

Supplementary Information

Site- and enantioselective B–H functionalization of carboranes

Kyungsup Lee^{1,6}, Gisela A. González-Montiel^{2,6}, Hyeonsik Eom¹, Tae Hyeon Kim¹, Hee Chan Noh¹, Abdikani Omar Farah², Henry R. Wise², Dongwook Kim^{3,4}, Paul Ha-Yeon Cheong^{2*}, Phil Ho Lee^{1,5*}

Corresponding authors: Paul Ha-Yeon Cheong, paulc@science.oregonstate.edu;
Phil Ho Lee, phlee@kangwon.ac.kr

¹Department of Chemistry, Kangwon National University, Chuncheon, 24341, Republic of Korea.

²Department of Chemistry, Oregon State University, 153 Gilbert Hall, Corvallis, Oregon, 97331-2145, United States.

³Department of Chemistry, Korea Advanced Institute of Science and Technology, Daejeon, 34141, Republic of Korea.

⁴Center for Catalytic Hydrocarbon Functionalizations, Institute for Basic Science, Daejeon, 34141, Republic of Korea.

⁵Institute for Molecular Science and Fusion Technology, Kangwon National University, Chuncheon, 24341, Republic of Korea.

⁶These authors contributed equally to this work.

*Corresponding authors. Email: phlee@kangwon.ac.kr (P.H.L.)
paulc@science.oregonstate.edu (P.H.-Y.C.)

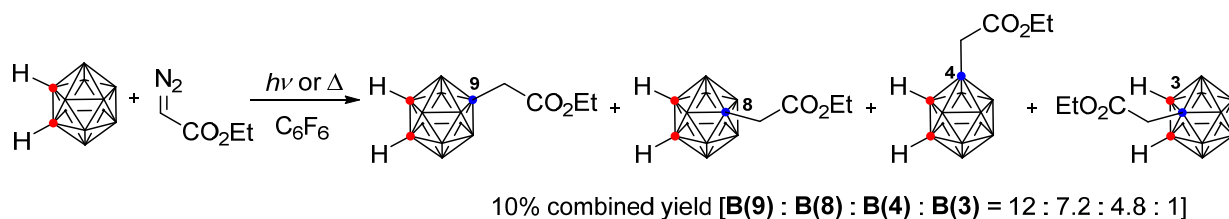
Table of Contents

1. Experimental Section.....	S3
2. Previously Reported Reactions of Carboranes with Carbenes.....	S4
3. Preparation of Carborane Derivatives.....	S5
4. Preparation of Diazo Compounds	S7
5. Detailed Screening of Reaction Conditions	S10
6. General Procedure of the Rh(II)-Catalyzed B(9)-Alkylation of Carboranes.....	S32
7. Larger Scale Procedure of One-Pot Reaction	S49
8. Comparison Experiments.....	S51
9. General Procedure of Functional Group Transformation	S53
10. Mechanistic Experiments	S56
11. Computational Section	S61
12. References.....	S109
13. X-ray Crystallography.....	S110
14. Crude ^1H NMR Spectra for Regioisomeric Ratio Determination	S120
15. HPLC Spectra for Enantiomeric Excess Determination.....	S152
16. ^1H , ^{13}C , ^{11}B , and ^{19}F NMR Data.....	S197

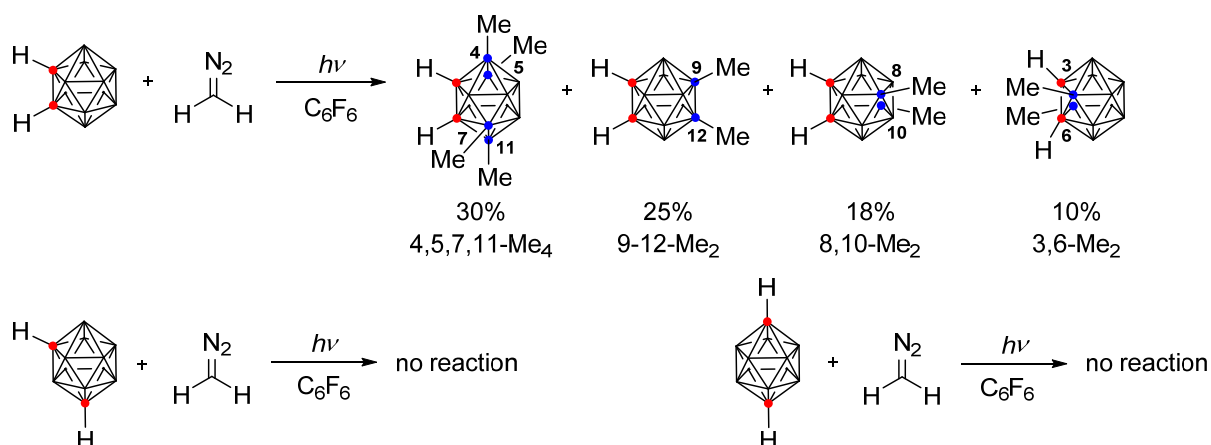
1. Experimental Section

Commercial available reagents were used without purification. Carboranes¹⁻⁴ 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 KMnO₄. 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), ¹³C{¹H} NMR (100 MHz), ¹¹B NMR (128 MHz), ¹¹B{¹H} NMR (128 MHz), and ¹⁹F 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 ¹³C{¹H} (chloroform-*d*), δ 29.8 for ¹³C{¹H} (acetone-*d*₆), and δ 49.0 for ¹³C{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 °C 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 N₂ 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.

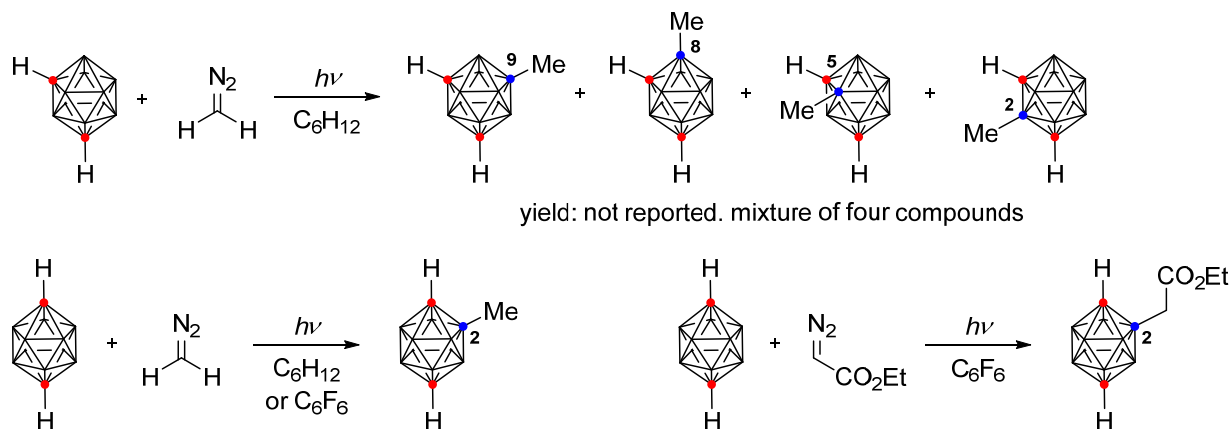
2. Previously Reported Reactions of Carboranes with Carbenes



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).

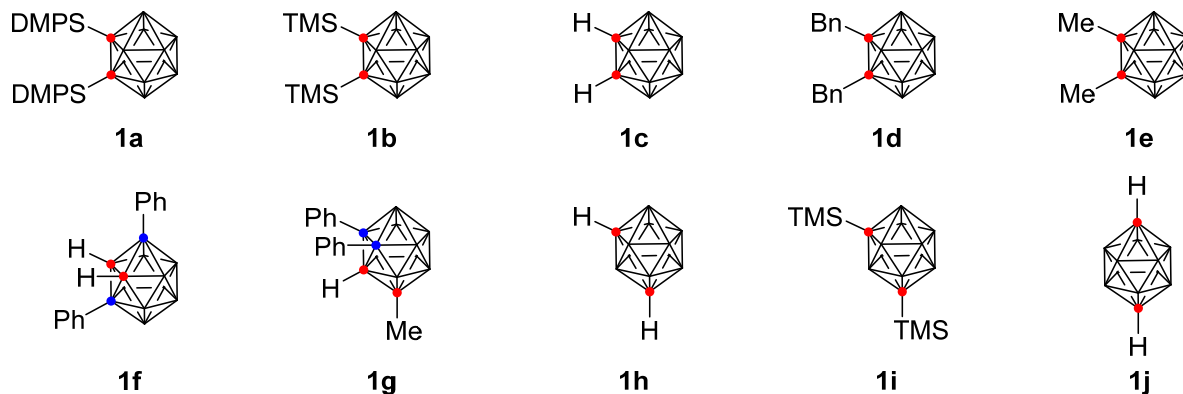


Yuan, K. & Jones, M. Jr. *Tetrahedron Lett.* **33**, 7481-7484 (1992).

Fig. S1. Previously reported reactions of carboranes with carbenes

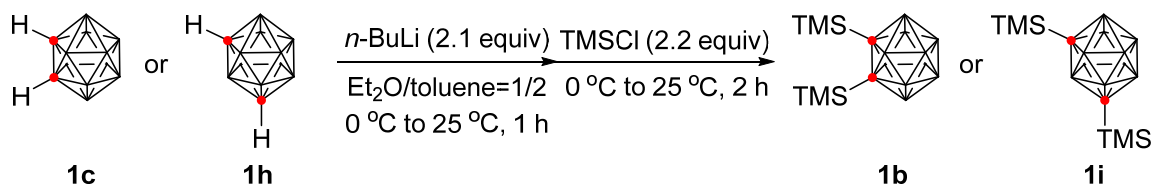
3. Preparation of Carborane Derivatives

List of carboranes

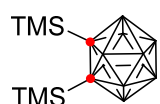


1c, **1h**, and **1j** are commercially available. **1a**, **1d**, **1e**, **1f**, and **1g** were synthesized via the known procedure¹⁻⁴.

General Procedure for the **1b** and **1i**

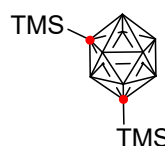


o-Carborane **1c** or *m*-carborane **1h** (432.7 mg, 3.0 mmol, 1.0 equiv) were dissolved in Et₂O/toluene (3 mL/6 mL) and stirred at 0 °C. *n*-BuLi (1.6 M in hexane, 3.9 mL, 6.3 mmol, 2.1 equiv) was slowly added to the reaction mixture. The resulting solution was stirred at 25 °C for 1 h. After the reaction 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 Et₂O (3 x 20 mL). The organic phase was dried over MgSO₄. 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; ¹H NMR (400 MHz, CDCl₃) δ 0.32 (s, 18H); ¹H{¹¹B} NMR (400 MHz, CDCl₃) 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); ¹³C{¹H} NMR (100

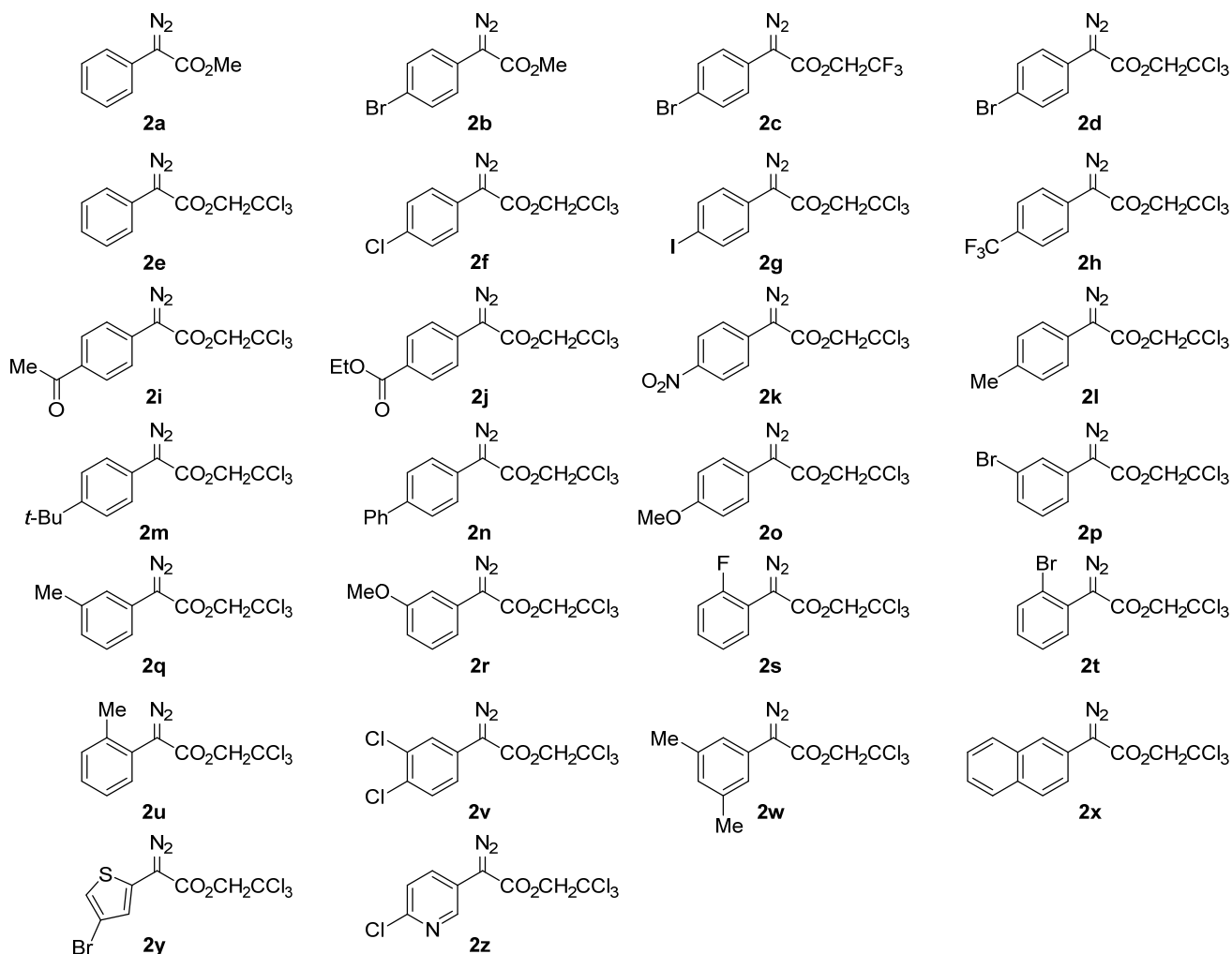
MHz, CDCl₃) δ 74.8, 1.72; ¹¹B{¹H} NMR (128 MHz, CDCl₃) δ 1.84 (2B), -5.73 (2B), -8.89 (4B), -11.15 (2B); IR (film): 2983, 2957, 2613, 2574, 2560, 1744, 1256, 846, 759 cm⁻¹; HRMS (FAB) *m/z*: [M-CH₃]⁺ Calcd for C₇H₂₅B₁₀Si₂⁺ 275.2420; Found 275.2421.



1i: Yield: 493.5 mg (57%); *R_f* = 0.70 (Hexane); White solid; Melting point: 53-55 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.12 (s, 18H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 68.0, -0.65; ¹¹B{¹H} NMR (128 MHz, CDCl₃) 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-CH₃]⁺ Calcd for C₇H₂₅B₁₀Si₂⁺ 275.2420; Found 275.2423.

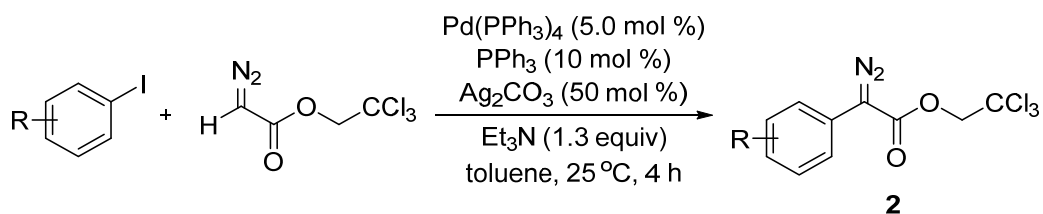
4. Preparation of Diazo Compounds

List of diazo compounds



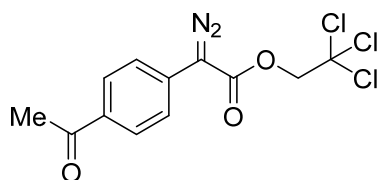
Diazo compounds were synthesized via the known procedure^{5,6}.

General Procedure A for the Diazo Compounds

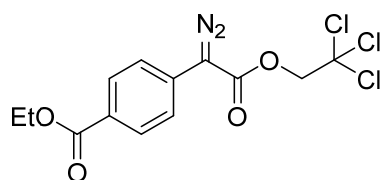


Aryl iodide (3.0 mmol, 1.0 equiv), Pd(PPh₃)₄ (173.3 mg, 0.15 mmol, 5.0 mol %), PPh₃ (78.7 mg, 0.30 mmol, 10 mol %), and Ag₂CO₃ (413.7 mg, 1.5 mmol, 0.5 equiv) were dissolved in toluene (12 mL)

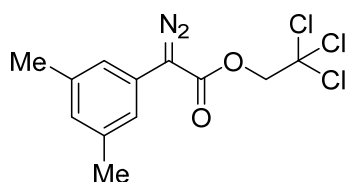
under a N₂ atmosphere, followed by addition of Et₃N (0.55 mL, 3.9 mmol, 1.3 equiv) and 2,2,2-trichloroethyl 2-diazoacetate (847.9 g, 3.9 mmol, 1.3 equiv). The resulting mixture was stirred at 25 °C for 4 h and then filtered through a pad of silica gel, washed with EtOAc. The crude product was purified by column chromatography on silica gel.



2i: Yield: 744.7 mg (74%); R_f = 0.40 (Et₂O:Hexane = 1:10); Yellow solid; Melting point: 60-62 °C; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C{¹H} NMR (100 MHz, CDCl₃) 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 C₁₂H₁₀Cl₃N₂O₃⁺ 334.9757; Found 334.9758.

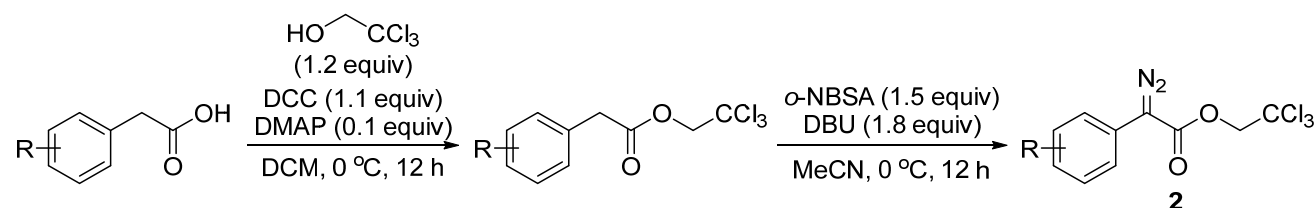


2j: Yield: 767.2 mg (80%); R_f = 0.35 (Et₂O:Hexane = 1:10); Yellow solid; Melting point: 85-87 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 8.7 Hz, 2H), 7.58 (d, J = 8.7 Hz, 2H), 4.93 (s, 2H), 4.38 (q, J = 7.1 Hz, 3H), 1.40 (t, J = 7.1 Hz, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 166.1, 162.7, 130.4, 130.0, 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 C₁₃H₁₂Cl₃N₂O₄⁺ 364.9863; Found 364.9861.



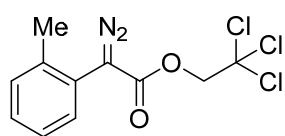
2w: Yield: 858.8 mg (89%); R_f = 0.40 (Et₂O:Hexane = 1:10); Yellow solid; Melting point: 85-87 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.11 (s, 2H), 6.86 (s, 1H), 4.91 (s, 2H), 2.33 (s, 6H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 163.7, 138.9, 128.3, 124.3, 122.0, 95.2, 73.9, 21.6; IR (film): 2952, 2919, 2085, 1710, 1252, 1141, 1097, 839, 711 cm⁻¹; HRMS (FAB) m/z : [M]⁺ Calcd for C₁₂H₁₁Cl₃N₂O₂⁺ 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 N₂ 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 Et₂O (30 mL) followed by adding saturated NH₄Cl(aq) solution (30 mL). The solution was extracted with Et₂O (3 x 30 mL) and the organic phase was dried over MgSO₄. 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 (Et₂O:Hexane = 1:15); Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.43-7.41 (m, 1H), 7.31-7.25 (m, 3H), 4.89 (s, 2H), 2.24 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) 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 C₁₁H₁₀Cl₃N₂O₂⁺ 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

^aReaction 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 N₂ atmosphere. The resulting solution was stirred for additional 10 min.

^bIsolated and combined yield of **3aa-B(9)** and **4aa-B(8)**. ^cRatios were determined from crude ¹H NMR.

^dDetermined by chiral HPLC analysis. ^eRh₂(S-TCPTTL)₄ (1.0 mol %) was used. ^fRh₂(S-TCPTTL)₄ (0.5 mol %) was used. ^g**2a** (1.5 equiv) was used.

Table S1-entry 1

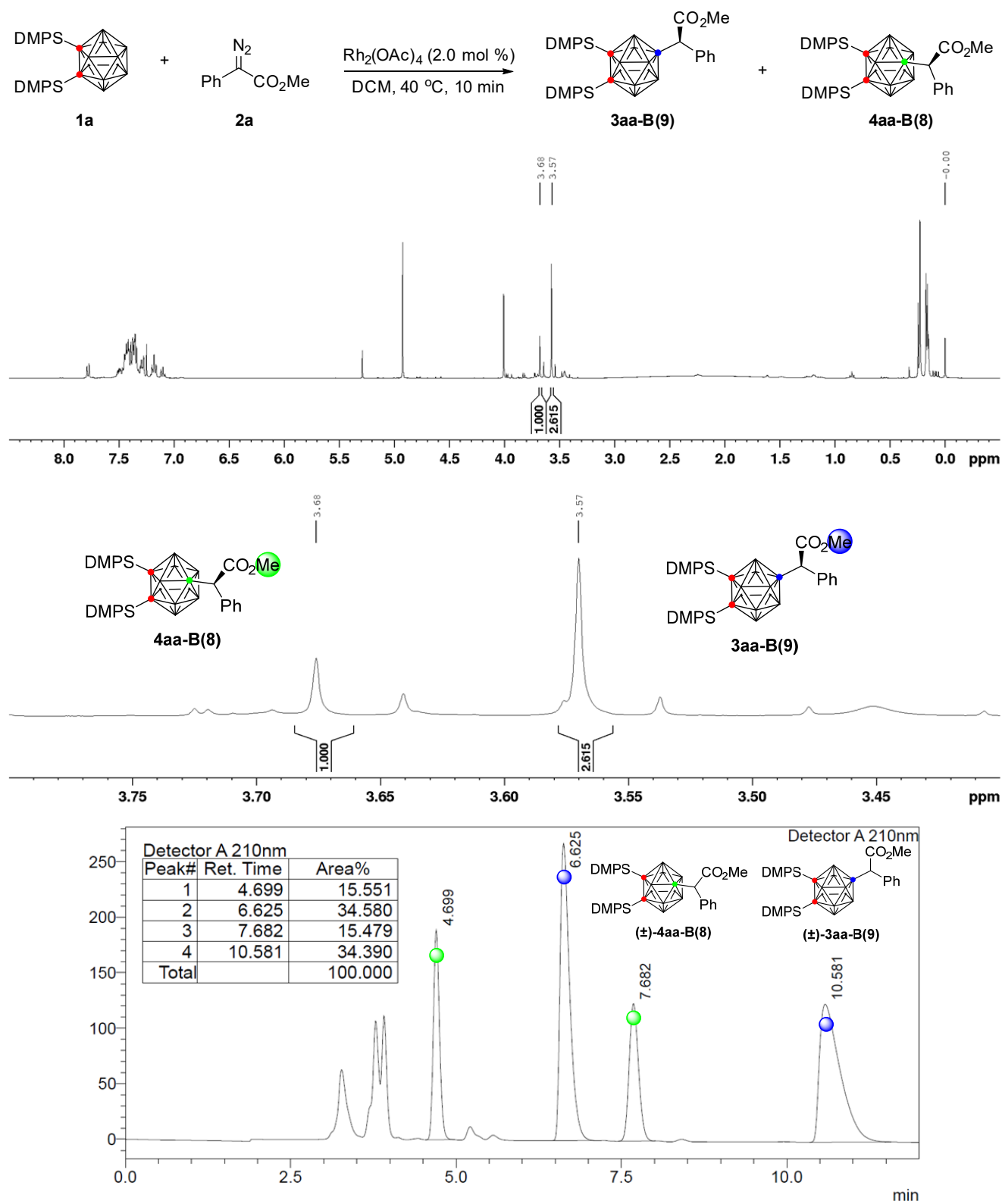


Table S1-entry 2

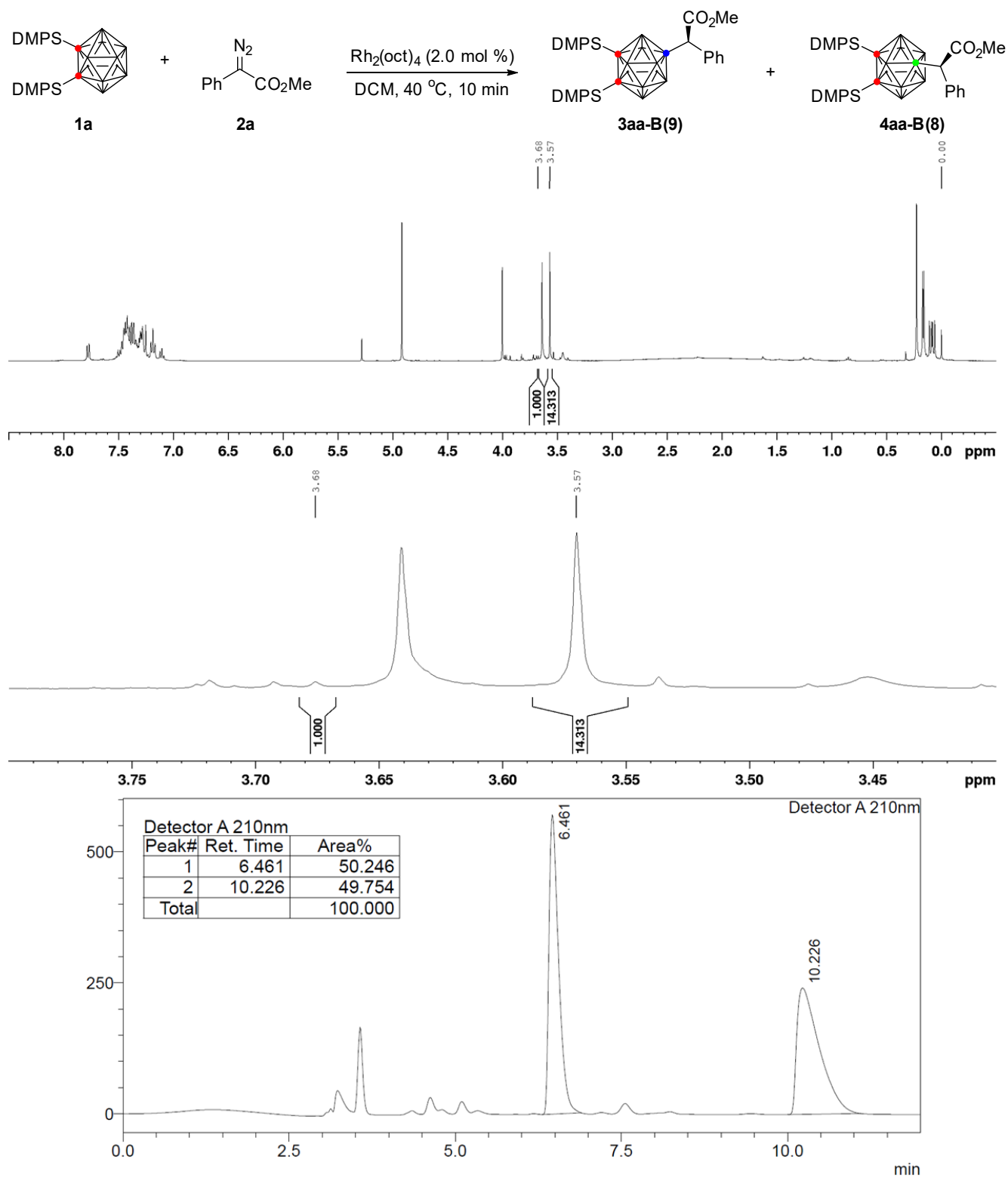


Table S1-entry 3

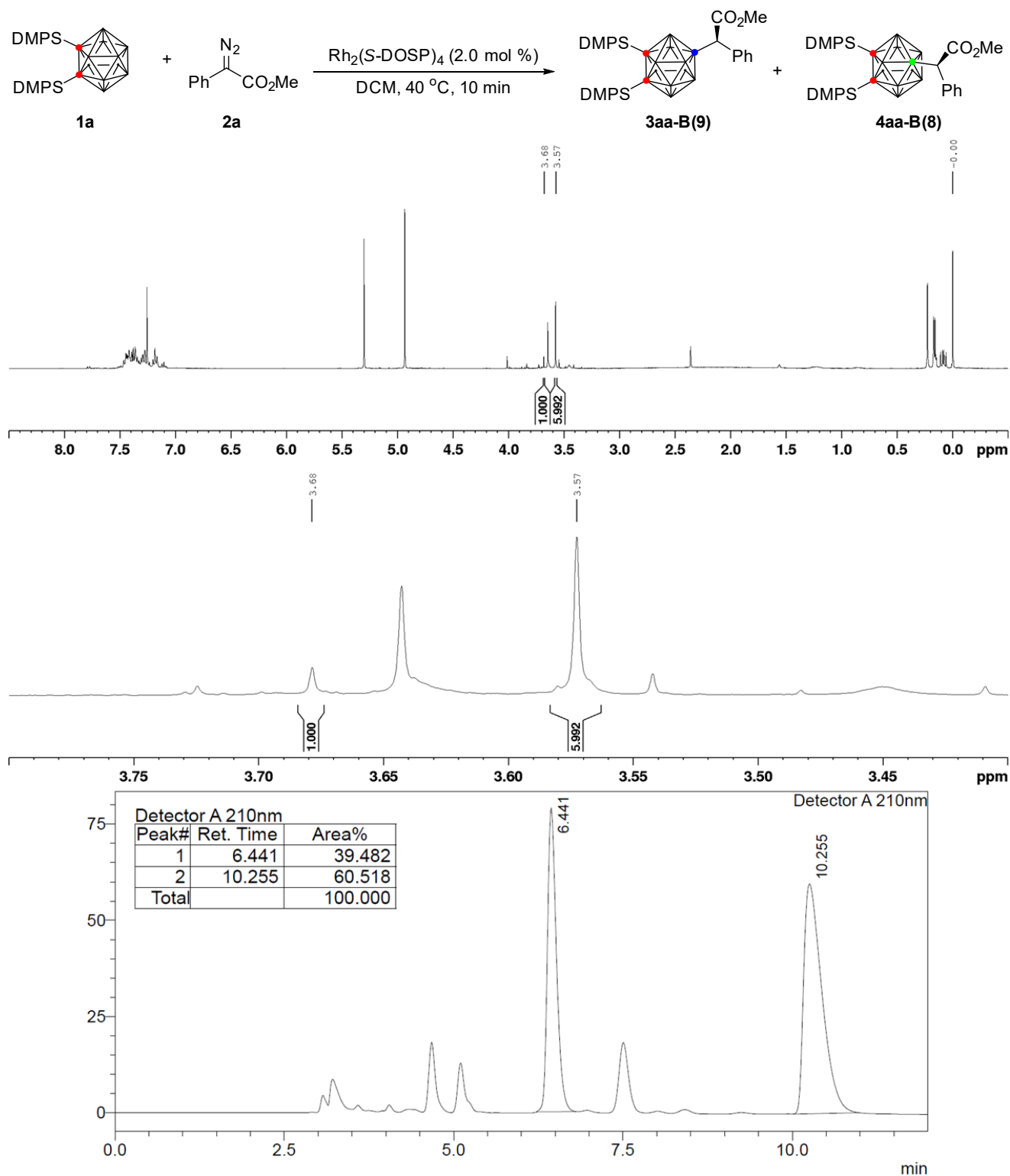


Table S1-entry 4

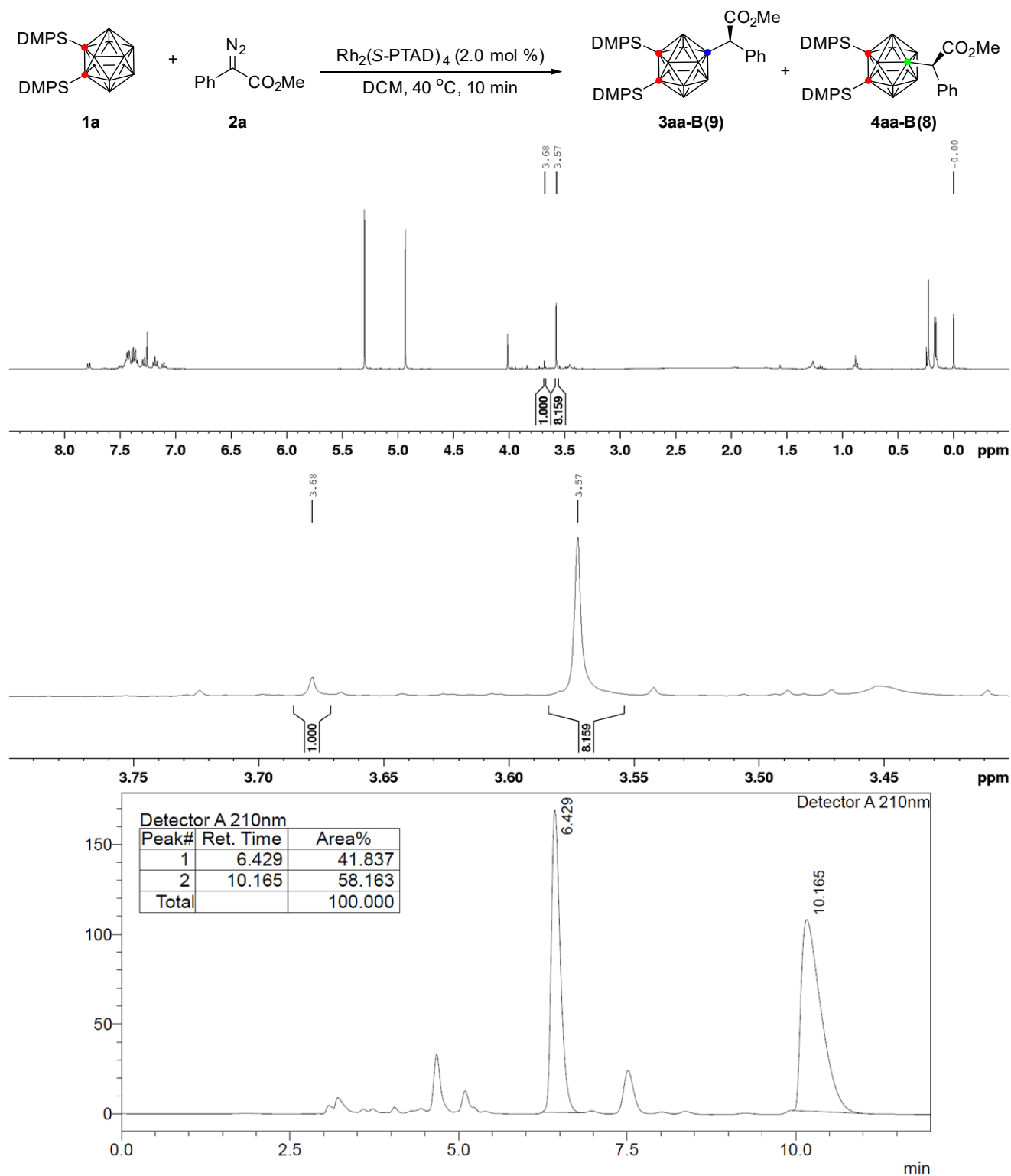


Table S1-entry 5

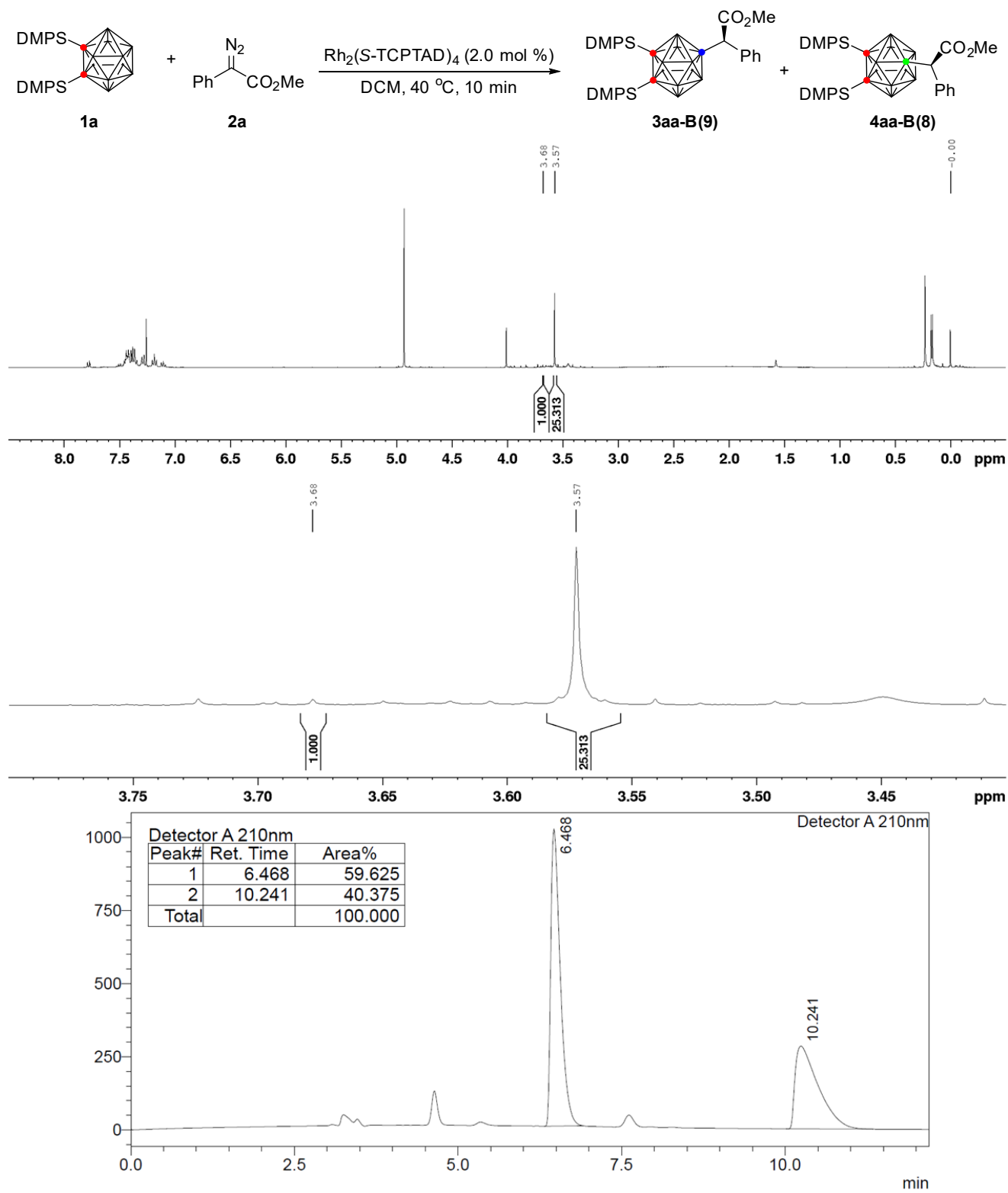


Table S1-entry 6

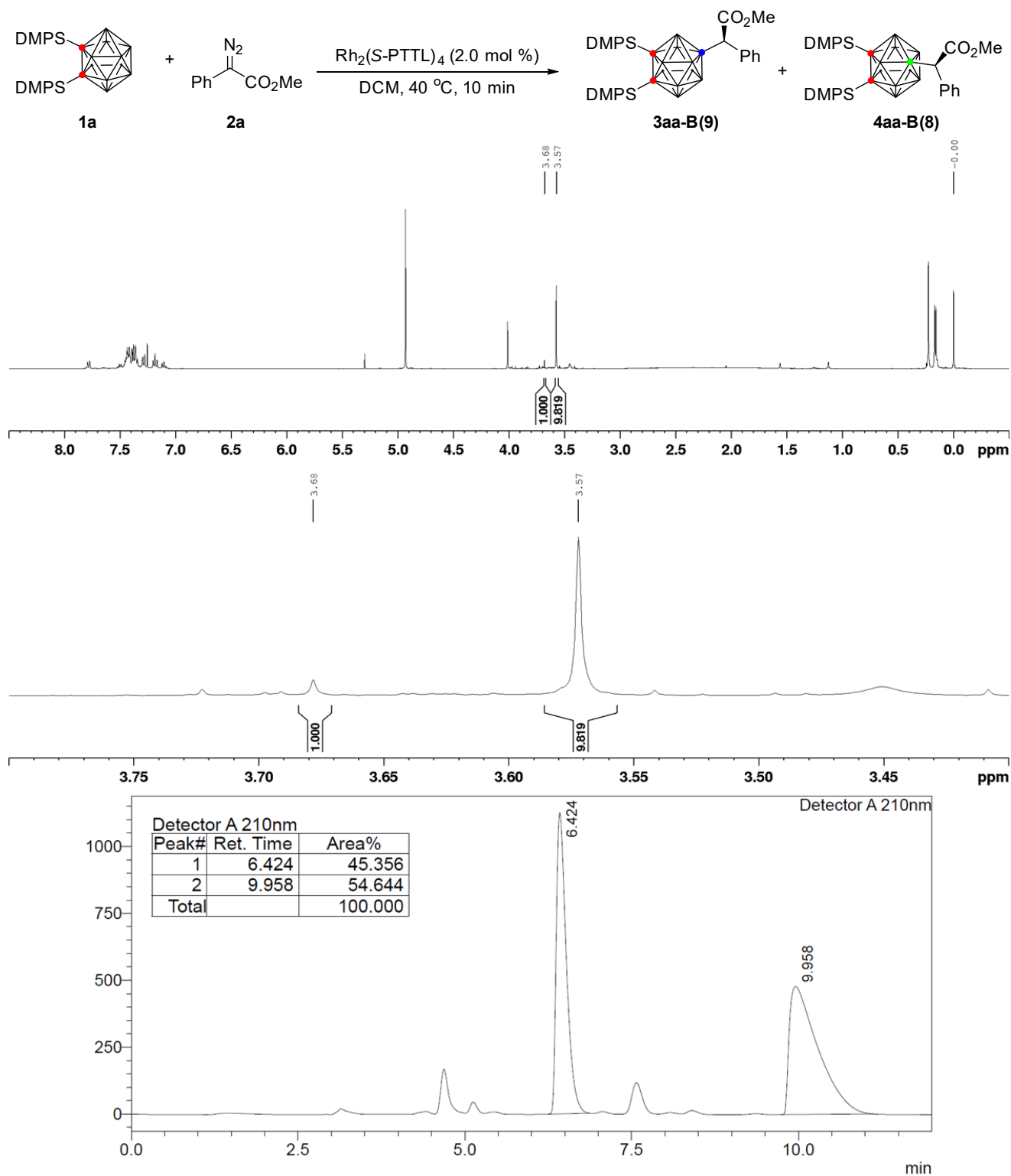


Table S1-entry 7

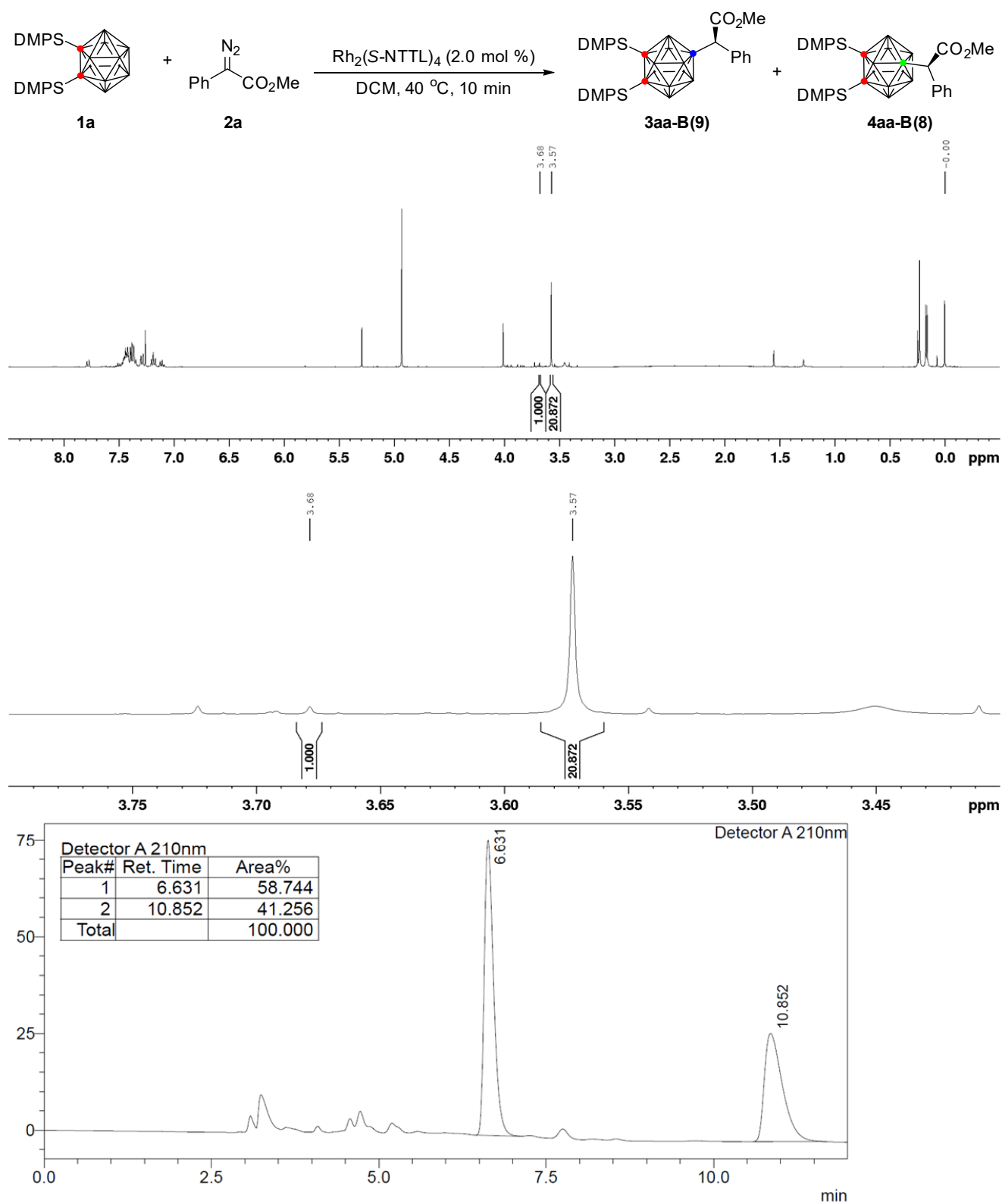


Table S1-entry 8

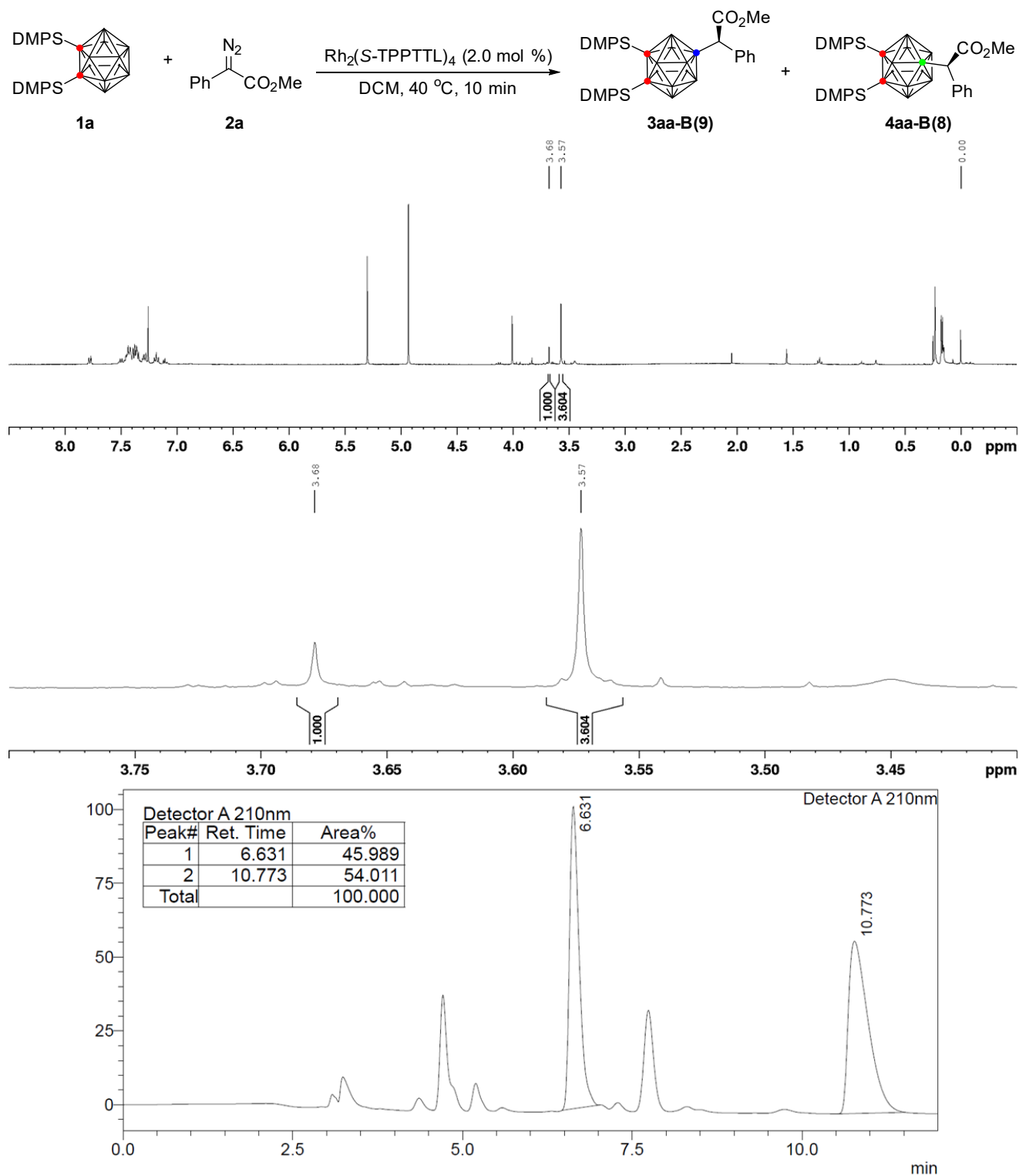


Table S1-entry 9

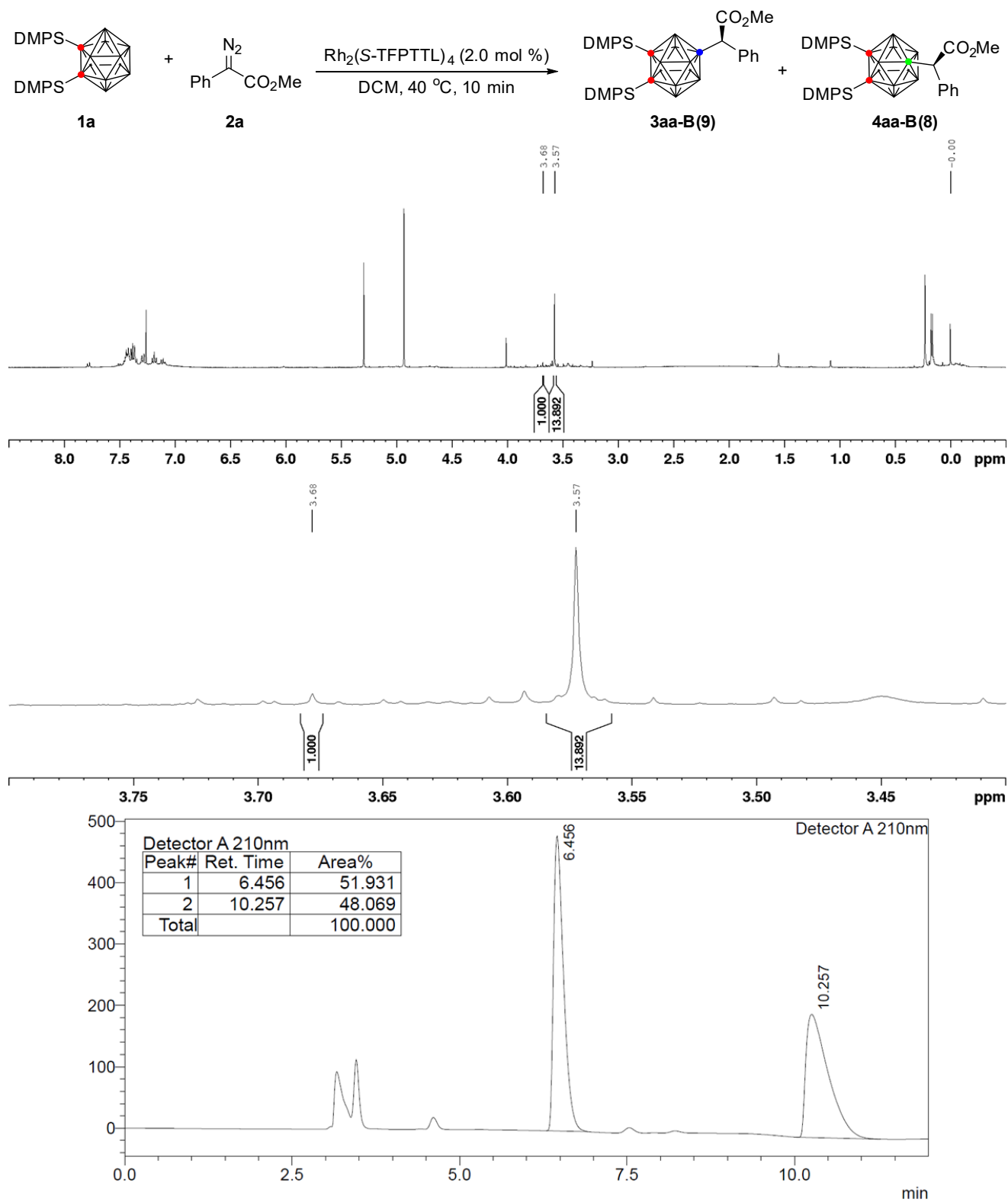


Table S1-entry 10

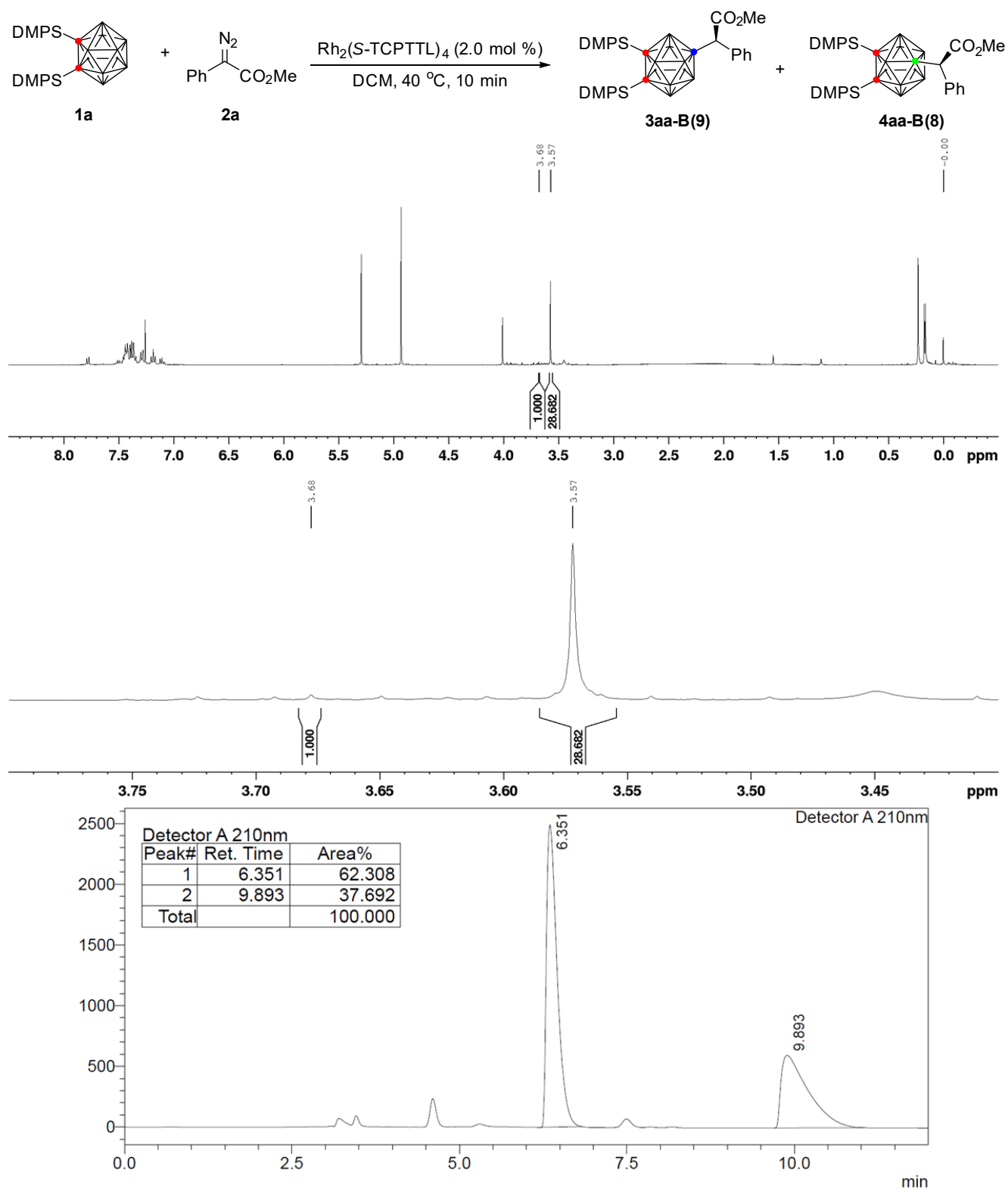


Table S1-entry 11

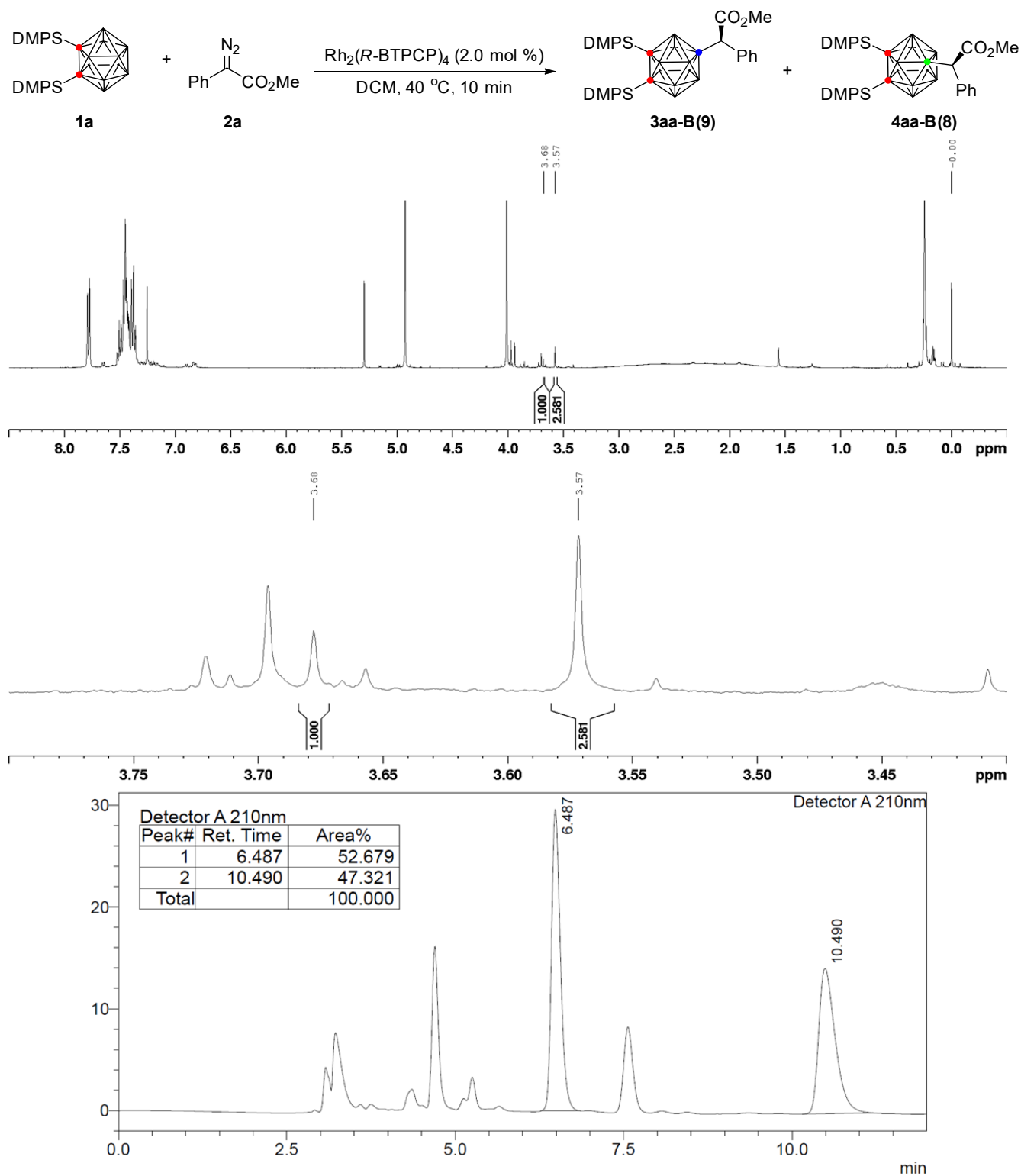


Table S1-entry 12

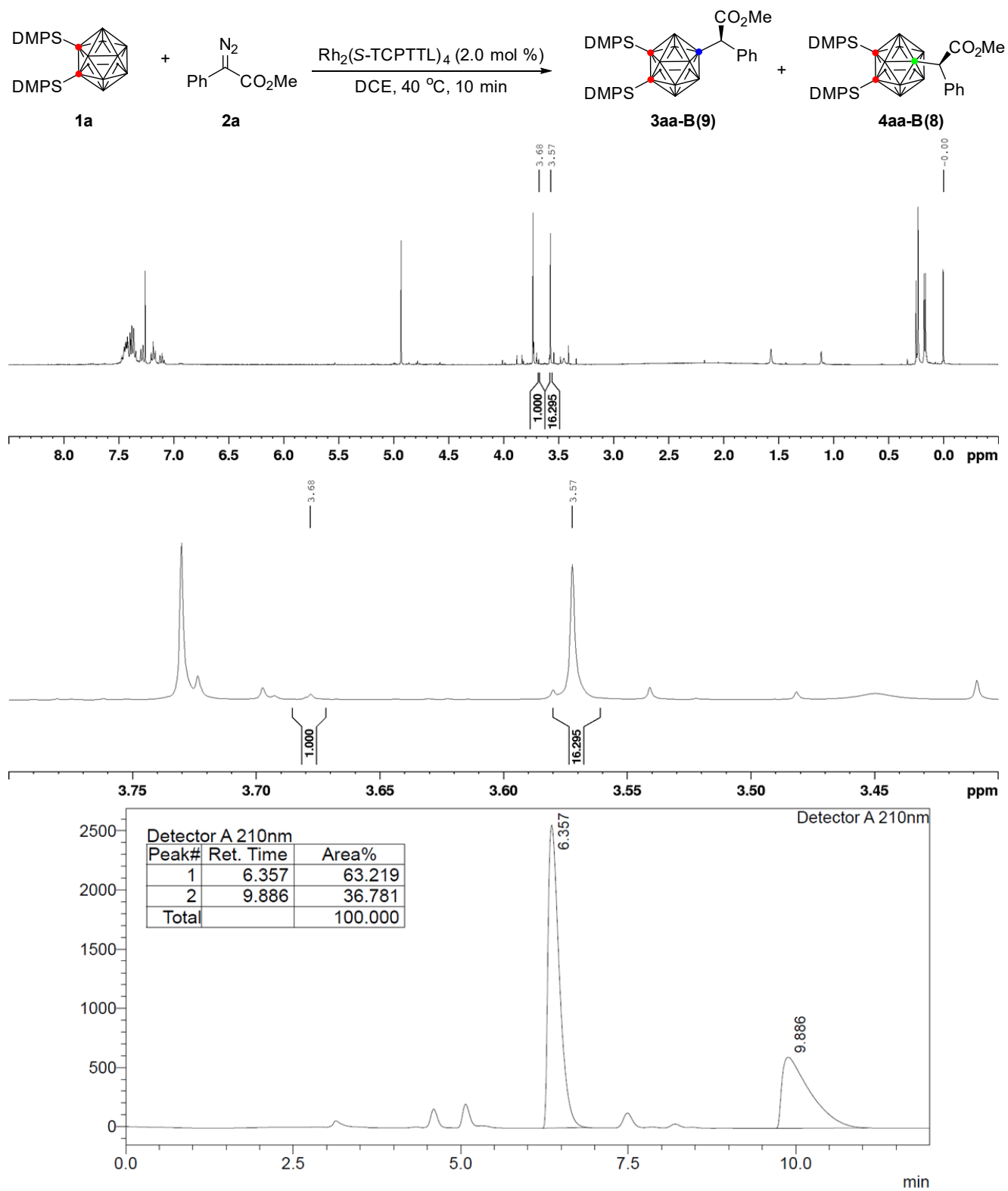


Table S1-entry 13

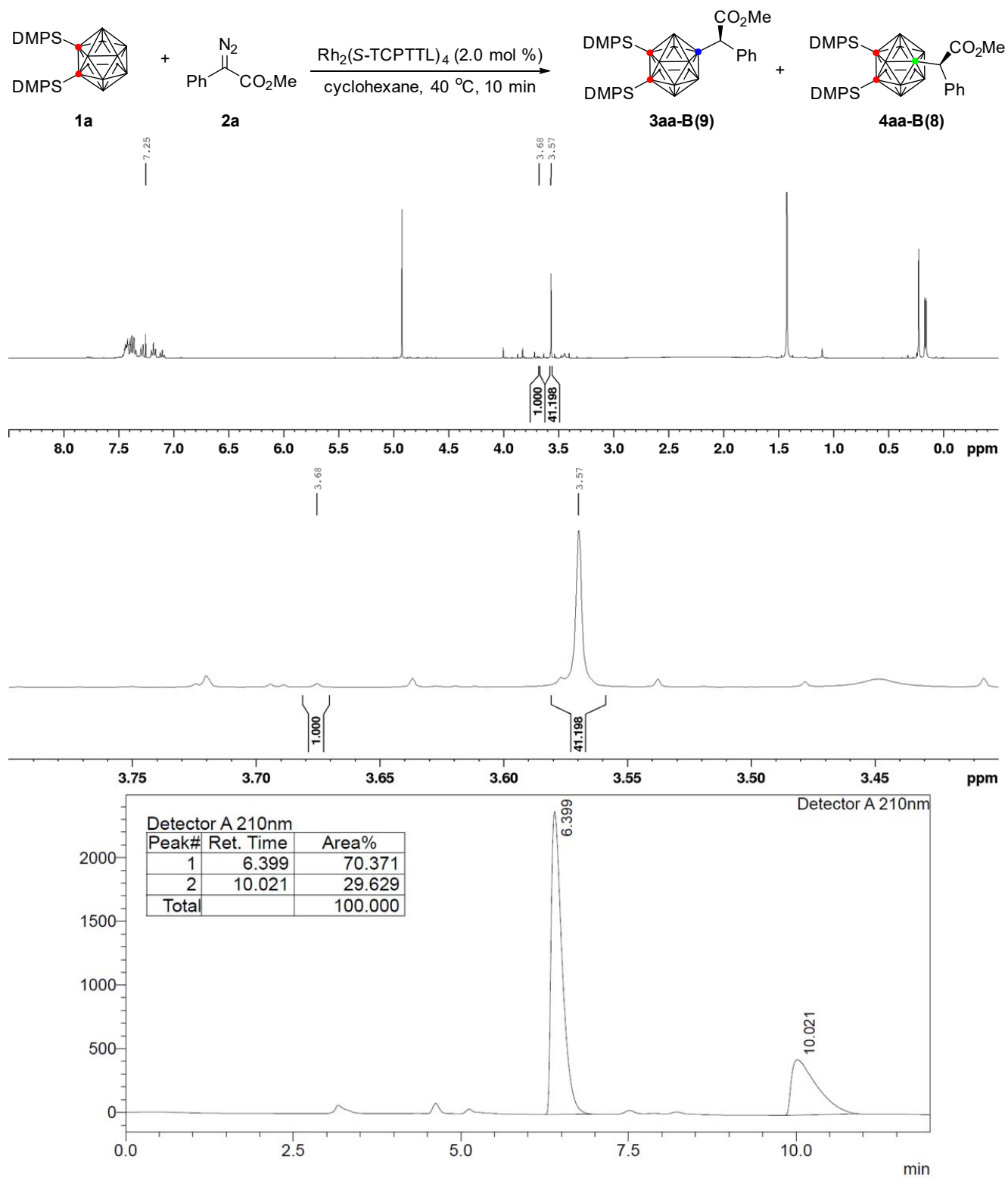


Table S1-entry 14

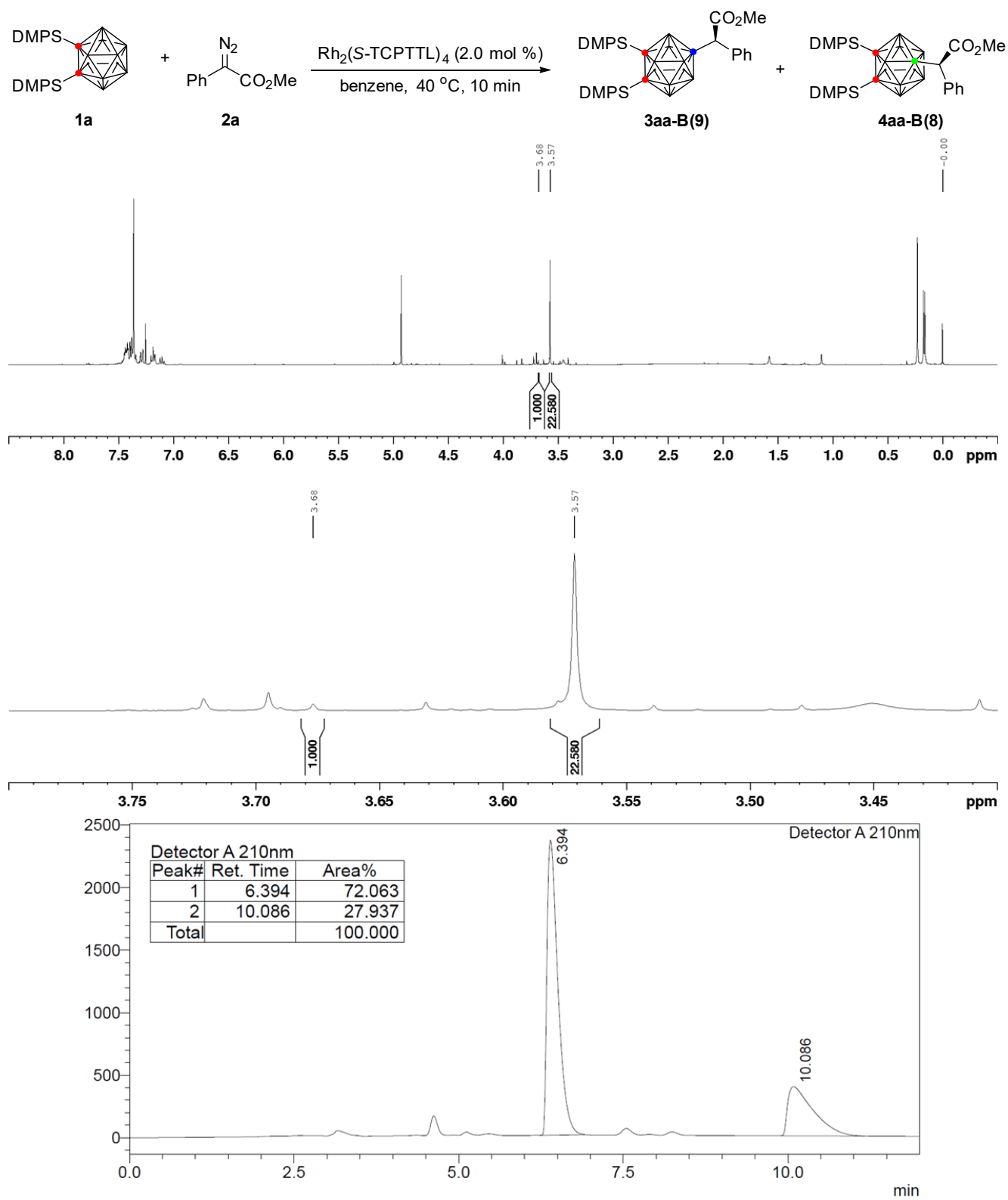


Table S1-entry 15

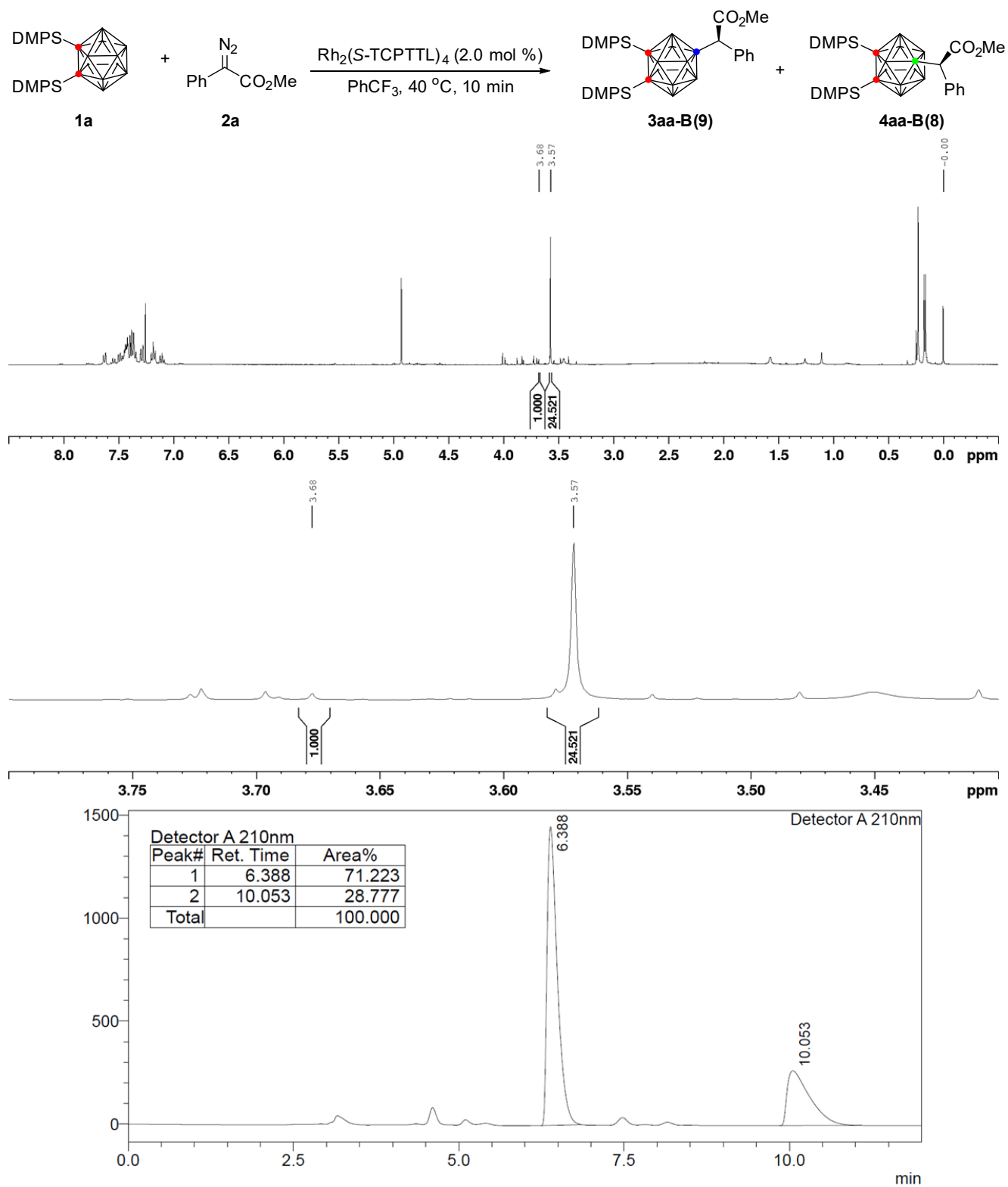


Table S1-entry 17

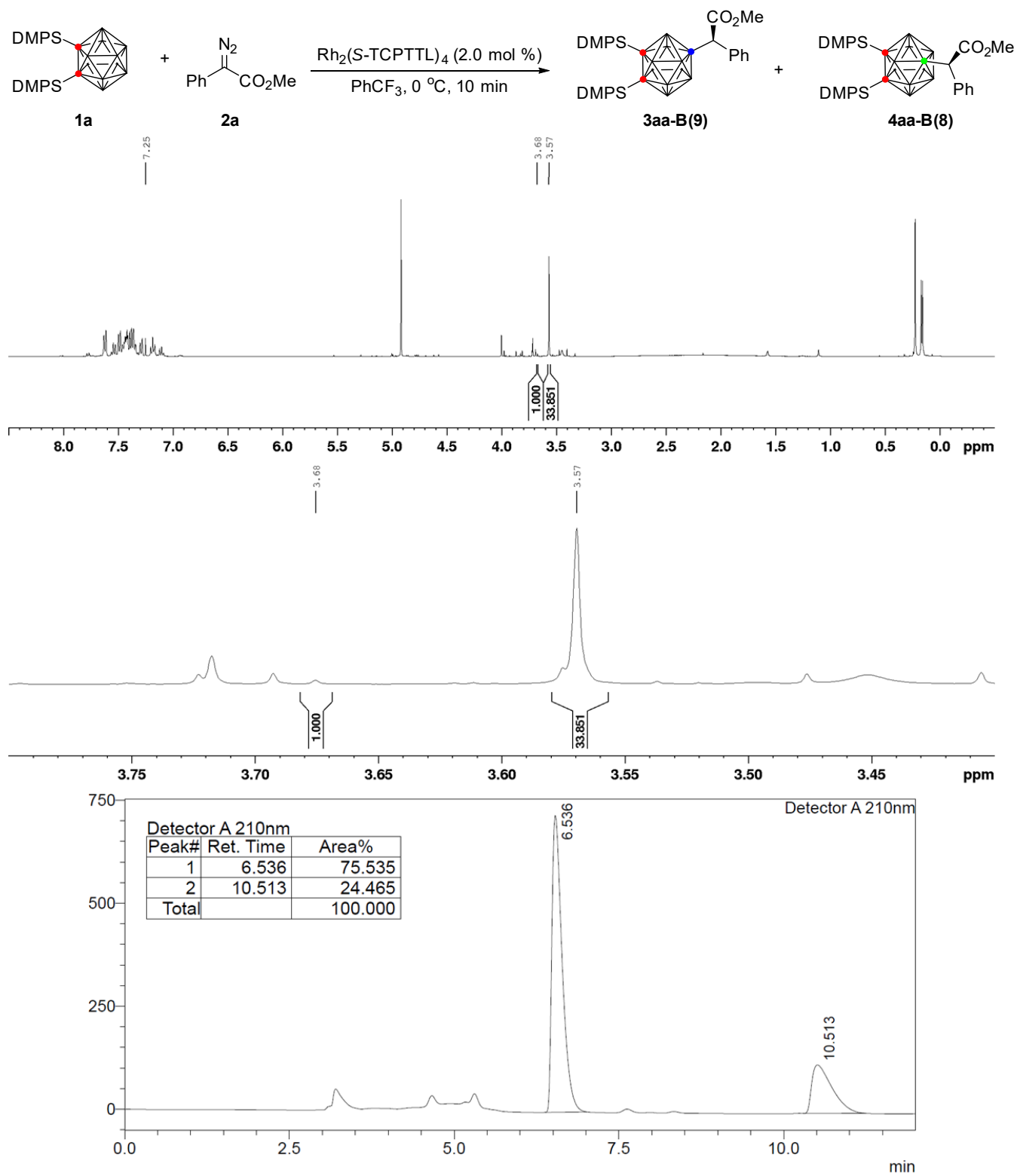


Table S1-entry 18

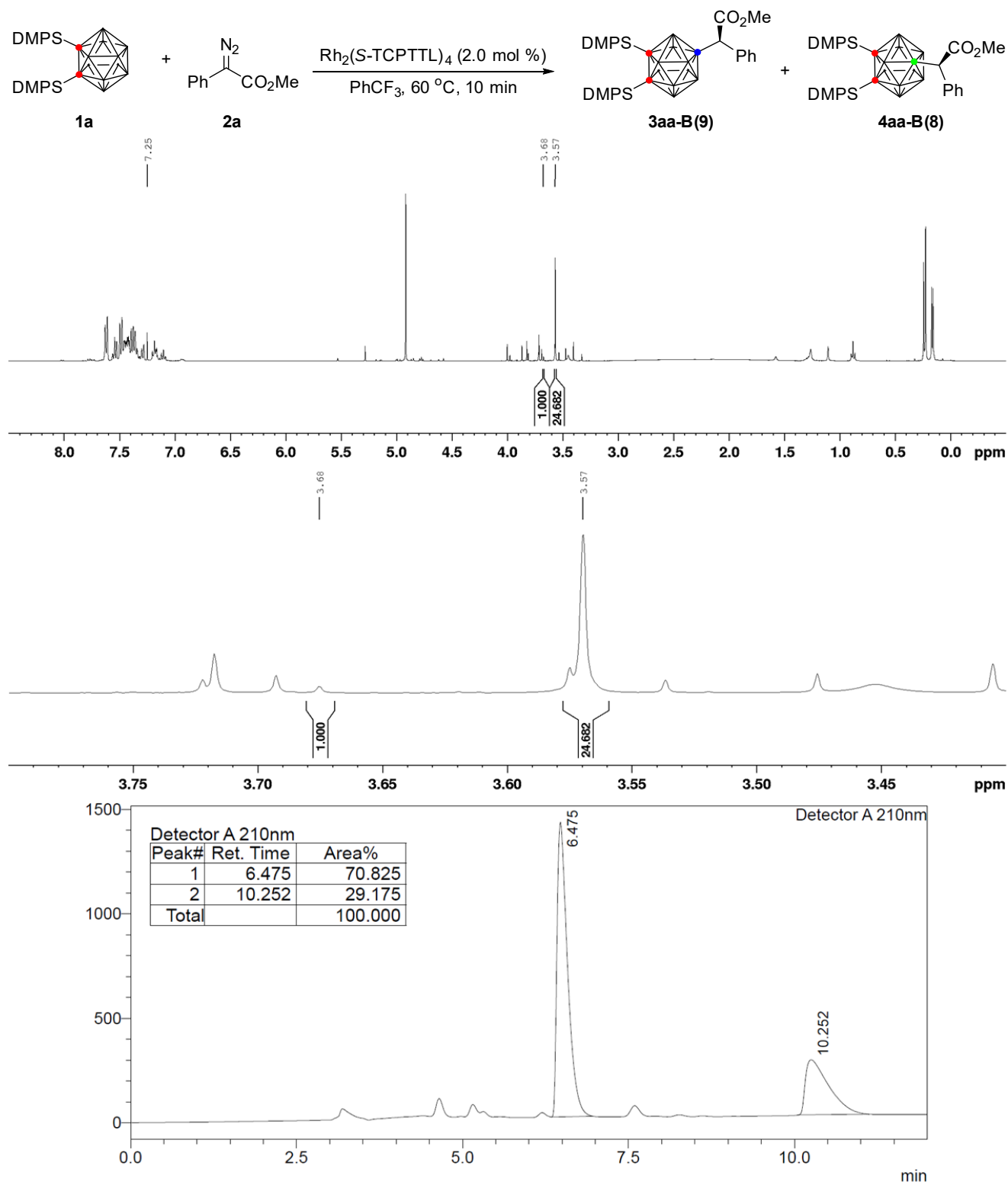


Table S1-entry 19

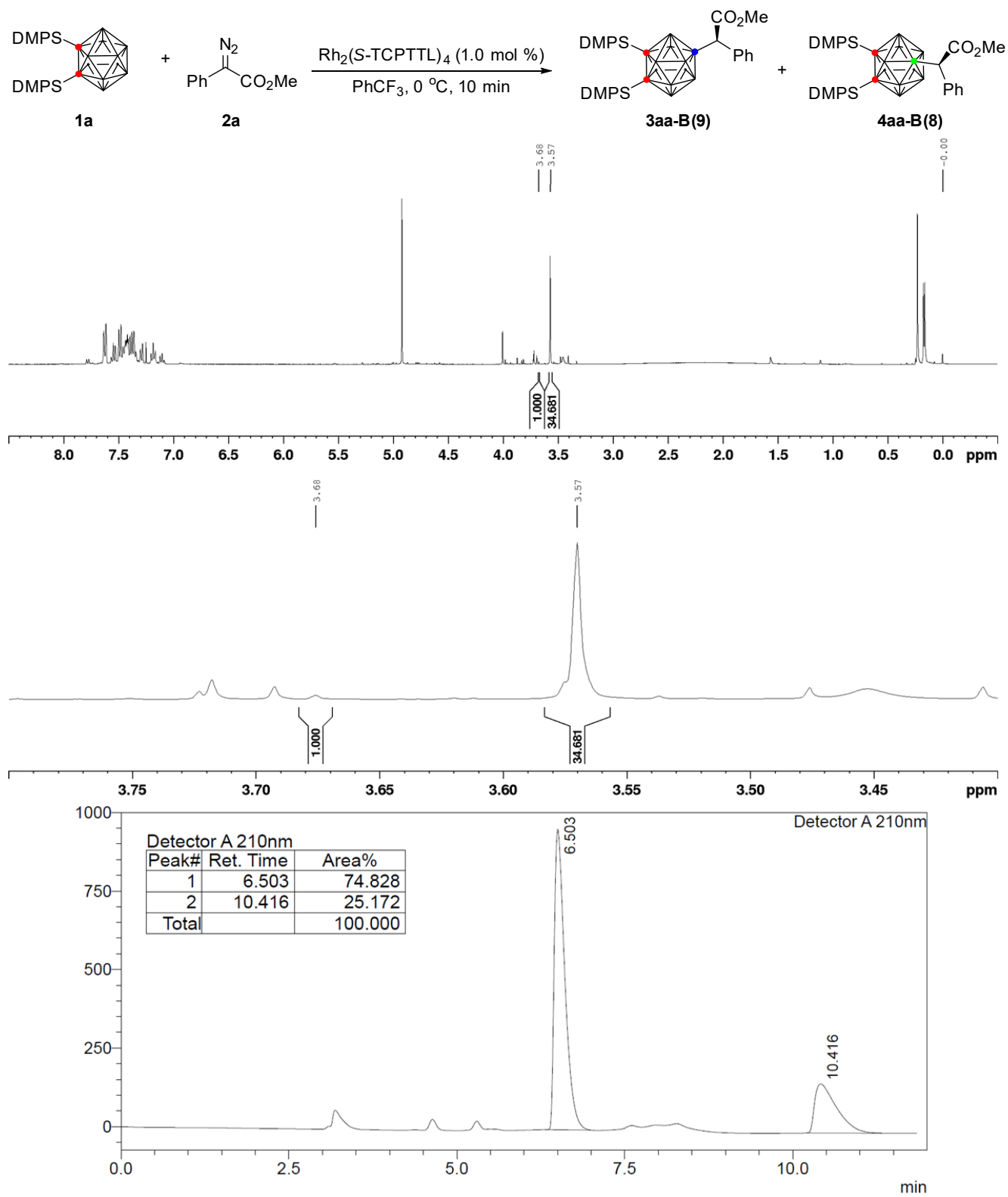


Table S1-entry 20

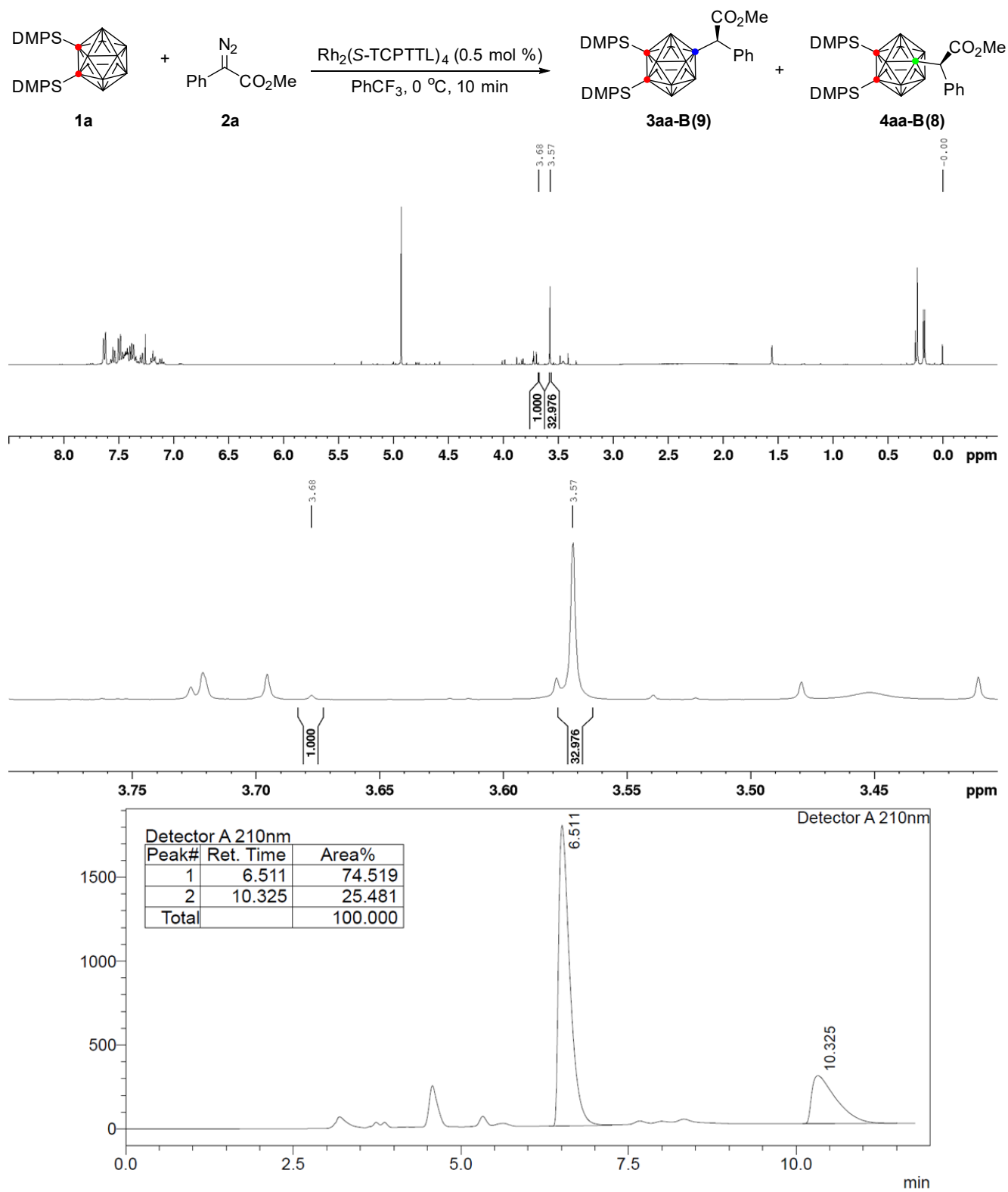
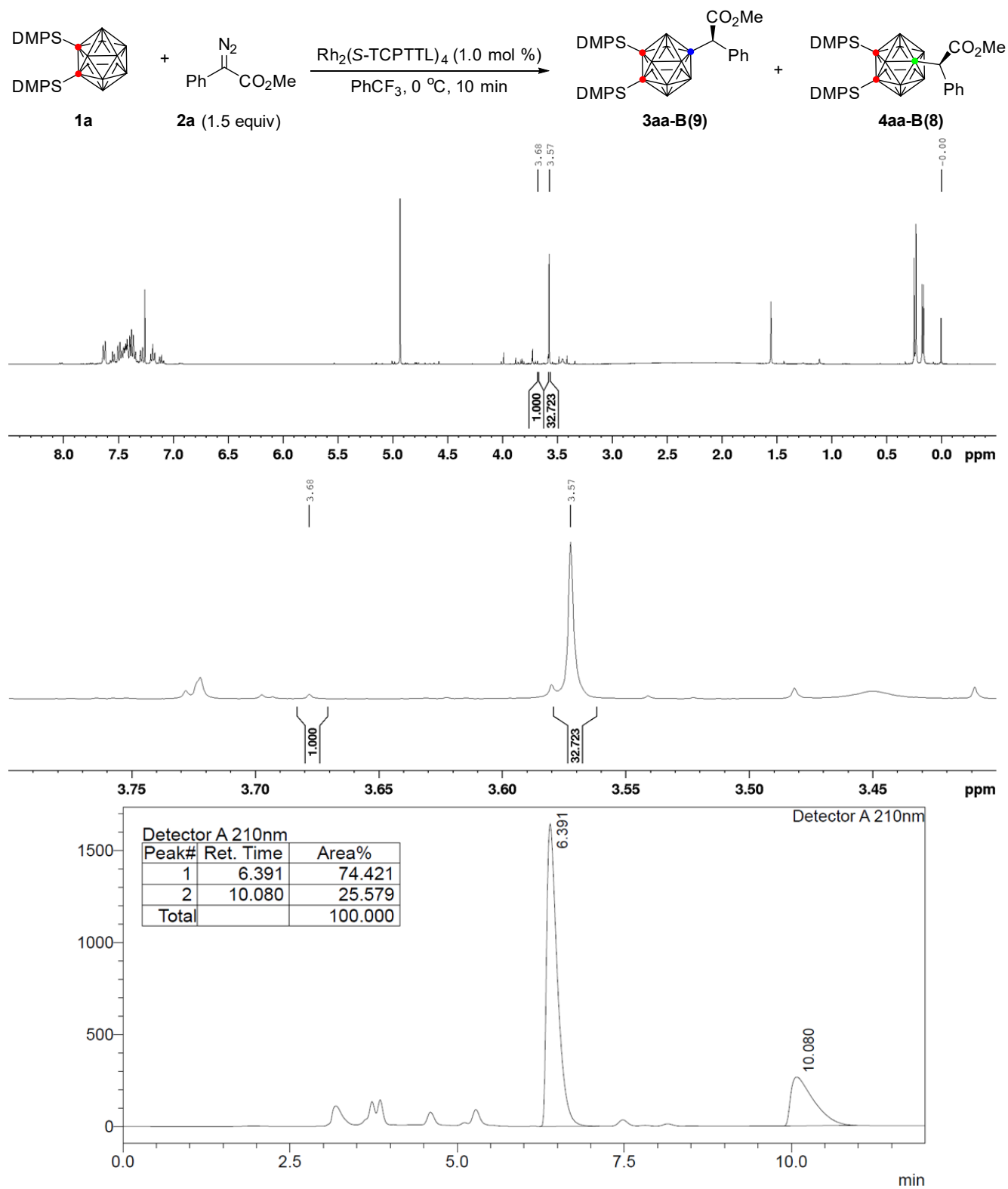
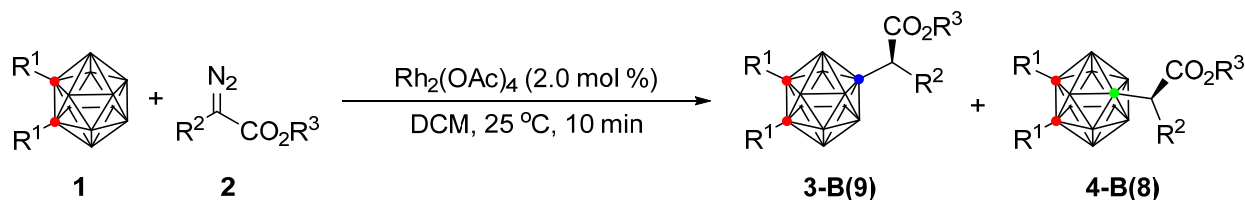


Table S1-entry 21



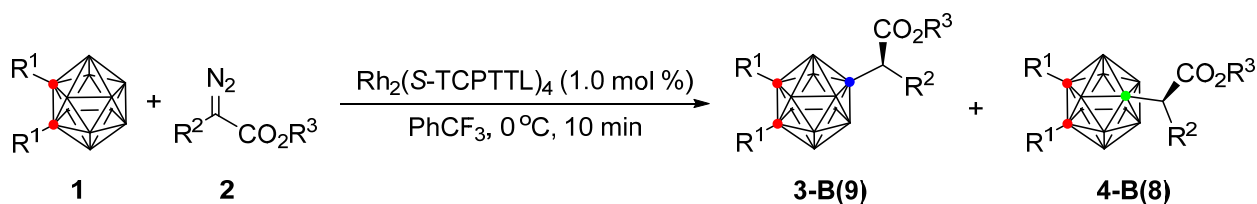
6. General Procedure of the Rh(II)-Catalyzed B(9)-Alkylation of Carboranes

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

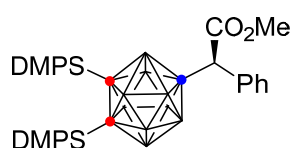


An oven dried test tube equipped with a magnetic stirrer was charged with *o*-carborane **1** (0.2 mmol, 1.0 equiv) and $Rh_2(OAc)_4$ (2.0 mol %) in DCM (1.5 mL) and stirred at 25 °C under a N_2 atmosphere. The diazo **2** (2.0 equiv) in DCM (1.5 mL) was added to the reaction mixture dropwise via syringe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

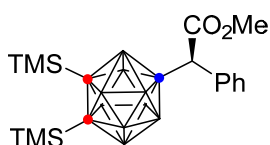


An oven dried test tube equipped with a magnetic stirrer was charged with *o*-carborane **1** (0.2 mmol, 1.0 equiv) and $Rh_2(S-TCPTTL)_4$ (1.0 mol %) in $PhCF_3$ (1.5 mL) and stirred at 0 °C under a N_2 atmosphere. The diazo **2** (2.0 equiv) in $PhCF_3$ (1.5 mL) was added to the reaction mixture dropwise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



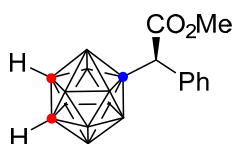
3aa: Yield: 109.9 mg (98%); Regioisomeric ratio (r.r.) = 35:1 (determined from crude 1H NMR analysis of the racemic product and the chiral product); R_f = 0.30 (Et_2O :Hexane = 1:15); White solid; Melting point: 67–68 °C; 1H NMR (400 MHz, $CDCl_3$) δ 7.47–7.34 (m, 10H), 7.30–7.28 (m, 2H), 7.20–7.16 (m,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

(100 MHz, CDCl₃) 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; ¹¹B{¹H} NMR (128 MHz, CDCl₃) 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 C₂₇H₄₀B₁₀O₂Si₂⁺ 562.3497; Found 562.3502; [α]_D²⁵: +22.5° (c = 0.24, CH₂Cl₂, 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..



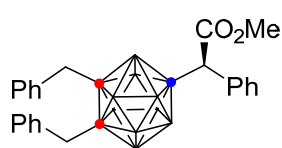
3ba: Yield: 84.7 mg (97%); Regioisomeric ratio (r.r.) = 22:1 (determined from crude ¹H NMR analysis of the racemic product and the chiral product); R_f = 0.35 (Et₂O:Hexane = 1:10); White solid; Melting point: 86-88 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, J = 7.29 Hz, 2H), 7.24 (t, J = 7.38 Hz, 2H), 7.13 (t, J = 7.32

Hz, 1H), 3.64 (s, 3H), 3.50 (s, 1H), 0.29 (s, 9H), 0.26 (s, 9H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 175.1, 140.7, 128.8, 127.8, 125.6, 73.6, 67.9, 51.2, 46.6, 1.8, 1.6; ¹¹B{¹H} NMR (128 MHz, CDCl₃) 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 C₁₇H₃₆B₁₀O₂Si₂⁺ 438.3184; Found 438.3184; [α]_D²⁵: +13.6° (c = 0.68, CH₂Cl₂, 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..

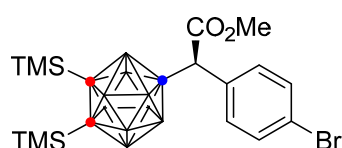


3ca: Yield: 56.1 mg (96%); Regioisomeric ratio (r.r.) = 7.3:1 (determined from crude ¹H NMR analysis of the racemic product and the chiral product); R_f = 0.30 (Et₂O:Hexane = 1:2); White solid; Melting point: 94-96 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.36 (d, J = 7.76 Hz, 2H), 7.25 (t, J = 7.38 Hz, 2H), 7.15 (t, J = 7.25 Hz,

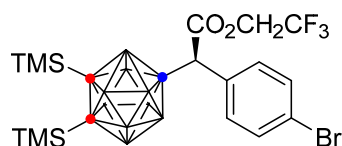
1H), 3.64 (s, 3H), 3.45 (s, 3H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 175.0, 140.5, 128.7, 128.0, 125.8, 53.3, 51.3, 49.6, 45.3; ¹¹B{¹H} NMR (128 MHz, CDCl₃) δ 7.04 (1B), -2.17 (1B), -9.03 (2B), -14.37 (4B), -15.50 (2B); IR (film): 3060, 2947, 2594, 1715, 1430, 1205, 1148, 1026, 698 cm⁻¹; HRMS (EI) m/z : [M]⁺ Calcd for C₁₁H₂₀B₁₀O₂⁺ 294.2394; Found 294.2397; [α]_D²⁵: +31.3° (c = 0.18, CH₂Cl₂, 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 ^1H 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 °C; ^1H 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); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}]^+$ Calcd for $\text{C}_{25}\text{H}_{32}\text{B}_{10}\text{O}_2^+$ 474.3333; Found 474.3334; $[\alpha]_D^{25}$: +11.3° (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..

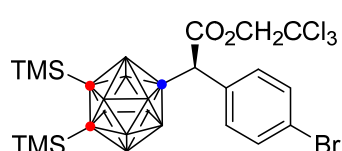


3bb: Yield: 99.2 mg (96%); Regioisomeric ratio (r.r.) = 36:1 (determined from crude ^1H NMR analysis of the racemic product and the chiral product); R_f = 0.35 (Et_2O :Hexane = 1:10); White solid; Melting point: 124-126 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.36 (d, J = 8.56 Hz, 2H), 7.26 (d, J = 8.53 Hz, 2H), 3.65 (s, 3H), 3.46 (s, 1H), 0.29 (s, 9H), 0.27 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}]^+$ Calcd for $\text{C}_{17}\text{H}_{35}\text{B}_{10}\text{BrO}_2\text{Si}_2^+$ 516.2290; Found 516.2292; $[\alpha]_D^{25}$: +9.0° (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..



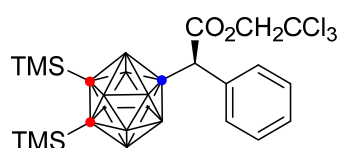
3bc: Yield: 113.7 mg (97%); Regioisomeric ratio (r.r.) = 48:1 (determined from crude ^1H NMR analysis of the racemic product and the chiral product); R_f = 0.35 (CH_2Cl_2 :Hexane = 1:2); White solid; Melting point: 86-88 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.38 (d, J = 8.52 Hz, 2H), 7.24 (d, J = 8.52 Hz, 2H), 4.48-4.31 (m, 2H), 3.54 (s, 1H), 0.30 (s, 9H), 0.26 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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 C₁₈H₃₄B₁₀BrF₃O₂Si₂⁺ 584.2163; Found 584.2164; [α]_D²⁵: +18.8° (c = 1.01, CH₂Cl₂, 90% e.e.); HPLC (DAICEL IA column, 4% CH₂Cl₂ 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..



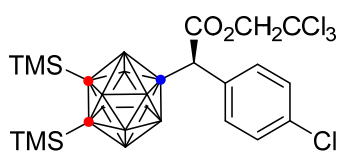
3bd: Yield: 121.5 mg (96%); Regioisomeric ratio (r.r.) = 25:1 (determined from crude ¹H NMR analysis of the racemic product and the chiral product); R_f = 0.35 (CH₂Cl₂:Hexane = 1:2); White solid; Melting point: 66-68 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, J = 8.48 Hz, 2H), 7.27 (d, J = 8.56 Hz,

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); ¹³C{¹H} NMR (100 MHz, CDCl₃) 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; ¹¹B{¹H} NMR (128 MHz, CDCl₃) 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 C₁₈H₃₄B₁₀BrCl₃O₂Si₂⁺ 632.1277; Found 632.1274; [α]_D²⁵: +17.9° (c = 0.26, CH₂Cl₂, 99% e.e.); HPLC (DAICEL IA column, 4% CH₂Cl₂ 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..

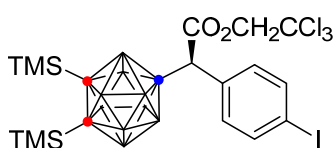


3be: Yield: 108.4 mg (98%); Regioisomeric ratio (r.r.) = 25:1 (determined from crude ¹H NMR analysis of the racemic product and the chiral product); R_f = 0.35 (CH₂Cl₂:Hexane = 1:2); Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.40 (d, J = 7.80 Hz, 2H), 7.25 (t, J = 11.22 Hz, 2H), 7.16 (t, J =

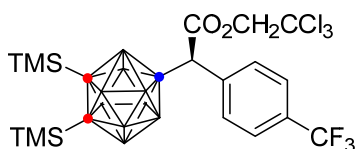
7.30 Hz, 1H), 4.75 (d, J = 11.94 Hz, 1H), 4.60 (d, J = 11.93 Hz, 1H), 3.64 (s, 1H), 0.29 (s, 9H), 0.25 (s, 9H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 173.1, 140.0, 128.7, 128.0, 125.8, 95.2, 74.7, 73.6, 68.2, 45.1, 1.8, 1.6; ¹¹B{¹H} NMR (128 MHz, CDCl₃) δ 10.31 (1B), 1.90 (1B), -5.51 (2B), -9.49 (4B), -11.80 (s, 2B); IR (film): 2957, 2610, 2575, 1744, 1254, 1126, 1053, 848, 720 cm⁻¹; HRMS (EI) m/z : [M]⁺ Calcd for C₁₈H₃₅B₁₀Cl₃O₂Si₂⁺ 554.2172; Found 554.2175; [α]_D²⁵: +15.7° (c = 0.21, CH₂Cl₂, 89% e.e.); HPLC (DAICEL IA column, 4% CH₂Cl₂ 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 ^1H 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 $^\circ\text{C}$; ^1H 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); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}]^+$ Calcd for $\text{C}_{18}\text{H}_{34}\text{B}_{10}\text{Cl}_4\text{O}_2\text{Si}_2^+$ 558.1782; Found 558.1785; $[\alpha]_D^{25}$: +8.2 $^\circ$ (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..

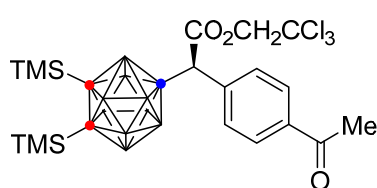


3bg: Yield: 131.8 mg (97%); Regioisomeric ratio (r.r.) = > 50:1 (determined from crude ^1H NMR analysis of the racemic product and the chiral product); R_f = 0.35 (CH_2Cl_2 :Hexane = 1:2); White solid; Melting point: 101-103 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.58 (d, J = 8.44 Hz, 2H), 7.15 (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); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}]^+$ Calcd for $\text{C}_{18}\text{H}_{34}\text{B}_{10}\text{Cl}_3\text{IO}_2\text{Si}_2^+$ 680.1138; Found 680.1139; $[\alpha]_D^{25}$: +25.1 $^\circ$ (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..

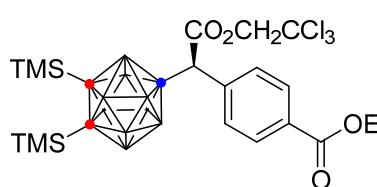


3bh: Yield: 114.5 mg (92%); Regioisomeric ratio (r.r.) = > 50:1 (determined from crude ^1H NMR analysis of the racemic product and the chiral product); R_f = 0.40 (CH_2Cl_2 :Hexane = 1:2); White solid; Melting point: 98-100 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.52 (s, 4H), 4.78 (d, J = 11.92 Hz, 1H), 4.59 (d, J = 11.92 Hz, 1H), 3.71 (s, 1H), 0.30 (s, 9H), 0.26 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3) δ 9.63 (1B), 1.69 (1B), -

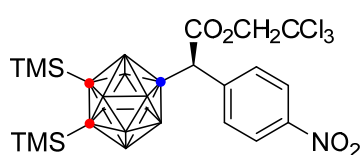
5.68 (2B), -9.53 (4B), -11.81 (2B); ^{19}F NMR (376 MHz, CDCl_3) δ -62.24; IR (film): 2957, 2615, 2575, 1741, 1322, 1256, 1119, 1064, 846 cm^{-1} ; HRMS (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{19}\text{H}_{34}\text{B}_{10}\text{Cl}_3\text{F}_3\text{O}_2\text{Si}_2^+$ 622.2046; Found 622.2047; $[\alpha]^{25}_{\text{D}}$: +21.8° ($c = 0.27$, 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..



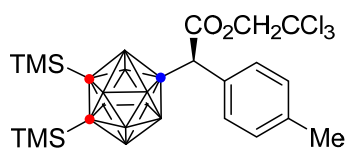
3bi: Yield: 105.8 mg (89%); Regioisomeric ratio (r.r.) = 29:1 (determined from crude ^1H NMR analysis of the racemic product and the chiral product); $R_f = 0.25$ (CH_2Cl_2 :Hexane = 1:1); Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 8.28$ Hz, 2H), 7.50 (d, $J = 8.28$ Hz, 2H), 4.78 (d, $J = 11.96$ 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); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{38}\text{B}_{10}\text{Cl}_3\text{O}_3\text{Si}_2^+$ 597.2356; Found 597.2359; $[\alpha]^{25}_{\text{D}}$: +12.0° ($c = 0.53$, 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..



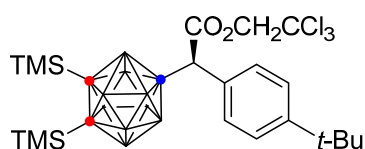
3bj: Yield: 122.2 mg (98%); Regioisomeric ratio (r.r.) = 47:1 (determined from crude ^1H NMR analysis of the racemic product and the chiral product); $R_f = 0.30$ (Et_2O :Hexane = 1:6); Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, $J = 8.48$ Hz, 2H), 7.48 (d, $J = 8.40$ Hz, 2H), 4.77 (d, $J = 11.94$ 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); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}]^+$ Calcd for $\text{C}_{21}\text{H}_{39}\text{B}_{10}\text{Cl}_3\text{O}_4\text{Si}_2^+$ 626.2383; Found 626.2383; $[\alpha]^{25}_{\text{D}}$: +9.8° ($c = 0.78$, 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 ^1H 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 $^\circ\text{C}$; ^1H 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); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}]^+$ Calcd for $\text{C}_{18}\text{H}_{34}\text{B}_{10}\text{Cl}_3\text{NO}_4\text{Si}_2^+$ 599.2022; Found 599.2020; $[\alpha]^{25}_{\text{D}}$: +16.1 $^\circ$ (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..

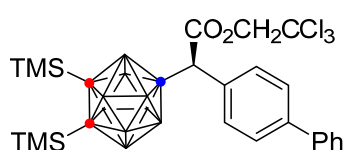


3bl: Yield: 112.1 mg (99%); Regioisomeric ratio (r.r.) = > 50:1 (determined from crude ^1H NMR analysis of the racemic product and the chiral product); R_f = 0.35 (CH_2Cl_2 :Hexane = 1:2); White solid; Melting point: 77-79 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.28 (d, J = 8.08 Hz, 2H), 7.07 (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); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}]^+$ Calcd for $\text{C}_{19}\text{H}_{37}\text{B}_{10}\text{Cl}_3\text{O}_2\text{Si}_2^+$ 568.2328; Found 568.2332; $[\alpha]^{25}_{\text{D}}$: +9.9 $^\circ$ (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..

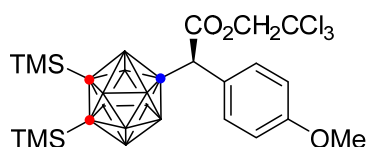


3bm: Yield: 106.2 mg (87%); Regioisomeric ratio (r.r.) = > 50:1 (determined from crude ^1H NMR analysis of the racemic product and the chiral product); R_f = 0.35 (CH_2Cl_2 :Hexane = 1:2); White solid; Melting point: 113-115 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.32 (d, J = 8.55 Hz, 2H), 7.27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

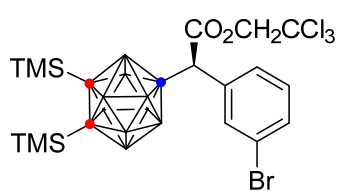
95.3, 74.7, 73.7, 68.1, 45.1, 34.4, 31.5, 1.8, 1.6; $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3) δ 10.37 (1B), 1.69 (1B), -5.57 (2B), -9.60 (4B), -11.98 (2B); IR (film): 2961, 2610, 2577, 1744, 1514, 1261, 1126, 1053, 848 cm^{-1} ; HRMS (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{22}\text{H}_{43}\text{B}_{10}\text{Cl}_3\text{O}_2\text{Si}_2^+$ 610.2798; Found 610.2802; $[\alpha]_D^{25}$: +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..



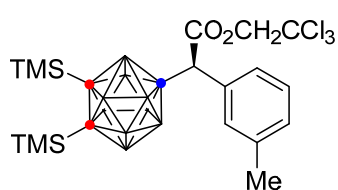
3bn: Yield: 117.3 mg (93%); Regioisomeric ratio (r.r.) = > 50:1 (determined from crude ^1H NMR analysis of the racemic product and the chiral product); R_f = 0.25 (CH_2Cl_2 :Hexane = 1:3); Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.61-7.57 (m, 2H), 7.52 (d, J = 8.48 Hz, 2H), 7.47 (d, J = 8.48 Hz, 2H), 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); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}]^+$ Calcd for $\text{C}_{24}\text{H}_{39}\text{B}_{10}\text{Cl}_3\text{O}_2\text{Si}_2^+$ 630.2485; Found 630.2486; $[\alpha]_D^{25}$: +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..



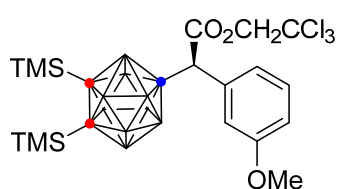
3bo: Yield: 107.7 mg (92%); Regioisomeric ratio (r.r.) = 29:1 (determined from crude ^1H NMR analysis of the racemic product and the chiral product); R_f = 0.40 (CH_2Cl_2 :Hexane = 1:1); Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, J = 8.72 Hz, 2H), 6.81 (d, J = 8.72 Hz, 2H), 4.74 (d, J = 11.92 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); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}]^+$ Calcd for $\text{C}_{19}\text{H}_{37}\text{B}_{10}\text{Cl}_3\text{O}_3\text{Si}_2^+$ 584.2277; Found 584.2274; $[\alpha]_D^{25}$: +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 ^1H NMR analysis of the racemic product and the chiral product); R_f = 0.30 (CH_2Cl_2 :Hexane = 1:2); Colorless oil; ^1H 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); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}]^+$ Calcd for $\text{C}_{18}\text{H}_{34}\text{B}_{10}\text{BrCl}_3\text{O}_2\text{Si}_2^+$ 632.1277; Found 632.1276; $[\alpha]_D^{25}$: +9.4° (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..

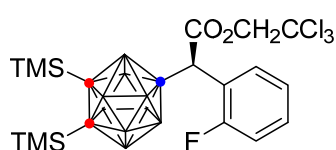


3bq: Yield: 113.5 mg (99%); Regioisomeric ratio (r.r.) = > 50:1 (determined from crude ^1H NMR analysis of the racemic product and the chiral product); R_f = 0.35 (CH_2Cl_2 :Hexane = 1:2); Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.23 (s, 1H), 7.19-7.12 (m, 2H), 6.97 (d, J = 6.95 Hz, 1H), 4.72 (d, 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); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}]^+$ Calcd for $\text{C}_{19}\text{H}_{37}\text{B}_{10}\text{Cl}_3\text{O}_2\text{Si}_2^+$ 568.2328; Found 568.2325; $[\alpha]_D^{25}$: +7.5° (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..



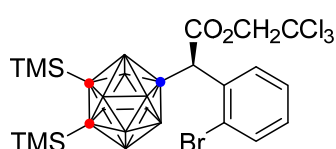
3br: Yield: 113.3 mg (97%); Regioisomeric ratio (r.r.) = 22:1 (determined from crude ^1H NMR analysis of the racemic product and the chiral product); R_f = 0.40 (CH_2Cl_2 :Hexane = 1:1); Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.19 (t, J = 7.92 Hz, 1H), 7.07 (s, 1H), 6.97 (d, J = 7.64 Hz, 1H), 6.75 (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); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}]^+$ Calcd for $\text{C}_{19}\text{H}_{37}\text{B}_{10}\text{Cl}_3\text{O}_3\text{Si}_2^+$ 584.2277; Found 584.2275; $[\alpha]_D^{25}$: +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..

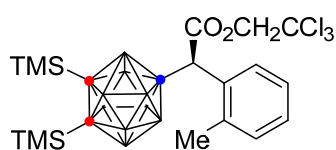


3bs: Yield: 101.6 mg (89%); Regioisomeric ratio (r.r.) = > 50:1 (determined from crude ^1H NMR analysis of the racemic product and the chiral product); R_f = 0.35 (CH_2Cl_2 :Hexane = 1:2); Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.87-7.83 (m, 1H), 7.16-7.07 (m, 2H), 7.00-6.95 (m, 1H), 4.78 (d, J = 12.0 Hz, 1H), 4.58 (d, J = 12.0 Hz, 1H), 4.14 (s, 1H), 0.30 (s, 9H), 0.26 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ 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;

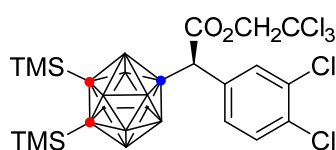
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3) δ 9.69 (1B), 1.73 (1B), -5.60 (2B), -9.45 (4B), -11.71 (2B); ^{19}F NMR (376 MHz, CDCl_3) δ -118.88; IR (film): 2959, 2613, 2575, 1744, 1256, 1126, 1049, 831, 751 cm^{-1} ; HRMS (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{18}\text{H}_{34}\text{B}_{10}\text{Cl}_3\text{FO}_2\text{Si}_2^+$ 572.2077; Found 572.2080; $[\alpha]_D^{25}$: +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..



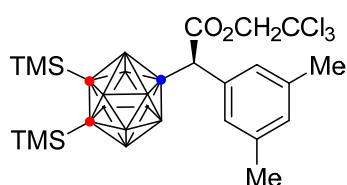
3bt: Yield: 122.8 mg (97%); Regioisomeric ratio (r.r.) = 18:1 (determined from crude ^1H NMR analysis of the racemic product and the chiral product); R_f = 0.30 (CH_2Cl_2 :Hexane = 1:2); White solid; Melting point: 42-44 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.89 (dd, J = 8.0 Hz, J = 1.7 Hz, 1H), 7.50 (dd, 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); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}]^+$ Calcd for $\text{C}_{18}\text{H}_{34}\text{B}_{10}\text{BrCl}_3\text{O}_2\text{Si}_2^+$ 632.1277; Found 632.1272; $[\alpha]_D^{25}$: +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 ^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: 84-86 $^\circ\text{C}$; ^1H 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); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}]^+$ Calcd for $\text{C}_{19}\text{H}_{37}\text{B}_{10}\text{Cl}_3\text{O}_2\text{Si}_2^+$ 568.2328; Found 568.2332; $[\alpha]_D^{25}$: +22.8 $^\circ$ (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..

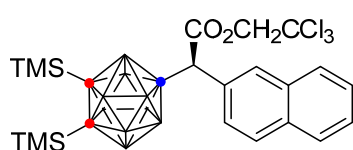


3bv: Yield: 115.5 mg (93%); Regioisomeric ratio (r.r.) = 45:1 (determined from crude ^1H NMR analysis of the racemic product and the chiral product); R_f = 0.30 (CH_2Cl_2 :Hexane = 1:2); White solid; Melting point: 125-127 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.54 (d, J = 1.9 Hz, 1H), 7.32 (d, 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); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}]^+$ Calcd for $\text{C}_{18}\text{H}_{33}\text{B}_{10}\text{Cl}_5\text{O}_2\text{Si}_2^+$ 622.1392; Found 622.1395; $[\alpha]_D^{25}$: +16.4 $^\circ$ (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..

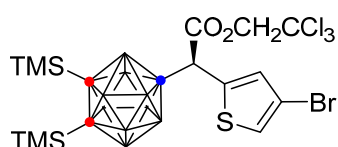


3bw: Yield: 110.5 mg (95%); Regioisomeric ratio (r.r.) = 38:1 (determined from crude ^1H NMR analysis of the racemic product and the chiral product); R_f = 0.35 (CH_2Cl_2 :Hexane = 1:2); White solid; Melting point: 103-105 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.02 (s, 2H), 6.80 (s, 1H), 4.70 (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); $^{13}\text{C}\{^1\text{H}\}$ 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,

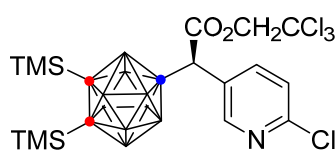
1.8, 1.6; $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3) δ 10.29 (1B), 1.79 (1B), -5.65 (2B), -9.60 (4B), -12.00 (2B); IR (film): 2959, 2912, 2613, 2570, 1741, 1254, 1122, 1053, 835 cm^{-1} ; HRMS (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{20}\text{H}_{39}\text{B}_{10}\text{Cl}_3\text{O}_2\text{Si}_2^+$ 582.2485; Found 582.2488; $[\alpha]_D^{25}$: +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..



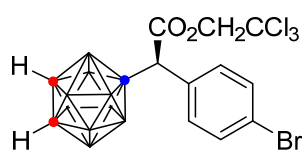
3bx: Yield: 105.3 mg (87%); Regioisomeric ratio (r.r.) = 46:1 (determined from crude ^1H NMR analysis of the racemic product and the chiral product); $R_f = 0.40$ (CH_2Cl_2 :Hexane = 1:2); White solid; Melting point: 114-116 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.82-7.74 (m, 4H), 7.61 (dd, $J = 8.6$ Hz, $J = 1.8$ 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); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}]^+$ Calcd for $\text{C}_{22}\text{H}_{37}\text{B}_{10}\text{Cl}_3\text{O}_2\text{Si}_2^+$ 604.2328; Found 604.2330.; $[\alpha]_D^{25}$: +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..



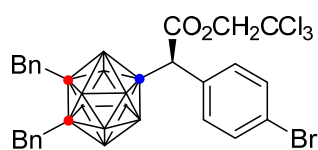
3by: Yield: 117.0 mg (92%); Regioisomeric ratio (r.r.) = > 50:1 (determined from crude ^1H NMR analysis of the racemic product and the chiral product); $R_f = 0.30$ (CH_2Cl_2 :Hexane = 1:2); Yellow solid; Melting point: 91-93 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.00 (d, $J = 1.0$ Hz, 2H), 6.83 (d, $J = 1.0$ 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); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{33}\text{B}_{10}\text{BrCl}_3\text{O}_2\text{SSi}_2^+$ 639.0919; Found 639.0922.; $[\alpha]_D^{25}$: +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 ^1H 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 $^\circ\text{C}$; ^1H 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); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{34}\text{B}_{10}\text{Cl}_4\text{NO}_2\text{Si}_2^+$ 590.1807; Found 590.1815.; $[\alpha]_D^{25}$: +11.4 $^\circ$ (c = 0.44, CH_2Cl_2 , 90% e.e.); HPLC (Reaction with $\text{Rh}_2(\text{R}/\text{S}\text{-TCPTTL})_4$ 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..

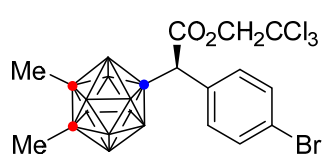


3cd: Yield: 87.9 mg (90%); Regioisomeric ratio (r.r.) = 5.2:1 (determined from crude ^1H NMR analysis of the racemic product and the chiral product); R_f = 0.35 (CH_2Cl_2 :Hexane = 1:1); White solid; Melting point: 113-115 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.40 (d, J = 8.6 Hz, 2H), 7.28 (d, 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); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{12}\text{H}_{19}\text{B}_{10}\text{BrCl}_3\text{O}_2^+$ 489.0565; Found 489.0562; $[\alpha]_D^{25}$: +29.4 $^\circ$ (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..

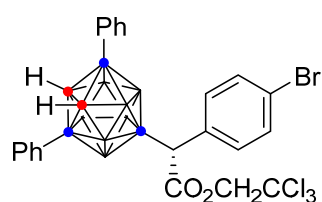


3dd: Yield: 125.5 mg (94%); Regioisomeric ratio (r.r.) = 6.3:1 (determined from crude ^1H NMR analysis of the racemic product and the chiral product); R_f = 0.25 (Et_2O :Hexane = 1:3); White solid; Melting point: 73-75 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.34 (m, 6H), 7.30 (d, J = 8.5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

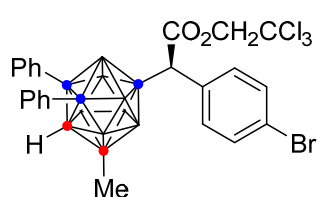
7.13 (m, 6H), 4.63 (d, $J = 11.9$ Hz, 1H), 4.43 (d, $J = 11.9$ Hz, 1H), 3.59 (s, 2H), 3.56 (s, 2H), 3.47 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 172.6, 138.9, 134.9, 134.7, 131.0, 130.4, 128.8, 128.5, 128.4, 119.8, 95.0, 78.5, 75.1, 74.5, 43.6, 41.5, 40.5; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{31}\text{B}_{10}\text{BrCl}_3\text{O}_2^+$ 669.1504; Found 669.1501; $[\alpha]_D^{25}$: +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 ^1H 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; ^1H 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); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{23}\text{B}_{10}\text{BrCl}_3\text{O}_2^+$ 517.0878; Found 517.0881; $[\alpha]_D^{25}$: +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..



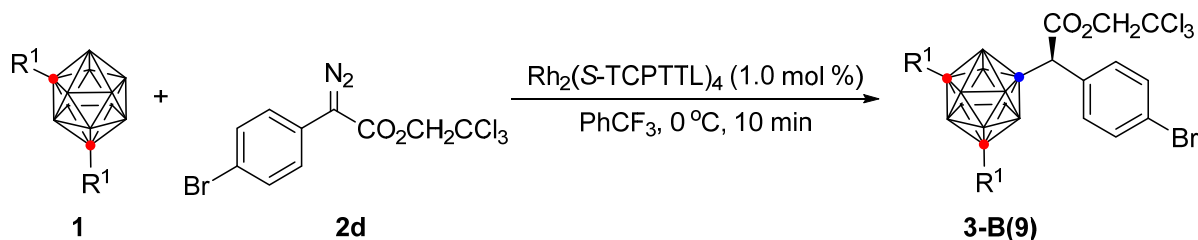
3fd: Yield: 113.9 mg (89%); $R_f = 0.30$ (Et_2O :Hexane = 1:6); White solid; Melting point: 123-125 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.55-7.52 (m, 4H), 7.43-7.39 (m, 4H), 7.36-7.32 (m, 6H), 4.75 (d, $J = 11.9$ Hz, 1H), 4.63 (d, $J = 11.9$ Hz, 1H), 3.83 (s, 1H), 3.76 (s, 1H), 3.71 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{27}\text{B}_{10}\text{BrCl}_3\text{O}_2^+$ 641.1191; Found 641.1193; $[\alpha]_D^{25}$: +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..



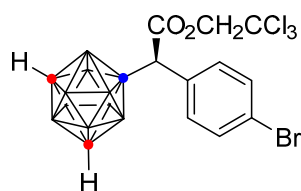
3gd: Yield: 126.8 mg (97%); R_f = 0.40 (Et₂O:Hexane = 1:1); White solid;

Melting point: 91-93 °C; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C{¹H} NMR (100 MHz, CDCl₃) 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; ¹¹B{¹H} NMR (128 MHz, CDCl₃) 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 C₂₅H₂₉B₁₀BrCl₃O₂⁺ 655.1342; Found 655.1350.; [α]_D²⁵: +22.1° (c = 0.60, CH₂Cl₂, 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



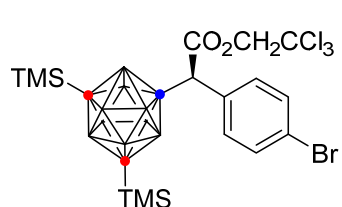
An oven dried test tube equipped with a magnetic stirrer was charged with *m*-carborane **1** (0.2 mmol, 1.0 equiv) and Rh₂(S-TCPTTL)₄ (1.0 mol %) in PhCF₃ (1.5 mL) and stirred at 0 °C under a N₂ atmosphere. The diazo **2d** (2.0 equiv) in PhCF₃ (1.5 mL) was added to the reaction mixture dropwise via 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 (CH₂Cl₂:Hexane = 1:2); Colorless oil;

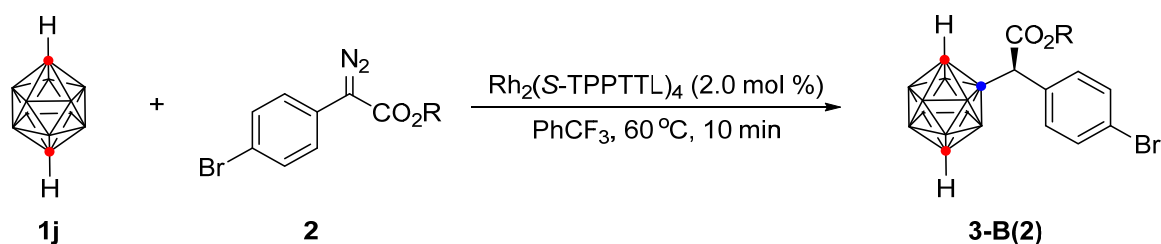
¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 4.76 (d, J = 11.9 Hz, 1H), 4.66 (d, J = 12.0 Hz, 1H), 3.78 (s, 1H), 2.91 (s, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 172.6, 138.9, 131.3, 130.4, 120.2, 94.9, 74.8, 54.5, 42.1; ¹¹B{¹H} NMR (128 MHz, CDCl₃) δ -0.58 (1B), -6.46 (2B), -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 C₁₂H₁₉B₁₀BrCl₃O₂⁺ 489.0565; Found 489.0562.; [α]_D²⁵:

+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..

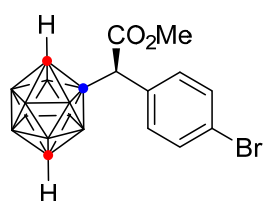


3id: Yield: 116.5 mg (92%); $R_f = 0.25$ (CH_2Cl_2 :Hexane = 1:2); White solid; Melting point: 88-90 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.5$ Hz, 2H), 4.76 (d, $J = 12.0$ Hz, 1H), 4.63 (d, $J = 11.9$ Hz, 1H), 3.77 (s, 1H), 0.08 (s, 18H); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{35}\text{B}_{10}\text{BrCl}_3\text{O}_2\text{Si}_2^+$ 633.1355; Found 633.1357.; $[\alpha]_D^{25}$: +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

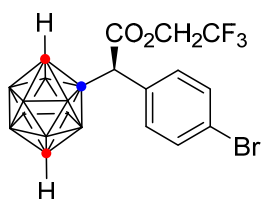


An oven dried test tube equipped with a magnetic stirrer was charged with *p*-carborane **1j** (0.2 mmol, 1.0 equiv) and $\text{Rh}_2(\text{S-TPPTTL})_4$ (2.0 mol %) in PhCF_3 (1.5 mL) and stirred at 60 °C under a N_2 atmosphere. The diazo **2** (2.0 equiv) in PhCF_3 (1.5 mL) was added to the reaction 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 ^1H NMR. The crude product was purified by column chromatography on silica gel to afford product **3**.

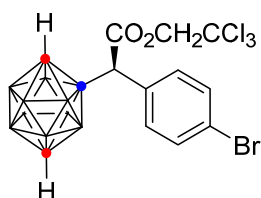


3jb: Yield: 42.1 mg (57%); $R_f = 0.30$ (Et_2O :Hexane = 1:6); White solid; Melting point: 143-145 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.42 (d, $J = 8.5$ Hz, 2H), 7.30 (d, $J = 8.5$ Hz, 2H), 3.73 (s, 1H), 3.70 (s, 3H), 2.76 (s, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100

MHz, CDCl₃) δ 173.7, 137.7, 131.6, 130.4, 120.5, 65.7, 63.7, 52.0, 41.7; ¹¹B{¹H} NMR (128 MHz, CDCl₃) 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 C₁₁H₂₀B₁₀BrO₂⁺ 373.1572; Found 373.1578.; [α]_D²⁵: +24.3° (c = 0.23, CH₂Cl₂, 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..

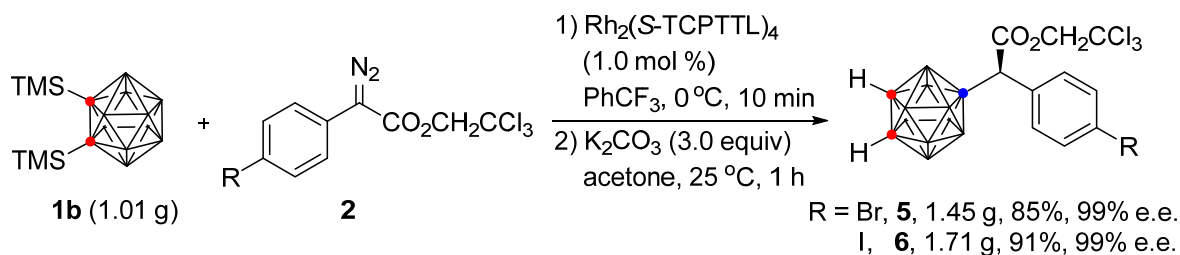


3jc: Yield: 54.6 mg (62%); R_f = 0.40 (Et₂O:Hexane = 1:6); Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, J = 8.6 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 4.56-4.39 (m, 2H), 3.82 (s, 1H), 2.79 (s, 1H), 2.70 (s, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 171.7, 136.7, 131.8, 130.2, 123.1 (q, J = 277.1 Hz), 121.0, 65.6, 63.9, 60.8 (q, J = 36.6 Hz), 41.3; ¹¹B{¹H} NMR (128 MHz, CDCl₃) δ -6.05 (1B), -13.92 (2B), -14.67 (6B), -16.86 (1B); ¹⁹F NMR (376 MHz, CDCl₃) δ -73.40; IR (film): 3060, 2610, 1748, 1485, 1278, 1161, 1134, 1117, 973 cm⁻¹; HRMS (FAB) m/z : [M+H]⁺ Calcd for C₁₂H₁₉B₁₀BrF₃O₂⁺ 441.1446; Found 441.1456.; [α]_D²⁵: +22.3° (c = 1.96, CH₂Cl₂, 97% e.e.); HPLC (DAICEL IA column, 4% CH₂Cl₂ 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 (Et₂O:Hexane = 1:6); White solid; Melting point: 92-94 °C; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 171.6, 136.9, 131.7, 130.4, 120.9, 94.7, 75.0, 65.7, 63.9, 42.0; ¹¹B{¹H} NMR (128 MHz, CDCl₃) 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 C₁₂H₁₉B₁₀BrCl₃O₂⁺ 489.0559; Found 489.0568.; [α]_D²⁵: +23.9° (c = 0.28, CH₂Cl₂, 96% e.e.); HPLC (DAICEL IA column, 15% CH₂Cl₂ 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



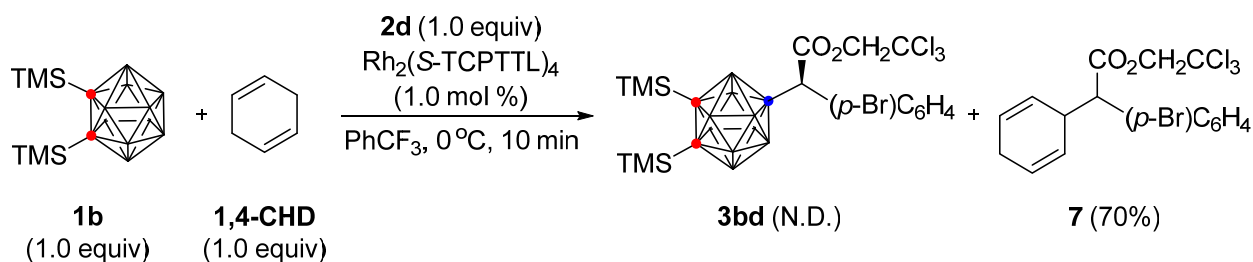
An oven dried flask equipped with a magnetic stirrer was charged with *o*-carborane **1** (1.01 g, 3.50 mmol, 1.0 equiv) and $\text{Rh}_2(\text{S-TCPTTL})_4$ (1.0 mol %) in PhCF_3 (26 mL) and stirred at 0 °C under a N_2 atmosphere. The diazo **2** (2.0 equiv) in PhCF_3 (26 mL) was added to the reaction 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; ^1H 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); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{12}\text{H}_{19}\text{B}_{10}\text{BrCl}_3\text{O}_2^+$ 489.0565; Found 489.0562; $[\alpha]_D^{25}$: +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; ^1H 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); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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)

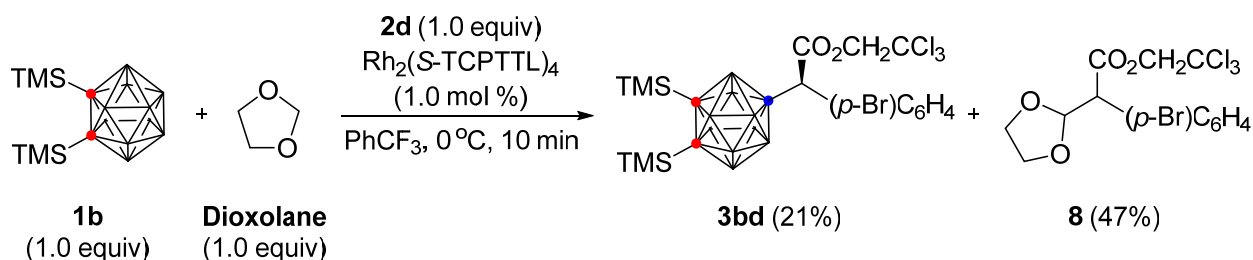
m/z : $[M+H]^+$ Calcd for $C_{12}H_{19}B_{10}Cl_3IO_2^+$ 537.0420; Found 537.0430; $[\alpha]^{25}_D$: $+11.5^\circ$ ($c = 0.56$, CH_2Cl_2 , 99% e.e.); HPLC (DAICEL IA column, 20% CH_2Cl_2 in hexane, 1.0 mL/min, 3 mg/mL, 30 min, UV 210 nm) retention times of 12.393 min (minor) and 13.292 min (major) 99%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

8. Comparison Experiments



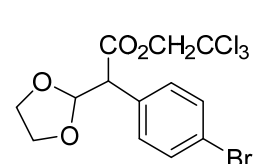
An oven dried test tube equipped with a magnetic stirrer was charged with **1b** (57.7 mg, 0.2 mmol, 1.0 equiv) and $\text{Rh}_2(\text{S-TCPTTL})_4$ (1.0 mol %) in PhCF_3 (1.5 mL) and stirred at 0 °C under a N_2 atmosphere, followed by addition of 1,4-cyclohexadiene (19 μL , 0.2 mmol, 1.0 equiv). The 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%).

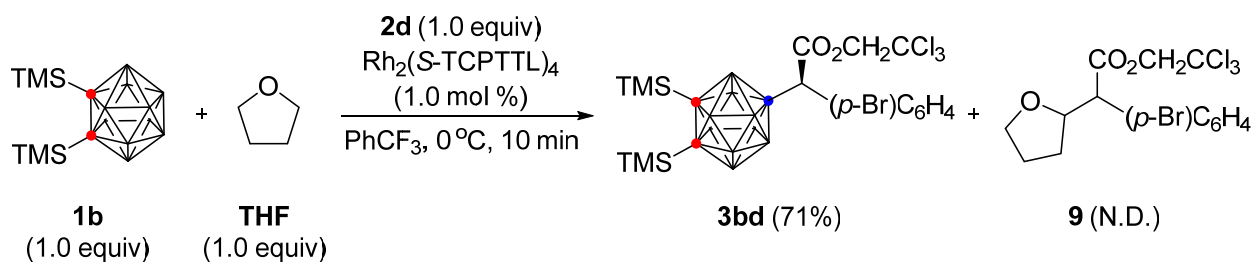
7: Yield: 70.2 mg (70%); $R_f = 0.30$ (CH_2Cl_2 :Hexane = 1:2); Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.46 (d, $J = 8.4$ Hz, 2H), 7.25 (d, $J = 8.9$ Hz, 2H), 5.83-5.81 (m, 1H), 5.75-5.72 (m, 2H), 5.32-5.29 (m, 1H), 4.79 (d, $J = 12.0$ Hz, 1H), 4.69 (d, $J = 11.9$ Hz, 1H), 3.55 (s, 2H), 2.62-2.60 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ 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 : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{15}\text{BrCl}_3\text{O}_2^+$ 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 $\text{Rh}_2(\text{S-TCPTTL})_4$ (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

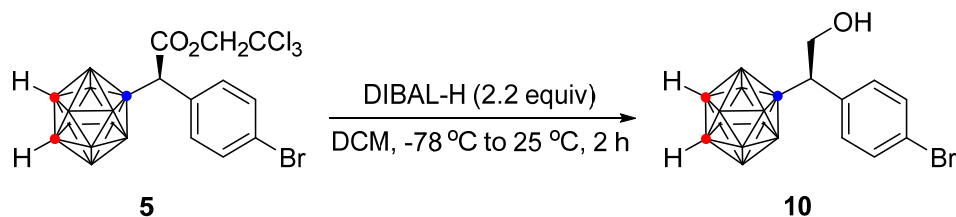
3 min. Then, the reaction mixture was stirred at 0 °C for 10 min. The crude product was concentrated under reduced pressure and purified by column chromatography on silica gel to afford **3bd** (21%) and **8** (47%).

 **8**: Yield: 39.4 mg (47%); R_f = 0.35 (CH_2Cl_2 :Hexane = 1:1); Colorless oil; ^1H 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); $^{13}\text{C}\{^1\text{H}\}$ 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 : $[\text{M}-\text{H}_2+\text{H}]^+$ Calcd for $\text{C}_{13}\text{H}_{11}\text{BrCl}_3\text{O}_4^+$ 414.8901; Found 414.8904.

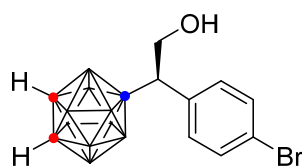


An oven dried test tube equipped with a magnetic stirrer was charged with **1b** (57.7 mg, 0.2 mmol, 1.0 equiv) and $\text{Rh}_2(\text{S-TCPTTL})_4$ (1.0 mol %) in PhCF_3 (1.5 mL) and stirred at 0 °C under a N_2 atmosphere, followed by addition of THF (16 μL , 0.2 mmol, 1.0 equiv). The diazo **2d** (74.5 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%).

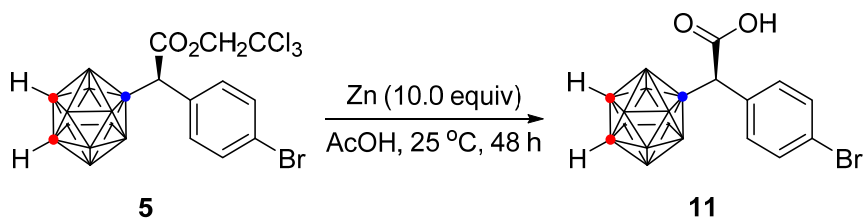
9. General Procedure of Functional Group Transformation



5 (97.7 mg, 0.2 mmol, 1.0 equiv) was dissolved in DCM (6 mL) and stirred at $-78\text{ }^\circ\text{C}$. 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 $25\text{ }^\circ\text{C}$ for 2 h. MeOH (6 mL) was added to the solution and stirred at $25\text{ }^\circ\text{C}$ 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.



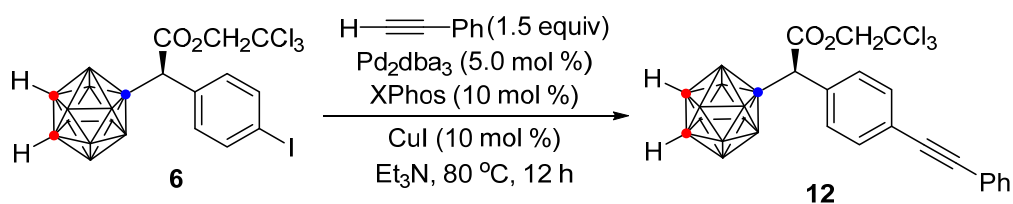
10: Yield: 51.5 mg (75%); $R_f = 0.35$ (EtOAc:Hexane = 1:3); White solid; Melting point: $135\text{--}137\text{ }^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.38 (d, $J = 8.4$ Hz, 2H), 6.99 (d, $J = 8.4$ Hz, 2H), 3.89 (t, $J = 11.4$ Hz, 1H), 3.87 (s, 1H), 3.47 (s, 2H), 2.54 (s, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 143.2, 131.5, 129.9, 119.0, 66.2, 53.3, 50.1, 40.0; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}-\text{H}_2\text{O}+\text{H}]^+$ Calcd for $\text{C}_{10}\text{H}_{18}\text{B}_{10}\text{Br}^+$ 327.1517; Found 327.1525; $[\alpha]_D^{25}$: -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 (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 $25\text{ }^\circ\text{C}$ 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.

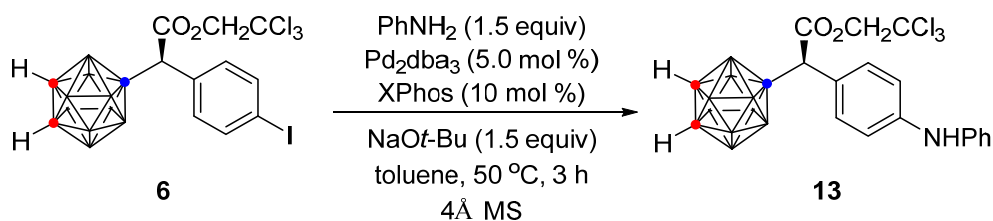
11: Yield: 63.6 mg (89%); R_f = 0.30 (Et₂O:Hexane = 2:1); White solid; Melting point: 238-240 °C; ¹H NMR (400 MHz, acetone-*d*₆) δ 10.44 (brs, 1H), 7.41 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 8.6 Hz, 2H), 4.49 (s, 2H), 3.45 (s, 1H); ¹³C{¹H} NMR (100 MHz, acetone-*d*₆) δ 175.0, 141.6, 131.6, 131.3, 119.6, 55.7, 51.8, 44.6; ¹¹B{¹H} 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 C₁₀H₁₈B₁₀BrO₂⁺ 359.1421; Found 359.1418; [α]_D²⁵: -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), Pd₂dba₃ (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 Et₃N (1 mL) under a N₂ atmosphere, followed by addition of phenylacetylene (33 μ L, 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 (CH₂Cl₂:Hexane = 1:2); White solid; Melting point: 133-135 °C; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C{¹H} NMR (100 MHz, CDCl₃) 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; ¹¹B{¹H} NMR (128 MHz, CDCl₃) δ 6.50 (1B), -2.14 (1B),

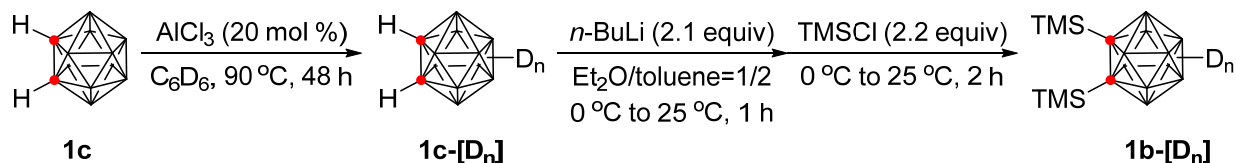
-9.03 (2B), -14.29 (4B), -15.45 (2B); IR (film): 3065, 2597, 1732, 1508, 1126, 1023, 755, 720, 689 cm^{-1} ; HRMS (FAB) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{24}\text{B}_{10}\text{Cl}_3\text{O}_2^+$ 511.1767; Found 511.1770; $[\alpha]_{\text{D}}^{25}$: +30.1° ($c = 0.13$, CH_2Cl_2 , 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 %), NaOt-Bu (33.7 mg, 0.30 mmol, 1.5 equiv), and 4 Å 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 $^\circ\text{C}$ 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.

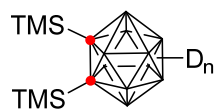
13: Yield: 68.3 mg (68%); $R_f = 0.40$ (CH_2Cl_2 :Hexane = 2:1); Yellow solid; Melting point: 85-87 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.29 (d, $J = 8.5$ Hz, 2H), 7.26-7.22 (m, 2H), 7.04-6.99 (m, 4H), 6.89 (t, $J = 7.3$ Hz, 1H), 5.63 (s, 1H), 4.72 (d, $J = 12.0$ Hz, 1H), 4.62 (d, $J = 12.0$ Hz, 1H), 3.59 (s, 1H), 3.49 (s, 2H); $^{13}\text{C}\{^1\text{H}\}$ 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; $^{11}\text{B}\{^1\text{H}\}$ 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 : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{25}\text{B}_{10}\text{Cl}_3\text{NO}_2^+$ 502.1876; Found 502.1877; $[\alpha]_{\text{D}}^{25}$: +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



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); $^1\text{H}\{^{11}\text{B}\}$ 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).

