Supplementary Information

Site- and enantioselective B−H functionalization of carboranes

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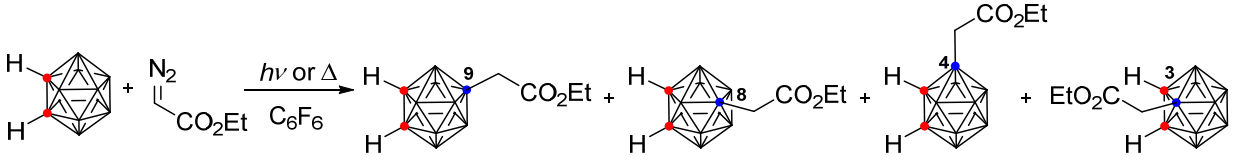
1. Experimental Section

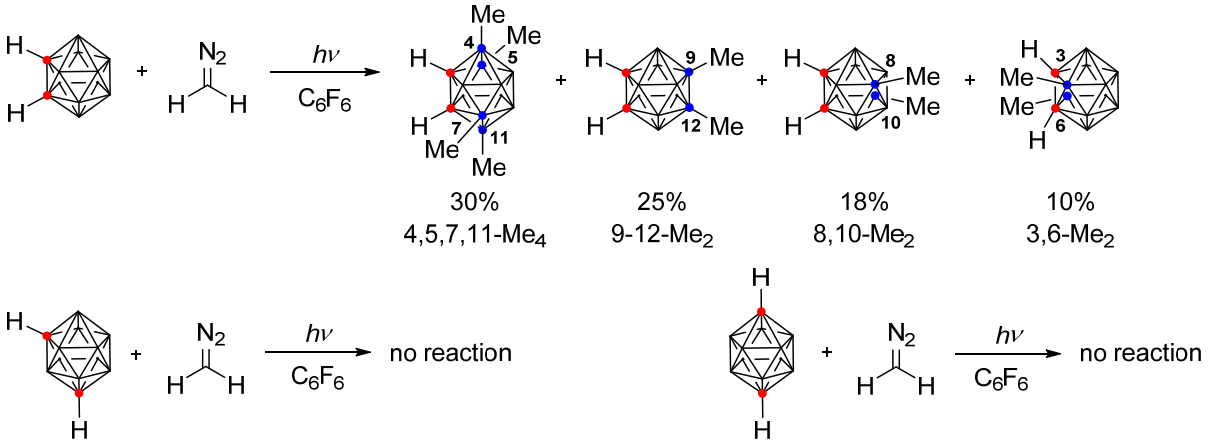
Commercial available reagents were used without purification. Carboranes[1-4] and diazo compounds[5,6] were prepared according to literature methods. All reaction mixtures were stirred magnetically and were monitored by thin-layer chromatography using silica gel pre-coated glass plates, which were visualized with UV light, and then developed using a solution of $KMnO_4$. For reactions that require heating, oil bath was used as the source of heating. Flash column chromatography was carried out using silica gel (230-400 mesh). ^1H NMR (400 MHz), $^{13}C\{^1H\}$ NMR (100 MHz), ^{11}B NMR (128 MHz), $^{11}B\{^1H\}$ NMR (128 MHz), and ^{19}F NMR (377 MHz) spectra were recorded on NMR spectrometer. Deuterated chloroform, acetone, and methanol were used as the solvent and chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent [δ 7.26 for ^1H (chloroform-*d*), δ 2.05 for ^1H (acetone-d_6), δ 3.31 for ^1H (methanol-d_4), δ 77.2 for $^{13}C\{^1H\}$ (chloroform-*d*), δ 29.8 for $^{13}C\{^1H\}$ (acetone-d_6), and δ 49.0 for $^{13}C\{^1H\}$ (methanol-d_4)]. Infrared spectra were recorded on FT-IR spectrometer as either a thin film pressed between two sodium chloride plates or as a solid suspended in a potassium bromide disk. High resolution mass spectra (HRMS) was obtained by fast atom bombardment (FAB) using a double focusing magnetic sector mass spectroscopy and electron impact (EI) ionization technique (magnetic sector - electric sector double focusing mass analyzer) from the KBSI (Korea Basic Science Institute Daegu Center) and performed on the Synapt G2-HDMS mass spectrometer (Waters, Manchester, U.K.), which was operated on the MassLynx 4.1 software from the KBSI (Korea Basic Science Institute, Ochang, Center of Research Equipment). Melting points were determined in open capillary tube. Circular dichroism spectra were recorded on a JASCO J-715 spectrometer. Enantiomeric excess was determined by HPLC analysis using the corresponding commercial chiral column as stated in the experimental procedures at 40 ^oC with UV detector at 210 or 254 nm. Single-crystal X-ray diffraction data were collected on a Bruker D8 QUEST with coated Parabar oil under N_2 gas stream at 173 K. The diffraction data were integrated, scaled, and reduced by using the Bruker APEX3 software. The crystal structures were solved by the SHELX structure solution program and refined by full-matrix least-squares calculations with the SHELXL. Specific rotation was measured on the JASCO P-2000 at 589 nm.

2. Previously Reported Reactions of Carboranes with Carbenes

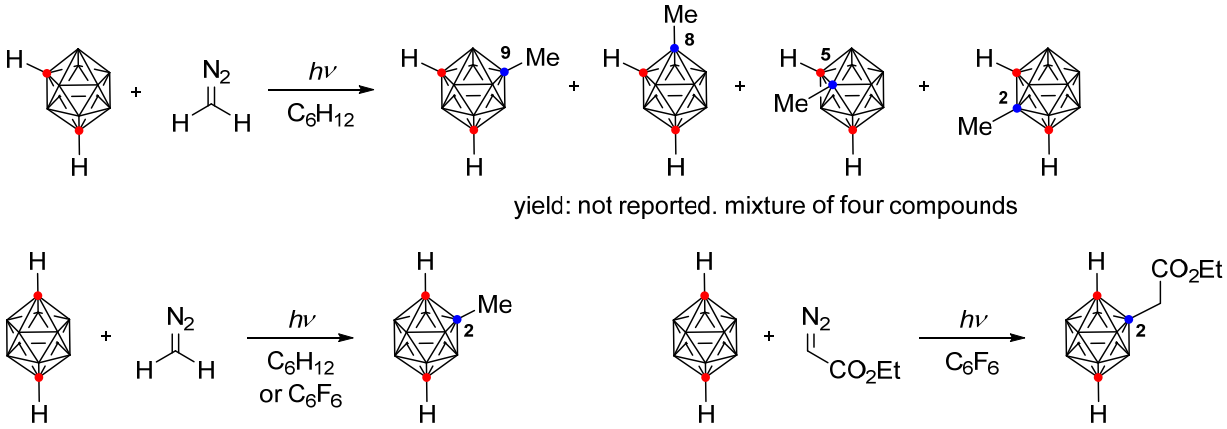


10% combined yield [**B(9)** : **B(8)** : **B(4)** : **B(3)** = 12 : 7.2 : 4.8 : 1]

Zheng, G.-X. & Jones, M. Jr. *J. Am. Chem. Soc.* **105**, 6487-6488 (1983).



Sung, D. D., Lee, J. D. & Choi, S. K. *Bull. Korean Chem. Soc.* **8**, 63-68 (1987).

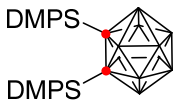


Yuan, K. & Jones, M. Jr. *Tetrahedron Lett.* **33**, 7481-7484 (1992).

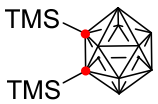
Fig. S1. Previously reported reactions of carboranes with carbenes

3. Preparation of Carborane Derivatives

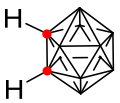
List of carboranes



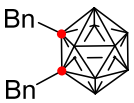
1a



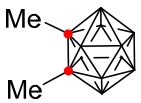
1b



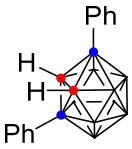
1c



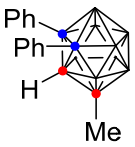
1d



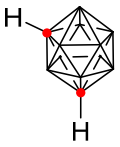
1e



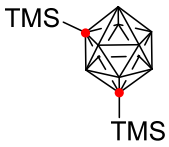
1f



1g



1h

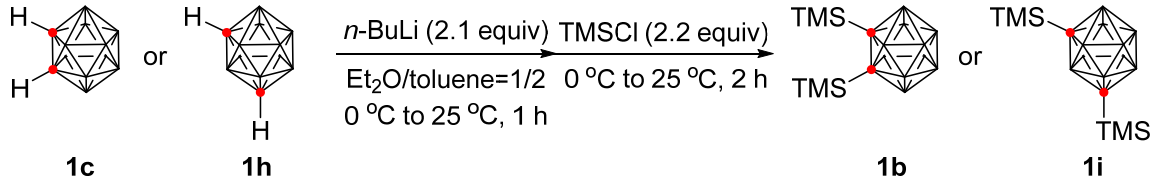


1i

1j

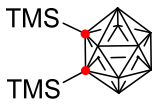
1c, **1h**, and **1j** are commercially available. **1a**, **1d**, **1e**, **1f**, and **1g** were synthesized via the known procedure[1-4].

General Procedure for the 1b and 1i



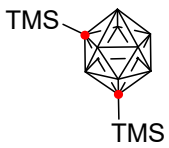
1c **1h** **1b** **1i**

o-Carborane **1c** or *m*-carborane **1h** (432.7 mg, 3.0 mmol, 1.0 equiv) were dissolved in Et_2O/toluene (3 mL/6 mL) and stirred at 0 °C. *n*-BuLi (1.6 M in hexane, 3.9 mL, 6.3 mmol, 2.1 equiv) was slowly added to the reaction mixture. The resulting solution was stirred at 25 °C for 1 h. After the reaction mixture was cooled to 0 °C, TMSCl (0.84 mL, 6.6 mmol, 2.2 equiv) was slowly added and stirred at 25 °C for 2 h. Then, the reaction was quenched with water (20 mL) and extracted with Et_2O (3 x 20 mL). The organic phase was dried over $MgSO_4$. The crude product was purified by column chromatography on silica gel and then concentrated under vacuum to give the **1b** or **1i** as a white solid.



1b: Yield: 796.48 mg (92%); R_f = 0.60 (Hexane); White solid; Melting point: 137-139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.32 (s, 18H); ^{1}H{^{11}B} NMR (400 MHz, $CDCl_3$) δ 2.47 (s, 2H), δ 2.38 (s, 2H), δ 2.31 (s, 2H), δ 2.15 (s, 4H), δ 0.32 (s, 18H); ^{13}C{^{1}H} NMR (100

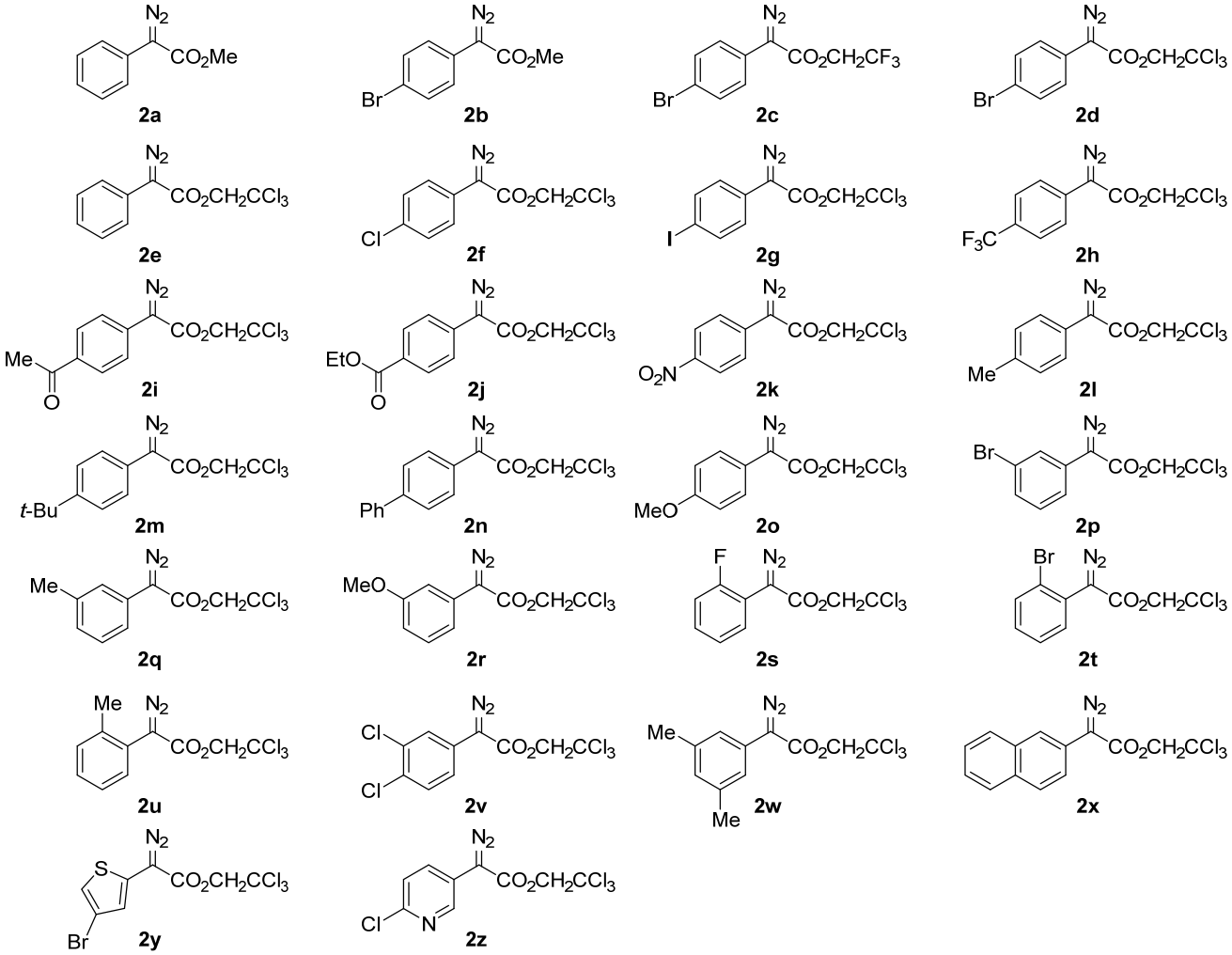
MHz, $CDCl_3$) δ 74.8, 1.72; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 1.84 (2B), -5.73 (2B), -8.89 (4B), -11.15 (2B); IR (film): 2983, 2957, 2613, 2574, 2560, 1744, 1256, 846, 759 cm^{-1}; HRMS (FAB) *m/z*: $[M\text{-}CH_3]^+$ Calcd for $C_7H_{25}B_{10}Si_2^+$ 275.2420; Found 275.2421.



1i: Yield: 493.5 mg (57%); R_f = 0.70 (Hexane); White solid; Melting point: 53-55 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 0.12 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 68.0, -0.65; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ -2.87 (2B), -7.51 (2B), -9.65 (4B), -13.89 (2B); IR (film): 2961, 2899, 2590, 1252, 1097, 859, 841, 824, 790 cm^{-1}; HRMS (FAB) *m/z*: $[M\text{-}CH_3]^+$ Calcd for $C_7H_{25}B_{10}Si_2^+$ 275.2420; Found 275.2423.

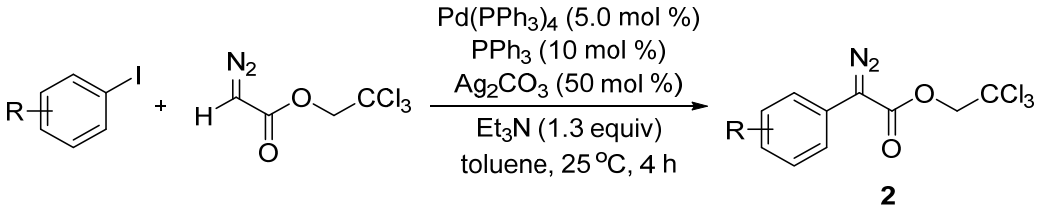
4. Preparation of Diazo Compounds

List of diazo compounds



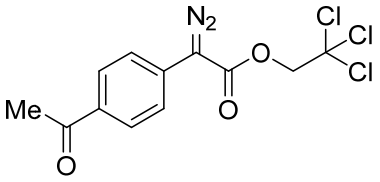
Diazo compounds were synthesized via the known procedure[5 6].

General Procedure A for the Diazo Compounds

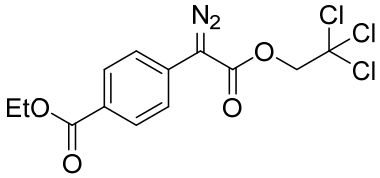


Aryl iodide (3.0 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (173.3 mg, 0.15 mmol, 5.0 mol %), PPh_3 (78.7 mg, 0.30 mmol, 10 mol %), and Ag_2CO_3 (413.7 mg, 1.5 mmol, 0.5 equiv) were dissolved in toluene (12 mL)

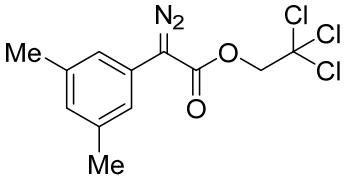
under a N_2 atmosphere, followed by addition of Et_3N (0.55 mL, 3.9 mmol, 1.3 equiv) and 2,2,2-trichloroethyl 2-diazoacetate (847.9 g, 3.9 mmol, 1.3 equiv). The resulting mixture was stirred at 25 °C for 4 h and then filtered through a pad of silica gel, washed with EtOAc. The crude product was purified by column chromatography on silica gel.



2i: Yield: 744.7 mg (74%); R_f = 0.40 (Et_2O:Hexane = 1:10); Yellow solid; Melting point: 60-62 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 8.7 Hz, 2H), 4.94 (s, 2H), 2.61 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 197.2, 162.7, 134.7, 130.4, 129.3, 123.3, 94.9, 74.1, 26.6; IR (film): 3005, 2957, 2097, 1715, 1677, 1598, 1269, 1236, 1141 cm^{-1}; HRMS (FAB) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{10}Cl_3N_2O_3^+$ 334.9757; Found 334.9758.

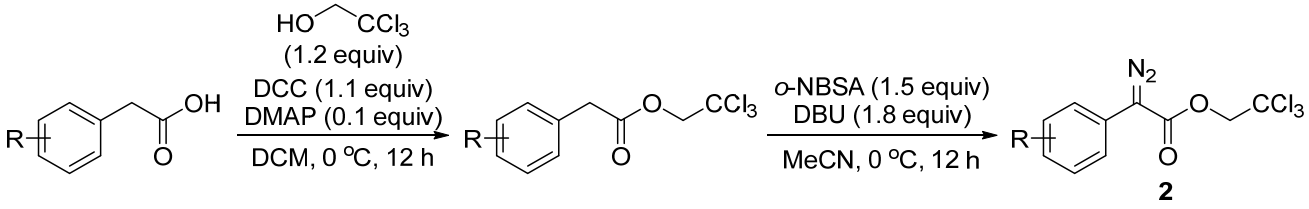


2j: Yield: 767.2 mg (80%); R_f = 0.35 (Et_2O:Hexane = 1:10); Yellow solid; Melting point: 85-87 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.7 Hz, 2H), 7.58 (d, J = 8.7 Hz, 2H), 4.93 (s, 2H), 4.38 (q, J = 7.1 Hz, 3H), 1.40 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.1, 162.7, 130.4, 130.0, 128.0, 123.1, 95.0, 74.0, 61.1, 14.5; IR (film): 2983, 2097, 1710, 1602, 1273, 1234, 1141, 1106, 766 cm^{-1}; HRMS (FAB) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{12}Cl_3N_2O_4^+$ 364.9863; Found 364.9861.



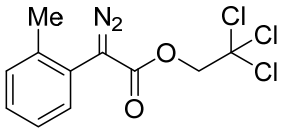
2w: Yield: 858.8 mg (89%); R_f = 0.40 (Et_2O:Hexane = 1:10); Yellow solid; Melting point: 85-87 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.11 (s, 2H), 6.86 (s, 1H), 4.91 (s, 2H), 2.33 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.7, 138.9, 128.3, 124.3, 122.0, 95.2, 73.9, 21.6; IR (film): 2952, 2919, 2085, 1710, 1252, 1141, 1097, 839, 711 cm^{-1}; HRMS (FAB) *m/z*: $[M]^+$ Calcd for $C_{12}H_{11}Cl_3N_2O_2^+$ 319.9886; Found 319.9890.

General Procedure B for the Diazo Compounds



Aryl acetic acid (1.0 equiv, 3.0 mmol) and 2,2,2-trichloroethanol (0.35 mL, 3.6 mmol, 1.2 equiv) were dissolved in DCM (6 mL) and stirred at 0 °C. DCC (680.9 mg, 3.3 mmol, 1.1 equiv) in DCM (2 mL) was added to the reaction mixture. DMAP (36.7 mg, 0.3 mmol, 0.1 equiv) was dissolved in DCM (2 mL) and added to the solution. The reaction was stirred for 12 h and warm to room temperature. The reaction mixture was filtered through silica gel and concentrated. The crude product was purified by column chromatography on silica gel and then concentrated under vacuum, yielding the ester as colorless oil, which is directly used for the following diazo transfer step.

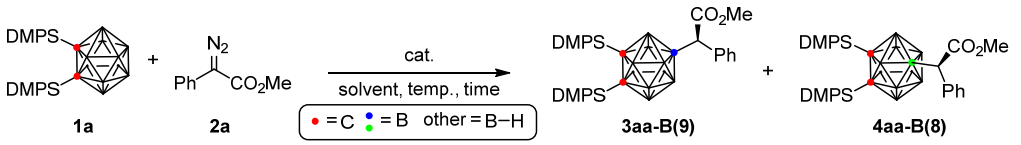
Ester and *o*-NBSA (*o*-nitrobenzenesulfonyl azide) (1026.8 mg, 4.5 mmol, 1.5 equiv) were dissolved in anhydrous MeCN (12 mL) under a N_2 atmosphere. The mixture was cooled to 0 °C and DBU (0.81 mL, 5.4 mmol, 1.8 equiv) was added dropwise to the solution. The reaction mixture was stirred for 12 h and it is quenched with Et_2O (30 mL) followed by adding saturated NH_4Cl(aq) solution (30 mL). The solution was extracted with Et_2O (3 x 30 mL) and the organic phase was dried over $MgSO_4$. The crude product was purified by column chromatography on silica gel and then concentrated under vacuum to give the pure diazo products.



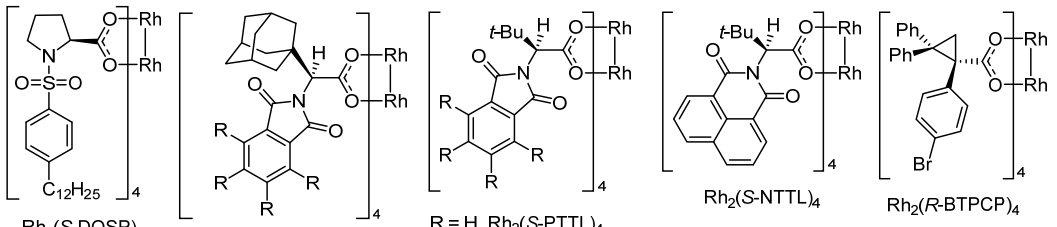
2u: Yield: 424.4 mg (46%); R_f = 0.35 (Et_2O:Hexane = 1:15); Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43-7.41 (m, 1H), 7.31-7.25 (m, 3H), 4.89 (s, 2H), 2.24 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.3, 138.0, 131.2, 131.0, 129.4, 126.6, 123.4, 95.3, 74.0, 20.0; IR (film): 2952, 2087, 1706, 1245, 1139, 1110, 754, 709, 570 cm^{-1}; HRMS (FAB) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_{10}Cl_3N_2O_2^+$ 306.9802; Found 306.9802.

5. Detailed Screening of Reaction Conditions

Table S1. Overall screening of reaction conditions[a]

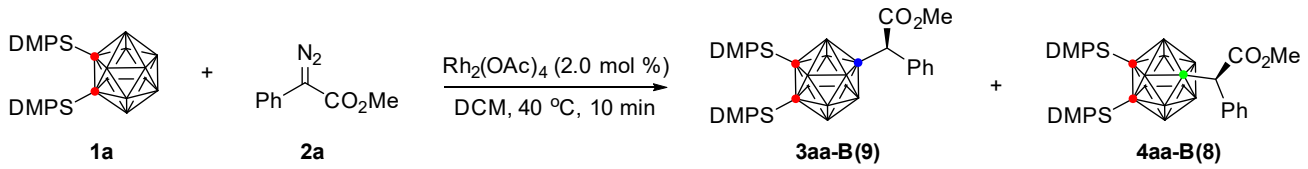


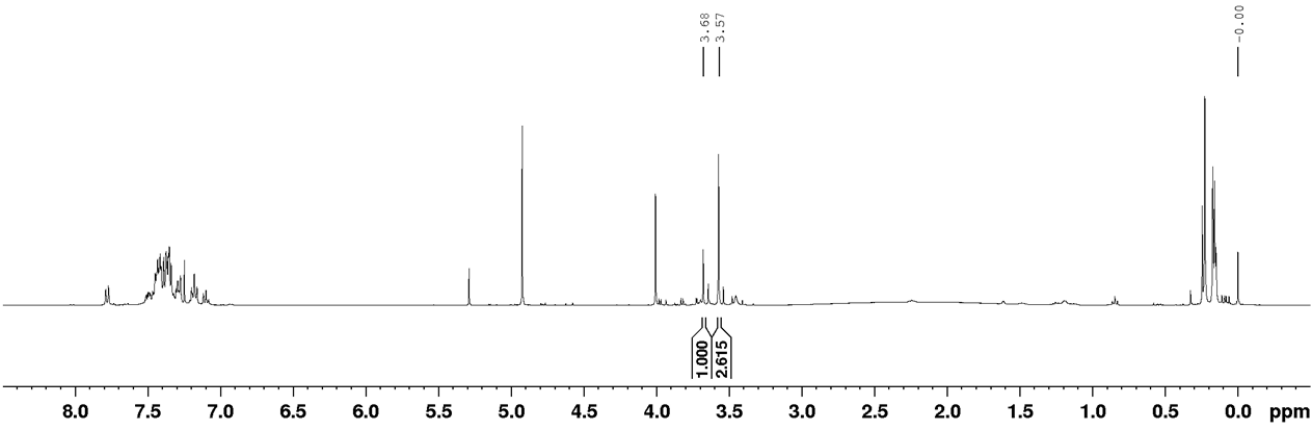
entry	cat.	solvent	temp. (°C)	time (min)	isolated yield (%)[b]	regioisomeric ratio (**3aa:4aa**)[c]	enantiomeric excess (%) (**3aa**)[d]
1	$Rh_2(OAc)_4$	DCM	40	10	87	2.6:1	0
2	$Rh_2(oct)_4$	DCM	40	10	71	14:1	0
3	Rh_2(*S*-DOSP)$_4$	DCM	40	10	81	6.0:1	-21
4	Rh_2(*S*-PTAD)$_4$	DCM	40	10	91	8.2:1	-16
5	Rh_2(*S*-TCPTAD)$_4$	DCM	40	10	86	25:1	19
6	Rh_2(*S*-PTTL)$_4$	DCM	40	10	97	9.8:1	-9
7	Rh_2(*S*-NTTL)$_4$	DCM	40	60	97	21:1	17
8	Rh_2(*S*-TPPTTL)$_4$	DCM	40	10	89	3.6:1	-8
9	Rh_2(*S*-TFPTTL)$_4$	DCM	40	10	85	14:1	4
10	Rh_2(*S*-TCPTTL)$_4$	DCM	40	10	98	29:1	25
11	Rh_2(*R*-BTPCP)$_4$	DCM	40	10	10	2.6:1	5
12	Rh_2(*S*-TCPTTL)$_4$	DCE	40	10	91	20:1	27
13	Rh_2(*S*-TCPTTL)$_4$	cyclohexane	40	10	97	42:1	41
14	Rh_2(*S*-TCPTTL)$_4$	benzene	40	10	98	23:1	44
15	Rh_2(*S*-TCPTTL)$_4$	$PhCF_3$	40	10	93	25:1	42
16	Rh_2(*S*-TCPTTL)$_4$	$PhCF_3$	-20	10	89	30:1	52
17	Rh_2(*S*-TCPTTL)$_4$	$PhCF_3$	0	10	97	34:1	51
18	Rh_2(*S*-TCPTTL)$_4$	$PhCF_3$	60	10	84	25:1	42
19[e]	Rh_2(*S*-TCPTTL)$_4$	$PhCF_3$	0	10	98	35:1	50
20[f]	Rh_2(*S*-TCPTTL)$_4$	$PhCF_3$	0	10	84	33:1	49
21[e,g]	Rh_2(*S*-TCPTTL)$_4$	$PhCF_3$	0	10	79	33:1	49

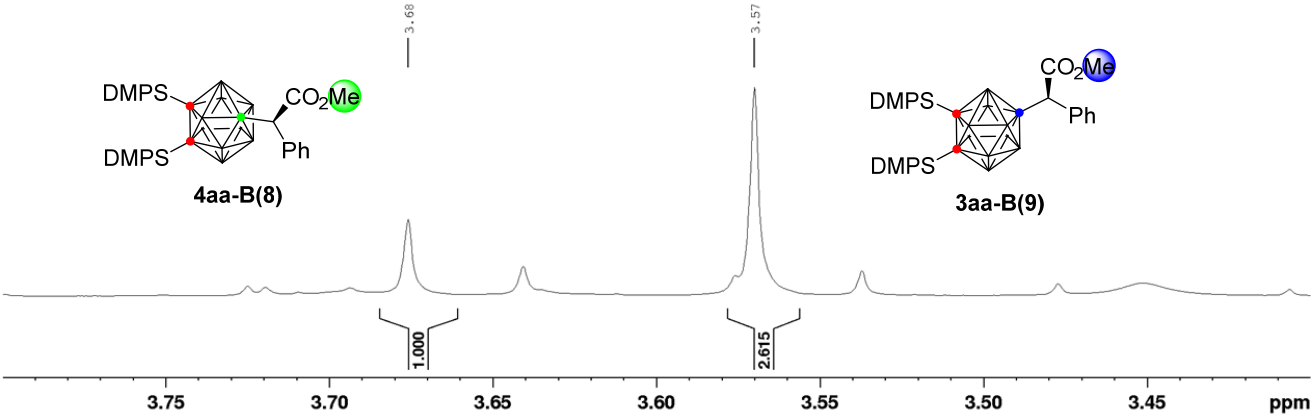


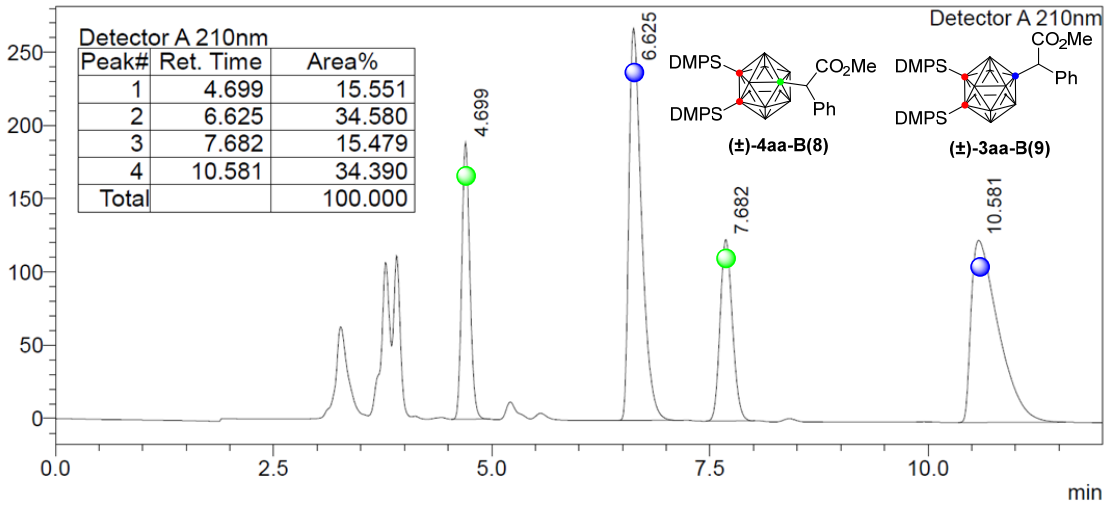
[a]Reaction conditions: After **1a** (0.20 mmol, 1.0 equiv) and catalyst (2.0 mol %) were dissolved in solvent (1.5 mL), a solution of **2a** (2.0 equiv) in solvent (1.5 mL) was added to the reaction mixture over a period of 3 min under a N_2 atmosphere. The resulting solution was stirred for additional 10 min. [b]Isolated and combined yield of **3aa-B(9)** and **4aa-B(8)**. [c]Ratios were determined from crude ^{1}H NMR. [d]Determined by chiral HPLC ananysis. [e]Rh_2(*S*-TCPTTL)$_4$ (1.0 mol %) was used. [f]Rh_2(*S*-TCPTTL)$_4$ (0.5 mol %) was used. [g]**2a** (1.5 equiv) was used.

Table S1-entry 1









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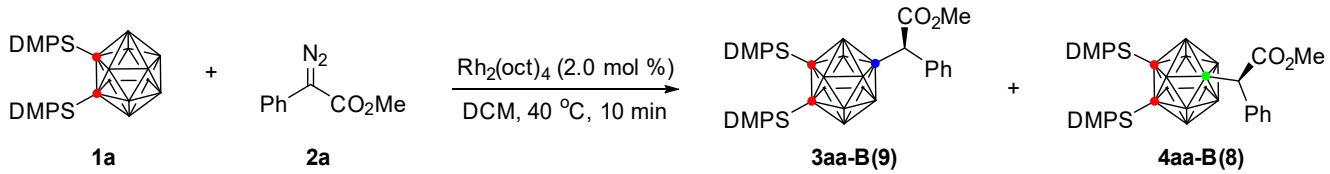

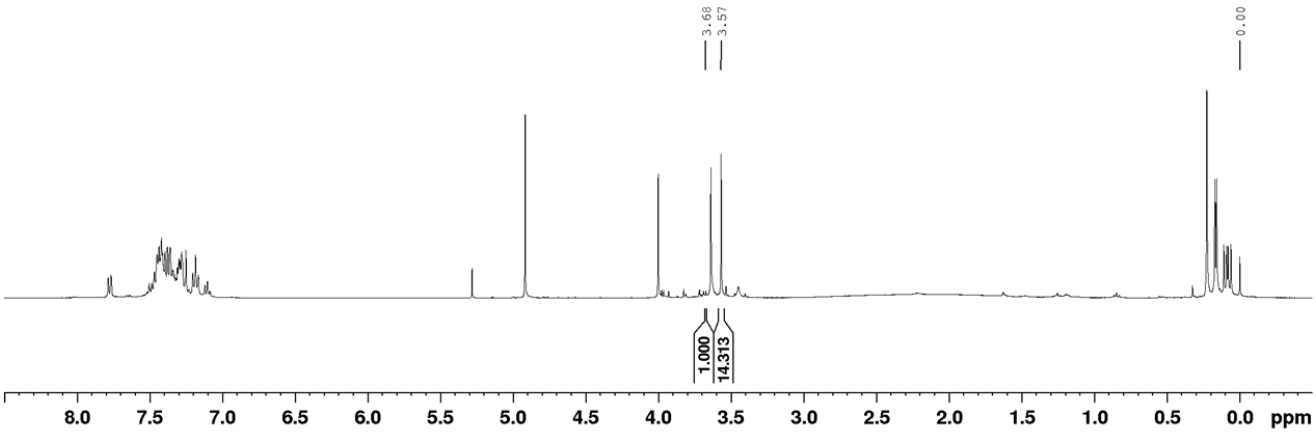

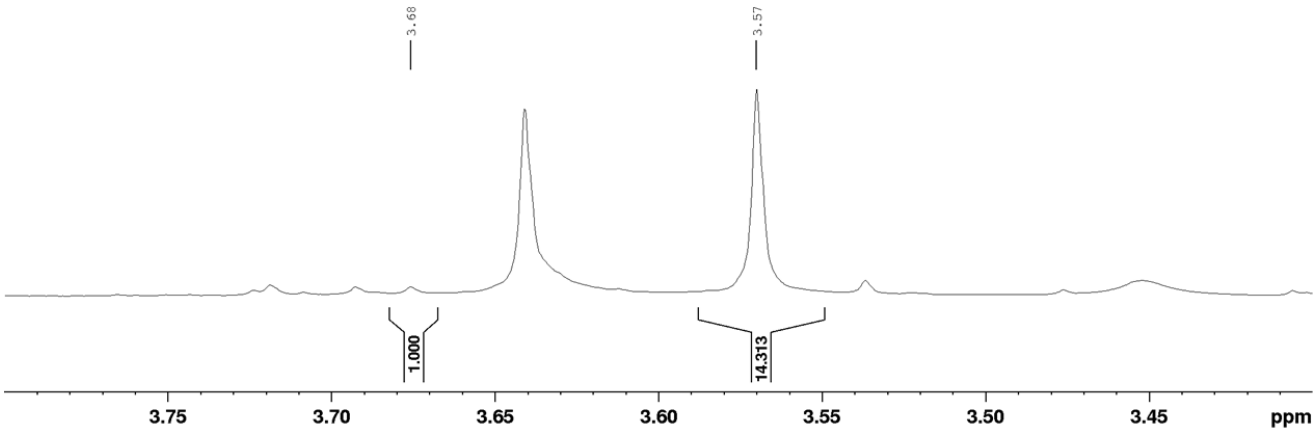

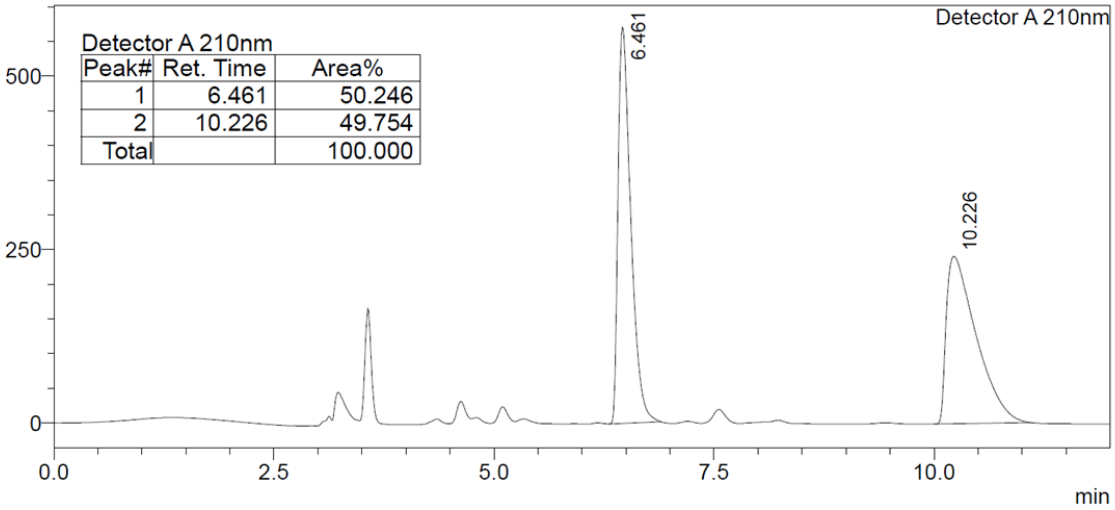

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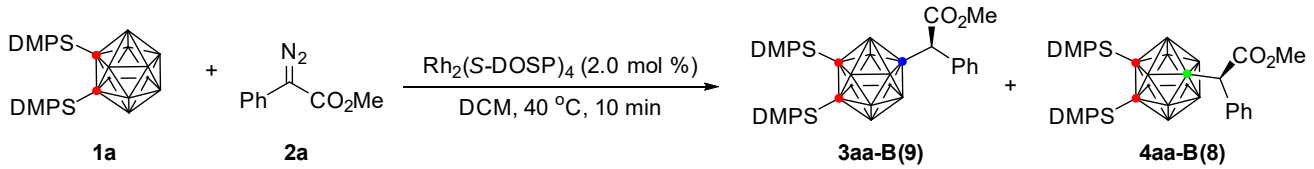

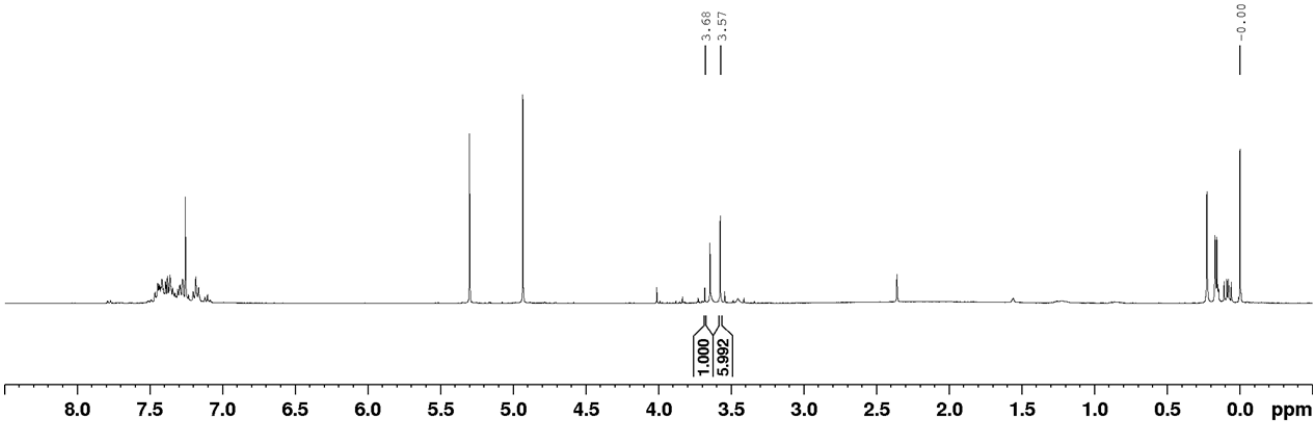

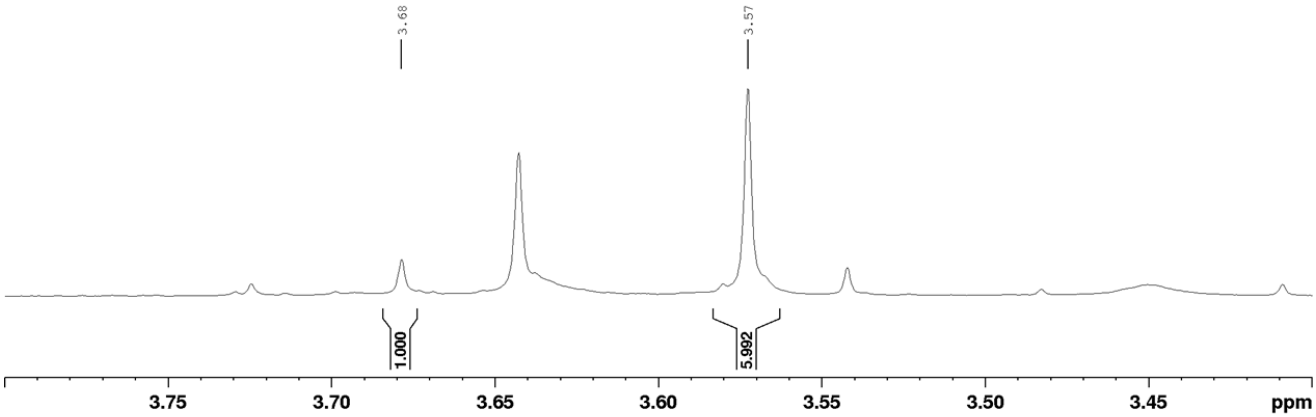

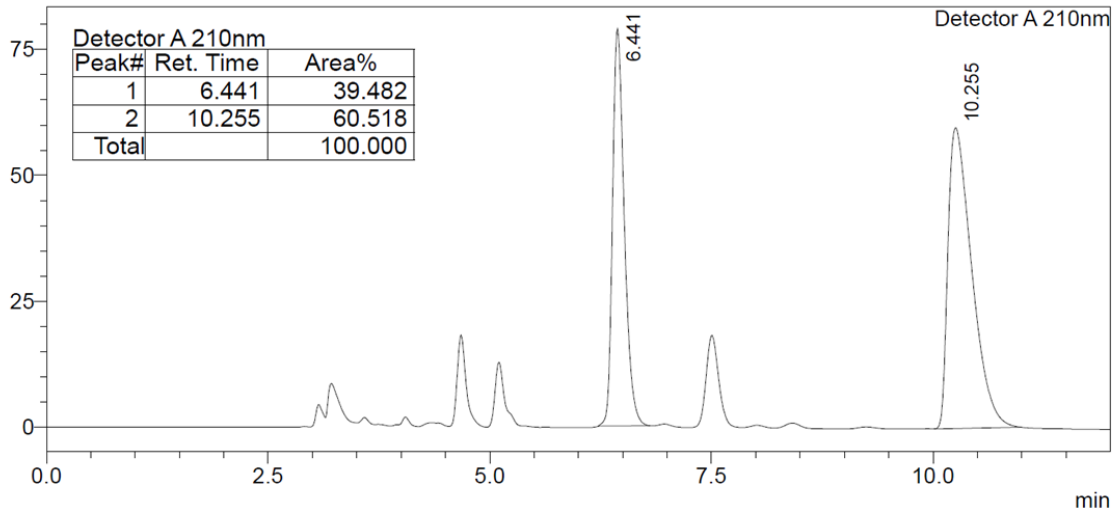

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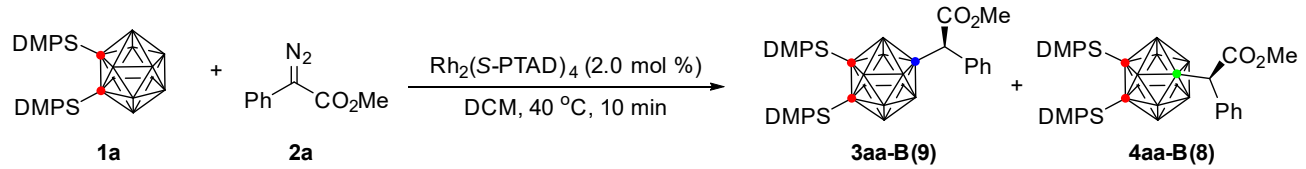

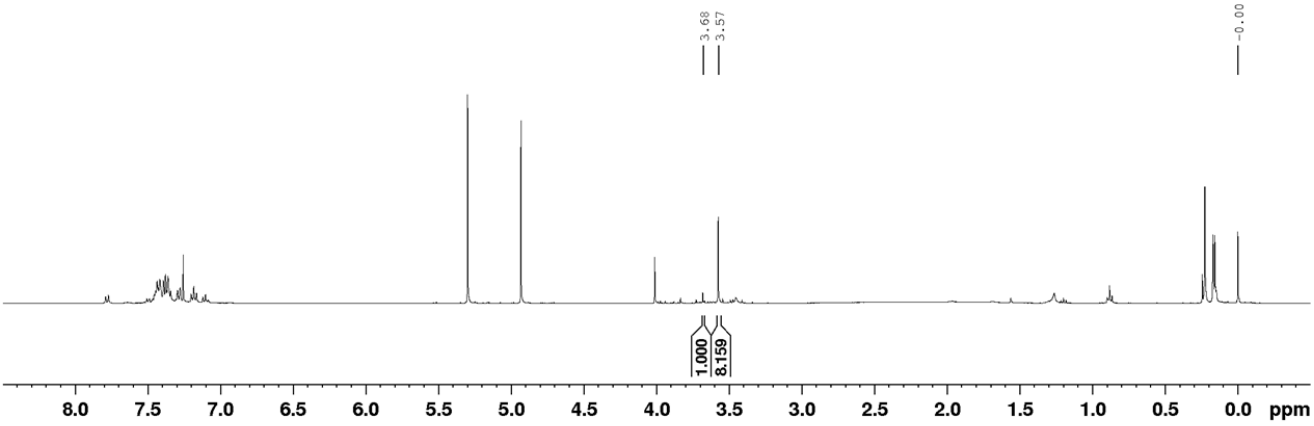

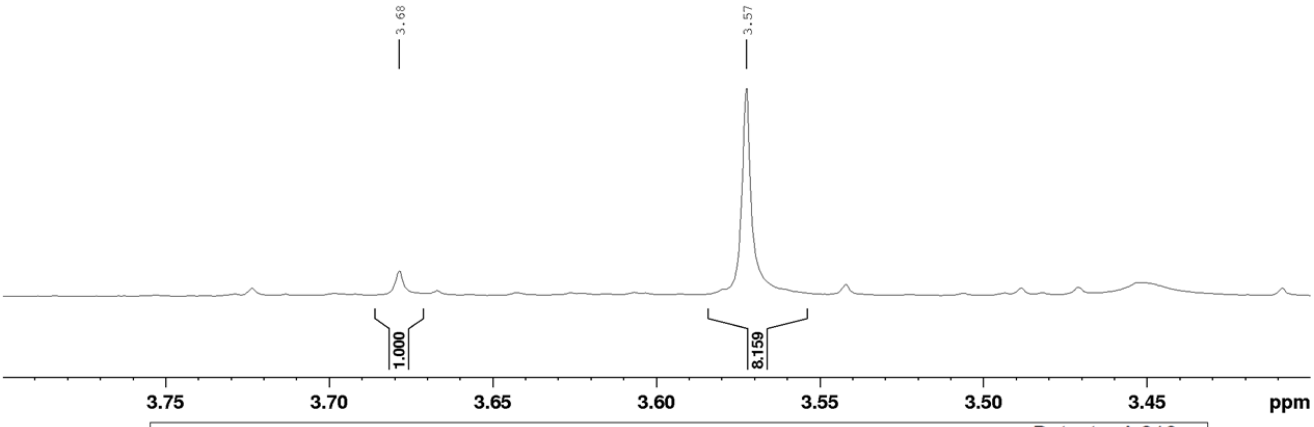

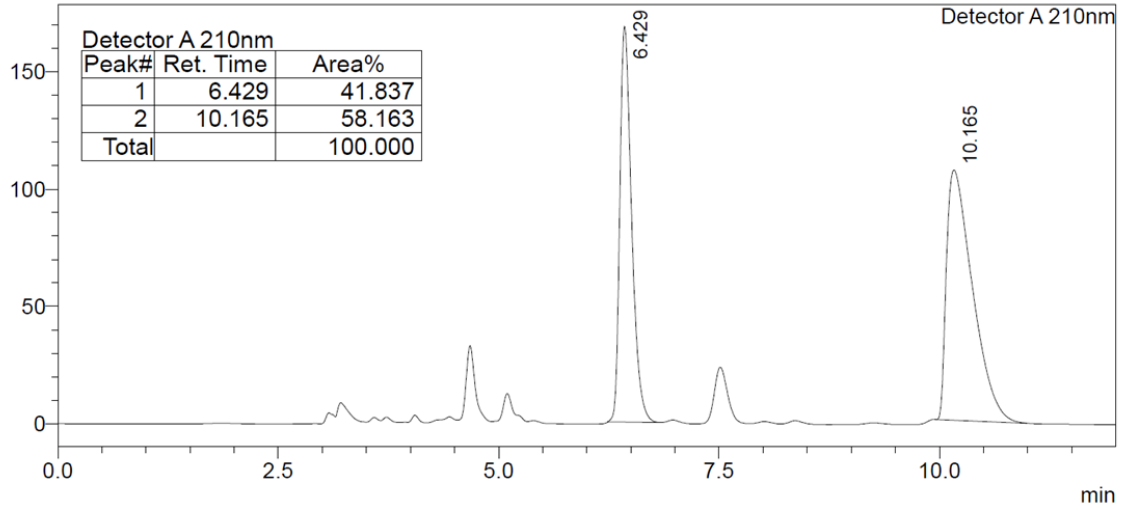

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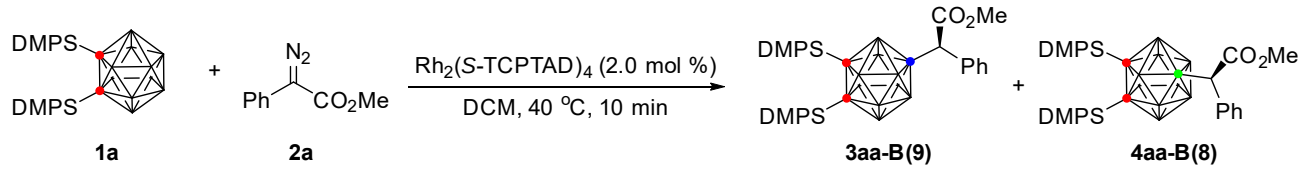

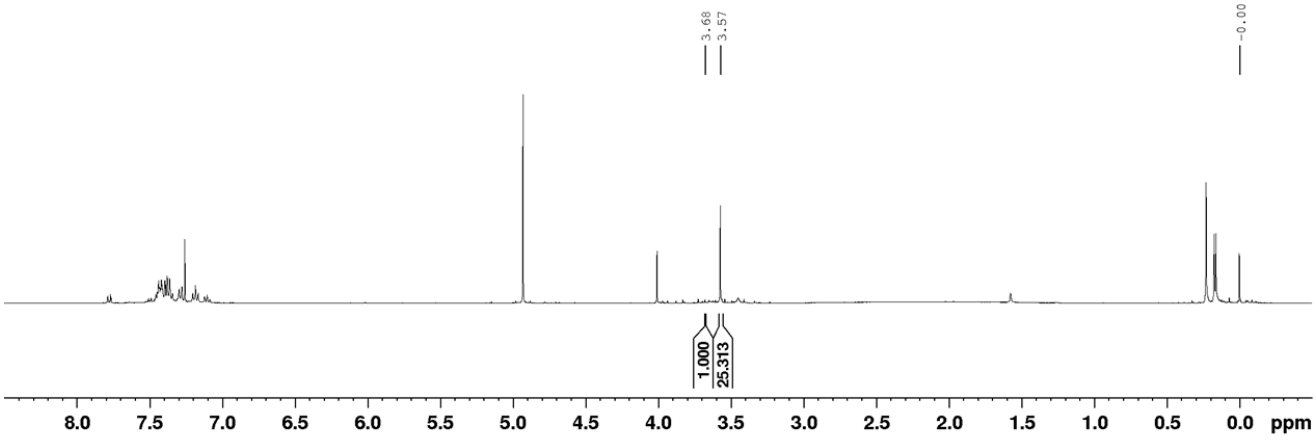

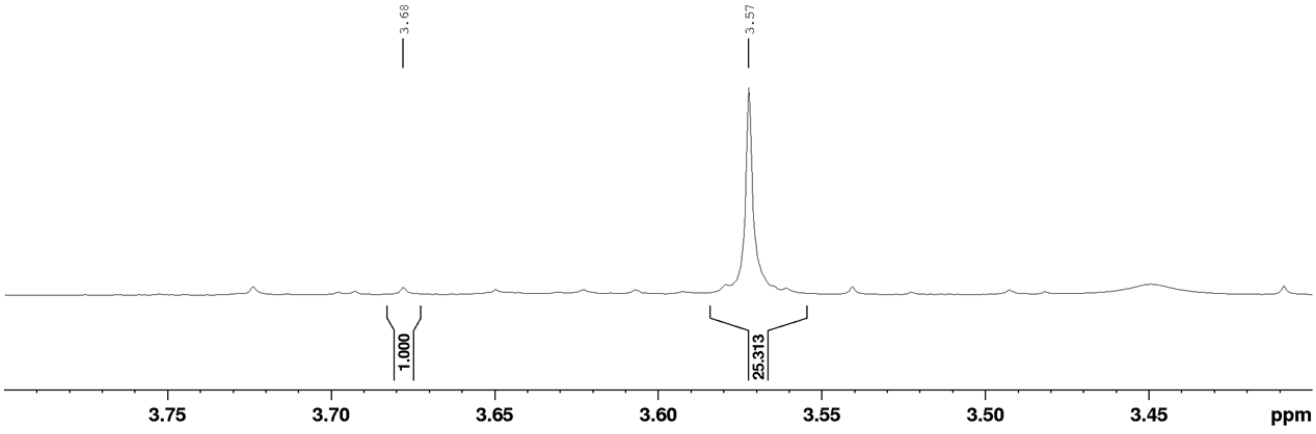

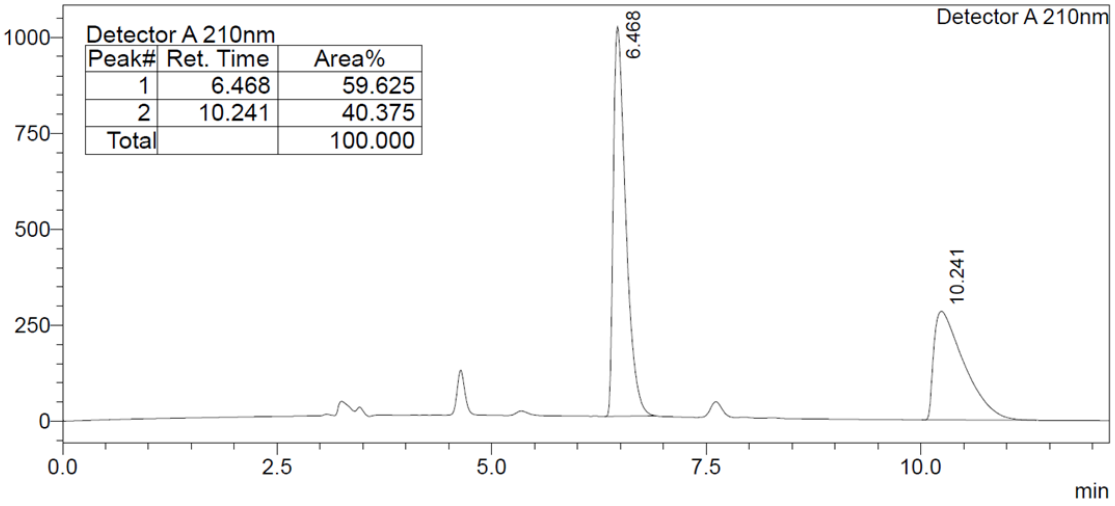

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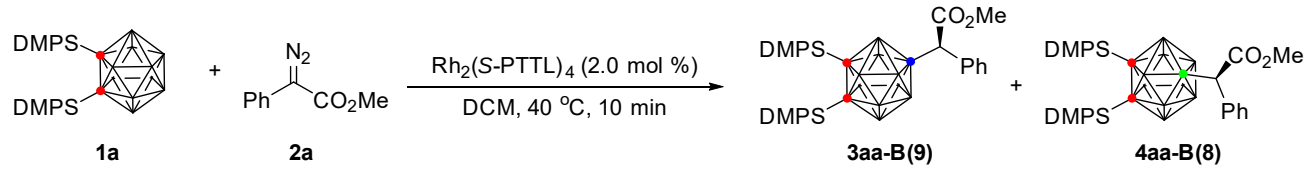

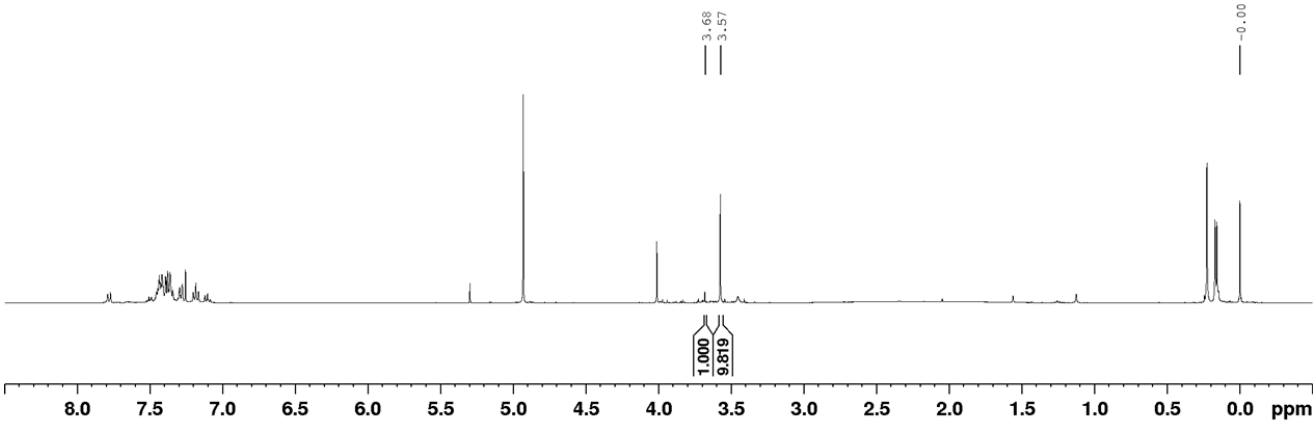

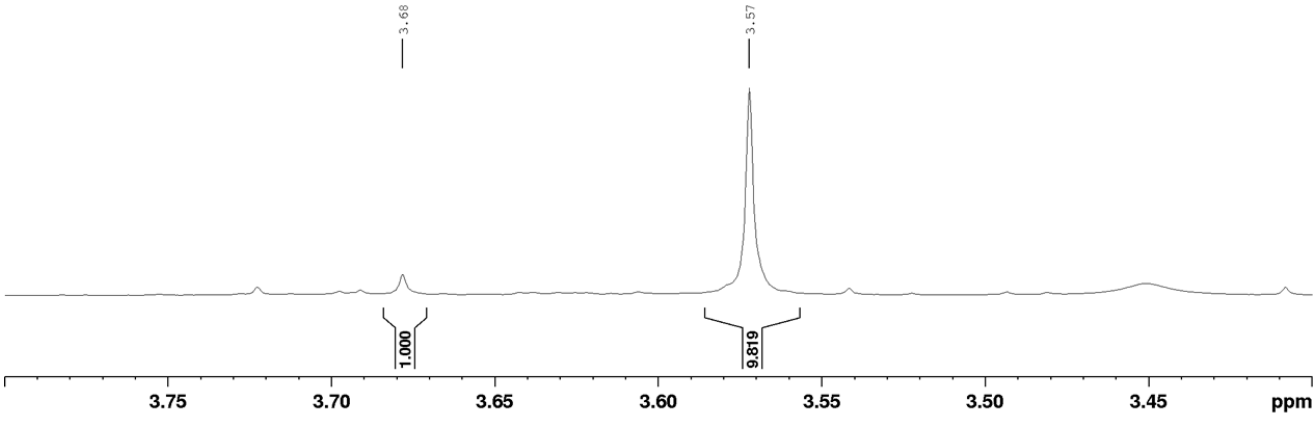

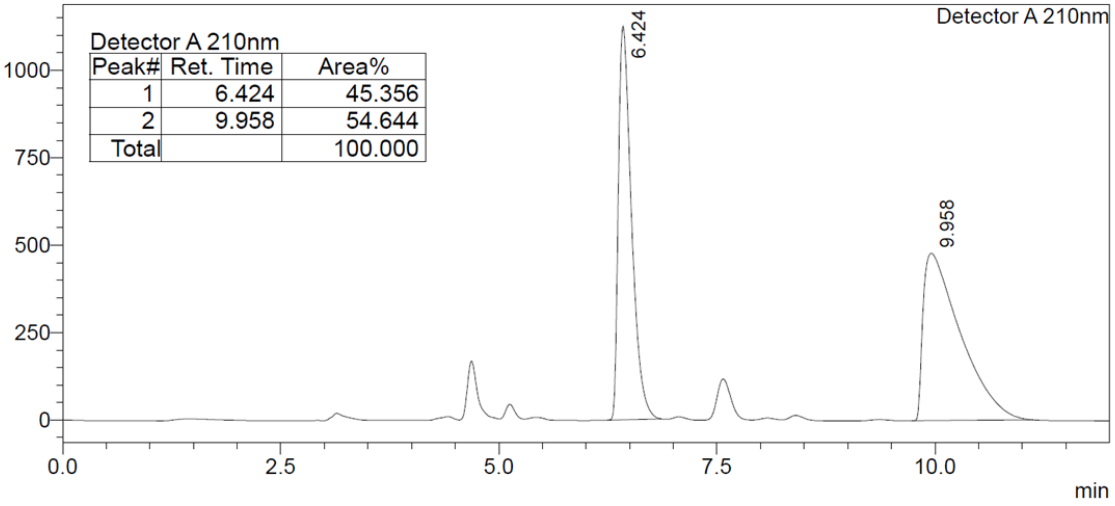

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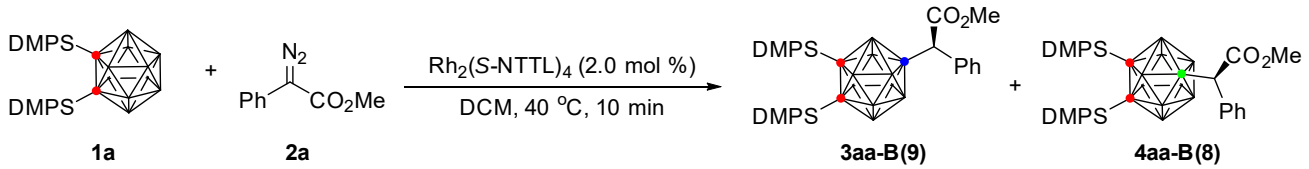

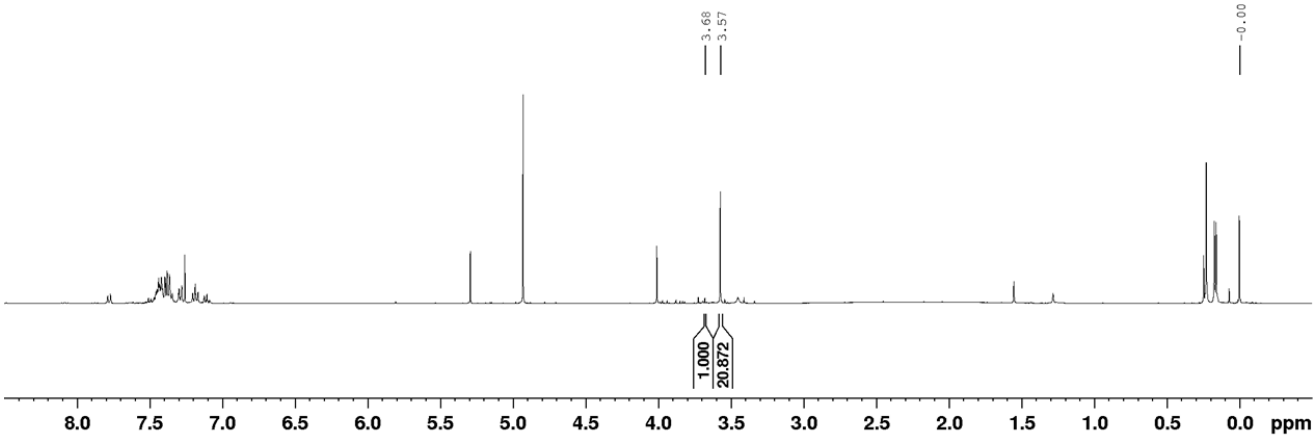

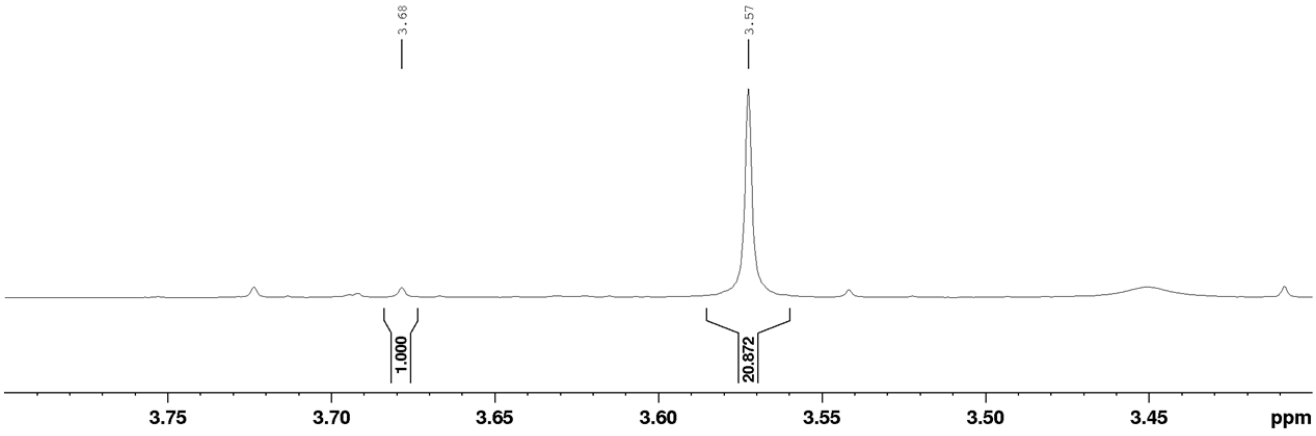

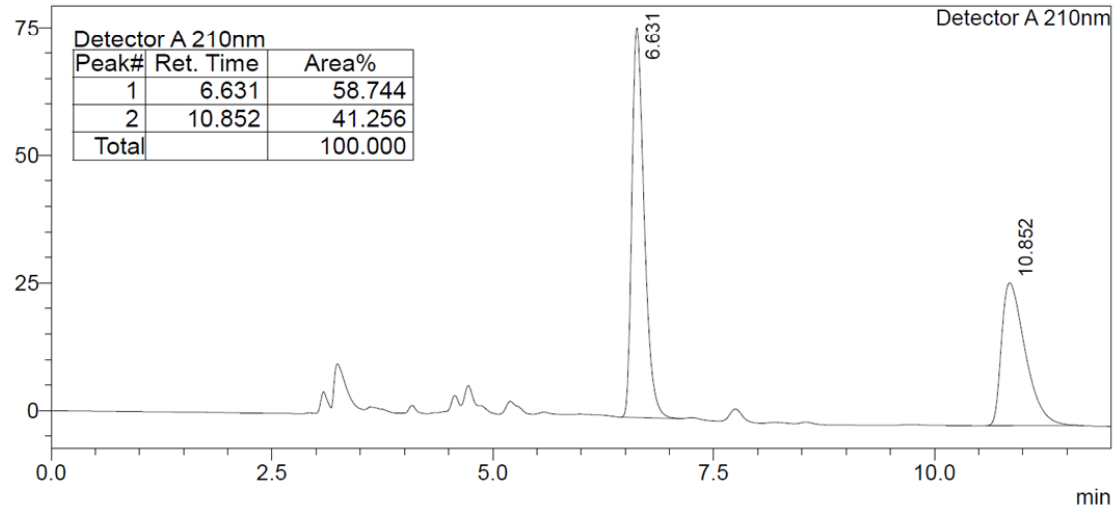

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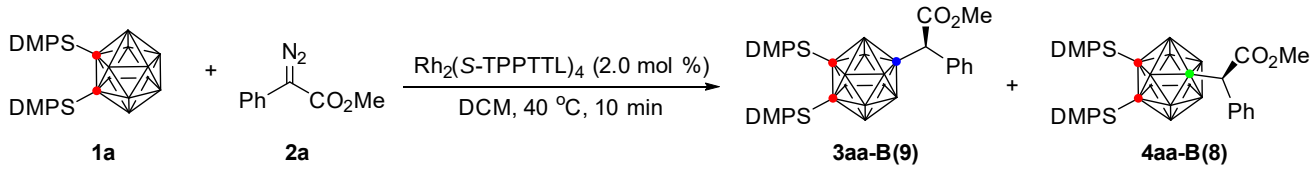

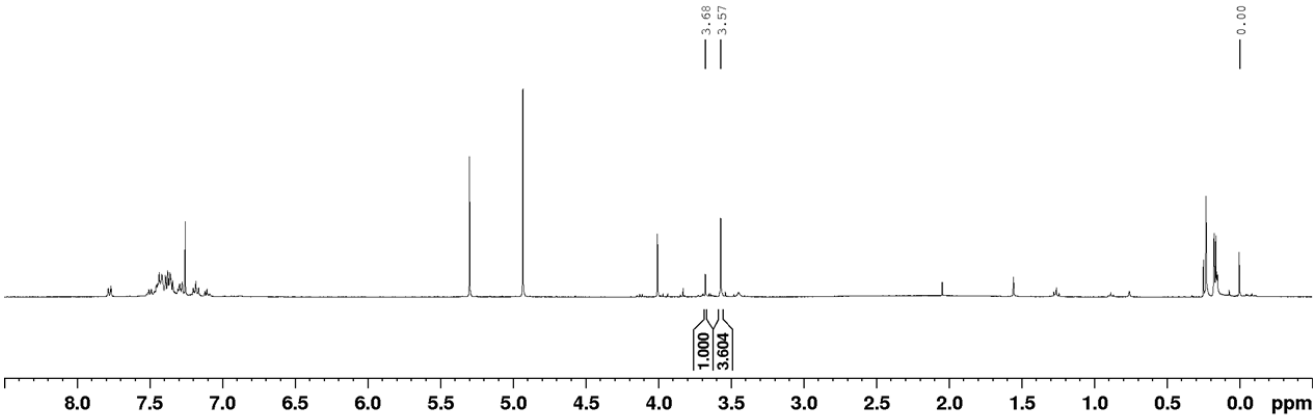

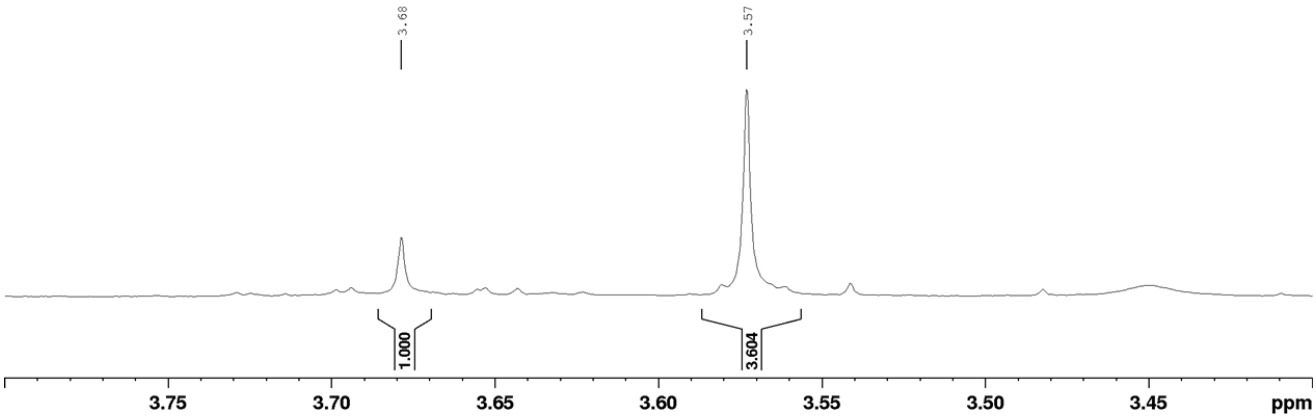

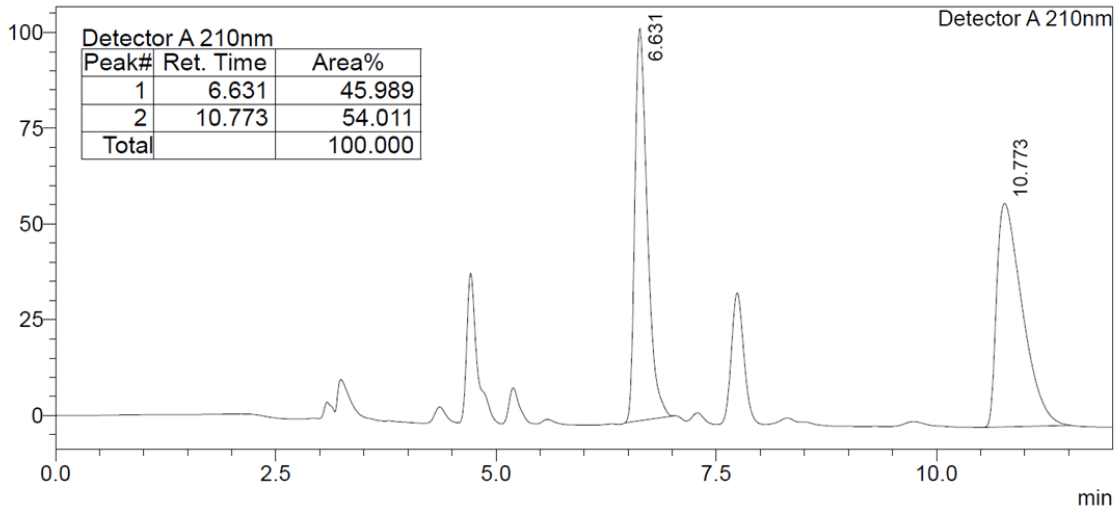

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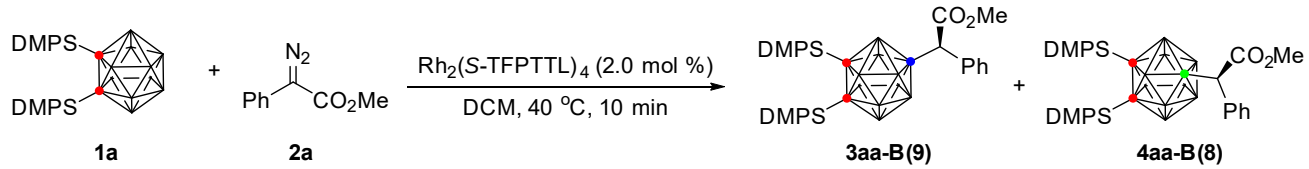

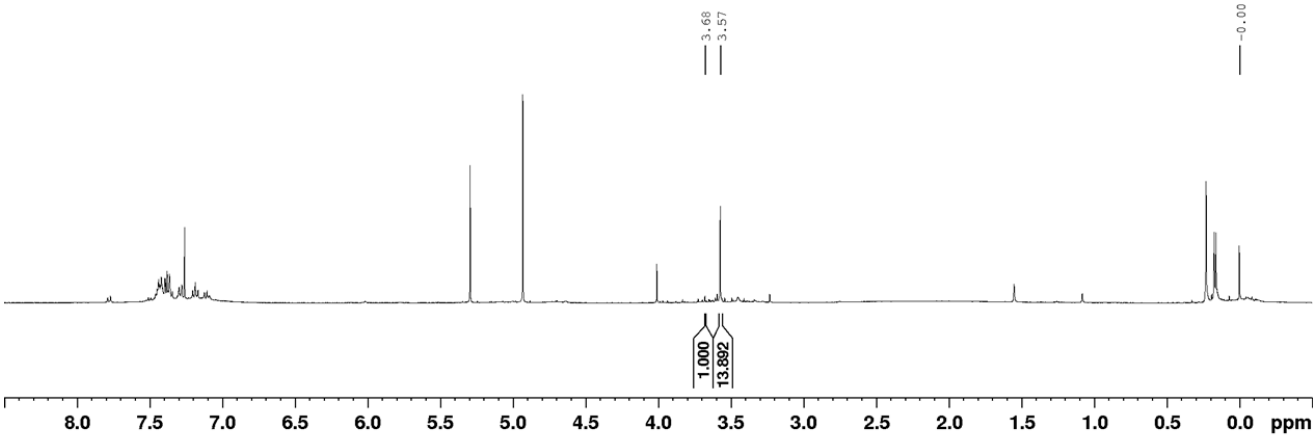

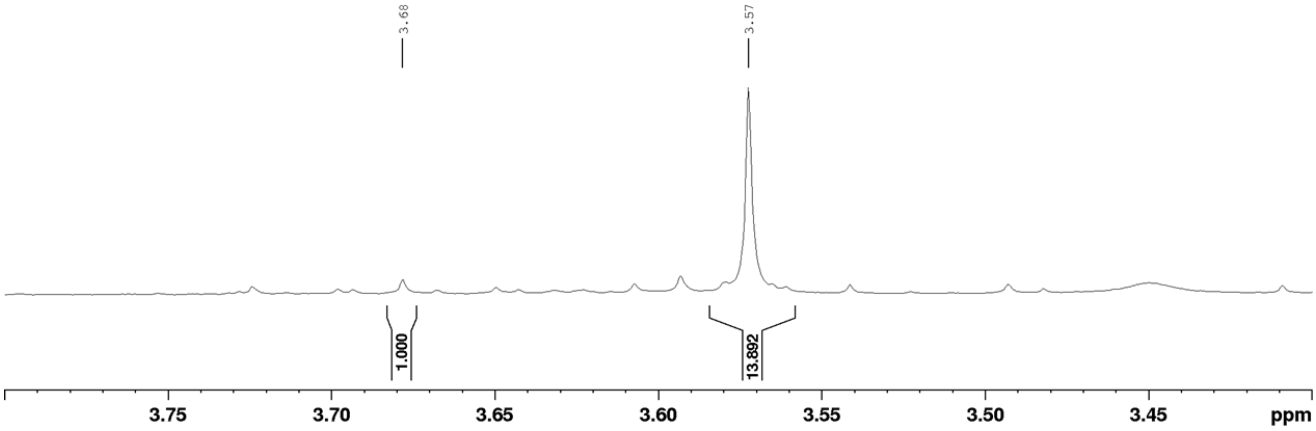

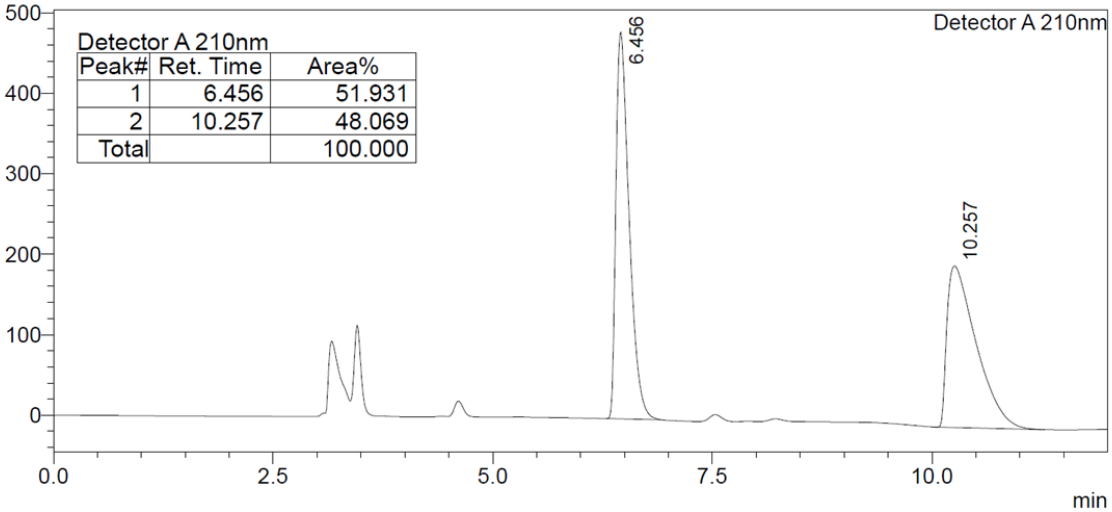

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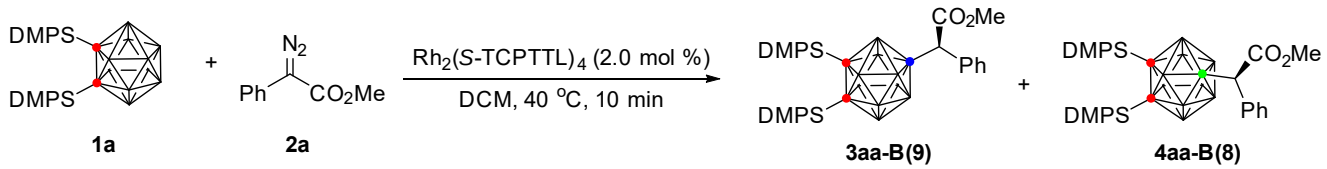

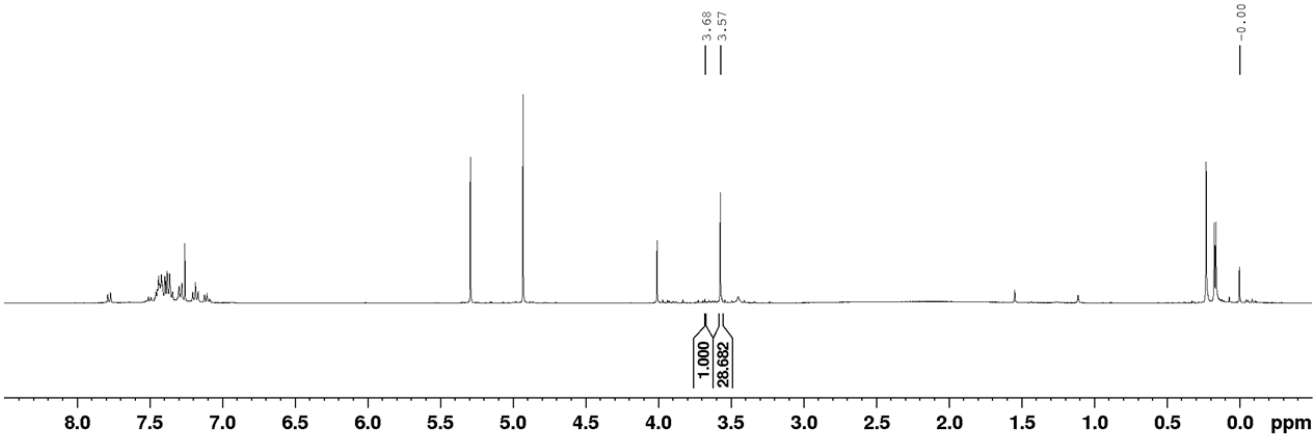

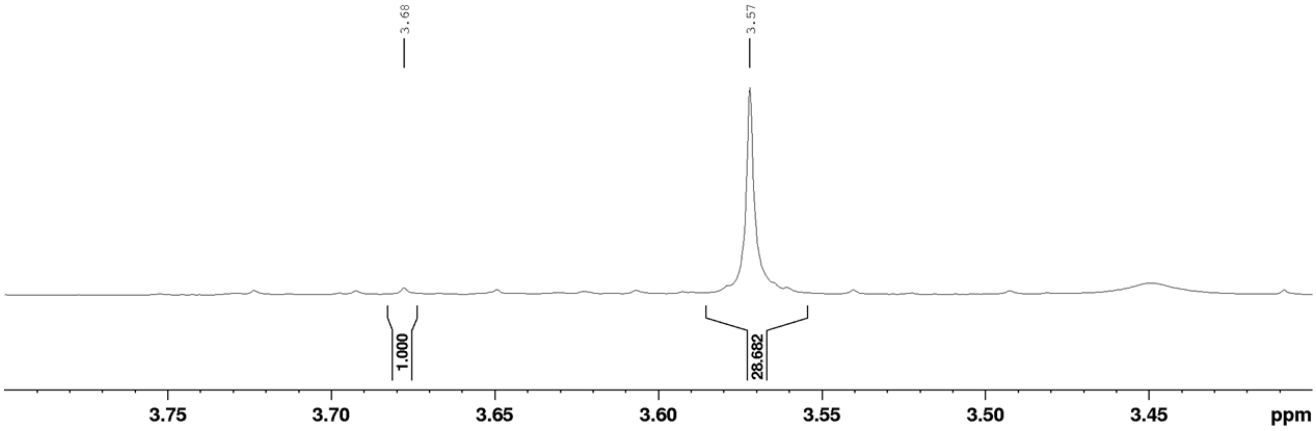

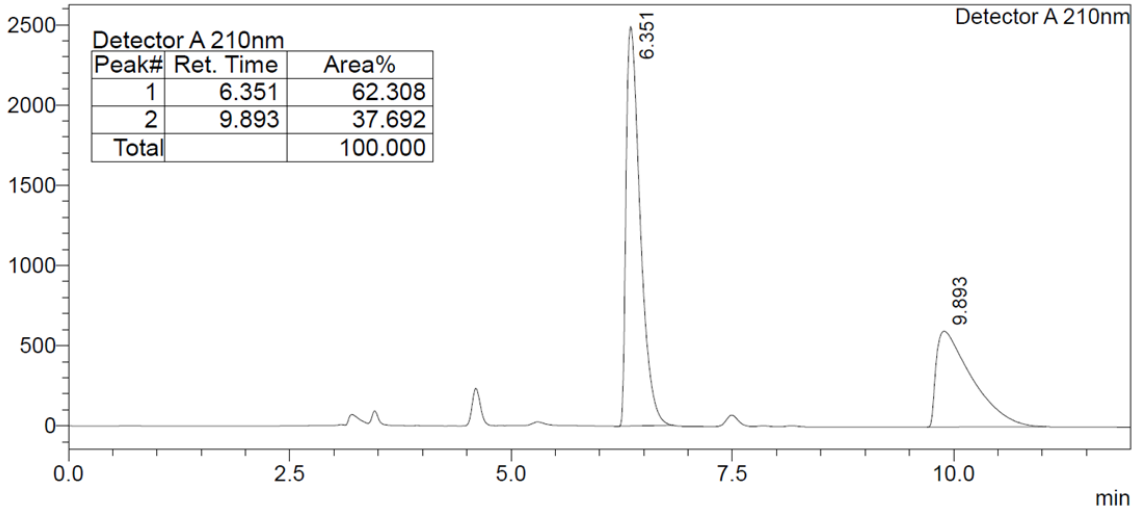

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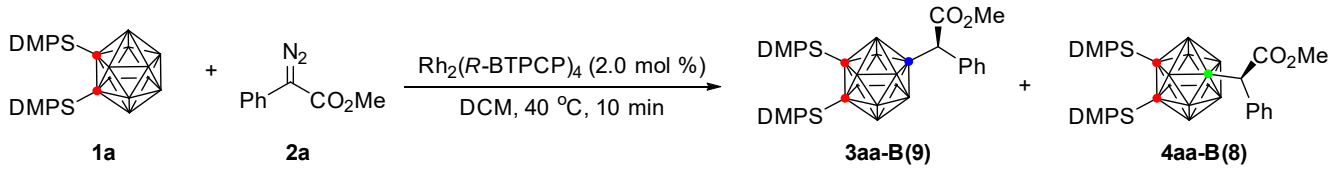

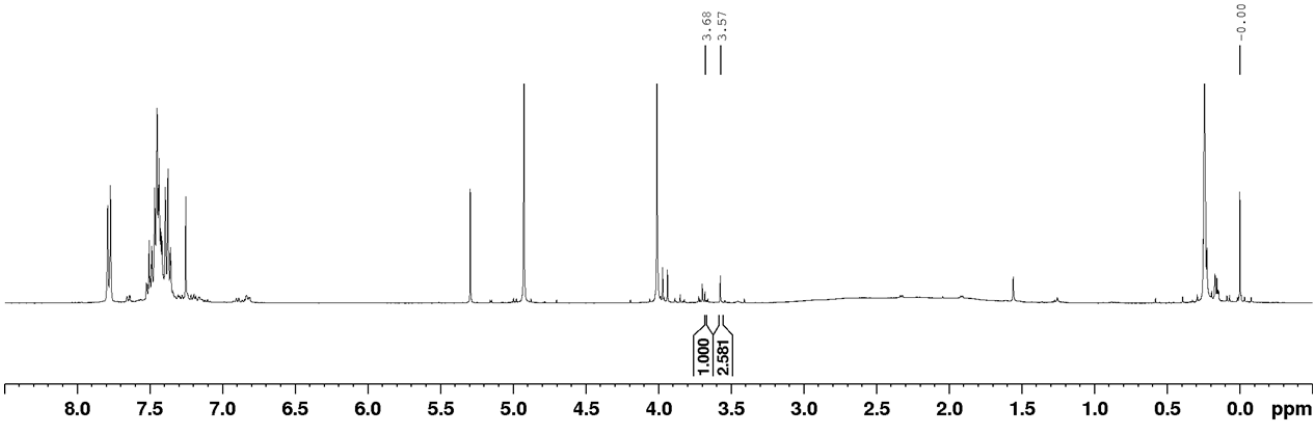

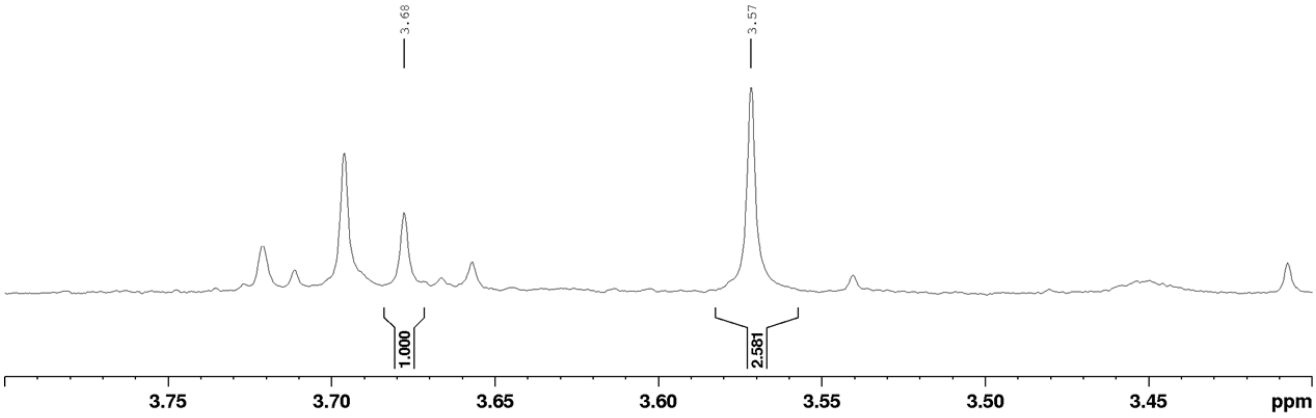

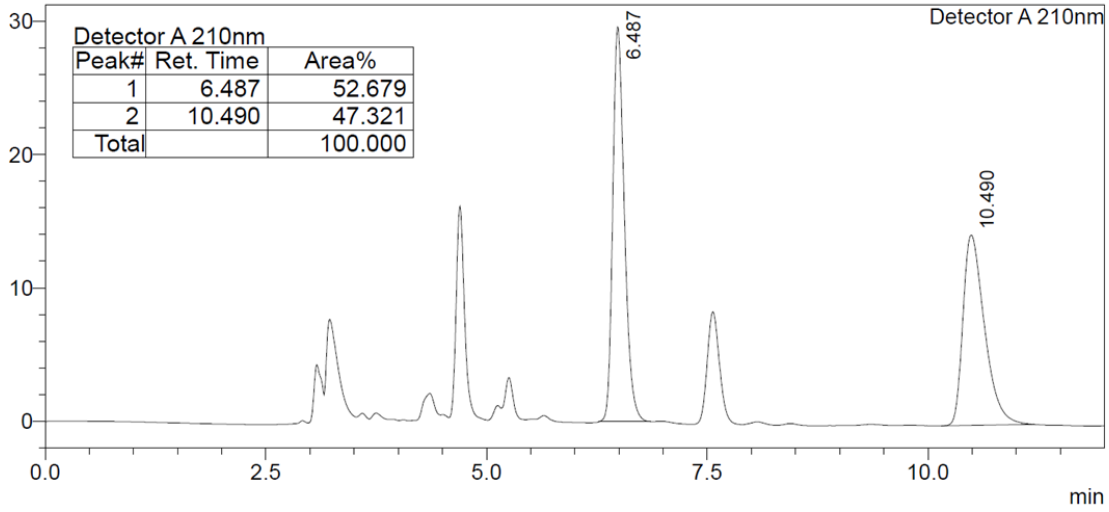

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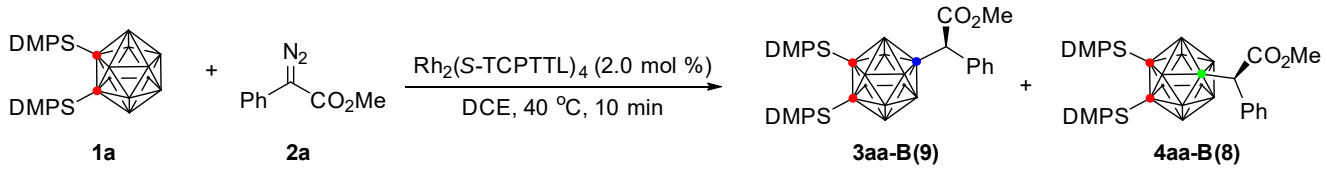
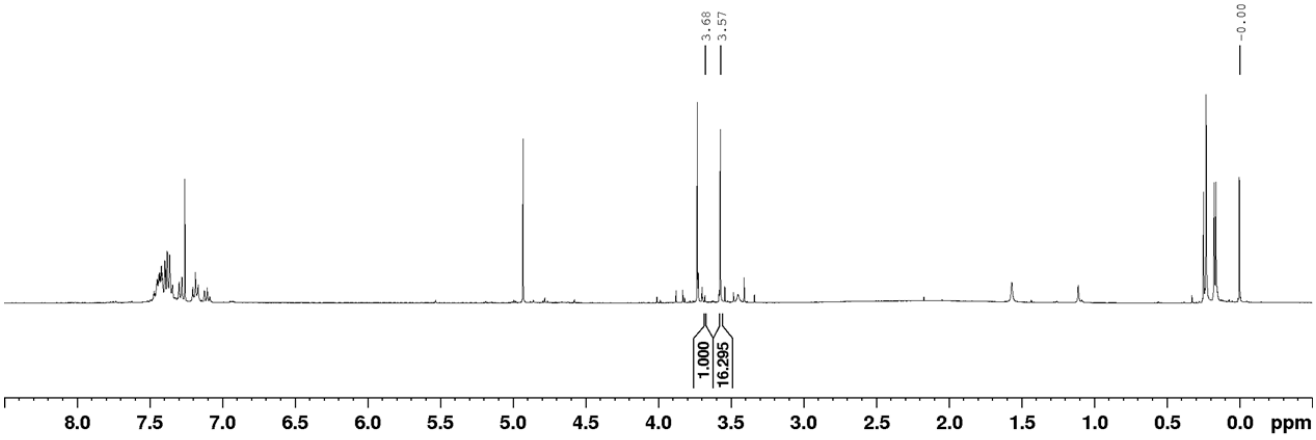
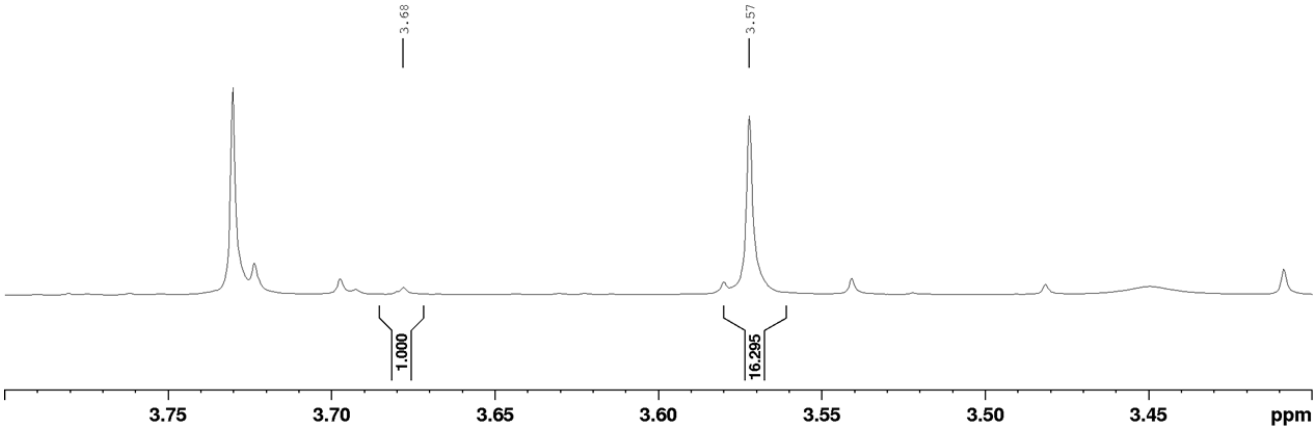






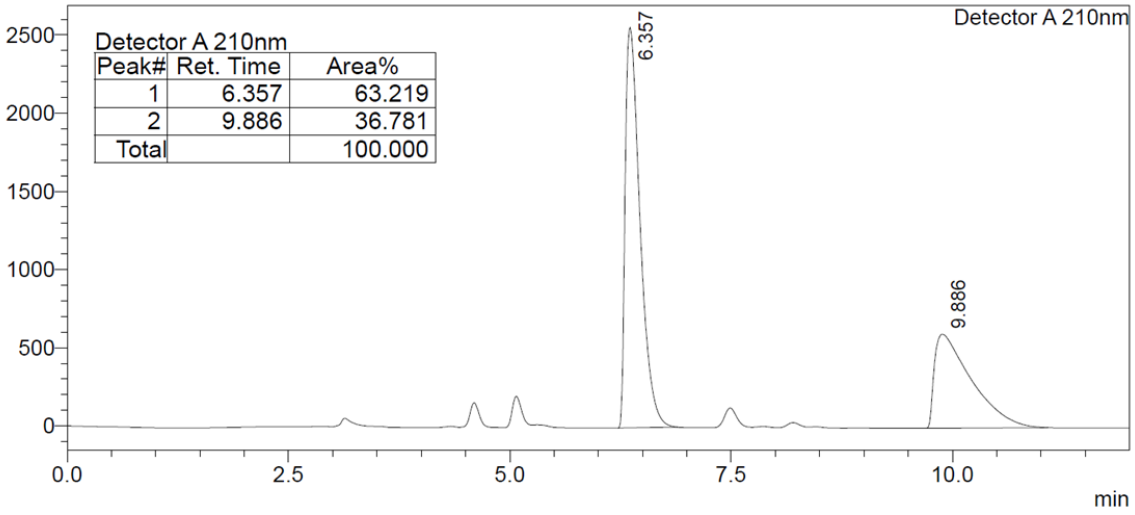
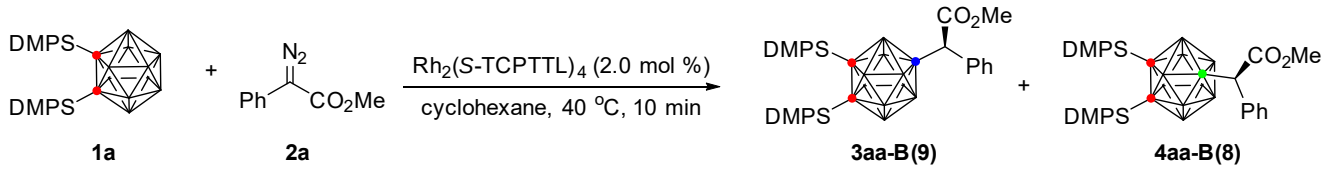
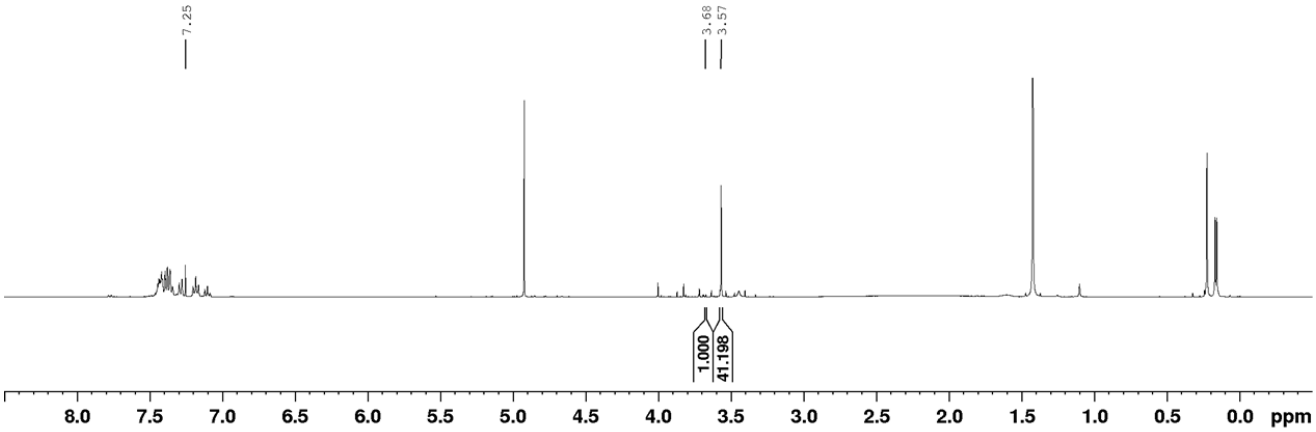
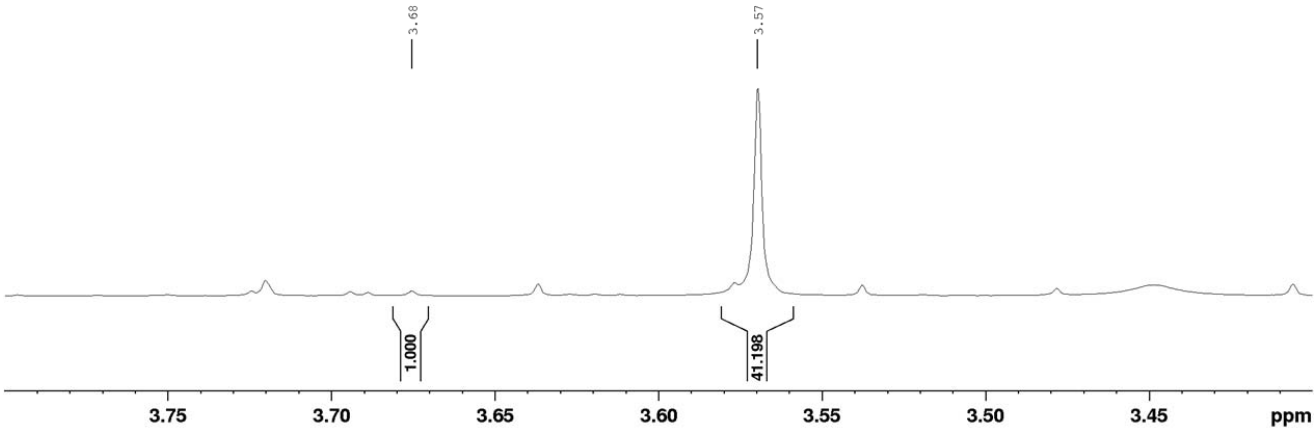


Table S1-entry 13







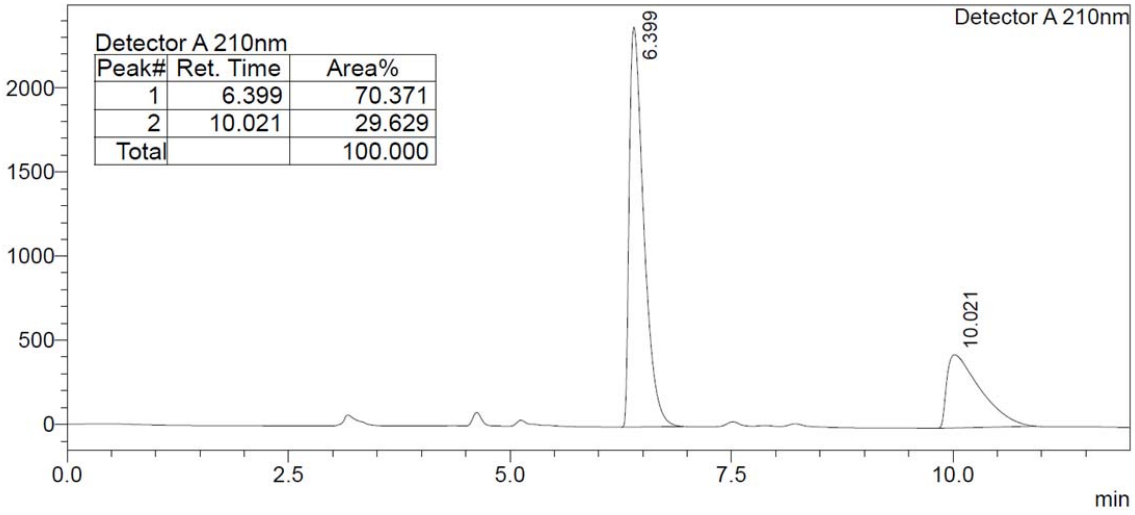
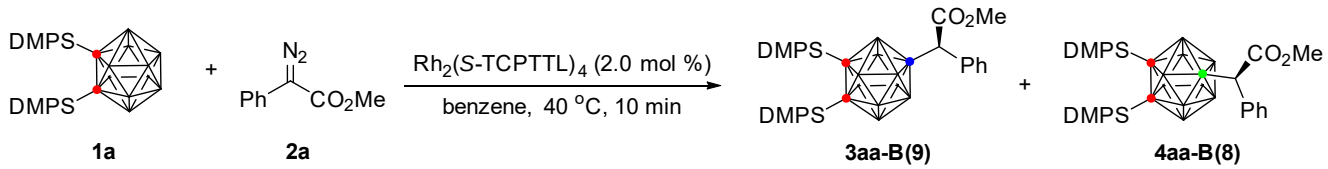
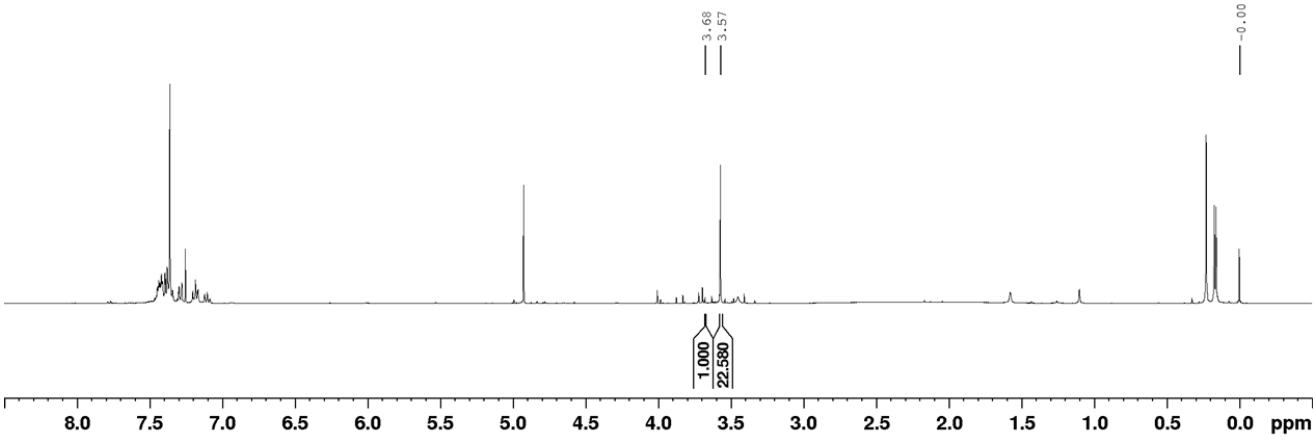
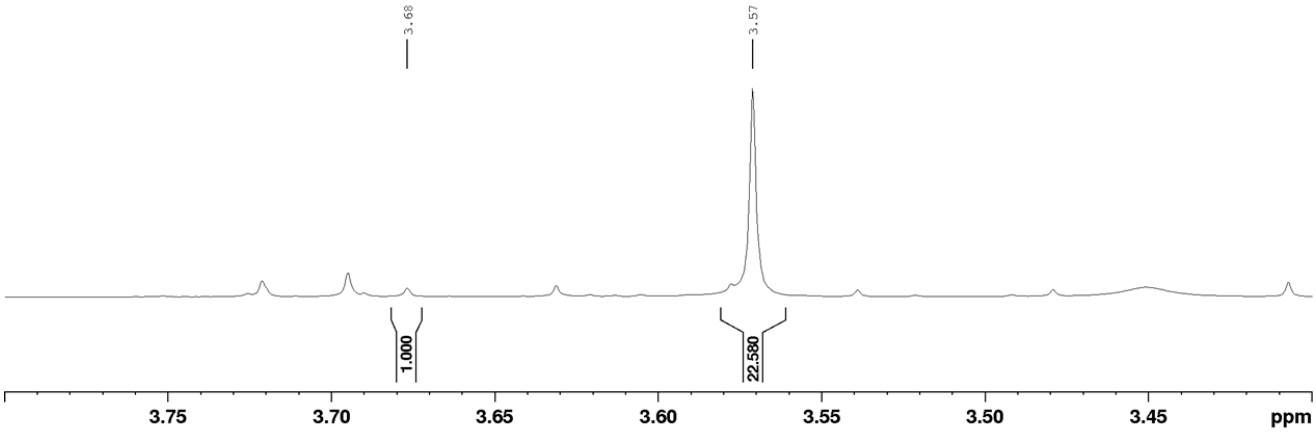


Table S1-entry 14







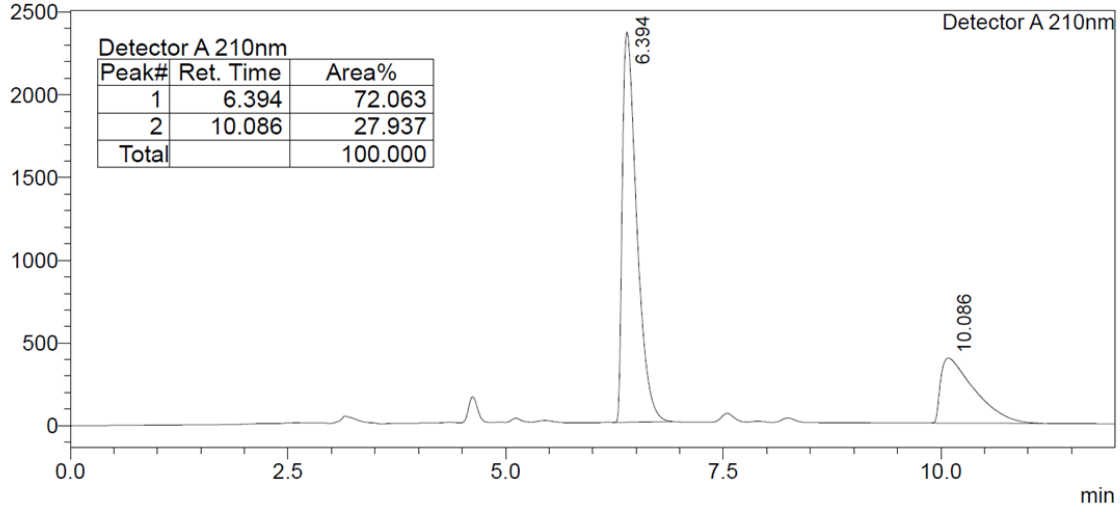
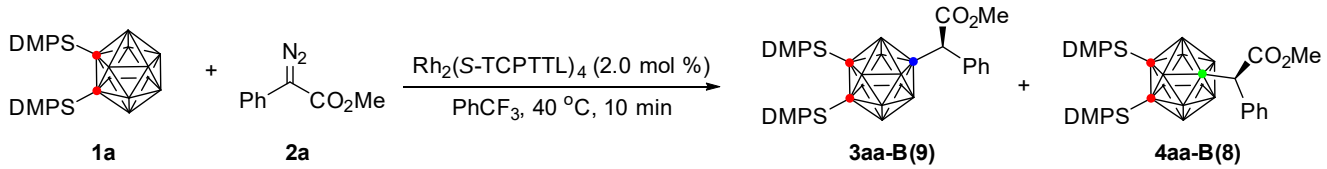
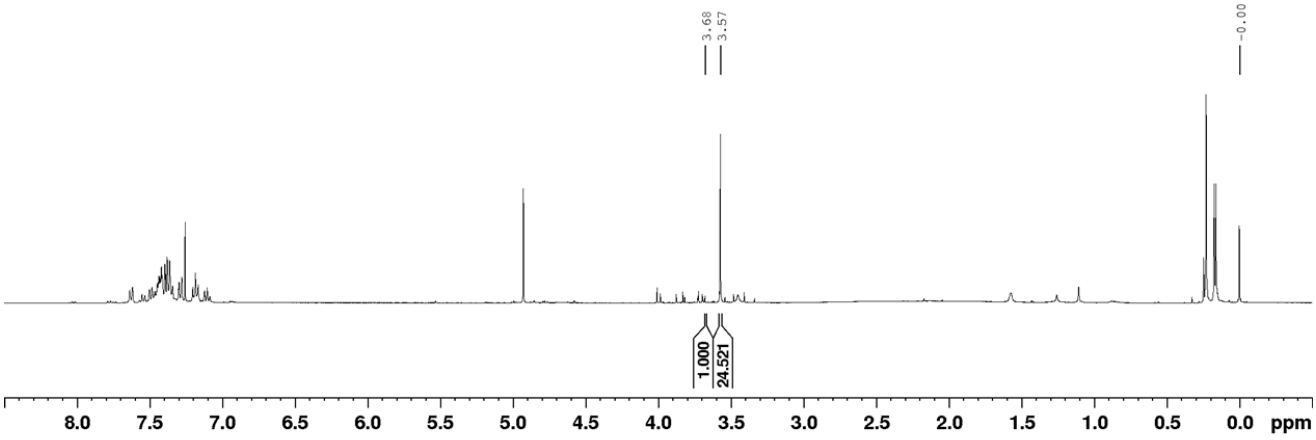
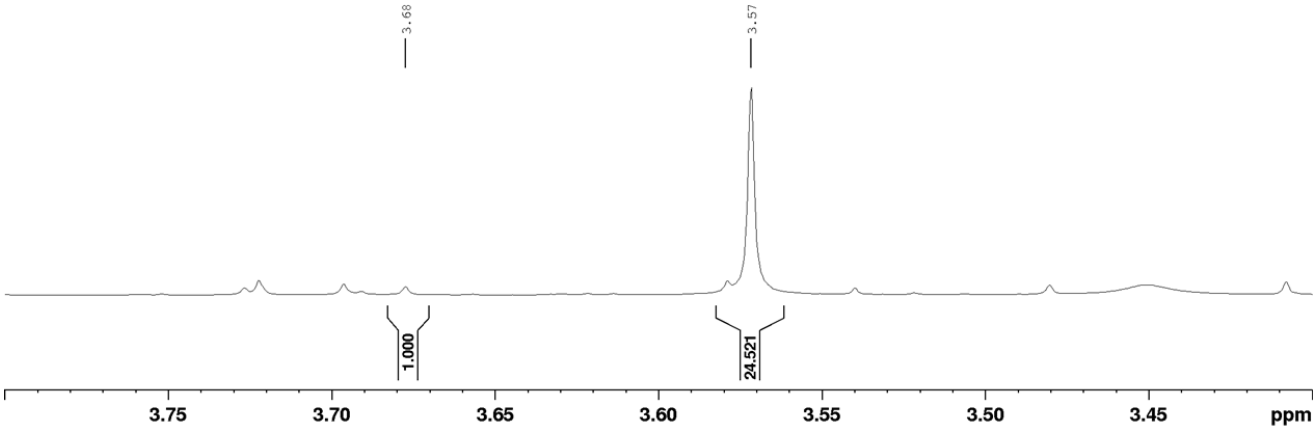
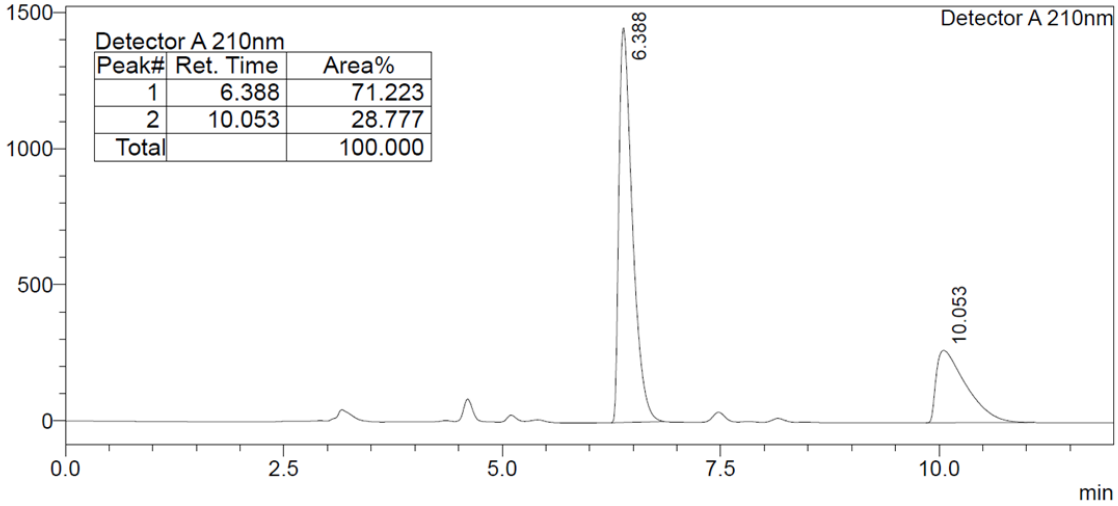


Table S1-entry 15









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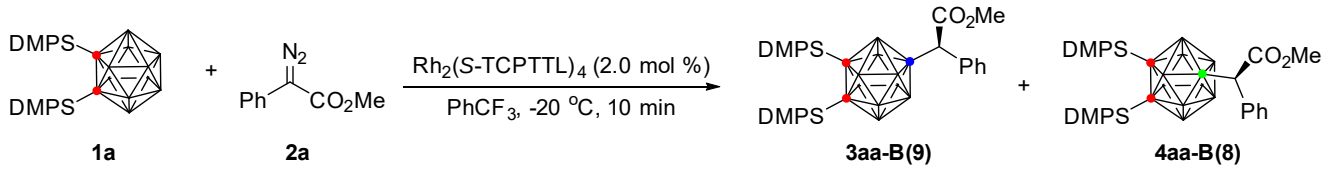
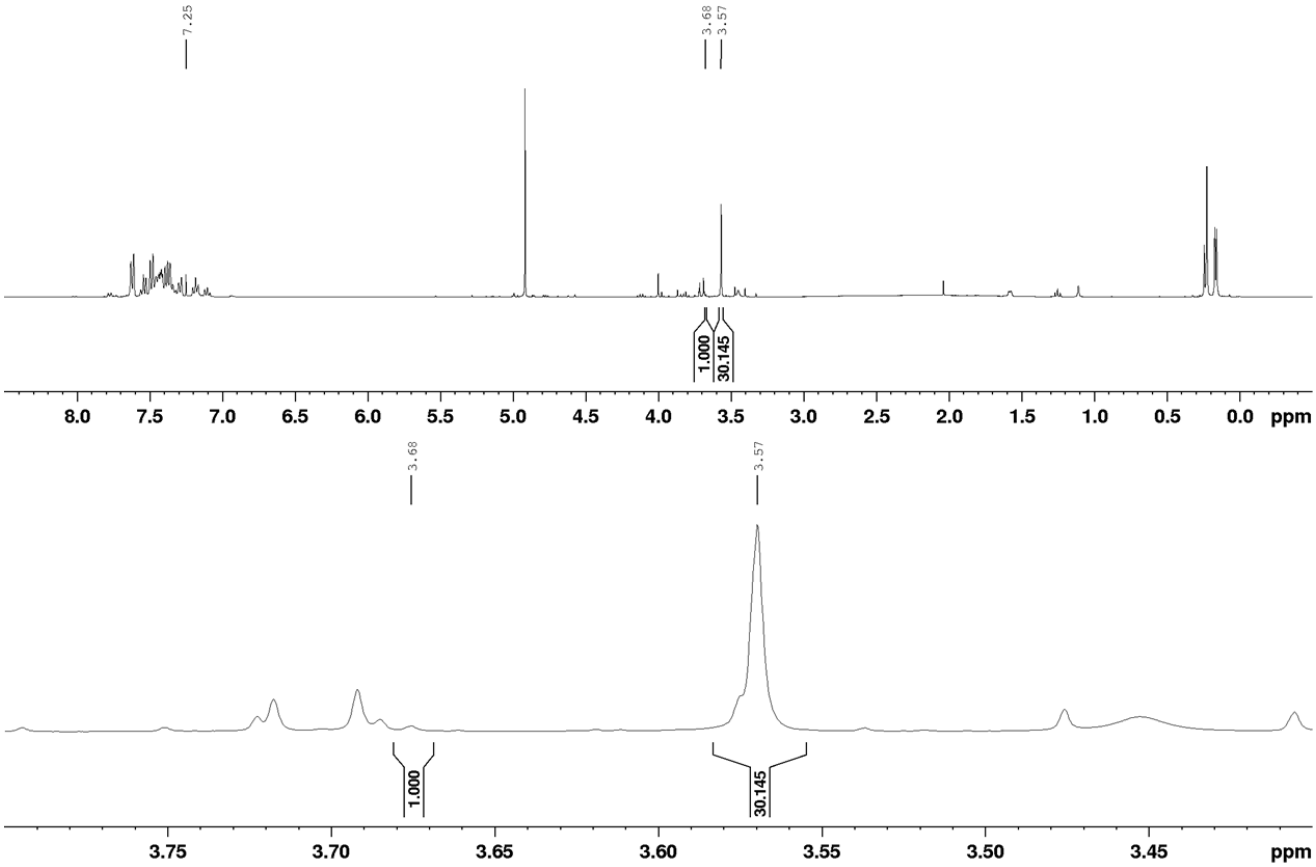




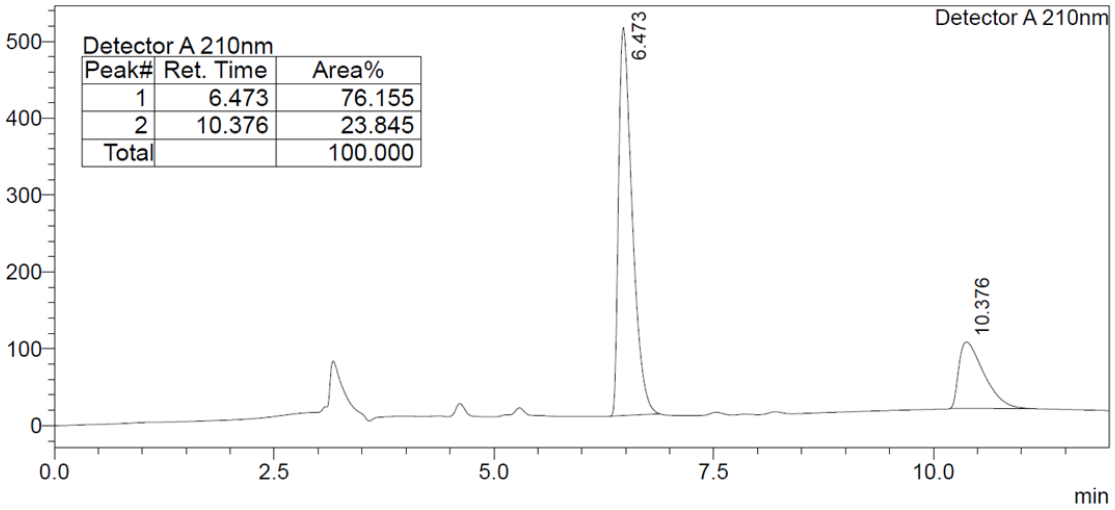
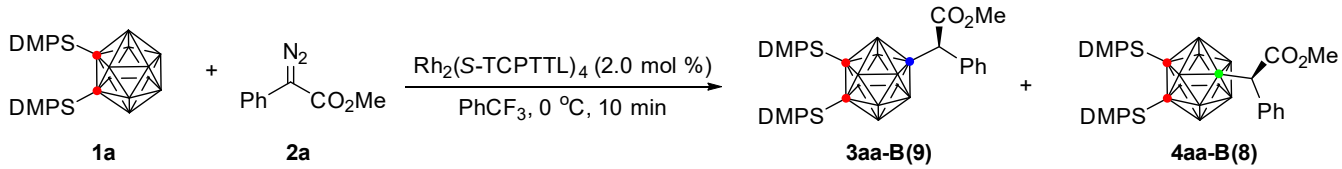
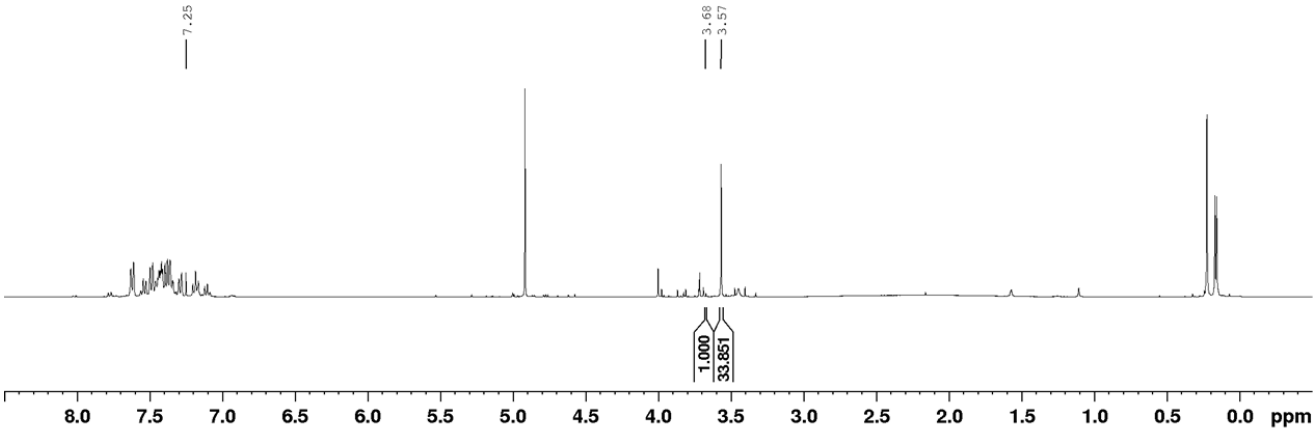
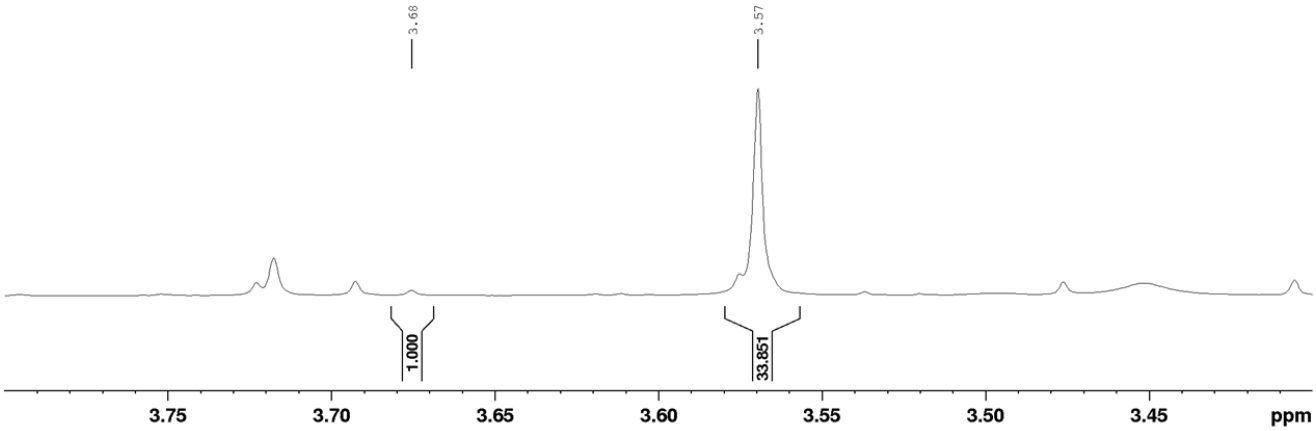


Table S1-entry 17







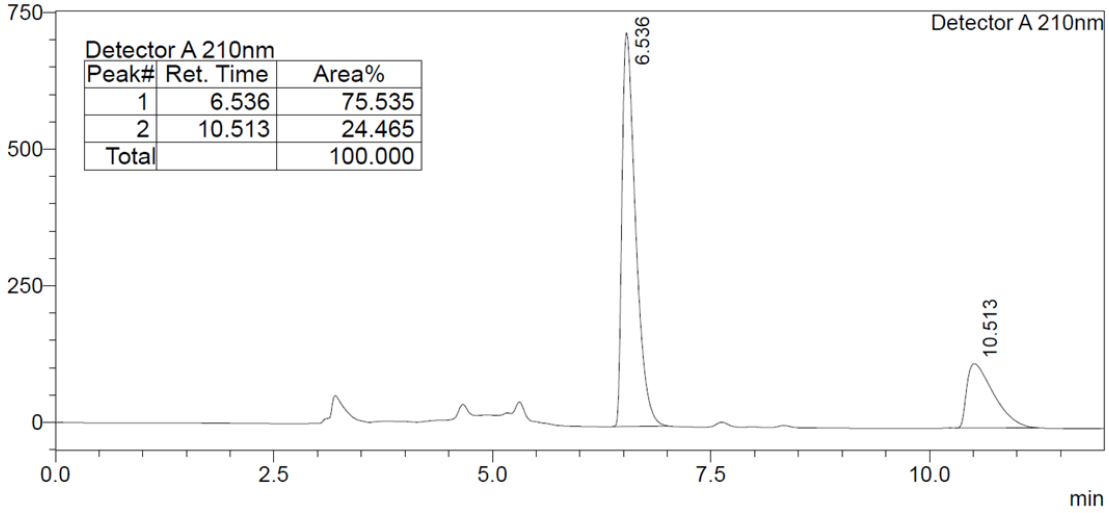
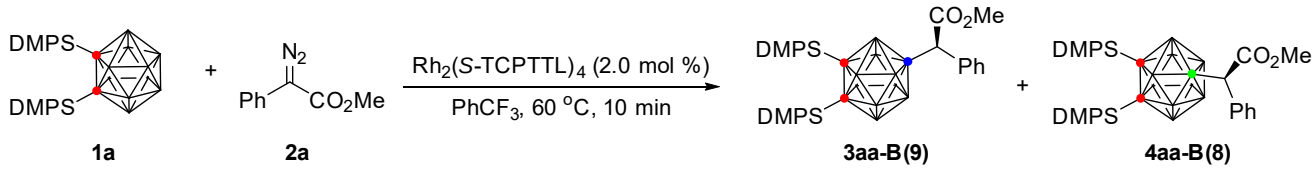
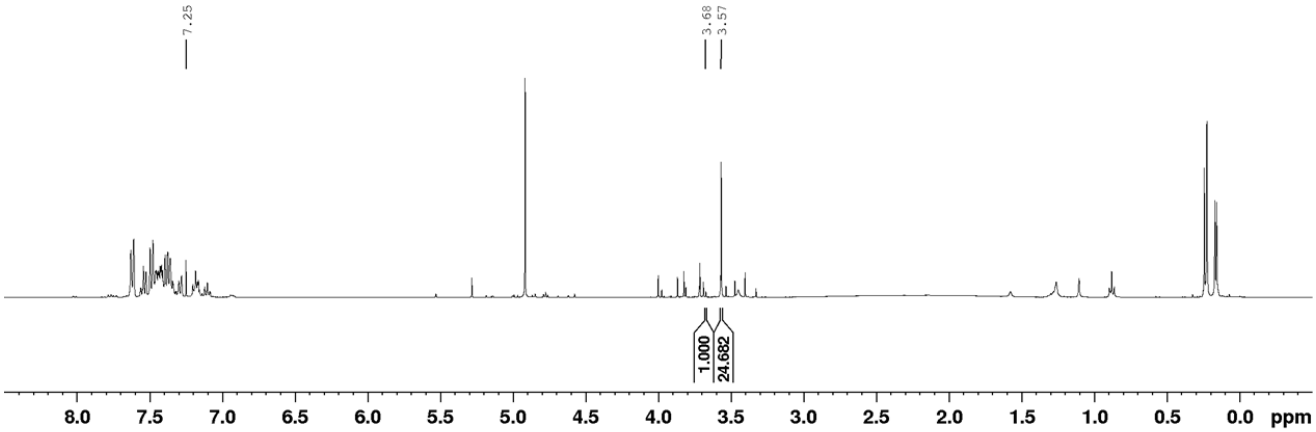
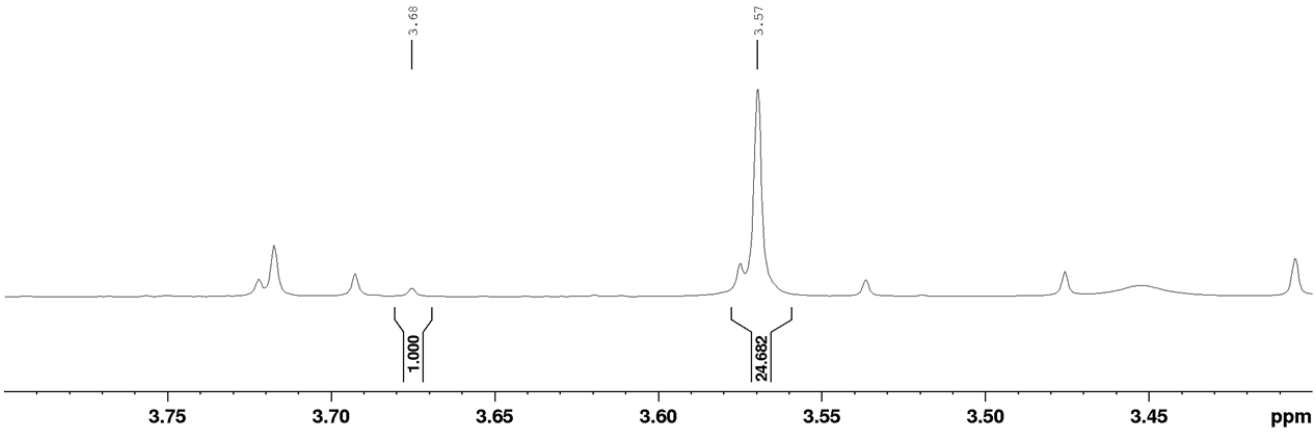


Table S1-entry 18







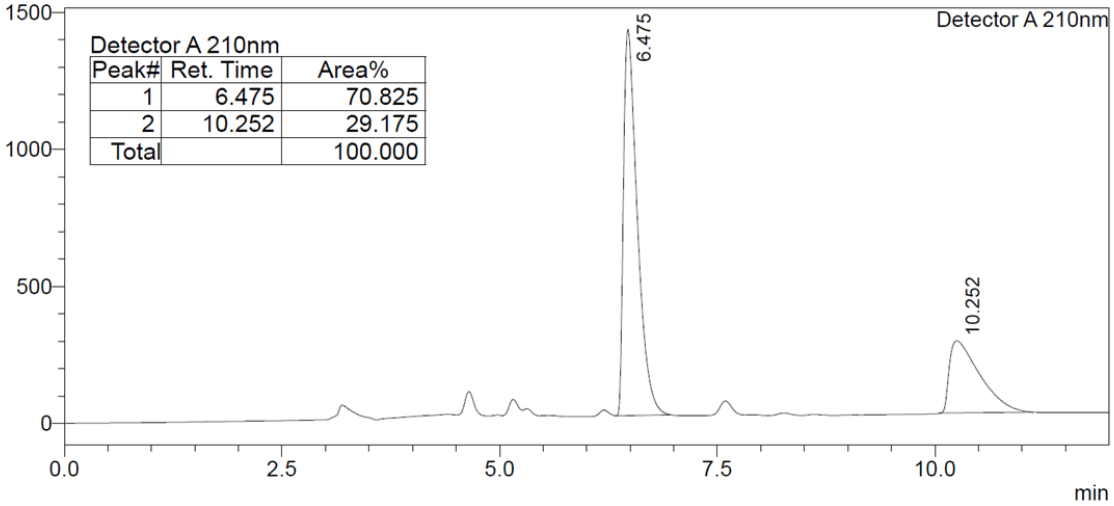
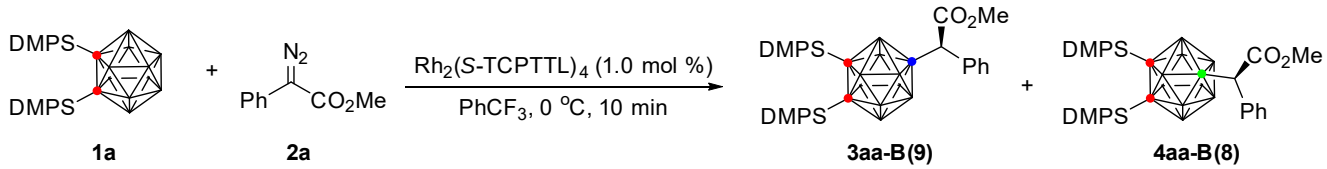
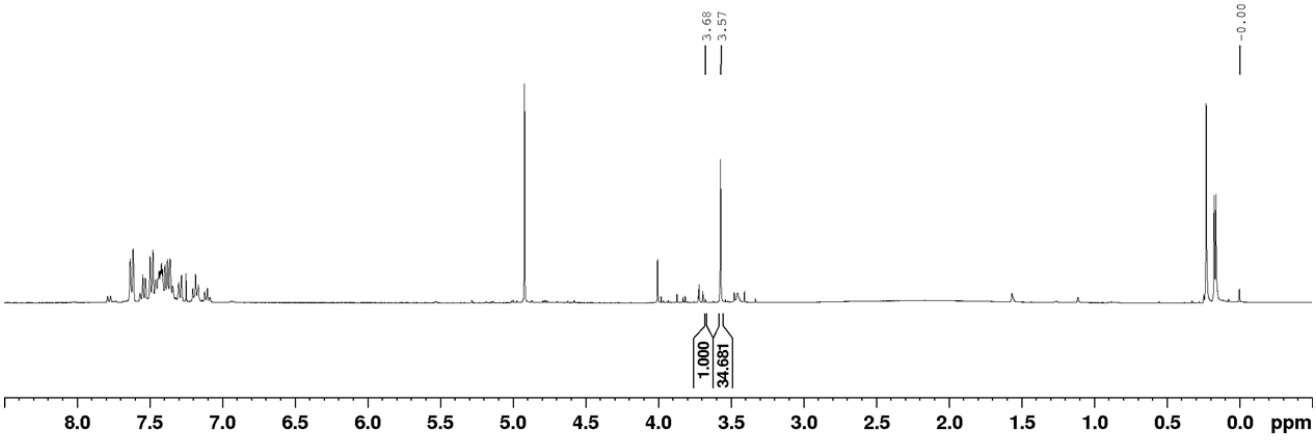
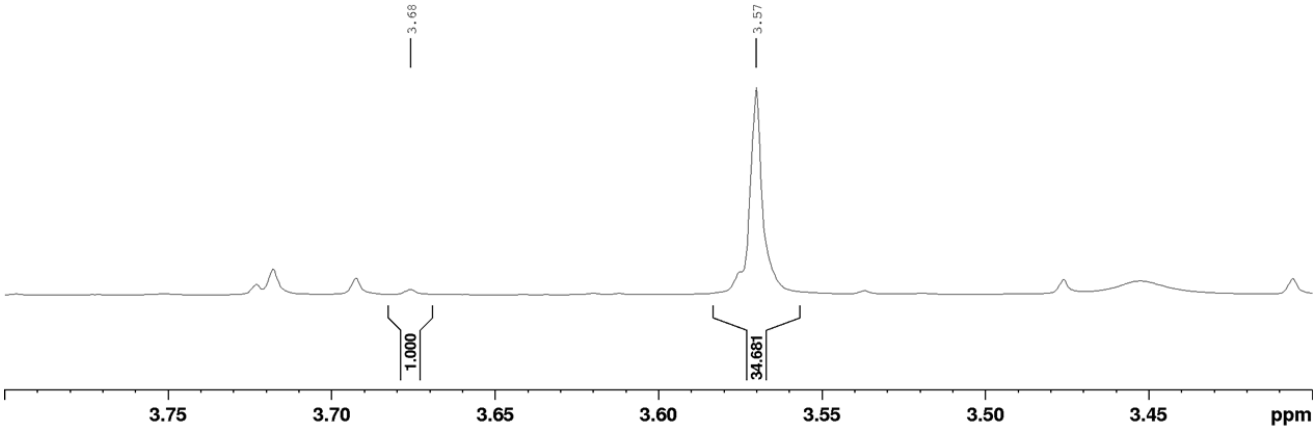
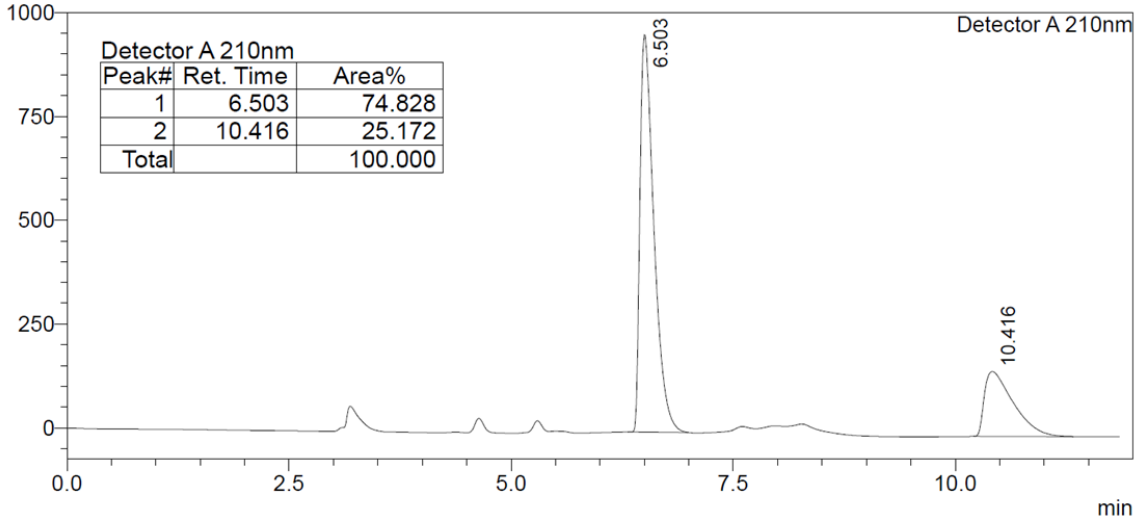


Table S1-entry 19









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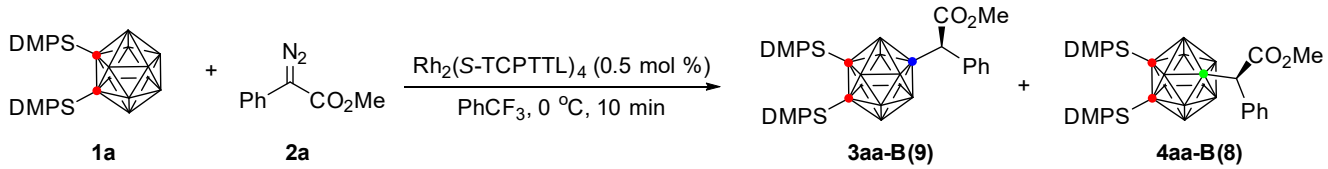
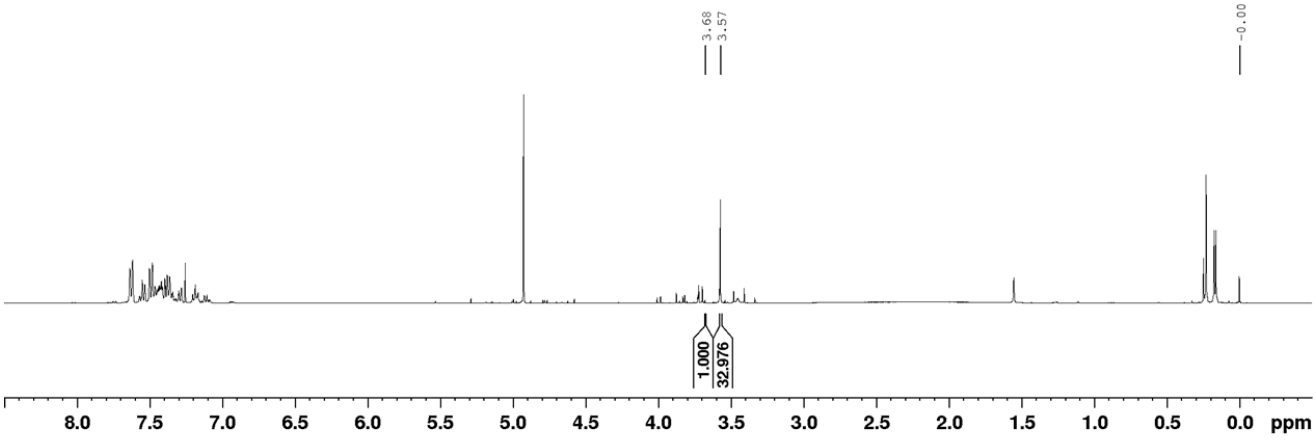
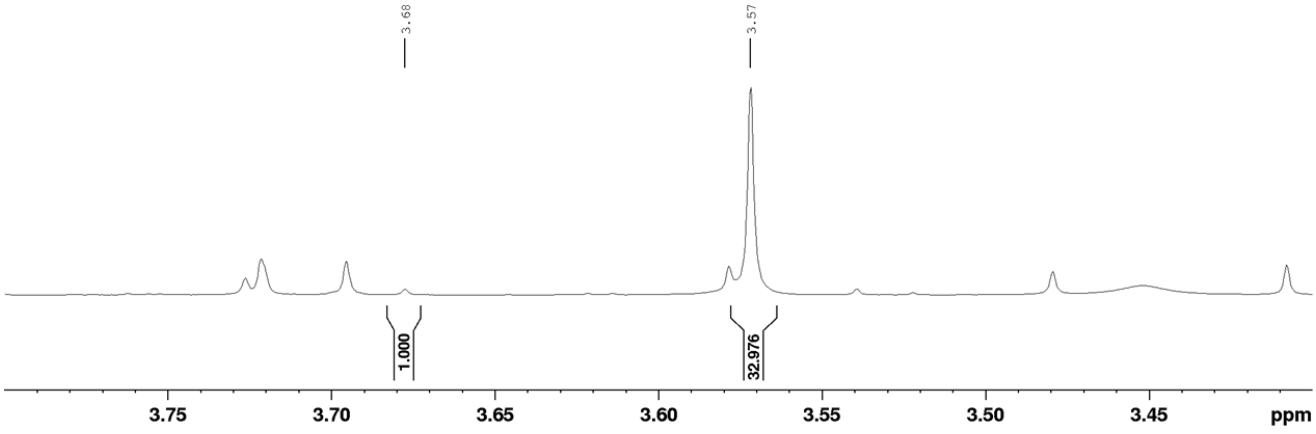






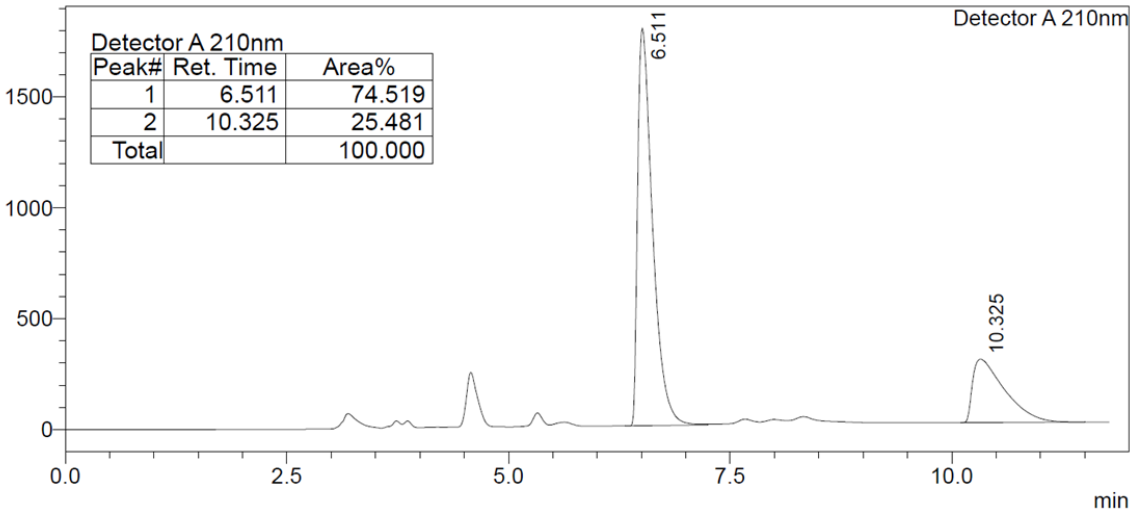
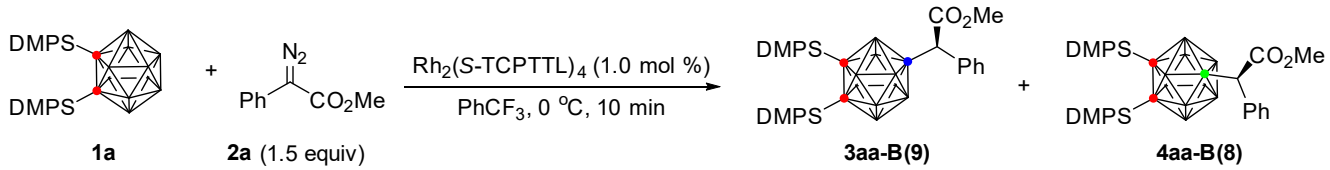
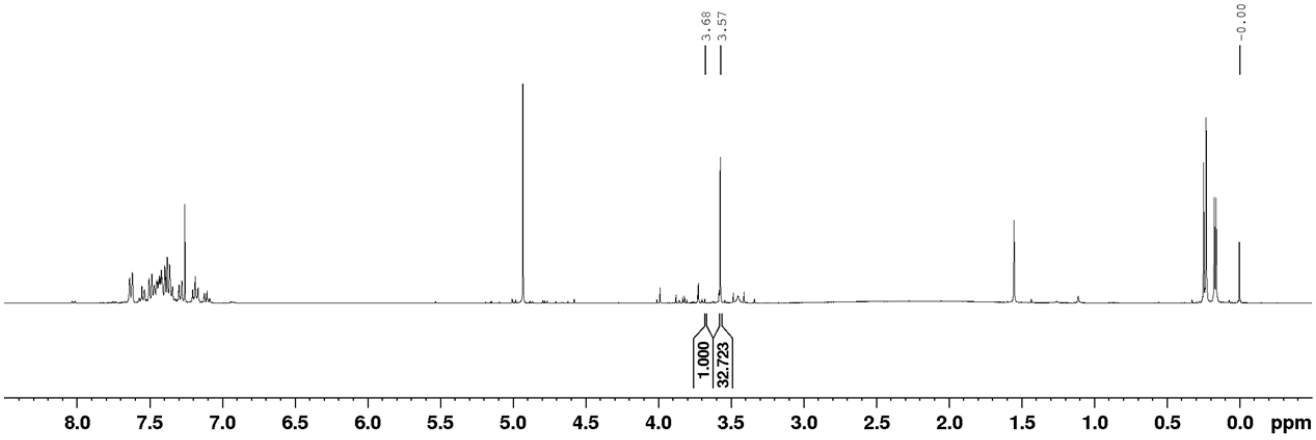
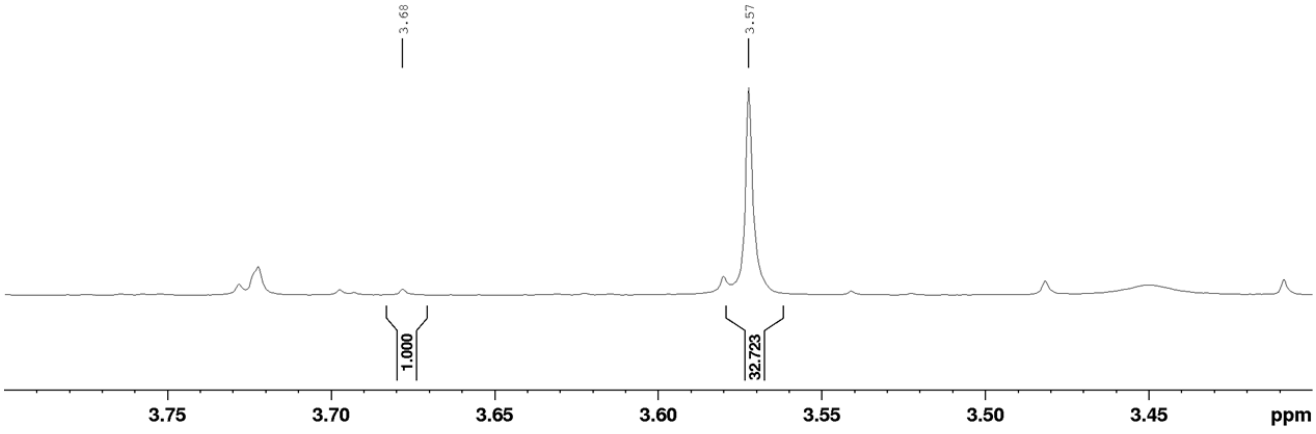
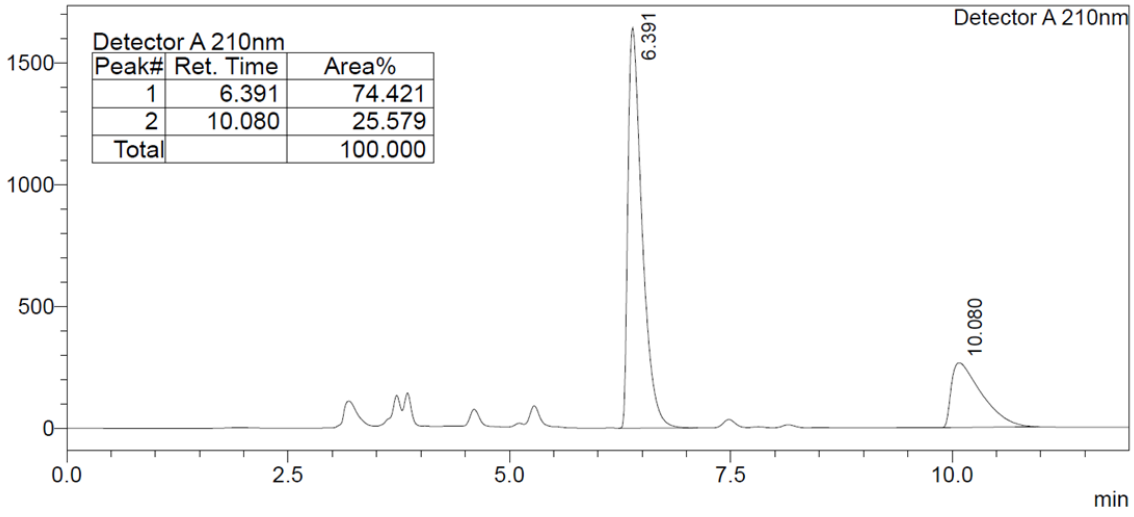


Table S1-entry 21



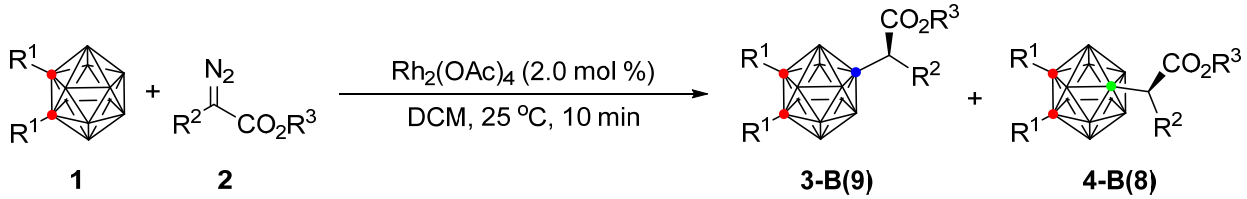






6. General Procedure of the Rh(II)-Catalyzed B(9)-Alkylation of Carboranes

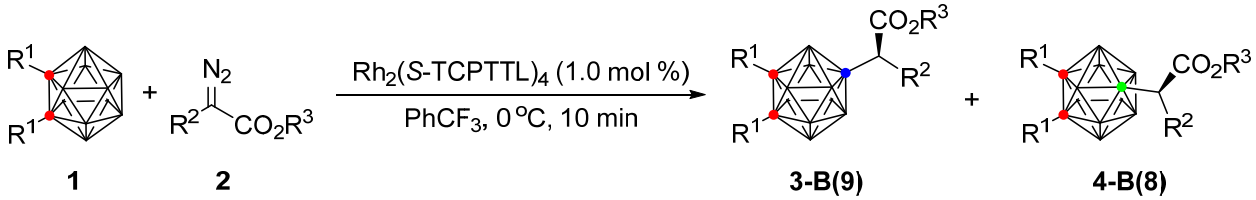
General Procedure for the Racemic B−H Insertion Product of *o*-Carboranes



1 **2** **3-B(9)** **4-B(8)**

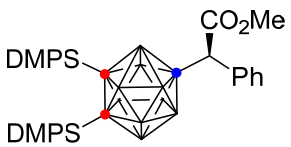
An oven dried test tube equipped with a magnetic stirrer was charged with *o*-carborane **1** (0.2 mmol, 1.0 equiv) and $Rh_2(OAc)_4$ (2.0 mol %) in DCM (1.5 mL) and stirred at 25 °C under a N_2 atmosphere. The diazo **2** (2.0 equiv) in DCM (1.5 mL) was added to the reaction mixture dropwise via syringe pump over 3 min. Then, the reaction mixture was stirred at 25 °C for 10 min and concentrated under reduced pressure for crude ^{1}H NMR. The crude product was purified by column chromatography on silica gel to afford product **3** and **4**.

General Procedure for the Chiral B−H Insertion Product of *o*-Carboranes



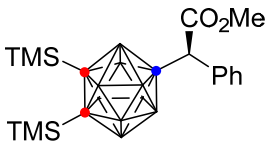
1 **2** **3-B(9)** **4-B(8)**

An oven dried test tube equipped with a magnetic stirrer was charged with *o*-carborane **1** (0.2 mmol, 1.0 equiv) and Rh_2(*S*-TCPTTL)$_4$ (1.0 mol %) in $PhCF_3$ (1.5 mL) and stirred at 0 °C under a N_2 atmosphere. The diazo **2** (2.0 equiv) in $PhCF_3$ (1.5 mL) was added to the reaction mixture dropwise via syringe pump over 3 min. Then, the reaction mixture was stirred at 0 °C for 10 min and concentrated under reduced pressure for crude ^{1}H NMR. The crude product was purified by column chromatography on silica gel to afford product **3** and **4**.

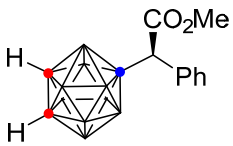


3aa: Yield: 109.9 mg (98%); Regioisomeric ratio (r.r.) = 35:1 (determined from crude ^{1}H NMR analysis of the racemic product and the chiral product); R_f = 0.30 (Et_2O:Hexane = 1:15); White solid; Melting point: 67-68 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.34 (m, 10H), 7.30-7.28 (m, 2H), 7.20-7.16 (m, 2H), 7.12-7.08 (m, 1H), 3.57 (s, 3H), 3.45 (s, 1H), 0.23 (s, 6H), 0.17 (s, 3H), 0.16 (s, 3H); ^{13}C{^{1}H} NMR

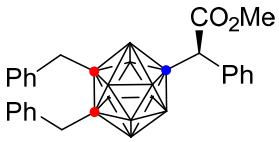
(100 MHz, $CDCl_3$) δ 175.0, 140.6, 135.5, 134.04, 134.01, 130.8, 130.7, 128.7, 127.98, 127.97, 127.8, 125.5, 73.6, 67.9, 51.2, 45.7, 0.25, 0.22, 0.11, 0.14; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 11.10 (1B), 2.28 (1B), -5.83 (2B), -9.35 - -11.14 (6B); IR (film): 2945, 2573, 1725, 1428, 1252, 1141, 1051, 818, 698 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{27}H_{40}B_{10}O_2Si_2^+$ 562.3497; Found 562.3502; $[\alpha]^{25}_D$: +22.5° (c = 0.24, CH_2Cl_2, 50% e.e.); HPLC (CHIRALPAK IB column, 4% *i*-PrOH in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 6.503 min (major) and 10.416 min (minor) 50% e.e..



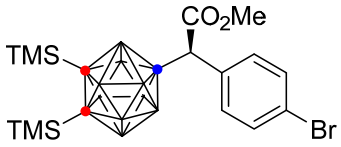
3ba: Yield: 84.7 mg (97%); Regioisomeric ratio (r.r.) = 22:1 (determined from crude ^1H NMR analysis of the racemic product and the chiral product); R_f = 0.35 (Et_2O:Hexane = 1:10); White solid; Melting point: 86-88 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.29 Hz, 2H), 7.24 (t, *J* = 7.38 Hz, 2H), 7.13 (t, *J* = 7.32 Hz, 1H), 3.64 (s, 3H), 3.50 (s, 1H), 0.29 (s, 9H), 0.26 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 175.1, 140.7, 128.8, 127.8, 125.6, 73.6, 67.9, 51.2, 46.6, 1.8, 1.6; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 10.75 (1B), 1.86 (1B), -5.54 (2B), -9.32 (4B), -11.82 (2B); IR (film): 2954, 2610, 2573, 1730, 1256, 1141, 1053, 837, 698 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{17}H_{36}B_{10}O_2Si_2^+$ 438.3184; Found 438.3184; $[\alpha]^{25}_D$: +13.6° (c = 0.68, CH_2Cl_2, 55% e.e.); HPLC (DAICEL IB column, 4% *i*-PrOH in hexane, 0.5 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 8.154 min (major) and 12.490 min (minor) 55% e.e..



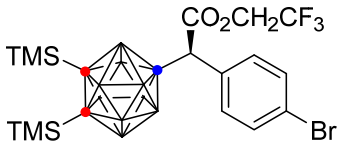
3ca: Yield: 56.1 mg (96%); Regioisomeric ratio (r.r.) = 7.3:1 (determined from crude ^1H NMR analysis of the racemic product and the chiral product); R_f = 0.30 (Et_2O:Hexane = 1:2); White solid; Melting point: 94-96 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.76 Hz, 2H), 7.25 (t, *J* = 7.38 Hz, 2H), 7.15 (t, *J* = 7.25 Hz, 1H), 3.64 (s, 3H), 3.45 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 175.0, 140.5, 128.7, 128.0, 125.8, 53.3, 51.3, 49.6, 45.3; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 7.04 (1B), -2.17 (1B), -9.03 (2B), -14.37 (4B), -15.50 (2B); IR (film): 3060, 2947, 2594, 1715, 1430, 1205, 1148, 1026, 698 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{11}H_{20}B_{10}O_2^+$ 294.2394; Found 294.2397; $[\alpha]^{25}_D$: +31.3° (c = 0.18, CH_2Cl_2, 65% e.e.); HPLC (DAICEL IB column, 15% *i*-PrOH in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 6.293 min (major) and 7.689 min (minor) 65% e.e..



3da: Yield: 94.4 mg (99%); Regioisomeric ratio (r.r.) = 14:1 (determined from crude ^{1}H NMR analysis of the racemic product and the chiral product); R_f = 0.30 (CH_2Cl_2:Hexane = 1:1); White solid; Melting point: 125-127 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.33 (m, 6H), 7.27-7.25 (m, 2H), 7.19-7.16 (m, 6H), 7.12-7.08 (m, 1H), 3.57 (d, J = 4.28 Hz, 4H), 3.53 (s, 3H), 3.37 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.0, 140.6, 135.0, 134.9, 130.4, 128.8, 128.73, 128.67, 128.27, 128.26, 127.8, 127.6, 78.3, 74.6, 51.1, 44.0, 41.5, 40.5; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 5.57 (1B), -4.08 (1B), -9.79 - -10.77 (8B); IR (film): 3029, 2945, 2606, 2577, 1724, 1494, 1141, 751, 696 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{25}H_{32}B_{10}O_2^+$ 474.3333; Found 474.3334; $[\alpha]^{25}_D$: +11.3^{o} (c = 0.23, CH_2Cl_2, 65% e.e.); HPLC (DAICEL IA column, 10% *i*-PrOH in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 7.602 min (major) and 8.429 min (minor) 65% e.e..

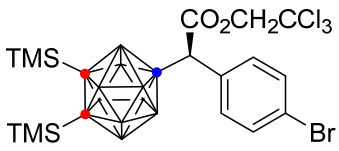


3bb: Yield: 99.2 mg (96%); Regioisomeric ratio (r.r.) = 36:1 (determined from crude ^{1}H NMR analysis of the racemic product and the chiral product); R_f = 0.35 (Et_2O:Hexane = 1:10); White solid; Melting point: 124-126 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.56 Hz, 2H), 7.26 (d, J = 8.53 Hz, 2H), 3.65 (s, 3H), 3.46 (s, 1H), 0.29 (s, 9H), 0.27 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.7, 139.7, 130.9, 130.5, 119.5, 73.7, 68.1, 51.3, 45.4, 1.8, 1.6; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 10.23 (1B), 1.71 (1B), -5.65 (2B), -9.47 (4B), -11.73 (2B); IR (film): 2947, 2615, 2573, 1728, 1485, 1256, 1143, 1051, 837 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{17}H_{35}B_{10}BrO_2Si_2^+$ 516.2290; Found 516.2292; $[\alpha]^{25}_D$: +9.0^{o} (c = 0.75, CH_2Cl_2, 86% e.e.); HPLC (DAICEL IA column, 4% *i*-PrOH in hexane, 0.5 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 9.192 min (minor) and 9.631 min (major) 86% e.e..

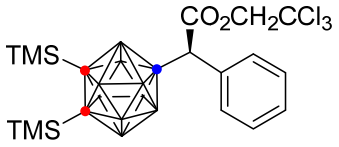


3bc: Yield: 113.7 mg (97%); Regioisomeric ratio (r.r.) = 48:1 (determined from crude ^{1}H NMR analysis of the racemic product and the chiral product); R_f = 0.35 (CH_2Cl_2:Hexane = 1:2); White solid; Melting point: 86-88 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.52 Hz, 2H), 7.24 (d, J = 8.52 Hz, 2H), 4.48-4.31 (m, 2H), 3.54 (s, 1H), 0.30 (s, 9H), 0.26 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.7, 138.8, 131.0, 130.4, 120.4 (q, J = 476.5 Hz), 119.8, 73.8, 68.5, 60.5 (q, J = 36.4), 44.3, 1.8, 1.6; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 9.61 (1B), 1.67 (1B), -5.74 (2B), -9.49 (4B), -11.71 (2B); ^{19}F NMR

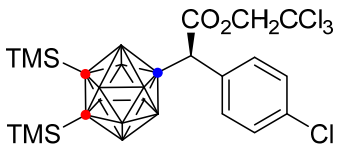
(376 MHz, CDCl3) δ -73.31; IR (film): 2961, 2615, 2575, 1746, 1280, 1256, 1165, 1128, 841 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{18}H_{34}B_{10}BrF_3O_2Si_2^+$ 584.2163; Found 584.2164; $[\alpha]^{25}_D$: +18.8° (c = 1.01, CH_2Cl_2, 90% e.e.); HPLC (DAICEL IA column, 4% CH_2Cl_2 in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 7.613 min (major) and 9.469 min (minor) 90% e.e..



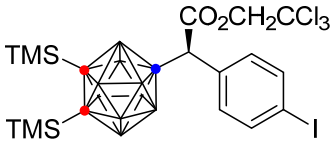
3bd: Yield: 121.5 mg (96%); Regioisomeric ratio (r.r.) = 25:1 (determined from crude ^{1}H NMR analysis of the racemic product and the chiral product); R_f = 0.35 (CH_2Cl_2:Hexane = 1:2); White solid; Melting point: 66-68 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.48 Hz, 2H), 7.27 (d, *J* = 8.56 Hz, 2H), 4.76 (d, *J* = 11.92 Hz, 1H), 4.58 (d, *J* = 11.92 Hz, 1H), 3.59 (s, 1H), 0.30 (s, 9H), 0.26 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.6, 139.0, 131.0, 130.5, 119.8, 95.1, 74.7, 73.8, 68.5, 45.4, 1.8, 1.6; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 9.73 (1B), 1.76 (1B), -5.72 (2B), -9.54 (4B), -11.80 (2B); IR (film): 2954, 2613, 2577, 1744, 1485, 1256, 1131, 1053, 850 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{18}H_{34}B_{10}BrCl_3O_2Si_2^+$ 632.1277; Found 632.1274; $[\alpha]^{25}_D$: +17.9° (c = 0.26, CH_2Cl_2, 99% e.e.); HPLC (DAICEL IA column, 4% CH_2Cl_2 in hexane, 0.5 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 18.373 min (minor) and 19.090 min (major) 99% e.e..



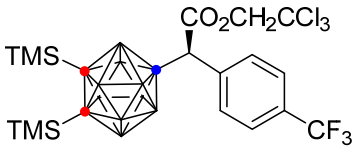
3be: Yield: 108.4 mg (98%); Regioisomeric ratio (r.r.) = 25:1 (determined from crude ^{1}H NMR analysis of the racemic product and the chiral product); R_f = 0.35 (CH_2Cl_2:Hexane = 1:2); Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.80 Hz, 2H), 7.25 (t, *J* = 11.22 Hz, 2H), 7.16 (t, *J* = 7.30 Hz, 1H), 4.75 (d, *J* = 11.94 Hz, 1H), 4.60 (d, *J* = 11.93 Hz, 1H), 3.64 (s, 1H), 0.29 (s, 9H), 0.25 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.1, 140.0, 128.7, 128.0, 125.8, 95.2, 74.7, 73.6, 68.2, 45.1, 1.8, 1.6; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 10.31 (1B), 1.90 (1B), -5.51 (2B), -9.49 (4B), -11.80 (s, 2B); IR (film): 2957, 2610, 2575, 1744, 1254, 1126, 1053, 848, 720 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{18}H_{35}B_{10}Cl_3O_2Si_2^+$ 554.2172; Found 554.2175; $[\alpha]^{25}_D$: +15.7° (c = 0.21, CH_2Cl_2, 89% e.e.); HPLC (DAICEL IA column, 4% CH_2Cl_2 in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 8.510 min (major) and 8.977 min (minor) 89% e.e..



3bf: Yield: 117.0 mg (99%); Regioisomeric ratio (r.r.) = > 50:1 (determined from crude ^{1}H NMR analysis of the racemic product and the chiral product); R_f = 0.35 (CH_2Cl_2:Hexane = 1:2); White solid; Melting point: 95-97 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.57 Hz, 2H), 7.23 (d, J = 8.58 Hz, 2H), 4.76 (d, J = 11.94 Hz, 1H), 4.58 (d, J = 11.93 Hz, 1H), 3.61 (s, 1H), 0.30 (s, 9H), 0.28 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.7, 138.4, 131.6, 130.0, 128.0, 95.1, 74.7, 73.7, 68.5, 45.4, 1.8, 1.6; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 9.84 (1B), 1.71 (1B), -5.69 (2B), -9.53 (4B), -11.79 (2B); IR (film): 2957, 2615, 2575, 1741, 1487, 1254, 1128, 1051, 831 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{18}H_{34}B_{10}Cl_4O_2Si_2^+$ 558.1782; Found 588.1785; $[\alpha]^{25}_D$: +8.2^{o} (c = 0.79, CH_2Cl_2, 99% e.e.); HPLC (DAICEL IA column, 4% CH_2Cl_2 in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 9.373 min (minor) and 9.689 min (major) 99% e.e..

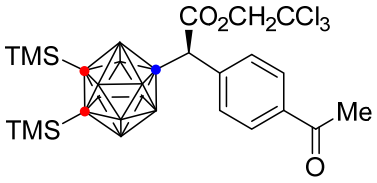


3bg: Yield: 131.8 mg (97%); Regioisomeric ratio (r.r.) = > 50:1 (determined from crude ^{1}H NMR analysis of the racemic product and the chiral product); R_f = 0.35 (CH_2Cl_2:Hexane = 1:2); White solid; Melting point: 101-103 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.44 Hz, 2H), 7.15 (d, J = 8.44 Hz, 2H), 4.76 (d, J = 11.92 Hz, 1H), 4.58 (d, J = 11.92 Hz, 1H), 3.57 (s, 1H), 0.30 (s, 9H), 0.26 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.5, 139.6, 136.9, 130.8, 95.1, 91.2, 74.6, 73.7, 68.5, 44.8, 1.8, 1.6; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 9.74 (1B), 1.72 (1B), -5.71 (2B), -9.54 (4B), -11.71 (2B); IR (film): 2959, 2613, 2575, 1744, 1481, 1256, 1128, 1051, 835 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{18}H_{34}B_{10}Cl_3IO_2Si_2^+$ 680.1138; Found 680.1139; $[\alpha]^{25}_D$: +25.1^{o} (c = 0.28, CH_2Cl_2, 99% e.e.); HPLC (DAICEL IF column, 5% *i*-PrOH in hexane, 0.5 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 9.413 min (minor) and 10.286 min (major) 99% e.e..

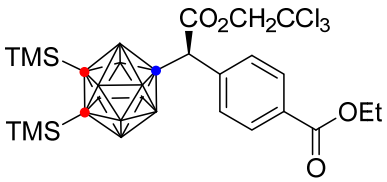


3bh: Yield: 114.5 mg (92%); Regioisomeric ratio (r.r.) = > 50:1 (determined from crude ^{1}H NMR analysis of the racemic product and the chiral product); R_f = 0.40 (CH_2Cl_2:Hexane = 1:2); White solid; Melting point: 98-100 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 4H), 4.78 (d, J = 11.92 Hz, 1H), 4.59 (d, J = 11.92 Hz, 1H), 3.71 (s, 1H), 0.30 (s, 9H), 0.26 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.4, 144.0, 128.9, 128.1 (q, J = 32.7 Hz), 124.9 (q, J = 3.9 Hz), 124.6 (q, J = 271.2 Hz), 95.1, 74.7, 73.9, 68.7, 45.8, 1.8, 1.6; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 9.63 (1B), 1.69 (1B), -

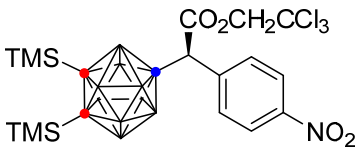
5.68 (2B), -9.53 (4B), -11.81 (2B); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.24; IR (film): 2957, 2615, 2575, 1741, 1322, 1256, 1119, 1064, 846 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{19}H_{34}B_{10}Cl_3F_3O_2Si_2^+$ 622.2046; Found 622.2047; $[\alpha]^{25}_D$: +21.8^o (c = 0.27, CH_2Cl_2, 98% e.e.); HPLC (DAICEL IF column, 4% CH_2Cl_2 in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 11.962 min (minor) and 12.568 min (major) 98% e.e..



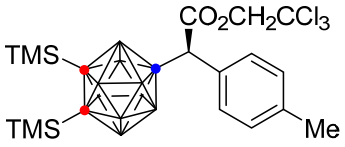
3bi: Yield: 105.8 mg (89%); Regioisomeric ratio (r.r.) = 29:1 (determined from crude ^{1}H NMR analysis of the racemic product and the chiral product); R_f = 0.25 (CH_2Cl_2:Hexane = 1:1); Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.28 Hz, 2H), 7.50 (d, *J* = 8.28 Hz, 2H), 4.78 (d, *J* = 11.96 Hz, 1H), 4.60 (d, *J* = 11.92 Hz, 1H), 3.72 (s, 1H), 2.58 (s, 3H), 0.30 (s, 9H), 0.26 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.2, 172.3, 145.7, 134.9, 128.8, 128.2, 95.1, 74.7, 73.8, 68.6, 26.7, 1.8, 1.6; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 9.59 (1B), 1.70 (1B), -5.70 (2B), -9.53 (4B), -11.72 (2B); IR (film): 2961, 2615, 2575, 1744, 1679, 1254, 1124, 835, 718 cm^{-1}; HRMS (FAB) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{38}B_{10}Cl_3O_3Si_2^+$ 597.2356; Found 597.2359; $[\alpha]^{25}_D$: +12.0^o (c = 0.53, CH_2Cl_2, 96% e.e.); HPLC (DAICEL IA column, 4% *i*-PrOH in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 6.936 min (minor) and 8.020 min (major) 96% e.e..



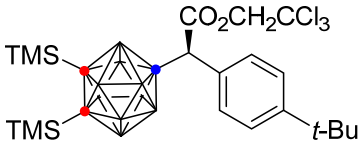
3bj: Yield: 122.2 mg (98%); Regioisomeric ratio (r.r.) = 47:1 (determined from crude ^{1}H NMR analysis of the racemic product and the chiral product); R_f = 0.30 (Et_2O:Hexane = 1:6); Colorless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.48 Hz, 2H), 7.48 (d, *J* = 8.40 Hz, 2H), 4.77 (d, *J* = 11.94 Hz, 1H), 4.60 (d, *J* = 11.92 Hz, 1H), 4.35 (q, *J* = 7.12 Hz, 2H), 3.71 (s, 1H), 1.33 (t, *J* = 7.12 Hz, 1H), 0.29 (s, 9H), 0.28 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.4, 166.9, 145.2, 129.3, 128.6, 128.0, 95.1, 74.7, 73.7, 68.6, 60.8, 45.4, 14.5, 1.7, 1.6; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 9.65 (1B), 1.73 (1B), -5.72 (2B), -9.56 (4B), -11.82 (2B); IR (film): 2981, 2615, 2575, 1744, 1715, 1271, 1104, 1053, 841 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{21}H_{39}B_{10}Cl_3O_4Si_2^+$ 626.2383; Found 626.2383; $[\alpha]^{25}_D$: +9.8^o (c = 0.78, CH_2Cl_2, 98% e.e.); HPLC (DAICEL IE column, 6% *i*-PrOH in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 10.191 min (major) and 15.788 min (minor) 98% e.e..



3bk: Yield: 82.7 mg (69%); Regioisomeric ratio (r.r.) = > 50:1 (determined from crude ^{1}H NMR analysis of the racemic product and the chiral product); R_f = 0.30 (CH_2Cl_2:Hexane = 1:1); White solid; Melting point: 134-136 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.76 Hz, 2H), 7.57 (d, J = 8.80 Hz, 2H), 4.80 (d, J = 11.92 Hz, 1H), 4.60 (d, J = 11.92 Hz, 1H), 3.77 (s, 1H), 0.30 (s, 9H), 0.26 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.8, 147.7, 146.2, 129.3, 123.2, 94.9, 74.7, 74.0, 69.0, 45.7, 1.7, 1.6; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 9.16 (1B), 1.62 (1B), -5.75 (2B), -9.49 (4B), -11.63 (2B); IR (film): 2959, 2616, 2577, 1741, 1518, 1342, 1256, 1131, 841 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{18}H_{34}B_{10}Cl_3NO_4Si_2^+$ 599.2022; Found 599.2020; $[\alpha]^{25}_D$: +16.1^{o} (c = 0.47, CH_2Cl_2, 93% e.e.); HPLC (Both TMS groups were removed with K_2CO_3 for better separation), (DAICEL IE column, 15% *i*-PrOH in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 6.329 min (major) and 10.340 min (minor) 93% e.e..

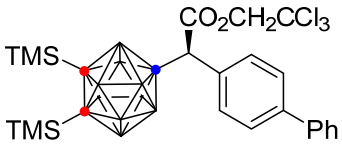


3bl: Yield: 112.1 mg (99%); Regioisomeric ratio (r.r.) = > 50:1 (determined from crude ^{1}H NMR analysis of the racemic product and the chiral product); R_f = 0.35 (CH_2Cl_2:Hexane = 1:2); White solid; Melting point: 77-79 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.08 Hz, 2H), 7.07 (d, J = 7.92 Hz, 2H), 4.73 (d, J = 11.92 Hz, 1H), 4.59 (d, J = 11.92 Hz, 1H), 3.60 (s, 1H), 2.30 (s, 3H), 0.29 (s, 9H), 0.26 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.2, 136.9, 135.2, 128.65, 128.62, 95.3, 74.6, 73.6, 68.1, 44.6, 21.1, 1.8, 1.6; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 10.27 (1B), 1.78 (1B), -5.64 (2B), -9.58 (4B), -11.89 (2B); IR (film): 2959, 2613, 2573, 1744, 1509, 1252, 1124, 1053, 848 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{19}H_{37}B_{10}Cl_3O_2Si_2^+$ 568.2328; Found 568.2332; $[\alpha]^{25}_D$: +9.9^{o} (c = 0.87, CH_2Cl_2, 94% e.e.); HPLC (DAICEL IA column, 4% CH_2Cl_2 in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 8.708 min (major) and 9.325 min (minor) 94% e.e..

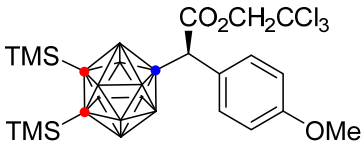


3bm: Yield: 106.2 mg (87%); Regioisomeric ratio (r.r.) = > 50:1 (determined from crude ^{1}H NMR analysis of the racemic product and the chiral product); R_f = 0.35 (CH_2Cl_2:Hexane = 1:2); White solid; Melting point: 113-115 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.55 Hz, 2H), 7.27 (d, J = 8.58 Hz, 2H), 4.73 (d, J = 11.94 Hz, 1H), 4.57 (d, J = 11.94 Hz, 1H), 3.62 (s, 1H), 1.29 (s, 3H), 0.29 (s, 9H), 0.24 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.3, 148.5, 136.9, 128.2, 124.8,

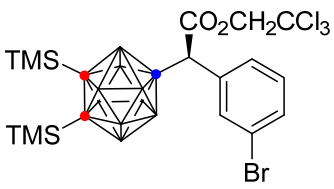
95.3, 74.7, 73.7, 68.1, 45.1, 34.4, 31.5, 1.8, 1.6; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 10.37 (1B), 1.69 (1B), -5.57 (2B), -9.60 (4B), -11.98 (2B); IR (film): 2961, 2610, 2577, 1744, 1514, 1261, 1126, 1053, 848 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{22}H_{43}B_{10}Cl_3O_2Si_2^+$ 610.2798; Found 610.2802; $[\alpha]^{25}_D$: +11.0° (c = 0.40, CH_2Cl_2, 98% e.e.); HPLC (DAICEL IB column, 4% CH_2Cl_2 in hexane, 0.5 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 9.196 min (major) and 9.910 min (minor) 98% e.e..



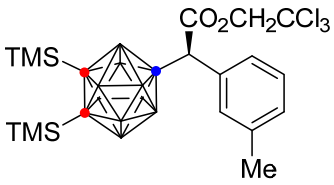
3bn: Yield: 117.3 mg (93%); Regioisomeric ratio (r.r.) = > 50:1 (determined from crude ^1H NMR analysis of the racemic product and the chiral product); R_f = 0.25 (CH_2Cl_2:Hexane = 1:3); Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.61-7.57 (m, 2H), 7.52 (d, *J* = 8.48 Hz, 2H), 7.47 (d, *J* = 8.48 Hz, 2H), 7.42 (t, *J* = 7.62 Hz, 2 H), 7.31 (t, *J* = 7.34 Hz, 1 H), 4.77 (d, *J* = 11.96 Hz, 1H), 4.61 (d, *J* = 11.92 Hz, 1H), 3.69 (s, 1H), 0.30 (s, 9H), 0.26 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.1, 141.3, 139.1, 138.6, 129.1, 128.8, 127.1, 127.0, 126.6, 95.2, 74.7, 73.7, 68.3, 45.3, 1.8, 1.6,; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 10.23 (1B), 1.91 (1B), -5.53 (2B), -9.47 (4B), -11.65 (2B); IR (film): 2959, 2613, 2575, 1741, 1485, 1256, 1124, 1055, 837 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{24}H_{39}B_{10}Cl_3O_2Si_2^+$ 630.2485; Found 630.2486; $[\alpha]^{25}_D$: +9.4° (c = 0.84, CH_2Cl_2, 99% e.e.); HPLC (DAICEL IA column, 4% *i*-PrOH in hexane, 0.5 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 8.941 min (minor) and 9.518 min (major) 99% e.e..



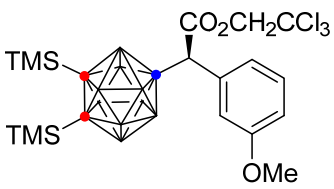
3bo: Yield: 107.7 mg (92%); Regioisomeric ratio (r.r.) = 29:1 (determined from crude ^1H NMR analysis of the racemic product and the chiral product); R_f = 0.40 (CH_2Cl_2:Hexane = 1:1); Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.72 Hz, 2H), 6.81 (d, *J* = 8.72 Hz, 2H), 4.74 (d, *J* = 11.92 Hz, 1H), 4.58 (d, *J* = 11.96 Hz, 1H), 3.78 (s, 3H), 3.58 (s, 1H), 0.29 (s, 9H), 0.26 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.3, 157.8, 132.2, 129.7, 113.3, 95.2, 74.6, 73.6, 68.1, 55.3, 44.2, 1.8, 1.6; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 10.34 (1B), 1.76 (1B), -5.65 (2B), -9.58 (4B), -11.93 (2B); IR (film): 2954, 2835, 2613, 2575, 1744, 1508, 1254, 1122, 835 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{19}H_{37}B_{10}Cl_3O_3Si_2^+$ 584.2277; Found 584.2274; $[\alpha]^{25}_D$: +21.9° (c = 0.42, CH_2Cl_2, 97% e.e.); HPLC (DAICEL IB column, 4% *i*-PrOH in hexane, 0.5 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 8.162 min (major) and 10.091 min (minor) 97% e.e..



3bp: Yield: 115.4 mg (91%); Regioisomeric ratio (r.r.) = > 50:1 (determined from crude ^{1}H NMR analysis of the racemic product and the chiral product); R_f = 0.30 (CH_2Cl_2:Hexane = 1:2); Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (t, J = 1.78 Hz, 1H), 7.31-7.29 (m, 2H), 7.13 (t, J = 7.86 Hz, 1H), 4.75 (d, J = 11.92 Hz, 1H), 4.60 (d, J = 11.92 Hz, 1H), 3.59 (s, 1H), 0.30 (s, 9H), 0.27 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.4, 142.1, 131.7, 129.4, 128.9, 127.4, 122.0, 95.1, 74.7, 73.8, 68.6 , 45.4, 1.8, 1.6; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 9.76 (1B), 1.75 (1B), -5.66 (2B), -9.51 (4B), -11.81 (2B); IR (film): 2957, 2613, 2575, 1744, 1256, 1128, 1053, 850, 720 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{18}H_{34}B_{10}BrCl_3O_2Si_2^+$ 632.1277; Found 632.1276; $[\alpha]^{25}_D$: +9.4^o (c = 0.93, CH_2Cl_2, 80% e.e.); HPLC (DAICEL IA column, 4% CH_2Cl_2 in hexane, 0.7 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 11.119 min (major) and 11.959 min (minor) 80% e.e..

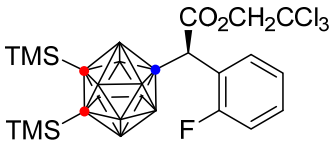


3bq: Yield: 113.5 mg (99%); Regioisomeric ratio (r.r.) = > 50:1 (determined from crude ^{1}H NMR analysis of the racemic product and the chiral product); R_f = 0.35 (CH_2Cl_2:Hexane = 1:2); Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 1H), 7.19-7.12 (m, 2H), 6.97 (d, J = 6.95 Hz, 1H), 4.72 (d, J = 11.94 Hz, 1H), 4.60 (d, J = 11.92 Hz, 1H), 3.59 (s, 1H), 2.32 (s, 3H), 0.29 (s, 9H), 0.26 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.1, 139.8, 137.3, 129.5, 127.8, 126.6, 125.8, 95.3, 74.6, 73.6, 68.2, 45.4, 21.7, 1.8, 1.6; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 10.22 (1B), 1.78 (1B), -5.64 (2B), -9.60 (4B), -12.01 (2B); IR (film): 2957, 2615, 2575, 1744, 1254, 1124, 1053, 841, 718 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{19}H_{37}B_{10}Cl_3O_2Si_2^+$ 568.2328; Found 568.2325; $[\alpha]^{25}_D$: +7.5^o (c = 0.90, CH_2Cl_2, 94% e.e.); HPLC (Both TMS groups were removed with K_2CO_3 for better separation), (DAICEL IB column, 5% *i*-PrOH in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 11.271 min (major) and 12.540 min (minor) 94% e.e..

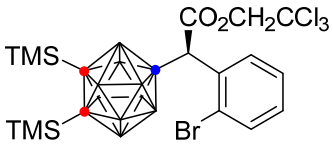


3br: Yield: 113.3 mg (97%); Regioisomeric ratio (r.r.) = 22:1 (determined from crude ^{1}H NMR analysis of the racemic product and the chiral product); R_f = 0.40 (CH_2Cl_2:Hexane = 1:1); Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, J = 7.92 Hz, 1H), 7.07 (s, 1H), 6.97 (d, J = 7.64 Hz, 1H), 6.75 (dd, J = 8.16 Hz, J = 2.40 Hz, 1H), 4.76 (d, J = 11.92 Hz, 1H), 4.63 (d, J = 11.96 Hz, 1H), 3.83 (s, 3H), 3.65 (s, 1H), 0.32 (s, 9H), 0.28 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.9, 159.3, 141.4, 128.8, 121.2,

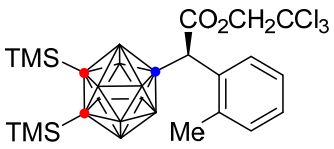
114.0, 111.8, 95.2, 74.7, 73.6, 68.2, 55.3, 45.8, 1.8, 1.6; $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) δ 10.15 (1B), 1.78 (1B), -5.62 (2B), -9.58 (4B), -11.91 (2B); IR (film): 2954, 2615, 2575, 1746, 1598, 1254, 1126, 1053, 841 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{19}H_{37}B_{10}Cl_3O_3Si_2^+$ 584.2277; Found 584.2275; $[\alpha]^{25}_D$: +9.7° (c = 0.66, CH_2Cl_2, 85% e.e.); HPLC (DAICEL IB column, 4% CH_2Cl_2 in hexane, 0.7 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 13.116 min (major) and 18.474 min (minor) 85% e.e..



