Supplementary Information

Nanoporous gold-catalyzed borylation of $C(sp^3)$–O bonds in dialkyl ethers and its mechanistic elucidation

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1. General Information

^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL JNM AL 400 (400 MHz) and JEOL JNM AL 600 (600 MHz) spectrometers. ^{1}H NMR spectra are reported as follows: chemical shifts are reported in ppm from the solvent resonance or tetramethylsilane (TMS) as the internal standard ($CDCl_3$: 7.26 ppm, TMS: 0.00ppm), multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, bs = broad singlet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on JEOL JNM AL 400 (100 MHz) spectrometer with complete proton decoupling, and chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm). High-resolution mass spectrometry data were obtained on a Bruker Daltonics SolariX spectrometer with dithranol (DIT) as the matrix and an FT-ICR-MS analyzer. Column chromatography was carried out employing silica gel 60 N (spherical, neutral, 40~100 μm, KANTO Chemical Co.) and Silica gel 60 (Merck). Gel permeation chromatography (GPC) was performed on JAI LaboACE LC7080 Plus with JAIGEL-2HR-40 ($CHCl_3$ as eluent). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F254 (Merck).

Materials

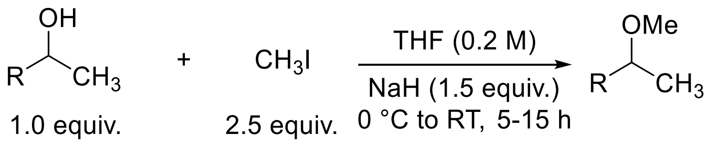
Unless otherwise noted, materials were purchased from Wako Pure Chemical Industries, Ltd., Tokyo Chemical Industry Co., LTD., Aldrich Inc., and other commercial suppliers and were used without purification. Toluene (Super dry solvent) was purchased from Wako Pure Chemical Industries. Dichloromethane, tetrahydrofuran and diethyl ether were supplied from Kanto Chemical Co., Inc. as "Dehydrated solvent system". Other solvents were purchased from commercial suppliers as dehydrated solvents, and used under nitrogen atmosphere. The epoxides (**3a**, **3g,** and **3i**), acetals (**7a** and **7b**), and B_2pin_2 were purchased and used as received. Other starting materials were prepared according to literature methods. Au (99.99%) and Ag (99.99%) are purchased from Tanaka Kikinzoku Hanbai K.K. and Mitsuwa's Pure Chemicals, respectively. The known starting ether substrates were prepared according to the reported literatures. The corresponding products **2**, **4**, **6** and **8** were characterized by ^{1}H NMR, ^{13}C NMR and/or HRMS and the known compounds were confirmed according to the reported literatures.

2. Fabrication of AuNPore catalyst[1]

Au/Ag alloy (30:70, in at.%) was fabricated by melting Au (99.99%) and Ag (99.99%) using electric arc-melting furnace under argon atmosphere, which was rolled down to thickness of 0.04 mm. The resulting foil was annealed at 850 ºC for 20 h. The foil was cut into small pieces (5 × 2 mm square). Treatment of the resulting chips (67.1 mg) with 70 wt% nitric acid (68 mL) for 18 h at room temperature in a shaking apparatus resulted in the formation of the nanoporous structure by selective leaching of silver. The material was washed with pure water and acetone successively. Drying of the material under reduced pressure gave the nanoporous gold (30.2 mg) with undetectable Ag component from energy dispersive X-ray spectroscopy (EDX) analysis.

3. Synthesis of starting ether and acetal substrates, and analytic data

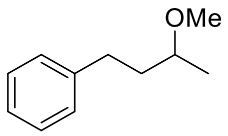
3.1 Synthetic procedure of alkyl methyl ethers 1 and analytic data



To a stirring suspension of NaH (7.5 mmol, 1.5 equiv.) in THF (0.2 M) was added the alcohol substrates (5 mmol, 1.0 equiv) at 0 °C. After 5 min, MeI (12.5 mmol, 2.5 equiv.) was added one portion at 0 °C, then the reaction was warmed to room temperature and stirred until completion of the reaction. Upon completion, the mixture was cooled to 0 °C and quenched by the dropwise addition of a saturated aqueous solution of NH_4Cl (caution: H_2 evolution). The aqueous layer was extracted with ethyl acetate (3×20 mL), and the combined organic layers were dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture was purified by flash chromatography to give the desired product ethers.[2]

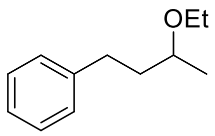
Analytic data of 1

(3-Methoxybutyl)benzene (**1a**)[3]



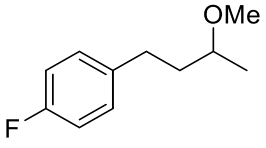
Colorless oil; yield 67%, 0.55 g (3.35 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.25 (m, 2H), 7.20–7.15 (m, 3H), 3.35–3.25 (m, 4H), 2.72–2.63 (m, 2H), 1.90–1.78 (m, 1H), 1.76–1.65 (m, 1H), 1.16 (d, J = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.33, 128.39, 128.28, 125.65, 75.89, 55.91, 38.14, 31.67, 18.94.

(3-Ethoxybutyl)benzene (**1a'**)[4]



Colorless oil; yield 70%, 0.62 g (3.23 mmol); prepared using EtI instead of using MeI, Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.20 (m, 2H), 7.18–7.13 (m, 3H), 3.58–3.50 (m, 1H), 3.42–3.32 (m, 2H), 2.77–2.59 (m, 2H), 1.89–1.79 (m, 1H), 1.73–1.64 (m, 1H), 1.20 (t, J = 7.0 Hz, 3H), 1.15 (d, J = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.32, 128.31, 128.17, 125.54, 74.14, 63.47, 38.34, 31.73, 19.64, 15.57.

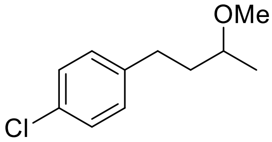
1-Fluoro-4-(3-methoxybutyl)benzene (**1b**)[5]



Colorless oil; yield 65%, 0.59 g (3.01 mmol); Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15–7.13 (m, 2H), 6.98–6.93 (m, 2H), 3.32 (s, 3H), 3.30–3.24 (m, 1H), 2.74–2.56

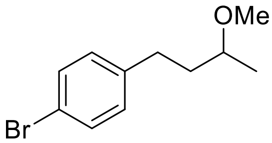
(m, 2H), 1.85–1.75 (m, 1H), 1.74–1.61 (m, 1H), 1.16 (d, J = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.15 (d, $^1J_{CF}$ = 244 Hz), 137.90 (d, $^4J_{CF}$ = 3.36 Hz), 129.67 (d, $^3J_{CF}$ = 7.74 Hz), 114.98 (d, $^2J_{CF}$ = 21.2 Hz), 75.75, 55.93, 38.33, 30.85, 18.90.

1-Chloro-4-(3-methoxybutyl)benzene (**1c**)



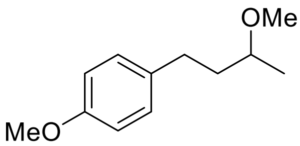
Colorless oil; yield 55%, 0.54 g (2.55 mmol); Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.19 (m, 2H), 7.12–7.08 (m, 2H), 3.31 (s, 3H), 3.29–3.23 (m, 1H), 2.74–2.55 (m, 2H), 1.84–1.77 (m, 1H), 1.72–1.61 (m, 1H), 1.14 (d, J = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.72, 131.31, 129.69, 128.31, 75.63, 55.86, 38.07, 30.97, 18.83. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{11}H_{15}ClNaO$: 221.0703, found: 221.0703.

1-Bromo-4-(3-methoxybutyl)benzene (**1d**)



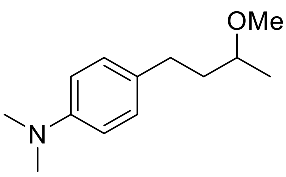
Colorless oil; yield 60%, 0.73 g (2.91 mmol); Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.35 (m, 2H), 7.08–7.02 (m, 2H), 3.31 (s, 3H), 3.30–3.22 (m, 1H), 2.72–2.54 (m, 2H), 1.84–1.73 (m, 1H), 1.72–1.60 (m, 1H), 1.15 (d, J = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.24, 131.27, 130.13, 75.63, 55.90, 37.99, 31.04, 18.86. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{11}H_{15}BrNaO$: 265.0198, found: 265.0198.

1-Methoxy-4-(3-methoxybutyl)benzene (**1e**)[6]



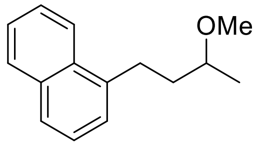
Colorless oil; yield 70%, 0.68 g (3.26 mmol); Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 3.76 (s, 3H), 3.32 (s, 4H), 2.71–2.52 (m, 2H), 1.85–1.76 (m, 1H), 1.71–1.60 (m, 1H), 1.15 (d, J = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.57, 134.26, 129.16, 113.61, 75.79, 55.81, 55.07, 38.34, 30.66, 18.85.

4-(3-Methoxybutyl)-*N*,*N*-dimethylaniline (**1f**)



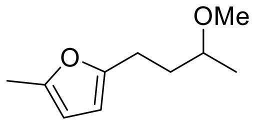
Colorless oil; yield 20%, 0.21 g (0.95 mmol);[7] Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, J = 8.3 Hz, 2H), 6.75 (d, J = 8.6 Hz, 2H), 3.39–3.32 (m, 4H), 2.96 (s, 6H), 2.72–2.59 (m, 2H), 1.94–1.84 (m, 1H), 1.78–1.65 (m, 1H), 1.22 (d, J = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.81, 130.31, 128.82, 112.86, 75.84, 55.75, 40.74, 38.33, 30.47, 18.85. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{13}H_{21}NaO$: 230.1515, found: 230.1515.

1-(3-Methoxybutyl)naphthalene (**1g**)



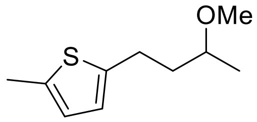
Colorless oil; yield 45%, 0.53 g (2.32 mmol); Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.66–7.55 (m, 2H), 7.55–7.43 (m, 2H), 3.53–3.49 (m, 4H), 3.40–3.30 (m, 1H), 3.26–3.17 (m, 1H), 2.14–2.03 (m, 1H), 2.01–1.92 (m, 1H), 1.31 (d, J = 6.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 13C NMR (100 MHz, $CDCl_3$) δ 138.39, 133.77, 131.78, 128.60, 126.39, 125.80, 125.59, 125.40, 125.25, 123.73, 75.99, 55.86, 37.47, 28.61, 18.82. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{15}H_{18}NaO$: 237.1249, found: 237.1250.

2-(3-Methoxybutyl)-5-methylfuran (**1h**)



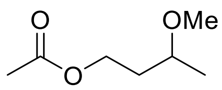
Colorless oil; yield 70%, 0.59 g (3.24 mmol);[8] Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84–5.82(m, 2H), 3.35–3.28 (m, 4H), 2.71–2.55 (m, 2H), 2.24 (s, 3H), 1.87–1.67 (m, 2H), 1.15 (d, J = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.06, 150.05, 105.66, 105.21, 75.76, 55.89, 34.69, 23.92, 18.80, 13.37. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{10}H_{16}NaO_2$: 191.1042, found: 191.1042.

2-(3-Methoxybutyl)-5-methylthiophene (**1i**)



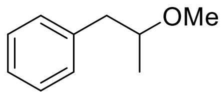
Colorless oil; yield 60%, 0.55 g (2.78 mmol);[8] Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57–6.51 (m, 2H), 3.32 (s, 4H), 2.88–2.75 (m, 2H), 2.42 (s, 3H), 1.92–1.78 (m, 1H), 1.78–1.65 (m, 1H), 1.15 (d, J = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.90, 137.17, 124.55, 123.74, 75.57, 55.97, 38.36, 25.94, 18.87, 15.22. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{10}H_{16}NaOS$: 207.0814, found: 207.0814.

3-Methoxybutyl acetate (**1j**)



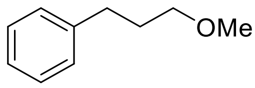
Colorless oil; yield 85%, 0.62 g (3.88 mmol);[9] Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19–4.11 (m, 2H), 3.48–3.35 (m, 1H), 3.32 (s, 3H), 2.05 (s, 3H), 1.88–1.68 (m, 2H), 1.17 (d, J = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.04, 73.62, 61.43, 56.03, 35.44, 20.92, 19.00. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_7H_{14}NaO_3$: 169.0835, found: 169.0835.

(2-Methoxypropyl)benzene (**1k**)[10]



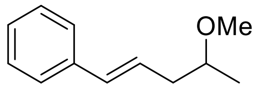
Colorless oil; yield 75%, 0.56 g (3.4 mmol); Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.22 (m, 2H), 7.21–7.14 (m, 3H), 3.55–3.47 (m, 1H), 3.31 (s, 3H), 2.93–2.88 (m, 1H), 2.61–2.58 (m, 1H), 1.11 (d, J = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.88, 129.30, 128.12, 125.96, 76.68, 42.62, 18.79.

(3-Methoxypropyl)benzene (**1m**)[11]



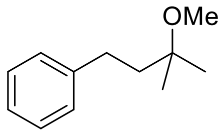
Colorless oil; yield 65%, 0.49 g (3.27 mmol); Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.26 (m, 2H), 7.22–7.15 (m, 3H), 3.38 (t, J = 6.4 Hz, 2H), 3.33 (s, 3H), 2.73–2.64 (m, 2H), 1.93–1.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.94, 128.43, 128.29, 125.74, 71.88, 58.52, 32.28, 31.23.

(*E*)-(4-Methoxypent-1-en-1-yl)benzene (**1l**)



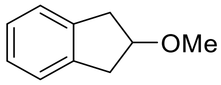
Colorless oil; yield 60%, 0.53 g (3.01 mmol);[12] Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.32 (m, 2H), 7.28 (dd, J = 8.3, 6.9 Hz, 2H), 7.22–7.16 (m, 1H), 6.43 (d, J = 15.9 Hz, 1H), 6.22 (dt, J = 15.8, 7.2 Hz, 1H), 3.47–3.39 (m, 1H), 3.36 (s, 3H), 2.51–2.41 (m, 1H), 2.38–2.28 (m, 1H), 1.18 (d, J = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.55, 131.96, 128.42, 126.96, 126.64, 125.98, 76.62, 56.11, 39.69, 19.00. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{12}H_{16}NaO$: 199.1093, found: 199.1093.

(3-Methoxy-3-methylbutyl)benzene (**1n**)[3]



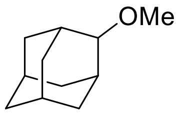
Colorless oil; yield 62%, 0.55 g (2.86 mmol);[13] Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.25 (m, 2H), 7. 20–7.14 (m, 3H), 3.22 (s, 3H), 2.68–2.58 (m, 2H), 1.84–1.71 (m, 2H), 1.21 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.79, 128.28, 128.21, 125.57, 125.57, 74.27, 49.09, 41.64, 30.20, 25.02.

2-Methoxy-2,3-dihydro-1H-indene (**1o**)[3]



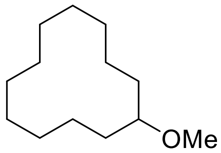
Colorless oil; yield 72%, 0.53 g (3.58 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.18 (dd, J = 5.3, 3.5 Hz, 2H), 7.17–7.11 (m, 2H), 4.26–4.21 (m, 1H), 3.37 (s, 3H), 3.17–3.12 (m, 2H), 3.00–2.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.78, 126.48, 124.66, 81.84, 56.54, 38.93.

(*1r,3r,5r,7r*)-2-Methoxyadamantane (**1p**)[3]



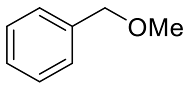
Colorless oil; yield 79%, 0.66 g (4.13 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.36–3.31 (m, 4H), 2.03 (d, J = 12.8 Hz, 4H), 1.89–1.74 (m, 4H), 1.74–1.60 (m, 4H), 1.47 (d, J = 12.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 83.21, 55.23, 37.56, 36.46, 31.40, 31.28, 27.43, 27.39.

Methoxycyclododecane (**1q**)[14]



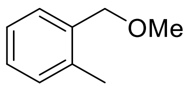
Colorless oil; yield 66%, 0.65 g (3.28 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.33–3.28 (m, 4H), 1.65–1.57 (m, 2H), 1.50–1.44 (m, 2H), 1.43–1.27 (m, 19H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 78.77, 56.13, 28.31, 24.83, 24.39, 23.09, 22.99, 20.52.

(Methoxymethyl)benzene (**1r**)[15]



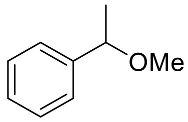
Colorless oil; yield 86%, 0.52 g (4.26 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.23 (m, 5H), 4.43 (s, 2H), 3.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.07, 128.25, 127.59, 127.51, 74.56, 57.92.

1-(Methoxymethyl)-2-methylbenzene (**1s**)[16]



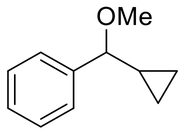
Colorless oil; yield 75%, 0.51 g (3.75 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 7.2 Hz, 1H), 7.22–7.12 (m, 3H), 4.44 (s, 2H), 3.38 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.54, 136.00, 130.14, 128.45, 127.73, 125.68, 72.97, 58.07, 18.63.

(1-Methoxyethyl)benzene (**1t**)[16]



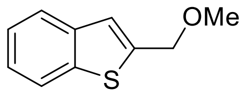
Colorless oil; yield 76%, 0.52 g (3.75 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.23 (m, 5H), 4.28 (q, *J* = 6.5 Hz, 1H), 3.21 (s, 3H), 1.43 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.45, 128.35, 127.37, 126.10, 79.56, 56.32, 23.82.

(Cyclopropyl(methoxy)methyl)benzene (**1u**)



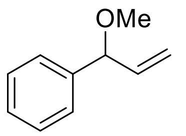
Colorless oil; yield 50%, 0.41 g (2.53 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.20 (m, 2H), 7.17–7.11 (m, 1H), 7.09–7.03 (m, 2H), 3.46–3.32 (m, 5H), 1.83–1.78 (m, 1H), 1.46–1.36 (m, 1H), 1.00–0.90 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.51, 128.25, 125.78, 125.52, 76.00, 58.32, 22.38, 21.35, 13.95. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{11}H_{14}NaO$: 185.0936, found: 185.0936.

2-(Methoxymethyl)benzo[b]thiophene (**1v**)[17]



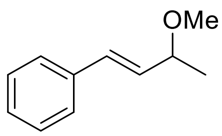
Colorless oil; yield 65%, 0.58 g (3.26 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.35–7.23 (m, 2H), 7.18 (s, 1H), 4.69 (s, 2H), 3.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.95, 140.15, 139.37, 124.18, 124.16, 123.40, 122.53, 122.35, 69.71, 57.92.

(1-Methoxyallyl)benzene (**1w**)[18]



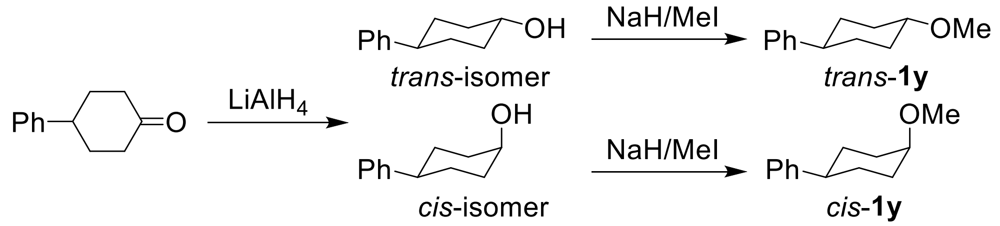
Colorless oil; yield 55%, 0.41 g (2.77 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.25 (m, 5H), 5.97–5.90 (m, 1H), 5.31–5.17 (m, 2H), 4.62 (d, *J* = 6.7 Hz, 1H), 3.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.84, 138.73, 128.44, 127.64, 126.79, 116.32, 84.70, 56.37.

(*E*)-(3-Methoxybut-1-en-1-yl)benzene **1x**[19]



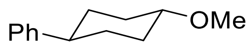
Colorless oil; yield 70%, 0.58 g (3.58 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, CDCl3) δ 7.37 (d, J = 7.4 Hz, 2H), 7.31–7.27 (m, 2H), 7.23–7.19 (m, 1H), 6.51 (d, J = 16.0 Hz, 1H), 6.07 (dd, J = 15.9, 7.6 Hz, 1H), 3.91–3.77 (m, 1H), 3.30 (s, 3H), 1.32 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.46, 131.25, 131.21, 128.41, 127.49, 126.29, 77.93, 55.84, 21.33.

Synthesis of *trans*-1y and *cis*-1y[20]



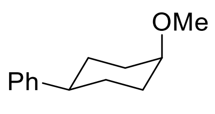
To a suspension of $LiAlH_4$ (0.95 g, 25 mmol, 1 equiv) in Et_2O (25 mL), 4-phenylcyclohexanone (4.36 g, 25 mmol) in Et_2O (40 mL) was added dropwise. The reaction was stirred for 30 min at rt. After dilution with Et_2O (30 mL), the mixture was cooled to 0 °C and water (2.5 mL) and aqueous NaOH (10%, 2.5 mL) were added, followed by water (2.5 mL). The white precipitate was removed by filtration on a pad of celite and washed with Et_2O. After filtration and concentration under reduced pressure, and the corresponding alcohols of *trans*-4-phenylcyclohexanol (3.10 g, 70%) and *cis*-4-phenylcyclohexanol (0.35 g, 9%) were isolated as white solids using silica gel column chromatography with pentane/Et_2O (4/6 to 5/5). *trans*-4-Phenylcyclohexanol and *cis*-4-phenylcyclohexanol were further converted to the desired ethers, *trans*-**1y** and *cis*-**1y**, by methylation using NaH and MeI.

trans-4-Methoxycyclohexyl)benzene (*trans*-**1y**)[21]



Colorless oil; yield 60%, 0.57 g (3 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.25 (m, 2H), 7.23–7.15 (m, 3H), 3.39 (s, 3H), 3.24–3.17 (m, 1H), 2.55–2.47 (m, 1H), 2.21–2.16 (m, 2H), 1.98–1.92 (m, 2H), 1.55–1.45 (m, 2H), 1.42–1.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.65, 128.31, 126.72, 126.00, 79.17, 55.69, 43.69, 32.39, 32.19.

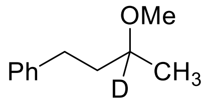
cis-4-Methoxycyclohexyl)benzene (*cis*-**1y**)[21]



Colorless oil; yield 55%, 0.2 g (1.05 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.19 (m, 4H), 7.19–7.11 (m, 1H), 3.54–3.45 (m, 1H), 3.32 (s, 3H), 2.55–2.47 (m, 1H), 2.11–1.99 (m, 2H), 1.88–1.72 (m, 2H), 1.64–1.60 (m, 2H), 1.56–1.43 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.46, 128.18, 126.79, 125.76, 74.20, 55.53, 43.97, 29.66, 28.04.

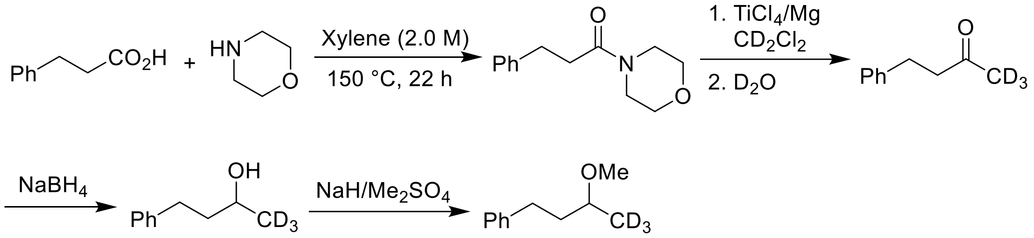
Synthesis of deuterated ethers 1a-*d*1

(3-Methoxybutyl-3-*d*)benzene (**1a-*d*1**)



1a-*d*1 was prepared by reduction of the commercially available 4-phenylbutan-2-one with $NaBD_4$, followed by methylation of the resulting 4-phenylbutan-2-d-2-ol with MeI in the presence of NaH. Colorless oil; yield 60%, 0.41 g (2.48 mmol); Hexane/EtOAc = 20/1; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29–7.22 (m, 2H), 7.20–7.12 (m, 3H), 3.31 (s, 3H), 2.76–2.57 (m, 2H), 1.88–1.79 (m, 1H), 1.72–1.65 (m, 1H), 1.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.26, 128.32, 128.21, 125.58, 75.31 (t, J = 21.4 Hz), 55.76, 37.98, 31.58, 18.74. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{11}H_{15}DNaO$: 188.1156, found: 188.1156.

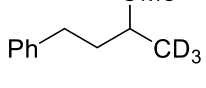
Synthesis of 1a-*d*3



1a-*d*3

The 3-phenylpropanoic acid (1.5 g, 10 mmol) was added to an oven dried 25 mL Schlenk tube, followed by the morpholine (0.87 g, 10 mmol) and 5 mL toluene. The tube was then sealed and heated at 150 °C for 22 hours. After cooling to room temperature, the solvent was removed on a rotary evaporator and the resulting amide product was used directly for the next step.[22] To a 0 °C suspension consisting of Mg (0.576 g, 24 mmol) and $TiCl_4$ (4.5 mmol, 1 M in toluene, 4.5 mL) was added a toluene (6 mL) solution of the amide (0.657 g, 3 mmol) over a 5-min period, followed by CD_2Cl_2 (0.9 mL) and THF (15 mL). The resulting green-black mixture was stirred for an additional 1 h at 0 °C. Then, a solution of D_2O/acetone (1/1, 6mL) was added. After stirring for 30 seconds at 0 °C, the mixture was diluted with CH_2Cl_2 (40 mL). The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography on silica gel using 1/15 ethyl acetate/hexane (1/15) as eluent, affording the corresponding deuterated ketone product, 4-phenylbutan-2-one-1,1,1-*d*3, in 60% (272 mg) yield with a 95/5 ratio of deuterated (-CD_3) and protonated (-CH_3) mixture as a colorless oil.[23] 4-Phenylbutan-2-one-1,1,1-*d*3 was used to prepare **1a-*d*3** using $NaBH_4$-mediated reduction, followed by methylation of the corresponding alcohol with Me_2SO_4/NaH.[3]

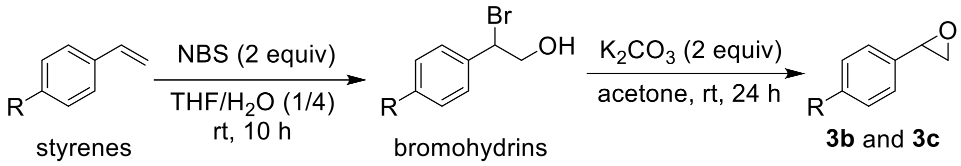
(3-Methoxybutyl-4,4,4-*d*3)benzene**1a-*d*3**



Colorless oil; yield 60% (**1a-*d*3/1a** = 83/17), 100 mg (0.60 mmol); Hexane/EtOAc = 50/1; ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.29–7.27 (m, 2H), 7.19–7.15 (m, 3H), 3.32 (s, 3H), 3.30–3.27 (m, 1H), 2.75–2.60 (m, 2H), 1.88–1.79 (m, 1H), 1.74–1.65 (m, 1H), 1.15–1.12 (m, CH_3, 0.15 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.33, 128.37, 128.27, 125.64, 75.73, 55.89, 38.05, 31.64, 18.92–17.89 (m). HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{11}H_{13}D_3NaO$: 190.1282, found: 190.1281.

3.2 Synthetic procedure of cyclic ethers 3 and analytic data

Synthesis epoxides 3b and 3c[24]

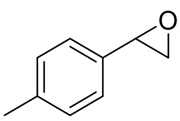


To a suspension of substituted styrenes (10 mmol) in THF/water (15 mL, V/V=1/4) solution was added *N*-bromosuccinimide (20 mmol, 2 equiv) and the reaction mixture stirred at room temperature for 10 h. At the end of reaction, 20 mL of aq. $NaHSO_3$ (0.01 M) was added to the reaction mixture, and then the crude product was extracted using 3×20 mL of ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4. After filtration, the solvent was then evaporated off and the crude bromohydrins was used directly for the next step. A mixture of bromohydrin (5 mmol), potassium carbonate (10 mmol, 2 equiv) and acetone (25 mL) was stirred for 24 hours at room temperature under N_2 atmosphere. After reaction, acetone was removed in vacuum and the residue was diluted with water (30 mL) and extracted with ethyl acetate (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, which were subsequently removed under reduced pressure with low temperature. Then the mixture was purified by flash column chromatography on silica gel and eluted with hexane/ethyl acetate (50/1) to give the corresponding epoxides **3** as a colorless oil.

Analytic data of 3

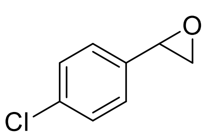
3a is commercially available.

2-(*p*-Tolyl)oxirane (**3b**)[25]



Colorless oil; yield 60%, 0.40 g (2.99 mmol); Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19–7.12 (m, 4H), 3.82 (dd, *J* = 4.0, 2.6 Hz, 1H), 3.11 (dd, *J* = 5.5, 4.1 Hz, 1H), 2.78 (dd, *J* = 5.5, 2.6 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.90, 134.47, 129.13, 125.40, 52.26, 51.03, 21.11.

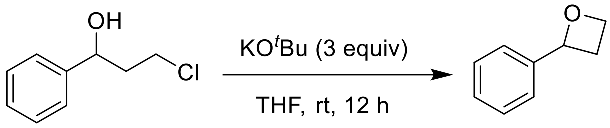
2-(4-Chlorophenyl)oxirane (**3c**)[25]



Colorless oil; yield 60%, 0.46 g (2.99 mmol); Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.28 (m, 2H), 7.23–7.18 (m, 2H), 3.83 (dd, *J* = 4.0, 2.6 Hz, 1H), 3.14 (dd, *J* =

5.4, 4.1 Hz, 1H), 2.75 (dd, J = 5.5, 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.14, 133.88, 128.66, 126.79, 51.73, 51.20.

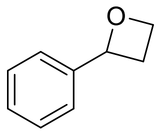
Synthesis of 3d[26]



3d

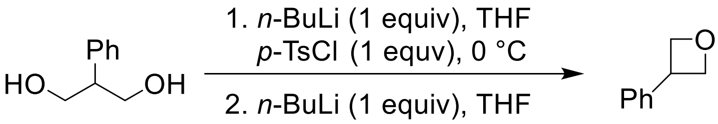
3-Chloro-1-phenylpropan-1-ol (0.85 g, 5 mmol) was added to a solution of potassium *tert*-butoxide (1.68 g, 15 mmol) and tetrahydrofuran (30 mL). The resulting mixture was stirred at room temperature for 12 h. The reaction was quenched by saturated NH_4Cl solution (5 mL) and then extracted with diethyl ether (3 × 15 mL). The combined organic layers were washed with brine (30 mL) and dried over anhydrous Na_2SO_4. After filtration and concentration under reduced pressure, the residue was purified by flash silica gel chromatography to produce the product **3d** in 50% yield (0.34 g) as a colorless oil.

2-Phenyloxetane (**3d**)[26]



Colorless oil; yield 50%, 0.34 g (2.54 mmol); Hexane/EtOAc = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.41 (m, 2H), 7.41–7.35 (m, 2H), 7.32–7.26 (m, 1H), 5.80 (t, J = 7.5 Hz, 1H), 4.82 (td, J = 8.0, 5.9 Hz, 1H), 4.65 (dt, J = 9.2, 5.8 Hz, 1H), 3.05–2.97 (m, 1H), 2.70–2.65 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.49, 128.41, 127.73, 125.15, 82.83, 68.16, 30.64.

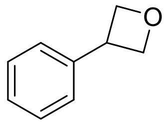
Synthesis of 3e[27]



3e

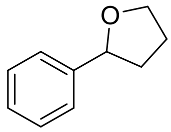
2-Phenylpropane-1,3-diol (0.76 g, 5 mmol, 1 equiv.) was dissolved in THF (40 mL, 0.125 M) and cooled to 0 °C. 2.5 mL of *n*-BuLi in hexanes (2.5 M, 5 mmol, 1 equiv) was added dropwise and the resulting suspension was stirred at 0 °C for 15 minutes before *p*-toluenesulfonyl chloride (0.95 g, 5 mmol, 1 equiv) was added in 3 portions. The reaction was allowed to continue at 0 °C for 1 hour and then 2 mL of *n*-BuLi in hexanes (2.5 M solution, 5 mmol, 1 equiv) was added over 2 minutes. The reaction was warmed to 50 °C and then stirred for 12 h. The reaction was cooled to room temperature and diluted with Et_2O, followed by quenched by the addition of water. The organic layer was removed and the aqueous layer was extracted with Et_2O (3×15 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and concentration under vacuum, the residue was purified by flash column chromatography to afford the oxetane **3e** in 57% yield (0.38 g) as a colorless oil.

3-Phenyloxetane (**3e**)[27]



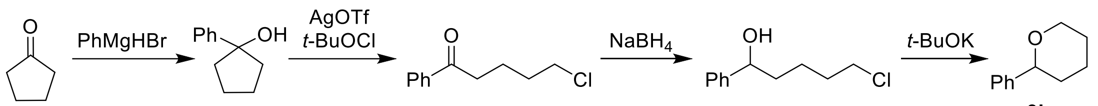
Colorless oil; yield 57%, 0.38 g (2.84 mmol); Hexane/EtOAc = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.33 (m, 4H), 7.30–7.23 (m, 1H), 5.07 (dd, *J* = 8.4, 6.1 Hz, 2H), 4.78 (dd, *J* = 6.8, 6.1 Hz, 2H), 4.26–4.19 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 141.48, 128.69, 126.97, 126.74, 78.86, 40.26.

2-Phenyltetrahydrofuran (**3f**)[28]



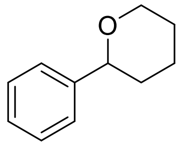
Colorless oil; yield 35%, 0.26 g (1.77 mmol); Hexane/EtOAc = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.29 (m, 4H), 7.27–7.20 (m, 1H), 4.88 (t, *J* = 7.2 Hz, 1H), 4.13–4.02 (m, 1H), 3.95–3.90 (m, 1H), 2.35–2.27 (m, 1H), 2.03–1.93 (m, 2H), 1.85–1.73 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.38, 128.20, 127.02, 125.54, 80.58, 68.58, 34.54, 25.95.

Synthesis of 3h[26,29,30]



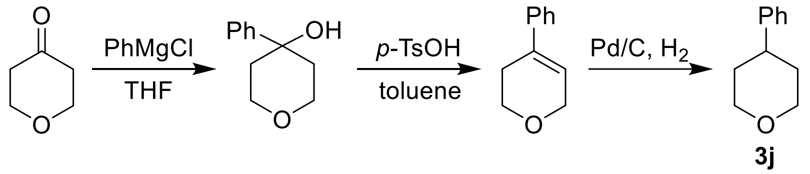
To a CH_2Cl_2 (25 mL) solution of cyclopentanone (1.0 mL, 11.84 mmol) in a 300-mL round-bottom flask, phenylmagnesium bromide (5.8 ml, 19.8 mmol) was added dropwise over 1.5 h at 0 °C. The solution was allowed to warm to room temperature. After reaction, the solution was cooled to 0 °C and quenched with saturated NH_4Cl (30 mL). After extraction with CH_2Cl_2 (3 x 20 mL), the combined organic layers were dried over Na_2SO_4. Ater filtration and concentration under reduced pressure, the desired 1-phenylcyclopentan-1-ol was obtained as a colorless oil and used directly for the next step. To a mixture of 1-Phenylcyclopentan-1-ol (10 mmol, 1.0 equiv), AgOTf (0.1 mmol, 0.1 equiv), and 1,10-phenanthroline (0.2 mmol, 0.2 equiv) in a dry Schlenk tube under N_2, dry acetonitrile (7.0 mL) was added, followed by the addition of *t*-BuOCl (30 mmol, 3.0 equiv). The reaction mixture was stirred at room temperature for 48 h. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (hexane/Et_2O = 50/1, v/v), affording 5-chloro-1-phenylpentan-1-one as a white solid. A solution of 5-chloro-1-phenylpentan-1-one (3 mmol) in MeOH (10 mL) was cooled to 0 °C, and $NaBH_4$ (2.0 equiv. 10 mmol) was added portion wise over 10 min. The suspension was stirred at 0 °C for an additional 1 h, and then slowly quenched by the dropwise addition of a saturated aqueous solution of NH_4Cl (caution: H_2 evolution). The mixture was poured into a separatory funnel containing H_2O (20 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and concentration under reduced pressure, the residue was purified by column chromatography through silica gel, eluting with hexanes/EtOAc (5/1 to 2/1), affording **3h** in 65% yield as a colorless oil.

2-Phenyltetrahydro-2H-pyran (**3h**)[28]



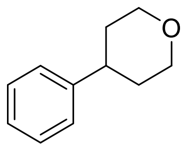
Colorless oil; yield 65%, 0.32 g (1.98 mmol); Hexane/EtOAc = 30/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.27 (m, 4H), 7.27–7.21 (m, 1H), 4.35–4.27 (m, 1H), 4.17–4.09 (m, 1H), 3.64–3.58 (m, 1H), 1.96–1.91 (m, 1H), 1.84–1.81 (m, 1H), 1.75–1.52 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.29, 128.22, 127.22, 125.79, 80.10, 68.95, 33.99, 25.85, 23.98.

Synthesis of 3j[31]



To a THF (5 mL) solution of tetrahydro-4*H*-pyran-4-one (0.46 mL, 5.0 mmol, 1.0 equiv) was added PhMgCl (1.0 M in diethyl ether, 6.0 mL, 1.2 equiv) at -78 ºC. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. After the reaction was completed, saturated aqueous NH_4Cl was added, and then the aqueous layer was separated and extracted with Et_2O. The combined organic layers were washed with brine and dried over Na_2SO_4. After filtration and concentration under reduced pressure gave 1-phenylcyclohexan-1-ol as a colorless oil. To a solution of this alcohol (0.73 g) in toluene (5 mL) was added *p*-TsOH (68.8 mg, 0.4 mmol) and the mixture was refluxed for 3 h. After cooling the mixture to room temperature, saturated aqueous $NaHCO_3$ was added. The aqueous layer was separated and extracted with ethyl acetate. The organic layer was combined, washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (EtOAc/hexane =1/20) to give 4-phenyl-5,6-dihydro-2*H*-pyran (0.61 g, 3.8 mmol) as a white solid. To an ethyl acetate solution of 4-phenyl-5,6-dihydro-2*H*-pyran (0.61 g, 3.8 mmol) in a round-bottomed flask was added Pd/C (200 mg, 5 mol%). The atmosphere was then purged with hydrogen and the reaction mixture was stirred vigorously under a balloon pressure atmosphere of hydrogen for 3 h. The solution was then filtered through Celite and the solvent was evaporated. The residue was purified by flash column chromatography (EtOAc/hexane = 1/20), giving the desired 4-phenyltetrahydropyran **3j** in 66% yield as a white solid.

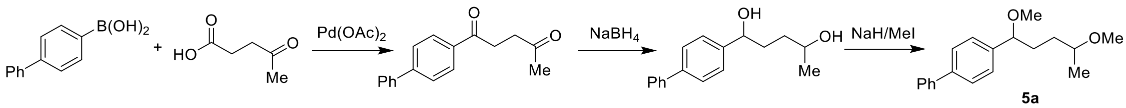
4-Phenyltetrahydro-2H-pyran (**3j**)[31]



White solid; yield 66%, 0.41 g (2.53 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.26 (m, 2H), 7.22 (d, *J* = 7.9 Hz, 3H), 4.09–4.05 (m, 2H), 3.55–3.49 (m, 2H), 2.82–2.67 (m, 1H), 1.90–1.69 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.81, 128.46, 126.68, 126.25, 68.35, 41.53, 33.89.

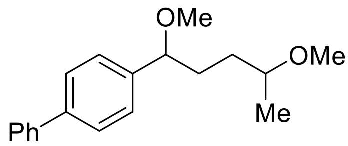
3.3 Synthetic procedure of diols 5a-5c and acetal 7c and analytic data

Synthesis of diols 5a[32]



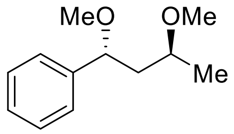
A 100-mL round-bottomed flask equipped with a pressure equalizer and a magnetic stirring bar was charged with $Pd(OAc)_2$ (67.3 mg, 0.30 mmol), tris(4-methoxyphenyl)phosphine (123 mg, 0.35 mmol), 4-oxopentanoic acid (1.16 g, 10 mmol), and 4-biphenylboronic acid (2.38 g, 12 mmol). Subsequently, THF (40 mL), water (45 mg, 2.5 mmol), and pivalic anhydride (2.79 g, 15 mmol) were added through a syringe. The reaction vessel was purged with argon and the brown reaction mixture was heated at 60 °C overnight. After removal of the volatiles under vacuum, the residue was taken up in a minimum amount of hexane and filtered through aluminum oxide by using hexane/Et_2O (100/0 to 90/10) as eluent. After removal of the volatiles and crystallization of the residue from hexane, 1-(biphenyl-4-yl)pentane-1,4-dione (1.76 g, 75 %) was obtained in 75% yield (1.76 g) as a white solid, which was determined by the reported literature.[33] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09–8.02 (m, 2H), 7.72–7.66 (m, 2H), 7.66–7.59 (m, 2H), 7.50–7.42 (m, 2H), 7.42–7.36 (m, 1H), 3.31 (t, *J* = 6.3 Hz, 2H), 2.91 (t, *J* = 6.3 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.49, 198.21, 145.91, 139.95, 135.41, 129.04, 128.74, 128.32, 127.36, 127.32, 37.20, 32.54, 30.23.
5a was prepared from 1-(biphenyl-4-yl)pentane-1,4-dione as a 1:1 mixture of *syn*- and *anti*-isomers using $NaBH_4$ in methanol, as described in the synthesis of **5h**.

4-(1,4-Dimethoxypentyl)-1,1'-biphenyl (**5a**)



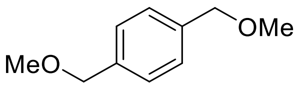
Colorless oil; yield 45%, 0.38 g (1.34 mmol), *syn*:*anti* = 50:50; Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.54 (m, 4H), 7.47–7.40 (m, 2H), 7.38–7.30 (m, 3H), 4.19–4.04 (m, 1H), 3.32–3.26 (m, 4H), 3.25–3.26 (m, 3H), 1.98–1.55 (m, 3H), 1.55–1.31 (m, 1H), 1.11 (dd, *J* = 8.1, 6.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.41, 141.32, 140.89, 140.38, 128.72, 127.19, 127.11, 127.04, 83.92, 83.72, 76.68, 76.51, 56.73, 56.68, 55.99, 55.94, 34.29, 33.73, 32.80, 32.20, 19.04, 18.96. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{19}H_{24}NaO_2$: 307.1668, found: 307.1668.

anti-1,3-Dimethoxybutyl)benzene (**5b**)



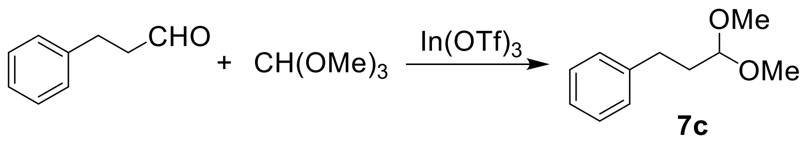
The **5b** was prepared from the commercially available 1-phenylbutan-1,3-dione as an *anti*-isomer through $NaBH_4$-mediated reduction, followed by methylation with MeI.
Colorless oil; yield 60%, 0.58 g (2.99 mmol); Hexane/EtOAc = 20/1; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37–7.23 (m, 5H), 4.33 (dd, *J* = 9.7, 3.6 Hz, 1H), 3.57 (m, 1H), 3.37 (s, 3H), 3.22 (s, 3H), 1.84–1.64 (m, 2H), 1.14 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.63, 128.39, 127.39, 126.42, 80.24, 73.43, 56.71, 56.29, 46.38, 19.29. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{12}H_{18}NaO_2$: 217.1199, found: 217.1199.

1,4-Bis(methoxymethyl)benzene (**5c**)[34]



The **5c** was prepared from 1,4-phenylenedimethanol through methylation with MeI.
Colorless oil; yield 72%, 0.60 g (3.61 mmol); Hexane/EtOAc = 20/1; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 4H), 4.43 (s, 4H), 3.36 (s, 6H). ^{13}C NMR (10 MHz, $CDCl_3$) δ 137.43, 127.61, 74.24, 57.84.

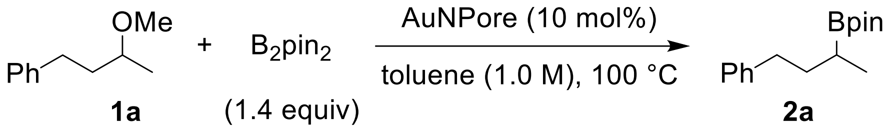
Synthesis of acetal 7c[35]



To a mixture of 3-phenylpropanal (0.67 g, 5 mmol, 1.0 equiv) and trimethyl orthoformate (1.06 g, 10 mmol) in dichloromethane (30 mL) was added indium triflate (14.1 mg, 0.5 mol%) at room temperature and the reaction mixture was stirred for 3 min. At this time, an additional indium triflate (14.1 mg, 0.5 mol%) was added and the reaction mixture was stirred for an additional 15 min. The mixture was passed through a short plug of neutral alumina, which was washed with dichloromethane (2×15 mL), and the solvent was removed under reduced pressure to give (3,3-dimethoxypropyl)benzene **7c** in 50% yield (0.45 g) as a colorless oil.
^1H NMR (400 MHz, $CDCl_3$) δ 7.29–7.25 (m, 2H), 7.20–7.16 (m, 3H), 4.36 (t, *J* = 5.7 Hz, 1H), 3.32 (s, 6H), 2.71–2.59 (m, 2H), 1.98–1.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.52, 128.30, 125.78, 103.61, 52.58, 33.99, 30.77.

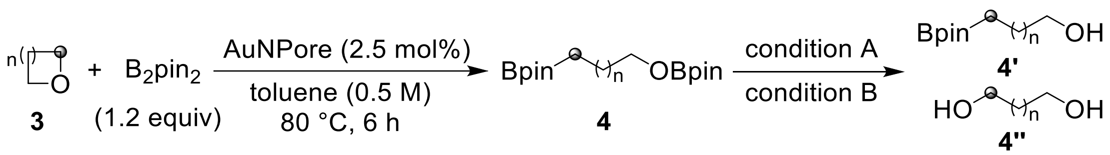
4. General procedure for the AuNPore-catalyzed borylation of ethers

Alkyl methyl acyclic ethers



To a solution of dialkyl ether **1a** (0.3 mmol, 1.0 equiv) and B_2pin_2 (0.42 mmol, 1.4 equiv) in toluene (1 M, 0.3 mL) was added AuNPore (10 mol%, 5.9 mg) in a 3 mL reactor vial with screwed cap at room temperature. The reaction mixture was stirred under nitrogen atmosphere on an aluminum-block for 6 h at 100 ºC. After cooling to room temperature, the AuNPore catalyst was recovered by simple filtration and the filtrate was evaporated. The resulting residual was purified by silica gel chromatography to afford **2a** in 80% yield (62.4 mg) as a colorless oil. The recovered AuNPore catalyst was washed with acetone and dried under vacuum for reuse.

Cyclic alkyl ethers



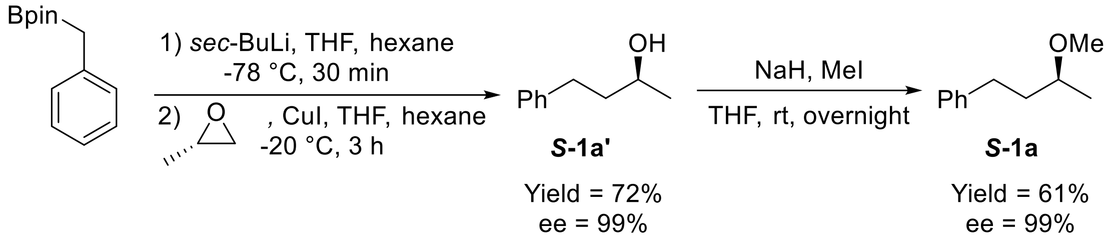
To a solution of ether **3** (0.3 mmol, 1.0 equiv) and B_2pin_2 (0.36 mmol, 1.2 equiv) in toluene (0.5 M, 0.6 mL) was added AuNPore (2.5 mol%, 1.5 mg) in a 3 mL reactor vial with screwed cap at room temperature. The reaction mixture was stirred under nitrogen atmosphere for 6 h at 80 ºC. After reaction, the AuNPore catalyst was recovered by simple filtration and the filtrate was evaporated.

Condition A: for **4a-4f** and **4h-4j**; The above residue containing boronic esters **4** was diluted with ethyl acetate (5 mL) and then a diluted aq. HCl (0.1 M, 10 mL) was added, which was stirred at room temperature for 2 h. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (2 × 5 mL). The combined organic layer was dried over anhydrous Na_2SO_4. After filtration and concentration of the filtrate, the residue was purified by a silica gel chromatography (ethyl acetate/ hexanes = 1/20 as eluent), affording the desired hydroxyl-tethered alkylboronic esters **4a'-4c'** and **4h'-4j'**.

Condition B: for **4d'-4f'**; After concentration of the filtrate obtained from condition A, the residue was diluted with THF (2 mL) and was cooled to 0 °C. Then, a mixture of NaOH (2 M in H_2O)/H_2O_2 (30% in H_2O) (2:1 v/v, 0.9 mL) was added dropwise and stirred at room temperature for 2 h. The organic layer was separated and the aqueous phase was extracted with Et_2O (2 × 5 mL). The combined organic layer was dried over anhydrous Na_2SO_4. After filtration and concentration of the filtrate, the residue was purified by silica gel column chromatography (*n*-hexane/AcOEt: 2/1), affording the corresponding diols **4d''-4f''**.

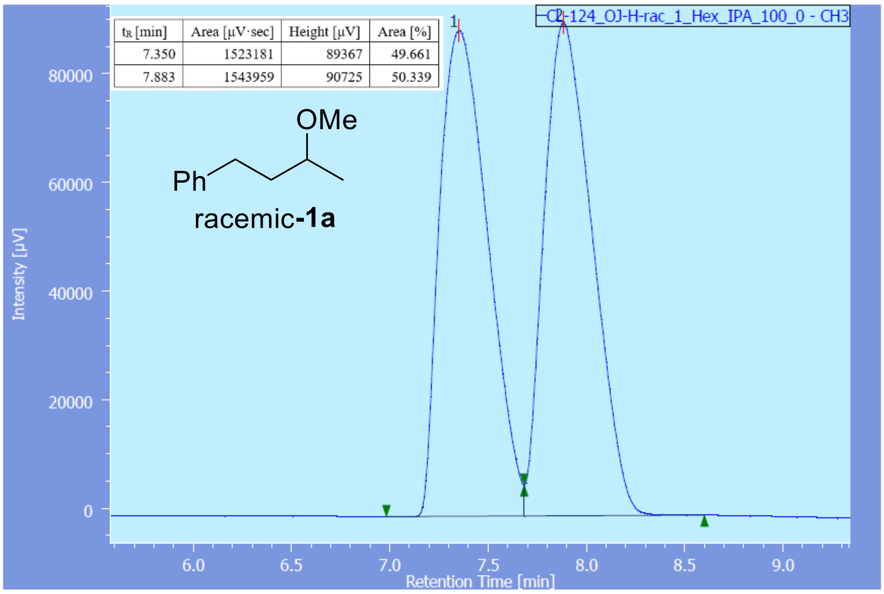
5. Borylation of chiral alkyl methyl ether

Synthesis of chiral alkyl methyl ether (*S*-1a)

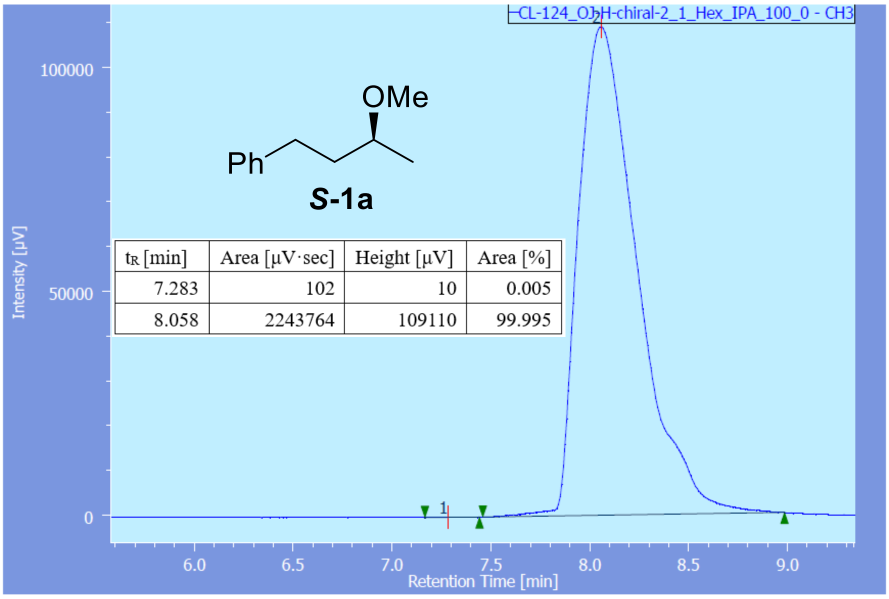


(*S*)-4-phenylbutan-2-ol (***S*-1a'**) was prepared according to the literature procedure with commercially available benzyl boronic pinacol ester (BnBpin), (*S*)-2-methyloxirane and freshly opened *sec*-BuLi solution.[36] Two 25 mL round bottom flasks, both with magnetic stir bars, were flame dried under vacuum. Copper iodide (CuI) (4.8 mg, 0.025, mmol, 0.050 equiv) was added to one of the flasks. Both flasks were covered with new septum, sealed with parafilm, and purged three times with argon gas. Benzyl boronic pinacol ester (BnBpin) (280 µL, 1.25 mmol, 2.5 equiv) and 5 mL of dry THF were added to the empty flask. Both flasks were cooled to -78°C in a dry ice bath with acetone and *sec*-BuLi (3 M in hexane) (1.0 mmol, 2.0 equiv) was added to the BnBpin to make the nucleophilic boronate complex. The reaction stirred for 30 minutes before the boronate were transferred via syringe to the flask containing CuI. Immediately after the nucleophile transfer, the epoxide (0.50 mmol, 1.0 eq) was added and the reaction was allowed to stir for 15 minutes at -78 °C. The reaction was then removed from the cold bath and left to stir for 2 hours and 45 minutes. At completion, the reaction was quenched with 0.3 mL of sat. NH_4Cl (aq). The reaction mixture was then worked up (10 mL sat. NH_4Cl, 3 × 10 mL EtOAc, 10 mL brine), dried over Na_2SO_4, concentrated under reduced pressure and purified on silica gel column (9/1: hexane/AcOEt) to afford ***S*-1a'** in 46% yield (35 mg, 0.23 mmol) as a colorless oil. Analysis of enantiomeric excess using chiral HPLC with Chiralpak IB as stationary phase and *n*-hexane/^{i}PrOH (97/3) as mobile phase at a flow rate of 0.7 mL.min^{-1} (T = 30 °C) with a wavelength of 254 nm.[37]

(*S*)-(3-methoxybutyl)benzene (***S*-1a**) with 99% ee was prepared by methylation of ***S*-1a'** using MeI and NaH. Analysis of enantiomeric excess of ***S*-1a** using chiral HPLC with Chiralcel OJ-H as stationary phase and *n*-hexane (100%) as mobile phase at a flow rate of 1 mL.min^{-1} (T = 30 °C) with a wavelength of 254 nm.

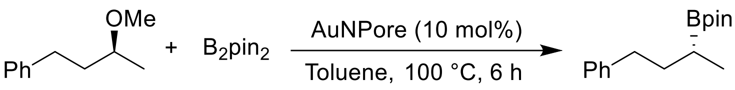


t_R [min]	Area [µV·sec]	Height [µV]	Area [%]
7.350	1523181	89367	49.661
7.883	1543959	90725	50.339



t_R [min]	Area [µV·sec]	Height [µV]	Area [%]
7.283	102	10	0.005
8.058	2243764	109110	99.995

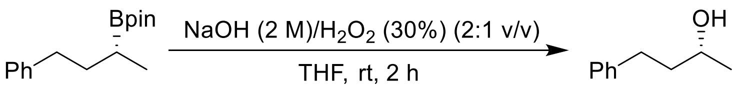
Borylation of chiral alkyl methyl ether *S*-1a



***S*-1a** ***R*-2a**, 70%

The borylation of ***S*-1a** with B_2pin_2 was conducted under standard conditions as described in general procedure of **1a**, affording ***R*-2a** in a 70% isolated yield.

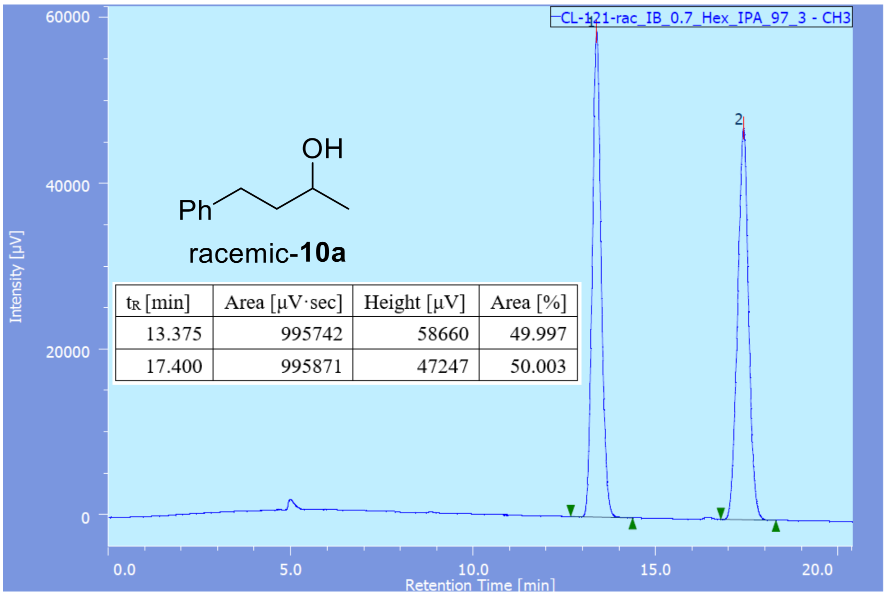
Hydroxylation of alkyl boronic ester *R*-2a



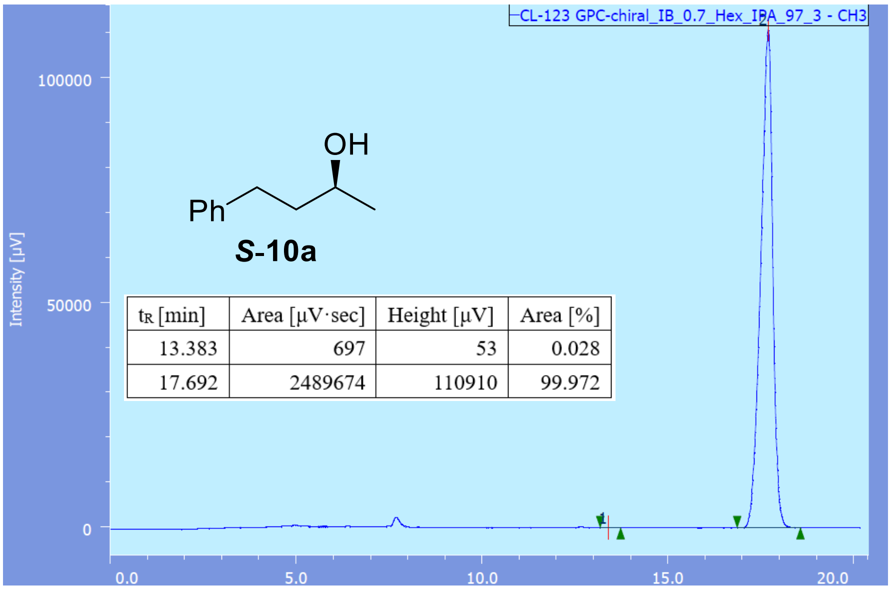
***R*-2a** ***R*-10a**, 60% ee

A solution of ***R*-2a** (56 mg, 2.15 mmol) in THF (1.3 mL) was cooled to 0 °C and a solution of

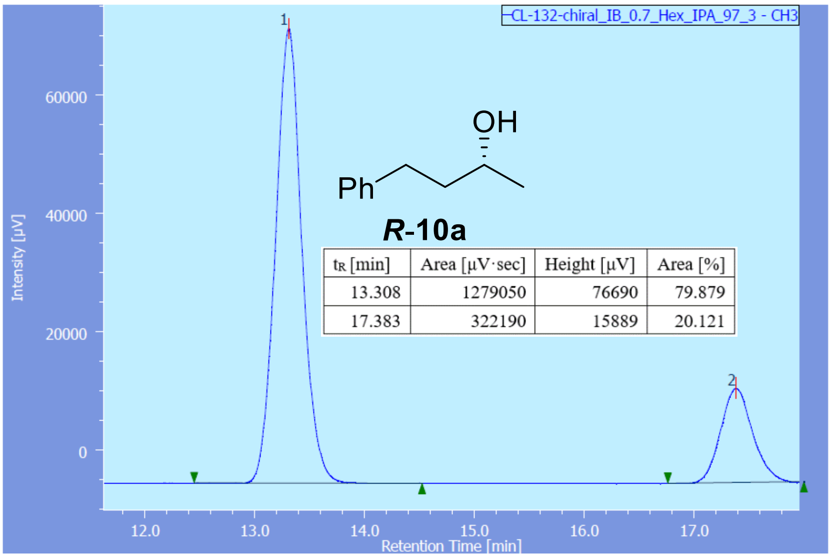
NaOH (2 M)/H_2O_2 (30%) (2:1 v/v, 0.9 mL) was added dropwise, and then allowed to stir at room temperature for 2 h. After reaction, the layers were separated and the aqueous phase was extracted with Et_2O (2 × 5 mL). The combined organic layer was dried over $MgSO_4$, and concentrated. The residue was purified by silica gel column chromatography using *n*-hexane/AcOEt (9/1) as eluent, affording ***R*-10a** in 96% yield (31 mg, 2.06 mmol) as a colorless oil. Analysis of enantiomeric excess was calculated to be 60%, which was measured using chiral HPLC with Chiralpak IB as stationary phase and *n*-hexane/^{i}PrOH (97/3) as mobile phase at a flow rate of 0.7 mL.min^{-1} (T = 30 °C) with a wavelength of 254 nm.[37]



tR [min]	Area [µV·sec]	Height [µV]	Area [%]
13.375	995742	58660	49.997
17.400	995871	47247	50.003



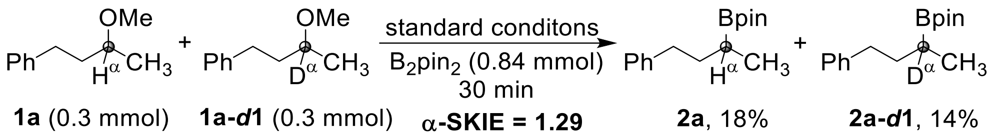
tR [min]	Area [µV·sec]	Height [µV]	Area [%]
13.383	697	53	0.028
17.692	2489674	110910	99.972



t_R [min]	Area [µV·sec]	Height [µV]	Area [%]
13.308	1279050	76690	79.879
17.383	322190	15889	20.121

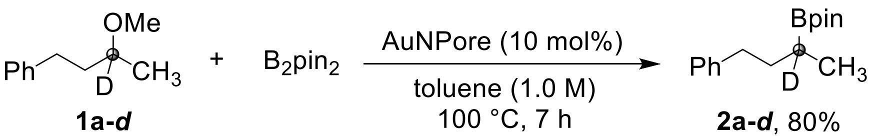
6. Study of secondary kinetic isotope effects (SKIEs)

Competitive borylation using deuterated ether 1a-*d*1 and protonated 1a



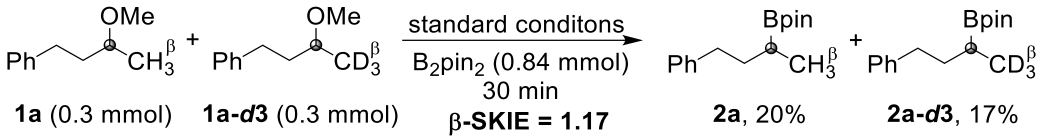
To a solution of ether **1a** (0.3 mmol, 1.0 equiv), **1a-*d*1** (0.3 mmol, 1.0 equiv) and B_2pin_2 (0.84 mmol, 1.5 equiv) in toluene (1 M, 0.3 mL) was added AuNPore (10 mol%, 5.9 mg) at room temperature. The reaction mixture was stirred under nitrogen atmosphere for 30 min at 100 ºC. The reaction mixture was transferred to a flask and evaporated. The ^1H NMR yields of **2a** and **2a-*d*1** were 18% and 14%, respectively, which were determined using dibromomethane as an internal standard. Thus, the SKIE value was calculated to be 1.29.

4,4,5,5-Tetramethyl-2-(4-phenylbutan-2-yl-2-d)-1,3,2-dioxaborolane (2a-*d*)



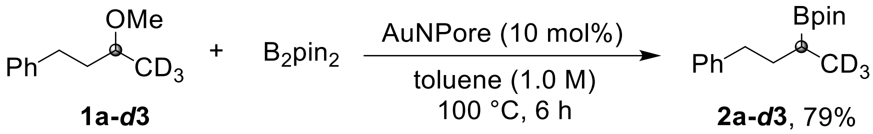
The borylation of **1a-*d*1** with B_2pin_2 was conducted under standard conditions as described in general procedure of **1a**, after 7 h, affording **2a-*d*1** in an 80% isolated yield. Colorless oil; yield 80%, 62.6 mg (0.24 mmol); Hexane/EtOAc = 50/1; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29–7.22 (m, 2H), 7.21–7.12 (m, 3H), 2.67–2.56 (m, 2H), 1.84–1.70 (m, 1H), 1.64–1.52 (m, 1H), 1.24 (s, 12H), 1.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.05, 128.40, 128.16,125.47, 82.84, 35.27, 35.18, 24.77, 24.71, 15.30. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{16}H_{24}DBNaO_2$: 284.1903, found: 284.1902.

Competitive borylation using deuterated ether 1a-*d*3 and protonated 1a



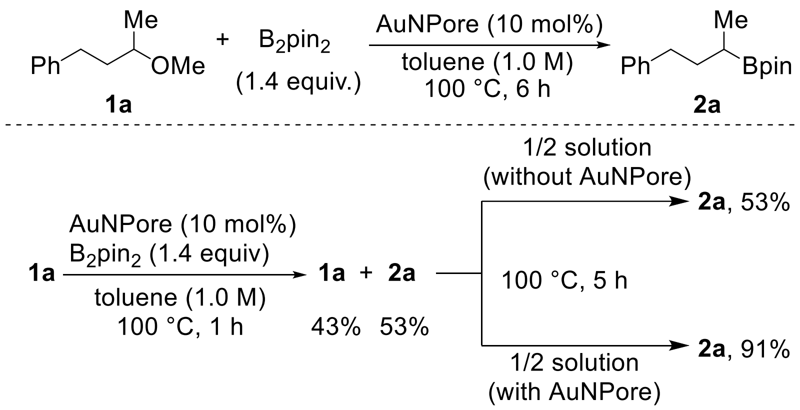
To a solution of ether **1a** (0.284 mmol), **1a-*d*3** (0.316 mmol, containing 5% of **1a**) and B_2pin_2 (0.84 mmol, 2.8 equiv) in toluene (1 M, 0.3 mL) was added AuNPore (10 mol%, 5.9 mg) at room temperature. The reaction mixture was stirred under nitrogen atmosphere for 30 min at 100 ºC. The resulting mixture was transferred to a flask and evaporated. The ^{1}H NMR yields of **2a** and **2a-*d*3** were 20% and 17%, respectively, which were determined using dibromomethane as an internal standard. Thus, the SKIE value was calculated to be 1.17.

4,4,5,5-Tetramethyl-2-(4-phenylbutan-2-yl-1,1,1-d3)-1,3,2-dioxaborolane (2a-*d*3)



The borylation of **1a-*d*3** with B_2pin_2 was conducted under standard conditions as described in general procedure of **1a**, after 6 h, affording **2a-*d*3** in a 79% isolated yield. Colorless oil; yield 79%, 62 mg (0.24 mmol); Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.22 (m, 2H), 7.21–7.12 (m, 3H), 2.64–2.58 (m, 2H), 1.87–1.68 (m, 1H), 1.65–1.51 (m, 1H), 1.25 (s, 12H), 1.09–1.03 (m, 1H), 1.01–0.97 (CH_3, m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.09, 128.42, 128.18, 125.48, 82.87, 35.31, 35.22, 24.79, 24.74, 17.16–15.88 (m), 15.31–14.12 (m). HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{16}H_{22}D_3BNaO_2$: 286.2028, found: 286.2028.

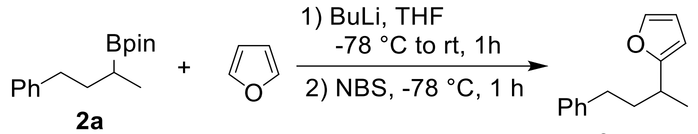
7. Leaching experiments



The toluene solution of **1a** and $B_2(pin)_2$ in the presence of the AuNPore catalyst (10 mol%) was stirred at 100 ºC for 1 h. At this time, the^{1}H NMR yield of **2a** was 55%. A part of the supernatant was transferred to the other reaction vial. This supernatant without AuNPore catalyst was continuously heated at 100 ºC for 5 h, affording **2a** in a 55% ^{1}H NMR yield. On the other hand, the residual containing the AuNPore catalyst gave **2a** in a 91% ^{1}H NMR yield after heating at 100 ºC for 5 h. ^{1}H NMR yields are shown using CH_2Br_2 as an internal standard.

8. Derivatization of alkylboronic esters

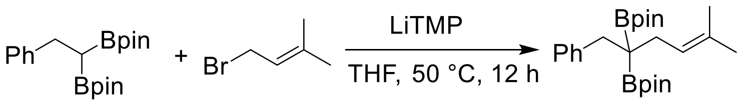
Coupling of with Furan[38]



2a **9a**, 76%

A solution of furan (44 µL, 0.6 mmol, 1.2 equiv) in THF (2.0 mL) was cooled to –78 °C and then treated with *n*-BuLi (0.37 mL, 0.6 mmol, 1.2 equiv, 1.6 M in hexane). The cooling bath was removed and the mixture was stirred at room temperature for 1 h. The mixture was cooled to –78 °C and a THF (1.0 mL) solution of **2a** (130 mg, 0.5 mmol, 1.0 equiv) was added dropwise. The mixture was stirred at –78 °C for 1 h. Then, a THF (2.0 mL) solution of furan (0.6 mmol, 1.2 equiv) in was added dropwise. After 1 h at –78 °C, $Na_2S_2O_3$ saturated solution (2 mL) was added and the reaction mixture was allowed to warm to room temperature. The reaction mixture was diluted with Et_2O and water. The layers were separated and the aqueous layer was extracted with Et_2O. The combined organic layer was dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by column chromatography on silica gel eluting with *n*-hexane, affording 2-(4-phenylbutan-2-yl)furan (**9a**). Colorless oil, 76% yield, 95mg (0.48 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.28 (m, 3H), 7.17–7.15 (m, 3H), 6.29–6.27 (m, 1H), 6.01–5.98 (m, 1H), 2.83 (hex, *J* = 6.7 Hz, 1H), 2.58 (t, *J* = 8.06 Hz, 2H), 2.05–1.95 (m, 1H), 1.86–1.76 (m, 1H), 1.27 (d, *J* = 6.7 Hz, 3H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.24, 142.32, 140.69, 128.39, 128.29, 125.70, 109.84, 103.71, 37.49, 33.39, 32.68, 19.23.

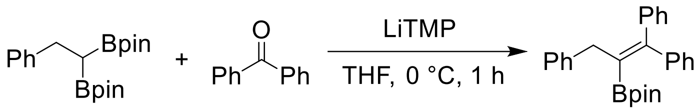
Coupling with 1-bromo-3-methylbut-2-ene[39]



8b **9b**, 82%

To a solution of 2,2'-(2-phenylethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**8b**) (86 mg, 0.24 mmol) in THF (0.5 mL) was added a THF solution of LiTMP (2,2,6,6-tetramethylpiperidyl lithium) at 0 °C, which was prepared from 2,2,6,6-tetramethylpiperidine (41 µL, 0.24 mmol) in THF (0.5 mL) with BuLi (1.6 M in hexane, 0.15 mL, 0.24 mmol) at -78 °C and stirred for 30 min and for 30 min at 0 °C. To the resulting solution was added 3,3-dimethylallyl bromide (23 µL, 0.2 mmol) dropwise at 0 °C and then heated at 50 °C for 12 h. After cooling to room temperature, the solvent was removed and the residue was purified using silica gel column chromatography with 100/1 then 50/1 hexane/EtOAc, affording the corresponding product 2,2'-(5-Methyl-1-phenylhex-4-ene-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**9b**). White solid, 82% yield, 83.9 mg (0.20 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21–7.14 (m, 4H), 7.11–7.07 (m, 1H), 5.20–5.16 (m, 1H), 2.95 (s, 2H), 2.20 (d, *J* = 6.9 Hz, 2H), 1.68 (s, 3H), 1.51 (s, 3H), 1.22 (s, 12H), 1.18 (s, 12H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.83, 131.73, 129.84, 127.58, 125.32, 123.93, 83.14, 34.79, 27.10, 26.06, 24.91, 24.89, 24.71, 24.69, 18.22. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{25}H_{40}B_2NaO_4$: 449.3004; found 449.3005.

Coupling with ketone



8b **9c**, 63%

To a solution of 2,2'-(2-phenylethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (86 mg, 0.24 mmol) in THF (0.5 mL) was added a THF solution (0.5 mL) of LiTMP, which was prepared from 2,2,6,6-tetramethylpiperidine (41 μL, 0.24 mmol) in THF (0.5 mL) with BuLi (1.6 M in hexane, 0.15 mL, 0.24 mmol) at -78 °C and stirred for 30 min and for 30 min at 0 °C. To the resulting mixture was added benzophenone (36.4 mg, 0.2 mmol). The reaction mixture was stirred for 1 h at rt, after which the solvent was removed and purified using silica gel column chromatography with 100/1 then 50/1 hexane/EtOAc to obtain the corresponding product 4,4,5,5-tetramethyl-2-(1,1,3-triphenylprop-1-en-2-yl)-1,3,2-dioxaborolane (**9c**).[40] White solid, 63% yield, 60 mg (0.15 mmol); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.14 (m, 15H), 3.62 (s, 2H), 0.89 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.08, 144.30, 141.93, 141.08, 129.33, 129.01, 128.96, 128.12, 128.09, 127.73, 127.12, 126.95, 125.79, 83.27, 39.52, 24.35.

9. DFT computation data for mechanistic elucidation

9.1 Method

Computational studies were carried out using the Gaussian16 program package[1] with the DFT method. The M06 functional and def2-SVP basis set were applied to all atoms. IRC calculations were performed for all optimized transition states to confirm their connectivity to the corresponding reactants and products. Natural bond orbital (NBO) analysis was conducted using the NBO 7.0 program.[2]

1. Gaussian 16, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.
2. NBO 7.0.10, E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, P. Karafiloglou, C. R. Landis, and F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI (2018).