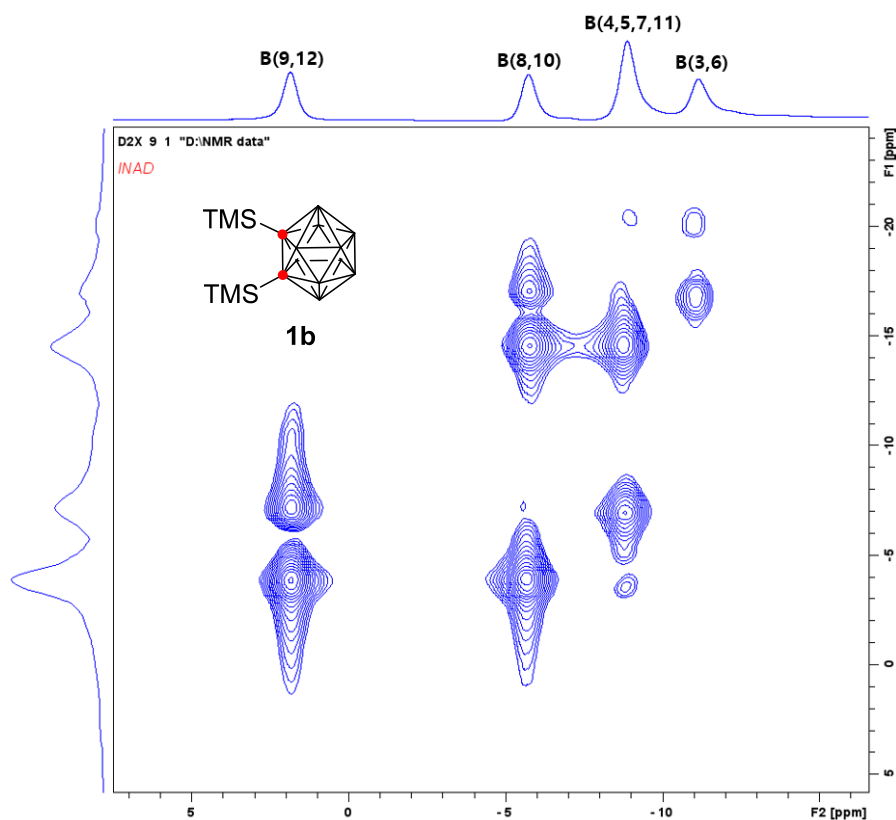


Fig. S2. $^{11}\text{B}\{^1\text{H}\}\text{-}^{11}\text{B}\{^1\text{H}\}$ INADEQUATE NMR for **1b**

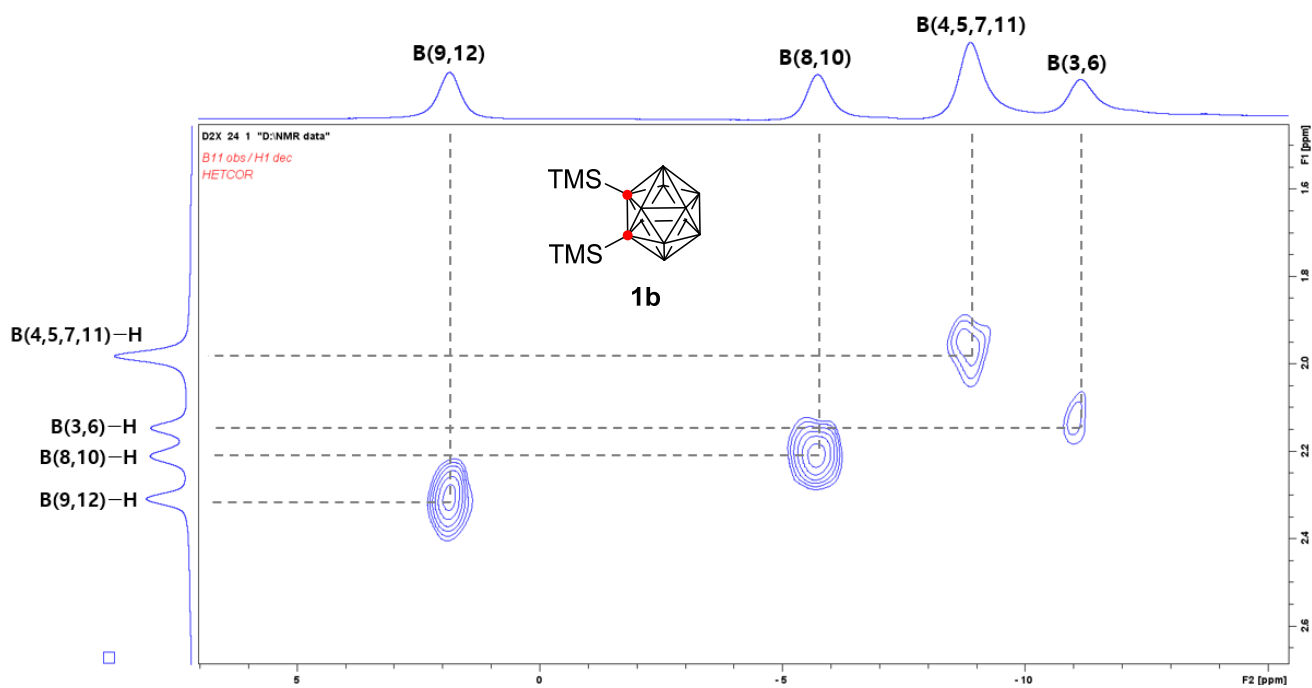


Fig. S3. $^{11}\text{B}\{^1\text{H}\}\text{-}^1\text{H}\{^{11}\text{B}\}$ HETCOR NMR for **1b**

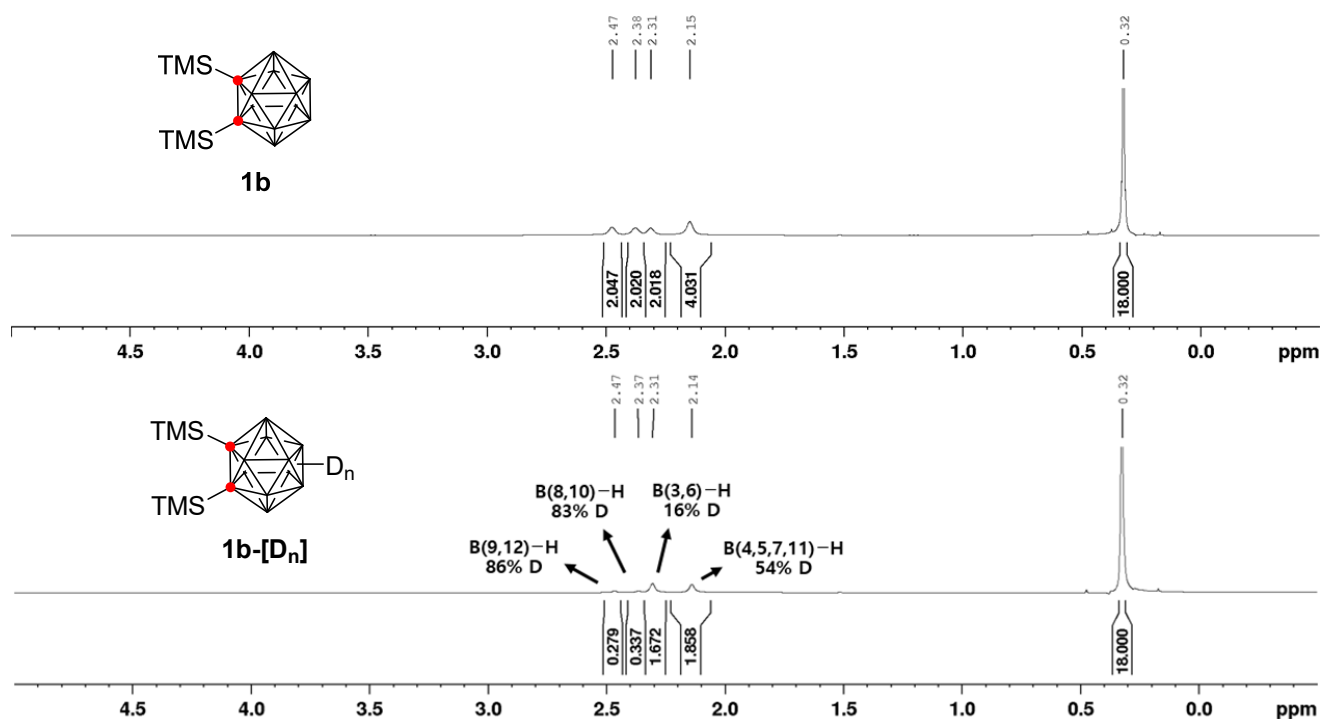


Fig. S4. Comparison of $^1\text{H}\{^{11}\text{B}\}$ NMR of **1b** (top) and **1b-[D_n]** (bottom)

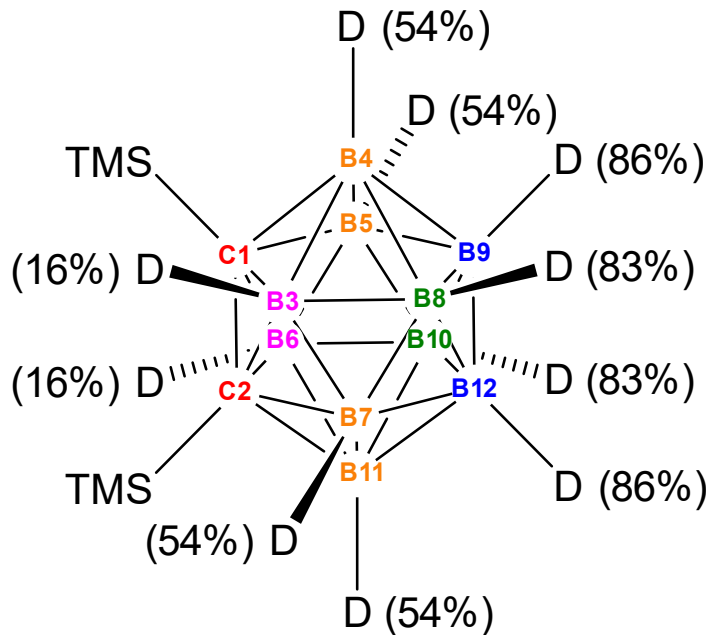
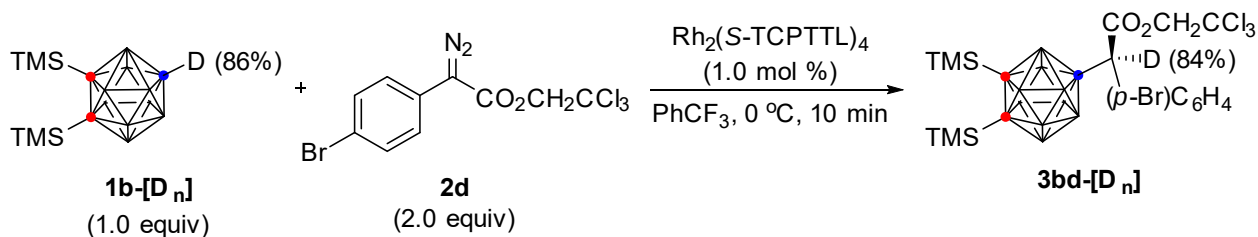


Fig. S5. Deuterated *o*-carborane **1b-[D_n]**



3bd-[D_n]: Yield: 123.8 mg (98%); $R_f = 0.35$ (CH_2Cl_2 :Hexane = 1:2); White solid; ^1H 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).

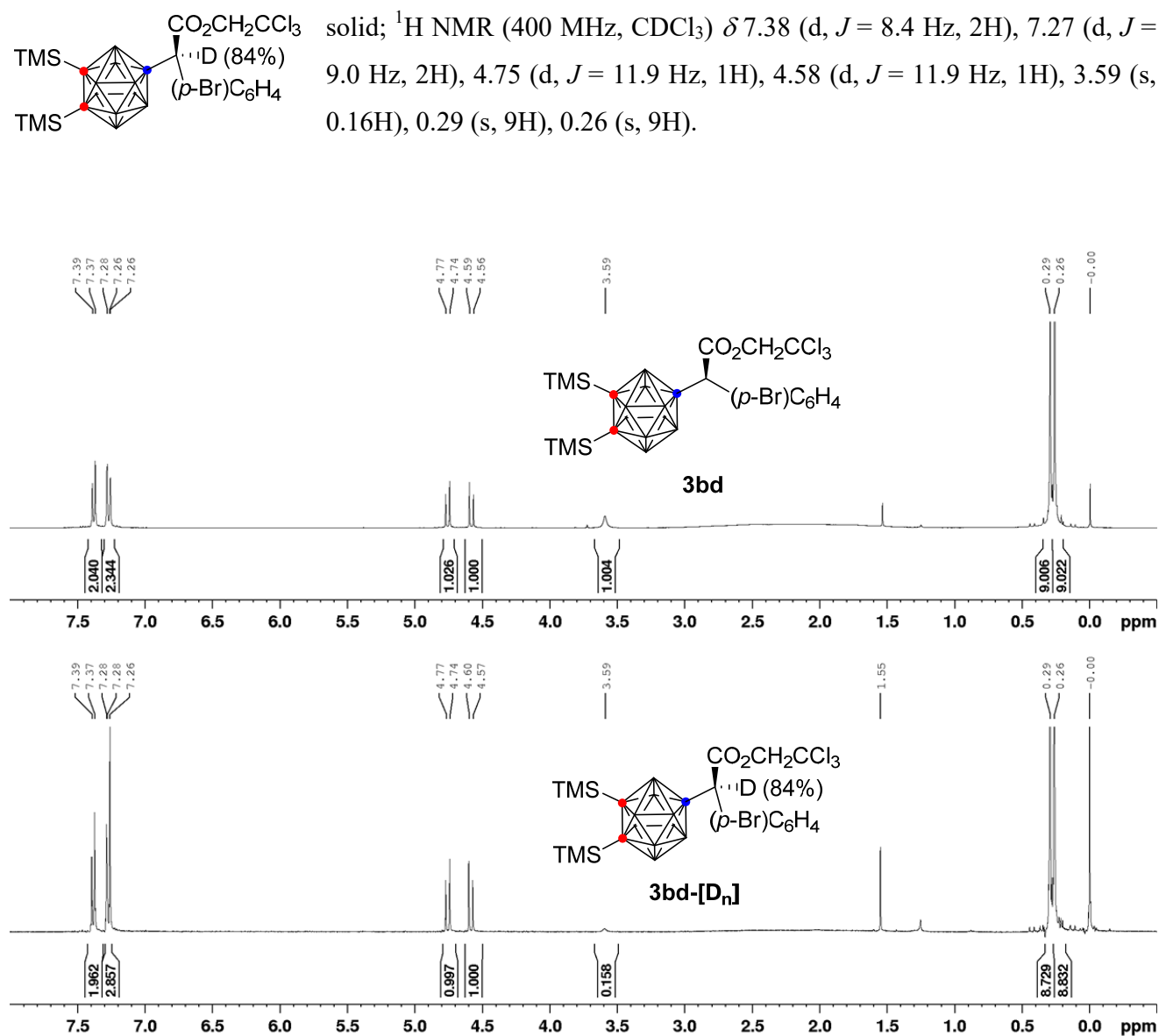
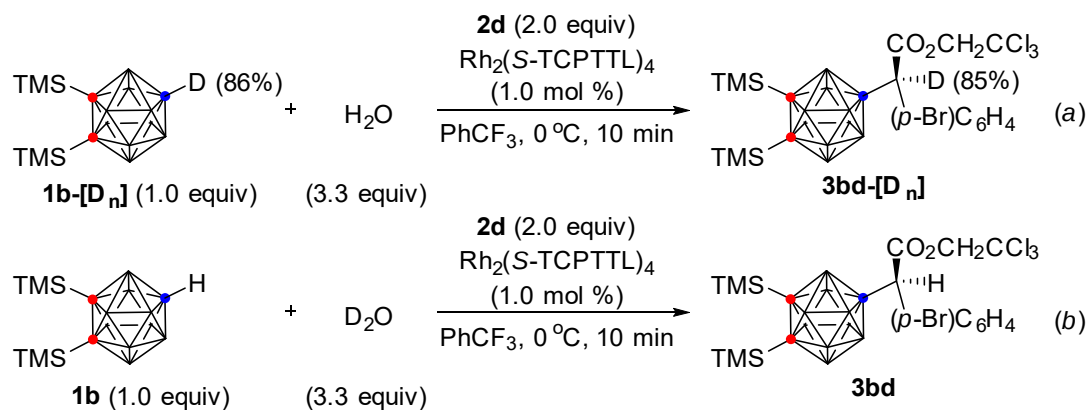


Fig. S6. Comparison of ^1H NMR of **3bd** (top) and **3bd-[D_n]** (bottom)



An oven dried test tube equipped with a magnetic stirrer was charged with **1b** or **1b**-[D_n] (0.2 mmol, 1.0 equiv) and $\text{Rh}_2(\text{S-TCPTTL})_4$ (1.0 mol %) in PhCF_3 (1.5 mL) and stirred at 0 °C under a N₂ atmosphere, followed by addition of H₂O or D₂O (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.

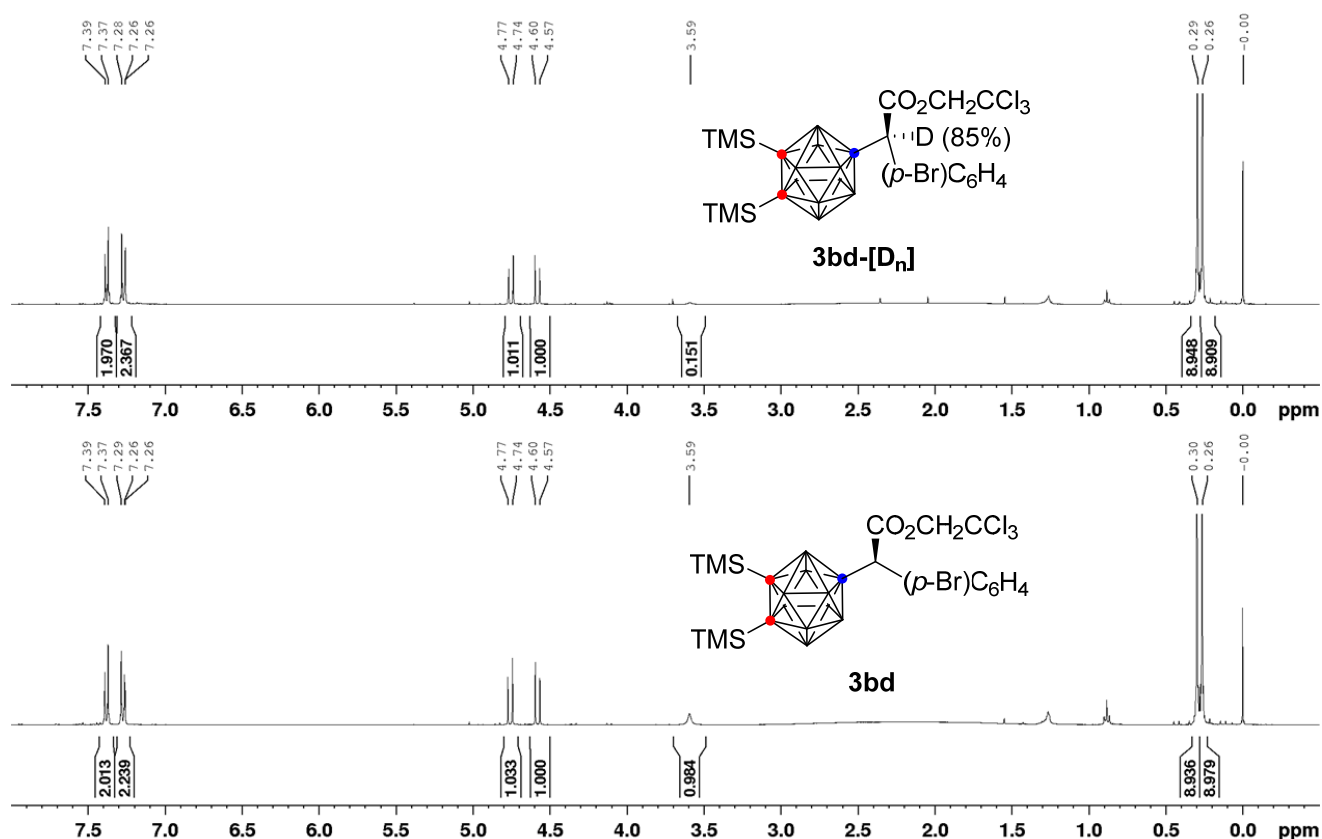


Fig. S7. Comparison of ¹H NMR of the product (a) (top) and (b) (bottom)

11. Computational Section

General information and computational procedures

All computations were performed using density functional theory (DFT) as implemented in the Gaussian 16 software package⁷. Structures were optimized using PBE^{8,9}-D3BJ¹⁰/LANL2DZ¹¹ (Rh, Br, Cl) & 6-31G(d)¹²⁻¹⁴ for all other atoms with CPCM(C₆H₆) solvation corrections^{15,16} at 0 °C. Single point calculations were performed at PBE-D3BJ/def2-TZVP level of theory¹⁷. Conformational search was performed using Schrödinger Macromodel¹⁸. Figures were rendered in MacPyMOL v1.7.4.2¹⁹. 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 Rh₂(*S*-TCPTTL)₄ to afford the dirhodium carbenoid intermediate **I** ($\Delta G = 0.0$ 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)-B(9)}**), $\Delta G^\ddagger = 6.92$ kcal/mol) leads to the formation of the ground state product complex **III** ($\Delta G = -37.5$ kcal/mol). In contrast, the enantiomeric minor (*S*)-B(9)-TS (**II-TS_{(S)-B(9)}**), $\Delta G^\ddagger = 8.96$ kcal/mol) leads to the respective product complex **III** ($\Delta G = -36.0$ kcal/mol), and the regioisomeric minor (*R*)-B(8)-TS (**II-TS_{(R)-B(8)}**), $\Delta G^\ddagger = 9.00$ kcal/mol) leads to the respective product complex **III** ($\Delta G = -29.7$ kcal/mol). A second diazo compound **2d** releases the major product (*R*)-**3bd** ($\Delta G = -51.1$ kcal/mol), as well as molecular nitrogen gas, resulting in regeneration of the dirhodium carbenoid **I** for the next catalytic cycle.

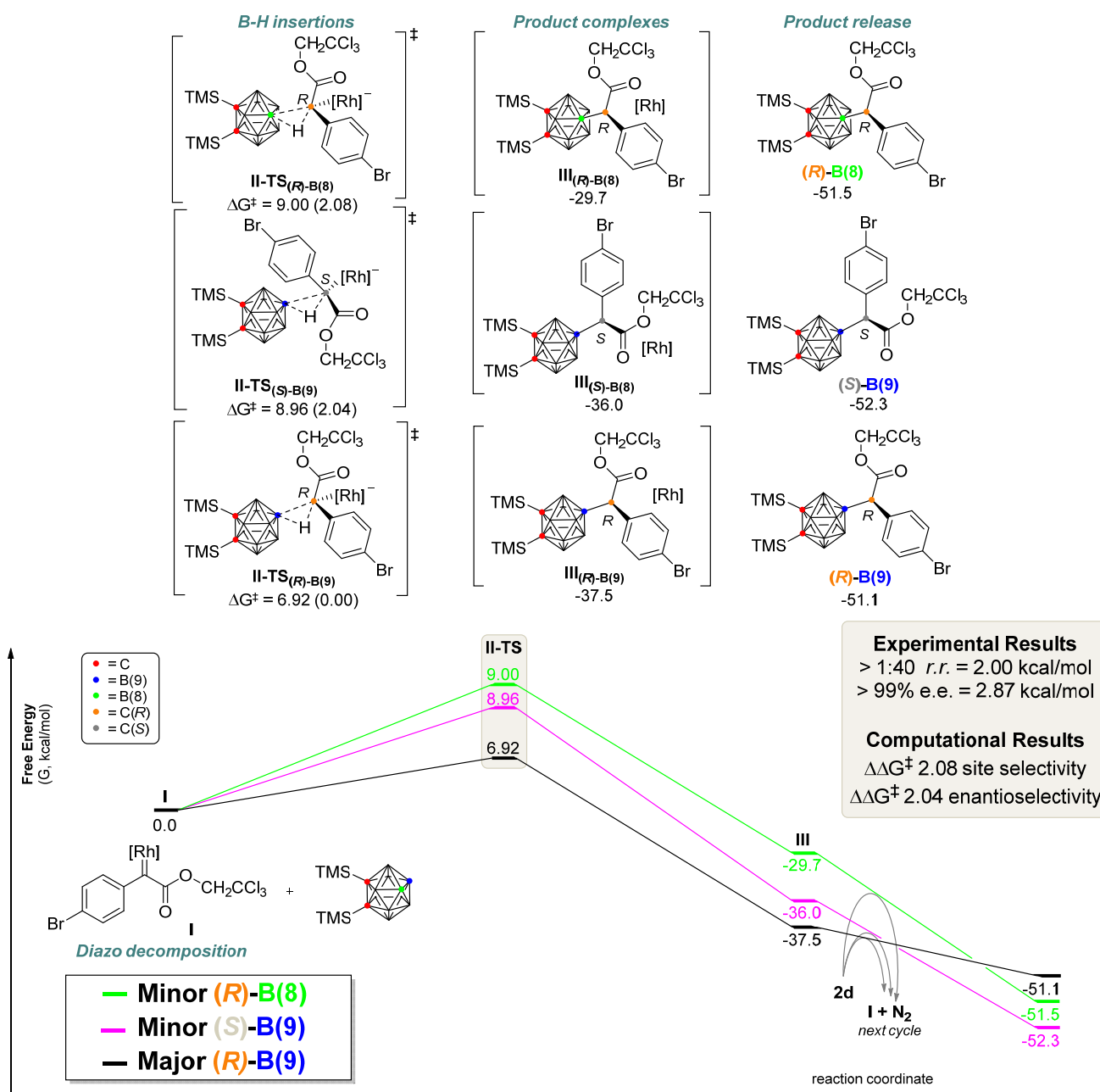


Fig. S8. The complete reaction coordinate diagram for the formation of the products

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

Supporting Information: N₂

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

pbepbe/6-31g(d)/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 5D 7F
#N Geom=AllCheck Guess=TChek 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
=====

pbepbe/6-31g(d)/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 5D 7F
#N Geom=AllCheck Guess=TChek 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

Optimization completed.	{Found	1	times}
Item	Max Val.	Criteria	Pass?
Force	0.00001 0.00045	[YES]	0.00000 0.00030 [YES]
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	Coordinates (Angstroms)		
Type	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: Rh₂(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

Supporting Information: dirhodium carbenoid intermediate I

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 Coordinates (Angstroms)
Type 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

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)-B(9)})

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
```

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

Charge = 0 Multiplicity = 1

SCF Energy= -5776.18133065 Predicted Change= -3.969515D-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	0.00298	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

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)-B(9)})

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 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

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	Coordinates (Angstroms)		
Type	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)-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

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

```
# pbe/bpbe/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= 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

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

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= C74H74B10BrCl19N4O18Rh2Si2 C1[X(C74H74B10BrCl19N4O18Rh2Si2)]

#Atoms= 204

Charge = 0 Multiplicity = 1

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

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

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

pbe/pbe/genecp/auto empirical dispersion=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= C74H74B10BrCl19N4O18Rh2Si2 C1[X(C74H74B10BrCl19N4O18Rh2Si2)]

#Atoms= 204

Charge = 0 Multiplicity = 1

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

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 Coordinates (Angstroms)

Type	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

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
```

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

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

=====

```
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	Coordinates (Angstroms)		
Type	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,yc) 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 Coordinates (Angstroms)
Type 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

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

pbe/pbe/genecp/auto empirical dispersion=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 Type	Coordinates (Angstroms)		
	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)-B(9)}

Movie S2: II-TS_{(S)-B(9)}

Movie S3: II-TS_{(R)-B(8)}

12. References

1. Núñez, R. et al. Synthesis of Small Carboranylsilane Dendrons as Scaffolds for Multiple Functionalizations. *Org. Lett.* **8**, 4549-4552 (2006).
2. Jaiswal, K., Volodarsky, S. & Kampel, V. A Self-Catalyzed Reaction of 1,2-Dibenzoyl *o*-Carborane with Hydrosilanes – Formation of New Hydrofuranes. *Chem. Commun.* **55**, 10448-10451 (2019).
3. Tang, C., Zhang, J., Zhang, J. & Xie, Z. Regioselective Nucleophilic Alkylation/Arylation of B–H Bonds in *o*-Carboranes: An Alternative Method for Selective Cage Boron Functionalization. *J. Am. Chem. Soc.* **140**, 16423-16427 (2018).
4. Armstrong, A. F. & Valliant, J. F. Microwave-Assisted Synthesis of Tricarbonyl Rhenacarboranes: Steric and Electronic Effects on the 1,2 → 1,7 Carborane Cage Isomerization. *Inorg. Chem.* **46**, 2148-2158 (2007).
5. Liao, K., Negretti, S., Musaev, D. G., Bacsá, J. & Davies, H. M. L. Site-selective and stereoselective functionalization of unactivated C–H bonds. *Nature* **533**, 230-234 (2016).
6. Fu, L., Mighion, J. D., Voight, E. A. & Davies, H. M. L. Synthesis of 2,2,2-Trichloroethyl Aryl- and Vinyl diazoacetates by Palladium-Catalyzed Cross-Coupling. *Chem. Eur. J.* **23**, 3272-3275 (2017).
7. Frisch, M. J. et al. Gaussian 16. Gaussian, Inc.: Wallingford, CT, USA. **2016**, Revision C.01.
8. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865 (1996).
9. Perdew, J. P., Burke, K. & Ernzerhof, M. Errata: Generalized gradient approximation made simple. *Phys. Rev. Lett.* **78**, 1396 (1997).
10. Grimme, S., Ehrlich, S. & Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comp. Chem.* **32**, 1456-1465 (2011).
11. Hay, P. J. & Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. *J. Chem. Phys.* **82**, 270-283 (1985).
12. Ditchfield, R., Hehre, W. J. & Pople, J. A. Self-consistent molecular-orbital methods. IX. An extended Gaussian-type basis for molecular-orbital studies of organic molecules. *J. Chem. Phys.* **54**, 724-728 (1971).
13. Hehre, W. J., Ditchfield, R. & Pople, J. A. Self-consistent molecular orbital methods. XII. Further extensions of Gaussian-type basis sets for use in molecular orbital studies of organic molecules. *J. Chem. Phys.* **56**, 2257-2261 (1972).
14. Clark, T., Chandrasekhar, J. & Spitznagel, G. W. P. v. R. Schleyer, Efficient diffuse function-augmented basis sets for anion calculations. III. The 3-21+ G basis set for first-row elements, Li–F. *J. Comp. Chem.* **4**, 294-301 (1983).
15. Barone, V. & Cossi, M. Quantum calculation of molecular energies and energy gradients in solution by a conductor solvent model. *J. Phys. Chem. A*. **102**, 1995-2001 (1998).
16. Cossi, M., Rega, N., Scalmani, G. & Barone, V. Energies, structures, and electronic properties of molecules in solution with the C-PCM solvation model. *J. Comp. Chem.* **24**, 669-681 (2003).
17. Weigend, F. & Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **7**, 3297-3305 (2005).
18. Schrödinger Release 2019-4: MacroModel, Schrödinger, LLC, New York, NY, **2019**.
19. MacPyMOL: PyMOL v1.7.4.2, Schrödinger, LLC. (<http://www.pymol.org>)

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)

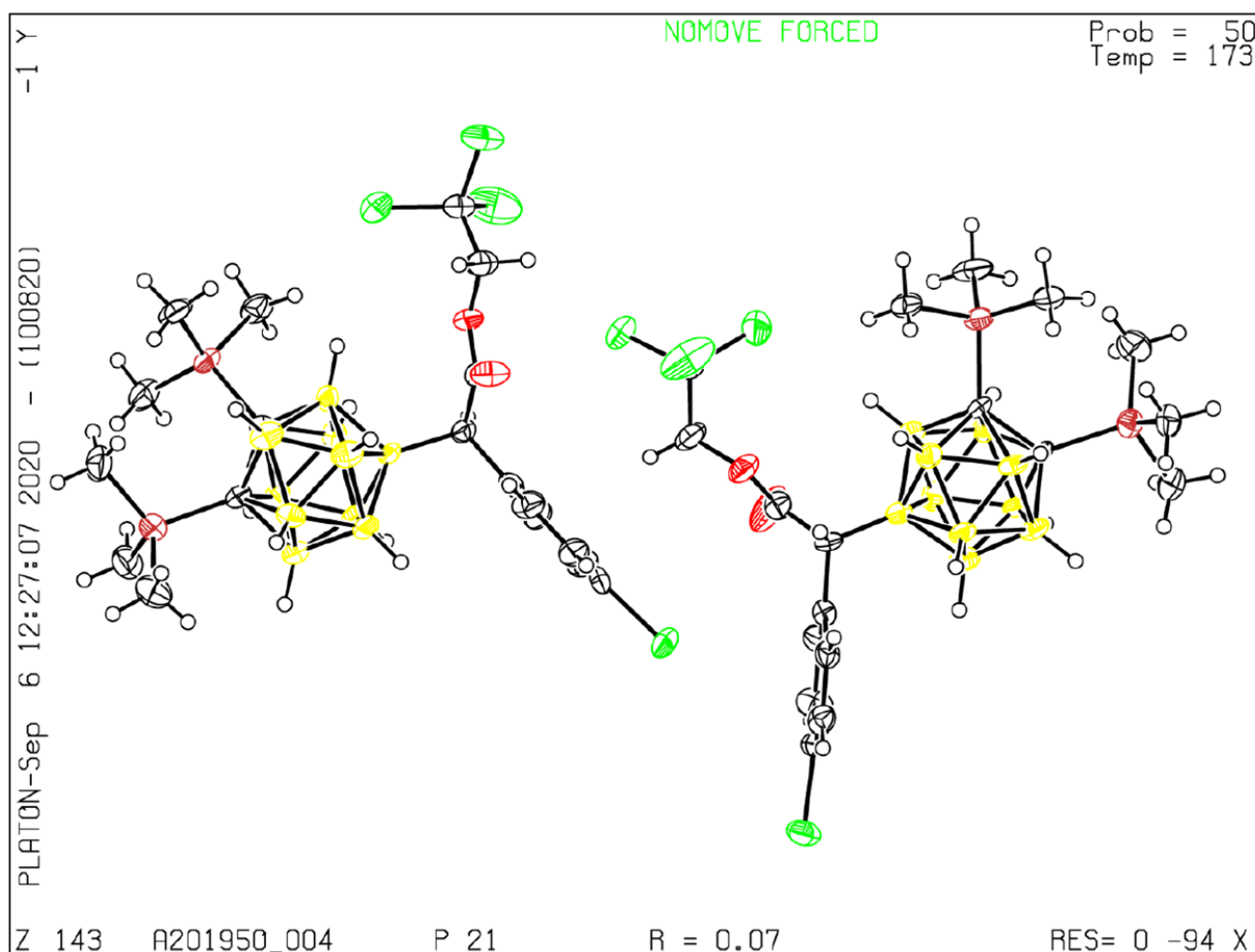


Table S2. Crystal data and structure refinement for (*R*)-3bd**.**

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	$a = 14.5216(8) \text{ \AA}$	$\alpha = 90^\circ$
	$b = 12.2531(8) \text{ \AA}$	$\beta = 107.513(5)^\circ$
	$c = 18.2279(12) \text{ \AA}$	$\gamma = 90^\circ$
Volume	$3093.0(3) \text{ \AA}^3$	
Z	4	
Density (calculated)	1.359 Mg/m^3	
Absorption coefficient	1.683 mm^{-1}	
F(000)	1288	
Crystal size	$0.337 \times 0.264 \times 0.156 \text{ mm}^3$	
Theta range for data collection	2.033 to 25.999°	
Index ranges	$-17 \leq h \leq 17$, $-15 \leq k \leq 15$, $-22 \leq l \leq 22$	
Reflections collected	26025	
Independent reflections	11989 [$R(\text{int}) = 0.0975$]	
Completeness to $\theta = 25.242^\circ$	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 [$I > 2\sigma(I)$]	$R1 = 0.0698$, $wR2 = 0.1035$	
R indices (all data)	$R1 = 0.1266$, $wR2 = 0.1193$	
Absolute structure parameter	0.013(7)	
Largest diff. peak and hole	0.578 and $-0.422 \text{ e} \cdot \text{\AA}^{-3}$	

(*R*)-**3gd**(CO₂H) (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**(CO₂H) suitable for X-ray diffraction within 2 day at room temperature. A block-like specimen of C₂₃H₂₇B₁₀BrO₂, 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)

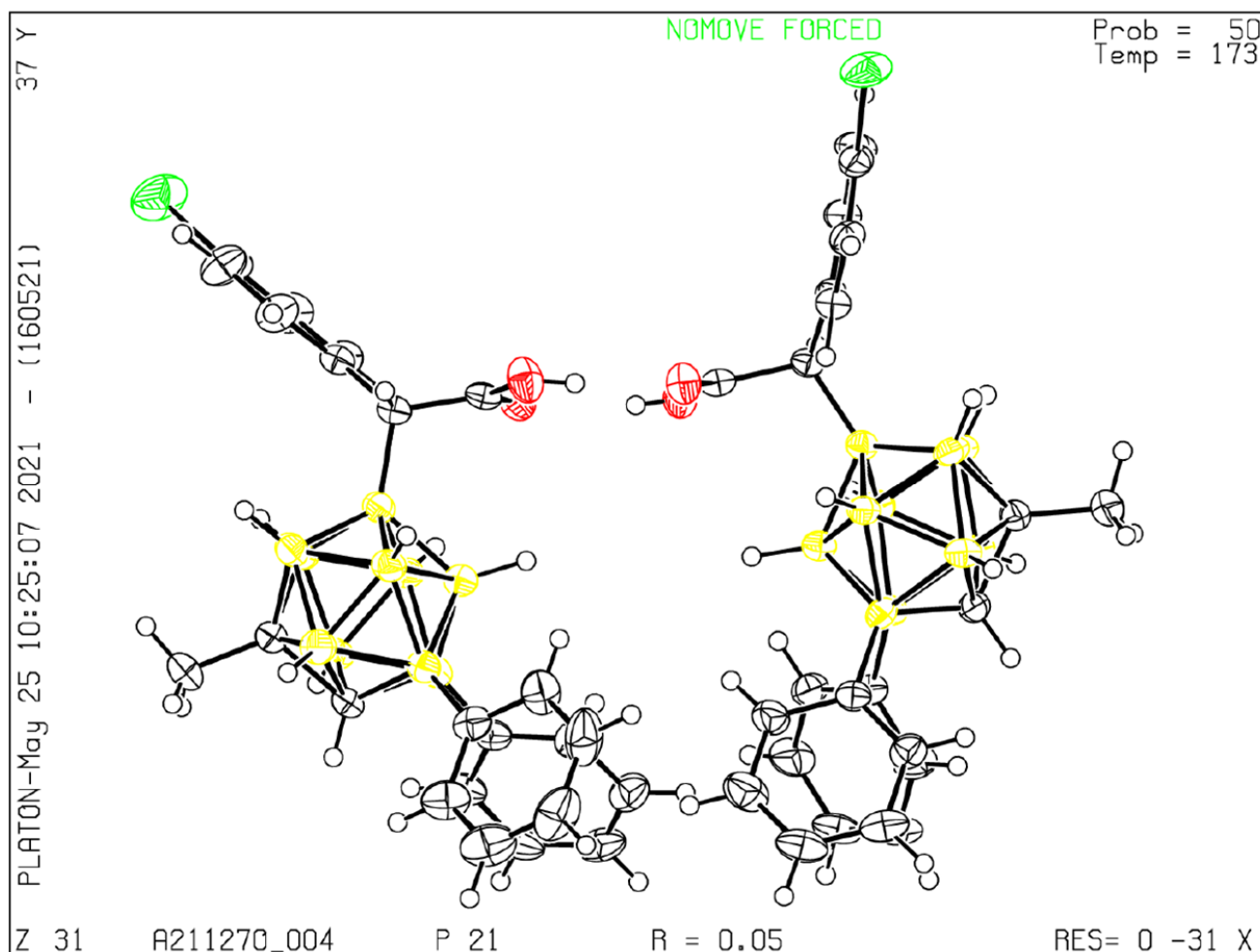


Table S4. Crystal data and structure refinement for (*R*)-3gd**.**

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	$a = 11.8606(8) \text{ \AA}$	$\alpha = 90^\circ$
	$b = 17.7171(11) \text{ \AA}$	$\beta = 98.8655(18)^\circ$
	$c = 12.5793(8) \text{ \AA}$	$\gamma = 90^\circ$
Volume	$2611.8(3) \text{ \AA}^3$	
Z	4	
Density (calculated)	1.331 Mg/m^3	
Absorption coefficient	1.595 mm^{-1}	
F(000)	1064	
Crystal size	$0.296 \times 0.052 \times 0.029 \text{ mm}^3$	
Theta range for data collection	2.480 to 26.493°	
Index ranges	$-14 \leq h \leq 14$, $-22 \leq k \leq 22$, $-15 \leq l \leq 15$	
Reflections collected	44248	
Independent reflections	10783 [$R(\text{int}) = 0.1066$]	
Completeness to $\theta = 25.242^\circ$	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 [$I > 2\sigma(I)$]	$R1 = 0.0476$, $wR2 = 0.0963$	
R indices (all data)	$R1 = 0.0847$, $wR2 = 0.1150$	
Absolute structure parameter	0.017(10)	
Largest diff. peak and hole	0.292 and $-0.469 \text{ e} \cdot \text{\AA}^{-3}$	

(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)

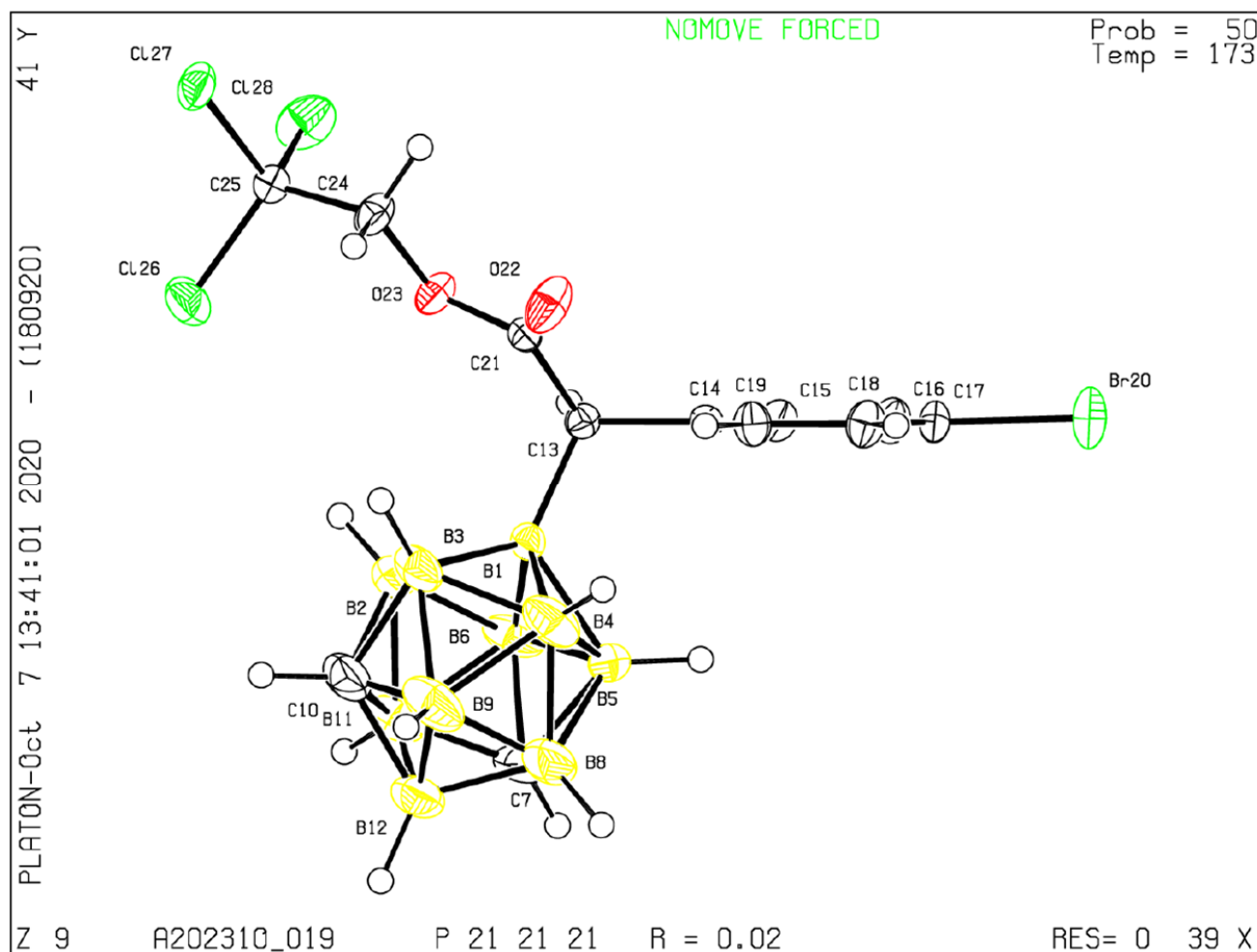


Table S5. Crystal data and structure refinement for (R)-3hd.

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	$a = 7.8684(4) \text{ \AA}$	$\alpha = 90^\circ$
	$b = 16.0219(8) \text{ \AA}$	$\beta = 90^\circ$
	$c = 17.0875(8) \text{ \AA}$	$\gamma = 90^\circ$
Volume	$2154.17(18) \text{ \AA}^3$	
Z	4	
Density (calculated)	1.507 Mg/m^3	
Absorption coefficient	2.287 mm^{-1}	
F(000)	968	
Crystal size	$0.309 \times 0.132 \times 0.082 \text{ mm}^3$	
Theta range for data collection	3.121 to 27.509° .	
Index ranges	$-10 \leq h \leq 10$, $-20 \leq k \leq 20$, $-22 \leq l \leq 22$	
Reflections collected	65329	
Independent reflections	4909 [$R(\text{int}) = 0.0414$]	
Completeness to $\theta = 25.242^\circ$	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 [$I > 2\sigma(I)$]	$R1 = 0.0238$, $wR2 = 0.0526$	
R indices (all data)	$R1 = 0.0275$, $wR2 = 0.0541$	
Absolute structure parameter	0.010(2)	
Largest diff. peak and hole	0.400 and $-0.336 \text{ e} \cdot \text{\AA}^{-3}$	

(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)

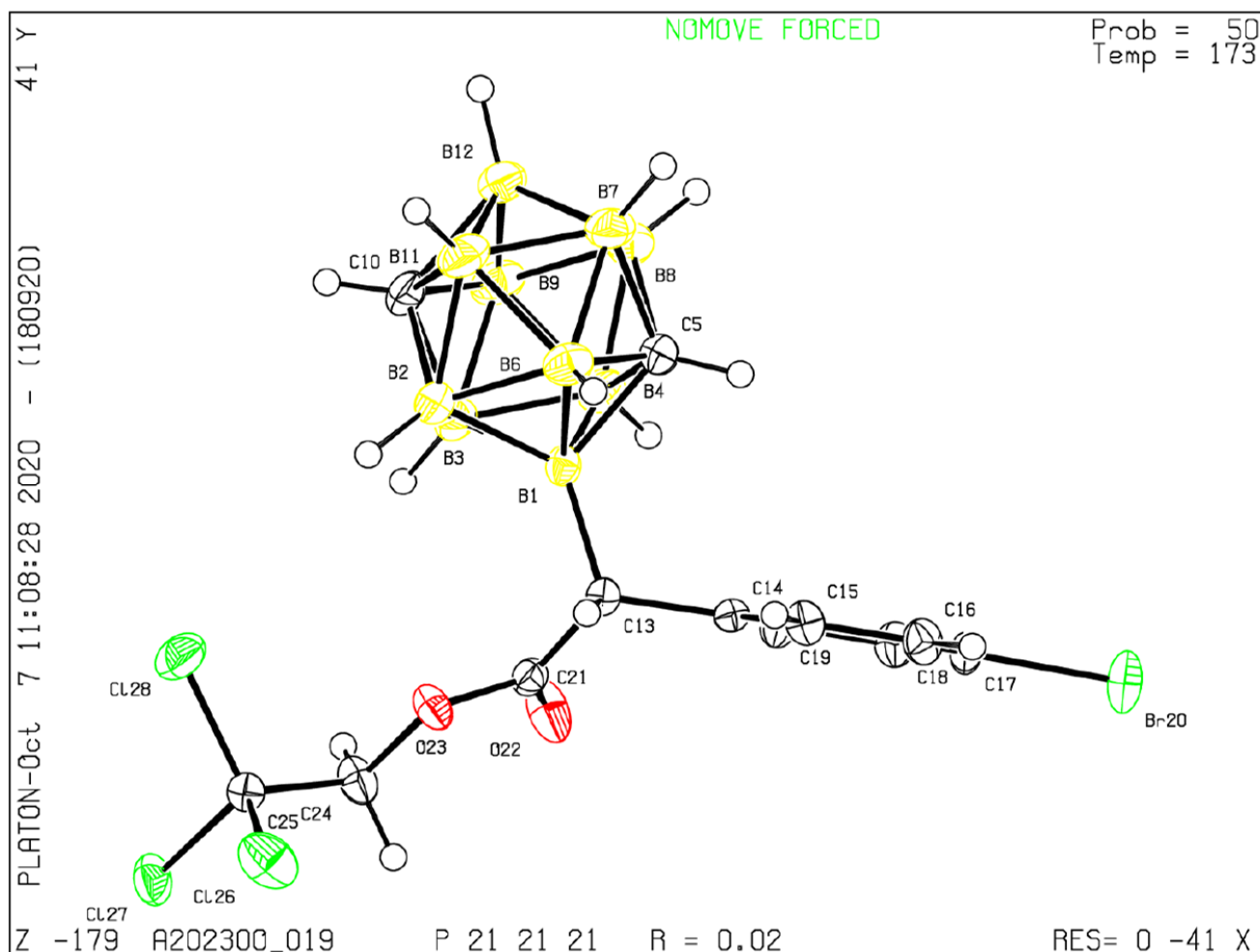


Table S6. Crystal data and structure refinement for (R)-3jd.

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	$a = 7.8717(3) \text{ \AA}$	$\alpha = 90^\circ$
	$b = 15.9248(6) \text{ \AA}$	$\beta = 90^\circ$
	$c = 17.0044(7) \text{ \AA}$	$\gamma = 90^\circ$
Volume	$2131.59(14) \text{ \AA}^3$	
Z	4	
Density (calculated)	1.523 Mg/m^3	
Absorption coefficient	2.311 mm^{-1}	
F(000)	968	
Crystal size	$0.298 \times 0.112 \times 0.067 \text{ mm}^3$	
Theta range for data collection	2.558 to 27.515°	
Index ranges	$-10 \leq h \leq 10$, $-20 \leq k \leq 20$, $-22 \leq l \leq 22$	
Reflections collected	54013	
Independent reflections	4855 [$R(\text{int}) = 0.0384$]	
Completeness to $\theta = 25.242^\circ$	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 [$I > 2\sigma(I)$]	$R1 = 0.0218$, $wR2 = 0.0487$	
R indices (all data)	$R1 = 0.0253$, $wR2 = 0.0501$	
Absolute structure parameter	0.024(2)	
Largest diff. peak and hole	0.316 and $-0.293 \text{ e} \cdot \text{\AA}^{-3}$	

(*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 C₁₈H₃₄B₁₀BrCl₃O₂Si₂, 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)

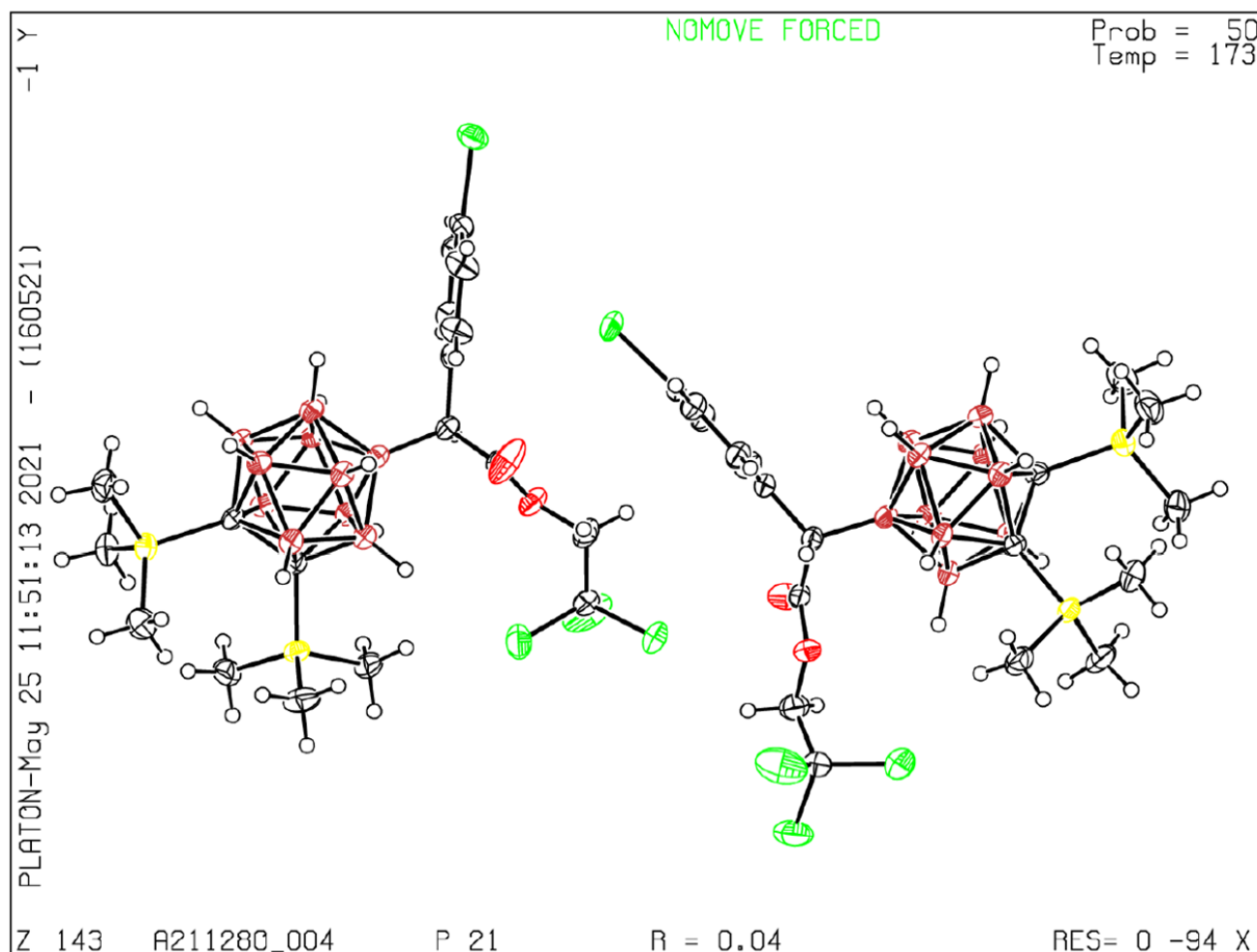
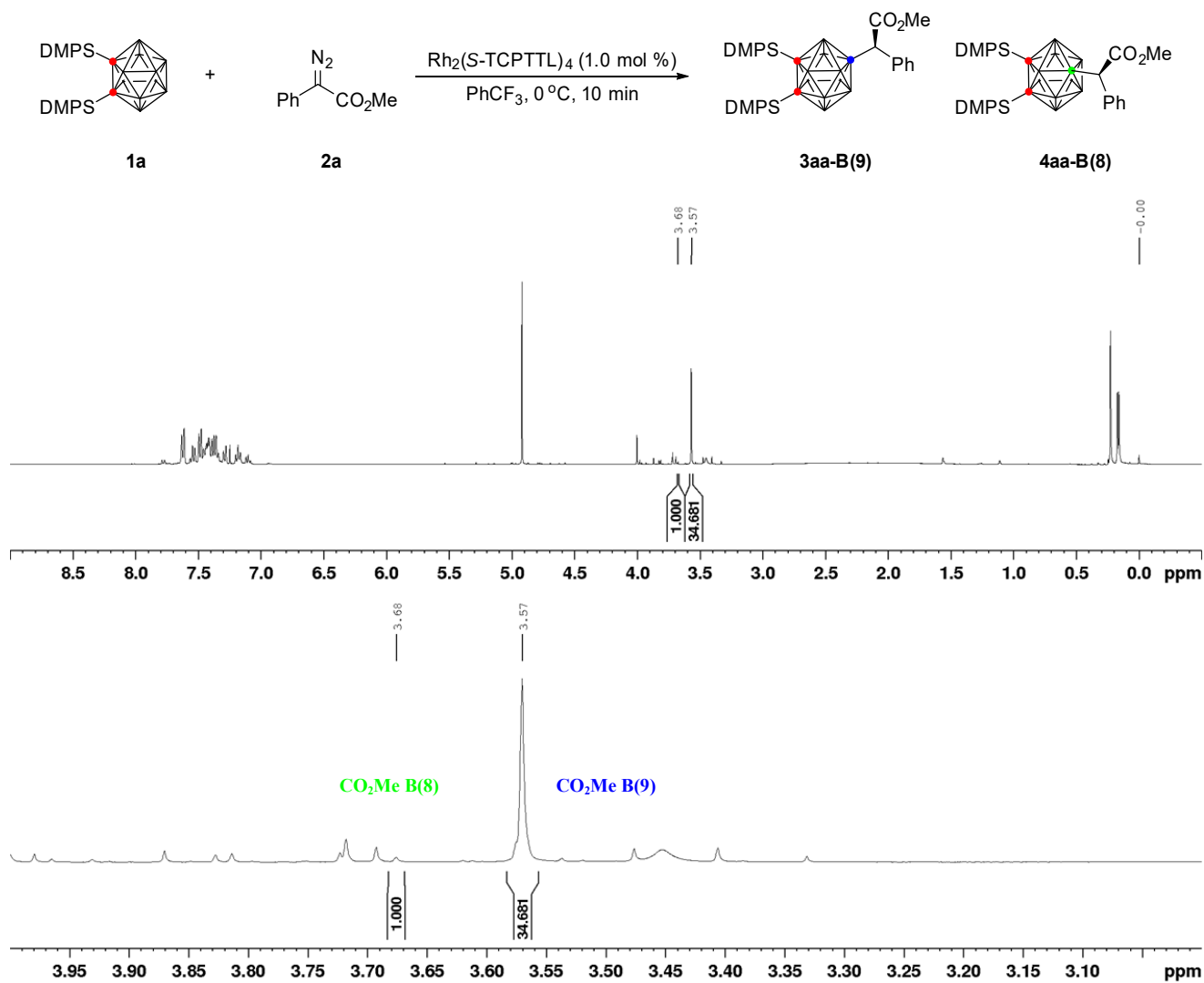


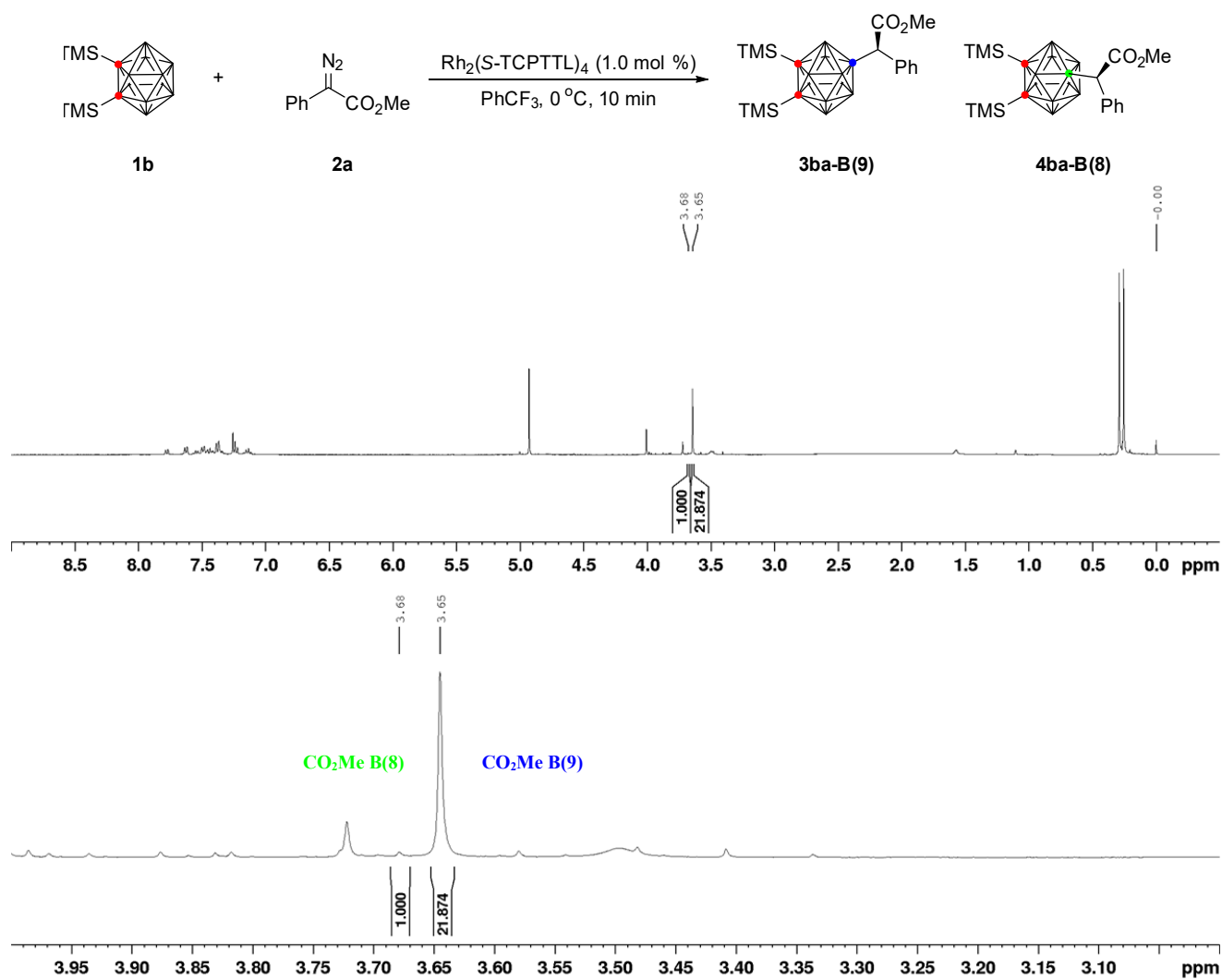
Table S3. Crystal data and structure refinement for (*S*)-3bd**.**

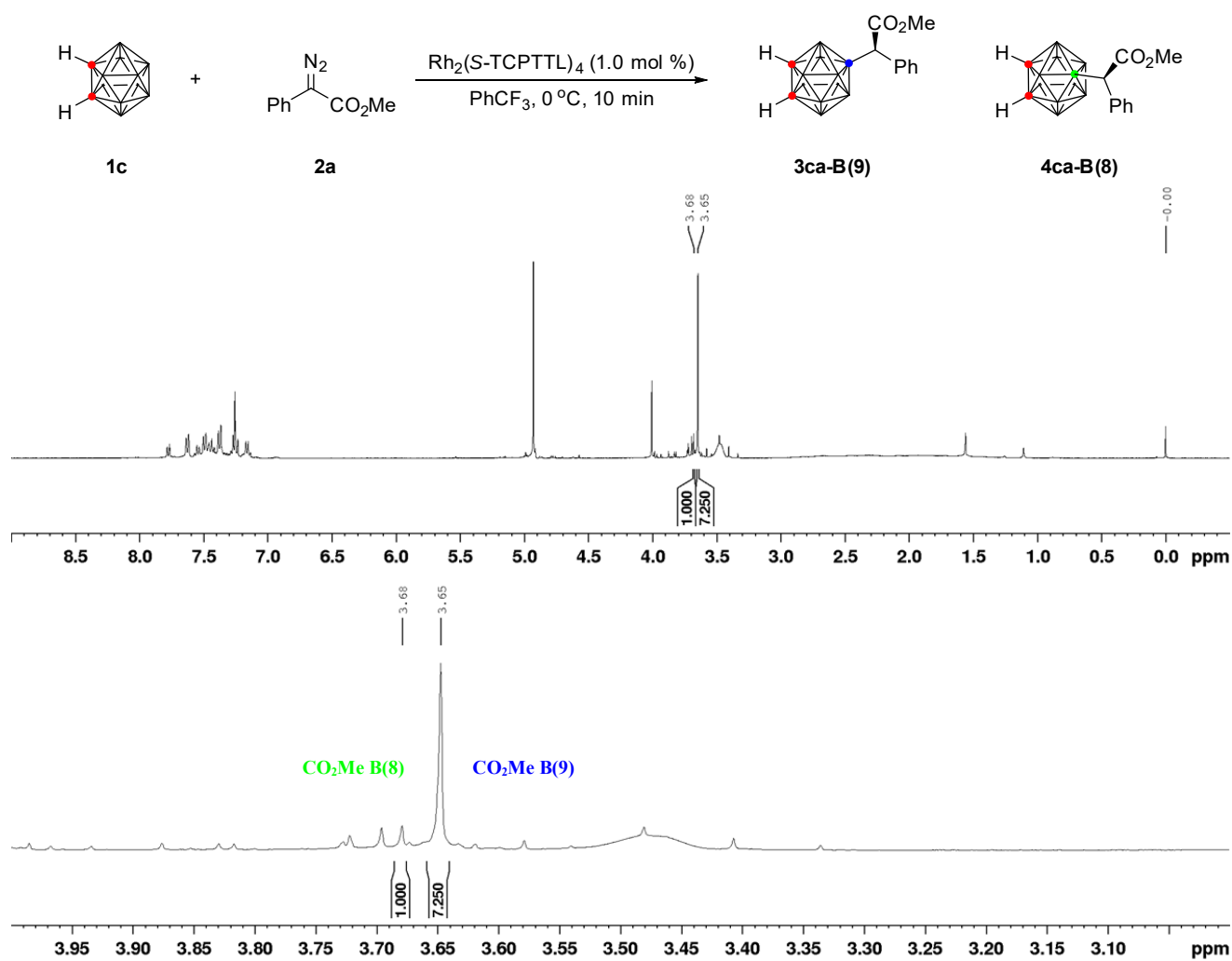
Empirical formula	C ₁₈ H ₃₄ B ₁₀ Br Cl ₃ O ₂ Si ₂
Formula weight	632.99
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic

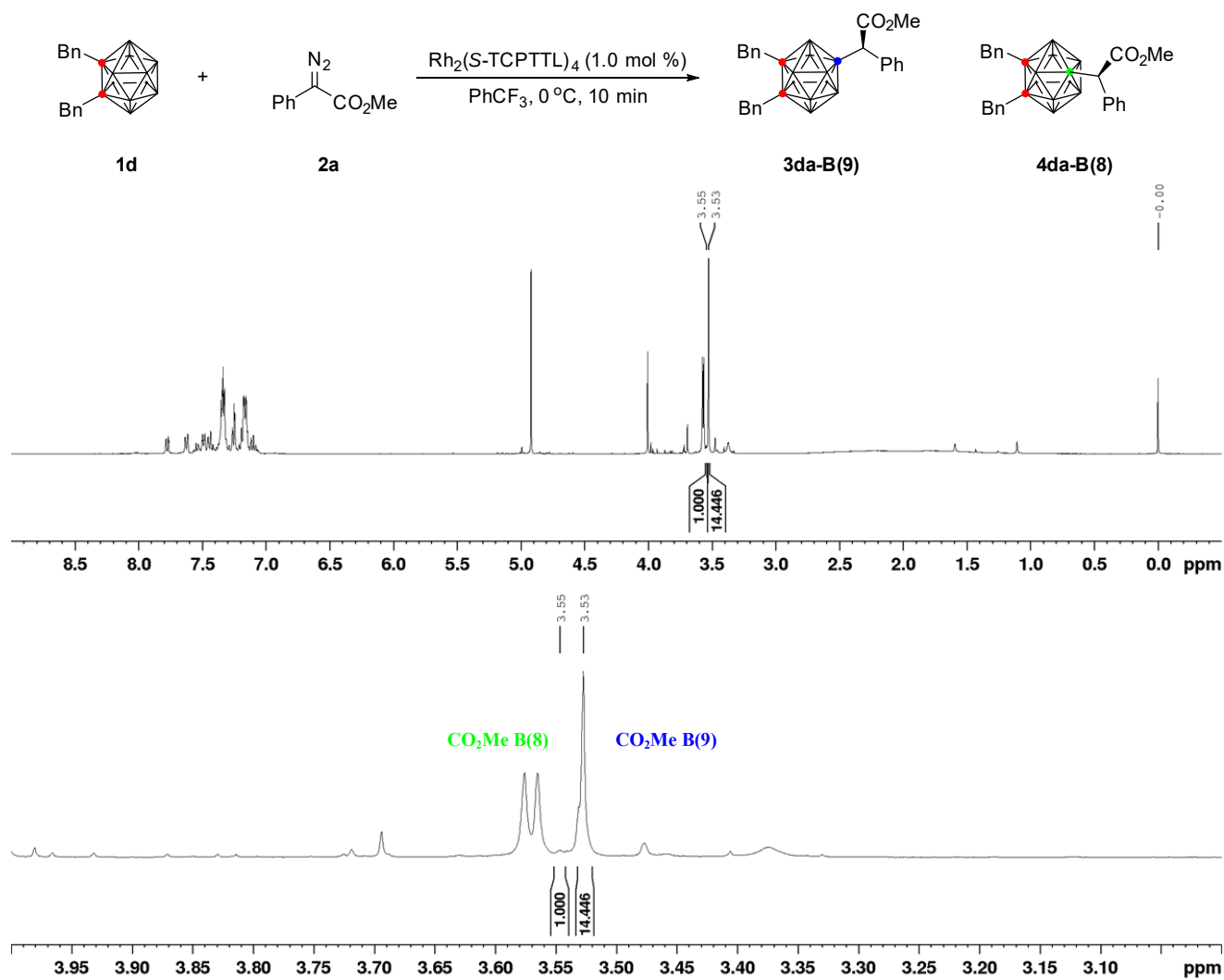
Space group	$P2_1$	
Unit cell dimensions	$a = 14.5317(6) \text{ \AA}$	$\alpha = 90^\circ$
	$b = 12.2602(5) \text{ \AA}$	$\beta = 107.5874(13)^\circ$
	$c = 18.2262(8) \text{ \AA}$	$\gamma = 90^\circ$
Volume	$3095.4(2) \text{ \AA}^3$	
Z	4	
Density (calculated)	1.358 Mg/m^3	
Absorption coefficient	1.682 mm^{-1}	
F(000)	1288	
Crystal size	$0.324 \times 0.135 \times 0.121 \text{ mm}^3$	
Theta range for data collection	2.709 to 27.523°	
Index ranges	$-17 \leq h \leq 18$, $-15 \leq k \leq 15$, $-22 \leq l \leq 23$	
Reflections collected	48533	
Independent reflections	13933 [$R(\text{int}) = 0.0548$]	
Completeness to $\theta = 25.242^\circ$	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 [$I > 2\sigma(I)$]	$R1 = 0.0396$, $wR2 = 0.0873$	
R indices (all data)	$R1 = 0.0538$, $wR2 = 0.0933$	
Absolute structure parameter	0.023(6)	
Largest diff. peak and hole	0.849 and $-0.634 \text{ e} \cdot \text{\AA}^{-3}$	

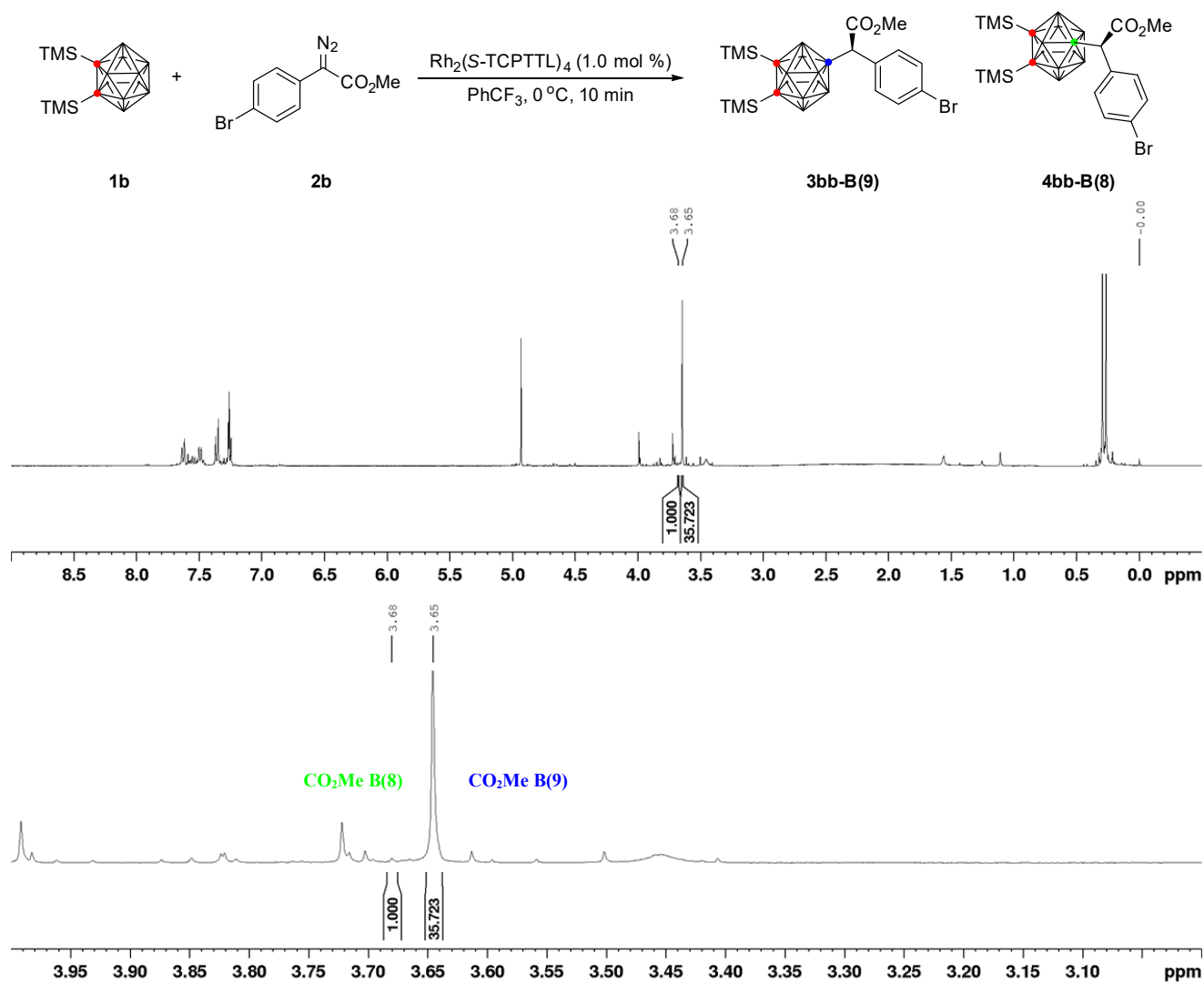
14. Crude ^1H NMR Spectra for Regioisomeric Ratio Determination

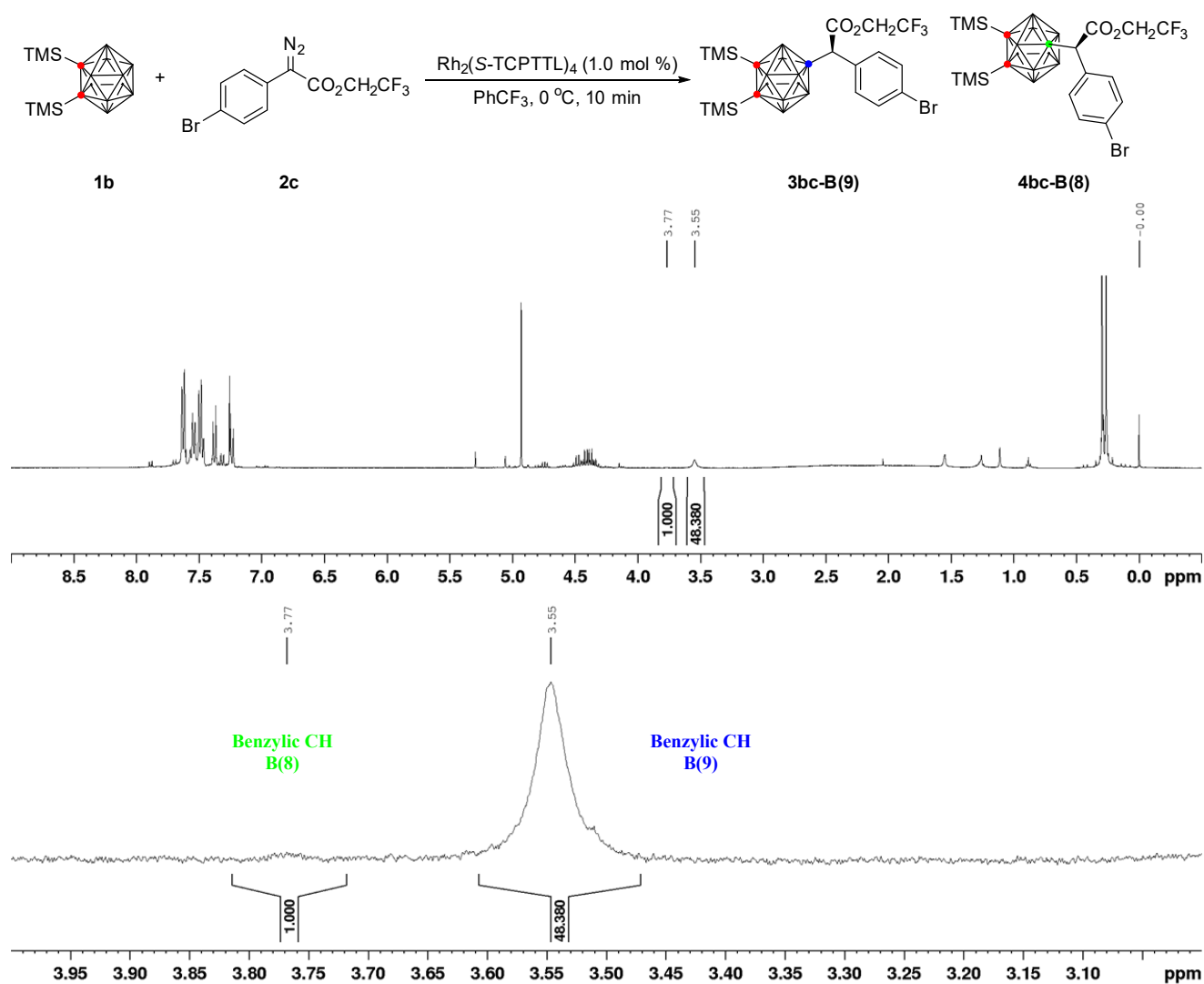


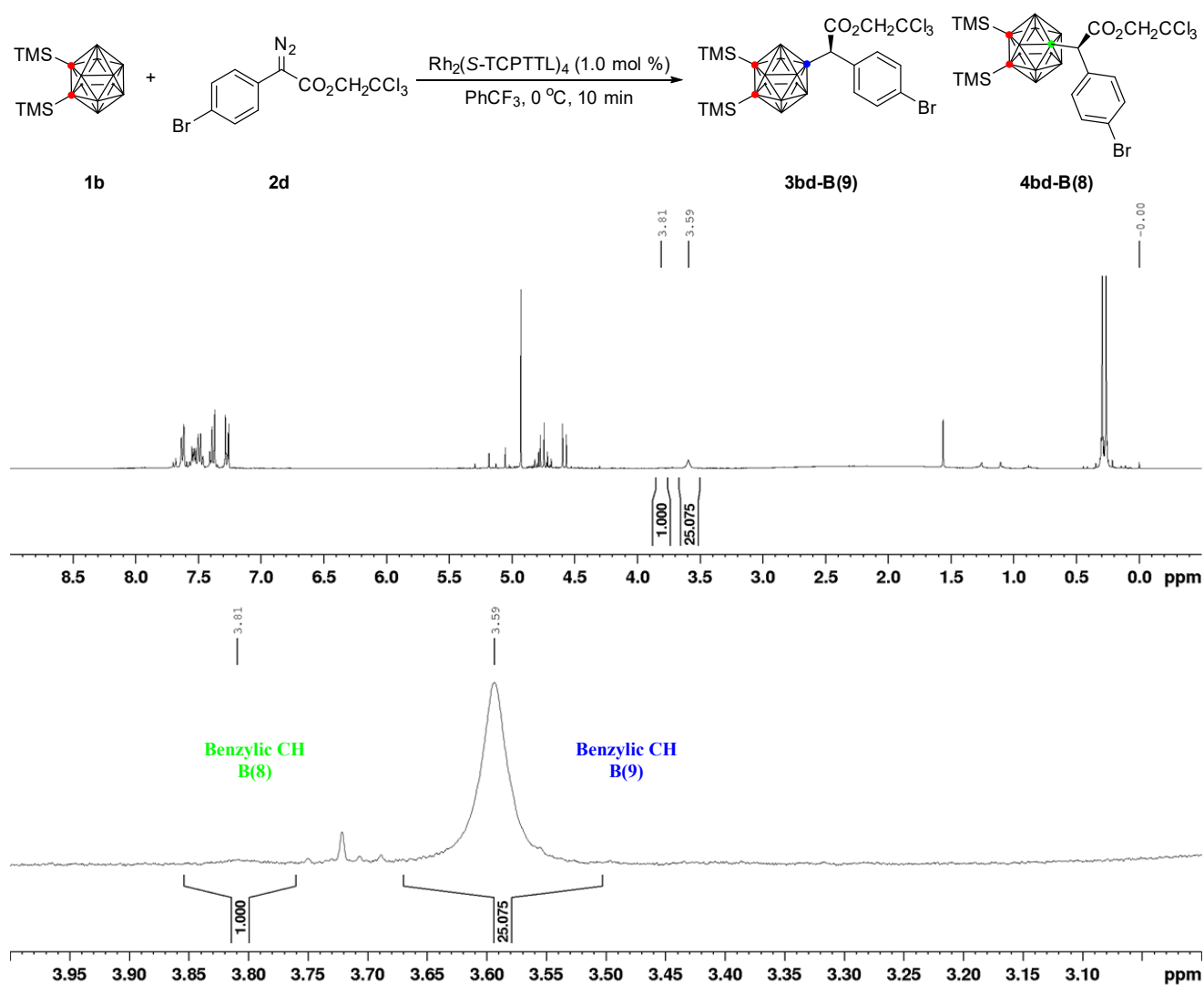


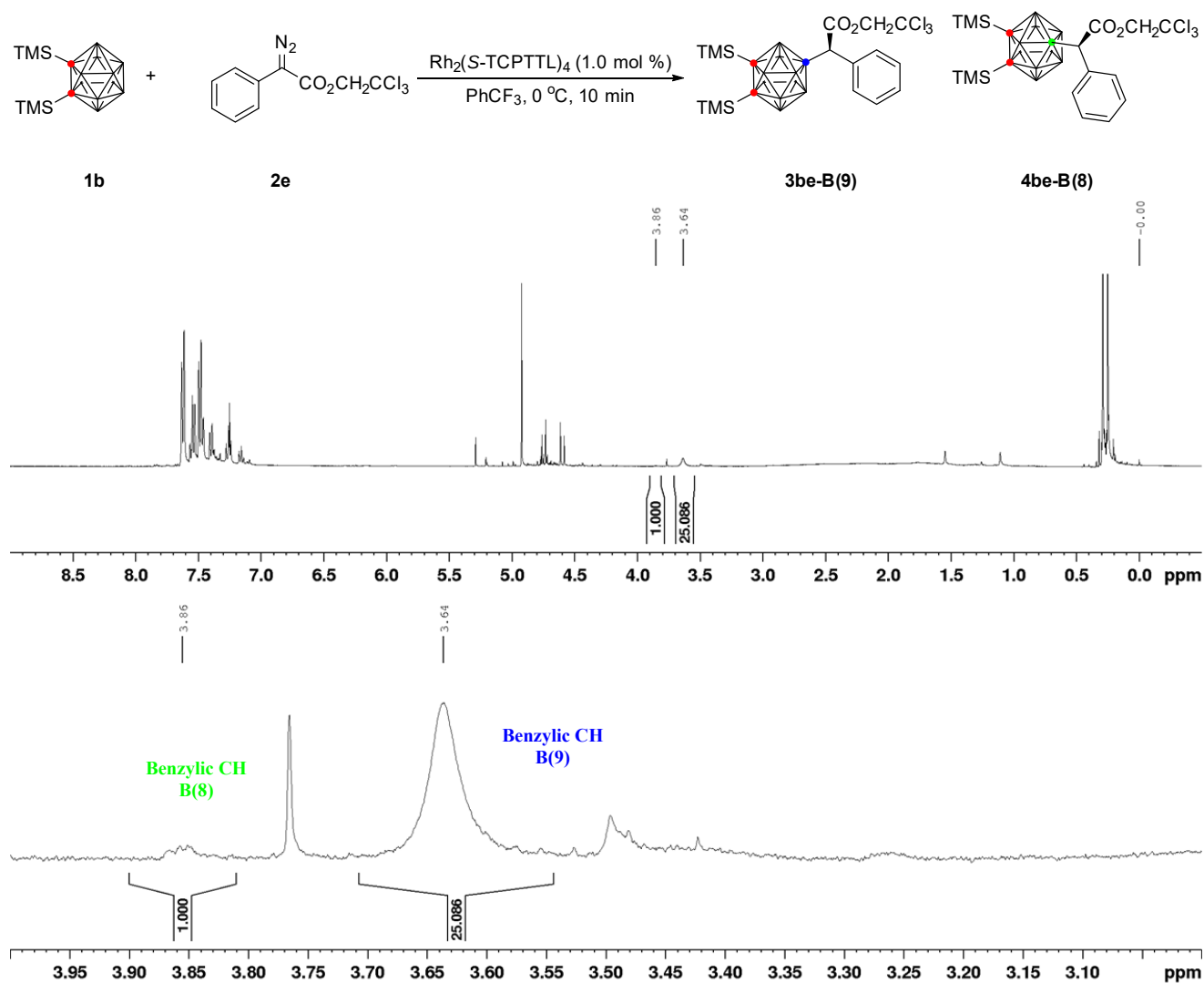


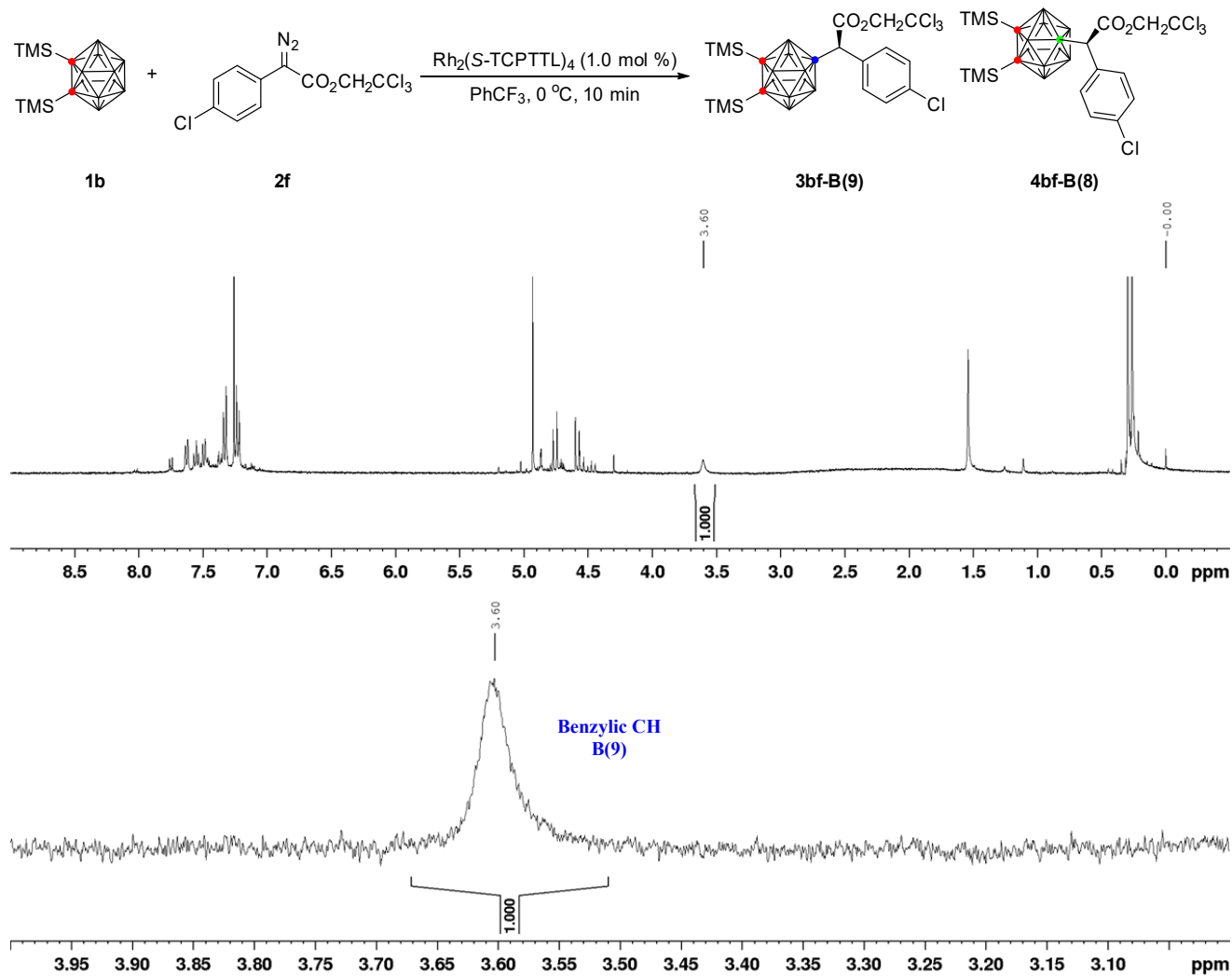


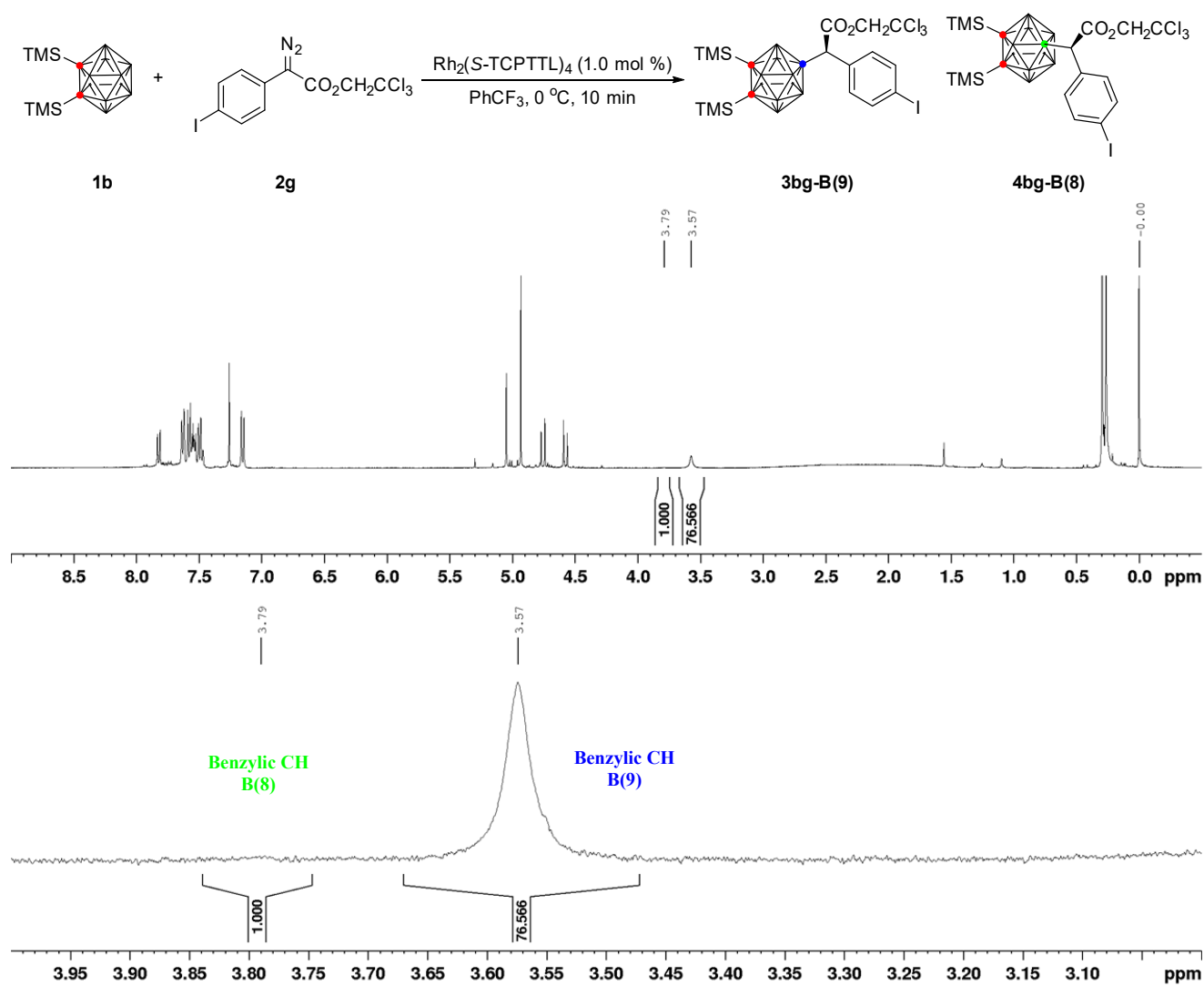


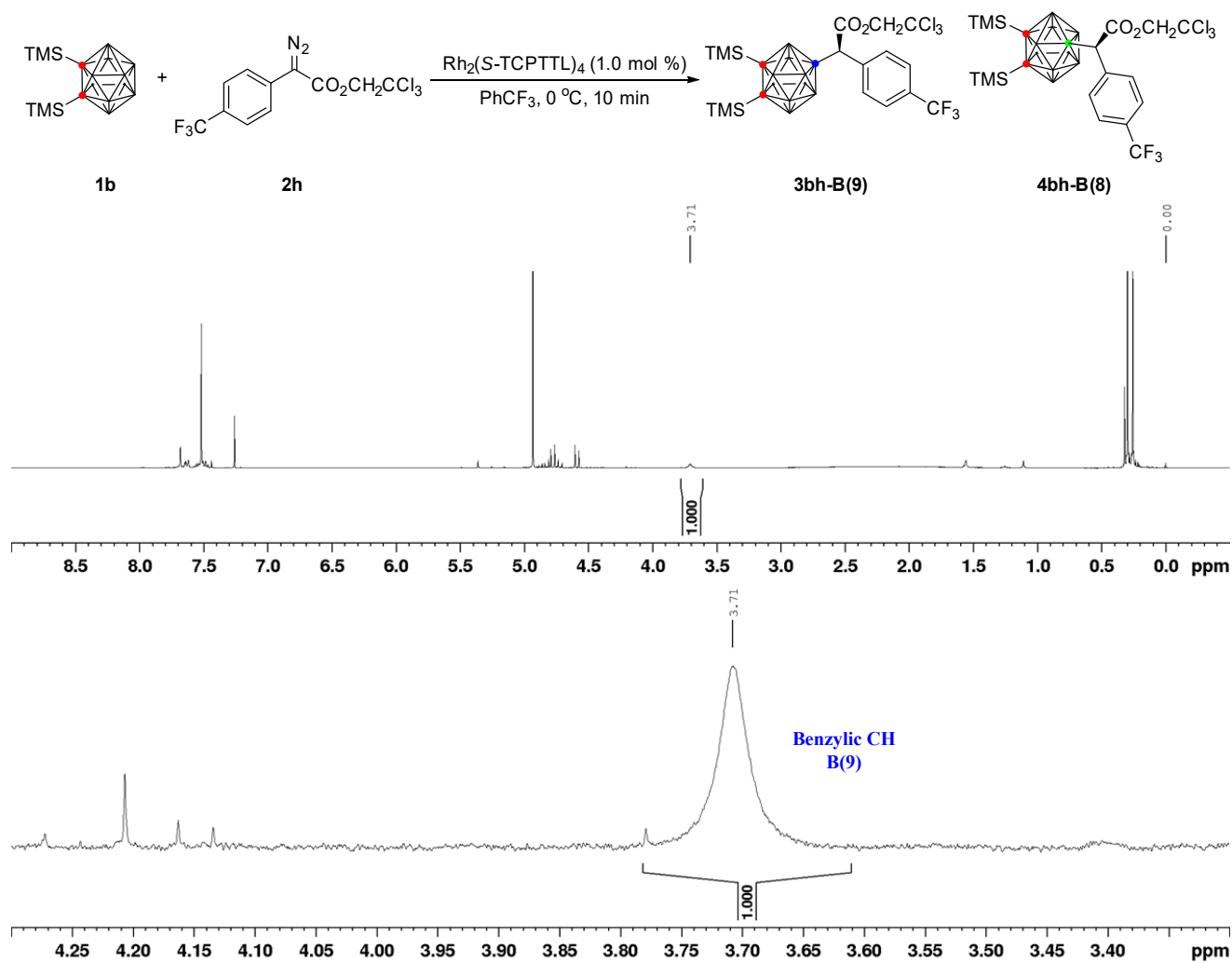


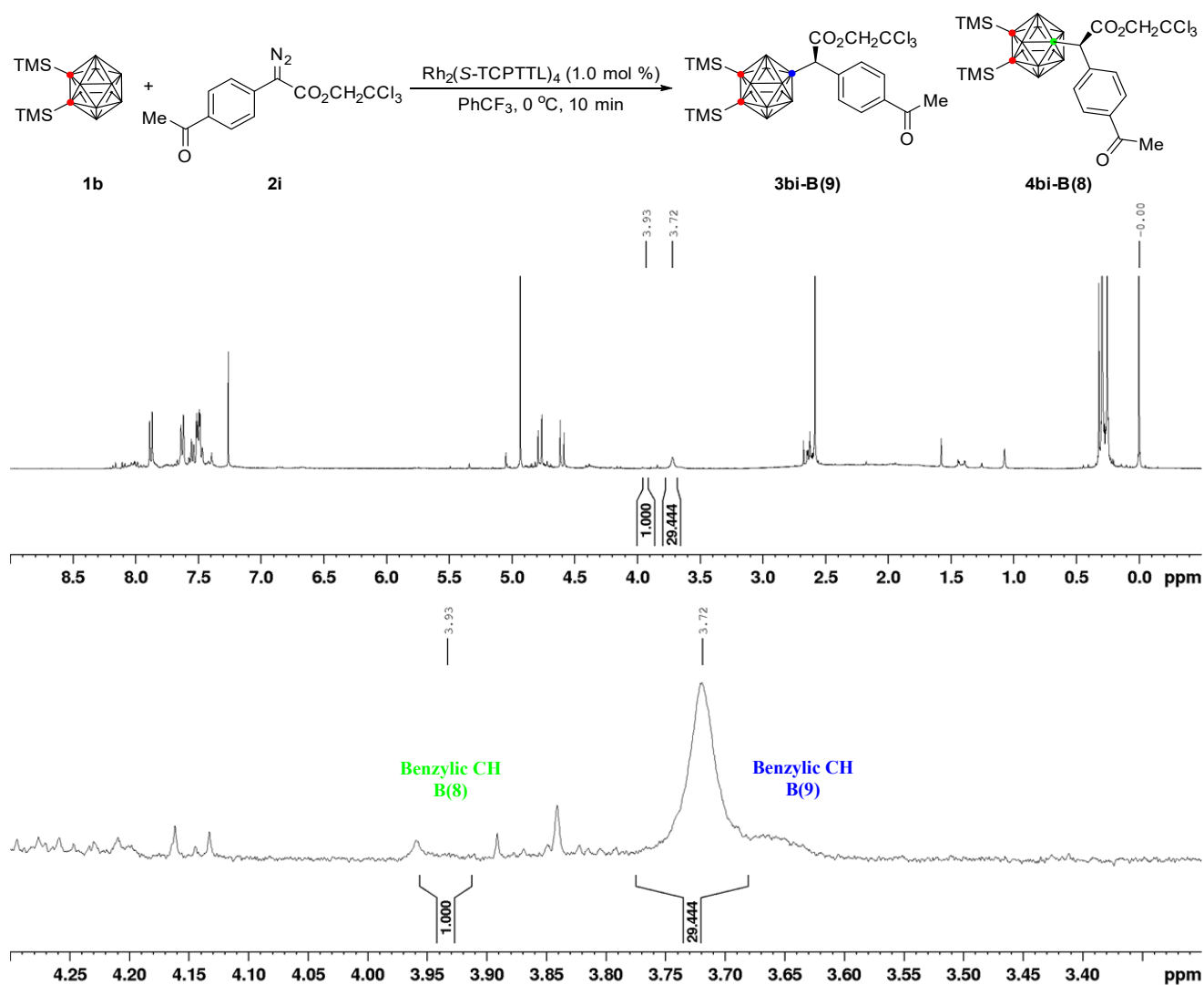


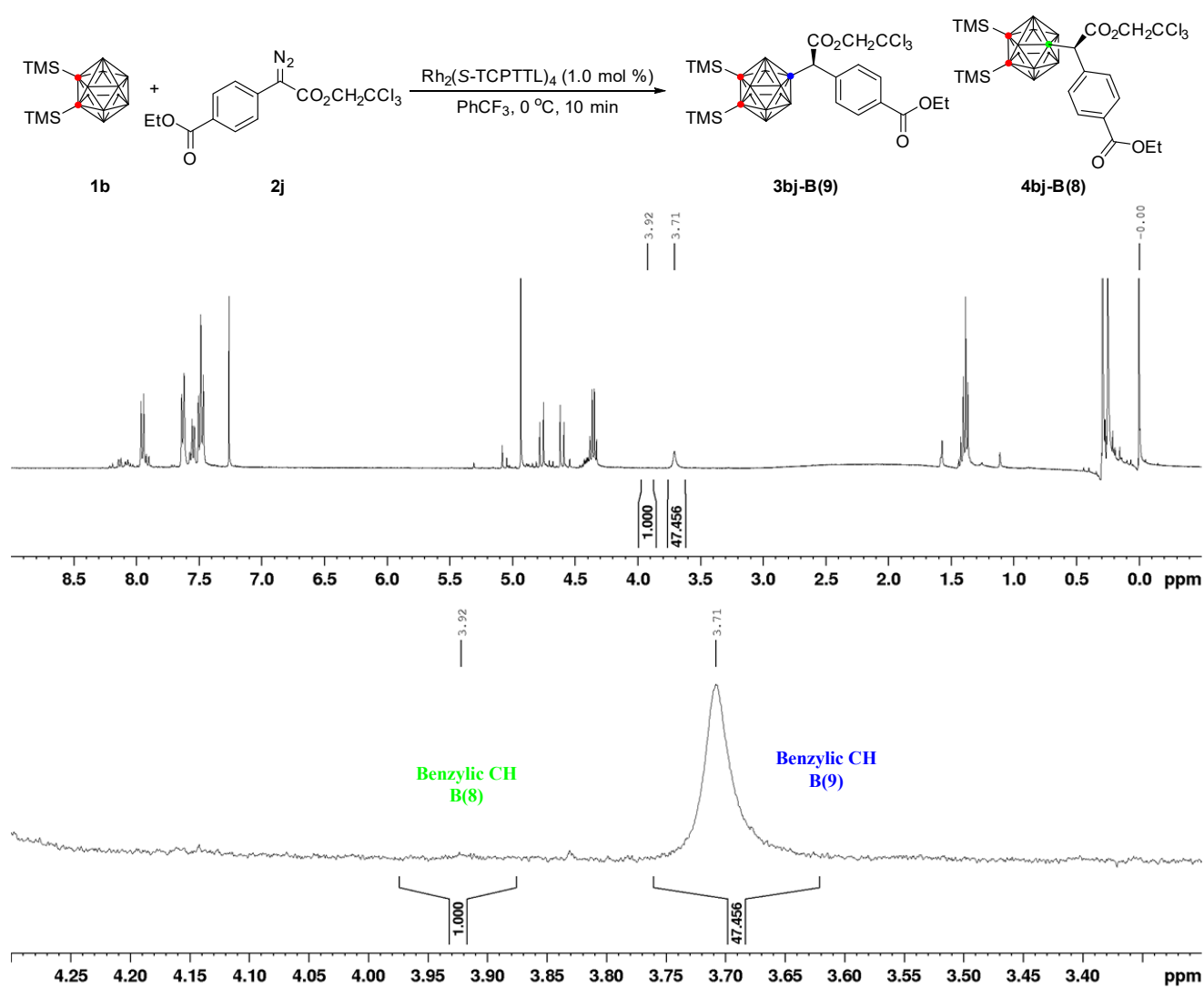


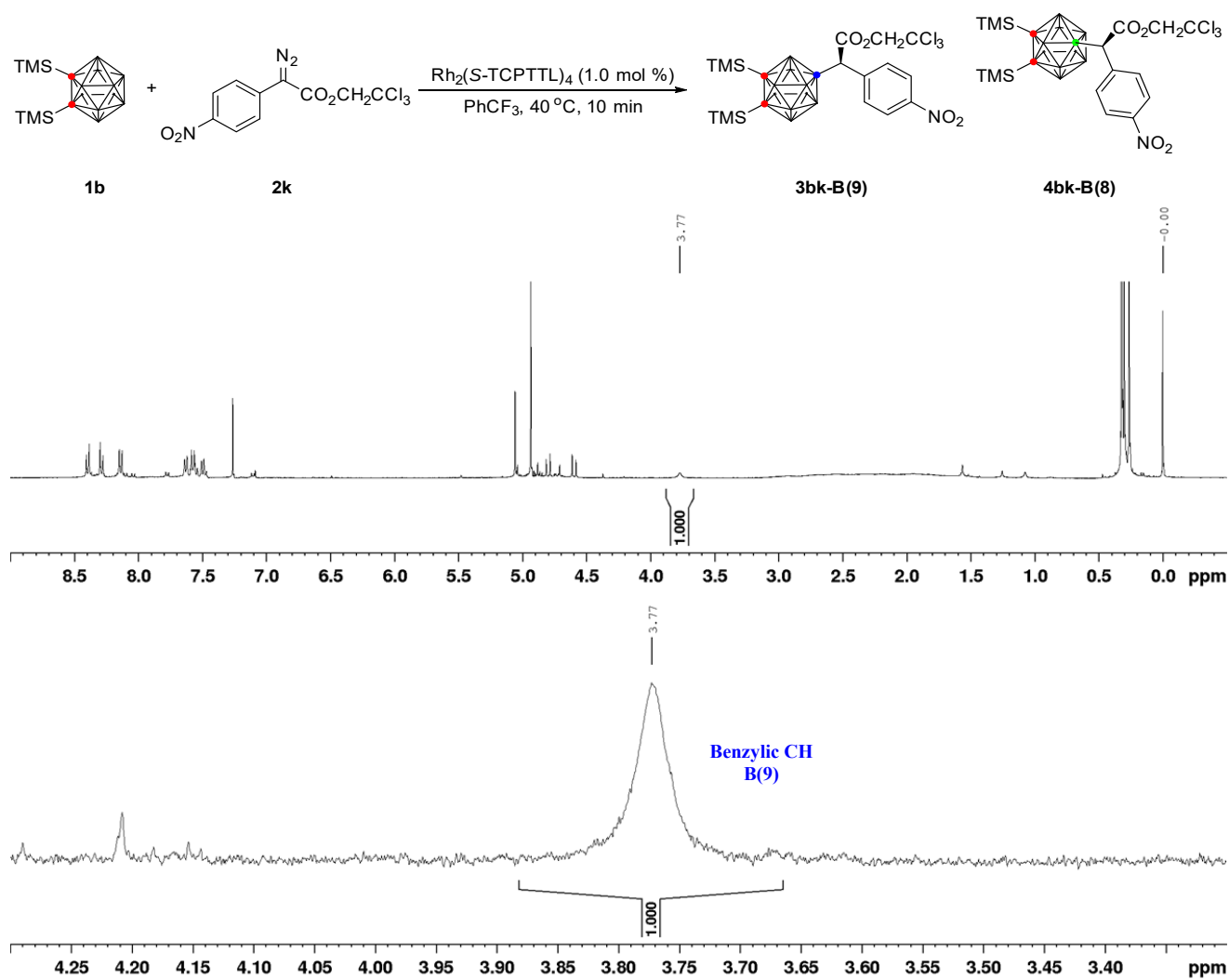


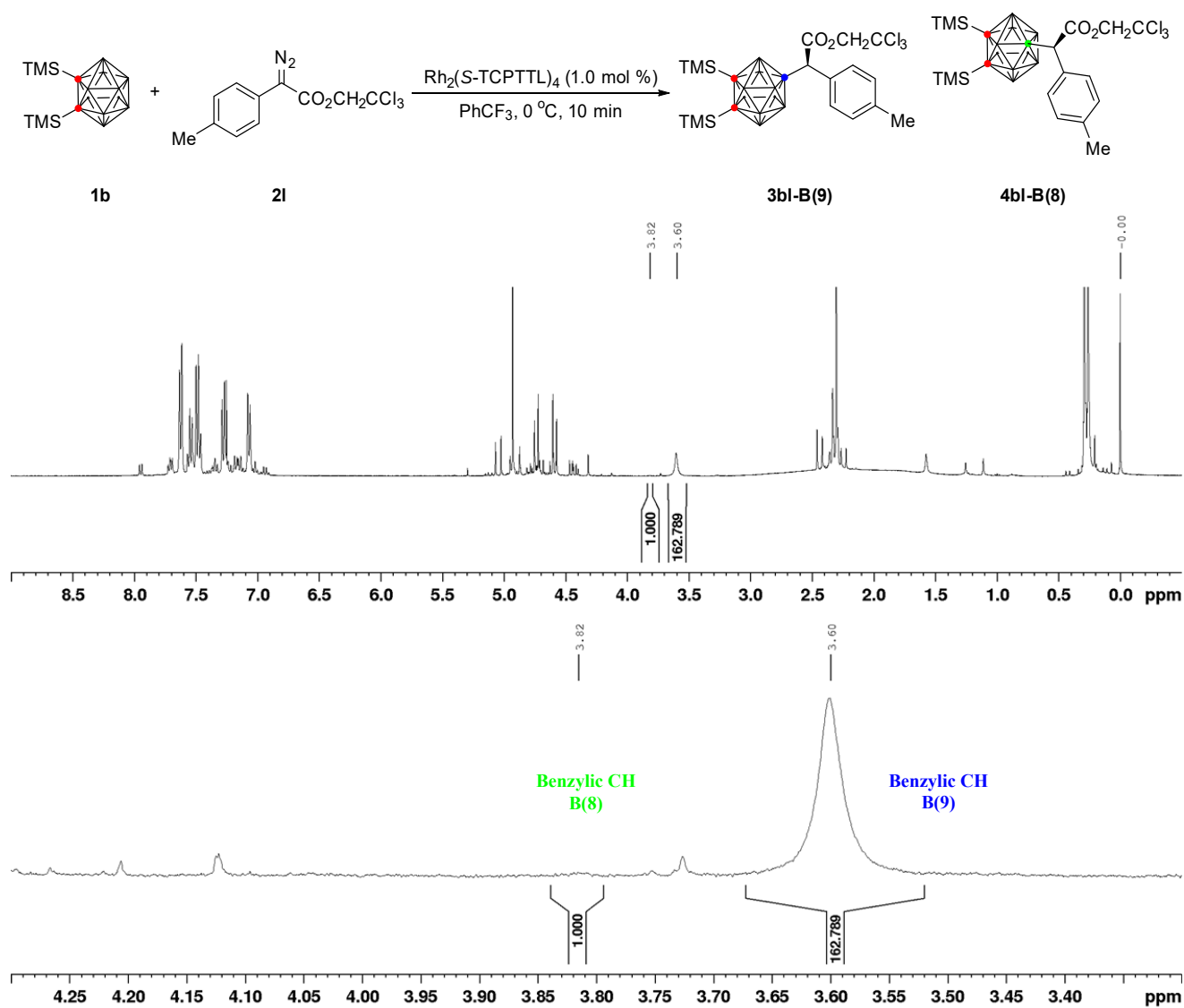


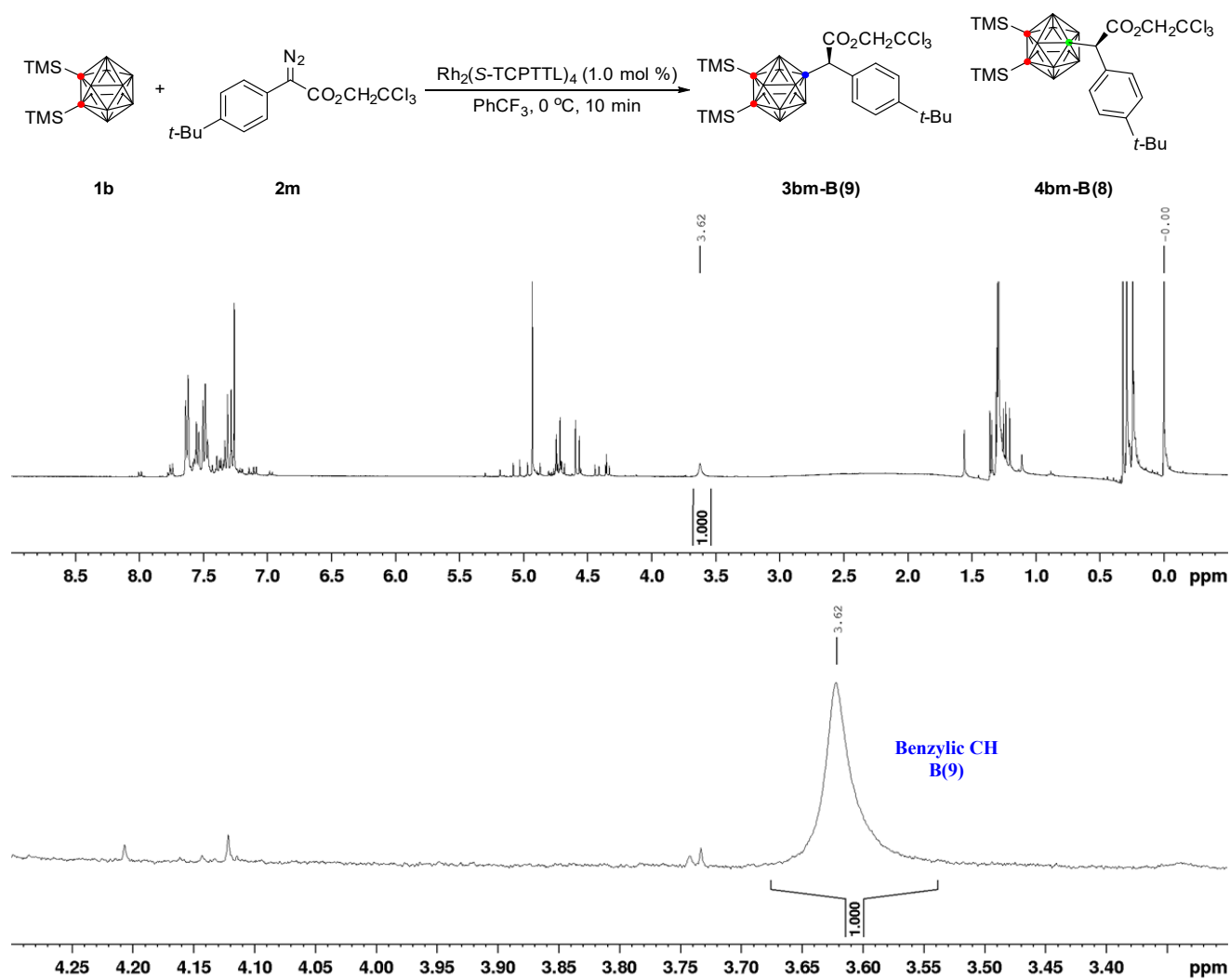


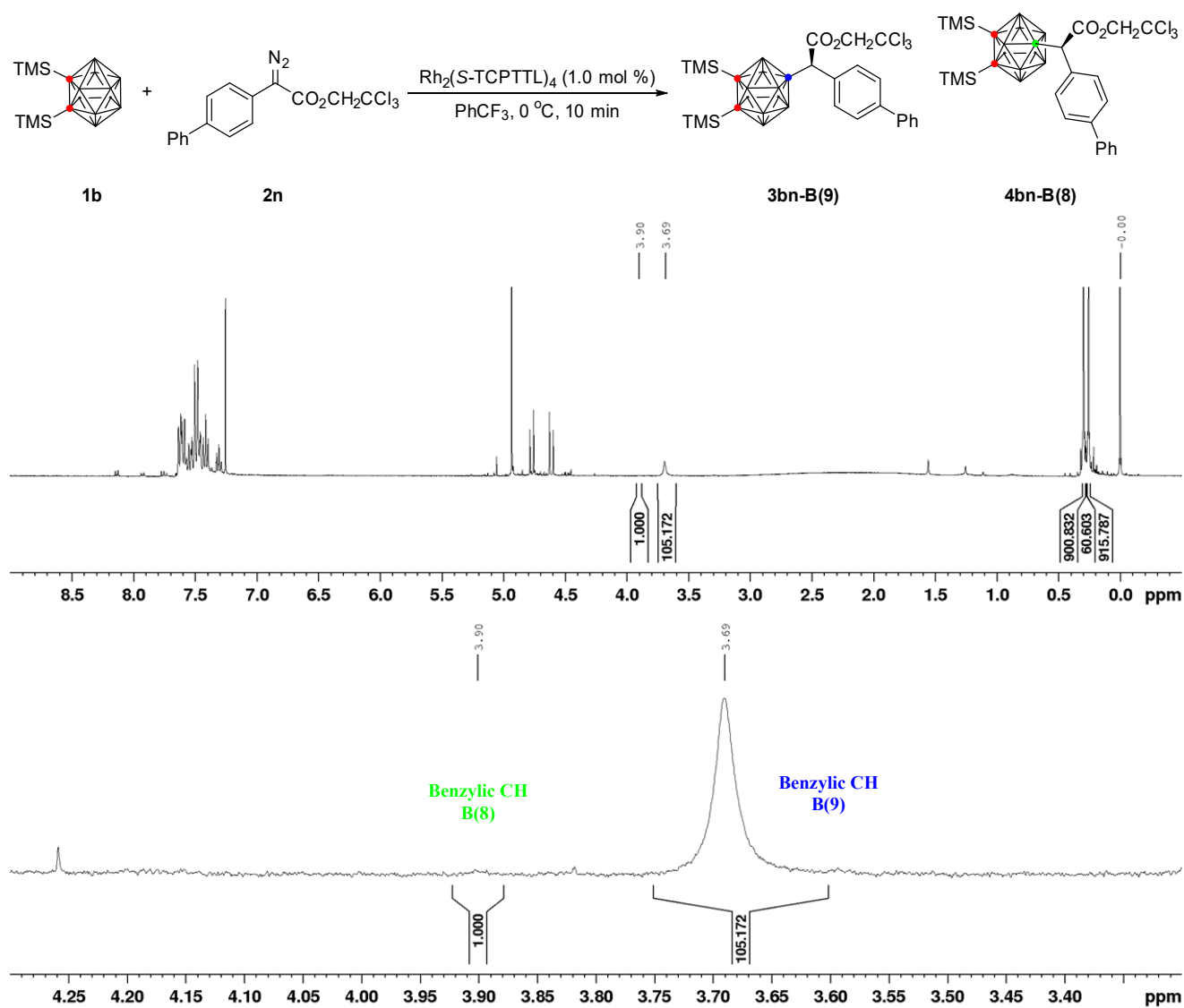


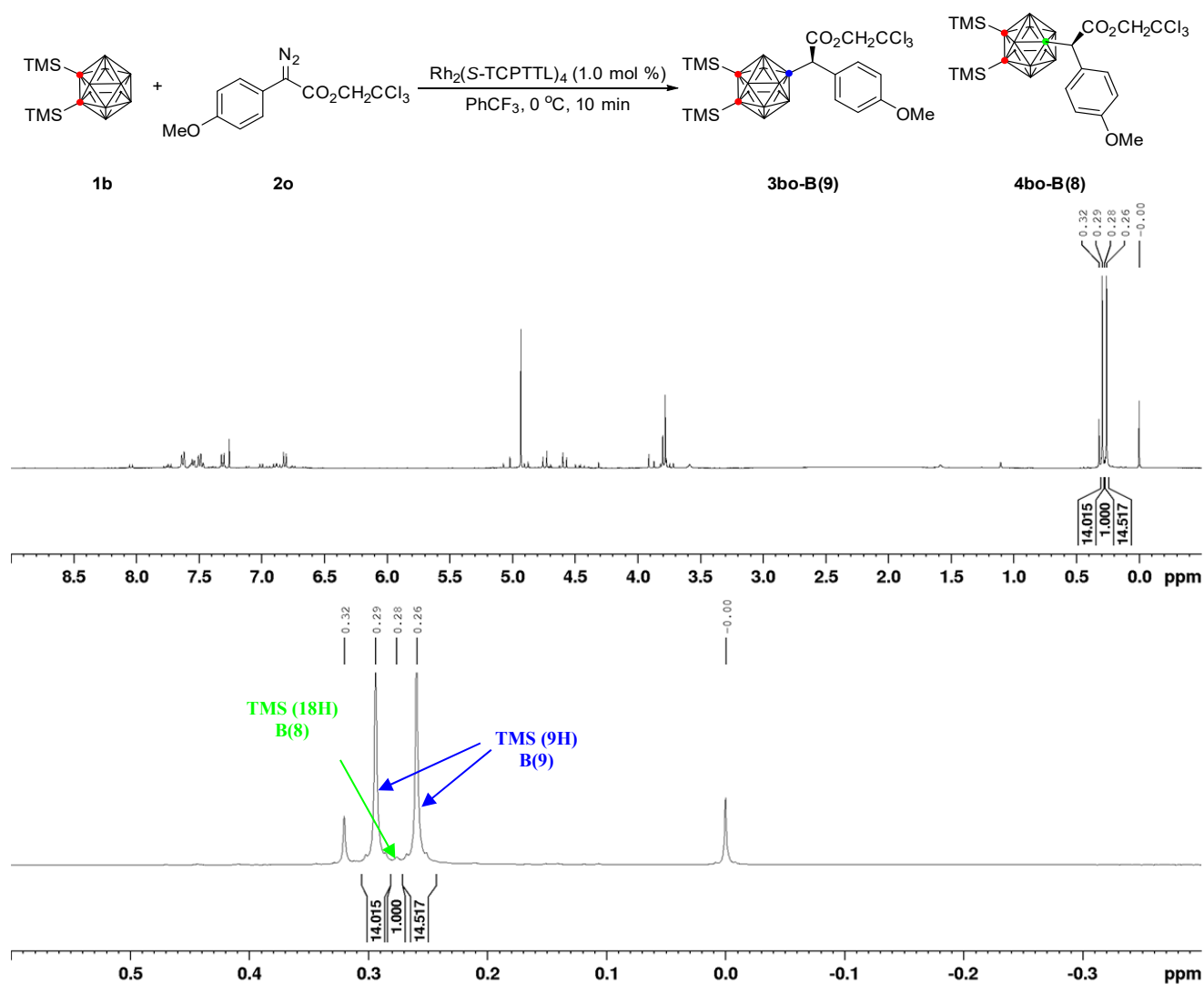


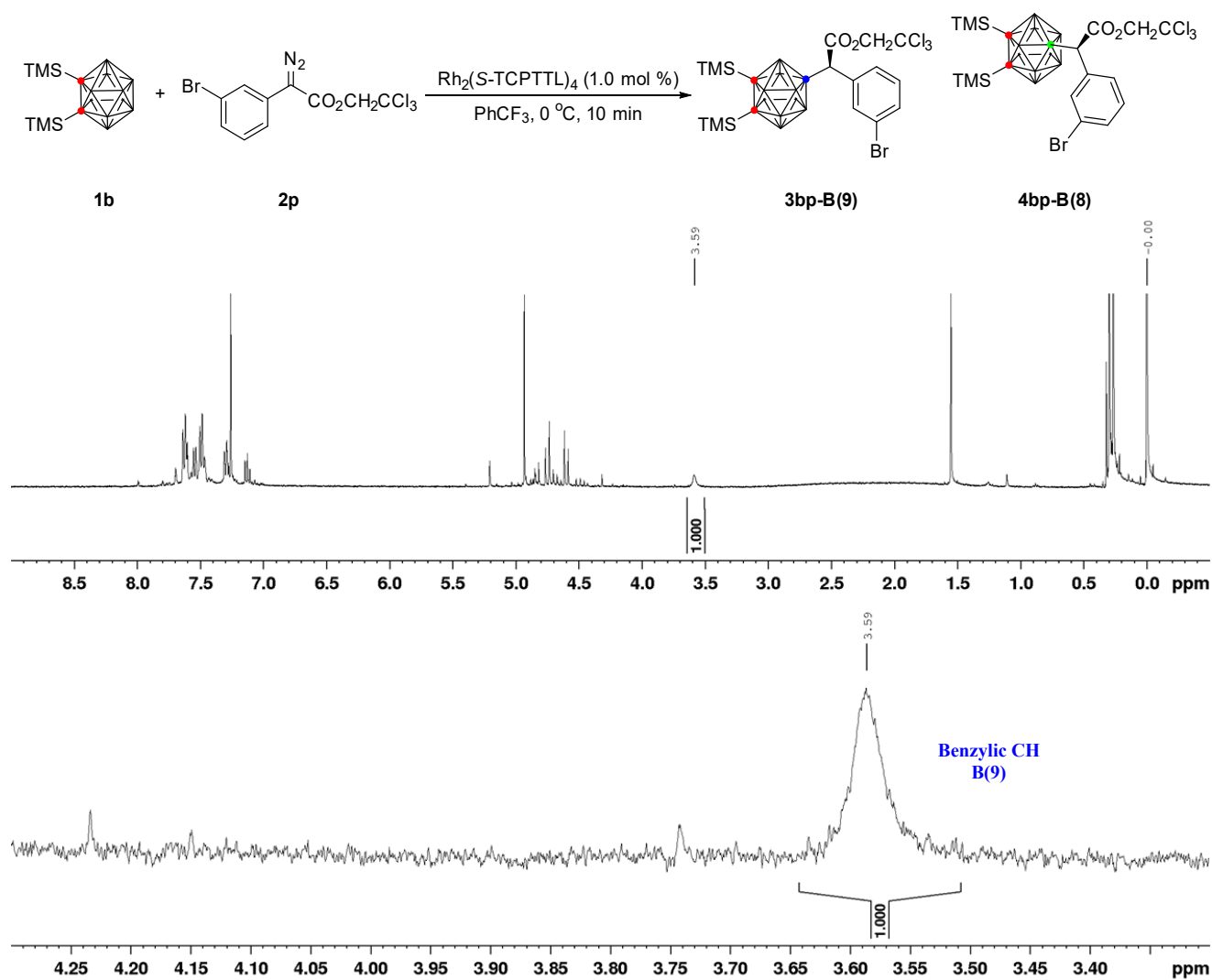


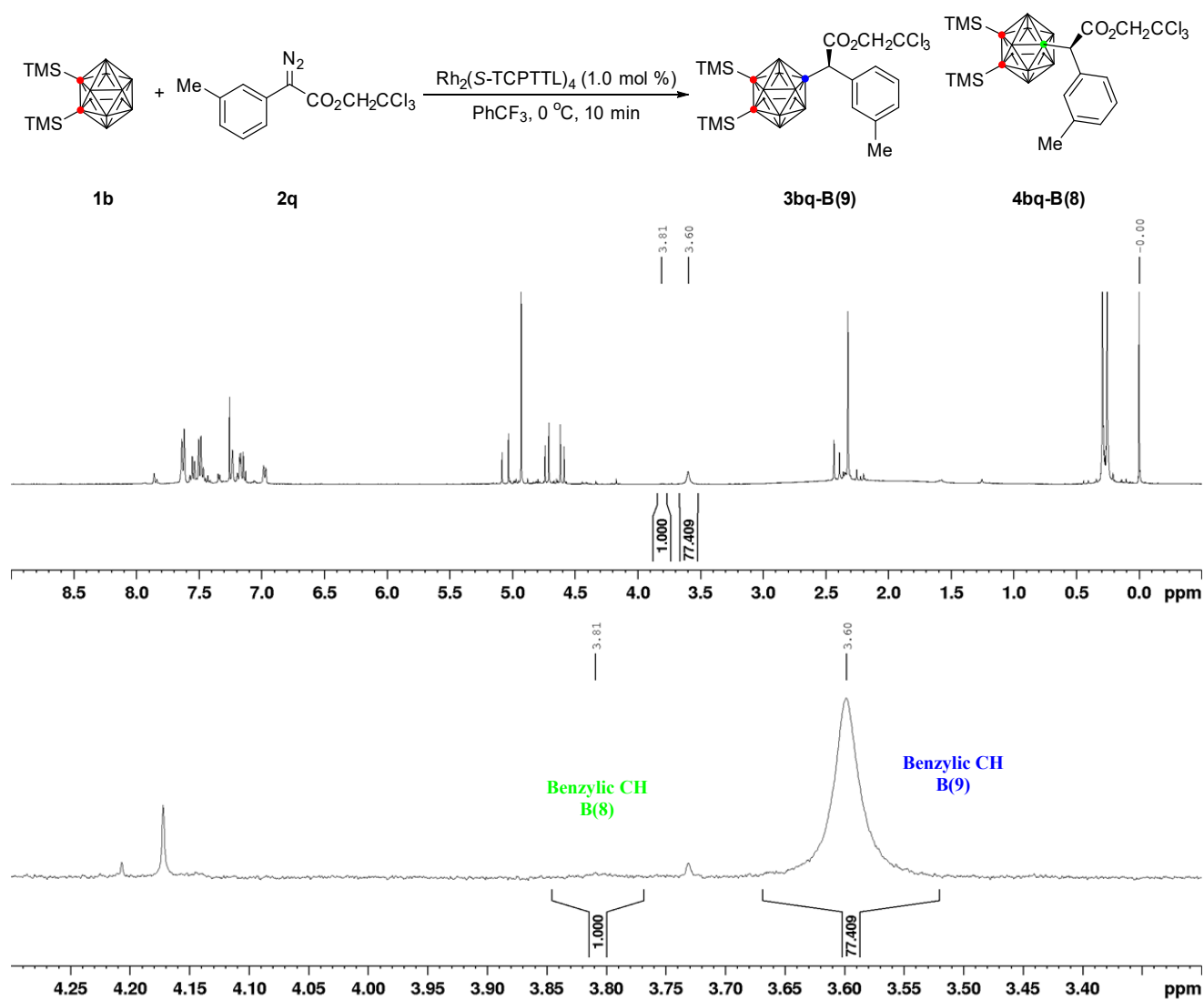


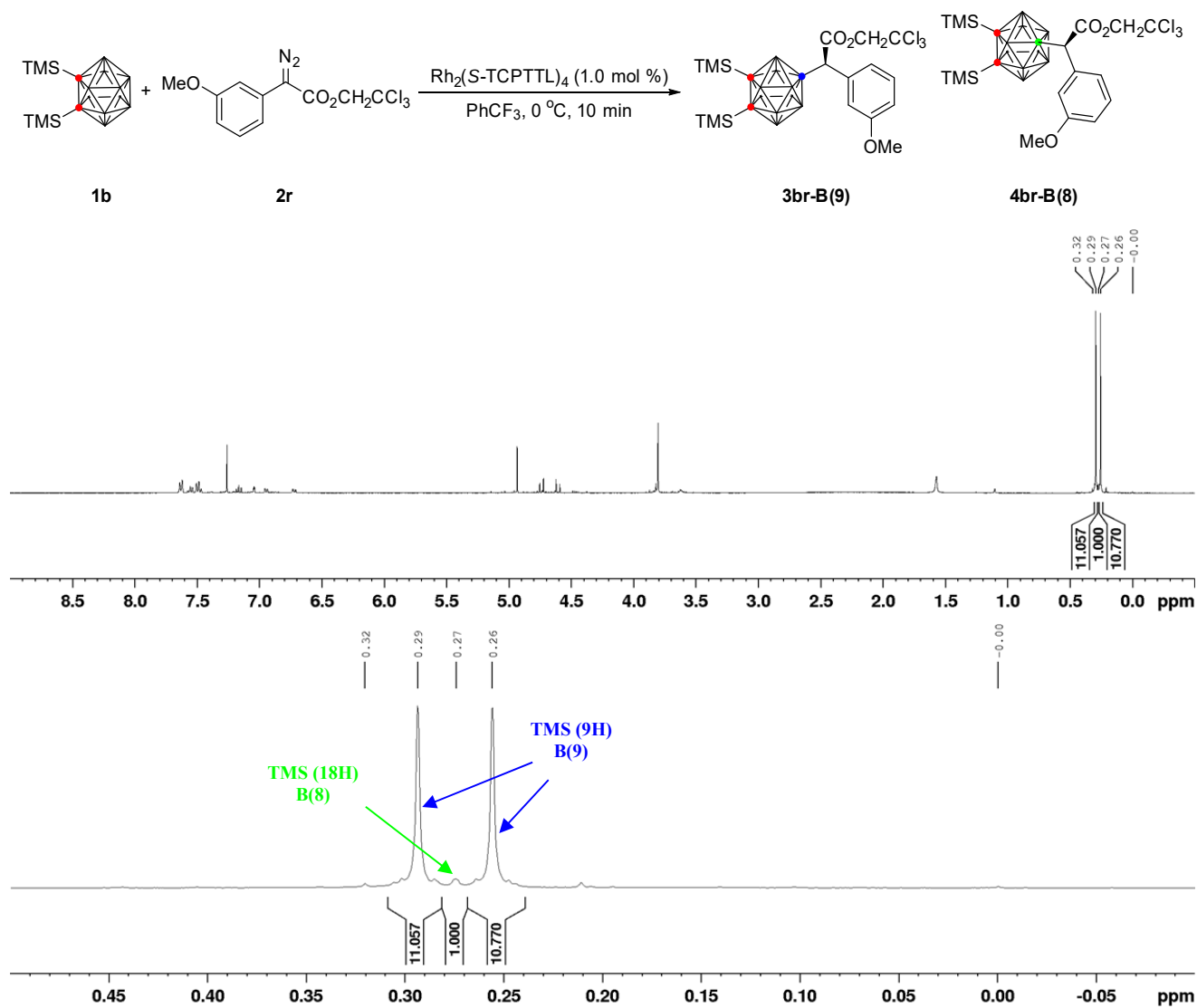


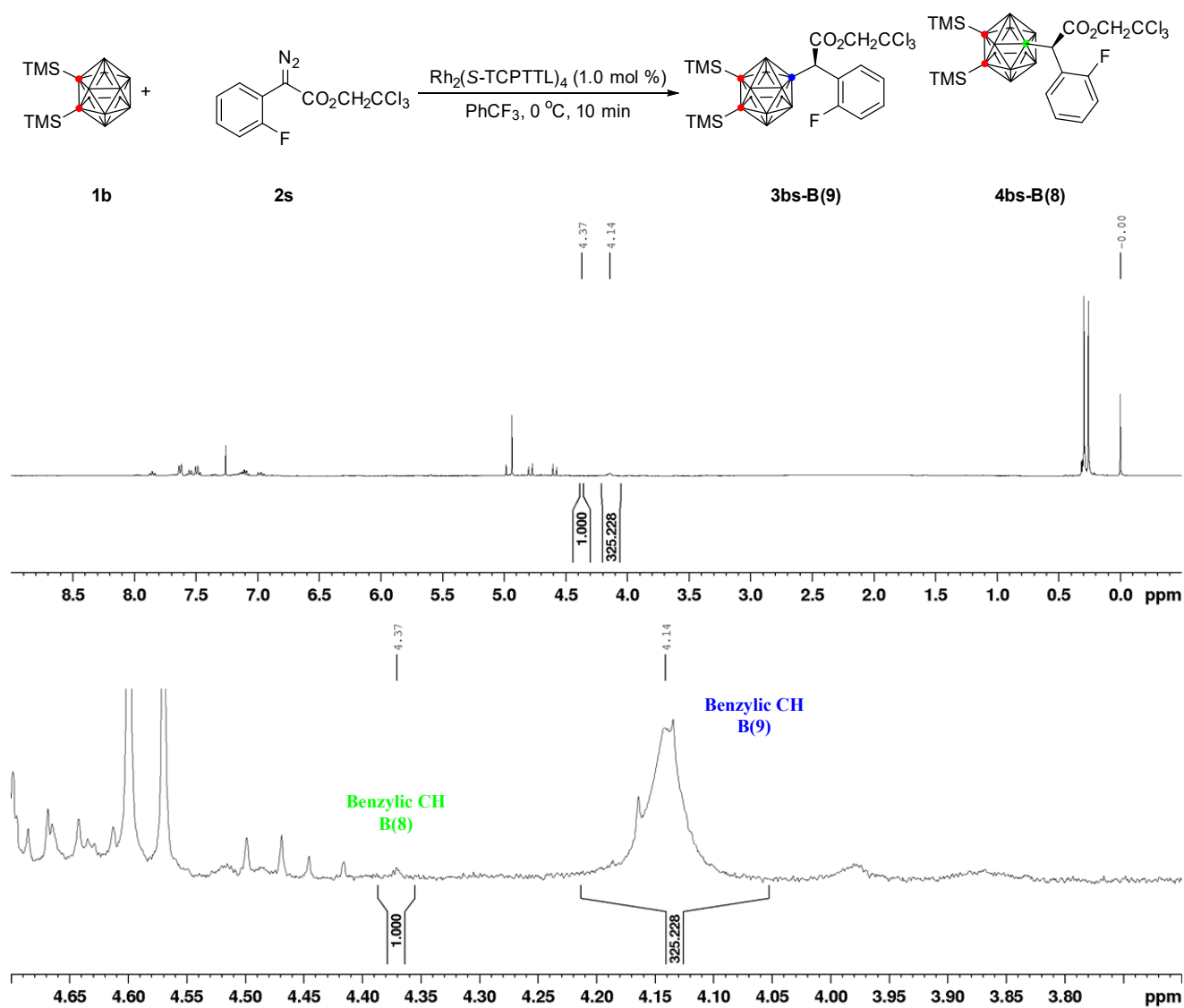


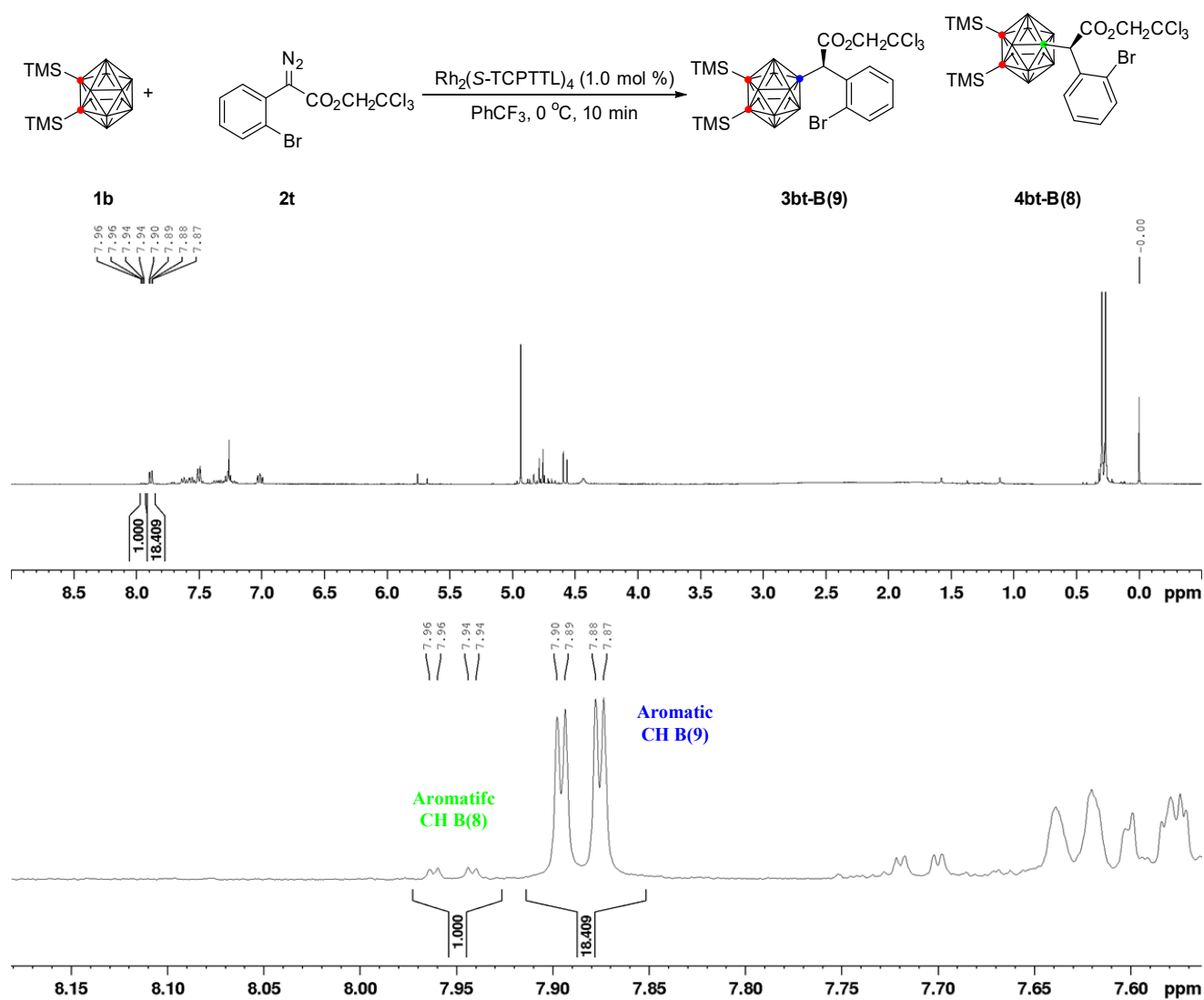


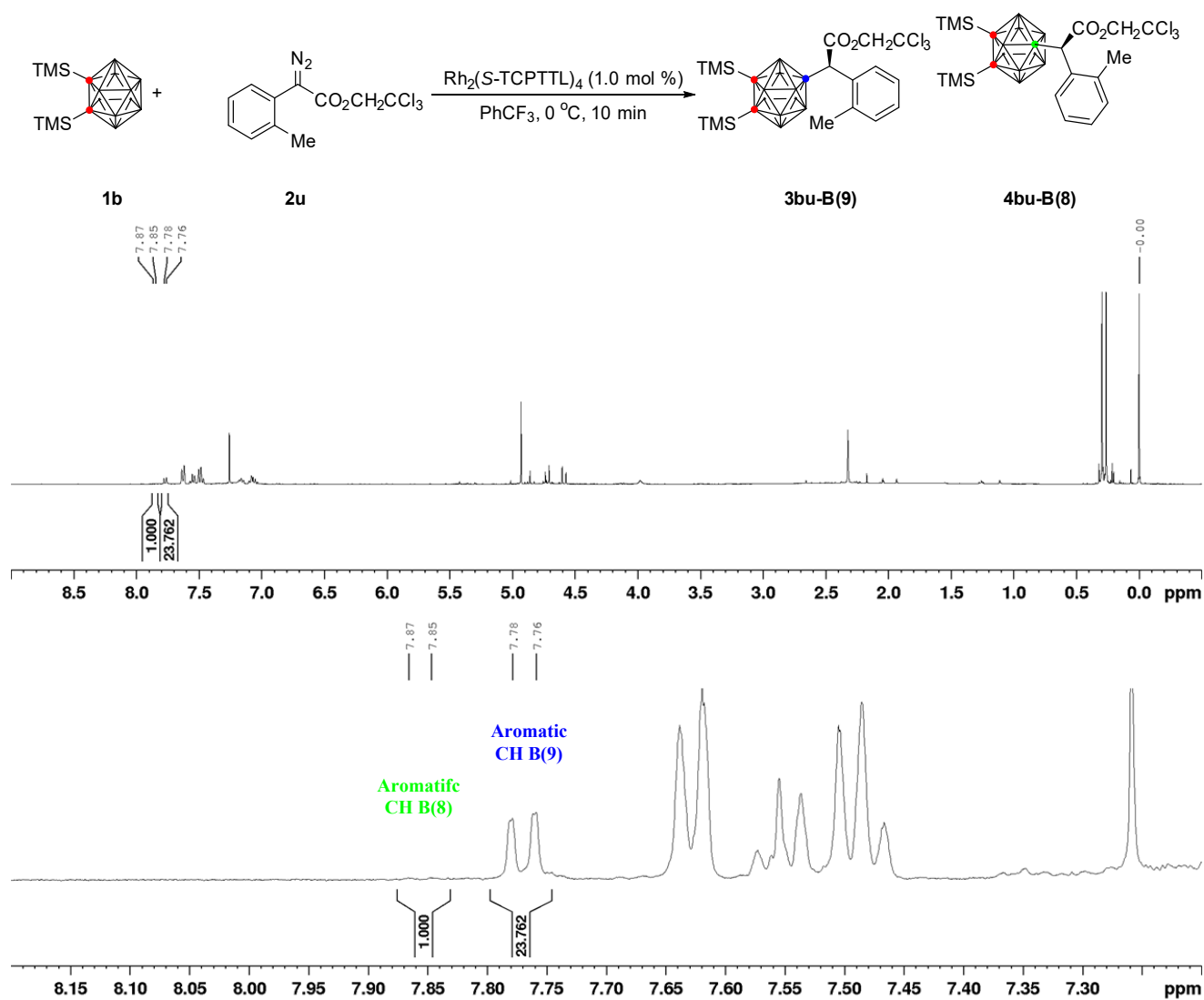


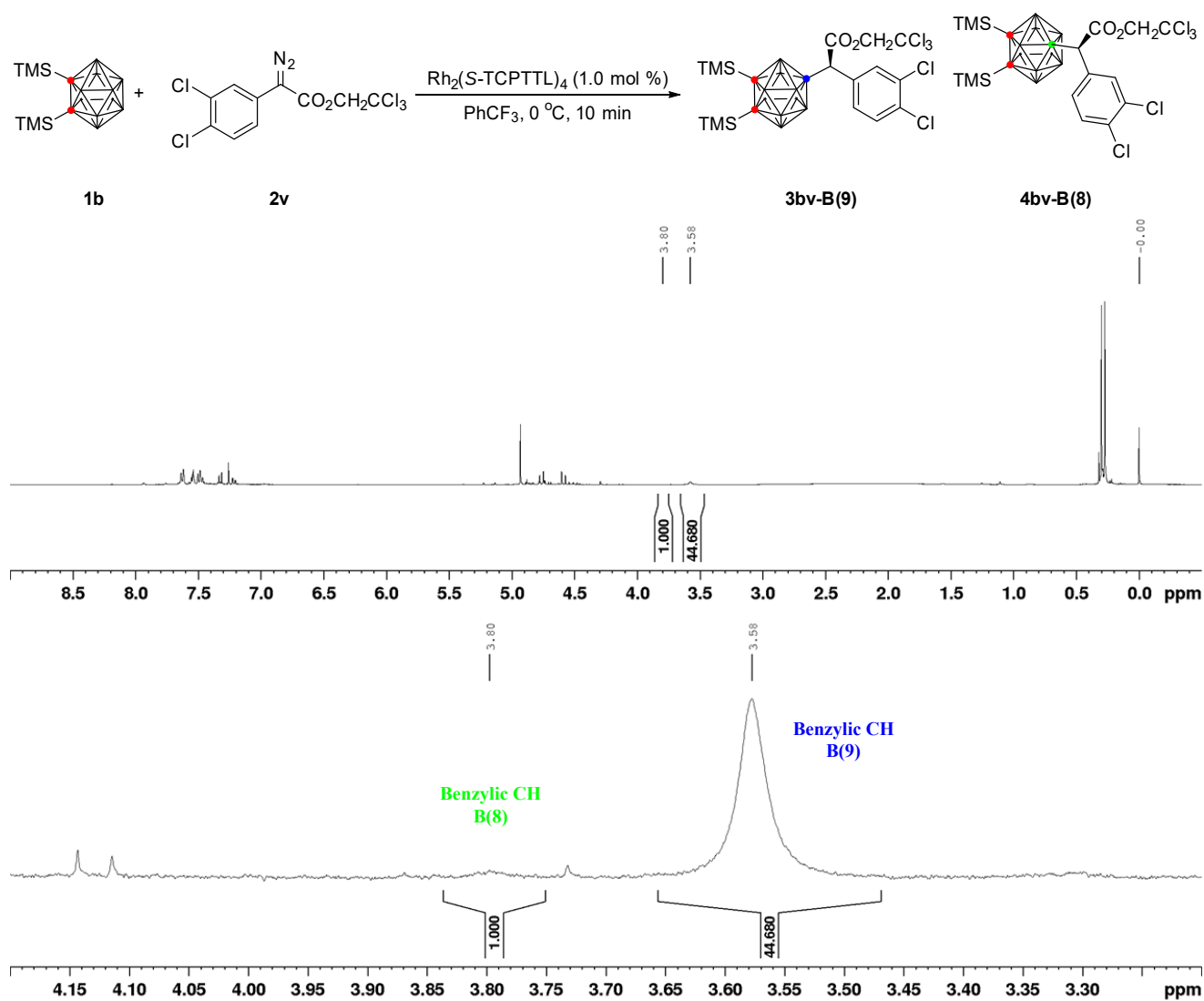


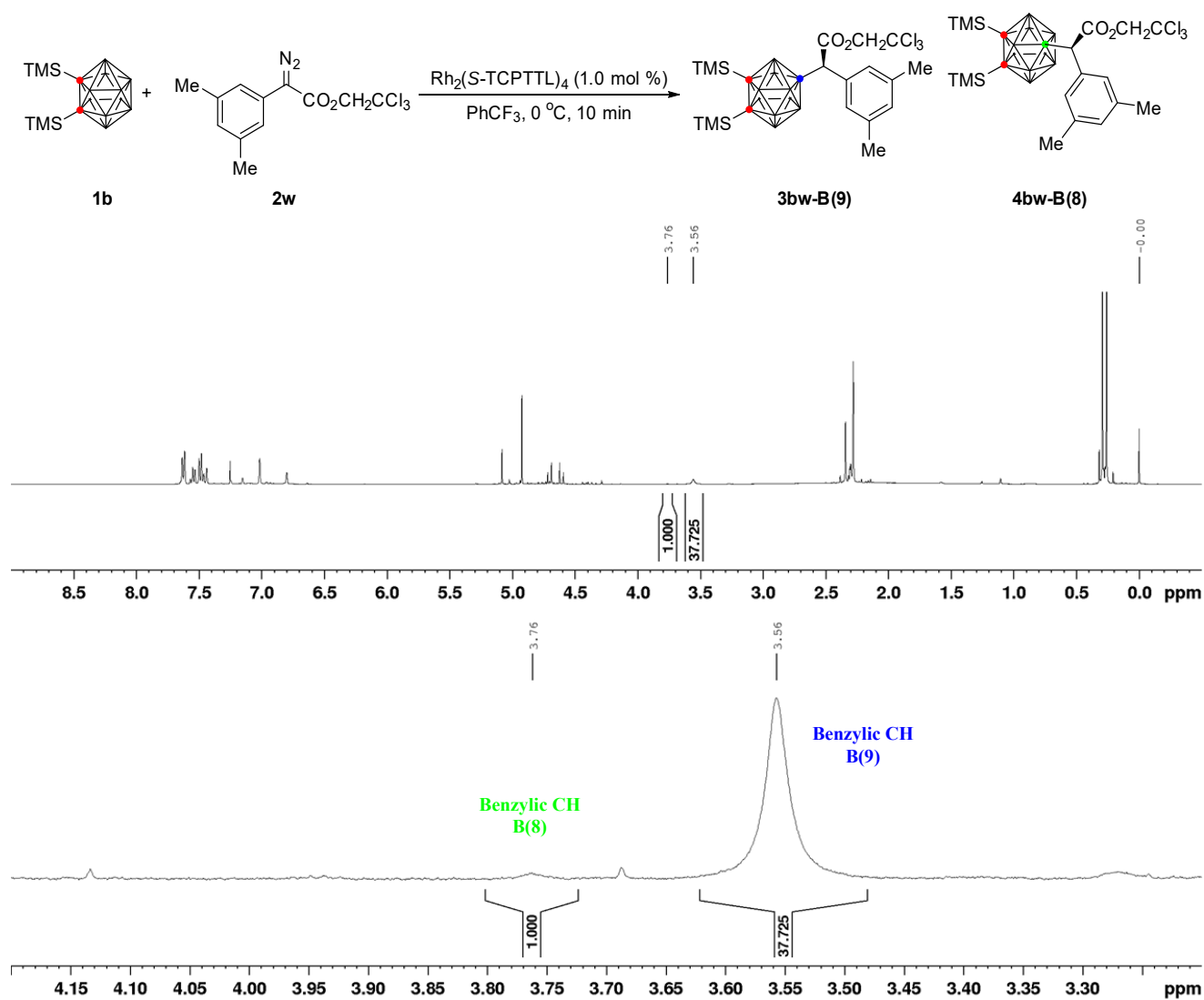


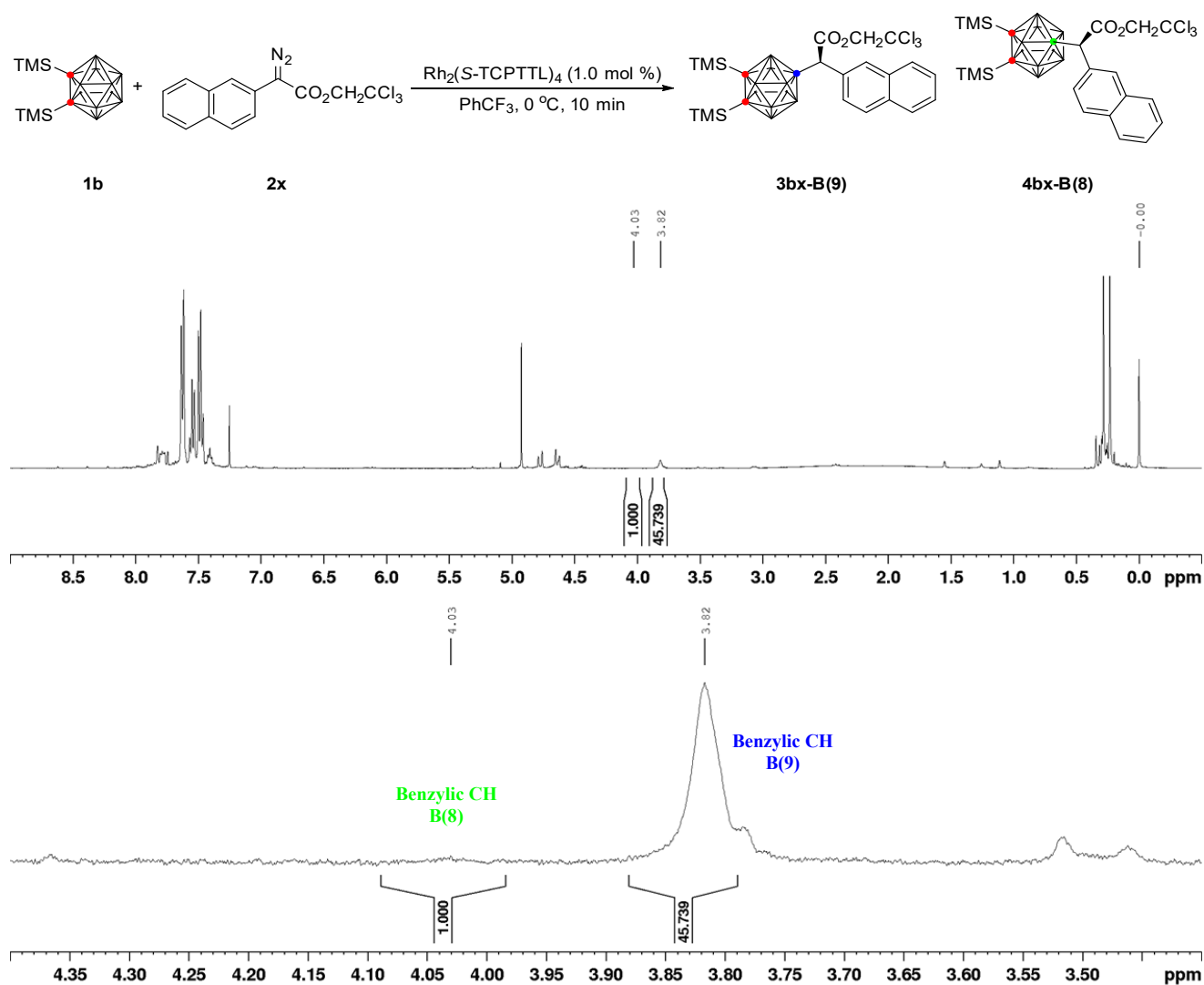


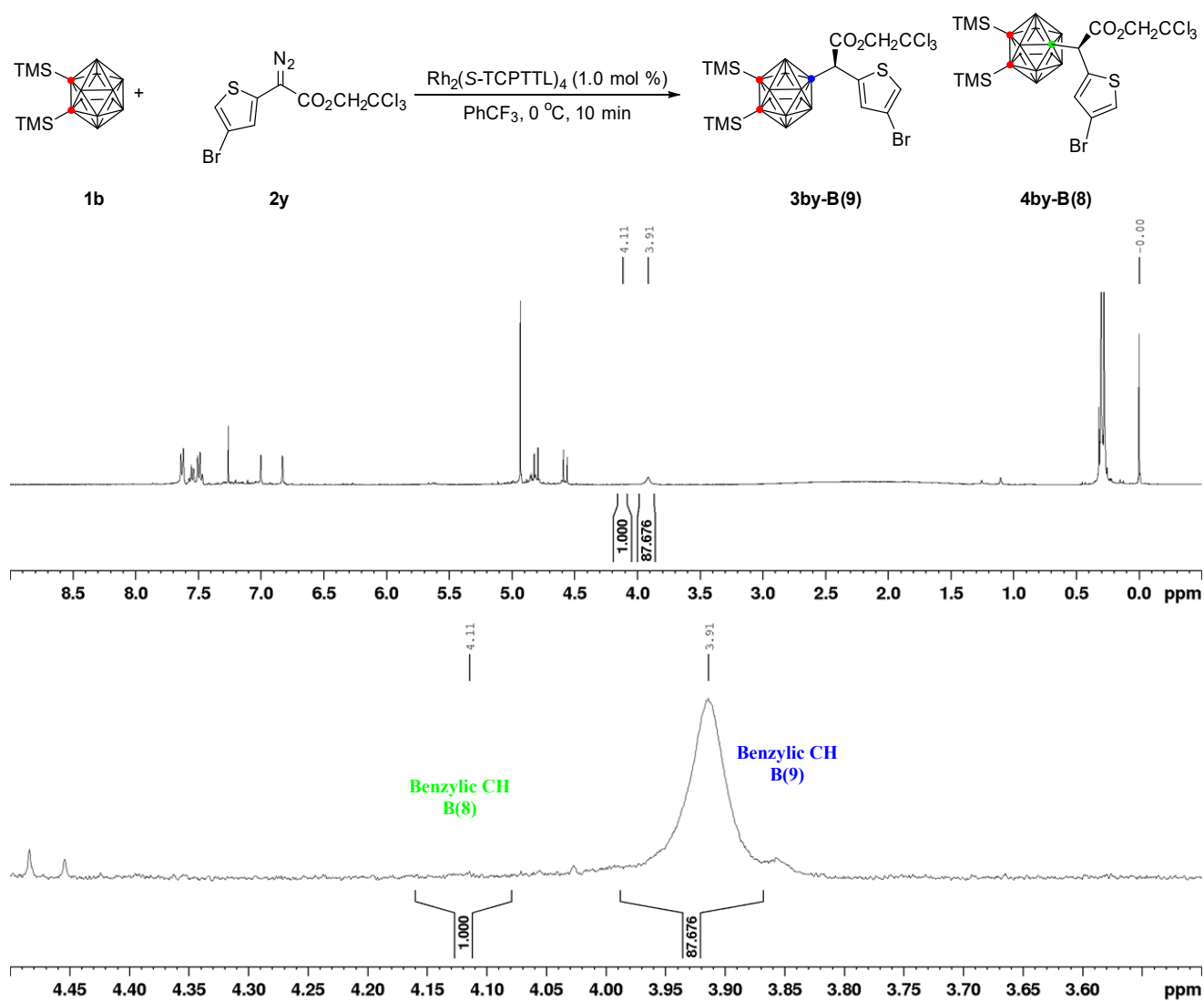


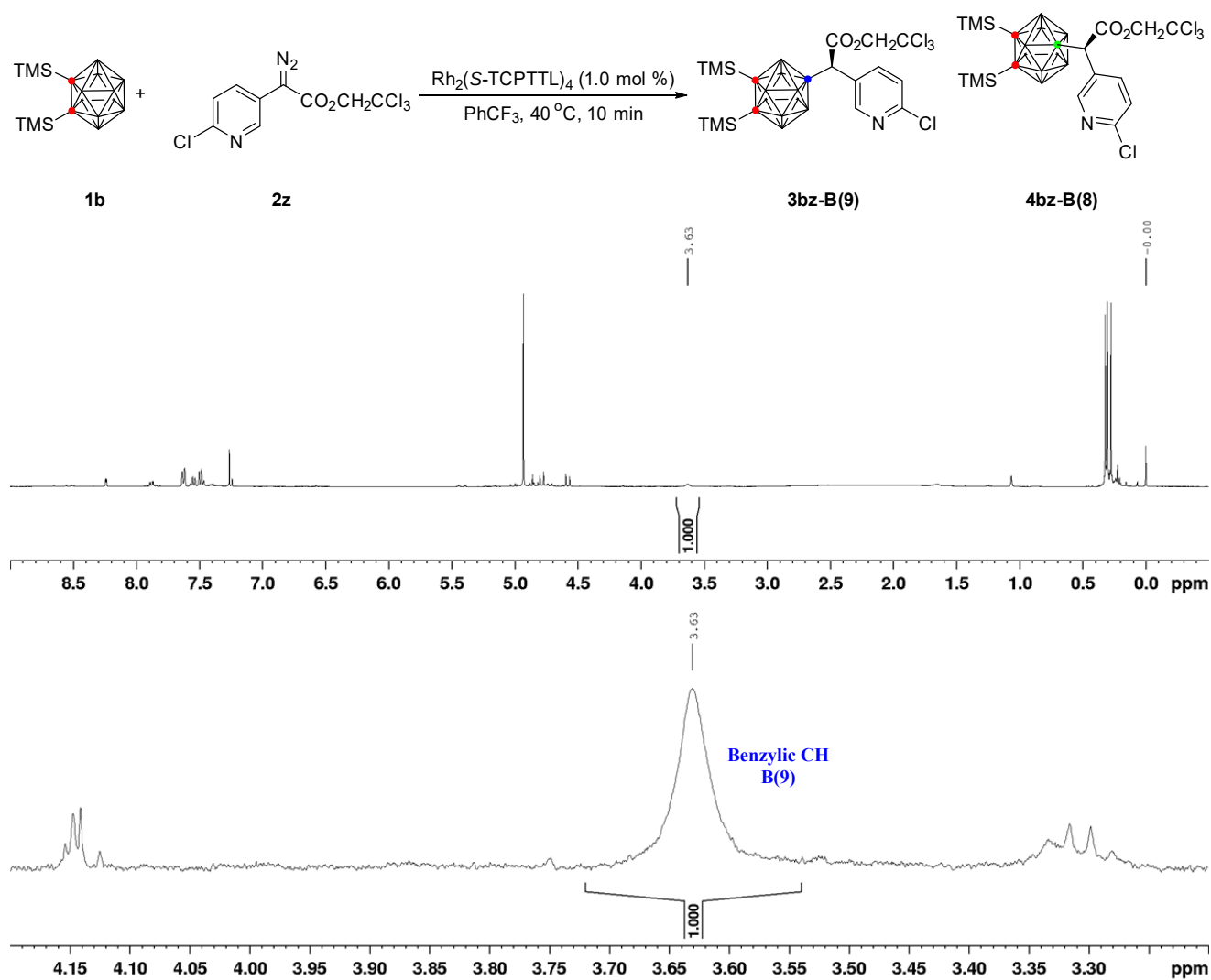


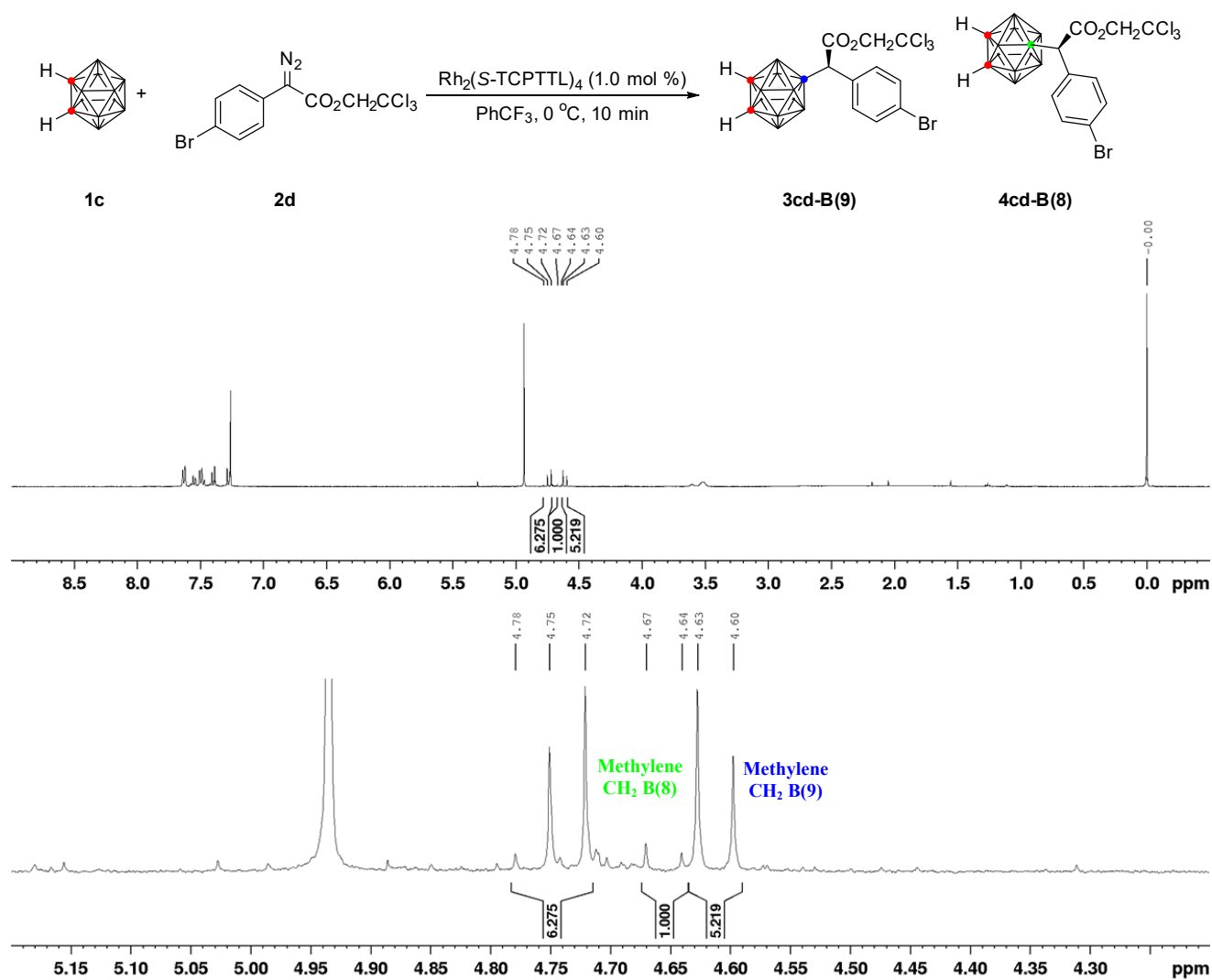


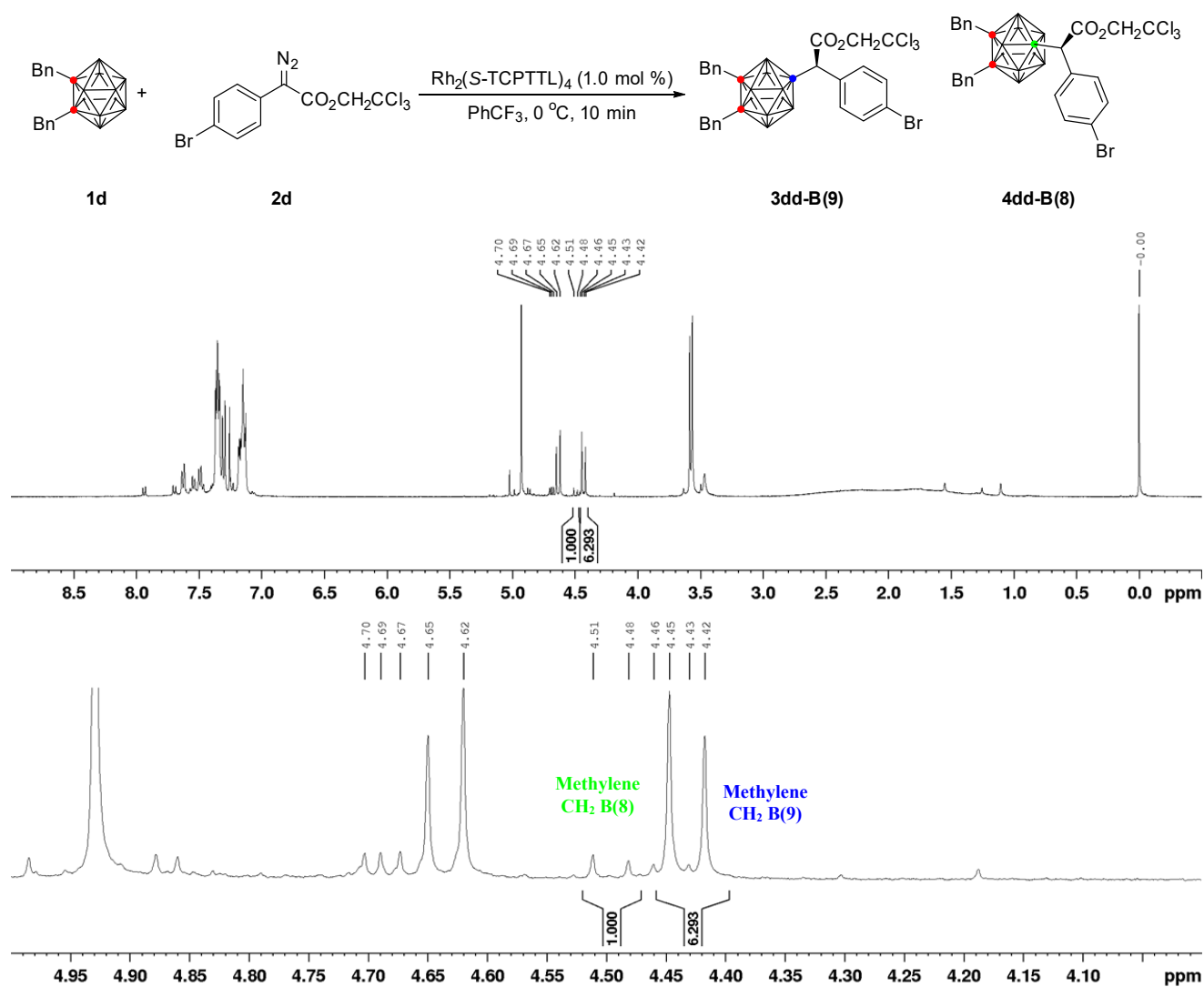


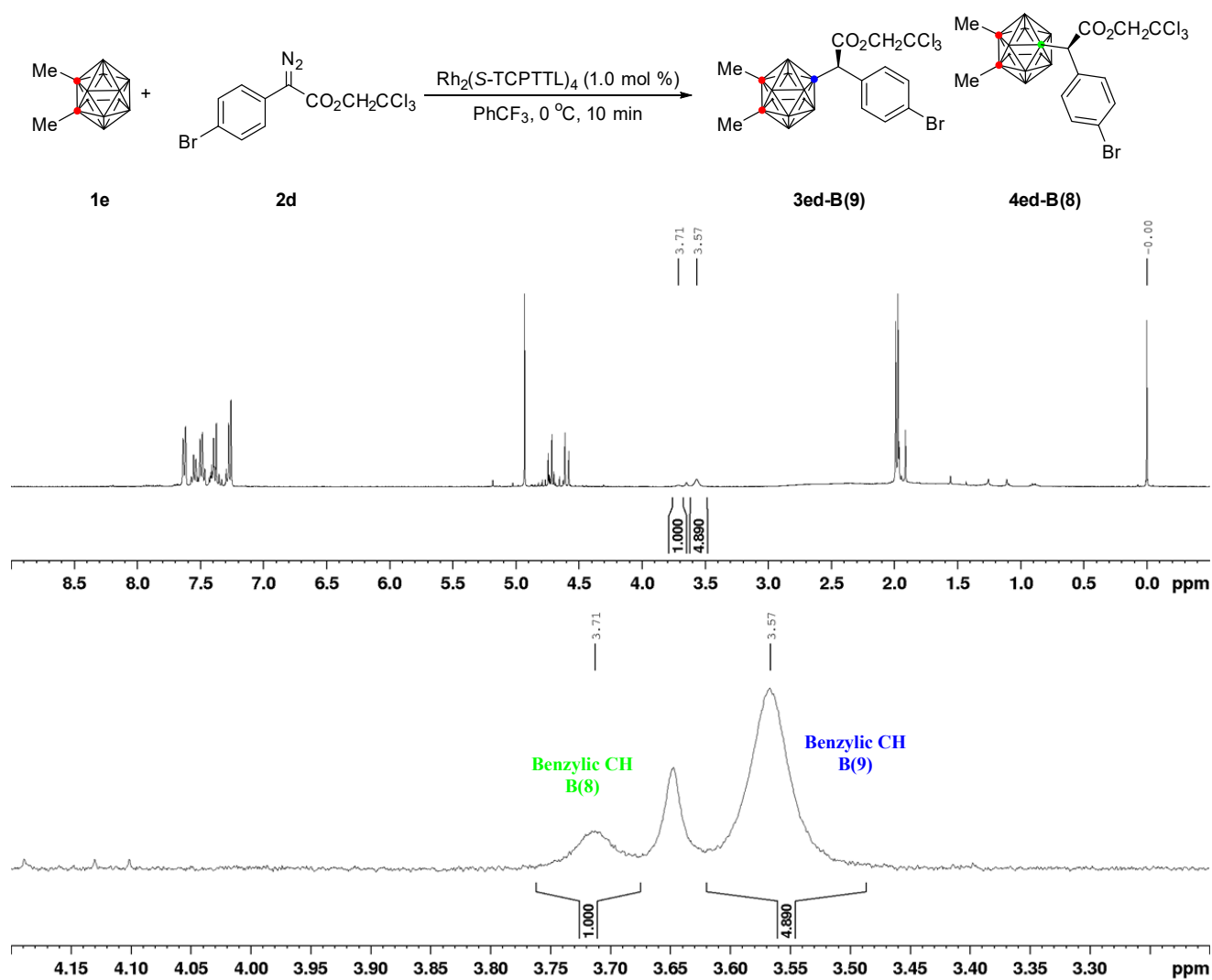




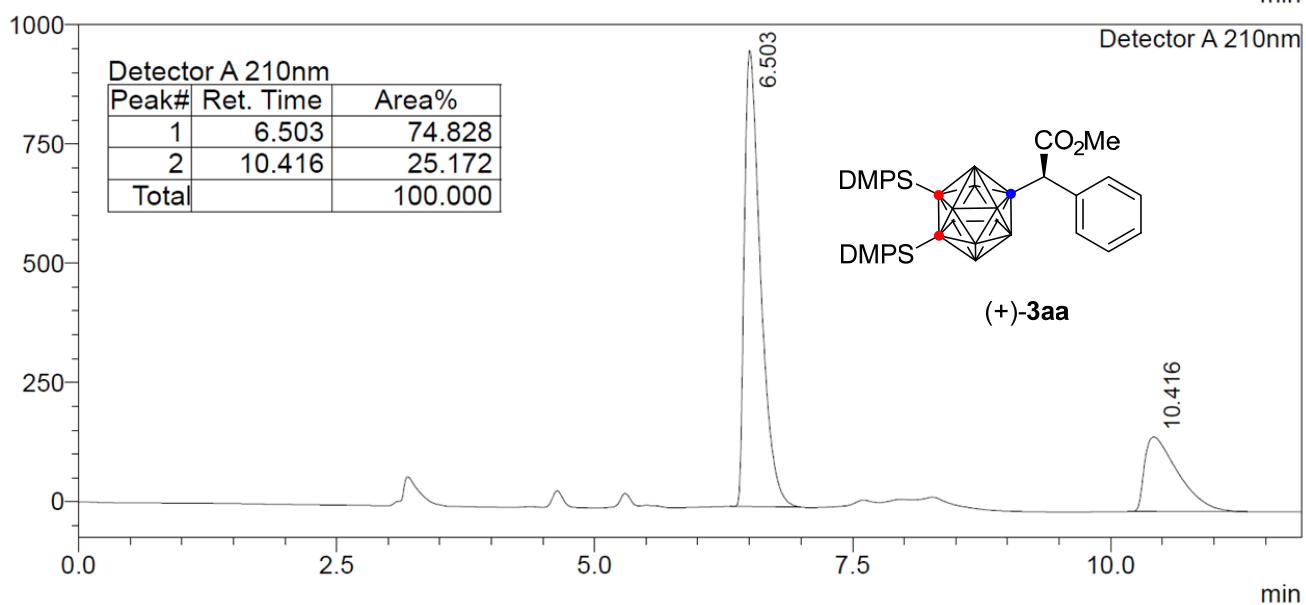
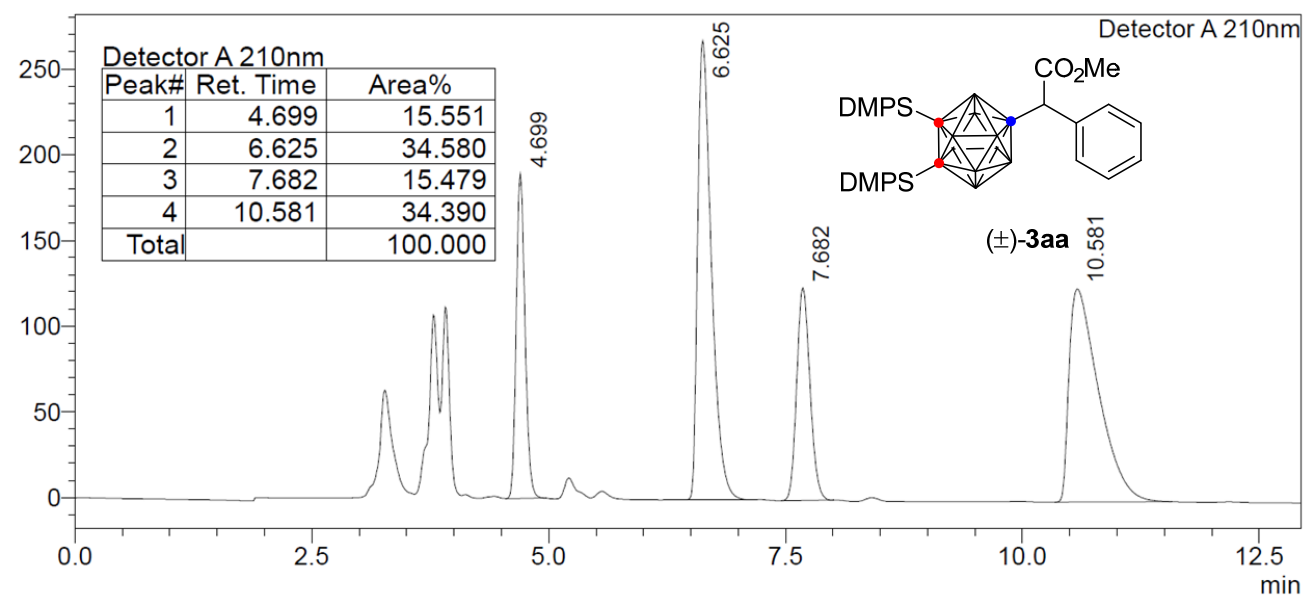


