Supporting Information

Nickel-Catalyzed Alkyl-Alkyl Cross-Coupling Reactions of Non-activated Secondary Alkyl Bromides with Aldehydes as Alkyl Carbanion Equivalents

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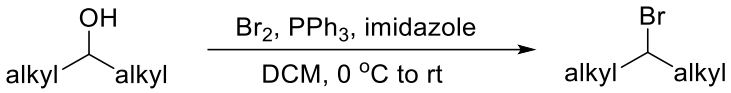
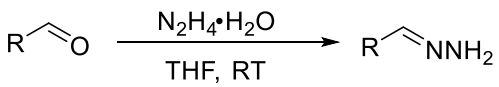
1. General Information

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under nitrogen. Unless otherwise noted, all reactions were carried out under a argon atmosphere. ^{1}H NMR spectra, ^{19}F NMR spectra, ^{13}C NMR spectra were recorded on a Bruker 300, 400 and 500 MHz spectrometer in $CDCl_3$. Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constant (Hz), and intergration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm). Tetrahydrofuran was distilled from sodium and benzophenone prior to use. Hydrazine hydrate was purchased from *Alfa Aesar*.

2. Preparation of substrates

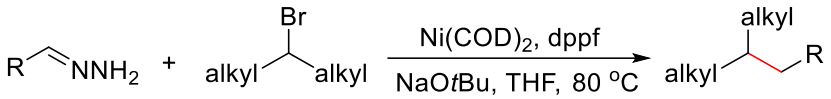


Under a nitrogen atmosphere, PPh_3 (1.25 equiv.), imidazole (1.25 equiv.), DCM (30 mL) were added to a 50 mL round-bottomed flask. Br_2 (1.16 equiv.) was added slowly at 0 °C and the mixture was stirring for 30 min. Then secondary alcohol (1 equiv.) in DCM (5 mL) was added dropwise at 0 °C and warming the mixture to ambient temperature. The mixture was concentrated under reduced pressure on a rotary evaporator to an approximate volume, and diluted with petroleum ether. The resulting solid was filtered, and the filtrate was concentrated and purified by column chromatography (petroleum ether) to give a colorless liquid. Spectroscopic data match those reported in the literature (**2a**[1], **2c**[2], **2d**[3], **2e**[4]). Other bromides were purchased.



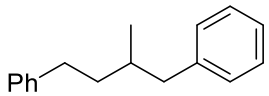
To a solution of aldehyde (20 mmol, 1.0 equiv.) in THF (20 mL) was added hydrazine hydrate (98% purity, 24 mmol, 1.2 equiv.) and the mixture stirred at room temperature for 0.5 h. After the aldehyde consumed completely, the mixture was then evaporated under reduced pressure at room temperature to provide the desired hydrazone and used directly without further purification.[5]

3. General procedure for the cross-coupling reaction of hydrazines and alkyl bromides.



$Ni(COD)_2$ (8.3 mg, 0.03 mmol), dppf (33 mg, 0.06 mmol), NaO^tBu (58 mg, 0.6 mmol) were added to a 10 mL sealing tube under a nitrogen atmosphere. Hydrazone (0.6 mmol, 2 equiv.), alkyl bromide (0.3 mmol) were added in THF (2 mL) and the mixture was stirring at 80 °C for 12 h. After alkyl bromide consumed completely, the resulting solid was filtered, and the filtrate was concentrated and purified by column chromatography (petroleum ether) to give a desired product.

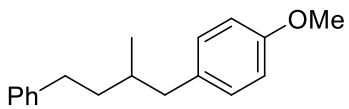
(2-methylbutane-1,4-diyl)dibenzene (**3a**):



3a

Prepared according to general procedure from benzylidenehydrazine **1a** (63 mg, 0.6 mmol) and (3-bromobutyl)benzene **2a** (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product **3a** as colorless oil (39 mg, 58%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.30 (m, 4H), 7.28-7.19 (m, 6H), 2.86-2.60 (m, 3H), 2.49 (dd, *J* = 12.0, 8.0 Hz, 1H), 1.92-1.71 (m, 2H), 1.64-1.48 (m, 1H), 0.99 (d, *J* = 12.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.85, 141.34, 129.24, 128.41, 128.34, 128.17, 125.74, 125.67, 43.59, 38.52, 34.67, 33.54, 19.44. HRMS (EI) calcd. for $[C_{17}H_{20}]^+$: 224.1565, found: 224.1563.

1-methoxy-4-(2-methyl-4-phenylbutyl)benzene (**3b**):

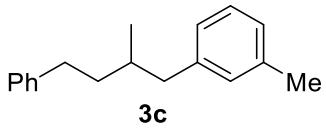


3b

Prepared according to general procedure from (4-methoxybenzylidene)hydrazine **1b** (90 mg, 0.6 mmol) and (3-bromobutyl)benzene **2a** (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product **3b** as colorless oil (46 mg, 61%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33-7.28 (m, 2H), 7.22-7.18 (m, 3H), 7.11-7.06 (m, 2H), 6.89-6.80 (m, 2H), 3.82 (s, 3H), 2.79-2.57 (m, 3H), 2.40 (dd, J = 15.0, 9.0 Hz, 1H), 1.84-1.64 (m, 2H), 1.56-1.45 (m, 1H), 0.95 (d, J = 6.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.73, 142.91, 133.39, 130.08, 128.40, 128.33, 125.64,

113.58, 55.26, 42.65, 38.44, 34.79, 33.55, 19.39. HRMS (EI) calcd. for $[C_{18}C_{22}O]^+$: 254.1671, found: 254.1672.

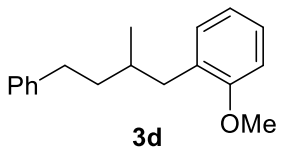
1-methyl-3-(2-methyl-4-phenylbutyl)benzene (**3c**):



3c

Prepared according to general procedure from (3-methylbenzylidene)hydrazine **1c** (80 mg, 0.6 mmol) and (3-bromobutyl)benzene **2a** (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product **3c** as colorless oil (37, 53%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.7 Hz, 2H), 7.29-7.20 (m, 4H), 7.07 (d, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 10.6 Hz, 2H), 2.84-2.62 (m, 3H), 2.45 (dd, *J* = 15.0, 10.0 Hz, 1H), 2.40 (s, 3H), 1.89-1.74 (m, 2H), 1.59-1.52 (m, 1H), 1.00 (d, *J* = 10.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.91, 141.29, 137.65, 130.05, 128.43, 128.34, 128.05, 126.48, 126.28, 125.66, 43.52, 38.57, 34.64, 33.55, 21.49, 19.49. HRMS (EI) calcd. for $[C_{18}C_{22}]^+$: 238.1722, found: 238.1721.