9.2 Cartesian coordinates

Table S1. Calculation data of intermediates (**IM**) and transition states (**TS**)

Au_{20}^{-} + $B_2(pin)_2$ (**IM0'**)

Au	-2.82623400	-1.90209400	3.65741700
Au	3.55231000	3.36992100	2.25154100
Au	-1.93123500	2.38828800	-3.99819800
Au	3.20565100	-3.88712000	-1.83099000
Au	1.53504000	-0.99207800	1.66903200
Au	-0.60276900	1.42142400	0.68302600
Au	1.98088500	0.79450200	-1.54709000
Au	-0.71083600	-1.23080000	-0.81255700
Au	-0.78885000	-0.01495600	3.21255200
Au	-0.32436300	0.17316900	-3.31050800
Au	1.47392100	-1.82871900	-2.68654400
Au	1.37450400	1.66762700	2.83231100
Au	-0.91522100	-2.65364600	1.72732300
Au	-0.18254700	2.80075900	-1.84160800
Au	1.69638500	3.15391000	0.14371900
Au	1.13291900	-3.34540900	0.00009000

Au	-2.79604600	-0.45777600	1.06552100
Au	-2.50426800	0.96099000	-1.47228300
Au	3.61160400	0.91799600	0.89631500
Au	3.49736800	-1.47039300	-0.44623200
B	-5.45766800	-0.74864700	-0.32577300
O	-5.47150600	-1.79095300	0.56656700
O	-5.48811700	-1.17744500	-1.62403000
C	-5.67265000	-3.01193400	-0.16844600
C	-5.28691300	-2.60441900	-1.63303500
C	-7.14323600	-3.36694500	-0.01093300
C	-4.80947100	-4.09846400	0.43640300
C	-6.16359700	-3.21099300	-2.70902200
C	-3.82632800	-2.85549700	-1.96584800
H	-7.38572700	-4.33112100	-0.48630700
H	-7.37442500	-3.44222100	1.06308000
H	-7.79407900	-2.58859100	-0.44077800
H	-5.14839300	-4.31262300	1.46259700
H	-4.88264700	-5.02881600	-0.15234500
H	-3.75153900	-3.79918400	0.49552400
H	-5.82153800	-2.86510100	-3.69691800
H	-6.09526800	-4.31209200	-2.69165800
H	-7.21793400	-2.92012500	-2.59700200
H	-3.60552900	-3.93059100	-2.06202500
H	-3.58121400	-2.36052800	-2.91993600
H	-3.15384500	-2.43154200	-1.20005800
B	-5.43199400	0.89298300	0.13404600
O	-5.05459300	1.90208200	-0.72221200
O	-5.79415000	1.37194100	1.36132700
C	-5.30744800	3.16577000	-0.07757900
C	-5.42050200	2.76200700	1.43320500
C	-6.61099900	3.68800300	-0.66086400
C	-4.17595000	4.11877400	-0.39750400
C	-6.48556000	3.51098100	2.20711500
C	-4.10129900	2.83475600	2.18395900
H	-6.86204400	4.68848100	-0.27321500
H	-6.50503800	3.75715800	-1.75468300
H	-7.44978400	3.00626900	-0.44652400
H	-4.15607500	4.32172800	-1.48073900
H	-4.31122500	5.07753600	0.13183800
H	-3.19327400	3.70258800	-0.12525700
H	-6.49097000	3.16349900	3.25206900
H	-6.27517600	4.59401800	2.20972800
H	-7.49081000	3.34695500	1.79334500
H	-3.78912400	3.87598500	2.36362900

H	-4.21604800	2.32965100	3.15698600
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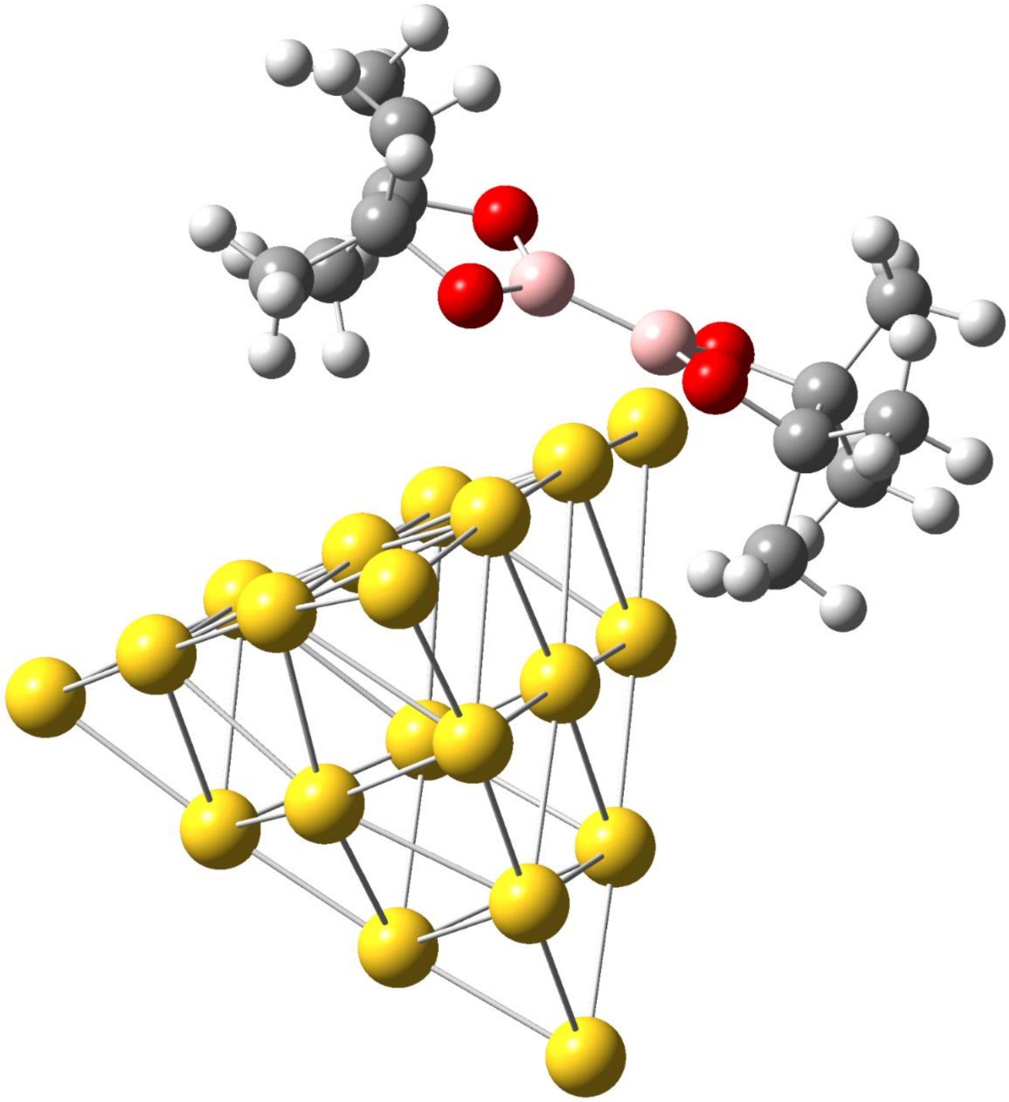
IM0'



Oxidative addition of $B_2(pin)_2$ (**TS_0**)

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Au	-0.09923600	4.86018200	-1.69147600
Au	3.42080300	-2.52641100	-3.37158800
Au	0.79294200	-1.90522500	0.63084500
Au	-0.72024100	0.77943200	1.12492400
Au	2.26081800	0.92577800	-0.20750200
Au	-0.43456300	-0.04513600	-1.73809400
Au	-1.73478900	-1.80846400	2.06987300
Au	1.04264100	2.40731500	-2.40764100
Au	2.24226100	-0.01428900	-2.97501400
Au	0.47728200	-0.68326700	3.29816800
Au	-1.77796300	-2.41374400	-0.85389000
Au	0.82396300	3.37590700	0.50088700
Au	1.84019300	1.85072800	2.52539900
Au	0.80012700	-2.65113400	-2.14434700
Au	-3.19585300	0.17584100	-0.70613700
Au	-1.67106500	2.56541700	-0.92684100
Au	3.24009900	-0.84406900	1.90180100
Au	3.38979300	-1.73935400	-0.70200900
B	-5.04163900	-0.82839400	-0.71047000
O	-5.77528200	-1.10716100	0.40964400
O	-5.61923400	-1.31717300	-1.85196000
C	-6.99107200	-1.75776800	-0.00212200
C	-6.65582300	-2.23251700	-1.45704700
C	-8.09041800	-0.70913600	0.04218200
C	-7.29768800	-2.87579900	0.97103400
C	-7.80304800	-2.12643700	-2.44003900
C	-6.06058500	-3.62966000	-1.51584700
H	-9.07744600	-1.13472200	-0.20221200
H	-8.13934900	-0.28880100	1.05966700
H	-7.87914200	0.11803400	-0.65489900
H	-7.52705000	-2.45156800	1.96137200
H	-8.17185500	-3.46098900	0.63660700
H	-6.43796700	-3.55317400	1.09241400
H	-7.47124100	-2.47884200	-3.42935000
H	-8.65161700	-2.75605400	-2.12119400
H	-8.15352400	-1.09105500	-2.55537200
H	-6.80994100	-4.40777000	-1.29738500
H	-5.66220100	-3.80085000	-2.52838800
H	-5.21781700	-3.74120200	-0.80893500
B	-4.00743900	2.03499700	-0.02757600
O	-4.81314800	2.91546400	-0.70592300

O	-4.04571800	2.22038800	1.33189400
C	-5.58036200	3.62400800	0.28805200
C	-4.68659700	3.48553600	1.56053800
C	-6.90508300	2.89040300	0.41974900
C	-5.80260300	5.04464800	-0.17898800
C	-5.44842900	3.42201100	2.86623600
C	-3.59287900	4.54048400	1.64647100
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H	-6.44677600	5.04788900	-1.07254100
H	-6.30211400	5.63814600	0.60615100
H	-4.85624300	5.53664400	-0.44543100
H	-4.73829500	3.33813700	3.70367100
H	-6.04626400	4.33793500	3.01445000
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H	-3.99437900	5.52663300	1.93253100
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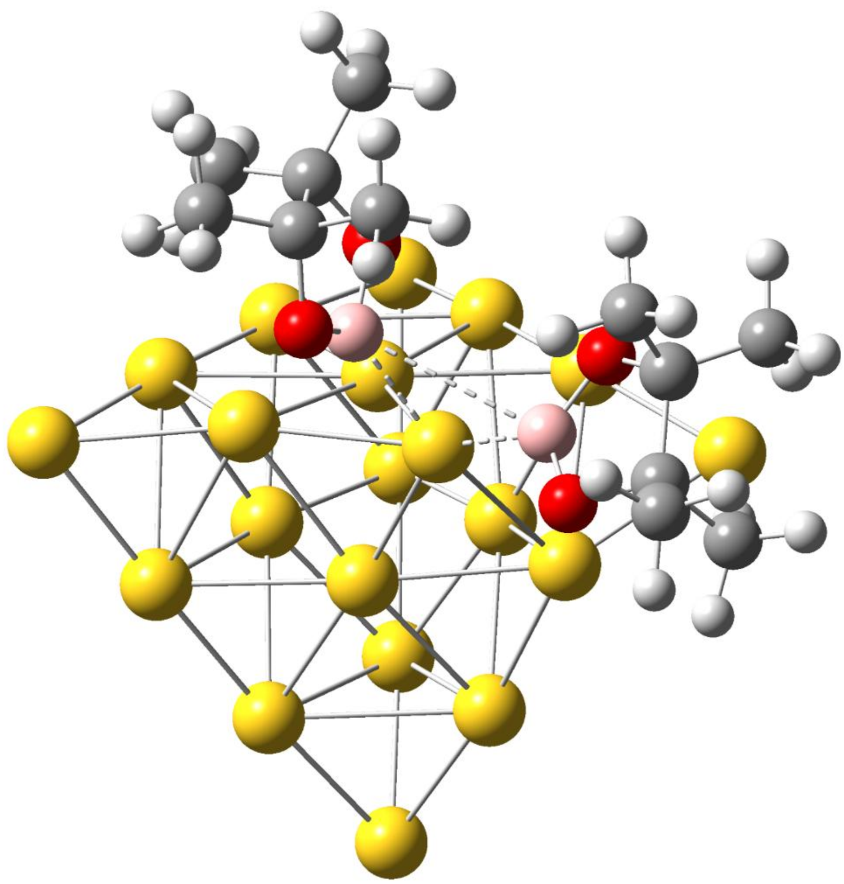
TS0



Au_{20}^{-}-$(B(pin))_2$ (**IM0**)

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Au	2.20011700	-4.69153500	-1.36434200
Au	0.90789500	-1.12086000	1.61462500
Au	-0.16859200	1.52677100	0.51489000
Au	2.16234400	0.12731400	-1.06918000
Au	-1.03845400	-0.89438600	-0.95838000
Au	-1.19673400	0.38570900	3.02264500
Au	0.29973100	0.18267300	-3.31216700
Au	1.26139500	-2.25491200	-2.45569400
Au	1.39896700	1.39030300	3.00300600
Au	-1.83017200	-2.12663200	1.55254400
Au	1.10493300	2.74819800	-1.83890200
Au	2.59857500	2.59481700	0.46782200
Au	0.09113800	-3.46137500	0.09023800
Au	-3.85825900	0.33195000	-0.91152300
Au	-1.85840800	1.93558200	-2.07867200
Au	3.66778500	-0.12384000	1.43447400
Au	3.03044300	-2.42929100	0.05215200
B	-5.23262300	-1.09542500	-0.24028700
O	-5.91794600	-0.97503600	0.96533500
O	-5.52008600	-2.29194400	-0.84226500
C	-6.82364600	-2.09008900	1.08603500
C	-6.19276700	-3.13151700	0.11055800
C	-8.18861300	-1.59634300	0.63279100
C	-6.88034500	-2.52501900	2.53430100
C	-7.19318600	-4.00189100	-0.62018200
C	-5.13183000	-4.00281900	0.76498200
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H	-8.46712000	-0.71971800	1.23856300
H	-8.16918100	-1.28232300	-0.42288700
H	-7.33992500	-1.72997600	3.14401600
H	-7.49136600	-3.43735200	2.64643000
H	-5.87696400	-2.71928100	2.94278200
H	-6.65714500	-4.70313400	-1.27880000
H	-7.79287000	-4.59394200	0.09262900
H	-7.87304200	-3.40793300	-1.24745200
H	-5.57139100	-4.74538400	1.45086200
H	-4.57885200	-4.53779700	-0.02341300
H	-4.39548200	-3.39853200	1.32480200
B	-3.17405700	2.72226700	-0.56250100
O	-4.15905900	3.65831400	-0.72046500

O	-2.66439300	2.73204400	0.72278000
C	-4.47937200	4.17135200	0.59031000
C	-3.16218300	3.90752600	1.38420200
C	-5.65721700	3.36138900	1.10819500
C	-4.85664000	5.63067300	0.46578500
C	-3.34556600	3.60838800	2.85505800
C	-2.10886000	4.98862700	1.19221200
H	-6.02100900	3.74214700	2.07662100
H	-6.47818700	3.42728600	0.37665400
H	-5.39889300	2.29439400	1.21954700
H	-5.79687200	5.72552500	-0.10022800
H	-5.01032000	6.07775300	1.46305300
H	-4.08467400	6.20688500	-0.06396300
H	-2.36288200	3.40196500	3.31289400
H	-3.79836300	4.46890300	3.37764800
H	-3.97225200	2.71795000	3.01610800
H	-2.36709200	5.91814400	1.72560400
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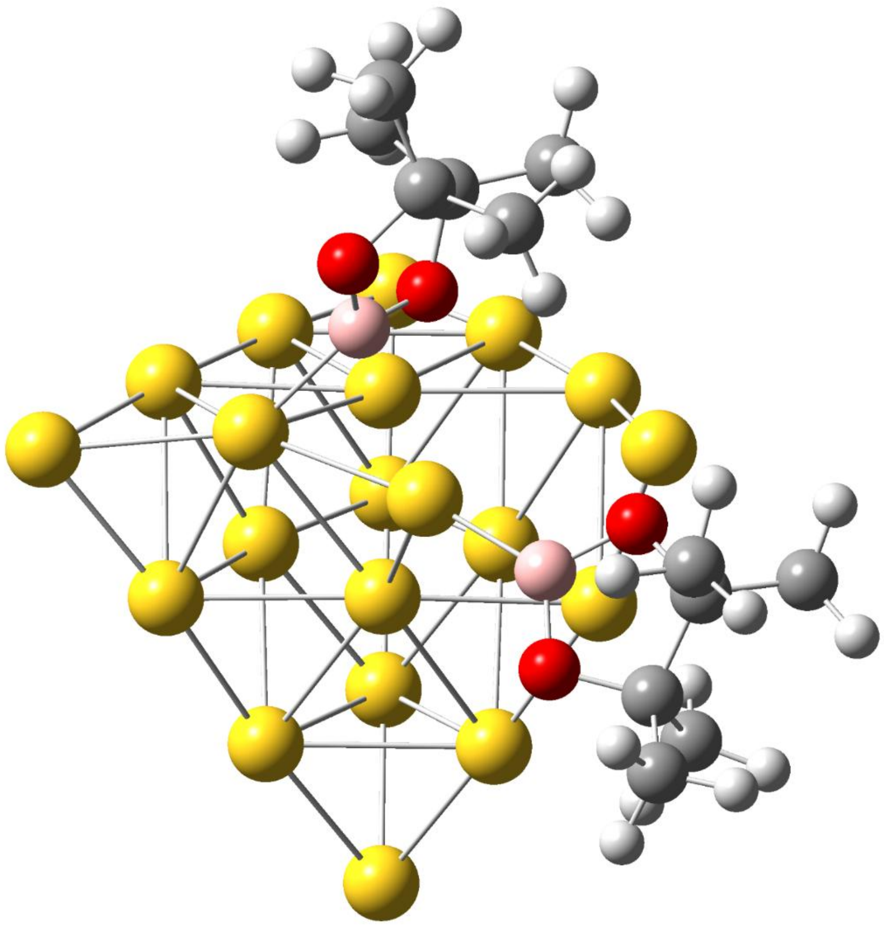
IM0



Au_{20}^{-}-$(B(pin))_2$ + *i*PrOMe (**IM1**)

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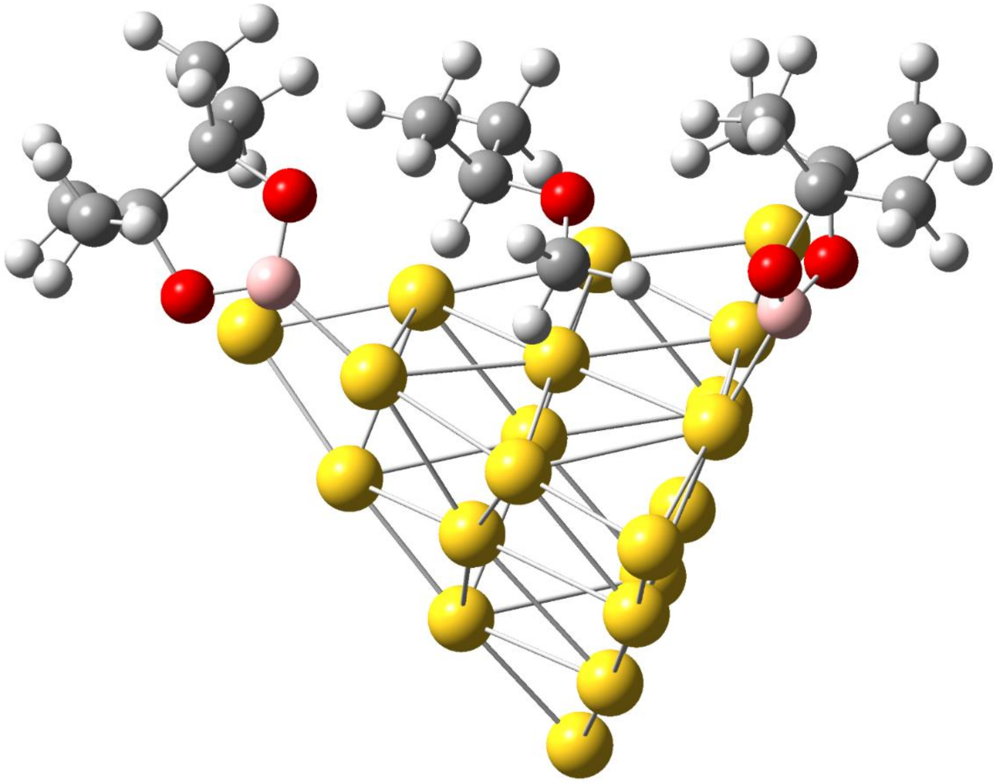
Au	5.59259200	0.60602400	-0.51392000
Au	1.37774200	-1.73310500	0.12167100
Au	-1.37060800	-0.20566500	0.09151200
Au	1.19186700	1.20648600	1.36099400
Au	0.70336500	0.91244100	-1.72733000
Au	-1.15010500	-3.25727700	-0.97562900
Au	0.85488300	3.52120900	-0.40316500
Au	3.15050000	2.00280100	-0.72629900
Au	-0.78403600	-2.51665000	1.80796500
Au	1.23518900	-2.11688000	-2.69927300
Au	-1.41099900	2.53025200	1.30541000
Au	-1.13103000	0.27696200	2.91558100
Au	3.42506900	-0.81306500	-1.67334500
Au	-1.37231500	-0.68901400	-2.72187500
Au	-2.22160200	1.94281300	-1.75032600
Au	1.64909000	-1.14969600	2.99398000
Au	3.69103800	-0.26508200	1.35887300
B	-2.65854100	-4.29605300	0.07176400
O	-2.62793000	-4.53633000	1.42767300
O	-3.86582900	-4.61223100	-0.47473400
C	-4.00210400	-4.64564800	1.86521700
C	-4.70790000	-5.15377900	0.56799200
C	-4.44424100	-3.24825500	2.26788800
C	-4.06379800	-5.58565500	3.04718700
C	-6.11174700	-4.62450200	0.36970400
C	-4.67570800	-6.66513200	0.42315400
H	-5.45775700	-3.25033300	2.70226000
H	-3.74454900	-2.85561800	3.02643000
H	-4.43595800	-2.56211100	1.40440300
H	-3.53082400	-5.13431800	3.89972300
H	-5.10997100	-5.75939000	3.35233300
H	-3.59160600	-6.55461100	2.83078000
H	-6.54207900	-5.05243700	-0.55046900
H	-6.76088100	-4.91386200	1.21433800
H	-6.11421500	-3.52829900	0.26823800
H	-5.35993600	-7.15656000	1.13421400
H	-4.98899200	-6.93085600	-0.59866400
H	-3.65983900	-7.06202600	0.57865100
B	-3.59152400	3.48821600	-1.37215600
O	-3.47686300	4.80975600	-1.72323700

O	-4.74642900	3.26271800	-0.65121000
C	-4.68888600	5.48834900	-1.35774400
C	-5.30495600	4.53421600	-0.28376400
C	-5.53421900	5.59109600	-2.61809300
C	-4.34169300	6.87190200	-0.85130400
C	-6.81597800	4.43156000	-0.31091600
C	-4.84125700	4.83693300	1.13262700
H	-6.45864400	6.16801600	-2.44992100
H	-4.94440400	6.09823400	-3.39762400
H	-5.80388300	4.59333600	-2.99958600
H	-3.92689000	7.47455500	-1.67491500
H	-5.23748300	7.38852900	-0.46506000
H	-3.58210700	6.83324300	-0.05450800
H	-7.14944900	3.72808500	0.47018100
H	-7.28187900	5.41110000	-0.10636000
H	-7.18779600	4.05925400	-1.27672300
H	-5.28875600	5.76484300	1.52486900
H	-5.13772200	4.00268800	1.78950400
H	-3.74119100	4.92388900	1.19132000
O	-5.06210000	-1.43597100	-0.60937600
C	-4.82805700	-1.84488500	-1.92293400
H	-3.95283200	-1.31375600	-2.36302200
H	-4.60045900	-2.92142100	-1.90752400
H	-5.69687500	-1.67021600	-2.58957400
C	-5.23853500	-0.03569900	-0.44467200
H	-4.44448000	0.48789800	-1.02695800
C	-6.59331400	0.42464700	-0.94533800
H	-7.40097300	-0.05626900	-0.36555200
H	-6.67228900	1.51730700	-0.83390600
H	-6.74672300	0.18916200	-2.01062800
C	-5.04374400	0.28206300	1.01684000
H	-4.03910200	-0.02899700	1.35643600
H	-5.13333100	1.36880100	1.17749600
H	-5.79803700	-0.23914400	1.63325300

IM1

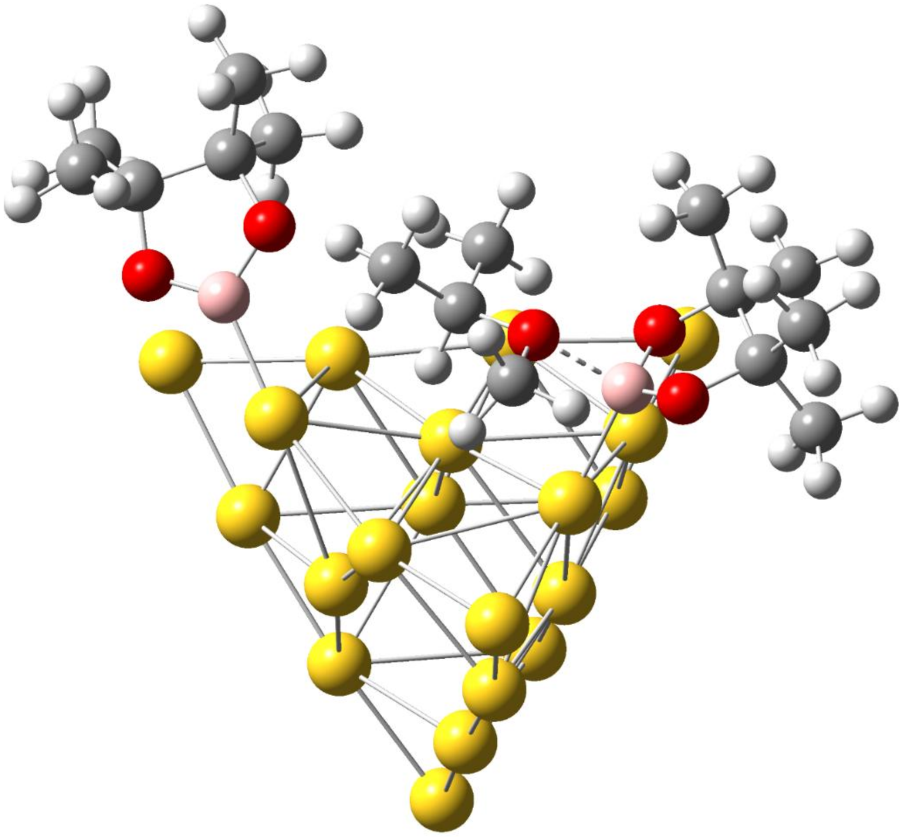


Acid-base complexation (**TS$_{1-2}$**)

Au	-2.37618100	-2.56644200	-3.71150000
Au	-1.45990900	-0.99469000	4.61460600
Au	1.46840500	5.17124600	0.07590100
Au	5.21770900	-2.15720100	-0.30205000
Au	0.32682900	-2.24544100	0.27731400
Au	-1.15190600	0.46857600	-0.01436400
Au	1.65234000	0.60429100	1.31088600
Au	1.20634100	0.59660700	-1.79389700
Au	-2.62779600	-1.96763500	-0.88436800
Au	2.62359900	2.75131300	-0.45324400
Au	3.82026200	0.26154800	-0.65081500
Au	-1.92395600	-1.64909100	1.89728300
Au	0.12300600	-2.69066200	-2.51380300
Au	-0.00040800	3.00535000	0.97492100
Au	-0.84344400	1.07354000	2.79643300
Au	2.62309300	-2.37259300	-1.44249100
Au	-1.22024900	-0.07994000	-2.91954500
Au	-1.17242600	2.66316300	-1.97294100
Au	0.84466500	-1.53889400	3.09333700
Au	3.08339700	-1.89834300	1.51986100
B	-4.62395500	-1.72962000	-0.02394300
O	-4.69931600	-1.40868400	1.32625900
O	-5.56421600	-2.70071800	-0.34998900
C	-5.87631100	-2.03125300	1.86315800
C	-6.07409300	-3.22858500	0.88264000
C	-7.01031300	-1.01920000	1.80355900
C	-5.59938000	-2.41996000	3.29928300
C	-7.51443500	-3.64826400	0.68208800
C	-5.22457000	-4.43694500	1.24738000
H	-7.92998600	-1.40658700	2.27242300
H	-6.70157600	-0.11318600	2.34994700
H	-7.23125600	-0.72470700	0.76560100
H	-5.46439100	-1.51180900	3.90904200
H	-6.43997800	-2.99742700	3.72155100
H	-4.67754200	-3.01437100	3.38840100
H	-7.55982300	-4.49940600	-0.01583100
H	-7.96404700	-3.96744000	1.63815900
H	-8.12200300	-2.83422100	0.26126800
H	-5.60295400	-4.95179500	2.14553800
H	-5.24295600	-5.14676000	0.40547900
H	-4.17294400	-4.15318700	1.41798300
B	-1.96453200	4.50117400	-1.34497800
O	-1.39779900	5.74778600	-1.44759200

O	-3.14665800	4.55686800	-0.62878800
C	-2.30384100	6.71520500	-0.89402500
C	-3.21930500	5.83762600	0.01761300
C	-3.05030500	7.34314000	-2.06088400
C	-1.50309700	7.76965600	-0.16076700
C	-4.66899300	6.27041700	0.08037300
C	-2.67382000	5.65880000	1.42676900
H	-3.71821600	8.15711100	-1.73360800
H	-2.31461400	7.75935100	-2.76677600
H	-3.64641600	6.59227900	-2.60373700
H	-0.89311200	8.33874500	-0.88076600
H	-2.16715000	8.47903400	0.36305500
H	-0.81640100	7.31908800	0.57239700
H	-5.22996600	5.57682300	0.72832900
H	-4.76115000	7.28427900	0.50672600
H	-5.14493500	6.26035900	-0.91103100
H	-2.76307800	6.58042800	2.02499200
H	-3.24293300	4.86027300	1.93094100
H	-1.61396000	5.34642500	1.41823800
O	-5.28470200	-0.21255300	-0.99382400
C	-5.57768900	-0.60361200	-2.32862300
H	-4.68755700	-0.49356100	-2.97635600
H	-5.87162100	-1.66023900	-2.30190700
H	-6.40842800	-0.00500900	-2.73229100
C	-4.62834600	1.09147700	-0.88614600
H	-3.58991600	0.95179700	-1.26064100
C	-5.32351200	2.13335700	-1.73375200
H	-6.39312900	2.20752200	-1.46672700
H	-4.84372000	3.10292300	-1.52668400
H	-5.23379600	1.95079100	-2.81527500
C	-4.58555400	1.51990400	0.55900000
H	-4.03814700	0.81215300	1.19702900
H	-4.07442000	2.49632900	0.60450900
H	-5.60877400	1.63268800	0.95971100

TS_{1-2}: B-O: 1.92 Å

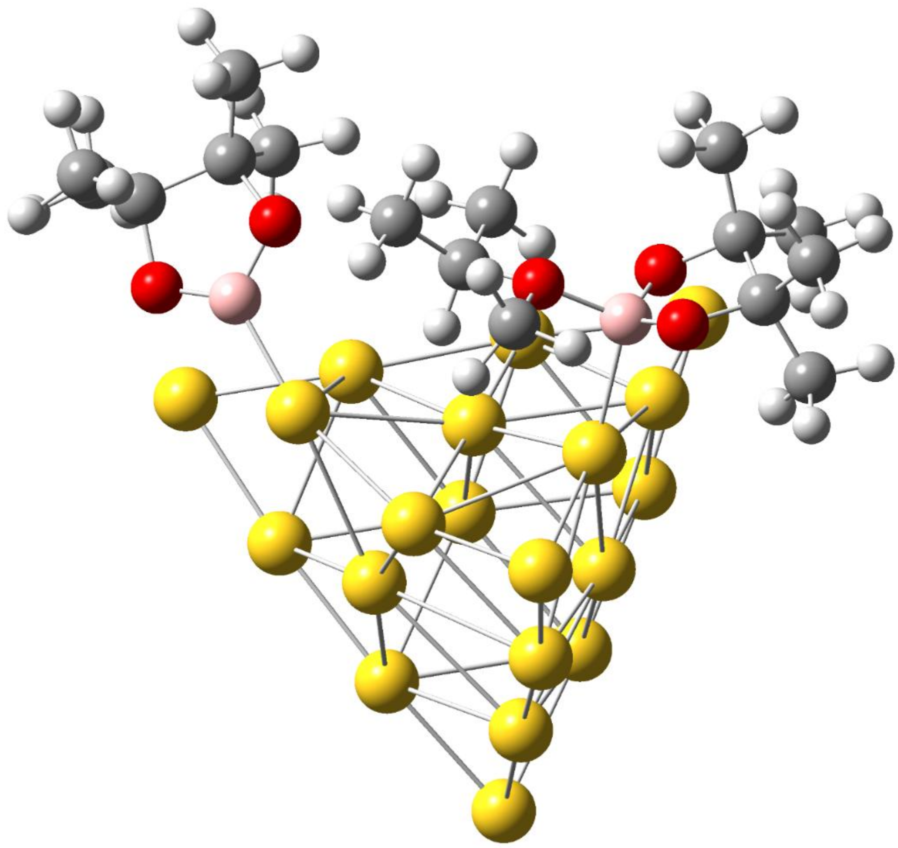


Acid-base complex (**IM2**)

Au	-2.31075600	-2.76010800	-3.59205200
Au	-1.38248500	-0.89417200	4.66518500
Au	1.29148300	5.21930800	-0.07711900
Au	5.29812700	-1.97590100	-0.28768100
Au	0.38229500	-2.24987200	0.31116400
Au	-1.16904600	0.42649500	0.00892500
Au	1.64163700	0.68625500	1.27495800
Au	1.15971400	0.59909100	-1.82008200
Au	-2.59888600	-1.99538700	-0.79441600
Au	2.52766200	2.82582000	-0.55189400
Au	3.80144300	0.37372600	-0.69552400
Au	-1.84317800	-1.68123600	1.96596200
Au	0.23160900	-2.73323400	-2.48426300
Au	-0.08548700	3.02305900	0.89334000
Au	-0.83955100	1.13008000	2.79488100
Au	2.69933700	-2.31636300	-1.39317000
Au	-1.24830600	-0.19774500	-2.90155800
Au	-1.31555600	2.56291300	-2.01261400
Au	0.90958300	-1.43681900	3.11109900
Au	3.15189300	-1.75780300	1.53352600
B	-4.75837700	-1.62036900	-0.10777900
O	-4.81049000	-1.41912000	1.27234800
O	-5.55172000	-2.71967200	-0.46617100
C	-5.76909000	-2.33289800	1.81767600
C	-5.81322800	-3.45601200	0.73239900
C	-7.08638100	-1.58060300	1.94416500
C	-5.29592200	-2.78744000	3.18159700
C	-7.15567400	-4.14424600	0.59428700
C	-4.71997900	-4.50093200	0.90585400
H	-7.87217500	-2.19267400	2.41703500
H	-6.92330500	-0.69043800	2.57262200
H	-7.44778600	-1.23927100	0.96005700
H	-5.28668200	-1.93261600	3.87740000
H	-5.96686400	-3.56113300	3.59340700
H	-4.27105600	-3.18854700	3.14397900
H	-7.09321500	-4.92617400	-0.17915000
H	-7.44498800	-4.62750100	1.54319200
H	-7.94807400	-3.44112200	0.29974600
H	-4.92788700	-5.17145800	1.75553100
H	-4.66618200	-5.10767000	-0.01236100
H	-3.72766900	-4.04217600	1.05342300
B	-2.17155500	4.36878600	-1.37048900
O	-1.67719200	5.64203300	-1.50751400

O	-3.32399200	4.37437500	-0.60045400
C	-2.60024900	6.56946500	-0.91616700
C	-3.43516600	5.65653500	0.03789600
C	-3.42377600	7.15981900	-2.05024000
C	-1.81570300	7.66068100	-0.21975000
C	-4.90220500	6.01519100	0.15210400
C	-2.83007800	5.52055600	1.42715100
H	-4.11231500	7.94465400	-1.69568800
H	-2.73853300	7.60583400	-2.78794500
H	-4.00870600	6.38149400	-2.56603500
H	-1.26231500	8.25301100	-0.96617800
H	-2.48729000	8.34216000	0.33087600
H	-1.07921900	7.24254600	0.48403900
H	-5.40249500	5.29921500	0.82555800
H	-5.03131100	7.02606100	0.57586000
H	-5.41378800	5.97385300	-0.82084800
H	-2.94610600	6.44228700	2.02051800
H	-3.33701500	4.69857900	1.95964800
H	-1.75621200	5.26396600	1.38299000
O	-5.23454800	-0.36413500	-0.96911500
C	-5.46026600	-0.70435600	-2.35354600
H	-4.55686600	-0.47419600	-2.94344200
H	-5.66405900	-1.77911000	-2.39420400
H	-6.32818900	-0.14225100	-2.71929000
C	-4.65622100	1.01163400	-0.78089400
H	-3.61874200	0.93378700	-1.16727900
C	-5.44849600	2.00392900	-1.59399300
H	-6.51663400	1.98403400	-1.31489100
H	-5.04118200	2.99969100	-1.35929600
H	-5.34889400	1.86795900	-2.68059100
C	-4.63581600	1.38798800	0.67479500
H	-3.99897200	0.73245800	1.28271700
H	-4.21953000	2.40859900	0.72252200
H	-5.65401700	1.38976100	1.09994100

IM2

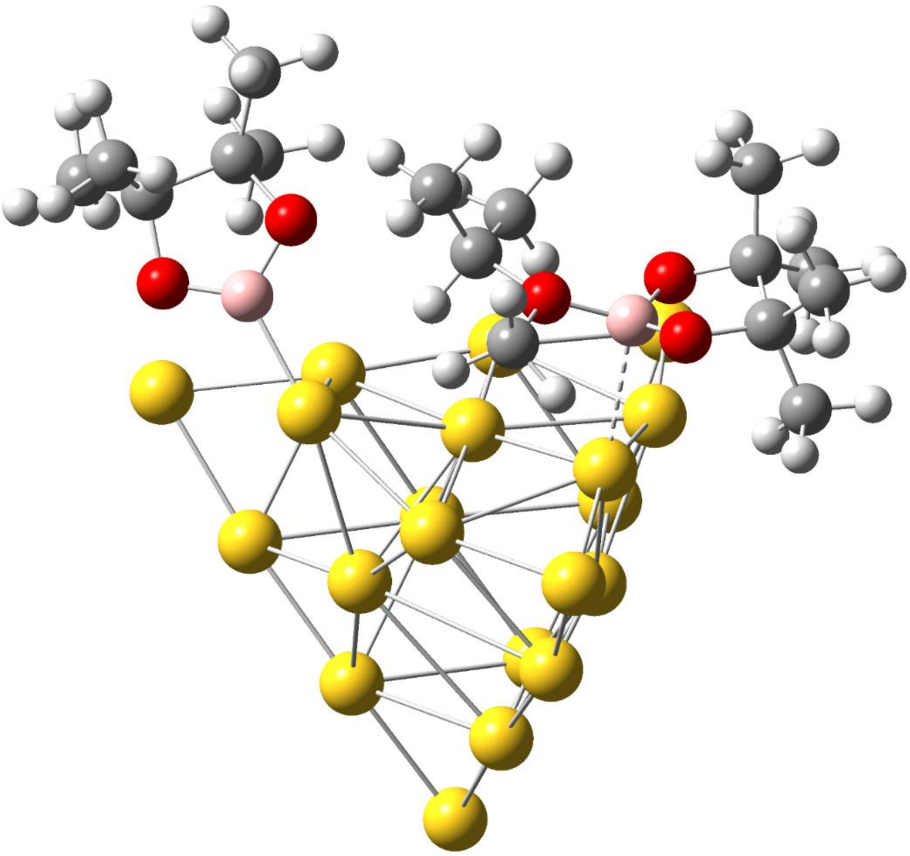


Elimination of boryloxonium (**TS$_{2\text{-}3}$**)

Au	-1.96693300	-3.25856700	-3.41381800
Au	-1.09485100	-0.87943900	4.76878100
Au	0.49367700	5.36102400	-0.20013800
Au	5.51699400	-1.17670300	-0.45416000
Au	0.76781600	-2.23224400	0.41293800
Au	-1.23025800	0.23507800	0.08266500
Au	1.54527000	0.95638200	1.19986400
Au	0.95946200	0.79557500	-1.87754900
Au	-2.17973500	-2.34211700	-0.63553000
Au	2.07400000	3.17262700	-0.68113800
Au	3.65402500	0.90489400	-0.83209300
Au	-1.46307600	-1.95296000	2.12354100
Au	0.57147700	-2.84192400	-2.35826900
Au	-0.52736400	2.98080100	0.78581400
Au	-0.90672700	1.09155400	2.81409900
Au	2.96004700	-1.95225600	-1.39399200
Au	-1.24855300	-0.53446000	-2.82363900
Au	-1.79398900	2.21496700	-2.05093800
Au	1.20457500	-1.19520600	3.12749600
Au	3.43929200	-1.17834600	1.48307900
B	-4.67147700	-2.01086400	-0.08858800
O	-4.71878400	-1.97796300	1.27663200
O	-5.23027300	-3.14536100	-0.63007000
C	-5.42578600	-3.15624400	1.70708200
C	-5.35003300	-4.09364900	0.44871500
C	-6.84097400	-2.70246000	2.03050800
C	-4.75121700	-3.70509600	2.94468100
C	-6.59573700	-4.92174400	0.21023800
C	-4.13165200	-5.00236900	0.43535900
H	-7.45986800	-3.52209500	2.42997100
H	-6.78931700	-1.90894300	2.79291300
H	-7.34125000	-2.28426300	1.14077200
H	-4.84738000	-2.98346500	3.77188400
H	-5.21770900	-4.65472500	3.25768400
H	-3.67463700	-3.87037800	2.78048400
H	-6.45378300	-5.54854300	-0.68395900
H	-6.78567800	-5.59069600	1.06651100
H	-7.48435900	-4.29567600	0.04630400
H	-4.23566700	-5.81993600	1.16670500
H	-4.02948000	-5.44198400	-0.56993500
H	-3.19667400	-4.45699300	0.64959500
B	-2.91158700	3.89020900	-1.45233400
O	-2.67123900	5.20288600	-1.77107700

O	-3.95505000	3.79301700	-0.54009400
C	-3.67250400	6.02634100	-1.15701200
C	-4.21838200	5.10707700	-0.01844700
C	-4.71088300	6.33169900	-2.22609100
C	-3.02544200	7.30843800	-0.67872900
C	-5.70299400	5.24143600	0.25247200
C	-3.44917100	5.24018300	1.28693800
H	-5.48579400	7.02794700	-1.86470000
H	-4.20331600	6.79325900	-3.08746100
H	-5.19938500	5.41022400	-2.58208100
H	-2.68062200	7.89445100	-1.54552300
H	-3.74132800	7.92630200	-0.10918700
H	-2.14739900	7.10587900	-0.04582000
H	-5.99545600	4.55058100	1.06134700
H	-5.95202800	6.26506100	0.58151700
H	-6.31020500	5.00360300	-0.63374500
H	-3.66311300	6.19432600	1.79577300
H	-3.73722700	4.41583300	1.96071100
H	-2.35845500	5.16328600	1.12983300
O	-4.94112700	-0.77696500	-0.87795500
C	-4.95780000	-0.94408800	-2.31983300
H	-4.28341700	-0.19233000	-2.76000000
H	-4.57112800	-1.94474800	-2.54926400
H	-5.99020000	-0.82977200	-2.67567400
C	-4.83787000	0.67753100	-0.43378300
H	-3.90956600	1.02315800	-0.93113500
C	-6.04925700	1.39019600	-0.96940400
H	-6.97740500	0.95842900	-0.55737500
H	-5.96554800	2.44020300	-0.65400300
H	-6.10268700	1.39496400	-2.06806100
C	-4.69160700	0.81011600	1.05114800
H	-3.82014400	0.26735800	1.44570800
H	-4.51583400	1.88568500	1.22395600
H	-5.59574200	0.49241500	1.59429000

$TS_{2\text{-}3}$: B-Au: 2.57 Å

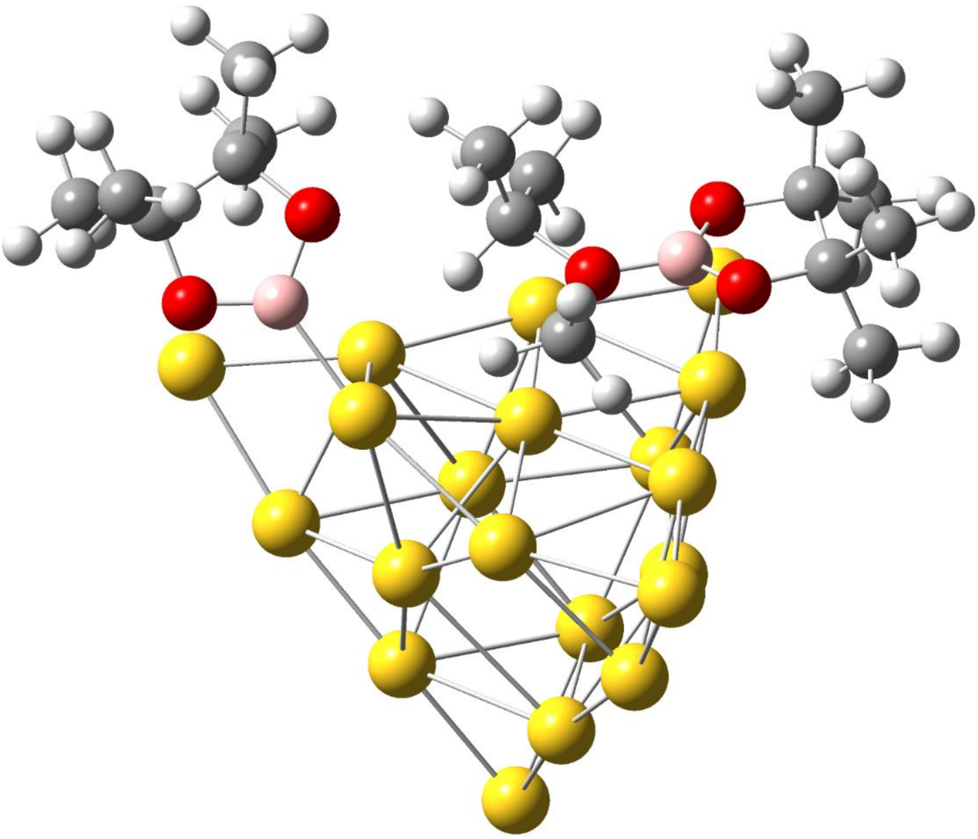


Boryloxonium (**IM3**)

Au	-1.31599500	-3.67221300	-3.44887000
Au	-1.05307500	-1.35962400	4.58481500
Au	-0.47882100	5.42311300	0.21425700
Au	5.57751500	-0.16346400	-0.38026000
Au	1.33163000	-2.28428900	0.42802600
Au	-1.17228400	-0.04635000	-0.01109300
Au	1.37712600	1.35718300	1.44428100
Au	0.78354700	1.16108400	-1.82062700
Au	-1.34616200	-2.81322200	-0.77244700
Au	1.44615400	3.59177600	-0.47510600
Au	3.39382600	1.62464900	-0.62974100
Au	-1.17511200	-2.25340700	1.93199700
Au	1.17120600	-2.75331100	-2.43052700
Au	-1.13712400	2.74213700	0.69780300
Au	-1.12645600	0.79371600	2.75719500
Au	3.22834800	-1.26221200	-1.48320500
Au	-0.95461100	-0.74942800	-2.86587000
Au	-2.17037900	1.81390000	-2.12920000
Au	1.33129400	-1.09483100	3.07463600
Au	3.51721600	-0.58482100	1.47709200
B	-4.74887000	-2.41316500	0.16929800
O	-4.76634000	-2.41807000	1.50925600
O	-4.97393400	-3.58732200	-0.44723300
C	-5.16984200	-3.75504900	1.90541500
C	-4.94283700	-4.60317400	0.59440600
C	-6.62943100	-3.64207300	2.30954000
C	-4.32324200	-4.18009900	3.08260500
C	-6.03674700	-5.60718800	0.30240800
C	-3.59076800	-5.28336100	0.52585800
H	-7.02425800	-4.59899300	2.68475500
H	-6.71645400	-2.89626200	3.11487000
H	-7.26063400	-3.30823000	1.46931800
H	-4.53506800	-3.53034000	3.94633900
H	-4.55068000	-5.22111100	3.36680500
H	-3.24645700	-4.09209300	2.86620100
H	-5.79923500	-6.14455800	-0.62840000
H	-6.10045300	-6.34991100	1.11481300
H	-7.02088400	-5.13336800	0.17869600
H	-3.53068800	-6.12260800	1.23634200
H	-3.43856800	-5.67499400	-0.49281800
H	-2.76047600	-4.58490300	0.73020400
B	-3.57914200	3.31959300	-1.72957400
O	-3.48259700	4.61567100	-2.16626000

O	-4.63869600	3.18322900	-0.83670600
C	-4.58450300	5.37287700	-1.65100600
C	-5.06352200	4.50156100	-0.44604100
C	-5.61575600	5.46896300	-2.76541200
C	-4.09337900	6.75463000	-1.27383400
C	-6.56251400	4.49485600	-0.22534500
C	-4.35915500	4.84081500	0.85797300
H	-6.47229700	6.10446100	-2.48532300
H	-5.13349300	5.90772100	-3.65283600
H	-5.99045700	4.47219700	-3.04920800
H	-3.79376800	7.30071600	-2.18227000
H	-4.88562800	7.33507200	-0.76956500
H	-3.21170500	6.70145100	-0.61515200
H	-6.80676400	3.86821100	0.65008900
H	-6.93299200	5.51303900	-0.01536600
H	-7.10853700	4.09839400	-1.09441900
H	-4.69136500	5.80984700	1.26490200
H	-4.58280900	4.06041200	1.60472900
H	-3.26124300	4.86990500	0.73558700
O	-4.64800900	-1.22757400	-0.61453500
C	-4.51389000	-1.39915200	-2.06178200
H	-4.12891100	-0.44859700	-2.46039500
H	-3.76898400	-2.19037000	-2.23381400
H	-5.49493800	-1.66677100	-2.47724500
C	-4.95166000	0.22042800	-0.15755500
H	-4.21035000	0.78730600	-0.75041700
C	-6.36300800	0.50880500	-0.57442000
H	-7.07860800	-0.13500700	-0.03325200
H	-6.56806900	1.55974100	-0.32475700
H	-6.51678000	0.40319300	-1.65922700
C	-4.67805500	0.40610800	1.29946200
H	-3.68057600	0.03479200	1.58781000
H	-4.66553600	1.49954300	1.44786000
H	-5.44544500	-0.04166400	1.94740300

IM3

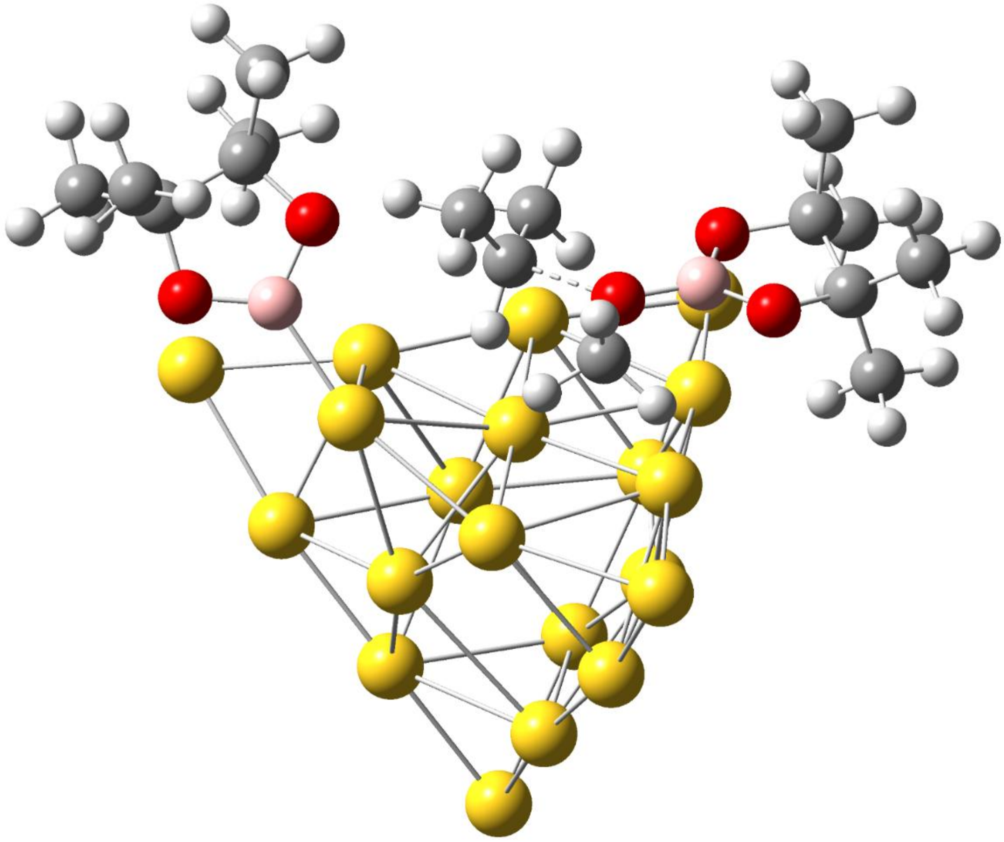


Carbocation formation (**TS$_{3\text{-}4}$**)

Au	-3.30410200	-2.26505300	-3.32018700
Au	-1.48092100	-0.52728500	4.65820900
Au	2.78154200	4.69244900	0.24700300
Au	4.47306100	-3.31318500	-0.51219400
Au	-0.18435100	-2.53942300	0.40451400
Au	-0.90828300	0.64625600	0.02424200
Au	2.00824800	0.35348300	1.45324600
Au	1.23283800	0.41921900	-1.94164200
Au	-2.74915800	-1.48956100	-0.67514400
Au	3.14188600	2.11018500	-0.62606300
Au	3.67487900	-0.59938600	-0.73993300
Au	-2.18306900	-1.11964600	2.00345100
Au	-0.66530200	-2.77723000	-2.44717500
Au	0.68443100	2.92760200	0.77303000
Au	-0.39567400	1.29628400	2.79458700
Au	1.89662300	-2.85856000	-1.56619600
Au	-1.42599700	0.06171800	-2.81696700
Au	-0.67097000	2.78537400	-2.06965000
Au	0.56865100	-1.65398400	3.06602700
Au	2.59549700	-2.48183700	1.39426600
B	-5.61444800	0.31705000	0.04177600
O	-5.44882000	0.49489400	1.37254100
O	-6.46295500	-0.67844400	-0.31165500
C	-6.38627000	-0.39149800	2.02658900
C	-6.74228500	-1.42732100	0.89571500
C	-7.56632500	0.47113900	2.44265200
C	-5.72274700	-0.99488700	3.24319900
C	-8.19544600	-1.85007400	0.86903900
C	-5.84990900	-2.65351600	0.88519600
H	-8.31288800	-0.10446300	3.01201800
H	-7.19892200	1.28584700	3.08590200
H	-8.06586500	0.92519100	1.57121700
H	-5.49377100	-0.20377400	3.97511800
H	-6.38989600	-1.72955200	3.72485200
H	-4.77033300	-1.48879600	2.99019400
H	-8.35151400	-2.57133600	0.05202100
H	-8.46957800	-2.34569700	1.81525100
H	-8.87449500	-1.00121300	0.70492900
H	-6.06971700	-3.31981700	1.73420700
H	-6.01957700	-3.20928600	-0.05092600
H	-4.77828900	-2.38834200	0.91555500
B	-0.95927300	4.81122300	-1.61195100
O	-0.21314300	5.87877500	-2.04026300

O	-1.91747700	5.23552500	-0.68893500
C	-0.76945000	7.08919200	-1.50948000
C	-1.59084500	6.57781300	-0.28552500
C	-1.64137200	7.69194400	-2.60107700
C	0.35780100	8.03708500	-1.16114800
C	-2.87731700	7.33013200	-0.01428800
C	-0.77212300	6.47941300	0.99121400
H	-2.05003200	8.67410900	-2.31056800
H	-1.02912200	7.82417600	-3.50667100
H	-2.47751300	7.02183200	-2.86053600
H	0.87031400	8.35643000	-2.08229600
H	-0.02551300	8.93806900	-0.65123200
H	1.10632200	7.55229600	-0.51731500
H	-3.39519900	6.87502900	0.84696500
H	-2.67213600	8.38494600	0.23688700
H	-3.56381500	7.30633200	-0.87425800
H	-0.54171800	7.47212700	1.41109300
H	-1.34486300	5.91044300	1.74306800
H	0.17625100	5.93628000	0.82597900
O	-5.05431000	1.16688200	-0.90705300
C	-5.19199400	0.85434200	-2.29704800
H	-4.26978900	1.16405500	-2.81552100
H	-5.29597000	-0.23394400	-2.42369700
H	-6.06906800	1.37535400	-2.71180900
C	-3.89184900	2.68778000	-0.60176400
H	-3.06782000	2.19494200	-1.15290400
C	-4.62778800	3.73992200	-1.31310700
H	-5.56892400	4.01052900	-0.81077100
H	-3.93321800	4.60272800	-1.25568900
H	-4.78395800	3.52245700	-2.37854900
C	-3.69452100	2.78470300	0.84120100
H	-3.28801200	1.86150500	1.28409000
H	-2.88398100	3.54530100	0.90272200
H	-4.57679000	3.15078500	1.38571500

TS$_{3\text{-}4}$: C-O: 1.94 Å

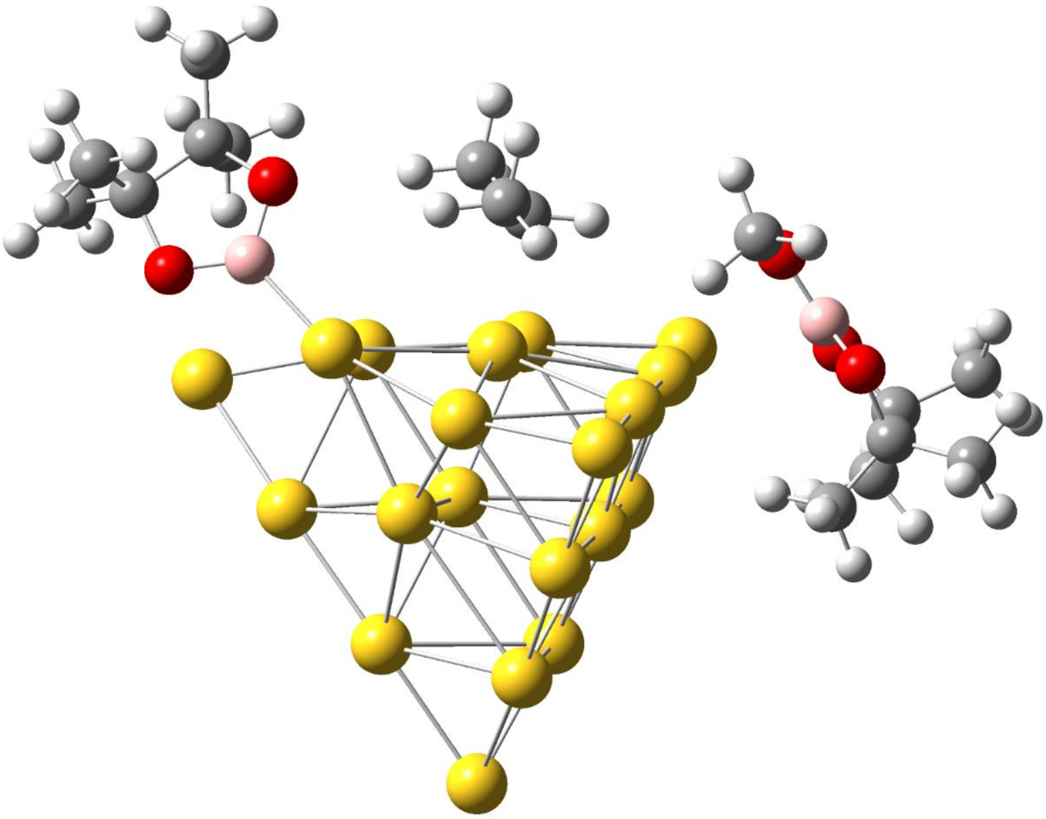


Carbocation (**IM4**)

Au	-2.41225200	2.15627800	-3.92959000
Au	-1.81472000	1.35214700	4.37744700
Au	5.37861600	-0.50015400	0.92422900
Au	-1.04732700	-5.37609800	-0.52330600
Au	-1.96912700	-0.64511500	-0.01656200
Au	0.46529700	1.83053700	0.04977300
Au	0.77246900	-1.29193500	1.31947800
Au	0.97700800	-0.78773900	-1.63526900
Au	-2.26035200	2.00496400	-1.14914300
Au	3.26056600	-1.87254300	-0.12481300
Au	1.07126200	-3.49217700	-0.61050300
Au	-2.12647000	1.74244700	1.60350500
Au	-2.00760400	-0.45309300	-2.91375700
Au	2.90635700	0.68528400	1.39741200
Au	0.59263700	1.12625900	2.89622300
Au	-1.60287100	-2.90243000	-1.79009100
Au	0.22312700	1.54044300	-2.90138600
Au	2.87637800	1.62091600	-1.68337500
Au	-1.67835200	-1.02555800	2.89382700
Au	-1.41248400	-3.24289700	1.26614400
B	-4.68316000	3.80990000	0.71250400
O	-4.79040100	3.04254800	1.84636200
O	-5.65017800	3.53268400	-0.22205700
C	-6.02242600	2.30858200	1.75609400
C	-6.35085100	2.35442800	0.21526100
C	-7.03896100	3.06160100	2.60401700
C	-5.81138800	0.91480200	2.31272600
C	-7.82361700	2.51853900	-0.10616600
C	-5.79398400	1.17054900	-0.56001500
H	-8.00782300	2.53739800	2.65126900
H	-6.64276400	3.15078200	3.62855000
H	-7.20818300	4.08106200	2.21856900
H	-5.57742000	0.97665700	3.38920700
H	-6.72306800	0.30332600	2.19321200
H	-4.97035600	0.39657300	1.82355600
H	-7.95945700	2.53863900	-1.19978900
H	-8.40584700	1.66995400	0.29274100
H	-8.23478100	3.45350500	0.30122300
H	-6.34414900	0.23987300	-0.34202000
H	-5.87611600	1.37852600	-1.64119700
H	-4.72474200	1.00179100	-0.34288600
B	4.69659000	2.48203400	-1.08800600
O	5.94893400	1.94371500	-1.26525800

O	4.76078300	3.67496200	-0.39421400
C	6.92619200	2.88589500	-0.79542700
C	6.08614200	3.80809000	0.14879000
C	7.46147200	3.61594000	-2.02016000
C	8.04606100	2.12841900	-0.11137000
C	6.48327800	5.27126300	0.13020000
C	6.03368900	3.31151000	1.58750100
H	8.28037000	4.31076700	-1.76378200
H	7.84843600	2.86911800	-2.73284300
H	6.66227900	4.18090300	-2.52866000
H	8.58476400	1.51515600	-0.85296000
H	8.77026500	2.82202700	0.35230700
H	7.65912300	1.44629700	0.66432500
H	5.83576100	5.83801800	0.81961200
H	7.52927800	5.39976900	0.46145100
H	6.37318300	5.71386400	-0.87198000
H	6.99612600	3.45310000	2.10954300
H	5.25610800	3.87649300	2.13043100
H	5.75864900	2.24136100	1.63915300
O	-3.73679000	4.76525300	0.57979600
C	-3.52255300	5.38545500	-0.66090000
H	-2.87072300	6.26086600	-0.51232300
H	-3.01733000	4.69636600	-1.36901600
H	-4.46673100	5.71859600	-1.12791300
C	0.58315400	4.18738700	0.33193600
H	-0.42238300	4.27375600	0.77913200
C	0.70861100	4.77907700	-1.03532200
H	0.72270200	5.88898800	-0.96245100
H	1.65647800	4.47914400	-1.52037400
H	-0.12628800	4.50101300	-1.70088100
C	1.71569600	4.45187000	1.27175000
H	1.58630700	3.94716200	2.24481000
H	2.68666900	4.14700300	0.83804900
H	1.78230000	5.54554100	1.46982200

IM4

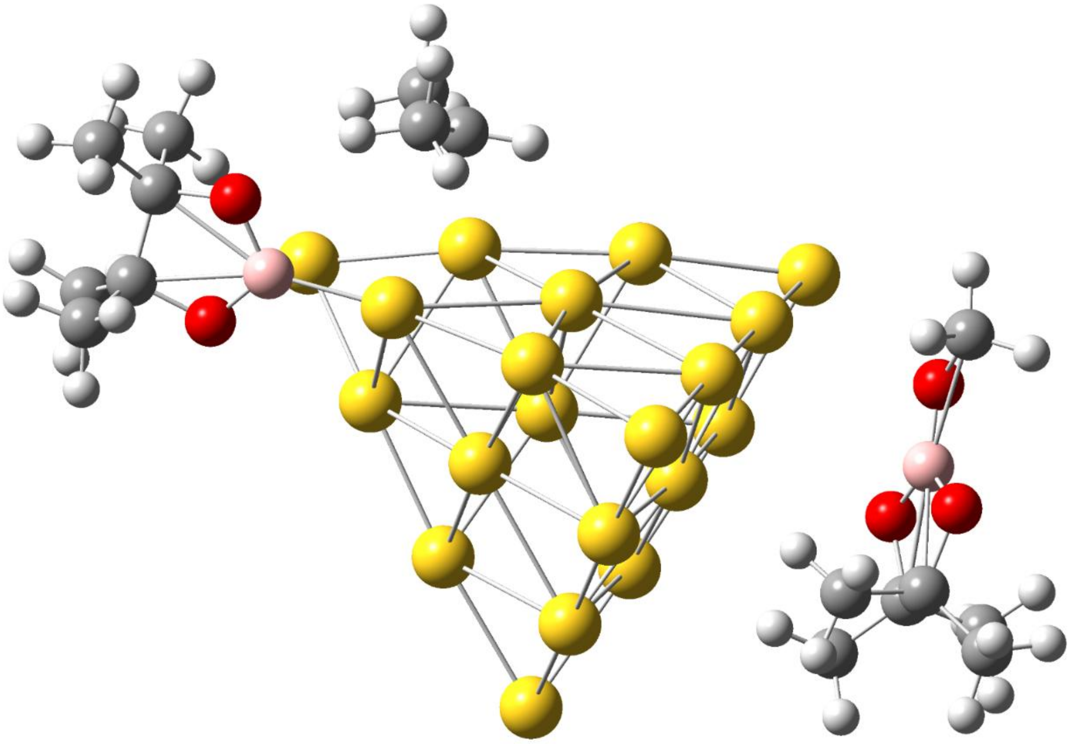


Addition of carbocation (**TS**$_{4\text{-}5}$)

Au	-1.73927300	4.73802200	-1.13549800
Au	-2.46021700	-1.66181100	4.17716600
Au	4.99207700	-1.96369600	1.02128000
Au	-1.25580100	-3.09432900	-3.95610500
Au	-2.03216100	0.01607800	-0.33896000
Au	0.66796900	1.11156900	1.37996400
Au	0.46819300	-1.81496600	0.34921900
Au	0.92443000	0.62196400	-1.60244700
Au	-2.00326300	2.70074100	0.77247700
Au	3.08597500	-1.24778600	-0.87233800
Au	1.00279000	-2.10868800	-2.52387300
Au	-2.24373000	0.60190400	2.49583800
Au	-1.55194700	2.18311800	-2.24008600
Au	2.65203600	-0.99734800	2.07386900
Au	0.11677400	-1.06143500	3.18141600
Au	-1.43134400	-0.39833700	-3.16680900
Au	0.66740100	3.24780400	-0.45024500
Au	3.20717200	1.83031000	-0.15085700
Au	-2.19756700	-2.29088900	1.46105300
Au	-1.76400600	-2.78254100	-1.22622000
B	-5.66699600	0.34746100	1.49360200
O	-5.38333800	-0.79120300	0.78899300
O	-6.42539200	1.25031600	0.79233300
C	-6.18774700	-0.75408800	-0.39942300
C	-6.47935700	0.77824100	-0.56591800
C	-7.44141800	-1.56606000	-0.10796700
C	-5.42349300	-1.37800700	-1.54575500
C	-7.83968900	1.10157500	-1.14555900
C	-5.39624600	1.50746700	-1.33976200
H	-8.09049100	-1.65403900	-0.99407500
H	-7.13937300	-2.57881900	0.20123500
H	-8.02744600	-1.12348800	0.71412200
H	-5.25045200	-2.44756800	-1.34115500
H	-5.99177200	-1.29371600	-2.48785400
H	-4.43614000	-0.91002000	-1.68697300
H	-7.95146100	2.19358100	-1.23673900
H	-7.94560000	0.66461400	-2.15288900
H	-8.65753100	0.73037200	-0.51102400
H	-5.40652200	1.25706500	-2.41319700
H	-5.54137900	2.59453700	-1.23111600
H	-4.39161300	1.27368500	-0.94651000
B	5.27381400	1.54962000	-0.39544300
O	5.85865600	0.67367200	-1.27798700

O	6.22469000	2.22946900	0.33714700
C	7.27989600	0.87238500	-1.25299000
C	7.49941000	1.60319700	0.11230800
C	7.62427900	1.73624400	-2.45665400
C	7.96292000	-0.47398900	-1.36664000
C	8.57539900	2.66909300	0.09477500
C	7.74080600	0.65181500	1.27285000
H	8.71171900	1.88311500	-2.56409500
H	7.24888300	1.23937700	-3.36485200
H	7.13760900	2.72247000	-2.39160400
H	7.75521900	-0.91090500	-2.35633600
H	9.05696700	-0.37344400	-1.25844100
H	7.59261600	-1.18156100	-0.60818500
H	8.65560800	3.12835100	1.09287600
H	9.55662400	2.23129000	-0.15815500
H	8.35025200	3.46956500	-0.62419300
H	8.72765500	0.16455400	1.21082000
H	7.69522000	1.22144900	2.21506000
H	6.96152900	-0.13159300	1.32016400
O	-5.26403100	0.53290700	2.77129000
C	-5.44738500	1.77613400	3.39451000
H	-5.03021200	1.71919900	4.41191900
H	-4.92280400	2.58308800	2.85081800
H	-6.51621900	2.04560600	3.46205800
C	3.29514600	2.95627500	2.71865600
H	2.23613100	2.91781600	3.01482000
C	3.81669800	4.24300300	2.19117900
H	4.04836300	4.95767500	3.01104600
H	4.75373500	4.08805800	1.62672300
H	3.09116300	4.74418100	1.52794000
C	4.22366100	1.98143400	3.34201800
H	3.74194800	1.00108300	3.51802600
H	5.11183300	1.81841400	2.70411200
H	4.59474200	2.33616200	4.32805600

TS$_{4-5}$: Au-C: 3.08 Å

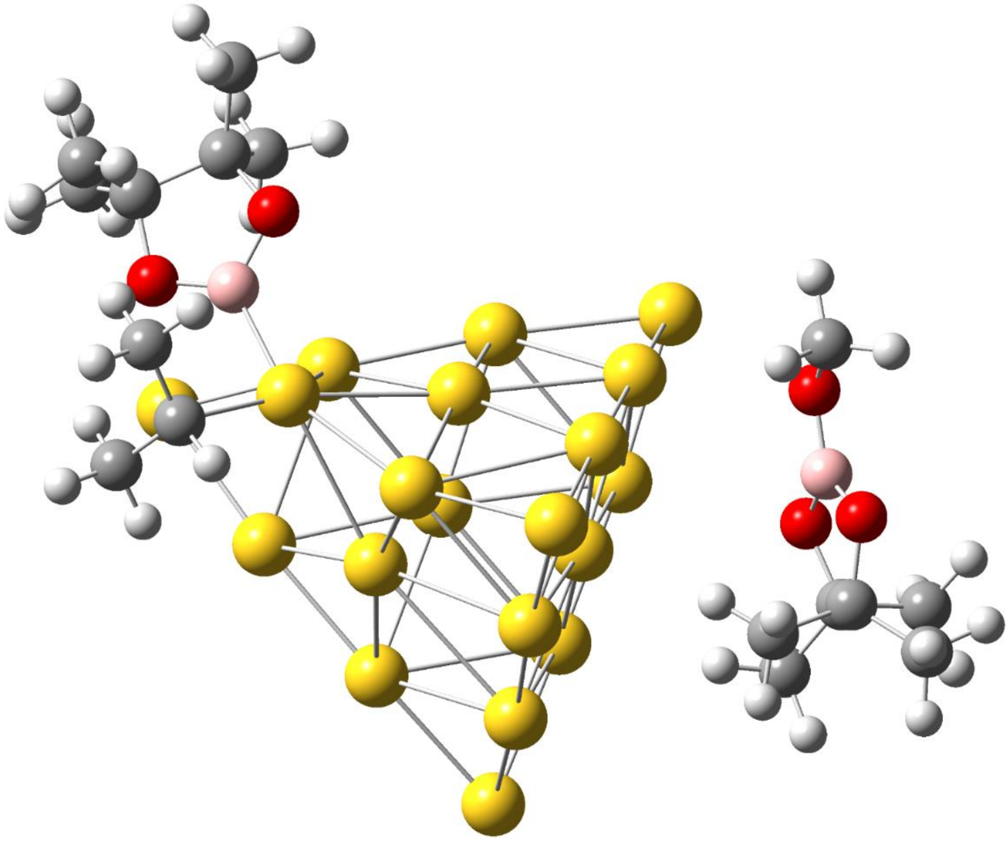


Organogold species (**IM5**)

Au	1.74691100	-3.26779500	-3.56624100
Au	1.28337600	-1.47589600	4.58225400
Au	-5.04110500	1.96129500	0.71451900
Au	2.49227200	4.61993200	-0.97898900
Au	1.97720100	-0.07765000	0.01553700
Au	-0.88405700	-1.58035600	0.21087300
Au	-0.48024500	1.52420900	1.27013500
Au	-0.77021700	0.72802300	-1.75679500
Au	1.55732400	-2.84879200	-0.81590700
Au	-2.64040800	2.55178800	-0.42246100
Au	-0.07387100	3.40416300	-0.97491200
Au	1.41352400	-2.25226600	1.88173300
Au	1.97995400	-0.56552500	-2.85006300
Au	-3.03222200	0.05124800	1.18139600
Au	-0.99045000	-0.69839500	3.01529400
Au	2.32537100	1.98921000	-1.98601100
Au	-0.67788600	-1.86997000	-2.76804700
Au	-3.20519300	-1.30639100	-1.49475600
Au	1.83386400	0.64208900	2.85159100
Au	2.19622600	2.67651100	1.02019400
B	4.88452000	-2.47653100	1.67805700
O	4.89784400	-1.13777500	1.95569100
O	5.76957300	-2.84331900	0.69660400
C	6.02476400	-0.58225000	1.26003600
C	6.26438300	-1.62411800	0.11262500
C	7.17276100	-0.52618800	2.25728700
C	5.68696900	0.81236100	0.78194500
C	7.71554200	-1.81614900	-0.27196300
C	5.42852000	-1.34709700	-1.12352300
H	8.06527300	-0.04079900	1.83054200
H	6.84766800	0.05649100	3.13322100
H	7.45361900	-1.53296900	2.60752700
H	5.53362100	1.47784000	1.64736400
H	6.50716600	1.22492300	0.16977400
H	4.75905300	0.83228600	0.18814600
H	7.78640900	-2.55250600	-1.08808600
H	8.14942900	-0.86802200	-0.63203400
H	8.32023900	-2.18479000	0.56935500
H	5.78253800	-0.46436800	-1.68064700
H	5.46708600	-2.22275500	-1.79175000
H	4.36776600	-1.18028500	-0.86699200
B	-4.84436100	-1.68267200	-0.20604200
O	-6.05588400	-1.04519200	-0.23856100

O	-4.84421200	-2.75365000	0.64969700
C	-6.97084900	-1.77126600	0.60340100
C	-6.01073900	-2.63987500	1.48498300
C	-7.85624100	-2.60262900	-0.31027000
C	-7.81041800	-0.77563800	1.37485000
C	-6.52270600	-4.02889800	1.80291600
C	-5.57778000	-1.95170300	2.77115000
H	-8.64714100	-3.12658400	0.25089700
H	-8.33725800	-1.93410500	-1.04243800
H	-7.26895900	-3.34876000	-0.86934300
H	-8.45279100	-0.21396100	0.67756700
H	-8.46099300	-1.28929200	2.10362300
H	-7.18389500	-0.04522800	1.90991400
H	-5.78025200	-4.56005600	2.41874400
H	-7.46546000	-3.97712300	2.37436200
H	-6.69138300	-4.62470500	0.89477400
H	-6.39436300	-1.91283300	3.51053300
H	-4.73670000	-2.51562300	3.20572300
H	-5.21803200	-0.92329000	2.58954200
O	4.08869900	-3.35196500	2.33753300
C	3.99727600	-4.68185700	1.89710400
H	3.32300600	-5.22691500	2.57511400
H	3.57913300	-4.73981800	0.87483600
H	4.98273600	-5.17941200	1.89526700
C	-4.45897800	-1.29533900	-3.31143300
H	-3.63799100	-1.42448200	-4.03961500
C	-5.07003700	0.07752500	-3.38688600
H	-5.63545600	0.19861200	-4.33504500
H	-5.77721900	0.24928300	-2.55633000
H	-4.30979600	0.87595400	-3.35198300
C	-5.44921200	-2.42293900	-3.39063500
H	-4.97692100	-3.41089200	-3.26539300
H	-6.23779100	-2.31570400	-2.62647000
H	-5.95991600	-2.42170700	-4.37639700

IM5

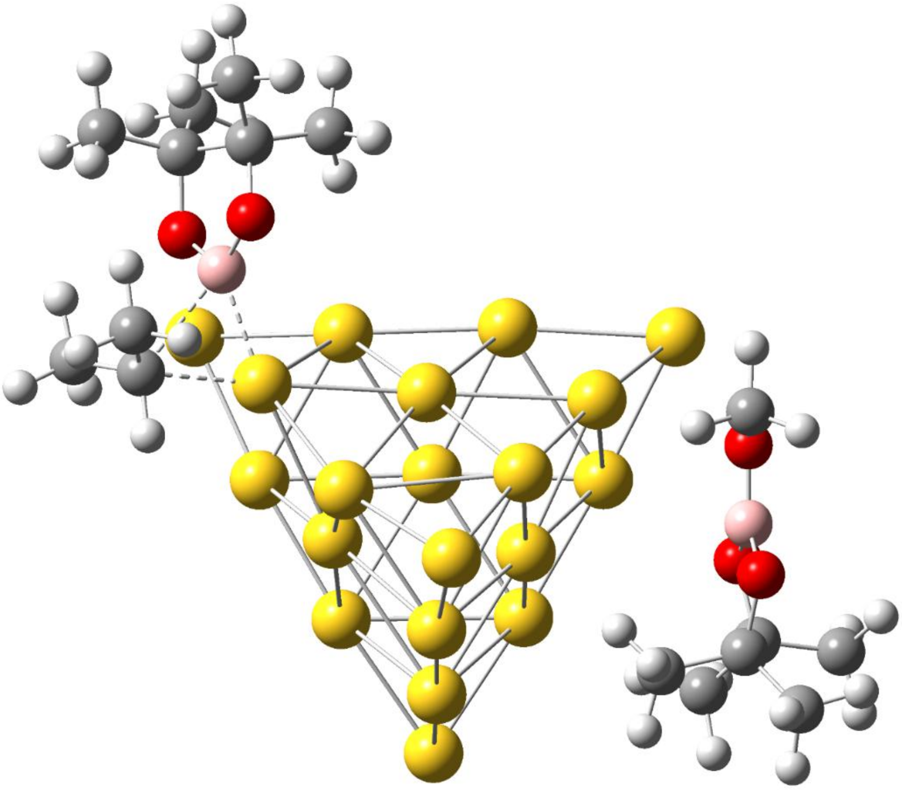


Reductive elimination (**TS**$_{5\text{-}6}$)

Au	1.52357500	-3.48679700	-3.43248000
Au	1.53530400	-1.26832200	4.61498400
Au	-5.02174100	1.98871200	0.68615500
Au	2.53704200	4.52636300	-1.30016400
Au	1.98026100	-0.12141900	-0.04293900
Au	-0.97286900	-1.47046500	0.35687300
Au	-0.35779200	1.65706400	1.26670100
Au	-0.74864500	0.68984800	-1.75198100
Au	1.37066900	-2.90199900	-0.70913300
Au	-2.60336400	2.53156900	-0.44419800
Au	-0.05532700	3.40535900	-1.07480000
Au	1.37493200	-2.16336000	1.95246300
Au	1.81526400	-0.73822800	-2.89007100
Au	-2.95080300	0.28319200	1.47582600
Au	-0.81949100	-0.45965700	3.16398500
Au	2.23821000	1.85016000	-2.15518200
Au	-0.83897900	-1.96923400	-2.64859700
Au	-3.23518400	-1.01510500	-1.29900000
Au	2.01289000	0.74818600	2.74959300
Au	2.34819600	2.66786100	0.79279300
B	4.81220000	-2.62354500	1.54774600
O	4.92360700	-1.27623400	1.75271300
O	5.62070700	-3.09546600	0.54514400
C	6.04596000	-0.83069000	0.97576900
C	6.16085700	-1.94165000	-0.12508400
C	7.24518800	-0.80012200	1.91187700
C	5.77141400	0.55752100	0.44177700
C	7.57532000	-2.24766200	-0.56819300
C	5.28255600	-1.67166200	-1.33275600
H	8.14401700	-0.40027300	1.41531400
H	7.00504400	-0.15156900	2.76870400
H	7.47764500	-1.80397600	2.30357600
H	5.69859500	1.27156200	1.27831600
H	6.58633000	0.88775500	-0.22499200
H	4.82003300	0.60759000	-0.11178100
H	7.55726300	-3.02656100	-1.34684900
H	8.04974300	-1.34936400	-0.99816000
H	8.19762600	-2.61384100	0.26118700
H	5.66173200	-0.84111600	-1.95030100
H	5.23436200	-2.57919300	-1.95620100
H	4.24857200	-1.42538100	-1.03424500
B	-4.99143500	-1.69416300	-0.41306000
O	-5.99250700	-0.96295700	0.15296700

O	-5.06185300	-3.02470700	-0.10458500
C	-6.85151400	-1.87225400	0.86698800
C	-5.93671800	-3.13167200	1.03519400
C	-8.06665200	-2.12552100	-0.00929200
C	-7.27033000	-1.21537000	2.16416200
C	-6.66363900	-4.45668800	0.97271900
C	-5.05589100	-3.07140100	2.27308700
H	-8.81324000	-2.75628100	0.50022100
H	-8.53837300	-1.15916200	-0.24947000
H	-7.78886400	-2.61024600	-0.95940900
H	-7.90791000	-0.34281700	1.94805100
H	-7.84733300	-1.91633600	2.79157800
H	-6.40145900	-0.85637000	2.73493300
H	-5.94295300	-5.27879800	1.10421600
H	-7.41421400	-4.52865500	1.77835100
H	-7.16664800	-4.60284000	0.00564500
H	-5.63454600	-3.22343900	3.19841500
H	-4.29343200	-3.86320700	2.20212000
H	-4.51638600	-2.11060400	2.34483100
O	4.00011800	-3.41215900	2.29153400
C	3.80639300	-4.75467700	1.93060500
H	3.14219800	-5.22182900	2.67368100
H	3.32663400	-4.83981600	0.93760200
H	4.75954500	-5.31089000	1.90159400
C	-4.88599400	-1.23460500	-2.82117800
H	-4.10864000	-0.88759000	-3.52961700
C	-6.00765800	-0.22581100	-2.80030600
H	-6.40223500	-0.08426800	-3.82617300
H	-6.84980500	-0.54132800	-2.16404400
H	-5.67309700	0.75784600	-2.43013800
C	-5.29272900	-2.63688000	-3.20526100
H	-4.43811300	-3.33245600	-3.18206800
H	-6.07018300	-3.05408700	-2.54259100
H	-5.70538100	-2.64170200	-4.23401400

TS$_{5\text{-}6}$: Au-B: 2.08 Å, Au-C: 2.26 Å, B-C: 2.45 Å

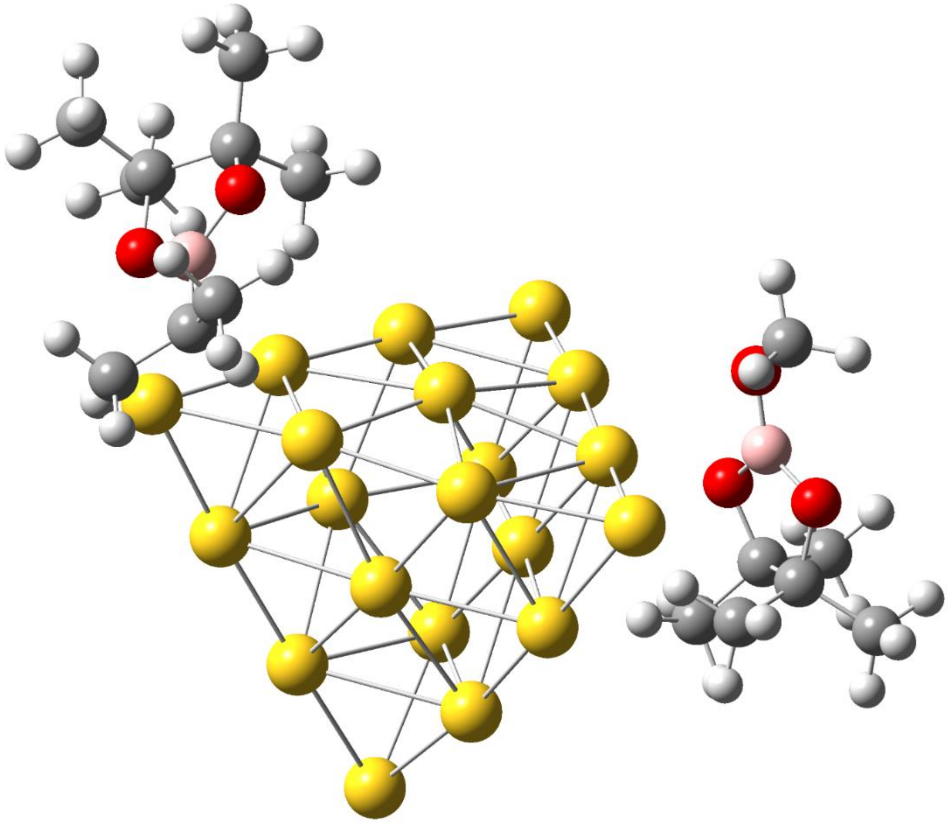


Au_{20}^{-} + *i*PrB(pin) + MeOB(pin) (**IM6**)

Au	0.99097500	-3.00401000	-4.07000500
Au	1.56244800	-2.15772400	4.23048300
Au	-4.85520500	1.41125000	0.23873700
Au	2.77931200	4.71878600	-0.41868600
Au	1.90353400	-0.15229900	-0.13158100
Au	-0.97858000	-1.56372200	0.17385000
Au	-0.24029900	1.60808800	1.71543200
Au	-0.43489500	1.20392300	-1.70834300
Au	1.25170200	-2.73414300	-1.31546800
Au	-2.37261200	2.61151500	-0.04894900
Au	0.17378800	3.66785500	-0.33549900
Au	1.43425600	-2.54001700	1.45166000
Au	1.63658000	-0.29540200	-3.06936800
Au	-2.78556800	0.17656300	1.68774900
Au	-0.69177100	-0.97543800	3.03781800
Au	2.36789400	2.15770700	-1.80091900
Au	-1.04674900	-1.42008200	-2.79344000
Au	-3.02725700	-0.15371800	-1.29675500
Au	2.07635100	0.20506600	2.77954100
Au	2.53837600	2.38605200	1.13634600
B	4.54424600	-3.57038500	0.76584100
O	4.84049000	-2.44451700	1.48123900
O	5.26657100	-3.69325700	-0.39278500
C	5.97994800	-1.83644000	0.85352100
C	5.93446100	-2.43421000	-0.59713500
C	7.20376000	-2.28232500	1.63932900
C	5.84105800	-0.33126100	0.91484600
C	7.29112500	-2.69144200	-1.21677500
C	5.07422700	-1.62117100	-1.54700800
H	8.12581300	-1.80370200	1.27196300
H	7.06454100	-2.00097200	2.69480000
H	7.33407700	-3.37608900	1.59628500
H	5.88919400	0.00620000	1.96294200
H	6.65643000	0.16065400	0.35757500
H	4.87680900	0.01130000	0.50640100
H	7.16094600	-3.09992100	-2.23129900
H	7.86326000	-1.75204300	-1.30018100
H	7.88090700	-3.41430200	-0.63468500
H	5.53789500	-0.65826700	-1.81618000
H	4.90541900	-2.20102500	-2.46933600
H	4.08234100	-1.41024000	-1.10927700
B	-6.71033600	-1.47996700	-0.66274500
O	-6.83617300	-0.64349200	0.42494900

O	-6.67281100	-2.79657700	-0.29684200
C	-7.06921400	-1.46905000	1.58545400
C	-6.49077100	-2.84789900	1.13000500
C	-8.57486500	-1.49670200	1.79976600
C	-6.38781600	-0.86334300	2.79195800
C	-7.22544800	-4.05192500	1.67853300
C	-4.99927700	-2.98359700	1.38477100
H	-8.84757400	-2.05325700	2.71076300
H	-8.93683300	-0.46209600	1.90683600
H	-9.09647100	-1.95092200	0.94180300
H	-6.84664300	0.10963800	3.03249800
H	-6.50183500	-1.52196800	3.66975100
H	-5.31209800	-0.69037100	2.62406800
H	-6.74446900	-4.97337100	1.31480800
H	-7.18646800	-4.06174200	2.78098000
H	-8.27792700	-4.07378400	1.36091500
H	-4.76752900	-3.10652600	2.45536400
H	-4.62257300	-3.86678900	0.84505900
H	-4.43800200	-2.10917600	1.01244900
O	3.63071800	-4.47750000	1.18948700
C	3.22672400	-5.51442600	0.33233200
H	2.55106500	-6.18264800	0.88647800
H	2.67659600	-5.11871500	-0.54428400
H	4.08720500	-6.09814500	-0.03724900
C	-6.60358500	-0.98508500	-2.14732900
H	-5.50180400	-0.91426800	-2.31883000
C	-7.19340400	0.40222600	-2.35940400
H	-7.05066100	0.75108800	-3.39673500
H	-8.27843600	0.41476600	-2.15132200
H	-6.72757200	1.15243300	-1.69305700
C	-7.15945200	-2.00441200	-3.13505200
H	-6.70332600	-2.99724400	-2.99820300
H	-8.25068300	-2.12602900	-3.00830200
H	-6.98639000	-1.69131300	-4.17909200

IM6



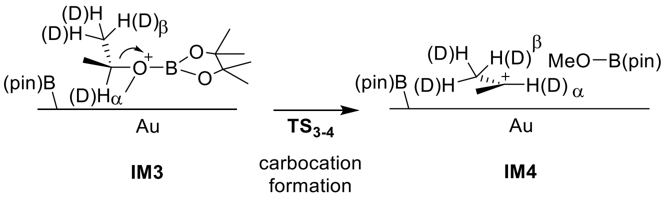
9.3 Summary

Table S2. Calculation summary of intermediates (**IM**) and transition states (**TS**)

	charge	mult.	*E* (au)	*G* (au)	ν_{imag} (cm^{-1})
Au_{20}^{-} + $B_2(pin)_2$ (**IM0'**)	-1	2	-3537.63662563	-3537.407017	-
Oxidative addition of $B_2(pin)_2$ (**TS$_0$**)	-1	2	-3537.59499964	-3537.363231	-41.8725
Au_{20}^{-}-(B(pin))$_2$ (**IM0**)	-1	2	-3537.60486121	-3537.376391	-
*i*PrOMe	0	1	-233.313762682	-233.207970	-
Au_{20}^{-}-(B(pin))$_2$ + *i*PrOMe (**IM1**)	-1	2	-3770.93518551	-3770.578589	-
Acid-base complexation (**TS$_{1-2}$**)	-1	2	-3770.92674904	-3770.568509	-139.0504
Acid-base complex (**IM2**)	-1	2	-3770.92891678	-3770.570140	-
Elimination of boryloxonium (**TS$_{2-3}$**)	-1	2	-3770.92722549	-3770.567241	-119.1726
Boryloxonium (**IM3**)	-1	2	-3770.93220669	-3770.573898	-
Carbocation formation (**TS$_{3-4}$**)	-1	2	-3770.92336946	-3770.569095	-173.8925
Carbocation (**IM4**)	-1	2	-3770.97745562	-3770.625306	-
Addition of carbocation (**TS$_{4-5}$**)	-1	2	-3770.96854576	-3770.618158	-15.9087
Organogold species (**IM5**)	-1	2	-3770.97497031	-3770.620743	-
Reductive elimination (**TS$_{5-6}$**)	-1	2	-3770.96890990	-3770.614932	-164.2218
Au_{20}^{-} + *i*PrB(pin) + MeOB(pin) (**IM6**)	-1	2	-3771.03997034	-3770.689078	-

9.4 Secondary kinetic isotope effects (SKIEs)

Table S3. Calculation of SKIE values



$$\mathrm{KIE} = \frac{k_H}{k_D} = exp\left(\frac{\Delta G_D^{\ddagger} - \Delta G_H^{\ddagger}}{RT}\right)$$

	IM3 (au)	**TS$_{3-4}$** (au)	$\Delta G^{\ddagger}$ (kcal/mol)	estimated KIE
all H	-3770.573898	-3770.569095	3.014	-
α-D	-3770.577459	-3770.572466	3.133	1.22
β-D_3	-3770.583890	-3770.579017	3.058	1.08

9.5 LUMO of IM4 (carbocation intermediate)

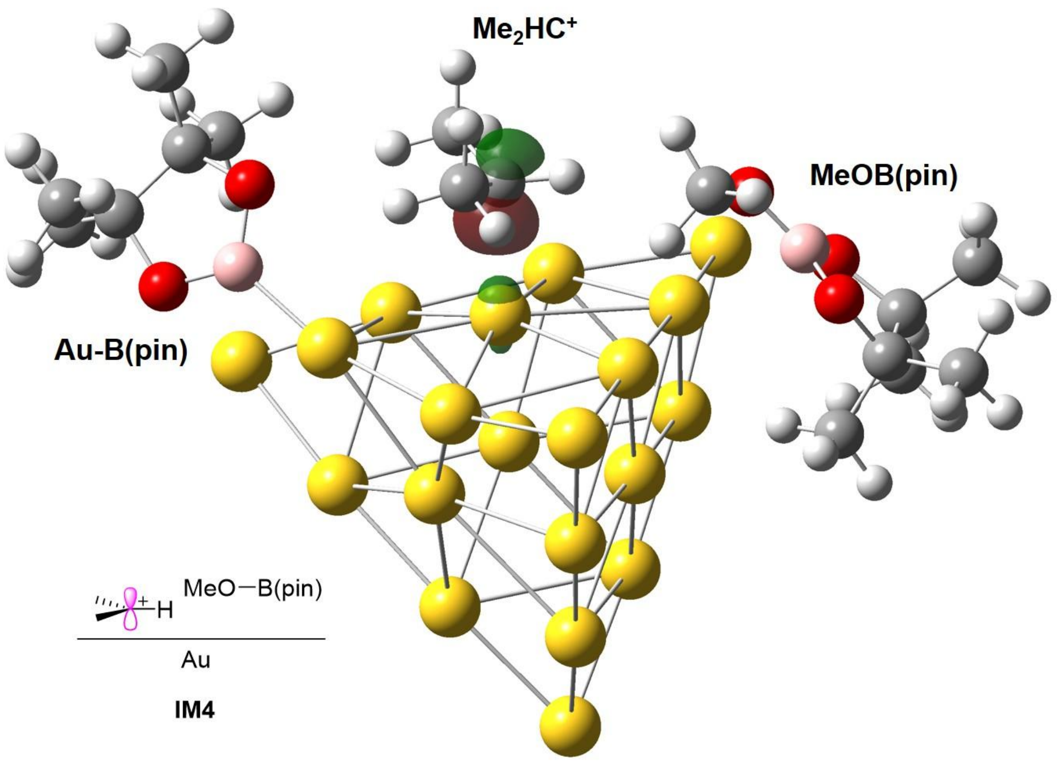
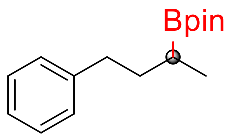


Figure S1. LUMO of **IM4**.

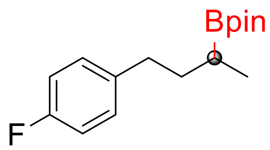
10. Analytic data of products

4,4,5,5-Tetramethyl-2-(4-phenylbutan-2-yl)-1,3,2-dioxaborolane (2a)[41]



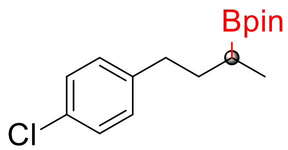
Colorless oil; yield 80%, 62.4 mg (0.24 mmol); Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.21 (m, 2H), 7.21–7.12 (m, 2H), 2.66–2.58 (m, 2H), 1.84–1.73 (m, 1H), 1.65–1.52 (m, 1H), 1.24 (s, 12H), 1.11–1.07 (m, 1H), 1.02 (d, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.05, 128.41, 128.17, 125.48, 82.84, 35.28, 35.27, 24.77, 24.71, 15.39.