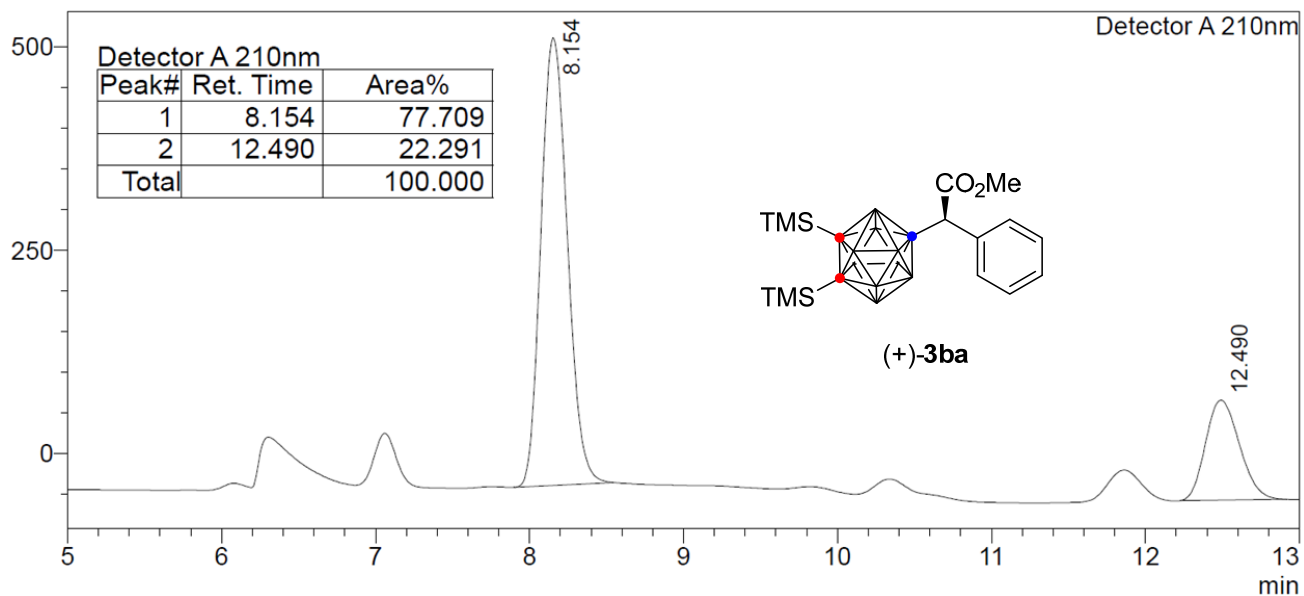
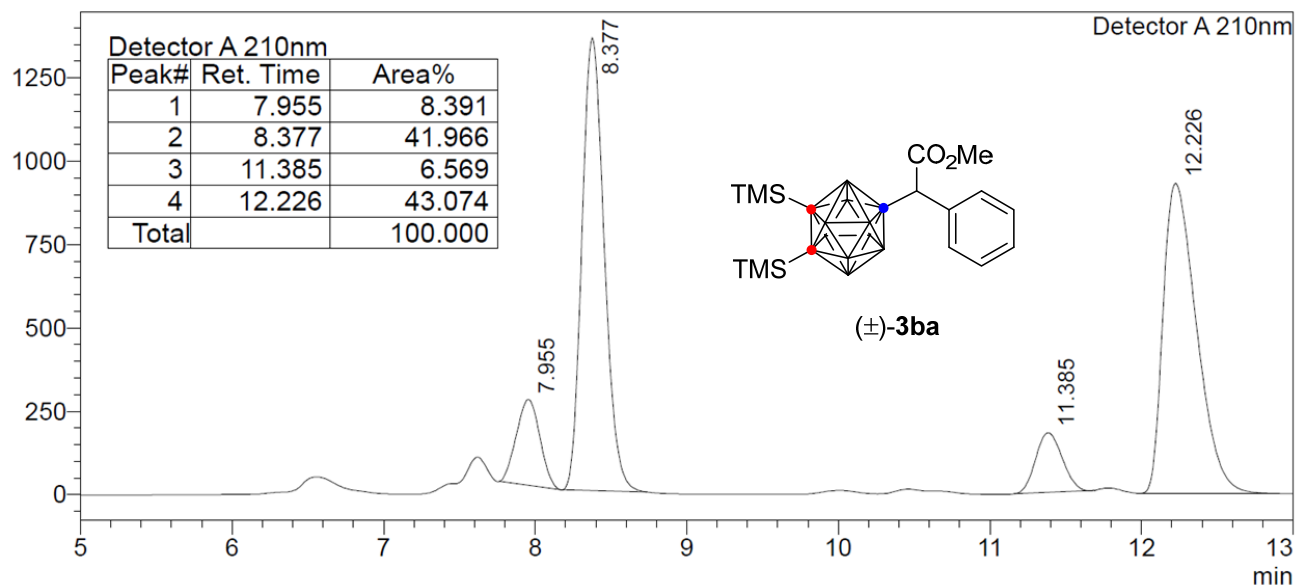


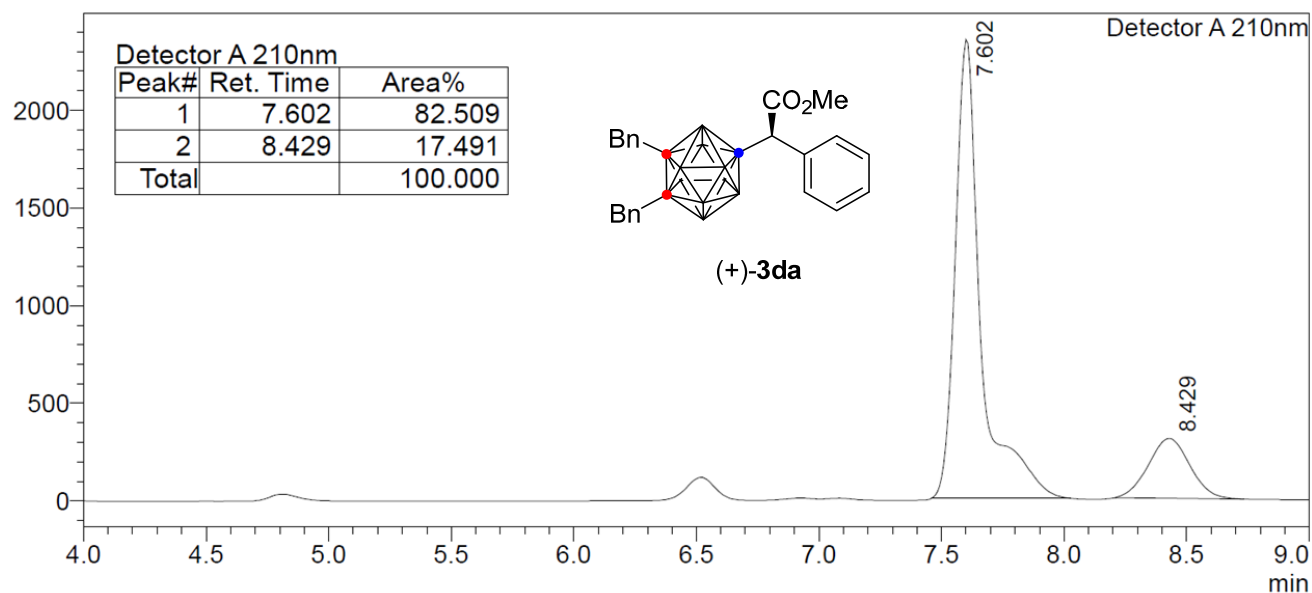
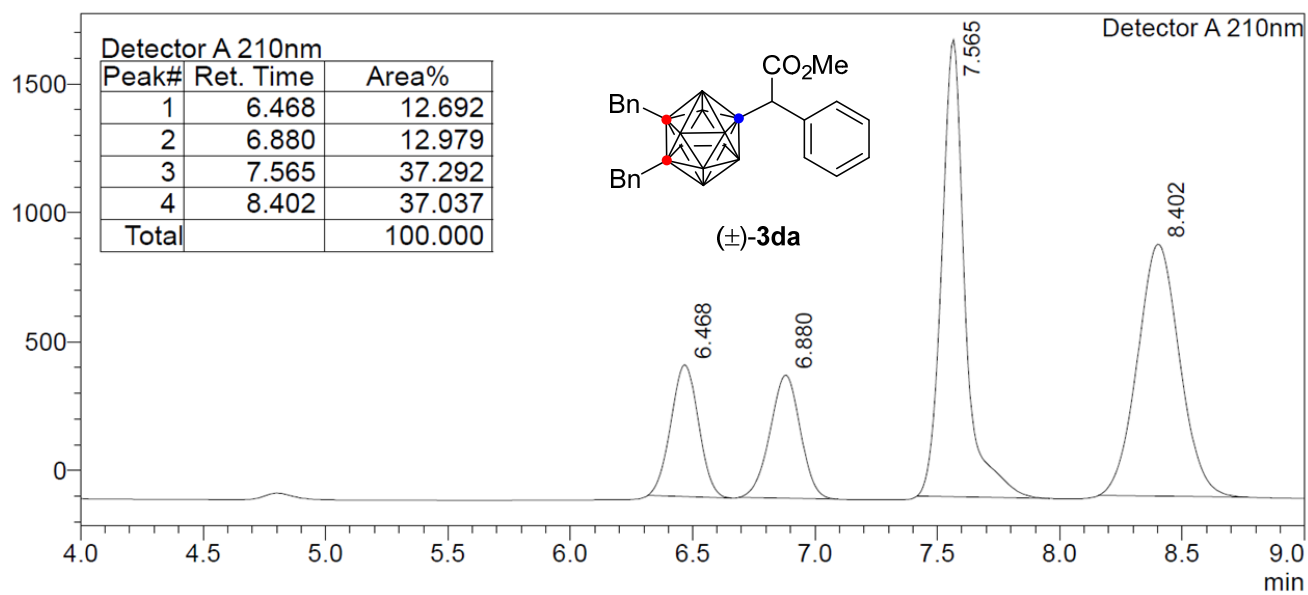


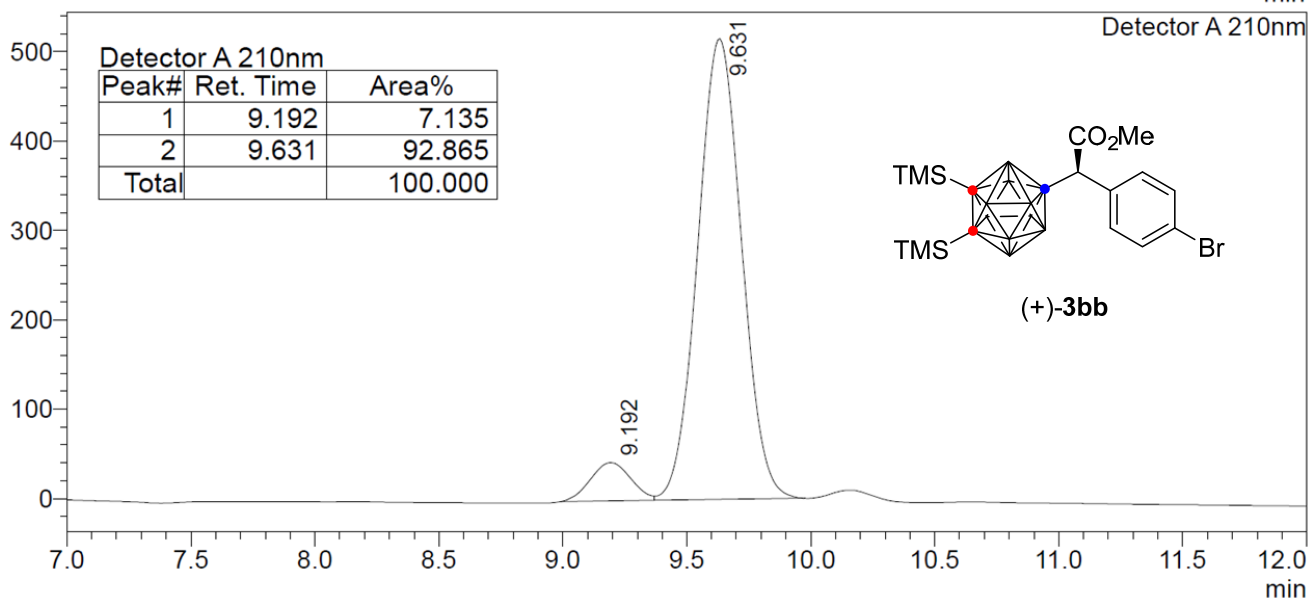
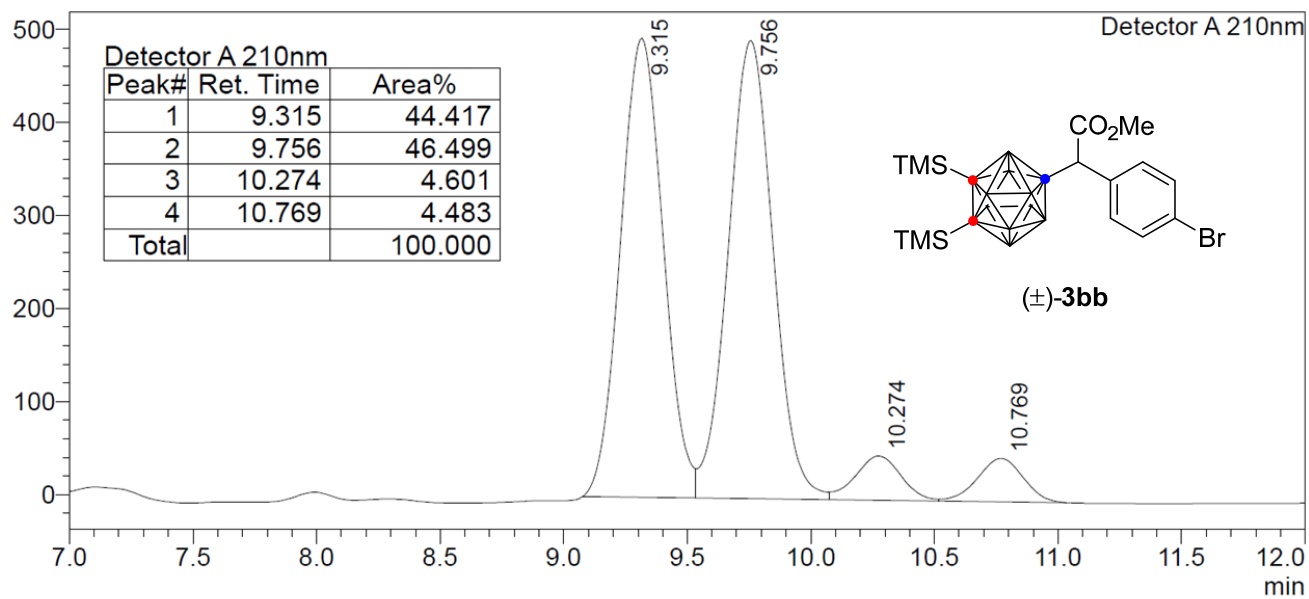


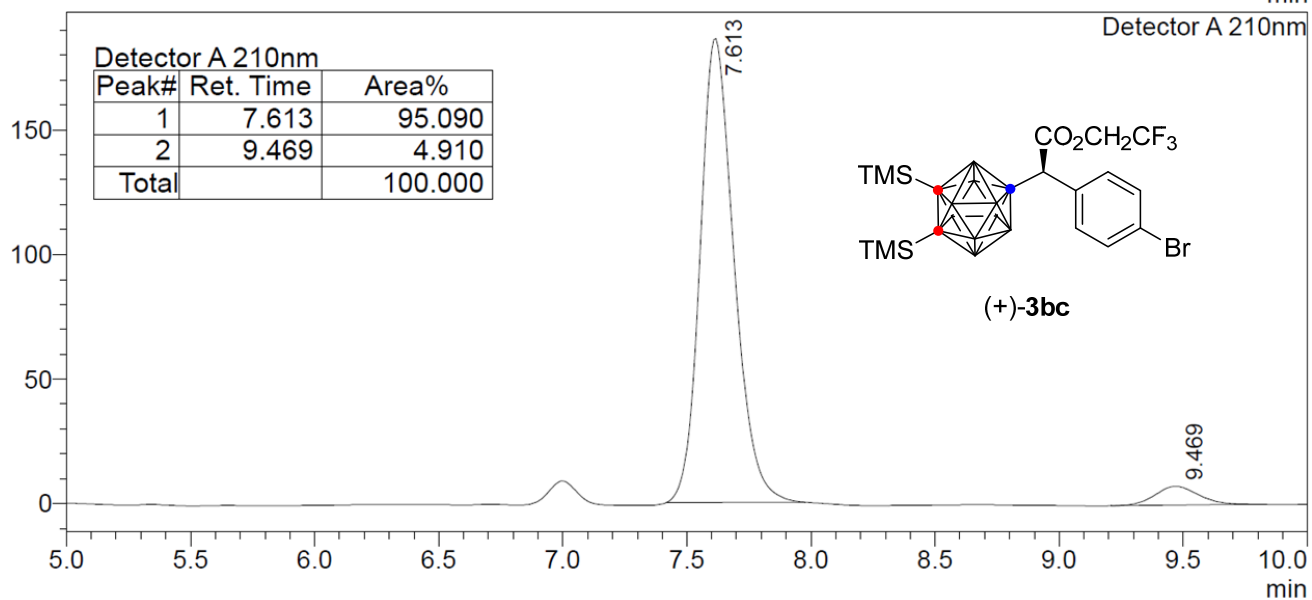
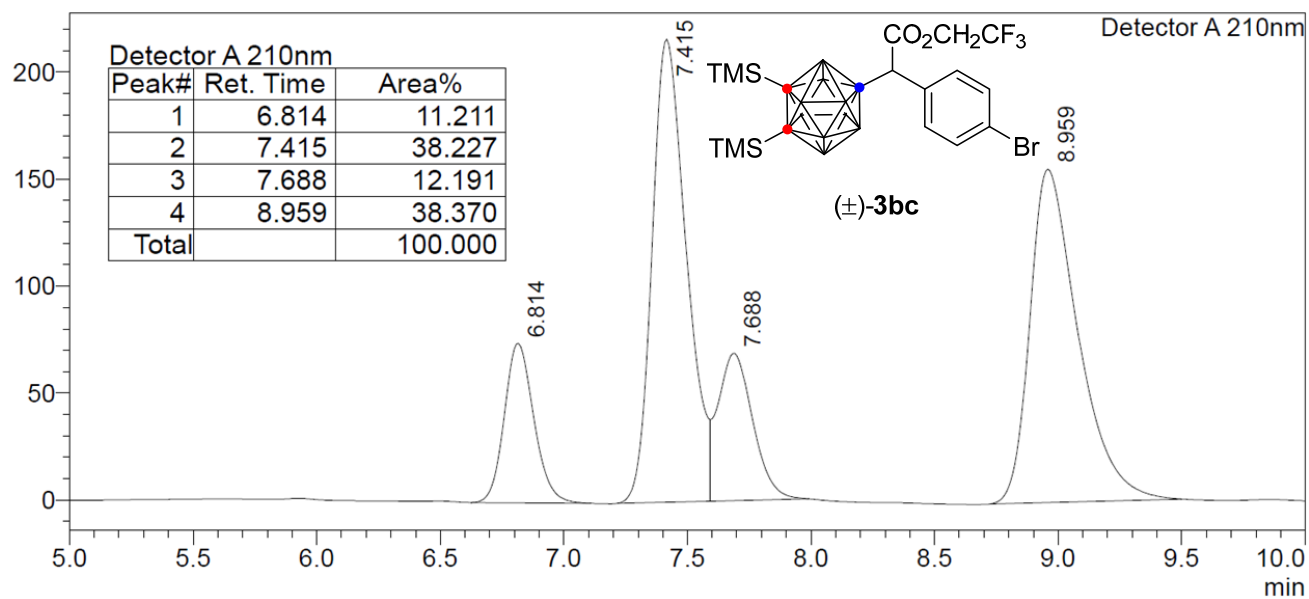
15. HPLC Spectra for Enantiomeric Excess Determination

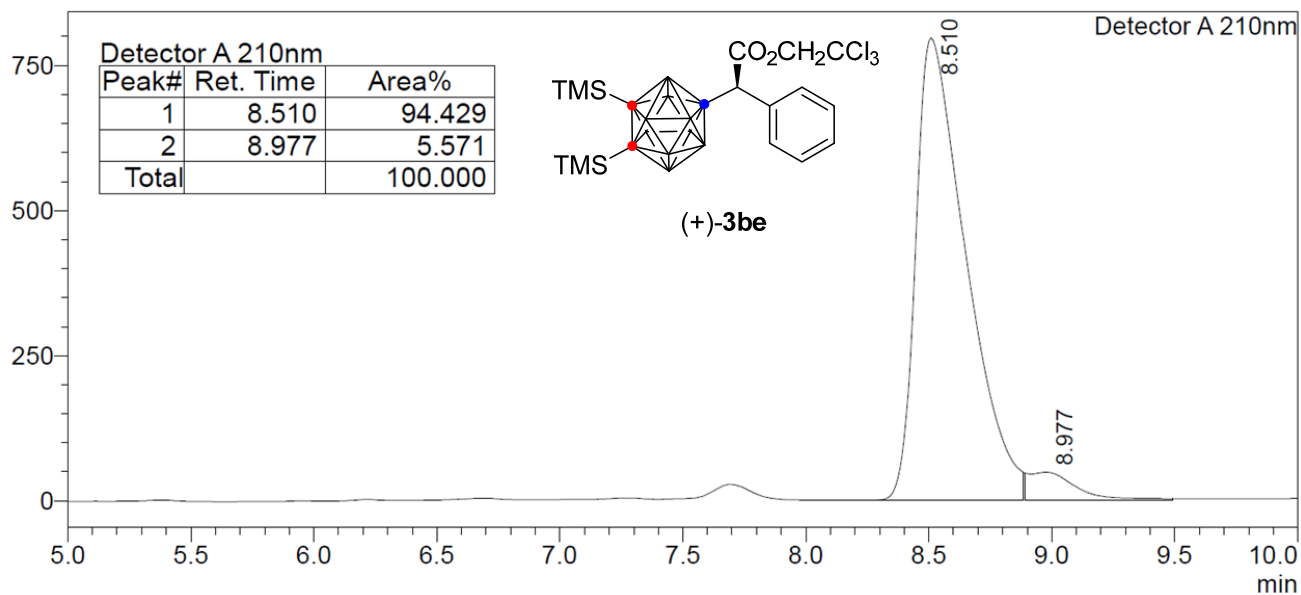
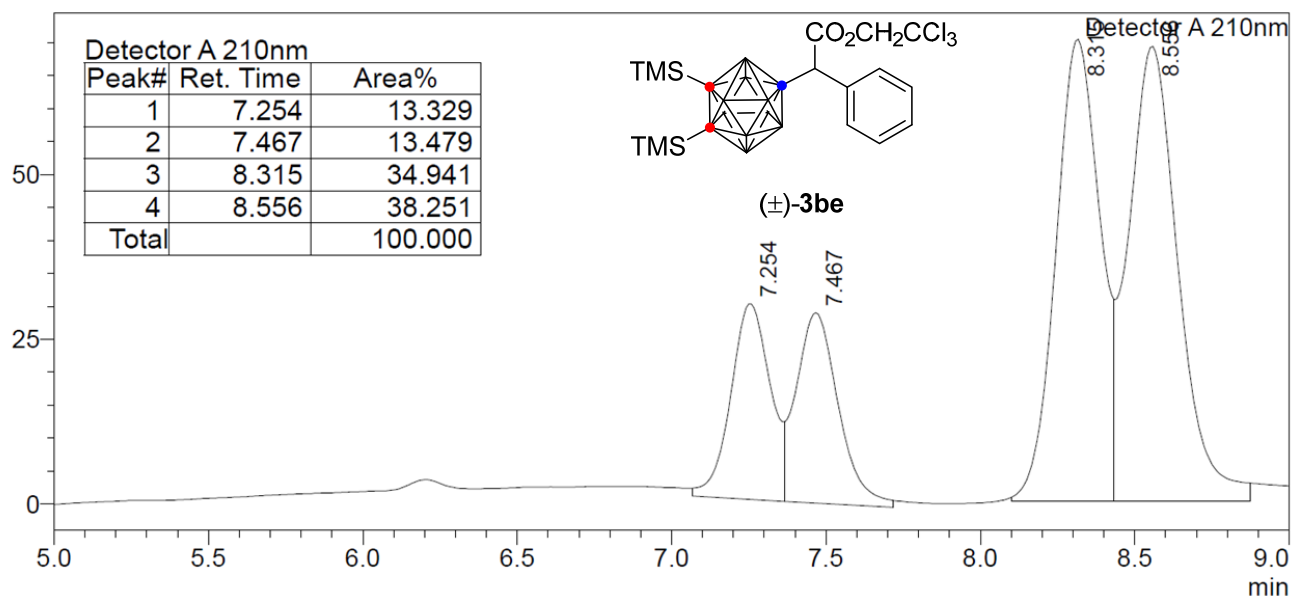


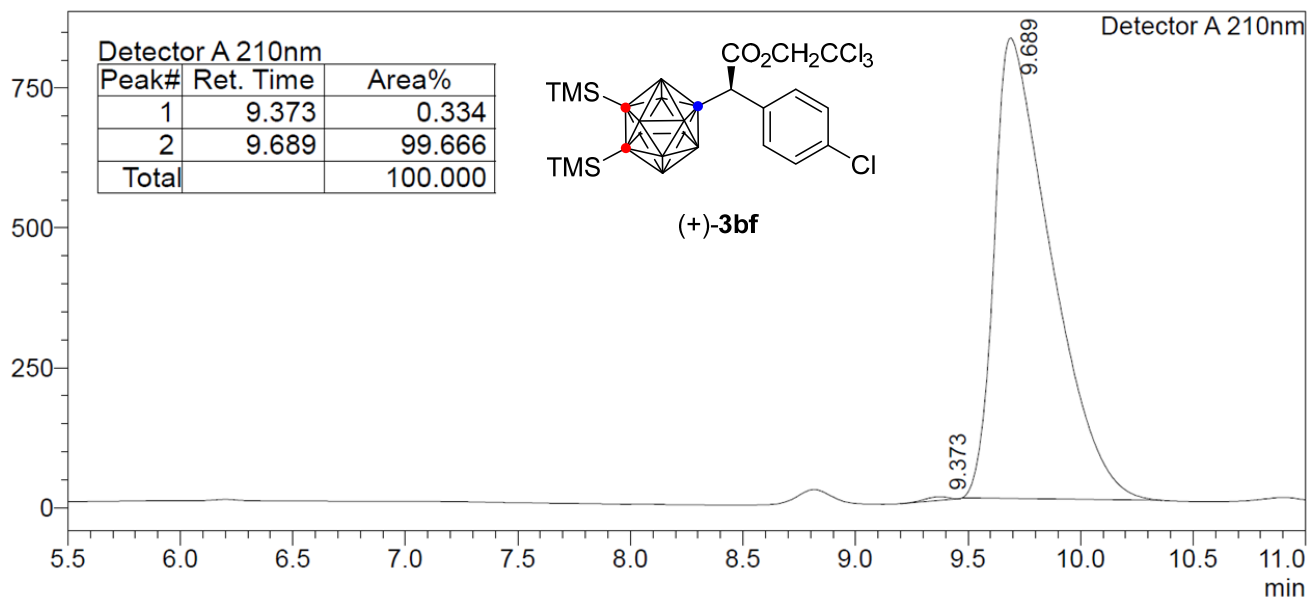
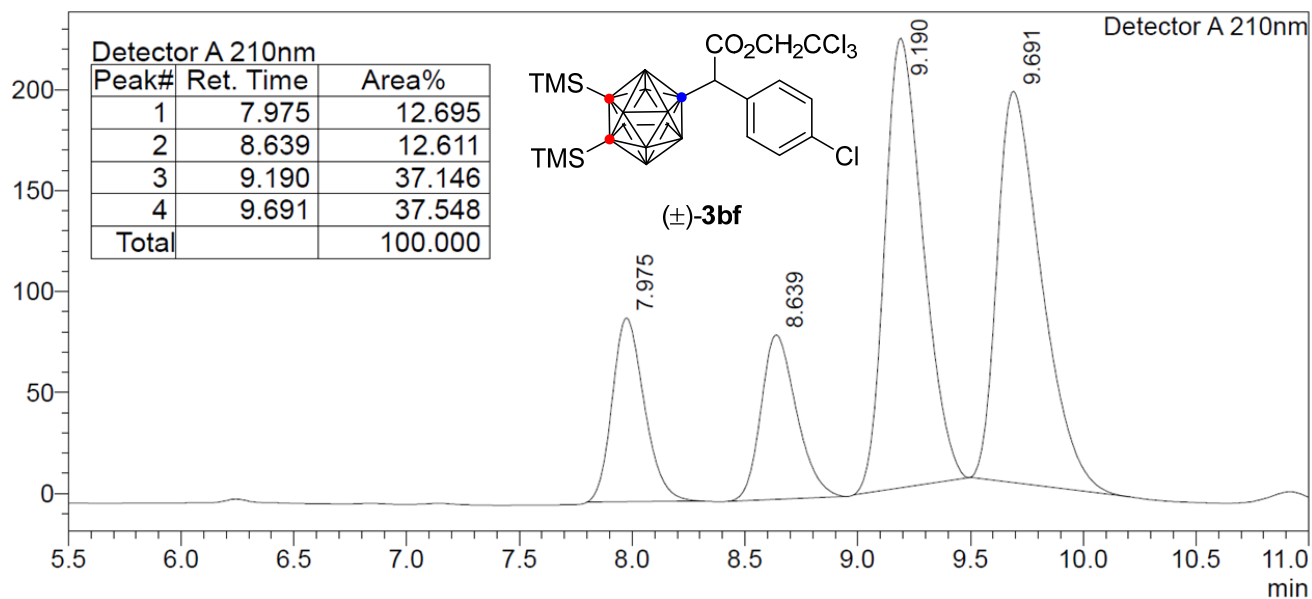


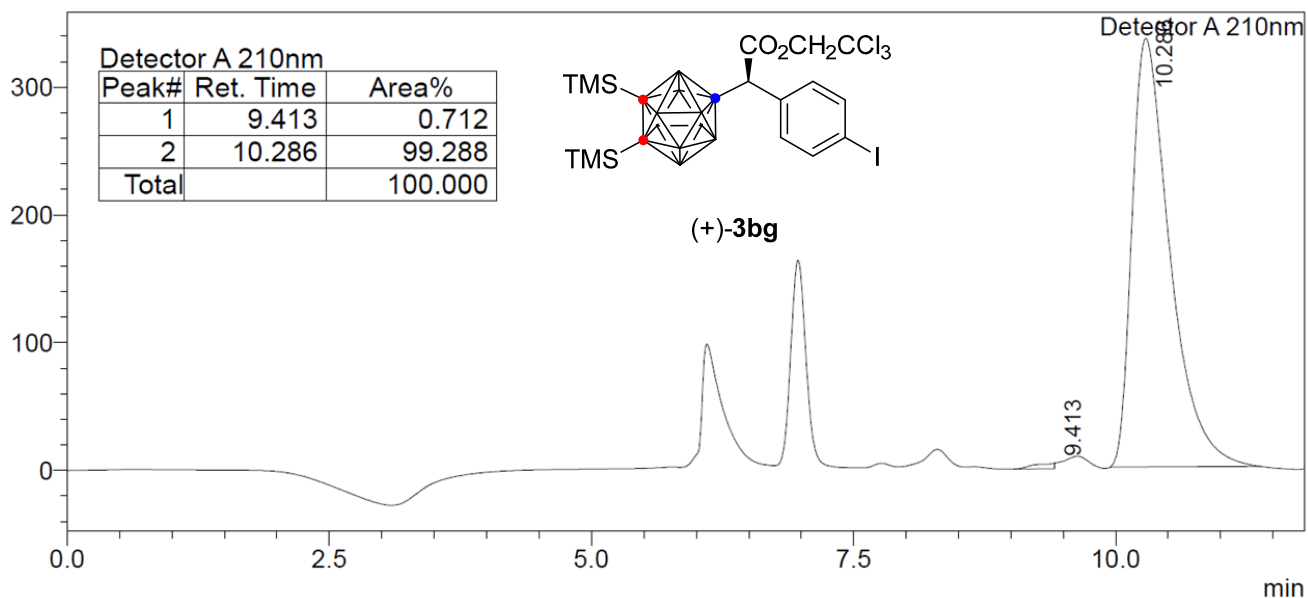
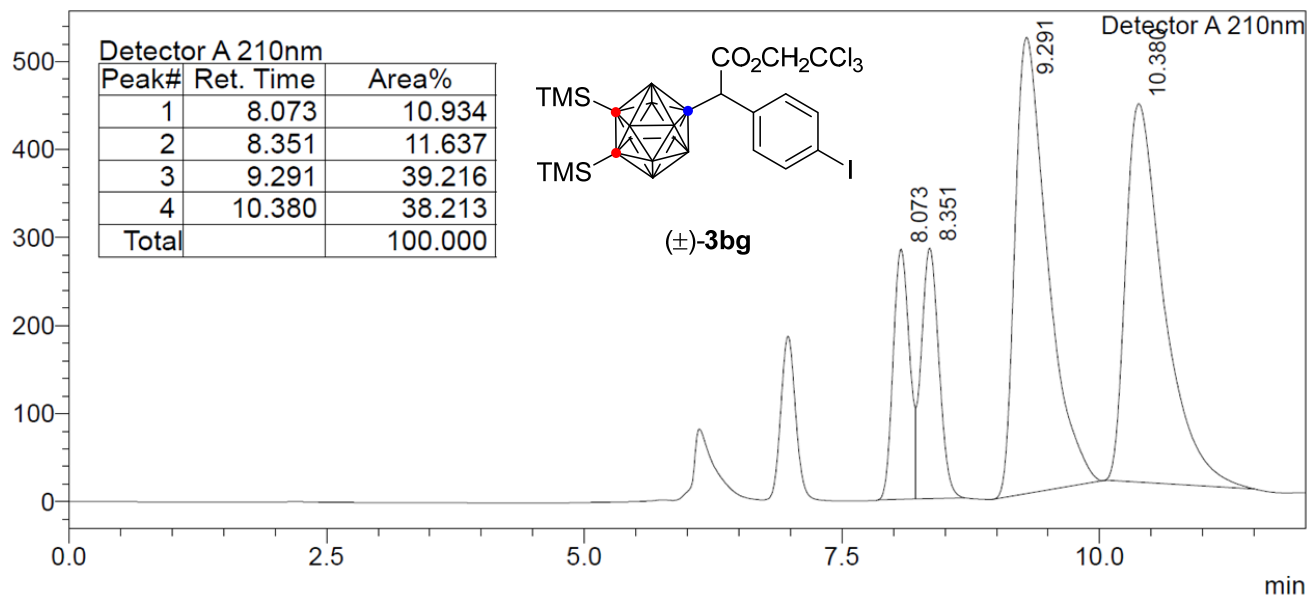


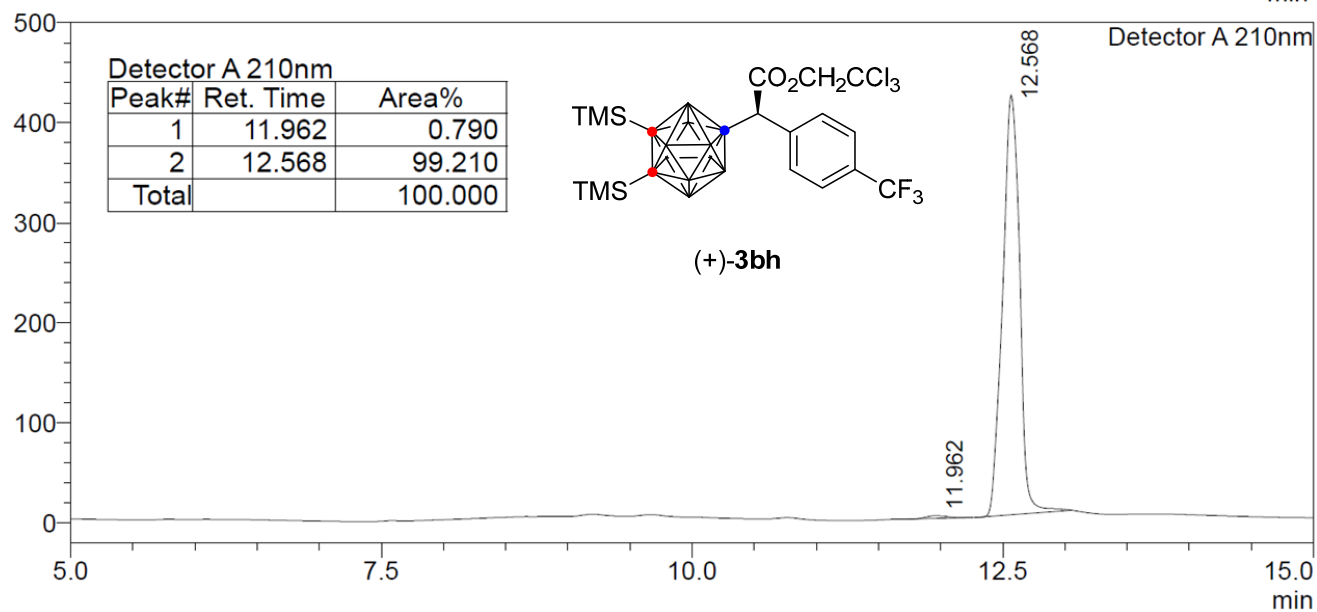
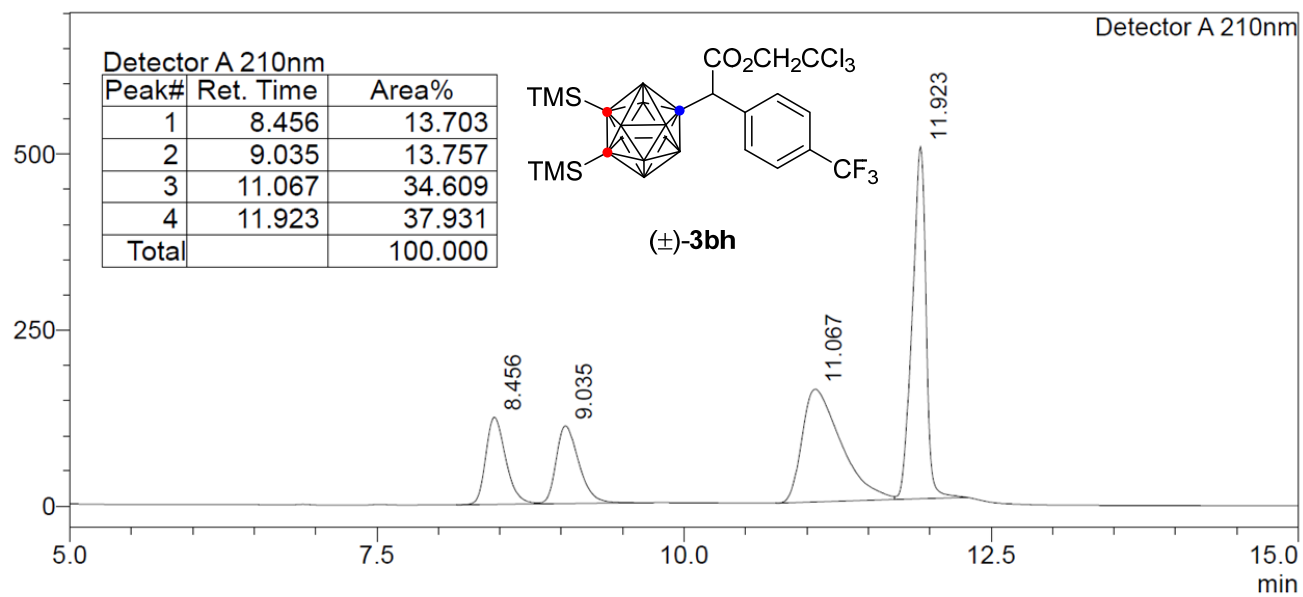


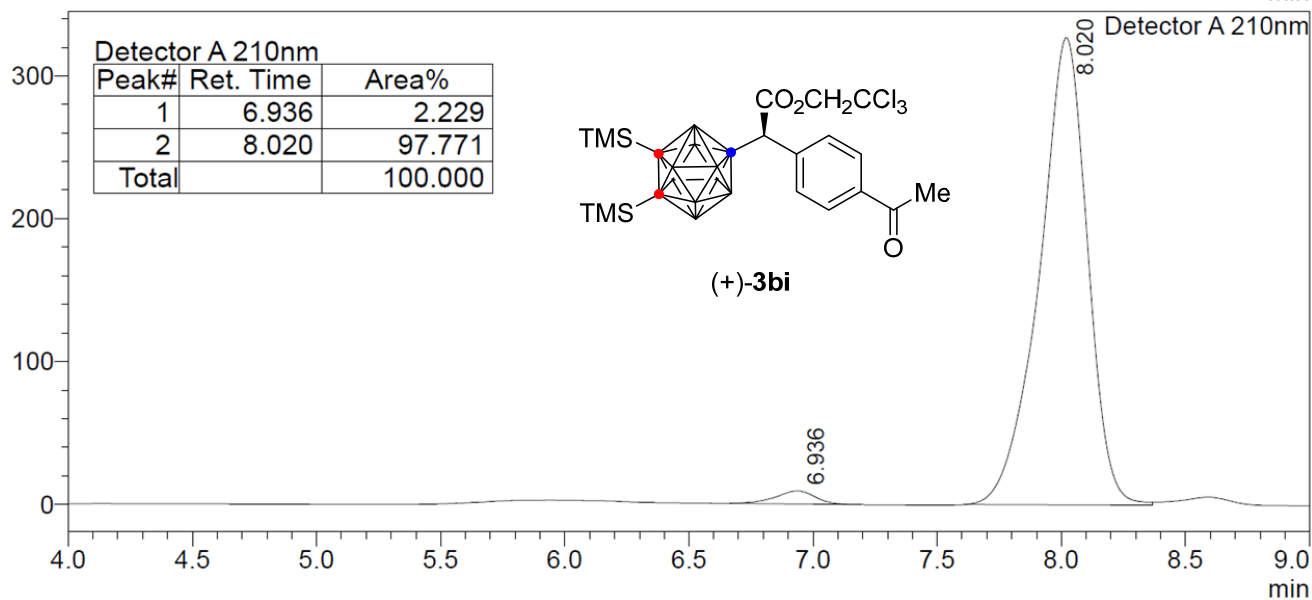
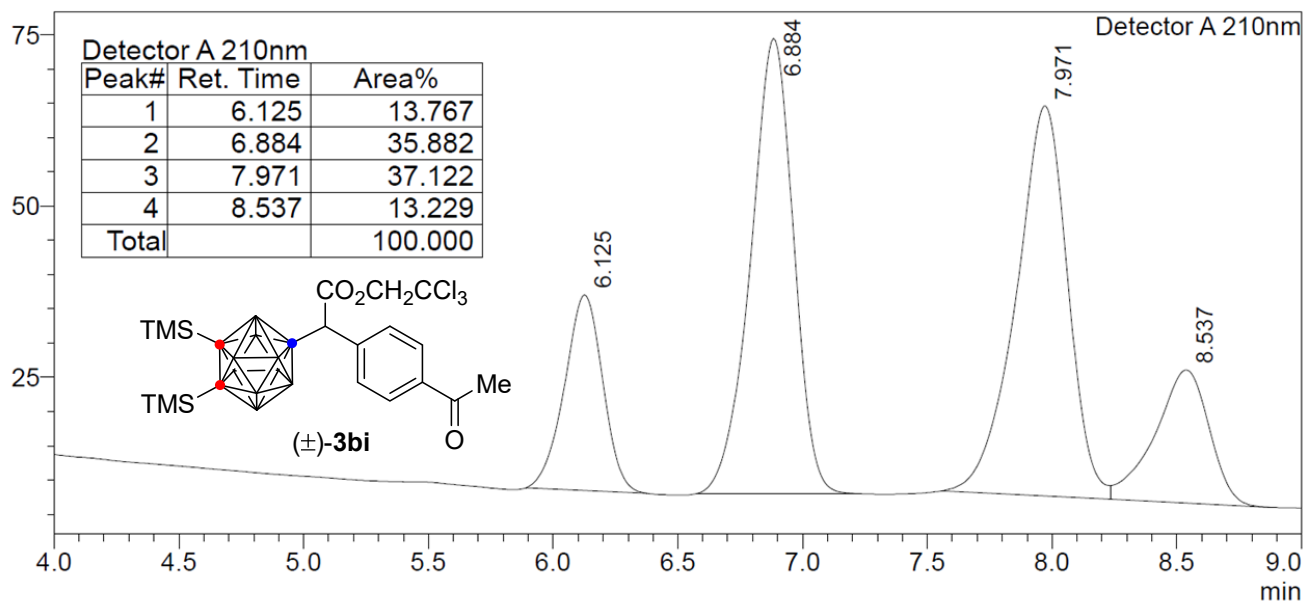


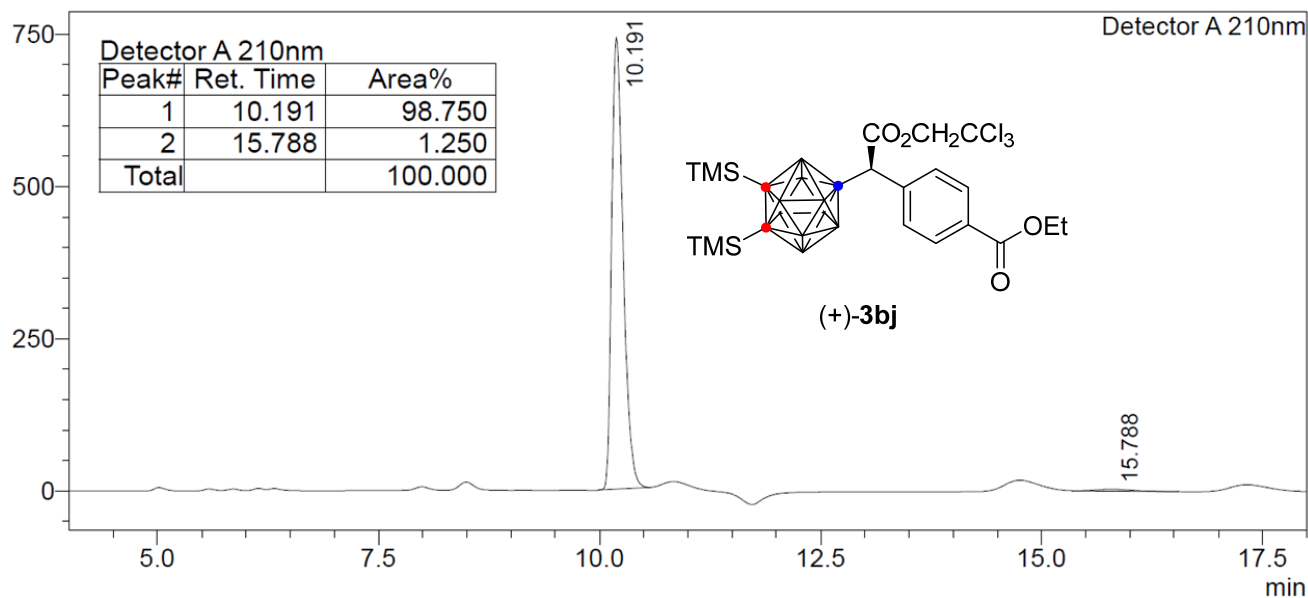
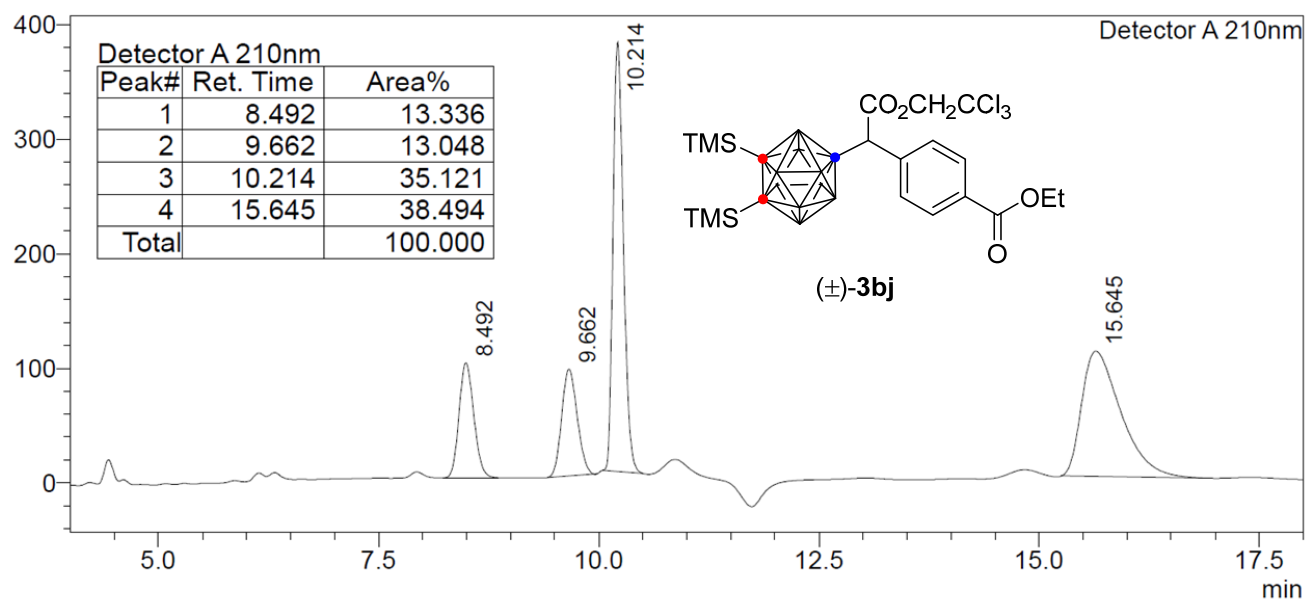


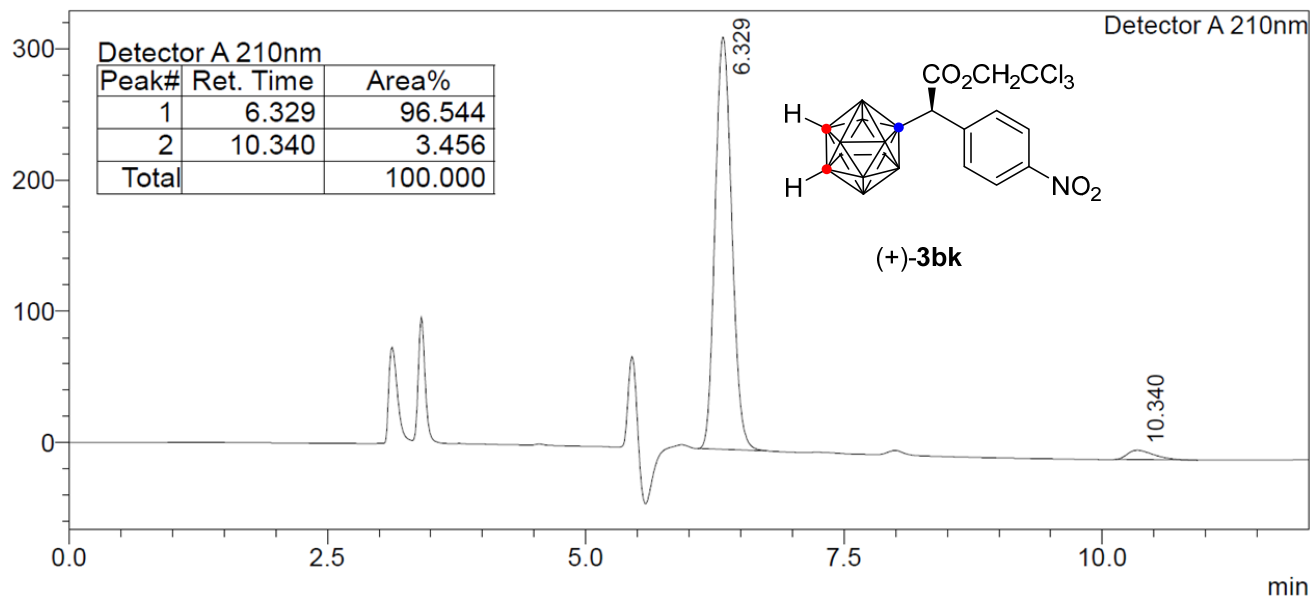
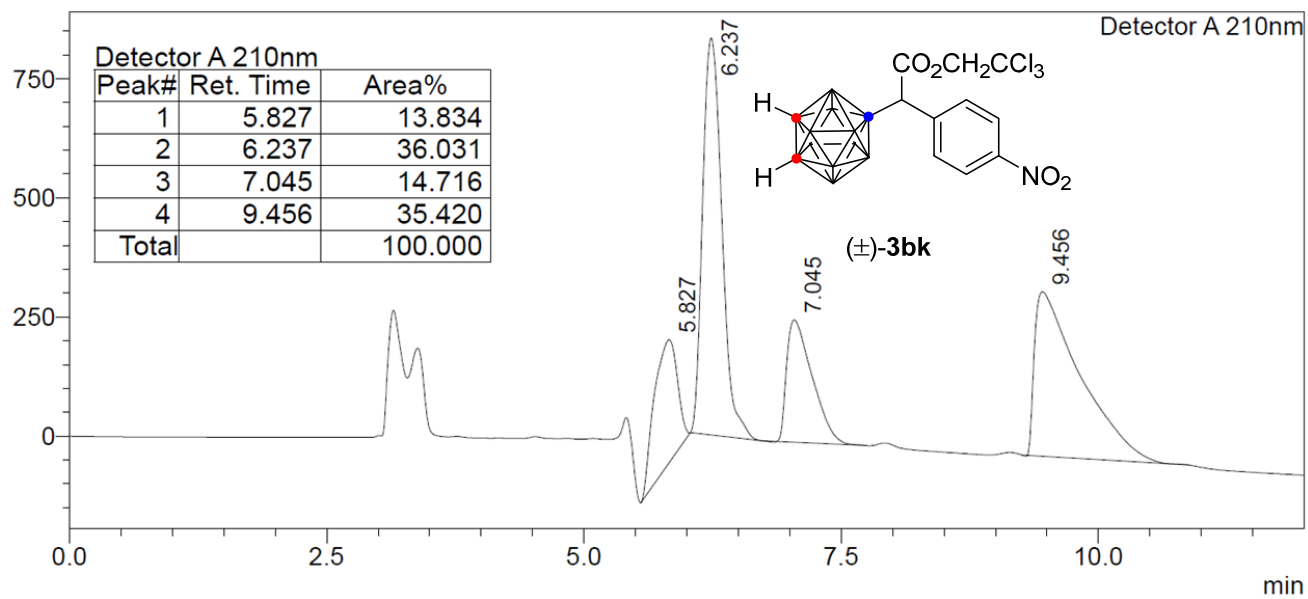


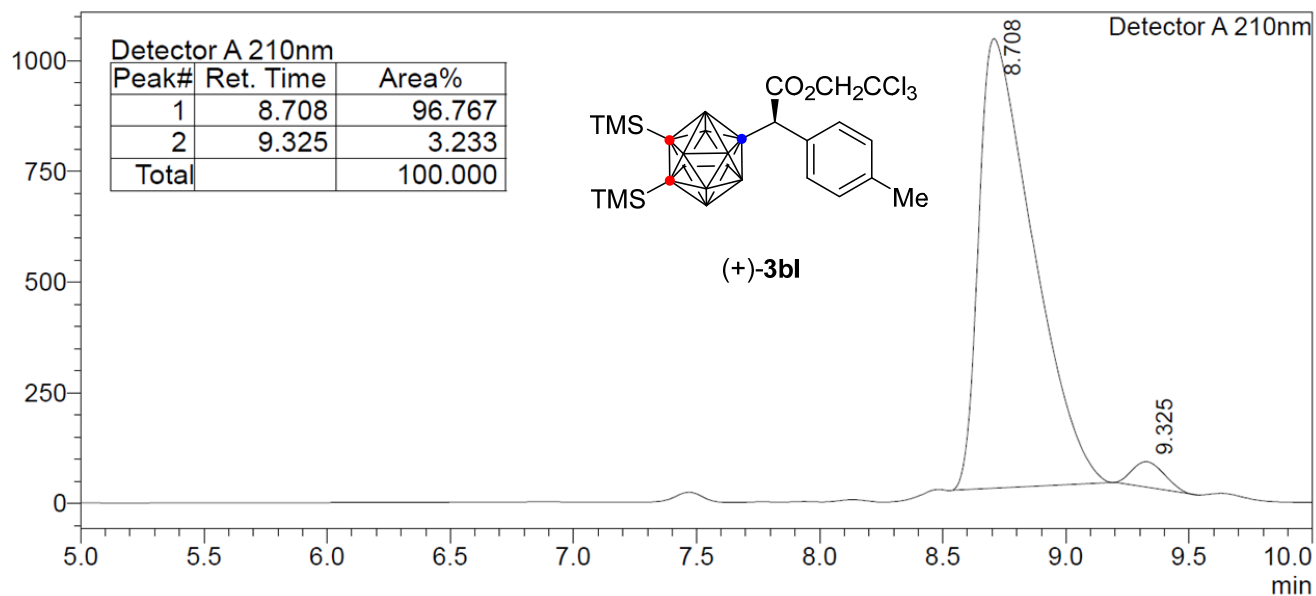
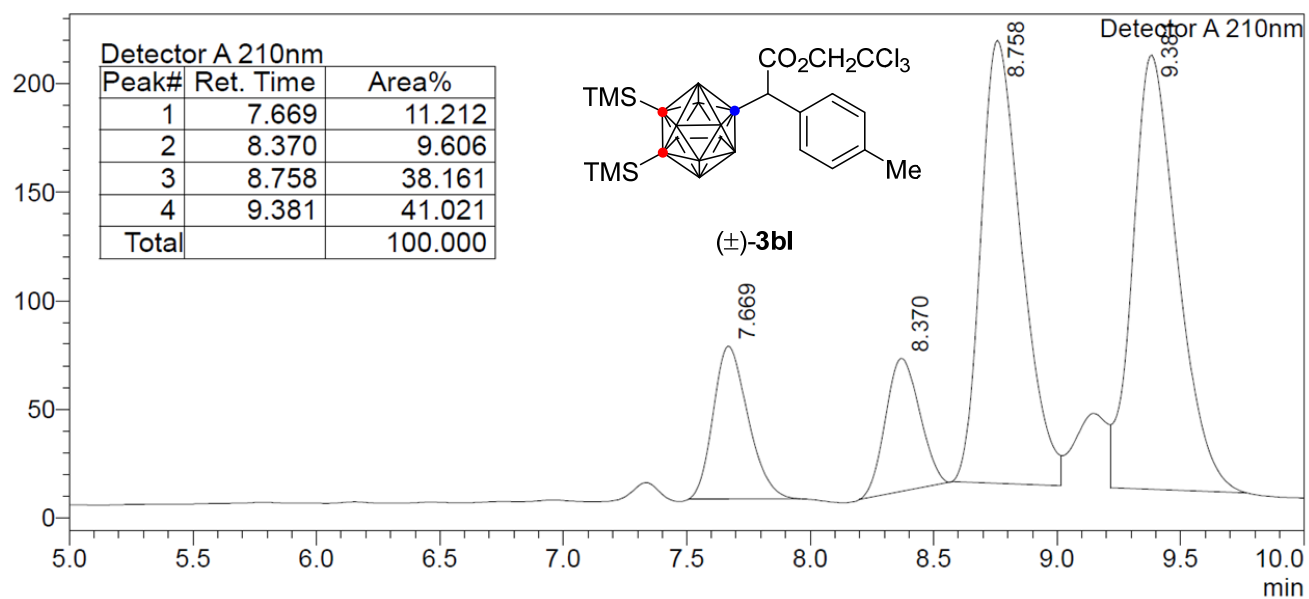


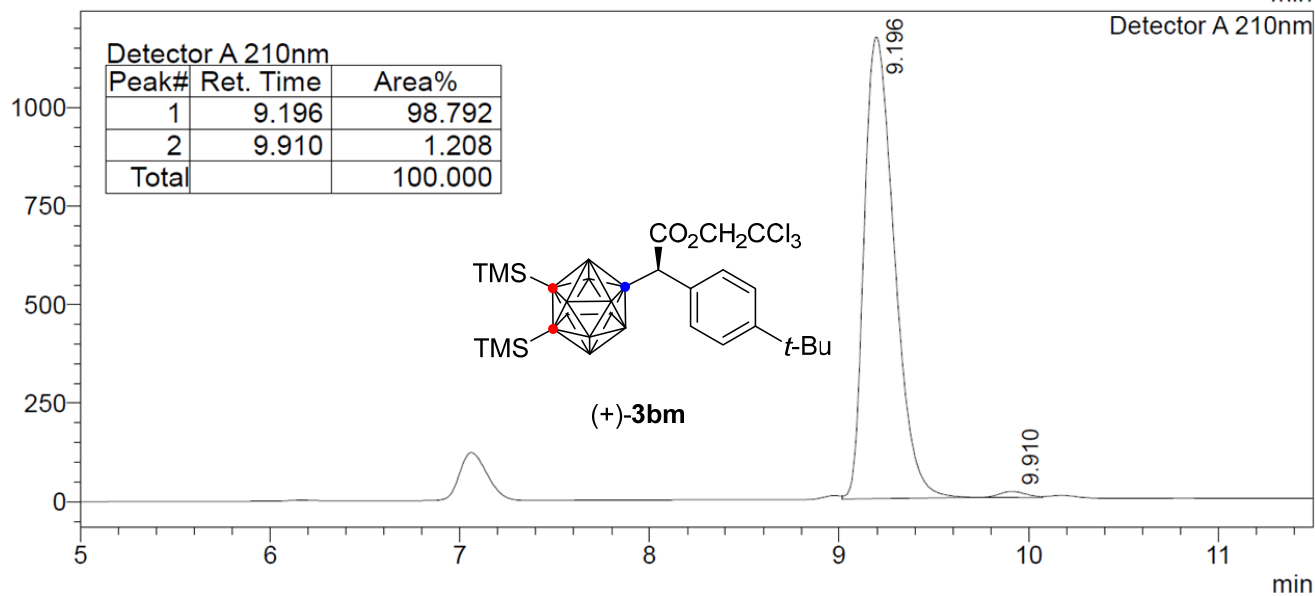
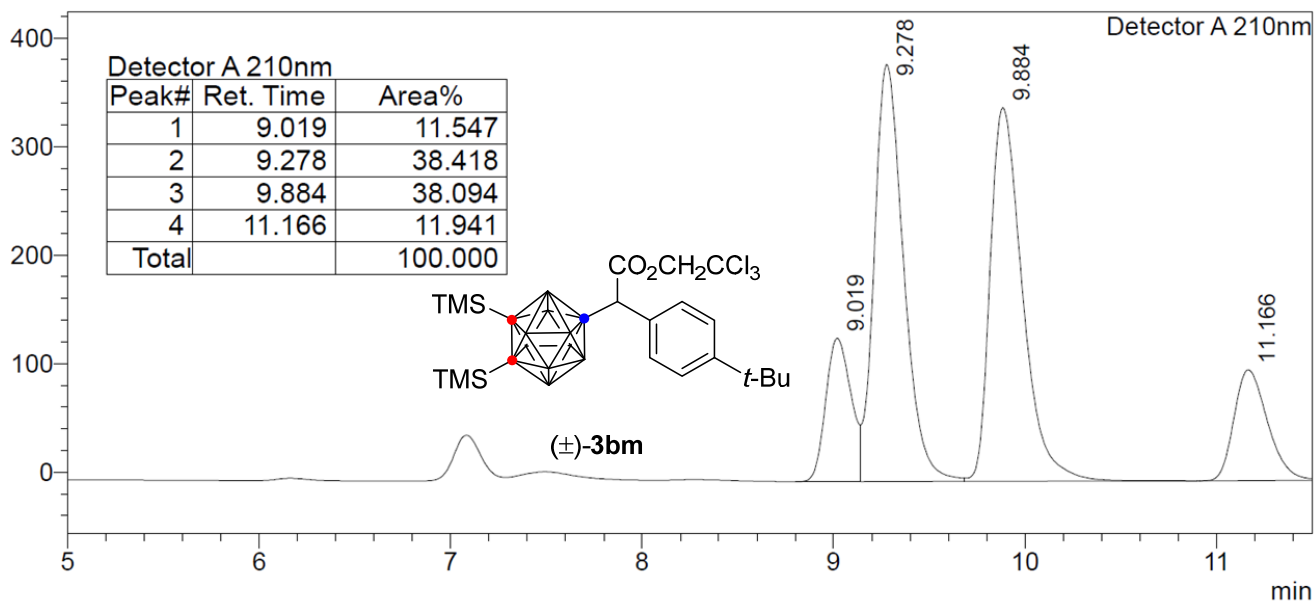


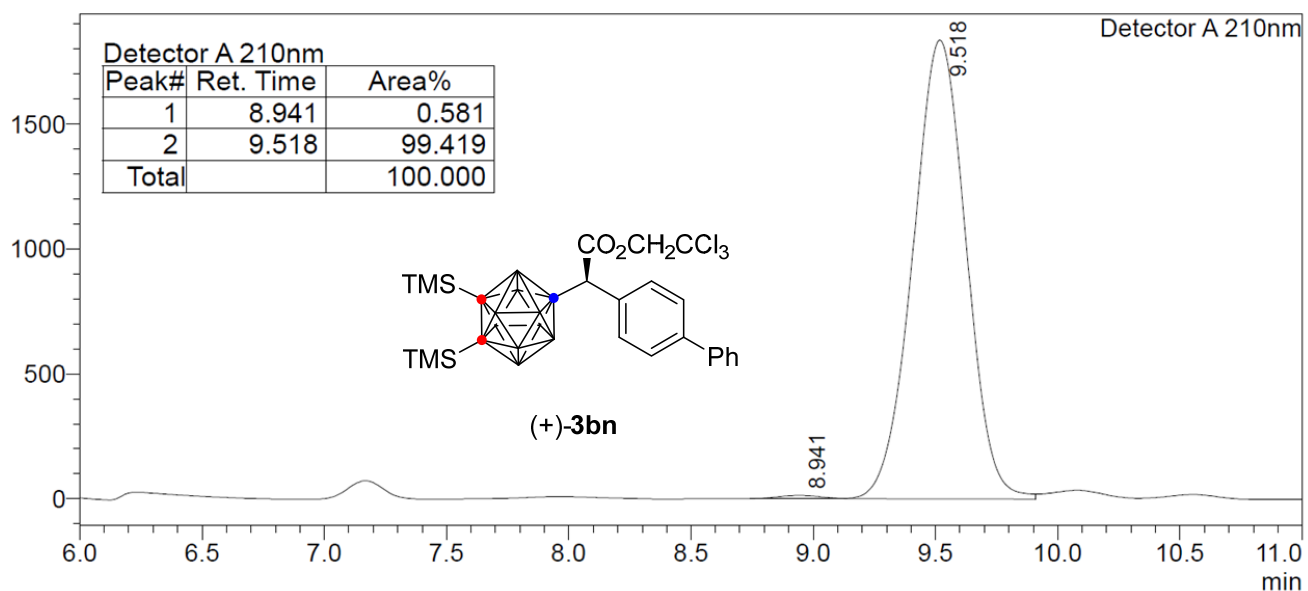
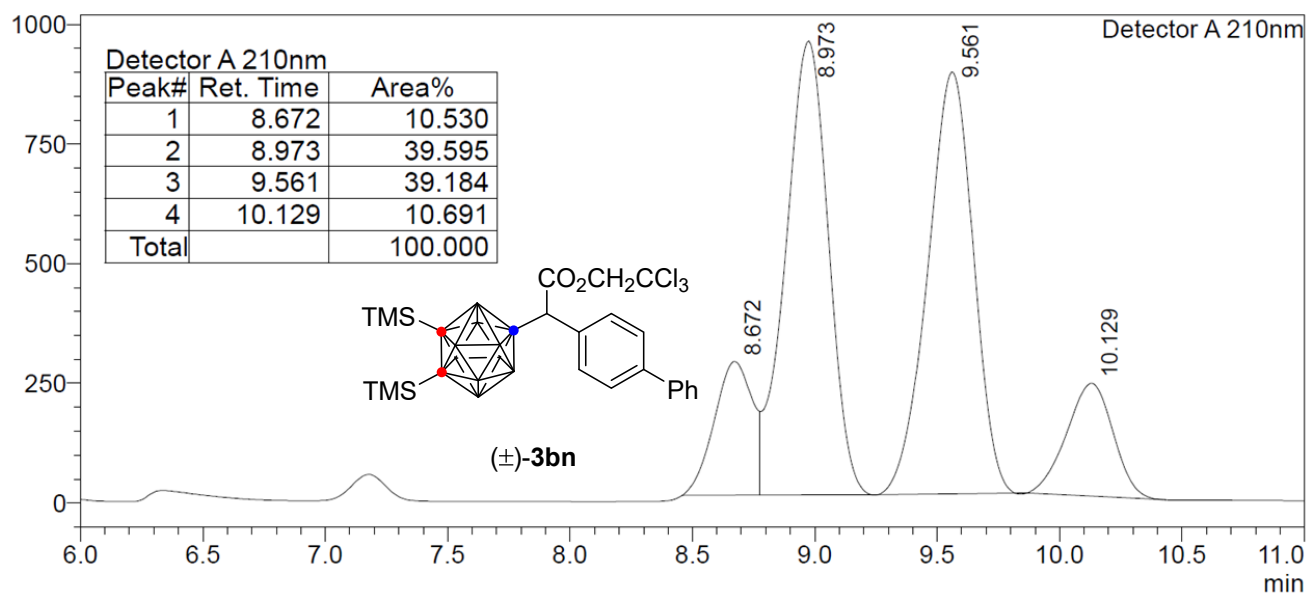


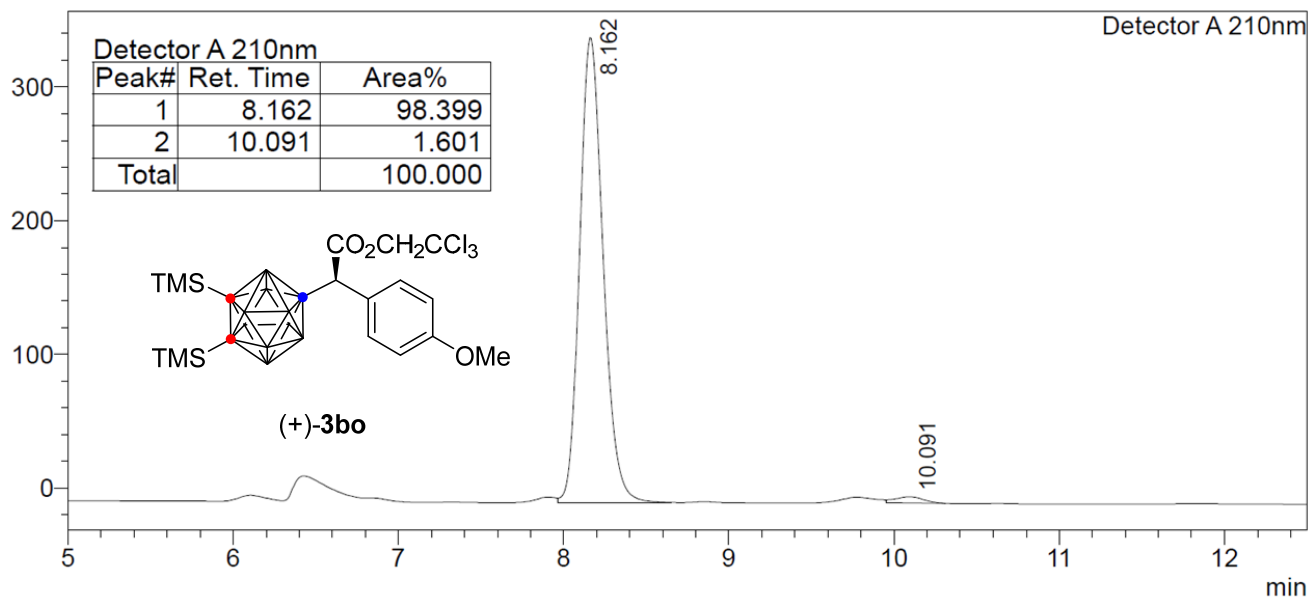
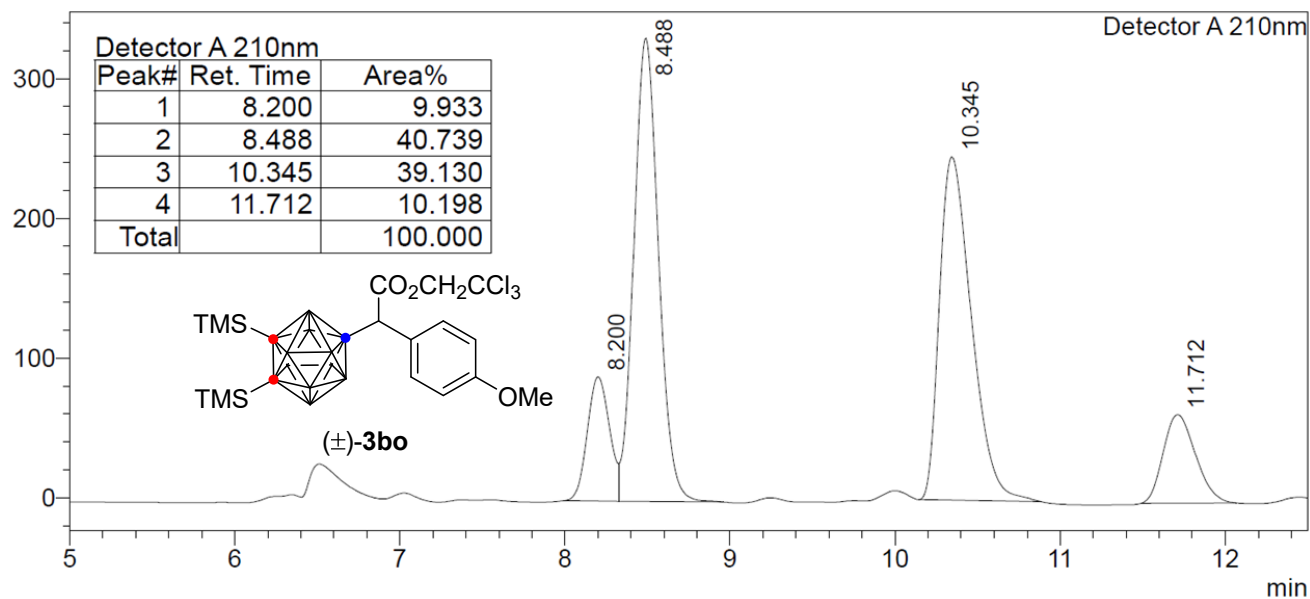


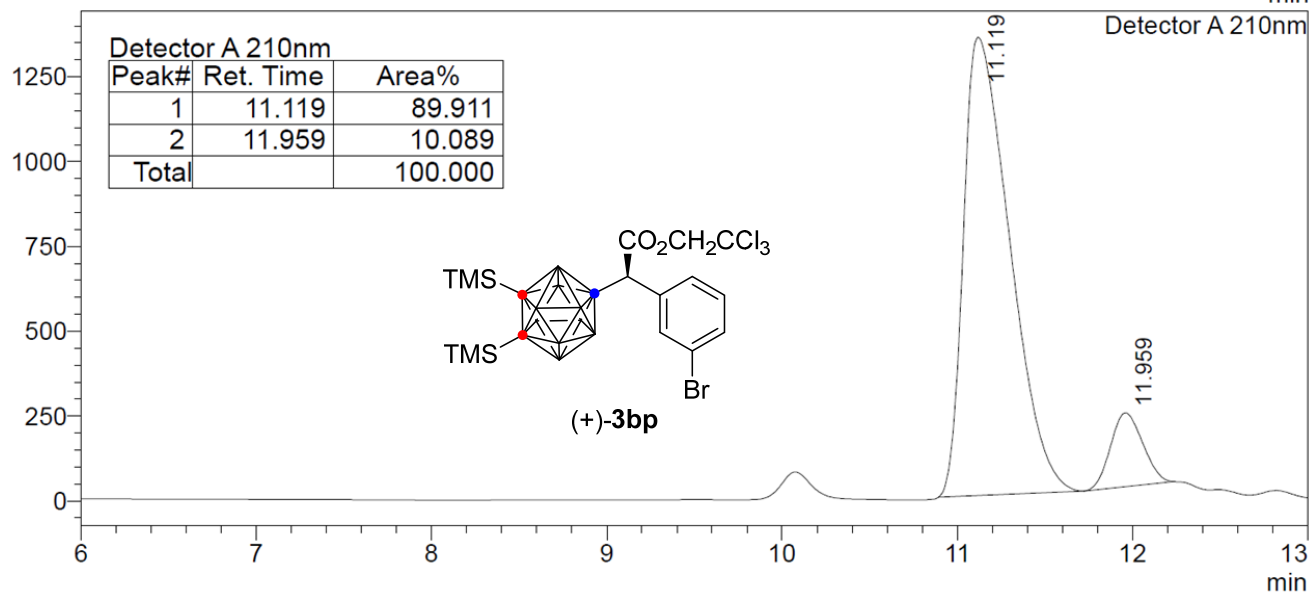
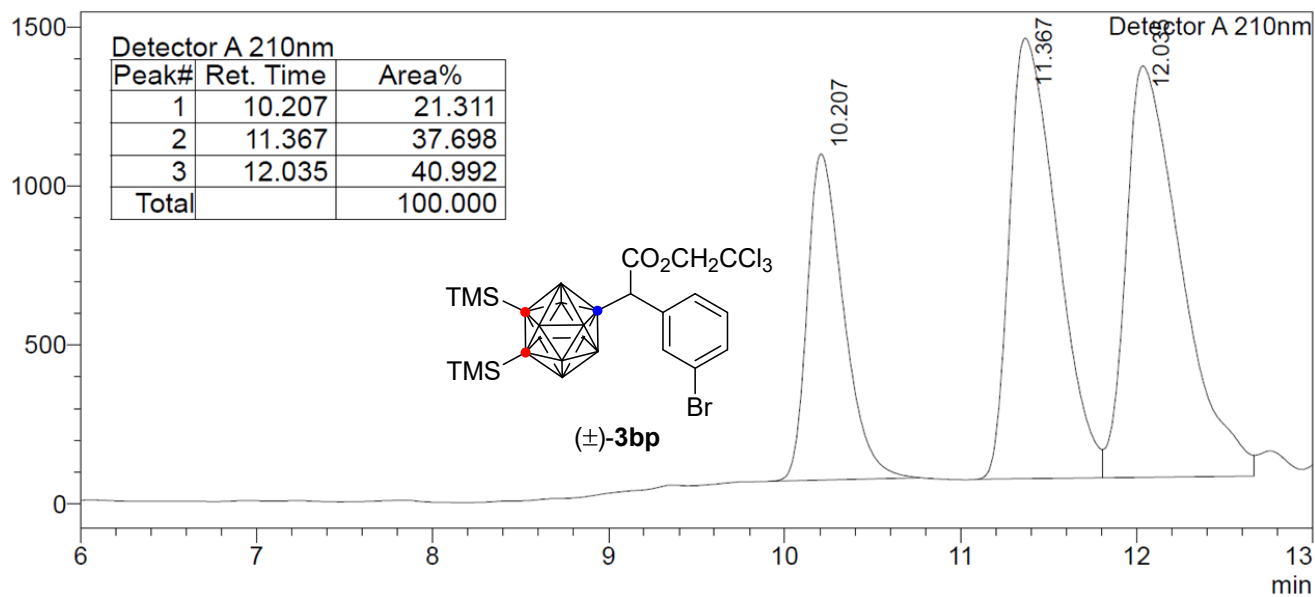


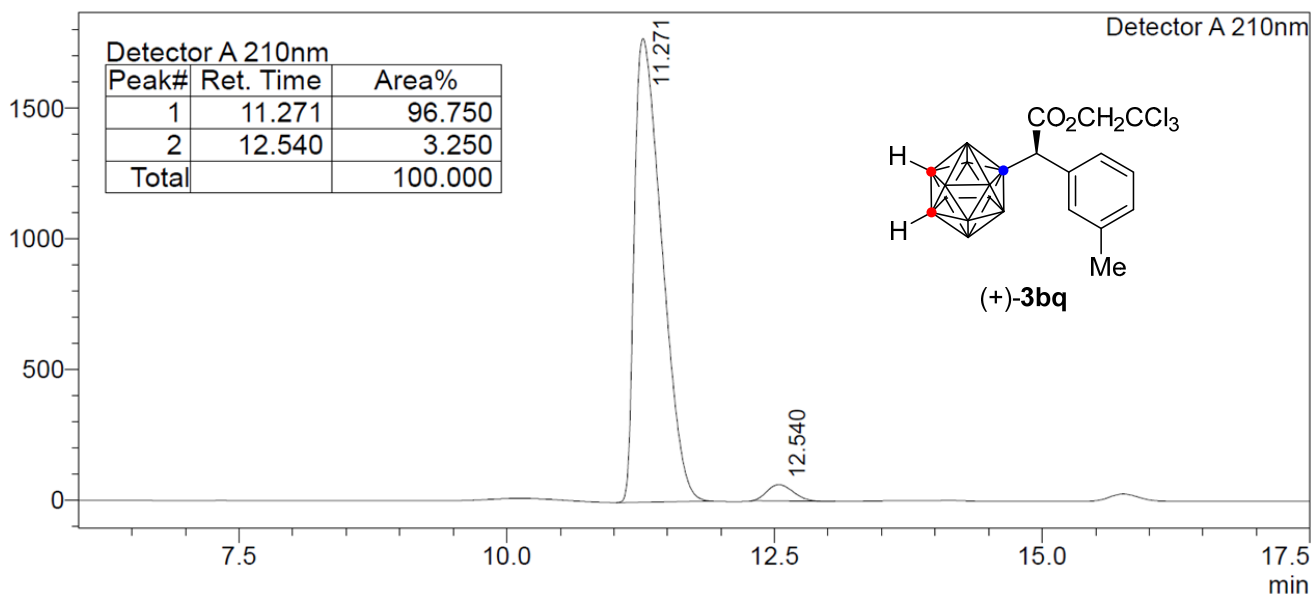
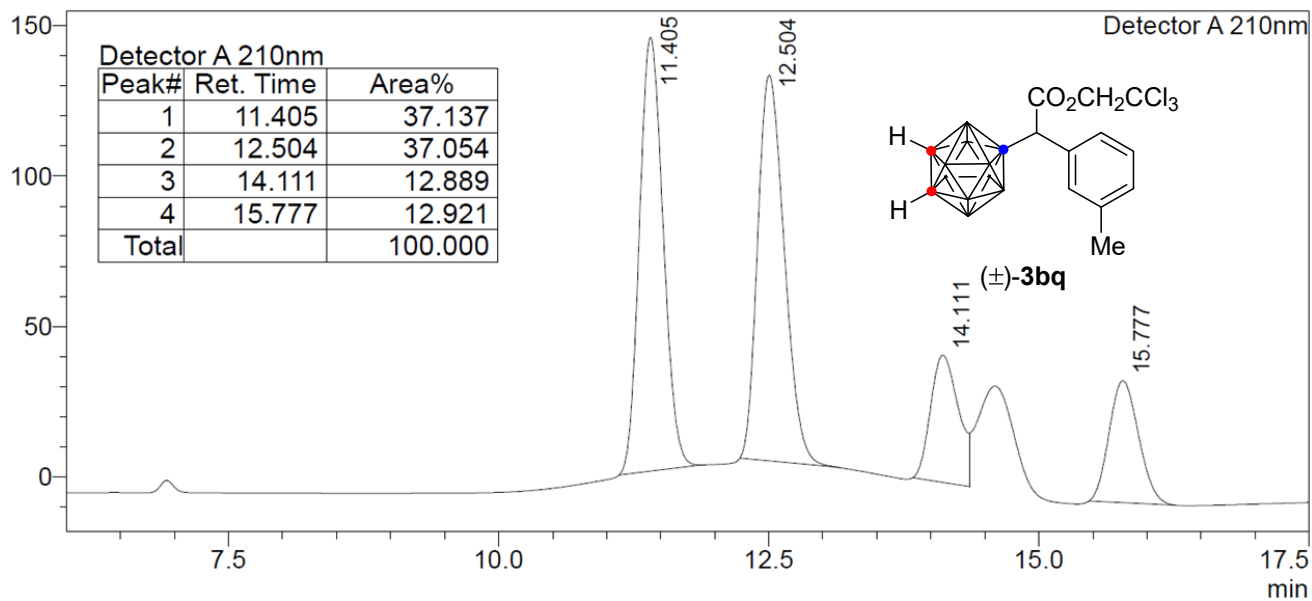


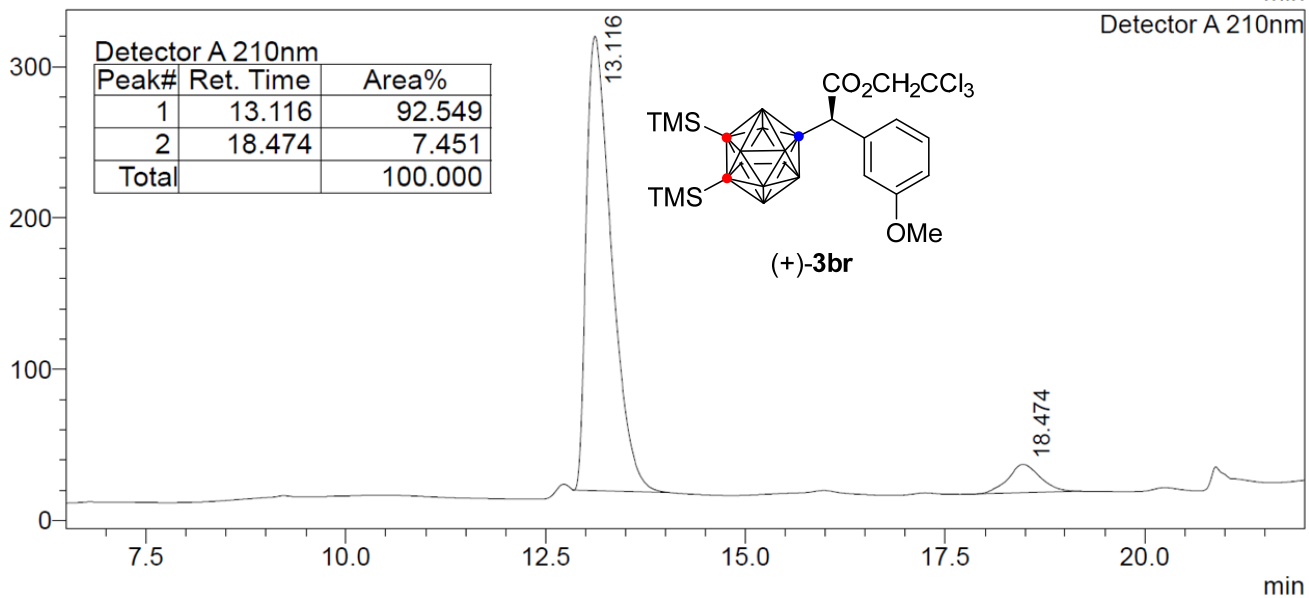
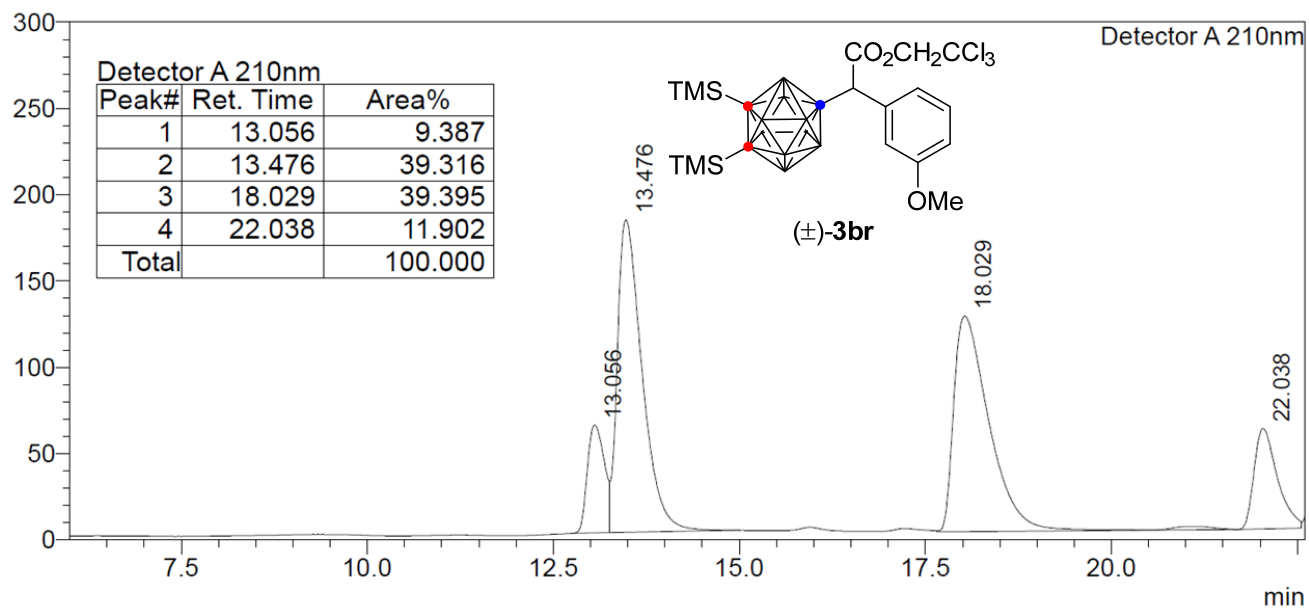


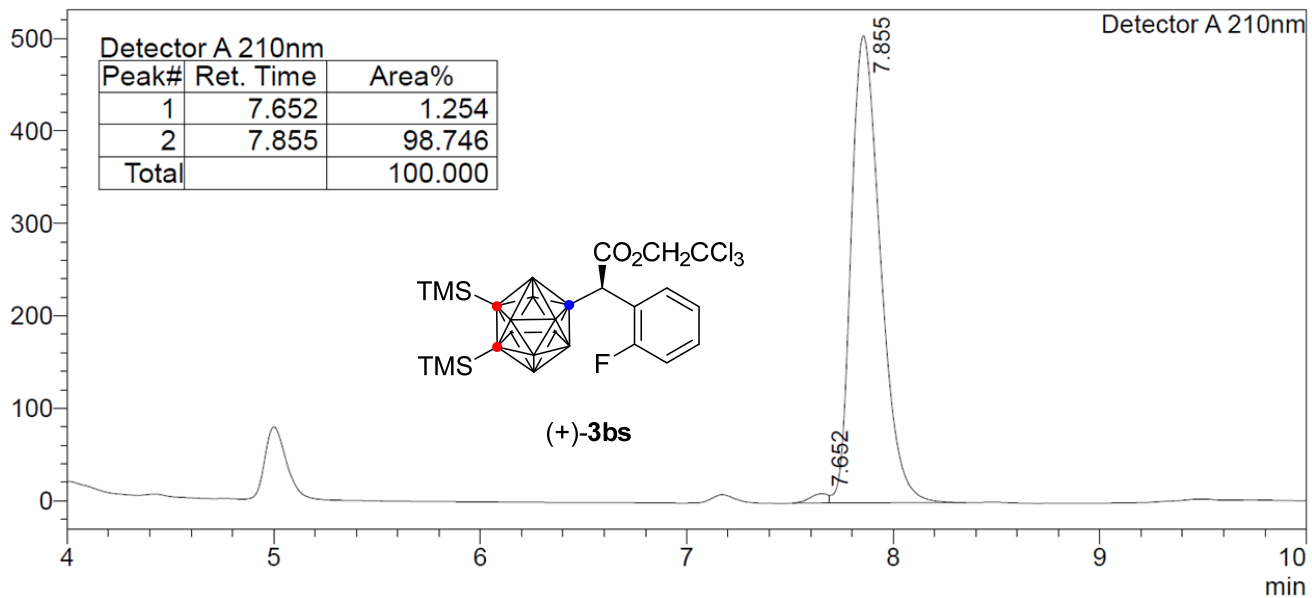
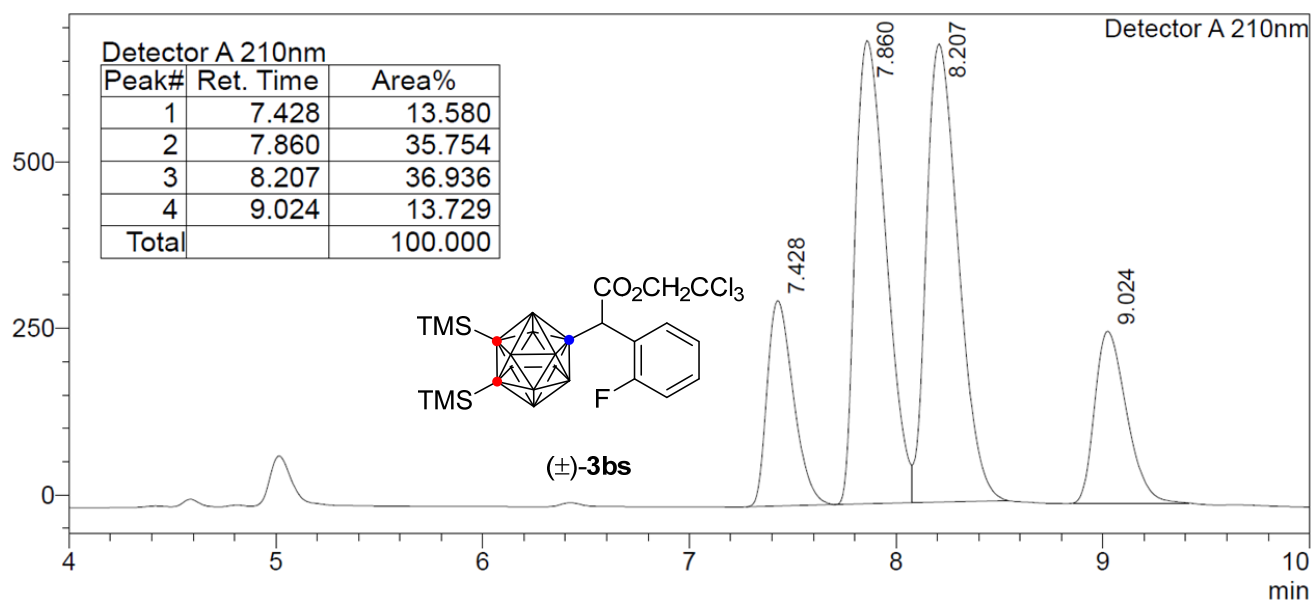


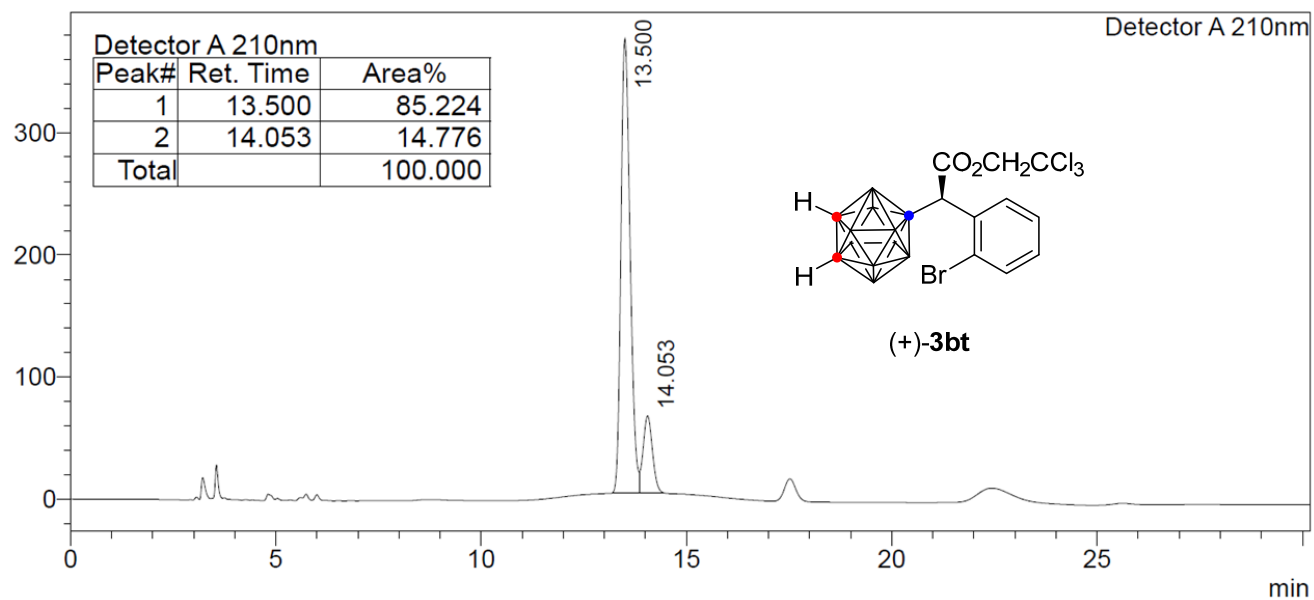
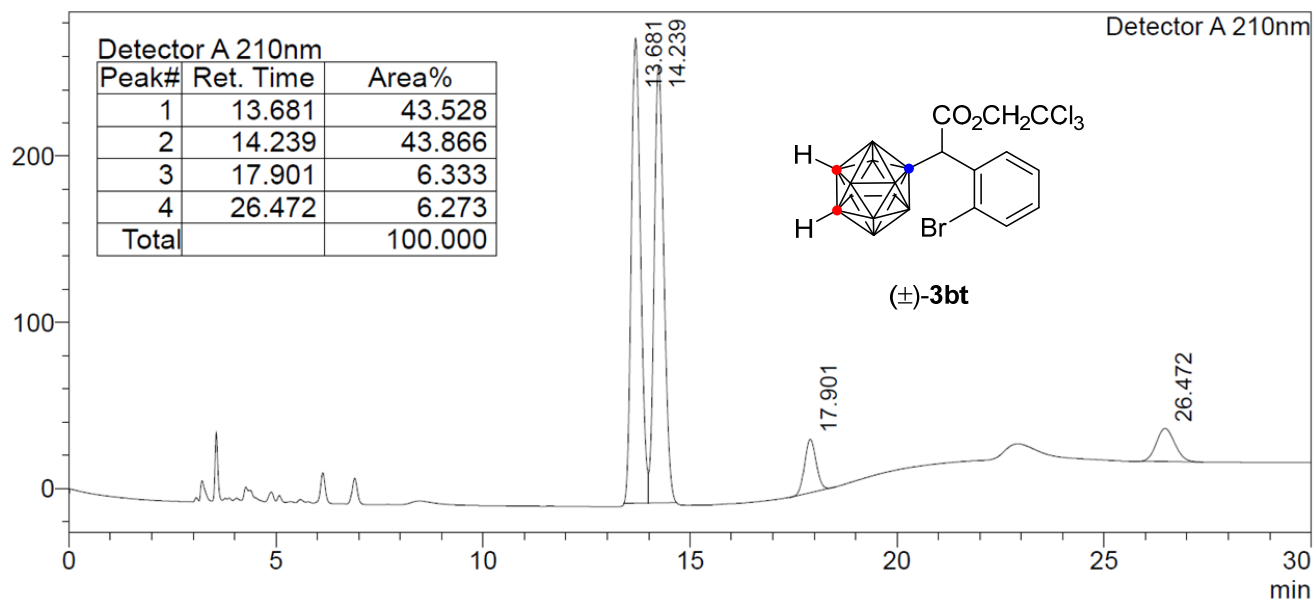


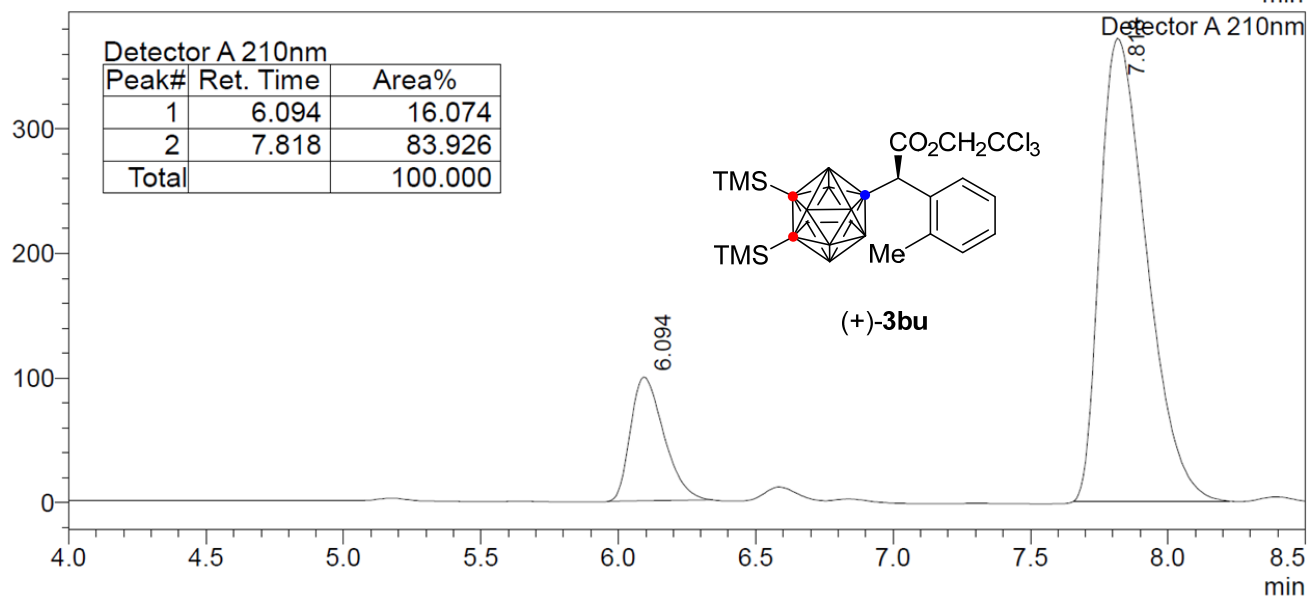
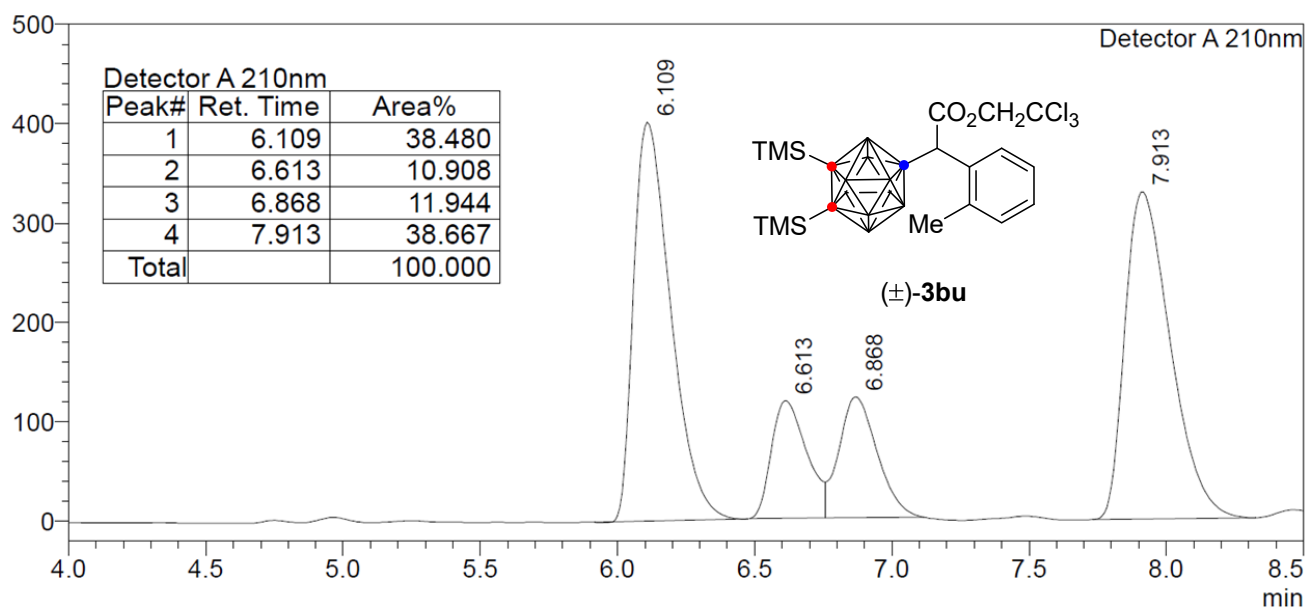


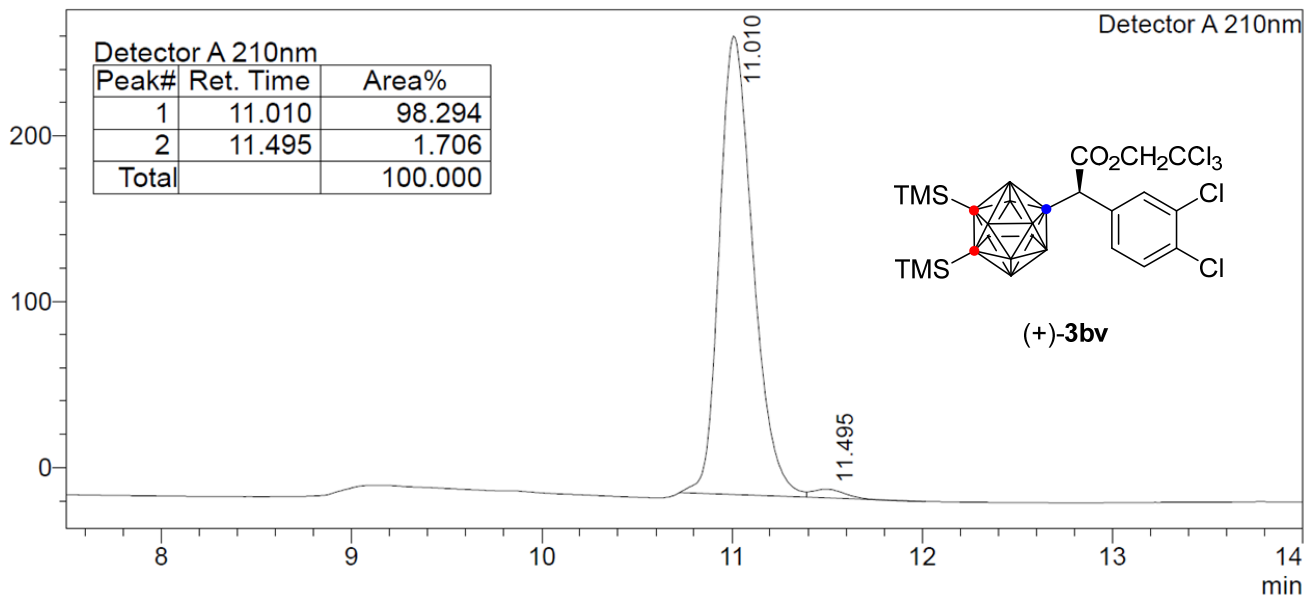
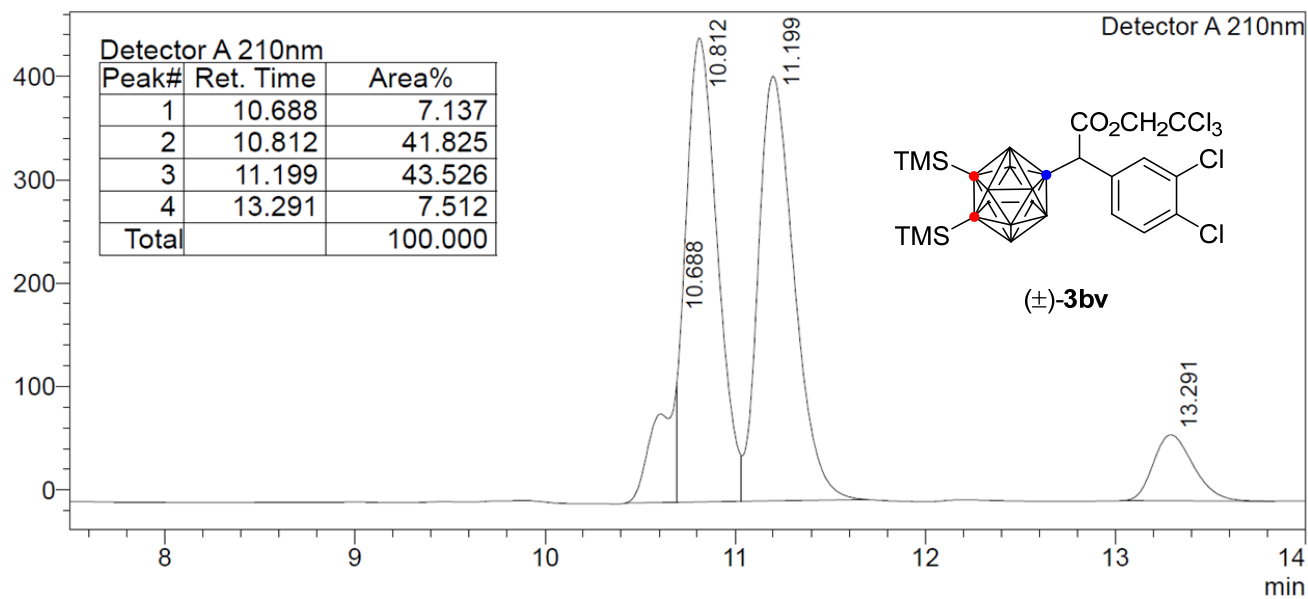


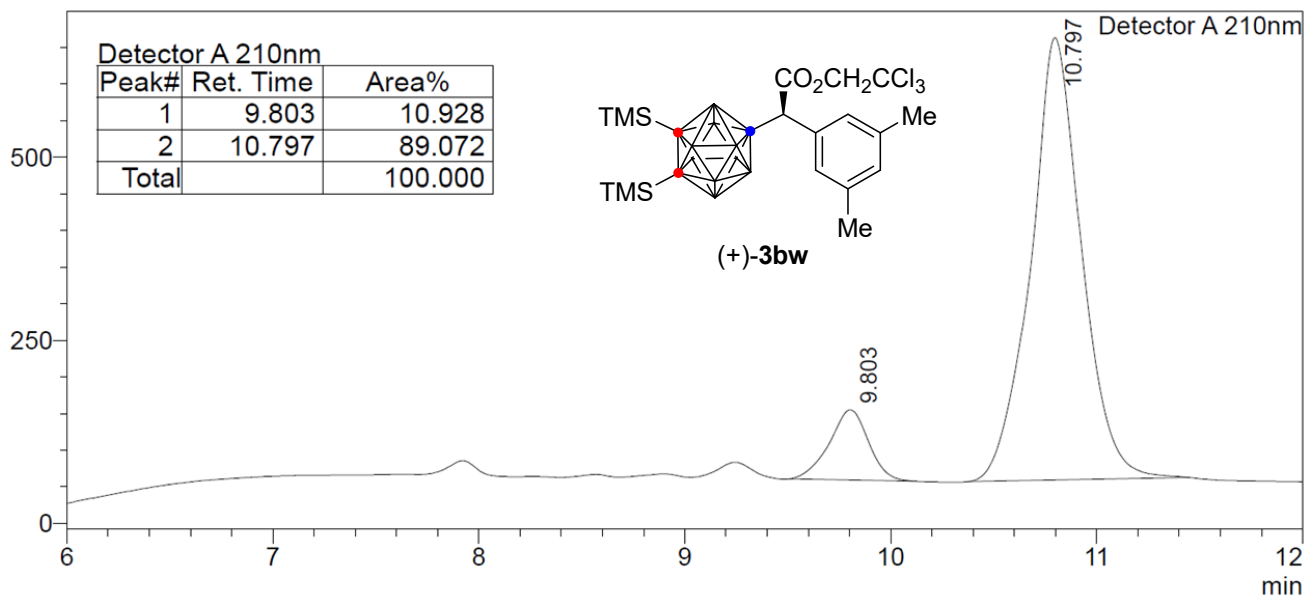
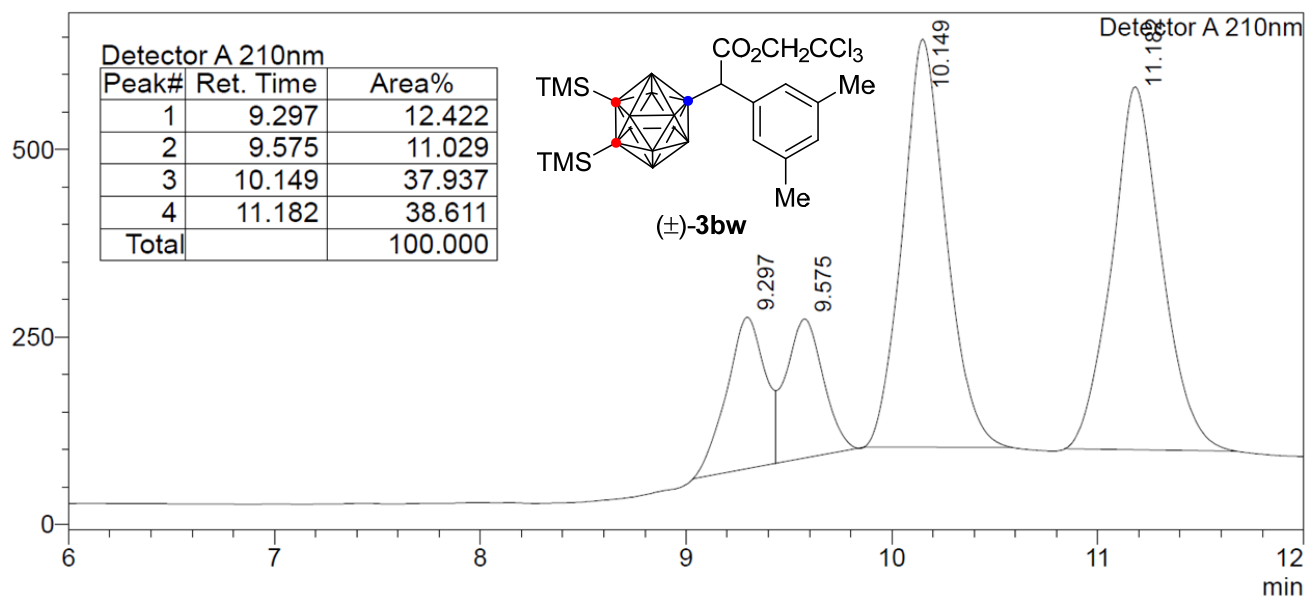


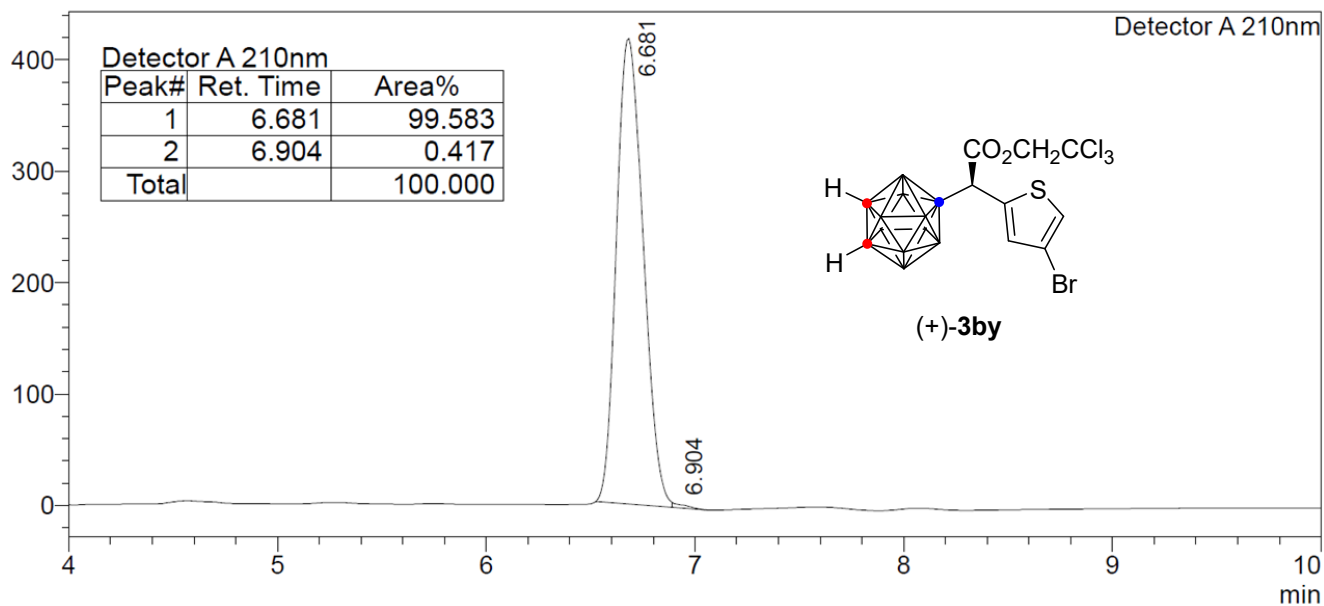
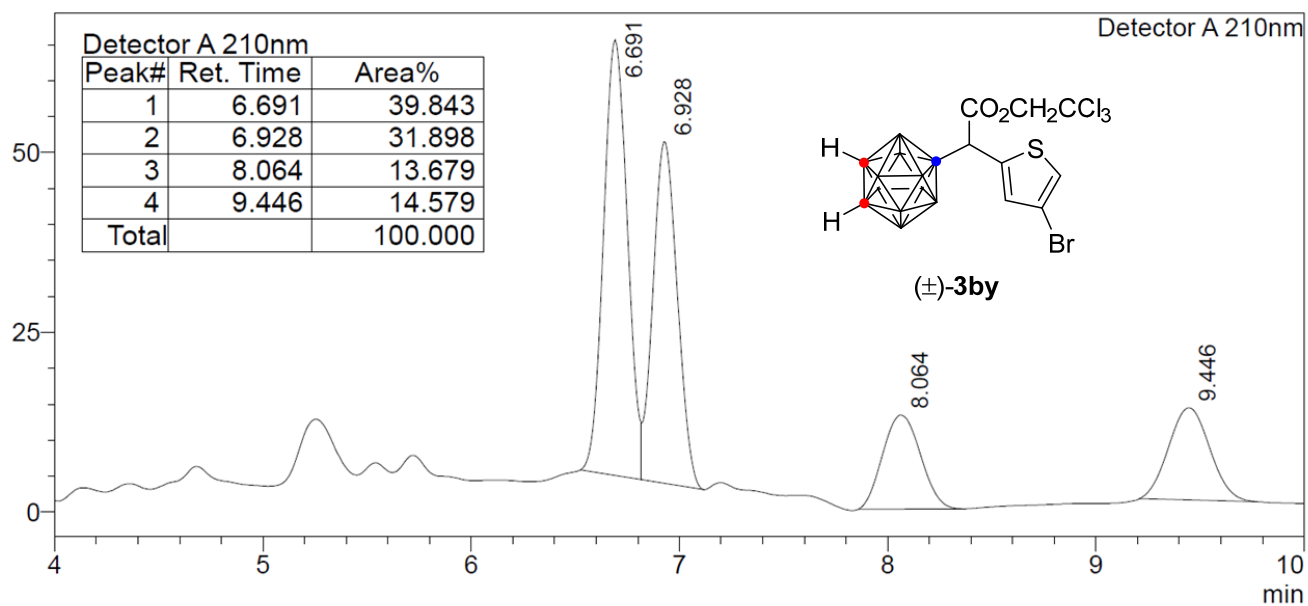


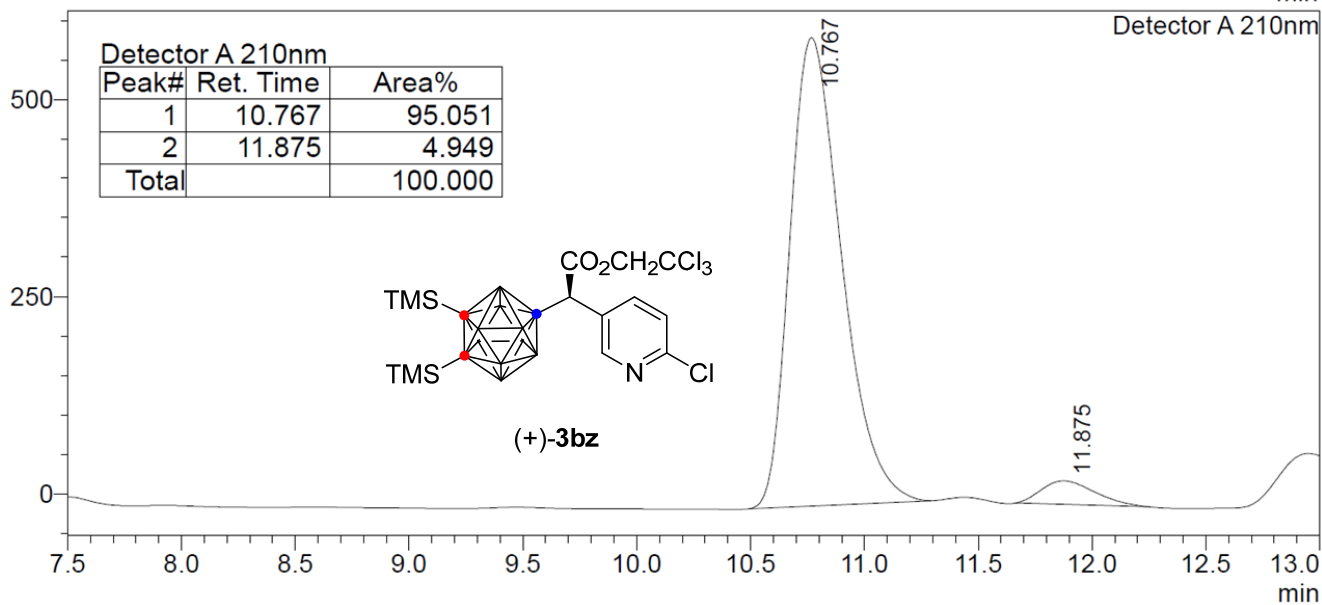
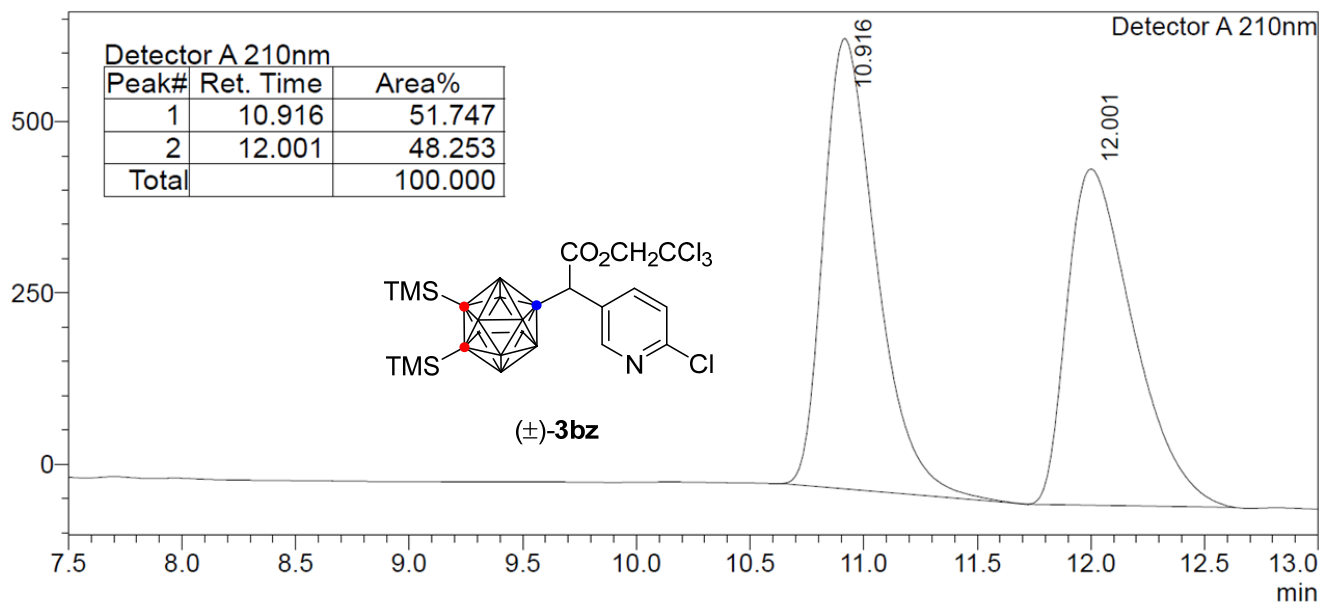


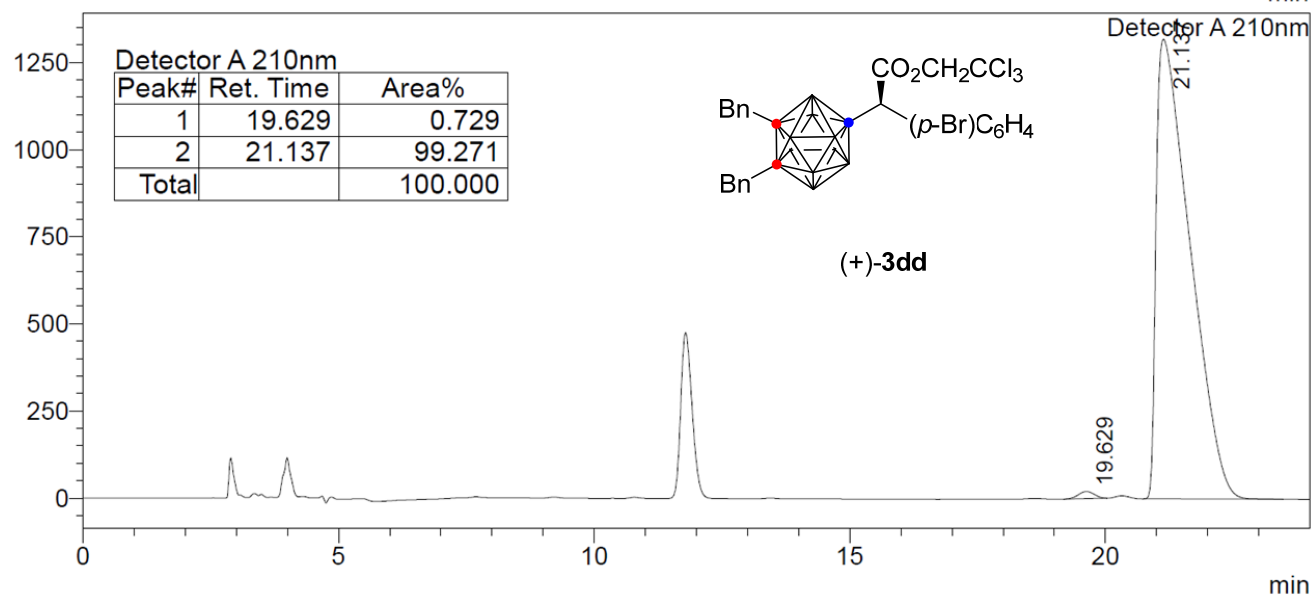
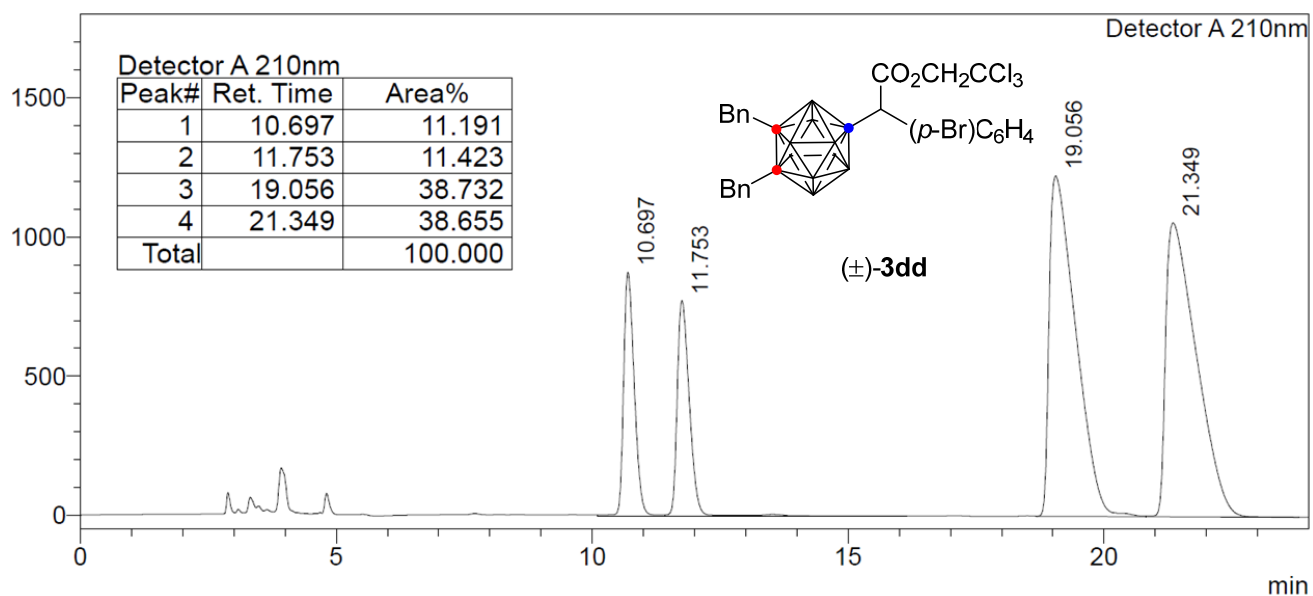


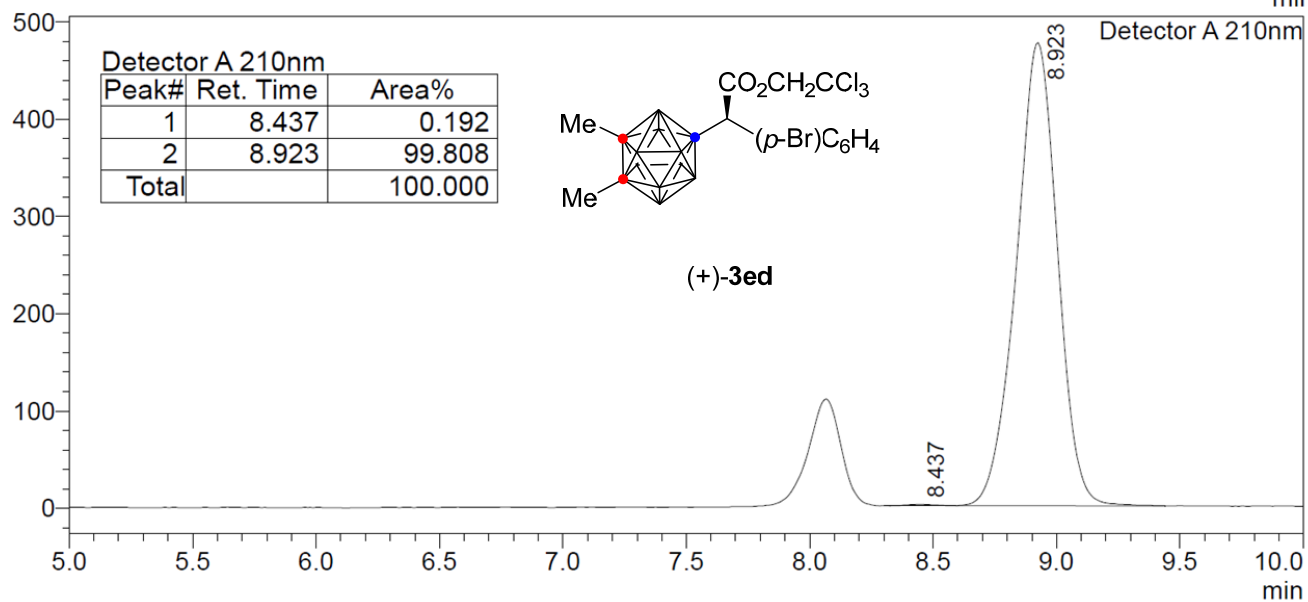
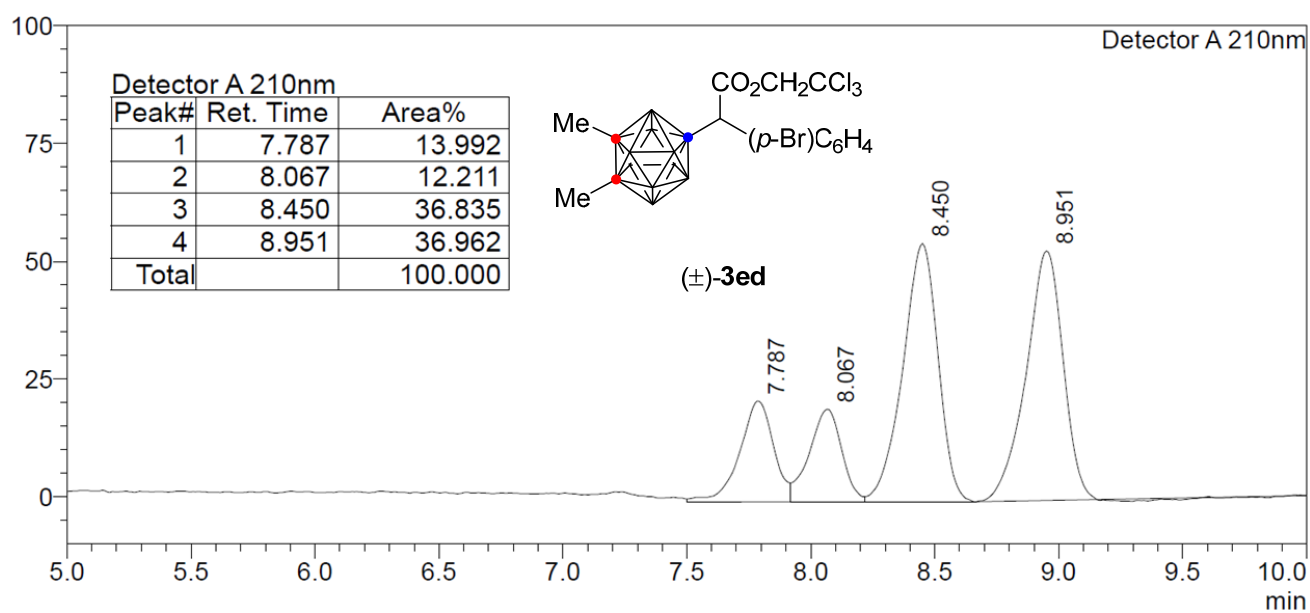