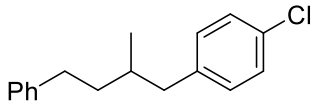
1-methoxy-2-(2-methyl-4-phenylbutyl)benzene (**3d**):



3d

Prepared according to general procedure from (2-methoxybenzylidene)hydrazine **1d** (90 mg, 0.6 mmol) and (3-bromobutyl)benzene **2d** (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product **3d** as colorless oil (41 mg, 54%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.29 (m, 2H), 7.26-7.18 (m, 4H), 7.14 (dd, *J* = 6.0, 1.5 Hz, 1H), 6.91 (dd, *J* = 12.0, 6.0 Hz, 2H), 3.83 (s, 3H), 2.85-2.59 (m, 3H), 2.47 (dd, *J* = 15.0, 8.1 Hz, 1H), 1.99-1.67 (m, 2H), 1.63-1.49 (m, 1H), 0.97 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.76, 143.19, 130.95, 129.91, 128.46, 128.27, 126.98, 125.56, 120.17, 110.32, 55.24, 38.85, 37.71, 33.53, 33.09, 19.70. HRMS (EI) calcd. for $[C_{18}C_{22}O]^+$: 254.1671, found: 254.1672.

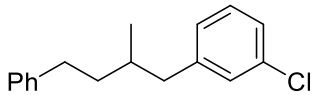
1-chloro-4-(2-methyl-4-phenylbutyl)benzene (**3e**):



3e

Prepared according to general procedure from (4-chlorobenzylidene)hydrazine **1e** (92 mg, 0.6 mmol) and (3-bromobutyl)benzene **2a** (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product **3e** as colorless oil (45mg, 59%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.16 (m, 7H), 7.09 (d, J = 9.0 Hz, 2H), 2.81-2.55 (m, 3H), 2.42 (dd, J = 15.0, 9.0 Hz, 1H), 1.86-1.63 (m, 2H), 1.57-1.43 (m, 1H), 0.95 (d, J = 6.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.64, 139.72, 131.44, 130.50, 129.87, 128.35, 128.25, 125.71, 42.85, 38.35, 34.54, 33.46, 19.29. HRMS (EI) calcd. for $[C_{17}H_{19}Cl]^+$: 258.1175, found: 258.1176.

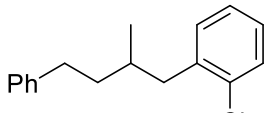
1-chloro-3-(2-methyl-4-phenylbutyl)benzene (**3f**):



3f

Prepared according to general procedure from (3-chlorobenzylidene)hydrazine **1f** (92 mg, 0.6 mmol) and (3-bromobutyl)benzene **2a** (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product **3f** as colorless oil (52 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.32 (m, 2H), 7.29-7.18 (m, 6H), 7.11-7.04 (m, 1H), 2.85-2.59 (m, 3H), 2.45 (dd, J = 15.0, 9.0 Hz, 1H), 1.93-1.68 (m, 2H), 1.60-1.50 (m, 1H), 0.99 (d, J = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.42, 142.63, 133.98, 129.42, 129.26, 128.40, 127.43, 125.99, 125.77, 43.22, 38.42, 34.49, 33.48, 19.35. HRMS (EI) calcd. for $[C_{17}H_{19}Cl]^+$: 258.1175, found: 258.1176.

1-chloro-2-(2-methyl-4-phenylbutyl)benzene (**3g**):

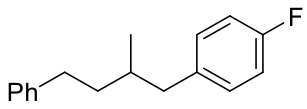


3g

Prepared according to general procedure from (2-chlorobenzylidene)hydrazine **1g** (92 mg, 0.6 mmol) and (3-bromobutyl)benzene **2a** (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product **3g** as colorless oil (41 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-

7.24 (m, 1H), 7.22-7.16 (m, 2H), 7.12-7.01 (m, 6H), 2.76 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.69-2.61 (m, 1H), 2.57-2.51 (m, 1H), 2.45 (dd, *J* = 16.0, 8.0 Hz, 1H), 1.87-1.79 (m, 1H), 1.66-1.61 (m, 1H), 1.52-1.41 (m, 1H), 0.86 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.80, 139.03, 134.32, 131.43, 129.51, 128.36, 128.31, 127.23, 126.42, 125.64, 40.99, 38.70, 33.48, 33.27, 19.38. HRMS (EI) calcd. for $[C_{17}H_{19}Cl]^+$: 258.1175, found: 258.1176.

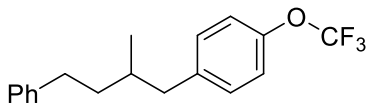
1-fluoro-4-(2-methyl-4-phenylbutyl)benzene (**3h**):



3h

Prepared according to general procedure from (4-fluorobenzylidene)hydrazine **1h** (83 mg, 0.6 mmol) and (3-bromobutyl)benzene **2a** (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product **3h** as colorless oil (45 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.25 (m, 2H), 7.21-7.12 (m, 3H), 7.10-7.02 (m, 2H), 6.99-6.90 (m, 2H), 2.76-2.51 (m, 3H), 2.39 (dd, *J* = 12.0, 8.0 Hz, 1H), 1.80-1.61 (m, 2H), 1.51-1.40 (m, 1H), 0.91 (d, *J* = 4.0 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.04. ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.45, 160.04, 142.69, 136.84 (d, *J* = 3.2 Hz), 130.41 (d, *J* = 7.7 Hz), 128.32 (d, *J* = 1.8 Hz), 125.67, 114.84 (d, *J* = 21.1 Hz), 42.67, 38.32, 34.65, 33.45, 19.27. HRMS (EI) calcd. for $[C_{17}H_{19}F]^+$: 242.1471, found: 242.1470.

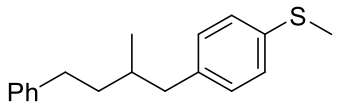
1-(2-methyl-4-phenylbutyl)-4-(trifluoromethoxy)benzene (**3i**):



3i

Prepared according to general procedure from (4-(trifluoromethoxy)benzylidene)hydrazine **1i** (122 mg, 0.6 mmol) and (3-bromobutyl)benzene **2a** (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product **3i** as colorless oil (56 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.22 (m, 2H), 7.21-7.07 (m, 7H), 2.78-2.64 (m, 2H), 2.62-2.55 (m, 1H), 2.41 (dd, *J* = 12.0, 8.0 Hz, 1H), 1.81-1.61 (m, 2H), 1.52-1.42 (m, 1H), 0.91 (d, *J* = 8.0 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.89. ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.39, 142.59, 140.02, 130.33, 128.35, 125.72, 121.84, 120.70, 119.29, 42.81, 38.33, 34.52, 33.43, 19.28. HRMS (EI) calcd. for $[C_{18}H_{19}F_3O]^+$: 308.1388, found: 308.1384.

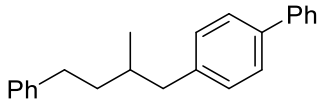
methyl(4-(2-methyl-4-phenylbutyl)phenyl)sulfane (**3j**):



3j

Prepared according to general procedure from (4-(methylthio)benzylidene)hydrazine **1j** (100 mg, 0.6 mmol) and (3-bromobutyl)benzene **2a** (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product **3j** as colorless oil (33 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.22 (m, 2H), 7.19-7.11 (m, 5H), 7.04 (d, *J* = 8.0 Hz, 2H), 2.75-2.52 (m, 3H), 2.45 (s, 3H), 2.37 (dd, *J* = 12.0, 8.0 Hz, 1H), 1.81-1.61 (m, 2H), 1.50-1.39 (m, 1H), 0.90 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.79, 138.46, 135.16, 129.78, 128.40, 128.36, 126.99, 125.70, 43.02, 38.44, 34.64, 33.53, 19.40, 16.37 (d, *J* = 3.8 Hz). HRMS (EI) calcd. for $[C_{18}H_{22}S]^+$: 270.1442, found: 270.1440.