2-(4-(4-fluorophenyl)butan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2b)



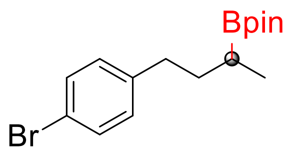
Colorless oil; yield 73%, 60.9 mg (0.22 mmol); Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15–7.10 (m, 2H), 6.97–6.91 (m, 2H), 2.63–2.53 (m, 2H), 1.82–1.69 (m, 1H), 1.61–1.49 (m, 1H), 1.25 (s, 12H), 1.10–0.99 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.09 (d, $^1J_{CF}$ = 242.0 Hz), 138.59 (d, $^4J_{CF}$ = 3.15 Hz), 129.68 (d, $^3J_{CF}$ = 7.73 Hz), 114.85 (d, $^2J_{CF}$ = 21.1 Hz), 83.04, 35.17, 34.76, 24.88, 24.83, 15.49. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{16}H_{24}BFNaO_2$: 301.1745, found: 301.1745.

2-(4-(4-Chlorophenyl)butan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c)



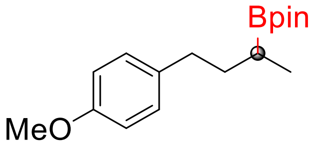
Colorless oil; yield 86%, 76.1 mg (0.26 mmol); Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (*d*, J = 8.3 Hz, 2H), 7.10 (*d*, J = 8.4 Hz, 2H), 2.62–2.54 (m, 2H), 1.82–1.69 (m, 1H), 1.61–1.50 (m, 1H), 1.24 (s, 12H), 1.10–0.96 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.43, 131.14, 129.75, 128.23, 82.89, 35.10, 34.57, 24.74, 24.69, 15.36. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{16}H_{24}BClNaO_2$: 317.1450, found: 317.1450.

2-(4-(4-Bromophenyl)butan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d)



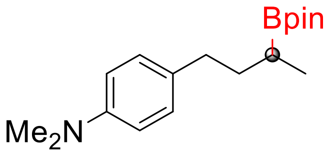
Colorless oil; yield 80%, 81.4 mg (0.24 mmol); Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.3 Hz, 2H), 7.05 (d, J = 8.3 Hz, 2H), 2.63–2.51 (m, 2H), 1.81–1.69 (m, 1H), 1.60–1.49 (m, 1H), 1.24 (s, 12H), 1.10–0.97 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.96, 131.19, 130.20, 119.17, 82.91, 35.04, 34.63, 24.75, 24.70, 15.36. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{16}H_{24}BBrNaO_2$: 361.0944, found: 361.0945.

2-(4-(4-Methoxyphenyl)butan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e)[42]



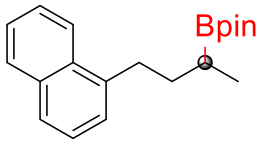
Colorless oil; yield 82%, 71.3 mg (0.25 mmol); Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 3.77 (s, 3H), 2.60–2.52 (m, 2H), 1.81–1.68 (m, 1H), 1.60–1.51 (m, 1H), 1.24 (s, 12H), 1.10–0.97 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.53, 135.15, 129.25, 113.59, 82.83, 55.19, 35.49, 34.32, 24.75, 24.70, 15.38.

N,N-Dimethyl-4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)aniline (2f)



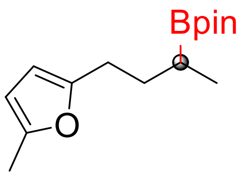
Colorless oil; yield 39%, 35.4 mg (0.12 mmol); Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.7 Hz, 2H), 6.69 (d, *J* = 8.7 Hz, 2H), 2.90 (s, 6H), 2.58–2.47 (m, 2H), 1.80–1.68 (m, 1H), 1.60–1.48 (m, 1H), 1.24 (s, 12H), 1.12–1.02 (m, 1H), 1.01 (d, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.91, 131.51, 128.97, 113.10, 99.91, 82.82, 41.03, 35.57, 34.22, 24.74, 15.39. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{18}H_{31}BNO_2$: 304.2442, found: 304.2442.

4,4,5,5-Tetramethyl-2-(4-(naphthalen-1-yl)butan-2-yl)-1,3,2-dioxaborolane (2g)



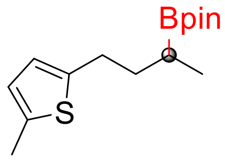
Colorless oil; yield 72%, 67 mg (0.22 mmol); Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17–8.15 (m, 1H), 7.84–7.82 (m, 1H), 7.69–7.67 (m, 1H), 7.53–7.42 (m, 2H), 7.41–7.29 (m, 2H), 3.15–3.01 (m, 2H), 1.97–1.83 (m, 1H), 1.79–1.66 (m, 1H), 1.28 (s, 12H), 1.24–1.17 (m, 1H), 1.10–1.08 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.32, 133.84, 131.94, 128.62, 126.31, 125.88, 125.56, 125.51, 125.28, 124.17, 82.97, 34.80, 32.72, 24.85, 24.77, 15.57. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{20}H_{27}BNaO_2$: 333.1996, found: 333.1996.

4,4,5,5-Tetramethyl-2-(4-(5-methylfuran-2-yl)butan-2-yl)-1,3,2-dioxaborolane (2h)[43]



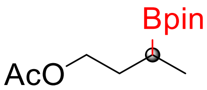
Colorless oil; yield 80%, 63.4 mg (0.24 mmol); Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85–5.82 (m, 2H), 2.59 (t, *J* = 8.0 Hz, 2H), 2.24 (s, 3H), 1.83–1.70 (m, 1H), 1.65–1.52 (m, 1H), 1.24 (s, 12H), 1.09–1.04 (m, 1H), 1.01–0.99 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.82, 149.89, 105.69, 105.01, 82.86, 31.50, 27.27, 24.72, 24.67, 15.27, 13.47.

4,4,5,5-Tetramethyl-2-(4-(5-methylthiophen-2-yl)butan-2-yl)-1,3,2-dioxaborolane (2i)



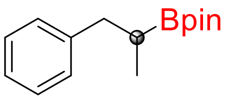
Colorless oil; yield 75%, 63 mg (0.23 mmol); Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.55–6.52 (m, 2H), 2.81–2.69 (m, 2H), 2.42 (s, 3H), 1.86–1.76 (m, 1H), 1.66–1.57 (m, 1H), 1.24 (s, 12H), 1.12–1.05 (m, 1H), 1.00 (d, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.66, 136.95, 124.51, 123.53, 82.89, 35.31, 29.32, 24.75, 24.71, 15.30, 15.25. HRMS (ESI) m/z [M+Na]$^+$ calcd for $C_{15}H_{25}NaBO_2S$: 303.1560, found: 303.1560.

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)butylacetate (2j)



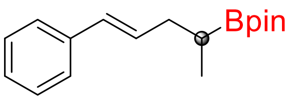
Yellow oil; yield 61%, 44 mg (0.18 mmol); Hexane/EtOAc = 95/5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.07 (t, J = 7.1 Hz, 2H), 2.0 (s, 3H), 1.81–1.73 (m, 1H), 1.61–1.53 (m, 1H), 1.21 (s, 12H), 1.13–1.04 (m, 1H), 0,97 (d, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.24, 83.07, 64.02, 31.70, 24.76, 24.68, 21.07, 15.30. HRMS (ESI) m/z [M + Na]$^+$ calcd for $C_{12}H_{23}BNaO_4$: 265.1581; found: 265.1581.

4,4,5,5-Tetramethyl-2-(1-phenylpropan-2-yl)-1,3,2-dioxaborolane (2k)[44]



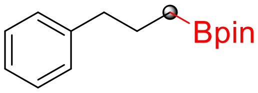
Colorless oil; yield 46%, 33.9 mg (0.14 mmol); Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.18 (m, 4H), 7.16–7.13 (m, 1H), 2.80 (dd, J = 13.6, 7.5 Hz, 1H), 2.54 (dd, J = 13.6, 8.3 Hz, 1H), 1.43–1.32 (m, 1H), 1.18 (d, J = 4.5 Hz, 1H), 0.96 (d, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.29, 128.87, 127.98, 125.53, 82.96, 38.93, 24.68, 24.66, 15.16.

(*E*)-4,4,5,5-Tetramethyl-2-(5-phenylpent-4-en-2-yl)-1,3,2-dioxaborolane (2l)



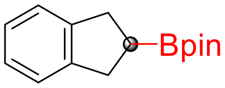
Colorless oil; yield 53%, 43 mg (0.16 mmol); Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.24 (m, 6H), 7.17–7.14 (m, 1H), 6.38 (d, J = 15.8 Hz, 1H), 6.29–6.16 (m, 1H), 2.41–2.28 (m, 1H), 2.28–2.16 (m, 1H), 1.24–1.23 (m, 1H), 1.23 (s, 12H), 1.02 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.96, 130.74, 130.28, 128.39, 126.65, 125.91, 82.99, 36.50, 24.79, 24.74, 15.21. HRMS (ESI) m/z [M+Na]$^+$ calcd for $C_{17}H_{25}NaBO_2$: 295.1839, found: 295.1840.

4,4,5,5-Tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane (2m)[45]



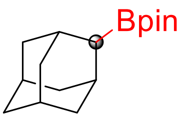
Colorless oil; yield 17%, 12.5 mg (0.05 mmol); Hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.23 (m, 2H), 7.18–7.13 (m, 3H), 2.65–2.53 (m, 2H), 1.77–1.68 (m, 2H), 1.24 (s, 12H), 0.90–0.87 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.66, 128.53, 128.14, 125.54, 82.90, 38.57, 26.09, 24.80.

2-(2,3-Dihydro-1*H*-inden-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2o)[46]



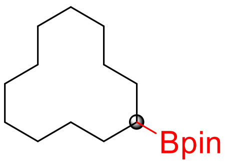
Colorless oil; yield 88%, 64.4 mg (0.26 mmol); Hexane/EtOAc = 99/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21–7.19 (m, 2H), 7.12–7.08 (m, 2H), 3.09–2.93 (m, 4H), 1.93–1.83 (m, 1H), 1.25 (s, 12H).^{13}C NMR (101 MHz, $CDCl_3$) δ 144.38, 125.86, 124.16, 83.22, 35.10, 24.75, 24.52.

2-((1r,3r,5r,7r)-adamantan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2p)[47]



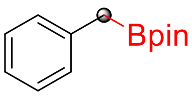
Colorless solid; yield 89%, 70 mg (0.27 mmol); Hexane/EtOAc = 99/1; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 2.12–2.03 (m, 2H), 1.86–1.65 (m, 12H), 1.38–1.31 (m, 1H), 1.22 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 82.68, 39.26, 36.20, 29.26, 28.17, 28.05, 24.75.

2-Cyclododecyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2q)[48]



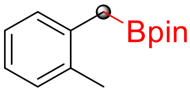
Colorless solid; yield 62%, 36.9 mg (0.19 mmol); Hexane/EtOAc = 99/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45–1.18 (m, 22H), 1.21 (s, 12H), 1.05–1.00 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 82.73, 24.86, 24.74, 24.23, 24.07, 23.41, 23.38, 23.35.

2-Benzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2r)[49]



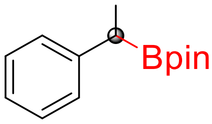
Colorless oil; yield 89%, 58.2 mg (0.27 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20–7.08 (m, 4H), 7.06–6.96 (m, 1H), 2.21 (s, 2H), 1.14 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.56, 128.92, 128.19, 124.76, 83.33, 24.65.

4,4,5,5-Tetramethyl-2-(2-methylbenzyl)-1,3,2-dioxaborolane (2s)[49]



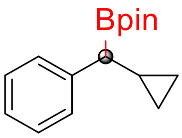
Colorless oil; yield 89%, 58.2 mg (0.25 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20–7.03 (m, 4H), 2.30 (s, 3H), 2.29 (s, 2H), 1.25 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.44, 135.81, 129.71, 129.38, 125.78, 125.08, 83.26, 24.65, 20.02.

4,4,5,5-Tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane (2t)[50]



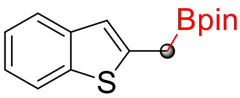
Colorless oil; yield 69%, 48 mg (0.21 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.21 (m, 4H), 7.14–7.11 (m, 1H), 2.43 (q, J = 7.5 Hz, 1H), 1.33 (d, J = 6.3 Hz, 3H), 1.20 (d, J = 5.4 Hz, 13H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.93, 128.27, 127.75, 125.05, 83.25, 24.58, 24.54, 17.01.

2-(Cyclopropyl(phenyl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2u)[51]



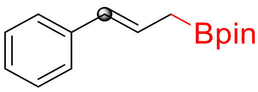
Colorless oil; yield 82%, 63.5 mg (0.25 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.25 (m, 4H), 7.18–7.11 (m, 1H), 1.72 (d, J = 9.7 Hz, 1H), 1.22 (d, J = 1.3 Hz, 12H), 0.59–0.54 (m, 1H), 0.52–0.39 (m, 1H), 0.28–0.22 (m, 1H), 0.12–0.02 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.04, 128.16 (2), 125.20, 83.27, 24.56, 24.54, 13.02, 4.98, 4.66.

2-(Benzo[*b*]thiophen-2-ylmethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2v)



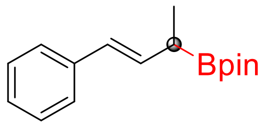
Colorless oil; yield 76%, 63 mg (0.23 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.9 Hz, 1H), 7.67–7.59 (m, 1H), 7.28–7.26 (m, 1H), 7.23–7.17 (m, 1H), 7.01 (s, 1H), 2.56 (s, 2H), 1.27 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.71, 140.63, 139.58, 123.84, 123.00, 122.41, 121.82, 121.17, 83.86, 24.72. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{15}H_{19}BNaO_2S$: 297.1091, found: 297.1091.

2-Cinnamyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2w)[52]



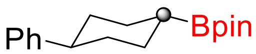
Colorless oil; yield 75%, 54.7 mg (0.23 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.29 (m, 2H), 7.26–7.24 (m, 2H), 7.156–7.13 (m, 1H), 6.41–6.22 (m, 2H), 1.87 (d, J = 7.1 Hz, 2H), 1.25 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.15, 130.21, 128.34, 126.46, 126.25, 125.79, 83.35, 24.76.

(*E*)-4,4,5,5-Tetramethyl-2-(4-phenylbut-3-en-2-yl)-1,3,2-dioxaborolane (2x)[53]



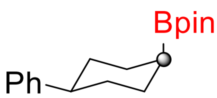
Colorless oil; yield 83%, 62.4 mg (0.25 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.33 (m, 2H), 7.31–7.23 (m, 2H), 7. 71–7.14 (m, 1H), 6.35–6.34 (m, 2H), 2.09–2.03 (m, 1H), 1.24 (s, 12H), 1.19 (d, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.23, 133.25, 128.35, 127.56, 126.45, 125.85, 83.24, 24.68, 24.61, 14.79.

4,4,5,5-Tetramethyl-2-((1r,4r)-4-phenylcyclohexyl)-1,3,2-dioxaborolane (*trans*-2y)[54]



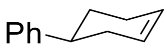
Colorless oil; yield 44%, 37.8 mg (0.13 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.25 (m, 2H), 7.22–7.13 (m, 3H), 2.52–2.46 (m, 1H), 1.95–1.87 (m, 4H), 1.49–1.32 (m, 4H), 1.25 (s, 12H), 0.97–0.92 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.04, 128.21, 126.79, 125.72, 82.82, 44.35, 35.01, 28.15, 24.72.

4,4,5,5-Tetramethyl-2-((1s,4s)-4-phenylcyclohexyl)-1,3,2-dioxaborolane (*cis*-2y)



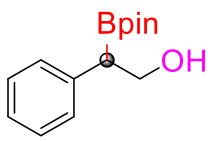
Colorless oil; yield 9%, 8 mg (0.03 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.26 (m, 2H), 7.21–7.12 (m, 3H), 2.53–2.41 (m, 1H), 2.02 (d, J = 10.1 Hz, 2H), 1.82 (d, J = 11.6 Hz, 2H), 1.61–1.46 (m, 4H), 1.38 (s, 1H), 1.29 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.92, 128.25, 126.79, 125.68, 83.01, 44.50, 33.31, 27.88, 24.85. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{18}H_{27}BNaO_2$: 309.1996, found: 309.1996.

1,2,3,6-Tetrahydro-1,1'-biphenyl (1y')[55]



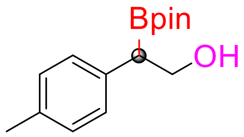
Colorless oil; yield 9%, 4.3 mg (0.027 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.27 (m, 2H), 7.26–7.17 (m, 3H), 5.82–5.72 (m, 2H), 2.85–2.75 (m, 1H), 2.34–2.23 (m, 1H), 2.23–2.09 (m, 3H), 1.98–1.89 (m, 1H), 1.82–1.69 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.35, 128.35, 126.98, 126.89, 126.78, 125.96, 40.15, 33.40, 29.71, 25.89.

2-Phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethan-1-ol (4a')



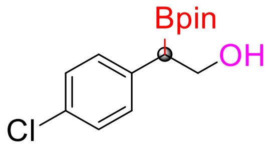
Colorless oil; yield 80%, 59.5 mg (0.24 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (m, 2H), 7.24–7.16 (m, 3H), 3.91 (q, J = 6.8 Hz, 2H), 2.65 (t, J = 7.4 Hz, 1H), 1.95 (s, 1H), 1.25 (s, 6H), 1.23 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.37, 128.98, 128.62, 125.98, 83.71, 65.32, 24.69, 24.60. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{14}H_{21}BNaO_3$: 271.1476, found: 271.1475.

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(p-tolyl)ethan-1-ol (4b')



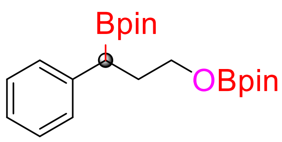
Colorless oil; yield 76%, 59.7 mg (0.23 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13–7.06 (m, 4H), 3.94–3.79 (m, 2H), 2.60 (t, J = 7.5 Hz, 1H), 2.29 (s, 3H), 2.10 (s, 1H), 1.24 (s, 6H), 1.22 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.36, 135.17, 129.18, 128.72, 83.47, 65.21, 24.88, 24.56, 24.50, 20.86. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{15}H_{23}BNaO_3$: 285.1632, found: 285.1632.

2-(4-Chlorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethan-1-ol (4c')



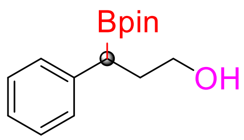
Colorless oil; yield 35%, 29.6 mg (0.11 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.24 (m, 2H), 7.19–7.14 (m, 2H), 3.95–3.82 (m, 2H), 2.62 (t, J = 7.2 Hz, 1H), 1.96 (s, 1H), 1.25 (s, 6H), 1.23 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.31, 131.75, 130.26, 128.69, 83.87, 65.07, 24.69, 24.60. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{14}H_{20}BClNaO_3$: 305.1086, found: 305.1086.

4,4,5,5-Tetramethyl-2-(1-phenyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)propyl)-1,3,2-dioxaborolane (4d)



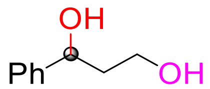
Due to oxy-borolane would undergo decomposition by silica, the **4d** was not purified. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.17 (m, 4H), 7.11 (m, 1H), 3.89–3.80 (m, 1H), 3.80–3.71 (m, 1H), 2.47 (t, J = 7.8 Hz, 1H), 2.19–2.10 (m, 1H), 1.92–1.88 (m, 1H), 1.25 (s, 6H), 1.23 (s, 6H), 1.19 (s, 6H), 1.17 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.42, 128.22, 128.08, 125.04, 83.10, 82.36, 63.90, 33.82, 24.80, 24.40, 24.37, 24.31.

3-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-ol (4d')



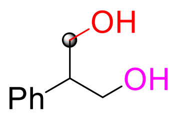
Due to alkyl boronates in the presence of OH would undergo self-oligomerization by silica, the crude **4d'** was not purified. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.17 (m, 4H), 7.13–7.11 (m, 1H), 3.64 (s, 1H), 3.59 (s, 1H), 2.43 (t, J = 7.8 Hz, 1H), 2.17–2.10 (m, 1H), 1.90–1.87 (m, 1H), 1.20 (s, 6H), 1.18 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.39, 128.23, 128.21, 125.21, 83.42, 75.26, 36.98, 24.35, 24.31.

1-Phenylpropane-1,3-diol (4d'')[56]



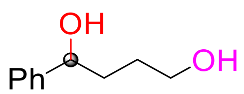
Colorless oil; yield 85%, 38.76 mg (0.26 mmol); Hexane/EtOAc = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.24 (m, 4H), 7.26–7.20 (m, 1H), 4.84 (dd, J = 8.5, 3.9 Hz, 1H), 4.04 (s, 1H), 3.77–3.67 (m, 3H), 1.99–1.77 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.06, 128.38, 127.42, 125.63, 73.25, 60.62, 40.27.

2-Phenylpropane-1,3-diol (4e'')[57]



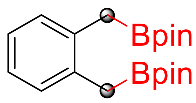
Colorless oil; yield 89%, 40.6 mg (0.27 mmol); Hexane/EtOAc = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.07 (m, 5H), 4.03–3.83 (m, 4H), 3.12–3.05 (m, 1H), 2.76 (brs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.23, 128.77, 127.99, 127.18, 66.00, 49.67.

1-Phenylbutane-1,4-diol (4f'')[58]



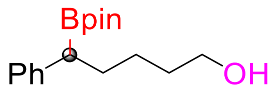
Colorless oil; yield 70%, 34.9 mg (0.21 mmol); Hexane/EtOAc = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.29 (m, 4H), 7.25–7.21 (m, 1H), 4.67–4.58 (m, 1H), 3.72 (brs, 1H), 3.61–3.50 (m, 2H), 1.80–1.75 (m, 2H), 1.66–1.53 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.65, 128.29, 127.27, 125.75, 74.07, 62.47, 36.22, 29.00.

1,2-Bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzene (4g)[59]



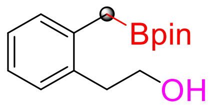
White solid; yield 75%, 77.3 mg (0.23 mmol); Hexane/EtOAc = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13–7.10 (m, 2H), 7.05–6.98 (m, 2H), 2.26 (s, 4H), 1.22 (s, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.87, 129.57, 125.07, 83.21, 24.70.

5-Phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-1-ol (4h')



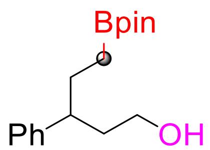
Colorless oil; yield 54%, 46.6 mg (0.16 mmol); Hexane/EtOAc = 3/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.15 (m, 4H), 7.15–7.07 (m, 1H), 3.58 (t, *J* = 6.7 Hz, 2H), 2.29 (t, *J* = 7.9 Hz, 1H), 2.01–1.78 (m, 2H), 1.71–1.60 (m, 1H), 1.60–1.48 (m, 2H), 1.35–1.27 (m, 2H), 1.18 (d, *J* = 8.3 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.09, 128.28, 128.22, 125.13, 83.27, 62.64, 32.53, 32.08, 25.23, 24.55, 24.51. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{17}H_{27}BNaO_3$: 313.1945, found: 313.1945.

2-(2-((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)phenyl)ethan-1-ol (4i')



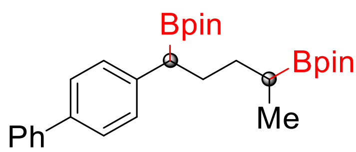
Colorless oil; yield 73%, 57.4 mg (0.22 mmol); Hexane/EtOAc = 2/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.33 (m, 4H), 7.29–7.26 (m, 1H), 4.67 (dd, *J* = 5.6; 7.6 Hz, 1H), 3.62 (t, *J* = 6.4 Hz, 2H), 1.95 (brs, 2H), 1.85–1.80 (m, 1H), 1.76–1.70 (m, 1H), 1.62–1.56 (m, 2H), 1.54–1.49 (m, 1H), 1.39–1.35 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.39, 135.92, 129.97, 129.75, 126.40, 125.28, 83.53, 74.94, 62.73, 36.27, 24.68, 24.54. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{15}H_{23}BNaO_3$: 285.1632, found: 285.1632.

3-Phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-1-ol (4j')



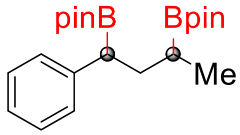
Colorless oil; yield 75%, 65 mg (0.23 mmol); Hexane/EtOAc = 5/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.24 (m, 2H), 7.20–7.12 (m, 3H), 3.64–3.36 (m, 2H), 2.65–2.57 (m, 1H), 1.99–1.88 (m, 1H), 1.87–1.73 (m, 2H), 1.70–1.60 (m, 1H), 1.22 (s, 12H), 0.67–0.62 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.93, 128.37, 127.77, 126.10, 82.95, 61.27, 44.67, 39.06, 30.85, 25.00, 24.79, 24.78. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{17}H_{27}BNaO_3$: 313.1945, found: 313.1945.

2,2'-(1-([1,1'-Biphenyl]-4-yl)pentane-1,4-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6a)



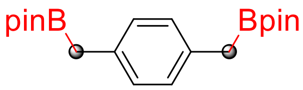
White solid; yield 75%, 107 mg (0.23 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.1 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.40–7.38 (m, 2H), 7.31–7.24 (m, 3H), 2.33 (td, *J* = 7.7, 2.0 Hz, 1H), 1.97–1.81 (m, 1H), 1.81–1.63 (m, 1H), 1.47–1.52 (m, 1H), 1.38–1.28 (m, 1H), 1.20 (d, *J* = 6.2 Hz, 24H), 1.09–0.99 (m, 1H), 0.95 (dd, *J* = 6.6, 2.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.73, 142.70, 141.22, 137.71, 128.69, 128.59, 126.84, 126.72, 83.18, 82.72, 32.90, 32.86, 31.97, 31.84, 24.72, 24.67, 24.62, 24.53, 15.48, 15.41. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{29}H_{42}B_2NaO_4$: 499.3161, found: 499.3161.

2,2'-(1-Phenylbutane-1,3-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6b)



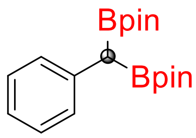
White solid; yield 46%, 53.3 mg (0.14 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.18 (m, 4H), 7.10-7.07 (m, 1H), 2.46–2.40 (m, 1H), 2.07–1.81 (m, 1H), 1.81–1.57 (m, 1H), 1.23–1.16 (m, 24H), 0.96 (d, J = 8.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.44, 143.33, 128.55, 128.48, 128.14, 128.12, 124.96, 124.93, 83.08, 82.69, 35.64, 35.35, 24.74, 24.70, 24.59, 24.54, 15.60, 15.18. HRMS (ESI) m/z $[M+Na]^+$ calcd for $C_{22}H_{36}B_2NaO_4$: 409.2691, found: 409.2691.

1,4-Bis((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzene (6c)[59]



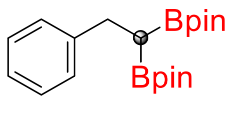
White solid; yield 85%, 91.5 mg (0.26 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (s, 4H), 2.23 (s, 4H), 1.22 (s, 24H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.66, 128.86, 83.22, 24.64. (benzylic carbon was not observed).

2,2'-(Phenylmethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (8a)[61]



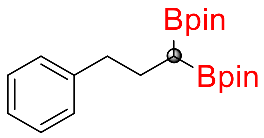
White solid; yield 49%, 50.7 mg (0.15 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.24 (m, 2H), 7.20 (dd, J = 8.5, 6.8 Hz, 2H), 7.10–7.04 (m, 1H), 2.30 (s, 1H), 1.23 (s, 12H), 1.21 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.48, 129.13, 127.92, 124.15, 83.33, 24.66, 24.57.

2,2'-(2-Phenylethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (8b)[62]



White solid; yield 72%, 77.3 mg (0.22 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 6.6 Hz, 4H), 7.14–7.07 (m, 1H), 2.88 (d, J = 8.3 Hz, 2H), 1.18–1.13 (m, 25H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.32, 127.93, 125.31, 83.07, 31.26, 24.74, 24.48.

2,2'-(3-Phenylpropane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (8c)[63]



White solid; yield 53%, 59.5 mg (0.3 mmol); Hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.22 (m, 2H), 7.20–7.11 (m, 3H), 2.65–2.53 (m, 2H), 1.92–1.80 (m, 2H), 1.24 (s, 12H), 1.23 (s, 12H), 0.81 (t, J = 7.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.87, 128.53, 128.06, 125.44, 82.93, 38.66, 27.94, 24.85, 24.45.

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12. NMR spectra of starting substrates and products

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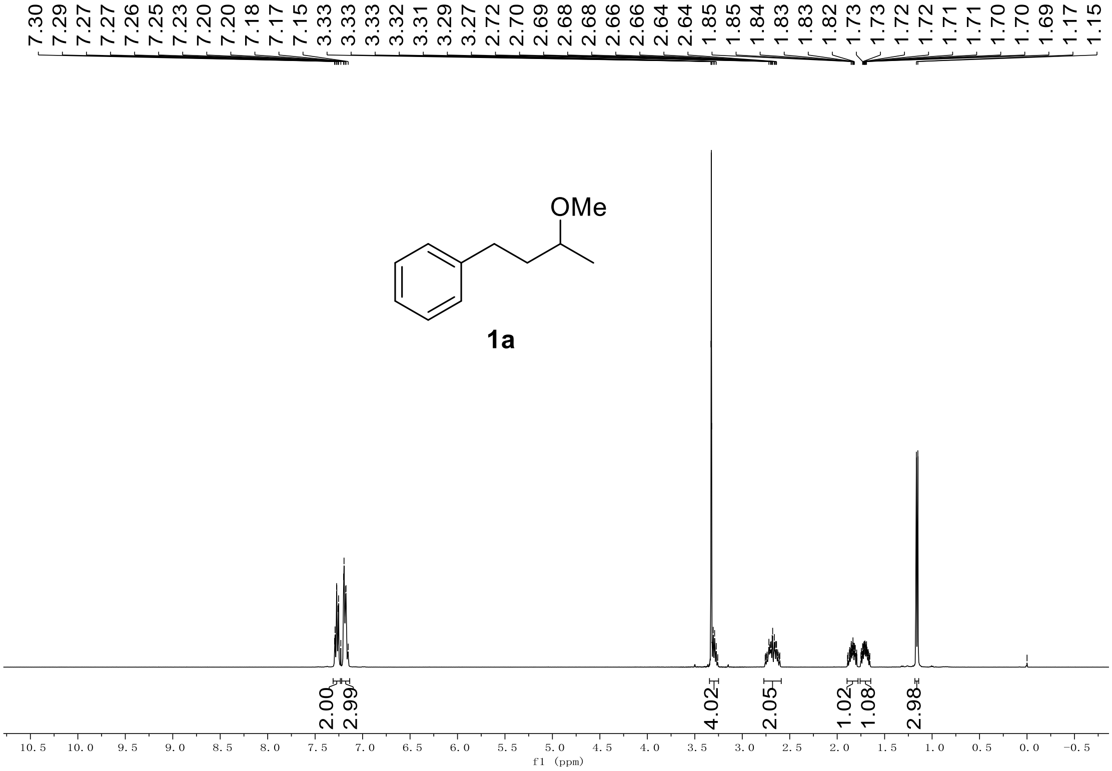

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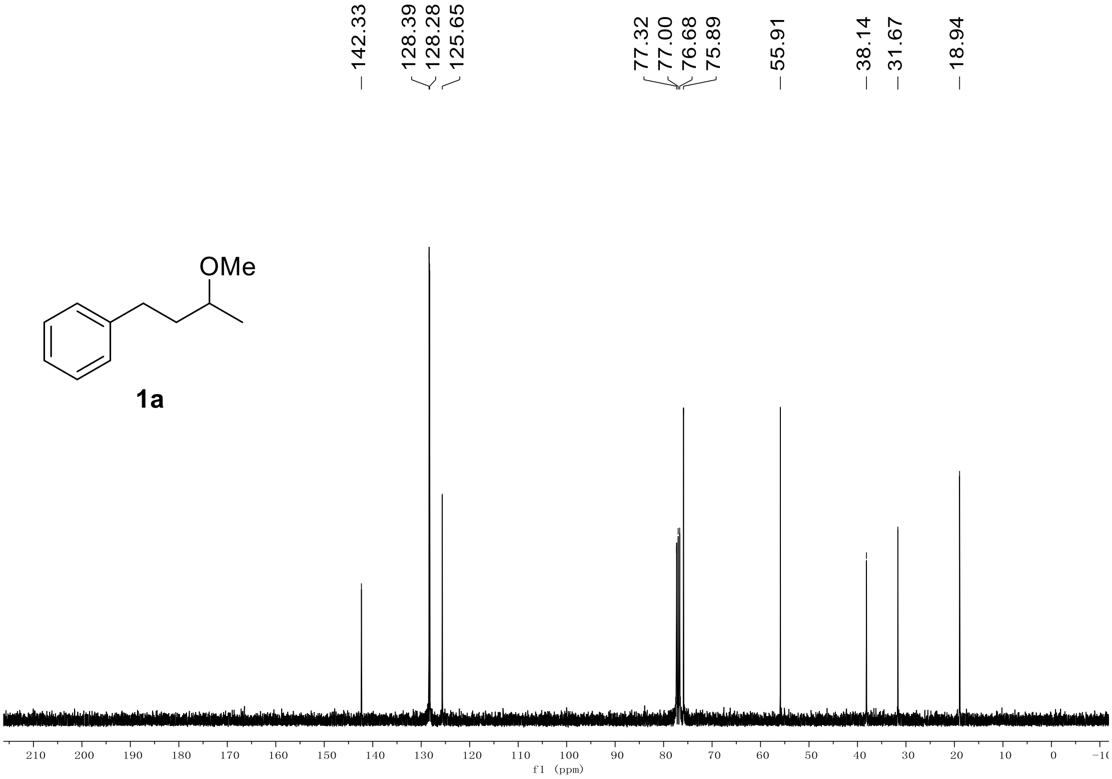

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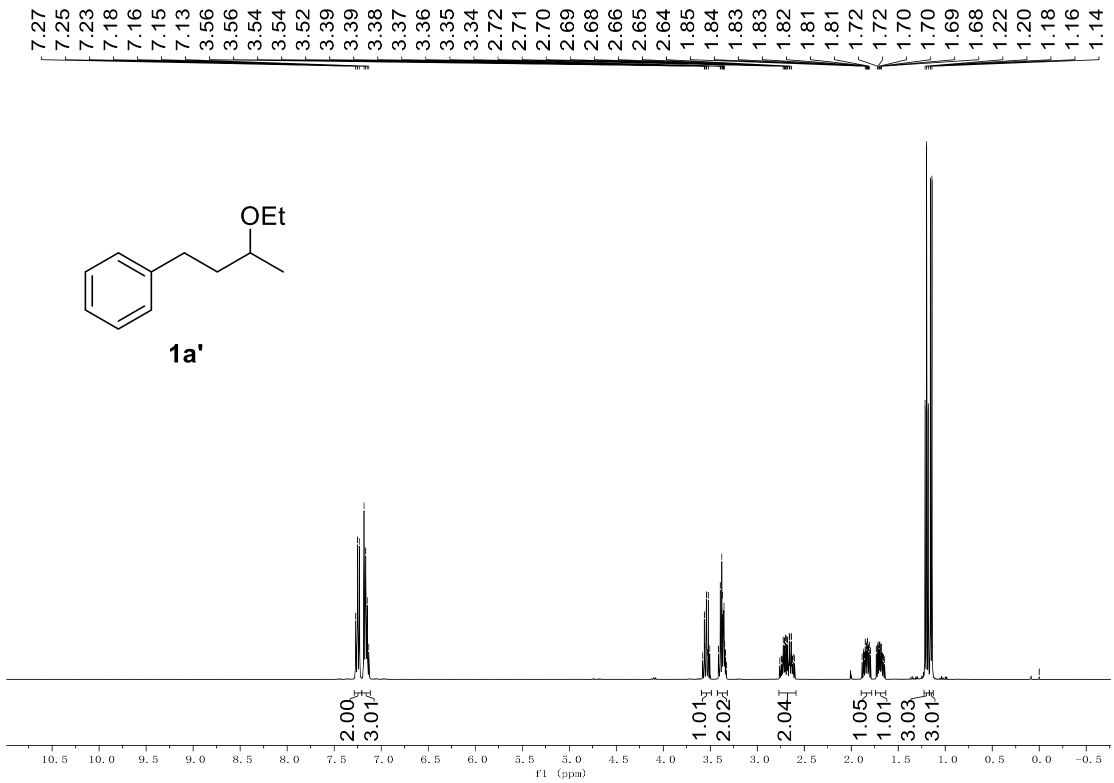

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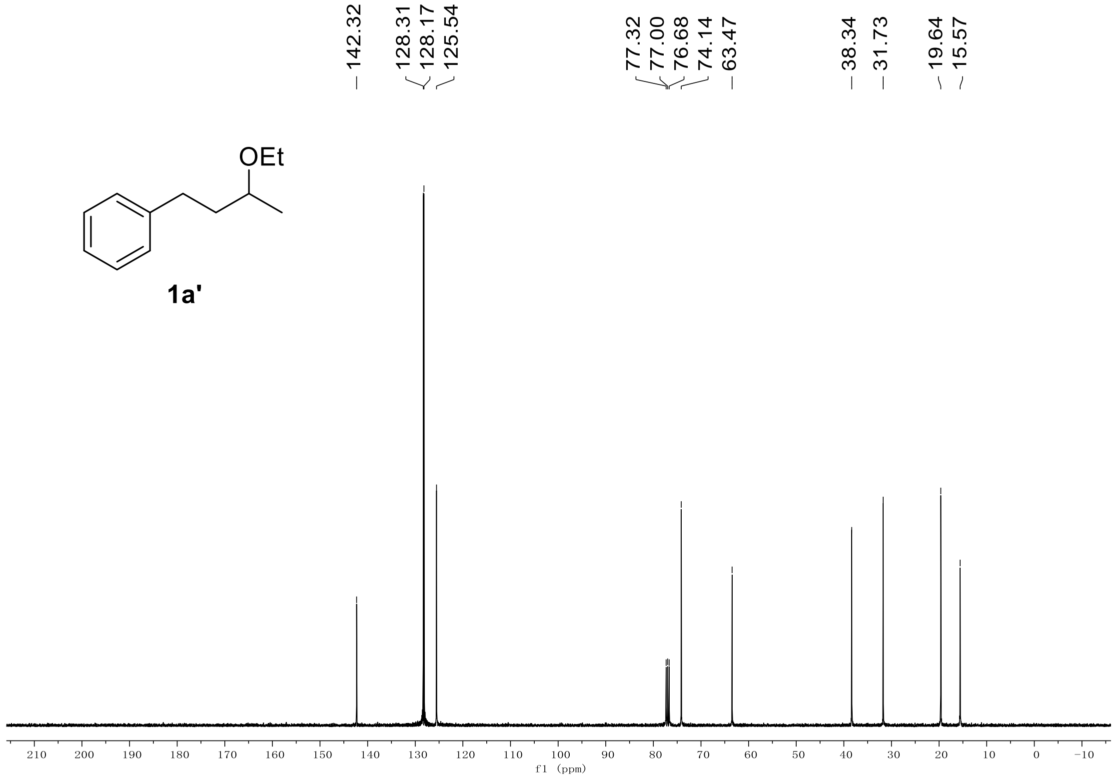

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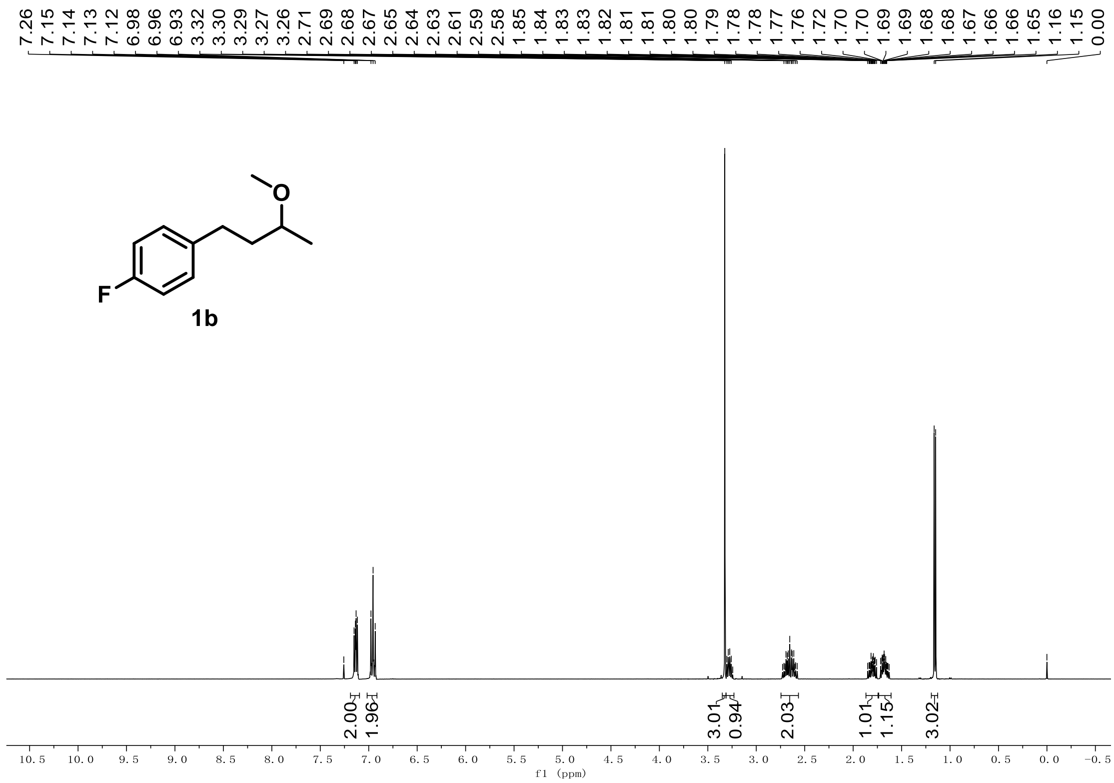

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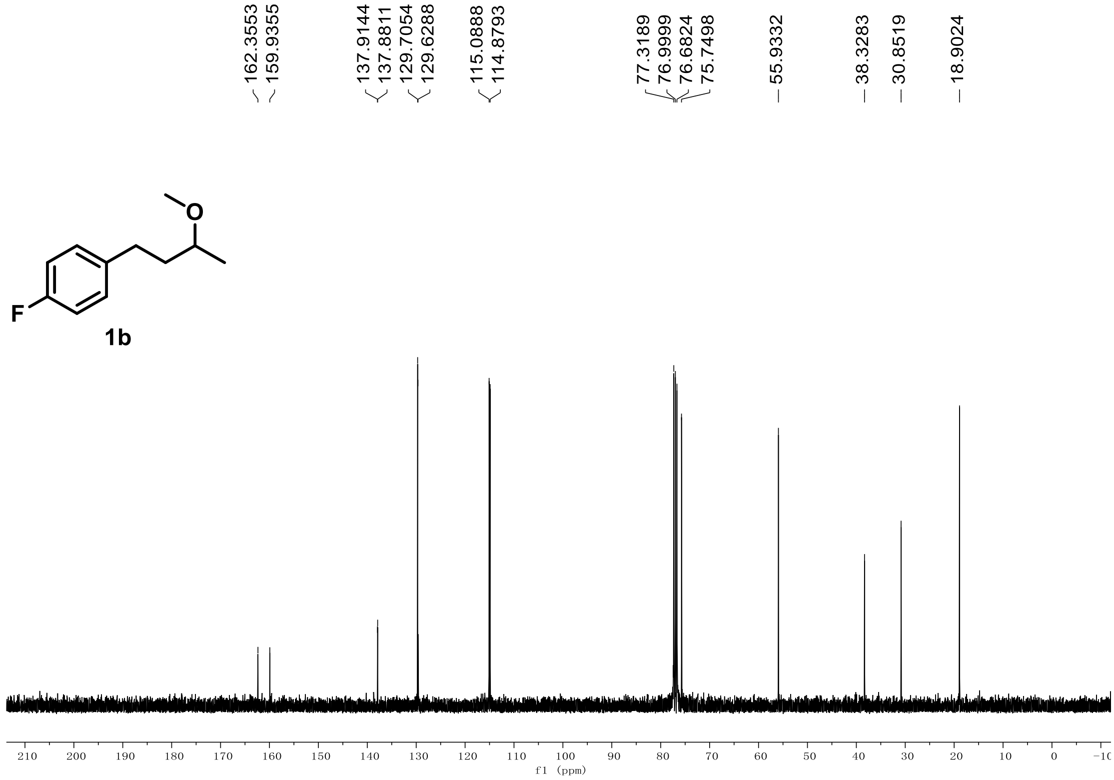

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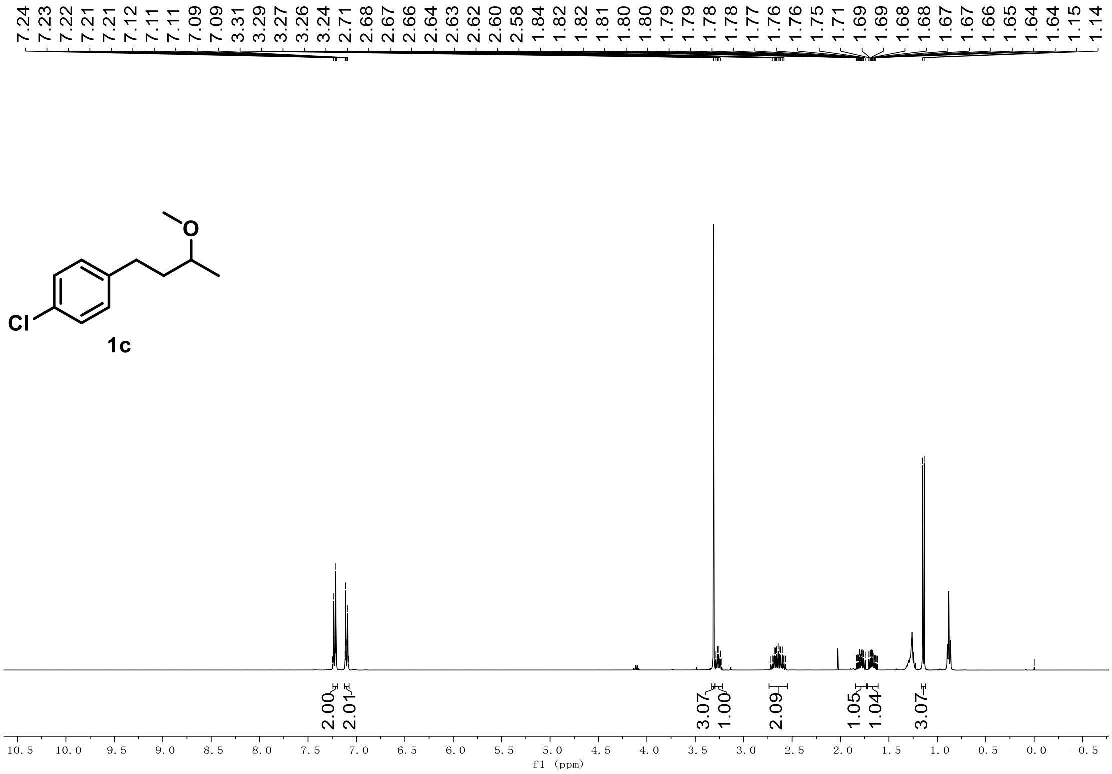

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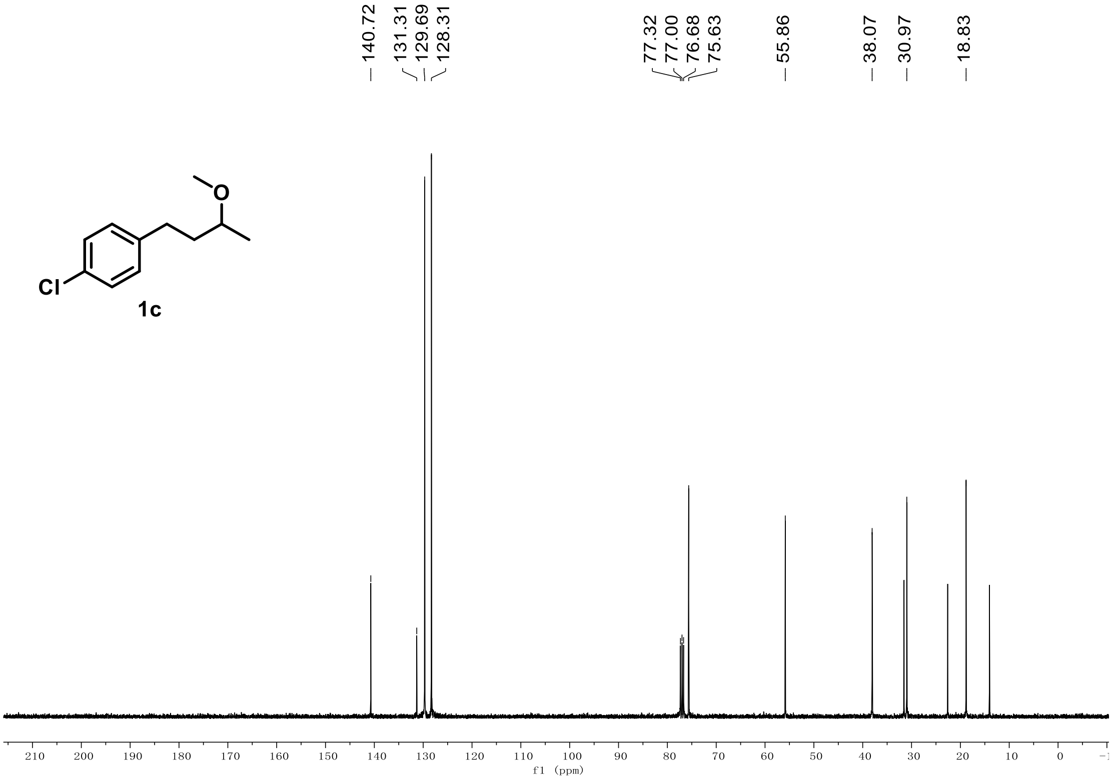

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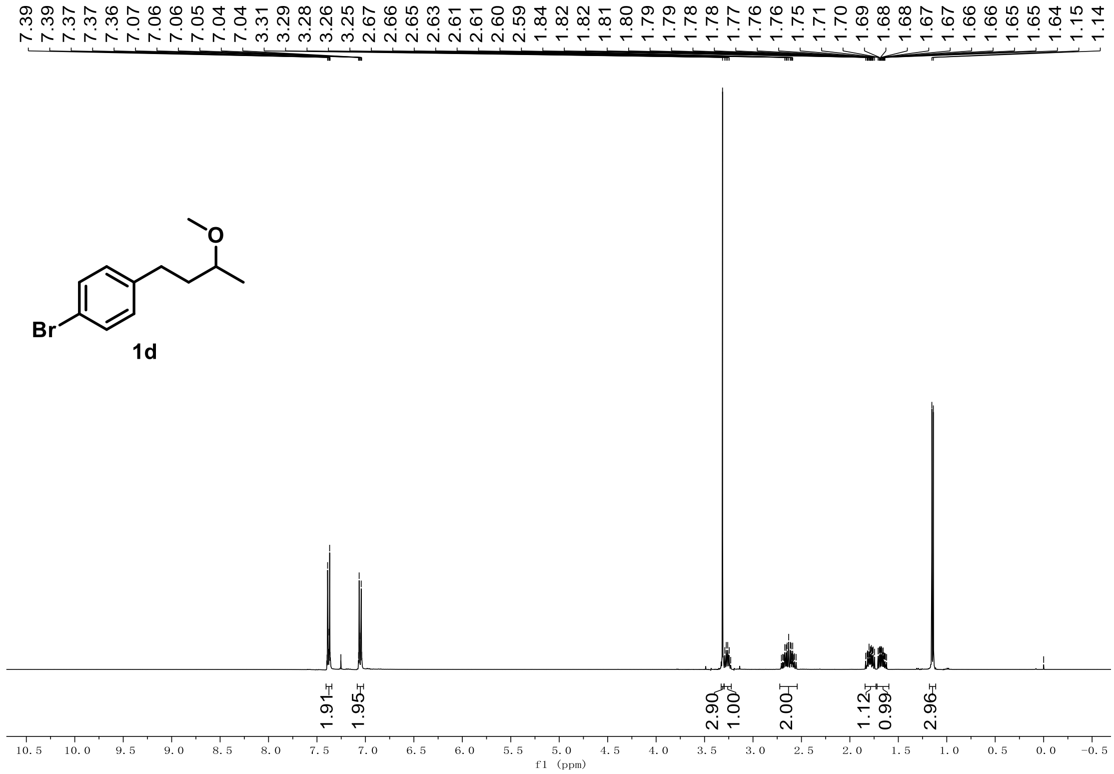

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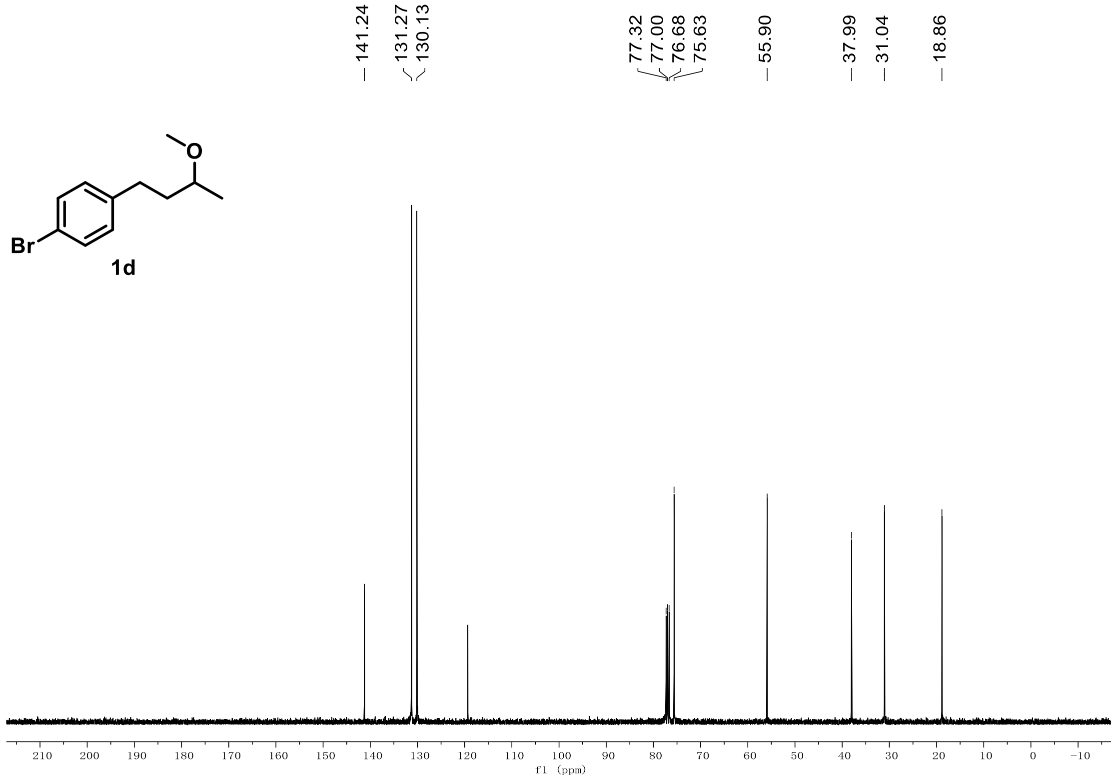

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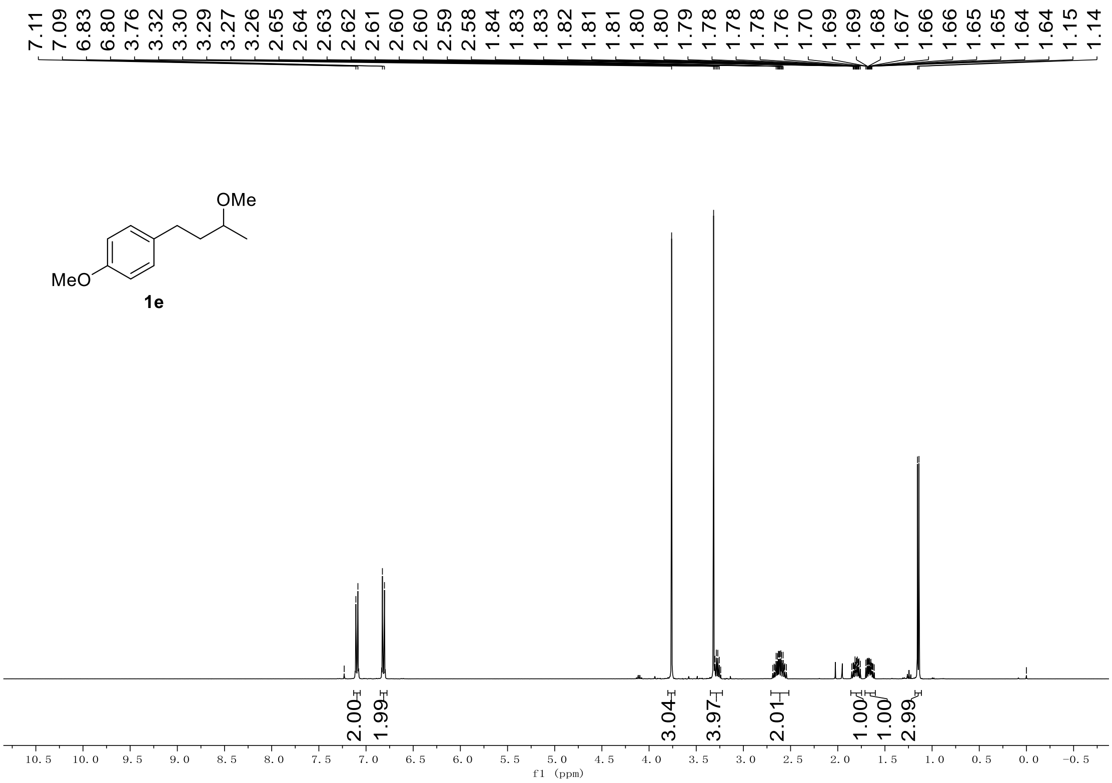

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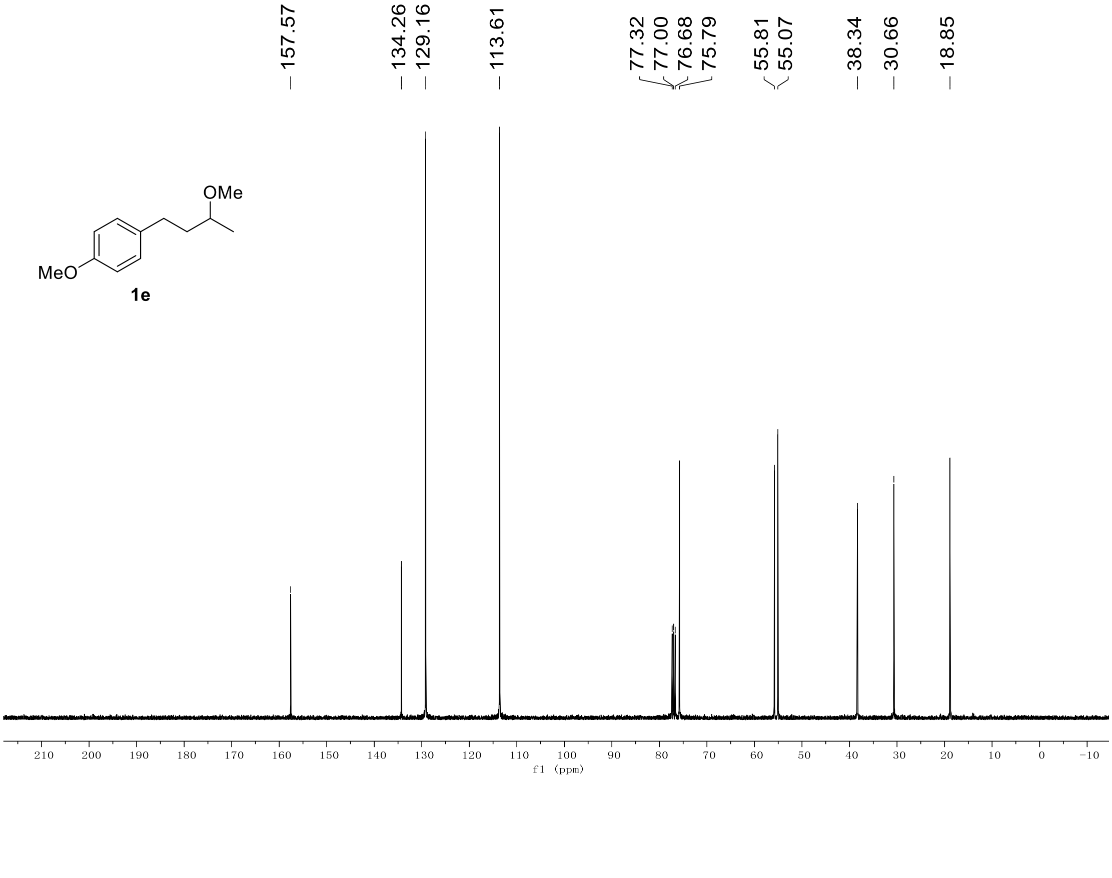

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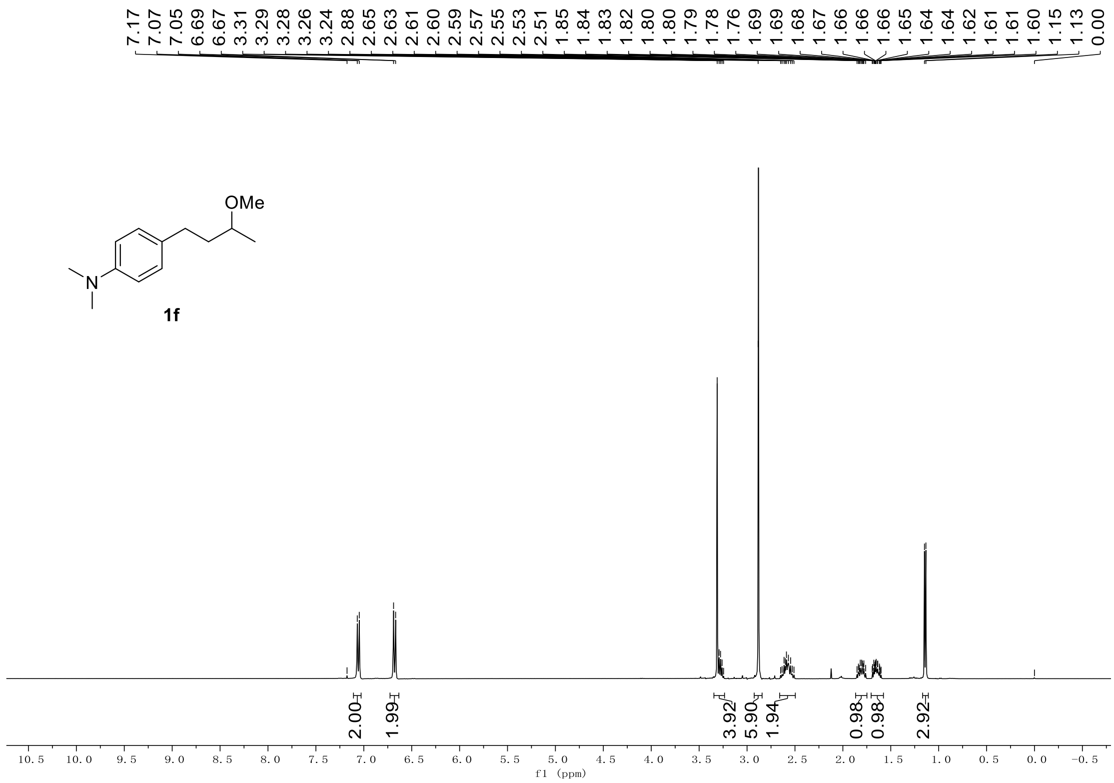

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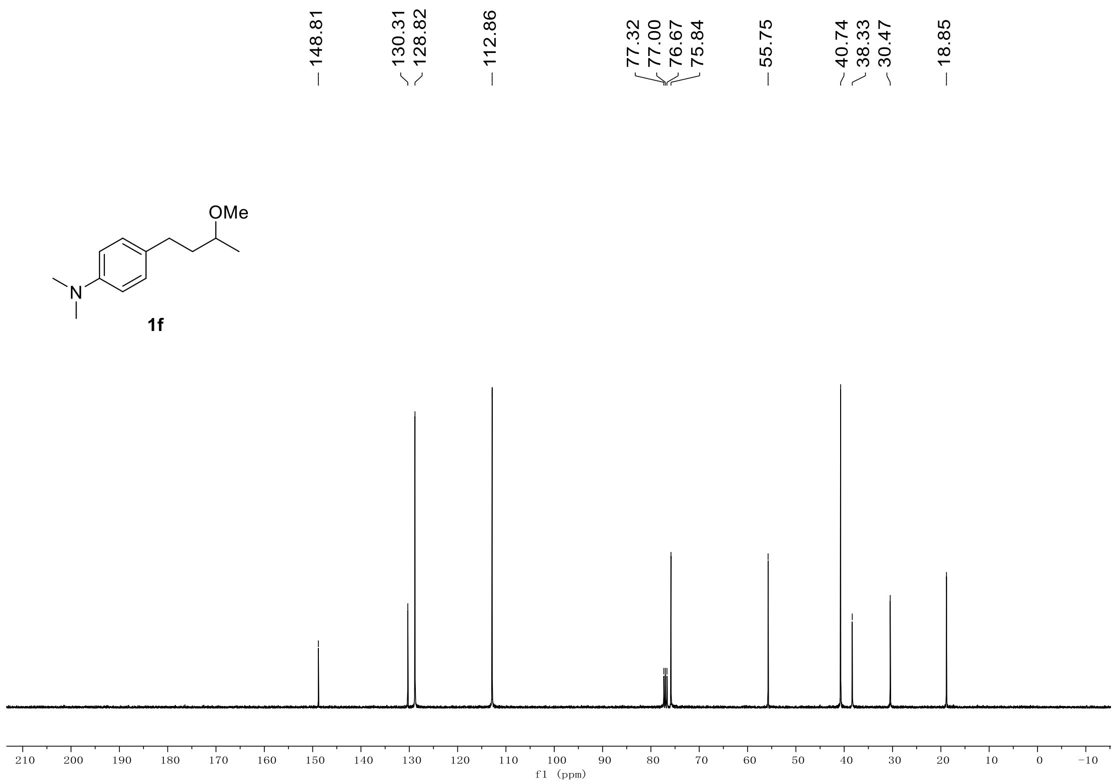

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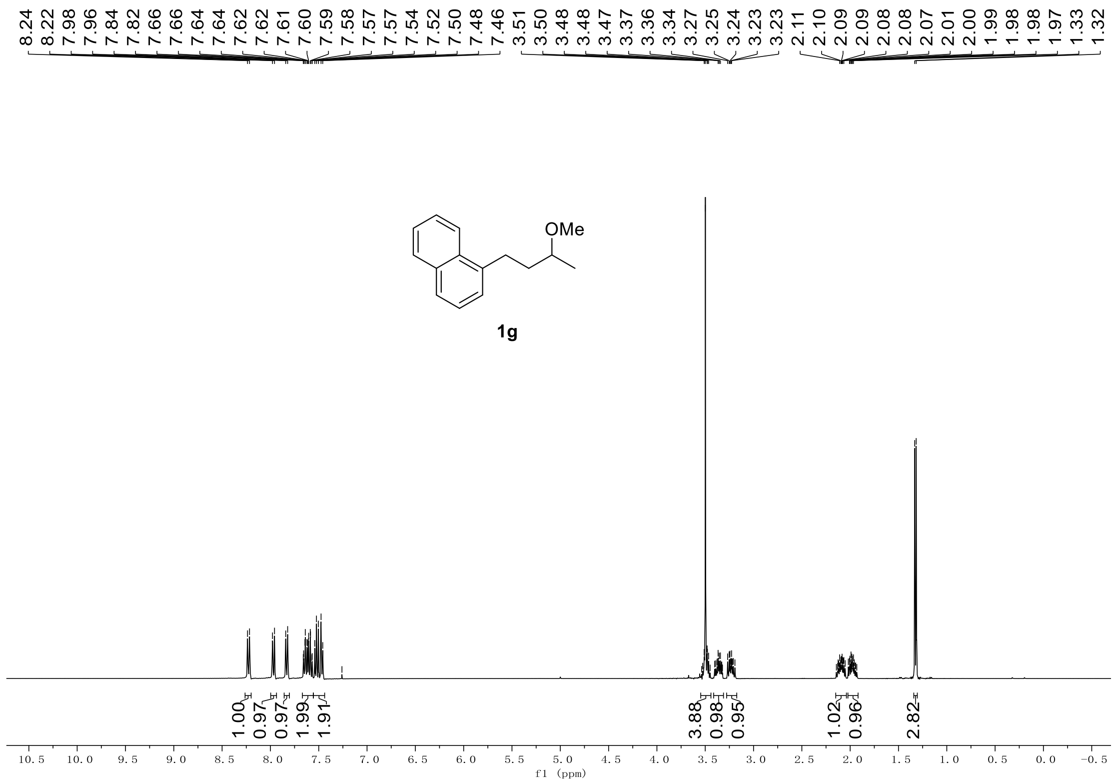

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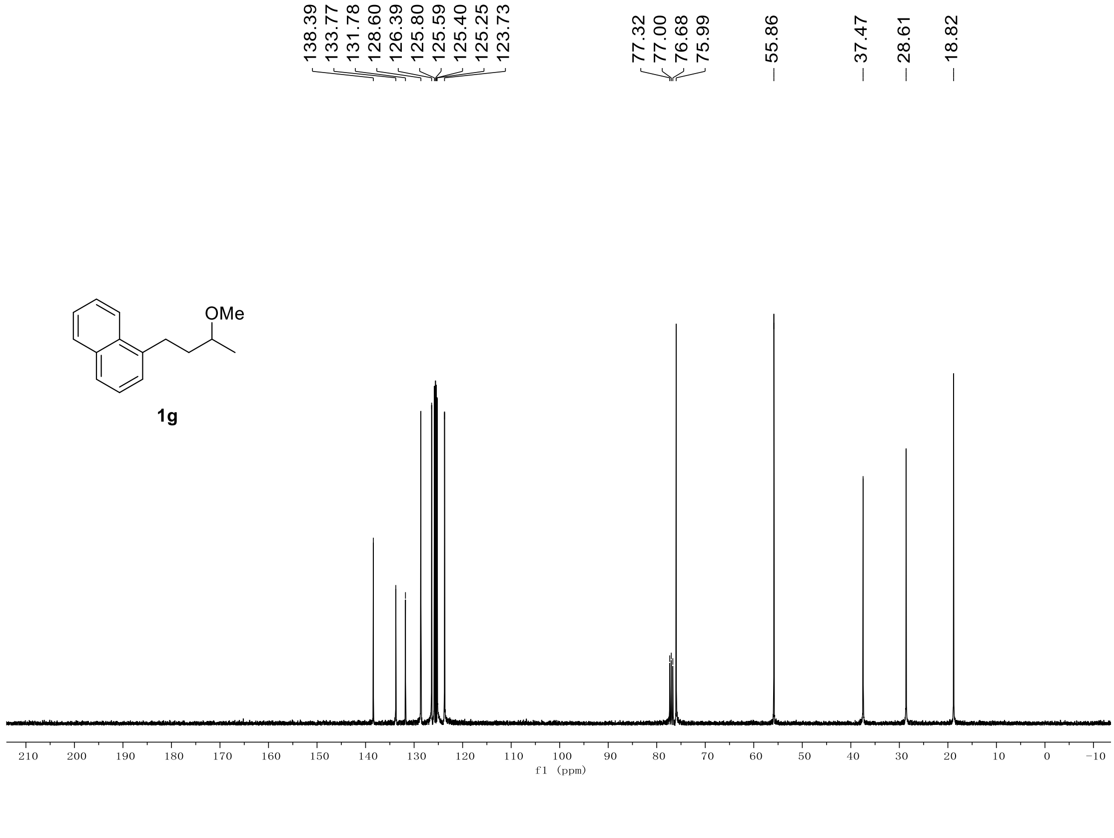

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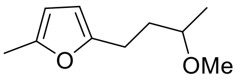

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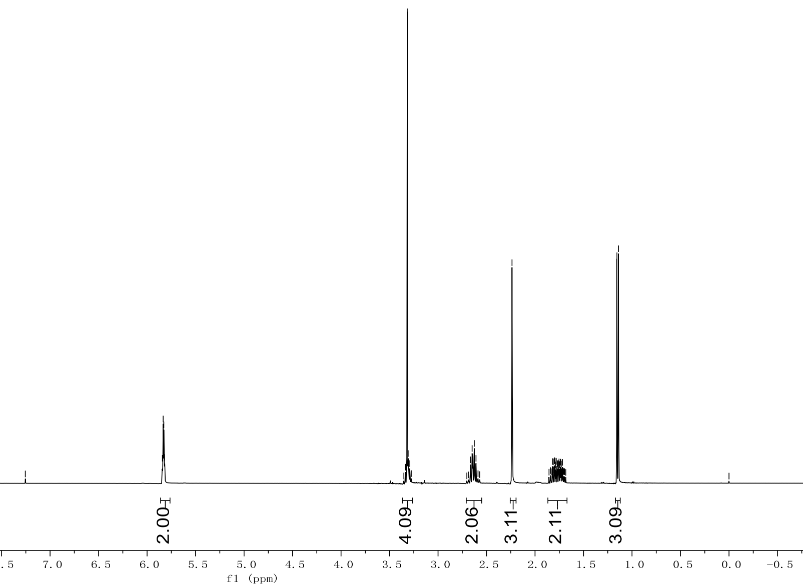

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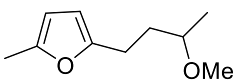

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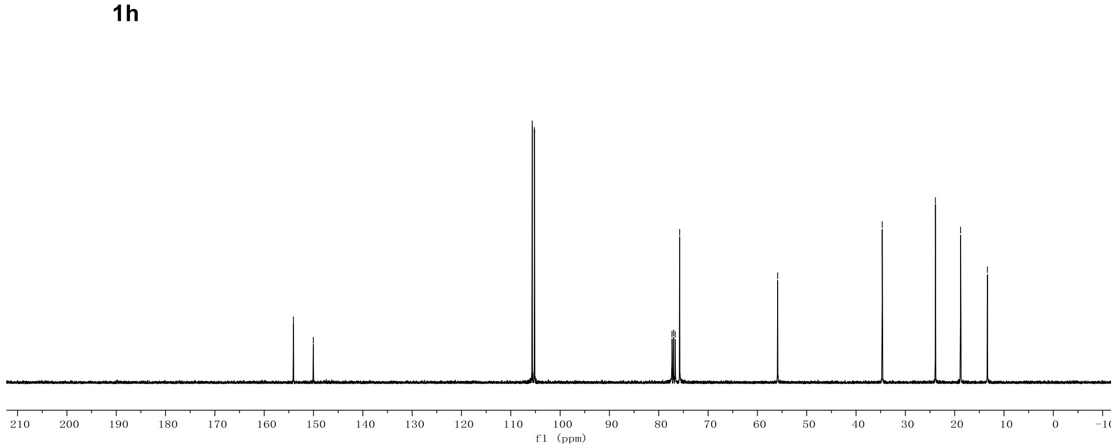

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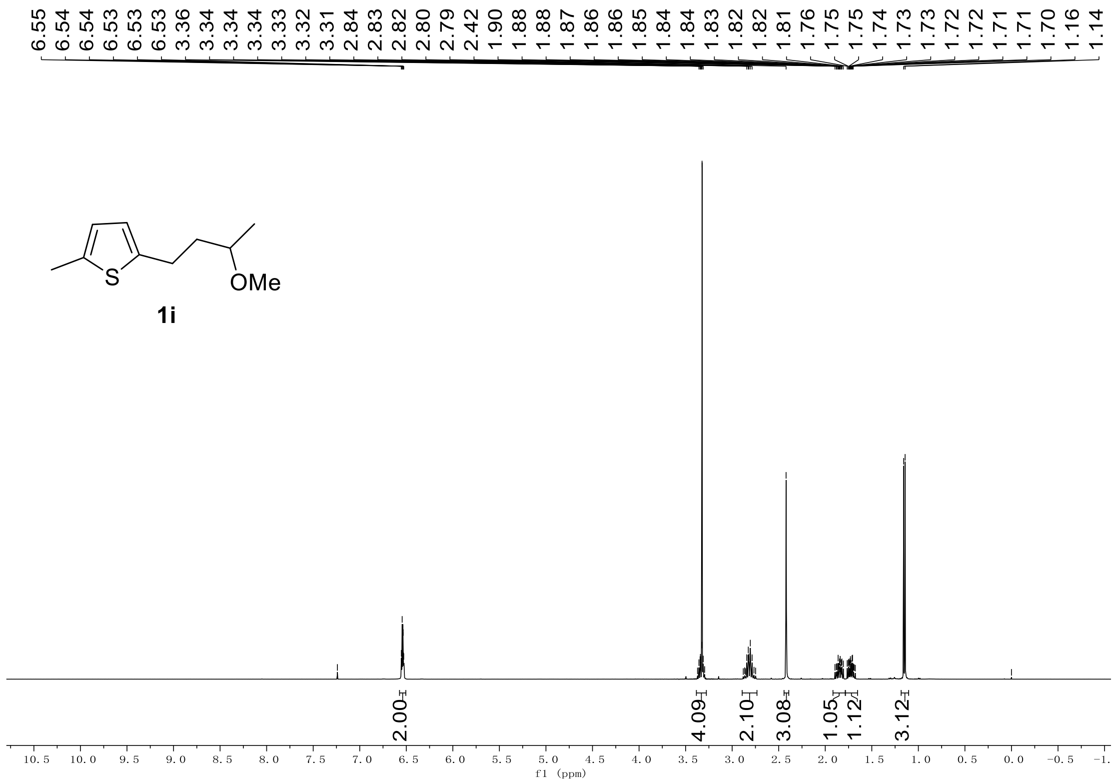

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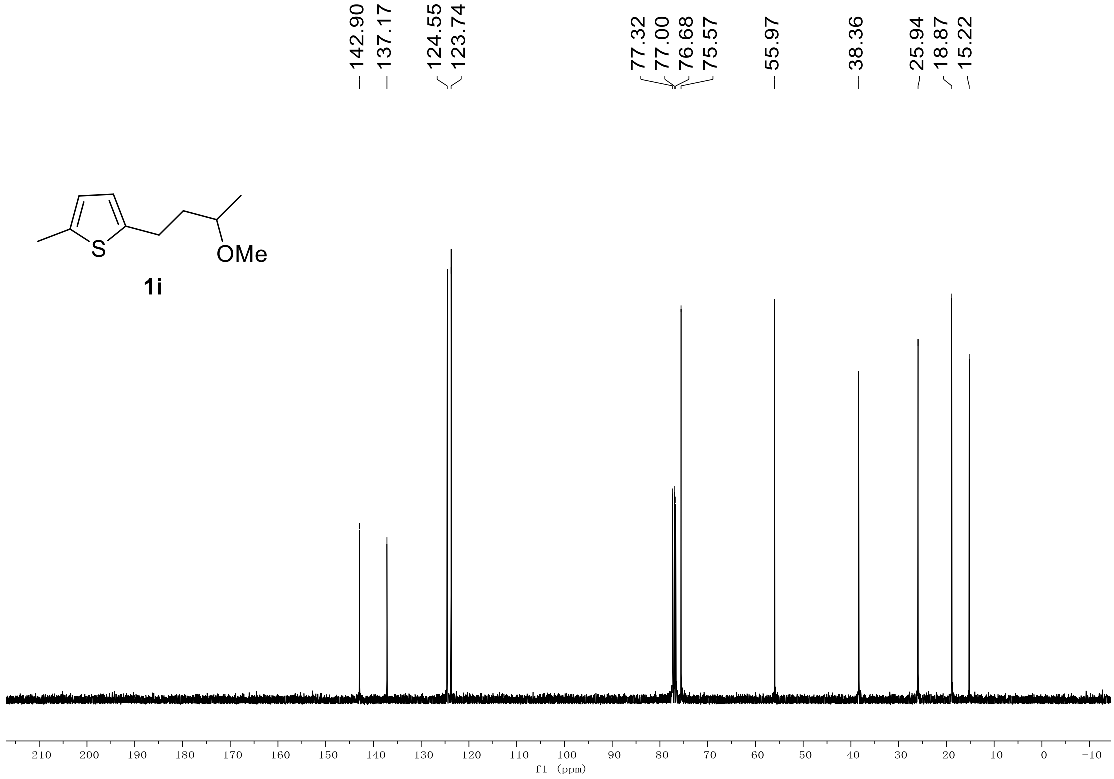

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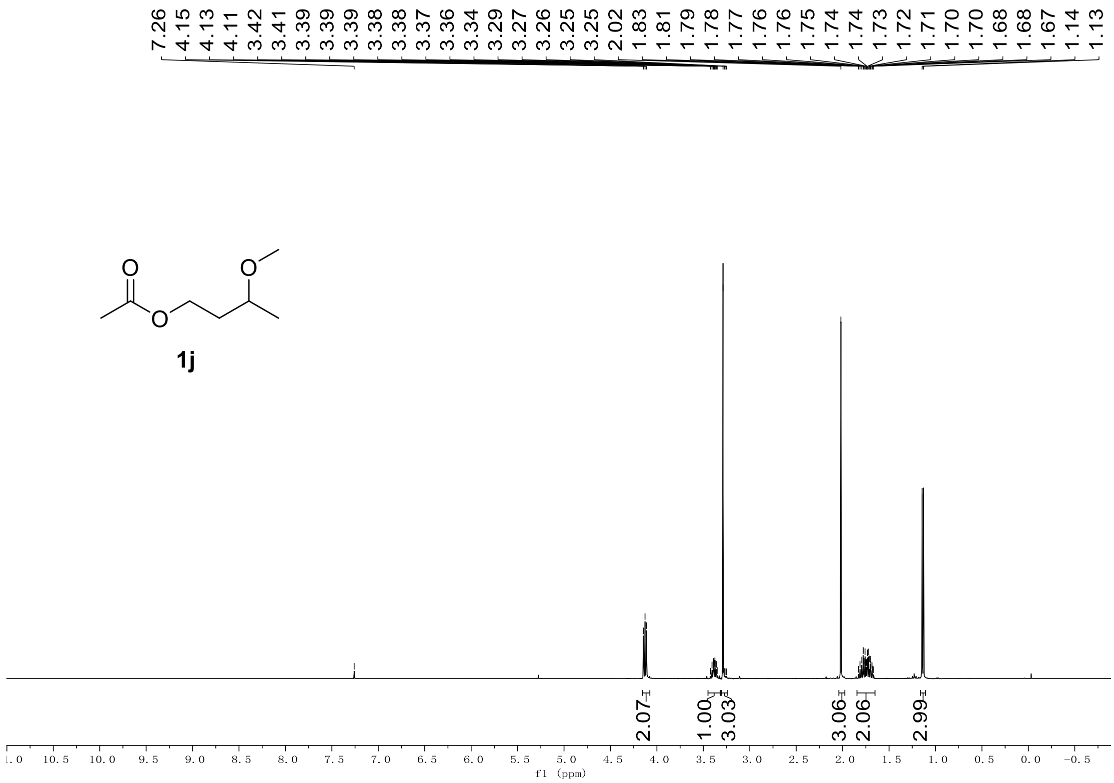

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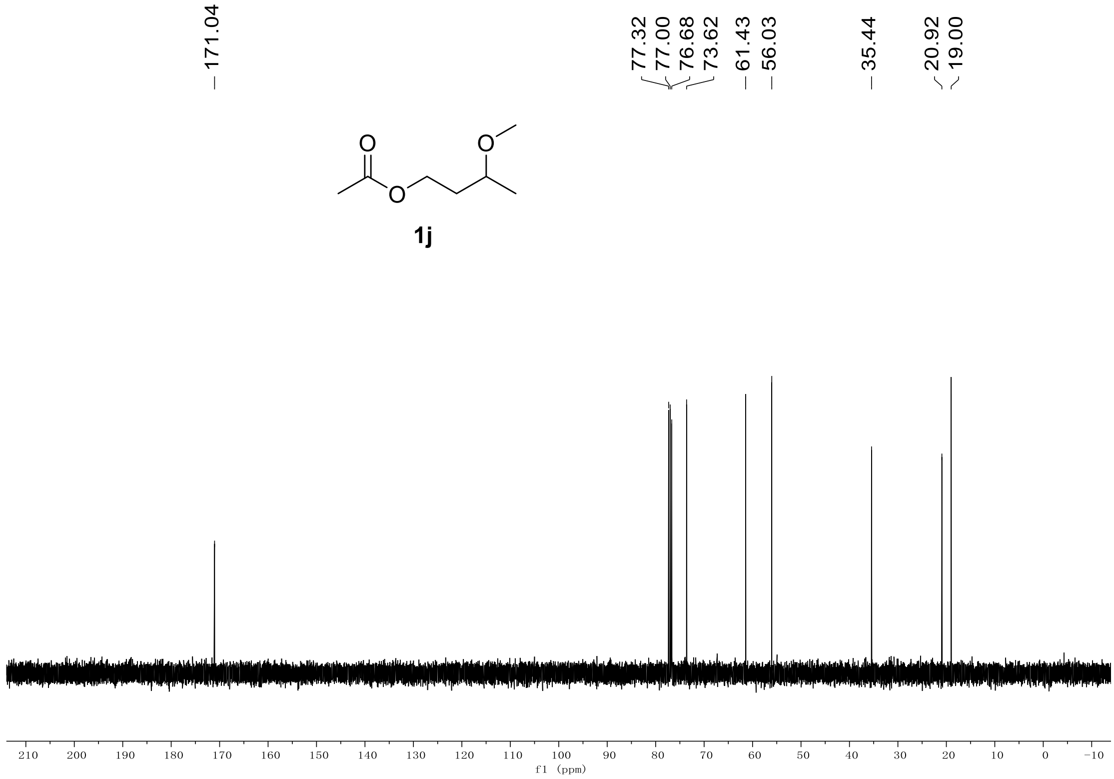