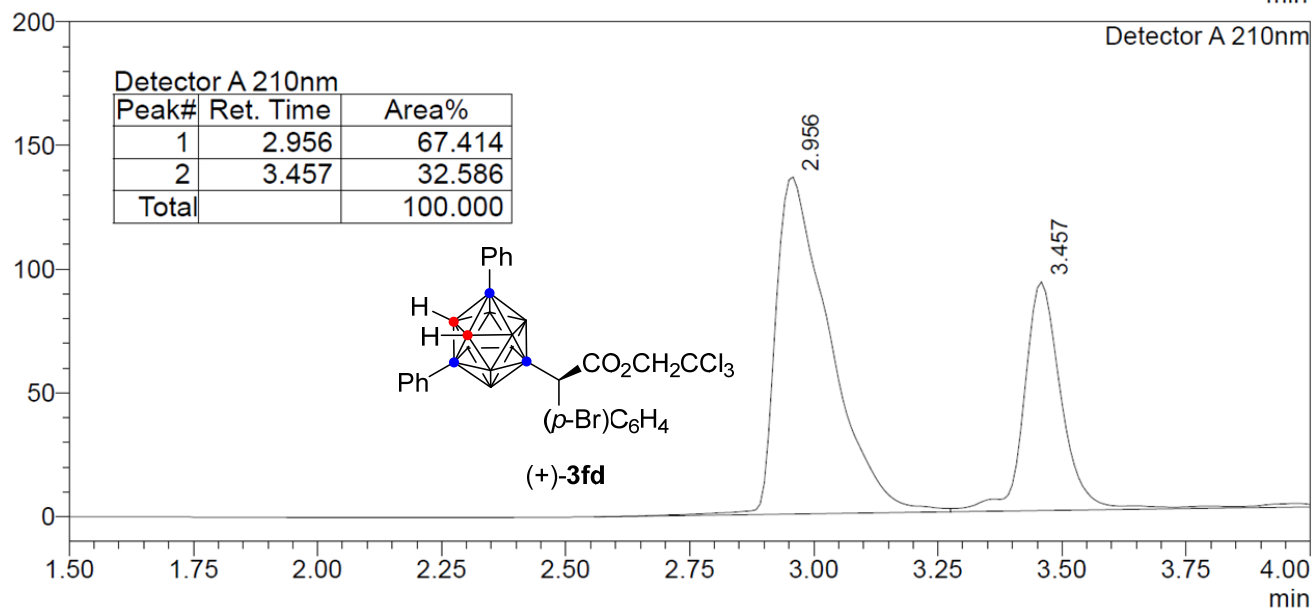
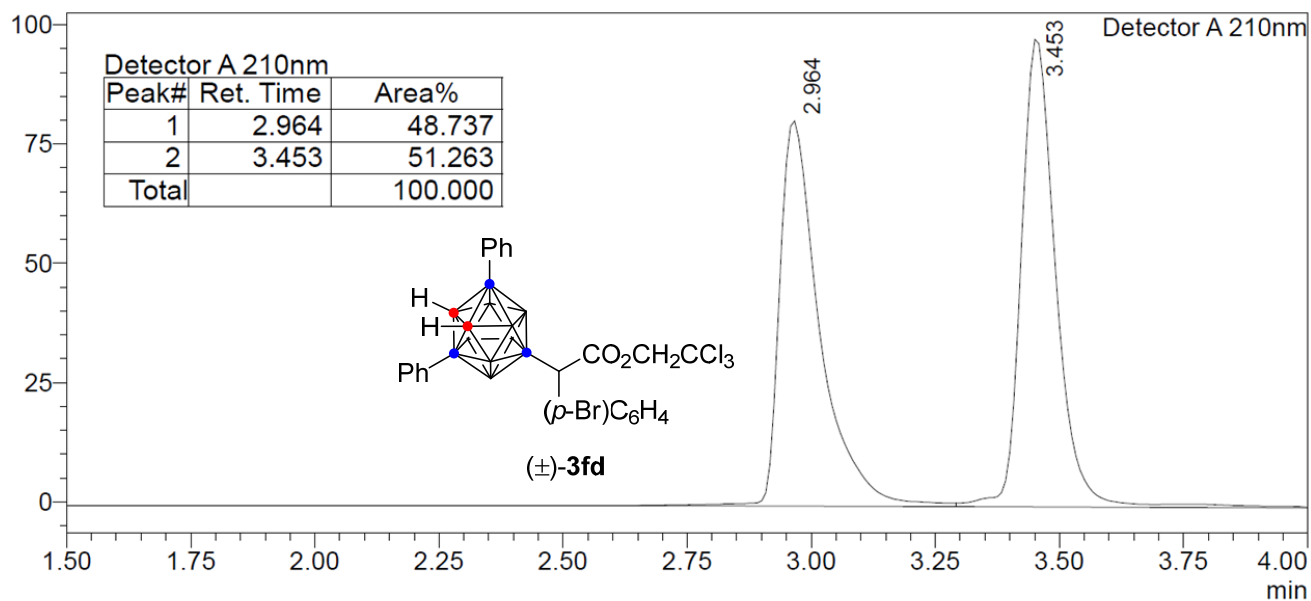


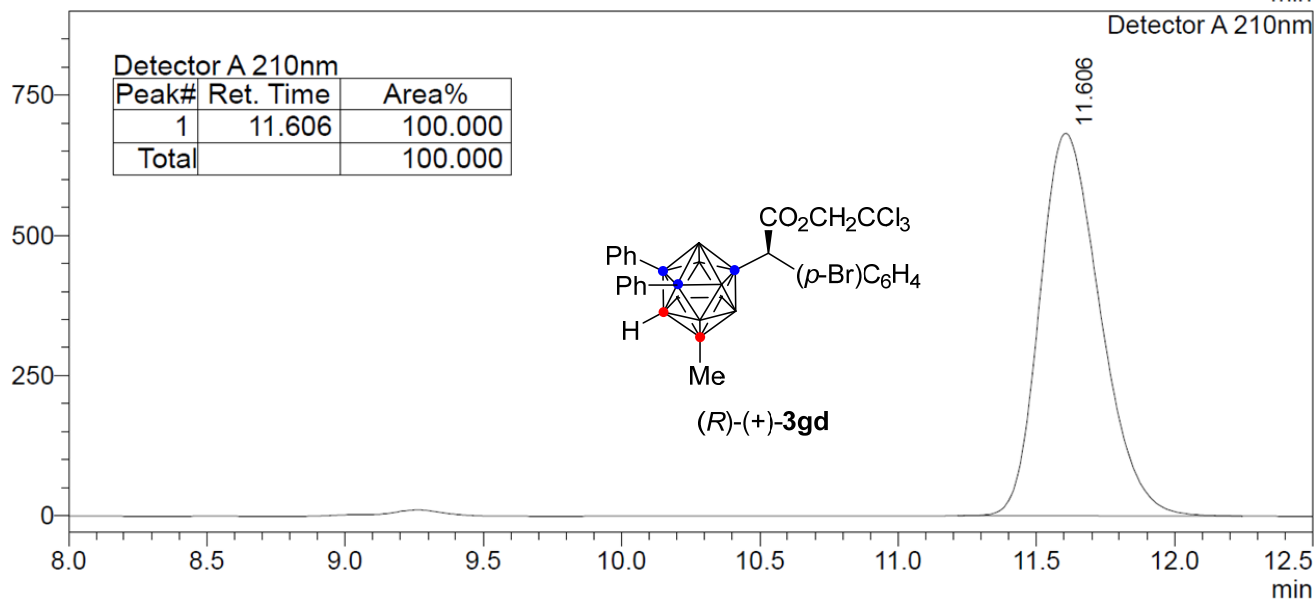
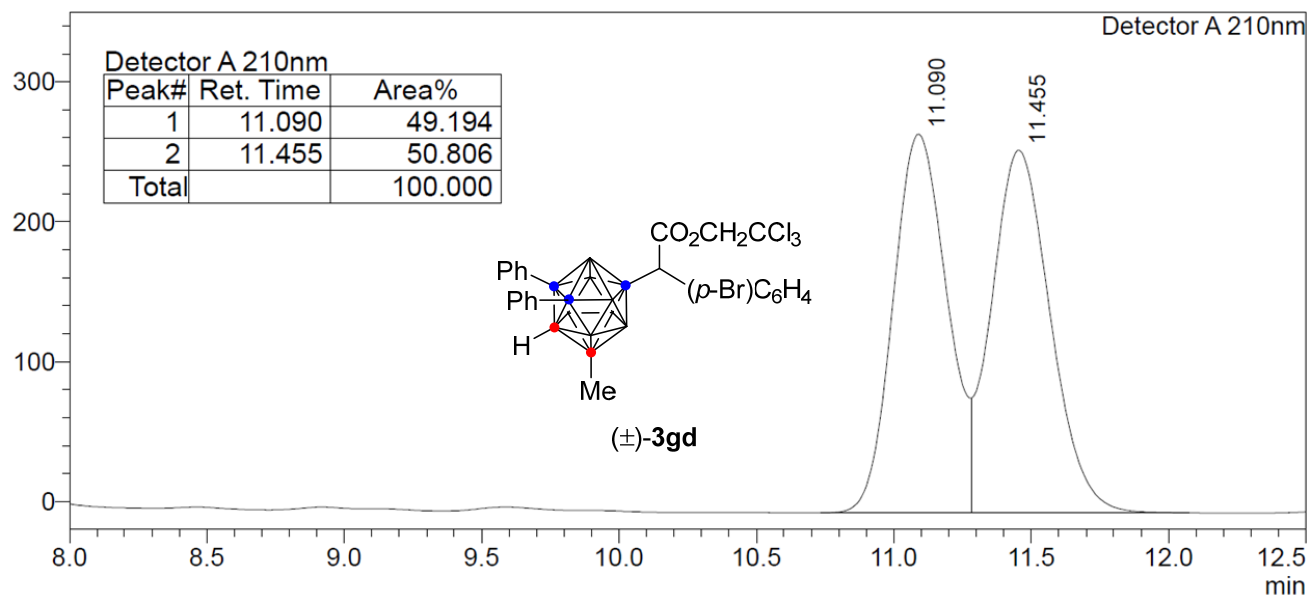


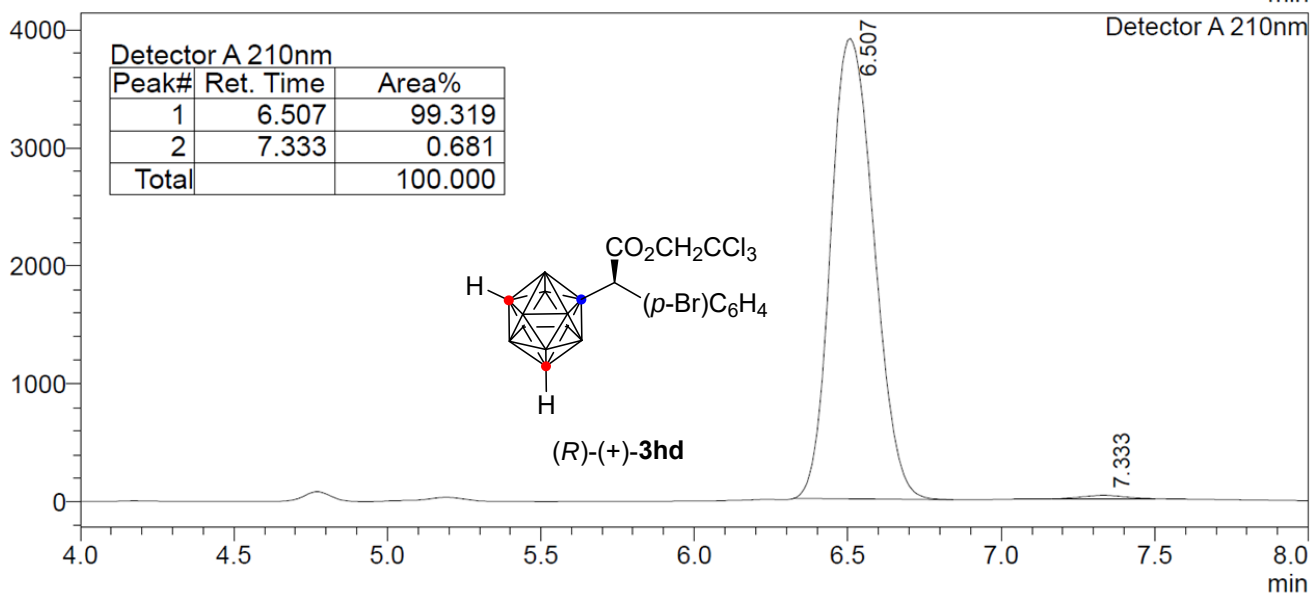
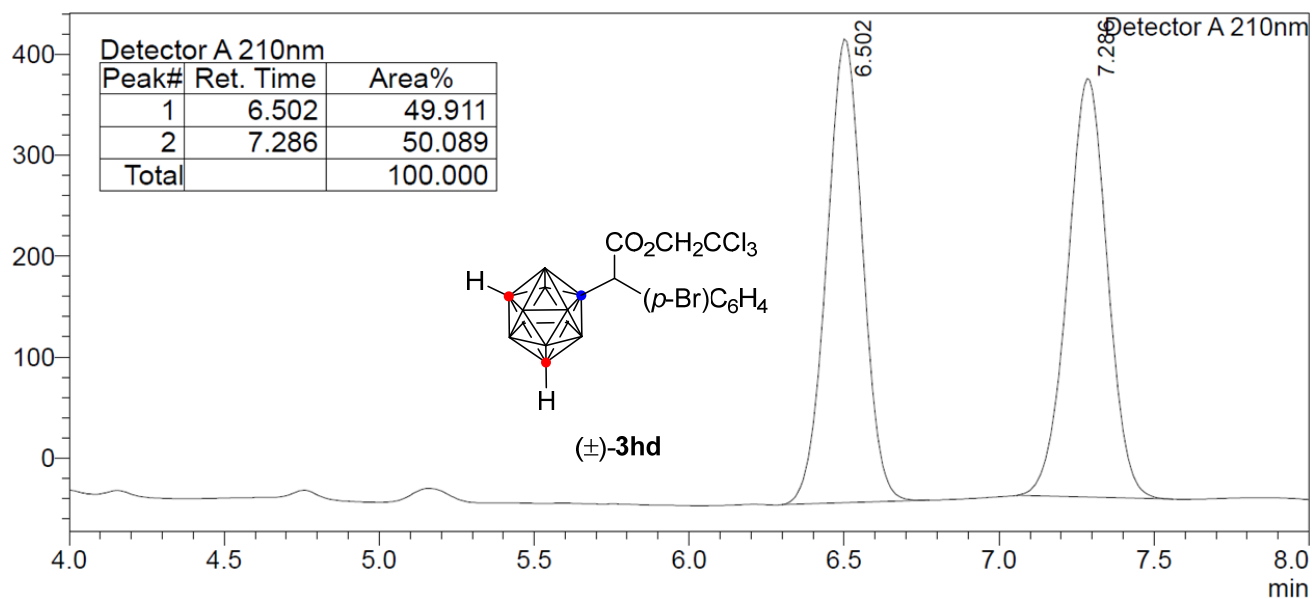


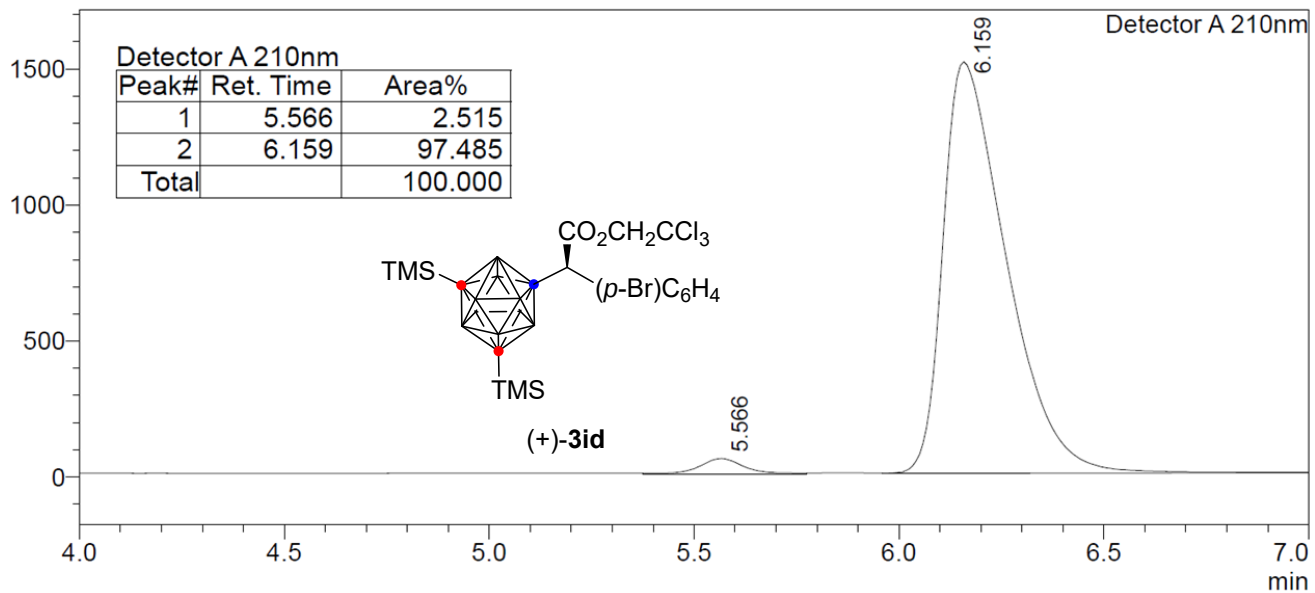
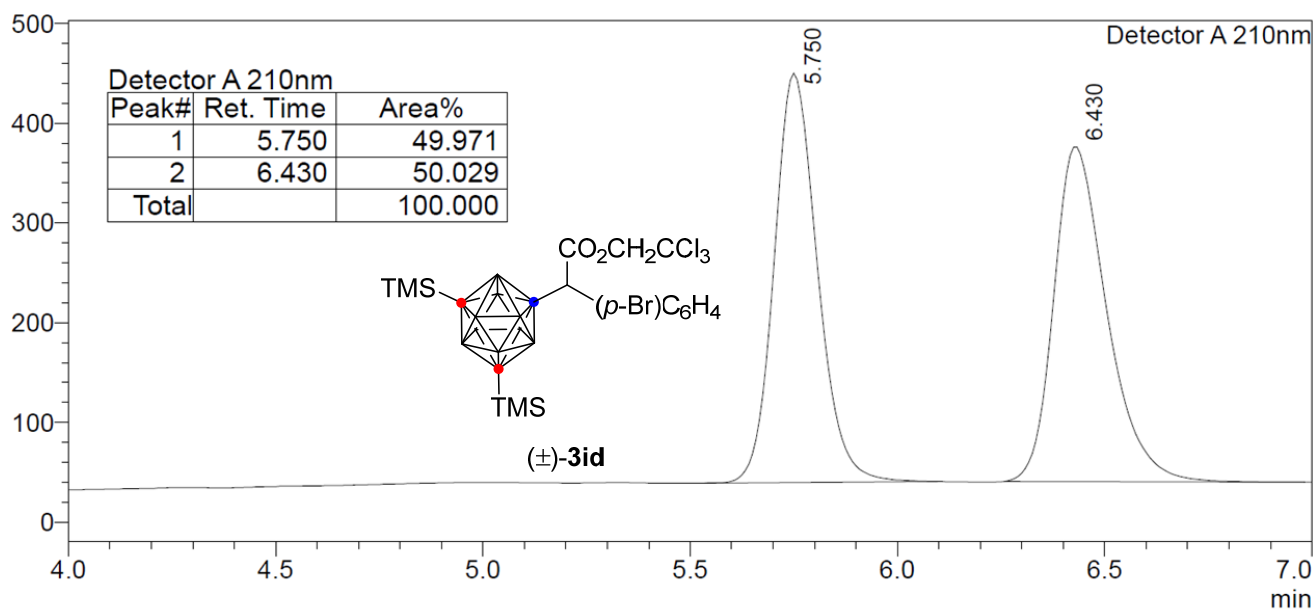


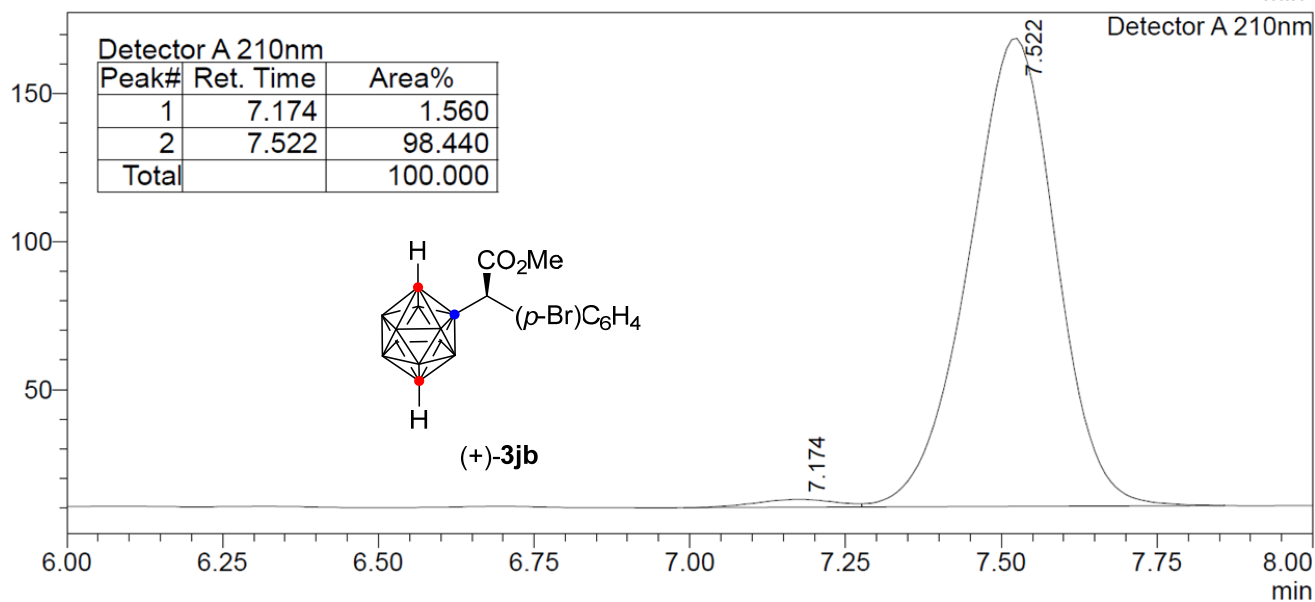
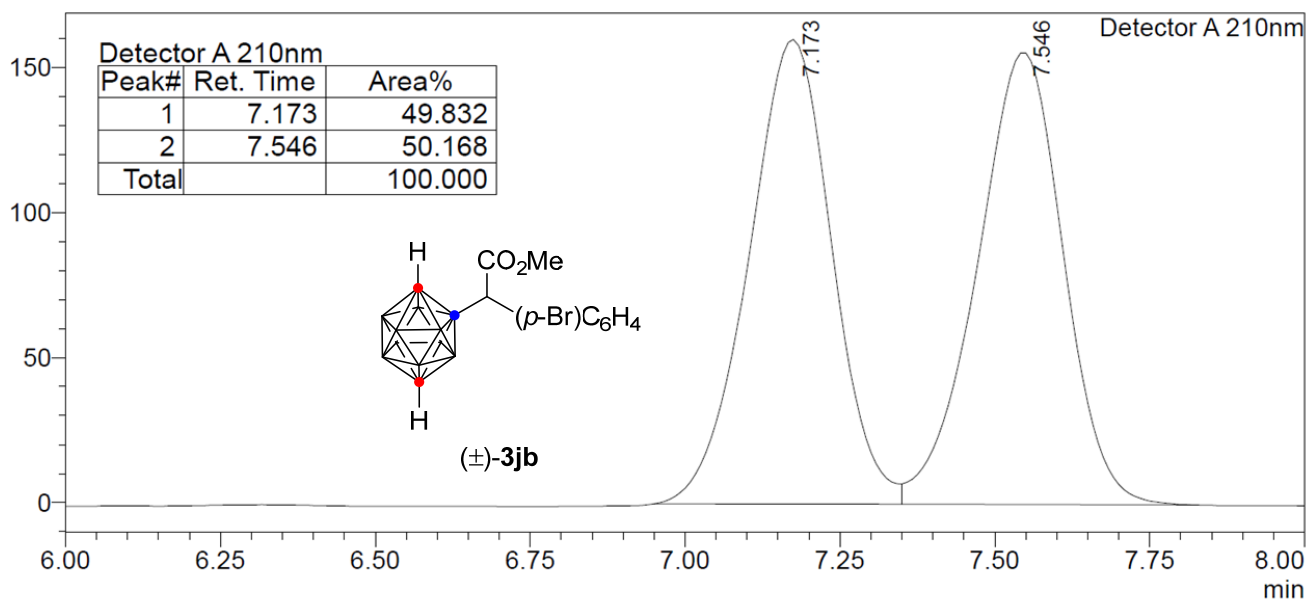


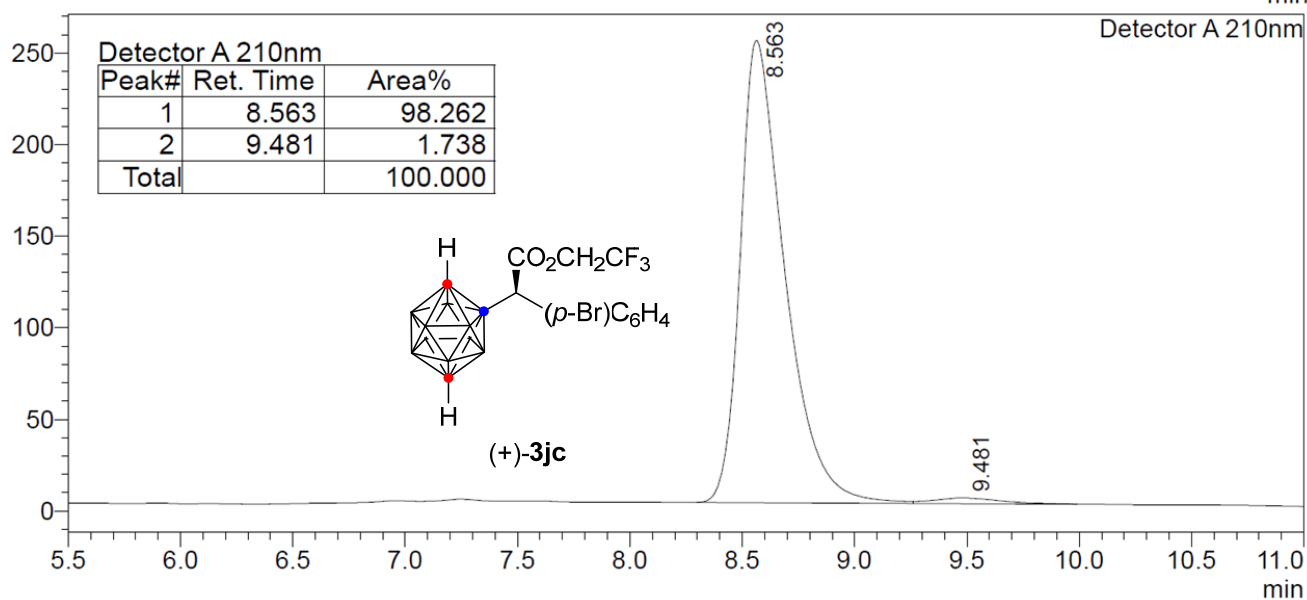
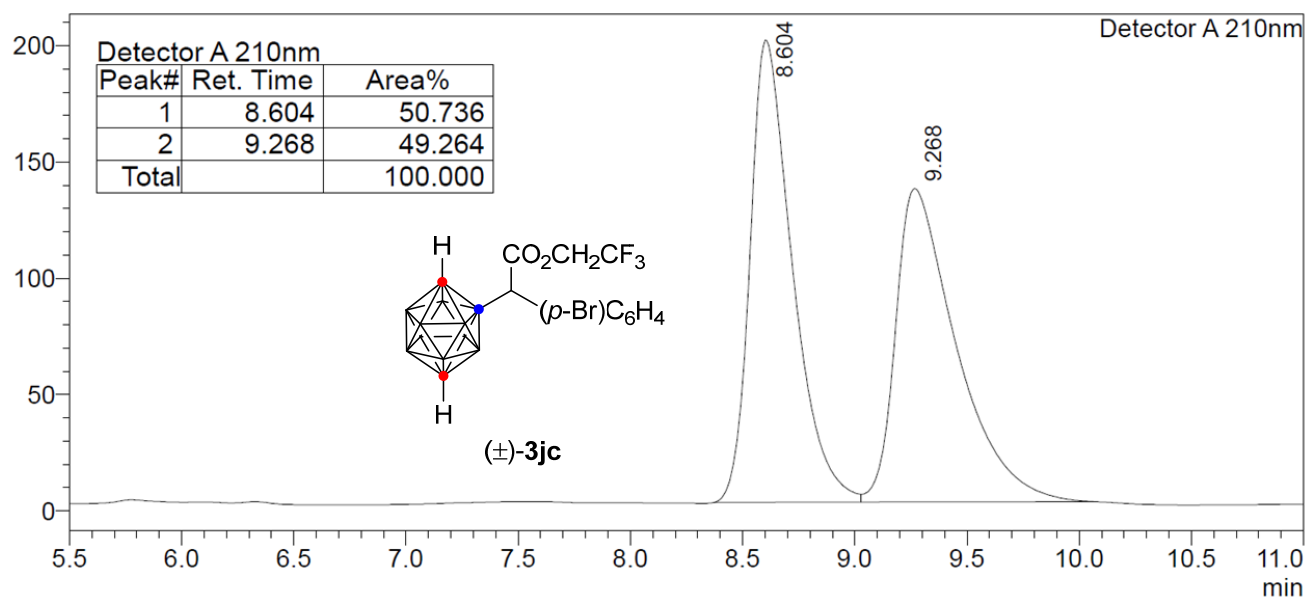


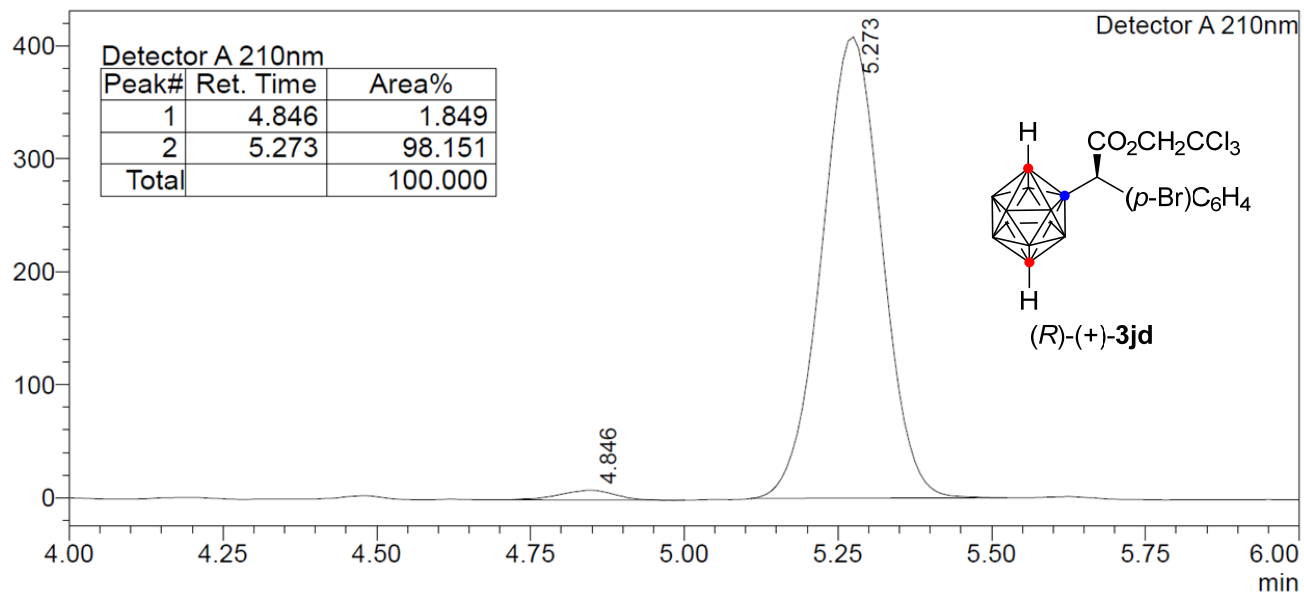
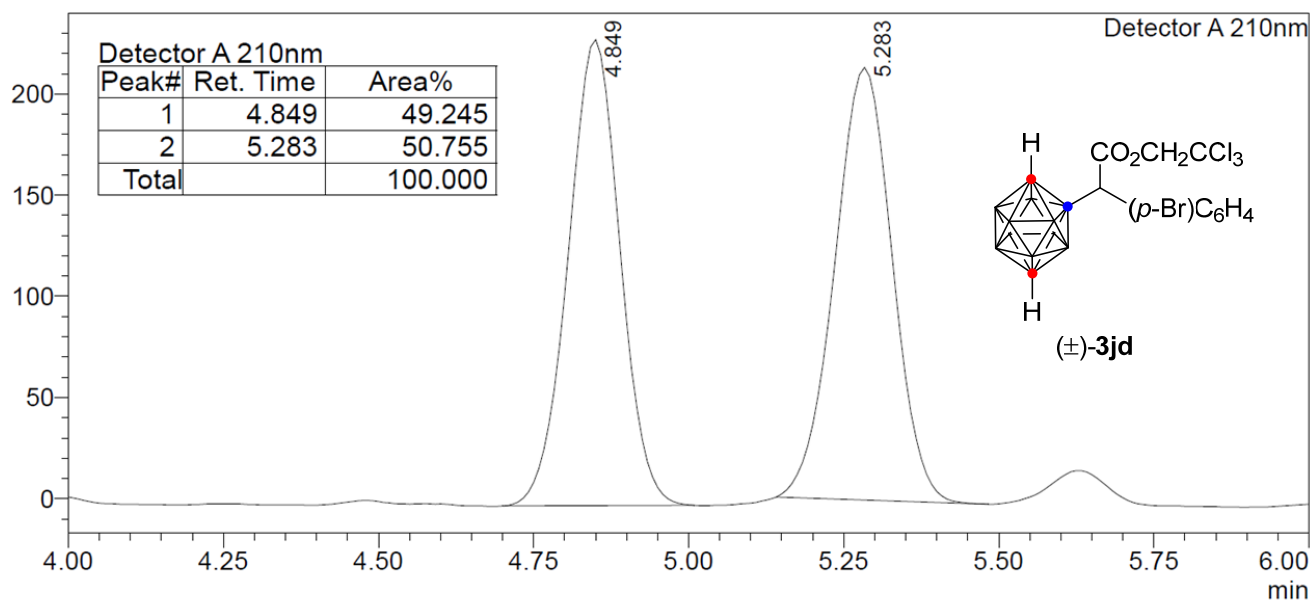


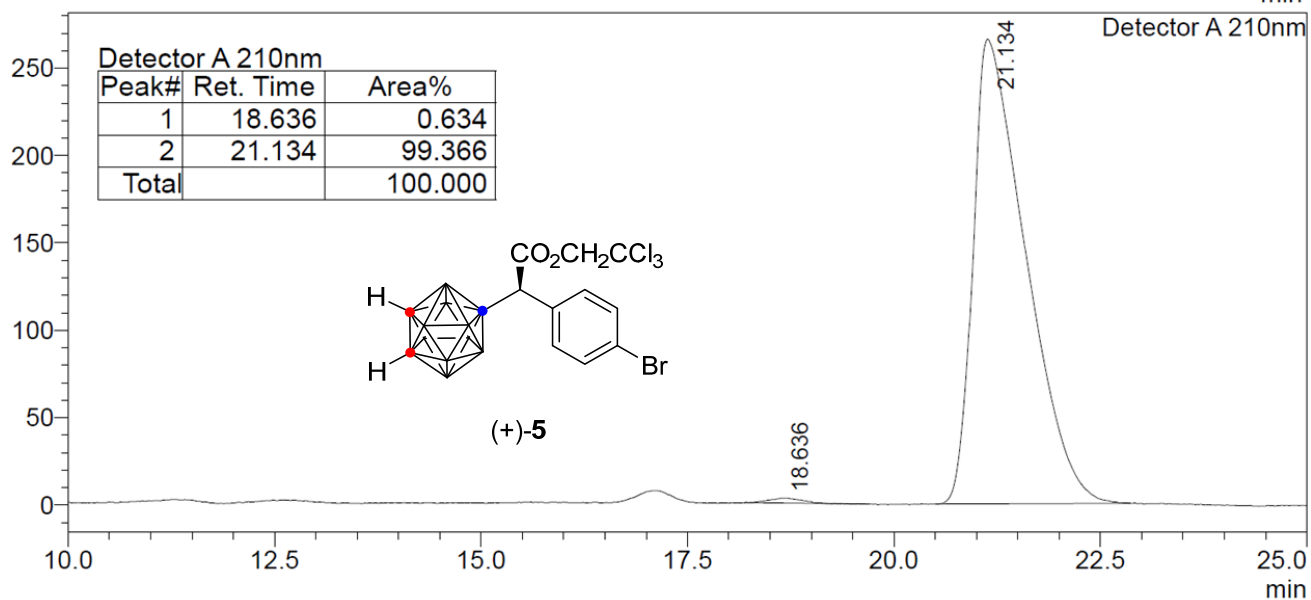
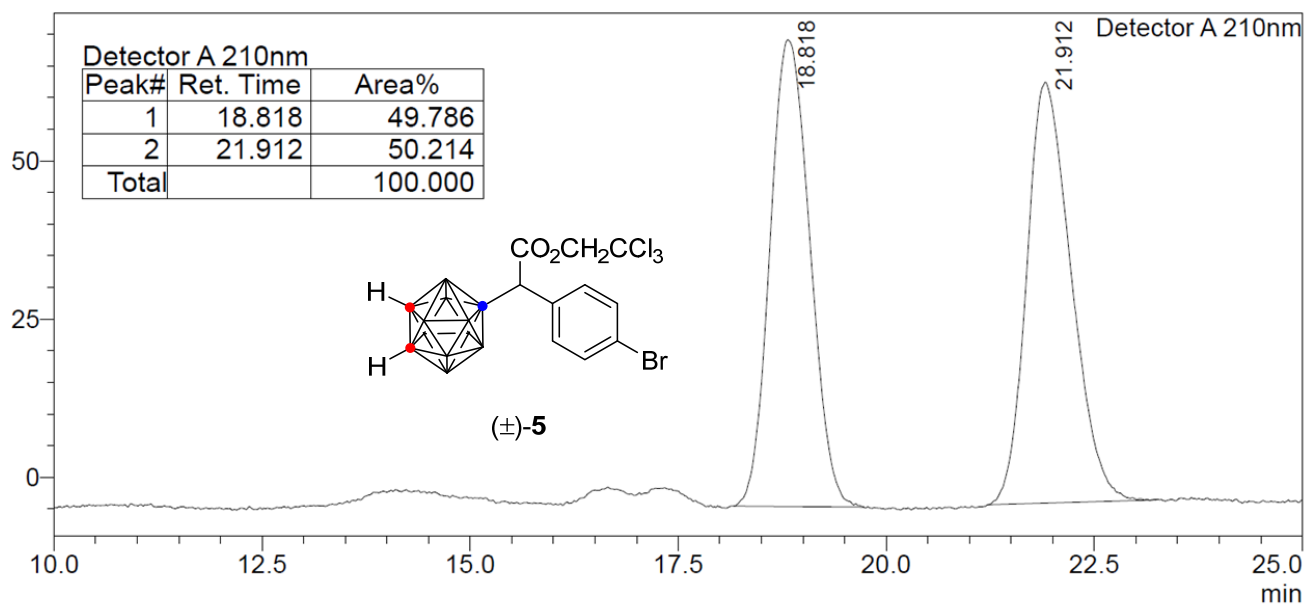


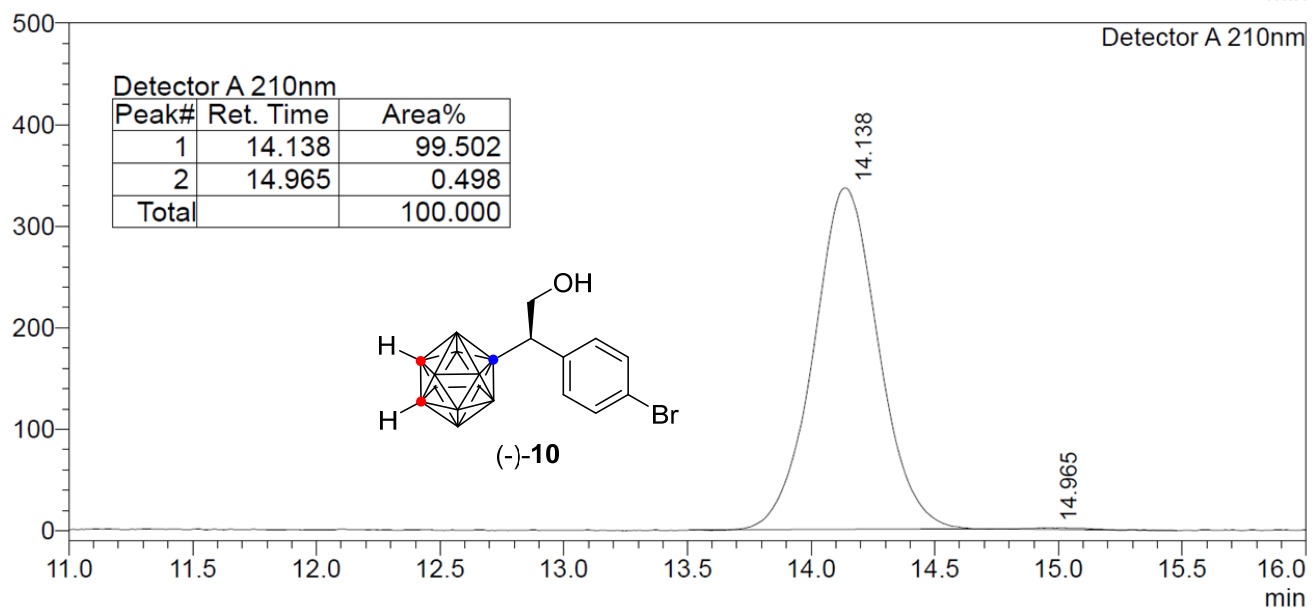
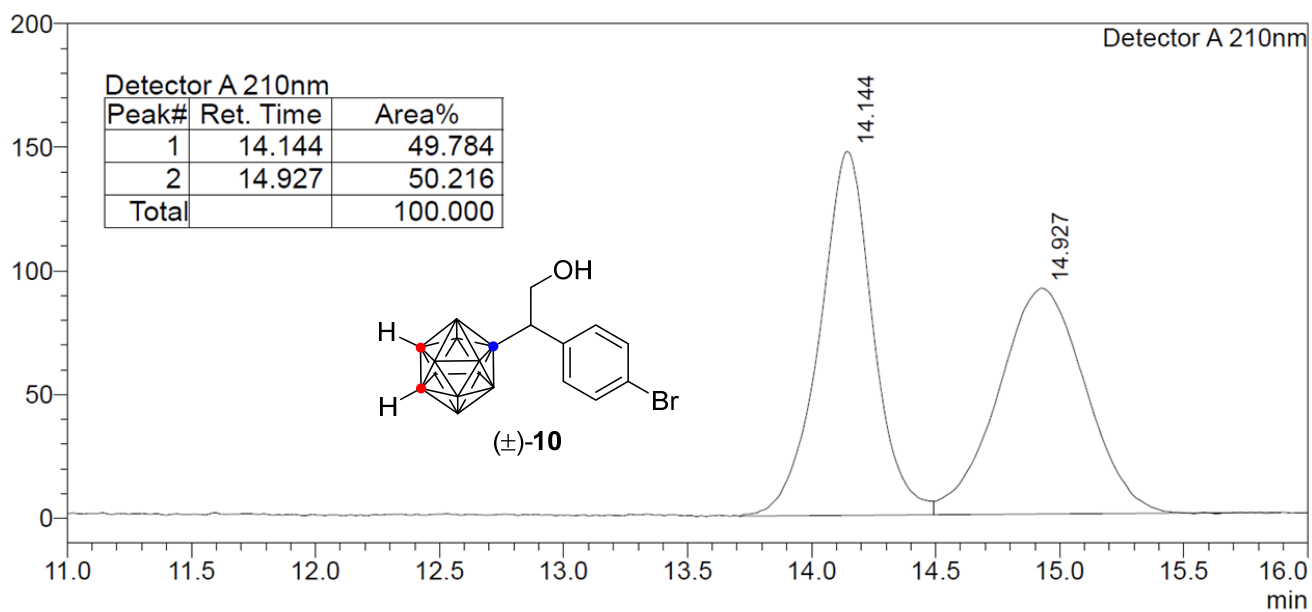


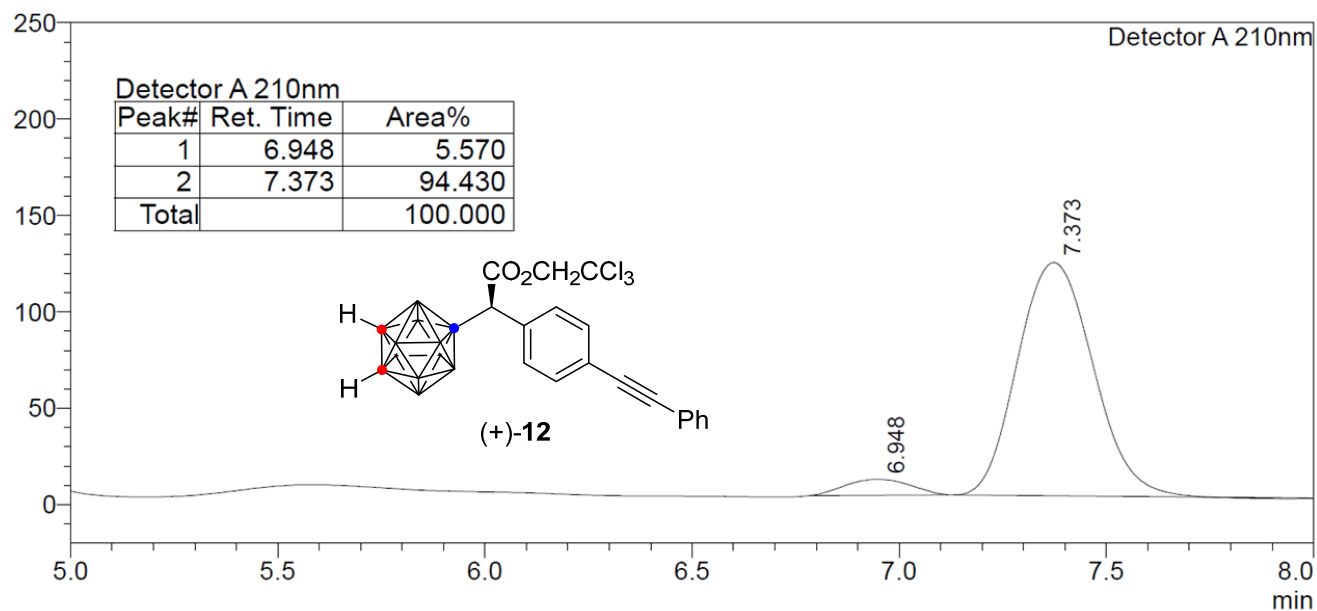
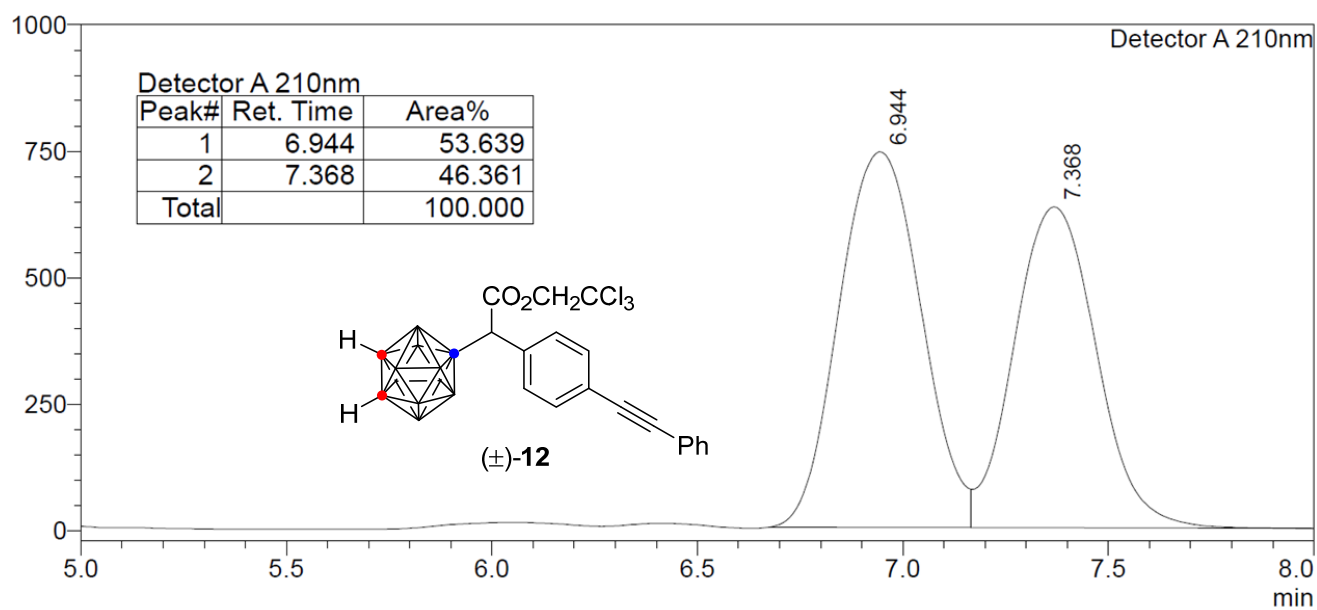


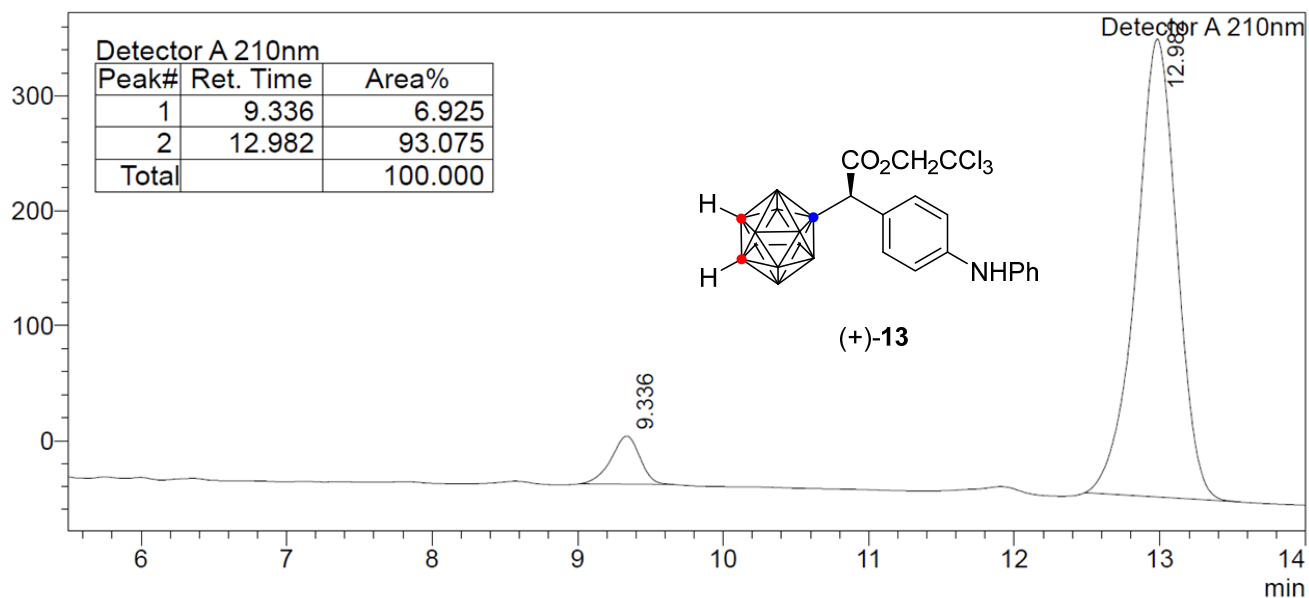
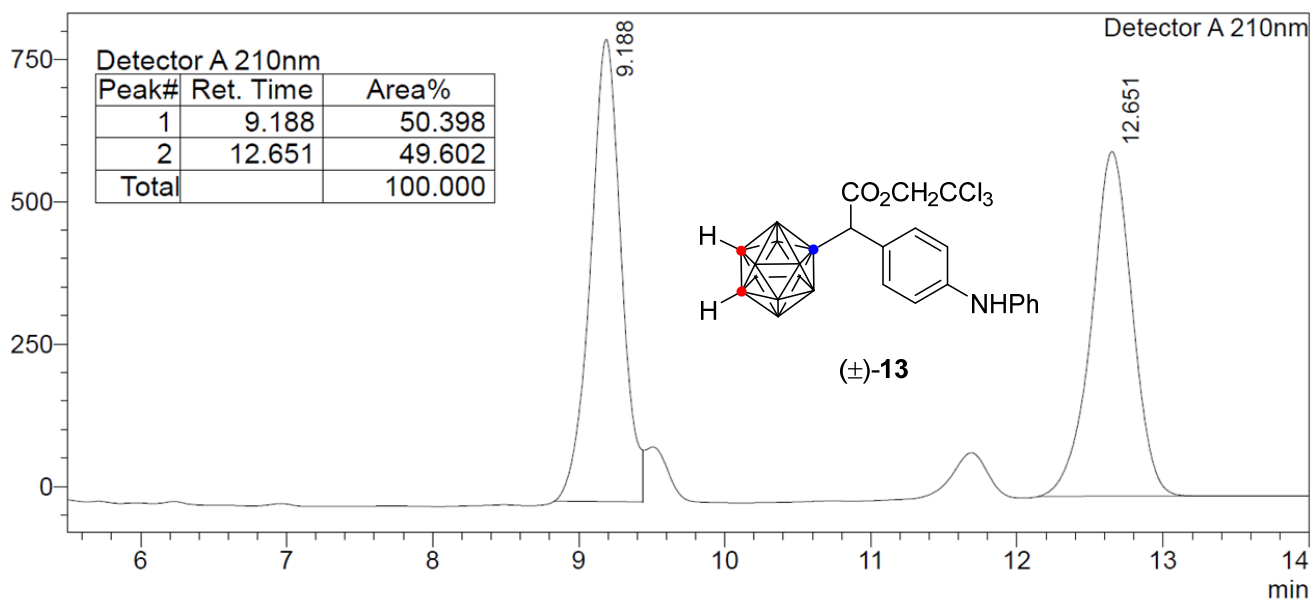






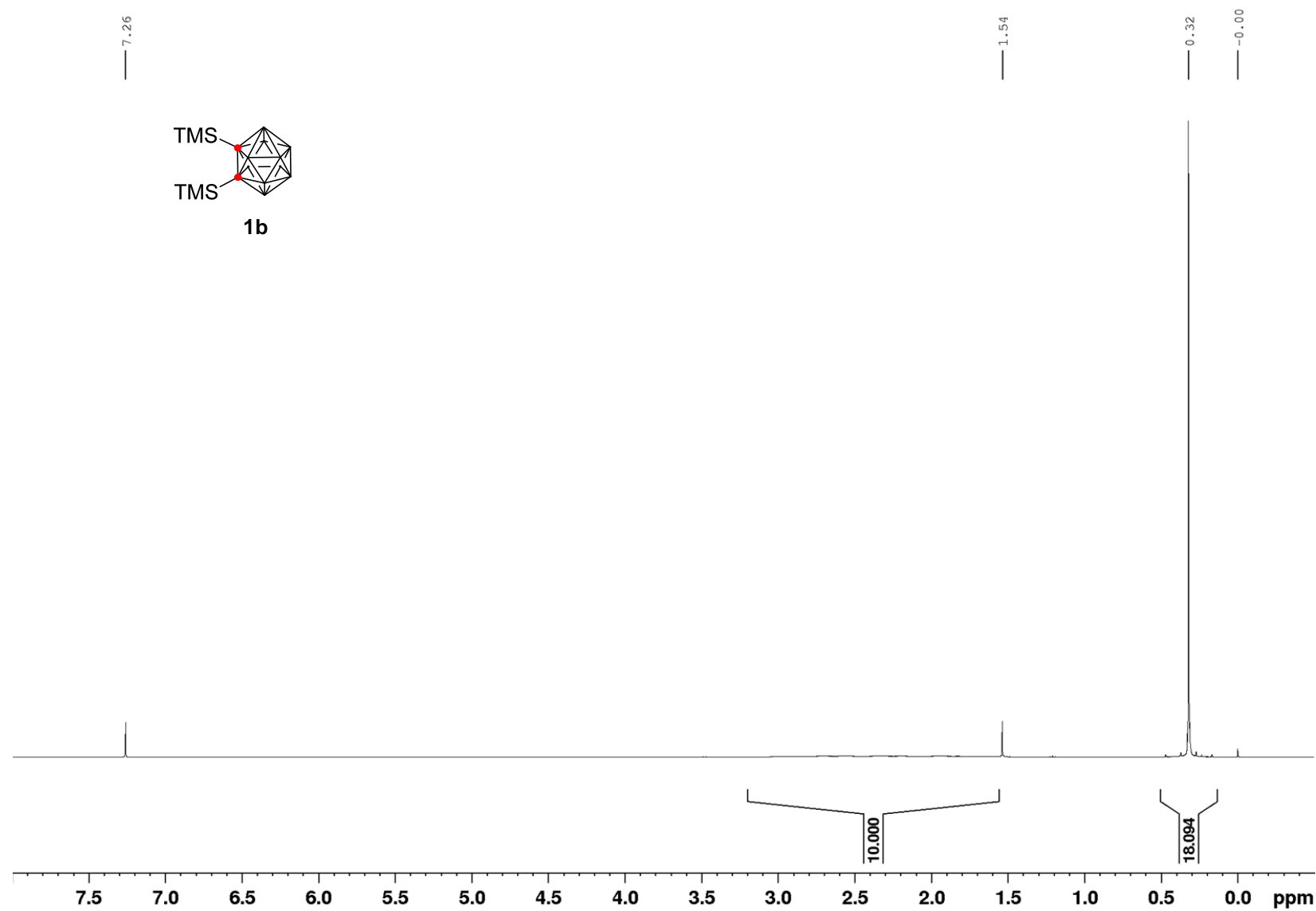




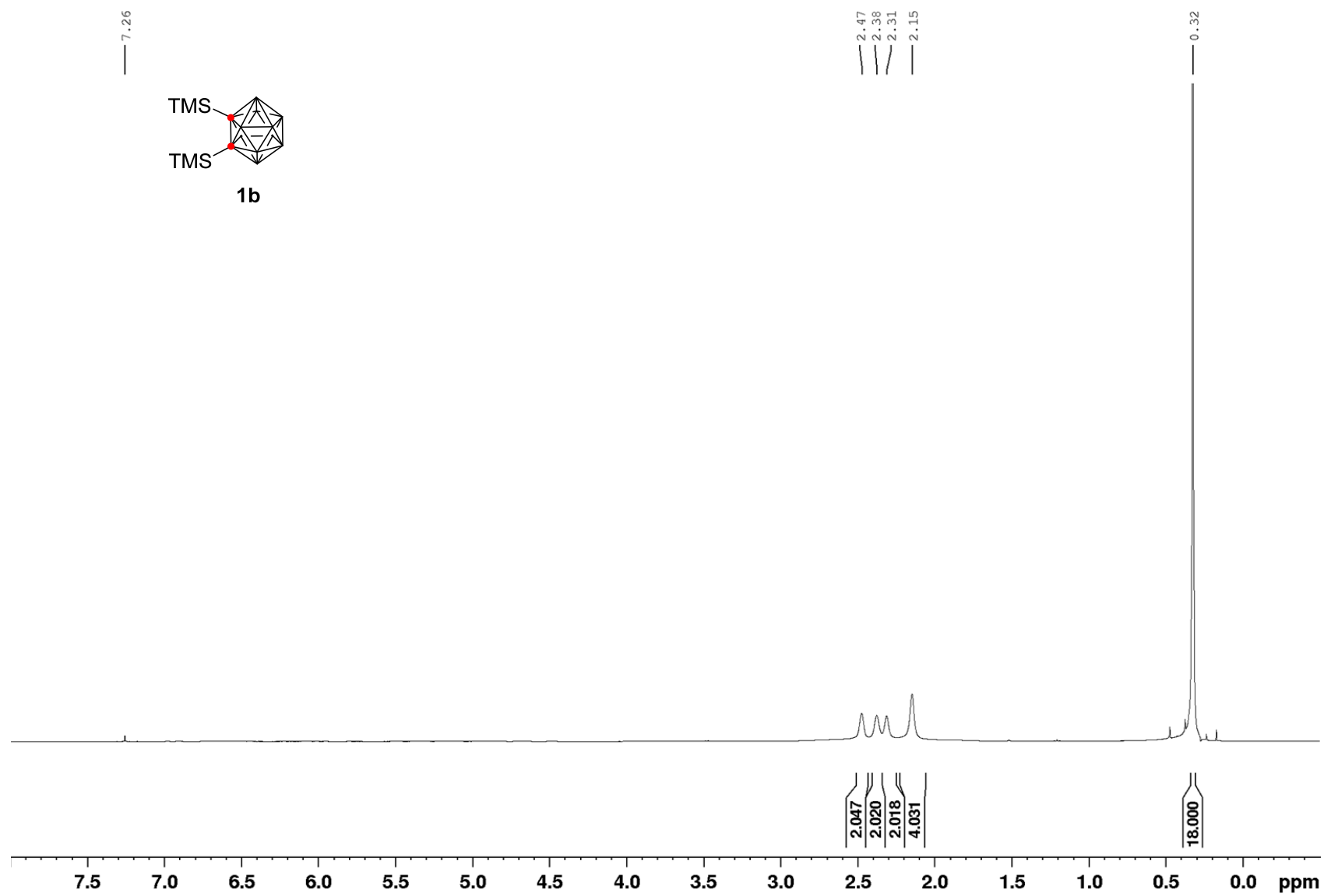


16. ^1H , ^{13}C , ^{11}B , and ^{19}F NMR Data

^1H NMR (400 MHz, CDCl_3)

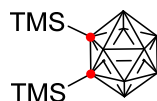


$^1\text{H}\{^{11}\text{B}\}$ NMR (400 MHz, CDCl_3)

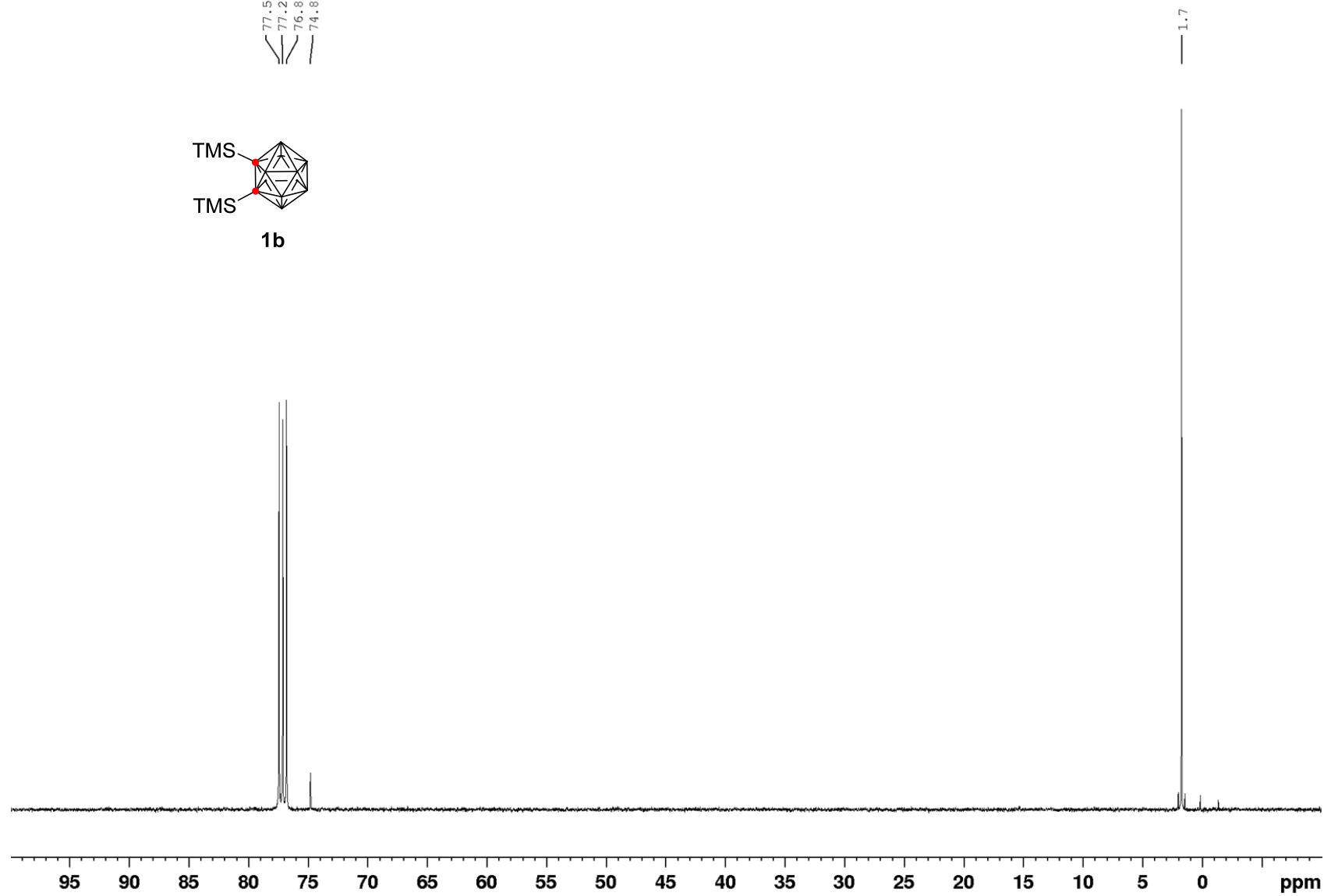


^{13}C NMR (100 MHz, CDCl_3)

77.5
77.2
76.8
74.8

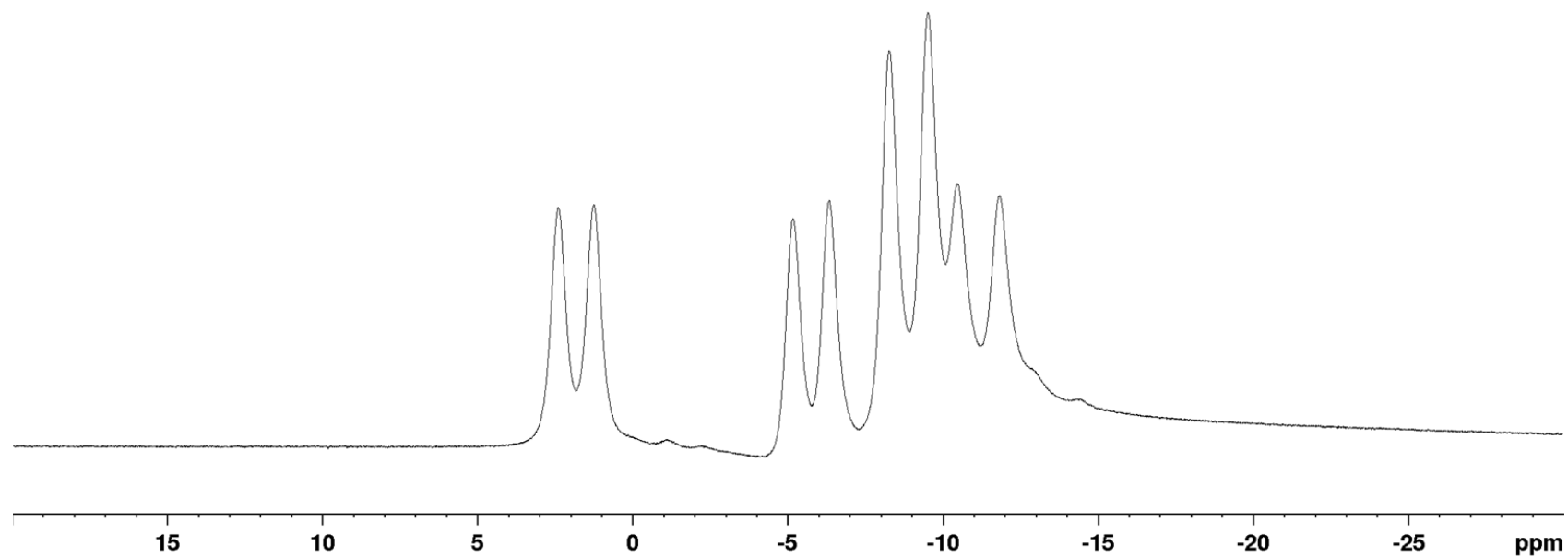
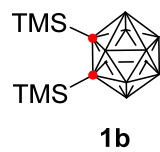


1b



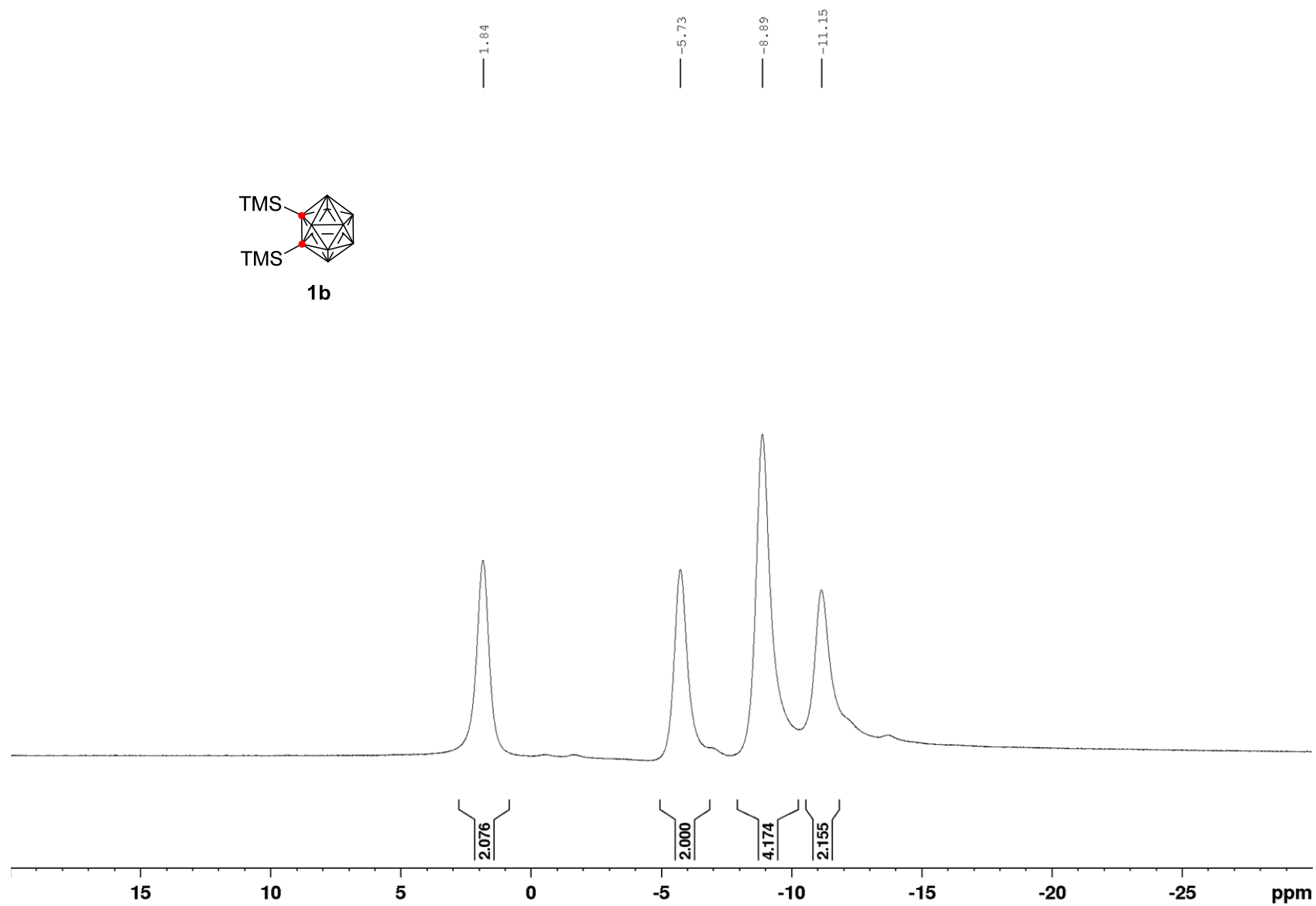
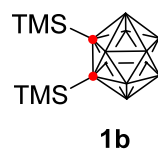
^{11}B NMR (128 MHz, CDCl_3)

2.41
1.25
-5.17
-6.33
-8.27
-9.52
-10.46
-11.83

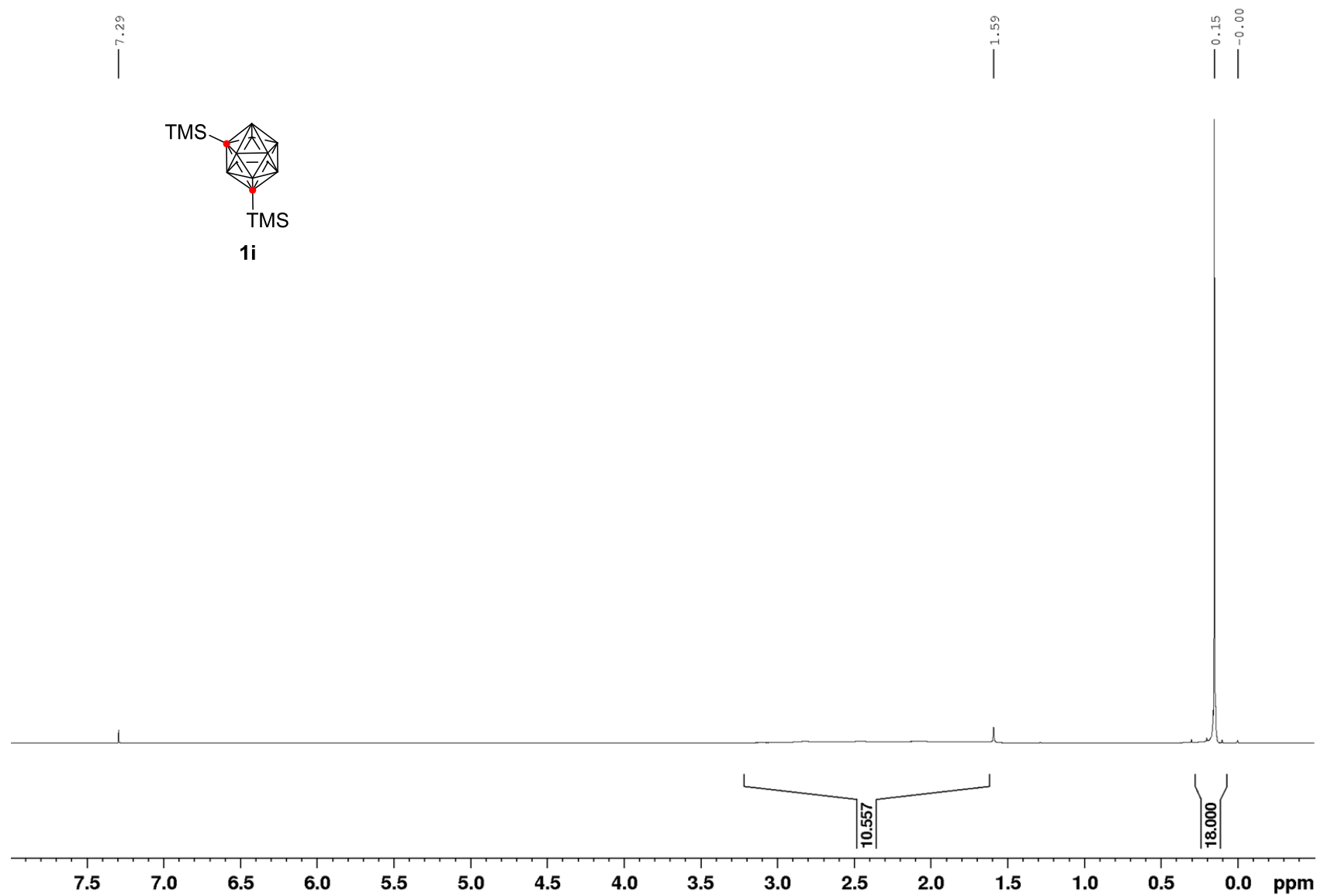


S200

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



^1H NMR (400 MHz, CDCl_3)

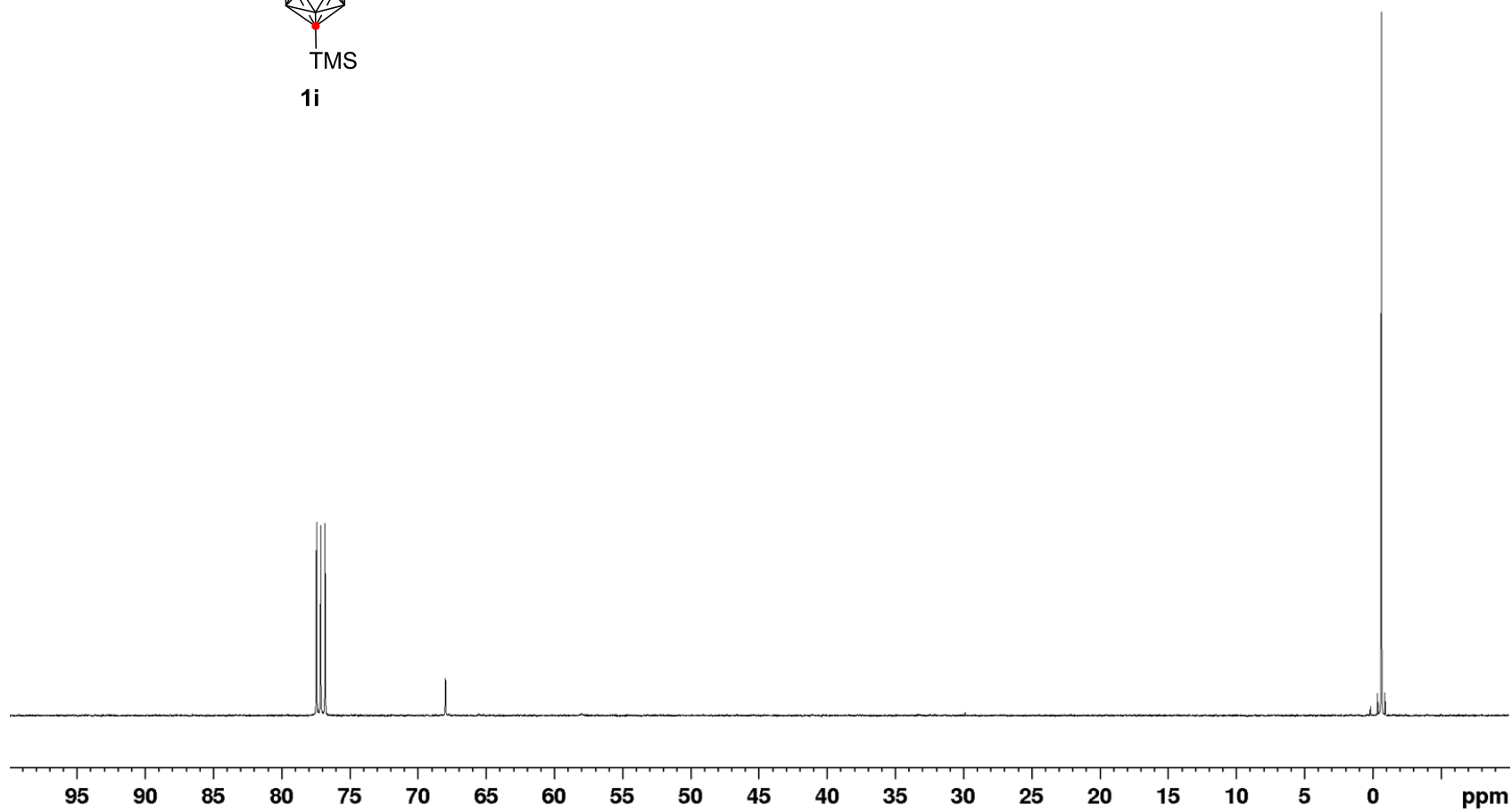
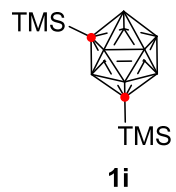


^{13}C NMR (100 MHz, CDCl_3)

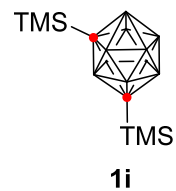
77.5
77.2
76.8

68.0

-0.6



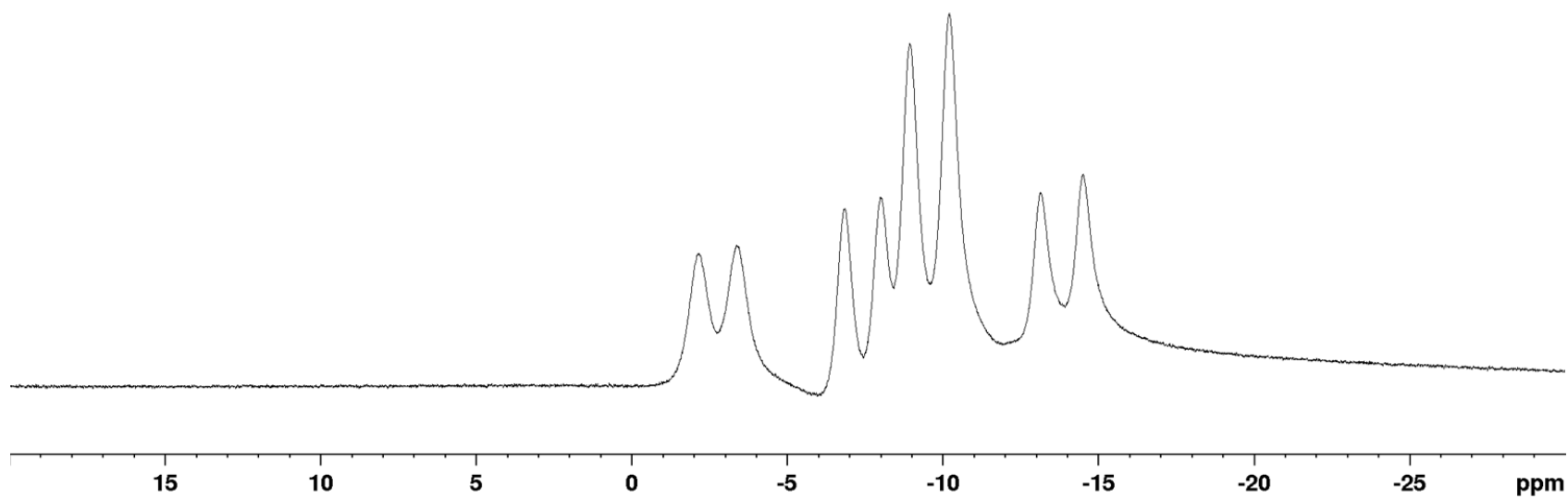
^{11}B NMR (128 MHz, CDCl_3)



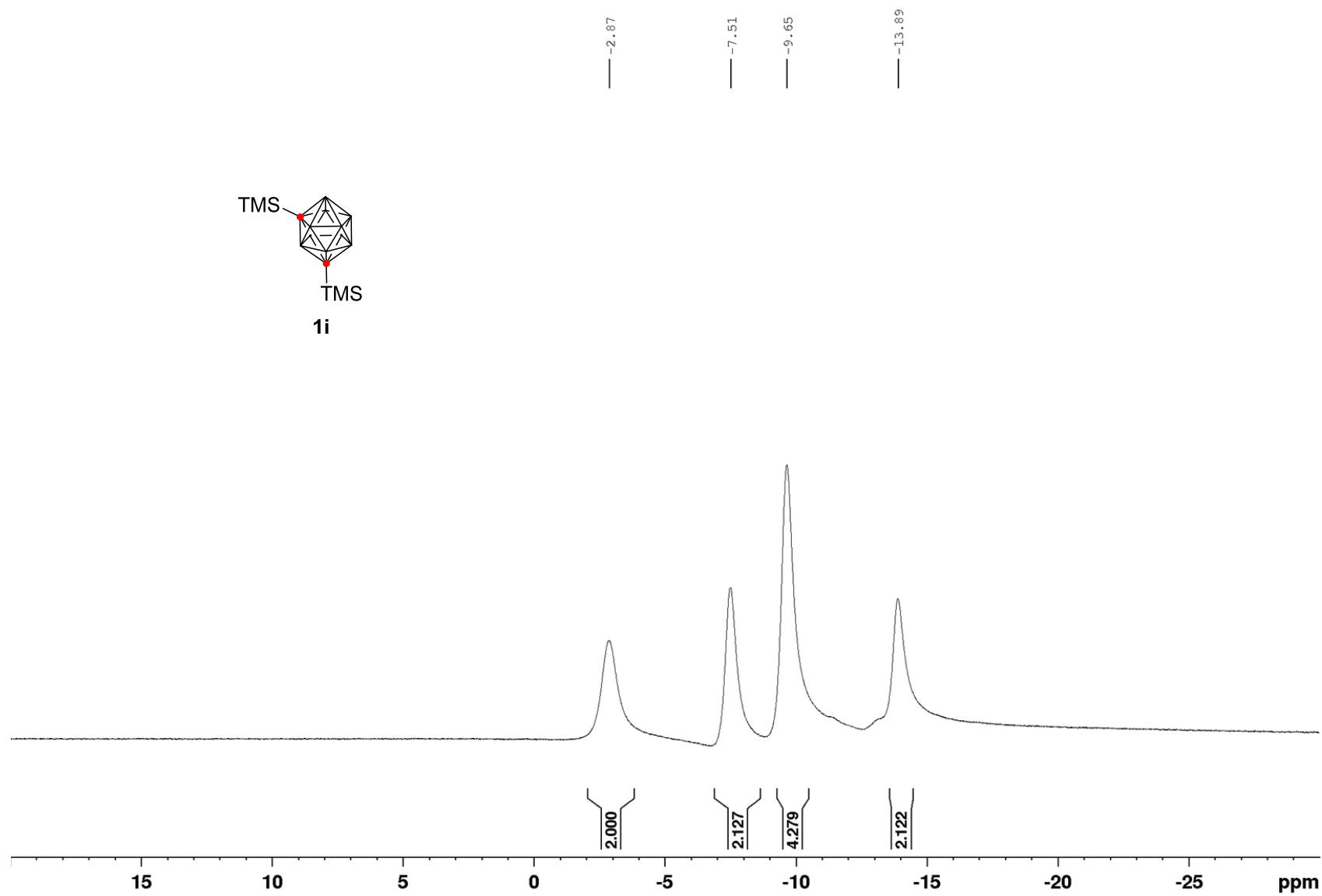
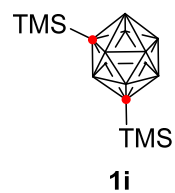
— -2.15
— -3.37

— -6.85
— -7.99
— -8.93
— -10.21

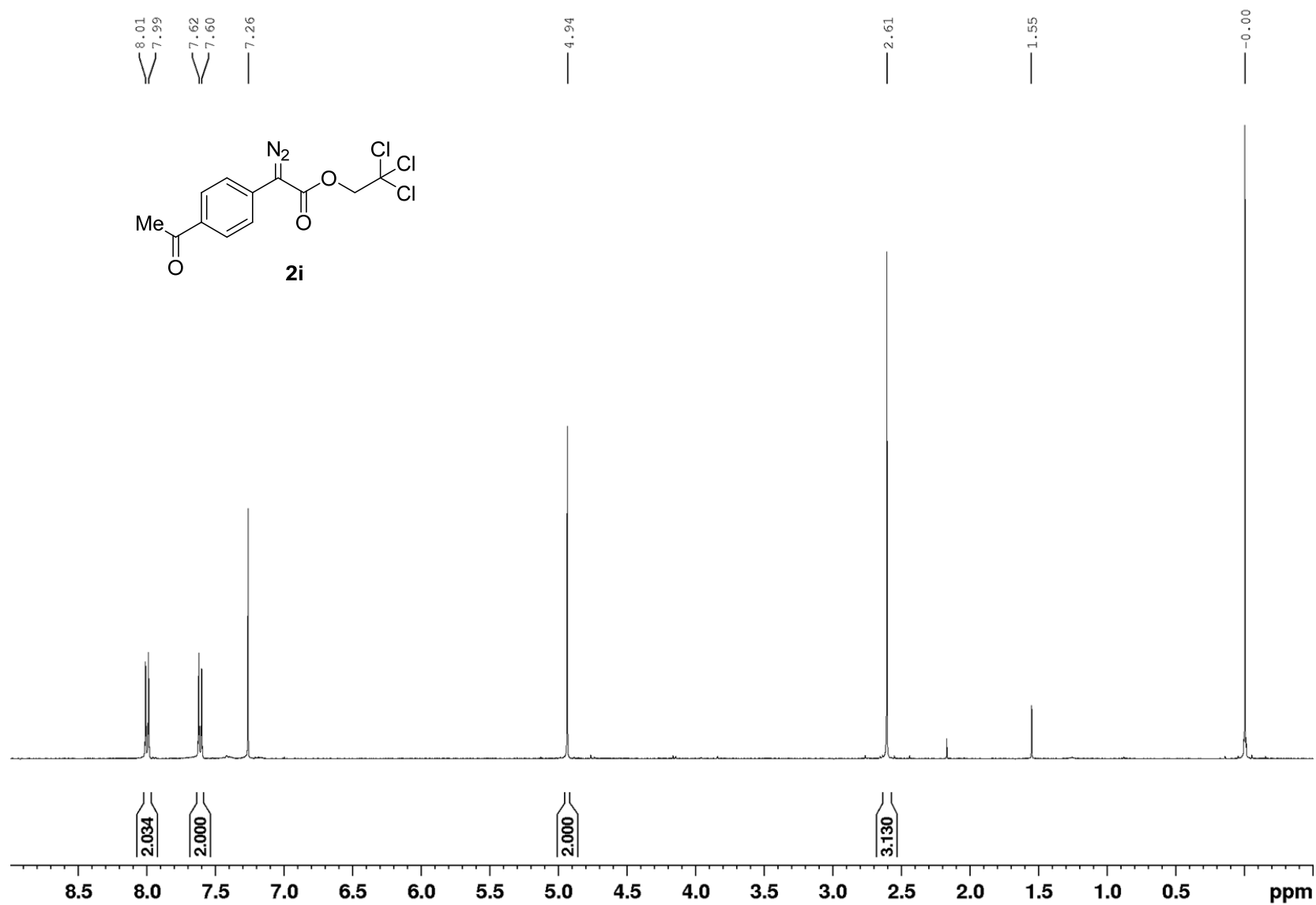
— -13.13
— -14.51



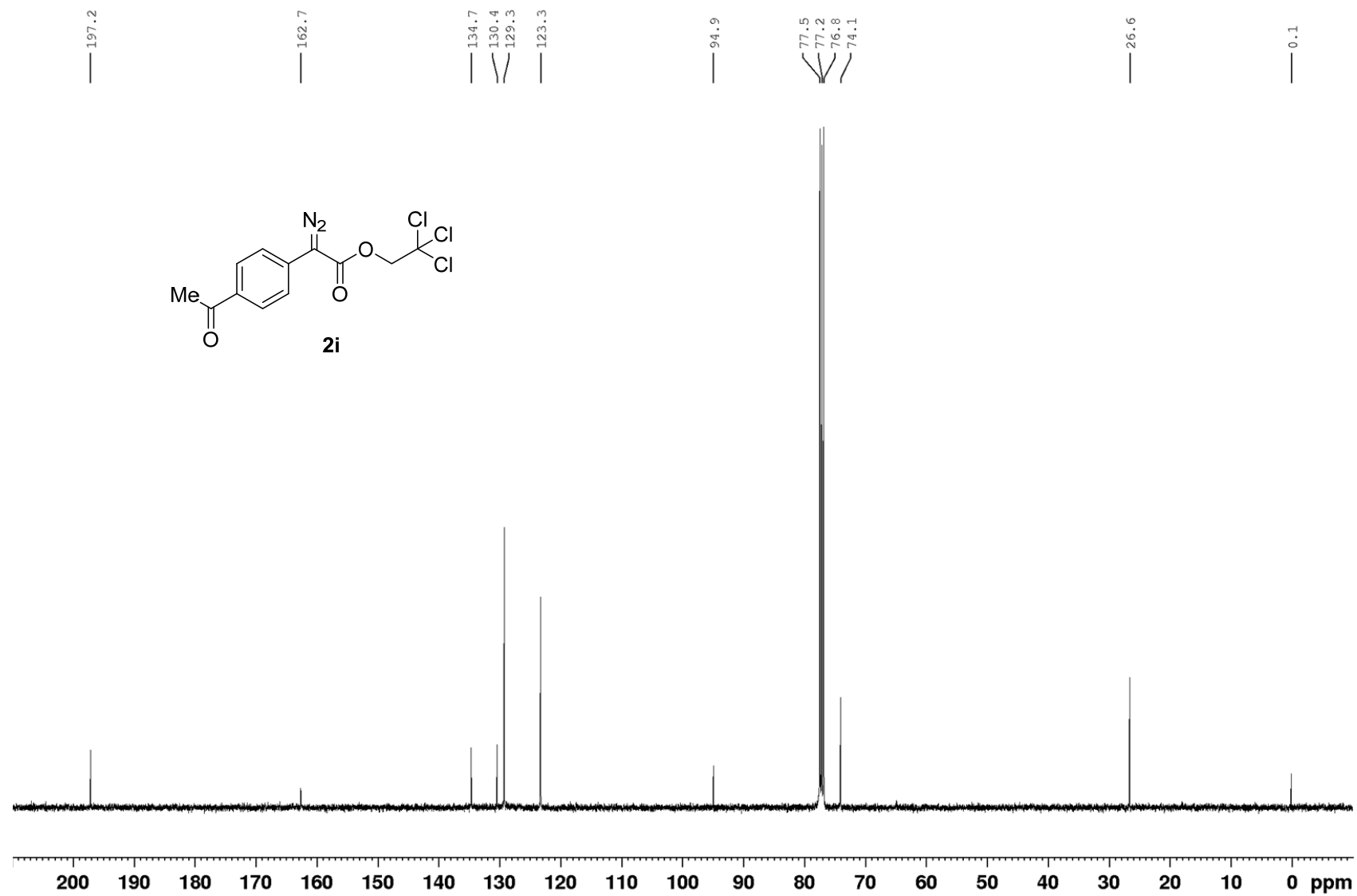
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



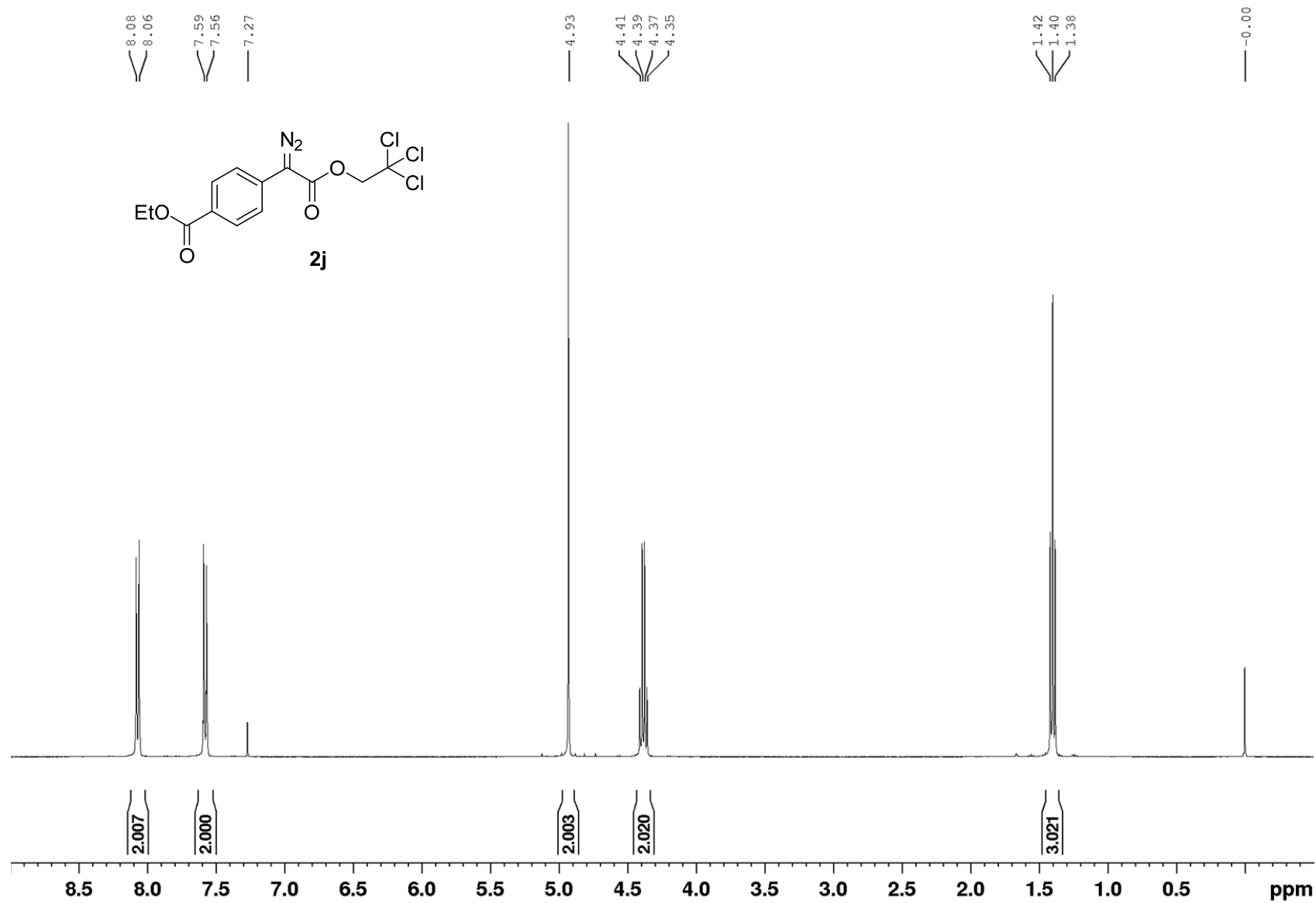
^1H NMR (400 MHz, CDCl_3)



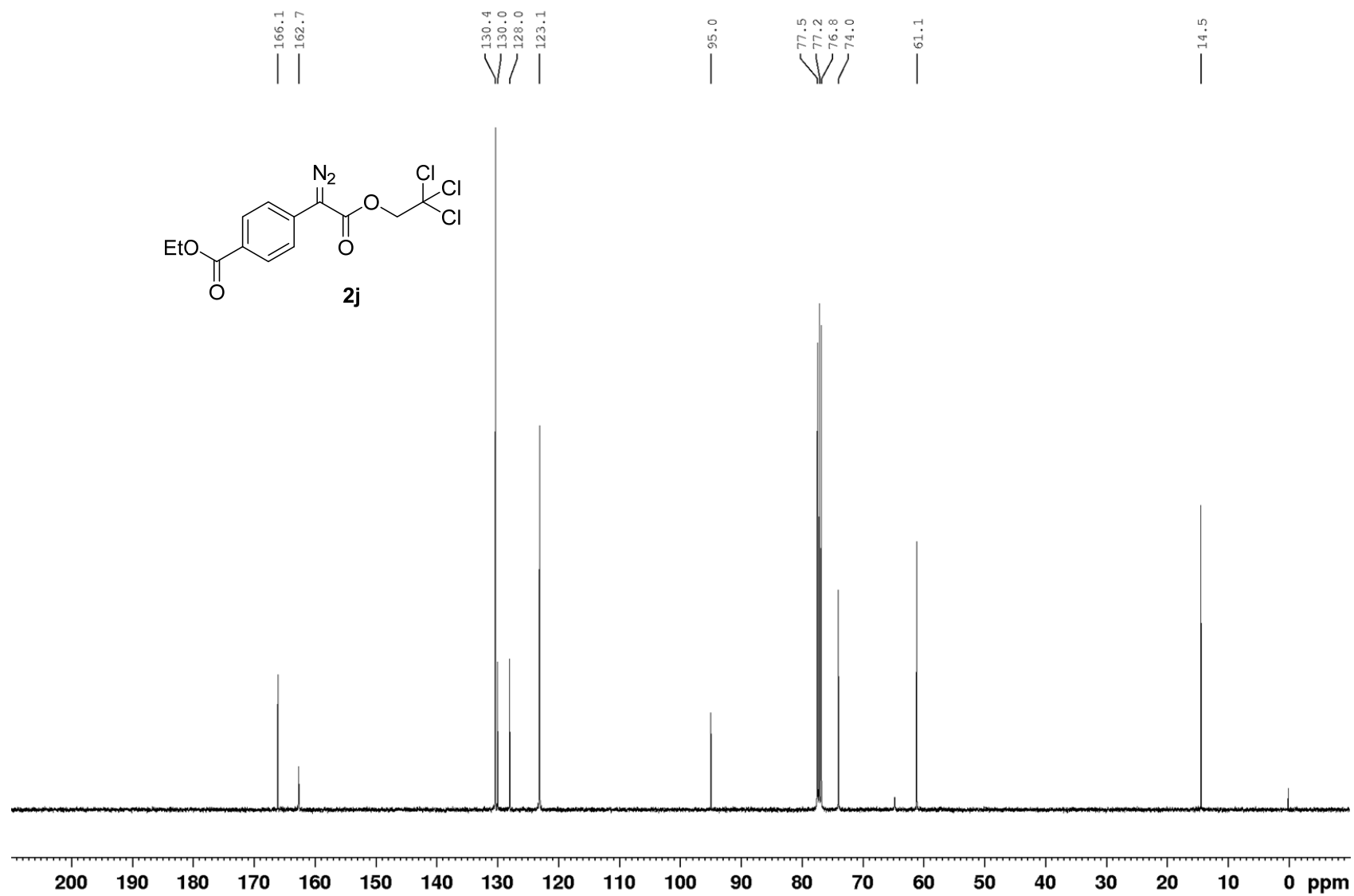
^{13}C NMR (100 MHz, CDCl_3)



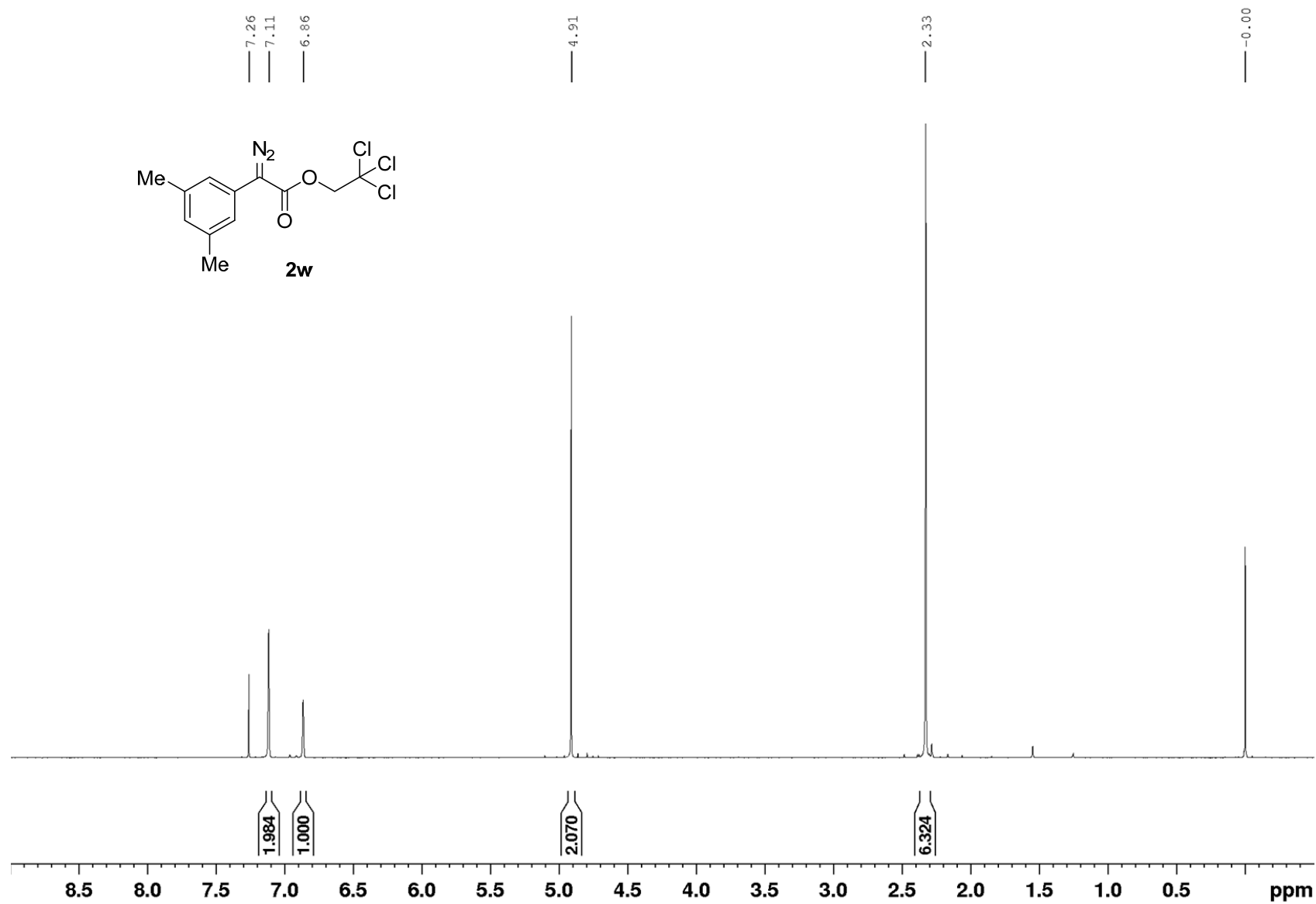
¹H NMR (400 MHz, CDCl₃)



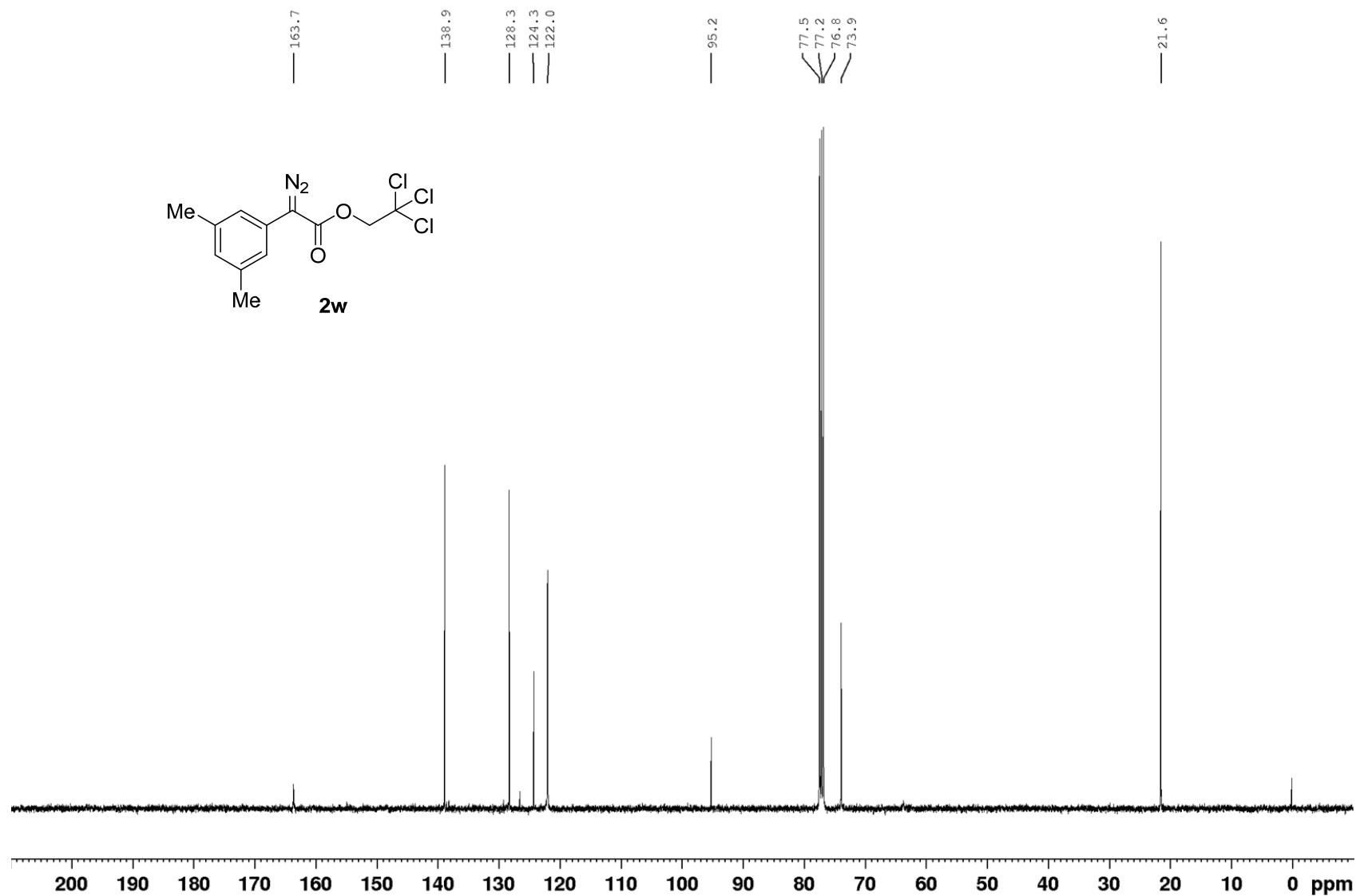
^{13}C NMR (100 MHz, CDCl_3)



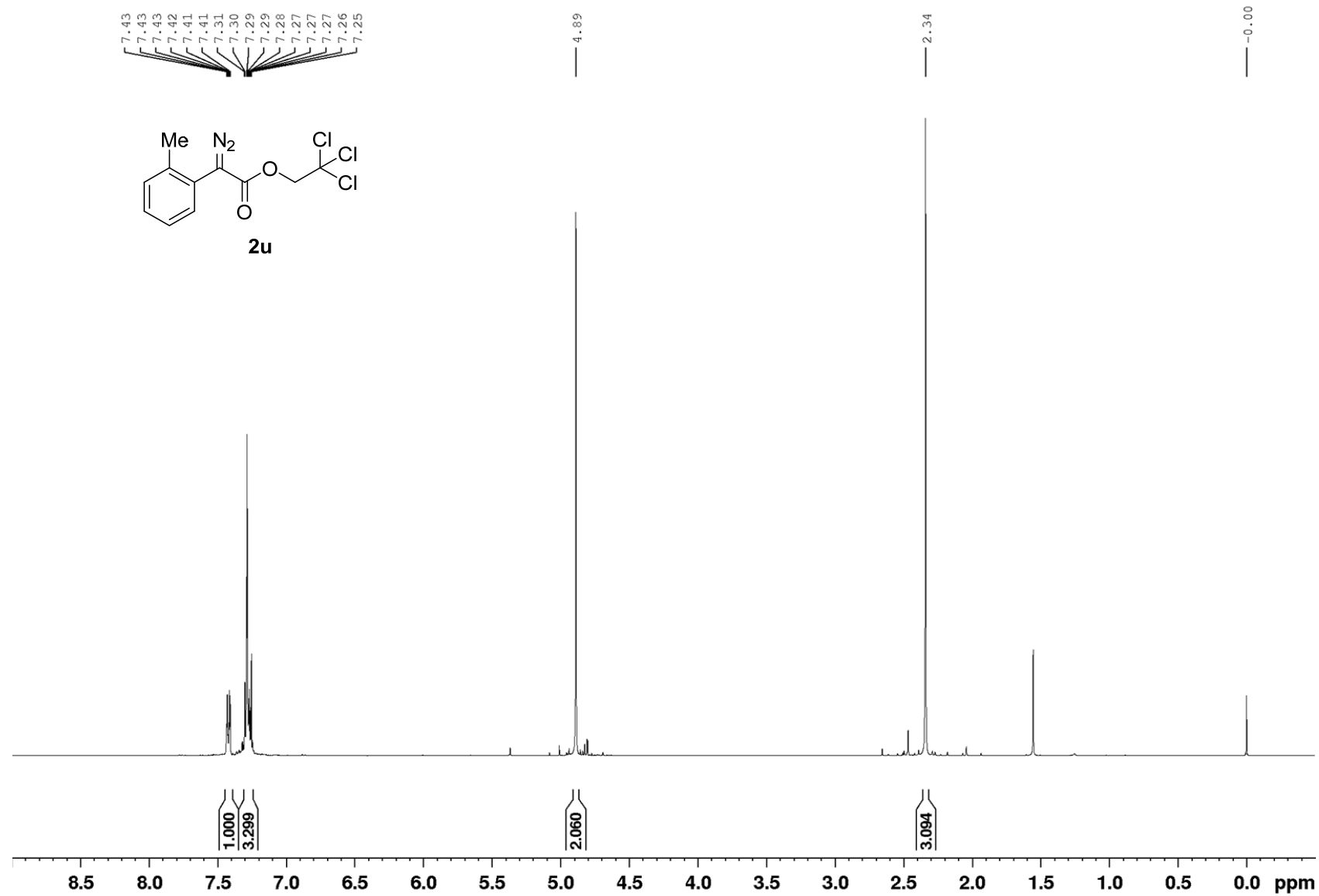
¹H NMR (400 MHz, CDCl₃)



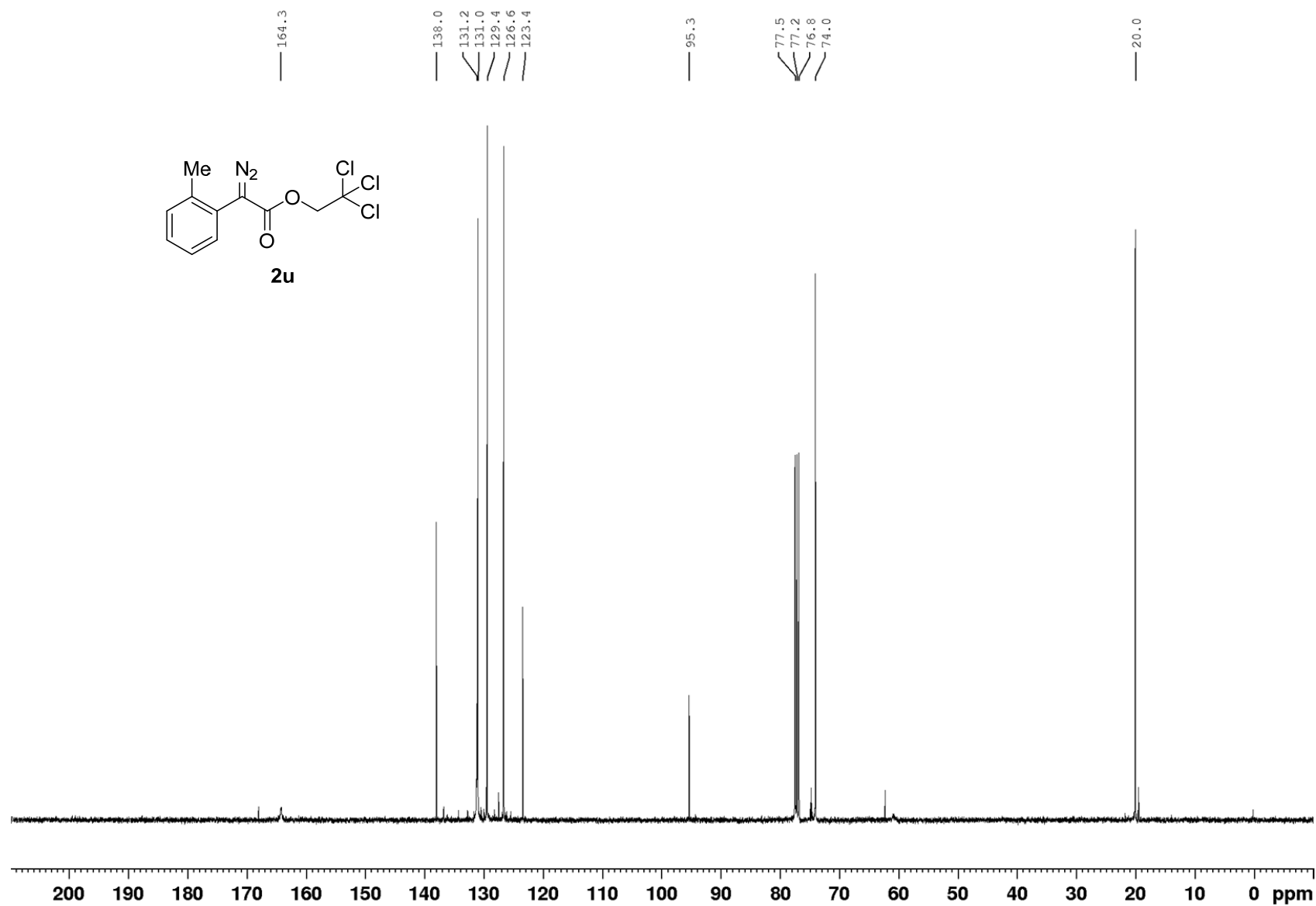
^{13}C NMR (100 MHz, CDCl_3)



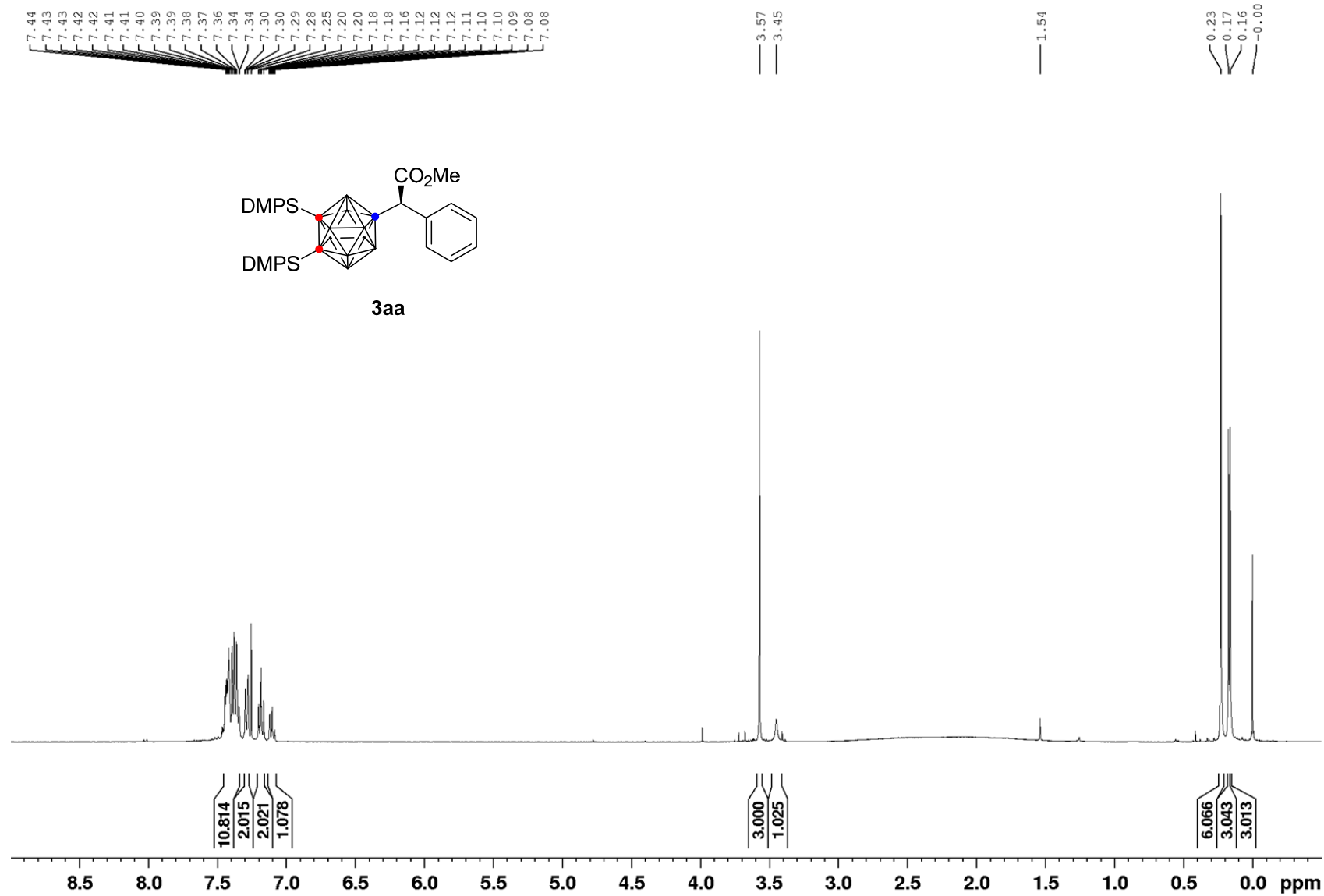
^1H NMR (400 MHz, CDCl_3)



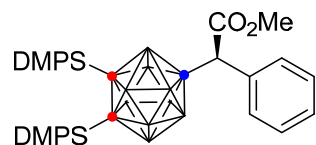
¹³C NMR (100 MHz, CDCl₃)



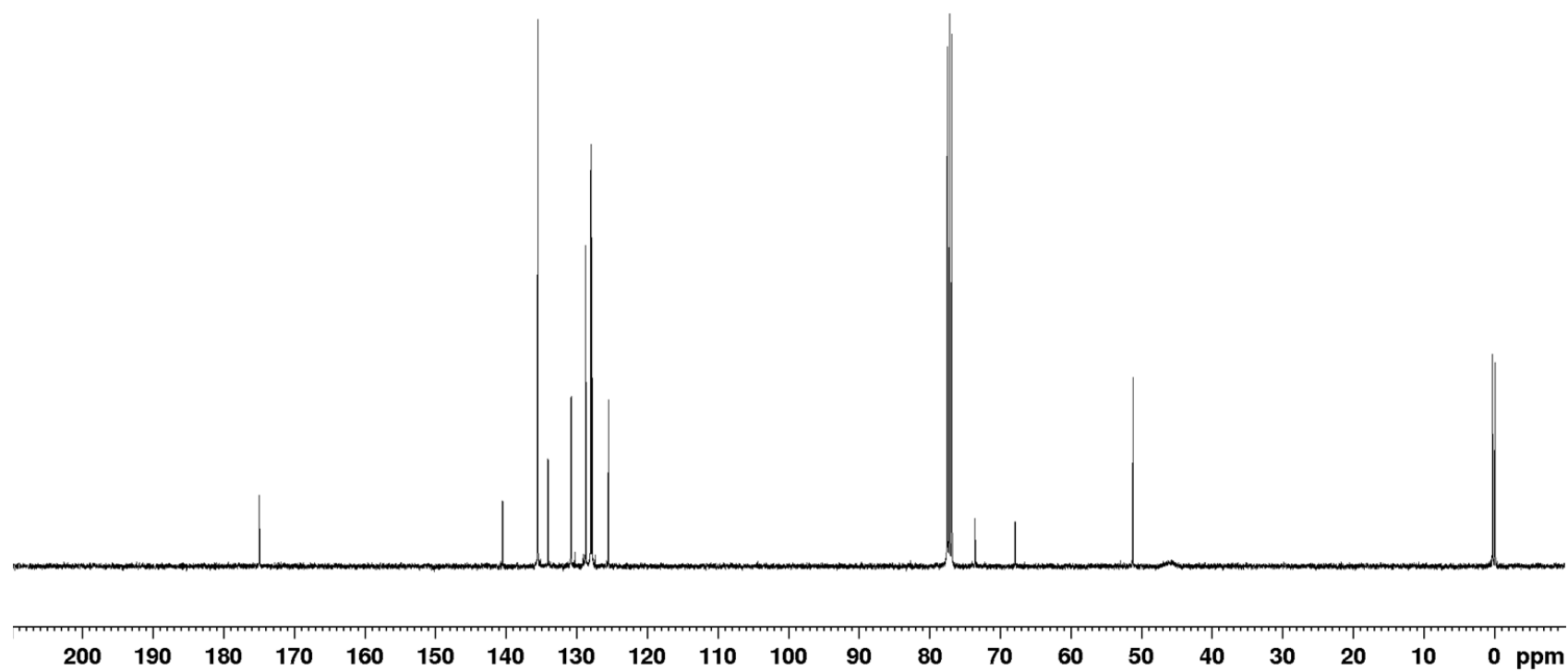
¹H NMR (400 MHz, CDCl₃)



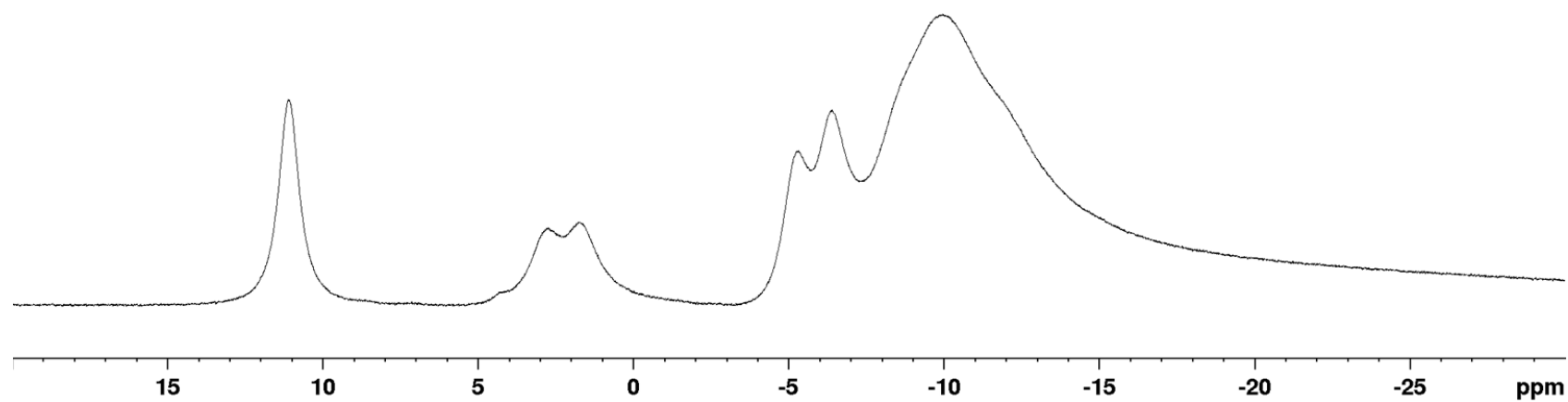
^{13}C NMR (100 MHz, CDCl_3)



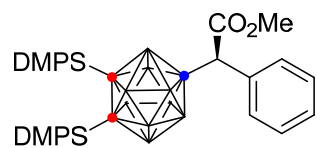
3aa



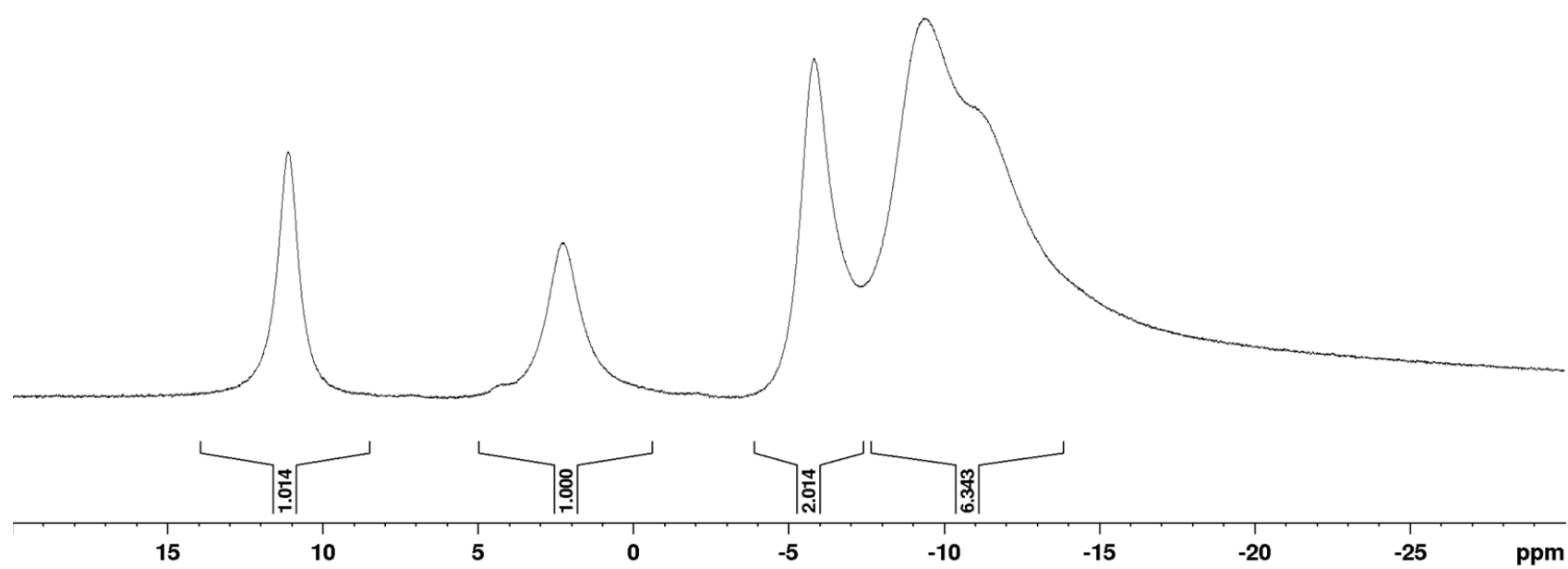
^{11}B NMR (128 MHz, CDCl_3)



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



3aa

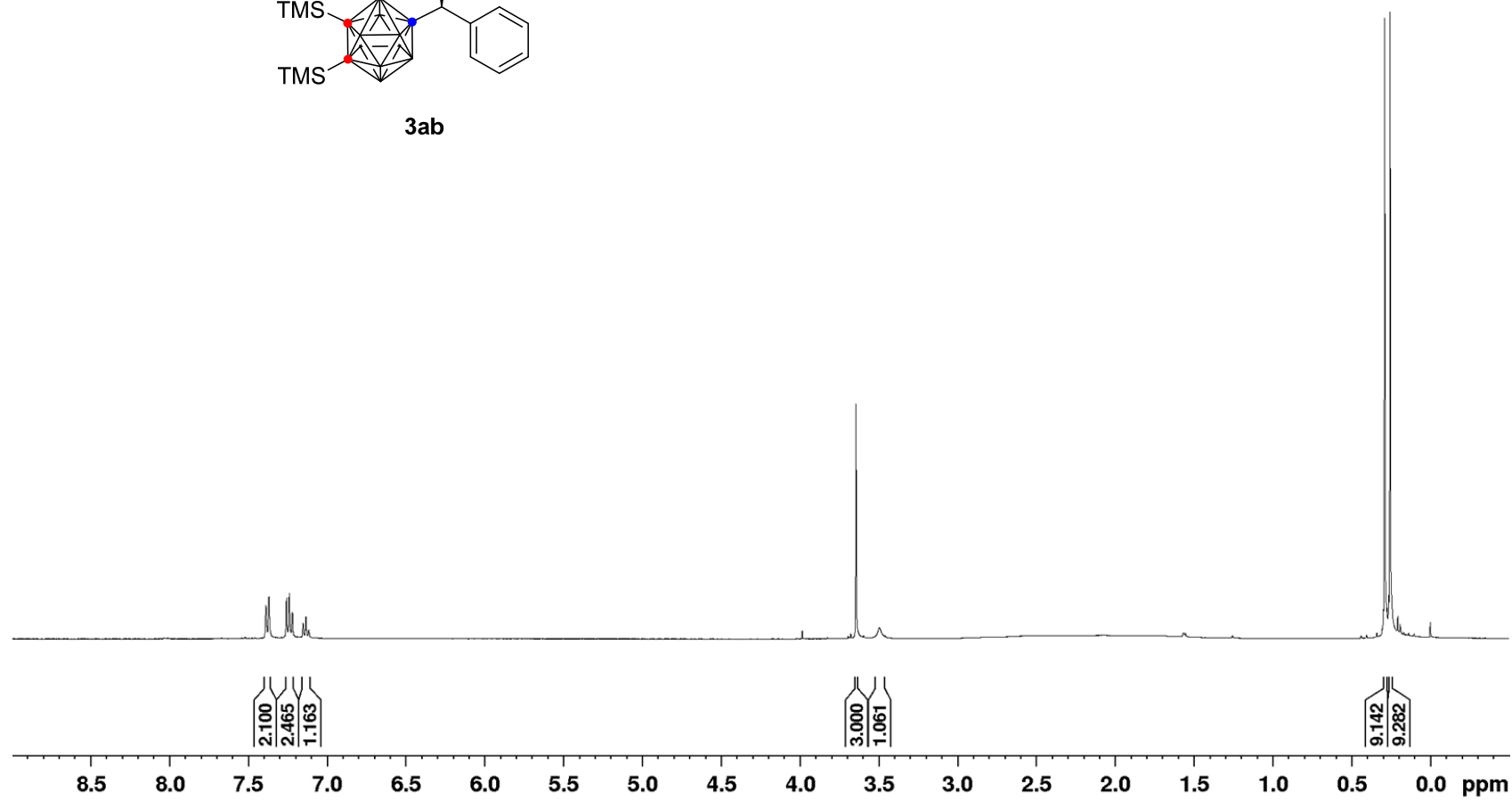
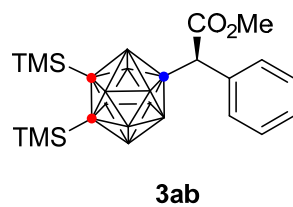


^1H NMR (400 MHz, CDCl_3)

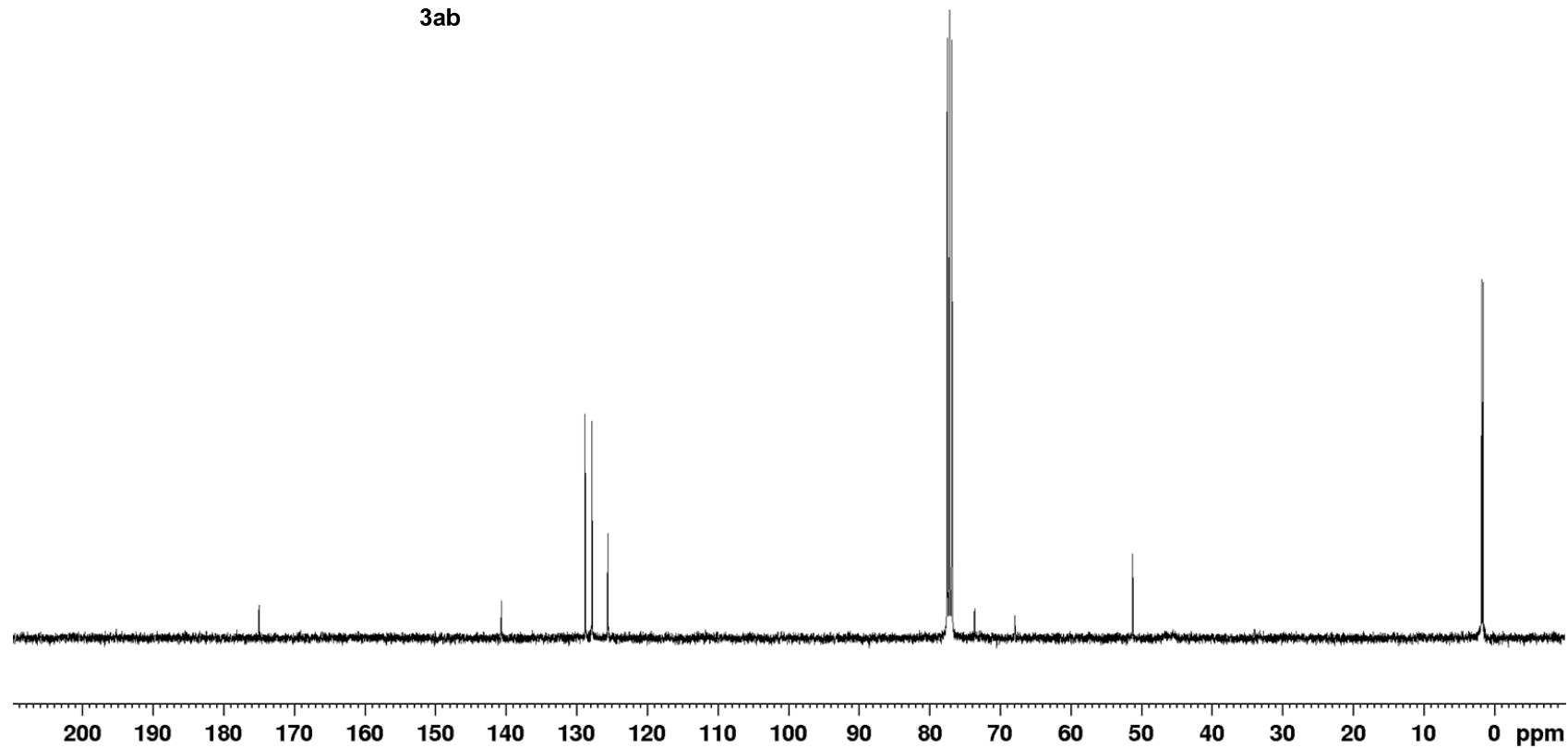
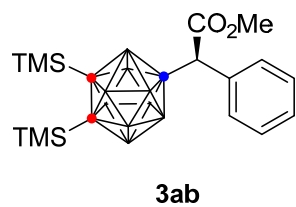
7.39
7.37
7.26
7.24
7.22
7.15
7.13
7.12

3.64
3.50

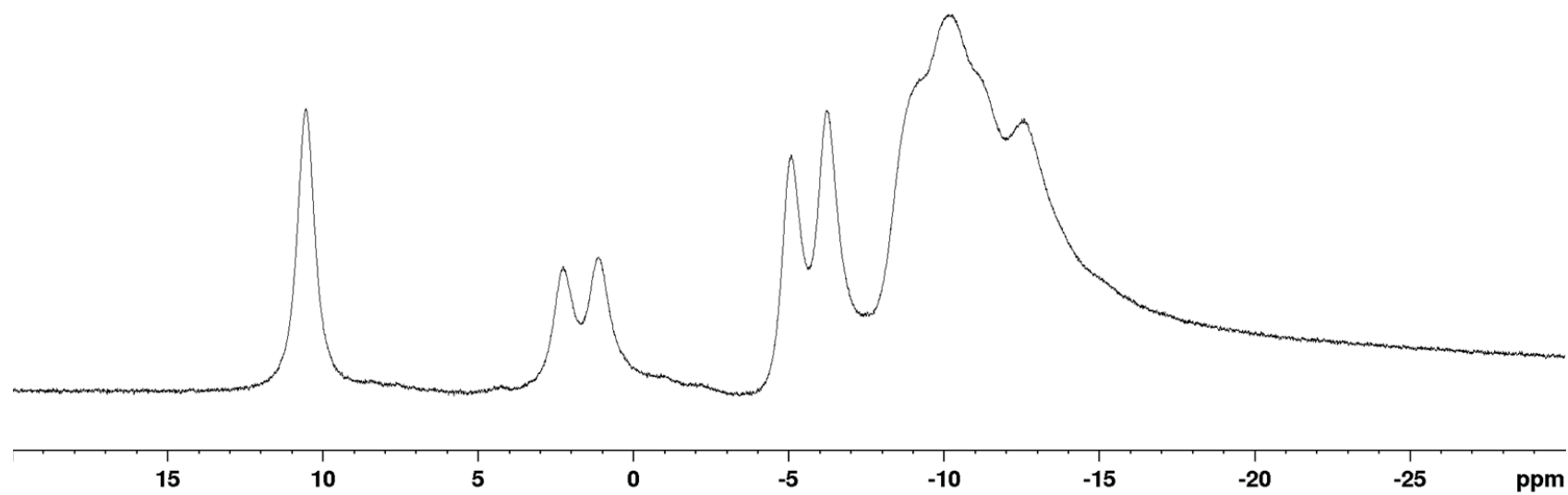
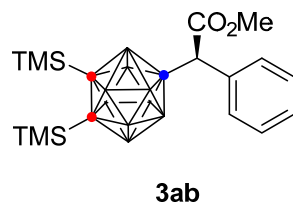
0.29
0.26
-0.00



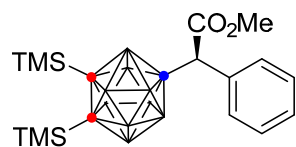
^{13}C NMR (100 MHz, CDCl_3)



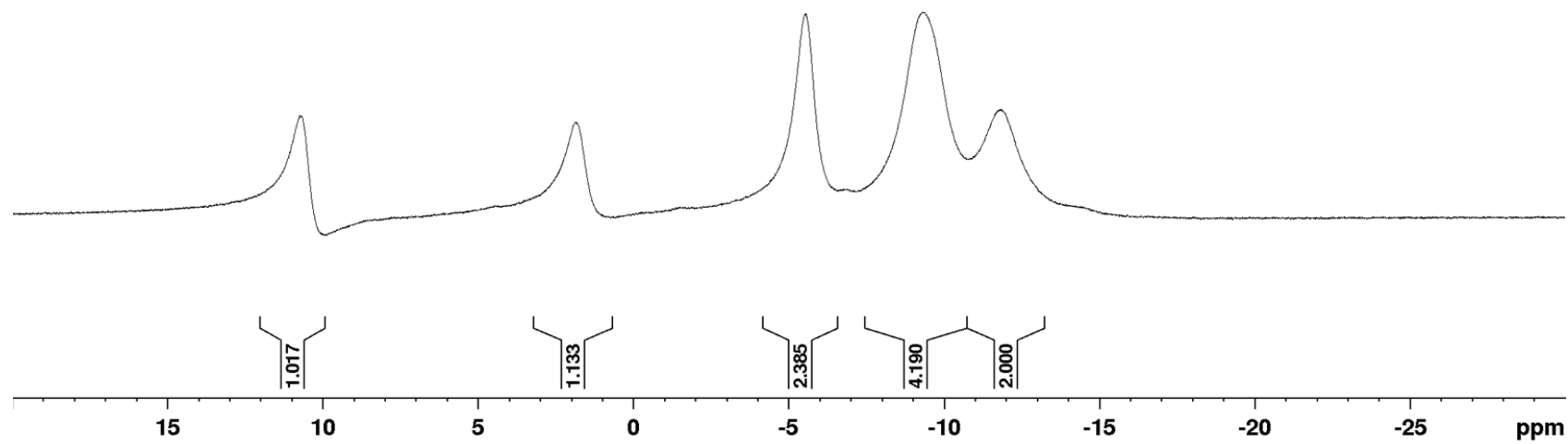
^{11}B NMR (128 MHz, CDCl_3)



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



3ab

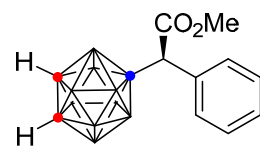


¹H NMR (400 MHz, CDCl₃)

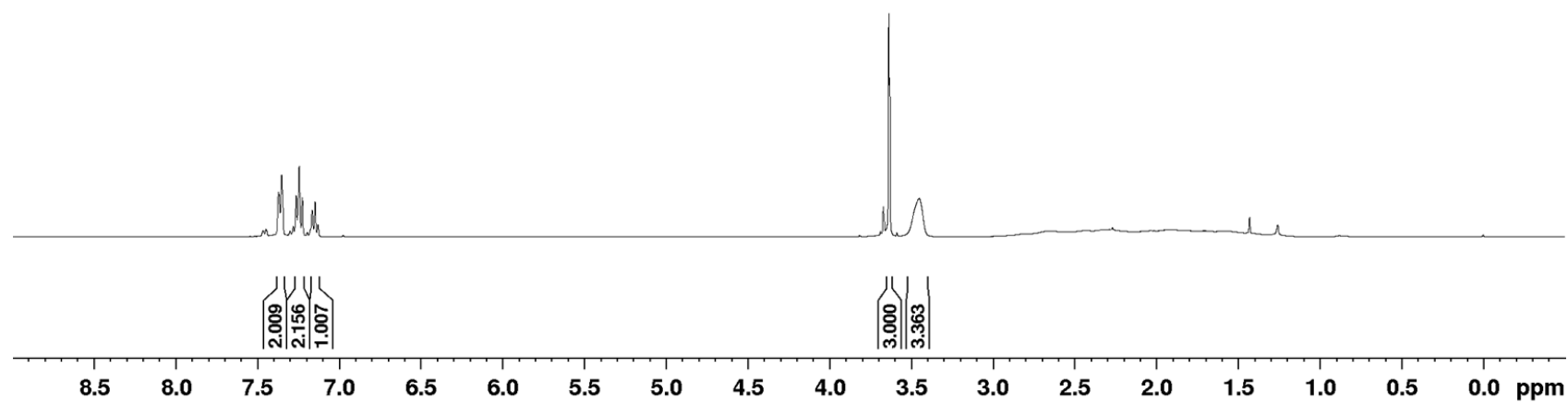
7.37
7.35
7.26
7.24
7.23
7.17
7.15
7.13

3.64
3.45

-0.00



3ca



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

— 175.0

— 140.5

128.7

128.0

125.8

77.5

77.2

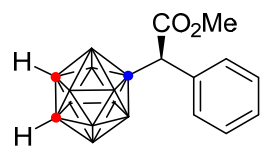
76.8

53.3

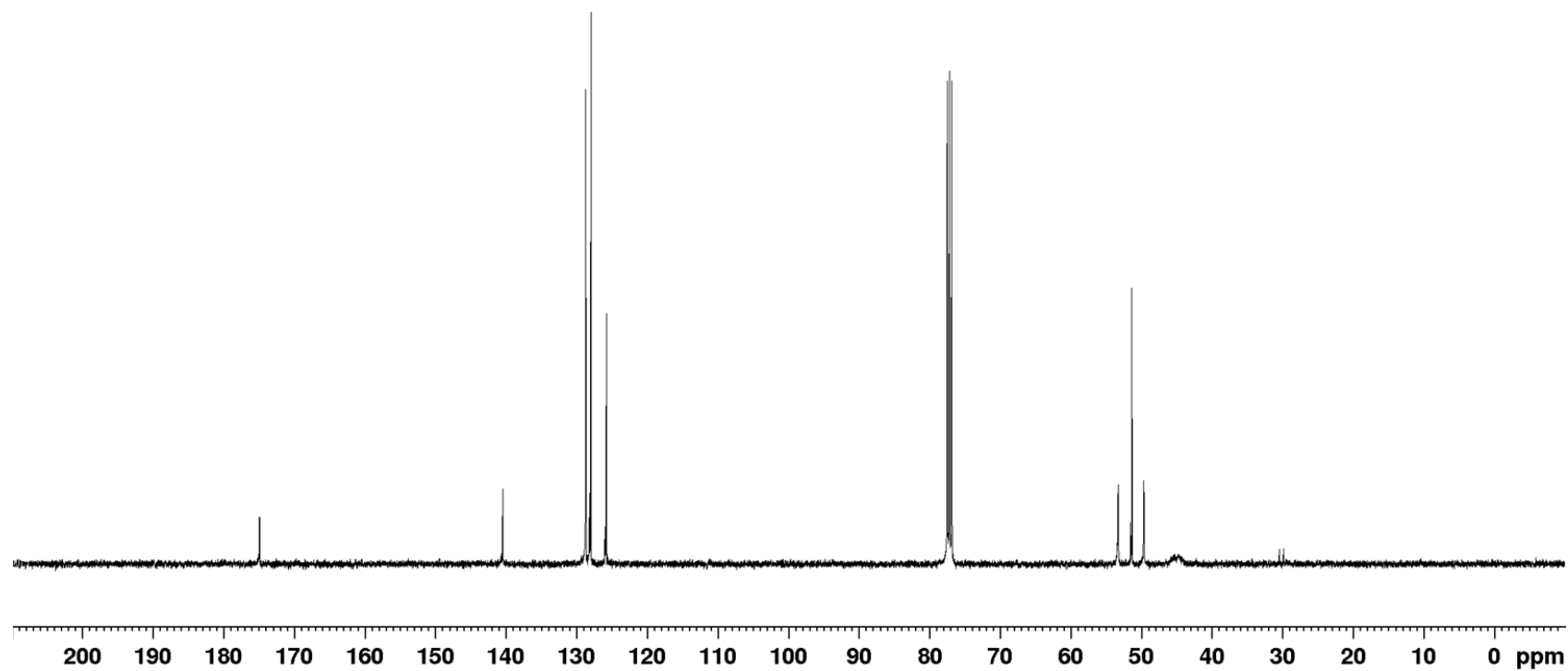
51.3

49.6

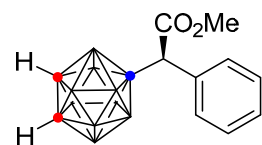
45.3



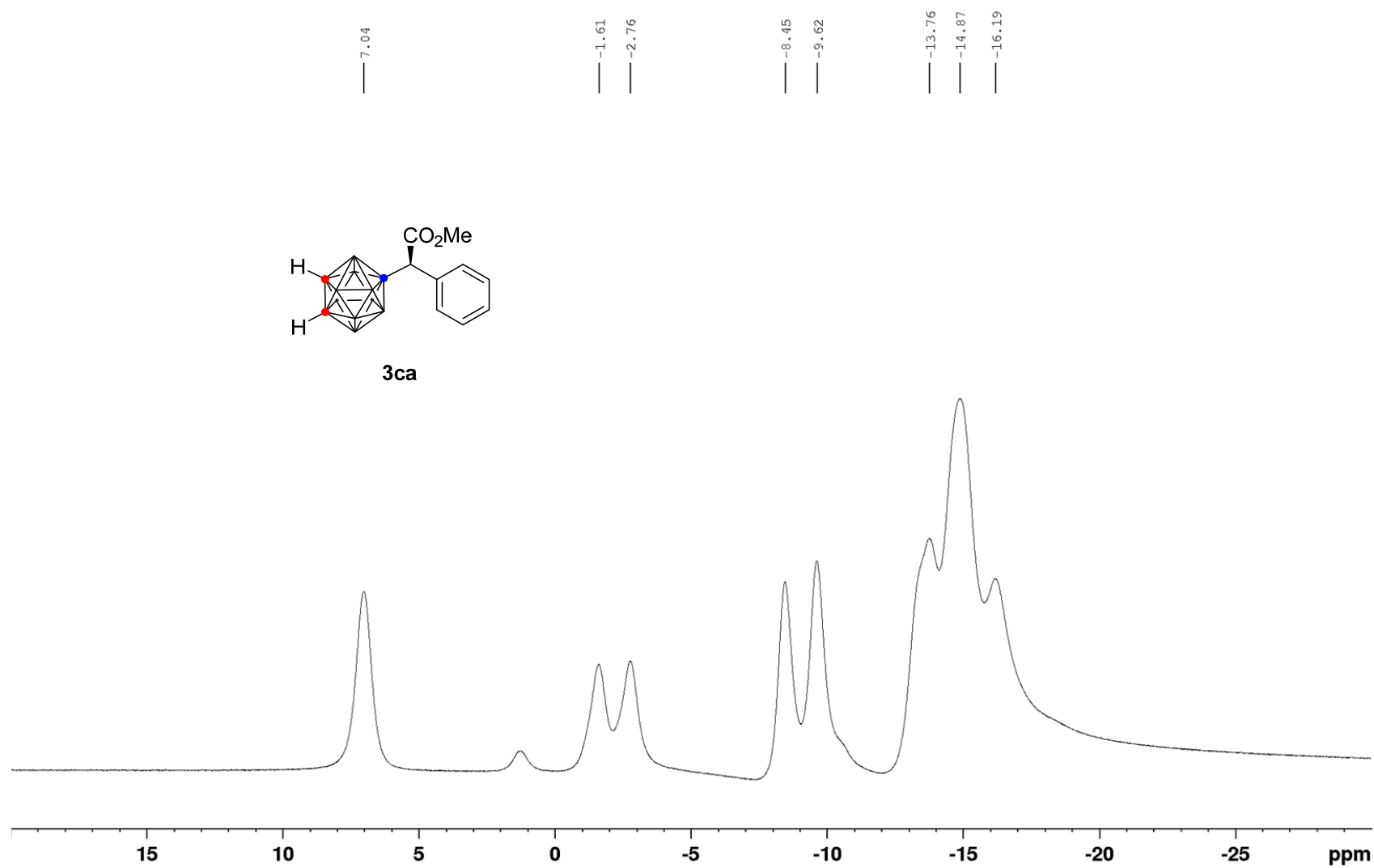
3ca



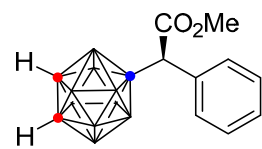
^{11}B NMR (128 MHz, CDCl_3)