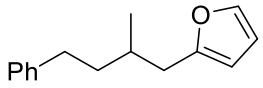
4-(2-methyl-4-phenylbutyl)-1,1'-biphenyl (**3k**):



3k

Prepared according to general procedure from ([1,1'-biphenyl]-4-ylmethylene)hydrazine **1k** (118 mg, 0.6 mmol) and (3-bromobutyl)benzene **2a** (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product **3k** as a white solid (55 mg, 62%), mp: 39-41 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72-7.66 (m, 2H), 7.60 (d, *J* = 5.0 Hz, 2H), 7.51 (t, *J* = 10.0 Hz, 2H), 7.41 (t, *J* = 5.0 Hz, 1H), 7.39-7.34 (m, 2H), 7.31-7.24 (m, 5H), 2.88-2.78 (m, 2H), 2.74-2.69 (m, 1H), 2.55 (dd, *J* = 10.0, 5.0 Hz, 1H), 1.97-1.87 (m, 1H), 1.87-1.77 (m, 1H), 1.66-1.57 (m, 1H), 1.05 (d, *J* = 5.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.86, 141.21, 140.51, 138.69, 129.69, 128.79, 128.45, 128.39, 127.06, 126.93, 125.73, 43.23, 38.56, 34.69, 33.58, 19.52. HRMS (EI) calcd. for $[C_{23}H_{24}]^+$: 300.1878, found: 300.1880.

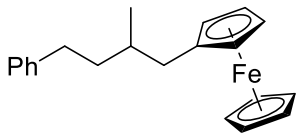
2-(2-methyl-4-phenylbutyl)furan (**3l**):



3l

Prepared according to general procedure from (furan-2-ylmethylene)hydrazine **1l** (66 mg, 0.6 mmol) and (3-bromobutyl)benzene **2a** (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product **3l** as colorless oil (27 mg, 42%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.31 (m, 1H), 7.31-7.27 (m, 2H), 7.22-7.17 (m, 3H), 6.30 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.00 (d, *J* = 3.2 Hz, 1H), 2.74-2.59 (m, 3H), 2.53 (dd, *J* = 15.0, 9.0 Hz, 1H), 1.97-1.84 (m, 1H), 1.78-1.63 (m, 1H), 1.55-1.45 (m, 1H), 0.99 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.20, 142.73, 140.80, 128.35, 128.29, 125.63, 110.04, 105.91, 38.37, 35.30, 33.42, 32.35, 19.58. HRMS (EI) calcd. for $[C_{15}H_{18}O]^+$: 214.1358, found: 214.1360.

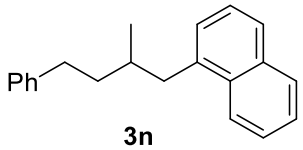
1-(2-methyl-4-phenylbutyl)-Ferrocene (**3m**):



3m

Prepared according to general procedure from **1m** (137 mg, 0.6 mmol) and (3-bromobutyl)benzene **2a** (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product **3m** as yellow oil (52 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.23 (m, 2H), 7.17-7.14 (m, 3H), 4.07 (s, 5H), 4.03 (s, 4H), 2.68-2.61 (m, 1H), 2.58-2.50 (m, 1H), 2.42 (dd, *J* = 12.0, 4.0 Hz, 1H), 2.23 (dd, *J* = 16.0, 8.0 Hz, 1H), 1.69-1.57 (m, 1H), 1.55-1.46 (m, 1H), 1.44-1.35 (m, 1H), 0.88 (d, *J* = 4.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.96, 128.39, 128.29, 125.60, 87.25, 69.42, 69.15, 68.57, 67.17, 38.45, 37.67, 35.01, 33.55, 19.63. HRMS (EI) calcd. for $[C_{21}H_{24}Fe]^+$: 332.1227, found: 332.1224.

1-(2-methyl-4-phenylbutyl)naphthalene (**3n**):

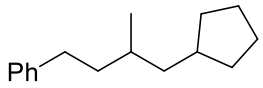


3n

Prepared according to general procedure from (naphthalen-1-ylmethylene)hydrazine **1n** (102 mg,

0.6 mmol) and (3-bromobutyl)benzene **2a** (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product **3n** as colorless oil (50 mg, 61%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04-7.97 (m, 1H), 7.90-7.87 (m, 1H), 7.76 (d, *J* = 6.0 Hz, 1H), 7.53-7.47 (m, 2H), 7.41 (dd, *J* = 15.0, 9.0 Hz, 1H), 7.35-7.28 (m, 3H), 7.24-7.20 (m, 3H), 3.23 (dd, *J* = 15.0, 6.0 Hz, 1H), 2.92-2.75 (m, 2H), 2.75-2.59 (m, 2H), 2.10-2.02 (m, 1H), 1.89-1.81 (m, 1H), 1.71-1.60 (m, 1H), 1.01 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.76, 137.43, 133.98, 132.22, 128.75, 128.37, 128.32, 127.23, 126.61, 125.66, 125.58, 125.33, 124.12, 40.90, 39.08, 33.88, 33.53, 19.88. HRMS (EI) calcd. for $[C_{21}H_{22}]^+$: 274.1722, found: 274.1723.

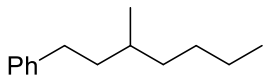
(4-cyclopentyl-3-methylbutyl)benzene (**3o**):



3o

Prepared according to general procedure from (cyclopentylmethylene)hydrazine **1o** (67 mg, 0.6 mmol) and (3-bromobutyl)benzene **2a** (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product **3o** as colorless oil (13 mg, 20%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.28 (m, 2H), 7.22-7.18 (m, 3H), 2.71-2.65 (m, 1H), 2.2-2.56 (m, 1H), 1.95-1.83 (m, 1H), 1.81-1.71 (m, 2H), 1.71-1.58 (m, 3H), 1.57-1.41 (m, 4H), 1.39-1.31 (m, 1H), 1.26-1.18 (m, 1H), 1.14-1.01 (m, 2H), 0.96 (d, *J* = 5.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.26, 128.36, 128.26, 125.52, 43.70, 39.33, 37.67, 33.46, 33.32, 32.66, 31.61, 25.15 (d, *J* = 1.0 Hz), 19.89. HRMS (EI) calcd. for $[C_{16}H_{24}]^+$: 216.1878, found: 216.1876.