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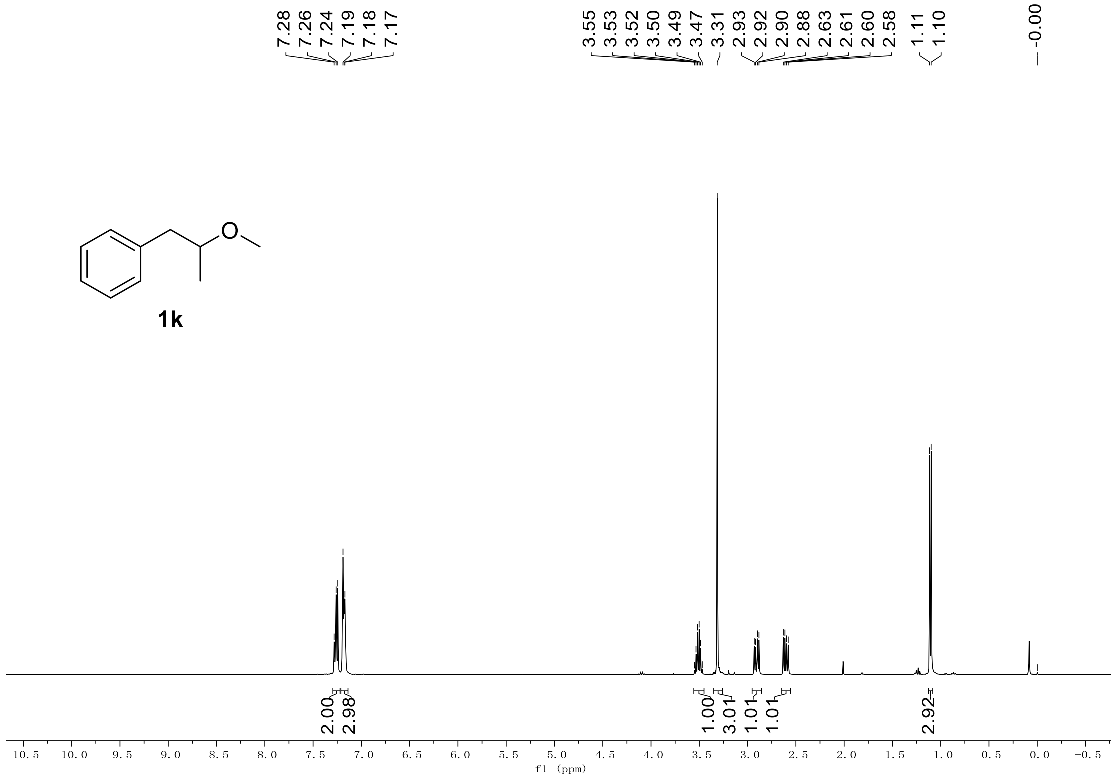

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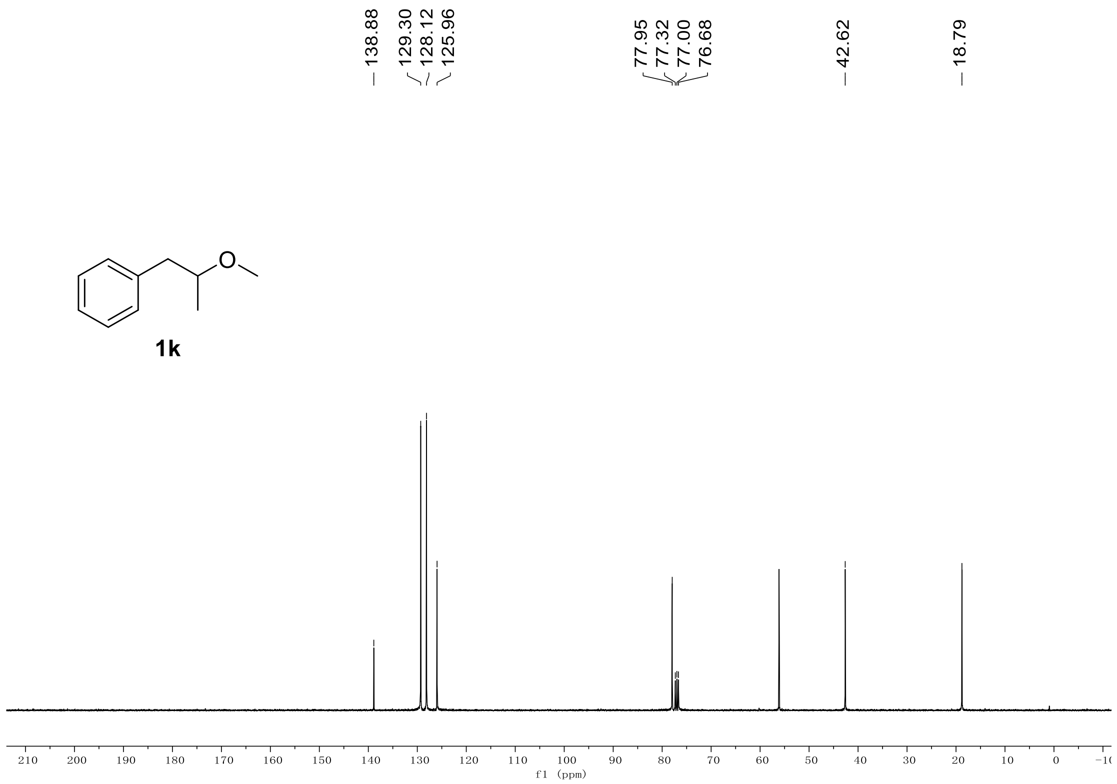

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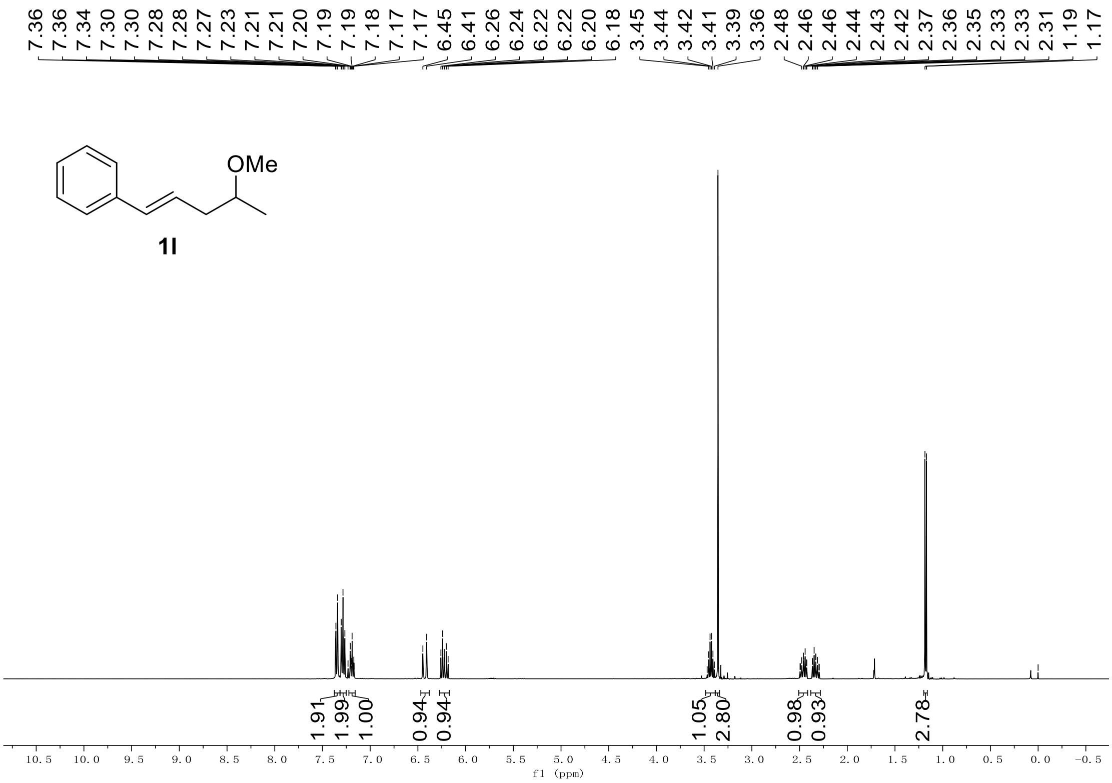

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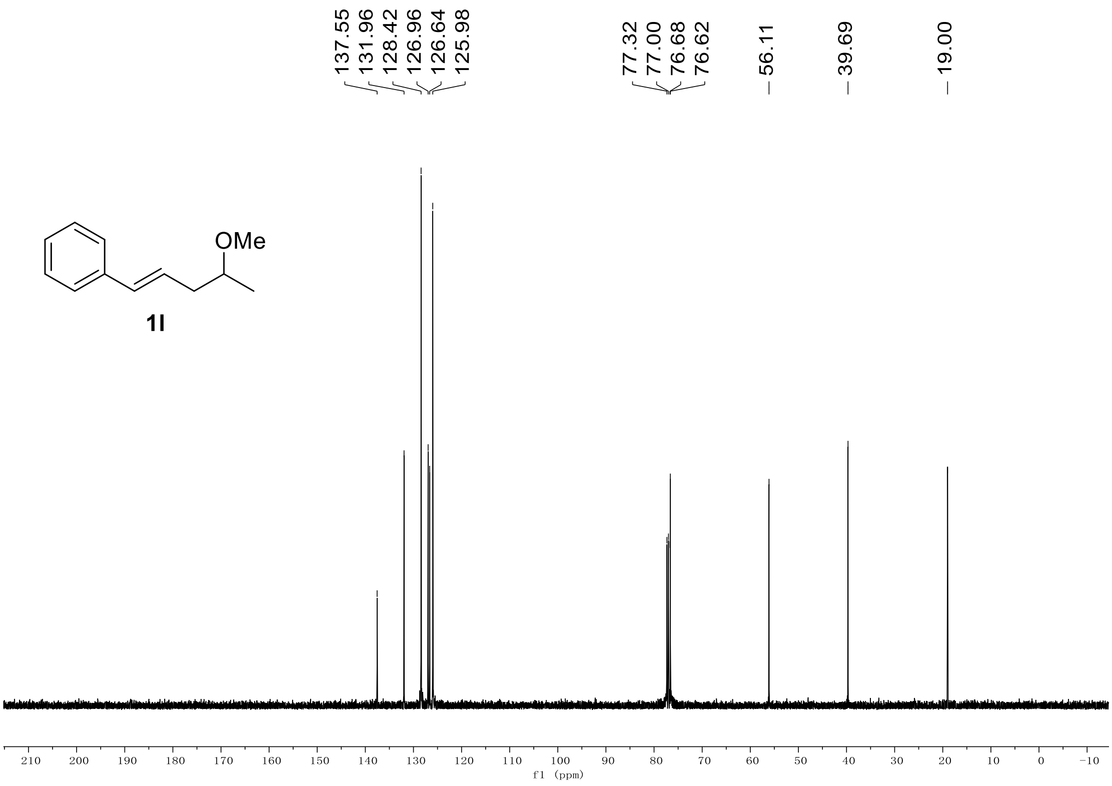

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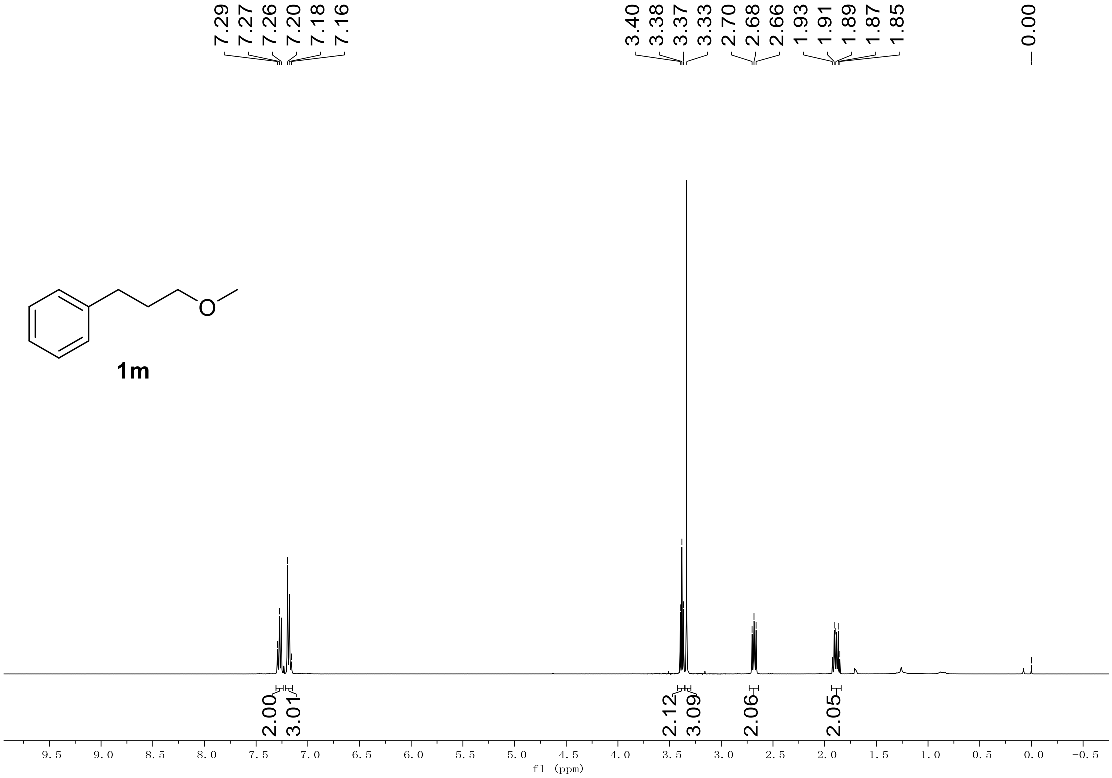

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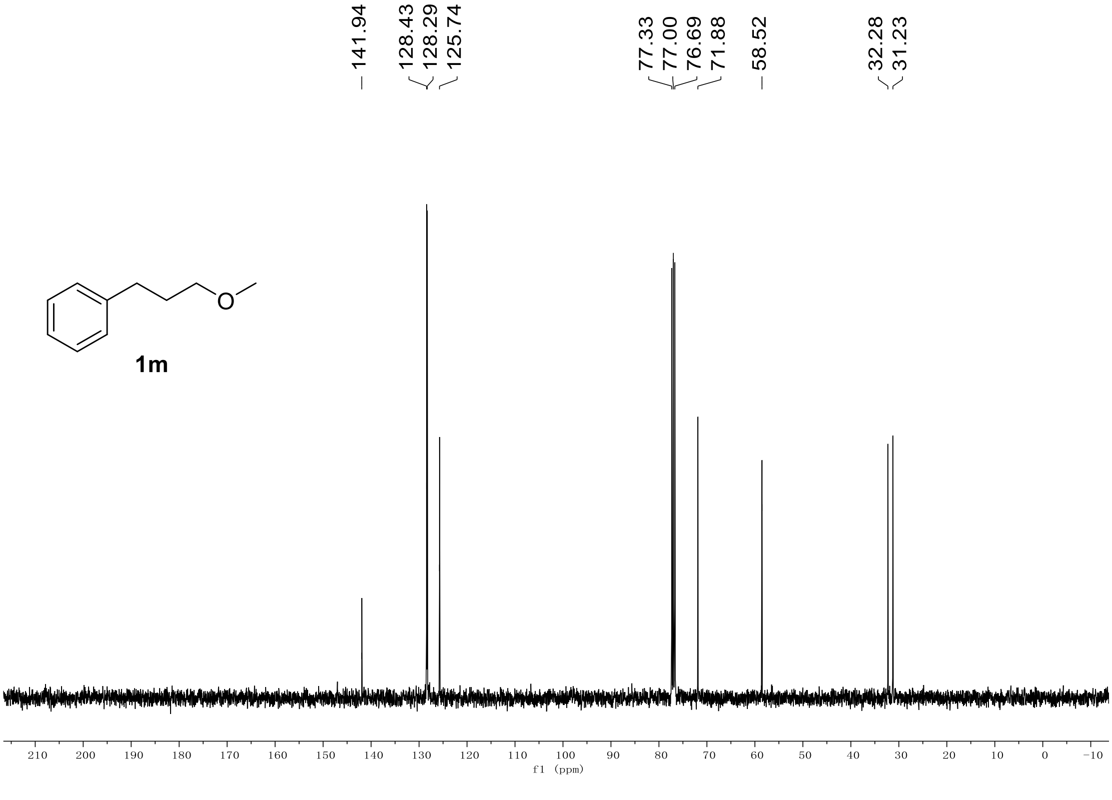

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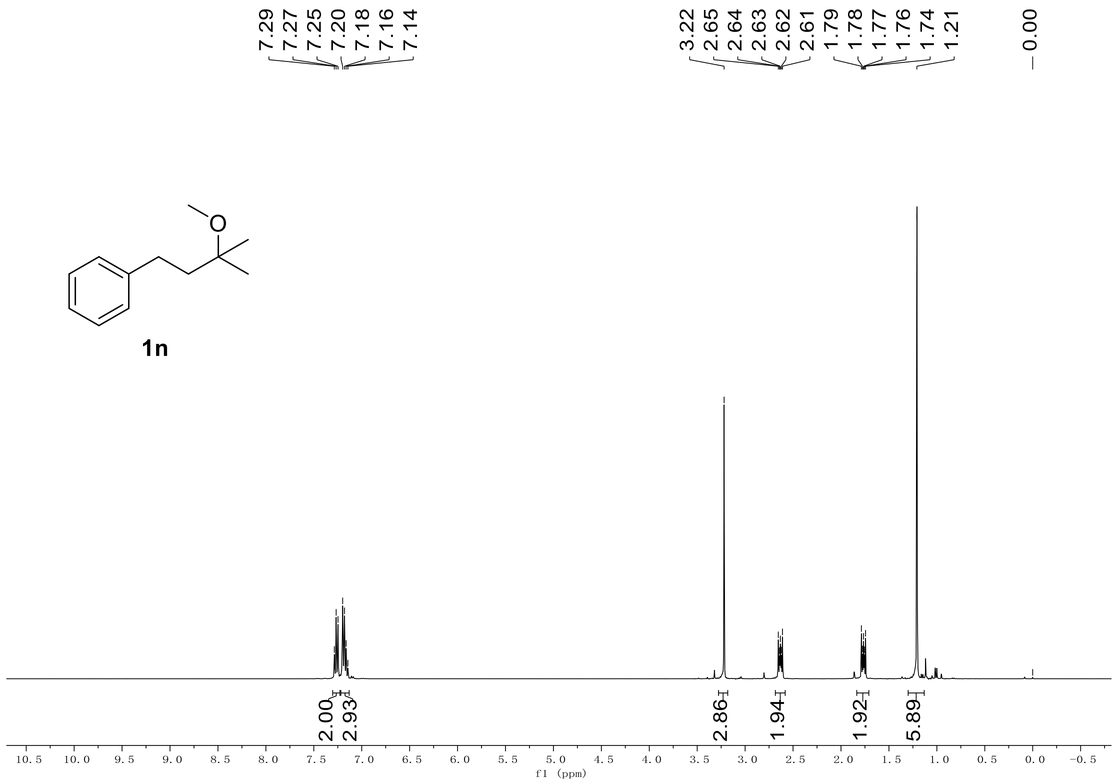

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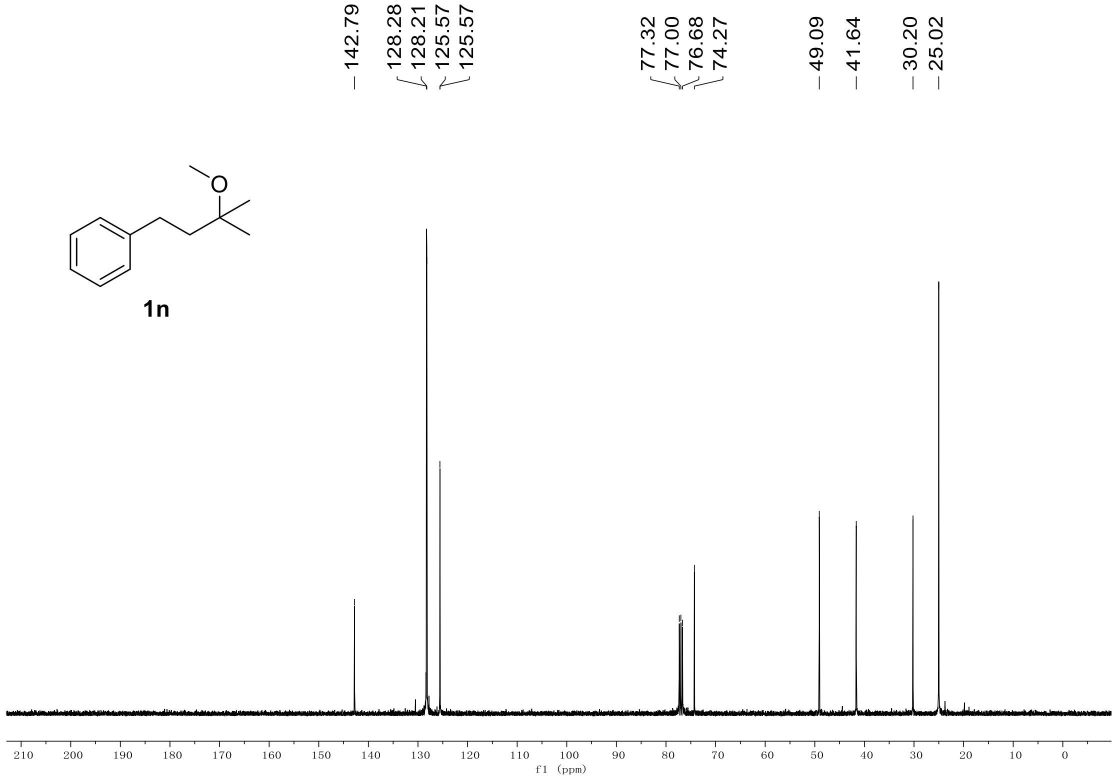

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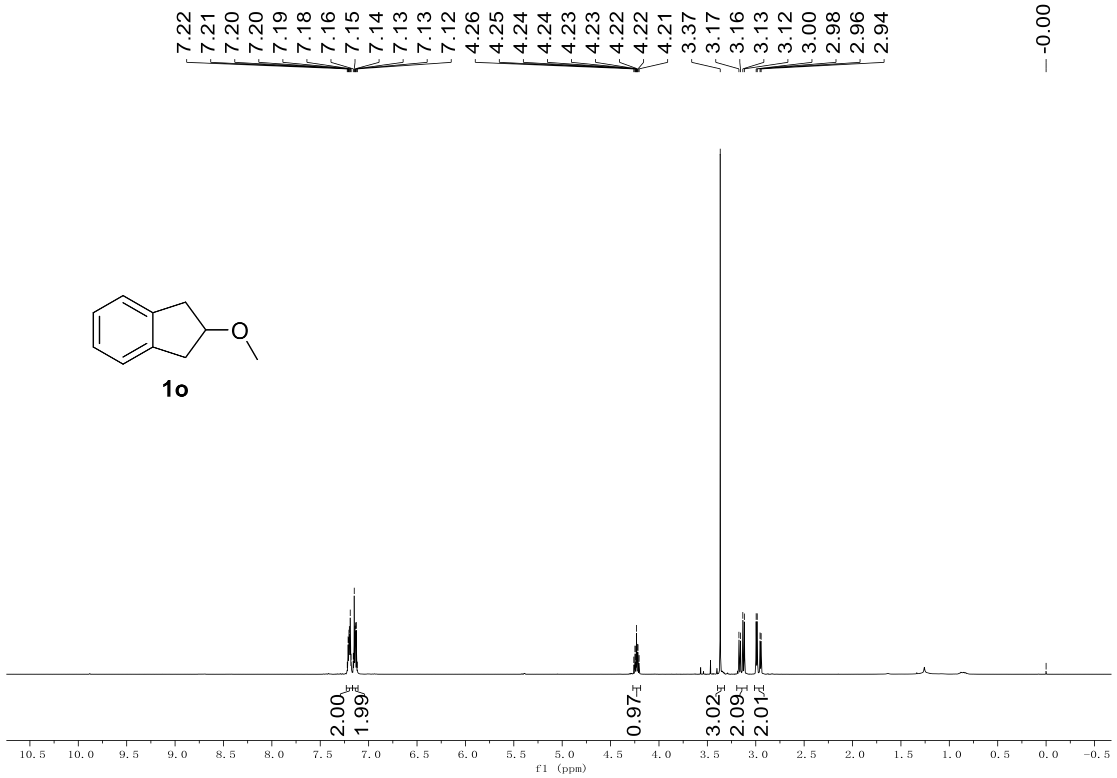

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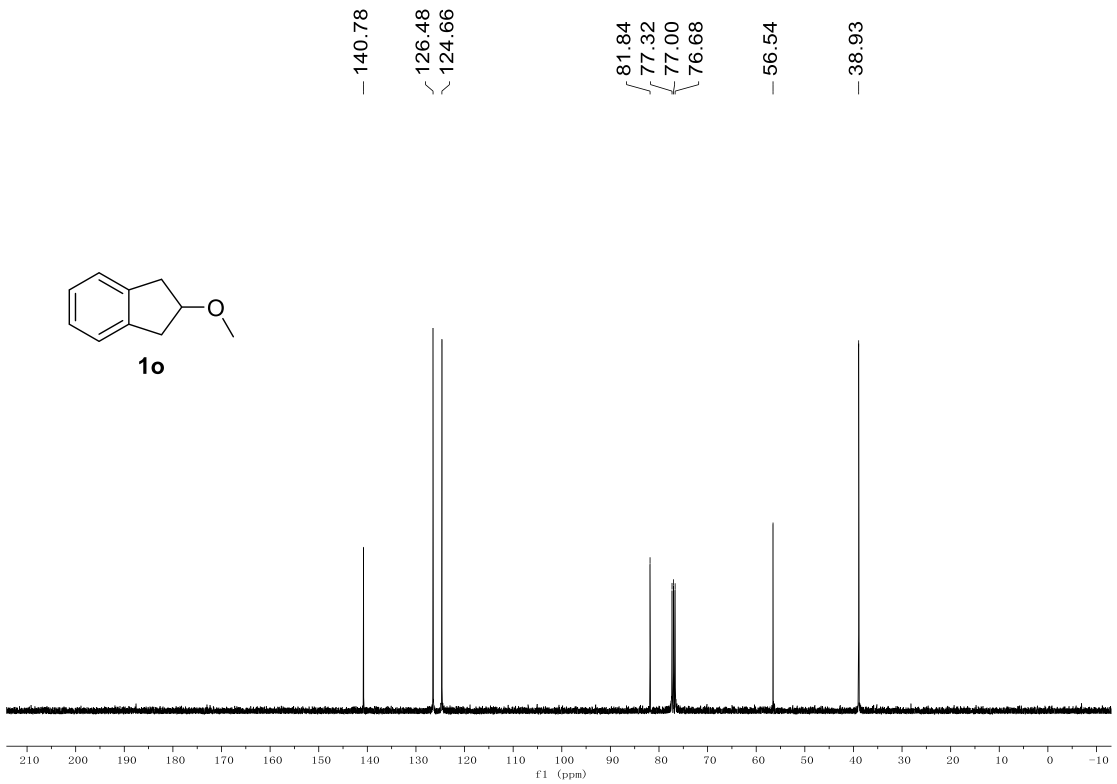

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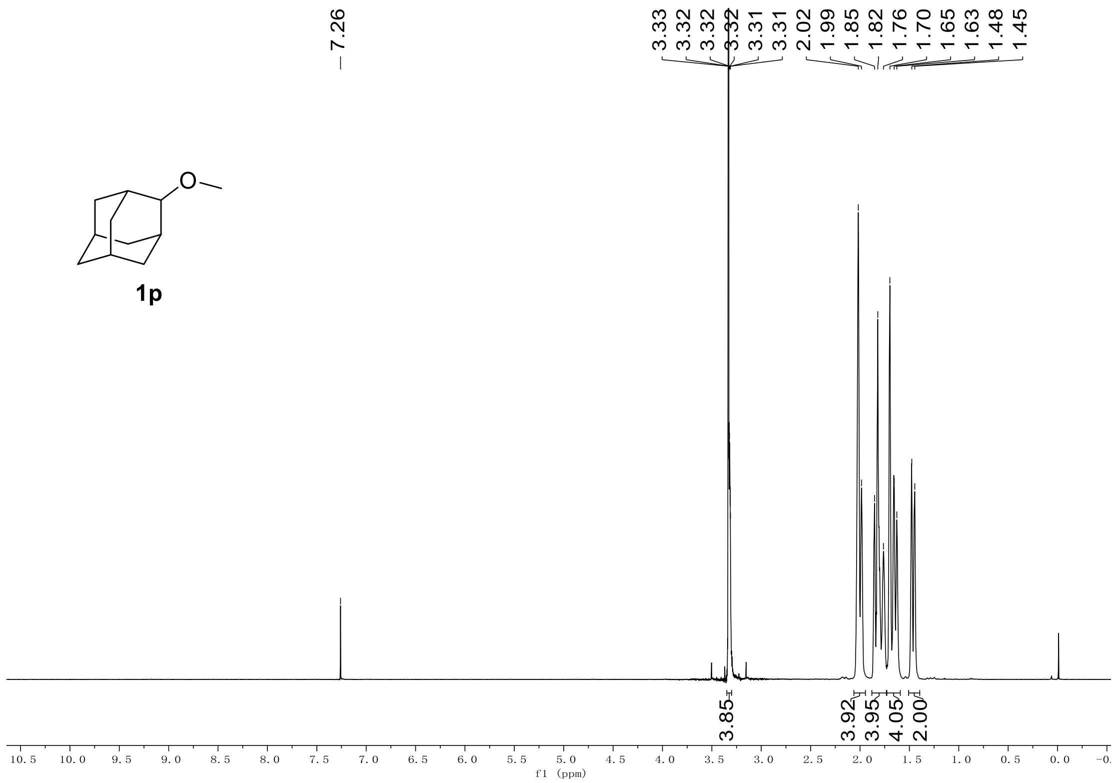

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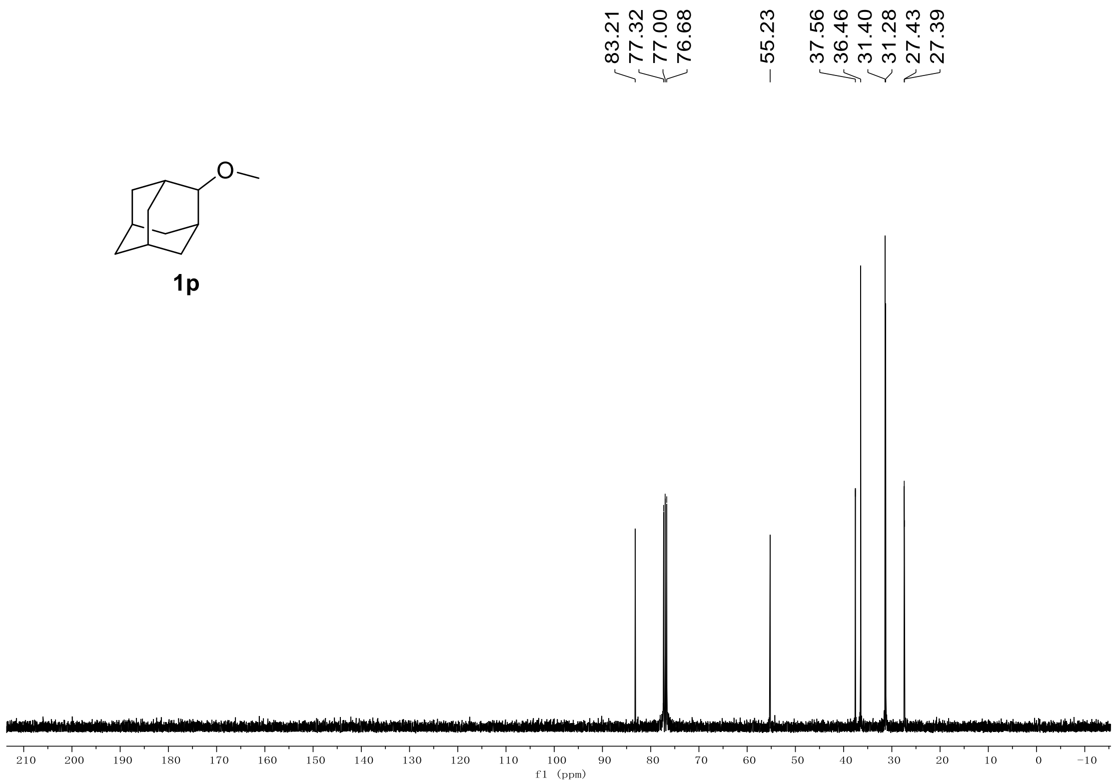

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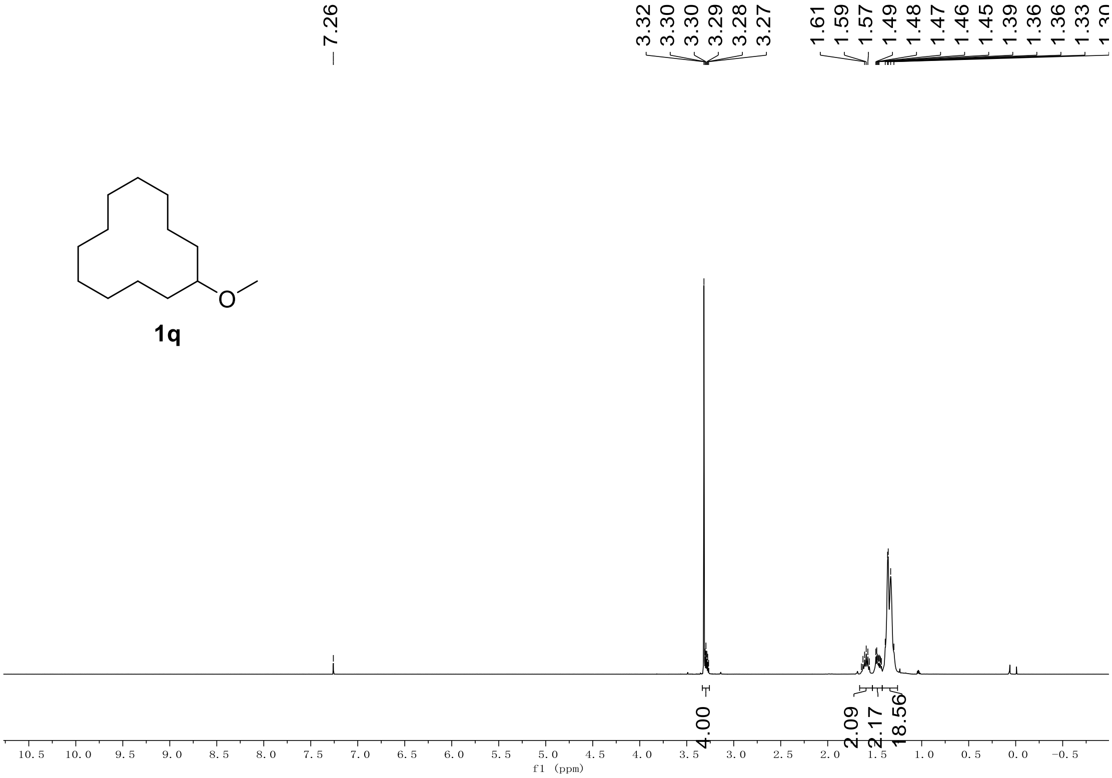

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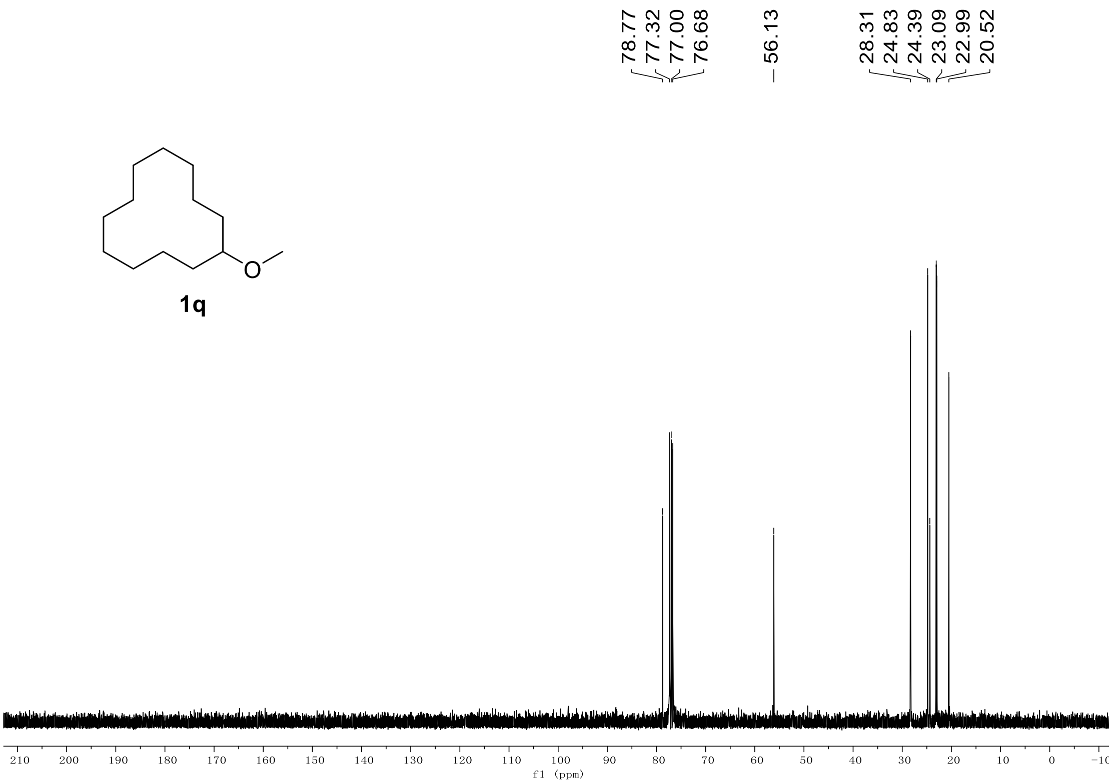

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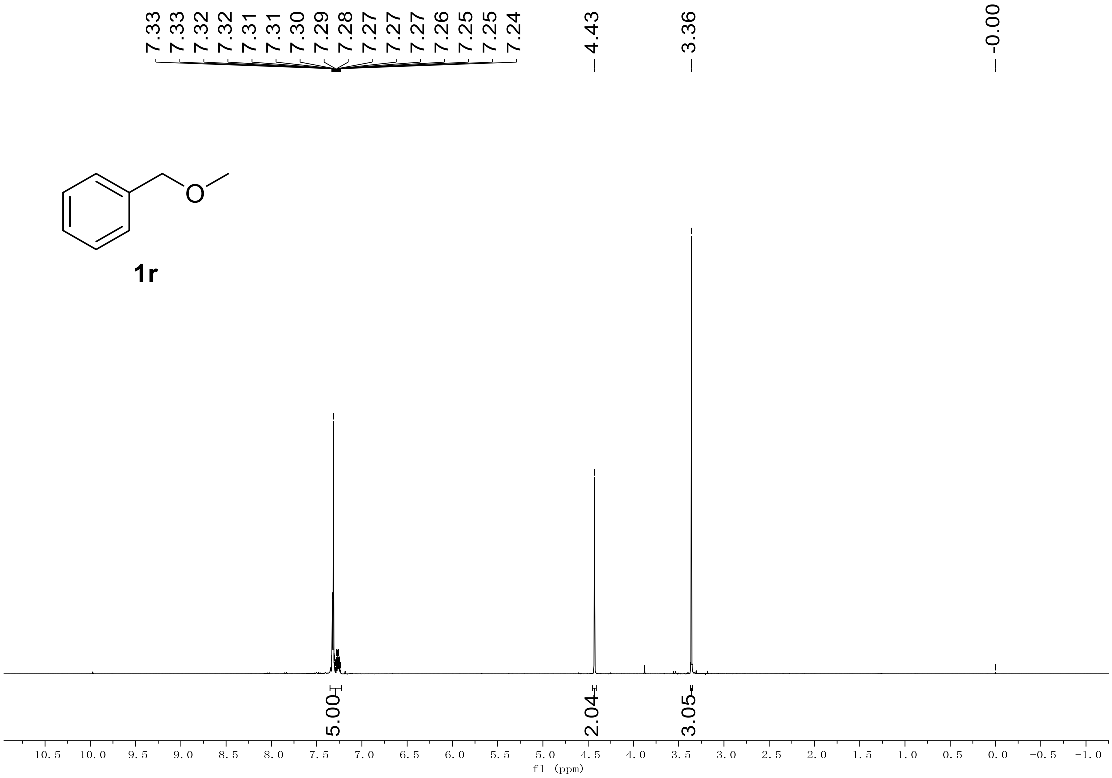

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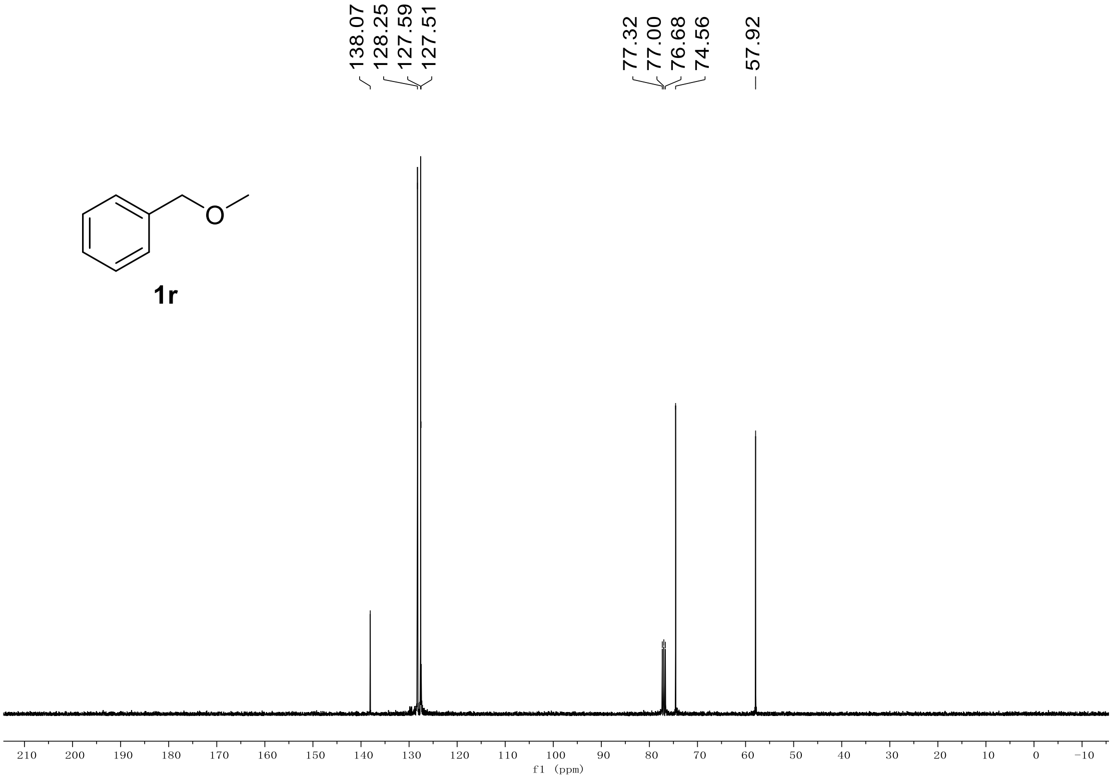

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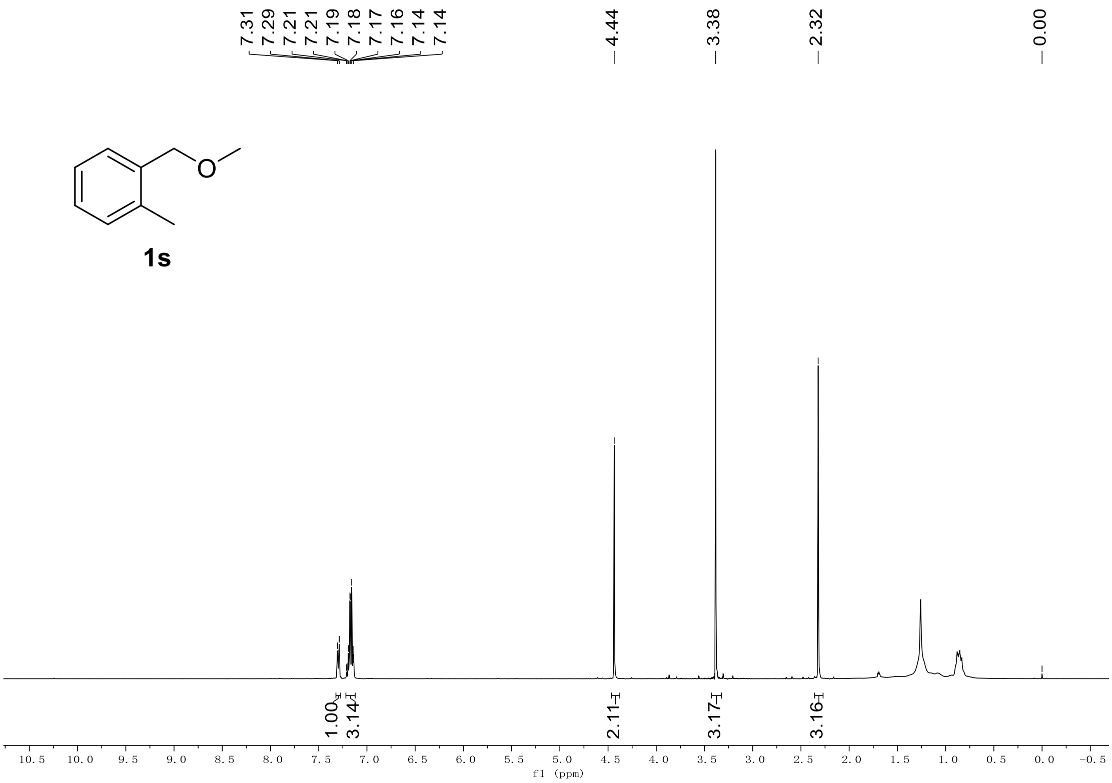

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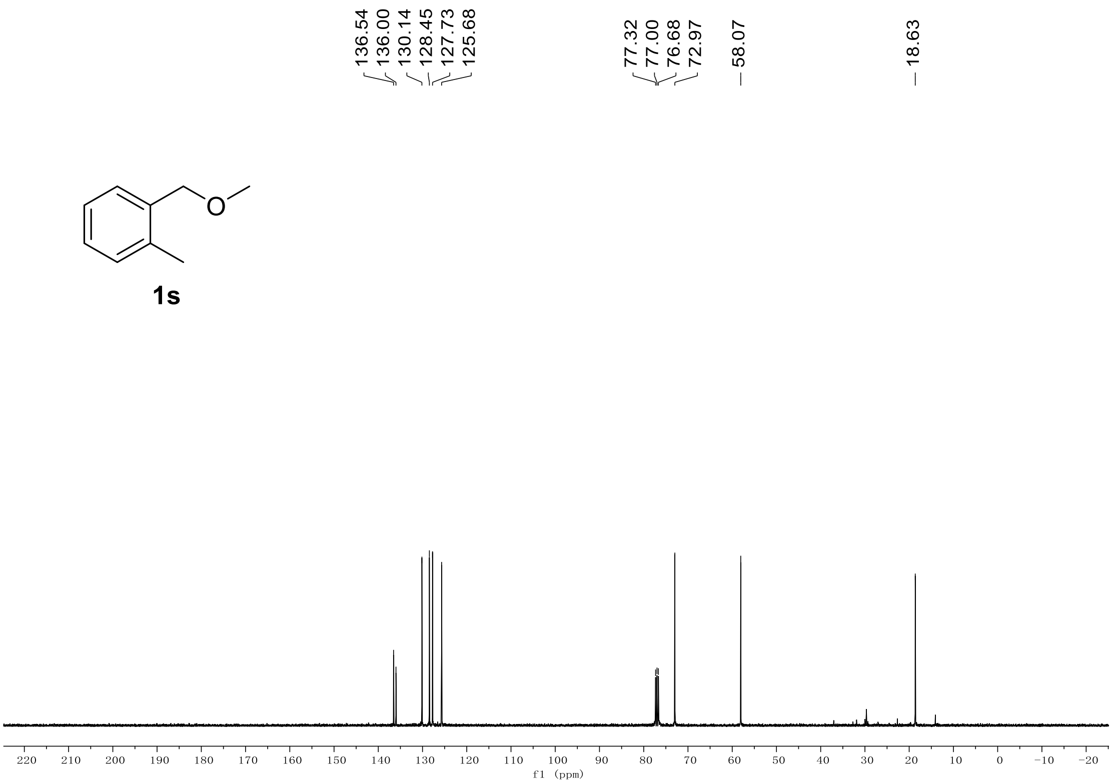

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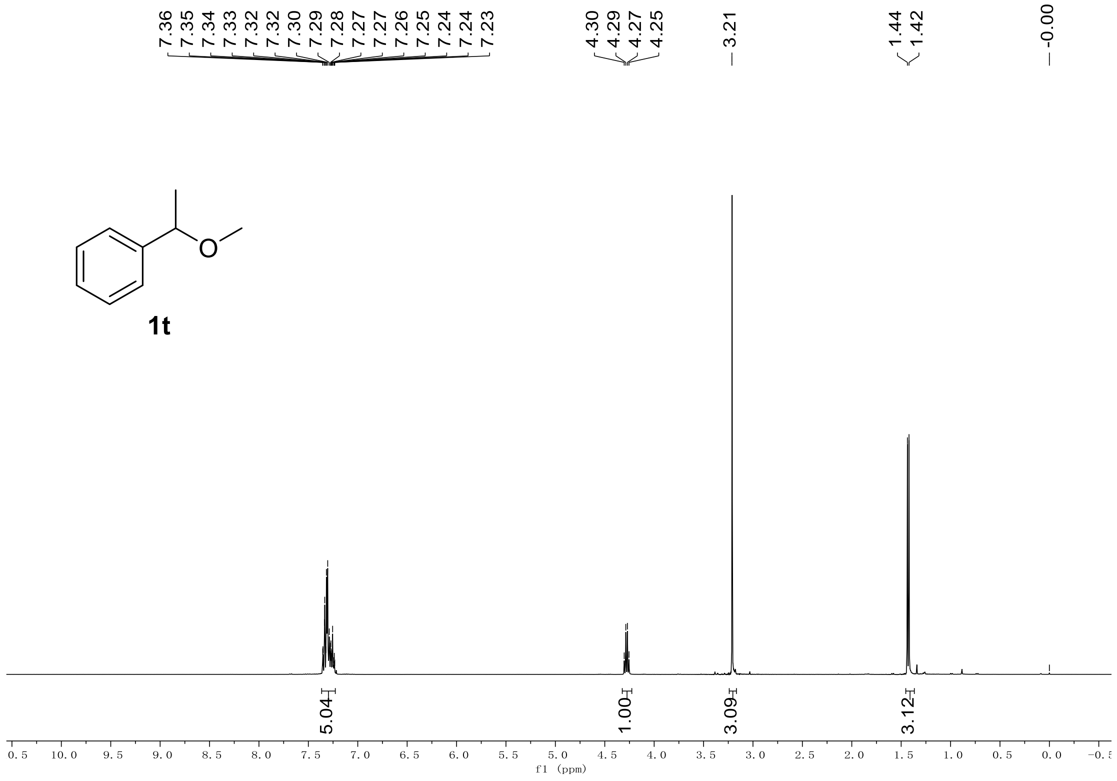

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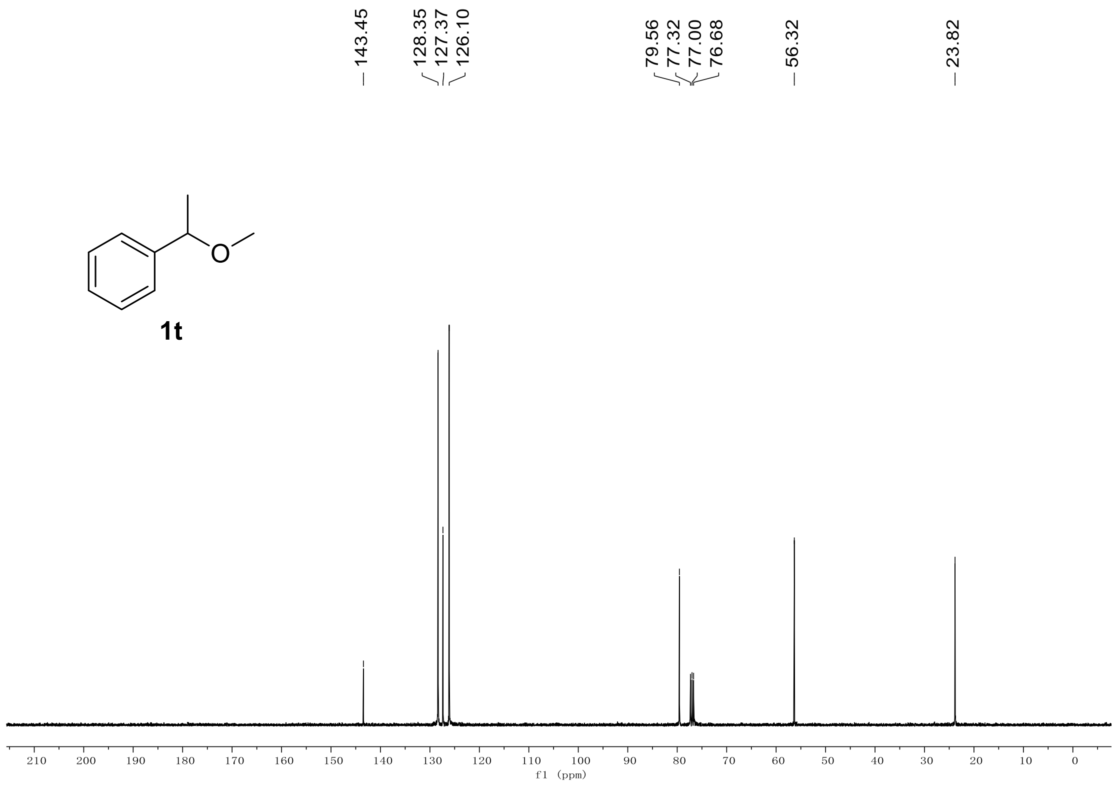

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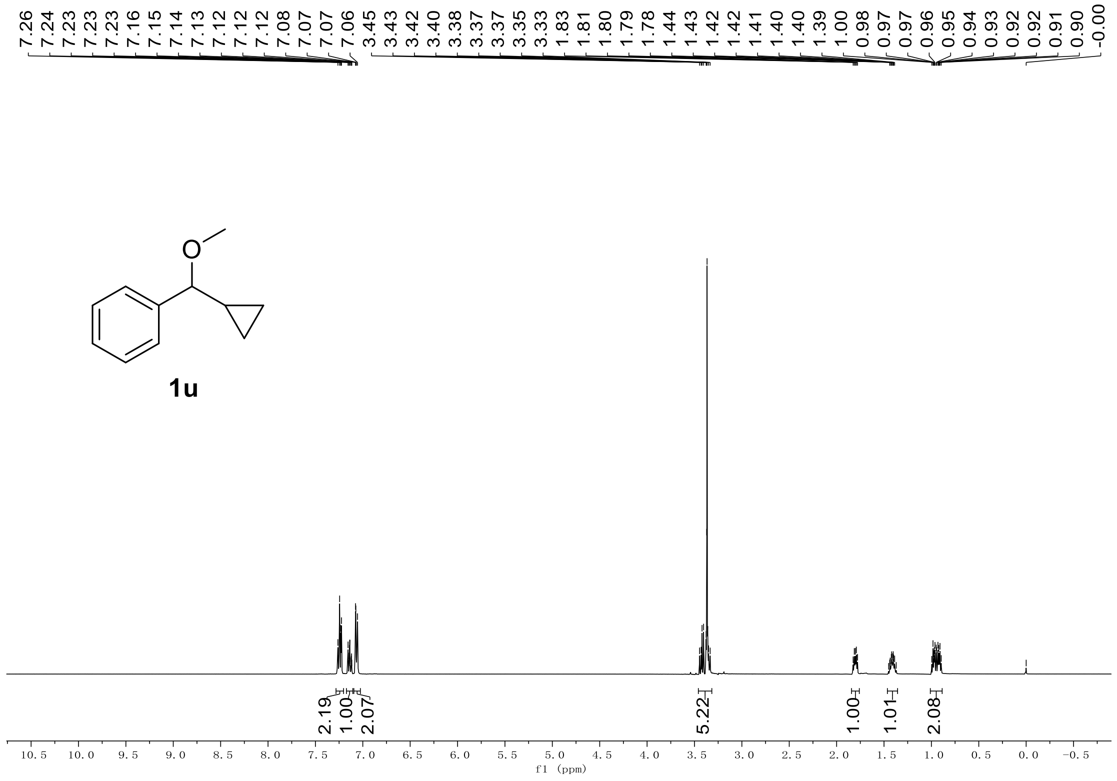

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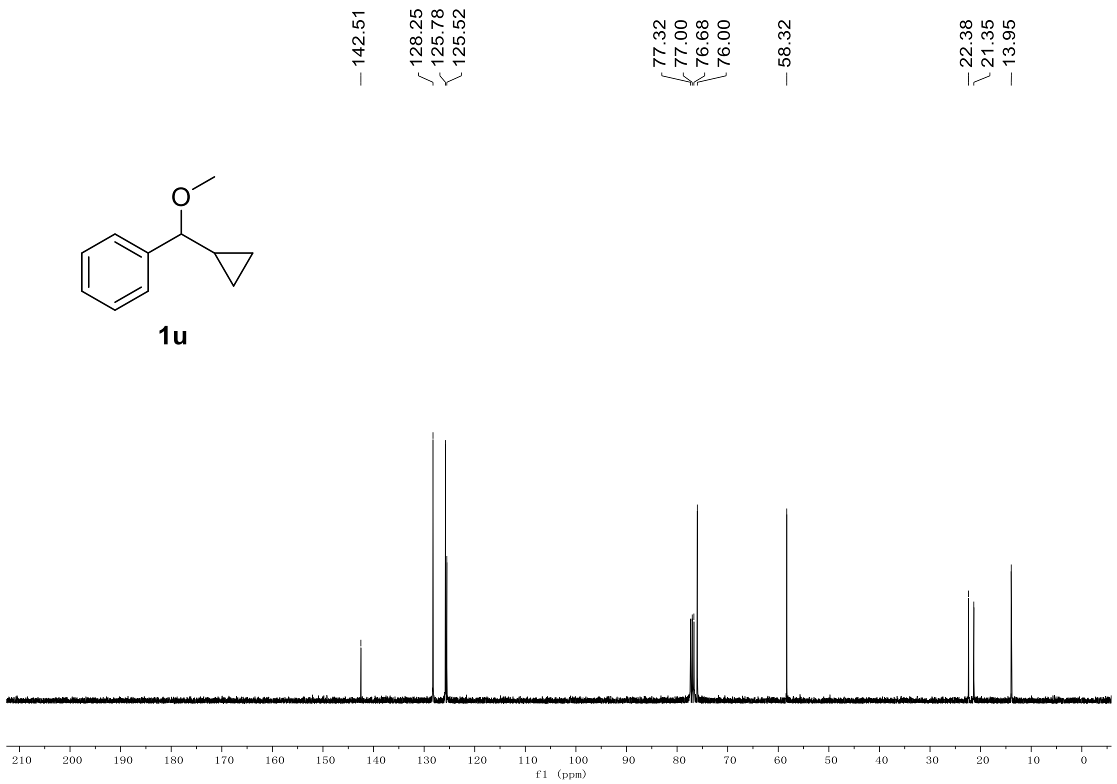

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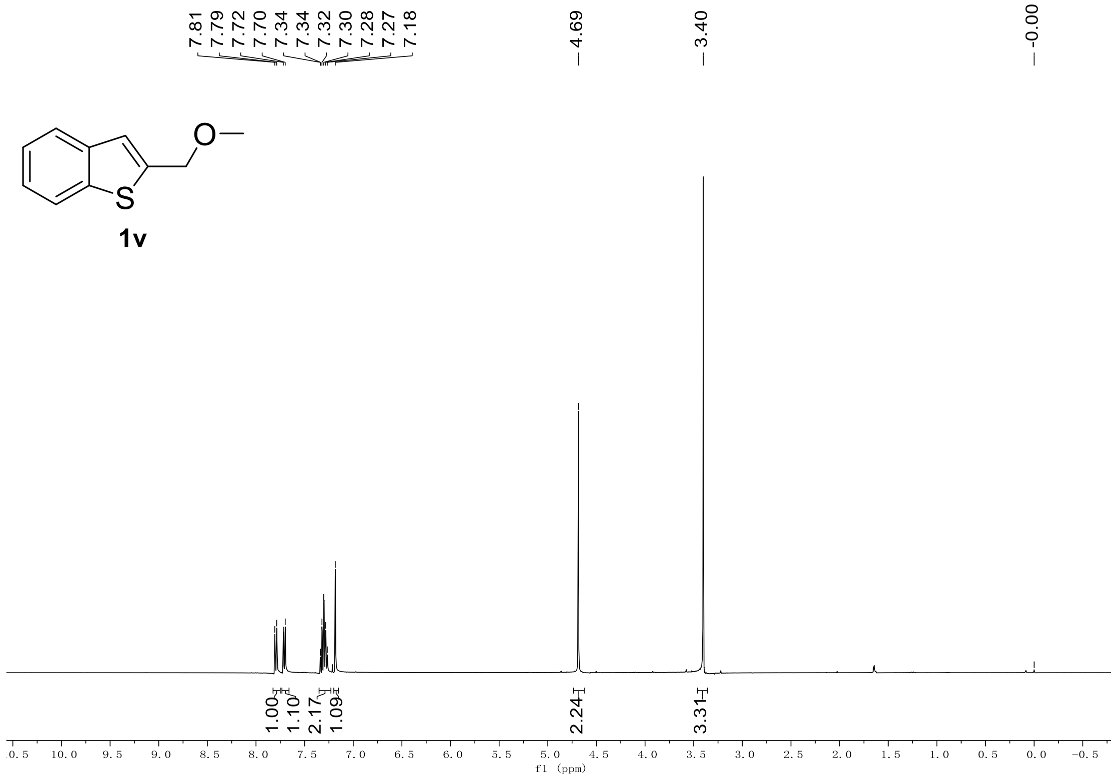

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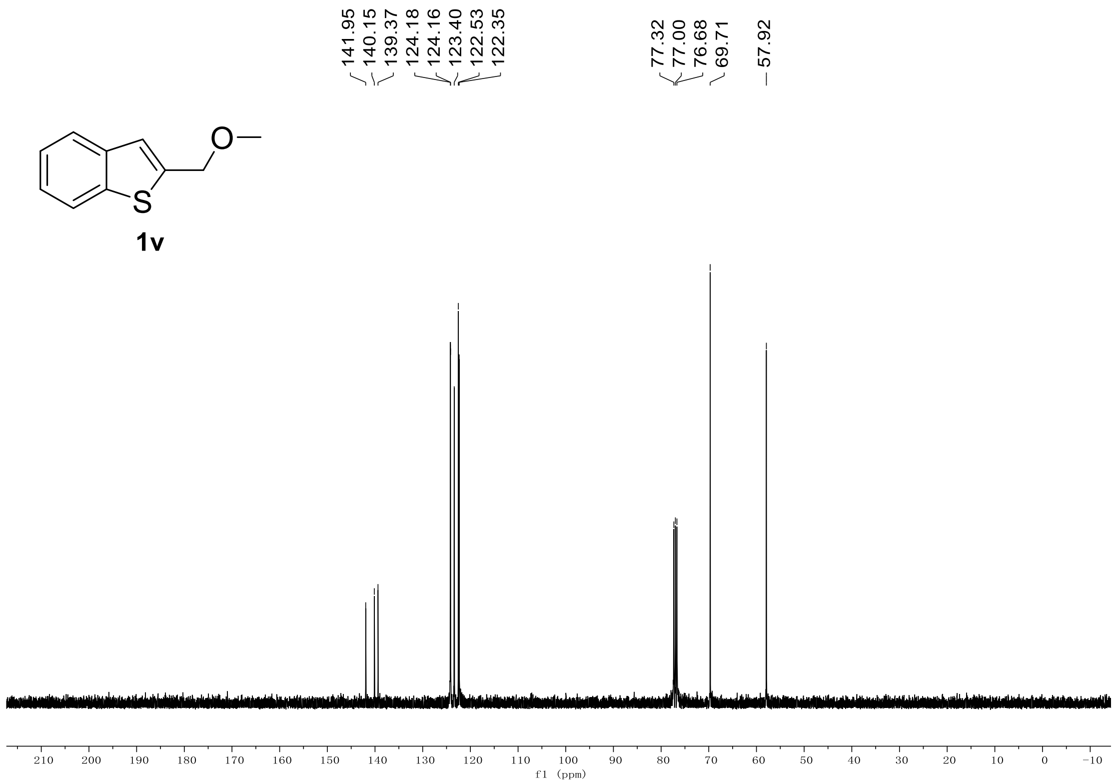

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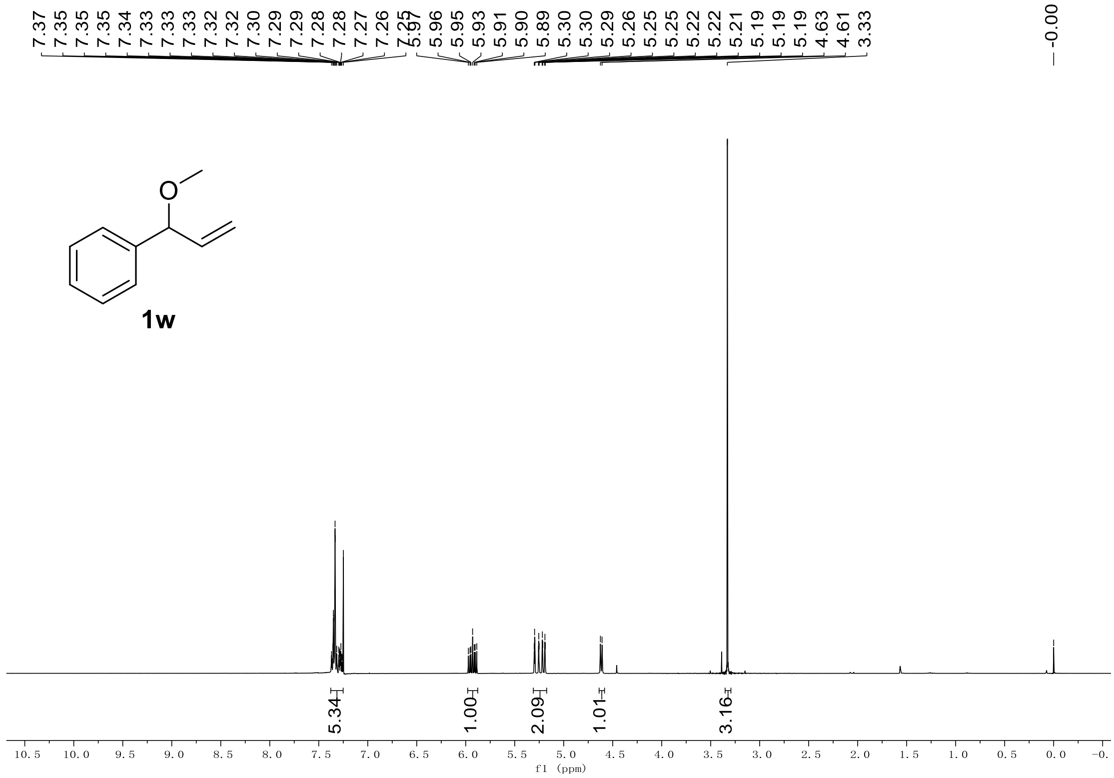

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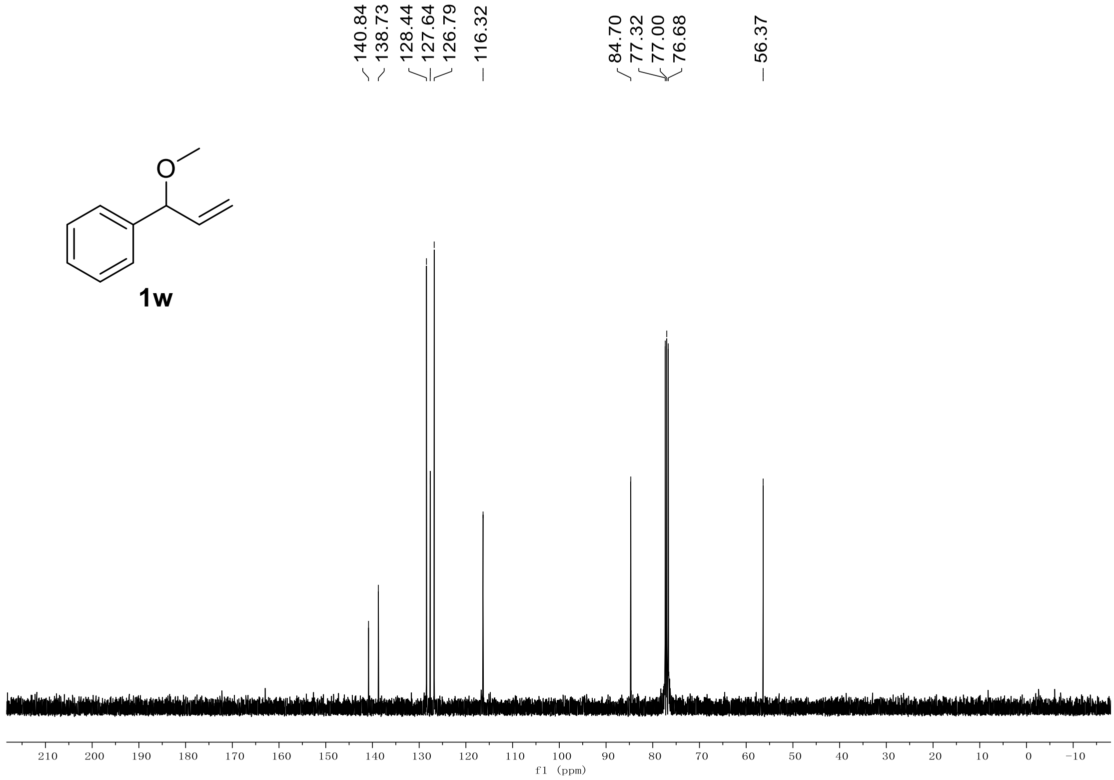

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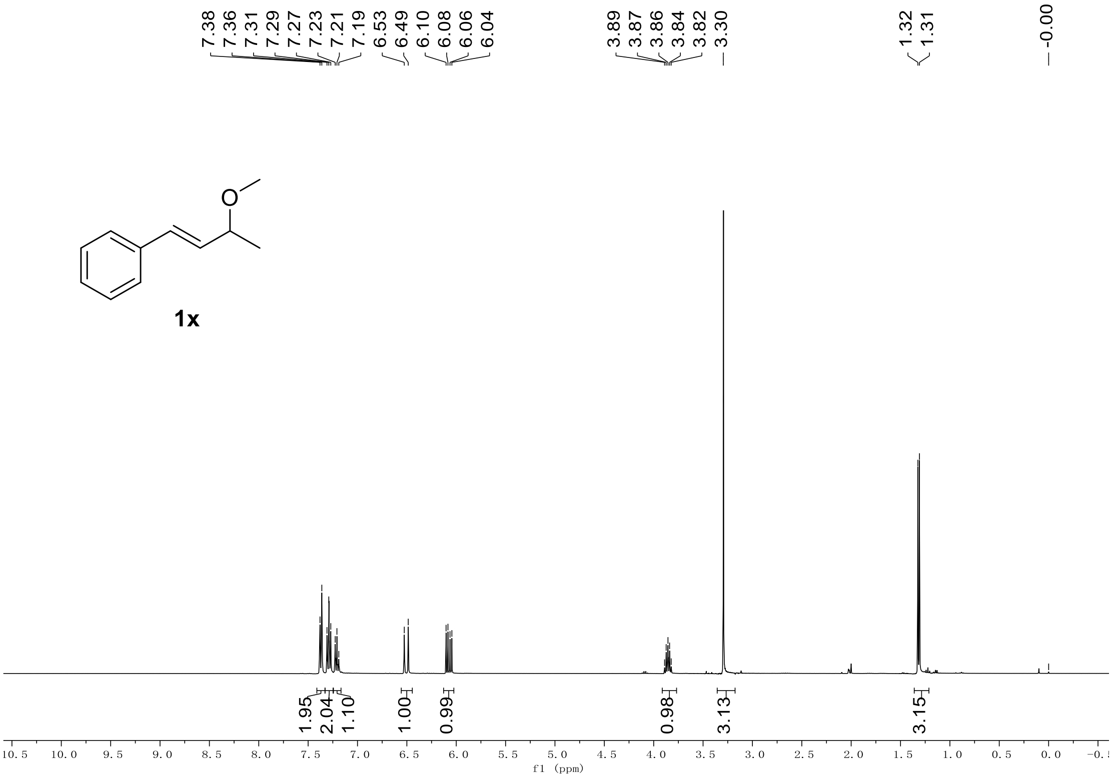

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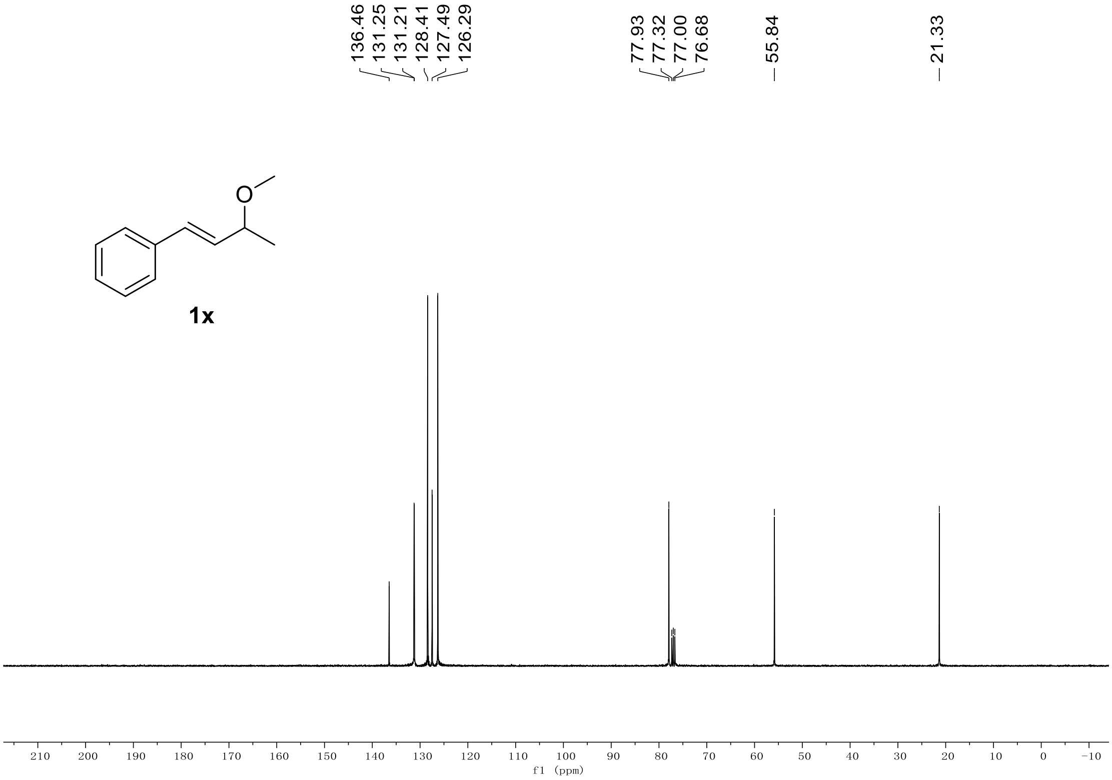

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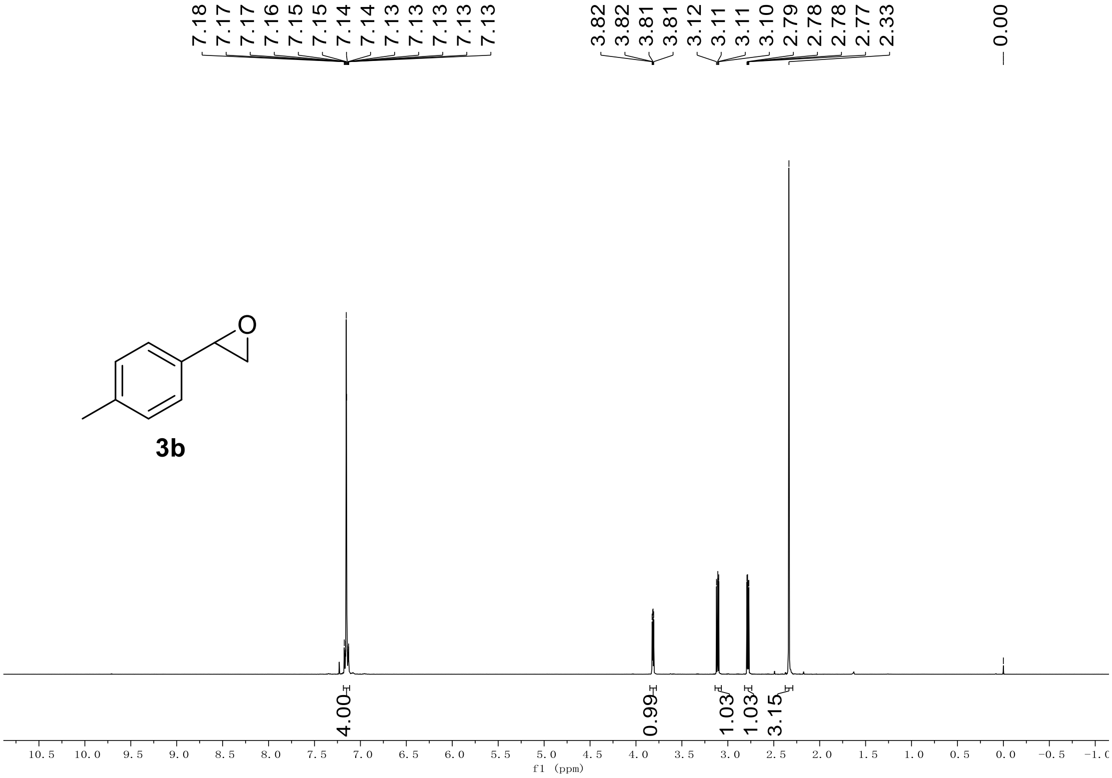
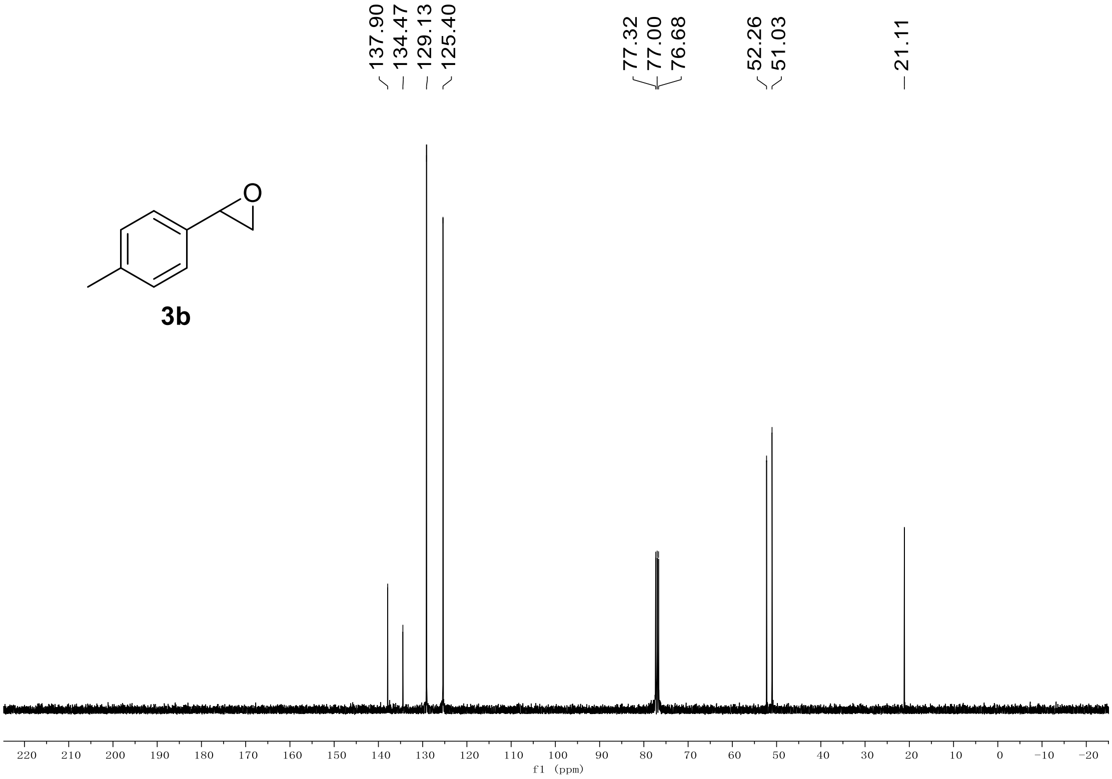


^{13}C NMR, 100 MHz, $CDCl_3$



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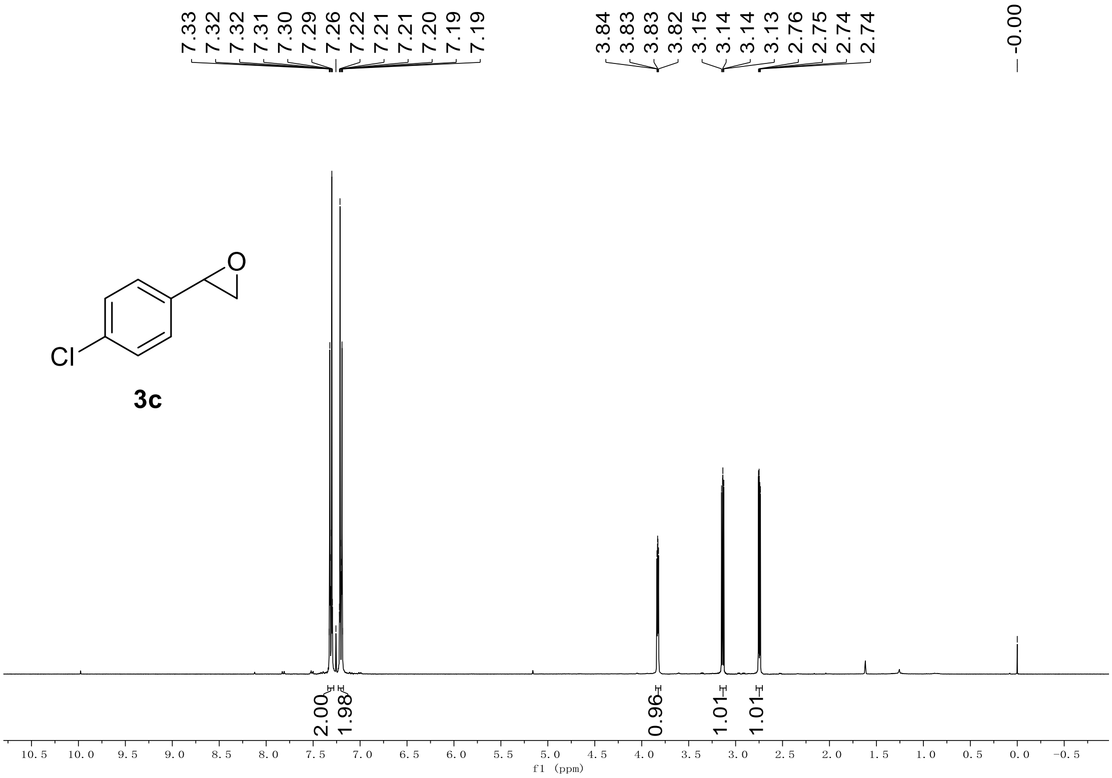

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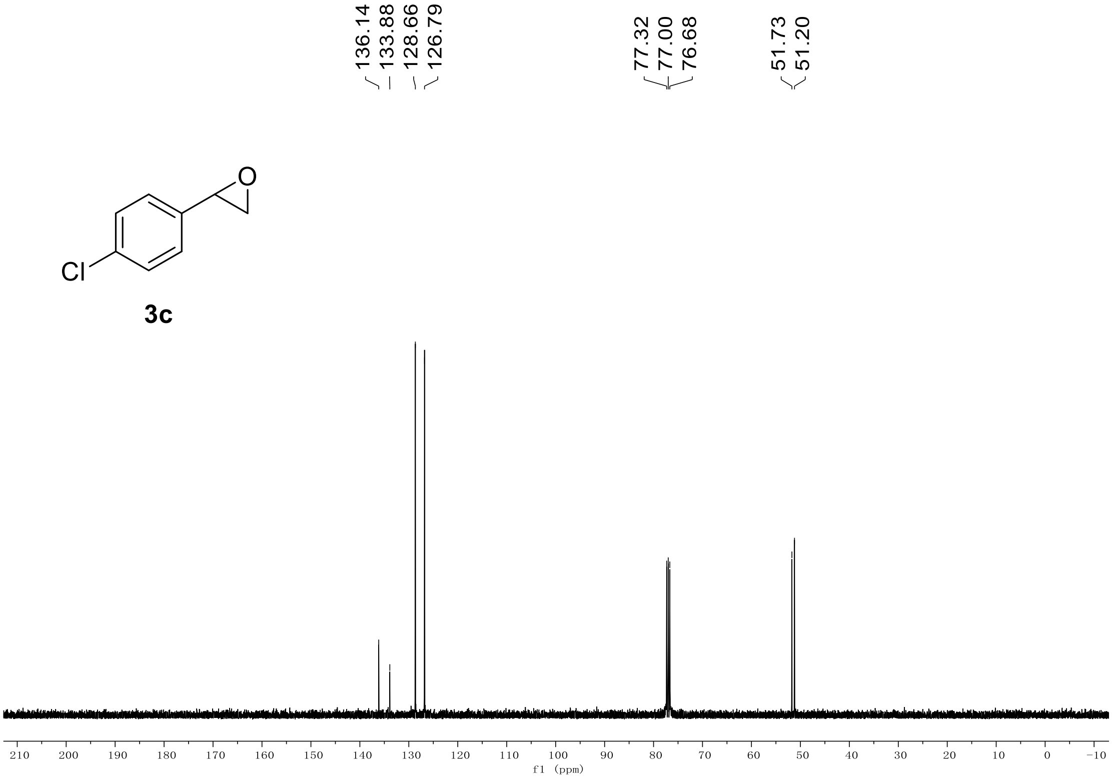