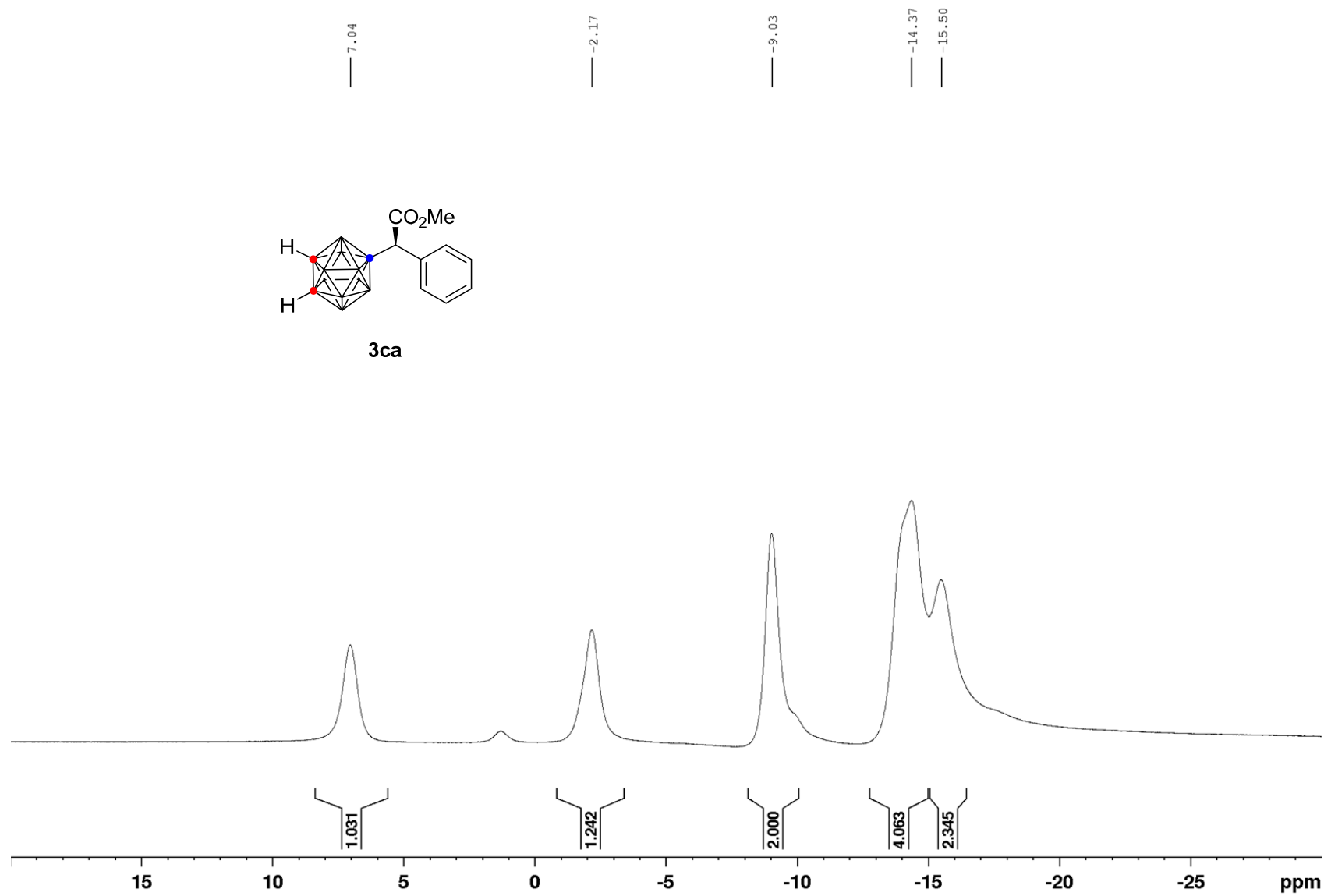
3ca



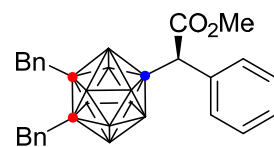
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



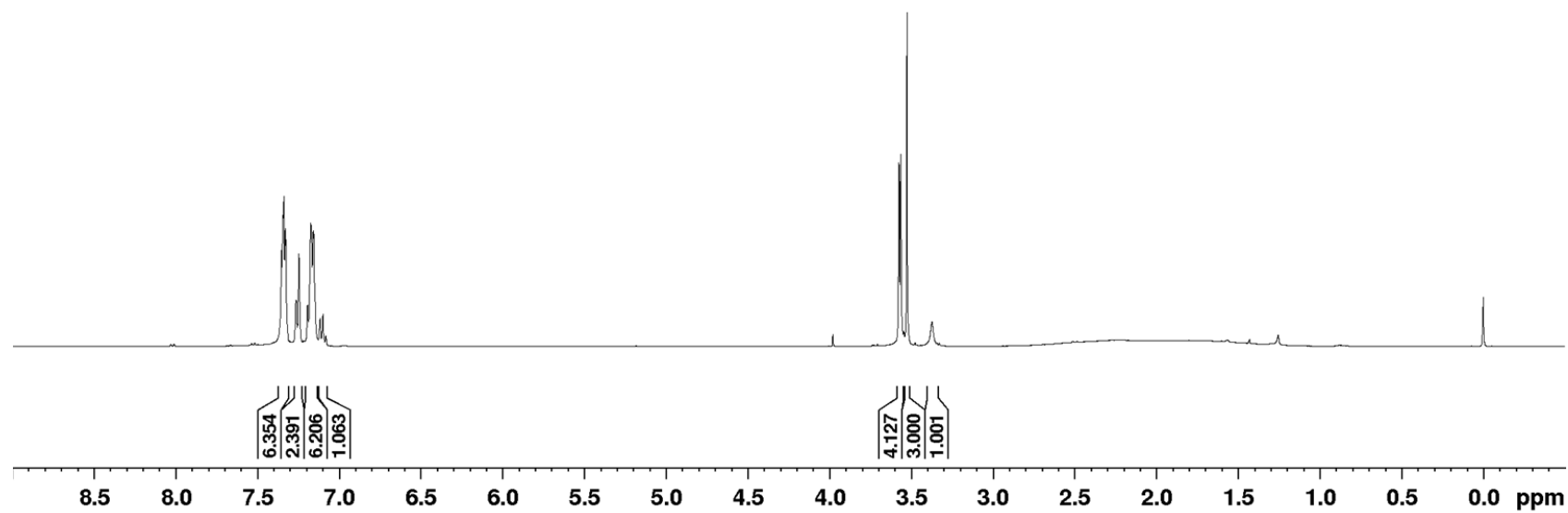
3ca



¹H NMR (400 MHz, CDCl₃)



3da



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

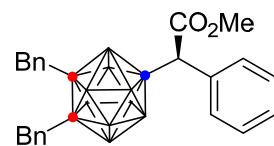
175.0

140.6
135.0
134.9
130.4
128.8
128.7
128.7
128.3
128.3
127.8
125.6

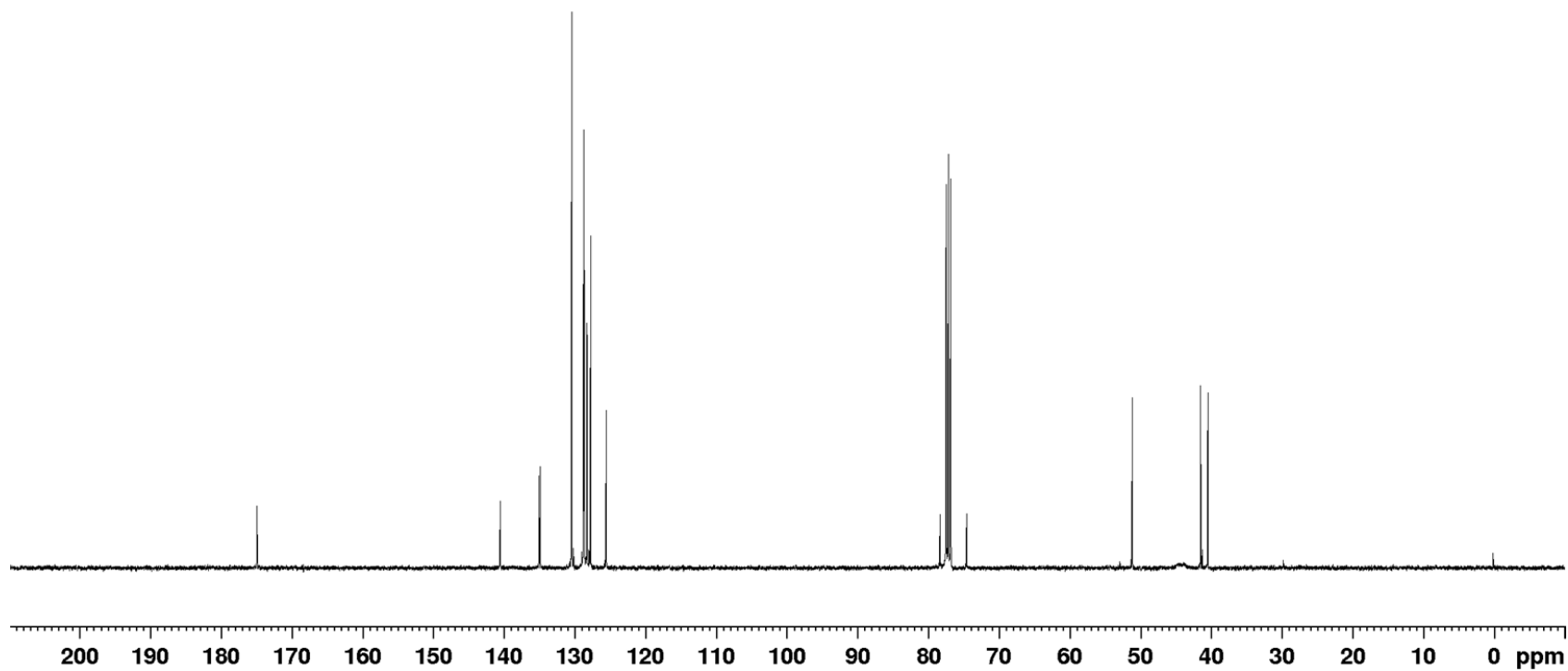
78.3
77.5
77.2
76.8
74.6

51.1

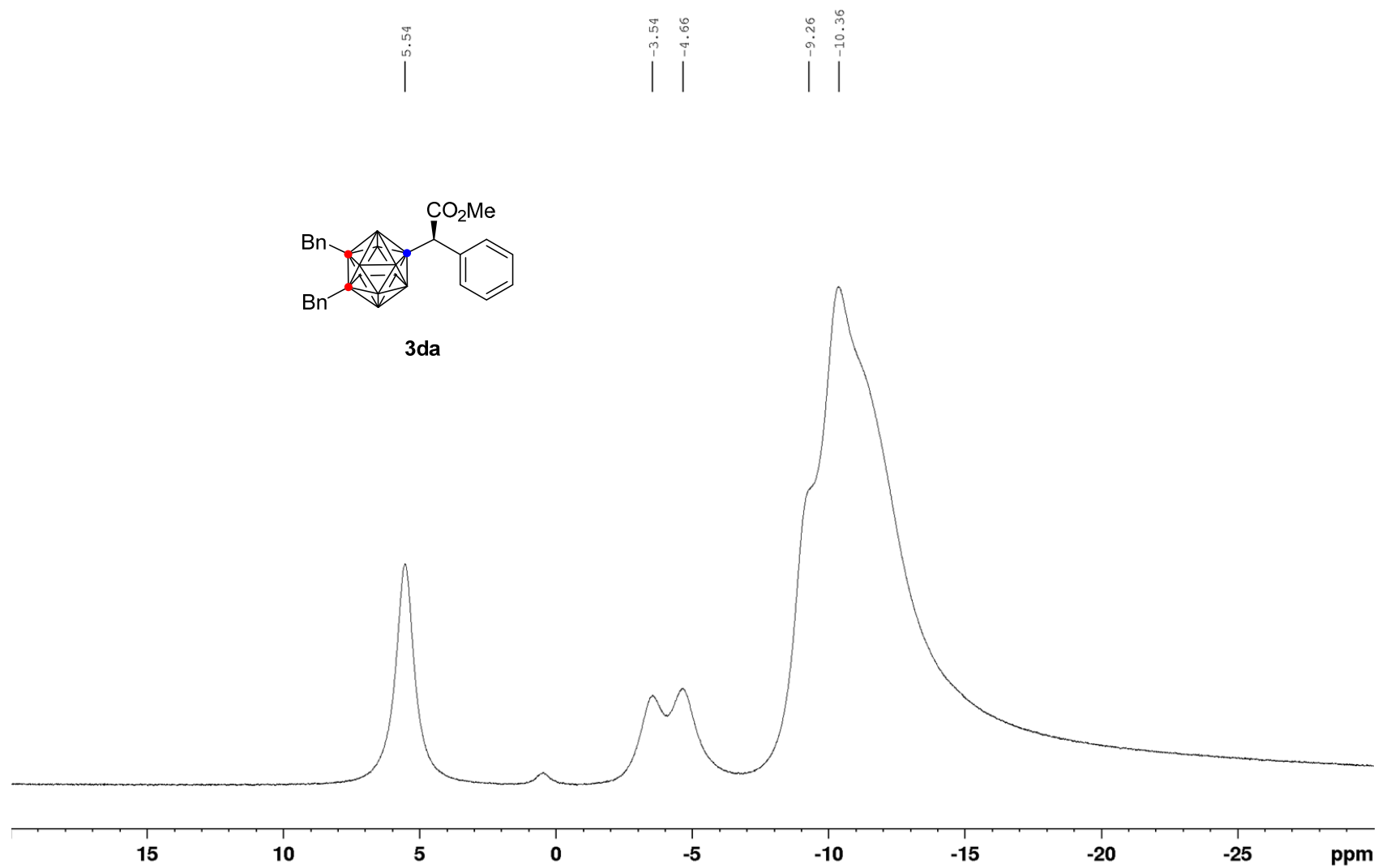
44.0
41.5
40.5



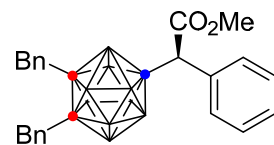
3da



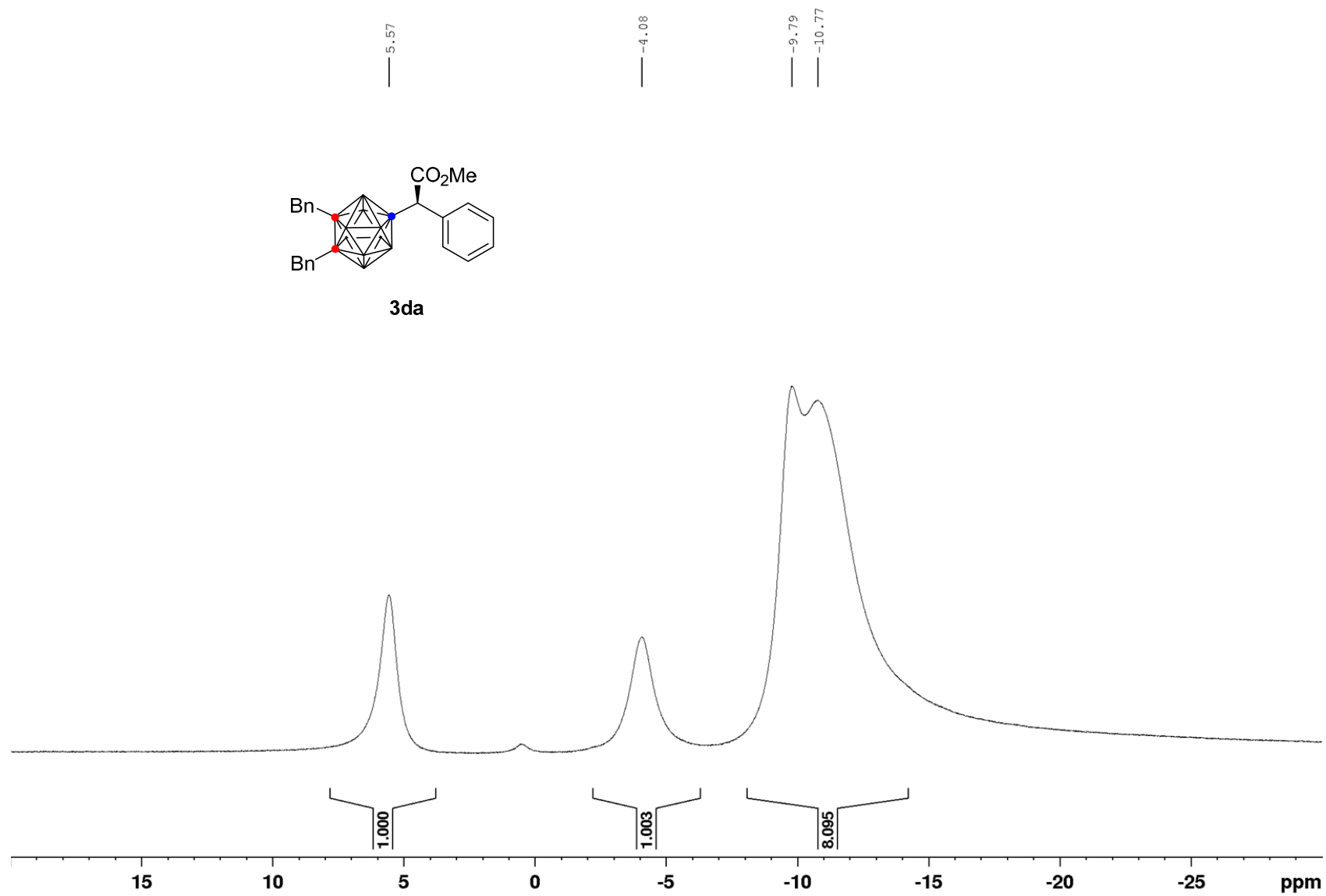
^{11}B NMR (128 MHz, CDCl_3)



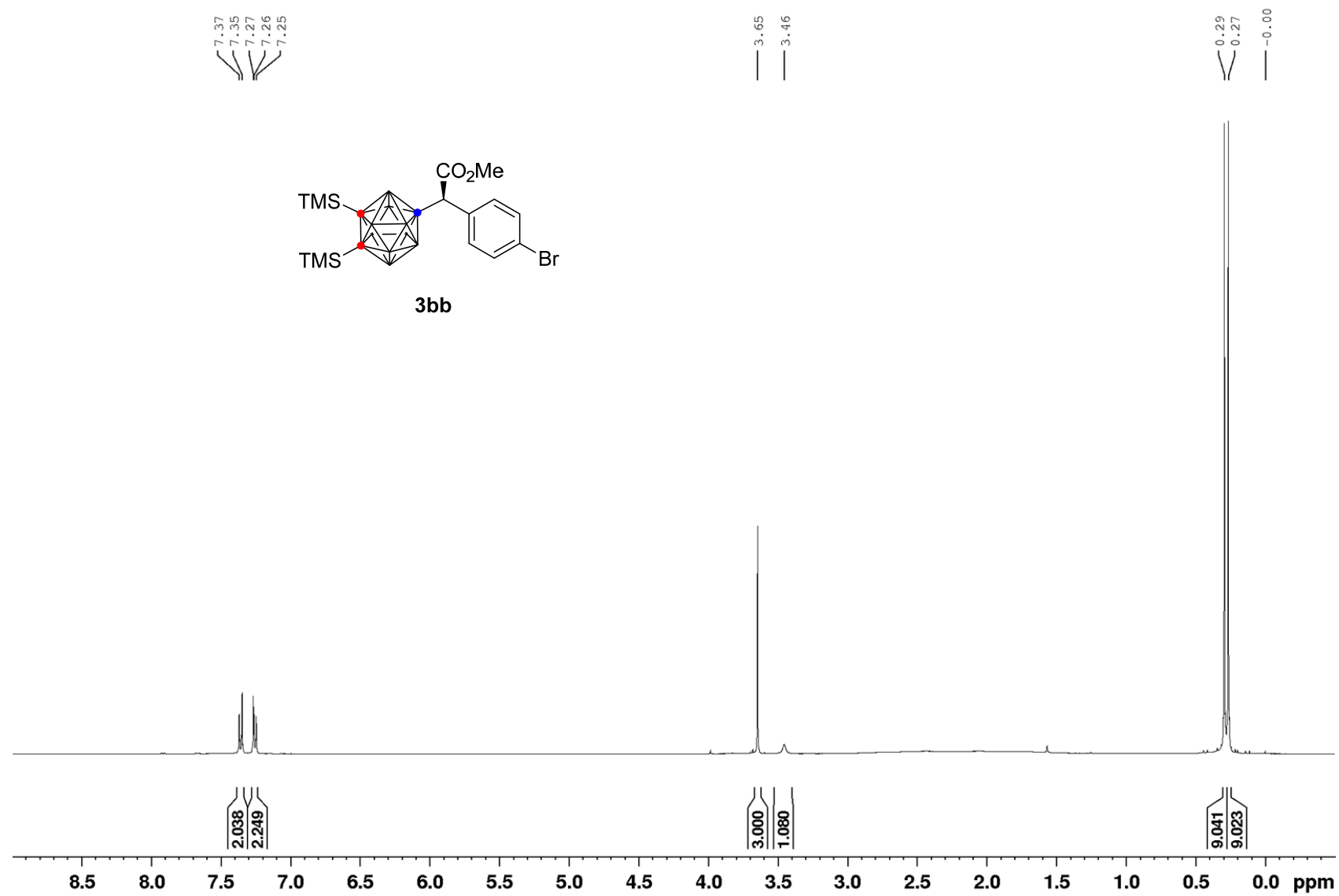
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



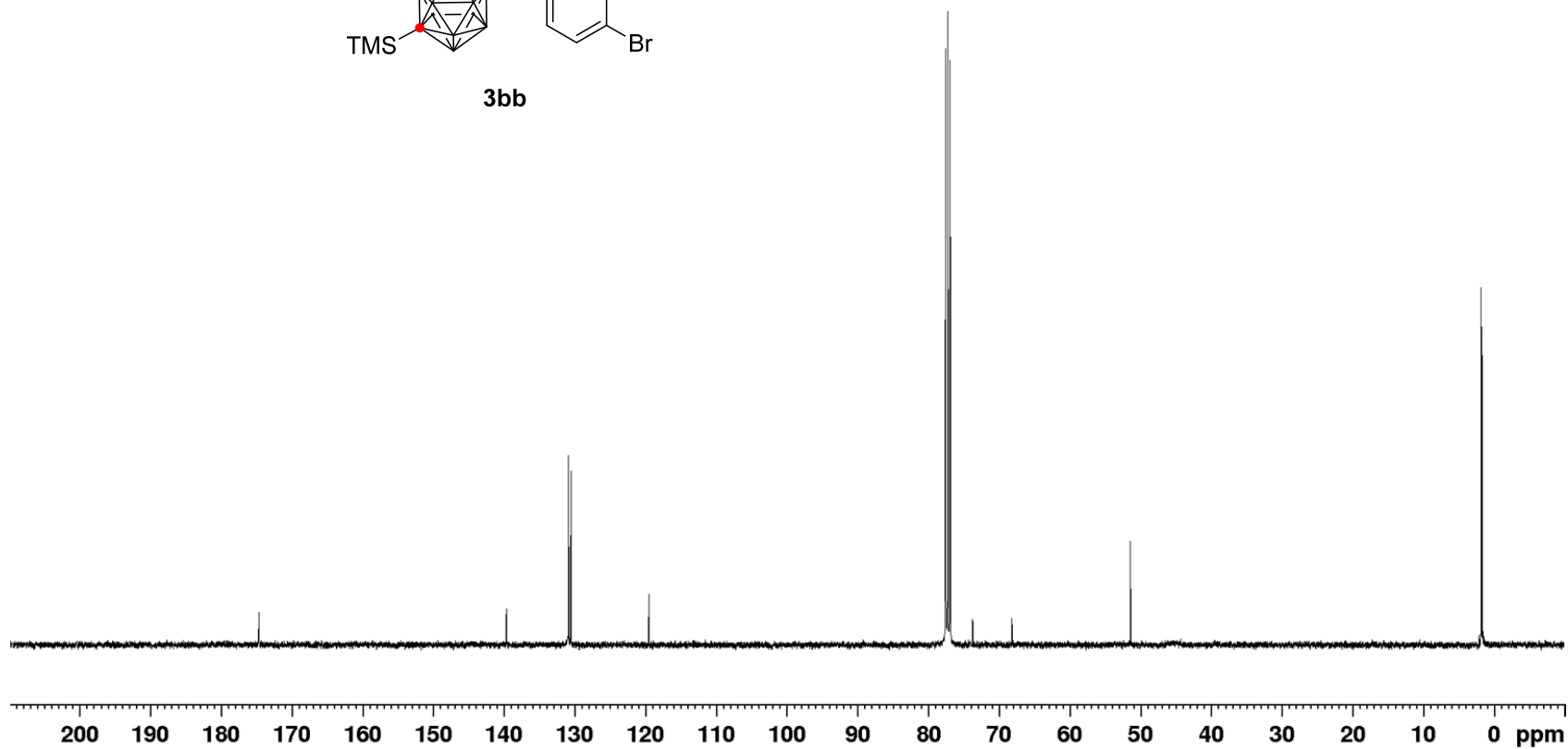
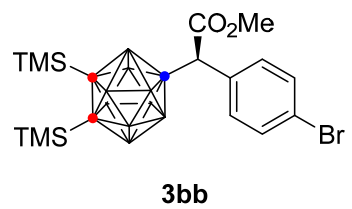
3da



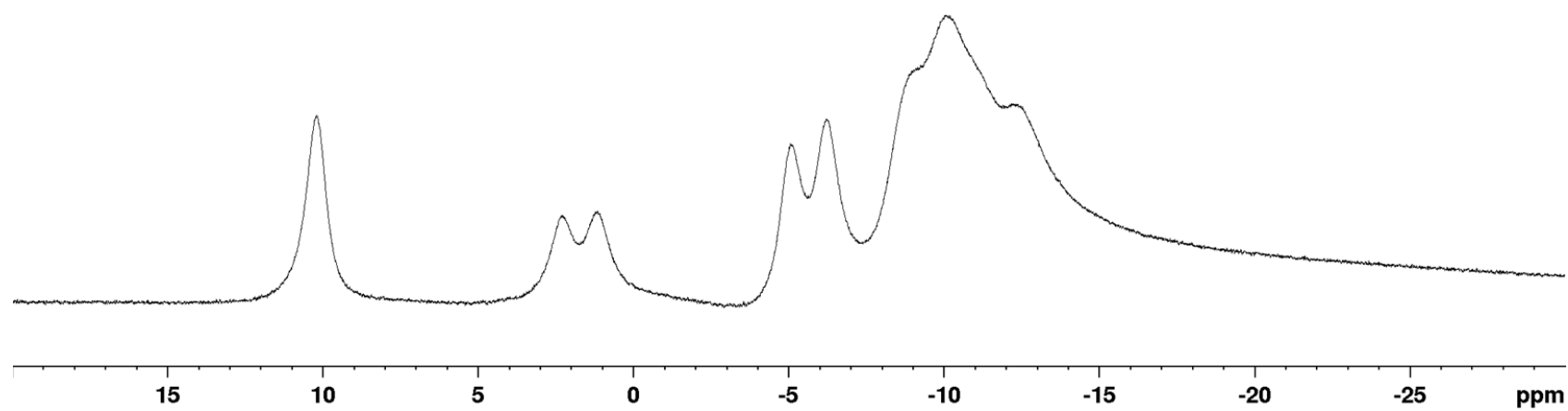
^1H NMR (400 MHz, CDCl_3)



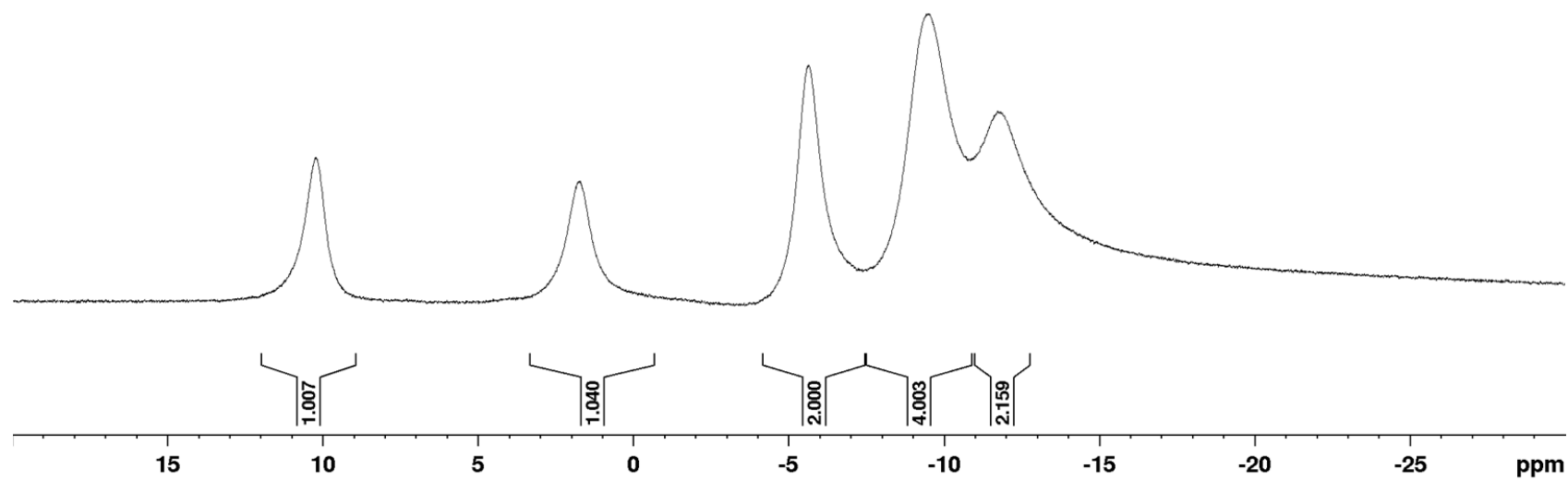
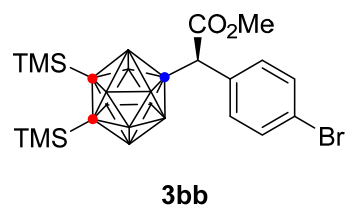
^{13}C NMR (100 MHz, CDCl_3)



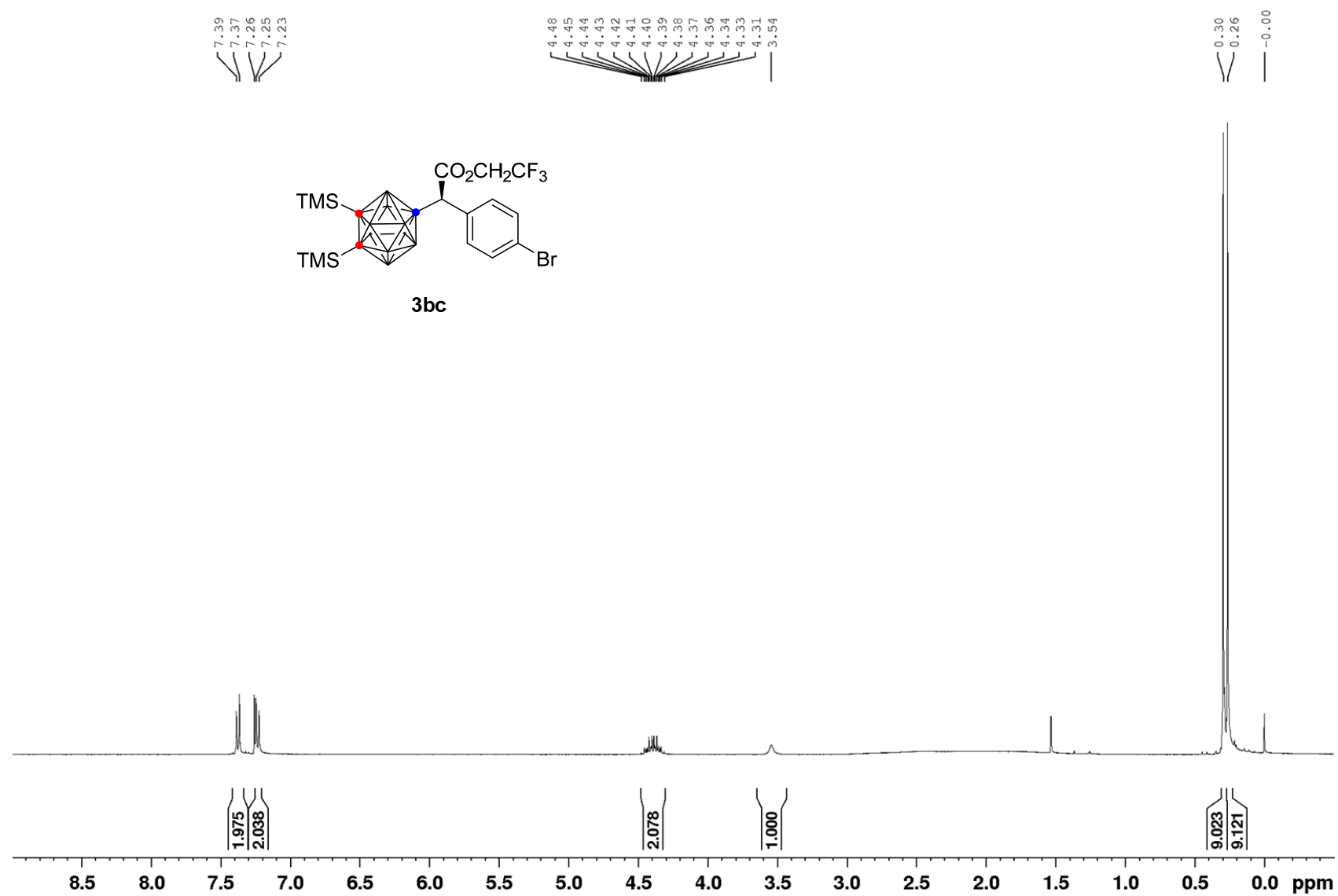
^{11}B NMR (128 MHz, CDCl_3)



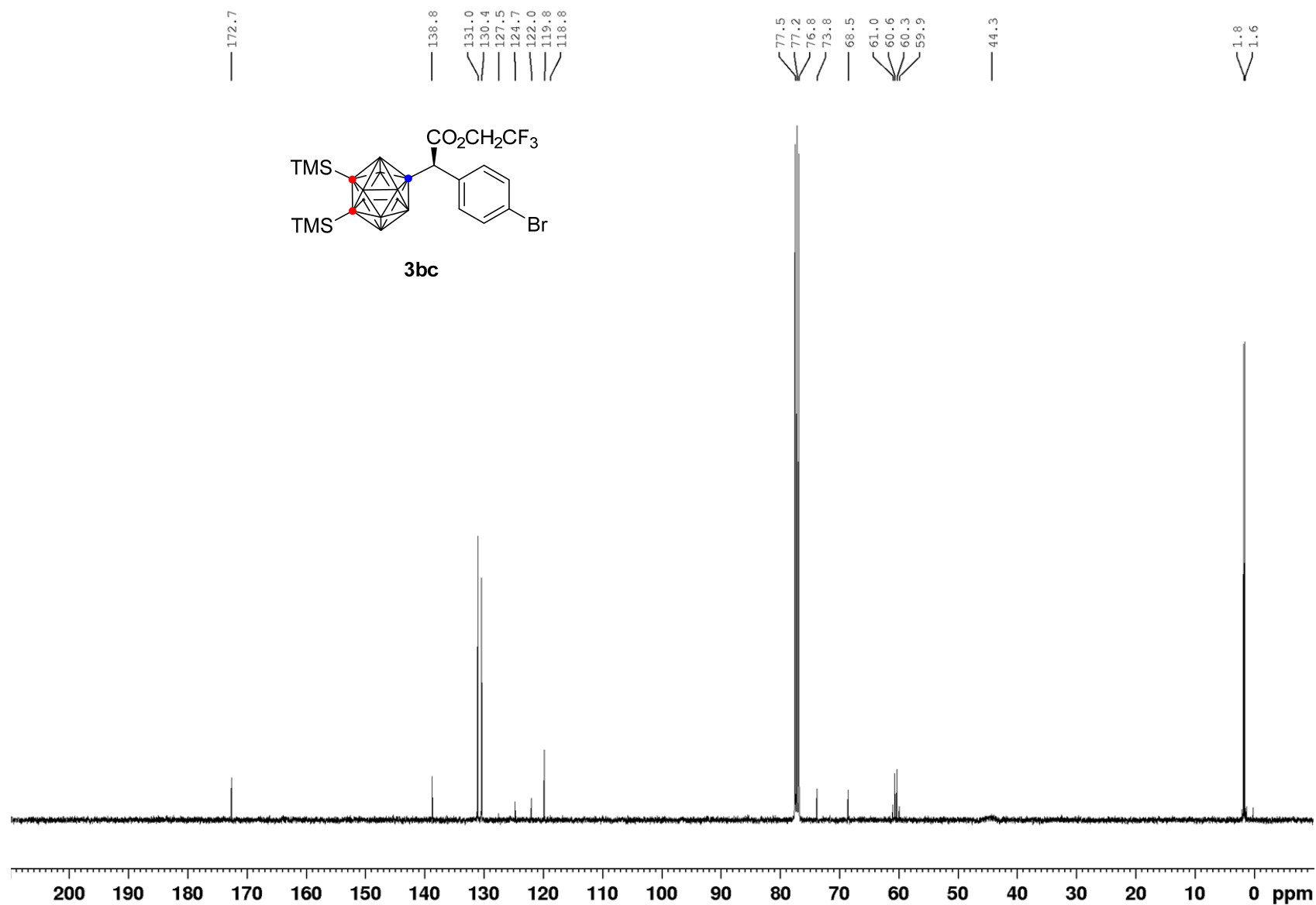
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



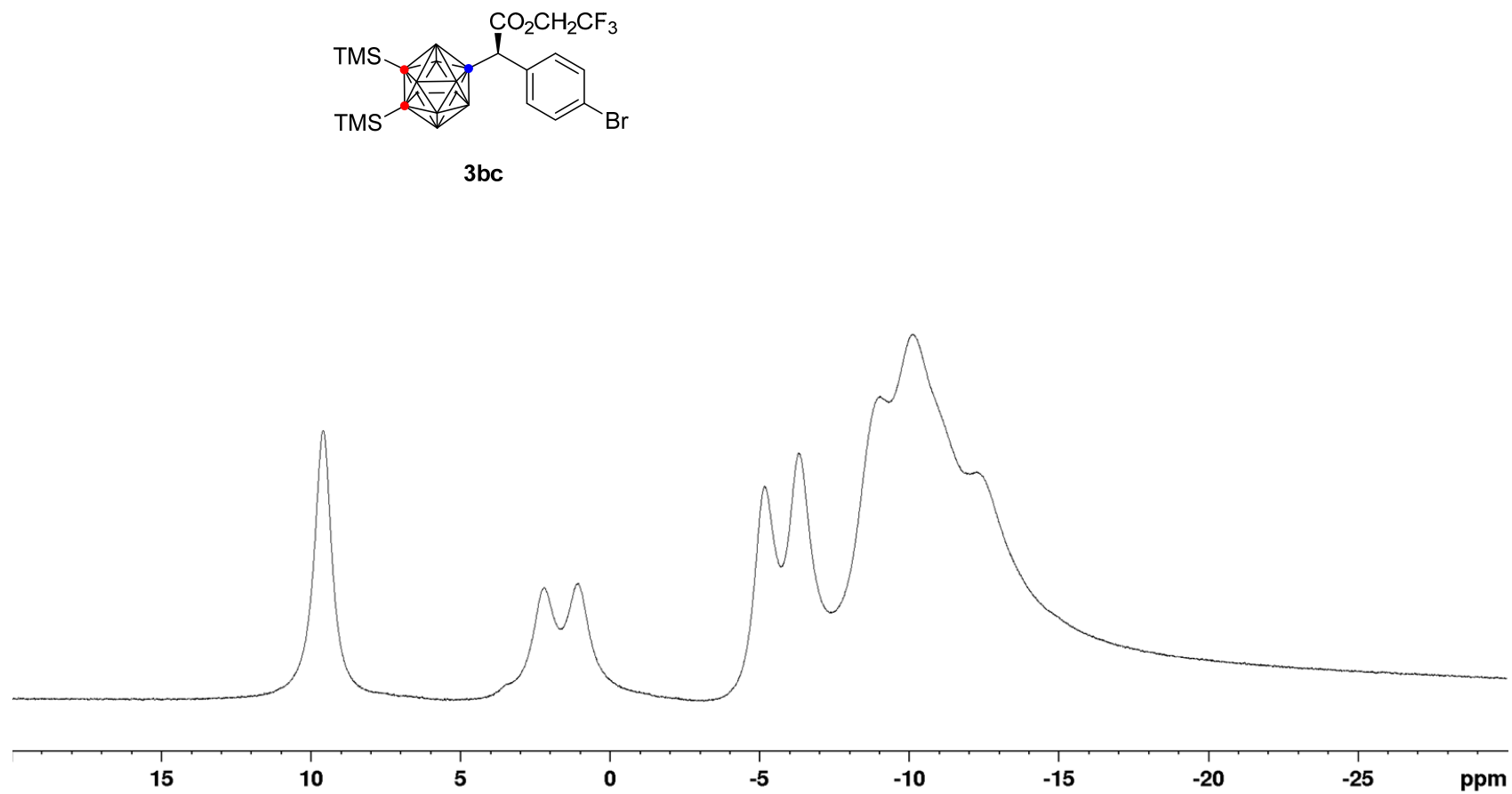
¹H NMR (400 MHz, CDCl₃)



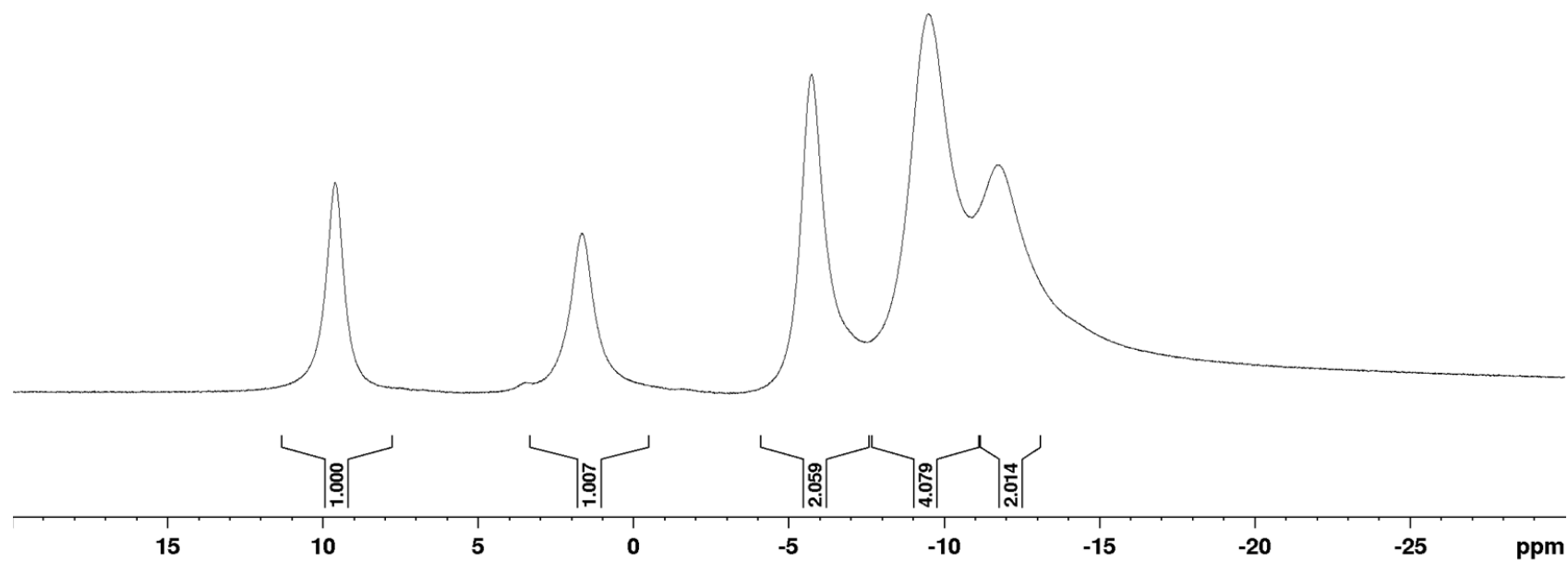
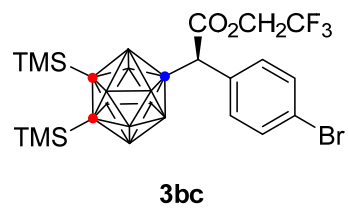
^{13}C NMR (100 MHz, CDCl_3)



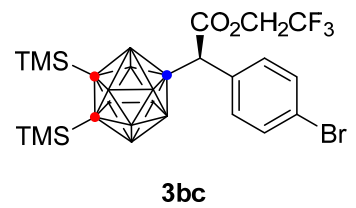
^{11}B NMR (128 MHz, CDCl_3)



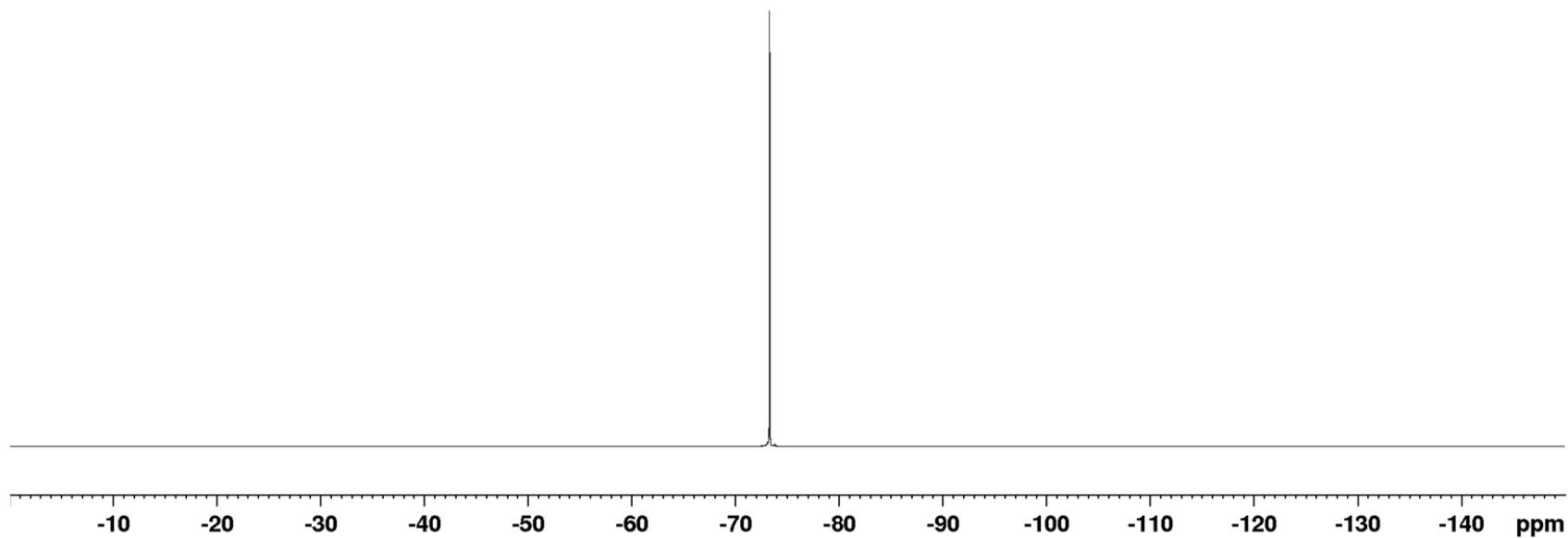
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



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



— -73.31



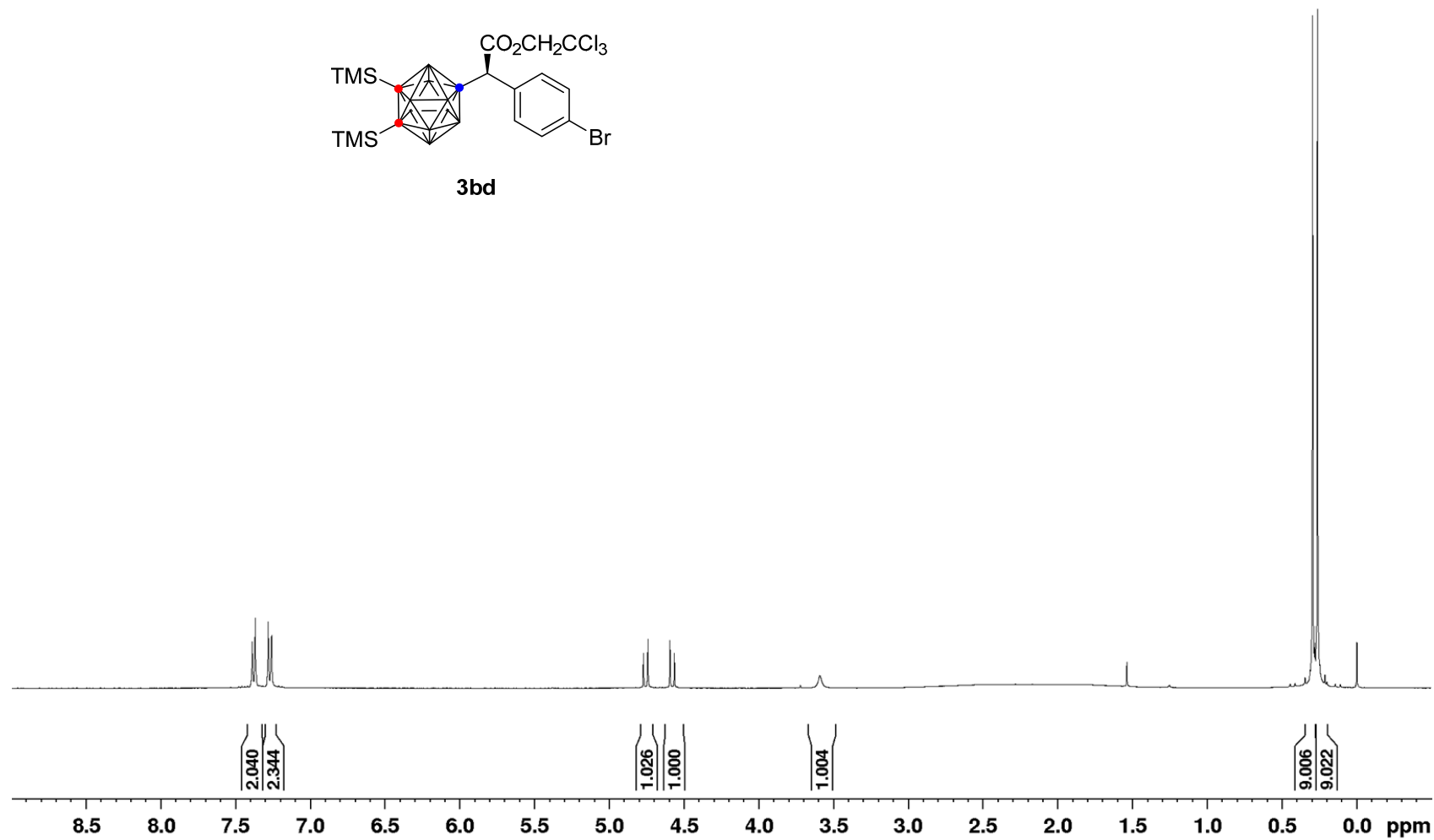
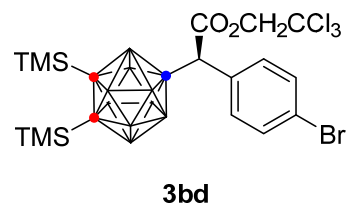
^1H NMR (400 MHz, CDCl_3)

7.39
7.37
7.28
7.26
7.26

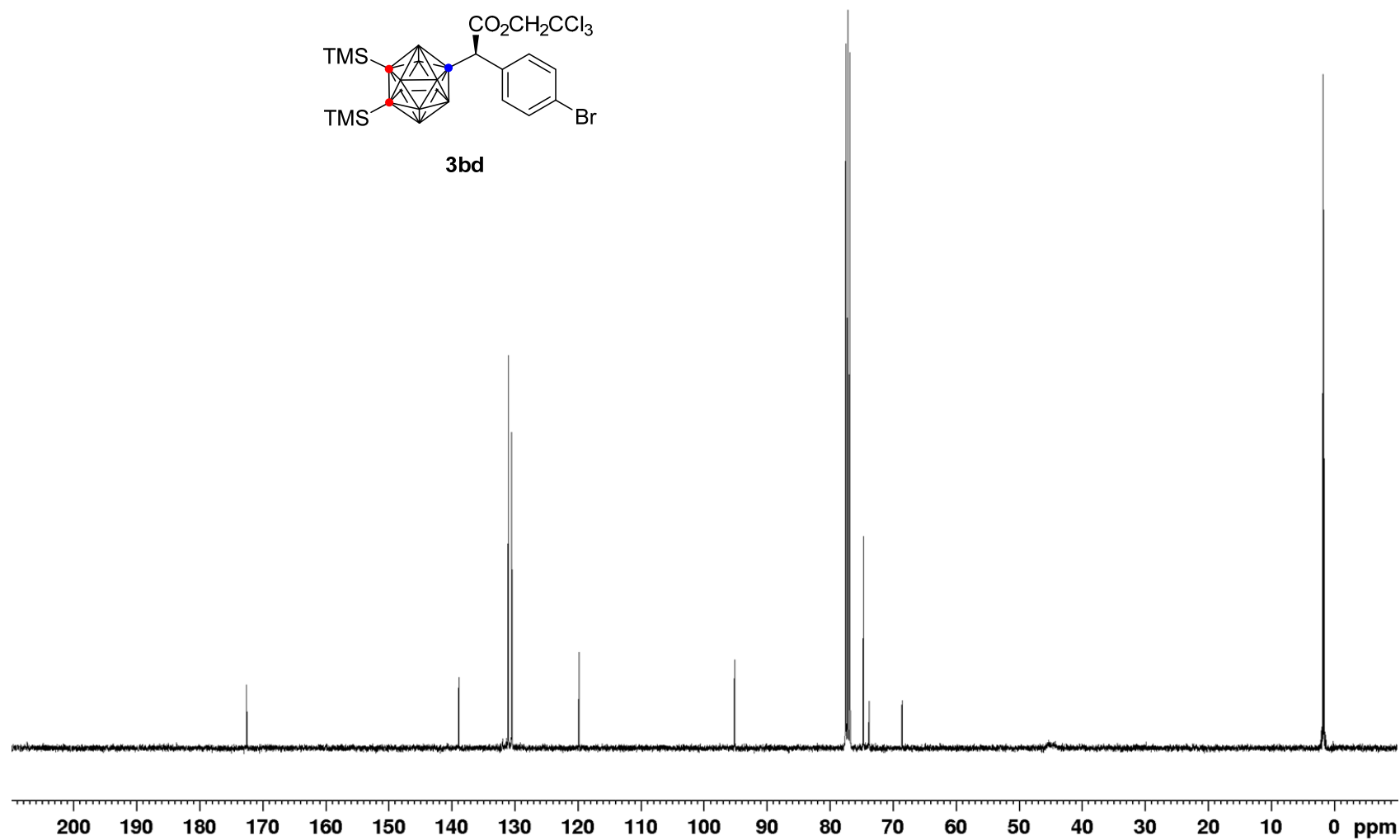
4.77
4.74
4.59
4.56

3.59

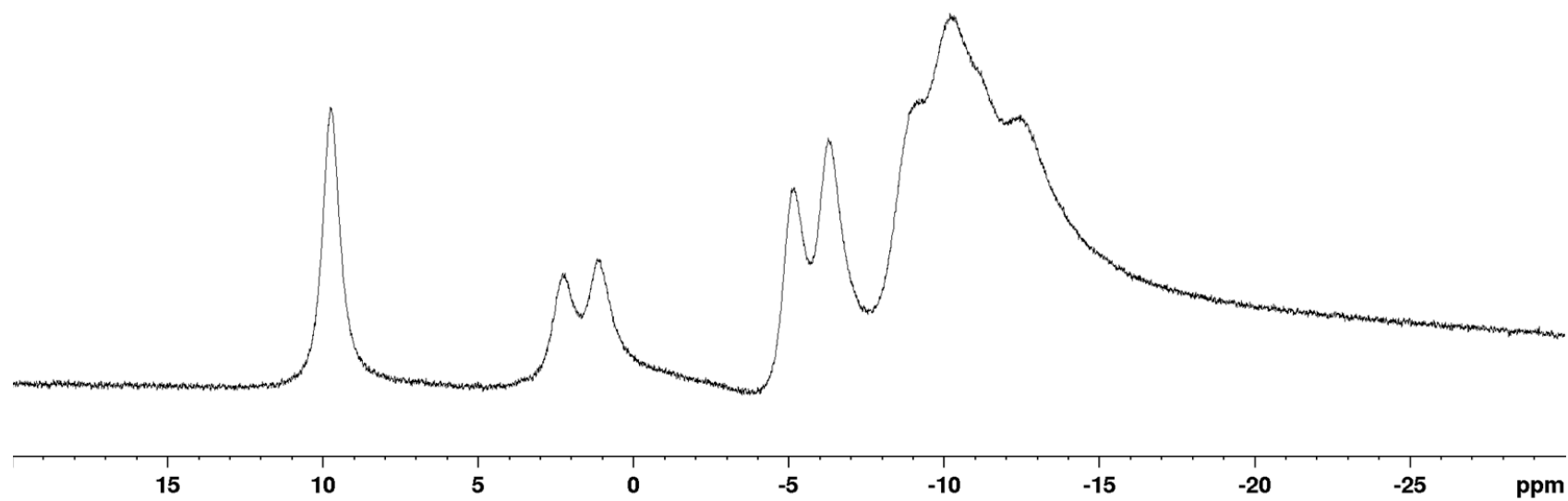
0.29
0.26
-0.00



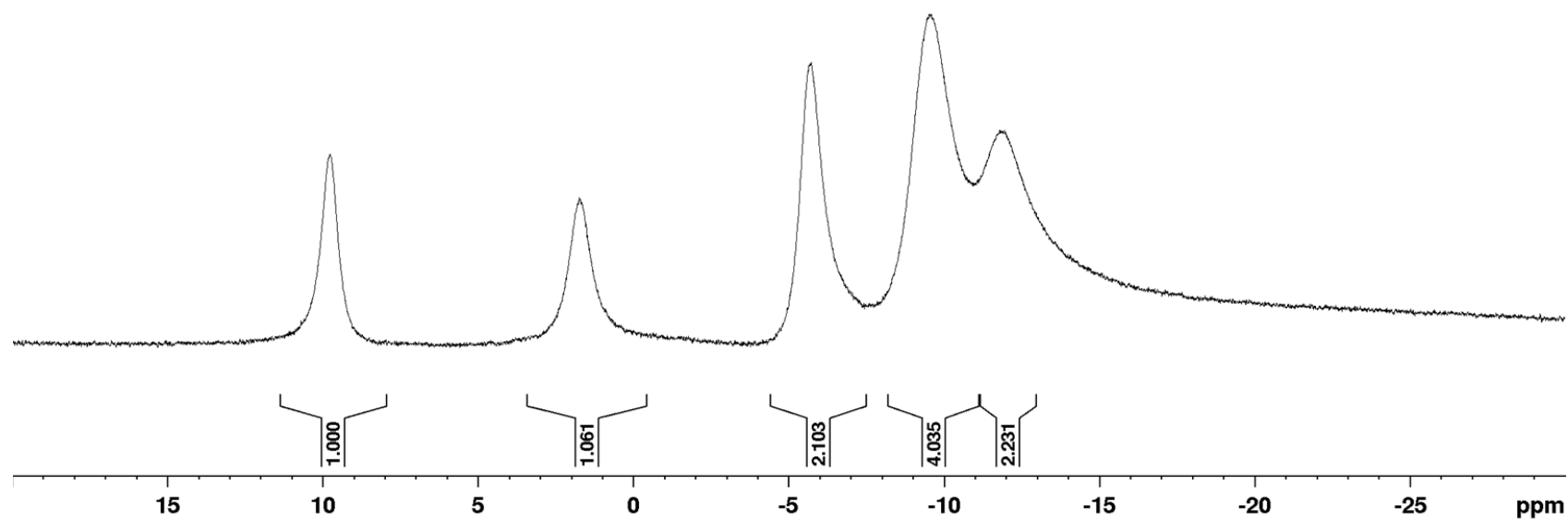
^{13}C NMR (100 MHz, CDCl_3)



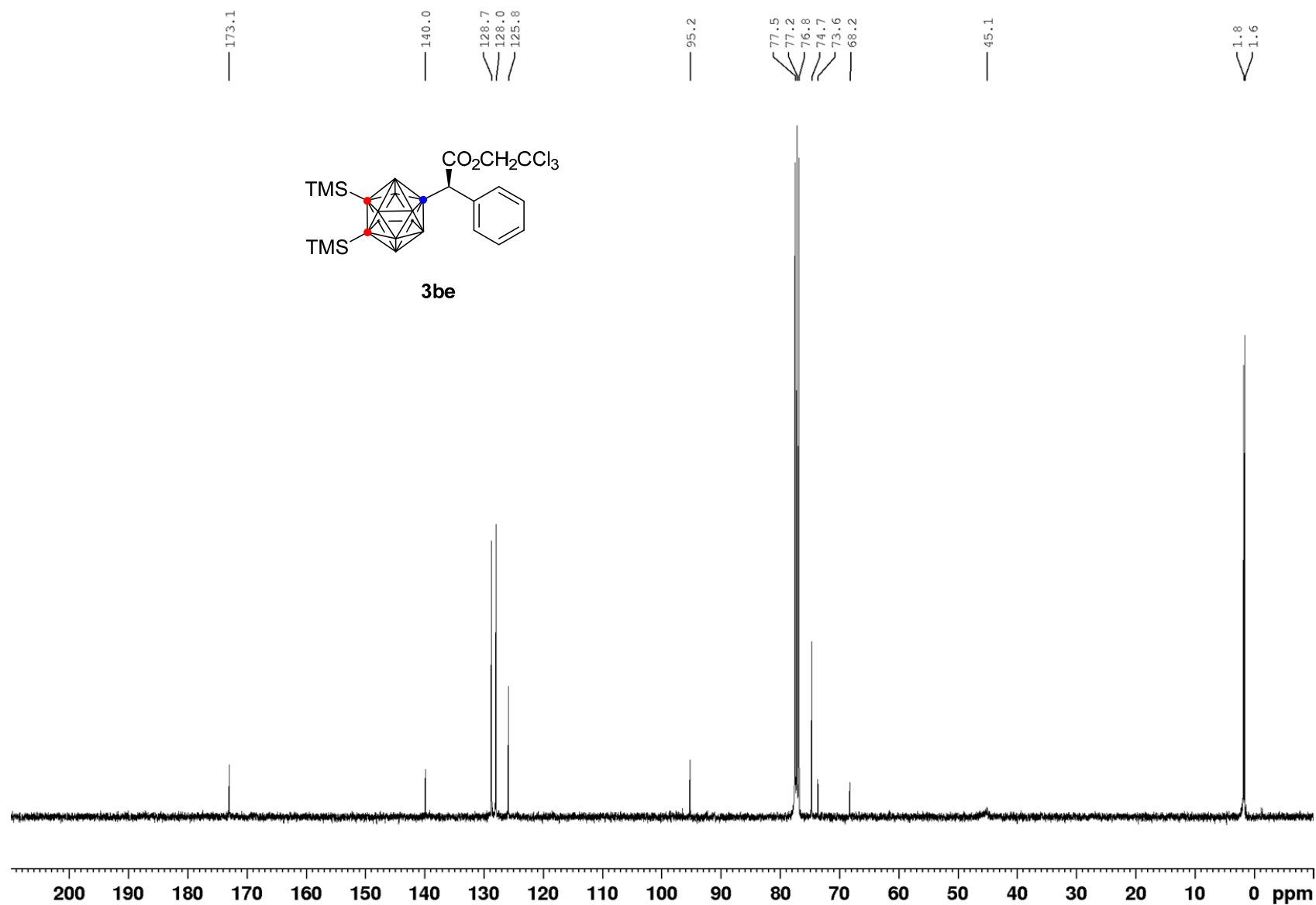
^{11}B NMR (128 MHz, CDCl_3)



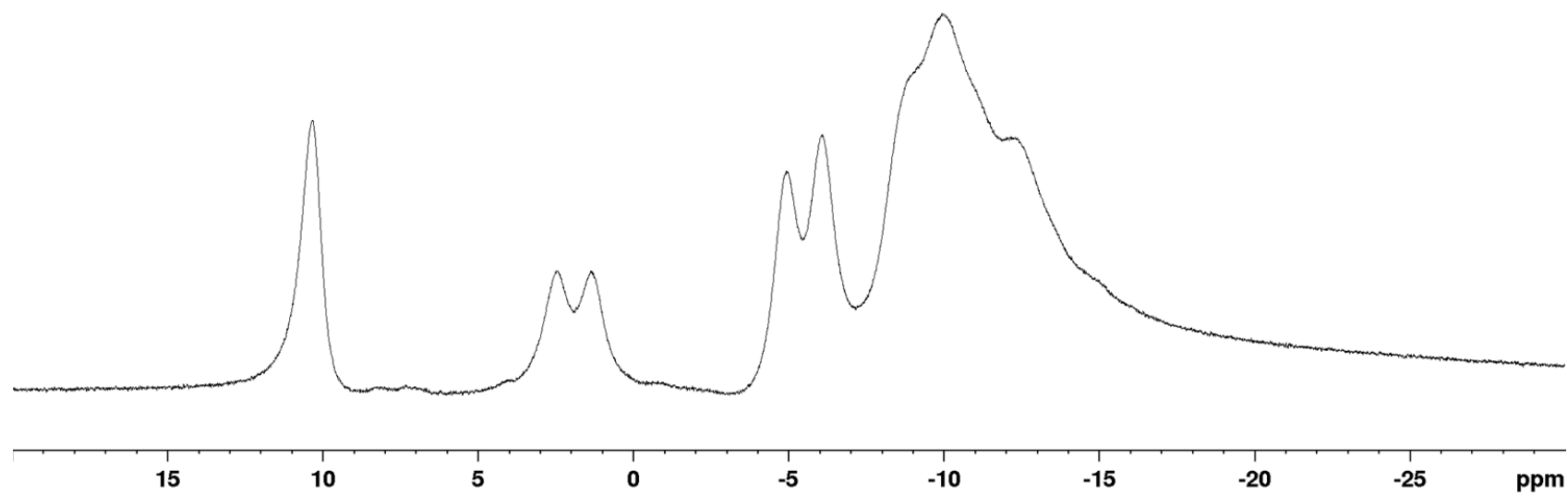
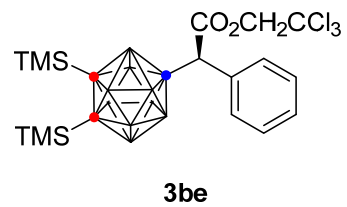
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



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

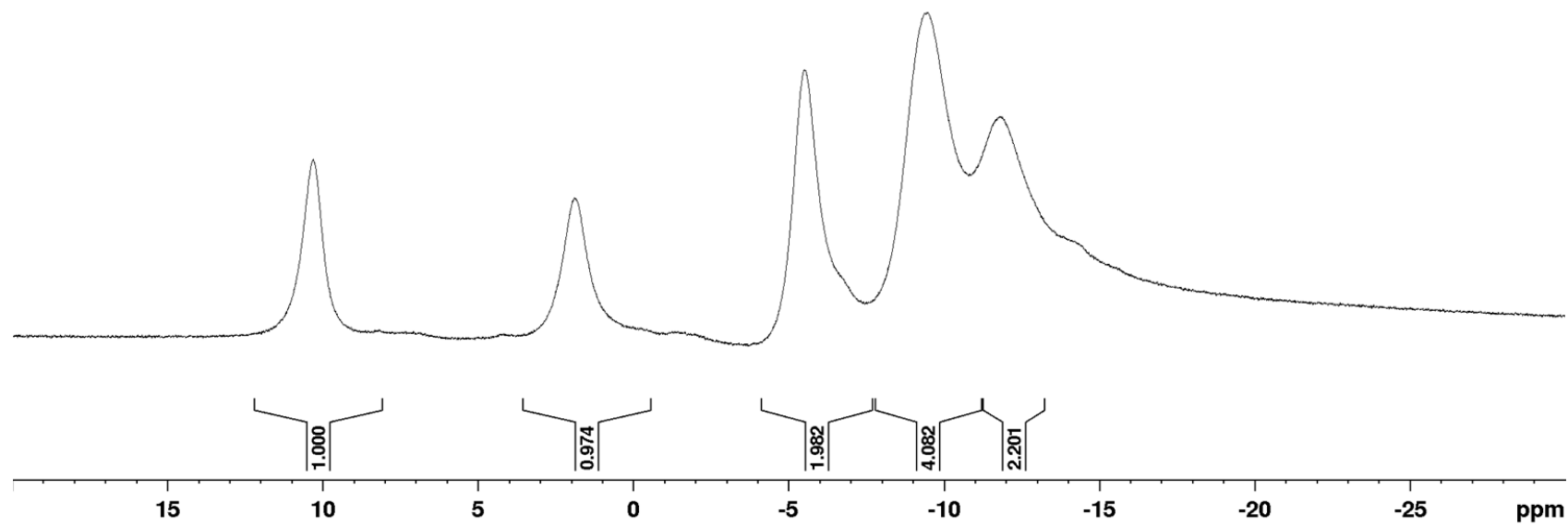
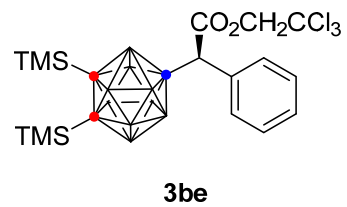


^{11}B NMR (128 MHz, CDCl_3)

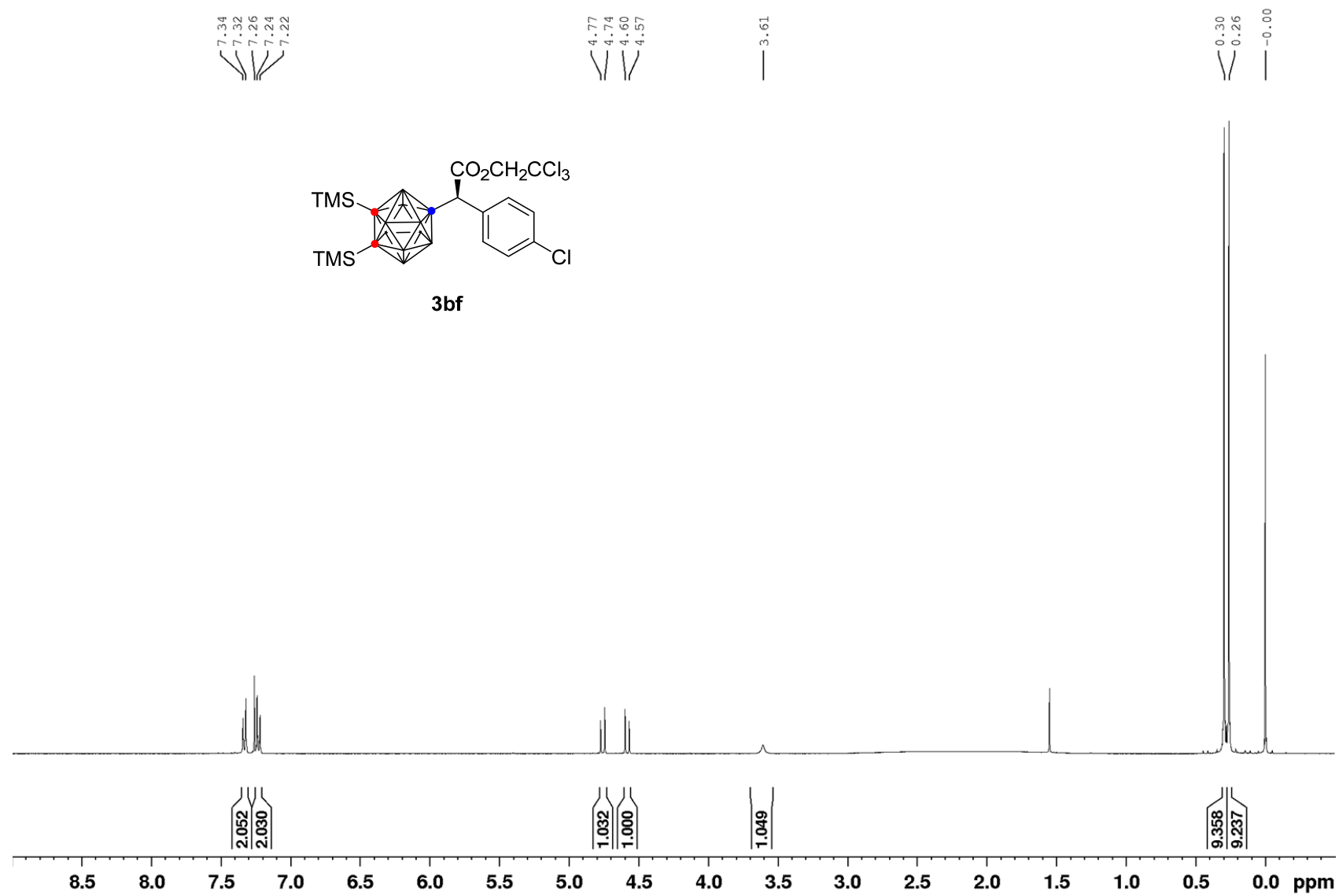


$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)

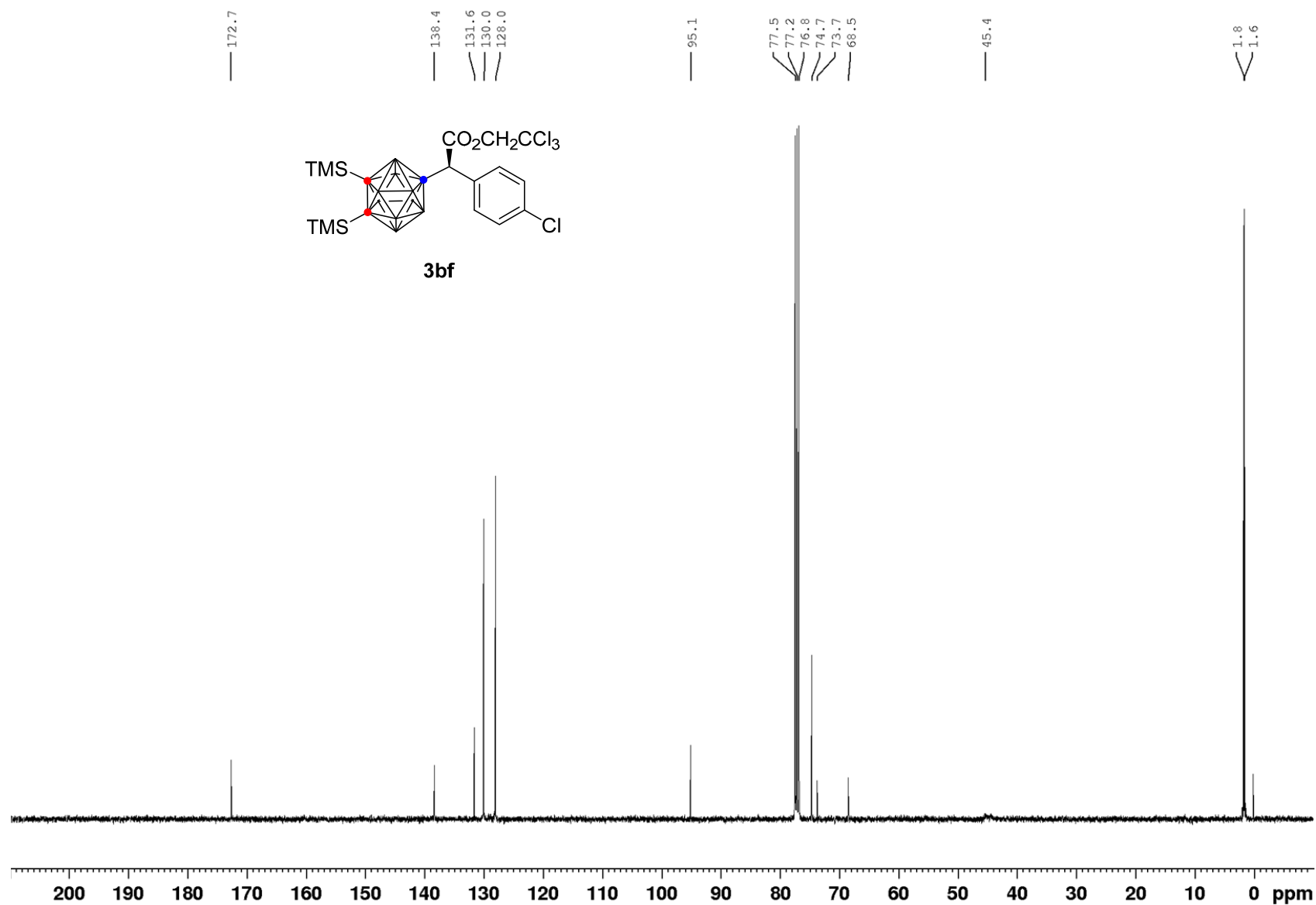
10.31
1.90
-5.51
-9.49
-11.80



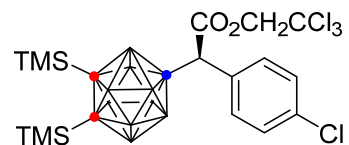
^1H NMR (400 MHz, CDCl_3)



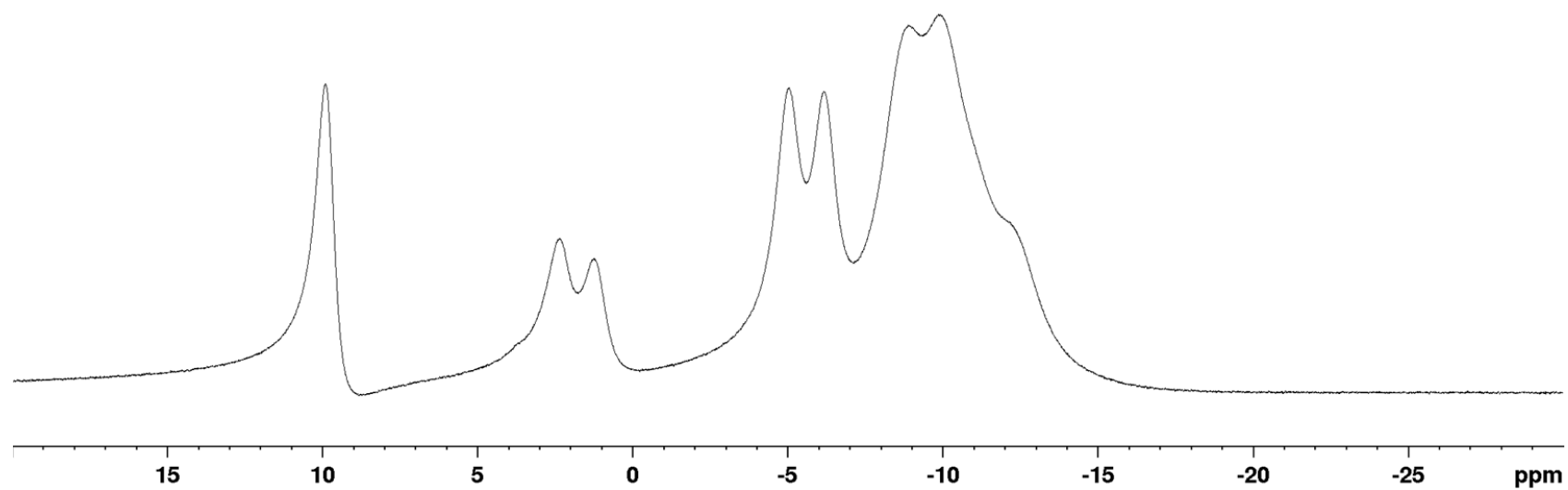
^{13}C NMR (100 MHz, CDCl_3)



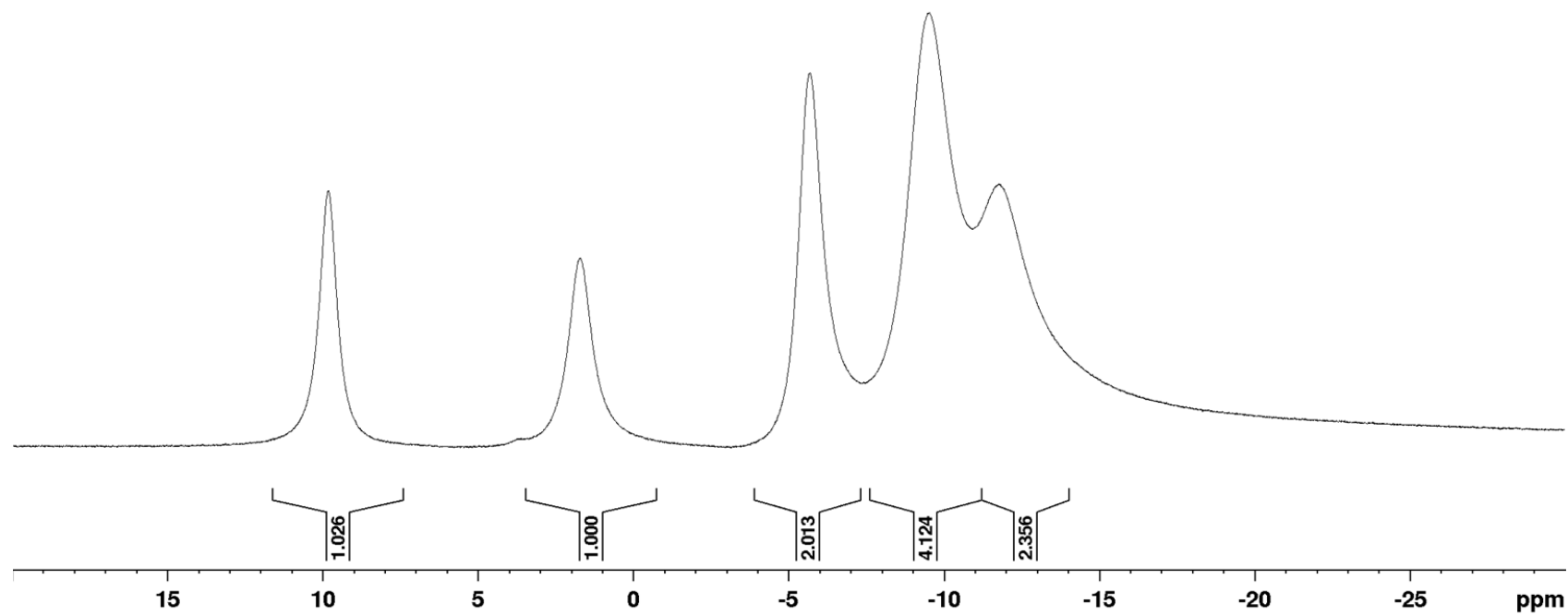
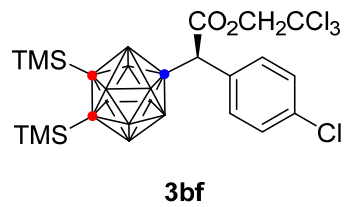
^{11}B NMR (128 MHz, CDCl_3)



3bf



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



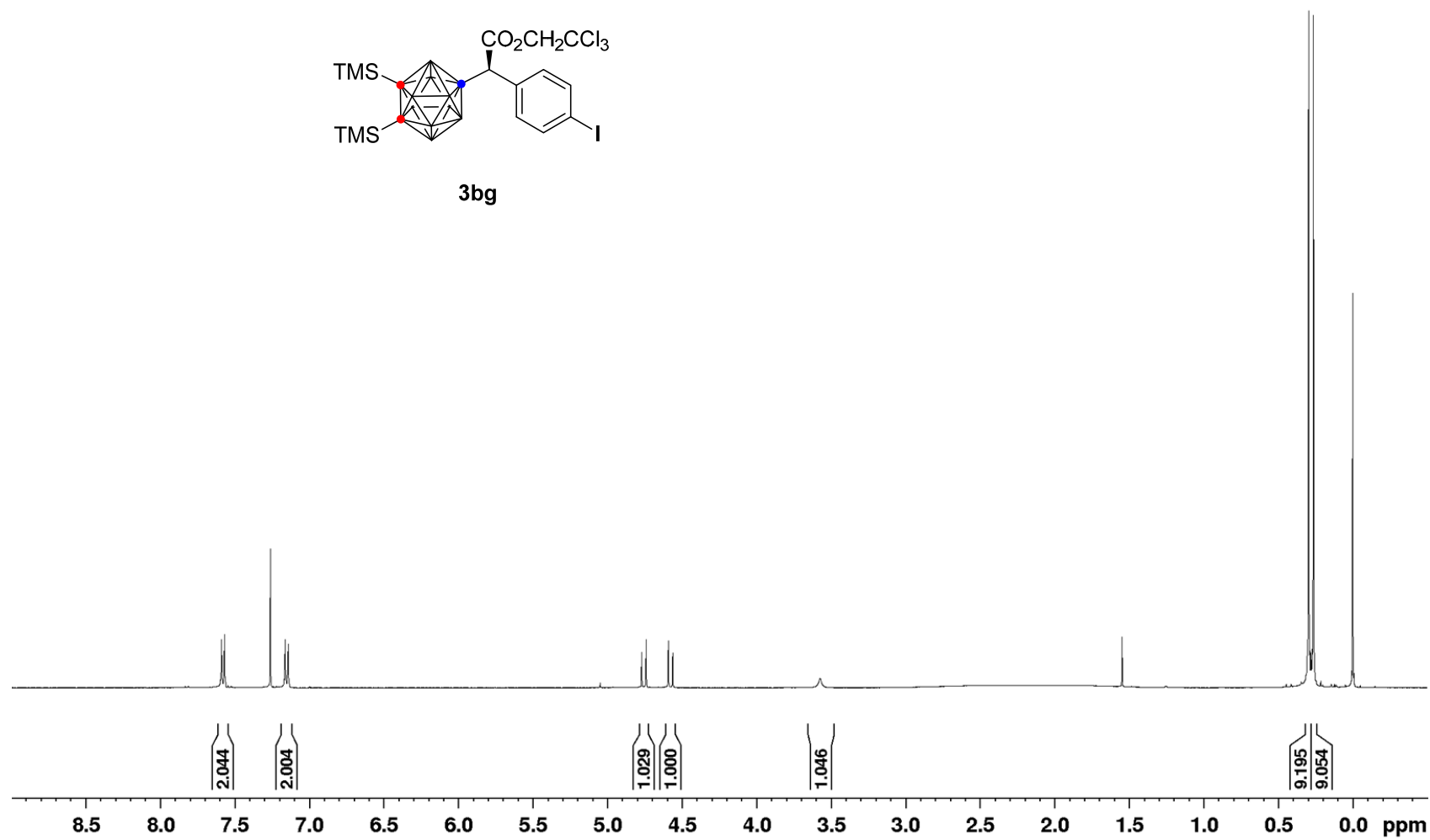
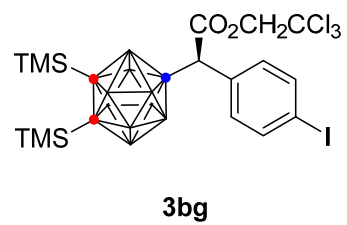
^1H NMR (400 MHz, CDCl_3)

7.59
7.57
7.26
7.16
7.14

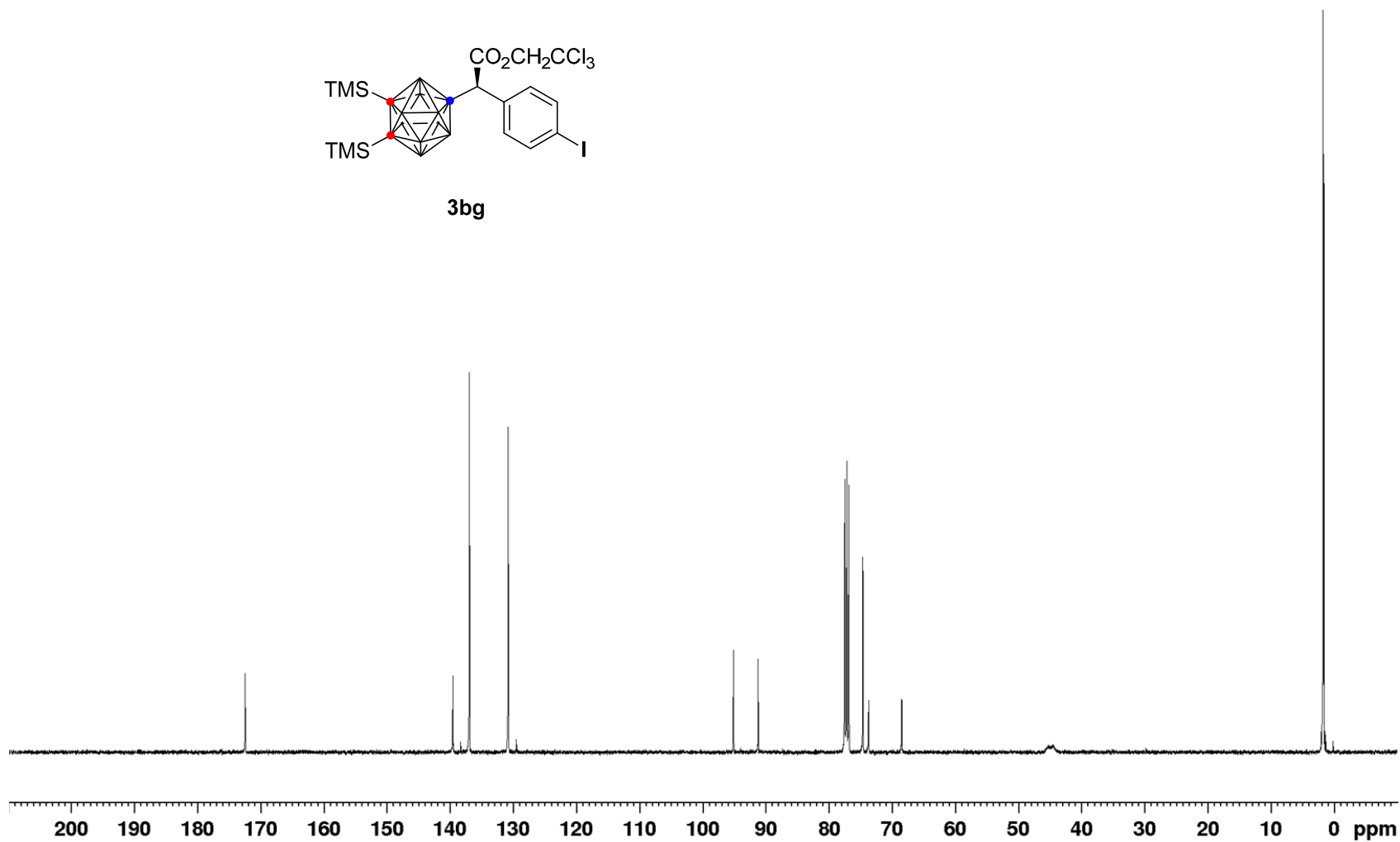
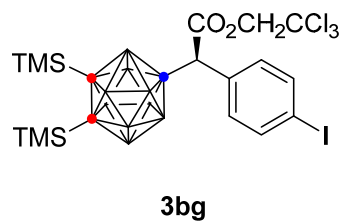
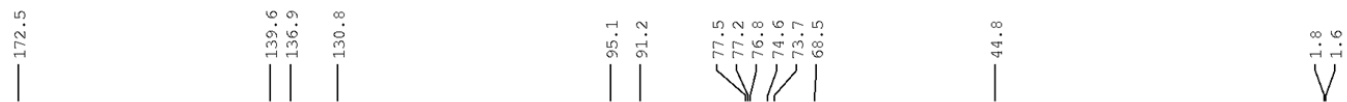
4.77
4.74
4.59
4.56

3.57

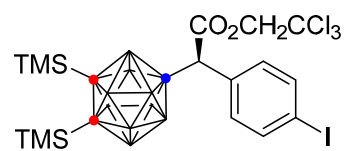
0.30
0.26
-0.00



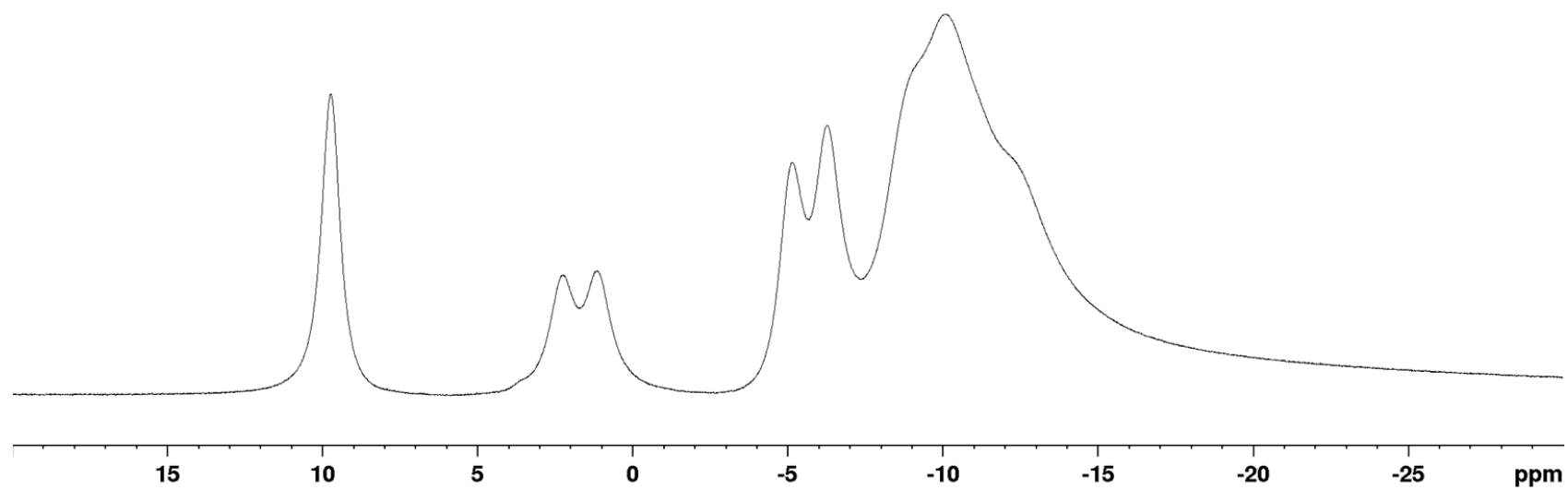
^{13}C NMR (100 MHz, CDCl_3)



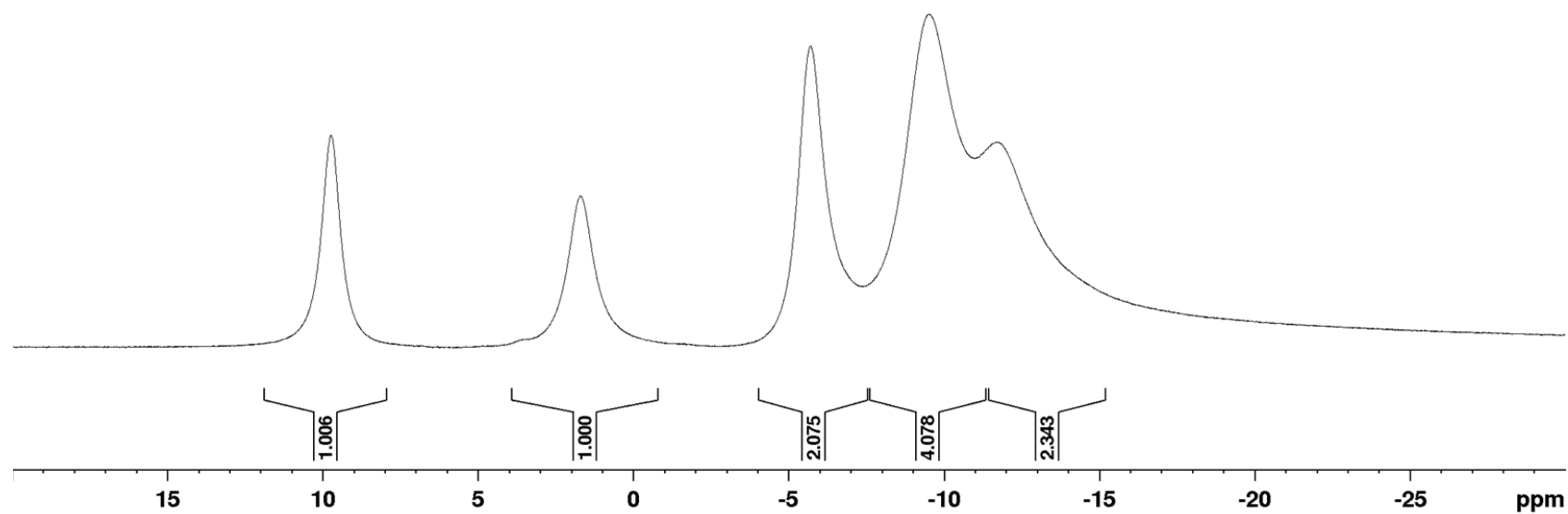
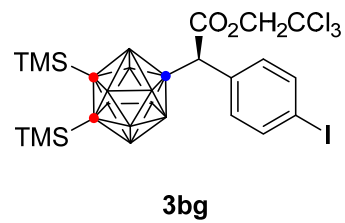
^{11}B NMR (128 MHz, CDCl_3)



3bg



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



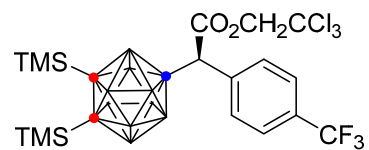
^1H NMR (400 MHz, CDCl_3)

7.52
7.26

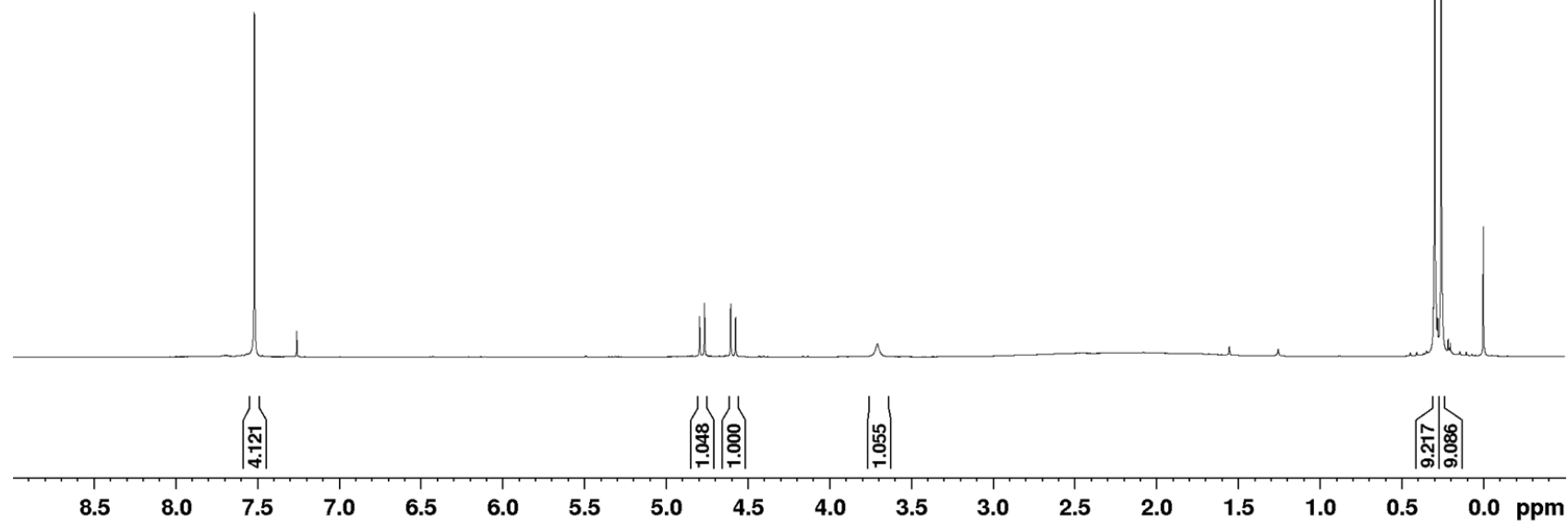
4.80
4.77
4.61
4.58

3.71

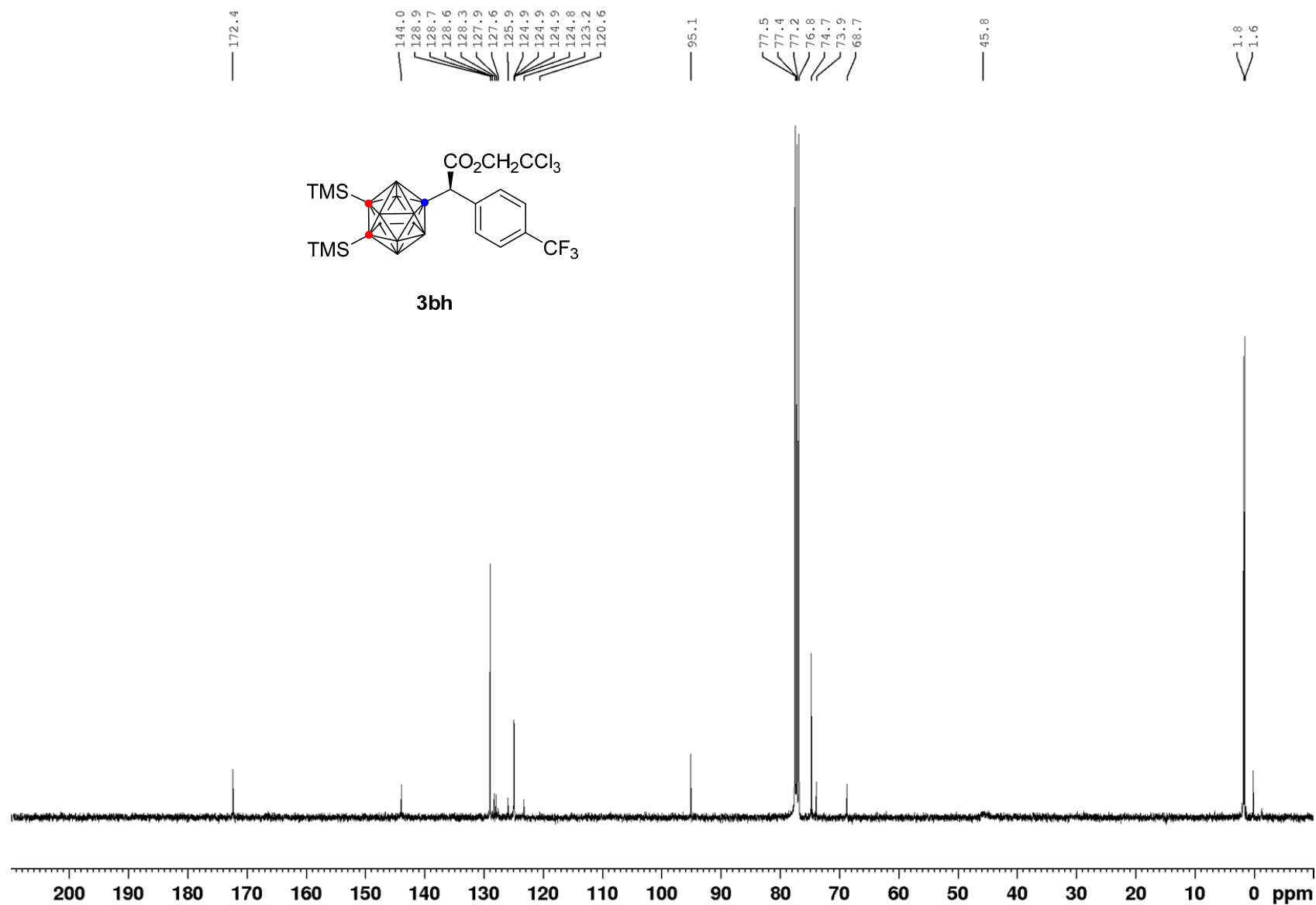
0.30
0.26
-0.00



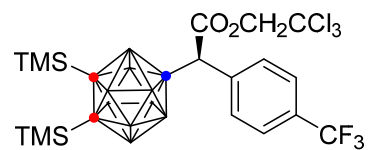
3bh



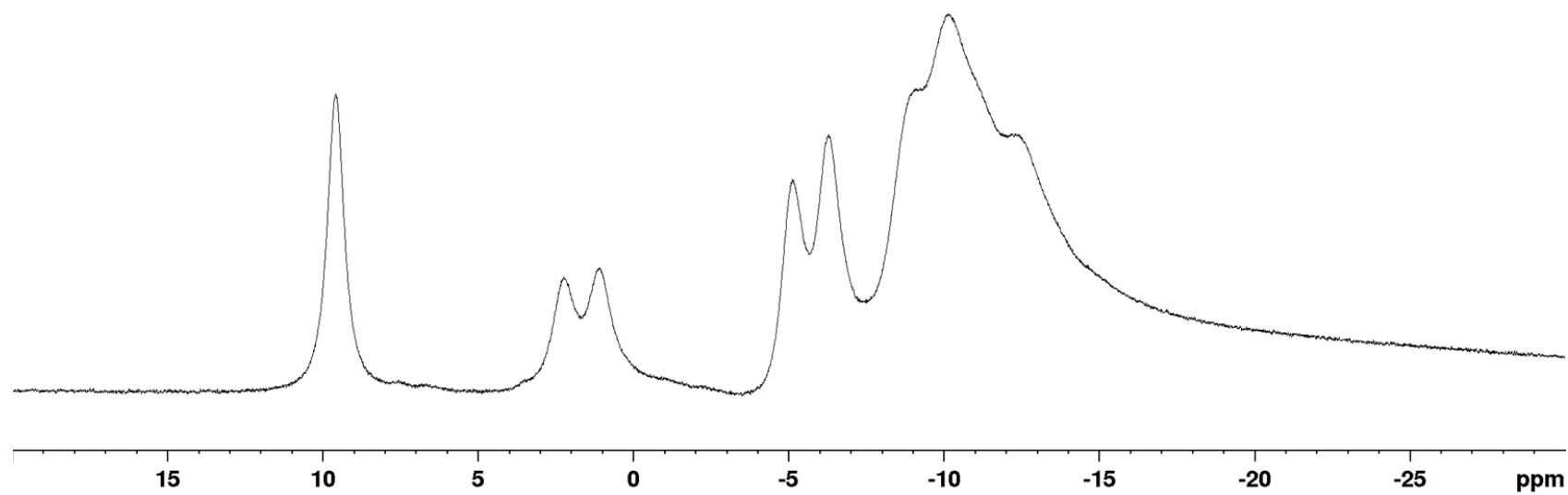
^{13}C NMR (100 MHz, CDCl_3)



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



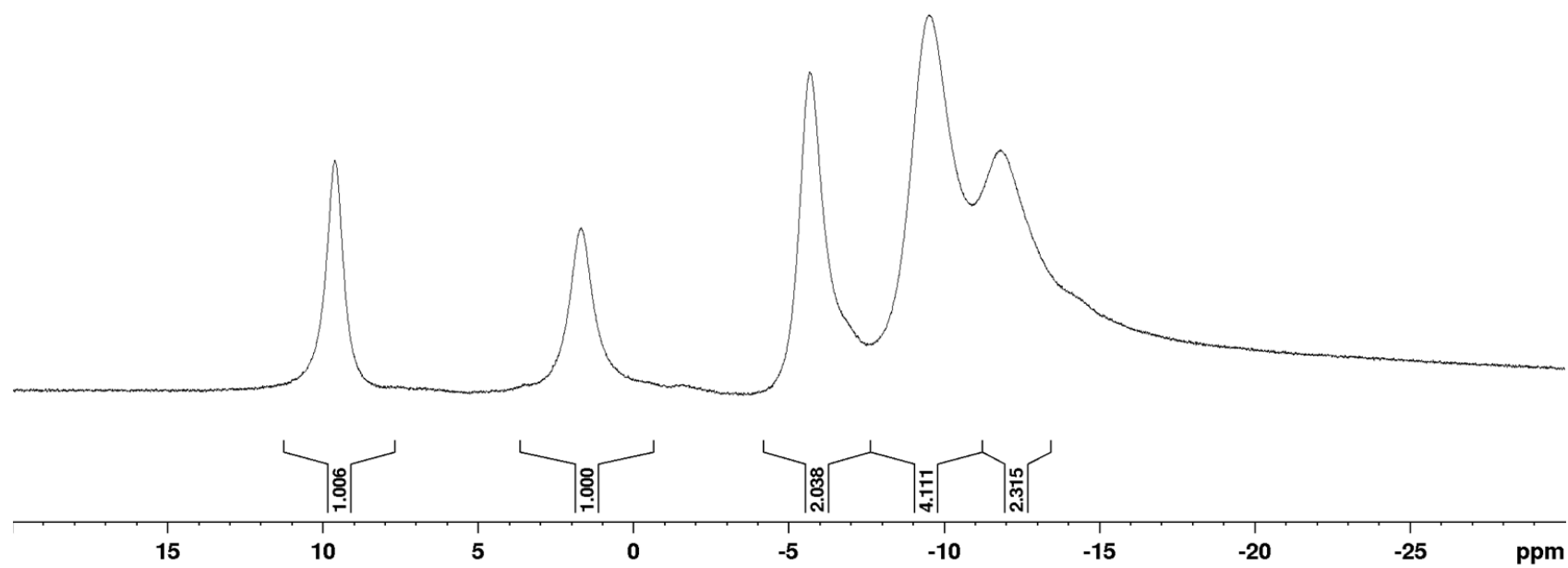
3bh



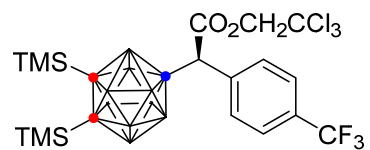
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



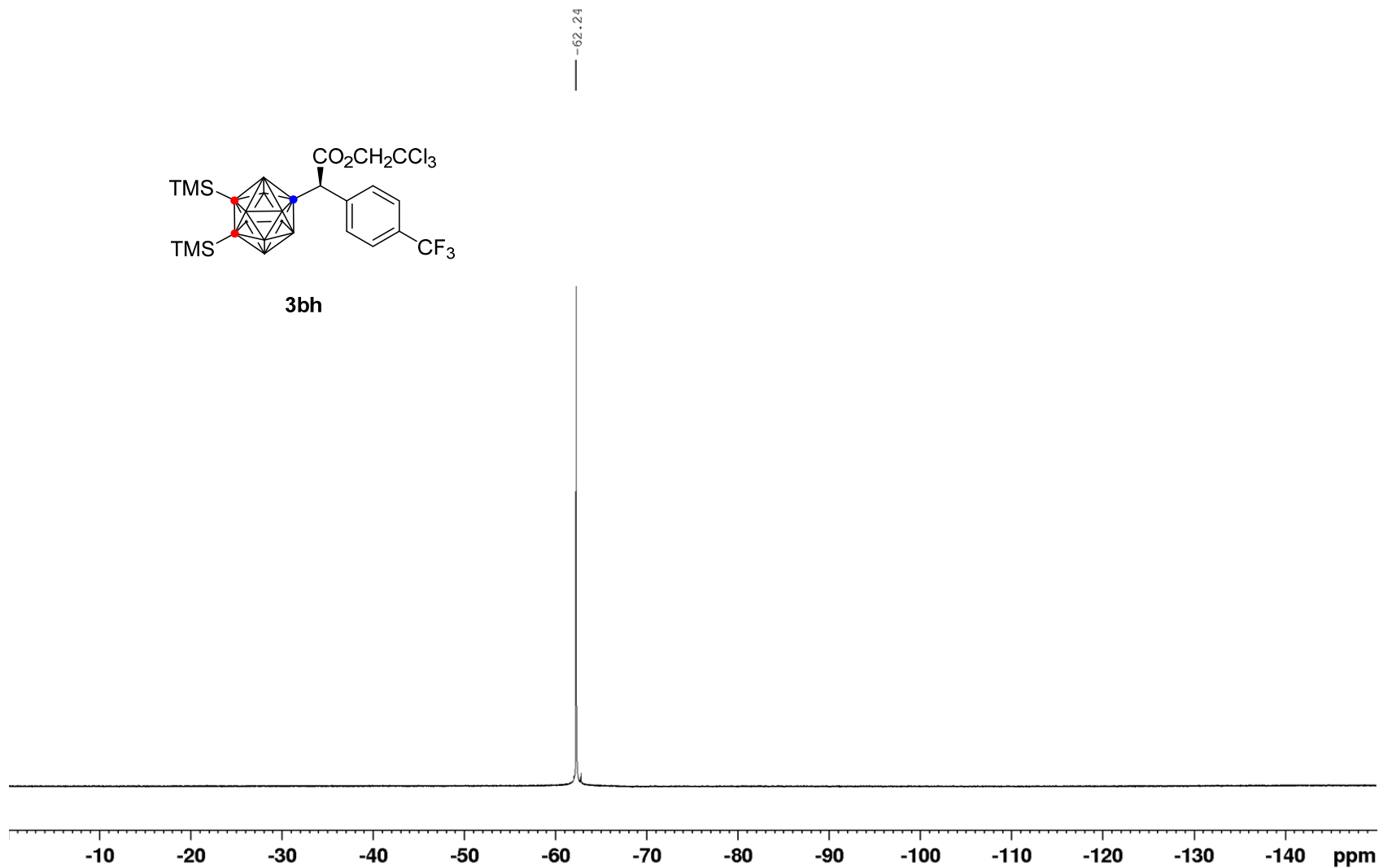
3bh



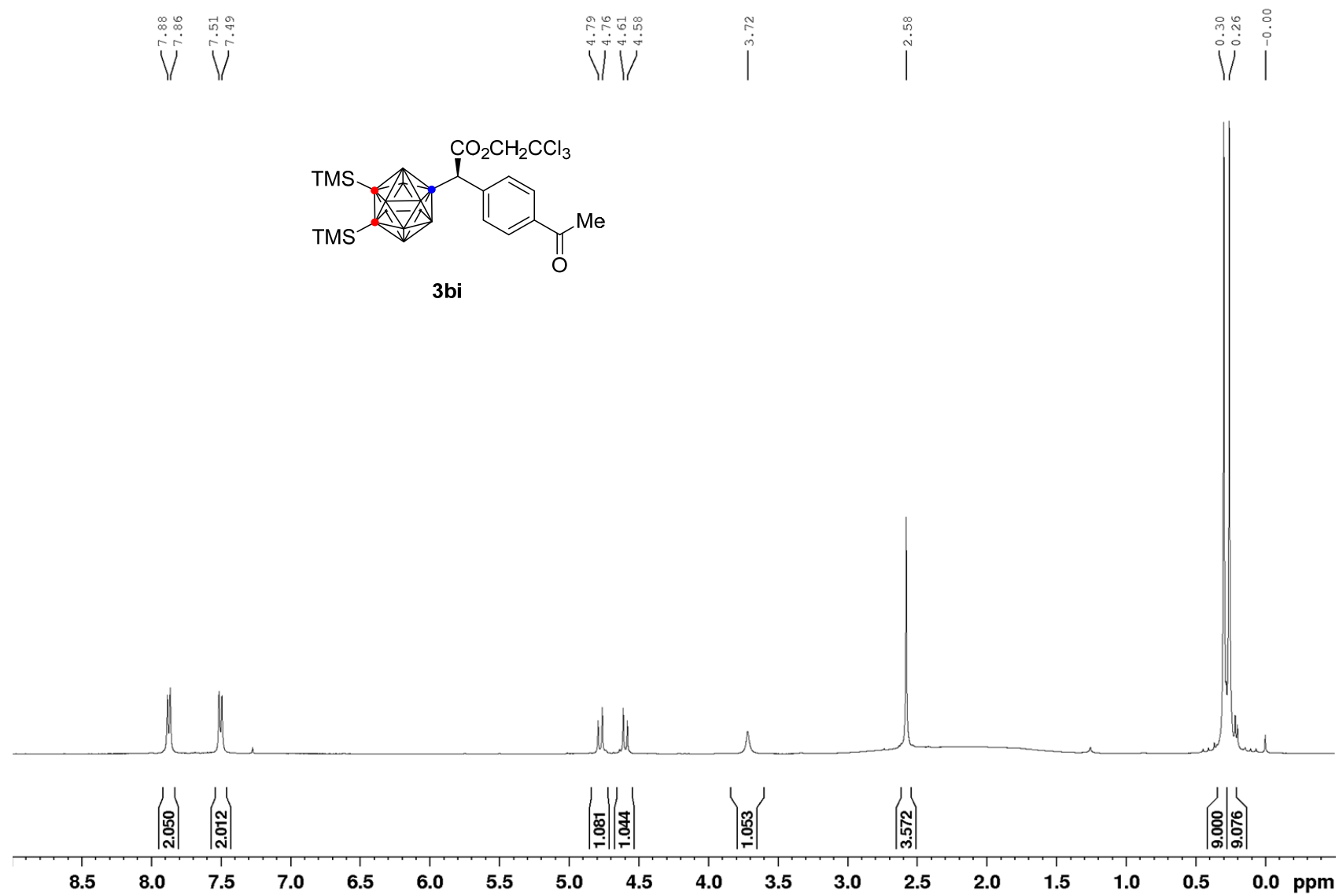
$^{19}\text{F}\{^1\text{H}\}$ NMR (377 MHz, CDCl_3)



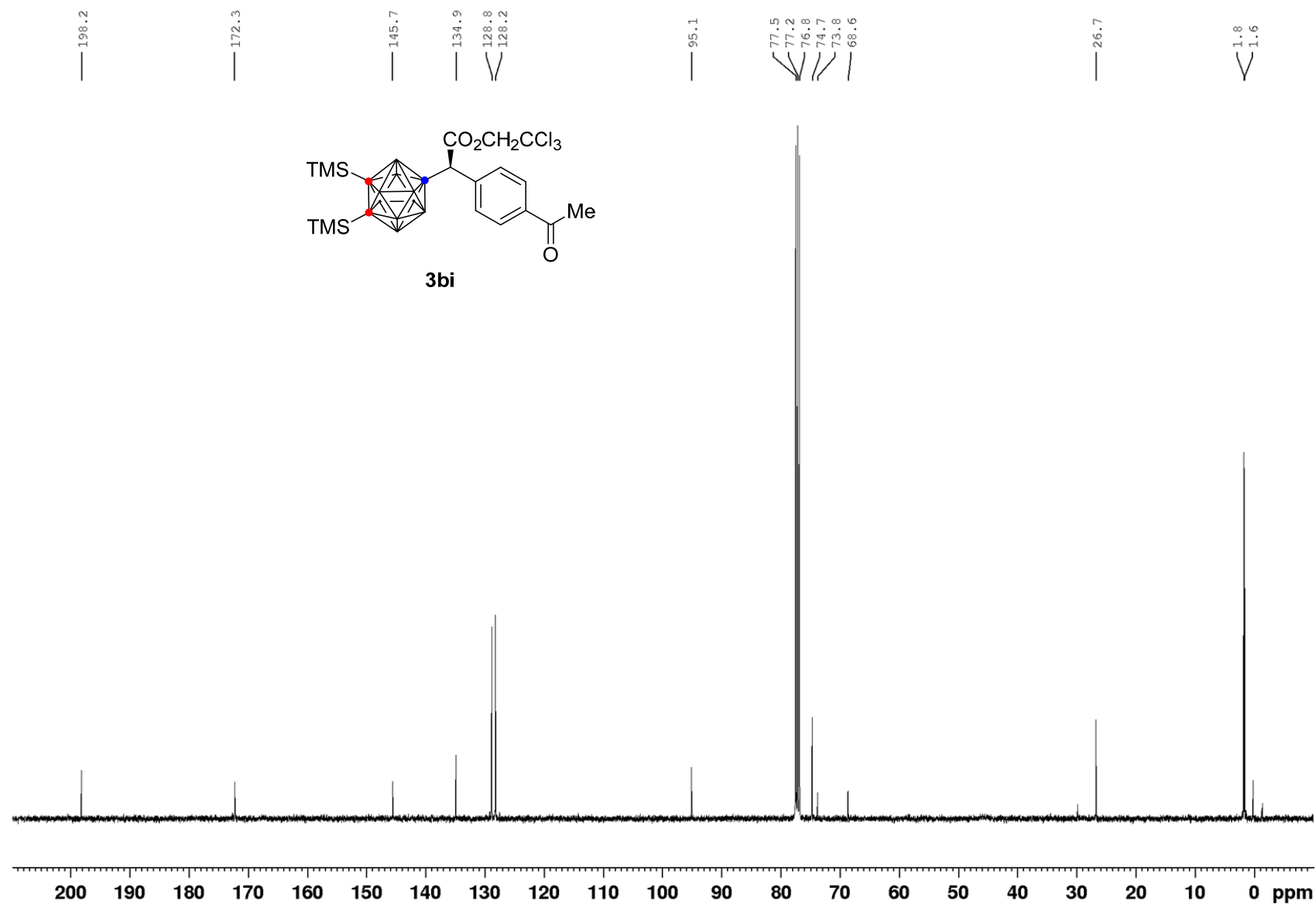
3bh



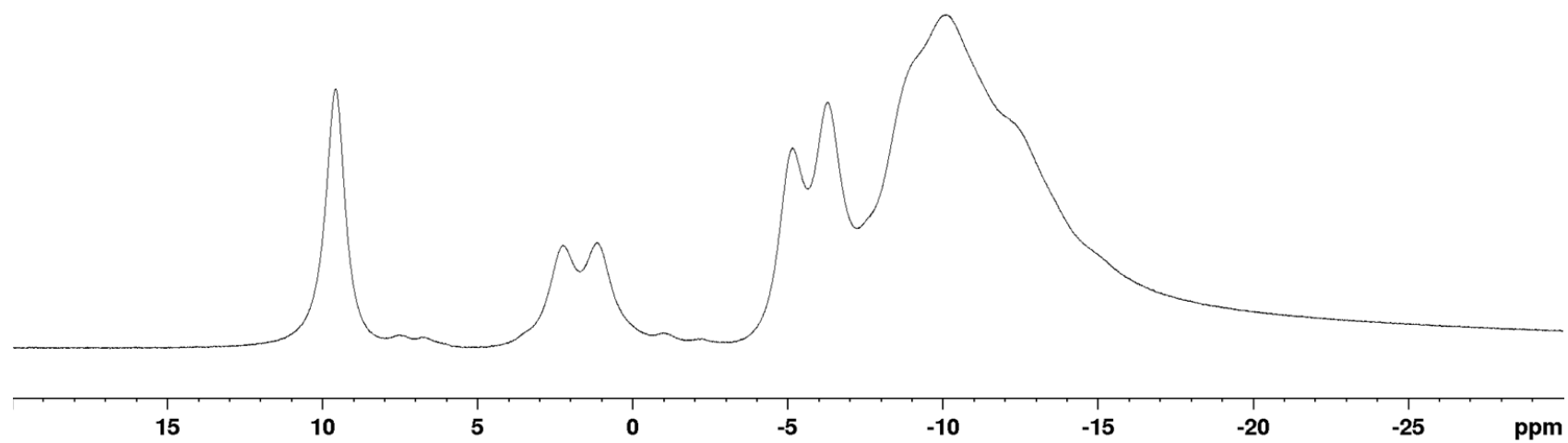
¹H NMR (400 MHz, CDCl₃)



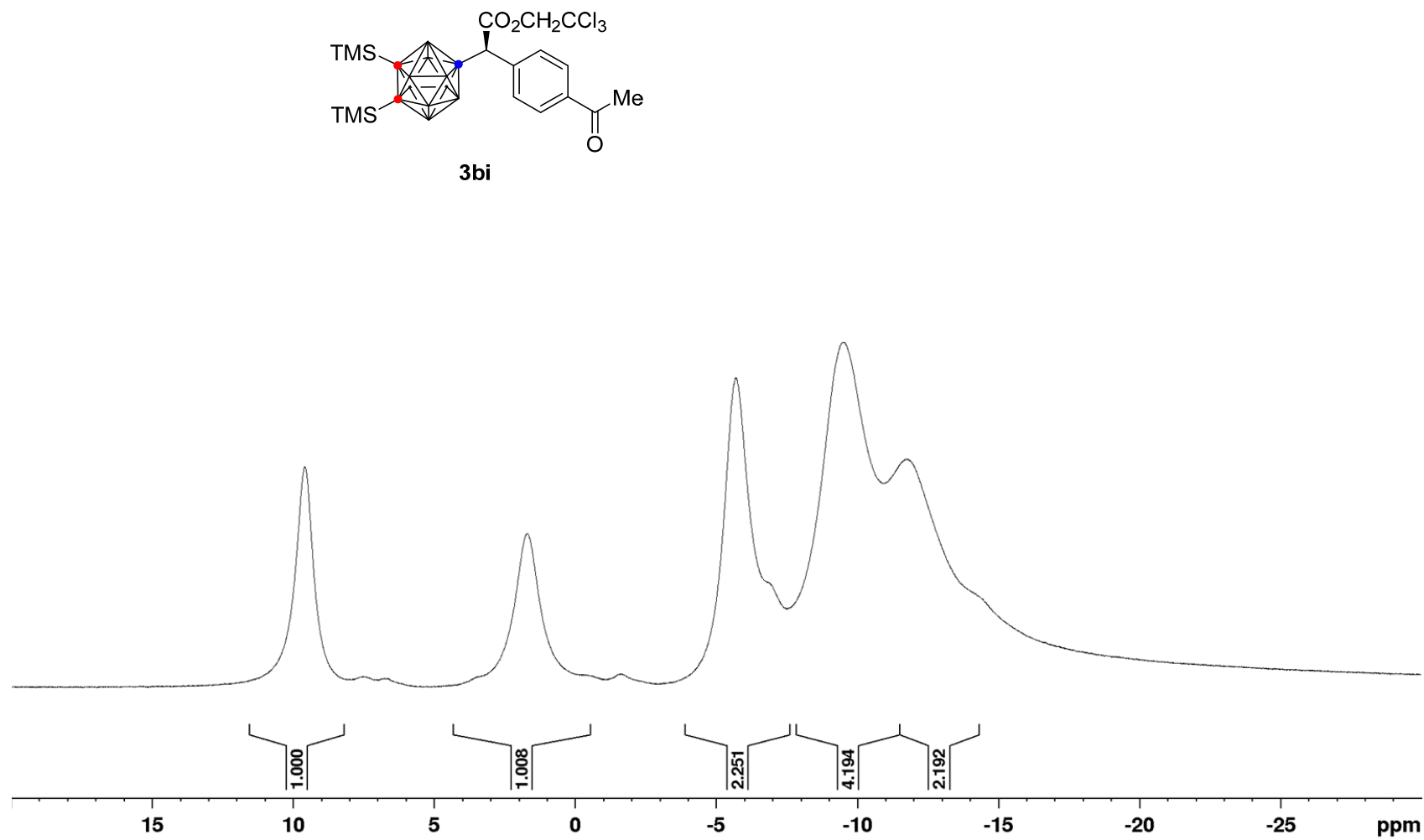
^{13}C NMR (100 MHz, CDCl_3)



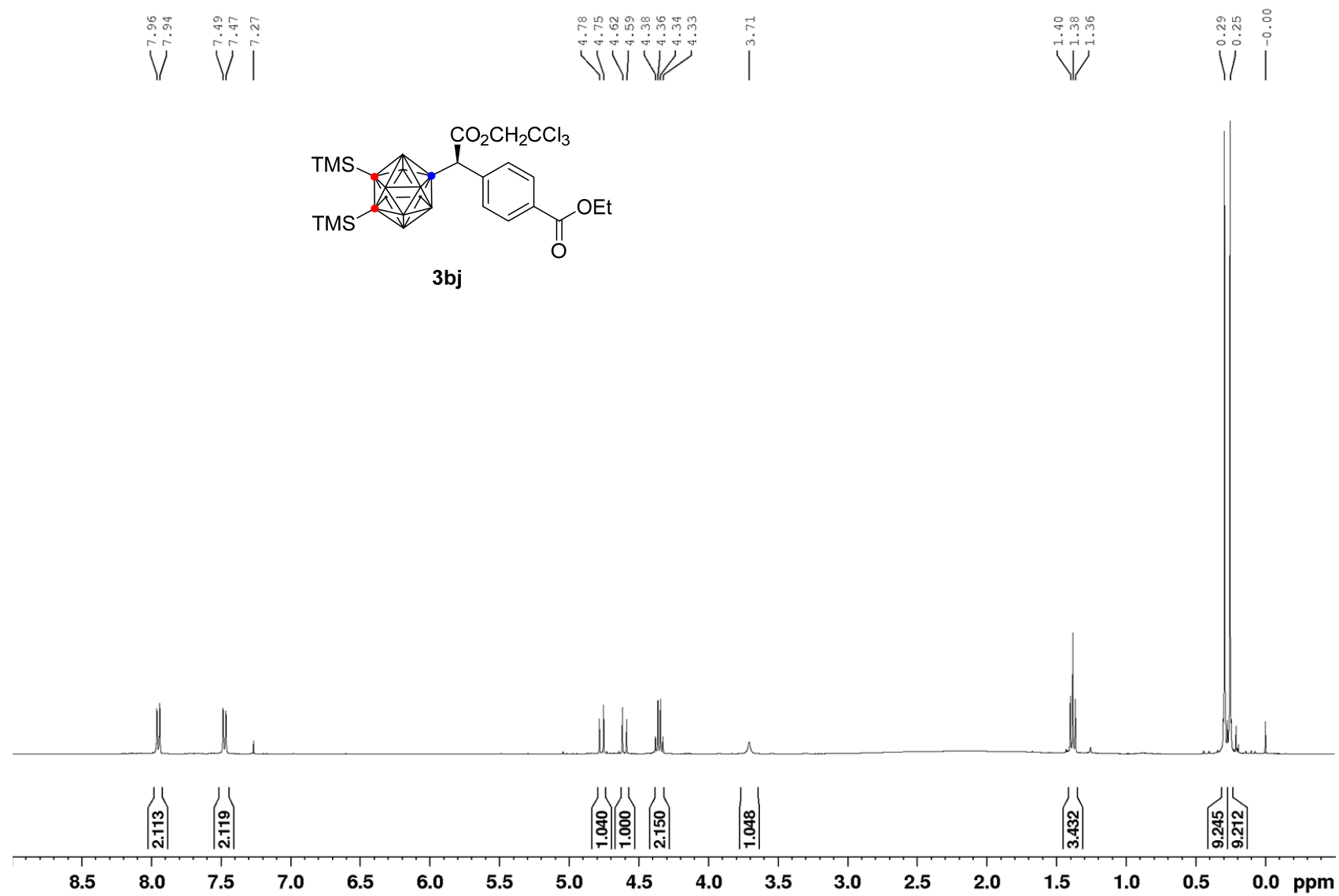
^{11}B NMR (128 MHz, CDCl_3)



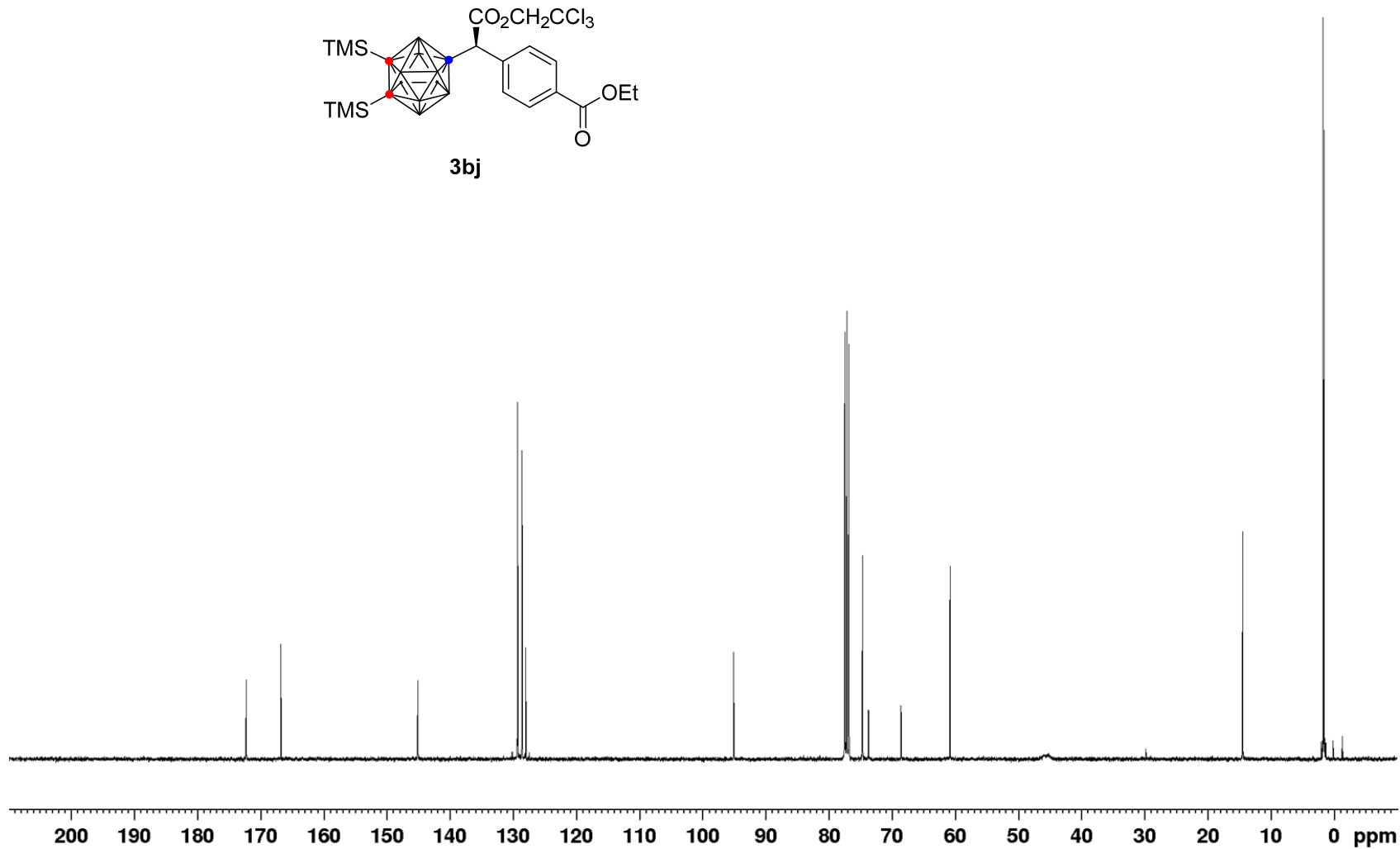
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



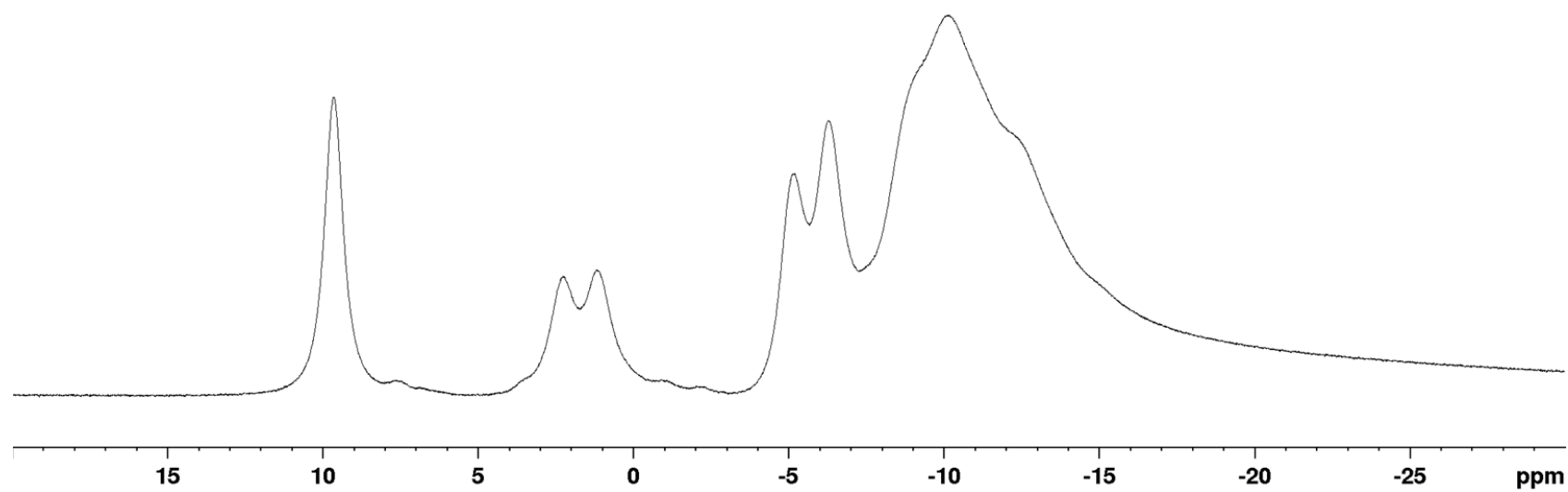
¹H NMR (400 MHz, CDCl₃)



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



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



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

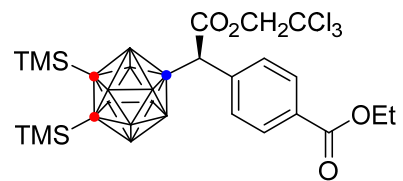
9.65

1.73

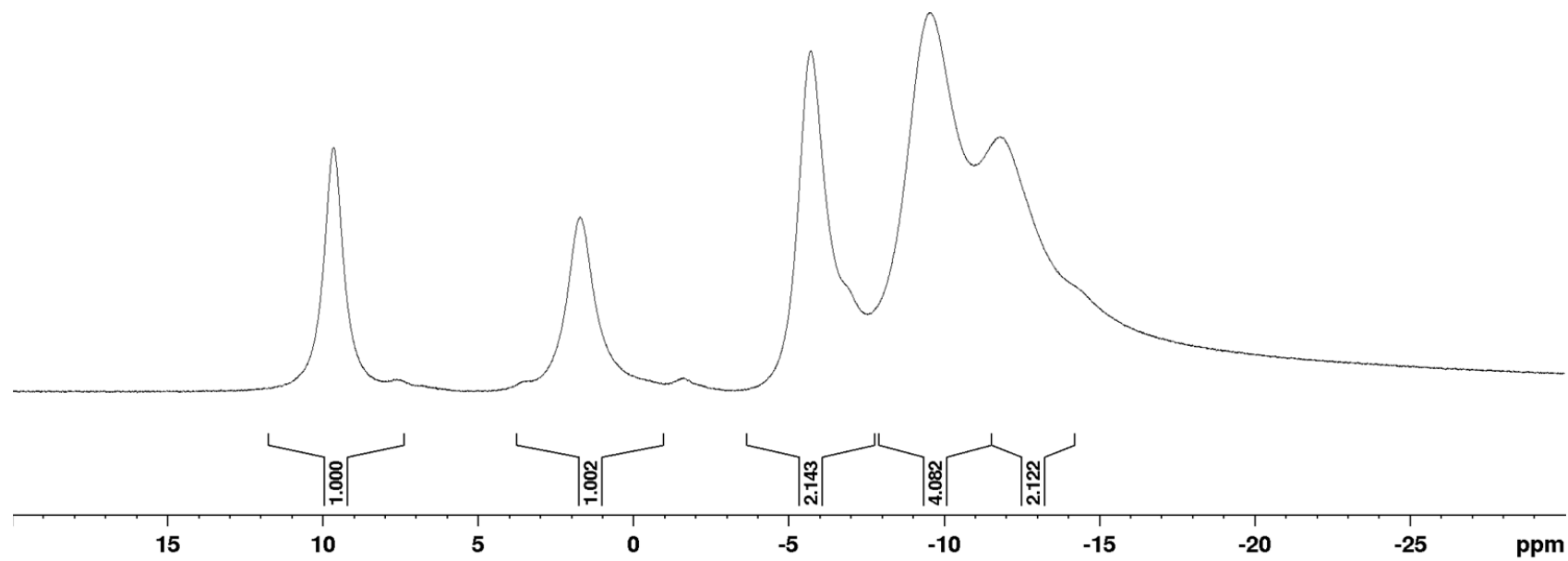
-5.72

-9.56

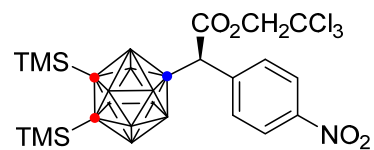
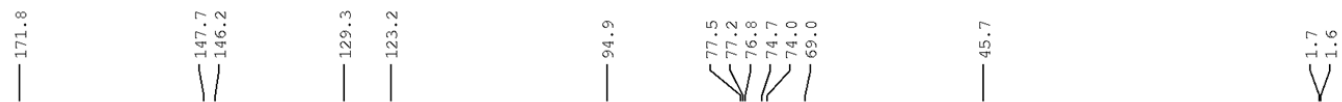
-11.82



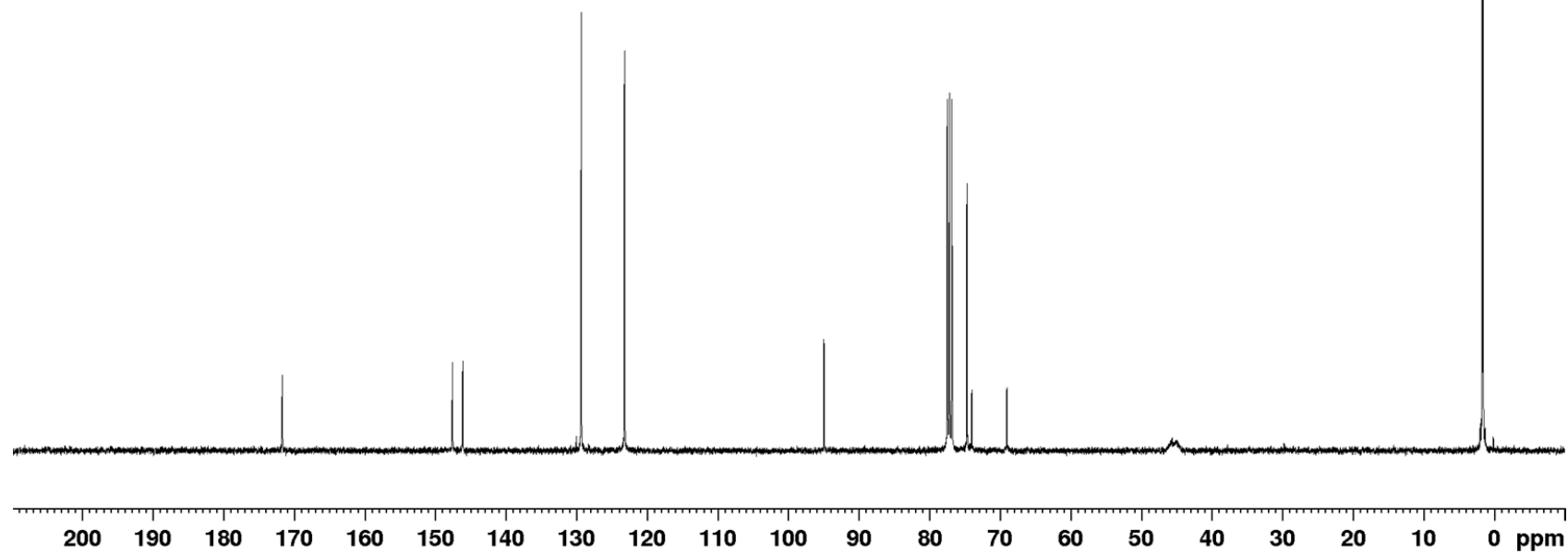
3bj



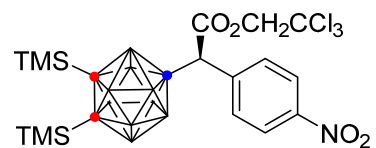
^{13}C NMR (100 MHz, CDCl_3)



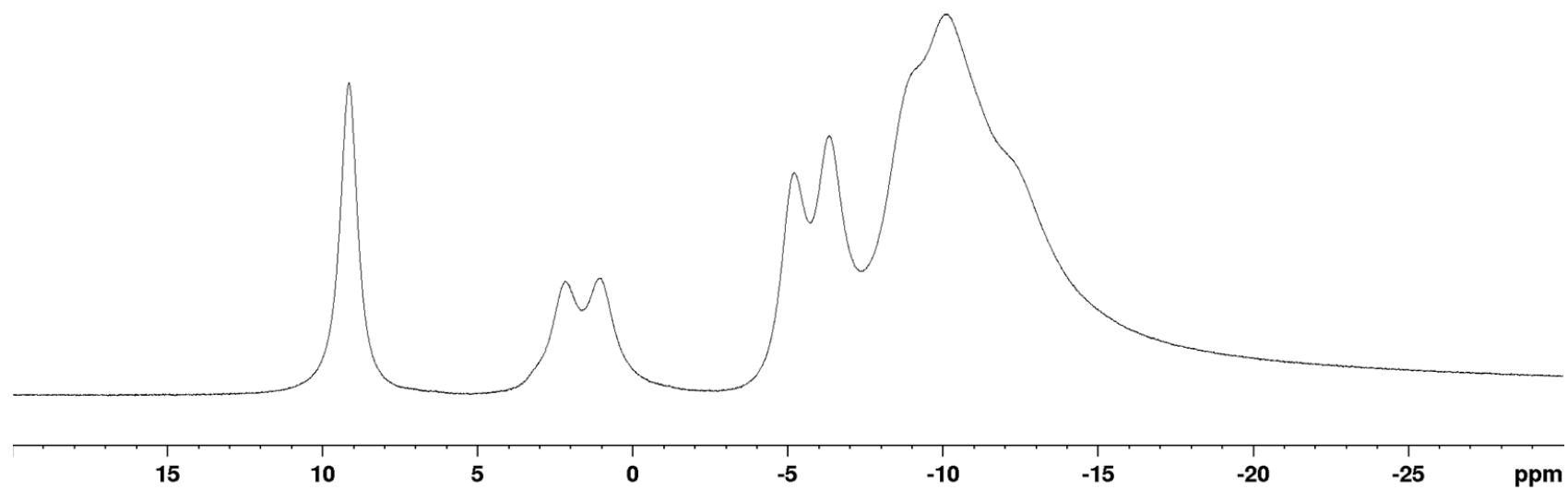
3bk



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



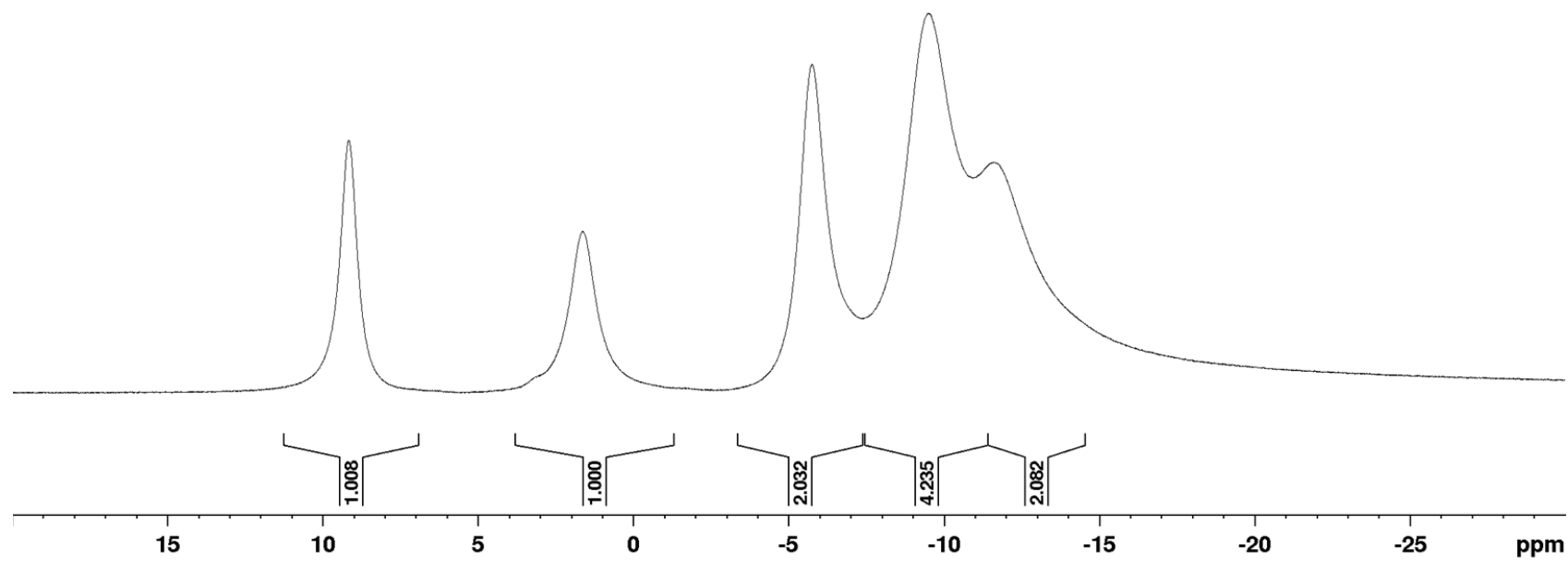
3bk



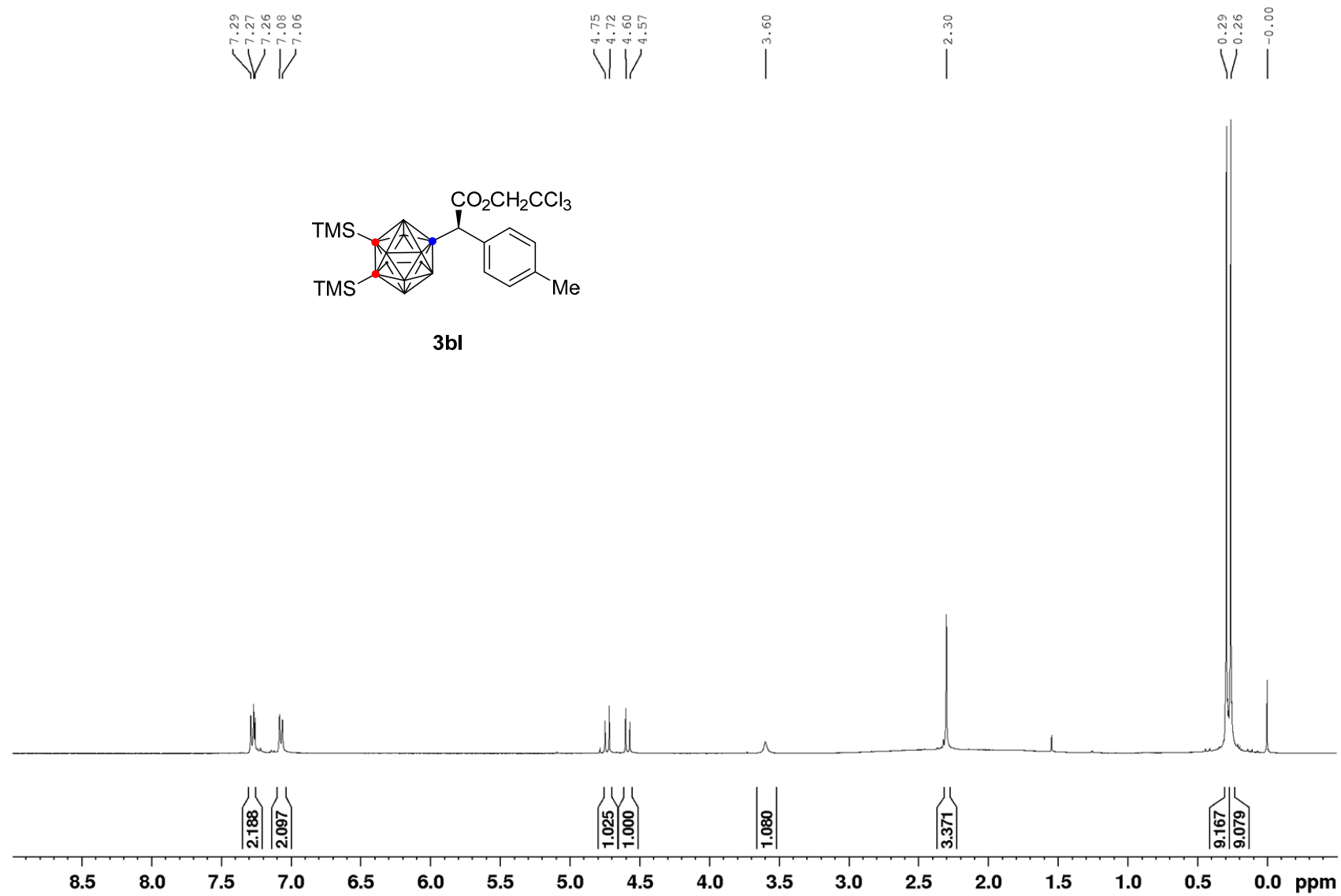
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



3bk



¹H NMR (400 MHz, CDCl₃)