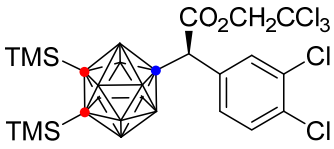
3bs: Yield: 101.6 mg (89%); Regioisomeric ratio (r.r.) = > 50:1 (determined from crude ^{1}H NMR analysis of the racemic product and the chiral product); R_f = 0.35 (CH_2Cl_2:Hexane = 1:2); Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.83 (m, 1H), 7.16-7.07 (m, 2H), 7.00-6.95 (m, 1H), 4.78 (d, *J* = 12.0 Hz, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 4.14 (s, 1H), 0.30 (s, 9H), 0.26 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 172.3, 159.5 (d, *J* = 244.2 Hz), 130.8 (d, *J* = 3.1 Hz), 127.1 (d, *J* = 8.1 Hz), 127.0 (d, *J* = 12.5 Hz), 123.5 (d, *J* = 3.4 Hz), 114.6 (d, *J* = 23.3 Hz), 95.1, 74.6, 73.7, 68.3, 35.2, 1.7, 1.6; $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) δ 9.69 (1B), 1.73 (1B), -5.60 (2B), -9.45 (4B), -11.71 (2B); ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.88; IR (film): 2959, 2613, 2575, 1744, 1256, 1126, 1049, 831, 751 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{18}H_{34}B_{10}Cl_3FO_2Si_2^+$ 572.2077; Found 572.2080; $[\alpha]^{25}_D$: +7.6° (c = 1.30, CH_2Cl_2, 97% e.e.); HPLC (DAICEL IB column, 5% CH_2Cl_2 in hexane, 0.7 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 7.652 min (minor) and 7.855 min (major) 97% e.e..



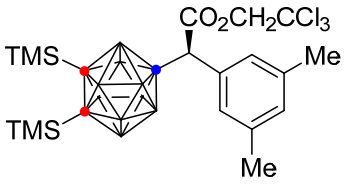
3bt: Yield: 122.8 mg (97%); Regioisomeric ratio (r.r.) = 18:1 (determined from crude ^{1}H NMR analysis of the racemic product and the chiral product); R_f = 0.30 (CH_2Cl_2:Hexane = 1:2); White solid; Melting point: 42-44 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.0 Hz, *J* = 1.7 Hz, 1H), 7.50 (dd, *J* = 8.0 Hz, *J* = 1.3 Hz, 1H), 7.29-7.25 (m, 1H), 7.03-6.99 (m, 1H), 4.77 (d, *J* = 11.9 Hz, 1H), 4.58 (d, *J* = 11.9 Hz, 1H), 4.43 (s, 1H), 0.30 (s, 9H), 0.27 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 172.5, 138.9, 132.3, 131.7, 127.3, 126.8, 124.2, 95.1, 74.7, 73.6, 68.6, 42.6, 1.8, 1.6; $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) δ 9.58 (1B), 1.67 (1B), -5.71 (2B), -9.49 (4B), -11.81 (2B); IR (film): 2959, 2613, 2577, 1741, 1254, 1131, 1051, 843, 744 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{18}H_{34}B_{10}BrCl_3O_2Si_2^+$ 632.1277; Found 632.1272; $[\alpha]^{25}_D$: +30.8° (c = 1.09, CH_2Cl_2, 70% e.e.); HPLC (Both TMS groups were removed with K_2CO_3 for better separation, DAICEL IB column, 5% *i*-PrOH in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 13.500 min (major) and 14.053 min (minor) 70% e.e..



3bu: Yield: 101.6 mg (89%); Regioisomeric ratio (r.r.) = 24:1 (determined from crude ^{1}H NMR analysis of the racemic product and the chiral product); R_f = 0.40 (CH_2Cl_2:Hexane = 1:2); White solid; Melting point: 84-86 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.76 (m, 1H), 7.18-7.14 (m, 1H), 7.10-7.03 (m, 2H), 4.72 (d, J = 11.9 Hz, 1H), 4.59 (d, J = 11.9 Hz, 1H), 3.98 (s, 1H), 2.32 (s, 3H), 0.30 (s, 9H), 0.26 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.2, 138.2, 134.9, 129.84, 129.80, 125.7, 125.6, 95.3, 74.6, 73.6, 68.3, 40.1, 20.6, 1.8, 1.6; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 10.04 (1B), 1.77 (1B), -5.68 (2B), -9.58 (4B), -11.87 (2B); IR (film): 2957, 2613, 2575, 1746, 1254, 1124, 1053, 837, 735 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{19}H_{37}B_{10}Cl_3O_2Si_2^+$ 568.2328; Found 568.2332; $[\alpha]^{25}_D$: +22.8^{o} (c = 0.19, CH_2Cl_2, 68% e.e.); HPLC (DAICEL IB column, 4% CH_2Cl_2 in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 6.094 min (minor) and 7.818 min (major) 68% e.e..

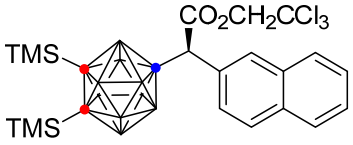


3bv: Yield: 115.5 mg (93%); Regioisomeric ratio (r.r.) = 45:1 (determined from crude ^{1}H NMR analysis of the racemic product and the chiral product); R_f = 0.30 (CH_2Cl_2:Hexane = 1:2); White solid; Melting point: 125-127 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 1.9 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.22 (dd, J = 8.3 Hz, J = 2.0 Hz, 1H), 4.77 (d, J = 11.9 Hz, 1H), 4.59 (d, J = 11.9 Hz, 1H), 3.58 (s, 1H), 0.30 (s, 9H), 0.28 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.2, 140.1, 131.8, 130.6, 129.8, 128.2, 95.0, 74.7, 73.9, 68.8, 44.6, 1.8, 1.6; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 9.46 (1B), 1.65 (1B), -5.77 (2B), -9.58 (4B), -11.81 (2B); IR (film): 2957, 2616, 2575, 1744, 1470, 1254, 1131, 1051, 841 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{18}H_{33}B_{10}Cl_5O_2Si_2^+$ 622.1392; Found 622.1395; $[\alpha]^{25}_D$: +16.4^{o} (c = 0.44, CH_2Cl_2, 97% e.e.); HPLC (DAICEL IB column, 4% CH_2Cl_2 in hexane, 0.5 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 11.010 min (major) and 11.495 min (minor) 97% e.e..

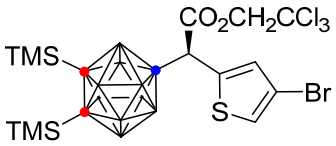


3bw: Yield: 110.5 mg (95%); Regioisomeric ratio (r.r.) = 38:1 (determined from crude ^{1}H NMR analysis of the racemic product and the chiral product); R_f = 0.35 (CH_2Cl_2:Hexane = 1:2); White solid; Melting point: 103-105 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (s, 2H), 6.80 (s, 1H), 4.70 (d, J = 12.0 Hz, 1H), 4.61 (d, J = 11.9 Hz, 1H), 3.55 (s, 1H), 2.28 (s, 6H), 0.29 (s, 9H), 0.26 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.1, 139.6, 137.2, 127.4, 126.6, 95.3, 74.6, 73.6, 68.1, 45.8, 21.6,

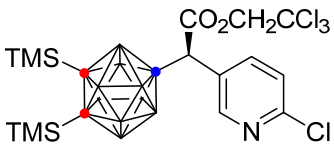
1.8, 1.6; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 10.29 (1B), 1.79 (1B), -5.65 (2B), -9.60 (4B), -12.00 (2B); IR (film): 2959, 2912, 2613, 2570, 1741, 1254, 1122, 1053, 835 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ Calcd for $C_{20}H_{39}B_{10}Cl_3O_2Si_2^+$ 582.2485; Found 582.2488; $[\alpha]^{25}_D$: +6.7° (c = 0.49, CH_2Cl_2, 78% e.e.); HPLC (DAICEL IA column, 4% CH_2Cl_2 in hexane, 0.7 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 9.803 min (minor) and 10.797 min (major) 78% e.e..



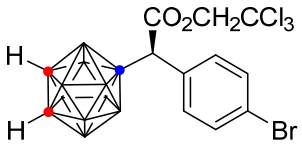
3bx: Yield: 105.3 mg (87%); Regioisomeric ratio (r.r.) = 46:1 (determined from crude ^1H NMR analysis of the racemic product and the chiral product); R_f = 0.40 (CH_2Cl_2:Hexane = 1:2); White solid; Melting point: 114-116 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82-7.74 (m, 4H), 7.61 (dd, *J* = 8.6 Hz, *J* = 1.8 Hz, 1H), 7.44-7.37 (m, 2H), 4.77 (d, *J* = 11.9 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 3.81 (s, 1H), 0.28 (s, 9H), 0.23 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.1, 137.5, 133.5, 132.1, 128.0, 127.9, 127.6, 127.3, 126.7, 125.7, 125.2, 95.2, 74.7, 73.6, 68.4, 45.2, 1.8, 1.6; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 10.13 (1B), 1.81 (1B), -5.66 (2B), -9.62 (4B), -11.95 (2B); IR (film): 2954, 2610, 2575, 1739, 1254, 1119, 1053, 835, 740 cm^{-1}; HRMS (FAB) *m/z*: $[M]^+$ Calcd for $C_{22}H_{37}B_{10}Cl_3O_2Si_2^+$ 604.2328; Found 604.2330.; $[\alpha]^{25}_D$: +13.3° (c = 0.67, CH_2Cl_2, 96% e.e.); HPLC (DAICEL IB column, 4% CH_2Cl_2 in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 8.605 min (major) and 9.577 min (minor) 96% e.e..



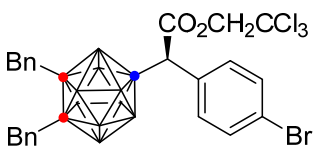
3by: Yield: 117.0 mg (92%); Regioisomeric ratio (r.r.) = > 50:1 (determined from crude ^1H NMR analysis of the racemic product and the chiral product); R_f = 0.30 (CH_2Cl_2:Hexane = 1:2); Yellow solid; Melting point: 91-93 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 1.0 Hz, 2H), 6.83 (d, *J* = 1.0 Hz, 2H), 4.81 (d, *J* = 11.9 Hz, 1H), 4.57 (d, *J* = 11.9 Hz, 1H), 3.91 (s, 1H), 0.30 (s, 9H), 0.28 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.9, 143.3, 127.0, 120.6, 108.6, 94.8, 74.9, 73.8, 68.5, 40.8, 1.8, 1.6; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 9.41 (1B), 1.58 (1B), -5.68 (2B), -9.58 (4B), -11.89 (2B); IR (film): 2959, 2619, 2575, 1744, 1516, 1258, 1132, 1053, 848 cm^{-1}; HRMS (FAB) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{33}B_{10}BrCl_3O_2SSi_2^+$ 639.0919; Found 639.0922.; $[\alpha]^{25}_D$: +27.6° (c = 0.95, CH_2Cl_2, 99% e.e.); HPLC (Both TMS groups were removed with K_2CO_3 for better separation, DAICEL IB column, 15% *i*-PrOH in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 6.681 min (major) and 6.904 min (minor) 99% e.e..



3bz: Yield: 68.4 mg (58%); Regioisomeric ratio (r.r.) = > 50:1 (determined from crude ^{1}H NMR analysis of the racemic product and the chiral product); R_f = 0.25 (CH_2Cl_2:Hexane = 1:1); White solid; Melting point: 99-101 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 2.4 Hz, 1H), 7.87 (dd, J = 8.4 Hz, J = 2.6 Hz, 2H), 7.25 (d, J = 8.0 Hz, 1H), 4.79 (d, J = 11.9 Hz, 1H), 4.58 (d, J = 11.9 Hz, 1H), 3.63 (s, 1H), 0.30 (s, 9H), 0.27 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.0, 149.3, 149.0, 139.2, 134.8, 123.5, 94.9, 74.8, 74.1, 69.0, 41.9, 1.8, 1.6; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 9.26 (1B), 1.61 (1B), -5.75 (2B), -9.49 (4B), -11.67 (2B); IR (film): 2957, 2616, 2575, 1744, 1458, 1256, 1134, 1104, 837 cm^{-1}; HRMS (FAB) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{34}B_{10}Cl_4NO_2Si_2^+$ 590.1807; Found 590.1815.; $[\alpha]^{25}_D$: +11.4^{o} (c = 0.44, CH_2Cl_2, 90% e.e.); HPLC (Reaction with Rh_2(*R*/*S*-TCPTTL)$_4$ as a catalyst and $PhCF_3$ as a solvent was conducted to get a racemic product, DAICEL ID column, 10% *i*-PrOH in hexane, 0.5 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 10.767 min (major) and 11.875 min (minor) 90% e.e..

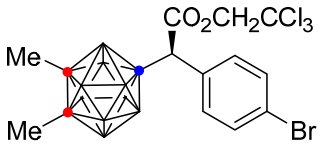


3cd: Yield: 87.9 mg (90%); Regioisomeric ratio (r.r.) = 5.2:1 (determined from crude ^{1}H NMR analysis of the racemic product and the chiral product); R_f = 0.35 (CH_2Cl_2:Hexane = 1:1); White solid; Melting point: 113-115 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.6 Hz, 2H), 7.28 (d, J = 8.6 Hz, 2H), 4.74 (d, J = 11.9 Hz, 1H), 4.61 (d, J = 11.9 Hz, 1H), 3.60 (s, 1H), 3.52 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.5, 138.7, 131.1, 130.4, 120.0, 94.9, 74.7, 53.3, 50.1, 44.1; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 6.36 (1B), -2.17 (1B), -9.04 (2B), -14.20 (4B), -15.35 (2B); IR (film): 3068, 2947, 2595, 2576, 1732, 1483, 1121, 1005, 719 cm^{-1}; HRMS (FAB) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{19}B_{10}BrCl_3O_2^+$ 489.0565; Found 489.0562; $[\alpha]^{25}_D$: +29.4^{o} (c = 0.24, CH_2Cl_2, 99% e.e.); HPLC (DAICEL IA column, 15% CH_2Cl_2 in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 18.532 min (major) and 21.477 min (minor) 99% e.e..

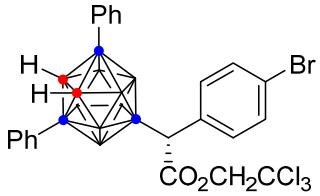


3dd: Yield: 125.5 mg (94%); Regioisomeric ratio (r.r.) = 6.3:1 (determined from crude ^{1}H NMR analysis of the racemic product and the chiral product); R_f = 0.25 (Et_2O:Hexane = 1:3); White solid; Melting point: 73-75 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.34 (m, 6H), 7.30 (d, J = 8.5 Hz, 2H), 7.19-

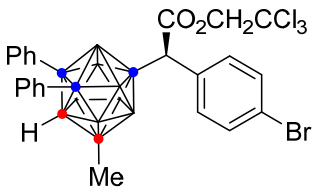
7.13 (m, 6H), 4.63 (d, J = 11.9 Hz, 1H), 4.43 (d, J = 11.9 Hz, 1H), 3.59 (s, 2H), 3.56 (s, 2H), 3.47 (s, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 172.6, 138.9, 134.9, 134.7, 131.0, 130.4, 128.8, 128.5, 128.4, 119.8, 95.0, 78.5, 75.1, 74.5, 43.6, 41.5, 40.5,; $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) δ 5.04 (1B), -3.92 (1B), -9.65 (6B), -10.70 (2B); IR (film): 3029, 2938, 2608, 2574, 1741, 1485, 1131, 751, 698 cm^{-1}; HRMS (FAB) *m/z*: $[M+H]^+$ Calcd for $C_{26}H_{31}B_{10}BrCl_3O_2^+$ 669.1504; Found 669.1501.; $[\alpha]^{25}_D$: +26.4° (c = 1.06, CH_2Cl_2, 99% e.e.); HPLC (DAICEL IB column, 25% *i*-PrOH in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 19.629 min (minor) and 21.137 min (major) 99% e.e..



3ed: Yield: 89.8 mg (97%); Regioisomeric ratio (r.r.) = 4.9:1 (determined from crude ^{1}H NMR analysis of the racemic product and the chiral product); R_f = 0.25 (Et_2O:Hexane = 1:6); White solid; Melting point: 89-91 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 4.73 (d, J = 11.9 Hz, 1H), 4.60 (d, J = 11.9 Hz, 1H), 3.57 (s, 1H), 1.99 (s, 3H), 1.97 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 172.7, 139.0, 131.1, 130.4, 119.9, 95.1, 74.8, 72.4, 49.2, 43.2, 23.5, 22.3; $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) δ 4.14 (1B), -4.73 (1B), -8.88 (2B), -10.01 (6B); IR (film): 2945, 2588, 1739, 1487, 1126, 1071, 1009, 985, 716 cm^{-1}; HRMS (FAB) *m/z*: $[M+H]^+$ Calcd for $C_{14}H_{23}B_{10}BrCl_3O_2^+$ 517.0878; Found 517.0881.; $[\alpha]^{25}_D$: +25.2° (c = 0.77, CH_2Cl_2, 99% e.e.); HPLC (DAICEL IA column, 15% CH_2Cl_2 in hexane, 0.7 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 8.437 min (minor) and 8.923 min (major) 99% e.e..

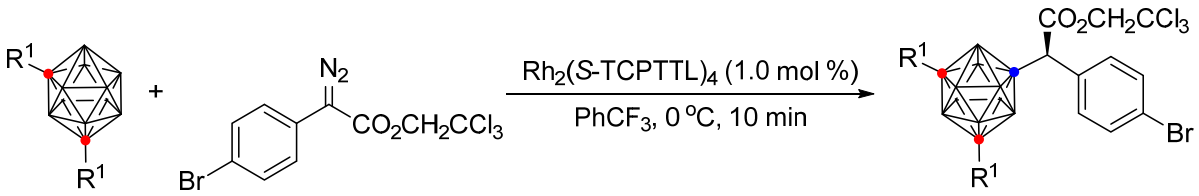


3fd: Yield: 113.9 mg (89%); R_f = 0.30 (Et_2O:Hexane = 1:6); White solid; Melting point: 123-125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.52 (m, 4H), 7.43-7.39 (m, 4H), 7.36-7.32 (m, 6H), 4.75 (d, J = 11.9 Hz, 1H), 4.63 (d, J = 11.9 Hz, 1H), 3.83 (s, 1H), 3.76 (s, 1H), 3.71 (s, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 172.6, 138.8, 133.2, 131.2, 130.5, 130.2, 128.5, 120.1, 95.0, 74.8, 57.8, 55.1, 44.2; $^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$) δ 6.52 (1B), -2.34 (1B), -4.45 (2B), -11.38 (2B), -13.79 (4B); IR (film): 3049, 2613, 2577, 1739, 1485, 1128, 1009, 740, 694 cm^{-1}; HRMS (FAB) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{27}B_{10}BrCl_3O_2^+$ 641.1191; Found 641.1193.; $[\alpha]^{25}_D$: +23.3° (c = 0.20, CH_2Cl_2, 35% e.e.); HPLC (DAICEL IB column, 15% *i*-PrOH in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 2.956 min (major) and 3.457 min (minor) 35% e.e..



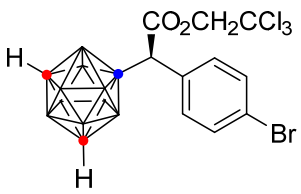
3gd: Yield: 126.8 mg (97%); R_f = 0.40 (Et_2O:Hexane = 1:1); White solid; Melting point: 91-93 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.6 Hz, 2H), 7.35 (d, J = 8.6 Hz, 2H), 7.21-7.10 (m, 10H), 4.75 (d, J = 12.0 Hz, 1H), 4.66 (d, J = 11.9 Hz, 1H), 3.98 (s, 1H), 3.70 (s, 1H), 2.10 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.6, 138.9, 132.8, 131.2, 130.5, 128.5, 127.8, 120.0, 95.1, 74.9, 67.7, 57.0, 44.2, 26.2; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ 5.62 (1B), -2.98 (2B), -6.42 (1B), -8.06 (2B), -11.51 (2B), -13.47 (2B); IR (film): 3051, 2592, 1732, 1485, 1254, 1131, 1007, 742, 694 cm^{-1}; HRMS (FAB) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{29}B_{10}BrCl_3O_2^+$ 655.1342; Found 655.1350.; $[\alpha]^{25}_D$: +22.1° (c = 0.60, CH_2Cl_2, 99% e.e.); HPLC (DAICEL IB column, 4% *i*-PrOH in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 11.606 min (major) 99% e.e..

General Procedure for the Chiral B−H Insertion Product of *m*-Carboranes



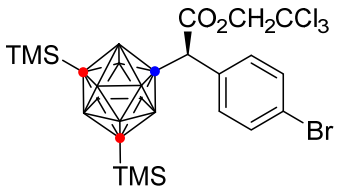
1 **2d** **3-B(9)**

An oven dried test tube equipped with a magnetic stirrer was charged with *m*-carborane **1** (0.2 mmol, 1.0 equiv) and Rh_2(*S*-TCPTTL)$_4$ (1.0 mol %) in $PhCF_3$ (1.5 mL) and stirred at 0 °C under a N_2 atmosphere. The diazo **2d** (2.0 equiv) in $PhCF_3$ (1.5 mL) was added to the reaction mixture dropwise via syringe pump over 3 min. Then, the reaction mixture was stirred at 0 °C for 10 min and concentrated under reduced pressure for crude ^1H NMR. The crude product was purified by column chromatography on silica gel to afford product **3**.



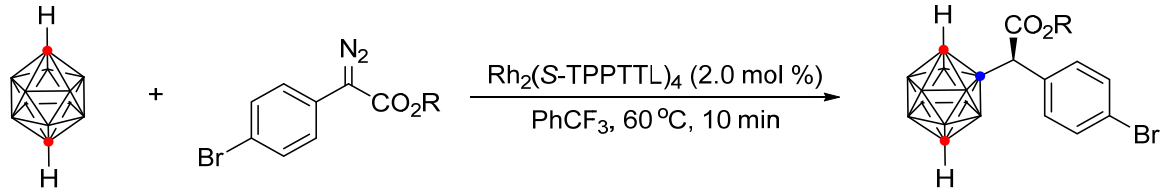
3hd: Yield: 74.1 mg (76%); R_f = 0.30 (CH_2Cl_2:Hexane = 1:2); Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 4.76 (d, J = 11.9 Hz, 1H), 4.66 (d, J = 12.0 Hz, 1H), 3.78 (s, 1H), 2.91 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.6, 138.9, 131.3, 130.4, 120.2, 94.9, 74.8, 54.5, 42.1; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ -0.58 (1B), -6.46 (2B), -9.96 (1B), -13.27 (2B), -13.71 (2B), -17.44 (1B), -19.38 (1B); IR (film): 3062, 2601, 1739, 1485, 1128, 1071, 1007, 802, 720 cm^{-1}; HRMS (FAB) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{19}B_{10}BrCl_3O_2^+$ 489.0565; Found 489.0562.; $[\alpha]^{25}_D$:

+9.6° (c = 1.02, CH_2Cl_2, 99% e.e.); HPLC (DAICEL IA column, 6% *i*-PrOH in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 6.507 min (major) and 7.333 min (minor) 99% e.e..



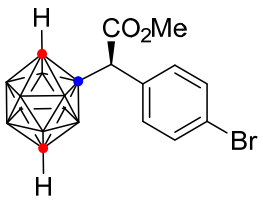
3id: Yield: 116.5 mg (92%); R_f = 0.25 (CH_2Cl_2:Hexane = 1:2); White solid; Melting point: 88-90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.5 Hz, 2H), 4.76 (d, J = 12.0 Hz, 1H), 4.63 (d, J = 11.9 Hz, 1H), 3.77 (s, 1H), 0.08 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.9, 139.2, 131.2, 130.5, 120.0, 95.1, 74.8, 67.6, 67.5, 42.7, -0.7; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 2.10 (1B), -2.81 (2B), -7.06 (1B), -10.04 (4B), -14.50 (1B), -16.02 (1B); IR (film): 2957, 2592, 1744, 1487, 1252, 1131, 1009, 846, 718 cm^{-1}; HRMS (FAB) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{35}B_{10}BrCl_3O_2Si_2^+$ 633.1355; Found 633.1357.; $[\alpha]^{25}_D$: +8.9° (c = 0.65, CH_2Cl_2, 95% e.e.); HPLC (DAICEL IA column, 4% CH_2Cl_2 in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 2.515 min (minor) and 6.159 min (major) 95% e.e..

General Procedure for the Chiral B−H Insertion Product of *p*-Carboranes



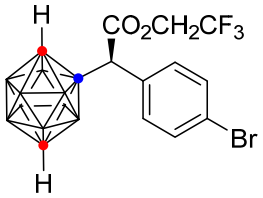
1j **2** **3-B(2)**

An oven dried test tube equipped with a magnetic stirrer was charged with *p*-carborane **1j** (0.2 mmol, 1.0 equiv) and Rh_2(*S*-TPPTTL)$_4$ (2.0 mol %) in $PhCF_3$ (1.5 mL) and stirred at 60 °C under a N_2 atmosphere. The diazo **2** (2.0 equiv) in $PhCF_3$ (1.5 mL) was added to the reaction mixture dropwise via syringe pump over 3 min. Then, the reaction mixture was stirred at 60 °C for 10 min and concentrated under reduced pressure for crude ^{1}H NMR. The crude product was purified by column chromatography on silica gel to afford product **3**.

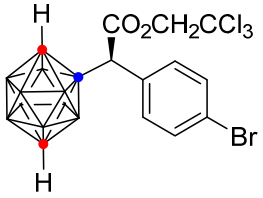


3jb: Yield: 42.1 mg (57%); R_f = 0.30 (Et_2O:Hexane = 1:6); White solid; Melting point: 143-145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 3.73 (s, 1H), 3.70 (s, 3H), 2.76 (s, 2H); ^{13}C{^{1}H} NMR (100

MHz, $CDCl_3$) δ 173.7, 137.7, 131.6, 130.4, 120.5, 65.7, 63.7, 52.0, 41.7; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ -5.80 (1B), -14.05 (2B), -14.89 (6B), -17.26 (1B); IR (film): 3058, 2943, 2610, 1730, 1430, 1205, 1150, 1007, 740 cm^{-1}; HRMS (FAB) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_{20}B_{10}BrO_2^+$ 373.1572; Found 373.1578.; $[\alpha]^{25}_D$: +24.3° (c = 0.23, CH_2Cl_2, 97% e.e.); HPLC (DAICEL IA column, 5% *i*-PrOH in hexane, 0.7 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 7.174 min (minor) and 7.522 min (major) 97% e.e..

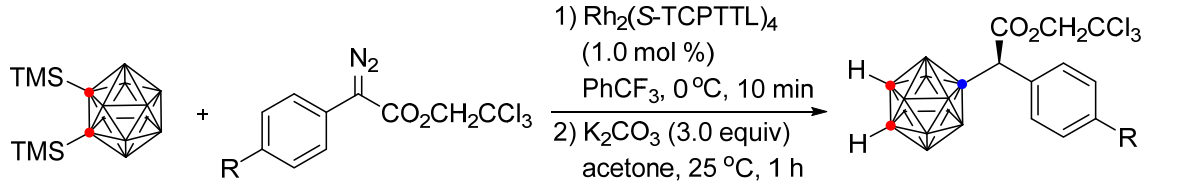


3jc: Yield: 54.6 mg (62%); R_f = 0.40 (Et_2O:Hexane = 1:6); Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 4.56-4.39 (m, 2H), 3.82 (s, 1H), 2.79 (s, 1H), 2.70 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.7, 136.7, 131.8, 130.2, 123.1 (q, *J* = 277.1 Hz), 121.0, 65.6, 63.9, 60.8 (q, *J* = 36.6 Hz), 41.3; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ -6.05 (1B), -13.92 (2B), -14.67 (6B), -16.86 (1B); ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.40; IR (film): 3060, 2610, 1748, 1485, 1278, 1161, 1134, 1117, 973 cm^{-1}; HRMS (FAB) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{19}B_{10}BrF_3O_2^+$ 441.1446; Found 441.1456.; $[\alpha]^{25}_D$: +22.3° (c = 1.96, CH_2Cl_2, 97% e.e.); HPLC (DAICEL IA column, 4% CH_2Cl_2 in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 8.563 min (major) and 9.481 min (minor) 97% e.e..

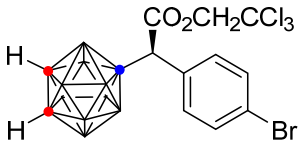


3jd: Yield: 59.5 mg (61%); R_f = 0.40 (Et_2O:Hexane = 1:6); White solid; Melting point: 92-94 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.71 (d, *J* = 12.0 Hz, 1H), 3.86 (s, 1H), 2.80 (s, 1H), 2.79 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.6, 136.9, 131.7, 130.4, 120.9, 94.7, 75.0, 65.7, 63.9, 42.0; $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$) δ -5.92 (1B), -13.90 (2B), -14.69 (6B), -16.85 (1B); IR (film): 3055, 2604, 1746, 1485, 1134, 1117, 1073, 1007, 716 cm^{-1}; HRMS (FAB) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{19}B_{10}BrCl_3O_2^+$ 489.0559; Found 489.0568.; $[\alpha]^{25}_D$: +23.9° (c = 0.28, CH_2Cl_2, 96% e.e.); HPLC (DAICEL IA column, 15% CH_2Cl_2 in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 4.846 min (minor) and 5.273 min (major) 96% e.e..

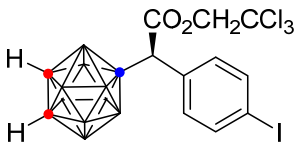
7. Larger Scale Procedure of One-Pot Reaction



An oven dried flask equipped with a magnetic stirrer was charged with *o*-carborane **1** (1.01 g, 3.50 mmol, 1.0 equiv) and Rh_2(*S*-TCPTTL)$_4$ (1.0 mol %) in $PhCF_3$ (26 mL) and stirred at 0 °C under a N_2 atmosphere. The diazo **2** (2.0 equiv) in $PhCF_3$ (26 mL) was added to the reaction mixture dropwise via syringe pump over 3 min. Then, the reaction mixture was stirred at 0 °C for 10 min. After K_2CO_3 (10.5 mmol, 3.0 equiv) and acetone (52 mL) were added, the resulting mixture was stirred at 25 °C for 1 h. The reaction mixture was filtered through a pad of Celite, washed with EtOAc, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford product **5** and **6**.



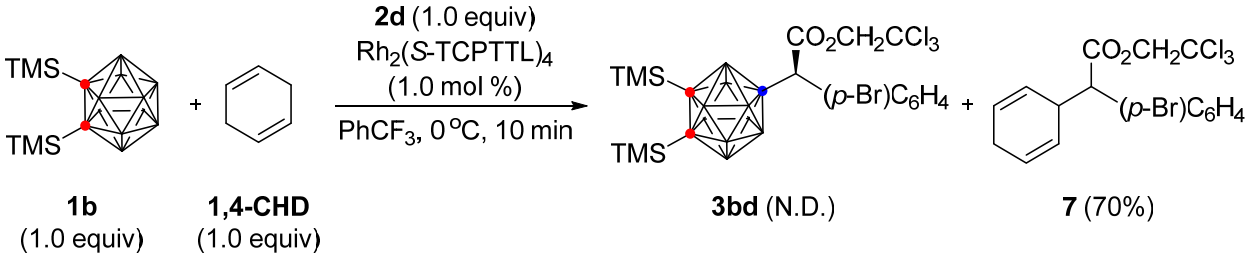
5: Yield: 1.45 g (85%); R_f = 0.35 (CH_2Cl_2:Hexane = 1:1); White solid; Melting point: 116-118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 4.73 (d, J = 11.9 Hz, 1H), 4.61 (d, J = 11.9 Hz, 1H), 3.60 (s, 1H), 3.51 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.5, 138.7, 131.1, 130.4, 120.0, 94.9, 74.7, 53.3, 50.1, 44.1; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 6.36 (1B), -2.17 (1B), -9.04 (2B), -14.20 (4B), -15.35 (2B); IR (film): 3069, 2599, 1730, 1483, 1267, 1132, 1024, 1007, 723 cm^{-1}; HRMS (FAB) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{19}B_{10}BrCl_3O_2^+$ 489.0565; Found 489.0562; $[\alpha]^{25}_D$: +32.07° (c = 1.00, CH_2Cl_2, 99% e.e.); HPLC (DAICEL IA column, 15% CH_2Cl_2 in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 18.532 min (major) and 21.477 min (minor) 99% e.e..



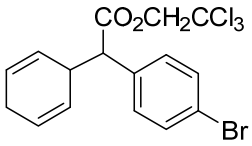
6: Yield: 1.74 g (91%); R_f = 0.35 (Et_2O:Hexane = 1:2); White solid; Melting point: 138-140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.3 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 4.73 (d, J = 11.9 Hz, 1H), 4.61 (d, J = 12.0 Hz, 1H), 3.58 (s, 1H), 3.51 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.5, 139.4, 137.2, 130.8, 95.0, 91.5, 74.7, 53.3, 50.1, 44.0; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 6.38 (1B), -2.15 (1B), -9.03 (2B), -14.25 (4B), -15.44 (2B); IR (film): 3064, 2945, 2593, 1727, 1482, 1128, 1021, 1007, 715 cm^{-1}; HRMS (FAB)

m/z: $[M+H]^+$ Calcd for $C_{12}H_{19}B_{10}Cl_3IO_2^+$ 537.0420; Found 537.0430; $[\alpha]^{25}_D$: +11.5° (c = 0.56, CH_2Cl_2, 99% e.e.); HPLC (DAICEL IA column, 20% CH_2Cl_2 in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 12.393 min (minor) and 13.292 min (major) 99% e.e..

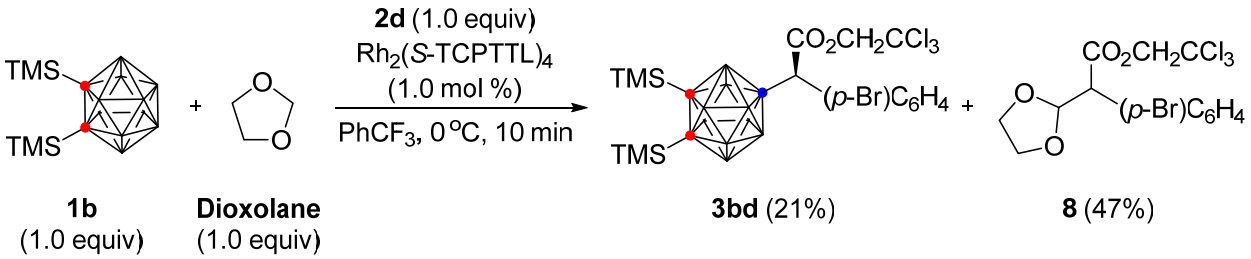
8. Comparison Experiments



An oven dried test tube equipped with a magnetic stirrer was charged with **1b** (57.7 mg, 0.2 mmol, 1.0 equiv) and Rh_2(*S*-TCPTTL)$_4$ (1.0 mol %) in $PhCF_3$ (1.5 mL) and stirred at 0 °C under a N_2 atmosphere, followed by addition of 1,4-cyclohexadiene (19 μL, 0.2 mmol, 1.0 equiv). The diazo **2d** (74.5 mg, 0.2 mmol, 1.0 equiv) in $PhCF_3$ (1.5 mL) was added to the reaction mixture dropwise via syringe pump over 3 min. Then, the reaction mixture was stirred at 0 °C for 10 min. The crude product was concentrated under reduced pressure and purified by column chromatography on silica gel to afford **7** (70%).

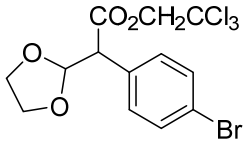


7: Yield: 70.2 mg (70%); R_f = 0.30 (CH_2Cl_2:Hexane = 1:2); Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.9 Hz, 2H), 5.83-5.81 (m, 1H), 5.75-5.72 (m, 2H), 5.32-5.29 (m, 1H), 4.79 (d, J = 12.0 Hz, 1H), 4.69 (d, J = 11.9 Hz, 1H), 3.55 (s, 2H), 2.62-2.60 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.9, 134.9, 131.8, 130.7, 127.1, 126.9, 125.9, 125.0, 121.9, 94.8, 74.3, 57.6, 38.4, 26.5; IR (film): 2957, 1748, 1693, 1585, 1485, 1165, 1131, 1009, 718 cm^{-1}; HRMS (FAB) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{15}BrCl_3O_2^+$ 422.9321; Found 422.9315.

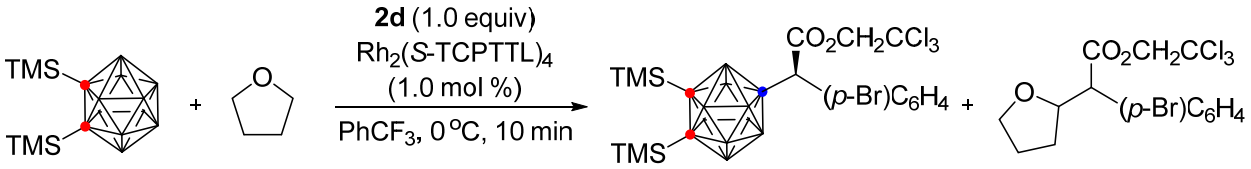


An oven dried test tube equipped with a magnetic stirrer was charged with **1b** (57.7 mg, 0.2 mmol, 1.0 equiv) and Rh_2(*S*-TCPTTL)$_4$ (1.0 mol %) in $PhCF_3$ (1.5 mL) and stirred at 0 °C under a N_2 atmosphere, followed by addition of dioxolane (14 μL, 0.2 mmol, 1.0 equiv). The diazo **2d** (74.5 mg, 0.2 mmol, 1.0 equiv) in $PhCF_3$ (1.5 mL) was added to the reaction mixture dropwise via syringe pump over

3 min. Then, the reaction mixture was stirred at 0 °C for 10 min. The crude product was concentrated under reduced pressure and purified by column chromatography on silica gel to afford **3bd** (21%) and **8** (47%).



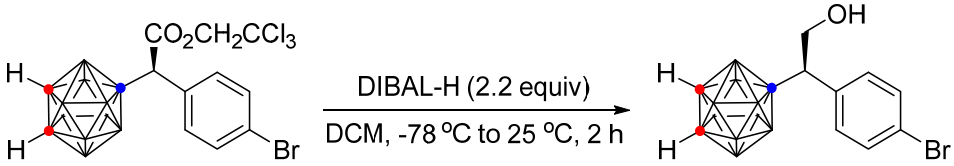
8: Yield: 39.4 mg (47%); R_f = 0.35 (CH_2Cl_2:Hexane = 1:1); Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 5.50 (d, J = 6.5 Hz, 1H), 4.78 (s, 2H), 3.95-3.84 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.7, 132.2, 131.9, 130.9, 122.6, 104.0, 94.6, 74.3, 65.53, 65.51, 55.8; IR (film): 2888, 1748, 1487, 1131, 1071, 1009, 762, 711, 570 cm^{-1}; HRMS (FAB) *m/z*: $[M-H_2+H]^+$ Calcd for $C_{13}H_{11}BrCl_3O_4^+$ 414.8901; Found 414.8904.



1b (1.0 equiv) **THF** (1.0 equiv) **3bd** (71%) **9** (N.D.)

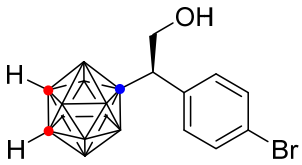
An oven dried test tube equipped with a magnetic stirrer was charged with **1b** (57.7 mg, 0.2 mmol, 1.0 equiv) and Rh_2(*S*-TCPTTL)$_4$ (1.0 mol %) in $PhCF_3$ (1.5 mL) and stirred at 0 °C under a N_2 atmosphere, followed by addition of THF (16 μL, 0.2 mmol, 1.0 equiv). The diazo **2d** (74.5 mg, 0.2 mmol, 1.0 equiv) in $PhCF_3$ (1.5 mL) was added to the reaction mixture dropwise via syringe pump over 3 min. Then, the reaction mixture was stirred at 0 °C for 10 min. The crude product was concentrated under reduced pressure and purified by column chromatography on silica gel to afford **3bd** (71%).

9. General Procedure of Functional Group Transformation

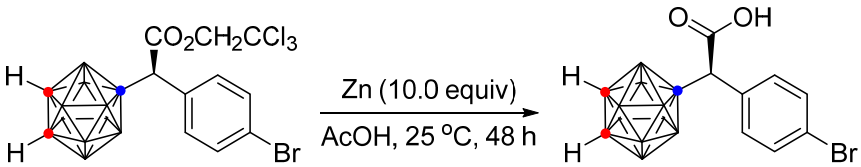


5 **10**

5 (97.7 mg, 0.2 mmol, 1.0 equiv) was dissolved in DCM (6 mL) and stirred at -78 °C. DIBAL-H (1.0 M in hexane, 0.44 mL, 0.44 mmol, 2.2 equiv) was slowly added to the reaction mixture. The resulting solution was stirred at 25 °C for 2 h. MeOH (6 mL) was added to the solution and stirred at 25 °C for 30 min. Then, the reaction was quenched with water (20 mL). After concentrated under reduced pressure, the reaction mixture was extracted with DCM (3 x 20 mL). The organic phase was dried over $MgSO_4$. The crude product was purified by column chromatography on silica gel and then concentrated under vacuum to give the **10** as a white solid.



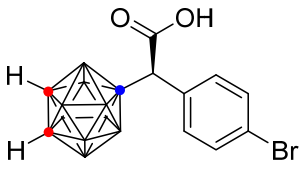
10: Yield: 51.5 mg (75%); R_f = 0.35 (EtOAc:Hexane = 1:3); White solid; Melting point: 135-137 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 8.4 Hz, 2H), 3.89 (t, J = 11.4 Hz, 1H), 3.87 (s, 1H), 3.47 (s, 2H), 2.54 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.2, 131.5, 129.9, 119.0, 66.2, 53.3, 50.1, 40.0; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 7.33 (1B), -2.64 (1B), -9.48 (2B), -14.28 (4B), -15.43 (2B); IR (film): 3055, 2885, 2588, 2359, 1483, 1273, 1263, 1011, 749 cm^{-1}; HRMS (FAB) *m/z*: $[M-H_2O+H]^+$ Calcd for $C_{10}H_{18}B_{10}Br^+$ 327.1517; Found 327.1525; $[\alpha]^{25}_D$: -4.2° (c = 0.18, CH_2Cl_2, 99% e.e.); HPLC (DAICEL IA column, 50% CH_2Cl_2 in hexane, 0.7 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 14.138 min (major) and 14.965 min (minor) 99% e.e..



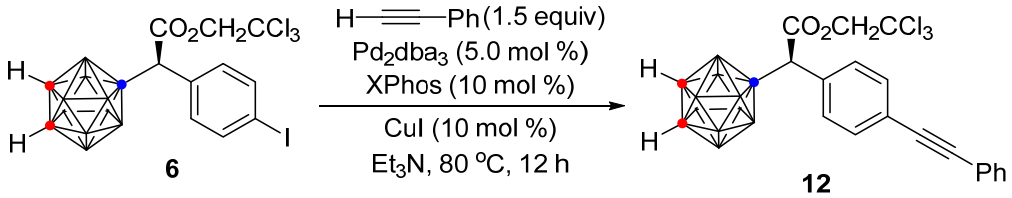
5 **11**

5 (97.7 mg, 0.2 mmol, 1.0 equiv) and Zn (130.8 mg, 2.0 mmol, 10 equiv) were dissolved in AcOH (4 mL). The resulting solution was stirred at 25 °C for 48 h. Then, the reaction was quenched with water (20 mL). The mixture was extracted with EtOAc (3 x 20 mL). The organic phase was dried over $MgSO_4$.

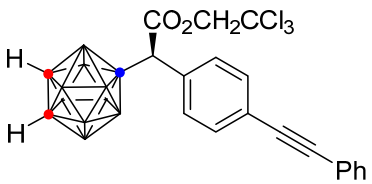
The crude product was purified by column chromatography on silica gel and then concentrated under vacuum to give the **11** as a white solid.



11: Yield: 63.6 mg (89%); R_f = 0.30 (Et_2O:Hexane = 2:1); White solid; Melting point: 238-240 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 10.44 (brs, 1H), 7.41 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 8.6 Hz, 2H), 4.49 (s, 2H), 3.45 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6) δ 175.0, 141.6, 131.6, 131.3, 119.6, 55.7, 51.8, 44.6; ^{11}B{^{1}H} NMR (128 MHz, acetone-d_6) δ 6.30 (1B), -2.92 (1B), -9.39 (2B), -13.84 (2B), -14.55 (2B), -15.23 (2B); IR (film): 3077, 3062, 2599, 2579, 1682, 1485, 1276, 1026, 1007 cm^{-1}; HRMS (FAB) *m/z*: $[M+H]^+$ Calcd for $C_{10}H_{18}B_{10}BrO_2^+$ 359.1421; Found 359.1418.; $[\alpha]^{25}_D$: -5.2° (c = 0.50, MeOH, 99% e.e.); HPLC (DAICEL IE column, 20% *i*-PrOH in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 4.712 min (major) 99% e.e..

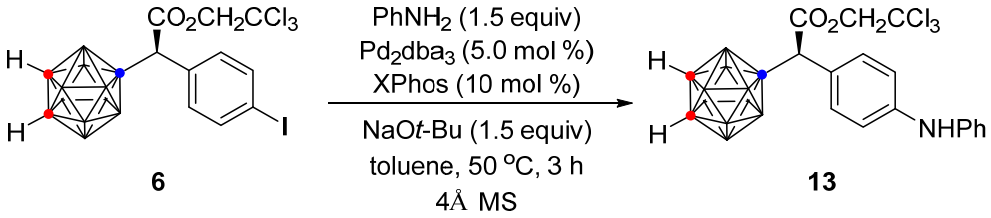


6 (107.2 mg, 0.2 mmol, 1.0 equiv), Pd_2dba_3 (9.2 mg, 0.01 mmol, 5.0 mol %), XPhos (9.6 mg, 0.02 mmol, 10 mol %), and CuI (3.8 mg, 0.02 mmol, 10 mol %) were dissolved in Et_3N (1 mL) under a N_2 atmosphere, followed by addition of phenylacetylene (33 μL, 0.3 mmol, 1.5 equiv). The resulting mixture was stirred at 80 °C for 12 h and then filtered through a short pad of silica gel, washed with EtOAc. The crude product was purified by column chromatography on silica gel and then concentrated under vacuum to give the **12** as a white solid.

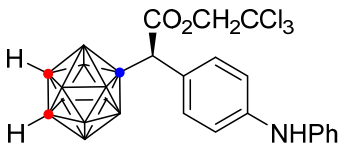


12: Yield: 87.8 mg (86%); R_f = 0.25 (CH_2Cl_2:Hexane = 1:2); White solid; Melting point: 133-135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.50 (m, 2H), 7.45 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 8.3 Hz, 2H), 7.37-7.30 (m, 3H), 4.74 (d, J = 11.9 Hz, 1H), 4.64 (d, J = 11.9 Hz, 1H), 3.65 (s, 1H), 3.50 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.5, 140.2, 131.7, 131.4, 128.7, 128.5, 128.2, 123.6, 120.9, 95.0, 89.7, 89.2, 74.8, 53.3, 50.0, 44.4; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 6.50 (1B), -2.14 (1B),

-9.03 (2B), -14.29 (4B), -15.45 (2B); IR (film): 3065, 2597, 1732, 1508, 1126, 1023, 755, 720, 689 cm^{-1}; HRMS (FAB) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{24}B_{10}Cl_3O_2^+$ 511.1767; Found 511.1770; $[\alpha]^{25}_D$: +30.1° (c = 0.13, CH_2Cl_2, 89% e.e.); HPLC (DAICEL IC column, 5% *i*-PrOH in hexane, 0.7 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 6.948 min (minor) and 7.373 min (major) 89% e.e..

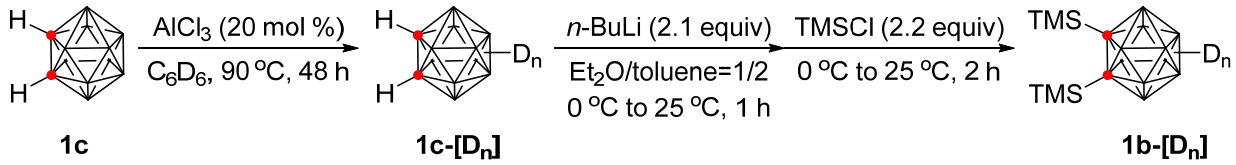


6 (107.2 mg, 0.2 mmol, 1.0 equiv), Pd_2dba_3 (9.2 mg, 0.01 mmol, 5.0 mol %), XPhos (9.6 mg, 0.02 mmol, 10 mol %), NaO*t*-Bu (33.7 mg, 0.30 mmol, 1.5 equiv), and 4Å molecular sieve (100 mg) were stirred in toluene (2 mL) under a N_2 atmosphere, followed by addition of $PhNH_2$ (27 μL, 0.3 mmol, 1.5 equiv). The resulting mixture was stirred at 50 °C for 3 h and then filtered through a short pad of silica gel, washed with EtOAc. The crude product was purified by column chromatography on silica gel and then concentrated under vacuum to give the **13** as a yellow solid.



13: Yield: 68.3 mg (68%); R_f = 0.40 (CH_2Cl_2:Hexane = 2:1); Yellow solid; Melting point: 85-87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.5 Hz, 2H), 7.26-7.22 (m, 2H), 7.04-6.99 (m, 4H), 6.89 (t, J = 7.3 Hz, 1H), 5.63 (s, 1H), 4.72 (d, J = 12.0 Hz, 1H), 4.62 (d, J = 12.0 Hz, 1H), 3.59 (s, 1H), 3.49 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.2, 143.7, 141.0, 132.7, 129.6, 129.4, 120.6, 118.0, 117.4, 95.1, 74.7, 53.2, 49.8, 44.0; ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$) δ 6.91 (1B), -2.13 (1B), -9.00 (2B), -14.43 (4B), -15.56 (2B); IR (film): 3389, 3058, 2916, 2848, 2599, 1595, 1511, 1128, 747 cm^{-1}; HRMS (FAB) *m/z*: $[M+H]^+$ Calcd for $C_{18}H_{25}B_{10}Cl_3NO_2^+$ 502.1876; Found 502.1877; $[\alpha]^{25}_D$: +30.1° (c = 0.18, CH_2Cl_2, 86% e.e.); HPLC (DAICEL IA column, 20% *i*-PrOH in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 9.336 min (minor) and 12.982 min (major) 86% e.e..

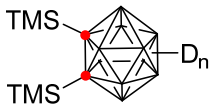
10. Mechanistic Experiments



1c **1c-[D_n]** **1b-[D_n]**

o-Carborane **1c** (432.7 mg, 3.0 mmol, 1.0 equiv) and $AlCl_3$ (80.0 mg, 0.60 mmol, 20 mol %) were dissolved in C_6D_6 (6 mL) and stirred at 90 °C for 48 h under a N_2 atmosphere. Then, the reaction was quenched with water (20 mL) and extracted with Et_2O (3 x 20 mL). The organic phase was dried over $MgSO_4$. The crude product was purified by column chromatography on silica gel and then concentrated under vacuum to give the **1c-[D_n]** as a white solid.

Deuterated *o*-Carborane **1c-[D_n]** was dissolved in Et_2O/toluene (3 mL/6 mL) and stirred at 0 °C. *n*-BuLi (1.6 M in hexane, 3.9 mL, 6.3 mmol, 2.1 equiv) was slowly added to the reaction mixture. The resulting solution was stirred at 25 °C for 1 h. After the reaction mixture was cooled to 0 °C, TMSCl (0.84 mL, 6.6 mmol, 2.2 equiv) was slowly added and stirred at 25 °C for 2 h. Then, the reaction was quenched with water (20 mL) and extracted with Et_2O (3 x 20 mL). The organic phase was dried over $MgSO_4$. The crude product was purified by column chromatography on silica gel and then concentrated under vacuum to give the **1b-[D_n]** as a white solid.



1b-[D_n]: Yield: 770.5 mg (89%); R_f = 0.60 (Hexane); White solid; ^1H NMR (400 MHz, $CDCl_3$) δ 0.32 (s, 18H); $^1H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$) δ 2.47 (B(9,12)−H, s, 0.28H), δ 2.37 (B(8,10)−H, s, 0.34H), δ 2.31 (B(3,6)−H, s, 1.67H), δ 2.14 (B(4,5,7,11)−H, s, 1.86H), δ 0.32 (s, 18H).

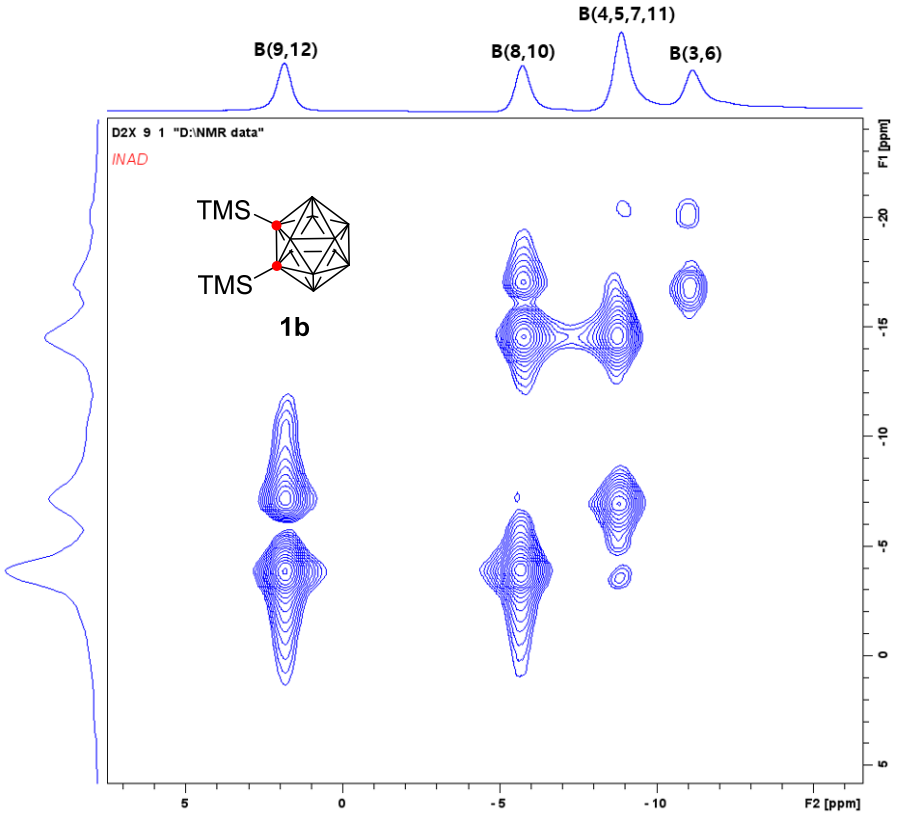


Fig. S2. $^{11}B\{^{1}H\}$-$^{11}B\{^{1}H\}$ INADEQUATE NMR for **1b**

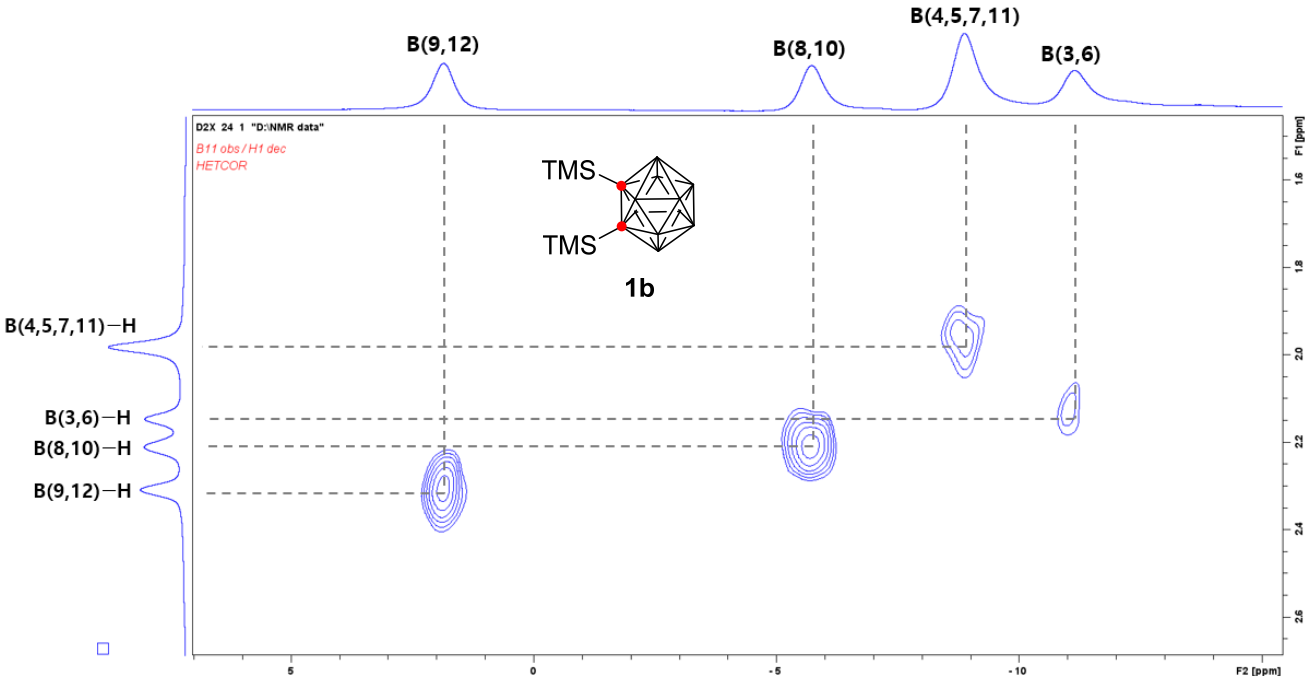


Fig. S3. $^{11}B\{^{1}H\}$-$^{1}H\{^{11}B\}$ HETCOR NMR for **1b**

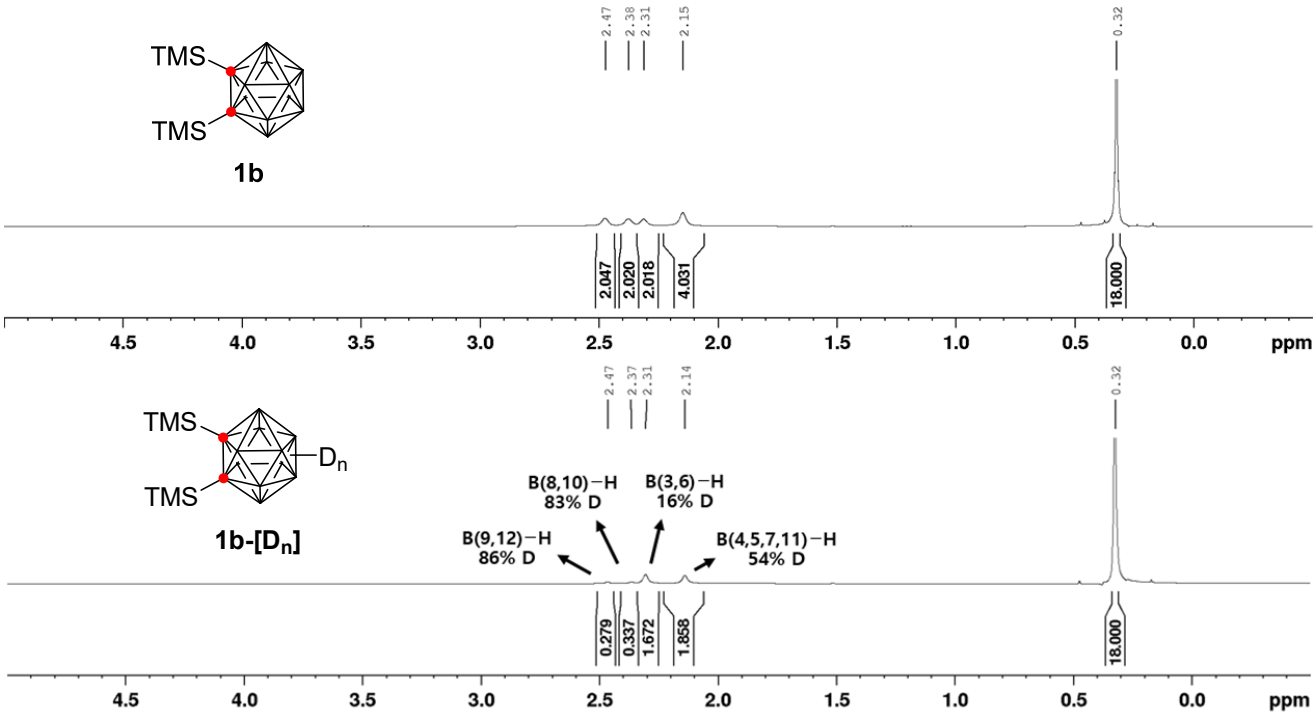


Fig. S4. Comparison of $^{1}H\{^{11}B\}$ NMR of **1b** (top) and **1b-[D$_n$]** (bottom)

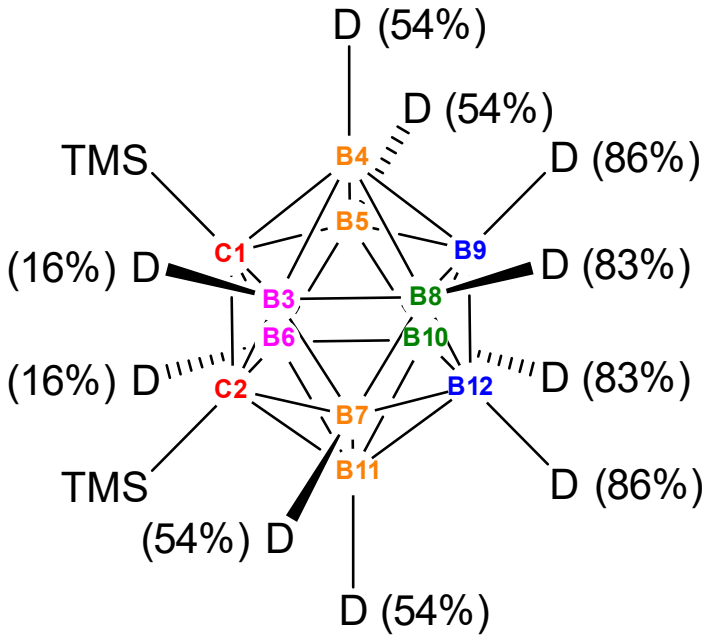
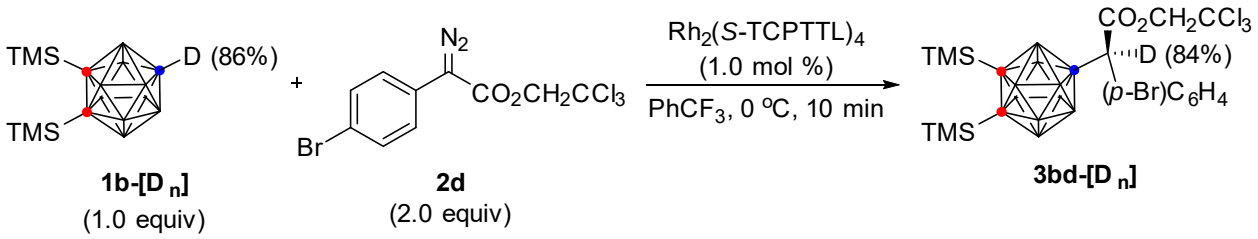
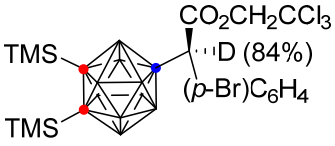


Fig. S5. Deuterated *o*-carborane **1b-[D$_n$]**





3bd-[D$_n$]: Yield: 123.8 mg (98%); R_f = 0.35 (CH_2Cl_2:Hexane = 1:2); White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 9.0 Hz, 2H), 4.75 (d, J = 11.9 Hz, 1H), 4.58 (d, J = 11.9 Hz, 1H), 3.59 (s, 0.16H), 0.29 (s, 9H), 0.26 (s, 9H).

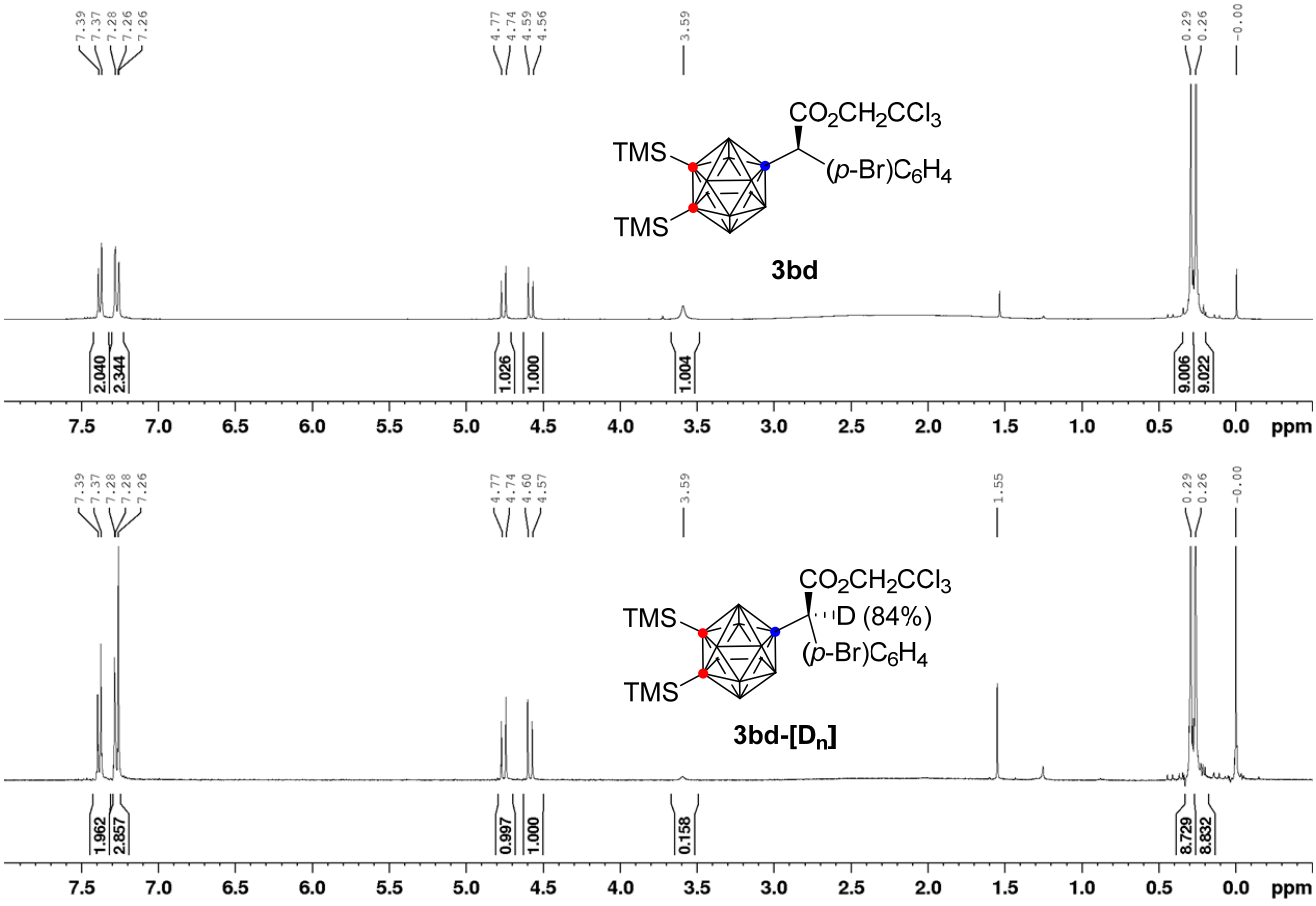
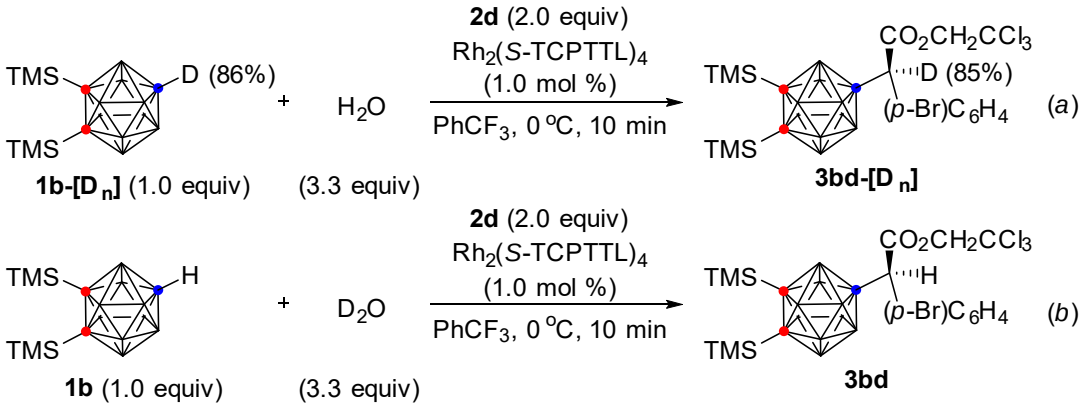


Fig. S6. Comparison of ^{1}H NMR of **3bd** (top) and **3bd-[D$_n$]** (bottom)



An oven dried test tube equipped with a magnetic stirrer was charged with **1b-[D$_n$]** or **1b** (0.2 mmol, 1.0 equiv) and Rh_2(*S*-TCPTTL)$_4$ (1.0 mol %) in $PhCF_3$ (1.5 mL) and stirred at 0 °C under a N_2 atmosphere, followed by addition of H_2O or D_2O (0.66 mmol, 3.3 equiv). The diazo **2d** (74.5 mg, 0.2 mmol, 1.0 equiv) in $PhCF_3$ (1.5 mL) was added to the reaction mixture dropwise via syringe pump over 3 min. Then, the reaction mixture was stirred at 0 °C for 10 min. The crude product was concentrated under reduced pressure and purified by column chromatography on silica gel.

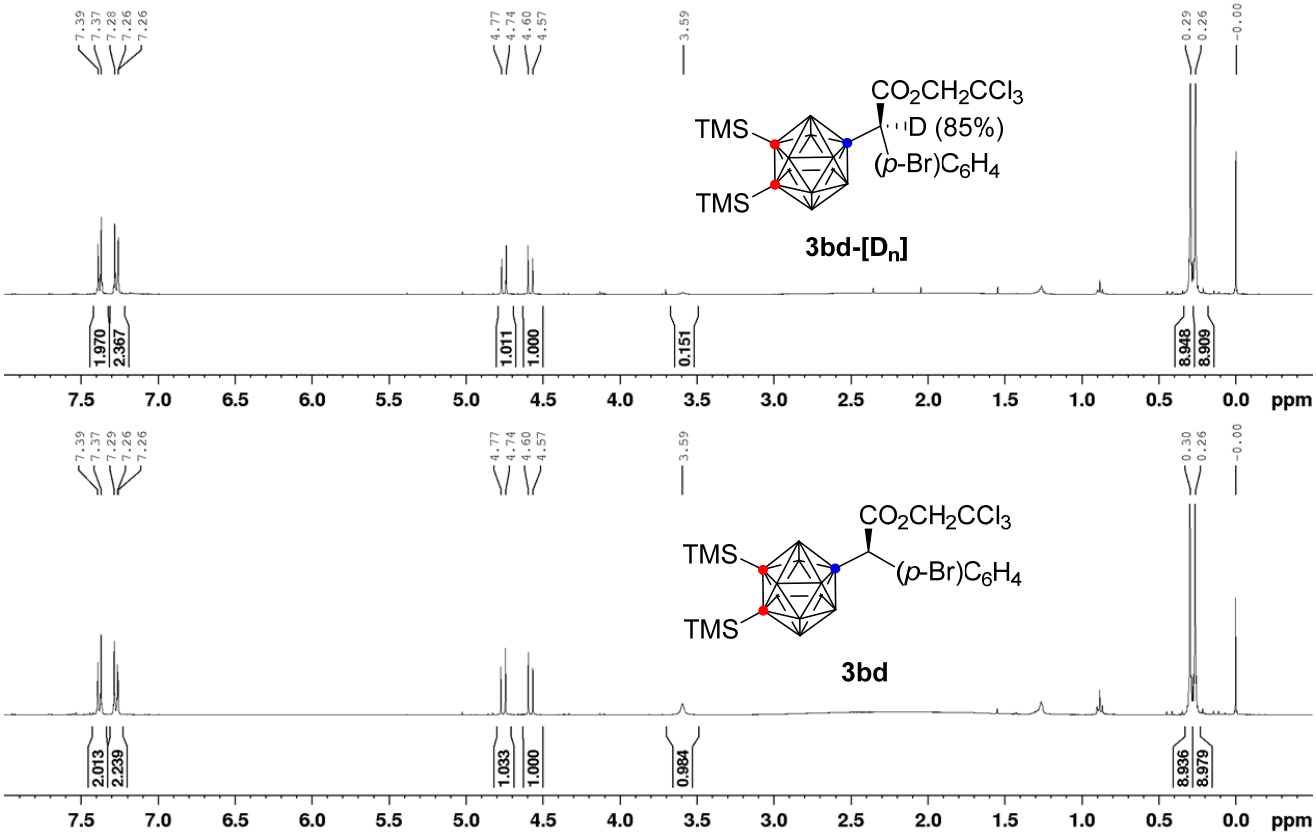


Fig. S7. Comparison of ^{1}H NMR of the product (*a*) (top) and (*b*) (bottom)

11. Computational Section

General information and computational procedures

All computations were performed using density functional theory (DFT) as implemented in the Gaussian 16 software package[7]. Structures were optimized using PBE[8,9]-D3BJ[10]/LANL2DZ[11] (Rh, Br, Cl) & 6-31G(d)[12-14] for all other atoms with CPCM(C_6H_6) solvation corrections[15,16] at 0 °C. Single point calculations were performed at PBE-D3BJ/def2-TZVP level of theory[17]. Conformational search was performed using Schrödinger Macromodel[18]. Figures were rendered in MacPyMOL v1.7.4.2[19]. All energy values are free energies reported in kcal/mol, and all distances are in Ångströms (Å).

Complete reaction coordinate diagram for the formation of the products

The mechanism for the formation of product of (*R*)-**3bd** begins with the diazo compound **2d** decomposition by the dirhodium catalyst Rh_2(*S*-TCPTTL)$_4$ to afford the dirhodium carbenoid intermediate **I** (ΔG = 0.0 kcal/mol) with the release of molecular nitrogen gas. The highly reactive dirhodium carbenoid **I** undergoes B−H bond insertion with incoming *o*-carborane **1b**, forming a selective three-member transition state (TS). Formation of the major (*R*)-B(9)-TS (**II-TS$_{(R)\text{-B(9)}}$**, $\Delta G^{‡}$ = 6.92 kcal/mol) leads to the formation of the ground state product complex **III** (ΔG = –37.5 kcal/mol). In contrast, the enantiomeric minor (*S*)-B(9)-TS (**II-TS$_{(S)\text{-B(9)}}$**, $\Delta G^{‡}$ = 8.96 kcal/mol) leads to the respective product complex **III** (ΔG = –36.0 kcal/mol), and the regioisomeric minor (*R*)-B(8)-TS (**II-TS$_{(R)\text{-B(8)}}$**, $\Delta G^{‡}$ = 9.00 kcal/mol) leads to the respective product complex **III** (ΔG = –29.7 kcal/mol). A second diazo compound **2d** releases the major product (*R*)-**3bd** (ΔG = –51.1 kcal/mol), as well as molecular nitrogen gas, resulting in regeneration of the dirhodium carbenoid **I** for the next catalytic cycle.

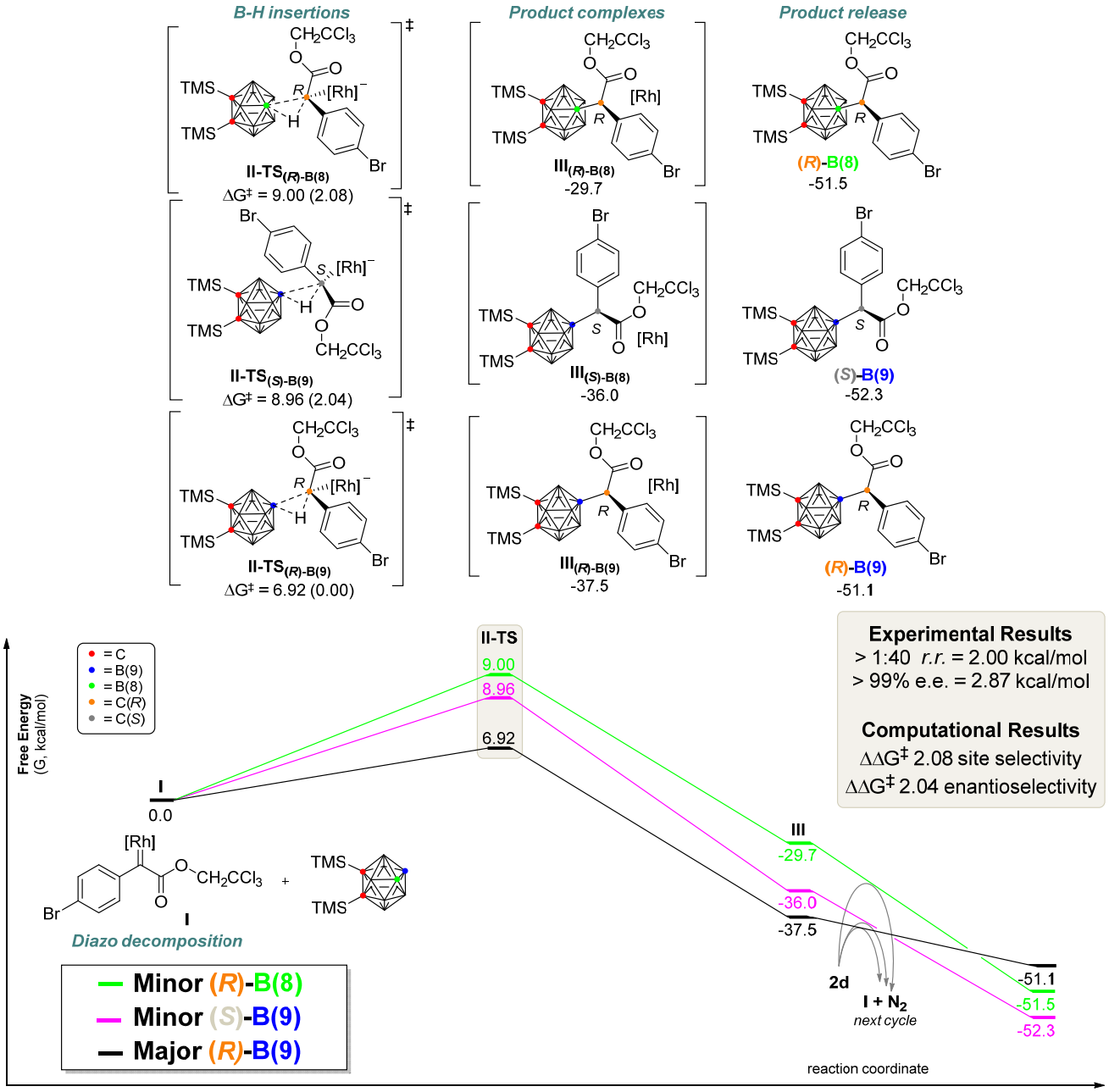


Fig. S8. The complete reaction coordinate diagram for the formation of the products

Computed structures, electronic energies, and thermal corrections as well as the input parameters

Supporting Information: N_2

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========

# pbepbe/6-31g(d)/auto empiricaldispersion=gd3bj
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scrf=(solvent=benzene,cpcm) opt=(gdiis,maxcycle=250) freq=noraman
Temperature=273.15 5D 7F
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq

---

Pointgroup= D*H Stoichiometry= N2 D*H[C*(N.N)] #Atoms= 2
Charge = 0 Multiplicity = 1

SCF Energy= -109.403638405 Predicted Change= -3.500890D-10

==========

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00003	0.00045	[YES]	0.00003	0.00030	[YES]
Displ	0.00001	0.00180	[YES]	0.00001	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
N	0.000000	0.000000	0.558296
N	0.000000	0.000000	-0.558296

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -109.403638405 Predicted Change= -3.500890D-10
Zero-point correction (ZPE)= -109.3982 0.00537
Internal Energy (U)= -109.3960 0.00754
Enthalpy (H)= -109.3952 0.00840
Gibbs Free Energy (G)= -109.4149 -0.01127
Entropy (S)= 7.206e-05

Frequencies -- 2360.2712

Supporting Information: 1a

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========

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scrf=(solvent=benzene,cpcm) opt=(gdiis,maxcycle=250) freq=noraman
Temperature=273.15 5D 7F
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/6-31G(d)/Auto Freq

---
Pointgroup= C1 Stoichiometry= C8H28B10Si2 C1[X(C8H28B10Si2)] #Atoms= 48
Charge = 0 Multiplicity = 1

SCF Energy= -1148.32150750 Predicted Change= -2.068049D-08
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Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
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Displ	0.00204	0.00180	[NO]	0.00204	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
B	1.448172	1.710236	-0.855046
H	2.476781	1.562667	-1.449722
B	0.888009	3.157728	0.017491
H	1.548501	4.158407	0.030789
B	-0.031571	2.595199	1.446875
H	-0.053186	3.178255	2.493671
B	0.031507	2.595165	-1.446914
H	0.053108	3.178196	-2.493724
B	-0.023744	0.812942	1.424242
B	-1.448214	1.710222	0.855026
H	-2.476819	1.562645	1.449707
B	-1.411551	1.719485	-0.915786
H	-2.411608	1.589374	-1.554737
B	0.023722	0.812909	-1.424237
H	0.040675	0.067462	-2.355535
B	-0.888085	3.157707	-0.017544
H	-1.548602	4.158371	-0.030866
C	-0.851796	0.364233	-0.018595
H	-0.040680	0.067516	2.355557
H	2.411567	1.589467	1.554720
B	1.411508	1.719540	0.915767
C	0.851783	0.364253	0.018608
Si	-2.013330	-1.203018	0.001544
Si	2.013359	-1.202970	-0.001515
C	-3.728548	-0.624962	-0.541622
H	-4.438101	-1.457613	-0.384619
H	-4.080770	0.239205	0.044765
H	-3.754916	-0.351934	-1.608970
C	-2.138695	-1.847865	1.771678
H	-2.522611	-1.056503	2.438190
H	-2.857139	-2.686671	1.795691
H	-1.182935	-2.205120	2.183955
C	-1.442748	-2.519904	-1.227440
H	-1.305180	-2.084875	-2.232085
H	-0.513744	-3.036507	-0.943682
H	-2.239540	-3.281914	-1.300966
C	1.443028	-2.519742	1.227705

H	0.514002	-3.036415	0.944153
H	2.239863	-3.281711	1.301184
H	1.305608	-2.084609	2.232326
C	2.138442	-1.848023	-1.771593
H	2.856906	-2.686810	-1.795631
H	1.182619	-2.205355	-2.183659
H	2.522217	-1.056728	-2.438265
C	3.728648	-0.624800	0.541307
H	4.438200	-1.457448	0.384285
H	4.080748	0.239310	-0.045238
H	3.755180	-0.351647	1.608618

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1148.32150750 Predicted Change= -2.068049D-08
Zero-point correction (ZPE)= -1147.9481 0.37337
Internal Energy (U)= -1147.9284 0.39307
Enthalpy (H)= -1147.9275 0.39393
Gibbs Free Energy (G)= -1147.9898 0.33162
Entropy (S)= 0.00022814

Frequencies -- 50.1808 88.5132 110.2916

Supporting Information: 2d

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========

# pbepbe/genecp/auto empiricaldispersion=gd3bj
scf=(maxcycle=300,direct,vshift=200,tight,yqc) density=current
scrf=(solvent=benzene,cpcm) opt=(gdiis,maxcycle=250) freq=noraman
Temperature=273.15
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/GenECP/Auto Freq

---

Pointgroup= C1 Stoichiometry= C10H6BrCl3N2O2 C1[X(C10H6BrCl3N2O2)] #Atoms= 24
Charge = 0 Multiplicity = 1

SCF Energy= -701.882672006 Predicted Change= -2.328691D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00005	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00471	0.00180	[NO]	0.00471	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
Br	-6.109054	-0.485688	0.255432
C	-4.192308	-0.091778	0.030062
C	-3.313161	-1.129168	-0.288578
C	-1.950637	-0.848492	-0.447765

C	-3.743262	1.221991	0.193383
C	-2.381741	1.494791	0.031500
C	-1.464766	0.468463	-0.290361
C	-0.030064	0.772872	-0.456444
C	1.026740	-0.171212	-0.824378
O	2.237983	0.492758	-0.951169
C	3.381223	-0.331128	-1.155418
C	4.256657	-0.334320	0.106698
Cl	3.373331	-1.072763	1.523532
Cl	5.755137	-1.322602	-0.240995
Cl	4.763798	1.360497	0.564577
O	0.884968	-1.372210	-1.016361
N	0.372468	2.017405	-0.246498
N	0.699610	3.102078	-0.056389
H	-3.676668	-2.152129	-0.412558
H	-1.257937	-1.654155	-0.694709
H	-4.439286	2.026490	0.442029
H	-2.041572	2.527265	0.159378
H	3.076142	-1.364380	-1.384120
H	3.967429	0.095864	-1.982821

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -701.882672006 Predicted Change= -2.328691D-08
Zero-point correction (ZPE)= -701.7389 0.14372
Internal Energy (U)= -701.7233 0.15936
Enthalpy (H)= -701.7224 0.16022
Gibbs Free Energy (G)= -701.7842 0.09841
Entropy (S)= 0.00022632

Frequencies -- 17.9859 22.2659 30.6017

Supporting Information: Rh_2(*S*-TCPTTL)$_4$

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========

# pbepbe/genecp/auto empiricaldispersion=gd3bj
scf=(maxcycle=300,direct,vshift=200,tight,yqc) density=current
scrf=(solvent=benzene,cpcm) opt=(gdiis,maxcycle=250) freq=noraman
Temperature=273.15
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/GenECP/Auto Freq

---

Pointgroup= C1 Stoichiometry= C56H40Cl16N4O16Rh2 C1[X(C56H40Cl16N4O16Rh2)] #Atoms= 134
Charge = 0 Multiplicity = 1

SCF Energy= -4035.28671154 Predicted Change= -2.368616D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]

Displ 0.00303 || 0.00180 [NO] 0.00303 || 0.00180 [YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	-2.419767	-0.323244	-2.283859
O	-1.989178	0.302745	-0.127698
O	-1.911700	3.069463	-1.284757
O	-5.487979	1.719980	1.315694
O	-1.333741	-2.939703	-1.553882
O	-0.736870	-2.221664	0.537863
O	-3.332858	-2.738288	2.537720
O	-4.296497	-4.175534	-1.769605
O	0.164029	0.571691	-3.174414
O	0.620287	1.303499	-1.054520
O	3.335283	0.713827	-3.326432
O	2.479784	4.561193	-0.914163
O	1.328139	-2.048615	-2.494601
O	1.836778	-1.181492	-0.440441
O	5.660606	-0.912594	-0.146519
O	2.347030	-4.074470	0.419676
C	-2.702432	0.280102	-1.193098
C	-4.050040	1.026881	-1.091471
H	-4.703852	0.385730	-0.467049
C	-2.729436	3.078574	-0.374236
C	-2.793652	3.972207	0.827266
C	-3.894292	3.577309	1.611296
C	-4.545067	2.404547	0.942950
C	-4.198171	4.234512	2.798783
C	-3.378986	5.311350	3.210485
C	-2.269907	5.700075	2.428717
C	-1.971297	5.021775	1.223954
C	-4.844941	1.328526	-2.405876
C	-6.099902	2.138384	-2.012815
H	-5.837279	3.135863	-1.621175
H	-6.699689	1.614138	-1.248217
H	-6.733522	2.283796	-2.904132
C	-5.311991	-0.007299	-3.018888
H	-4.466678	-0.635444	-3.336065
H	-5.947209	0.194571	-3.898302
H	-5.919654	-0.578124	-2.298257
C	-4.024721	2.123158	-3.437583
H	-3.115148	1.577890	-3.731961
H	-3.722418	3.109258	-3.050909
H	-4.639171	2.285502	-4.340403
C	-1.295342	-3.039138	-0.278042
C	-2.107190	-4.154406	0.405501
H	-1.849244	-4.070675	1.474380
C	-3.953018	-2.898084	1.497319
C	-5.288434	-2.353652	1.105050
C	-5.590401	-2.832711	-0.181910

C	-4.424951	-3.647495	-0.675285
C	-6.799784	-2.516076	-0.792755
C	-7.694877	-1.649644	-0.122314
C	-7.380650	-1.149537	1.159756
C	-6.171297	-1.522870	1.790253
C	-1.830934	-5.636949	-0.002060
C	-2.978263	-6.508010	0.546397
H	-2.711372	-7.573423	0.440016
H	-3.916265	-6.338849	-0.008398
H	-3.163345	-6.310005	1.617305
C	-1.654882	-5.887020	-1.512642
H	-1.508949	-6.969908	-1.674166
H	-0.767525	-5.363789	-1.904568
H	-2.533627	-5.558164	-2.084169
C	-0.513490	-6.018839	0.712260
H	-0.232505	-7.051902	0.444379
H	-0.621335	-5.969239	1.810954
H	0.320109	-5.357294	0.422367
C	0.611029	1.422169	-2.332119
C	1.226661	2.756060	-2.799968
H	0.767813	3.509676	-2.133717
C	3.557403	1.716325	-2.657791
C	4.801586	2.073353	-1.902398
C	4.509292	3.175381	-1.077342
C	3.114324	3.630236	-1.387302
C	5.452173	3.657216	-0.174864
C	6.710778	3.016682	-0.096810
C	7.019337	1.946000	-0.962578
C	6.061393	1.485667	-1.893564
C	0.989388	3.245059	-4.259209
C	1.607669	2.336276	-5.337590
H	1.228111	1.306482	-5.261586
H	2.706890	2.304740	-5.265943
H	1.348232	2.735291	-6.334191
C	1.604849	4.656801	-4.368936
H	2.700803	4.631510	-4.240134
H	1.185197	5.342227	-3.611741
H	1.393281	5.076216	-5.367332
C	-0.535921	3.347058	-4.471794
H	-1.006823	2.351754	-4.472197
H	-0.740586	3.825287	-5.445130
H	-1.015083	3.951949	-3.682717
C	2.114956	-1.831441	-1.512698
C	3.578917	-2.299959	-1.600372
H	4.144688	-1.388186	-1.876306
C	4.996815	-1.781780	0.400451
C	4.998599	-2.202137	1.837110
C	3.990953	-3.168708	2.009242
C	3.320214	-3.383228	0.684090
C	3.746586	-3.728750	3.258631
C	5.540302	-2.337941	4.185449

C	5.775155	-1.776312	2.909496
C	3.960521	-3.388235	-2.656078
C	5.448097	-3.738153	-2.436371
H	5.787163	-4.418377	-3.236119
H	5.608930	-4.246565	-1.470390
H	6.083631	-2.835479	-2.461155
C	3.110274	-4.668571	-2.554539
H	3.256145	-5.183093	-1.591979
H	3.404555	-5.362090	-3.361823
H	2.036544	-4.447442	-2.665304
C	3.807071	-2.768211	-4.063731
H	4.367477	-1.821334	-4.149388
H	2.752418	-2.563364	-4.300747
H	4.203213	-3.472552	-4.815694
N	-3.504787	-3.672622	0.392891
N	-3.826348	2.205391	-0.252327
N	4.027912	-2.584487	-0.233648
N	2.636590	2.742613	-2.381351
C	4.531399	-3.310411	4.358364
Rh	-0.568855	-1.223188	-2.428346
Cl	-1.245521	7.032998	2.964765
Cl	-3.736134	6.167058	4.711656
Cl	-0.556907	5.487797	0.270324
Cl	-5.574765	3.736978	3.793431
Cl	5.092548	5.031861	0.880563
Cl	7.904976	3.557757	1.085224
Cl	8.603125	1.175660	-0.873587
Cl	6.488290	0.211472	-3.045472
Cl	2.474075	-4.937395	3.488342
Cl	4.245183	-3.998661	5.957833
Cl	6.504024	-1.818729	5.569228
Cl	7.028805	-0.543055	2.698140
Cl	-5.799982	-0.930016	3.412408
Cl	-8.500876	-0.059122	1.973058
Cl	-9.205764	-1.172226	-0.900567
Cl	-7.226179	-3.164514	-2.384459
Rh	-0.057953	-0.441647	-0.221860

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -4035.28671154 Predicted Change= -2.368616D-08
Zero-point correction (ZPE)= -4034.4128 0.87382
Internal Energy (U)= -4034.3297 0.95696
Enthalpy (H)= -4034.3288 0.95783
Gibbs Free Energy (G)= -4034.5377 0.74900
Entropy (S)= 0.00076451

Frequencies -- 4.9863 6.4766 7.3816

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016
==========
# pbepbe/genecp/auto empiricaldispersion=gd3bj
scf=(maxcycle=300,direct,vshift=200,tight,yqc) density=current
scrf=(solvent=benzene,cpcm) opt=(gdiis,maxcycle=250) freq=noraman
Temperature=273.15
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/GenECP/Auto Freq
---
Pointgroup= C1 Stoichiometry= C66H46BrCl19N4O18Rh2 C1[X(C66H46BrCl19N4O18Rh2)] #Atoms= 156
Charge = 0 Multiplicity = 1

SCF Energy= -4627.83550306 Predicted Change= -1.168350D-08
==========
Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00203	0.00180	[NO]	0.00203	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	-1.499169	1.123255	-3.734777
O	-1.467731	1.256883	-1.448897
O	-0.347126	4.026265	-2.231176
O	-4.342058	3.234377	-0.075800
O	-1.406552	-1.826432	-3.531923
O	-1.444389	-1.601309	-1.252254
O	-4.188904	-4.365005	0.150714
O	-4.215502	-0.611448	-2.550954
O	1.388305	1.191493	-3.817233
O	1.504042	1.286662	-1.531437
O	4.225015	0.022126	-2.948501
O	4.251447	3.855100	-0.367692
O	1.452272	-1.795104	-3.595579
O	1.497439	-1.576533	-1.319350
O	4.586286	-3.232630	0.094718
O	0.291820	-4.292071	-1.248218
C	-1.873834	1.602282	-2.619114
C	-2.961716	2.692399	-2.552404
H	-3.837458	2.183801	-2.104258
C	-1.230169	4.146826	-1.391996
C	-1.159665	4.781745	-0.037150
C	-2.376128	4.535030	0.623415
C	-3.251066	3.744448	-0.297624
C	-2.568286	4.933843	1.940690
C	-1.521366	5.606768	2.609226
C	-0.303565	5.862302	1.943512
C	-0.118984	5.442723	0.606034
C	-3.454484	3.353550	-3.874431
C	-4.513239	4.408921	-3.488961

H	-4.068941	5.236143	-2.909407
H	-5.326086	3.965790	-2.886452
H	-4.958334	4.836656	-4.403475
C	-4.134279	2.263468	-4.732820
H	-3.405501	1.521186	-5.091543
H	-4.613113	2.734760	-5.608624
H	-4.913637	1.729345	-4.161619
C	-2.326210	4.028638	-4.676195
H	-1.535305	3.308933	-4.938680
H	-1.864264	4.855918	-4.113800
H	-2.743755	4.443996	-5.610299
C	-1.826093	-2.115688	-2.365081
C	-2.877385	-3.233390	-2.194099
H	-2.416743	-3.947786	-1.486616
C	-4.562117	-3.299718	-0.318429
C	-5.656850	-2.390885	0.156015
C	-5.683454	-1.261592	-0.684596
C	-4.586354	-1.410090	-1.699502
C	-6.616711	-0.247670	-0.488422
C	-7.519329	-0.352517	0.595808
C	-7.486873	-1.480707	1.442884
C	-6.552781	-2.517468	1.212677
C	-3.300920	-4.040726	-3.463719
C	-4.298619	-5.132473	-3.018829
H	-4.541236	-5.775808	-3.881834
H	-5.244991	-4.697895	-2.653203
H	-3.880449	-5.768026	-2.220014
C	-3.968715	-3.164710	-4.540535
H	-4.233171	-3.796080	-5.406995
H	-3.298831	-2.362045	-4.882148
H	-4.900617	-2.705798	-4.169108
C	-2.043972	-4.734790	-4.032172
H	-2.340959	-5.422881	-4.842426
H	-1.527448	-5.325561	-3.255330
H	-1.329114	-4.005816	-4.441518
C	1.858377	1.627714	-2.721011
C	2.966864	2.700300	-2.707406
H	2.577220	3.499237	-2.049591
C	4.613869	0.843752	-2.127085
C	5.662237	0.680105	-1.066133
C	5.620589	1.812817	-0.231885
C	4.602530	2.764465	-0.790422
C	6.446188	1.907541	0.884390
C	7.336798	0.844538	1.166291
C	7.394822	-0.280562	0.314515
C	6.560341	-0.355263	-0.825735
C	3.372059	3.373622	-4.053556
C	3.962811	2.386508	-5.077332
H	3.252868	1.580991	-5.316593
H	4.896299	1.928557	-4.709755
H	4.203192	2.931862	-6.006958

C	4.423984	4.455931	-3.727730
H	5.356577	4.012657	-3.337616
H	4.047388	5.177272	-2.981879
H	4.676478	5.011079	-4.647247
C	2.117942	4.063069	-4.634169
H	1.358915	3.327555	-4.941960
H	2.405025	4.657148	-5.518924
H	1.656158	4.742955	-3.897673
C	1.846212	-2.120838	-2.433859
C	2.885561	-3.246089	-2.231311
H	3.840816	-2.715756	-2.046613
C	3.428783	-3.622460	0.172470
C	2.601522	-3.848676	1.398142
C	1.277145	-4.090481	0.992537
C	1.247303	-4.117528	-0.505434
C	0.249188	-4.186993	1.926825
C	1.897351	-3.802055	3.704061
C	2.932915	-3.745867	2.744956
C	3.155389	-4.246383	-3.393657
C	4.165802	-5.288639	-2.869694
H	4.462969	-5.961228	-3.692405
H	3.729315	-5.905239	-2.065671
H	5.076607	-4.804322	-2.474795
C	1.884641	-4.959514	-3.888496
H	1.420555	-5.563052	-3.092367
H	2.145629	-5.632532	-4.724023
H	1.135295	-4.236872	-4.248081
C	3.808978	-3.465681	-4.556038
H	4.706202	-2.917736	-4.216927
H	3.109810	-2.739250	-4.996811
H	4.119950	-4.174161	-5.343209
N	-4.014618	-2.670144	-1.455805
N	-2.541330	3.641206	-1.510947
N	2.575886	-3.860517	-0.926374
N	4.097285	2.138898	-1.953049
C	0.563047	-4.012638	3.295017
Rh	-0.016475	-0.325601	-3.732642
Cl	1.002680	6.689831	2.795392
Cl	-1.726068	6.111570	4.288454
Cl	1.430205	5.723401	-0.199889
Cl	-4.074060	4.564564	2.798829
Cl	6.387349	3.316866	1.950352
Cl	8.389926	0.926620	2.578205
Cl	8.518563	-1.591539	0.670590
Cl	6.707850	-1.722041	-1.938279
Cl	-1.422634	-4.458589	1.431202
Cl	-0.726828	-4.030748	4.500314
Cl	2.268698	-3.579086	5.415646
Cl	4.610784	-3.522448	3.259081
Cl	-6.528579	-3.934171	2.270218
Cl	-8.606481	-1.588083	2.800315

Cl	-8.681893	0.937276	0.901694
Cl	-6.693113	1.155330	-1.562209
Rh	0.031071	-0.139192	-1.278070
C	0.101067	0.103712	0.696638
C	1.227858	-0.010623	1.573911
C	-1.126708	0.725853	1.235100
C	2.546829	-0.243251	1.076709
C	1.064333	0.138949	2.987903
O	-2.172954	-0.141928	1.390309
O	-1.187770	1.936464	1.429962
C	3.643007	-0.277538	1.934364
H	2.692420	-0.376353	0.005160
C	2.154188	0.105094	3.851674
H	0.064096	0.291247	3.404061
C	-3.422429	0.447713	1.768594
C	3.436721	-0.074034	3.307962
H	4.646011	-0.464689	1.546182
H	2.018728	0.232276	4.928013
H	-3.393774	1.542177	1.660394
H	-4.195075	0.023063	1.112799
C	-3.770101	0.094563	3.218285
Br	4.981370	0.002702	4.494355
Cl	-2.599615	0.862627	4.398255
Cl	-5.445820	0.734934	3.574422
Cl	-3.754492	-1.709955	3.487757

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

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SCF Energy= -4627.83550306 Predicted Change= -1.168350D-08
Zero-point correction (ZPE)= -4626.8267 1.00879
Internal Energy (U)= -4626.7286 1.10689
Enthalpy (H)= -4626.7277 1.10775
Gibbs Free Energy (G)= -4626.9673 0.86810
Entropy (S)= 0.00087735

Frequencies -- 5.5658 9.0803 11.4259

Supporting Information: major (*R*)-B(9)-TS (II-TS$_{(R)\text{-B(9)}}$)

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

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# pbepbe/genecp/auto empiricaldispersion=gd3bj
scf=(maxcycle=300,direct,vshift=200,tight,yqc) density=current
scrf=(cpcm,solvent=benzene) opt=(gdiis,maxcycle=250,ts,calcfc,noeigentest)
freq=noraman Temperature=273.15
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/GenECP/Auto Freq

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Pointgroup= C1 Stoichiometry= C74H74B10BrCl19N4O18Rh2Si2 C1[X(C74H74B10BrCl19N4O18Rh2Si2)]
#Atoms= 204

Charge = 0 Multiplicity = 1

SCF Energy= -5776.18133065 Predicted Change= -3.969515D-08

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Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00298	0.00180	[NO]	0.00298	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	0.355114	2.842036	-3.774499
O	0.063212	2.607164	-1.516059
O	-1.153027	0.352050	-4.203028
O	-1.480524	0.174318	-1.939888
O	2.806587	1.303145	-3.587294
O	2.545451	0.991863	-1.331271
O	1.329274	-1.156321	-4.052874
O	0.910697	-1.444619	-1.820524
C	0.114716	3.281944	-2.605050
C	-0.194941	4.781916	-2.405818
H	-1.255604	4.820521	-2.089453
C	-0.053047	5.736632	-3.631624
C	1.364930	5.728538	-4.232961
H	2.116569	6.065000	-3.499591
H	1.400234	6.419547	-5.093691
H	1.648352	4.723081	-4.579120
C	-0.394106	7.165711	-3.157183
H	0.347871	7.541428	-2.431652
H	-1.390359	7.209993	-2.684220
H	-0.391859	7.849498	-4.023298
C	-1.094368	5.314537	-4.691898
H	-1.106464	6.055621	-5.509963
H	-2.109669	5.271158	-4.257697
H	-0.859425	4.327695	-5.117392
C	-1.860297	0.139401	-3.167138
C	-3.340388	-0.255735	-3.352826
H	-3.418075	-1.284023	-2.951844
C	-3.929568	-0.283124	-4.802802
C	-3.180135	-1.357027	-5.621509
H	-3.665975	-1.463484	-6.607254
H	-3.206325	-2.337040	-5.116157
H	-2.126833	-1.082306	-5.777890
C	-5.412319	-0.703766	-4.701385
H	-5.528810	-1.662692	-4.167500
H	-6.020388	0.056006	-4.180266
H	-5.827734	-0.822166	-5.716750
C	-3.845207	1.080955	-5.514418
H	-4.252036	0.980082	-6.536187
H	-2.805265	1.433190	-5.584716

H	-4.438650	1.851793	-4.995377
C	3.228272	1.245454	-2.385904
C	4.717772	1.559503	-2.118188
H	4.710029	2.463739	-1.482005
C	5.624038	1.866356	-3.357493
C	7.056583	2.152762	-2.856380
H	7.524833	1.256459	-2.414060
H	7.073665	2.957731	-2.102772
H	7.682081	2.463890	-3.710637
C	5.094392	3.147626	-4.040026
H	5.010586	3.976862	-3.315413
H	4.105846	2.986779	-4.493608
H	5.798806	3.456758	-4.831870
C	5.677702	0.696510	-4.359288
H	6.330272	0.972956	-5.206253
H	4.678941	0.452756	-4.750161
H	6.101409	-0.211650	-3.897356
C	1.242390	-1.852194	-2.992538
C	1.612877	-3.349576	-3.046864
H	2.453697	-3.459336	-2.337463
C	2.081496	-3.946276	-4.416356
C	3.376742	-3.223696	-4.847566
H	3.776634	-3.709844	-5.754557
H	4.145939	-3.279003	-4.058732
H	3.192550	-2.162820	-5.071315
C	2.415114	-5.438690	-4.199628
H	1.516983	-6.030377	-3.950616
H	3.156031	-5.579817	-3.394116
H	2.836591	-5.855199	-5.130426
C	1.012931	-3.832259	-5.520911
H	0.722584	-2.785427	-5.693336
H	1.420985	-4.244229	-6.460773
H	0.105678	-4.408923	-5.274184
Rh	0.836222	0.842867	-3.964819
Rh	0.515567	0.585453	-1.545158
C	0.307704	0.425610	0.614382
C	1.444837	-0.114614	1.406627
C	-0.259469	1.722950	1.051757
C	2.088487	-1.304431	0.995746
C	1.846875	0.473513	2.629376
O	-1.640535	1.779202	1.040154
O	0.444770	2.696535	1.303099
C	3.037395	-1.933800	1.808857
H	1.811932	-1.759785	0.042565
C	2.826591	-0.120557	3.433092
H	1.381007	1.400121	2.970182
C	-2.198210	3.079134	1.208186
C	3.385317	-1.334530	3.023421
H	3.479261	-2.884351	1.501727
H	3.119626	0.340072	4.379524
H	-2.990896	3.197715	0.457338

H	-1.427295	3.848772	1.066692
C	-2.819731	3.294967	2.596901
Br	4.668918	-2.238540	4.214225
Cl	-3.556151	4.965485	2.622682
Cl	-1.577986	3.176061	3.934138
Cl	-4.159142	2.098031	2.964353
H	-0.592715	-0.414010	0.438614
N	0.544170	5.223430	-1.214691
C	1.859102	4.828455	-0.896388
C	-0.110860	5.818092	-0.121544
O	2.622380	4.237907	-1.648689
C	2.085453	5.276535	0.516759
O	-1.292342	6.142622	-0.099078
C	0.910714	5.901892	0.971490
C	3.185162	5.125582	1.353750
C	0.826141	6.409841	2.263329
C	3.103921	5.618638	2.676542
Cl	4.642120	4.283130	0.817853
C	1.934347	6.263289	3.128210
Cl	-0.639037	7.218484	2.839926
Cl	4.470890	5.414105	3.776732
Cl	1.851409	6.876073	4.782856
N	5.258935	0.502430	-1.253458
C	4.978325	-0.866671	-1.389748
C	6.070056	0.774484	-0.132910
O	4.246942	-1.363522	-2.237147
C	5.750645	-1.550611	-0.300035
O	6.408827	1.884714	0.250645
C	6.413136	-0.564012	0.451592
C	5.880040	-2.896892	0.021701
C	7.223524	-0.908966	1.527870
C	6.707880	-3.264083	1.106719
Cl	4.990089	-4.145240	-0.867537
C	7.384012	-2.275459	1.851451
Cl	8.040183	0.327986	2.494352
Cl	6.876409	-4.963698	1.551695
Cl	8.414946	-2.748777	3.202216
N	0.516956	-4.113914	-2.438182
C	-0.844422	-3.931757	-2.727845
C	0.730959	-5.099417	-1.454118
O	-1.308258	-3.057612	-3.448343
C	-1.567143	-5.004124	-1.963869
O	1.809919	-5.378154	-0.951263
C	-0.621553	-5.699308	-1.188314
C	-2.909470	-5.367471	-1.951747
C	-1.008793	-6.756319	-0.371663
C	-3.310359	-6.465643	-1.156801
Cl	-4.112592	-4.479977	-2.897441
C	-2.366735	-7.150117	-0.363051
Cl	0.158215	-7.585250	0.669846
Cl	-5.004512	-6.964353	-1.132036

Cl	-2.895531	-8.476857	0.677044
N	-4.136342	0.555419	-2.425546
C	-5.043386	-0.017656	-1.512820
C	-3.997838	1.942051	-2.251083
O	-5.287752	-1.211690	-1.413546
C	-5.616684	1.136429	-0.740699
O	-3.187849	2.660724	-2.823062
C	-5.016347	2.318467	-1.212695
C	-6.578946	1.179723	0.261759
C	-5.392931	3.561518	-0.713132
C	-6.974427	2.435053	0.778174
Cl	-7.288059	-0.306549	0.914611
C	-6.394737	3.622589	0.283521
Cl	-4.634392	5.052609	-1.296924
Cl	-8.185592	2.520630	2.058671
Cl	-6.913817	5.182745	0.920904
B	-1.314525	-1.222771	1.301189
B	-3.046701	-0.976246	1.396288
B	-2.006796	-0.778545	2.835768
B	-2.353299	-2.308499	0.405810
B	-0.900650	-2.934685	1.263473
B	-0.693852	-1.981062	2.747278
H	-3.626765	-0.049637	0.925503
B	-3.754426	-2.592434	1.463658
B	-3.542092	-1.663943	2.961258
H	-1.855575	0.224202	3.460175
H	-2.449949	-2.335222	-0.783457
H	0.046751	-3.403004	0.706511
H	0.341603	-1.798242	3.300633
H	-4.861980	-2.865501	1.121249
H	-4.444565	-1.310955	3.653781
B	-2.447257	-3.784968	1.395577
H	-2.658115	-4.897823	1.026598
B	-1.432217	-3.583331	2.838115
H	-0.956472	-4.492650	3.442619
Si	-4.263653	-4.687957	3.722179
C	-5.203447	-3.979487	5.198042
C	-5.530986	-5.211028	2.425801
C	-3.185606	-6.172741	4.160949
H	-5.762493	-3.073340	4.908661
H	-5.940886	-4.735118	5.523686
H	-4.573102	-3.735359	6.065951
H	-5.063740	-5.517619	1.476756
H	-6.087630	-6.078971	2.823542
H	-6.257325	-4.410797	2.209862
H	-3.834027	-6.974166	4.557996
H	-2.682288	-6.566760	3.261343
H	-2.415037	-5.954004	4.915955
Si	-1.843876	-2.035484	5.627480
C	-3.273885	-0.998132	6.289281
C	-1.646502	-3.705168	6.485221

C	-0.237638	-1.067301	5.856273
H	-3.323739	-0.032774	5.756066
H	-4.256416	-1.486791	6.202697
H	-3.092426	-0.782878	7.357375
H	-2.561527	-4.315452	6.514922
H	-0.847980	-4.297796	6.006841
H	-1.337731	-3.515322	7.528953
H	-0.158249	-0.790680	6.923362
H	0.652594	-1.661074	5.592215
H	-0.219275	-0.138748	5.262365
C	-3.132537	-3.324904	2.889211
C	-2.092257	-2.249858	3.696909

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

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SCF Energy= -5776.18133065 Predicted Change= -3.969515D-08
Zero-point correction (ZPE)= -5774.7982 1.38313
Internal Energy (U)= -5774.6797 1.50157
Enthalpy (H)= -5774.6788 1.50244
Gibbs Free Energy (G)= -5774.9570 1.22426
Entropy (S)= 0.00101841

Frequencies -- -96.2871 6.6986 8.0238

Supporting Information: enantiomeric minor (*S*)-B(9)-TS (II-TS$_{(S)\text{-B(9)}}$)

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

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# pbepbe/genecp/auto empiricaldispersion=gd3bj
scf=(maxcycle=300,direct,vshift=200,tight,yqc) density=current
scrf=(cpcm,solvent=benzene) opt=(gdiis,maxcycle=250,ts,calcfc,noeigentest)
freq=noraman Temperature=273.15 iop(1/8=12)
#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk RPBEPBE/GenECP/Auto
Freq

Pointgroup= C1 Stoichiometry= C74H74B10BrCl19N4O18Rh2Si2 C1[X(C74H74B10BrCl19N4O18Rh2Si2)]
#Atoms= 204
Charge = 0 Multiplicity = 1

SCF Energy= -5776.18203269 Predicted Change= -8.309322D-09

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Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00101	0.00180	[YES]	0.00101	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	-0.016632	-2.456149	3.898790

O	-0.440963	-2.278641	1.657122
O	-0.458786	0.411611	4.219064
O	-0.999867	0.588597	2.000171
O	2.765144	-2.005132	3.363419
O	2.366255	-1.663109	1.131984
O	2.362912	0.896157	3.718692
O	1.833910	1.198316	1.508152
C	-0.511027	-2.859415	2.795659
C	-1.333865	-4.167179	2.810962
H	-2.392904	-3.848910	2.748308
C	-1.199800	-5.086540	4.073285
C	0.262567	-5.471617	4.366939
H	0.883154	-4.583610	4.558741
H	0.709791	-6.027711	3.526219
H	0.297325	-6.122258	5.258525
C	-2.014553	-6.375236	3.828753
H	-3.064740	-6.153250	3.575481
H	-2.001457	-6.989746	4.745199
H	-1.584421	-6.984123	3.014930
C	-1.823672	-4.354012	5.282198
H	-1.253137	-3.453091	5.549582
H	-1.839105	-5.032489	6.152949
H	-2.866537	-4.056672	5.068592
C	-1.191686	0.796485	3.252939
C	-2.431121	1.654214	3.595474
H	-2.227839	2.652222	3.163569
C	-2.763942	1.861023	5.114211
C	-1.608332	2.651577	5.768104
H	-1.892195	2.919969	6.800690
H	-1.403753	3.585180	5.215584
H	-0.680999	2.062612	5.800606
C	-4.042987	2.719685	5.226668
H	-3.946118	3.674193	4.682794
H	-4.932158	2.190979	4.841465
H	-4.230842	2.945294	6.290318
C	-3.001747	0.530135	5.854093
H	-3.231120	0.740671	6.913589
H	-2.116915	-0.121583	5.809849
H	-3.860661	-0.019491	5.432486
C	3.011190	-2.156792	2.122122
C	4.179289	-3.061652	1.676882
H	3.706195	-3.845196	1.056440
C	5.021846	-3.783050	2.776220
C	6.094645	-4.638680	2.068146
H	6.833444	-4.011919	1.539131
H	5.645485	-5.332368	1.336982
H	6.641420	-5.233996	2.819496
C	4.081989	-4.729352	3.554635
H	3.551353	-5.414827	2.870512
H	3.330469	-4.167861	4.129016
H	4.675729	-5.339664	4.257271

C	5.717324	-2.804101	3.741051
H	6.435993	-2.154934	3.212980
H	6.281344	-3.378391	4.497241
H	4.987246	-2.163728	4.257983
C	2.398710	1.524419	2.613796
C	3.237920	2.816608	2.517576
H	4.015947	2.602903	1.760801
C	3.977958	3.320161	3.799878
C	4.995182	2.241203	4.231872
H	5.621487	2.640413	5.048690
H	5.658532	1.957098	3.397003
H	4.490607	1.331816	4.588941
C	4.759352	4.598346	3.424614
H	4.084200	5.430047	3.157972
H	5.443411	4.424227	2.576061
H	5.361150	4.924787	4.289900
C	3.015687	3.643124	4.959032
H	2.415795	2.764350	5.238907
H	3.603042	3.962777	5.837860
H	2.328065	4.466408	4.702399
Rh	1.175591	-0.784611	3.855979
Rh	0.677241	-0.528008	1.463335
C	0.317300	-0.351076	-0.686850
C	-0.497773	-1.416430	-1.327208
C	1.647797	-0.045448	-1.271884
C	-1.747211	-1.772060	-0.767138
C	-0.107048	-2.038475	-2.536017
O	1.945268	1.301941	-1.339656
O	2.453880	-0.922207	-1.570253
C	-2.617383	-2.646772	-1.426841
H	-2.051174	-1.335457	0.186012
C	-0.962344	-2.920858	-3.206404
H	0.865047	-1.808781	-2.976119
C	3.308555	1.613502	-1.619562
C	-2.223532	-3.177062	-2.661112
H	-3.588718	-2.894615	-0.992314
H	-0.661890	-3.366248	-4.158034
H	3.630744	2.388515	-0.907091
H	3.928258	0.708413	-1.523517
C	3.503527	2.169259	-3.038203
Br	-3.512886	-4.235894	-3.704930
Cl	2.564520	3.707446	-3.316786
Cl	5.282056	2.574867	-3.238738
Cl	3.041902	0.958443	-4.325798
H	-0.342553	0.687494	-0.517491
N	-1.093818	-4.869881	1.546554
C	0.150856	-4.956778	0.891451
C	-2.143820	-5.396431	0.772813
O	1.228079	-4.612893	1.358365
C	-0.138443	-5.587441	-0.438221
O	-3.330816	-5.371212	1.072511

C	-1.499983	-5.940653	-0.466109
C	0.694826	-5.864703	-1.516541
C	-2.031289	-6.659661	-1.530696
C	0.149641	-6.539121	-2.633950
Cl	2.387725	-5.361207	-1.517536
C	-1.196678	-6.961056	-2.630893
Cl	-3.709274	-7.223885	-1.505295
Cl	1.165529	-6.865678	-4.042196
Cl	-1.838709	-7.860834	-4.006897
N	4.994922	-2.291720	0.729926
C	5.372706	-0.951795	0.906177
C	5.342276	-2.785435	-0.543406
O	5.080376	-0.245569	1.863197
C	6.173524	-0.594624	-0.312800
O	5.054002	-3.889701	-0.980601
C	6.135910	-1.690352	-1.195027
C	6.895531	0.551158	-0.628119
C	6.800968	-1.646618	-2.415477
C	7.610475	0.592978	-1.846682
Cl	6.928842	1.948700	0.461326
C	7.549927	-0.492865	-2.744534
Cl	6.727532	-3.003683	-3.548801
Cl	8.571289	2.016516	-2.257940
Cl	8.409134	-0.406082	-4.283183
N	2.401444	3.850523	1.893881
C	1.064235	4.123479	2.233713
C	2.833093	4.595516	0.781732
O	0.409573	3.533129	3.082764
C	0.640410	5.246466	1.331474
O	3.905728	4.450392	0.207633
C	1.708925	5.536022	0.461988
C	-0.554850	5.952572	1.254342
C	1.596743	6.532906	-0.501489
C	-0.684909	6.963898	0.274366
Cl	-1.913780	5.589904	2.326528
C	0.380507	7.247953	-0.603620
Cl	2.935626	6.914416	-1.592327
Cl	-2.199194	7.864900	0.133497
Cl	0.189049	8.492405	-1.841624
N	-3.571638	1.141461	2.825771
C	-3.851049	-0.219678	2.613923
C	-4.490052	1.988714	2.175374
O	-3.193909	-1.160669	3.039399
C	-5.103057	-0.250226	1.783502
O	-4.427167	3.208750	2.126043
C	-5.514269	1.076643	1.563388
C	-5.838848	-1.319996	1.284346
C	-6.694474	1.354139	0.883206
C	-7.031598	-1.051164	0.572740
Cl	-5.283210	-2.985746	1.485258
C	-7.464913	0.278772	0.384303

Cl	-7.246750	3.023837	0.650798
Cl	-7.968026	-2.381868	-0.107930
Cl	-8.959835	0.596256	-0.499728
B	-1.071980	1.498654	-1.399537
B	-1.929017	2.723094	-0.463186
B	-2.811844	1.375429	-1.220760
B	-0.570419	3.158700	-1.552453
B	-0.646723	2.075013	-2.995817
B	-2.035991	0.985175	-2.775577
H	-1.867009	2.841485	0.720160
B	-2.067580	4.118069	-1.541658
B	-3.452489	3.020572	-1.345288
H	-3.443162	0.556097	-0.632632
H	0.454240	3.597031	-1.132683
H	0.304077	1.718294	-3.619768
H	-2.141424	-0.098510	-3.262706
H	-2.204618	5.248142	-1.186384
H	-4.497223	3.354710	-0.883277
B	-1.268074	3.731397	-3.075720
H	-0.835279	4.589442	-3.781534
C	-3.428197	1.978165	-2.709402
B	-2.185184	2.410929	-3.824146
H	-2.402773	2.338906	-4.992942
C	-2.972540	3.610131	-2.890978
Si	-4.026226	5.038914	-3.718459
C	-4.708942	4.503232	-5.395273
C	-5.342369	5.593538	-2.486346
C	-2.847103	6.482614	-4.022453
H	-5.489023	3.729224	-5.351528
H	-5.148626	5.393481	-5.880097
H	-3.895845	4.139472	-6.046686
H	-6.063406	4.808916	-2.212214
H	-4.861701	5.954044	-1.560212
H	-5.904278	6.438031	-2.923701
H	-3.451858	7.345518	-4.356250
H	-2.302517	6.784738	-3.113533
H	-2.110664	6.260512	-4.811465
Si	-5.051646	1.147052	-3.427756
C	-6.581975	2.197908	-3.098367
C	-4.776963	0.783958	-5.258052
C	-5.245110	-0.492223	-2.521009
H	-6.643207	3.117027	-3.699541
H	-7.466738	1.581377	-3.338352
H	-6.657199	2.476387	-2.035048
H	-4.643056	1.682339	-5.879510
H	-3.892733	0.137386	-5.391714
H	-5.655114	0.232384	-5.638953
H	-6.142174	-1.006989	-2.909104
H	-4.377438	-1.151402	-2.679792
H	-5.376052	-0.354808	-1.437612

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -5776.18203269 Predicted Change= -8.309322D-09
Zero-point correction (ZPE)= -5774.7986 1.38336
Internal Energy (U)= -5774.6805 1.50146
Enthalpy (H)= -5774.6797 1.50232
Gibbs Free Energy (G)= -5774.9543 1.22769
Entropy (S)= 0.00100541

Frequencies -- -118.7097 10.4408 12.0997

Supporting Information: regioisomeric minor (*R*)-B(8)-TS (II-TS$_{(R)\text{-B(8)}}$)

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

# pbepbe/genecp/auto empiricaldispersion=gd3bj
scf=(maxcycle=300,direct,vshift=200,tight,yqc) density=current
scrf=(cpcm,solvent=benzene) opt=(gdiis,maxcycle=250,ts,calcfc,noeigentest)
freq=noraman Temperature=273.15
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/GenECP/Auto Freq

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Pointgroup= C1 Stoichiometry= C74H74B10BrCl19N4O18Rh2Si2 C1[X(C74H74B10BrCl19N4O18Rh2Si2)]
#Atoms= 204
Charge = 0 Multiplicity = 1

SCF Energy= -5776.18116847 Predicted Change= -4.507597D-09

Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00002 ||	0.00045	[YES]	0.00000 ||	0.00030	[YES]
Displ	0.00077 ||	0.00180	[YES]	0.00077 ||	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	1.909500	-2.133353	-3.837882
O	1.840593	-1.904039	-1.562267
O	1.624600	0.808465	-4.042887
O	1.579891	0.986017	-1.755860
O	-0.972858	-2.379482	-3.883742
O	-1.116981	-2.173821	-1.605936
O	-1.240612	0.503231	-4.123709
O	-1.338541	0.775276	-1.852558
C	2.278602	-2.415629	-2.654098
C	3.399946	-3.452798	-2.421160
H	4.256936	-2.868435	-2.032092
C	3.928055	-4.266267	-3.641218
C	2.821435	-5.070202	-4.349056
H	2.023821	-4.410378	-4.723536
H	2.364700	-5.811359	-3.672615

H	3.256602	-5.615201	-5.205317
C	5.010232	-5.236093	-3.119929
H	5.805150	-4.699814	-2.572716
H	5.473087	-5.763289	-3.971720
H	4.581980	-5.997012	-2.445075
C	4.590978	-3.277621	-4.625888
H	3.850089	-2.600363	-5.076236
H	5.087905	-3.841759	-5.434171
H	5.357614	-2.663938	-4.118932
C	1.956947	1.336145	-2.934223
C	2.886152	2.567579	-2.947427
H	2.302356	3.371401	-2.461502
C	3.376300	3.121931	-4.326321
C	2.146840	3.589828	-5.134895
H	2.489678	4.072404	-6.066863
H	1.549333	4.321859	-4.566265
H	1.492286	2.746025	-5.398665
C	4.267104	4.352898	-4.048456
H	3.741586	5.108441	-3.439373
H	5.198686	4.076125	-3.524916
H	4.551071	4.820959	-5.006527
C	4.187167	2.095608	-5.140792
H	4.483052	2.552396	-6.101814
H	3.596770	1.191195	-5.349384
H	5.110534	1.795121	-4.618463
C	-1.429906	-2.691569	-2.736074
C	-2.444768	-3.855120	-2.648383
H	-1.954651	-4.617119	-2.014818
C	-2.856794	-4.551833	-3.988735
C	-3.857379	-5.683034	-3.664951
H	-4.813932	-5.289035	-3.280130
H	-3.451666	-6.389245	-2.921517
H	-4.079986	-6.242462	-4.589768
C	-1.595426	-5.196168	-4.606720
H	-1.095554	-5.862835	-3.881726
H	-0.869590	-4.437537	-4.933131
H	-1.887165	-5.802957	-5.481566
C	-3.519802	-3.581141	-4.985325
H	-4.447362	-3.149334	-4.571601
H	-3.792064	-4.132482	-5.902651
H	-2.844898	-2.756847	-5.258005
C	-1.715331	1.010442	-3.058268
C	-2.919082	1.972088	-3.203599
H	-3.738282	1.492877	-2.637582
C	-3.448286	2.245485	-4.655766
C	-3.952965	0.915053	-5.257720
H	-4.433855	1.118838	-6.230389
H	-4.699353	0.439708	-4.598443
H	-3.132059	0.201326	-5.415314
C	-4.655095	3.206140	-4.567512
H	-4.361682	4.210960	-4.217272

H	-5.439983	2.820738	-3.895354
H	-5.091470	3.325596	-5.573933
C	-2.383440	2.885839	-5.568132
H	-1.496530	2.243771	-5.668335
H	-2.817470	3.047365	-6.570642
H	-2.060083	3.869516	-5.186892
Rh	0.337617	-0.801151	-4.028799
Rh	0.244648	-0.593060	-1.583999
C	0.216898	-0.562021	0.580437
C	-1.006552	-1.052142	1.270395
C	1.503371	-1.128469	1.051575
C	-2.277943	-0.615131	0.832835
C	-0.942219	-1.875690	2.420510
O	2.527301	-0.216685	1.202473
O	1.661280	-2.335635	1.204492
C	-3.430811	-0.897895	1.574535
H	-2.354157	-0.014587	-0.077137
C	-2.093399	-2.212731	3.140753
H	0.020501	-2.251244	2.771581
C	3.811693	-0.790019	1.446033
C	-3.318745	-1.683154	2.726649
H	-4.398366	-0.500212	1.263124
H	-2.025136	-2.847597	4.027393
H	3.815468	-1.860715	1.195586
H	4.530442	-0.253602	0.813546
C	4.271459	-0.644113	2.904498
Br	-4.925232	-2.029388	3.812305
Cl	3.150302	-1.491005	4.074600
Cl	5.932618	-1.397950	3.033810
Cl	4.415078	1.106950	3.419867
H	0.299327	0.694479	0.585766
N	2.994134	-4.277379	-1.272529
C	1.680164	-4.740791	-1.050744
C	3.770833	-4.316787	-0.100527
O	0.783261	-4.747518	-1.883113
C	1.638253	-5.173278	0.384609
O	4.897852	-3.848355	0.012634
C	2.910000	-4.957420	0.943661
C	0.575006	-5.600534	1.172325
C	3.150794	-5.200375	2.290814
C	0.795476	-5.803310	2.553778
Cl	-1.046346	-5.809022	0.502331
C	2.077441	-5.616120	3.109846
Cl	4.754164	-4.947692	2.997668
Cl	-0.554166	-6.261228	3.601094
Cl	2.332031	-5.868026	4.840289
N	-3.596217	-3.398370	-1.857418
C	-4.173917	-2.122099	-1.948826
C	-4.194175	-4.186791	-0.853634
O	-3.806234	-1.225876	-2.698072
C	-5.296797	-2.110343	-0.953171

O	-3.836143	-5.306035	-0.516527
C	-5.322805	-3.360703	-0.309821
C	-6.199795	-1.111537	-0.605433
C	-6.270316	-3.643351	0.667971
C	-7.168478	-1.383384	0.388311
Cl	-6.100501	0.508476	-1.315664
C	-7.212412	-2.646866	1.013426
Cl	-6.301491	-5.208971	1.489197
Cl	-8.307183	-0.124778	0.875218
Cl	-8.428285	-2.971057	2.249171
N	-2.629429	3.210144	-2.468572
C	-1.394623	3.879768	-2.484515
C	-3.583968	3.863857	-1.665725
O	-0.387272	3.493174	-3.062031
C	-1.591429	5.117394	-1.656863
O	-4.704022	3.446248	-1.403945
C	-2.921718	5.128229	-1.198766
C	-0.711097	6.140992	-1.321471
C	-3.401240	6.182599	-0.427868
C	-1.176108	7.200120	-0.507664
Cl	0.975277	6.114796	-1.848215
C	-2.517081	7.226132	-0.071158
Cl	-5.083789	6.229406	0.127453
Cl	-0.069732	8.482314	-0.014276
Cl	-3.079097	8.545453	0.958862
N	3.984658	2.302322	-2.012839
C	4.721456	1.107945	-1.959303
C	4.309995	3.187864	-0.966014
O	4.539540	0.120192	-2.659931
C	5.721172	1.304692	-0.854801
O	3.756971	4.255374	-0.744216
C	5.447223	2.537388	-0.232245
C	6.760618	0.493254	-0.409443
C	6.187983	2.959849	0.865676
C	7.546630	0.928916	0.683384
Cl	7.093606	-1.070824	-1.168885
C	7.249916	2.148202	1.328682
Cl	5.797551	4.468026	1.705112
Cl	8.889789	-0.061415	1.254262
Cl	8.198660	2.650140	2.728235
B	0.199576	1.675408	1.540802
B	1.520221	2.792357	1.841901
B	0.875601	1.734594	3.139245
B	0.150902	3.272534	0.808242
B	-1.324577	2.514228	1.459332
B	-0.891444	1.580609	2.917485
H	2.627022	2.642732	1.425025
B	0.760689	4.402605	2.048388
B	1.221759	3.441560	3.465450
H	1.424538	0.846313	3.712381
H	0.273589	3.448682	-0.364446

C	-1.541440	3.148977	3.040917
H	-2.281885	2.183023	0.836960
H	-1.517311	0.657557	3.324386
H	1.315258	5.428300	1.778426
B	-0.330312	4.301652	3.457502
H	2.040269	3.757361	4.272944
Si	-3.403030	3.363206	3.611825
H	-0.604576	5.175161	4.221041
C	-3.932413	2.041769	4.852020
C	-4.478957	3.087506	2.088494
C	-3.601256	5.126248	4.253043
H	-3.775357	1.032343	4.434633
H	-3.453594	2.092868	5.839992
H	-5.020756	2.163332	5.002758
H	-4.449942	2.035211	1.759978
H	-5.523037	3.323998	2.363141
H	-4.212433	3.721070	1.231262
H	-2.982369	5.336668	5.140080
H	-3.335741	5.856770	3.469247
H	-4.657865	5.295820	4.525644
B	-0.989510	4.208188	1.814617
H	-1.744976	5.063858	1.468946
C	-0.219570	2.693438	4.032388
Si	-0.276217	2.260787	5.938848
C	-1.227823	3.585754	6.890122
C	-0.937369	0.502821	6.128354
C	1.512153	2.275904	6.546814
H	-2.292631	3.669802	6.627044
H	-1.166033	3.353024	7.968329
H	-0.757396	4.572203	6.735834
H	-1.977840	0.366228	5.799297
H	-0.305211	-0.196024	5.552770
H	-0.873441	0.212922	7.192330
H	1.524191	1.876361	7.577222
H	2.169294	1.641290	5.929604
H	1.936007	3.292707	6.572240

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -5776.18116847 Predicted Change= -4.507597D-09
Zero-point correction (ZPE)= -5774.7977 1.38341
Internal Energy (U)= -5774.6795 1.50157
Enthalpy (H)= -5774.6787 1.50243
Gibbs Free Energy (G)= -5774.9543 1.22680
Entropy (S)= 0.0010091

Frequencies -- -83.8102 9.9172 12.0736

Supporting Information: major (*R*)-B(9) product complex III

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

# pbepbe/genecp/auto empiricaldispersion=gd3bj
scf=(maxcycle=300,direct,vshift=200,tight,yqc) density=current
scrf=(cpcm,solvent=benzene) opt=(gdiis,maxcycle=250) freq=noraman
Temperature=273.15
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/GenECP/Auto Freq

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Pointgroup= C1 Stoichiometry= C74H74B10BrCl19N4O18Rh2Si2 C1[X(C74H74B10BrCl19N4O18Rh2Si2)]
#Atoms= 204
Charge = 0 Multiplicity = 1

SCF Energy= -5776.25682257 Predicted Change= -2.214168D-07

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00025	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00654	0.00180	[NO]	0.00654	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	2.496951	-1.008232	-3.693806
O	2.274371	-0.852652	-1.421188
O	1.550019	1.692781	-4.057918
O	1.365636	1.921650	-1.790266
O	-0.239666	-2.000599	-3.869672
O	-0.502260	-1.778793	-1.604917
O	-1.192666	0.729232	-4.235371
O	-1.408425	0.954458	-1.967771
C	2.890377	-1.189399	-2.493069
C	4.272886	-1.833642	-2.260283
H	4.831204	-1.093356	-1.659631
C	5.142777	-2.169506	-3.518571
C	4.472253	-3.192427	-4.455808
H	4.312118	-4.160791	-3.951751
H	5.132676	-3.377070	-5.321351
H	3.502288	-2.828771	-4.825168
C	6.488486	-2.752689	-3.033576
H	6.360546	-3.734112	-2.544935
H	6.995644	-2.077463	-2.323915
H	7.151415	-2.902331	-3.902896
C	5.438371	-0.853878	-4.272323
H	6.147166	-1.057487	-5.093720
H	5.896499	-0.106633	-3.601527
H	4.524987	-0.415689	-4.700184
C	1.747536	2.299604	-2.952969
C	2.486090	3.655888	-2.987341
H	1.732260	4.405183	-2.678629
C	3.075541	4.121718	-4.360279
C	1.904243	4.338530	-5.344825

H	2.285601	4.811217	-6.266551
H	1.140306	5.008518	-4.911115
H	1.417729	3.390145	-5.614293
C	3.779174	5.480655	-4.153047
H	3.101602	6.229416	-3.709935
H	4.665942	5.389761	-3.502370
H	4.123871	5.860136	-5.130145
C	4.096060	3.120106	-4.934250
H	4.480619	3.503144	-5.895826
H	3.642768	2.132925	-5.107496
H	4.958376	2.991247	-4.258179
C	-0.640779	-2.391723	-2.723923
C	-1.336067	-3.763721	-2.613464
H	-0.700237	-4.354962	-1.928153
C	-1.521504	-4.611813	-3.916140
C	-2.204120	-5.939384	-3.519304
H	-3.233160	-5.779017	-3.153920
H	-1.639907	-6.471083	-2.733861
H	-2.264921	-6.596043	-4.403874
C	-0.129063	-4.940310	-4.497469
H	0.520754	-5.413375	-3.742184
H	0.379513	-4.037117	-4.865137
H	-0.247018	-5.643761	-5.340107
C	-2.387418	-3.905611	-4.977254
H	-2.454591	-4.548341	-5.872719
H	-1.954617	-2.938061	-5.272015
H	-3.414979	-3.731068	-4.617358
C	-1.796831	1.112361	-3.179878
C	-3.162222	1.816388	-3.306592
H	-3.884957	1.129229	-2.826448
C	-3.714948	2.126540	-4.733127
C	-3.942505	0.785438	-5.465614
H	-4.465505	0.975332	-6.418995
H	-4.565432	0.101360	-4.863052
H	-2.991272	0.278044	-5.684599
C	-5.081854	2.824524	-4.563527
H	-4.978659	3.813720	-4.084981
H	-5.774892	2.218912	-3.954599
H	-5.538930	2.979108	-5.555846
C	-2.782949	3.036709	-5.554882
H	-1.789061	2.582416	-5.685035
H	-3.225991	3.203407	-6.552577
H	-2.652478	4.021865	-5.077235
Rh	0.652886	-0.156673	-4.010229
Rh	0.429452	0.078134	-1.619431
C	-2.255422	-0.981656	1.588036
C	-3.707697	-0.649814	1.869275
C	-1.888451	-2.390464	1.993992
C	-4.428048	0.111188	0.933558
C	-4.318834	-0.949146	3.103042
O	-0.577968	-2.687001	1.646366

O	-2.628935	-3.218072	2.498321
C	-5.710883	0.601217	1.218161
H	-3.973316	0.357704	-0.031195
C	-5.607110	-0.487211	3.402684
H	-3.783076	-1.541824	3.847876
C	-0.210914	-4.056558	1.810349
C	-6.273839	0.297346	2.457563
H	-6.234900	1.215641	0.485232
H	-6.070592	-0.720510	4.364290
H	0.389300	-4.339888	0.933248
H	-1.110419	-4.687613	1.876500
C	0.637824	-4.294682	3.066589
Br	-8.057620	1.022946	2.902447
Cl	0.937794	-6.096485	3.210045
Cl	-0.194641	-3.737139	4.586483
Cl	2.269953	-3.456330	2.962401
H	-2.079598	-0.947171	0.494488
N	4.095686	-2.984038	-1.366171
C	3.071076	-3.937857	-1.481740
C	4.941736	-3.234796	-0.266639
O	2.142597	-3.891044	-2.278975
C	3.362272	-4.972639	-0.434623
O	5.853632	-2.512669	0.110528
C	4.484778	-4.547046	0.299284
C	2.741836	-6.183531	-0.148314
C	4.993305	-5.319208	1.337750
C	3.271801	-6.998259	0.878472
Cl	1.305144	-6.717611	-1.039303
C	4.383457	-6.561348	1.628645
Cl	6.376131	-4.769483	2.295479
Cl	2.536612	-8.562401	1.232886
Cl	5.005405	-7.565943	2.937954
N	-2.587524	-3.570153	-1.874077
C	-3.515348	-2.542432	-2.118304
C	-2.932521	-4.348838	-0.750780
O	-3.384660	-1.649865	-2.947591
C	-4.630364	-2.768943	-1.143723
O	-2.238905	-5.241085	-0.278403
C	-4.268684	-3.838661	-0.301831
C	-5.855565	-2.128968	-1.001129
C	-5.117840	-4.262117	0.715758
C	-6.730738	-2.549224	0.026104
Cl	-6.340261	-0.821425	-2.093190
C	-6.351638	-3.593701	0.895374
Cl	-4.697820	-5.627963	1.755144
Cl	-8.303046	-1.778081	0.214950
Cl	-7.438300	-4.083319	2.195904
N	-3.126970	2.981006	-2.412377
C	-2.044722	3.871664	-2.292857
C	-4.081291	3.156416	-1.392251
O	-1.038207	3.867027	-2.990297

C	-2.388663	4.769264	-1.139940
O	-5.086771	2.473832	-1.251078
C	-3.596648	4.316959	-0.577194
C	-1.721806	5.869530	-0.611826
C	-4.135707	4.929146	0.549635
C	-2.275871	6.523728	0.513082
Cl	-0.201685	6.443780	-1.310430
C	-3.463259	6.043042	1.103886
Cl	-5.613484	4.322310	1.307157
Cl	-1.475932	7.945597	1.191676
Cl	-4.102420	6.829301	2.548695
N	3.470615	3.655584	-1.896424
C	3.629502	4.746852	-1.021935
C	4.239207	2.543024	-1.508858
O	3.019005	5.805212	-1.085022
C	4.655901	4.313918	-0.015703
O	4.282844	1.470547	-2.096313
C	4.973487	2.967229	-0.271127
C	5.252002	5.000550	1.036606
C	5.845614	2.267450	0.556887
C	6.160096	4.311650	1.873392
Cl	4.885376	6.705056	1.348870
C	6.437260	2.947133	1.647369
Cl	6.183856	0.552567	0.297998
Cl	6.925083	5.149536	3.225671
Cl	7.517291	2.080865	2.741874
B	-1.308387	0.229526	2.153545
B	0.101875	0.802784	1.232437
B	0.349285	0.056478	2.811120
B	-1.367381	1.795954	1.300040
B	-2.020937	1.677719	2.954551
B	-0.972049	0.582914	3.865768
H	0.515080	0.152201	0.285975
B	0.233988	2.551886	1.398554
B	1.296926	1.492411	2.345639
H	0.950981	-0.949265	3.018933
H	-2.064367	1.968152	0.346133
H	-3.184443	1.783952	3.206517
H	-1.301750	-0.070312	4.808930
H	0.734546	3.291570	0.609336
H	2.484521	1.483260	2.241072
B	-1.064703	3.086190	2.476844
H	-1.470014	4.211107	2.447048
B	-0.806428	2.336882	4.066909
H	-0.995882	2.904876	5.097539
Si	1.471841	4.462484	3.552261
C	3.293362	4.111968	3.898975
C	1.353530	5.601677	2.058382
C	0.571805	5.305654	4.981381
H	3.728492	3.510574	3.083636
H	3.828258	5.077765	3.924309

H	3.492824	3.594852	4.848569
H	0.309912	5.727809	1.734160
H	1.737715	6.596181	2.346452
H	1.938007	5.258577	1.193034
H	1.081684	6.260797	5.201165
H	-0.465061	5.541009	4.684640
H	0.536506	4.715824	5.909183
Si	1.736931	0.938347	5.428310
C	3.467203	0.555627	4.776044
C	1.696874	2.307648	6.729944
C	1.047067	-0.611520	6.248124
H	3.423085	-0.284483	4.061224
H	3.960662	1.403045	4.276405
H	4.103581	0.241679	5.622637
H	2.175538	3.252039	6.434237
H	0.657640	2.524214	7.031460
H	2.227597	1.929300	7.622392
H	1.748708	-0.917165	7.045449
H	0.062865	-0.433720	6.711323
H	0.951495	-1.448849	5.540552
C	0.515591	2.828792	3.074994
C	0.577323	1.342785	3.906182

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

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SCF Energy= -5776.25682257 Predicted Change= -2.214168D-07
Zero-point correction (ZPE)= -5774.8691 1.38764
Internal Energy (U)= -5774.7506 1.50618
Enthalpy (H)= -5774.7497 1.50705
Gibbs Free Energy (G)= -5775.0269 1.22987
Entropy (S)= 0.00101475

Frequencies -- 8.5692 11.9764 13.0613

Supporting Information: minor (*S*)-B(9) product complex III

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

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# pbepbe/genecp/auto empiricaldispersion=gd3bj
scf=(maxcycle=300,direct,vshift=200,tight,yqc) density=current
scrf=(cpcm,solvent=benzene) opt=(gdiis,maxcycle=250) freq=noraman
Temperature=273.15
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/GenECP/Auto Freq

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Pointgroup= C1 Stoichiometry= C74H74B10BrCl19N4O18Rh2Si2 C1[X(C74H74B10BrCl19N4O18Rh2Si2)]
#Atoms= 204
Charge = 0 Multiplicity = 1

SCF Energy= -5776.25586211 Predicted Change= -6.599586D-07

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Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00009	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.01616	0.00180	[NO]	0.01616	0.00180	[NO]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	0.850528	1.054625	-4.550441
O	1.033983	1.387622	-2.296407
O	-2.020111	1.155042	-4.338872
O	-1.935547	1.386506	-2.067420
O	0.820112	-1.825513	-4.125734
O	1.055799	-1.475816	-1.878538
O	-2.041321	-1.785622	-3.944014
O	-1.889647	-1.516964	-1.678586
C	1.377948	1.583665	-3.516192
C	2.511373	2.611070	-3.731623
H	2.125753	3.569463	-3.332945
C	2.984336	2.877883	-5.203238
C	3.516777	1.611651	-5.902725
H	2.755488	0.818904	-5.944524
H	4.407968	1.209907	-5.392565
H	3.813628	1.868748	-6.934756
C	4.114032	3.930896	-5.163639
H	3.800783	4.850862	-4.642232
H	4.393845	4.197093	-6.197144
H	5.020262	3.544084	-4.666628
C	1.804929	3.477102	-5.999610
H	0.999013	2.744000	-6.147717
H	2.163482	3.803875	-6.991029
H	1.384441	4.361521	-5.487639
C	-2.327831	1.724660	-3.237104
C	-3.301390	2.917082	-3.307944
H	-4.318916	2.478491	-3.316709
C	-3.200427	3.836350	-4.580776
C	-3.823797	3.082229	-5.776035
H	-3.821491	3.738135	-6.663897
H	-4.871998	2.802689	-5.565757
H	-3.260146	2.168450	-6.015113
C	-4.039105	5.105622	-4.322208
H	-5.072557	4.855676	-4.025896
H	-3.595192	5.737747	-3.534363
H	-4.083477	5.705839	-5.246949
C	-1.750331	4.235955	-4.911290
H	-1.741919	4.870480	-5.814872
H	-1.128728	3.349584	-5.111858
H	-1.285861	4.800747	-4.087677
C	1.324386	-2.076464	-2.978962
C	2.408603	-3.176162	-2.888562
H	3.338021	-2.639621	-2.617270

C	2.708724	-3.997324	-4.187539
C	3.798686	-5.040805	-3.859311
H	3.439851	-5.795665	-3.139027
H	4.703309	-4.569584	-3.440492
H	4.079535	-5.571443	-4.785233
C	3.279304	-3.036803	-5.255507
H	4.134656	-2.463081	-4.856050
H	2.521645	-2.323018	-5.609785
H	3.637818	-3.623238	-6.119365
C	1.466405	-4.735304	-4.722679
H	1.072819	-5.449919	-3.980264
H	1.743979	-5.308230	-5.625029
H	0.660149	-4.035324	-4.987308
C	-2.356800	-2.063858	-2.738324
C	-3.345485	-3.225895	-2.501533
H	-2.765579	-3.971167	-1.925294
C	-3.914619	-3.949354	-3.770569
C	-2.736704	-4.605116	-4.526677
H	-3.132947	-5.233165	-5.343388
H	-2.146370	-5.252956	-3.854799
H	-2.060908	-3.854524	-4.960998
C	-4.864018	-5.077518	-3.310396
H	-5.770949	-4.680502	-2.822493
H	-4.370045	-5.770268	-2.609280
H	-5.191556	-5.652086	-4.193639
C	-4.699022	-2.997732	-4.694489
H	-4.064181	-2.183218	-5.072819
H	-5.089555	-3.568274	-5.555478
H	-5.563576	-2.551916	-4.173403
Rh	-0.610186	-0.361896	-4.284023
Rh	-0.450192	-0.038640	-1.899758
C	2.411758	-0.071271	1.098596
C	2.937626	1.309886	1.429974
C	3.320801	-1.254905	1.316686
C	2.607304	2.383895	0.582381
C	3.594408	1.594957	2.643412
O	4.628159	-0.900719	1.586140
O	2.960906	-2.418443	1.237649
C	2.893174	3.711042	0.938113
H	2.073612	2.187965	-0.355042
C	3.894410	2.912177	3.015637
H	3.869510	0.784094	3.321567
C	5.501166	-1.984894	1.907010
C	3.519573	3.952786	2.161173
H	2.635661	4.530707	0.264792
H	4.399529	3.118208	3.962599
H	5.005171	-2.948783	1.715374
H	6.406825	-1.895453	1.291085
C	5.908302	-1.900487	3.379492
Br	3.856625	5.817312	2.715276
Cl	4.459320	-2.081383	4.483931

Cl	7.087993	-3.251784	3.728945
Cl	6.720197	-0.303393	3.761659
H	2.168469	-0.118385	0.018093
N	3.616019	2.270742	-2.832088
C	4.128712	0.978940	-2.632084
C	4.260873	3.240675	-2.034919
O	3.692171	-0.045328	-3.143995
C	5.272139	1.146055	-1.676292
O	3.959032	4.424793	-1.991837
C	5.342705	2.502205	-1.305758
C	6.192203	0.224056	-1.191199
C	6.318421	2.952383	-0.422804
C	7.206383	0.672778	-0.314890
Cl	6.114550	-1.480713	-1.662551
C	7.253491	2.022656	0.089331
Cl	6.416370	4.651699	0.046371
Cl	8.443579	-0.453607	0.257340
Cl	8.500935	2.556608	1.216285
N	2.111438	-4.009123	-1.717121
C	0.817412	-4.379292	-1.314739
C	3.093674	-4.364377	-0.767091
O	-0.205084	-4.191516	-1.963796
C	0.979212	-5.018260	0.031517
O	4.289166	-4.129554	-0.864978
C	2.349762	-5.050883	0.340635
C	0.028615	-5.476083	0.938393
C	2.792429	-5.573189	1.550275
C	0.463606	-5.967539	2.188601
Cl	-1.698412	-5.394921	0.571842
C	1.840429	-6.026176	2.490165
Cl	4.519389	-5.647317	1.945717
Cl	-0.721290	-6.493147	3.389890
Cl	2.369726	-6.645463	4.057494
N	-4.391808	-2.771021	-1.578250
C	-4.992790	-1.498363	-1.602012
C	-4.870665	-3.572454	-0.523513
O	-4.724828	-0.600382	-2.389186
C	-5.994161	-1.506663	-0.479768
O	-4.460242	-4.685012	-0.224579
C	-5.947235	-2.768363	0.139411
C	-6.875641	-0.527562	-0.032673
C	-6.798993	-3.084323	1.192551
C	-7.724118	-0.823228	1.059734
Cl	-6.904556	1.076563	-0.763045
C	-7.689214	-2.094694	1.667665
Cl	-6.775109	-4.686897	1.944237
Cl	-8.813733	0.417408	1.686153
Cl	-8.738376	-2.439604	3.045937
N	-3.258372	3.641219	-2.035071
C	-2.108745	4.099845	-1.359983
C	-4.431996	3.816083	-1.278959

O	-0.965544	4.101588	-1.791711
C	-2.603557	4.600013	-0.028521
O	-5.561161	3.543400	-1.664474
C	-3.996563	4.411190	0.023565
C	-1.924613	5.182203	1.037375
C	-4.730198	4.775542	1.148224
C	-2.662154	5.589677	2.173685
Cl	-0.172036	5.413844	0.999541
C	-4.055863	5.377737	2.234564
Cl	-6.473816	4.484928	1.242191
Cl	-1.837184	6.366696	3.527981
Cl	-4.956927	5.865998	3.672303
B	0.974202	-0.315949	1.842207
B	-0.528992	0.089168	0.982349
B	0.016792	1.119449	2.299892
B	-0.184623	-1.596965	1.390866
B	0.563122	-1.607047	3.016758
B	0.688134	0.072795	3.559480
H	-0.481291	0.621370	-0.116070
B	-1.834610	-0.938076	1.568866
B	-1.705065	0.743215	2.138739
H	0.343408	2.257480	2.185280
H	0.044644	-2.419992	0.560162
H	1.337893	-2.439690	3.385307
H	1.481971	0.490336	4.349388
H	-2.818398	-1.246616	0.965051
H	-2.538553	1.573733	1.944695
B	-1.154369	-1.984216	2.821664
H	-1.655012	-3.034229	3.085353
C	-0.909993	0.677146	3.659450
B	-0.631808	-0.945880	4.160087
H	-0.774744	-1.228299	5.309822
C	-2.014034	-0.546701	3.228329
Si	-3.814424	-0.774449	3.939857
C	-3.886811	-0.560432	5.814909
C	-4.960884	0.414668	3.025089
C	-4.305143	-2.559416	3.576244
H	-3.735515	0.469917	6.168785
H	-4.891236	-0.882220	6.144966
H	-3.150208	-1.213196	6.313547
H	-4.746251	1.474857	3.231627
H	-4.887070	0.262133	1.934930
H	-6.004796	0.216899	3.325937
H	-5.376124	-2.684610	3.814959
H	-4.150382	-2.842398	2.523140
H	-3.736945	-3.267056	4.202011
Si	-1.146809	2.081263	4.997664
C	-2.826555	2.919047	4.794172
C	-0.878150	1.333095	6.709349
C	0.211174	3.356825	4.688450
H	-3.681268	2.307034	5.118925

H	-2.830922	3.847905	5.390786
H	-2.989547	3.202727	3.741183
H	-1.613176	0.560423	6.980057
H	0.128474	0.885093	6.772722
H	-0.935083	2.138944	7.462770
H	0.205884	4.073494	5.529735
H	1.211172	2.895560	4.637233
H	0.053879	3.928154	3.760584

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

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SCF Energy= -5776.25586211 Predicted Change= -6.599586D-07
Zero-point correction (ZPE)= -5774.8677 1.38809
Internal Energy (U)= -5774.7496 1.50623
Enthalpy (H)= -5774.7487 1.50710
Gibbs Free Energy (G)= -5775.0254 1.23038
Entropy (S)= 0.00101306

Frequencies -- 6.2195 9.5353 12.5876

Supporting Information: minor (*R*)-B(8) product complex III

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

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# pbepbe/genecp/auto empiricaldispersion=gd3bj
scf=(maxcycle=300,direct,vshift=200,tight,yqc) density=current
scrf=(cpcm,solvent=benzene) opt=(gdiis,maxcycle=250) freq=noraman
Temperature=273.15
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/GenECP/Auto Freq

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Pointgroup= C1 Stoichiometry= C74H74B10BrCl19N4O18Rh2Si2 C1[X(C74H74B10BrCl19N4O18Rh2Si2)]
#Atoms= 204
Charge = 0 Multiplicity = 1

SCF Energy= -5776.24378387 Predicted Change= -2.100812D-08

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Optimization completed. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00138	0.00180	[YES]	0.00138	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
O	1.494628	-2.245636	-4.007750
O	1.395913	-1.960324	-1.742225
O	1.458275	0.704269	-4.320092
O	1.413239	0.883080	-2.039325
O	-1.396979	-2.247620	-4.144605
O	-1.543809	-2.003774	-1.876815

O	-1.435992	0.638411	-4.411618
O	-1.523854	0.901697	-2.140797
C	1.819714	-2.535079	-2.807179
C	2.849886	-3.648031	-2.530540
H	3.760345	-3.114653	-2.192105
C	3.282189	-4.576921	-3.705980
C	2.095779	-5.315909	-4.352551
H	1.351720	-4.609602	-4.752789
H	1.587754	-5.975828	-3.630542
H	2.465157	-5.941887	-5.183886
C	4.278890	-5.609136	-3.136332
H	5.127711	-5.115924	-2.631152
H	4.678404	-6.227311	-3.958391
H	3.793464	-6.284511	-2.411196
C	4.017933	-3.717442	-4.758128
H	3.334194	-3.012032	-5.253422
H	4.457376	-4.376475	-5.526914
H	4.837342	-3.136774	-4.298015
C	1.846466	1.192159	-3.206793
C	2.920279	2.295609	-3.198643
H	2.446332	3.144598	-2.672097
C	3.452686	2.833404	-4.567202
C	2.270547	3.452297	-5.344228
H	2.652591	3.929458	-6.263446
H	1.755675	4.221046	-4.744095
H	1.529691	2.690318	-5.629082
C	4.473886	3.952481	-4.266760
H	4.038612	4.744229	-3.633174
H	5.373453	3.562089	-3.760188
H	4.800137	4.412043	-5.215354
C	4.139984	1.749379	-5.419504
H	4.473256	2.198571	-6.371689
H	3.455091	0.918621	-5.645040
H	5.031569	1.337975	-4.917806
C	-1.907255	-2.500128	-2.999666
C	-3.049968	-3.536655	-2.932495
H	-2.619074	-4.410927	-2.406571
C	-3.641969	-4.048125	-4.289296
C	-4.796721	-5.025046	-3.977266
H	-5.648360	-4.512838	-3.497324
H	-4.472010	-5.846423	-3.317127
H	-5.163095	-5.462897	-4.921489
C	-2.542955	-4.835709	-5.037317
H	-2.132051	-5.641821	-4.402946
H	-1.714143	-4.184790	-5.351042
H	-2.978448	-5.305046	-5.936475
C	-4.187838	-2.904103	-5.165794
H	-5.003261	-2.361677	-4.658354
H	-4.597703	-3.326331	-6.100102
H	-3.401926	-2.179357	-5.425457
C	-1.872876	1.183202	-3.340719

C	-2.973274	2.259013	-3.457041
H	-3.830428	1.847532	-2.892526
C	-3.485335	2.621271	-4.890917
C	-4.119470	1.357311	-5.513678
H	-4.604133	1.625523	-6.468430
H	-4.890416	0.931026	-4.847820
H	-3.368467	0.578720	-5.711380
C	-4.591301	3.690629	-4.753944
H	-4.193133	4.647893	-4.375523
H	-5.397999	3.361394	-4.077680
H	-5.029853	3.885814	-5.747449
C	-2.371040	3.177962	-5.798073
H	-1.555188	2.452351	-5.931196
H	-2.795282	3.416465	-6.789221
H	-1.943794	4.109063	-5.388242
Rh	0.042802	-0.789996	-4.271507
Rh	-0.065402	-0.543606	-1.890863
C	0.478108	-0.125585	1.351315
C	-0.646084	-0.957454	1.952666
C	1.772435	-0.926501	1.411365
C	-1.945283	-0.935528	1.416069
C	-0.431889	-1.663883	3.153794
O	2.877626	-0.152431	1.662264
O	1.834132	-2.133758	1.246485
C	-3.011101	-1.563762	2.077512
H	-2.151190	-0.403342	0.482588
C	-1.477470	-2.313825	3.819372
H	0.568794	-1.702787	3.594325
C	4.109202	-0.857730	1.817018
C	-2.761169	-2.238111	3.273438
H	-4.019055	-1.519383	1.663824
H	-1.291399	-2.859651	4.747054
H	3.996456	-1.917202	1.536311
H	4.857428	-0.371313	1.177602
C	4.596422	-0.762742	3.268300
Br	-4.260013	-3.102656	4.217401
Cl	3.395218	-1.499138	4.434752
Cl	6.174320	-1.676868	3.395736
Cl	4.894607	0.969716	3.768774
H	0.296473	0.012948	0.256687
N	2.394586	-4.360079	-1.328453
C	1.050000	-4.703419	-1.073290
C	3.178850	-4.388707	-0.158555
O	0.147116	-4.683762	-1.899912
C	0.990023	-5.052475	0.383264
O	4.342716	-4.015498	-0.084334
C	2.279656	-4.903277	0.922557
C	-0.090192	-5.383821	1.195530
C	2.515751	-5.101325	2.277178
C	0.132847	-5.567583	2.579212
Cl	-1.726325	-5.520662	0.542180

C	1.427994	-5.422876	3.118547
Cl	4.137432	-4.900419	2.961482
Cl	-1.220977	-5.960440	3.643689
Cl	1.682029	-5.615330	4.856882
N	-4.065793	-3.020624	-2.007270
C	-4.463762	-1.675422	-1.920494
C	-4.631580	-3.816590	-0.990449
O	-4.120495	-0.780928	-2.683317
C	-5.371347	-1.598550	-0.728295
O	-4.403337	-5.004046	-0.810487
C	-5.514973	-2.896317	-0.202702
C	-5.994718	-0.510409	-0.125606
C	-6.328852	-3.138619	0.899389
C	-6.794956	-0.736647	1.019123
Cl	-5.755515	1.134457	-0.727850
C	-6.977643	-2.044097	1.518746
Cl	-6.554677	-4.774081	1.528105
Cl	-7.561902	0.627659	1.836363
Cl	-8.005293	-2.309426	2.926223
N	-2.544055	3.431252	-2.683598
C	-1.232370	3.937418	-2.661873
C	-3.400619	4.127440	-1.808260
O	-0.284811	3.468469	-3.279093
C	-1.269206	5.123647	-1.744558
O	-4.560439	3.829861	-1.556181
C	-2.584093	5.261170	-1.262870
C	-0.269959	6.009544	-1.355869
C	-2.925280	6.301454	-0.405196
C	-0.598960	7.061410	-0.469263
Cl	1.395838	5.822517	-1.914939
C	-1.921443	7.211482	-0.002674
Cl	-4.574188	6.475223	0.219084
Cl	0.652222	8.179264	0.073809
Cl	-2.311636	8.515638	1.121849
N	3.988601	1.857100	-2.294157
C	4.565408	0.576884	-2.295380
C	4.453963	2.660549	-1.231430
O	4.233750	-0.356453	-3.016142
C	5.618869	0.611629	-1.226302
O	4.047485	3.780299	-0.961517
C	5.526394	1.849475	-0.561394
C	6.579122	-0.327316	-0.861842
C	6.371976	2.153453	0.500903
C	7.466189	-0.019772	0.197545
Cl	6.707570	-1.882123	-1.695119
C	7.354917	1.209301	0.884054
Cl	6.232315	3.686343	1.370095
Cl	8.711732	-1.176513	0.666093
Cl	8.447813	1.566024	2.220271
B	0.447899	1.400061	1.932158
B	1.756344	2.633220	1.914185

B	1.201440	1.909834	3.450579
B	0.333664	2.865385	0.888202
B	-1.080029	2.291630	1.781748
B	-0.562396	1.722609	3.377154
H	2.850871	2.423798	1.486143
B	1.005006	4.250962	1.791229
B	1.553721	3.641615	3.358210
H	1.802198	1.191134	4.191891
H	0.363371	2.786740	-0.306530
C	-1.216930	3.282296	3.172330
H	-2.082250	1.844914	1.318559
H	-1.169494	0.925704	4.018858
H	1.542374	5.184486	1.268117
B	0.002488	4.496889	3.244921
H	2.417605	4.130559	4.020977
Si	-3.044455	3.658190	3.745852
H	-0.234584	5.523643	3.803790
C	-3.554261	2.578665	5.210648
C	-4.188356	3.194760	2.314865
C	-3.186378	5.506444	4.101659
H	-3.394675	1.511033	4.980774
H	-3.042867	2.810891	6.156486
H	-4.637813	2.723318	5.372456
H	-4.240182	2.102327	2.175308
H	-5.205769	3.549417	2.561381
H	-3.900969	3.649928	1.354291
H	-2.542873	5.840525	4.930577
H	-2.923282	6.096887	3.207696
H	-4.232793	5.744308	4.363108
B	-0.744723	4.018327	1.710402
H	-1.533753	4.766571	1.222623
C	0.154542	3.059346	4.165566
Si	0.198512	3.076286	6.114091
C	-0.752849	4.552381	6.811044
C	-0.421720	1.407283	6.742784
C	2.010826	3.261019	6.616385
H	-1.842119	4.502267	6.663453
H	-0.564556	4.602431	7.898576
H	-0.387319	5.493829	6.366214
H	-1.478874	1.207853	6.511407
H	0.180947	0.592238	6.305646
H	-0.296956	1.368133	7.839587
H	2.083344	3.111862	7.709004
H	2.654998	2.512640	6.125905
H	2.405996	4.262865	6.382524

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

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SCF Energy= -5776.24378387 Predicted Change= -2.100812D-08
Zero-point correction (ZPE)= -5774.8565 1.38727

Internal Energy (U)= -5774.7378 1.50598
Enthalpy (H)= -5774.7369 1.50684
Gibbs Free Energy (G)= -5775.0150 1.22876
Entropy (S)= 0.00101808

Frequencies -- 12.0180 12.3423 14.3337

Supporting Information: (*R*)-B(9)-3bd

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========

# pbepbe/genecp/auto empiricaldispersion=gd3bj
scf=(maxcycle=300,direct,vshift=200,tight,yqc) density=current
scrf=(solvent=benzene,cpcm) opt=(gdiis,maxcycle=250) freq=noraman
Temperature=273.15
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/GenECP/Auto Freq

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Pointgroup= C1 Stoichiometry= C18H34B10BrCl3O2Si2 C1[X(C18H34B10BrCl3O2Si2)] #Atoms= 70
Charge = 0 Multiplicity = 1

SCF Energy= -1740.88695802 Predicted Change= -3.658170D-08

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Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00003	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00232	0.00180	[NO]	0.00232	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
B	1.974796	-2.477439	1.231918
H	2.346039	-3.382389	1.921508
B	0.374968	-2.263085	0.483889
H	-0.506714	-3.051230	0.670719
B	0.628757	-1.471975	-1.101277
H	-0.058551	-1.674901	-2.060358
B	0.938303	-1.141960	1.754193
H	0.461834	-1.096804	2.853239
B	2.380285	-1.212898	-1.297978
B	1.330460	0.123241	-0.794877
H	1.233428	1.071322	-1.518664
B	1.510057	0.328833	0.955063
H	1.525119	1.413190	1.451466
B	2.682147	-0.872659	1.514817
H	3.508401	-0.649692	2.345279
B	0.084178	-0.516926	0.309123
C	2.833712	-0.135908	-0.028255
H	3.009883	-1.210668	-2.310749
H	2.000348	-3.729727	-1.043650
B	1.776663	-2.683169	-0.515803
C	3.109159	-1.810282	0.134716

Si	4.170393	1.242369	-0.380458
Si	4.840761	-2.709898	0.099190
C	3.352240	2.902127	0.008070
H	4.027159	3.708187	-0.331946
H	2.391639	3.016273	-0.520616
H	3.172538	3.038779	1.086478
C	4.600446	1.216173	-2.217870
H	3.691429	1.373438	-2.823622
H	5.296171	2.046845	-2.432836
H	5.073309	0.280295	-2.551480
C	5.677304	1.062812	0.743370
H	5.373607	1.010825	1.802828
H	6.307621	0.188843	0.520601
H	6.302387	1.965529	0.620173
C	5.917320	-2.109231	-1.332088
H	6.292853	-1.081197	-1.219398
H	6.794013	-2.778624	-1.398315
H	5.374301	-2.178148	-2.290095
C	5.666311	-2.495910	1.783084
H	6.609808	-3.070334	1.793426
H	5.901163	-1.450128	2.033176
H	5.017870	-2.899339	2.579684
C	4.498081	-4.547534	-0.172307
H	5.446580	-5.098070	-0.036126
H	3.765984	-4.945355	0.549128
H	4.128152	-4.753936	-1.189690
C	-1.400368	0.163573	0.448960
H	-1.451013	0.543859	1.483342
C	-2.509401	-0.847820	0.243452
C	-2.920400	-1.287210	-1.029732
C	-3.111076	-1.423249	1.378306
C	-3.910101	-2.270602	-1.168607
H	-2.474054	-0.847136	-1.923483
C	-4.096743	-2.413126	1.262206
H	-2.800076	-1.099189	2.377672
C	-4.479771	-2.819966	-0.017657
H	-4.225101	-2.602147	-2.161099
H	-4.554309	-2.851720	2.152217
Br	-5.868539	-4.214524	-0.204653
C	-1.452470	1.361952	-0.460814
O	-1.813843	1.410505	-1.625207
O	-0.929065	2.459836	0.211719
C	-0.850724	3.669777	-0.533801
C	-1.782716	4.719328	0.082901
H	-1.149305	3.493893	-1.580112
H	0.181507	4.049717	-0.477689
Cl	-1.602621	6.275164	-0.867569
Cl	-1.348092	5.052849	1.828087
Cl	-3.524341	4.182075	0.015869

Statistical Thermodynamic Analysis

Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

SCF Energy= -1740.88695802 Predicted Change= -3.658170D-08
Zero-point correction (ZPE)= -1740.3747 0.51218
Internal Energy (U)= -1740.3401 0.54681
Enthalpy (H)= -1740.3392 0.54767
Gibbs Free Energy (G)= -1740.4400 0.44690
Entropy (S)= 0.00036893

Frequencies -- 11.0181 14.0373 17.4583

Supporting Information: (*S*)-B(9)-3bd

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

# pbepbe/genecp/auto empiricaldispersion=gd3bj
scf=(maxcycle=300,direct,vshift=200,tight,yqc) density=current
scrf=(cpcm,solvent=benzene) opt=(gdiis,maxcycle=250) freq=noraman
Temperature=273.15
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/GenECP/Auto Freq

---

Pointgroup= C1 Stoichiometry= C18H34B10BrCl3O2Si2 C1[X(C18H34B10BrCl3O2Si2)] #Atoms= 70
Charge = 0 Multiplicity = 1

SCF Energy= -1740.88657413 Predicted Change= -8.751363D-10

Optimization completed on the basis of negligible forces. {Found 2 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00000	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00216	0.00180	[NO]	0.00216	0.00180	[YES]

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	1.111419	-0.240084	-2.226197
C	1.988361	0.805941	-1.557493
C	1.570819	-1.678373	-2.175193
C	2.281275	1.980303	-2.277652
C	2.445957	0.712281	-0.227108
O	1.938364	-2.066058	-0.906874
O	1.569332	-2.457113	-3.116062
C	2.998708	3.038716	-1.701944
H	1.930834	2.080763	-3.310753
C	3.171633	1.754730	0.365688
H	2.240553	-0.183169	0.361314
C	2.296733	-3.444340	-0.796835
C	3.431917	2.906178	-0.381435
H	3.212468	3.943642	-2.275900
H	3.521838	1.665703	1.397153
H	1.493434	-4.090817	-1.185700
H	3.229316	-3.656499	-1.344839

C	2.512495	-3.742114	0.685810
Br	4.438367	4.387091	0.454527
Cl	0.985194	-3.490380	1.656104
Cl	3.016260	-5.495724	0.842569
Cl	3.829815	-2.695728	1.401579
H	1.062185	-0.011633	-3.303658
B	-0.429714	-0.164818	-1.682805
B	-1.579615	1.029985	-2.360601
B	-0.983857	1.215129	-0.707592
B	-1.810651	-0.716150	-2.659514
B	-1.375468	-1.593562	-1.165111
B	-0.860355	-0.390924	0.029950
H	-1.269682	1.808537	-3.217900
B	-3.201856	0.324994	-2.275618
B	-2.692065	1.513681	-1.056859
H	-0.318701	2.124779	-0.320805
H	-1.676774	-1.200007	-3.748056
H	-0.929882	-2.705525	-1.160431
H	-0.123057	-0.593479	0.947438
H	-4.123884	0.610325	-2.983403
H	-3.221595	2.570846	-0.900979
B	-3.071819	-1.284469	-1.549221
H	-3.893115	-2.125377	-1.756056
C	-2.210845	0.611974	0.321528
B	-2.494942	-1.075195	0.114330
H	-2.894206	-1.713805	1.038710
C	-3.534593	0.079698	-0.612518
Si	-5.416081	0.197253	-0.112315
C	-5.702978	-0.405386	1.654917
C	-6.012752	1.964745	-0.399207
C	-6.366066	-0.950031	-1.274482
H	-5.290037	0.253818	2.433119
H	-6.793713	-0.472119	1.818646
H	-5.282918	-1.415525	1.798080
H	-5.508679	2.711842	0.232286
H	-5.861244	2.251828	-1.453983
H	-7.096087	2.013960	-0.188968
H	-7.447028	-0.782447	-1.117294
H	-6.140037	-0.747481	-2.334127
H	-6.153627	-2.012409	-1.072834
Si	-2.252542	1.370756	2.120509
C	-3.598499	2.683784	2.301245
C	-2.418682	-0.042494	3.361087
C	-0.584835	2.217953	2.391295
H	-3.448123	3.191316	3.271158
H	-3.508308	3.447716	1.510058
H	-4.625768	2.289879	2.287540
H	-3.366439	-0.596365	3.279680
H	-1.591242	-0.761338	3.231224
H	-2.349571	0.369345	4.383734
H	-0.503625	2.483846	3.460911

H 0.266242 1.566367 2.134046
H -0.493504 3.145441 1.802823

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

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SCF Energy= -1740.88657413 Predicted Change= -8.751363D-10
Zero-point correction (ZPE)= -1740.3745 0.51203
Internal Energy (U)= -1740.3398 0.54675
Enthalpy (H)= -1740.3389 0.54762
Gibbs Free Energy (G)= -1740.4407 0.44584
Entropy (S)= 0.00037262

Frequencies -- 4.2904 12.6891 16.8003

Supporting Information: (*R*)-B(8)-3bd

Using Gaussian 16: ES64L-G16RevA.03 25-Dec-2016

==========

# pbepbe/genecp/auto empiricaldispersion=gd3bj
scf=(maxcycle=300,direct,vshift=200,tight,yqc) density=current
scrf=(cpcm,solvent=benzene) opt=(gdiis,maxcycle=250) freq=noraman
Temperature=273.15
#N Geom=AllCheck Guess=TCheck SCRF=Check GenChk RPBEPBE/GenECP/Auto Freq

---

Pointgroup= C1 Stoichiometry= C18H34B10BrCl3O2Si2 C1[X(C18H34B10BrCl3O2Si2)] #Atoms= 70
Charge = 0 Multiplicity = 1

SCF Energy= -1740.88768017 Predicted Change= -3.387122D-08

==========

Optimization completed. {Found 1 times}

Item	Max Val.	Criteria	Pass?	RMS Val.	Criteria	Pass?
Force	0.00001	0.00045	[YES]	0.00000	0.00030	[YES]
Displ	0.00434	0.00180	[NO]	0.00434	0.00180	[YES]

Atomic Coordinates (Angstroms)

Type	X	Y	Z
B	1.562254	-3.097214	1.703248
H	1.450310	-4.284257	1.651643
B	0.759347	-1.989184	2.830815
H	0.019850	-2.396375	3.683068
B	0.414325	-0.470806	1.951089
B	2.533226	-2.212791	2.888753
H	3.101058	-2.783390	3.775939
B	1.036085	-0.659866	0.289479
B	1.977899	0.232556	1.495558
H	2.169339	1.395471	1.308801
B	3.270898	-0.830930	2.060915
H	4.374554	-0.409350	2.251881

B	3.105029	-2.380661	1.206777
H	4.032062	-3.016144	0.808529
B	1.819541	-0.583704	3.059809
C	2.725212	-0.886896	0.436973
H	0.605729	-0.169236	-0.705842
H	-0.736145	-2.473910	0.659096
B	0.274532	-2.034244	1.121339
C	1.708250	-2.240053	0.220658
Si	3.959564	-0.142312	-0.879605
Si	1.471406	-3.276802	-1.417488
C	4.423778	1.586612	-0.276056
H	5.250311	1.960167	-0.907450
H	3.582555	2.292915	-0.365479
H	4.768517	1.584120	0.770810
C	3.148064	0.037687	-2.575977
H	2.183055	0.566218	-2.495660
H	3.813942	0.654519	-3.205984
H	2.977221	-0.912890	-3.102972
C	5.516916	-1.208321	-0.913021
H	5.975795	-1.244884	0.089942
H	5.337962	-2.243039	-1.242822
H	6.249143	-0.751147	-1.602238
C	0.314083	-2.321833	-2.563707
H	0.738085	-1.377817	-2.938300
H	0.070280	-2.956606	-3.434201
H	-0.630436	-2.087730	-2.041987
C	3.128062	-3.722864	-2.208053
H	3.668919	-2.872111	-2.648318
H	3.790143	-4.211432	-1.472654
H	2.935034	-4.450712	-3.016614
C	0.620936	-4.889547	-0.922673
H	0.336291	-5.425044	-1.846551
H	1.284536	-5.547473	-0.338544
H	-0.295091	-4.711657	-0.336163
H	1.864875	0.045727	4.078874
C	-0.910187	0.424567	2.296850
H	-1.126712	0.231651	3.360439
C	-2.113683	-0.017223	1.479270
C	-0.530967	1.886006	2.257162
C	-2.276070	0.259472	0.106408
C	-3.075105	-0.830876	2.109263
O	-0.219784	2.565717	3.222849
O	-0.491639	2.381987	0.973465
C	-3.360201	-0.259129	-0.615110
H	-1.555231	0.890621	-0.415176
C	-4.163623	-1.365878	1.405538
H	-2.967477	-1.066811	3.173613
C	-0.045807	3.735699	0.885159
C	-4.285833	-1.069988	0.046684
H	-3.474048	-0.032327	-1.678160
H	-4.896716	-1.998736	1.911519

C	-0.163574	4.156522	-0.577791
H	1.006186	3.823890	1.203693
H	-0.667525	4.400561	1.505979
Br	-5.807220	-1.817096	-0.968124
Cl	0.391350	5.892978	-0.718526
Cl	-1.880386	4.036792	-1.180237
Cl	0.897680	3.126229	-1.663233

Statistical Thermodynamic Analysis
Temperature= 273.150 Kelvin Pressure= 1.00000 Atm

==========

SCF Energy= -1740.88768017 Predicted Change= -3.387122D-08
Zero-point correction (ZPE)= -1740.3754 0.51222
Internal Energy (U)= -1740.3408 0.54683
Enthalpy (H)= -1740.3399 0.54770
Gibbs Free Energy (G)= -1740.4399 0.44777
Entropy (S)= 0.00036583

Frequencies -- 12.4280 16.4979 21.3299

Movie S1-S3

Movie S1: II-TS$_{(R)\text{-B(9)}}$

Movie S2: II-TS$_{(S)\text{-B(9)}}$

Movie S3: II-TS$_{(R)\text{-B(8)}}$

12. References

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13. X-ray Crystallography

(*R*)-**3bd** (20 mg) was dissolved in ether (1 mL) in 4 mL glass vial and hexane (2 mL) was slowly added to form a separate layer. The 4 mL vial was open cap. Vapor diffusion afforded crystals of the composition (*R*)-**3bd** suitable for X-ray diffraction within 2 day at room temperature. A block-like specimen of $C_{18}H_{34}B_{10}BrCl_3O_2Si_2$, approximate dimensions 0.100 mm x 0.100 mm x 0.150 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. (ellipsoid = 40%, CCDC = 2031747)

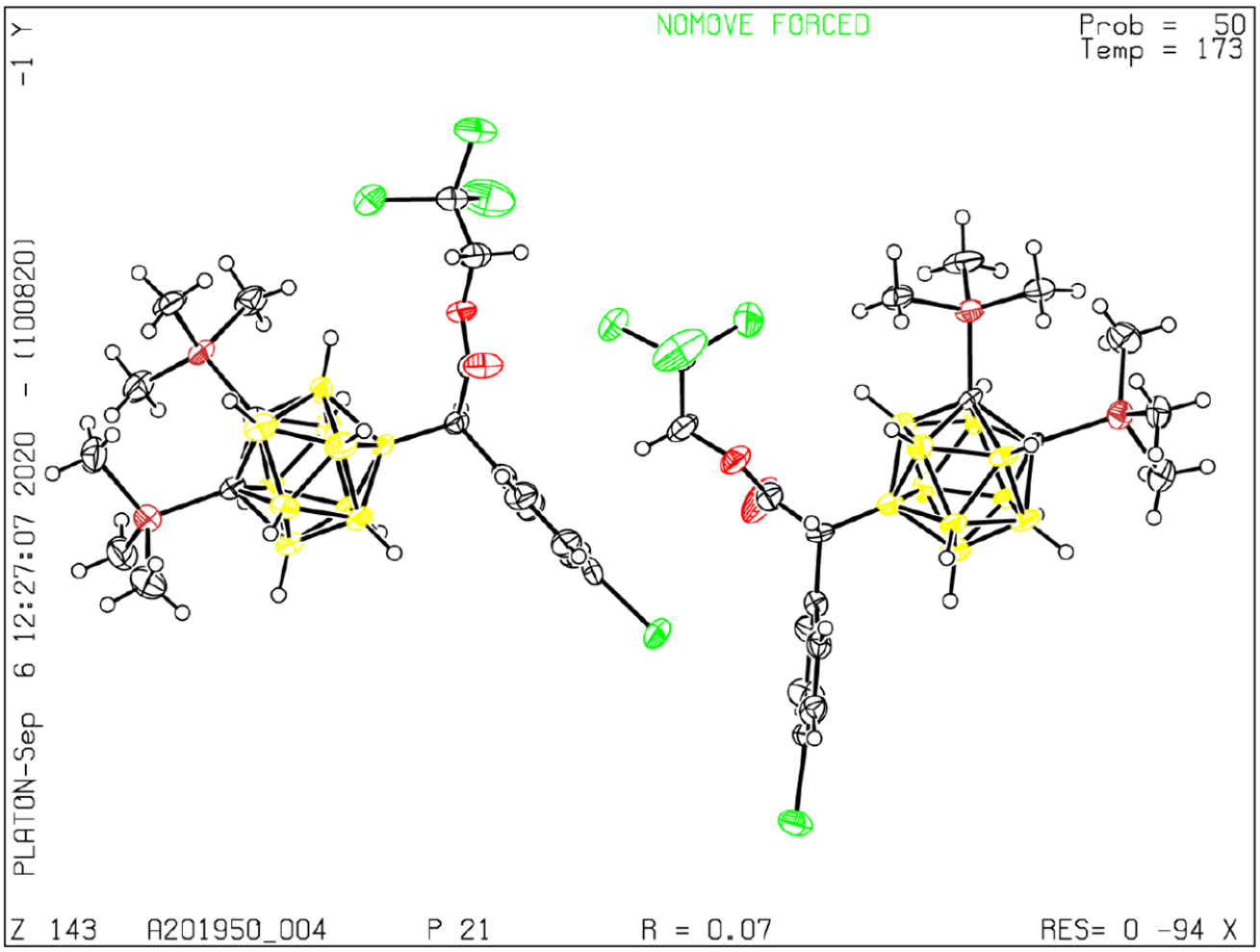


Table S2. Crystal data and structure refinement for (*R*)-3bd.

Empirical formula	$C_{18}H_{34}B_{10}BrCl_3O_2Si_2$
Formula weight	632.99
Temperature	173(2) K
Wavelength	0.71073 Å

Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 14.5216(8) Å	α = 90°
	b = 12.2531(8) Å	β = 107.513(5)°
	c = 18.2279(12) Å	γ = 90°
Volume	3093.0(3) $Å^3$	
Z	4	
Density (calculated)	1.359 Mg/m^3	
Absorption coefficient	1.683 mm^{-1}	
F(000)	1288	
Crystal size	0.337 x 0.264 x 0.156 mm^3	
Theta range for data collection	2.033 to 25.999°.	
Index ranges	–17<=h<=17, –15<=k<=15, –22<=l<=22	
Reflections collected	26025	
Independent reflections	11989 [R(int) = 0.0975]	
Completeness to theta = 25.242°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9917 and 0.3633	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11989 / 1 / 667	
Goodness-of-fit on F^2	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0698, wR2 = 0.1035	
R indices (all data)	R1 = 0.1266, wR2 = 0.1193	
Absolute structure parameter	0.013(7)	
Largest diff. peak and hole	0.578 and –0.422 $e \cdot Å^{-3}$	

(*R*)-**3gd**(CO_2H) (20 mg) was dissolved in ether (1 mL) in 4 mL glass vial and hexane (2 mL) was slowly added to form a separate layer. The 4 mL vial was open cap. Vapor diffusion afforded crystals of the composition (*R*)-**3gd**(CO_2H) suitable for X-ray diffraction within 2 day at room temperature. A block-like specimen of $C_{23}H_{27}B_{10}BrO_2$, approximate dimensions 0.100 mm x 0.100 mm x 0.100 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. (ellipsoid = 40%, CCDC = 2085991)

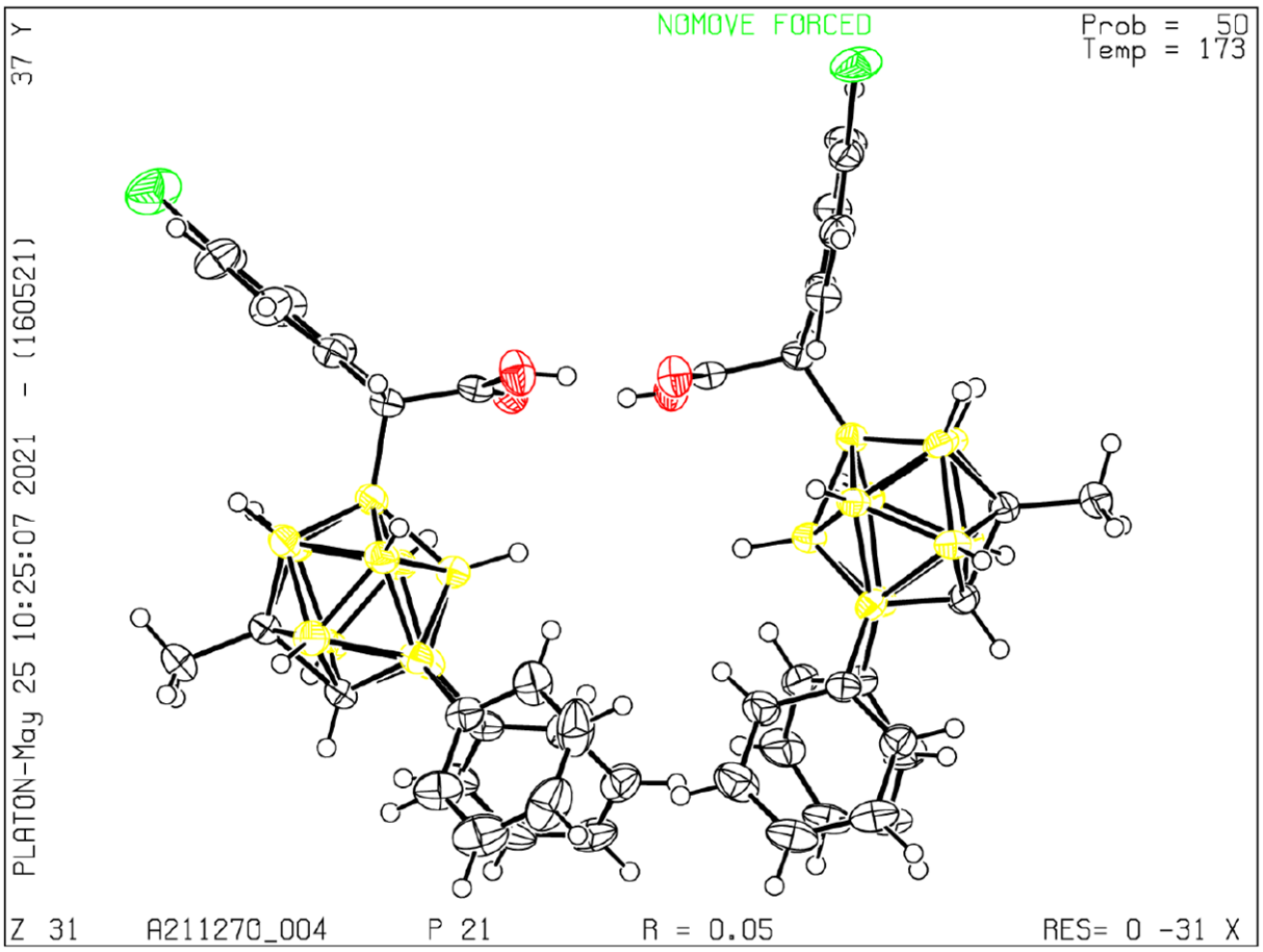


Table S3. Crystal data and structure refinement for (*R*)-3gd.

Empirical formula	$C_{23}\ H_{27}\ B_{10}\ Br\ O_2$
Formula weight	523.45
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic

Space group	$P2_1$	
Unit cell dimensions	a = 11.8606(8) Å	α = 90°
	b = 17.7171(11) Å	β = 98.8655(18)°
	c = 12.5793(8) Å	γ = 90°
Volume	2611.8(3) $Å^3$	
Z	4	
Density (calculated)	1.331 Mg/m^3	
Absorption coefficient	1.595 mm^{-1}	
F(000)	1064	
Crystal size	0.296 x 0.052 x 0.029 mm^3	
Theta range for data collection	2.480 to 26.493°.	
Index ranges	–14<=h<=14, –22<=k<=22, –15<=l<=15	
Reflections collected	44248	
Independent reflections	10783 [R(int) = 0.1066]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.4244	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10783 / 1 / 668	
Goodness-of-fit on F^2	1.020	
Final R indices [I>2sigma(I)]	R1 = 0.0476, wR2 = 0.0963	
R indices (all data)	R1 = 0.0847, wR2 = 0.1150	
Absolute structure parameter	0.017(10)	
Largest diff. peak and hole	0.292 and –0.469 $e \cdot Å^{-3}$	

(*R*)-3hd (20 mg) was dissolved in ether (1 mL) in 4 mL glass vial and hexane (2 mL) was slowly added to form a separate layer. The 4 mL vial was open cap. Vapor diffusion afforded crystals of the composition **(*R*)-3hd** suitable for X-ray diffraction within 2 day at room temperature. A block-like specimen of $C_{12}H_{18}B_{10}BrCl_3O_2$, approximate dimensions 0.100 mm x 0.100 mm x 0.150 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. (ellipsoid = 40%, CCDC = 2036998)

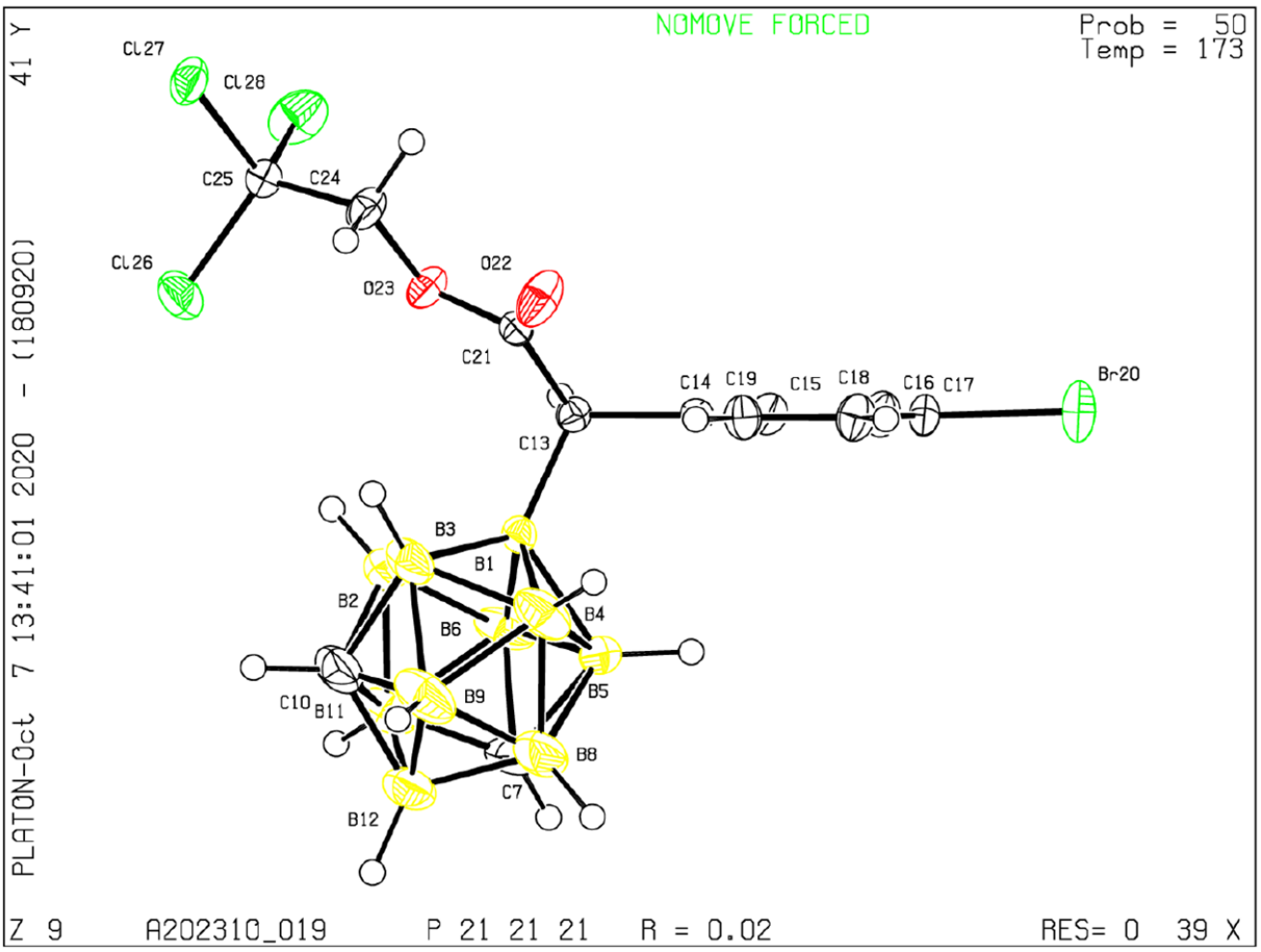


Table S4. Crystal data and structure refinement for (*R*)-3hd.