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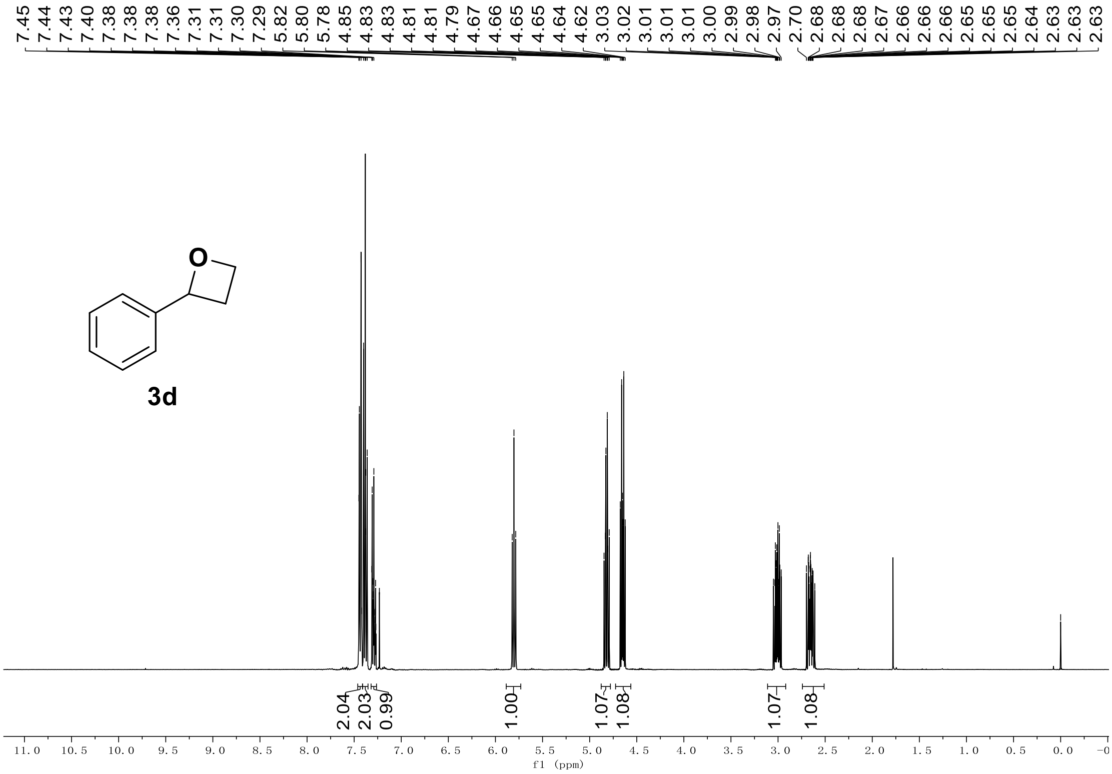

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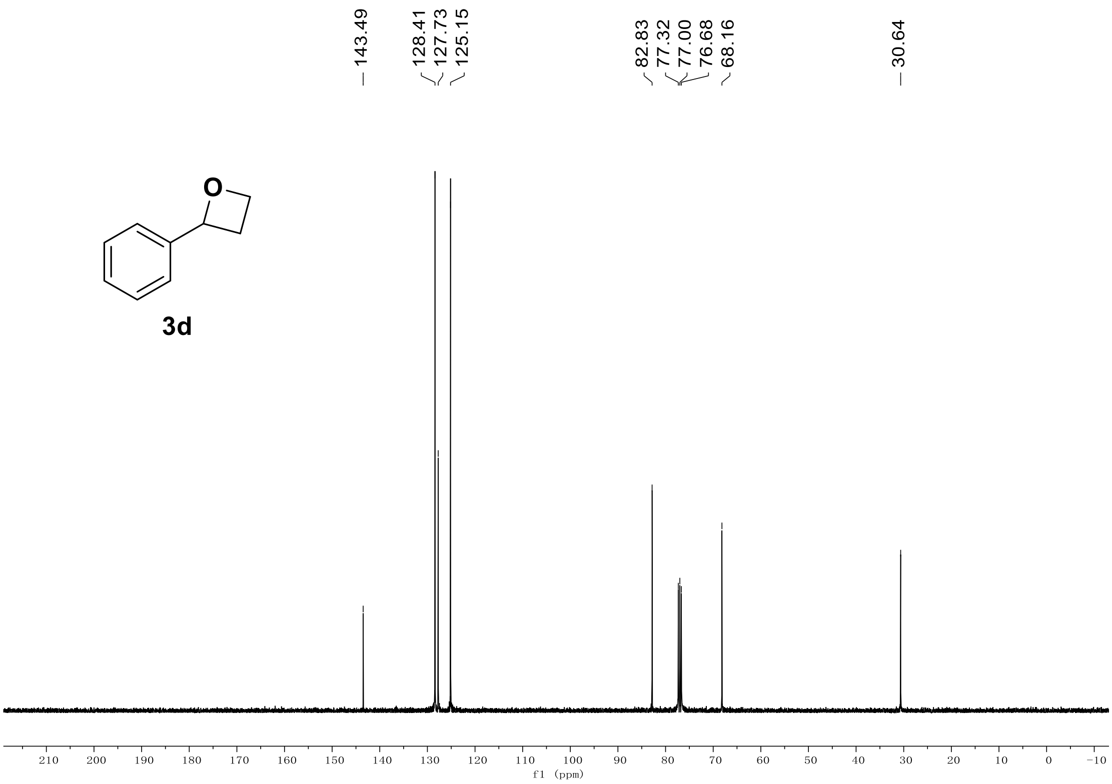

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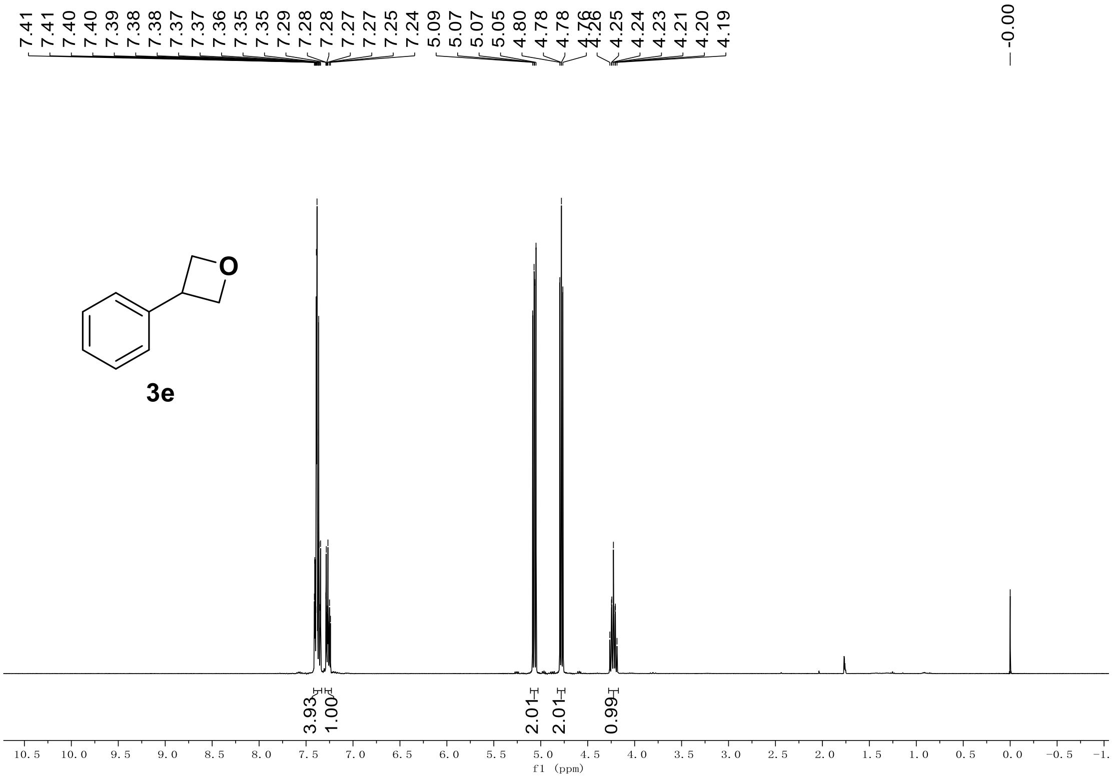

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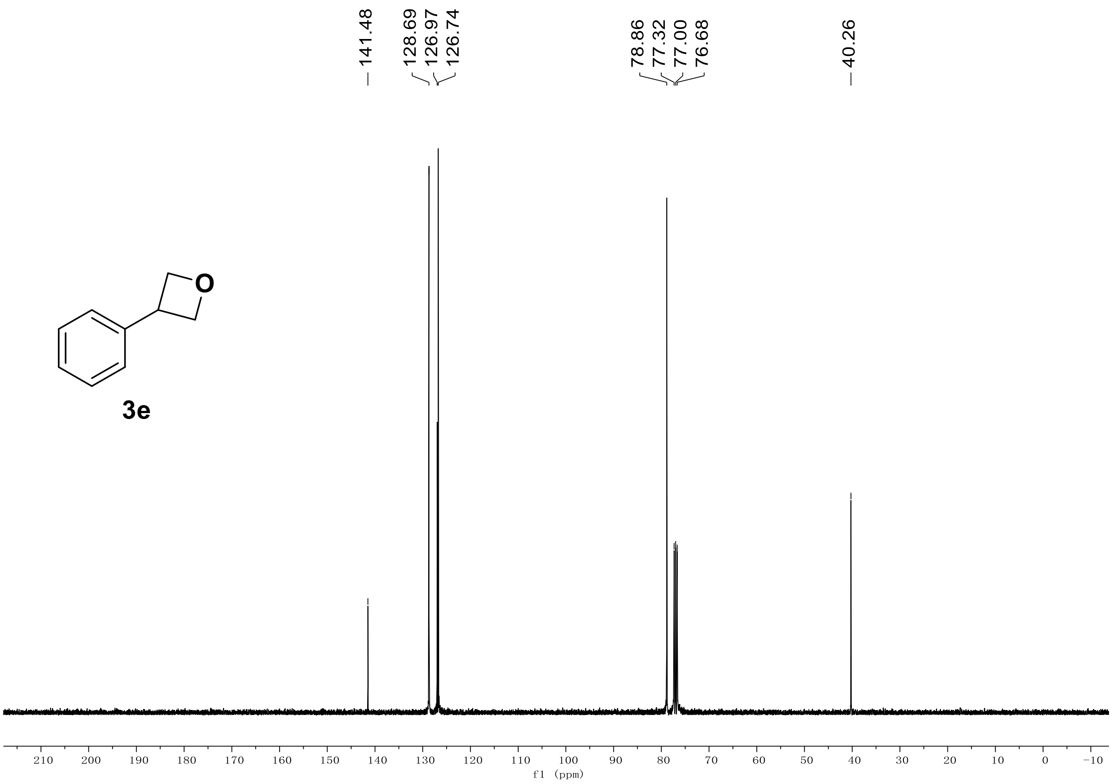

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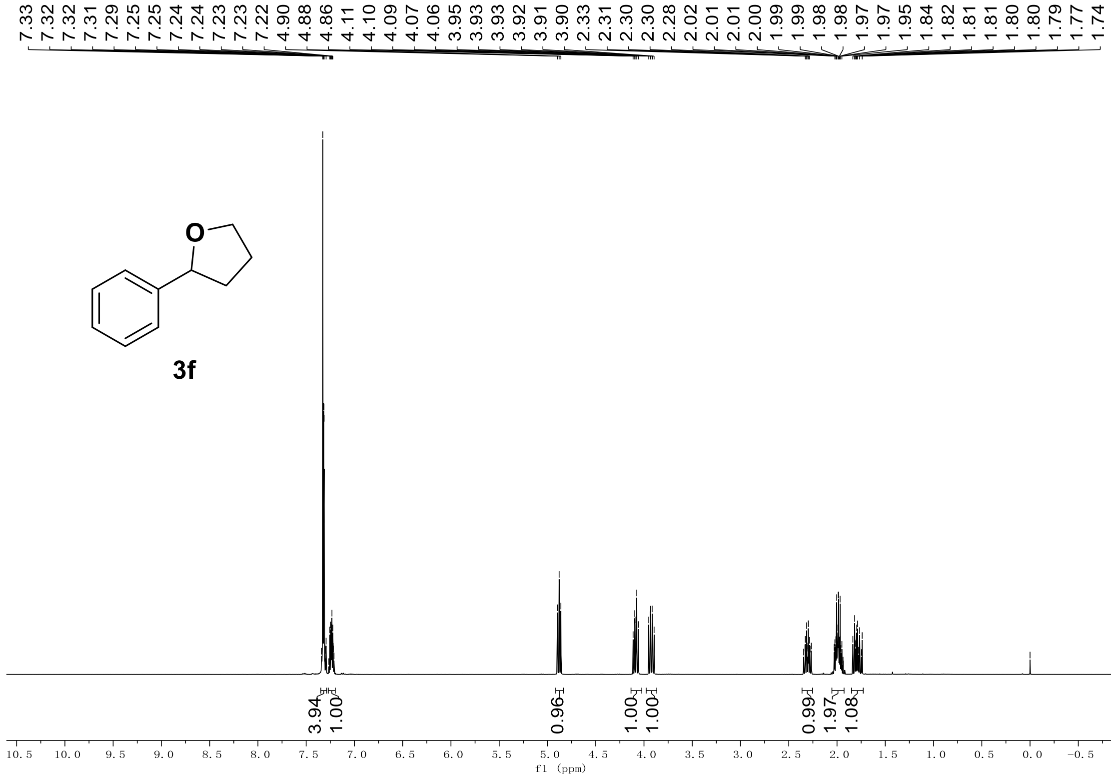

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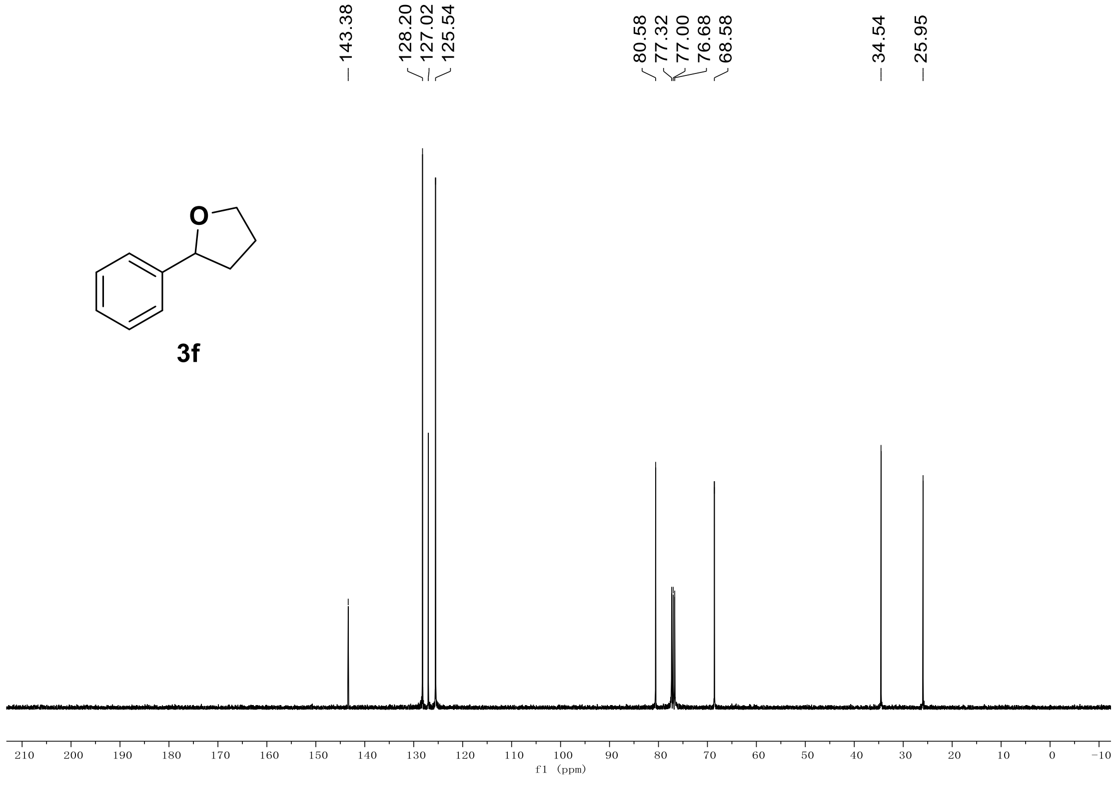

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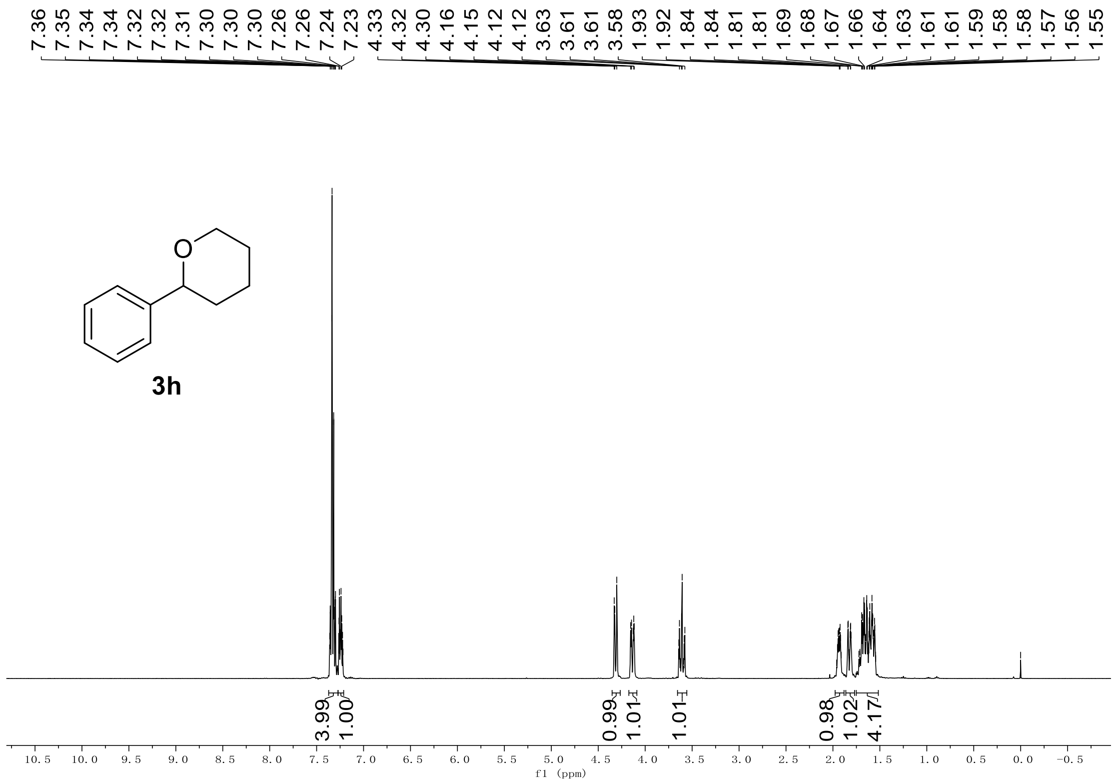

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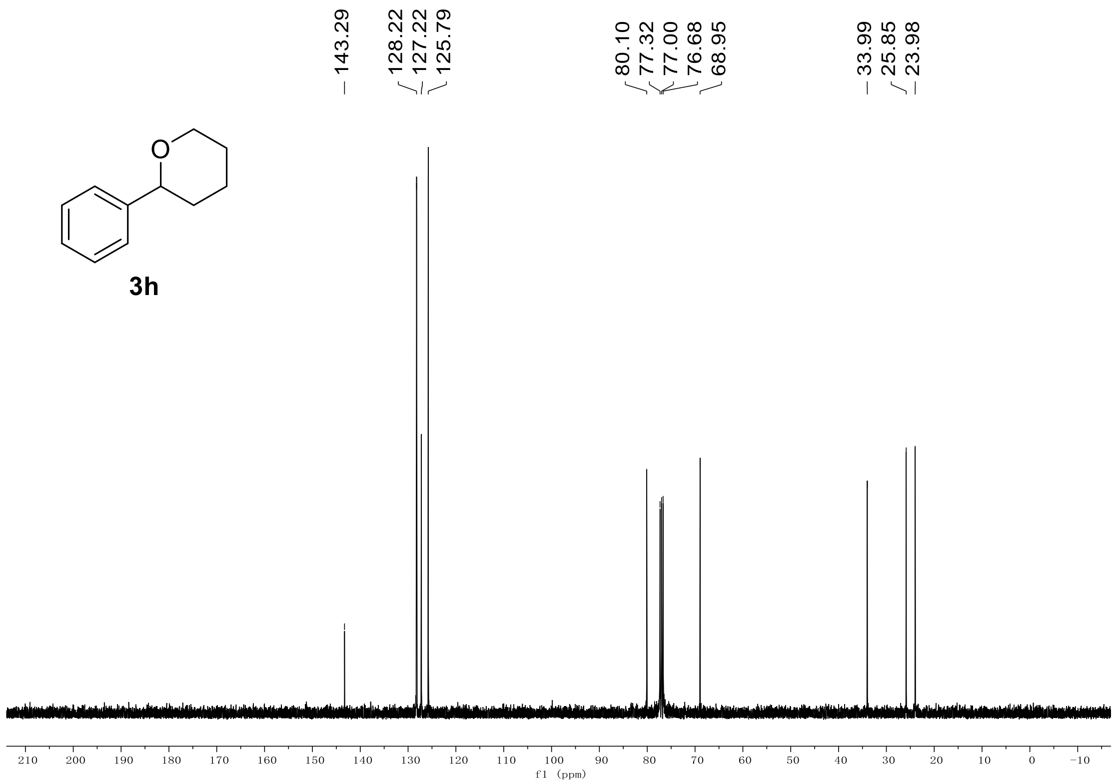

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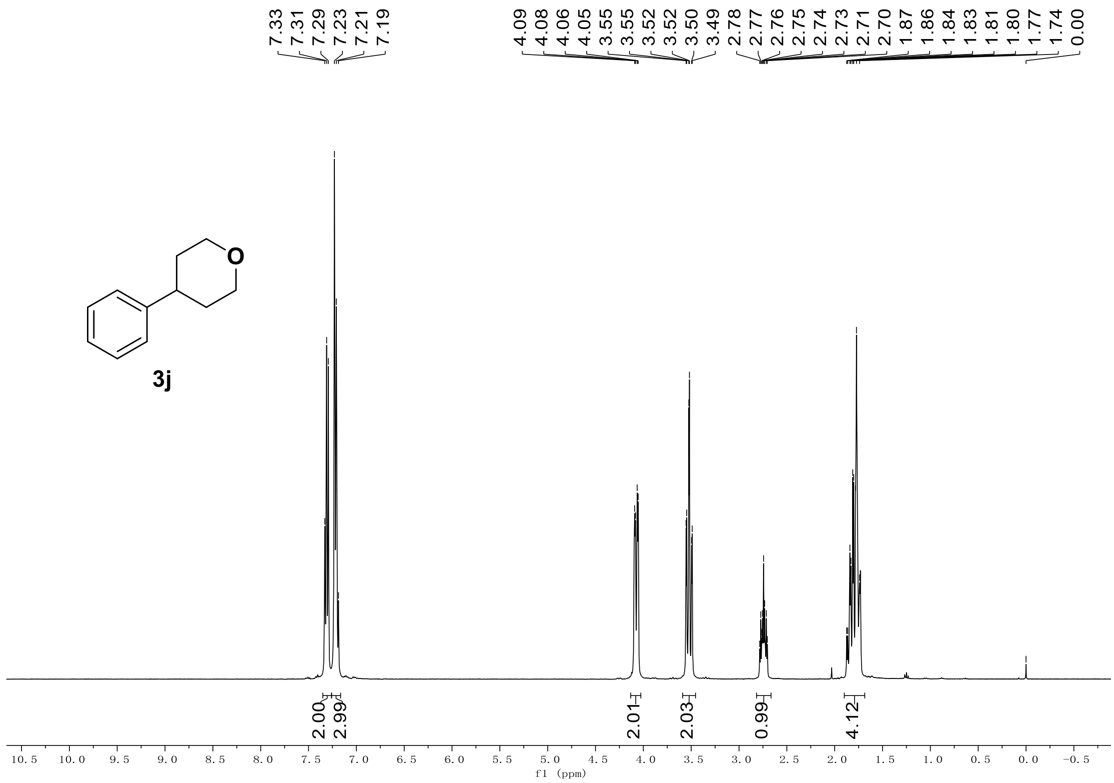

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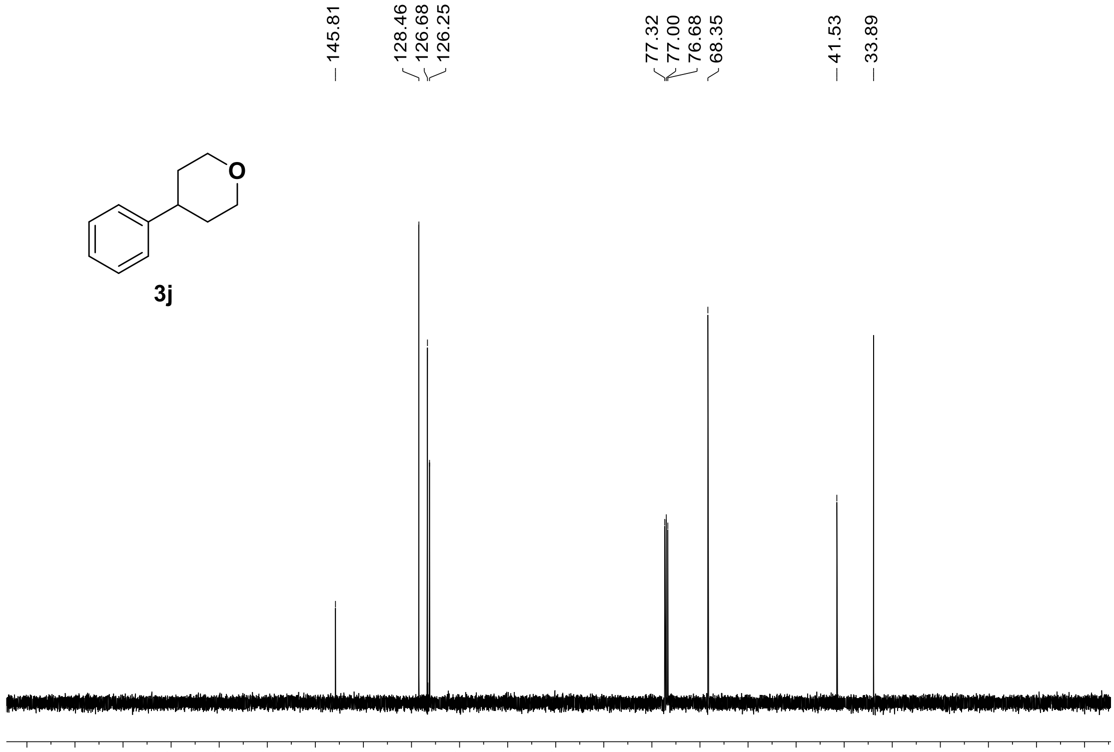

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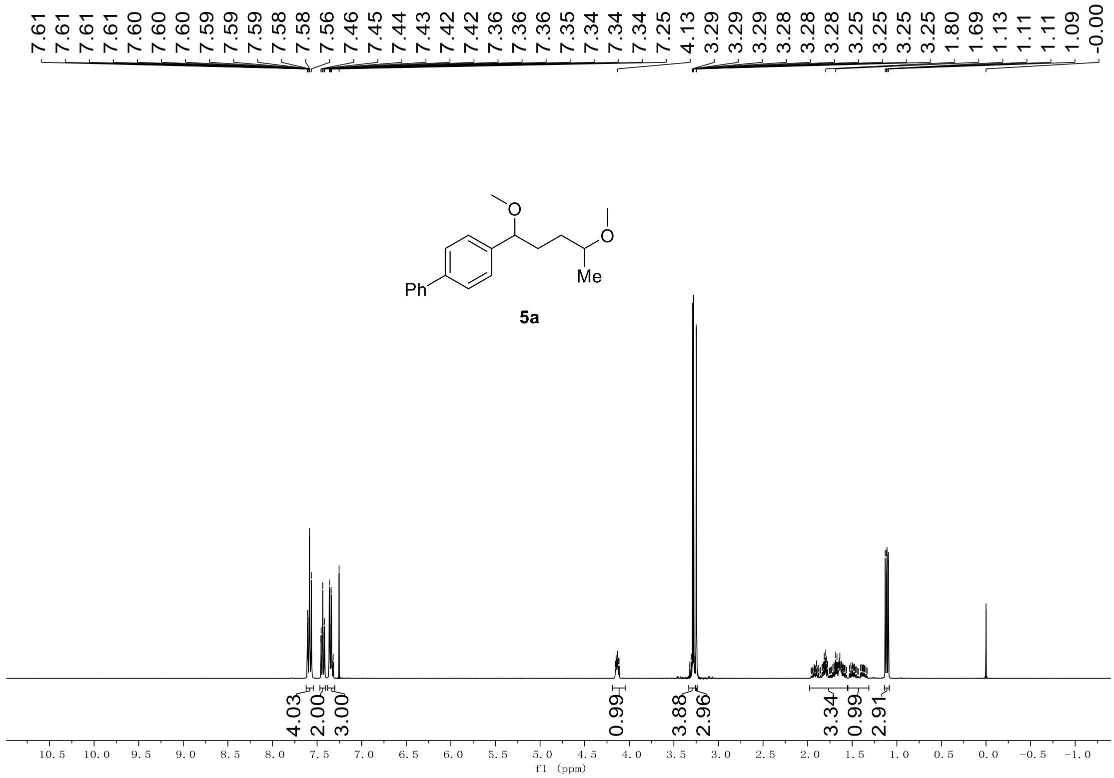

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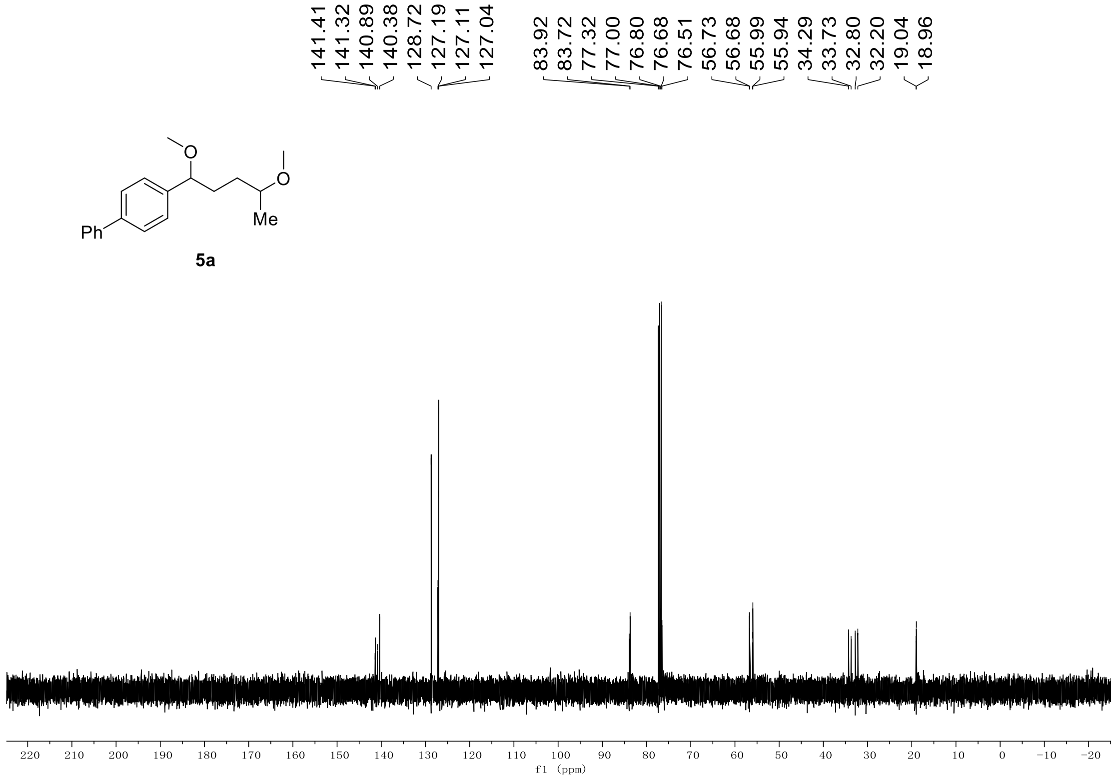

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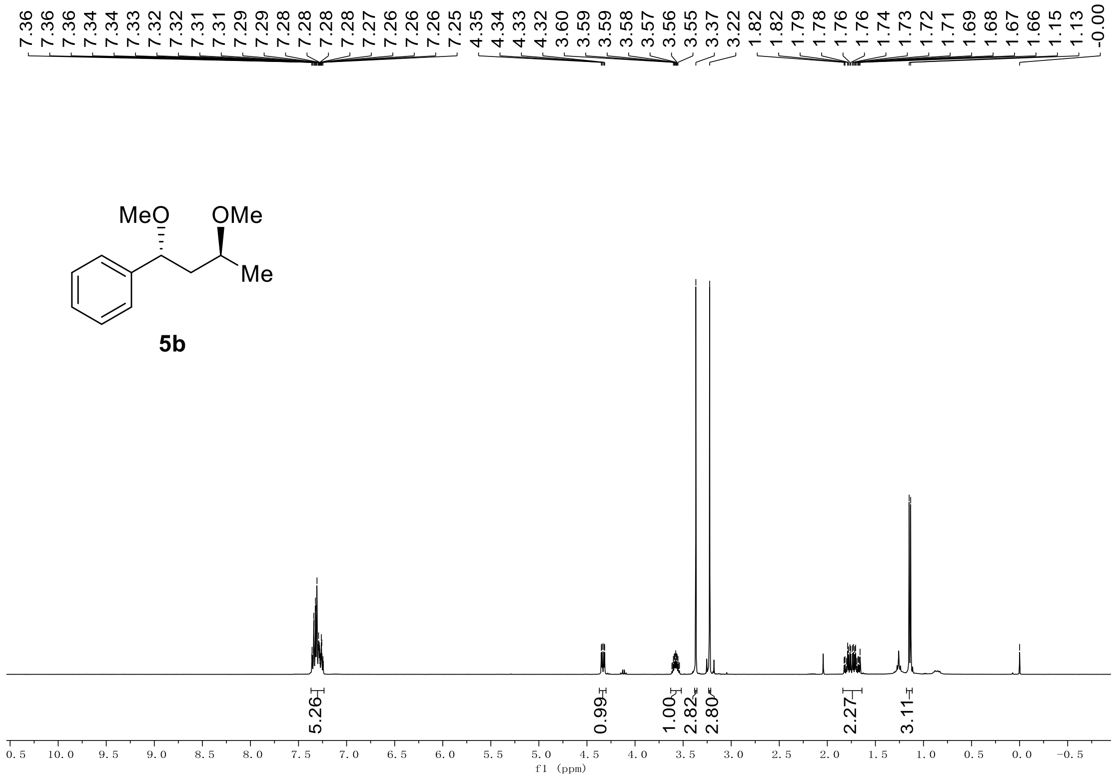

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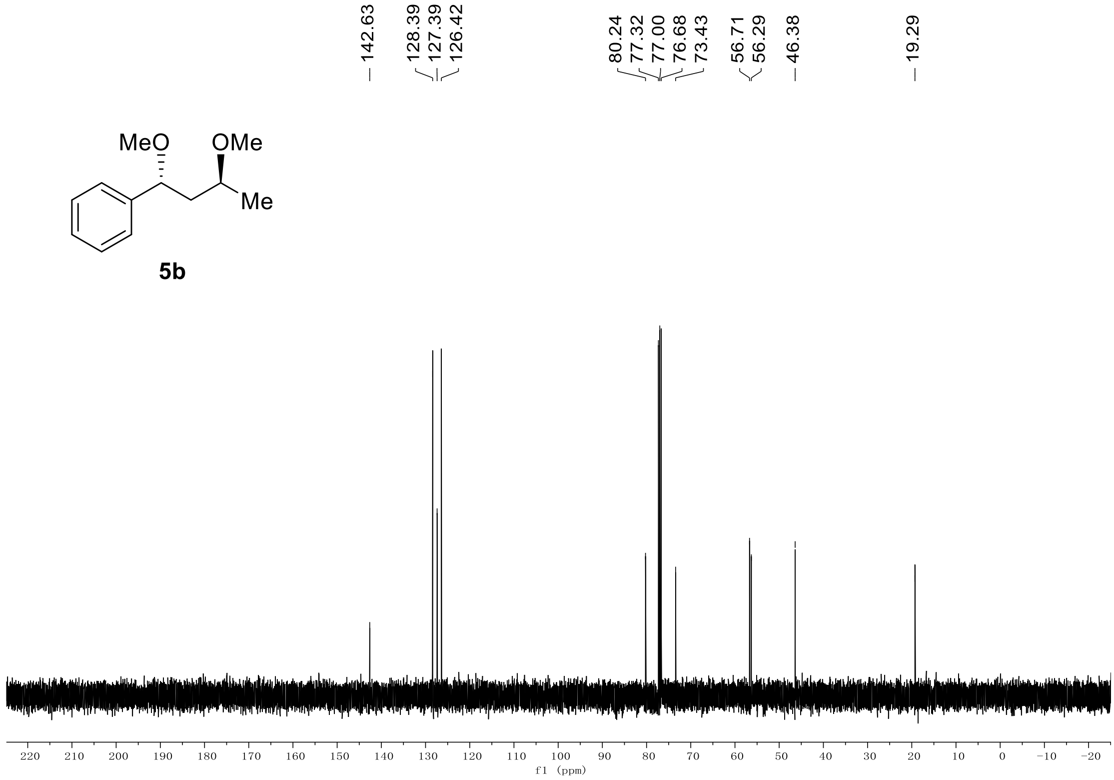

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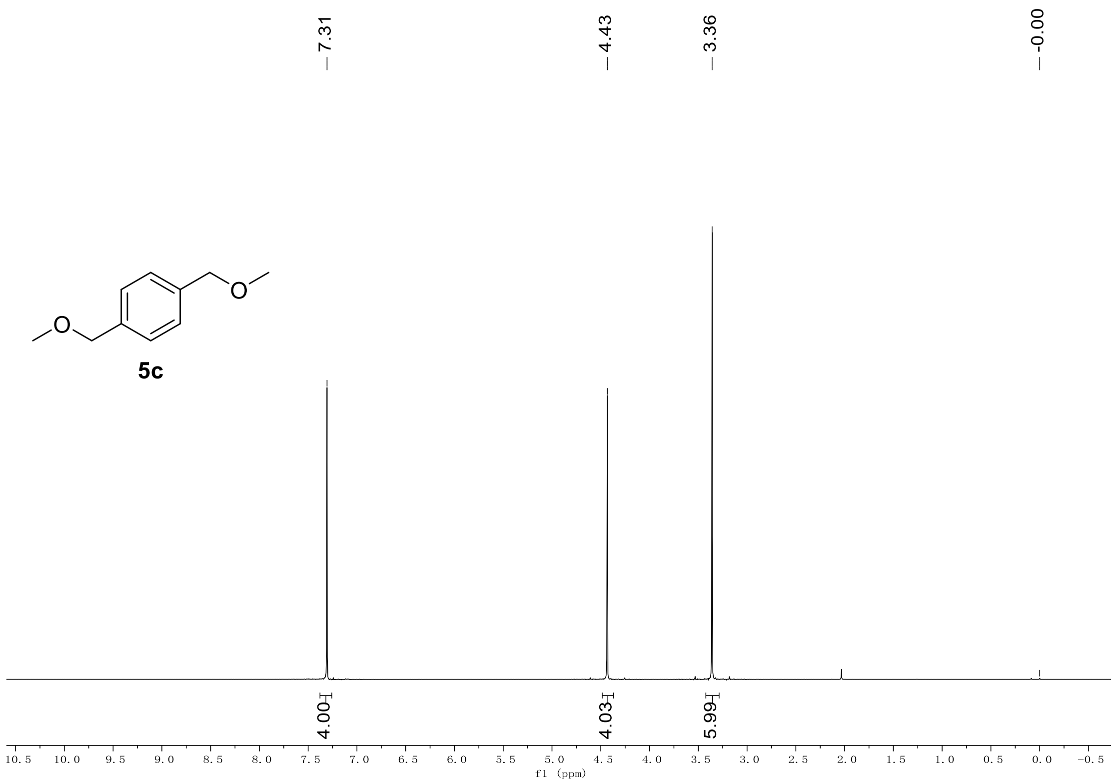

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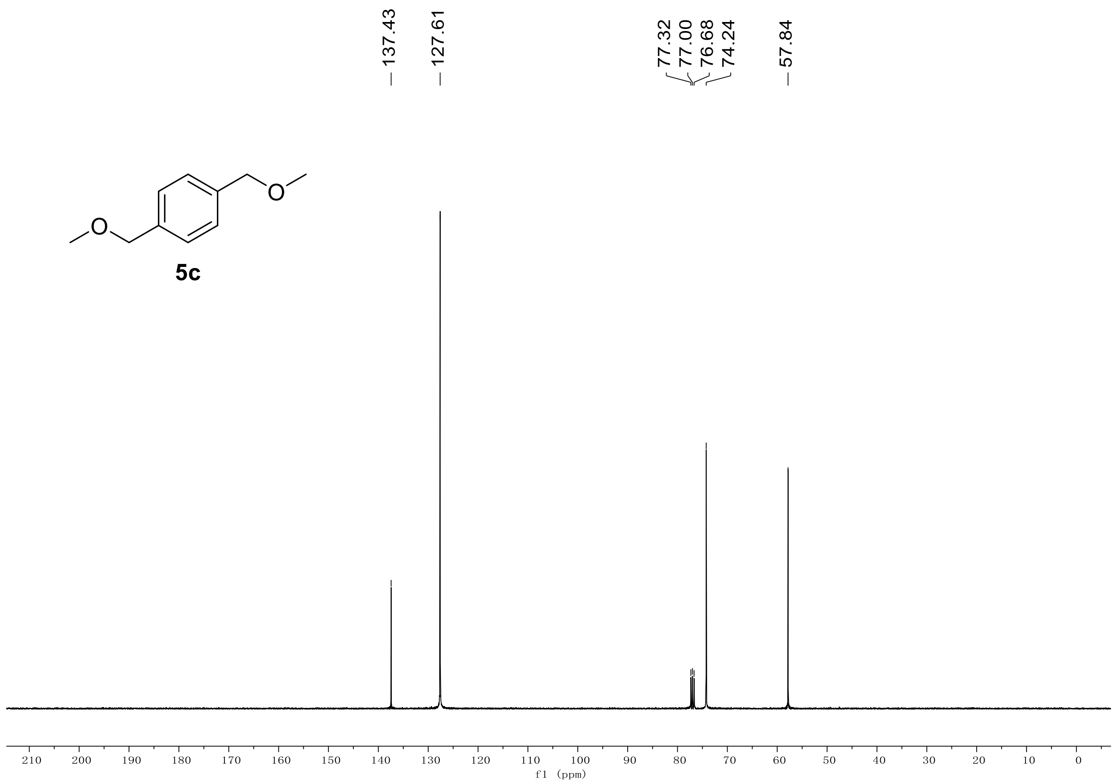

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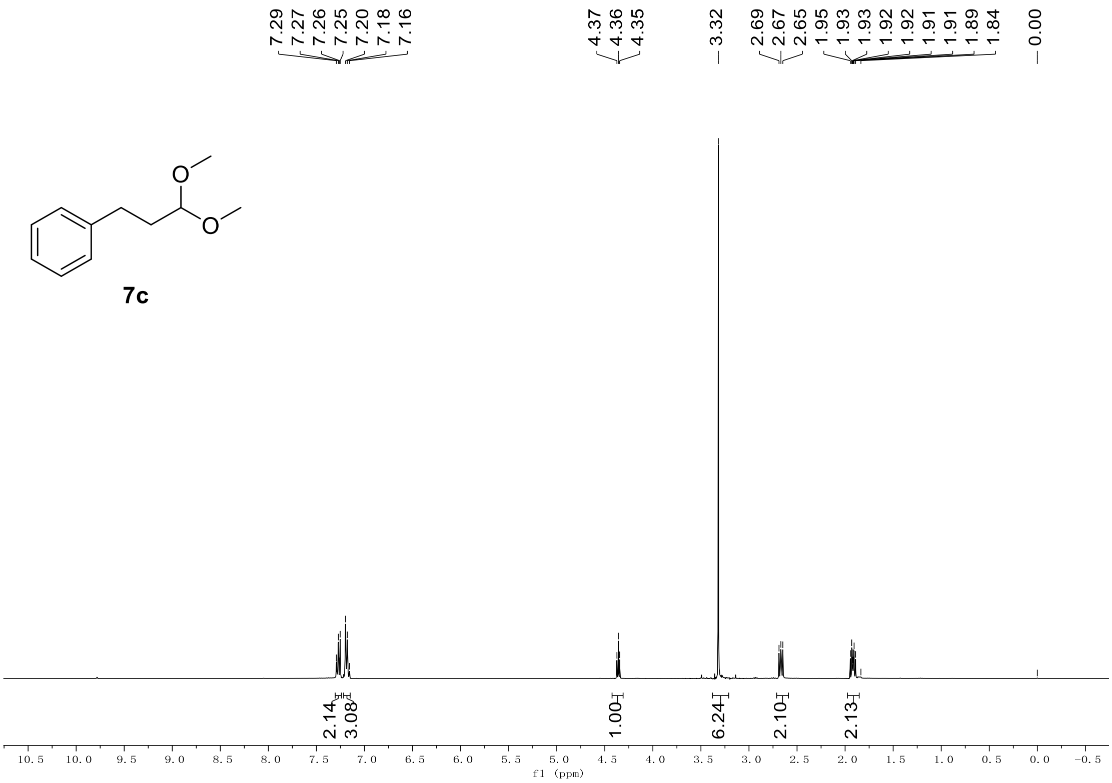

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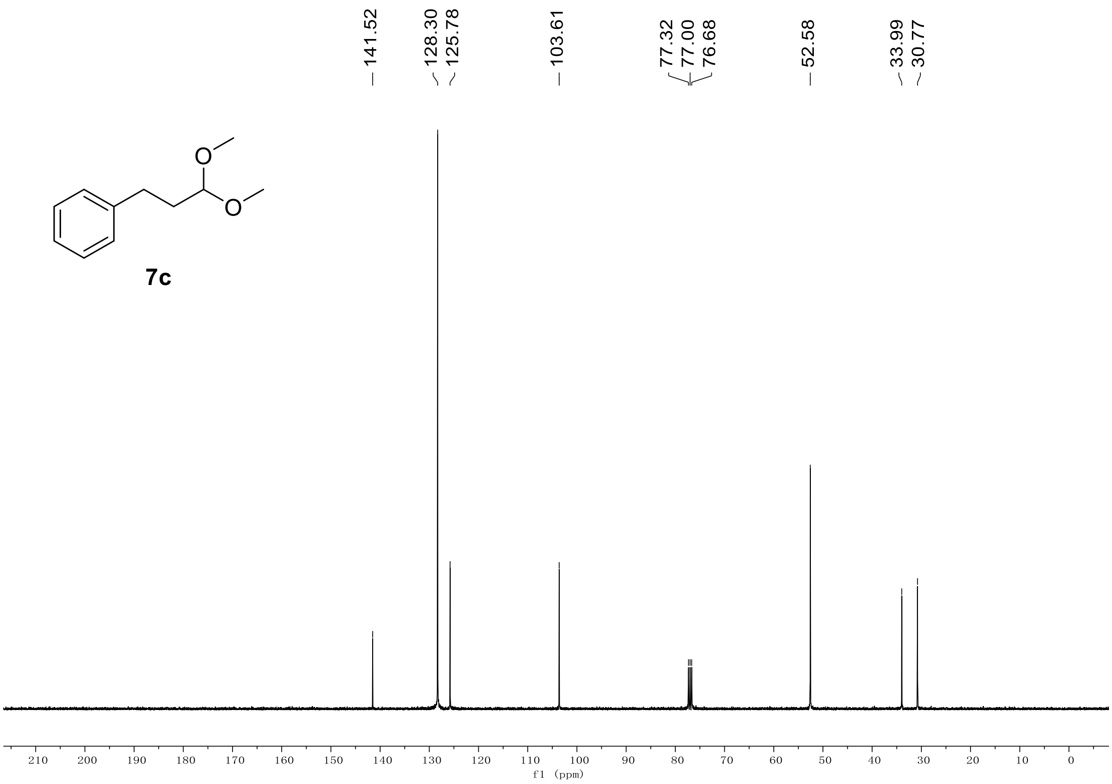

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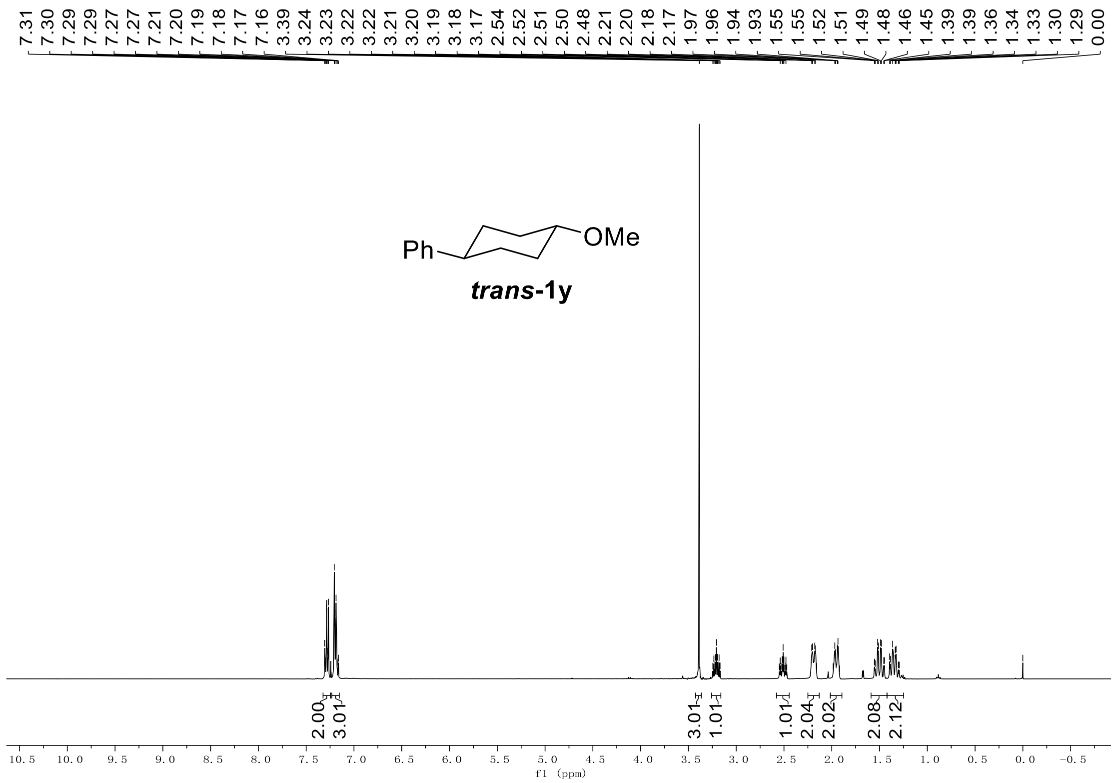

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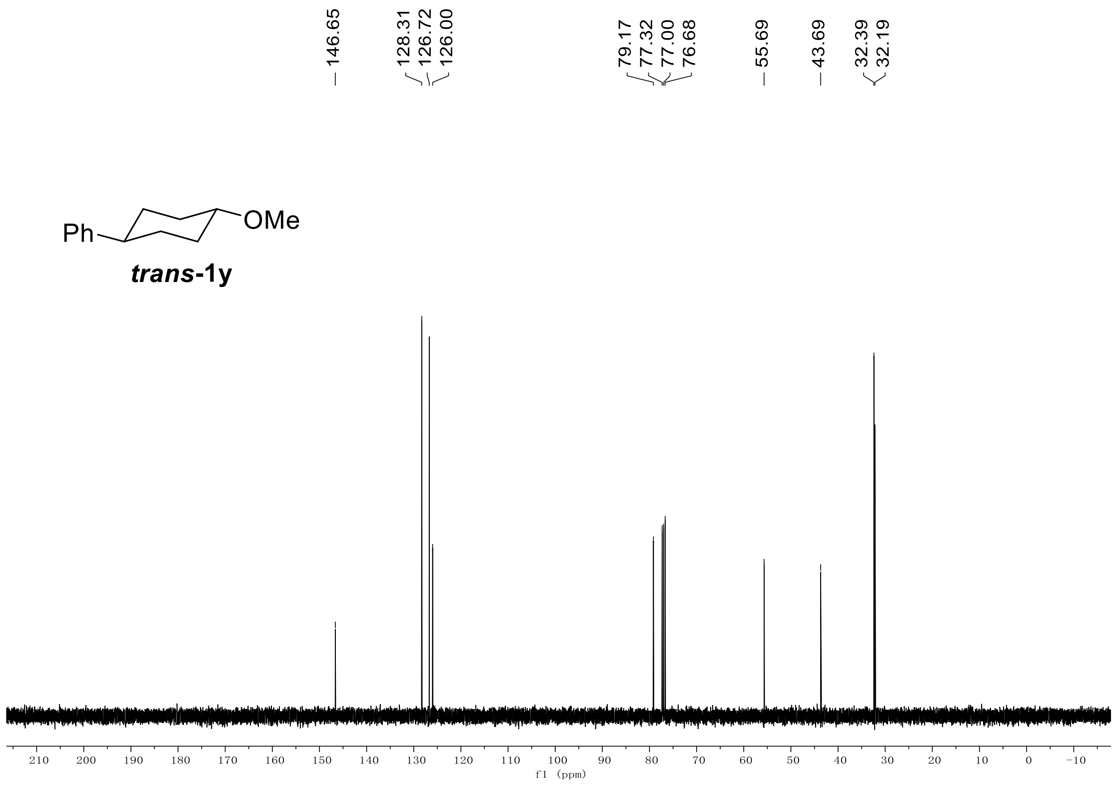

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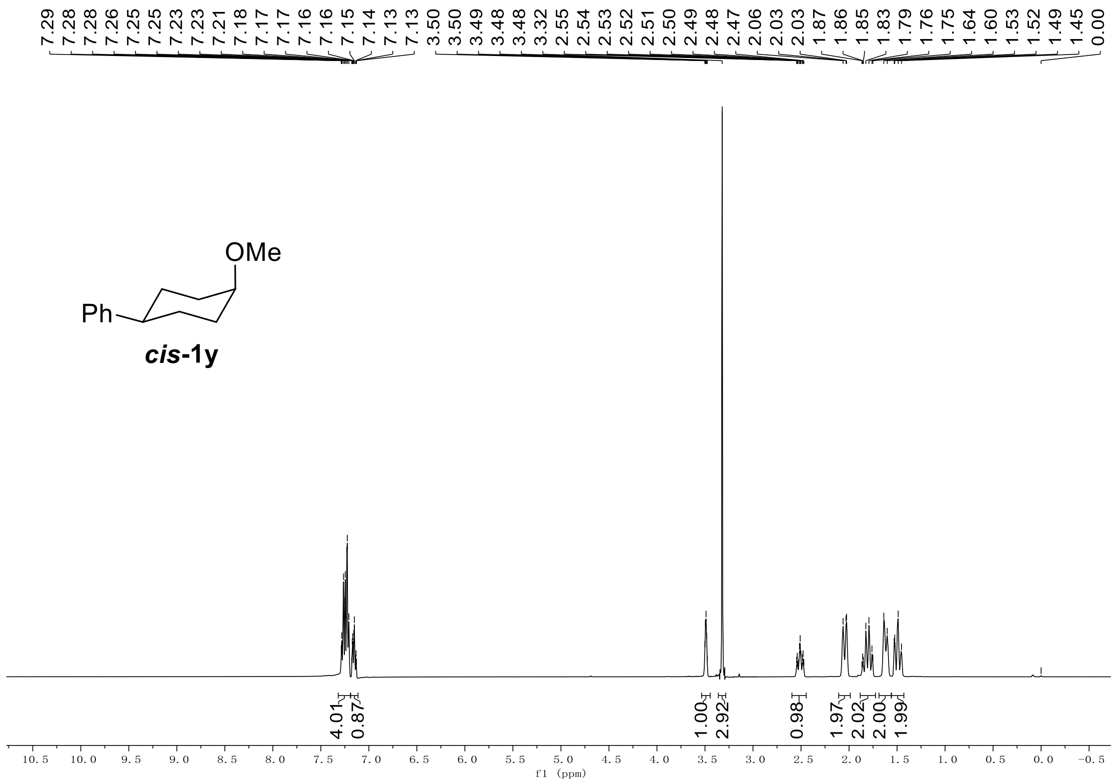

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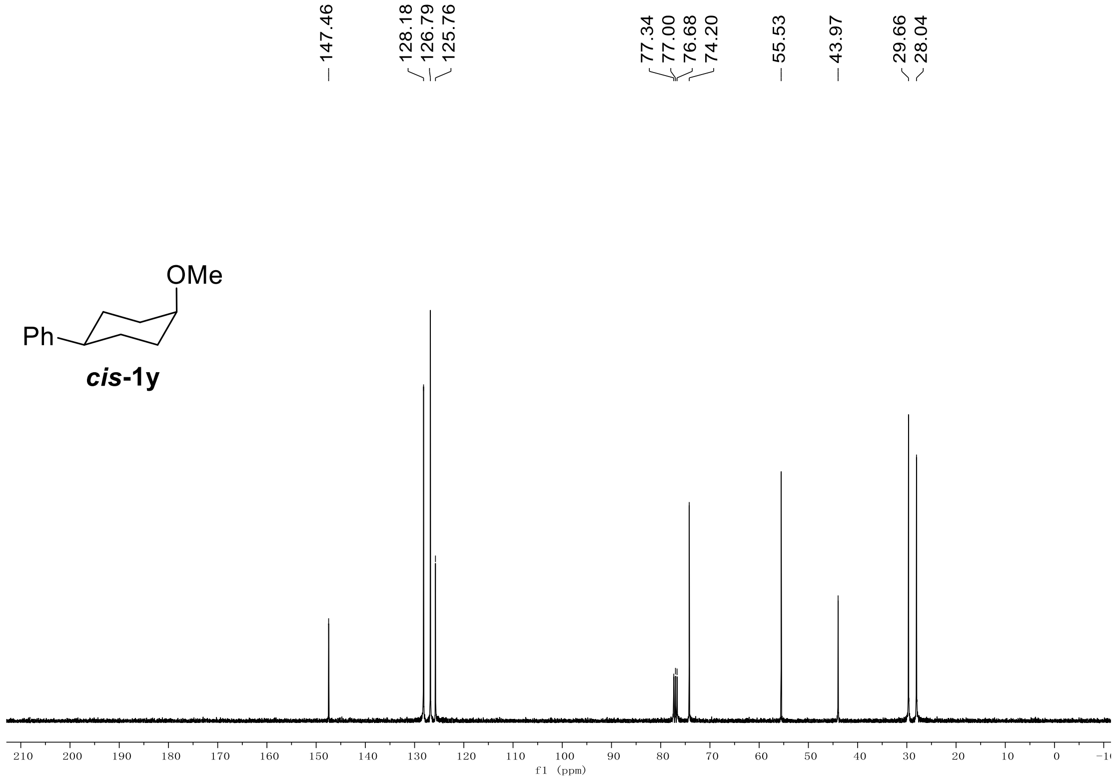

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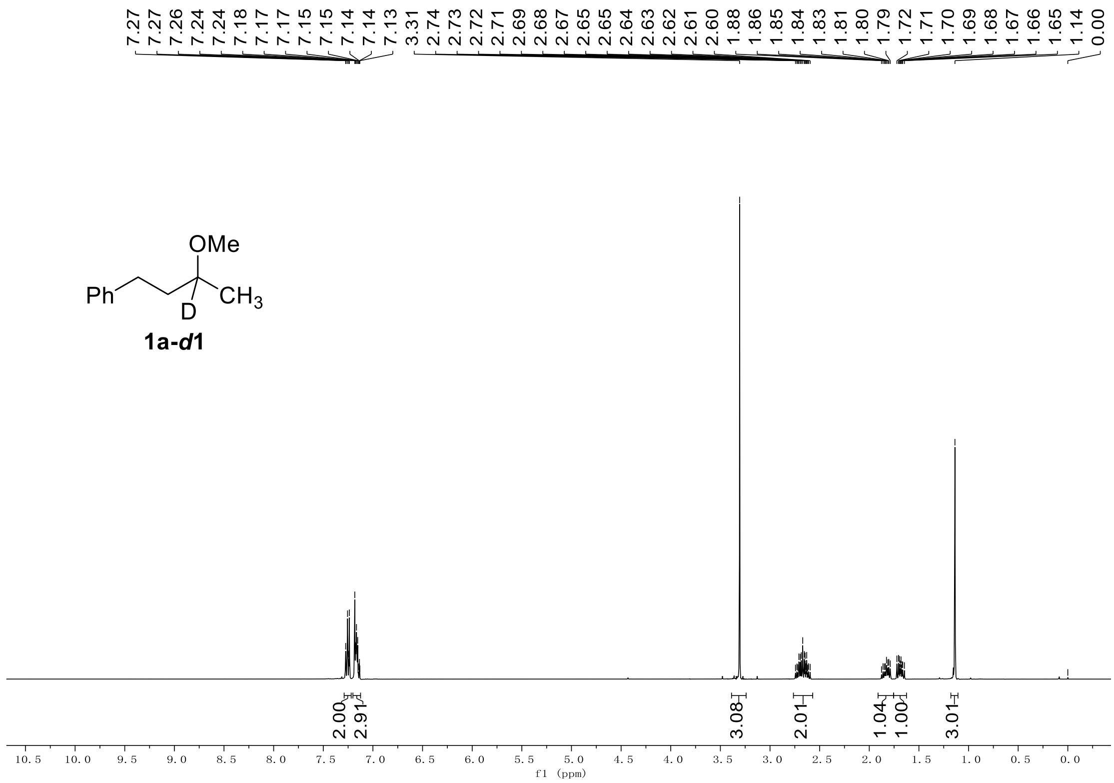

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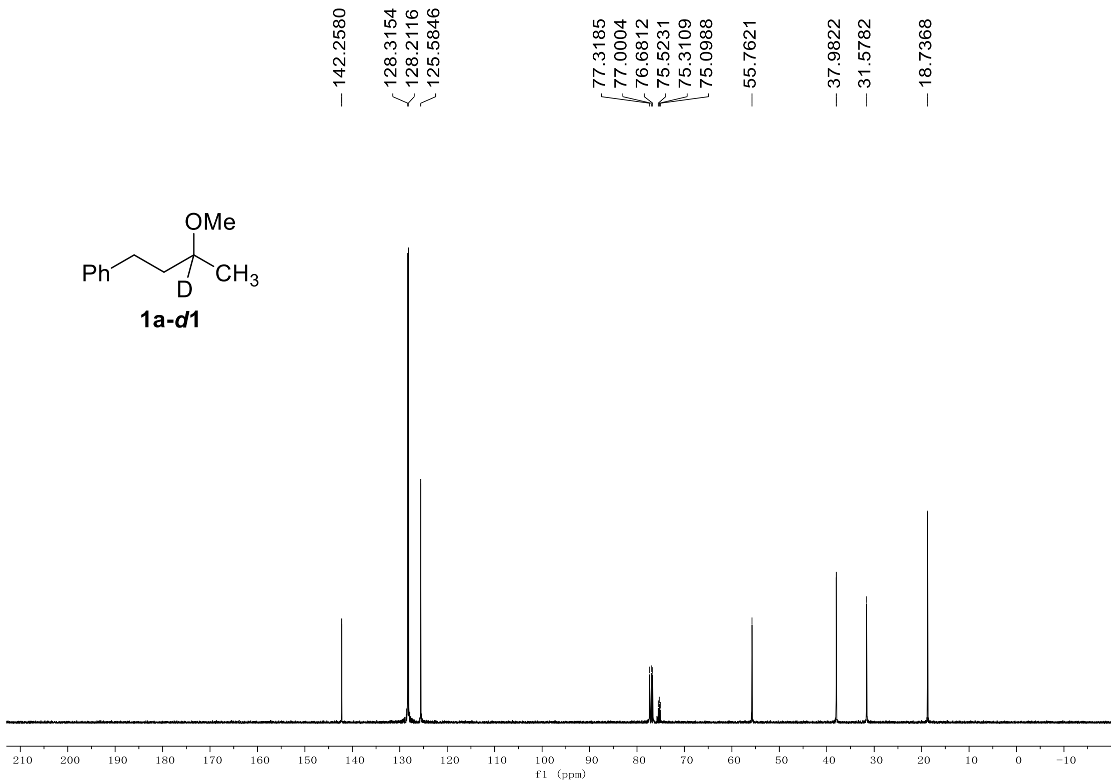

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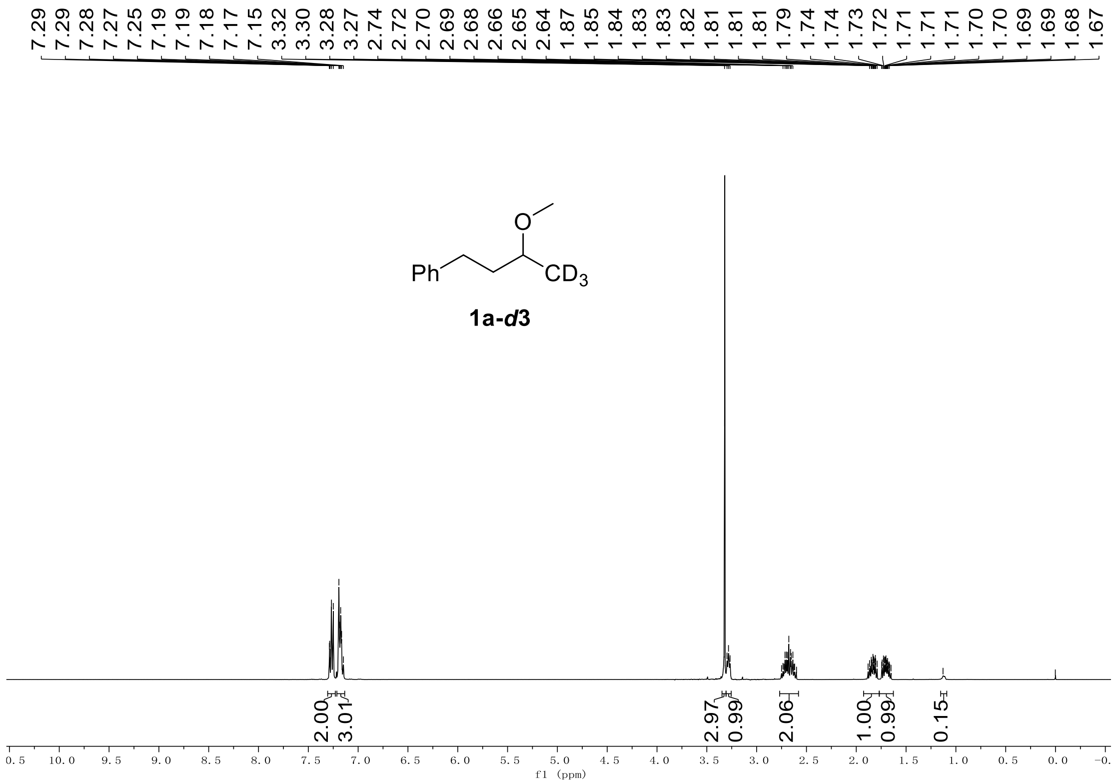

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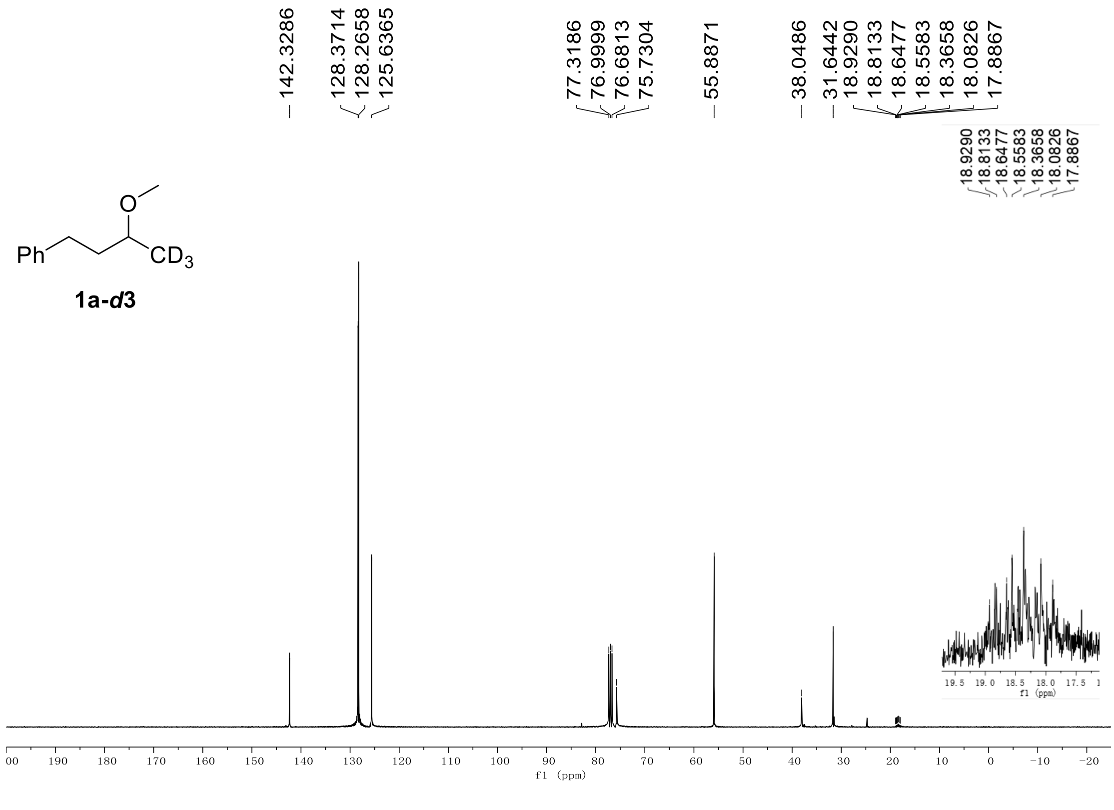

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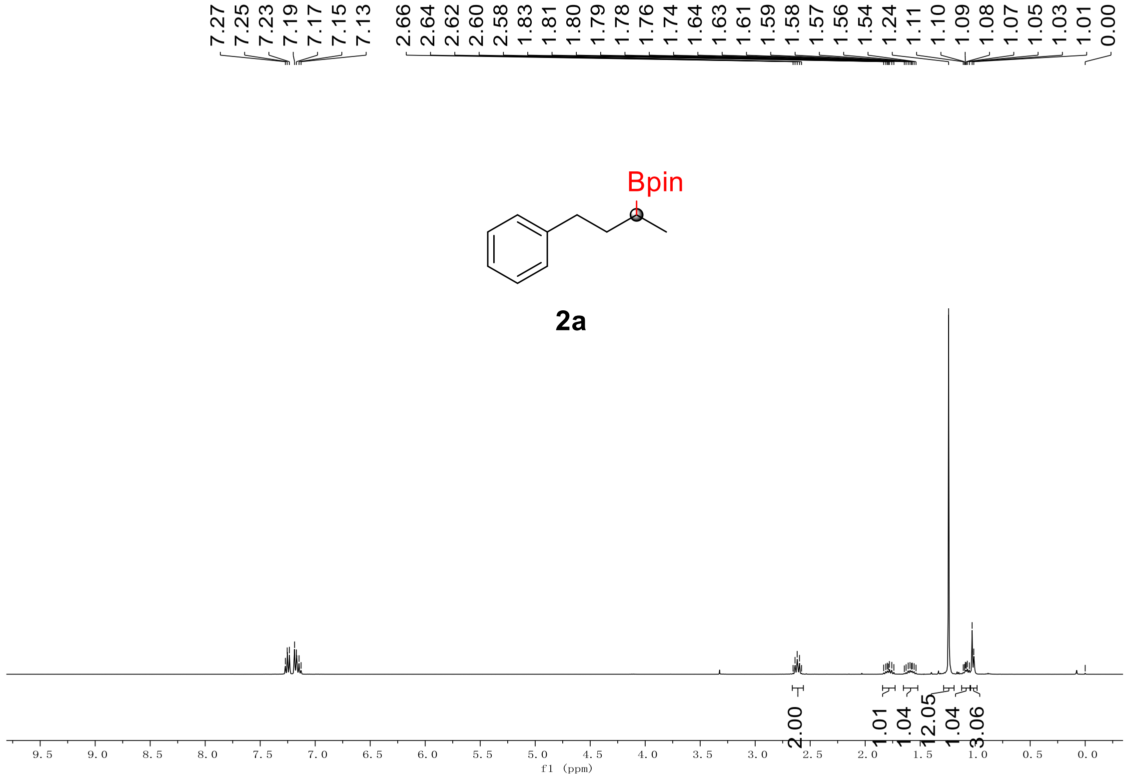

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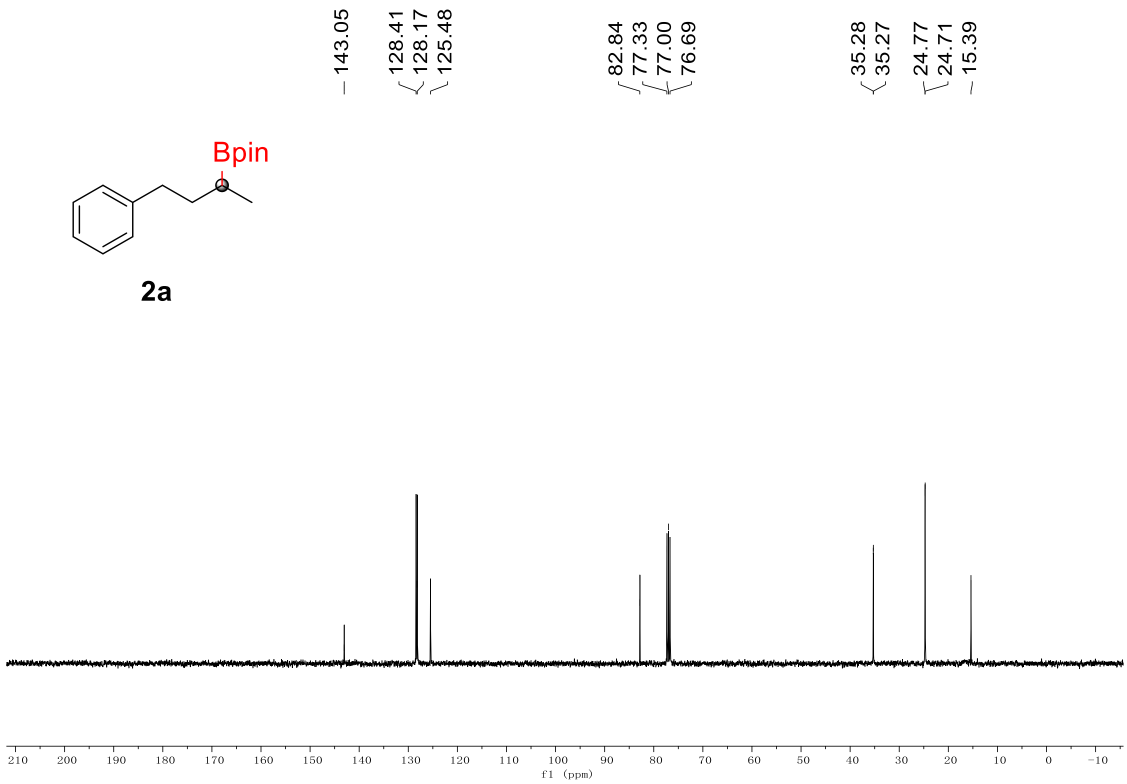

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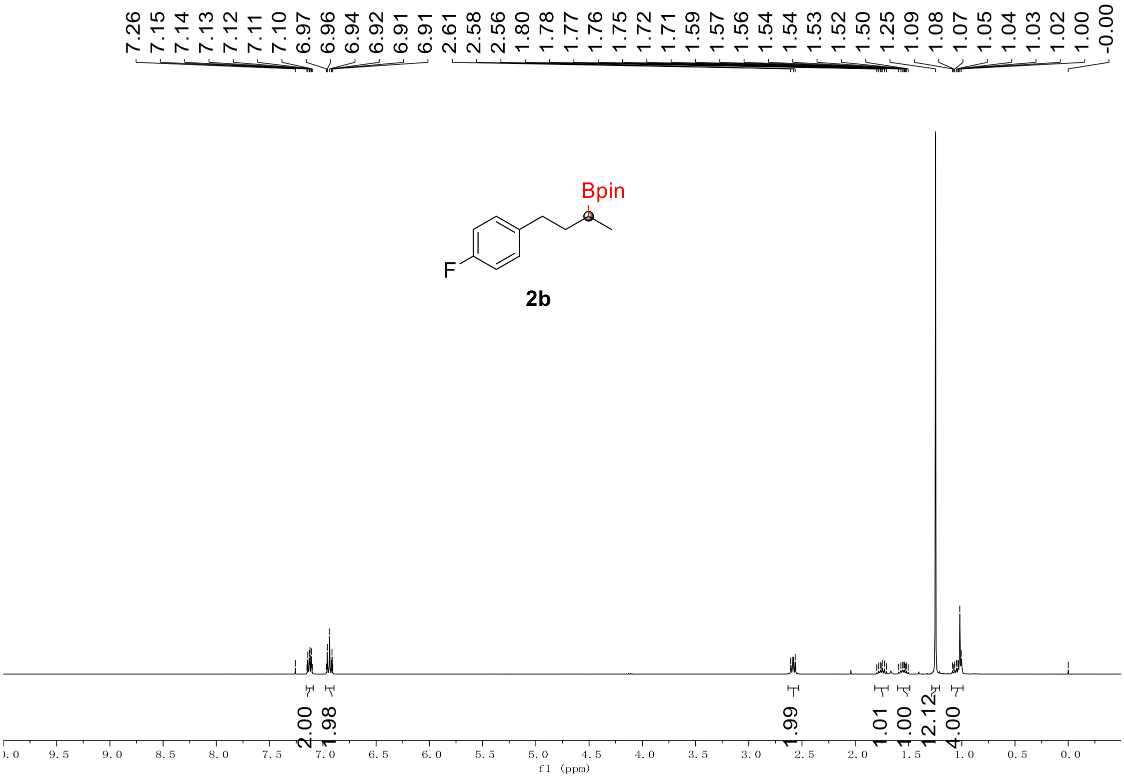

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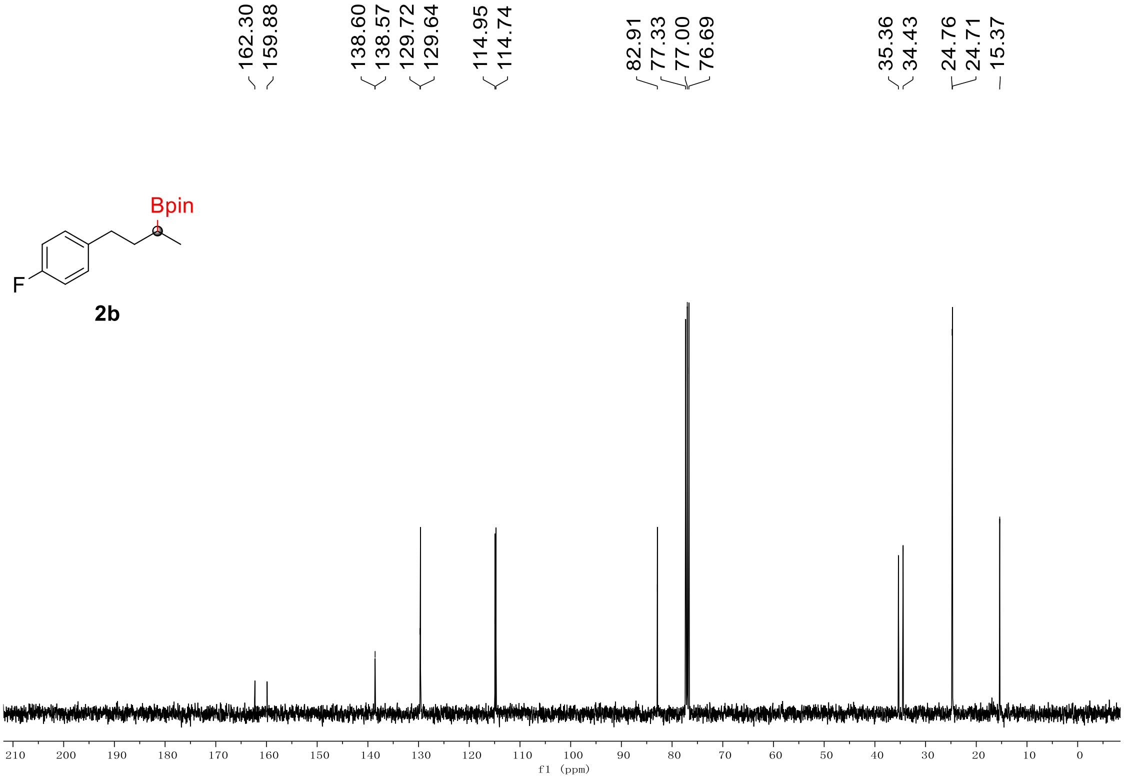

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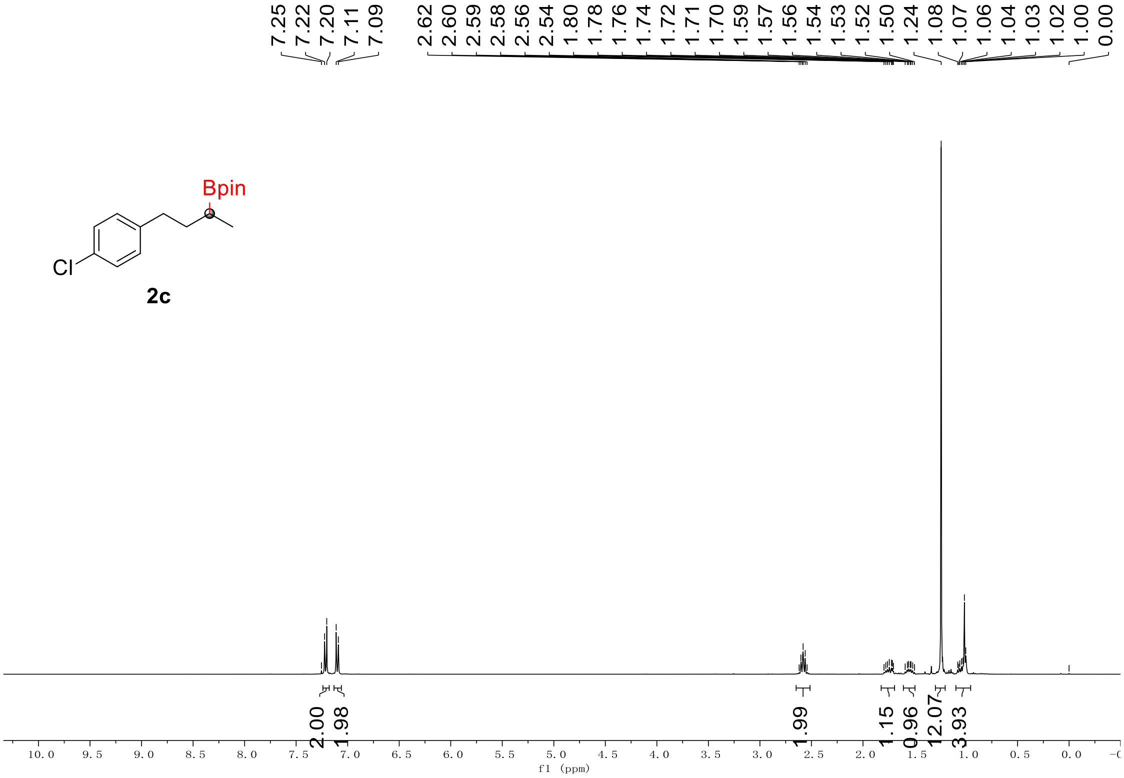

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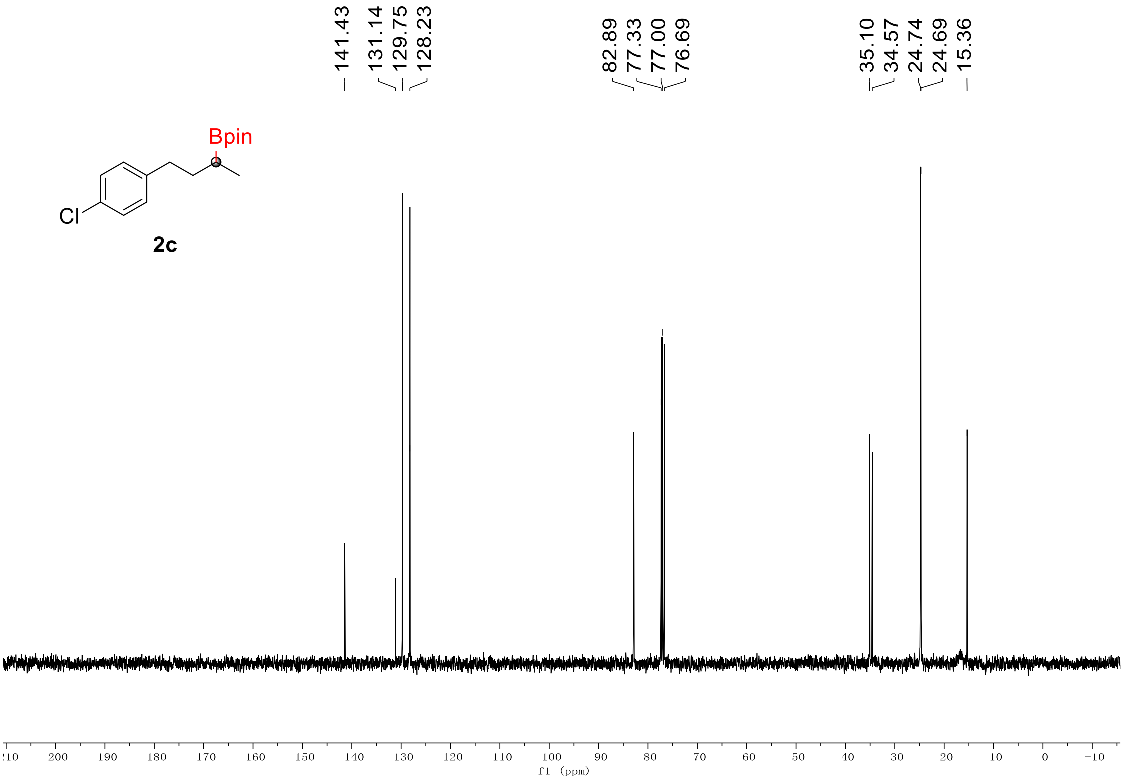