(3-methylheptyl)benzene (**3p**):[6]

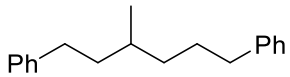


3p

Prepared according to general procedure from butylidenehydrazine **1p** (52 mg, 0.6 mmol) and (3-bromobutyl)benzene **2a** (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product **3p** as colorless oil (21mg, 38%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.28 (m, 2H), 7.23-7.19 (m, 3H), 2.72-2.67 (m, 1H), 2.63-2.57 (m, 1H), 1.72-1.62 (m, 1H), 1.53-1.44 (m, 2H), 1.41-1.28 (m, 5H), 1.24-1.15 (m, 1H), 0.97 (d, *J* = 5.0 Hz, 3H), 0.93 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.26, 128.37, 128.27, 125.53, 39.01, 36.64, 33.53, 32.53, 29.26, 23.06,

19.65, 14.19.

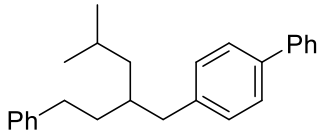
(3-methylhexane-1,6-diyl)dibenzene (**3q**):[7]



3q

Prepared according to general procedure from (3-phenylpropylidene)hydrazine **1q** (89 mg, 0.6 mmol) and (3-bromobutyl)benzene **2a** (72 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product **3q** as colorless oil (36 mg, 48%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.29 (m, 4H), 7.26-7.19 (m, 6H), 2.76-2.56 (m, 4H), 1.76-1.61 (m, 3H), 1.56-1.39 (m, 3H), 1.36-1.22 (m, 1H), 0.99 (d, J = 6.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.11, 142.87, 128.42, 128.38, 128.29, 128.28, 125.64, 125.58, 38.88, 36.57, 36.30, 33.49, 32.39, 28.95, 19.59.

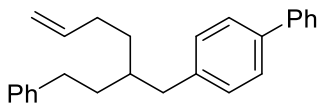
4-(4-methyl-2-phenethylpentyl)-1,1'-biphenyl (**4b**):



4b

Prepared according to general procedure from [(1,1'-biphenyl)-4-ylmethylene]hydrazine **1k** (118 mg, 0.6 mmol) and (3-bromo-5-methylhexyl)benzene **2b** (76 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product **4b** as colorless oil (53 mg, 52%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71-7.68 (m, 2H), 7.61 (d, J = 9.0 Hz, 2H), 7.52 (t, J = 6.0 Hz, 2H), 7.45-7.20 (m, 8H), 2.84-2.62 (m, 4H), 1.98-1.76 (m, 2H), 1.77-1.62 (m, 2H), 1.40-1.26 (m, 2H), 0.99 (d, J = 6.0 Hz, 3H), 0.94 (d, J = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.95, 141.19, 140.55, 138.60, 129.72, 128.80, 128.45, 128.36, 127.04, 126.93, 125.70, 43.37, 40.33, 36.91, 35.30, 32.84, 25.38, 23.08, 22.86. HRMS (EI) calcd. for $[C_{26}H_{30}]^{+}$: 342.2348, found: 342.2350.

4-(2-phenethylhex-5-en-1-yl)-1,1'-biphenyl (**4c**):

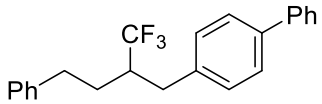


4c

Prepared according to general procedure from [(1,1'-biphenyl)-4-ylmethylene]hydrazine **1k** (118 mg, 0.6 mmol) and (3-bromohept-6-en-1-yl)benzene **2c** (76 mg, 0.3 mmol), after flash column

chromatography (petroleum ether) afforded the product **4c** as colorless oil (36 mg, 36%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.57 (m, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.34-7.28 (m, 1H), 7.25 (t, *J* = 8.0 Hz, 2H), 7.21-7.13 (m, 5H), 5.83-5.73 (m, 1H), 5.04-4.89 (m, 2H), 2.71-2.54 (m, 4H), 2.24-1.98 (m, 2H), 1.84-1.70 (m, 1H), 1.65-1.59 (m, 2H), 1.45 (dd, *J* = 16.0, 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.80, 141.15, 140.39, 139.04, 138.70, 129.68, 128.80, 128.43, 128.39, 127.08, 127.04, 126.98, 125.74, 114.50, 39.95, 38.81, 35.00, 33.00, 32.47, 30.99. HRMS (EI) calcd. for $[C_{26}H_{28}]^{+}$: 340.2191, found: 340.2194.

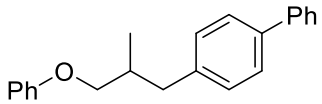
4-(4-phenyl-2-(trifluoromethyl)butyl)-1,1'-biphenyl (**4d**):



4d

Prepared according to general procedure from [(1,1'-biphenyl)-4-ylmethylene]hydrazine **1k** (118 mg, 0.6 mmol) and (3-bromo-4,4,4-trifluorobutyl)benzene **2d** (80 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product **4d** as colorless oil (45 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.57 (m, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.35-7.31 (m, 1H), 7.24-7.12 (m, 5H), 7.01 (d, *J* = 8.0 Hz, 2H), 3.08 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.73-2.64 (m, 2H), 2.63-2.53 (m, 1H), 2.50-2.35 (m, 1H), 2.00-1.87 (m, 1H), 1.82-1.73 (m, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -69.88. ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.98, 140.81, 139.61, 137.23, 129.80, 129.54, 128.87, 128.51, 128.42, 127.33, 127.07, 126.14, 43.89, 43.63, 33.94, 33.02, 29.09. HRMS (EI) calcd. for $[C_{23}H_{21}F_3]^{+}$: 354.1595, found: 354.1591.

4-(2-methyl-3-phenoxypropyl)-1,1'-biphenyl (**4e**):

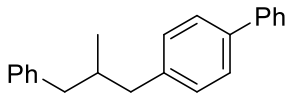


4e

Prepared according to general procedure from [(1,1'-biphenyl)-4-ylmethylene]hydrazine **1k** (118 mg, 0.6 mmol) and (2-bromopropoxy)benzene **2e** (64 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product **4e** as colorless oil (48 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.57 (m, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.34-7.22 (m, 5H), 6.97-6.86 (m, 3H), 3.87-3.74 (m, 2H), 2.91 (dd, *J* = 12.0, 8.0 Hz, 1H), 2.59 (dd, *J* = 12.0,

8.0 Hz, 1H), 2.34-2.22 (m, 1H), 1.05 (d, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.21, 141.09, 139.51, 138.91, 129.75, 129.49, 128.79, 127.10, 127.04, 120.61, 114.61, 71.92, 39.41, 35.27, 16.97. HRMS (EI) calcd. for $[C_{22}H_{22}O]^+$: 302.1671, found: 302.1668.

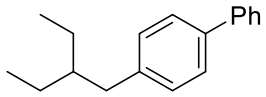
4-(2-methyl-3-phenylpropyl)-1,1'-biphenyl (**4f**):



4f

Prepared according to general procedure from [(1,1'-biphenyl)-4-ylmethylene]hydrazine **1k** (118 mg, 0.6 mmol) and (2-bromopropyl)benzene **2f** (119 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product **4f** as colorless oil (36 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.55 (m, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 8.0 Hz, 2H), 7.34-7.23 (m, 3H), 7.23-7.12 (m, 5H), 2.75-2.69 (m, 2H), 2.47-2.41 (m, 2H), 2.16-2.01 (m, 1H), 0.86 (d, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.28, 141.17, 140.46, 138.72, 129.65, 129.25, 128.78, 128.25, 127.04, 126.96, 125.84, 43.42, 43.00, 37.22, 19.30. HRMS (EI) calcd. for $[C_{22}H_{22}]^+$: 286.1722, found: 286.1723.