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

— 173.2

136.9

135.2

128.6

128.6

— 95.3

77.5

77.2

76.8

74.6

73.6

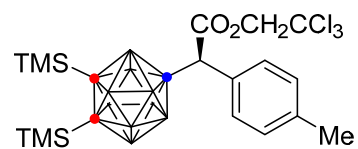
68.1

— 44.6

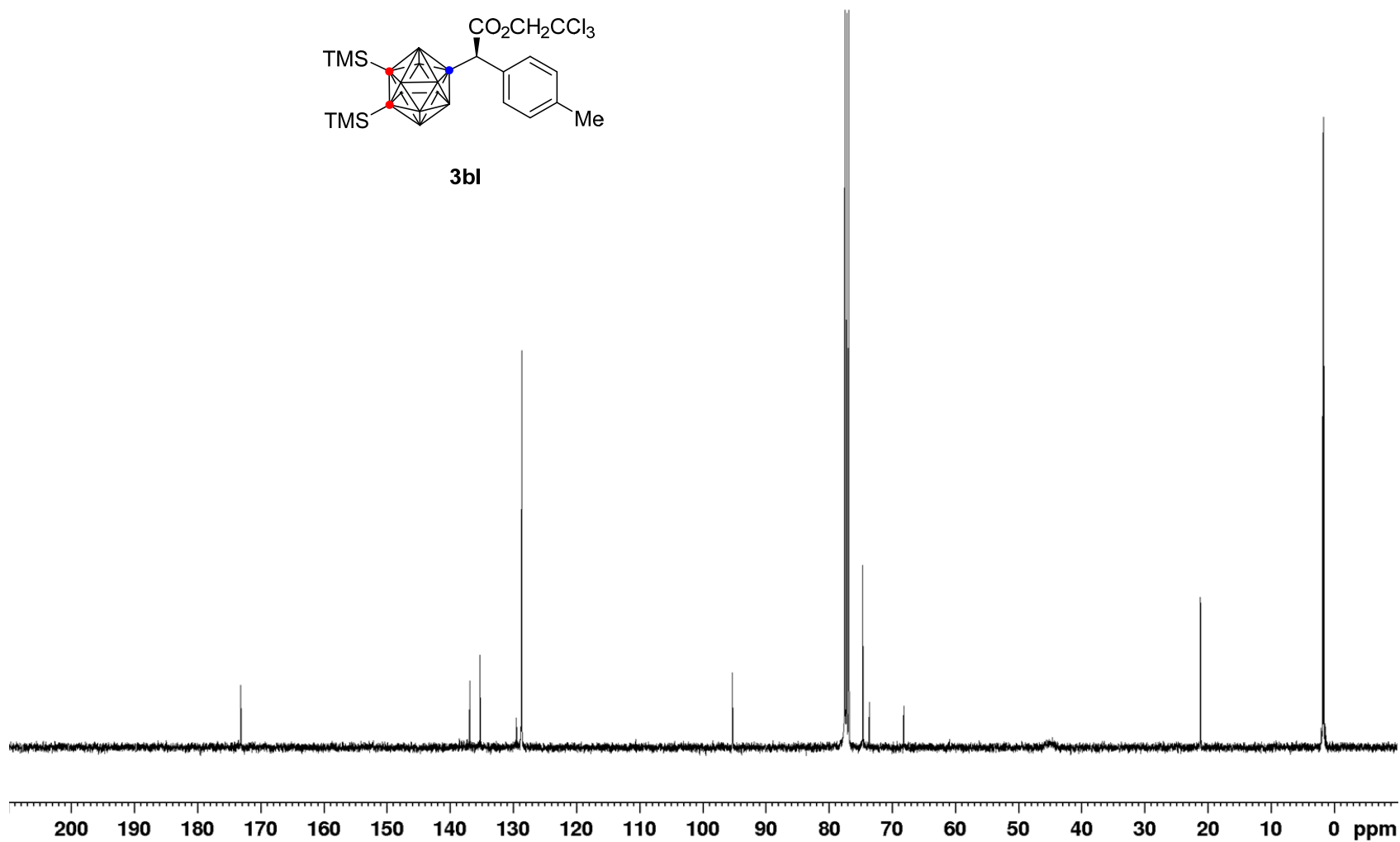
— 21.1

1.8

1.6



3bl



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

10.27

2.34

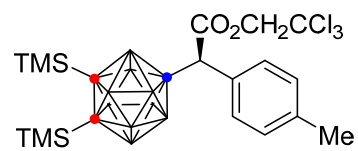
1.25

-5.08

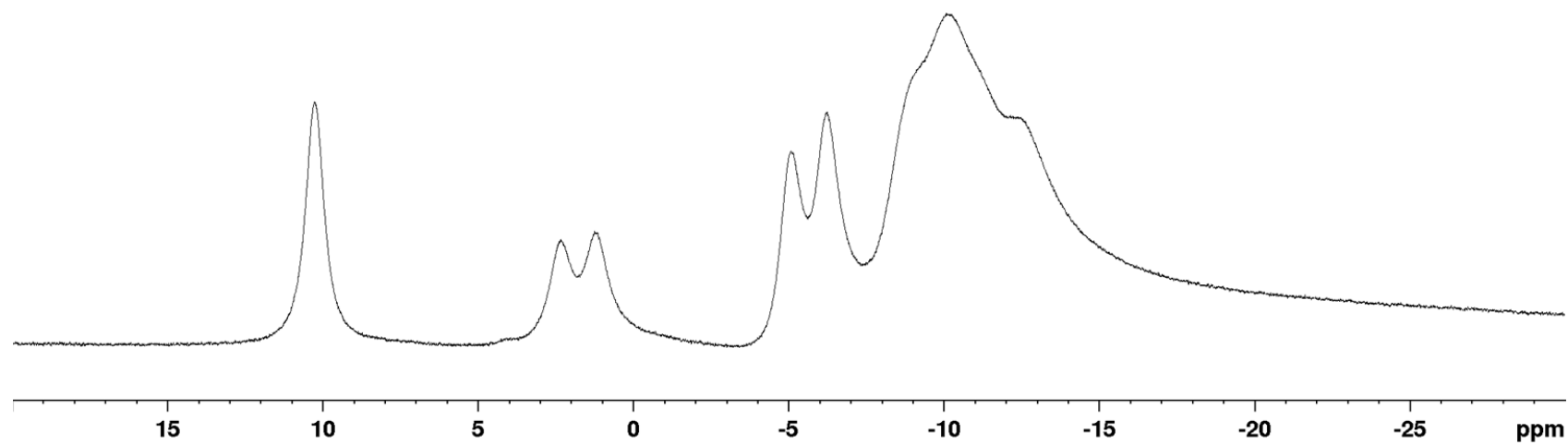
-6.24

-10.08

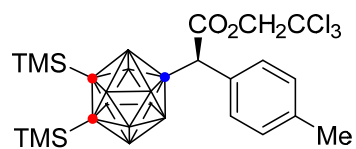
-12.09



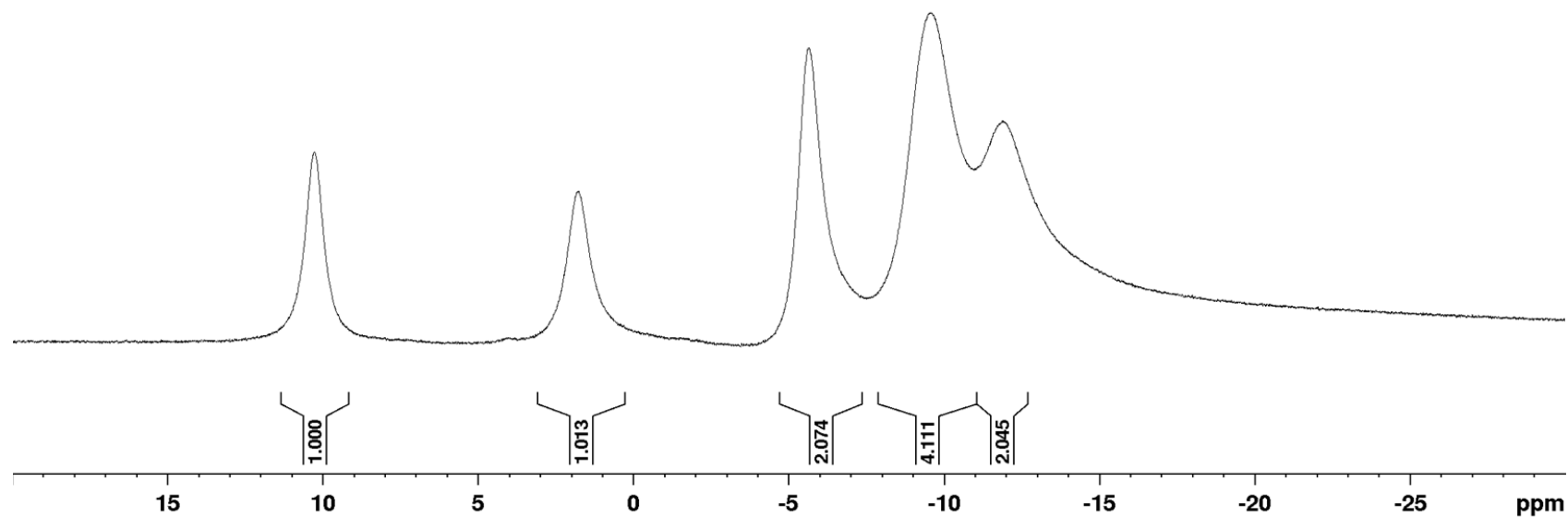
3bl



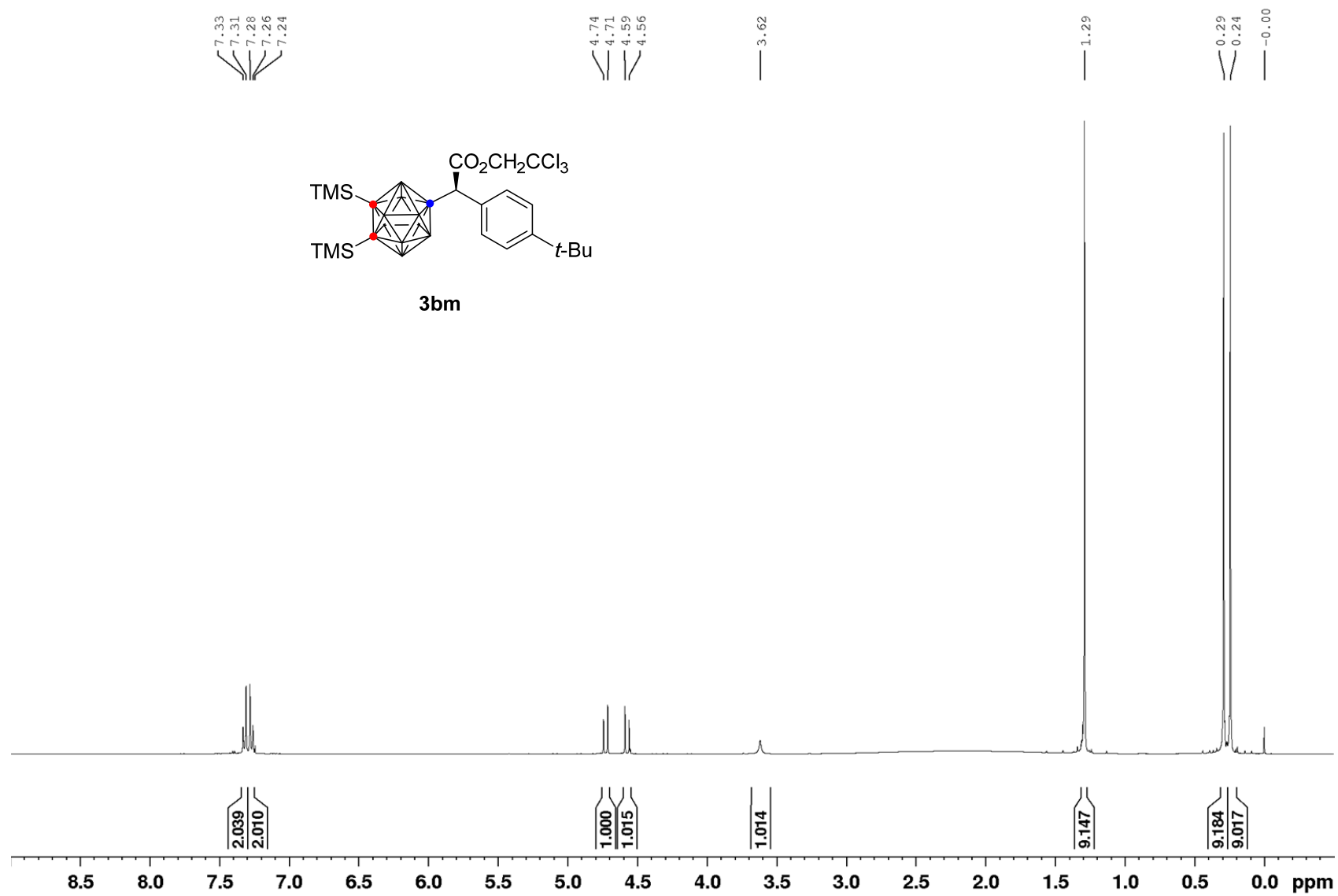
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



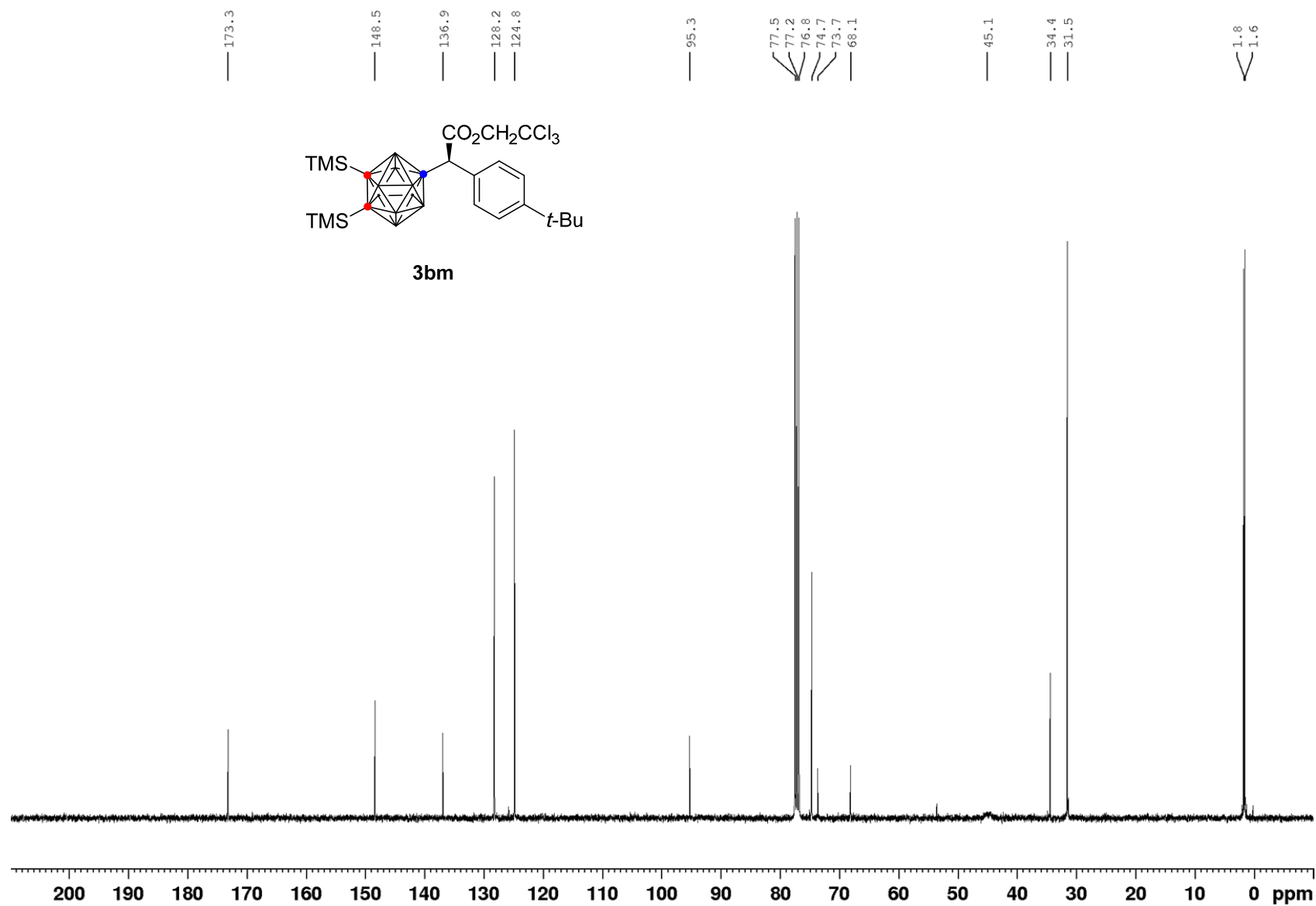
3bl



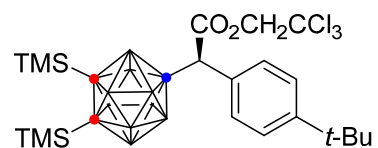
^1H NMR (400 MHz, CDCl_3)



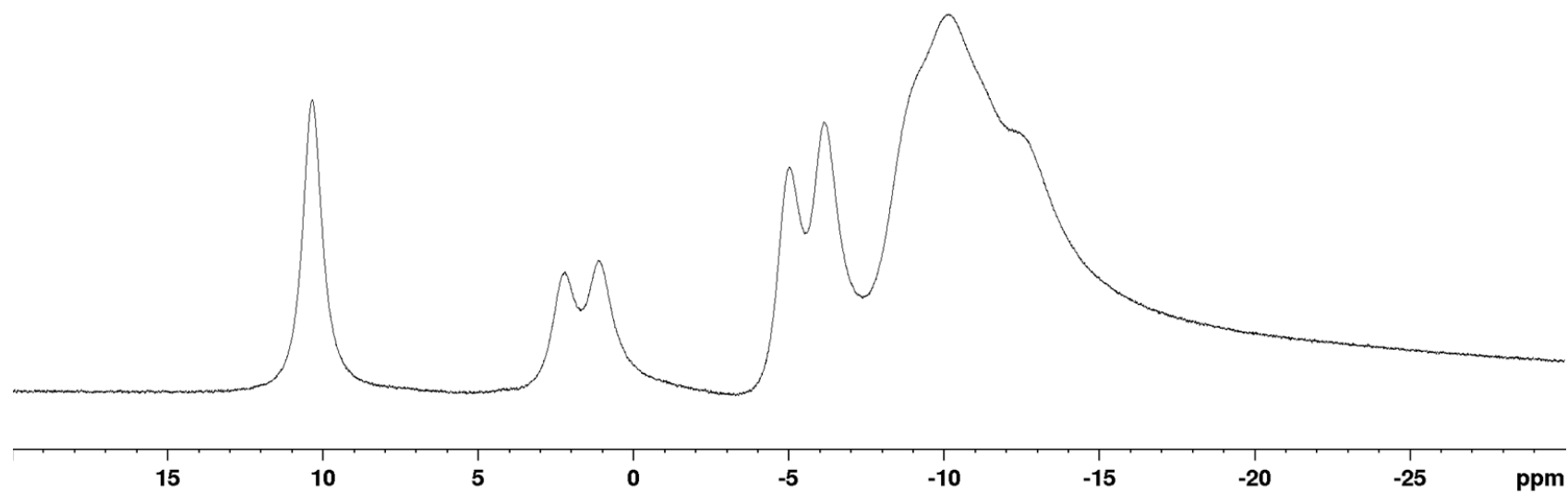
^{13}C NMR (100 MHz, CDCl_3)



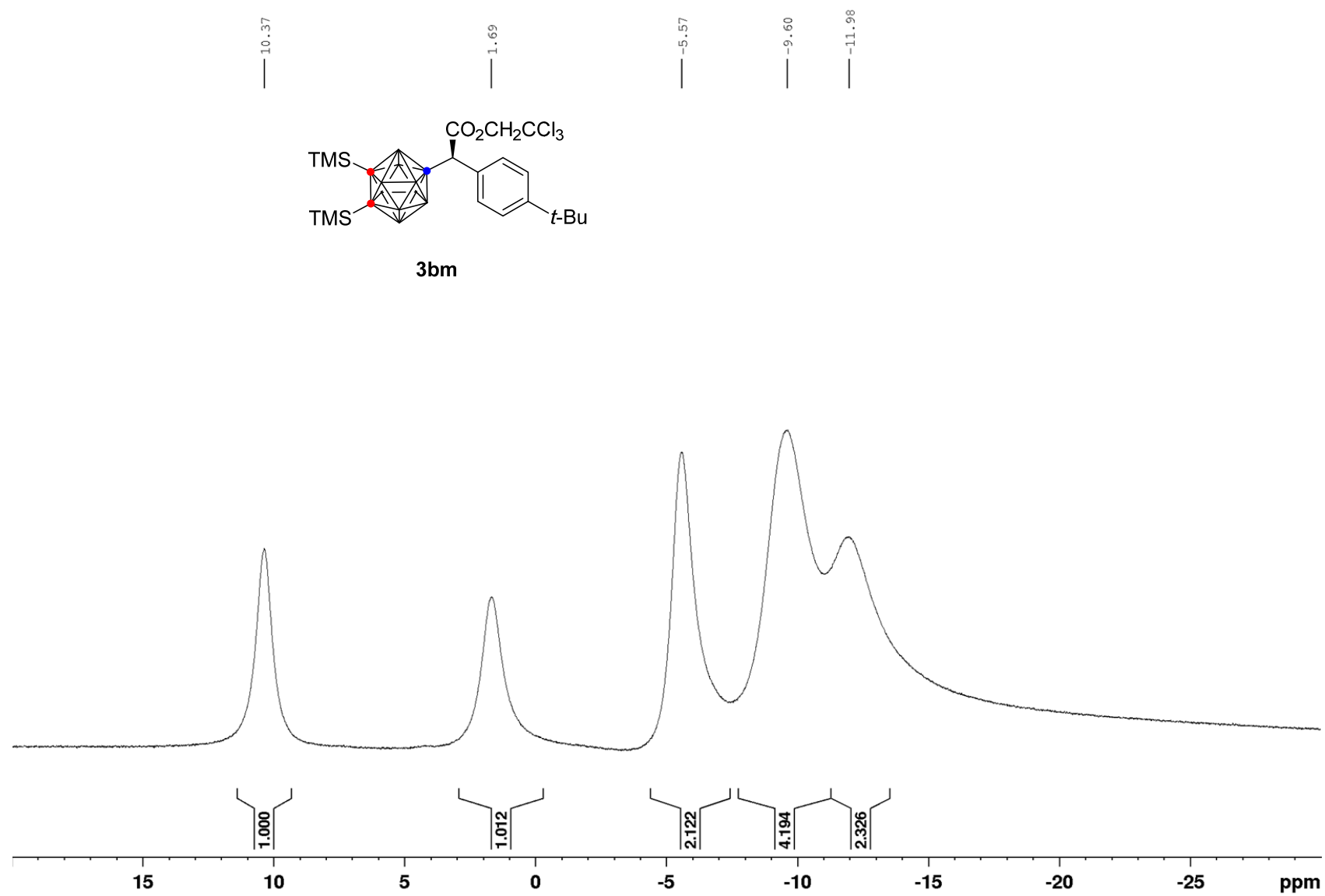
^{11}B NMR (128 MHz, CDCl_3)



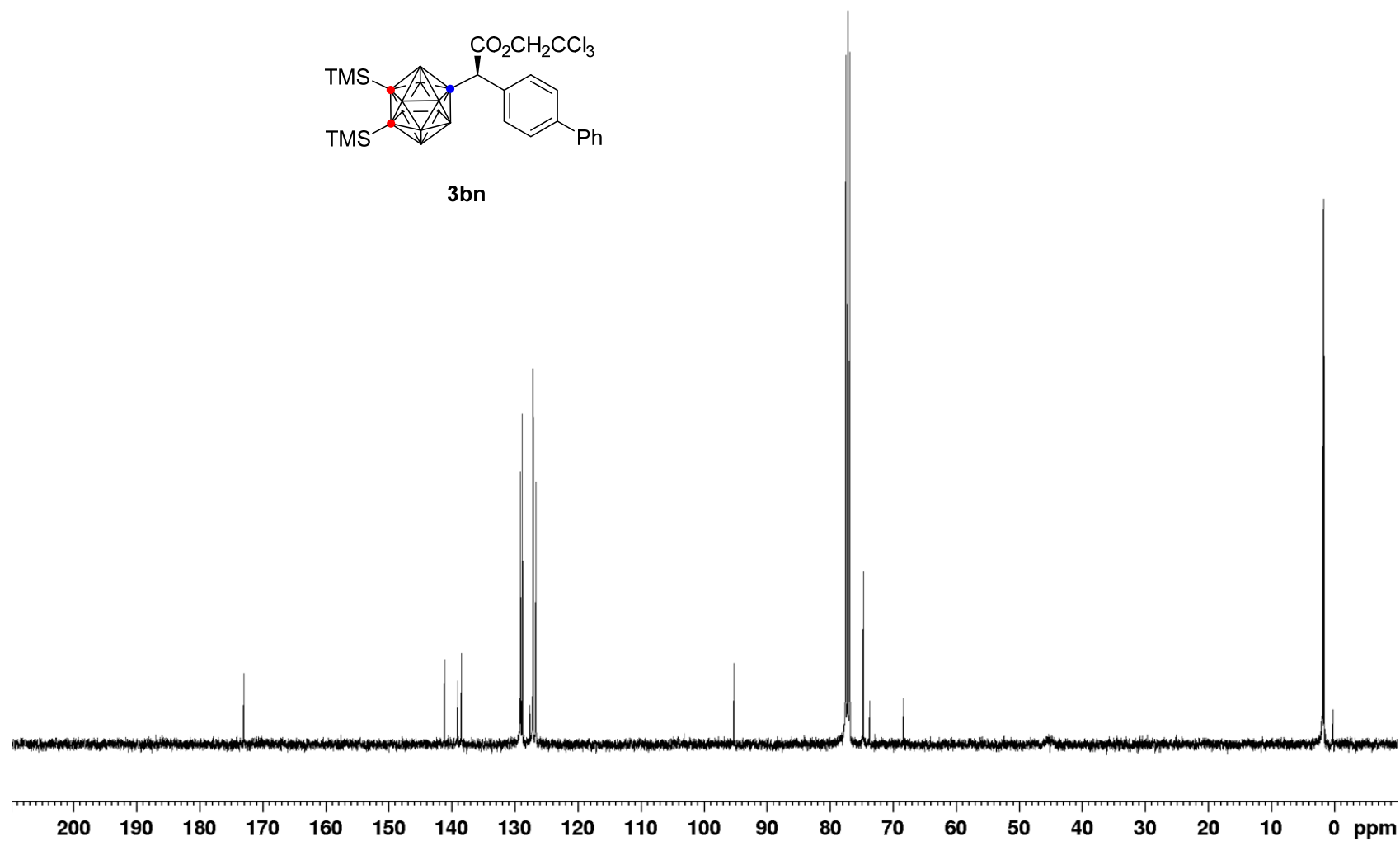
3bm



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



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



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

10.22

2.42

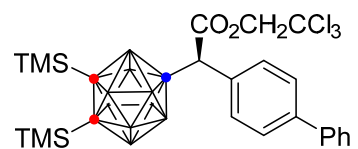
1.39

-5.05

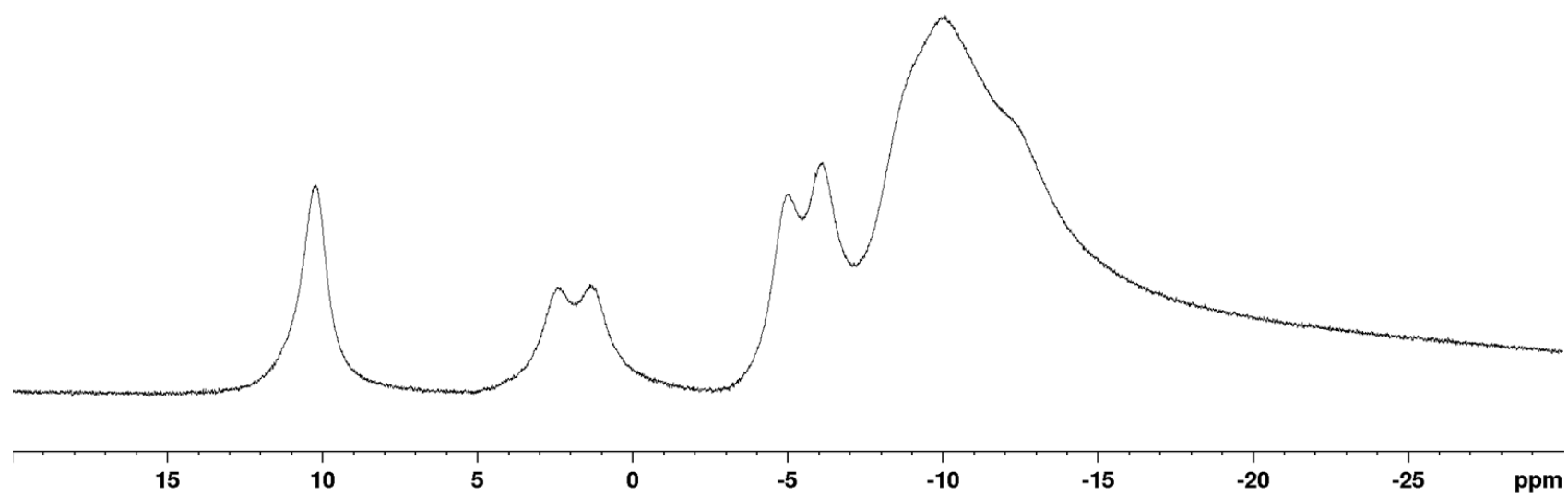
-6.10

-10.04

-12.30

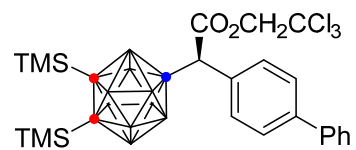


3bn

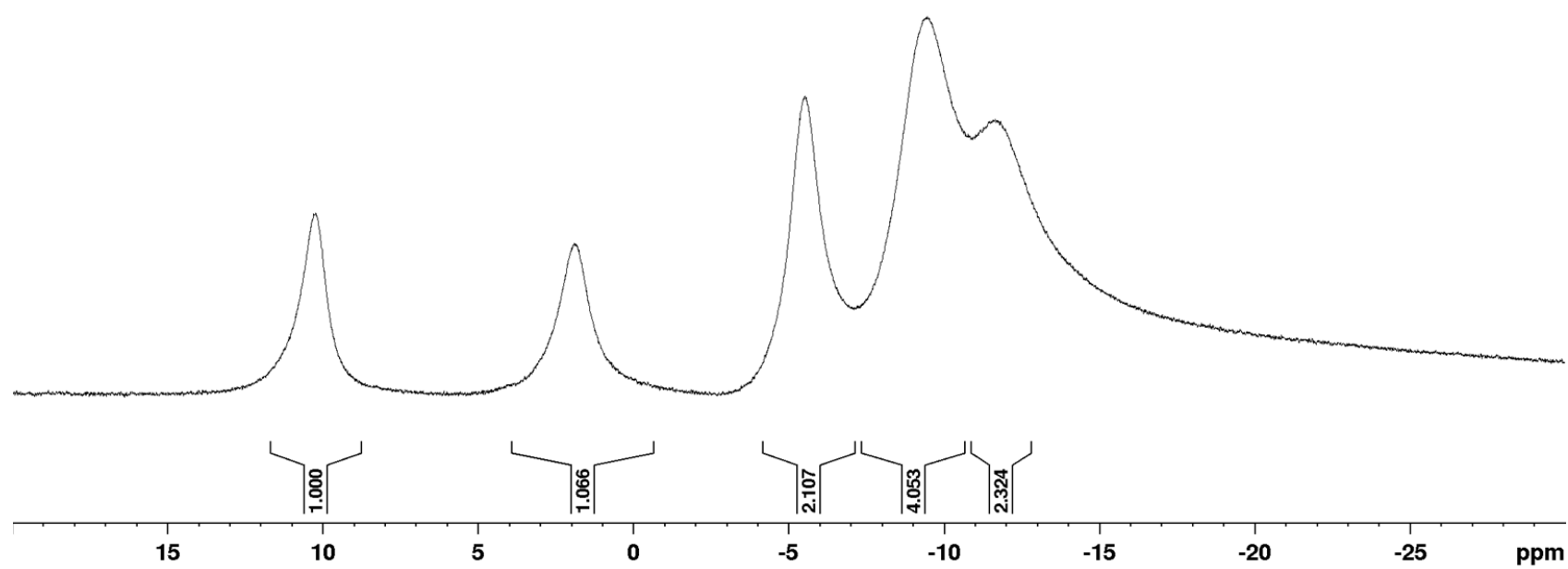


$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)

10.23
1.91
-5.53
-9.47
-11.65



3bn



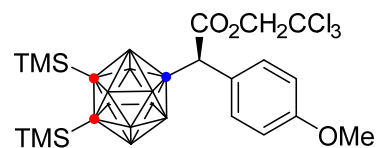
¹H NMR (400 MHz, CDCl₃)

7.32
7.30
7.26
6.82
6.80

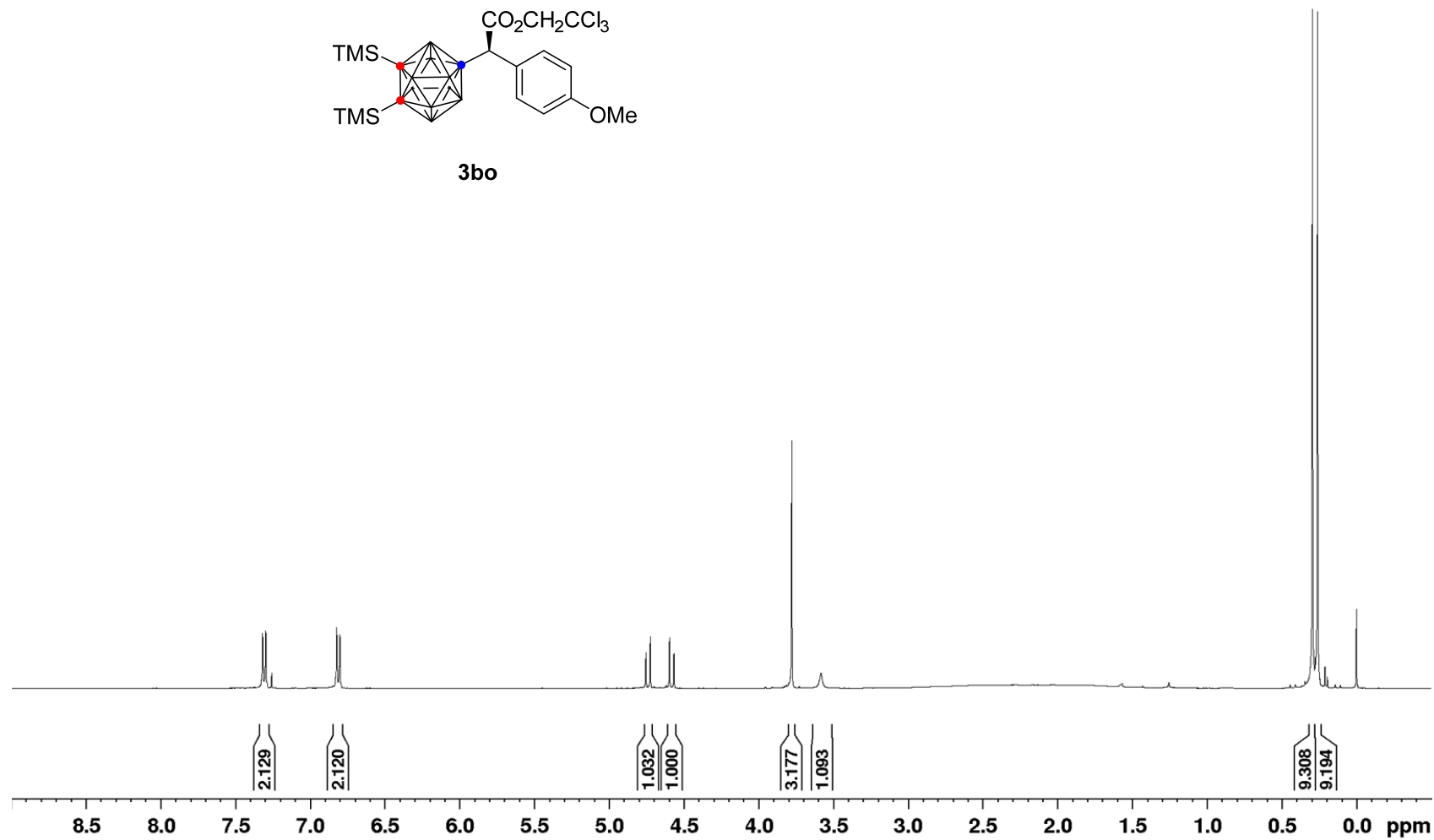
4.75
4.72
4.60
4.57

3.78
3.58

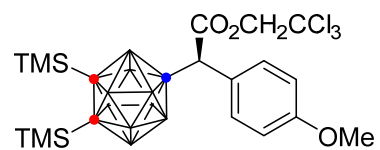
0.29
0.26
-0.00



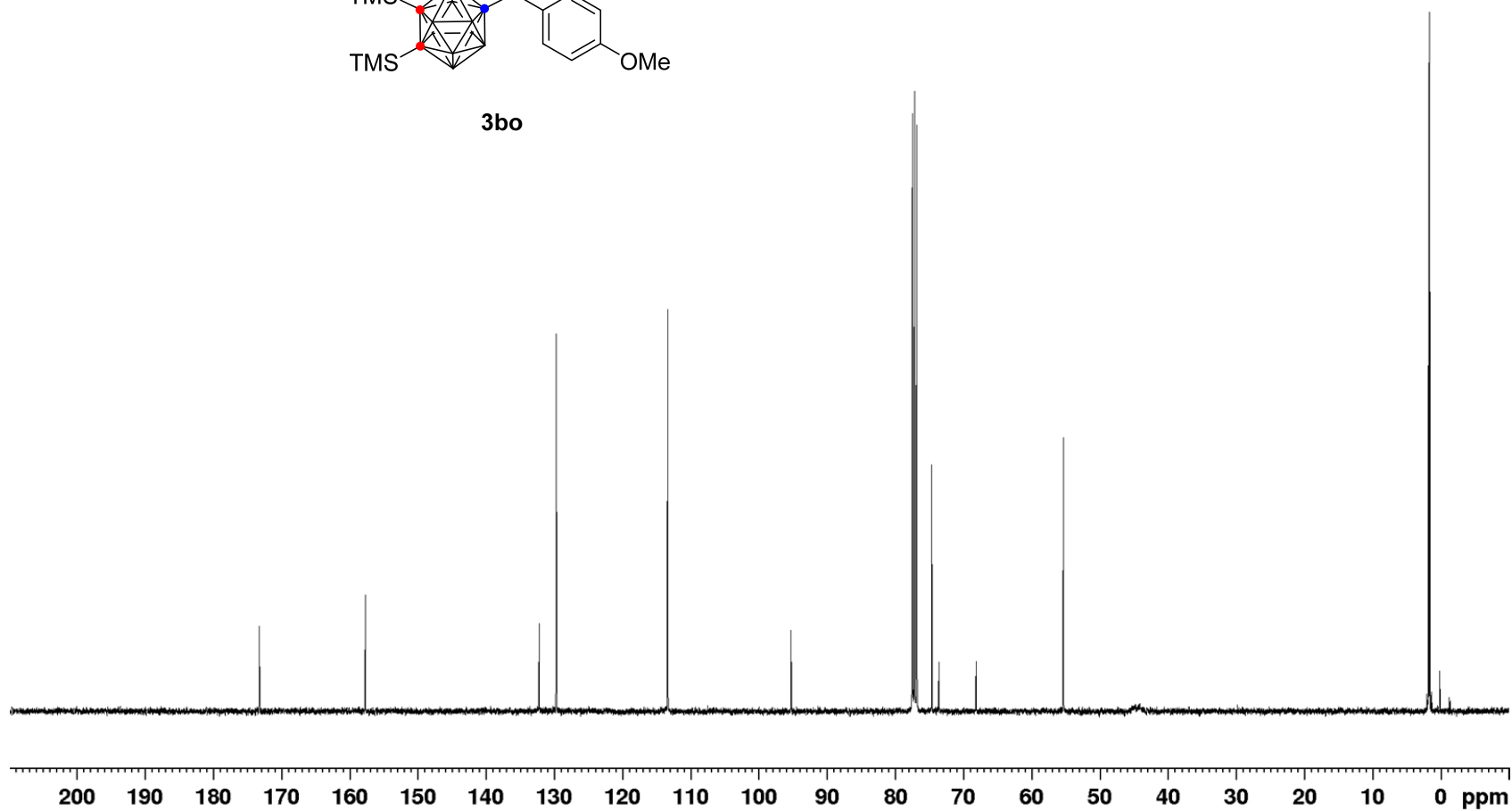
3bo



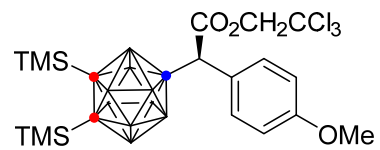
^{13}C NMR (100 MHz, CDCl_3)



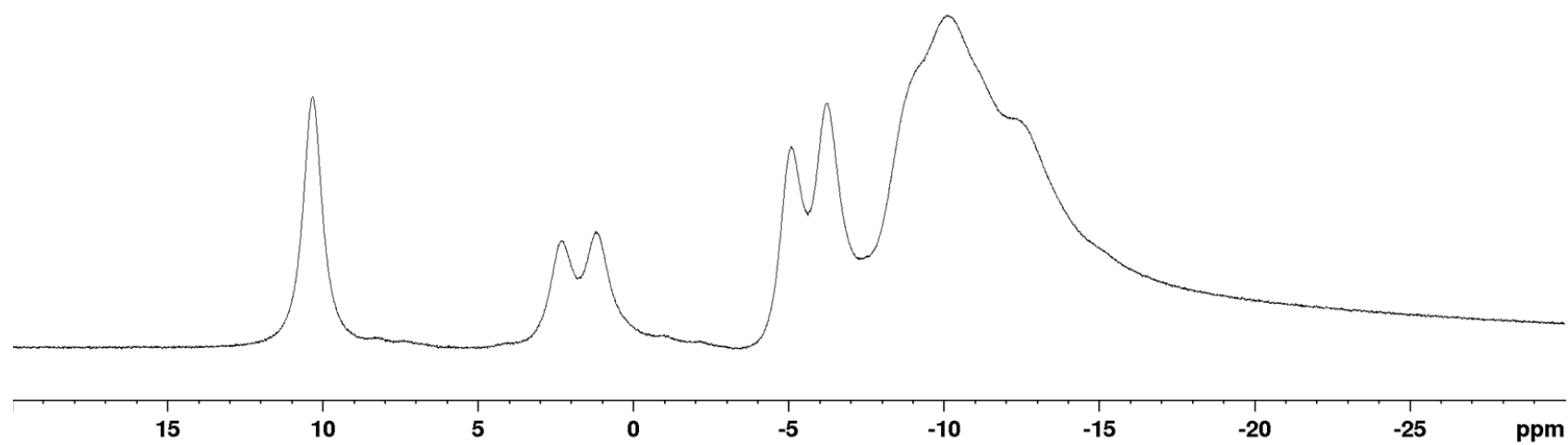
3bo



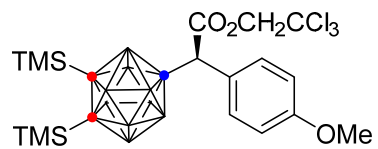
^{11}B NMR (128 MHz, CDCl_3)



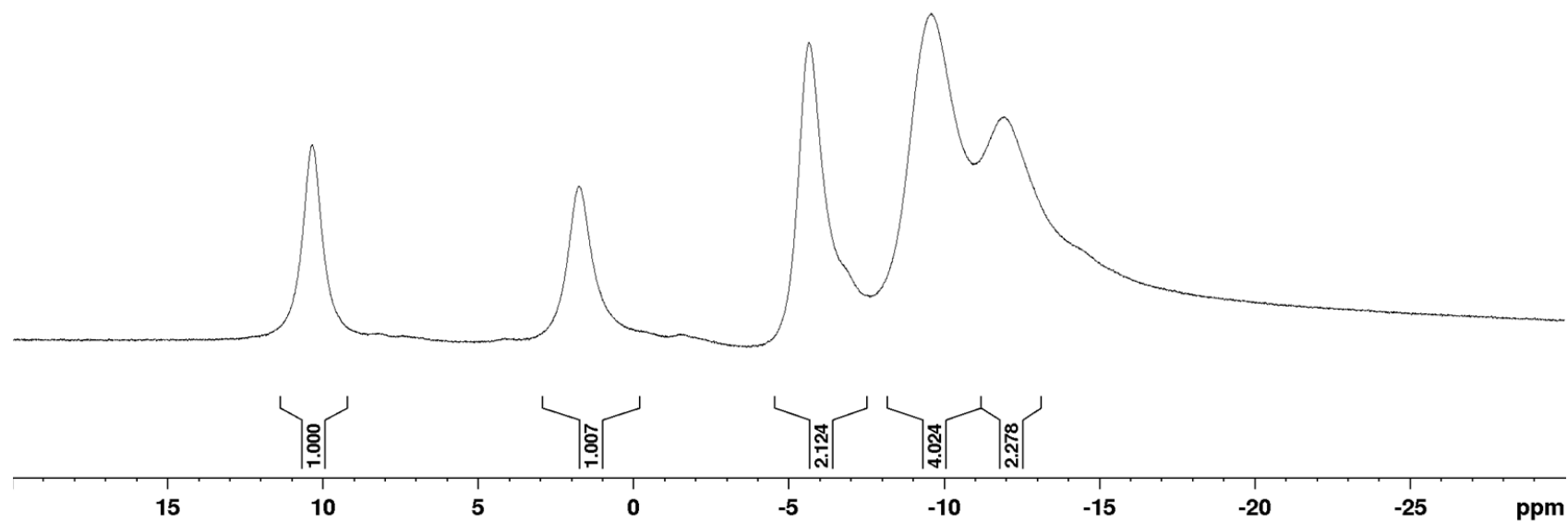
3bo



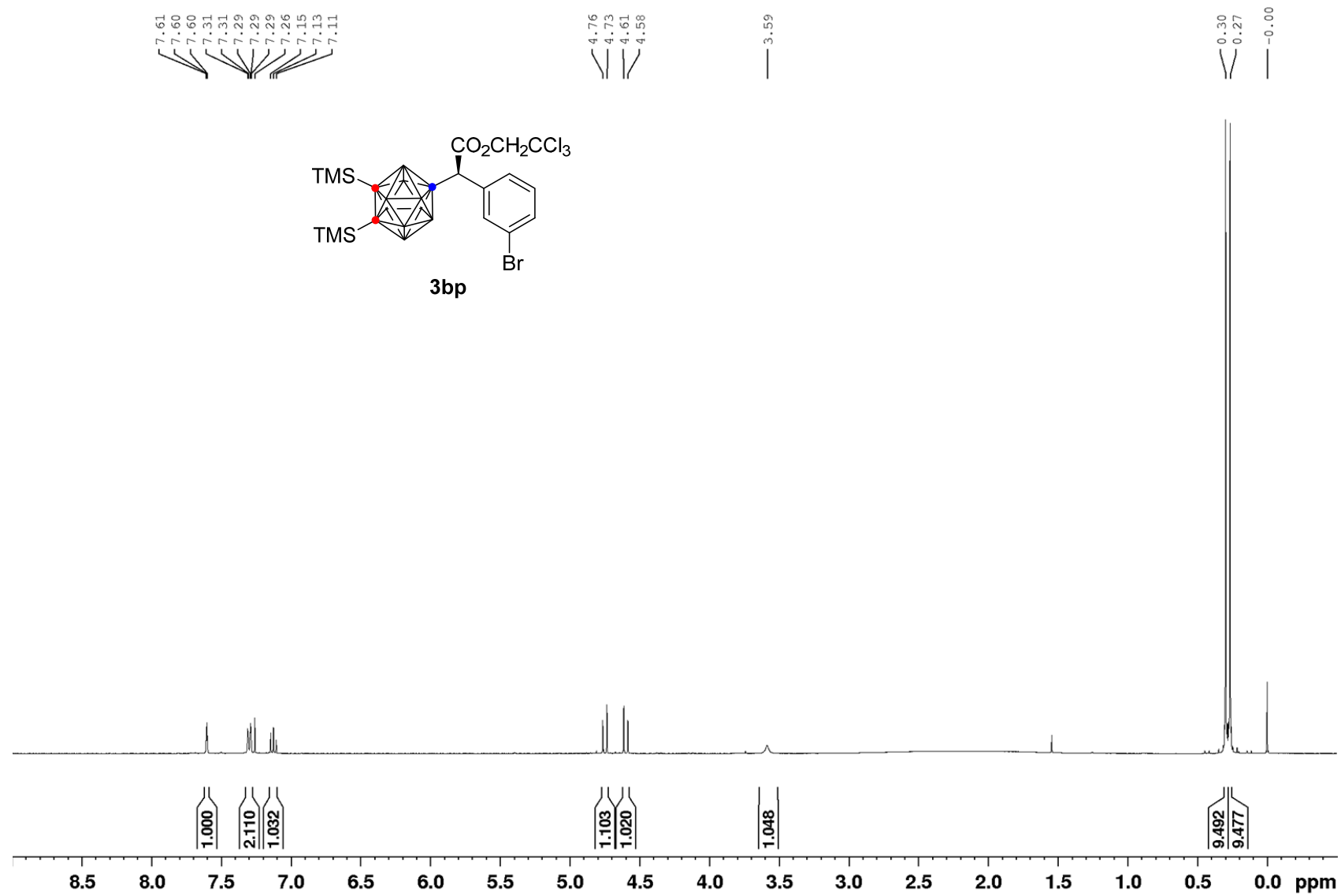
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



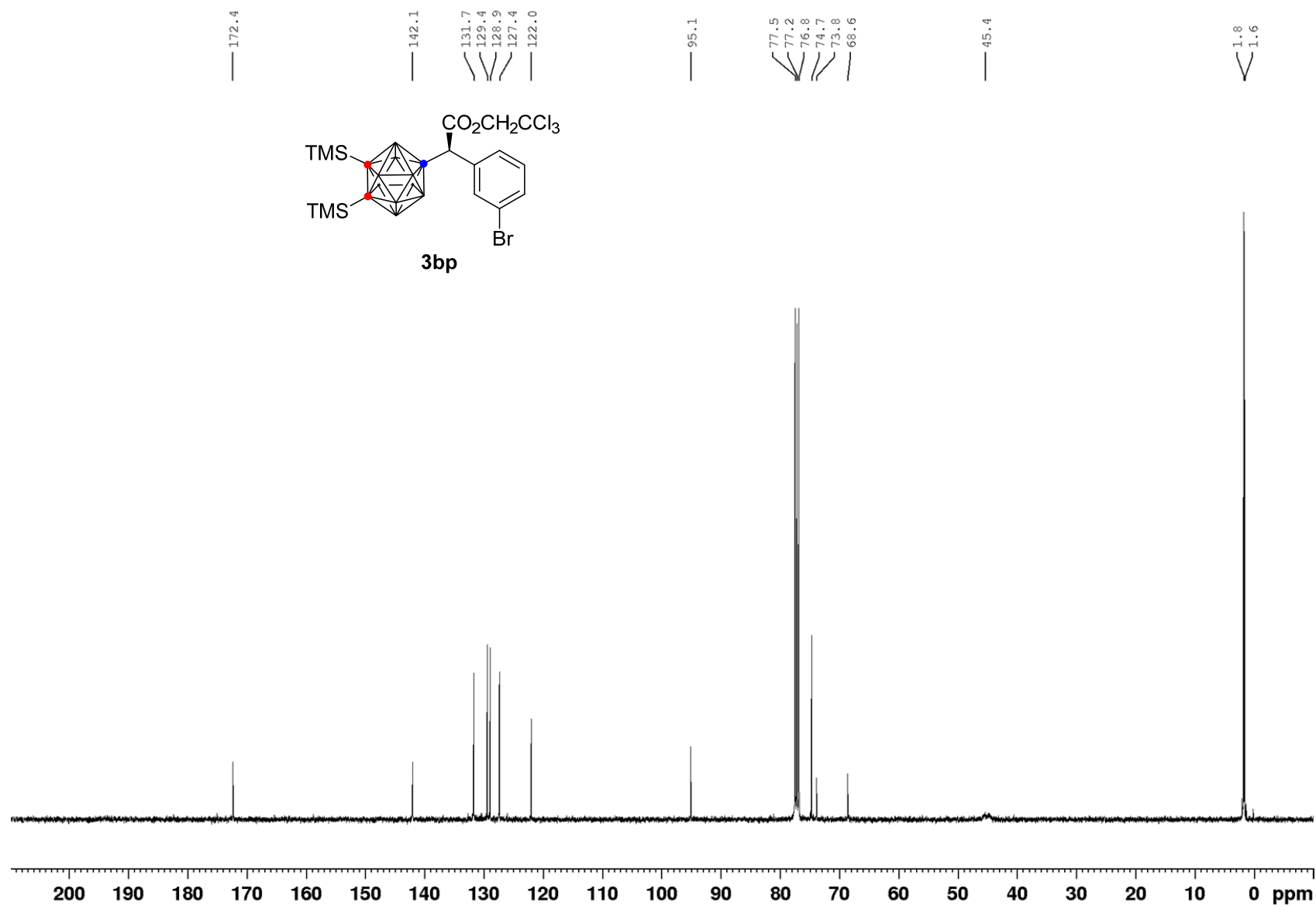
3bo



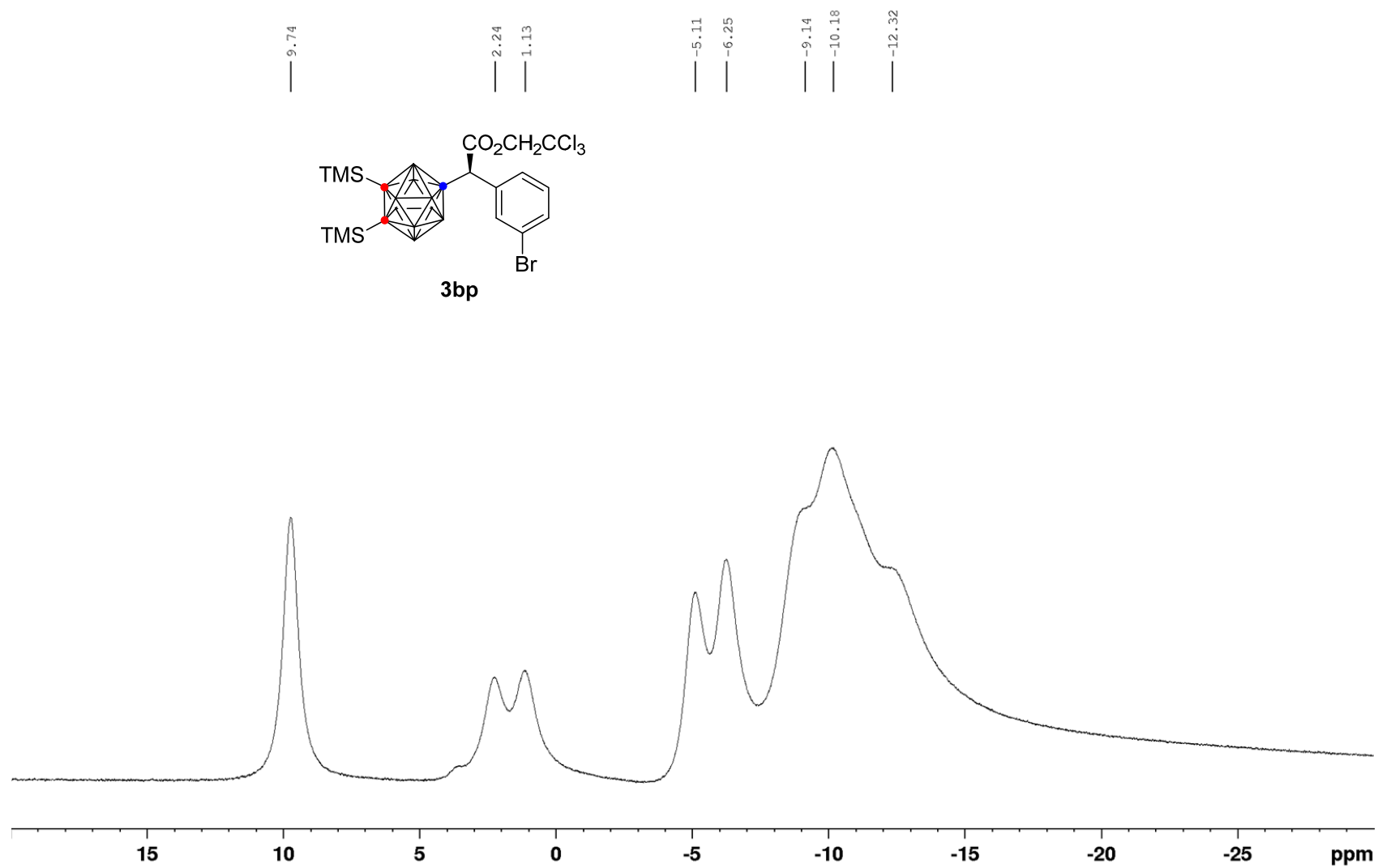
¹H NMR (400 MHz, CDCl₃)



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

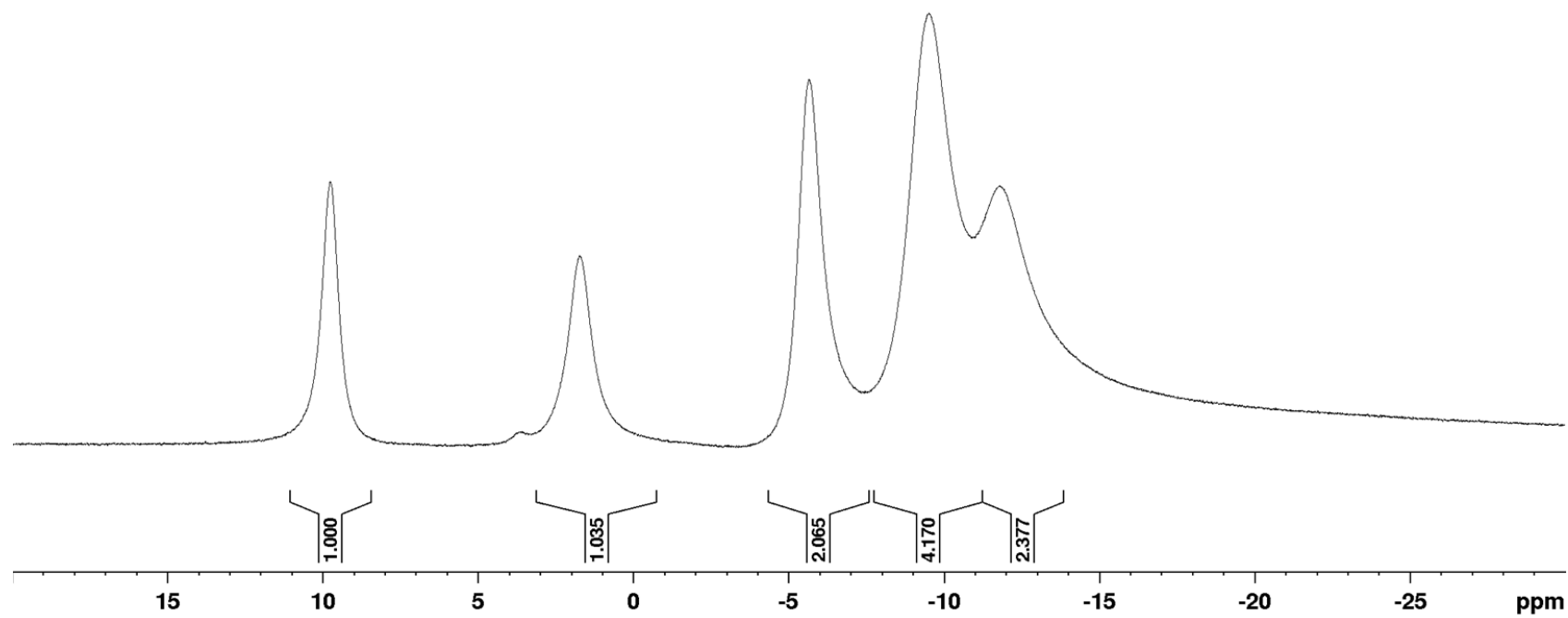
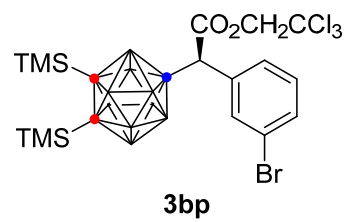


^{11}B NMR (128 MHz, CDCl_3)

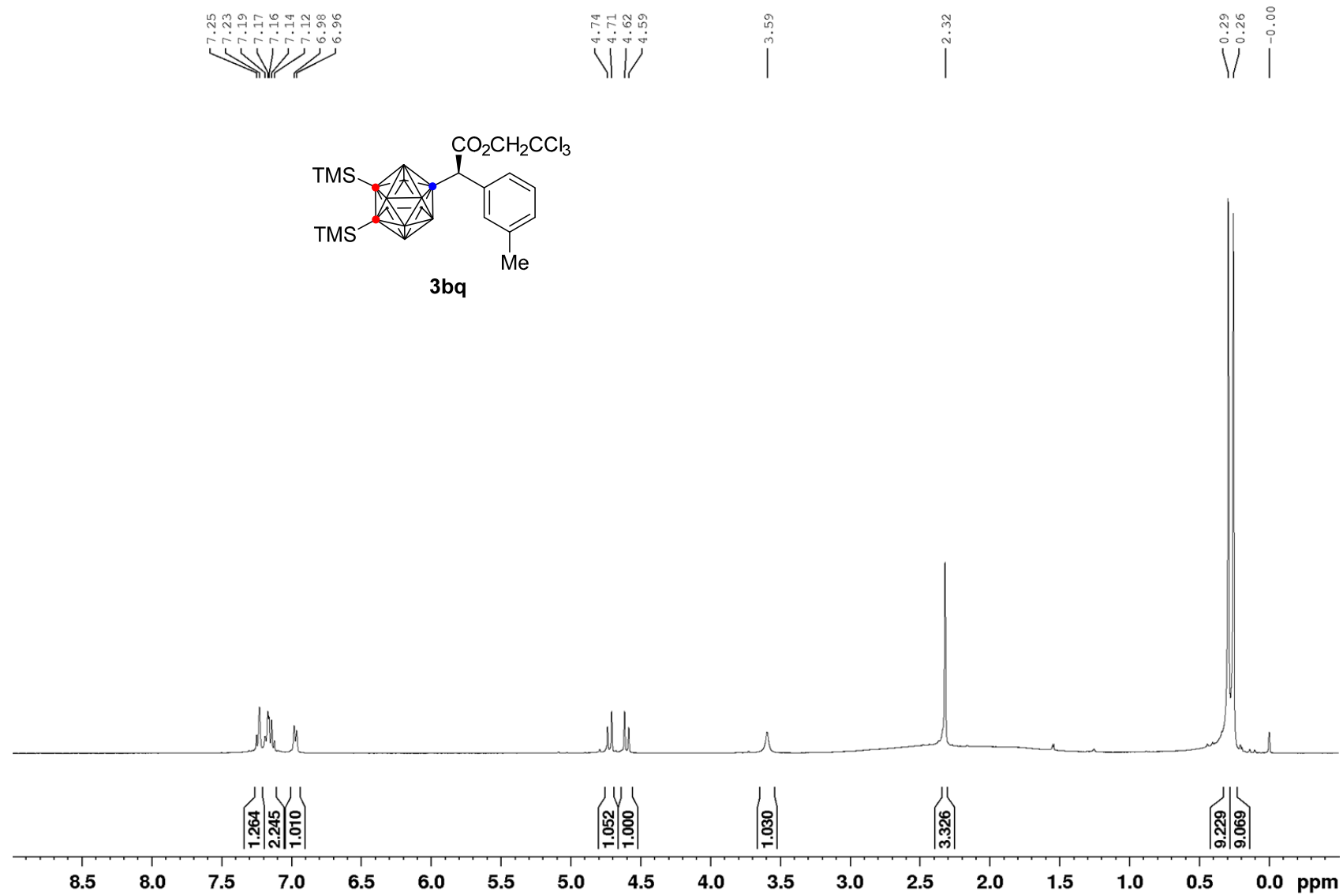


$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)

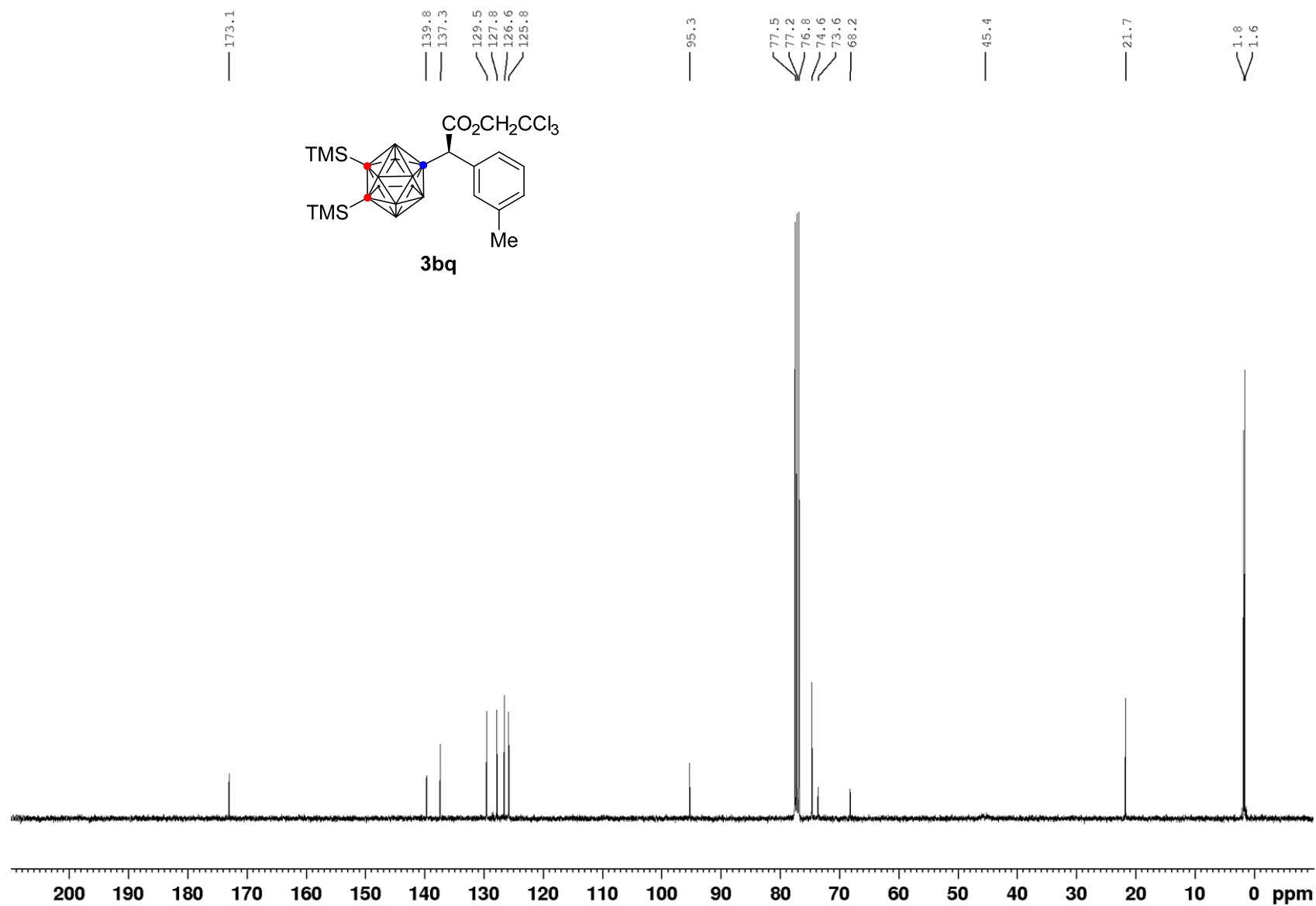
9.76
1.75
-5.66
-9.51
-11.81



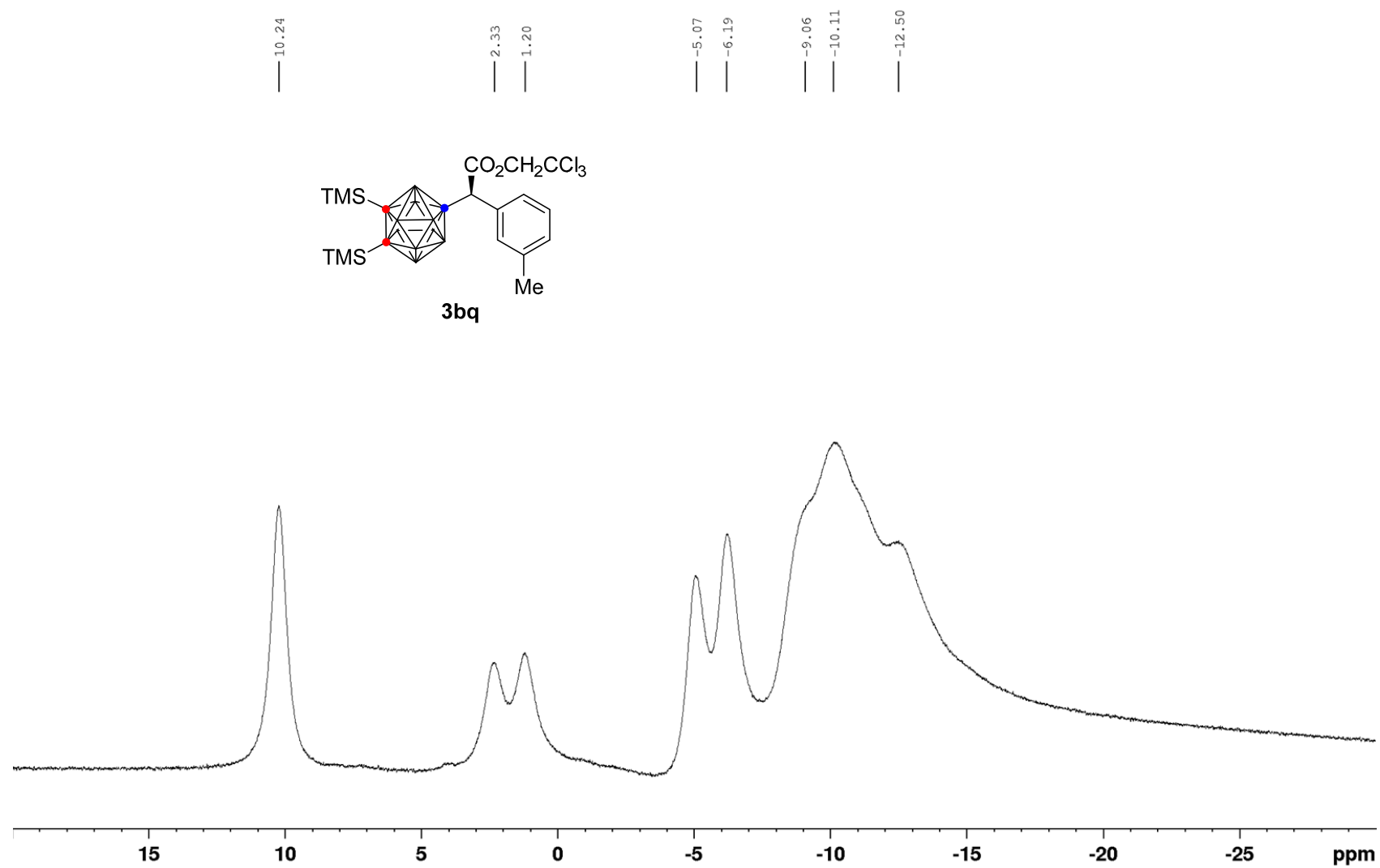
¹H NMR (400 MHz, CDCl₃)



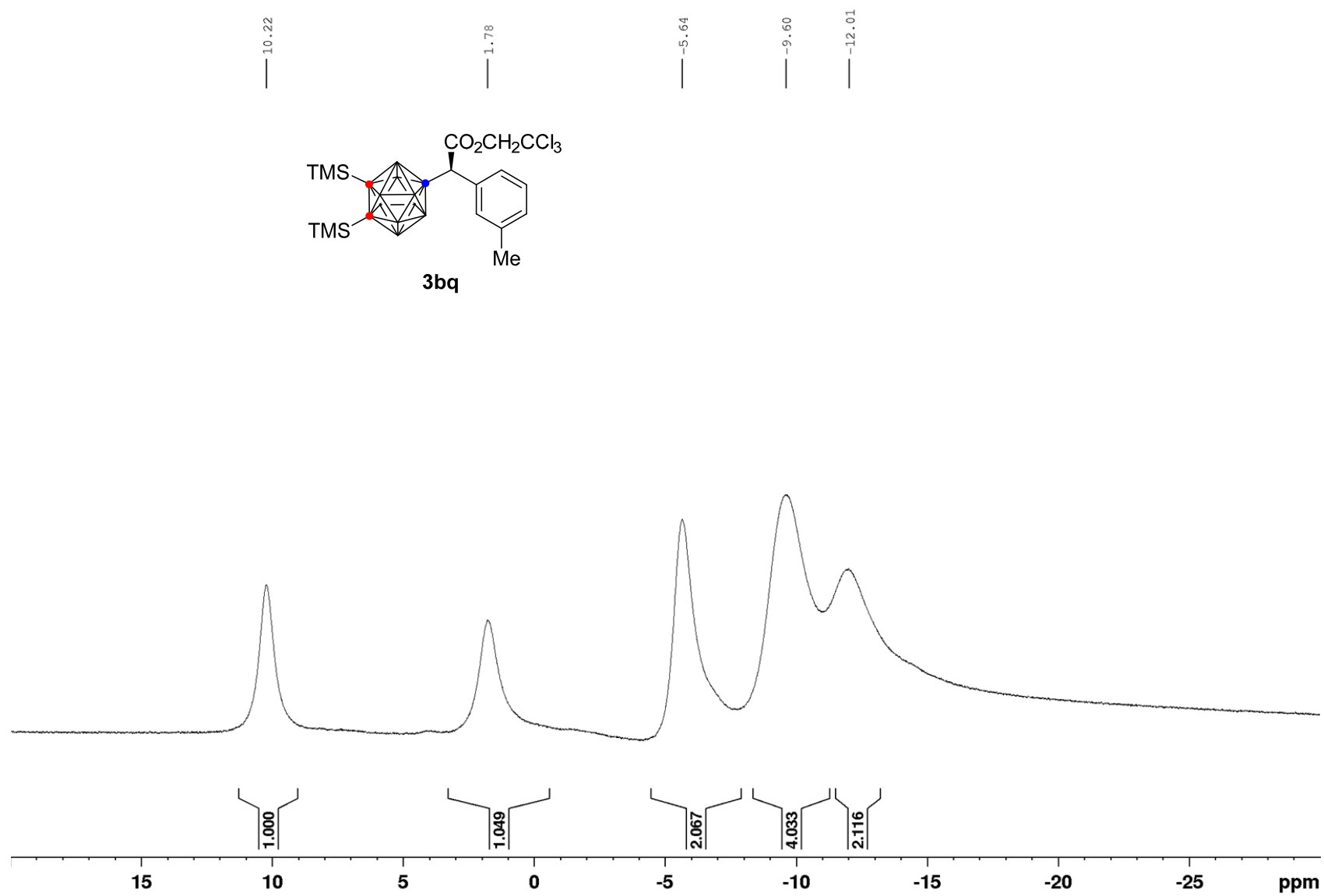
^{13}C NMR (100 MHz, CDCl_3)



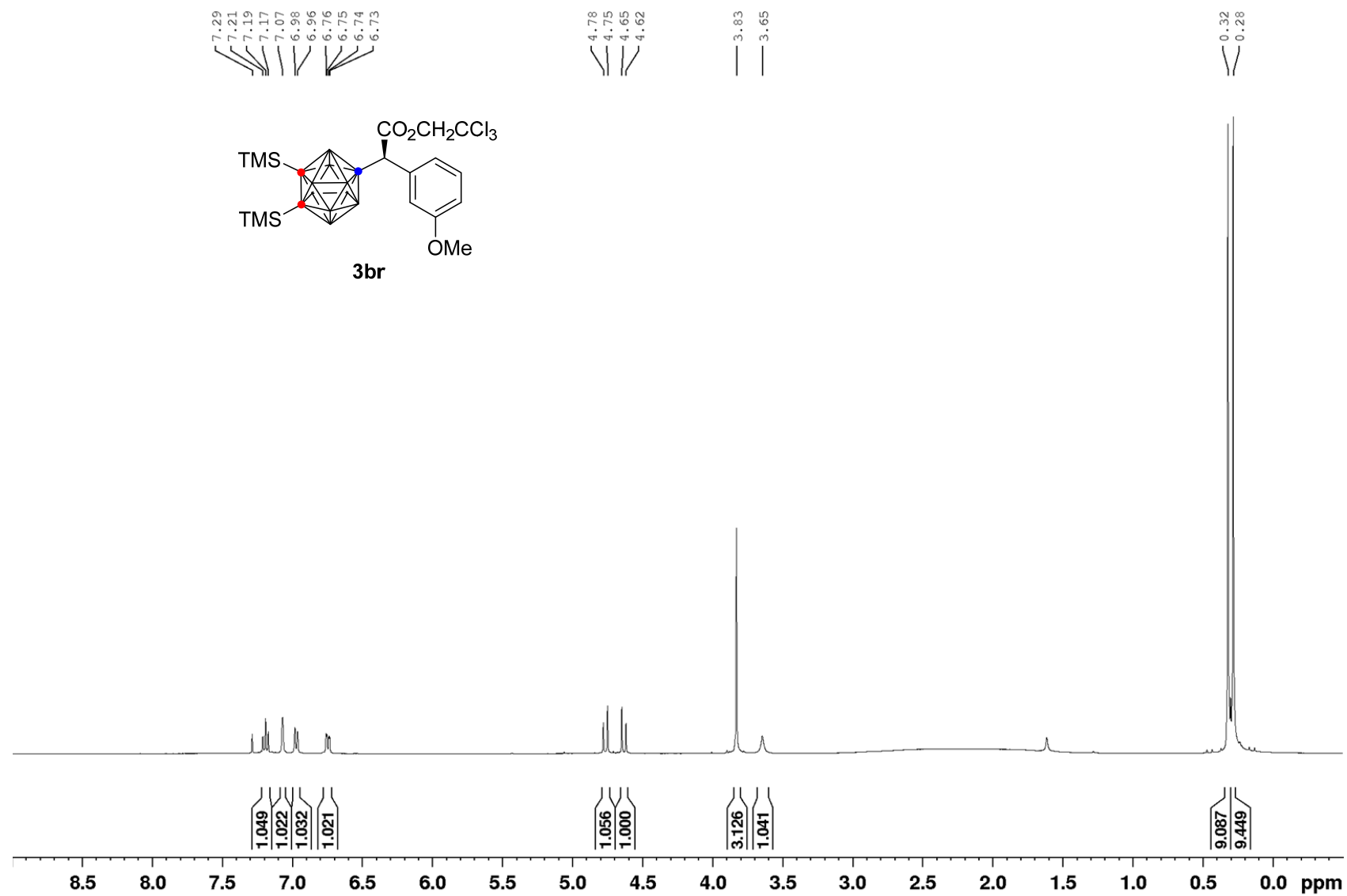
^{11}B NMR (128 MHz, CDCl_3)



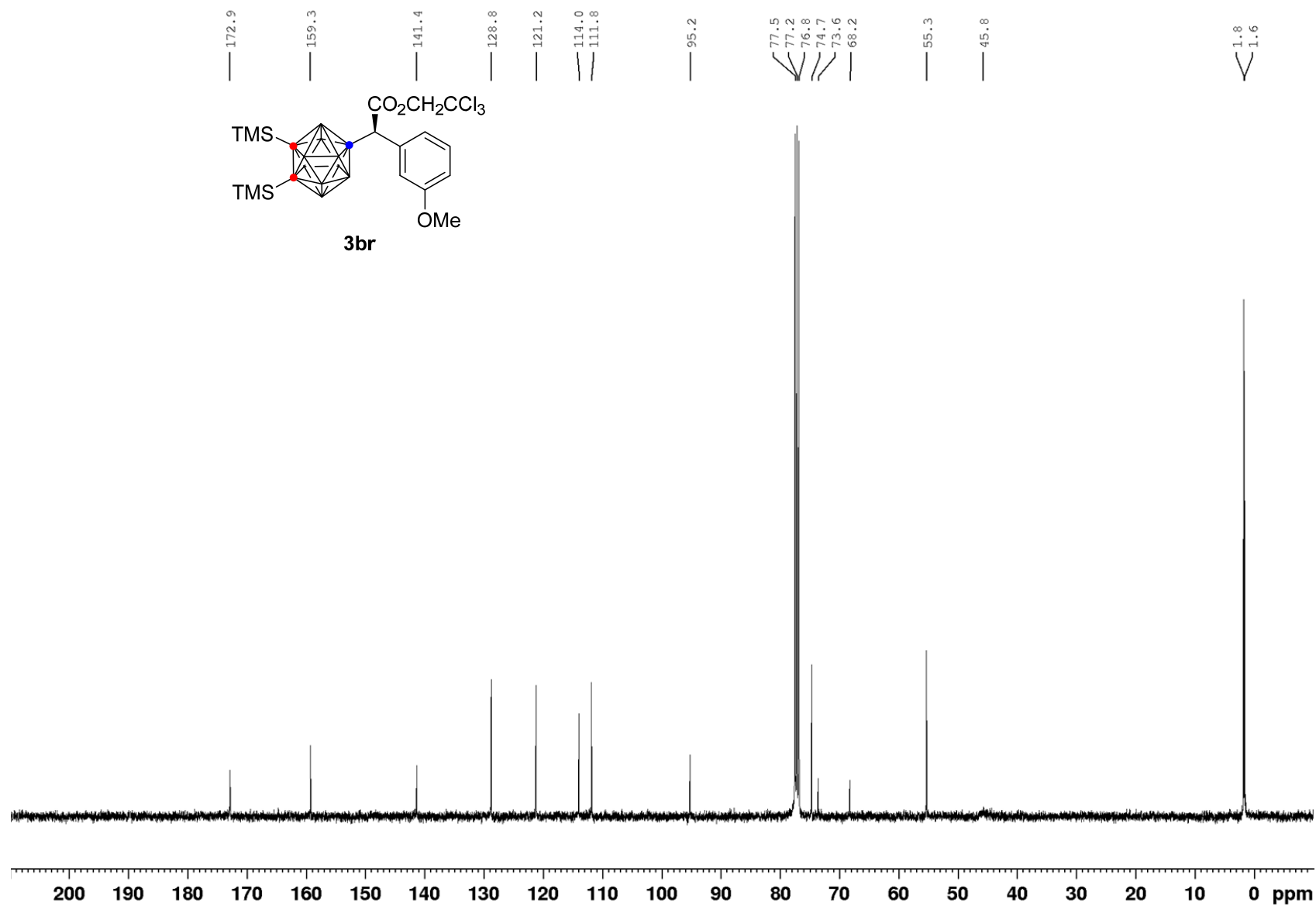
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



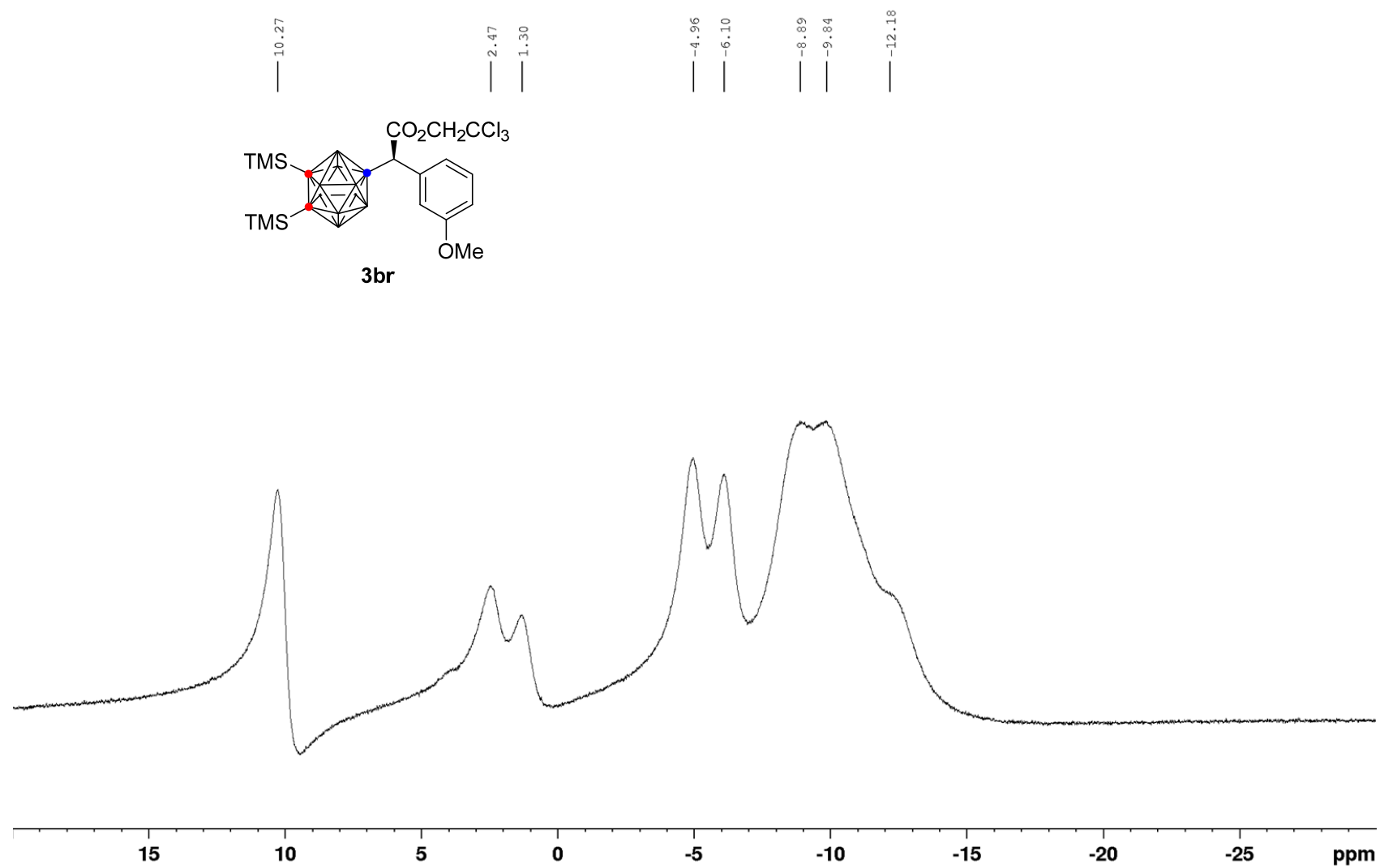
^1H NMR (400 MHz, CDCl_3)



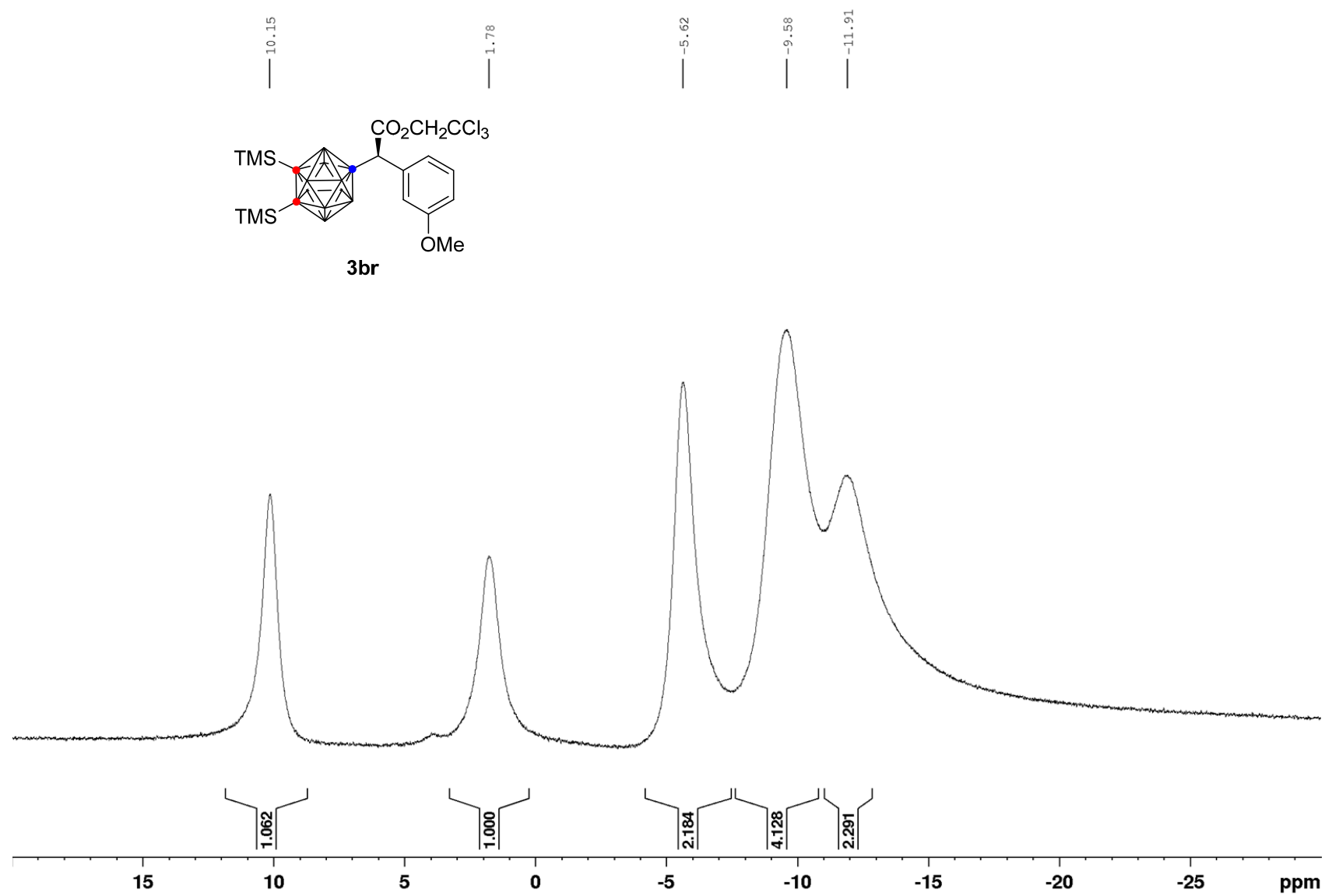
^{13}C NMR (100 MHz, CDCl_3)



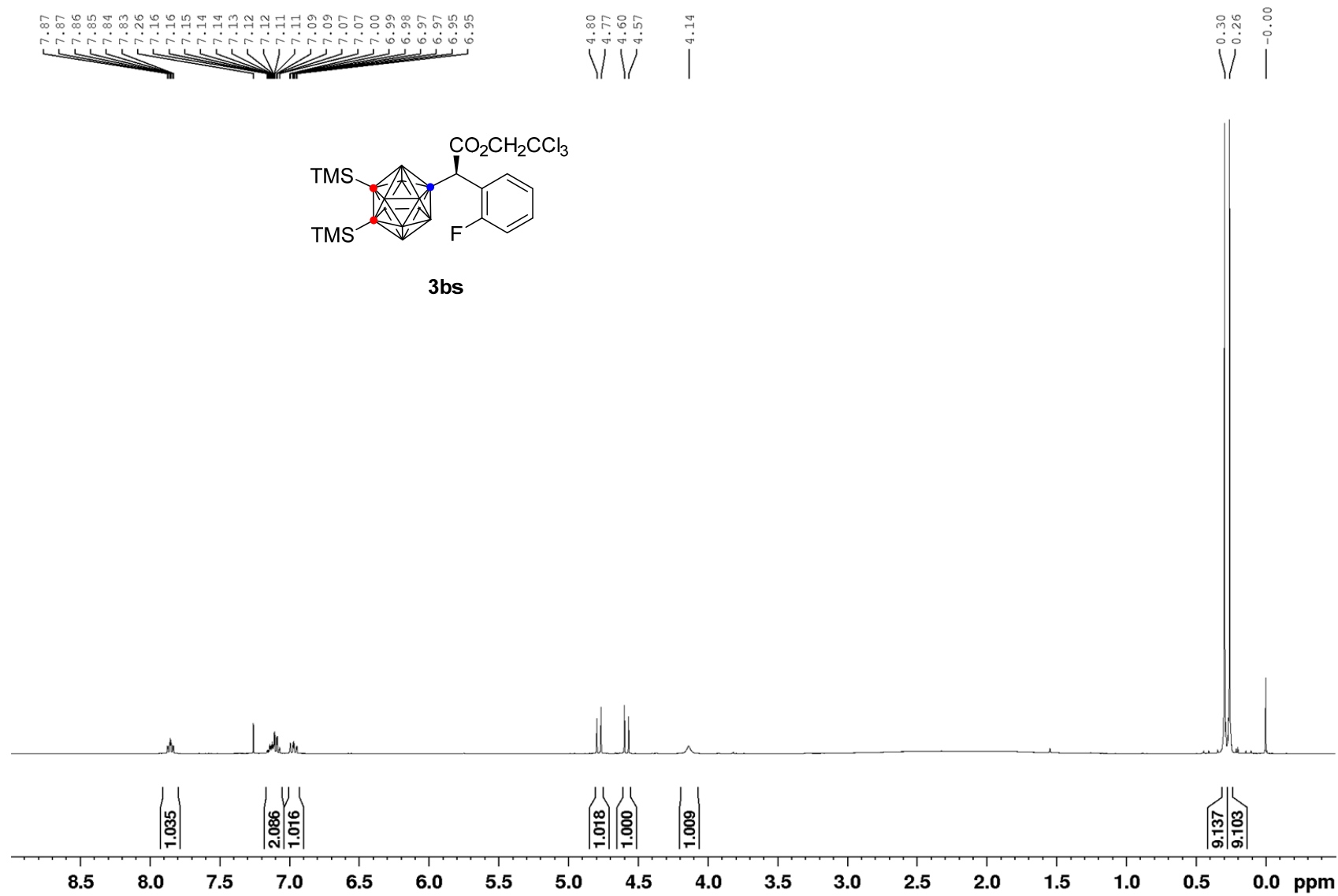
^{11}B NMR (128 MHz, CDCl_3)



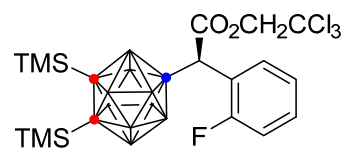
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



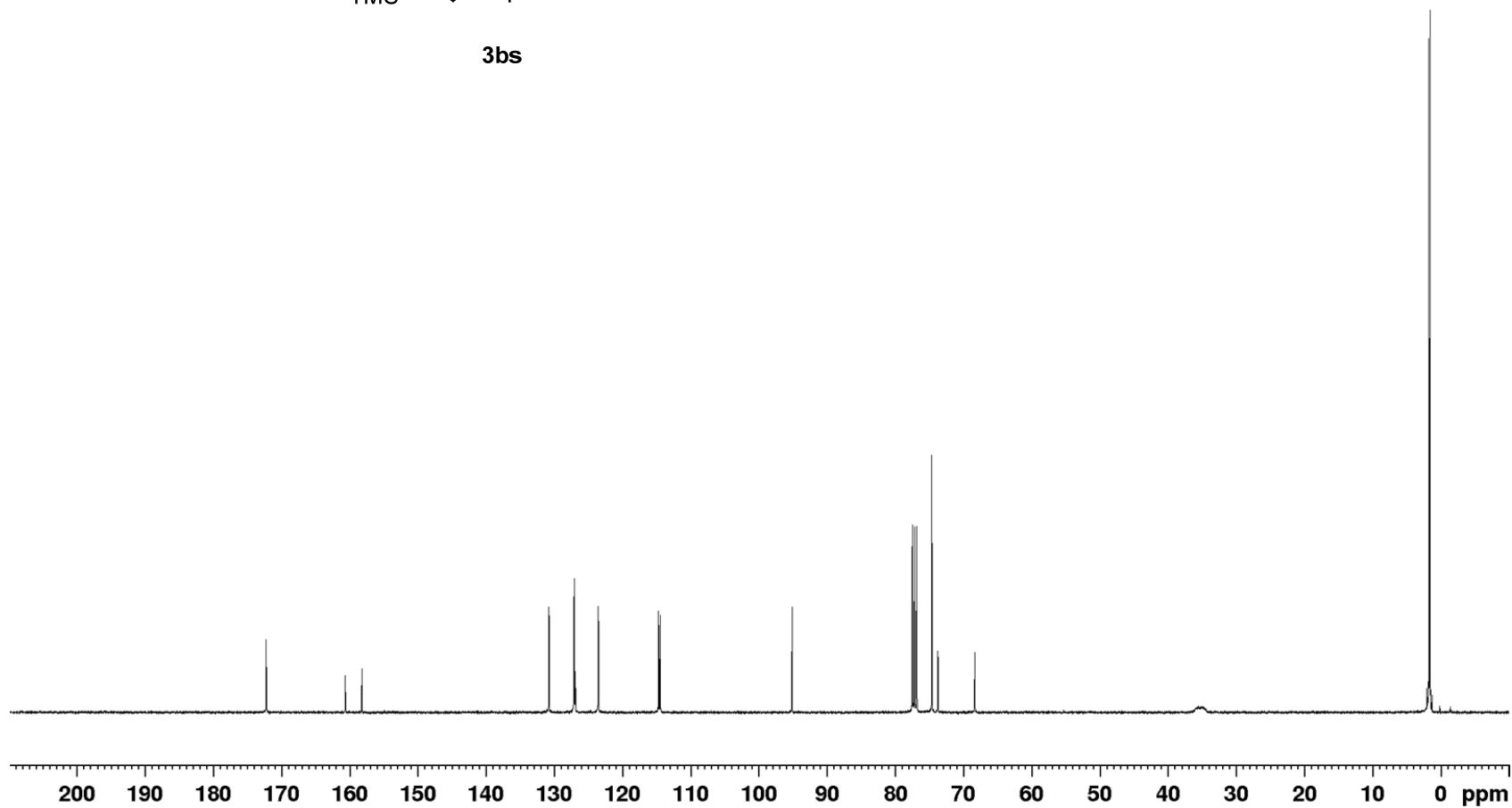
¹H NMR (400 MHz, CDCl₃)



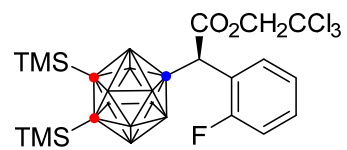
^{13}C NMR (100 MHz, CDCl_3)



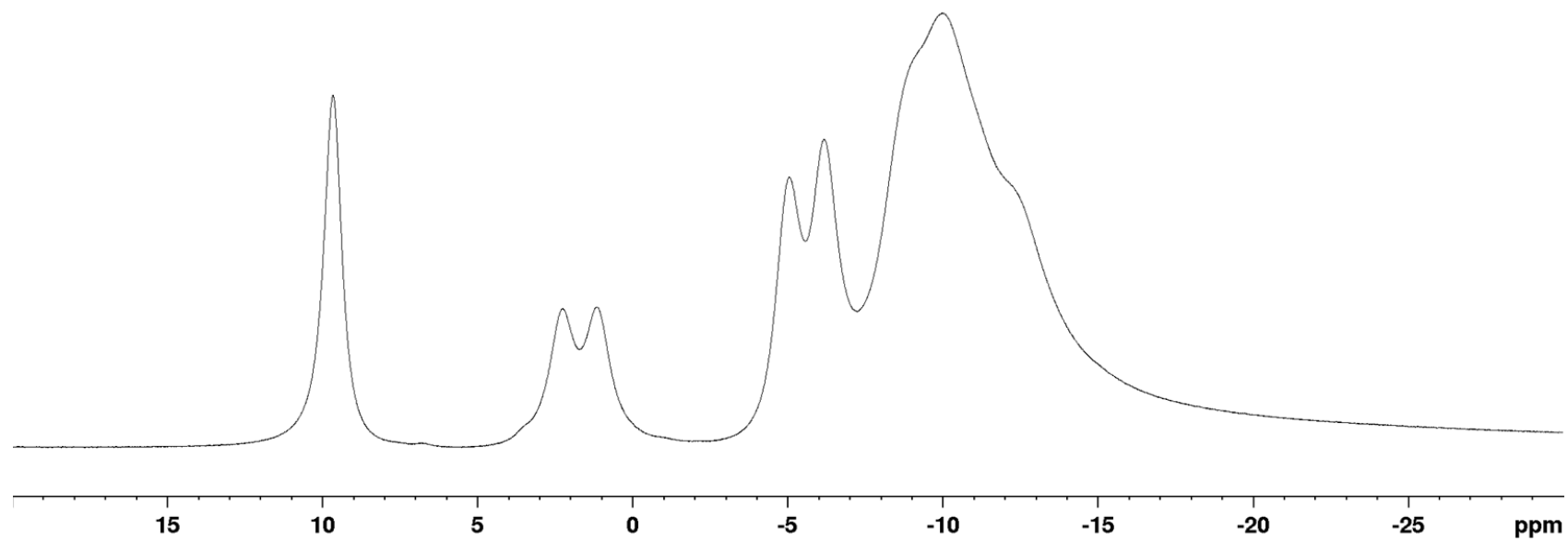
3bs



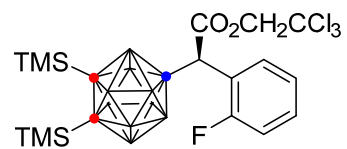
^{11}B NMR (128 MHz, CDCl_3)



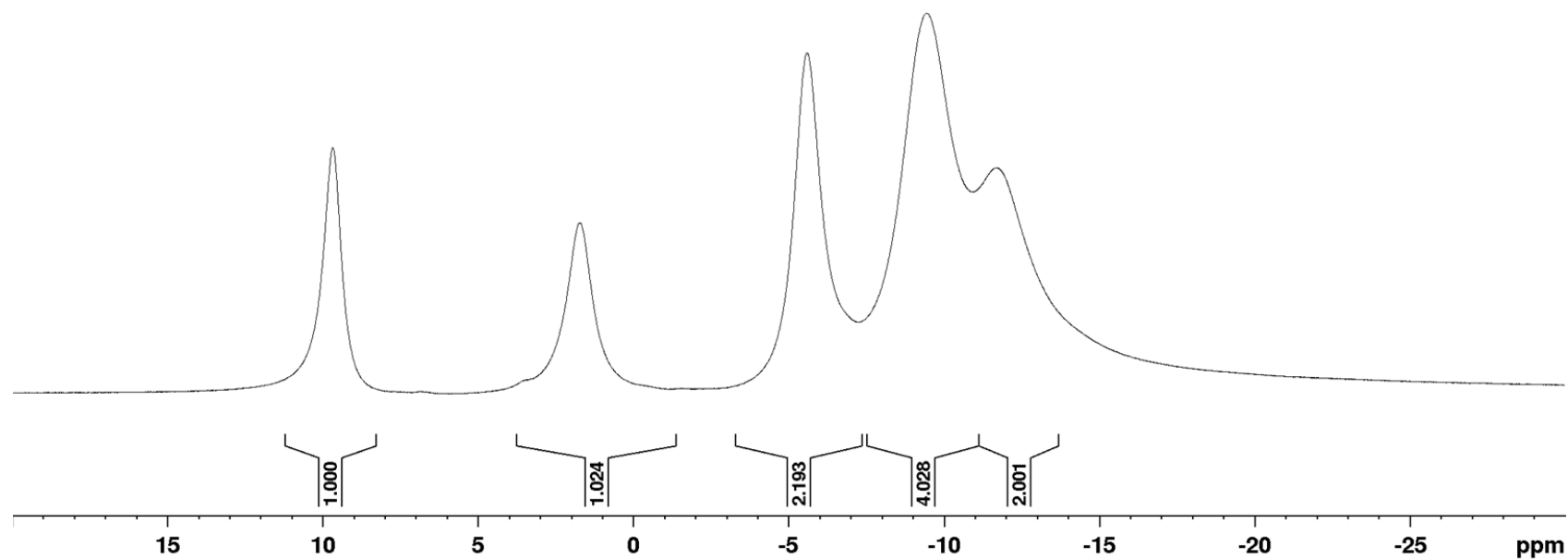
3bs



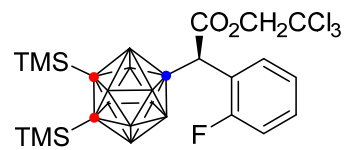
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



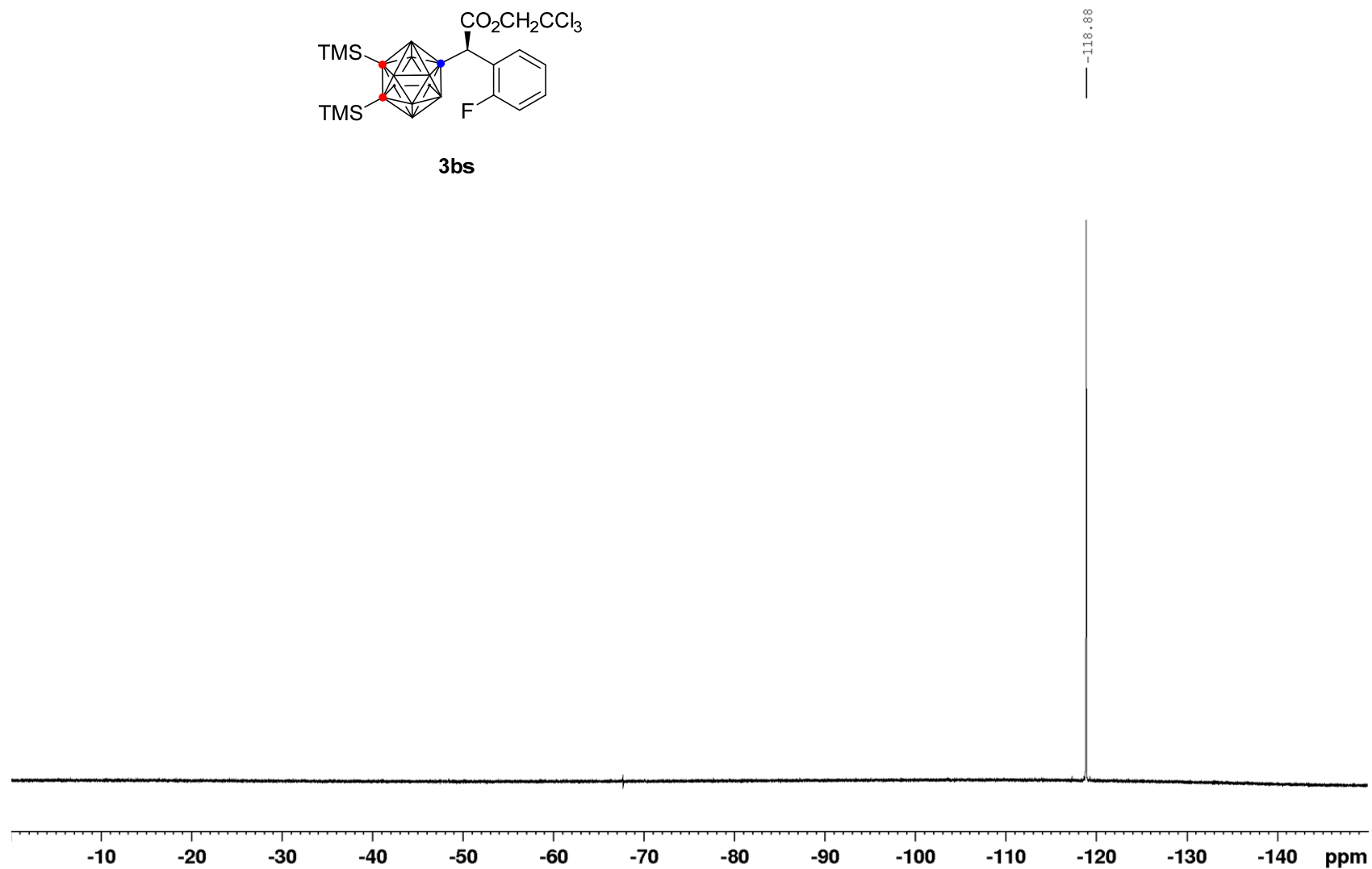
3bs



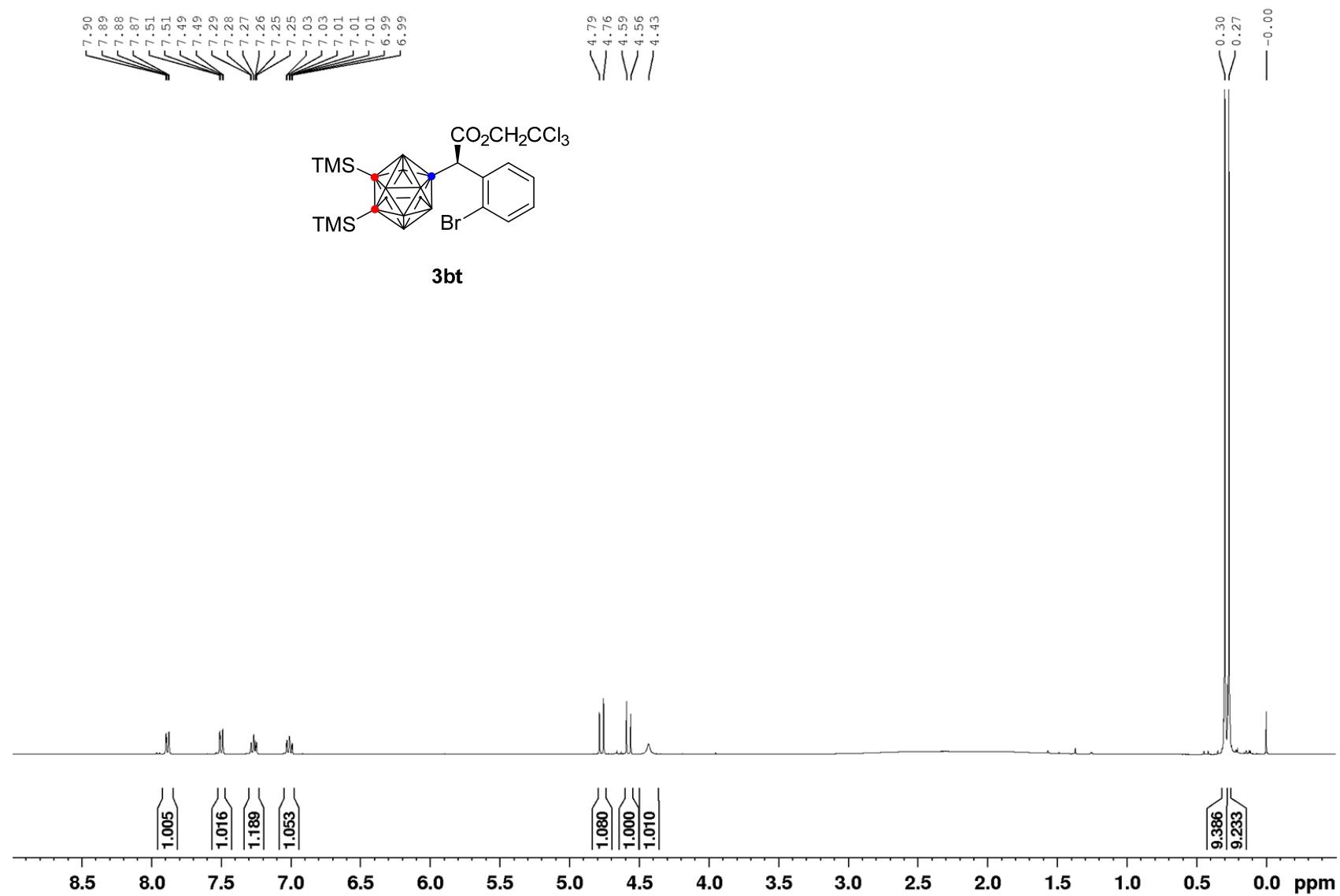
$^{19}\text{F}\{^1\text{H}\}$ NMR (377 MHz, CDCl_3)



3bs



^1H NMR (400 MHz, CDCl_3)



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

172.5

138.9

132.3

131.7

127.3

126.8

124.2

95.1

77.5

77.2

76.8

74.7

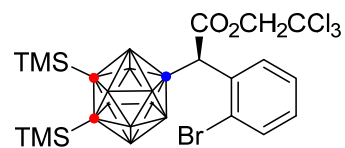
73.6

68.6

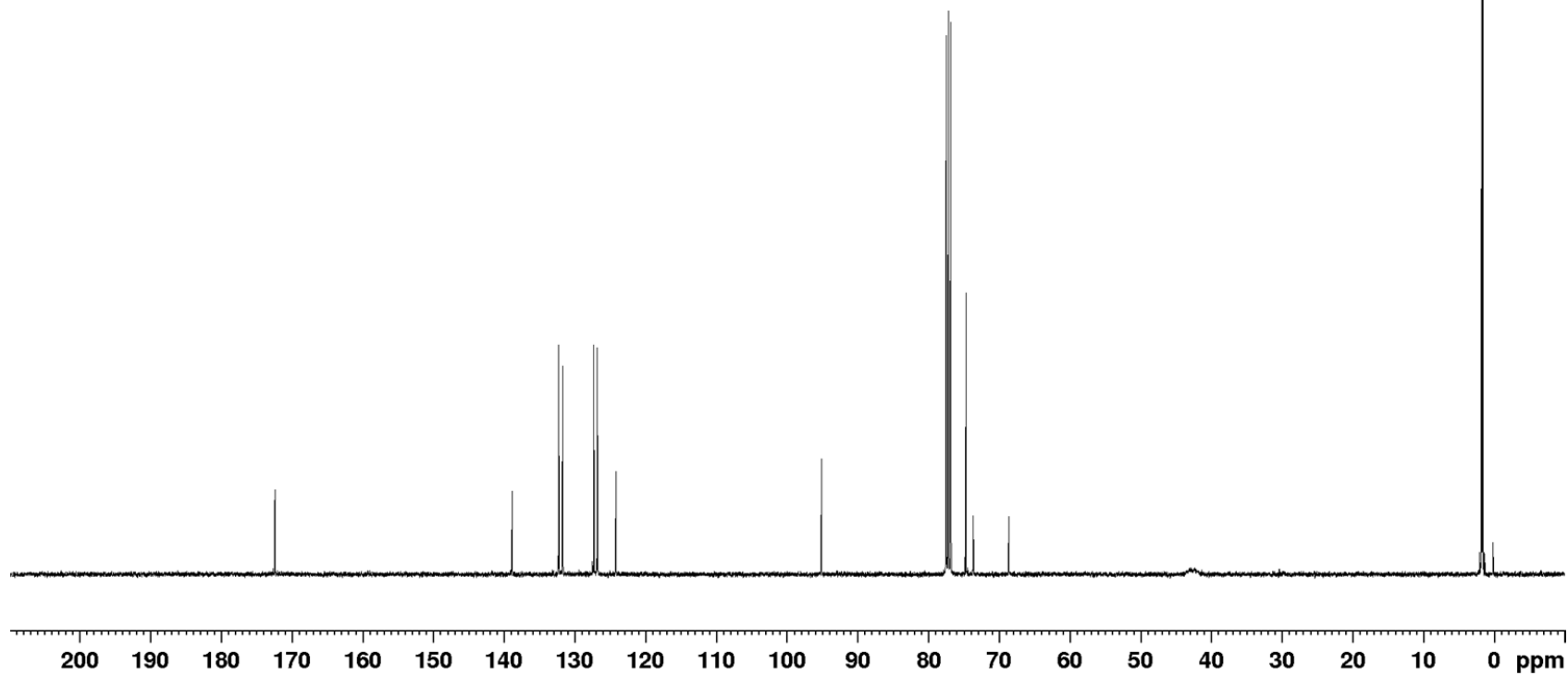
42.6

1.8

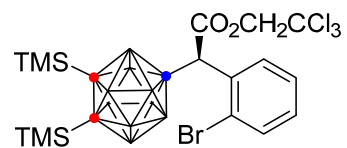
1.6



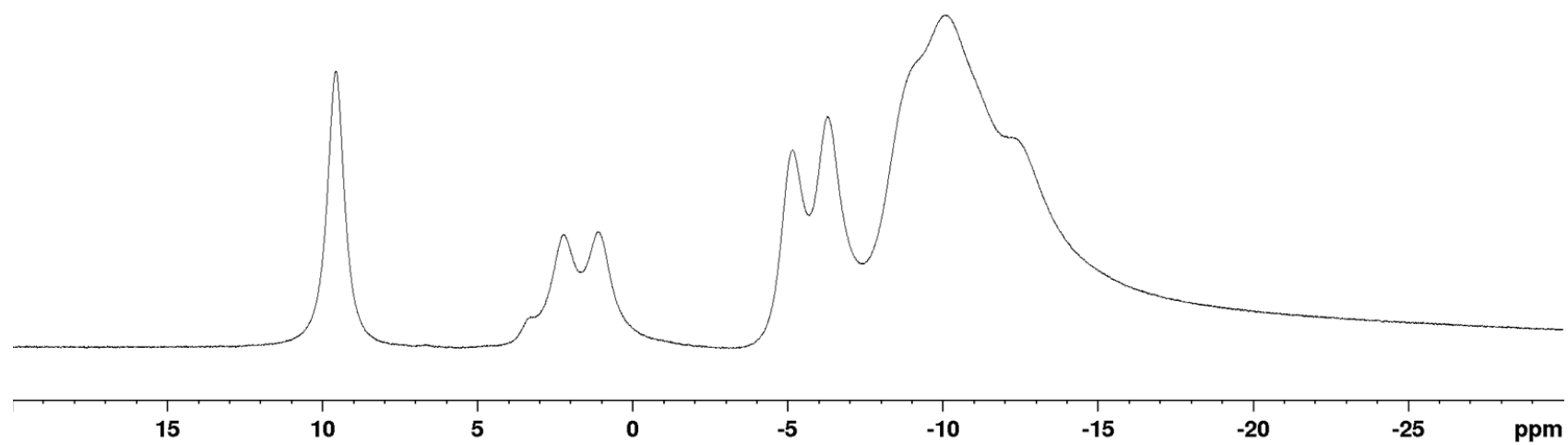
3bt



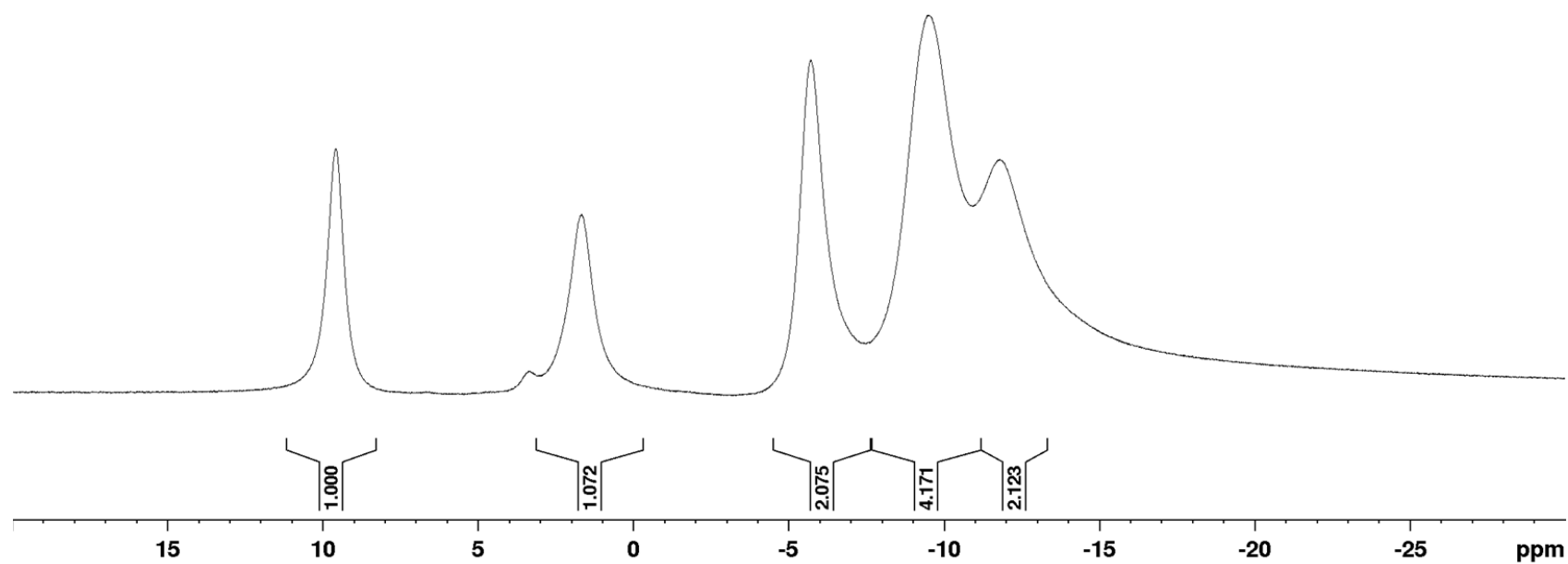
^{11}B NMR (128 MHz, CDCl_3)



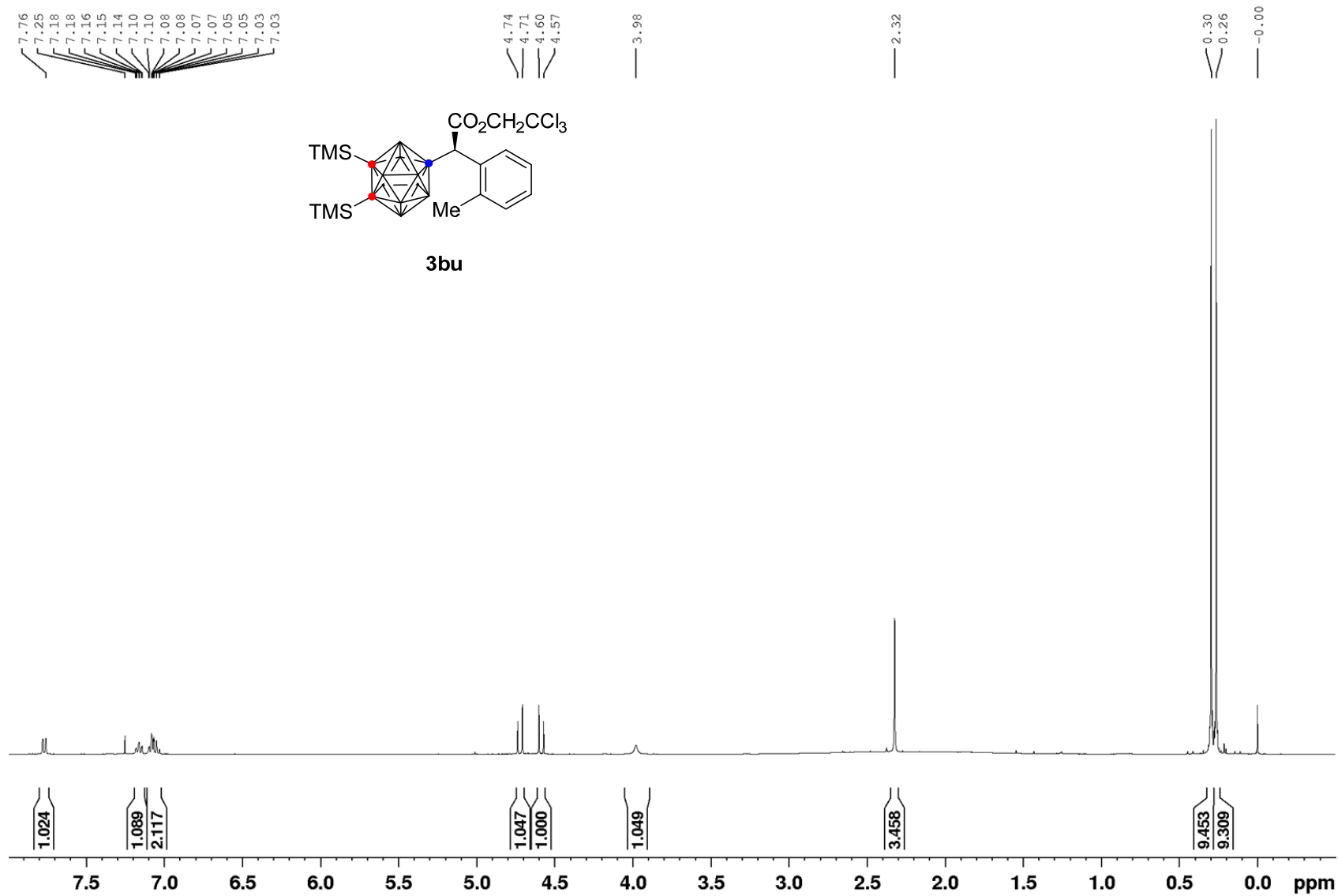
3bt



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



¹H NMR (400 MHz, CDCl₃)



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

— 173.2

— 138.2

— 134.9

— 129.8

— 129.8

— 125.7

— 125.6

— 95.3

— 77.5

— 77.2

— 76.8

— 74.6

— 73.6

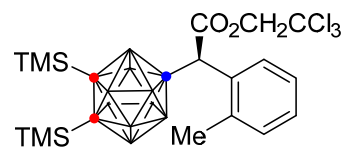
— 68.3

— 40.1

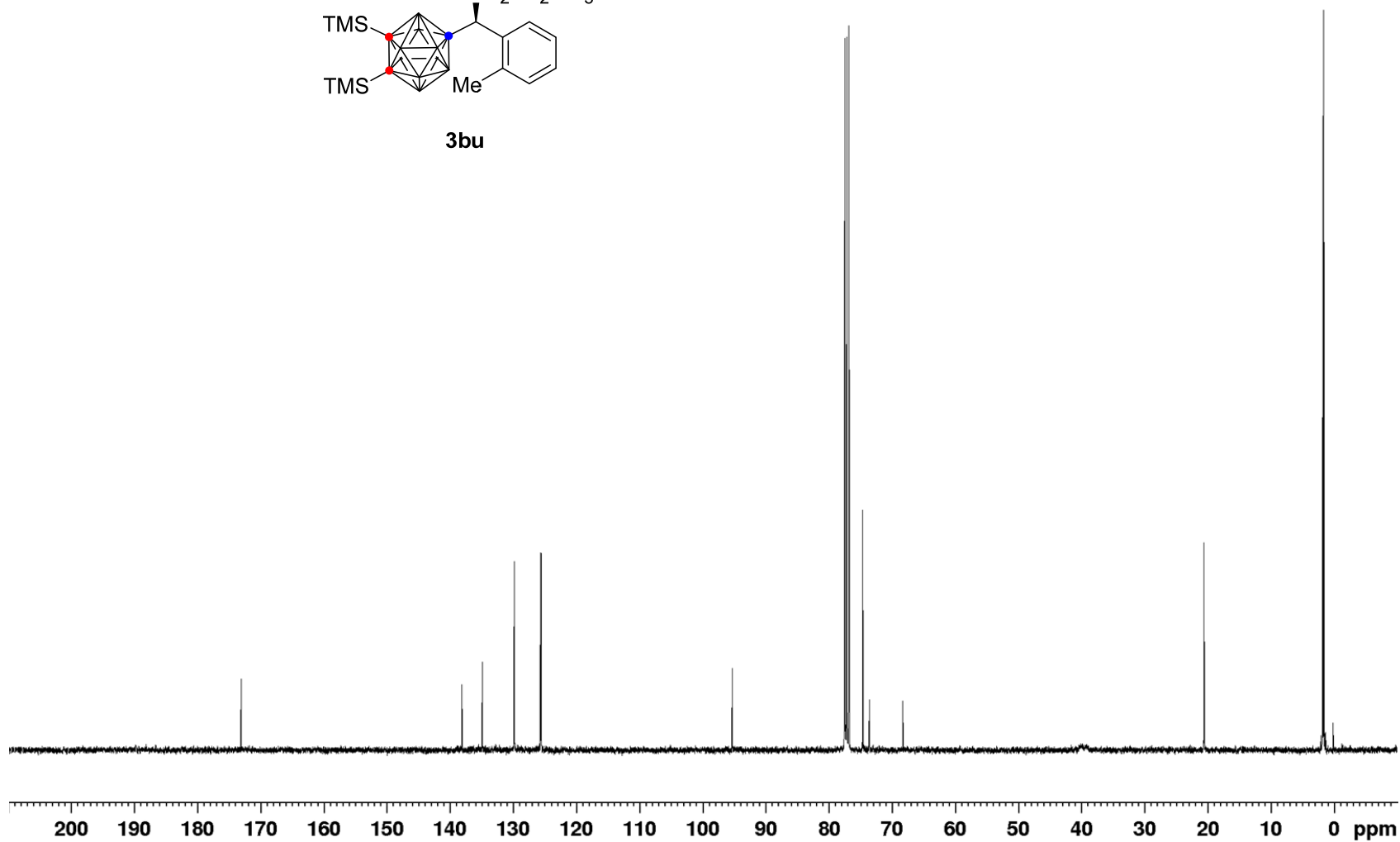
— 20.6

— 1.8

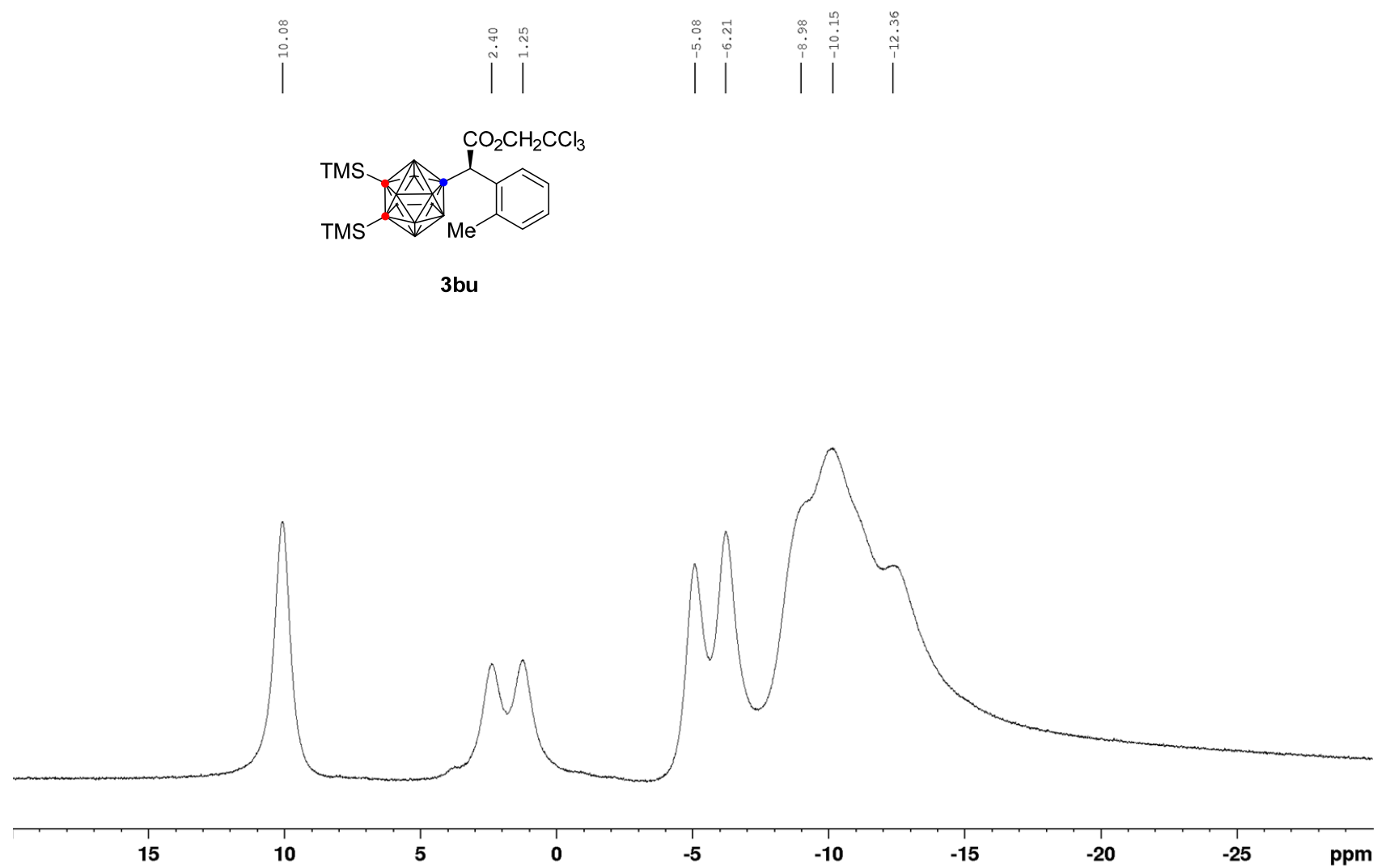
— 1.6



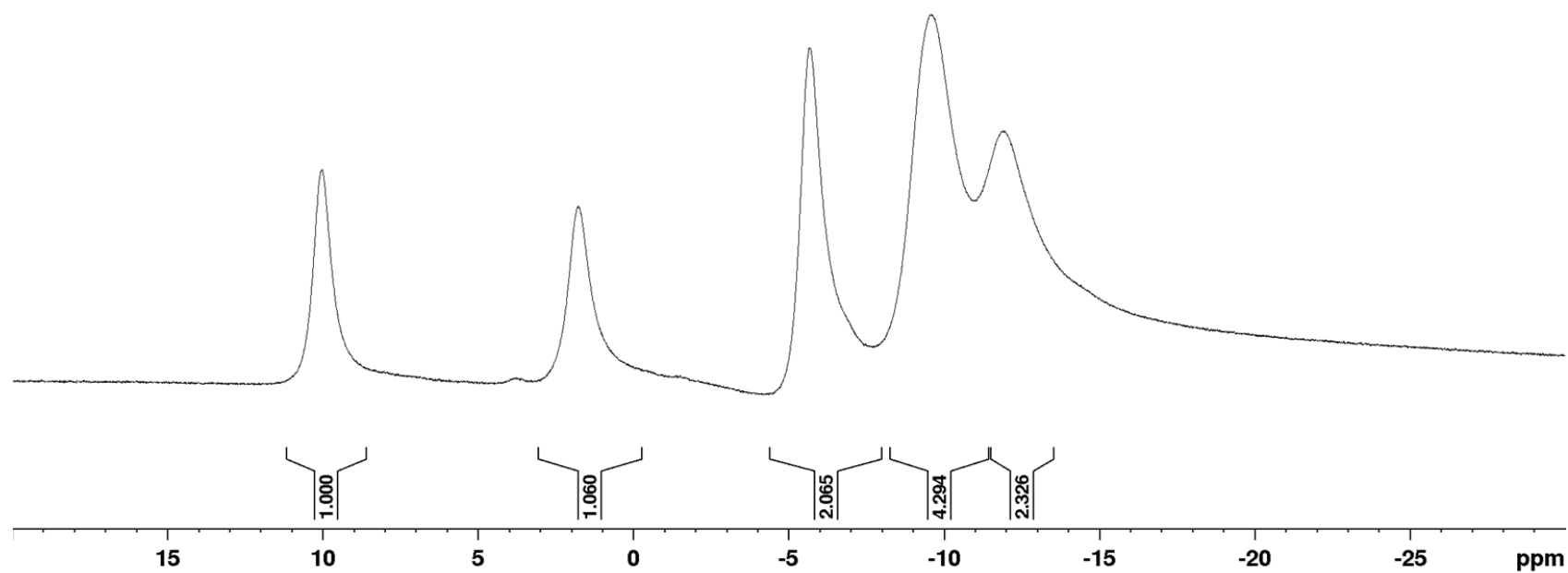
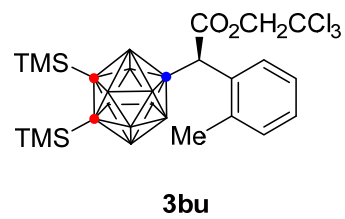
3bu



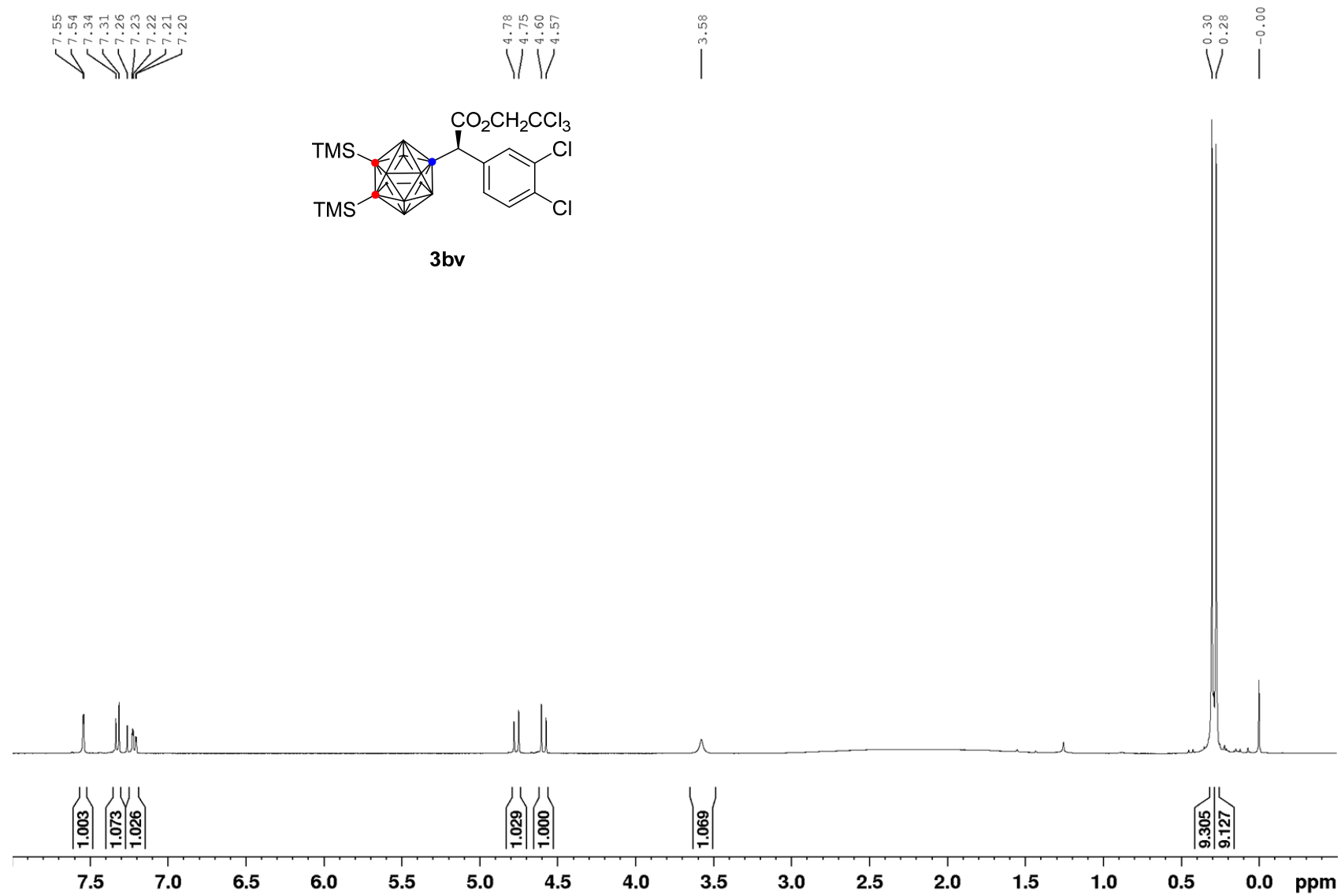
^{11}B NMR (128 MHz, CDCl_3)



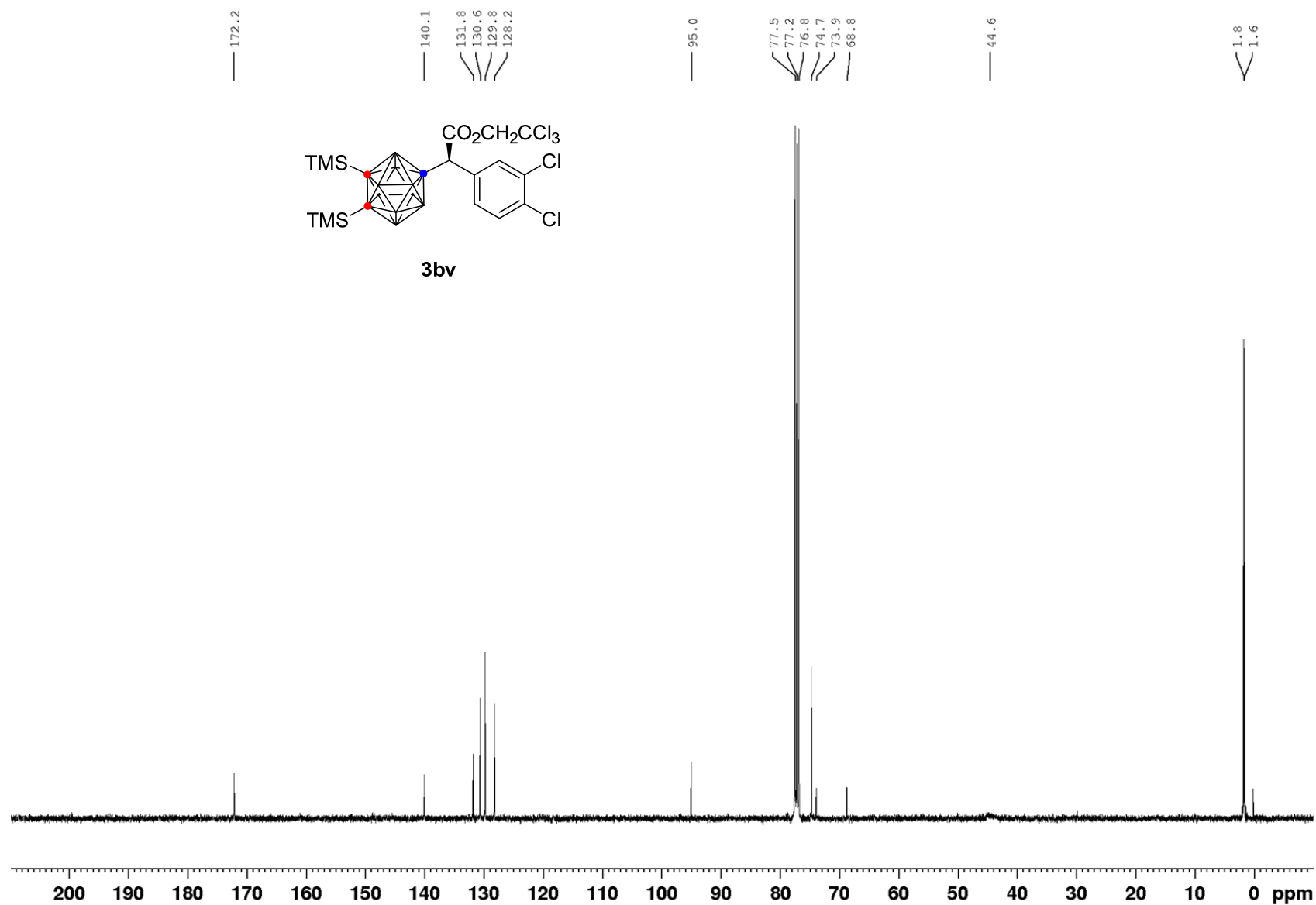
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



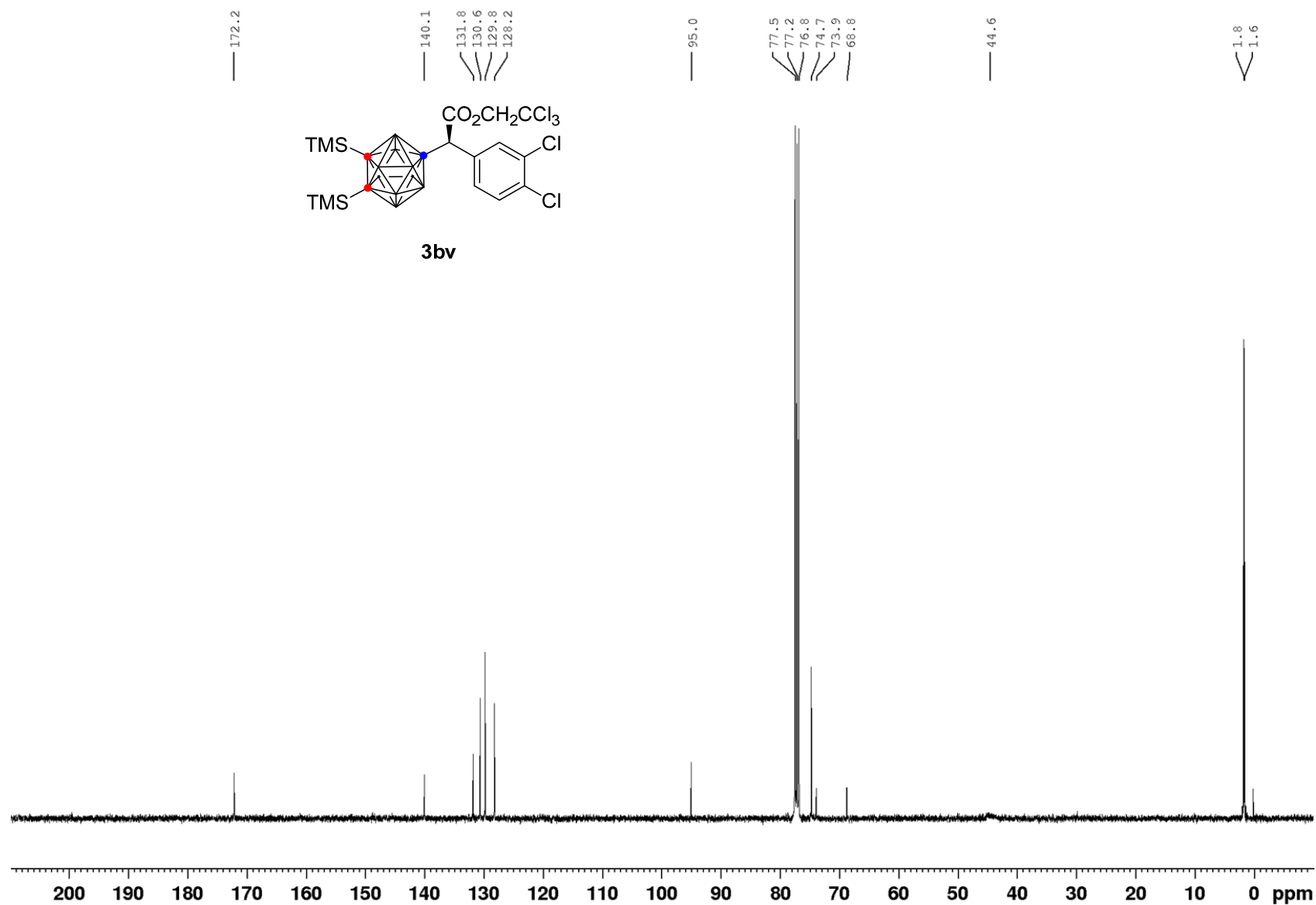
¹H NMR (400 MHz, CDCl₃)



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

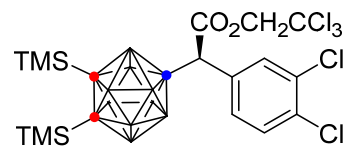


^{11}B NMR (128 MHz, CDCl_3)

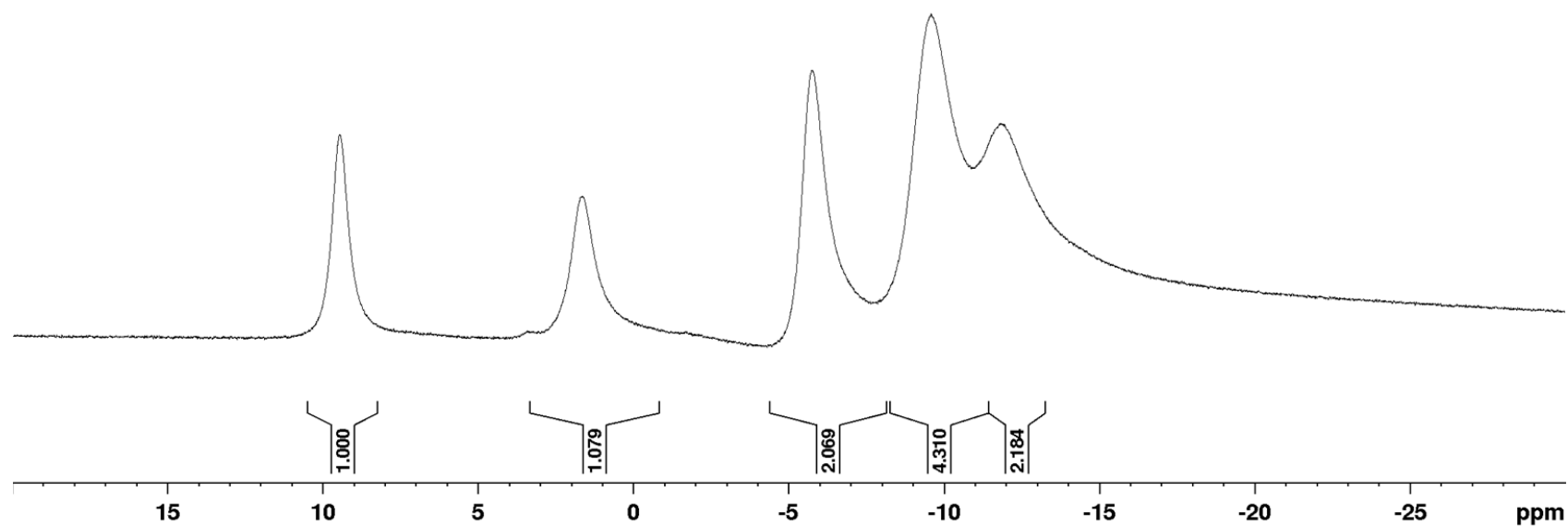


$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)

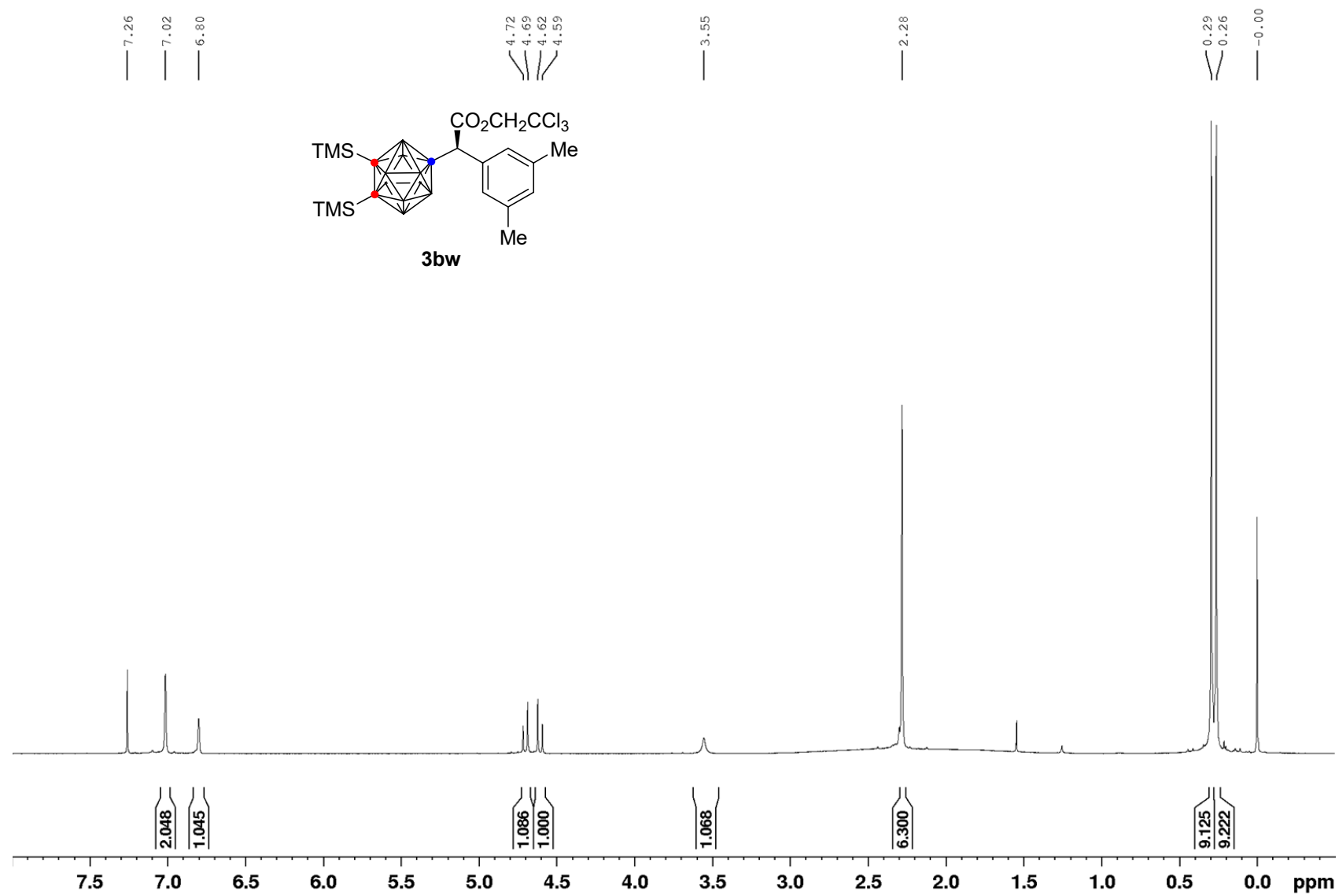
9.46 1.65 -5.77 -9.58 -11.81



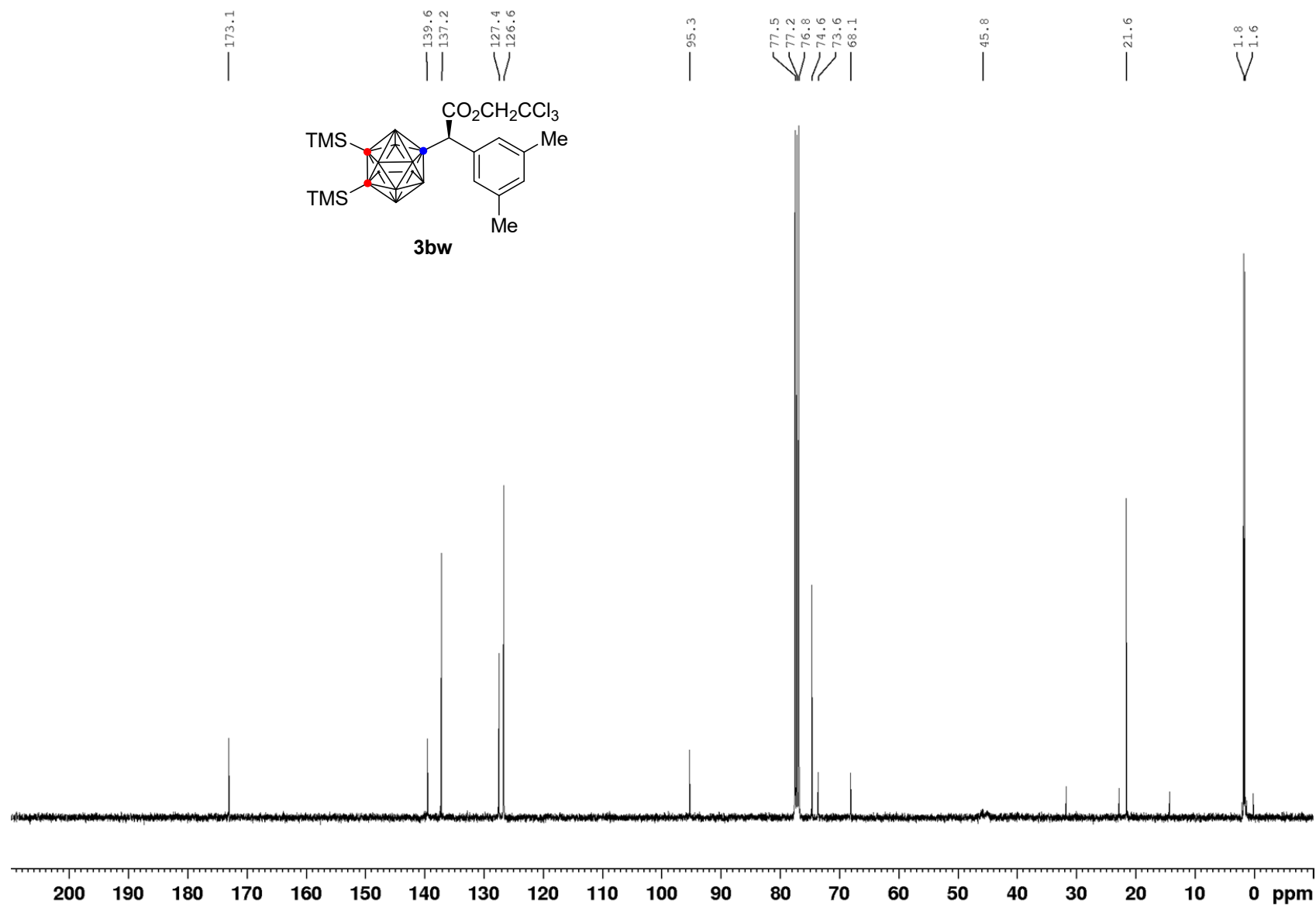
3bv



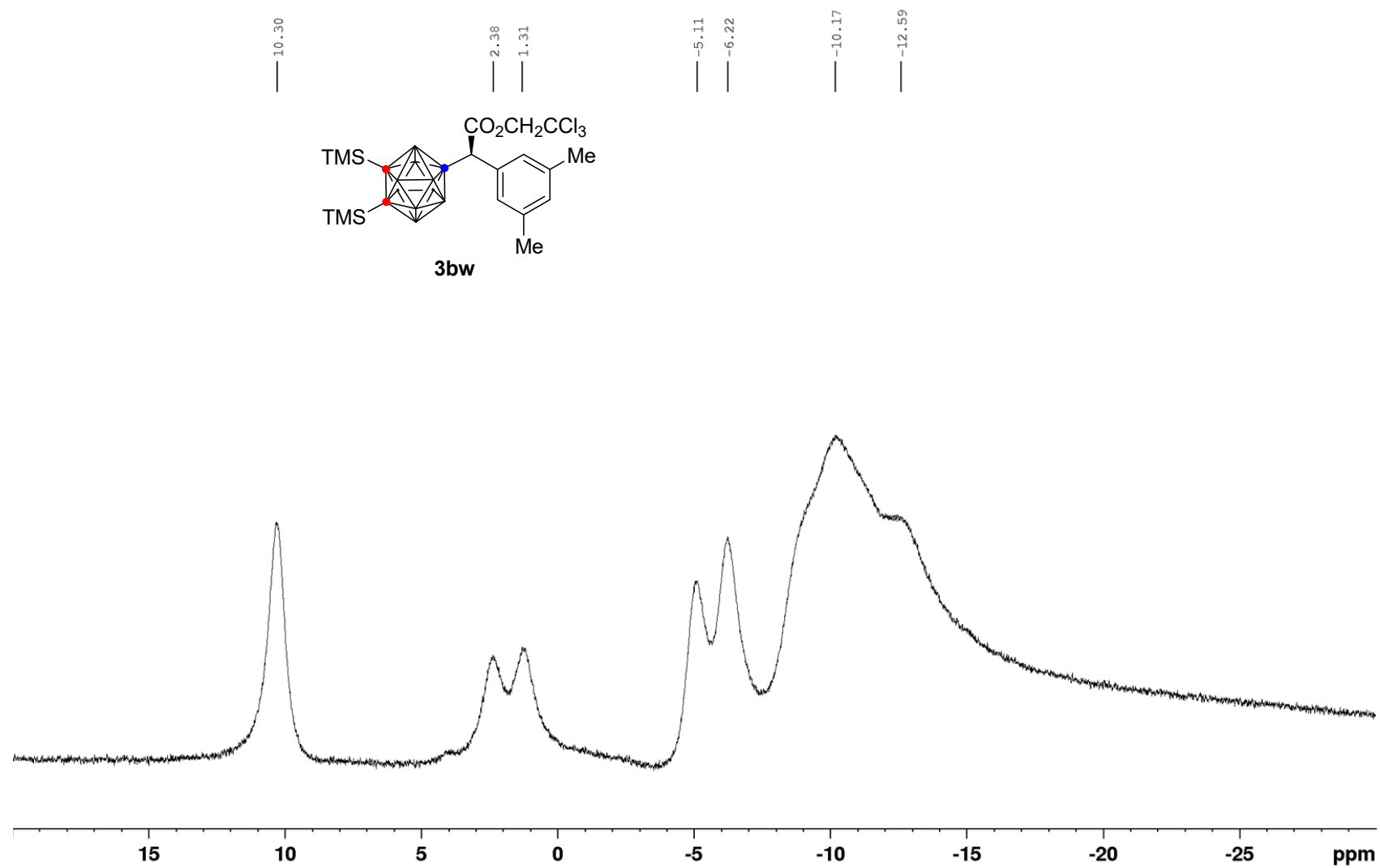
^1H NMR (400 MHz, CDCl_3)