Empirical formula	$C_{12}H_{18}B_{10}O_2Cl_3Br$
Formula weight	488.62
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic

Space group	$P2_12_12_1$	
Unit cell dimensions	a = 7.8684(4) Å	α = 90°
	b = 16.0219(8) Å	β = 90°
	c = 17.0875(8) Å	γ = 90°
Volume	2154.17(18) $Å^3$	
Z	4	
Density (calculated)	1.507 Mg/m^3	
Absorption coefficient	2.287 mm^{-1}	
F(000)	968	
Crystal size	0.309 x 0.132 x 0.082 mm^3	
Theta range for data collection	3.121 to 27.509°.	
Index ranges	–10<=h<=10, –20<=k<=20, –22<=l<=22	
Reflections collected	65329	
Independent reflections	4909 [R(int) = 0.0414]	
Completeness to theta = 25.242°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5224	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4909 / 0 / 259	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0238, wR2 = 0.0526	
R indices (all data)	R1 = 0.0275, wR2 = 0.0541	
Absolute structure parameter	0.010(2)	
Largest diff. peak and hole	0.400 and –0.336 $e \cdot Å^{-3}$	

(*R*)-3jd (20 mg) was dissolved in ether (1 mL) in 4 mL glass vial and hexane (2 mL) was slowly added to form a separate layer. The 4 mL vial was open cap. Vapor diffusion afforded crystals of the composition **(*R*)-3jd** suitable for X-ray diffraction within 2 day at room temperature. A block-like specimen of $C_{12}H_{18}B_{10}BrCl_3O_2$, approximate dimensions 0.100 mm x 0.100 mm x 0.150 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. (ellipsoid = 40%, CCDC = 2036999)

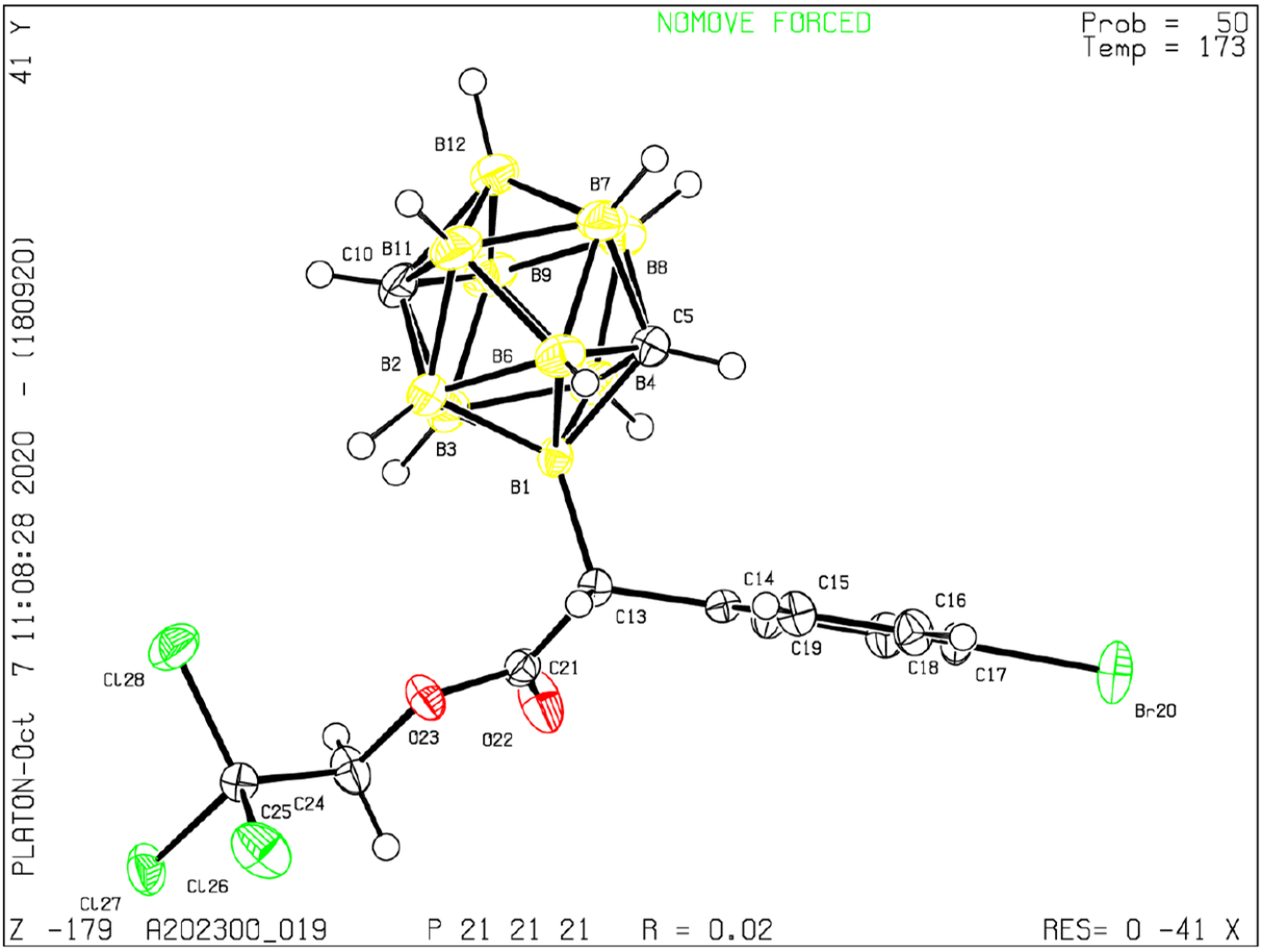


Table S5. Crystal data and structure refinement for (*R*)-3jd.

Empirical formula	$C_{12}H_{18}B_{10}O_2Cl_3Br$
Formula weight	488.62
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic

Space group	$P2_12_12_1$	
Unit cell dimensions	a = 7.8717(3) Å	α = 90°
	b = 15.9248(6) Å	β = 90°
	c = 17.0044(7) Å	γ = 90°
Volume	2131.59(14) $Å^3$	
Z	4	
Density (calculated)	1.523 Mg/m^3	
Absorption coefficient	2.311 mm^{-1}	
F(000)	968	
Crystal size	0.298 x 0.112 x 0.067 mm^3	
Theta range for data collection	2.558 to 27.515°.	
Index ranges	–10<=h<=10, –20<=k<=20, –22<=l<=22	
Reflections collected	54013	
Independent reflections	4855 [R(int) = 0.0384]	
Completeness to theta = 25.242°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5085	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4855 / 0 / 259	
Goodness-of-fit on F^2	1.060	
Final R indices [I>2sigma(I)]	R1 = 0.0218, wR2 = 0.0487	
R indices (all data)	R1 = 0.0253, wR2 = 0.0501	
Absolute structure parameter	0.024(2)	
Largest diff. peak and hole	0.316 and –0.293 $e \cdot Å^{-3}$	

(*S*)-**3bd** (20 mg) was dissolved in ether (1 mL) in 4 mL glass vial and hexane (2 mL) was slowly added to form a separate layer. The 4 mL vial was open cap. Vapor diffusion afforded crystals of the composition (*S*)-**3bd** suitable for X-ray diffraction within 2 day at room temperature. A block-like specimen of $C_{18}H_{34}B_{10}BrCl_3O_2Si_2$, approximate dimensions 0.100 mm x 0.100 mm x 0.150 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. (ellipsoid = 40%, CCDC = 2085990)

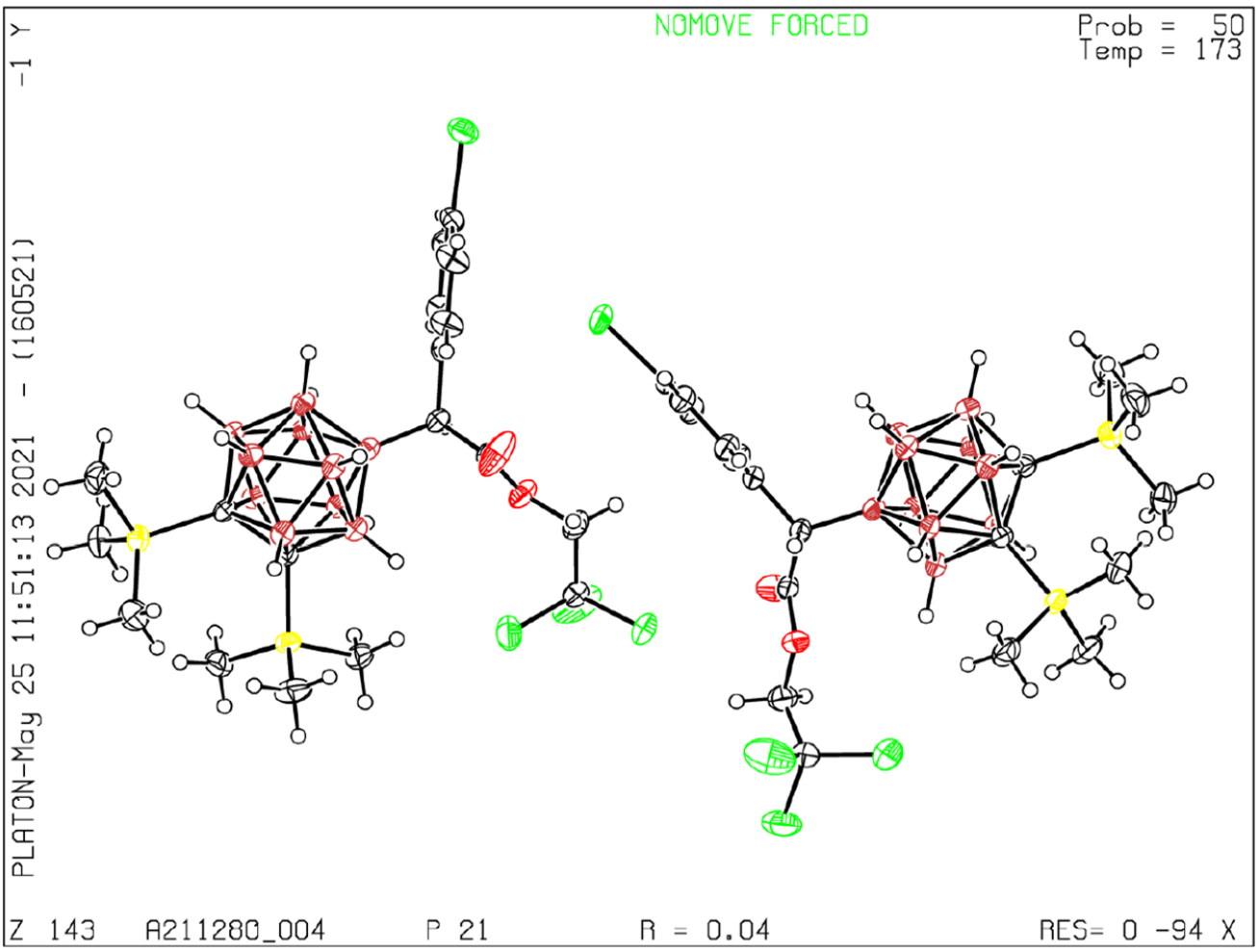
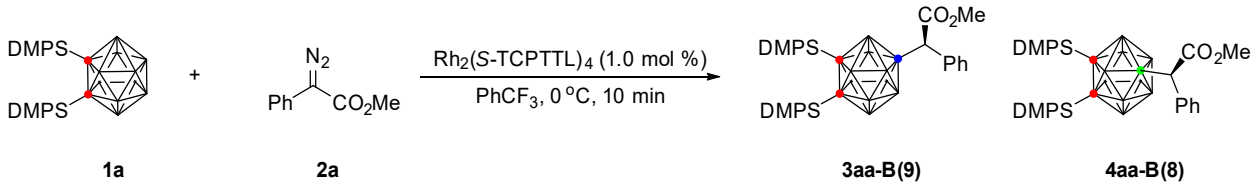


Table S6. Crystal data and structure refinement for (*S*)-3bd.

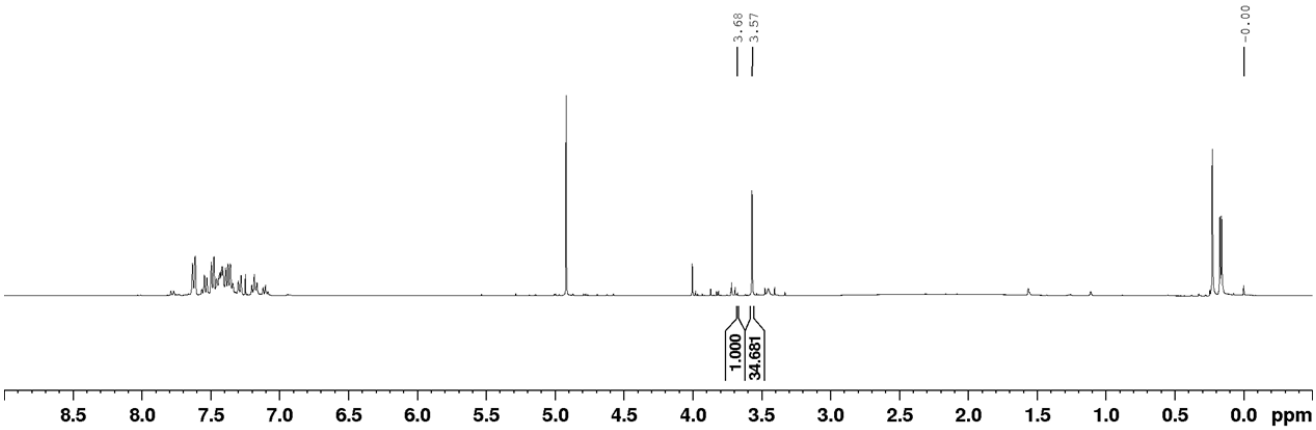
Empirical formula	$C_{18}\ H_{34}\ B_{10}\ Br\ Cl_3\ O_2\ Si_2$
Formula weight	632.99
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic

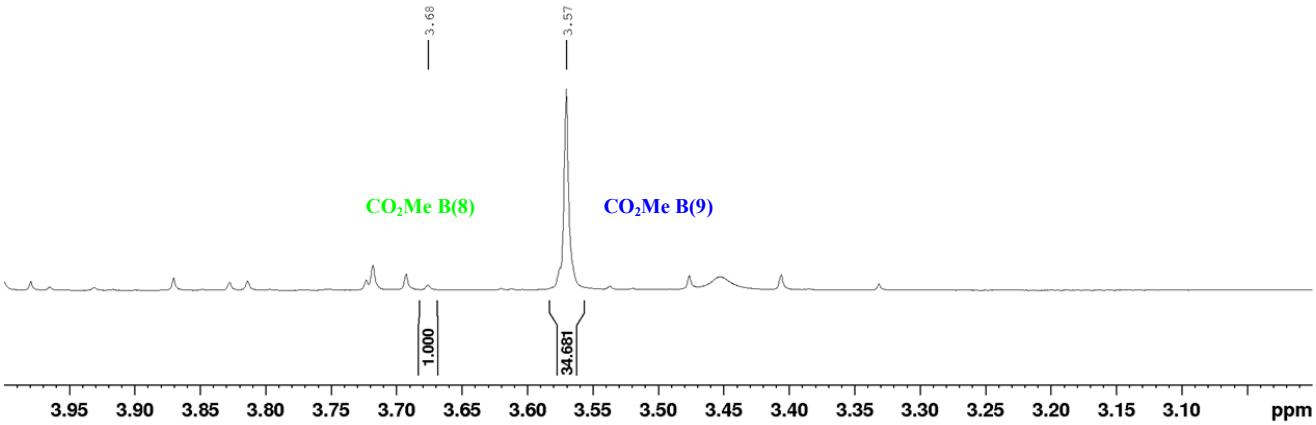
Space group	$P2_1$	
Unit cell dimensions	a = 14.5317(6) Å	α = 90°
	b = 12.2602(5) Å	β = 107.5874(13)°
	c = 18.2262(8) Å	γ = 90°
Volume	3095.4(2) $Å^3$	
Z	4	
Density (calculated)	1.358 Mg/m^3	
Absorption coefficient	1.682 mm^{-1}	
F(000)	1288	
Crystal size	0.324 x 0.135 x 0.121 mm^3	
Theta range for data collection	2.709 to 27.523°.	
Index ranges	–17<=h<=18, –15<=k<=15, –22<=l<=23	
Reflections collected	48533	
Independent reflections	13933 [R(int) = 0.0548]	
Completeness to theta = 25.242°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5227	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13933 / 1 / 668	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0396, wR2 = 0.0873	
R indices (all data)	R1 = 0.0538, wR2 = 0.0933	
Absolute structure parameter	0.023(6)	
Largest diff. peak and hole	0.849 and –0.634 $e \cdot Å^{-3}$	

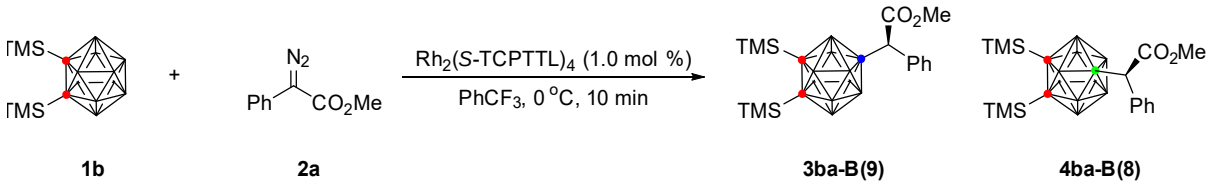
14. Crude ^{1}H NMR Spectra for Regioisomeric Ratio Determination



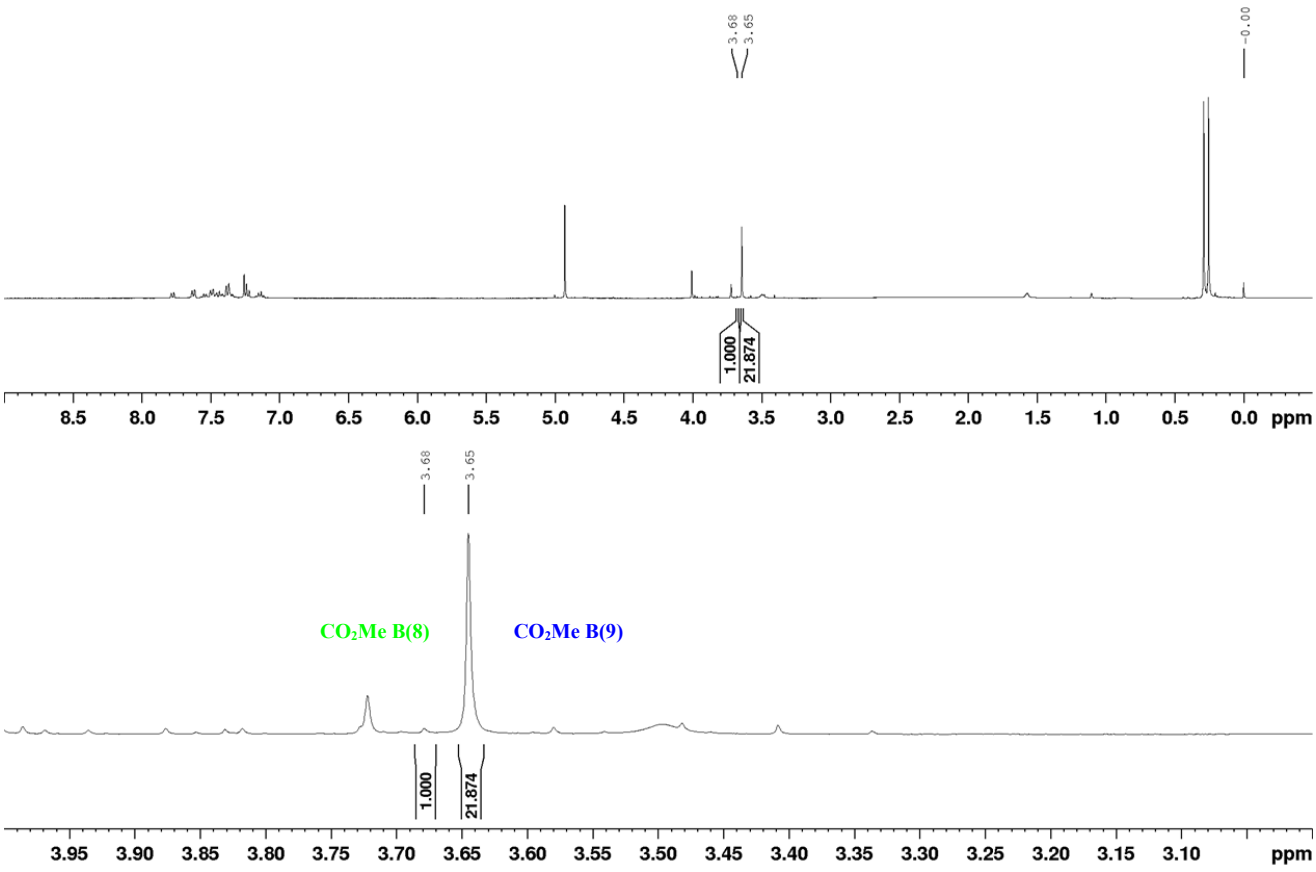
1a **2a** **3aa-B(9)** **4aa-B(8)**

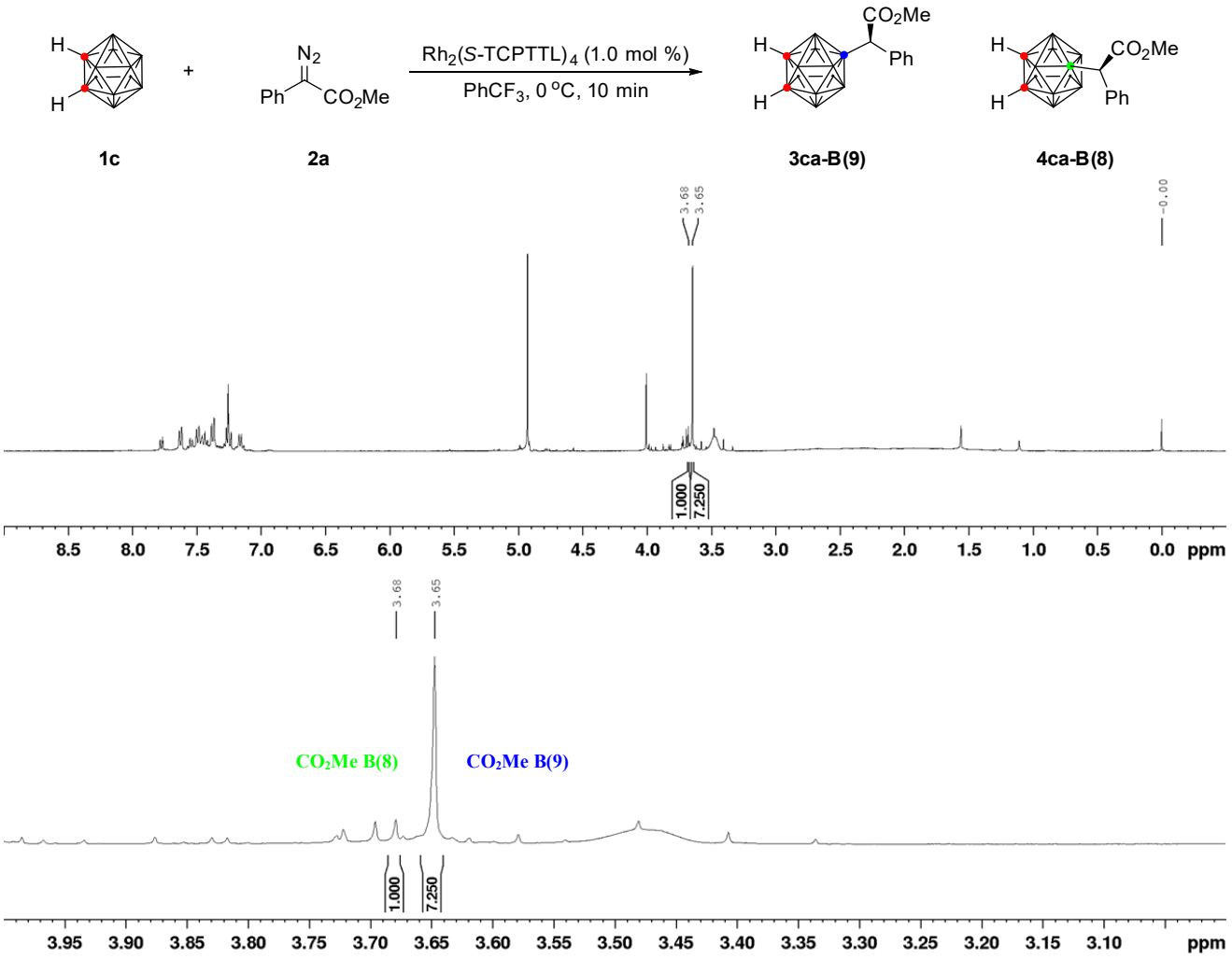


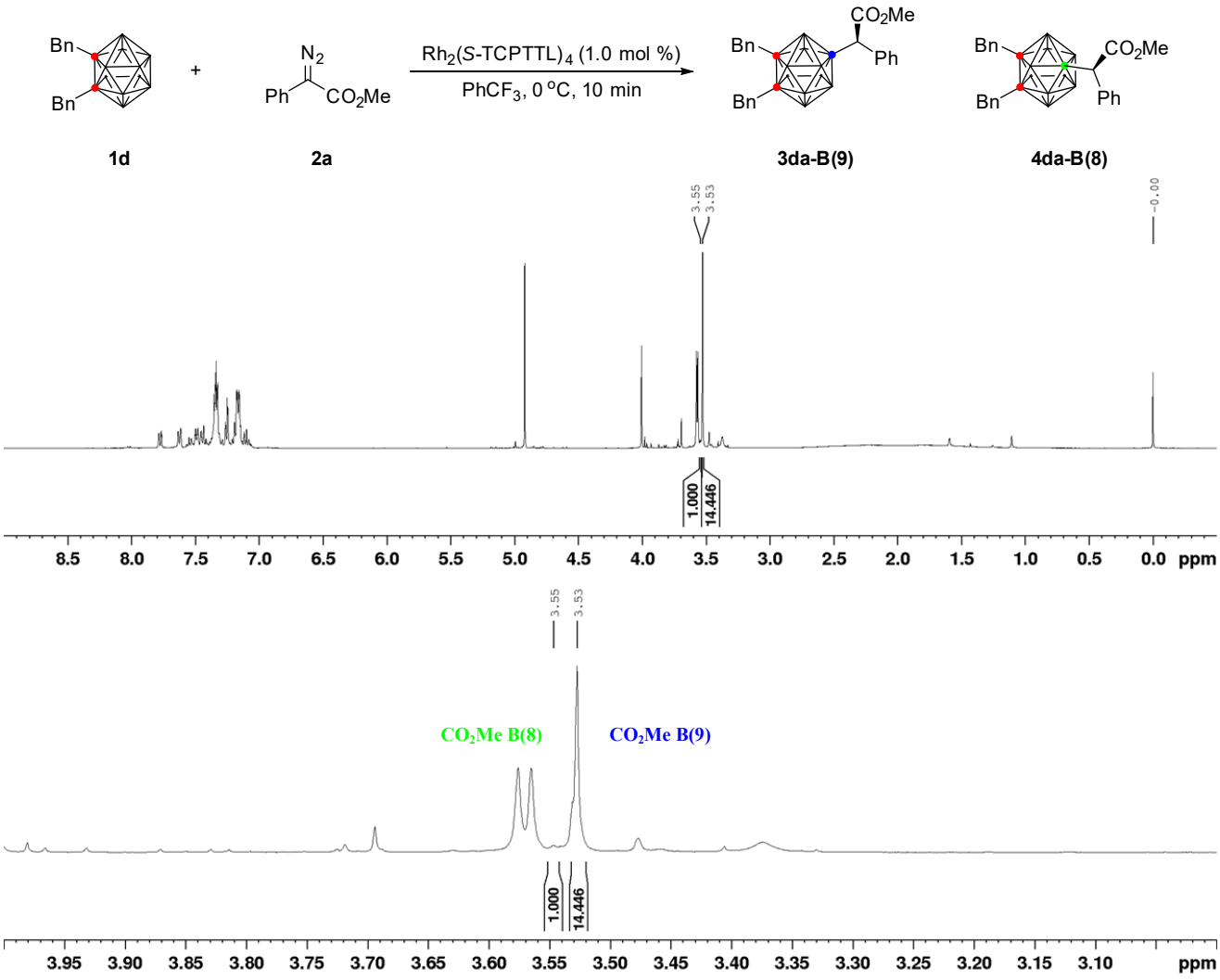


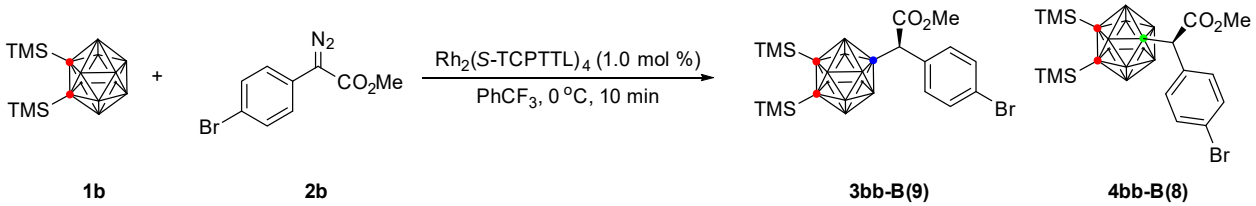


1b **2a** **3ba-B(9)** **4ba-B(8)**

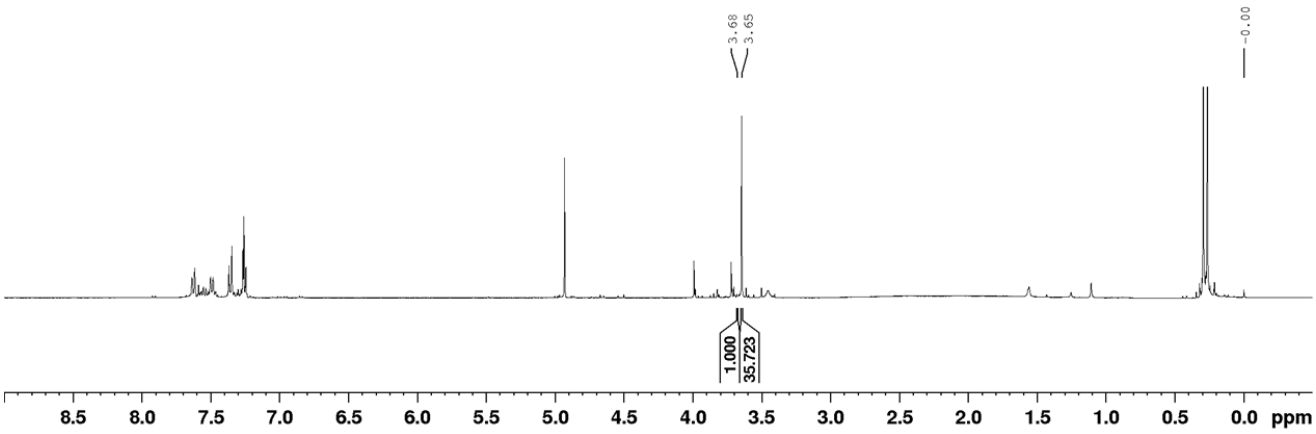


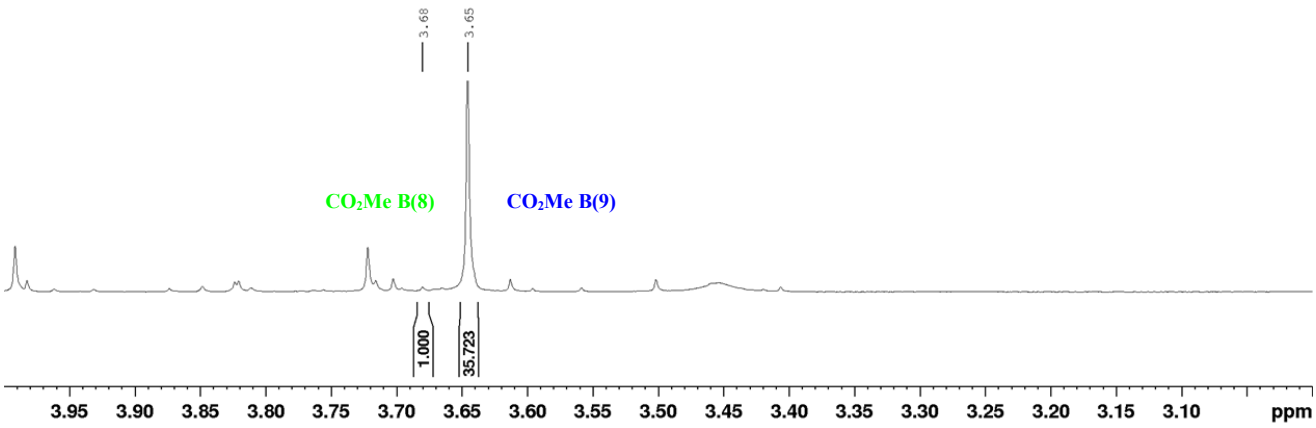

Rh2(S-TCPTTL)4 (1.0 mol %)
PhCF3, 0 °C, 10 min
1c
2a
3ca-B(9)
4ca-B(8)
CO2Me B(8)
CO2Me B(9)
ppm

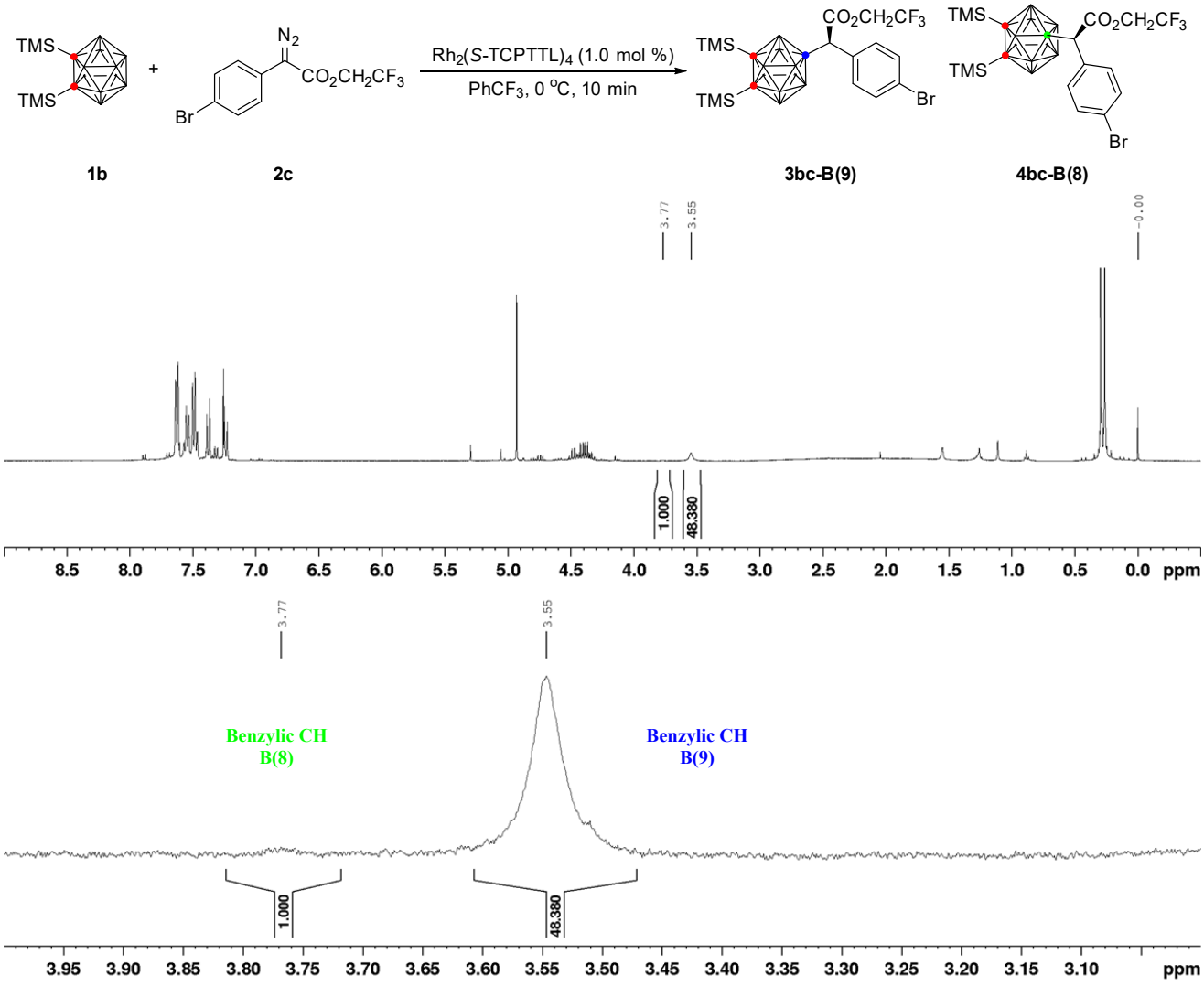

Bn
Bn
+
N2
Ph
CO2Me
Rh2(S-TCPTTL)4 (1.0 mol %)
PhCF3, 0 °C, 10 min
CO2Me
Ph
Bn
Bn
CO2Me
Ph
Bn
Bn
1d
2a
3da-B(9)
4da-B(8)
3.55
3.53
-0.00
1.000
14.446
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
3.55
3.53
CO2Me B(8)
CO2Me B(9)
1.000
14.446
3.95 3.90 3.85 3.80 3.75 3.70 3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30 3.25 3.20 3.15 3.10 ppm

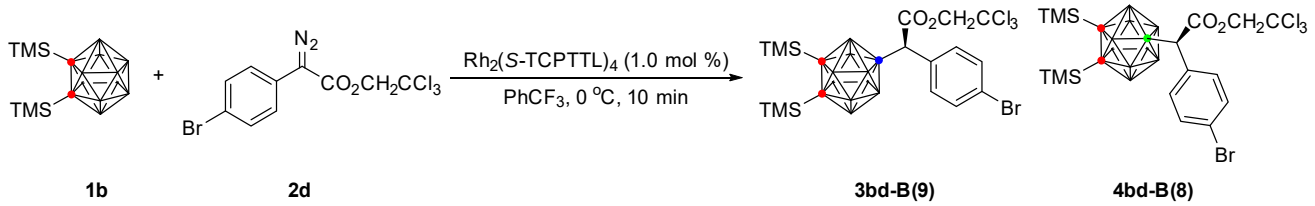


1b **2b** **3bb-B(9)** **4bb-B(8)**

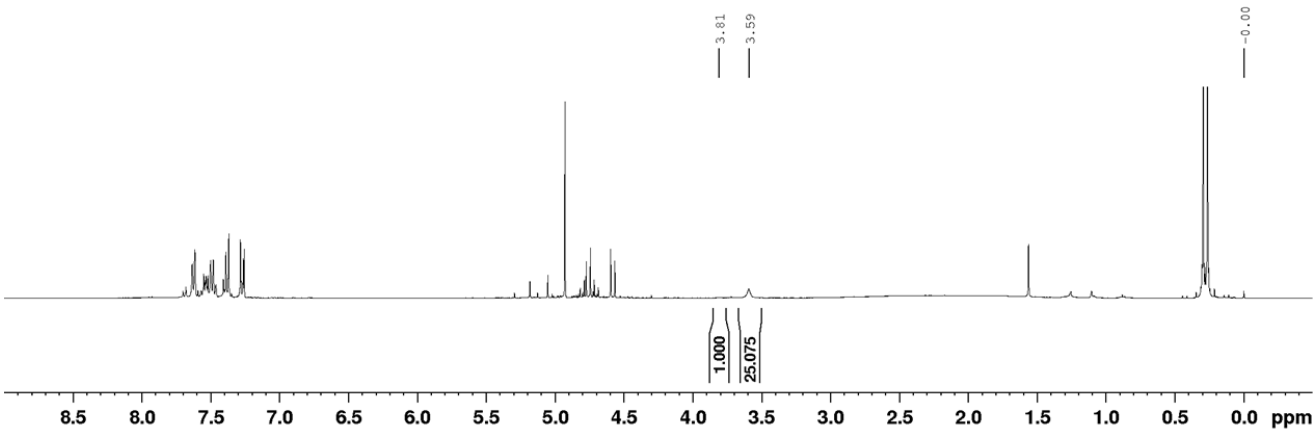


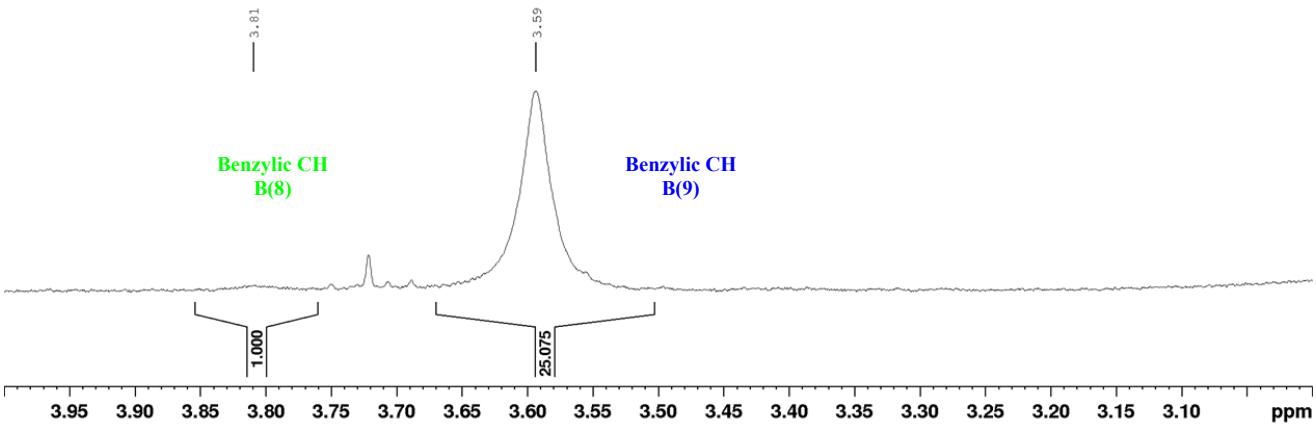


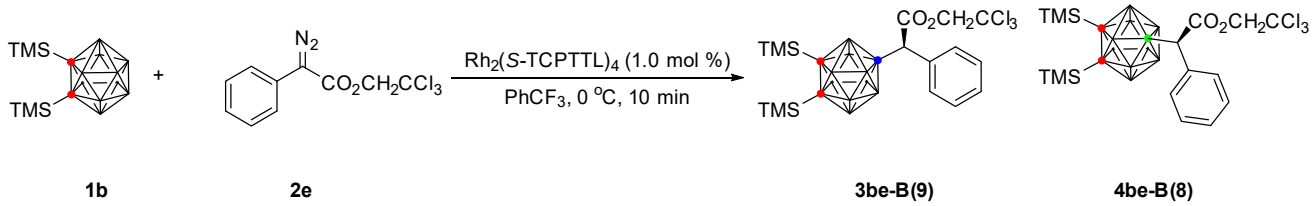

TMS
TMS
+
N2
CO2CH2CF3
Br
Rh2(S-TCPTTL)4 (1.0 mol %)
PhCF3, 0 °C, 10 min
CO2CH2CF3
TMS
TMS
Br
TMS
TMS
CO2CH2CF3
Br
1b
2c
3bc-B(9)
4bc-B(8)
3.77
3.55
0.00
1.000
48.380
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
Benzylic CH
B(8)
Benzylic CH
B(9)
1.000
48.380
3.95 3.90 3.85 3.80 3.75 3.70 3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30 3.25 3.20 3.15 3.10 ppm



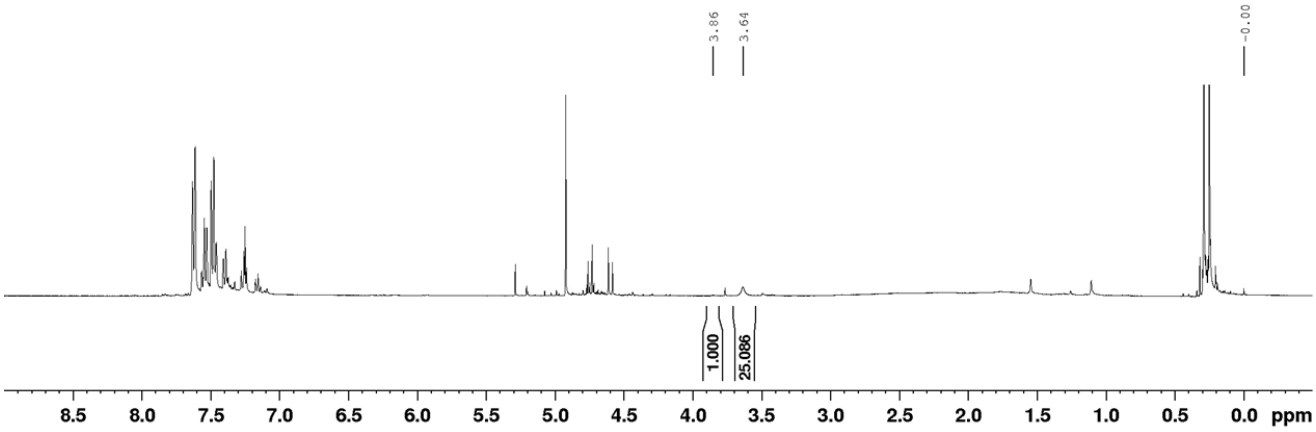
1b **2d** **3bd-B(9)** **4bd-B(8)**

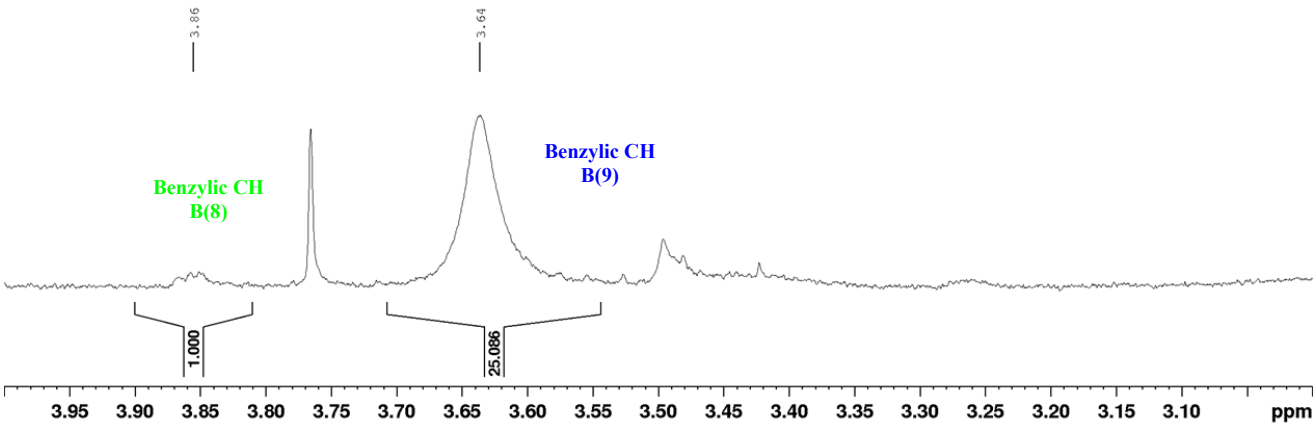


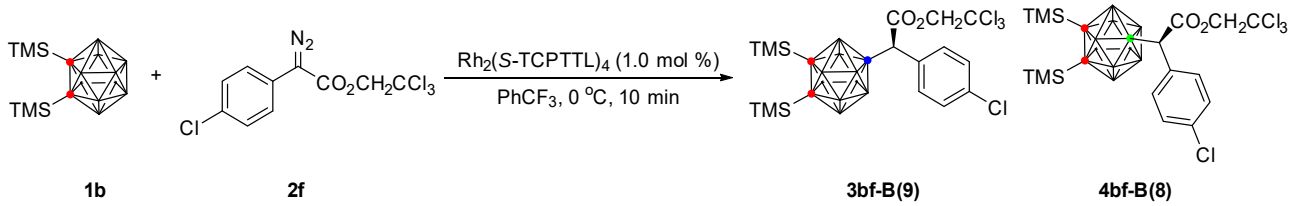




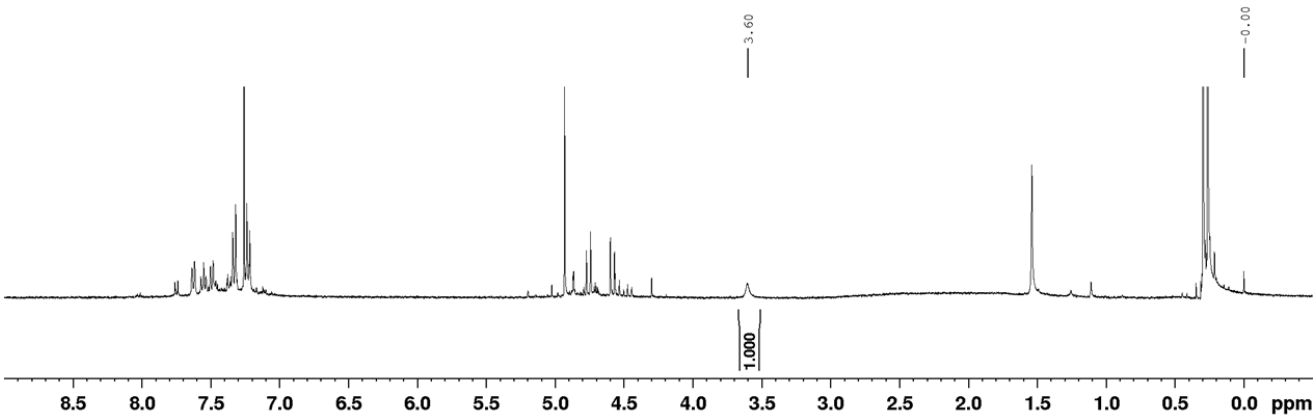
1b **2e** **3be-B(9)** **4be-B(8)**

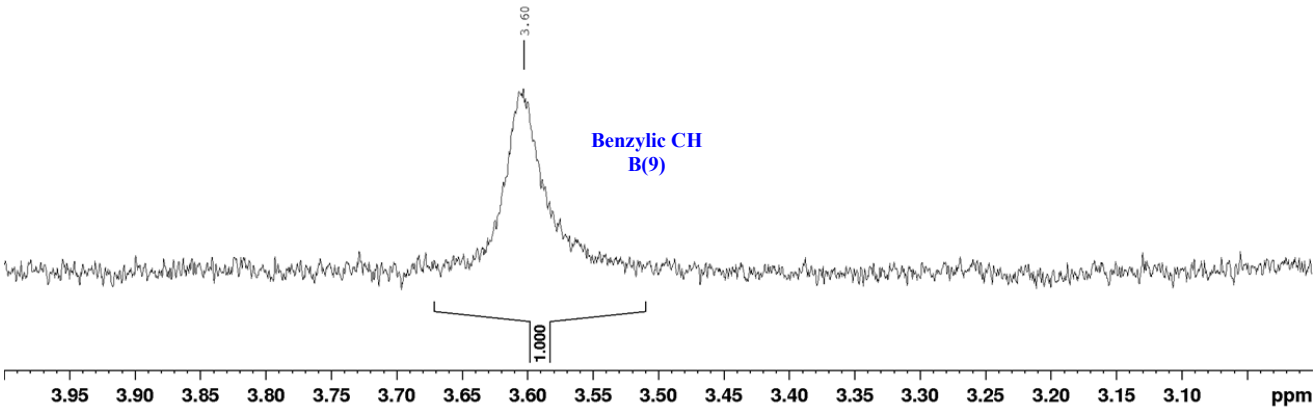


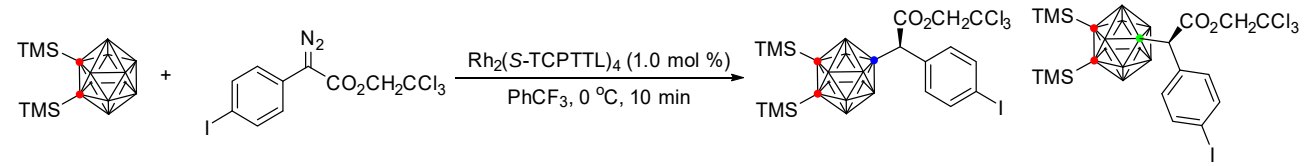




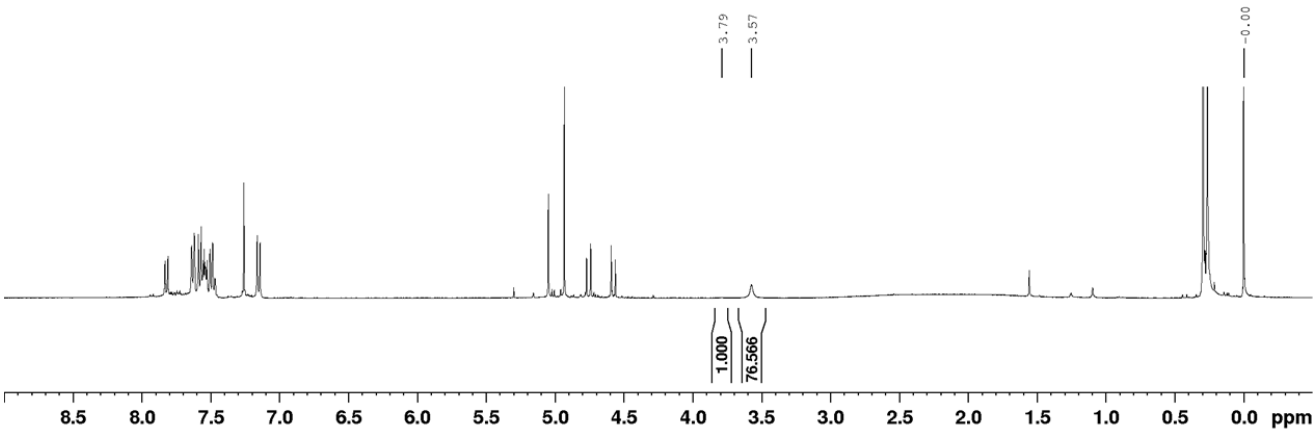
1b **2f** **3bf-B(9)** **4bf-B(8)**

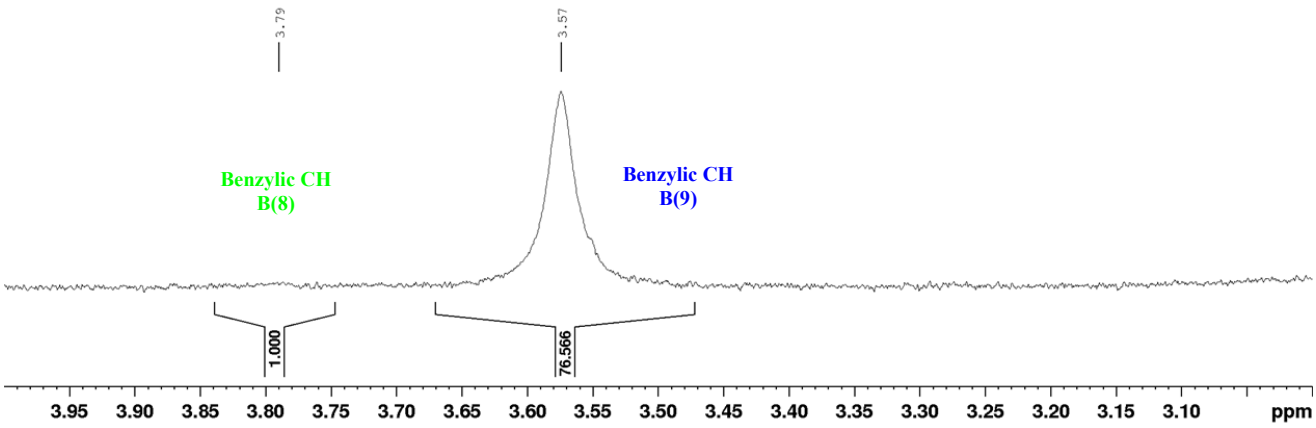


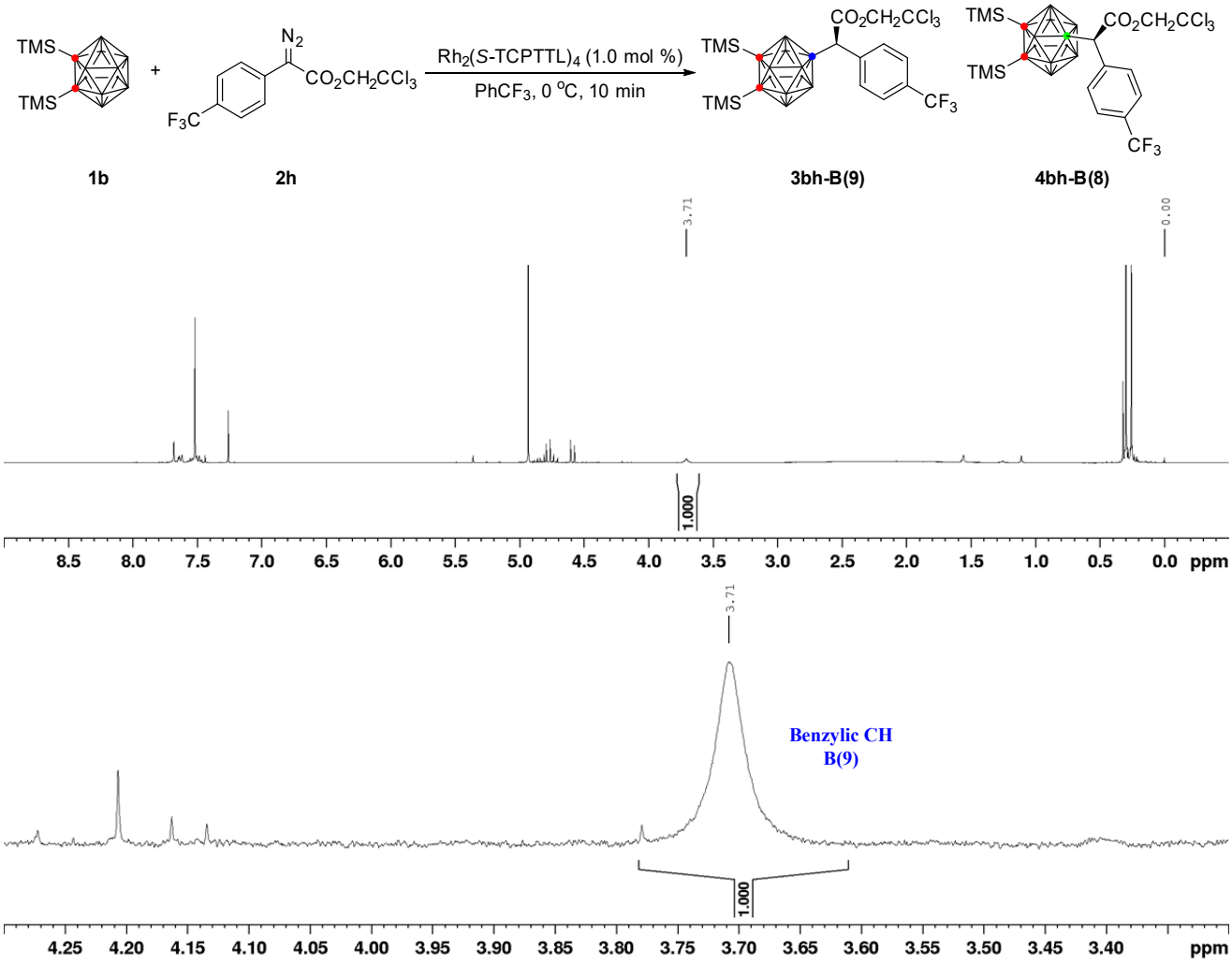


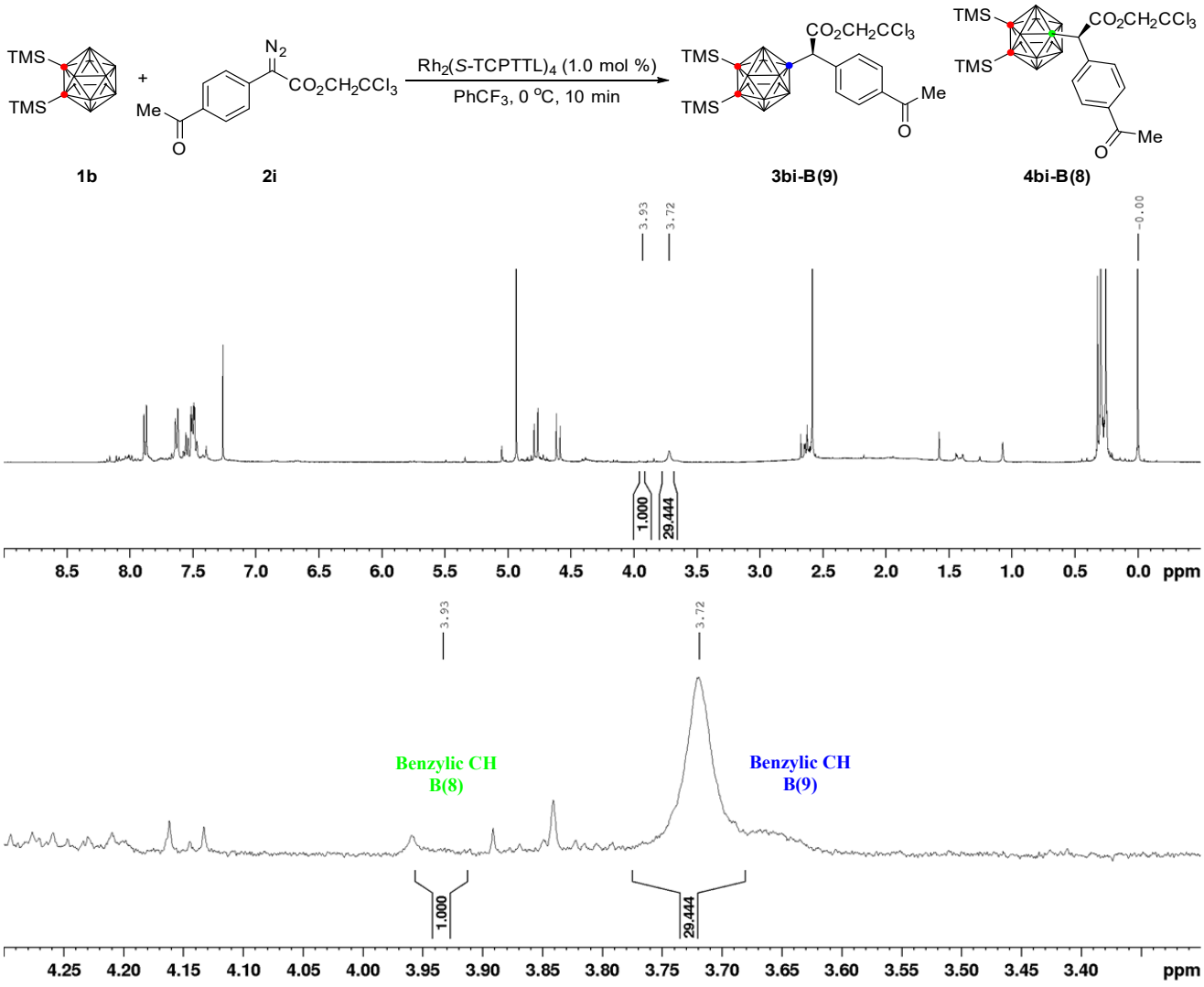


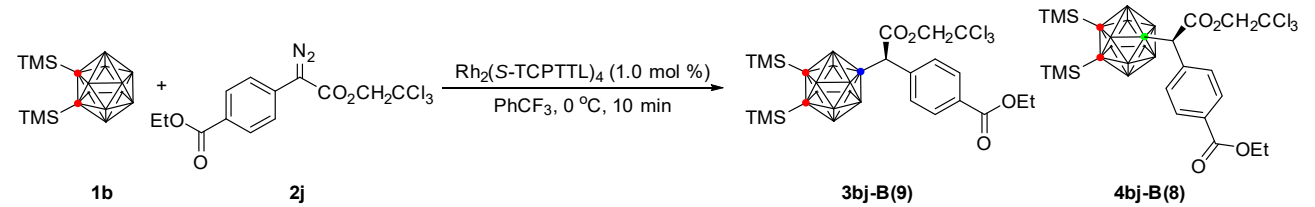
1b **2g** **3bg-B(9)** **4bg-B(8)**

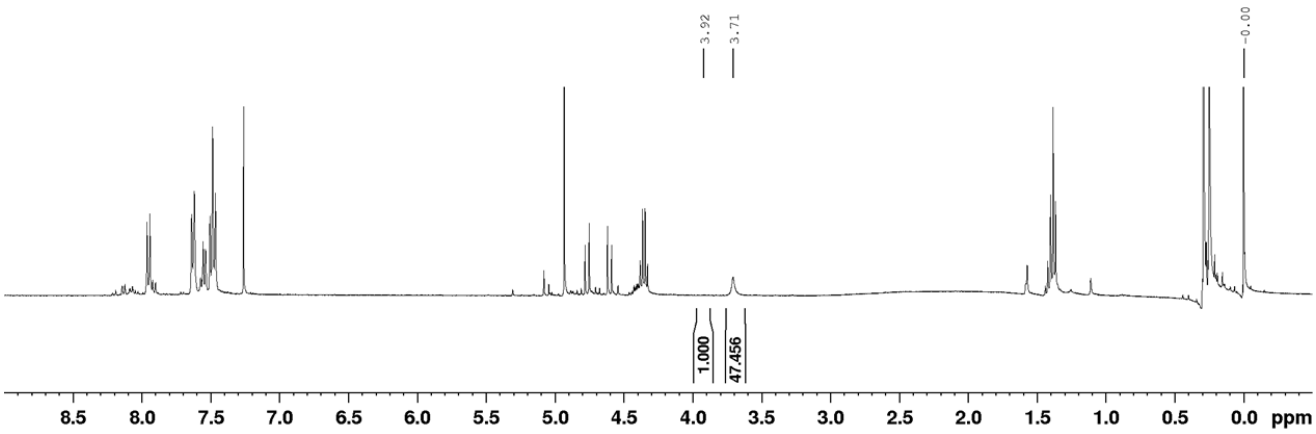


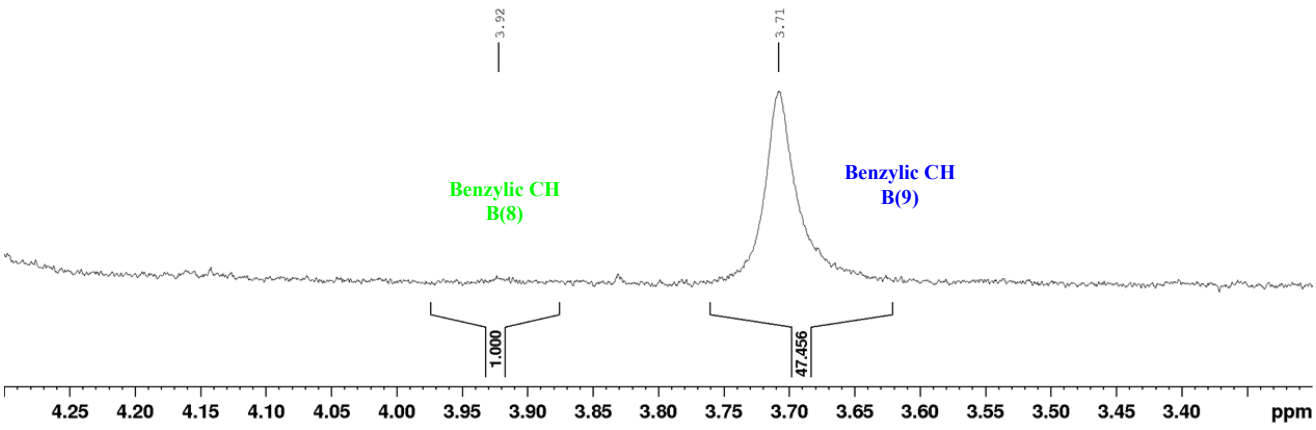


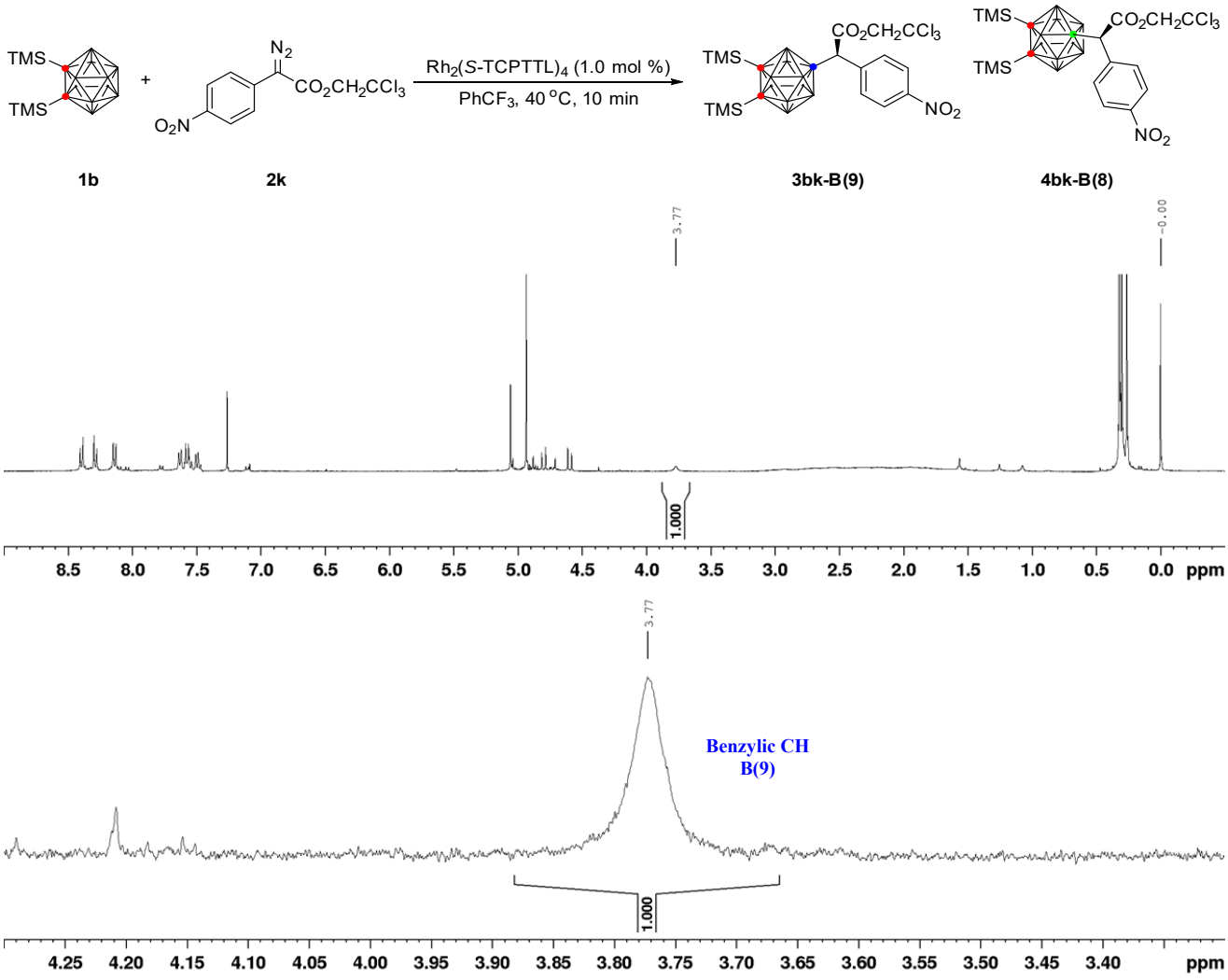

TMS
TMS
+
N2
CO2CH2CCl3
F3C
Rh2(S-TCPTTL)4 (1.0 mol %)
PhCF3, 0 °C, 10 min
CO2CH2CCl3
TMS
TMS
CF3
TMS
TMS
CO2CH2CCl3
CF3
1b
2h
3bh-B(9)
4bh-B(8)
3.71
0.00
1.000
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
3.71
Benzylic CH
B(9)
1.000
4.25 4.20 4.15 4.10 4.05 4.00 3.95 3.90 3.85 3.80 3.75 3.70 3.65 3.60 3.55 3.50 3.45 3.40 ppm

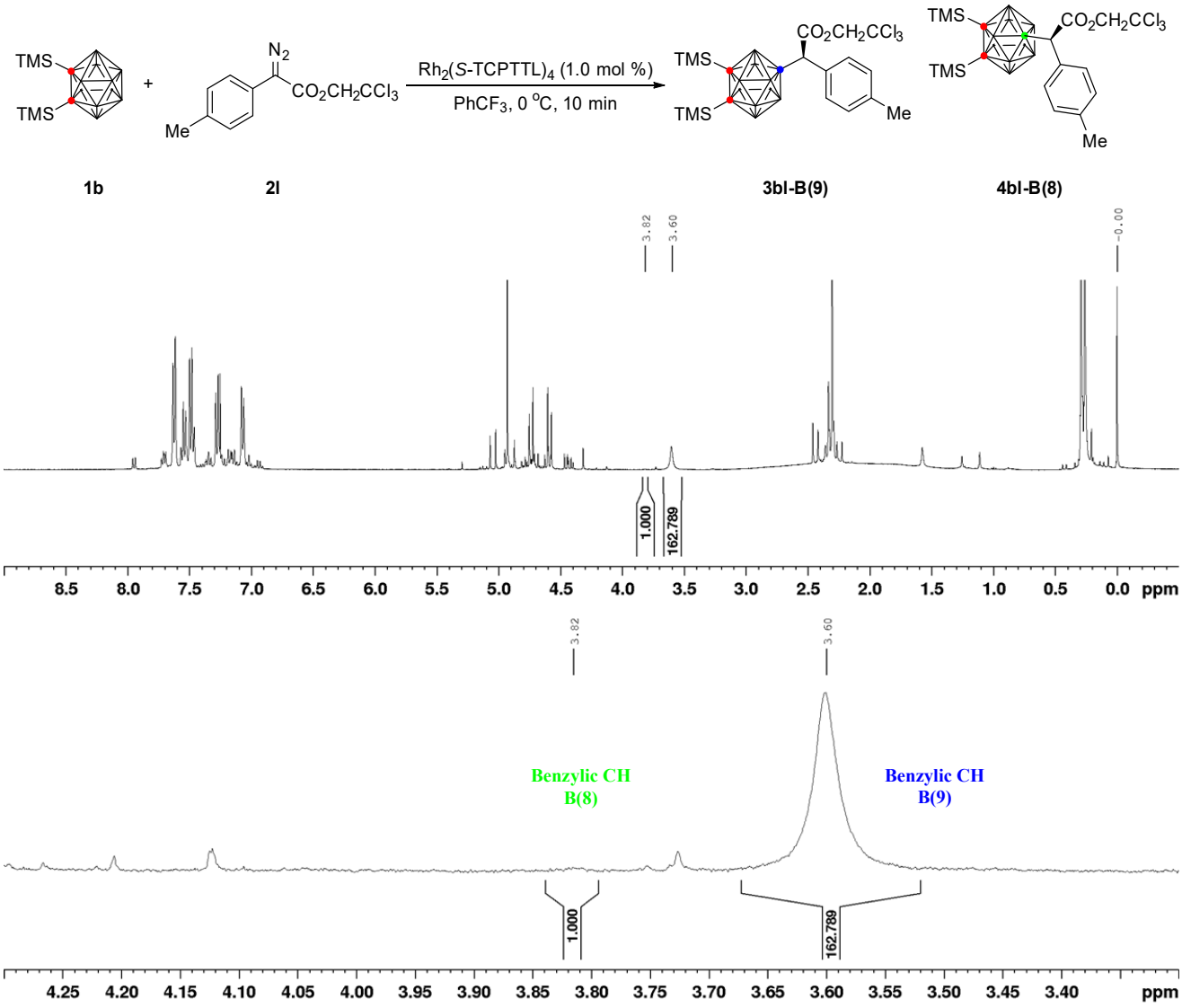

TMS
TMS
+
Me
O
N2
CO2CH2CCl3
Rh2(S-TCPTTL)4 (1.0 mol %)
PhCF3, 0 °C, 10 min
CO2CH2CCl3
Me
1b
2i
3bi-B(9)
4bi-B(8)
3.93
3.72
0.00
1.000
29.444
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
Benzylic CH
B(8)
Benzylic CH
B(9)
4.25 4.20 4.15 4.10 4.05 4.00 3.95 3.90 3.85 3.80 3.75 3.70 3.65 3.60 3.55 3.50 3.45 3.40 ppm

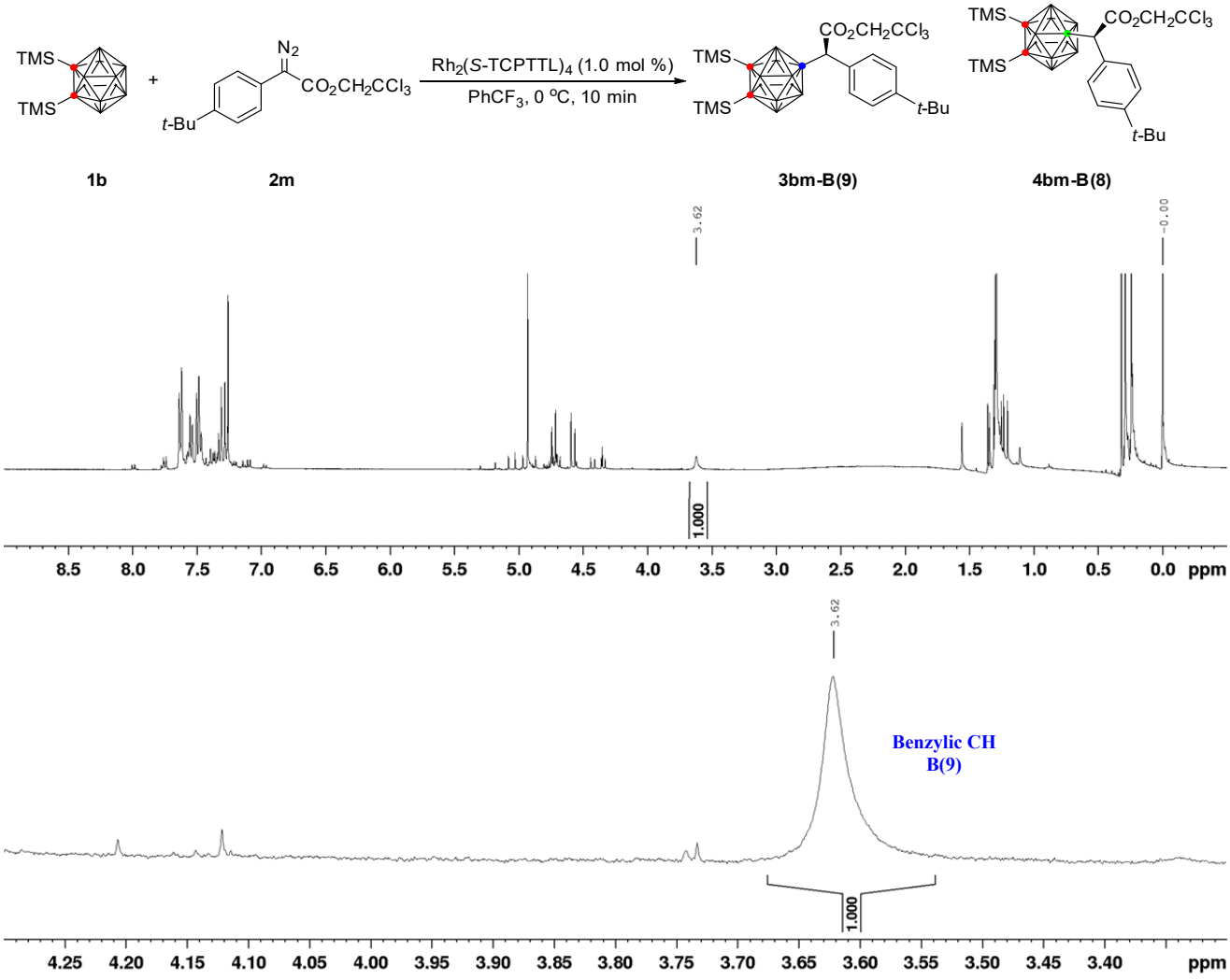

TMS
TMS
+
EtO
O
N2
CO2CH2CCl3
Rh2(S-TCPTTL)4 (1.0 mol %)
PhCF3, 0 °C, 10 min
CO2CH2CCl3
OEt
1b
2j
3bj-B(9)
4bj-B(8)

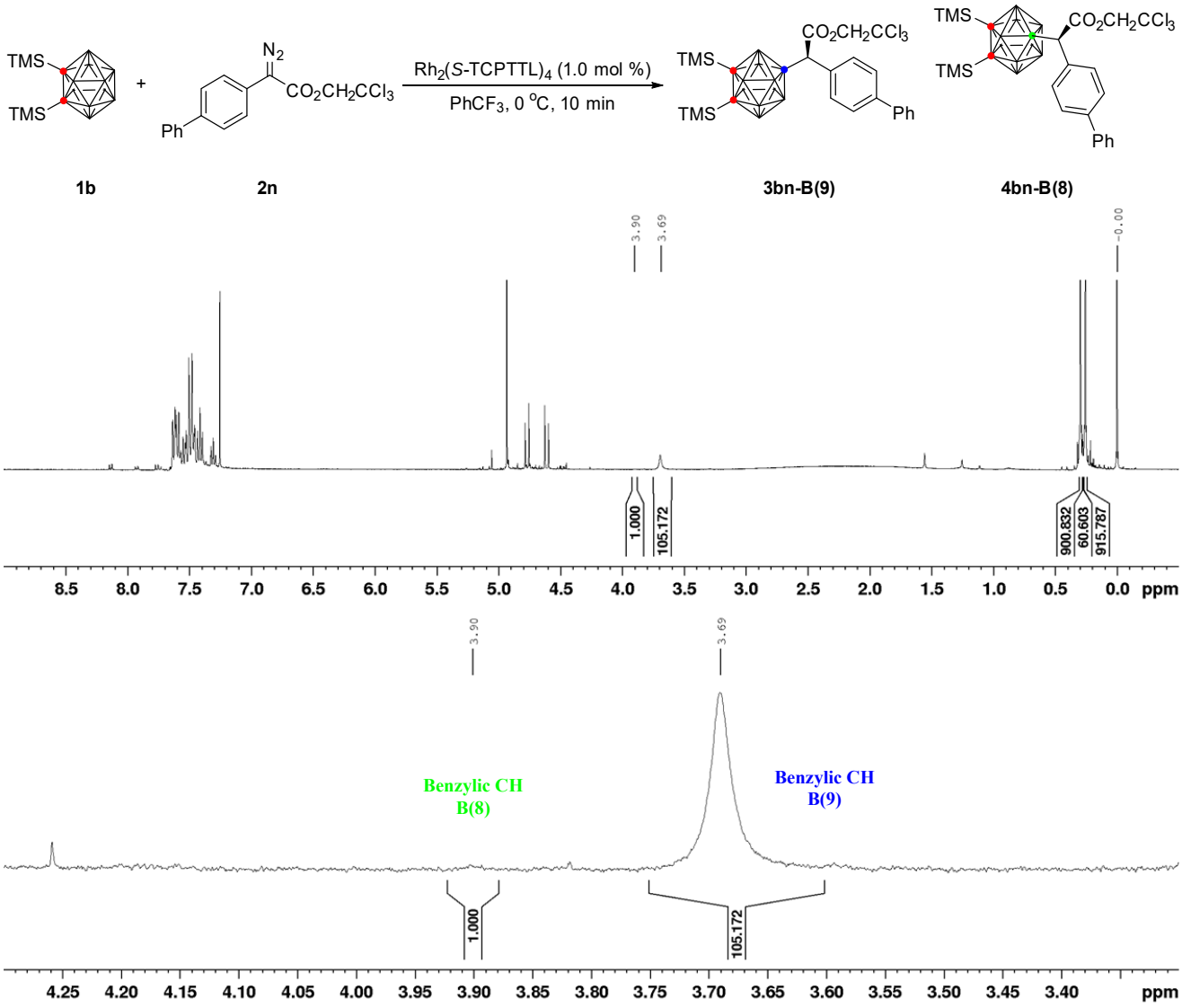

3.92
3.71
0.00
1.000
47.456
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

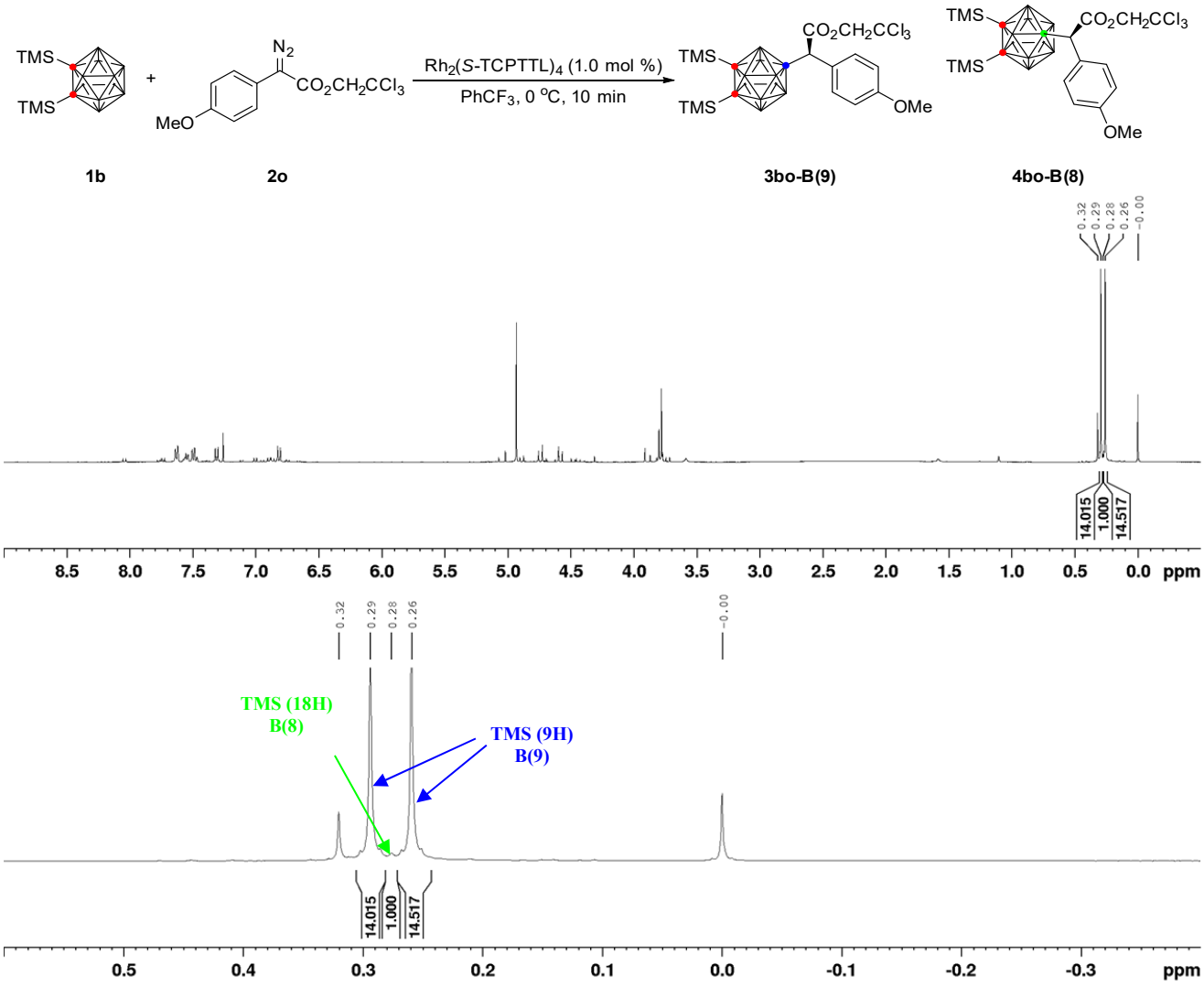

3.92
3.71
Benzylic CH
B(8)
Benzylic CH
B(9)
1.000
47.456
4.25 4.20 4.15 4.10 4.05 4.00 3.95 3.90 3.85 3.80 3.75 3.70 3.65 3.60 3.55 3.50 3.45 3.40 ppm

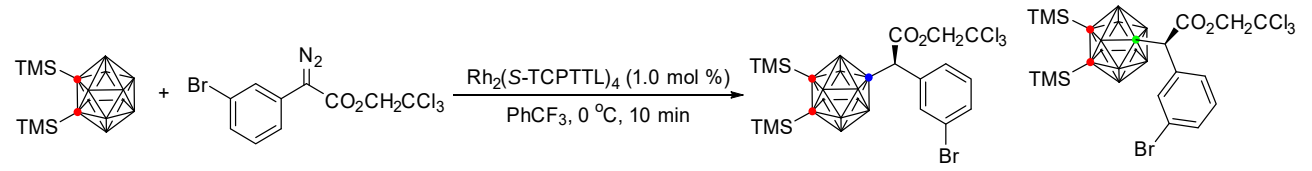

TMS
TMS
+
N_2
$CO_2CH_2CCl_3$
O_2N
Rh_2(S-TCPTTL)$_4$ (1.0 mol %)
$PhCF_3$, 40 °C, 10 min
$CO_2CH_2CCl_3$
NO_2
1b
2k
3bk-B(9)
4bk-B(8)
3.77
0.00
1.000
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
Benzylic CH
B(9)
4.25 4.20 4.15 4.10 4.05 4.00 3.95 3.90 3.85 3.80 3.75 3.70 3.65 3.60 3.55 3.50 3.45 3.40 ppm


TMS
TMS
+
N2
CO2CH2CCl3
Me
Rh2(S-TCPTTL)4 (1.0 mol %)
PhCF3, 0 °C, 10 min
CO2CH2CCl3
TMS
TMS
Me
CO2CH2CCl3
TMS
TMS
Me
1b
2l
3bl-B(9)
4bl-B(8)
3.82
3.60
0.00
1.000
162.789
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
3.82
3.60
Benzylic CH
B(8)
Benzylic CH
B(9)
1.000
162.789
4.25 4.20 4.15 4.10 4.05 4.00 3.95 3.90 3.85 3.80 3.75 3.70 3.65 3.60 3.55 3.50 3.45 3.40 ppm

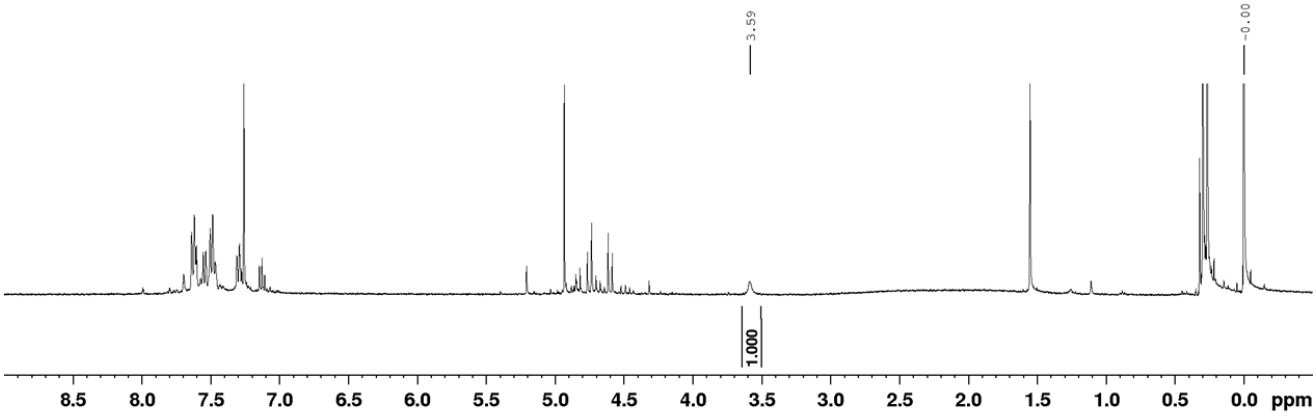

TMS
TMS
+
N2
CO2CH2CCl3
t-Bu
Rh2(S-TCPTTL)4 (1.0 mol %)
PhCF3, 0 °C, 10 min
CO2CH2CCl3
TMS
TMS
t-Bu
CO2CH2CCl3
TMS
TMS
t-Bu
1b
2m
3bm-B(9)
4bm-B(8)
3.62
0.00
1.000
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
3.62
Benzylic CH
B(9)
1.000
4.25 4.20 4.15 4.10 4.05 4.00 3.95 3.90 3.85 3.80 3.75 3.70 3.65 3.60 3.55 3.50 3.45 3.40 ppm

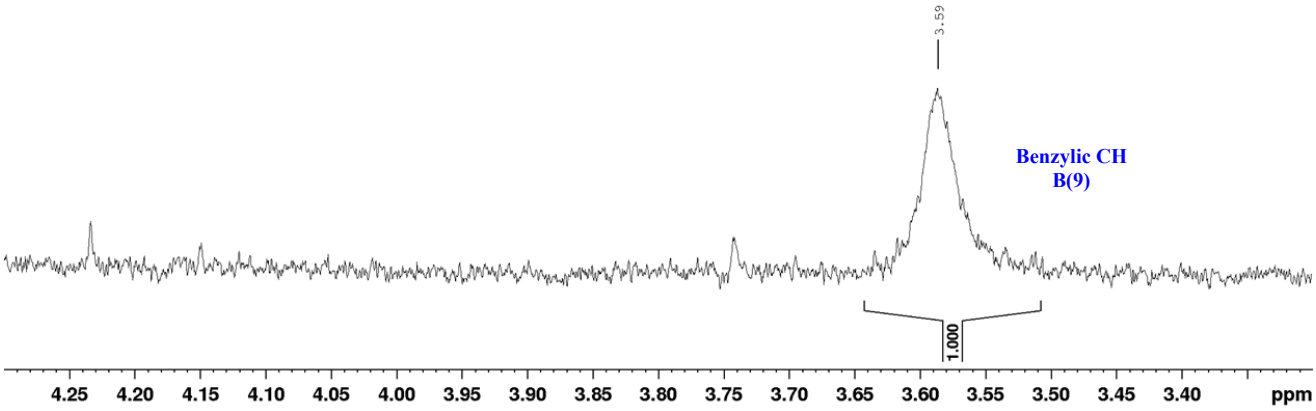

TMS
TMS
+
N2
CO2CH2CCl3
Ph
Rh2(S-TCPTTL)4 (1.0 mol %)
PhCF3, 0 °C, 10 min
CO2CH2CCl3
TMS
TMS
Ph
TMS
TMS
CO2CH2CCl3
Ph
1b
2n
3bn-B(9)
4bn-B(8)
3.90
3.69
0.00
1.000
105.172
900.832
60.603
915.787
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
Benzylic CH
B(8)
Benzylic CH
B(9)
1.000
105.172
4.25 4.20 4.15 4.10 4.05 4.00 3.95 3.90 3.85 3.80 3.75 3.70 3.65 3.60 3.55 3.50 3.45 3.40 ppm

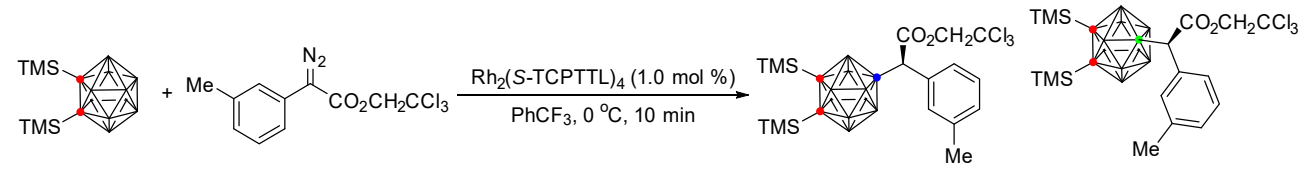

TMS
TMS
+
N2
CO2CH2CCl3
MeO
Rh2(S-TCPTTL)4 (1.0 mol %)
PhCF3, 0 °C, 10 min
CO2CH2CCl3
TMS
TMS
OMe
TMS
TMS
CO2CH2CCl3
OMe
1b
2o
3bo-B(9)
4bo-B(8)
0.32
0.29
0.28
0.26
-0.00
14.015
1.000
14.517
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
TMS (18H)
B(8)
TMS (9H)
B(9)
0.5 0.4 0.3 0.2 0.1 0.0 -0.1 -0.2 -0.3 ppm



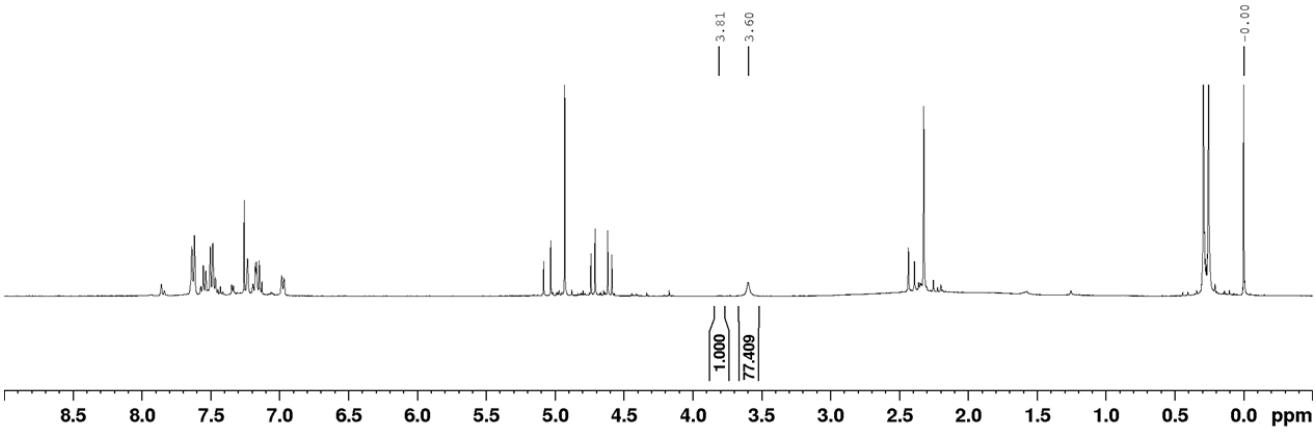
1b **2p** **3bp-B(9)** **4bp-B(8)**

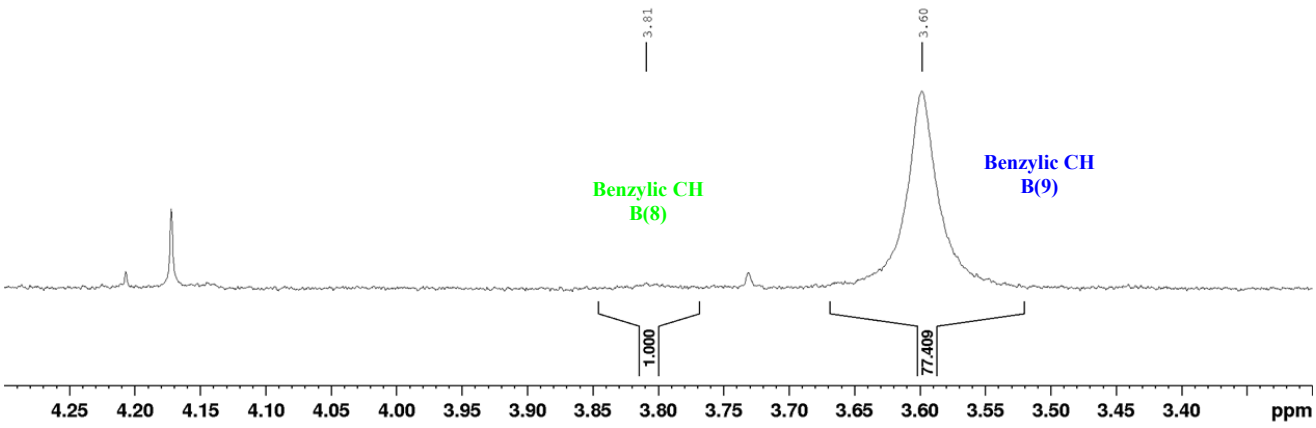


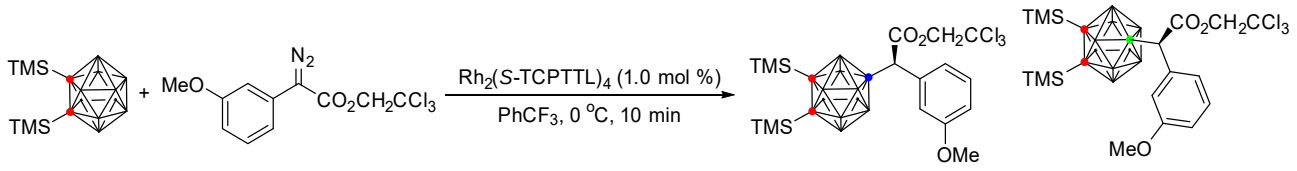




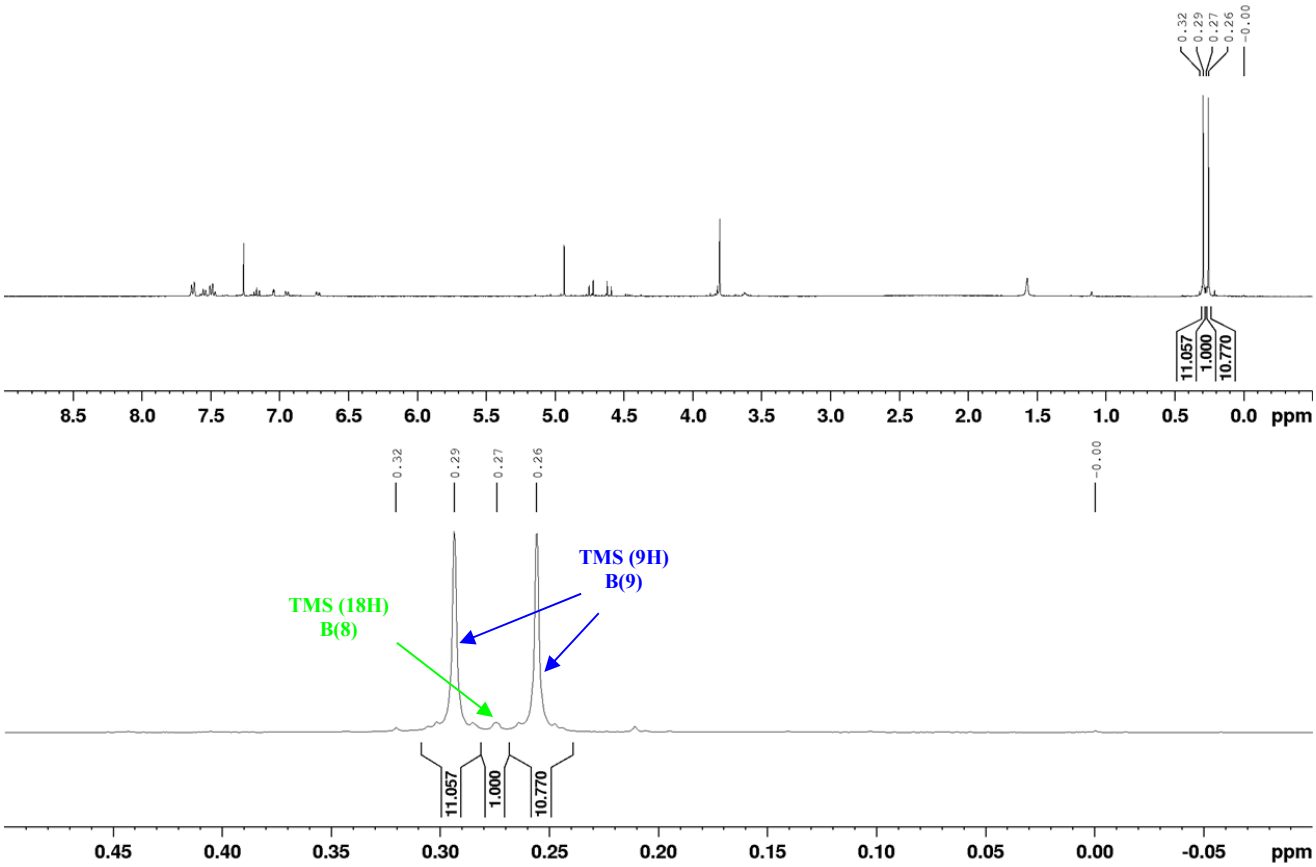
1b **2q** **3bq-B(9)** **4bq-B(8)**

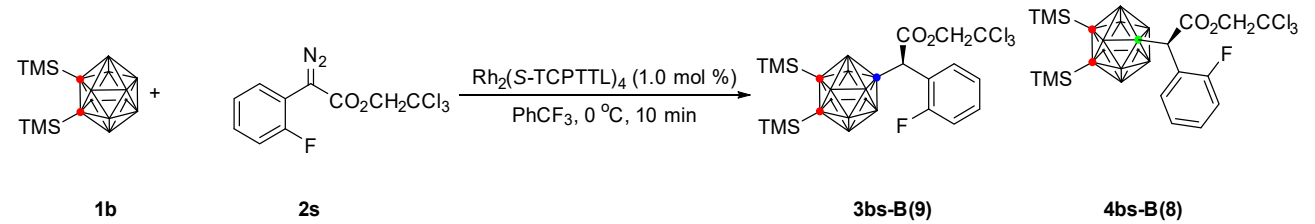




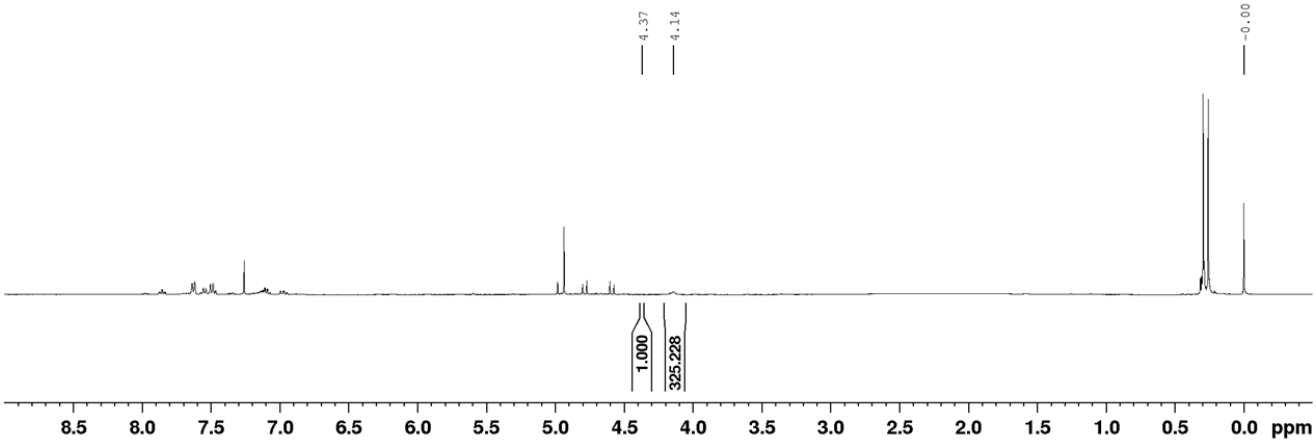


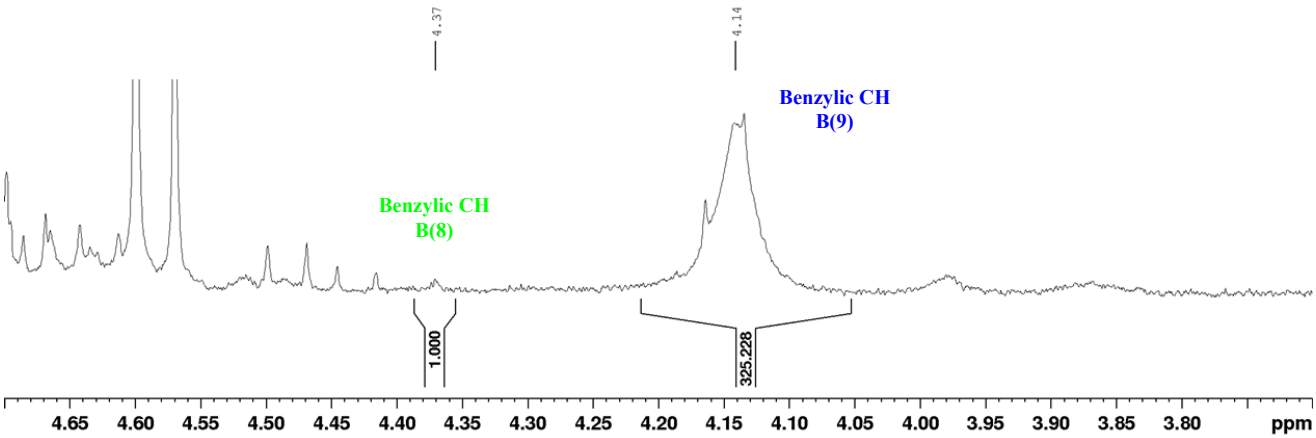
1b **2r** **3br-B(9)** **4br-B(8)**

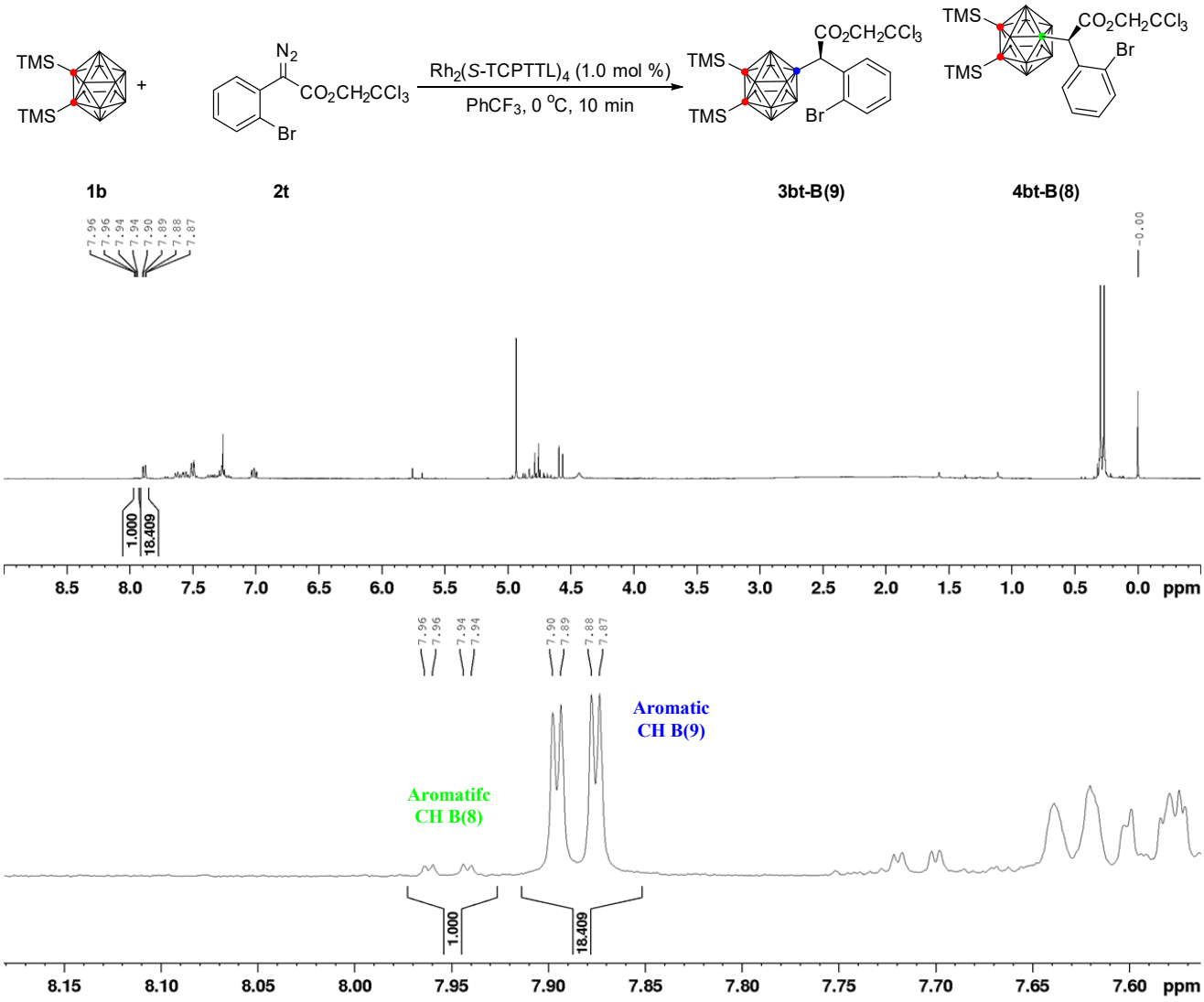


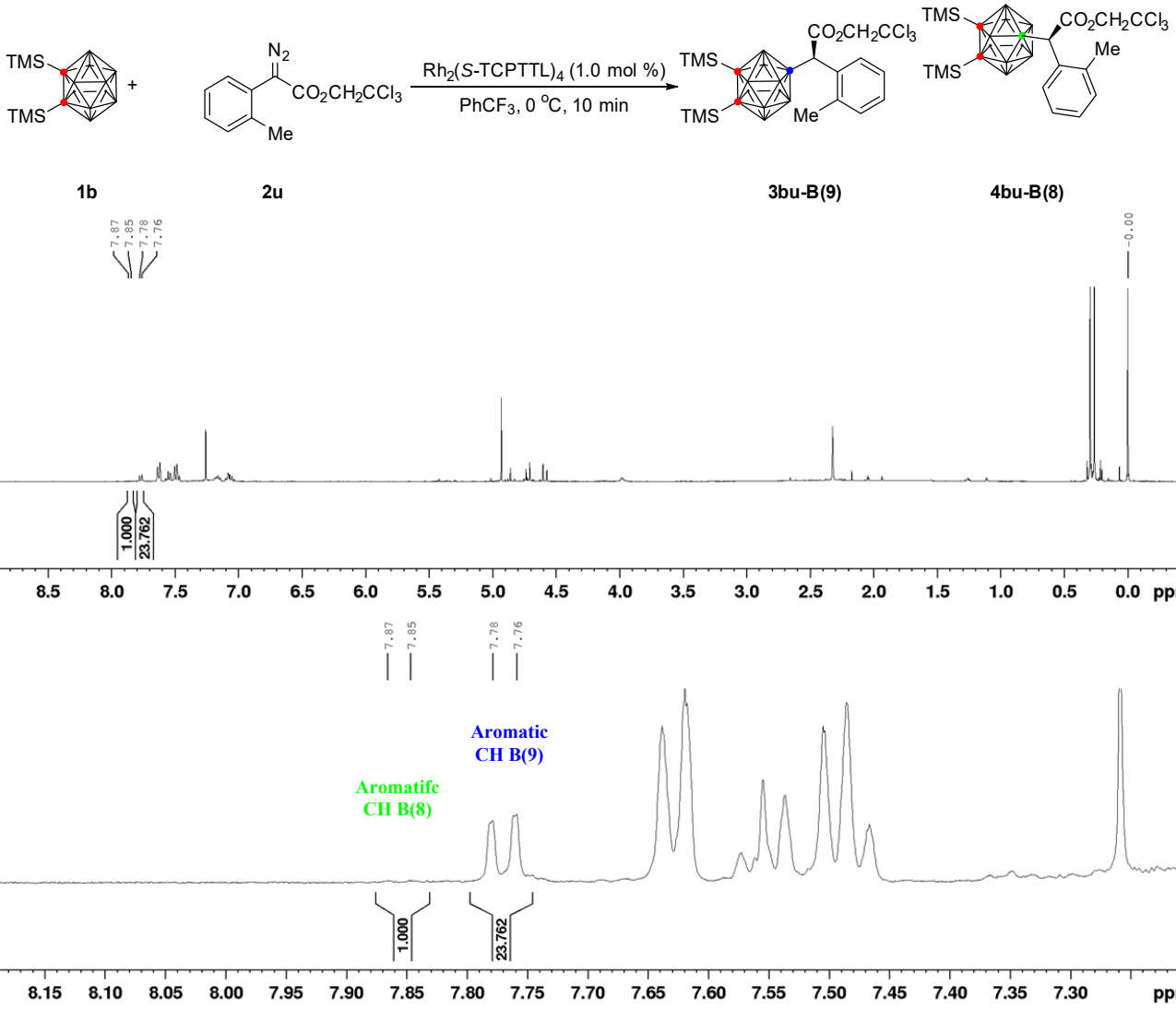


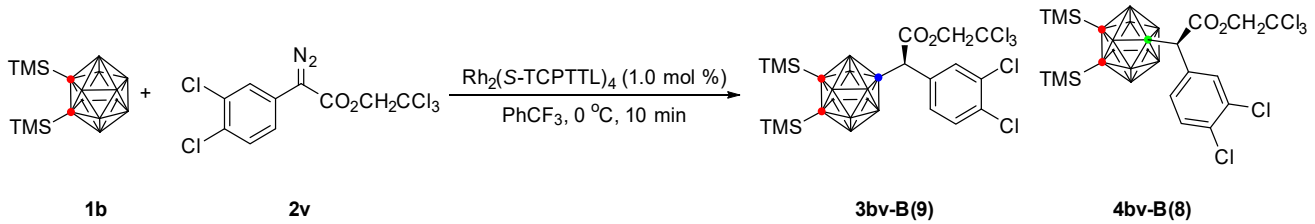
1b **2s** **3bs-B(9)** **4bs-B(8)**



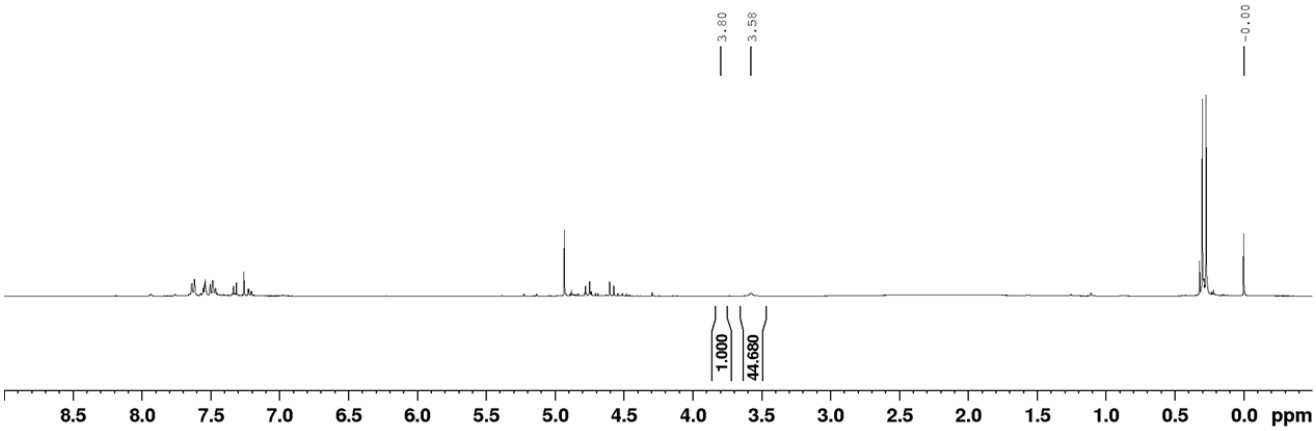


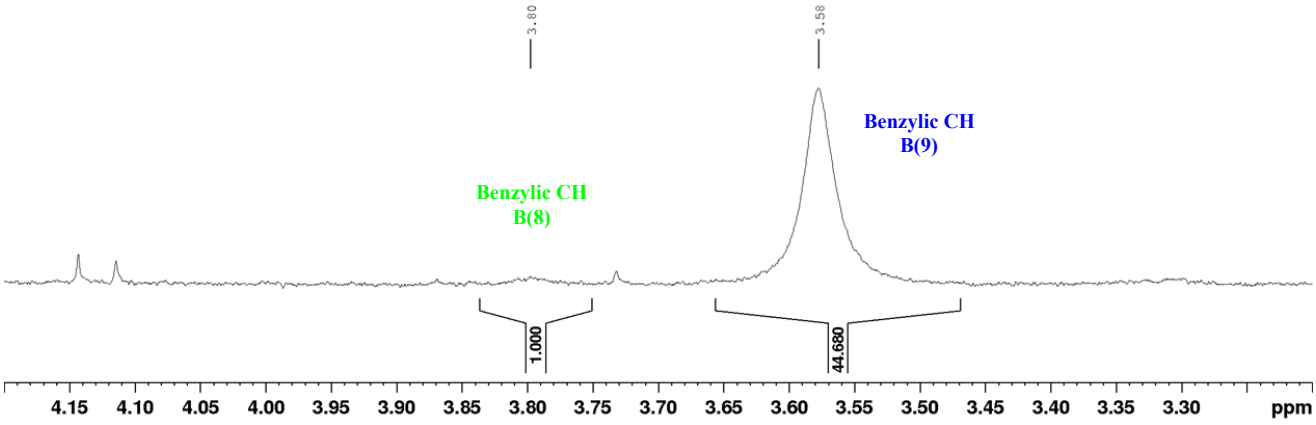

TMS
TMS
+
N2
CO2CH2CCl3
Br
Rh2(S-TCPTTL)4 (1.0 mol %)
PhCF3, 0 °C, 10 min
CO2CH2CCl3
TMS
TMS
Br
TMS
TMS
CO2CH2CCl3
Br
1b
2t
3bt-B(9)
4bt-B(8)
7.96
7.96
7.94
7.94
7.90
7.89
7.88
7.87
-0.00
1.000
18.409
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
7.96
7.96
7.94
7.94
7.90
7.89
7.88
7.87
Aromatic
CH B(9)
Aromatifc
CH B(8)
1.000
18.409
8.15
8.10
8.05
8.00
7.95
7.90
7.85
7.80
7.75
7.70
7.65
7.60
ppm

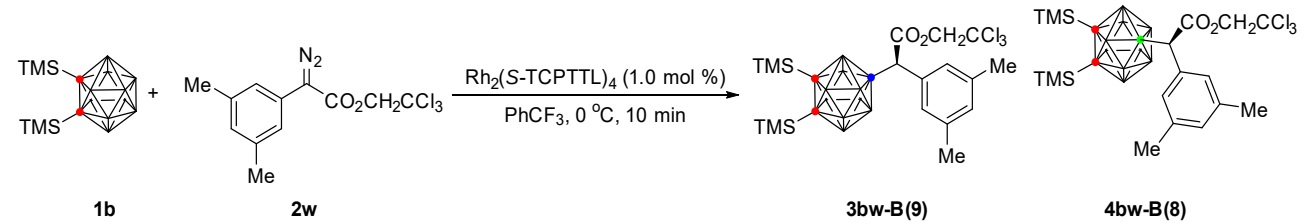

TMS
TMS
+
N2
CO2CH2CCl3
Me
Rh2(S-TCPTTL)4 (1.0 mol %)
PhCF3, 0 °C, 10 min
CO2CH2CCl3
TMS
TMS
Me
TMS
TMS
CO2CH2CCl3
Me
1b
2u
3bu-B(9)
4bu-B(8)
7.87
7.85
7.78
7.76
0.00
1.000
23.762
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
Aromatic
CH B(9)
Aromatifc
CH B(8)
1.000
23.762
8.15
8.10
8.05
8.00
7.95
7.90
7.85
7.80
7.75
7.70
7.65
7.60
7.55
7.50
7.45
7.40
7.35
7.30
ppm



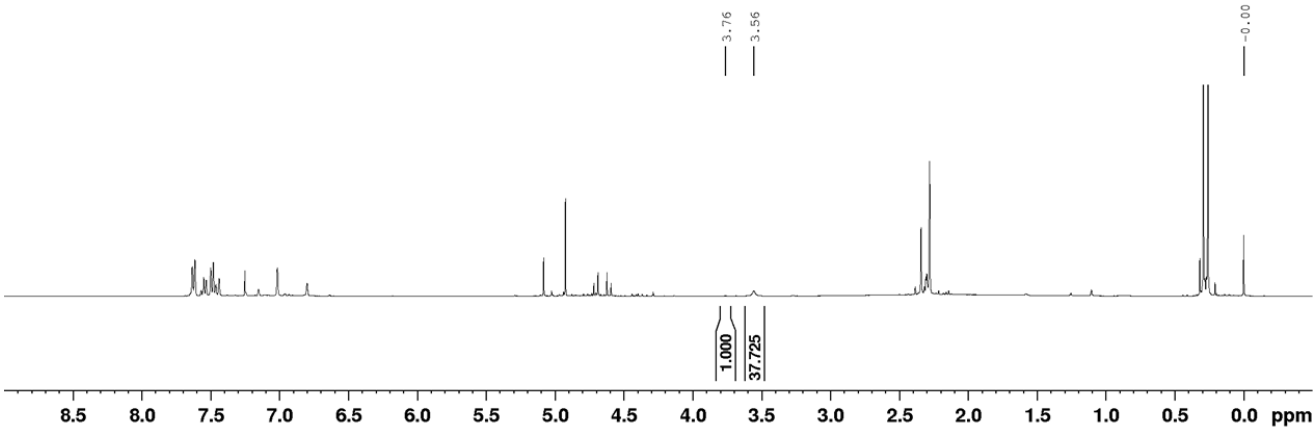
1b **2v** **3bv-B(9)** **4bv-B(8)**

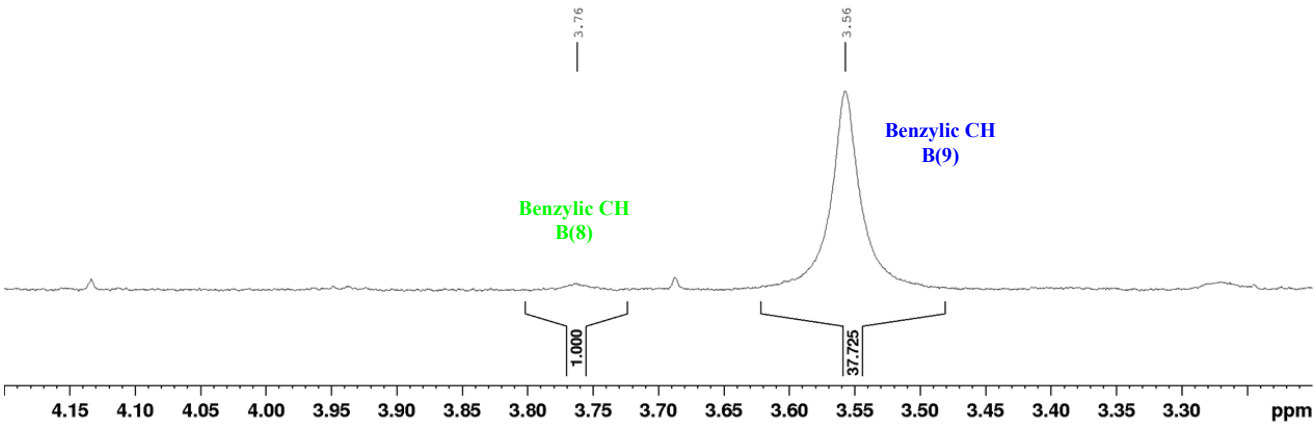


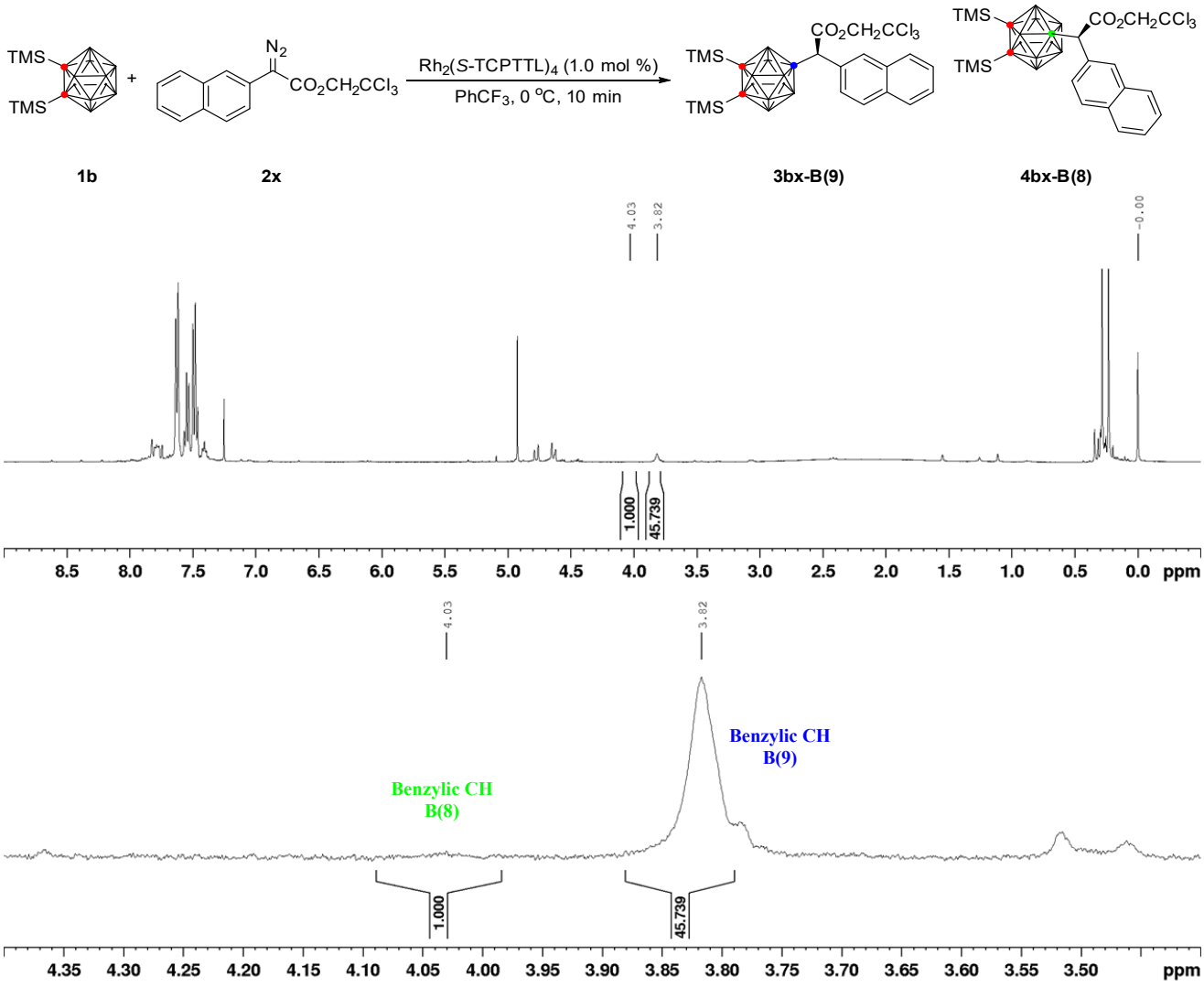


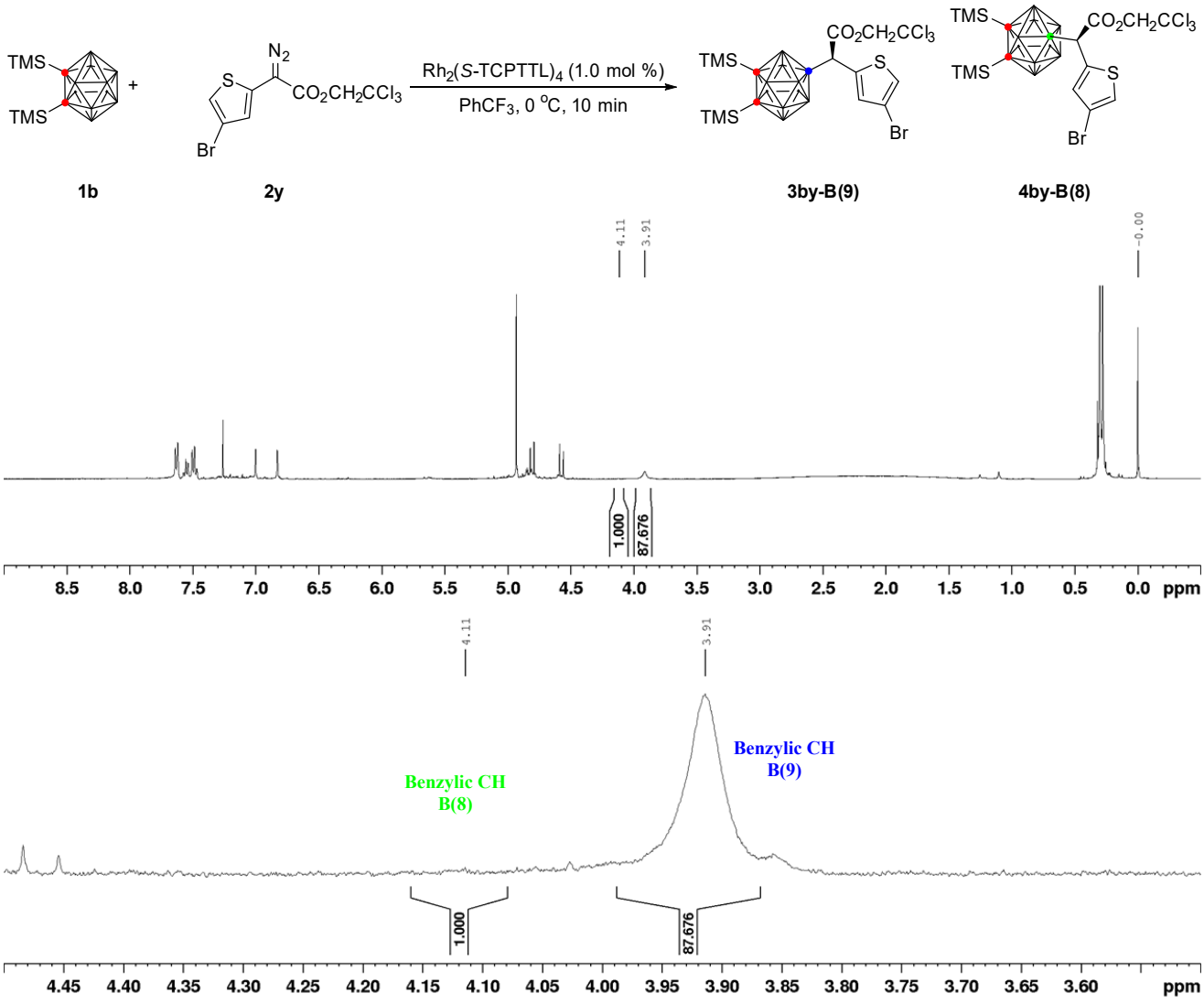


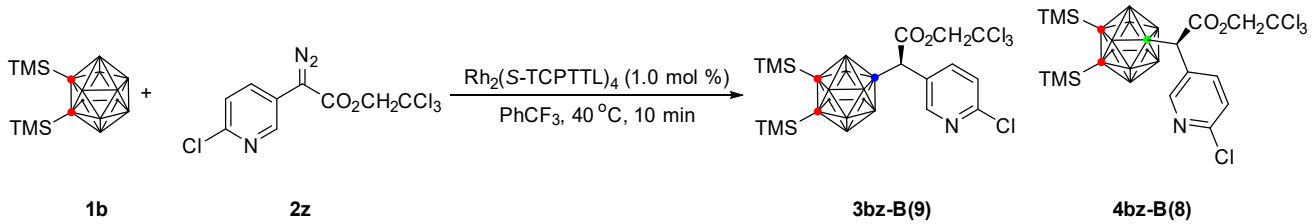
1b **2w** **3bw-B(9)** **4bw-B(8)**



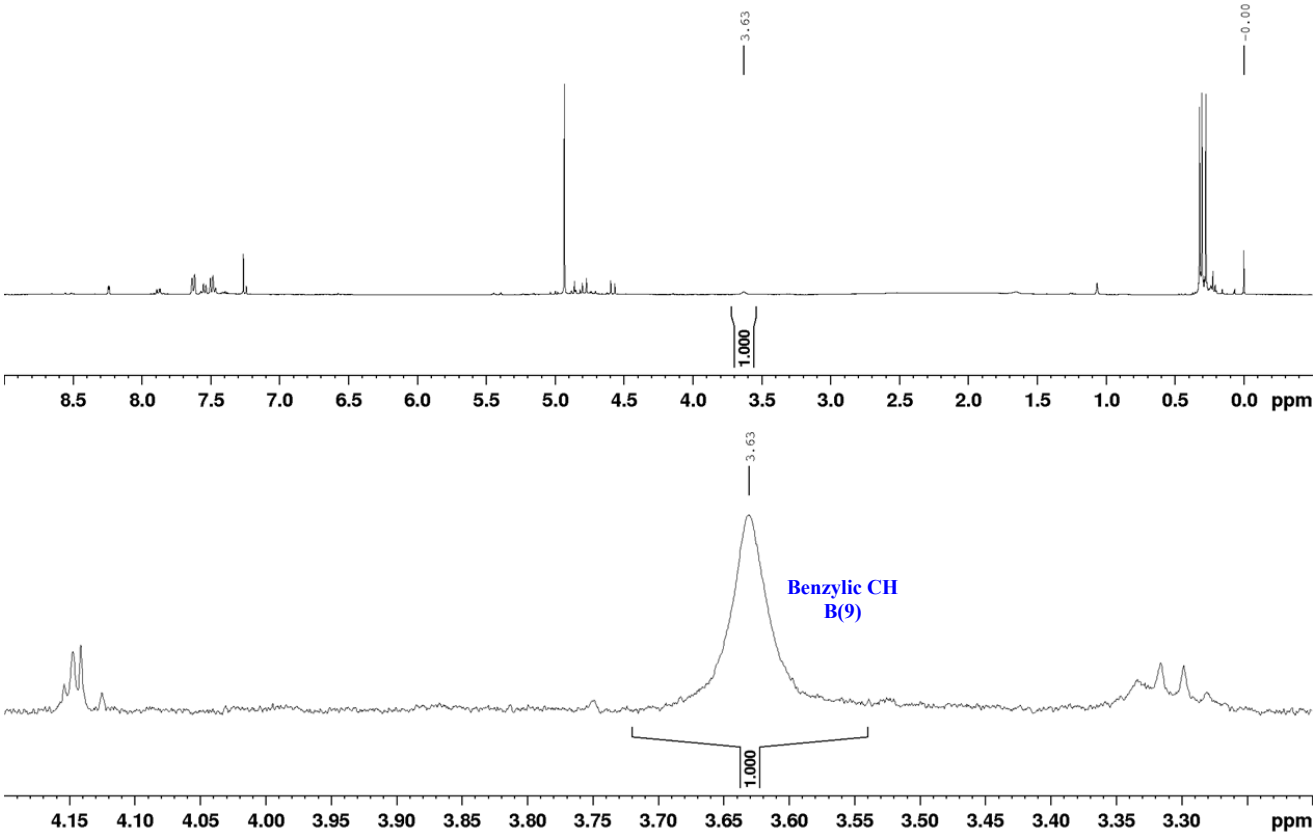


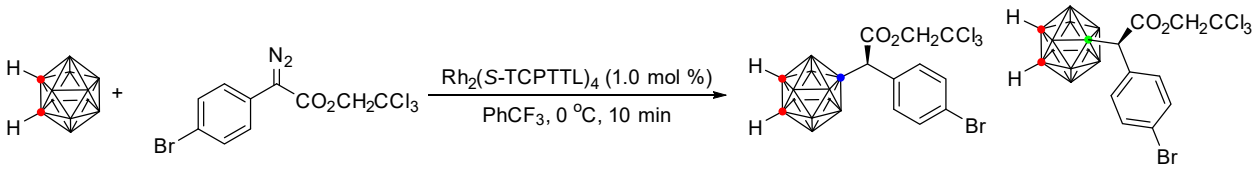

TMS
TMS
+
N2
CO2CH2CCl3
Rh2(S-TCPTTL)4 (1.0 mol %)
PhCF3, 0 °C, 10 min
CO2CH2CCl3
TMS
TMS
TMS
TMS
CO2CH2CCl3
1b
2x
3bx-B(9)
4bx-B(8)
4.03
3.82
0.00
1.000
45.739
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.03
3.82
Benzylic CH
B(9)
Benzylic CH
B(8)
1.000
45.739
4.35 4.30 4.25 4.20 4.15 4.10 4.05 4.00 3.95 3.90 3.85 3.80 3.75 3.70 3.65 3.60 3.55 3.50 ppm


TMS
TMS
+
N2
S
CO2CH2CCl3
Br
Rh2(S-TCPTTL)4 (1.0 mol %)
PhCF3, 0 °C, 10 min
CO2CH2CCl3
TMS
TMS
S
Br
CO2CH2CCl3
TMS
TMS
S
Br
1b
2y
3by-B(9)
4by-B(8)
4.11
3.91
0.00
1.000
87.676
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.11
3.91
Benzylic CH
B(8)
Benzylic CH
B(9)
1.000
87.676
4.45 4.40 4.35 4.30 4.25 4.20 4.15 4.10 4.05 4.00 3.95 3.90 3.85 3.80 3.75 3.70 3.65 3.60 ppm

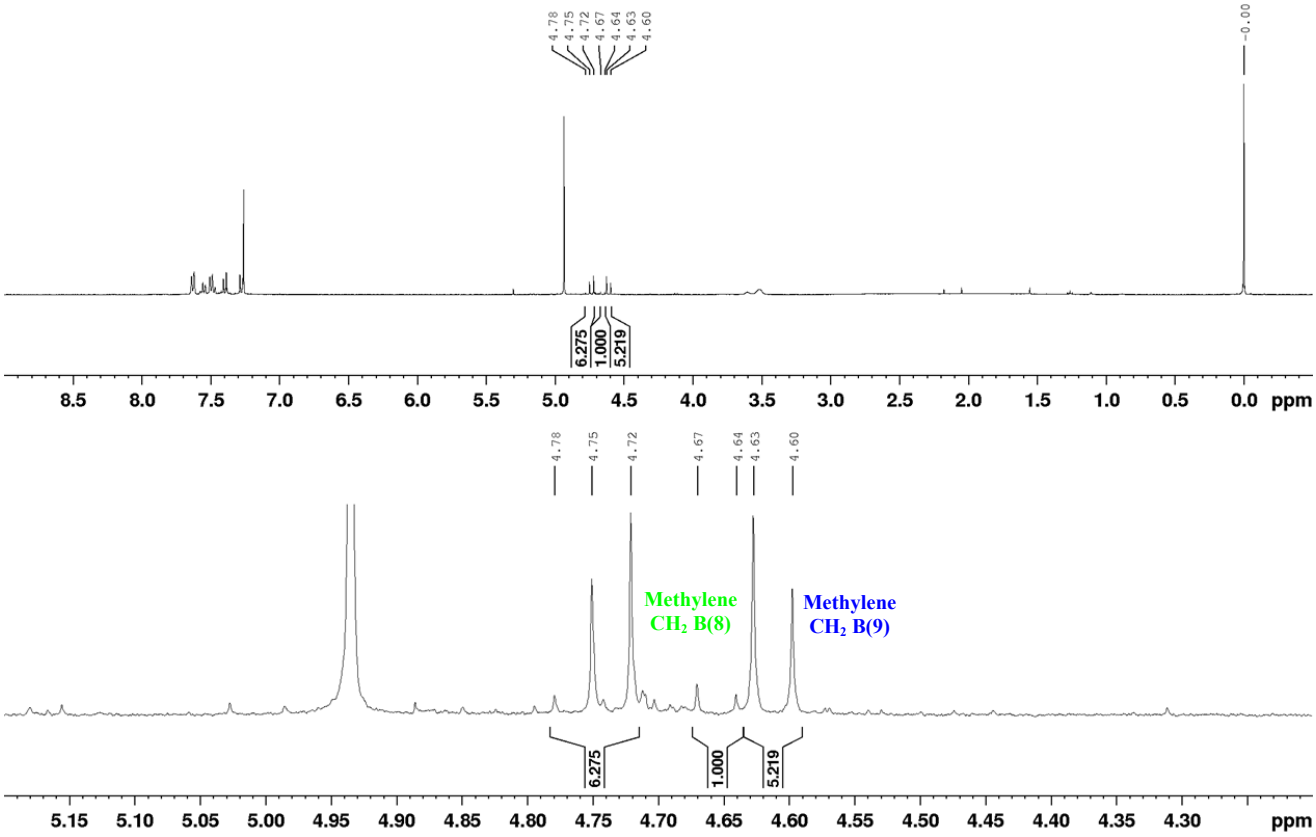


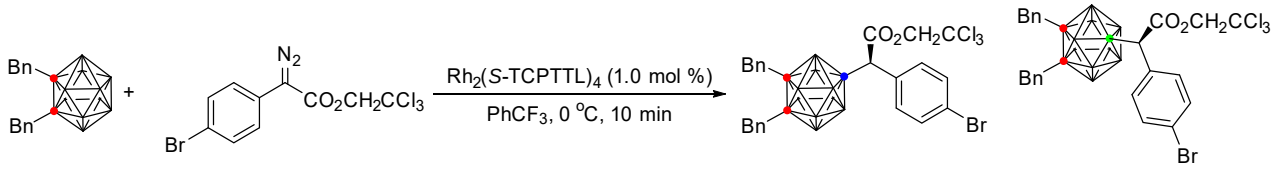
1b **2z** **3bz-B(9)** **4bz-B(8)**



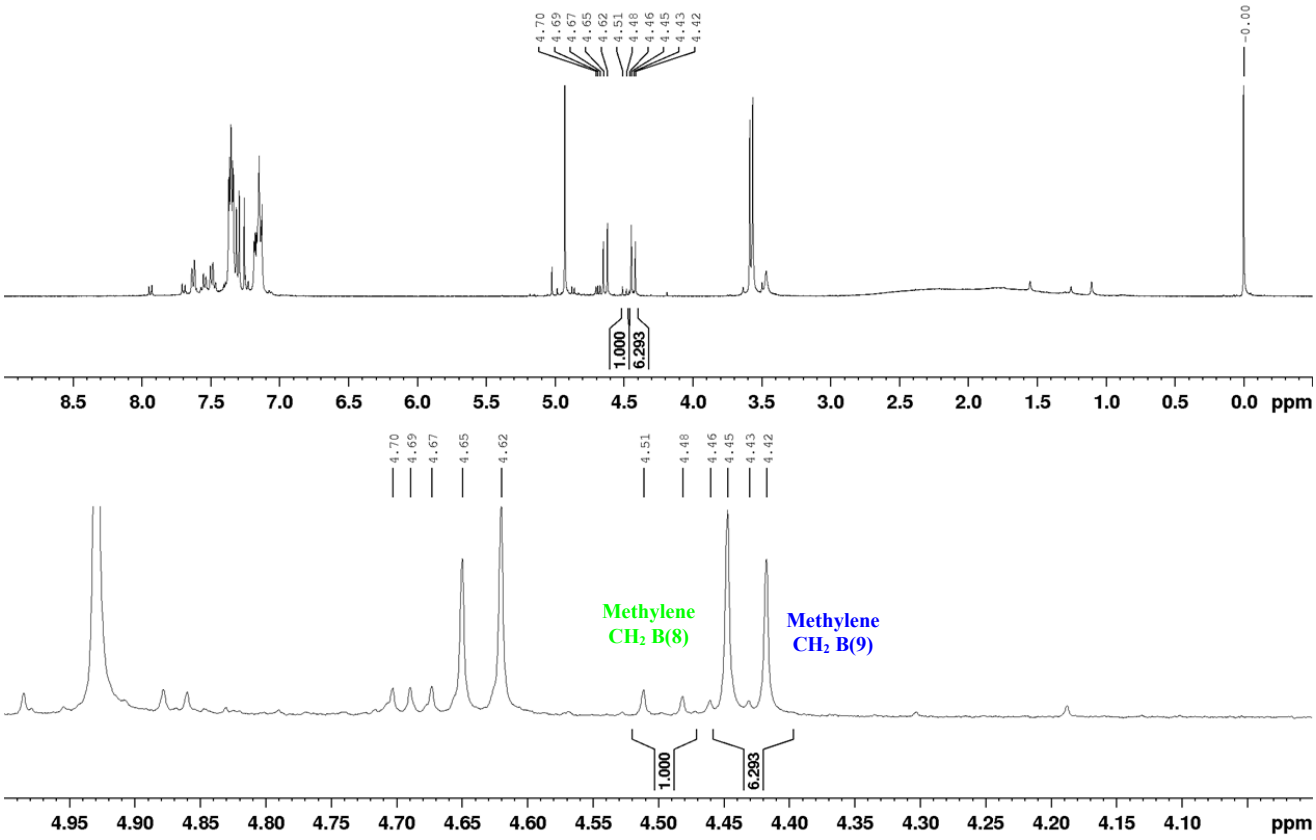


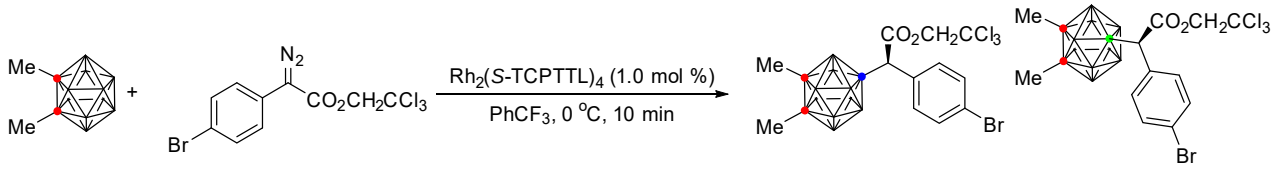
1c **2d** **3cd-B(9)** **4cd-B(8)**



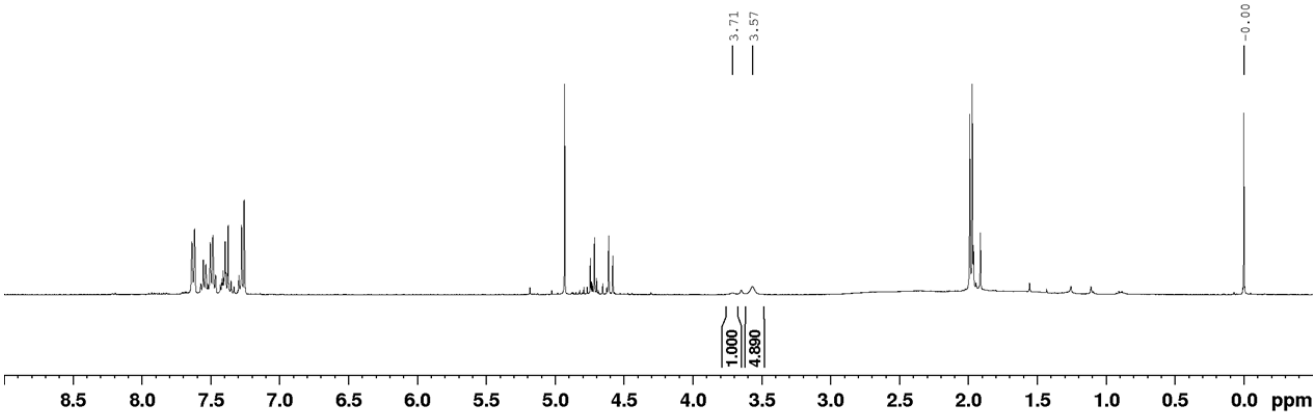


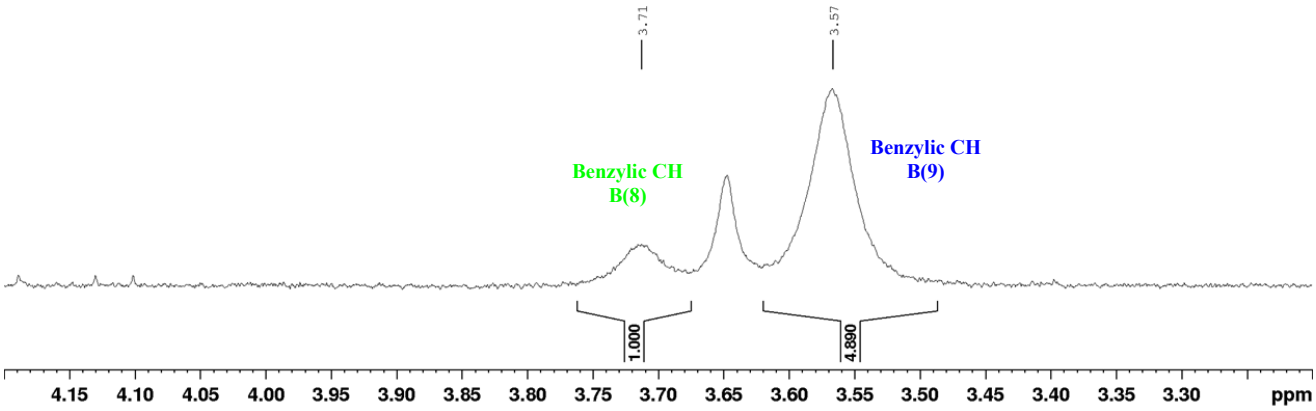
1d **2d** **3dd-B(9)** **4dd-B(8)**



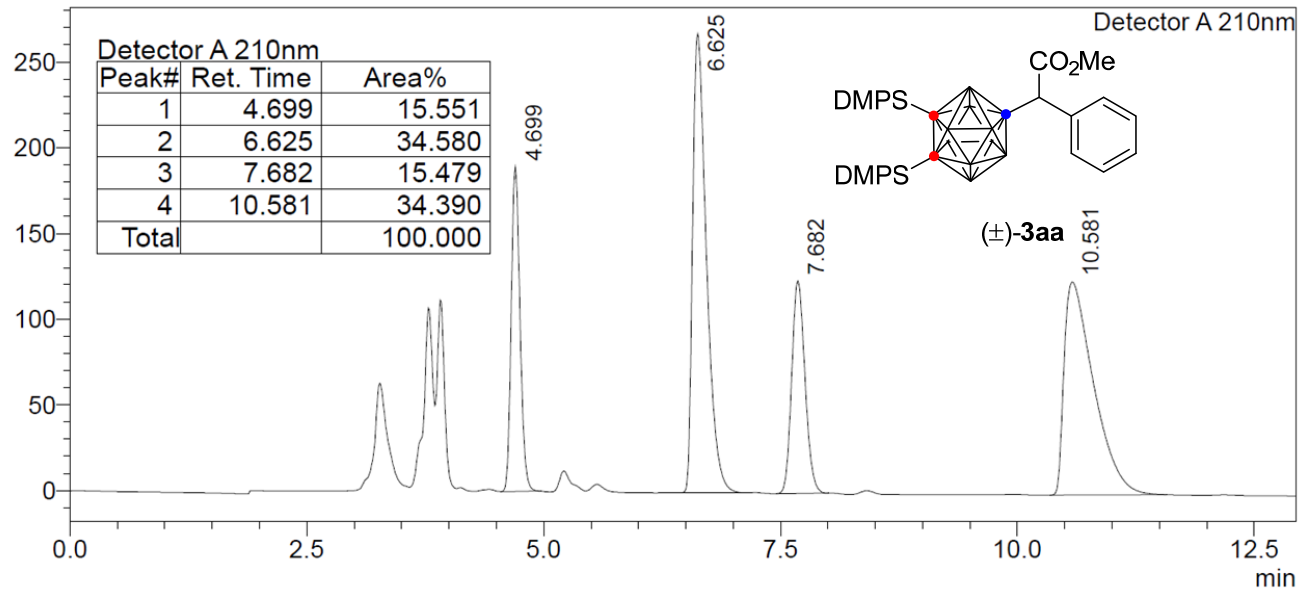


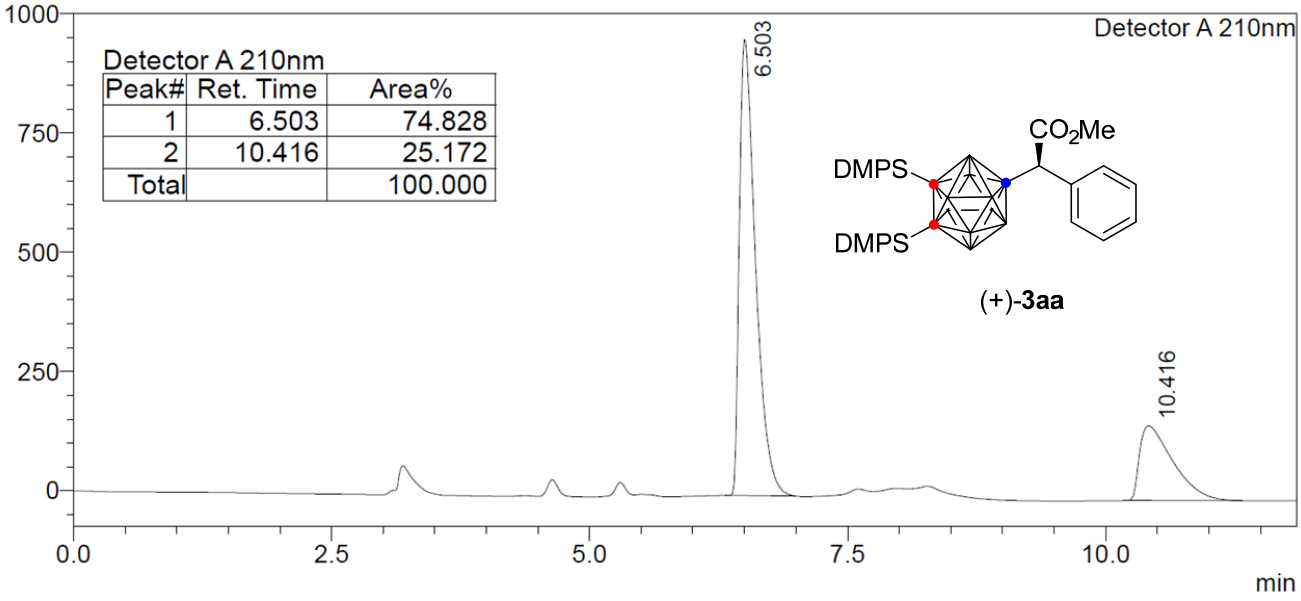
1e **2d** **3ed-B(9)** **4ed-B(8)**

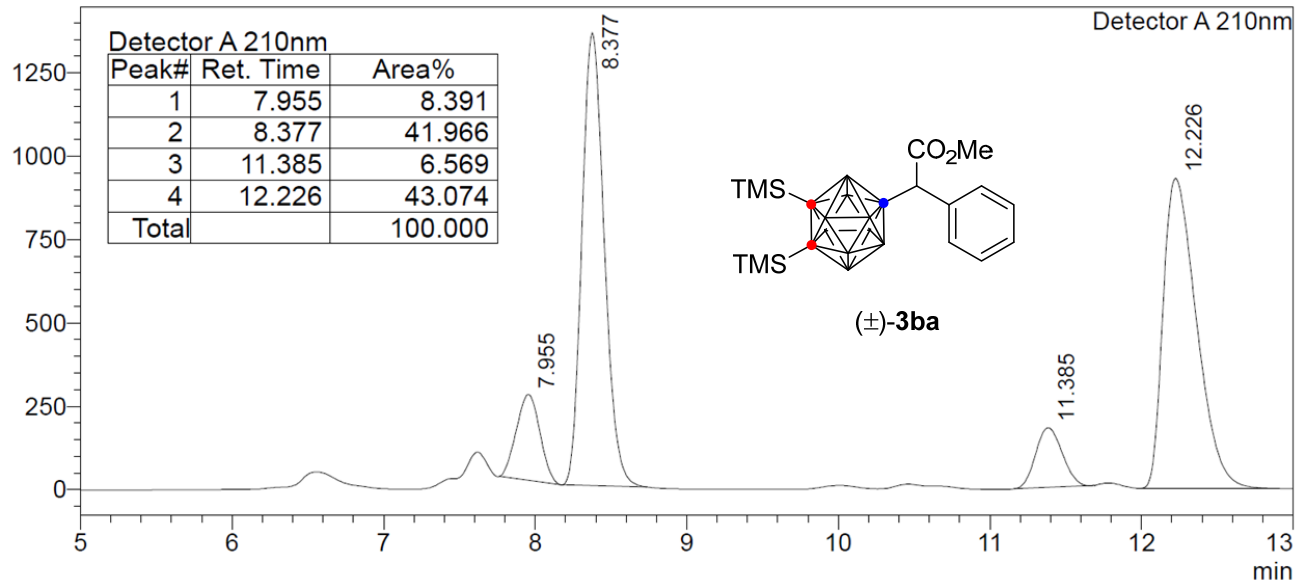


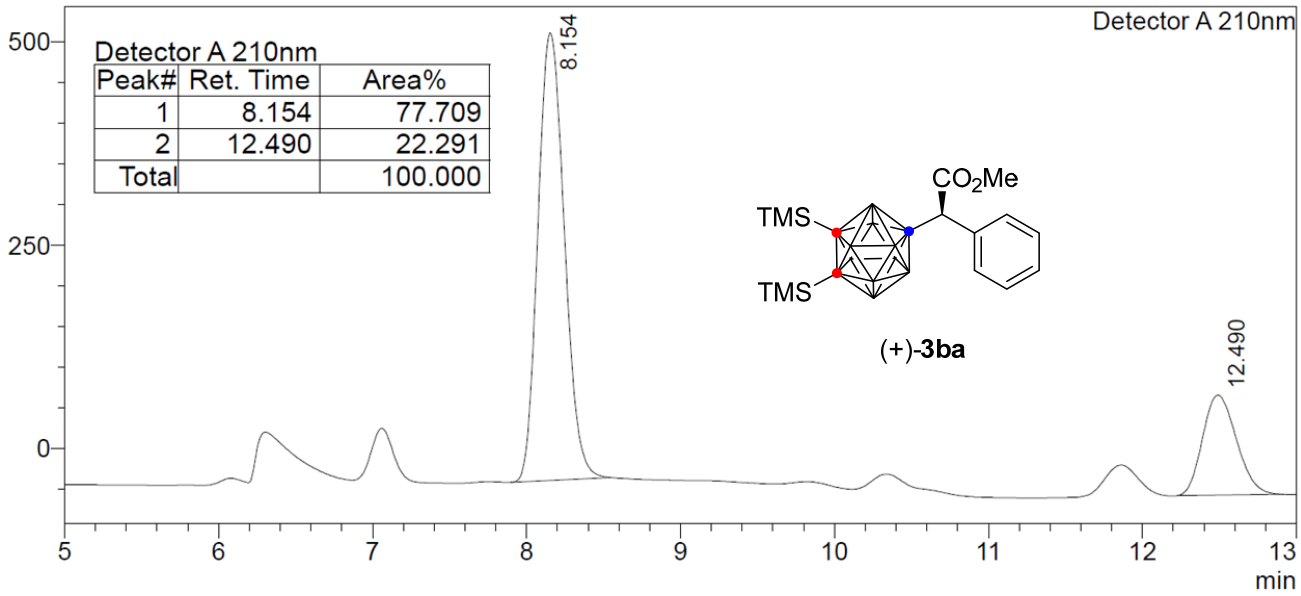


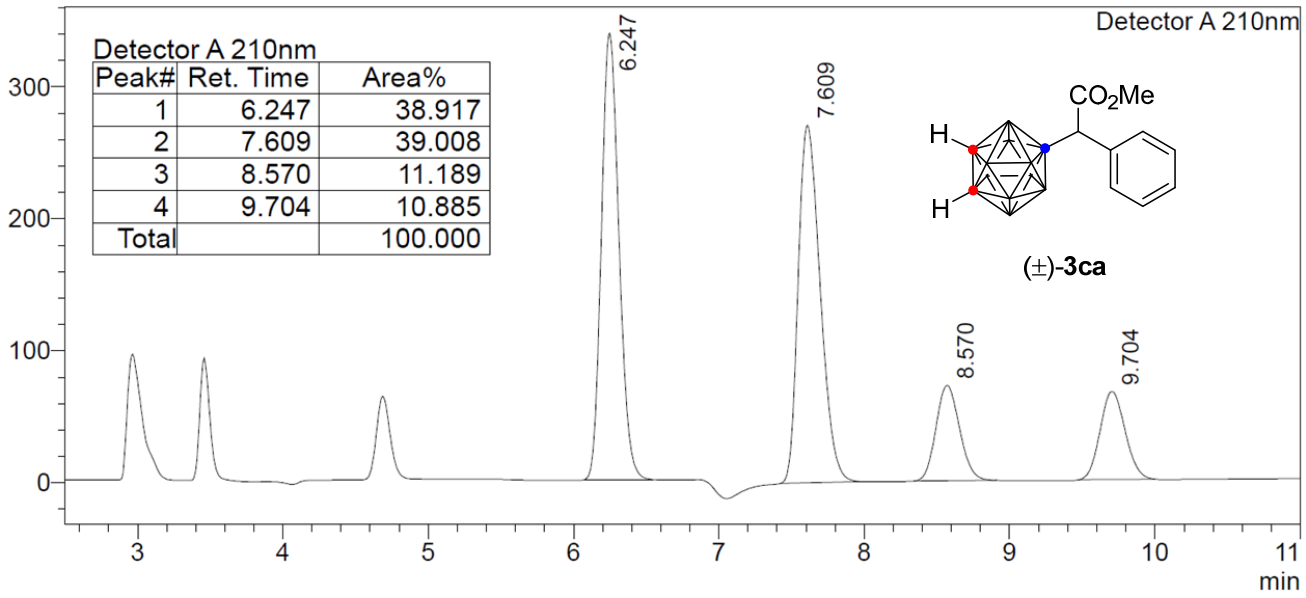
15. HPLC Spectra for Enantiomeric Excess Determination

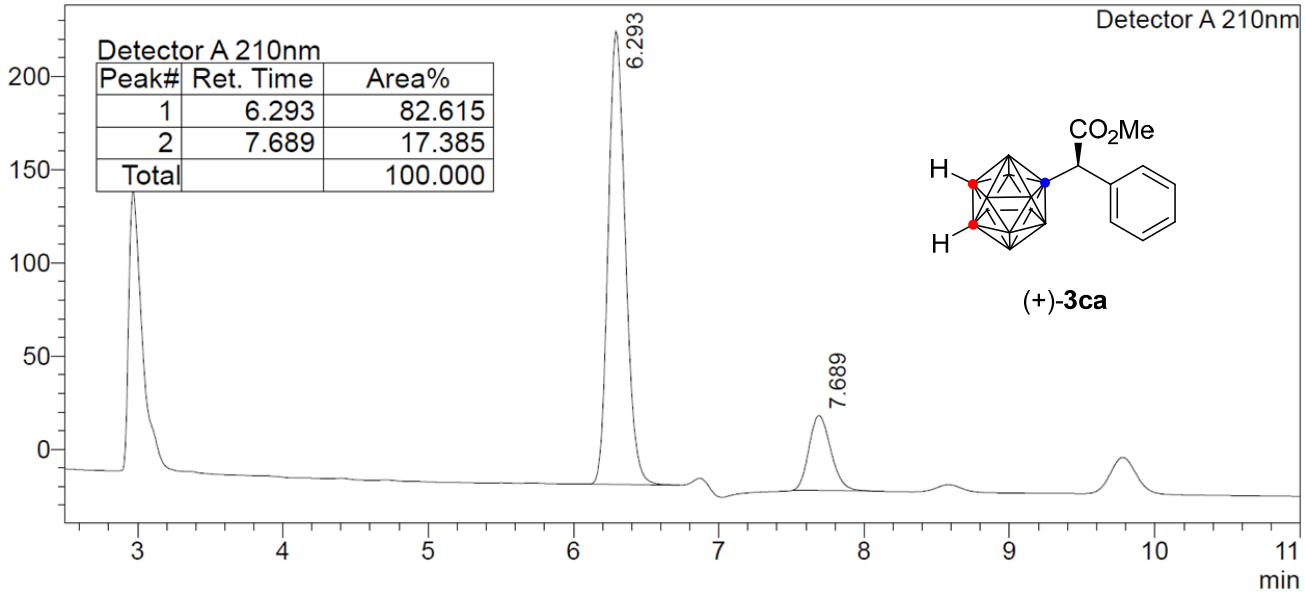


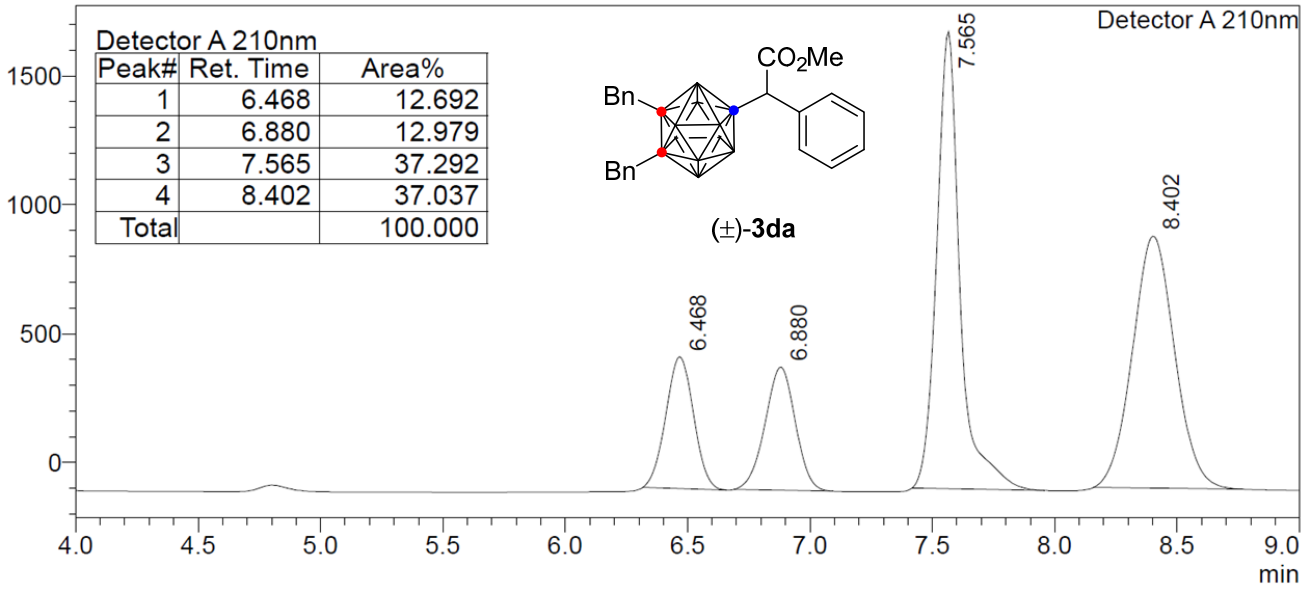


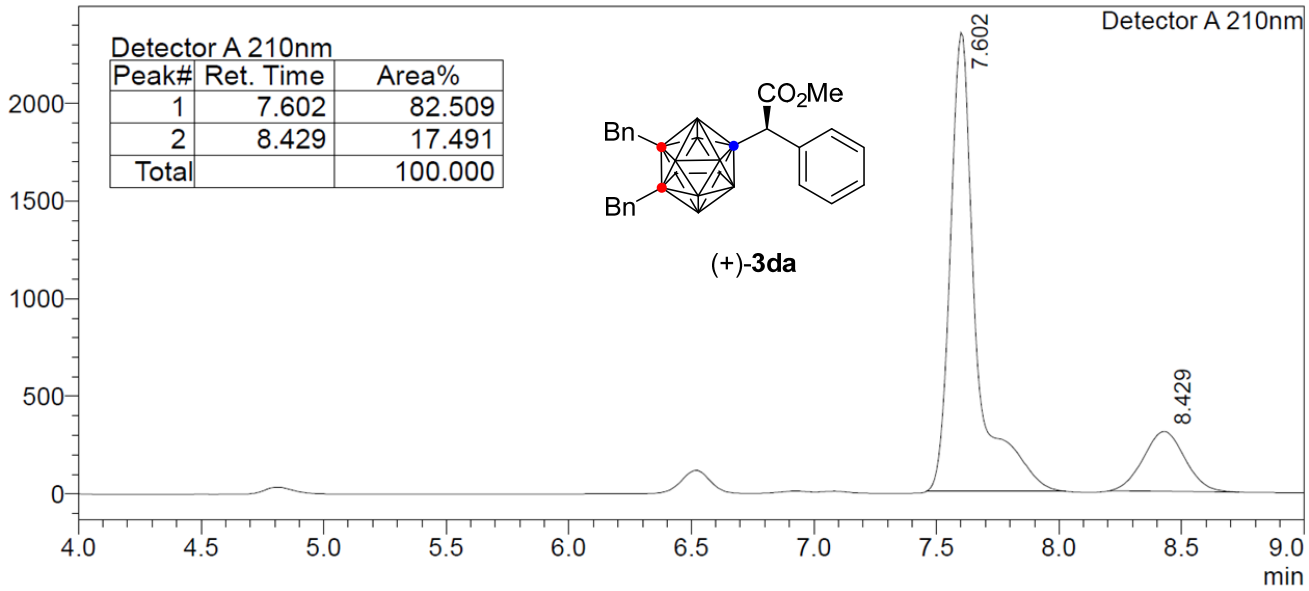

Detector A 210nm
Peak# Ret. Time Area%
1 7.955 8.391
2 8.377 41.966
3 11.385 6.569
4 12.226 43.074
Total 100.000
Detector A 210nm
8.377
7.955
11.385
12.226
1250
1000
750
500
250
0
5
6
7
8
9
10
11
12
13
min
TMS
TMS
CO2Me
(±)-3ba

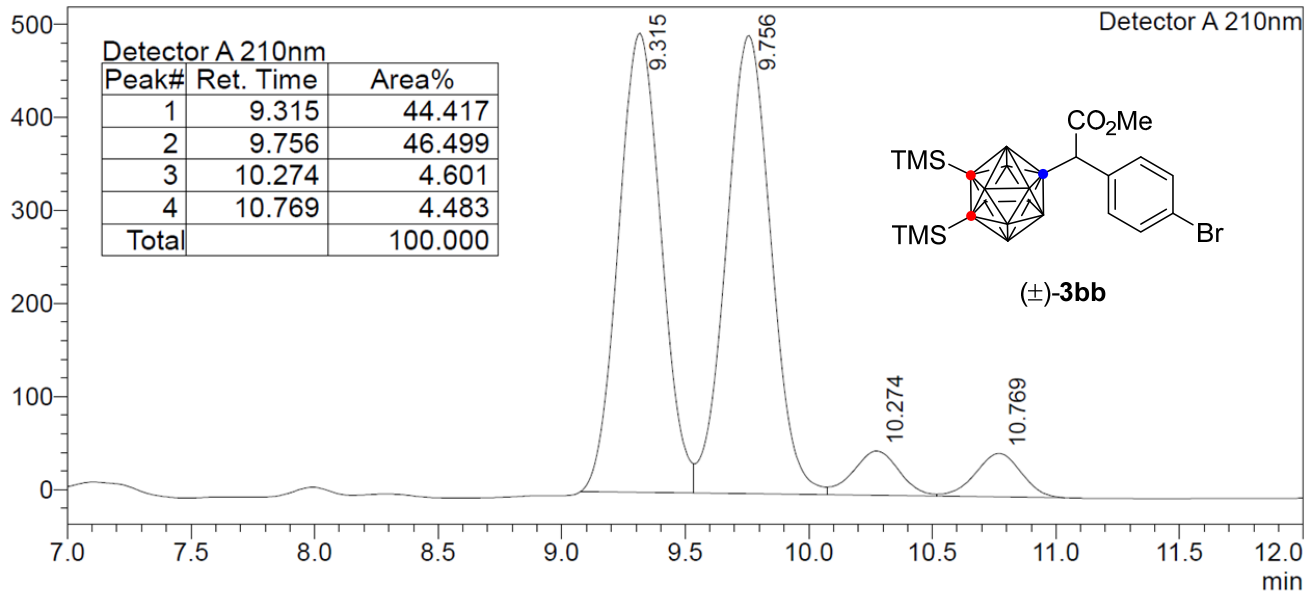

Detector A 210nm
Peak# Ret. Time Area%
1 8.154 77.709
2 12.490 22.291
Total 100.000
Detector A 210nm
8.154
12.490
500
250
0
5
6
7
8
9
10
11
12
13
min
TMS
TMS
CO2Me
(+)-3ba


Detector A 210nm
Peak# Ret. Time Area%
1 6.247 38.917
2 7.609 39.008
3 8.570 11.189
4 9.704 10.885
Total 100.000
6.247
7.609
8.570
9.704
CO2Me
H
H
(±)-3ca
min


Detector A 210nm
Peak# Ret. Time Area%
1 6.293 82.615
2 7.689 17.385
Total 100.000
6.293
7.689
CO2Me
H
H
(+)-3ca
min

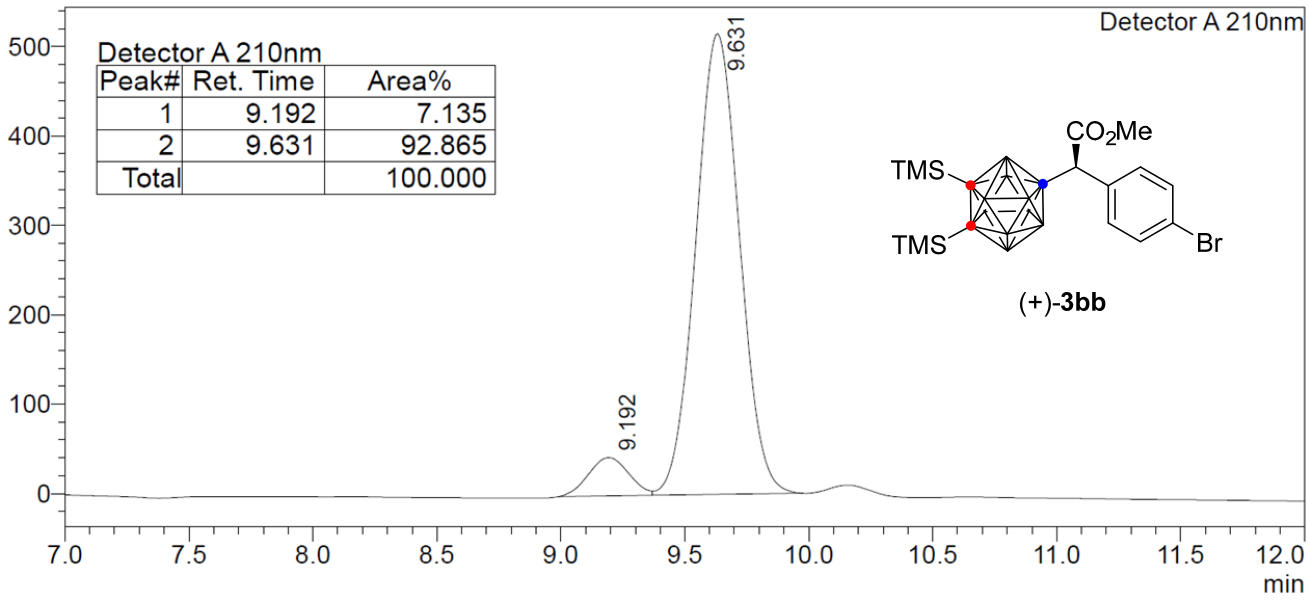

Detector A 210nm
Peak# Ret. Time Area%
1 6.468 12.692
2 6.880 12.979
3 7.565 37.292
4 8.402 37.037
Total 100.000
Bn
Bn
CO2Me
(±)-3da
6.468
6.880
7.565
8.402
1500
1000
500
0
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
min


Detector A 210nm
Peak# Ret. Time Area%
1 7.602 82.509
2 8.429 17.491
Total 100.000
Bn
Bn
CO2Me
(+)-3da
7.602
8.429
2000
1500
1000
500
0
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
min



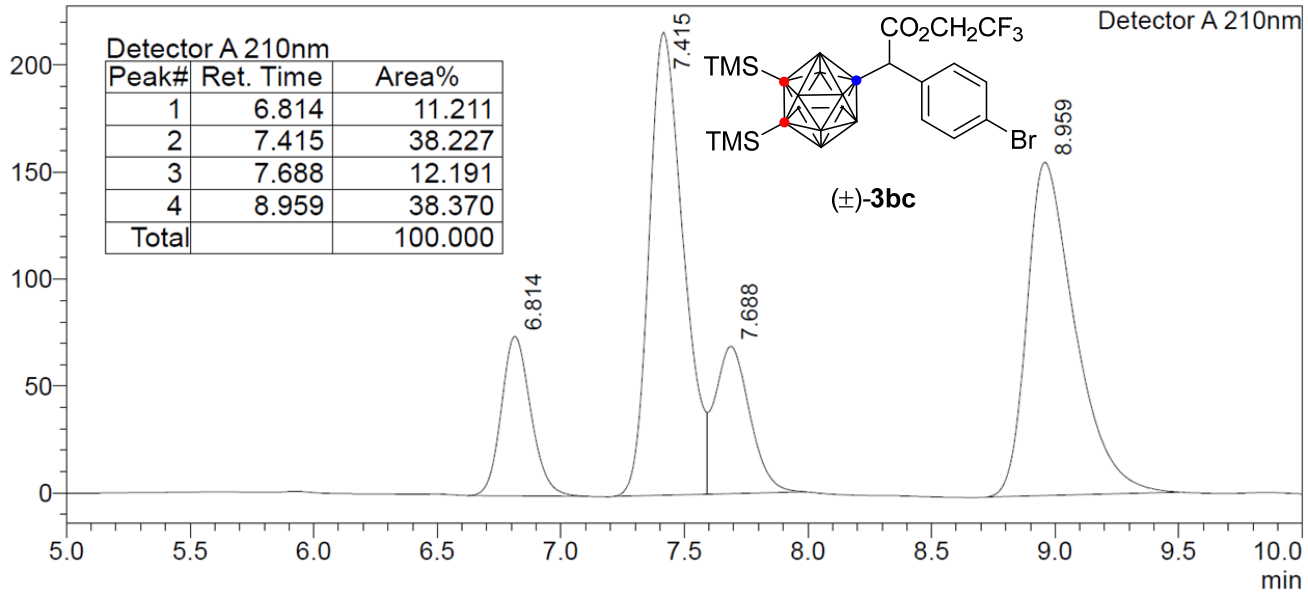
Detector A 210nm

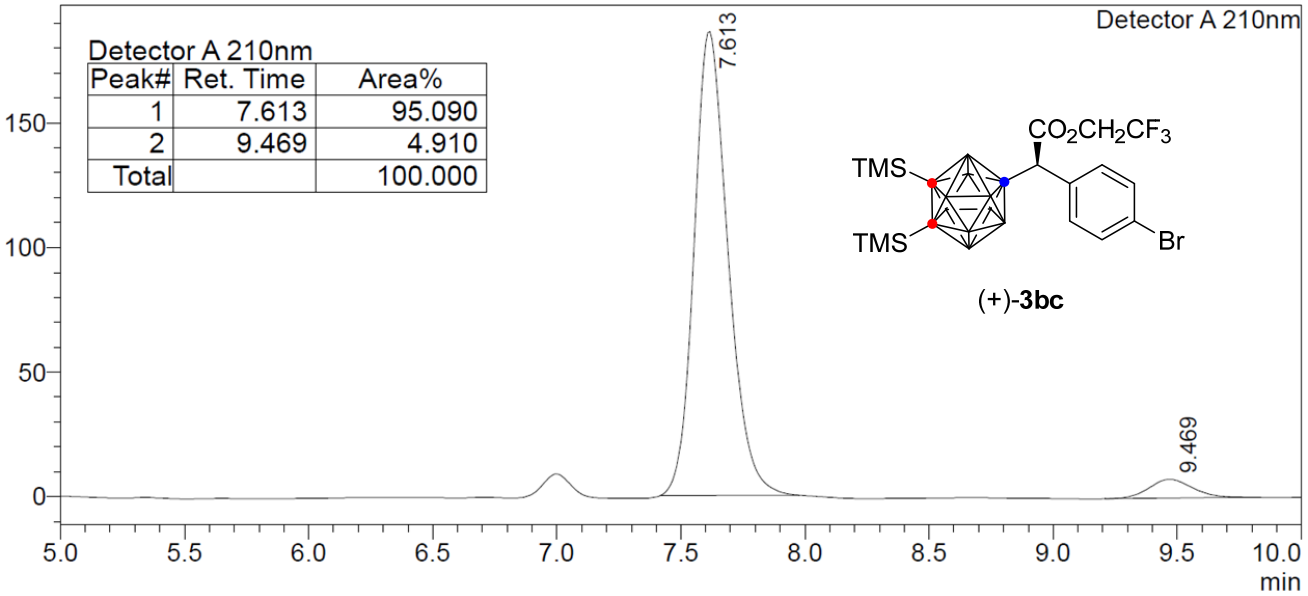
Peak#	Ret. Time	Area%
1	9.315	44.417
2	9.756	46.499
3	10.274	4.601
4	10.769	4.483
Total		100.000

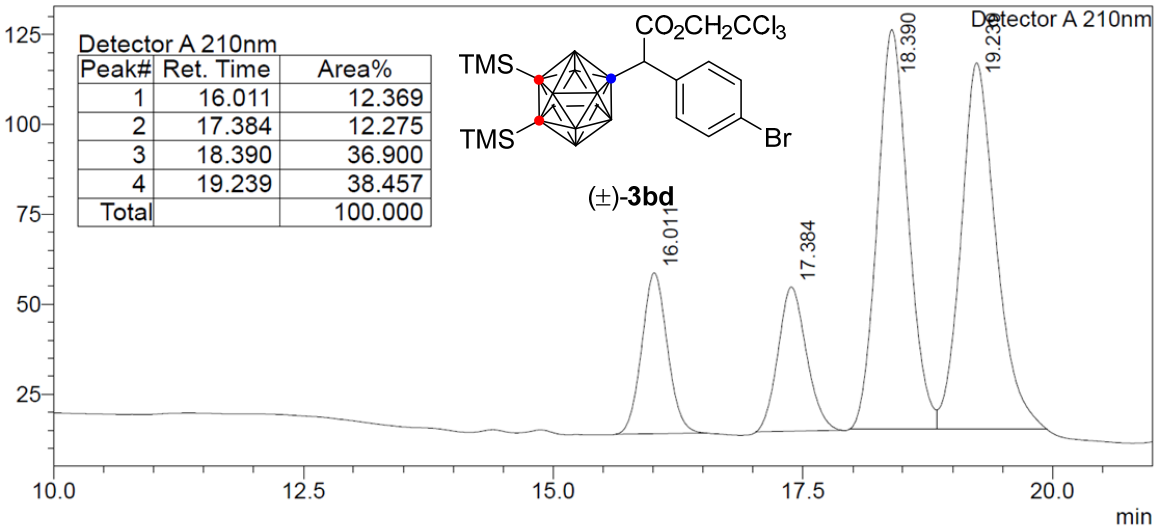


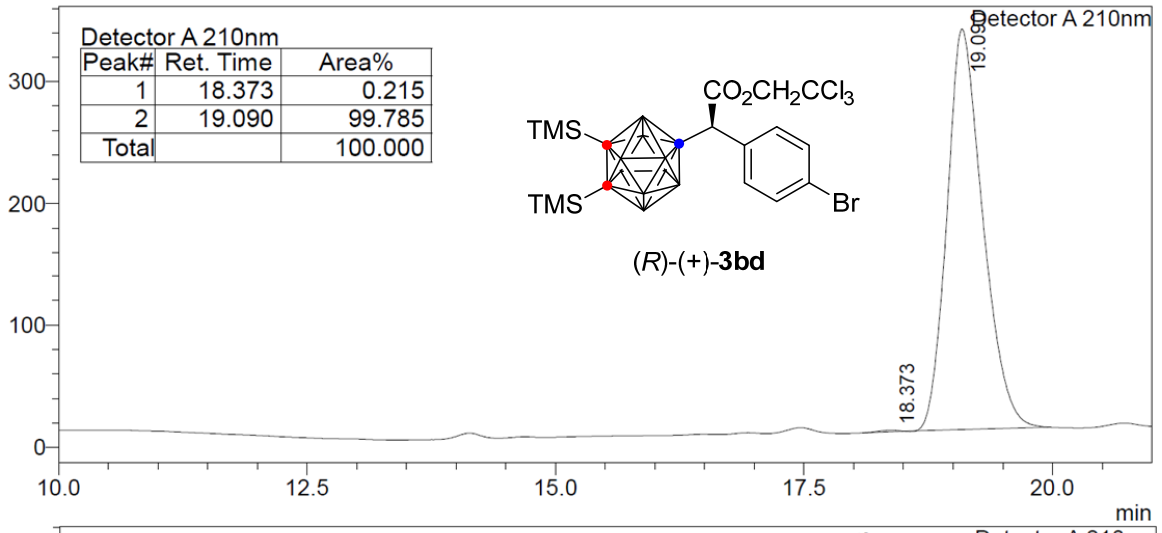
Detector A 210nm

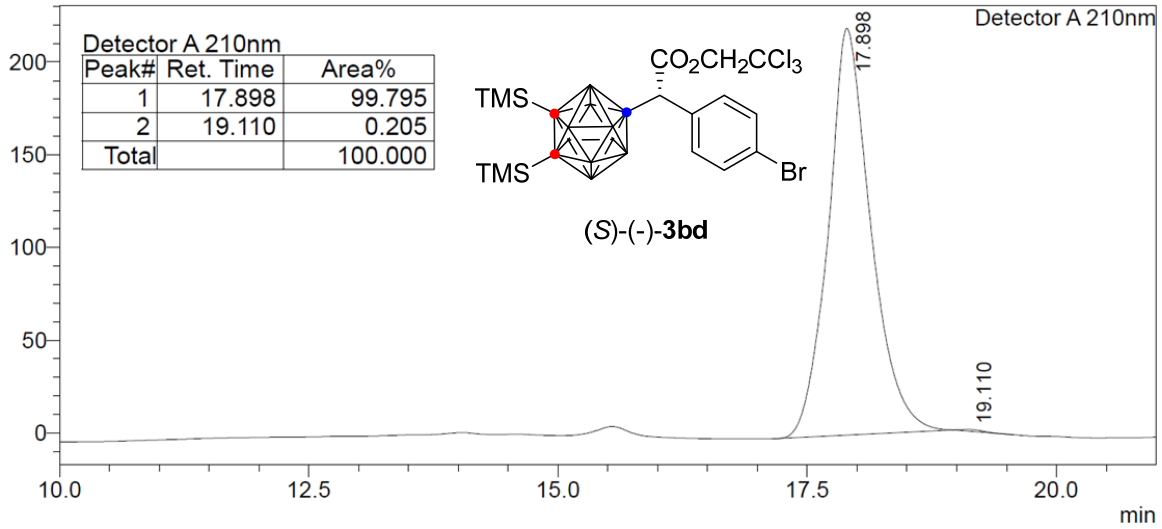
Peak#	Ret. Time	Area%
1	9.192	7.135
2	9.631	92.865
Total		100.000

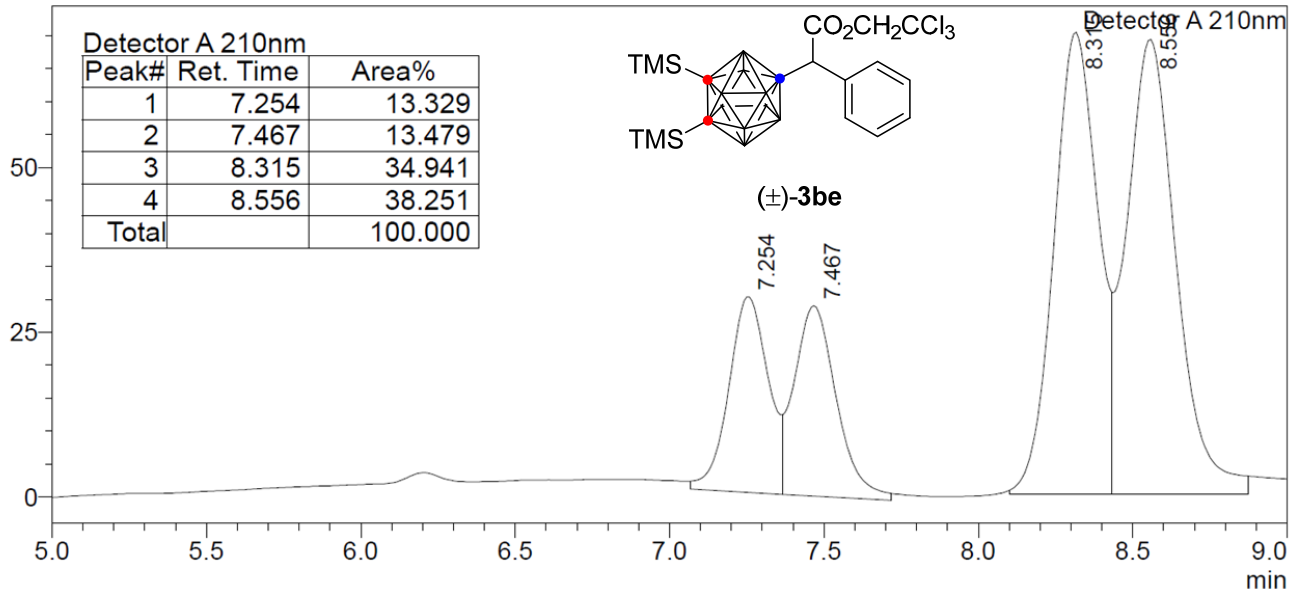

Detector A 210nm
Peak# Ret. Time Area%
1 6.814 11.211
2 7.415 38.227
3 7.688 12.191
4 8.959 38.370
Total 100.000
6.814
7.415
7.688
8.959
TMS
TMS
CO2CH2CF3
Br
(±)-3bc
min