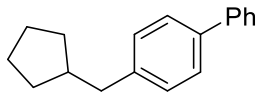
4-(2-ethylbutyl)-1,1'-biphenyl (**4g**):



4g

Prepared according to general procedure from [(1,1'-biphenyl)-4-ylmethylene]hydrazine **1k** (118 mg, 0.6 mmol) and 3-bromopentane **2g** (90 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product **4g** as colorless oil (37 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.55 (m, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 8.0 Hz, 2H), 7.34-7.27 (m, 1H), 7.24-7.18 (m, 2H), 2.57 (d, J = 4.0 Hz, 2H), 1.58-1.50 (m, 1H), 1.38-1.27 (m, 4H), 0.89 (t, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.21, 141.09, 138.47, 129.65, 128.74, 127.01, 126.98, 126.85, 42.65, 39.38, 25.02, 10.90. HRMS (EI) calcd. for $[C_{18}H_{22}]^+$: 238.1722, found: 238.1721.

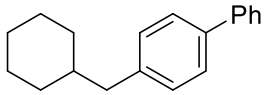
4-(cyclopentylmethyl)-1,1'-biphenyl (**4h**):



4h

Prepared according to general procedure from [(1,1'-biphenyl)-4-ylmethylene]hydrazine **1k** (118 mg, 0.6 mmol) and bromocyclopentane **2h** (45 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product **4h** as colorless oil (42 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.57 (m, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.34-7.27 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.64 (d, *J* = 8.0 Hz, 2H), 2.19-2.04 (m, 1H), 1.77-1.69 (m, 2H), 1.68-1.59 (m, 2H), 1.59-1.49 (m, 2H), 1.30-1.14 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.60, 141.24, 138.53, 129.27, 128.75, 127.03, 126.99, 126.93, 42.04, 41.79, 32.58, 25.01. HRMS (EI) calcd. for $[C_{18}H_{20}]^{+}$: 236.1565, found: 236.1563.

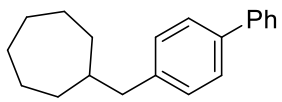
4-(cyclohexylmethyl)-1,1'-biphenyl (**4i**):[8]



4i

Prepared according to general procedure from [(1,1'-biphenyl)-4-ylmethylene]hydrazine **1k** (118 mg, 0.6 mmol) and bromocyclohexane **2i** (49 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product **4i** as colorless oil (46 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.56 (m, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.34-7.28 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.51 (d, *J* = 4.0 Hz, 2H), 1.76-1.61 (m, 5H), 1.59-1.52 (m, 1H), 1.29-1.12 (m, 3H), 1.01-0.91 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.22, 140.57, 138.53, 129.64, 128.73, 127.02, 126.97, 126.82, 43.81, 39.84, 33.24, 26.62, 26.38.

4-(cycloheptylmethyl)-1,1'-biphenyl (**4j**):

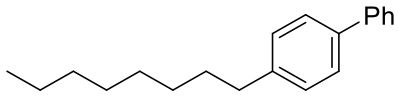


4j

Prepared according to general procedure from [(1,1'-biphenyl)-4-ylmethylene]hydrazine **1k** (118 mg, 0.6 mmol) and bromocycloheptane **2j** (53 mg, 0.3 mmol), after flash column chromatography

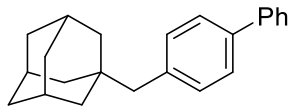
(petroleum ether) afforded the product **4j** as colorless oil (43 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.55 (m, 2H), 7.50 (d, *J* = 12.0 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.32-7.29 (m, 1H), 7.24-7.16 (m, 2H), 2.54 (d, *J* = 8.0 Hz, 2H), 1.85-1.54 (m, 7H), 1.52-1.34 (m, 4H), 1.25-1.16 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.22, 141.07, 138.53, 129.66, 128.75, 127.03, 127.00, 126.87, 44.21, 41.41, 34.52, 28.47, 26.42. HRMS (EI) calcd. for $[C_{20}H_{24}]^+$: 264.1878, found: 264.1877.

4-octyl-1,1'-biphenyl (**5**):[9]



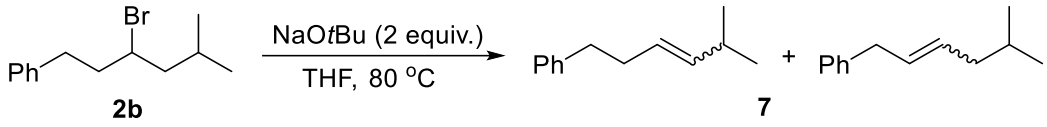
Prepared according to general procedure from [(1,1'-biphenyl)-4-ylmethylene]hydrazine **1k** (118 mg, 0.6 mmol) and 1-bromoheptane **2k** (53 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product **5** as colorless oil (23 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.57 (m, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.64 (t, *J* = 8.0 Hz, 2H), 1.68-1.64 (m, 2H), 1.41-1.20 (m, 10H), 0.88 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.15, 141.22, 138.55, 128.85, 128.72, 127.02, 127.01, 126.97, 35.66, 31.94, 31.56, 29.54, 29.43, 29.32, 22.72, 14.16.

(3r,5r,7r)-1-([1,1'-biphenyl]-4-ylmethyl)adamantine (**6**):



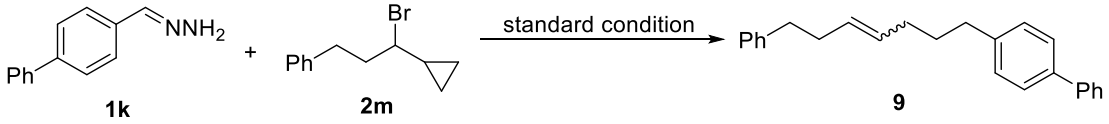
Prepared according to general procedure from [(1,1'-biphenyl)-4-ylmethylene]hydrazine **1k** (118 mg, 0.6 mmol) and (3r,5r,7r)-1-(bromomethyl)adamantane **2l** (53 mg, 0.3 mmol), after flash column chromatography (petroleum ether) afforded the product **6** as a white solid (40 mg, 45%), mp: 84-86 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.57 (m, 2H), 7.52-7.47 (m, 2H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.35-7.28 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 2H), 1.94 (s, 3H), 1.67 (d, *J* = 12.0 Hz, 3H), 1.58 (d, *J* = 8.0 Hz, 3H), 1.51 (d, *J* = 4.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.19, 138.52, 137.50, 131.03, 129.51, 128.72, 126.99, 126.23, 50.92, 42.44, 37.03, 33.64, 28.77. HRMS (EI) calcd. for $[C_{23}H_{26}]^+$: 302.2035, found: 302.2032.