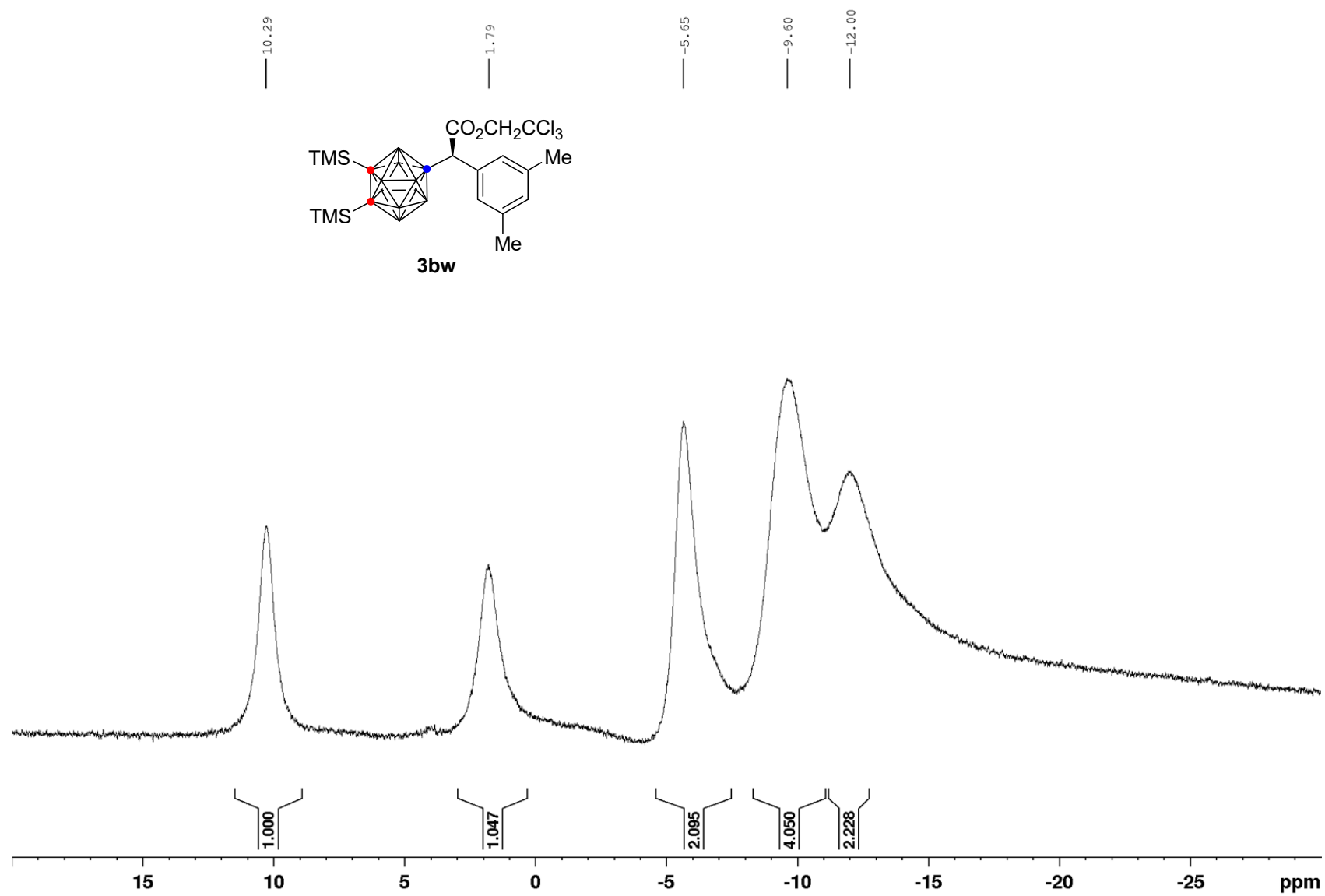
^{13}C NMR (100 MHz, CDCl_3)



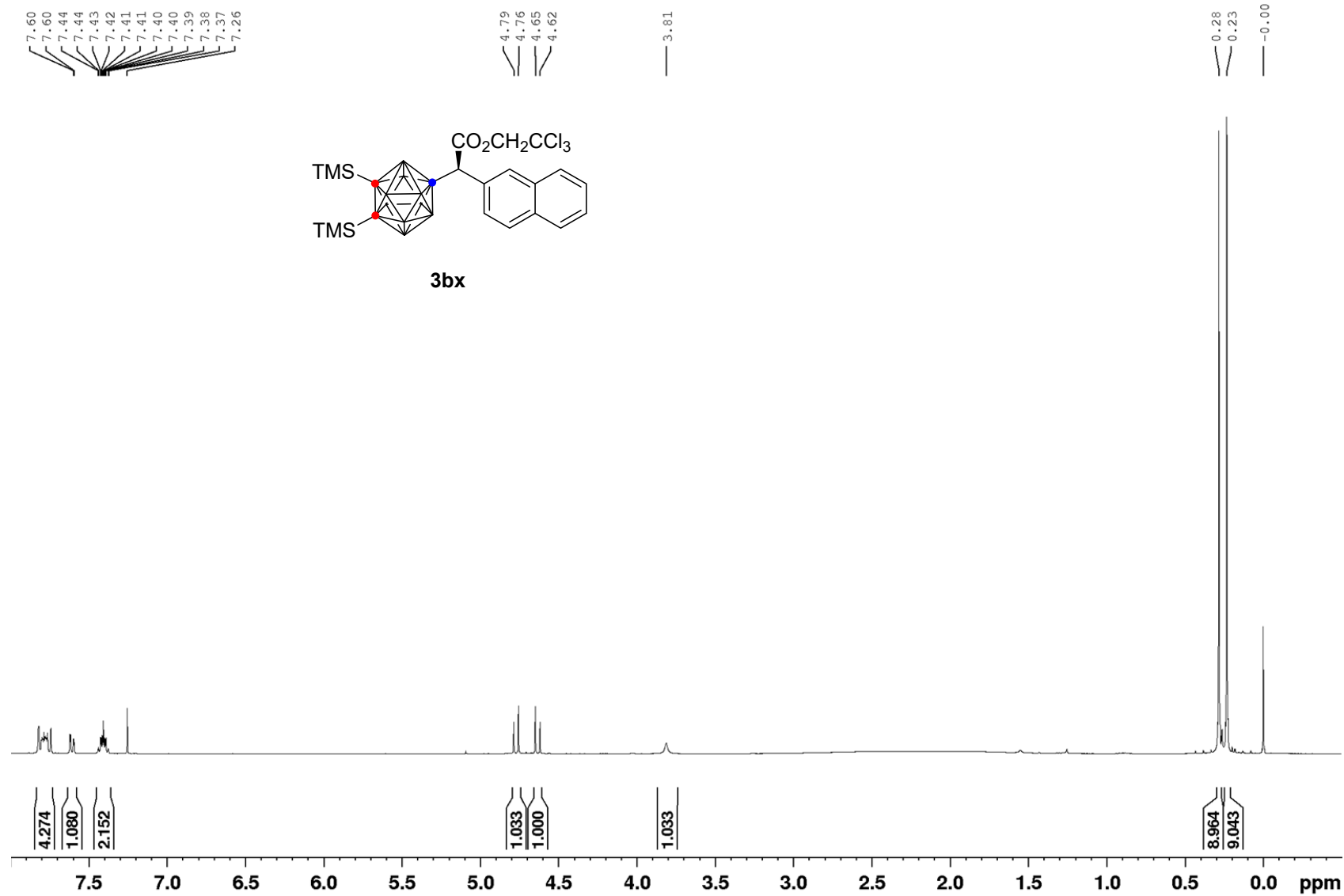
^{11}B NMR (128 MHz, CDCl_3)



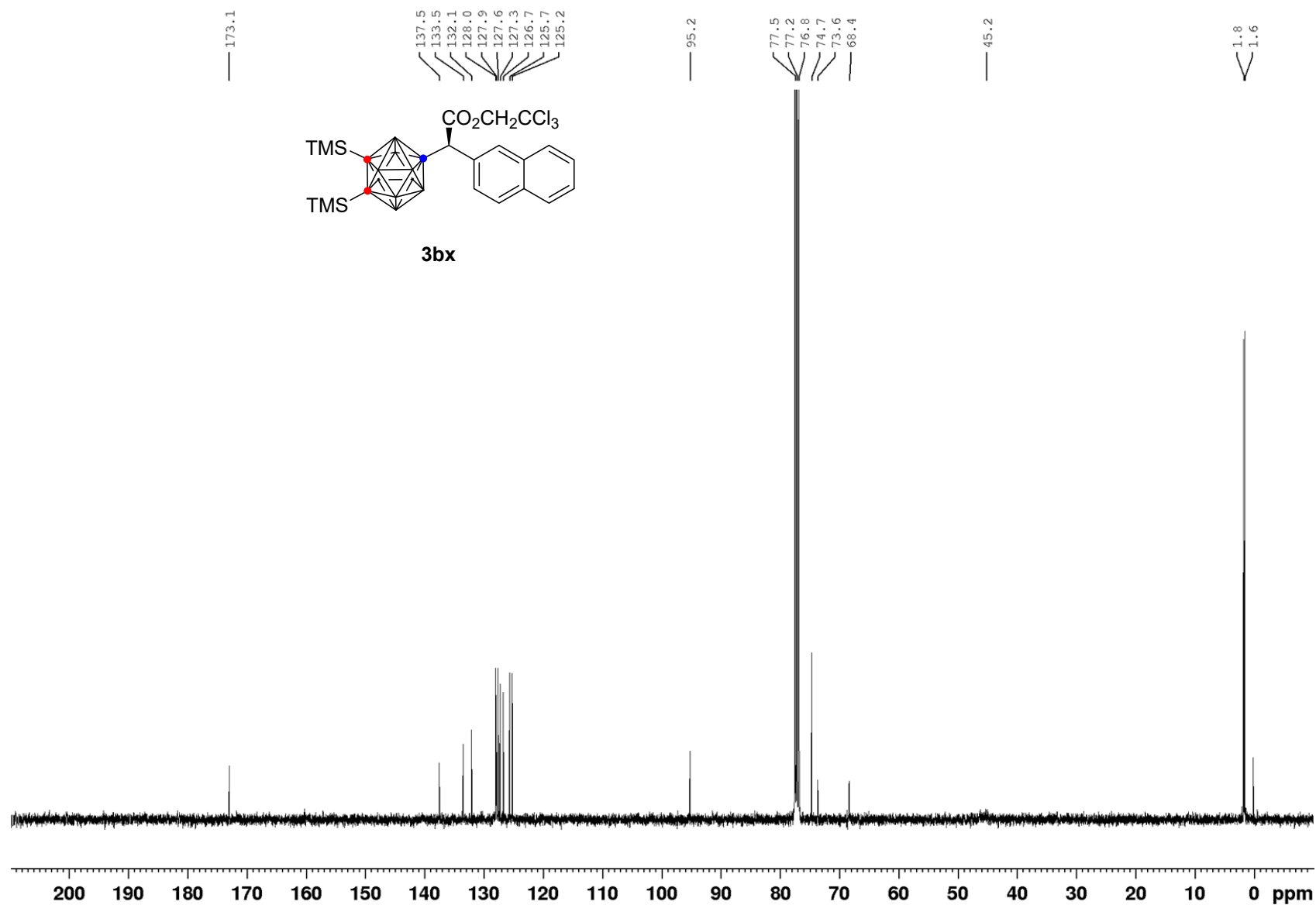
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



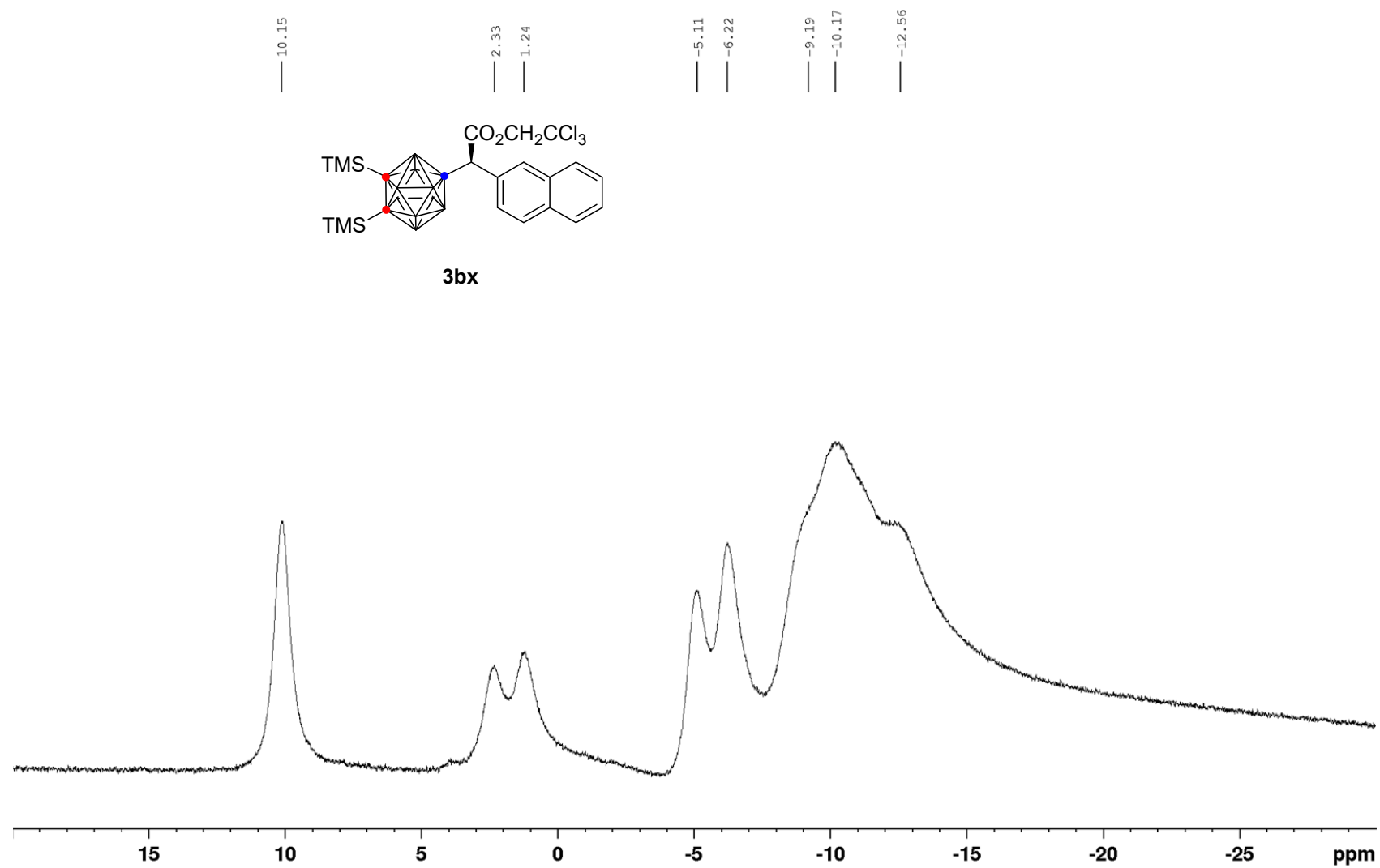
^1H NMR (400 MHz, CDCl_3)



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



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



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

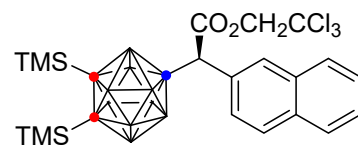
10.13

1.81

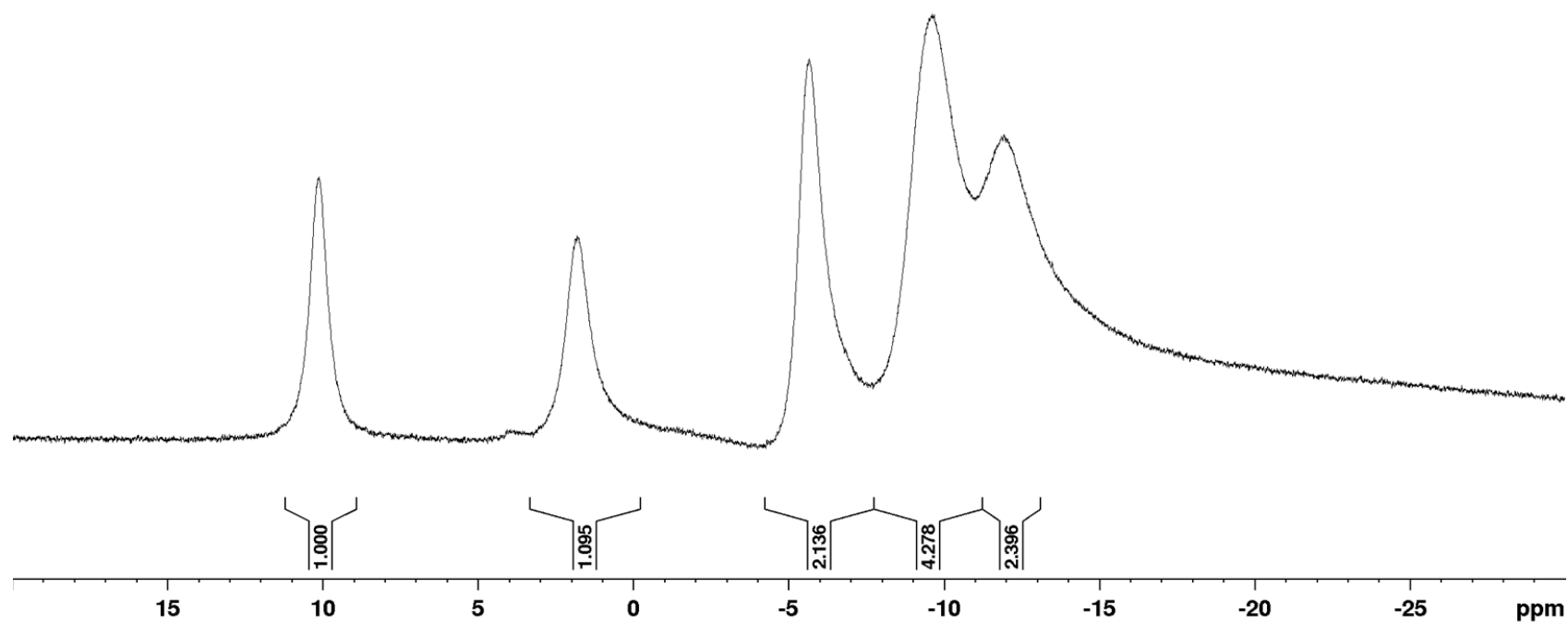
-5.66

-9.62

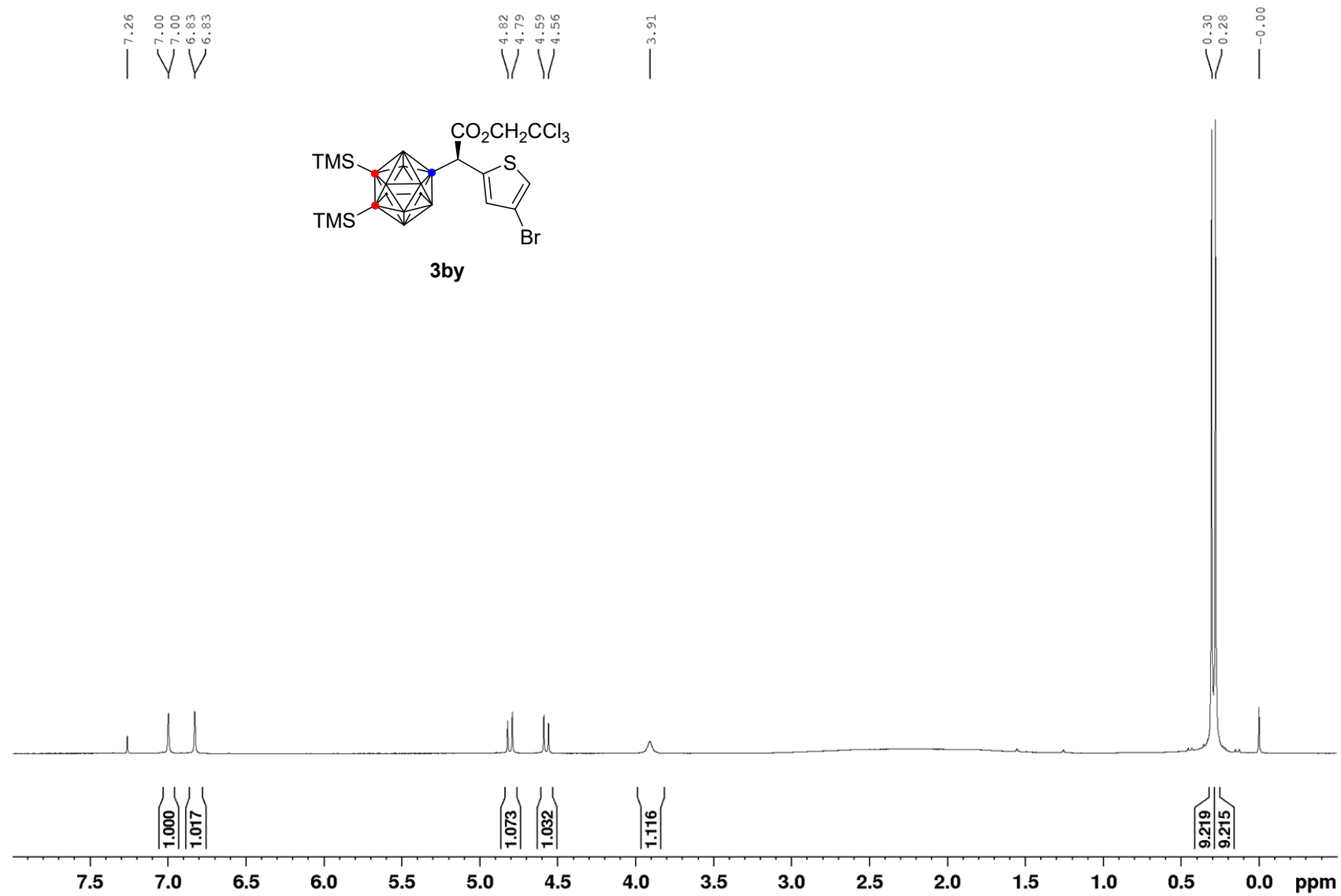
-11.95



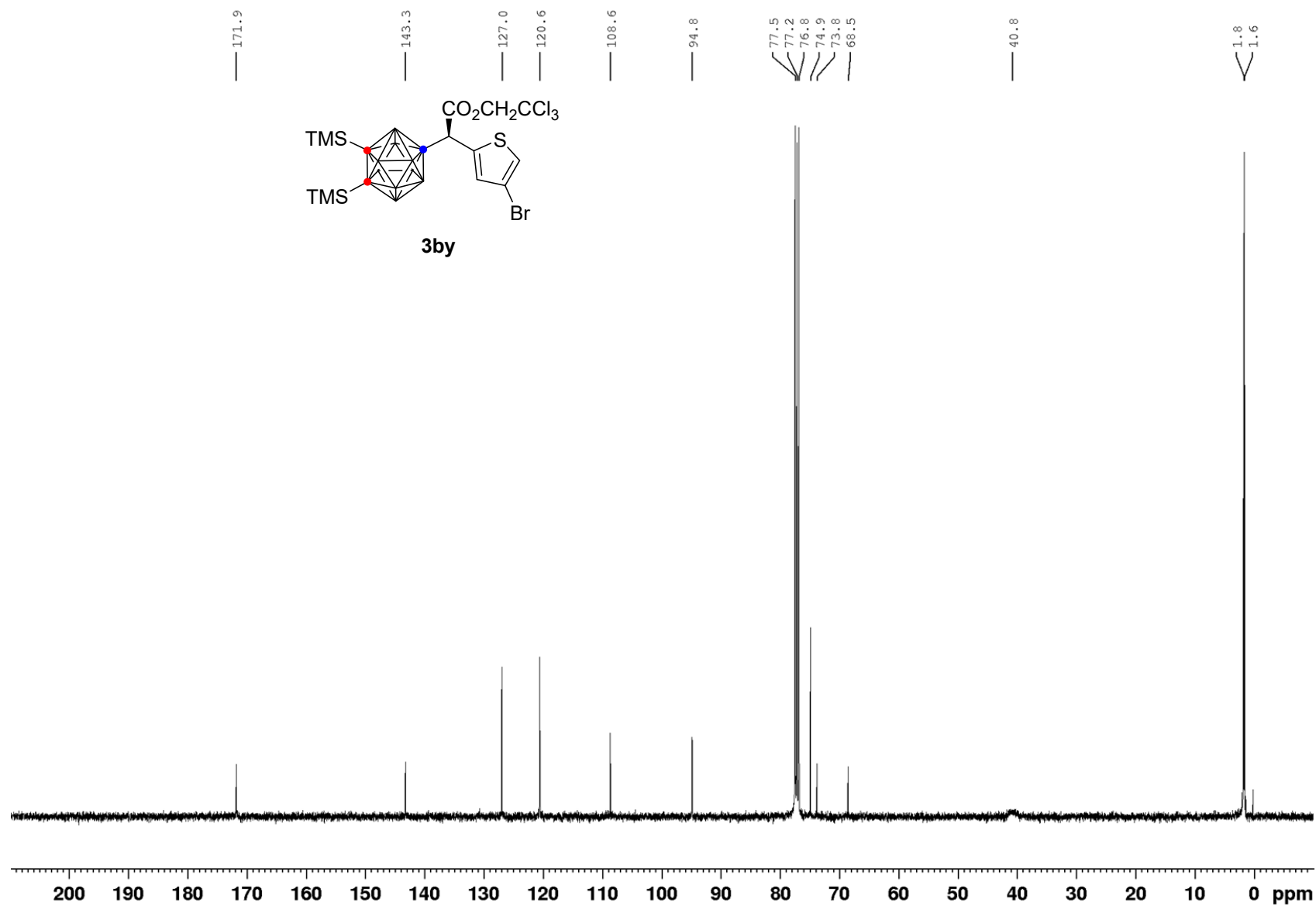
3bx



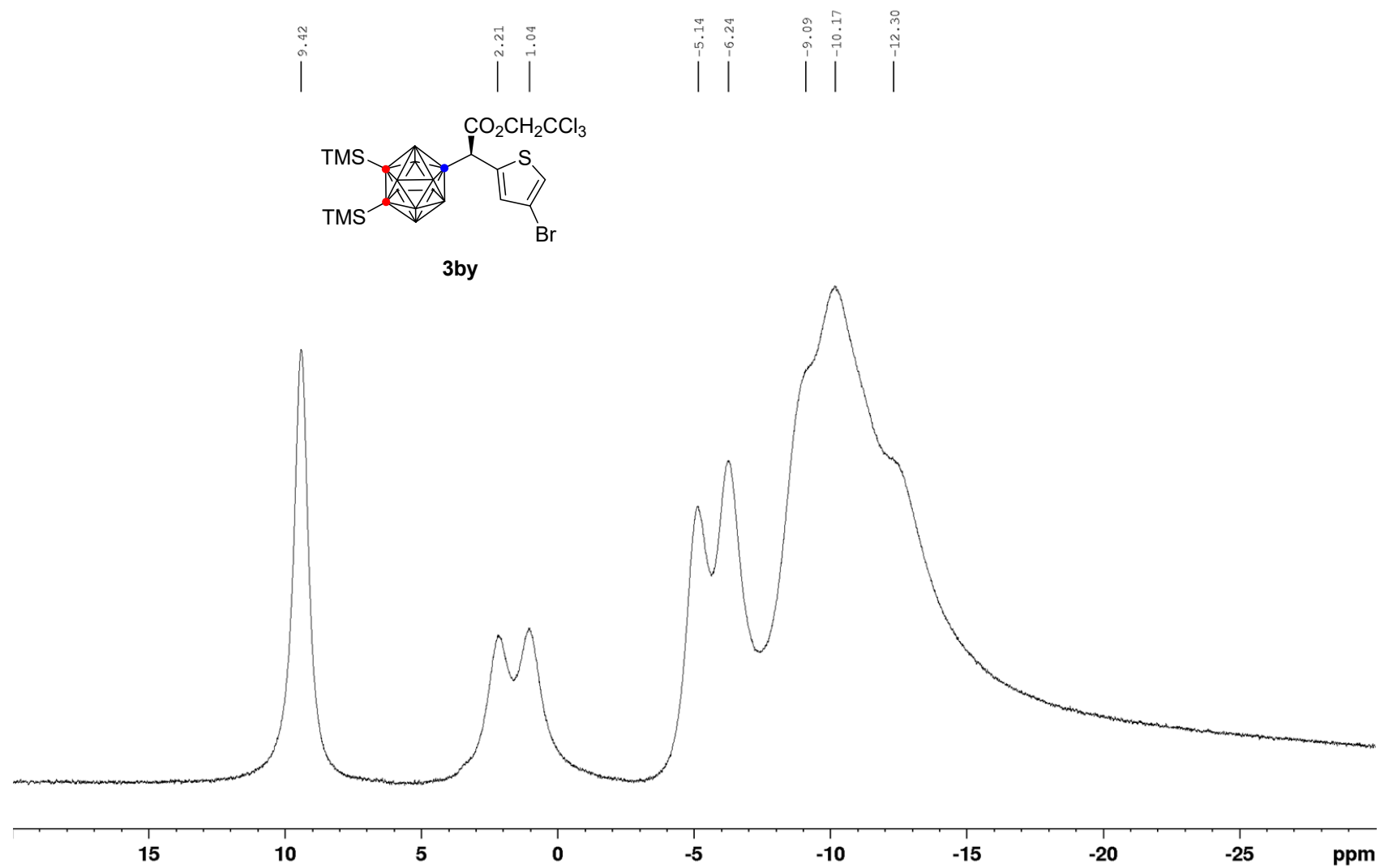
^1H NMR (400 MHz, CDCl_3)



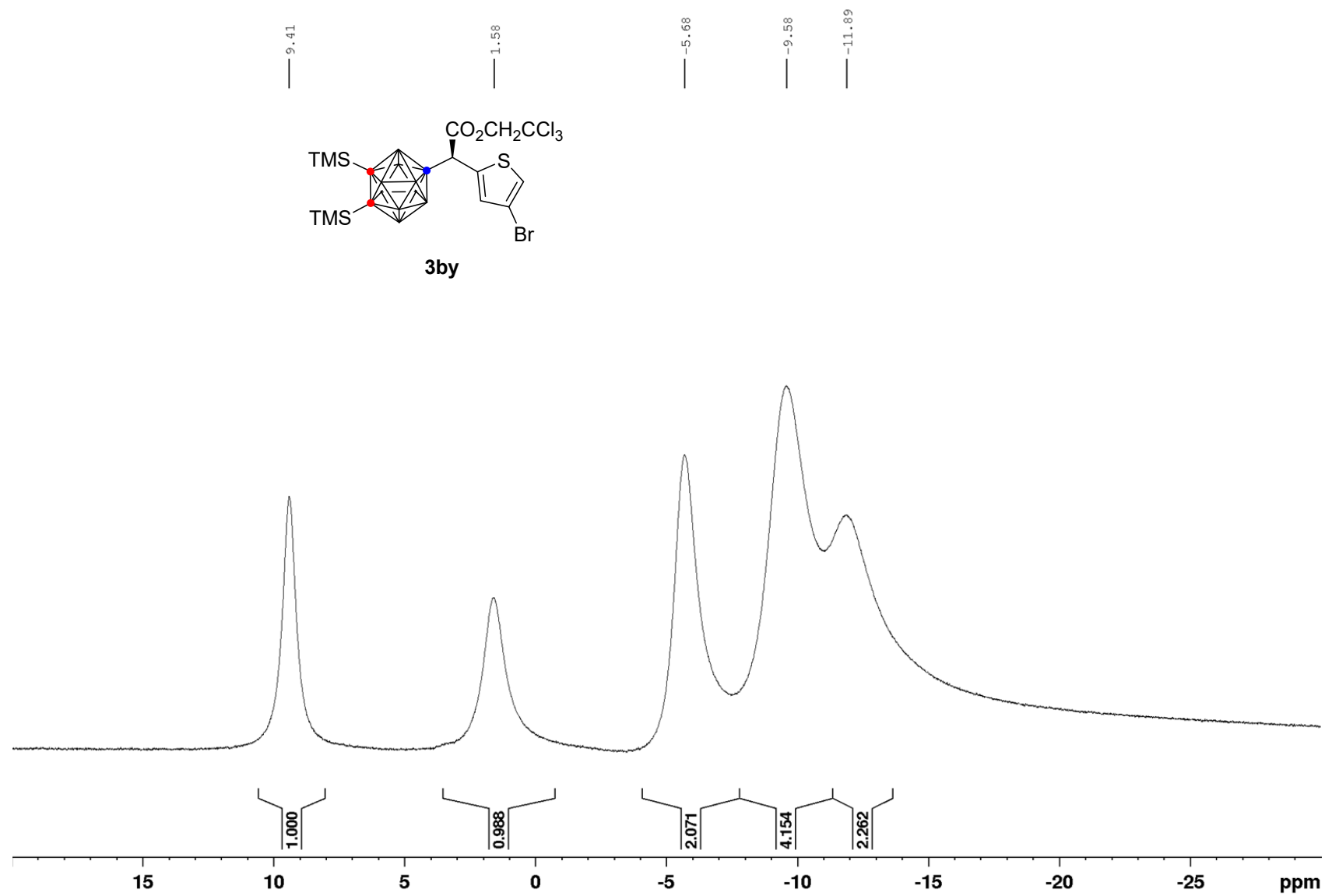
^{13}C NMR (100 MHz, CDCl_3)



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



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



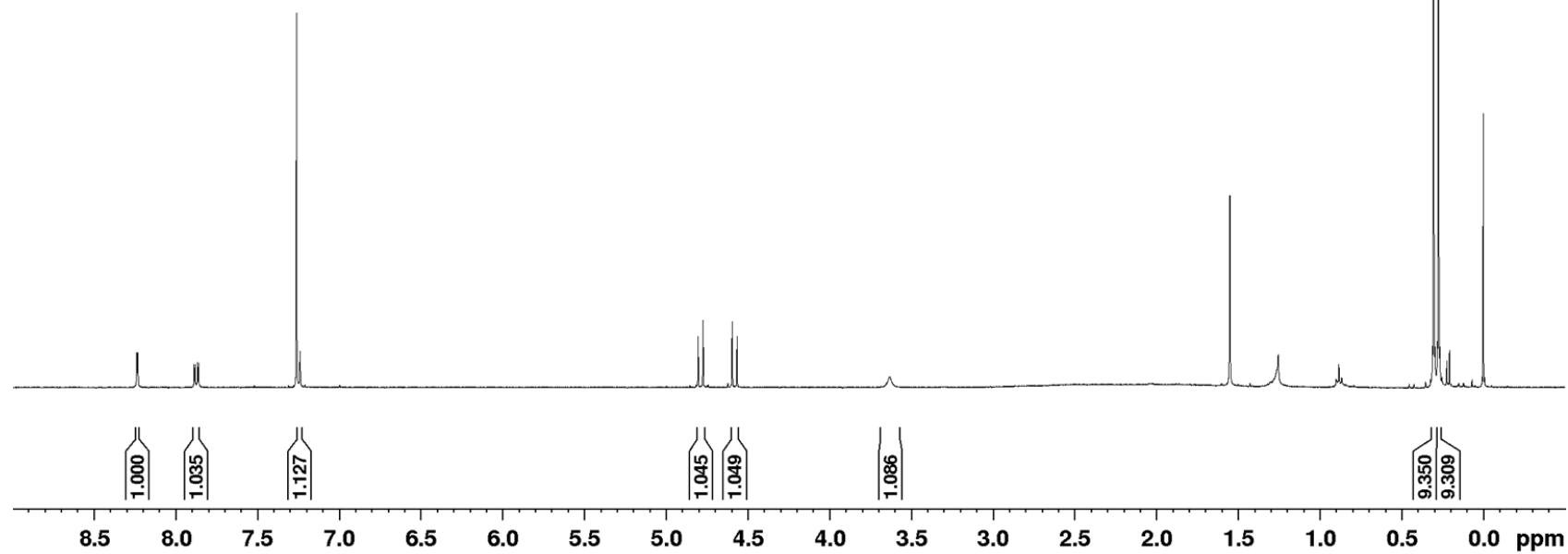
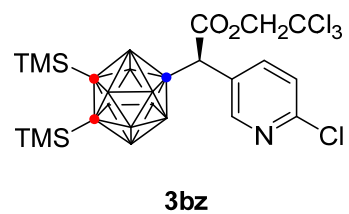
¹H NMR (400 MHz, CDCl₃)

8.24
8.23
7.89
7.88
7.87
7.86
7.26
7.26

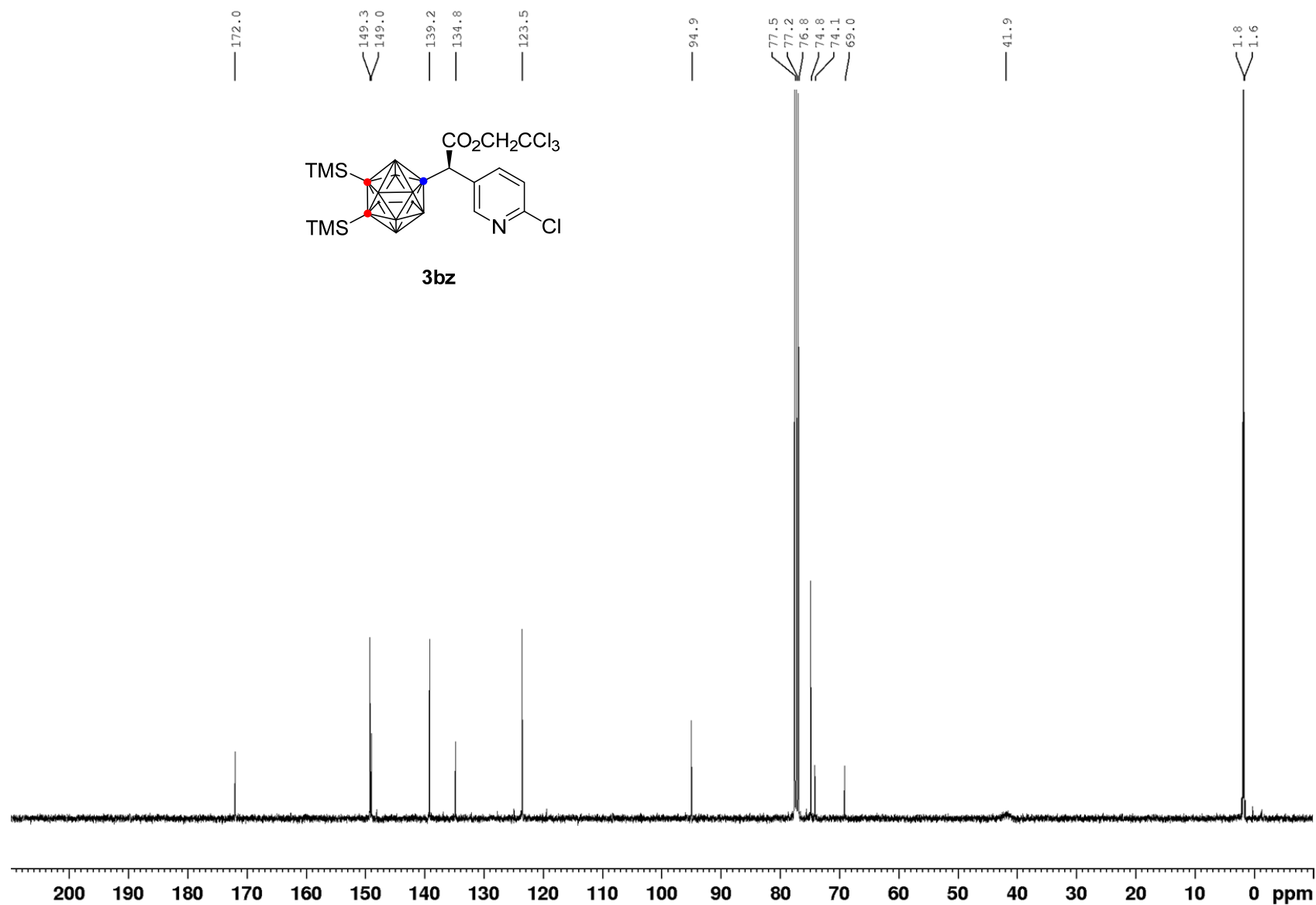
4.80
4.77
4.60
4.57

3.63

0.30
0.27
-0.00



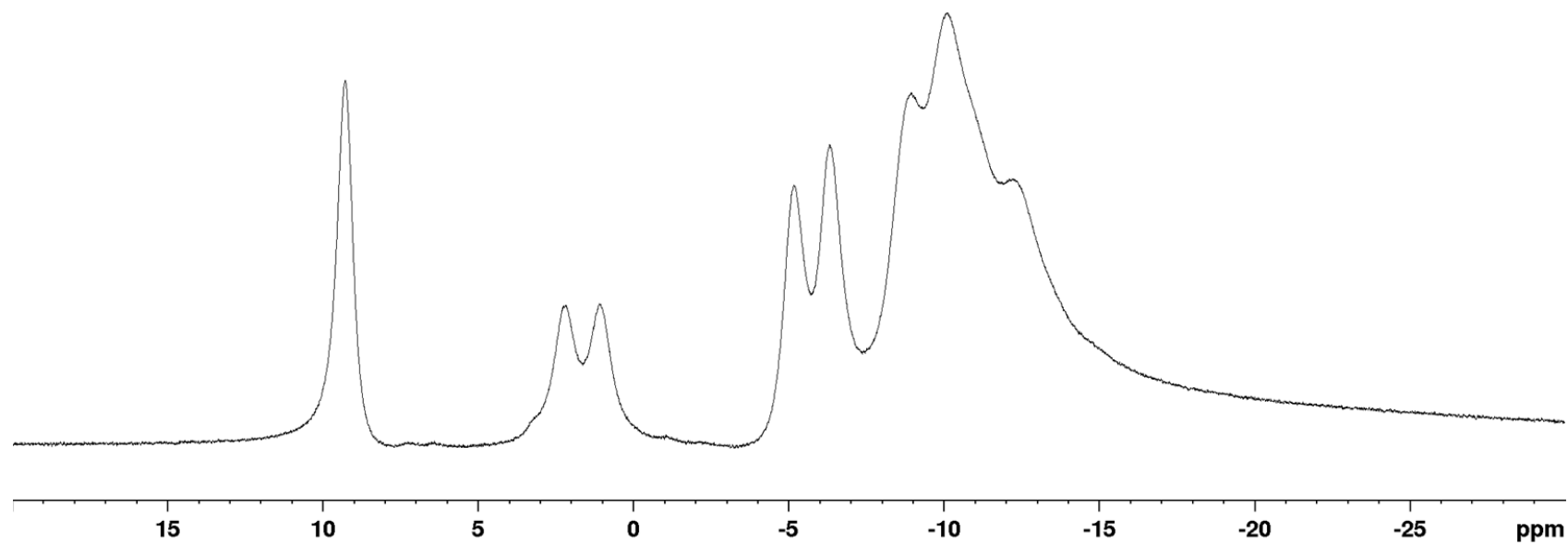
¹³C NMR (100 MHz, CDCl₃)



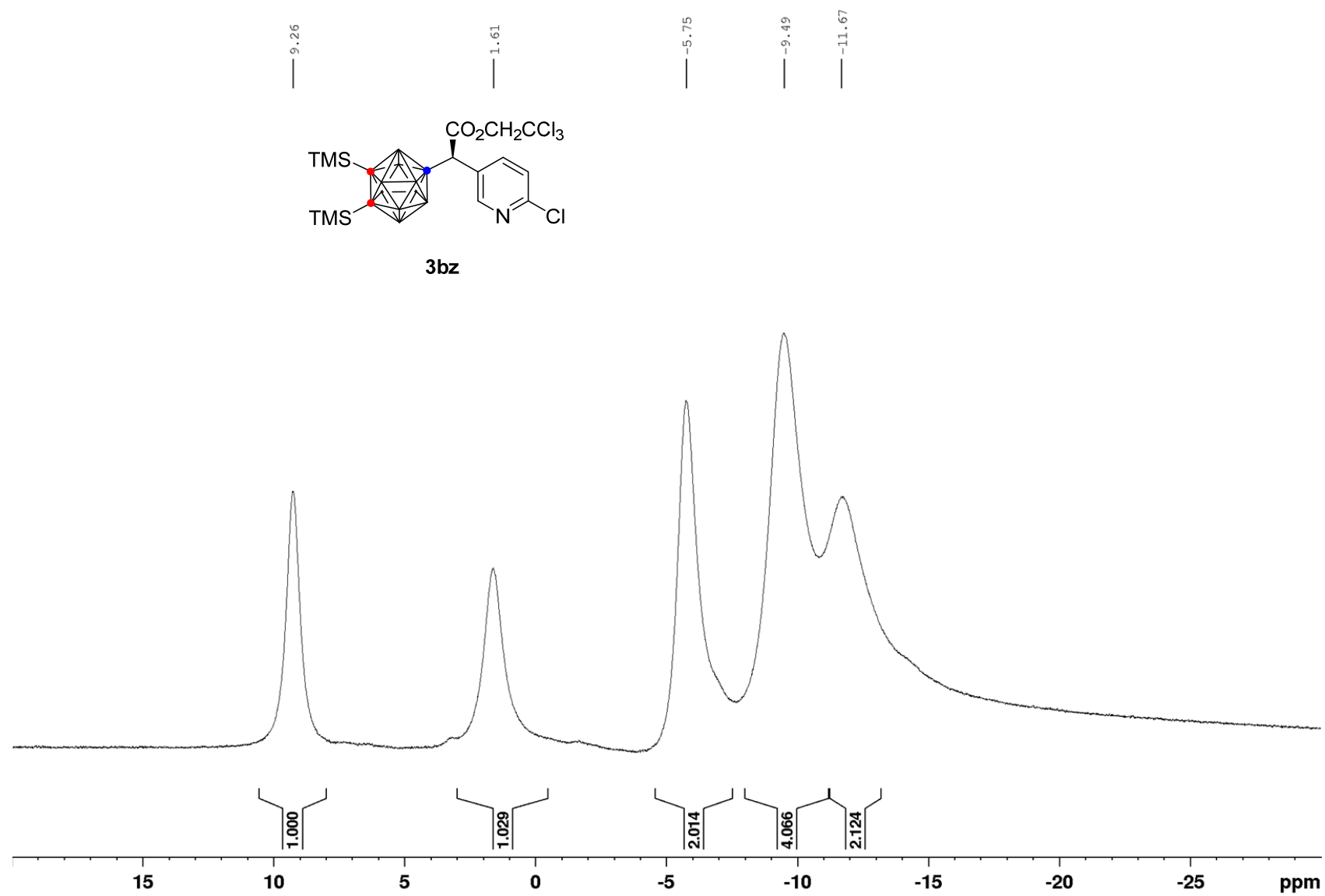
^{11}B NMR (128 MHz, CDCl_3)



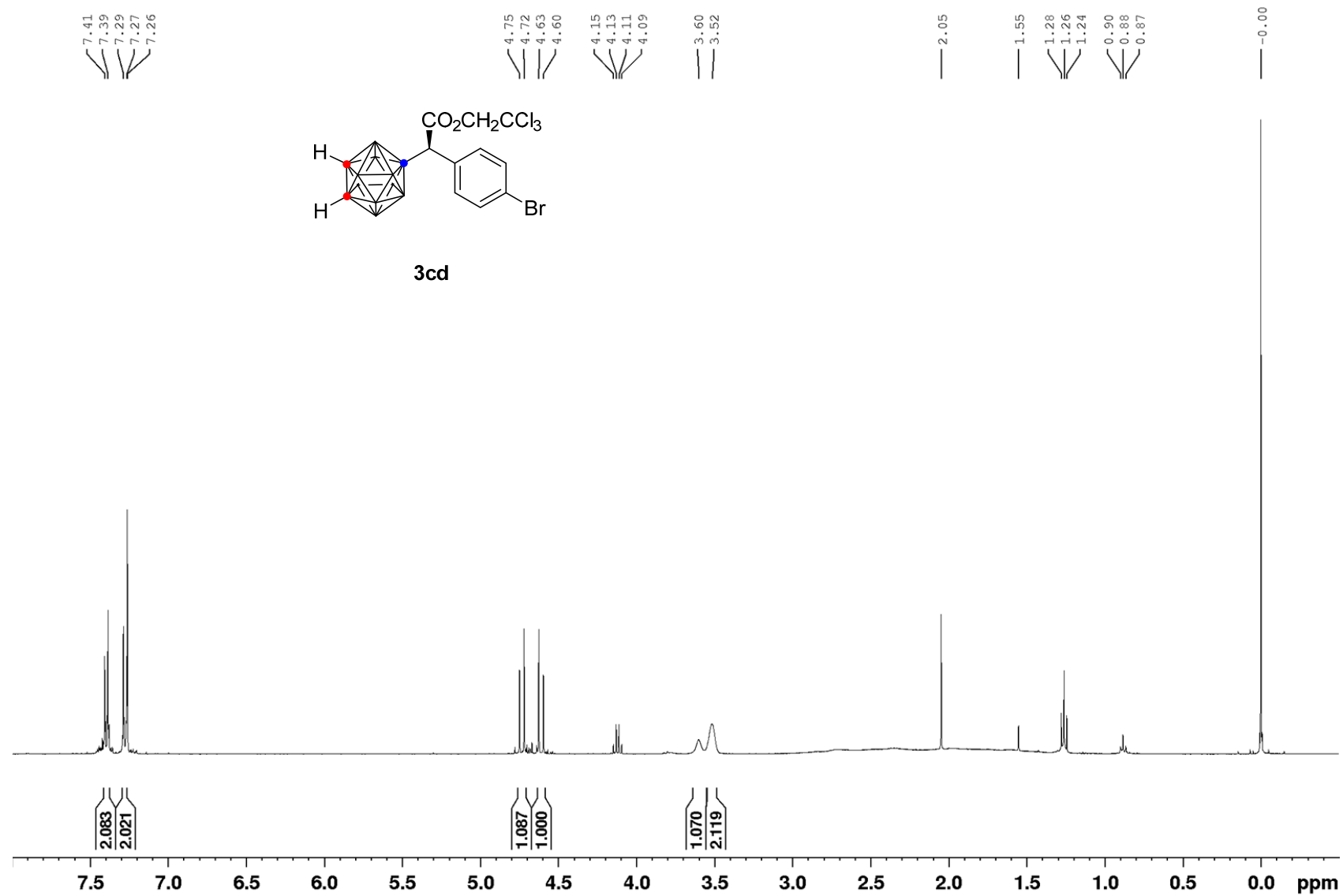
3bz



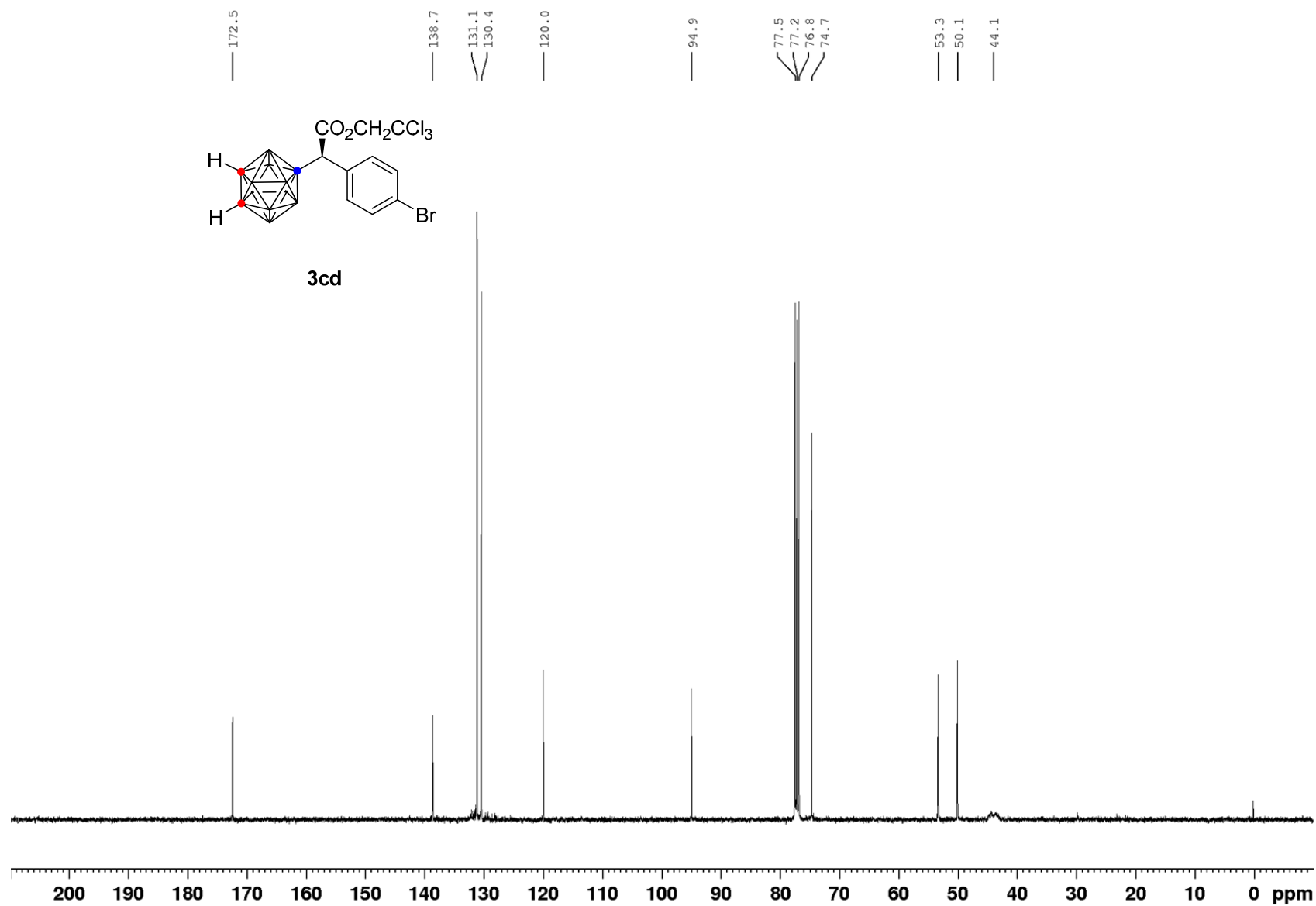
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



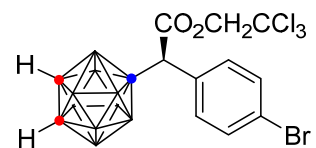
¹H NMR (400 MHz, CDCl₃)



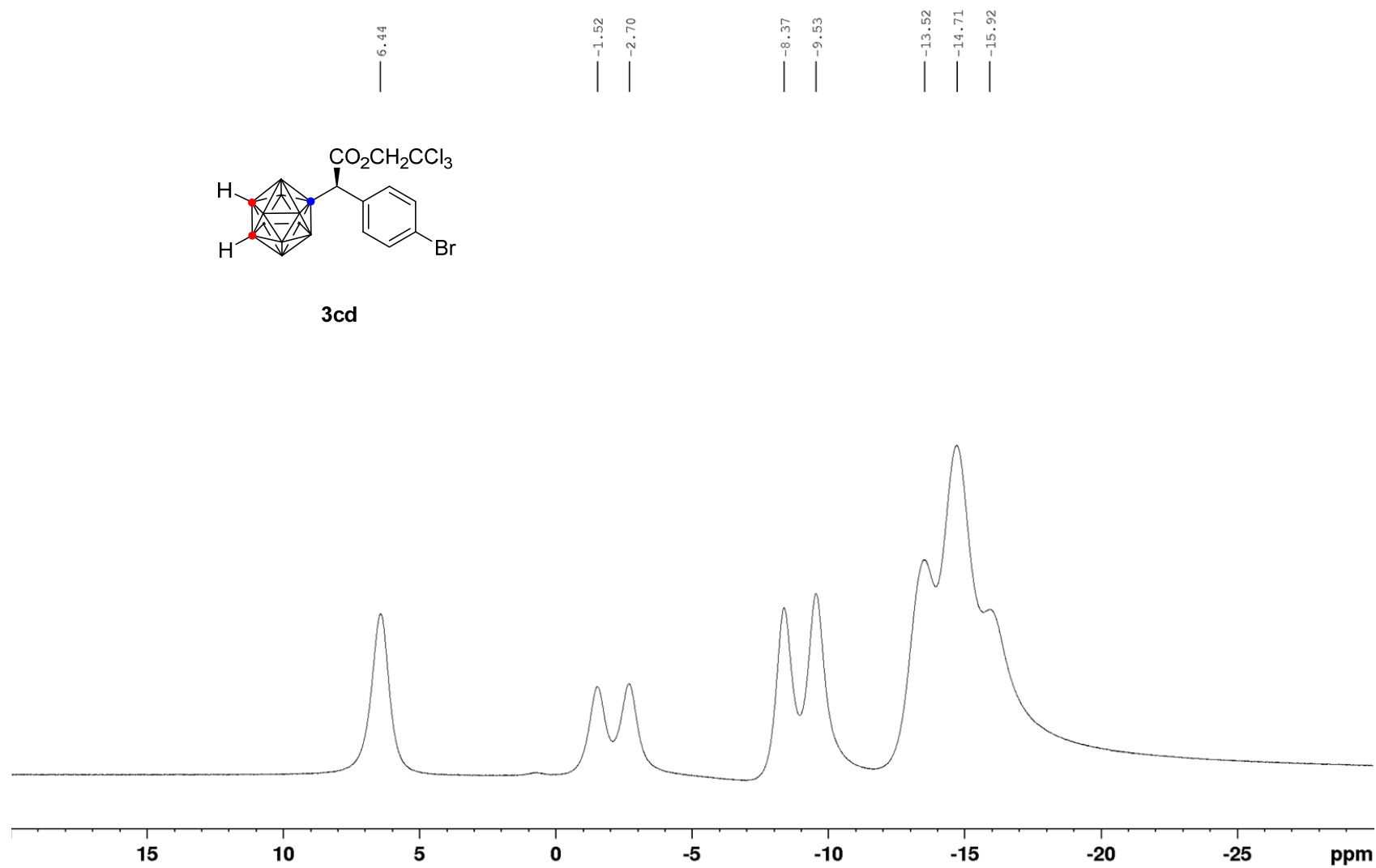
^{13}C NMR (100 MHz, CDCl_3)



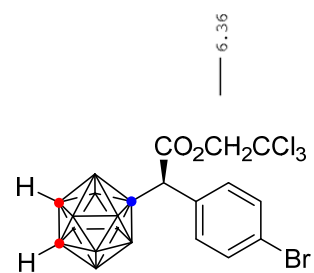
^{11}B NMR (128 MHz, CDCl_3)



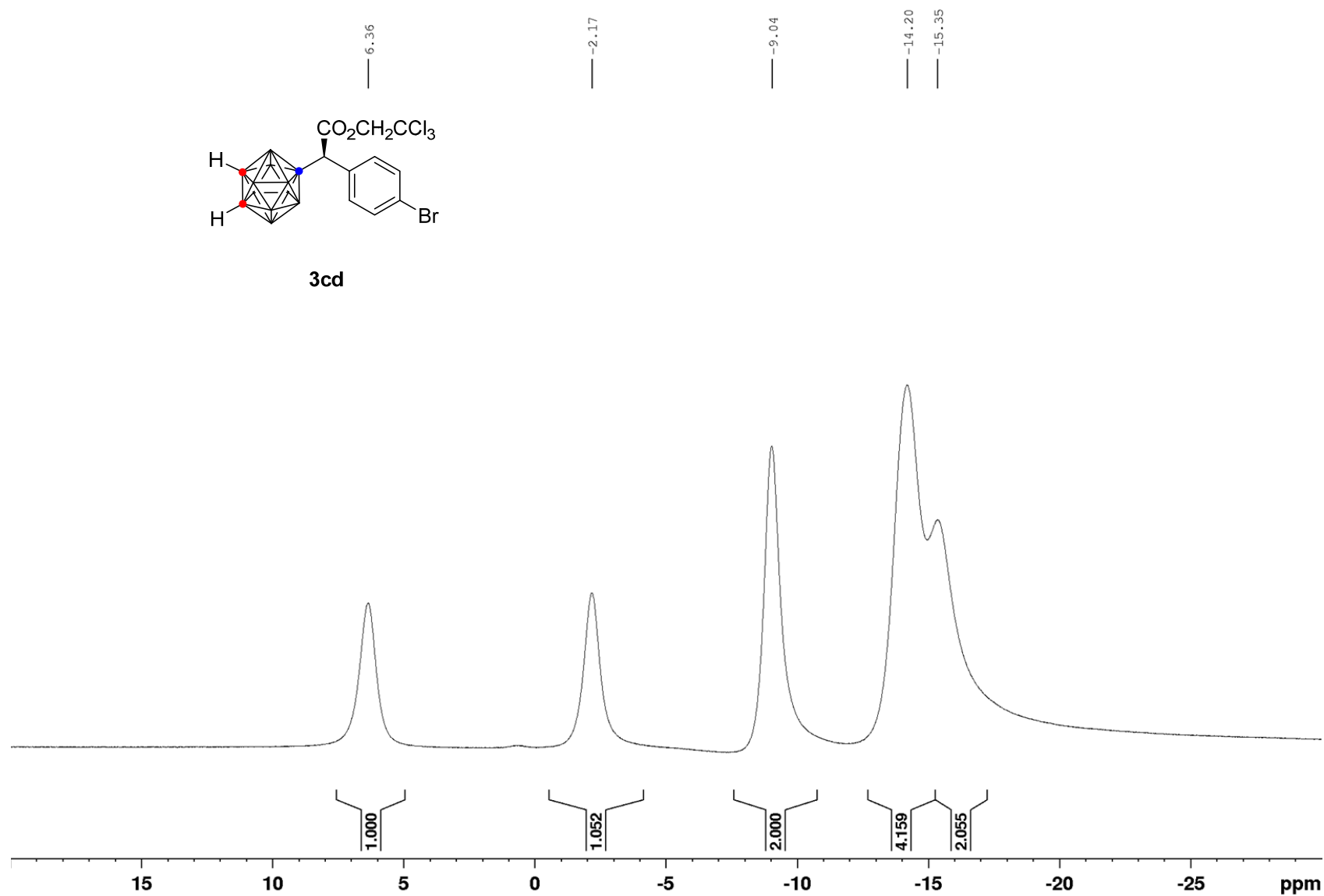
3cd



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



3cd



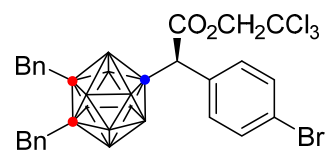
^1H NMR (400 MHz, CDCl_3)

7.36
7.35
7.34
7.34
7.31
7.29
7.19
7.18
7.17
7.16
7.16
7.15
7.14
7.13
7.13

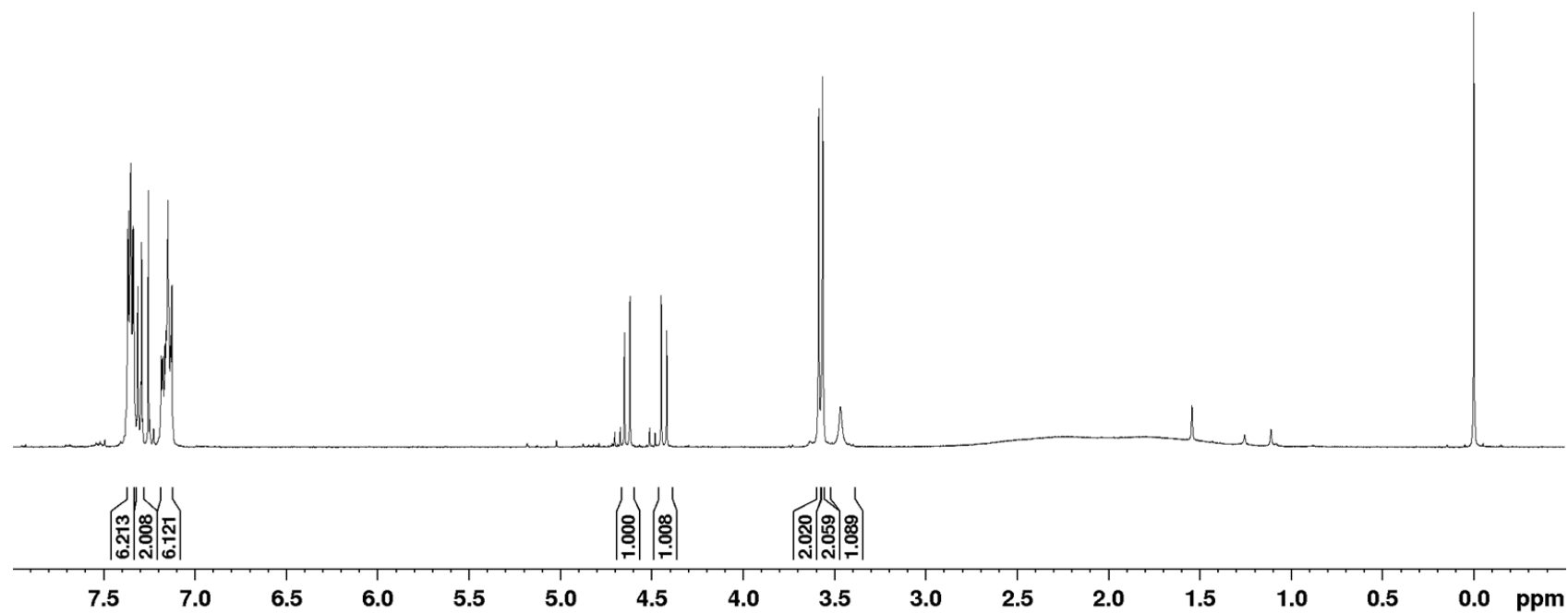
4.65
4.62
4.45
4.42

3.59
3.56
3.47

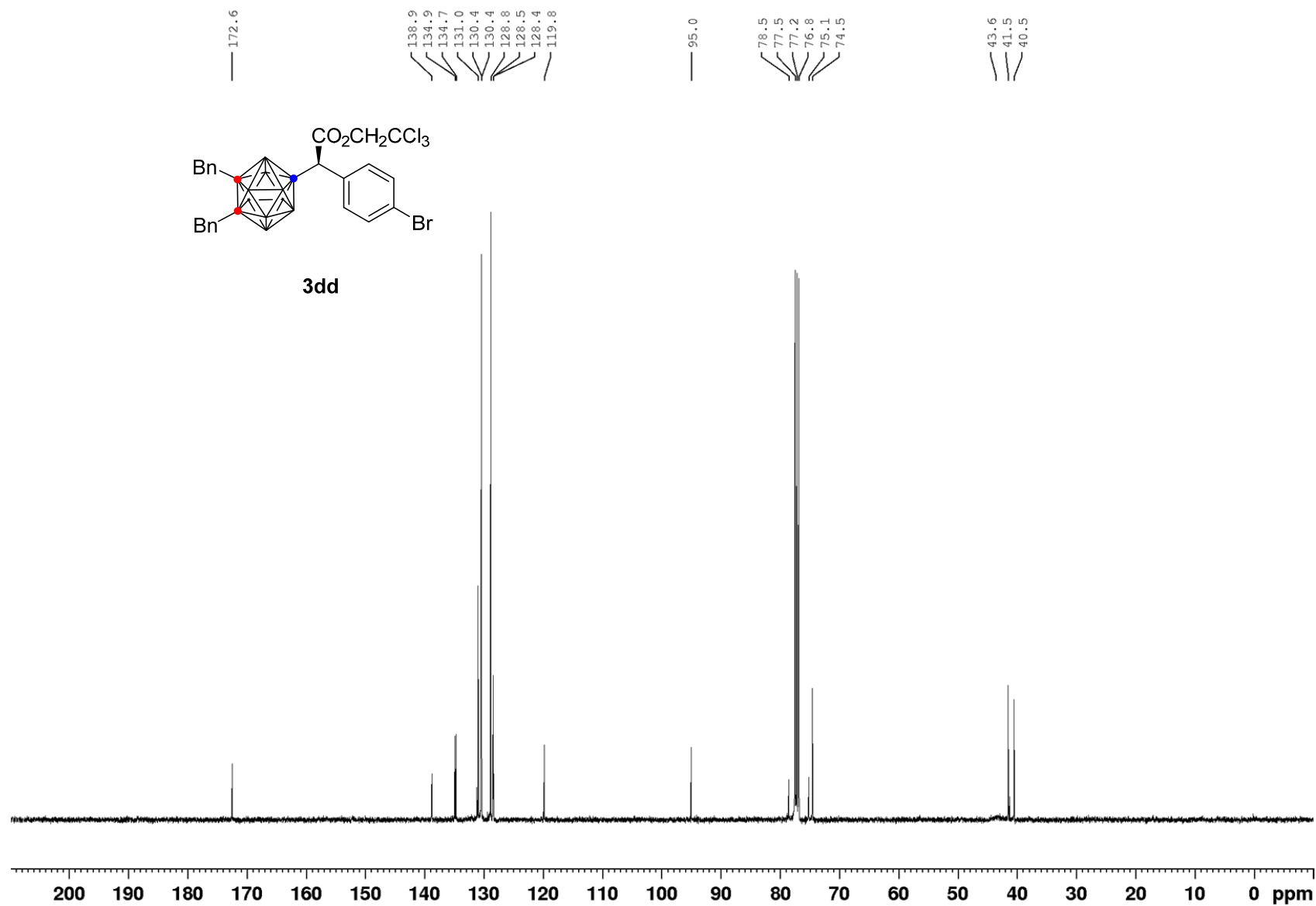
— 0.00



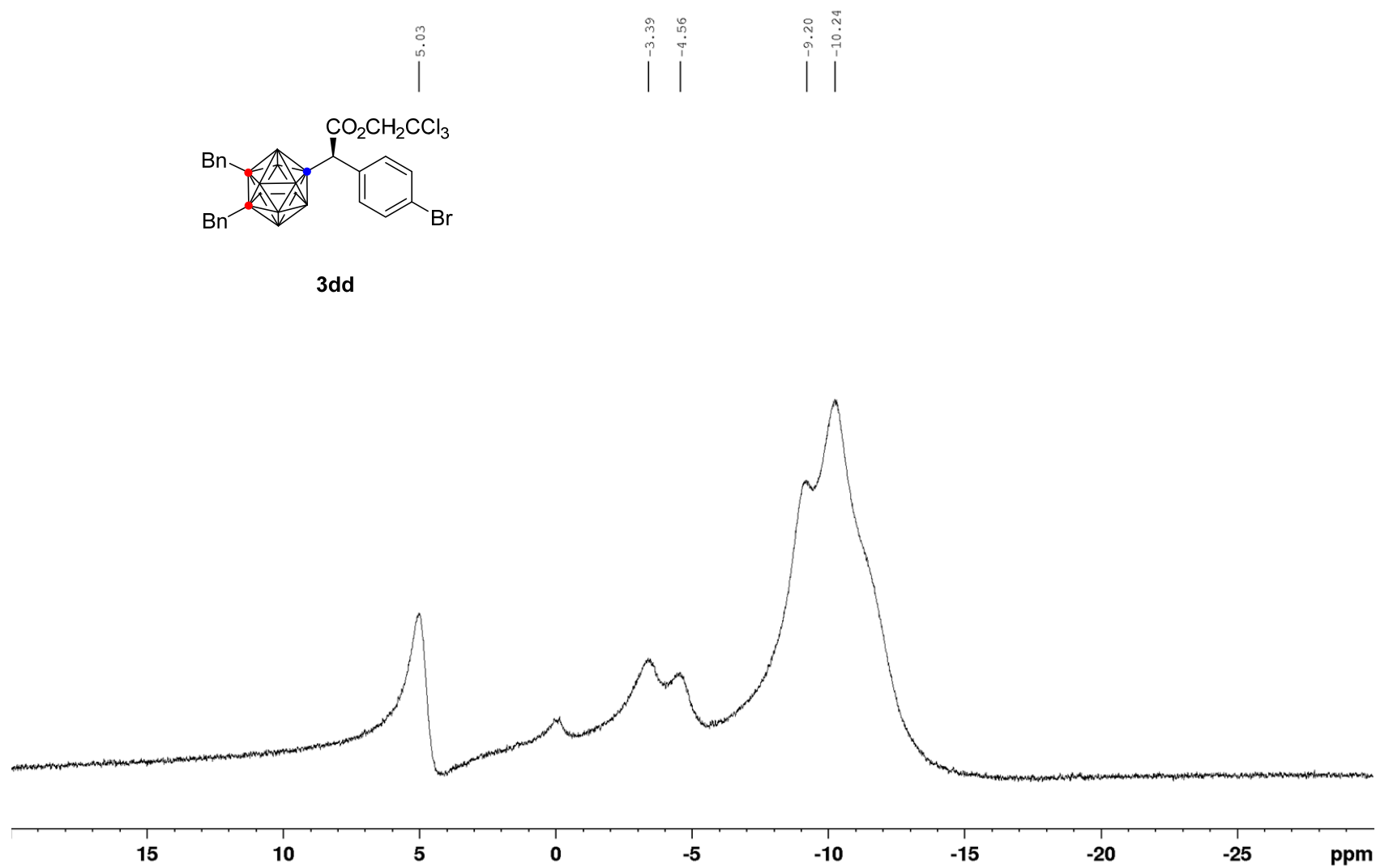
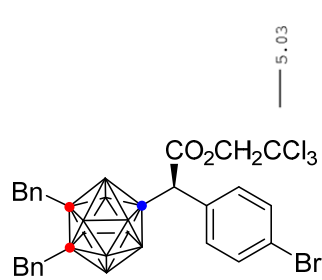
3dd



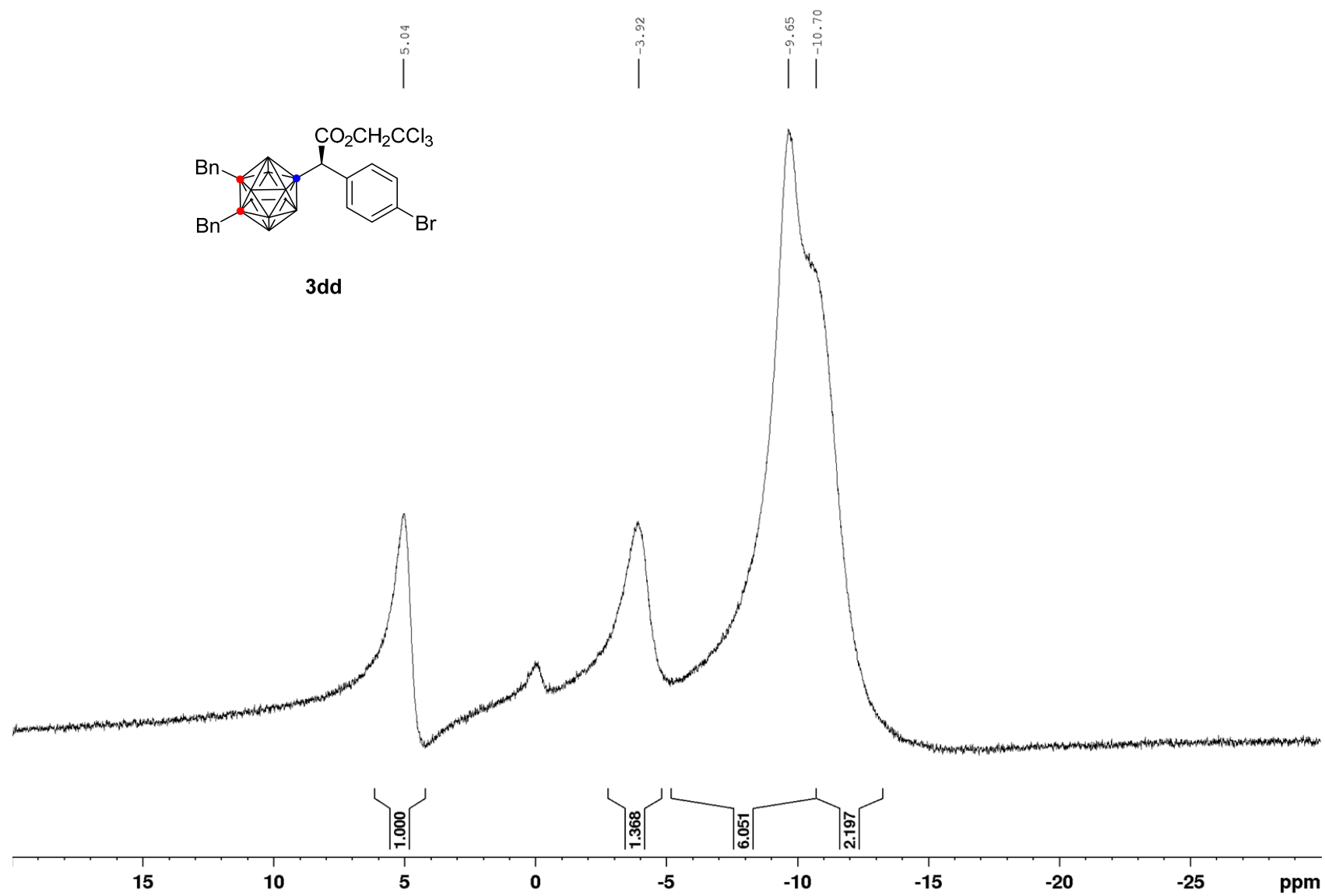
^{13}C NMR (100 MHz, CDCl_3)



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



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

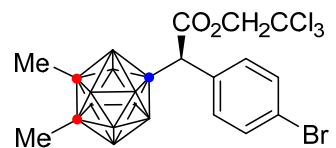


Chemical structure of **3ed** is shown above the spectrum. The structure is a complex molecule featuring a central core with two methyl groups (Me) and a side chain containing a carbonyl group (CO₂CH₂CCl₃) and a bromophenyl group (Br).

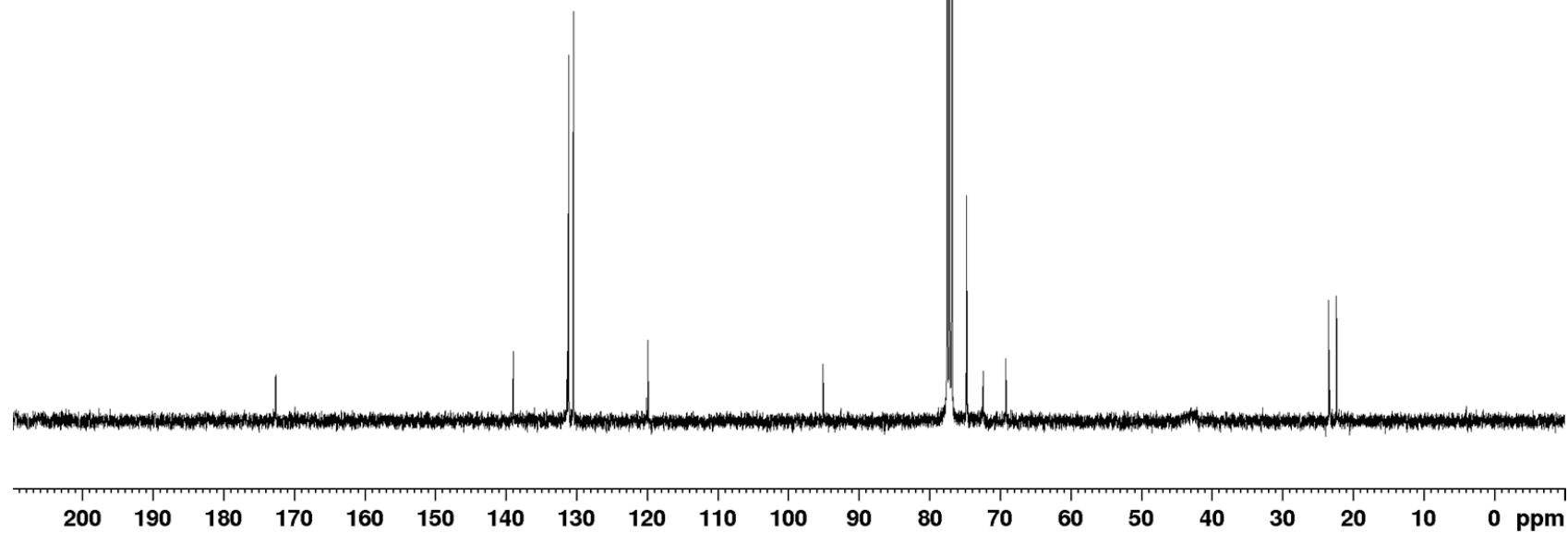
The ¹H NMR spectrum (CDCl₃) displays the following peaks and integrations:

- Aromatic region (7.25–7.40 ppm): Multiplet, integration 2.045 and 2.395.
- Aliphatic region (4.58–4.74 ppm): Multiplet, integration 1.067 and 1.000.
- Carbonyl region (3.57 ppm): Singlet, integration 1.038.
- Triplet region (1.99–2.00 ppm): Triplet, integration 3.071 and 3.179.
- Reference peak (0.00 ppm): Singlet, integration 1.000.

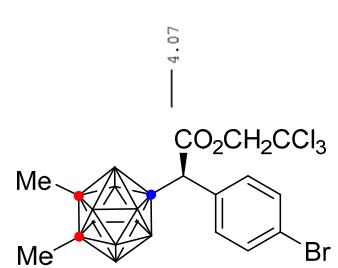
^{13}C NMR (100 MHz, CDCl_3)



3ed

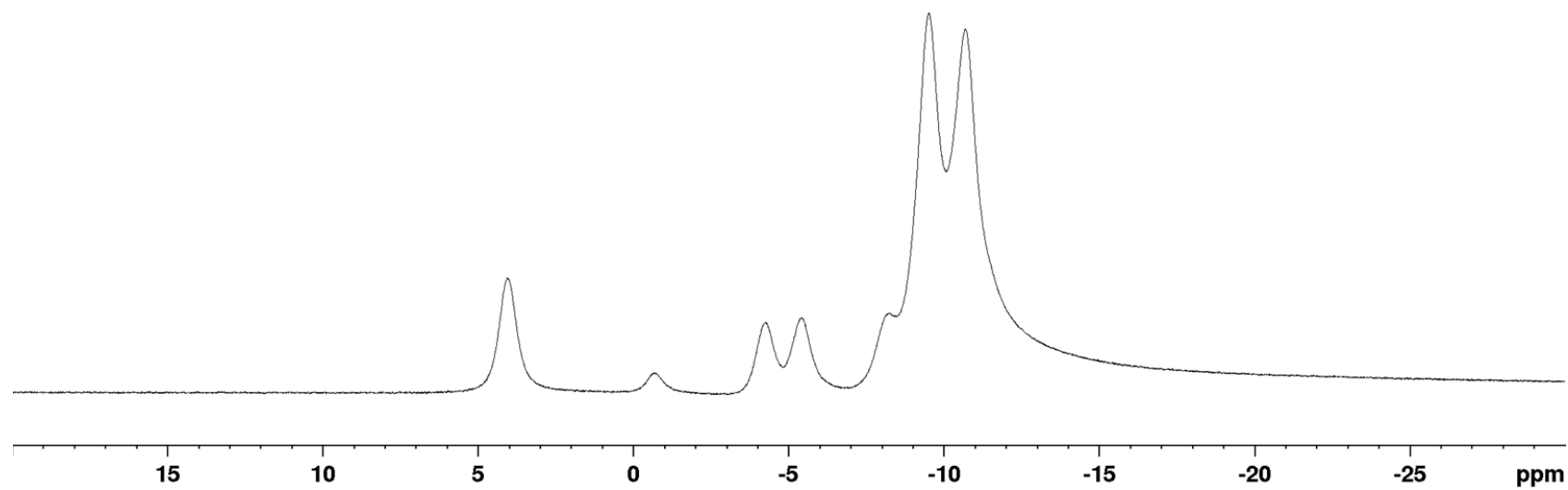


^{11}B NMR (128 MHz, CDCl_3)

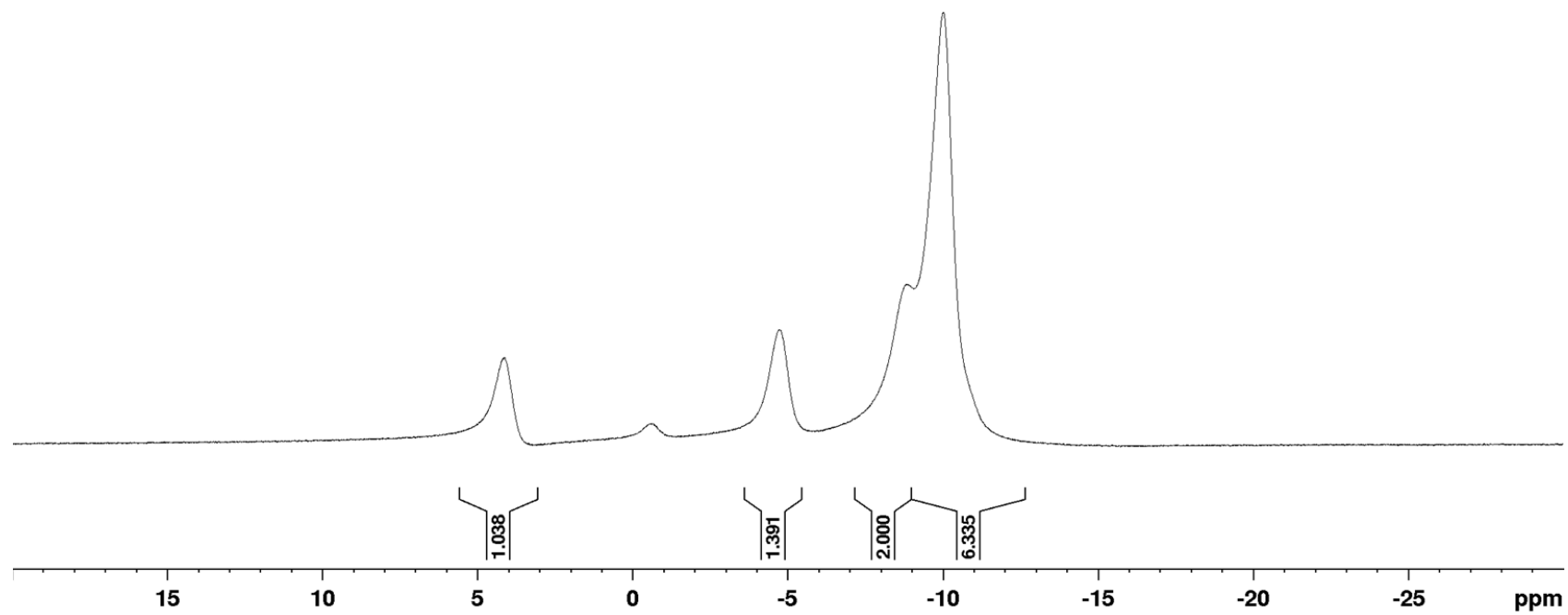
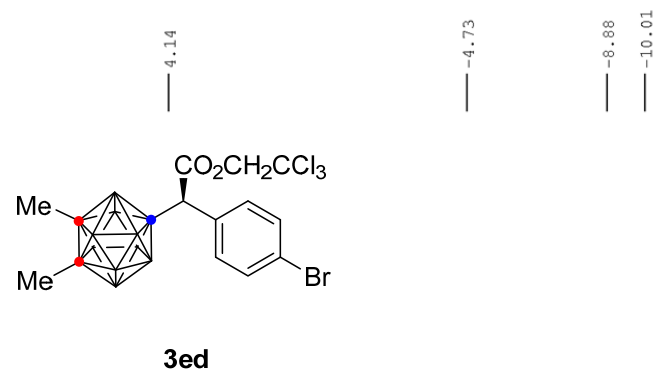


3ed

— 4.24
— 5.42
— 9.52
— 10.68



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

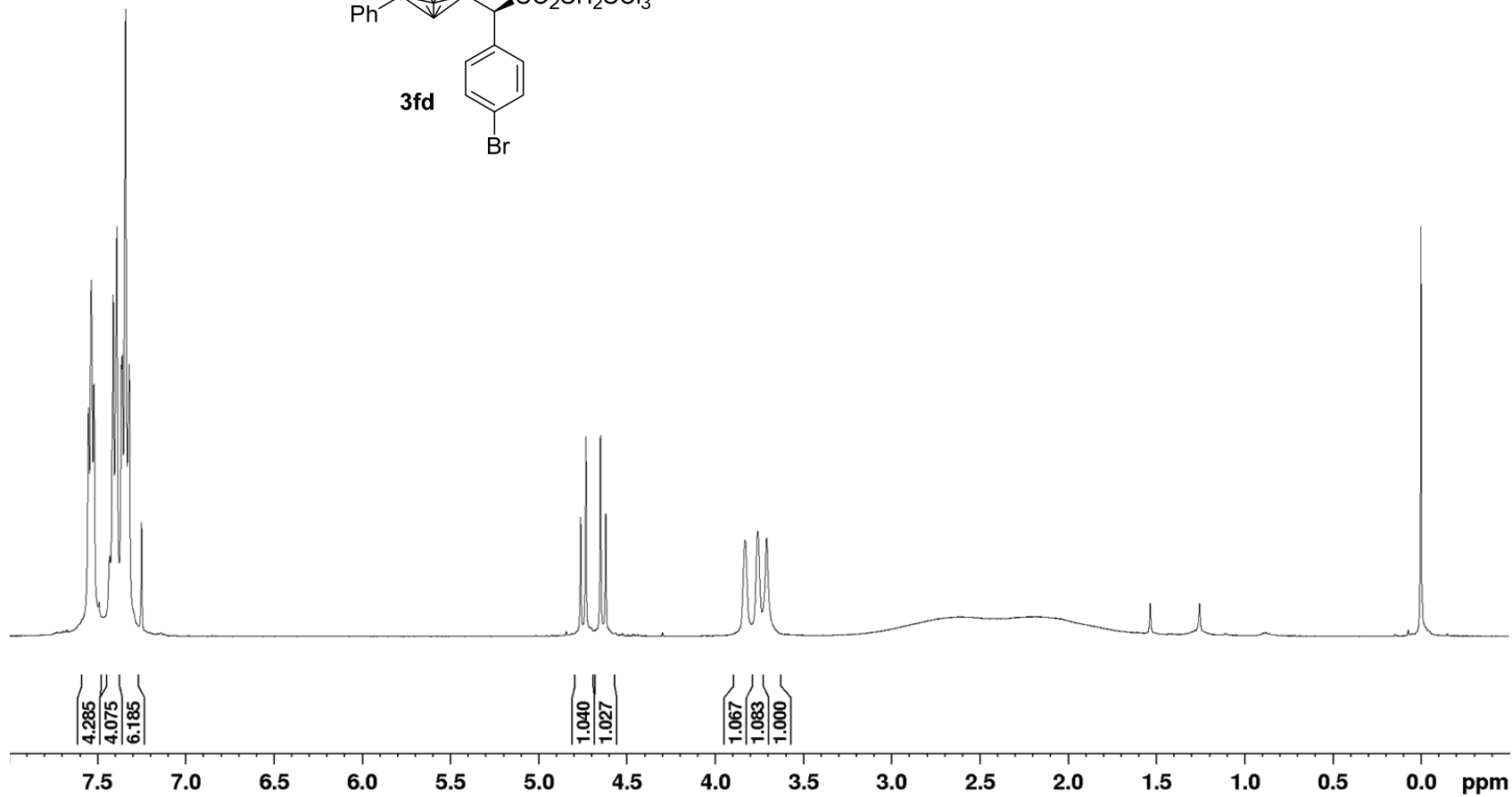
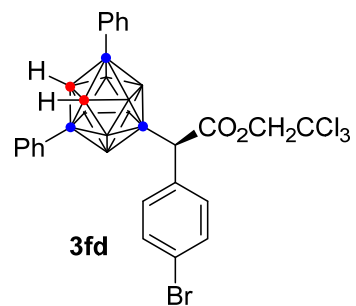


^1H NMR (400 MHz, CDCl_3)

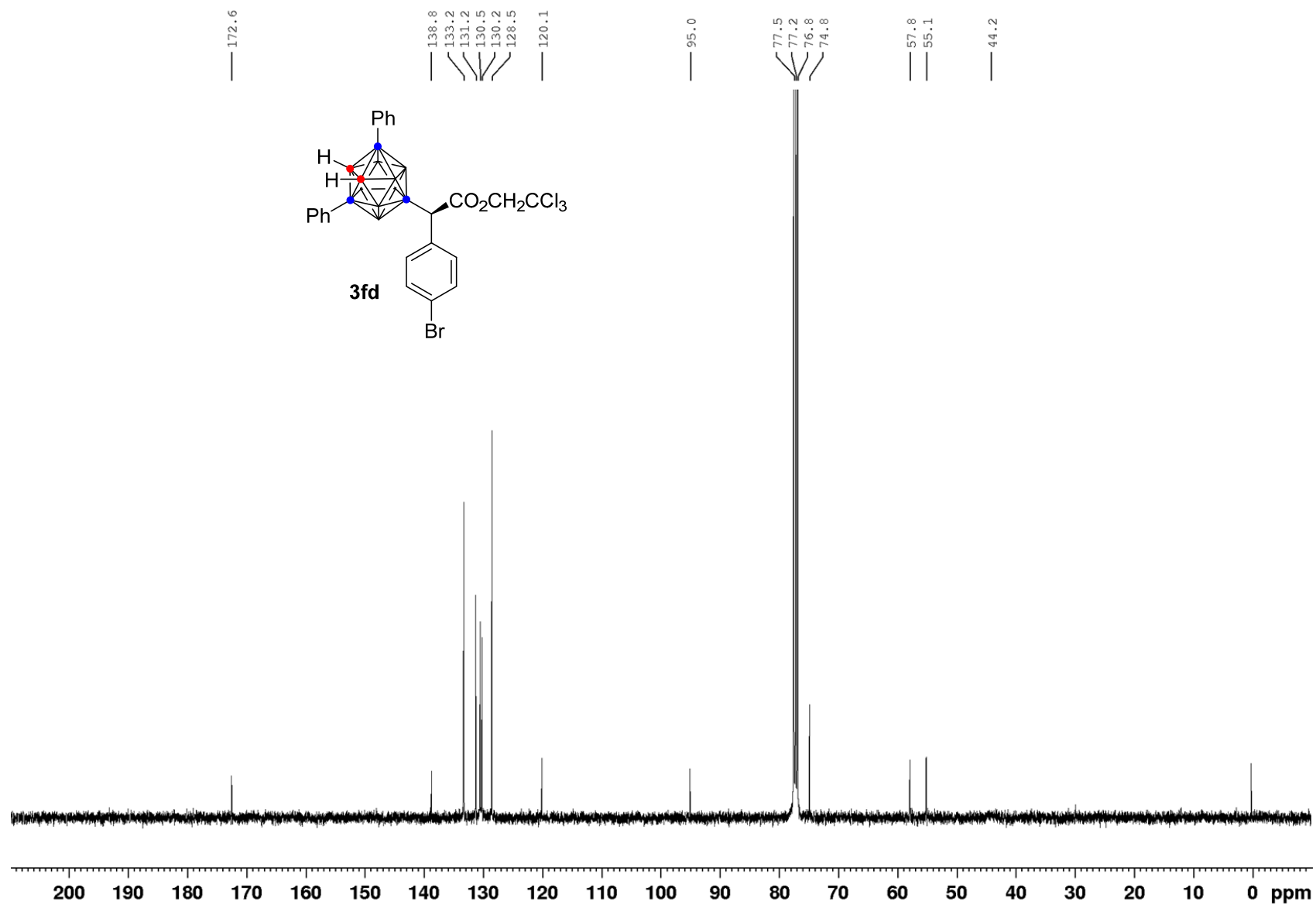
7.55
7.54
7.52
7.43
7.41
7.39
7.36
7.34
7.32
7.25

4.76
4.73
4.65
4.62

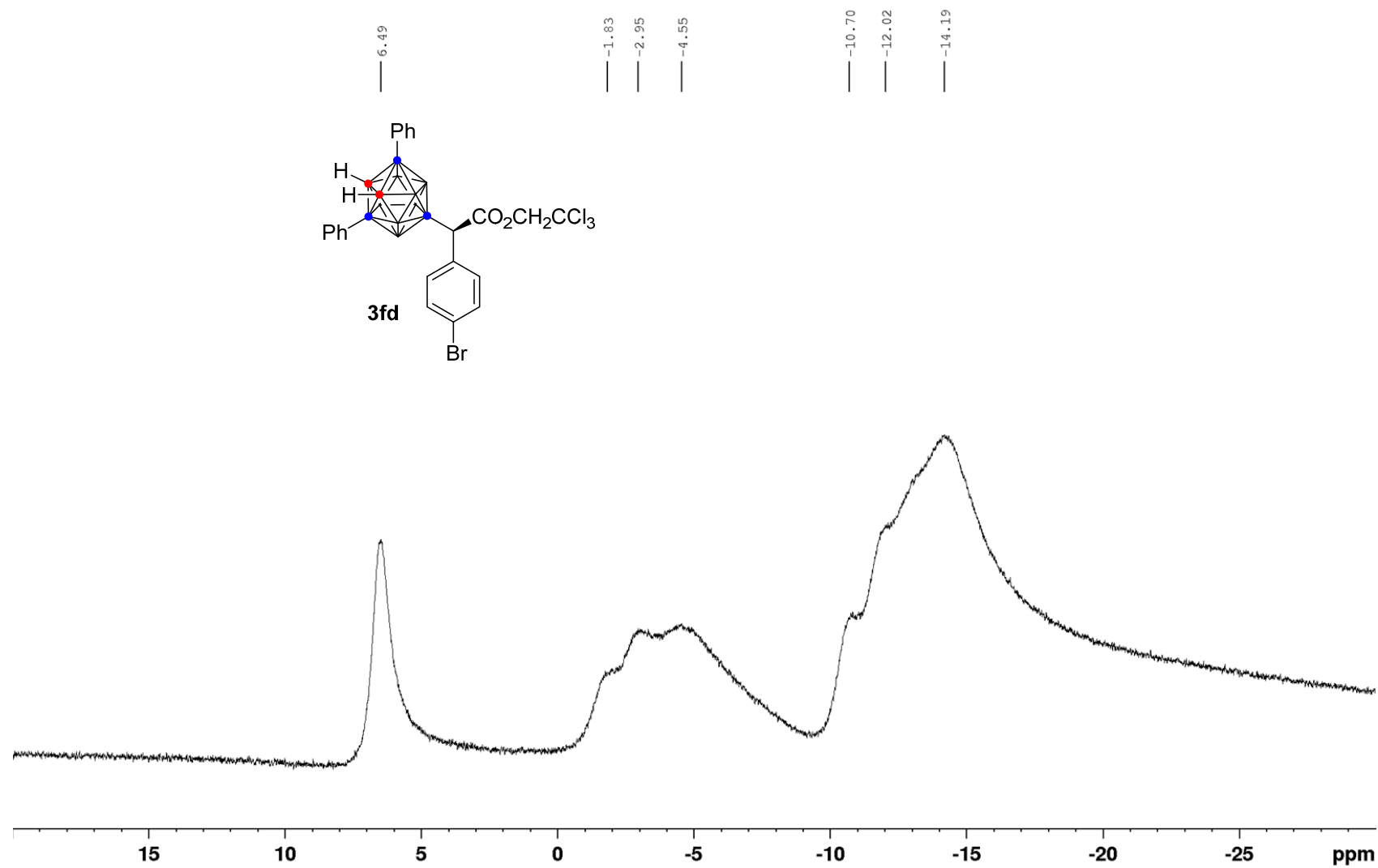
3.83
3.76
3.71



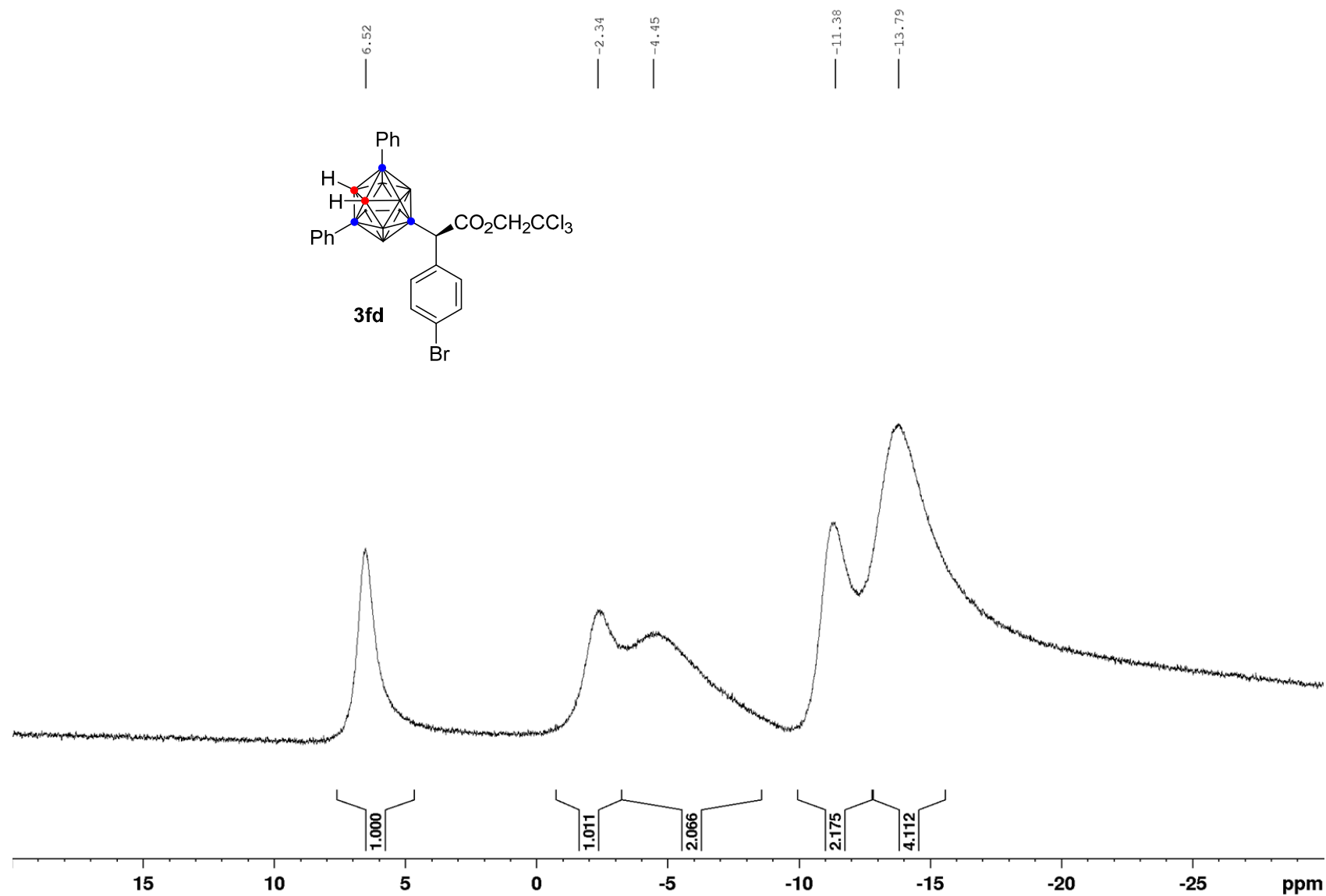
^{13}C NMR (100 MHz, CDCl_3)



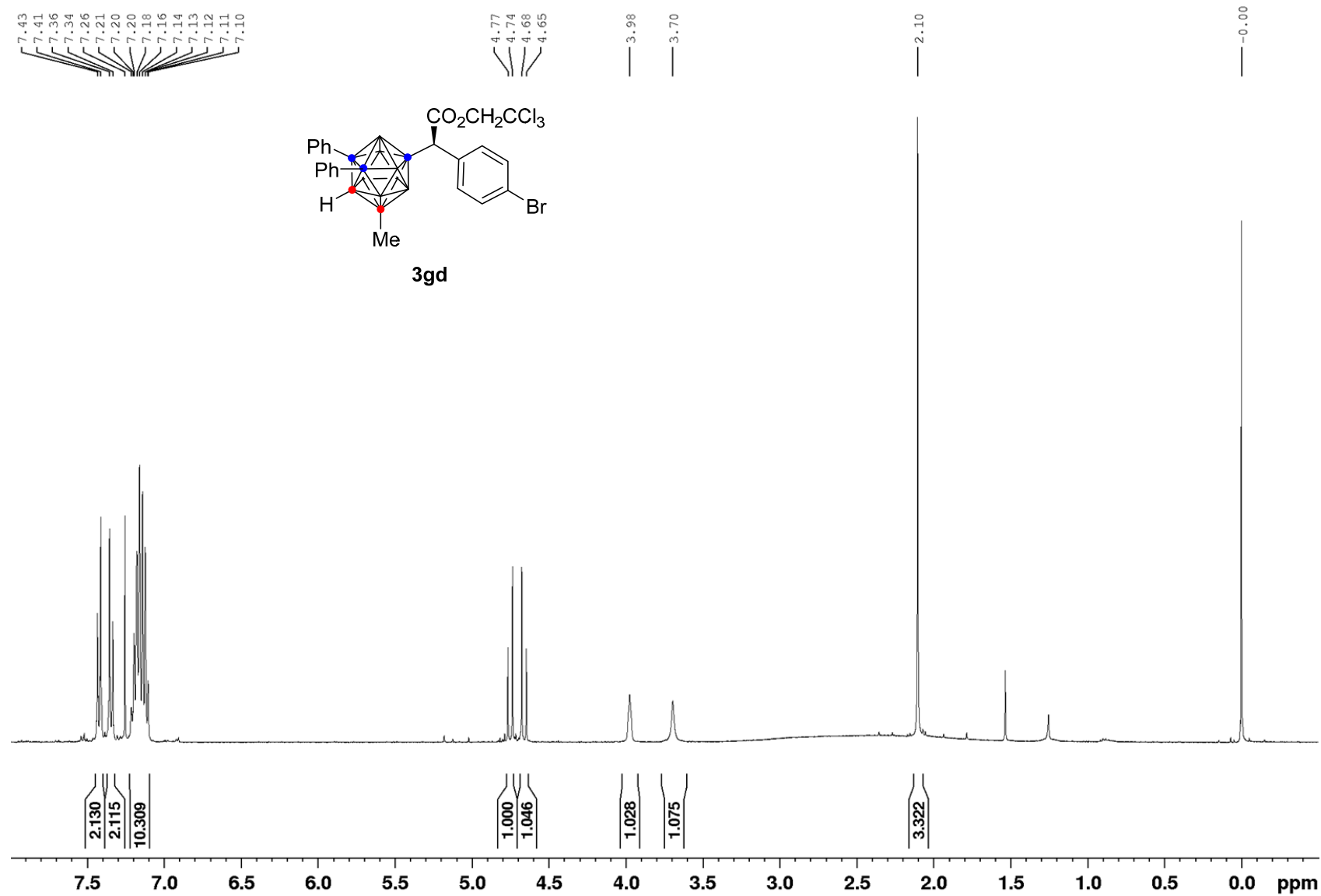
^{11}B NMR (128 MHz, CDCl_3)



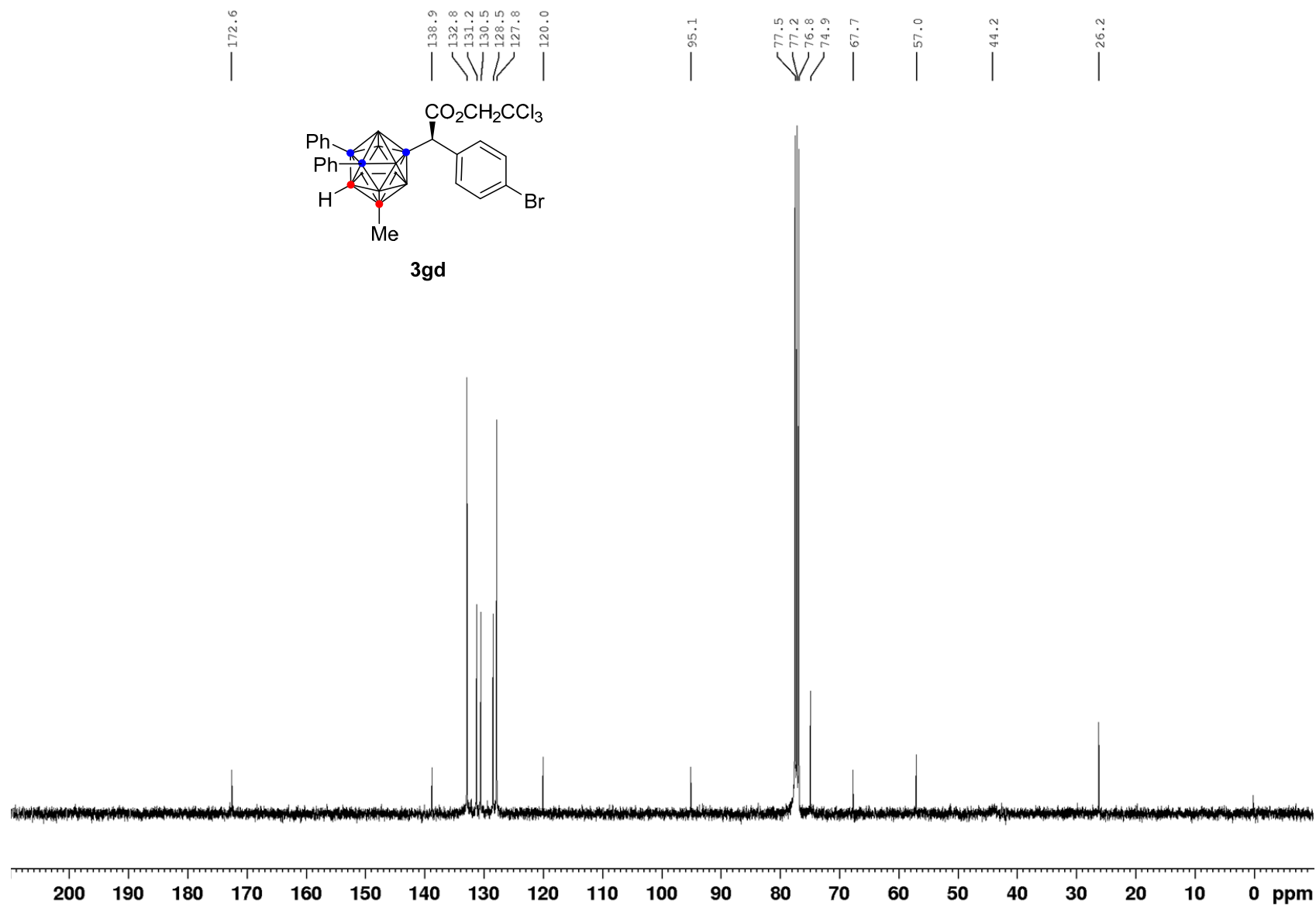
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



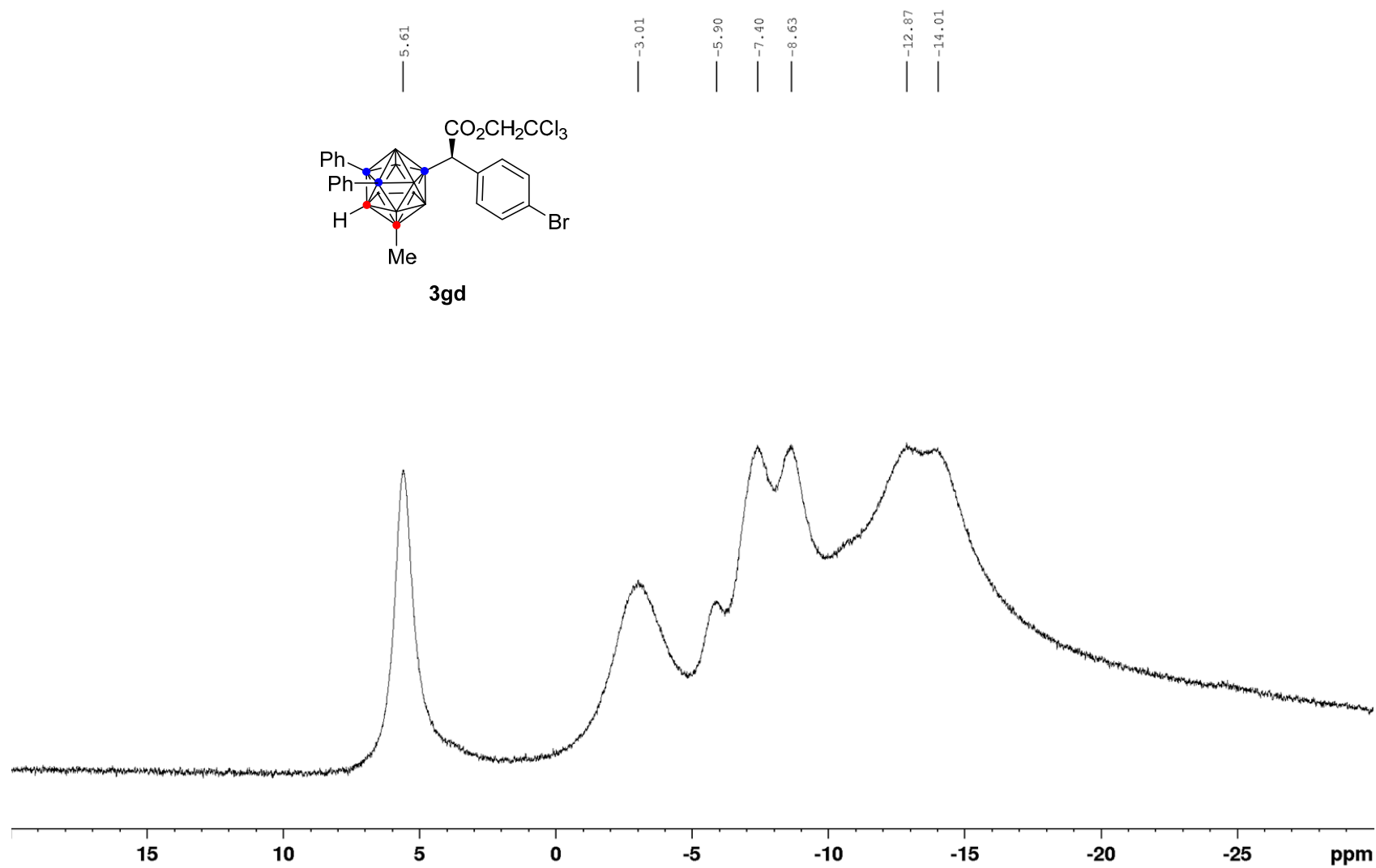
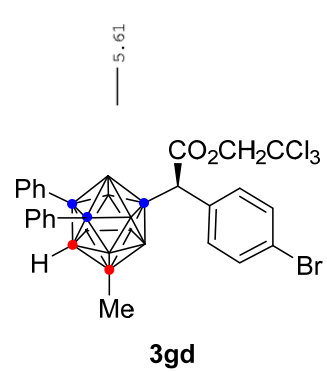
¹H NMR (400 MHz, CDCl₃)



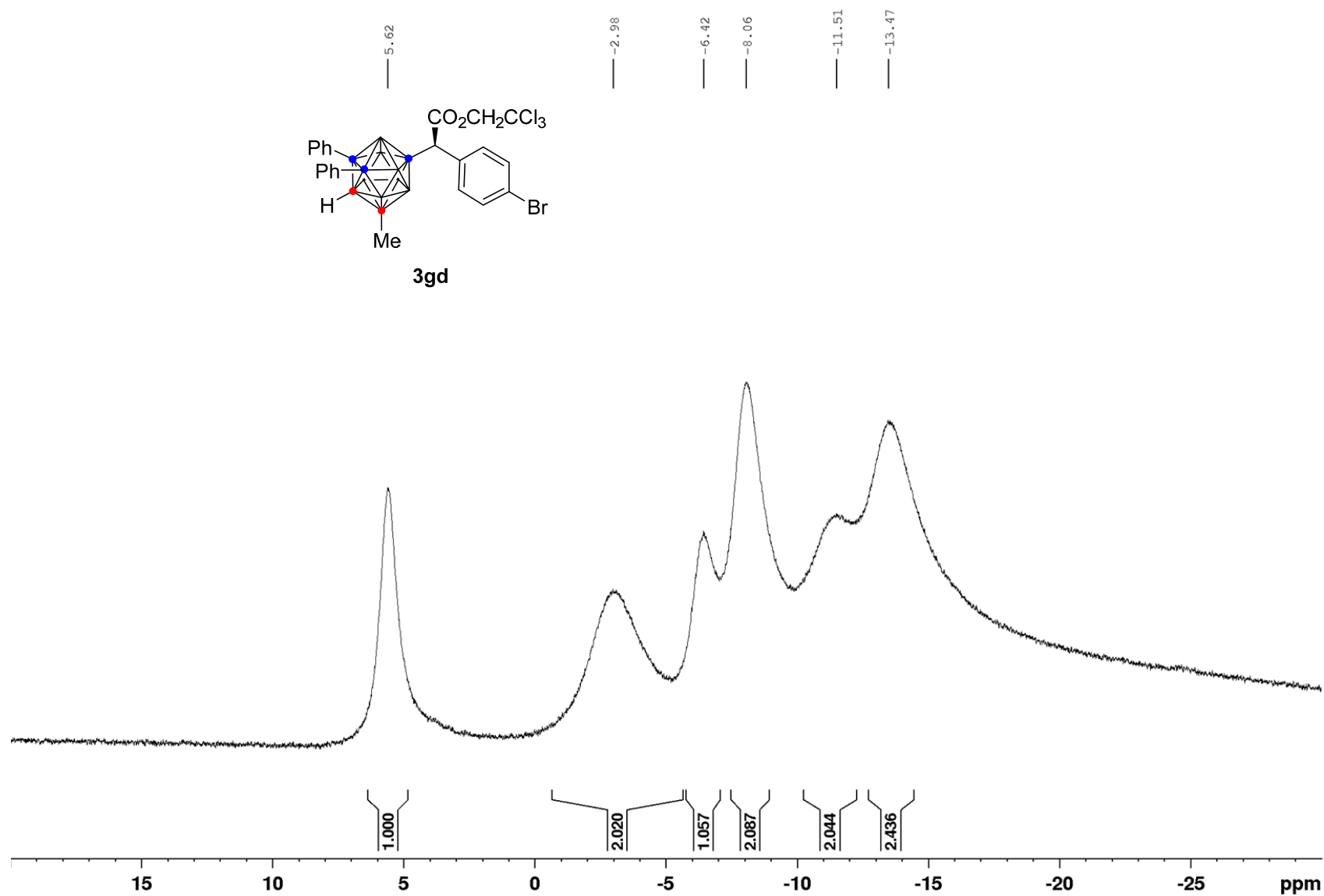
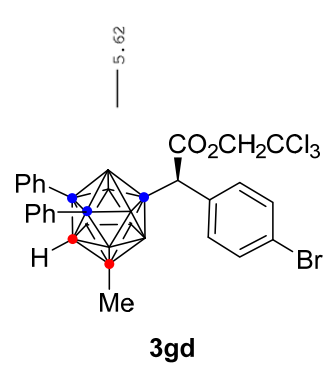
^{13}C NMR (100 MHz, CDCl_3)



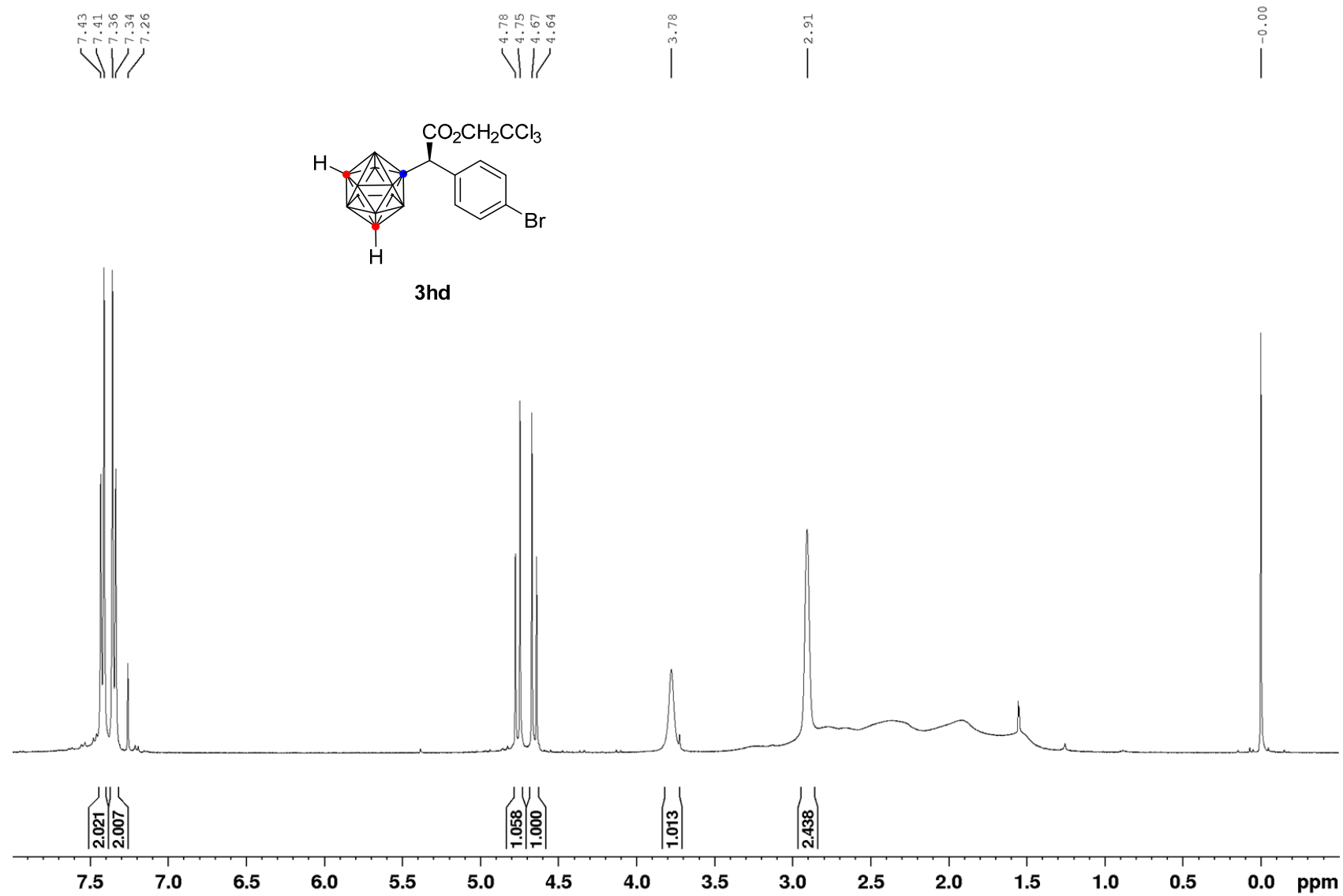
^{11}B NMR (128 MHz, CDCl_3)



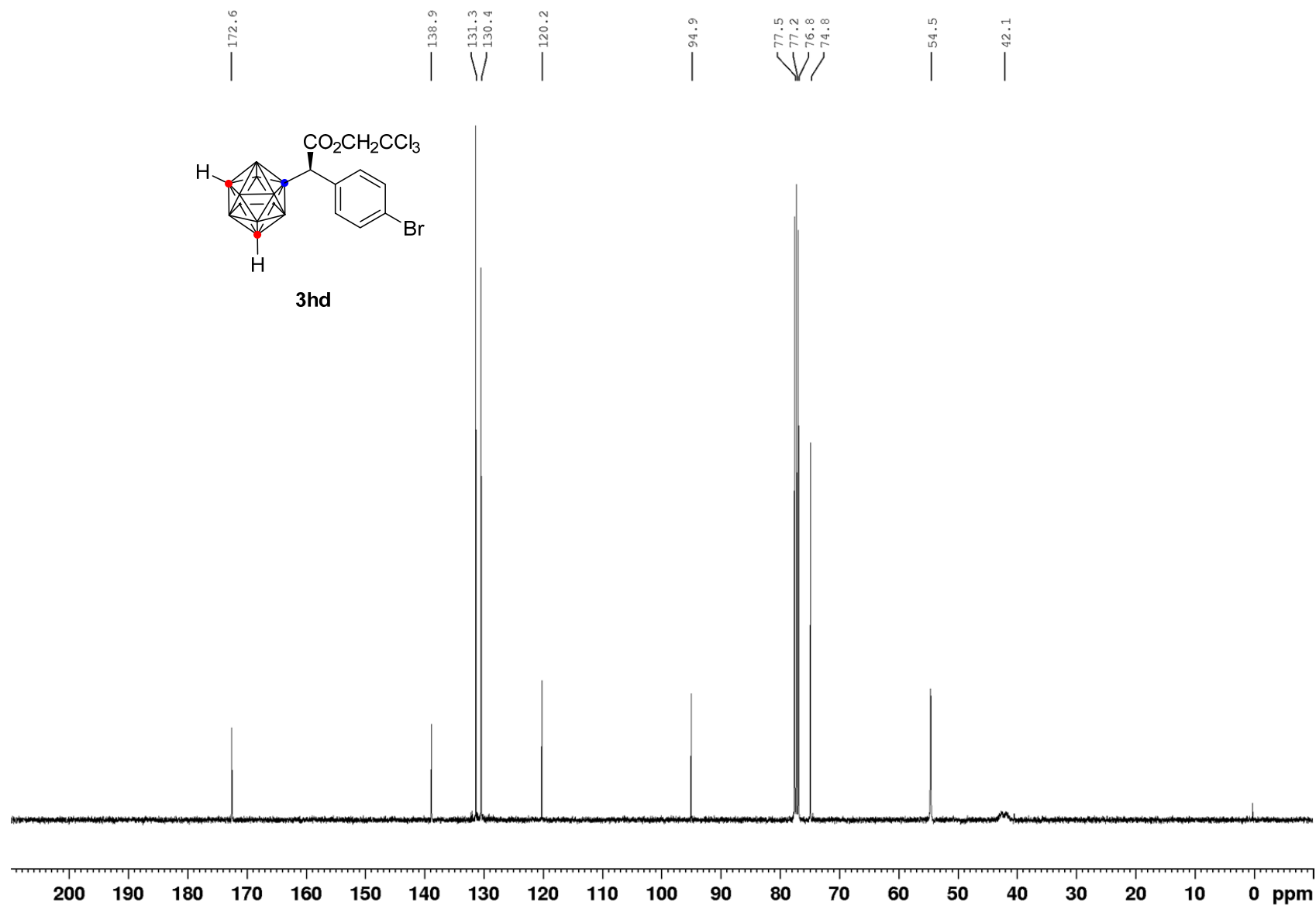
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



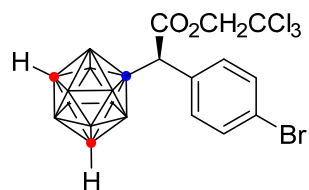
^1H NMR (400 MHz, CDCl_3)



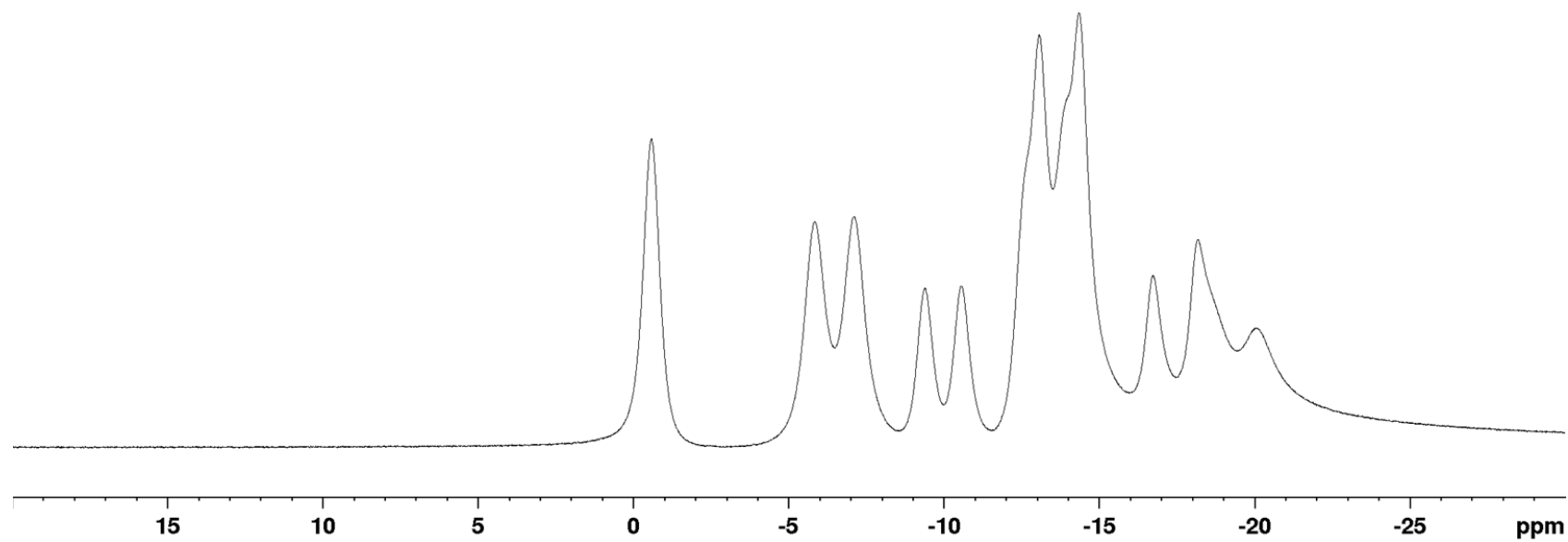
^{13}C NMR (100 MHz, CDCl_3)



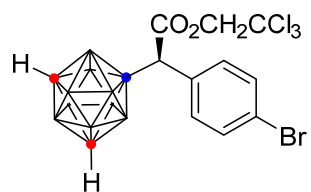
^{11}B NMR (128 MHz, CDCl_3)



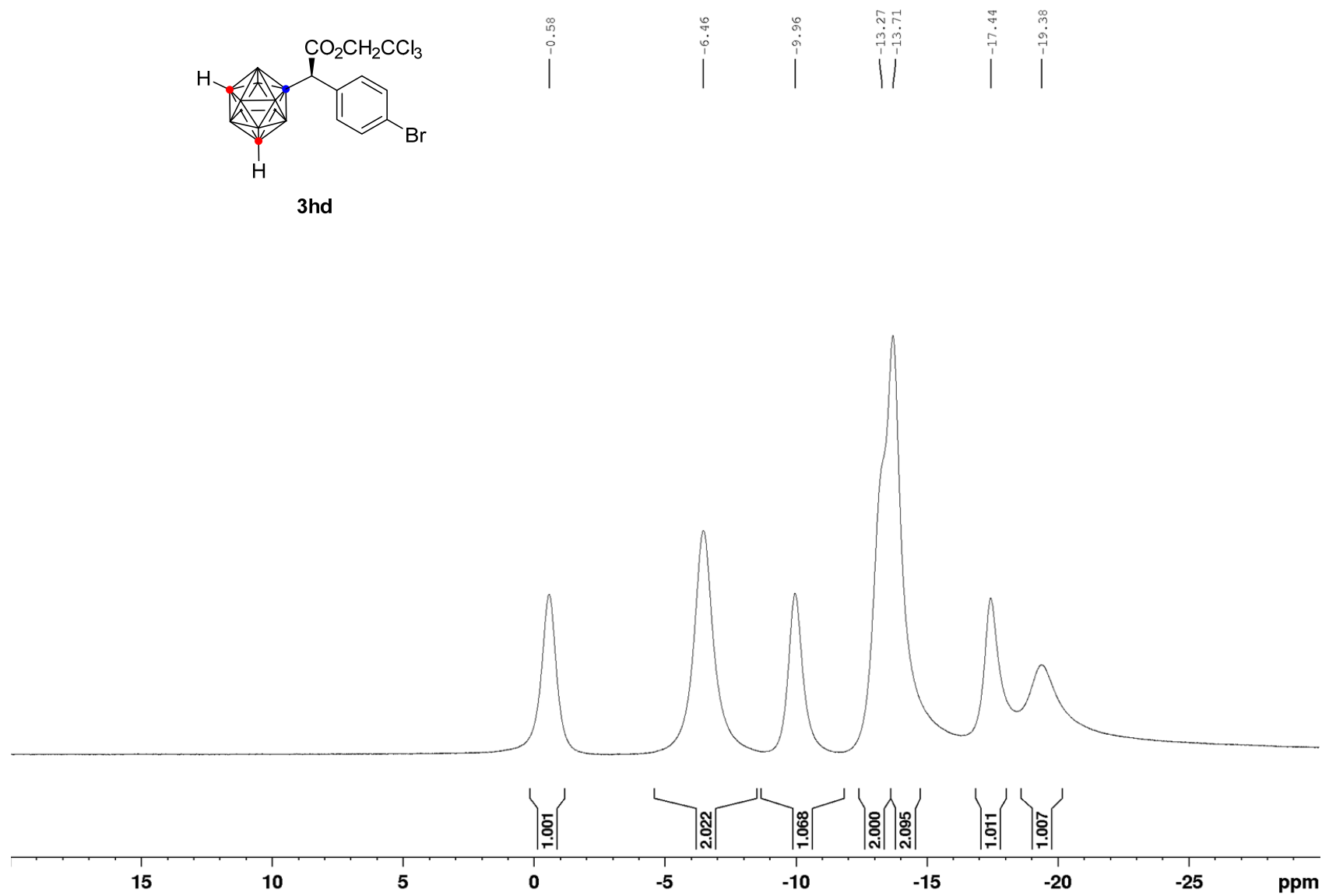
3hd



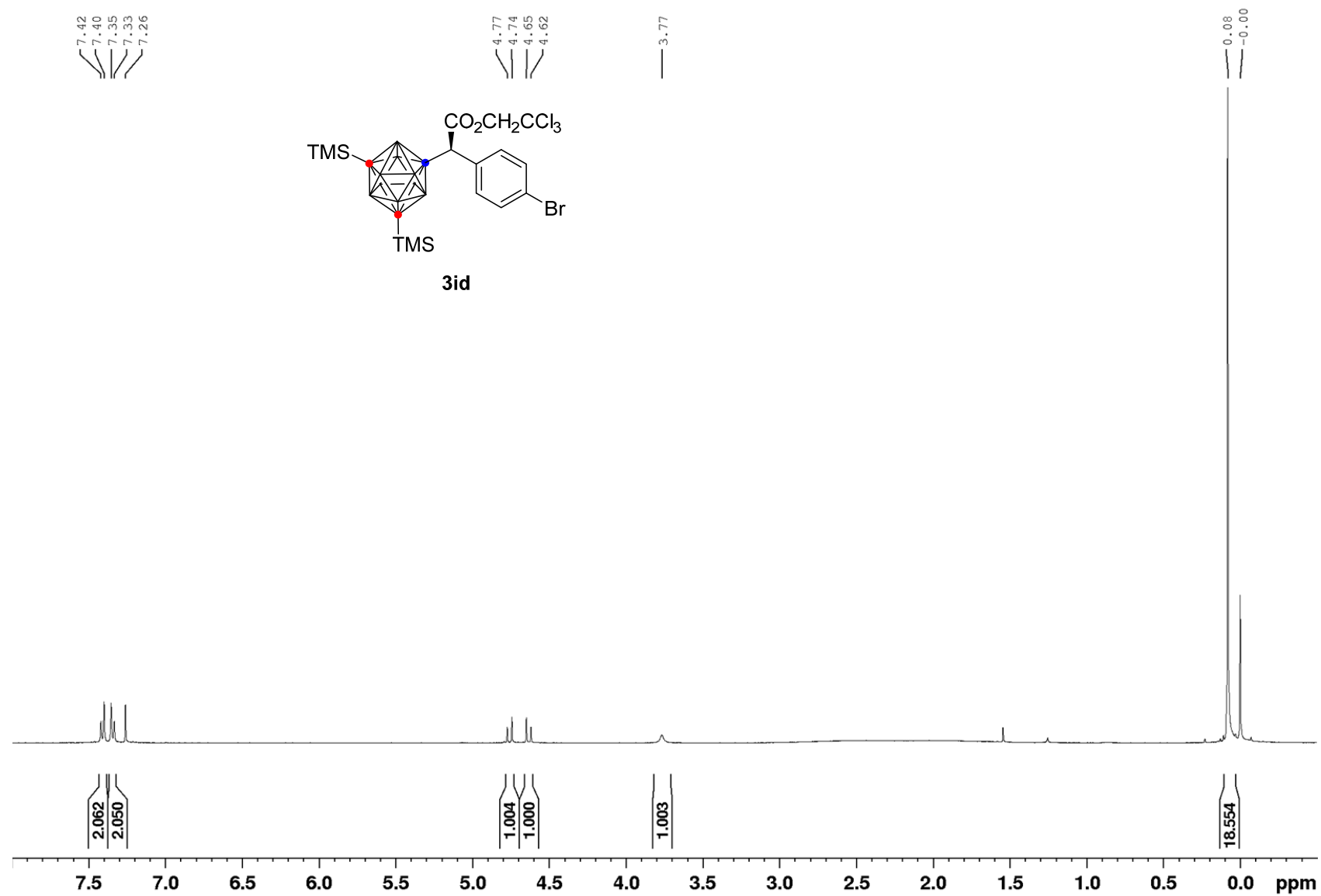
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



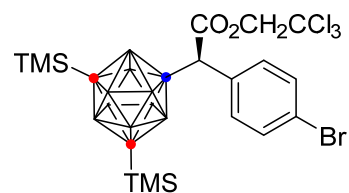
3hd



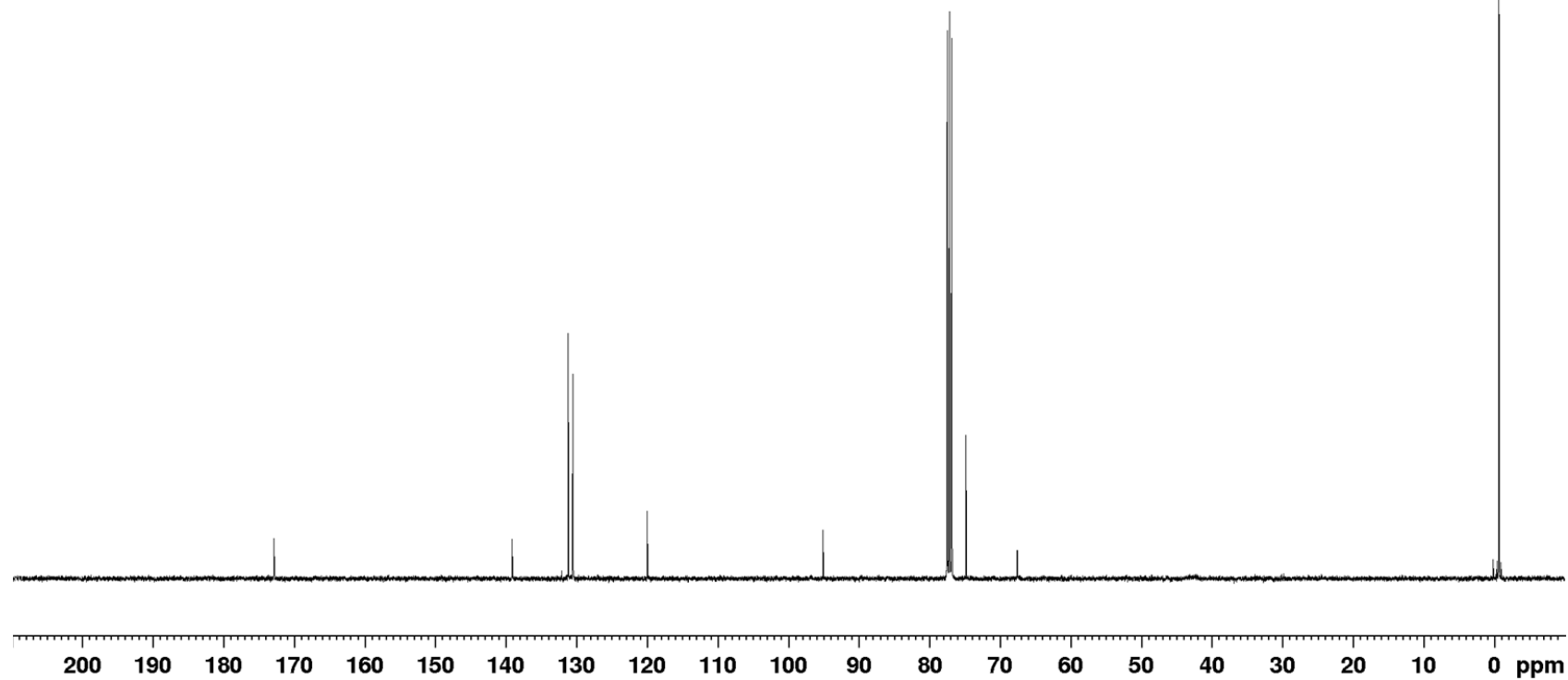
^1H NMR (400 MHz, CDCl_3)



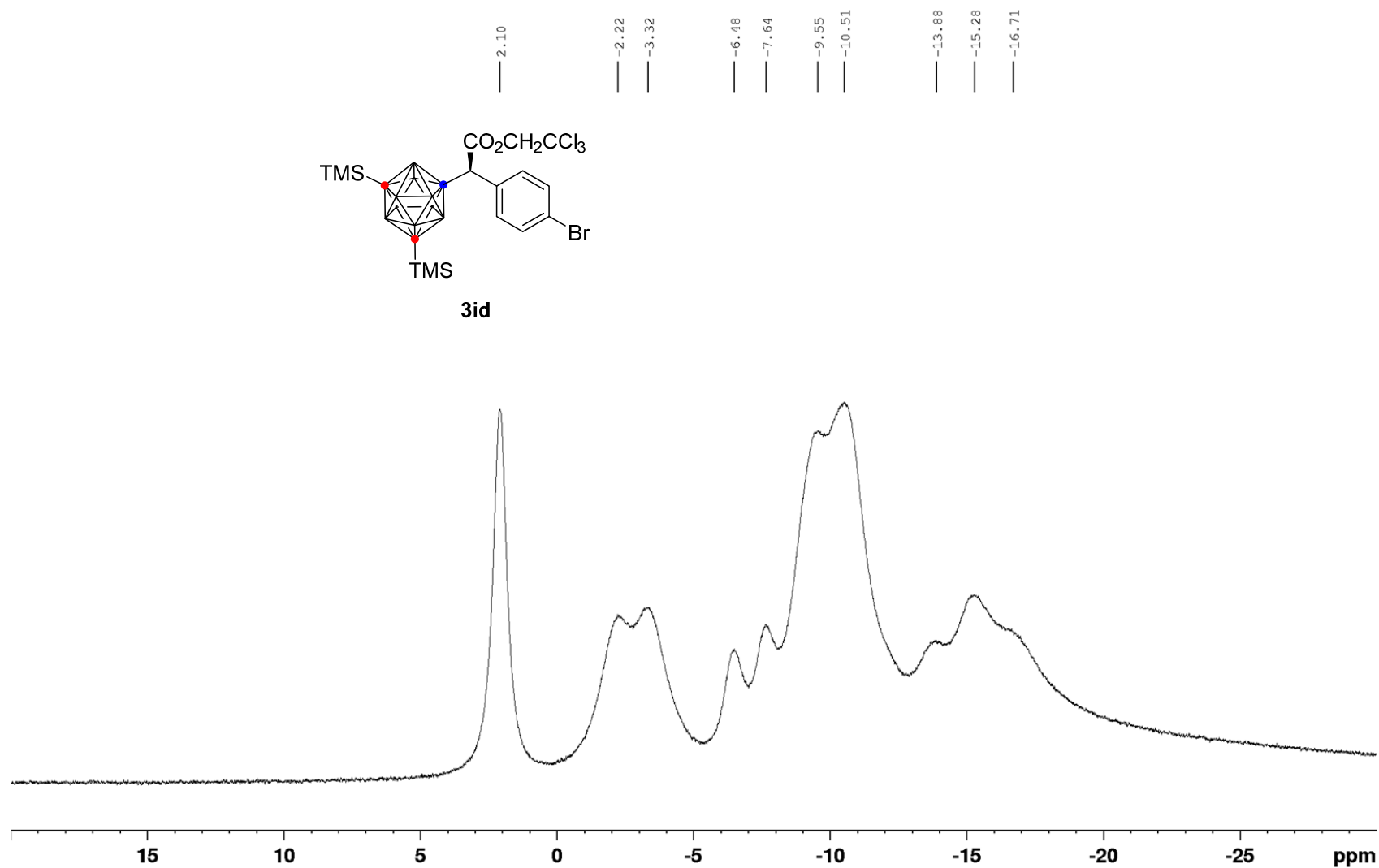
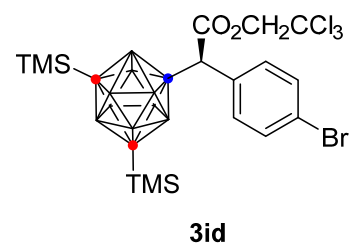
^{13}C NMR (100 MHz, CDCl_3)



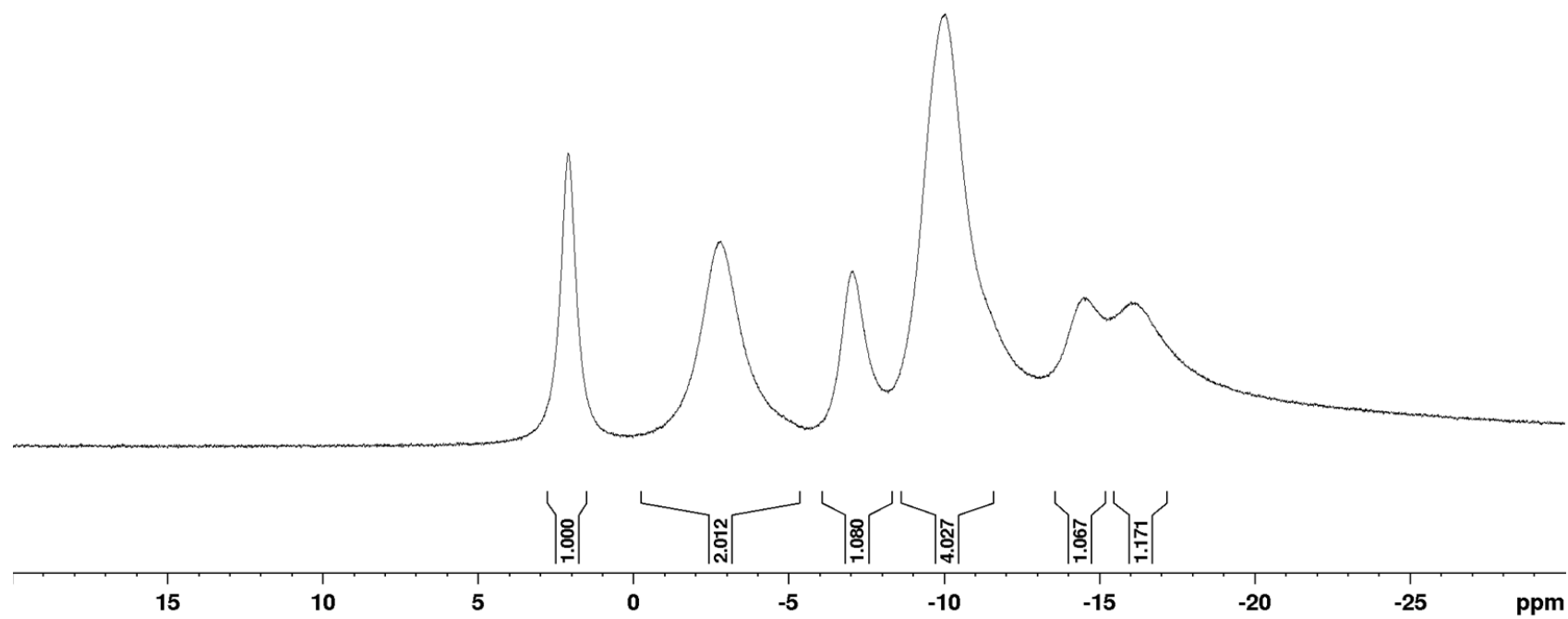
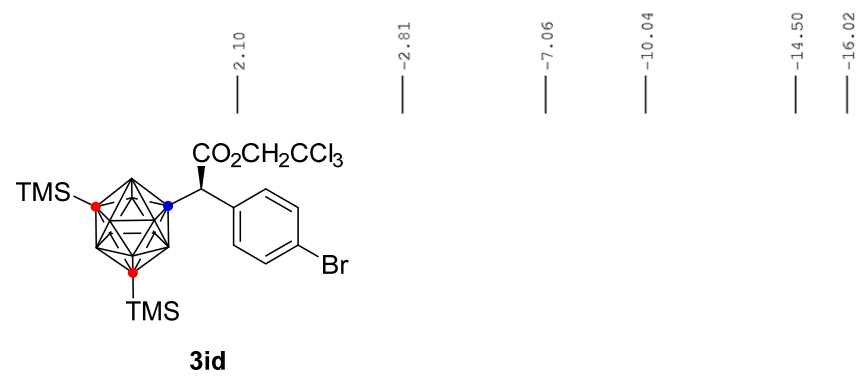
3id