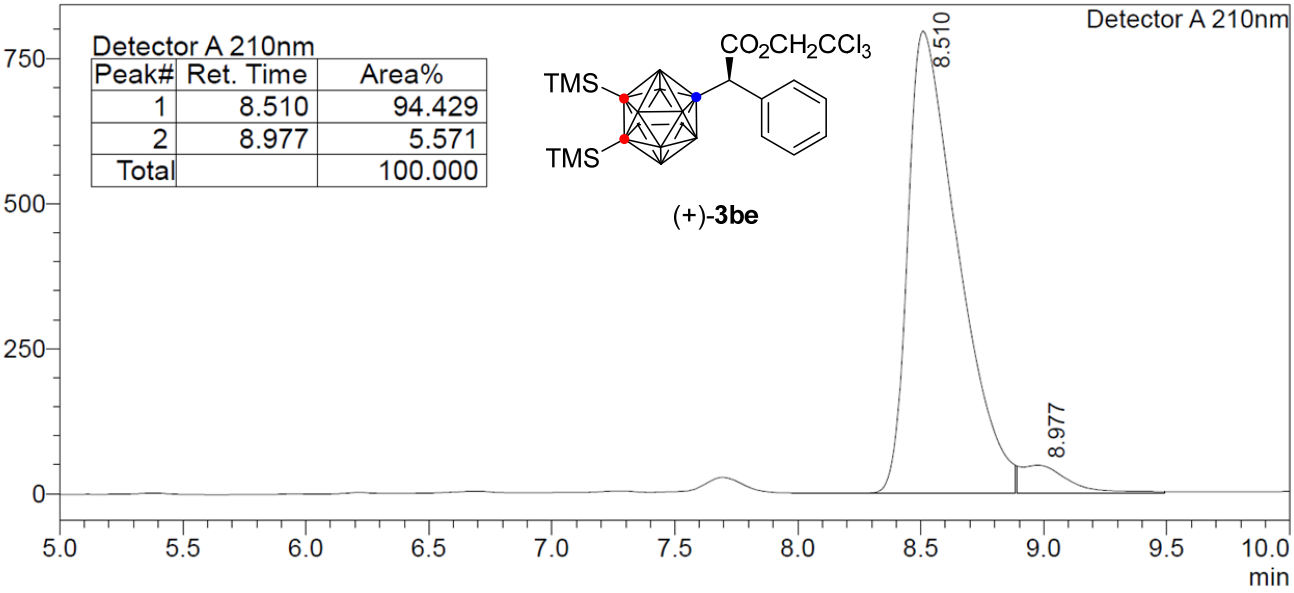

Detector A 210nm
Peak# Ret. Time Area%
1 7.613 95.090
2 9.469 4.910
Total 100.000
7.613
9.469
TMS
TMS
CO2CH2CF3
Br
(+)-3bc
min

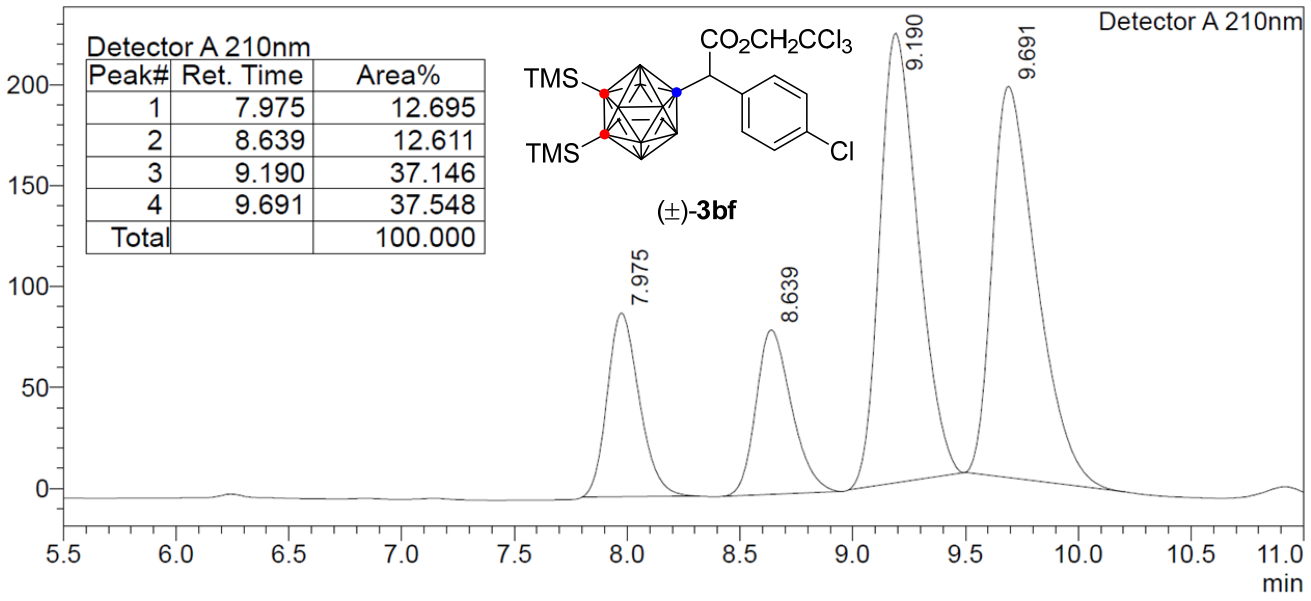

Detector A 210nm
Peak# Ret. Time Area%
1 16.011 12.369
2 17.384 12.275
3 18.390 36.900
4 19.239 38.457
Total 100.000
TMS
TMS
CO2CH2CCl3
Br
(±)-3bd
16.011
17.384
18.390
19.239
Detector A 210nm
125
100
75
50
25
10.0
12.5
15.0
17.5
20.0
min

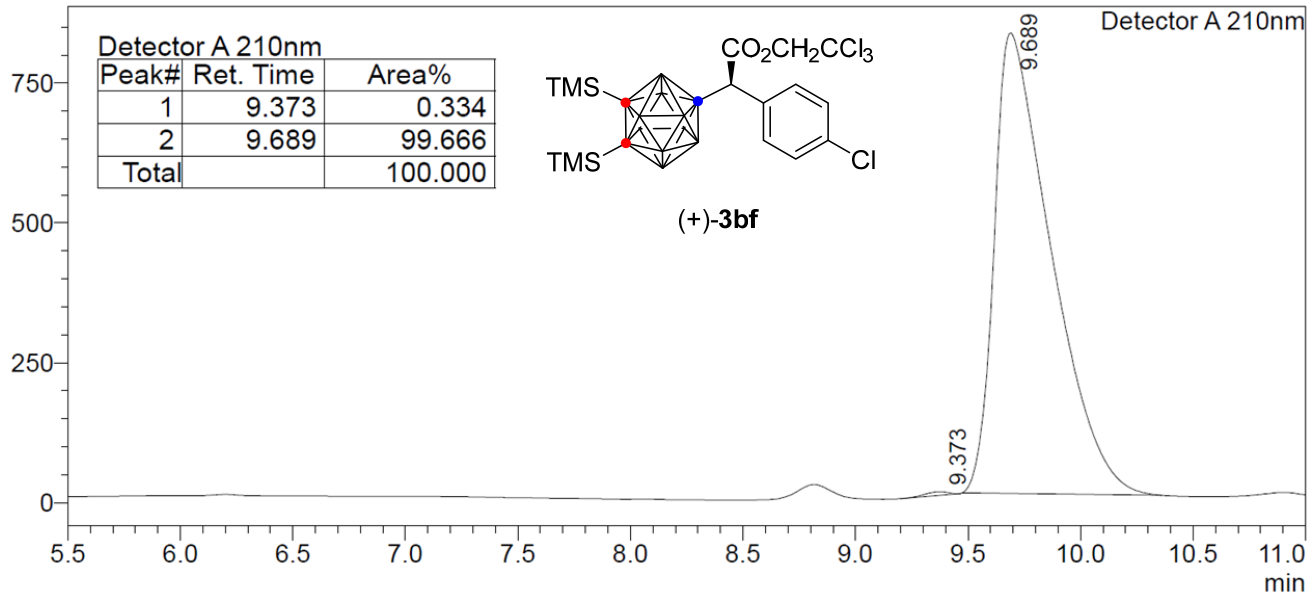

Detector A 210nm
Peak# Ret. Time Area%
1 18.373 0.215
2 19.090 99.785
Total 100.000
TMS
TMS
CO2CH2CCl3
Br
(R)-(+)-3bd
18.373
19.090
Detector A 210nm
300
200
100
0
10.0
12.5
15.0
17.5
20.0
min

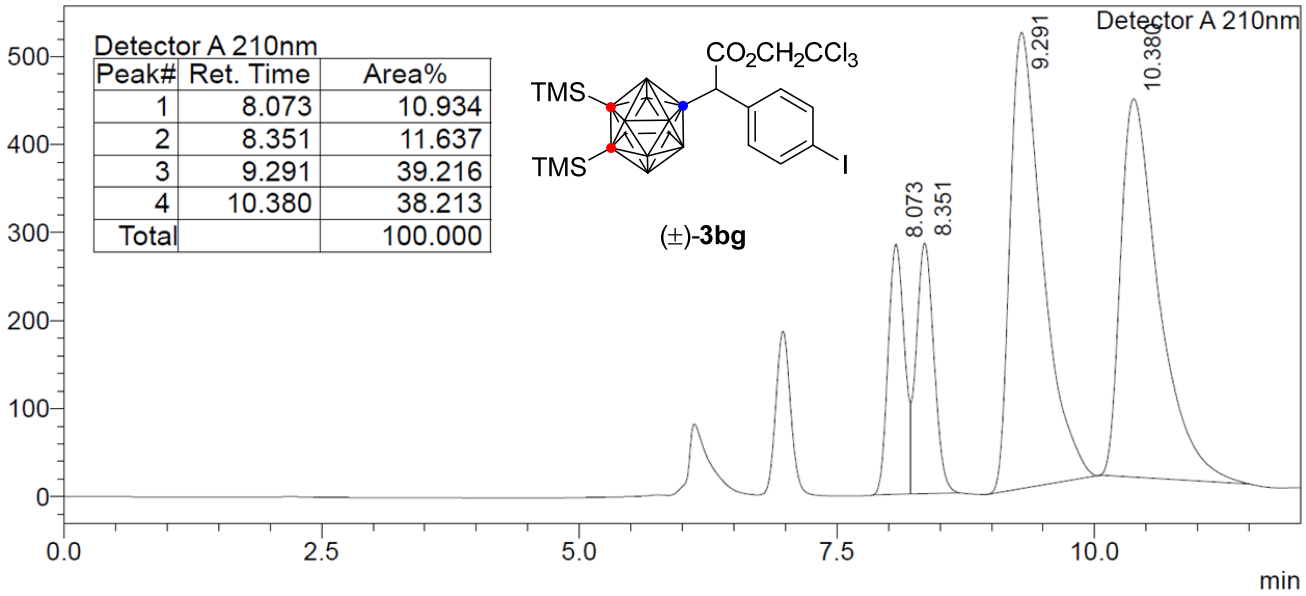

Detector A 210nm
Peak# Ret. Time Area%
1 17.898 99.795
2 19.110 0.205
Total 100.000
TMS
TMS
CO2CH2CCl3
Br
(S)-(-)-3bd
17.898
19.110
Detector A 210nm
200
150
100
50
0
10.0
12.5
15.0
17.5
20.0
min

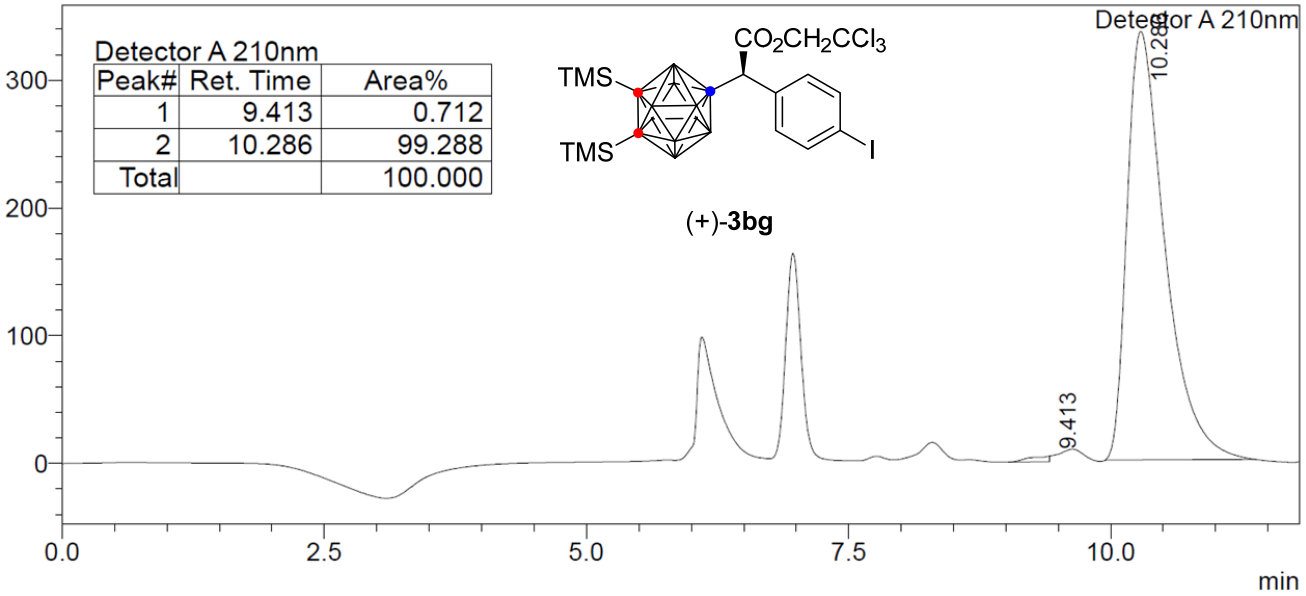

Detector A 210nm
Peak# Ret. Time Area%
1 7.254 13.329
2 7.467 13.479
3 8.315 34.941
4 8.556 38.251
Total 100.000
TMS
TMS
CO2CH2CCl3
(±)-3be
7.254
7.467
8.315
8.556
50
25
0
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
min

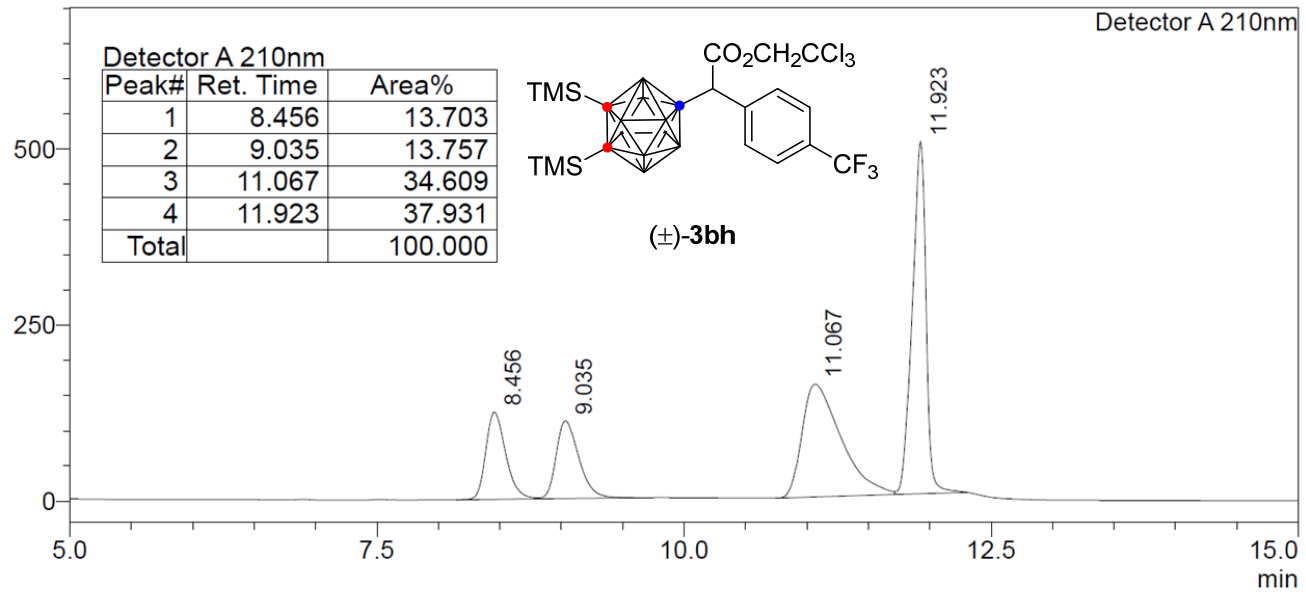

Detector A 210nm
Peak# Ret. Time Area%
1 8.510 94.429
2 8.977 5.571
Total 100.000
TMS
TMS
CO2CH2CCl3
(+)-3be
8.510
8.977
750
500
250
0
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
min

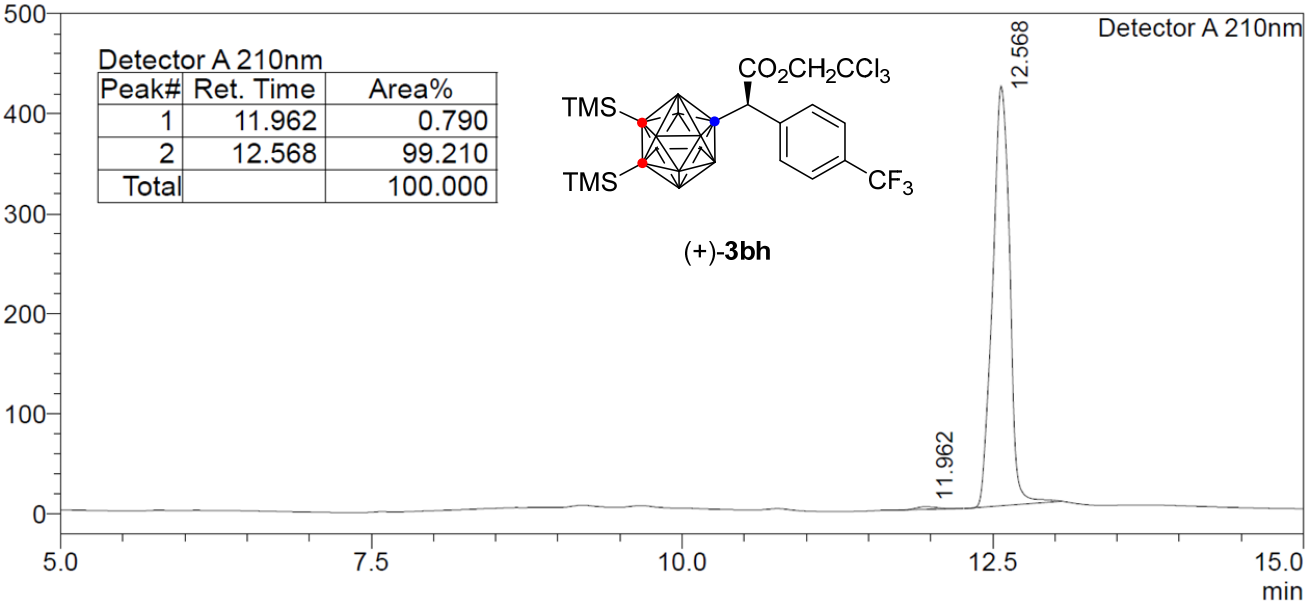

Detector A 210nm
Peak# Ret. Time Area%
1 7.975 12.695
2 8.639 12.611
3 9.190 37.146
4 9.691 37.548
Total 100.000
TMS
TMS
CO2CH2CCl3
Cl
(±)-3bf
7.975
8.639
9.190
9.691
Detector A 210nm
200
150
100
50
0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
min

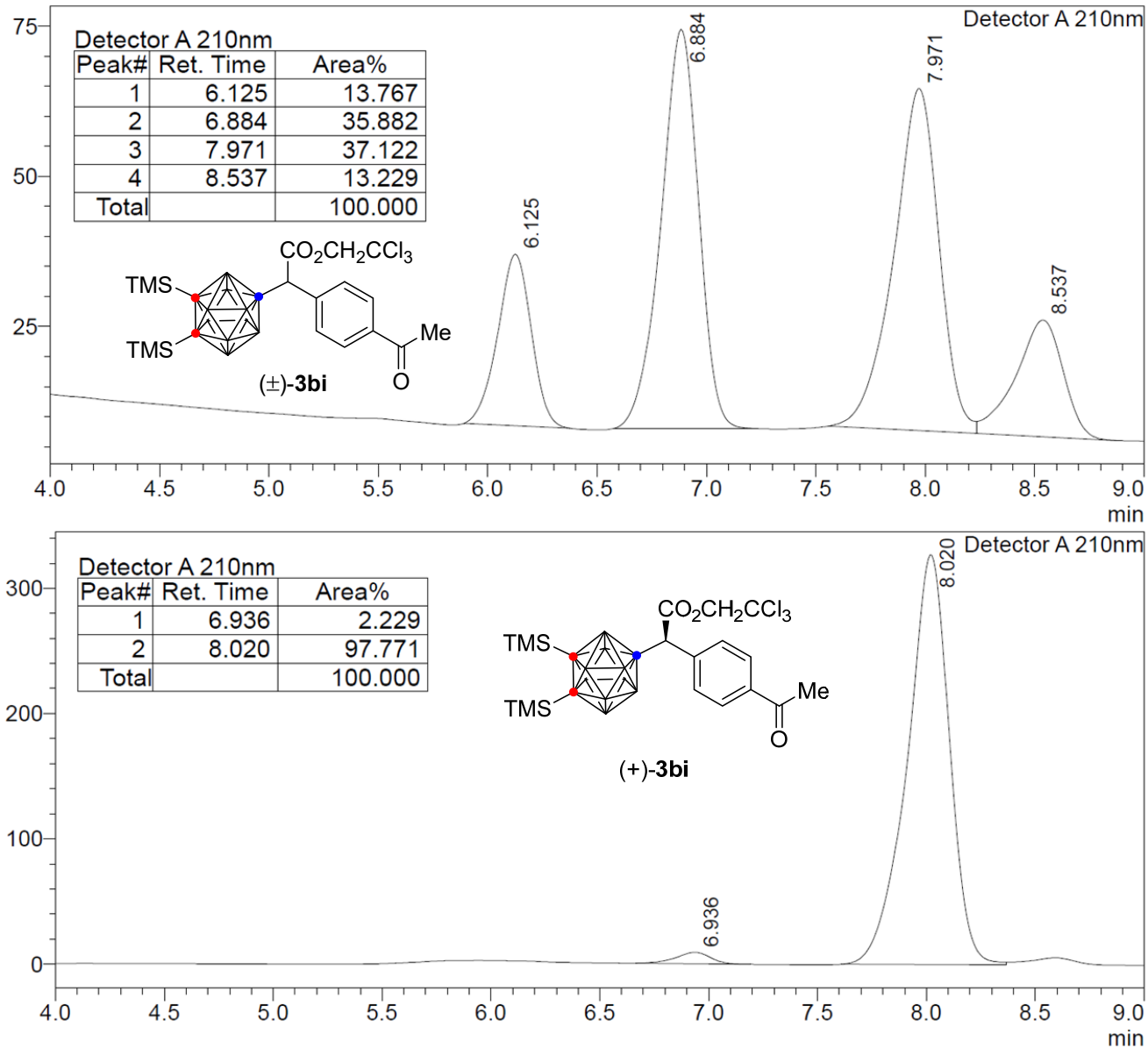

Detector A 210nm
Peak# Ret. Time Area%
1 9.373 0.334
2 9.689 99.666
Total 100.000
TMS
TMS
CO2CH2CCl3
Cl
(+)-3bf
9.373
9.689
Detector A 210nm
750
500
250
0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
min

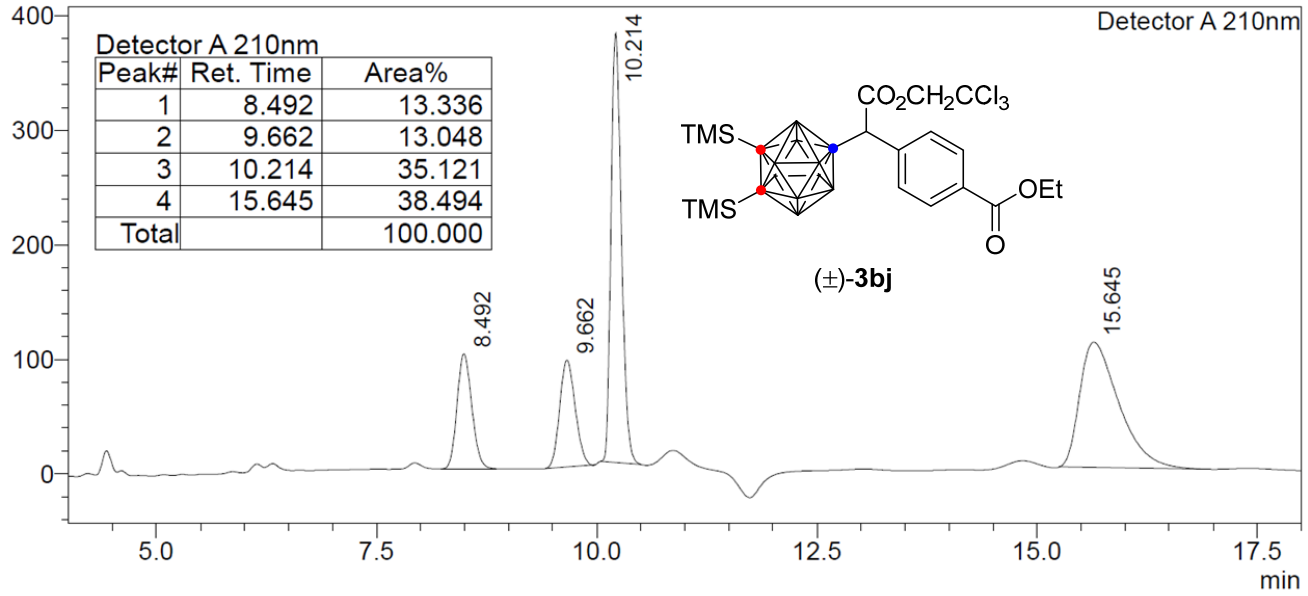

Detector A 210nm
Peak# Ret. Time Area%
1 8.073 10.934
2 8.351 11.637
3 9.291 39.216
4 10.380 38.213
Total 100.000
TMS
TMS
CO2CH2CCl3
I
(±)-3bg
8.073
8.351
9.291
10.380
Detector A 210nm
500
400
300
200
100
0
0.0
2.5
5.0
7.5
10.0
min

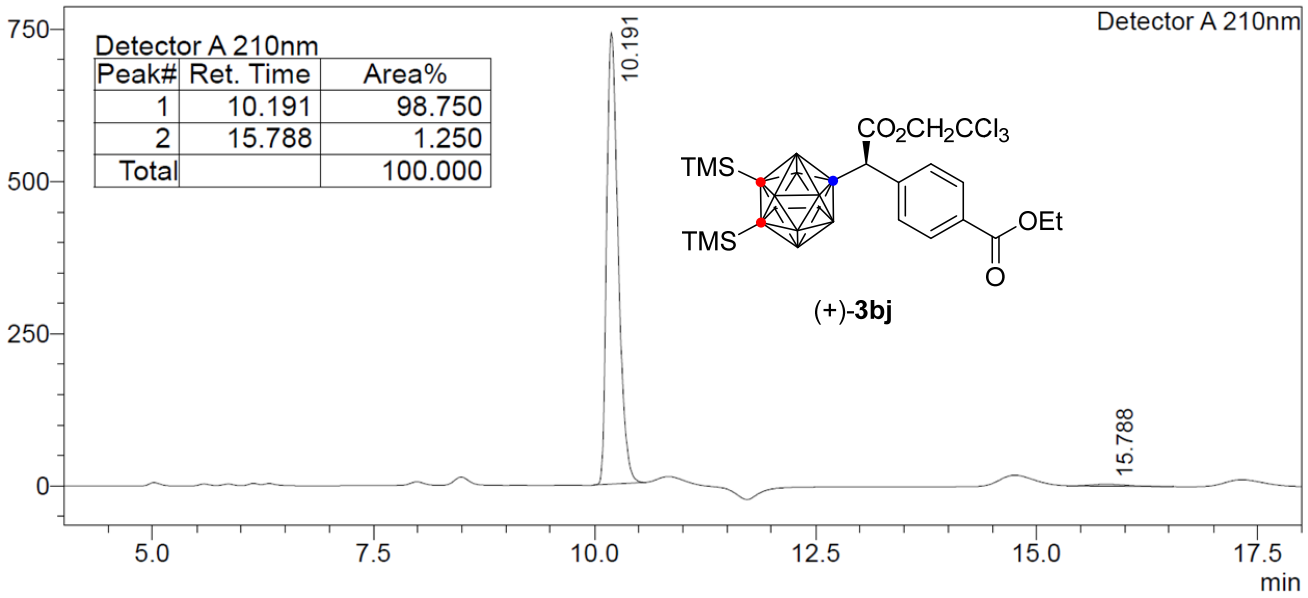

Detector A 210nm
Peak# Ret. Time Area%
1 9.413 0.712
2 10.286 99.288
Total 100.000
TMS
TMS
CO2CH2CCl3
I
(+)-3bg
9.413
10.286
Detector A 210nm
300
200
100
0
0.0
2.5
5.0
7.5
10.0
min

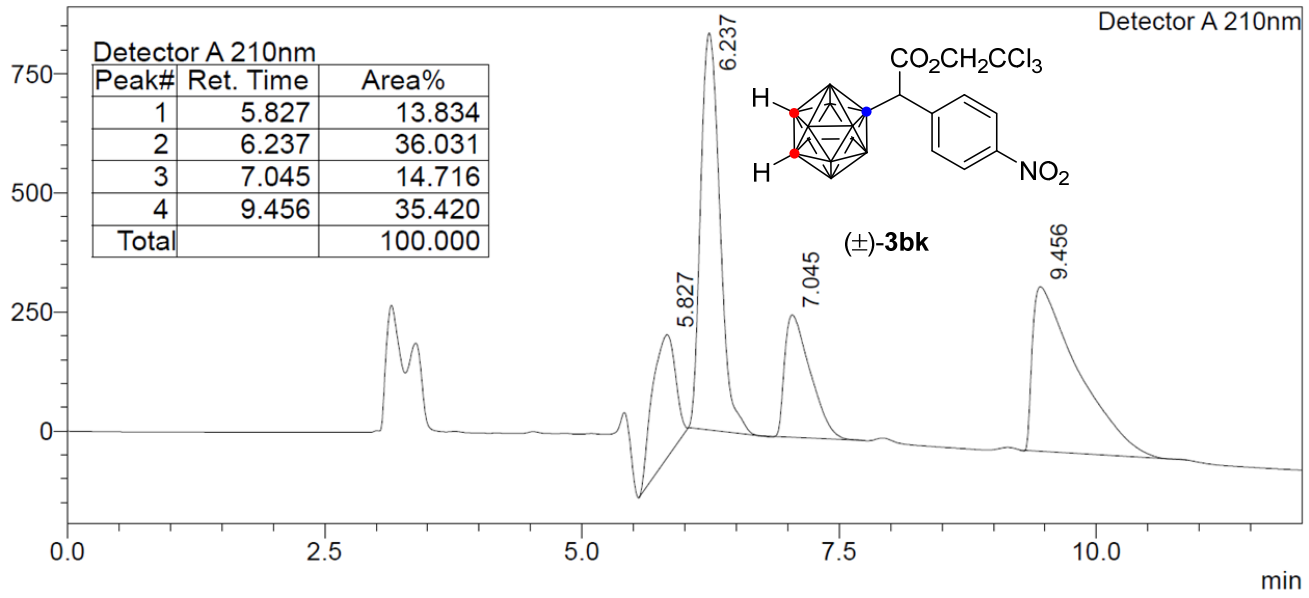

Detector A 210nm
Peak# Ret. Time Area%
1 8.456 13.703
2 9.035 13.757
3 11.067 34.609
4 11.923 37.931
Total 100.000
TMS
TMS
CO2CH2CCl3
CF3
(±)-3bh
8.456
9.035
11.067
11.923
500
250
0
5.0
7.5
10.0
12.5
15.0
min

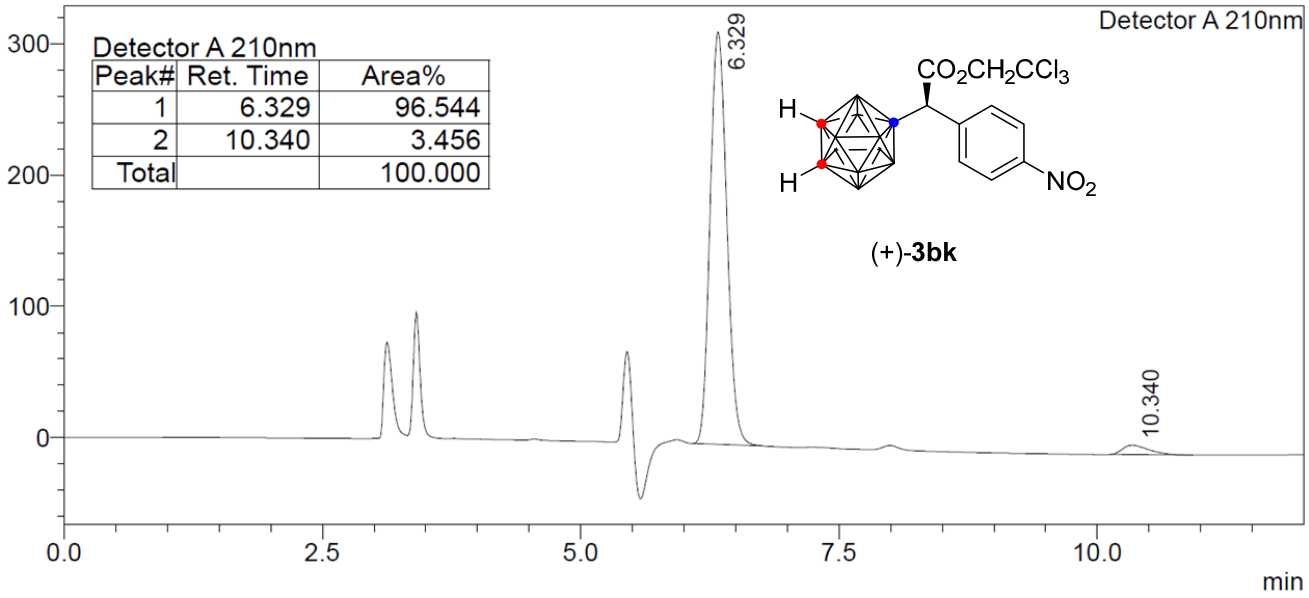

Detector A 210nm
Peak# Ret. Time Area%
1 11.962 0.790
2 12.568 99.210
Total 100.000
TMS
TMS
CO2CH2CCl3
CF3
(+)-3bh
11.962
12.568
500
400
300
200
100
0
5.0
7.5
10.0
12.5
15.0
min

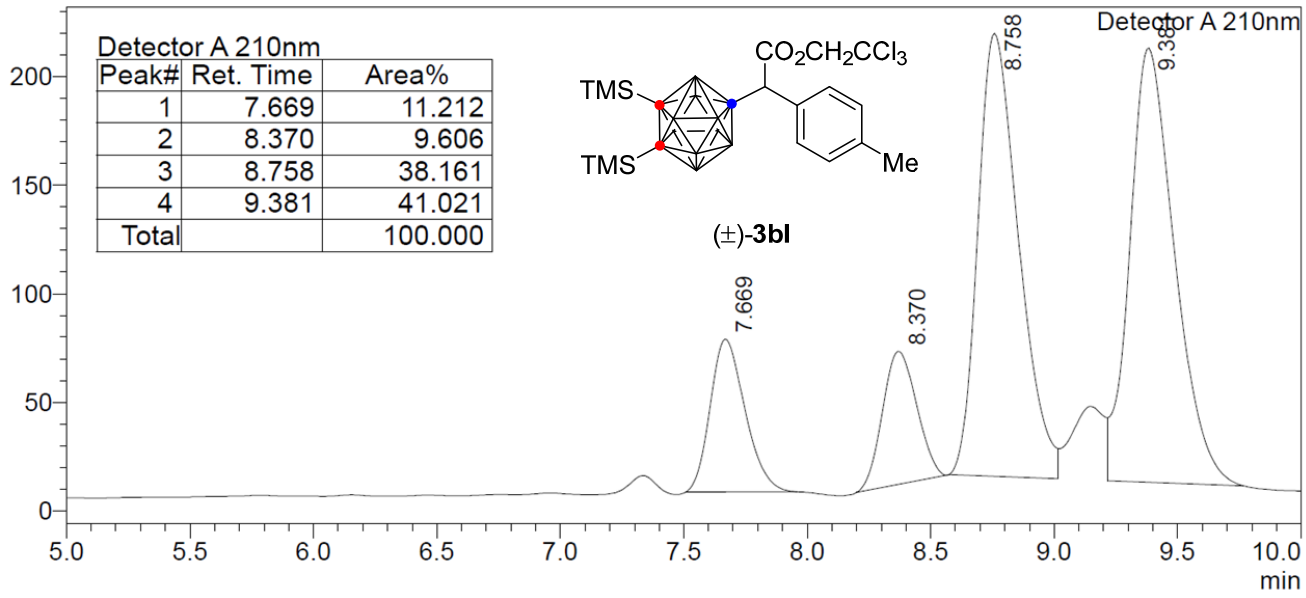

Detector A 210nm
Peak# Ret. Time Area%
1 6.125 13.767
2 6.884 35.882
3 7.971 37.122
4 8.537 13.229
Total 100.000
6.125
6.884
7.971
8.537
TMS
TMS
CO2CH2CCl3
Me
O
(±)-3bi
min
Detector A 210nm
Peak# Ret. Time Area%
1 6.936 2.229
2 8.020 97.771
Total 100.000
6.936
8.020
TMS
TMS
CO2CH2CCl3
Me
O
(+)-3bi
min

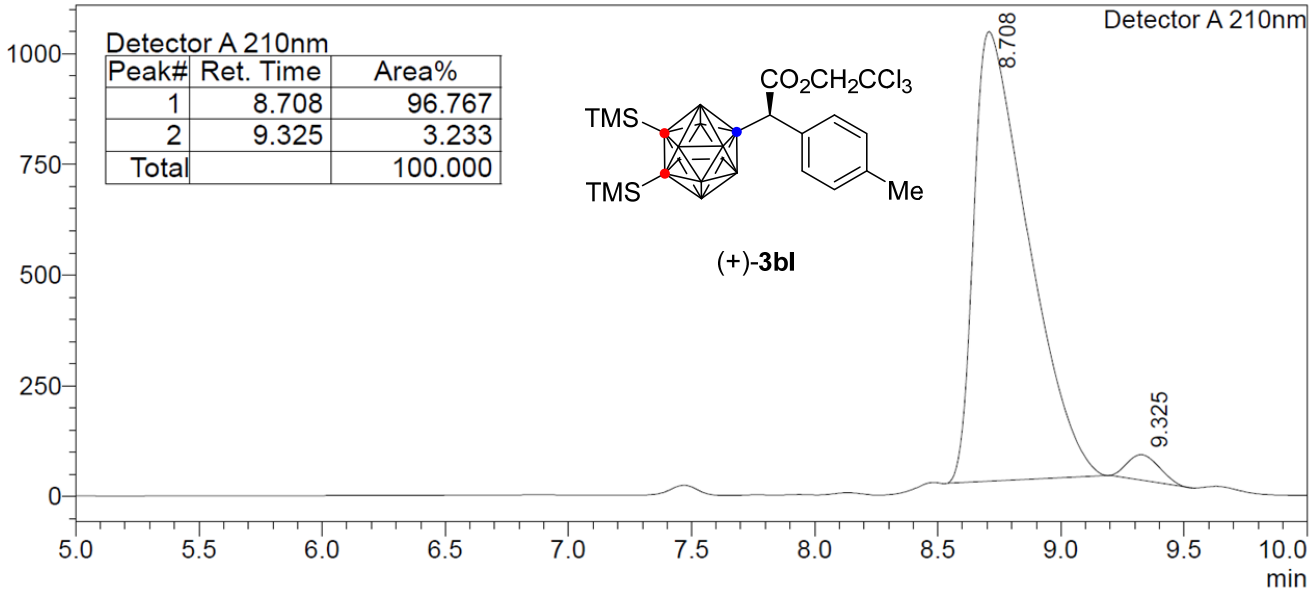

Detector A 210nm
Peak# Ret. Time Area%
1 8.492 13.336
2 9.662 13.048
3 10.214 35.121
4 15.645 38.494
Total 100.000
8.492
9.662
10.214
15.645
TMS
TMS
CO2CH2CCl3
OEt
O
(±)-3bj
min

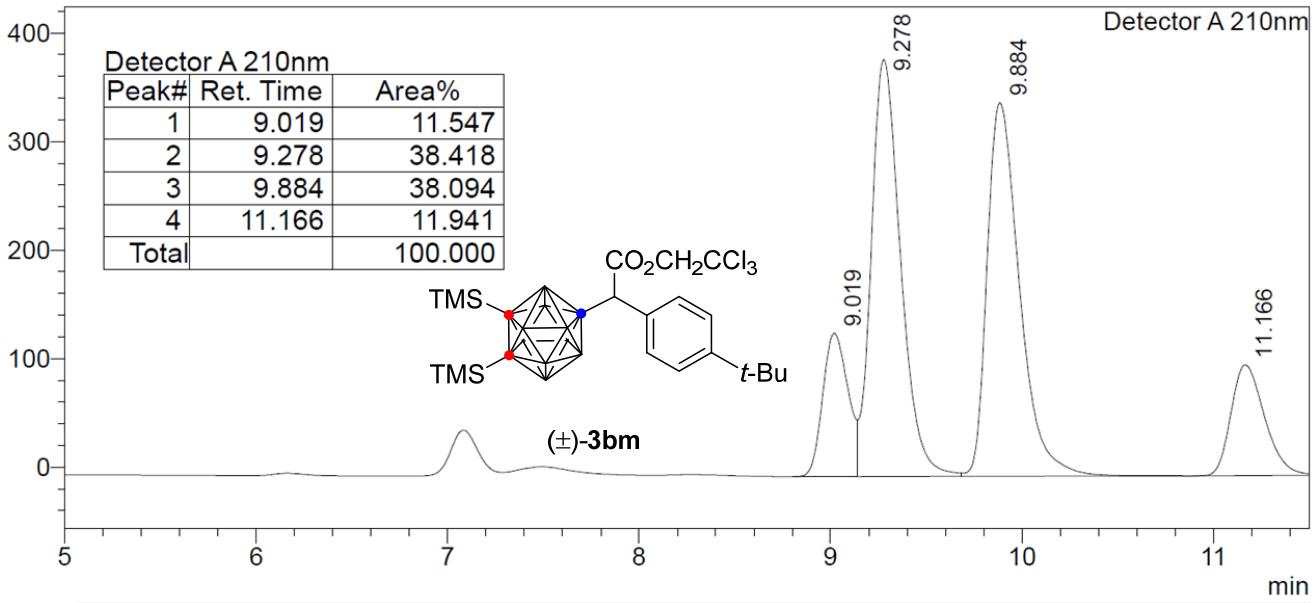

Detector A 210nm
Peak# Ret. Time Area%
1 10.191 98.750
2 15.788 1.250
Total 100.000
10.191
15.788
TMS
TMS
CO2CH2CCl3
OEt
O
(+)-3bj
min

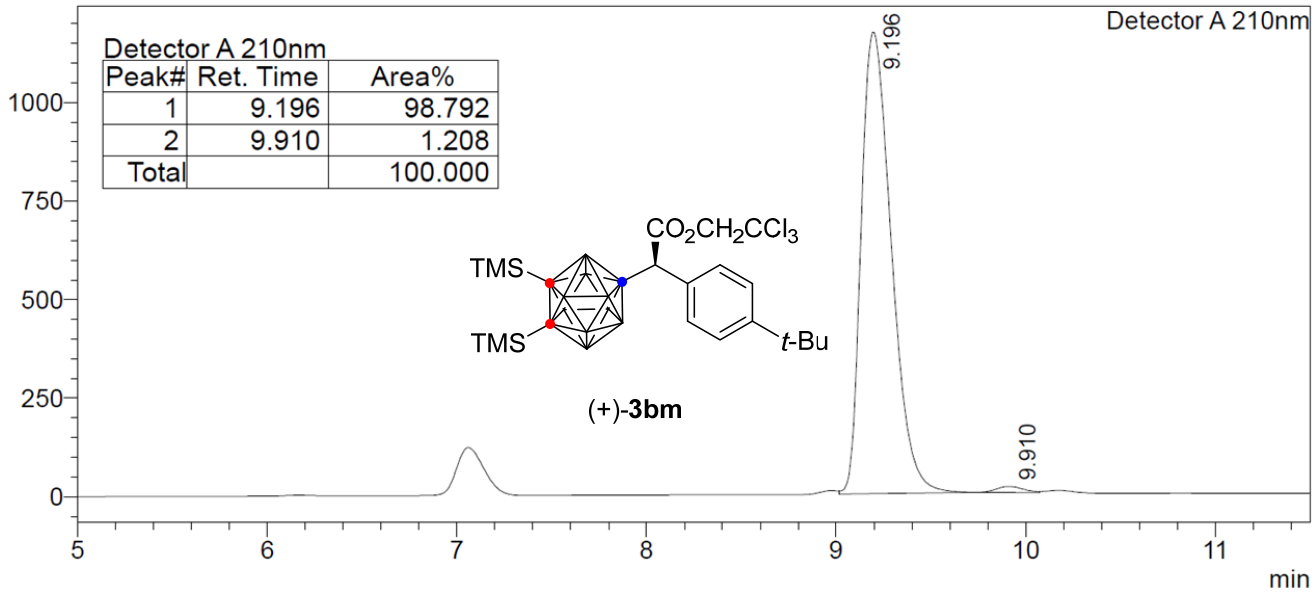

Detector A 210nm
Peak# Ret. Time Area%
1 5.827 13.834
2 6.237 36.031
3 7.045 14.716
4 9.456 35.420
Total 100.000
6.237
5.827
7.045
9.456
CO2CH2CCl3
H
H
NO2
(±)-3bk
750
500
250
0
0.0
2.5
5.0
7.5
10.0
min

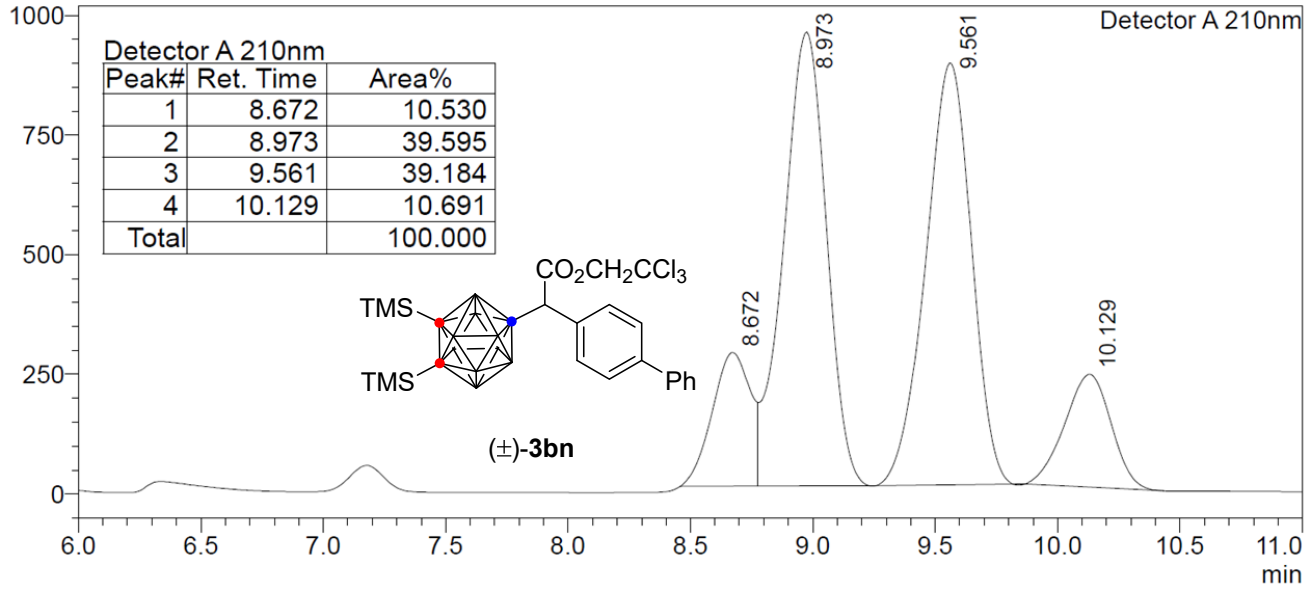

Detector A 210nm
Peak# Ret. Time Area%
1 6.329 96.544
2 10.340 3.456
Total 100.000
6.329
10.340
CO2CH2CCl3
H
H
NO2
(+)-3bk
300
200
100
0
0.0
2.5
5.0
7.5
10.0
min

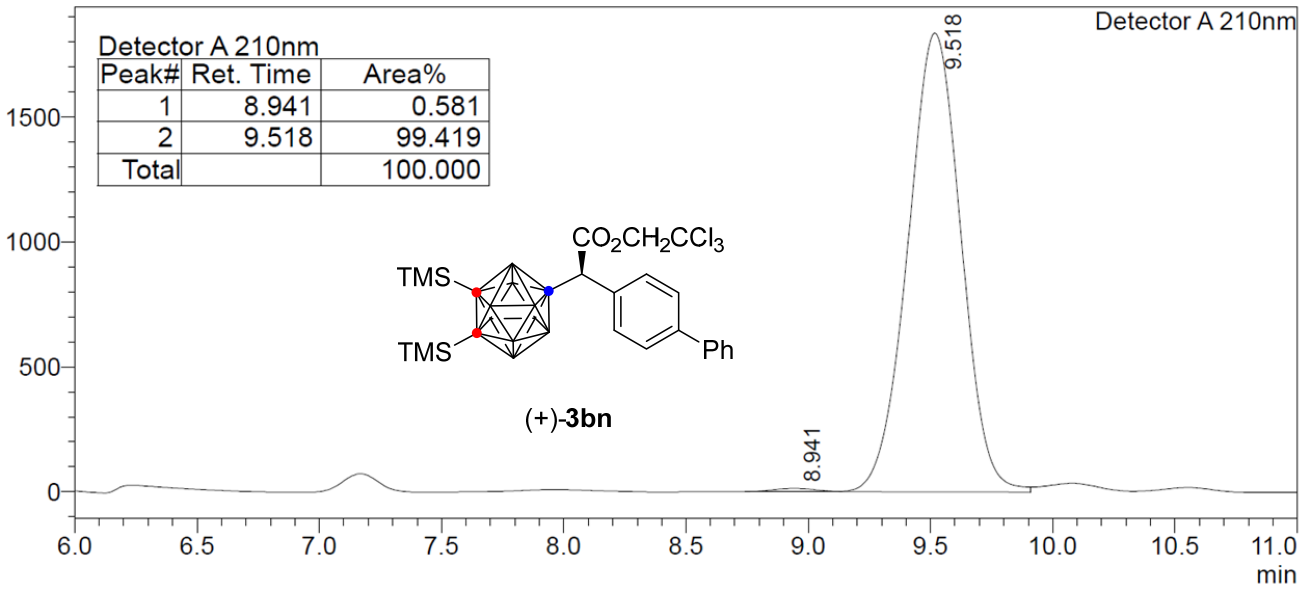

Detector A 210nm
Peak# Ret. Time Area%
1 7.669 11.212
2 8.370 9.606
3 8.758 38.161
4 9.381 41.021
Total 100.000
TMS
TMS
CO2CH2CCl3
Me
(±)-3bl
7.669
8.370
8.758
9.381
Detector A 210nm
200
150
100
50
0
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
min

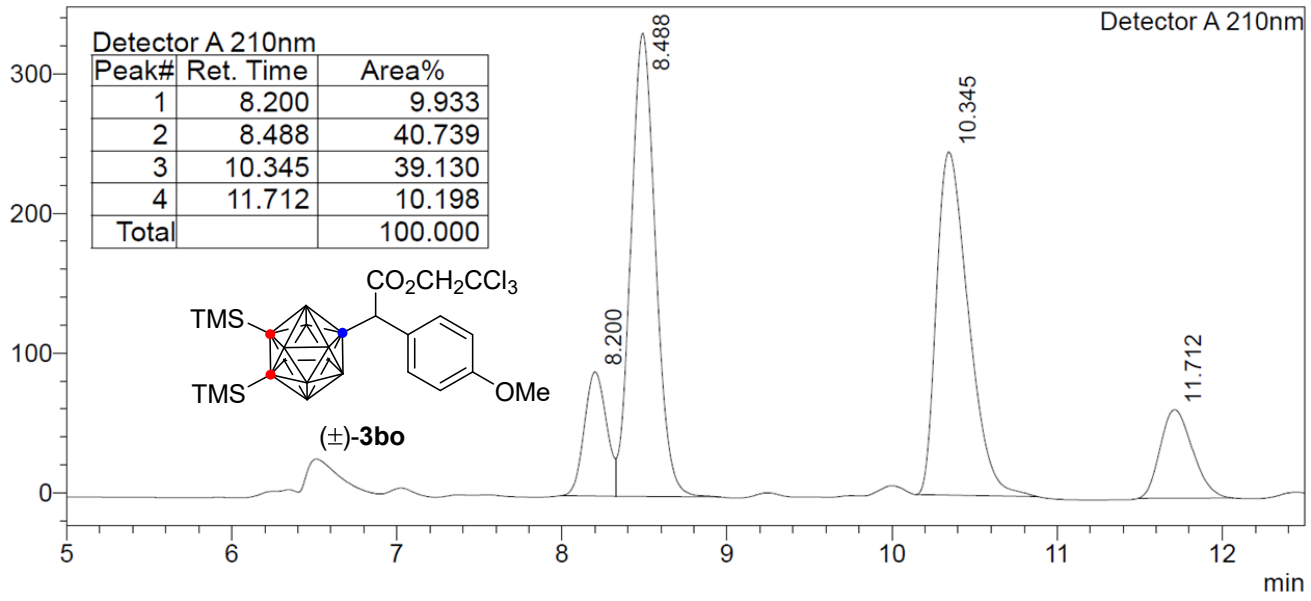

Detector A 210nm
Peak# Ret. Time Area%
1 8.708 96.767
2 9.325 3.233
Total 100.000
TMS
TMS
CO2CH2CCl3
Me
(+)-3bl
8.708
9.325
Detector A 210nm
1000
750
500
250
0
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
min

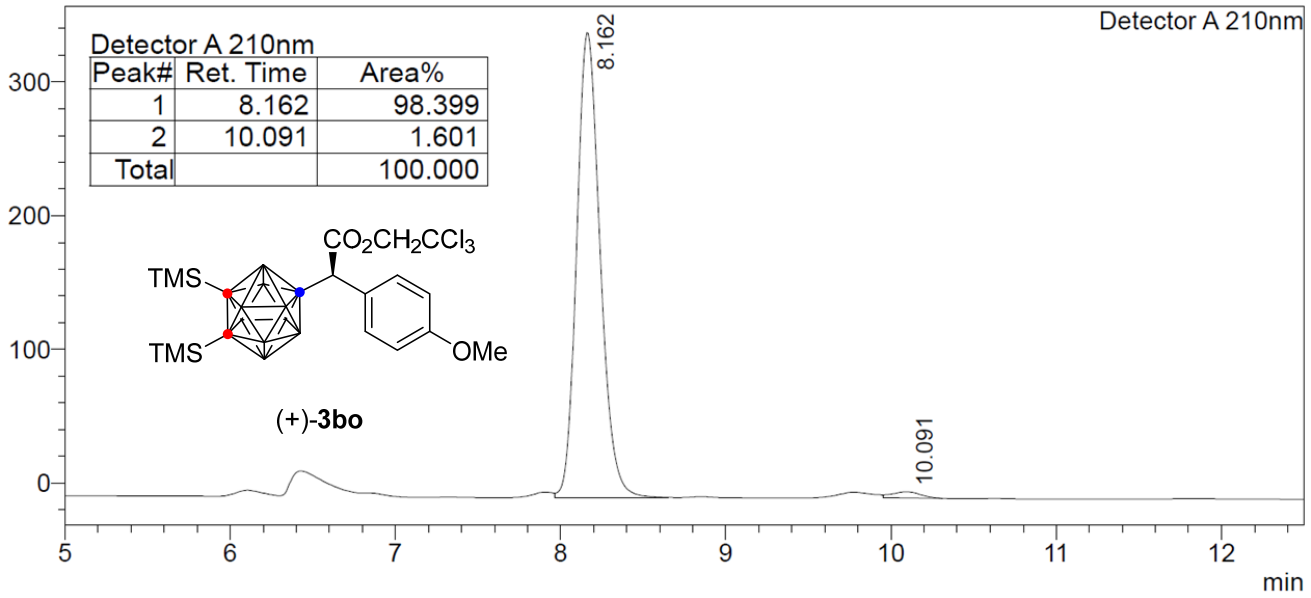

Detector A 210nm
Peak# Ret. Time Area%
1 9.019 11.547
2 9.278 38.418
3 9.884 38.094
4 11.166 11.941
Total 100.000
TMS
TMS
CO2CH2CCl3
t-Bu
(±)-3bm
9.019
9.278
9.884
11.166
Detector A 210nm
400
300
200
100
0
5
6
7
8
9
10
11
min

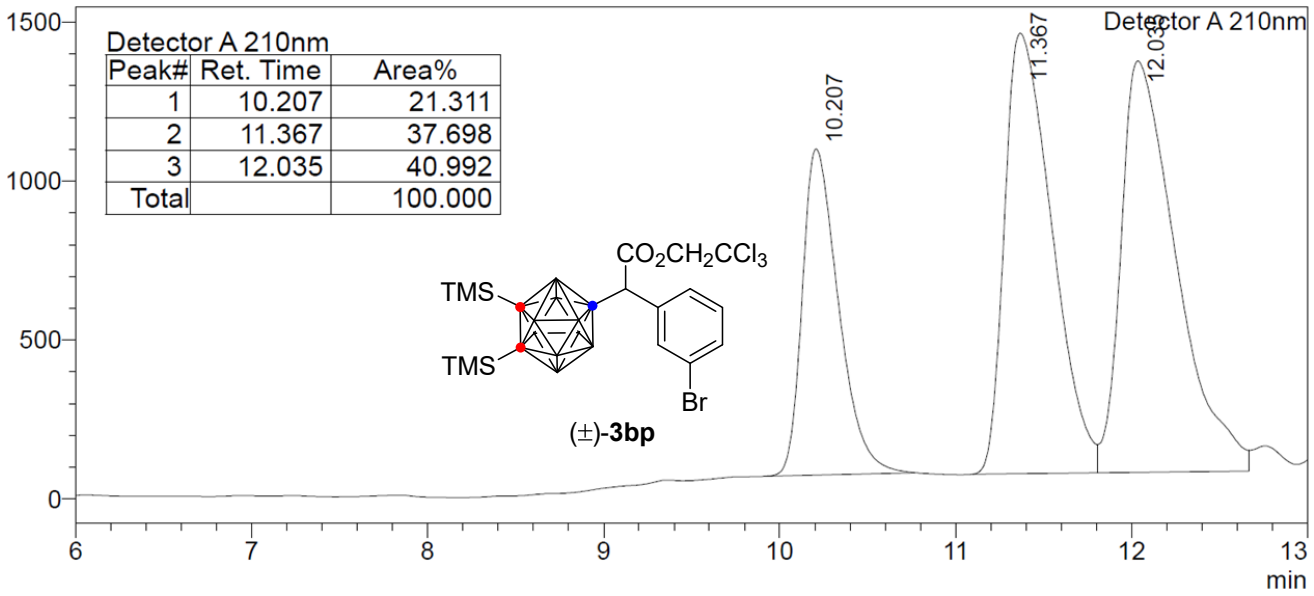

Detector A 210nm
Peak# Ret. Time Area%
1 9.196 98.792
2 9.910 1.208
Total 100.000
TMS
TMS
CO2CH2CCl3
t-Bu
(+)-3bm
9.196
9.910
Detector A 210nm
1000
750
500
250
0
5
6
7
8
9
10
11
min

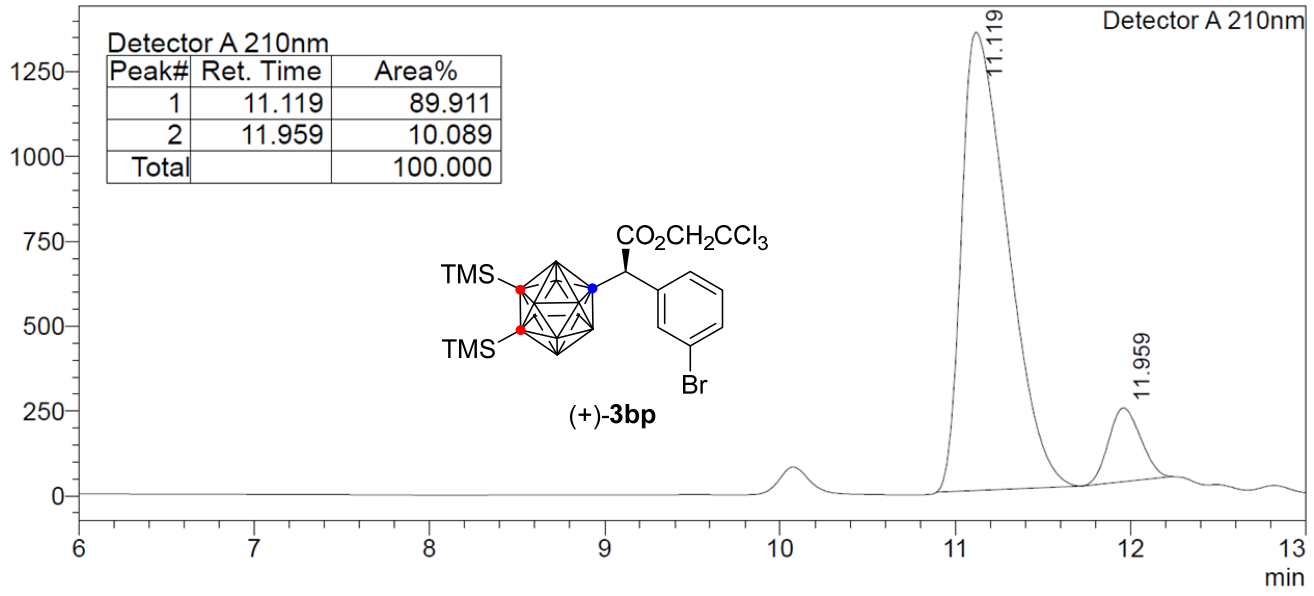

Detector A 210nm
Peak# Ret. Time Area%
1 8.672 10.530
2 8.973 39.595
3 9.561 39.184
4 10.129 10.691
Total 100.000
8.672
8.973
9.561
10.129
TMS
TMS
CO2CH2CCl3
Ph
(±)-3bn
min

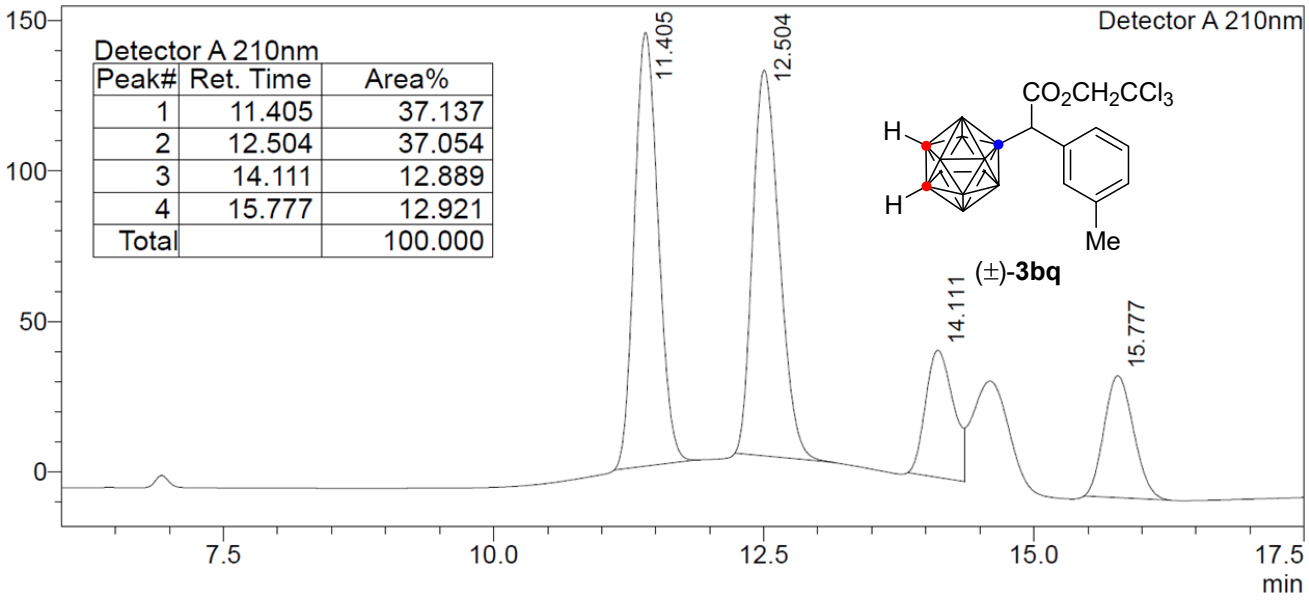

Detector A 210nm
Peak# Ret. Time Area%
1 8.941 0.581
2 9.518 99.419
Total 100.000
8.941
9.518
TMS
TMS
CO2CH2CCl3
Ph
(+)-3bn
min

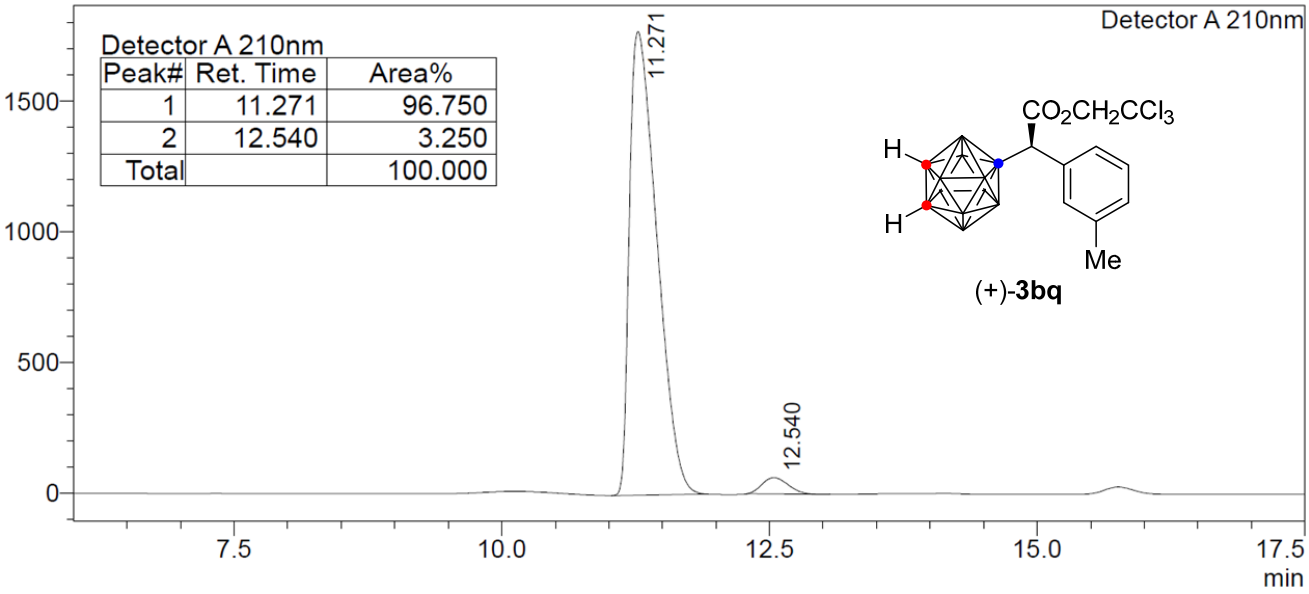

Detector A 210nm
Peak# Ret. Time Area%
1 8.200 9.933
2 8.488 40.739
3 10.345 39.130
4 11.712 10.198
Total 100.000
CO2CH2CCl3
TMS
TMS
OMe
(±)-3bo
8.200
8.488
10.345
11.712
300
200
100
0
5
6
7
8
9
10
11
12
min

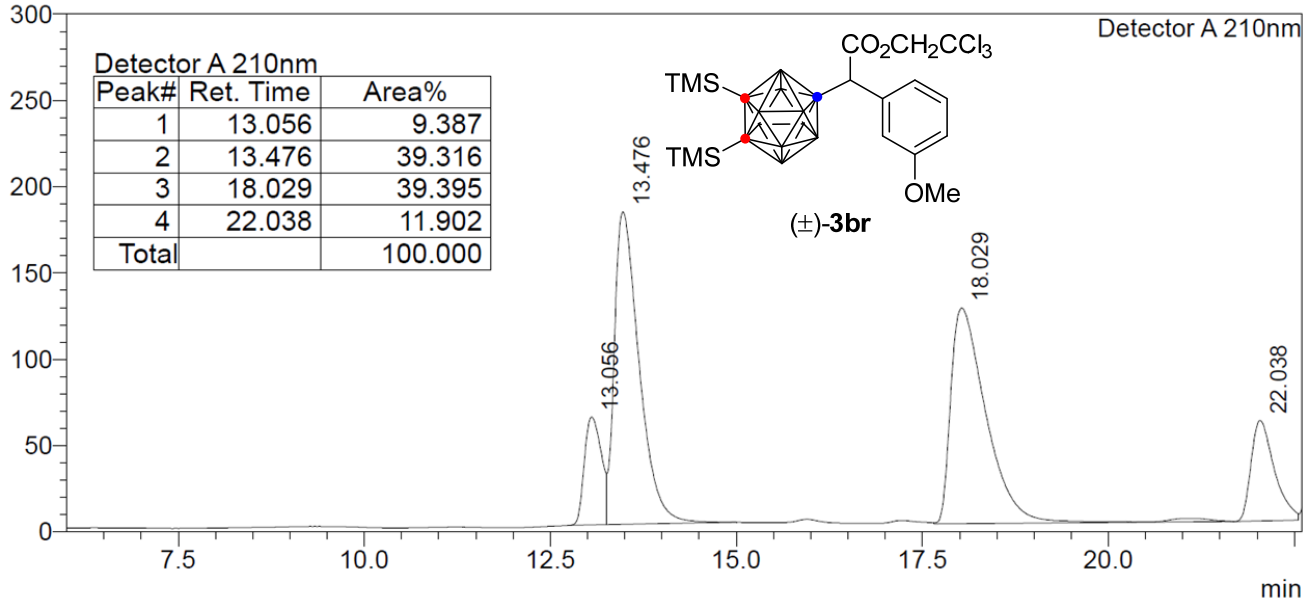

Detector A 210nm
Peak# Ret. Time Area%
1 8.162 98.399
2 10.091 1.601
Total 100.000
CO2CH2CCl3
TMS
TMS
OMe
(+)-3bo
8.162
10.091
300
200
100
0
5
6
7
8
9
10
11
12
min

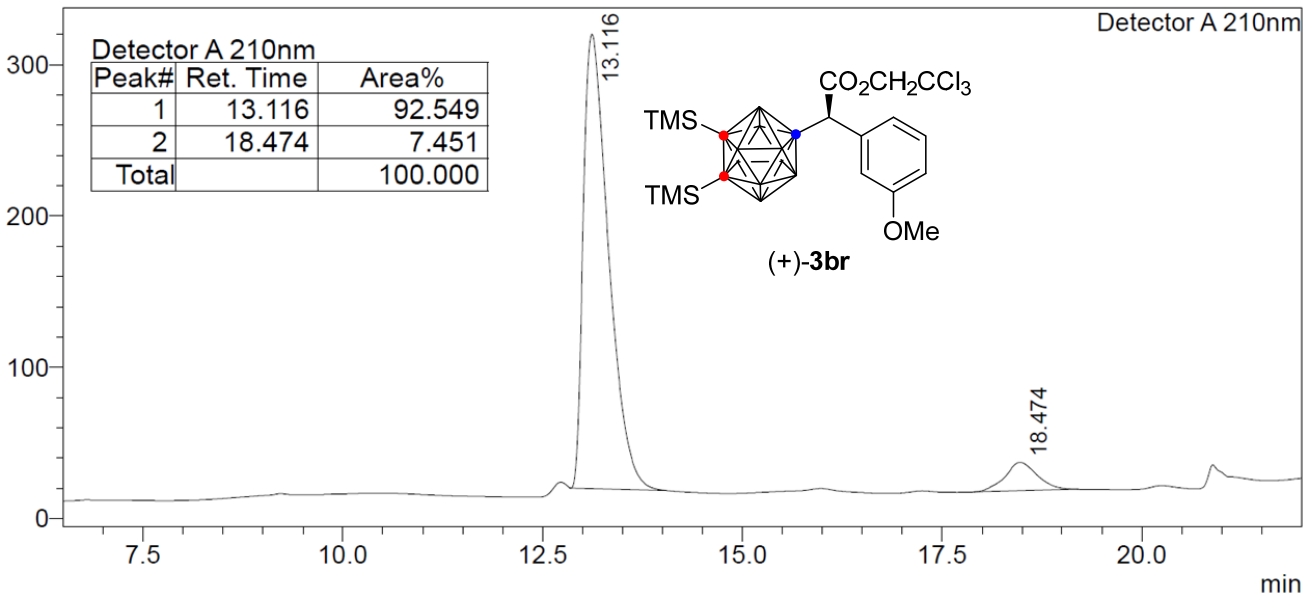

Detector A 210nm
Peak# Ret. Time Area%
1 10.207 21.311
2 11.367 37.698
3 12.035 40.992
Total 100.000
10.207
11.367
12.035
TMS
TMS
CO2CH2CCl3
Br
(±)-3bp
min

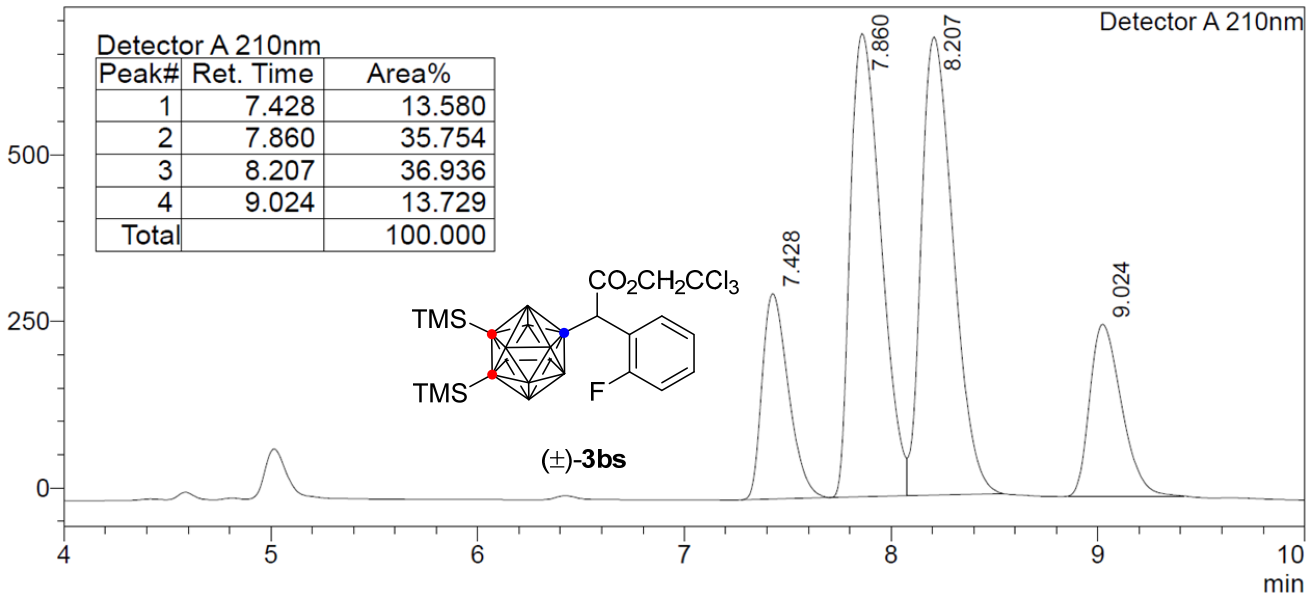

Detector A 210nm
Peak# Ret. Time Area%
1 11.119 89.911
2 11.959 10.089
Total 100.000
11.119
11.959
TMS
TMS
CO2CH2CCl3
Br
(+)-3bp
min

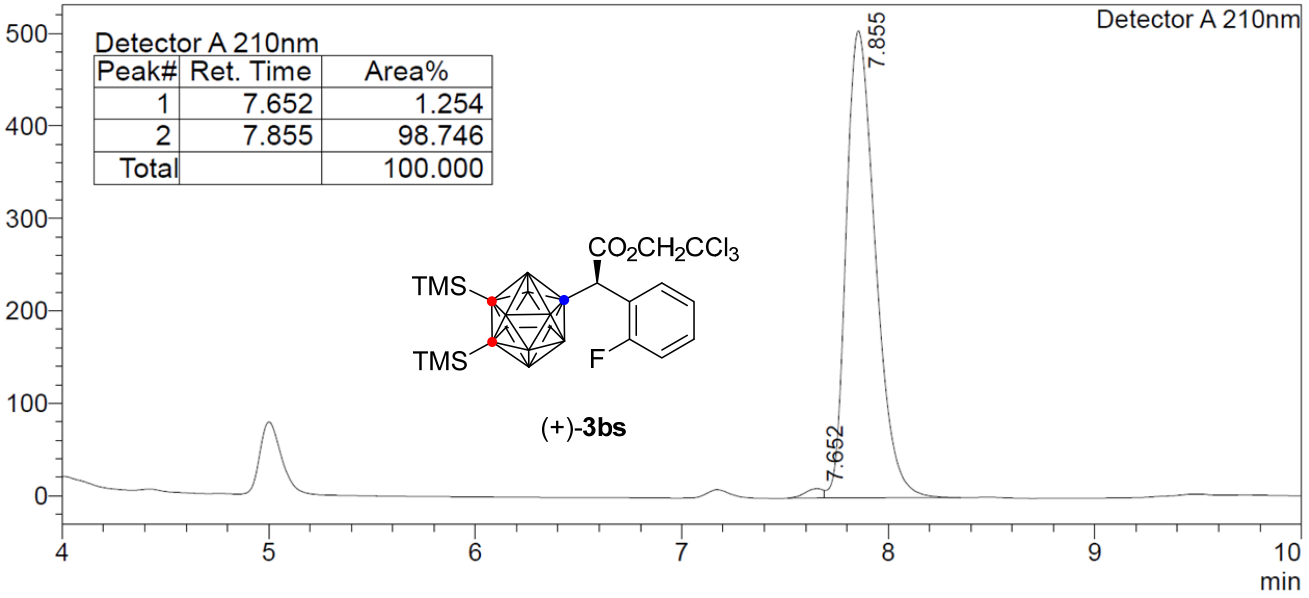

Detector A 210nm
Peak# Ret. Time Area%
1 11.405 37.137
2 12.504 37.054
3 14.111 12.889
4 15.777 12.921
Total 100.000
11.405
12.504
14.111
15.777
Detector A 210nm
150
100
50
0
7.5
10.0
12.5
15.0
17.5
min
H
H
CO2CH2CCl3
Me
(±)-3bq

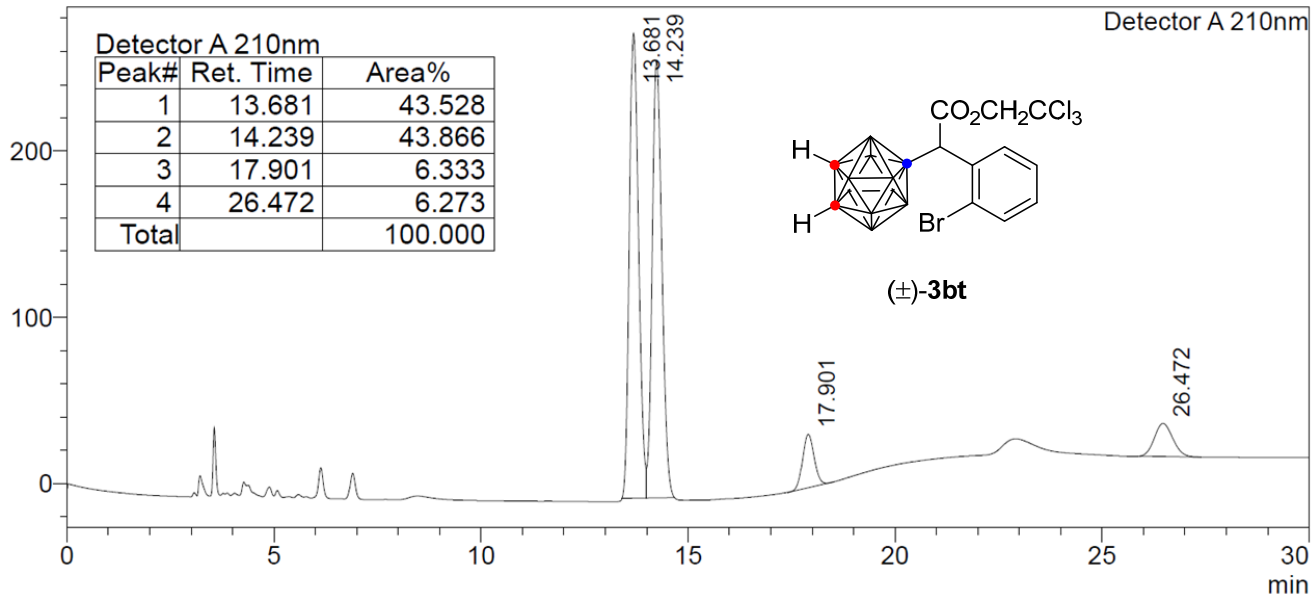

Detector A 210nm
Peak# Ret. Time Area%
1 11.271 96.750
2 12.540 3.250
Total 100.000
11.271
12.540
Detector A 210nm
1500
1000
500
0
7.5
10.0
12.5
15.0
17.5
min
H
H
CO2CH2CCl3
Me
(+)-3bq

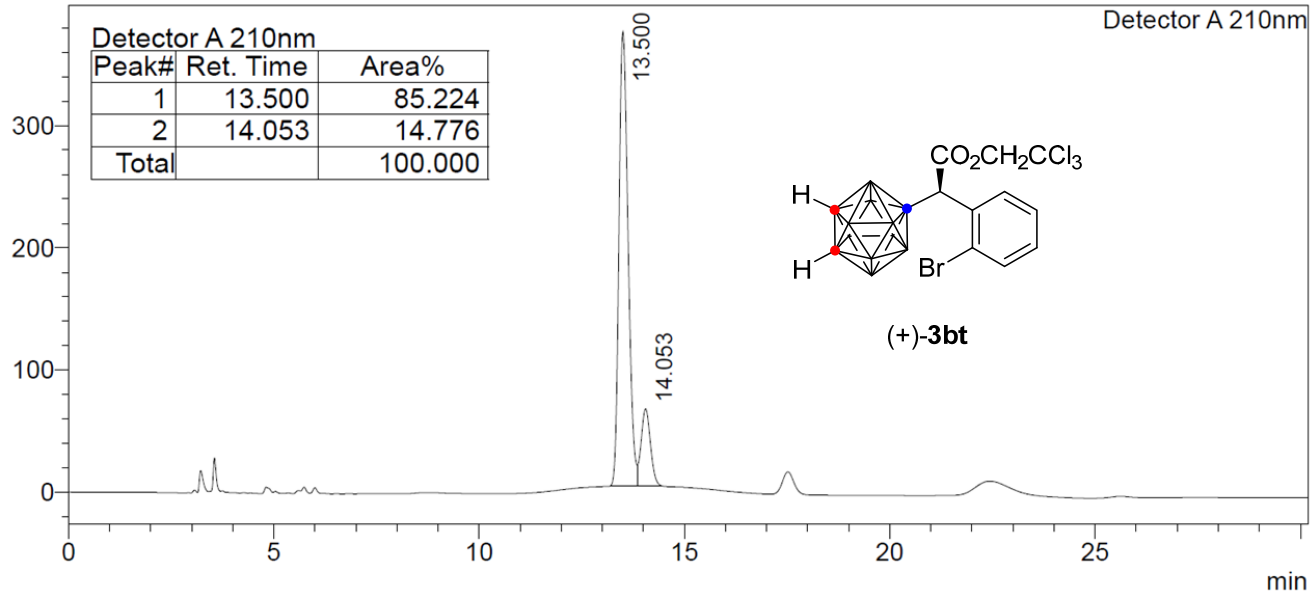

Detector A 210nm
Peak# Ret. Time Area%
1 13.056 9.387
2 13.476 39.316
3 18.029 39.395
4 22.038 11.902
Total 100.000
13.476
13.056
18.029
22.038
TMS
TMS
CO2CH2CCl3
OMe
(±)-3br
min

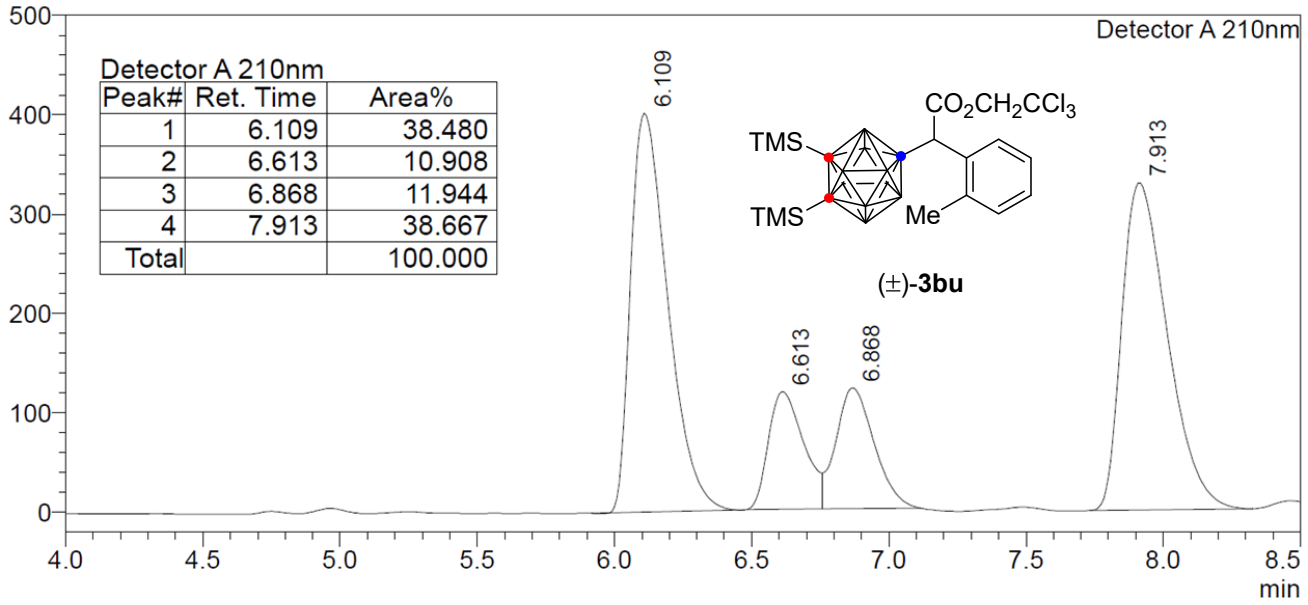

Detector A 210nm
Peak# Ret. Time Area%
1 13.116 92.549
2 18.474 7.451
Total 100.000
13.116
18.474
TMS
TMS
CO2CH2CCl3
OMe
(+)-3br
min


Detector A 210nm
Peak# Ret. Time Area%
1 7.428 13.580
2 7.860 35.754
3 8.207 36.936
4 9.024 13.729
Total 100.000
7.428
7.860
8.207
9.024
CO2CH2CCl3
TMS
TMS
F
(±)-3bs
500
250
0
4
5
6
7
8
9
10
min


Detector A 210nm
Peak# Ret. Time Area%
1 7.652 1.254
2 7.855 98.746
Total 100.000
7.652
7.855
CO2CH2CCl3
TMS
TMS
F
(+)-3bs
500
400
300
200
100
0
4
5
6
7
8
9
10
min

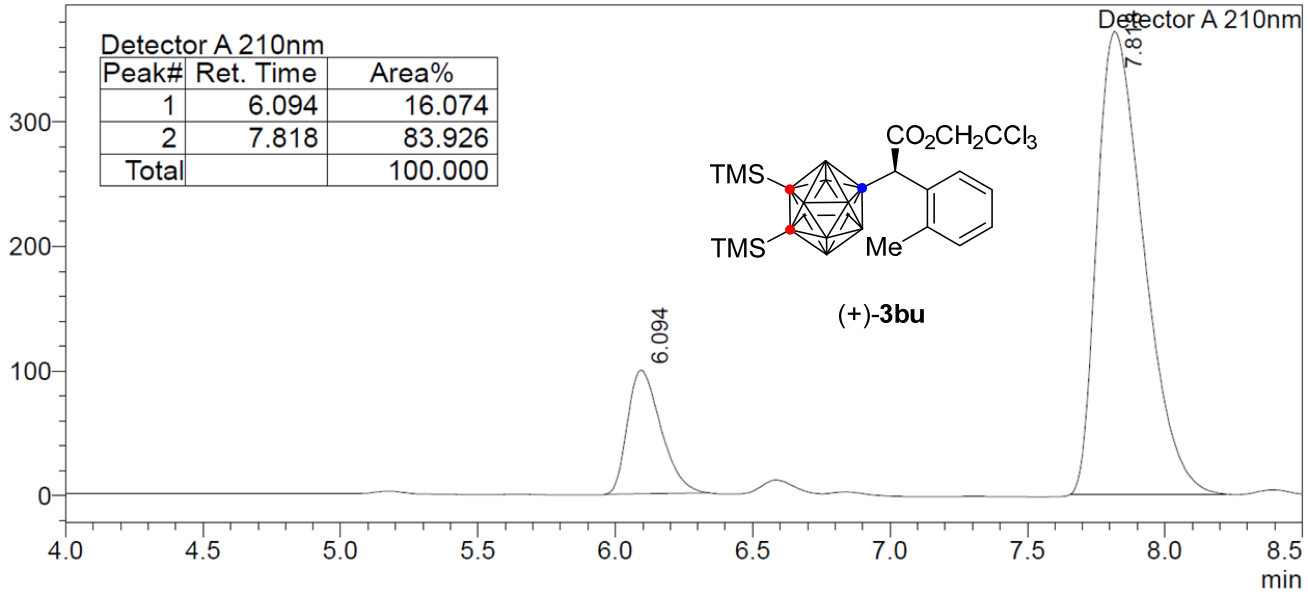

Detector A 210nm
Peak# Ret. Time Area%
1 13.681 43.528
2 14.239 43.866
3 17.901 6.333
4 26.472 6.273
Total 100.000
13.681
14.239
17.901
26.472
CO2CH2CCl3
H
H
Br
(±)-3bt
200
100
0
0
5
10
15
20
25
30
min


Detector A 210nm
Peak# Ret. Time Area%
1 13.500 85.224
2 14.053 14.776
Total 100.000
13.500
14.053
CO2CH2CCl3
H
H
Br
(+)-3bt
300
200
100
0
0
5
10
15
20
25
min



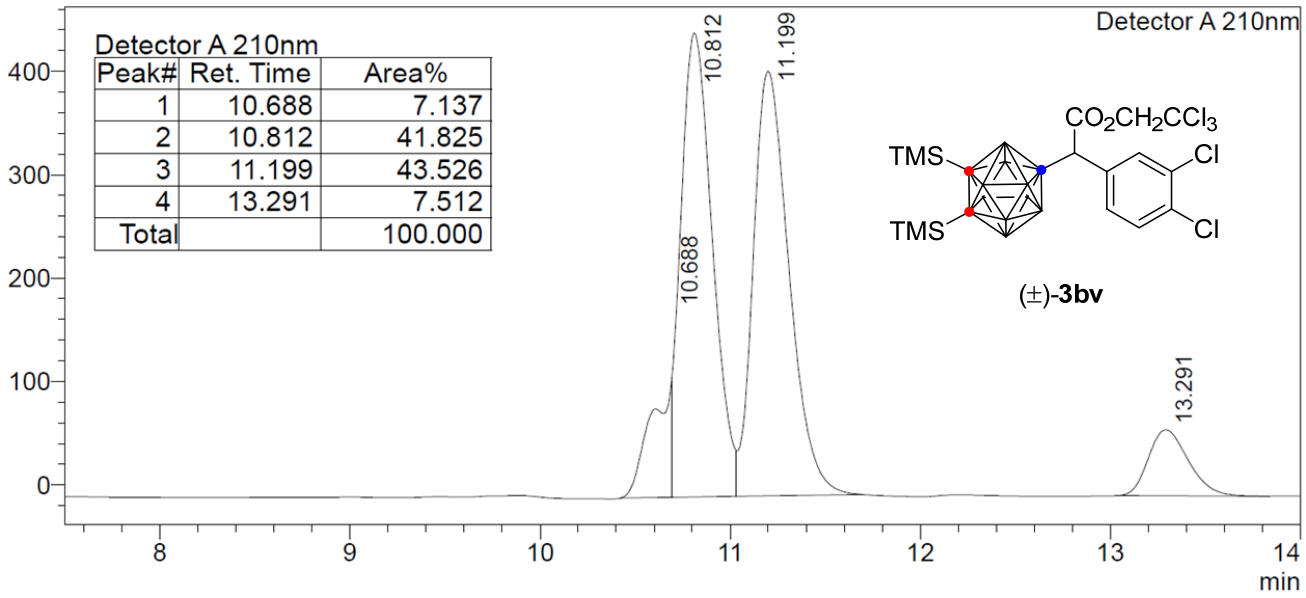
Detector A 210nm

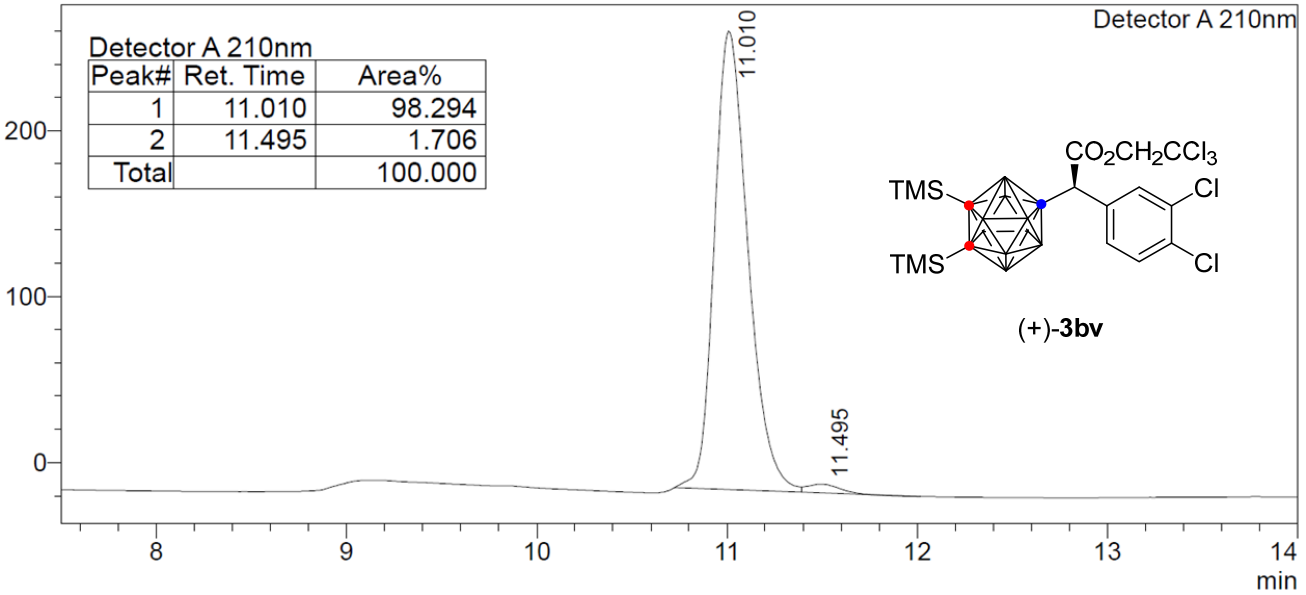
Peak#	Ret. Time	Area%
1	6.109	38.480
2	6.613	10.908
3	6.868	11.944
4	7.913	38.667
Total		100.000

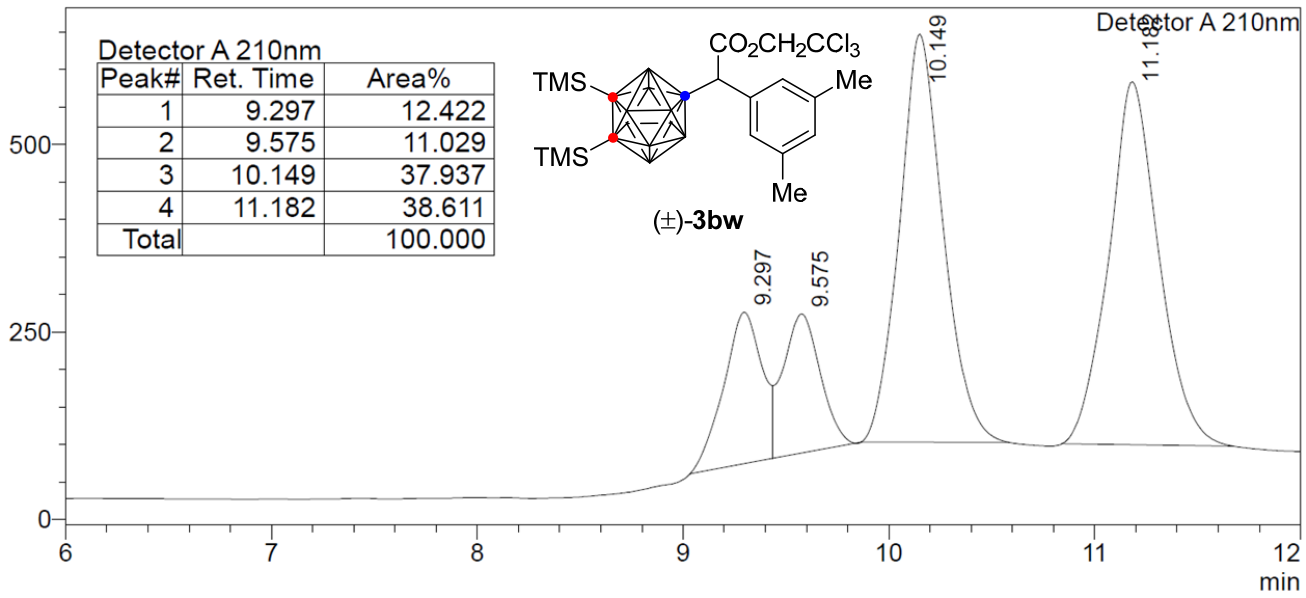


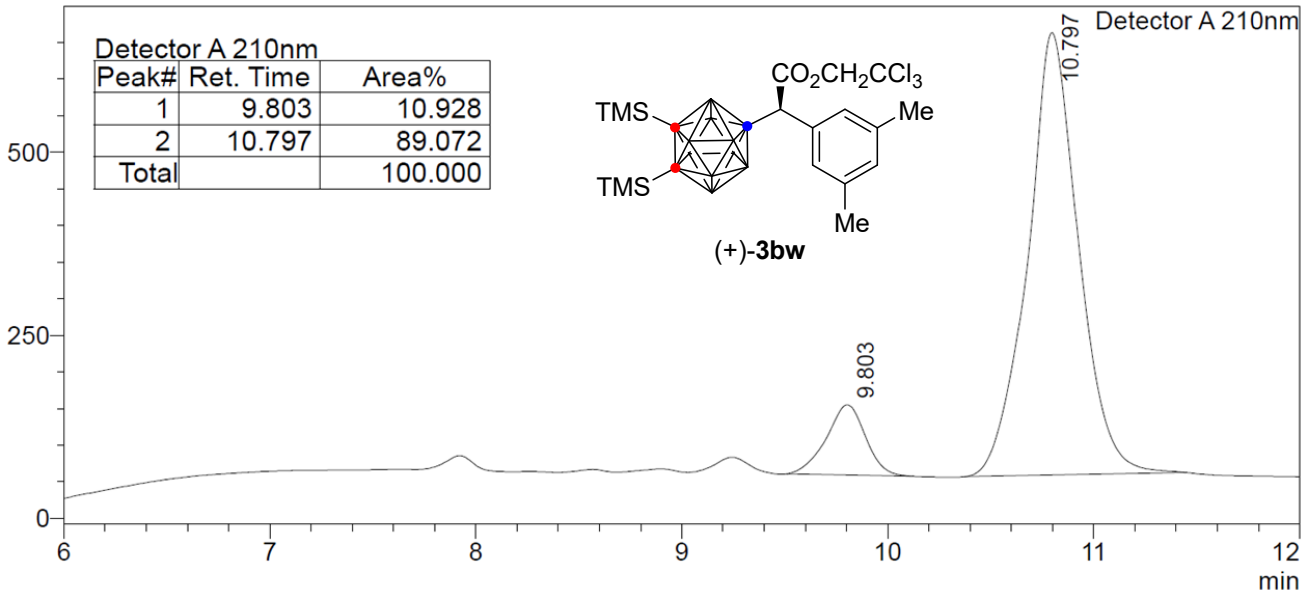
Detector A 210nm

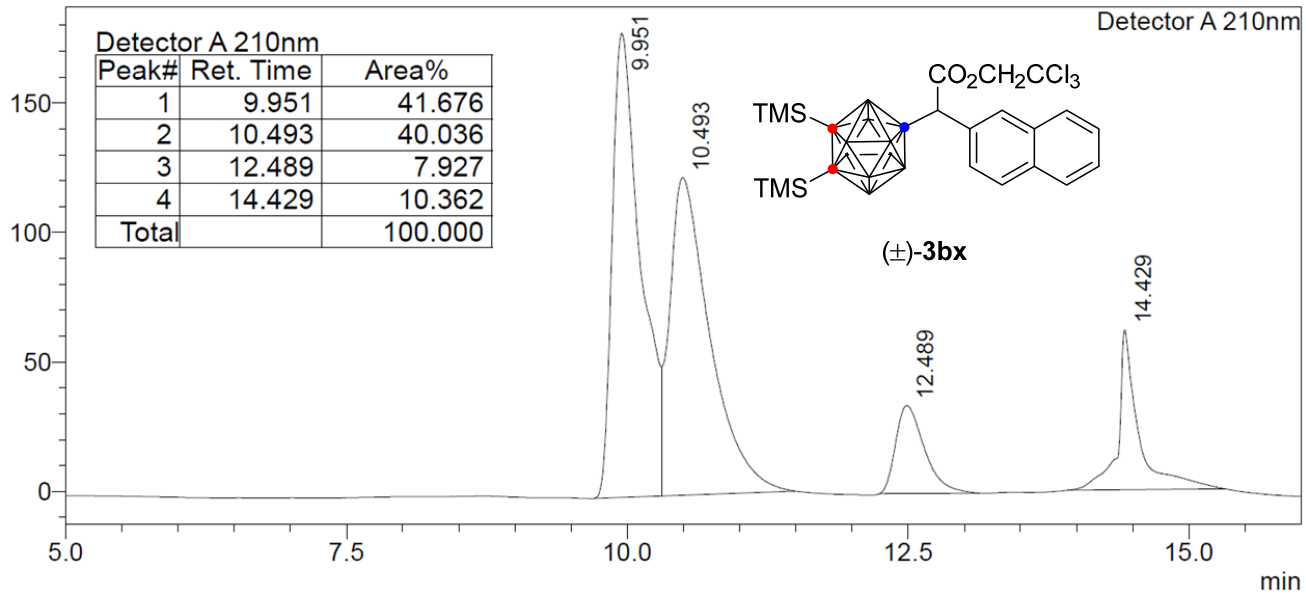
Peak#	Ret. Time	Area%
1	6.094	16.074
2	7.818	83.926
Total		100.000

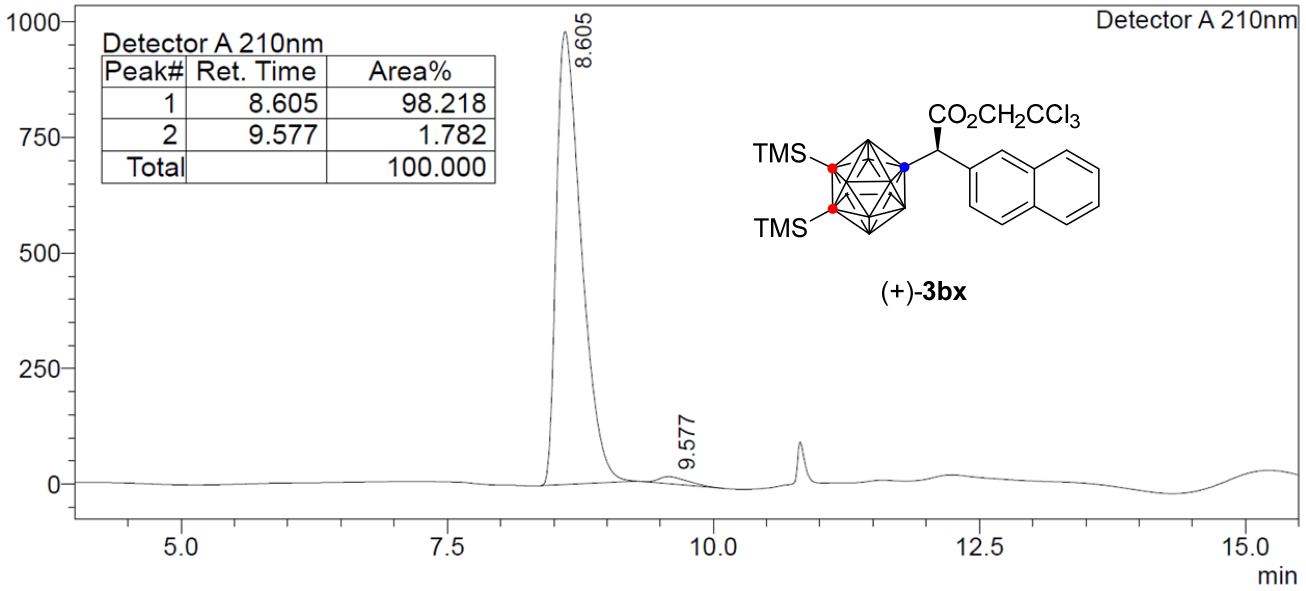

Detector A 210nm
Peak# Ret. Time Area%
1 10.688 7.137
2 10.812 41.825
3 11.199 43.526
4 13.291 7.512
Total 100.000
10.812
11.199
10.688
13.291
Detector A 210nm
CO2CH2CCl3
TMS
TMS
Cl
Cl
(±)-3bv
400
300
200
100
0
8
9
10
11
12
13
14
min

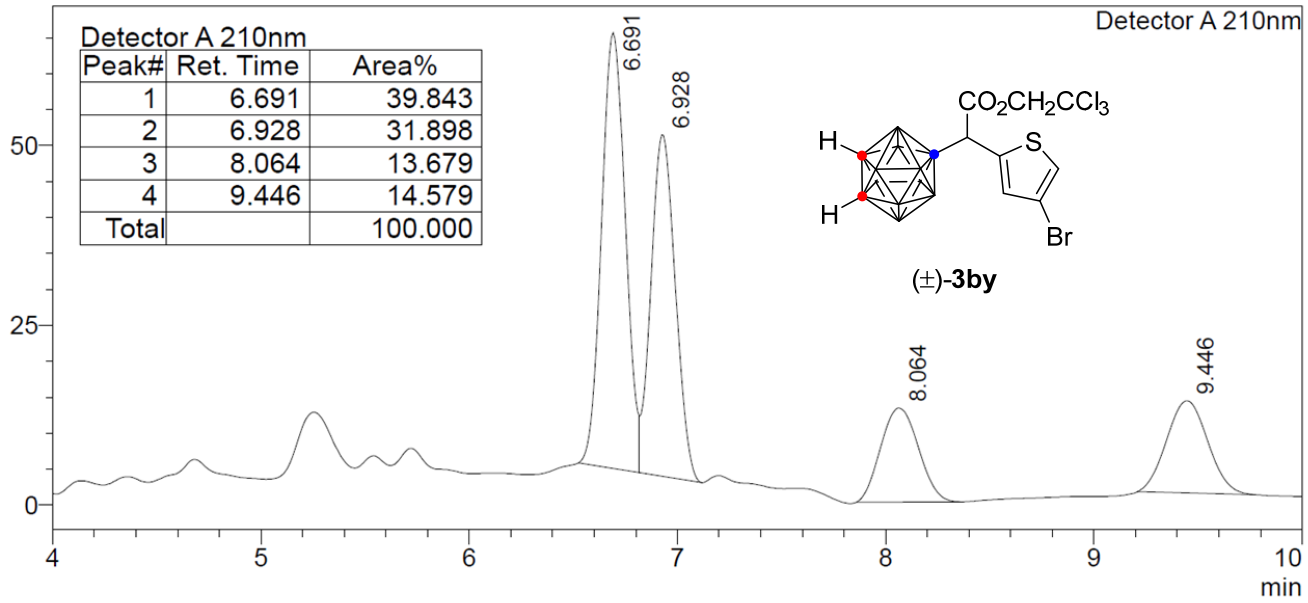

Detector A 210nm
Peak# Ret. Time Area%
1 11.010 98.294
2 11.495 1.706
Total 100.000
11.010
11.495
Detector A 210nm
CO2CH2CCl3
TMS
TMS
Cl
Cl
(+)-3bv
200
100
0
8
9
10
11
12
13
14
min


Detector A 210nm
Peak# Ret. Time Area%
1 9.297 12.422
2 9.575 11.029
3 10.149 37.937
4 11.182 38.611
Total 100.000
TMS
TMS
CO2CH2CCl3
Me
Me
(±)-3bw
9.297
9.575
10.149
11.182
Detector A 210nm
500
250
0
6
7
8
9
10
11
12
min

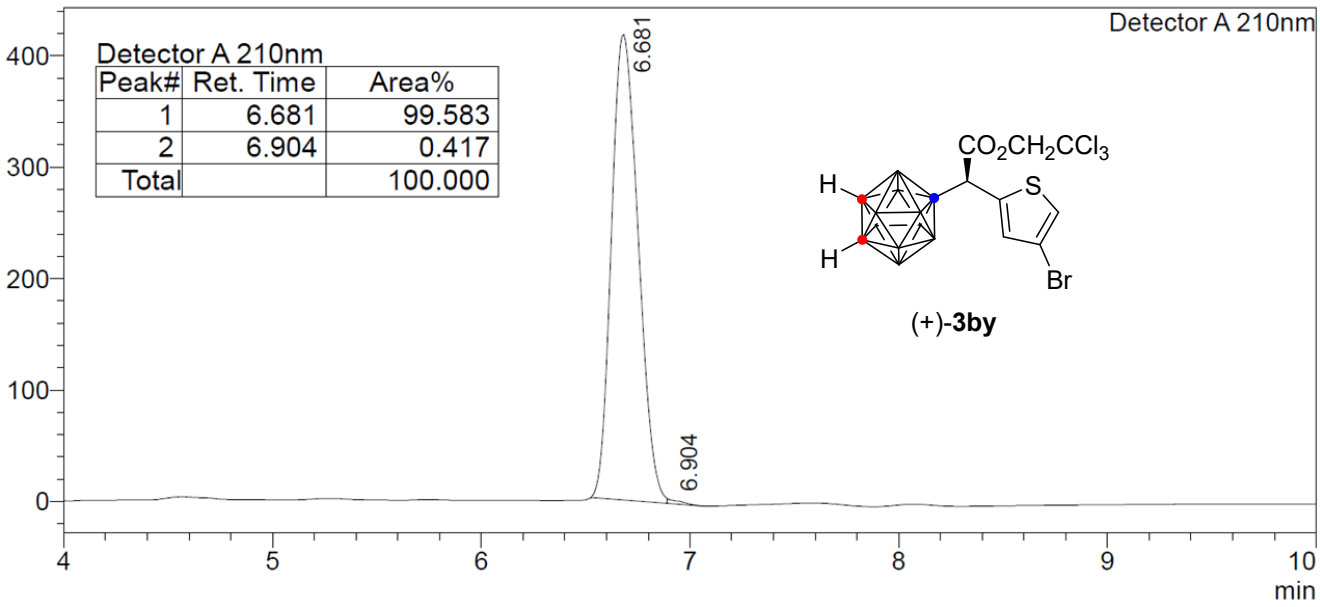

Detector A 210nm
Peak# Ret. Time Area%
1 9.803 10.928
2 10.797 89.072
Total 100.000
TMS
TMS
CO2CH2CCl3
Me
Me
(+)-3bw
9.803
10.797
Detector A 210nm
500
250
0
6
7
8
9
10
11
12
min


Detector A 210nm
Peak# Ret. Time Area%
1 9.951 41.676
2 10.493 40.036
3 12.489 7.927
4 14.429 10.362
Total 100.000
9.951
10.493
12.489
14.429
TMS
TMS
CO2CH2CCl3
(±)-3bx
150
100
50
0
5.0
7.5
10.0
12.5
15.0
min

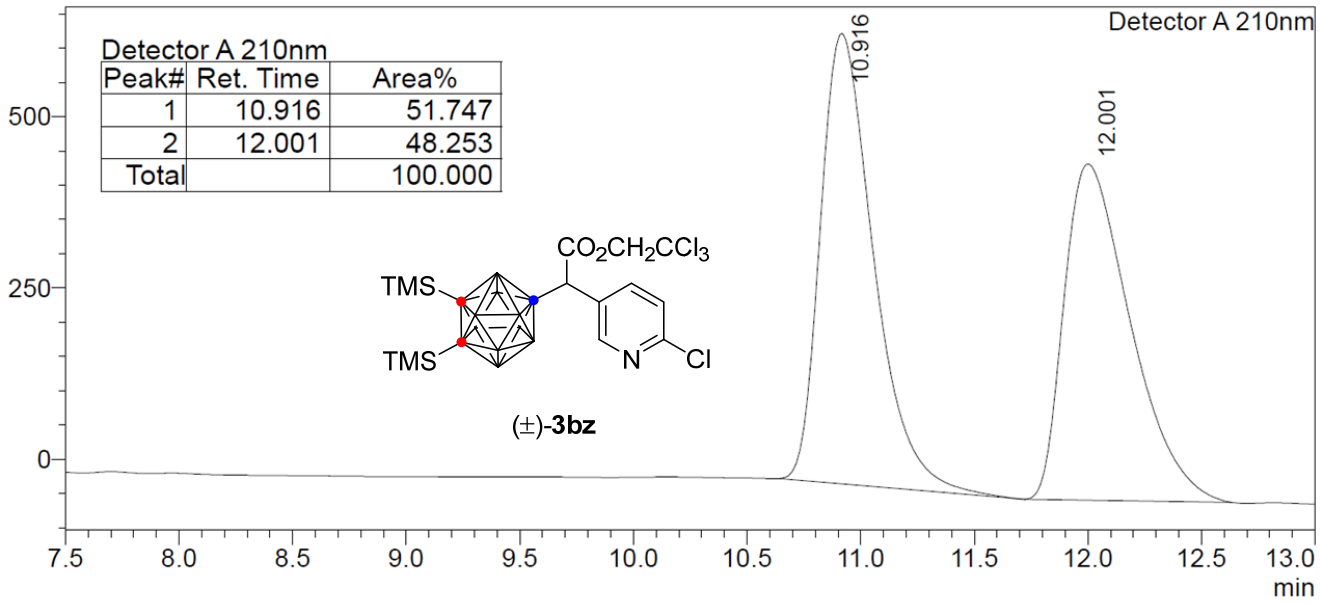

Detector A 210nm
Peak# Ret. Time Area%
1 8.605 98.218
2 9.577 1.782
Total 100.000
8.605
9.577
TMS
TMS
CO2CH2CCl3
(+)-3bx
1000
750
500
250
0
5.0
7.5
10.0
12.5
15.0
min

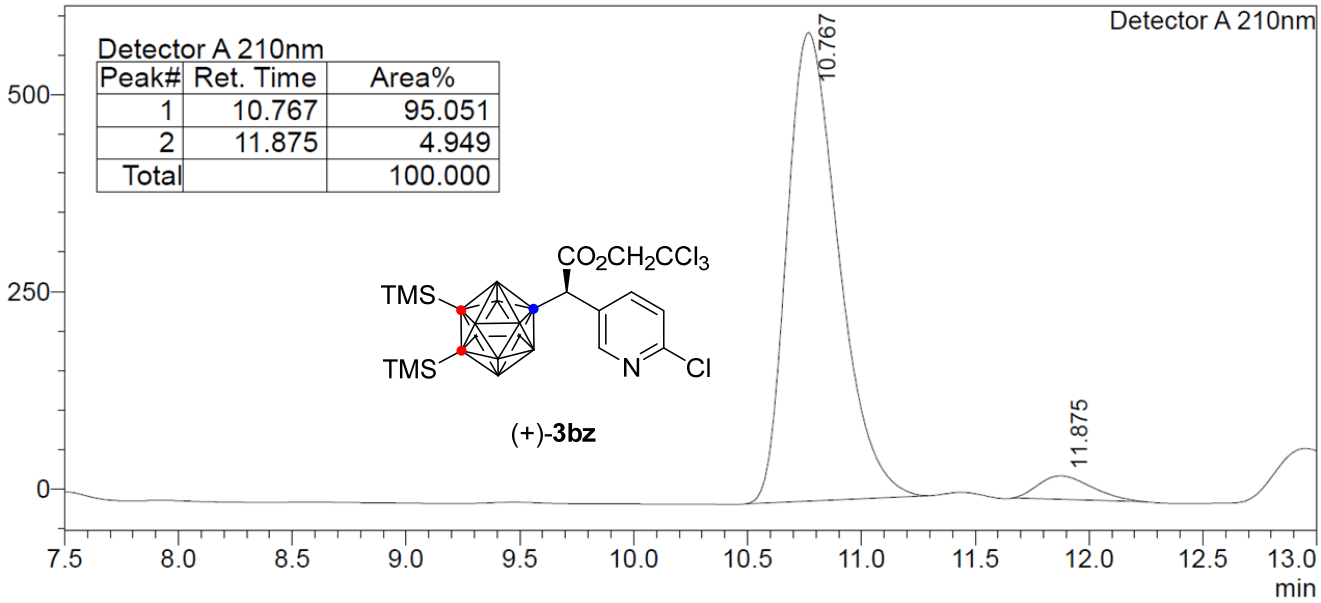

Detector A 210nm
Peak# Ret. Time Area%
1 6.691 39.843
2 6.928 31.898
3 8.064 13.679
4 9.446 14.579
Total 100.000
6.691
6.928
8.064
9.446
Detector A 210nm
50
25
0
4
5
6
7
8
9
10
min
H
H
S
Br
CO2CH2CCl3

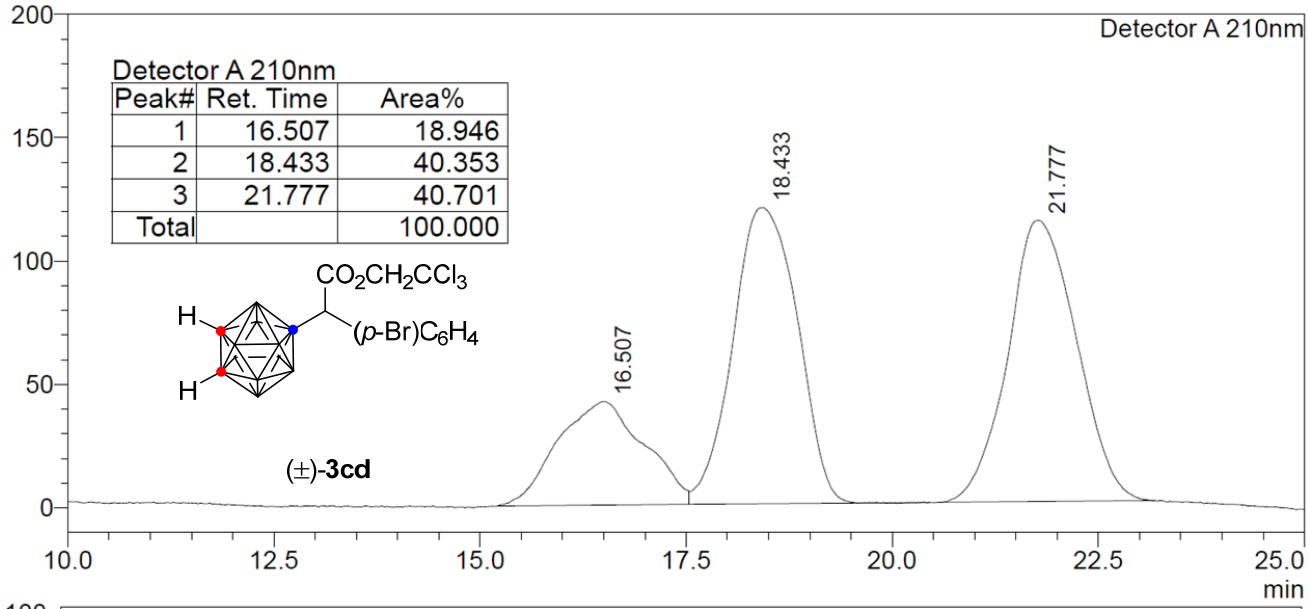
(±)-**3by**

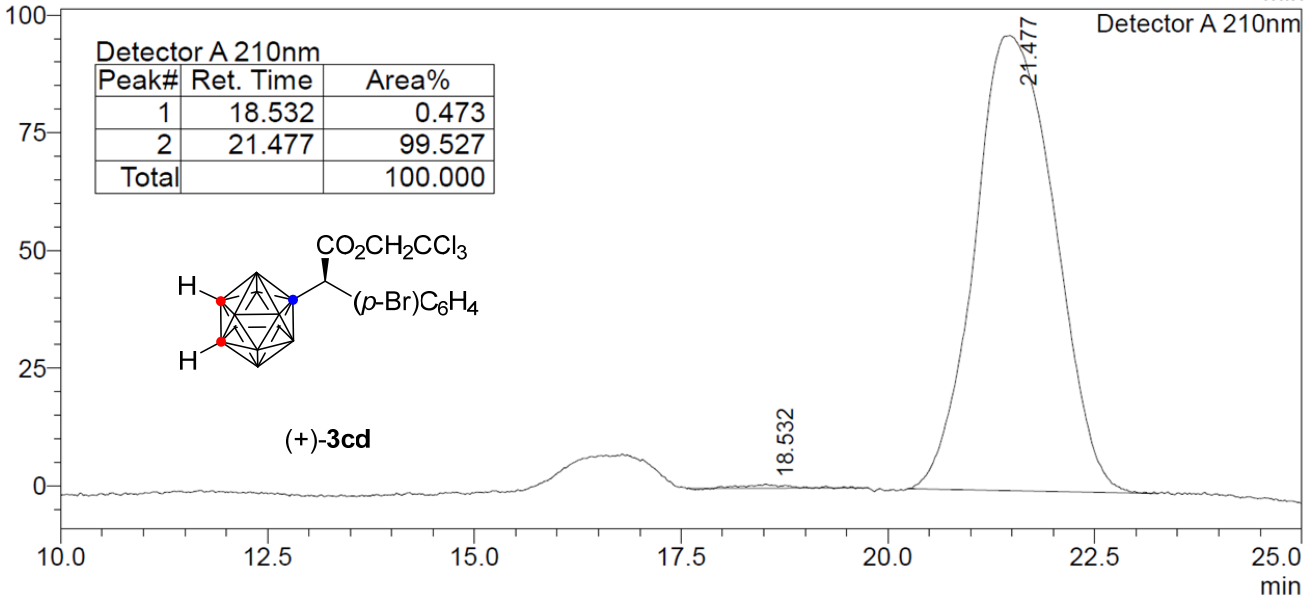

Detector A 210nm
Peak# Ret. Time Area%
1 6.681 99.583
2 6.904 0.417
Total 100.000
6.681
6.904
Detector A 210nm
400
300
200
100
0
4
5
6
7
8
9
10
min
H
H
S
Br
CO2CH2CCl3

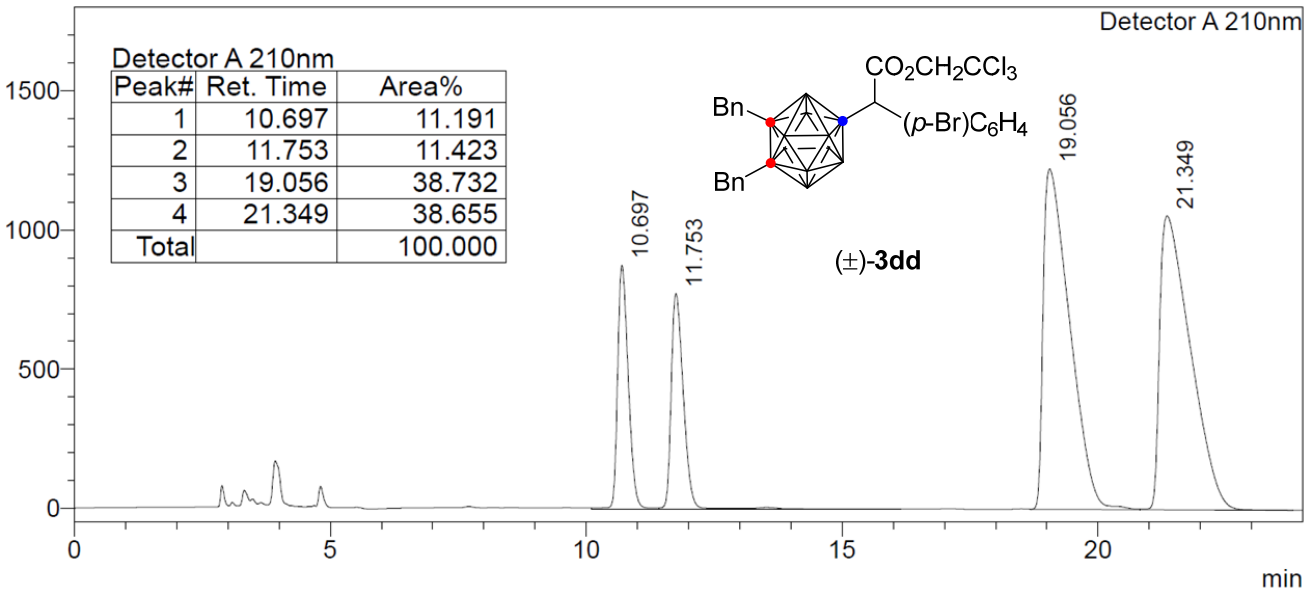
(+)-**3by**

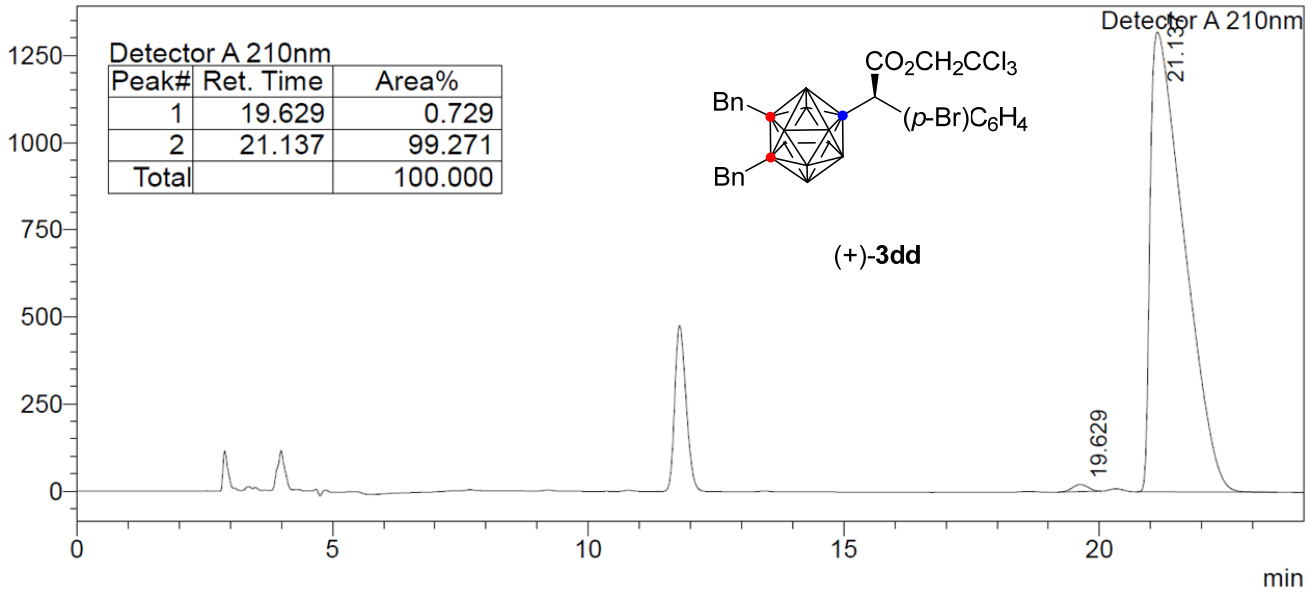

Detector A 210nm
Peak# Ret. Time Area%
1 10.916 51.747
2 12.001 48.253
Total 100.000
10.916
12.001
CO2CH2CCl3
TMS
TMS
N
Cl
(±)-3bz
500
250
0
7.5 8.0 8.5 9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0
min

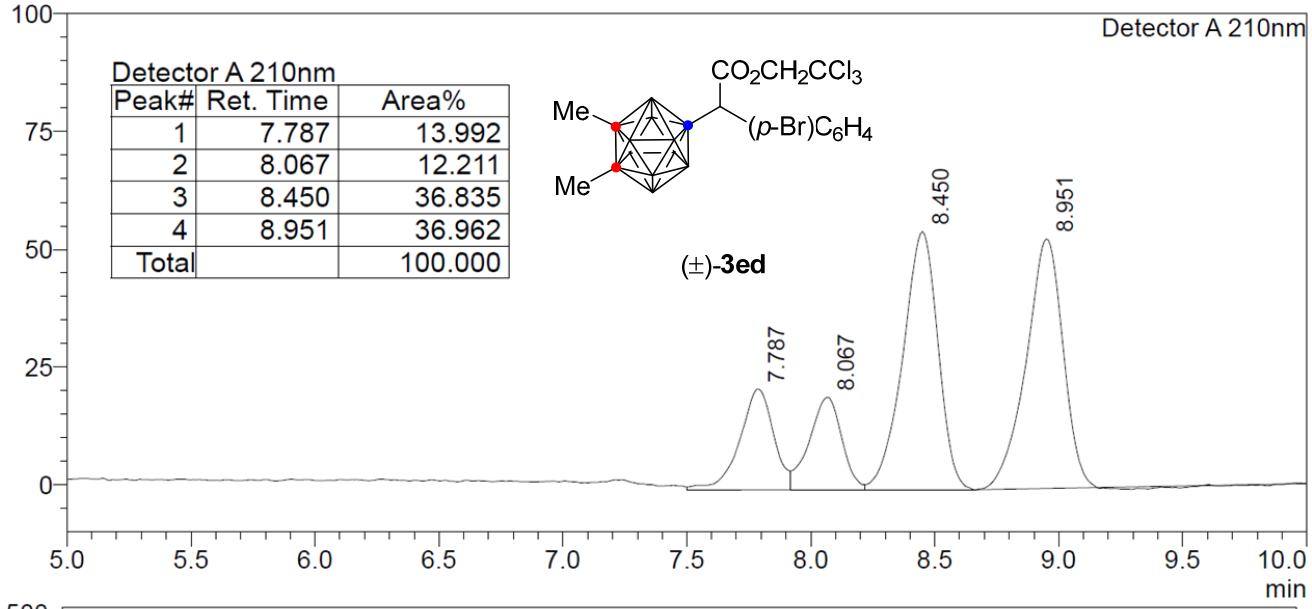

Detector A 210nm
Peak# Ret. Time Area%
1 10.767 95.051
2 11.875 4.949
Total 100.000
10.767
11.875
CO2CH2CCl3
TMS
TMS
N
Cl
(+)-3bz
500
250
0
7.5 8.0 8.5 9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0
min

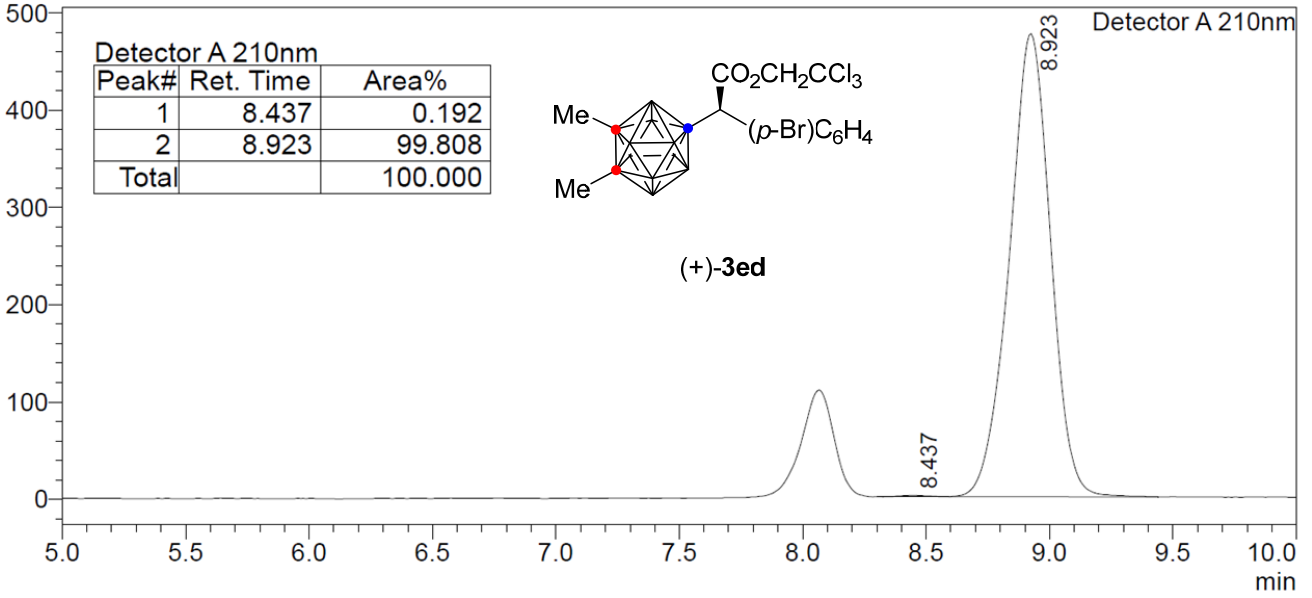

Detector A 210nm
Peak# Ret. Time Area%
1 16.507 18.946
2 18.433 40.353
3 21.777 40.701
Total 100.000
CO2CH2CCl3
H
H
(p-Br)C6H4
(±)-3cd
16.507
18.433
21.777
min

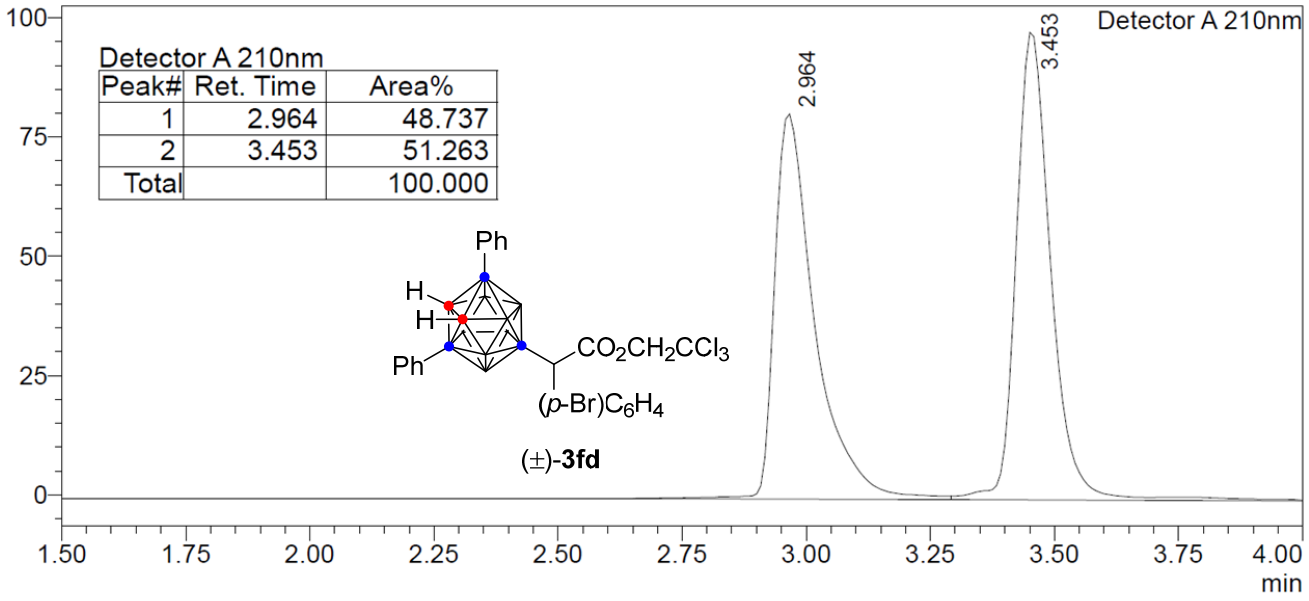

Detector A 210nm
Peak# Ret. Time Area%
1 18.532 0.473
2 21.477 99.527
Total 100.000
CO2CH2CCl3
H
H
(p-Br)C6H4
(+)-3cd
18.532
21.477
min

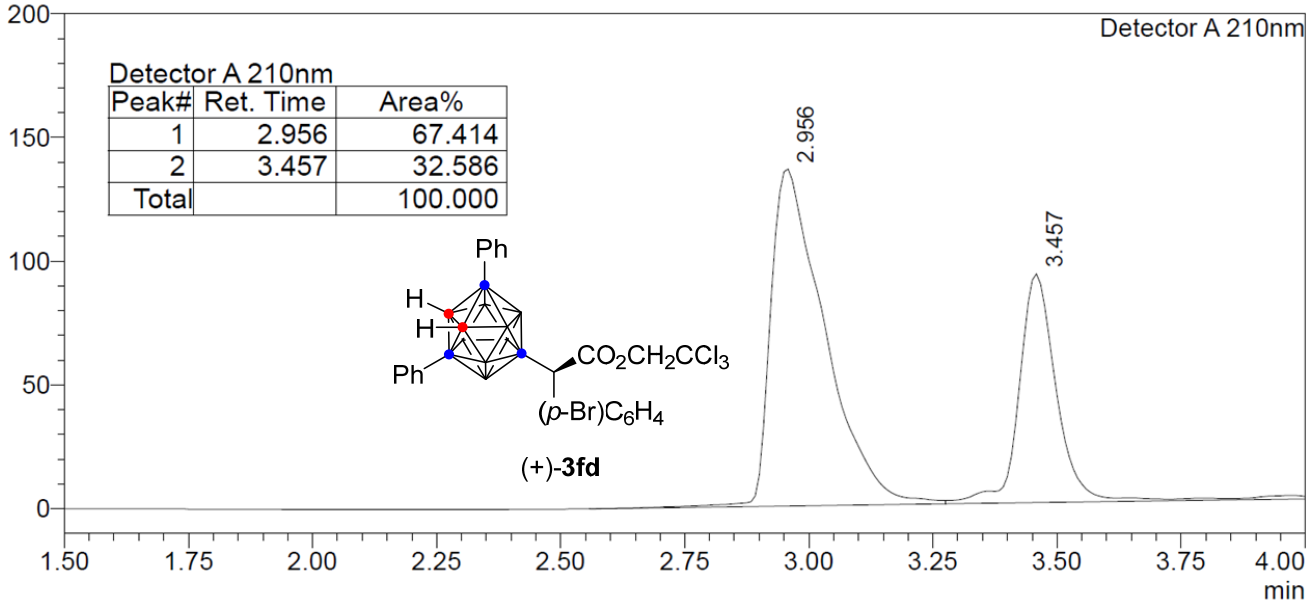

Detector A 210nm
Detector A 210nm
Peak# Ret. Time Area%
1 10.697 11.191
2 11.753 11.423
3 19.056 38.732
4 21.349 38.655
Total 100.000
CO2CH2CCl3
Bn
Bn
(p-Br)C6H4
(±)-3dd
10.697
11.753
19.056
21.349
1500
1000
500
0
0
5
10
15
20
min

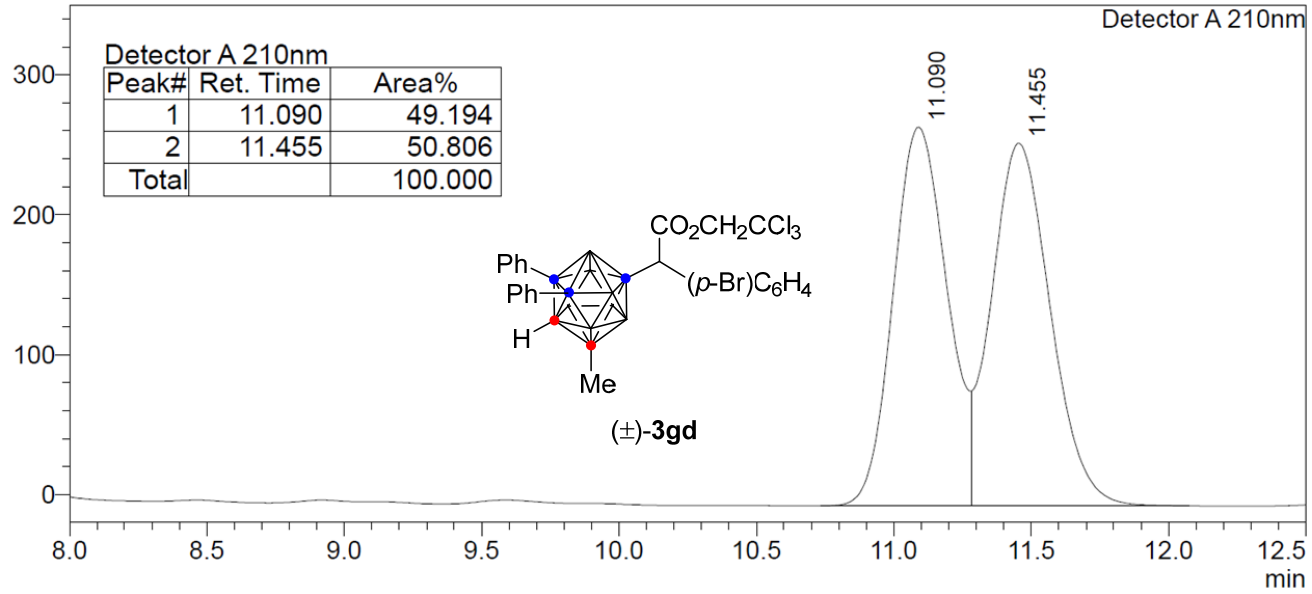

Detector A 210nm
Detector A 210nm
Peak# Ret. Time Area%
1 19.629 0.729
2 21.137 99.271
Total 100.000
CO2CH2CCl3
Bn
Bn
(p-Br)C6H4
(+)-3dd
21.137
19.629
1250
1000
750
500
250
0
0
5
10
15
20
min

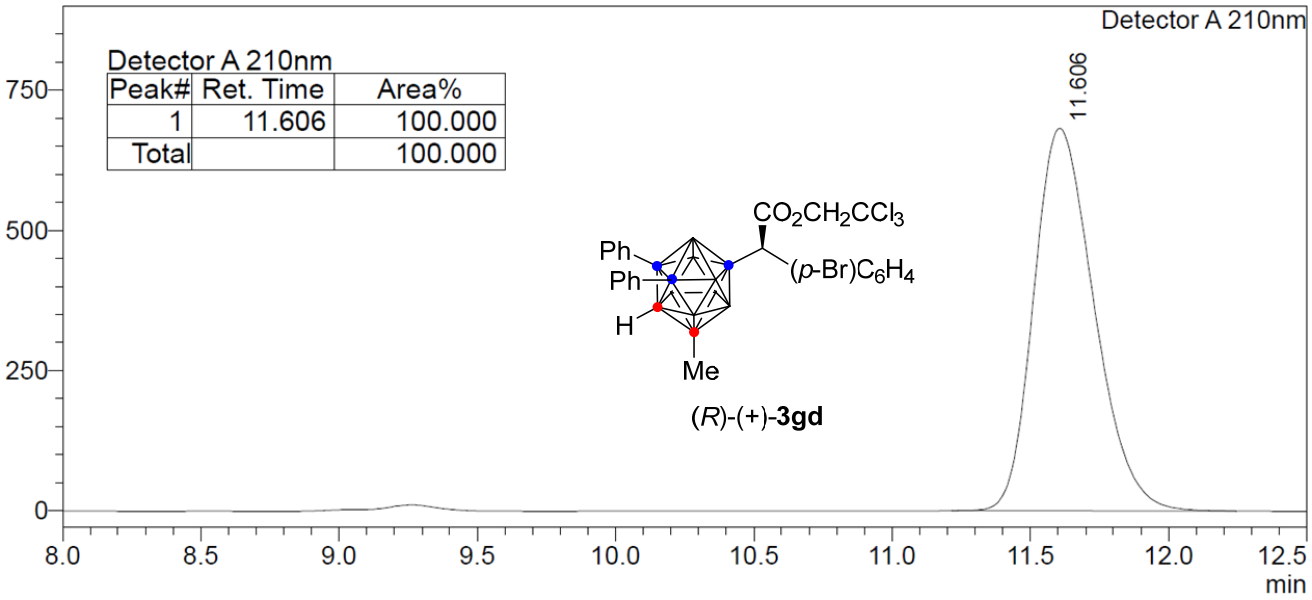

Detector A 210nm
Detector A 210nm
Peak# Ret. Time Area%
1 7.787 13.992
2 8.067 12.211
3 8.450 36.835
4 8.951 36.962
Total 100.000
Me
Me
CO2CH2CCl3
(p-Br)C6H4
(±)-3ed
7.787
8.067
8.450
8.951
100
75
50
25
0
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
min

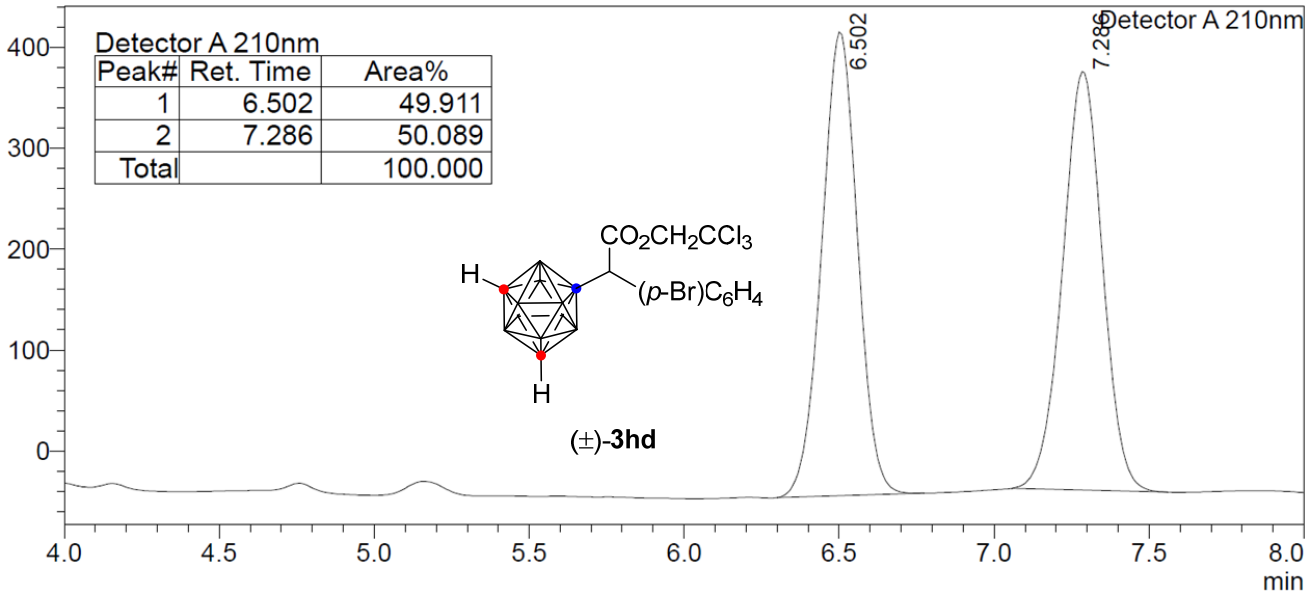

Detector A 210nm
Detector A 210nm
Peak# Ret. Time Area%
1 8.437 0.192
2 8.923 99.808
Total 100.000
Me
Me
CO2CH2CCl3
(p-Br)C6H4
(+)-3ed
8.437
8.923
500
400
300
200
100
0
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
min

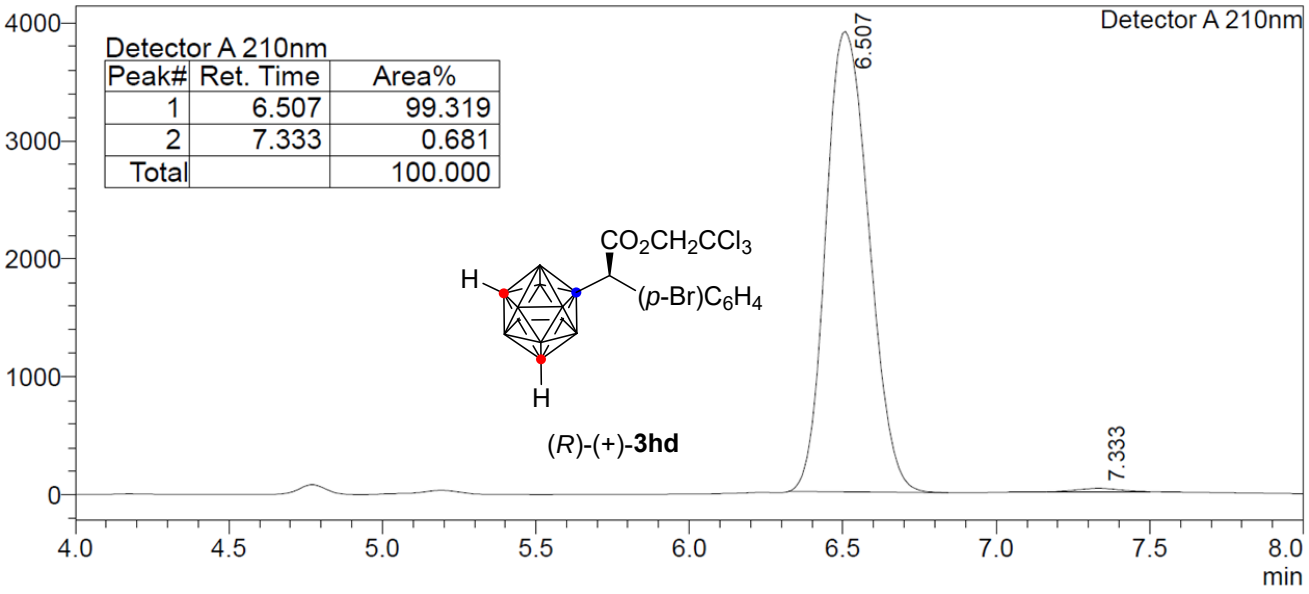

Detector A 210nm
Peak# Ret. Time Area%
1 2.964 48.737
2 3.453 51.263
Total 100.000
2.964
3.453
Ph
H
H
Ph
CO2CH2CCl3
(p-Br)C6H4
(±)-3fd
min

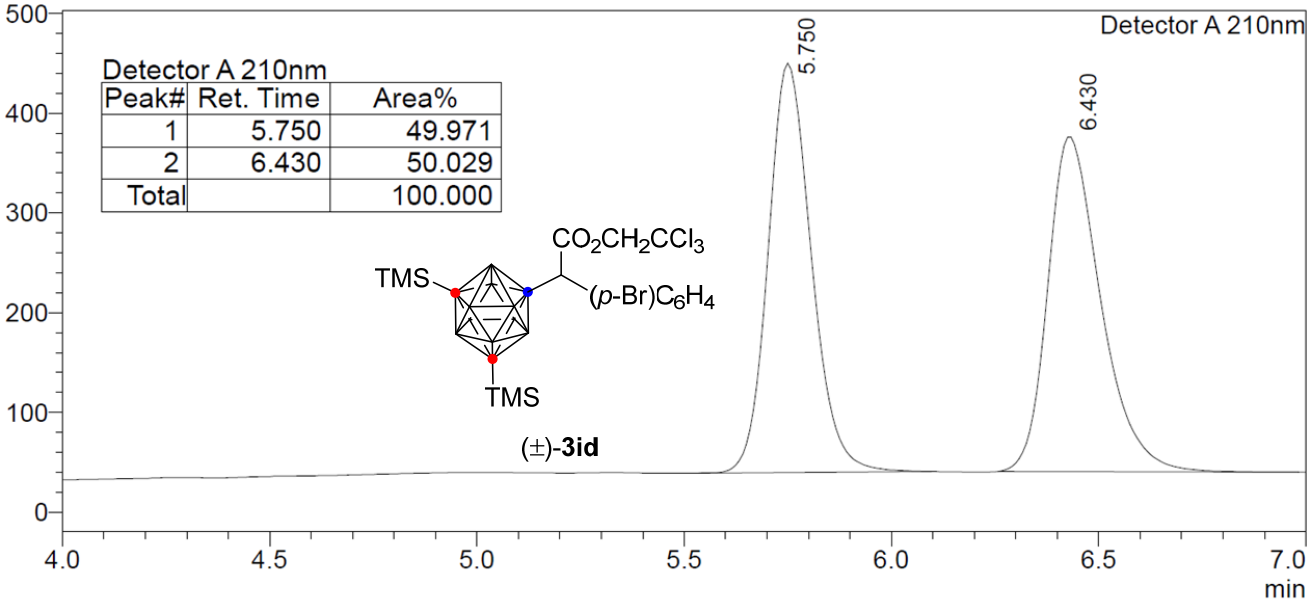

Detector A 210nm
Peak# Ret. Time Area%
1 2.956 67.414
2 3.457 32.586
Total 100.000
2.956
3.457
Ph
H
H
Ph
CO2CH2CCl3
(p-Br)C6H4
(+)-3fd
min

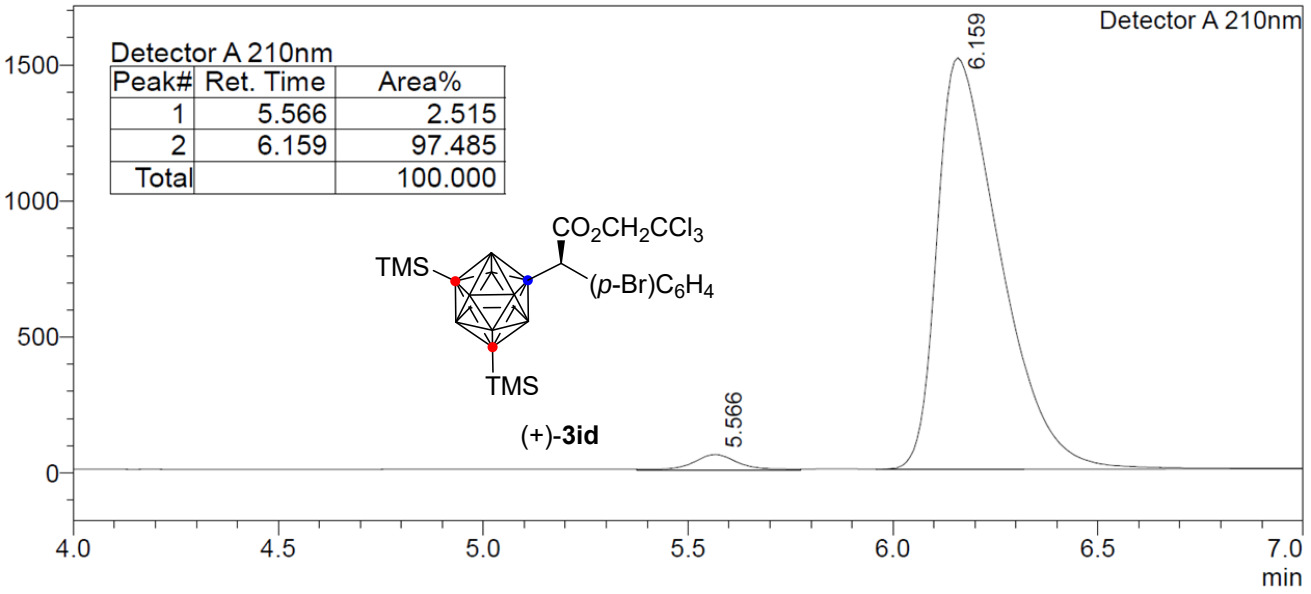

Detector A 210nm
Peak# Ret. Time Area%
1 11.090 49.194
2 11.455 50.806
Total 100.000
11.090
11.455
CO2CH2CCl3
Ph
Ph
H
Me
(p-Br)C6H4
(±)-3gd
300
200
100
0
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
12.0
12.5
min

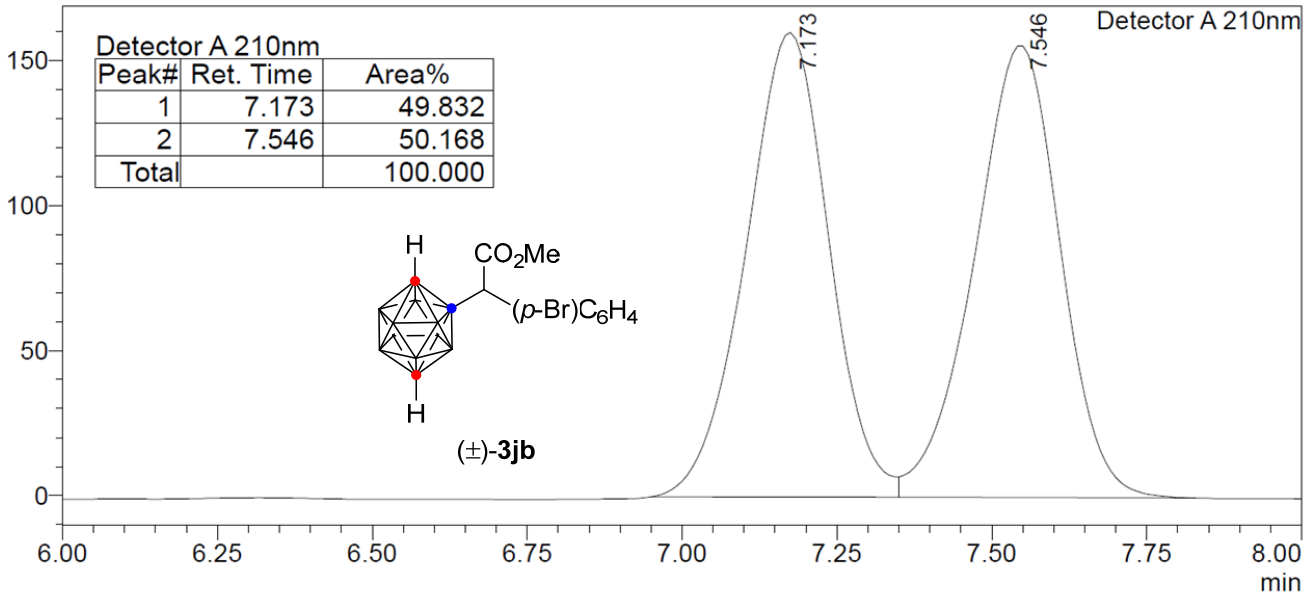

Detector A 210nm
Peak# Ret. Time Area%
1 11.606 100.000
Total 100.000
11.606
CO2CH2CCl3
Ph
Ph
H
Me
(p-Br)C6H4
(R)-(+)-3gd
750
500
250
0
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
12.0
12.5
min

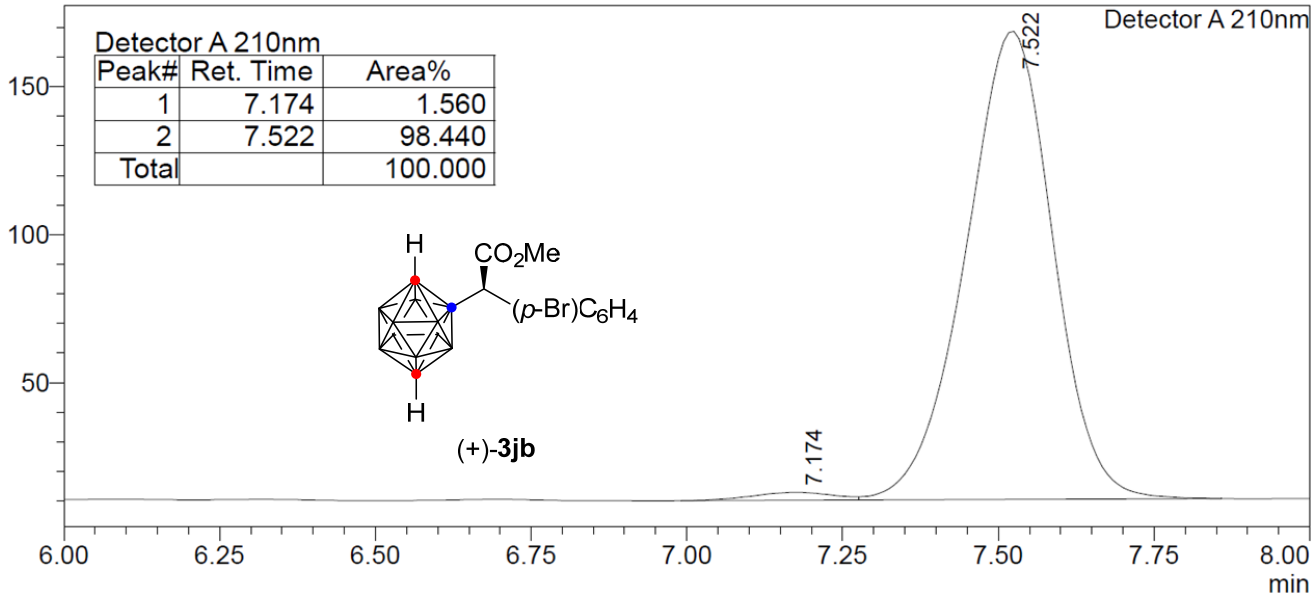

Detector A 210nm
Peak# Ret. Time Area%
1 6.502 49.911
2 7.286 50.089
Total 100.000
6.502
7.286
Detector A 210nm
CO2CH2CCl3
H
(p-Br)C6H4
H
(±)-3hd
400
300
200
100
0
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
min

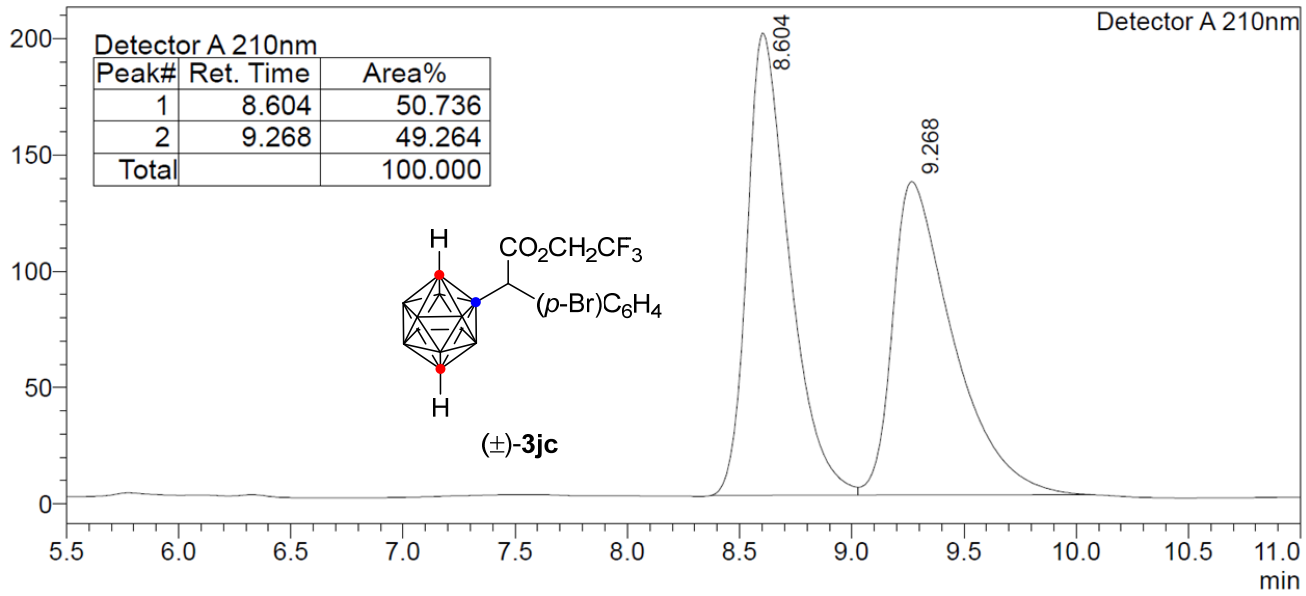

Detector A 210nm
Peak# Ret. Time Area%
1 6.507 99.319
2 7.333 0.681
Total 100.000
6.507
7.333
Detector A 210nm
CO2CH2CCl3
H
(p-Br)C6H4
H
(R)-(+)-3hd
4000
3000
2000
1000
0
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
min

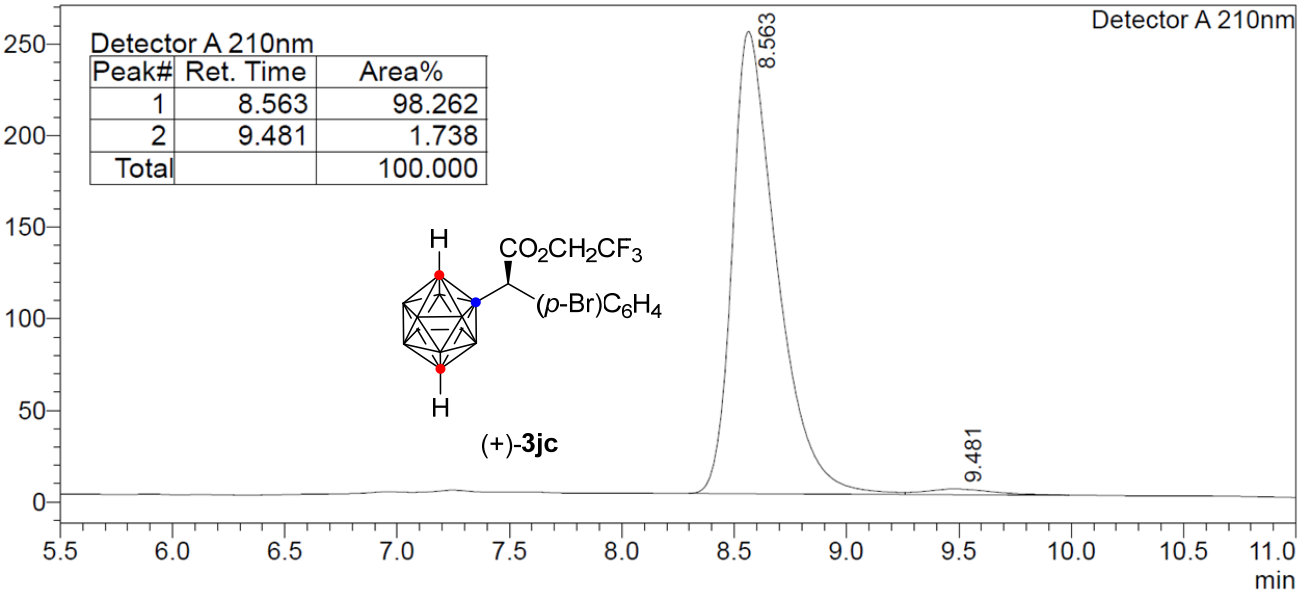

Detector A 210nm
Peak# Ret. Time Area%
1 5.750 49.971
2 6.430 50.029
Total 100.000
5.750
6.430
CO2CH2CCl3
TMS
(p-Br)C6H4
TMS
(±)-3id
500
400
300
200
100
0
4.0
4.5
5.0
5.5
6.0
6.5
7.0
min

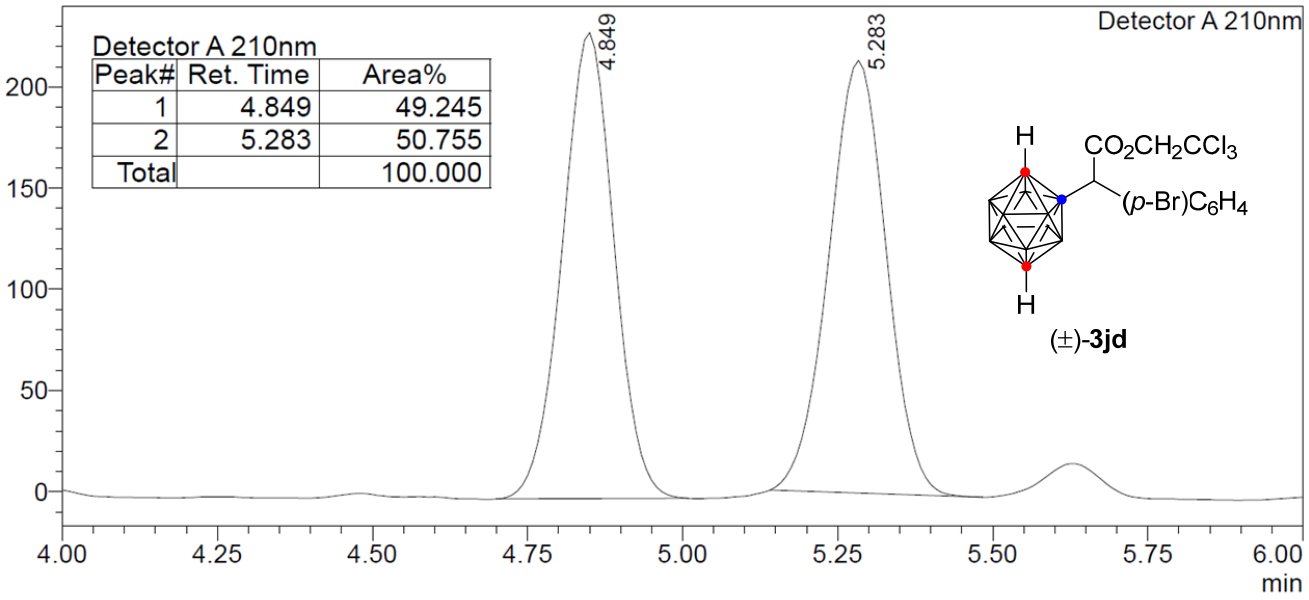

Detector A 210nm
Peak# Ret. Time Area%
1 5.566 2.515
2 6.159 97.485
Total 100.000
6.159
5.566
CO2CH2CCl3
TMS
(p-Br)C6H4
TMS
(+)-3id
1500
1000
500
0
4.0
4.5
5.0
5.5
6.0
6.5
7.0
min

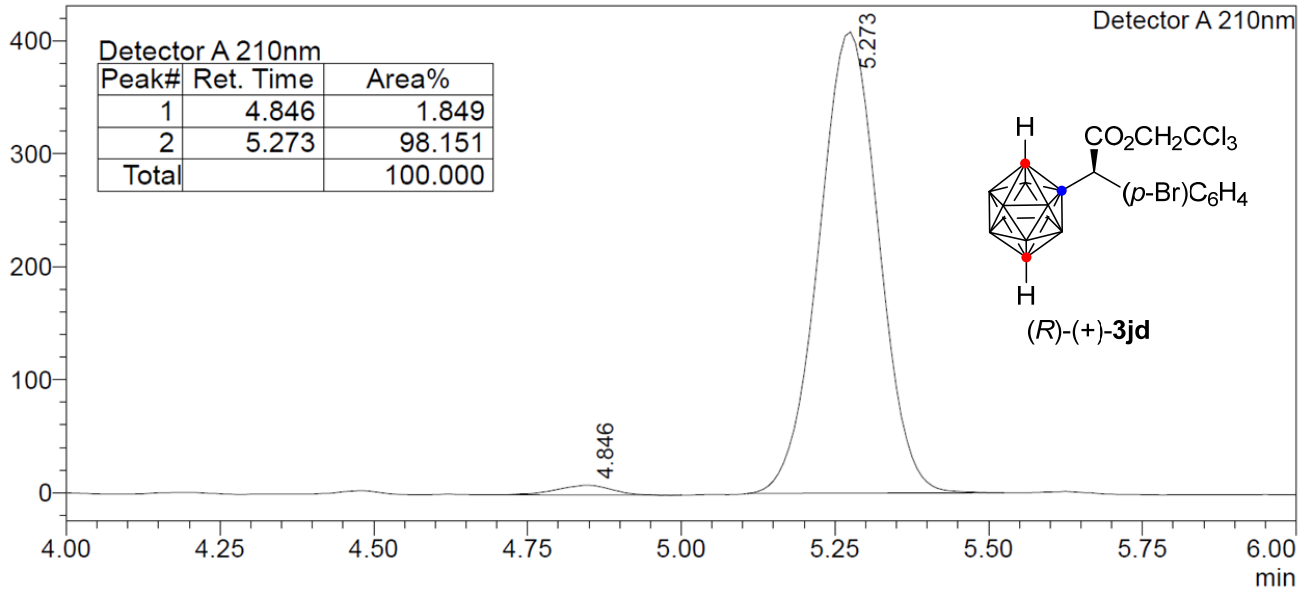

Detector A 210nm
Peak# Ret. Time Area%
1 7.173 49.832
2 7.546 50.168
Total 100.000
7.173
7.546
Detector A 210nm
H
CO2Me
(p-Br)C6H4
H
(±)-3jb
150
100
50
0
6.00
6.25
6.50
6.75
7.00
7.25
7.50
7.75
8.00
min

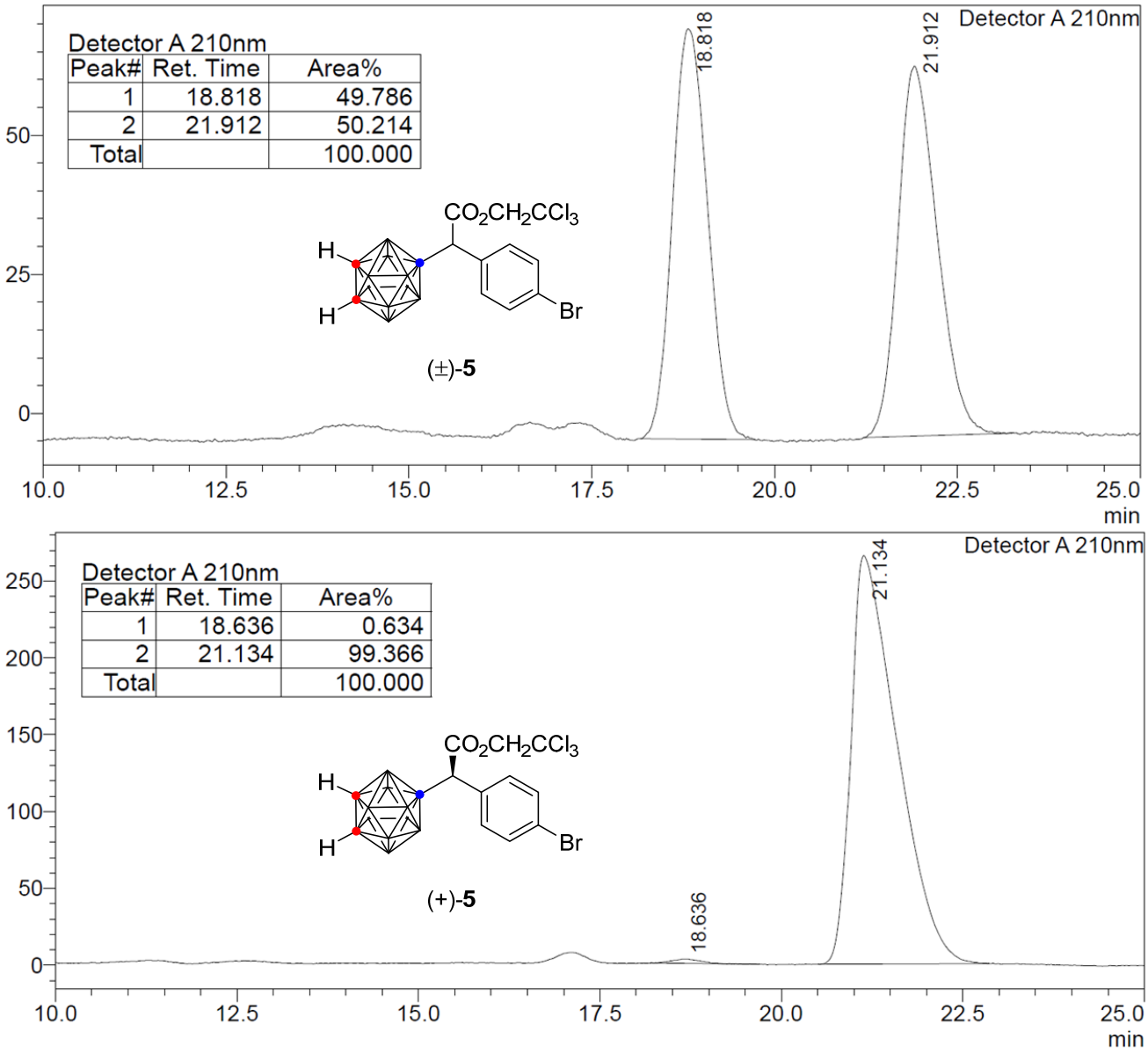

Detector A 210nm
Peak# Ret. Time Area%
1 7.174 1.560
2 7.522 98.440
Total 100.000
7.522
7.174
Detector A 210nm
H
CO2Me
(p-Br)C6H4
H
(+)-3jb
150
100
50
6.00
6.25
6.50
6.75
7.00
7.25
7.50
7.75
8.00
min

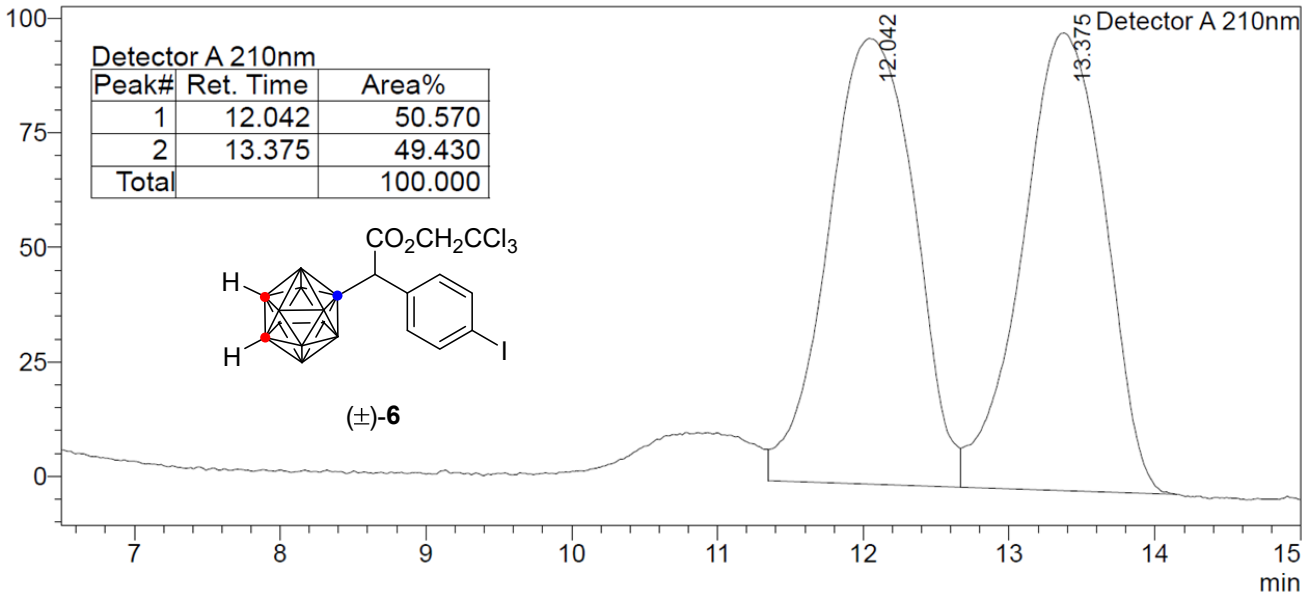

Detector A 210nm
Peak# Ret. Time Area%
1 8.604 50.736
2 9.268 49.264
Total 100.000
8.604
9.268
H
CO2CH2CF3
(p-Br)C6H4
H
(±)-3jc
Detector A 210nm
200
150
100
50
0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
min

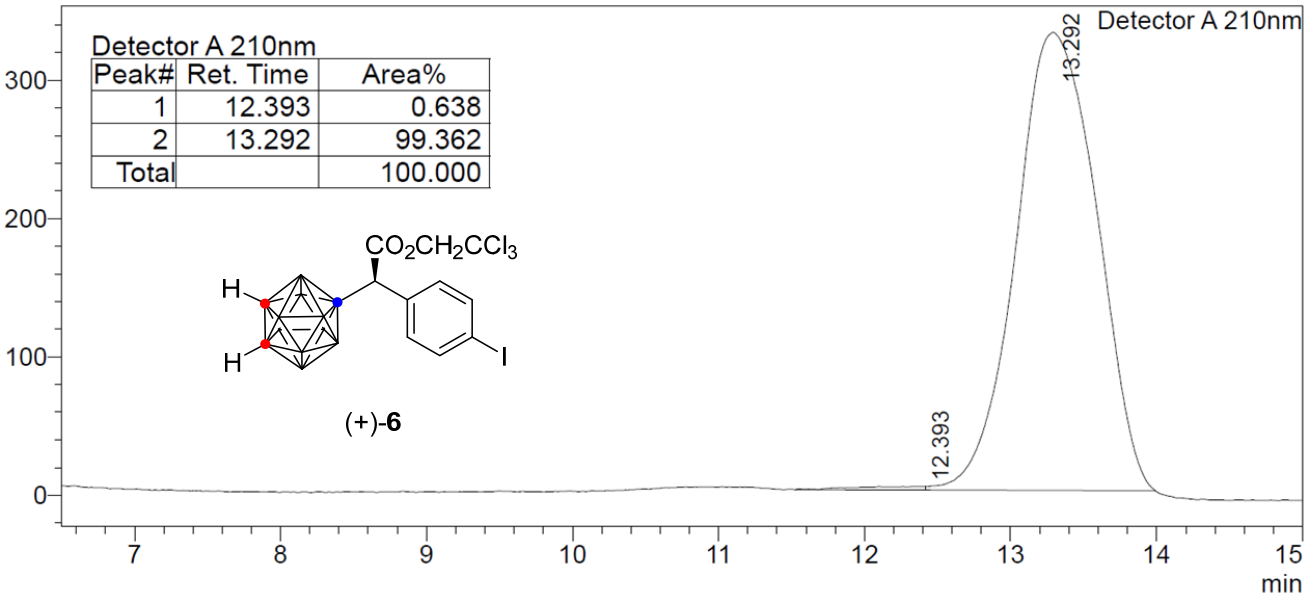

Detector A 210nm
Peak# Ret. Time Area%
1 8.563 98.262
2 9.481 1.738
Total 100.000
8.563
9.481
H
CO2CH2CF3
(p-Br)C6H4
H
(+)-3jc
Detector A 210nm
250
200
150
100
50
0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
min

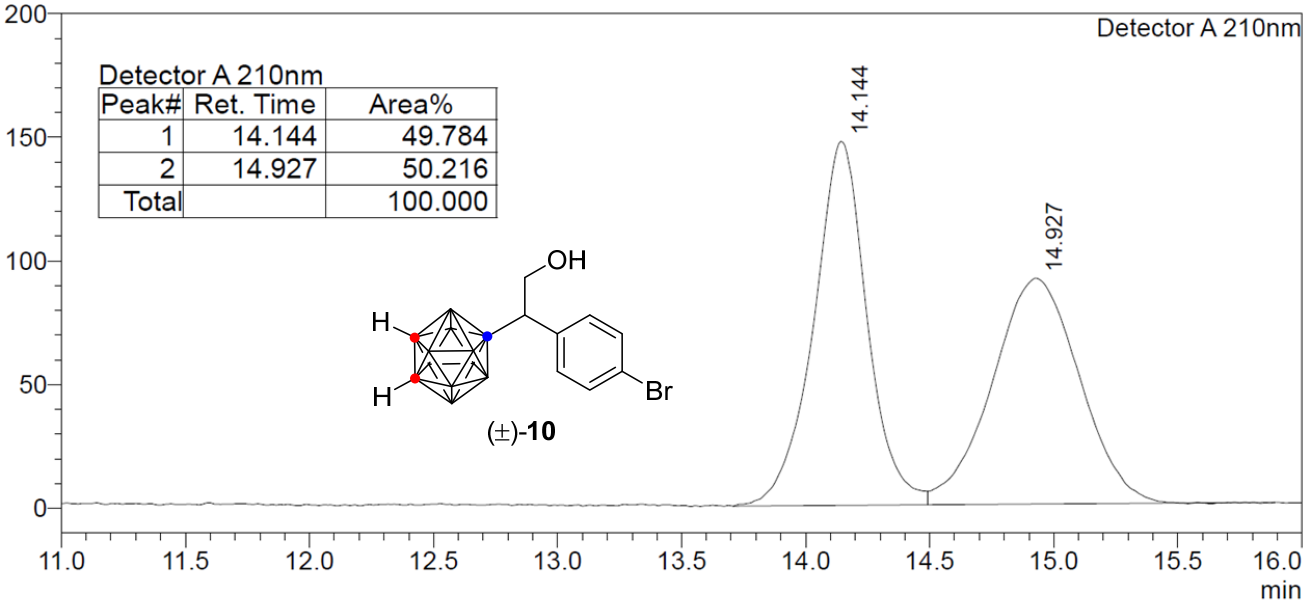

Detector A 210nm
Peak# Ret. Time Area%
1 4.849 49.245
2 5.283 50.755
Total 100.000
4.849
5.283
Detector A 210nm
H
CO2CH2CCl3
(p-Br)C6H4
H
(±)-3jd
200
150
100
50
0
4.00
4.25
4.50
4.75
5.00
5.25
5.50
5.75
6.00
min

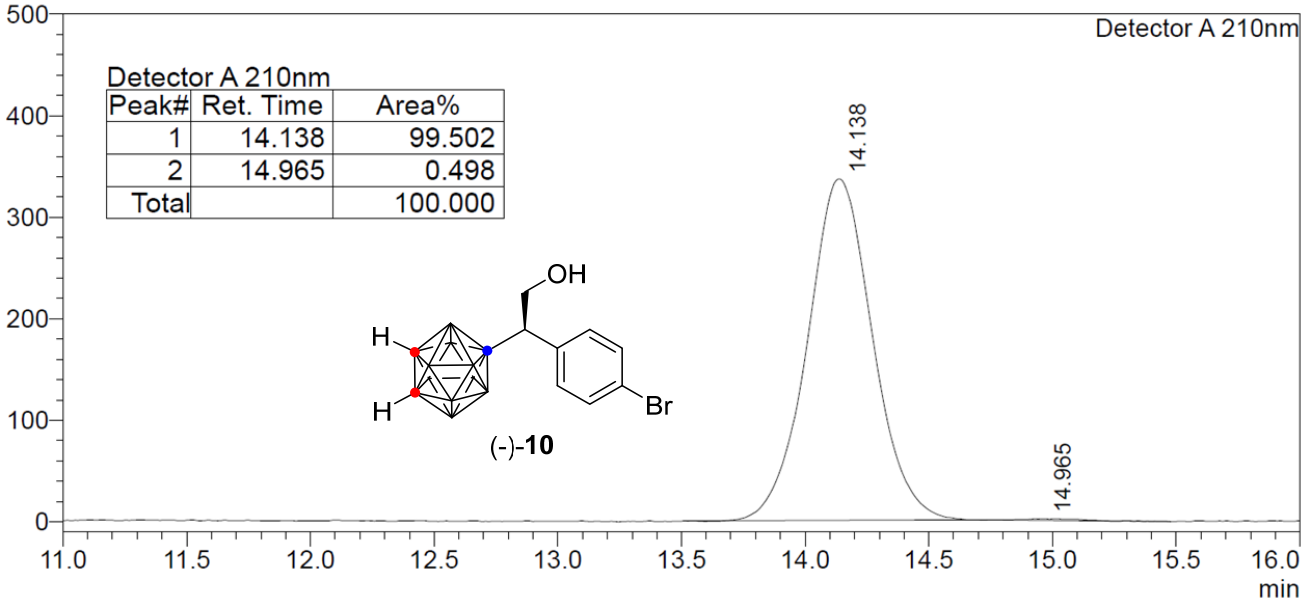

Detector A 210nm
Peak# Ret. Time Area%
1 4.846 1.849
2 5.273 98.151
Total 100.000
5.273
4.846
Detector A 210nm
H
CO2CH2CCl3
(p-Br)C6H4
H
(R)-(+)-3jd
400
300
200
100
0
4.00
4.25
4.50
4.75
5.00
5.25
5.50
5.75
6.00
min

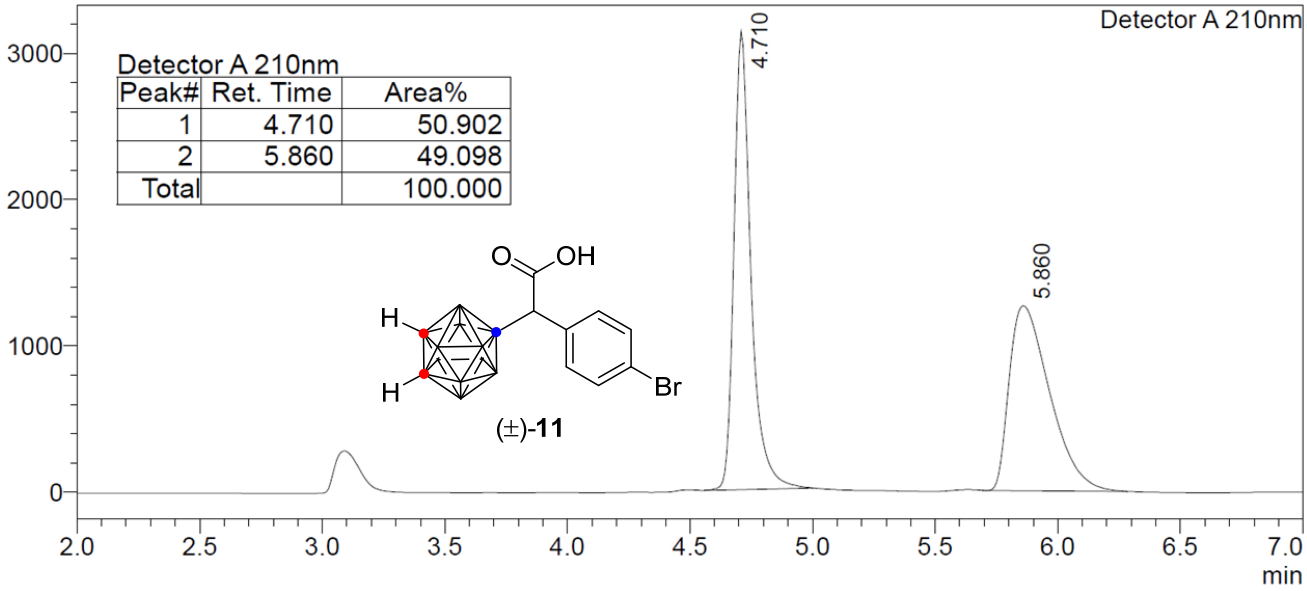

Detector A 210nm
Peak# Ret. Time Area%
1 18.818 49.786
2 21.912 50.214
Total 100.000
18.818
21.912
Detector A 210nm
50
25
0
10.0
12.5
15.0
17.5
20.0
22.5
25.0
min
CO2CH2CCl3
H
H
Br
(±)-5
Detector A 210nm
Peak# Ret. Time Area%
1 18.636 0.634
2 21.134 99.366
Total 100.000
21.134
18.636
Detector A 210nm
250
200
150
100
50
0
10.0
12.5
15.0
17.5
20.0
22.5
25.0
min
CO2CH2CCl3
H
H
Br
(+)-5