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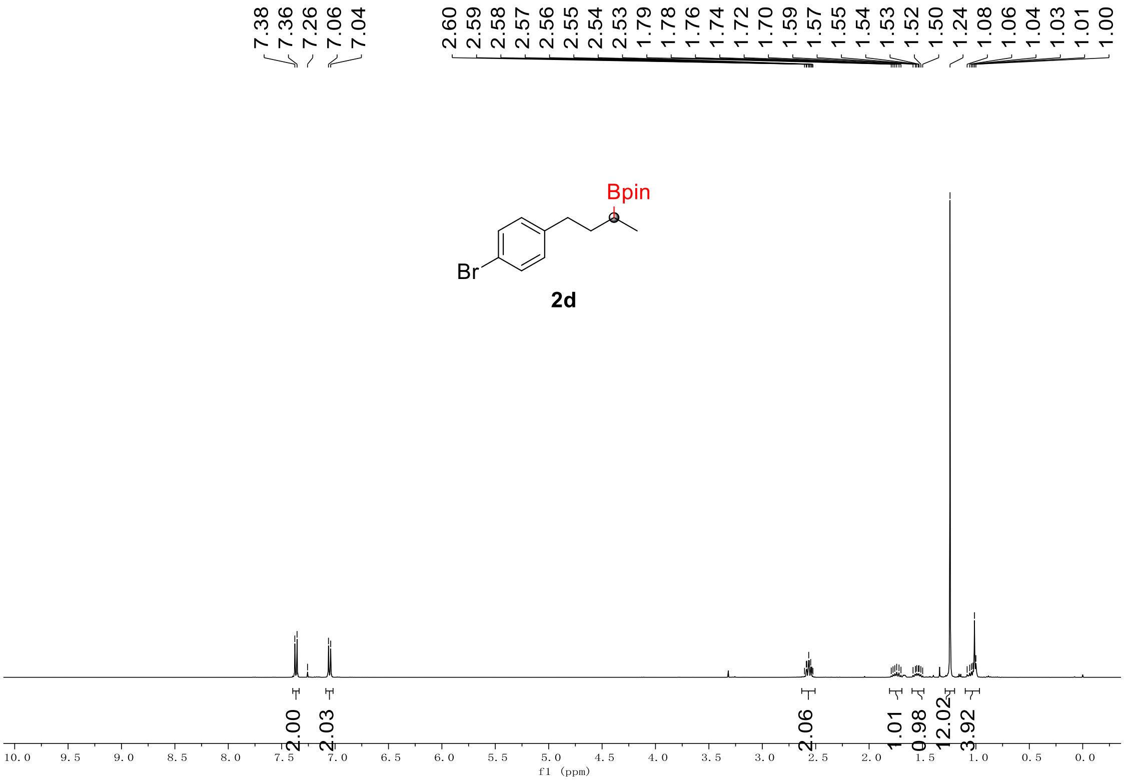

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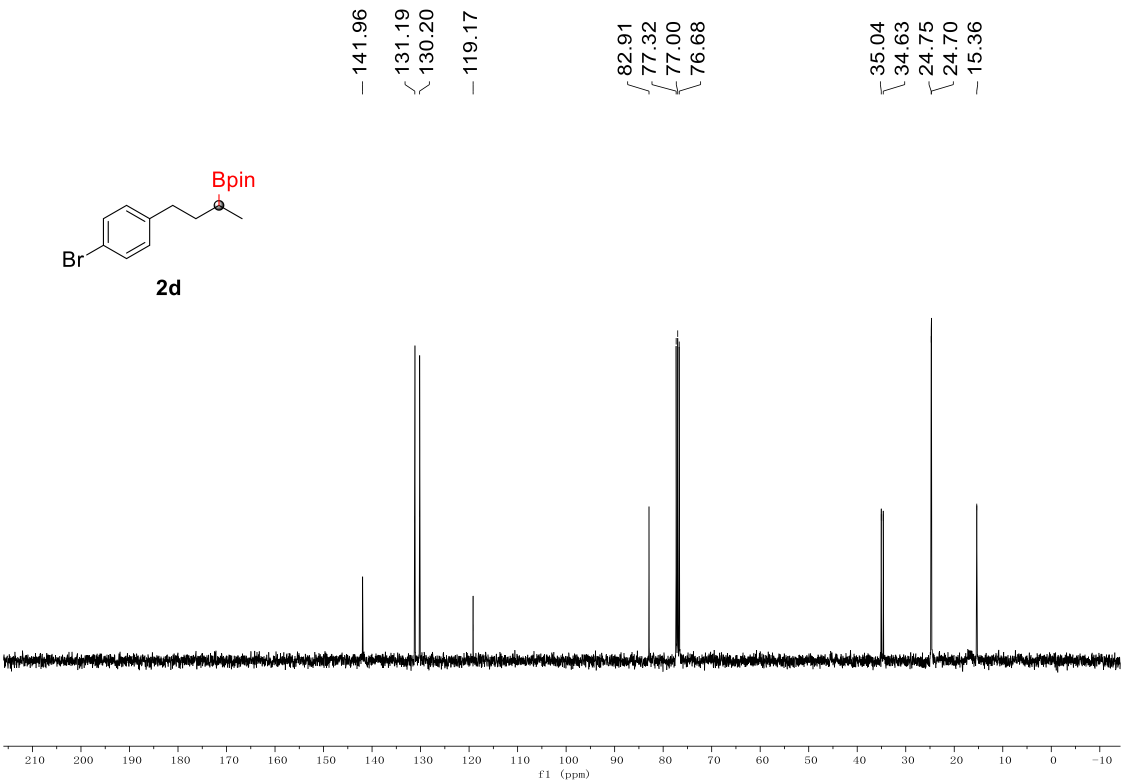

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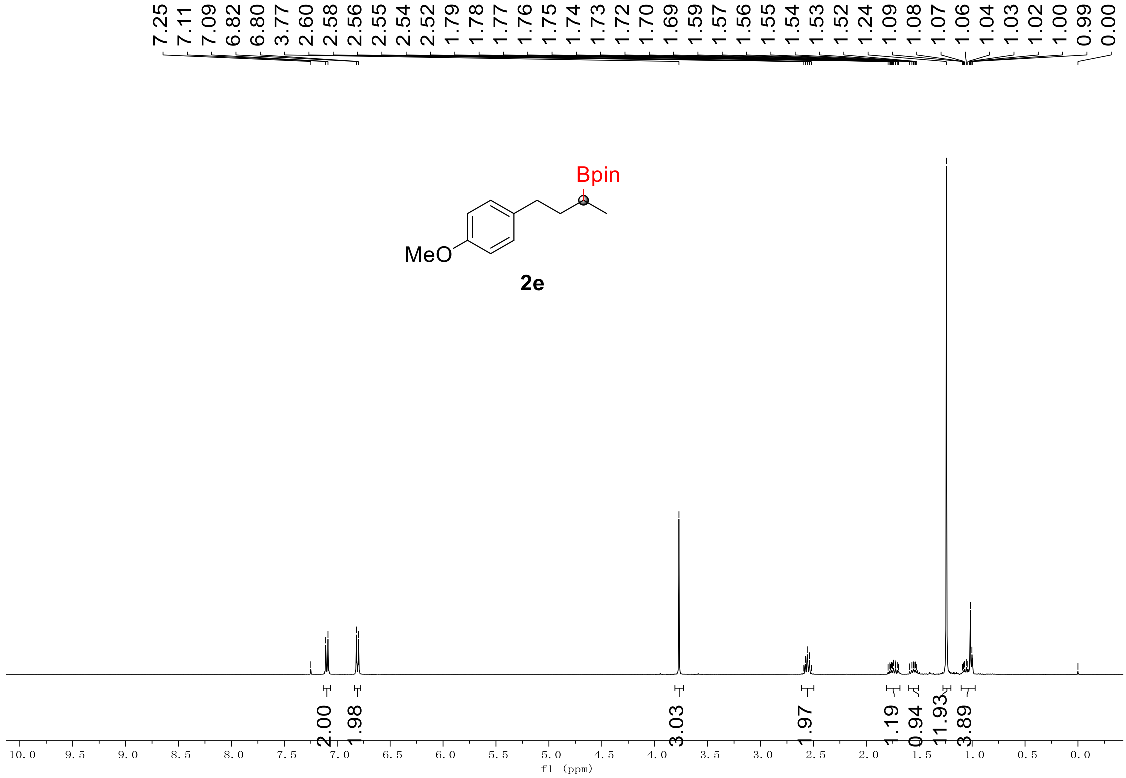

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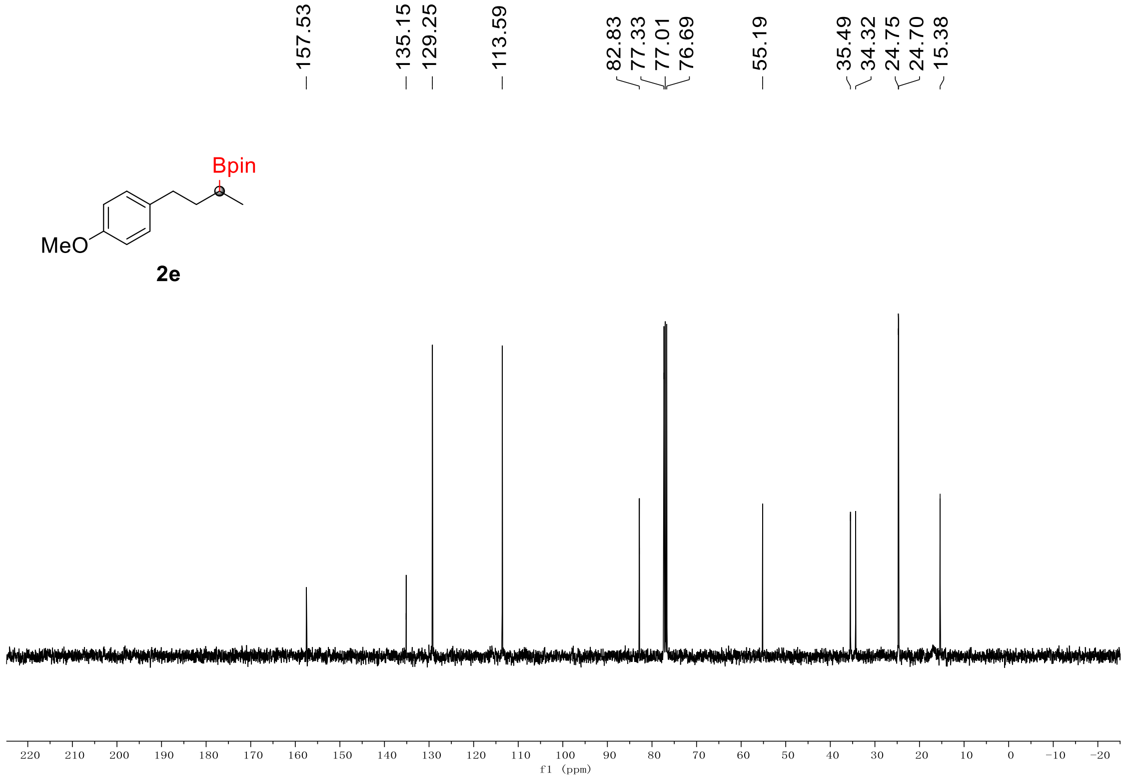

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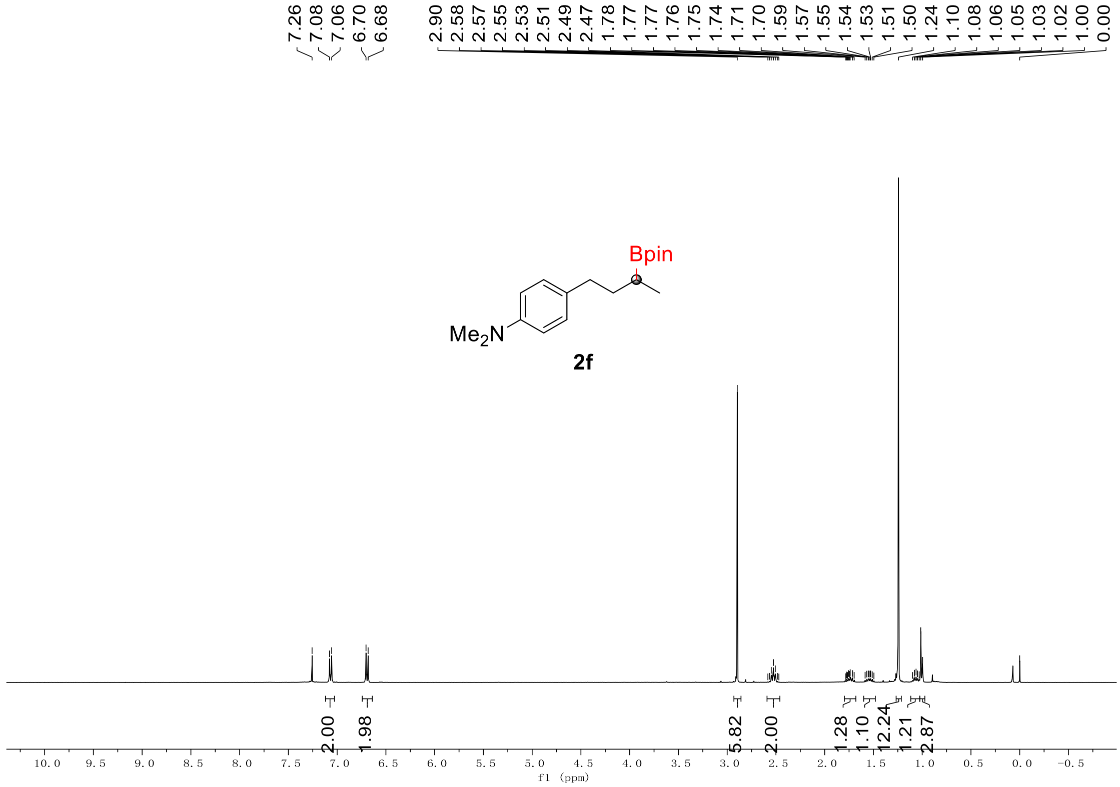

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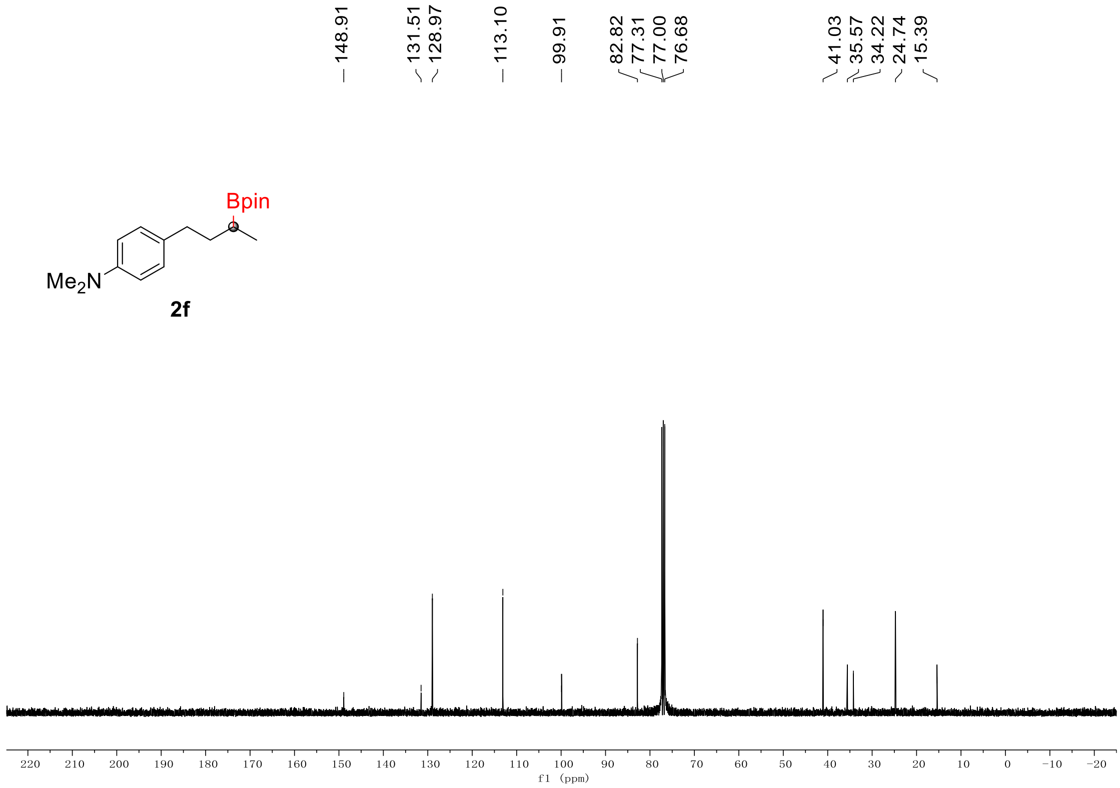

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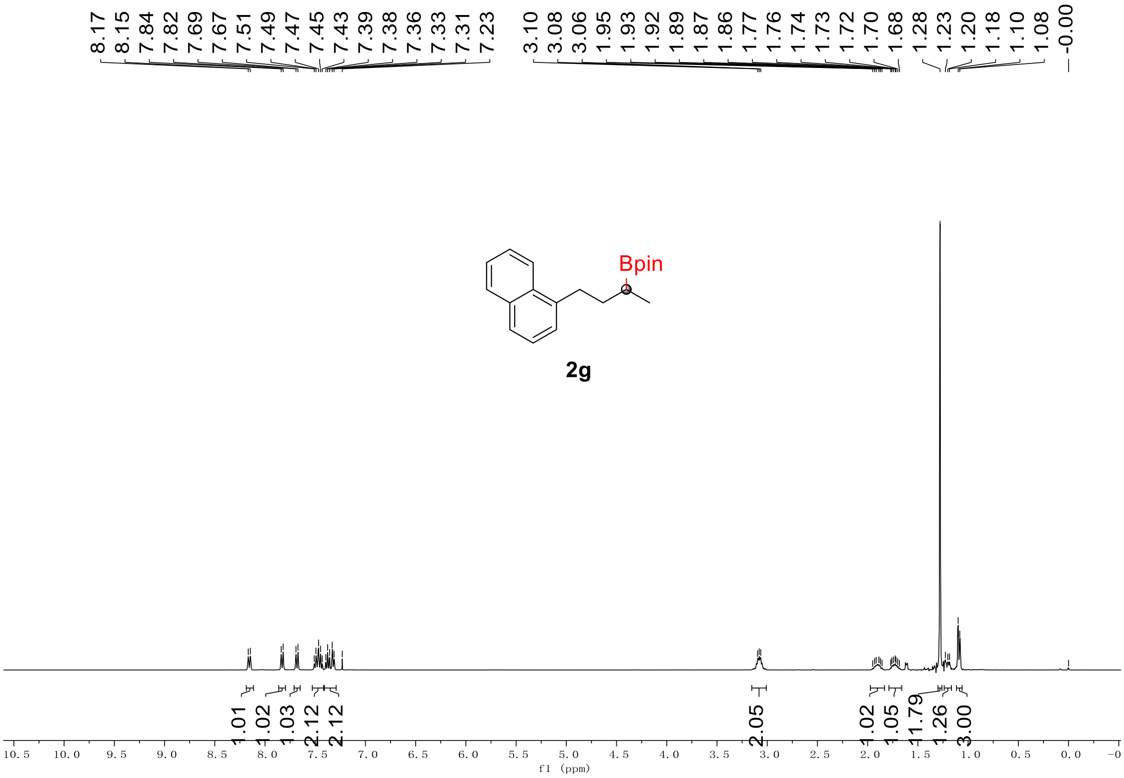

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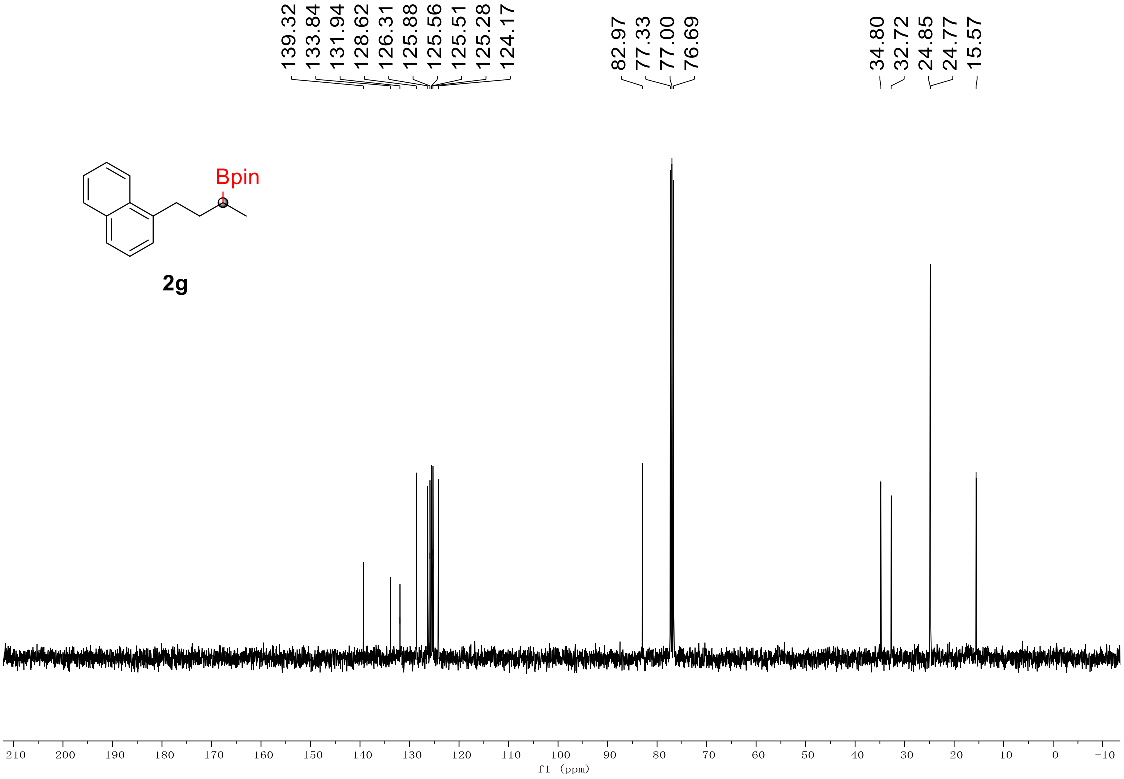

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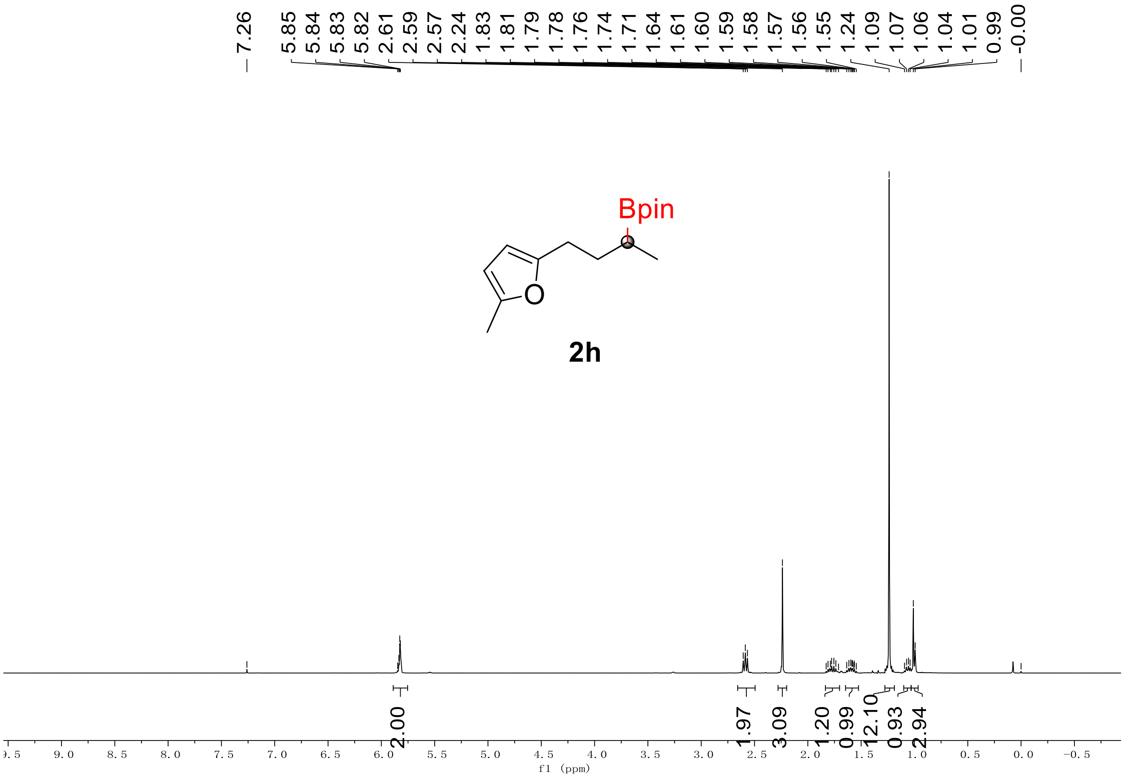

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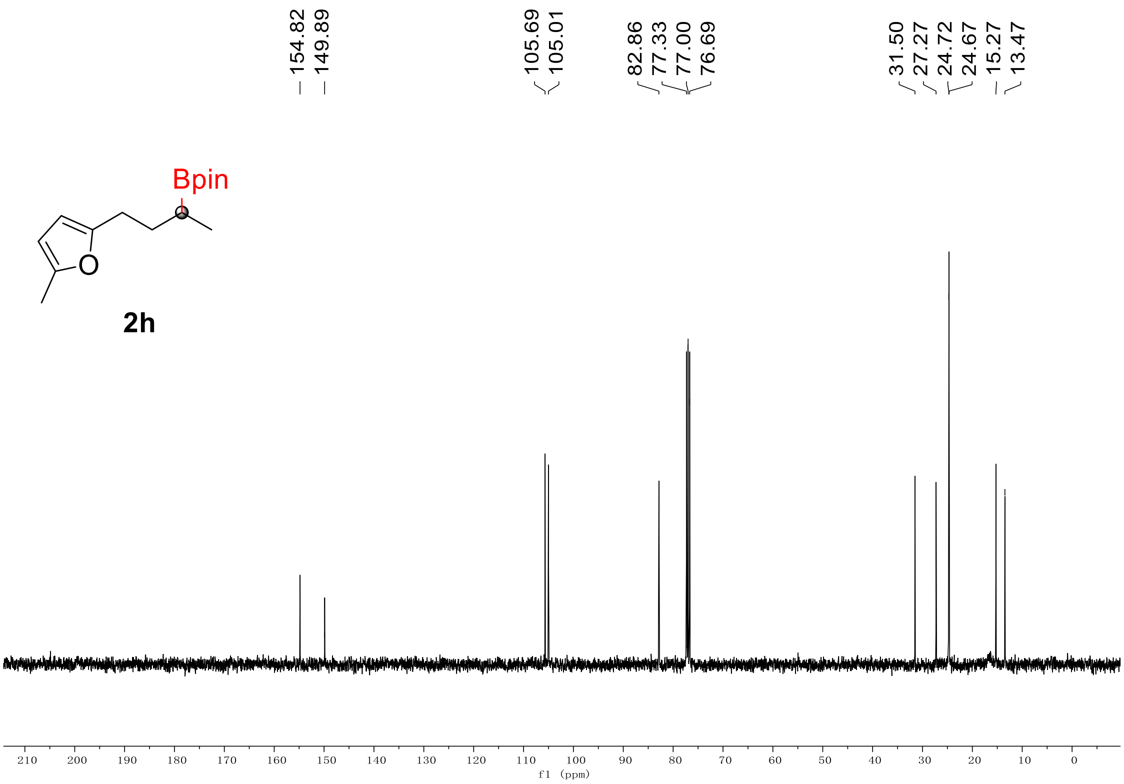

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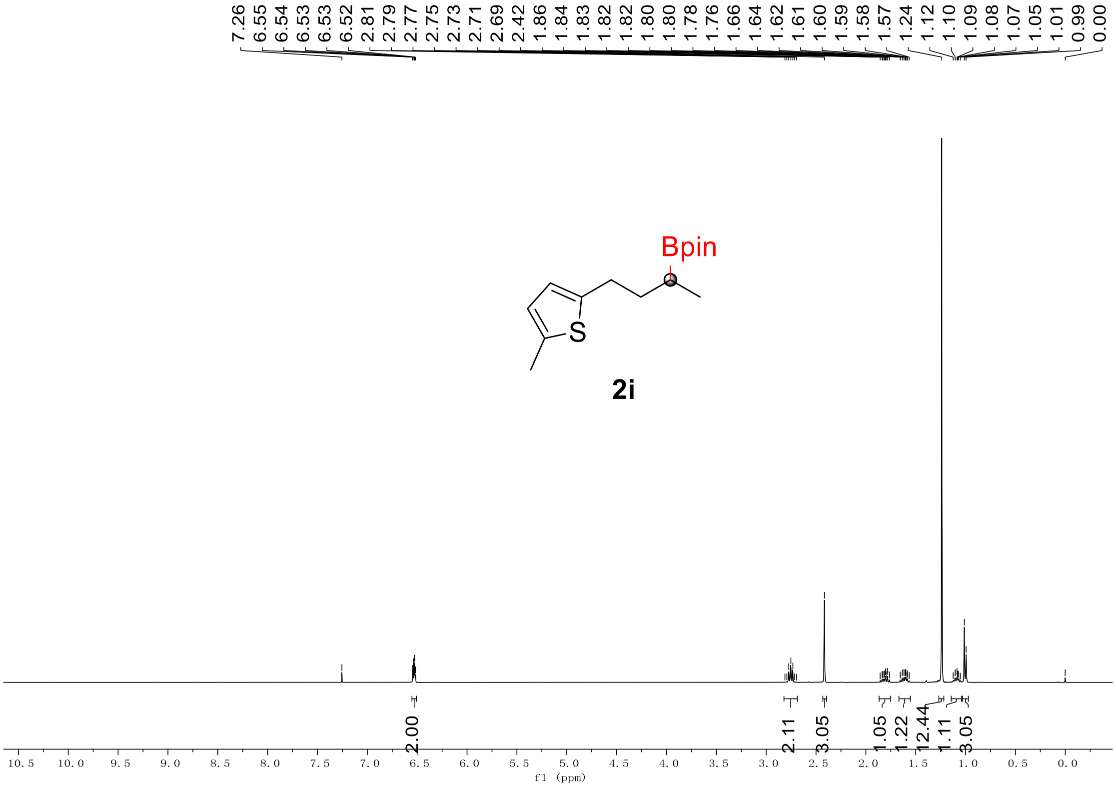

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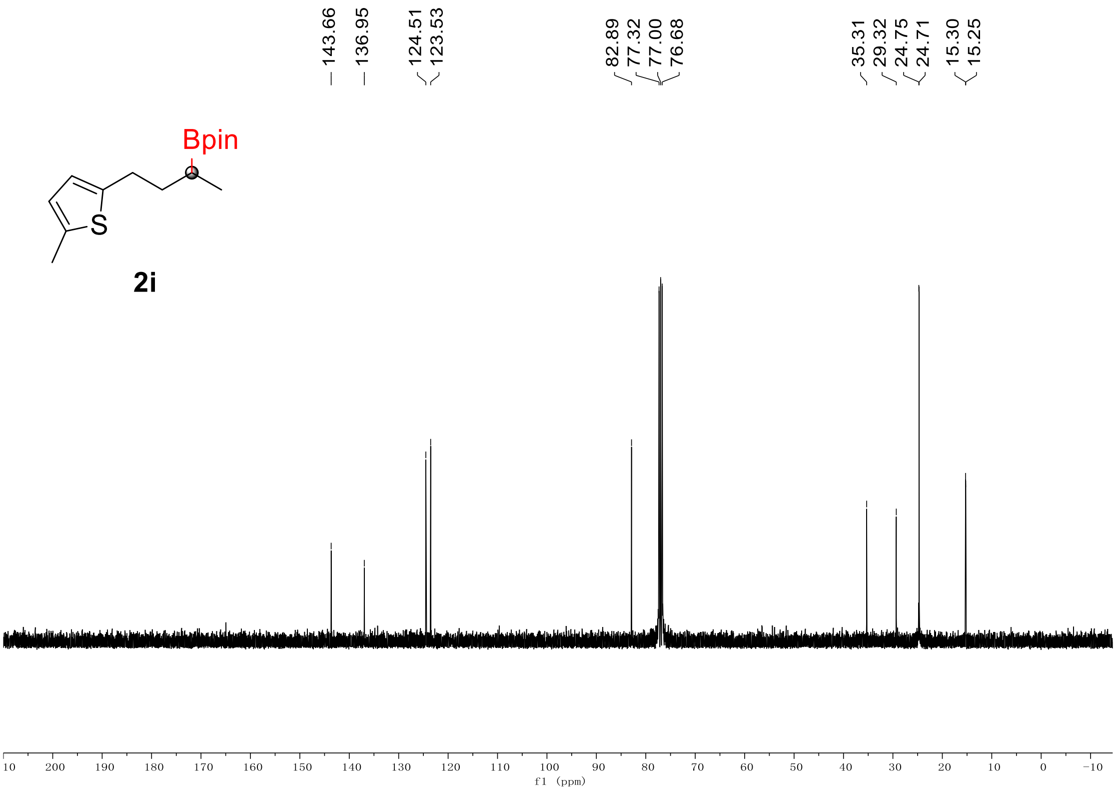

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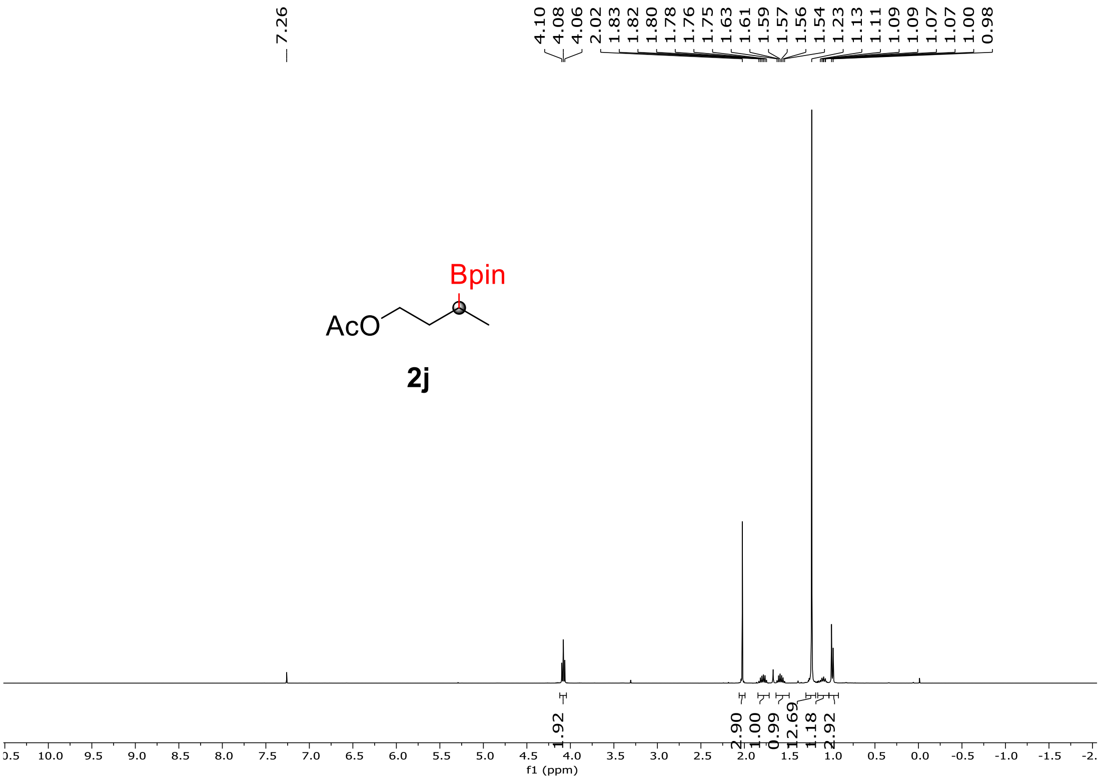

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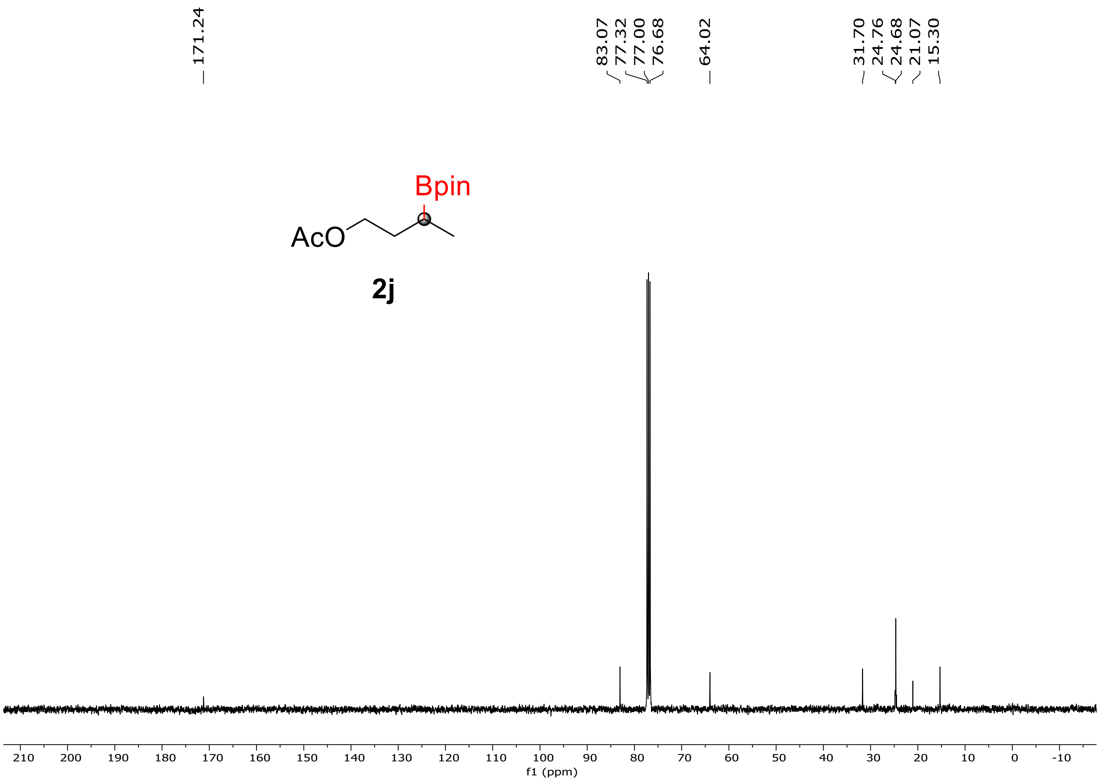

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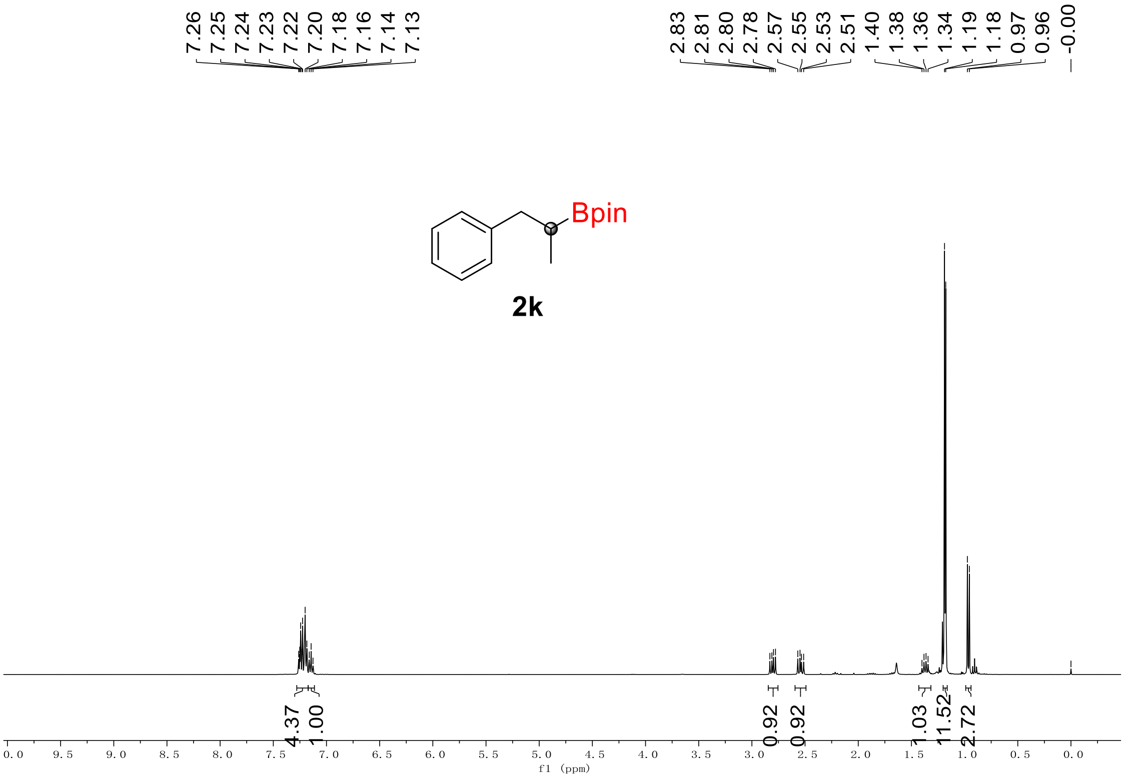

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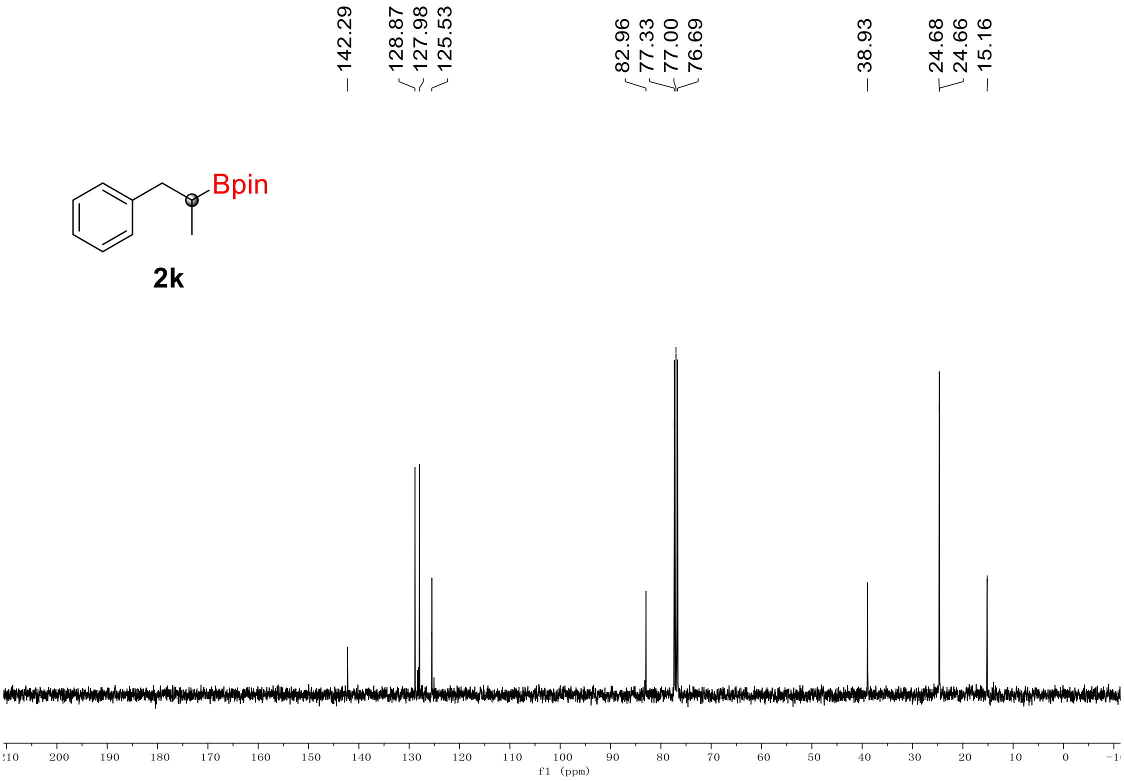

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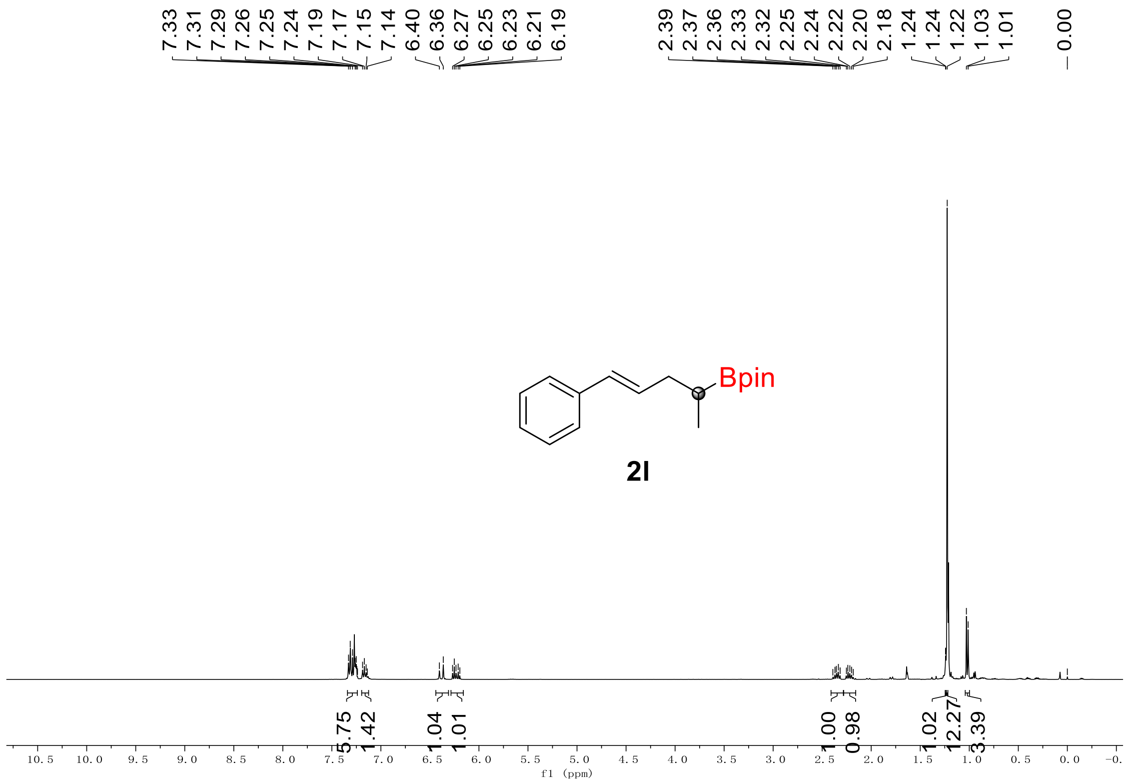

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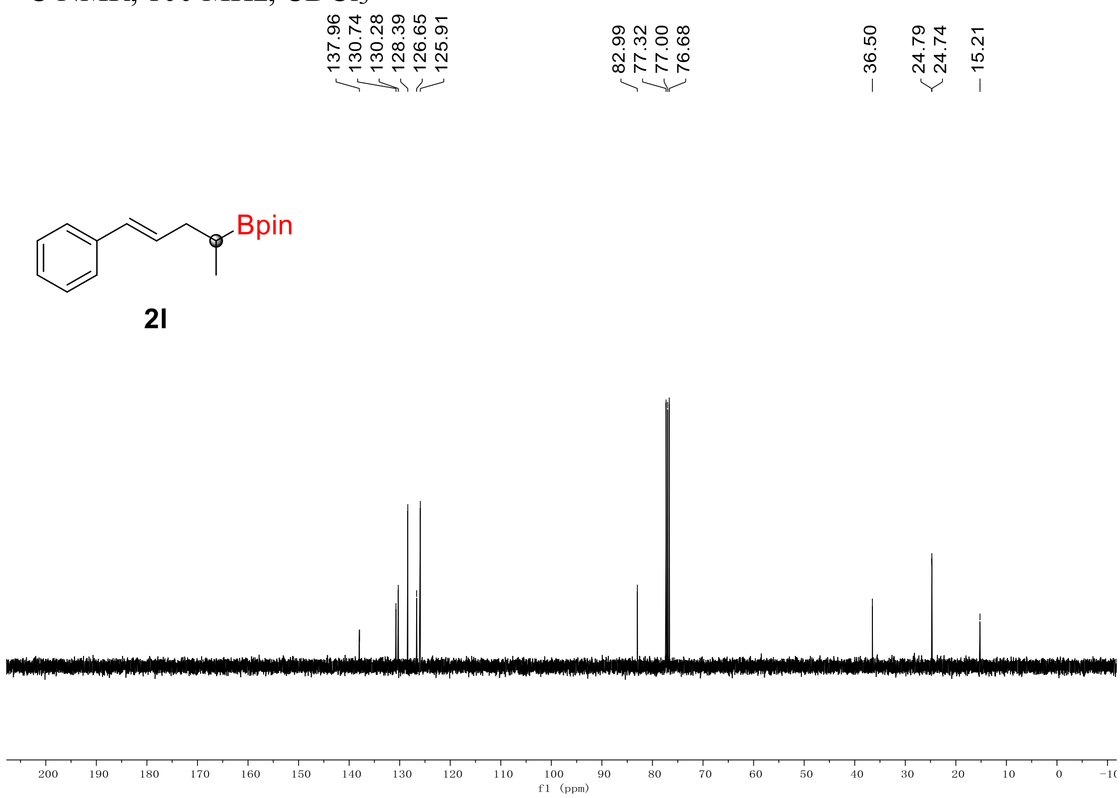

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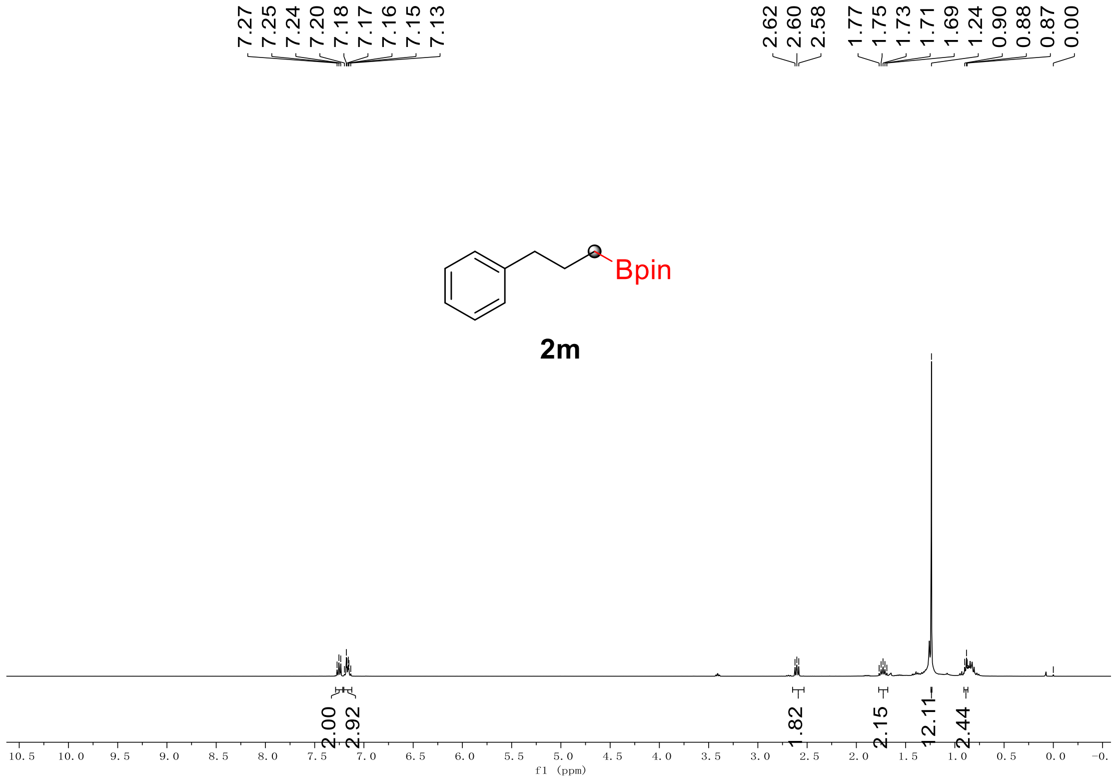

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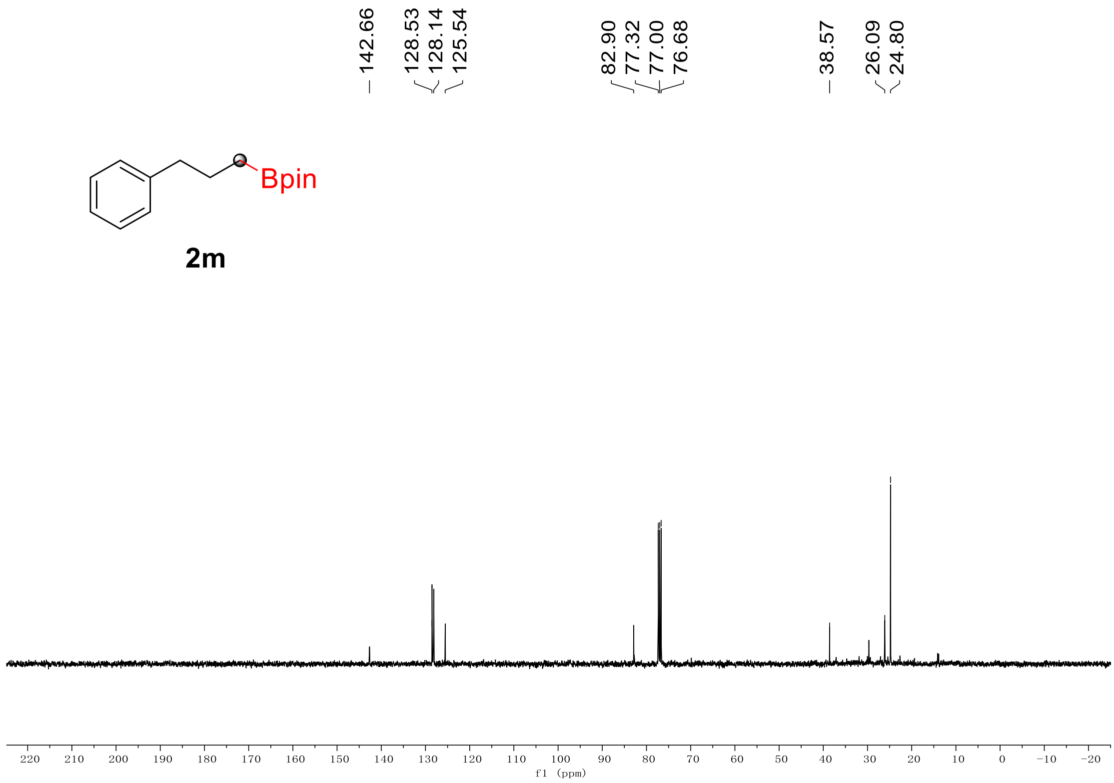

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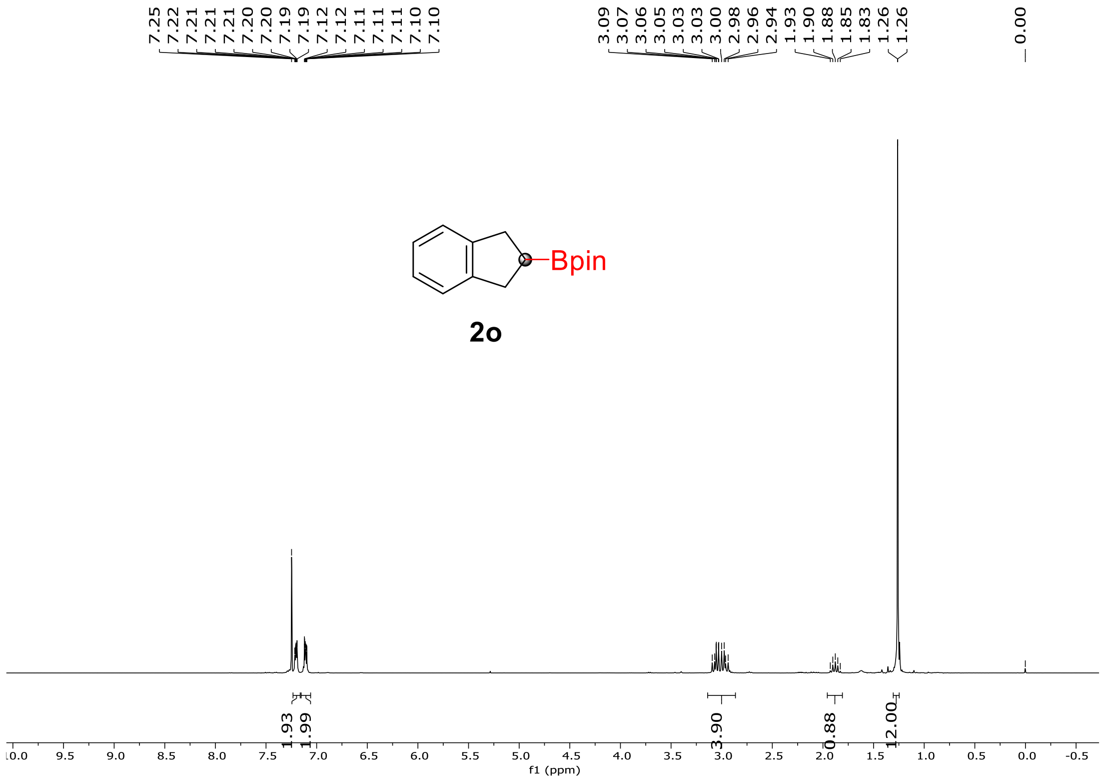

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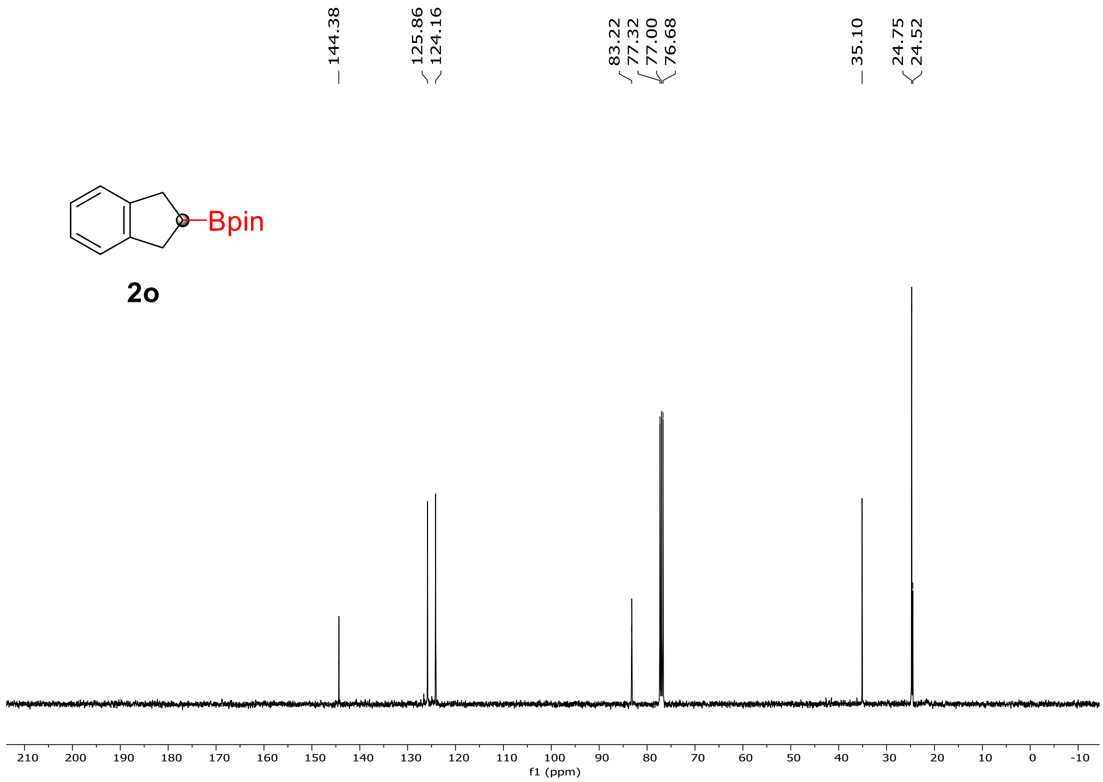

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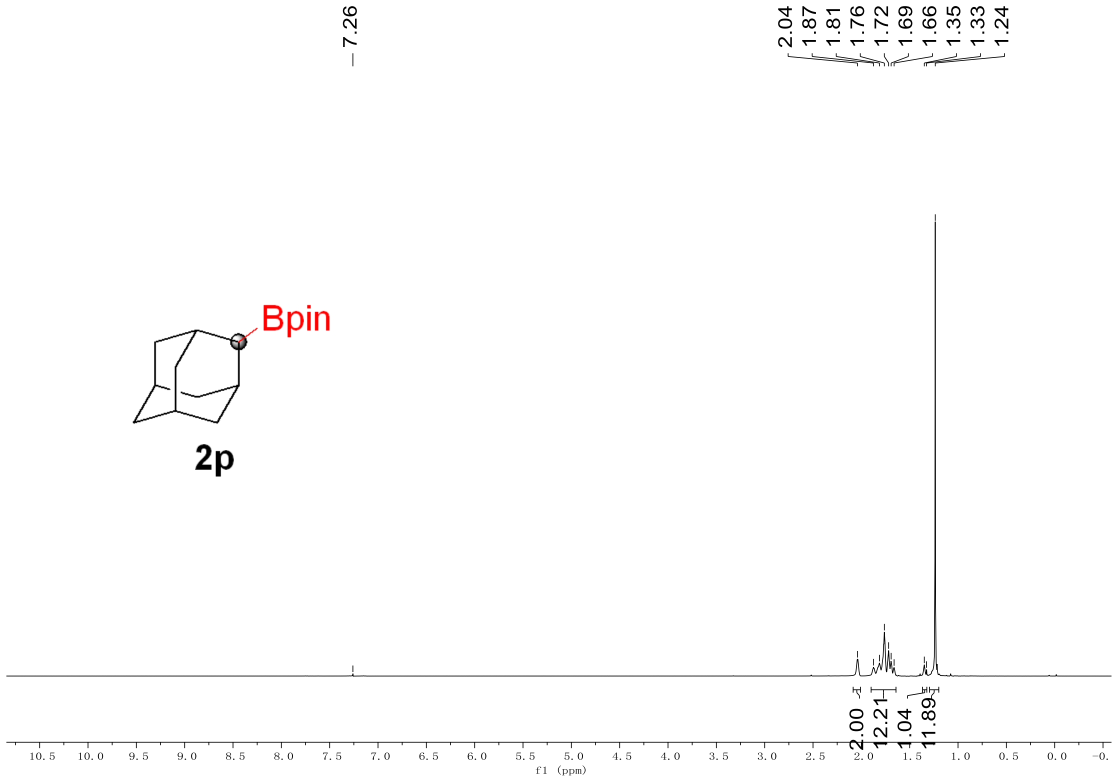

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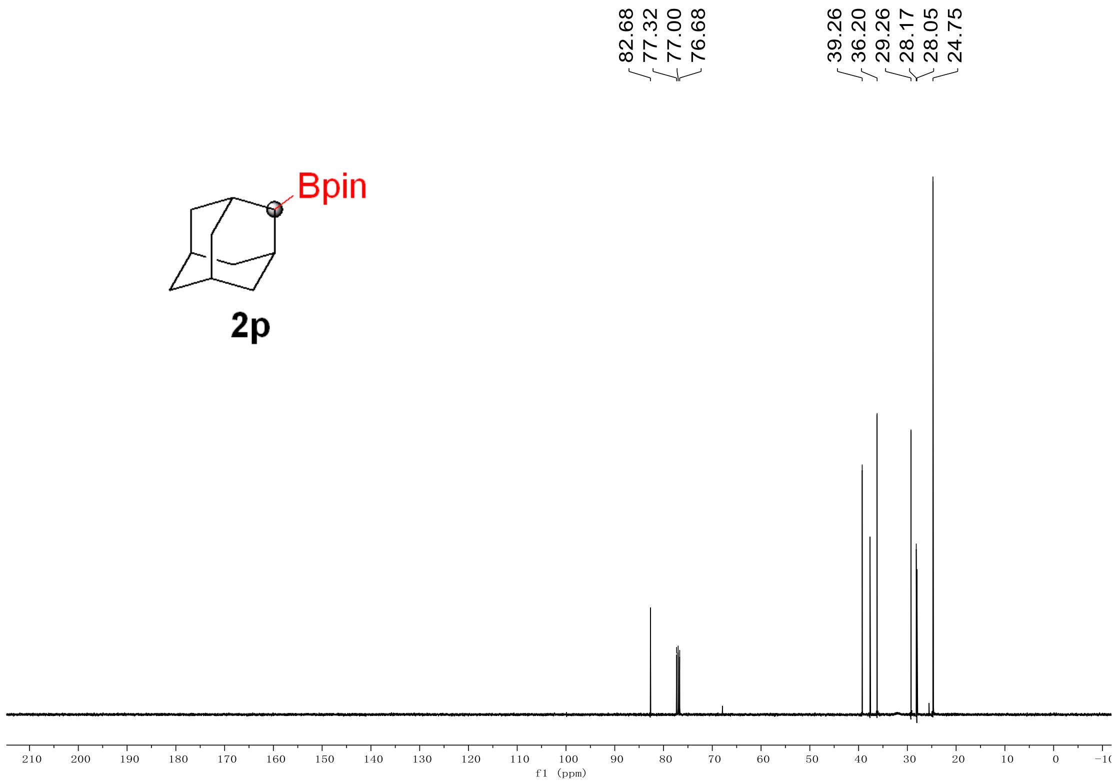

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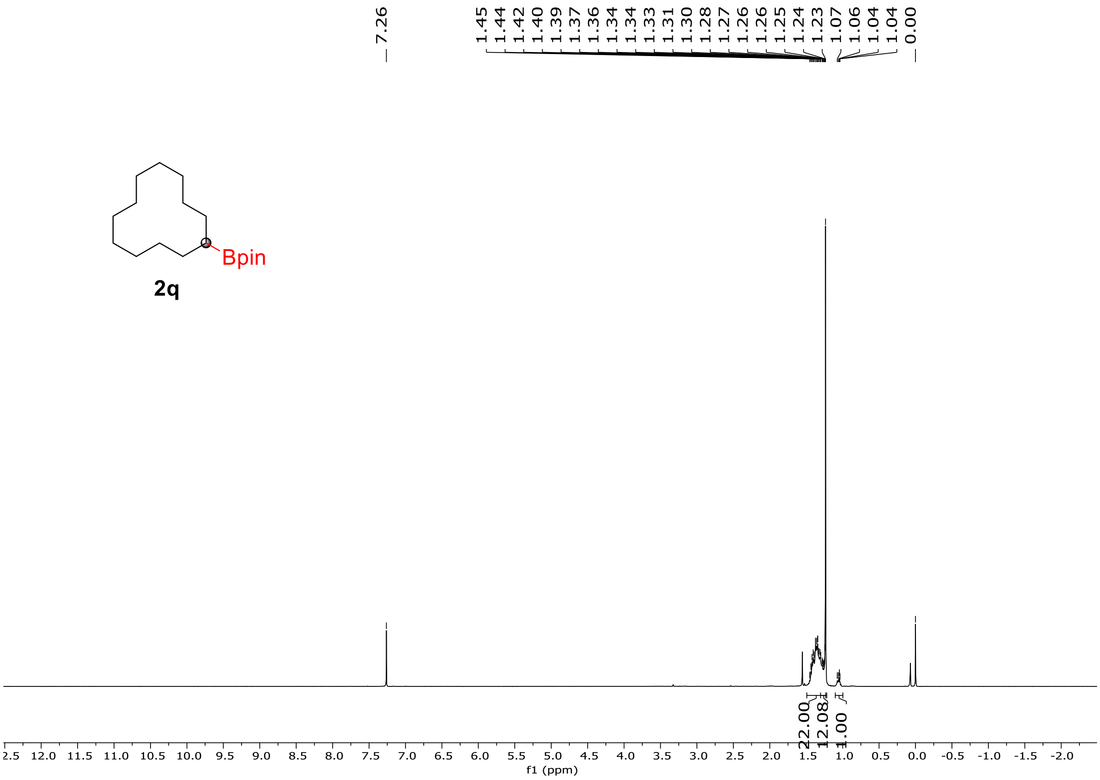

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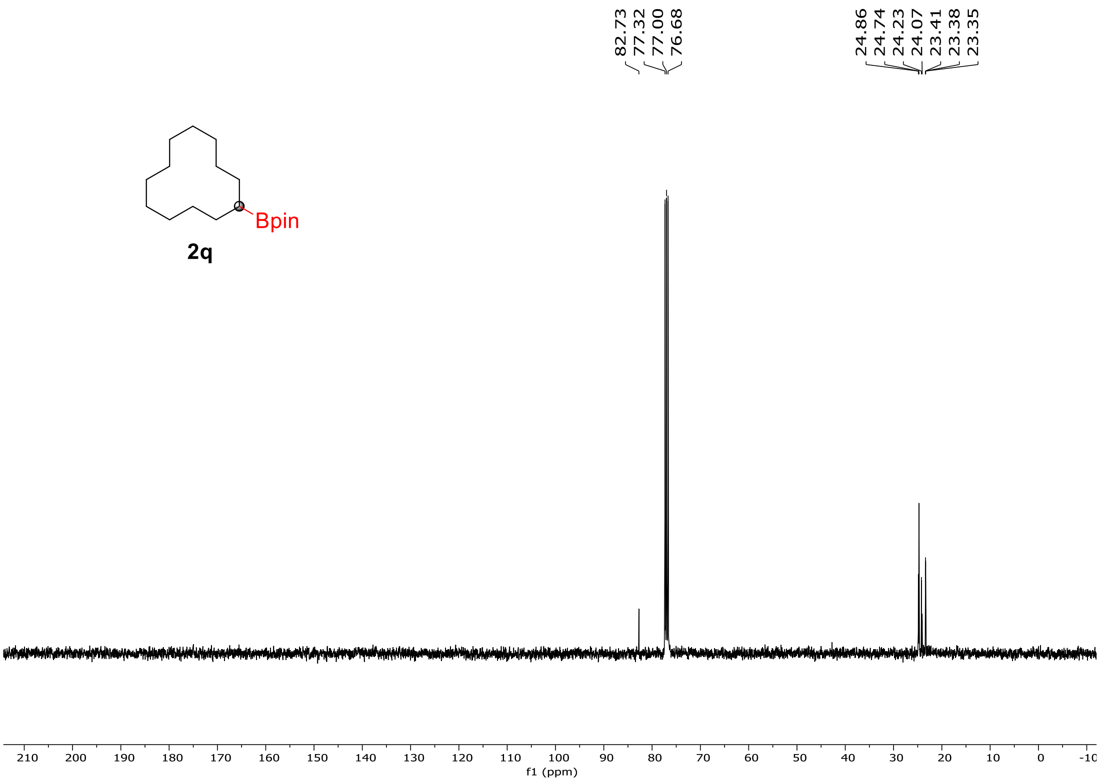

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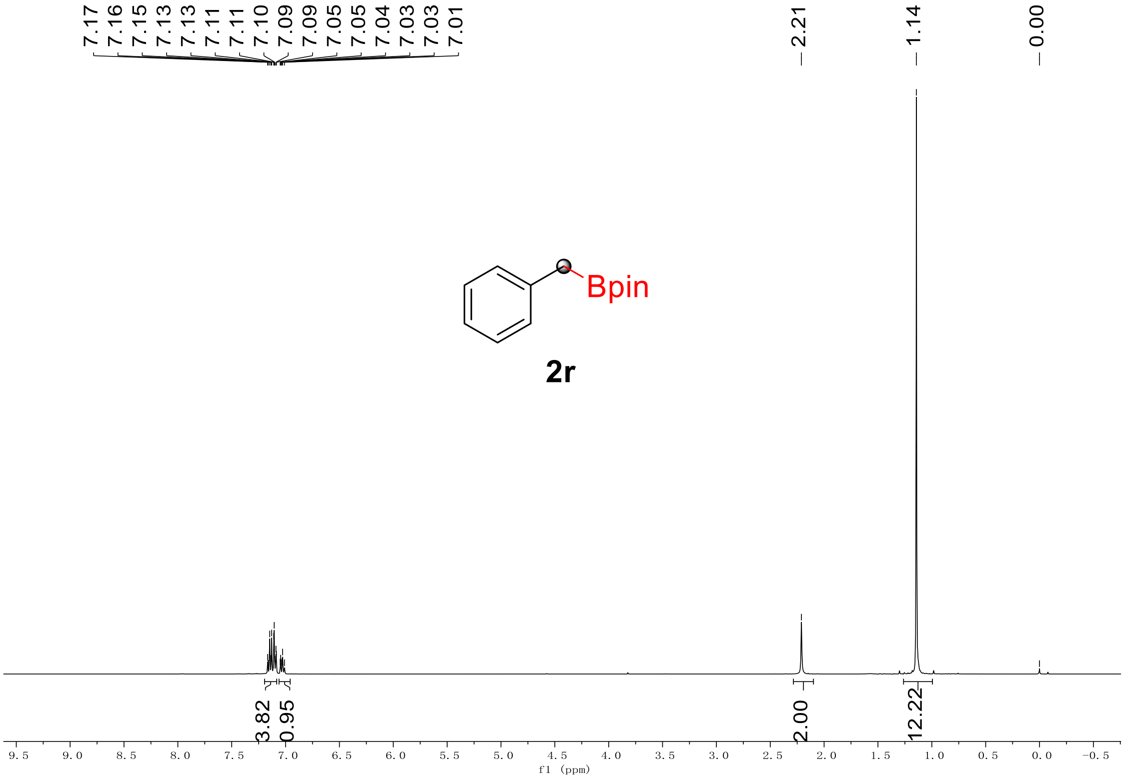

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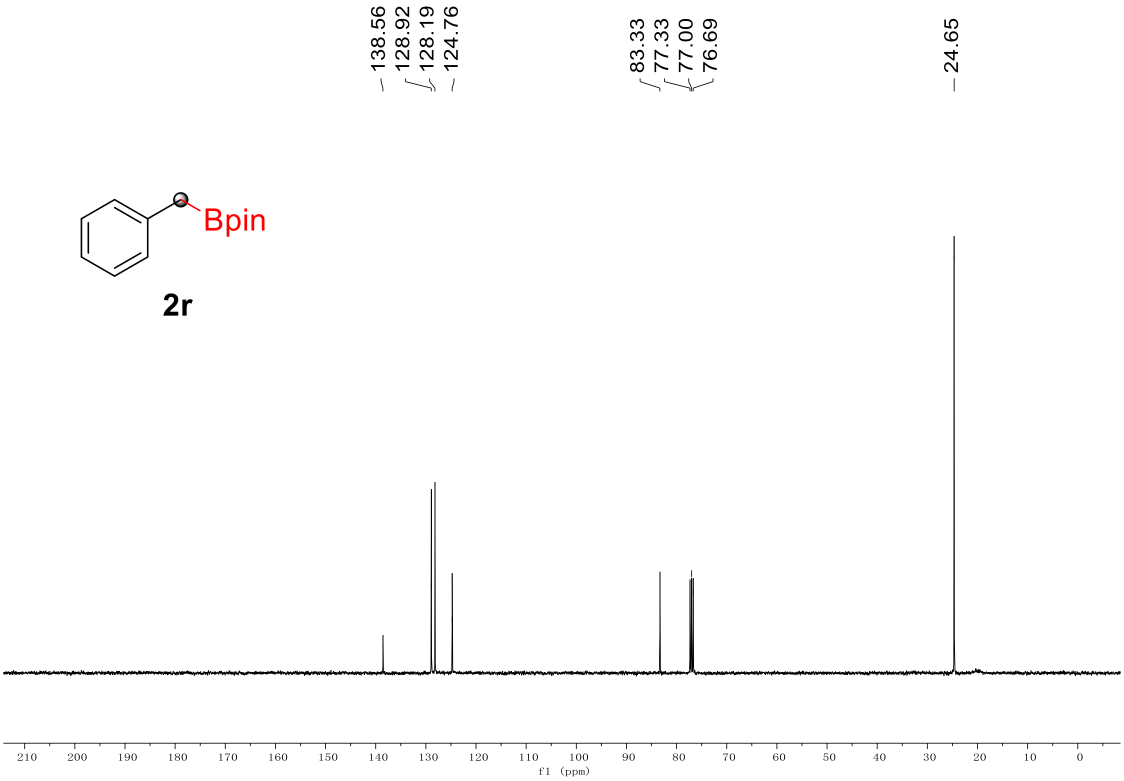

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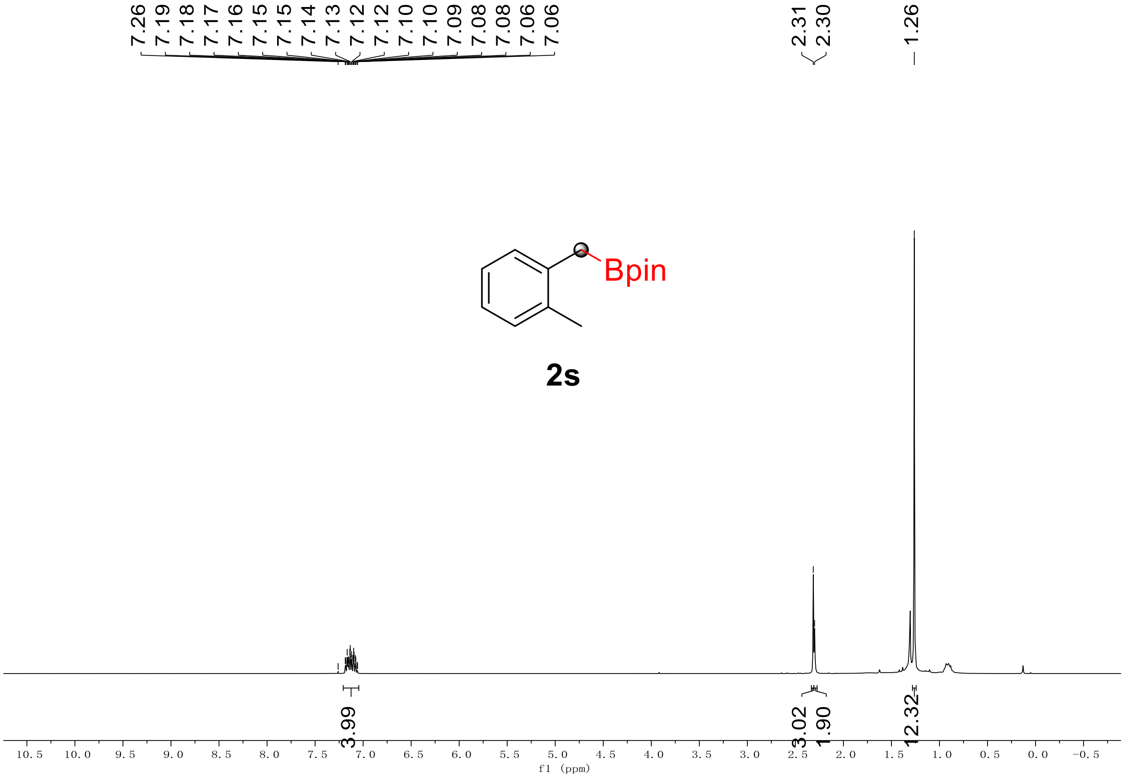

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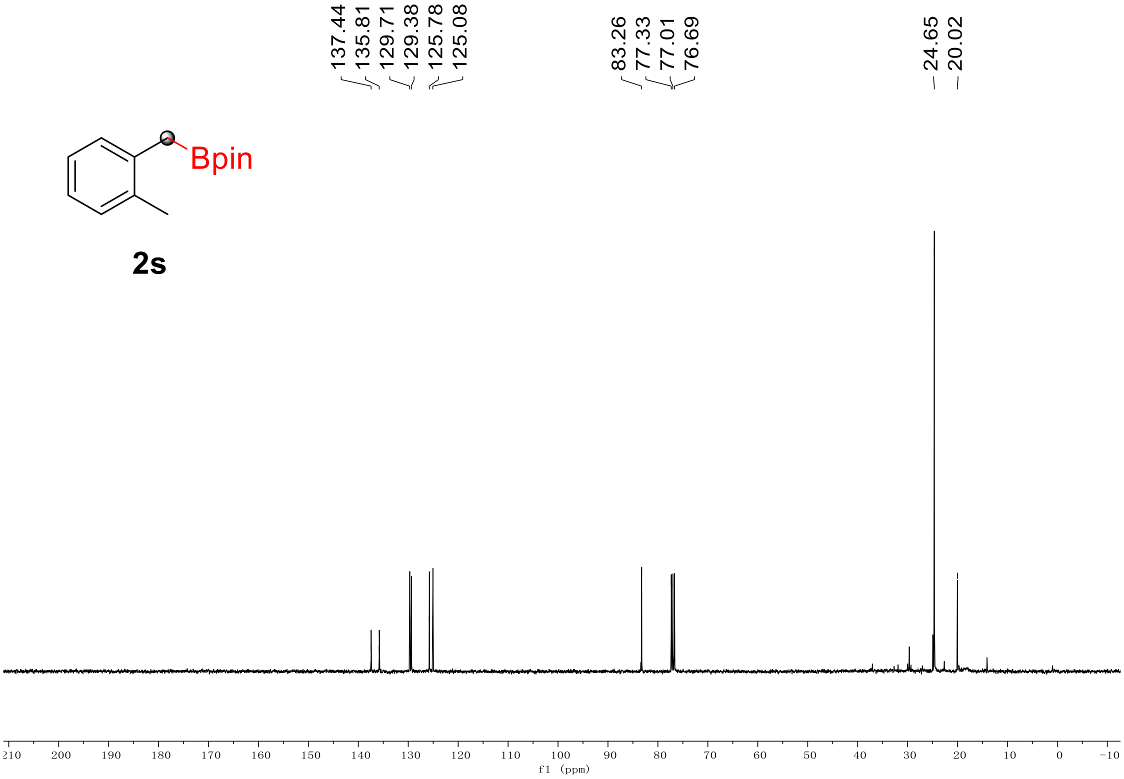
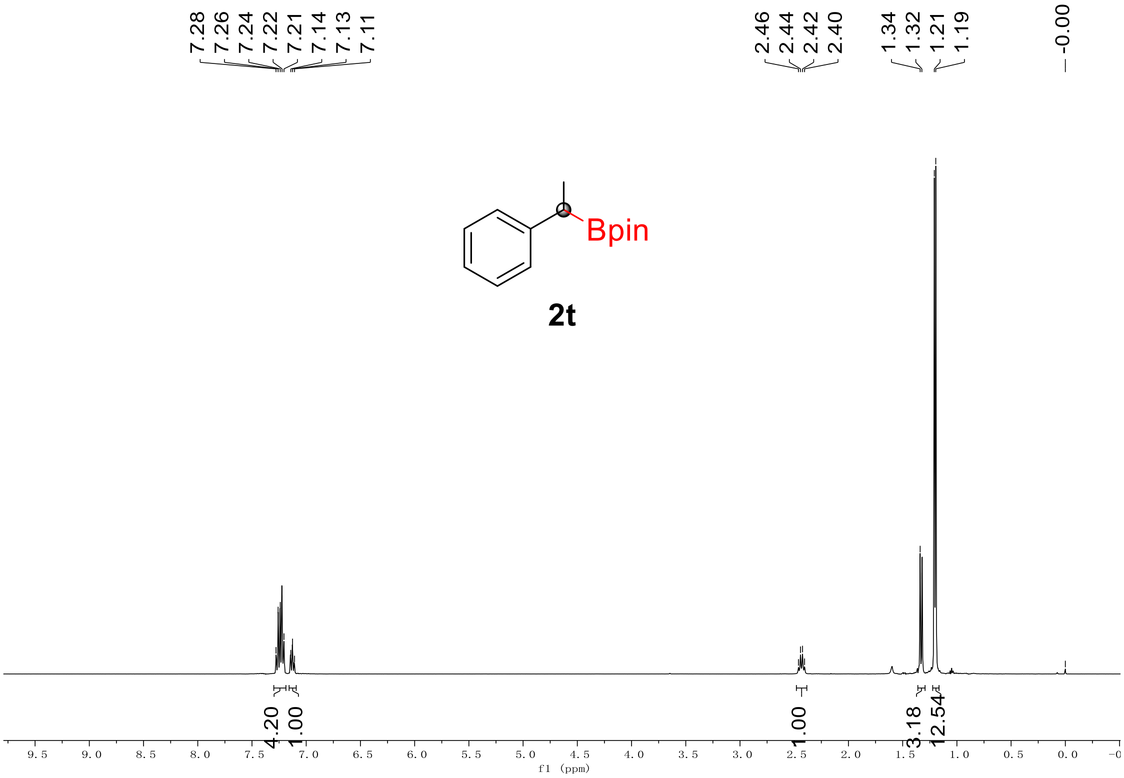
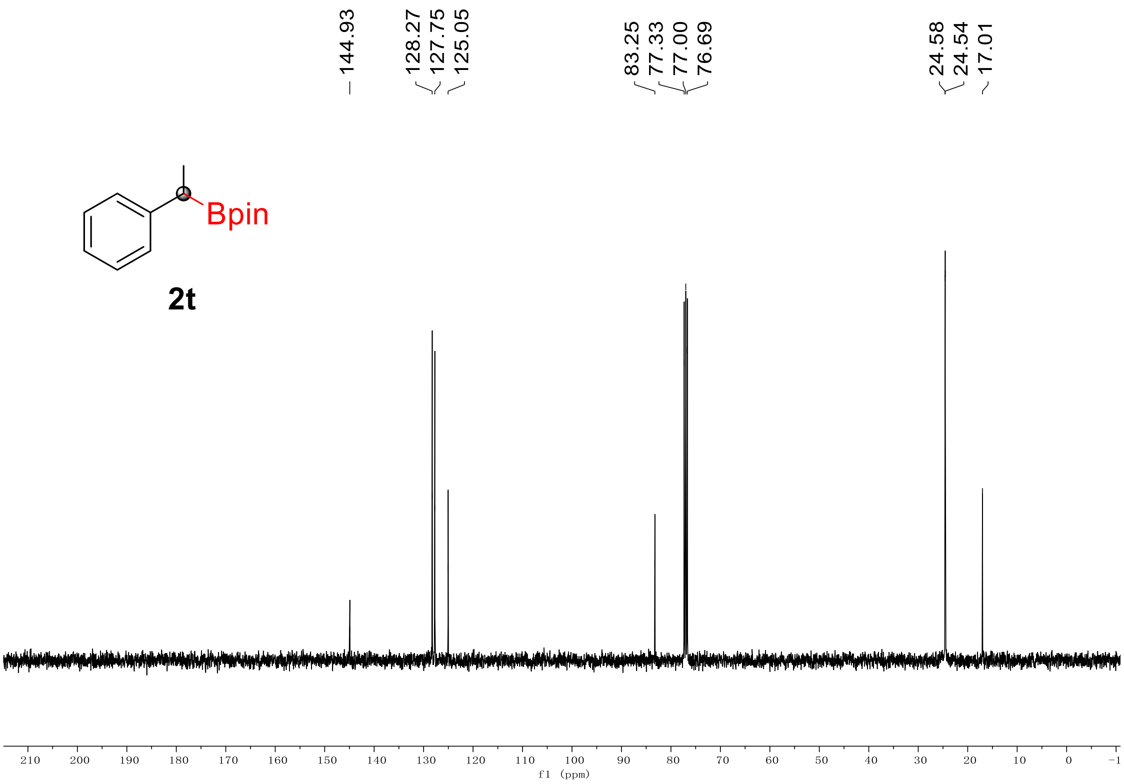