4. General procedure for eq. 3 and 5



2b **7**

NaO^{t}Bu (38 mg, 0.4 mmol), alkyl bromide **2b** (51 mg, 0.2 mmol) and THF (3 mL) were added to a 10 mL sealing tube under a nitrogen atmosphere and the mixture was stirring at 80 °C for 12 h. After alkyl bromide consumed completely, the resulting solid was filtered, and the filtrate was concentrated and purified by column chromatography (petroleum ether) to give a mixture product as colorless oil **7** (28 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.25 (m, 4H), 7.19-7.16 (m, 5H), 6.38 (d, *J* = 15.8 Hz, 0.27H), 6.25-6.18 (m, 1H), 5.63-5.43 (m, 2.33H), 5.40-5.39 (m, 0.92H), 3.40 (d, *J* = 6.9 Hz, 0.38H), 3.34 (d, *J* = 6.0 Hz, 1.92H), 2.70-2.62 (m, 1H), 2.31-2.20 (m, 2H), 2.04 (t, *J* = 6.9 Hz, 0.42H), 1.91 (t, *J* = 6.6 Hz, 1.96H), 1.69-1.57 (m, 1.44H), 1.36 (dd, *J* = 15.5, 6.8 Hz, 0.63H), 0.95 (d, *J* = 6.7 Hz, 3.41H), 0.92 (d, *J* = 6.7 Hz, 2H), 0.89 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.15, 138.30, 130.79, 129.85, 129.68, 129.56, 128.50, 128.47, 128.31, 128.19, 126.72, 126.24, 125.89, 125.83, 125.65, 41.90, 39.12, 38.55, 36.39, 36.23, 34.41, 33.58, 30.98, 30.89, 28.72, 28.67, 28.45, 27.56, 22.61, 22.51, 22.41, 22.30.



1k **2m** **9**

$Ni(COD)_2$ (8.3 mg, 0.03 mmol), dppf (33 mg, 0.06 mmol), NaO^{t}Bu (58 mg, 0.6 mmol) were added to a 10 mL sealing tube under a nitrogen atmosphere. Hydrazone **1k** (0.6 mmol, 2 equiv.), alkyl bromide **2m** (0.3 mmol) were added in THF (2 mL) and the mixture was stirring at 80 °C for 12 h. After alkyl bromide consumed completely, the resulting solid was filtered, and the filtrate was concentrated and purified by column chromatography (petroleum ether) to give a mixture product as colorless oil **9** (44 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.55 (m, 2H), 7.53-7.45 (m, 2H), 7.43-7.39 (m, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.26-7.06 (m, 7H), 5.57-5.16 (m, 2H), 2.77-1.98 (m, 7H), 1.80-1.63 (m, 1H), 1.02-0.80 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.78, 142.12, 141.78, 141.20, 140.11, 139.88, 138.66, 138.58, 136.19, 135.81, 134.78, 130.61, 130.00, 129.76, 129.73, 128.90, 128.72, 128.53, 128.44, 128.27, 128.23, 128.00, 127.88, 127.02, 127.00, 126.98, 126.80, 126.77, 126.73, 125.75,

125.71, 125.68, 125.61, 44.04, 43.45, 43.40, 41.95, 38.35, 36.23, 36.17, 35.93, 34.94, 34.41, 34.07, 33.63, 32.12, 31.19, 29.36, 20.91, 20.08, 17.99.