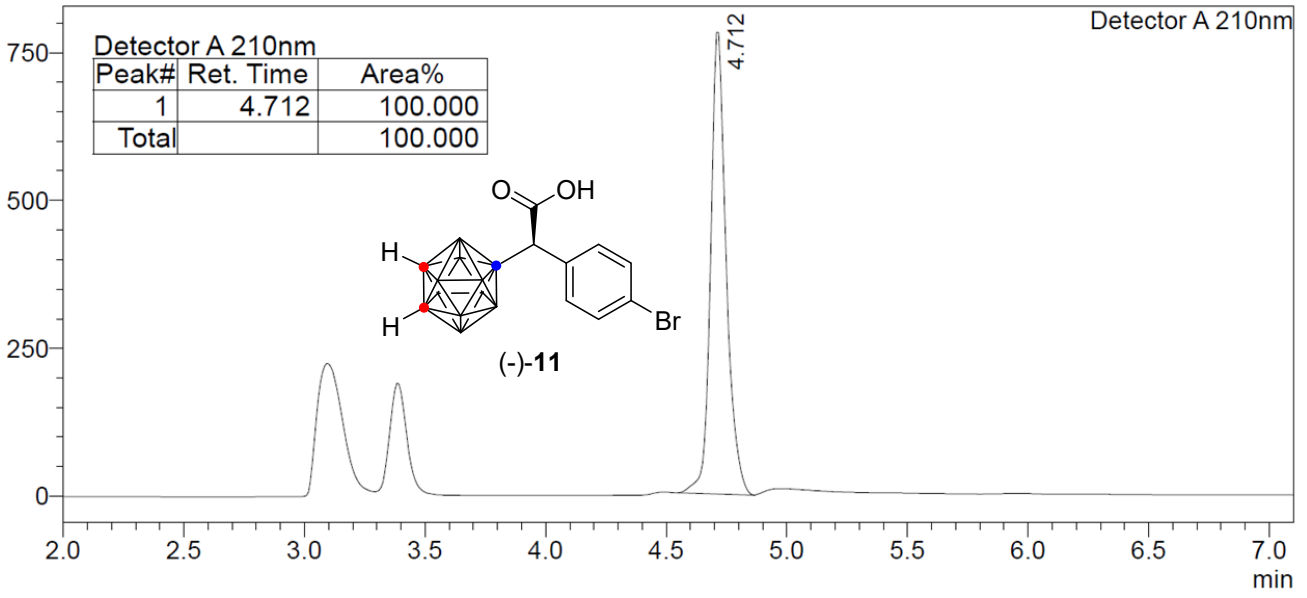

Detector A 210nm
Peak# Ret. Time Area%
1 12.042 50.570
2 13.375 49.430
Total 100.000
12.042
13.375
Detector A 210nm
CO2CH2CCl3
H
H
I
(±)-6
100
75
50
25
0
7
8
9
10
11
12
13
14
15
min

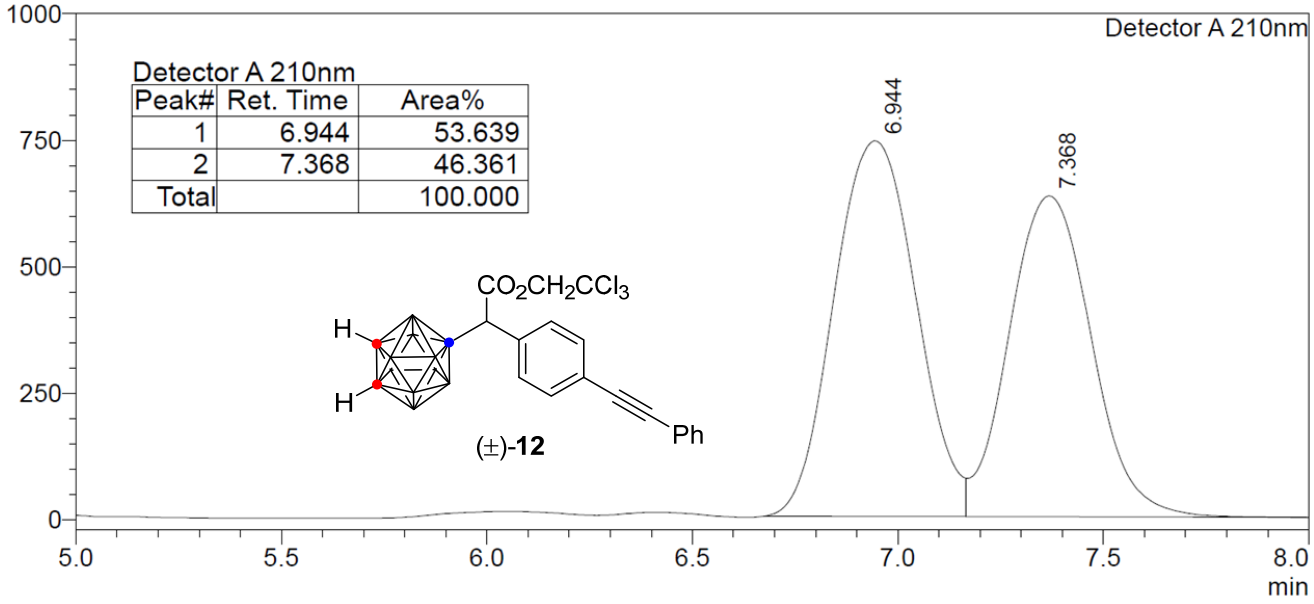

Detector A 210nm
Peak# Ret. Time Area%
1 12.393 0.638
2 13.292 99.362
Total 100.000
13.292
12.393
Detector A 210nm
CO2CH2CCl3
H
H
I
(+)-6
300
200
100
0
7
8
9
10
11
12
13
14
15
min

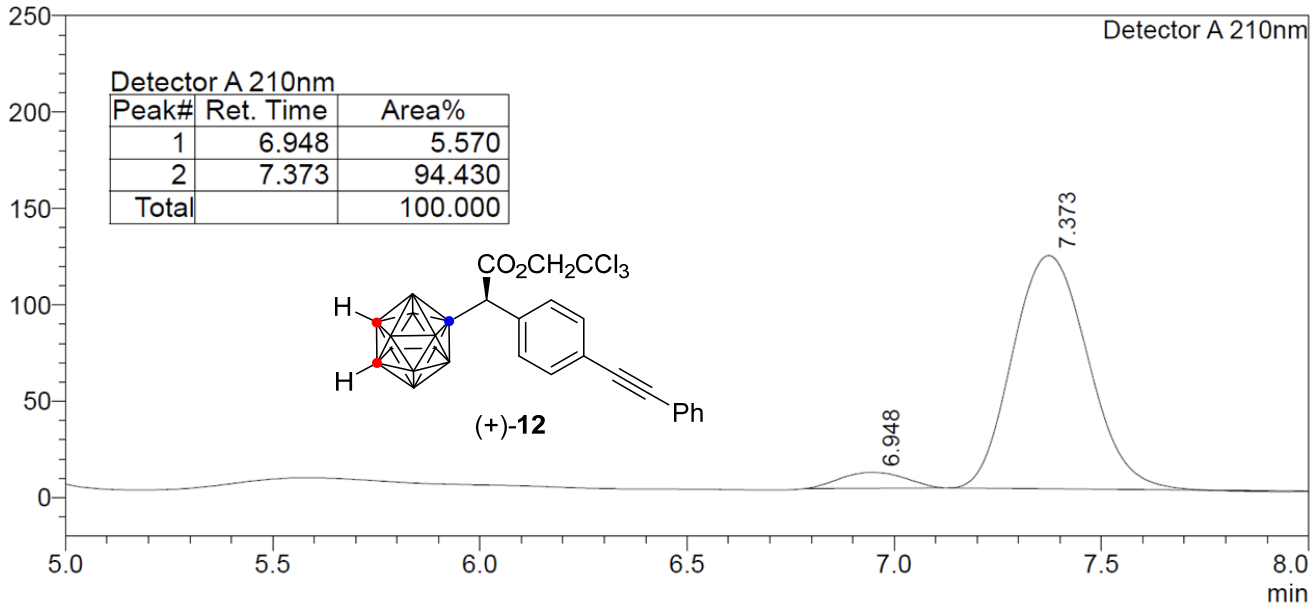

Detector A 210nm
Detector A 210nm
Peak# Ret. Time Area%
1 14.144 49.784
2 14.927 50.216
Total 100.000
14.144
14.927
OH
H
H
Br
(±)-10
200
150
100
50
0
11.0
11.5
12.0
12.5
13.0
13.5
14.0
14.5
15.0
15.5
16.0
min

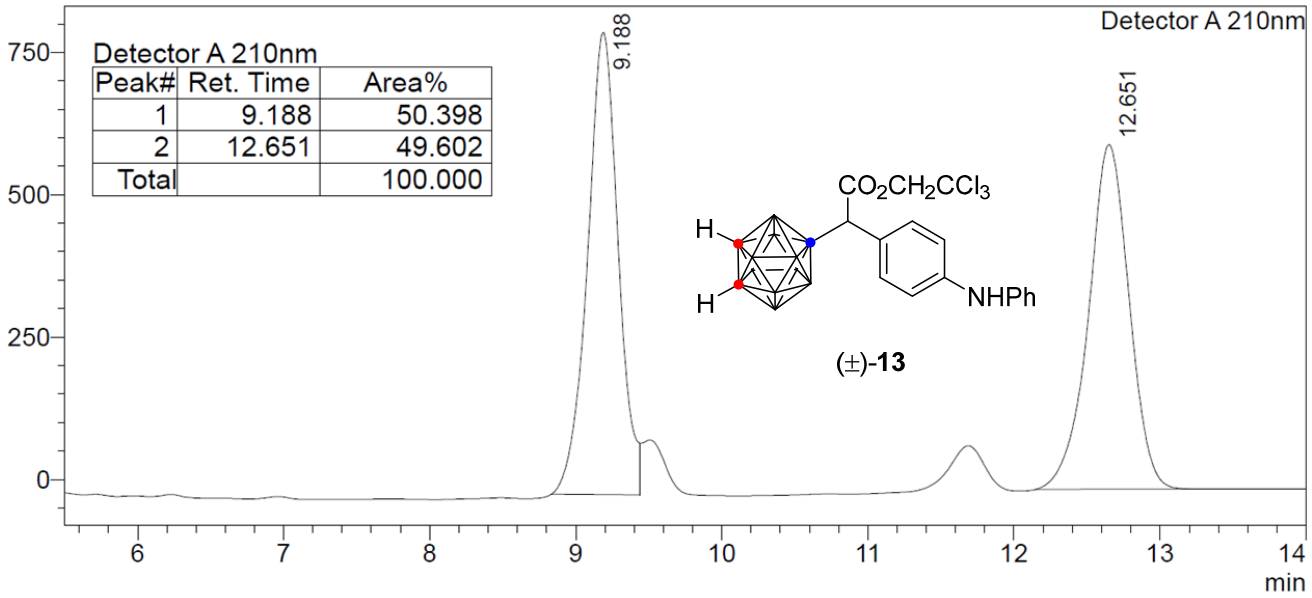

Detector A 210nm
Detector A 210nm
Peak# Ret. Time Area%
1 14.138 99.502
2 14.965 0.498
Total 100.000
14.138
14.965
OH
H
H
Br
(-)-10
500
400
300
200
100
0
11.0
11.5
12.0
12.5
13.0
13.5
14.0
14.5
15.0
15.5
16.0
min

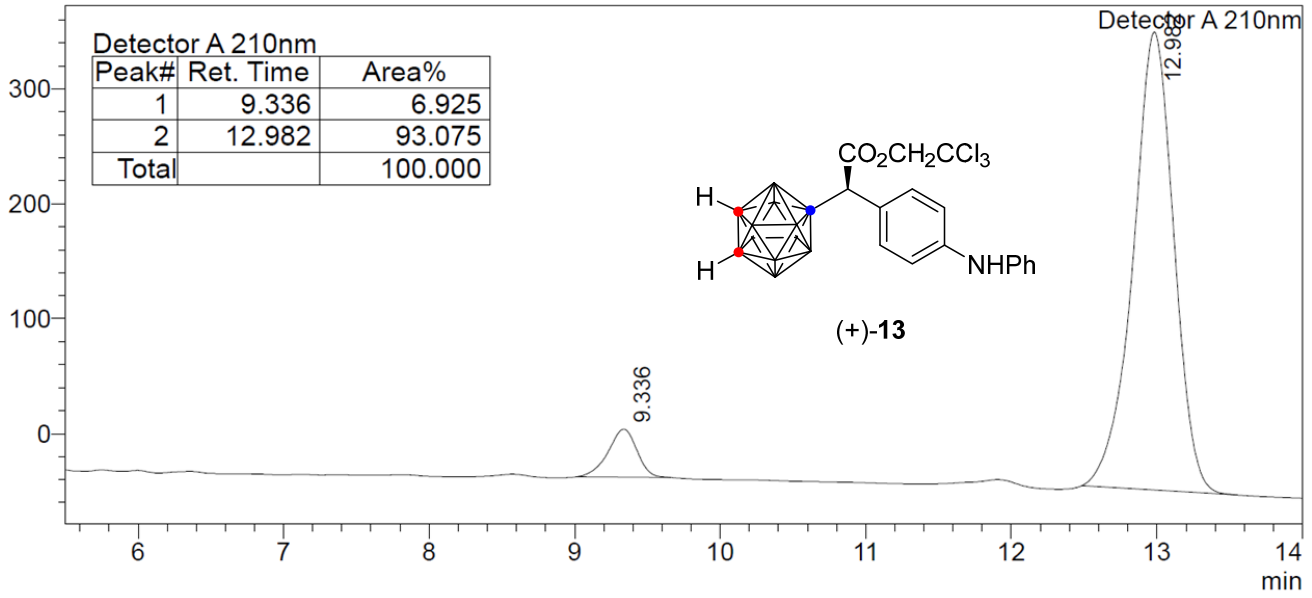

Detector A 210nm
4.710
5.860
Detector A 210nm
Peak# Ret. Time Area%
1 4.710 50.902
2 5.860 49.098
Total 100.000
O
OH
H
H
Br
(±)-11
3000
2000
1000
0
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
min


Detector A 210nm
4.712
Detector A 210nm
Peak# Ret. Time Area%
1 4.712 100.000
Total 100.000
O
OH
H
H
Br
(-)-11
750
500
250
0
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
min


Detector A 210nm
Detector A 210nm
Peak# Ret. Time Area%
1 6.944 53.639
2 7.368 46.361
Total 100.000
6.944
7.368
CO2CH2CCl3
H
H
Ph
(±)-12
1000
750
500
250
0
5.0
5.5
6.0
6.5
7.0
7.5
8.0
min

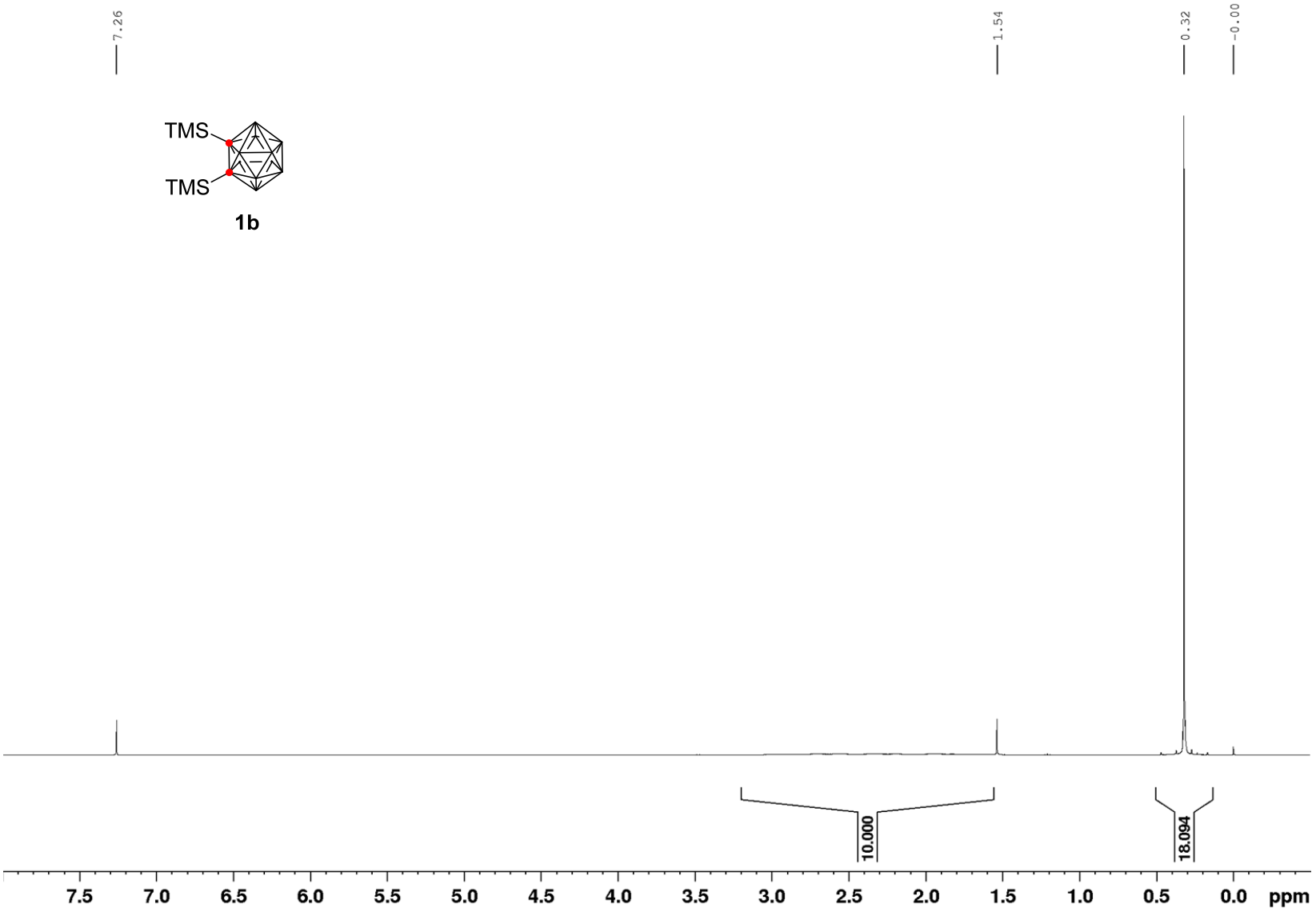

Detector A 210nm
Detector A 210nm
Peak# Ret. Time Area%
1 6.948 5.570
2 7.373 94.430
Total 100.000
6.948
7.373
CO2CH2CCl3
H
H
Ph
(+)-12
250
200
150
100
50
0
5.0
5.5
6.0
6.5
7.0
7.5
8.0
min


Detector A 210nm
Peak# Ret. Time Area%
1 9.188 50.398
2 12.651 49.602
Total 100.000
9.188
12.651
CO2CH2CCl3
H
H
NHPh
(±)-13
750
500
250
0
6
7
8
9
10
11
12
13
14
min

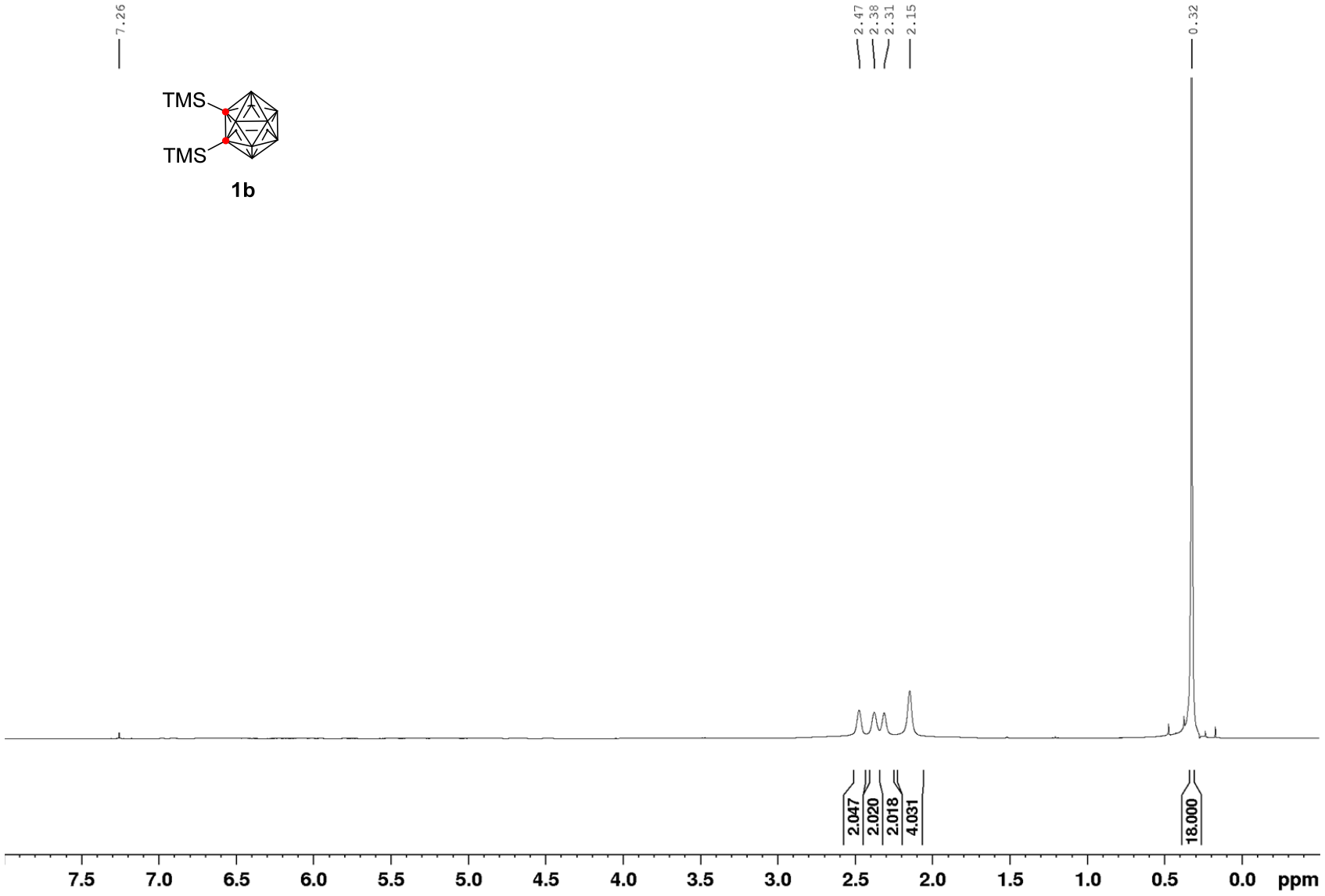

Detector A 210nm
Peak# Ret. Time Area%
1 9.336 6.925
2 12.982 93.075
Total 100.000
12.982
9.336
CO2CH2CCl3
H
H
NHPh
(+)-13
300
200
100
0
6
7
8
9
10
11
12
13
14
min

16. ^{1}H, ^{13}C, ^{11}B, and ^{19}F NMR Data

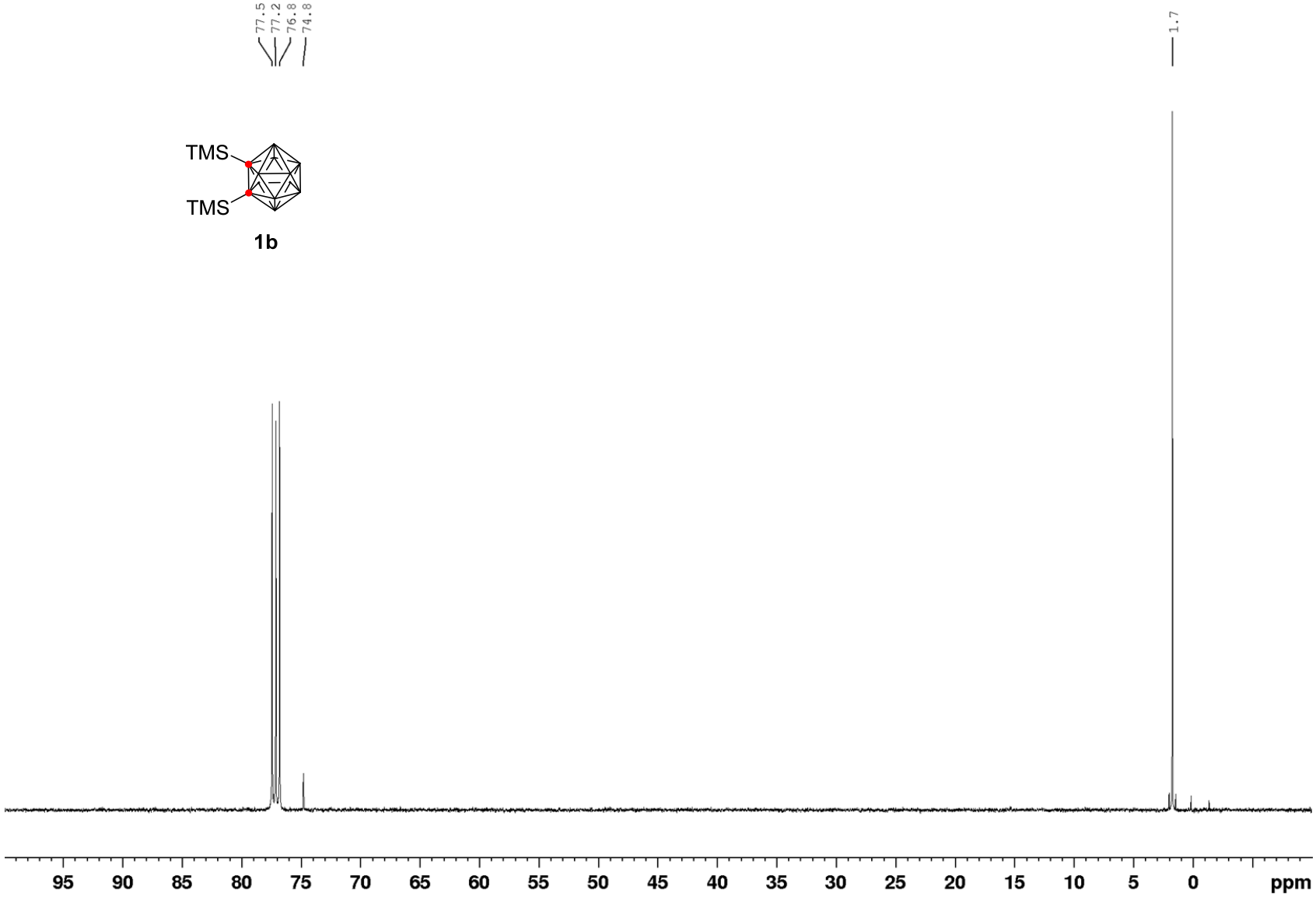
^{1}H NMR (400 MHz, $CDCl_3$)



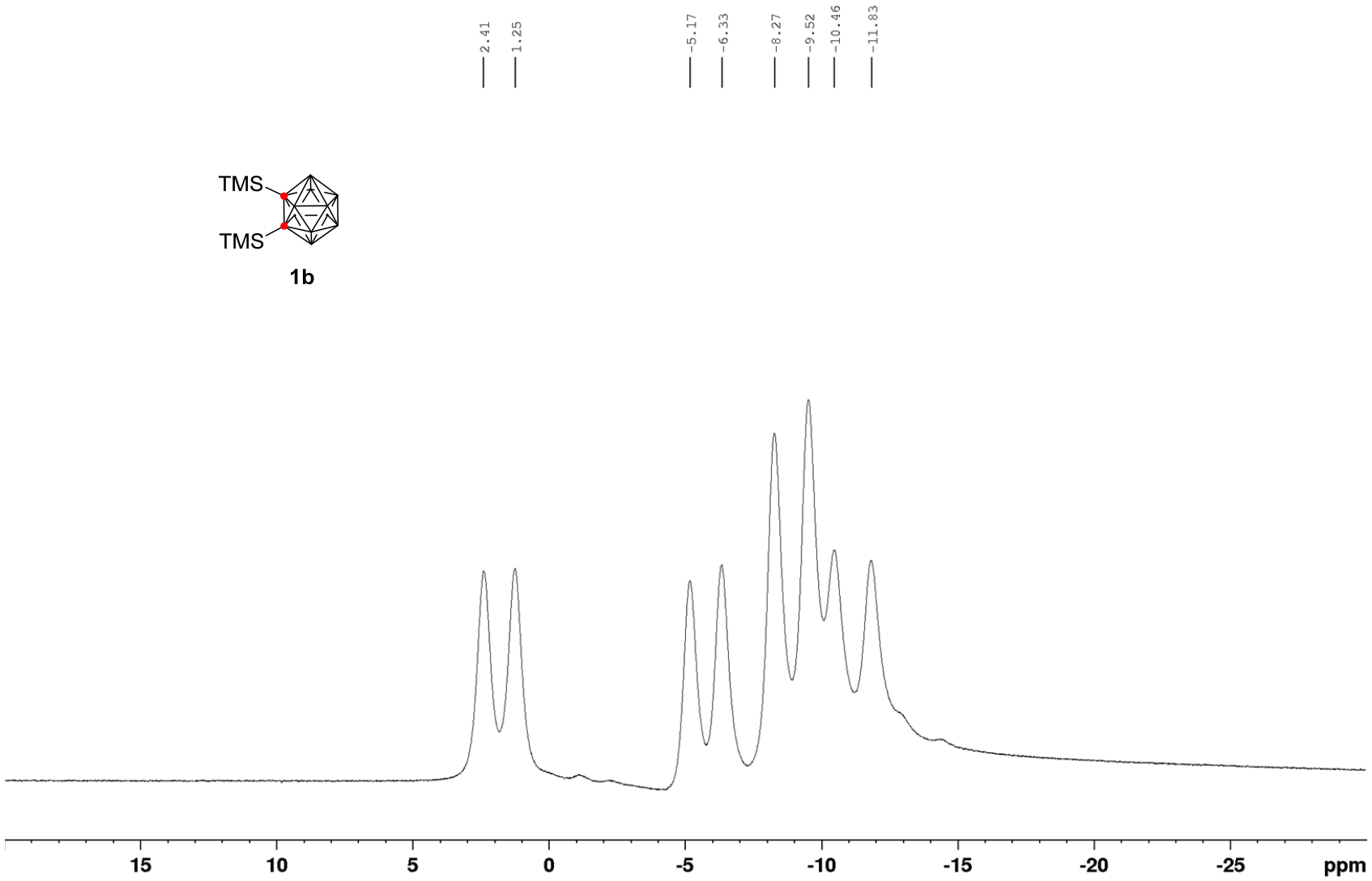
$^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$)



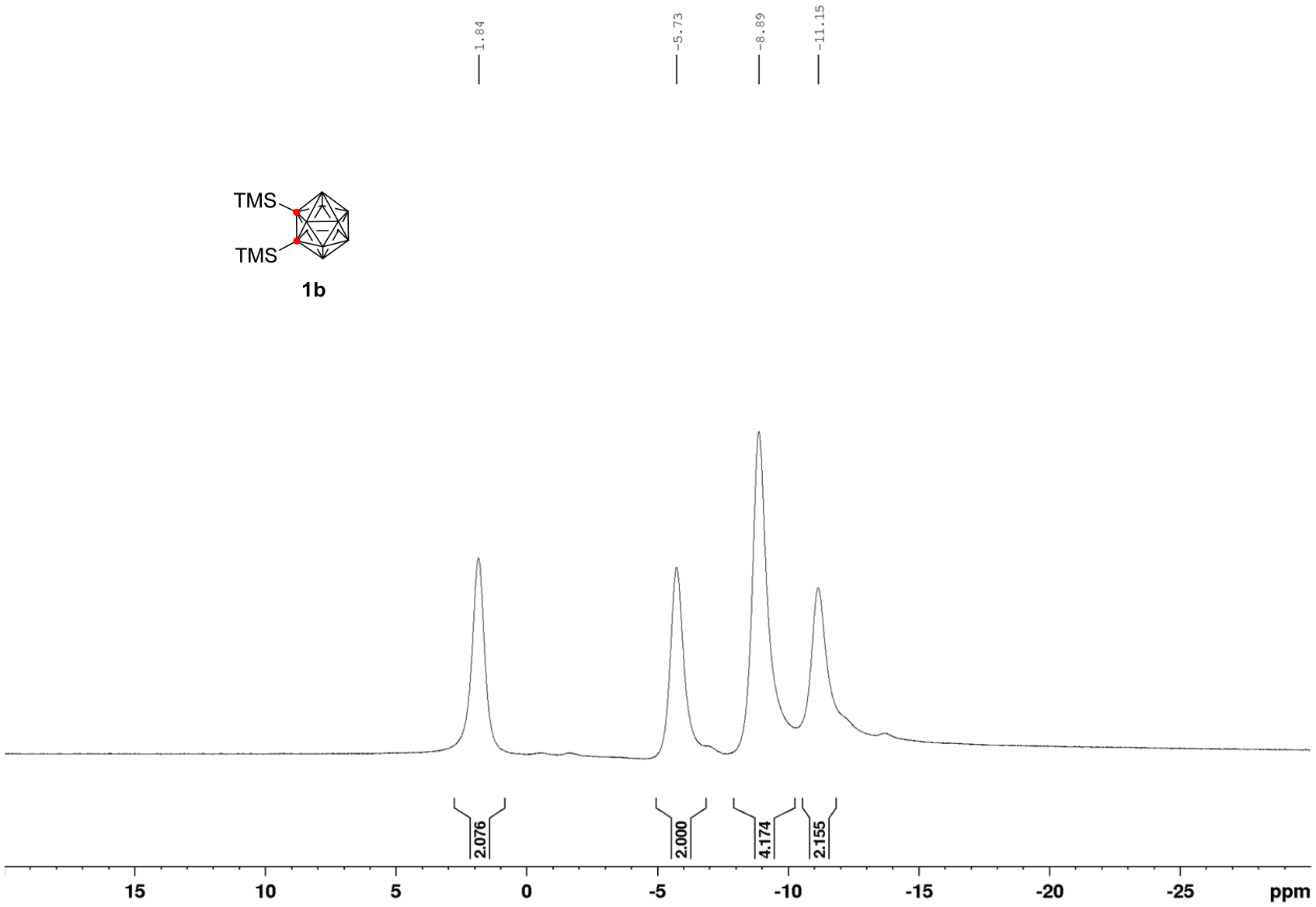
^{13}C NMR (100 MHz, $CDCl_3$)



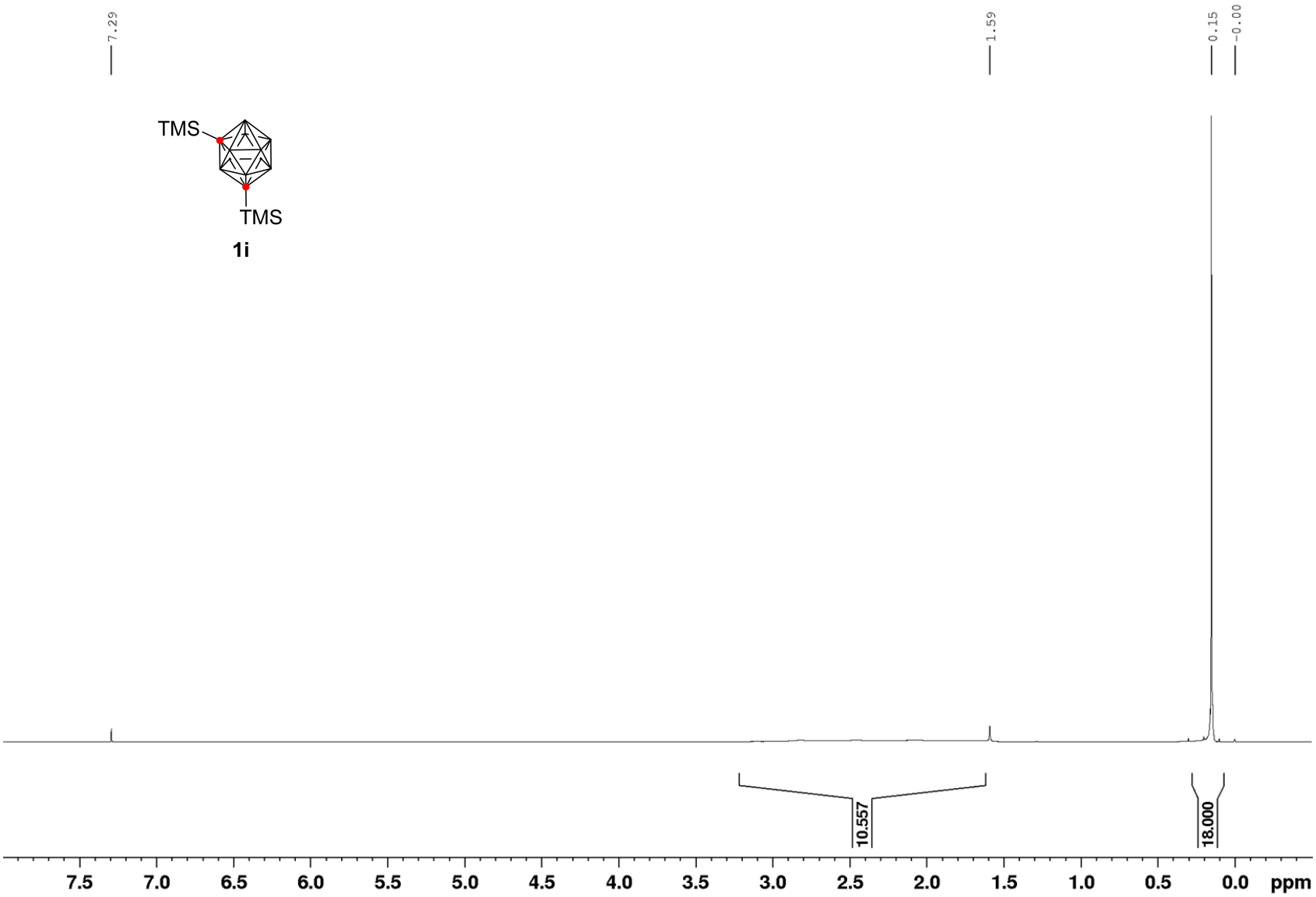
^{11}B NMR (128 MHz, $CDCl_3$)



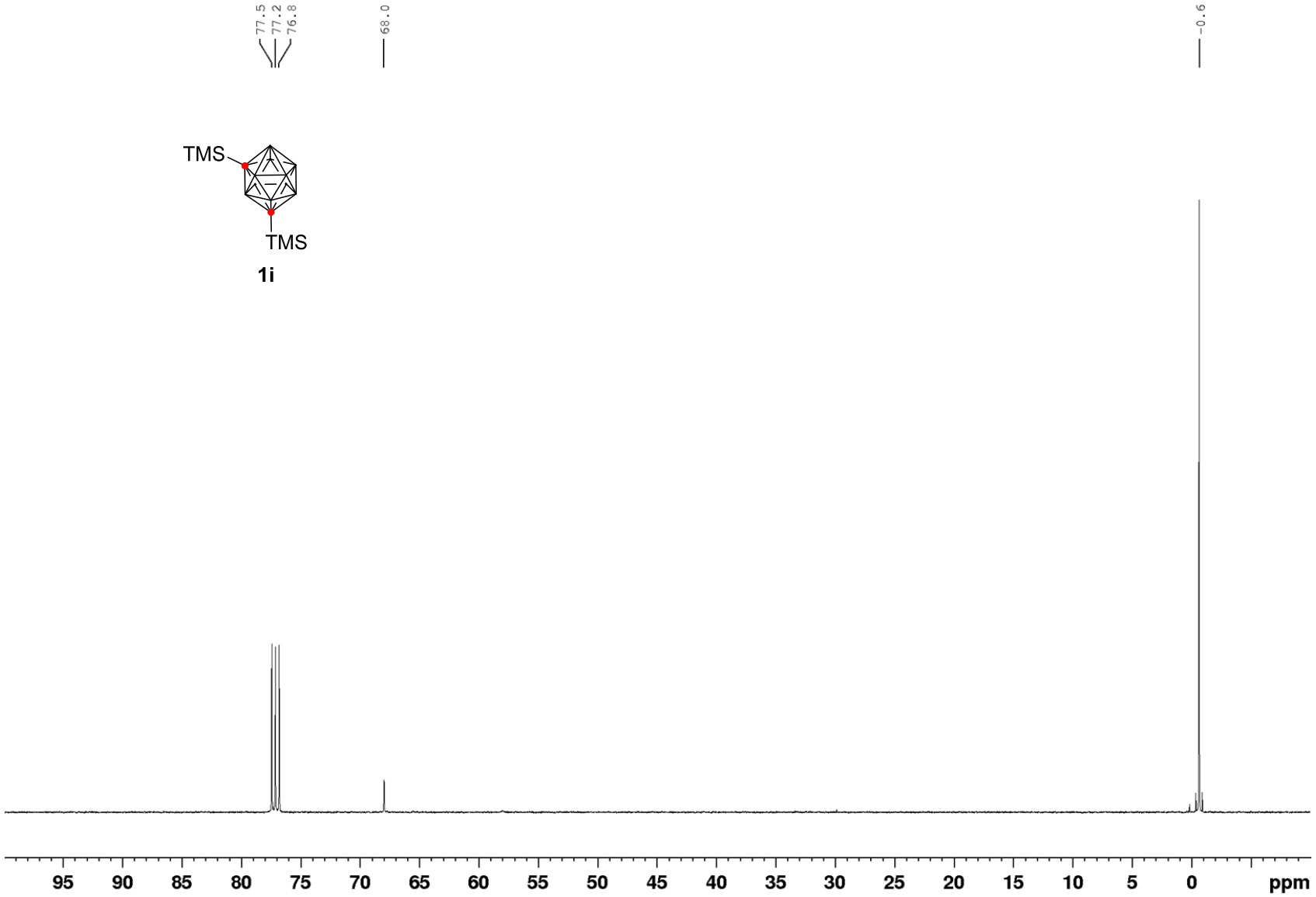
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

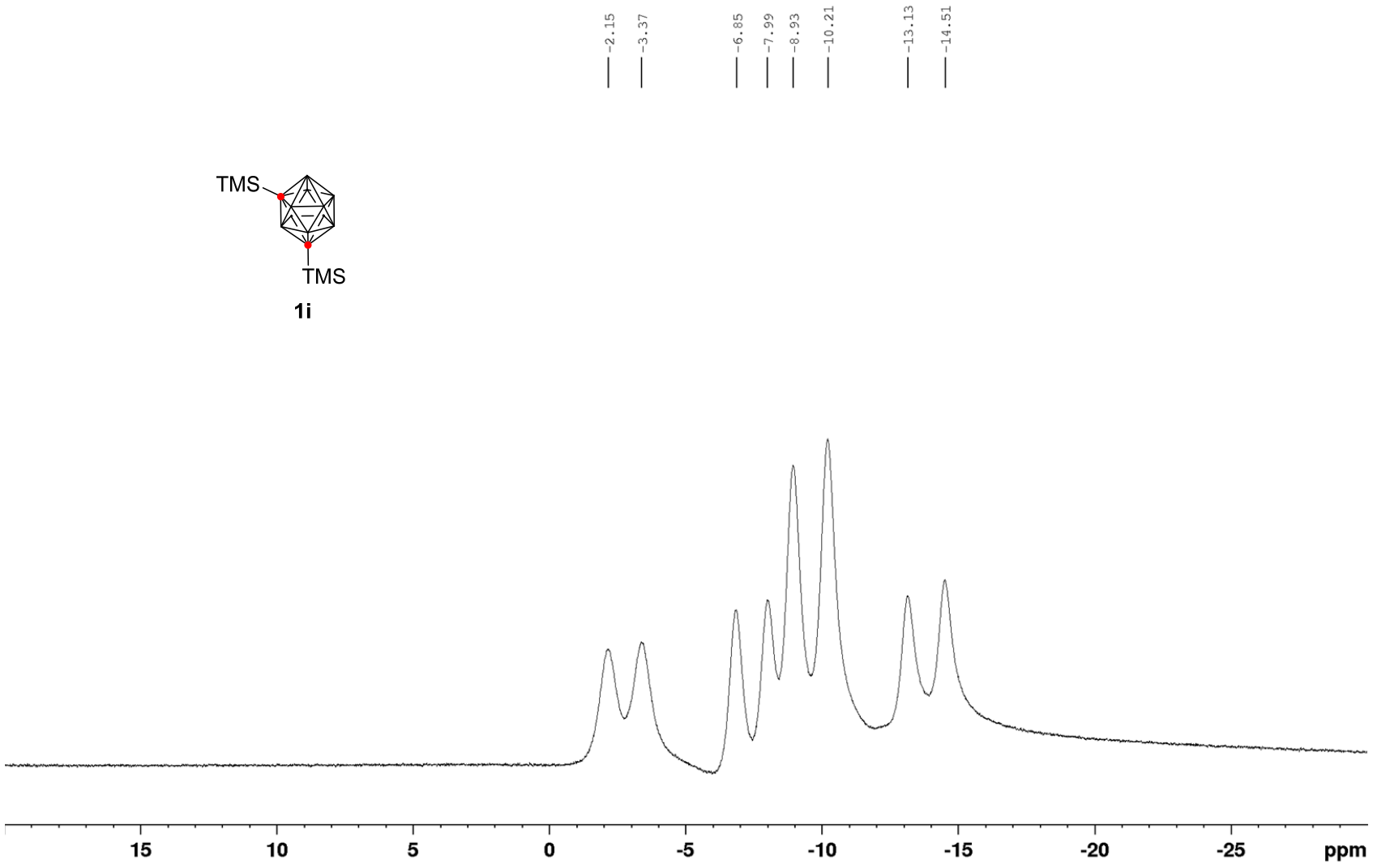


^{13}C NMR (100 MHz, $CDCl_3$)



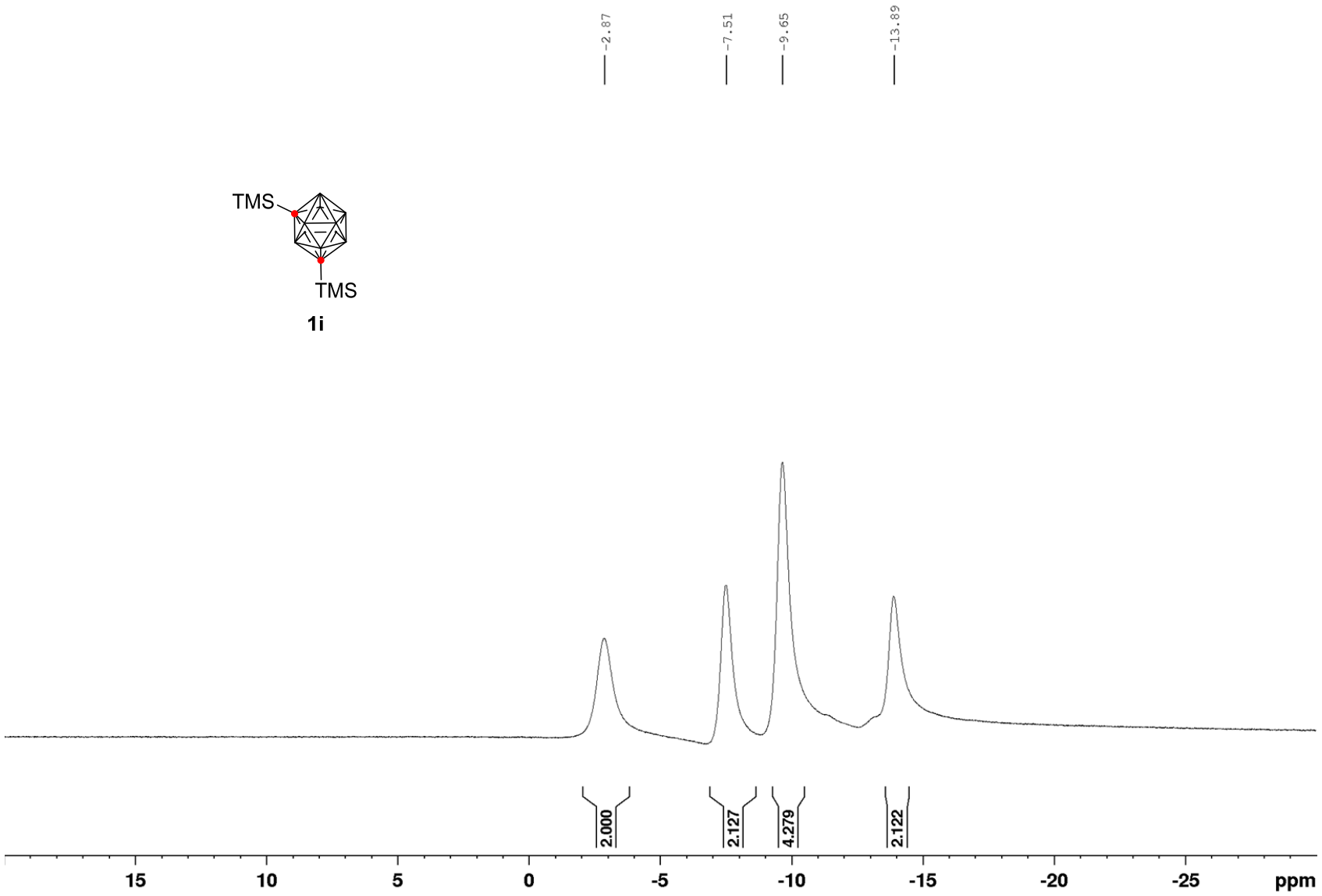
1i

^{11}B NMR (128 MHz, $CDCl_3$)

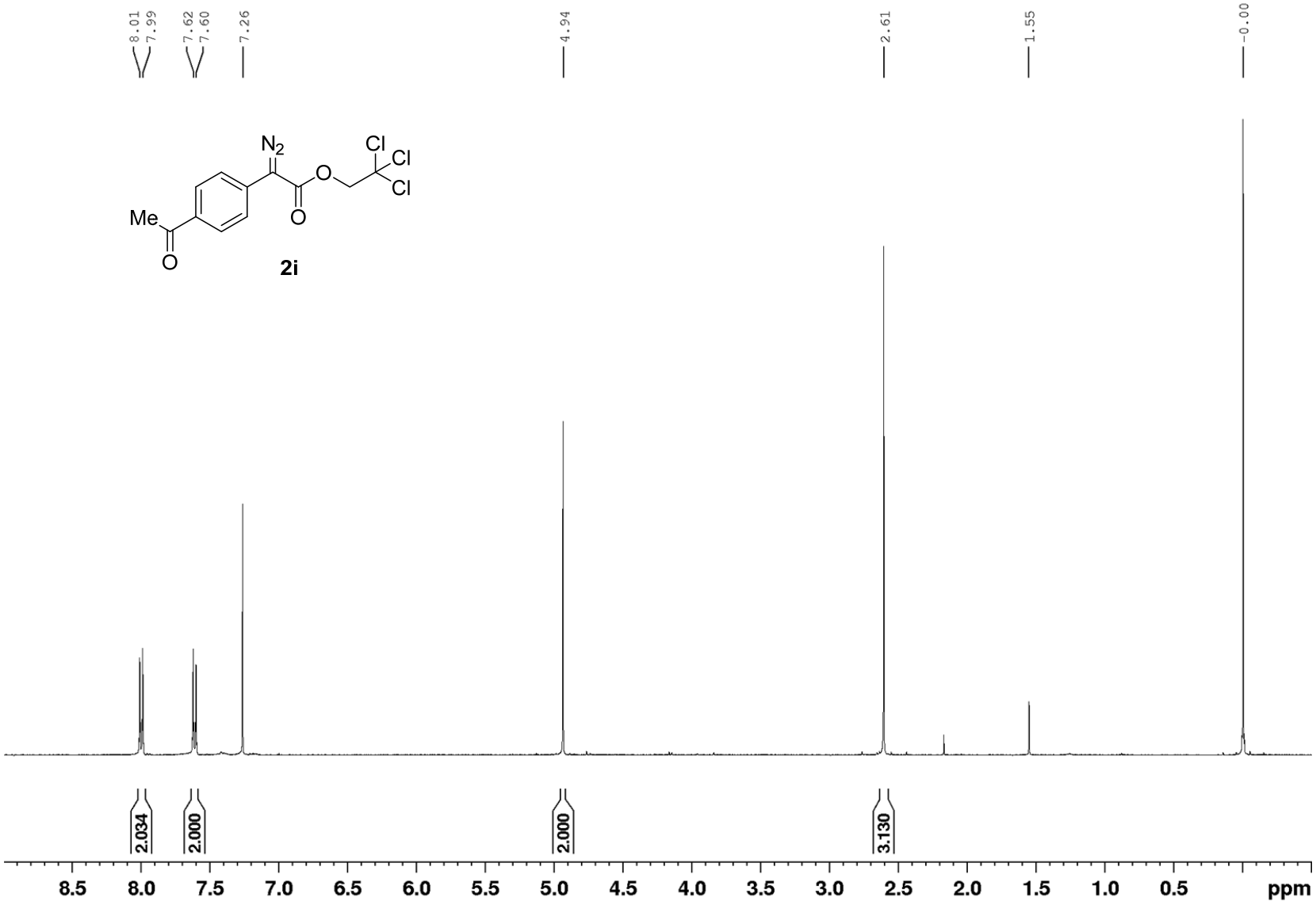


1i

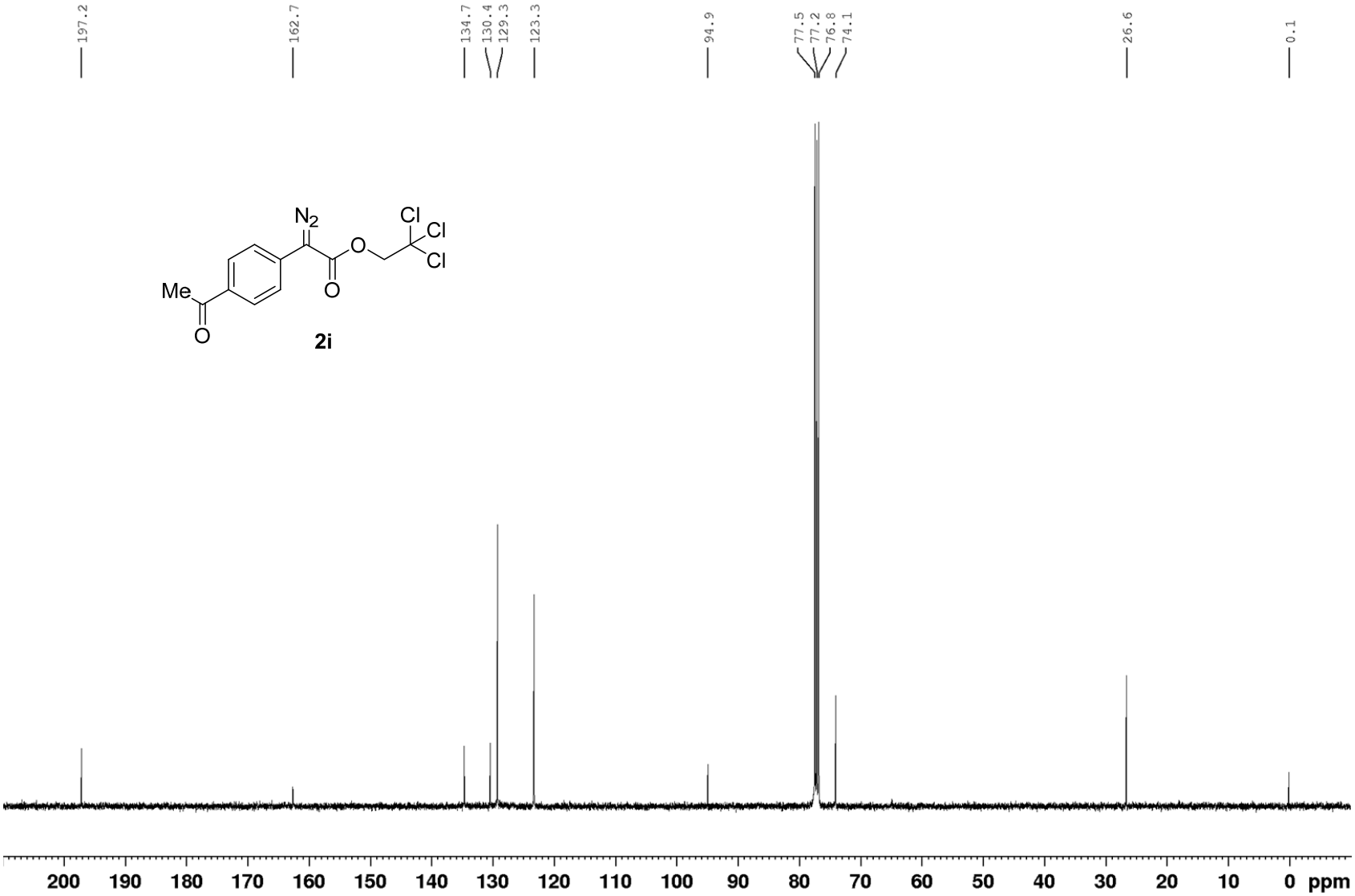
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

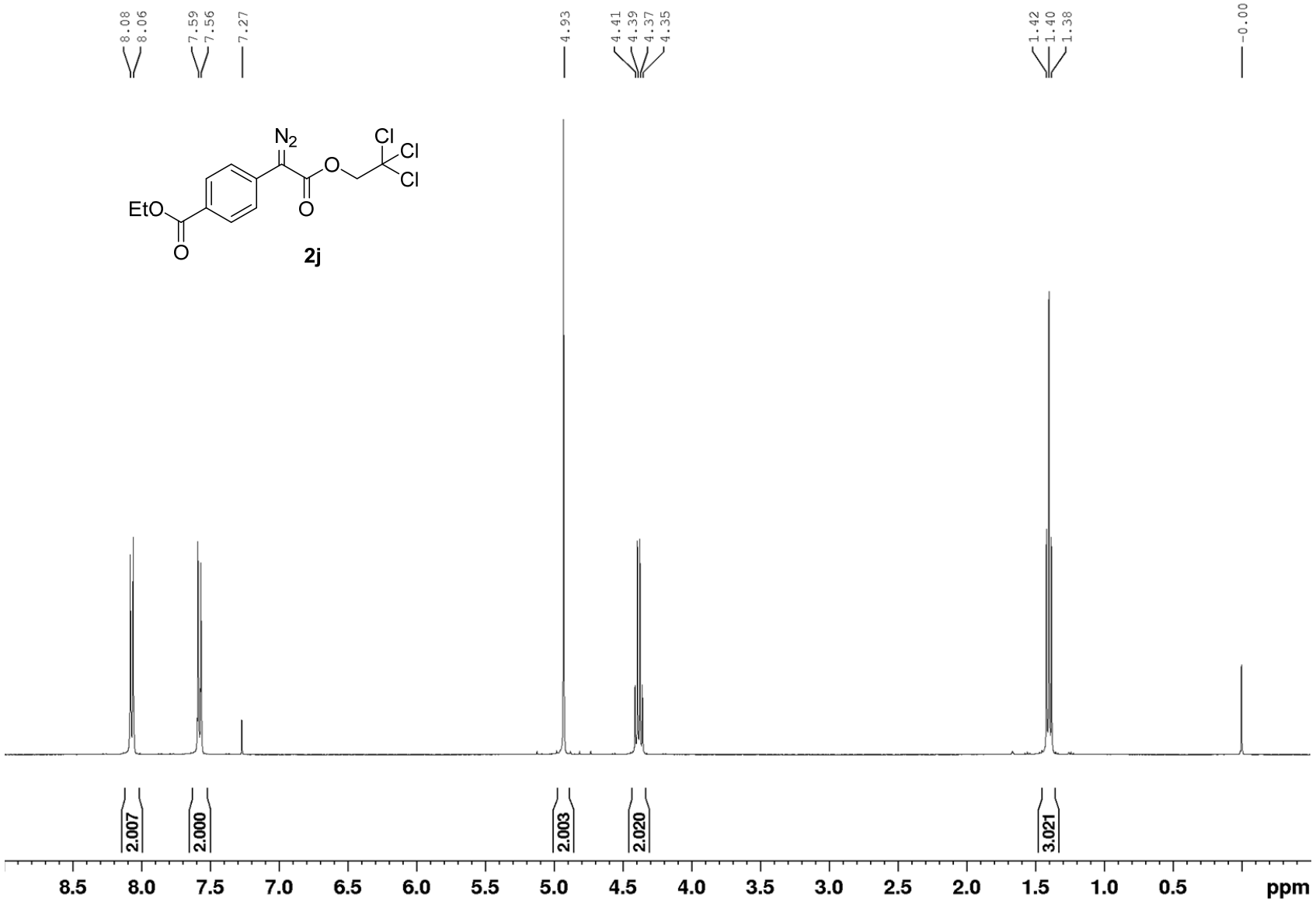


^{13}C NMR (100 MHz, $CDCl_3$)

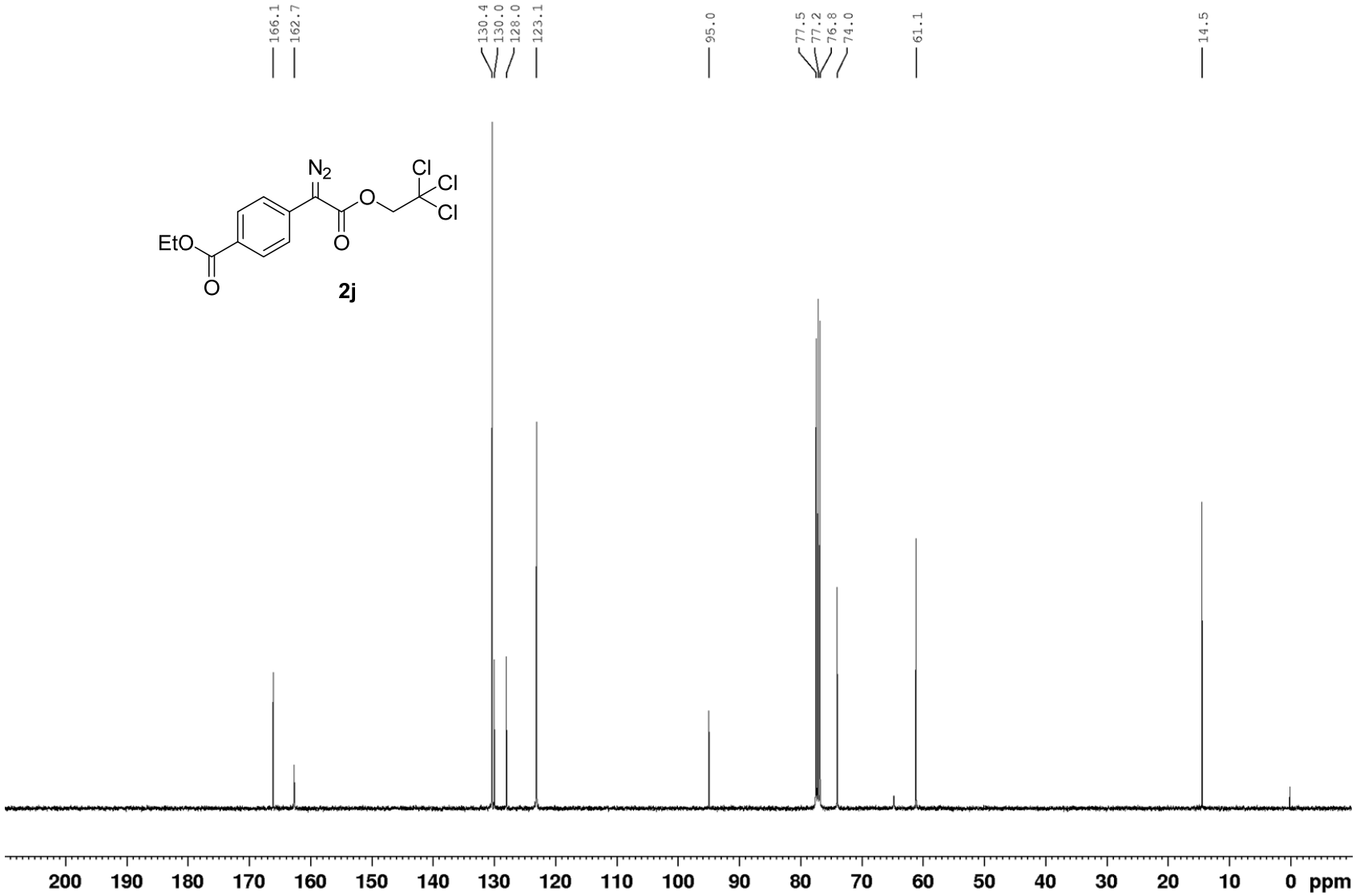


2i

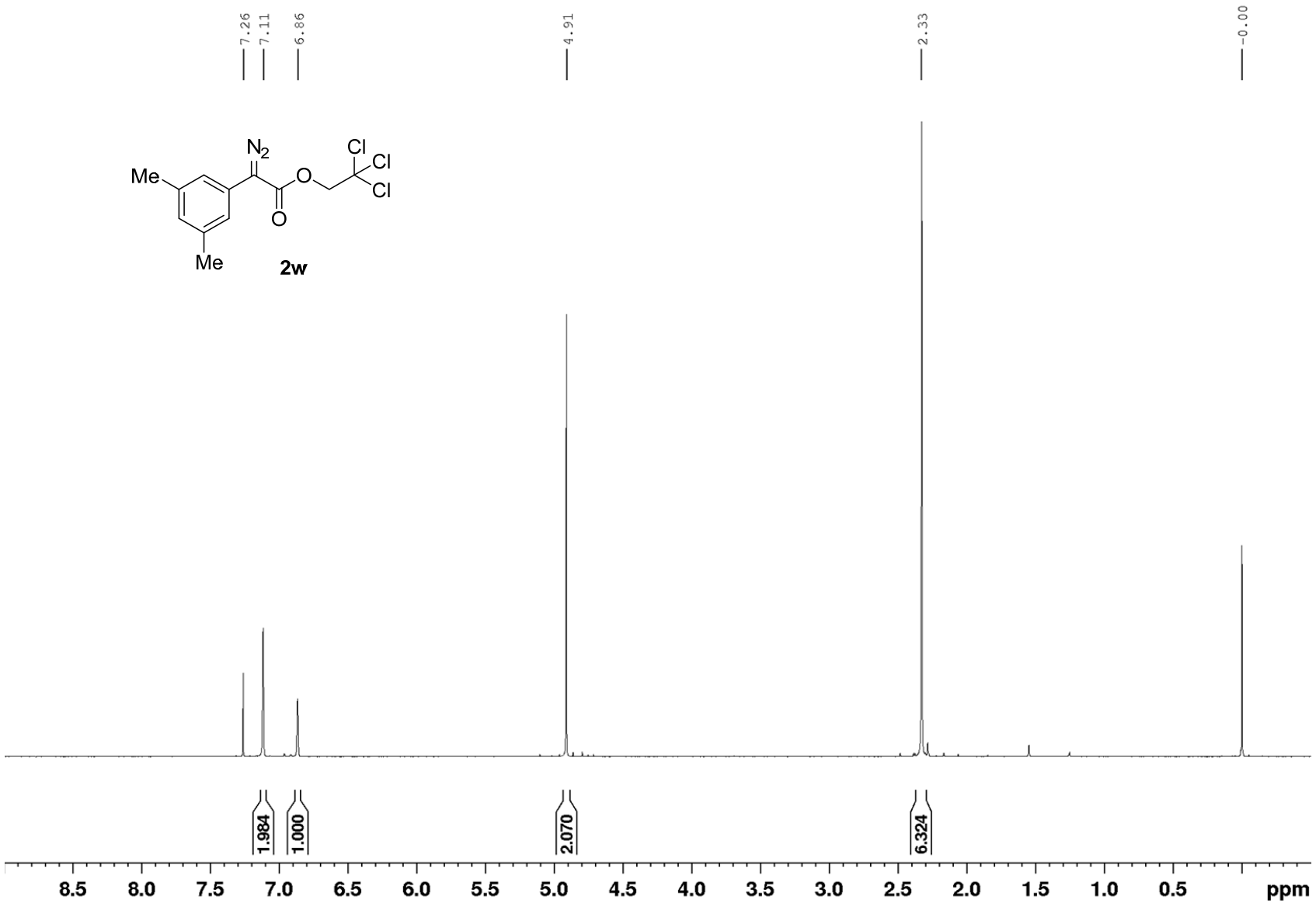
^{1}H NMR (400 MHz, $CDCl_3$)



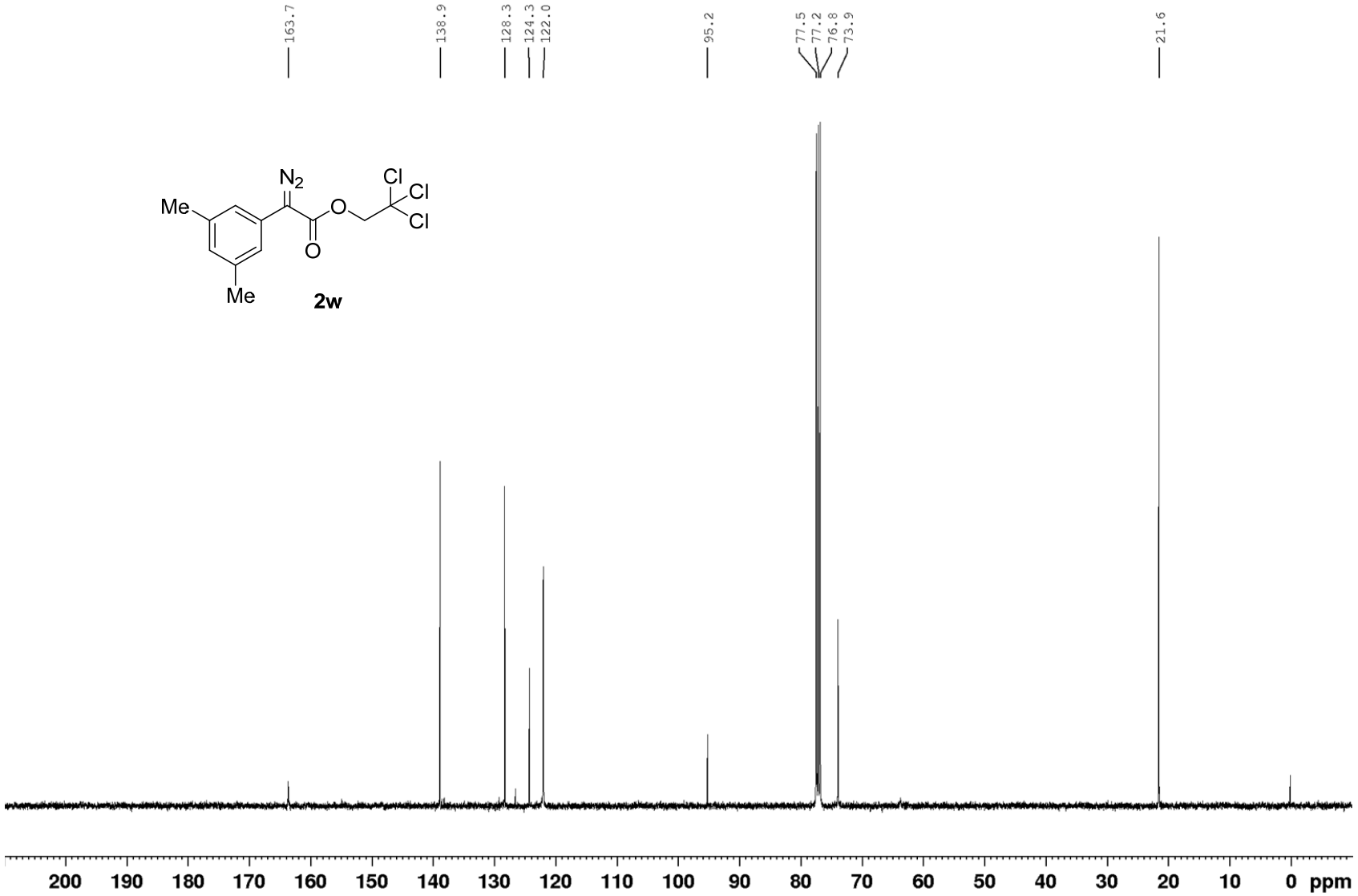
^{13}C NMR (100 MHz, $CDCl_3$)



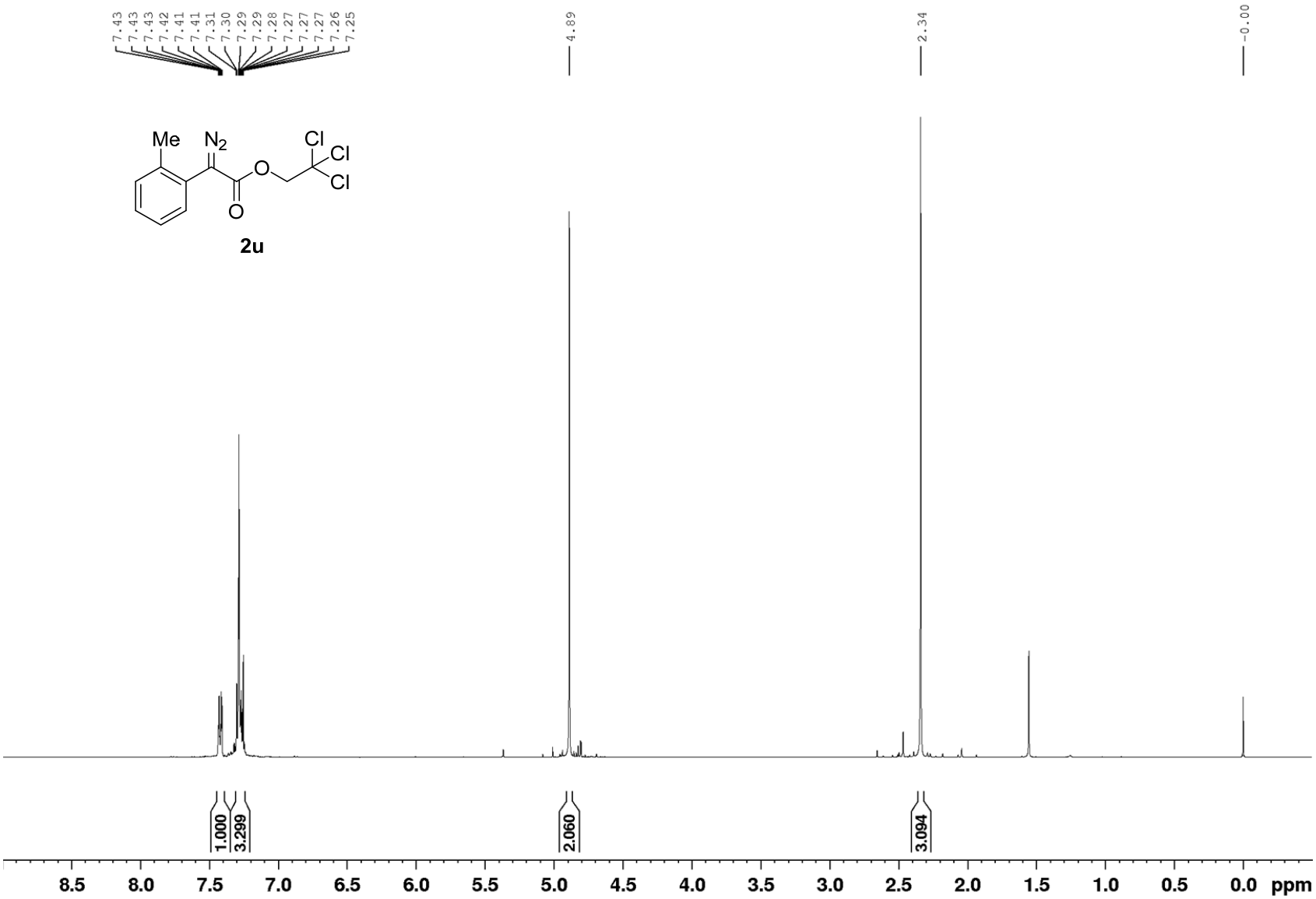
^{1}H NMR (400 MHz, $CDCl_3$)



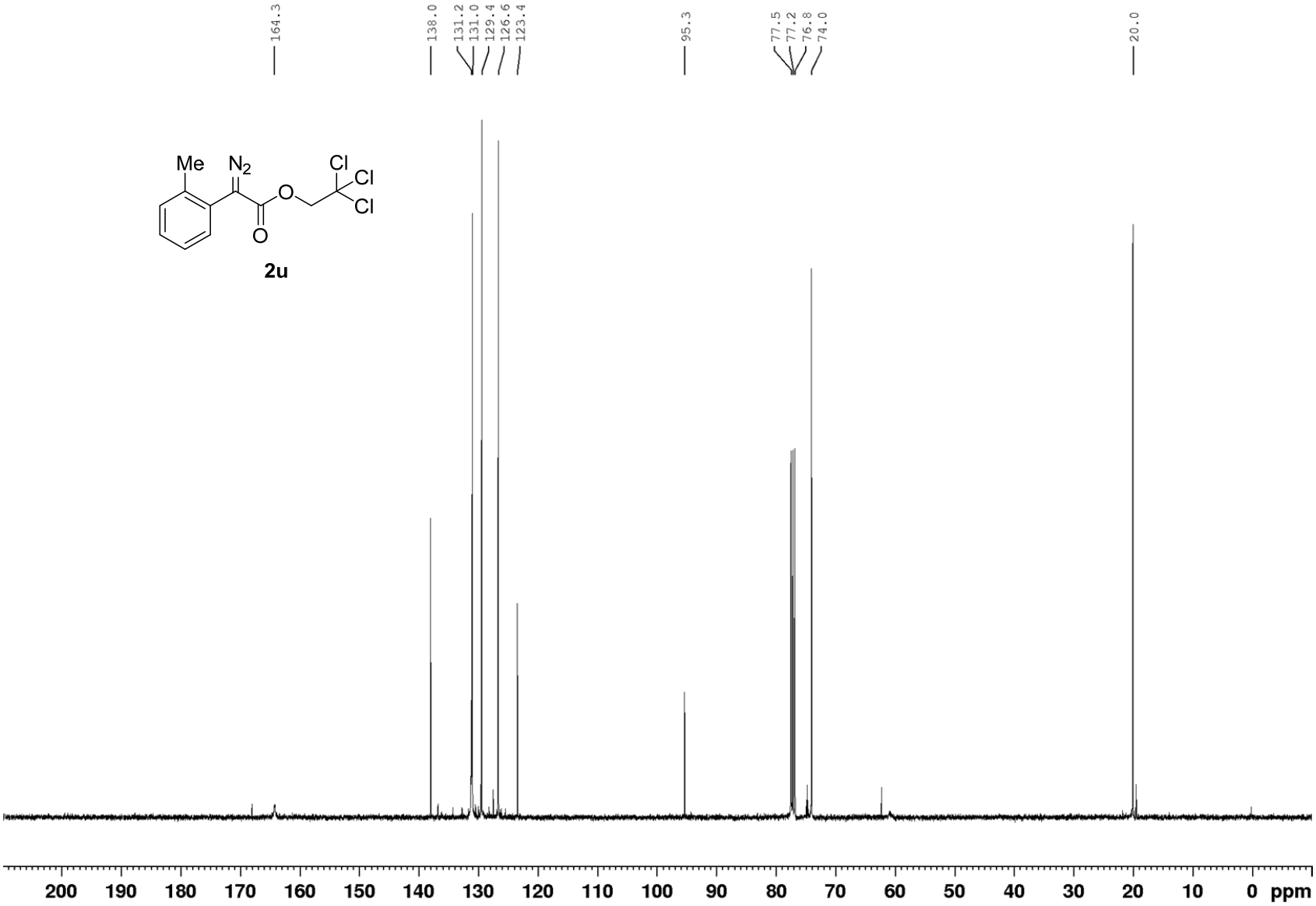
^{13}C NMR (100 MHz, $CDCl_3$)



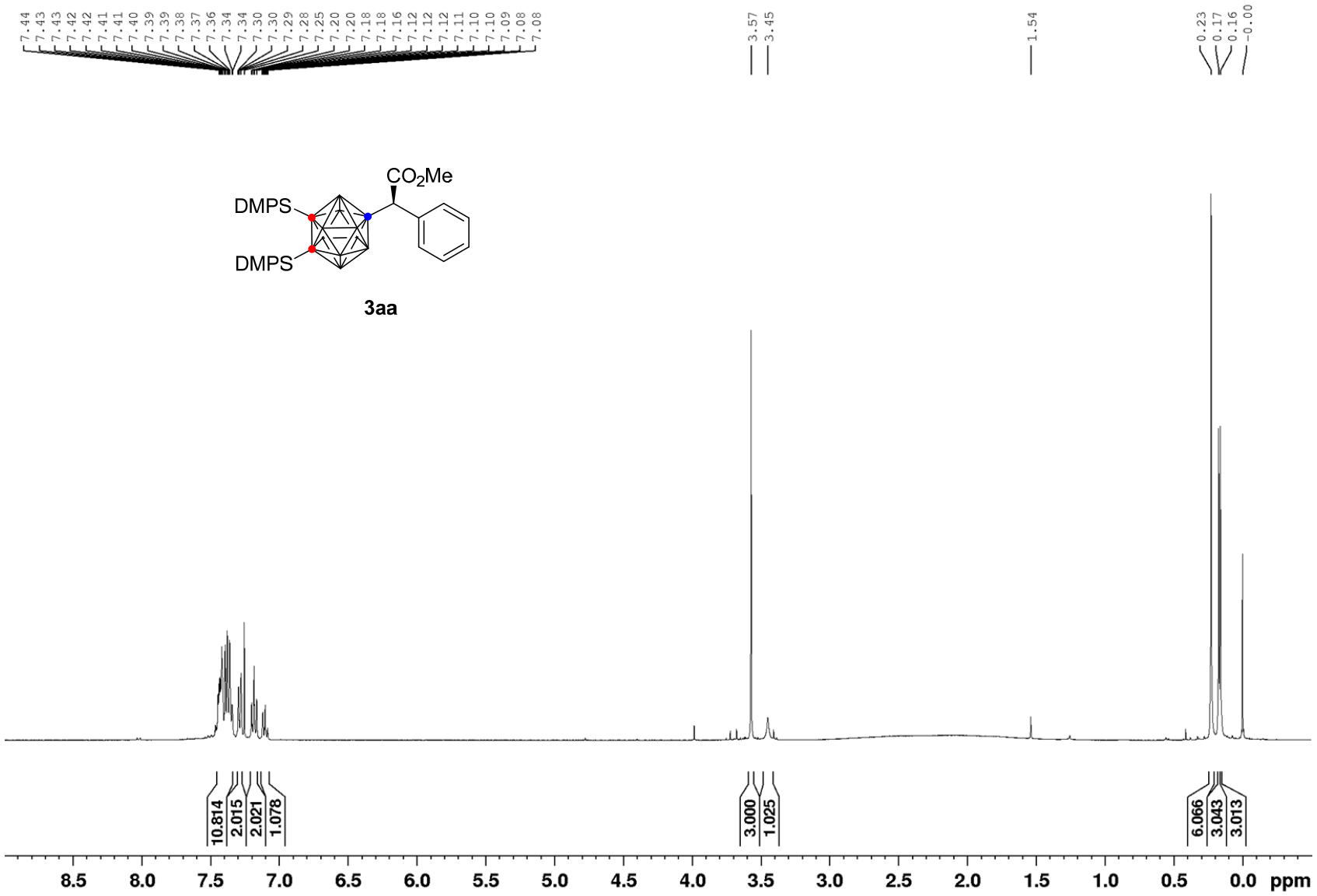
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

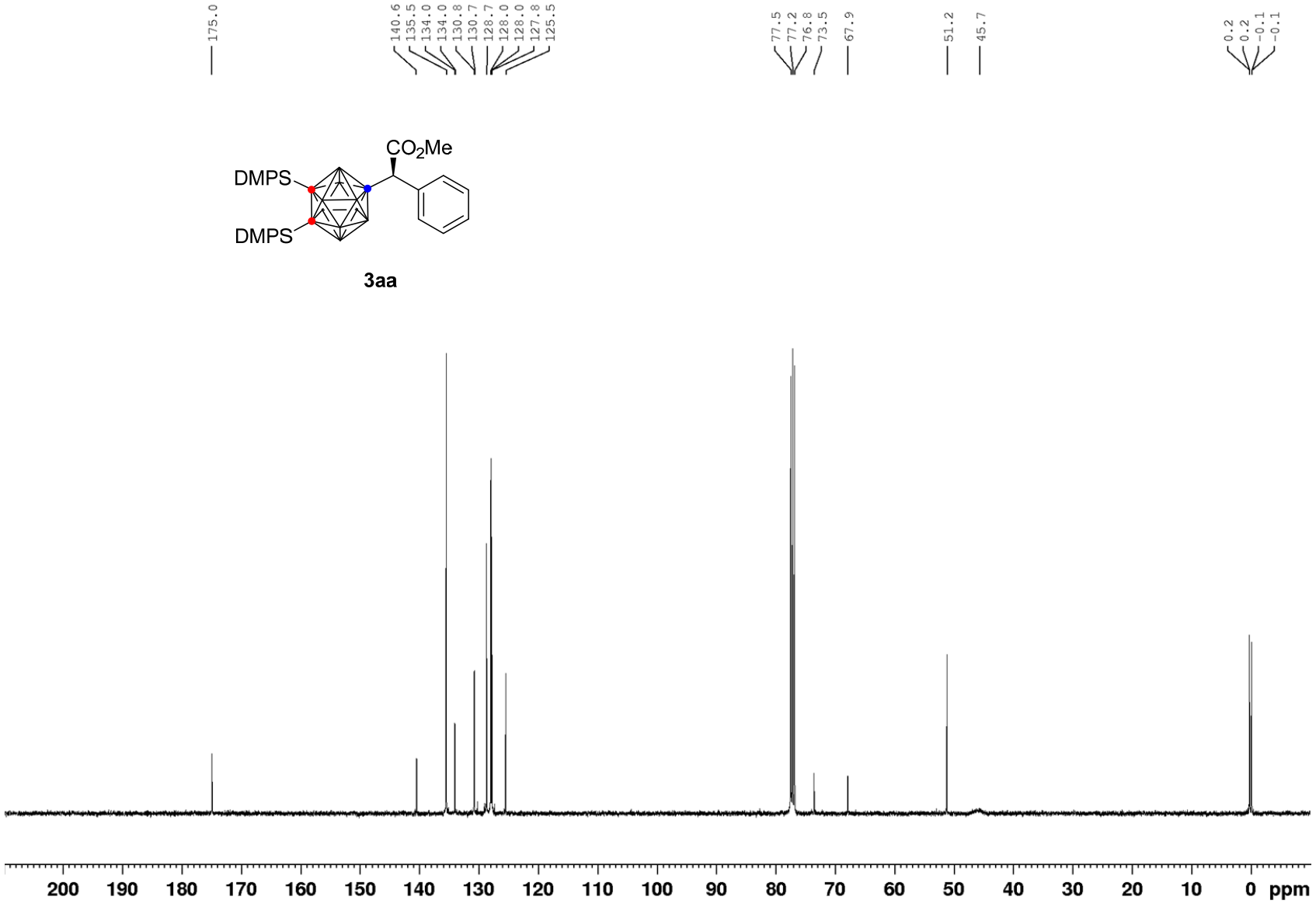


^{1}H NMR (400 MHz, $CDCl_3$)



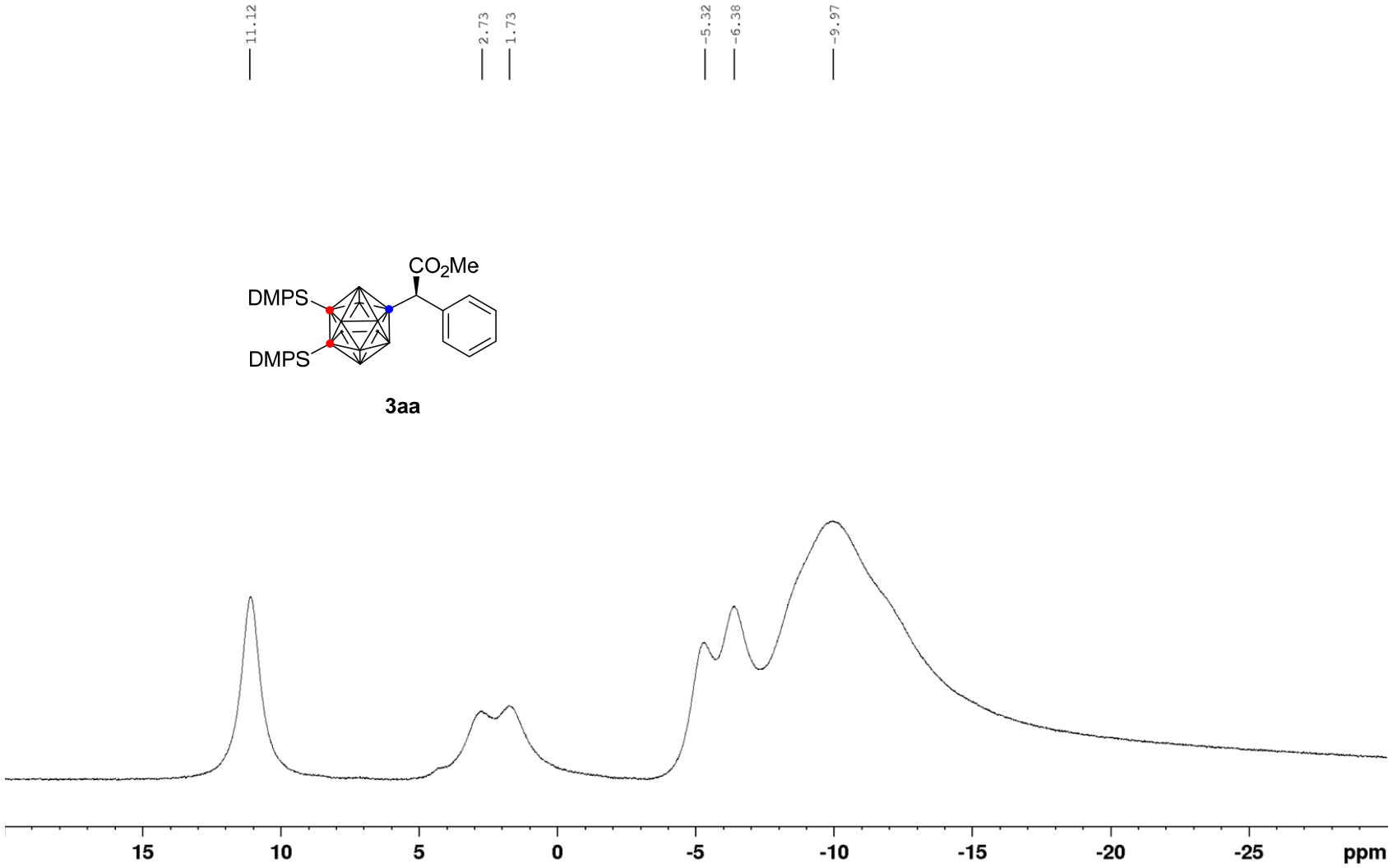
3aa

^{13}C NMR (100 MHz, $CDCl_3$)



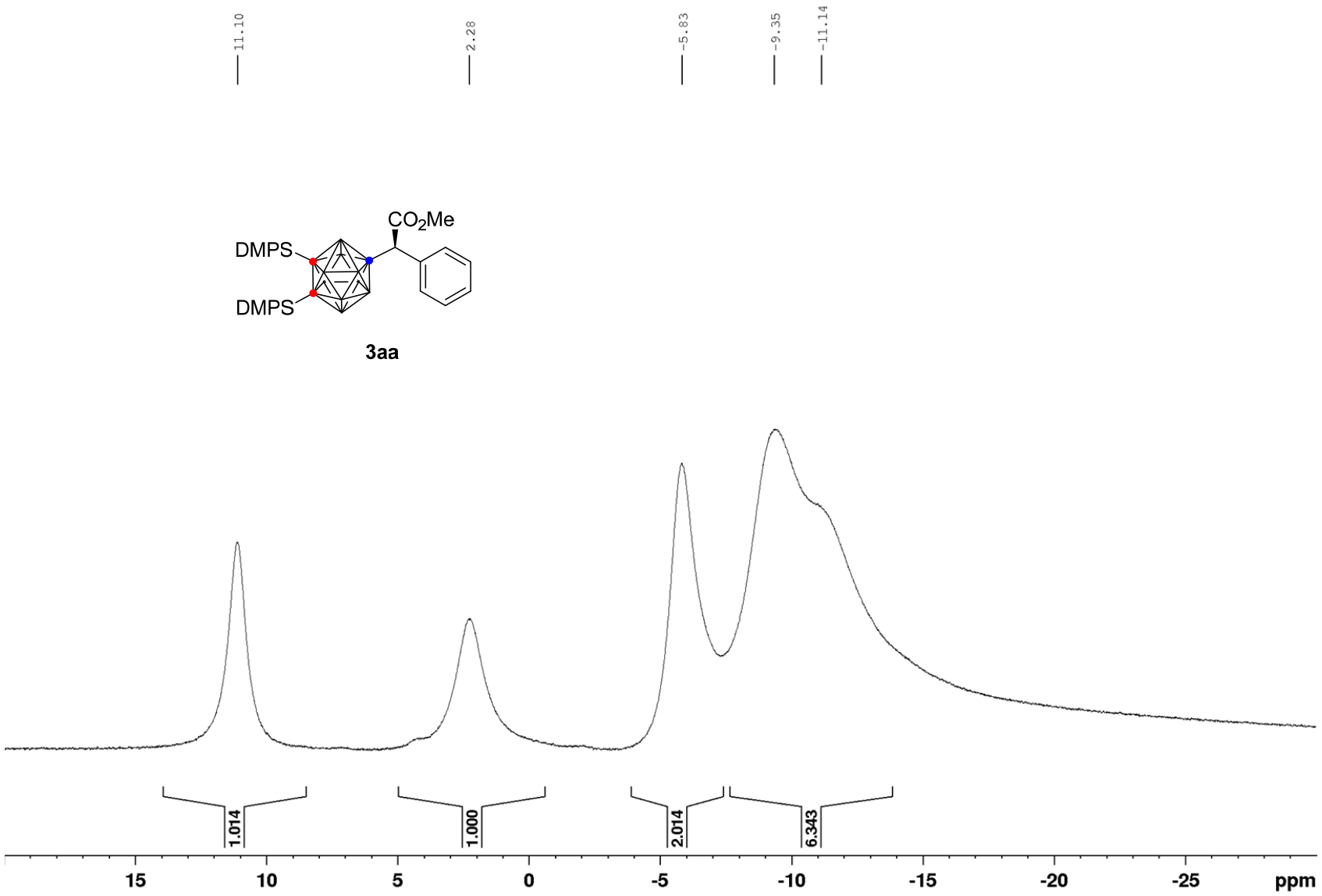
3aa

^{11}B NMR (128 MHz, $CDCl_3$)



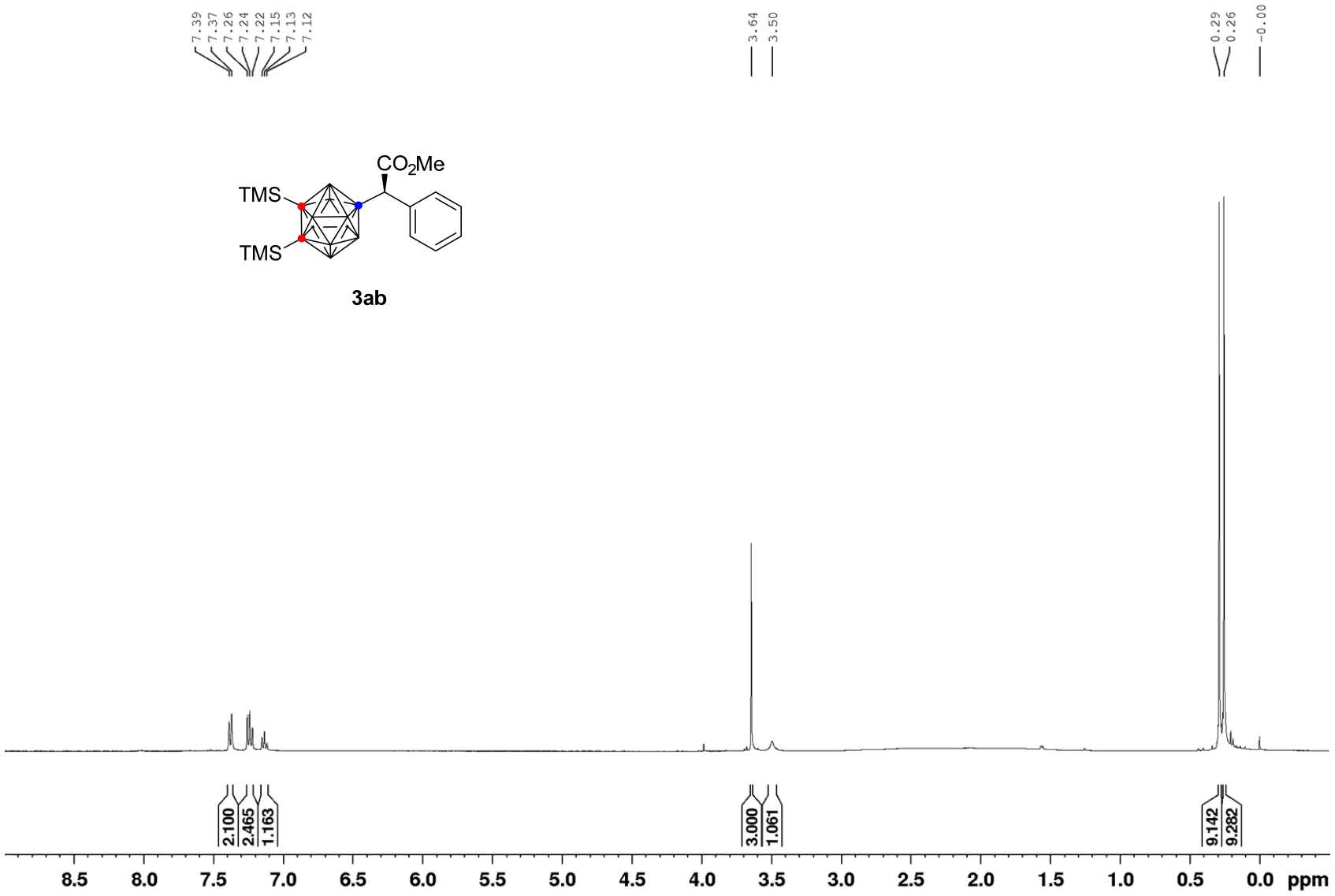
3aa

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



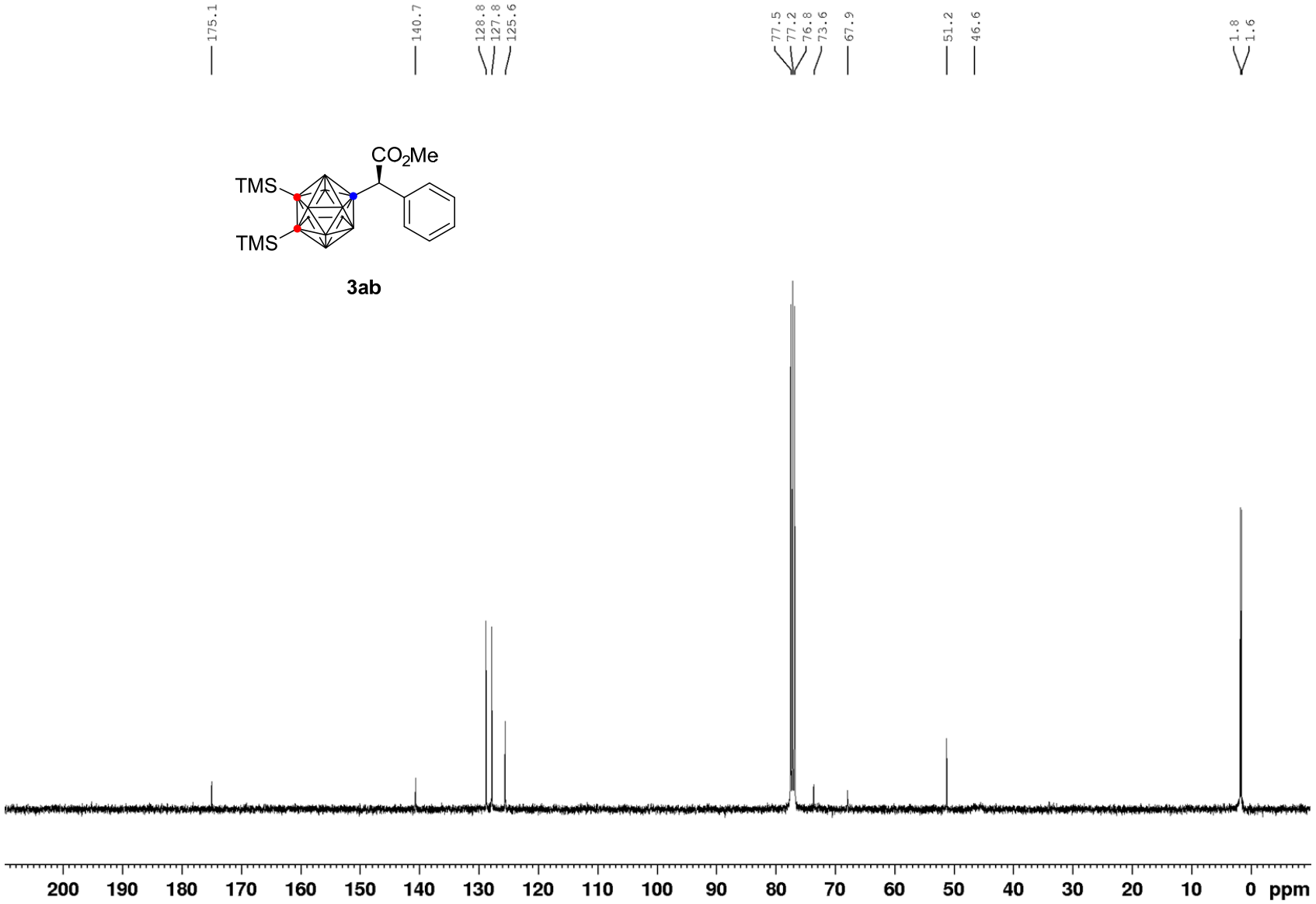
3aa

^{1}H NMR (400 MHz, $CDCl_3$)

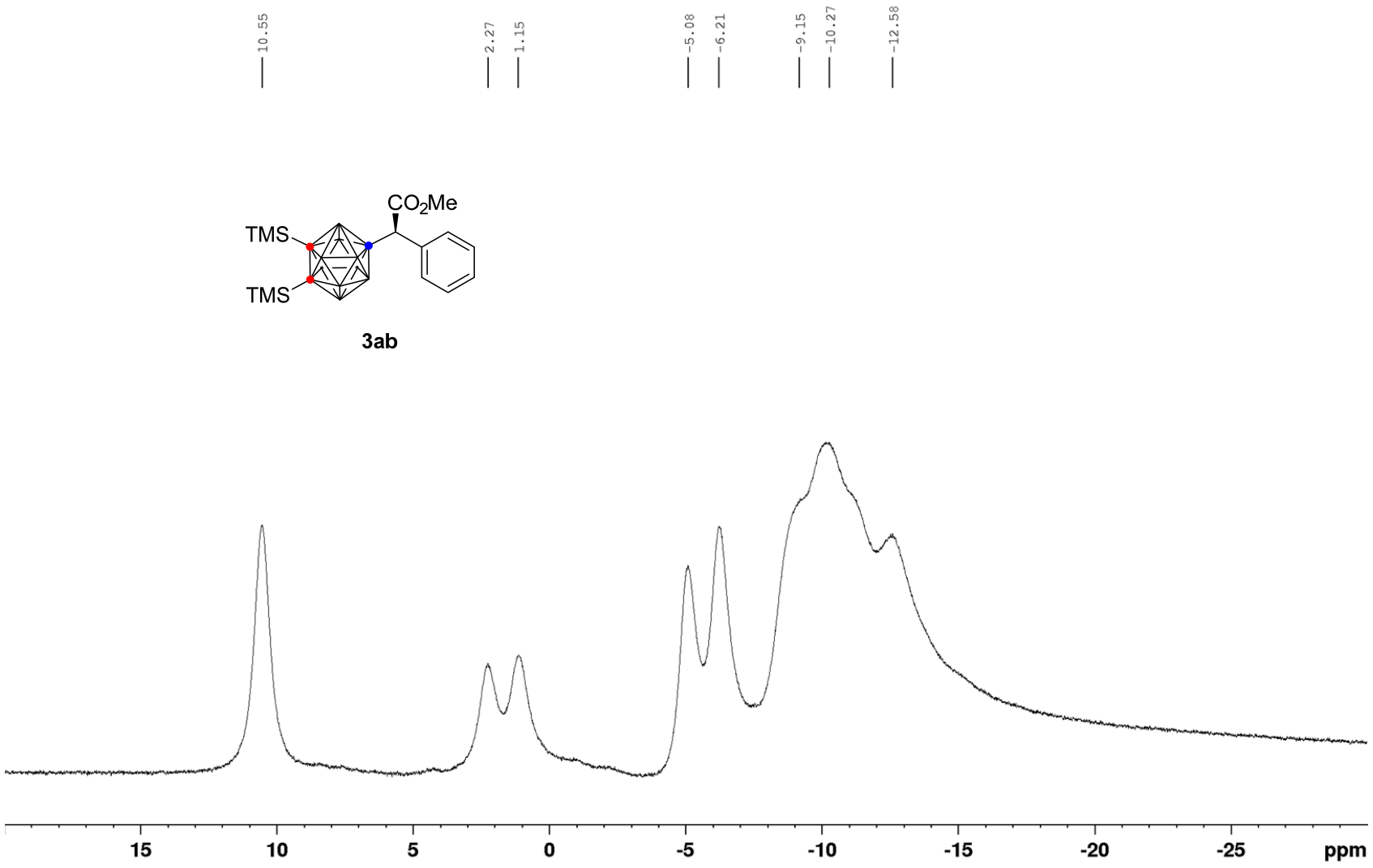


3ab

^{13}C NMR (100 MHz, $CDCl_3$)

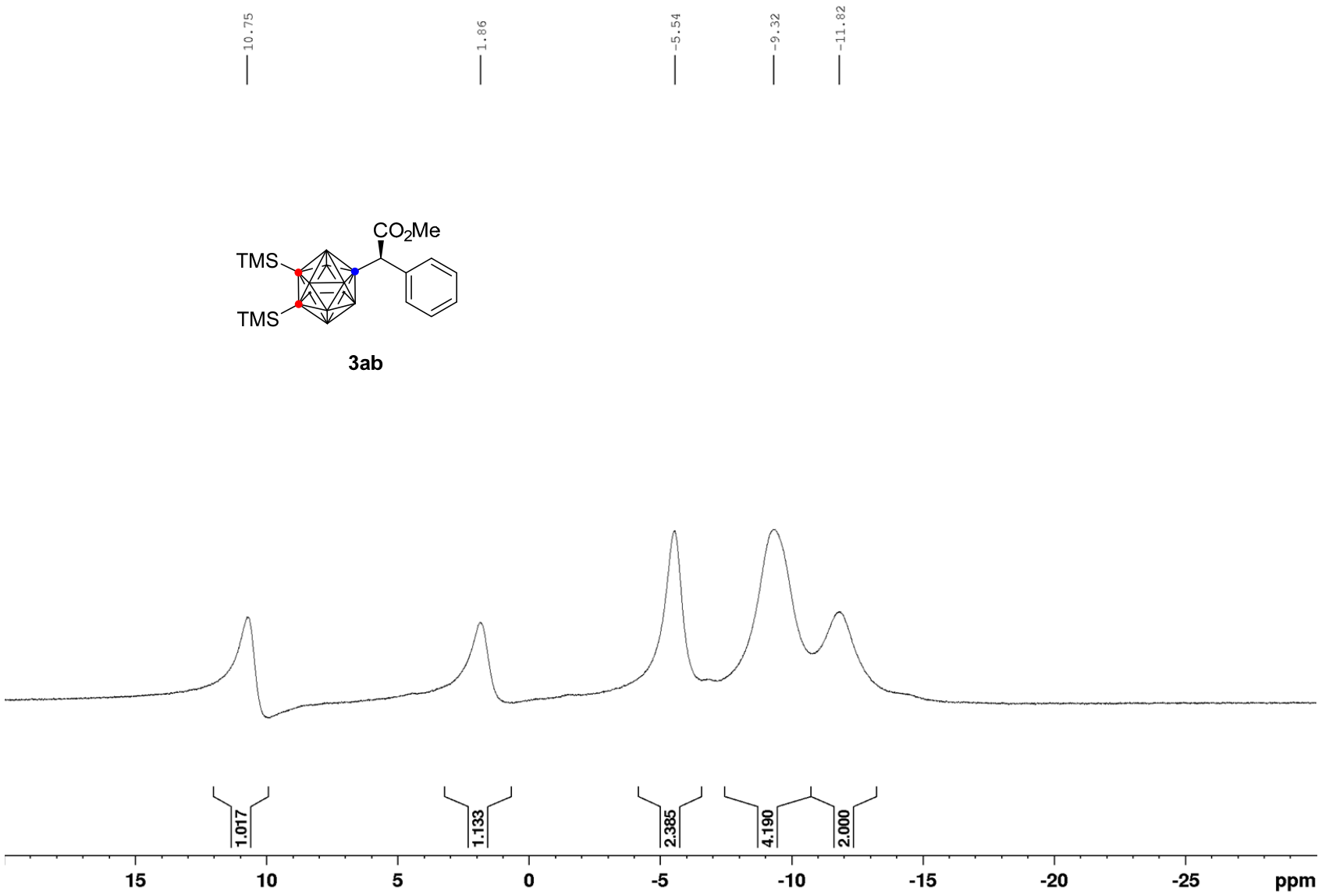


^{11}B NMR (128 MHz, $CDCl_3$)



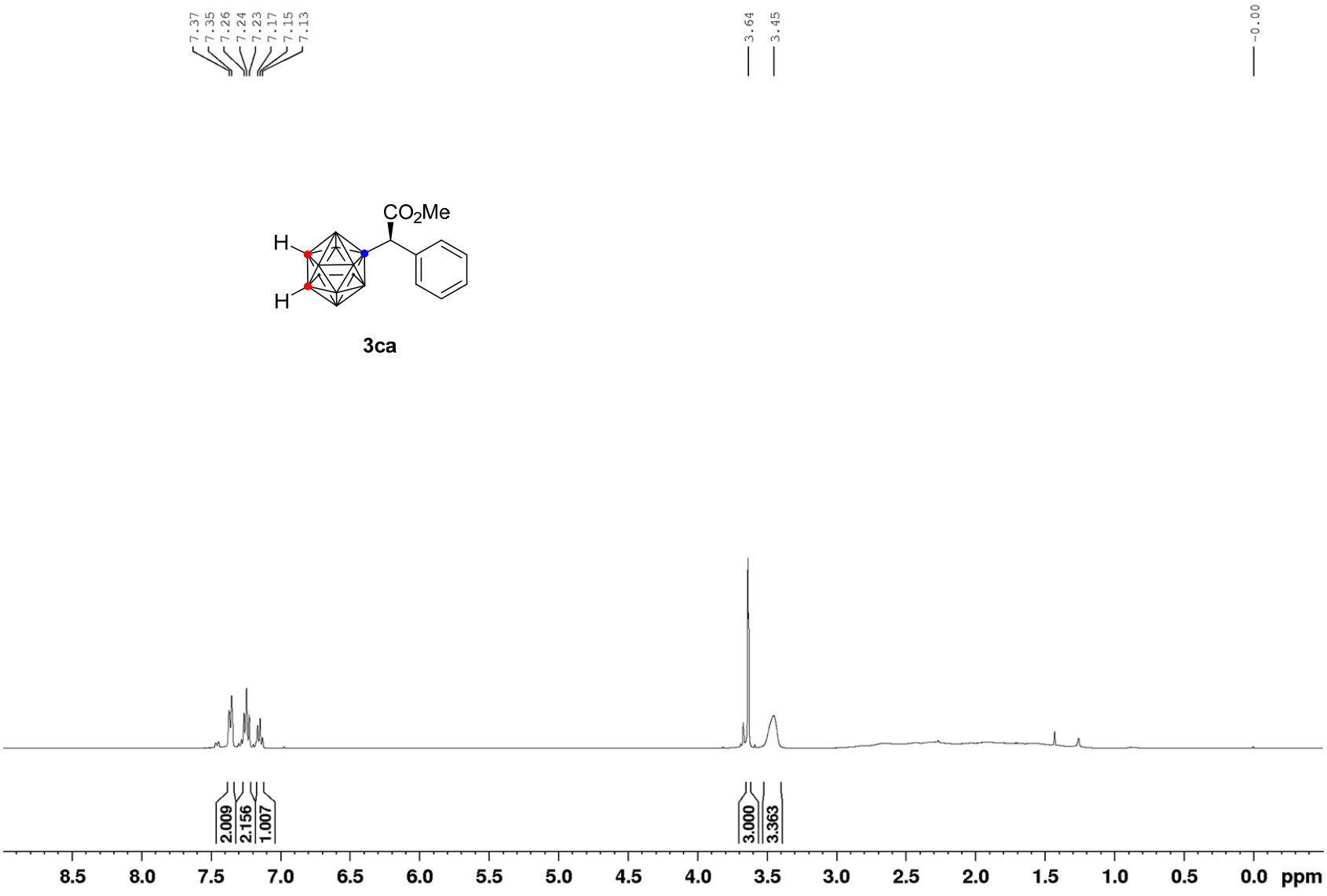
3ab

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



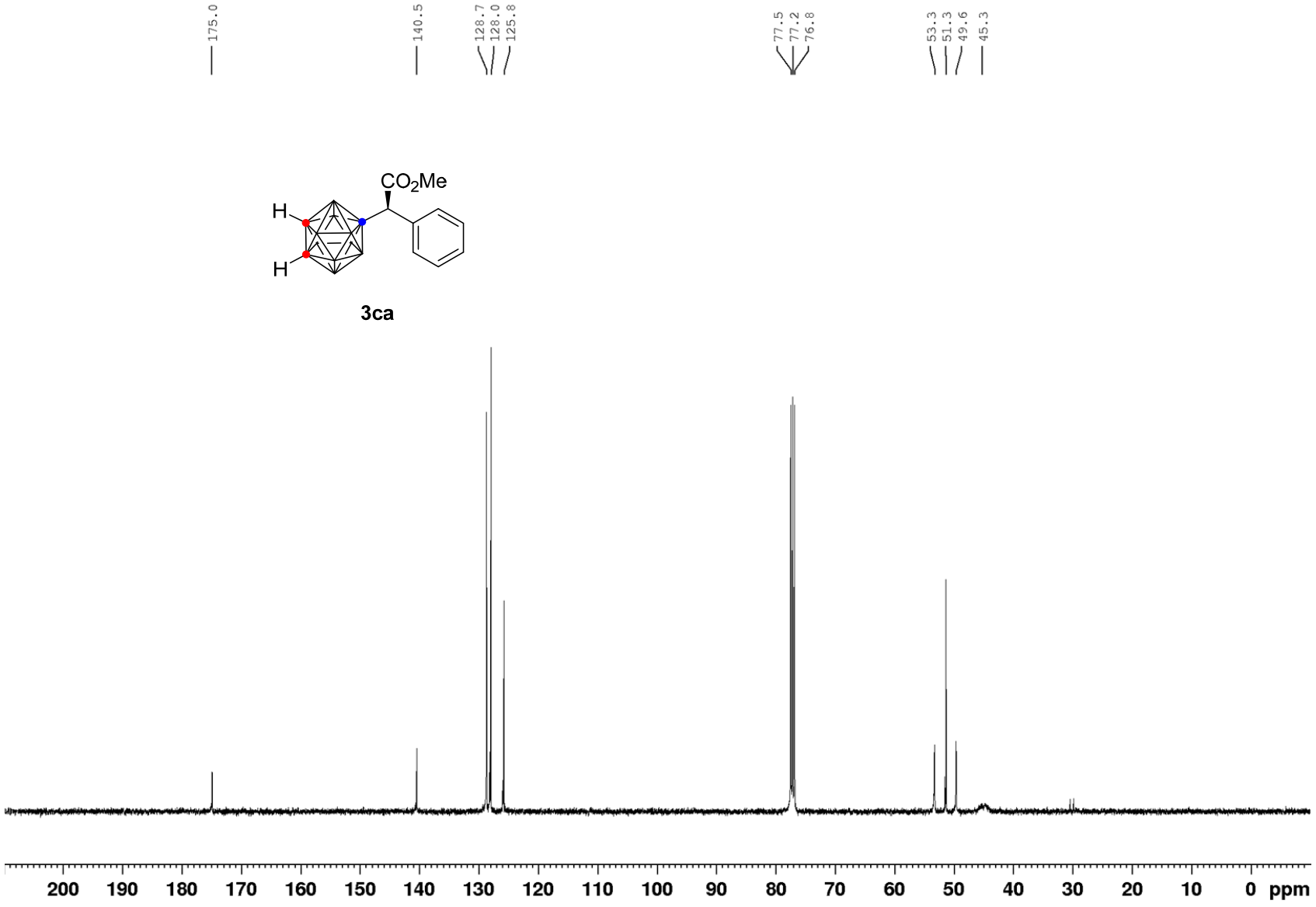
3ab

^{1}H NMR (400 MHz, $CDCl_3$)



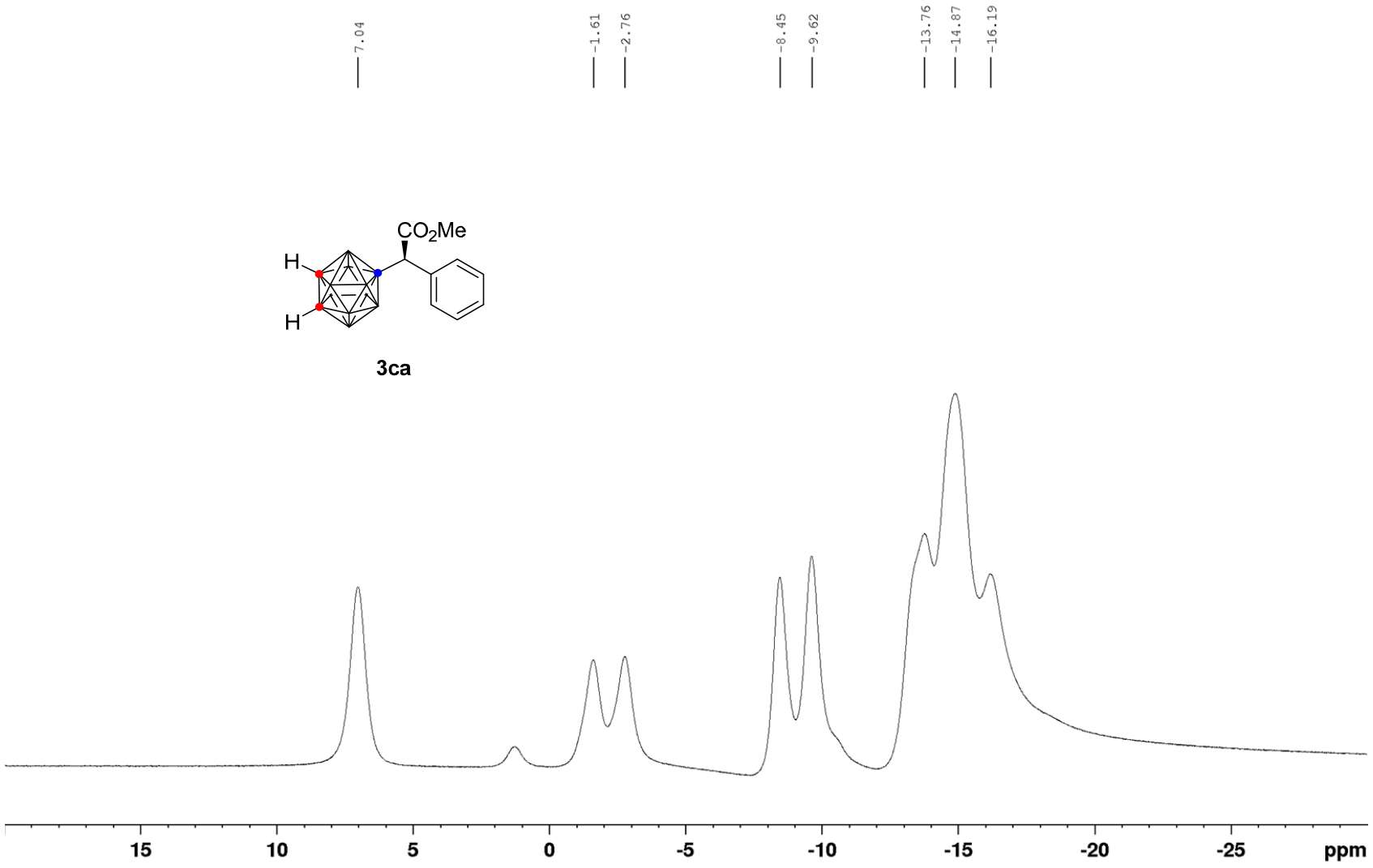
3ca

^{13}C NMR (100 MHz, $CDCl_3$)



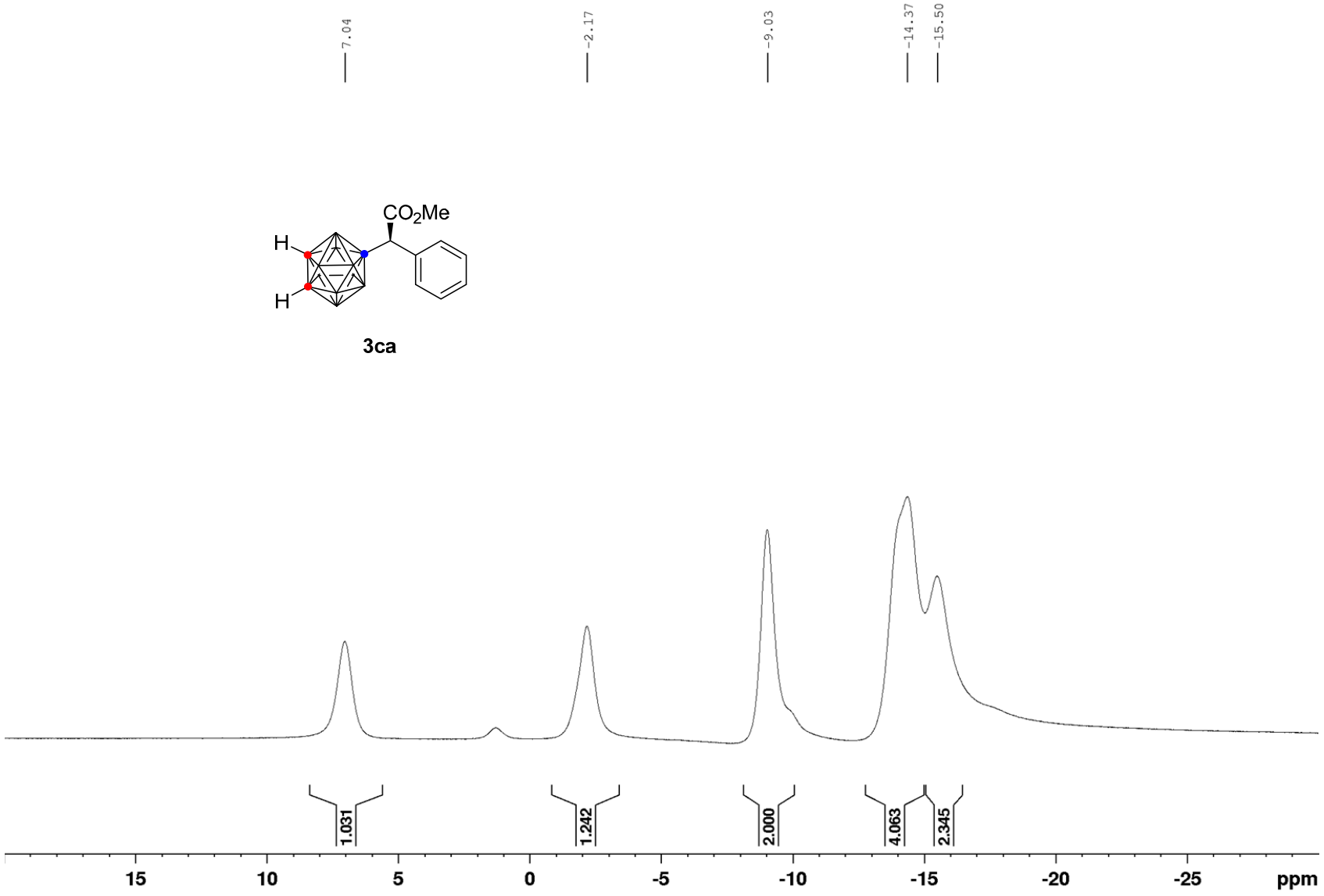
3ca

^{11}B NMR (128 MHz, $CDCl_3$)



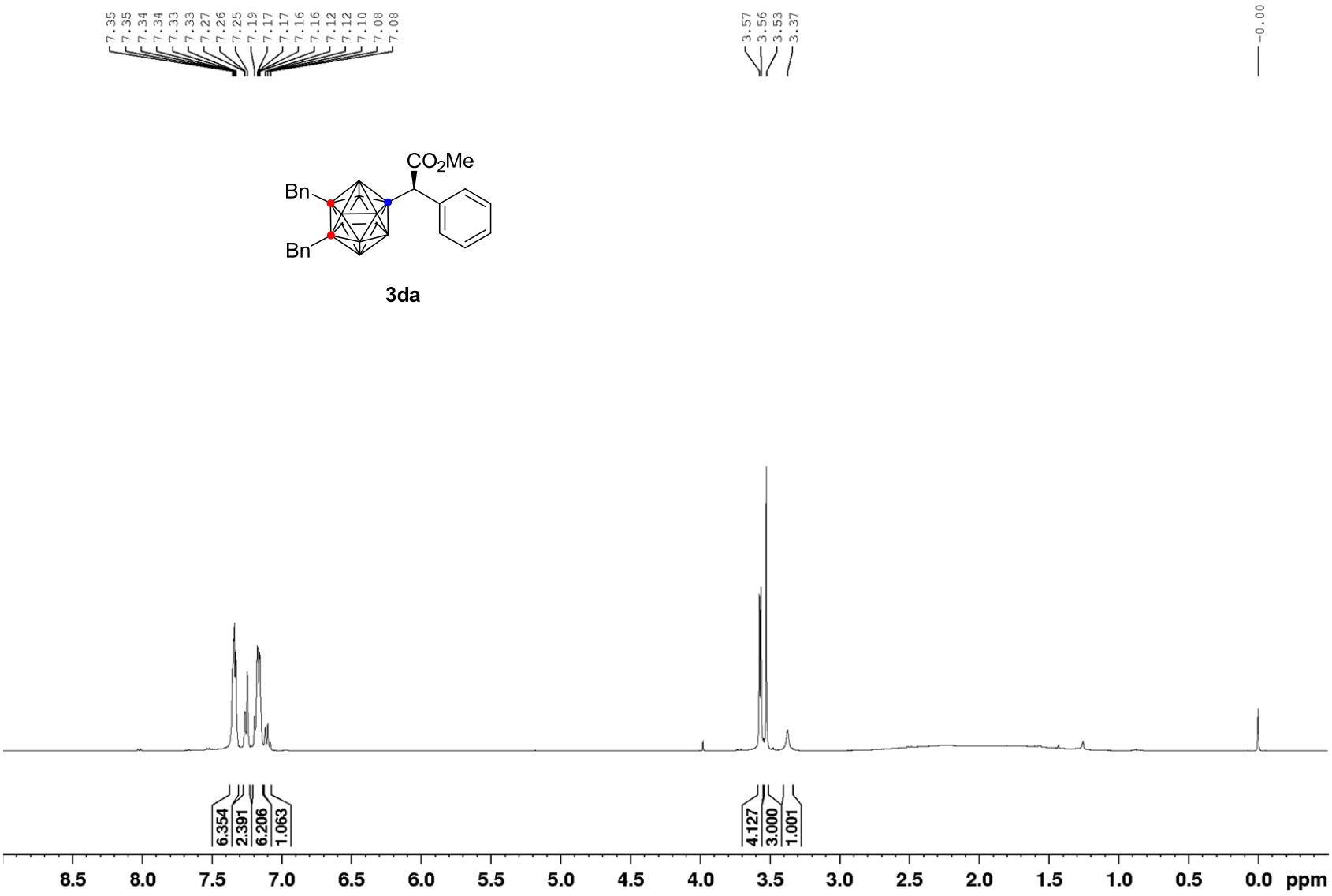
3ca

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



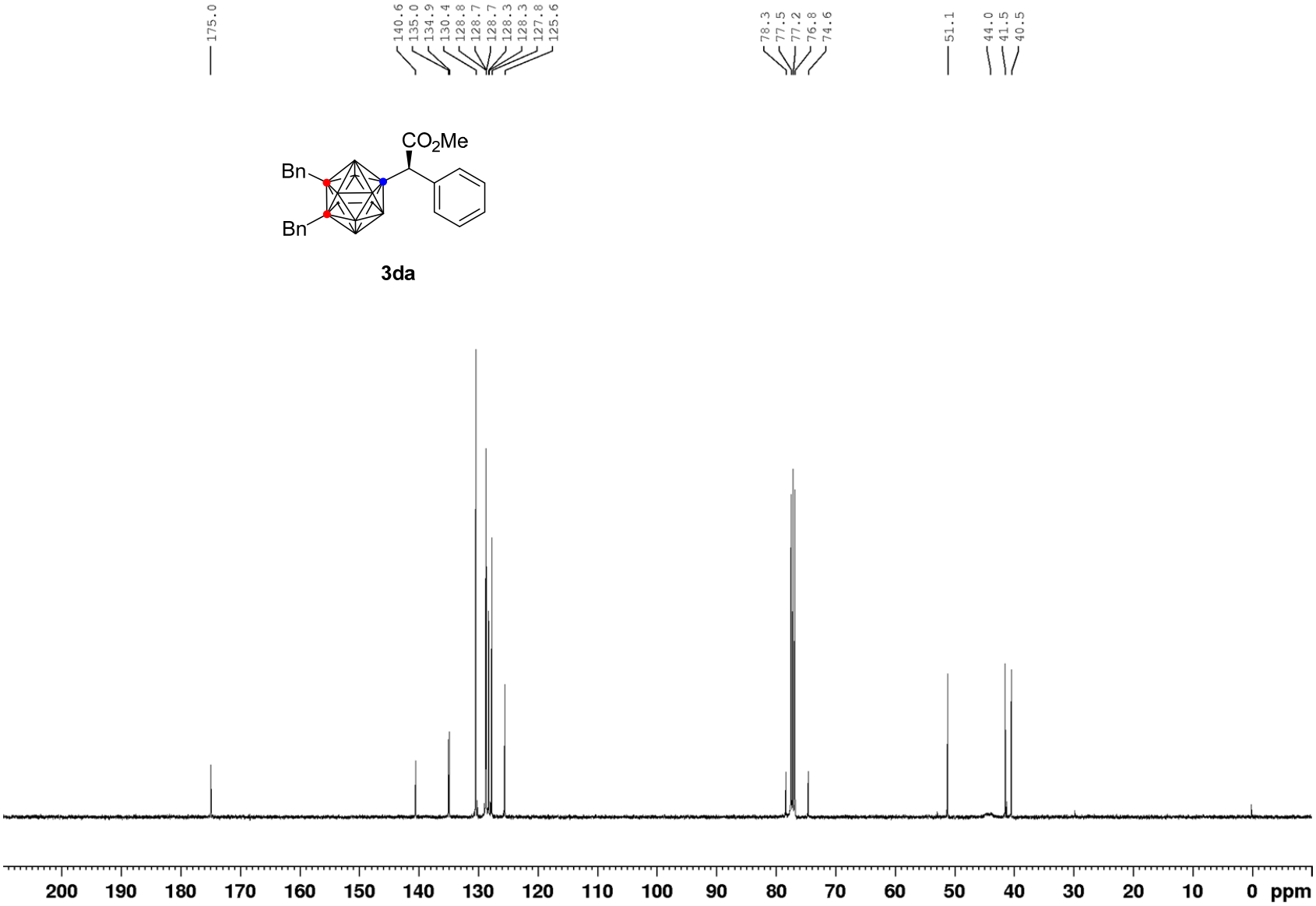
3ca

^{1}H NMR (400 MHz, $CDCl_3$)



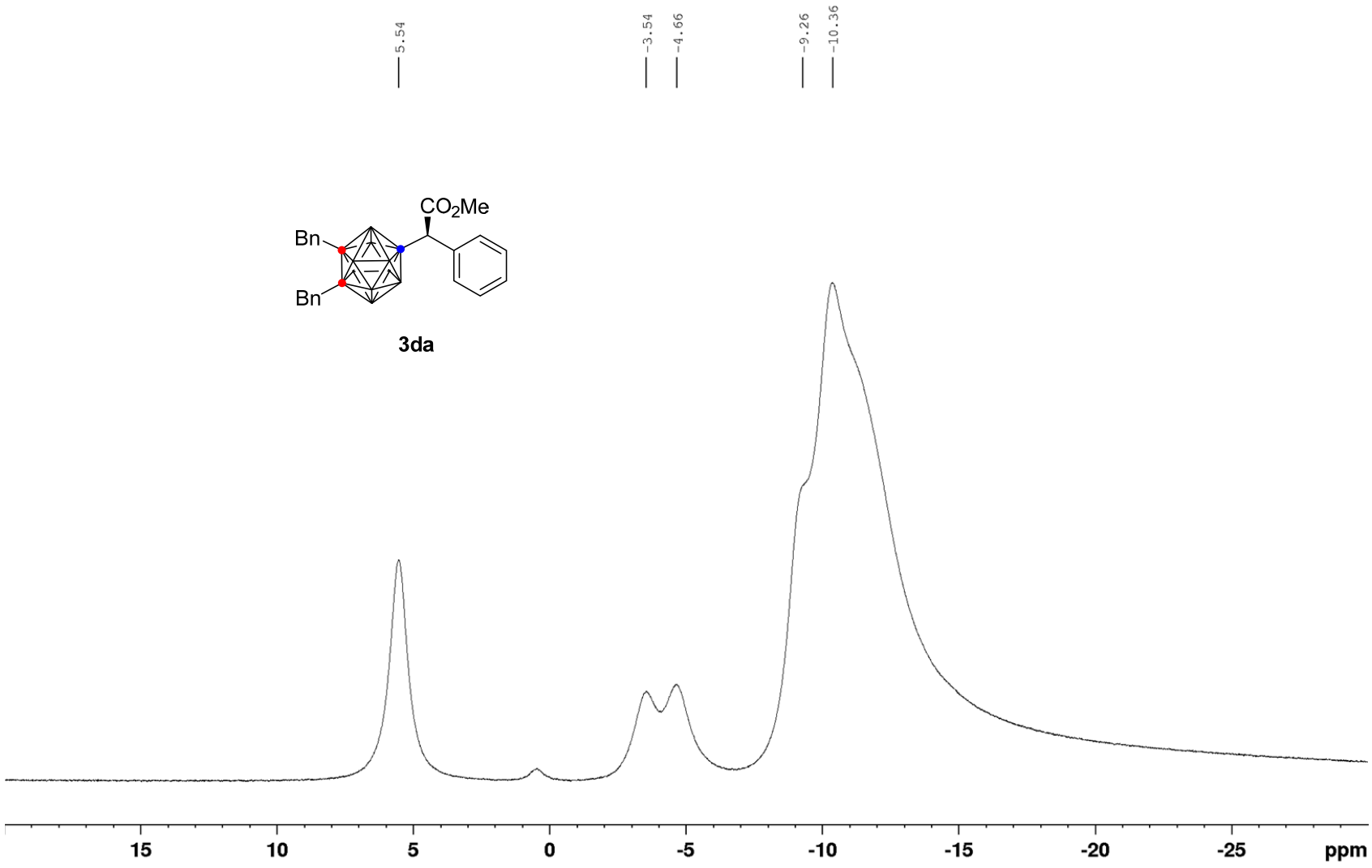
3da

^{13}C NMR (100 MHz, $CDCl_3$)

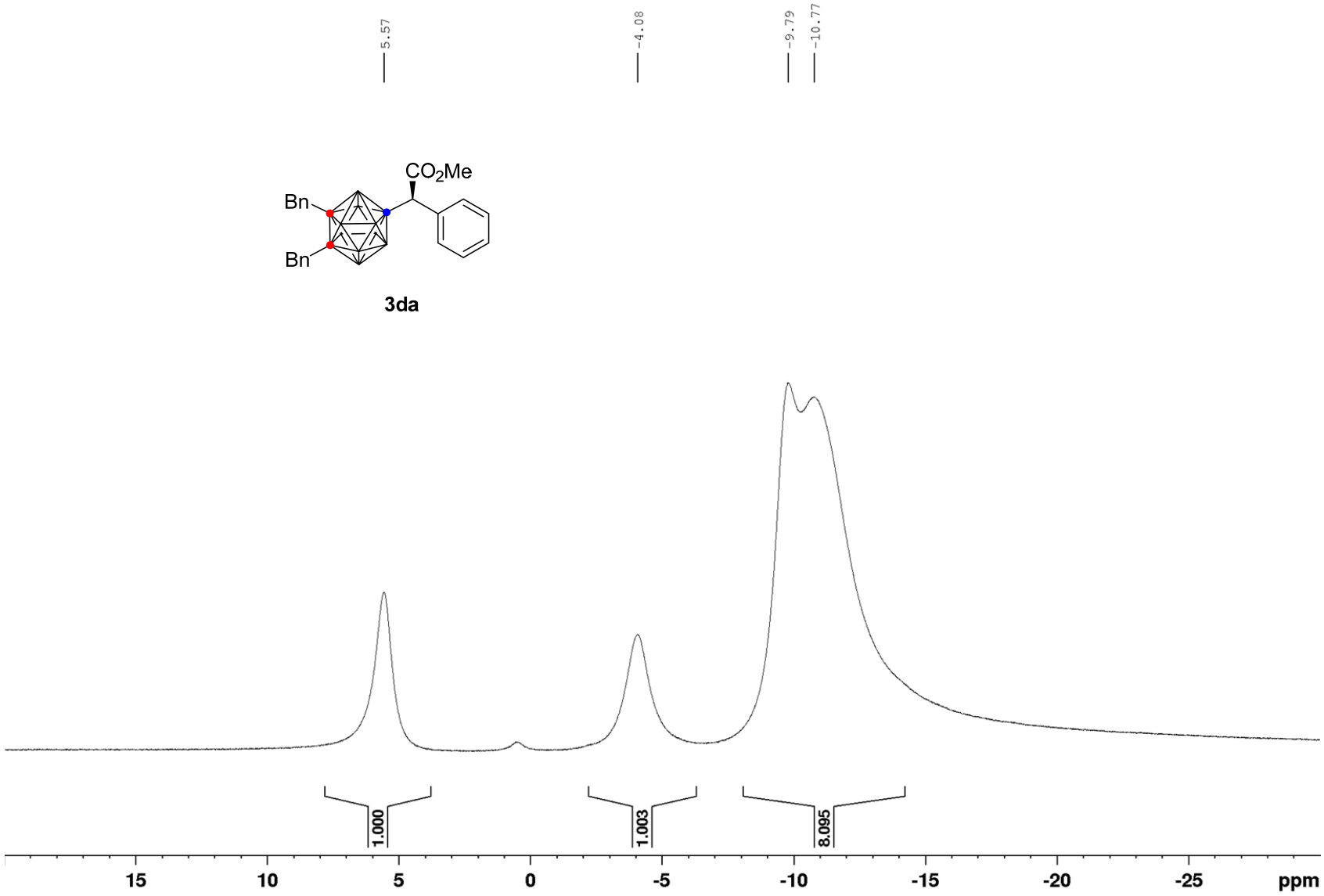


3da

^{11}B NMR (128 MHz, $CDCl_3$)

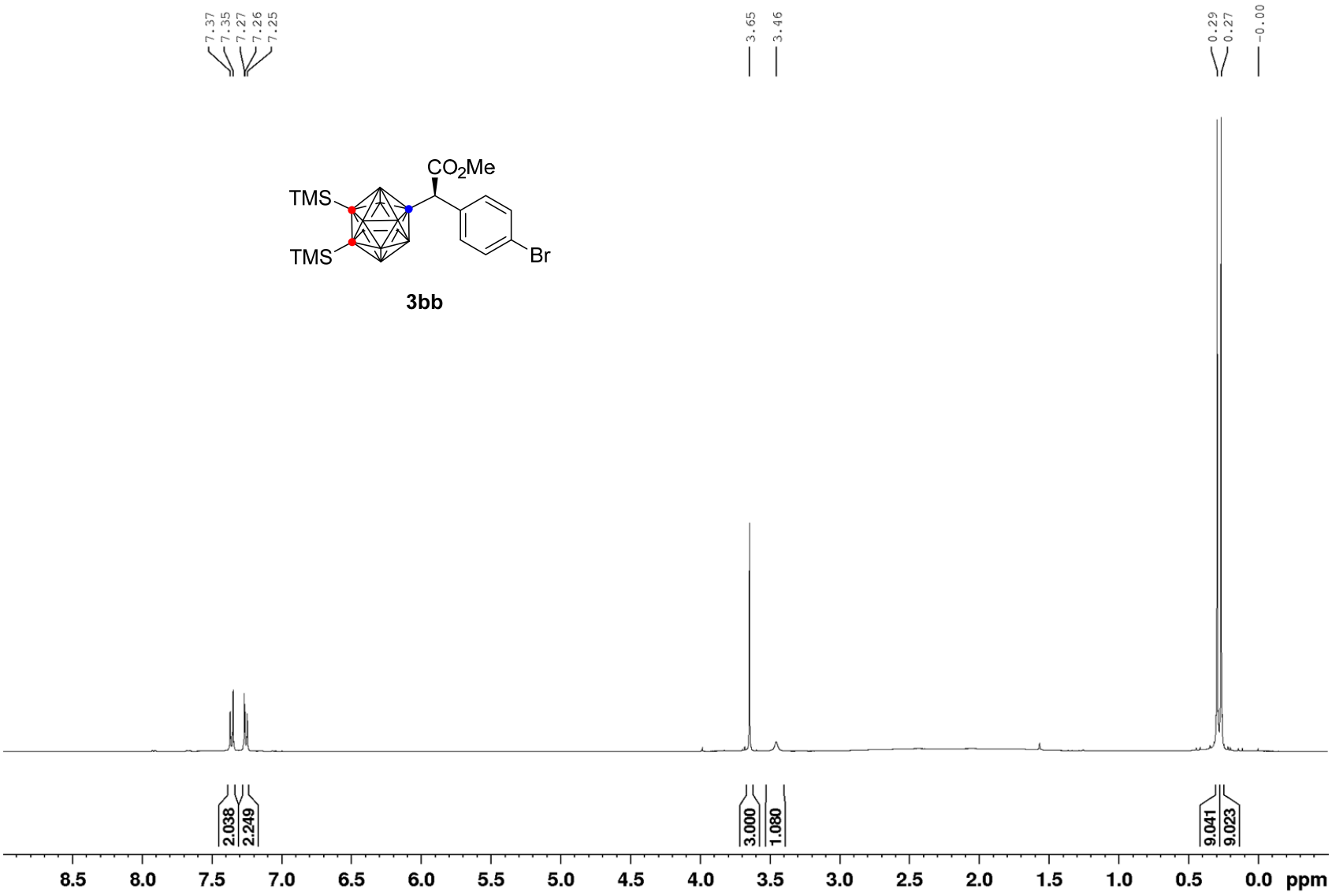


$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$)

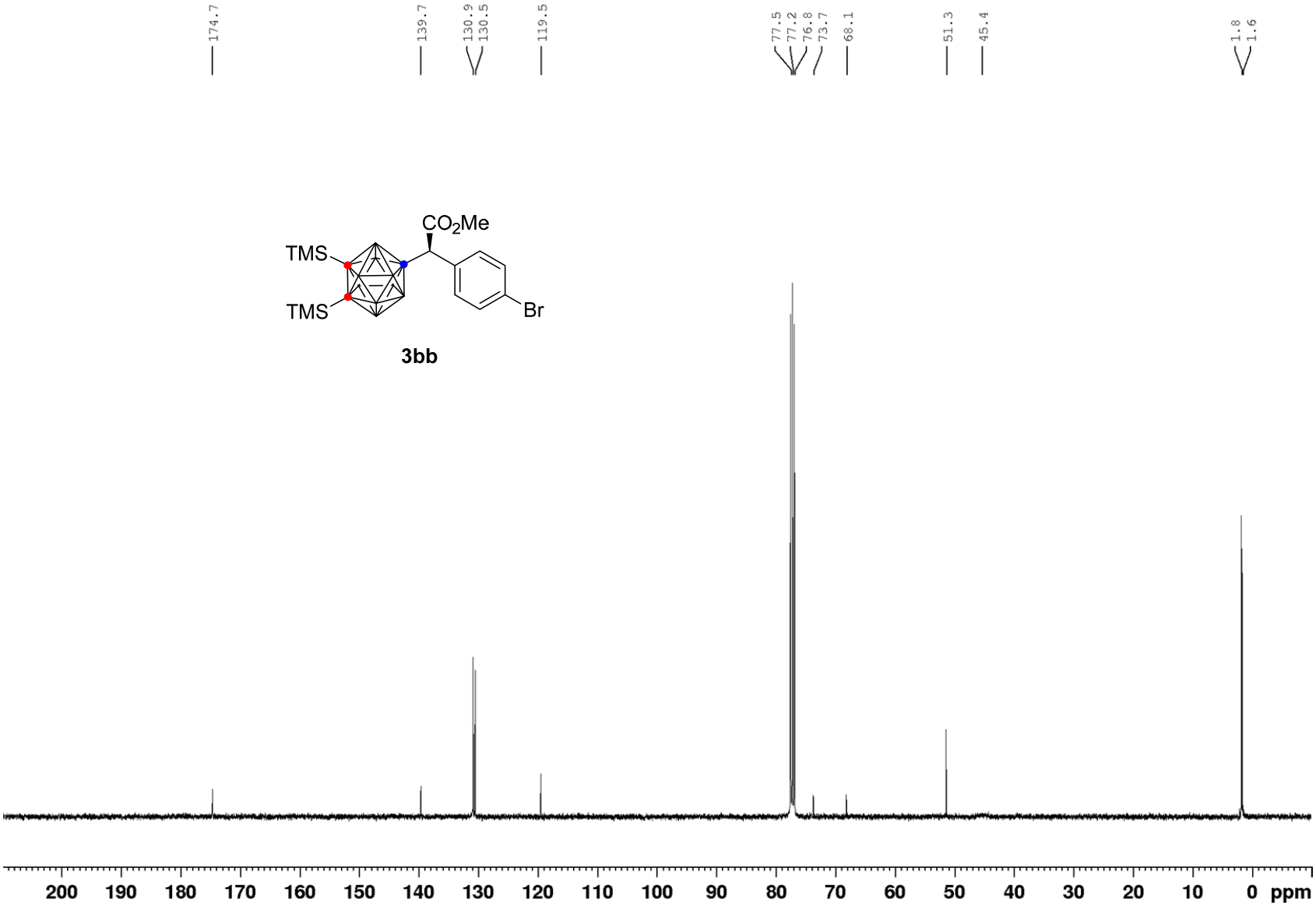


3da

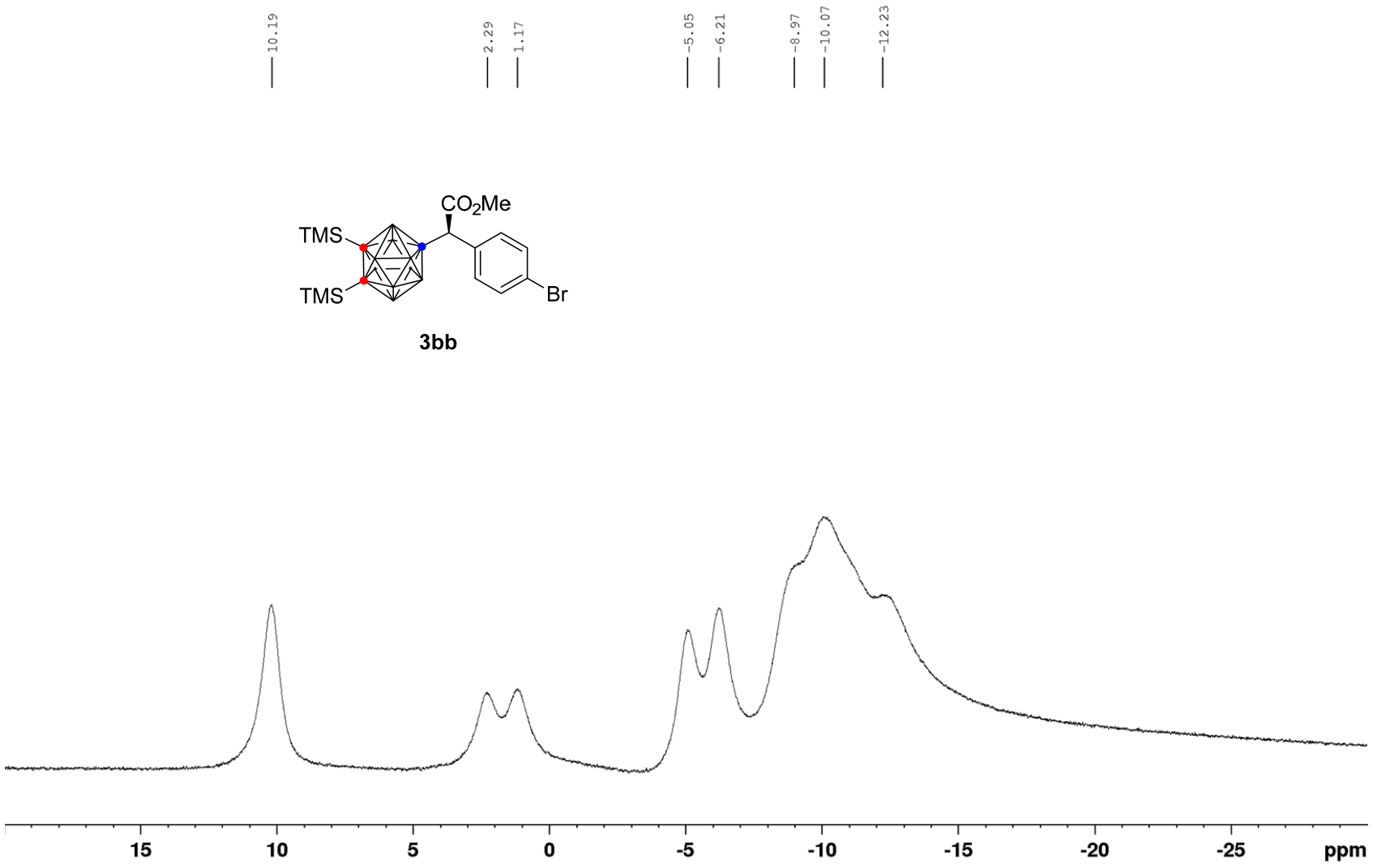
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

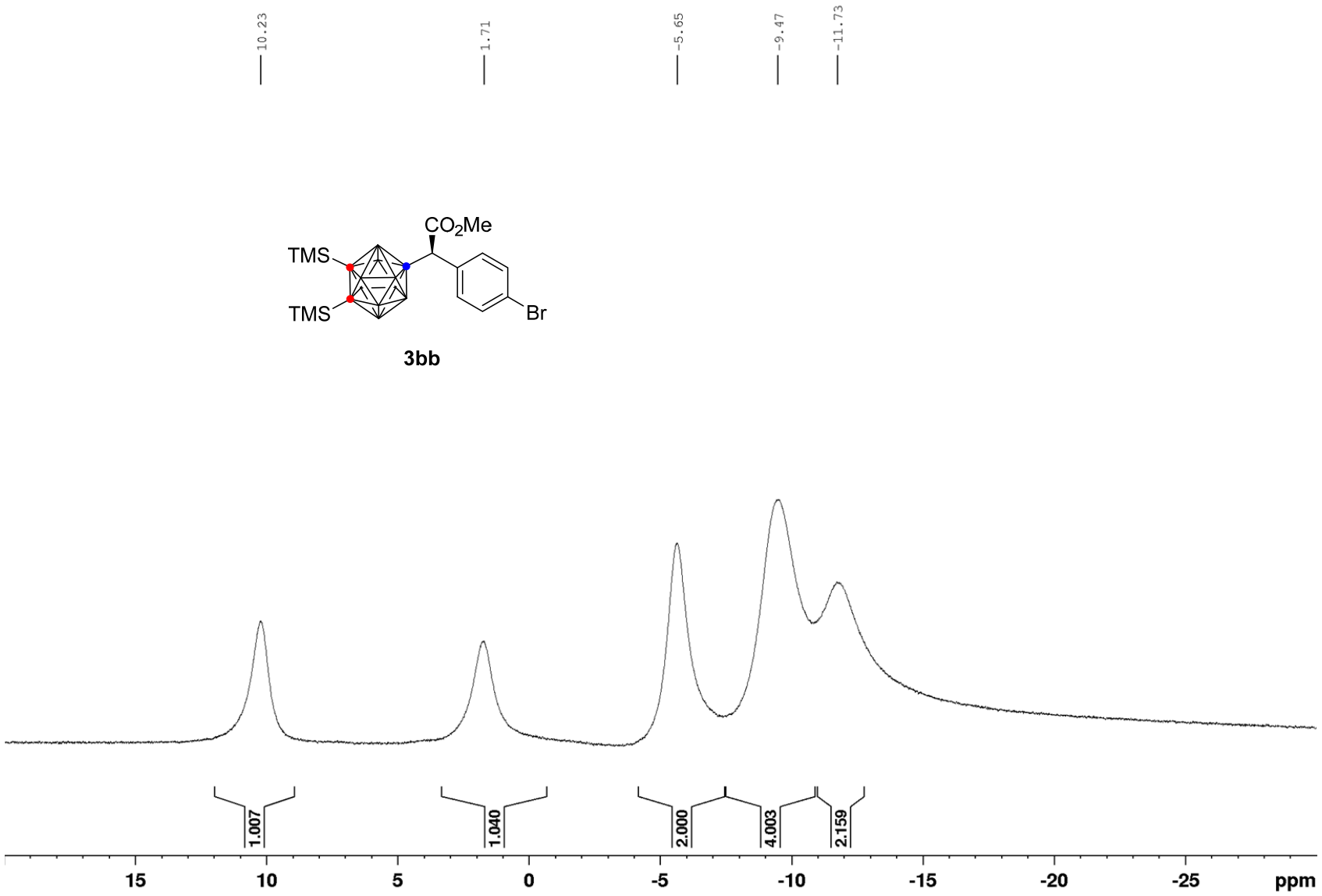


^{11}B NMR (128 MHz, $CDCl_3$)

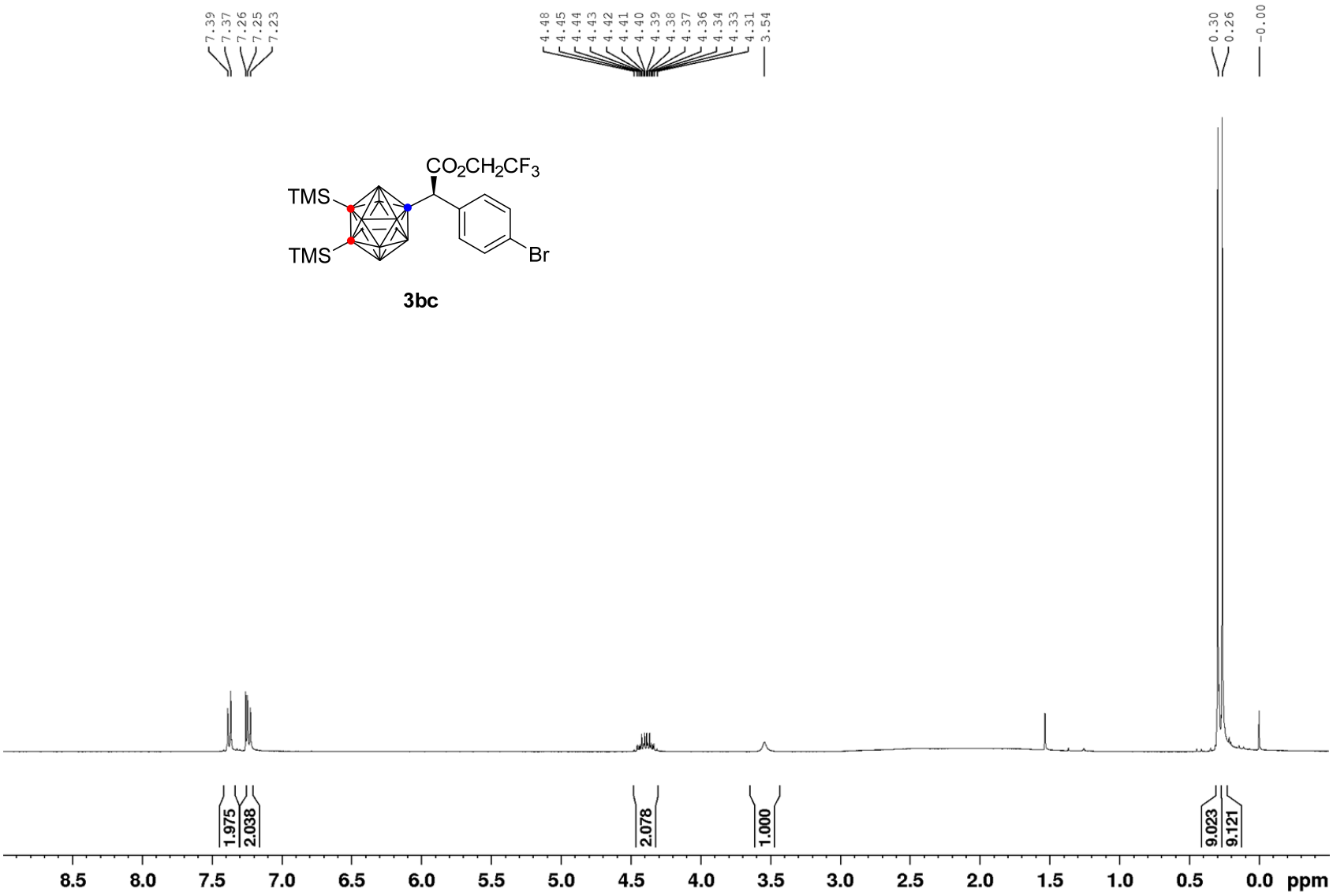


3bb

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

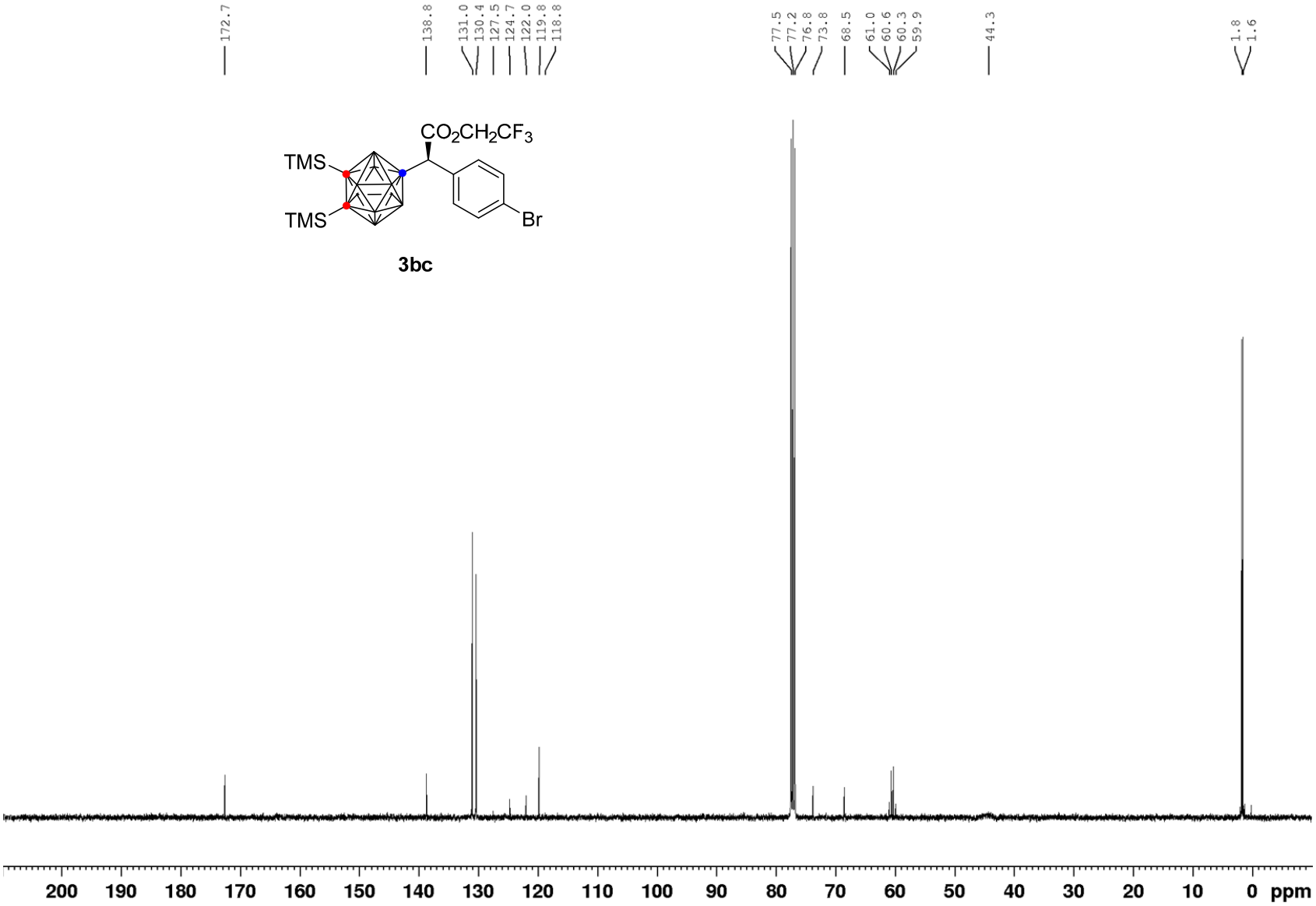


^{1}H NMR (400 MHz, $CDCl_3$)

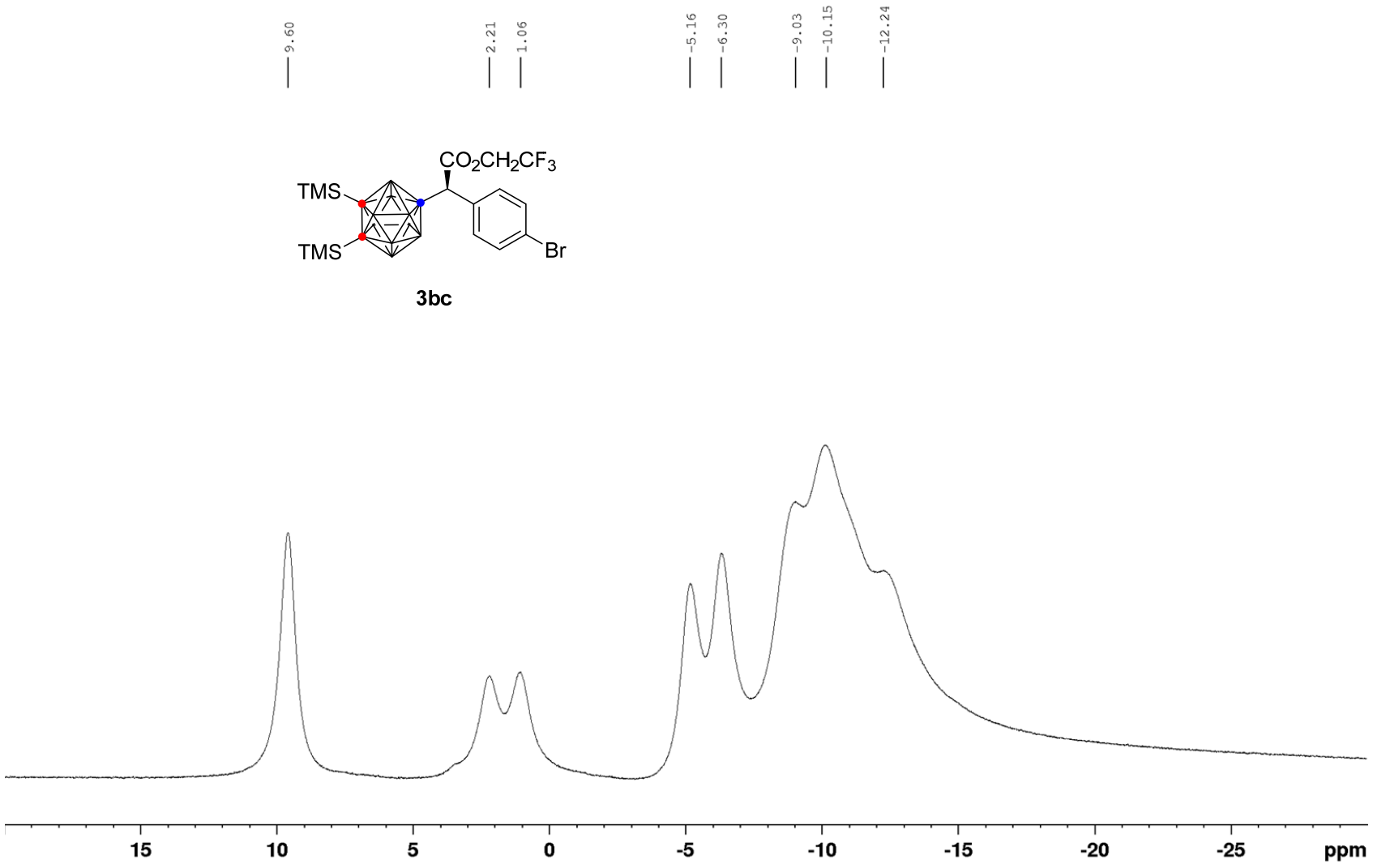


3bc

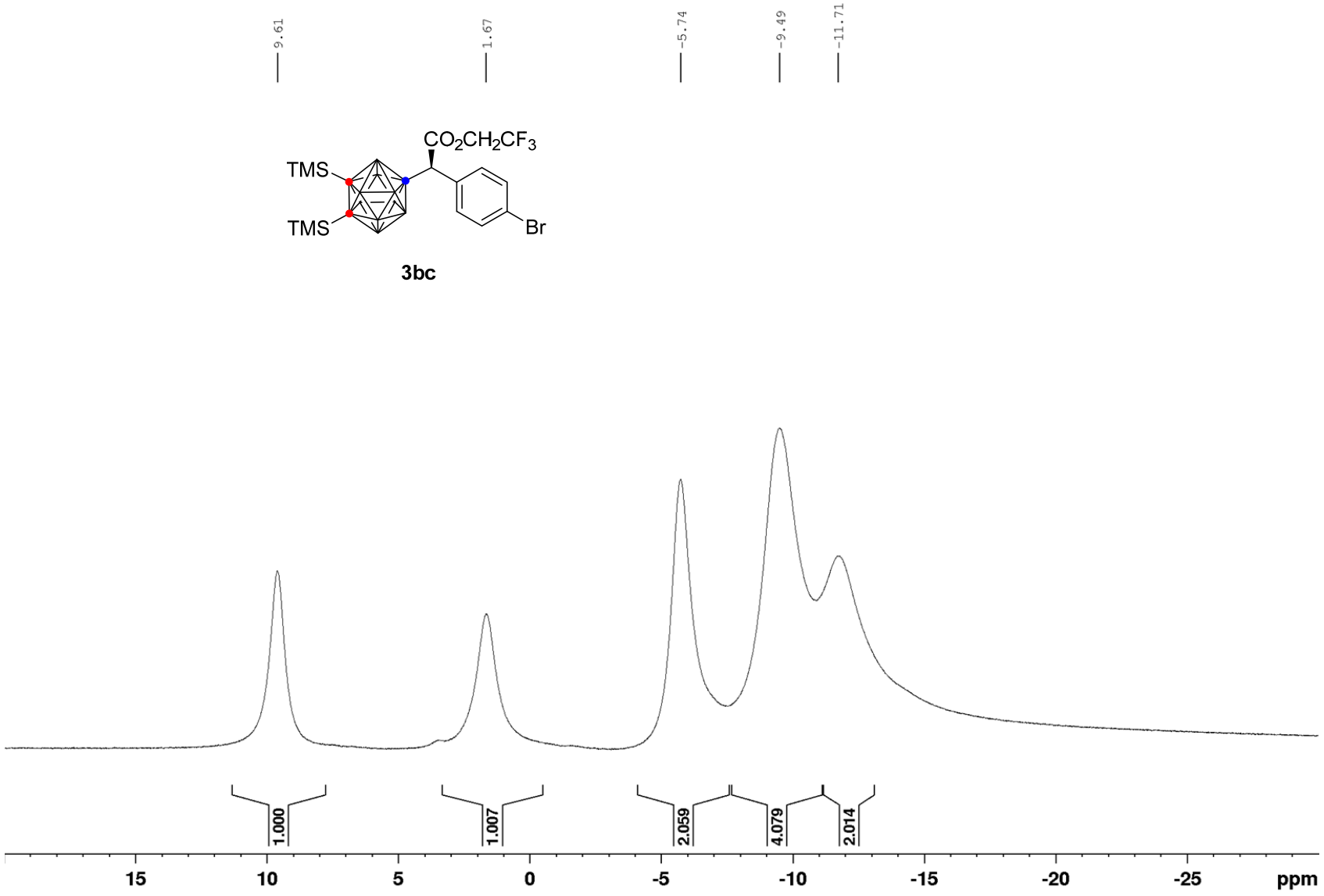
^{13}C NMR (100 MHz, $CDCl_3$)



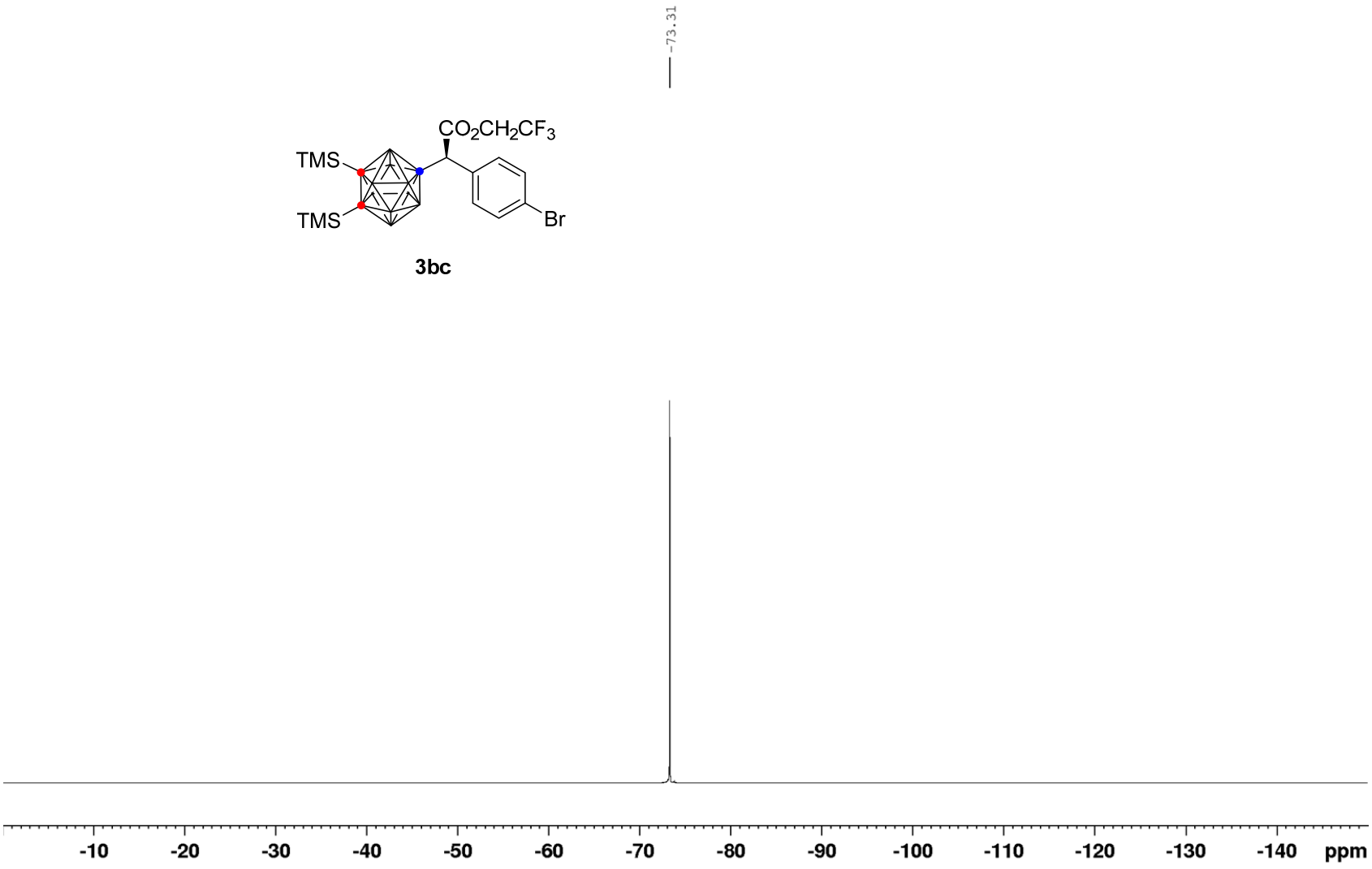
^{11}B NMR (128 MHz, $CDCl_3$)



$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

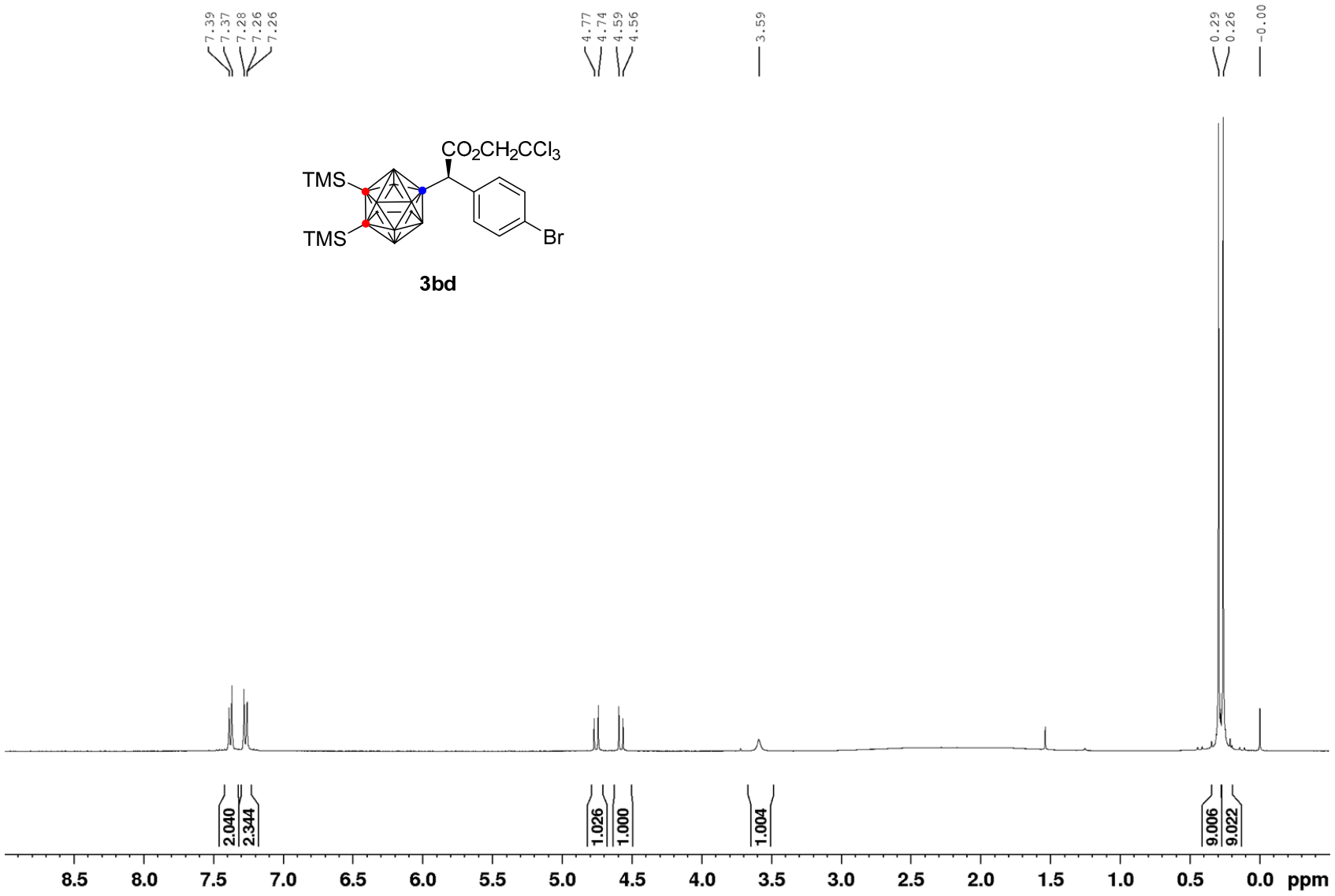


$^{19}F\{^{1}H\}$ NMR (377 MHz, $CDCl_3$)

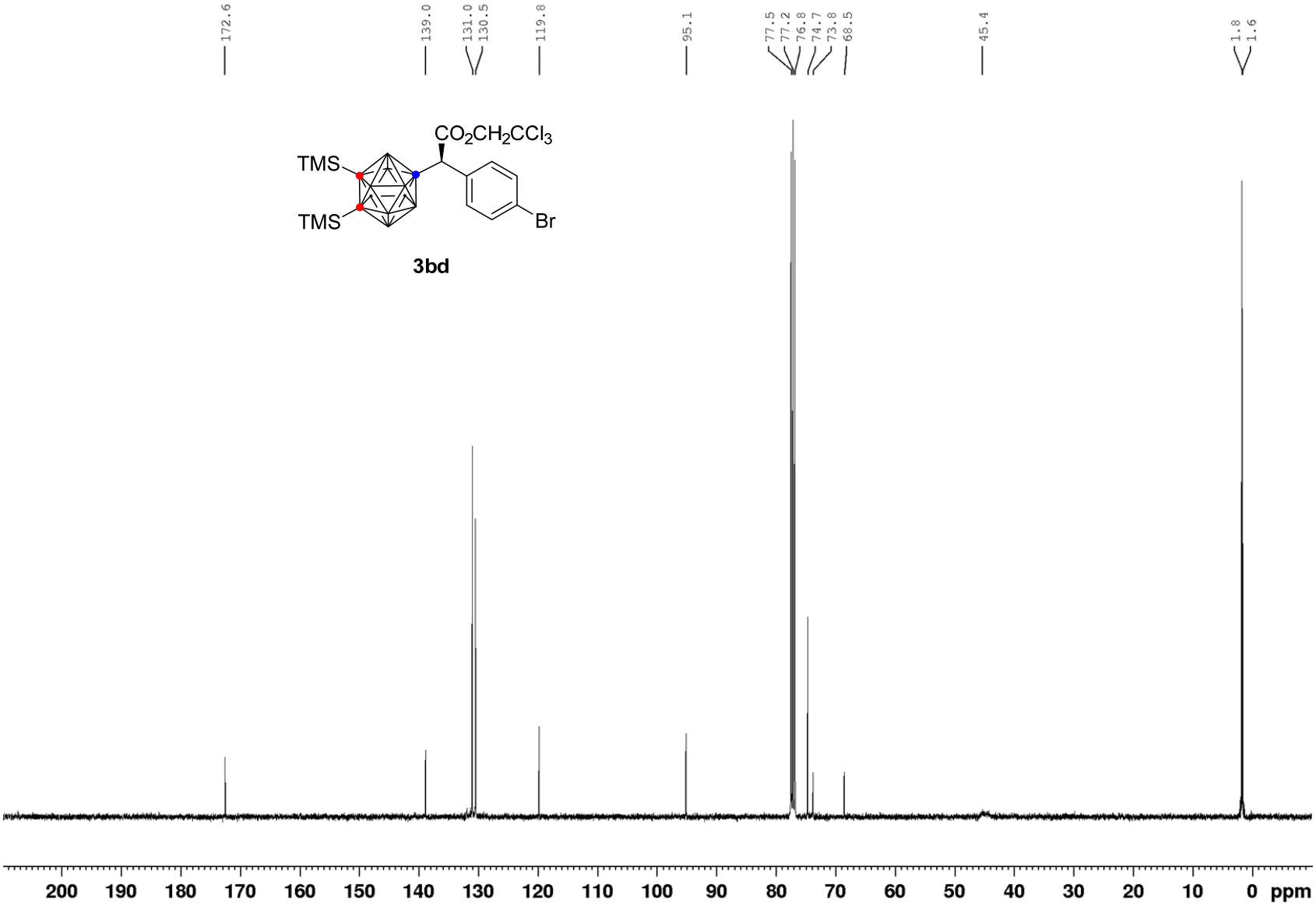


3bc

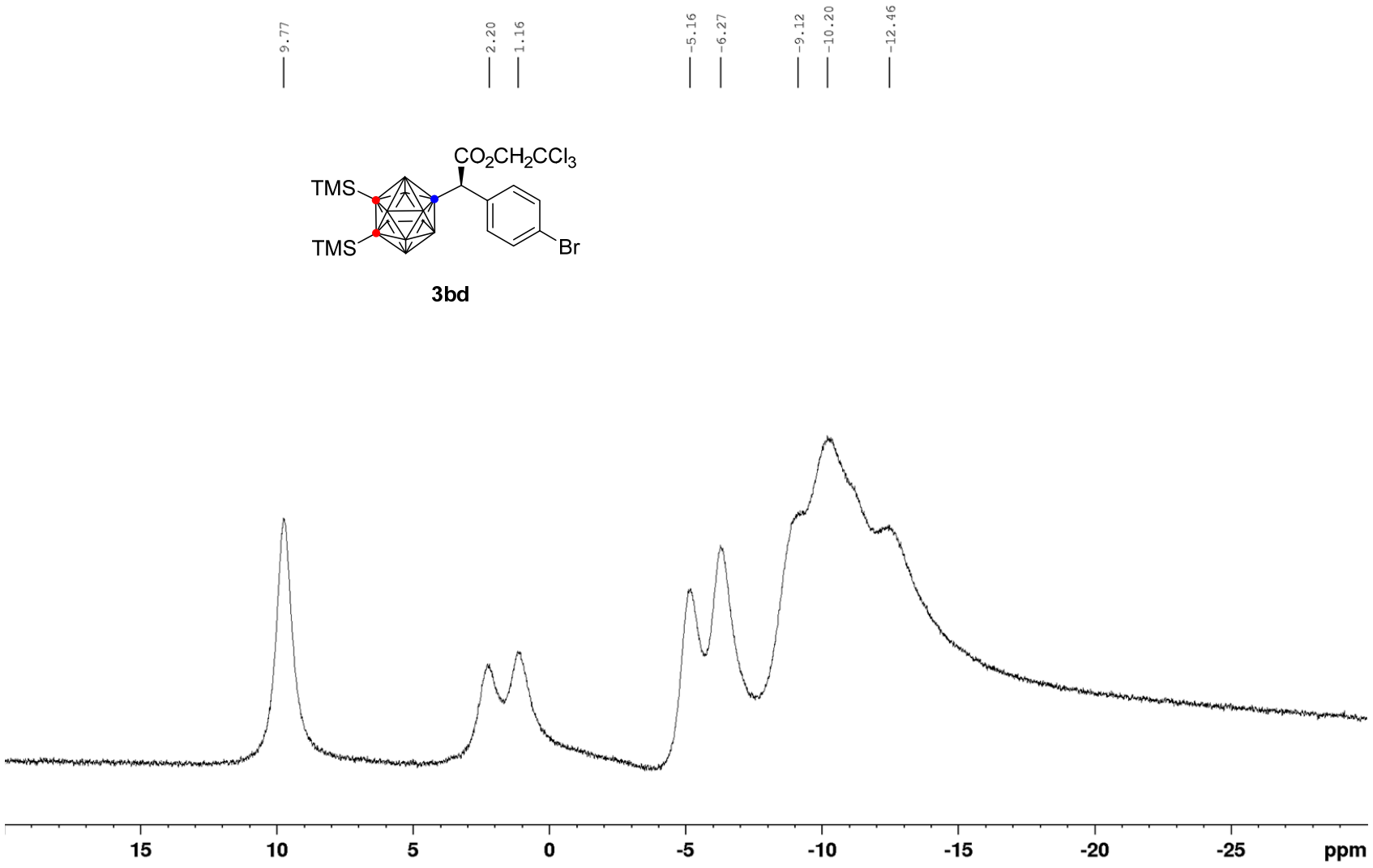
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

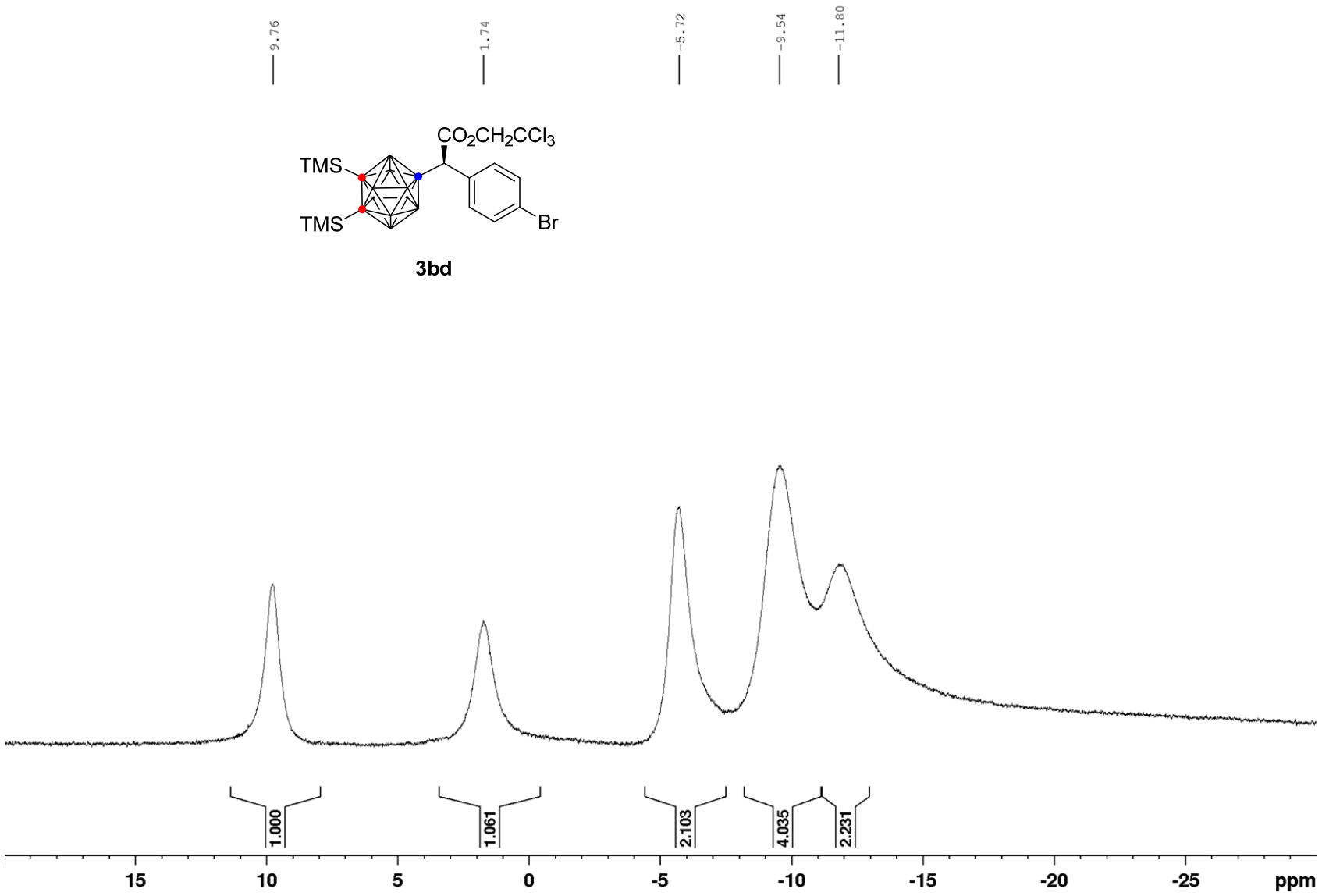


^{11}B NMR (128 MHz, $CDCl_3$)

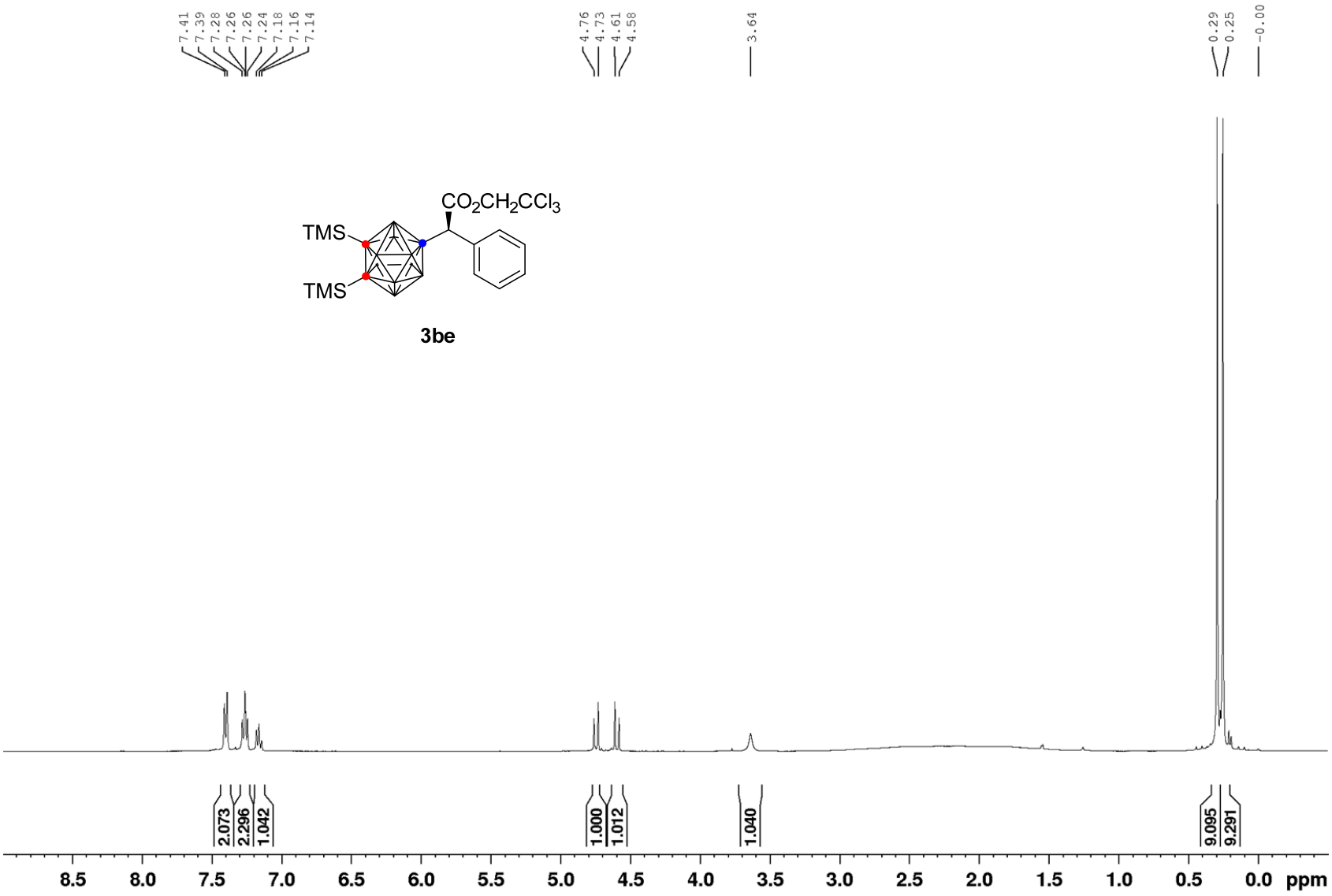


3bd

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

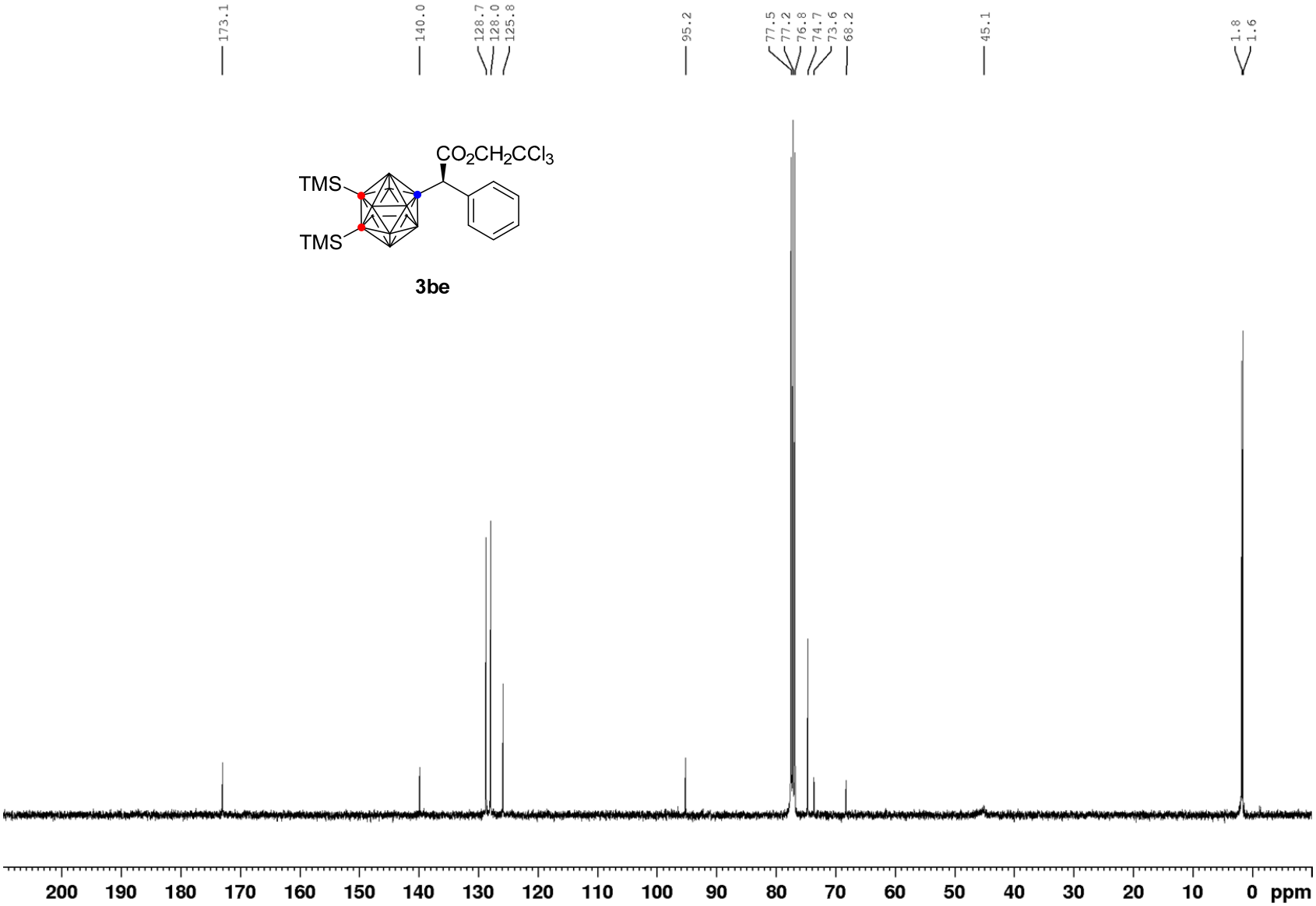


^{1}H NMR (400 MHz, $CDCl_3$)