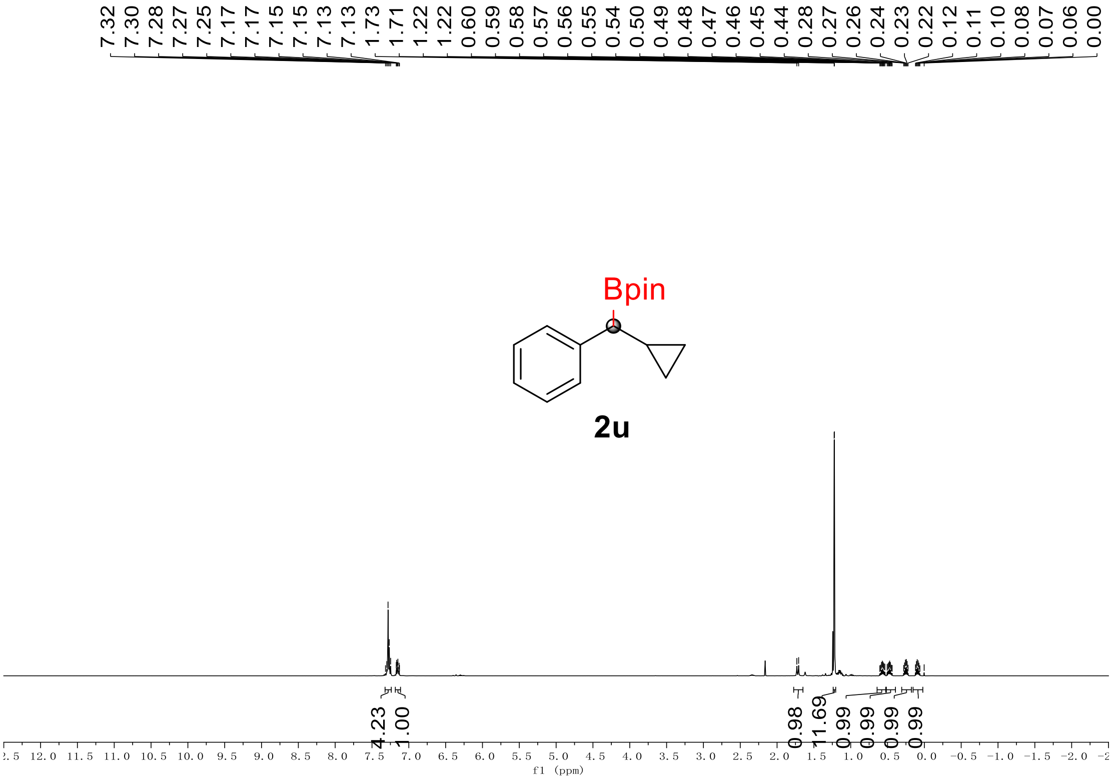
^{1}H NMR, 400 MHz, $CDCl_3$



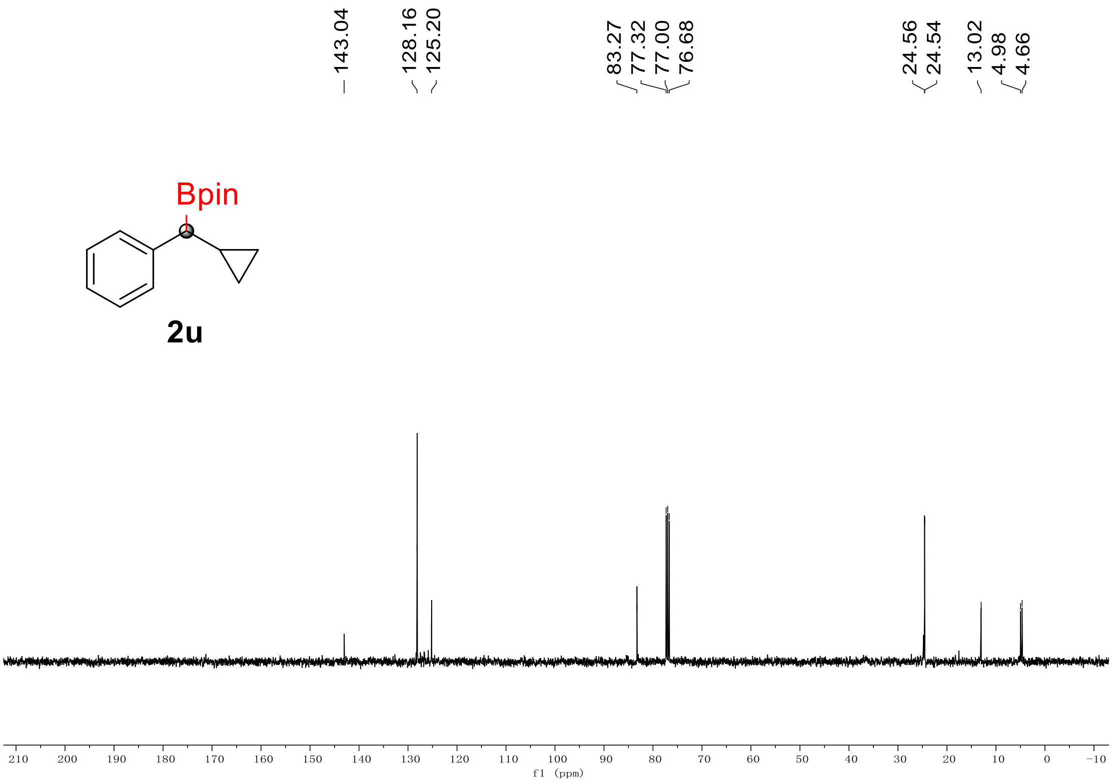
^{13}C NMR, 100 MHz, $CDCl_3$



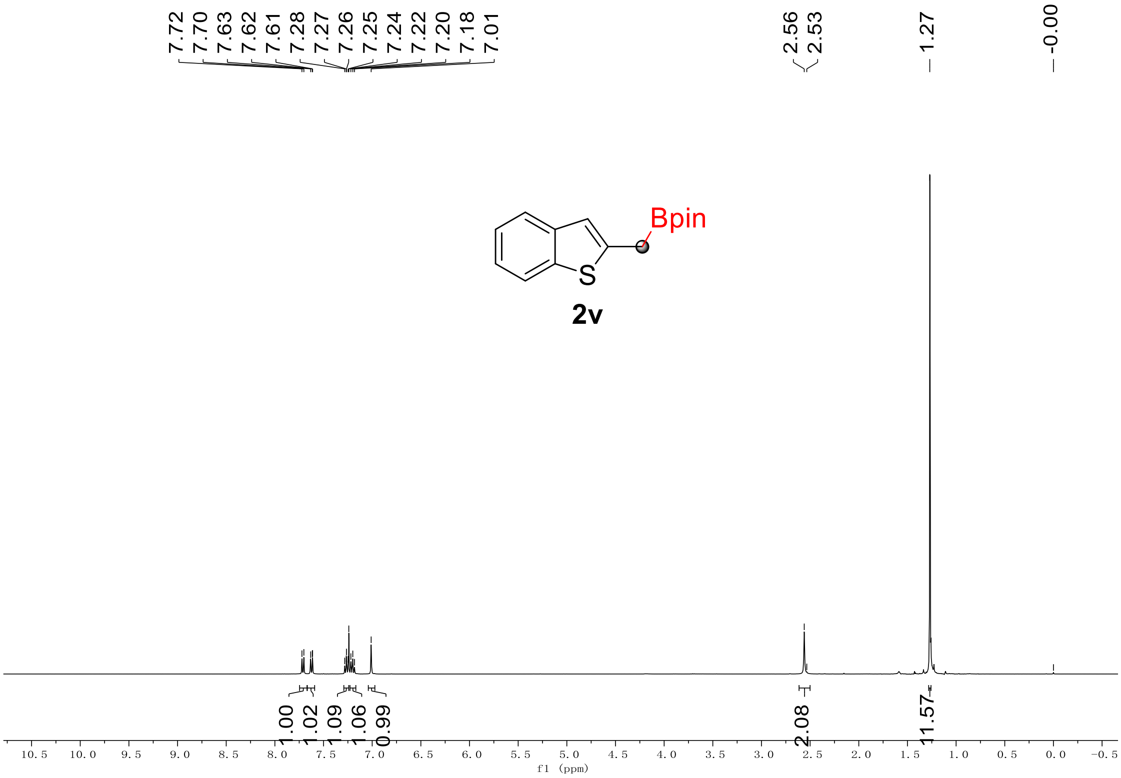
[1]H NMR, 400 MHz, $CDCl_3$



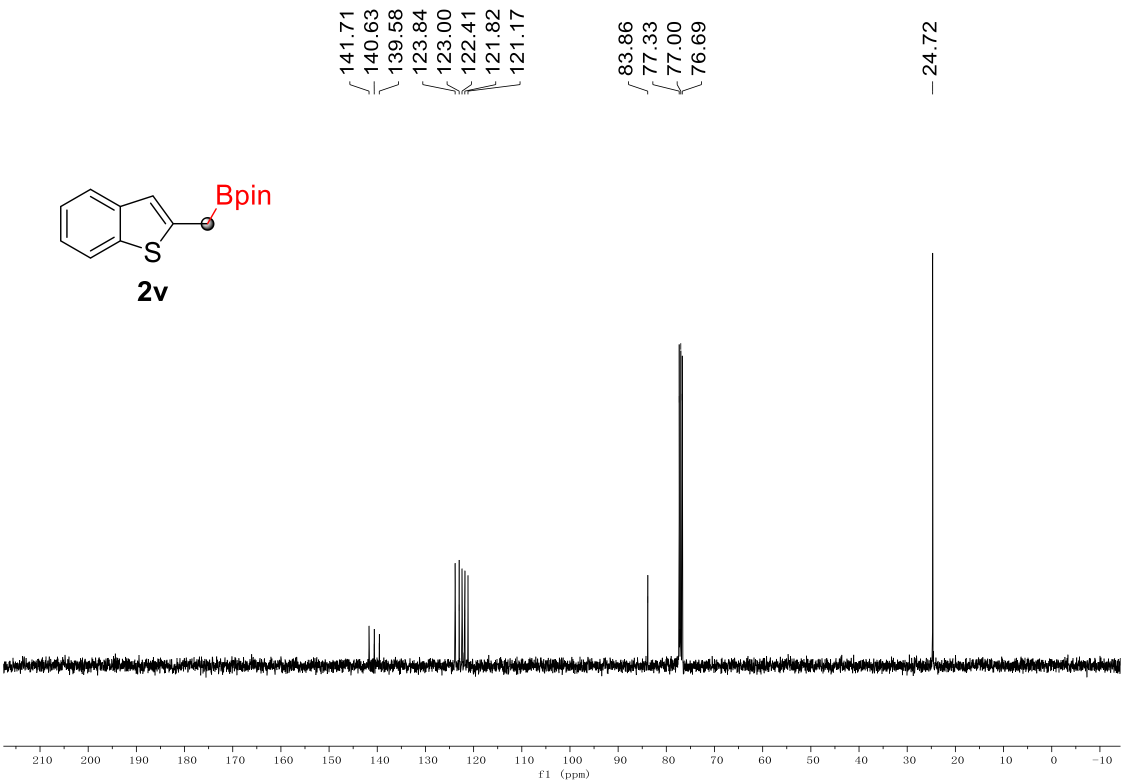
[13]C NMR, 100 MHz, $CDCl_3$



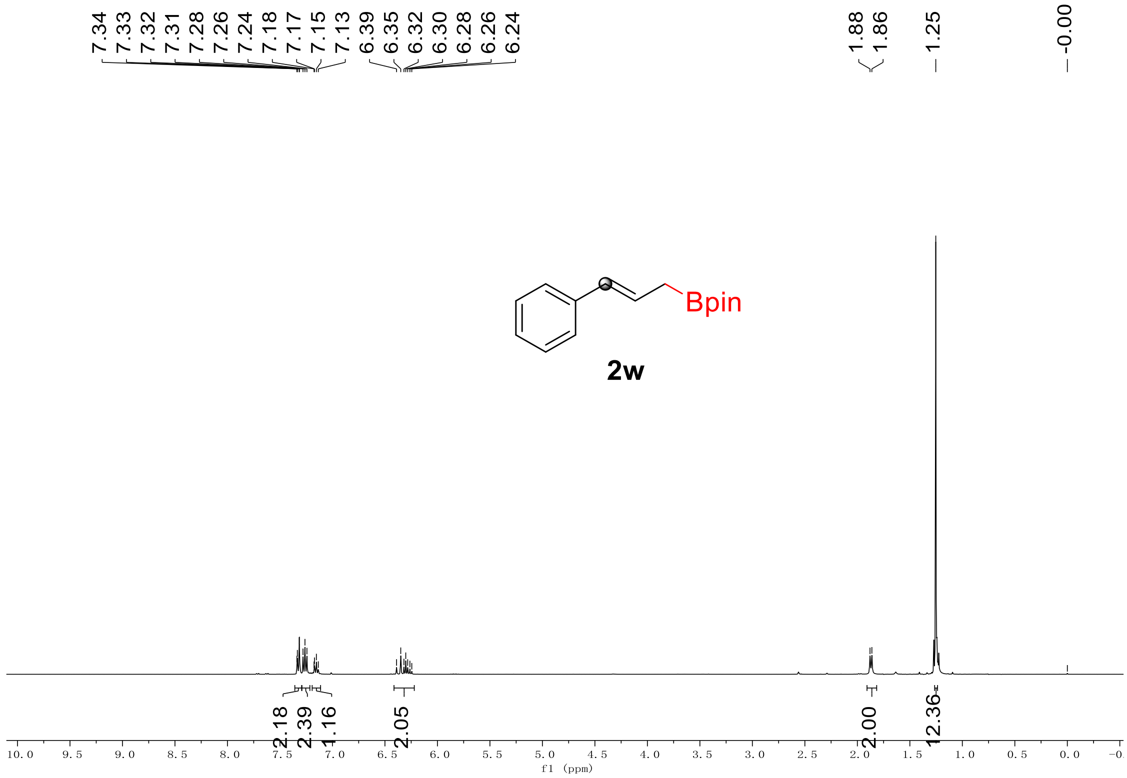
^{1}H NMR, 400 MHz, $CDCl_3$



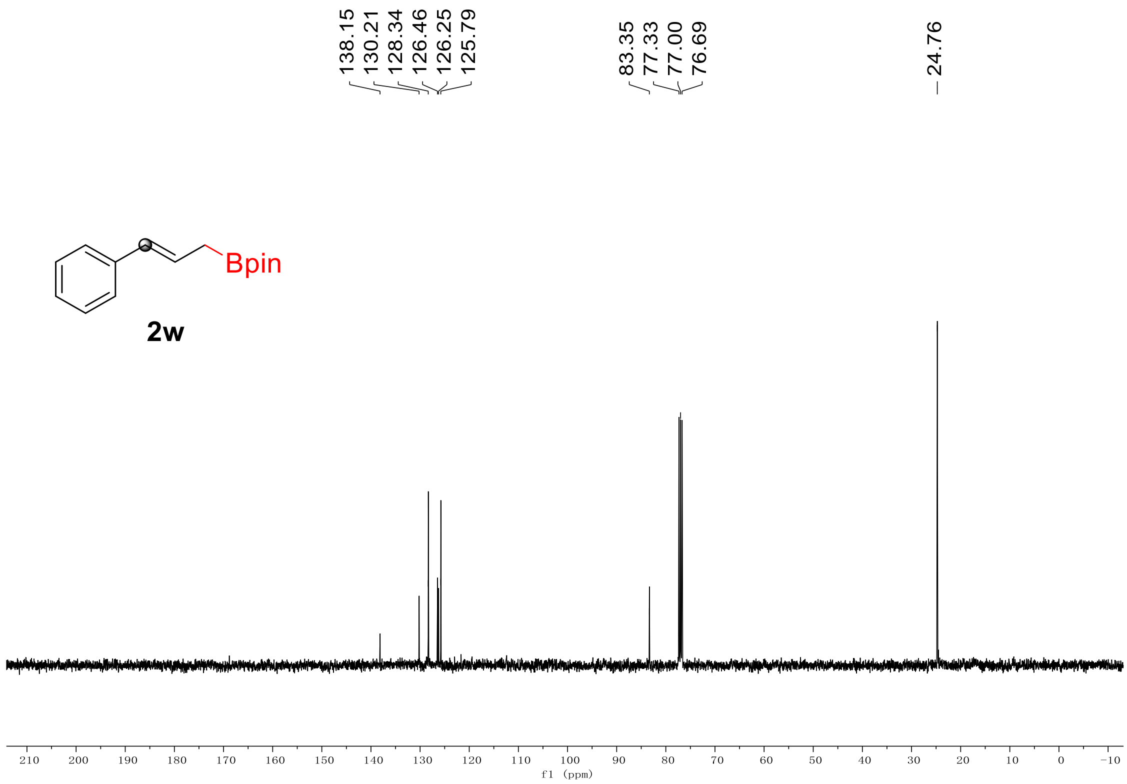
^{13}C NMR, 100 MHz, $CDCl_3$



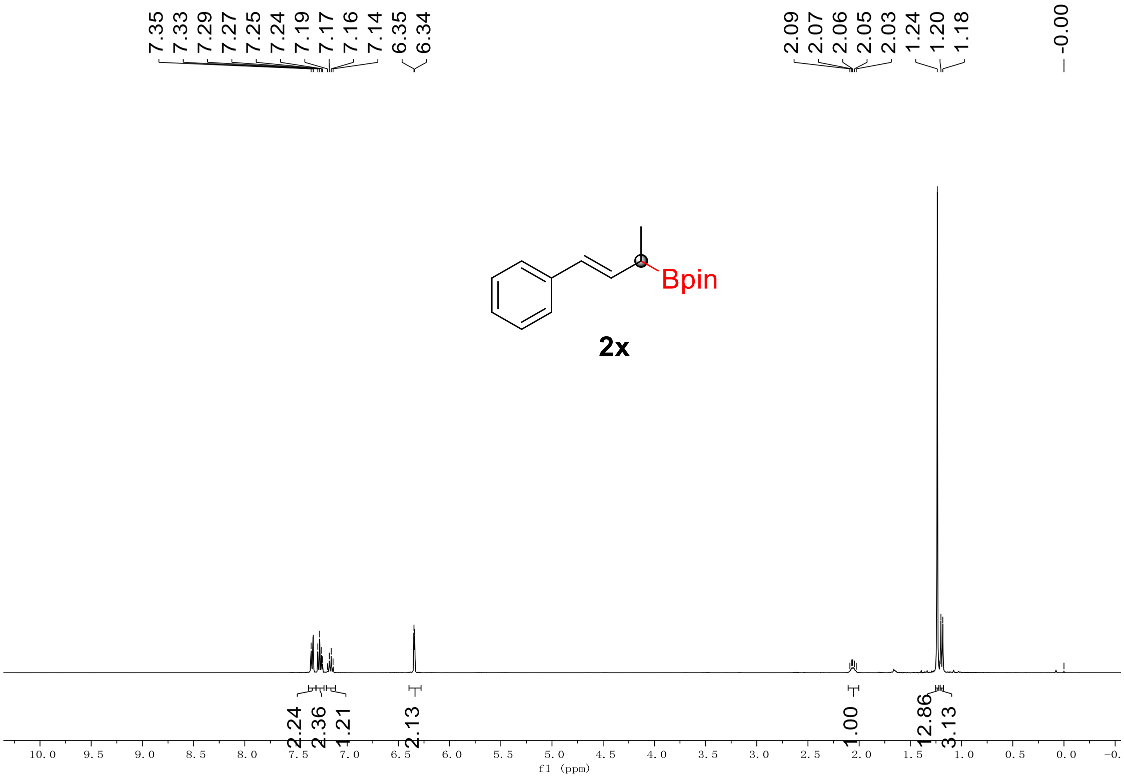
^{1}H NMR, 400 MHz, $CDCl_3$



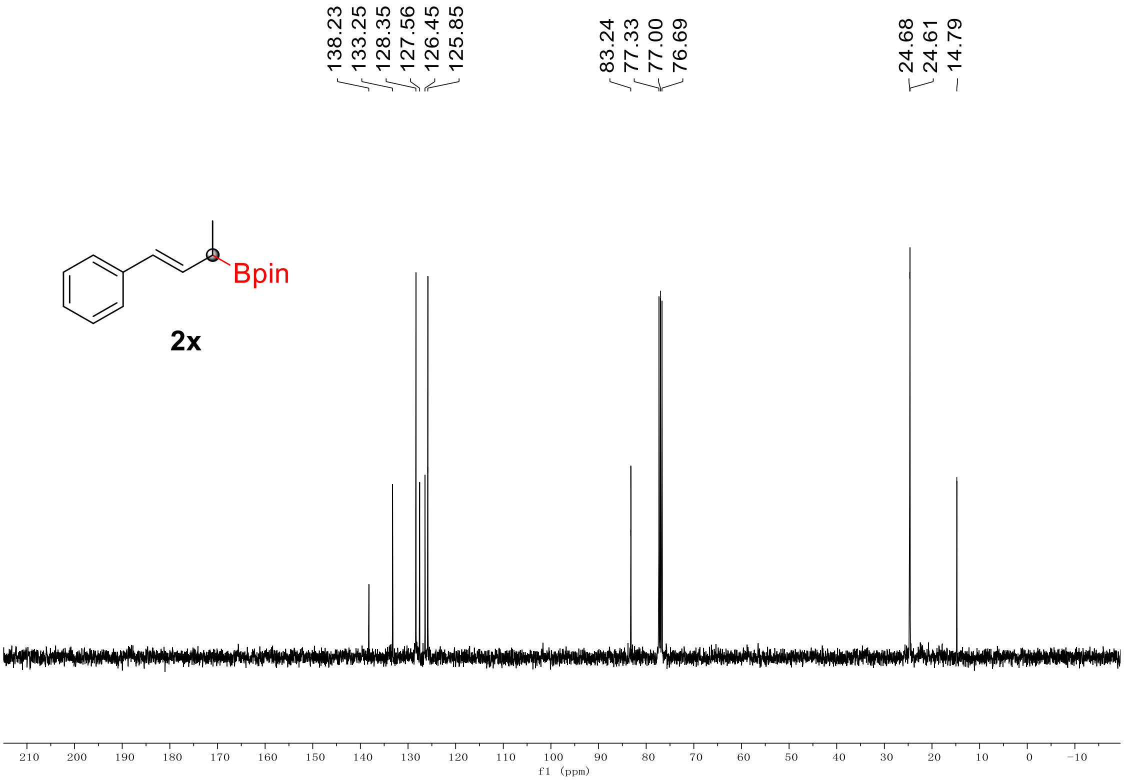
^{13}C NMR, 100 MHz, $CDCl_3$



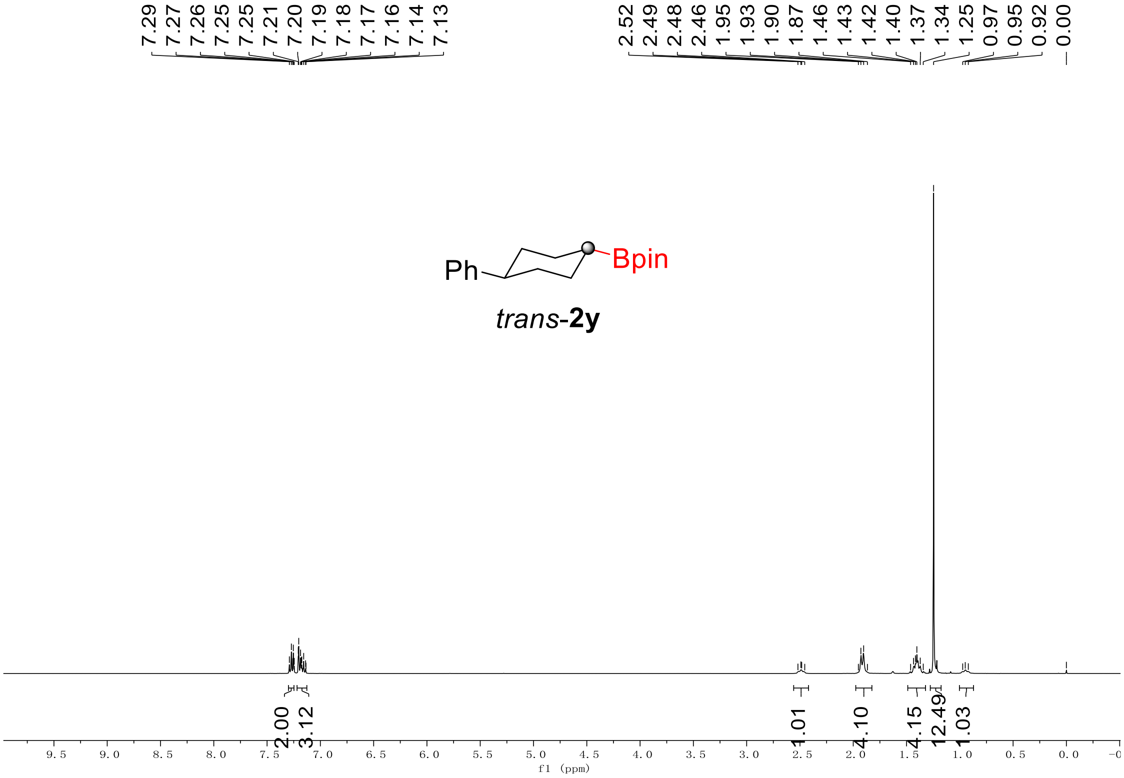
^{1}H NMR, 400 MHz, $CDCl_3$



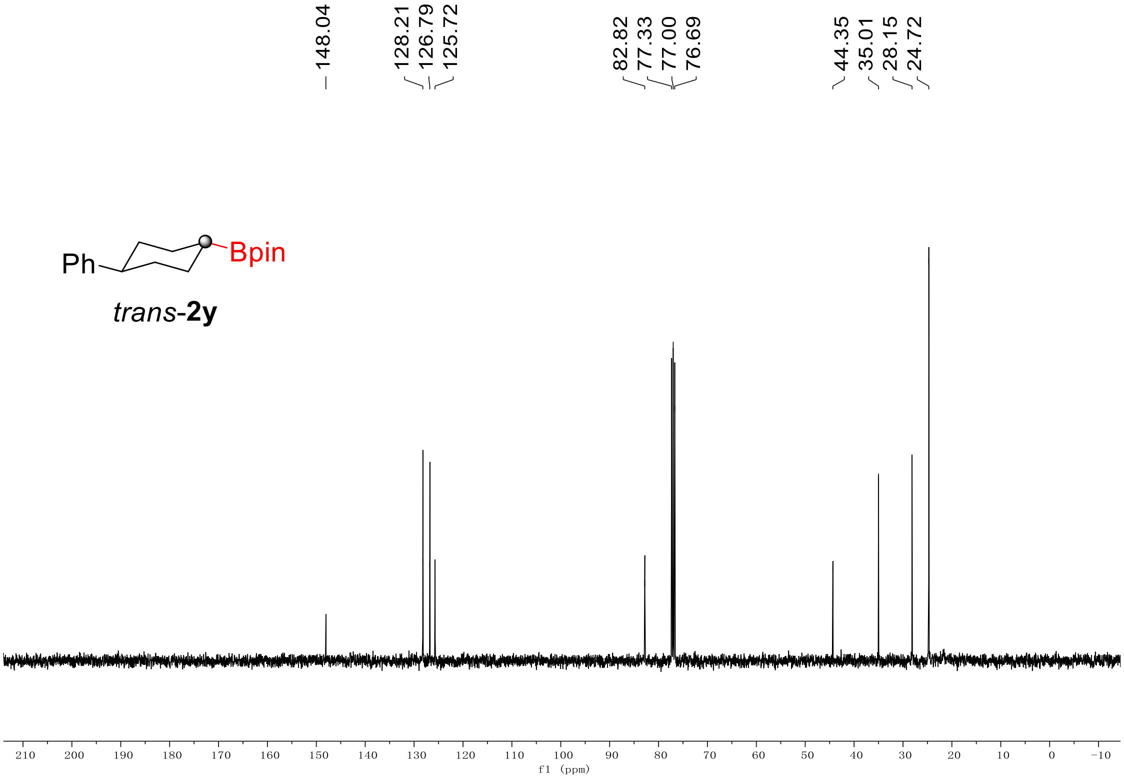
^{13}C NMR, 100 MHz, $CDCl_3$



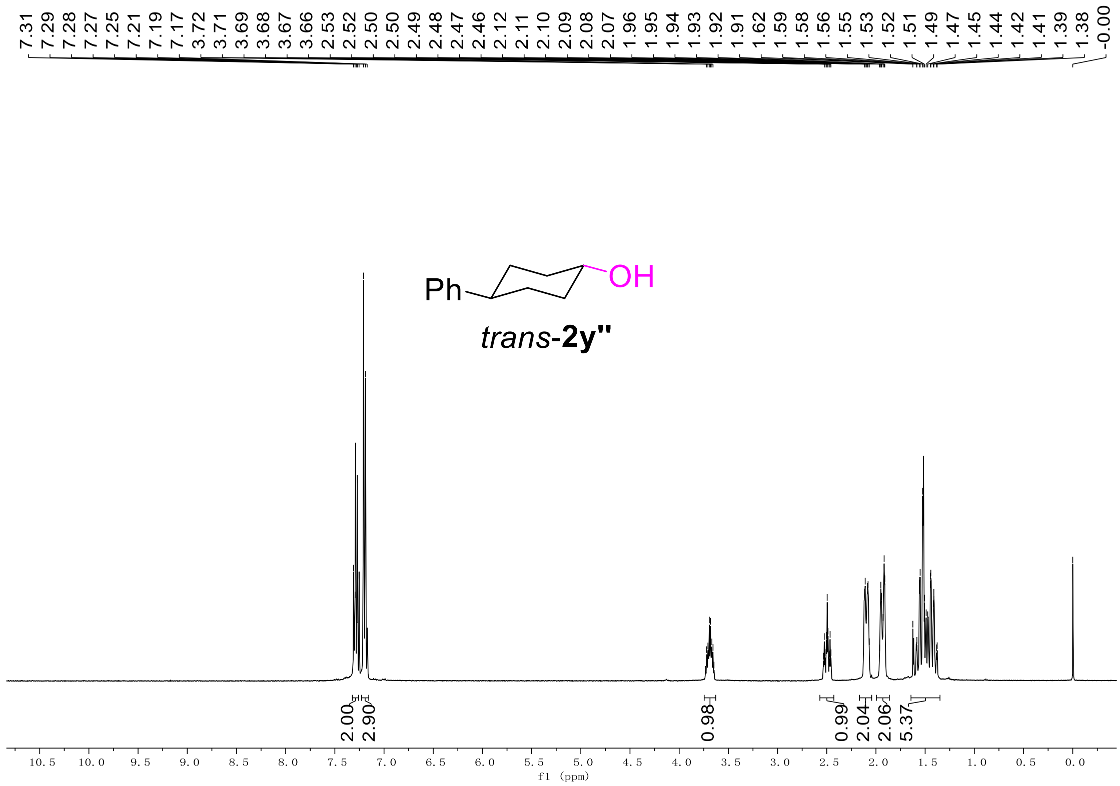
^{1}H NMR, 400 MHz, $CDCl_3$



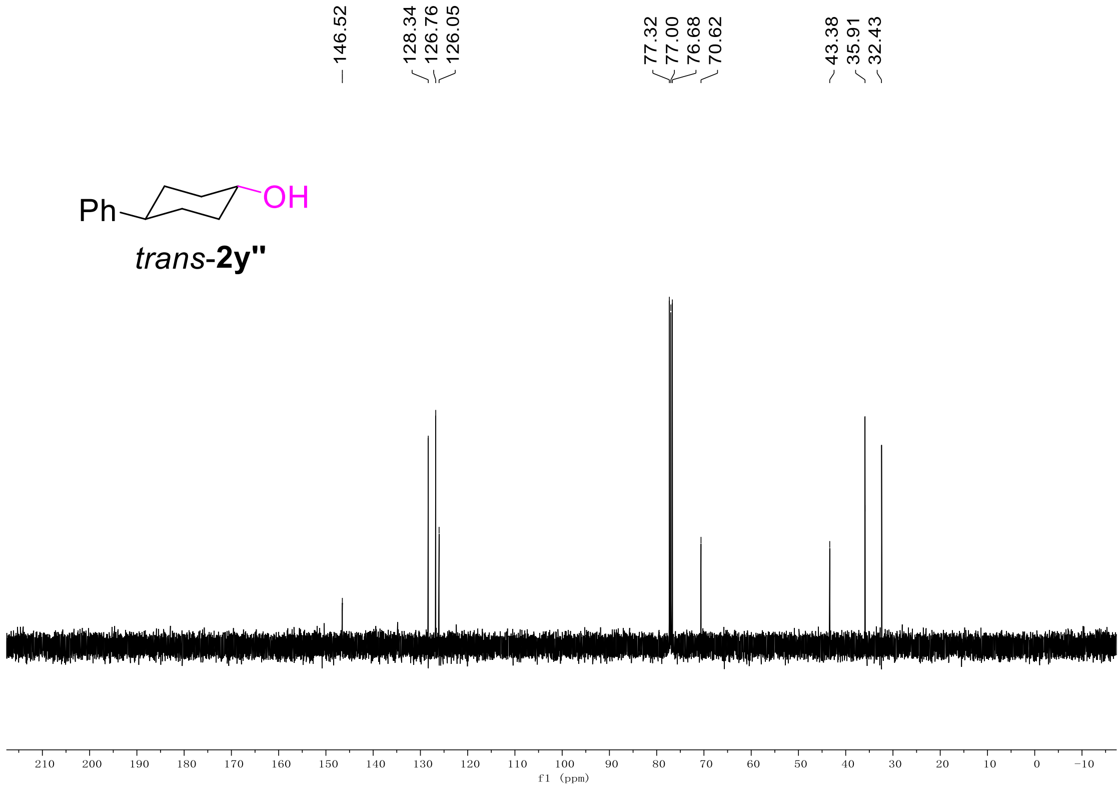
^{13}C NMR, 100 MHz, $CDCl_3$



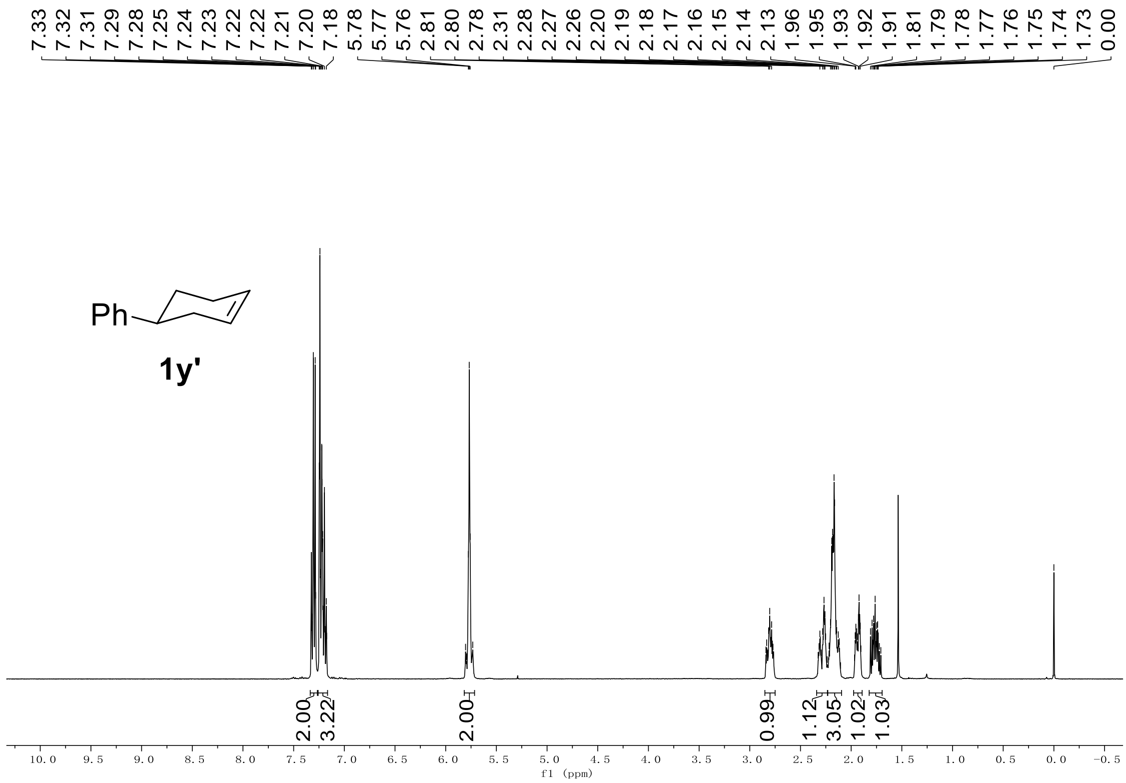
^{1}H NMR, 400 MHz, $CDCl_3$



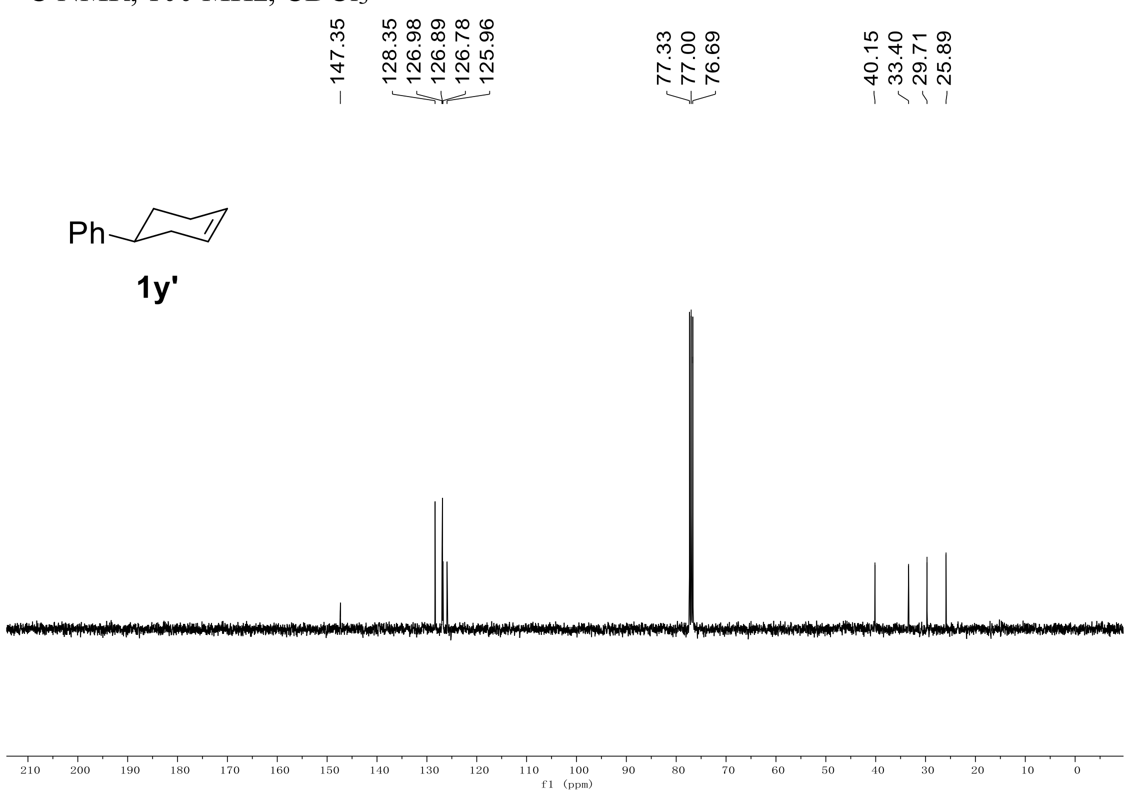
^{13}C NMR, 100 MHz, $CDCl_3$



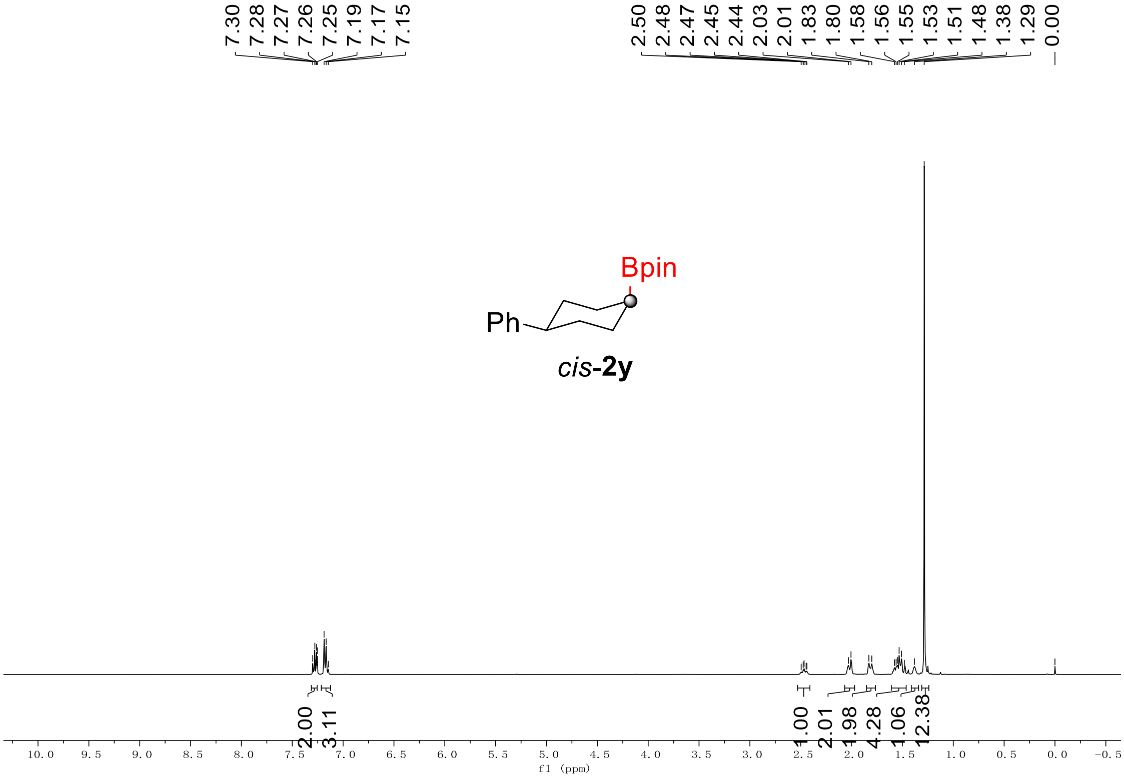
^{1}H NMR, 400 MHz, $CDCl_3$



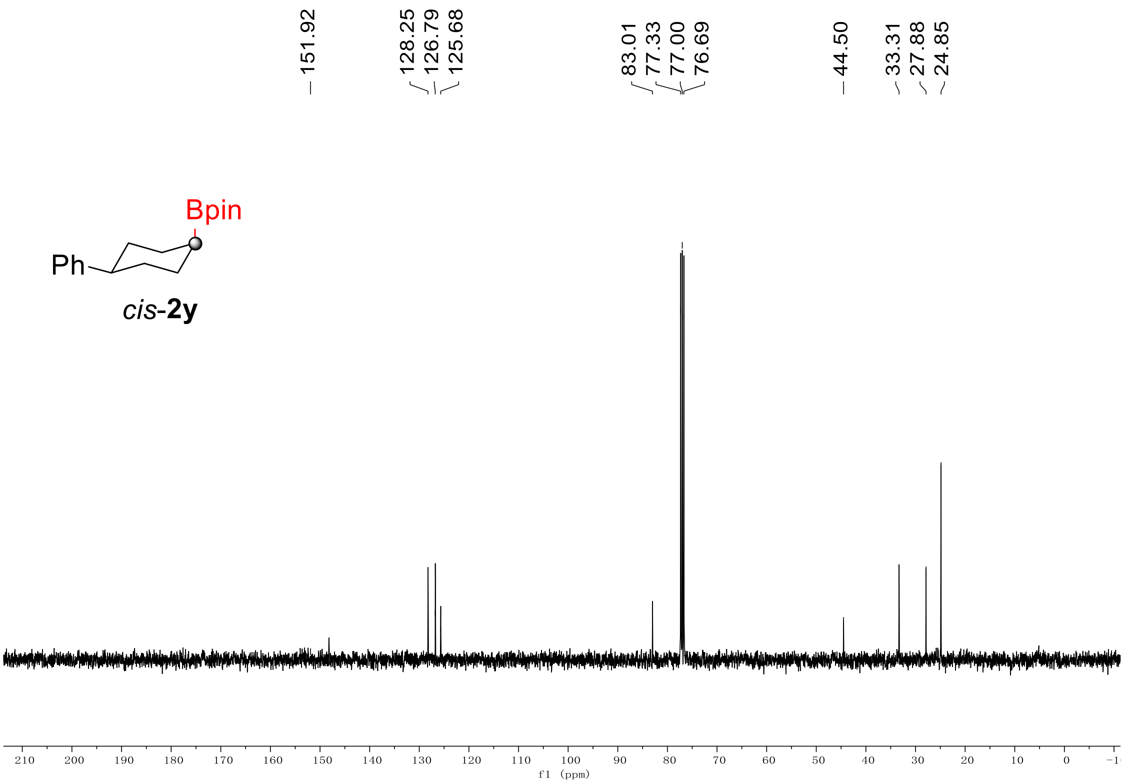
^{13}C NMR, 100 MHz, $CDCl_3$



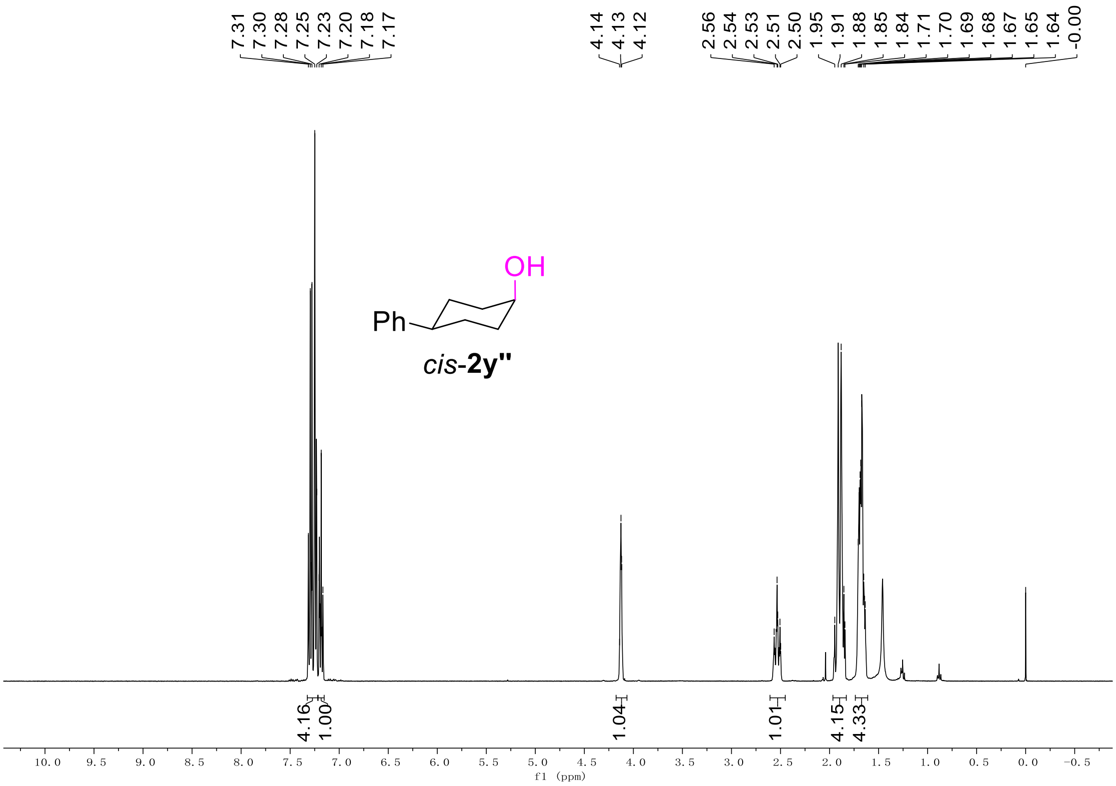
^{1}H NMR, 400 MHz, $CDCl_3$



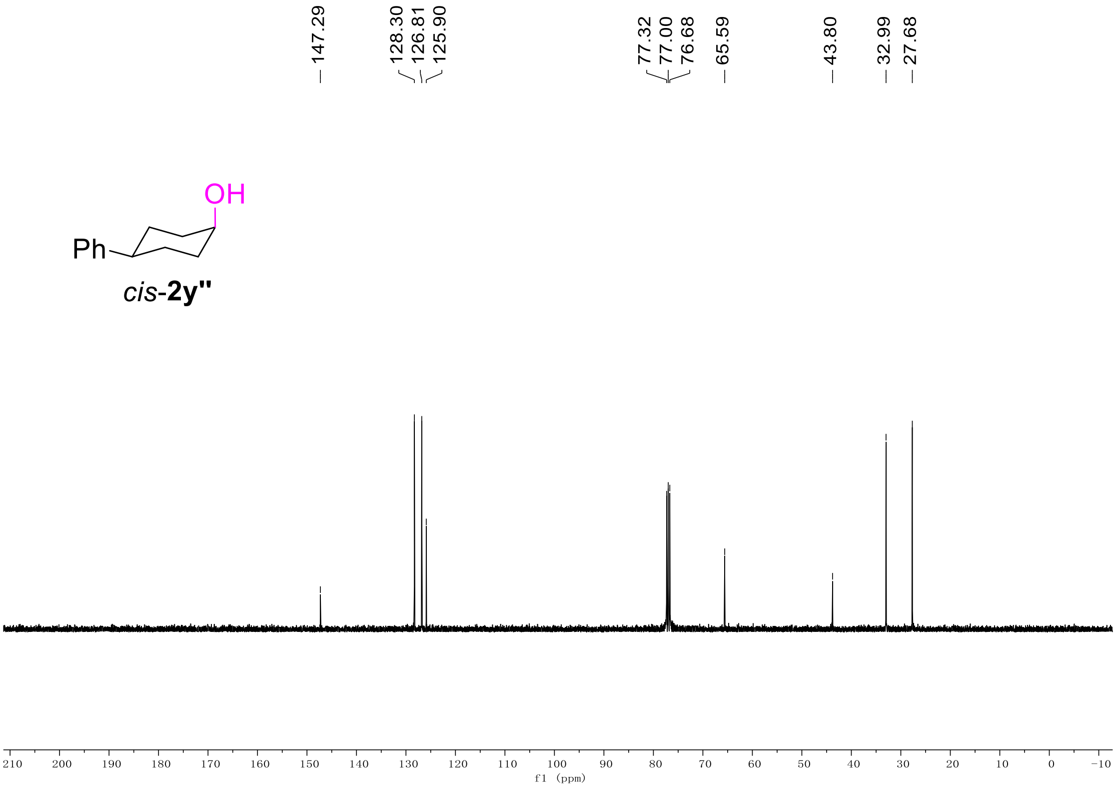
^{13}C NMR, 100 MHz, $CDCl_3$



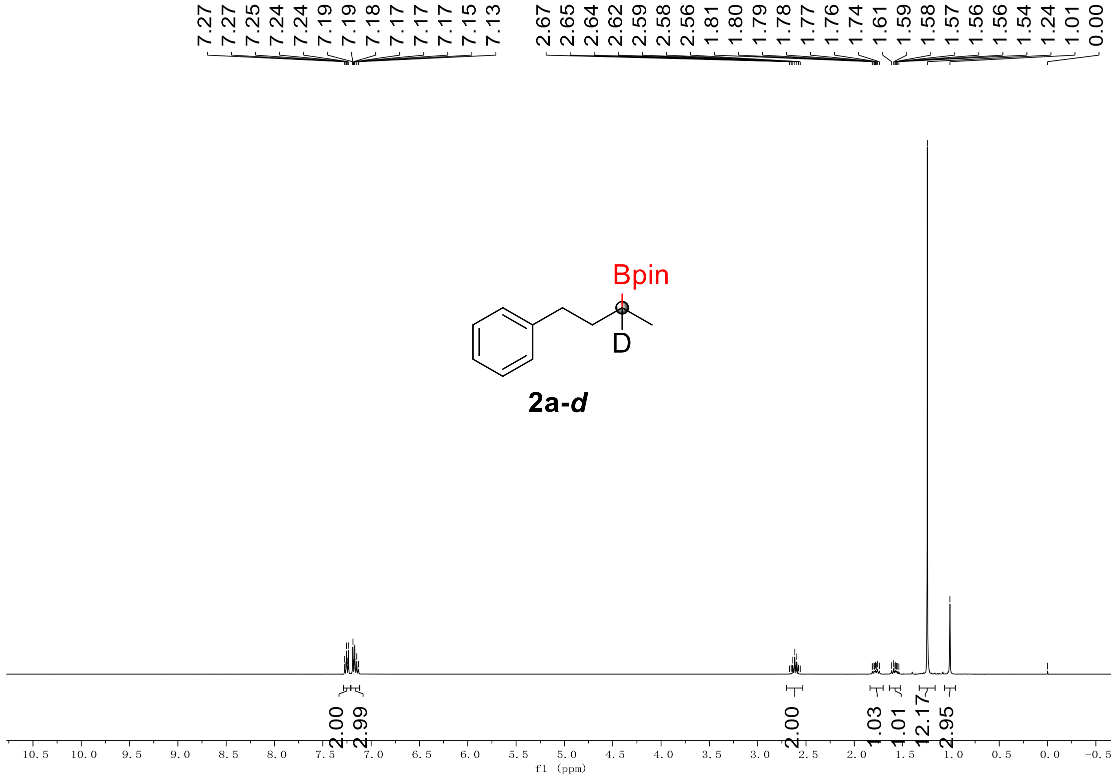
^1H NMR, 400 MHz, $CDCl_3$



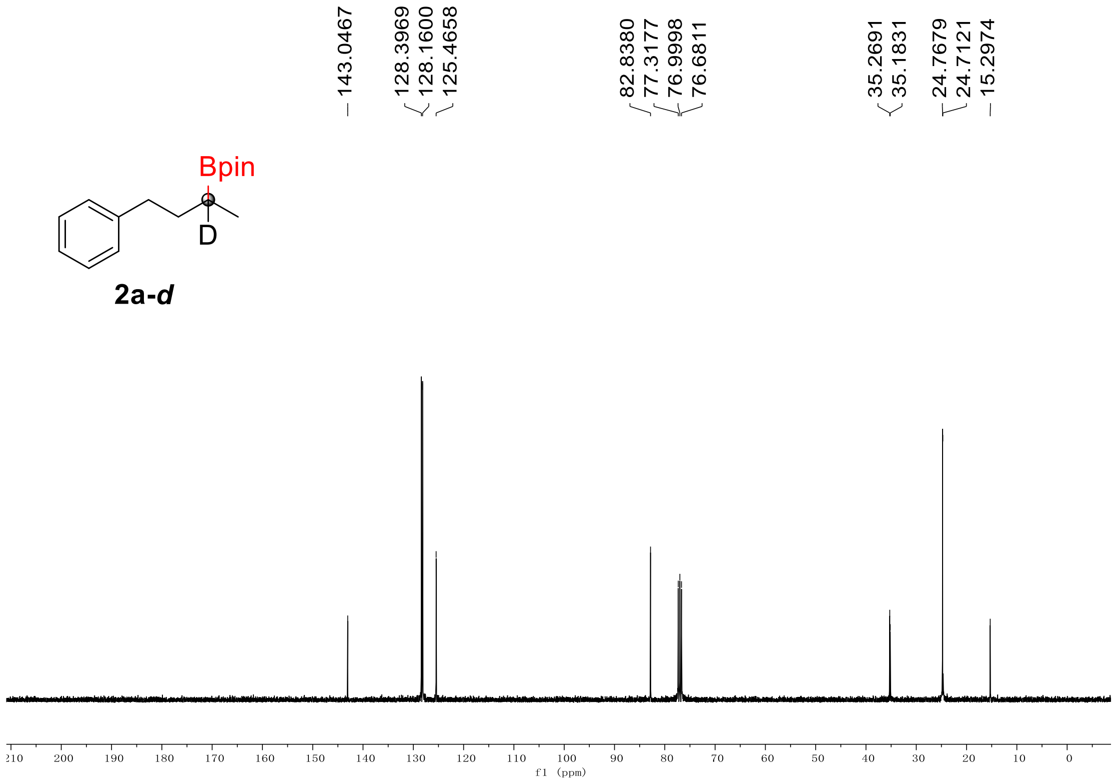
^{13}C NMR, 100 MHz, $CDCl_3$



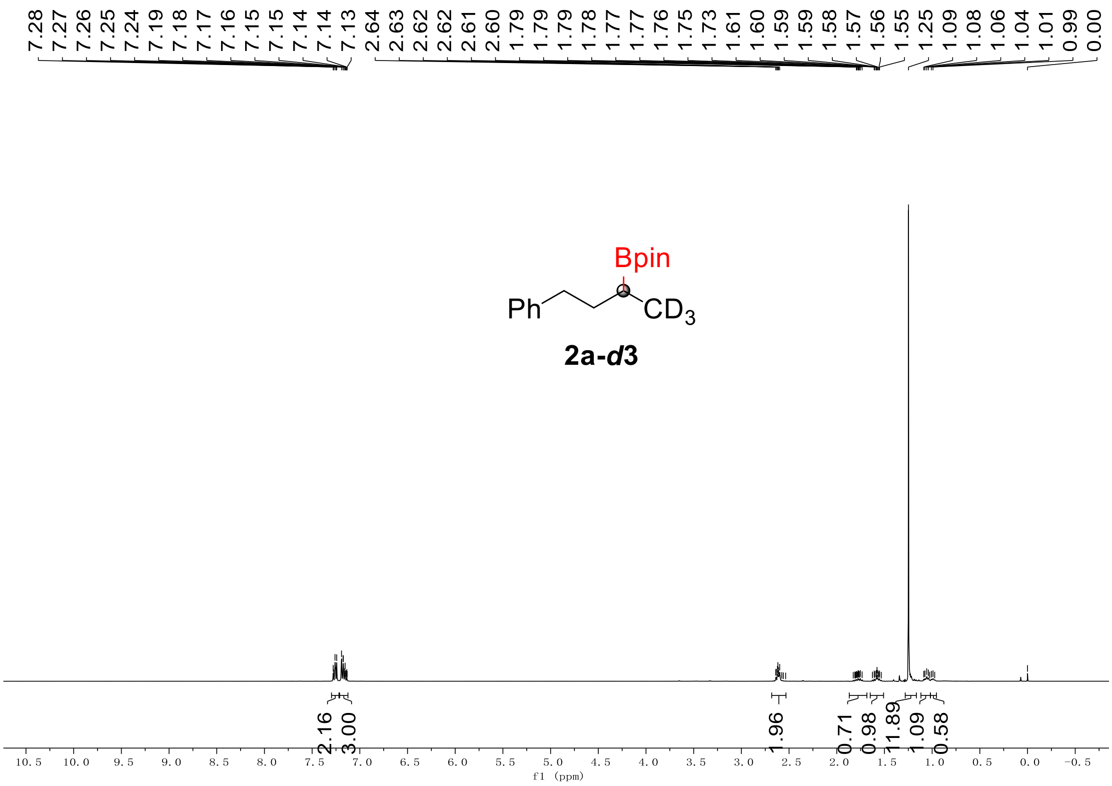
^{1}H NMR, 400 MHz, $CDCl_3$



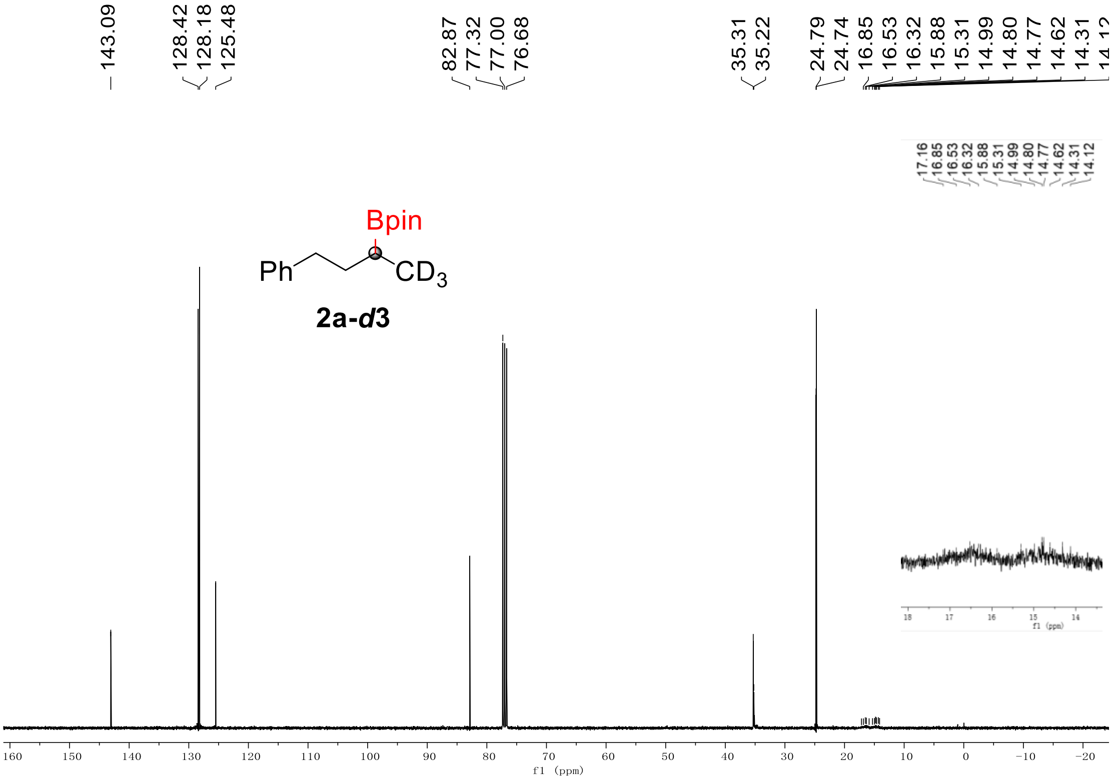
^{13}C NMR, 100 MHz, $CDCl_3$

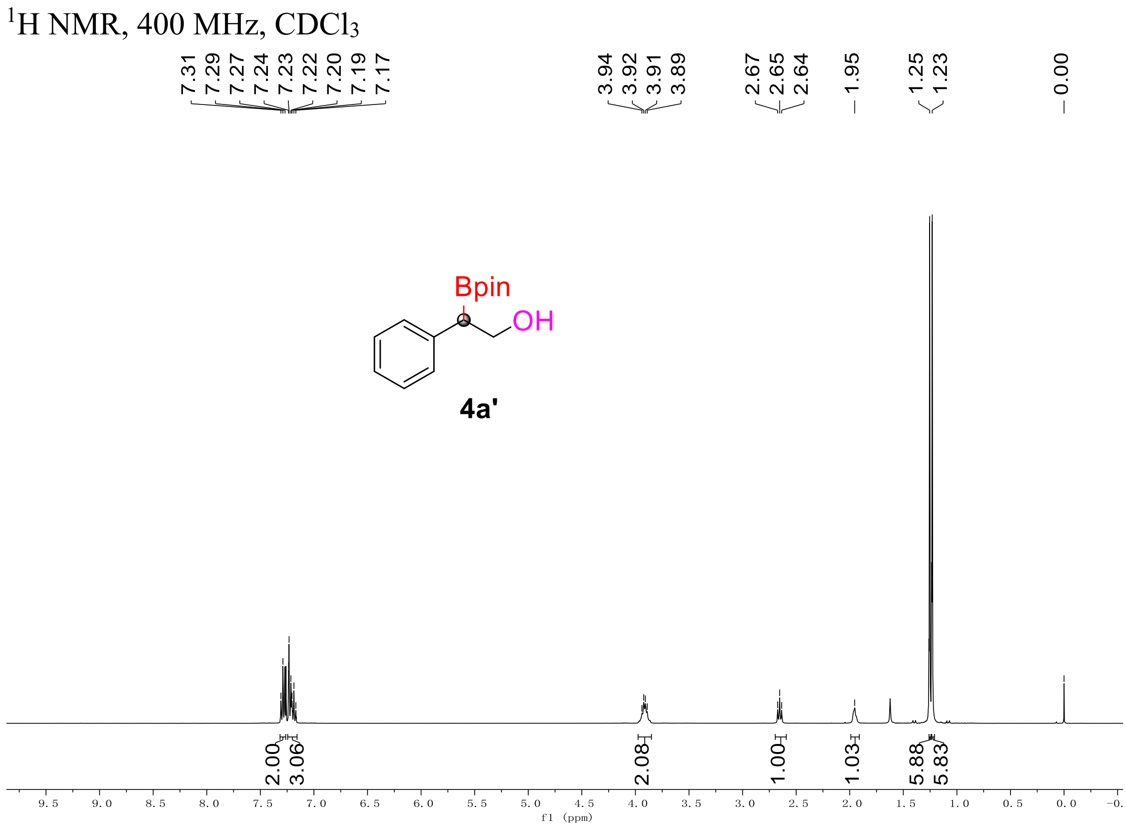


[1]H NMR, 400 MHz, $CDCl_3$

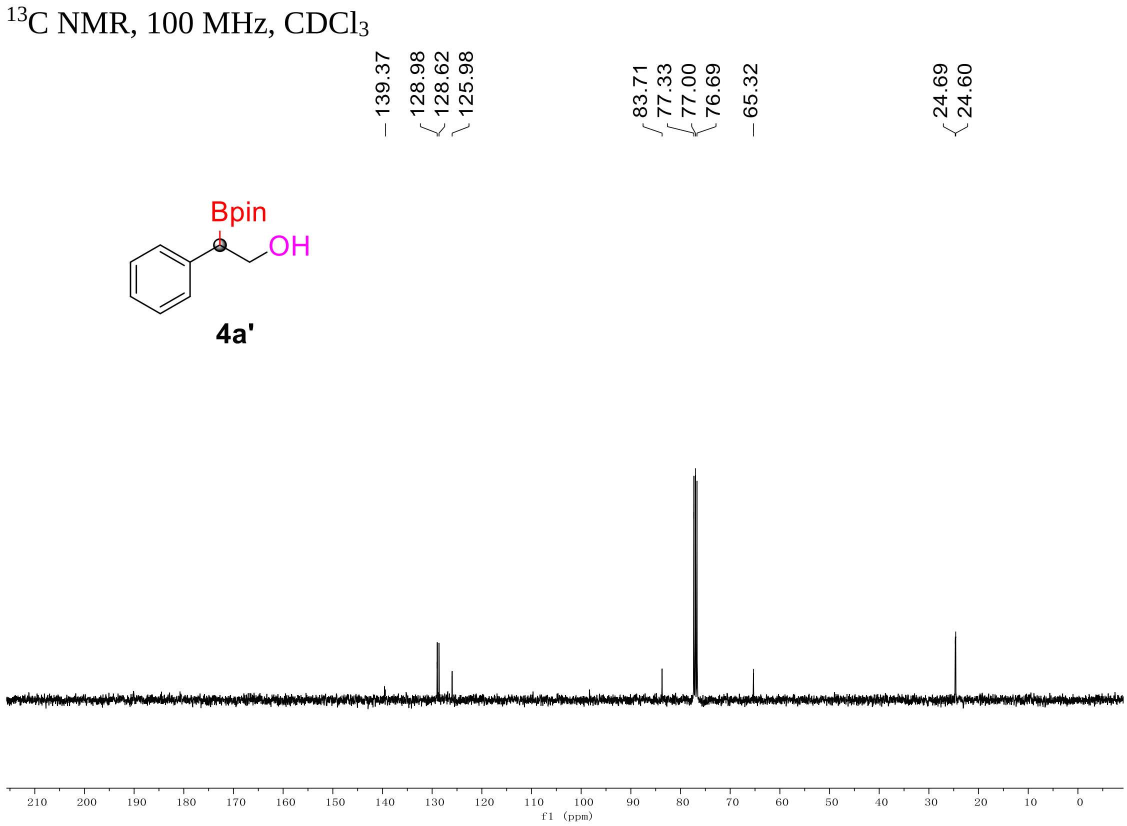


[13]C NMR, 100 MHz, $CDCl_3$



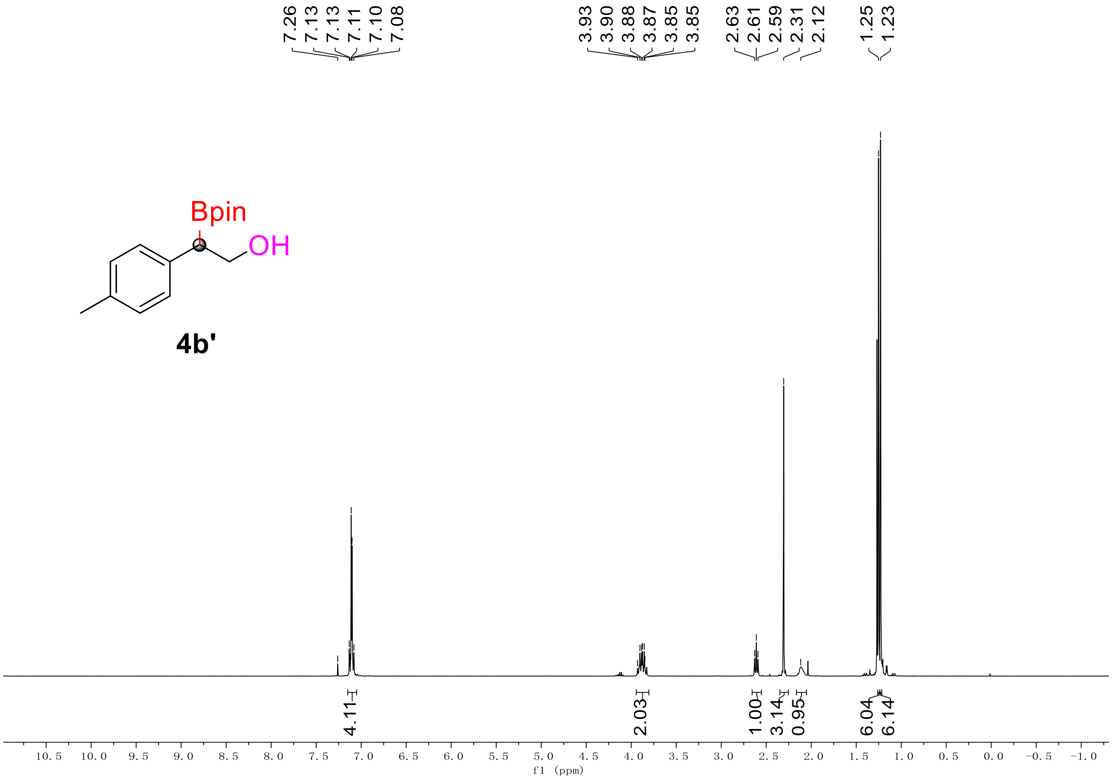


^{1}H NMR, 400 MHz, CDCl$_3$
7.31
7.29
7.27
7.24
7.23
7.22
7.20
7.19
7.17
3.94
3.92
3.91
3.89
2.67
2.65
2.64
1.95
1.25
1.23
0.00
Bpin
OH
4a'
2.00
3.06
2.08
1.00
1.03
5.88
5.83
f1 (ppm)

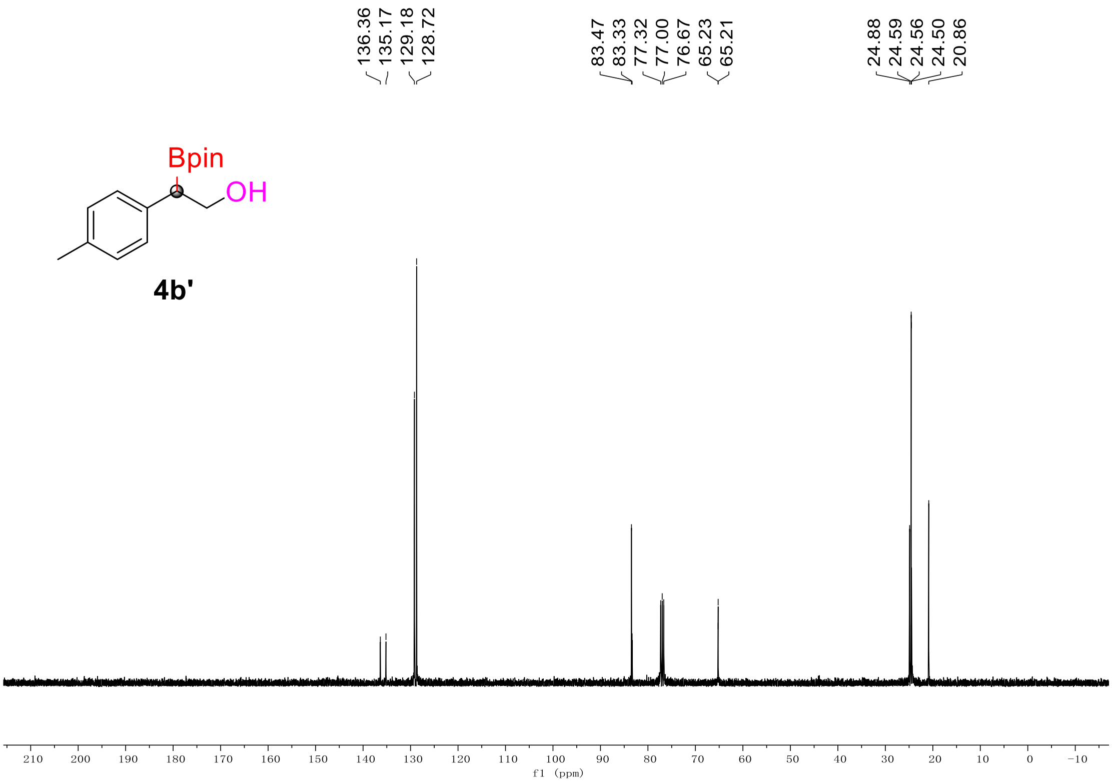


^{13}C NMR, 100 MHz, CDCl$_3$
139.37
128.98
128.62
125.98
83.71
77.33
77.00
76.69
65.32
24.69
24.60
Bpin
OH
4a'
f1 (ppm)