5. References

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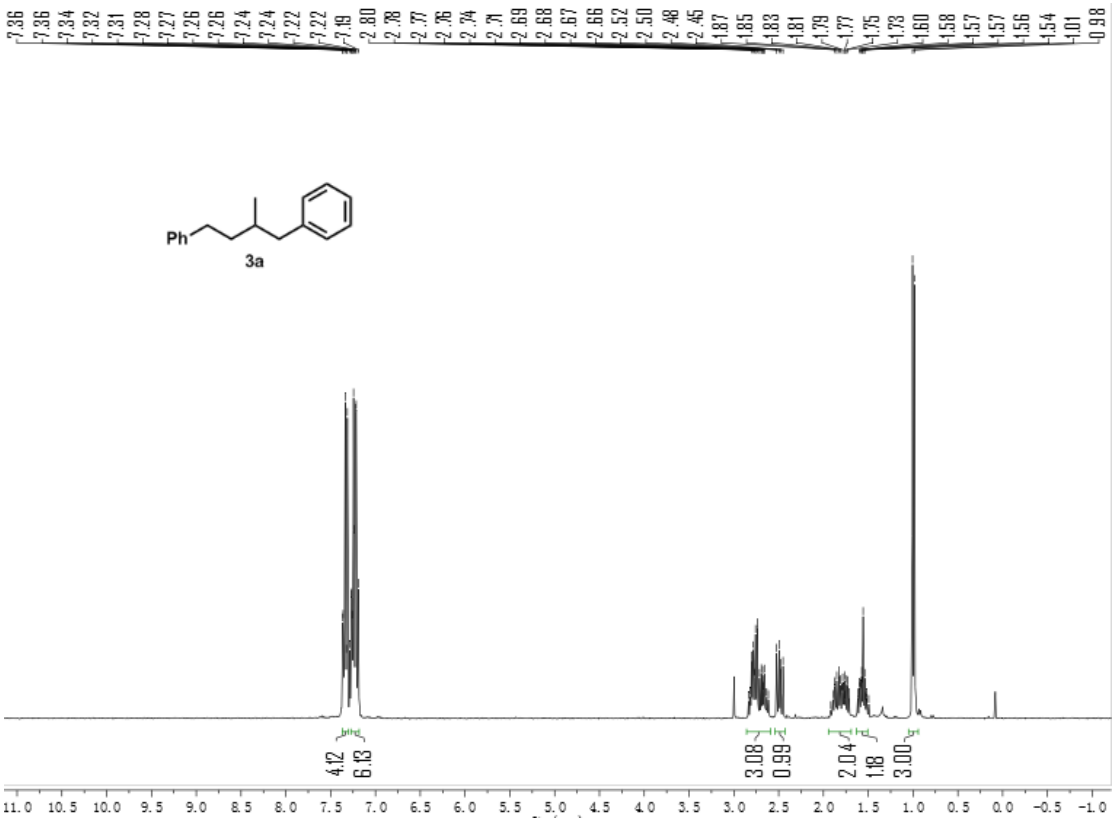
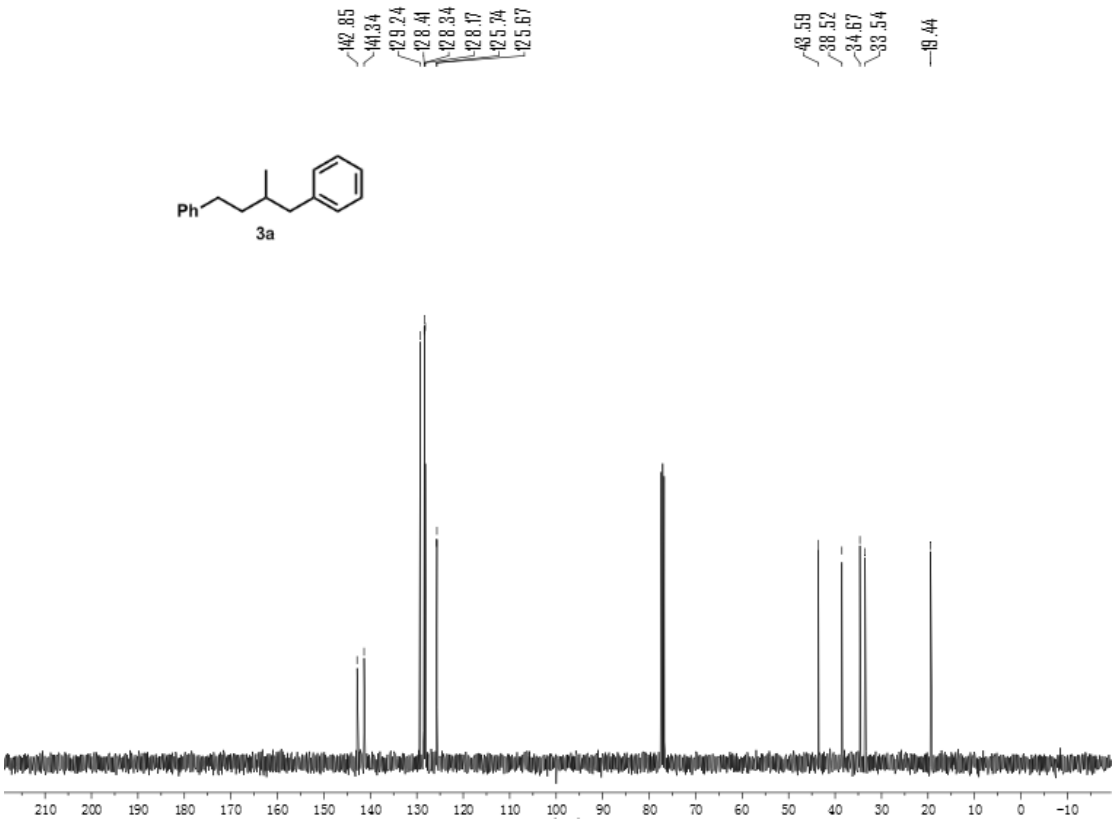
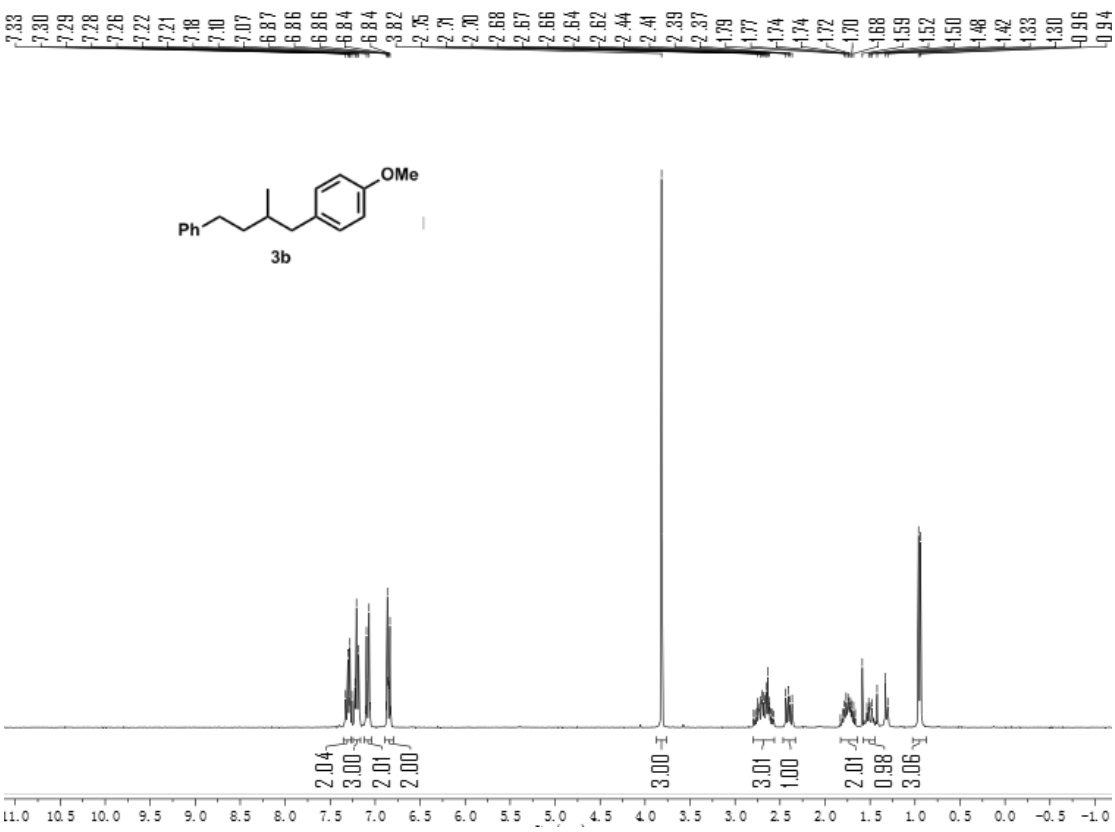
6. ^{1}H, ^{13}C, ^{19}F NMR Spectra