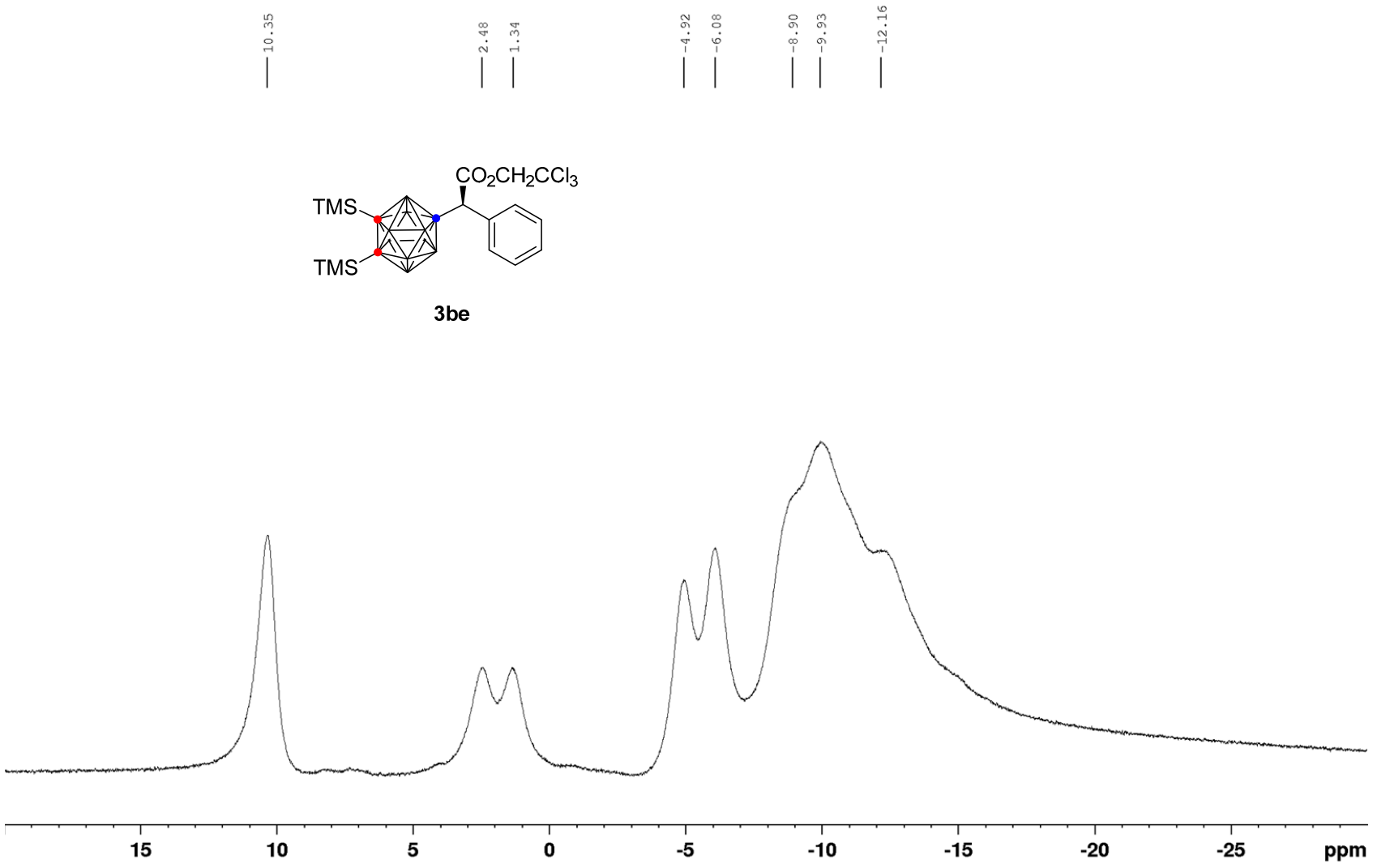


3be

^{13}C NMR (100 MHz, $CDCl_3$)

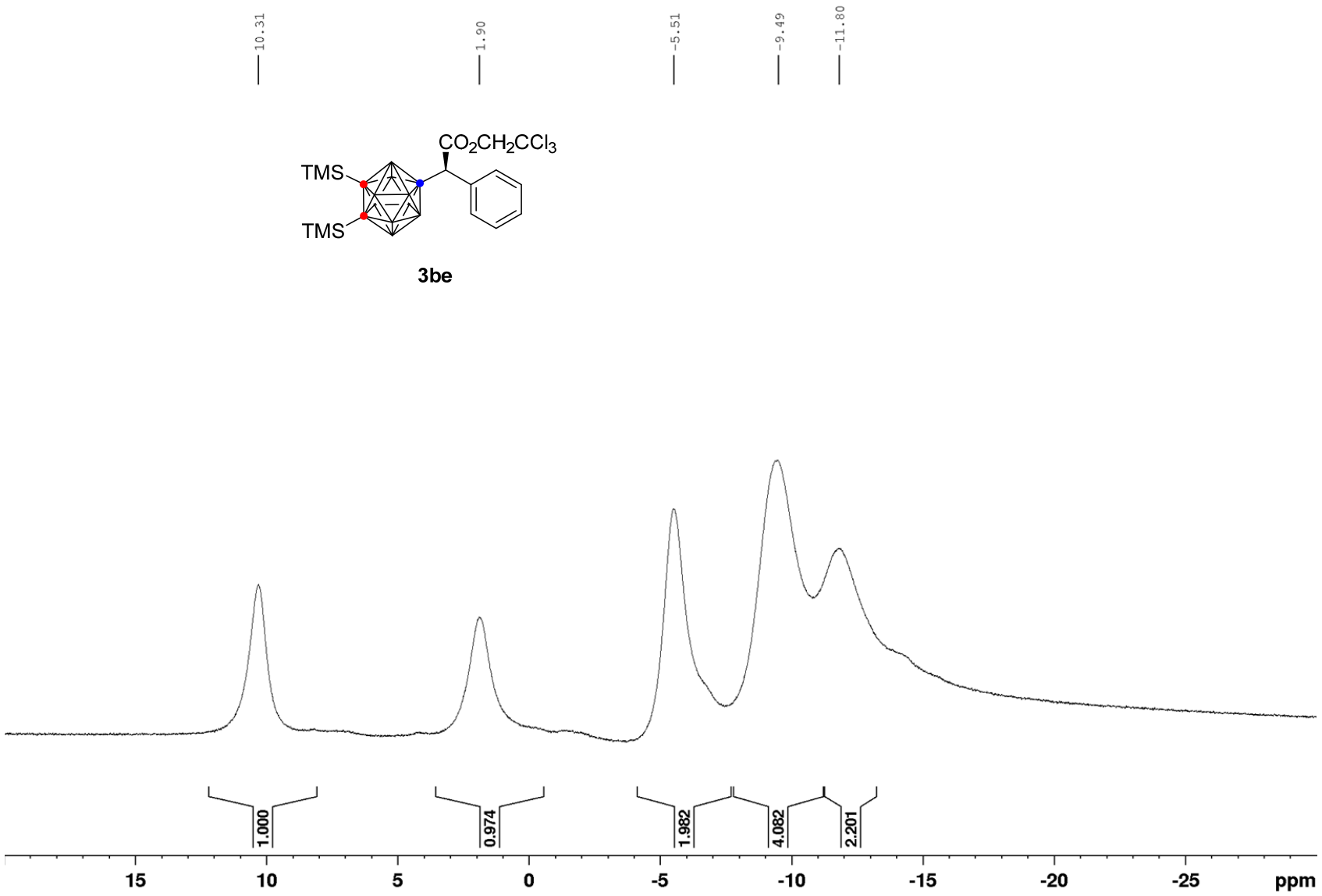


^{11}B NMR (128 MHz, $CDCl_3$)



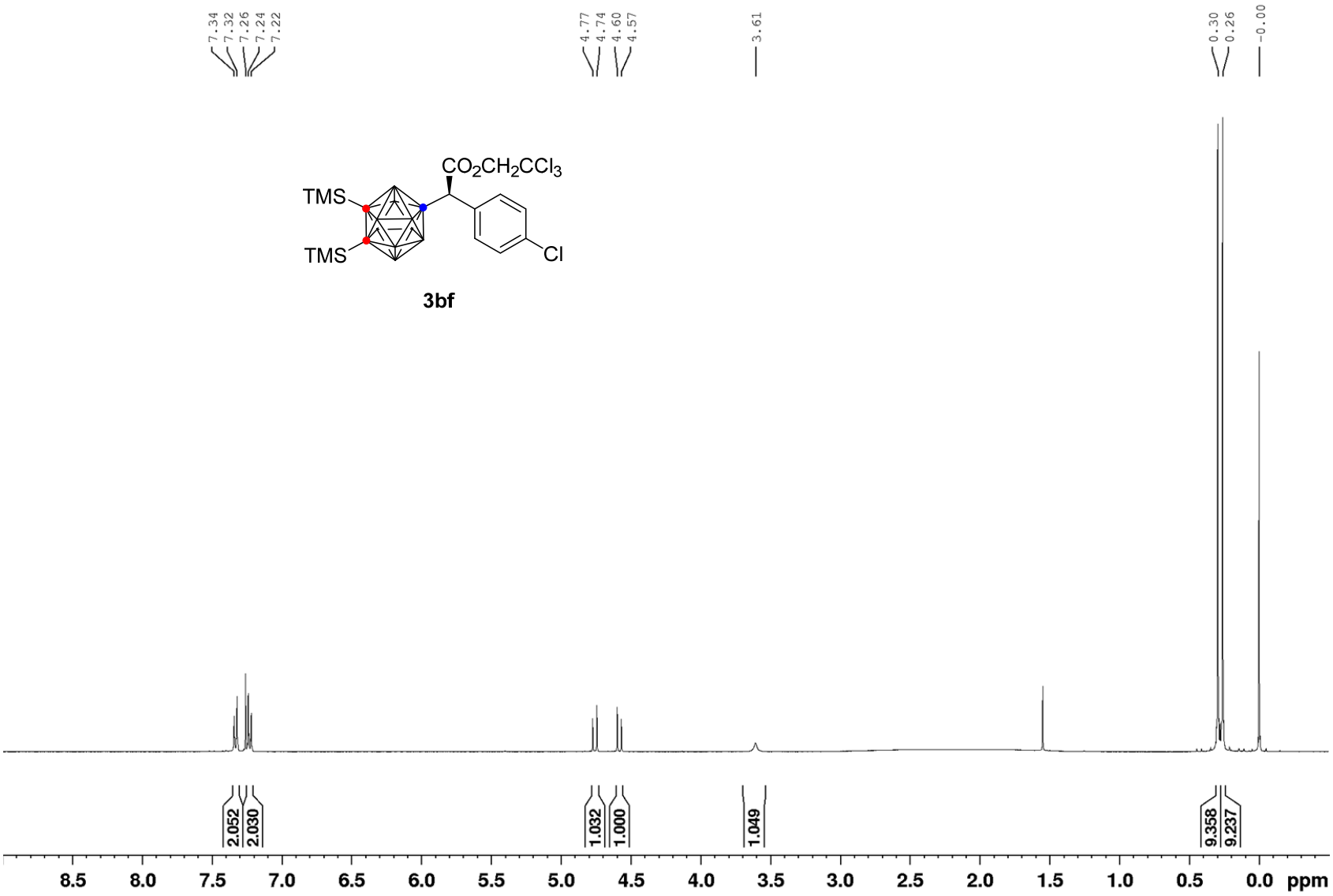
3be

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

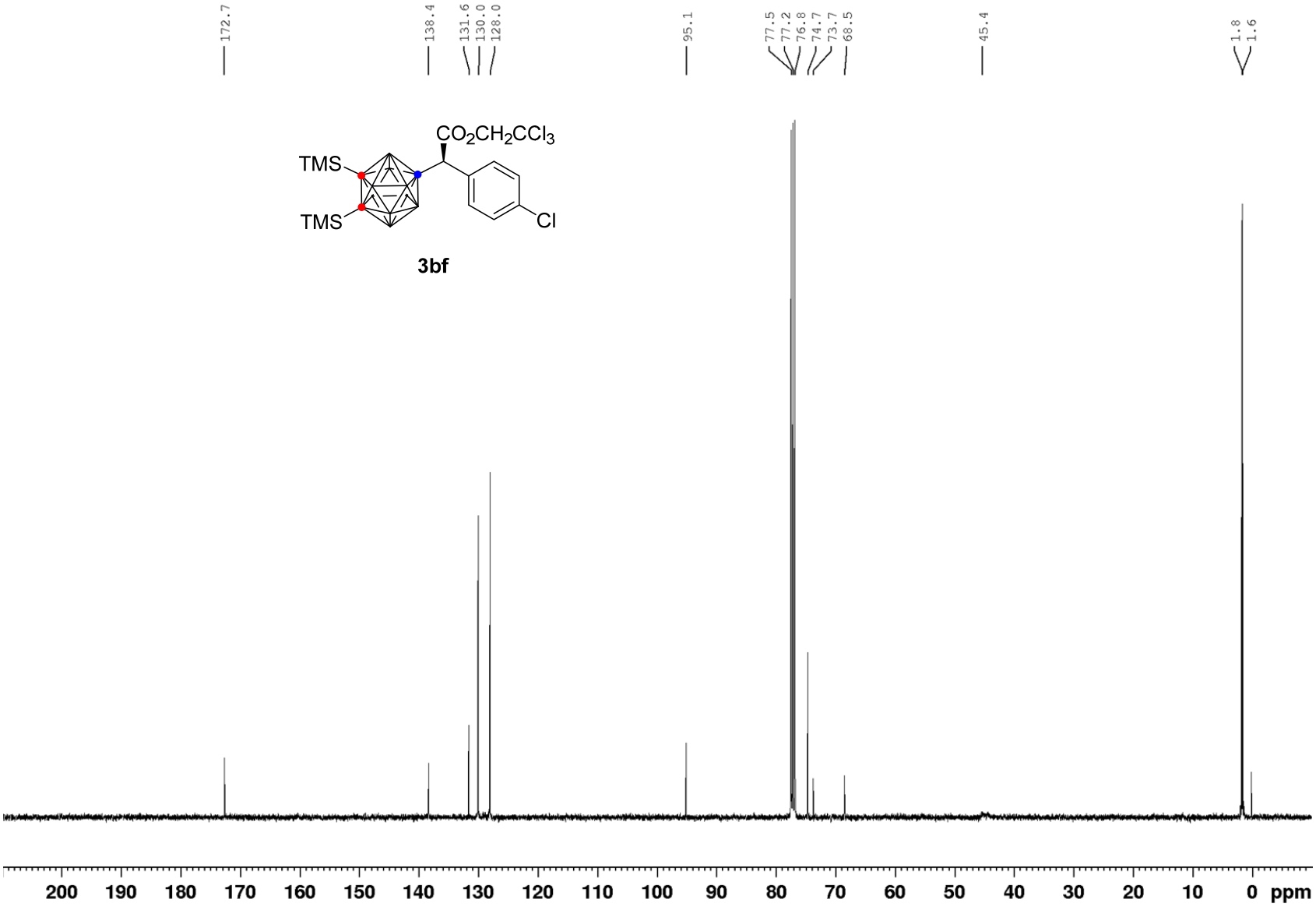


3be

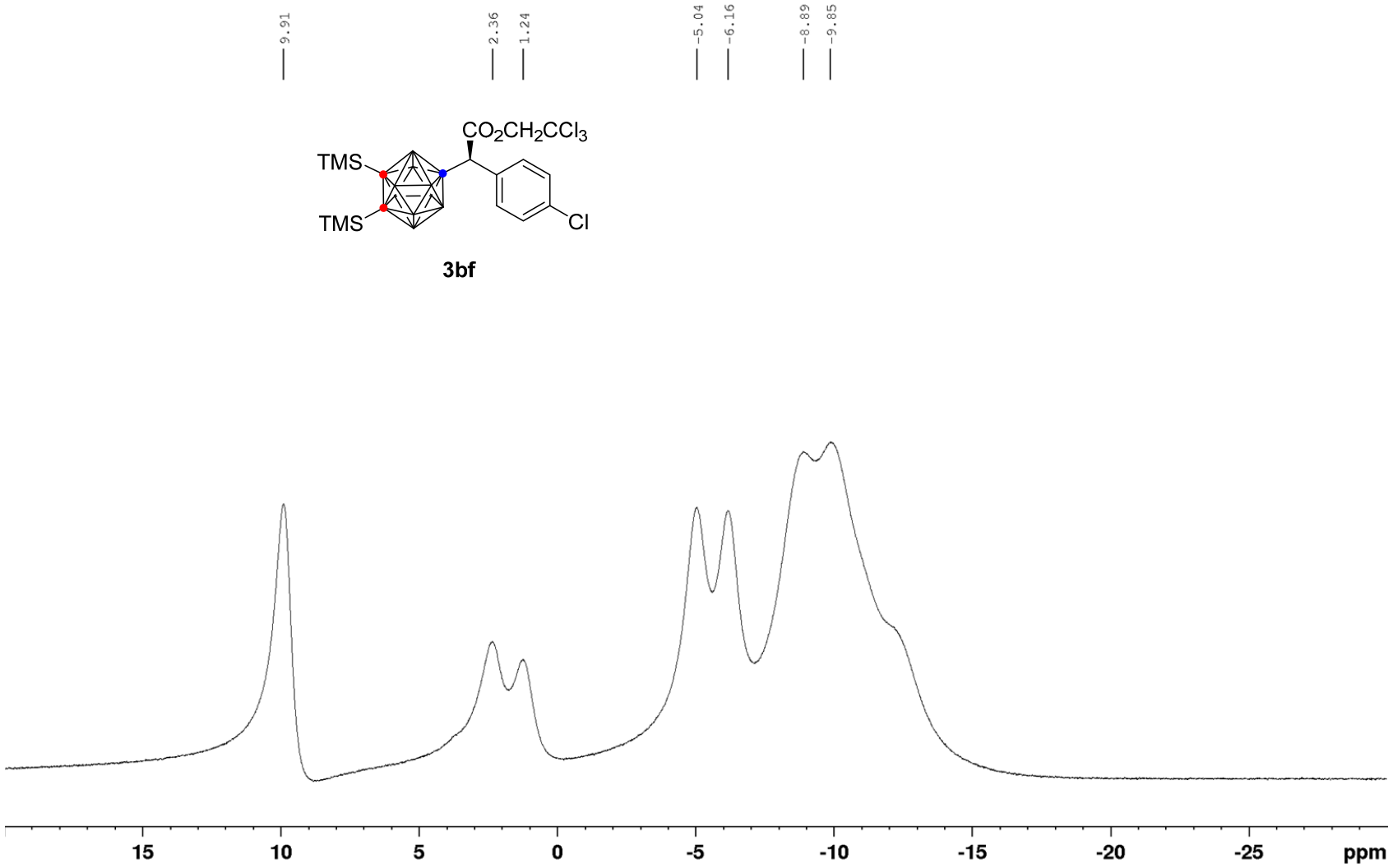
^{1}H NMR (400 MHz, $CDCl_3$)



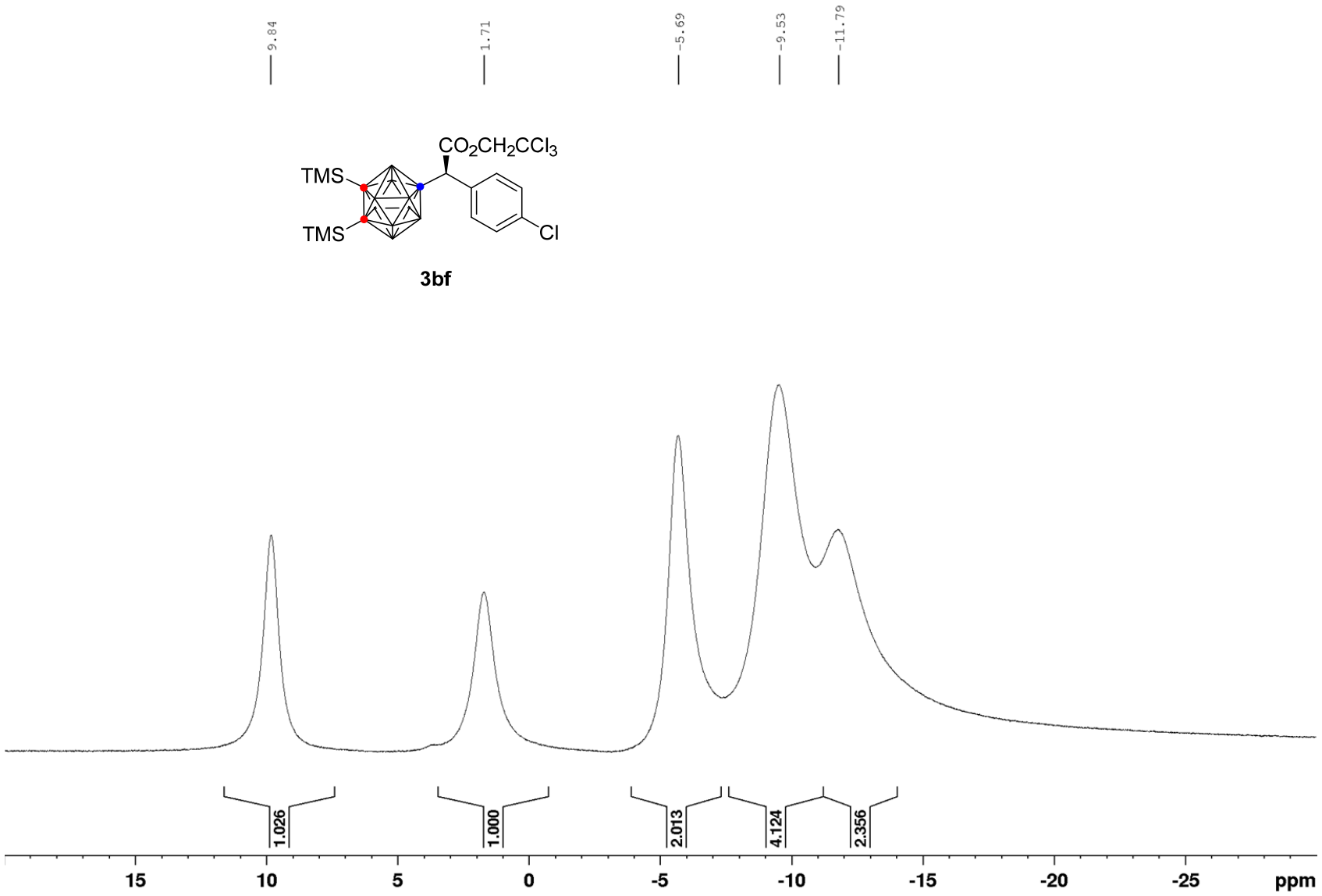
^{13}C NMR (100 MHz, $CDCl_3$)



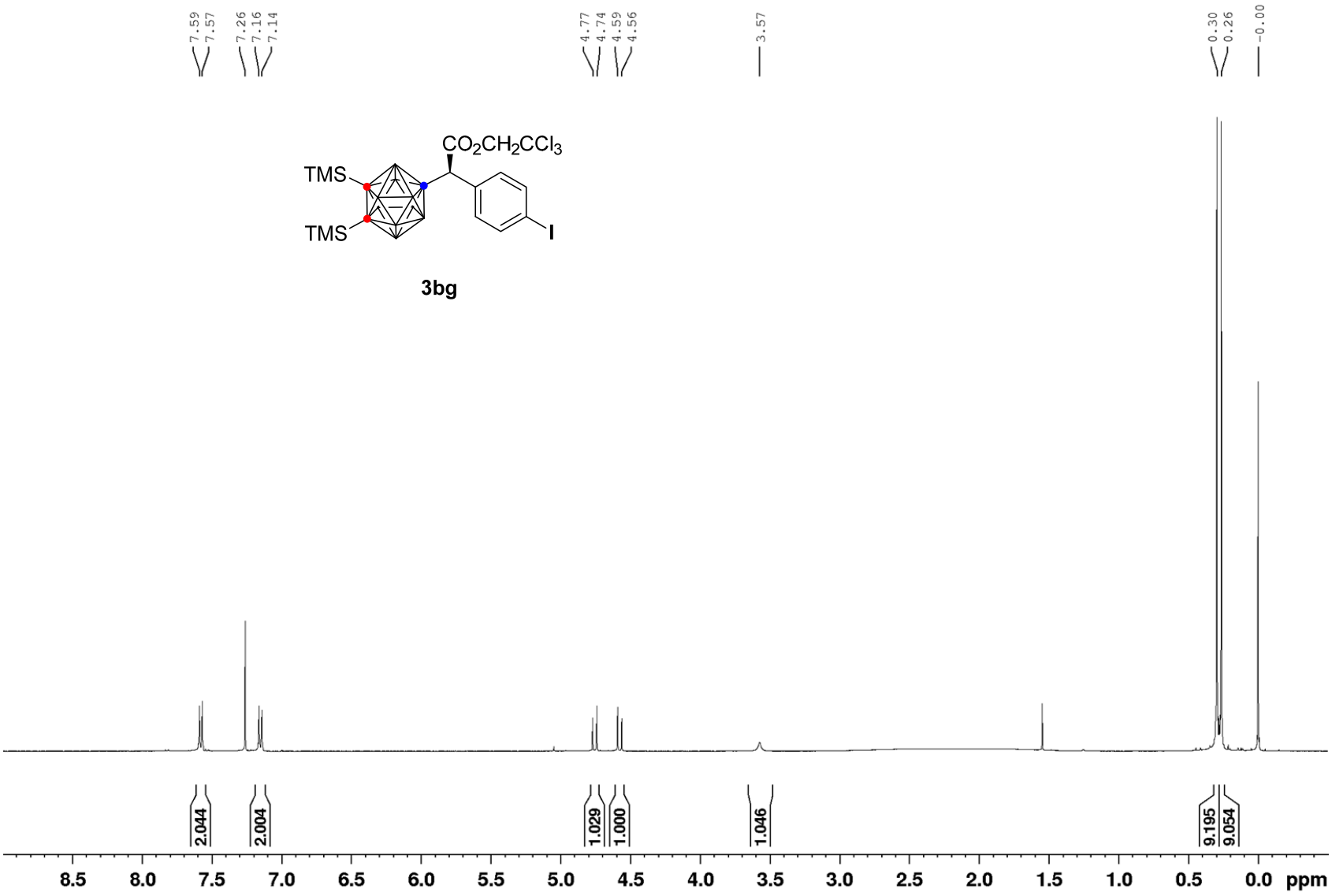
^{11}B NMR (128 MHz, $CDCl_3$)



$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

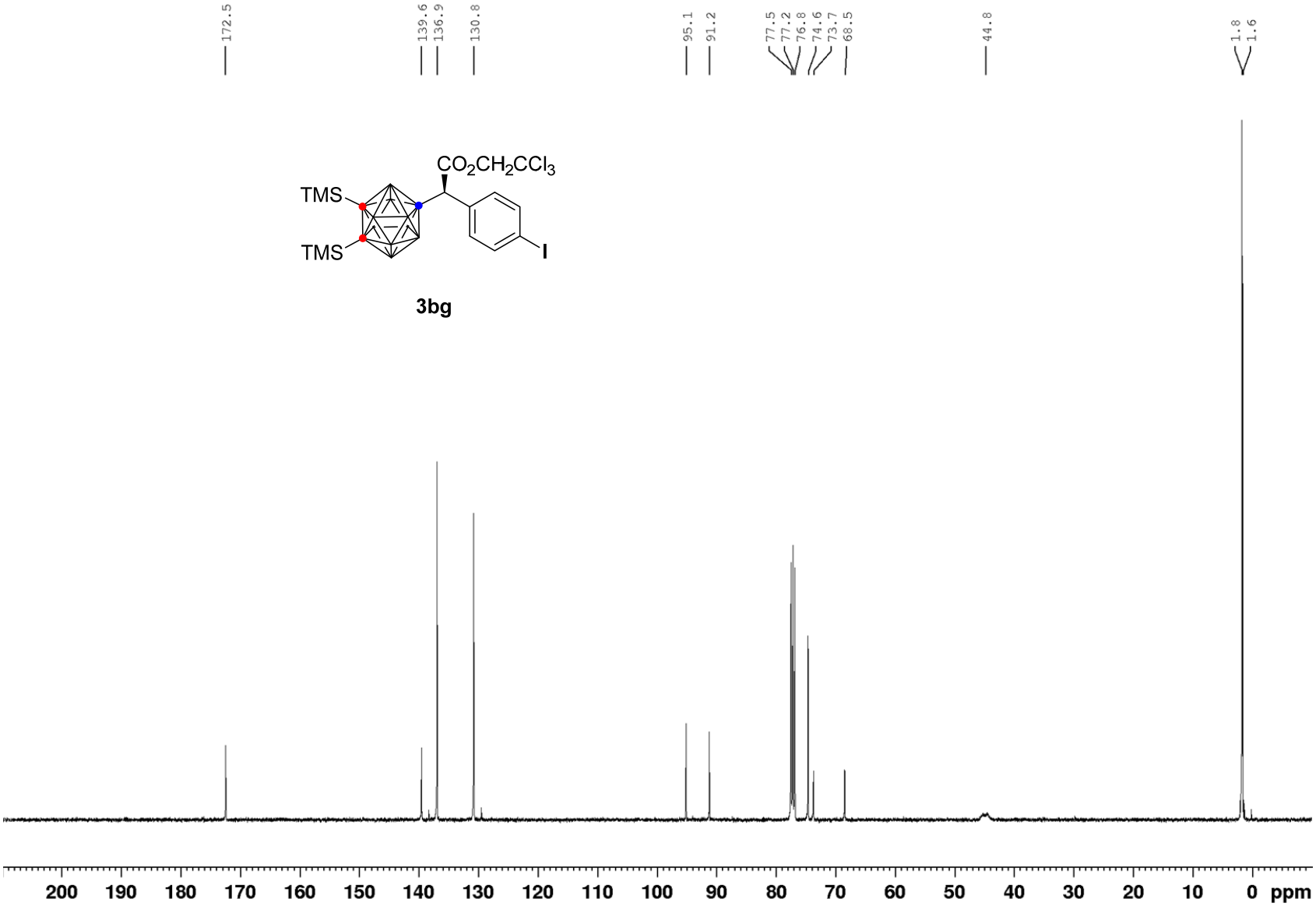


^{1}H NMR (400 MHz, $CDCl_3$)



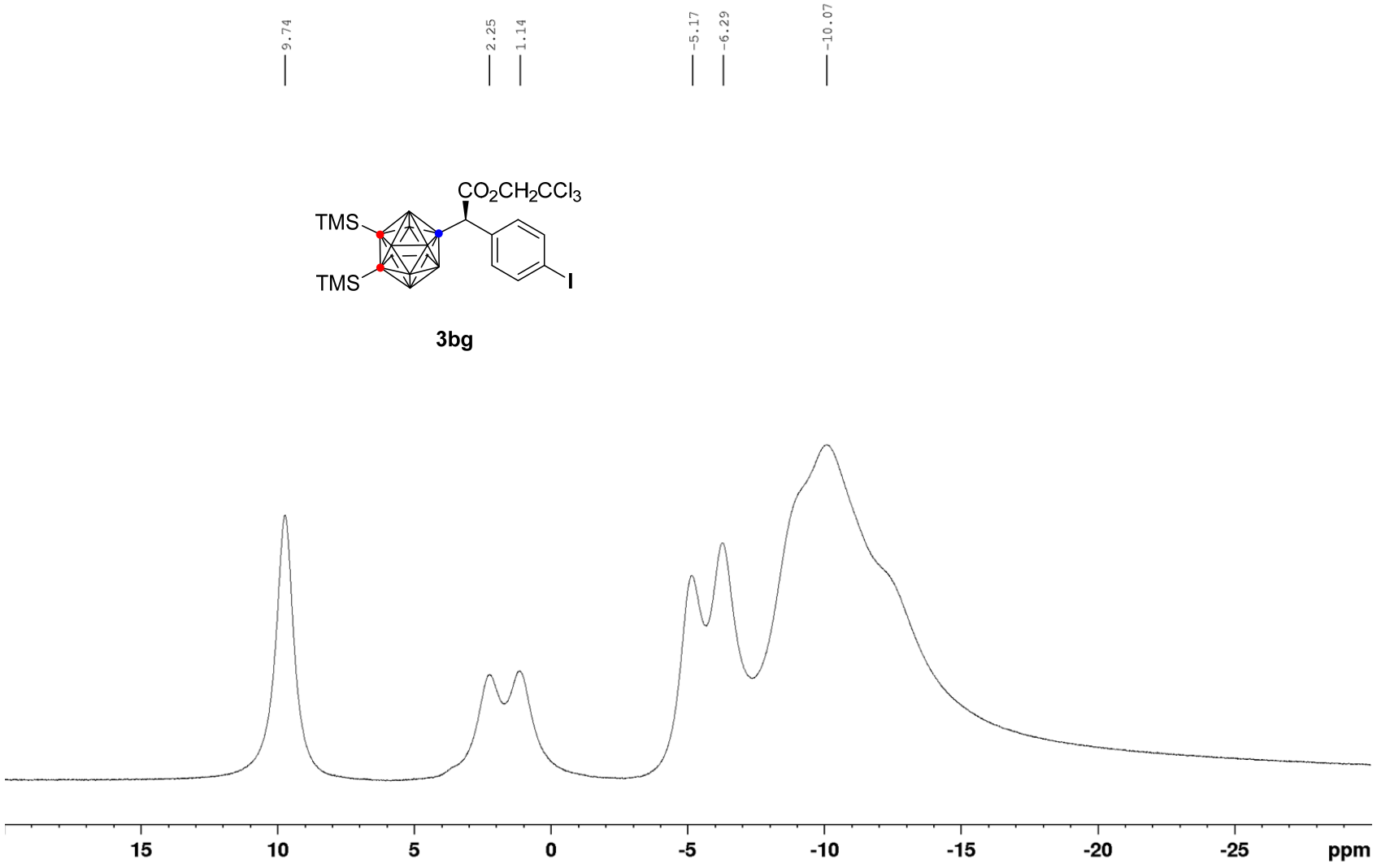
3bg

^{13}C NMR (100 MHz, $CDCl_3$)

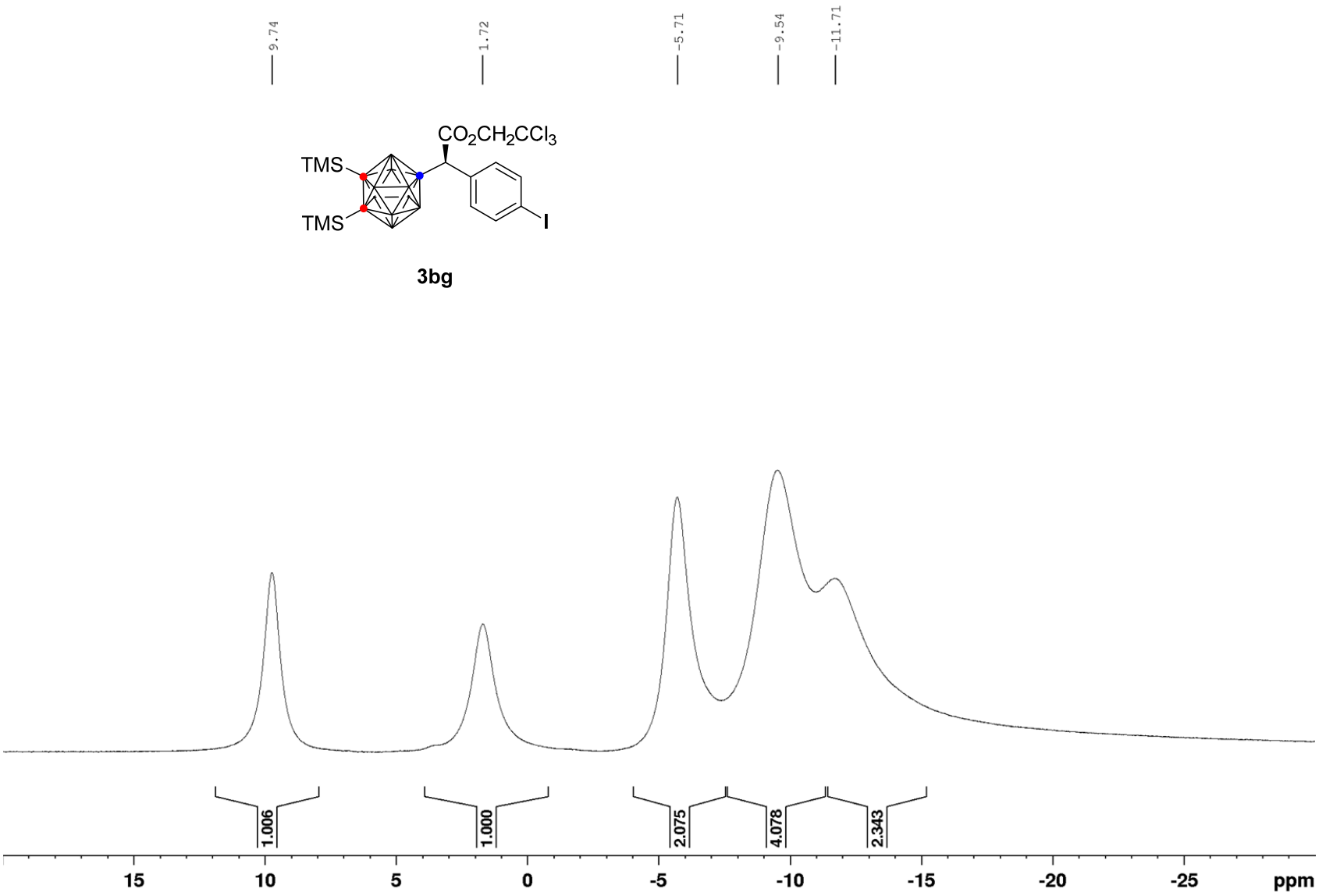


3bg

^{11}B NMR (128 MHz, $CDCl_3$)

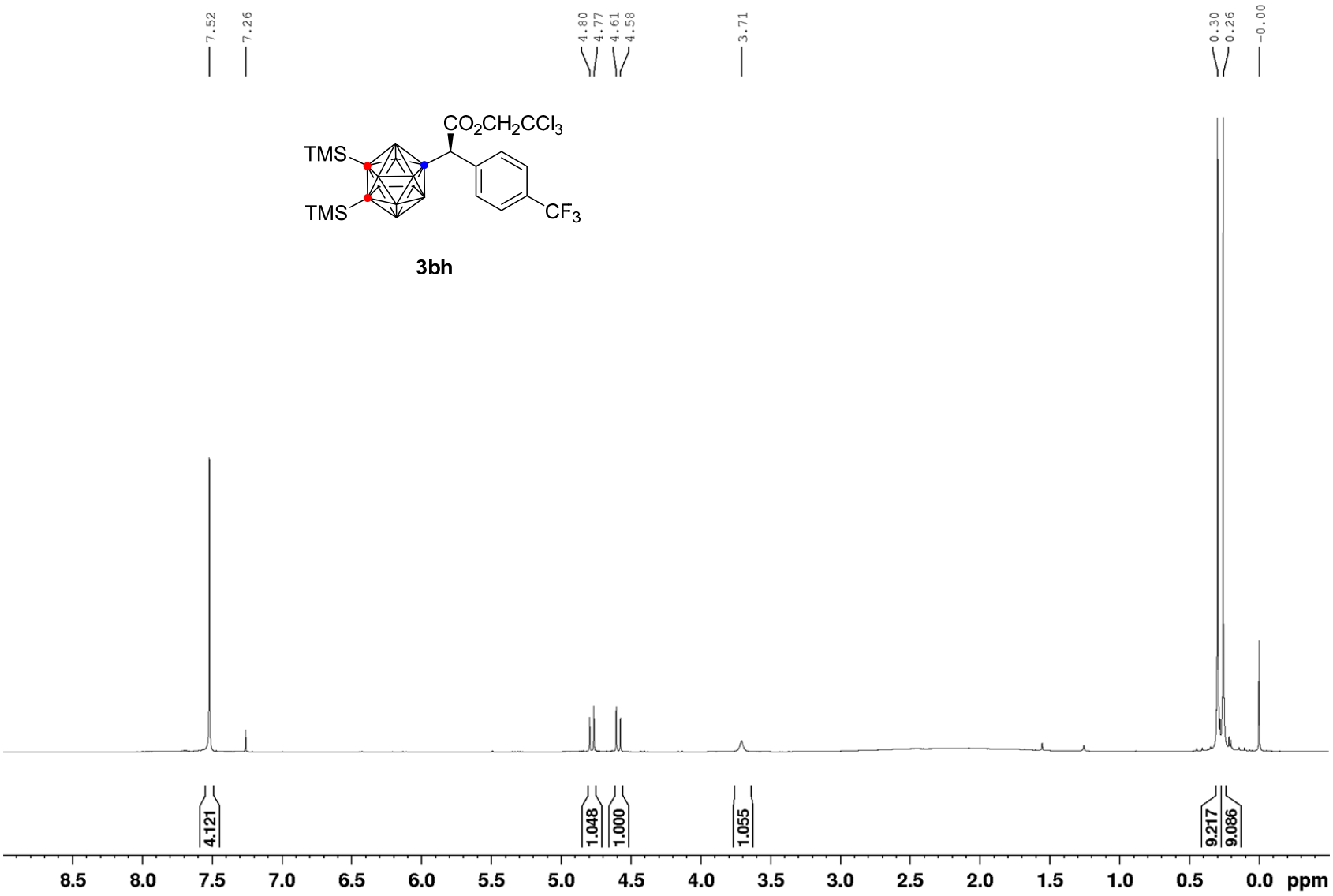


$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

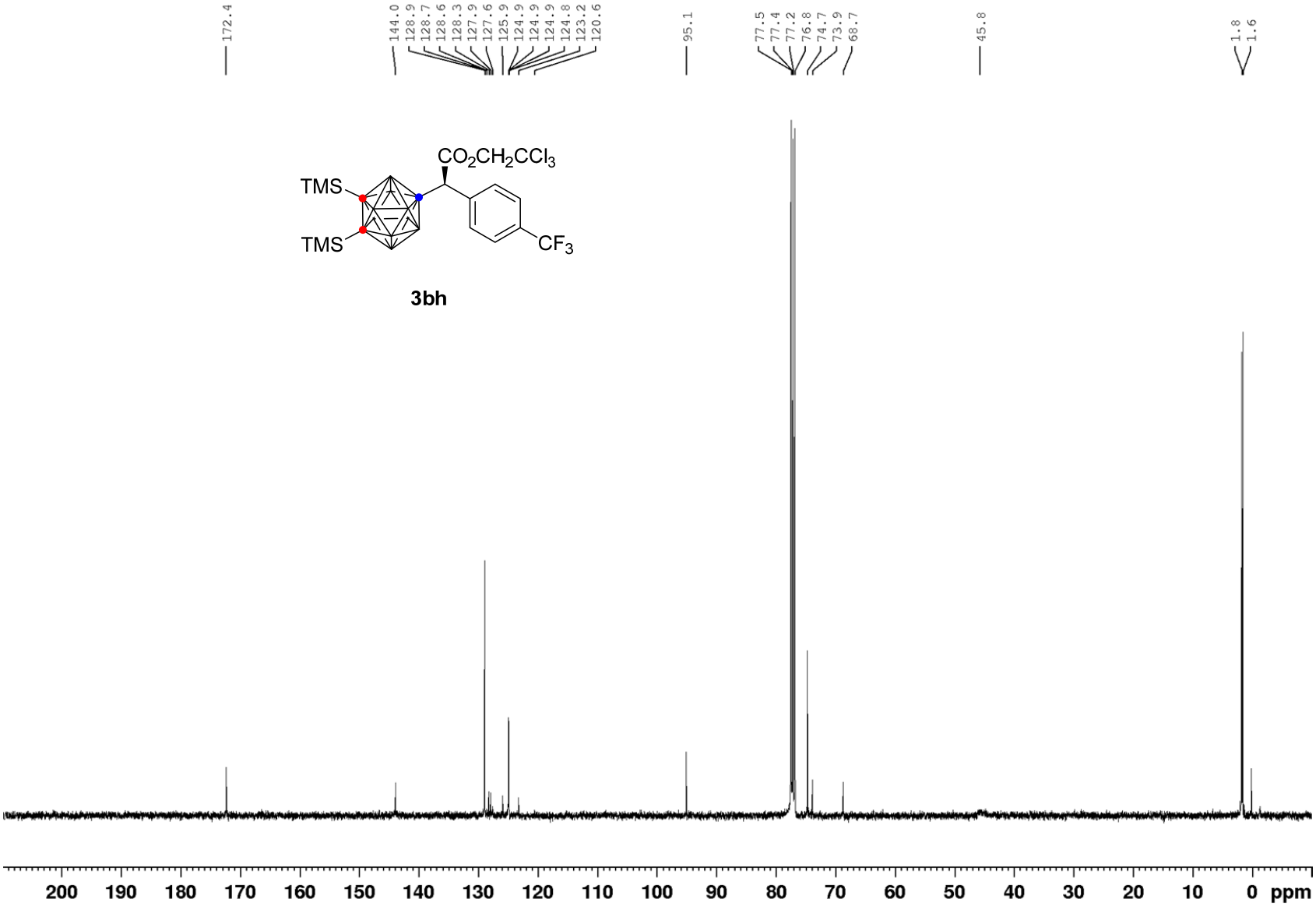


3bg

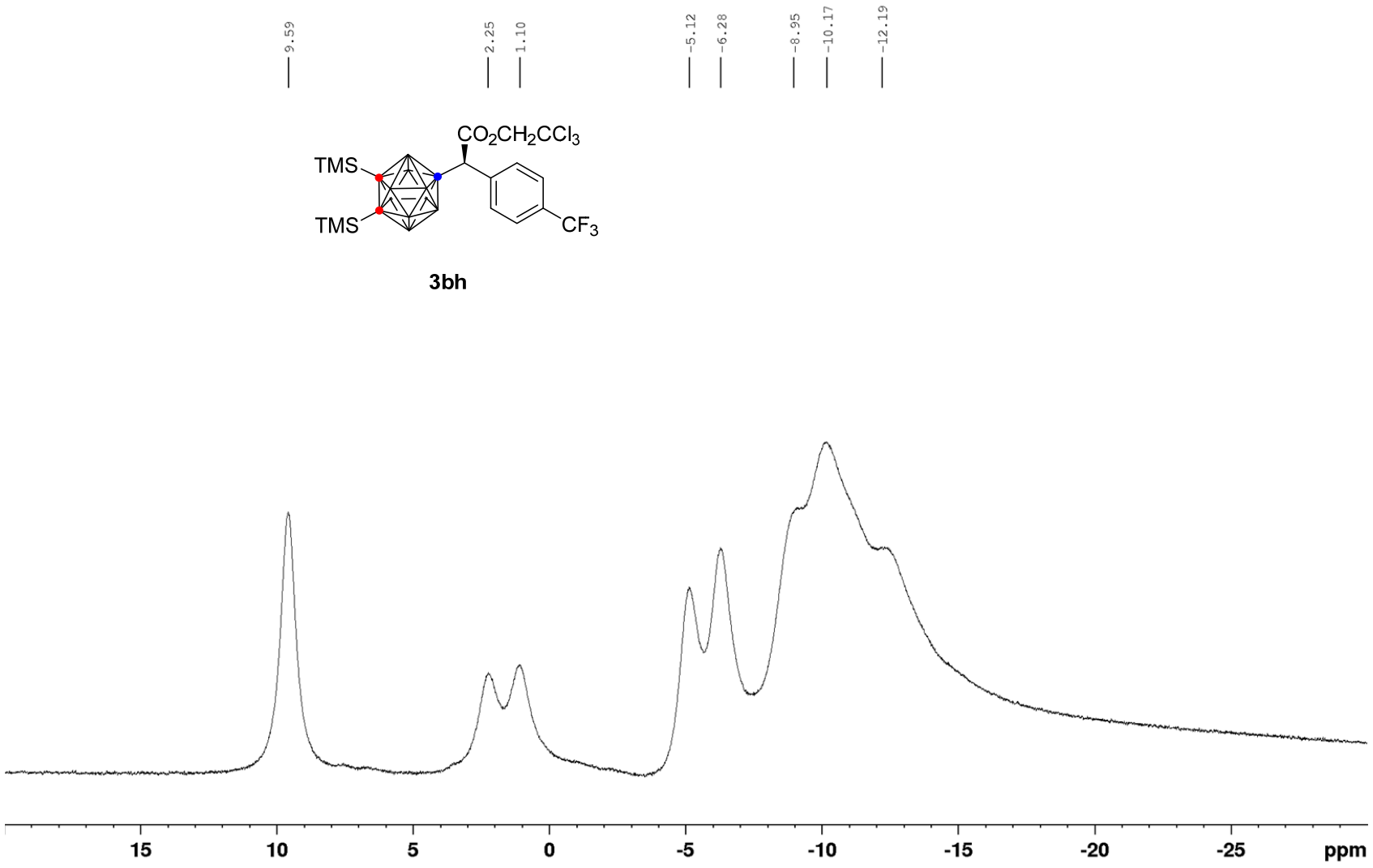
^{1}H NMR (400 MHz, $CDCl_3$)



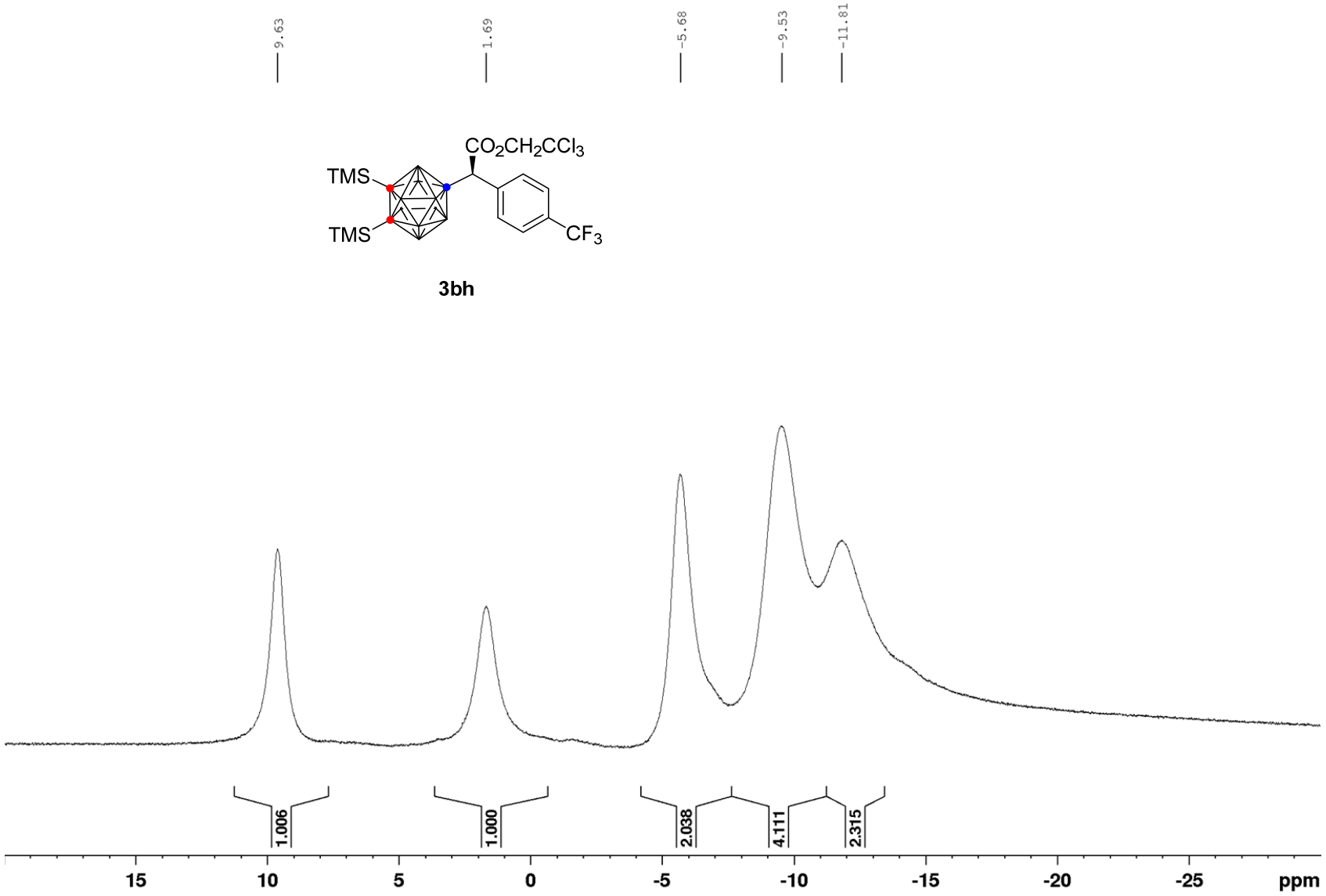
^{13}C NMR (100 MHz, $CDCl_3$)



^{11}B NMR (128 MHz, $CDCl_3$)

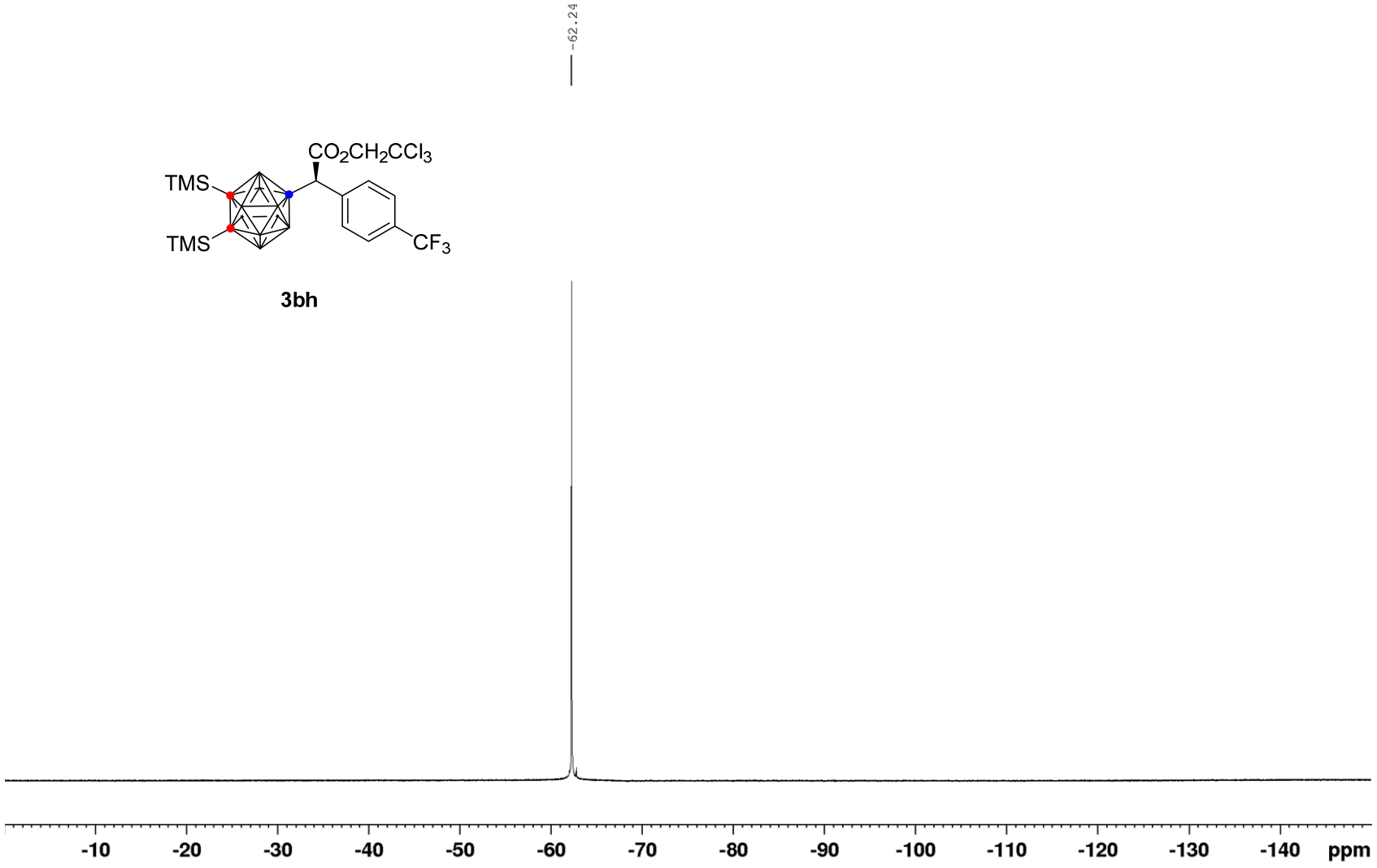


$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

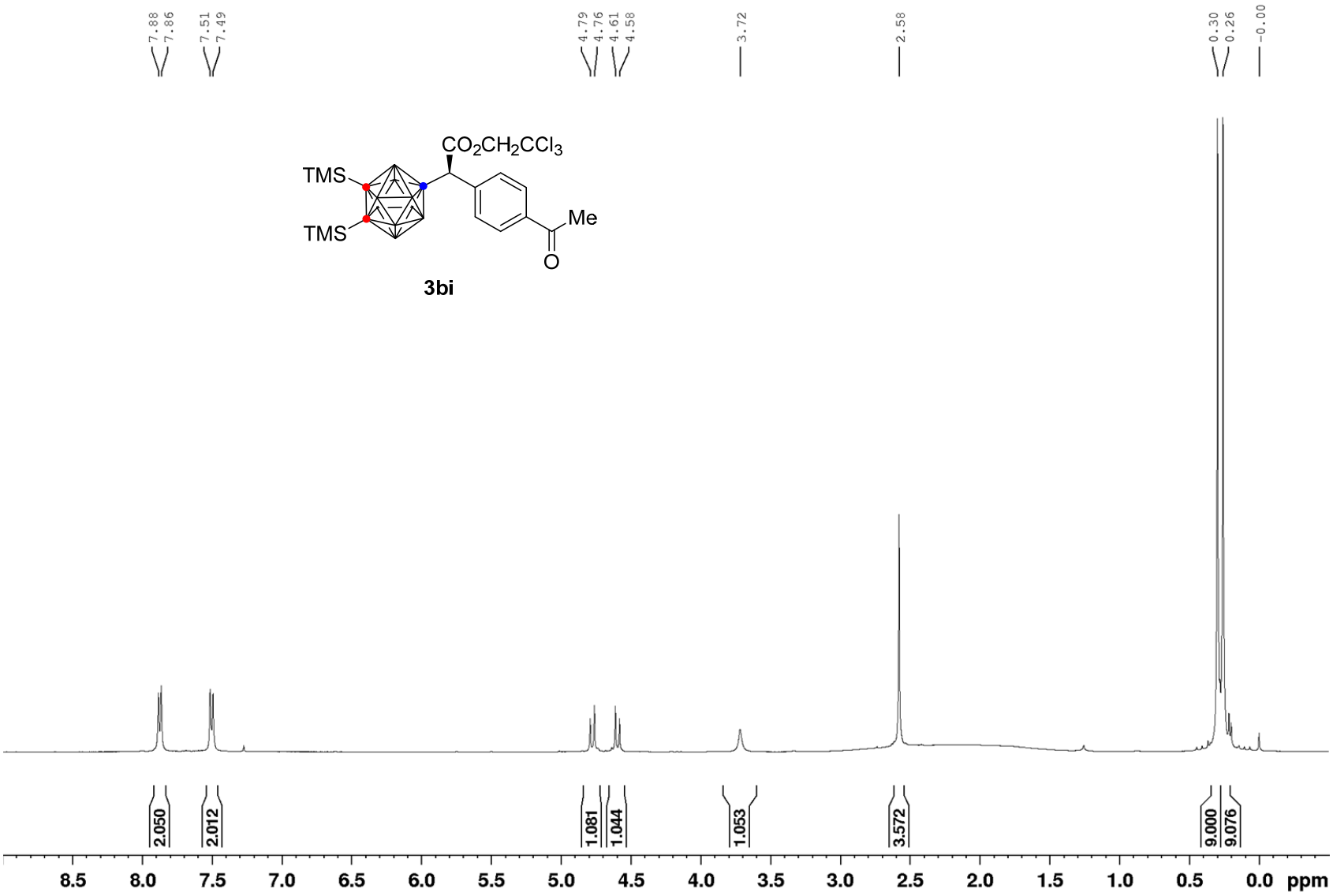


3bh

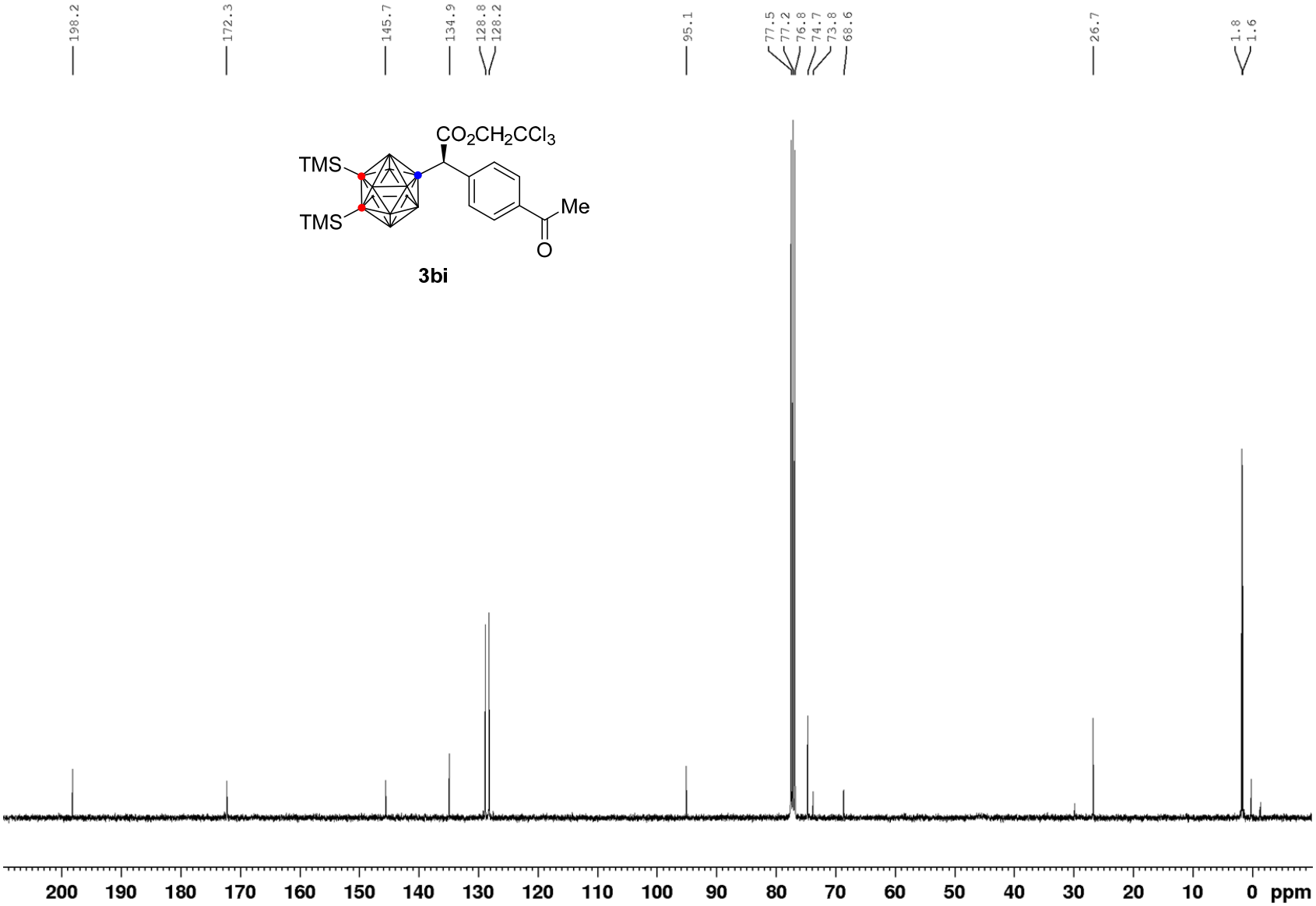
$^{19}F\{^{1}H\}$ NMR (377 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

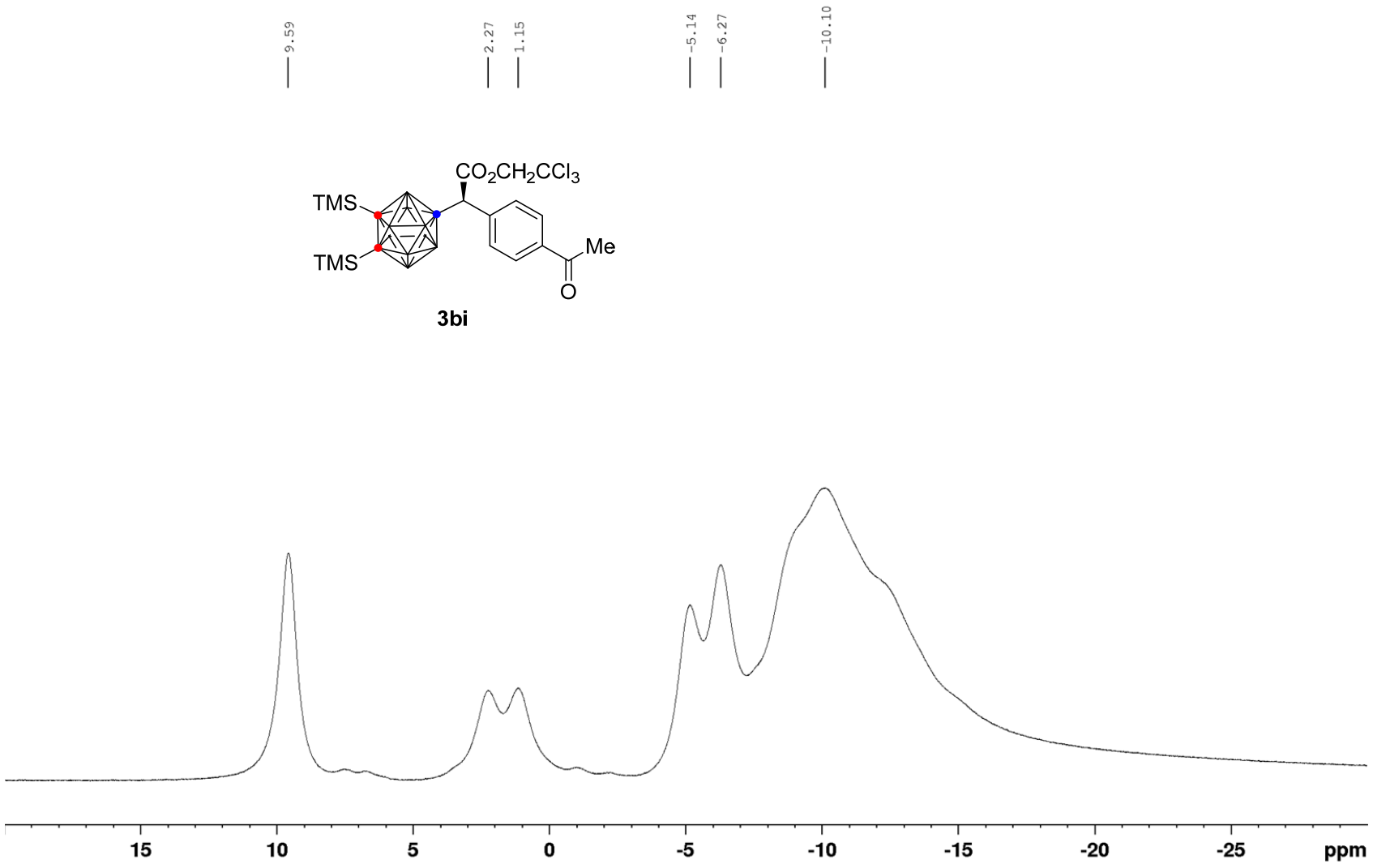


^{13}C NMR (100 MHz, $CDCl_3$)



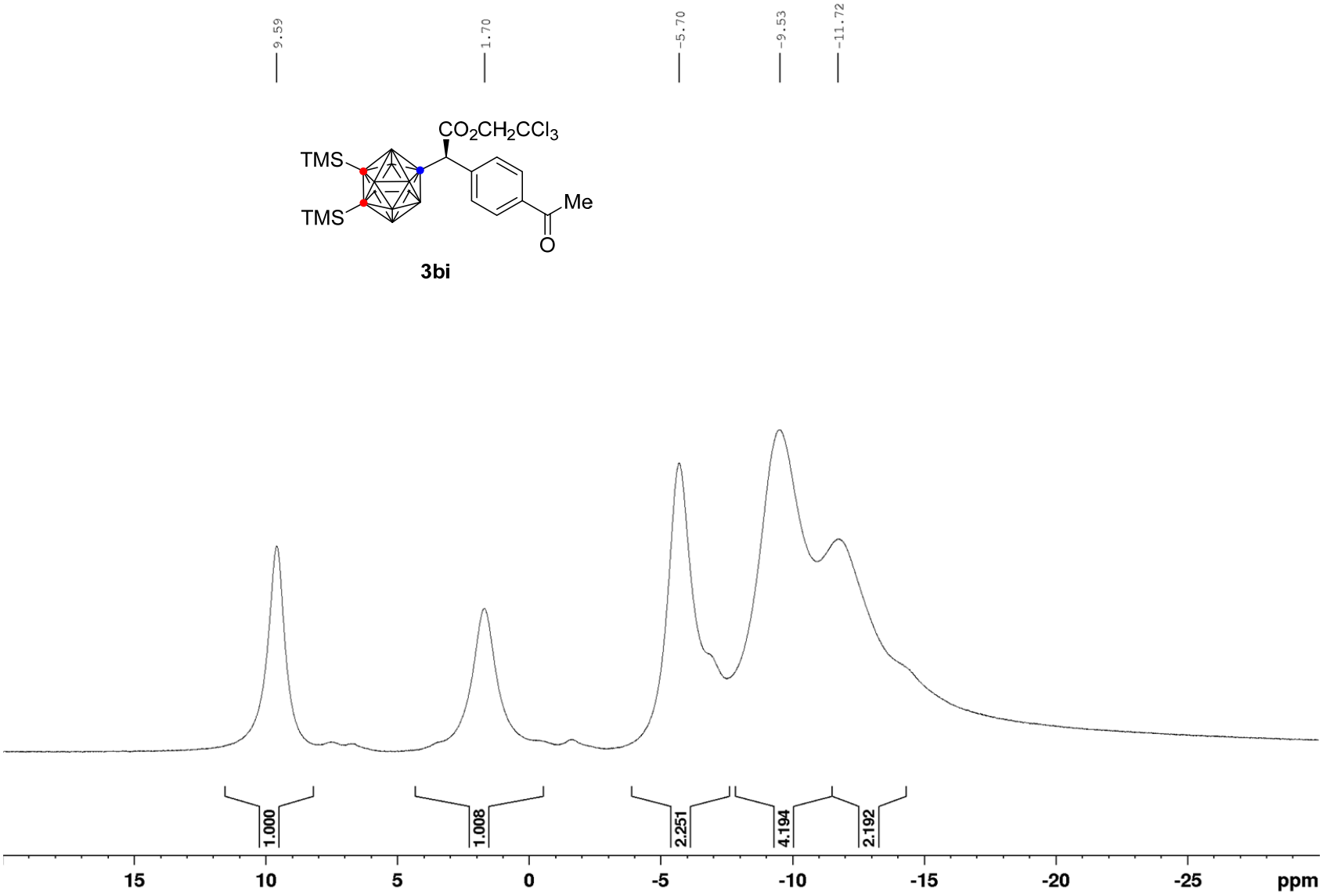
3bi

^{11}B NMR (128 MHz, $CDCl_3$)

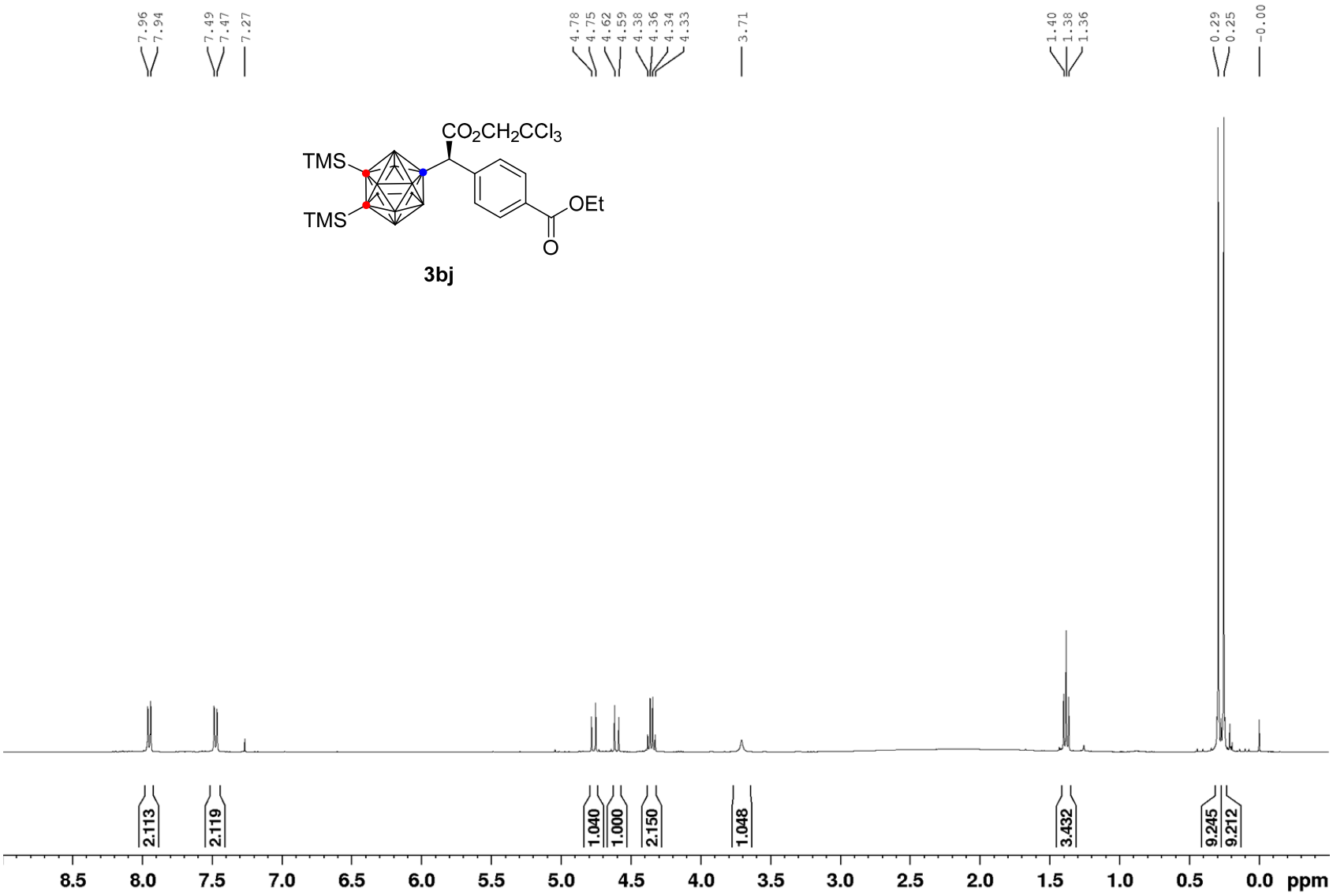


3bi

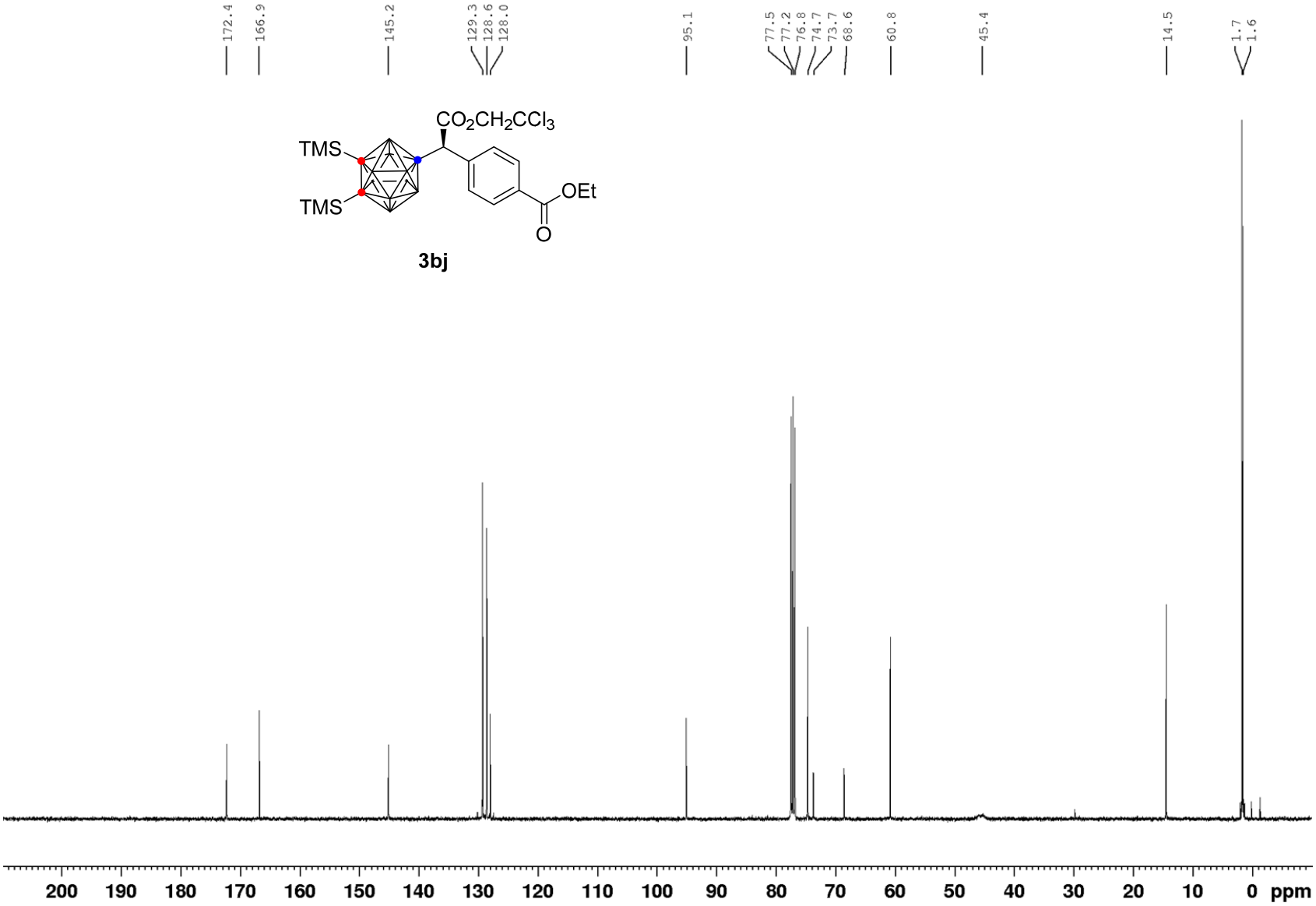
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



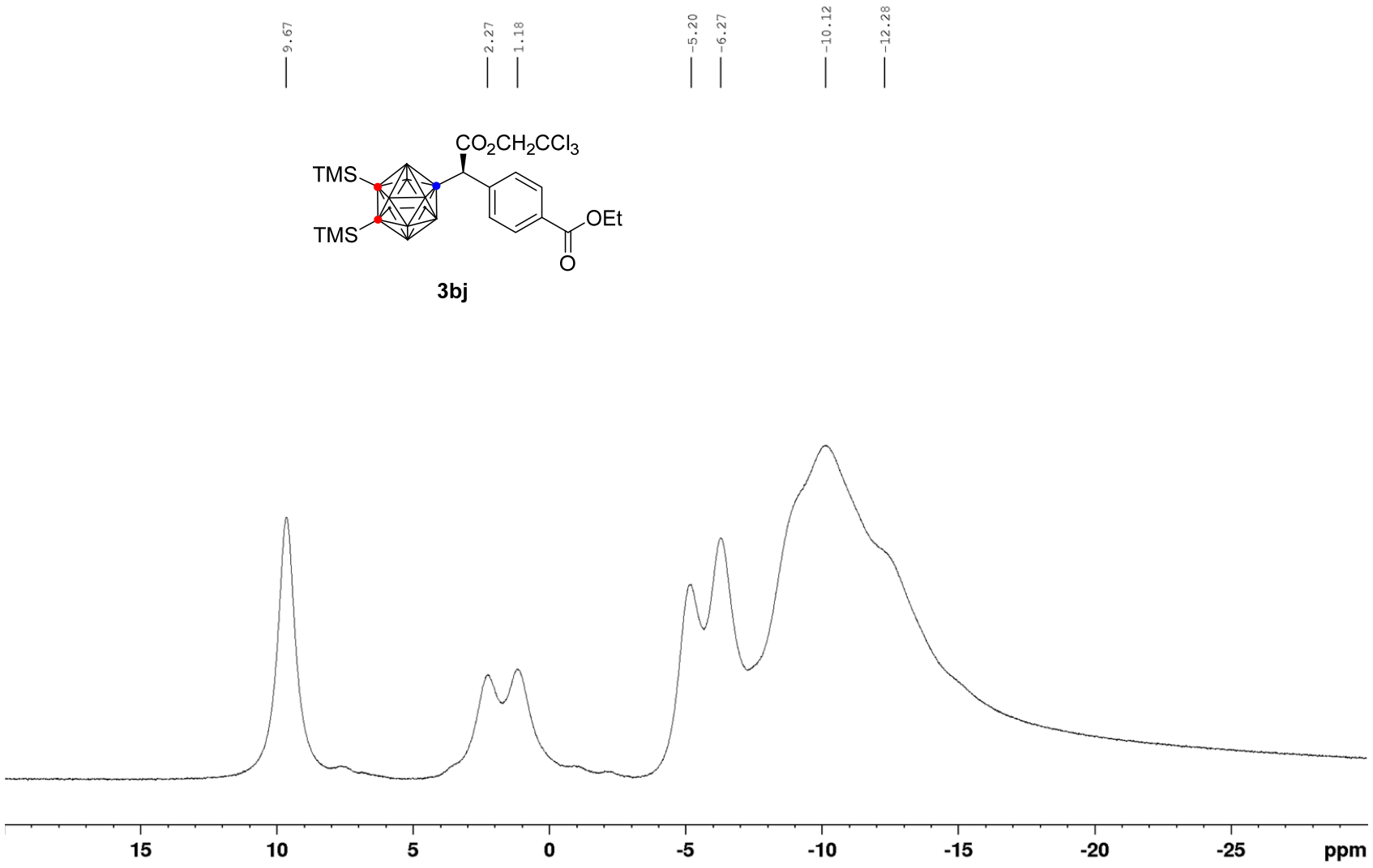
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

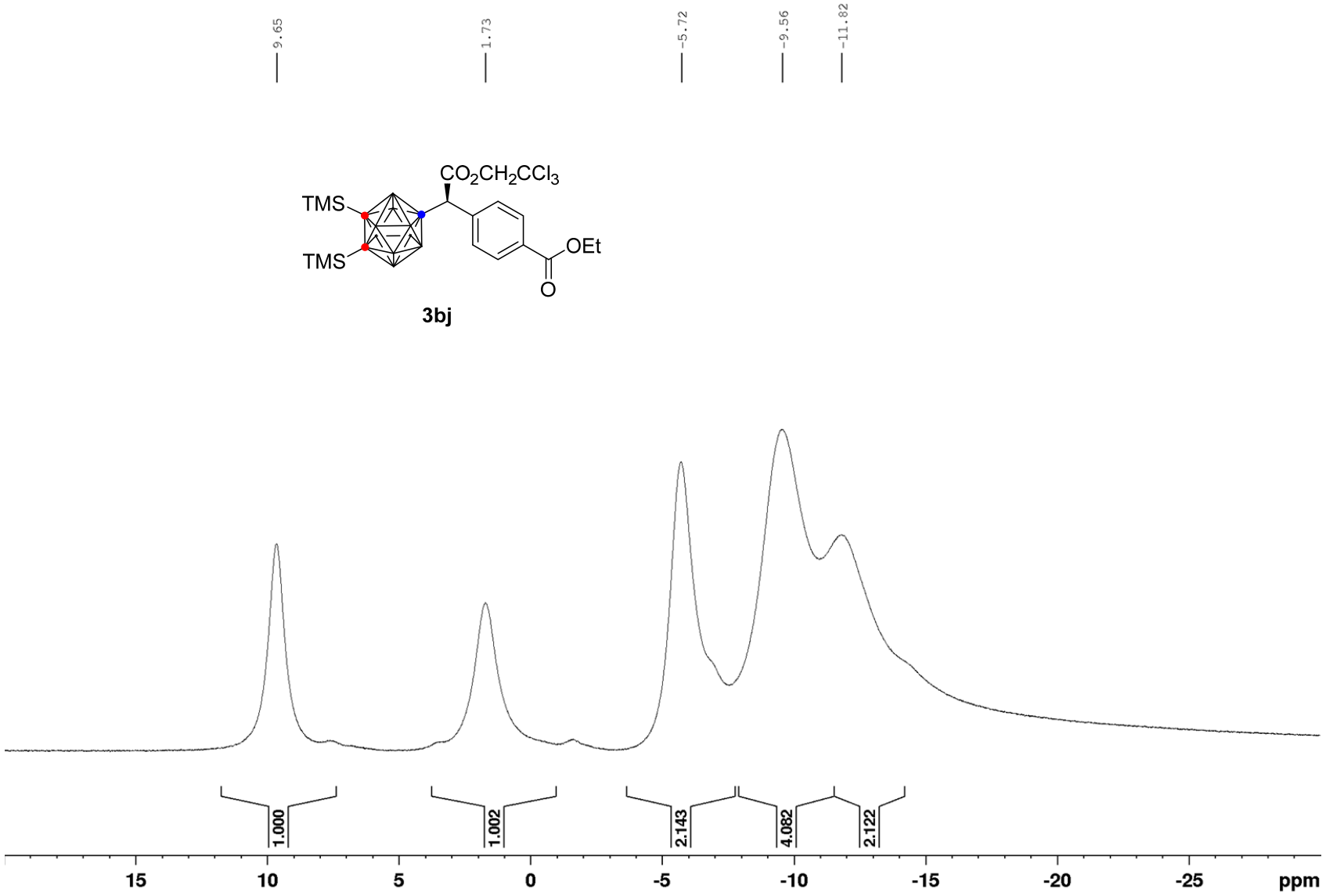


^{11}B NMR (128 MHz, $CDCl_3$)

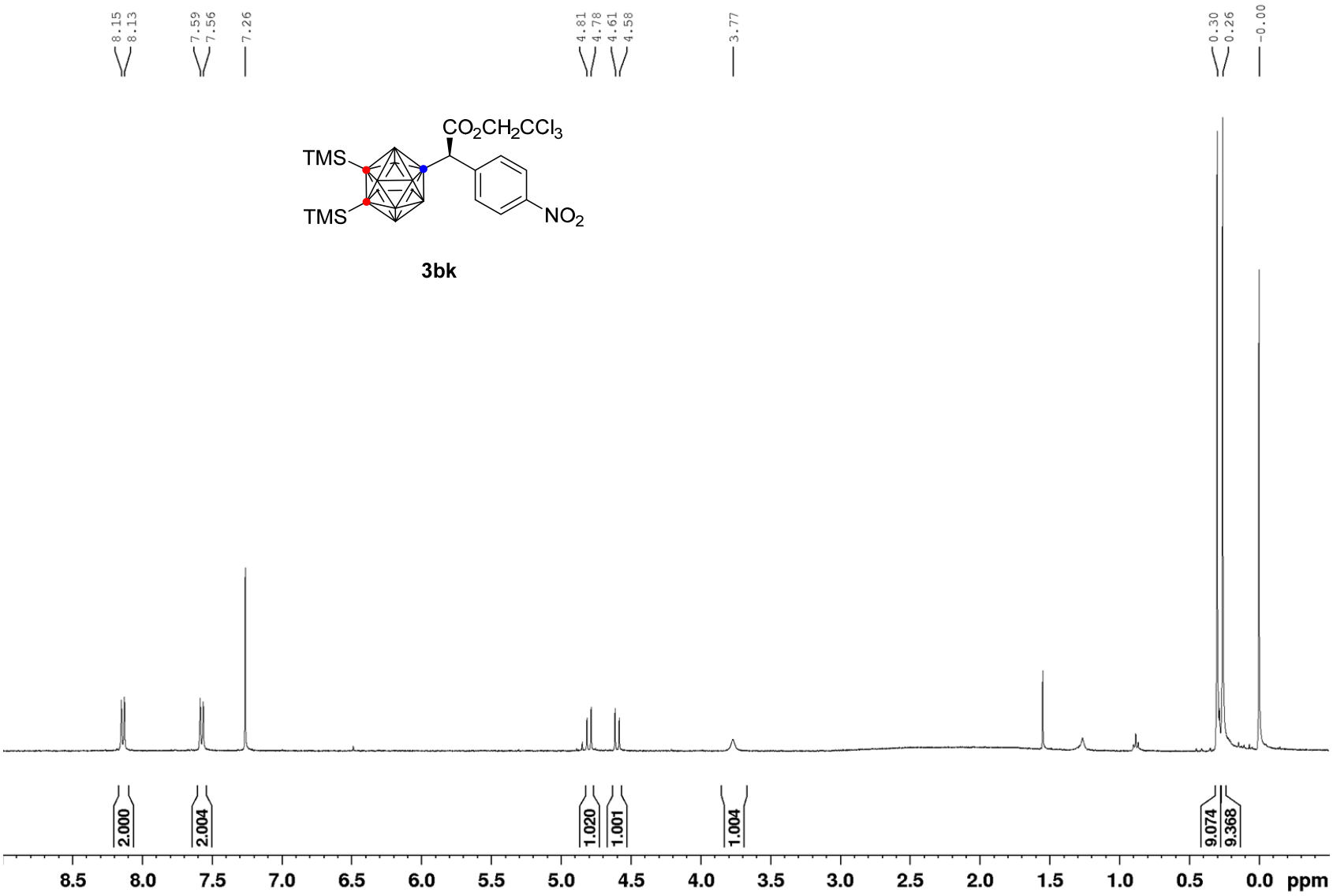


3bj

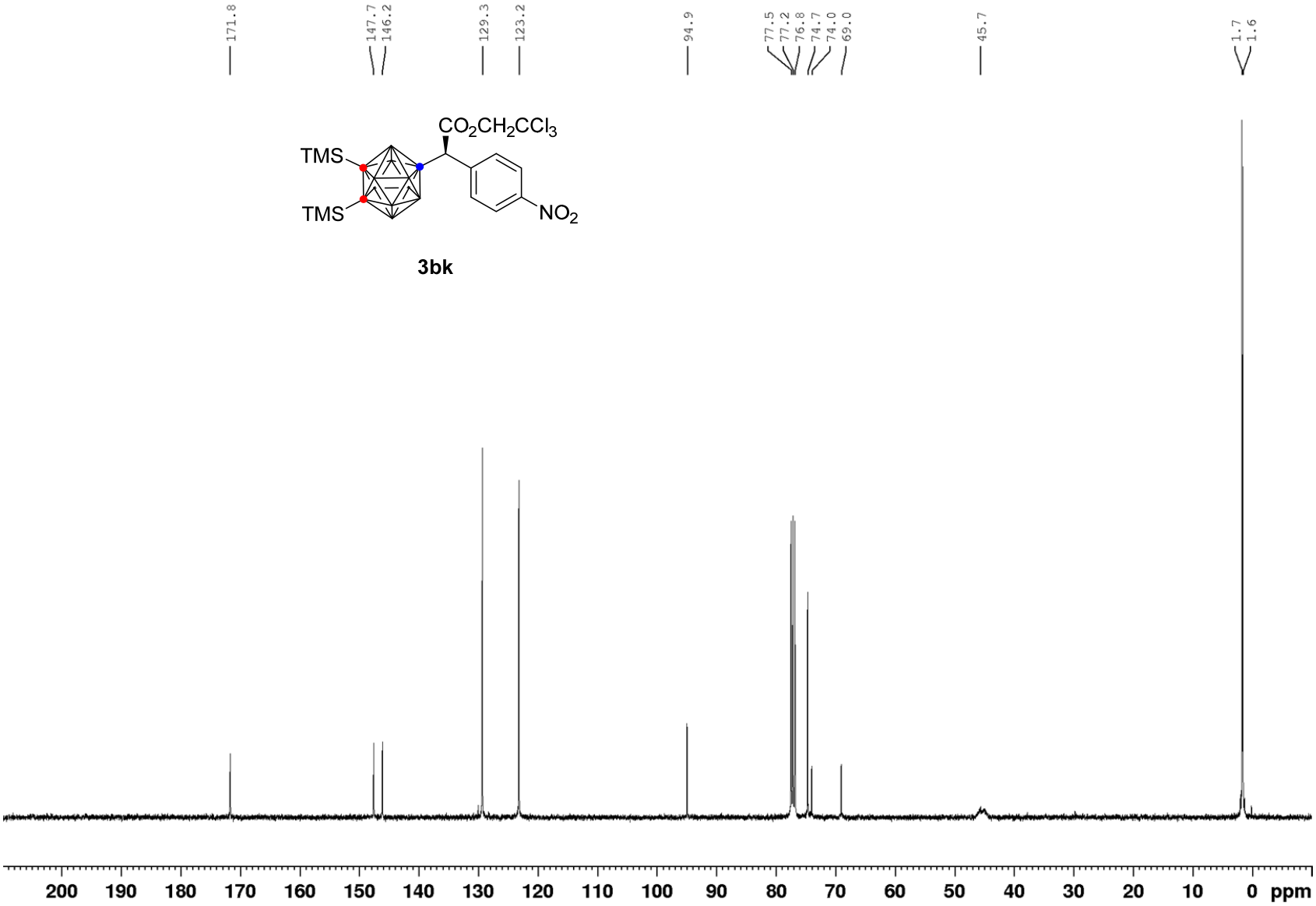
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

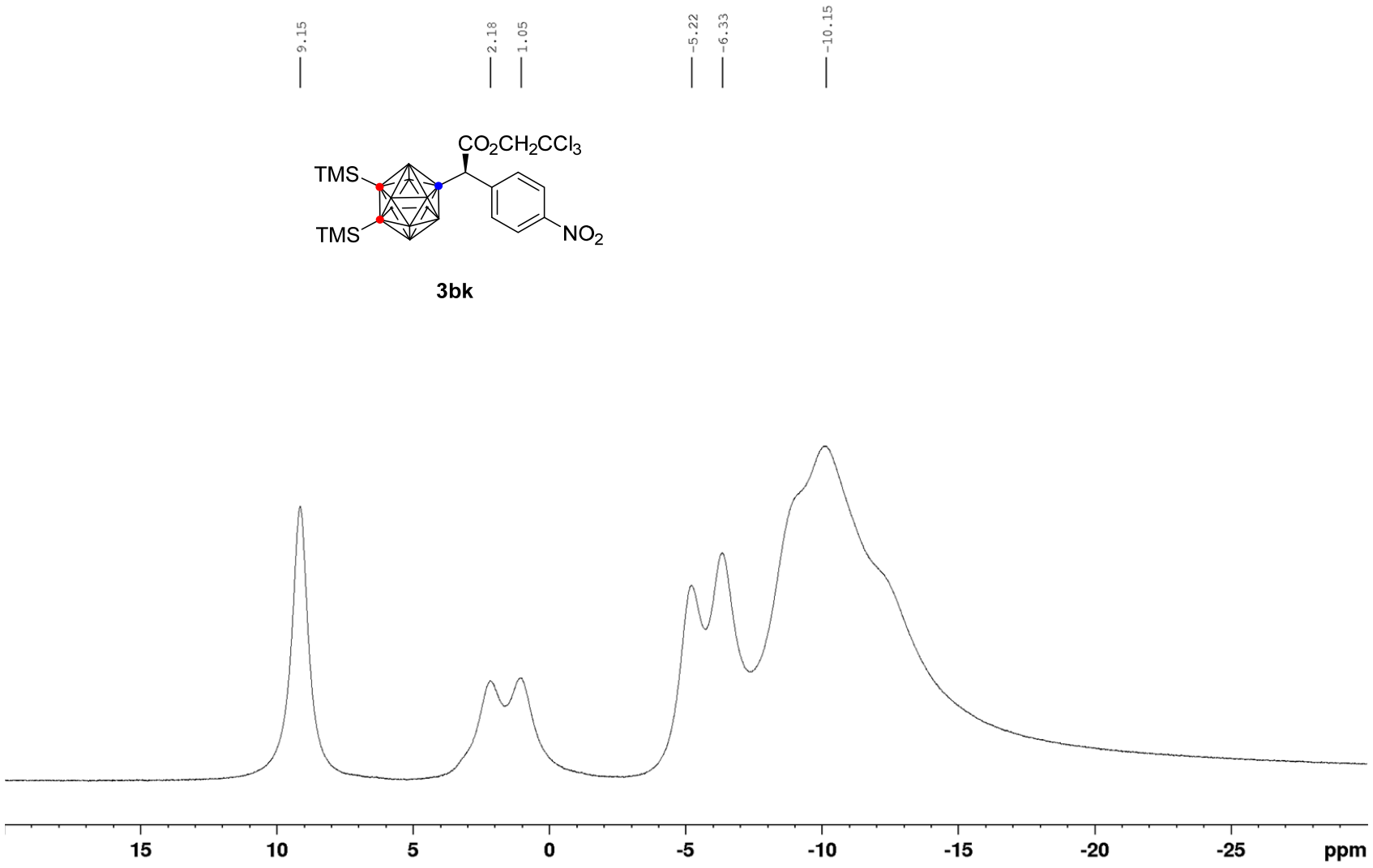


^{13}C NMR (100 MHz, $CDCl_3$)



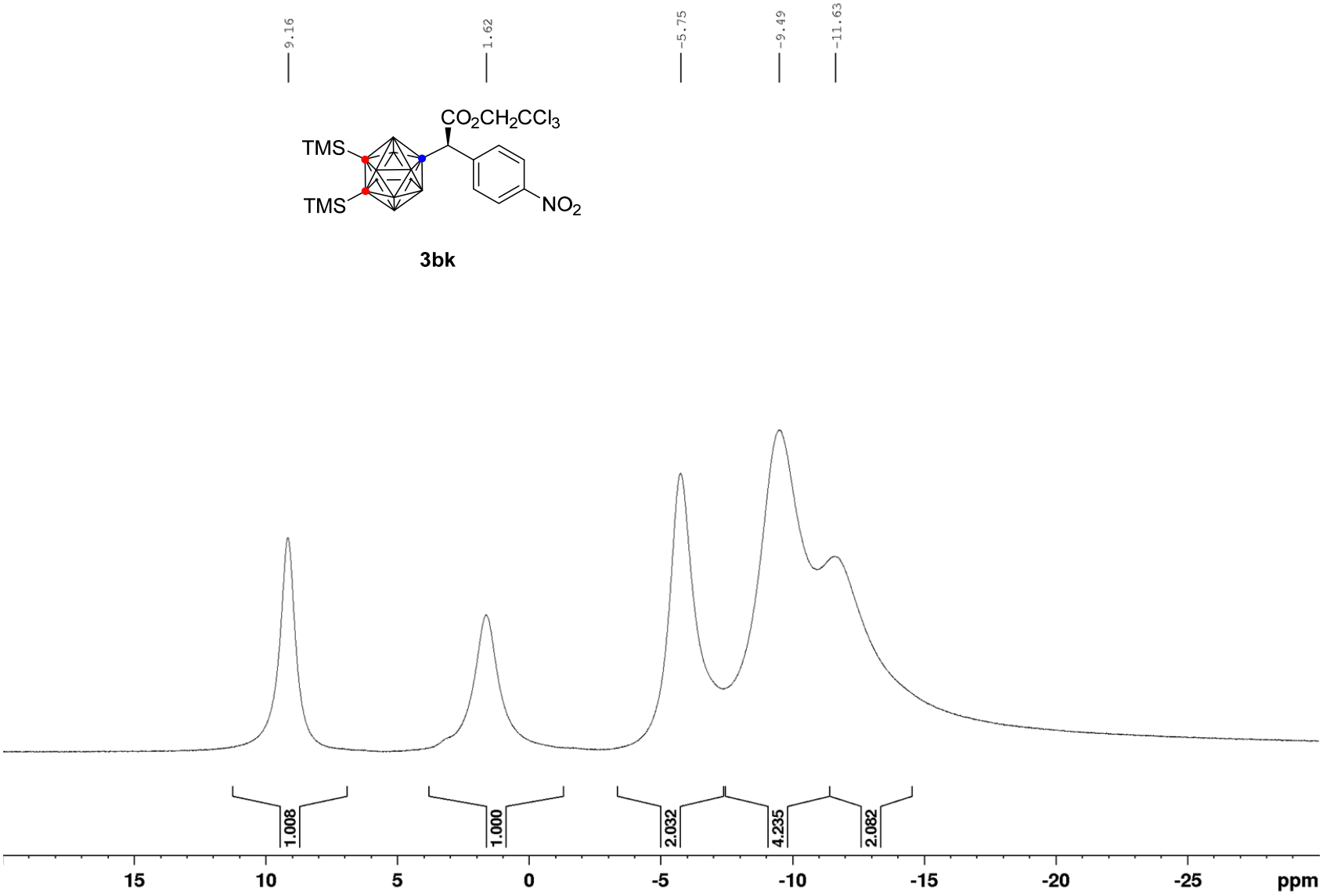
3bk

^{11}B NMR (128 MHz, $CDCl_3$)



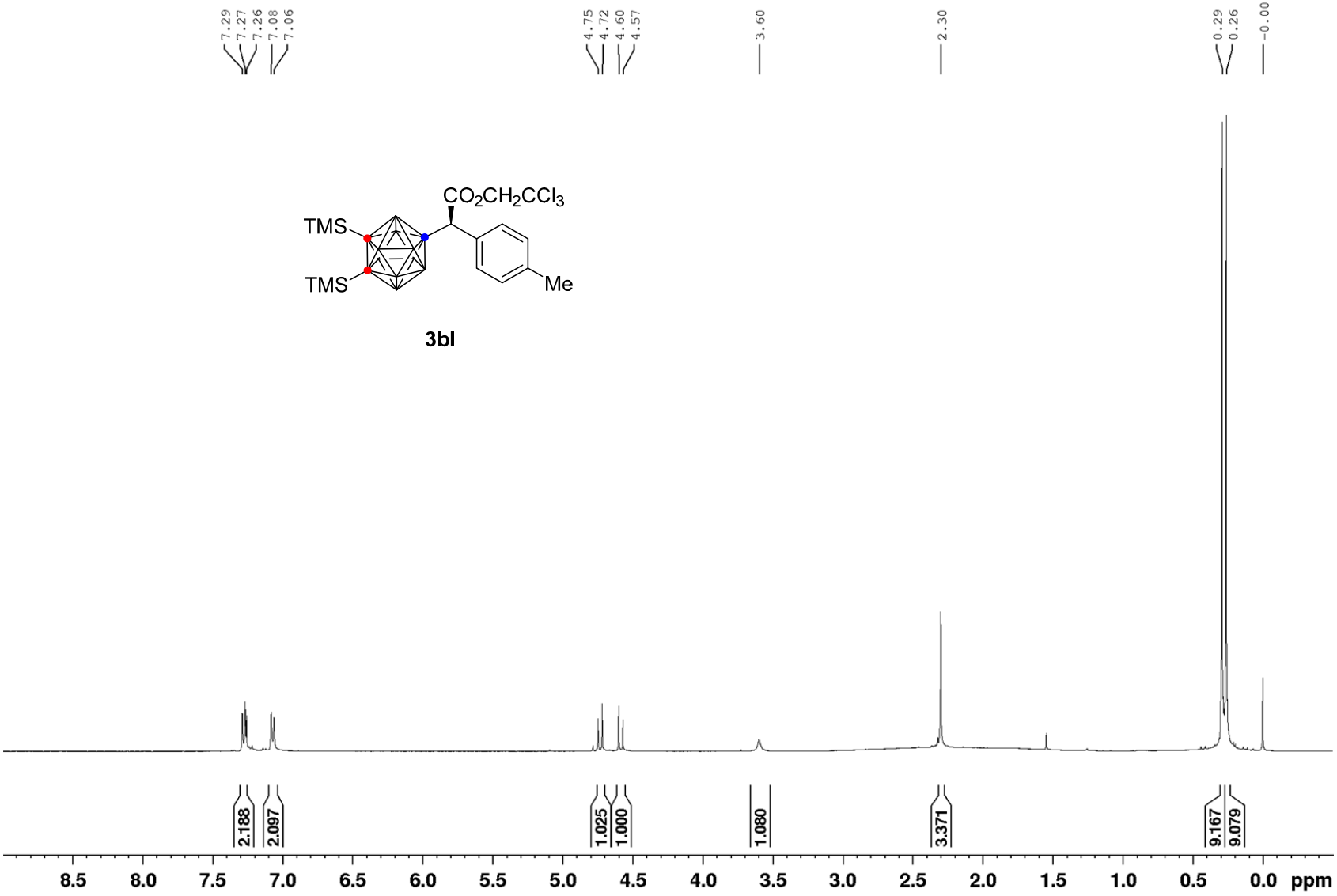
3bk

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



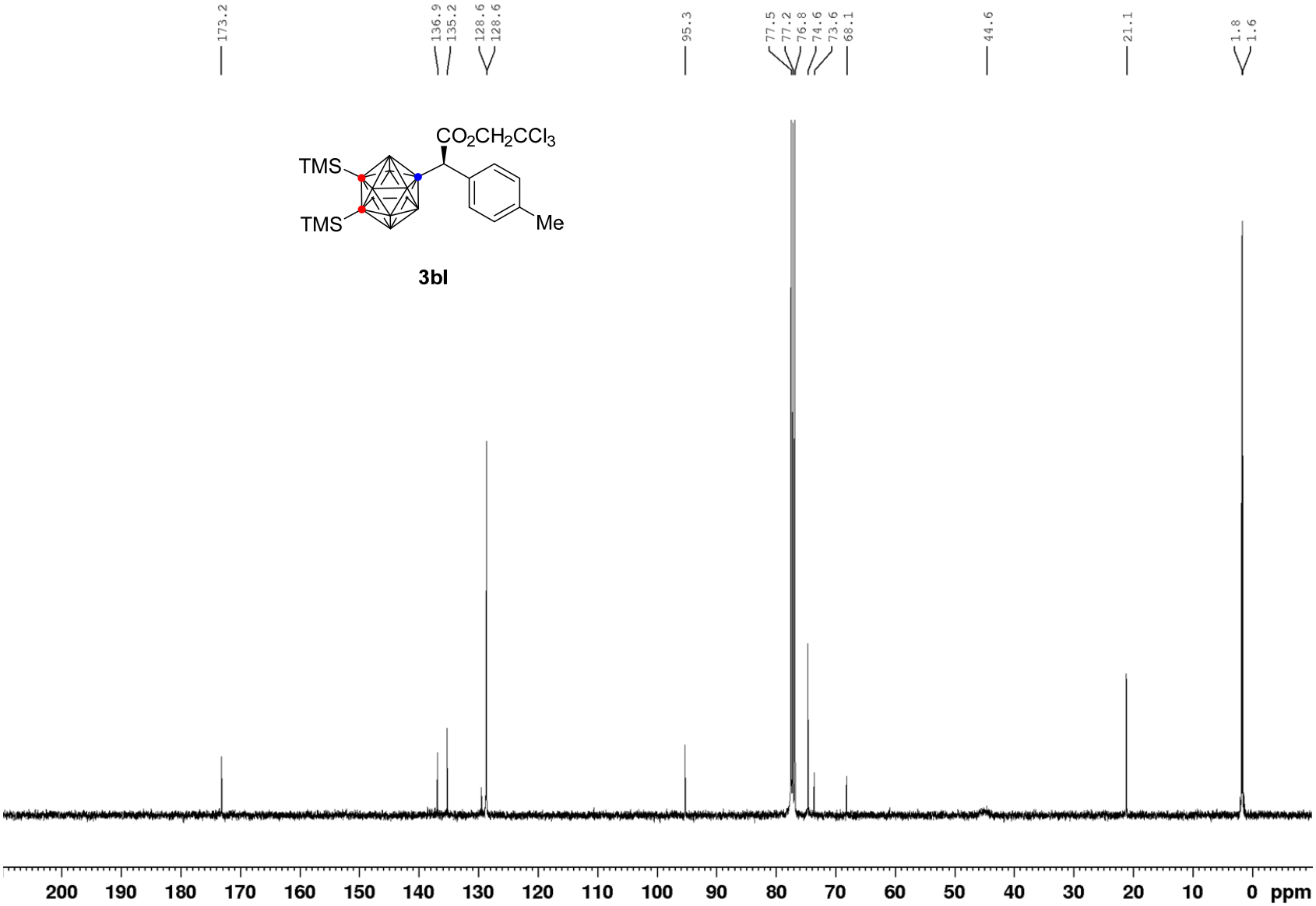
3bk

^{1}H NMR (400 MHz, $CDCl_3$)



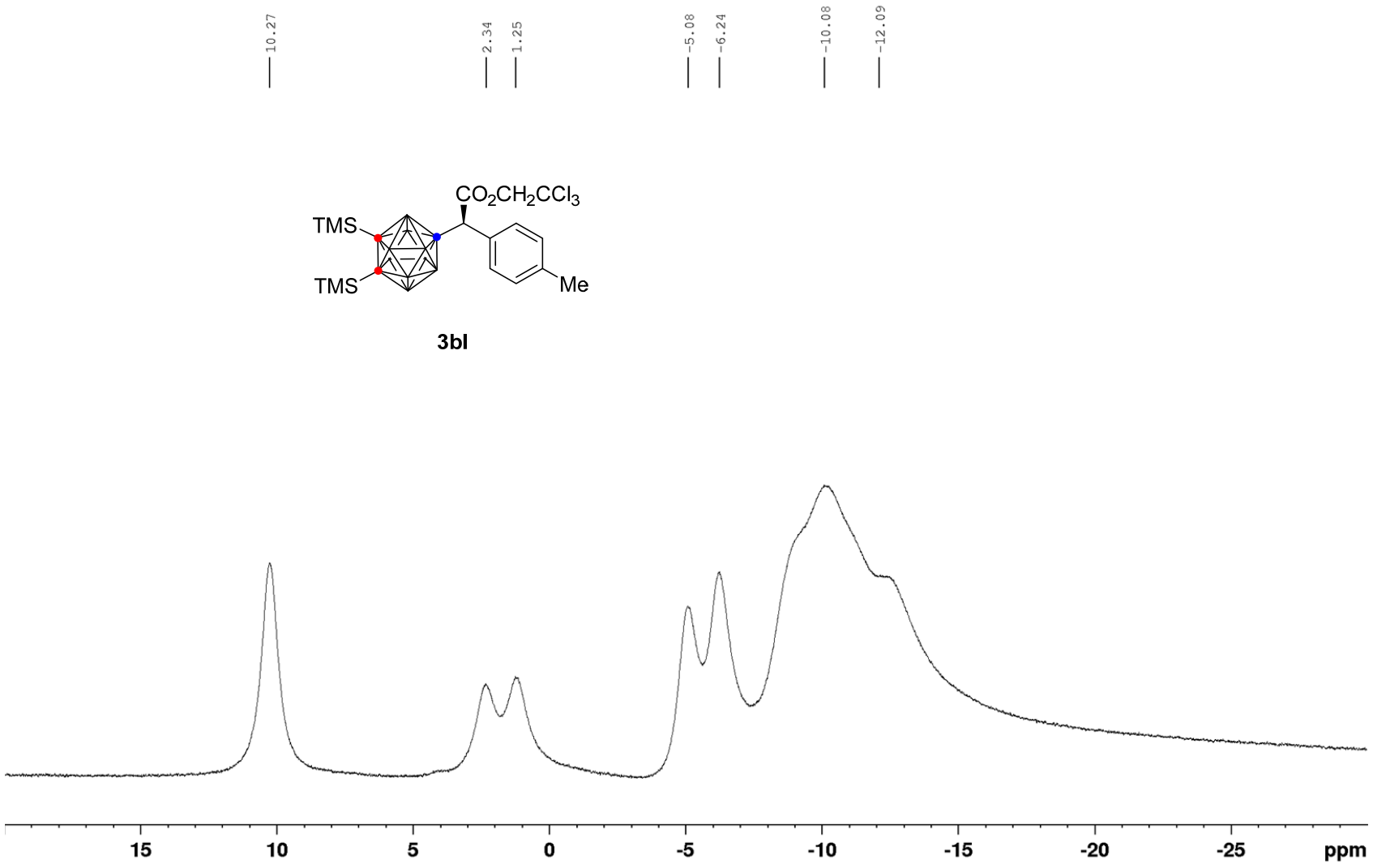
3bl

^{13}C NMR (100 MHz, $CDCl_3$)



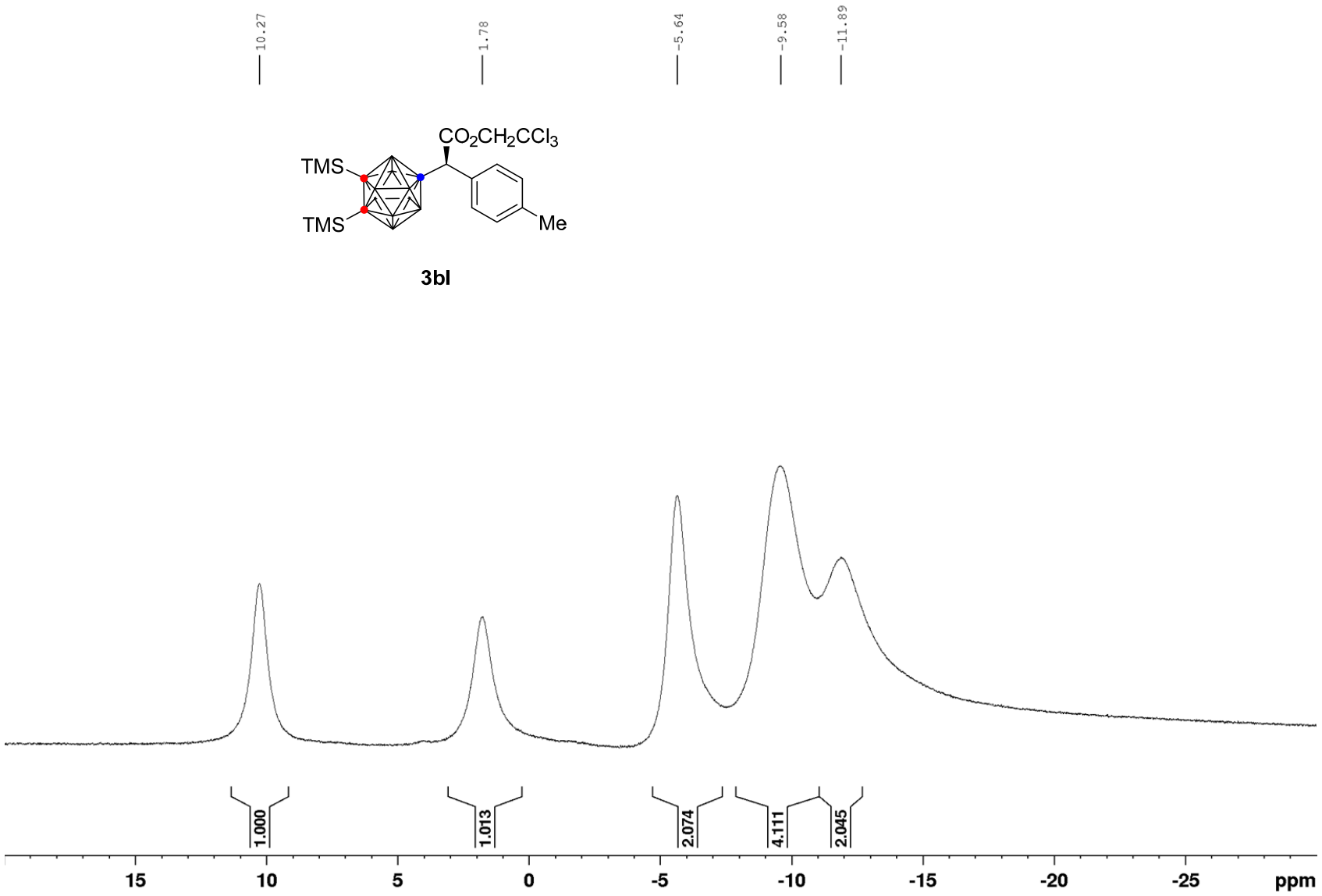
3bl

^{11}B NMR (128 MHz, $CDCl_3$)



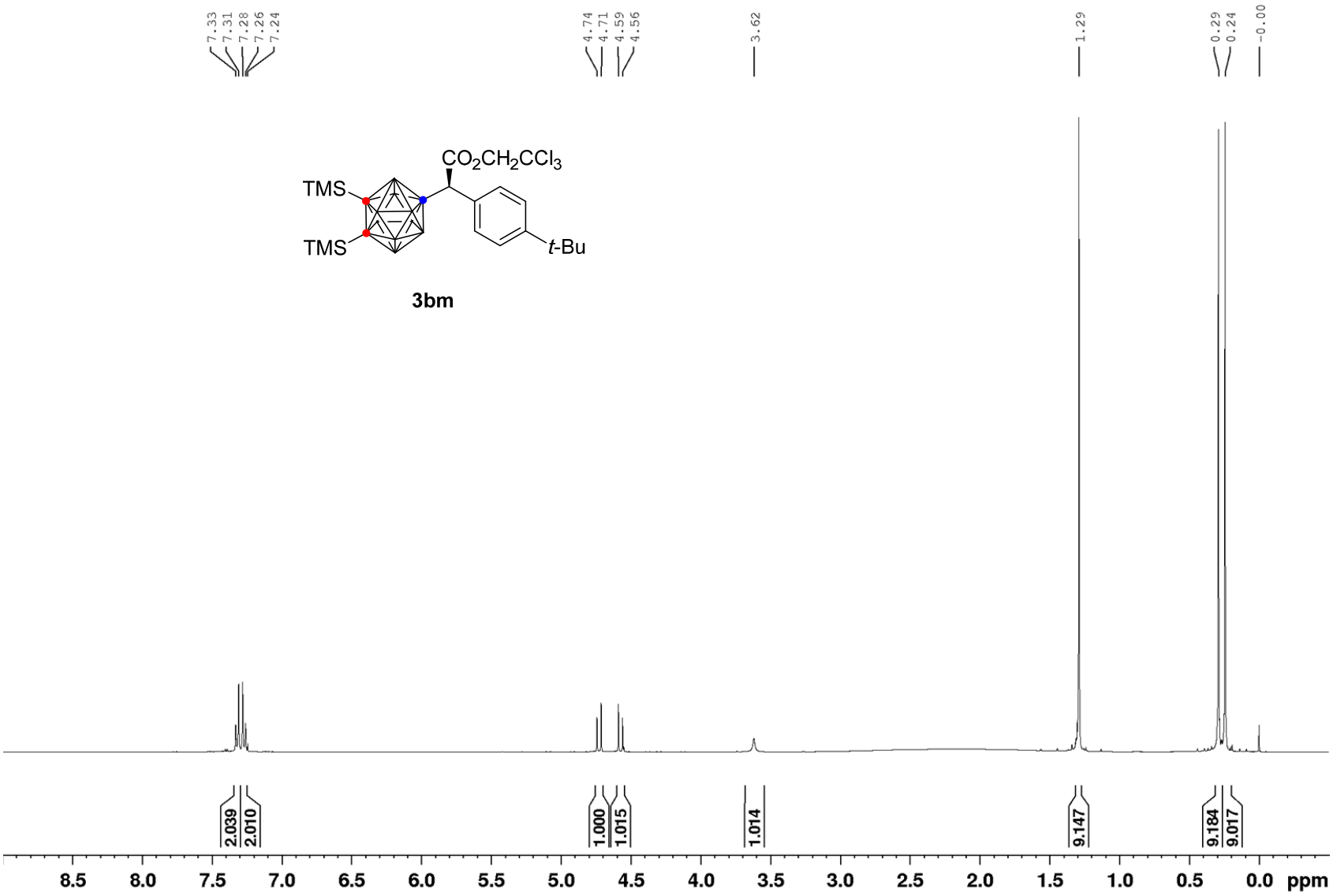
3bl

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

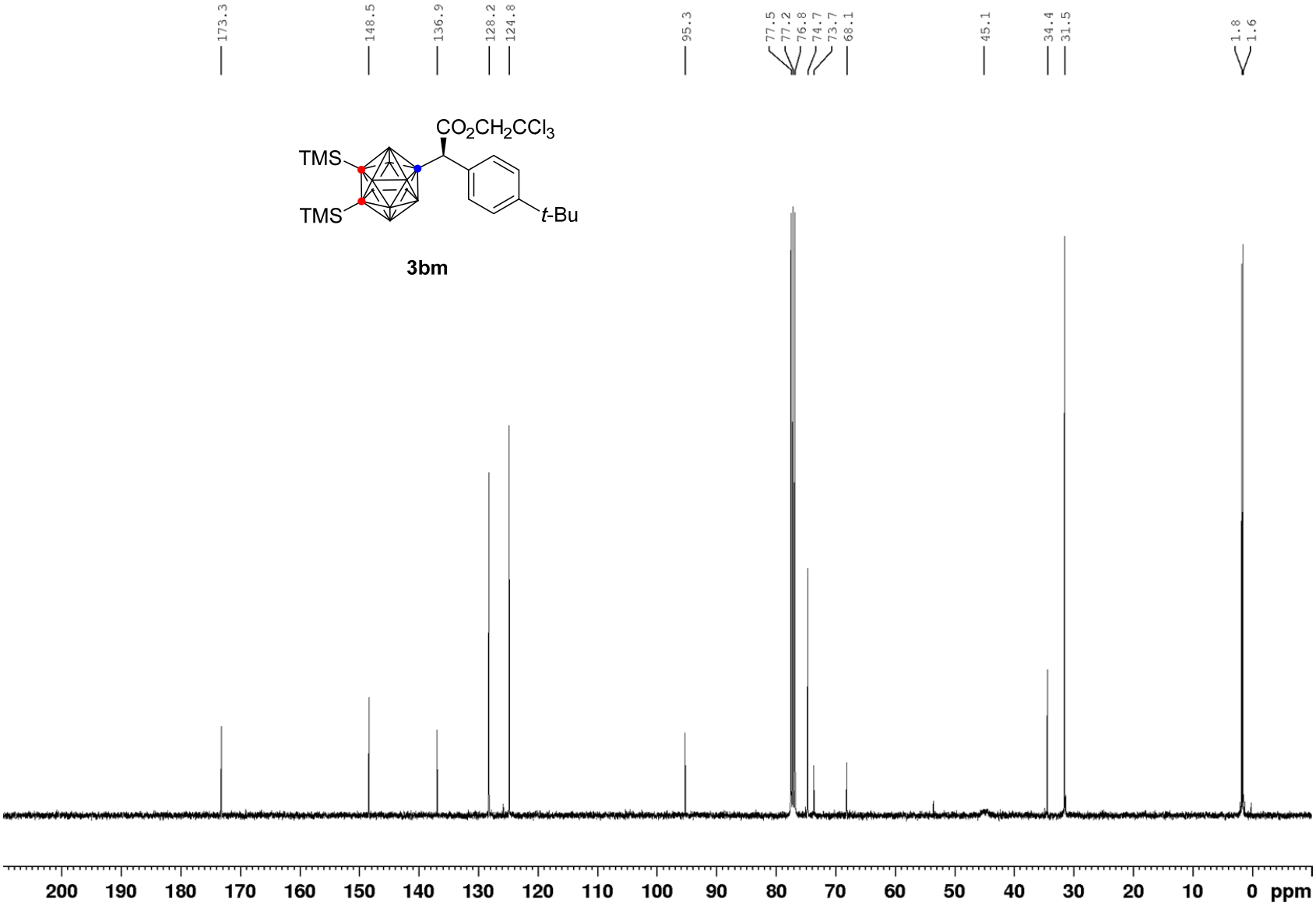


3bl

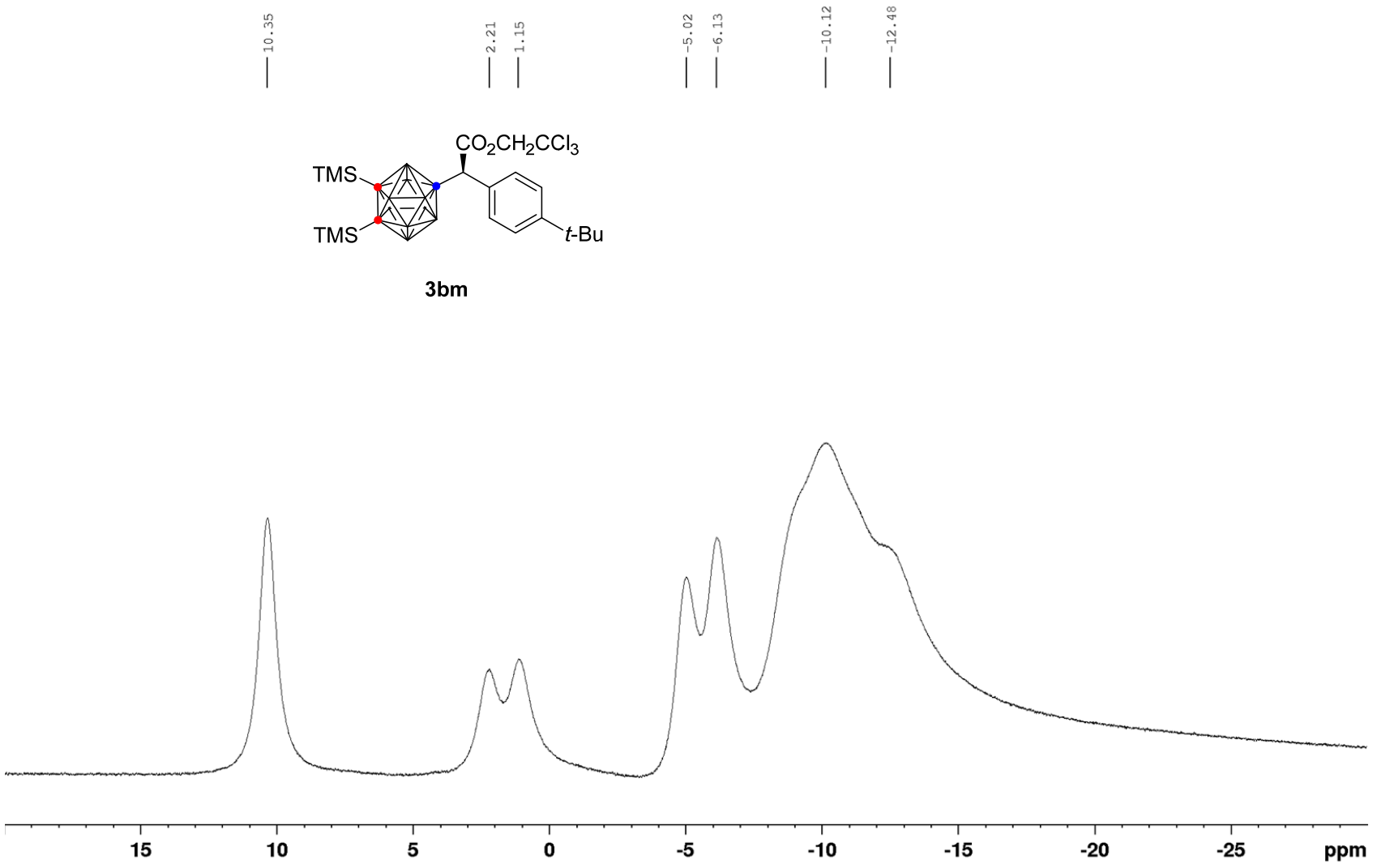
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

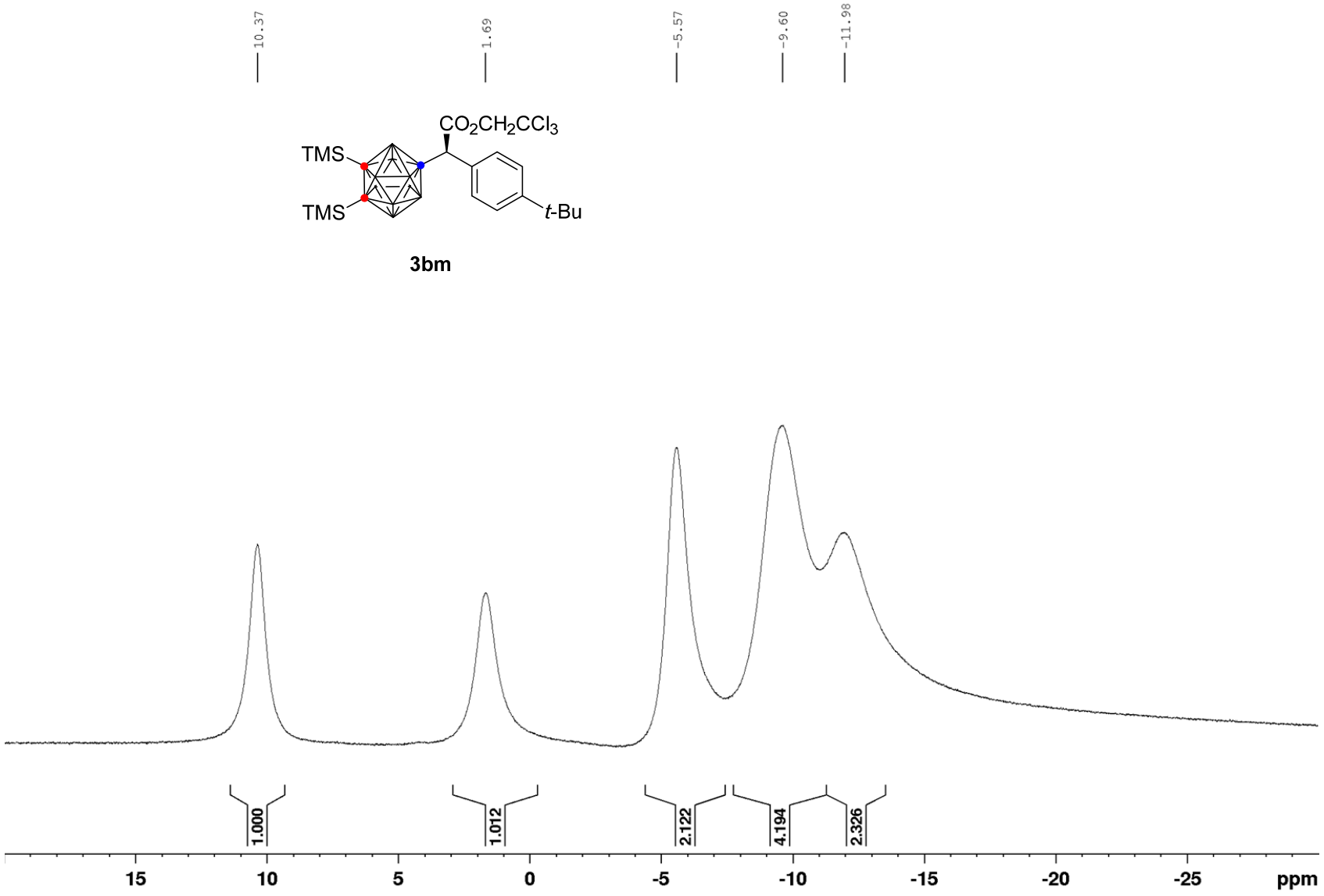


^{11}B NMR (128 MHz, $CDCl_3$)



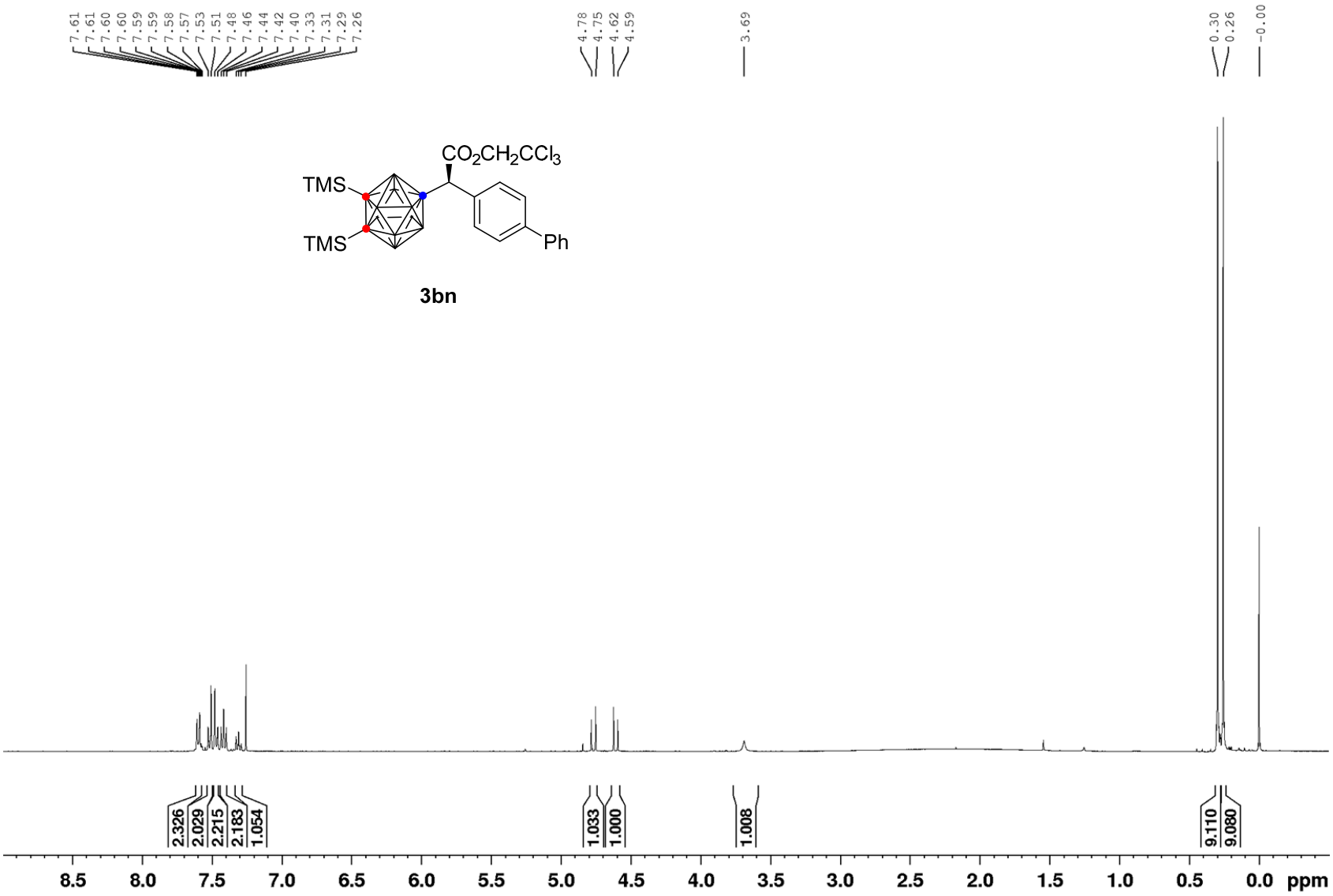
3bm

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



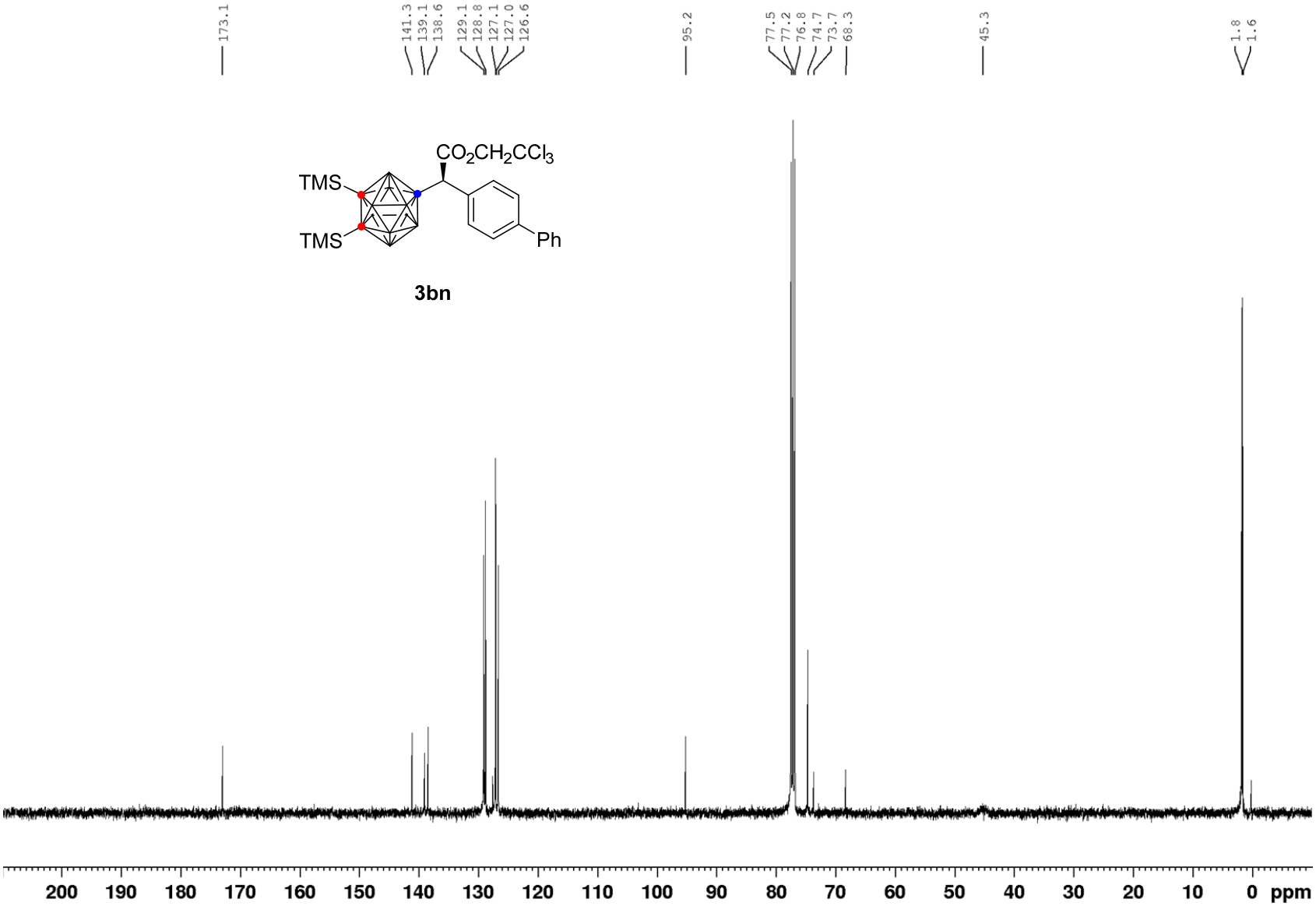
3bm

^{1}H NMR (400 MHz, $CDCl_3$)



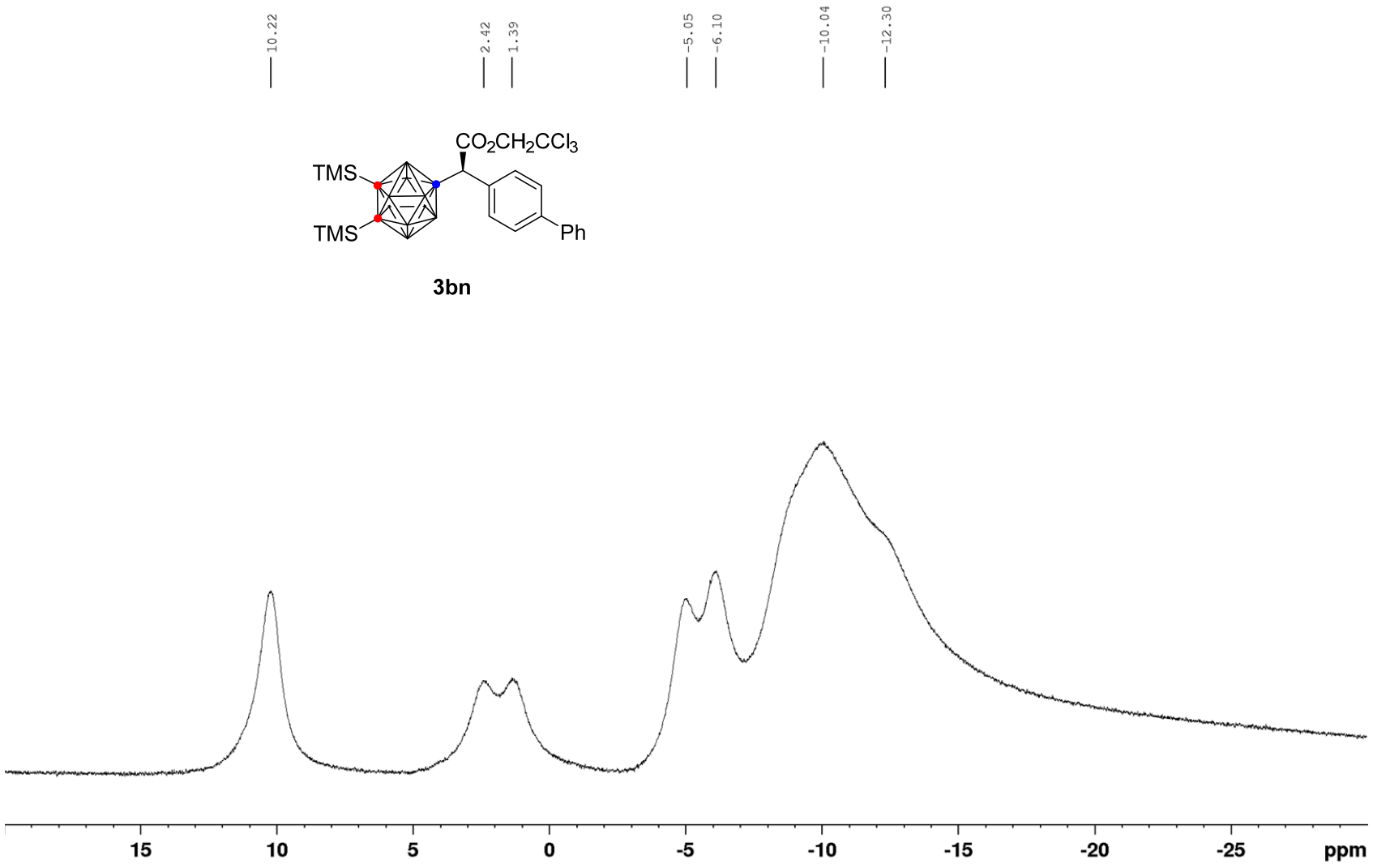
3bn

^{13}C NMR (100 MHz, $CDCl_3$)



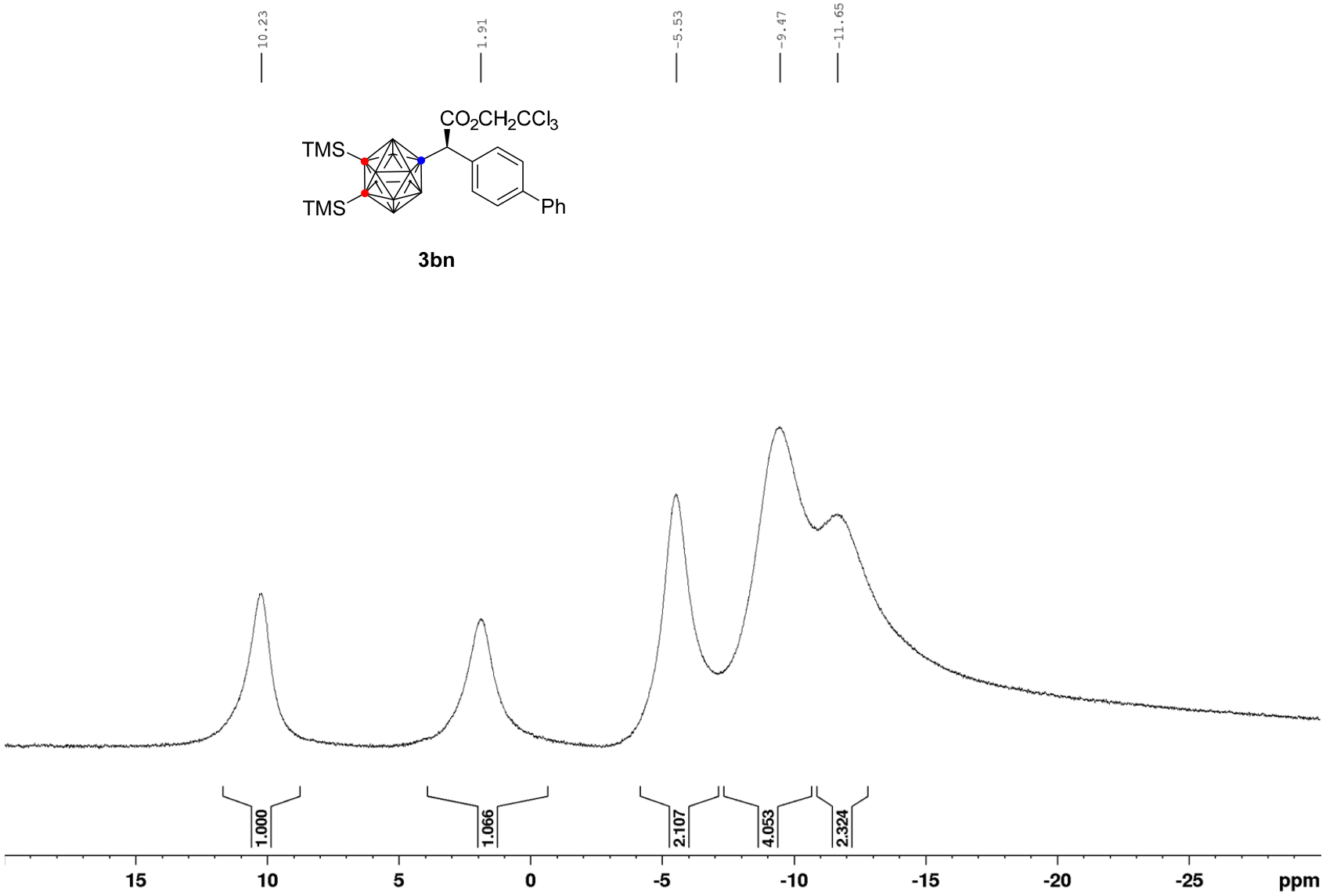
3bn

^{11}B NMR (128 MHz, $CDCl_3$)



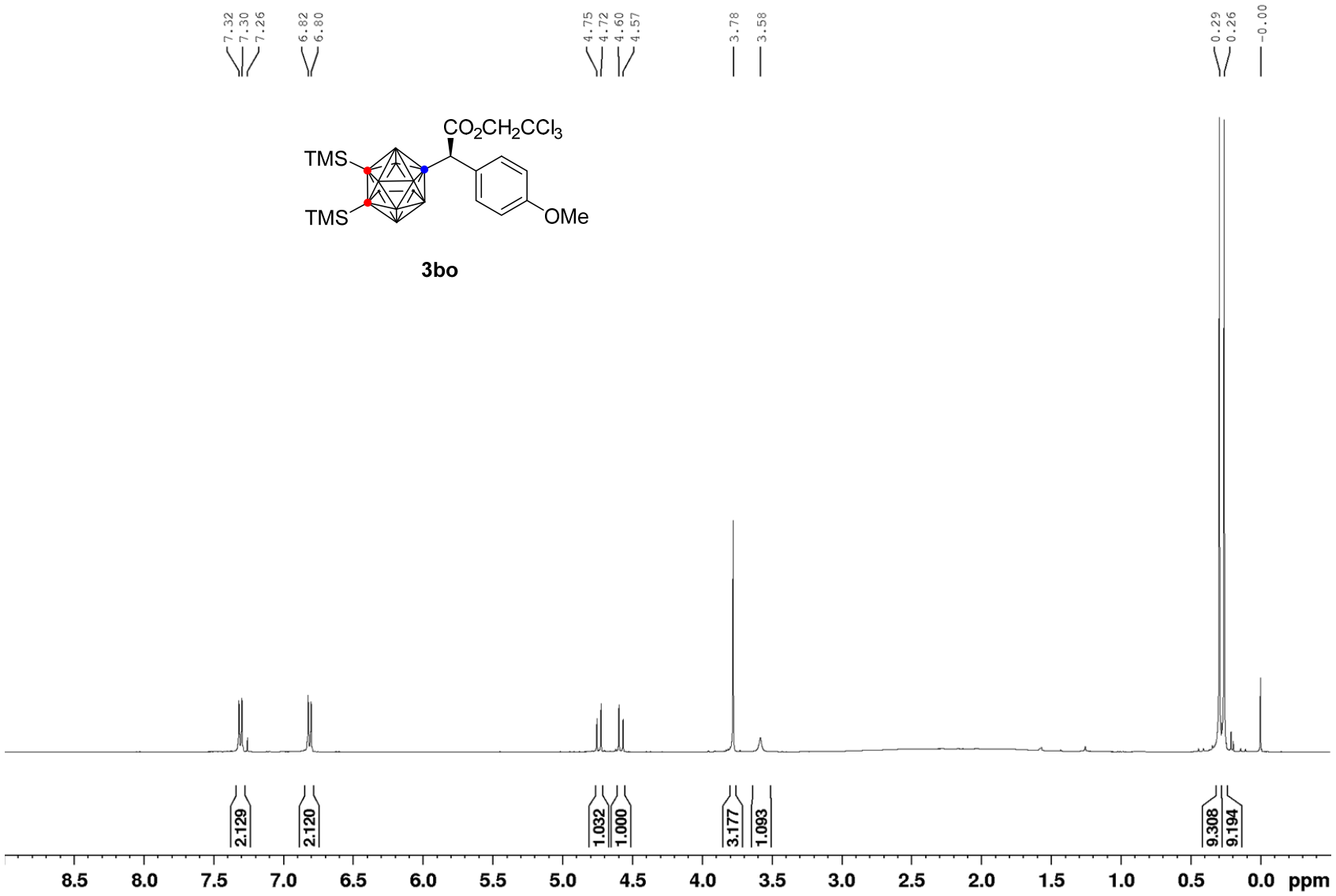
3bn

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

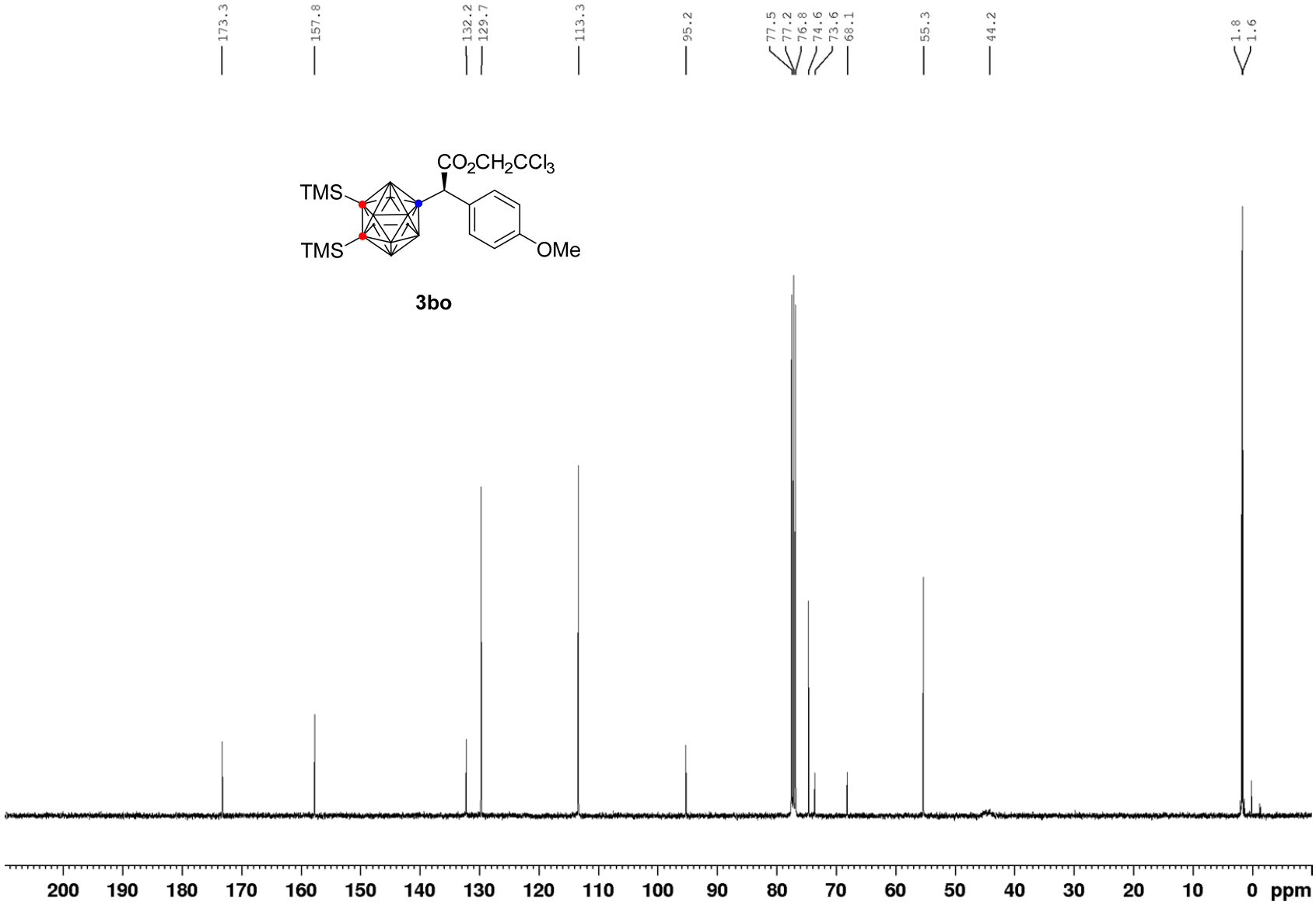


3bn

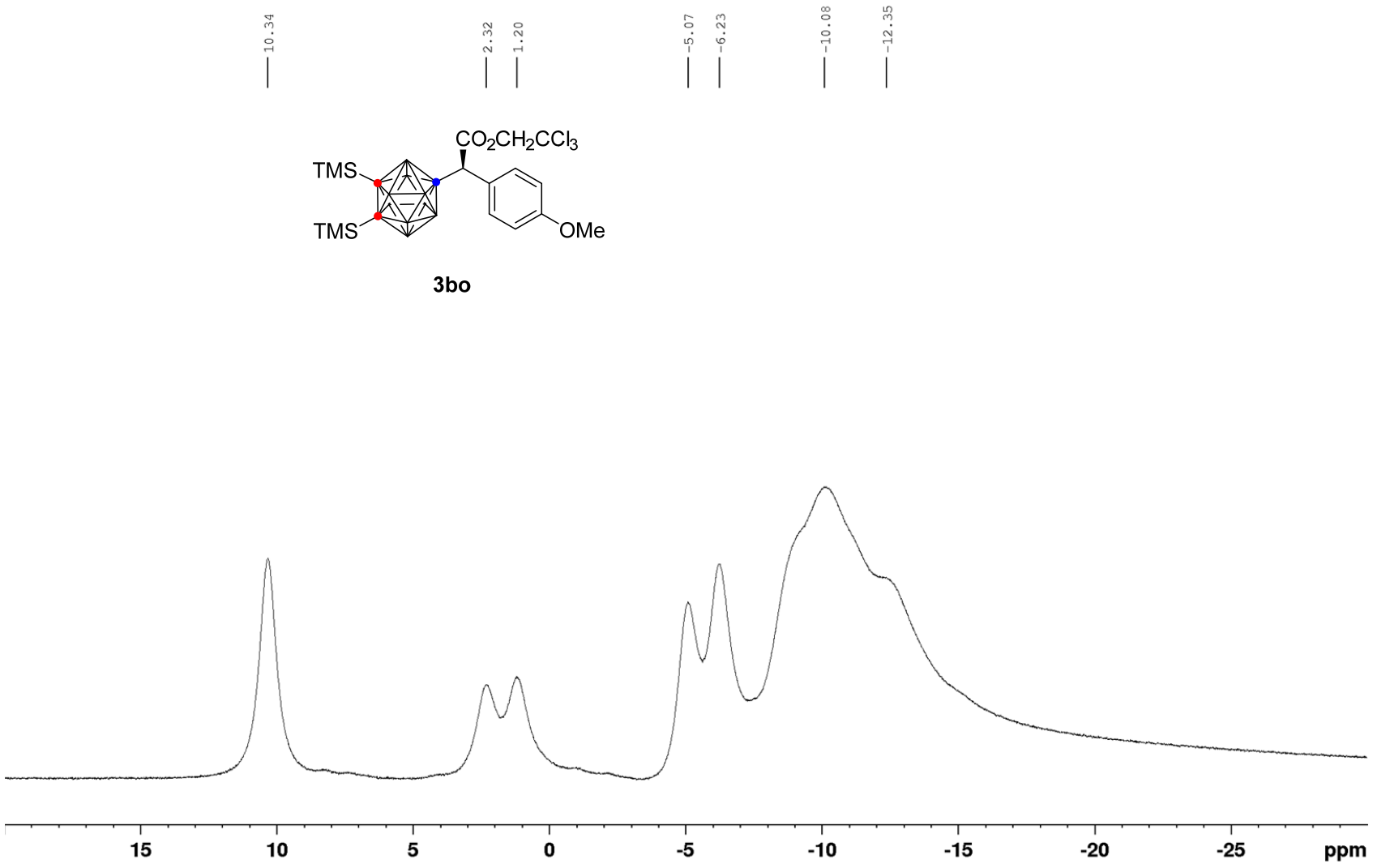
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

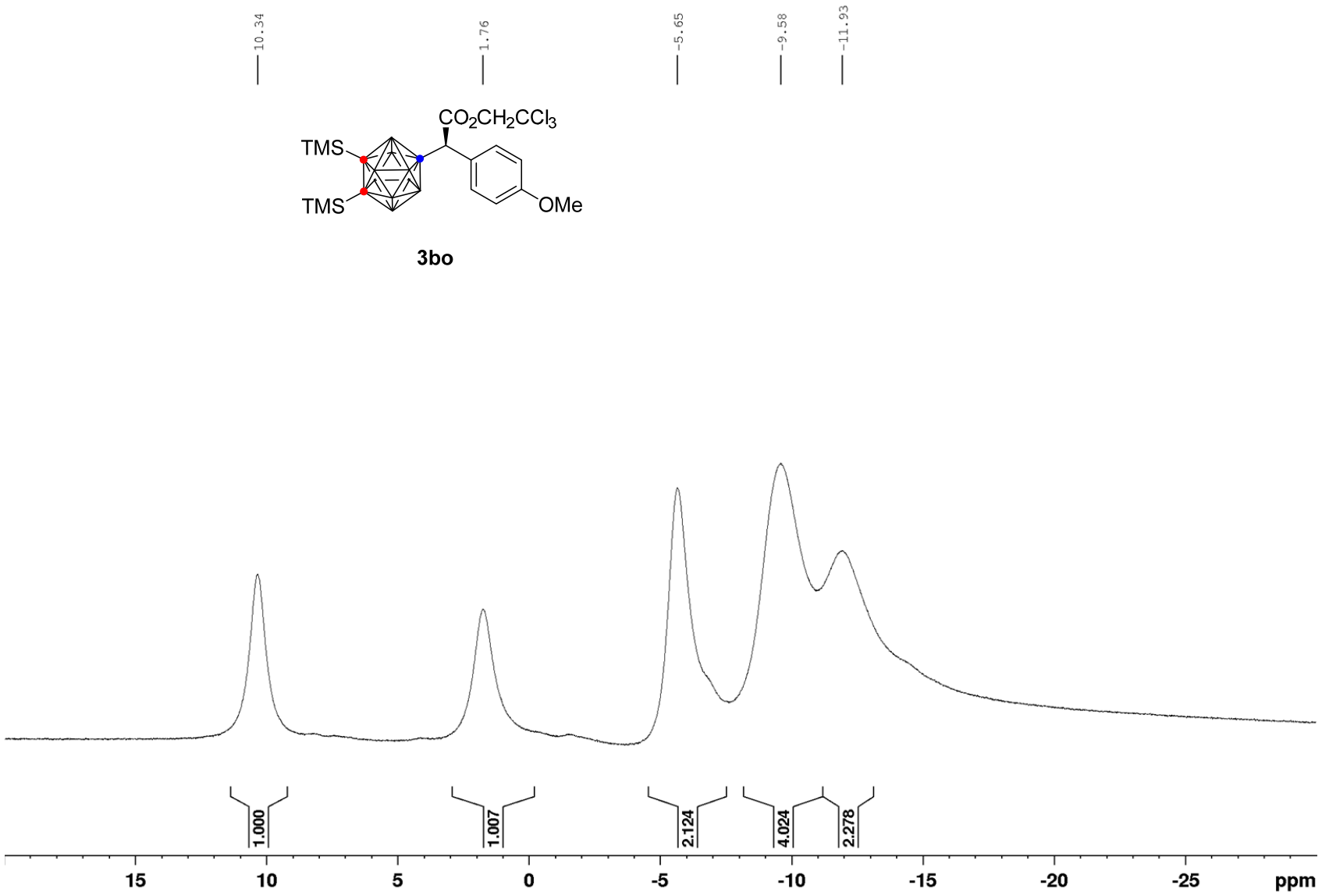


^{11}B NMR (128 MHz, $CDCl_3$)



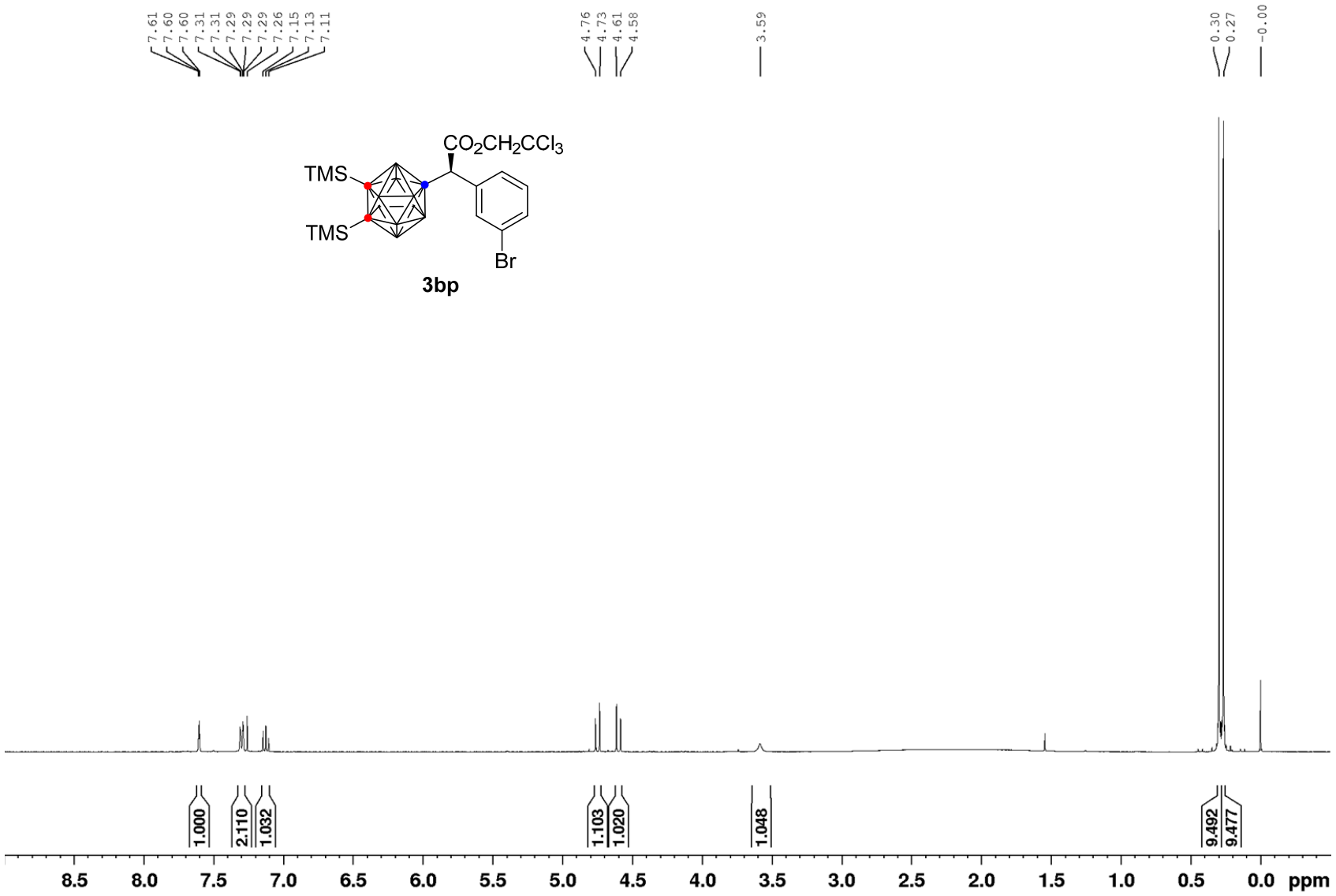
3bo

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

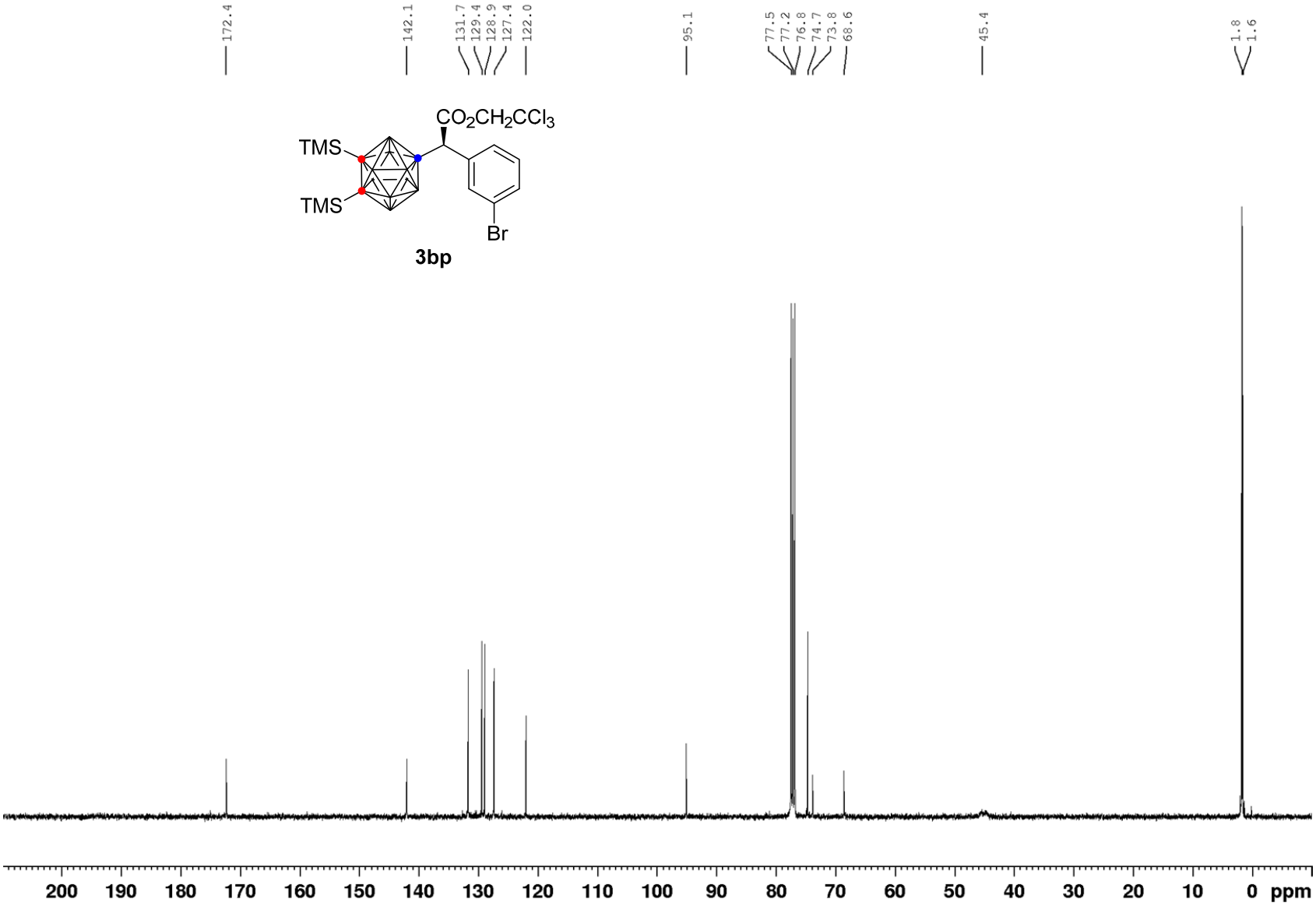


3bo

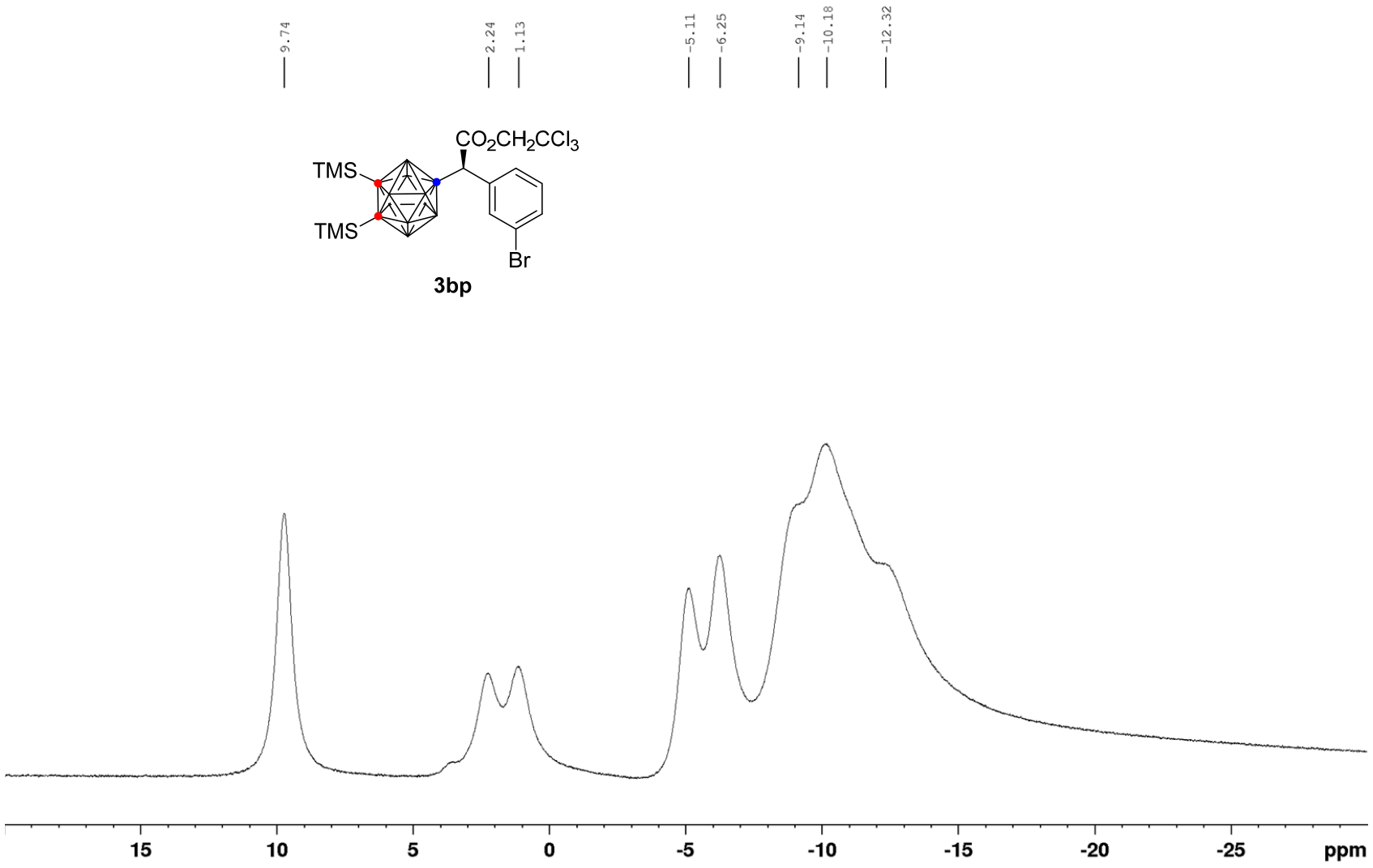
^{1}H NMR (400 MHz, $CDCl_3$)



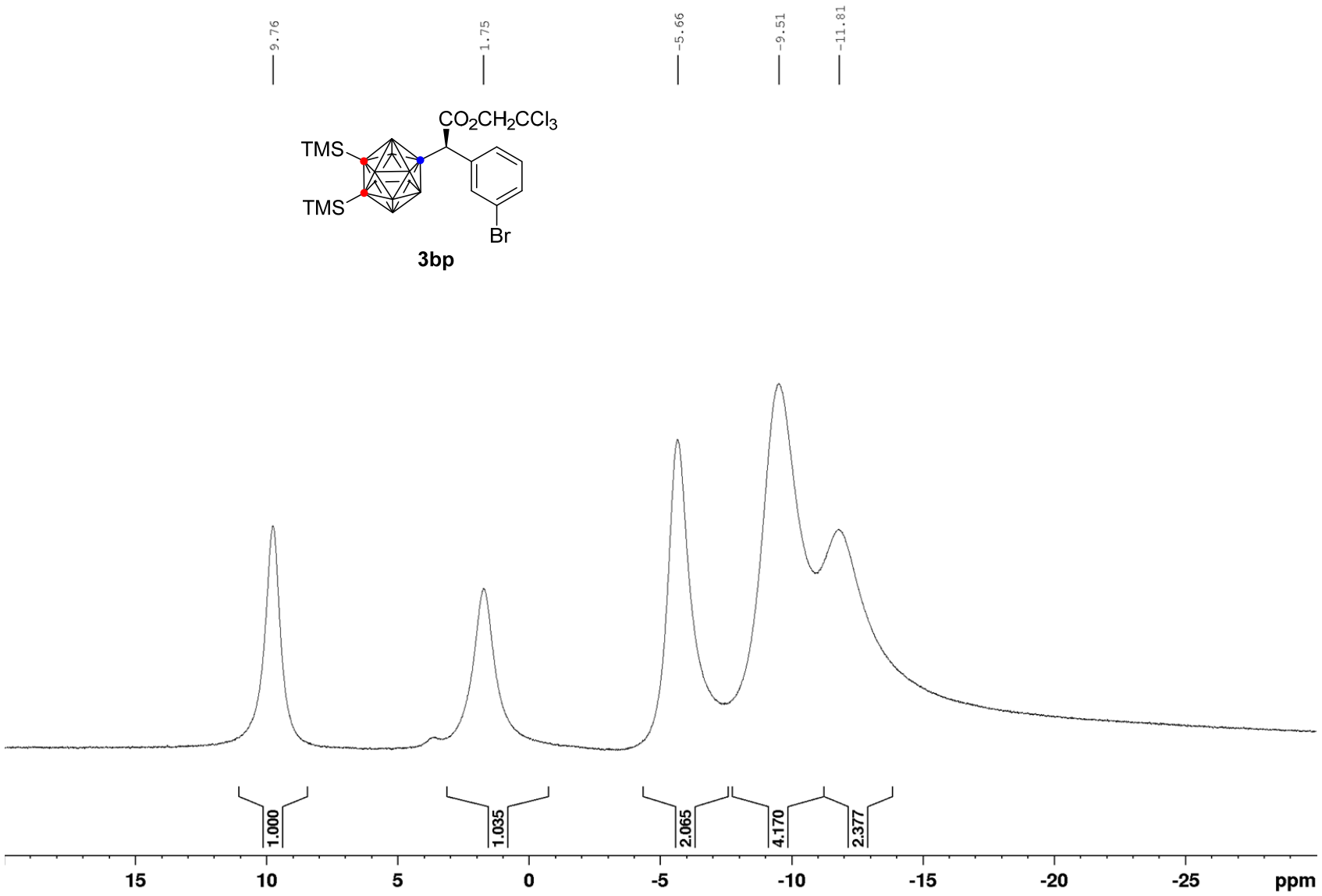
^{13}C NMR (100 MHz, $CDCl_3$)



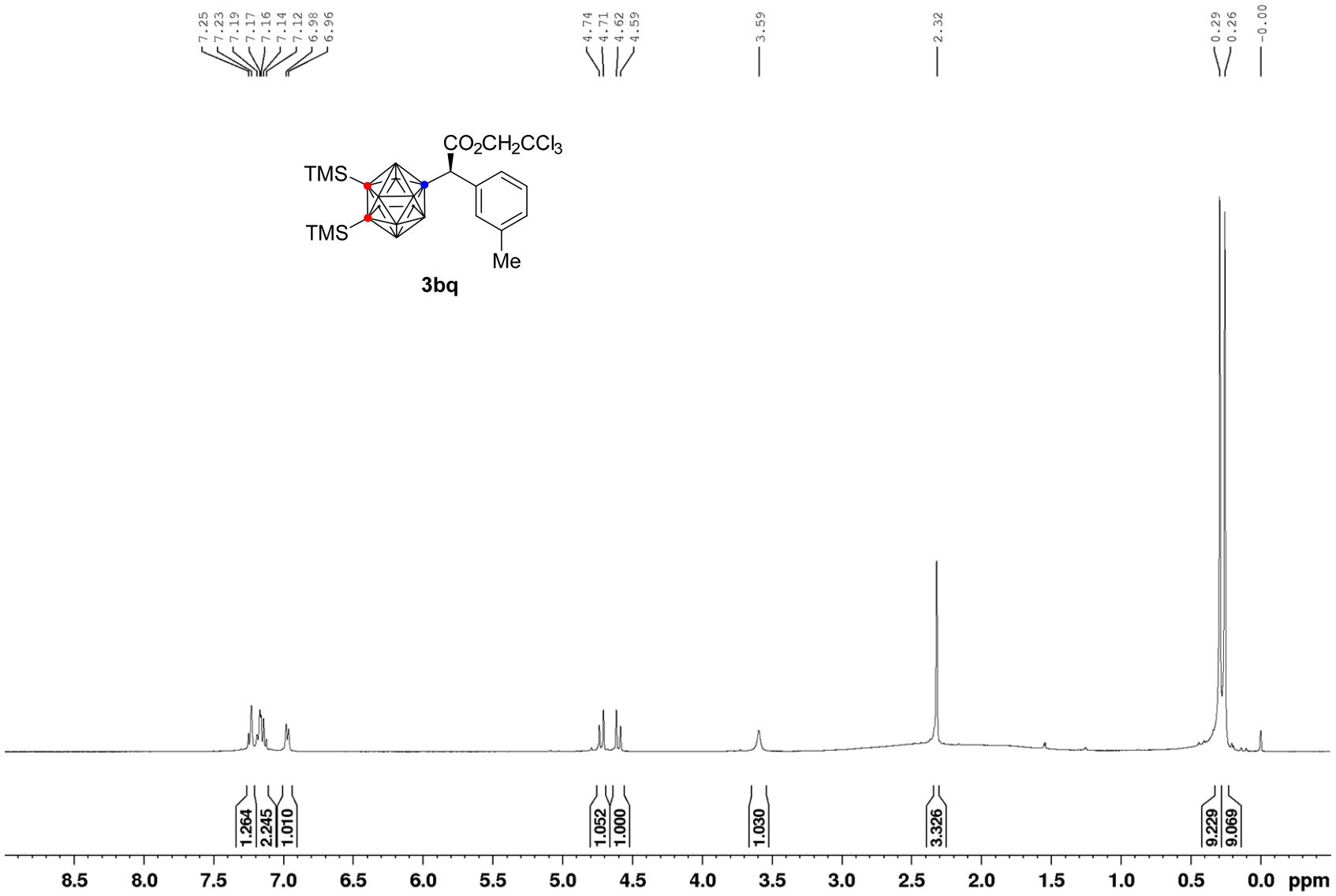
^{11}B NMR (128 MHz, $CDCl_3$)



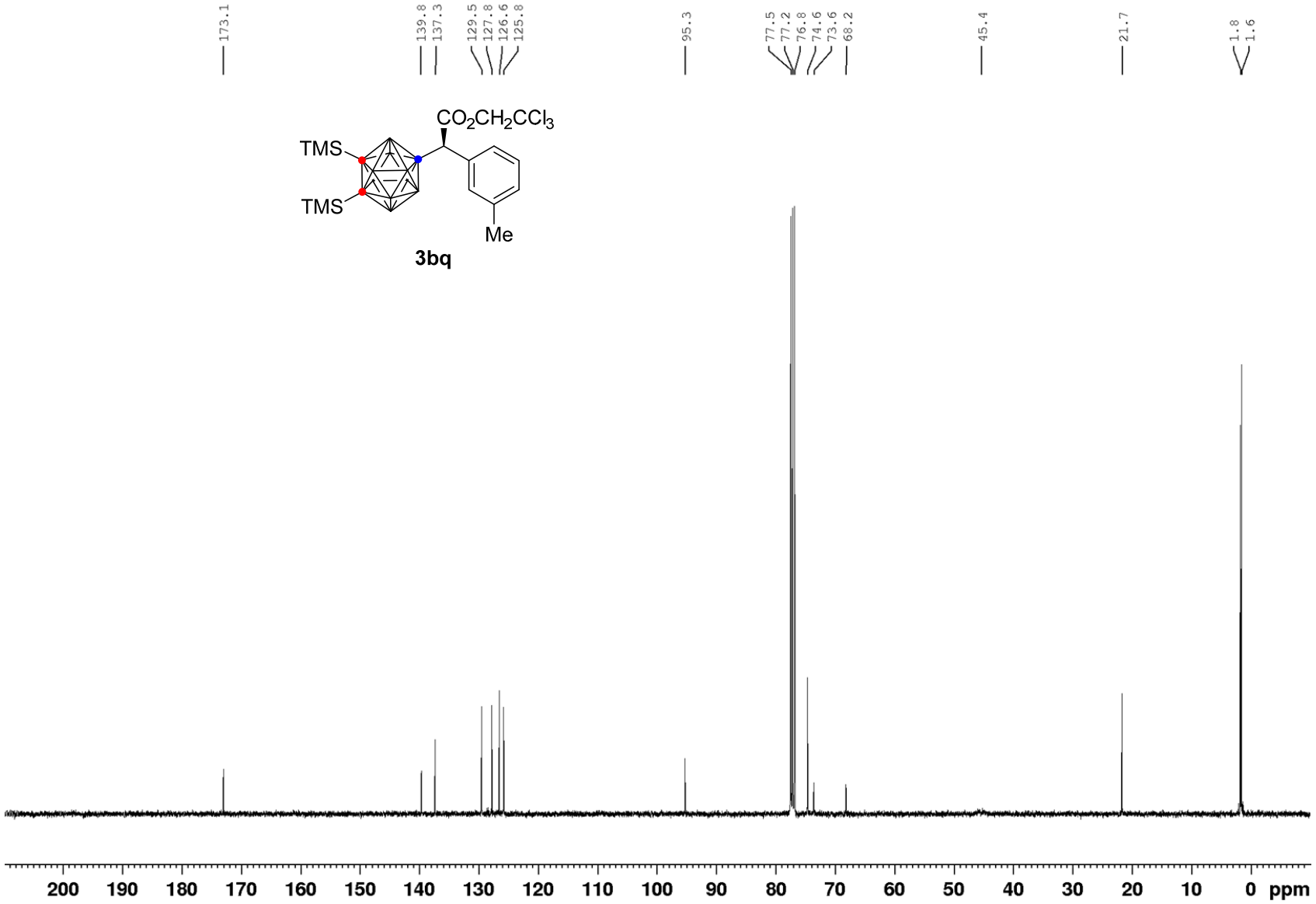
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



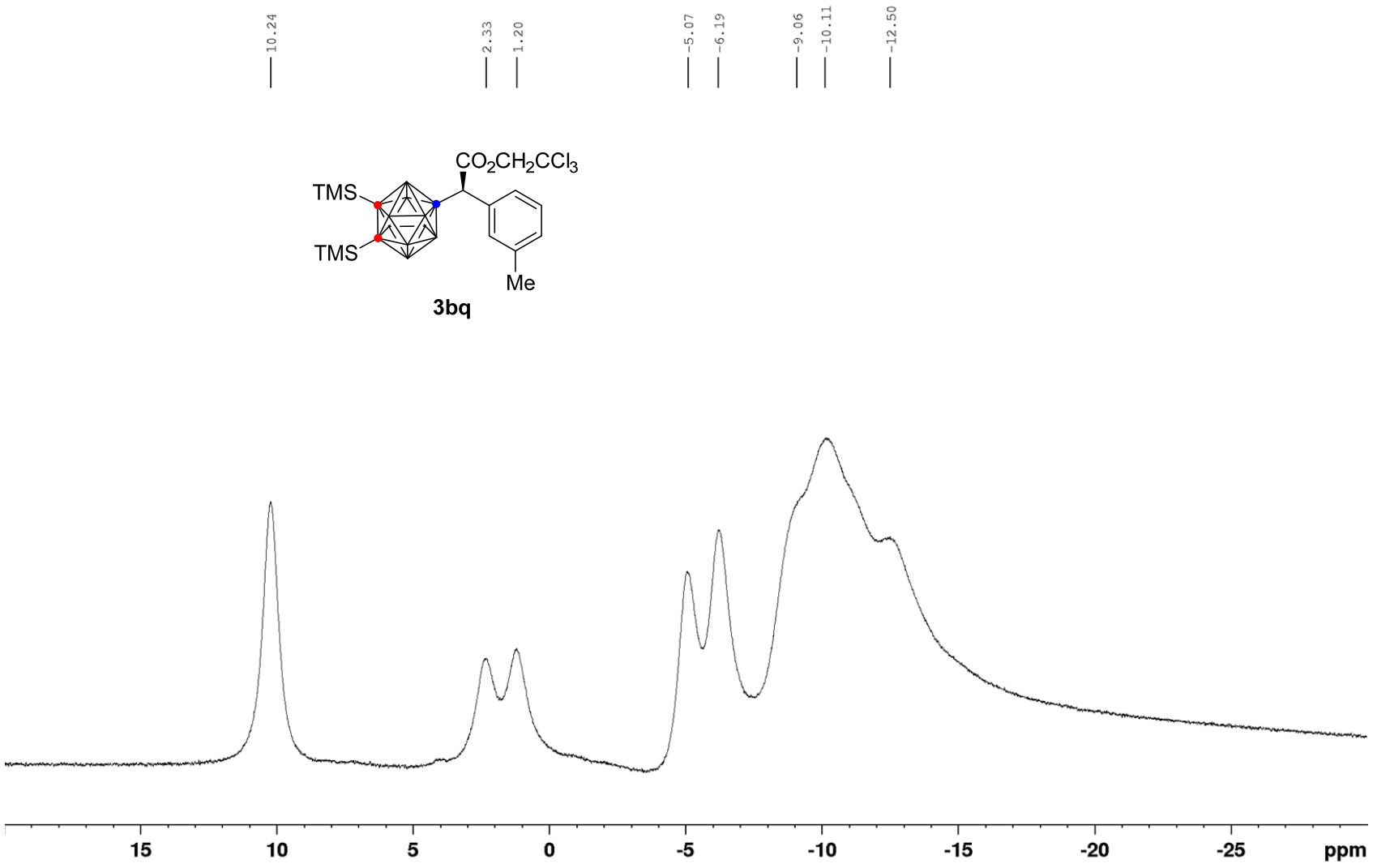
^{1}H NMR (400 MHz, $CDCl_3$)



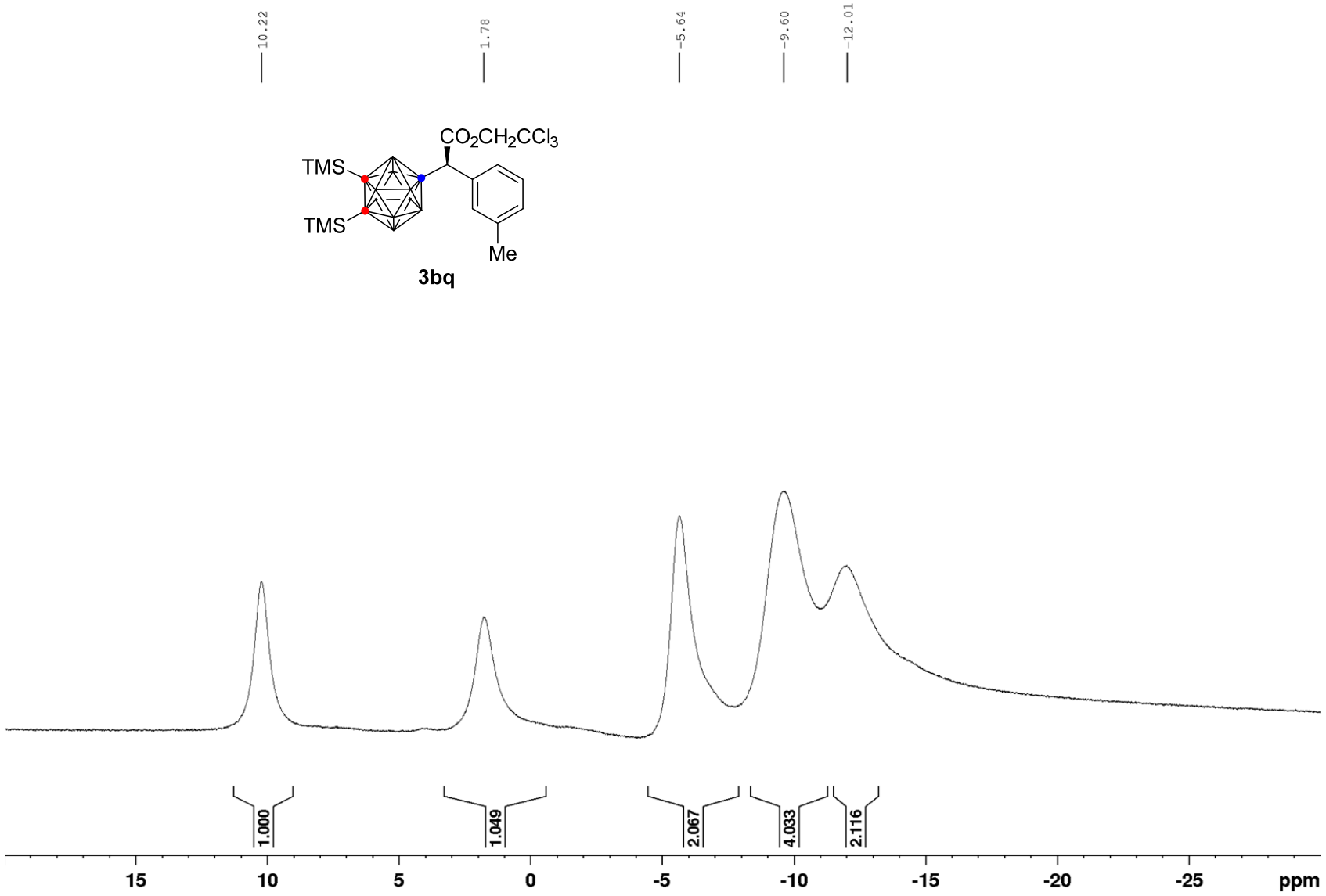
^{13}C NMR (100 MHz, $CDCl_3$)