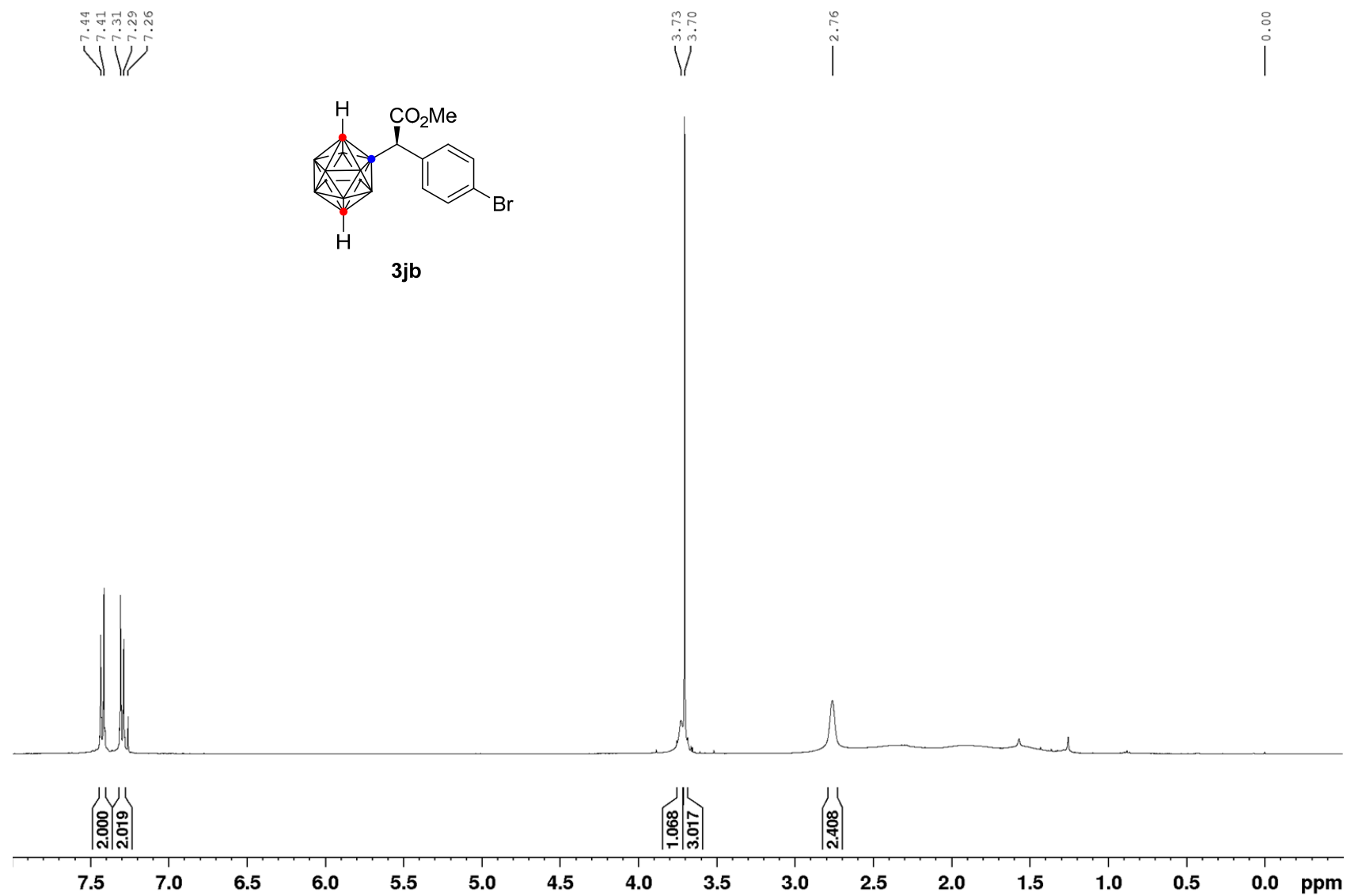
^{11}B NMR (128 MHz, CDCl_3)



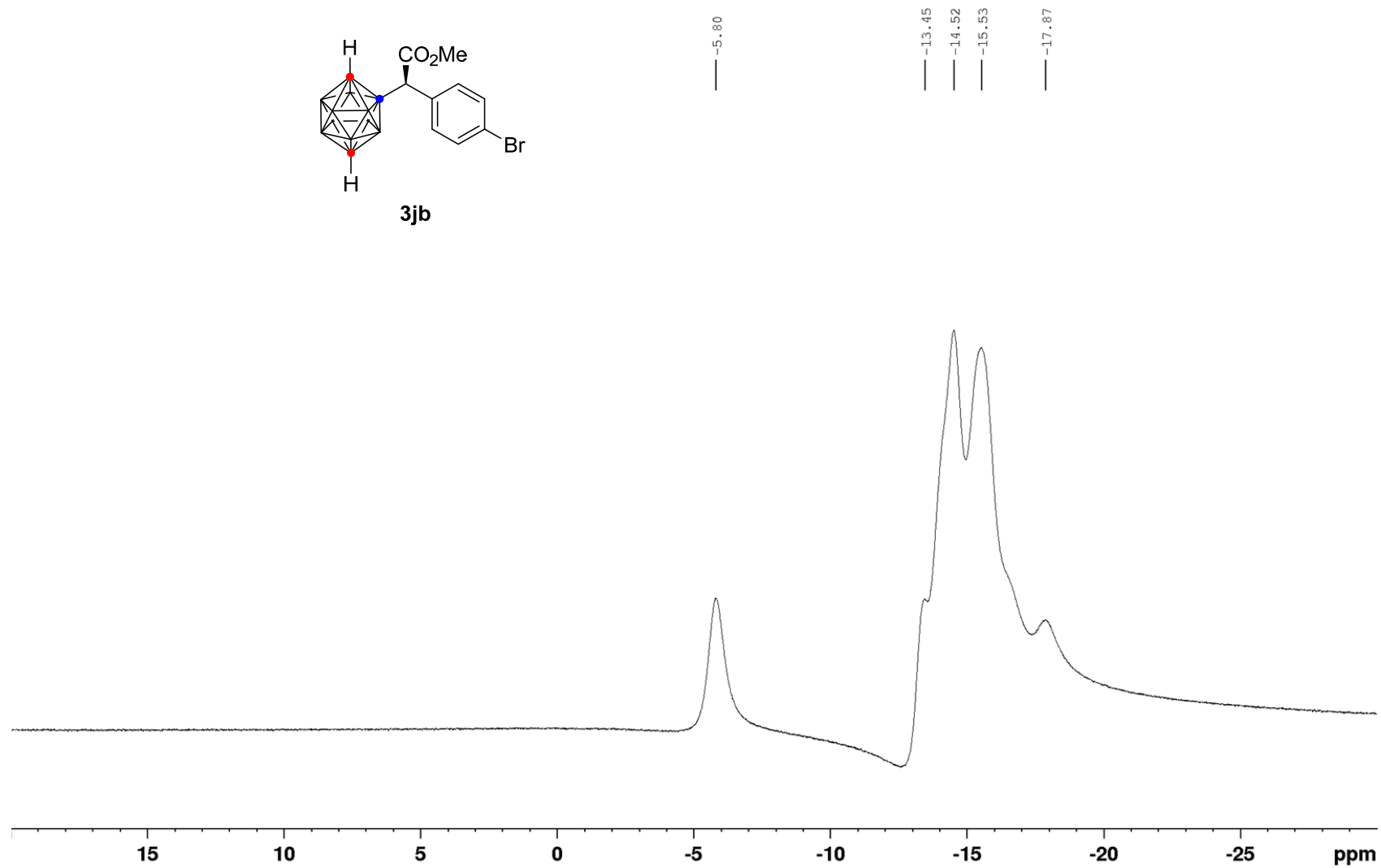
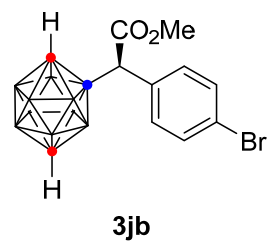
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



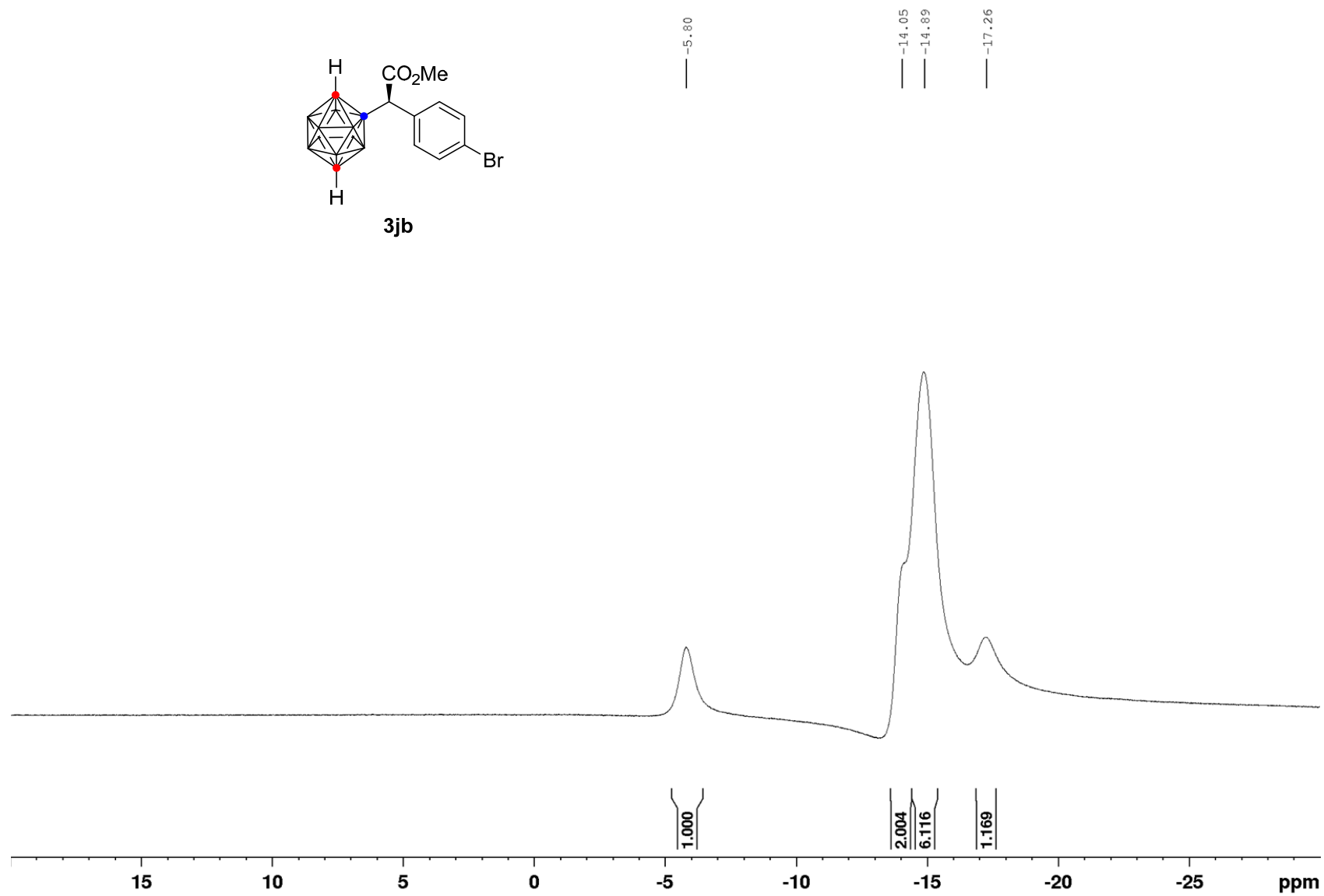
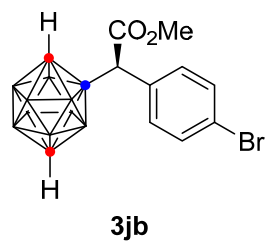
^1H NMR (400 MHz, CDCl_3)



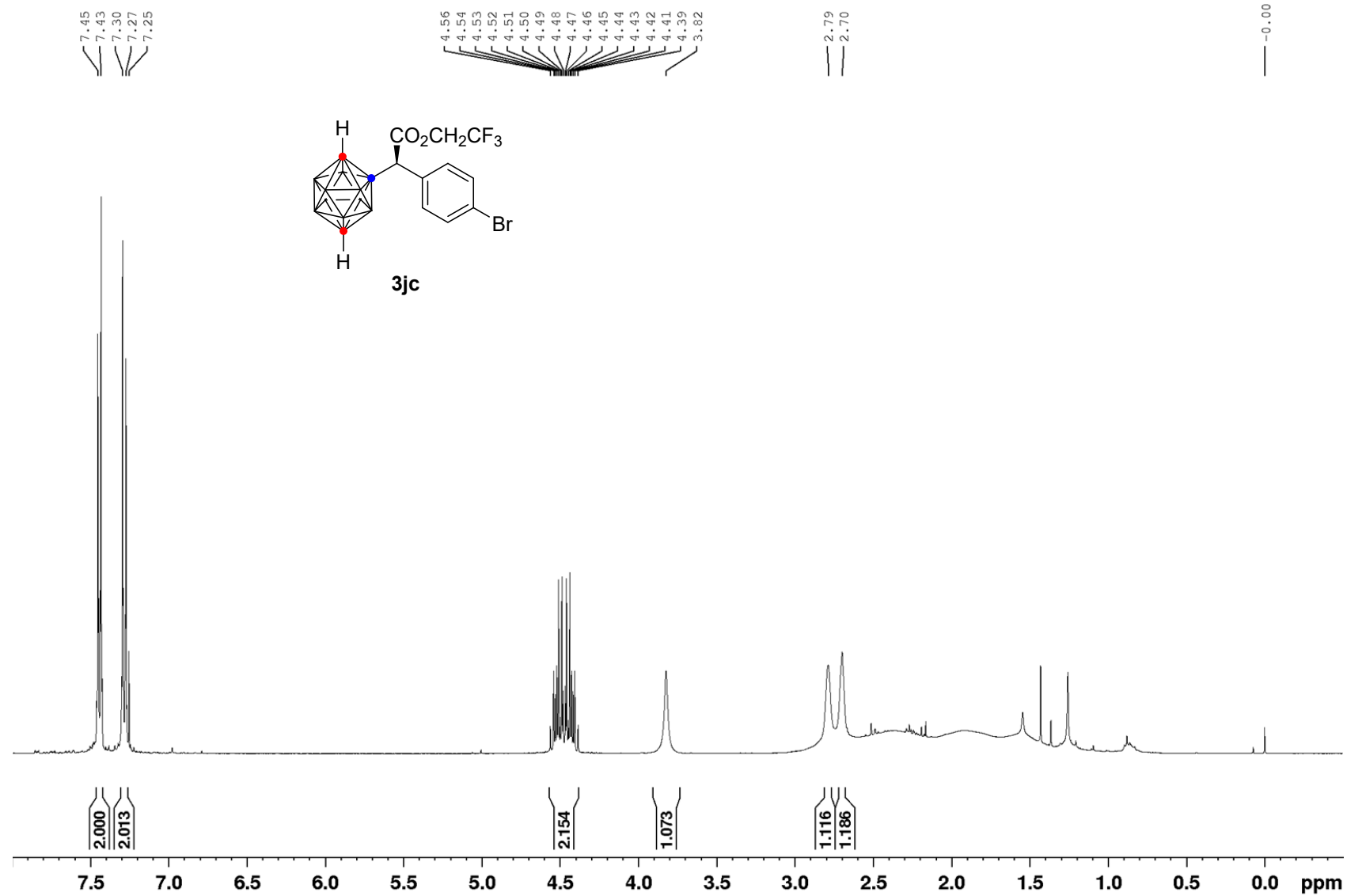
^{11}B NMR (128 MHz, CDCl_3)



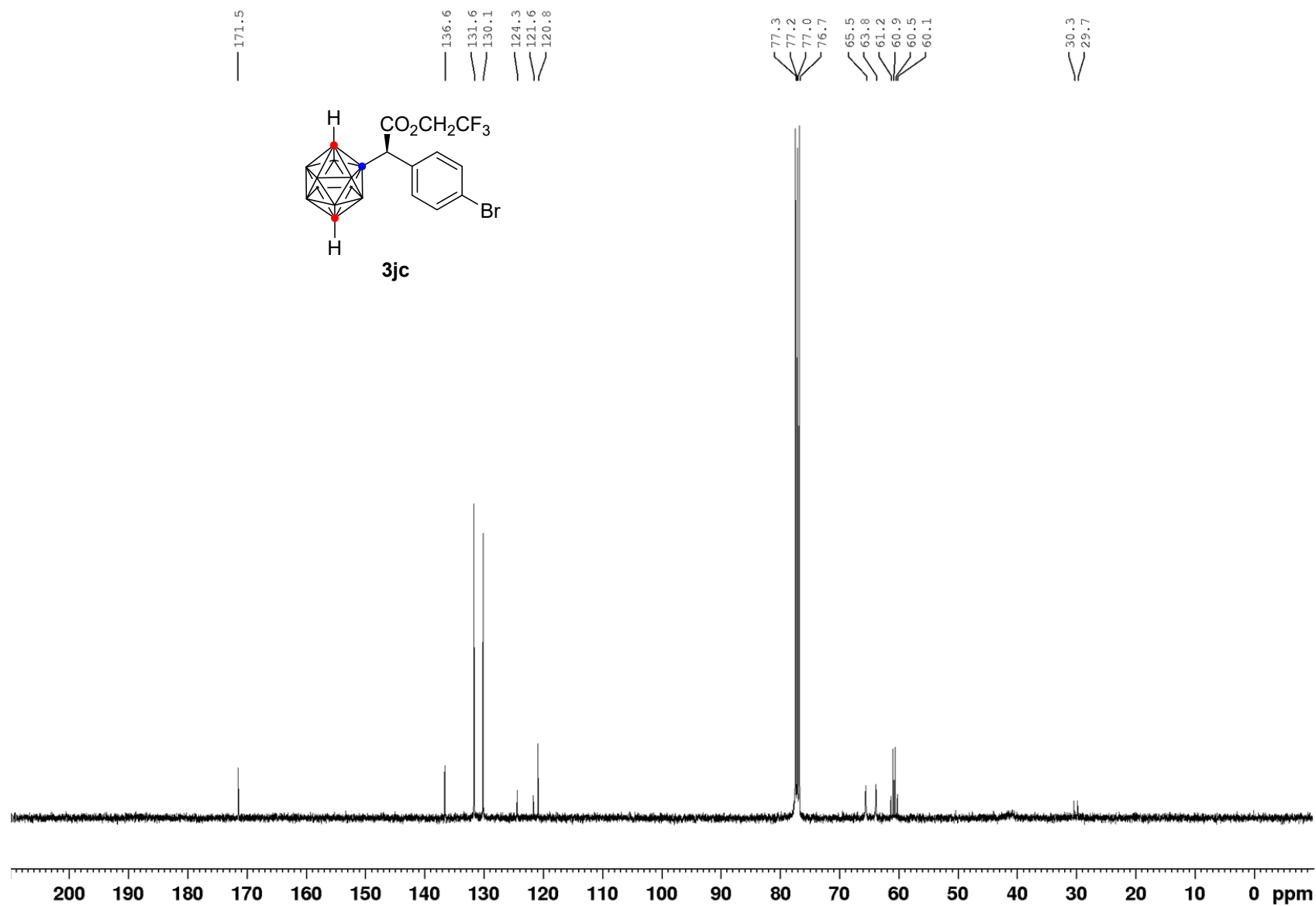
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



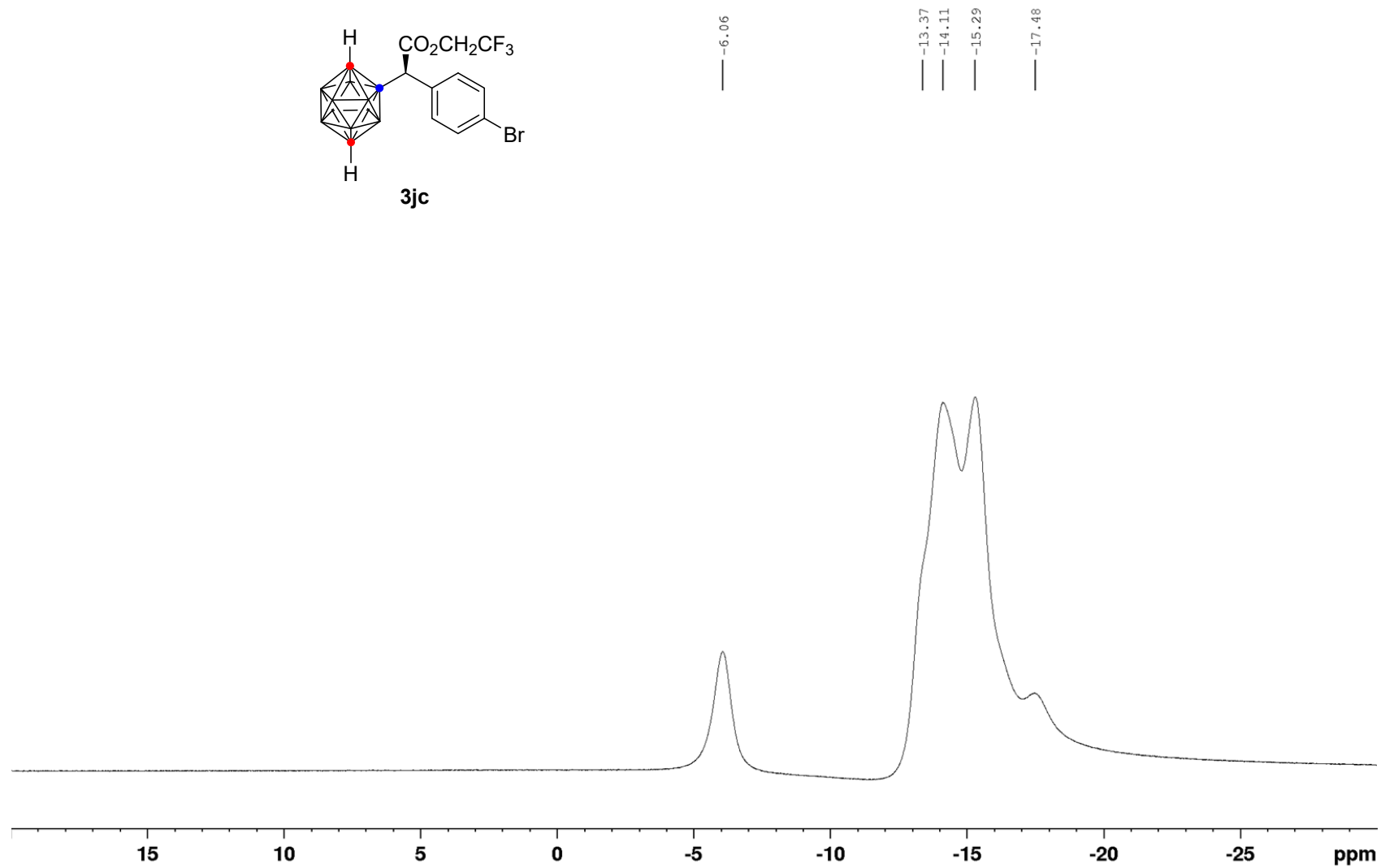
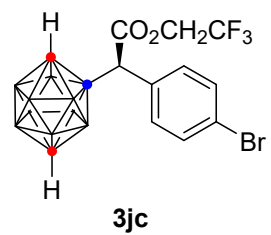
¹H NMR (400 MHz, CDCl₃)



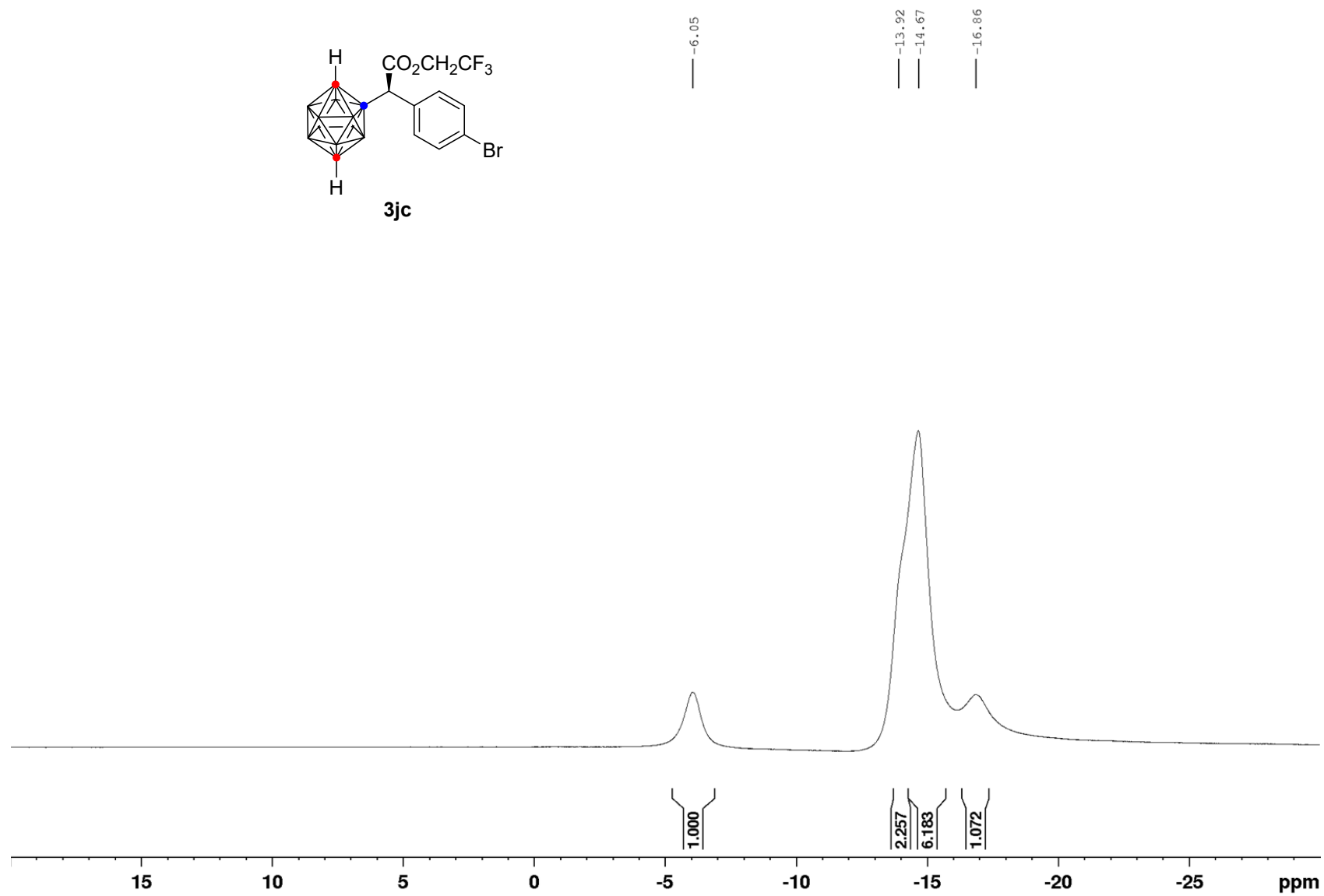
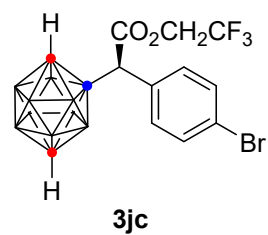
^{13}C NMR (100 MHz, CDCl_3)



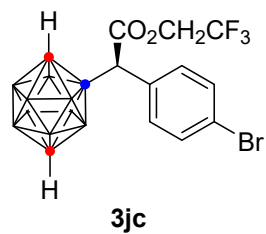
^{11}B NMR (128 MHz, CDCl_3)



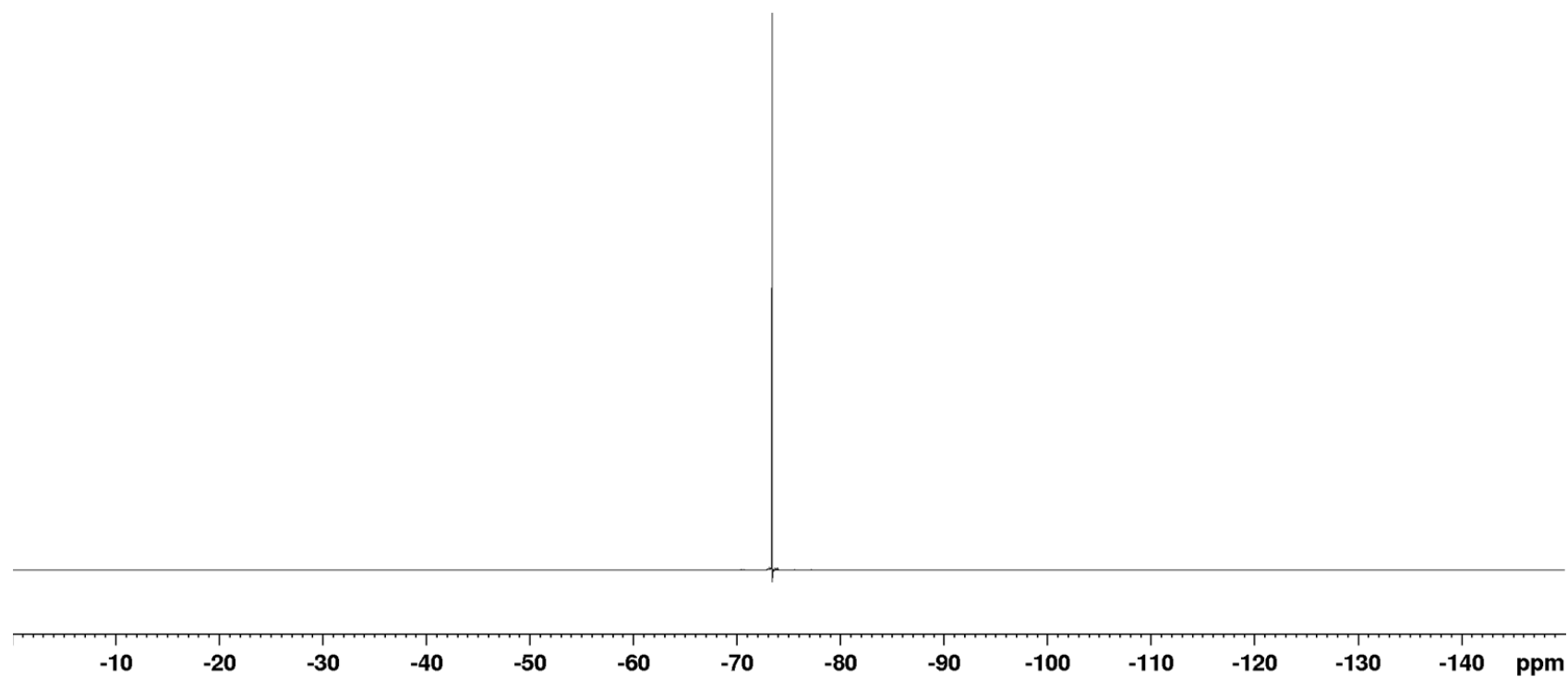
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



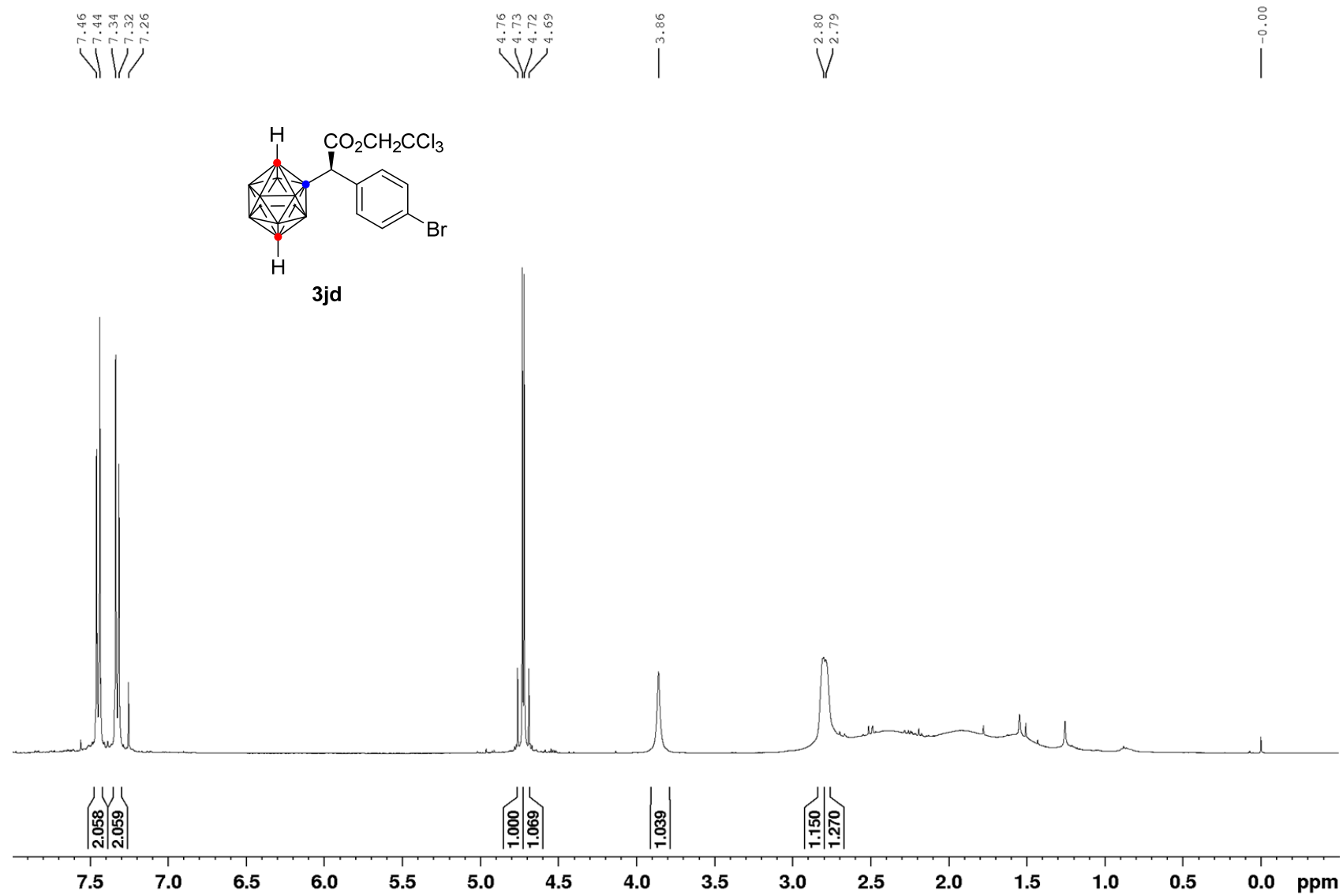
$^{19}\text{F}\{^1\text{H}\}$ NMR (377 MHz, CDCl_3)



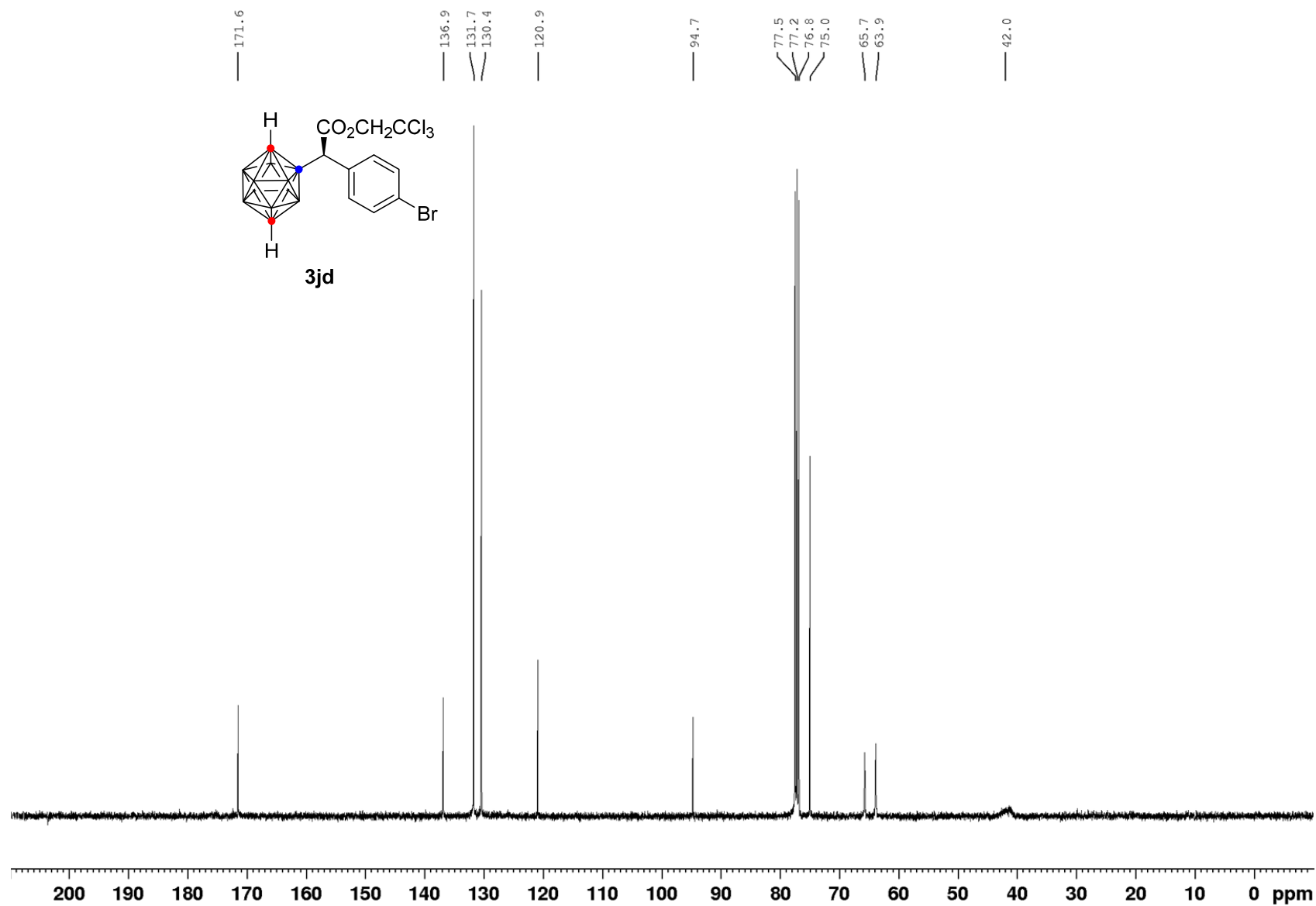
— -73.40



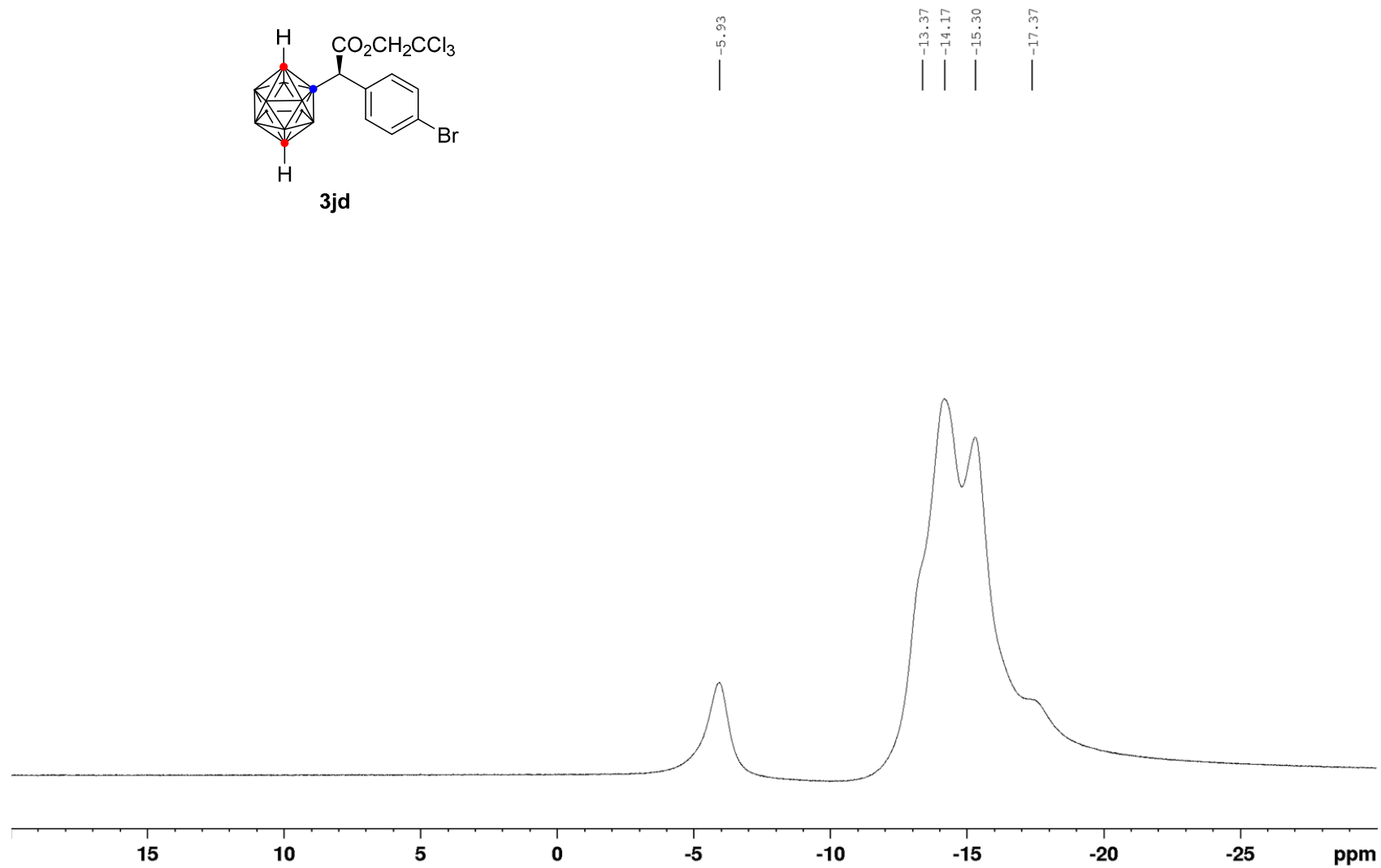
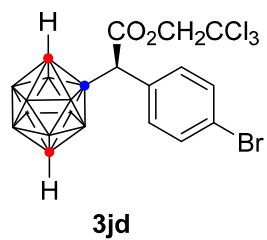
^1H NMR (400 MHz, CDCl_3)



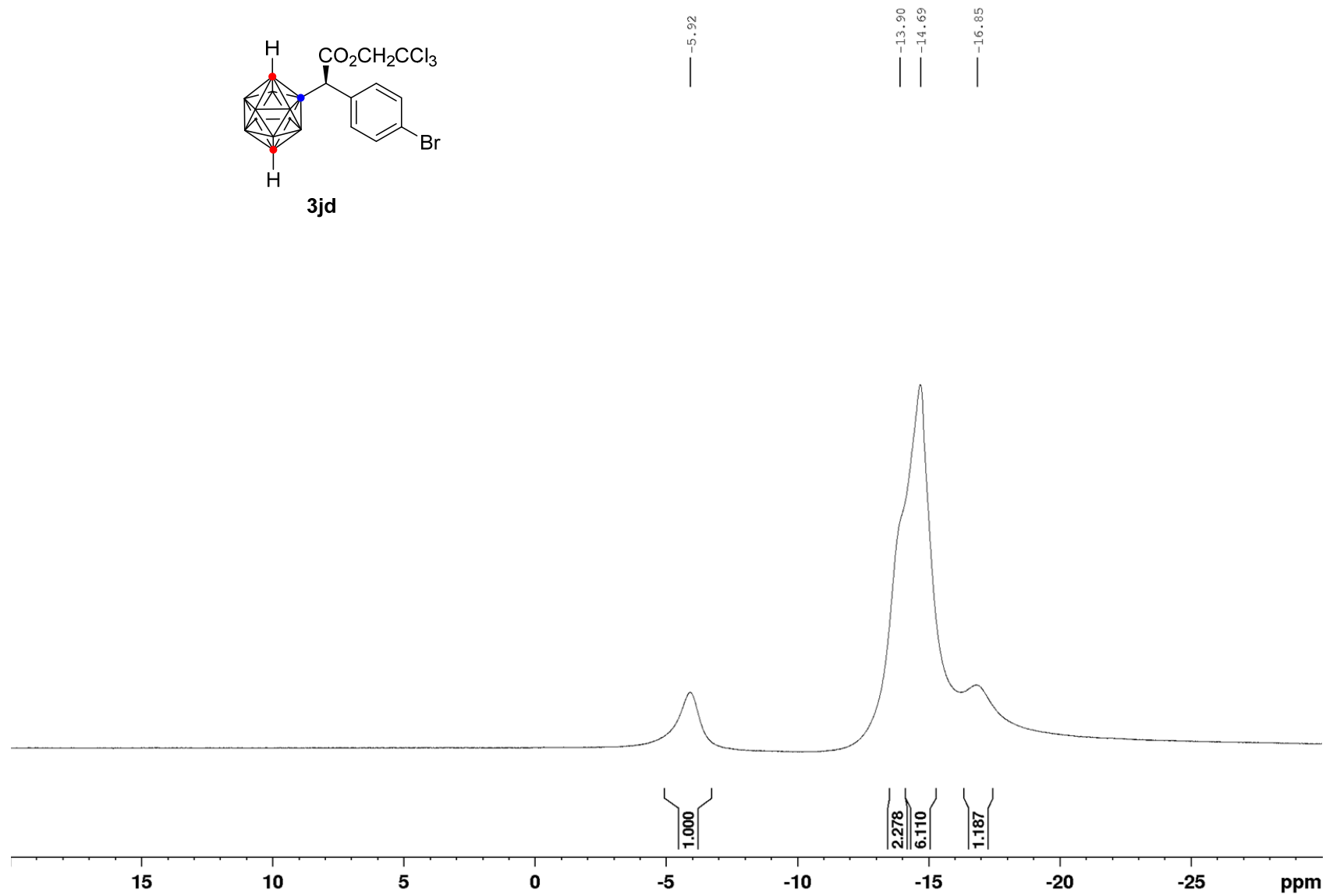
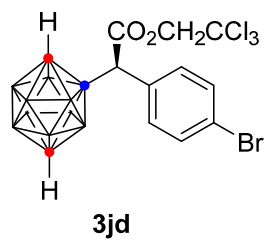
^{13}C NMR (100 MHz, CDCl_3)



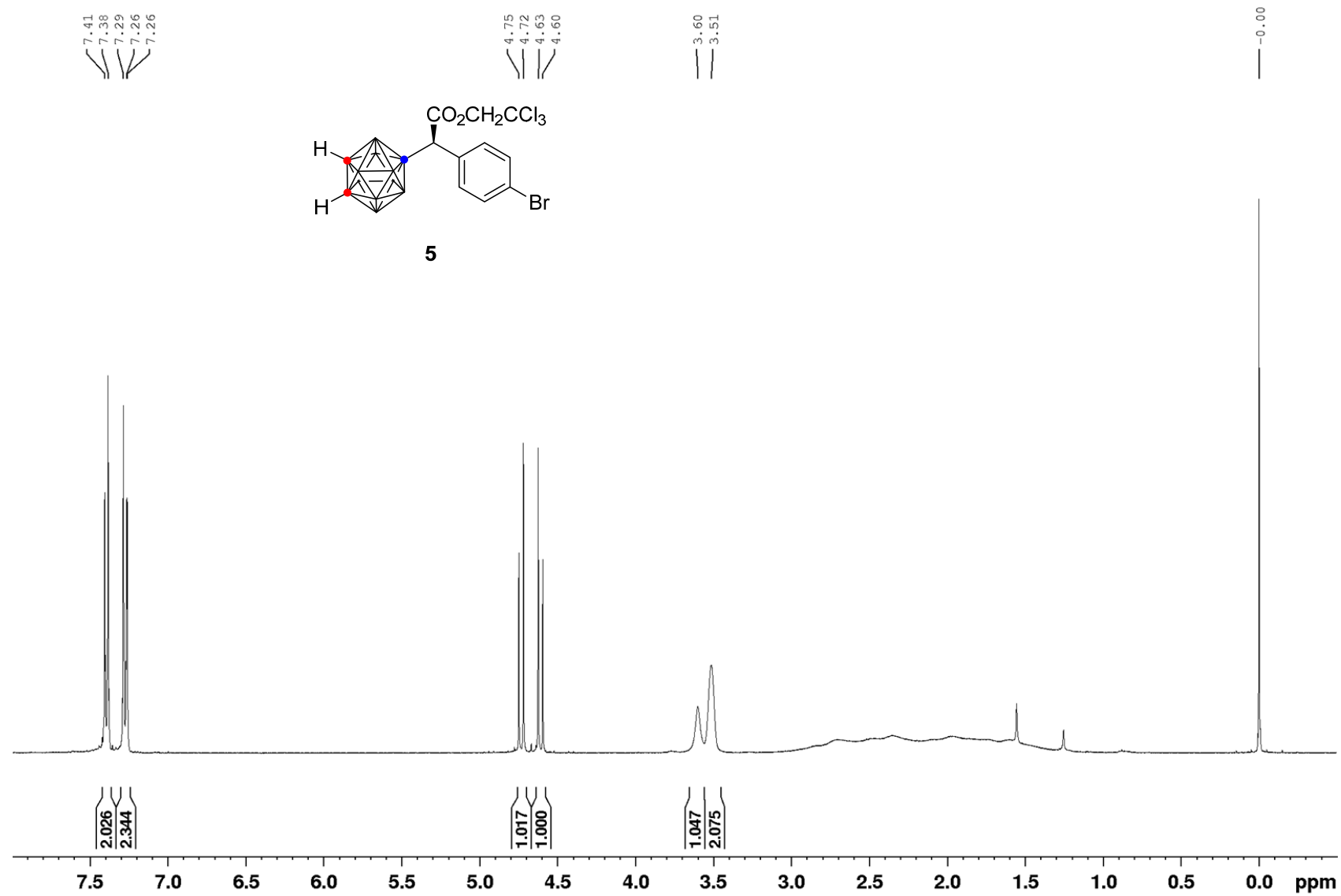
^{11}B NMR (128 MHz, CDCl_3)



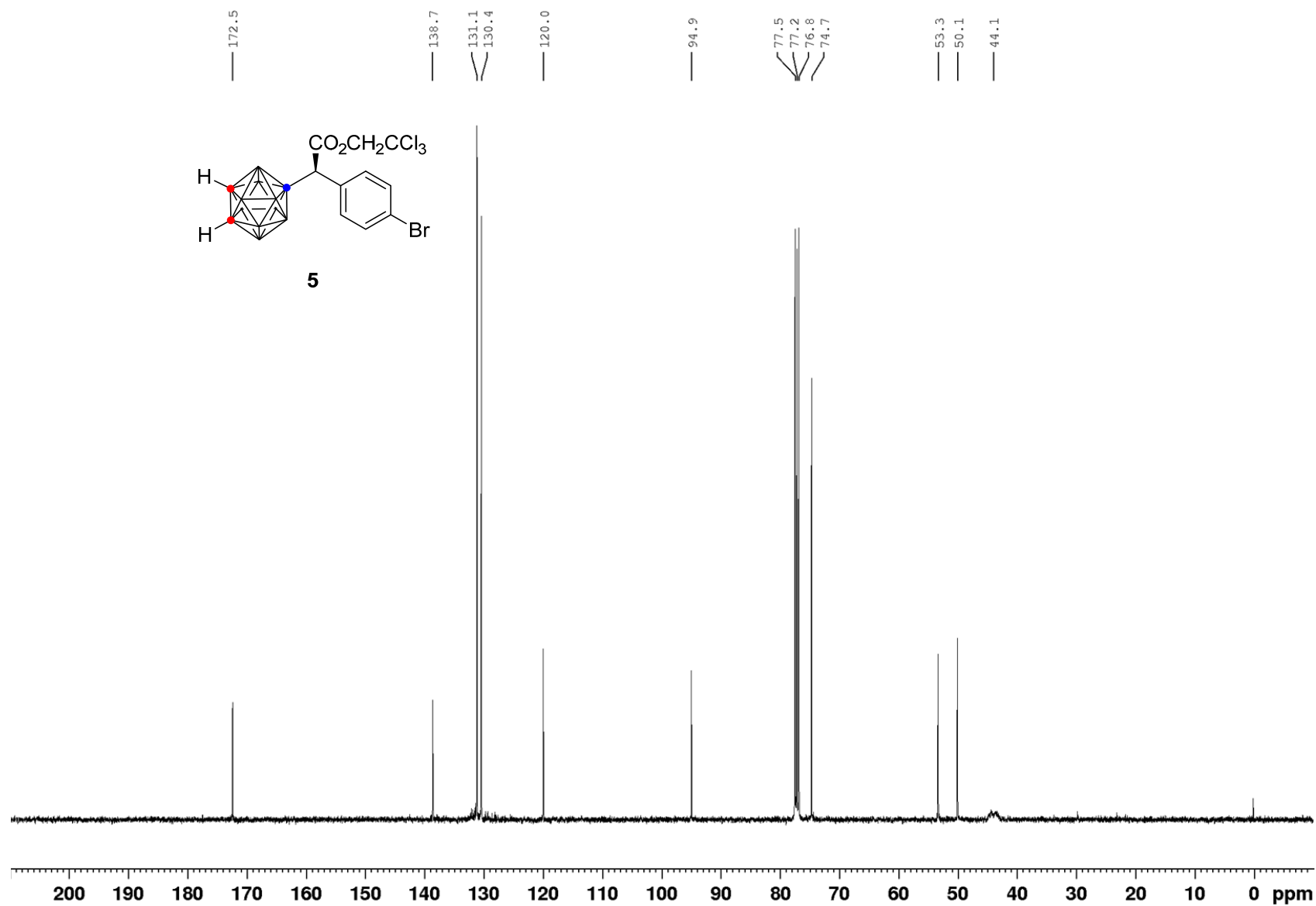
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



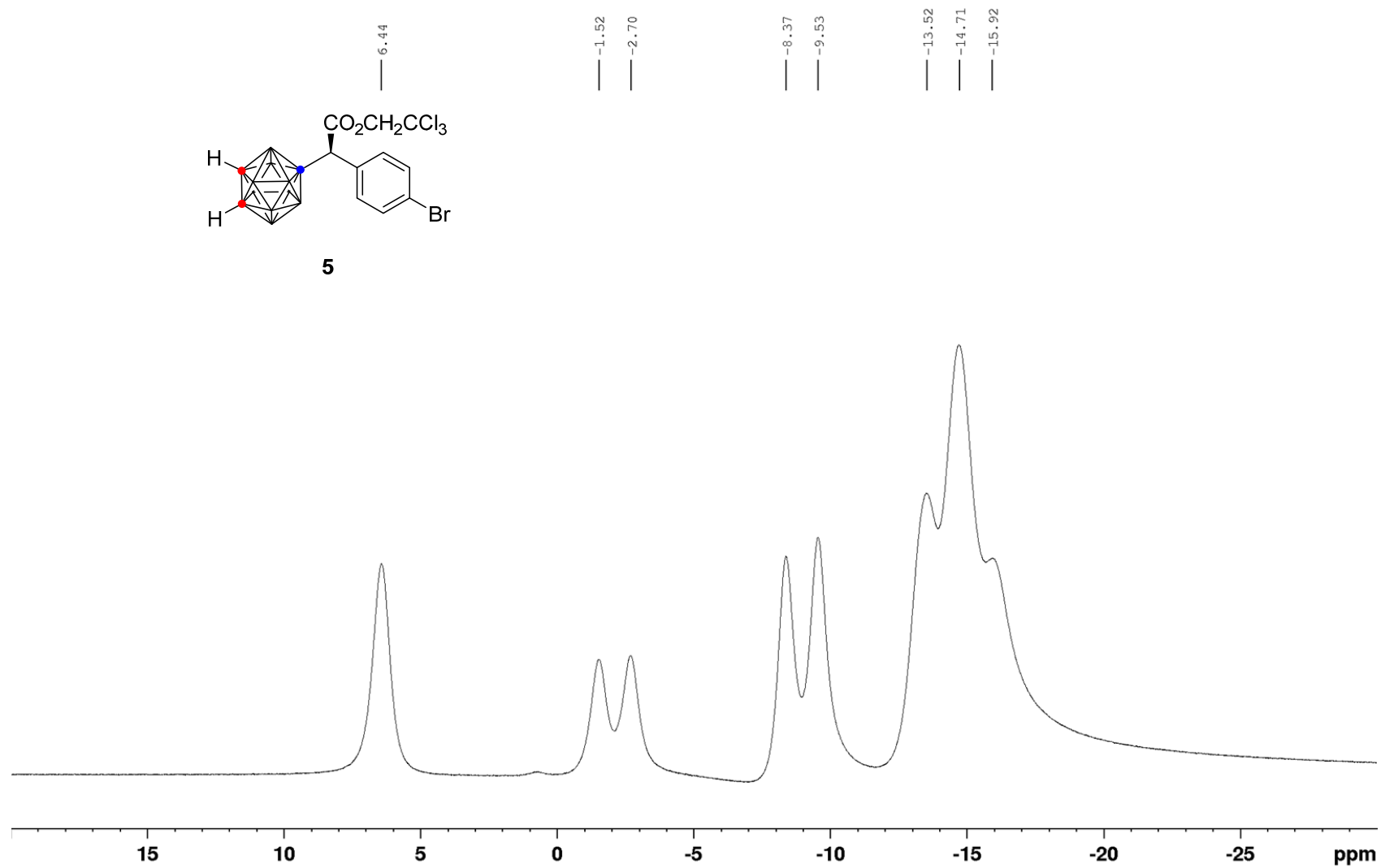
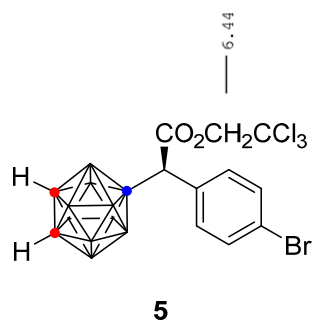
¹H NMR (400 MHz, CDCl₃)



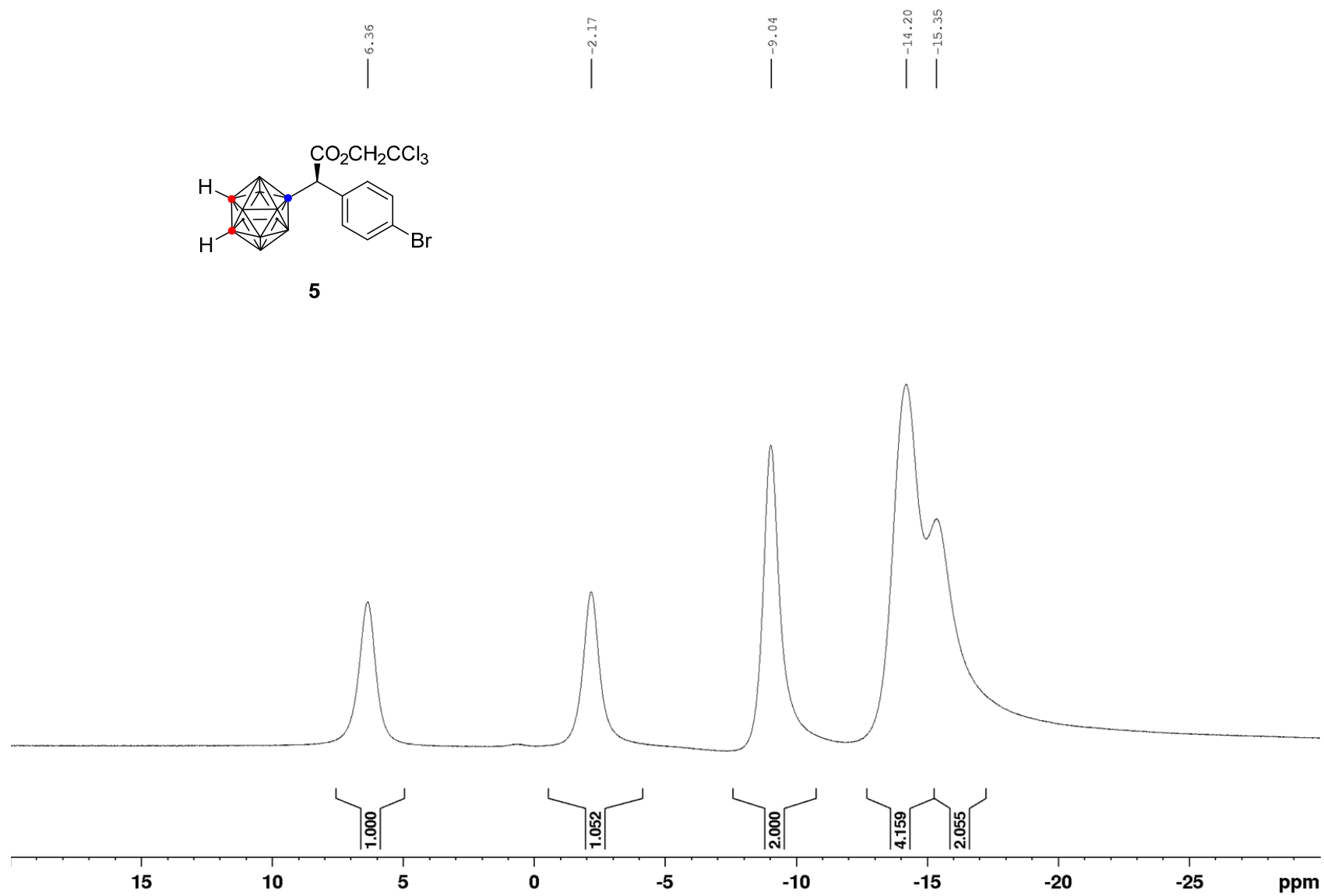
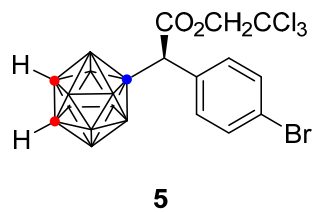
^{13}C NMR (100 MHz, CDCl_3)



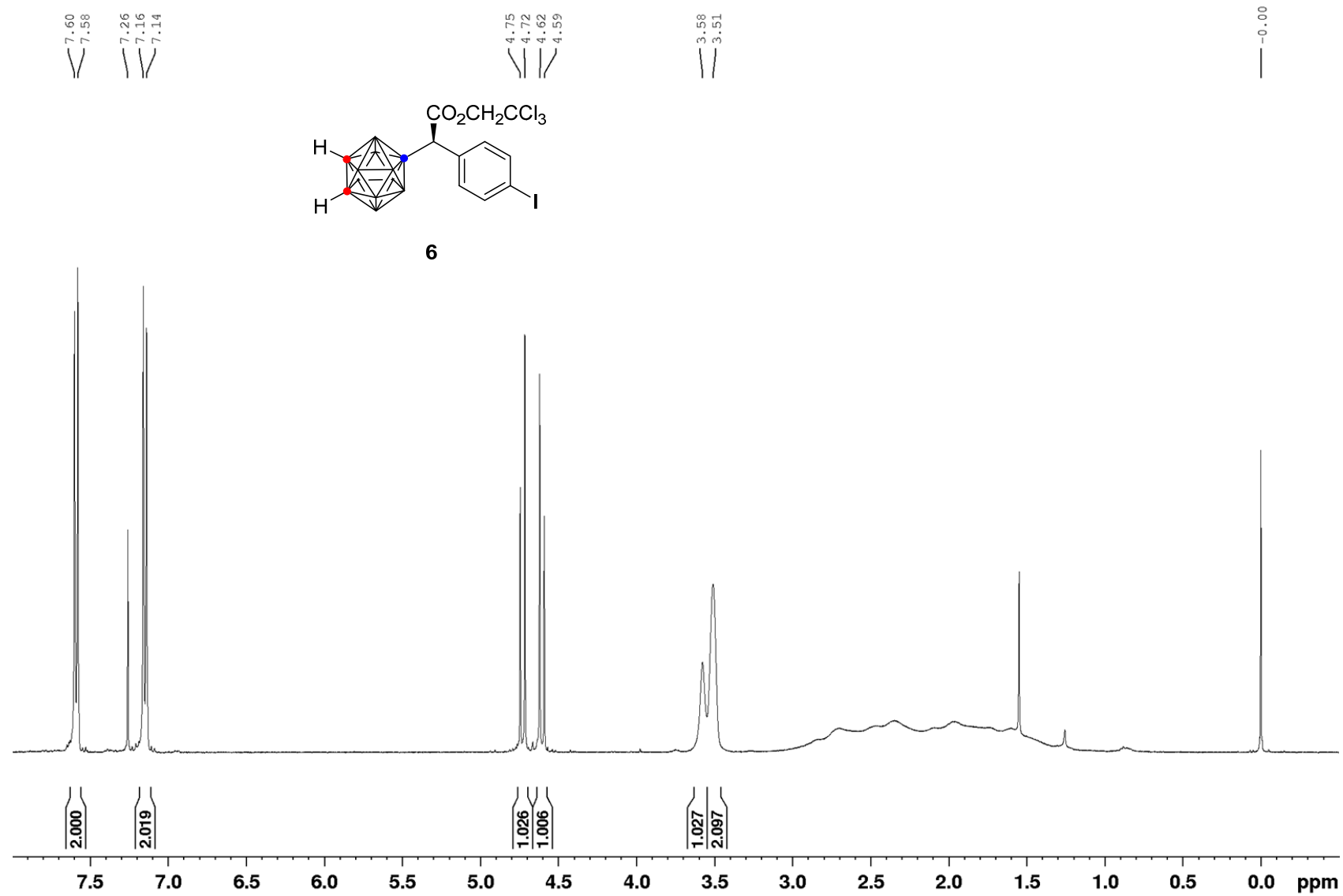
^{11}B NMR (128 MHz, CDCl_3)



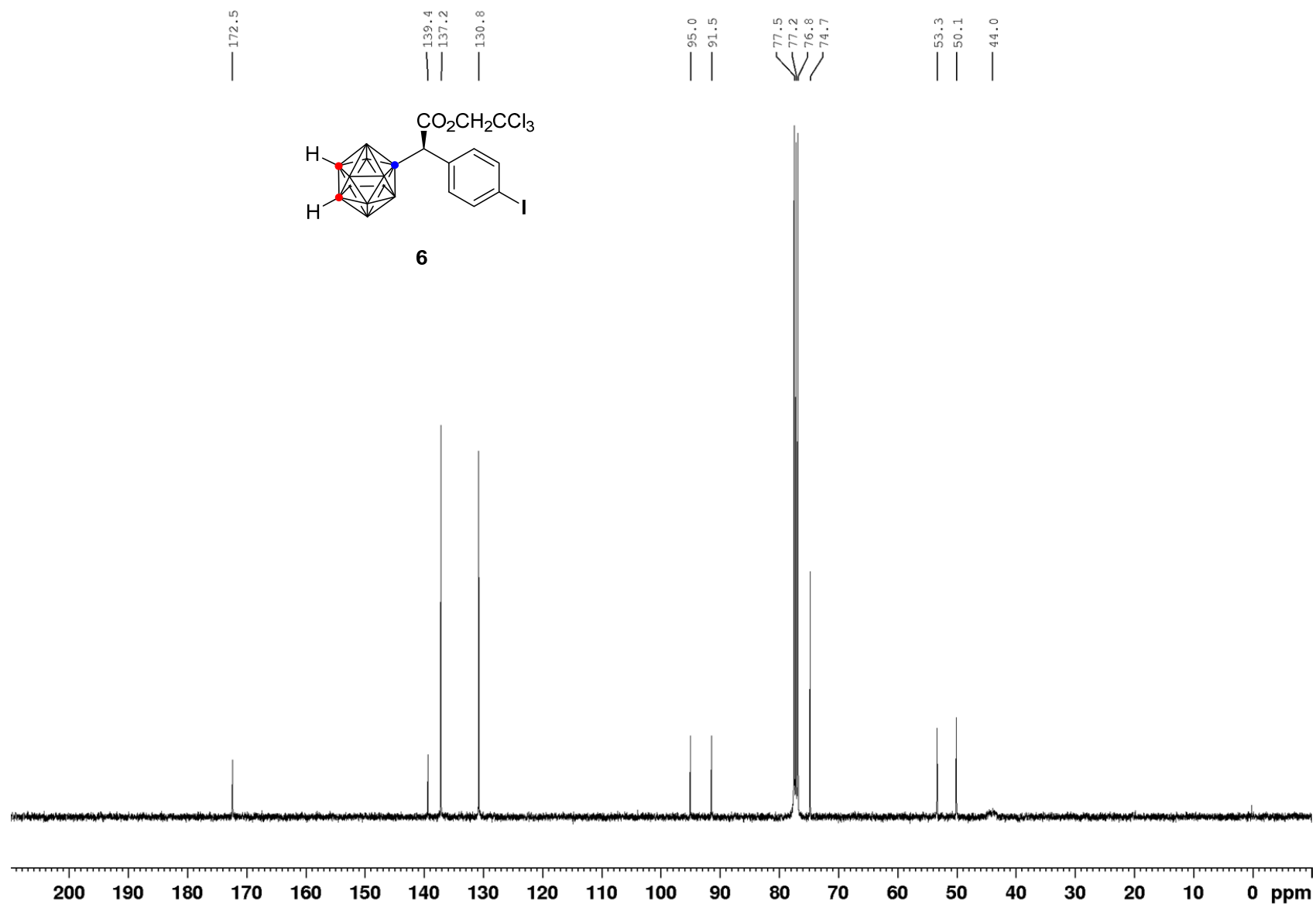
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



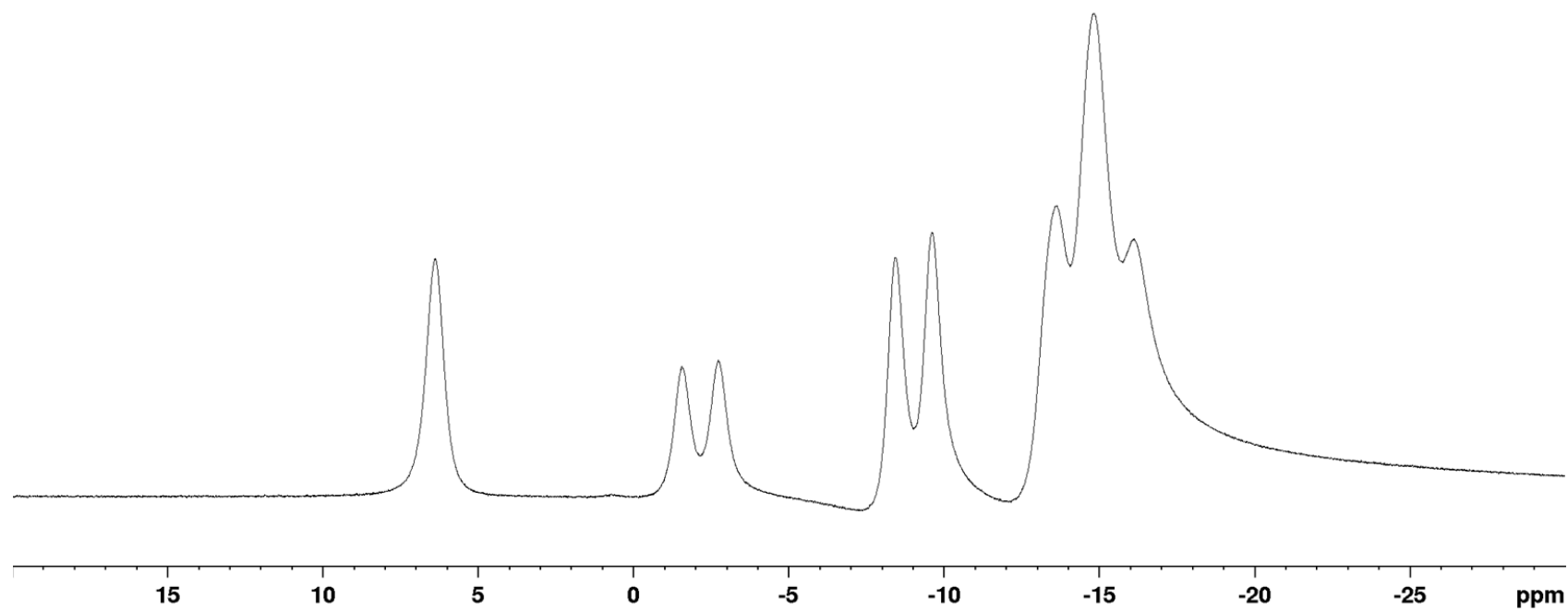
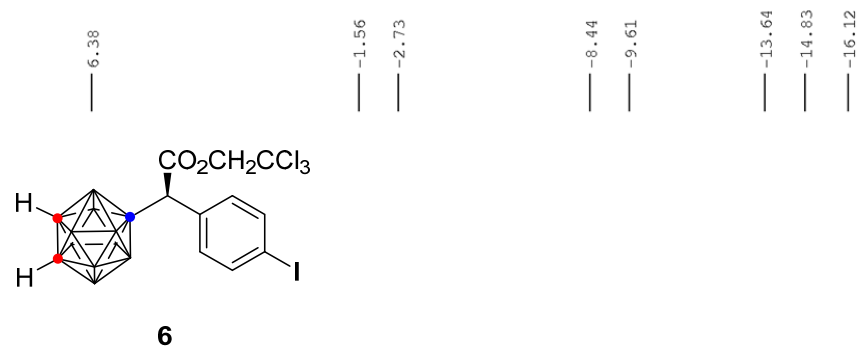
^1H NMR (400 MHz, CDCl_3)



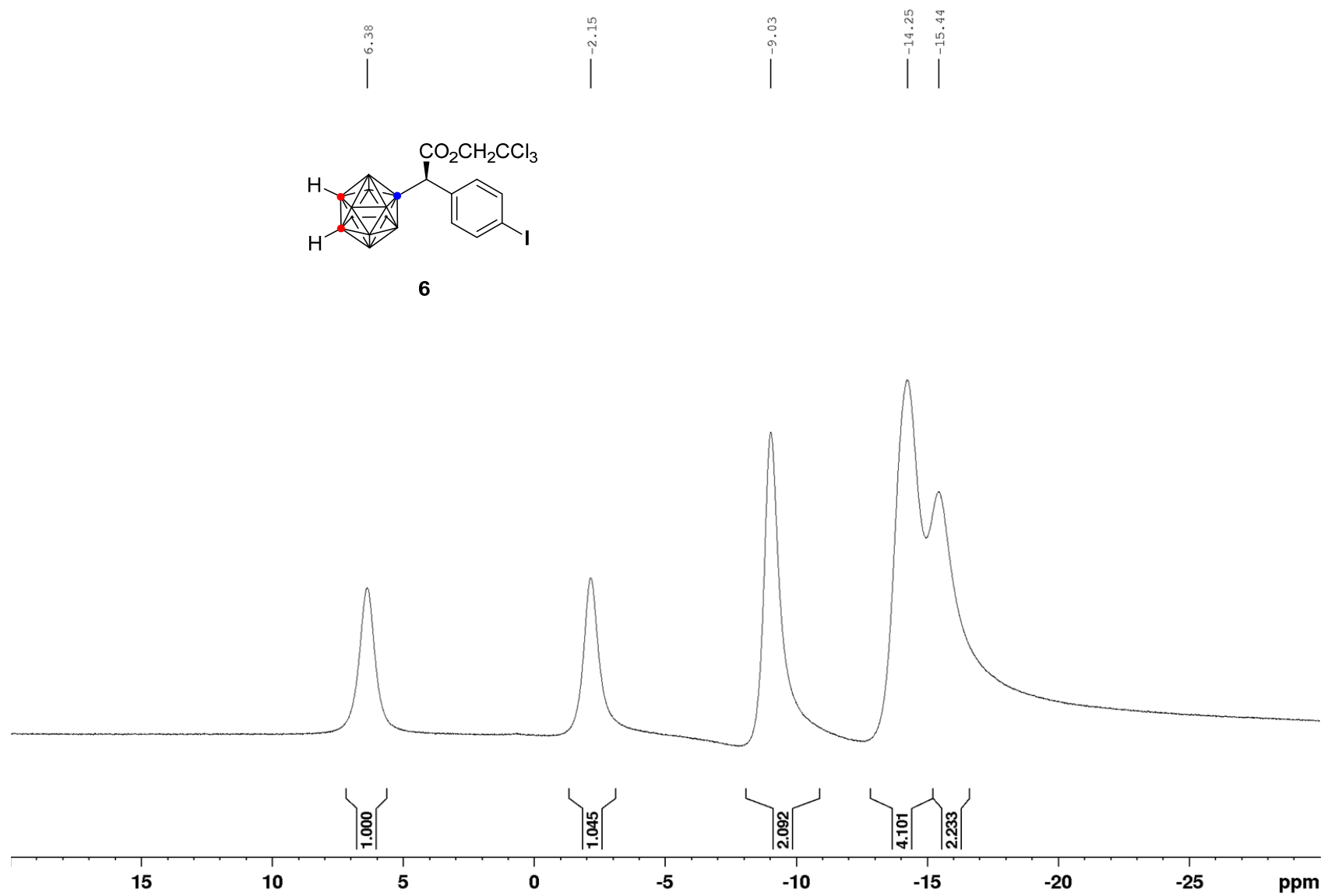
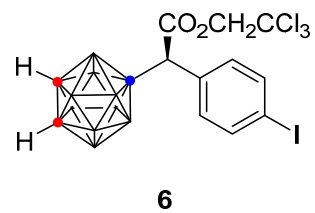
^{13}C NMR (100 MHz, CDCl_3)



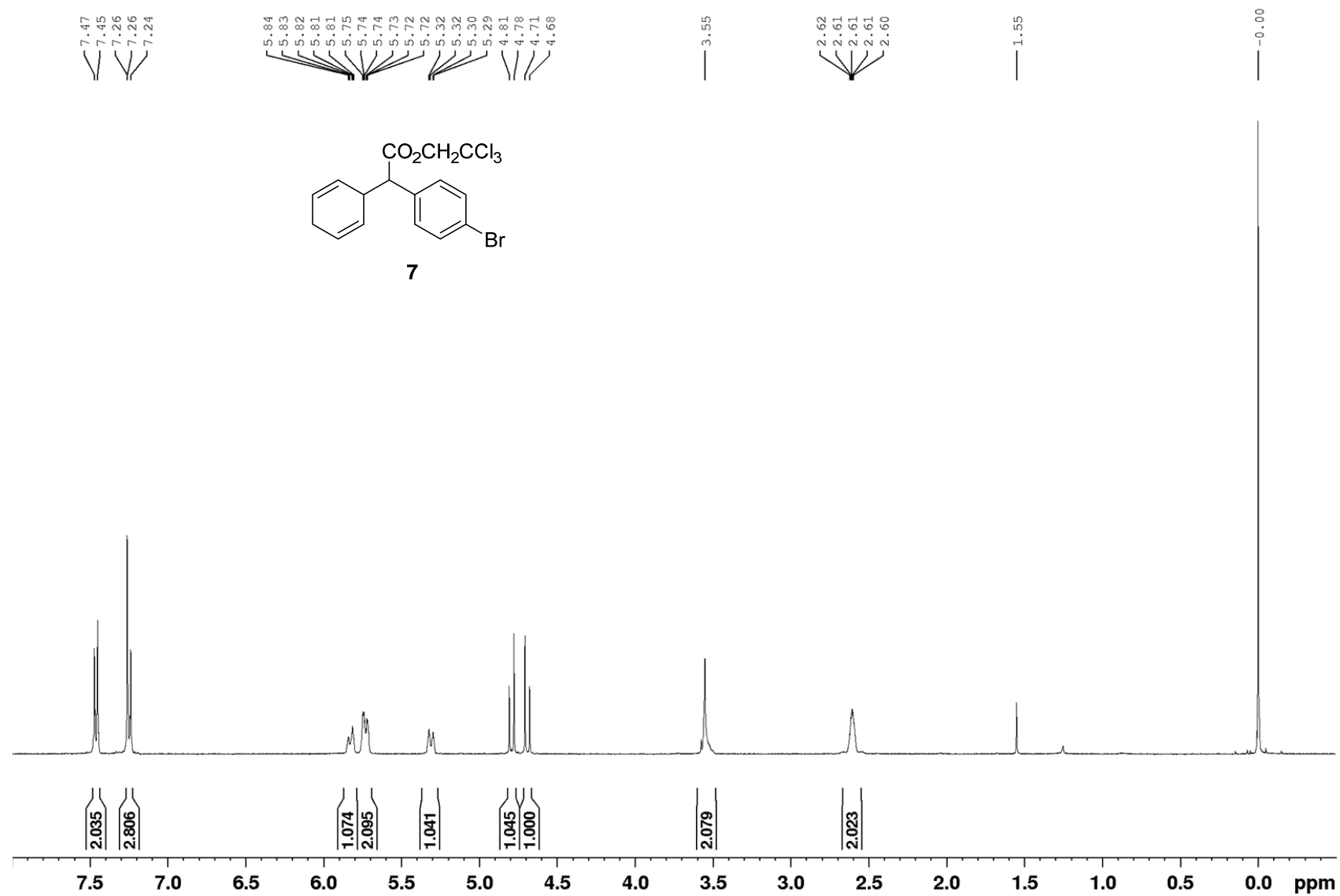
^{11}B NMR (128 MHz, CDCl_3)



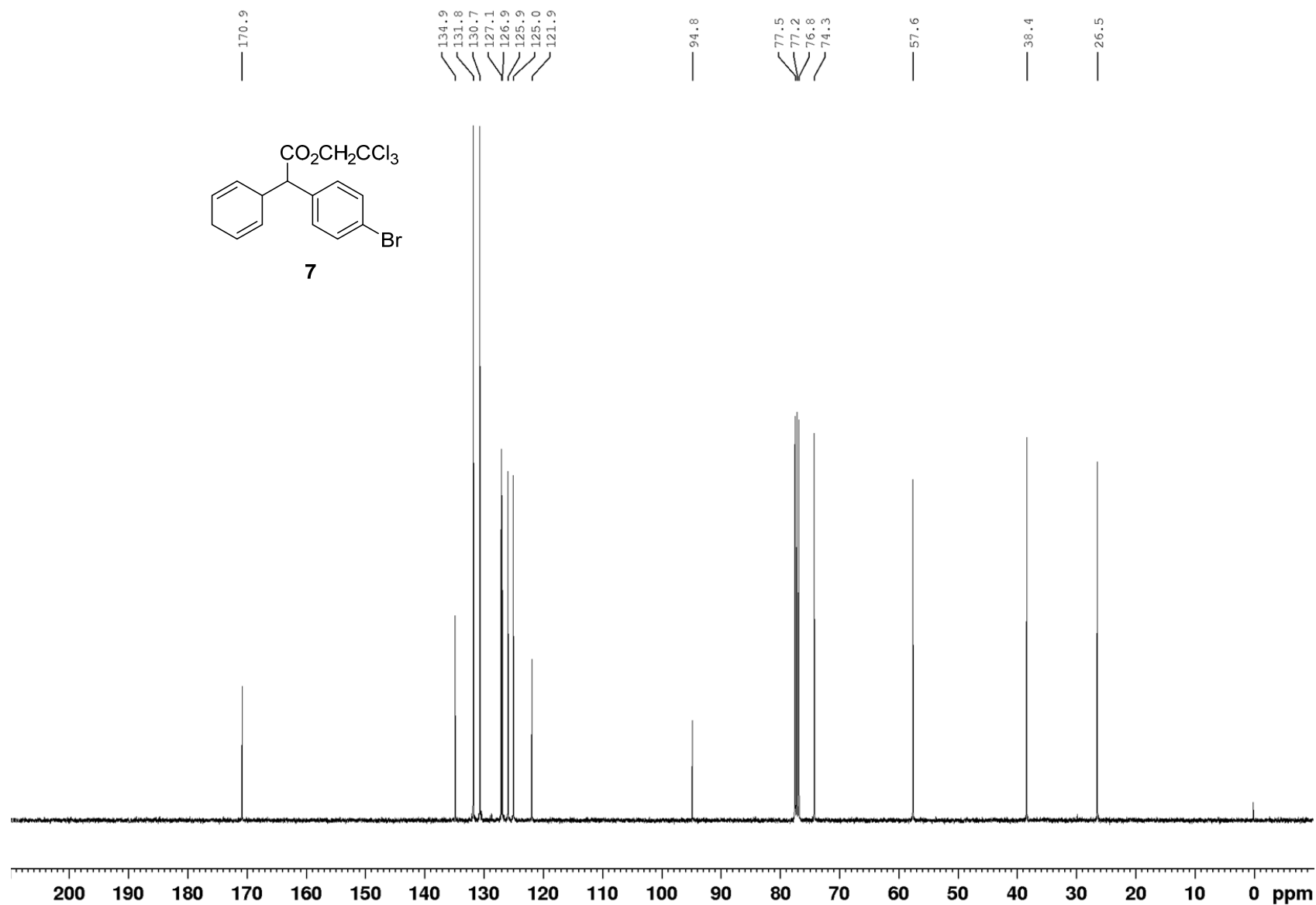
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



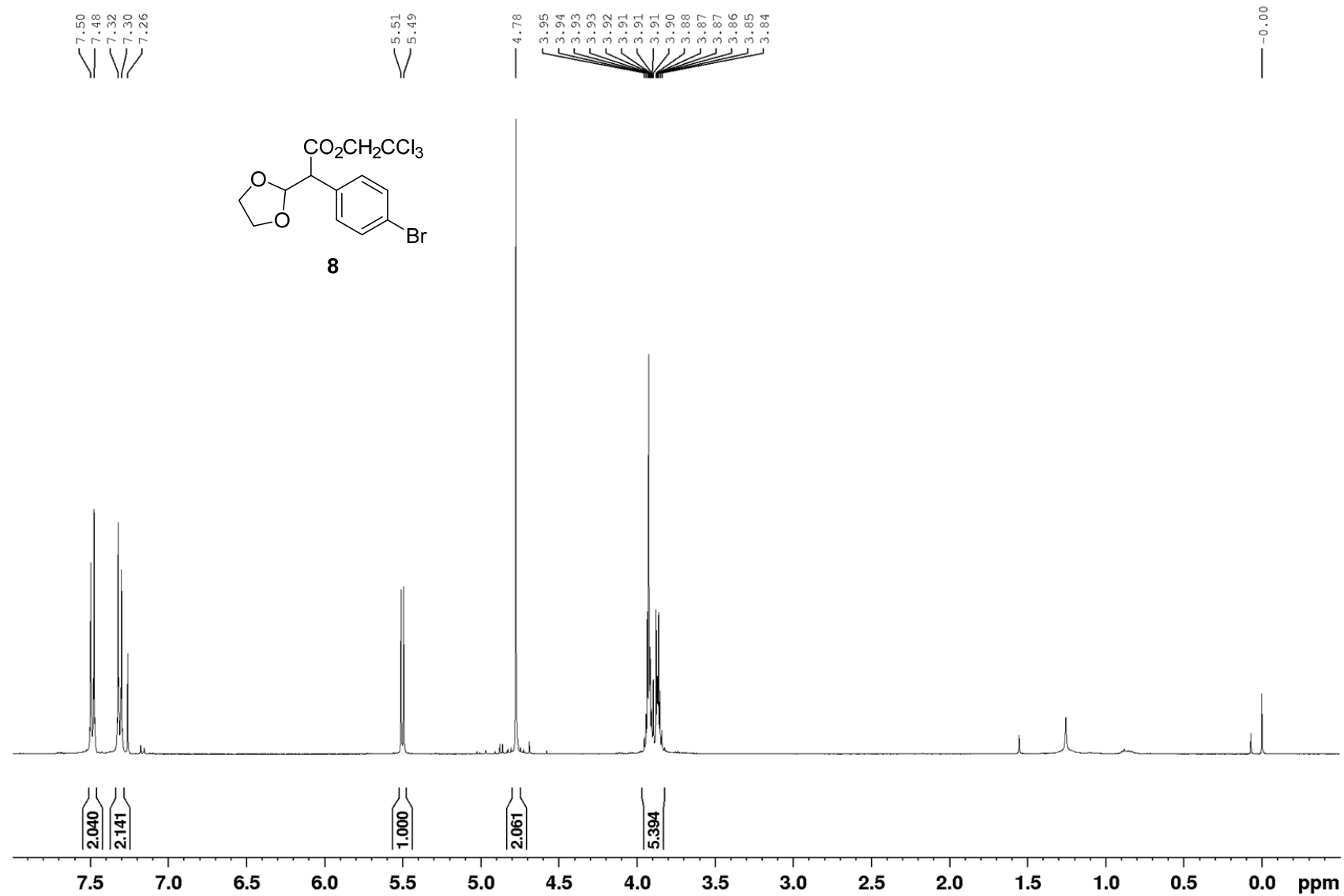
¹H NMR (400 MHz, CDCl₃)



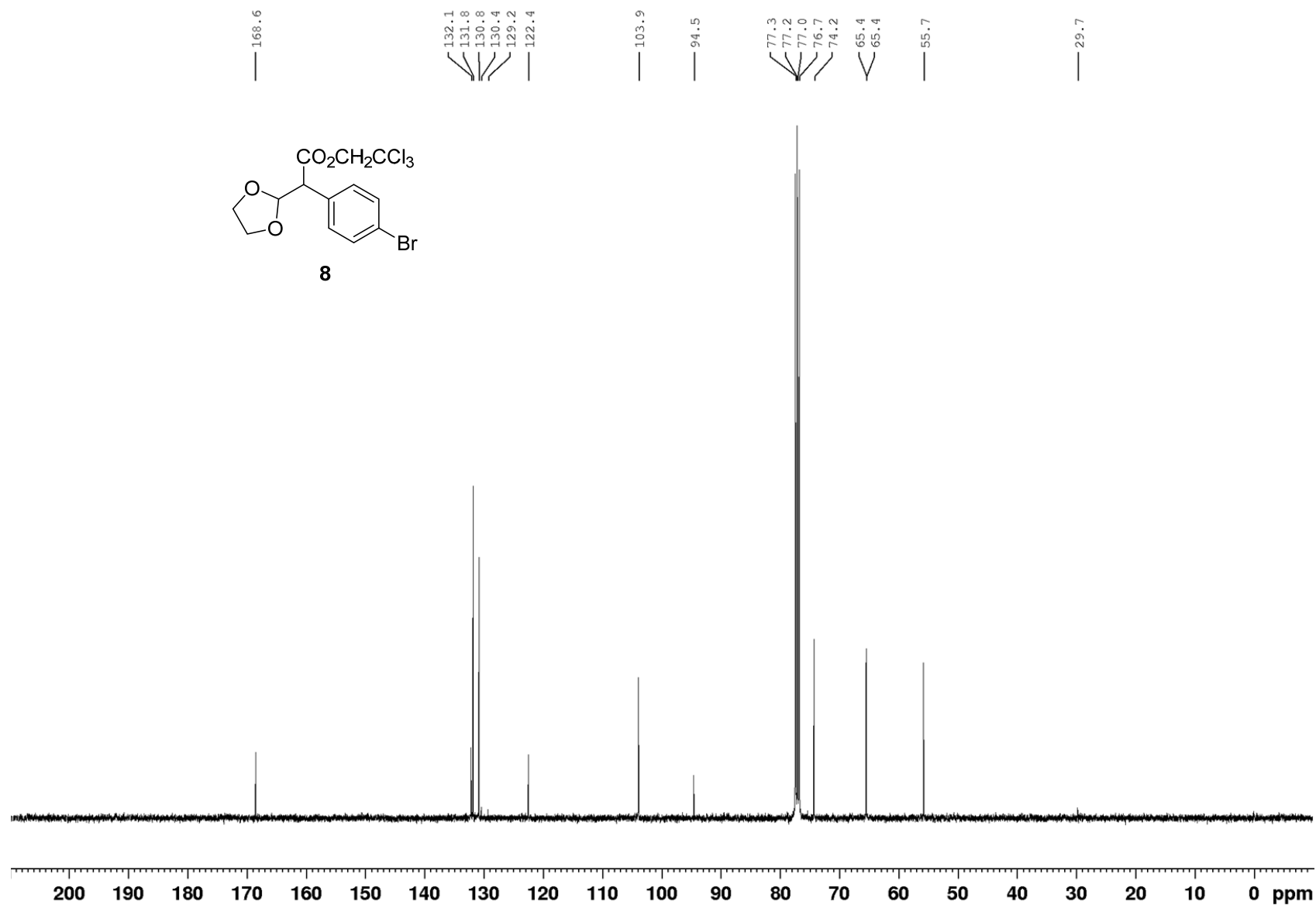
^{13}C NMR (100 MHz, CDCl_3)



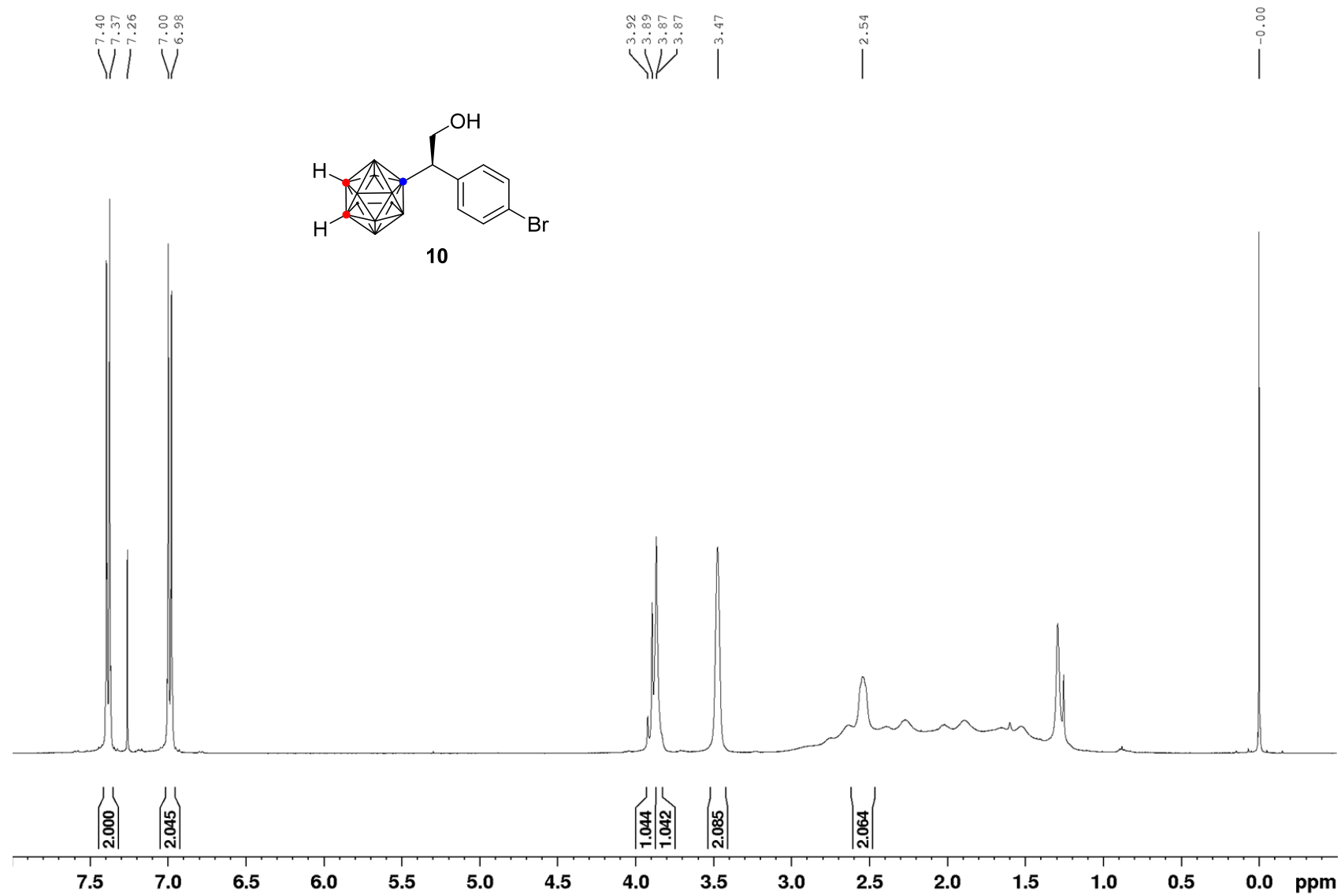
^1H NMR (400 MHz, CDCl_3)



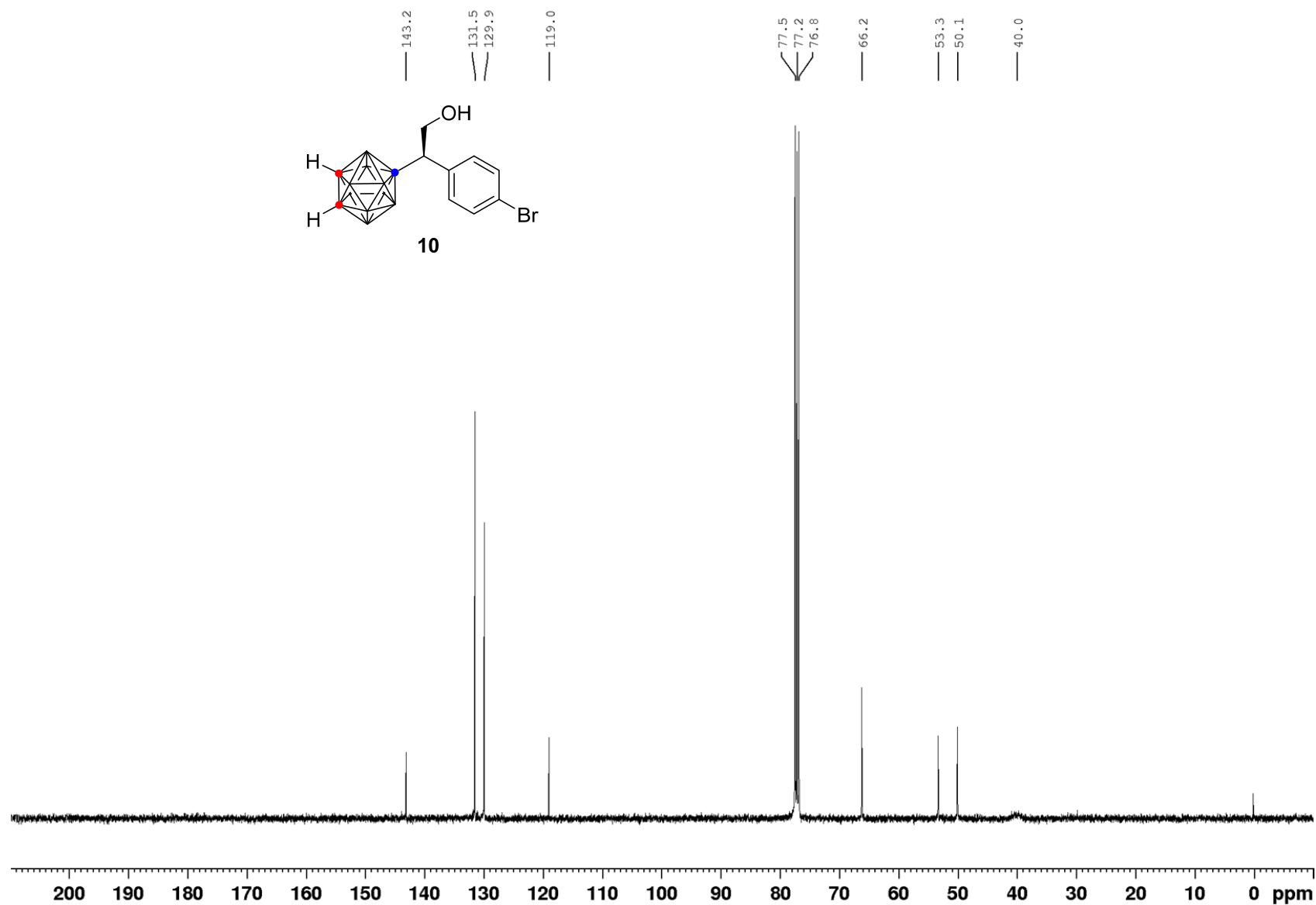
^{13}C NMR (100 MHz, CDCl_3)



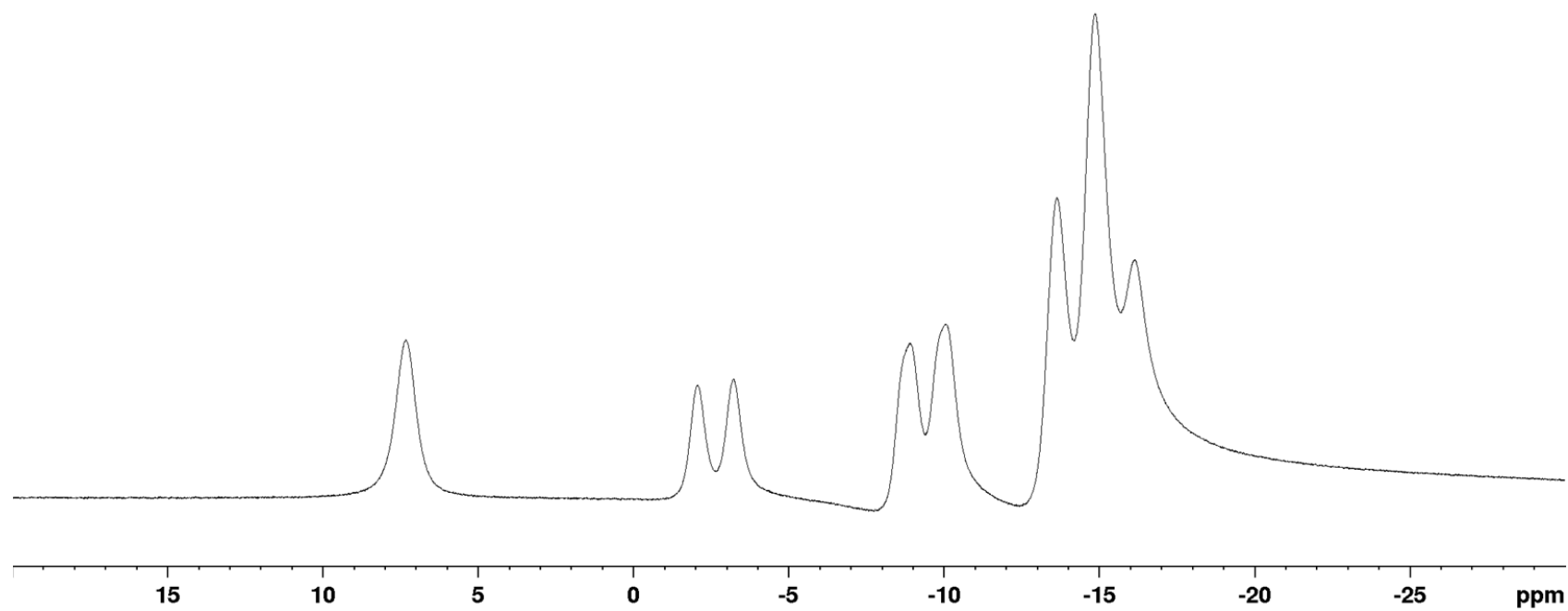
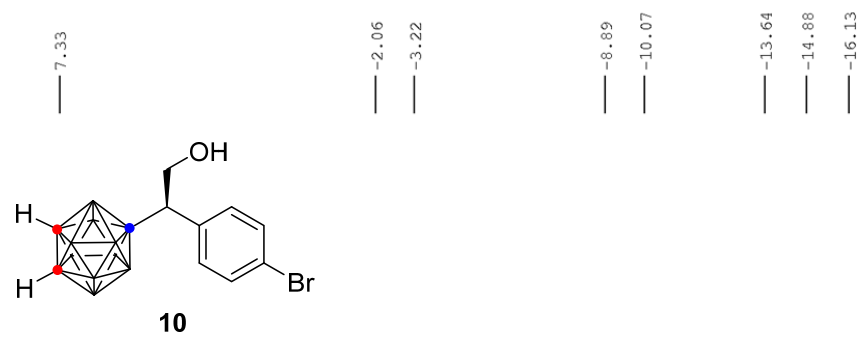
^1H NMR (400 MHz, CDCl_3)



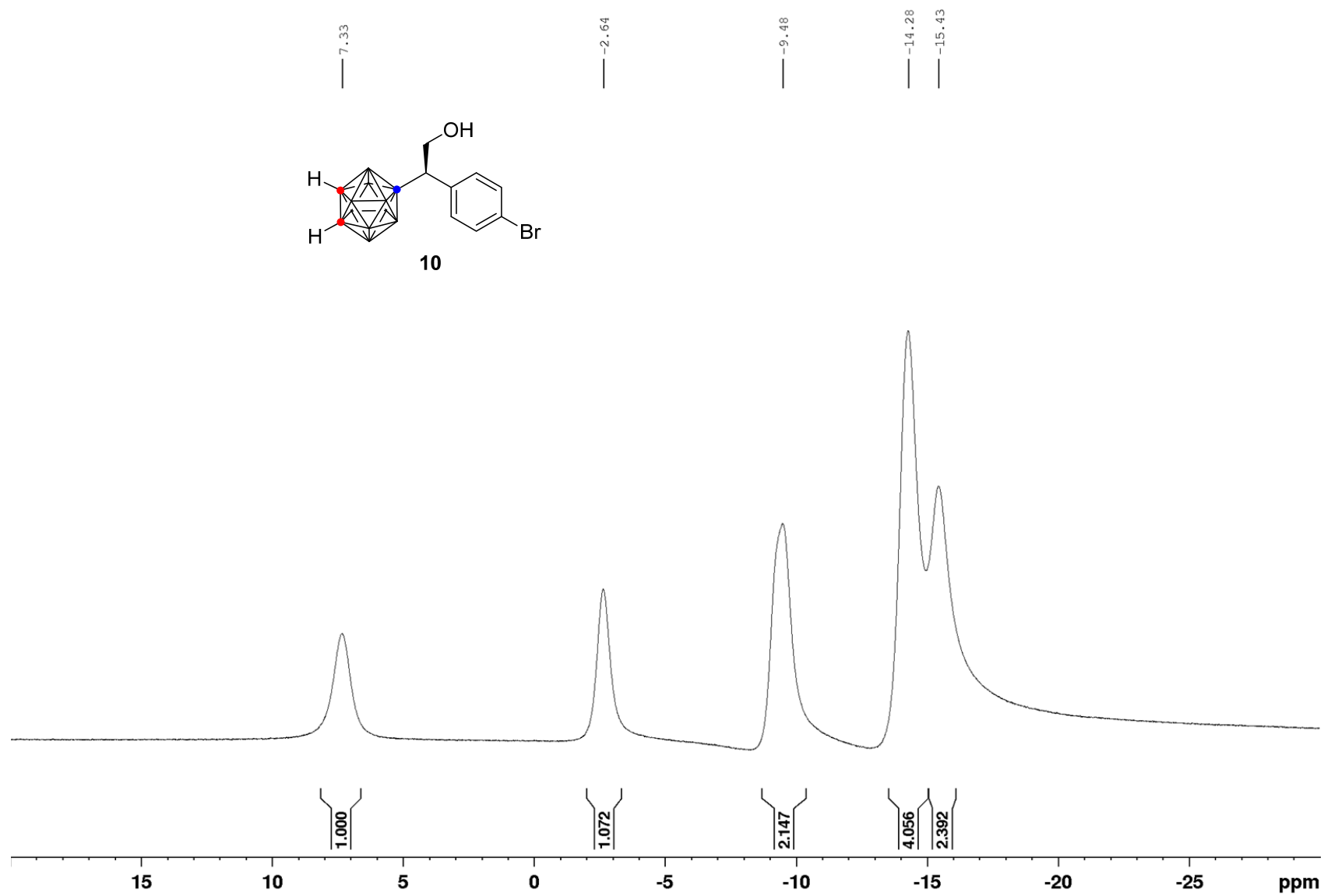
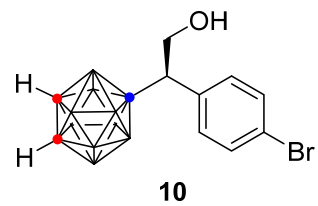
^{13}C NMR (100 MHz, CDCl_3)



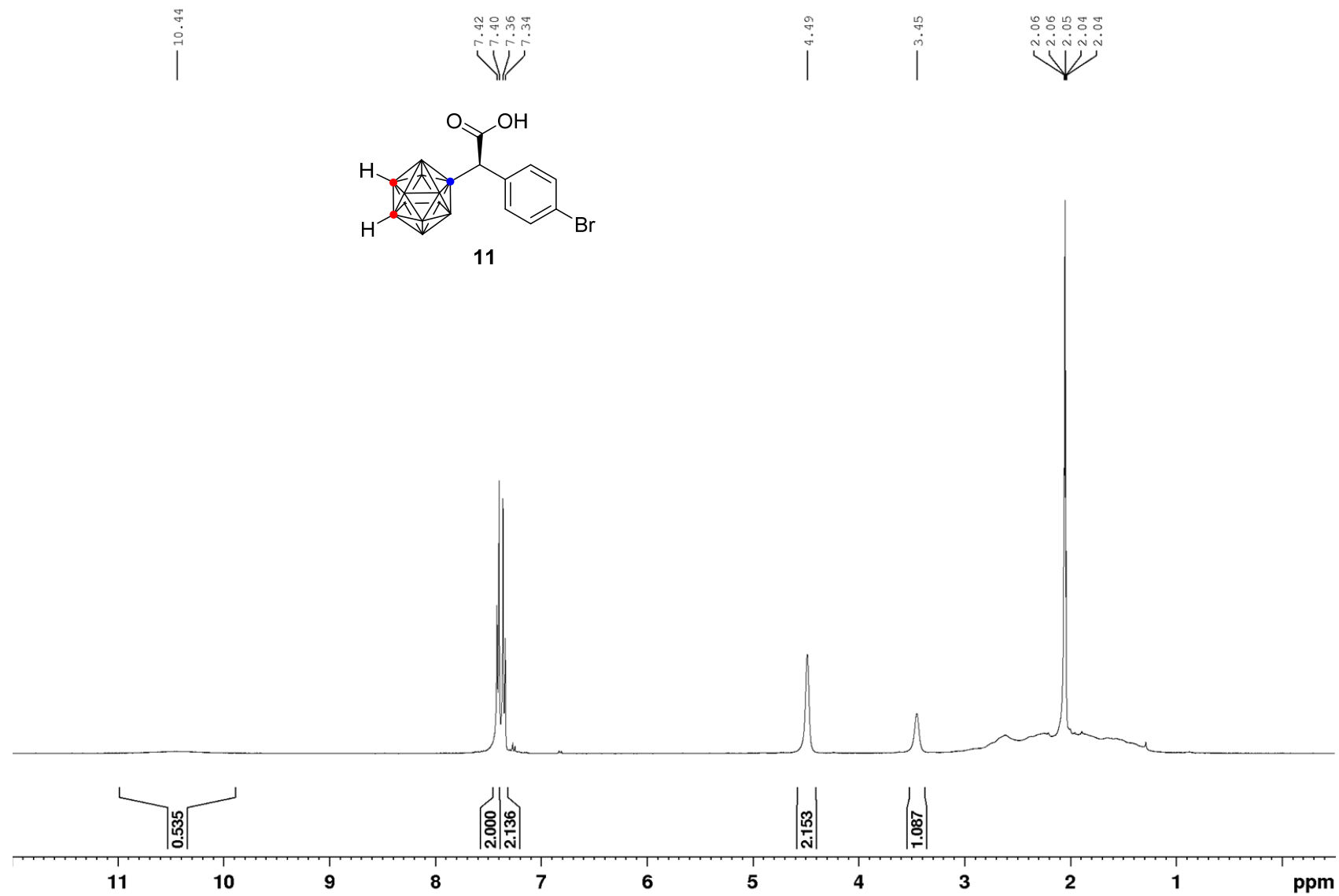
^{11}B NMR (128 MHz, CDCl_3)



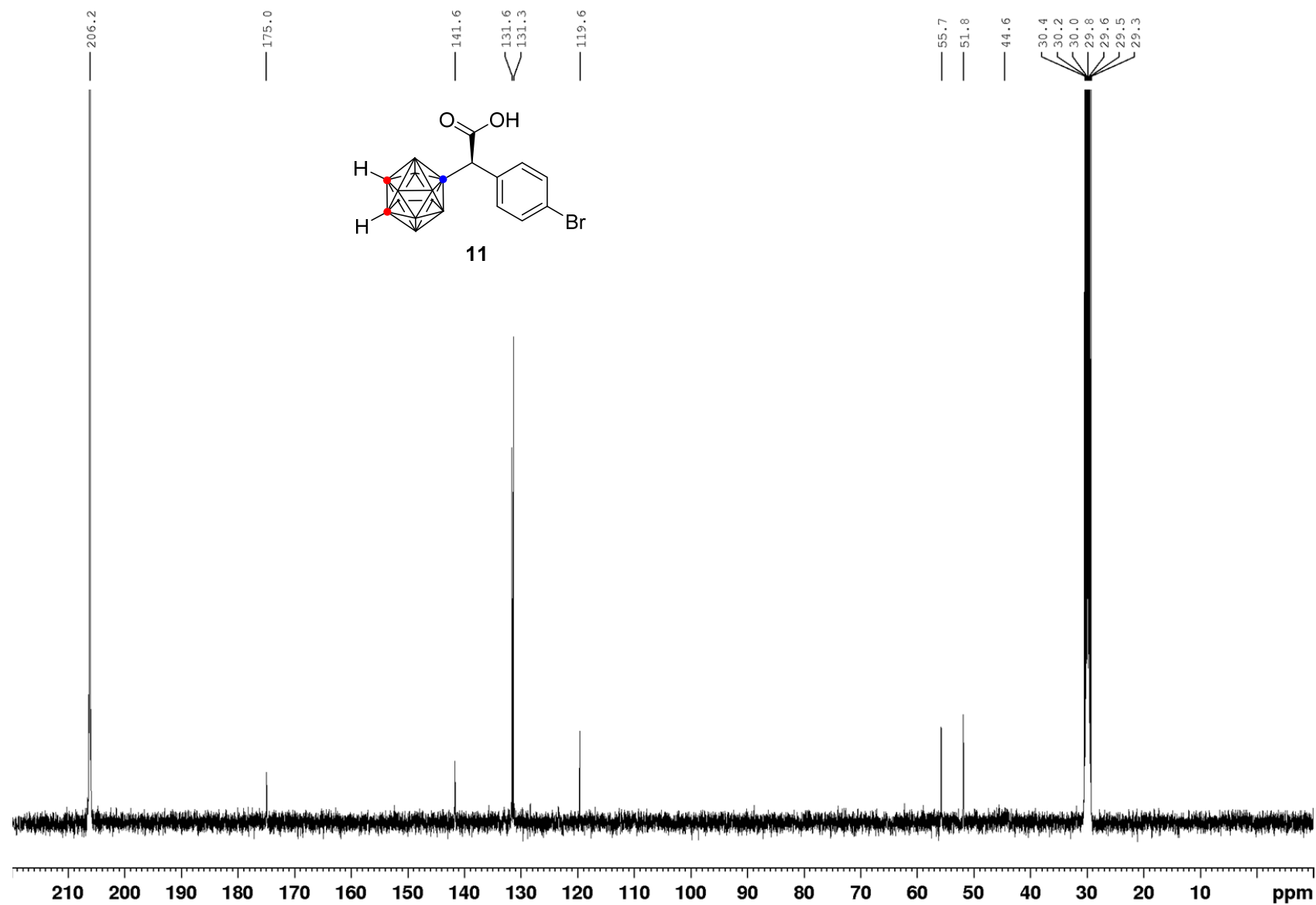
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



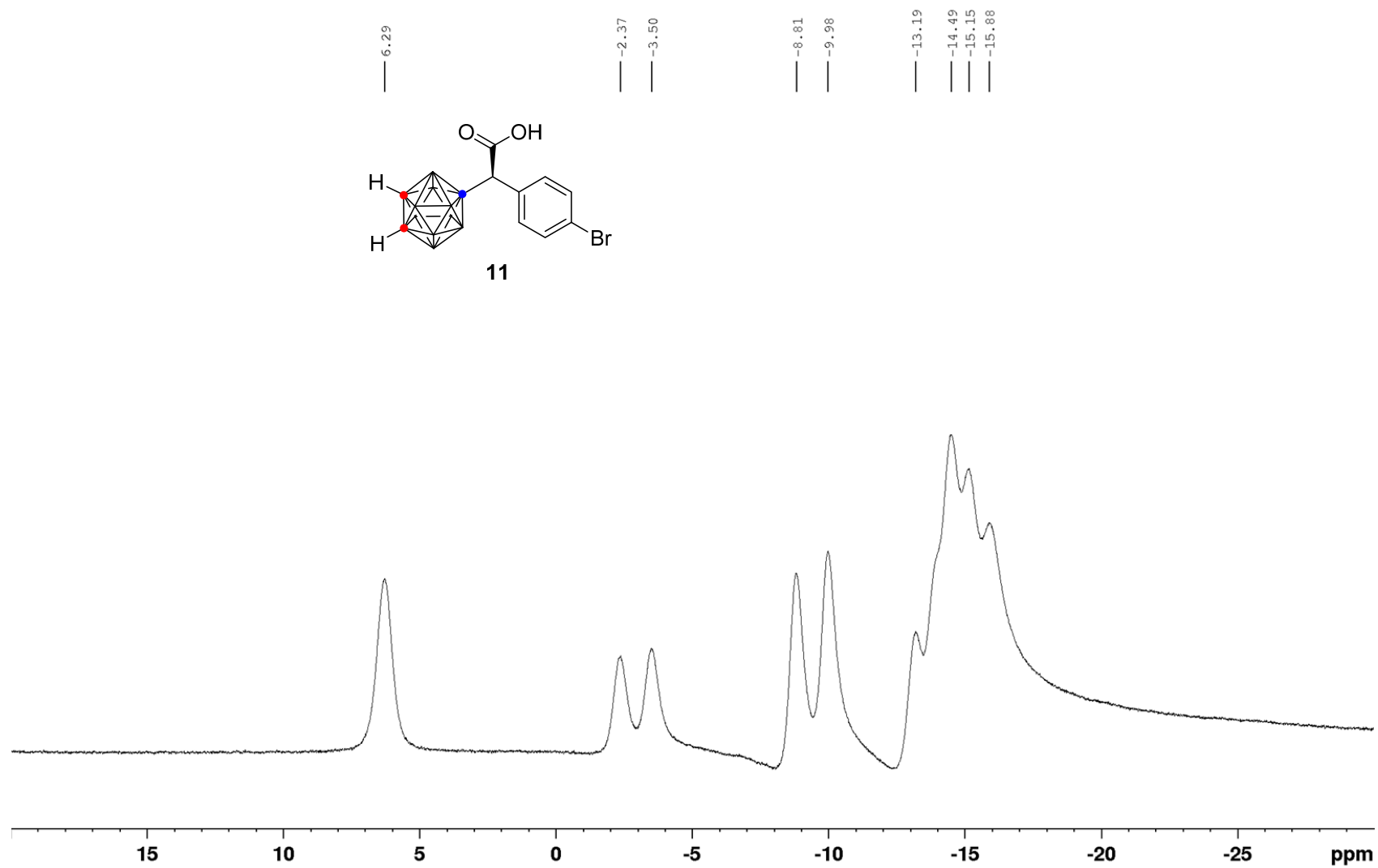
^1H NMR (400 MHz, acetone- d_6)



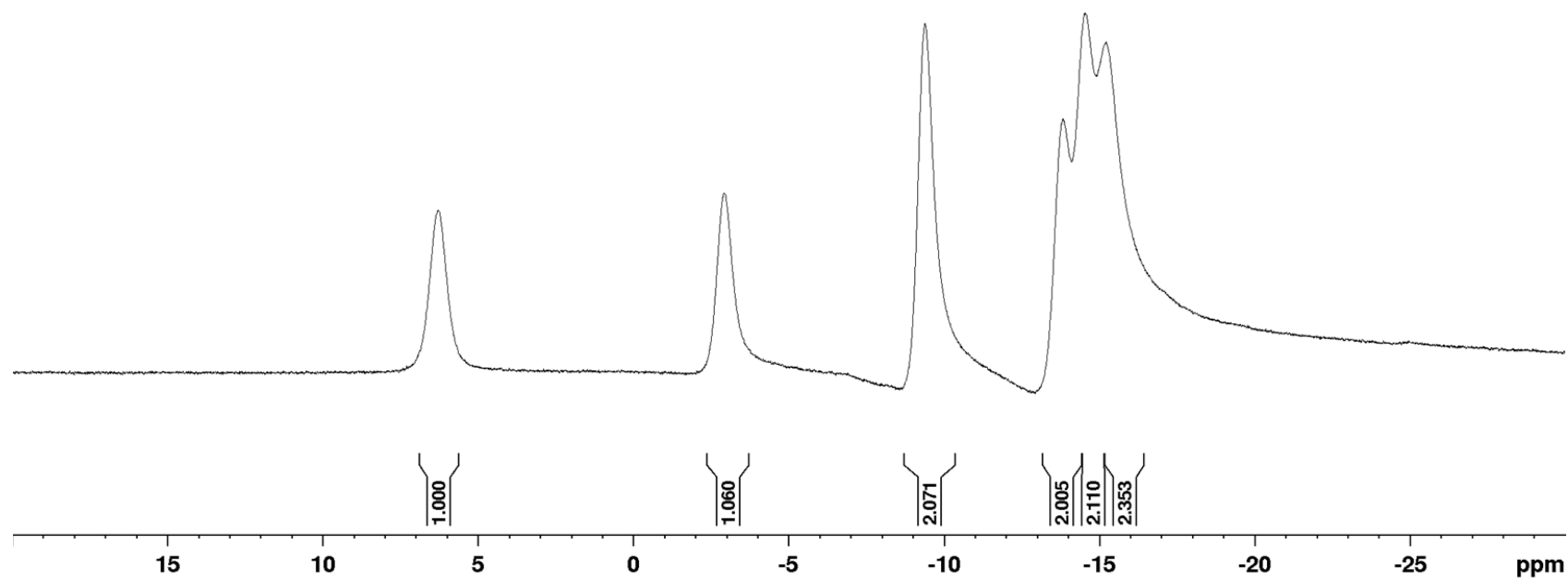
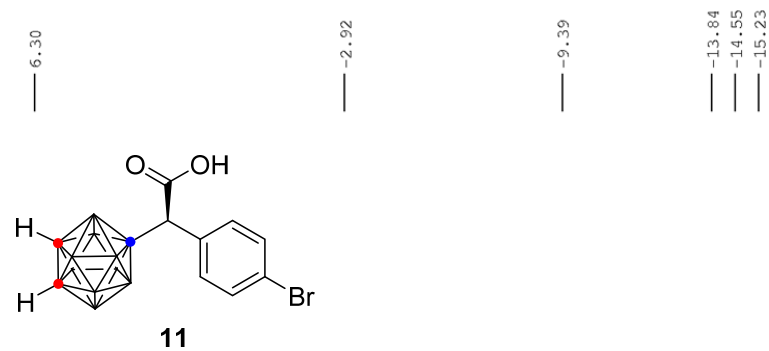
^{13}C NMR (100 MHz, acetone- d_6)



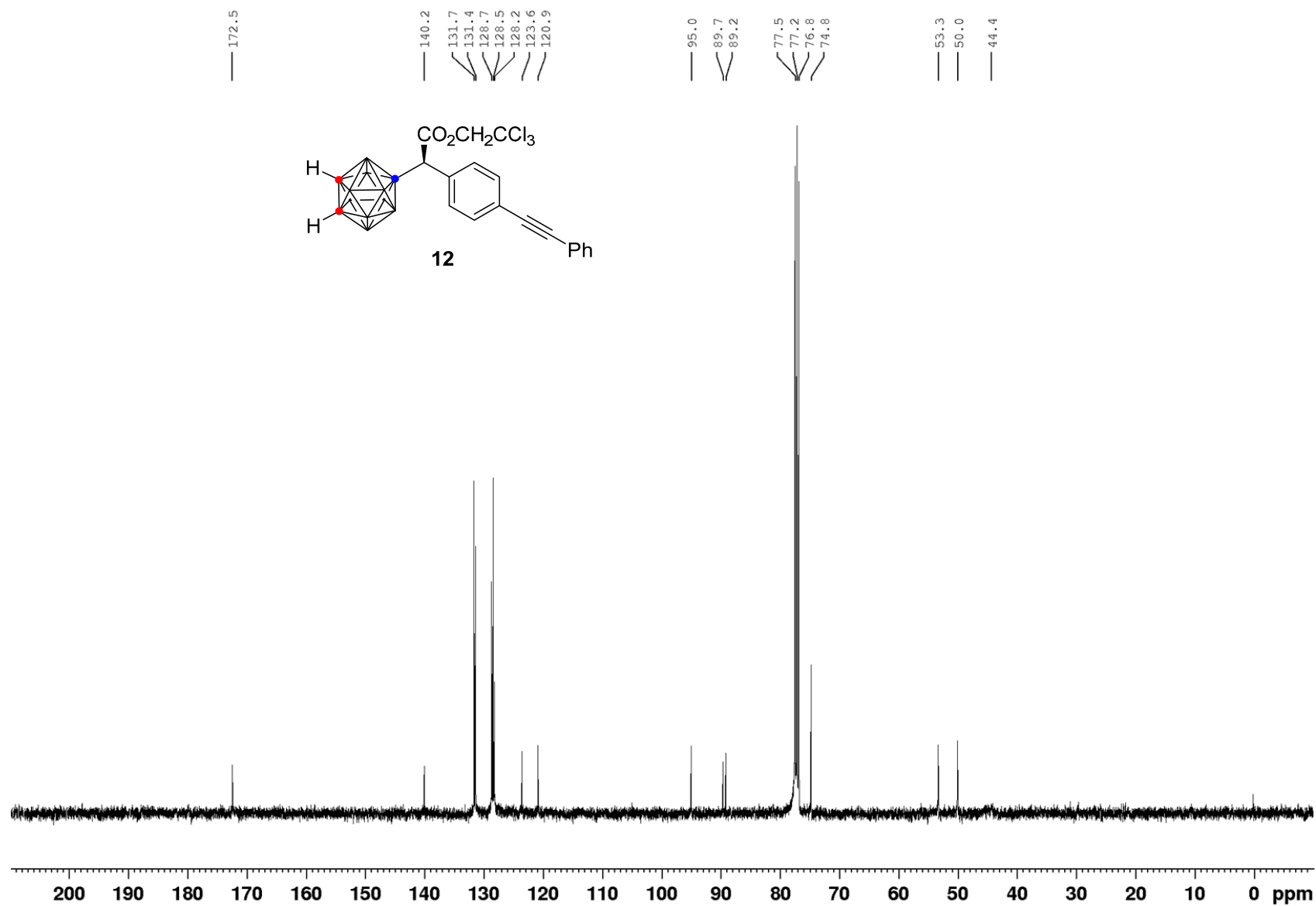
^{11}B NMR (128 MHz, acetone- d_6)



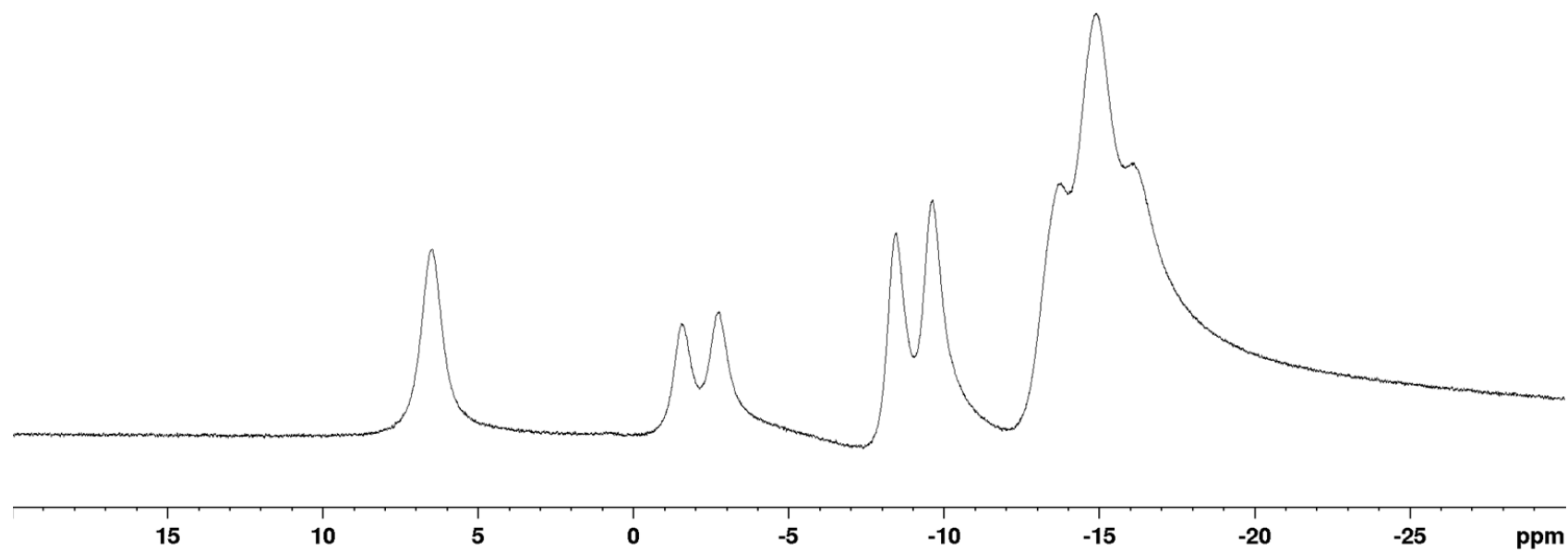
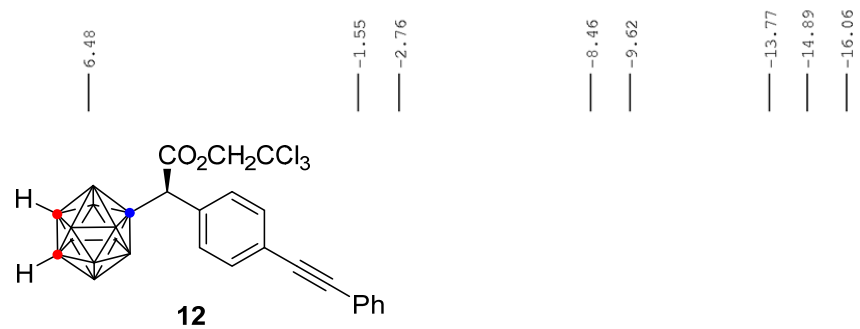
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, acetone- d_6)



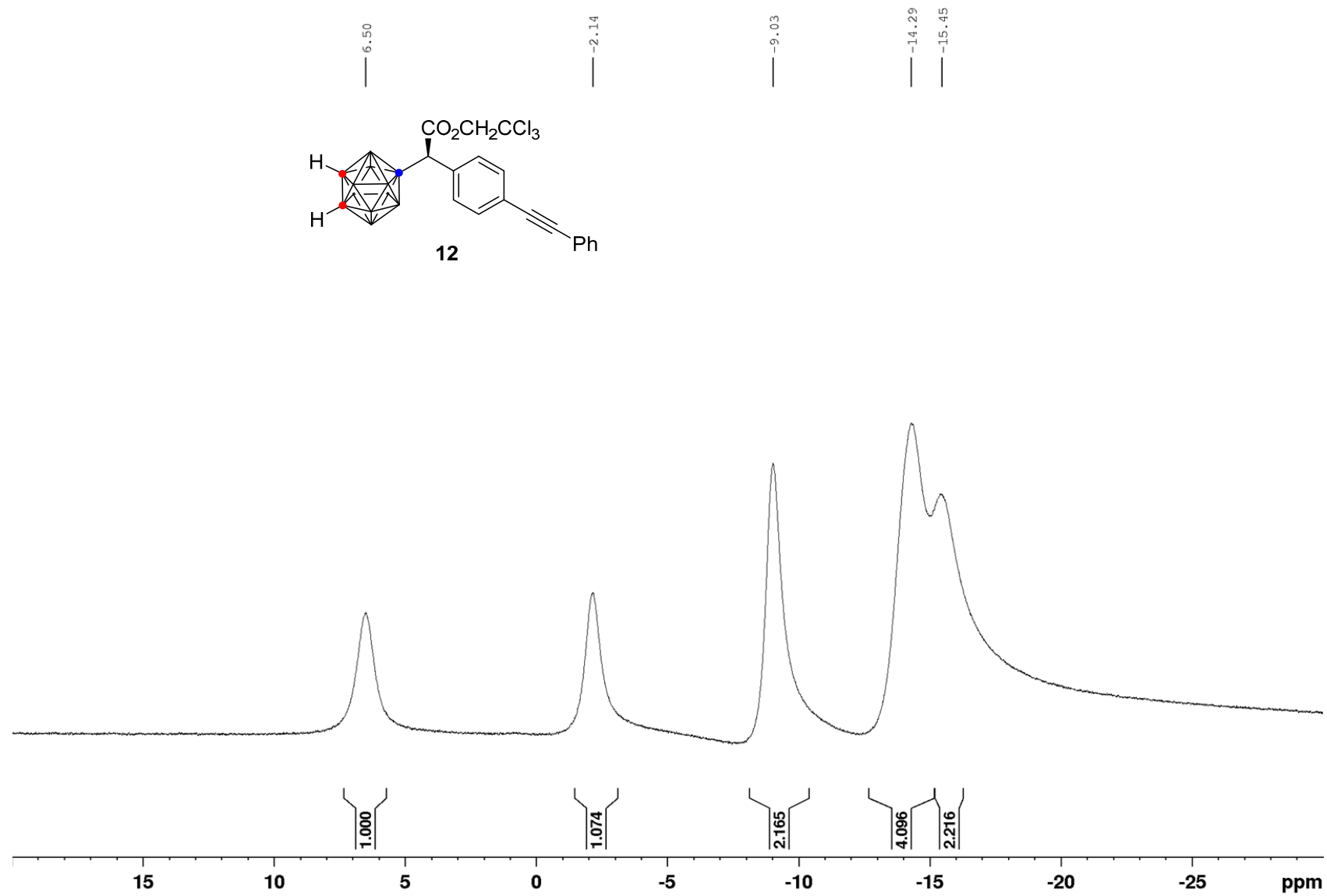
^{13}C NMR (100 MHz, CDCl_3)



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



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



^1H NMR (400 MHz, CDCl_3)

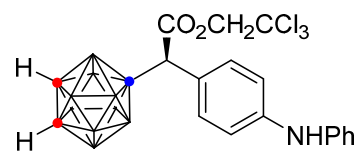
7.30
7.28
7.26
7.25
7.24
7.24
7.22
7.04
7.04
7.02
7.02
6.99
6.90
6.89
6.87

5.63

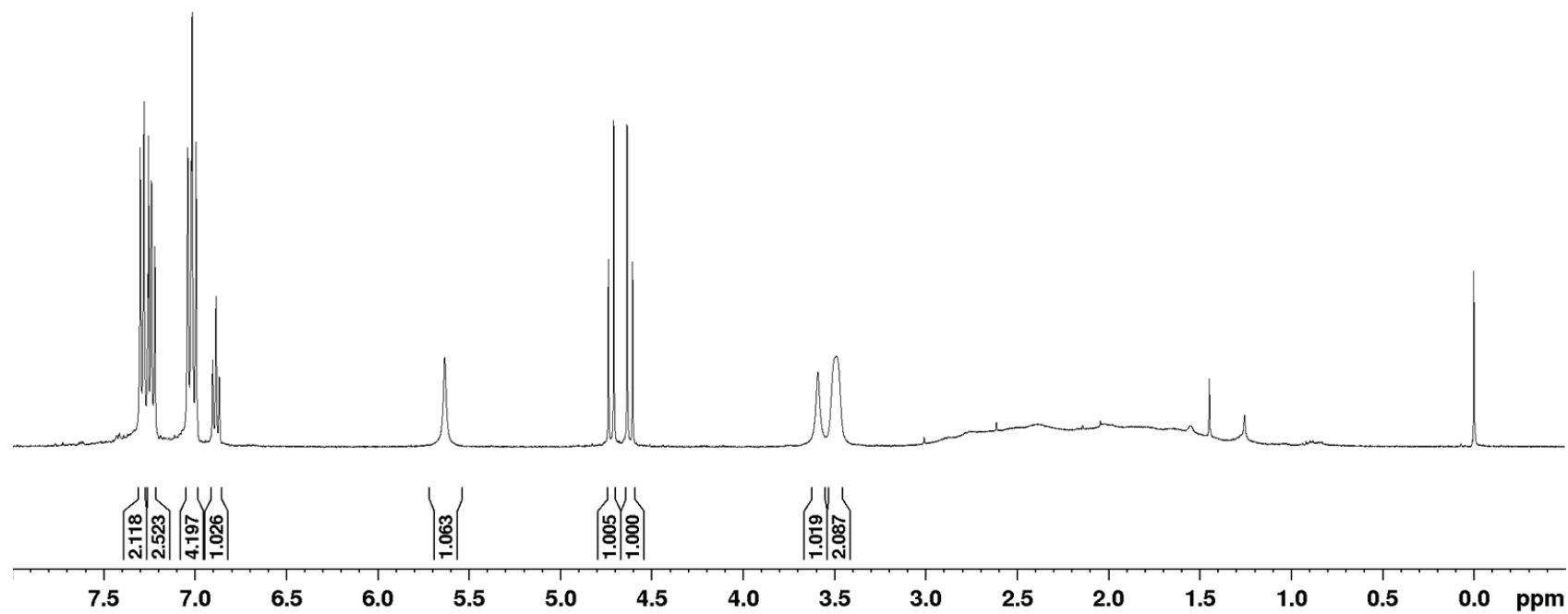
4.74
4.71
4.63
4.60

3.59
3.49

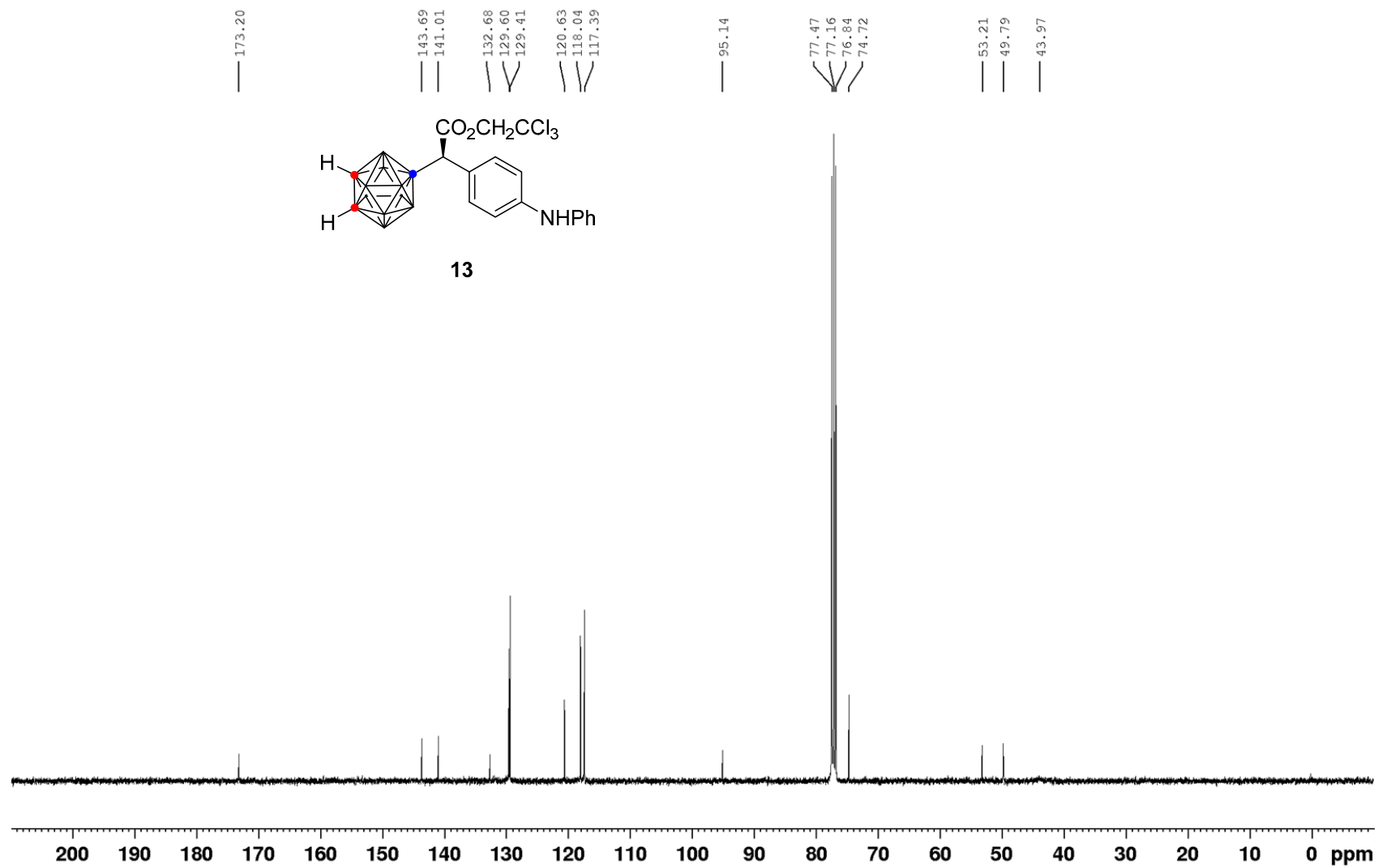
-0.00



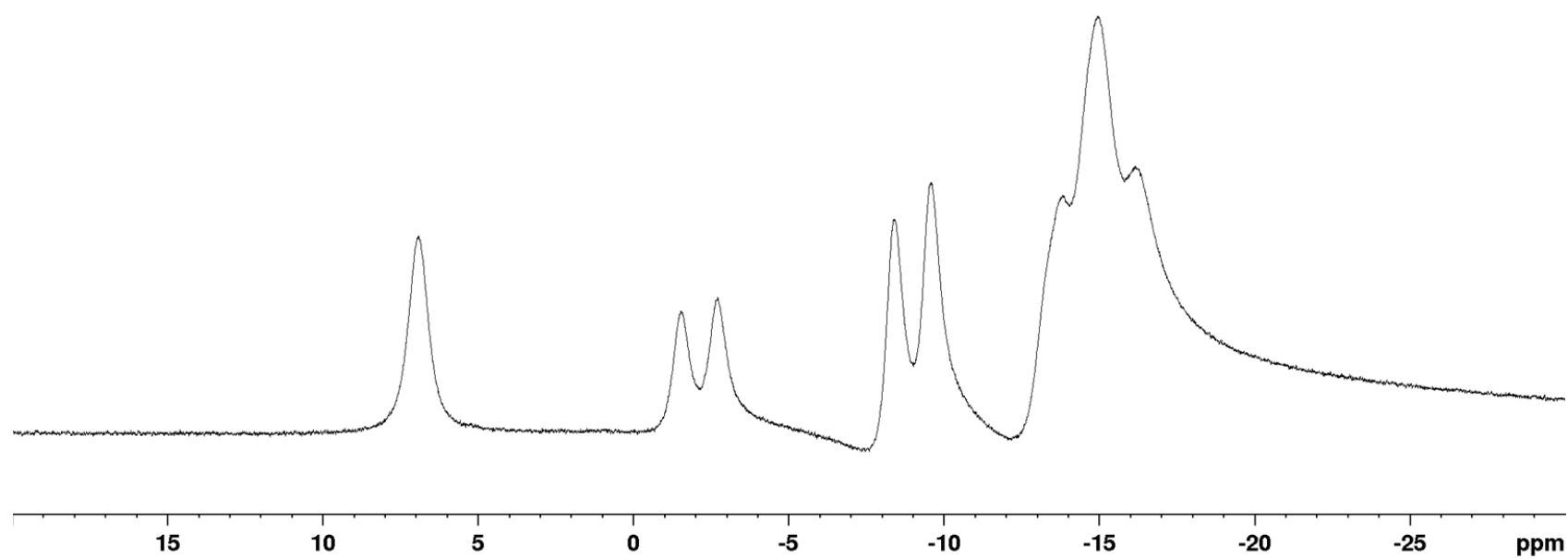
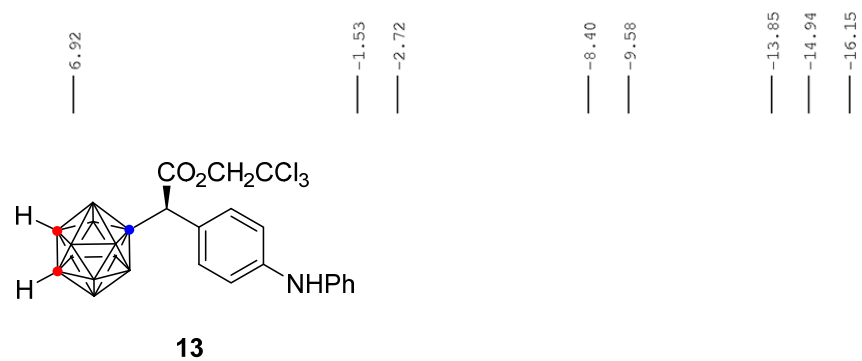
13



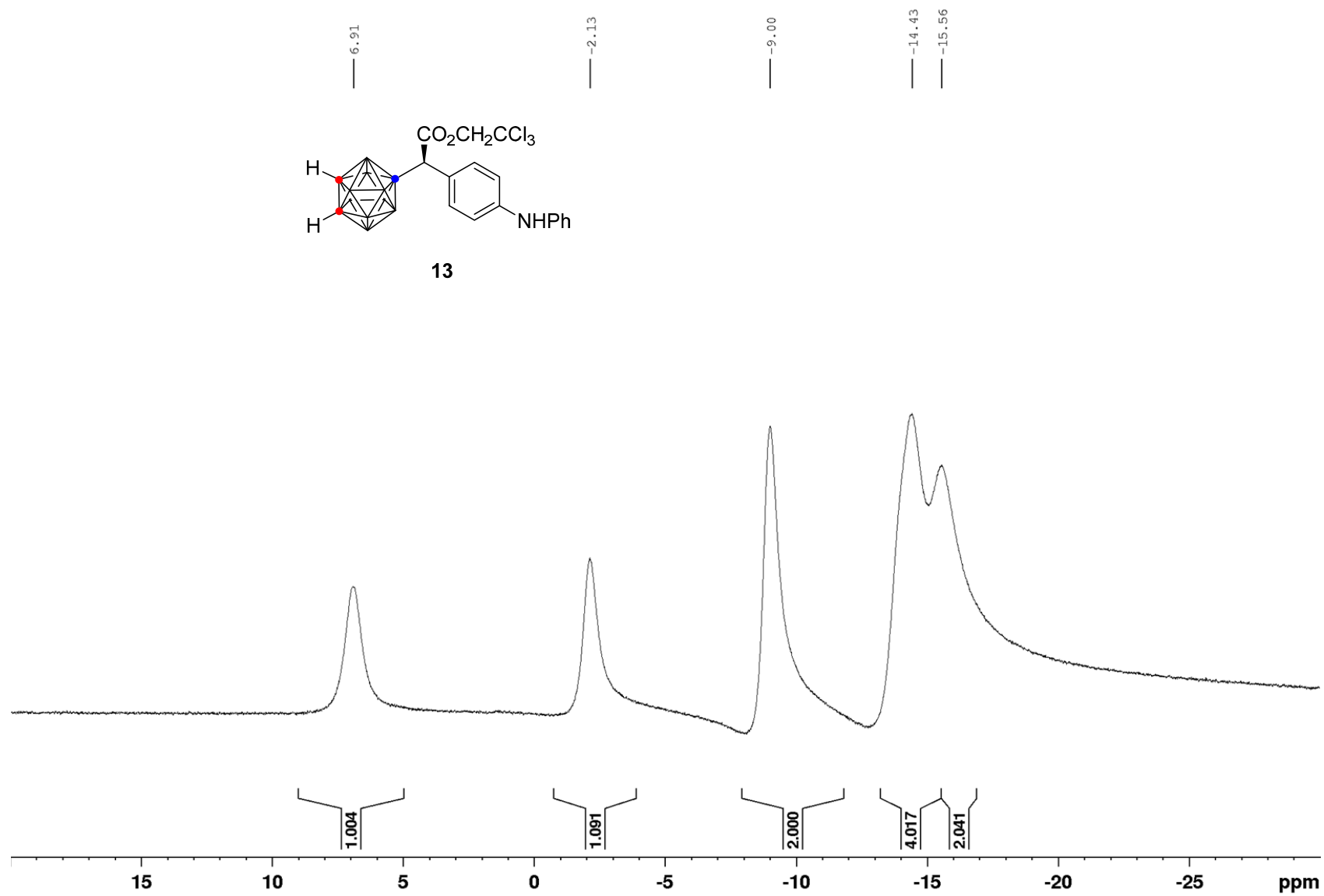
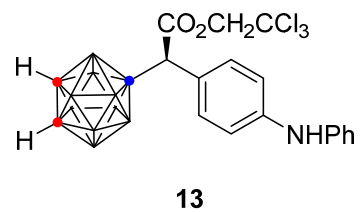
^{13}C NMR (100 MHz, CDCl_3)



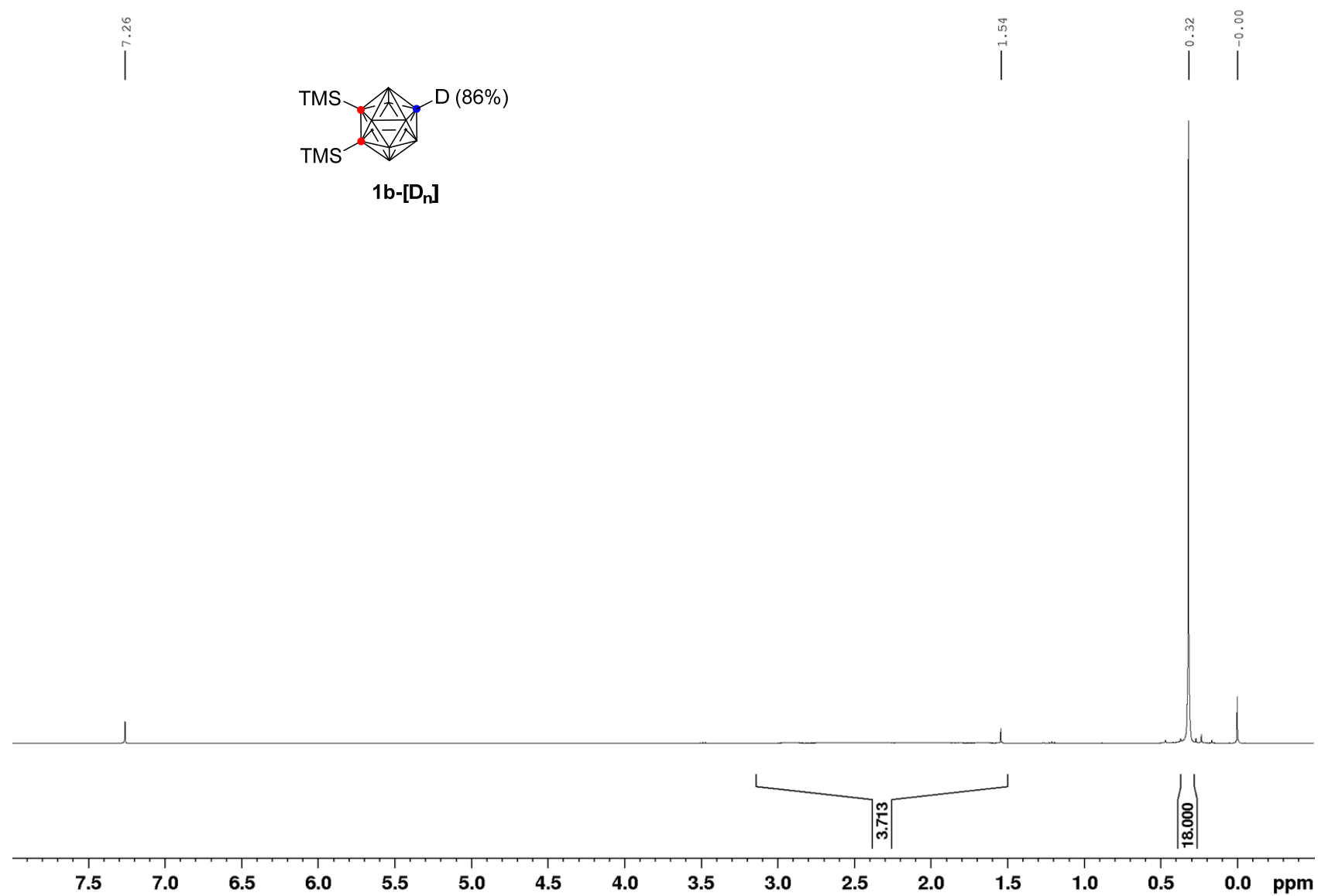
^{11}B NMR (128 MHz, CDCl_3)



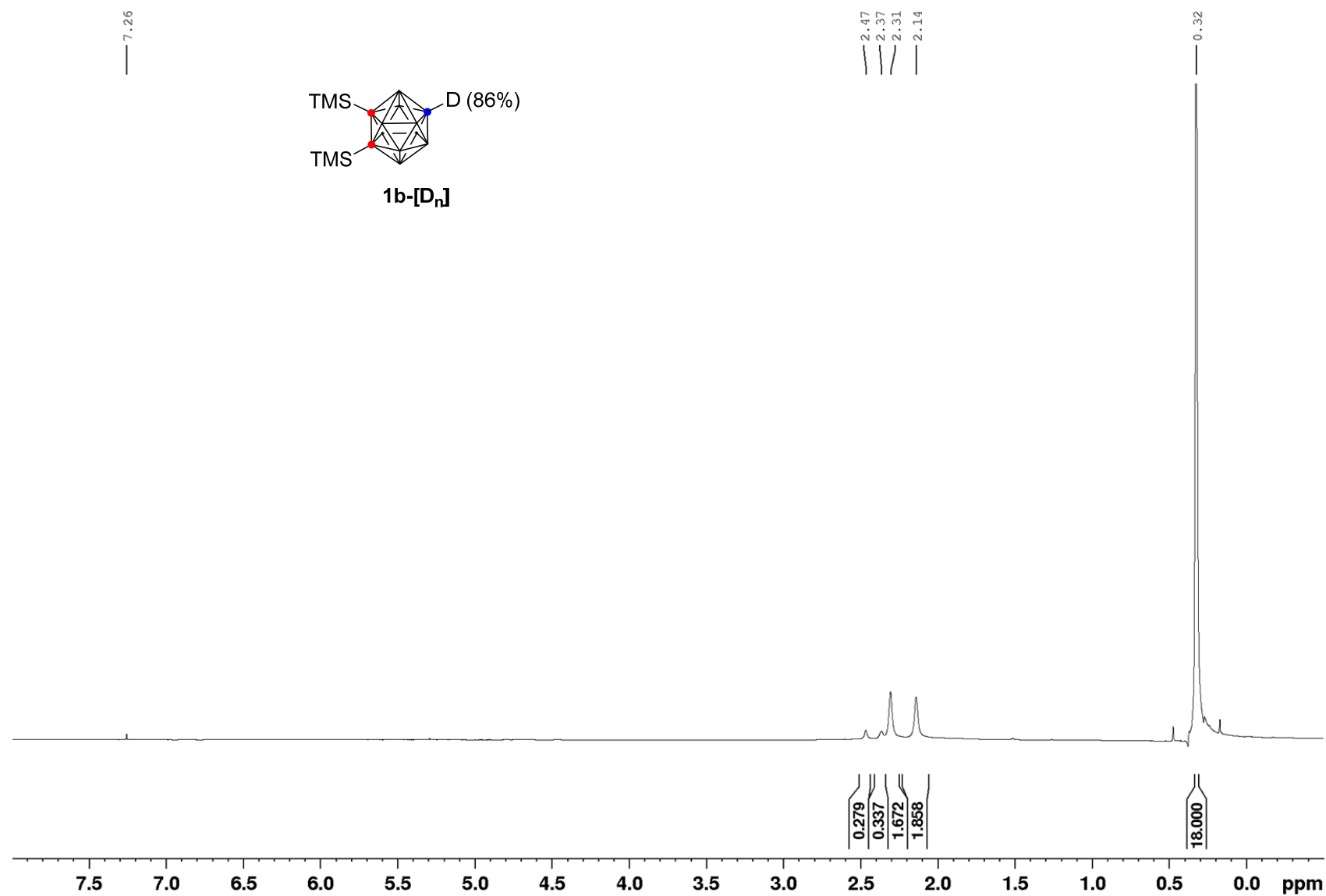
$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3)



^1H NMR (400 MHz, CDCl_3)



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



¹H NMR (400 MHz, CDCl₃)