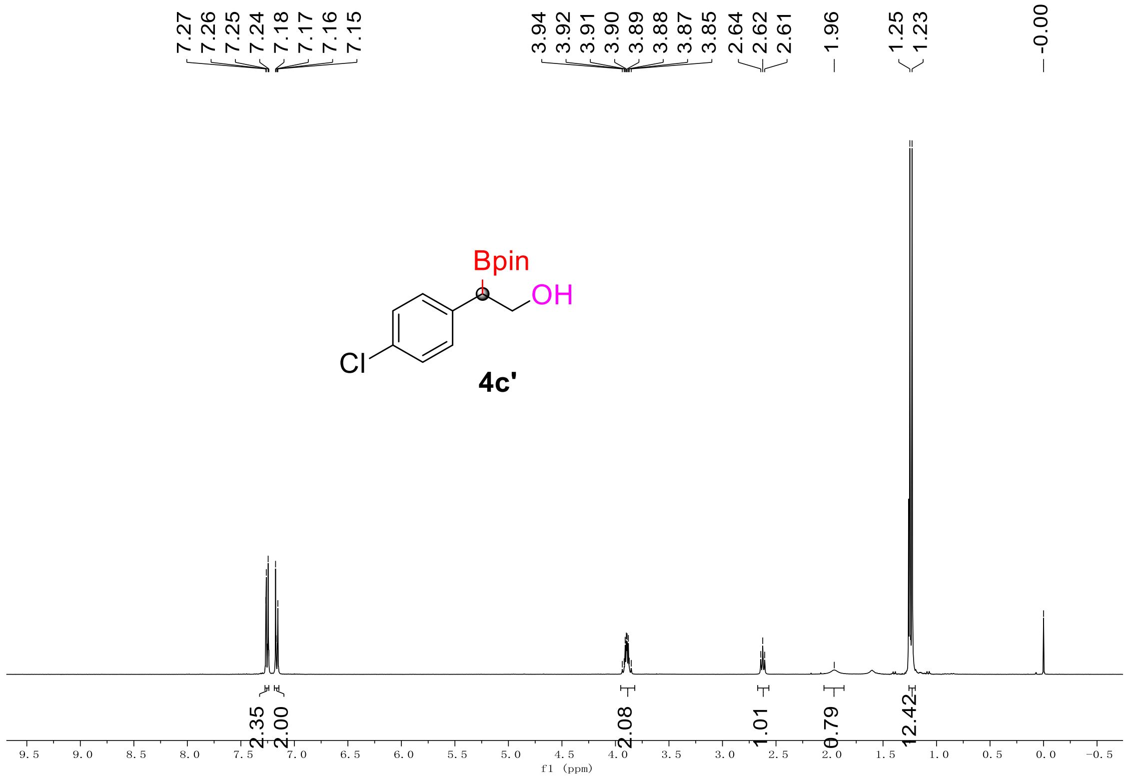
^{1}H NMR, 400 MHz, $CDCl_3$



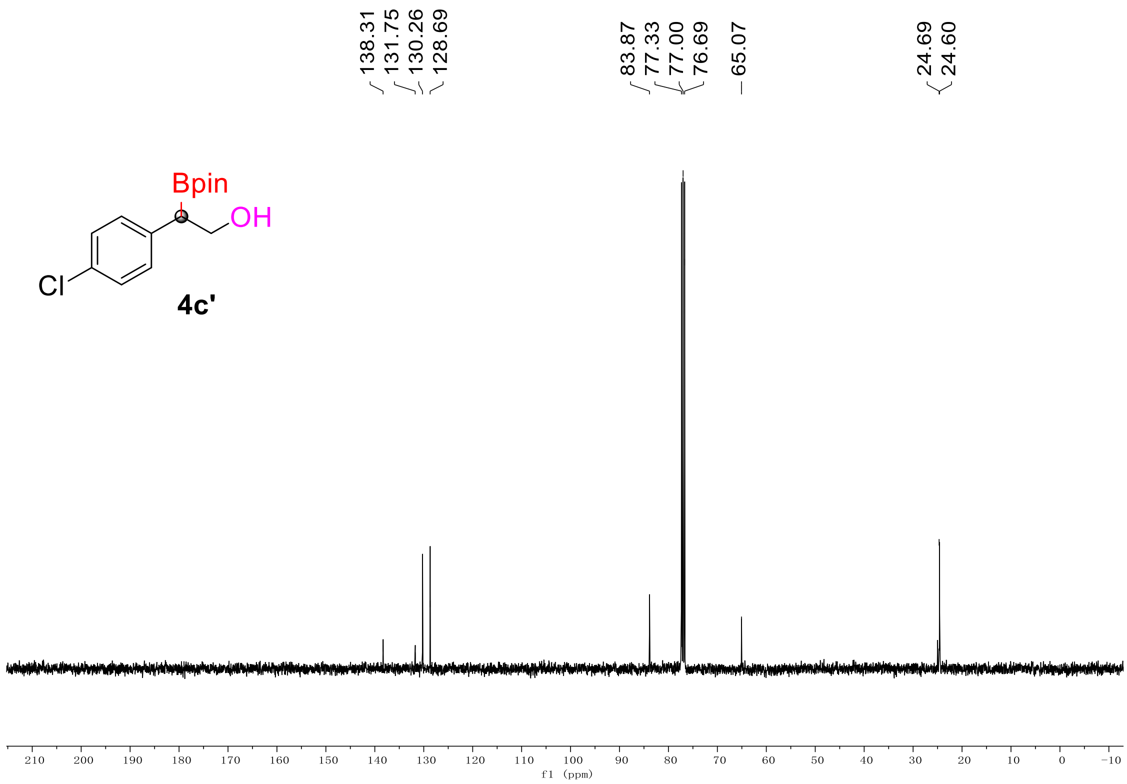
^{13}C NMR, 100 MHz, $CDCl_3$



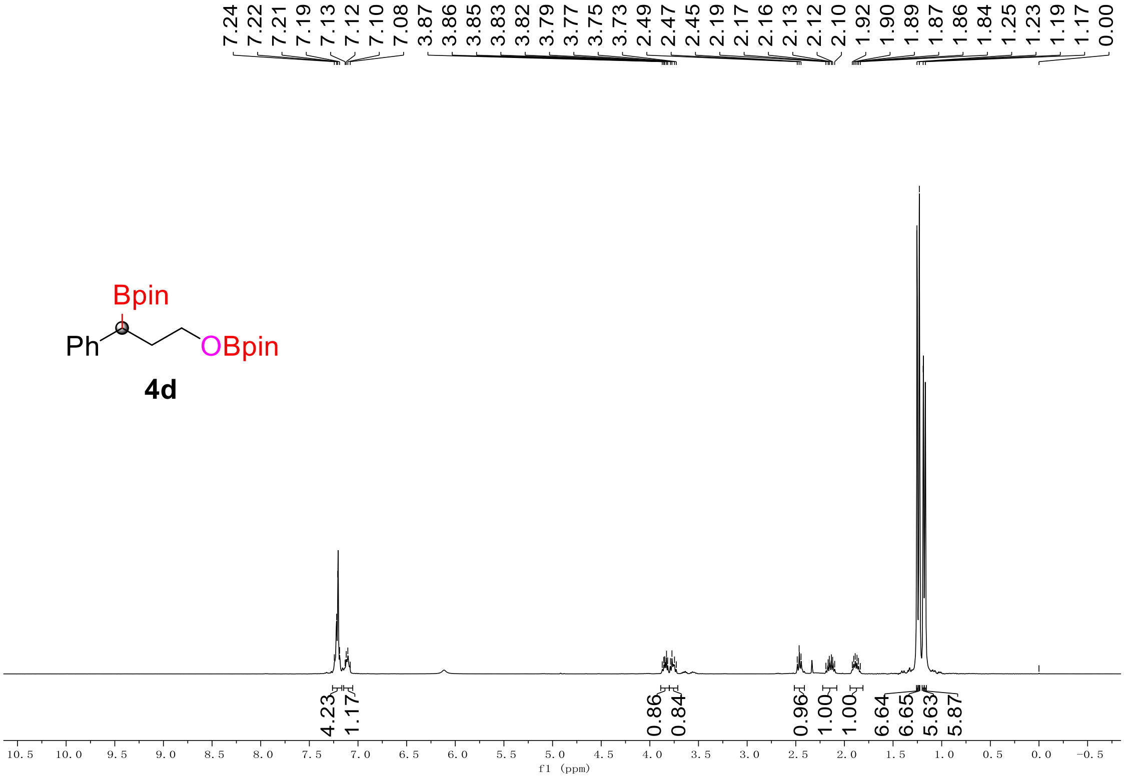
^{1}H NMR, 400 MHz, $CDCl_3$



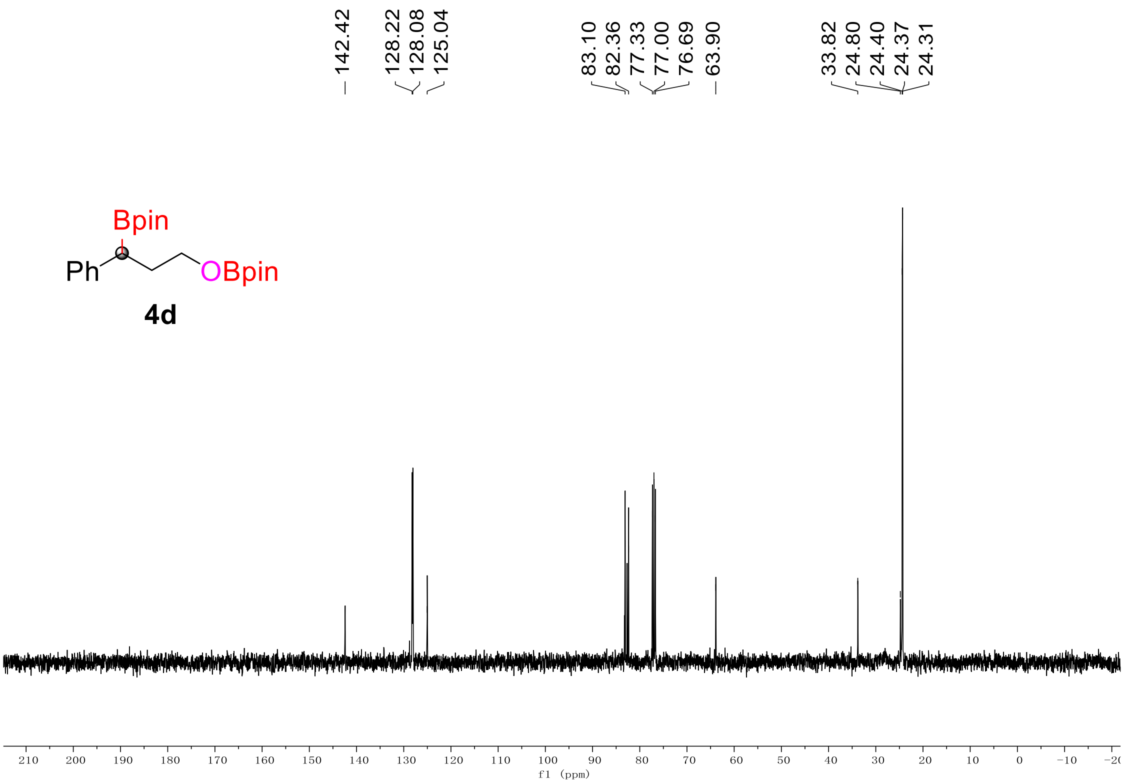
^{13}C NMR, 100 MHz, $CDCl_3$



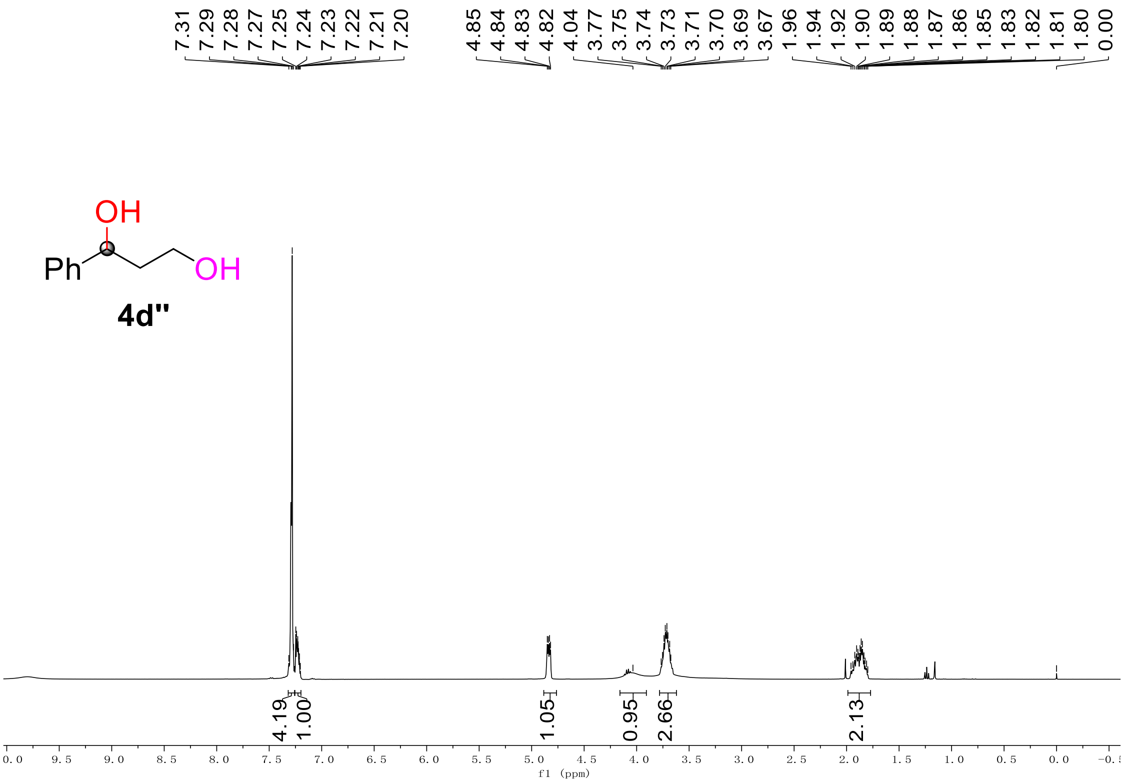
[1]H NMR, 400 MHz, $CDCl_3$



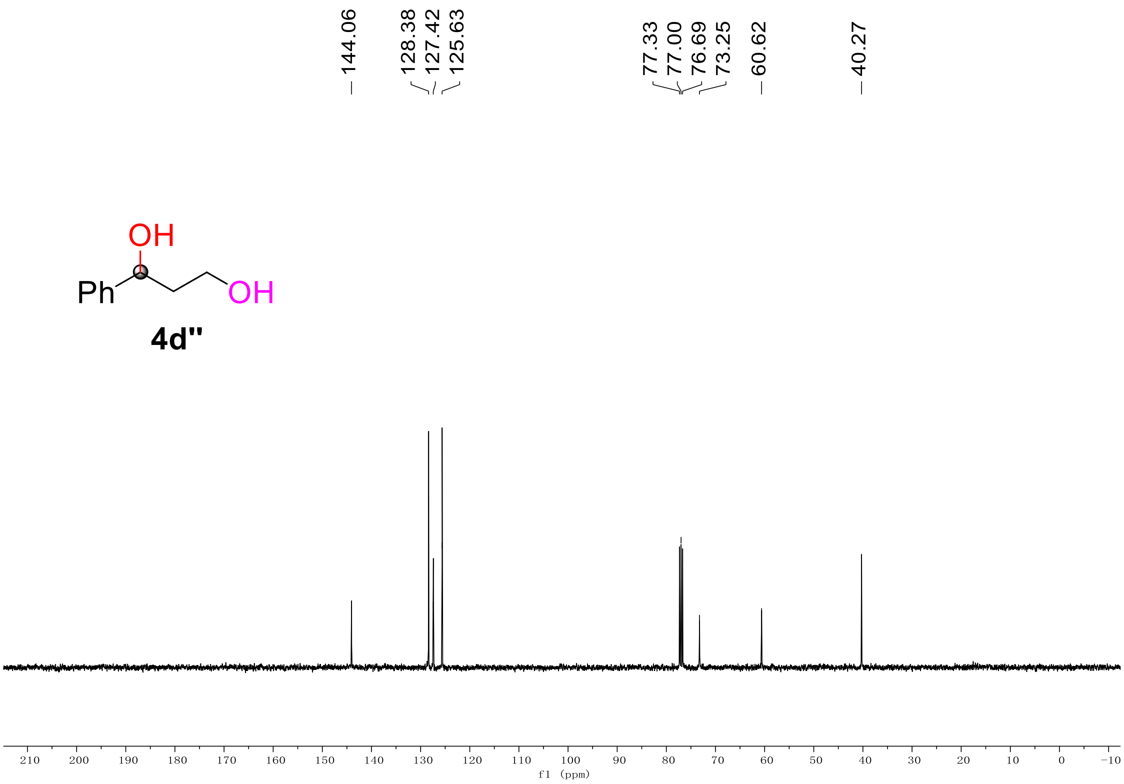
[13]C NMR, 100 MHz, $CDCl_3$



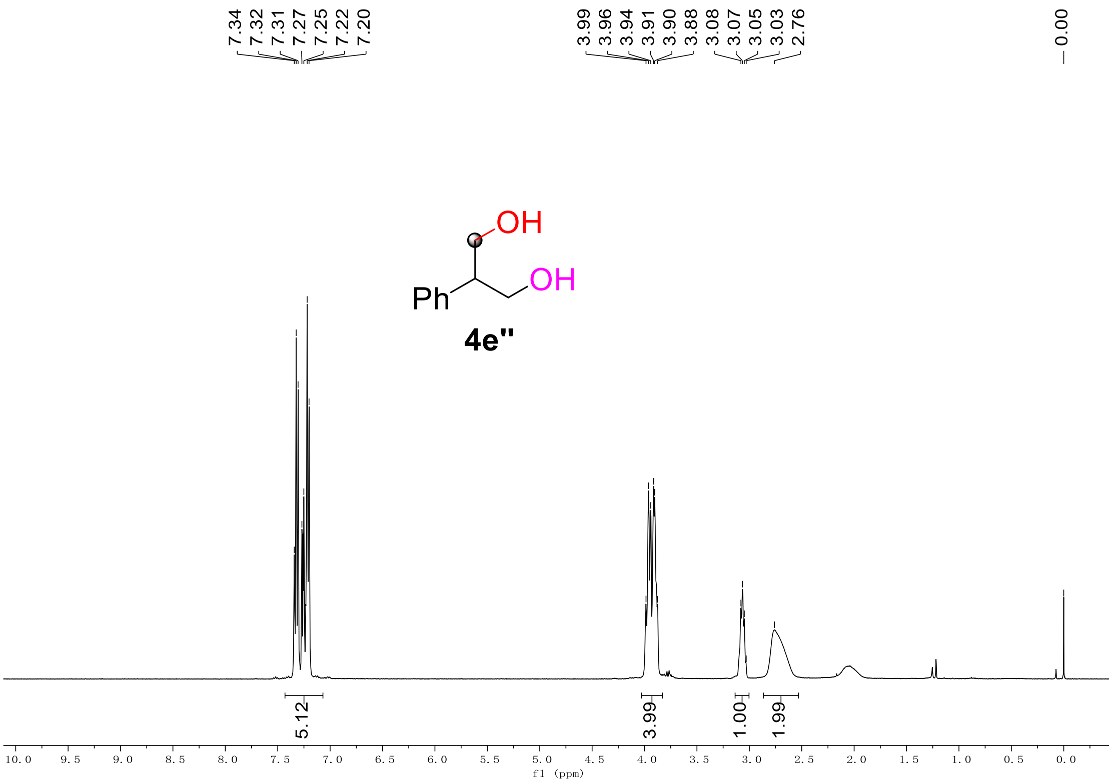
^{1}H NMR, 400 MHz, $CDCl_3$



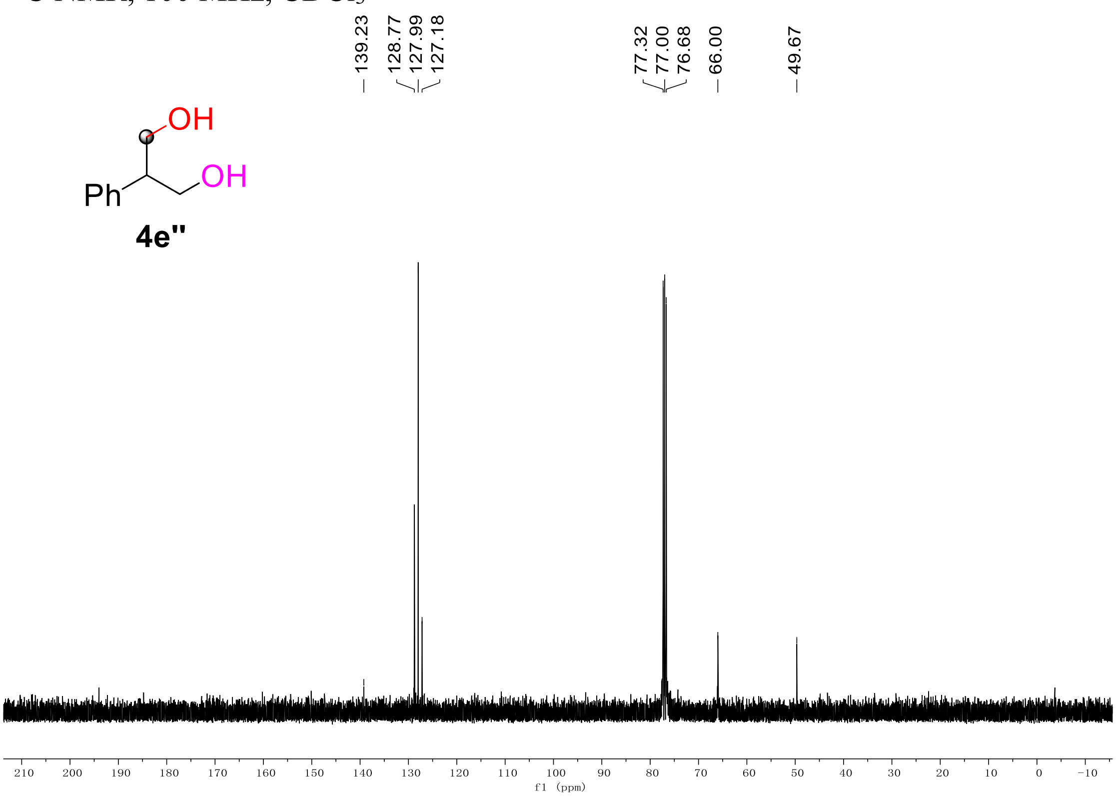
^{13}C NMR, 100 MHz, $CDCl_3$



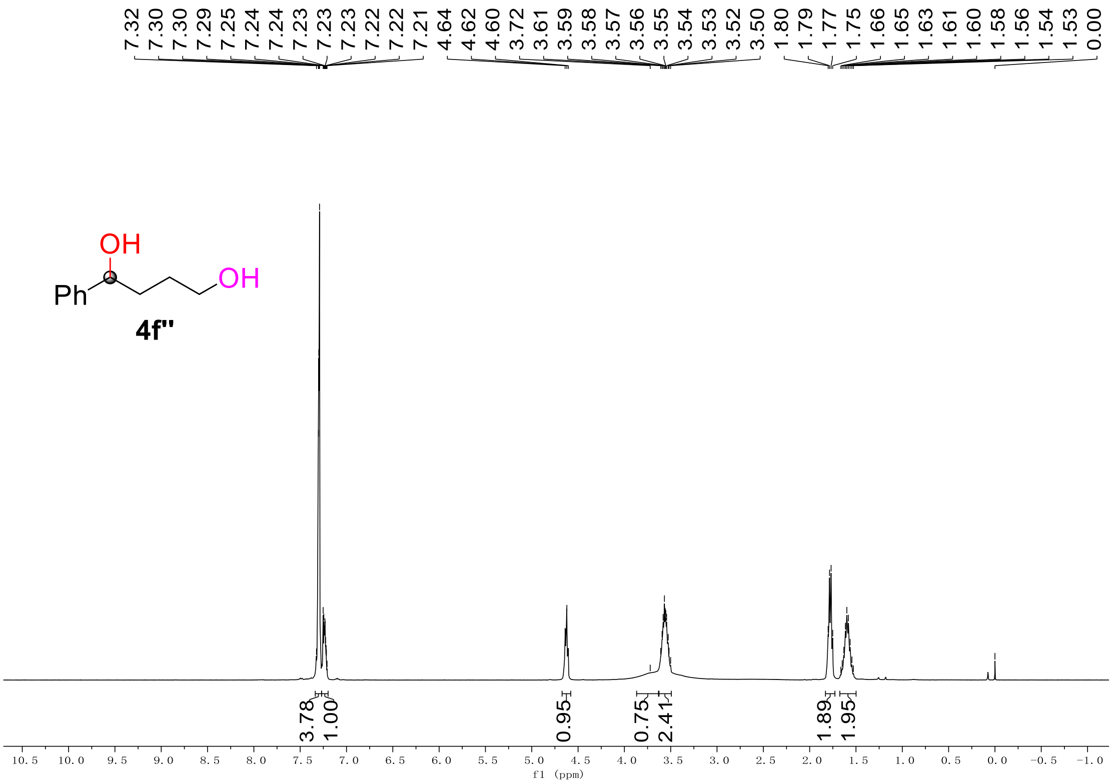
^{1}H NMR, 400 MHz, $CDCl_3$



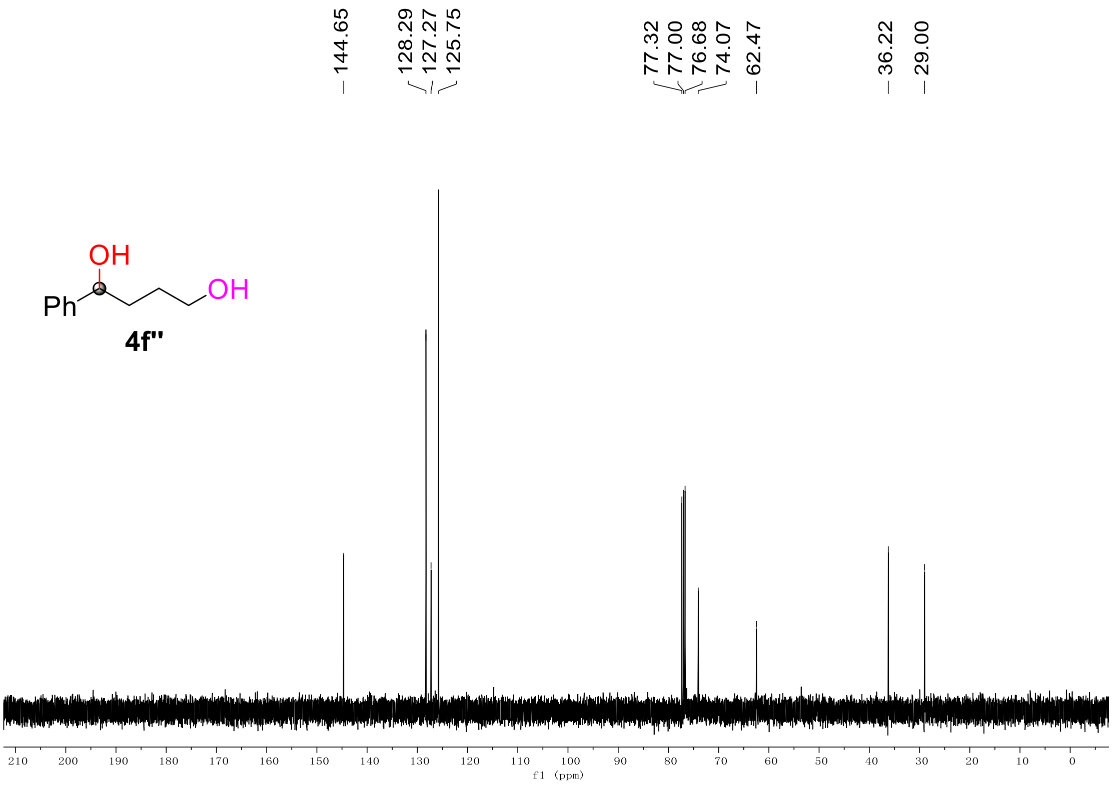
^{13}C NMR, 100 MHz, $CDCl_3$



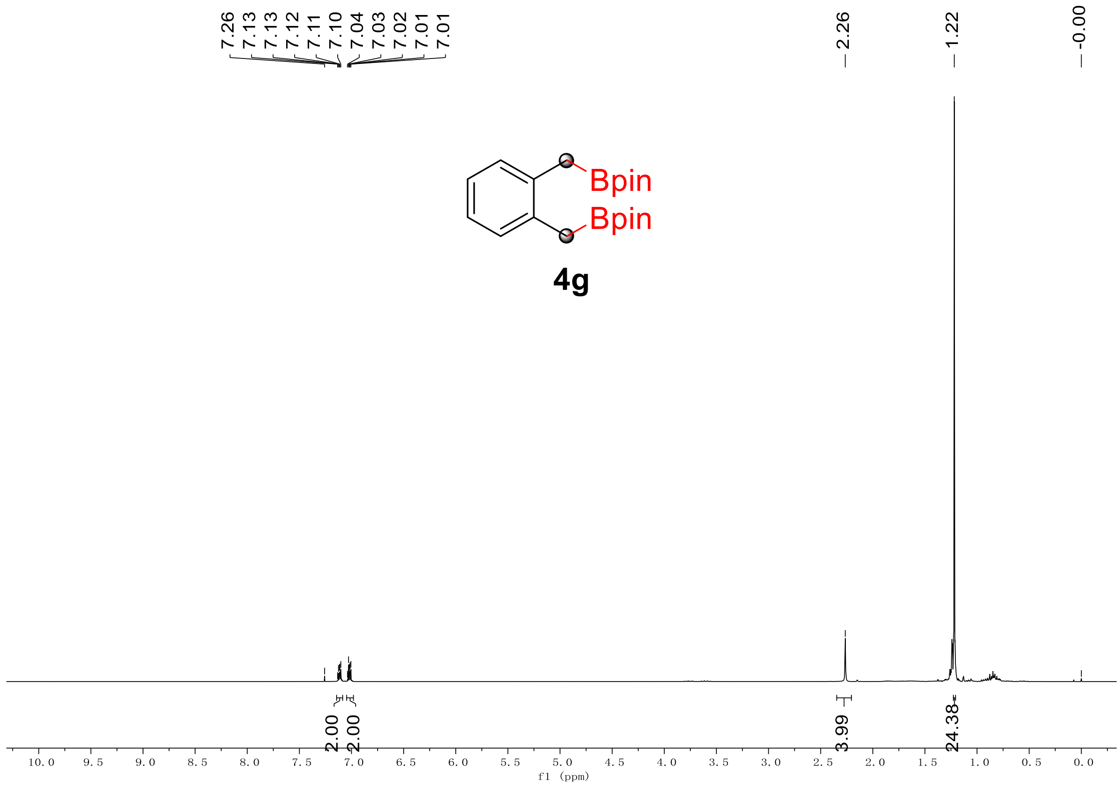
^{1}H NMR, 400 MHz, $CDCl_3$



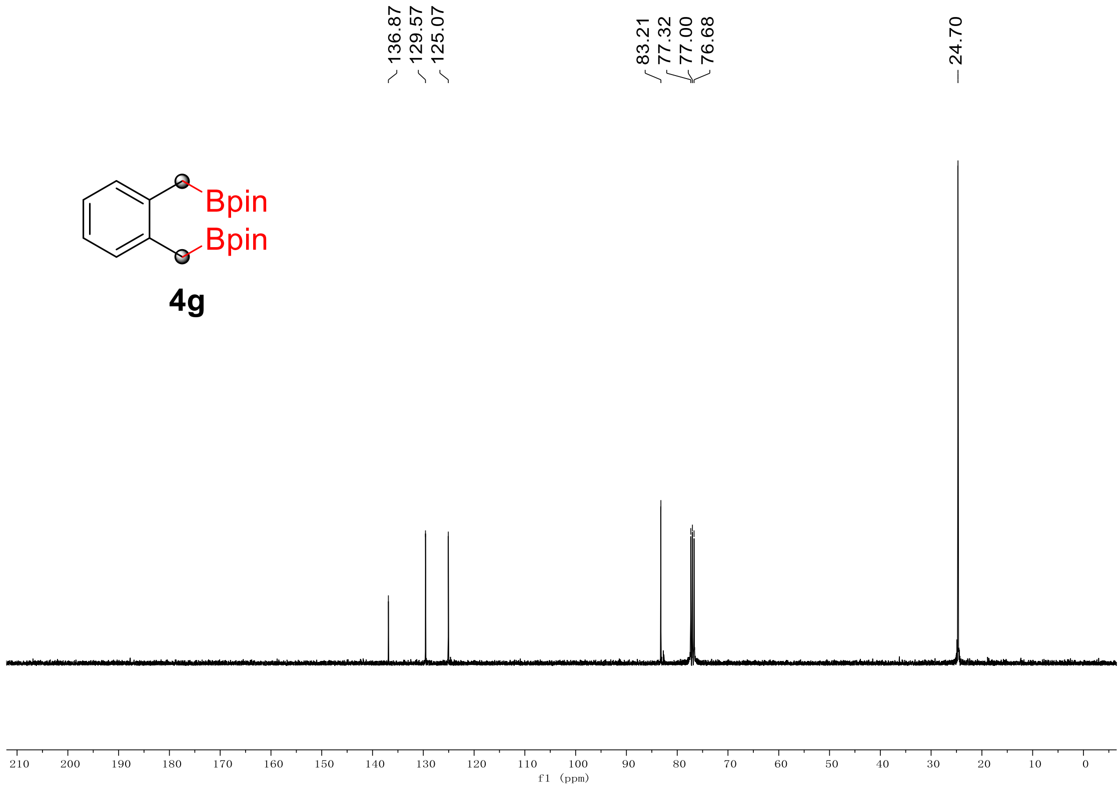
^{13}C NMR, 100 MHz, $CDCl_3$



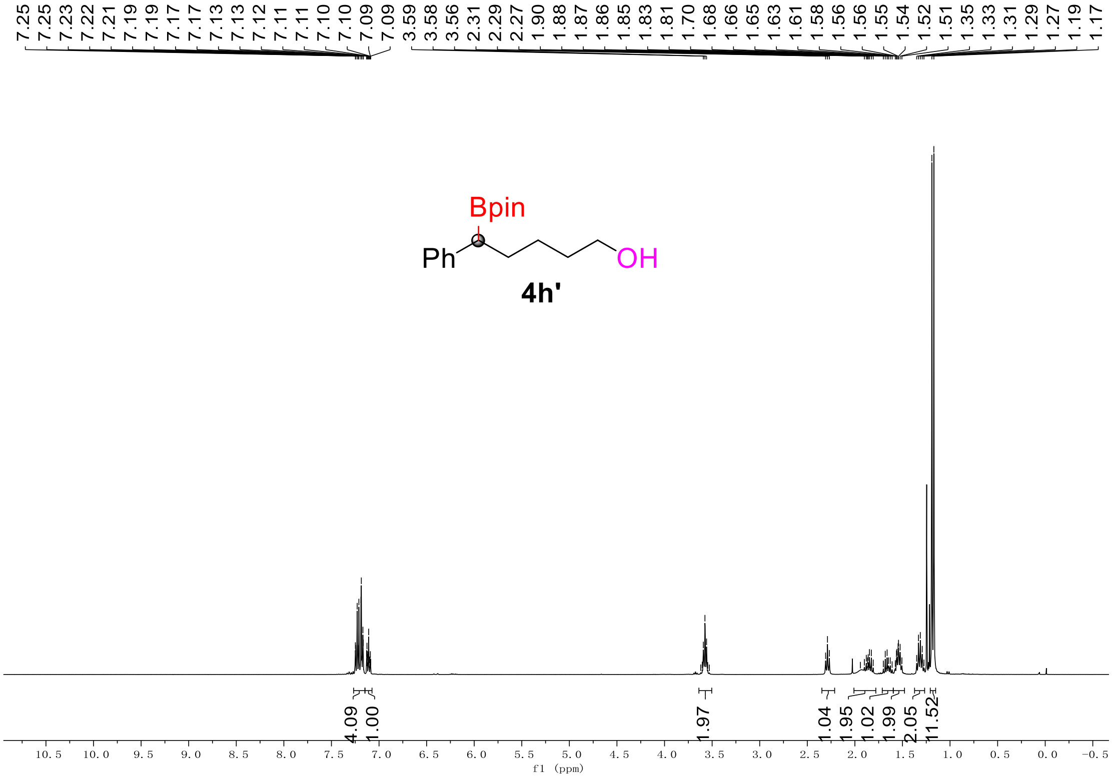
^{1}H NMR, 400 MHz, $CDCl_3$



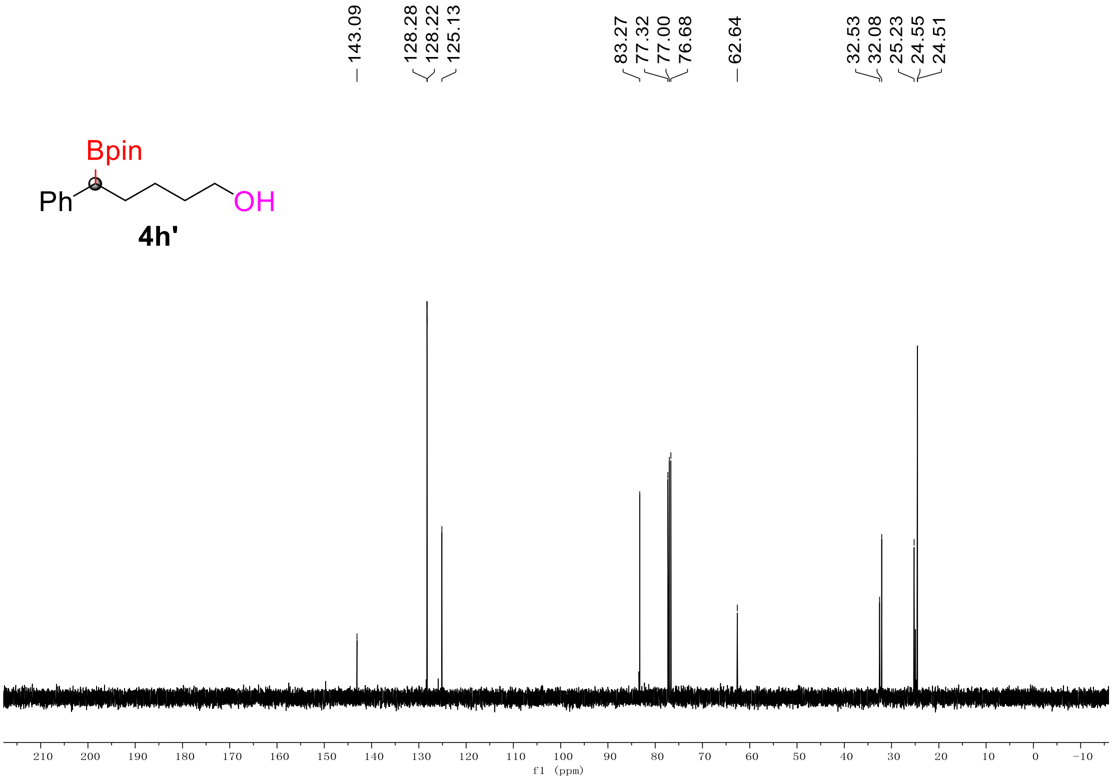
^{13}C NMR, 100 MHz, $CDCl_3$



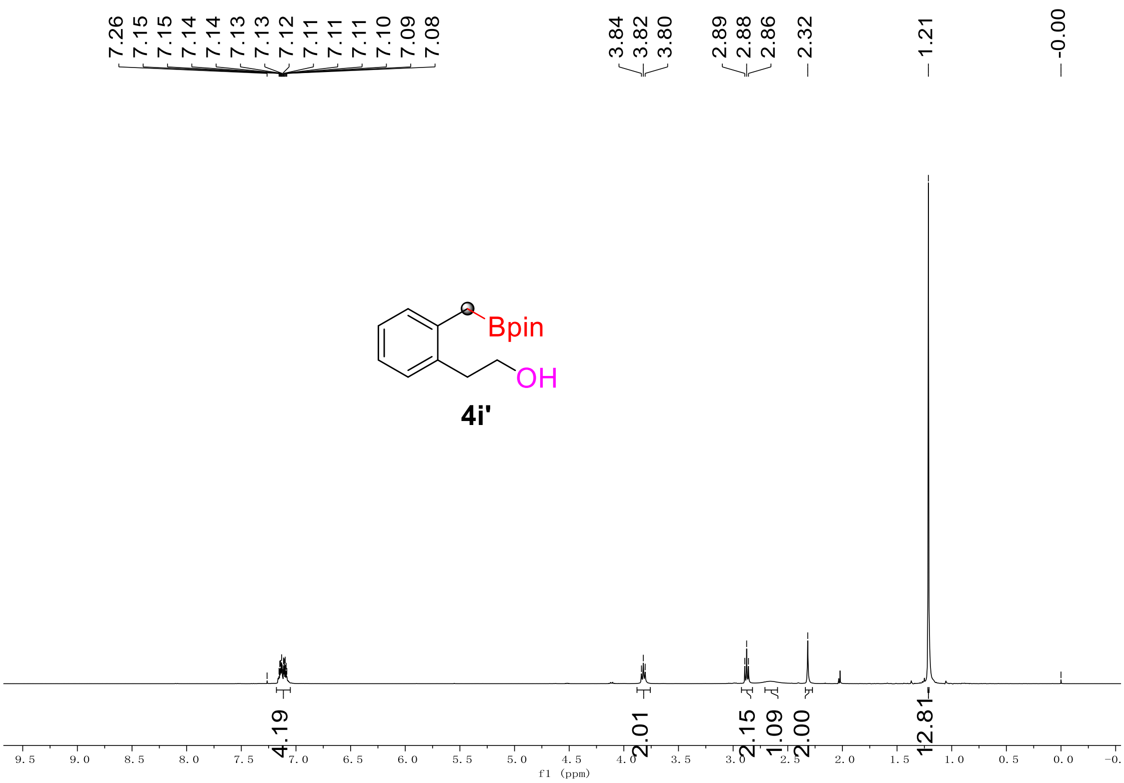
^{1}H NMR, 400 MHz, $CDCl_3$



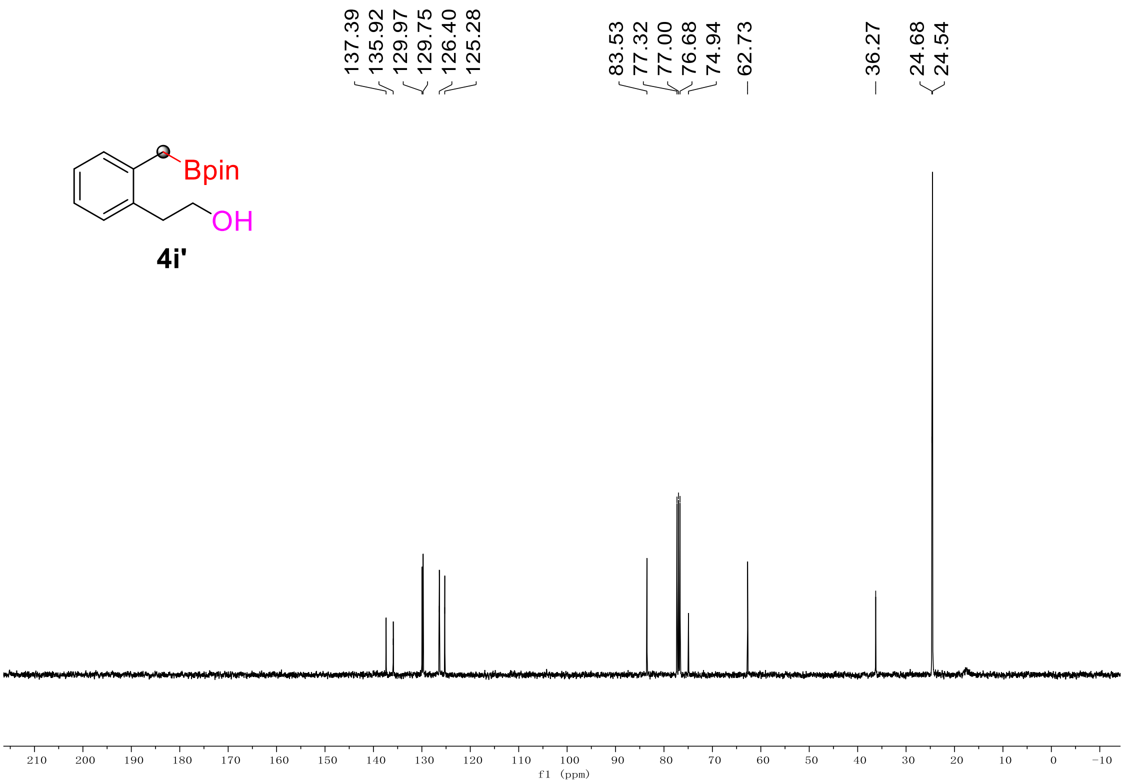
^{13}C NMR, 100 MHz, $CDCl_3$



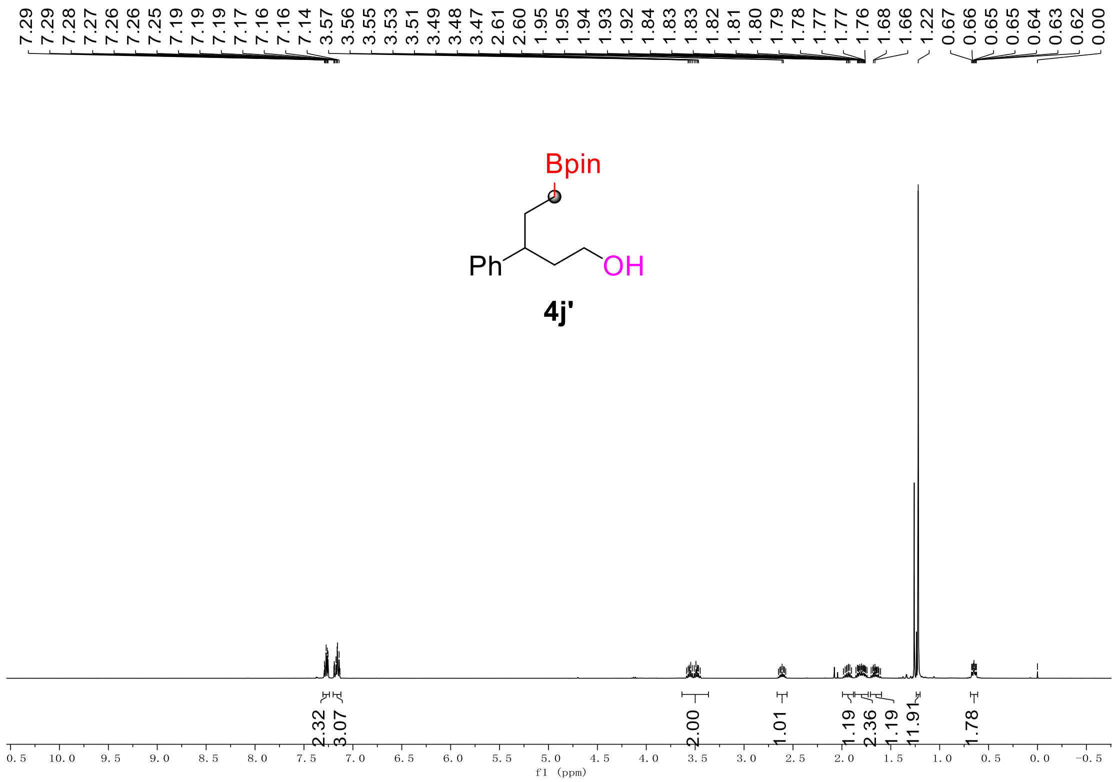
^{1}H NMR, 400 MHz, $CDCl_3$



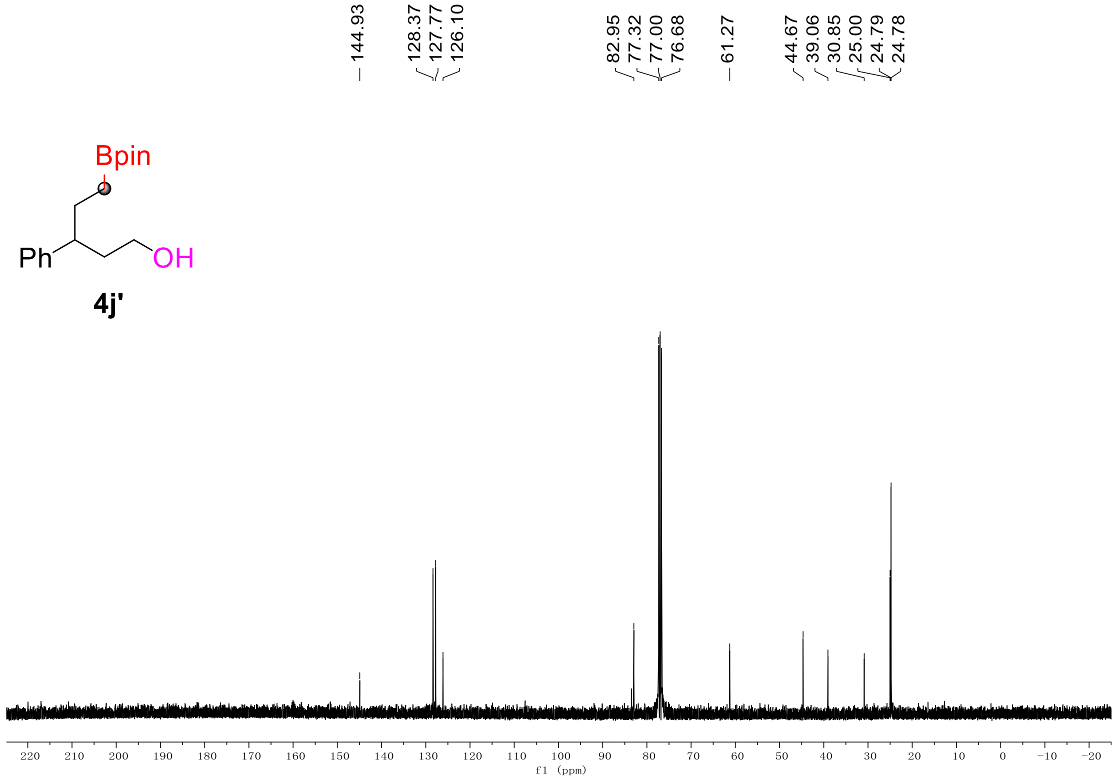
^{13}C NMR, 100 MHz, $CDCl_3$



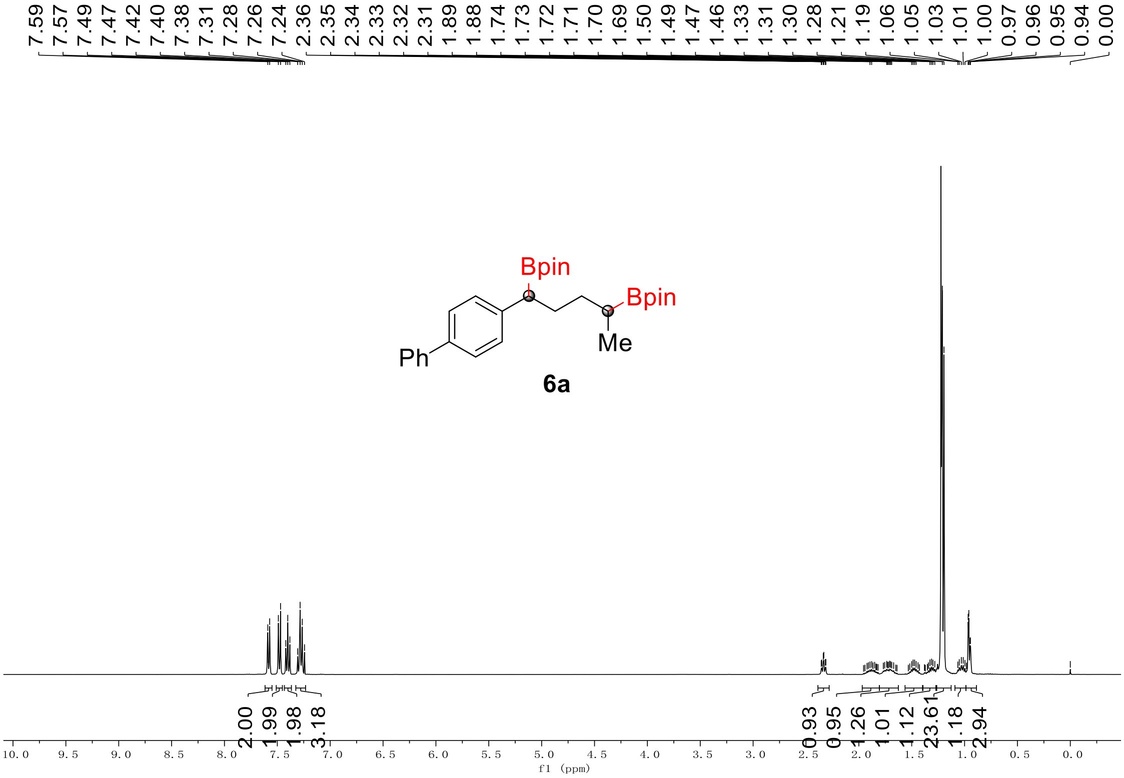
^{1}H NMR, 400 MHz, $CDCl_3$



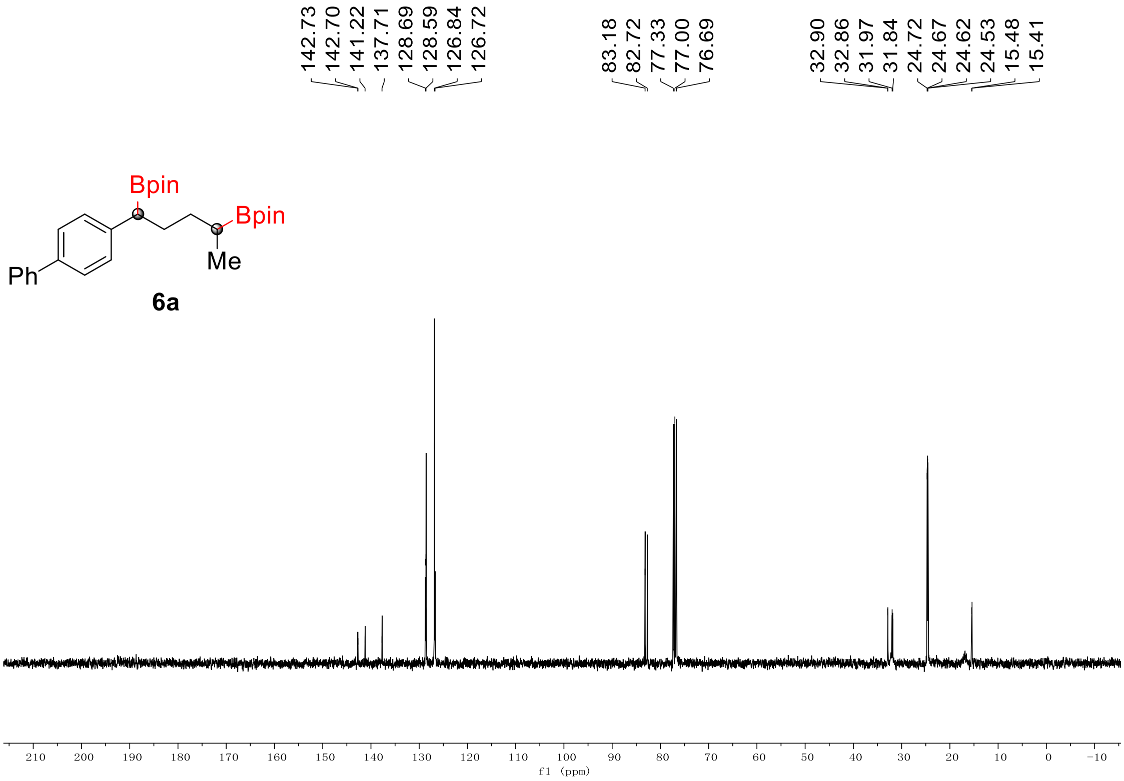
^{13}C NMR, 100 MHz, $CDCl_3$



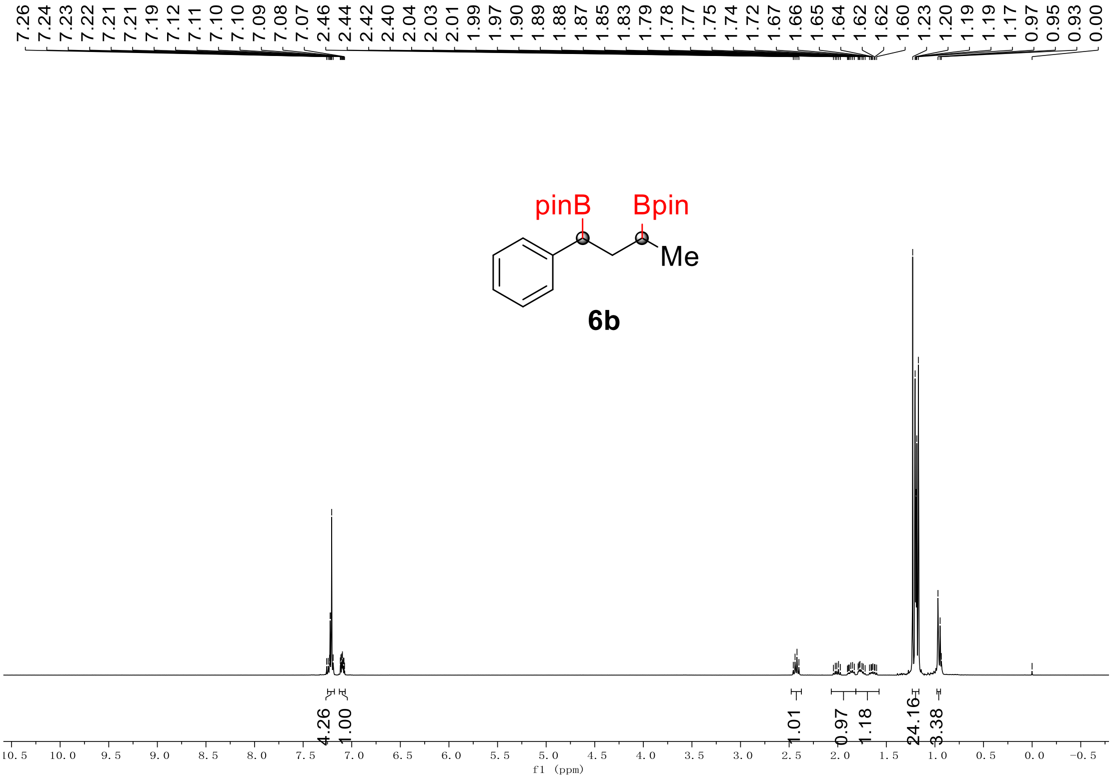
^{1}H NMR, 400 MHz, $CDCl_3$



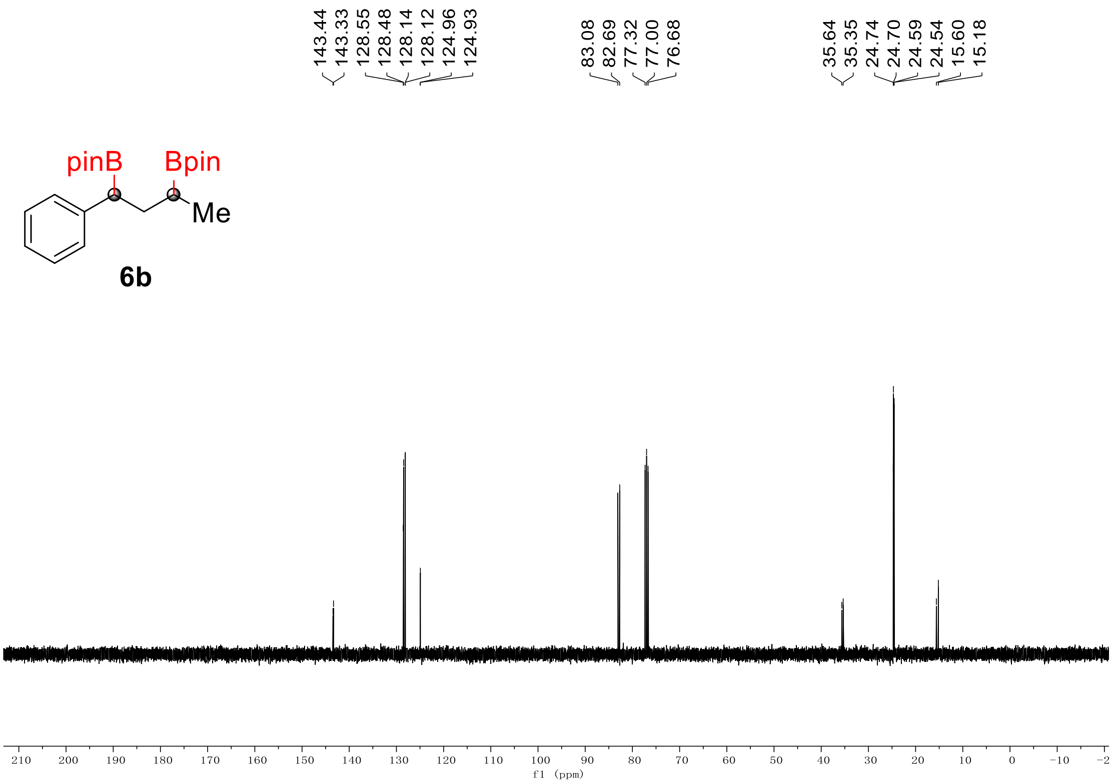
^{13}C NMR, 100 MHz, $CDCl_3$



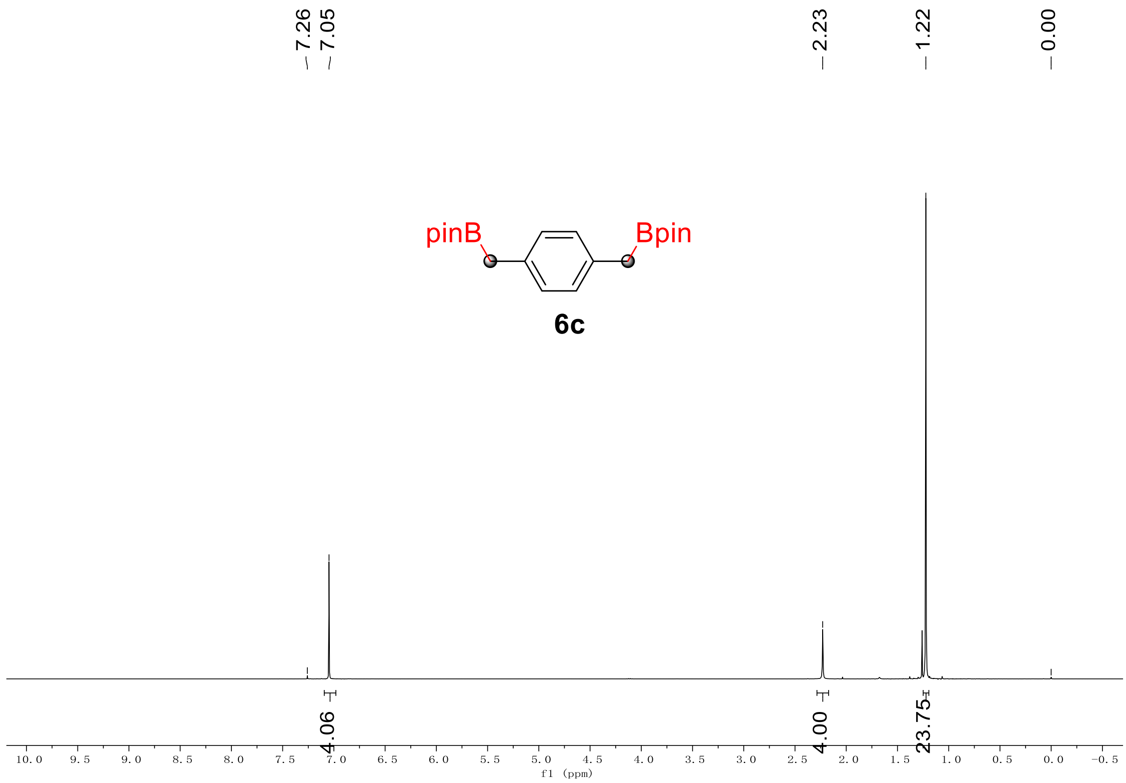
^1H NMR, 400 MHz, $CDCl_3$



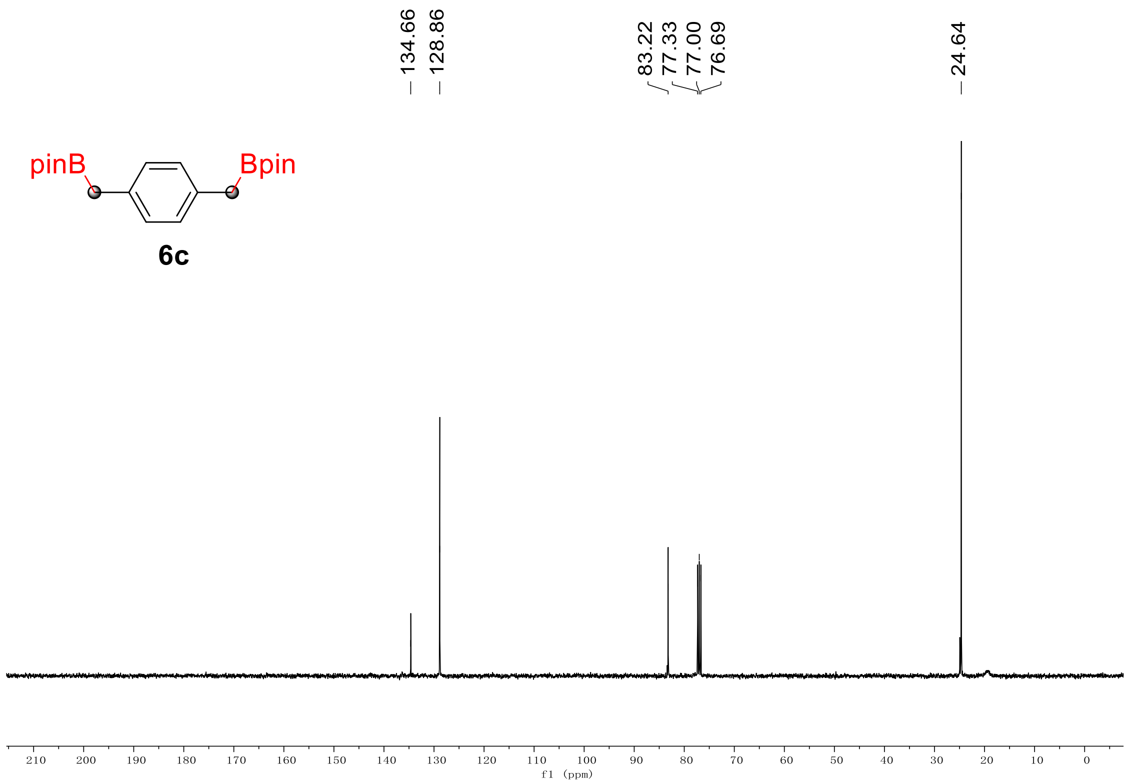
^{13}C NMR, 100 MHz, $CDCl_3$



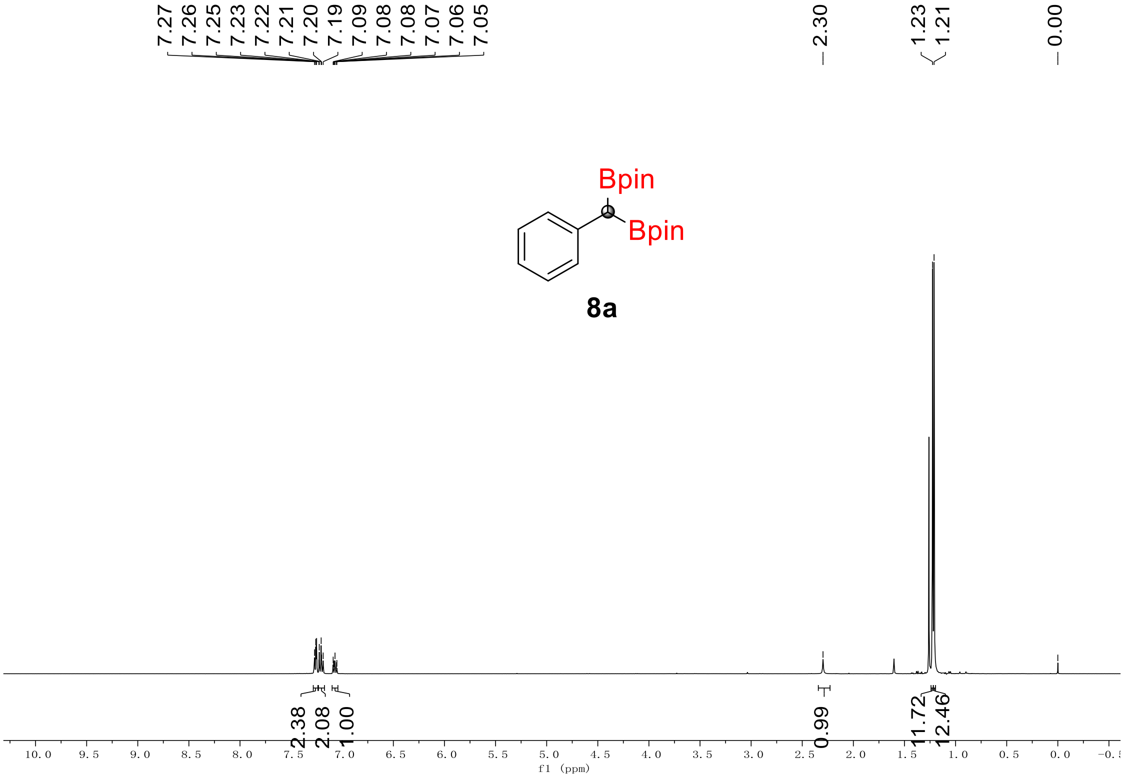
^{1}H NMR, 400 MHz, $CDCl_3$



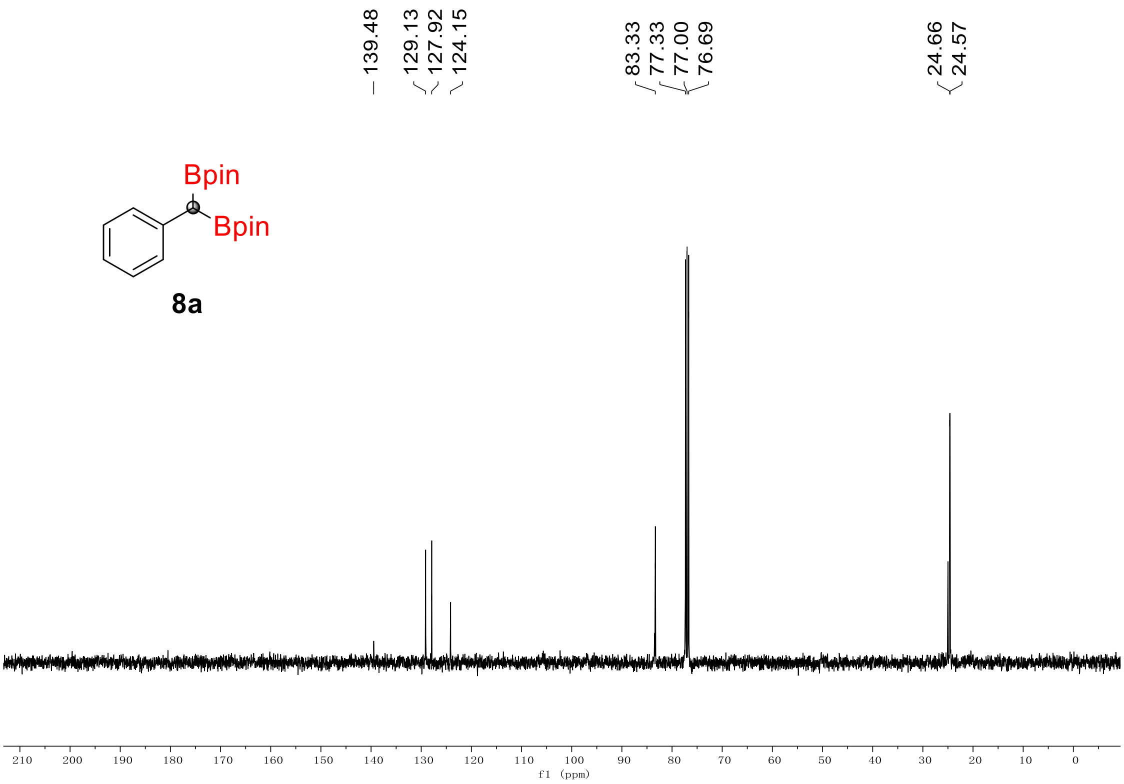
^{13}C NMR, 100 MHz, $CDCl_3$



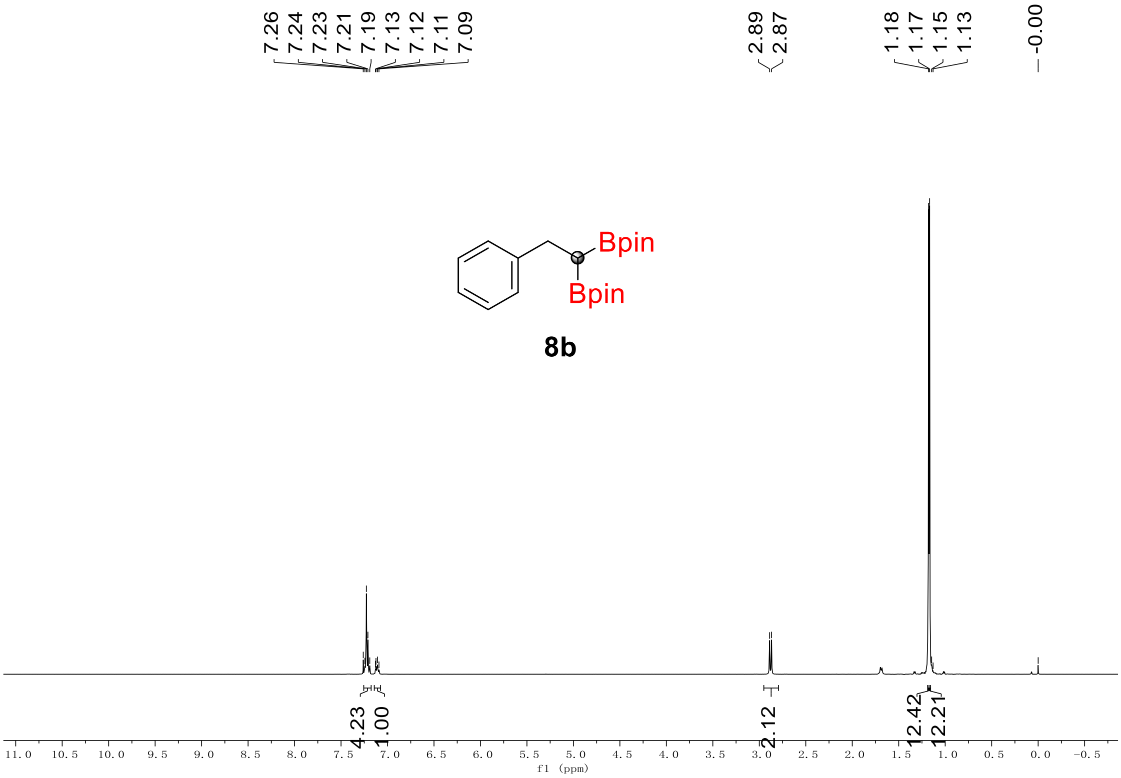
^{1}H NMR, 400 MHz, $CDCl_3$



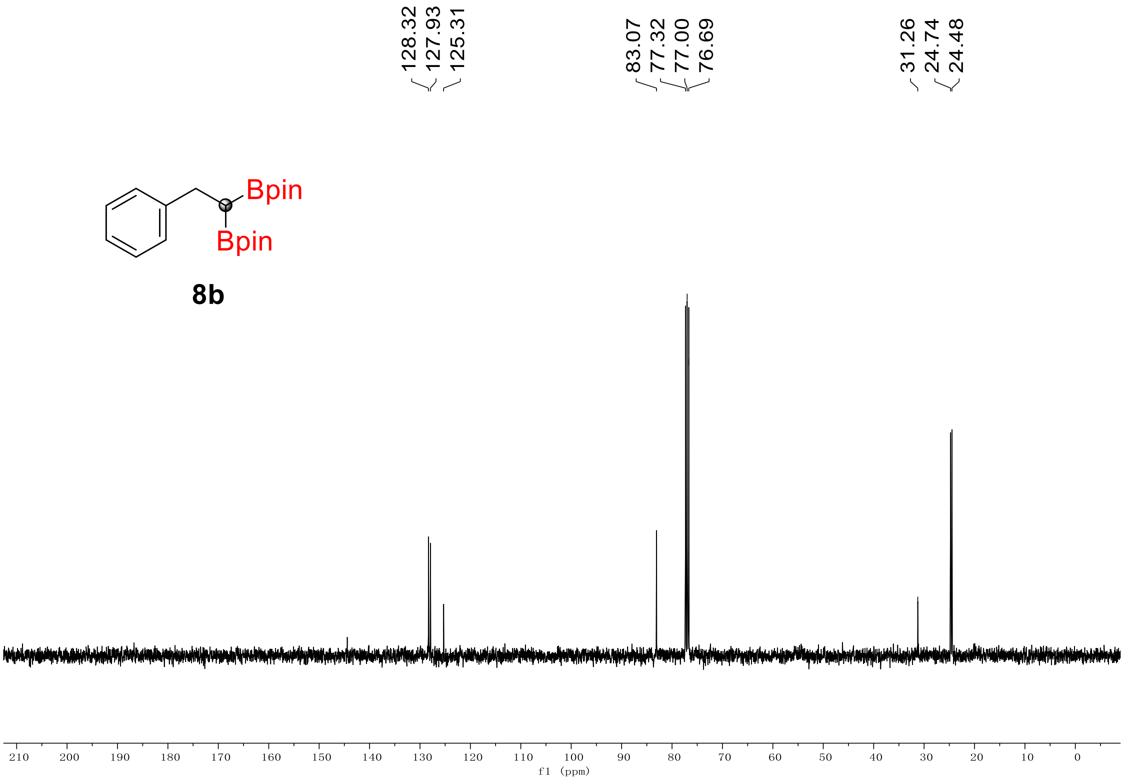
^{13}C NMR, 100 MHz, $CDCl_3$



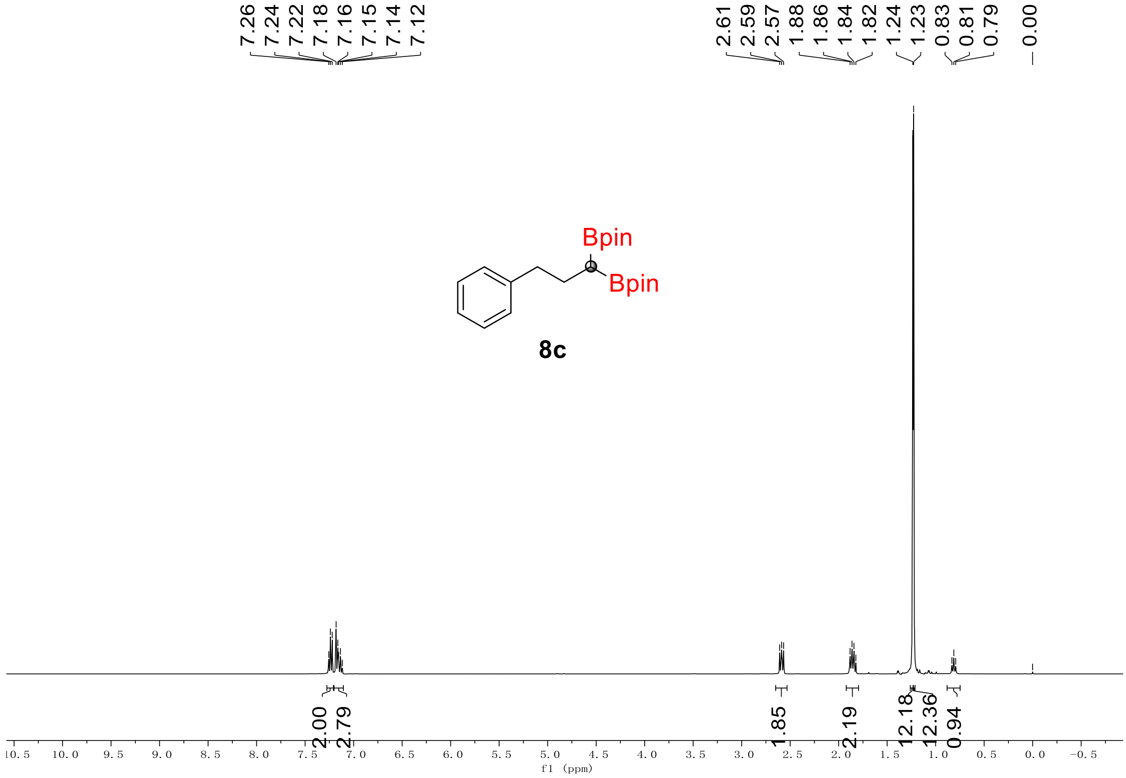
^{1}H NMR, 400 MHz, $CDCl_3$



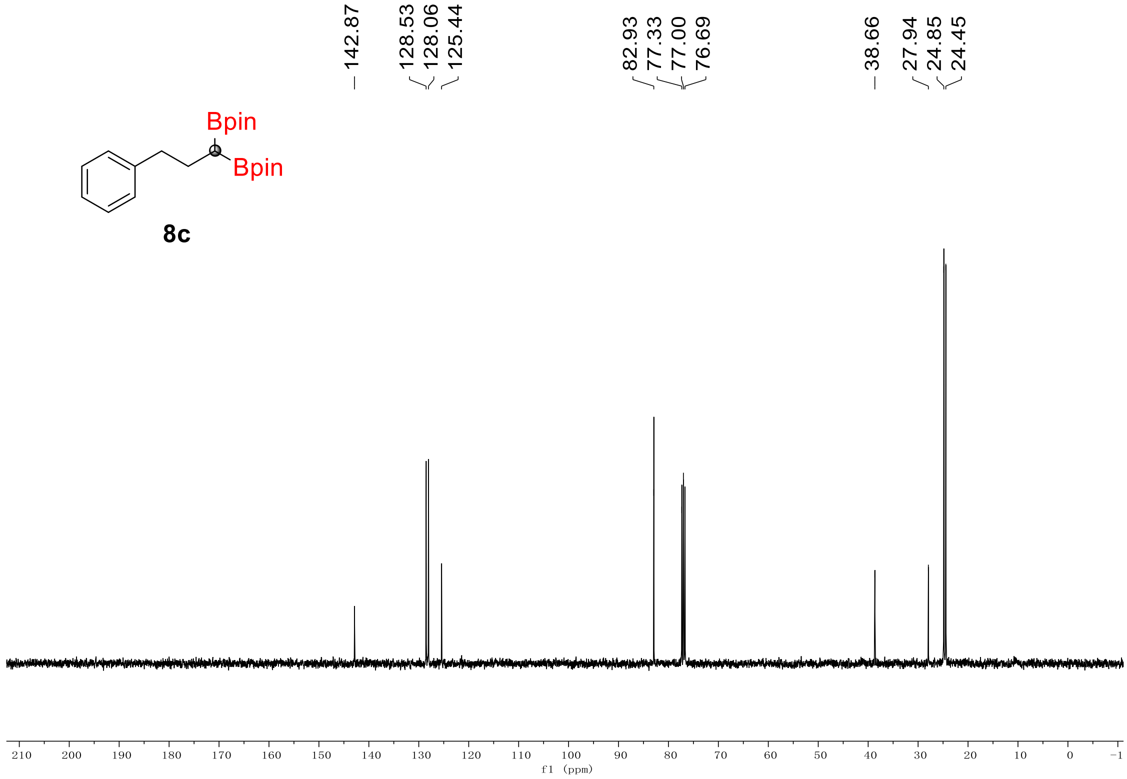
^{13}C NMR, 100 MHz, $CDCl_3$



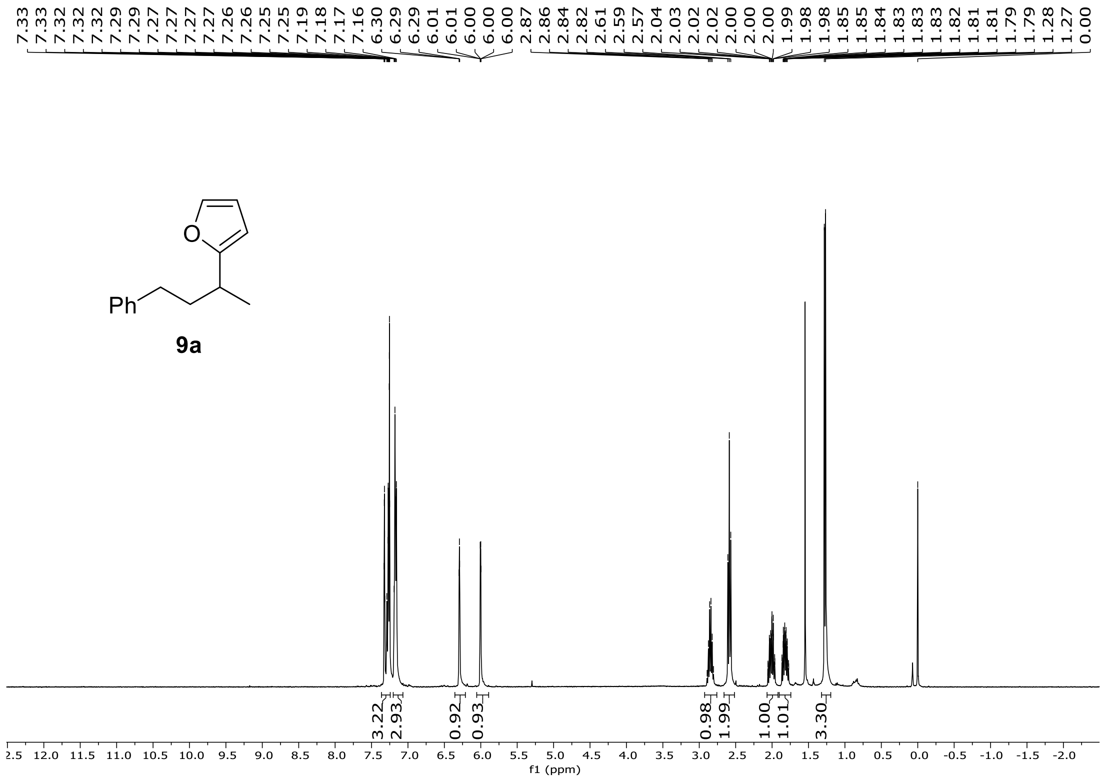
^{1}H NMR, 400 MHz, $CDCl_3$



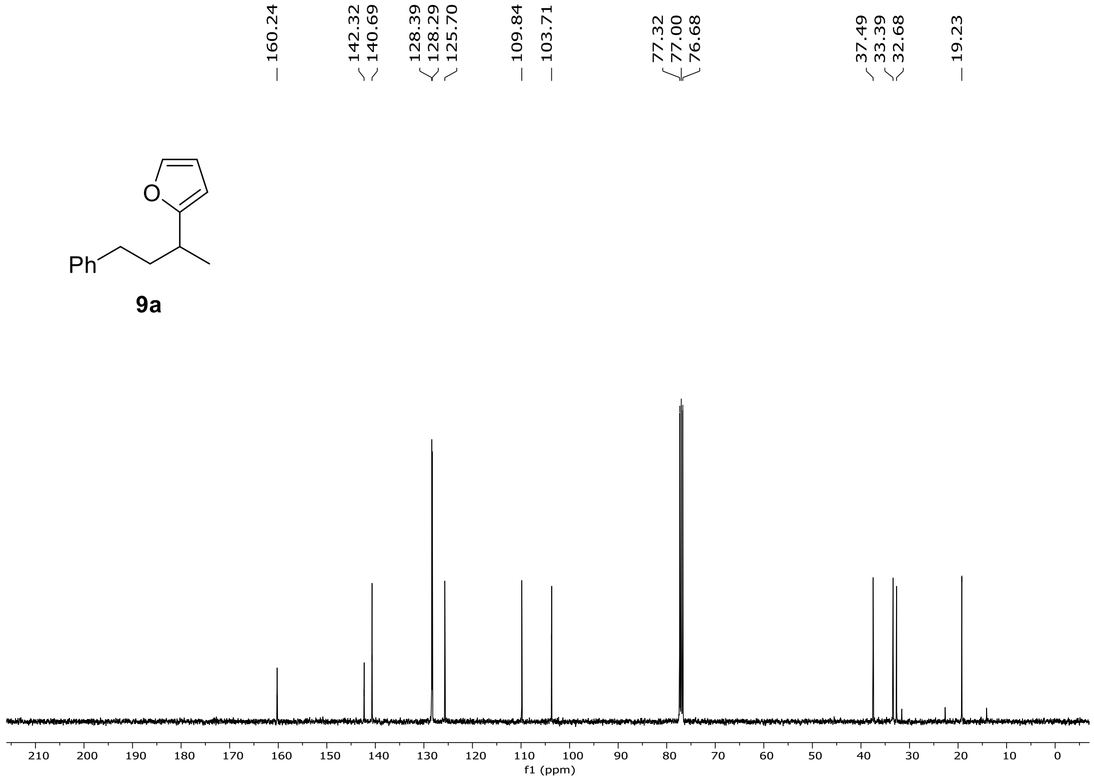
^{13}C NMR, 100 MHz, $CDCl_3$



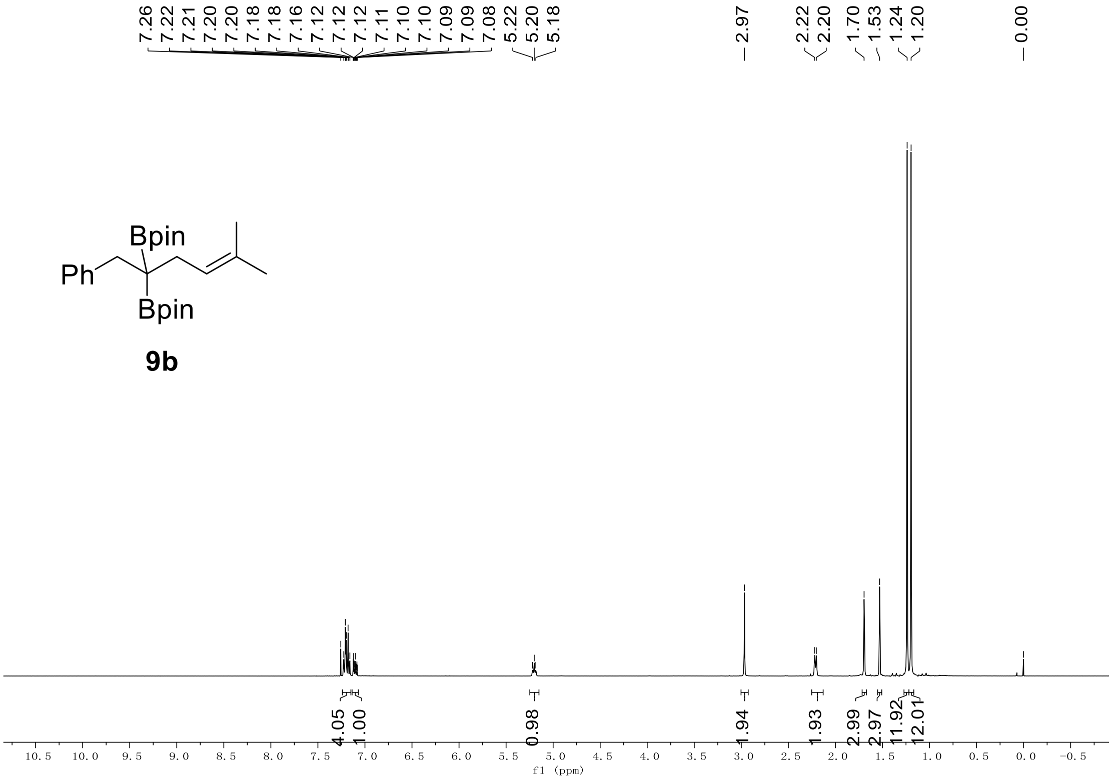
^{1}H NMR, 400 MHz, $CDCl_3$



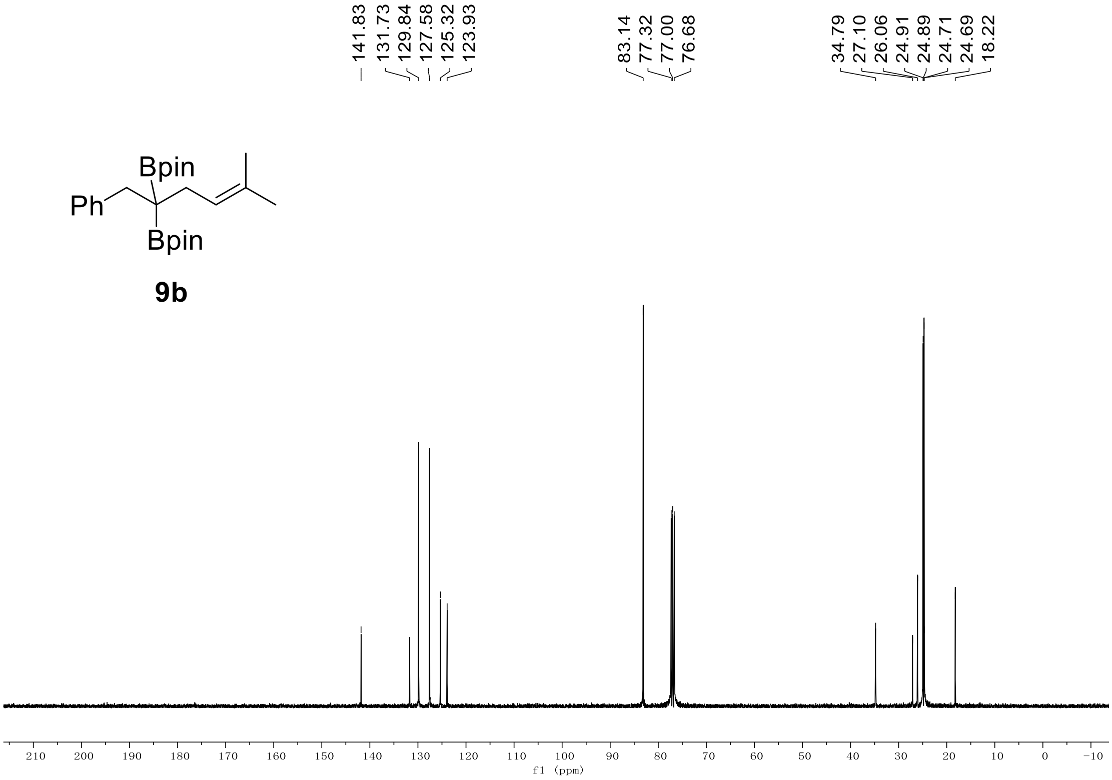
^{13}C NMR, 100 MHz, $CDCl_3$



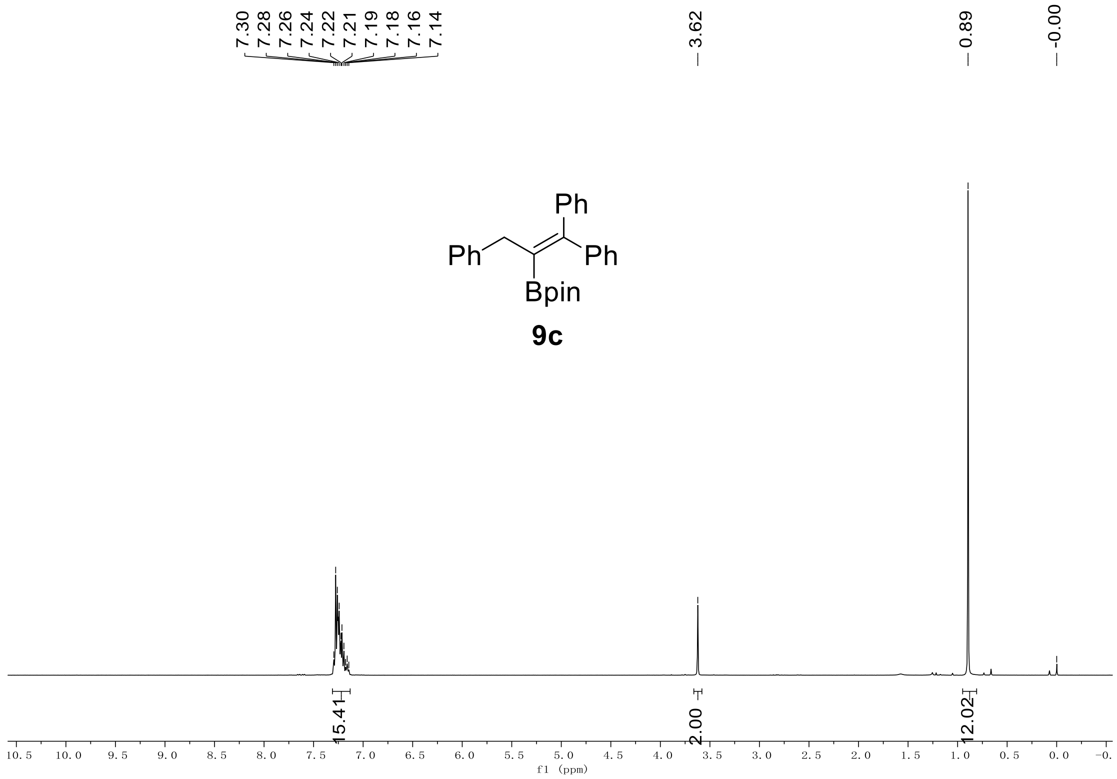
^{1}H NMR, 400 MHz, $CDCl_3$



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



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



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