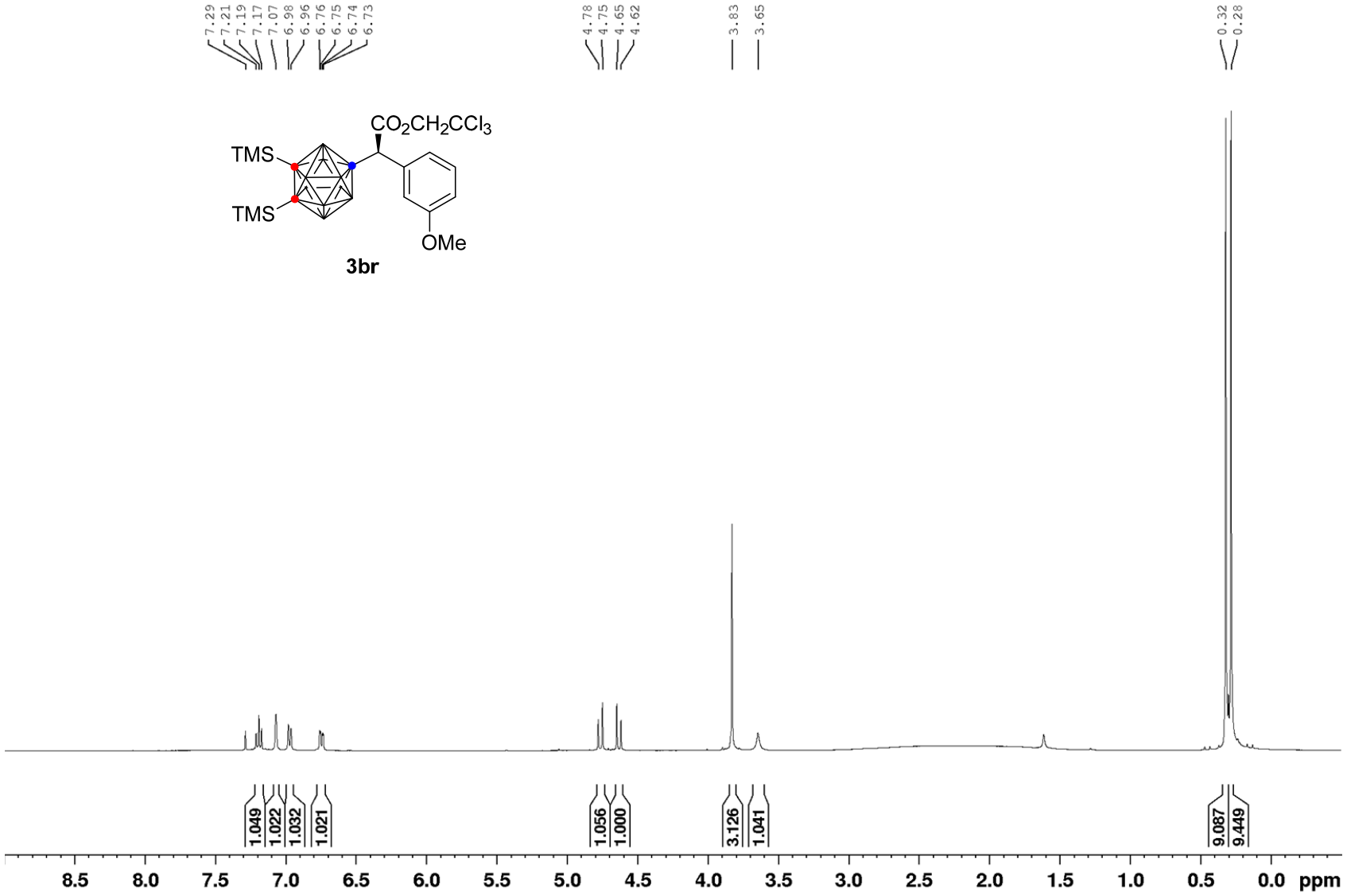
^{11}B NMR (128 MHz, $CDCl_3$)



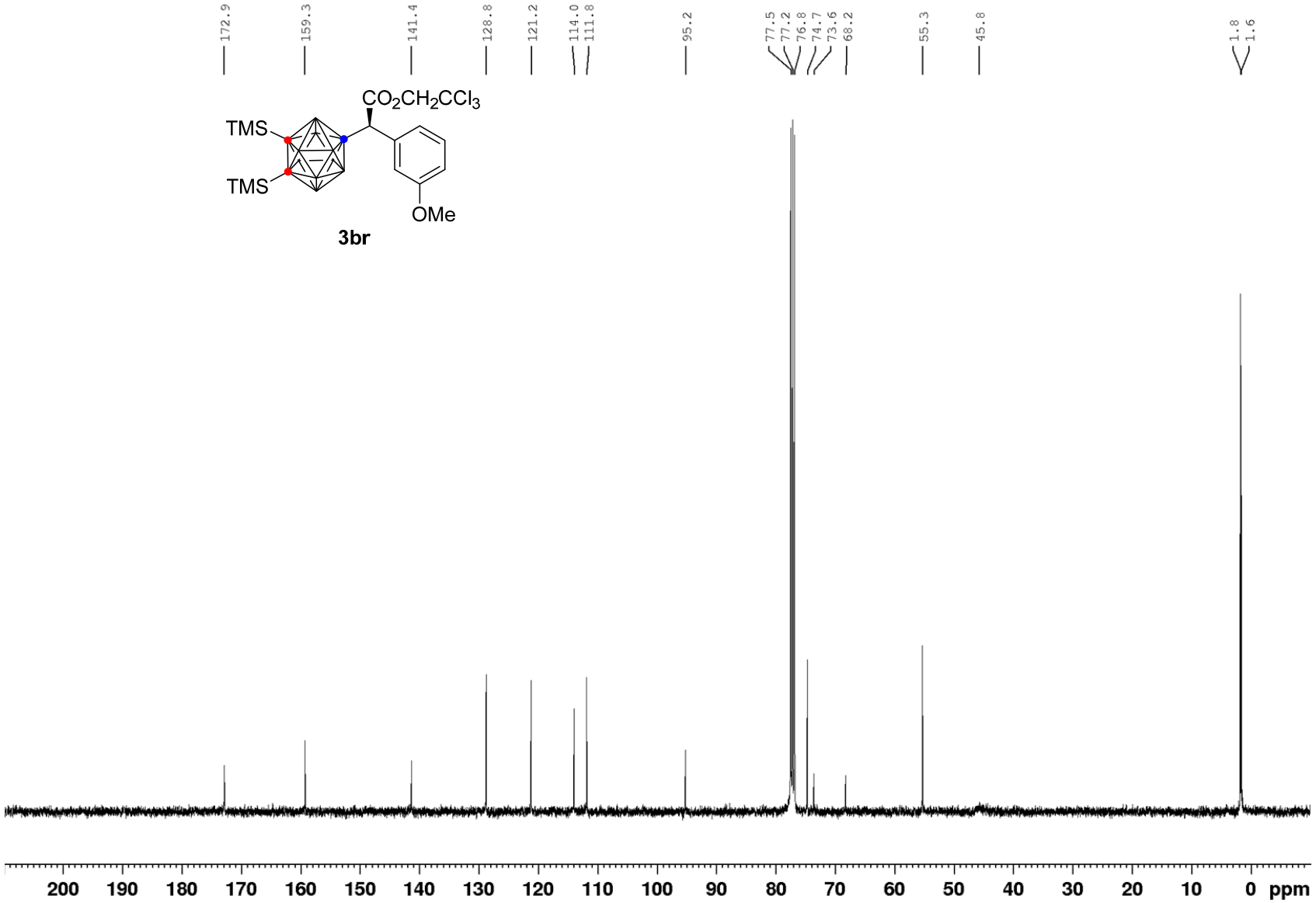
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



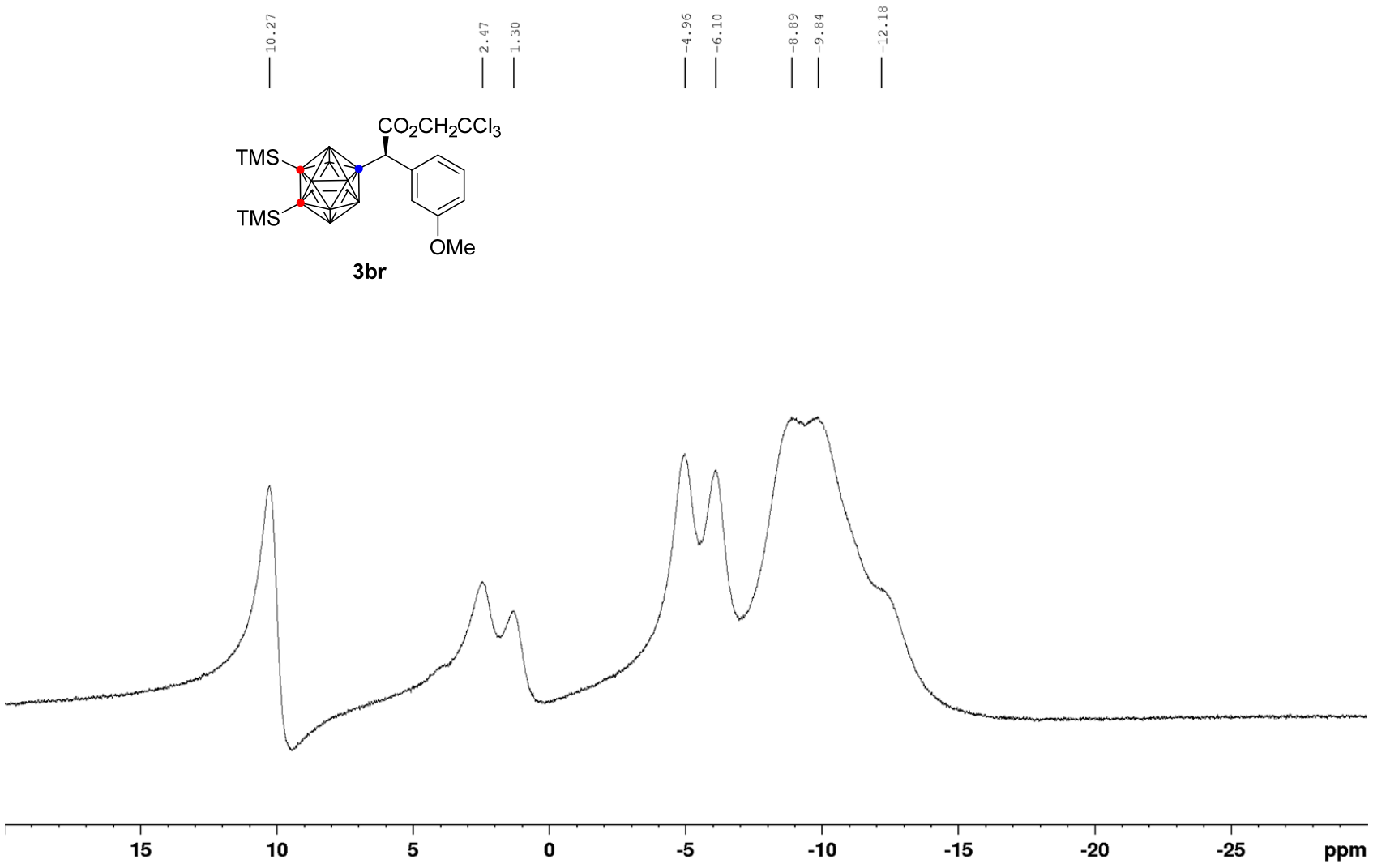
^{1}H NMR (400 MHz, $CDCl_3$)



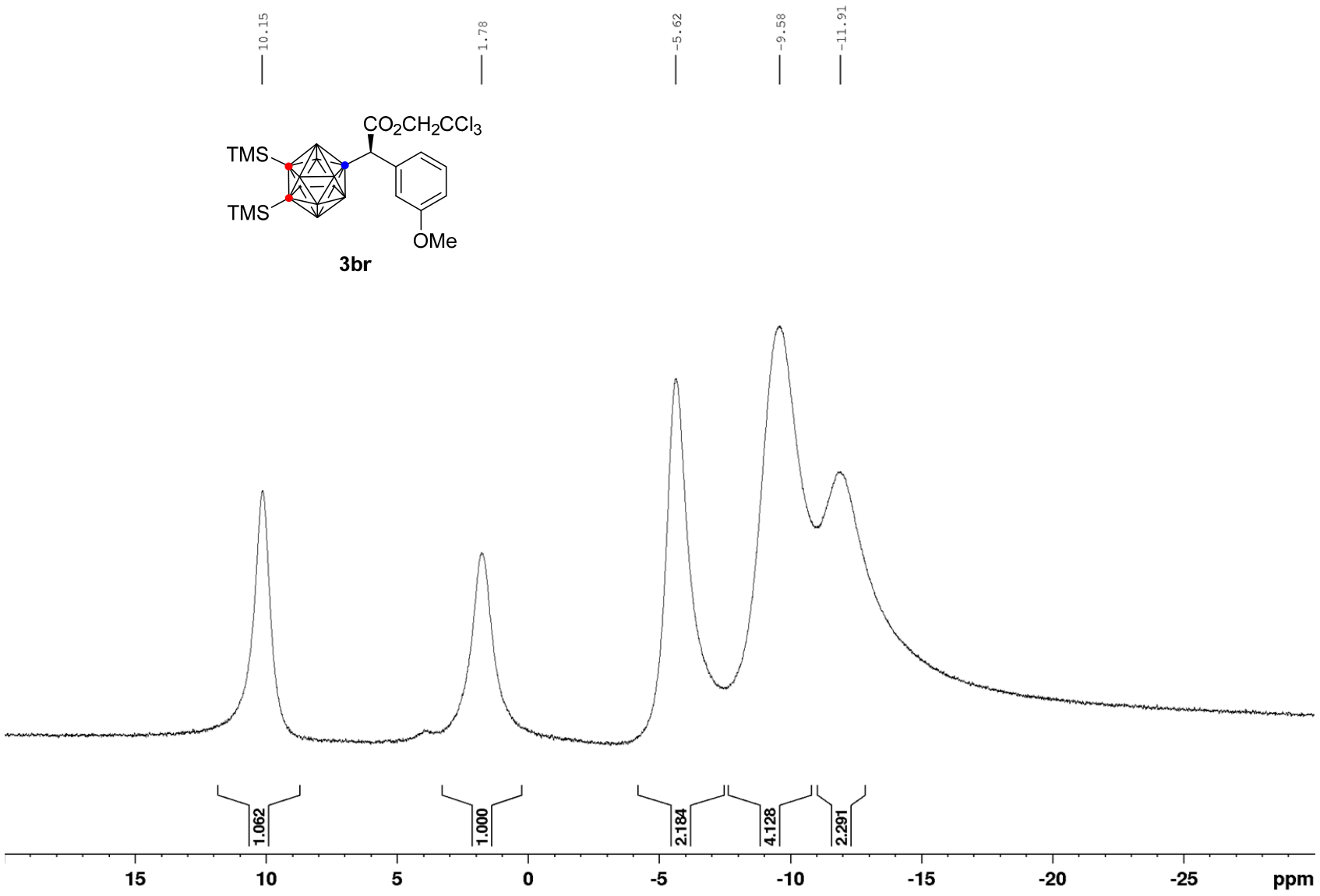
^{13}C NMR (100 MHz, $CDCl_3$)



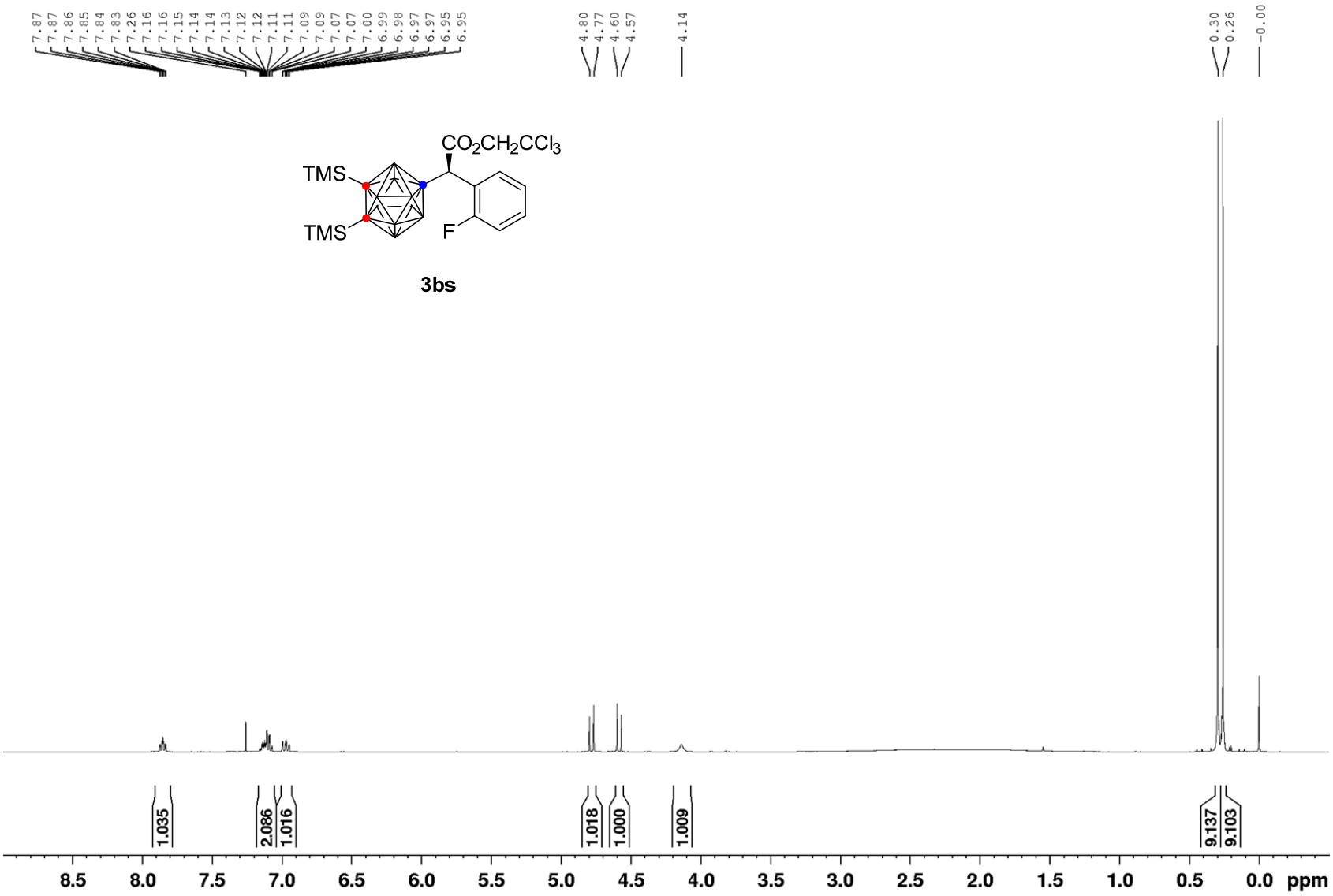
^{11}B NMR (128 MHz, $CDCl_3$)



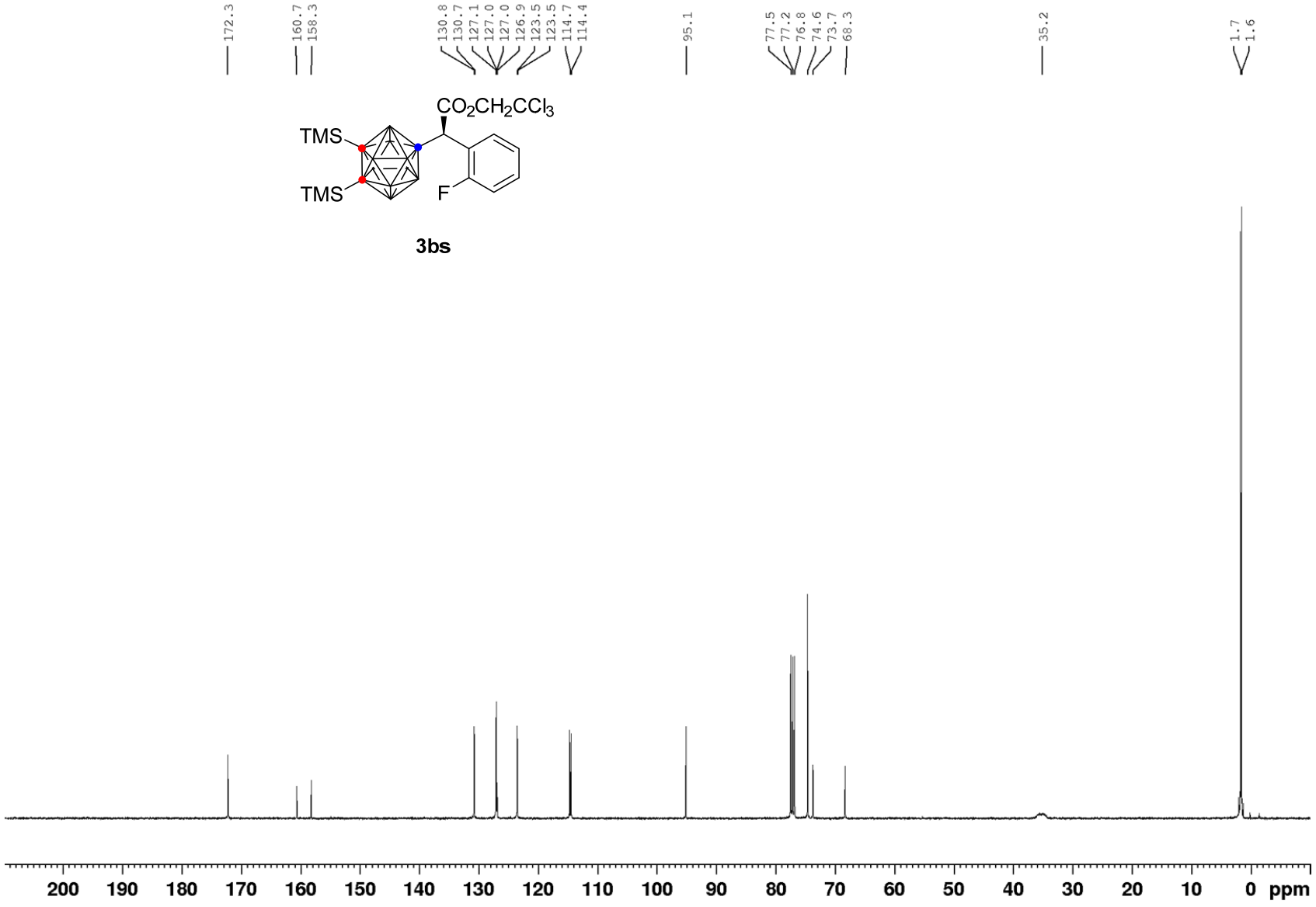
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

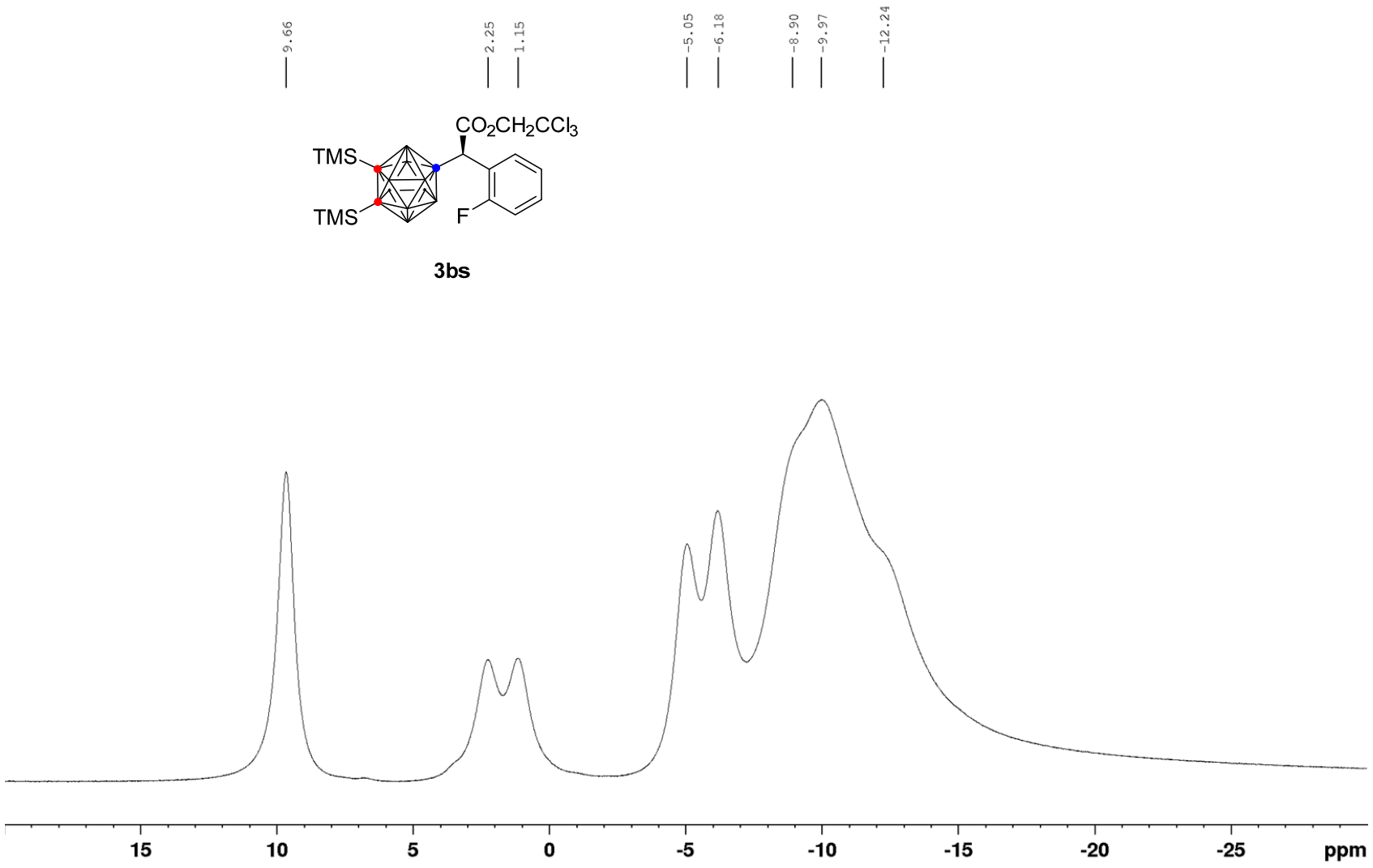


^{13}C NMR (100 MHz, $CDCl_3$)

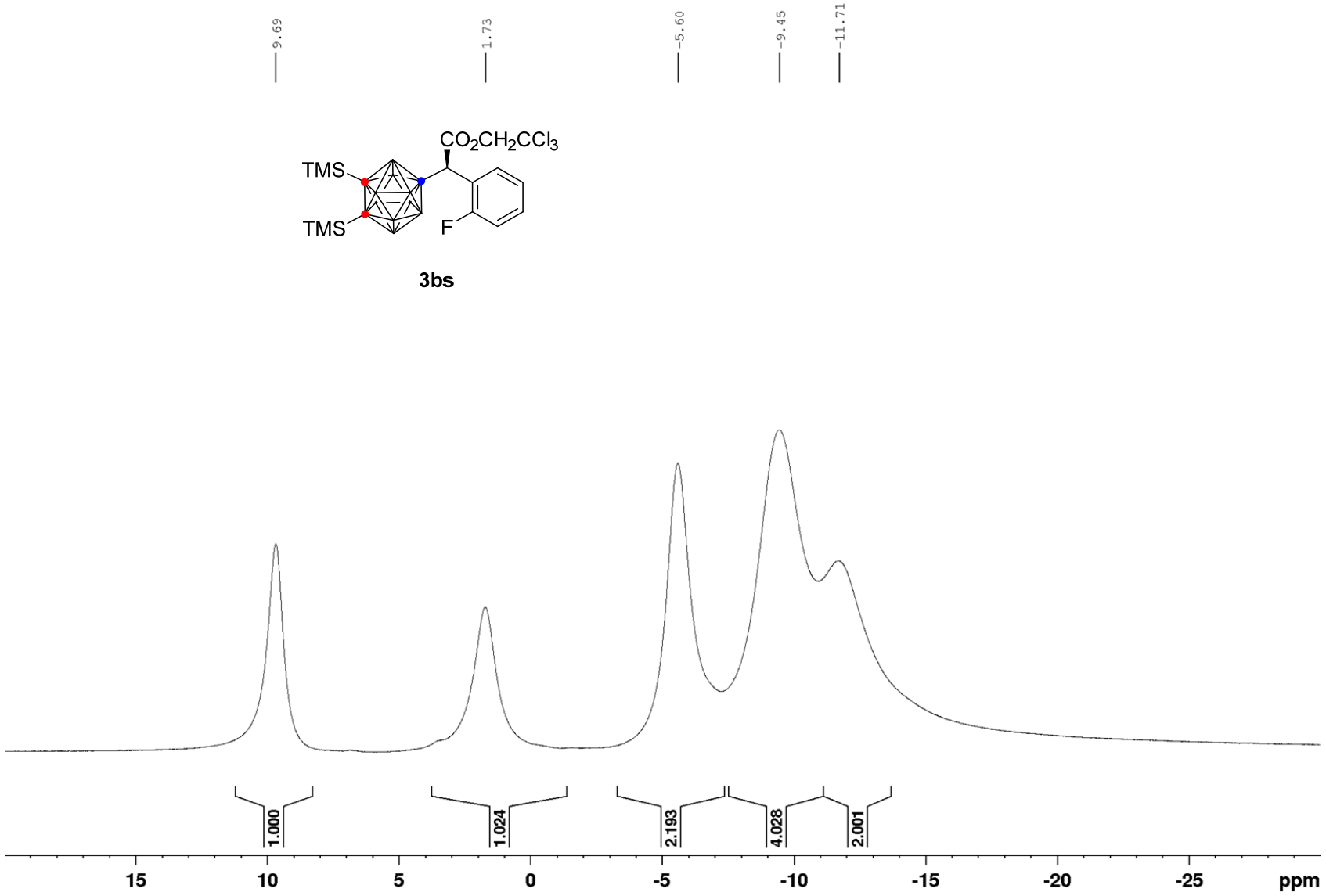


3bs

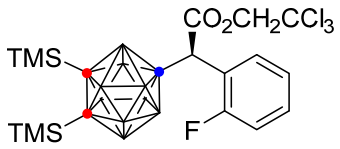
^{11}B NMR (128 MHz, $CDCl_3$)



$^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$)

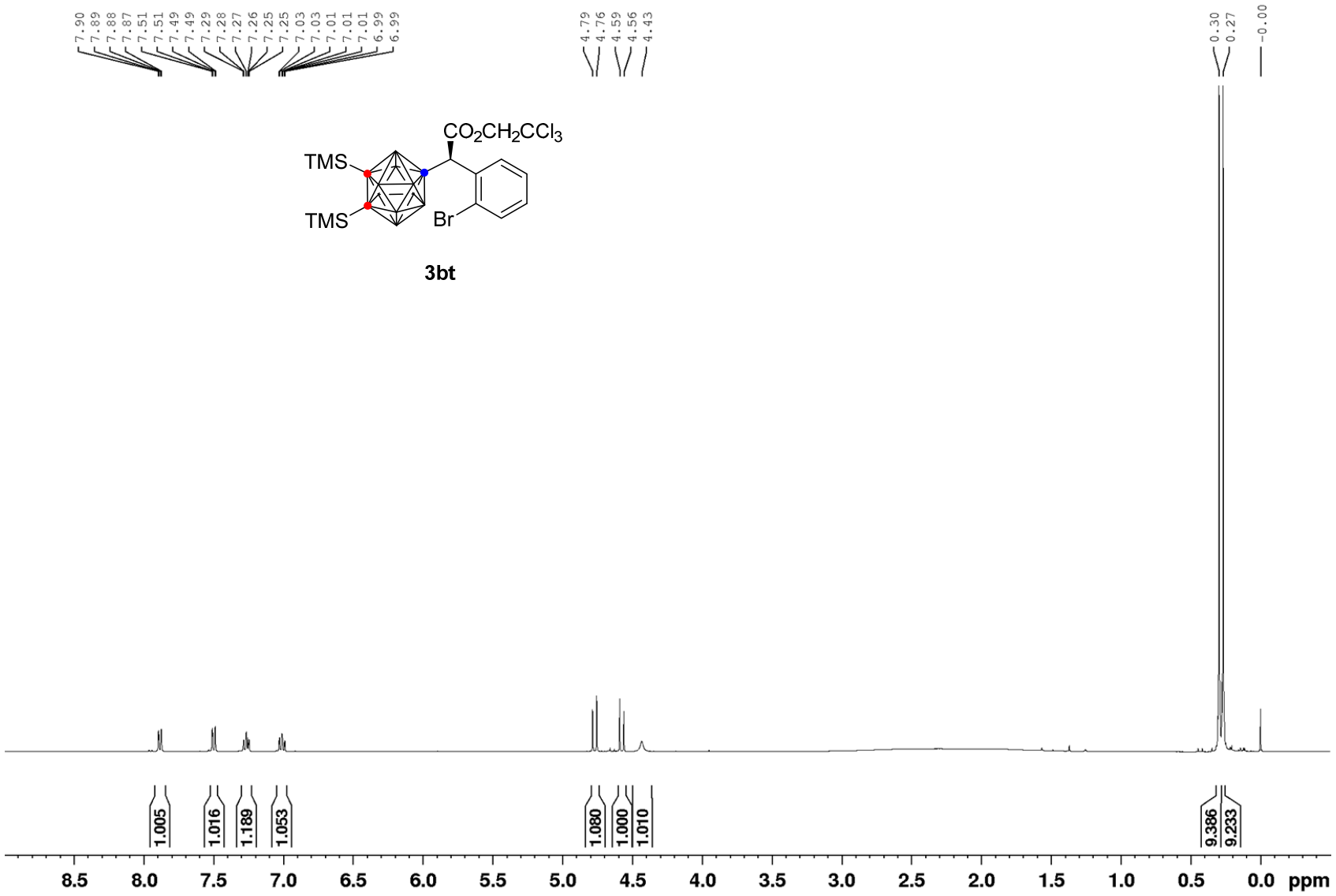


$^{19}F\{^{1}H\}$ NMR (377 MHz, $CDCl_3$)



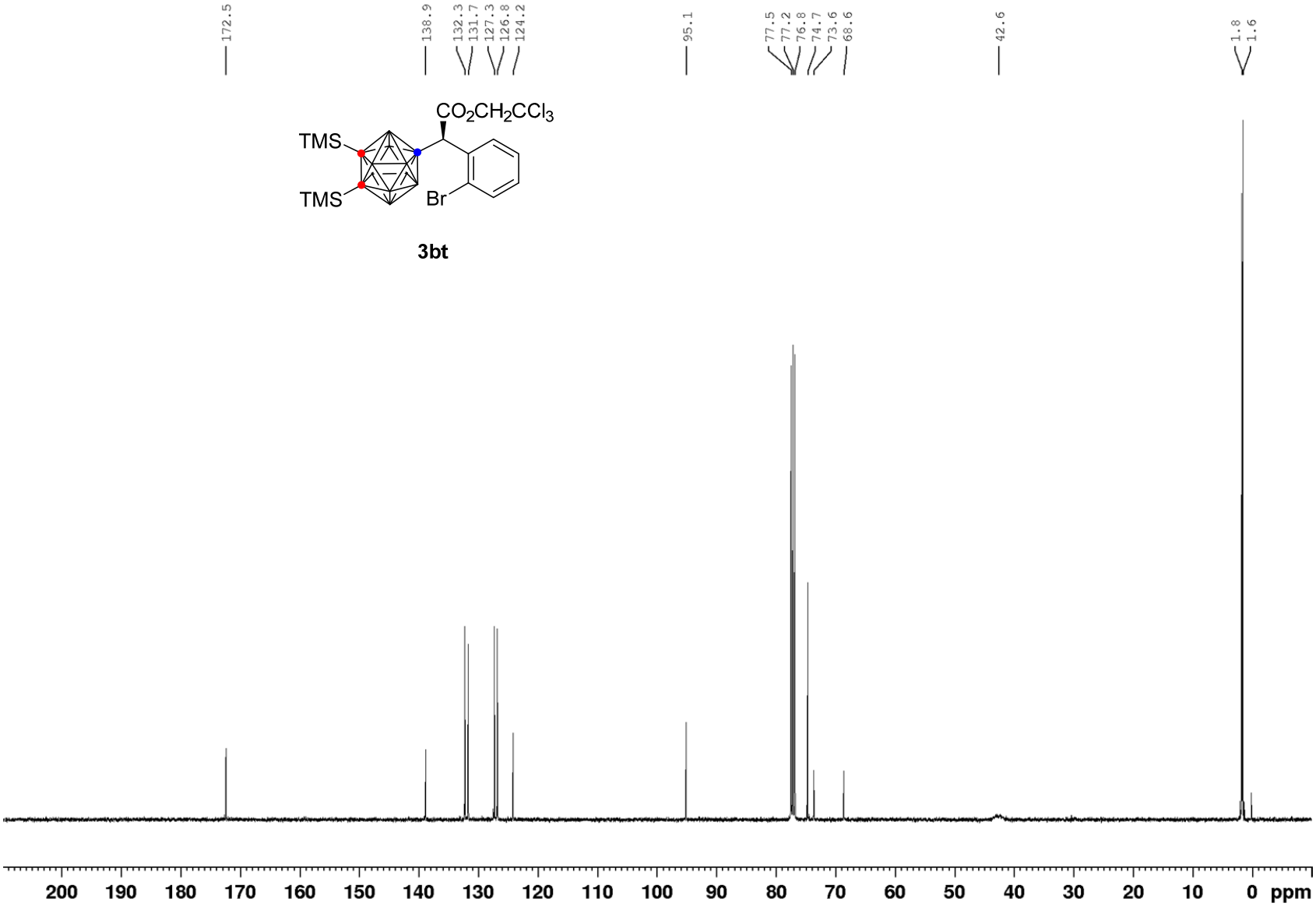
3bs

^{1}H NMR (400 MHz, $CDCl_3$)



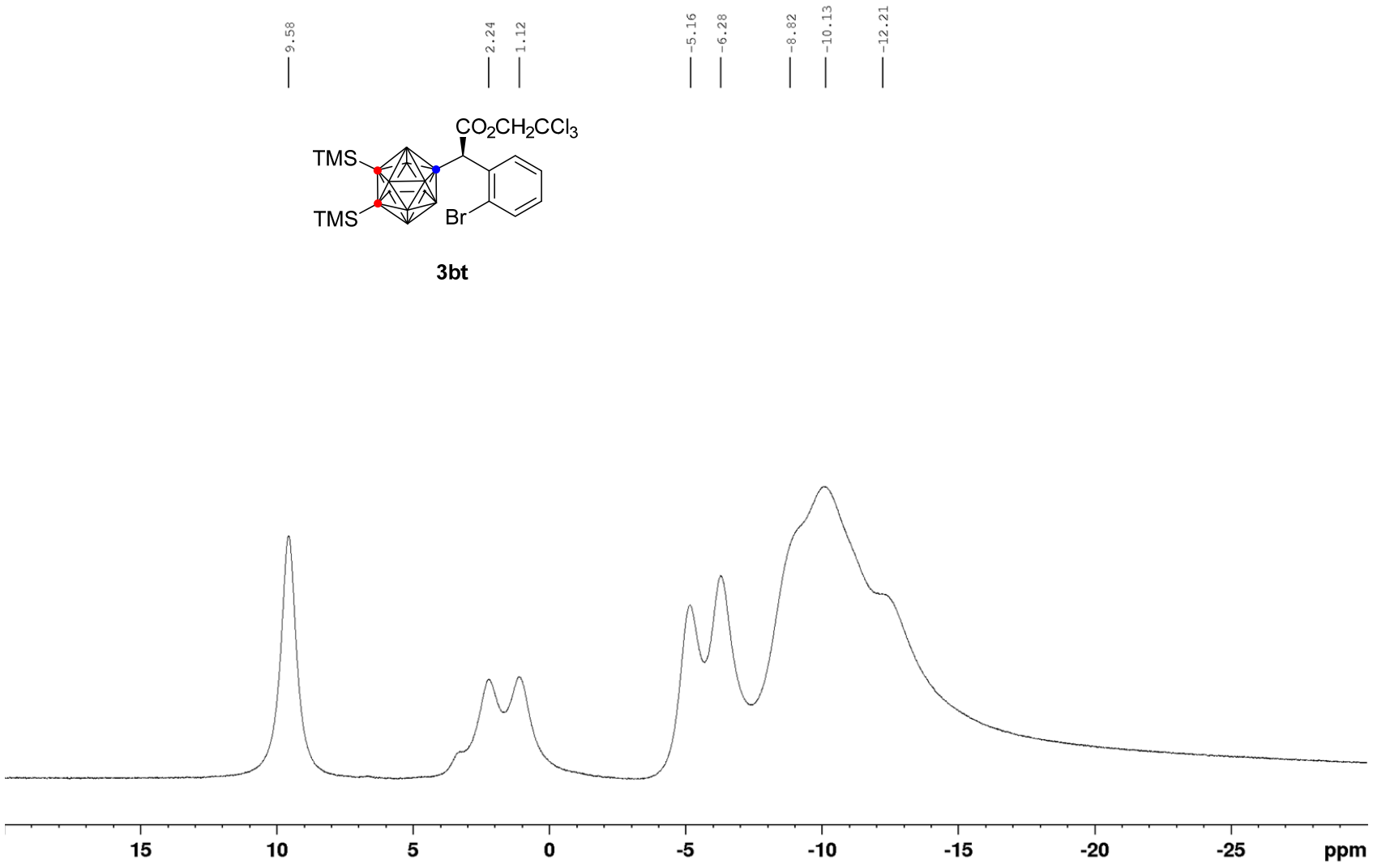
3bt

^{13}C NMR (100 MHz, $CDCl_3$)



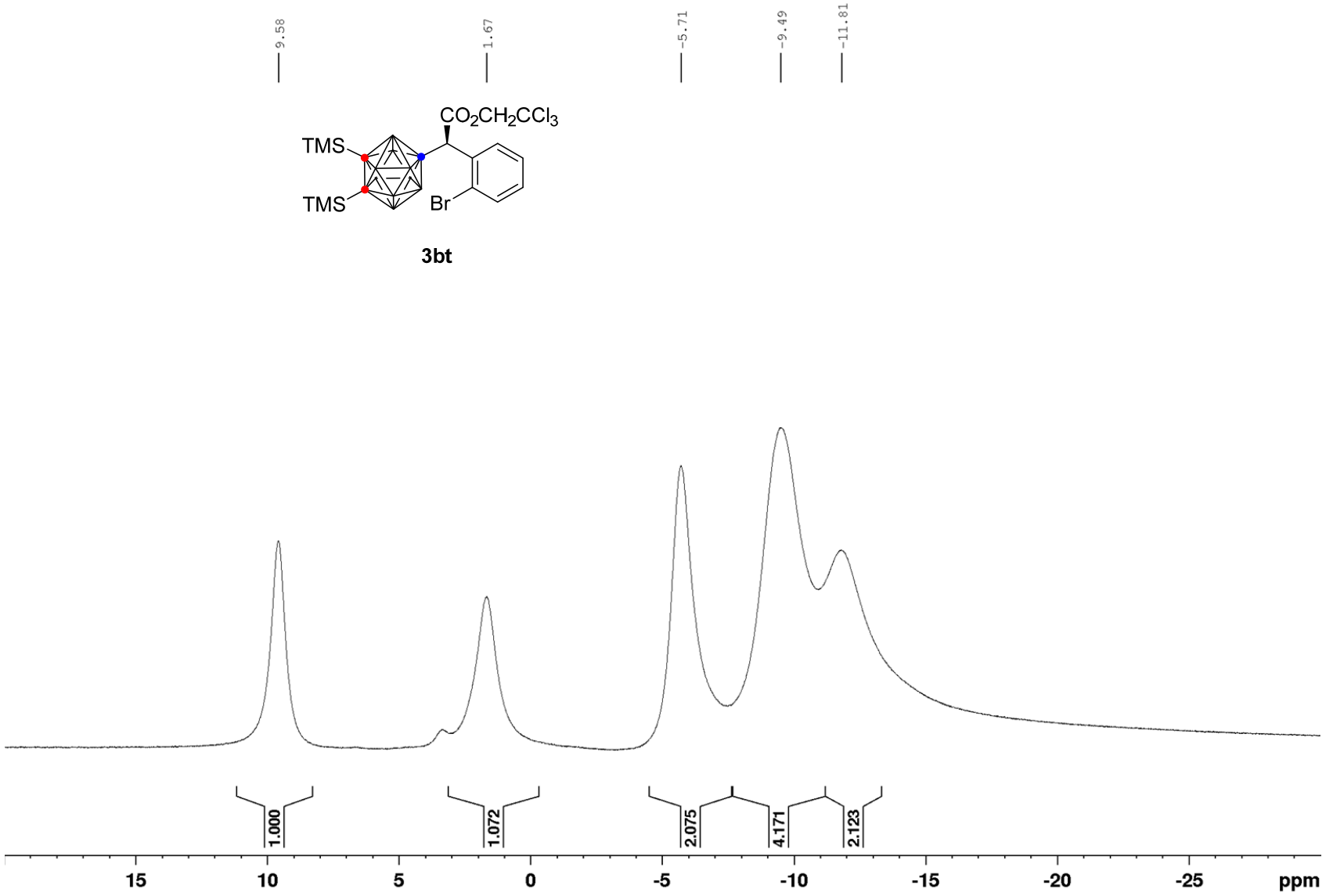
3bt

^{11}B NMR (128 MHz, $CDCl_3$)



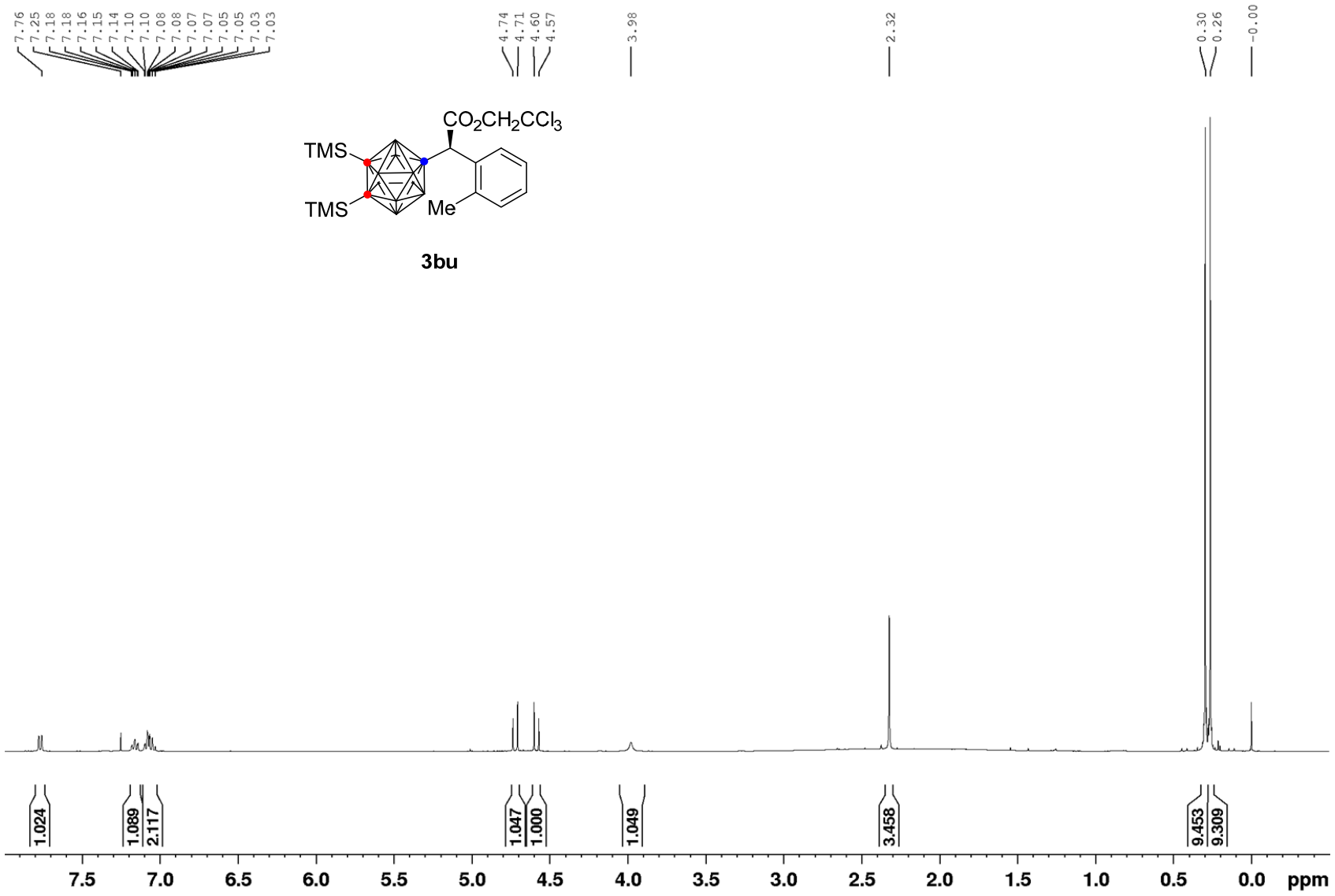
3bt

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



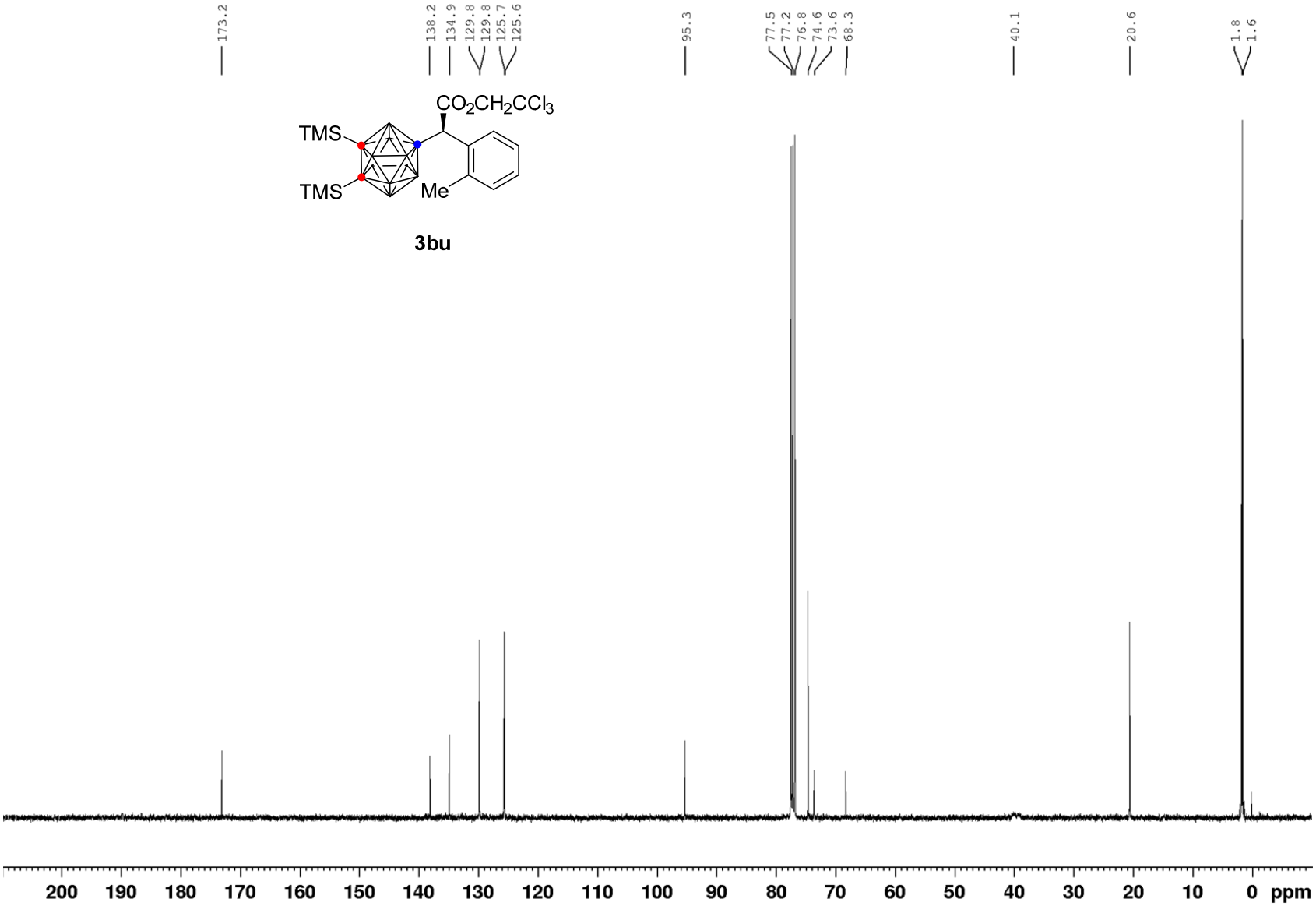
3bt

^{1}H NMR (400 MHz, $CDCl_3$)

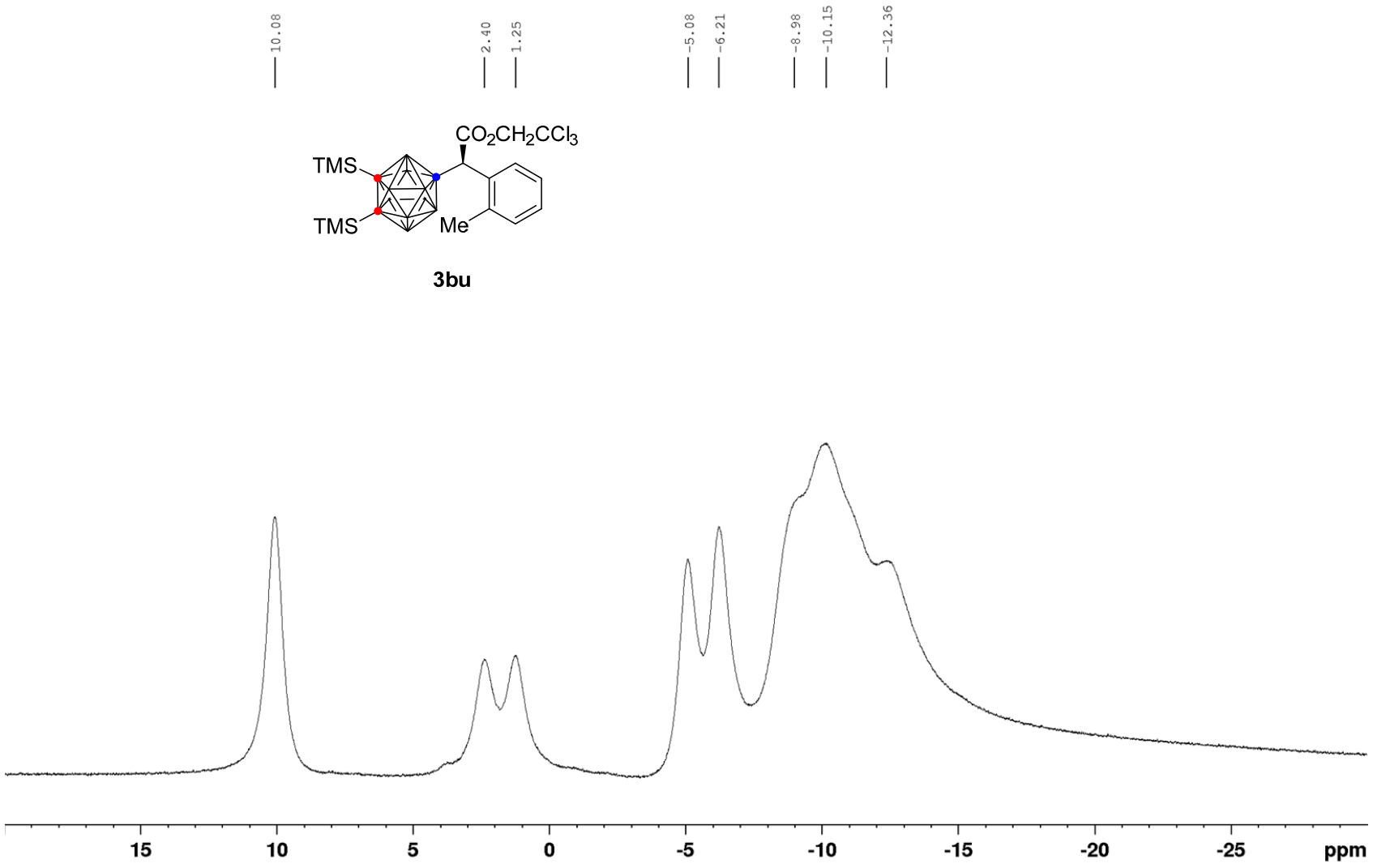


3bu

^{13}C NMR (100 MHz, $CDCl_3$)

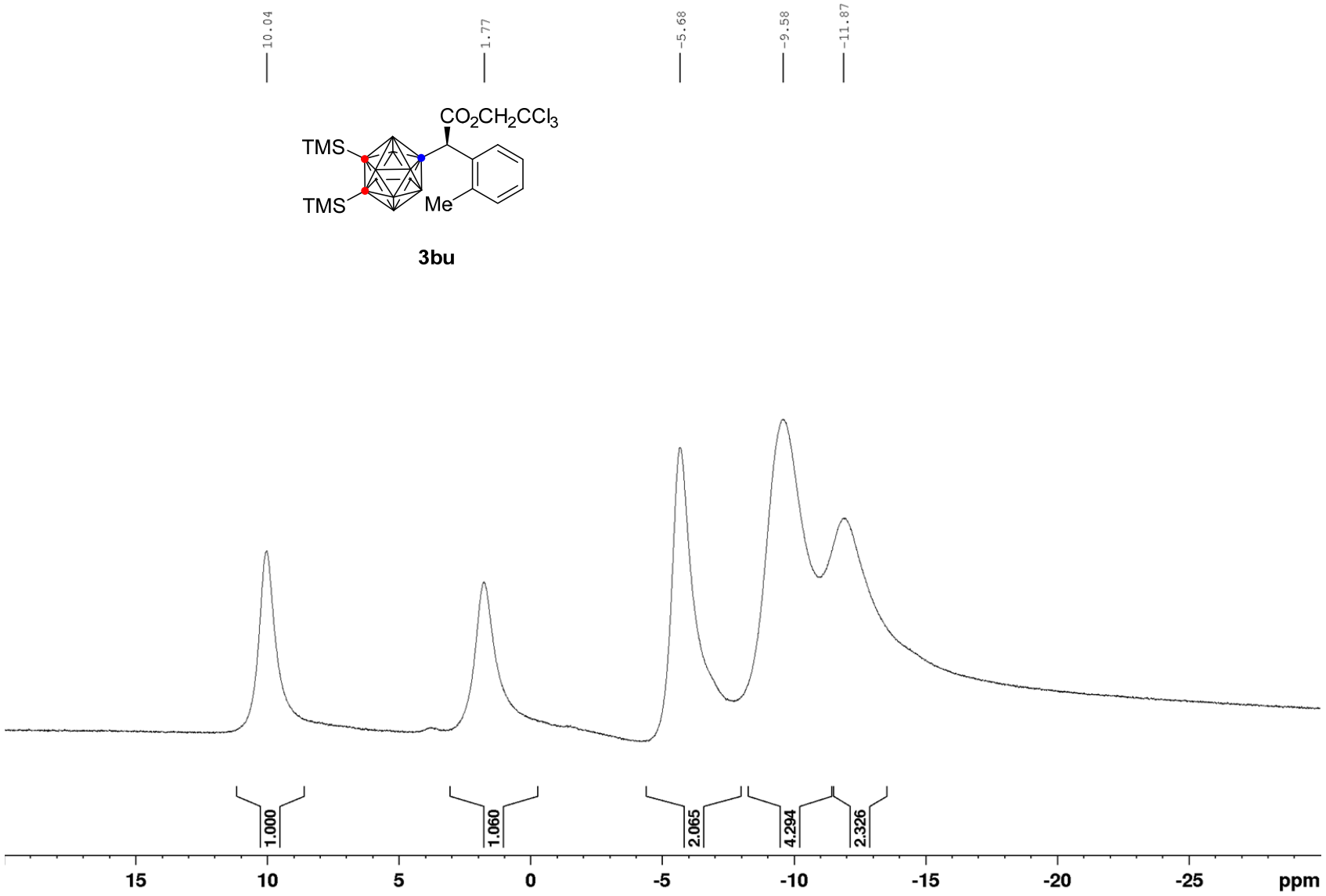


^{11}B NMR (128 MHz, $CDCl_3$)



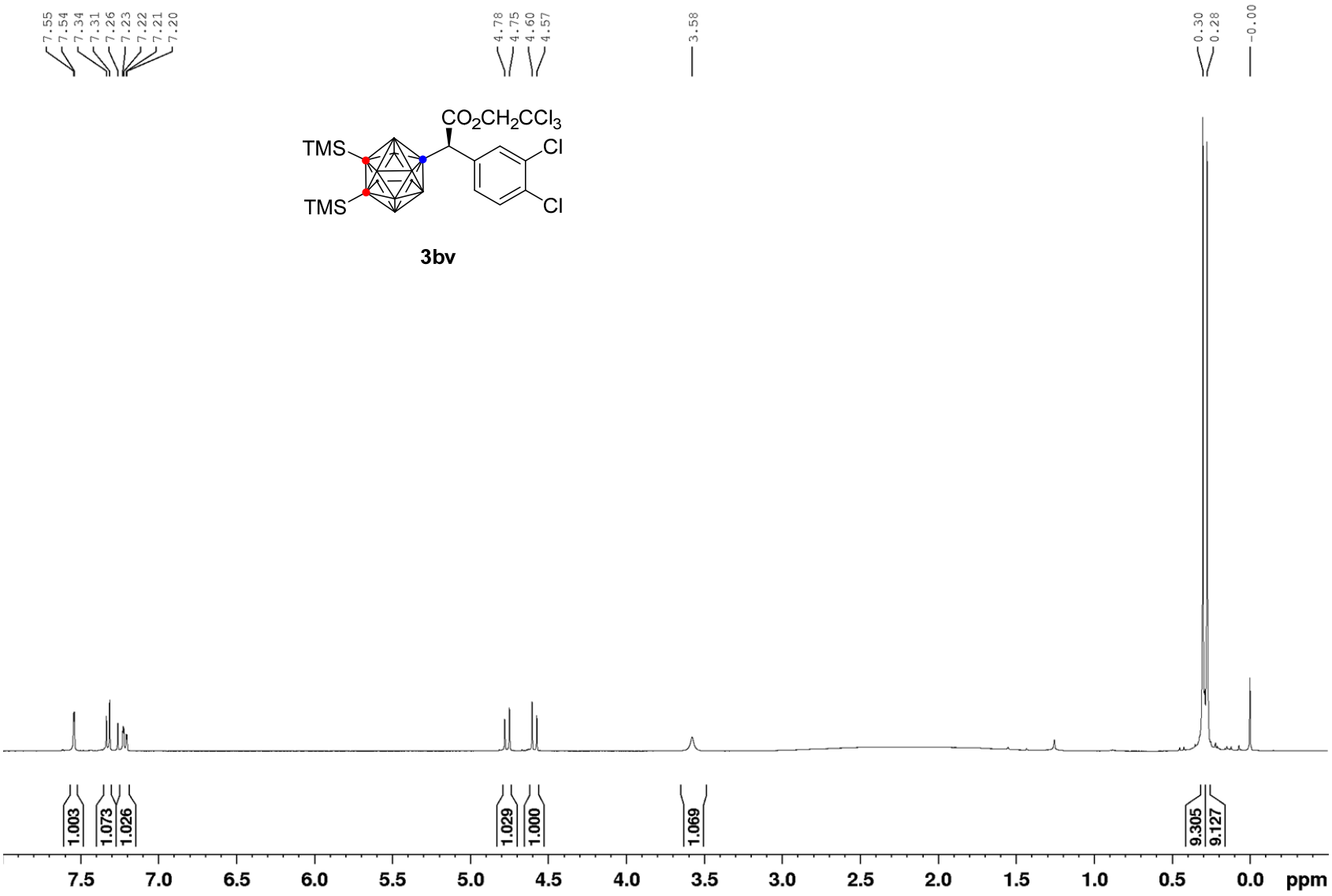
3bu

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



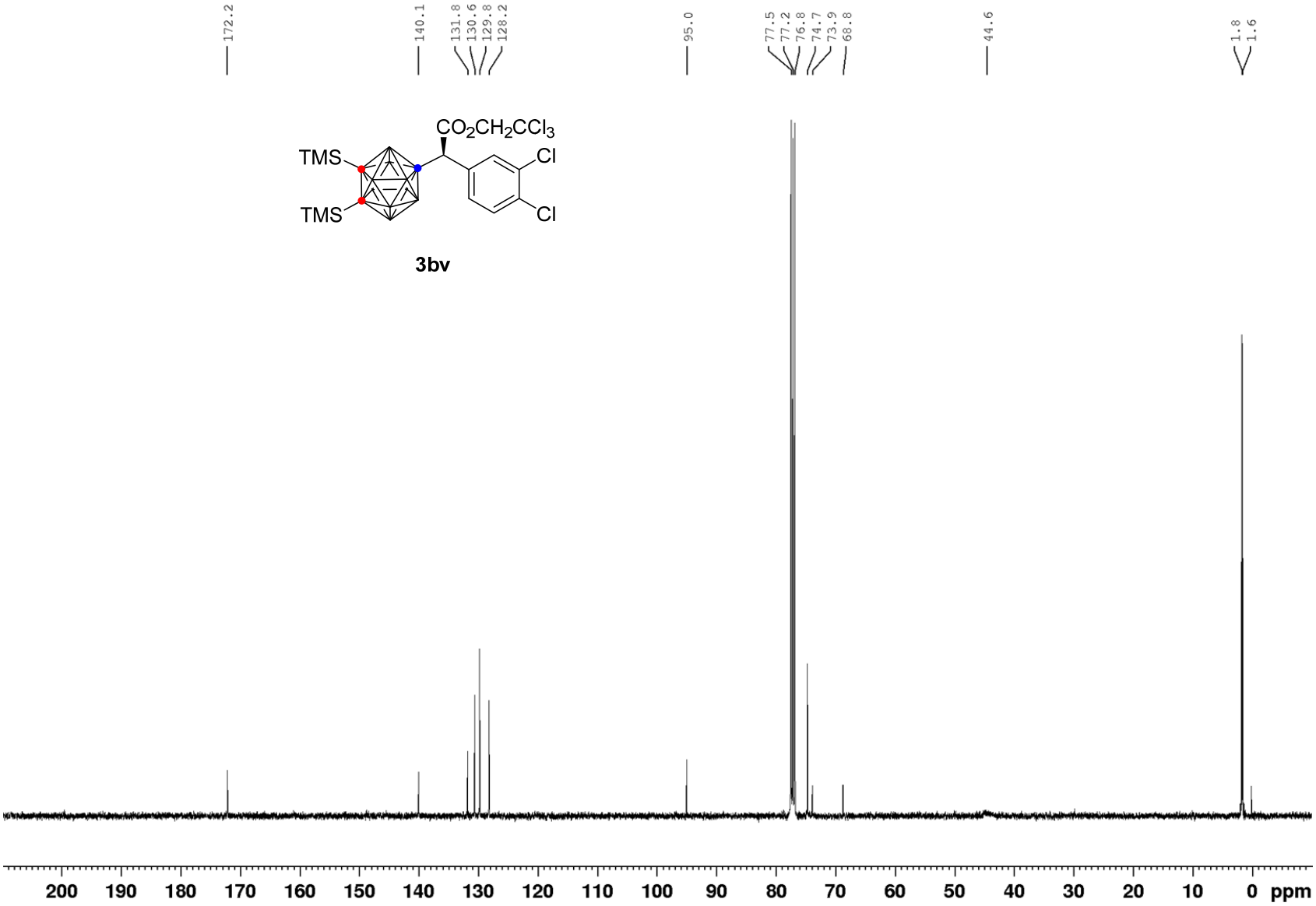
3bu

^{1}H NMR (400 MHz, $CDCl_3$)



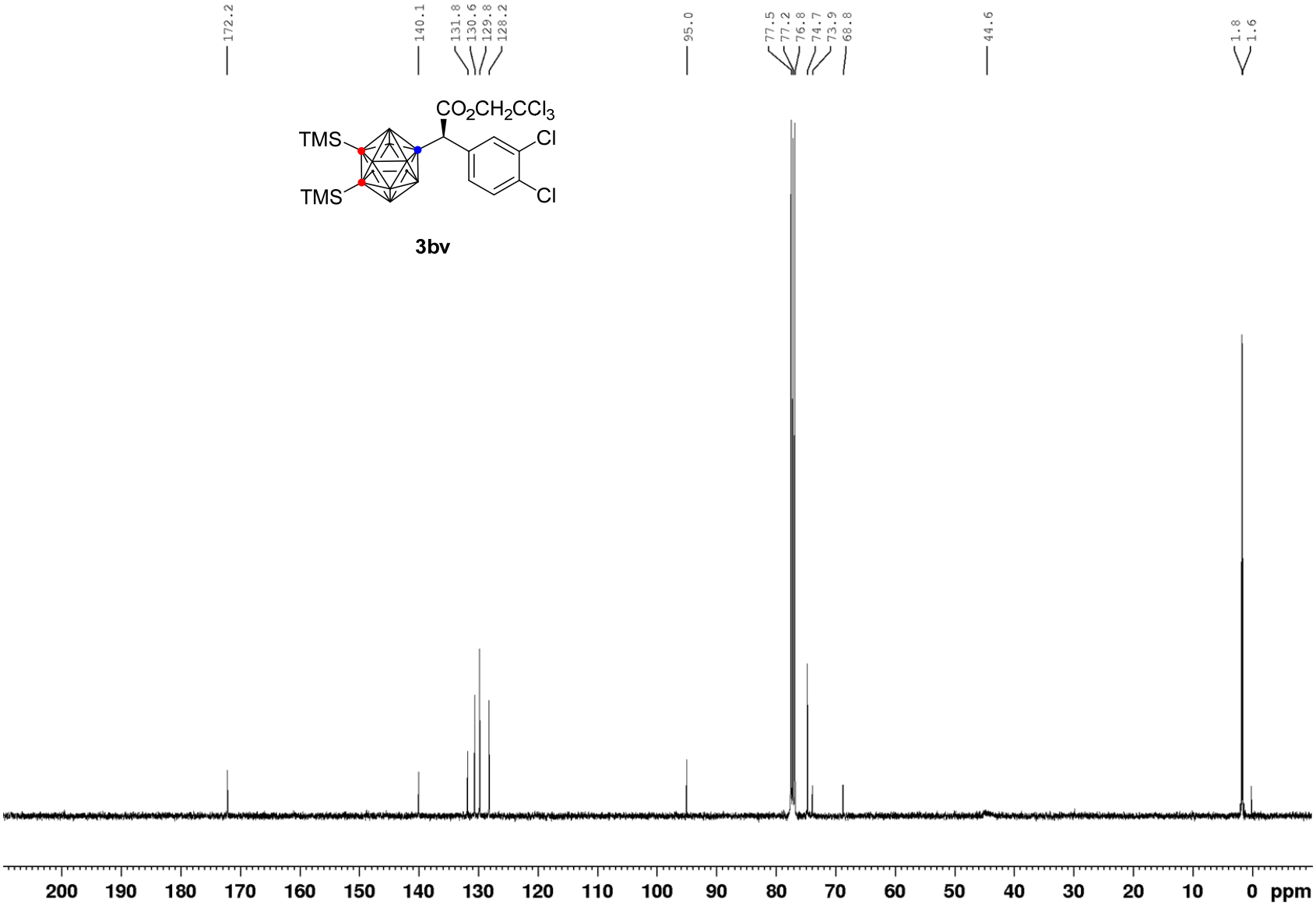
3bv

^{13}C NMR (100 MHz, $CDCl_3$)

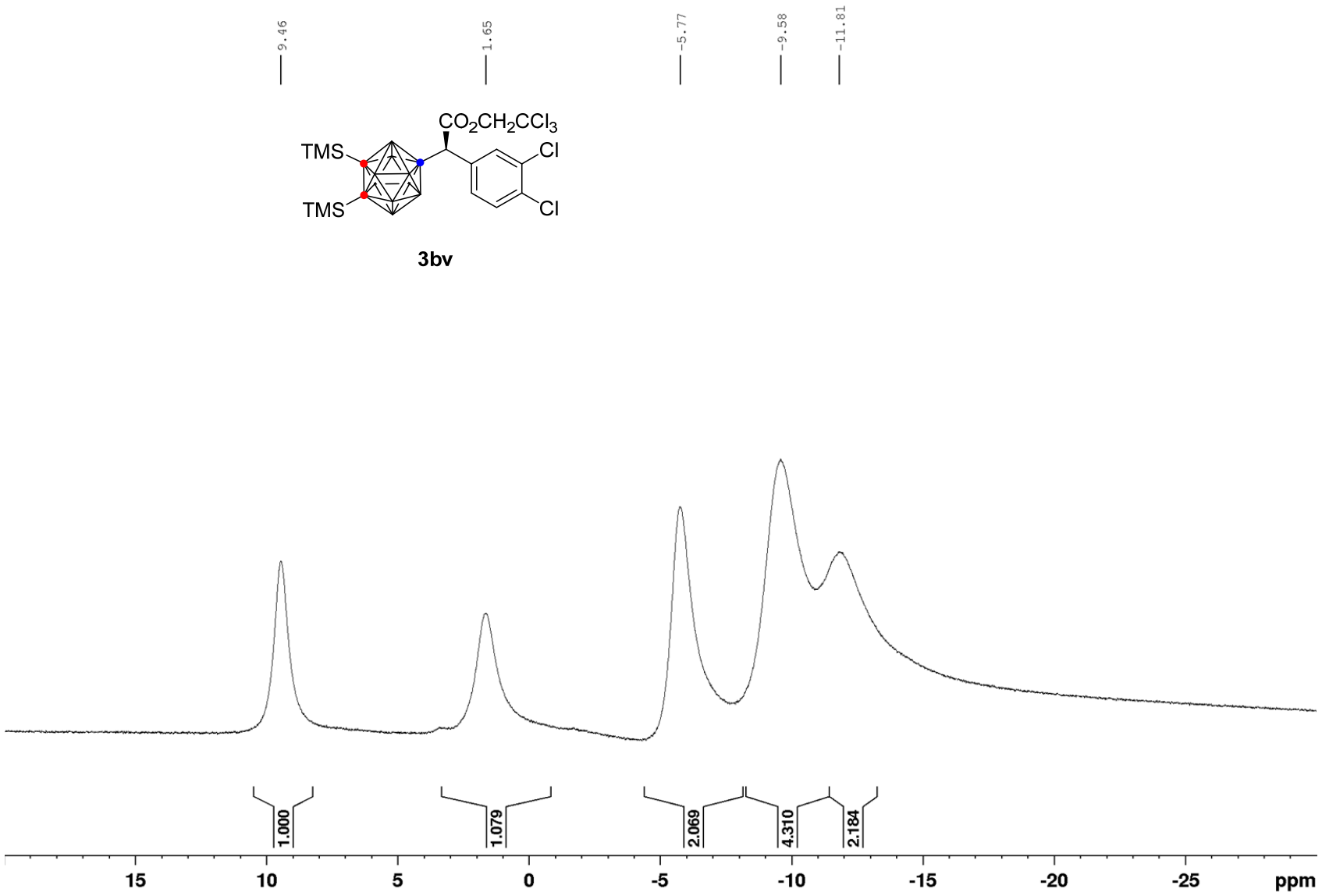


3bv

^{11}B NMR (128 MHz, $CDCl_3$)

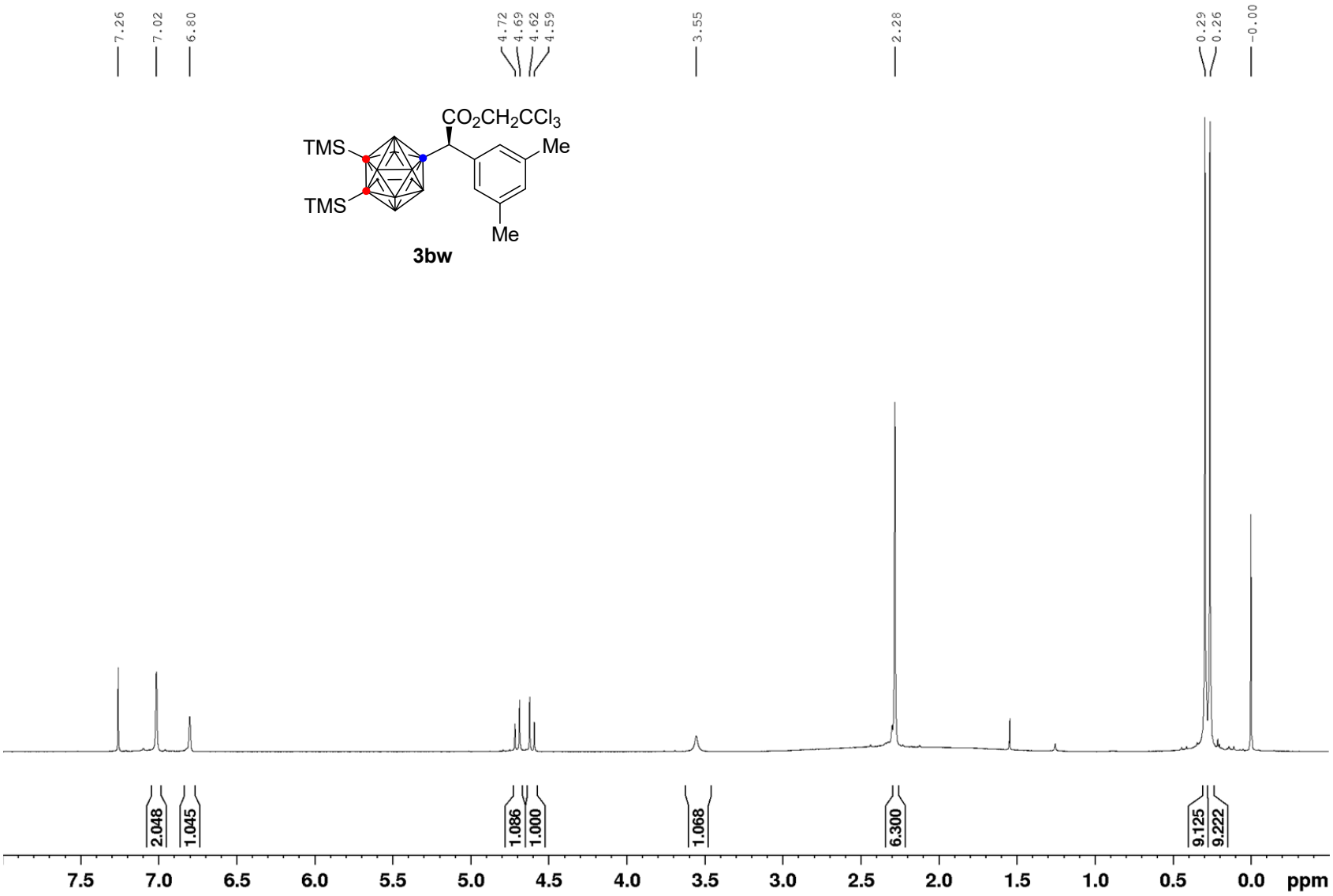


$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

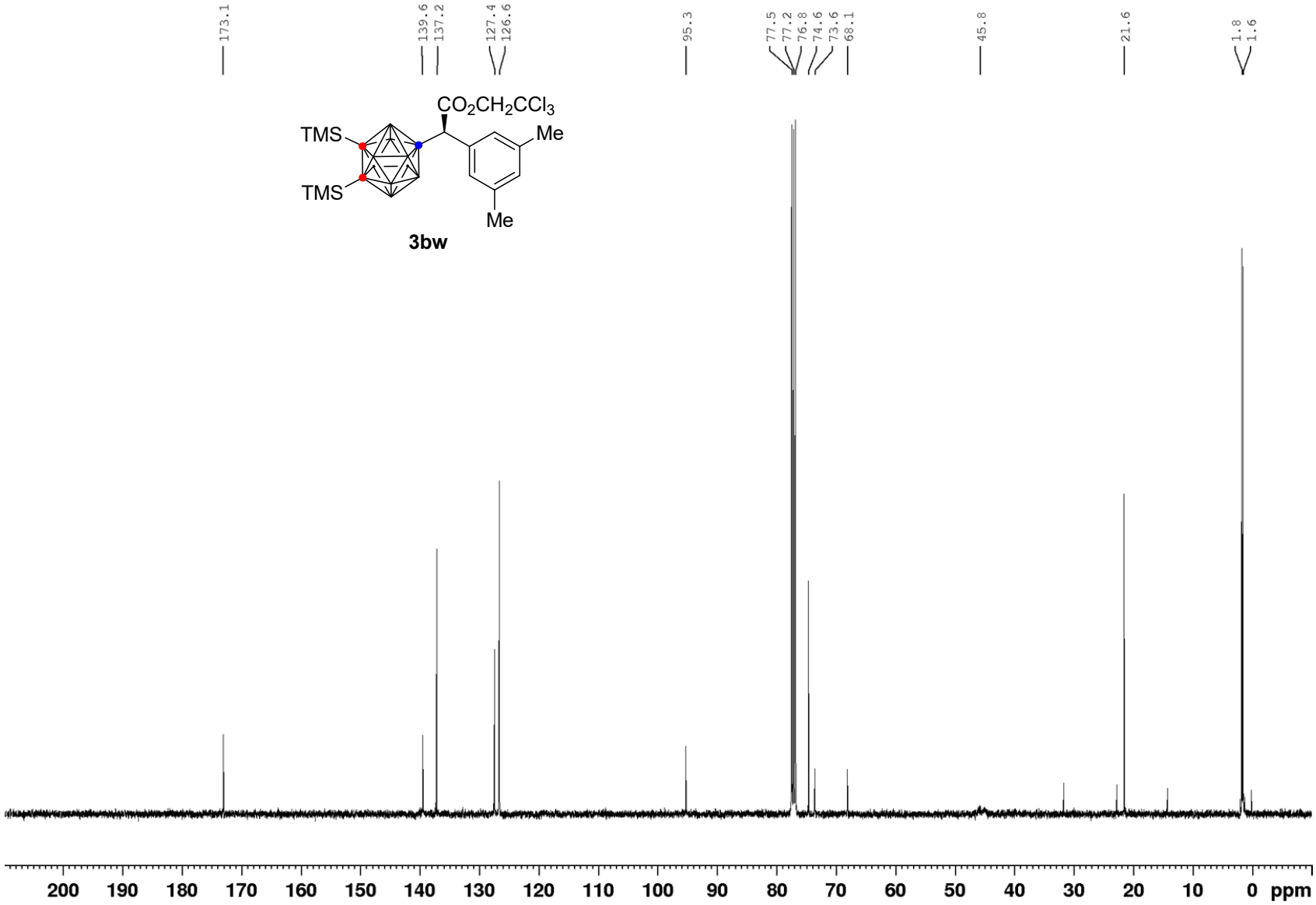


3bv

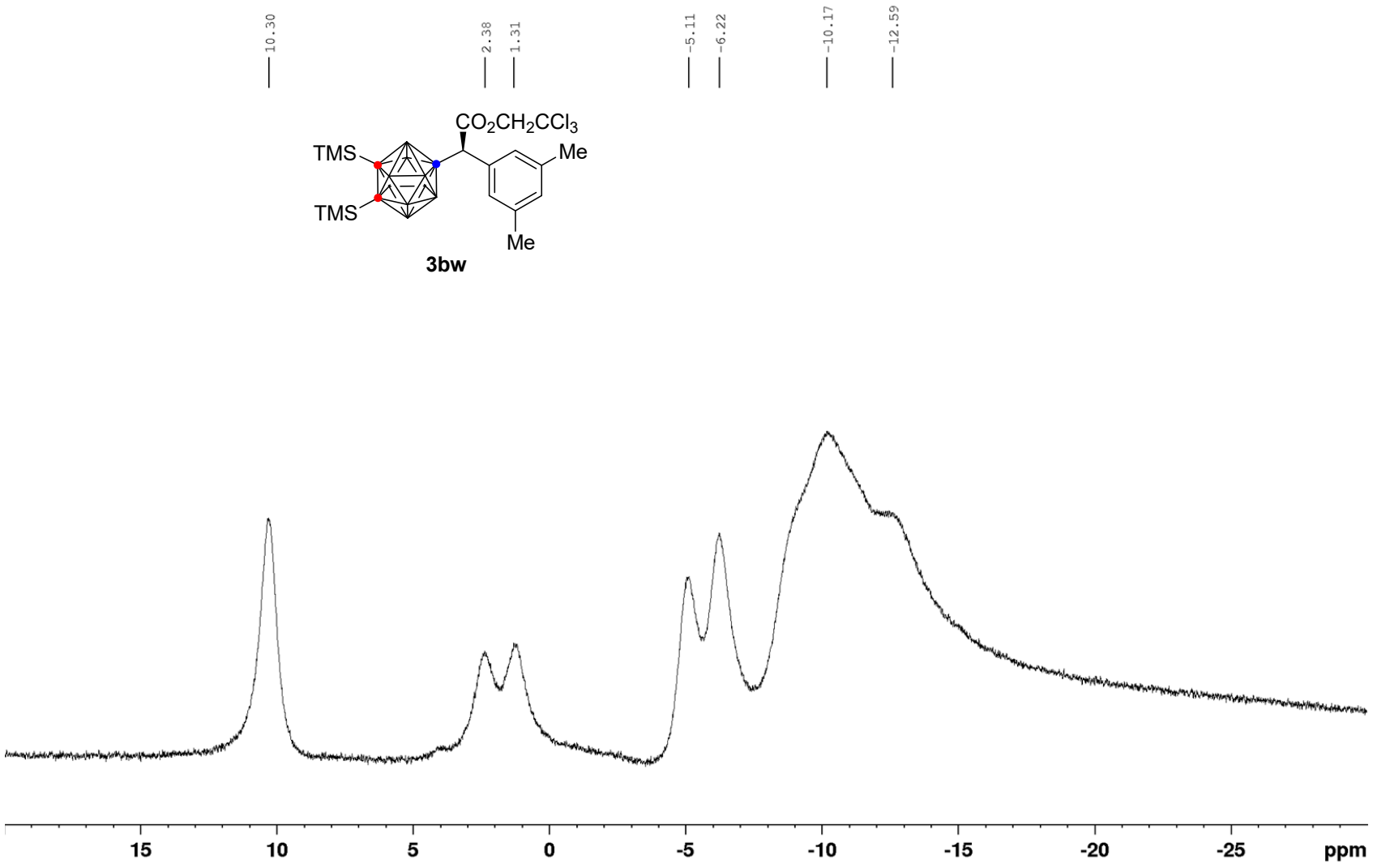
^{1}H NMR (400 MHz, $CDCl_3$)



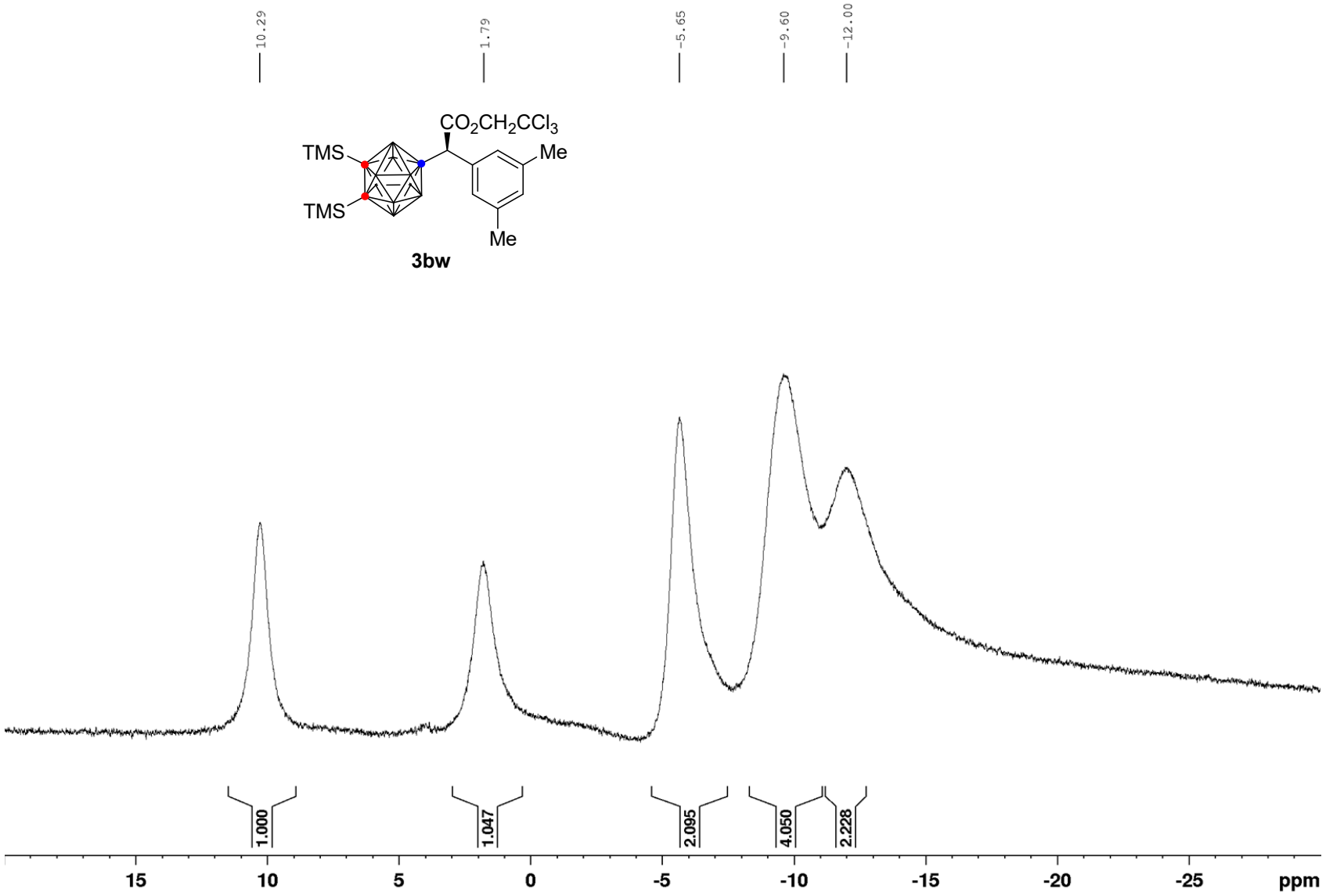
^{13}C NMR (100 MHz, $CDCl_3$)



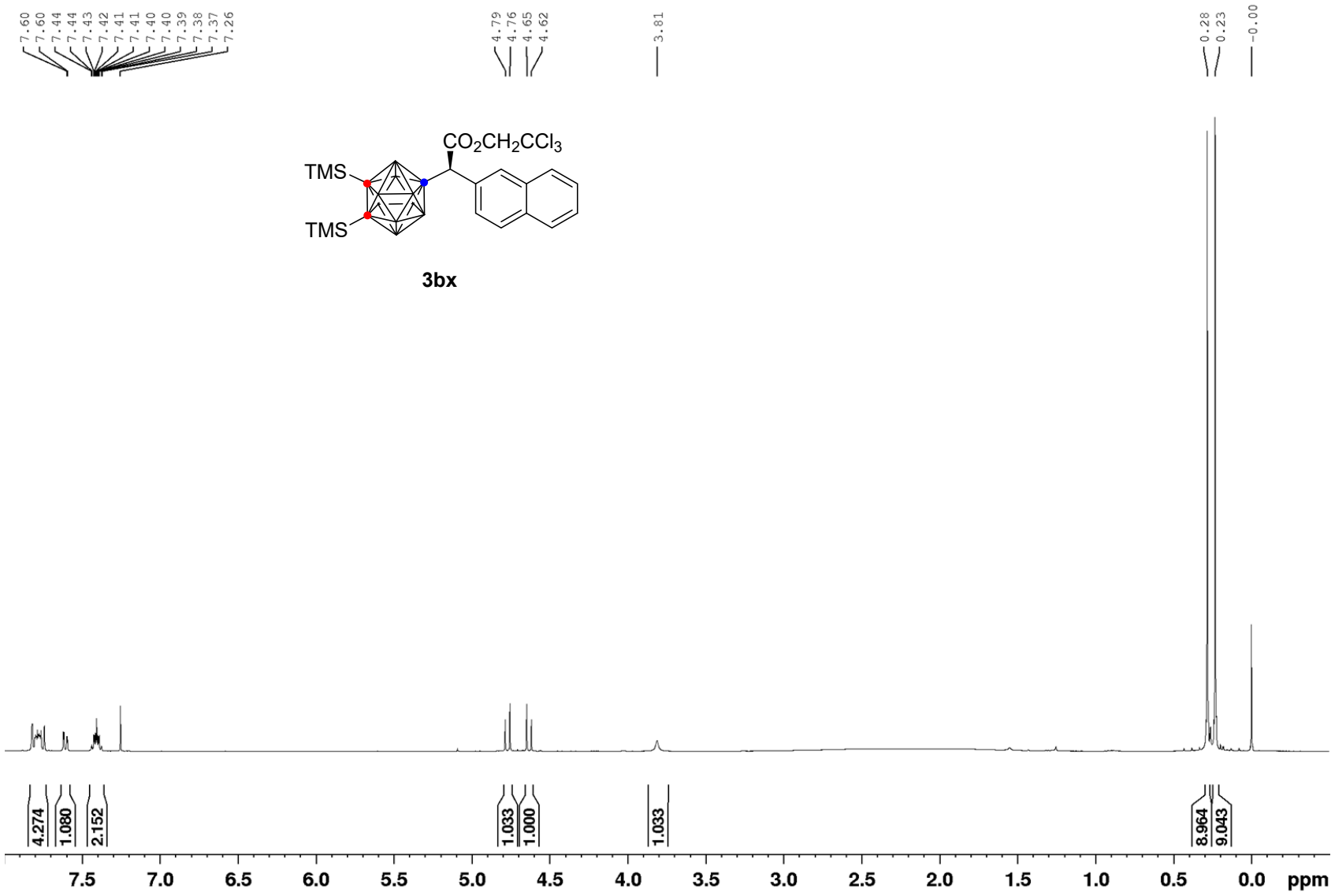
^{11}B NMR (128 MHz, $CDCl_3$)



$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

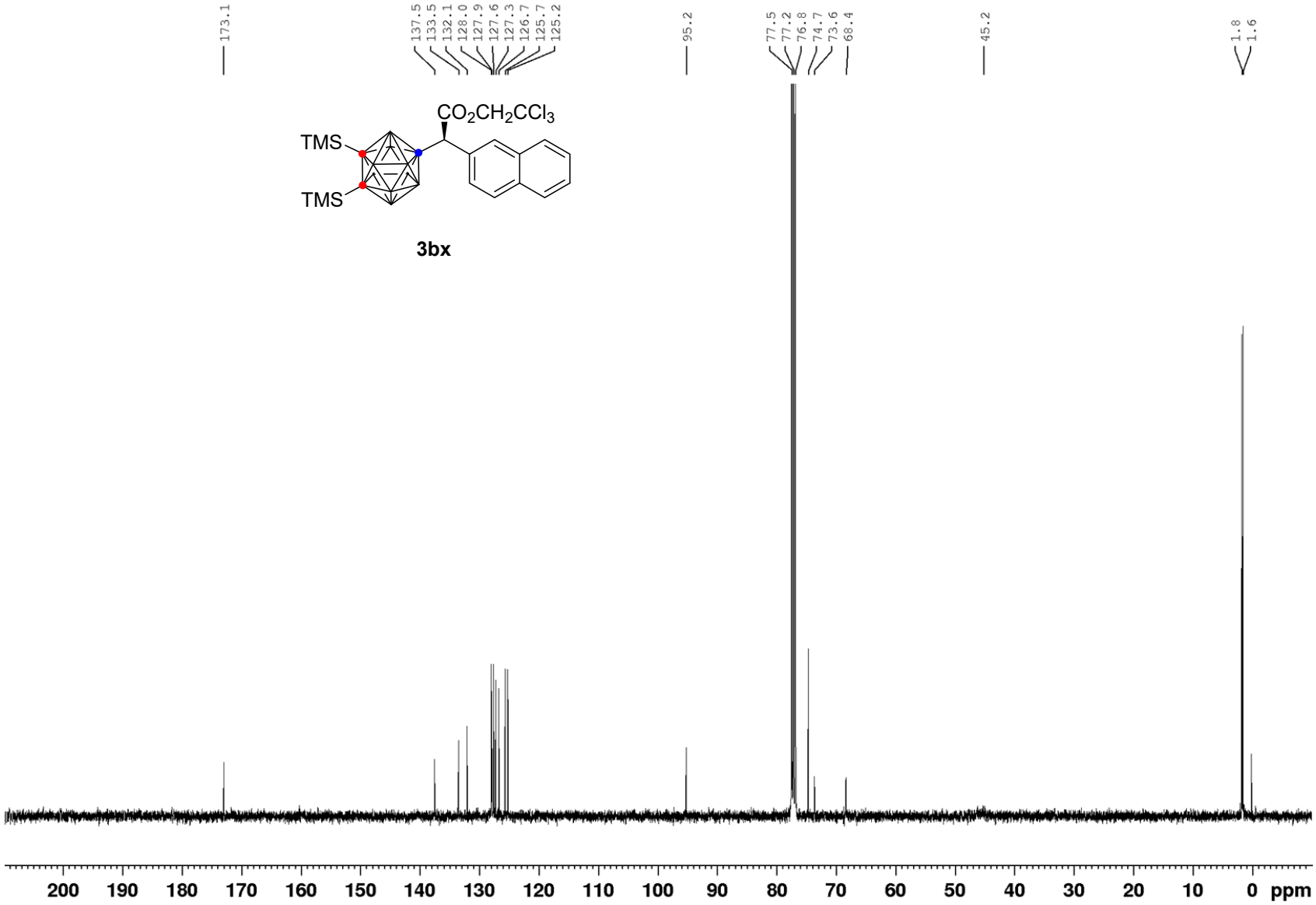


^{1}H NMR (400 MHz, $CDCl_3$)

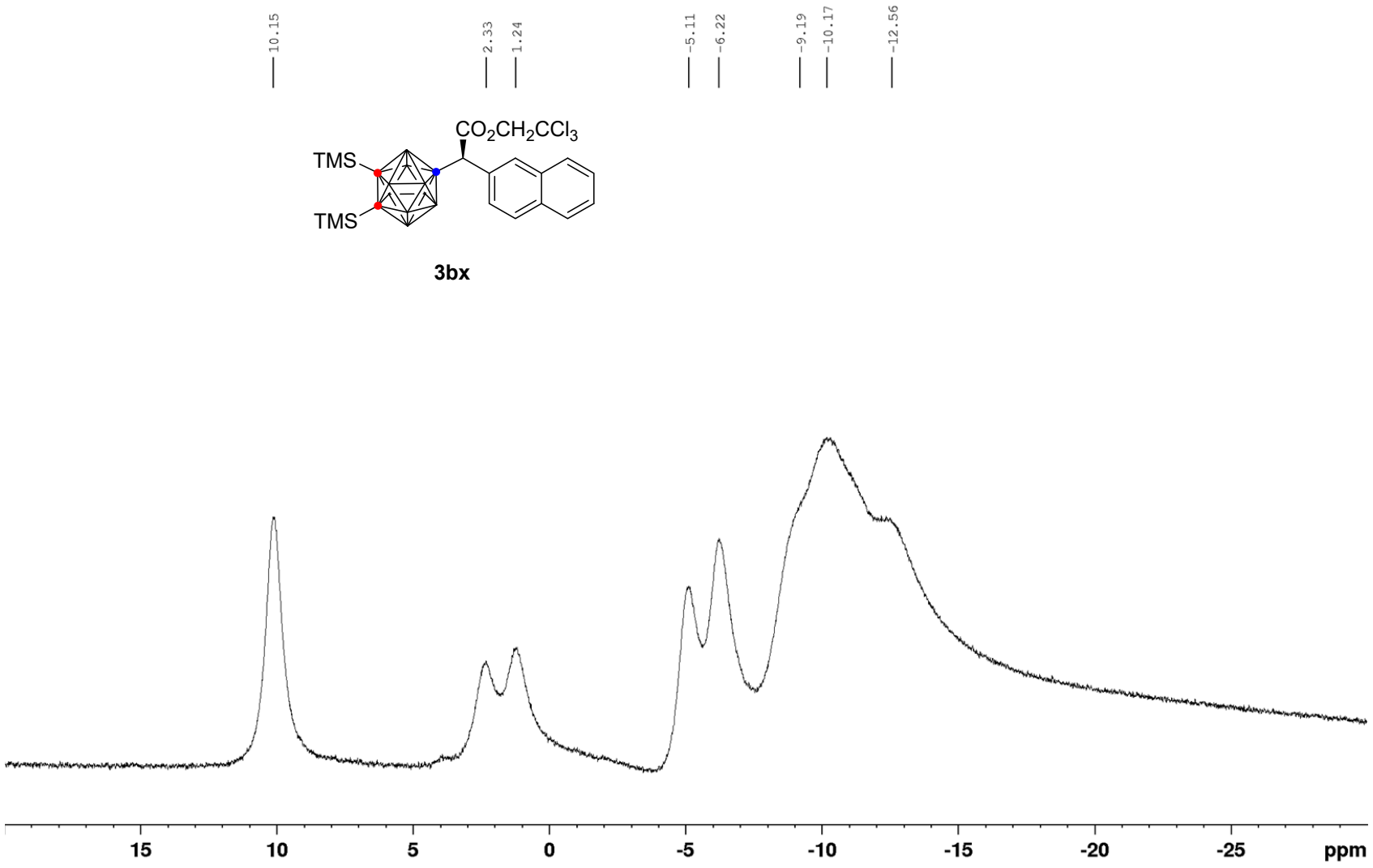


3bx

^{13}C NMR (100 MHz, $CDCl_3$)

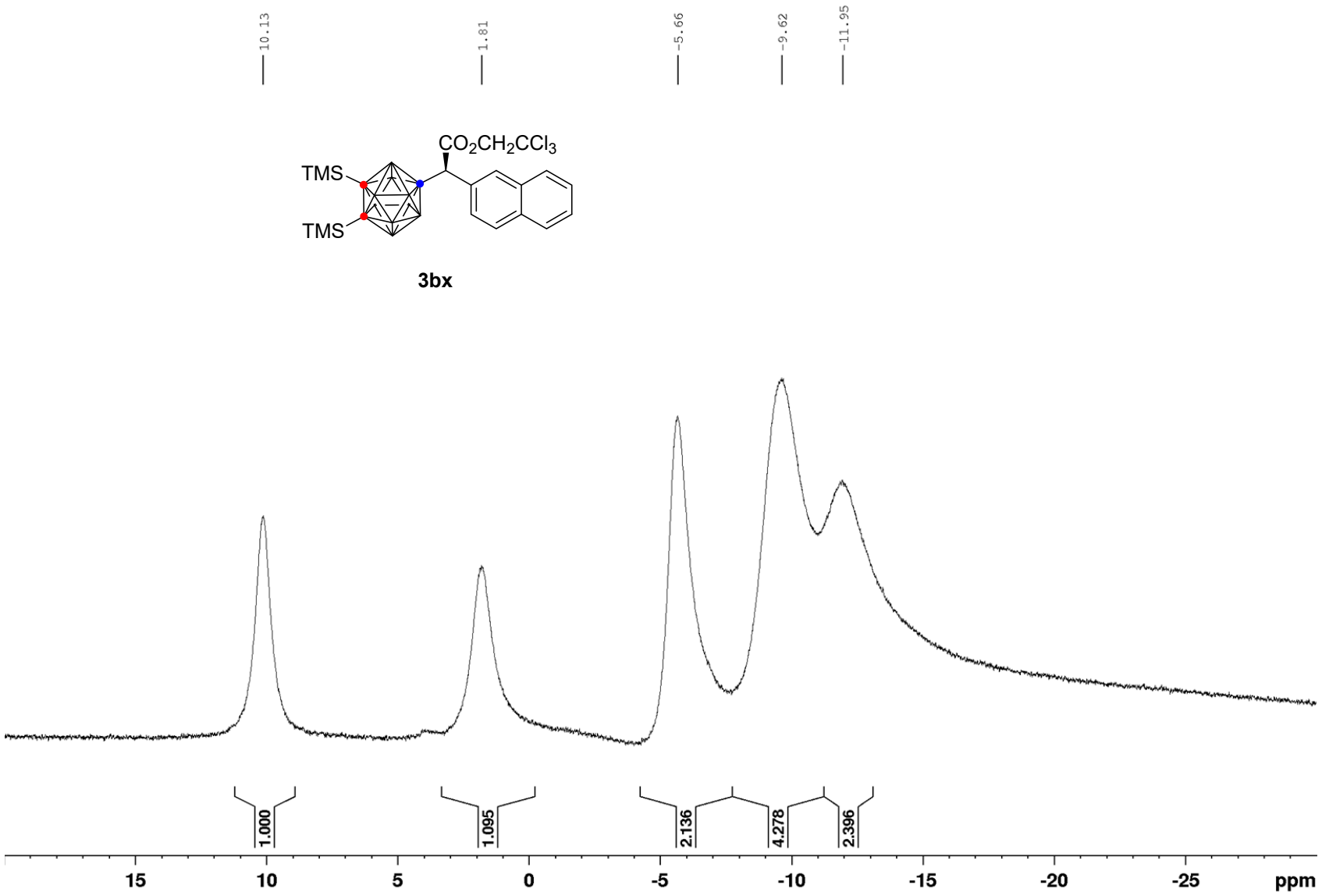


^{11}B NMR (128 MHz, $CDCl_3$)



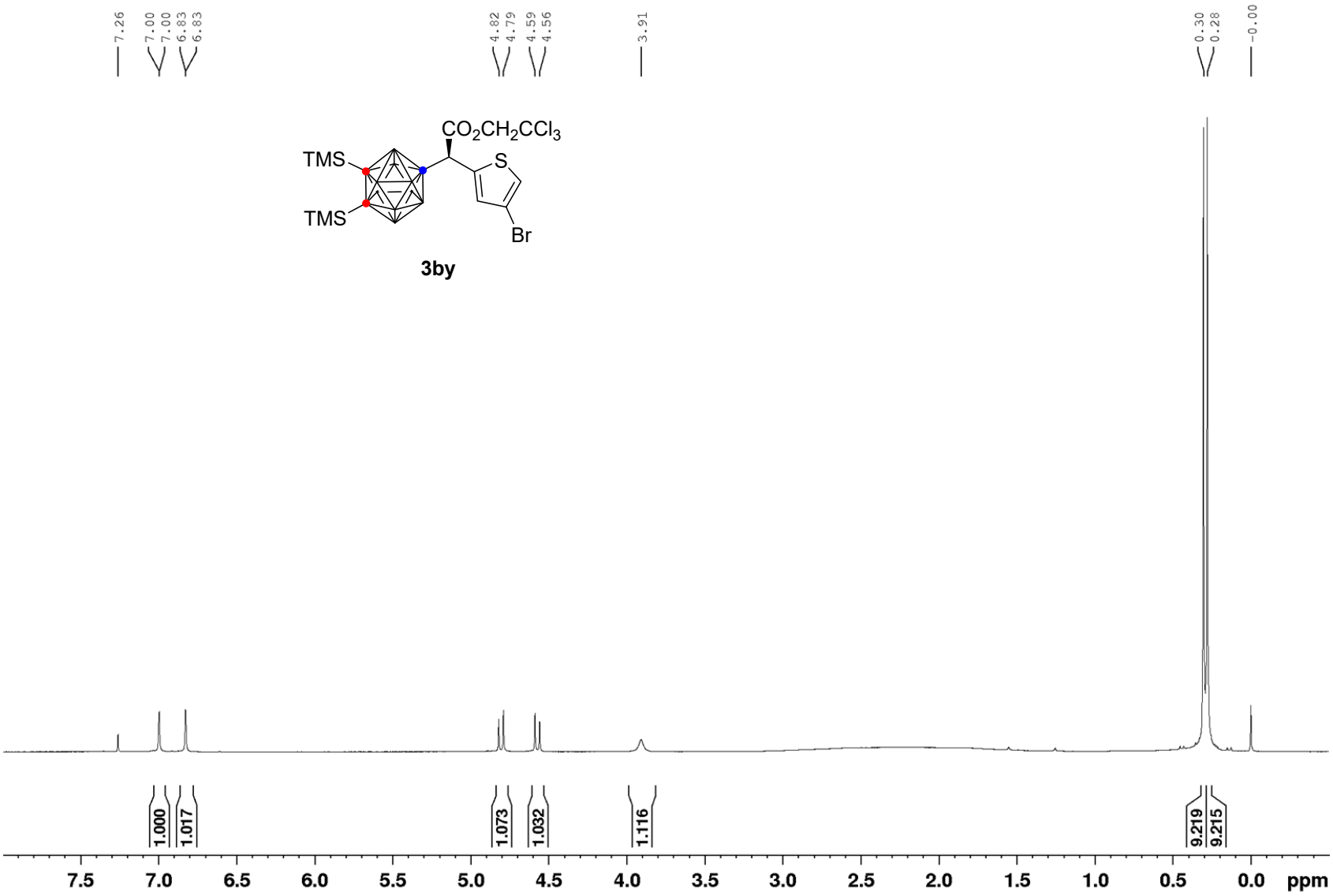
3bx

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

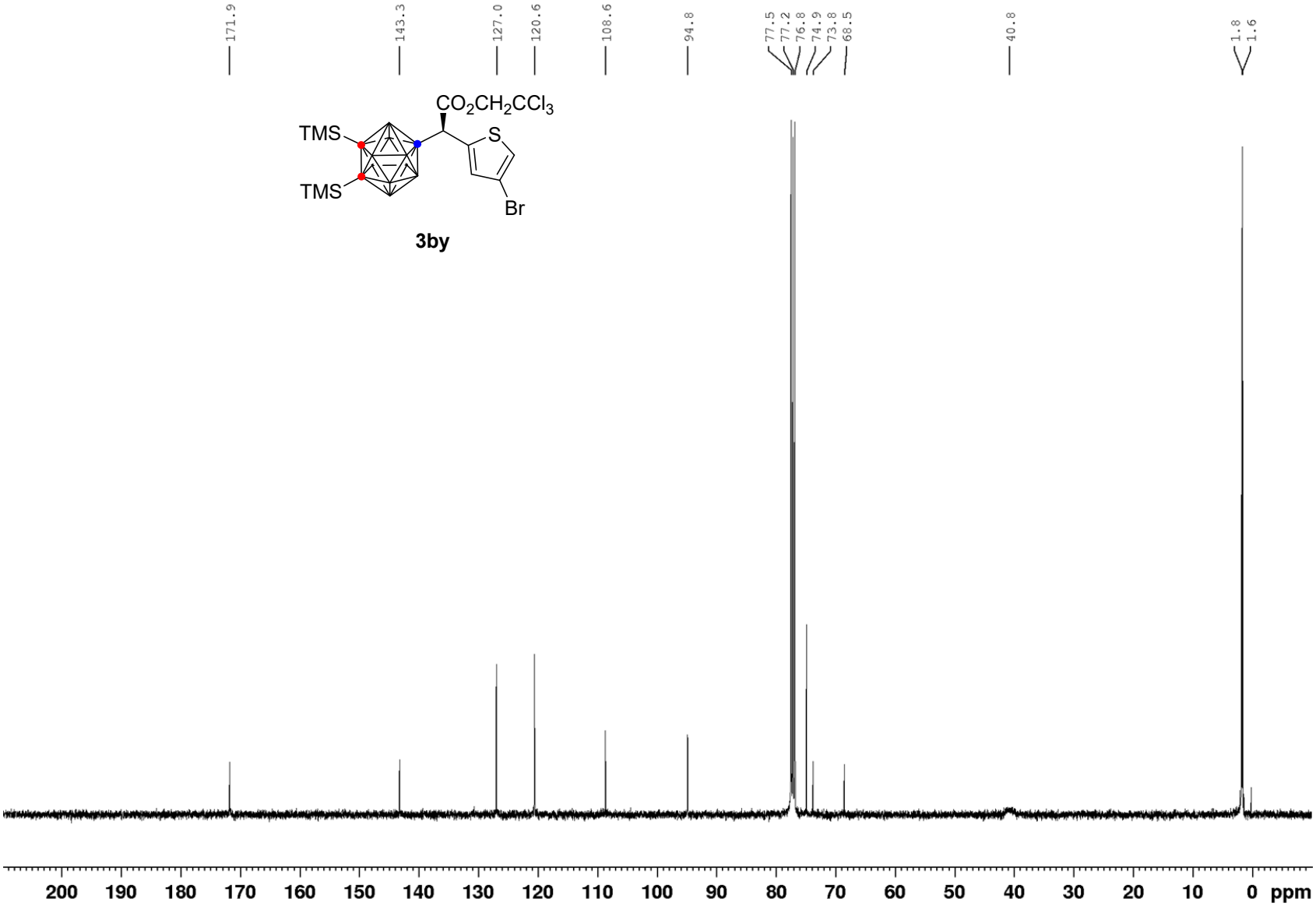


3bx

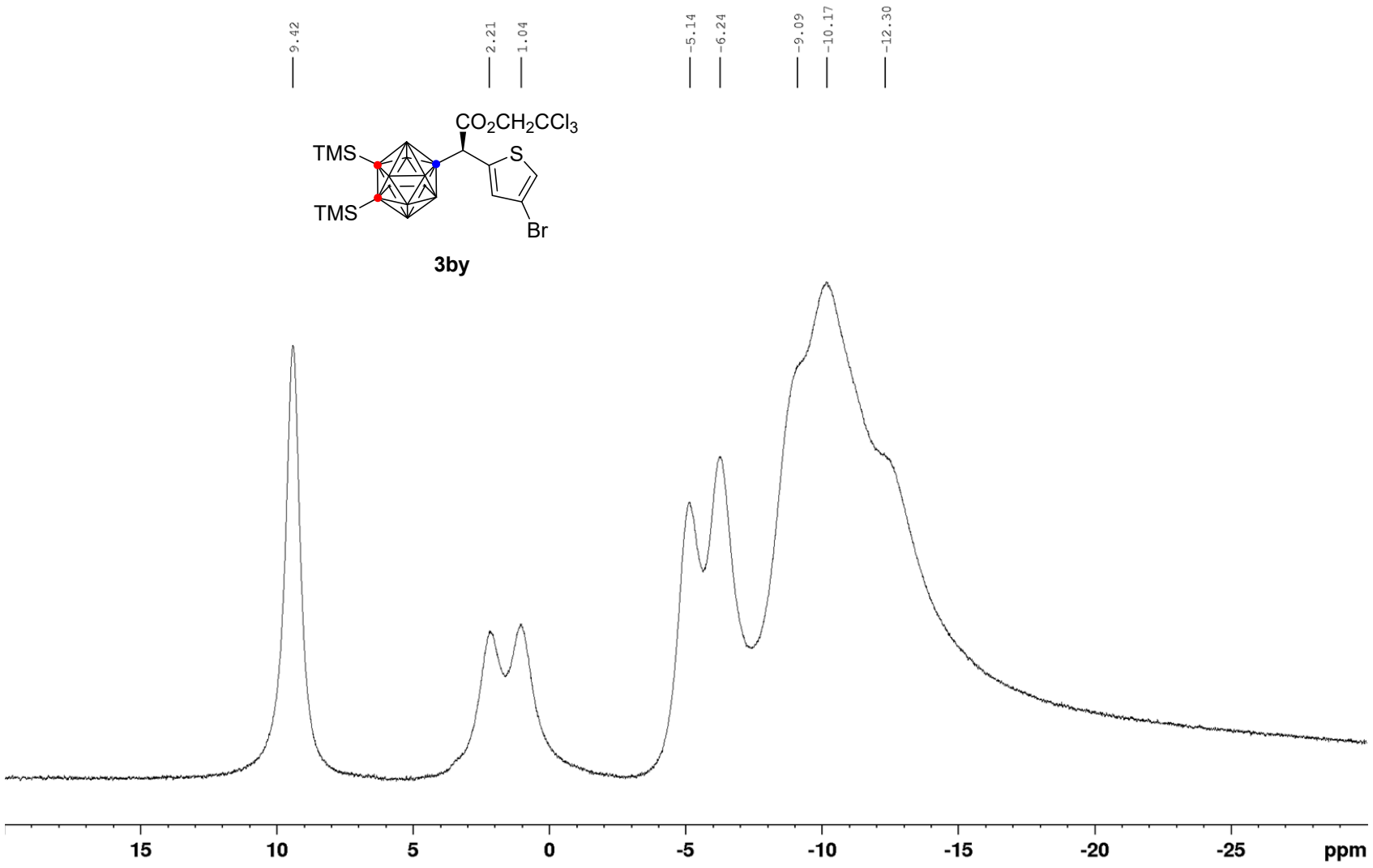
^{1}H NMR (400 MHz, $CDCl_3$)



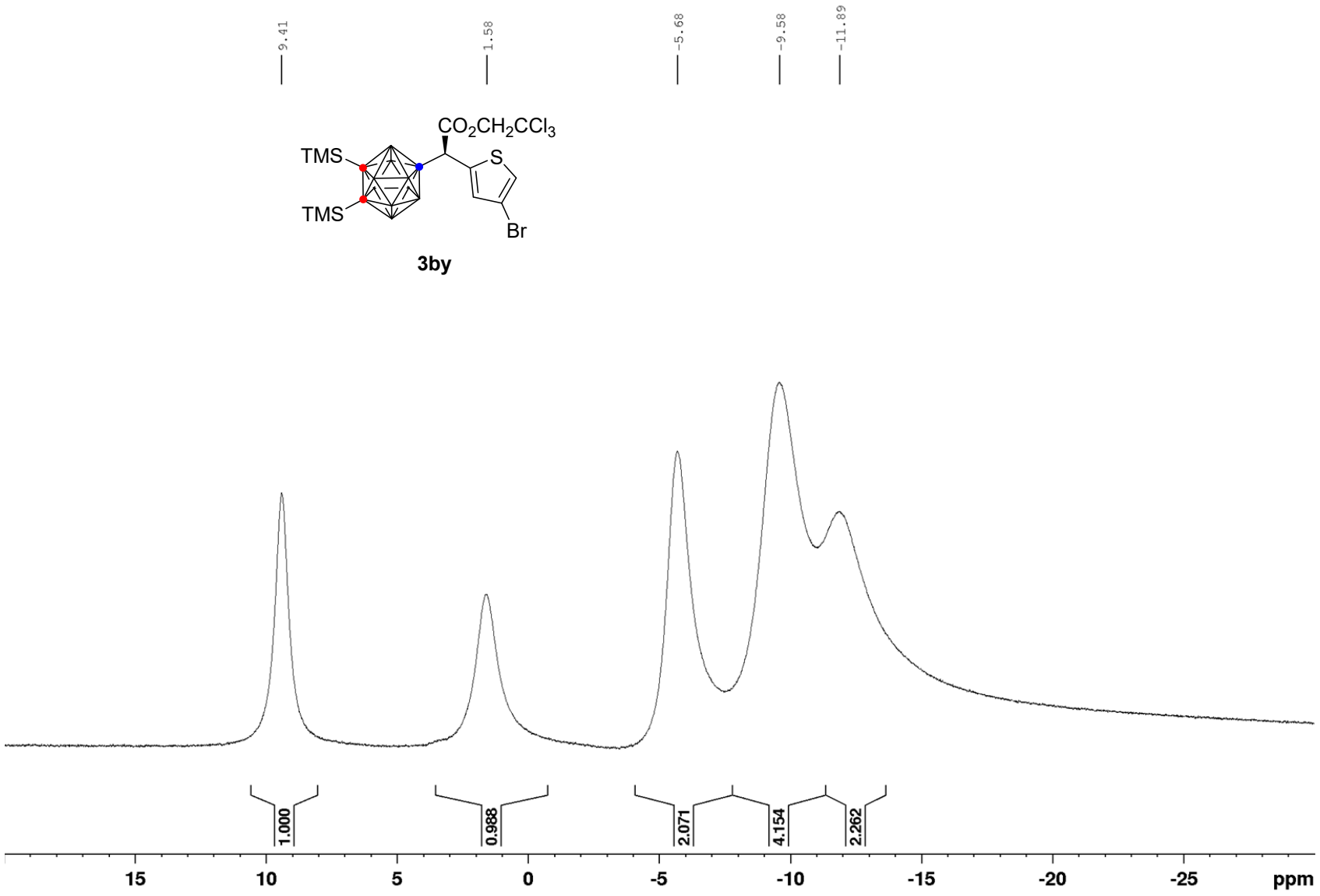
^{13}C NMR (100 MHz, $CDCl_3$)



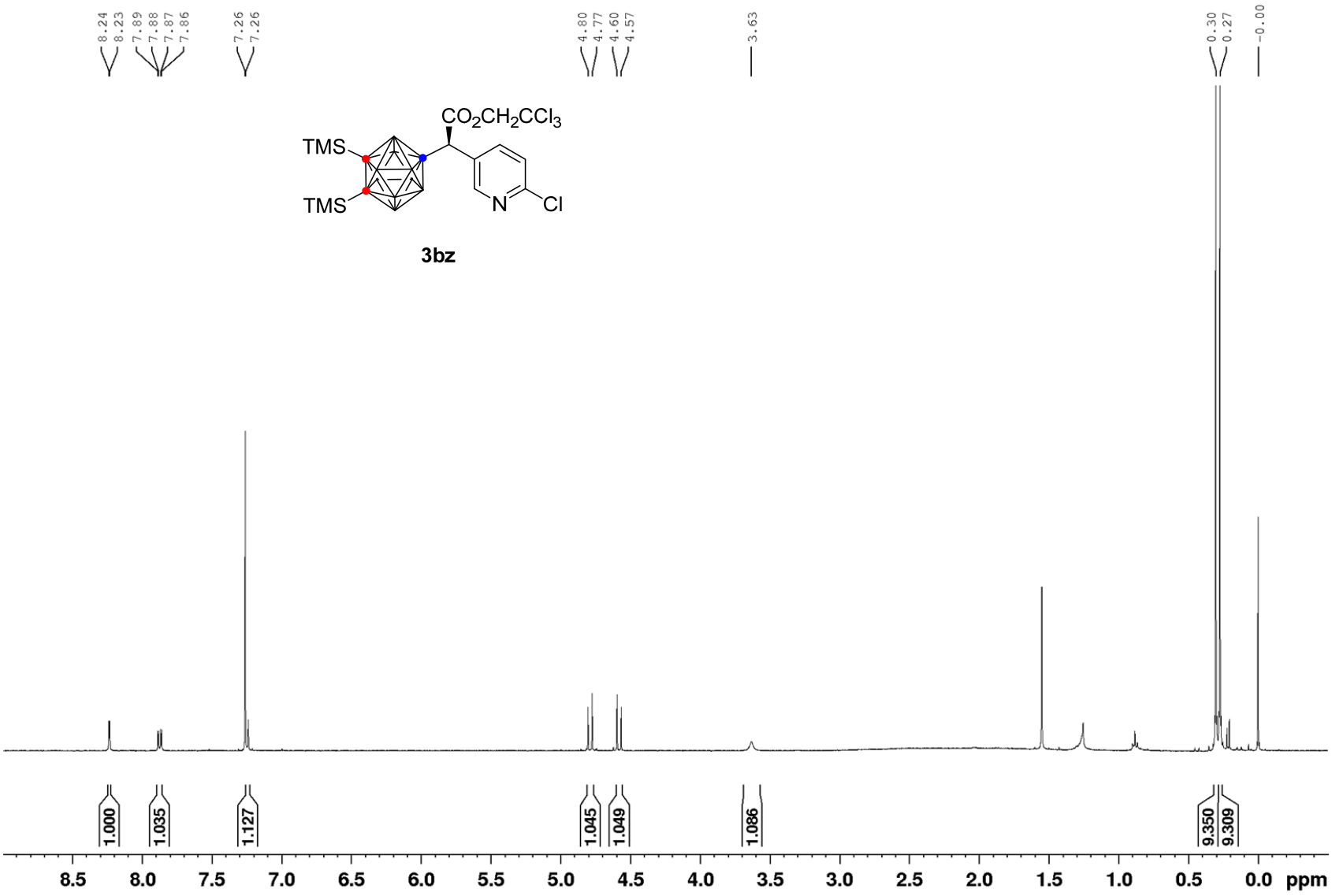
^{11}B NMR (128 MHz, $CDCl_3$)



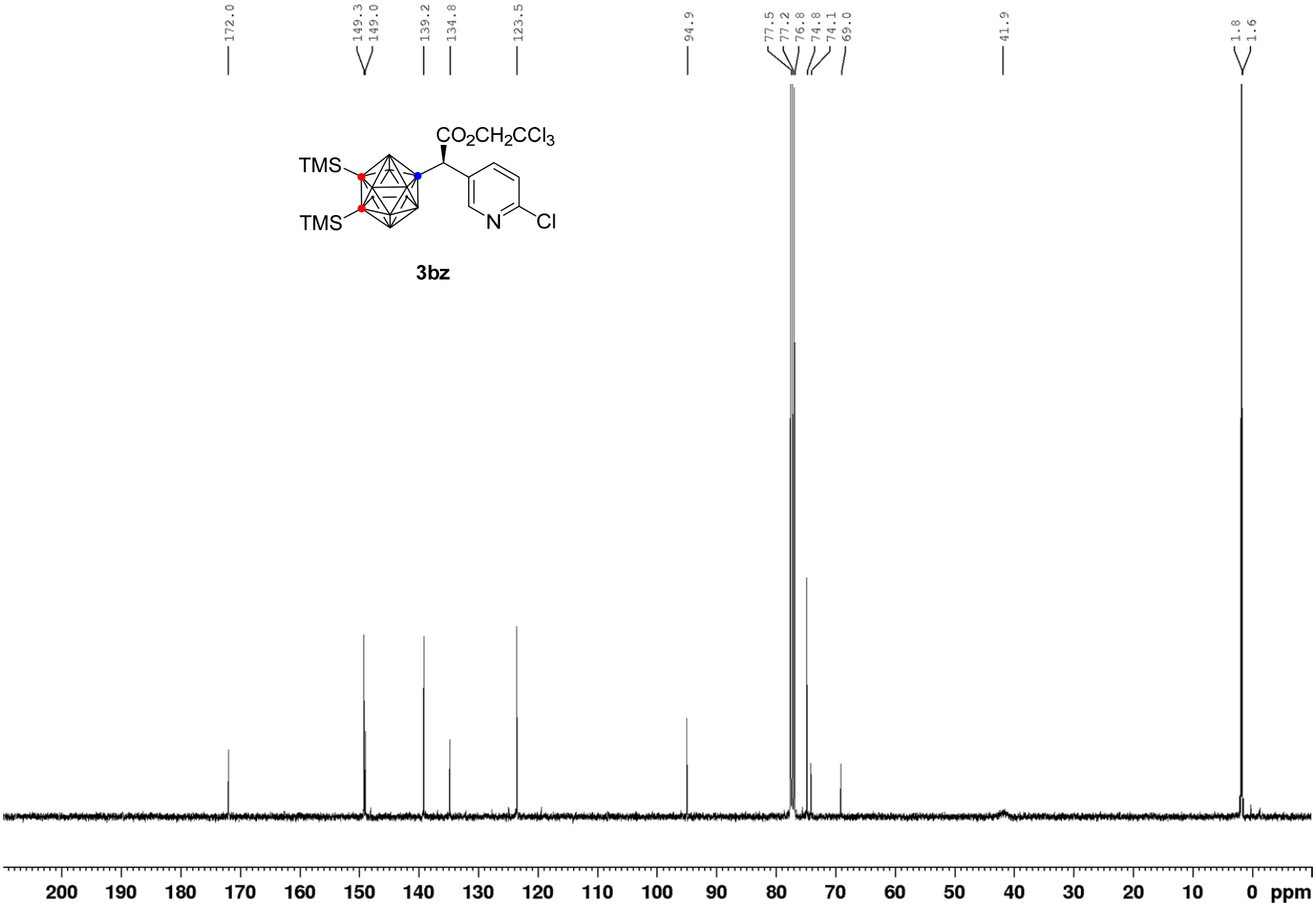
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



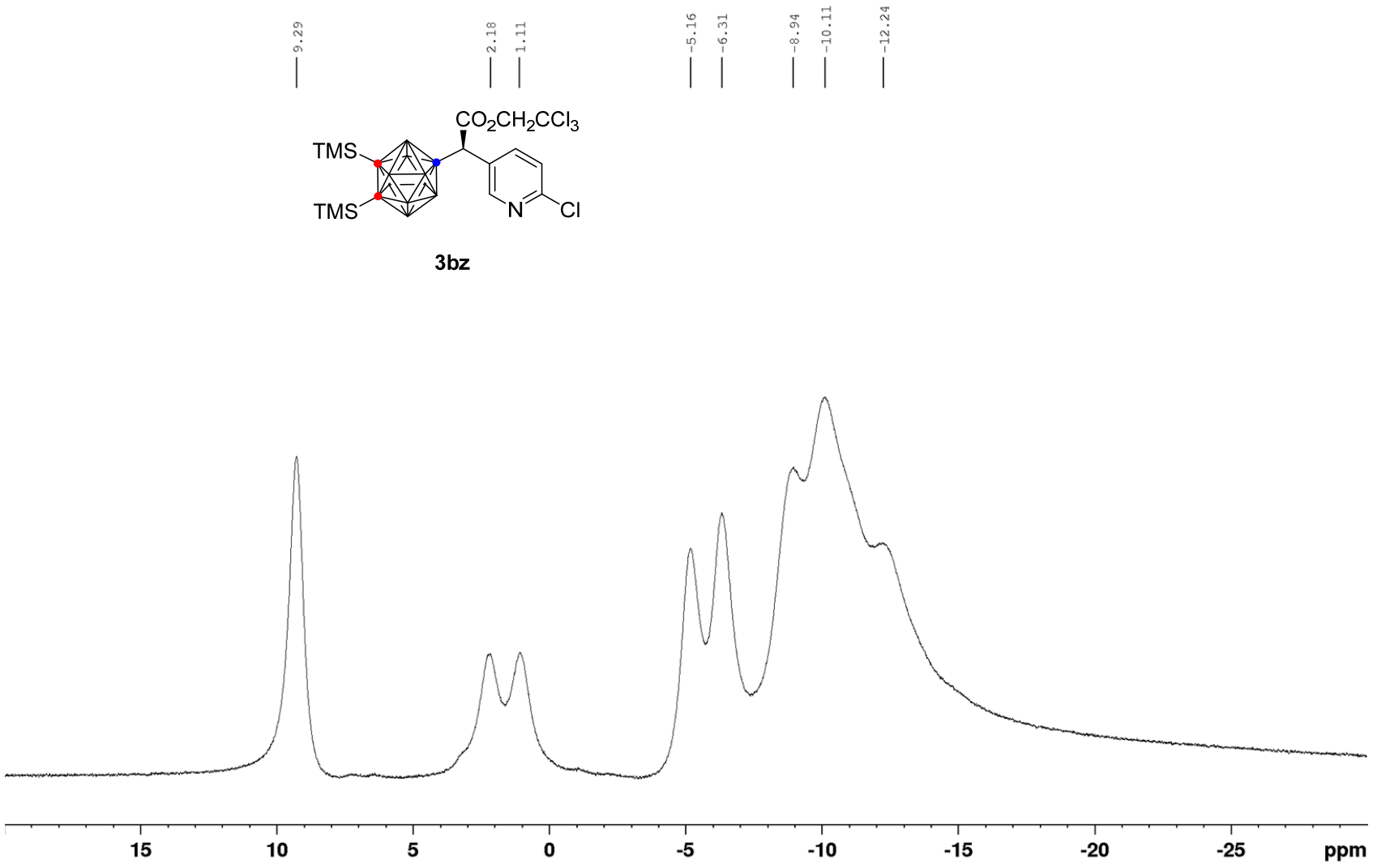
^{1}H NMR (400 MHz, $CDCl_3$)



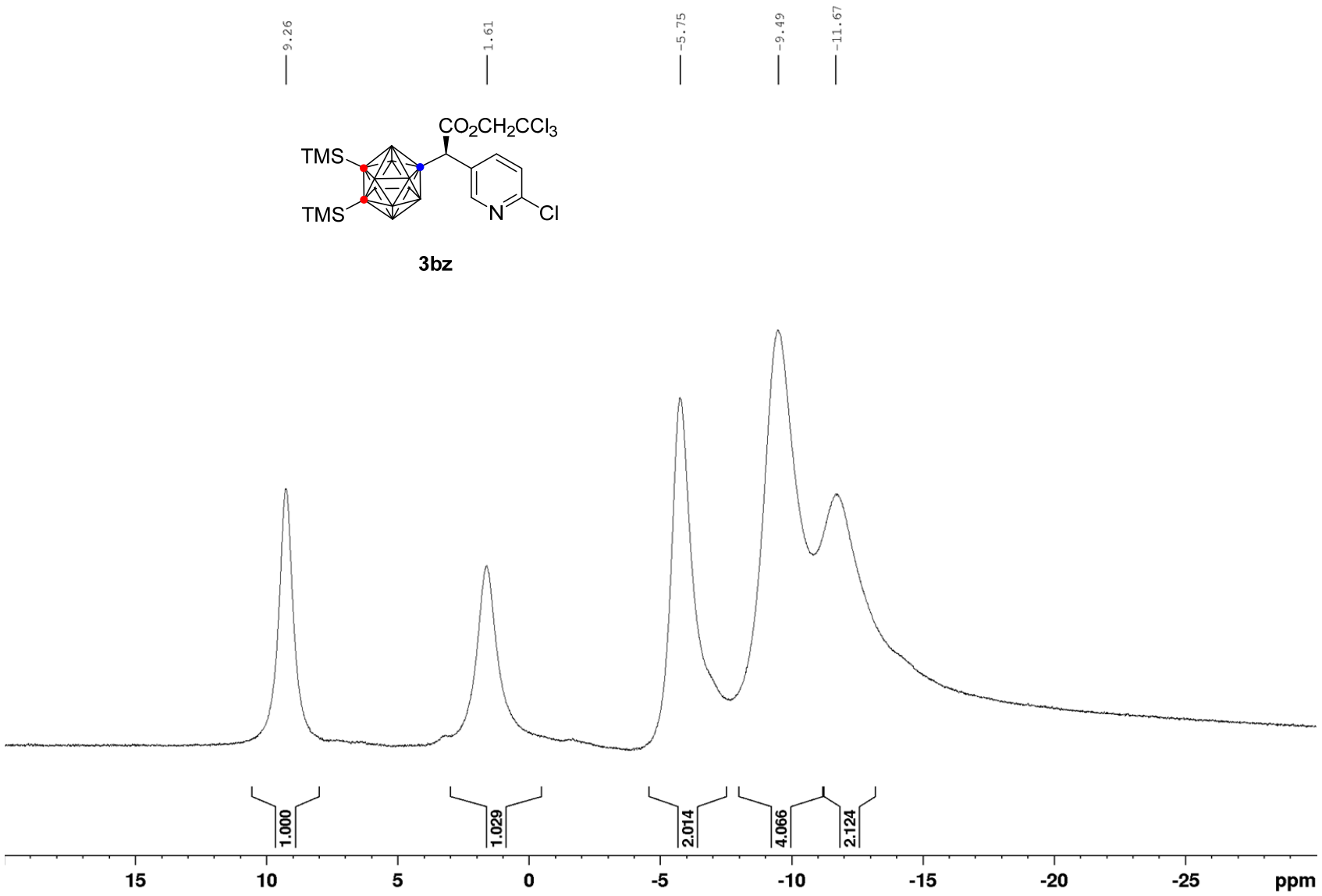
^{13}C NMR (100 MHz, $CDCl_3$)



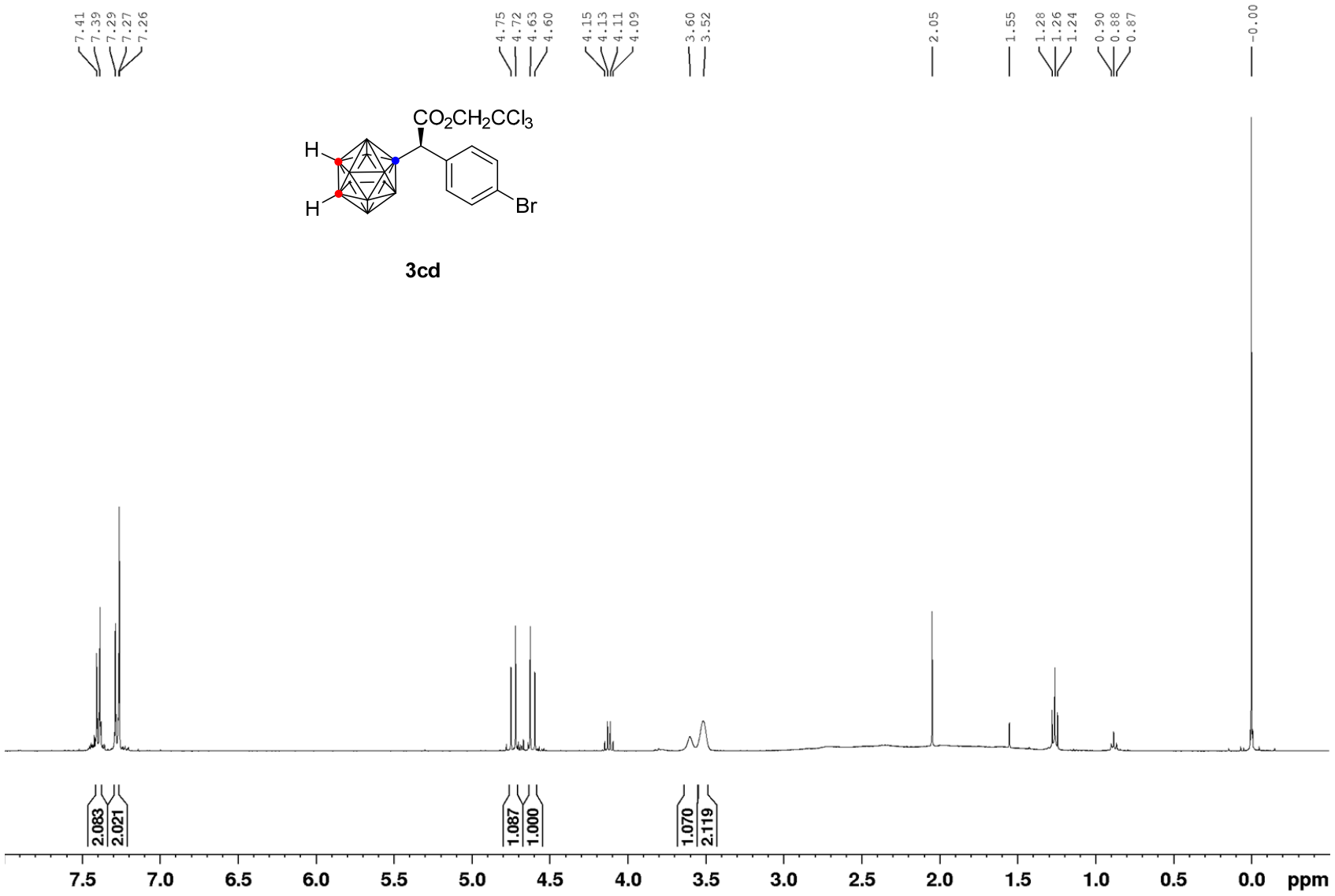
^{11}B NMR (128 MHz, $CDCl_3$)



$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

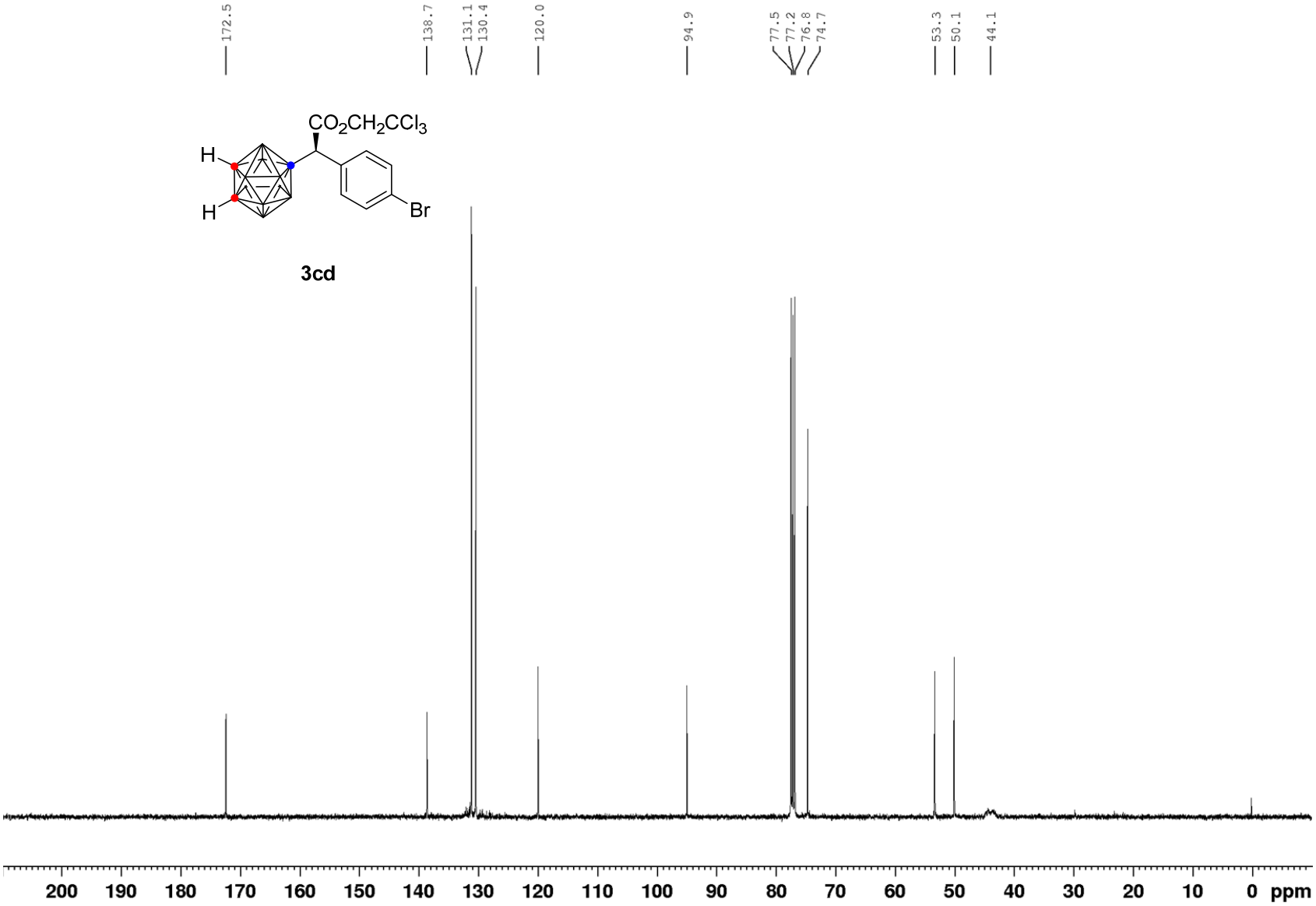


^{1}H NMR (400 MHz, $CDCl_3$)

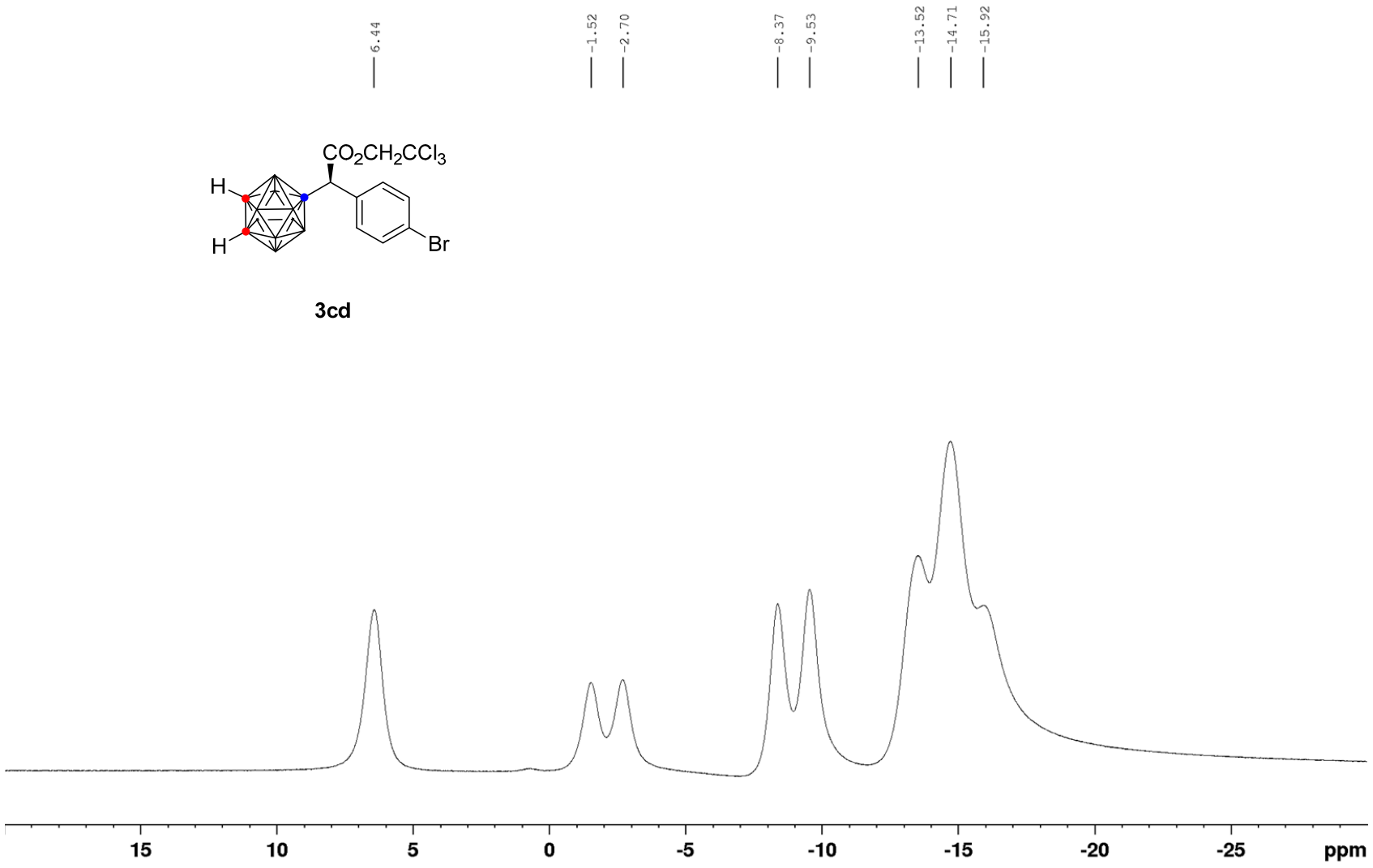


3cd

^{13}C NMR (100 MHz, $CDCl_3$)

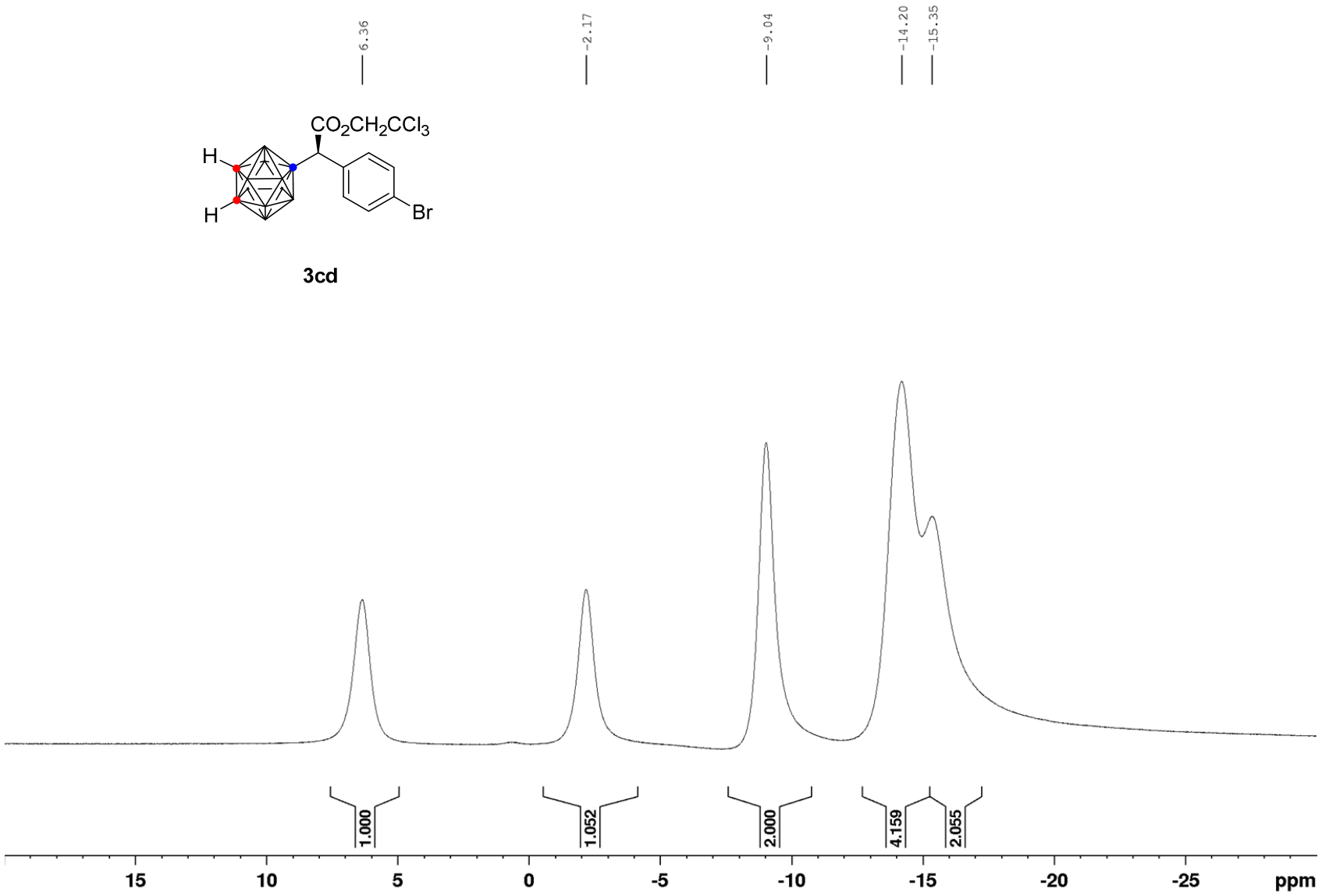


^{11}B NMR (128 MHz, $CDCl_3$)



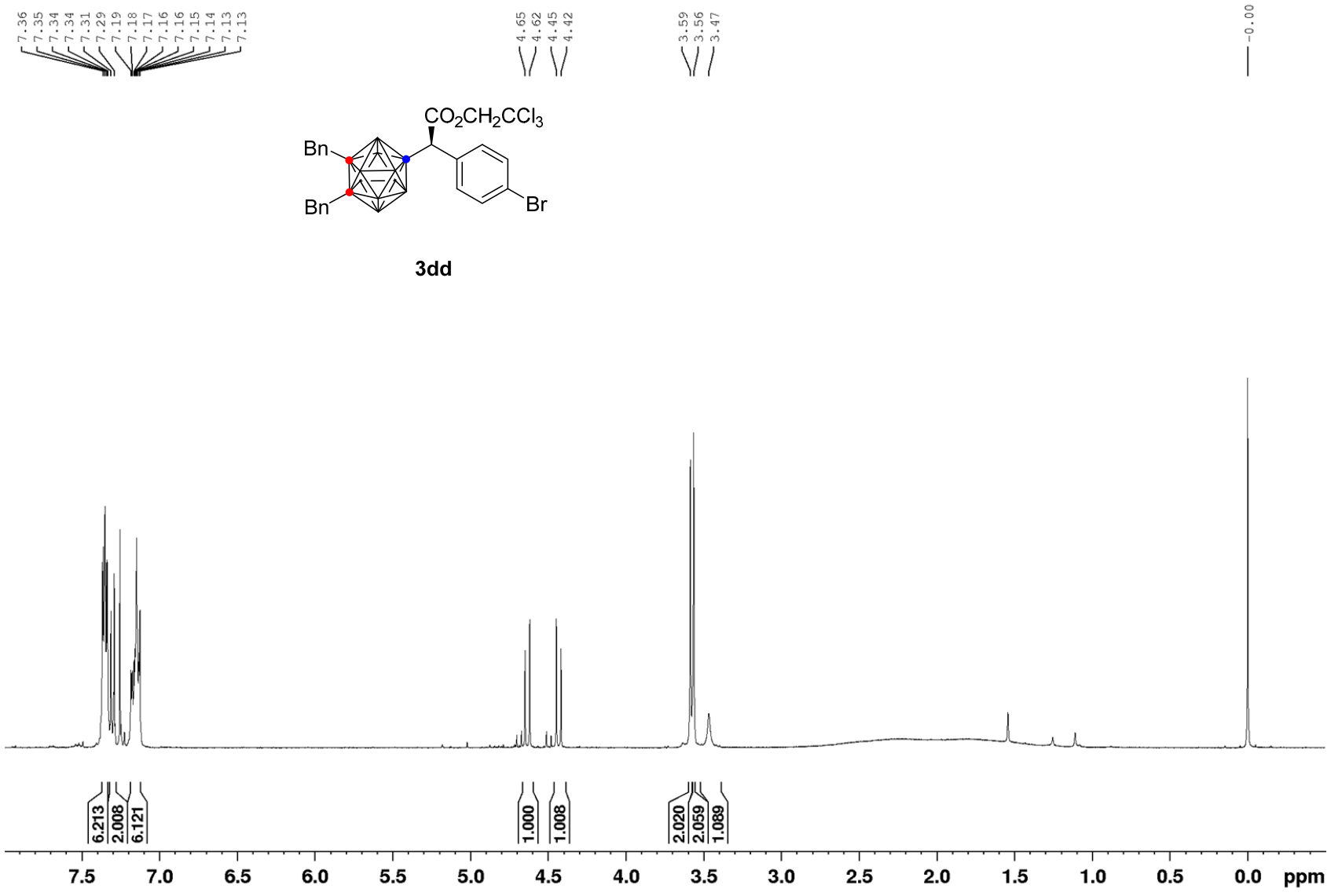
3cd

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



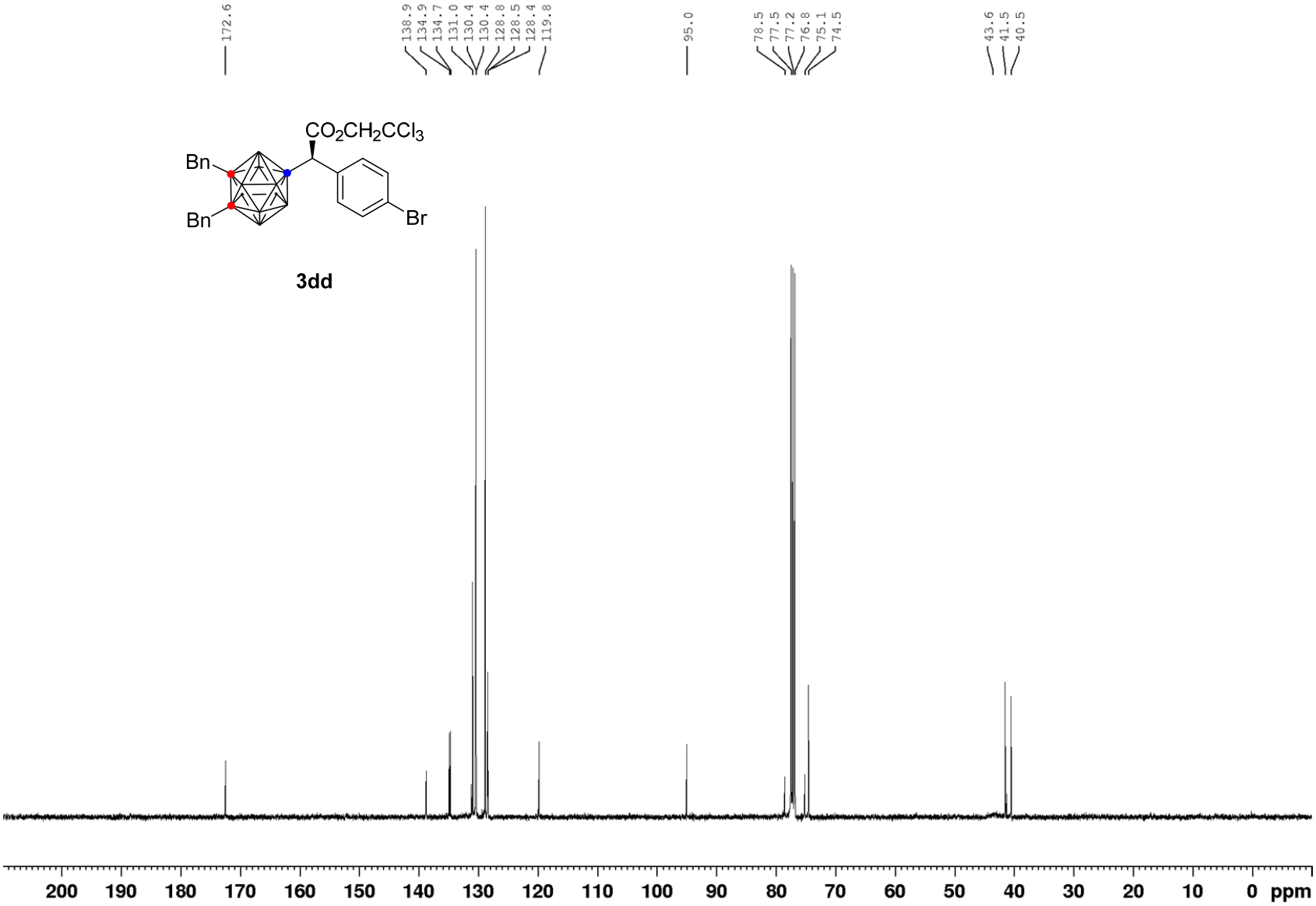
3cd

^{1}H NMR (400 MHz, $CDCl_3$)

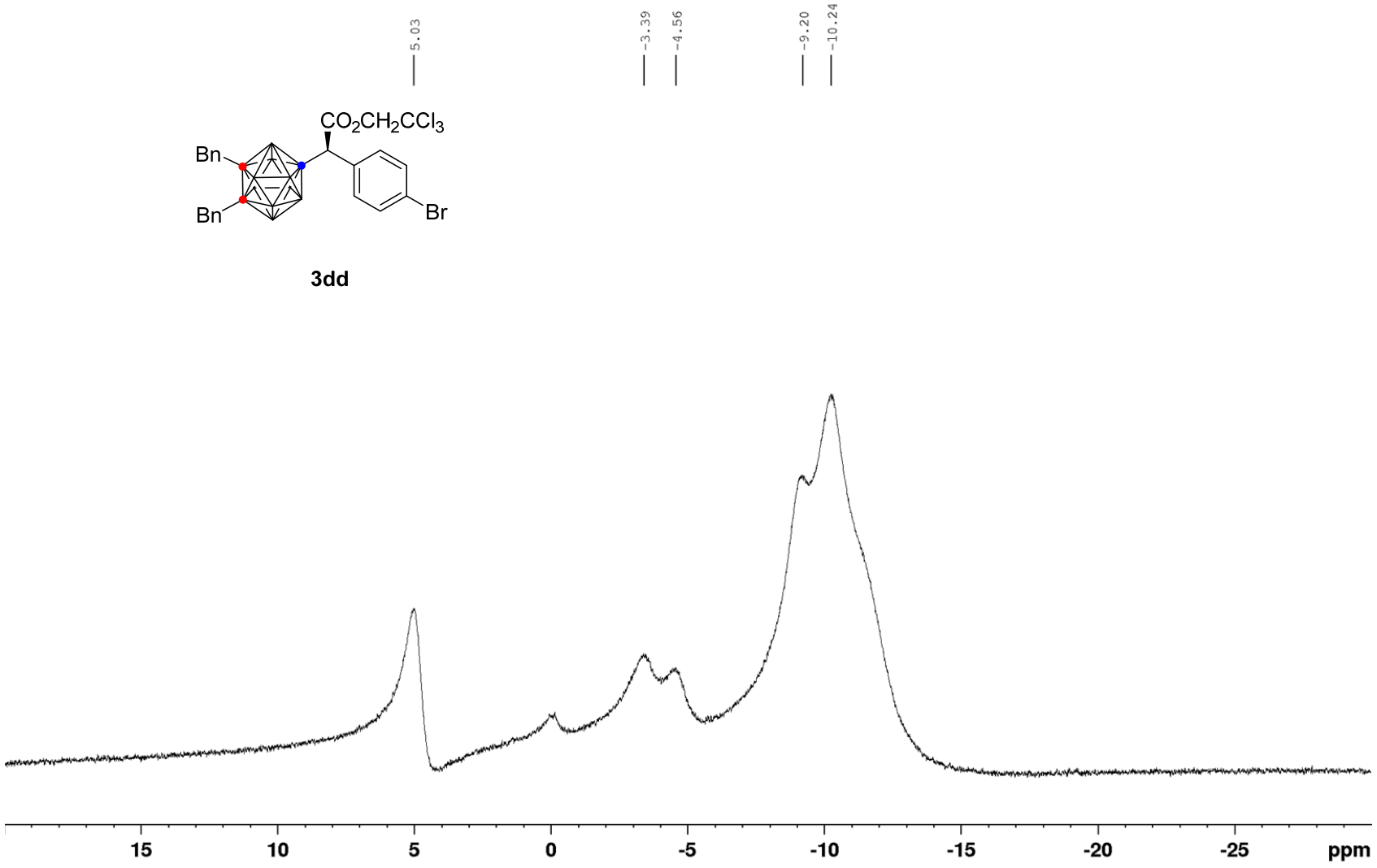


3dd

^{13}C NMR (100 MHz, $CDCl_3$)

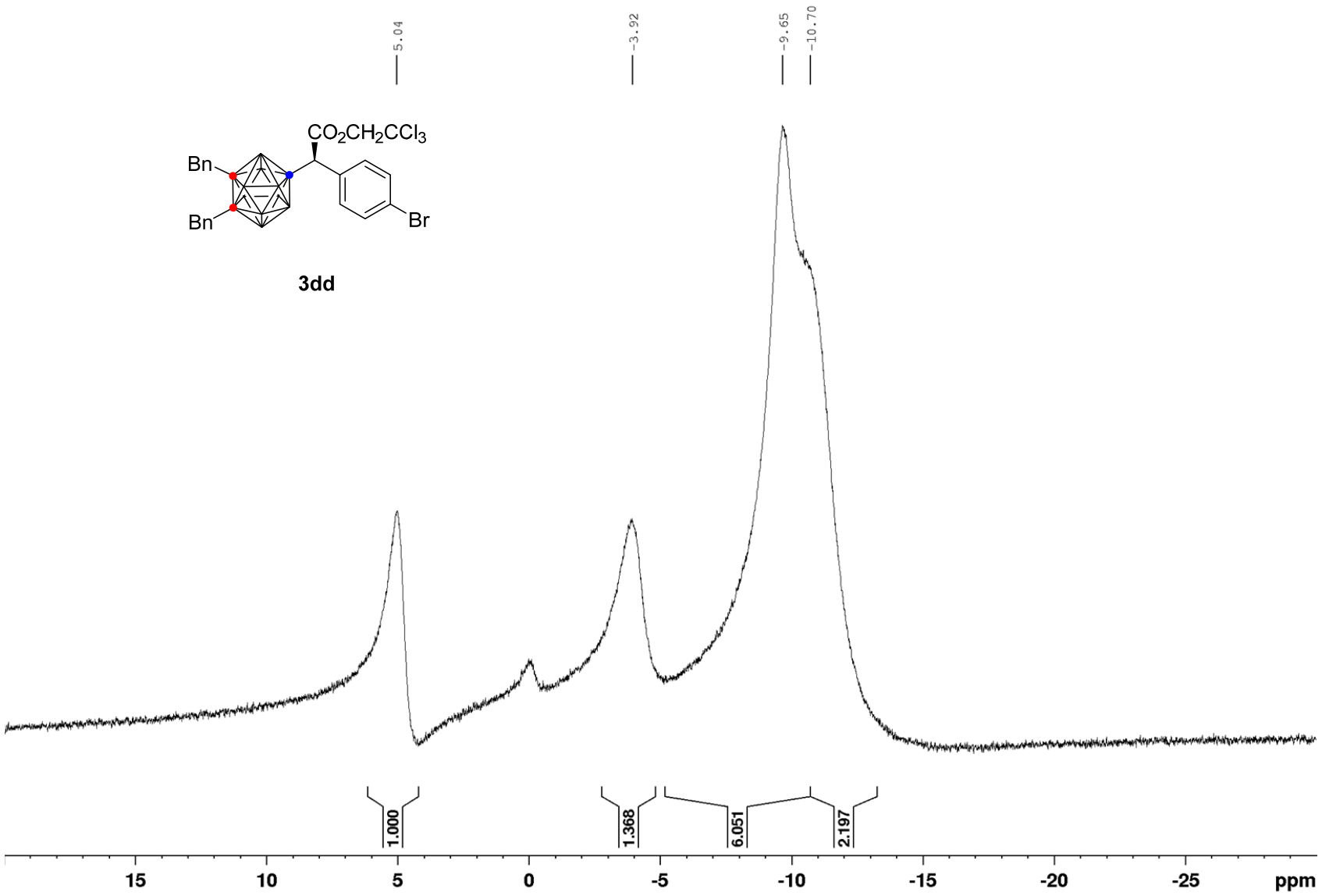


^{11}B NMR (128 MHz, $CDCl_3$)

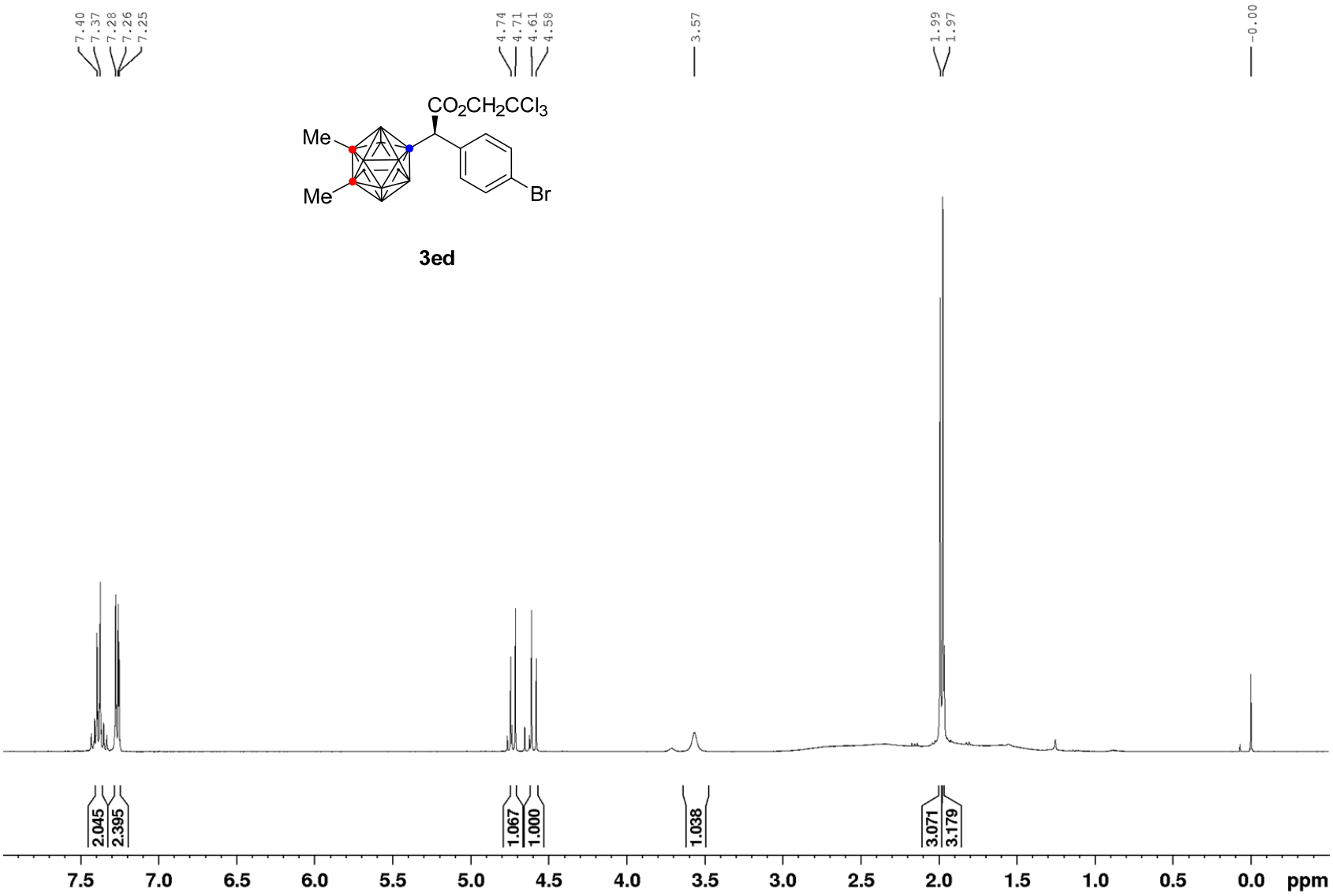


3dd

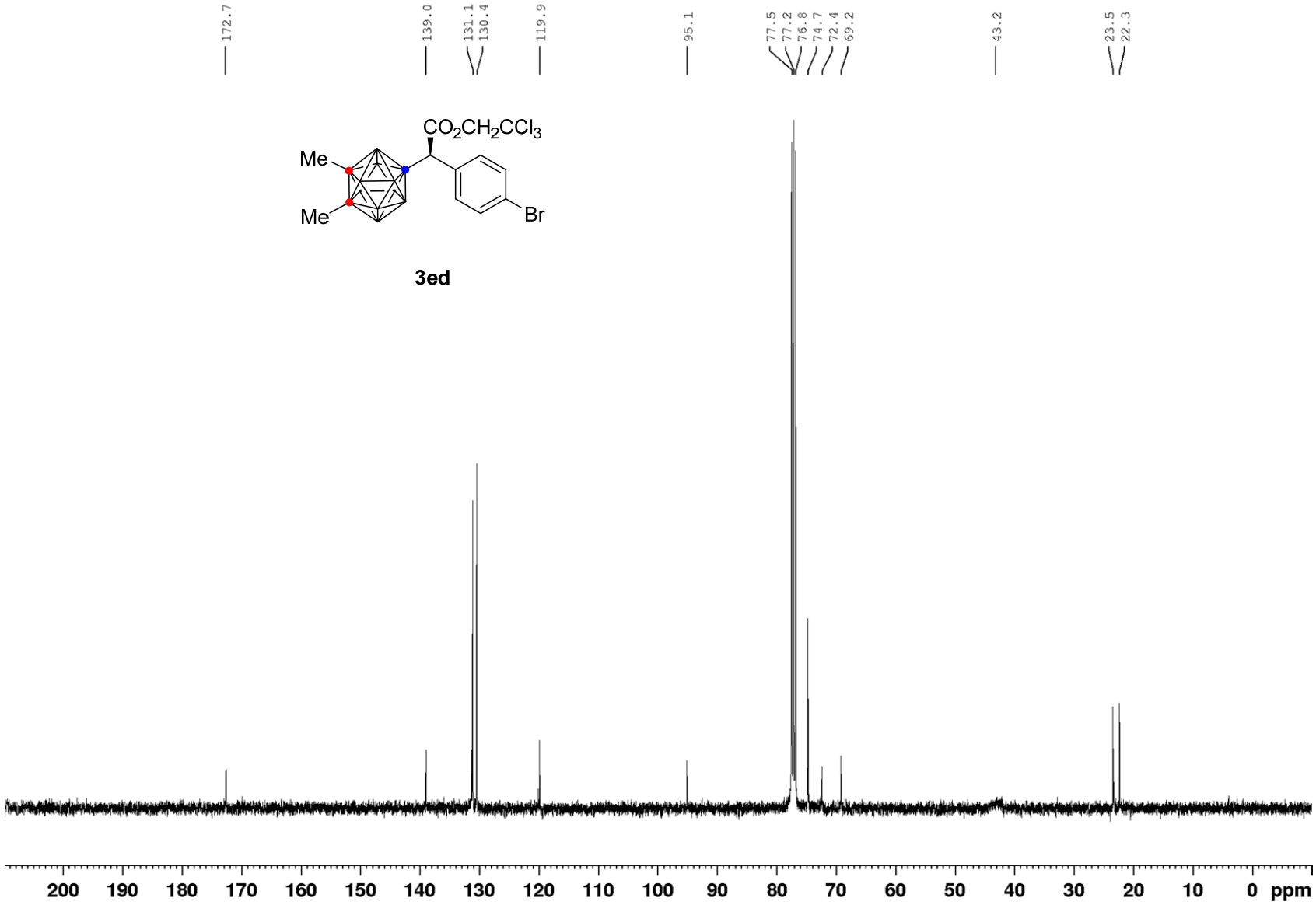
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



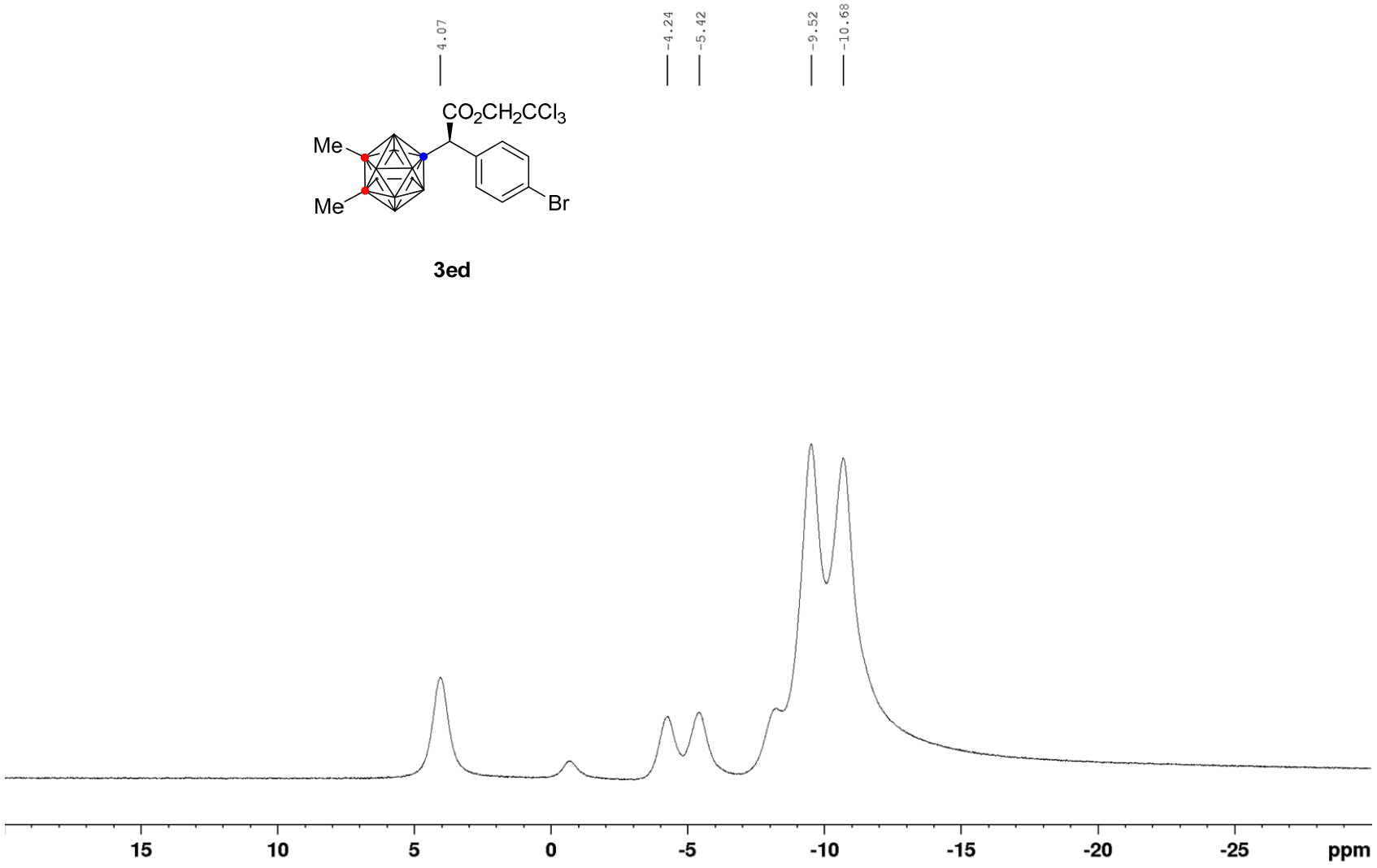
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

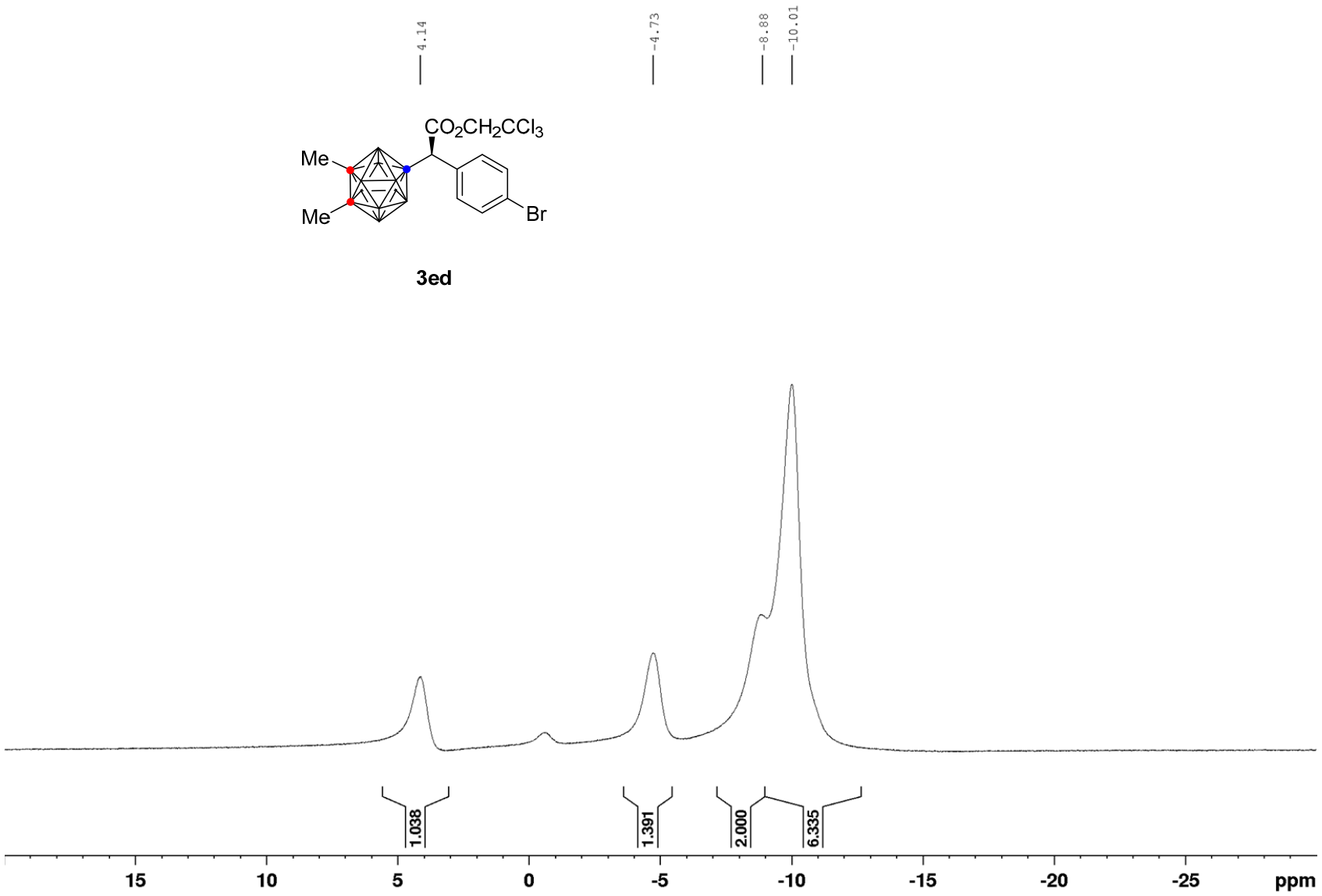


^{11}B NMR (128 MHz, $CDCl_3$)

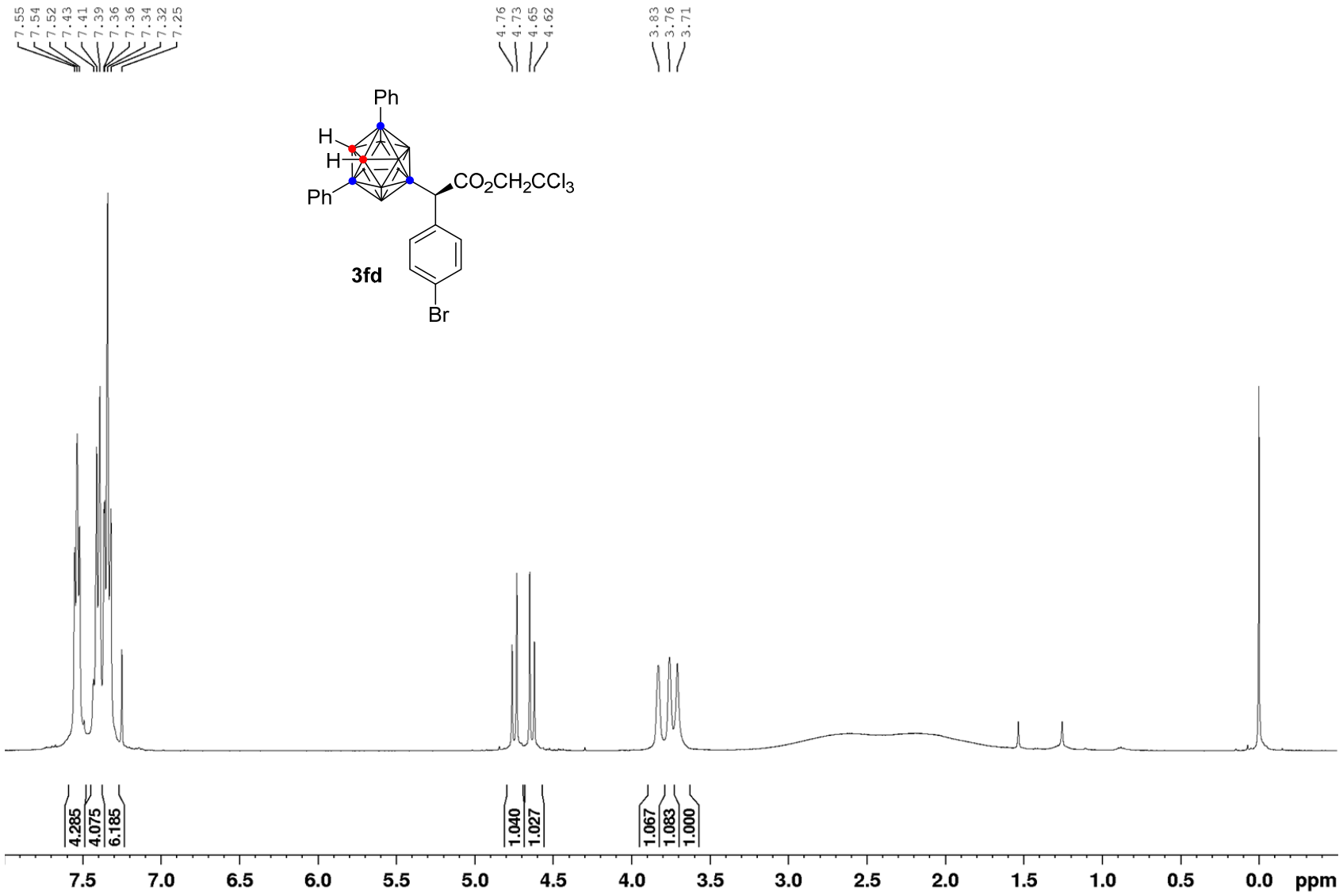


3ed

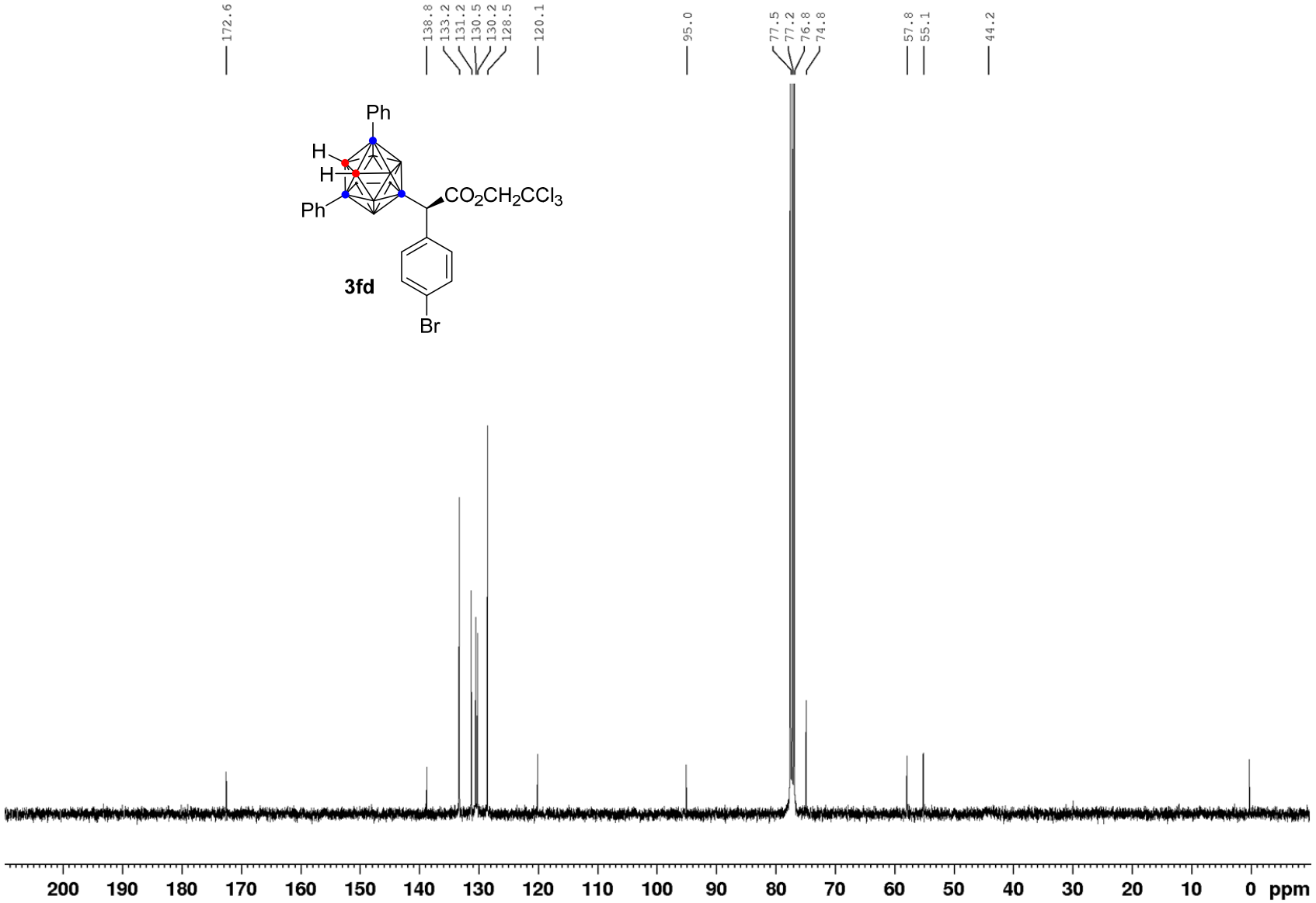
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



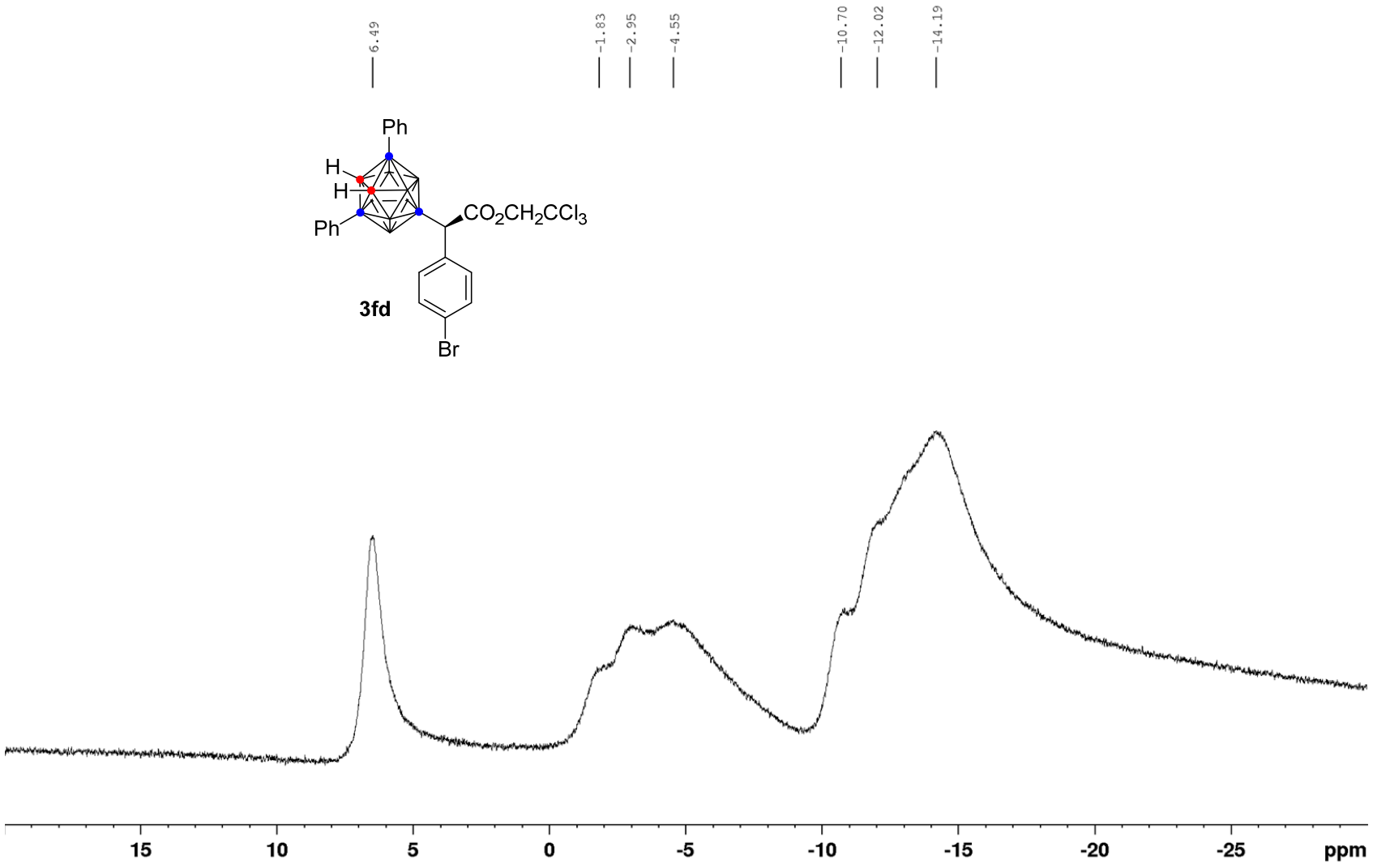
^{1}H NMR (400 MHz, $CDCl_3$)



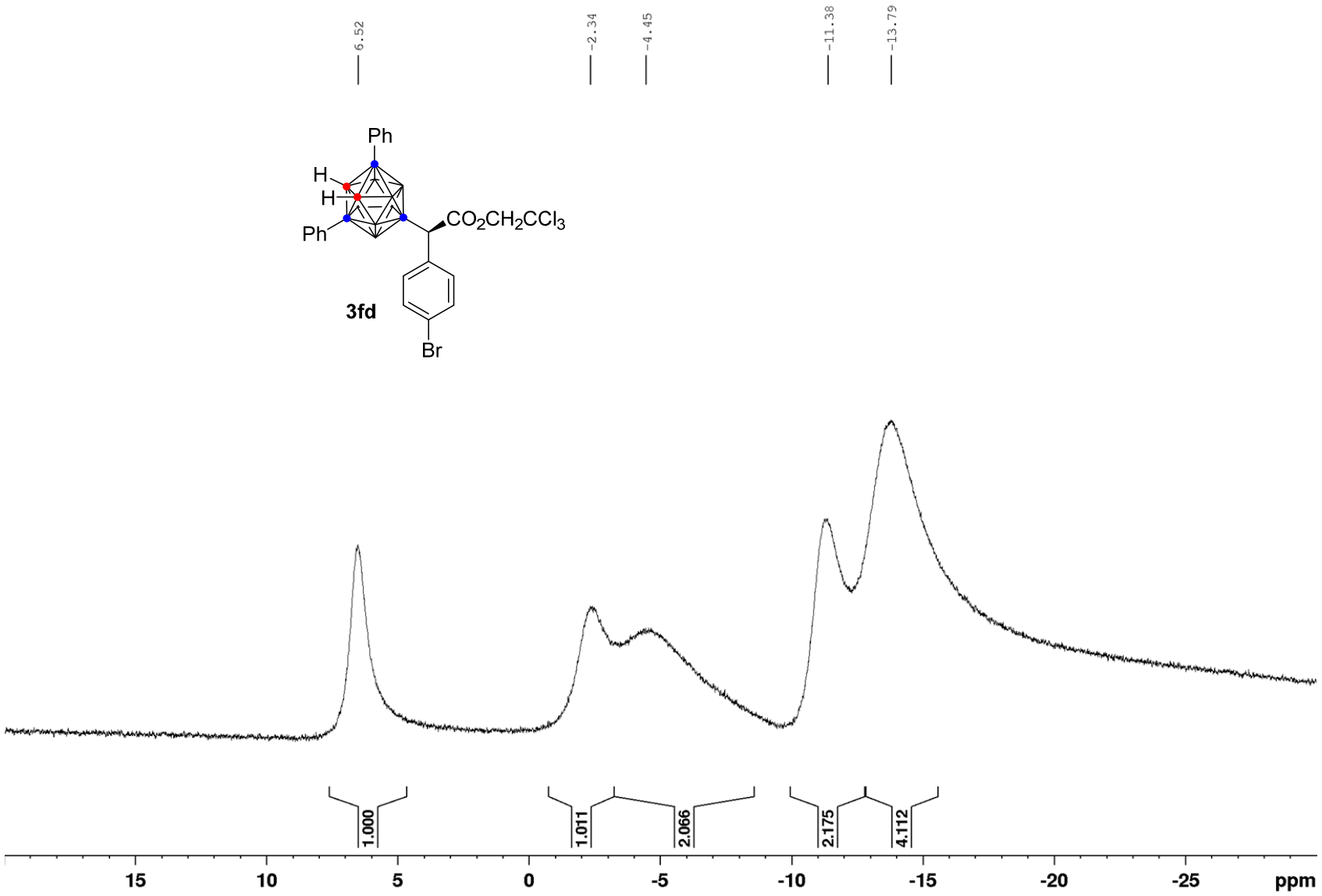
^{13}C NMR (100 MHz, $CDCl_3$)



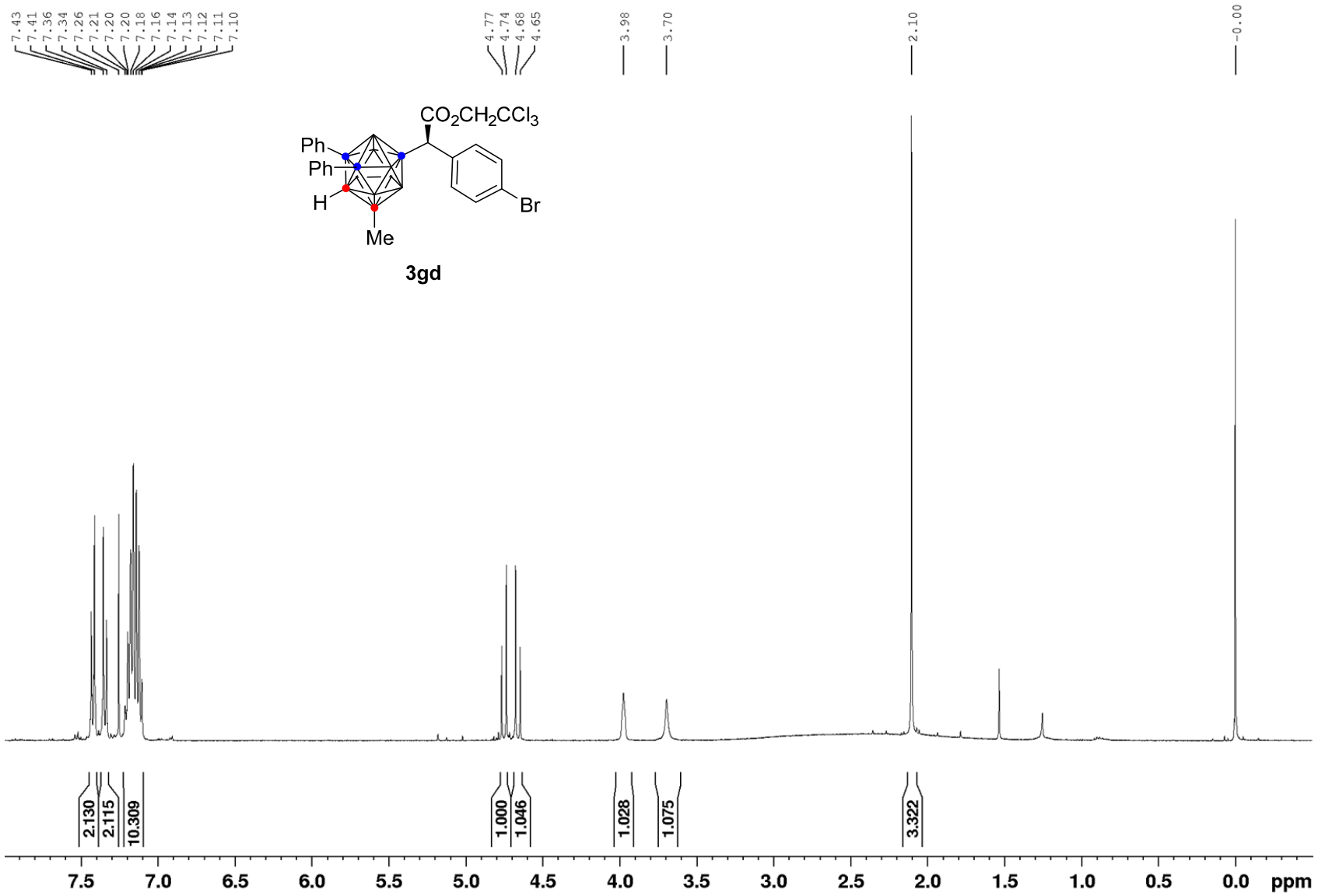
^{11}B NMR (128 MHz, $CDCl_3$)



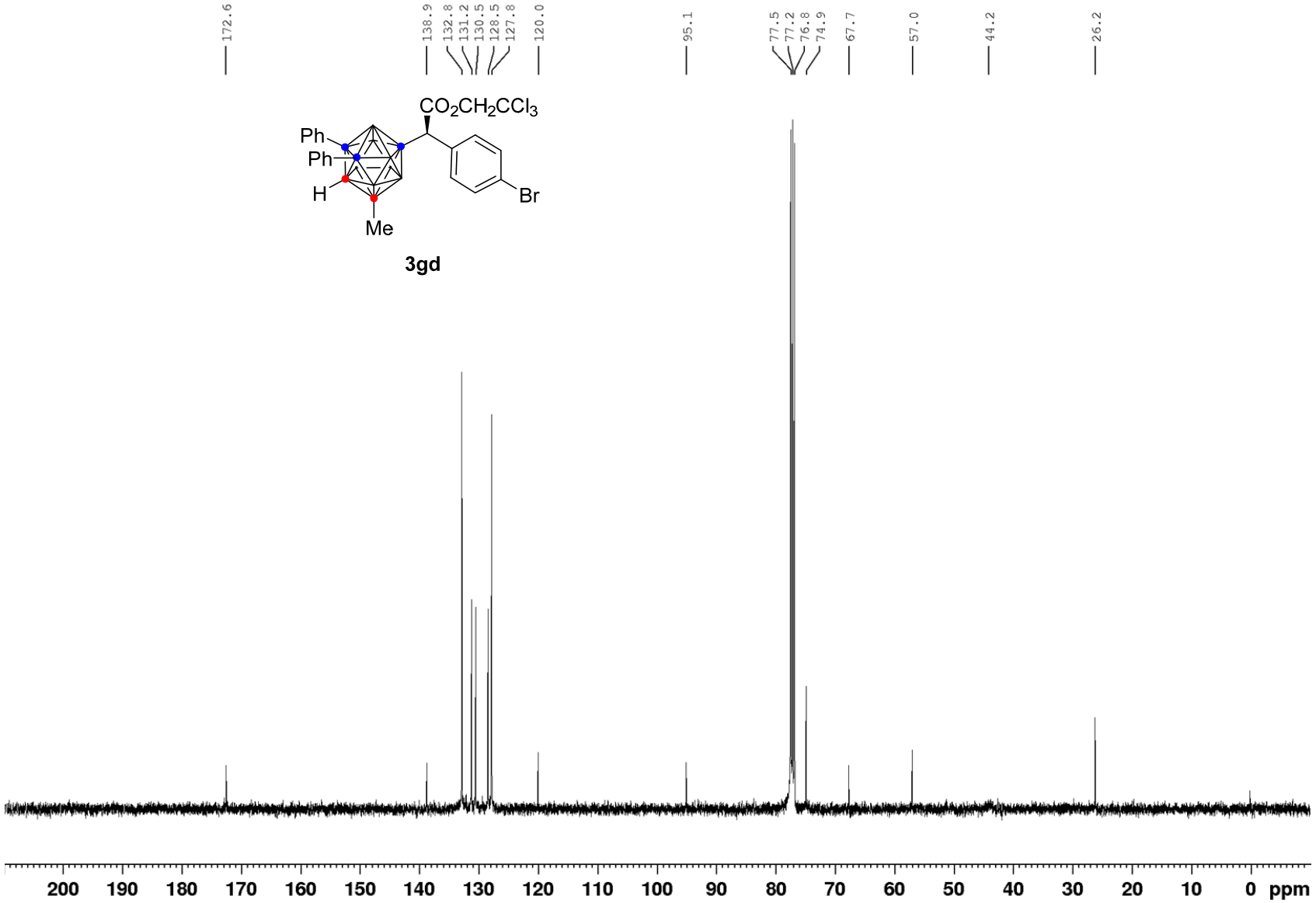
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



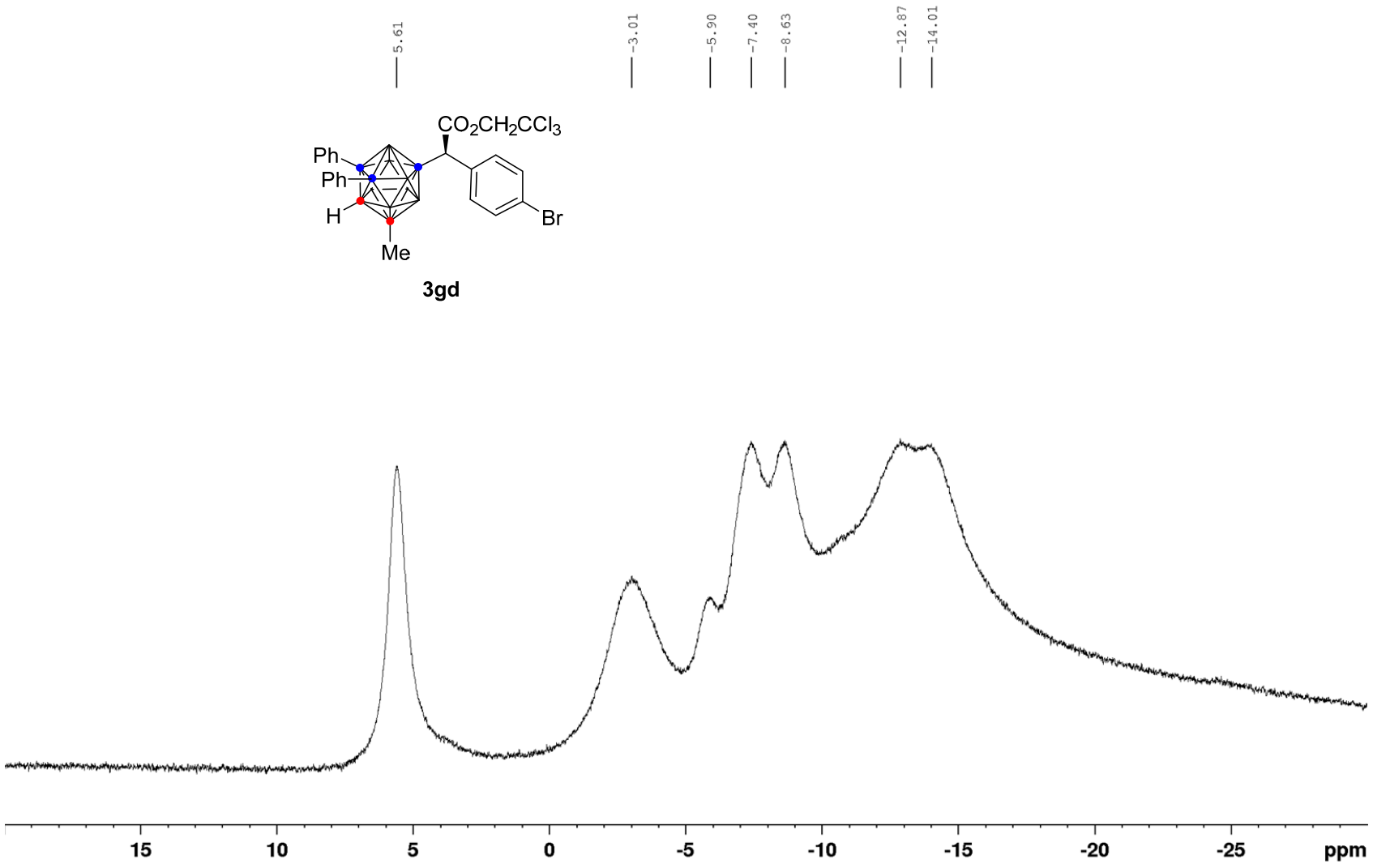
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

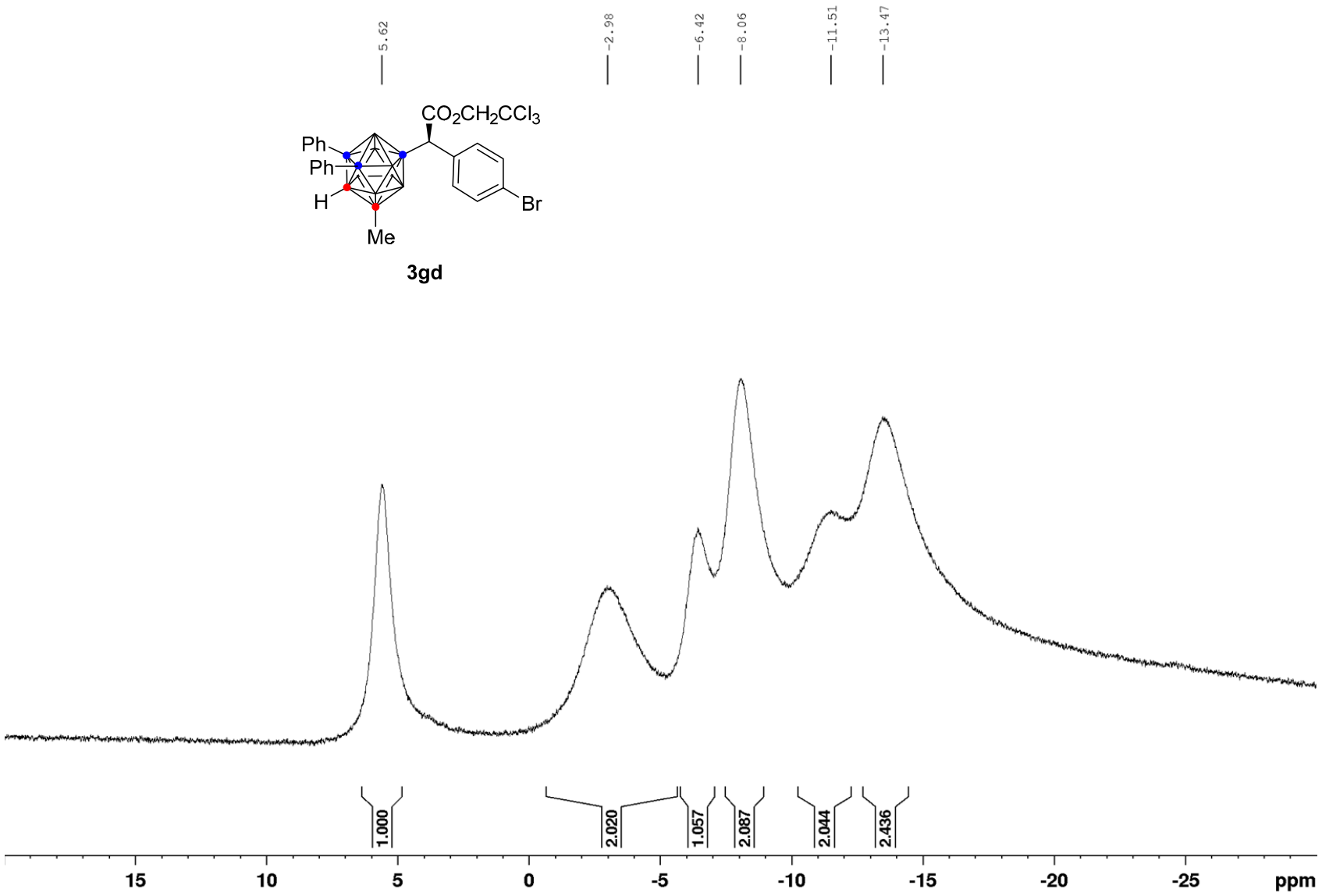


^{11}B NMR (128 MHz, $CDCl_3$)

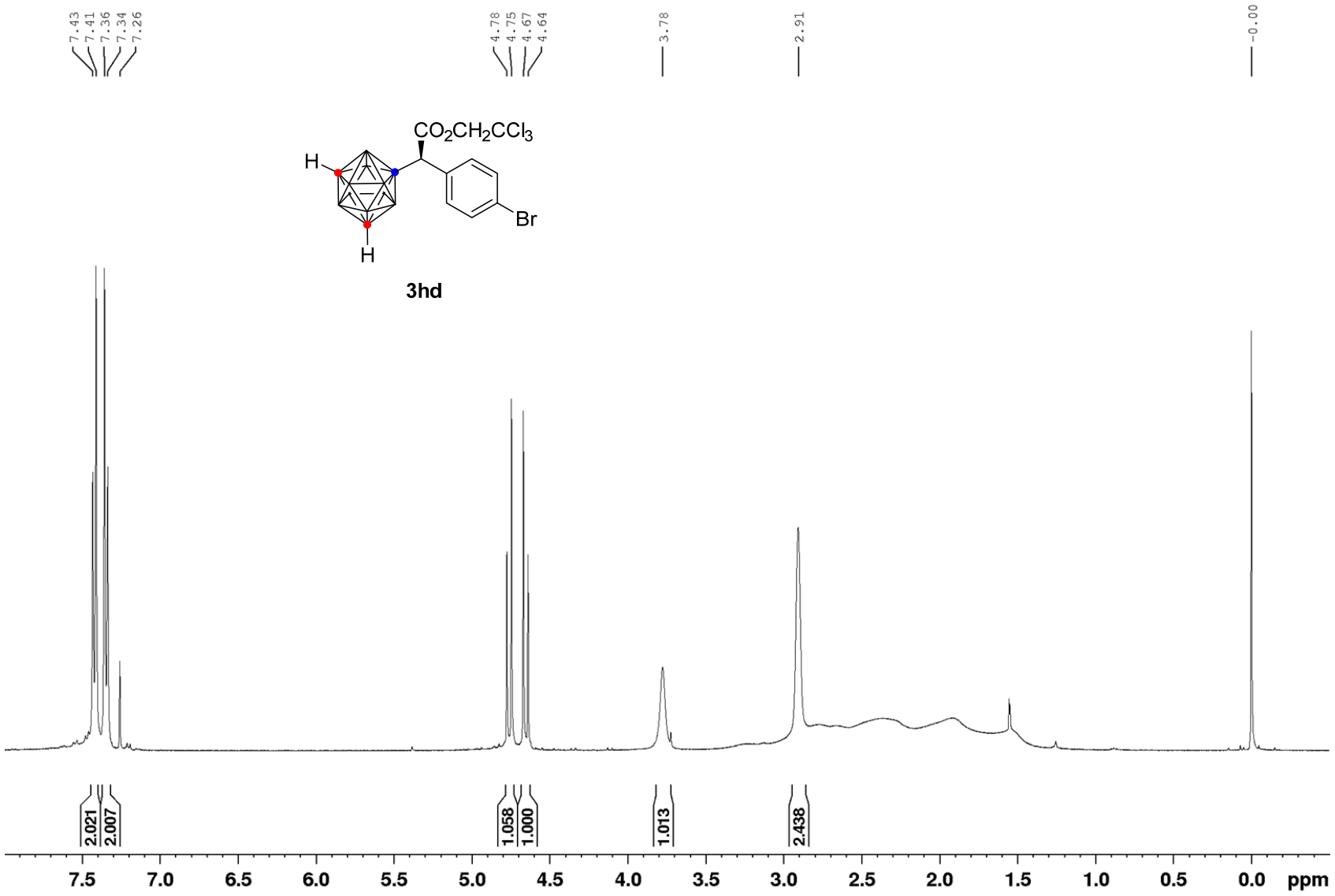


3gd

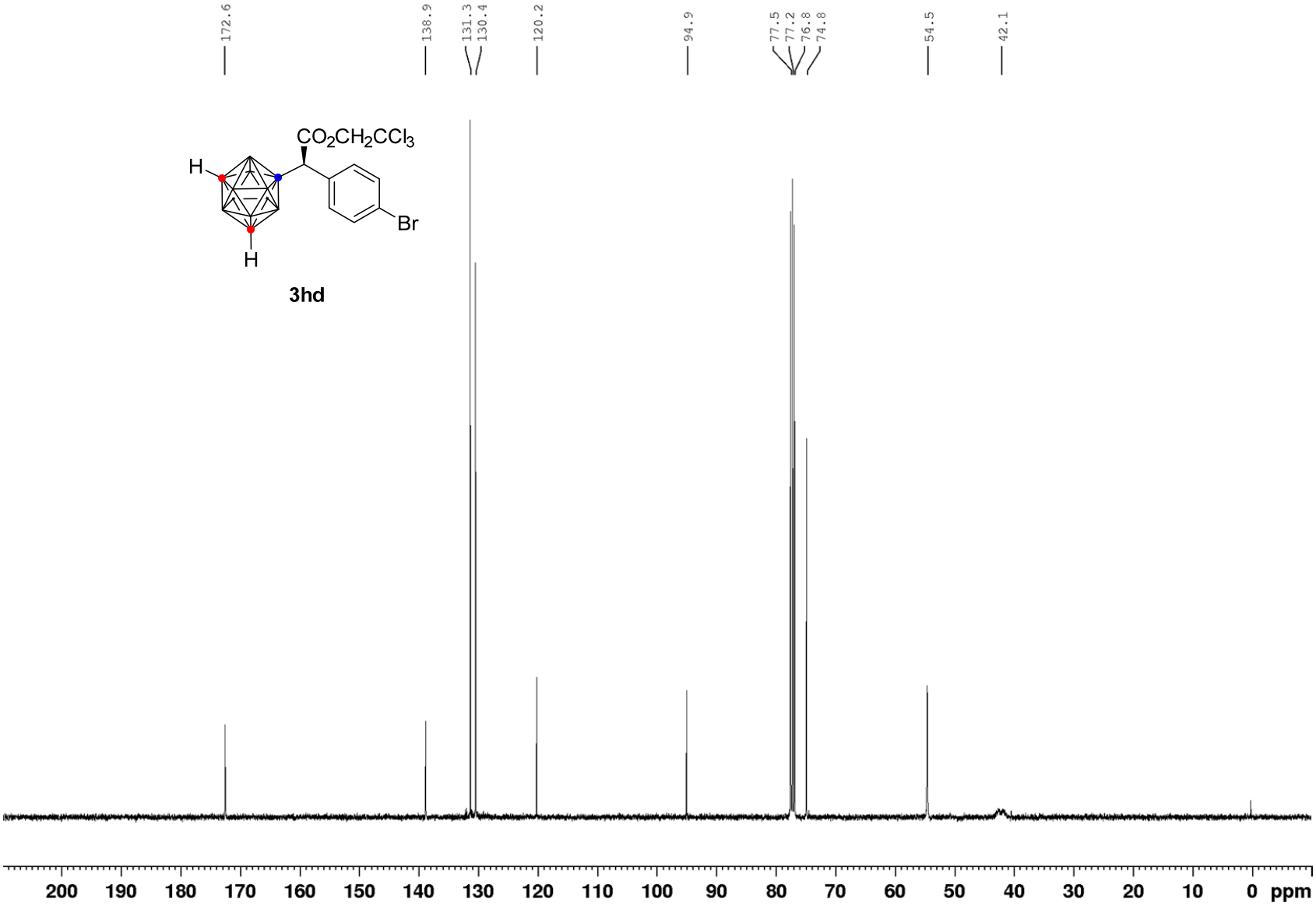
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



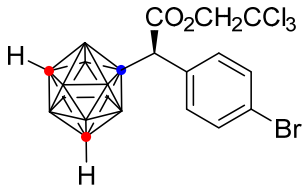
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

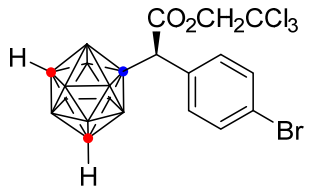


^{11}B NMR (128 MHz, $CDCl_3$)



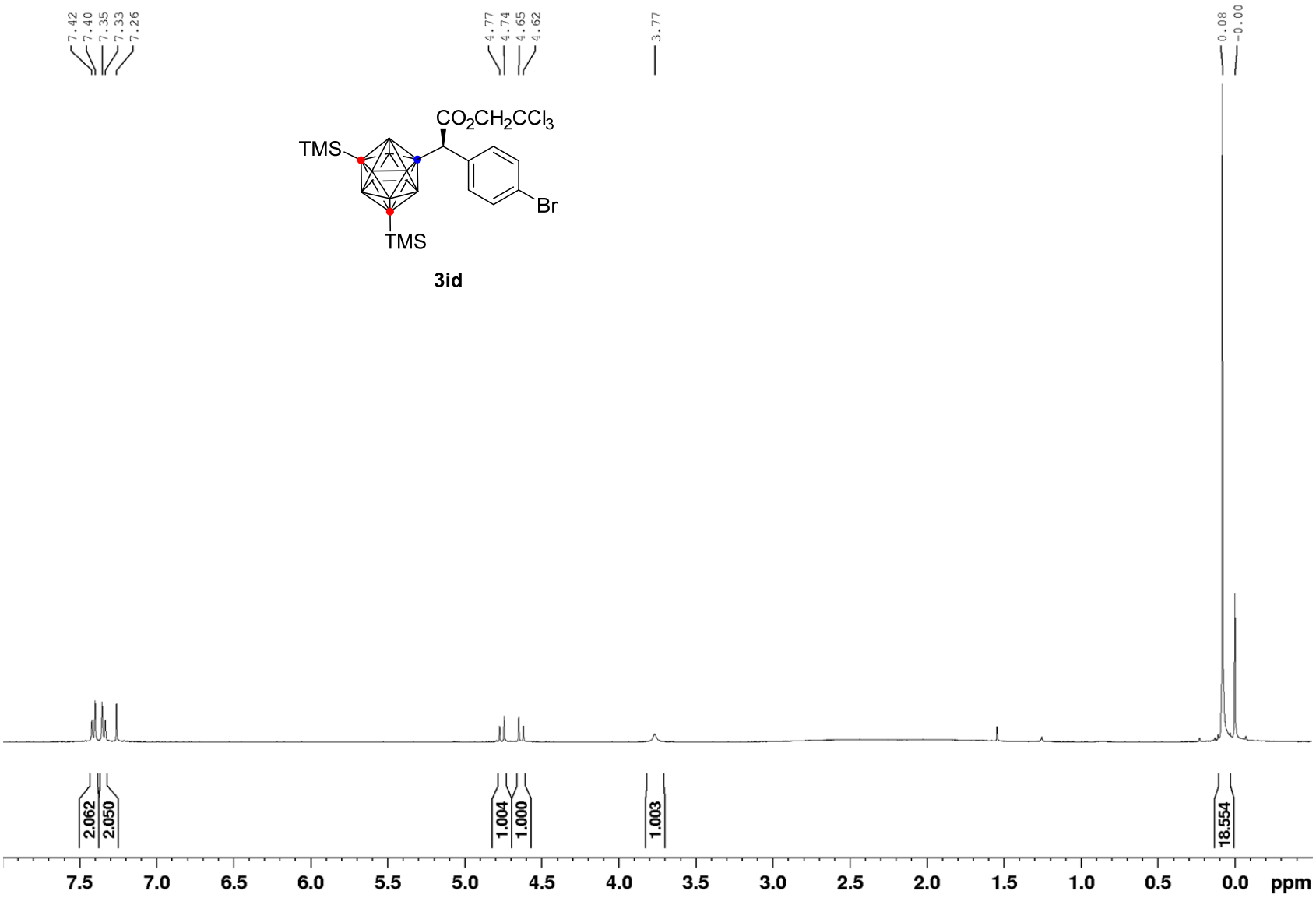
3hd

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



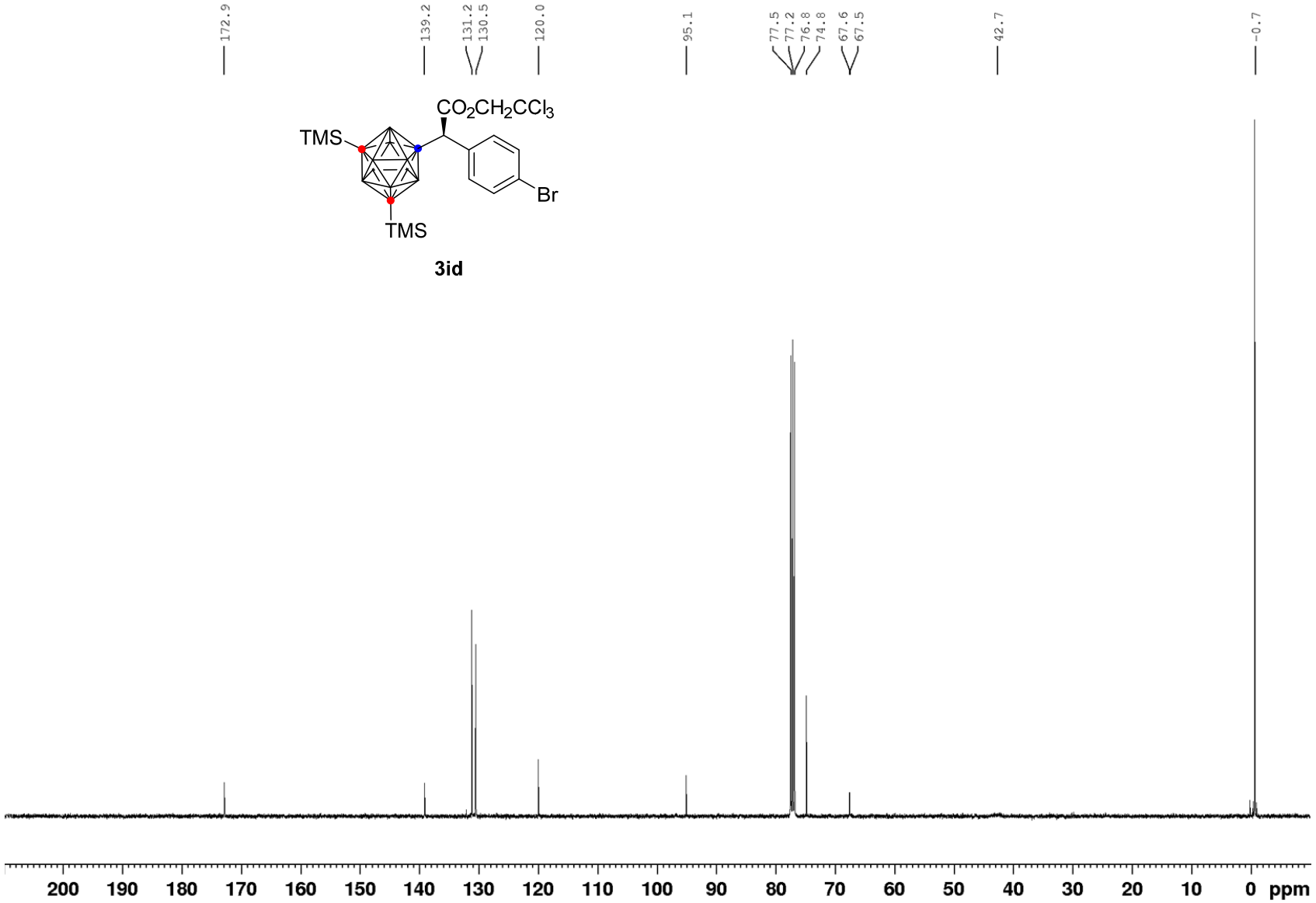
3hd

^{1}H NMR (400 MHz, $CDCl_3$)



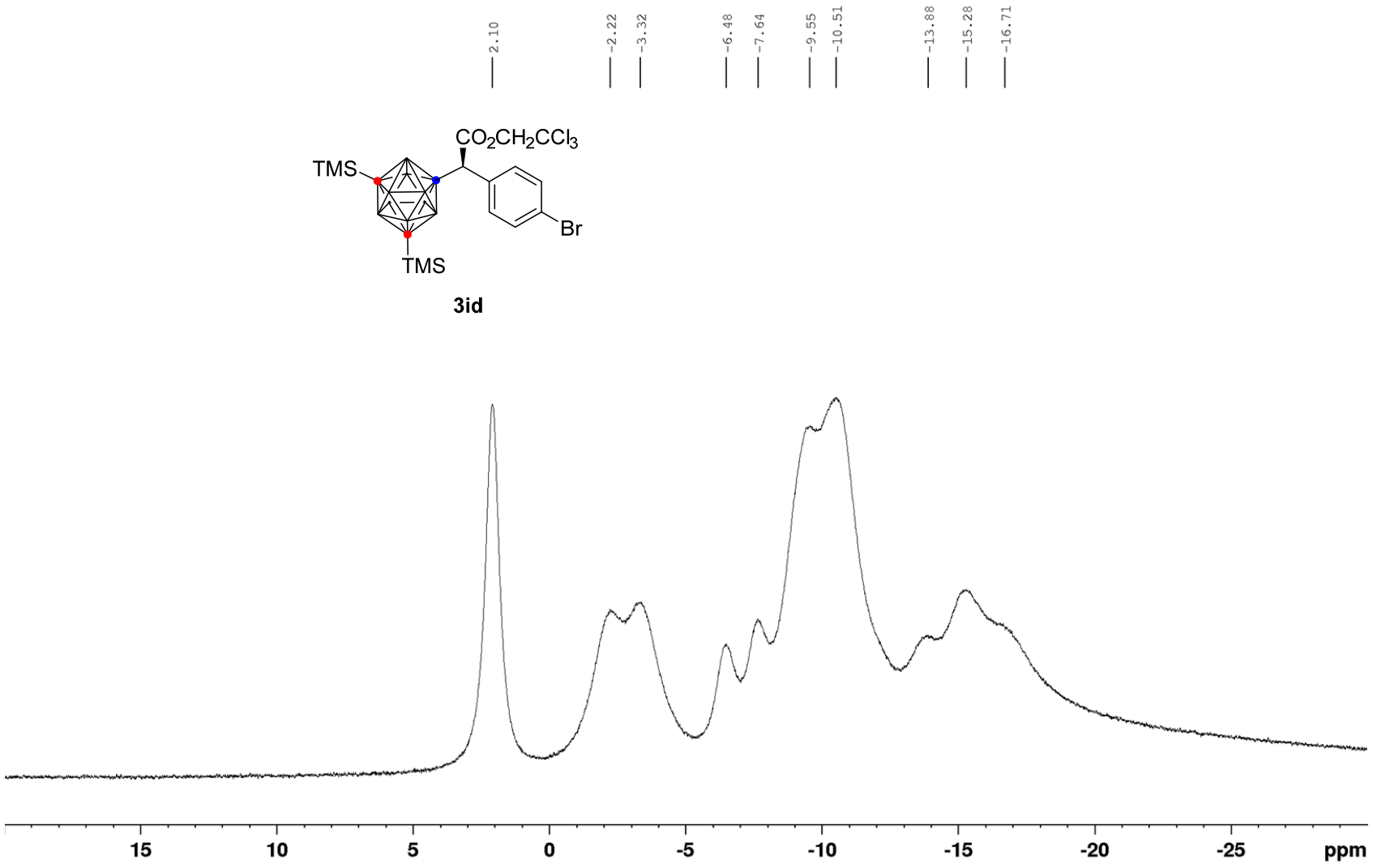
3id

^{13}C NMR (100 MHz, $CDCl_3$)



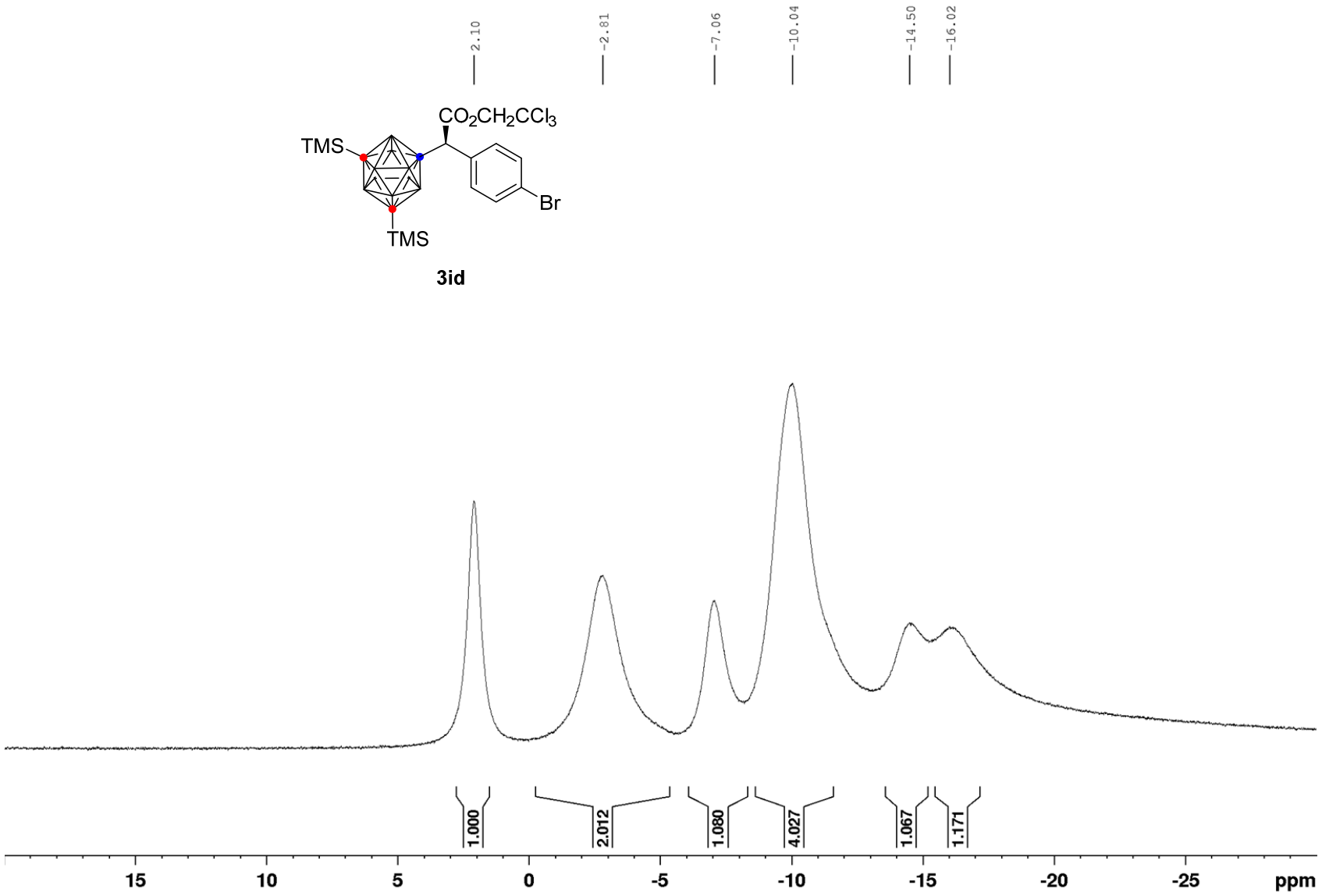
3id

^{11}B NMR (128 MHz, $CDCl_3$)

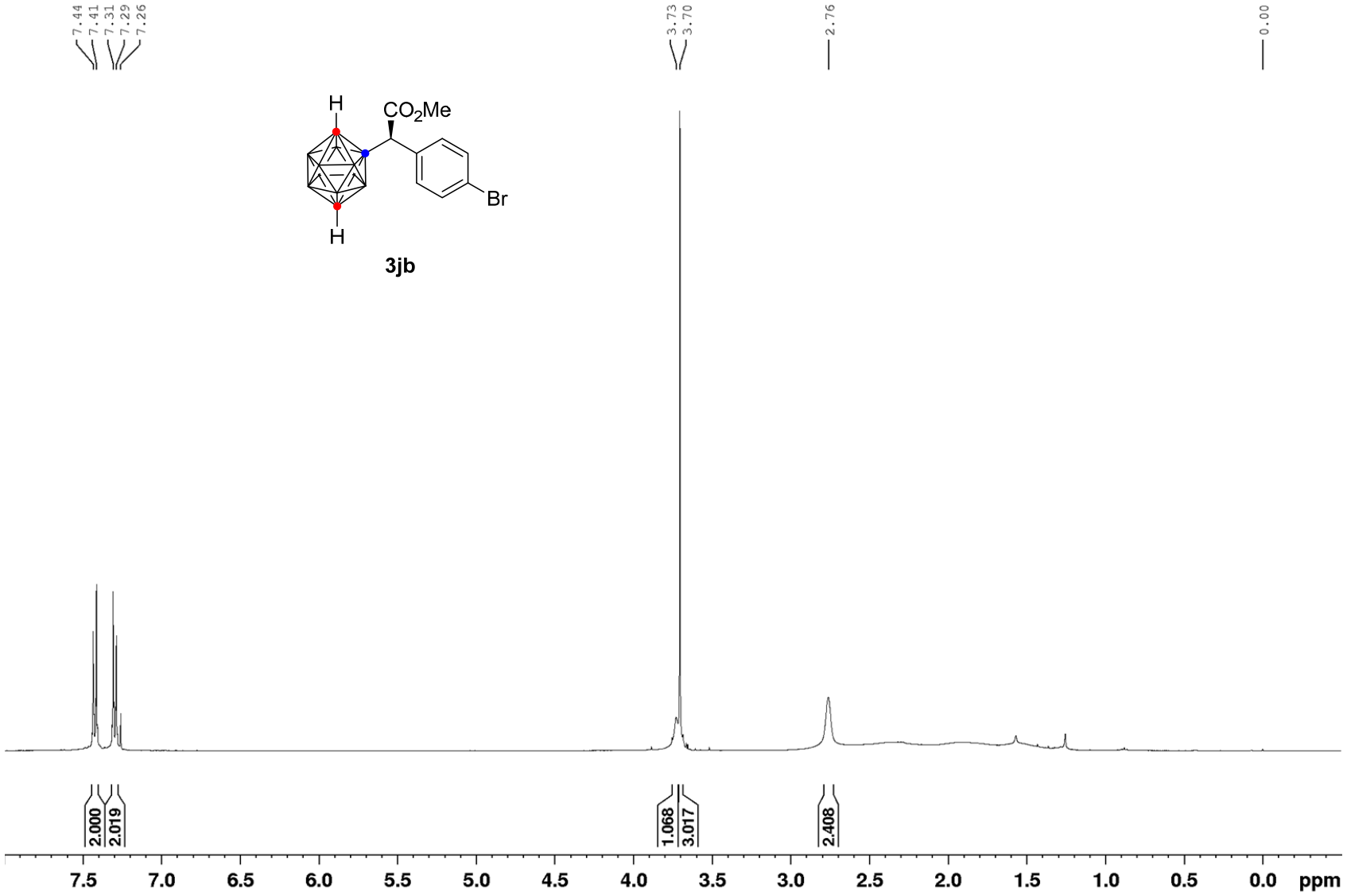


3id

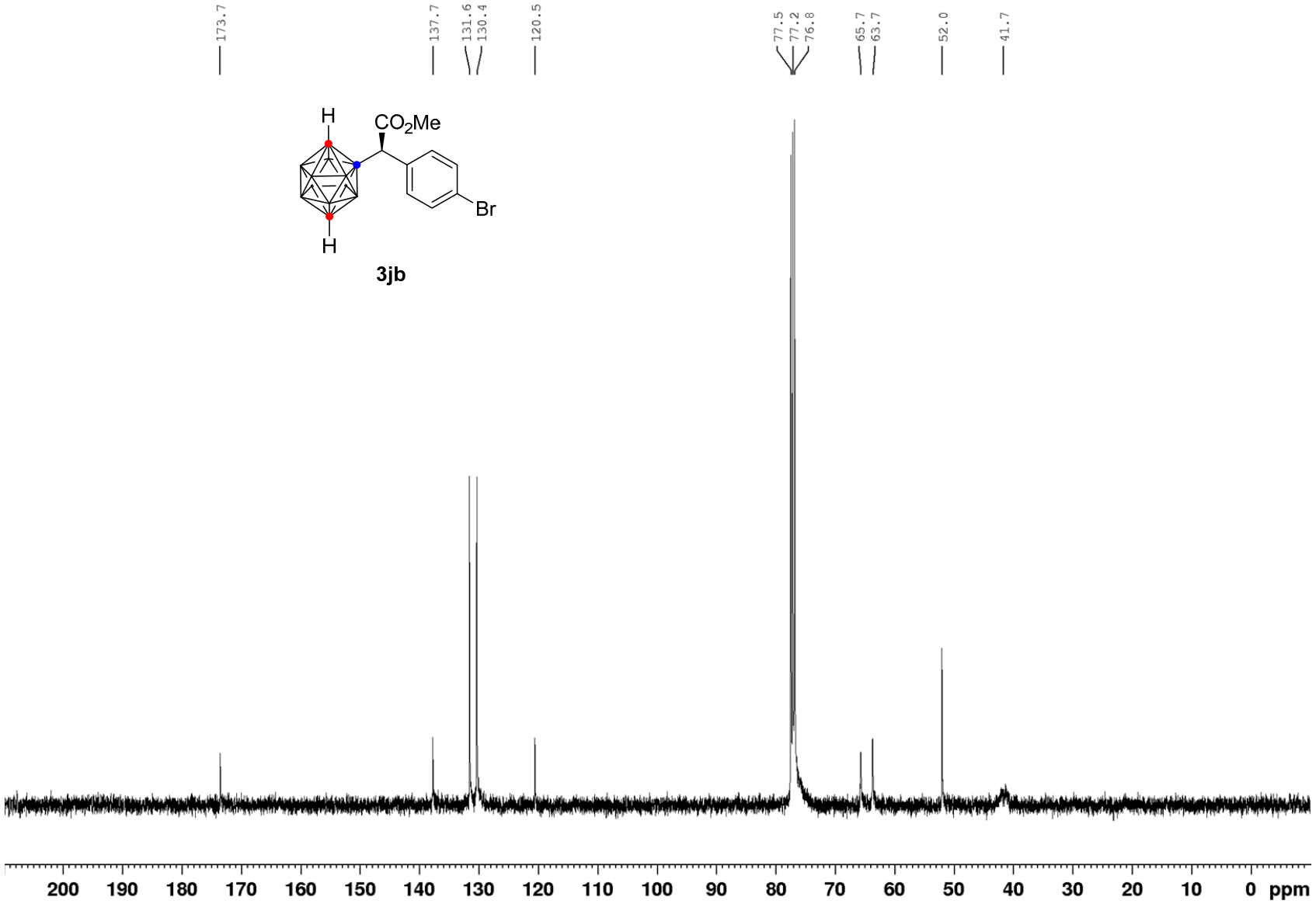
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



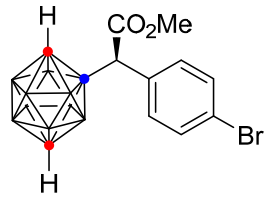
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

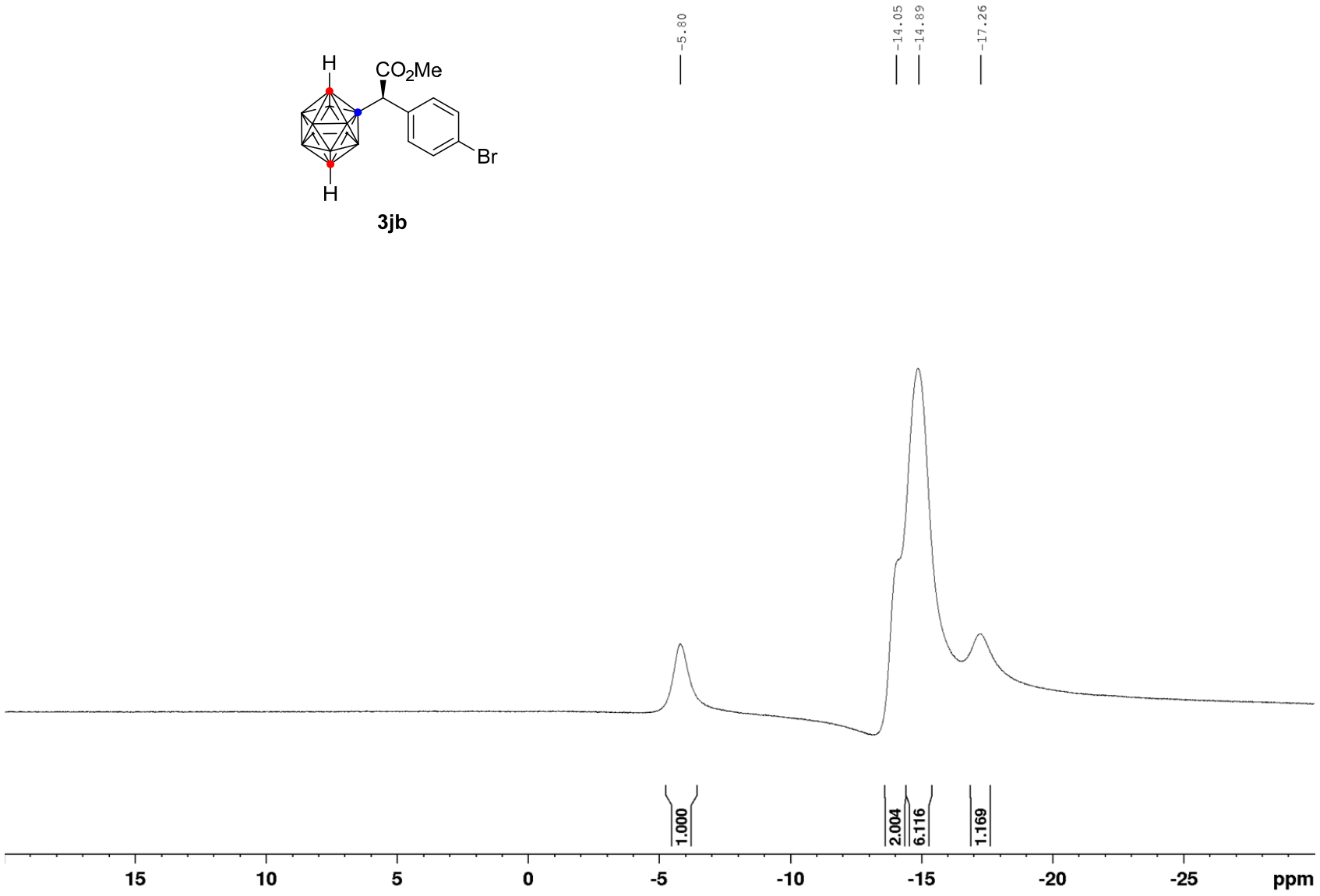


^{11}B NMR (128 MHz, $CDCl_3$)

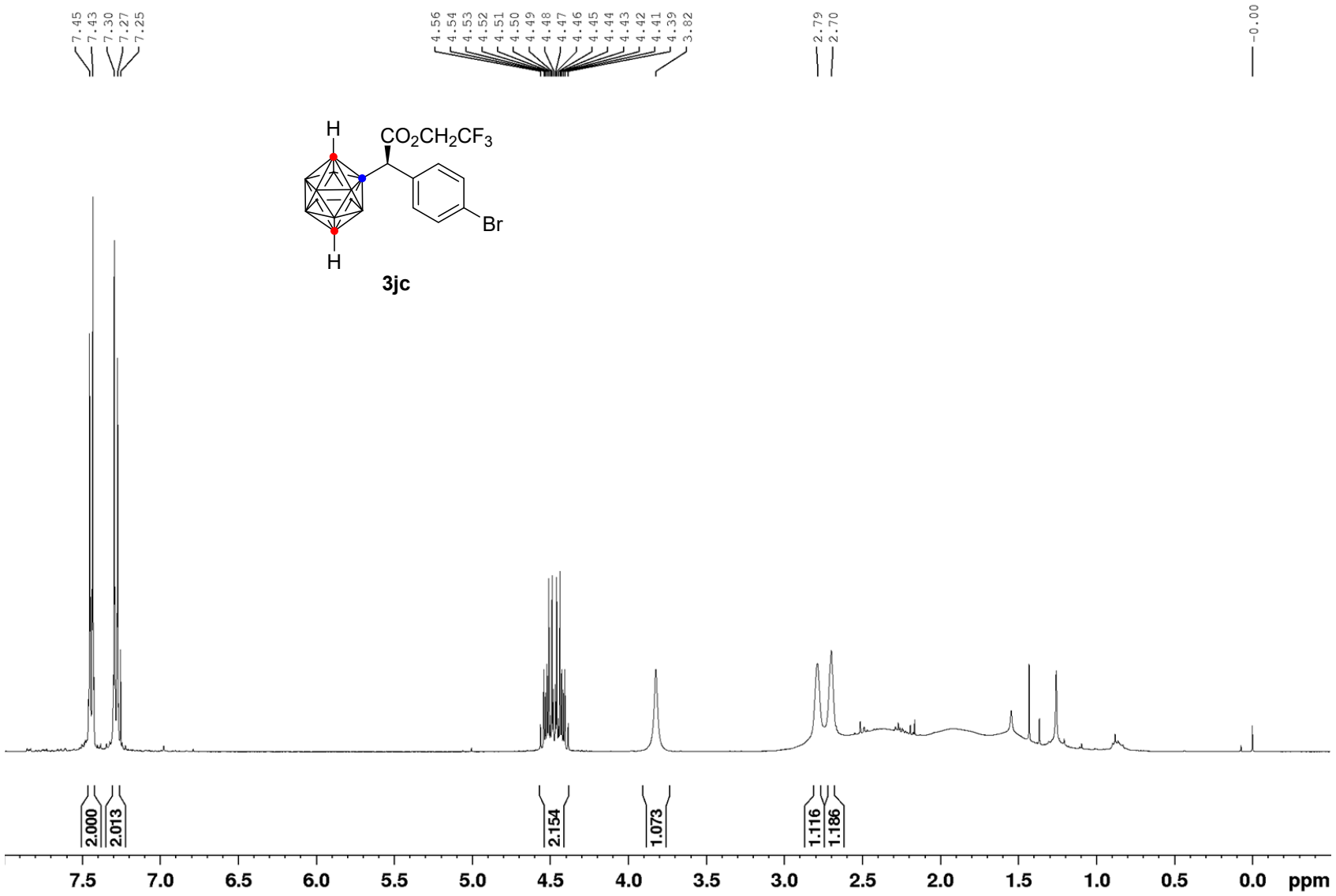


3jb

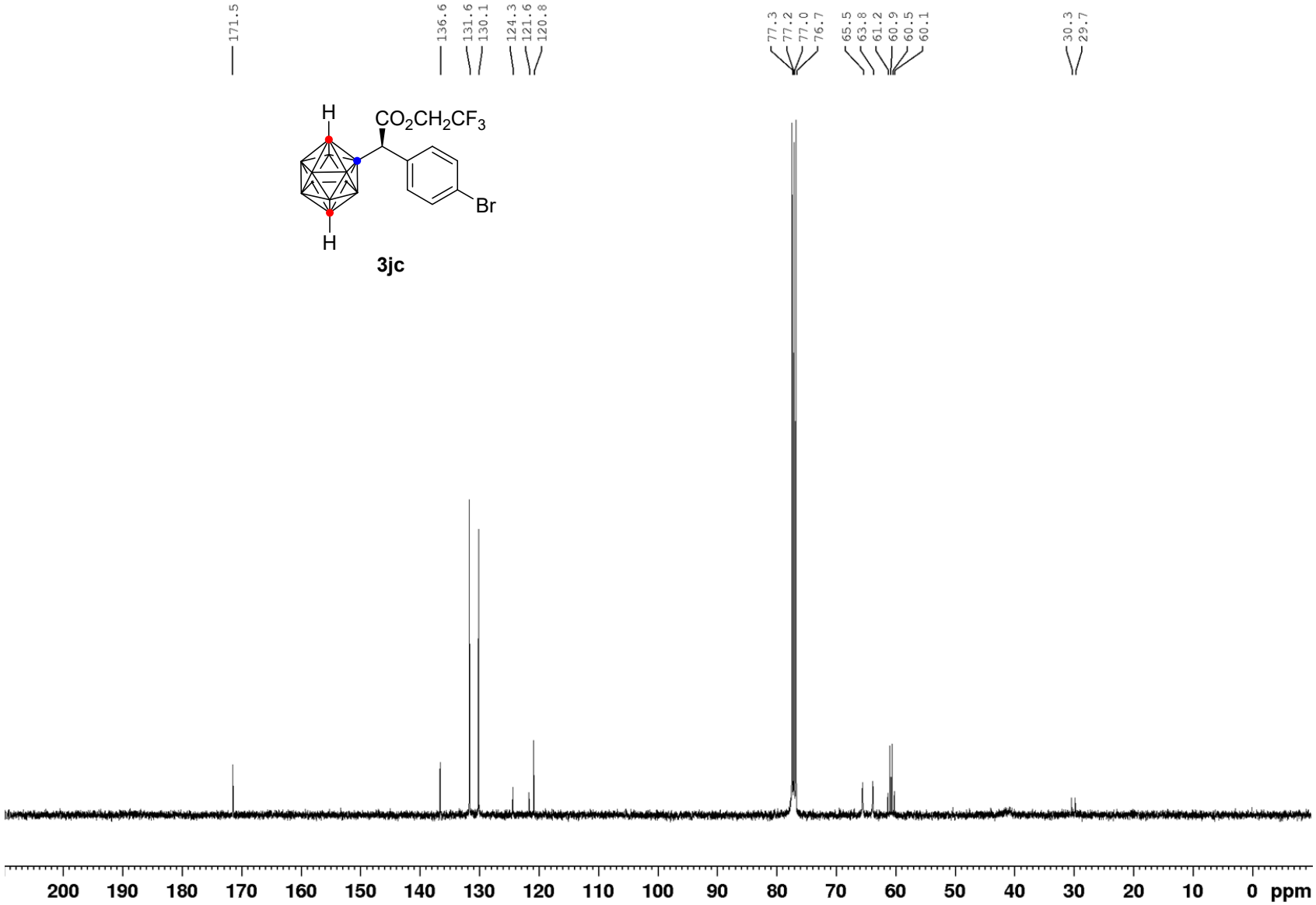
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



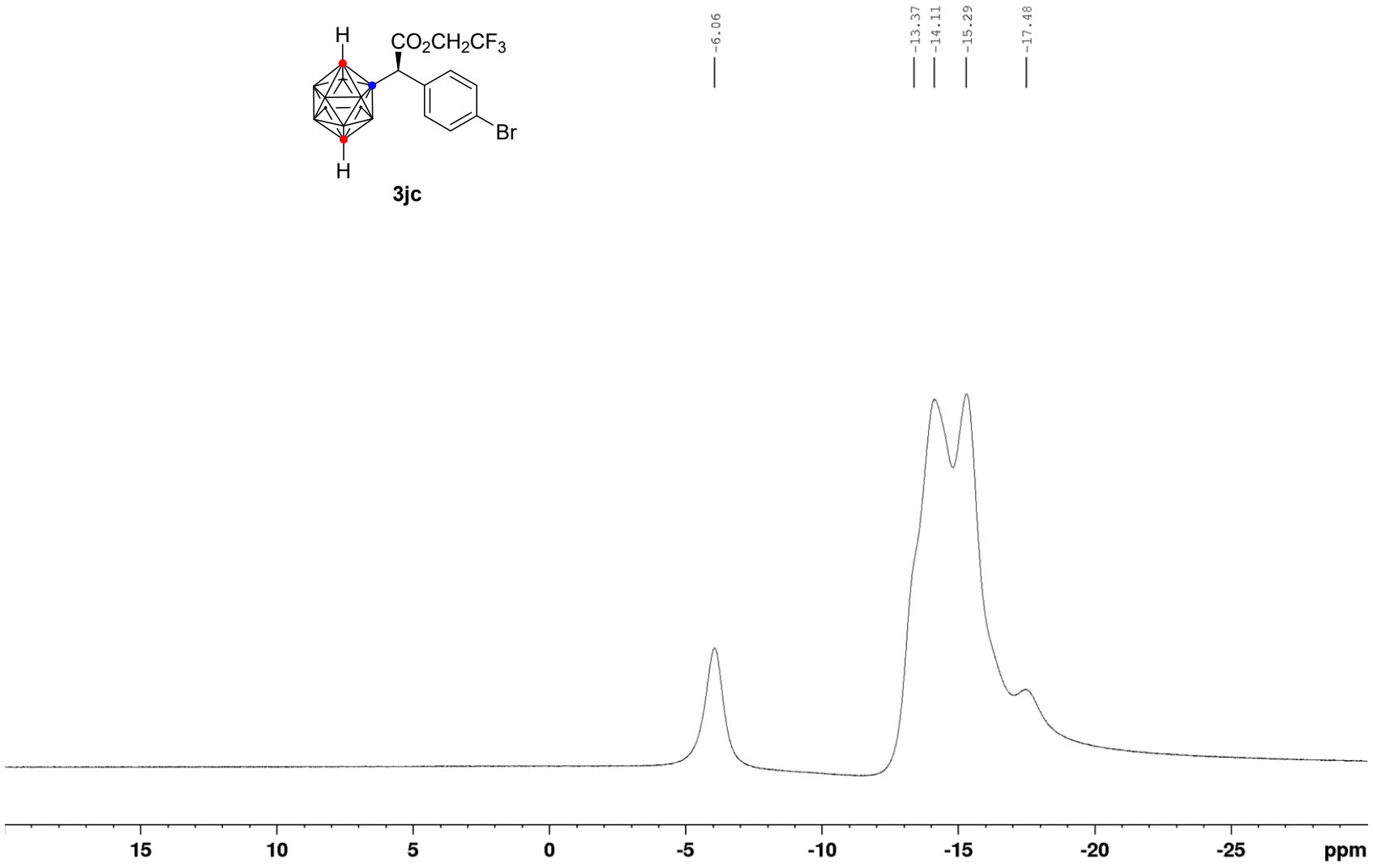
^{1}H NMR (400 MHz, $CDCl_3$)



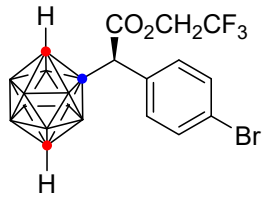
^{13}C NMR (100 MHz, $CDCl_3$)



^{11}B NMR (128 MHz, $CDCl_3$)

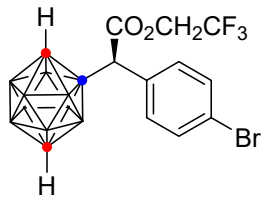


$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



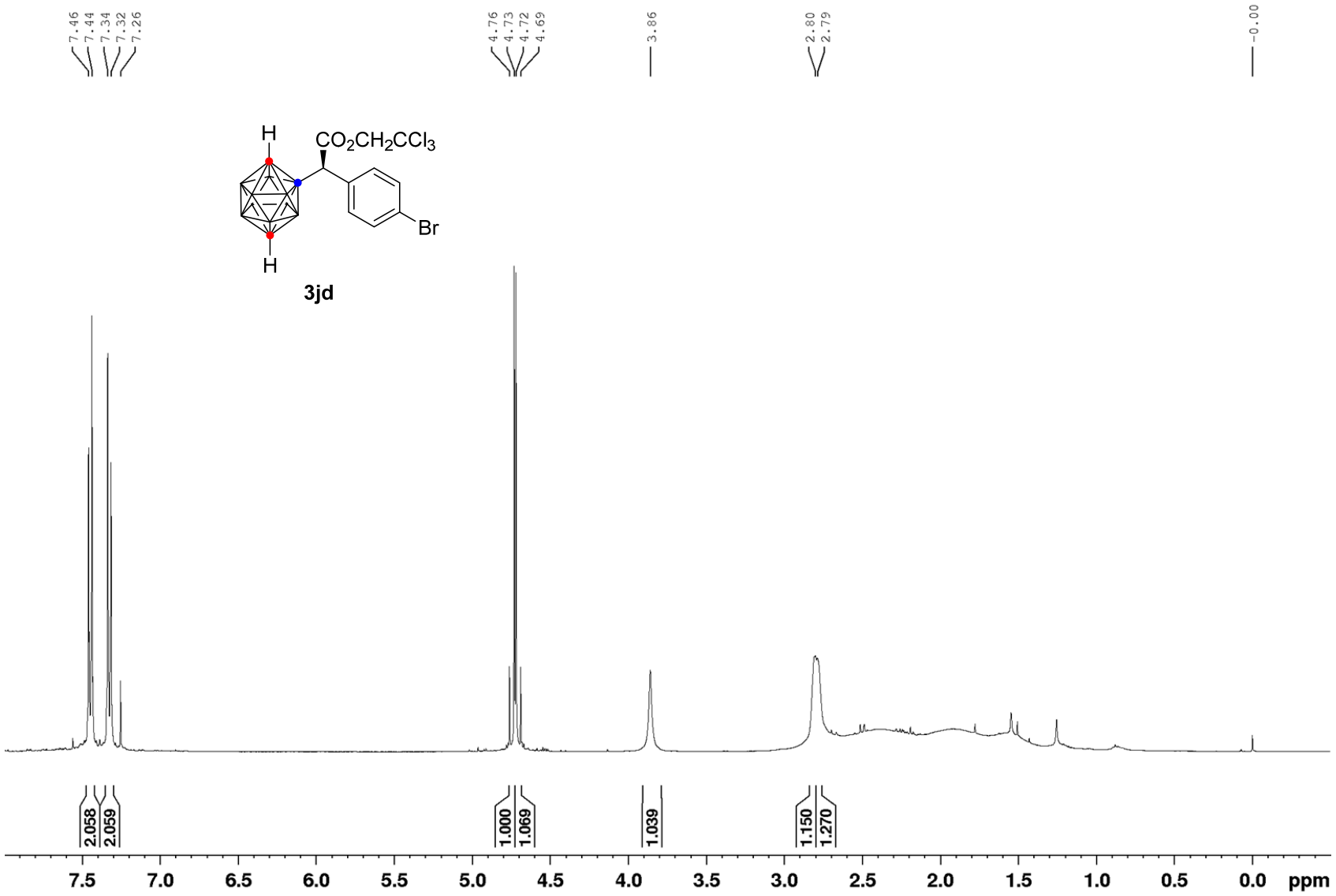
3jc

$^{19}F\{^{1}H\}$ NMR (377 MHz, $CDCl_3$)

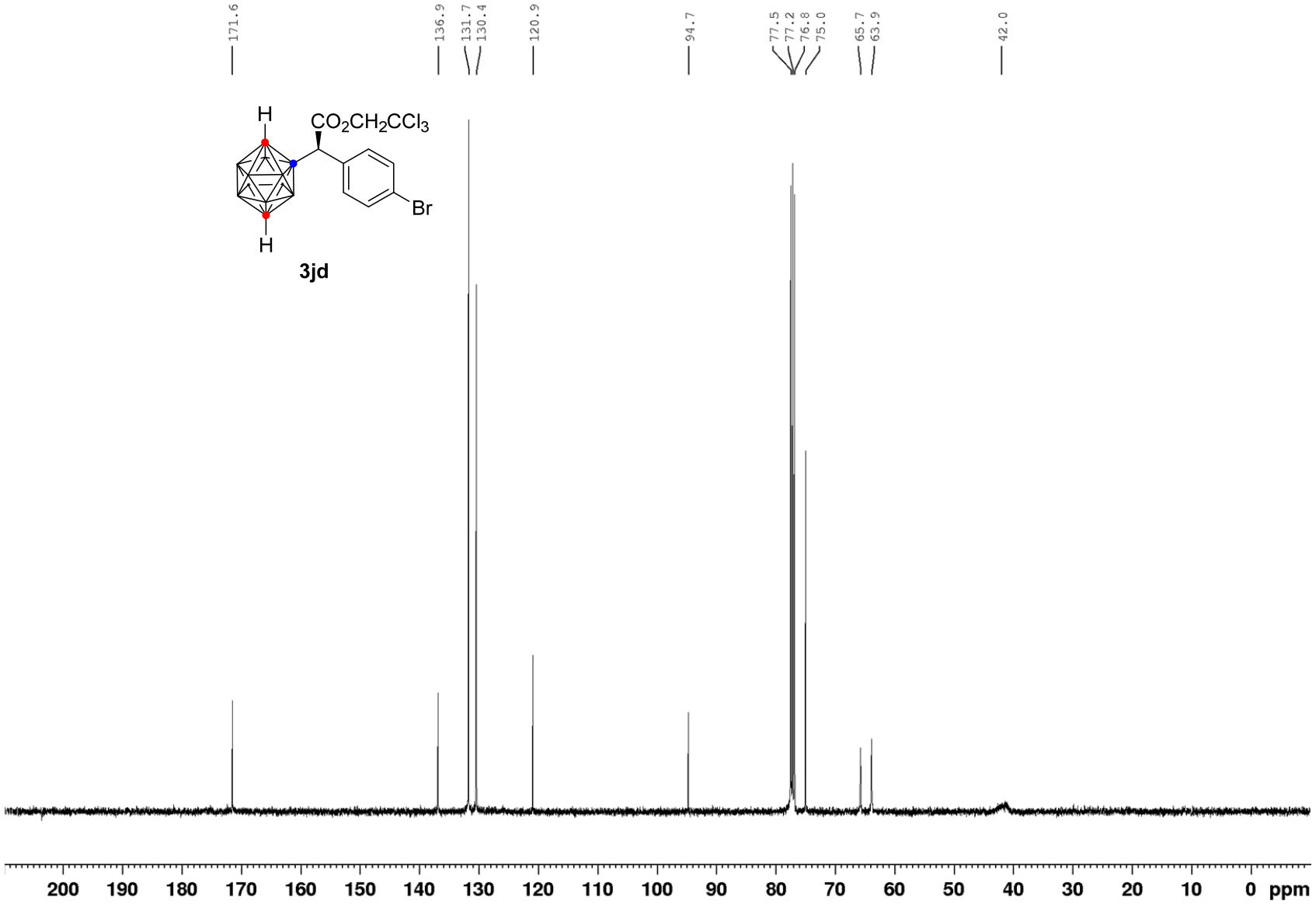


3jc

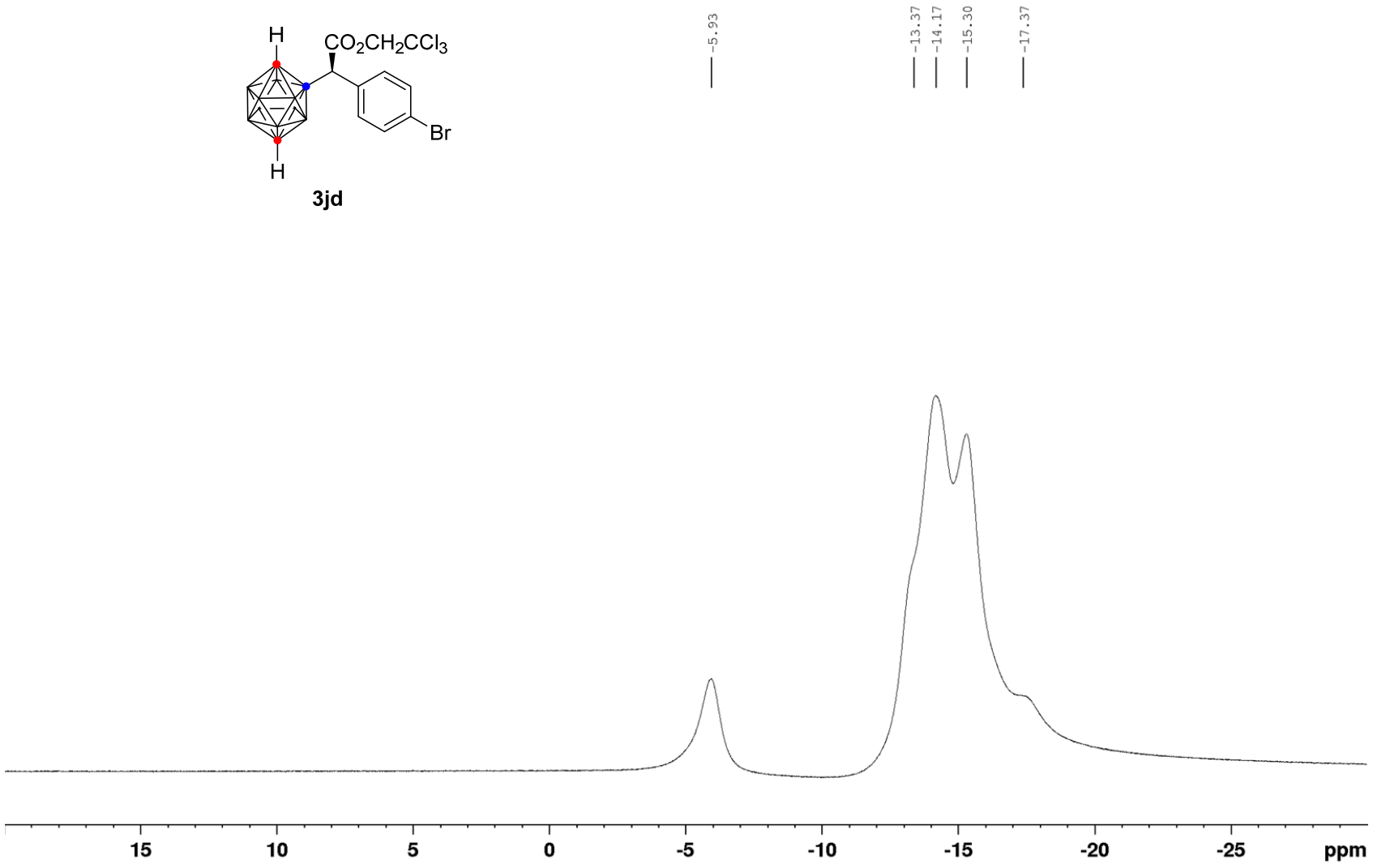
^{1}H NMR (400 MHz, $CDCl_3$)



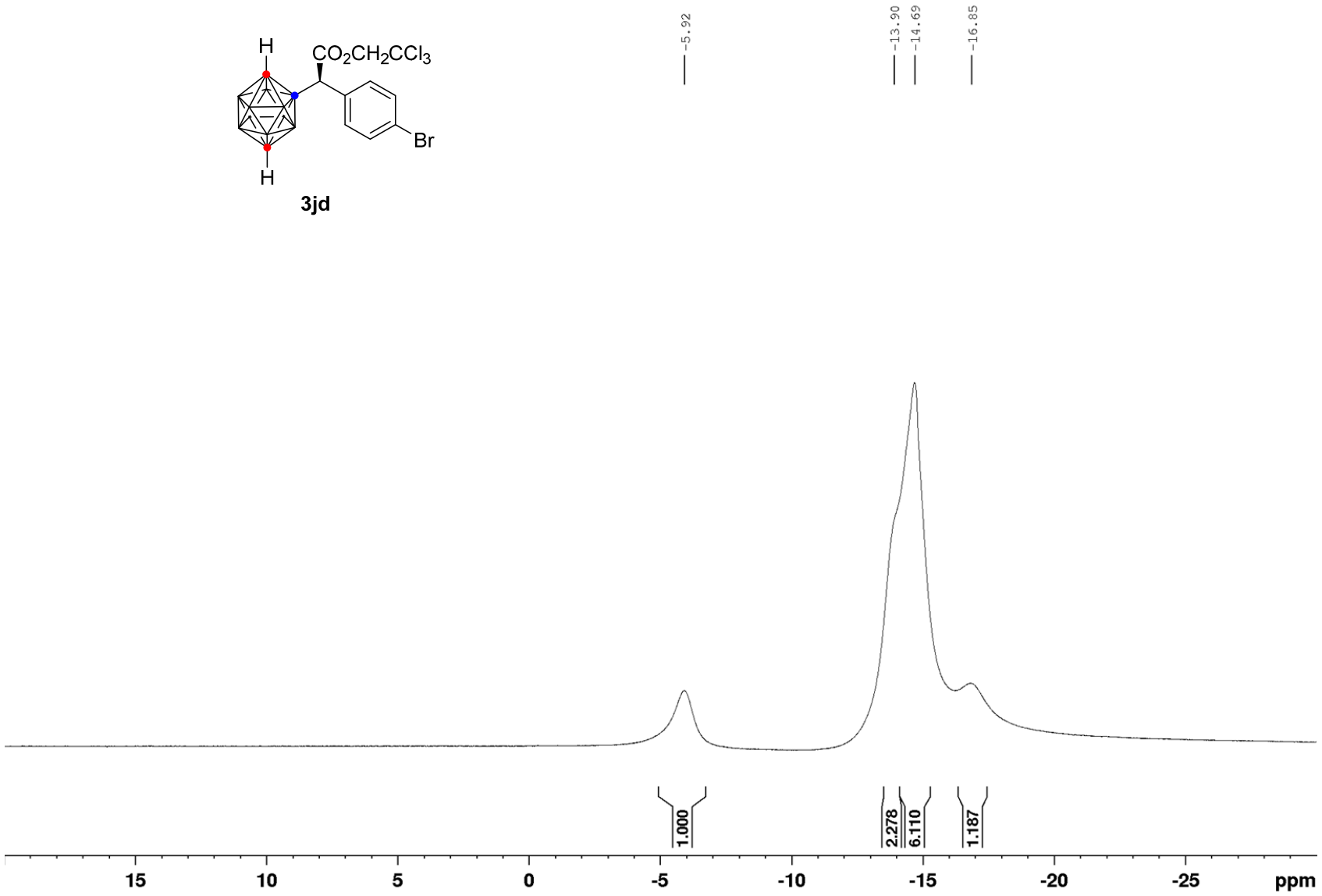
^{13}C NMR (100 MHz, $CDCl_3$)



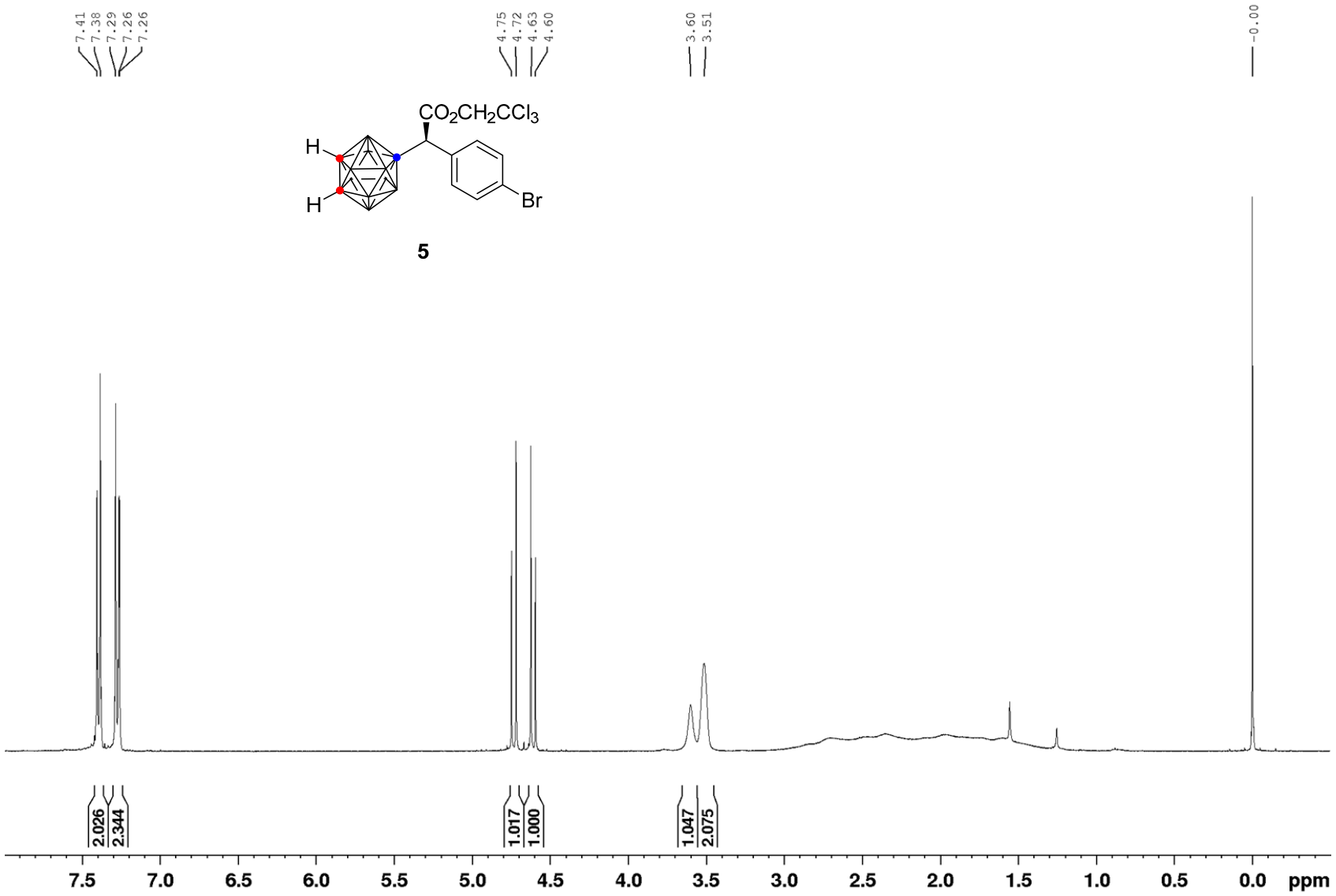
^{11}B NMR (128 MHz, $CDCl_3$)



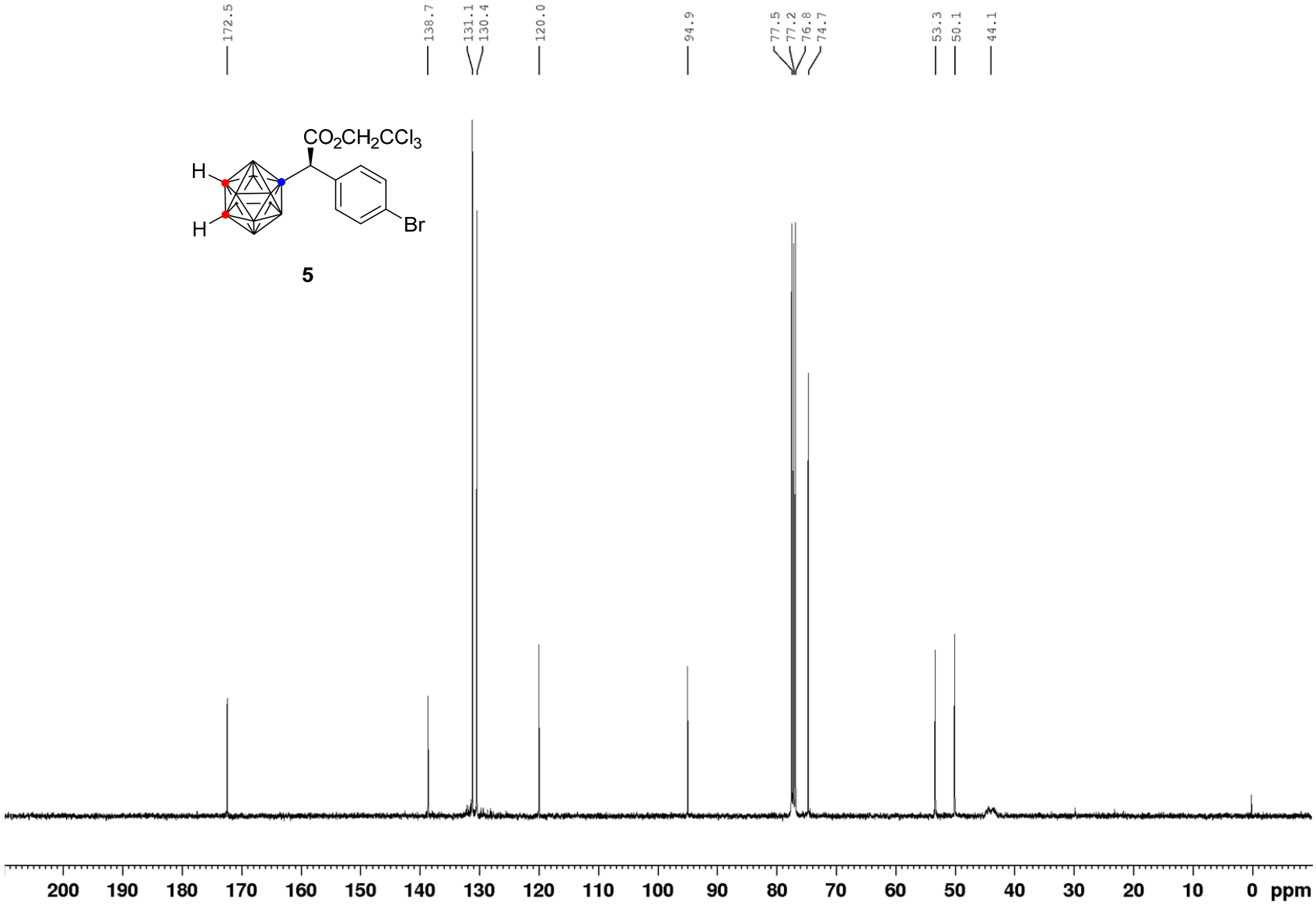
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



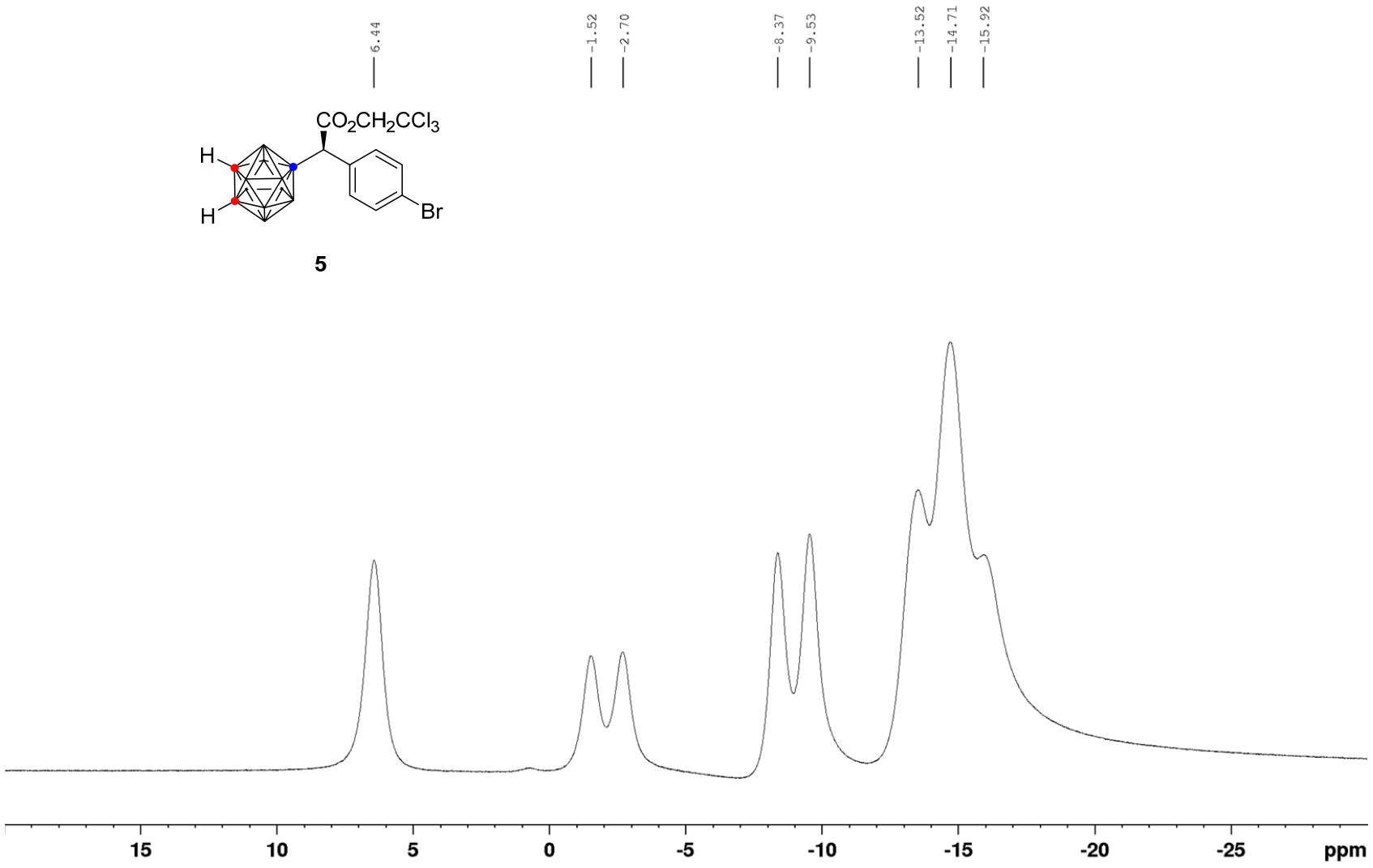
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

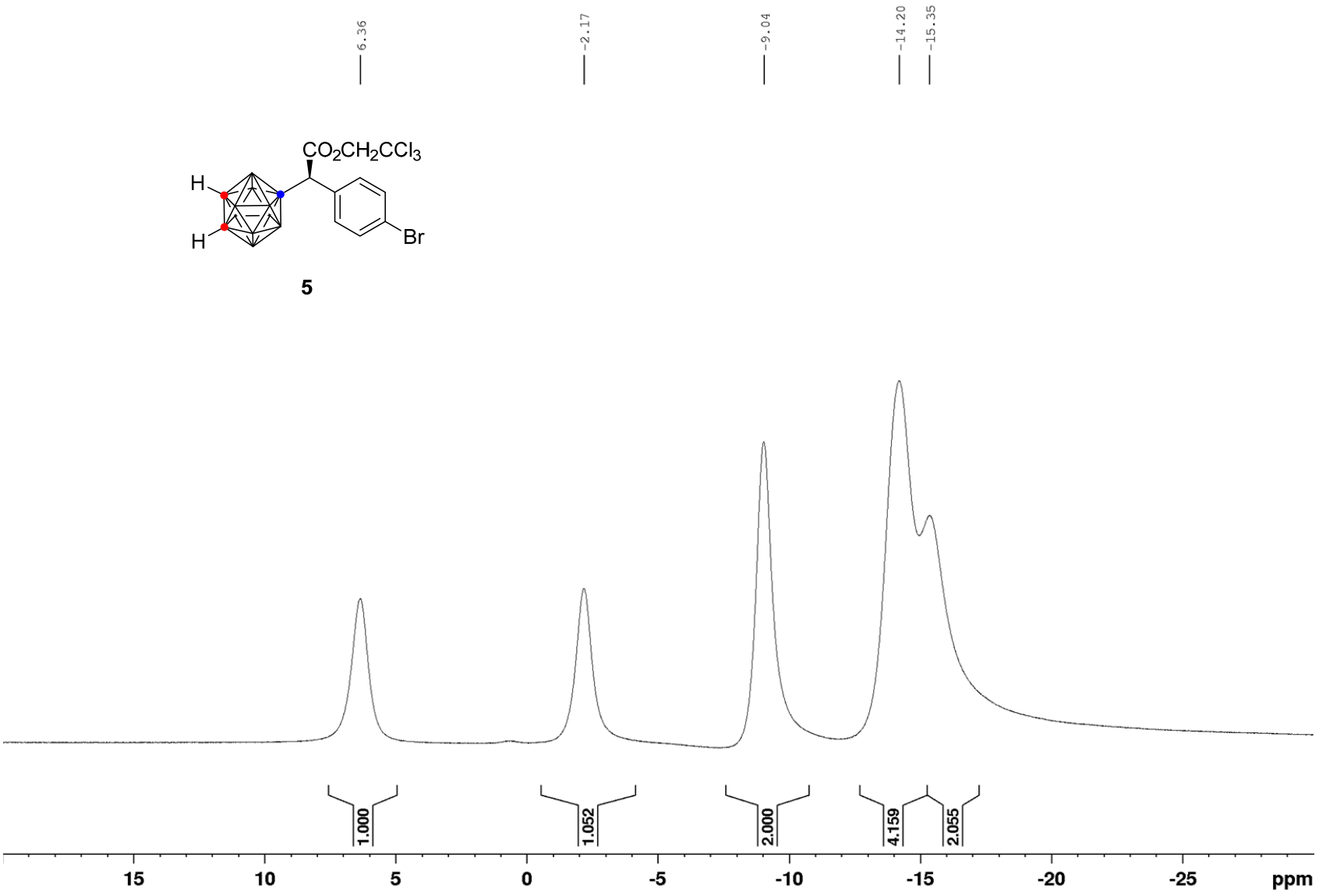


^{11}B NMR (128 MHz, $CDCl_3$)



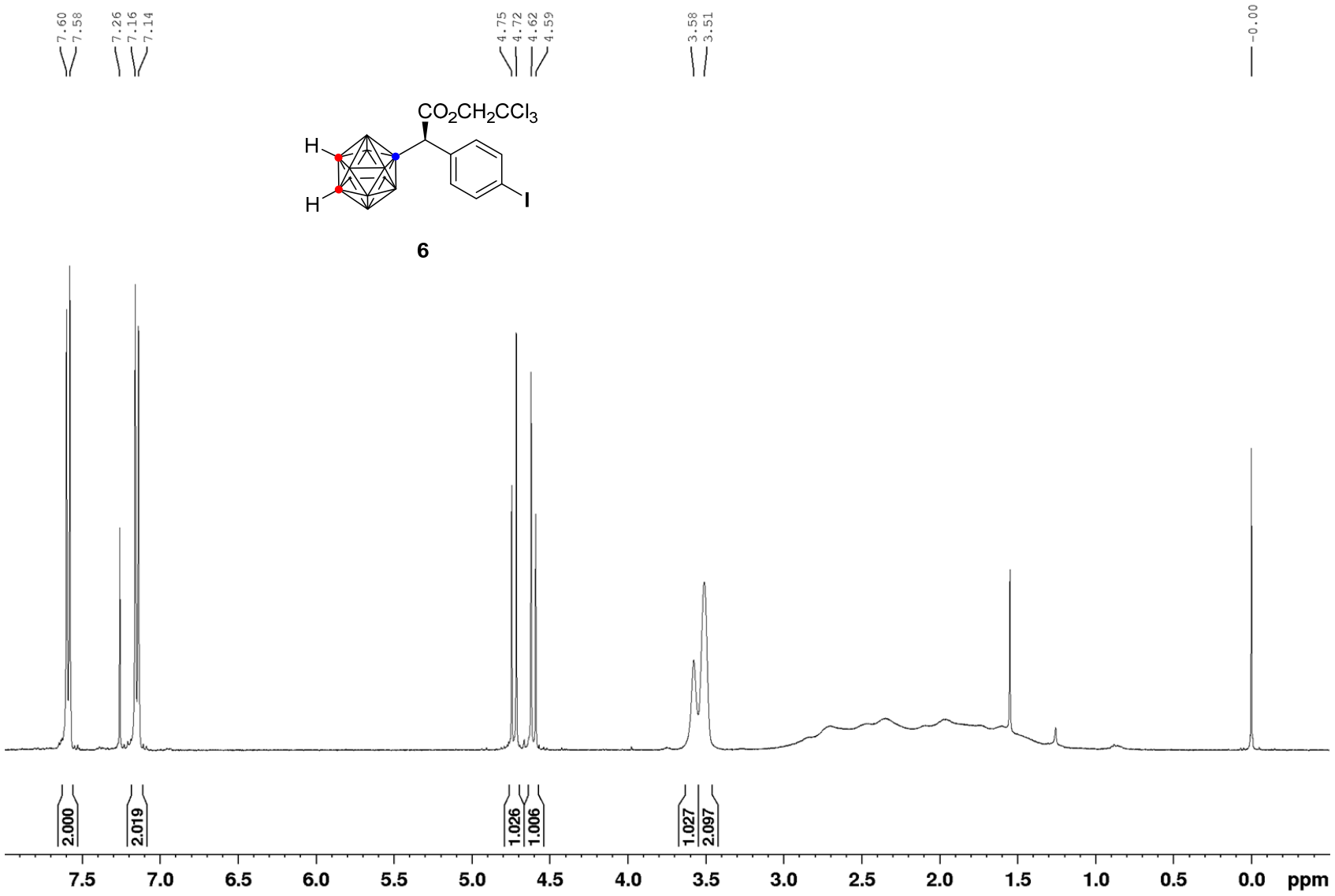
5

$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



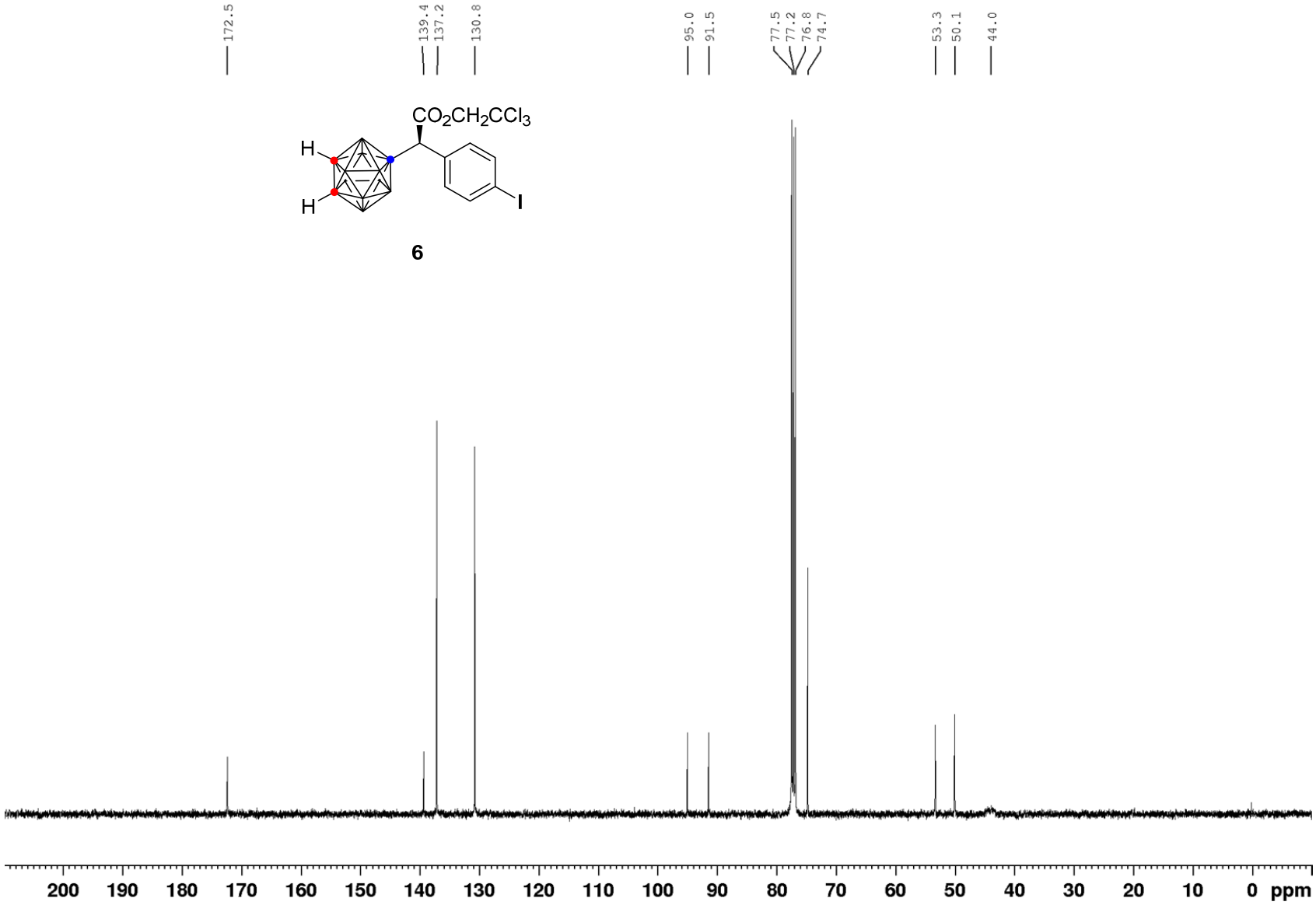
5

^{1}H NMR (400 MHz, $CDCl_3$)

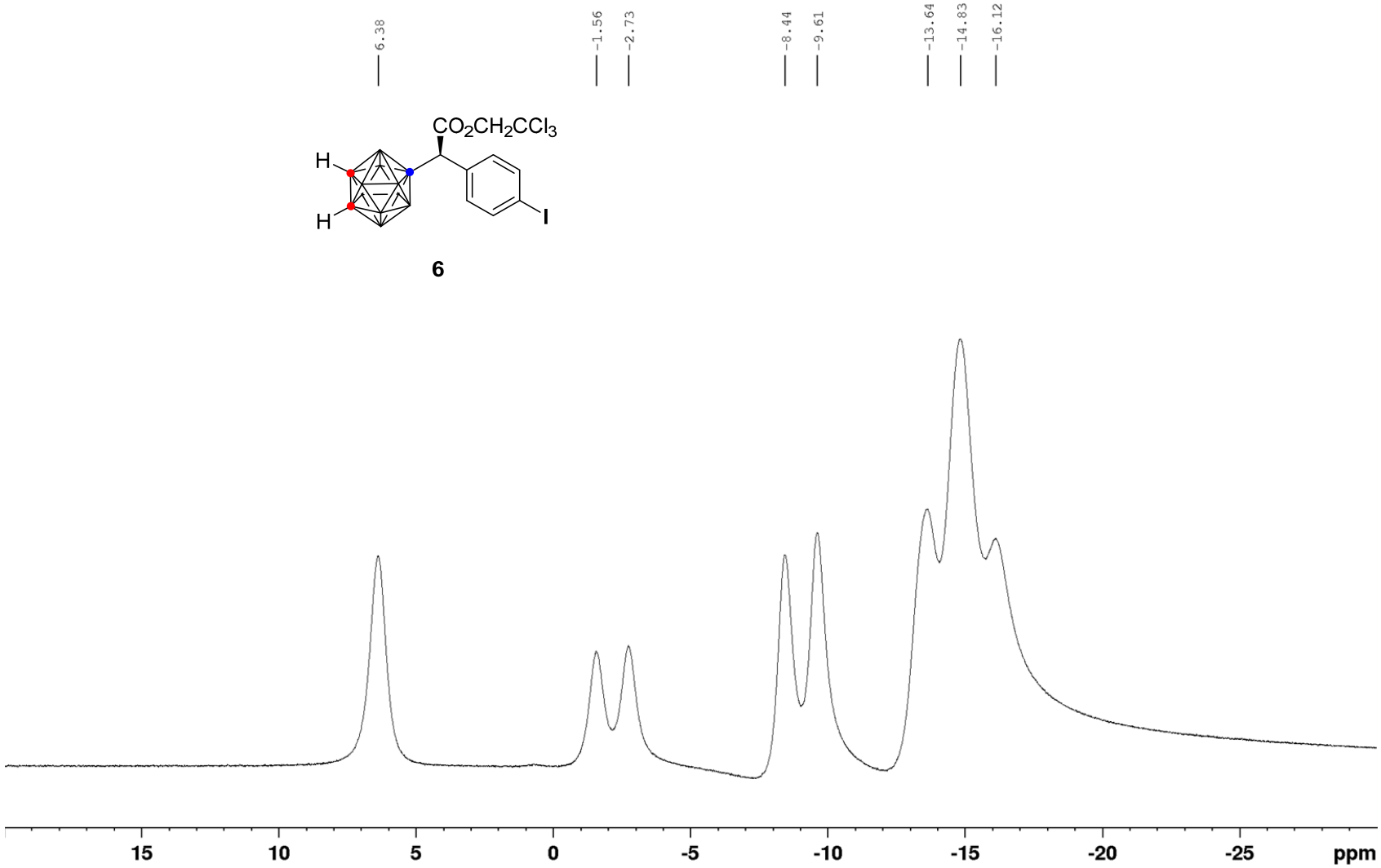


6

^{13}C NMR (100 MHz, $CDCl_3$)

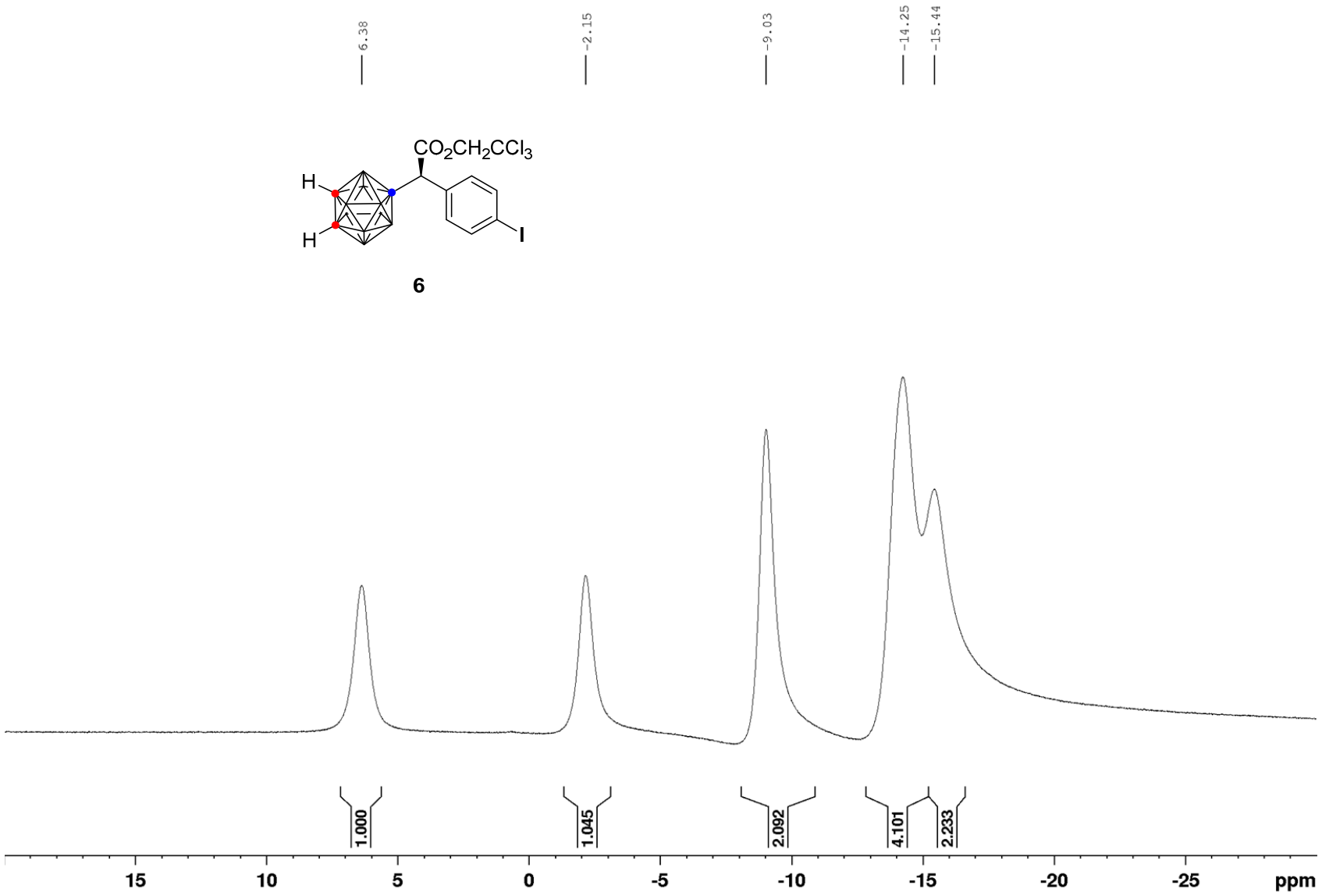


^{11}B NMR (128 MHz, $CDCl_3$)

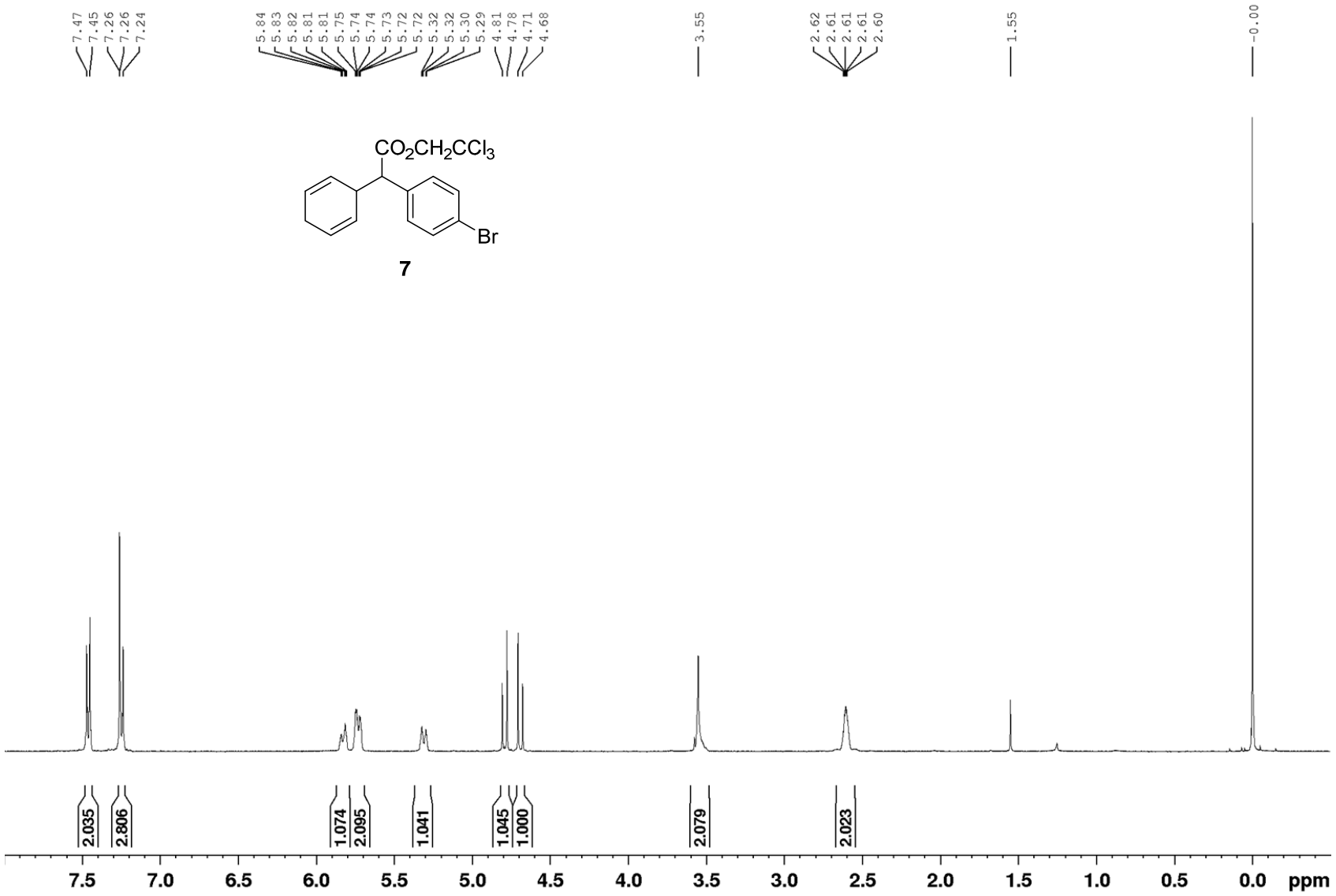


6

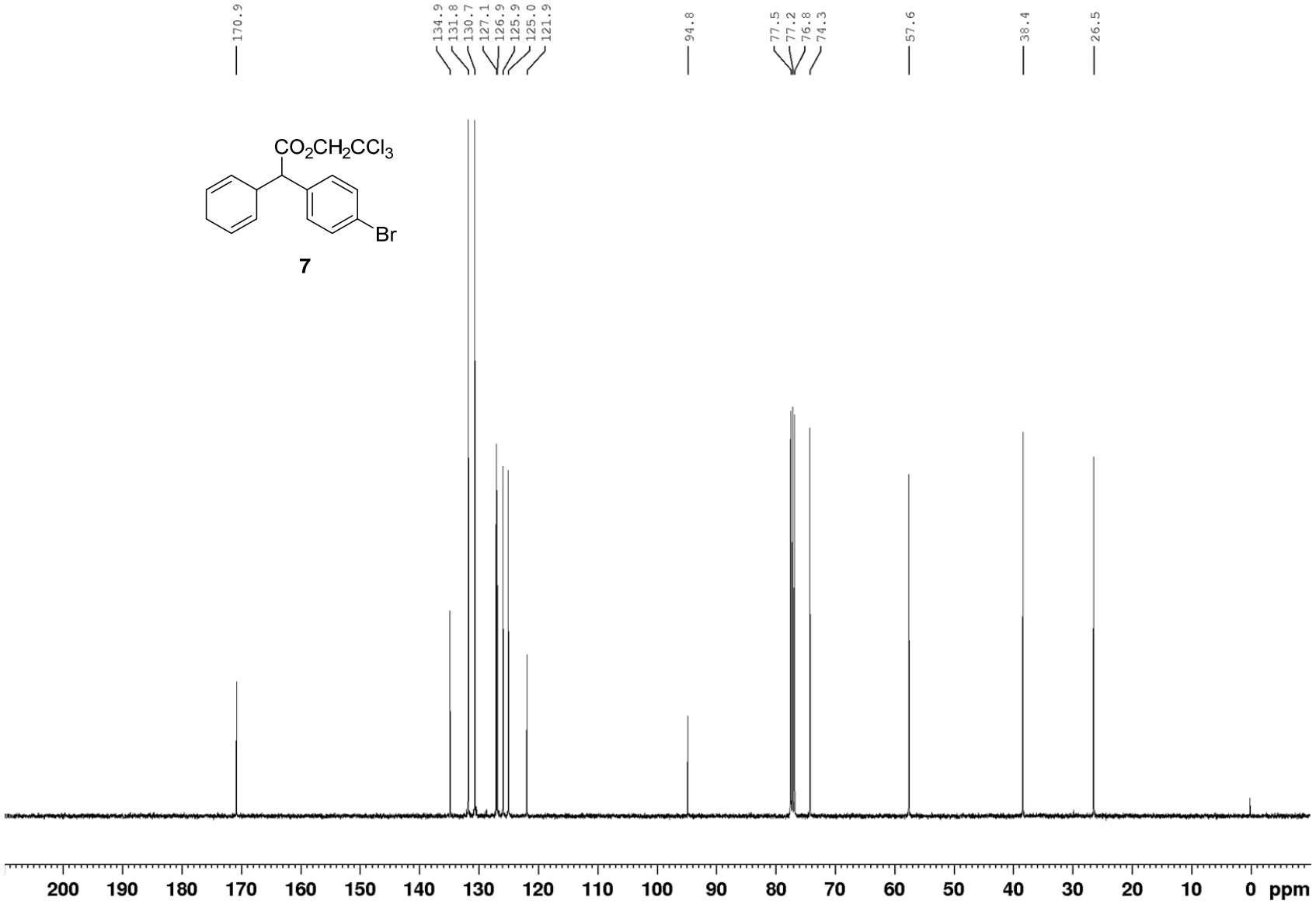
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



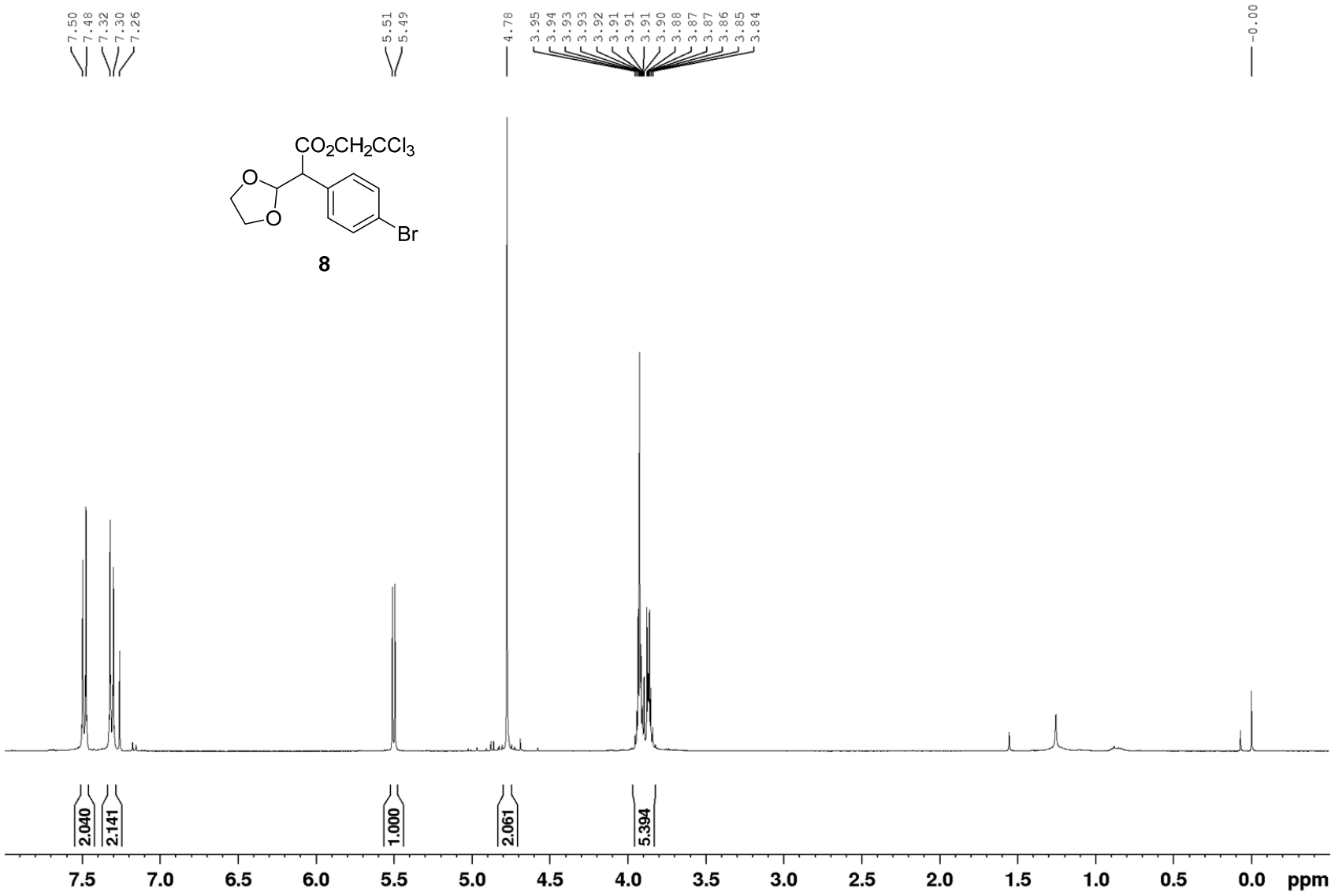
^{1}H NMR (400 MHz, $CDCl_3$)



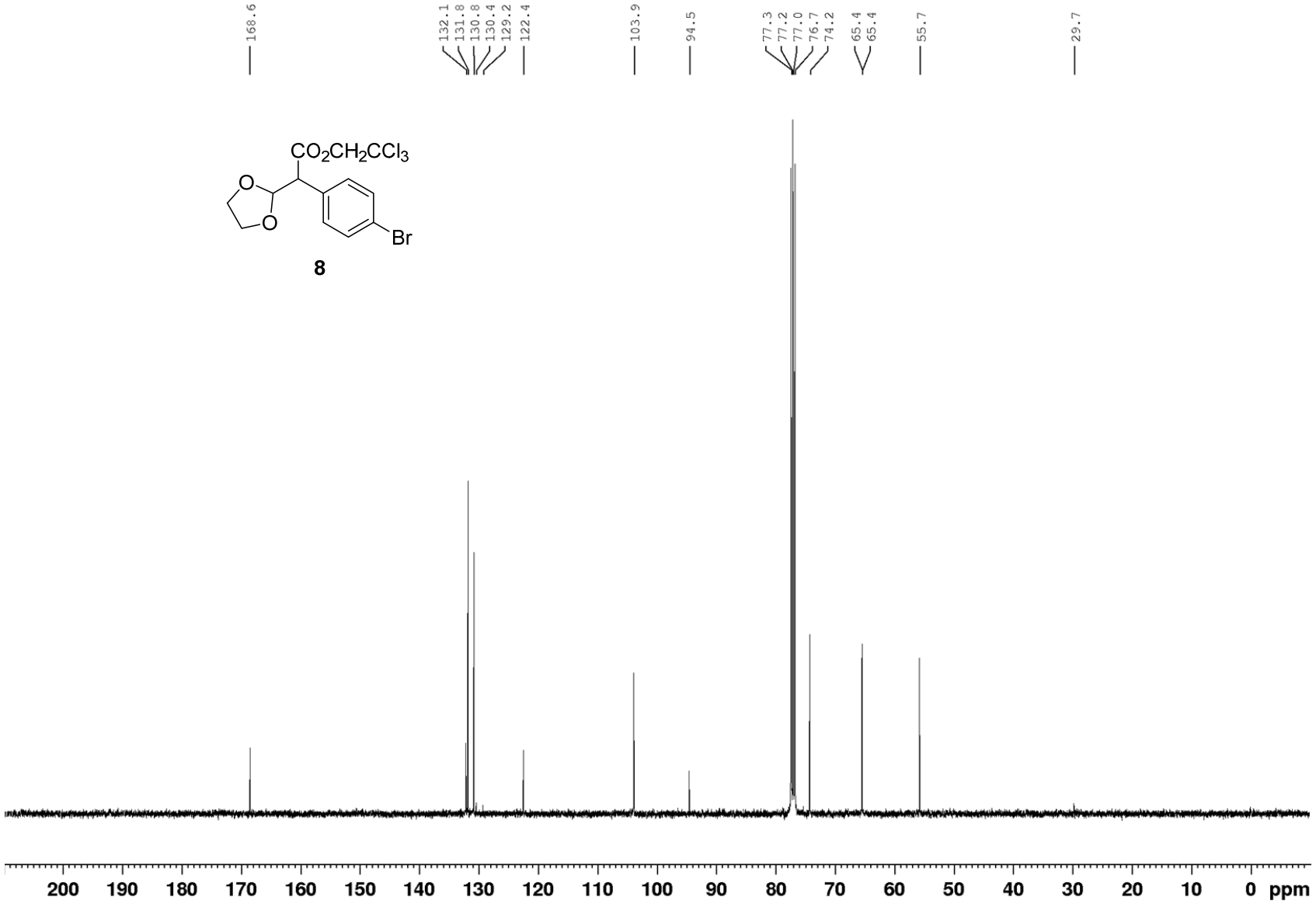
^{13}C NMR (100 MHz, $CDCl_3$)



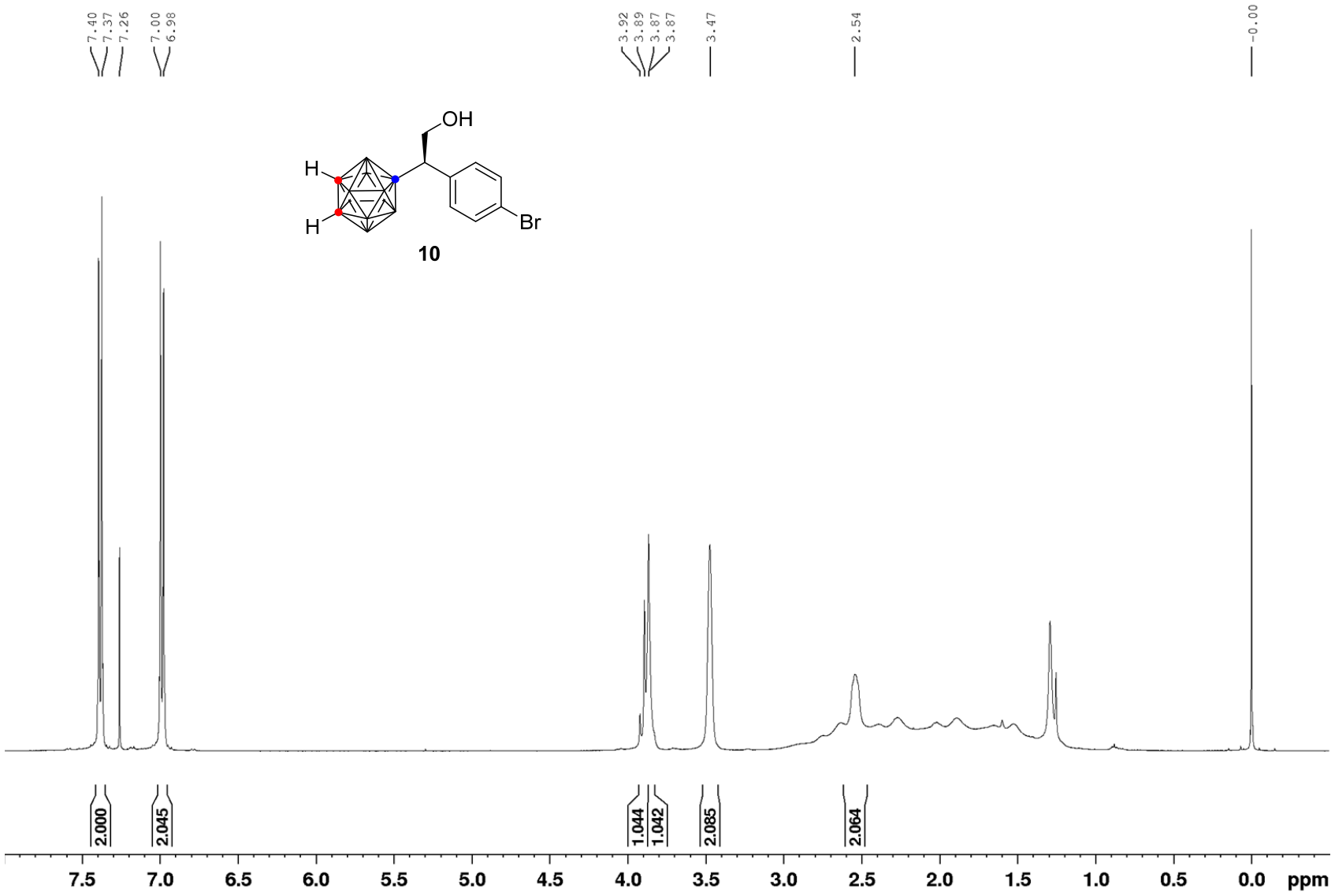
^{1}H NMR (400 MHz, $CDCl_3$)



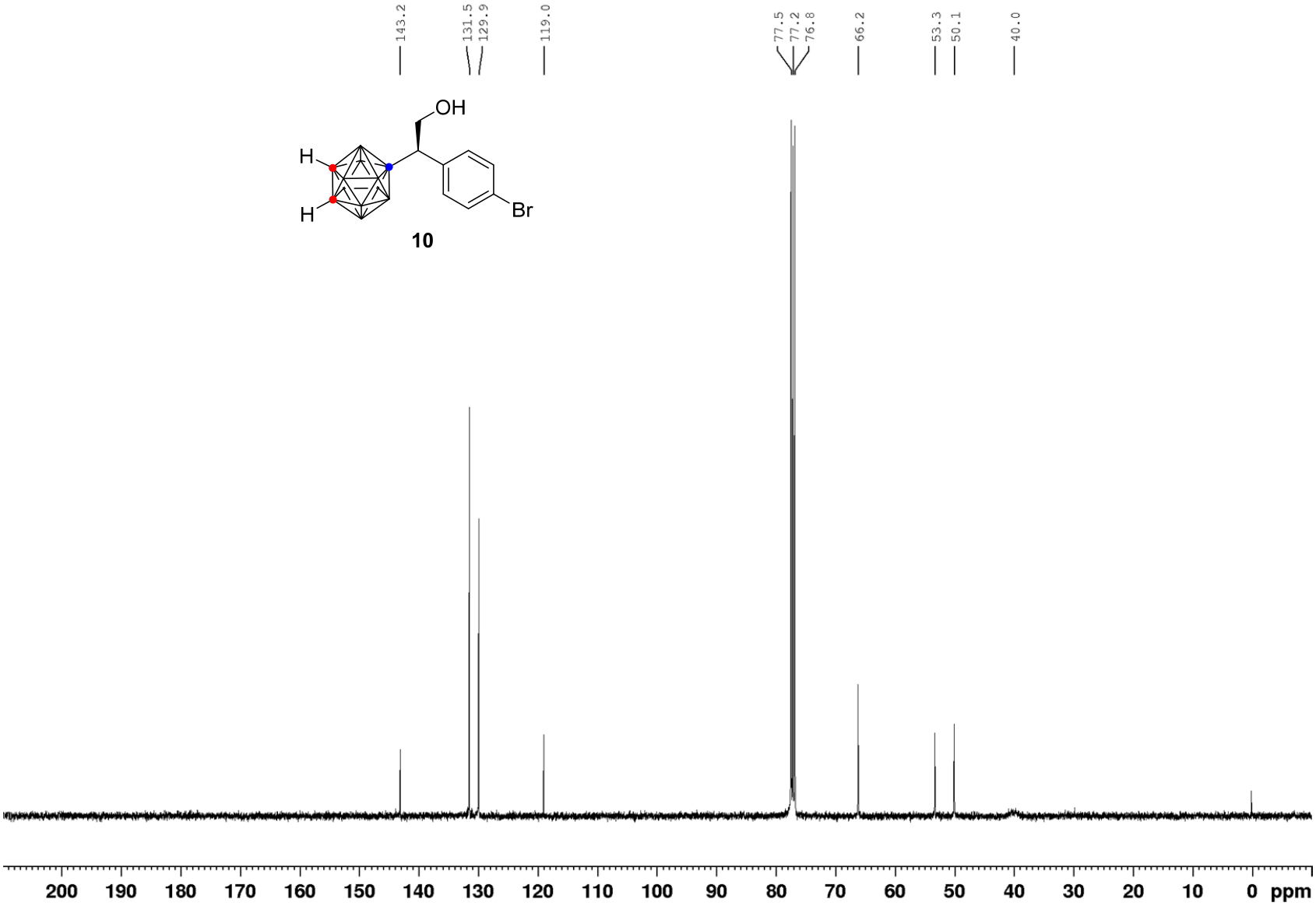
^{13}C NMR (100 MHz, $CDCl_3$)



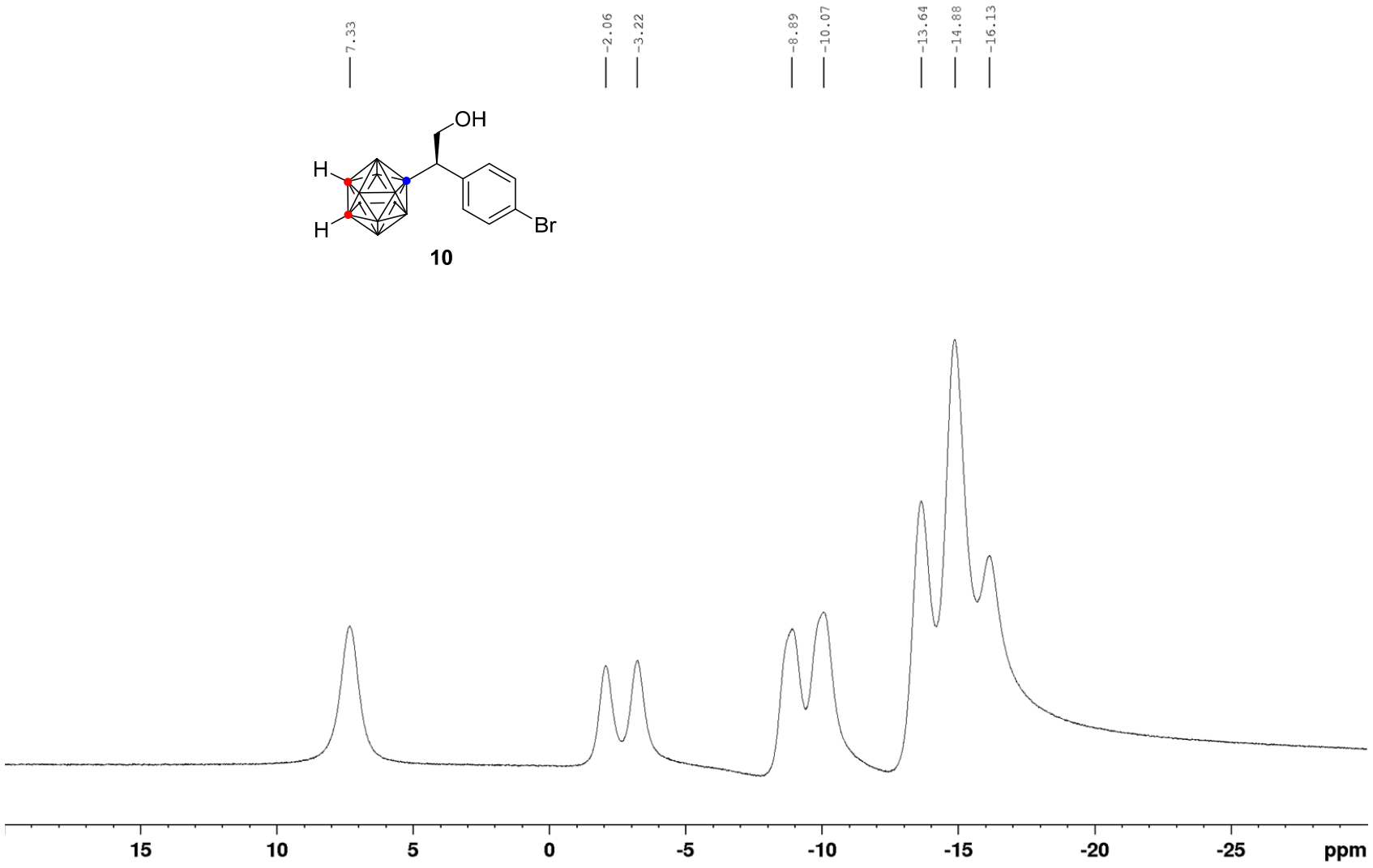
^{1}H NMR (400 MHz, $CDCl_3$)



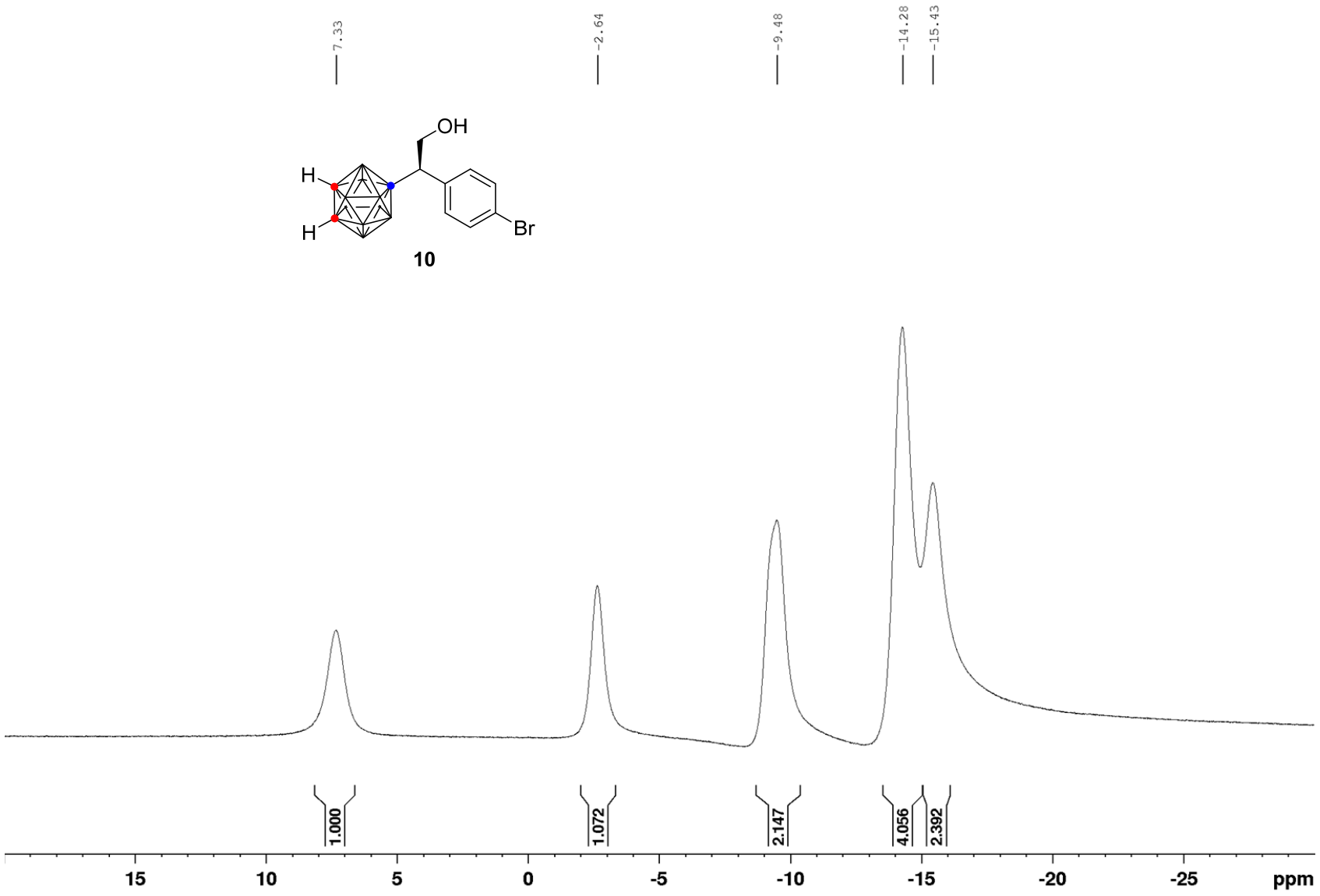
^{13}C NMR (100 MHz, $CDCl_3$)



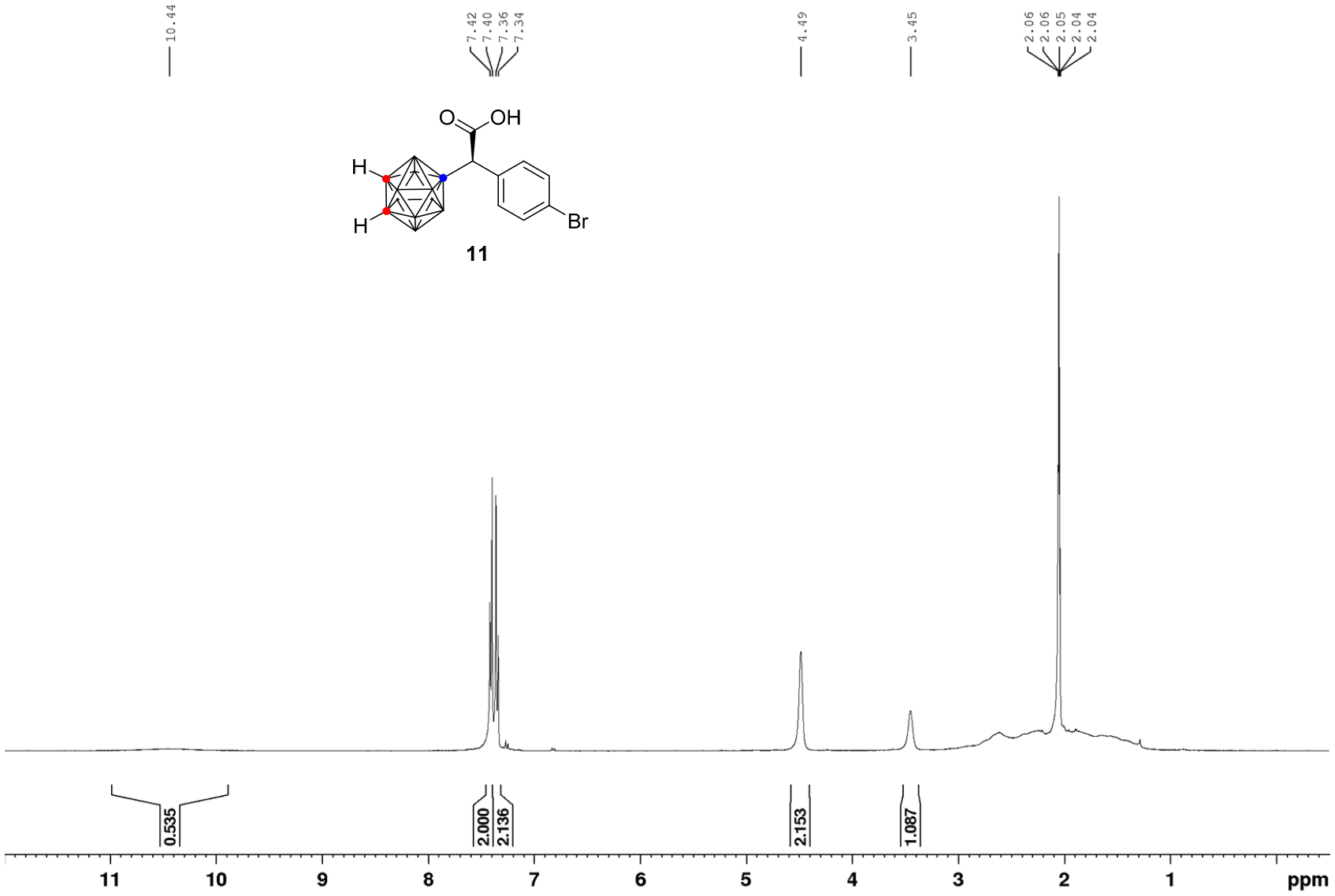
^{11}B NMR (128 MHz, $CDCl_3$)



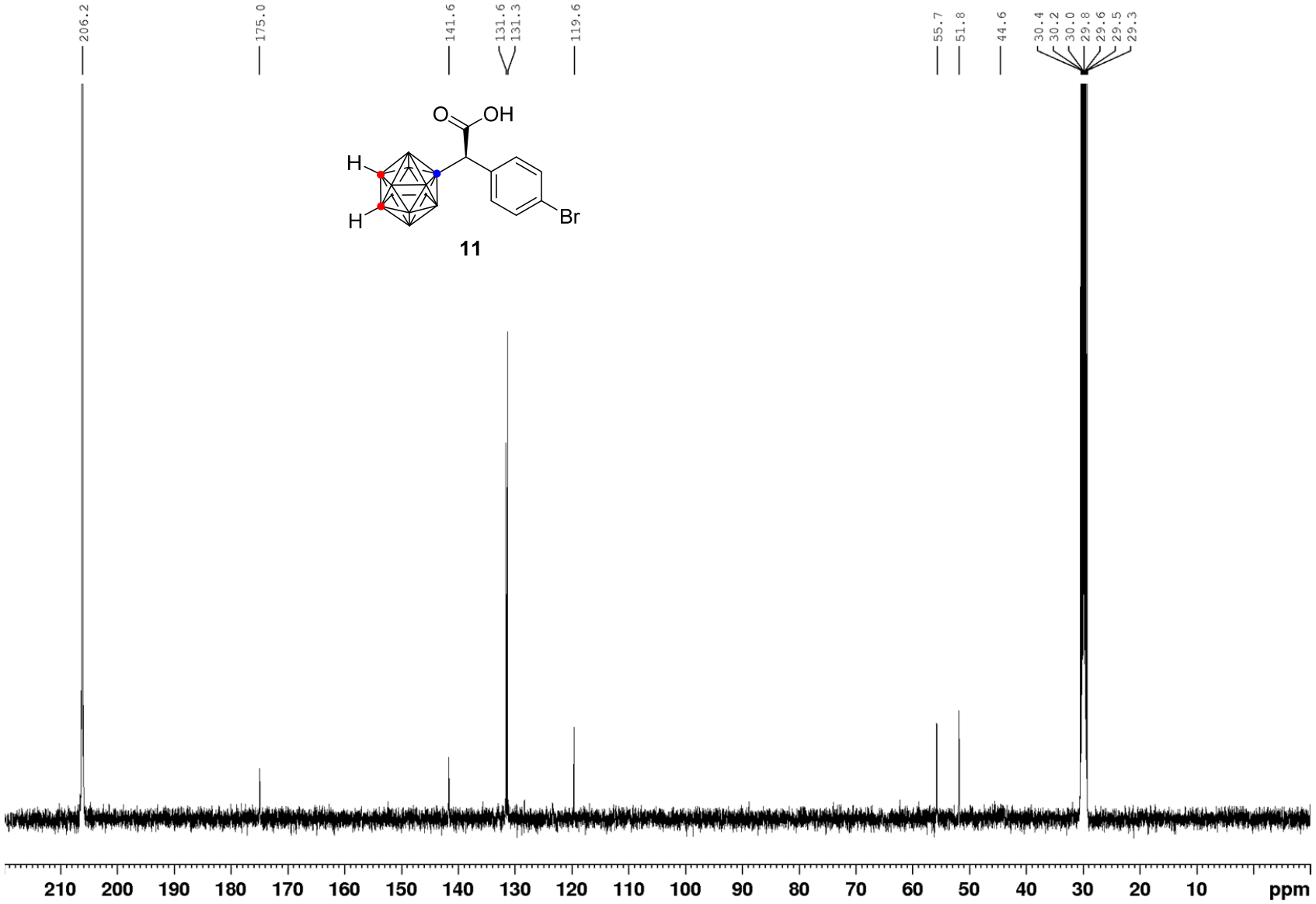
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



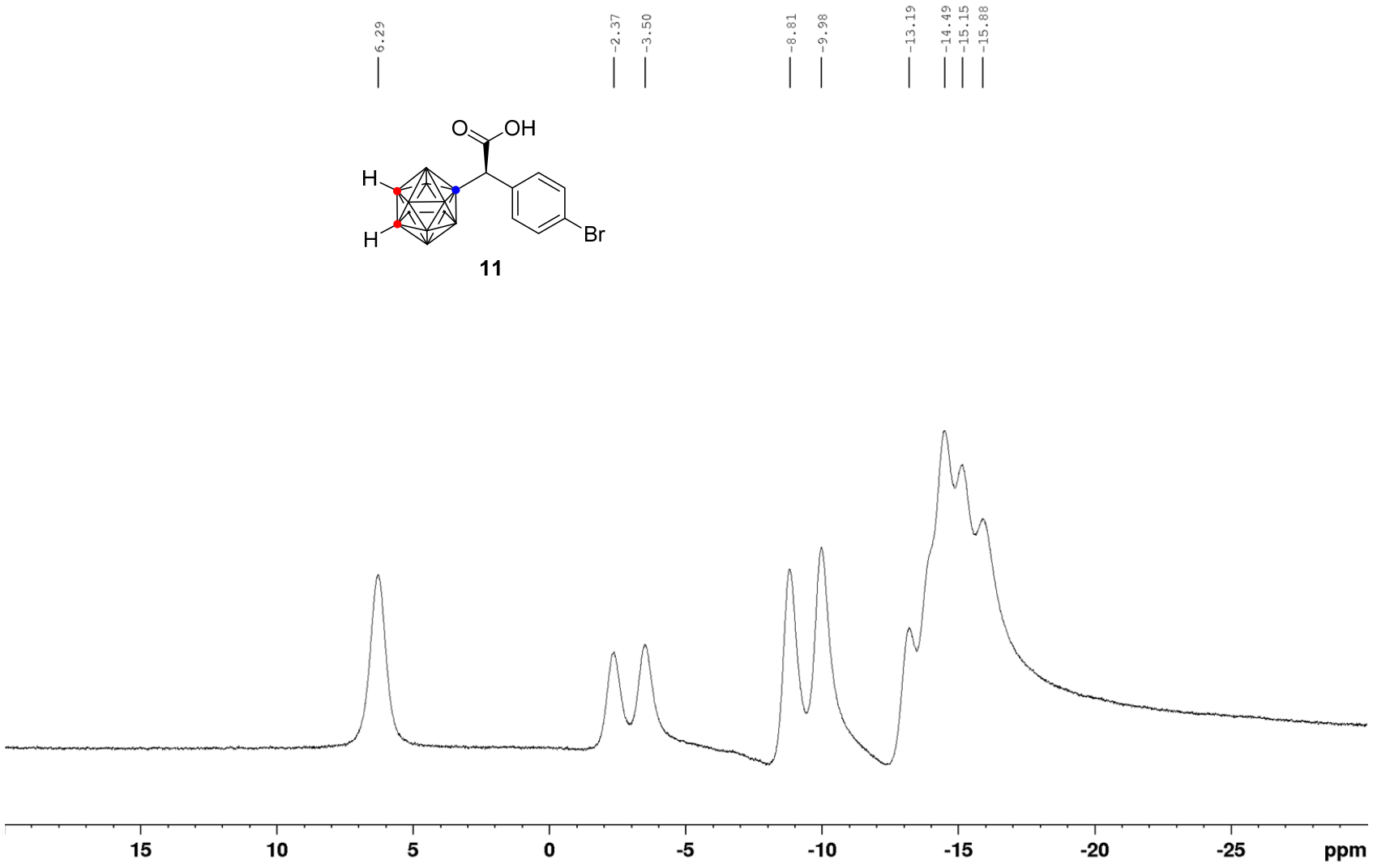
^{1}H NMR (400 MHz, acetone-d_6)



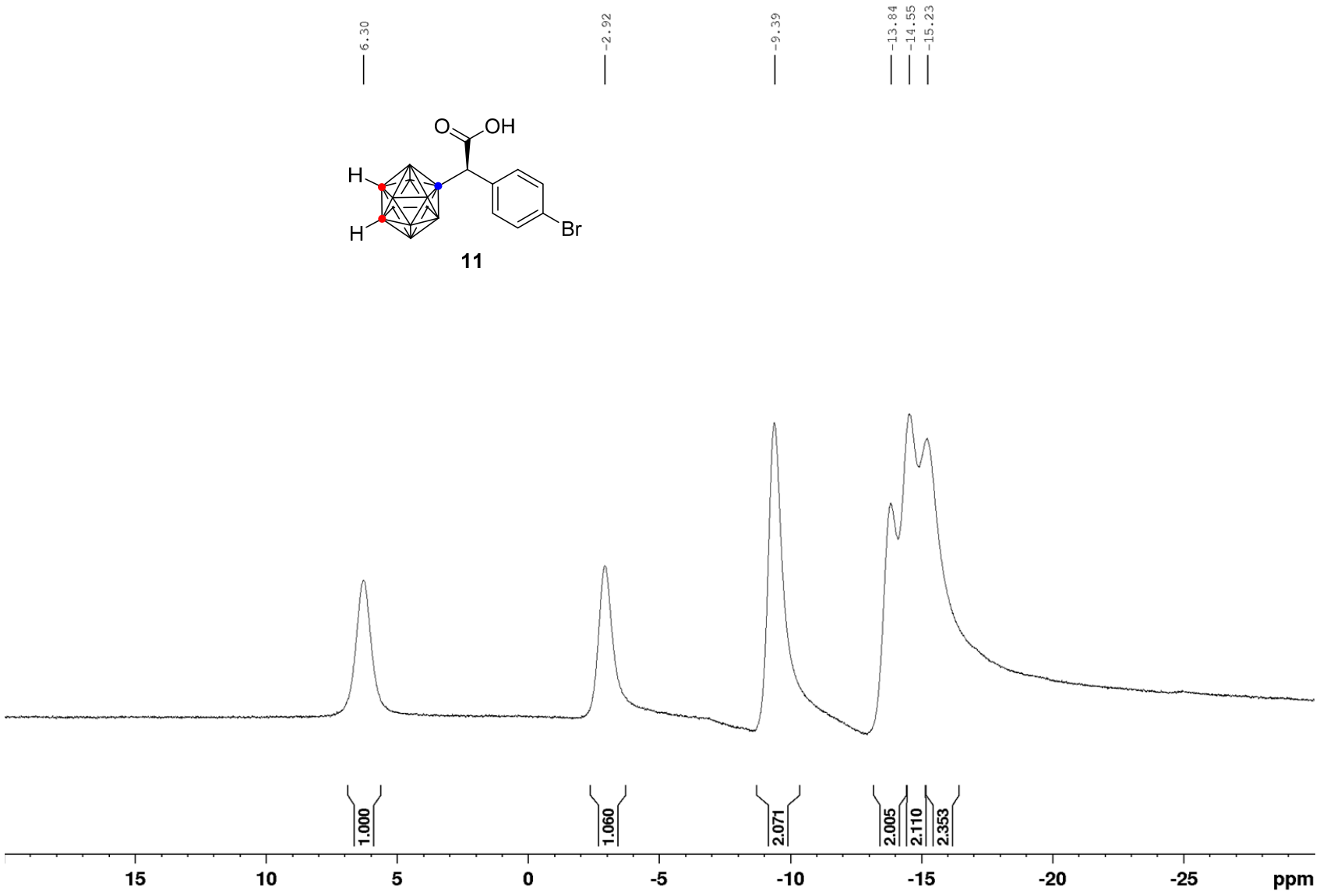
^{13}C NMR (100 MHz, acetone-d_6)



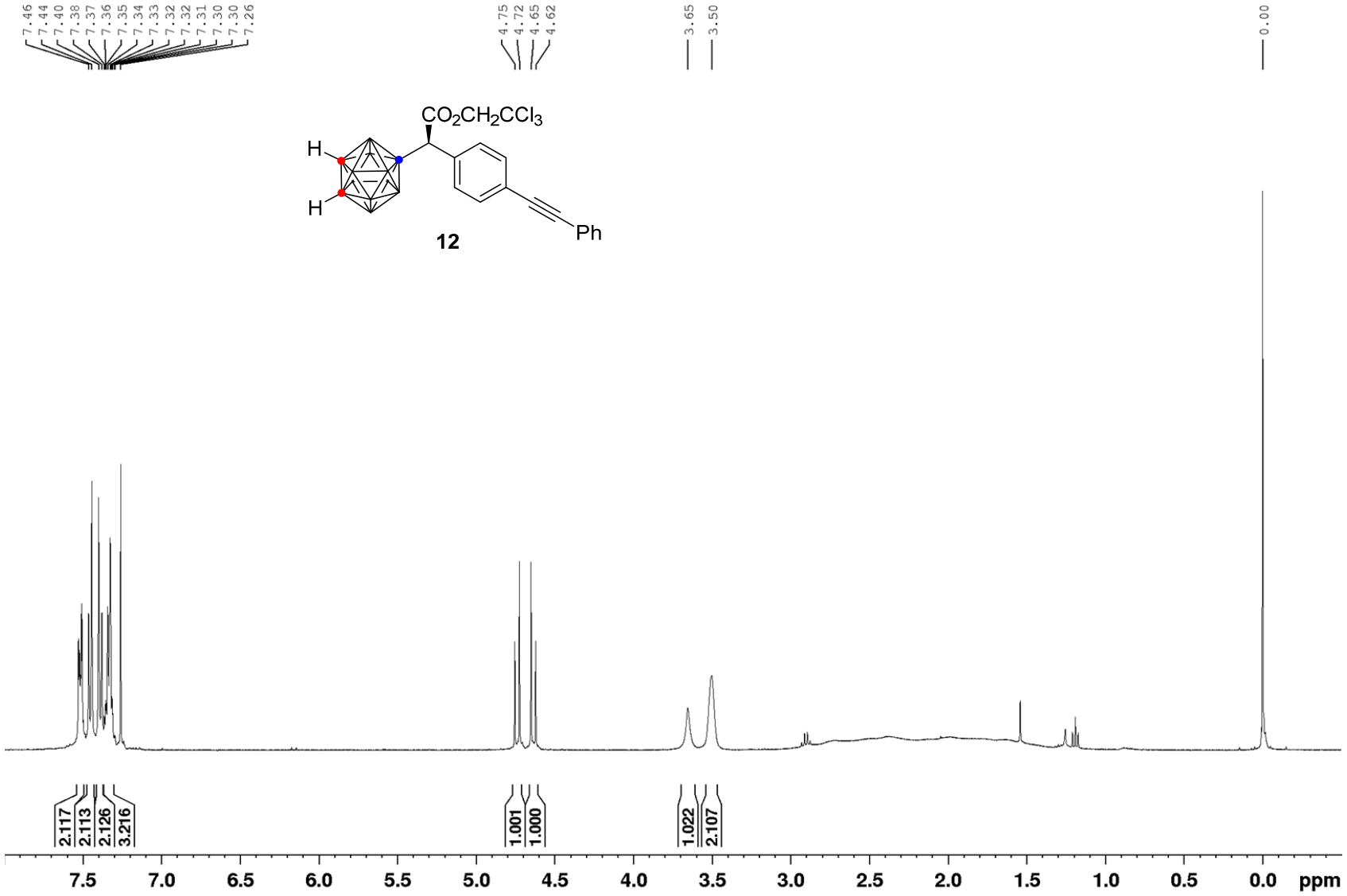
^{11}B NMR (128 MHz, acetone-d_6)



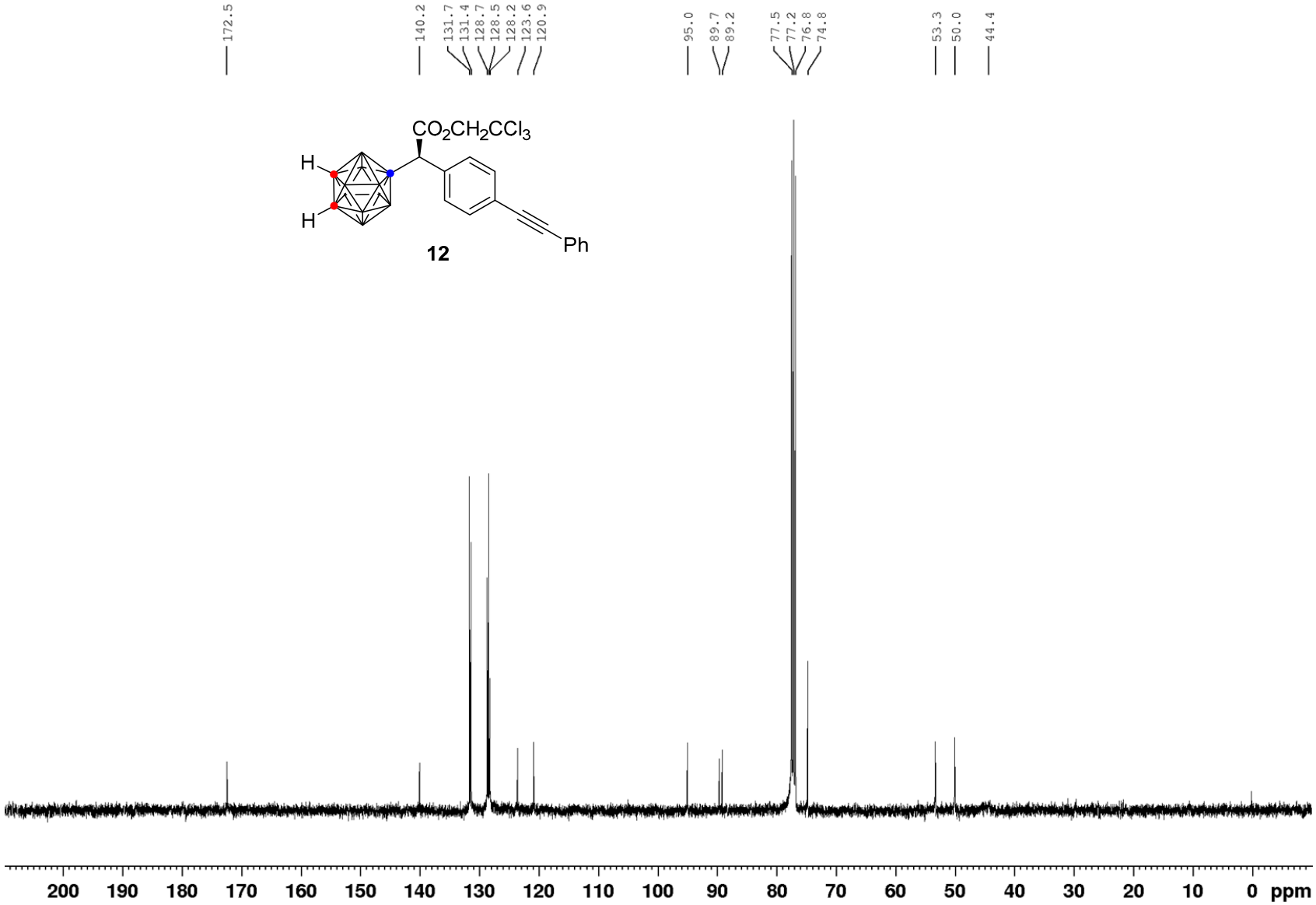
$^{11}B\{^{1}H\}$ NMR (128 MHz, acetone-d_6)



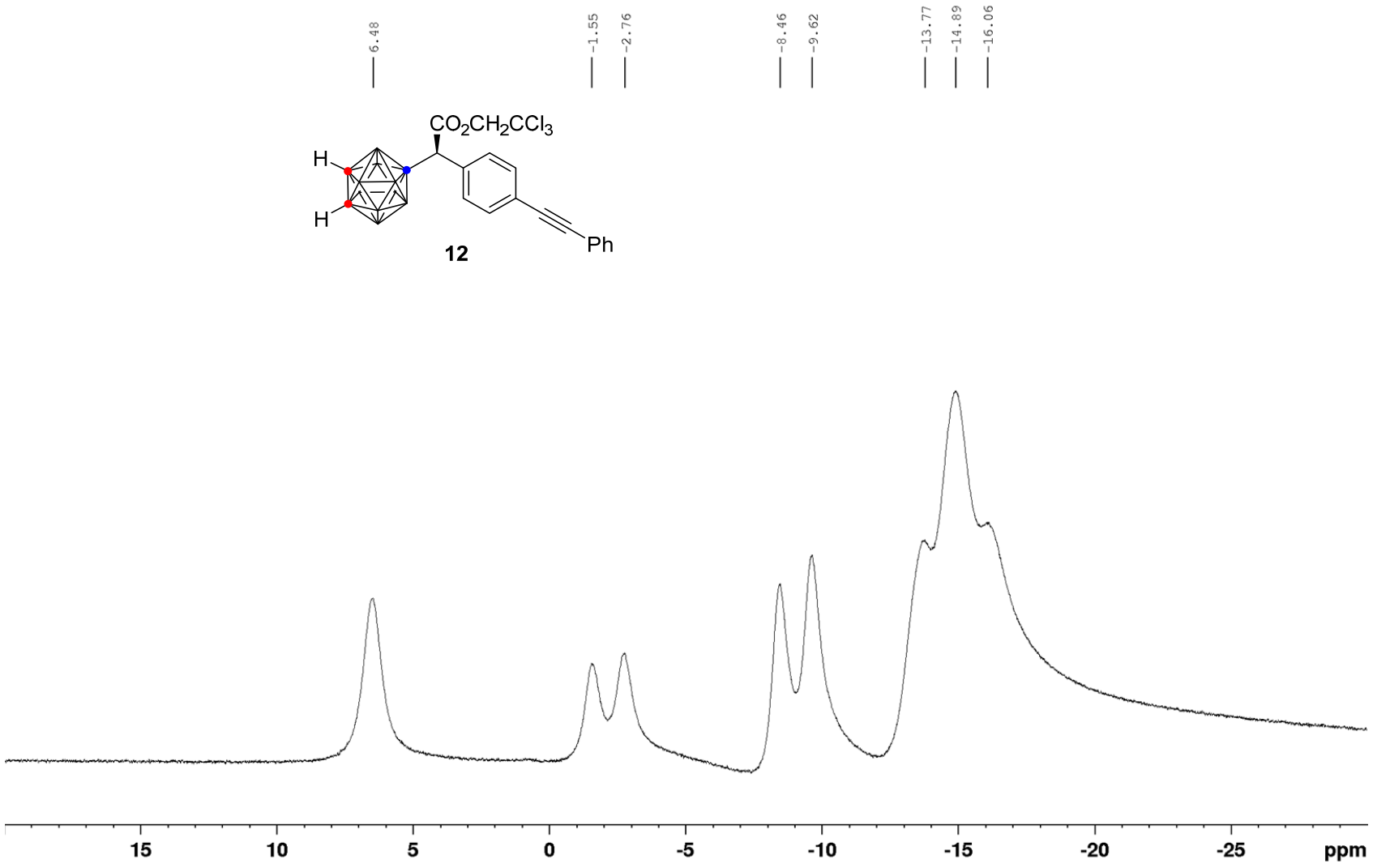
^{1}H NMR (400 MHz, $CDCl_3$)



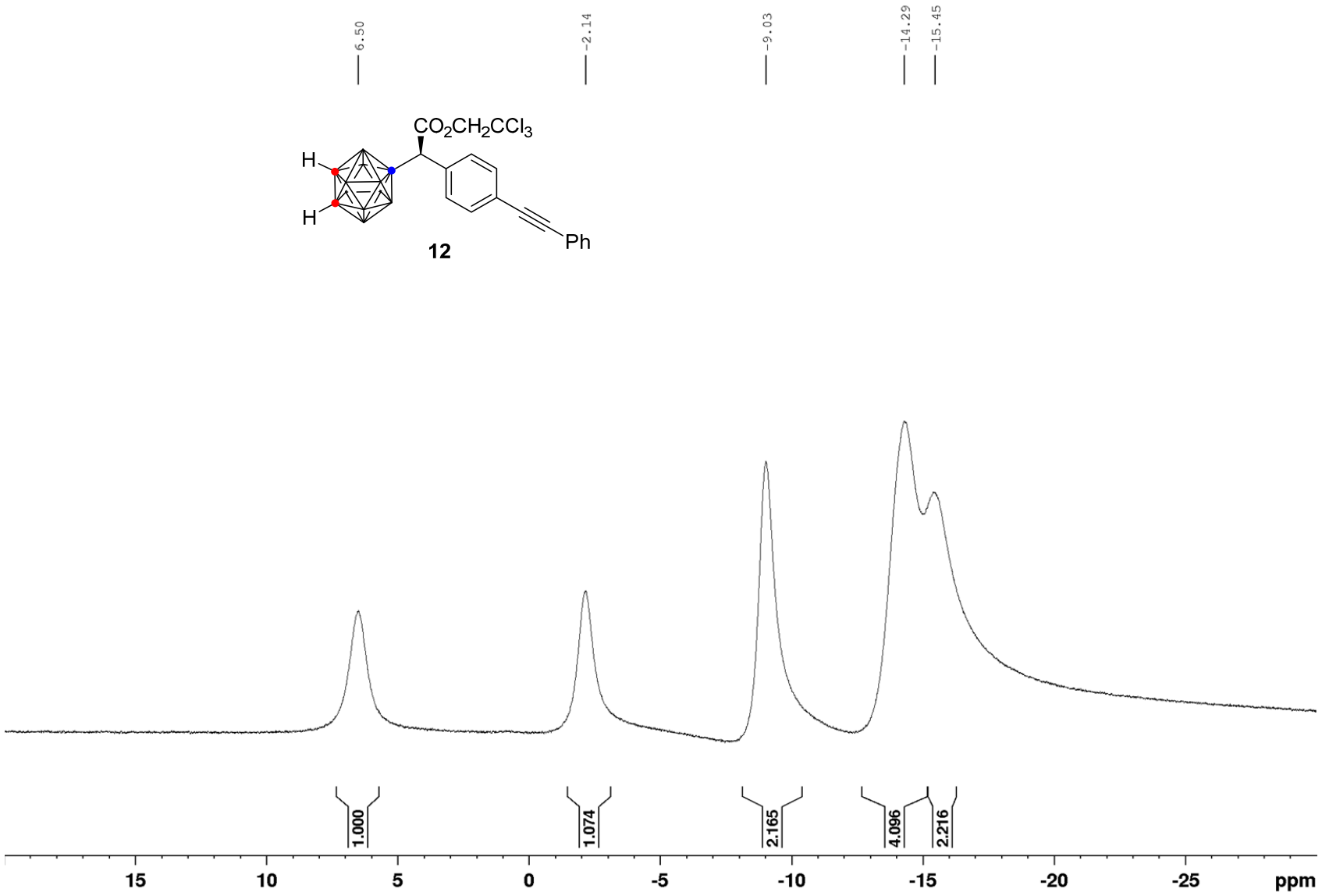
^{13}C NMR (100 MHz, $CDCl_3$)



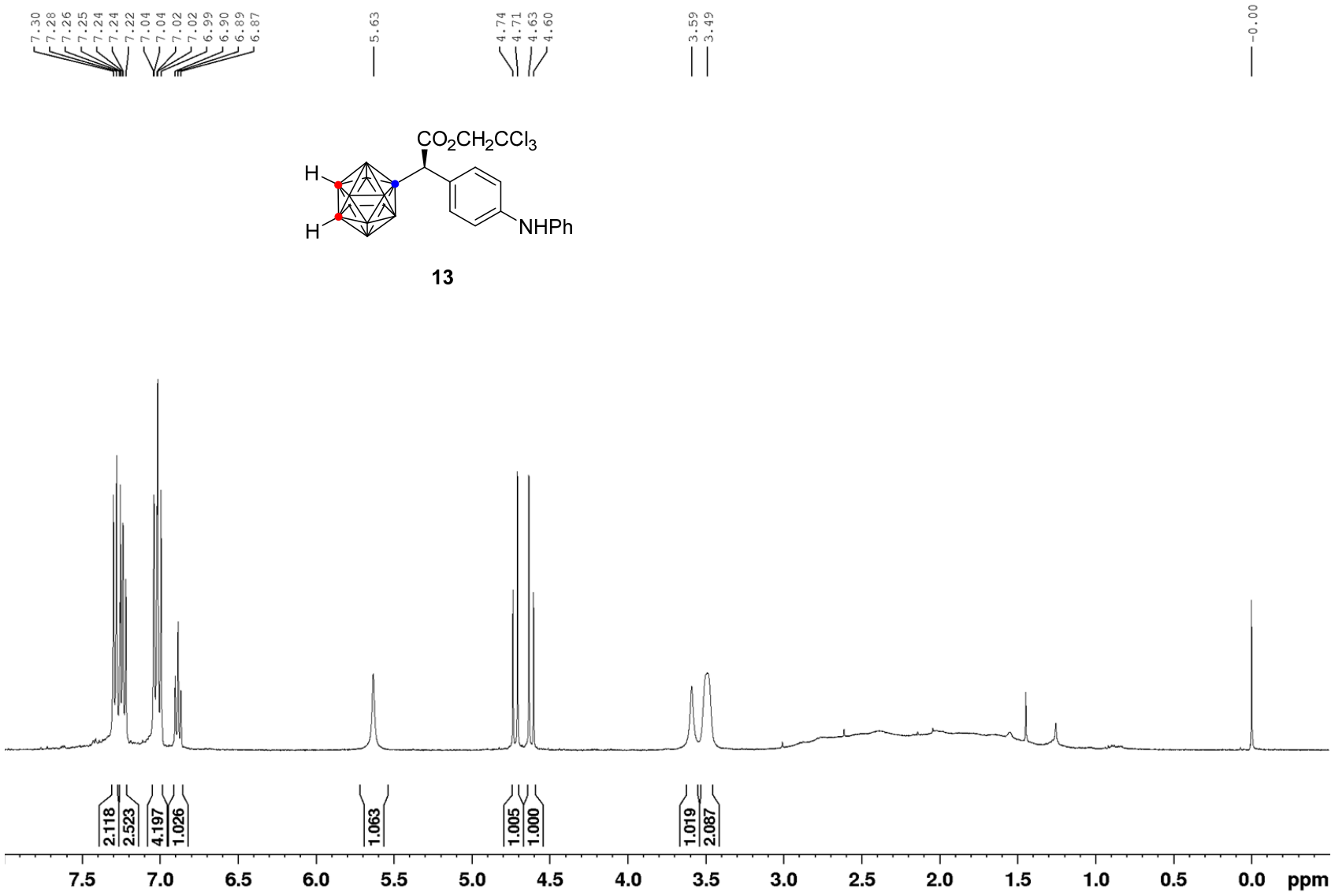
^{11}B NMR (128 MHz, $CDCl_3$)



$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)

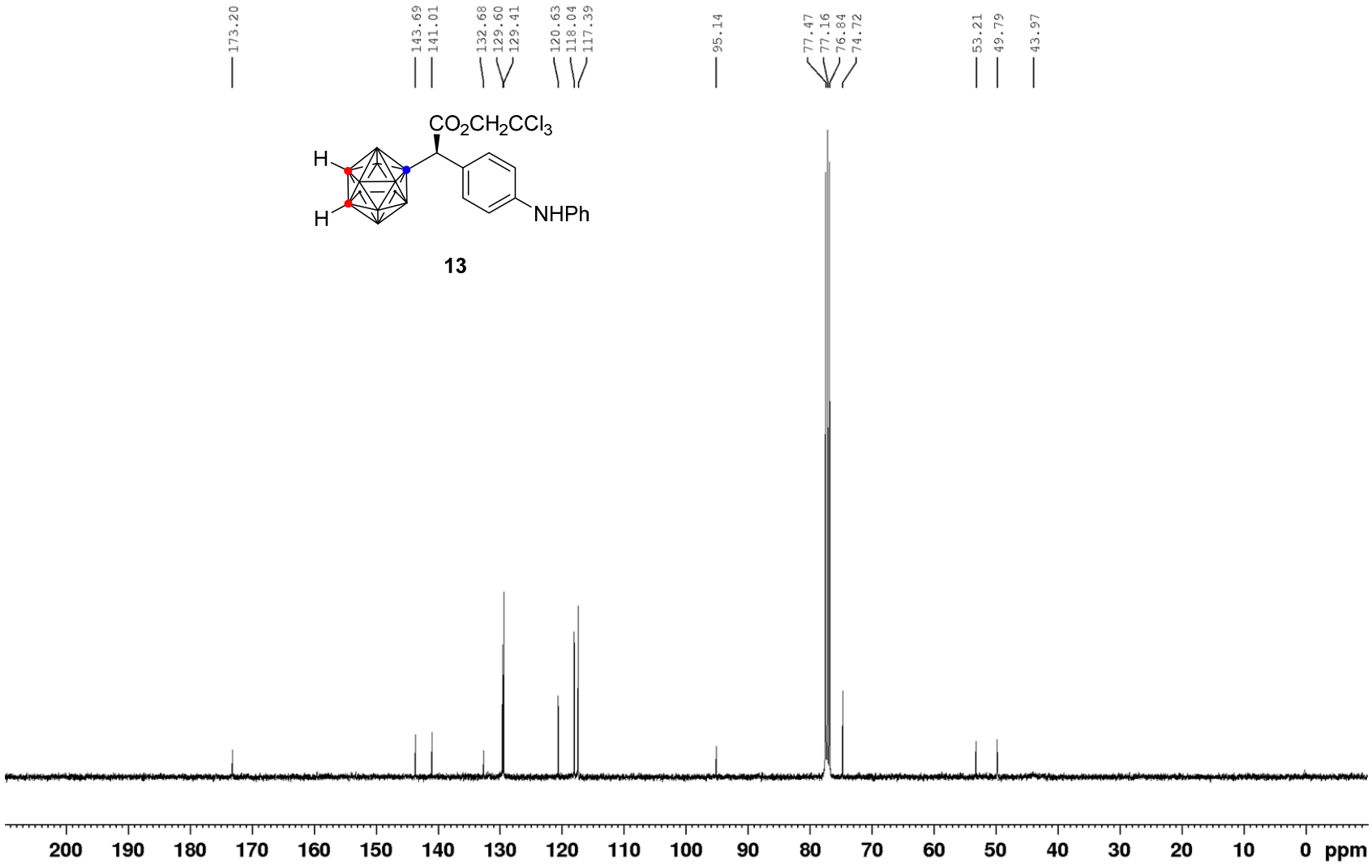


^{1}H NMR (400 MHz, $CDCl_3$)

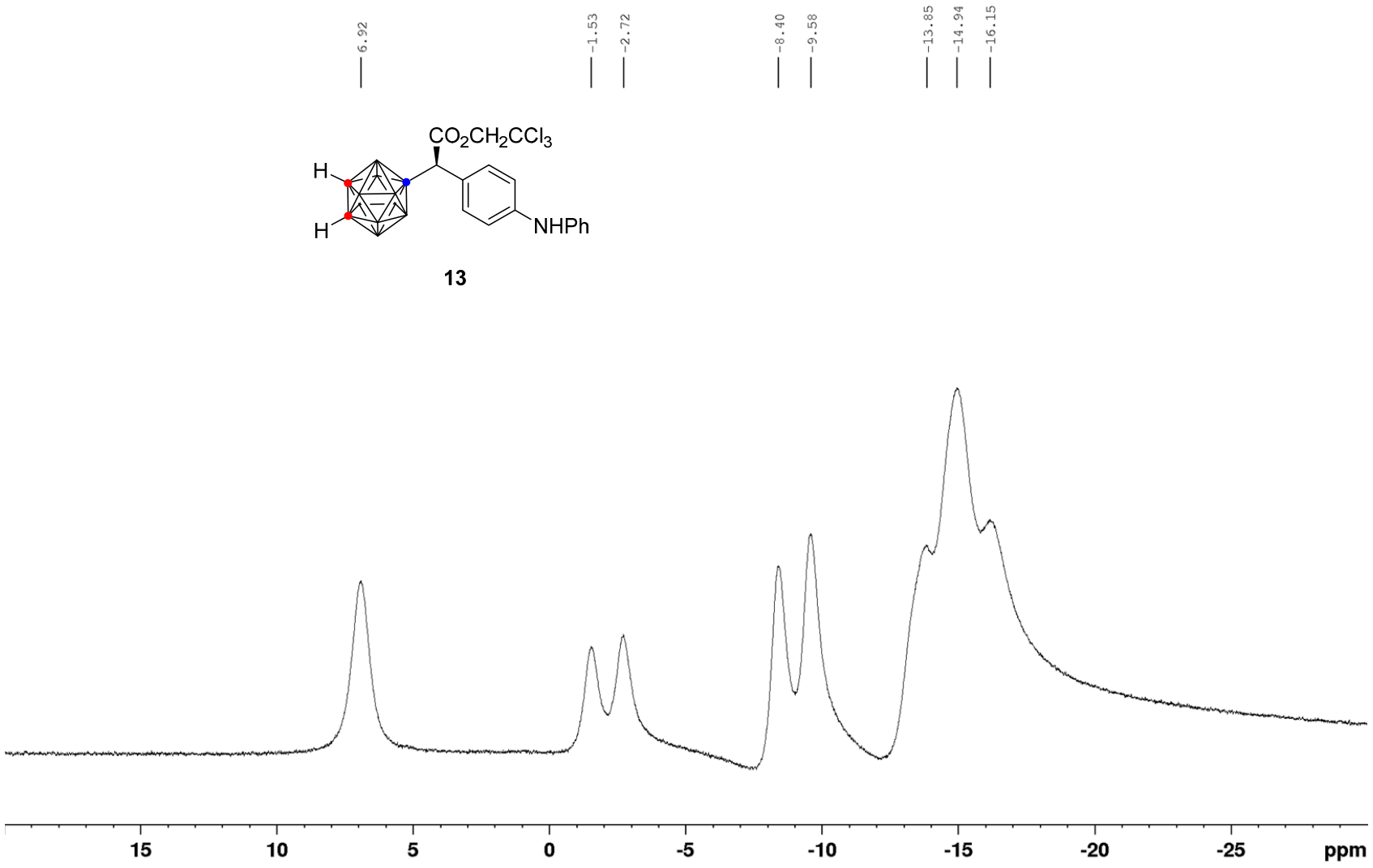


13

^{13}C NMR (100 MHz, $CDCl_3$)

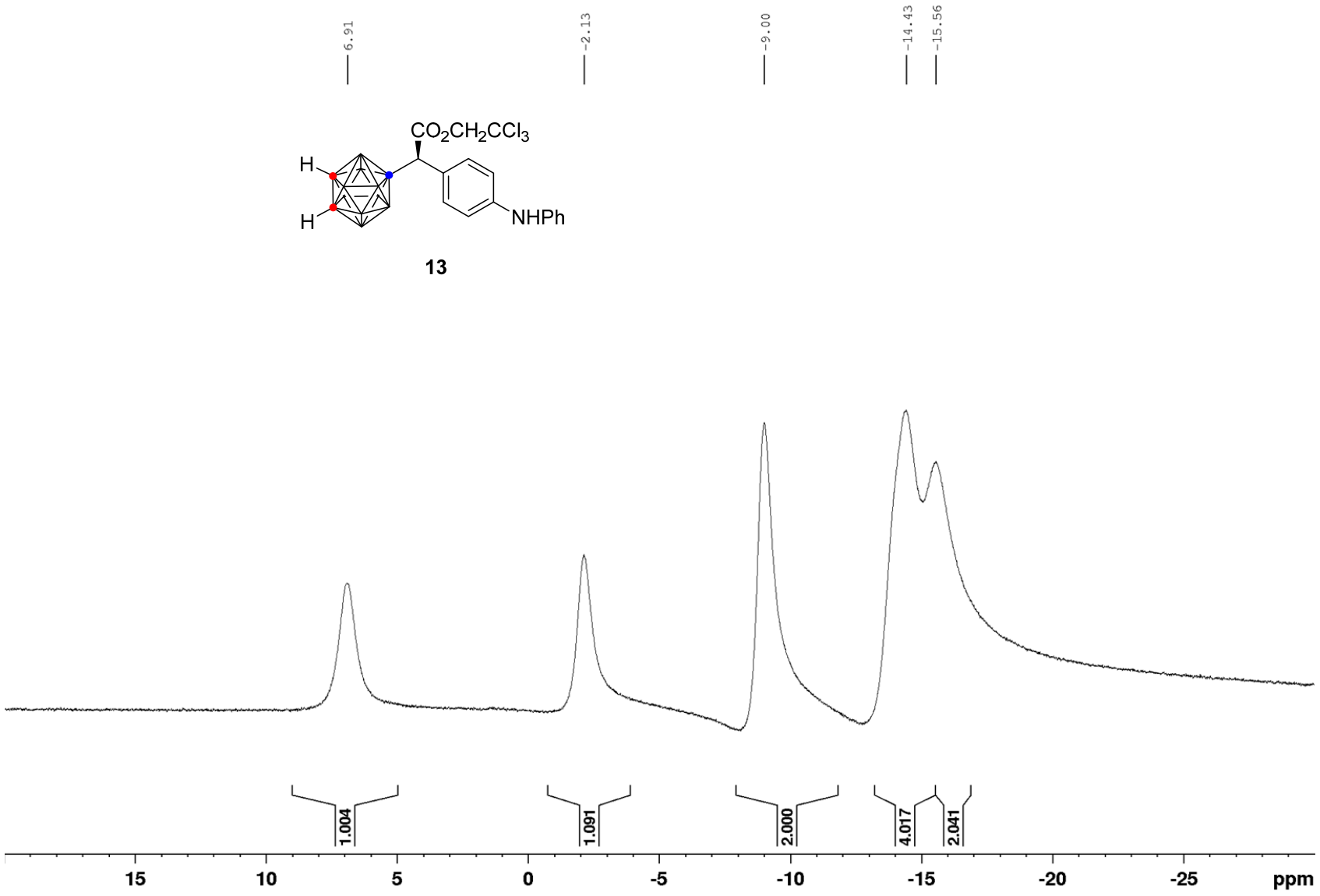


^{11}B NMR (128 MHz, $CDCl_3$)

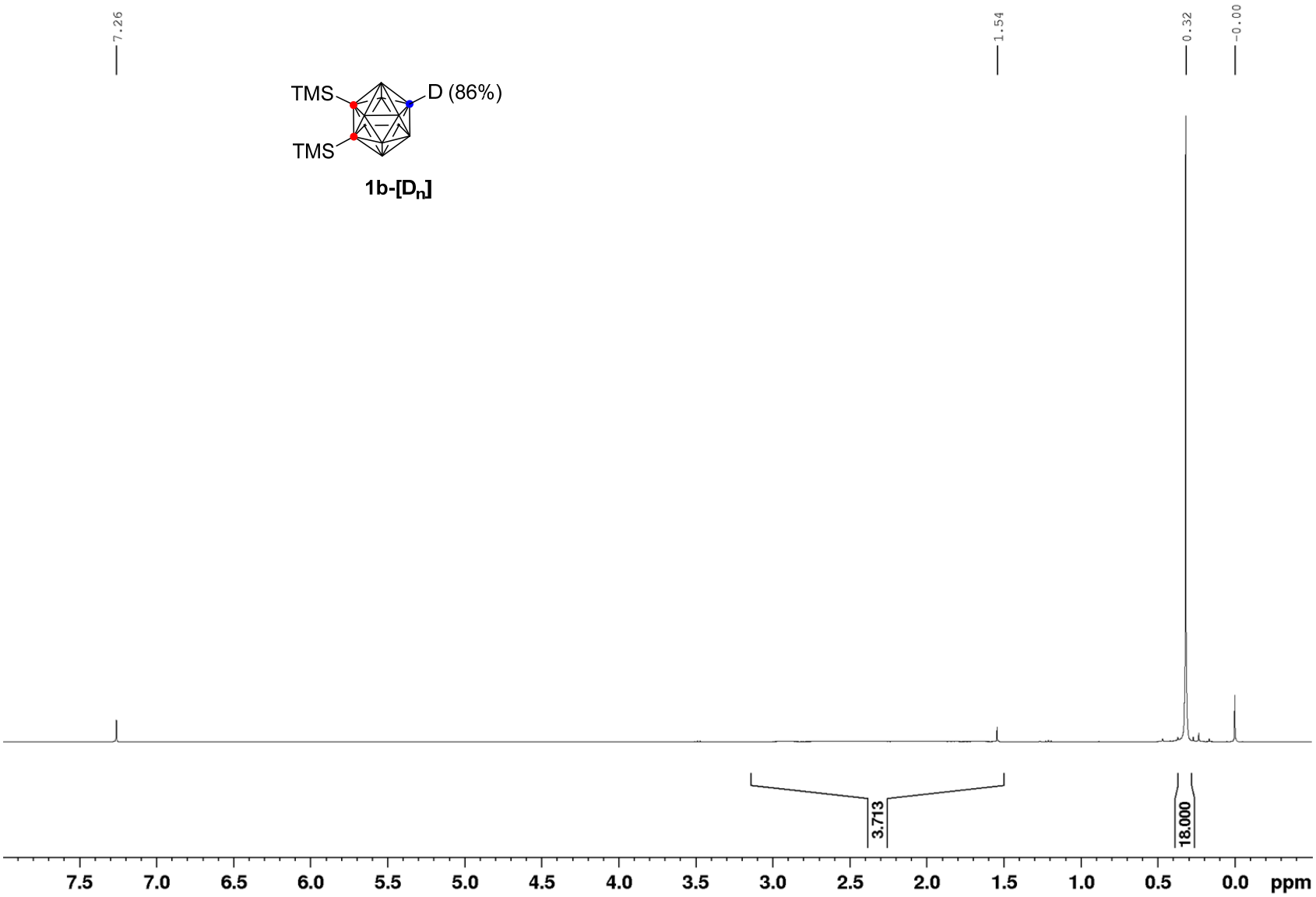


13

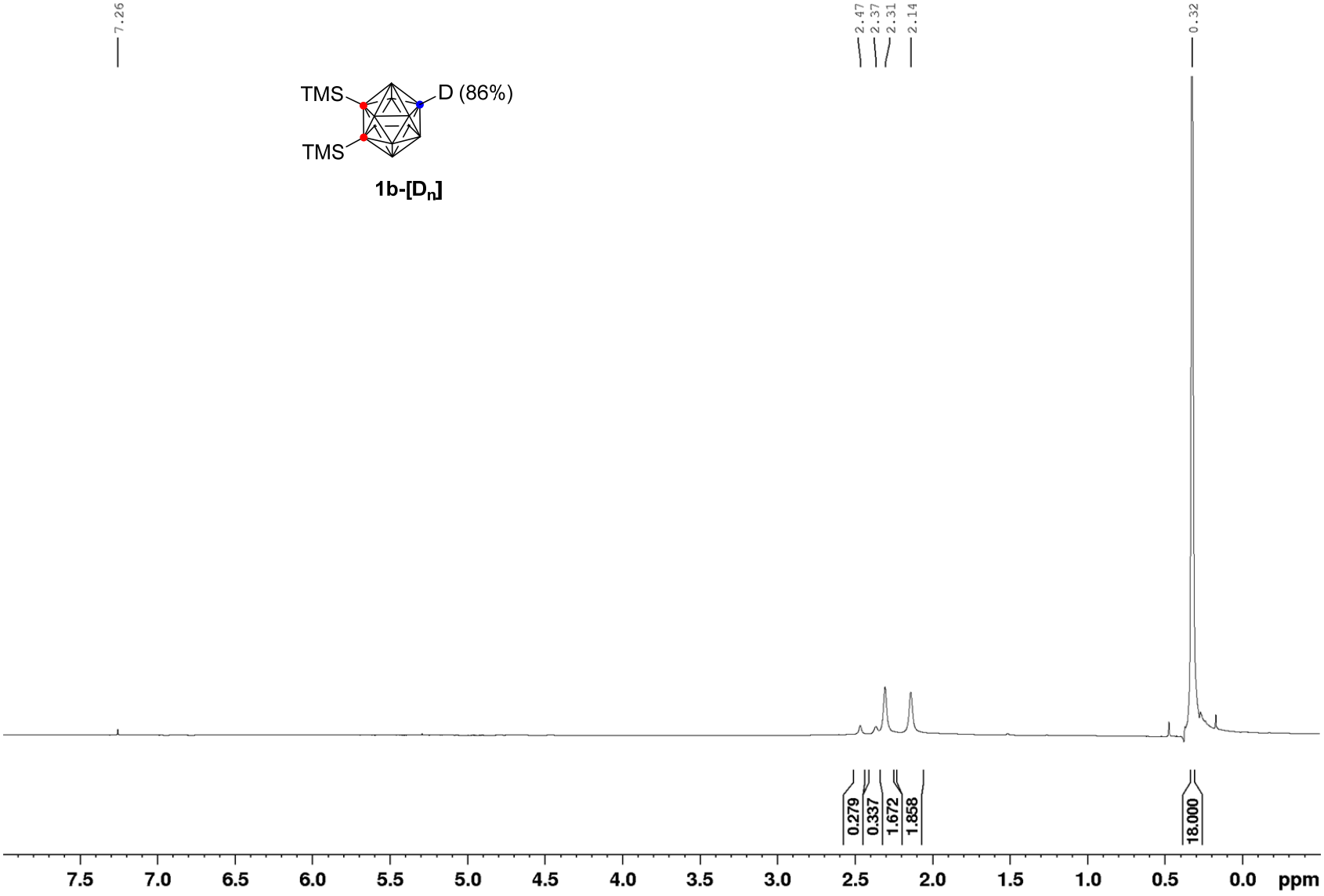
$^{11}B\{^{1}H\}$ NMR (128 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



$^{1}H\{^{11}B\}$ NMR (400 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)