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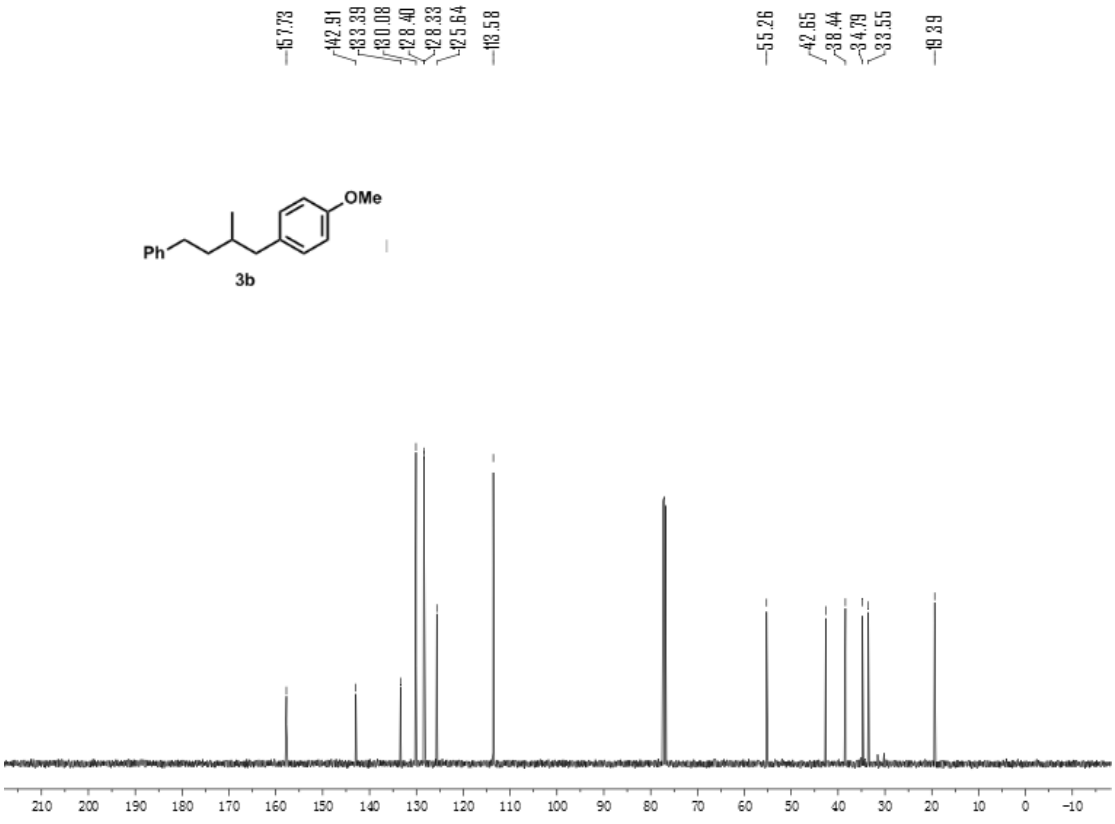
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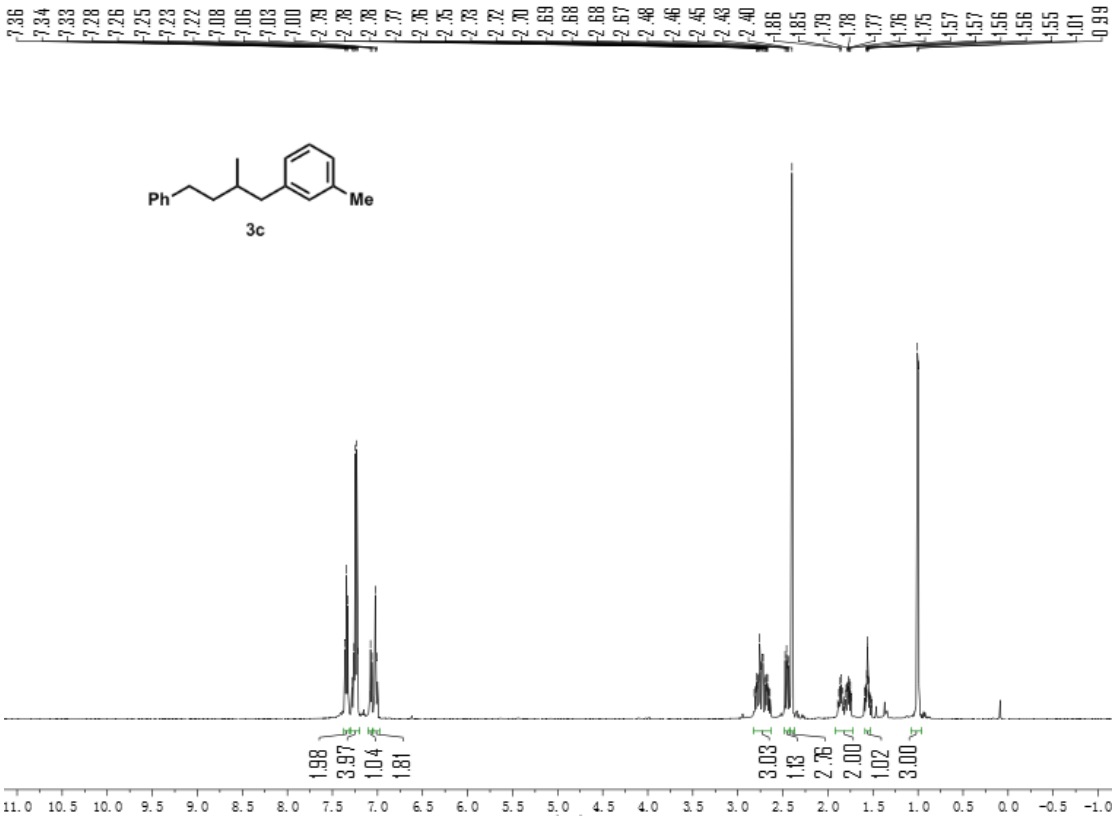
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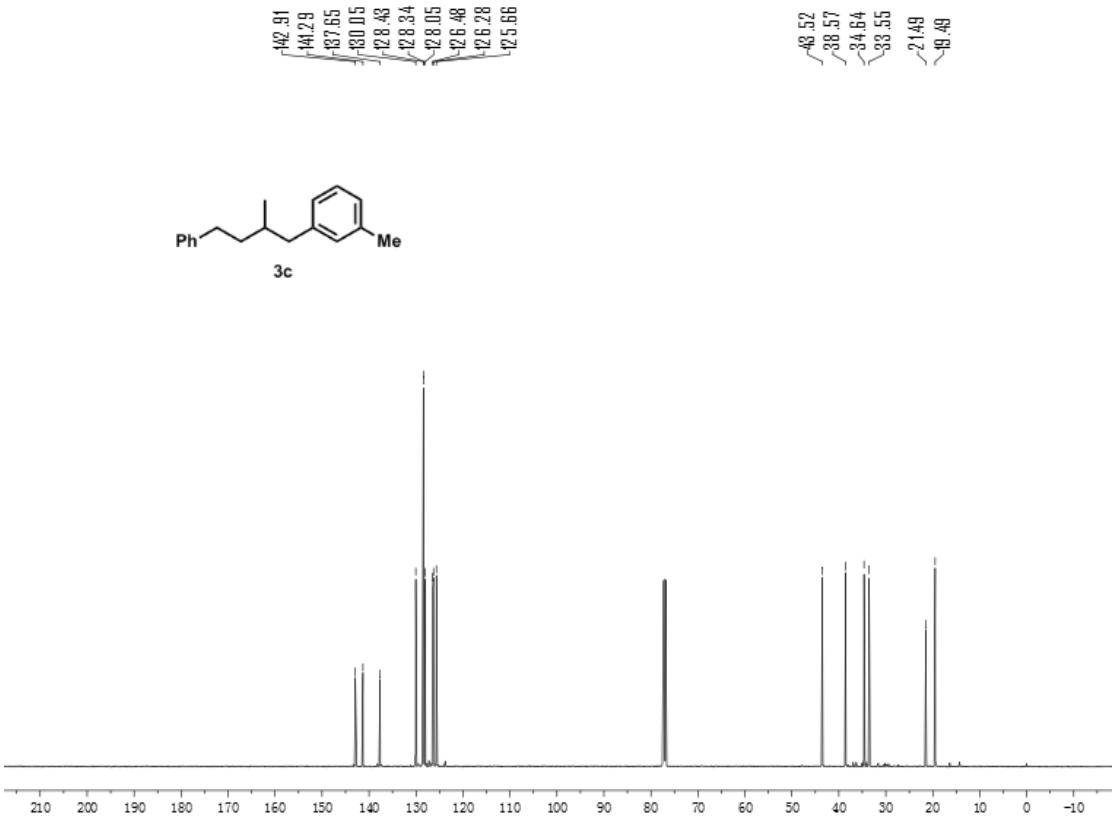
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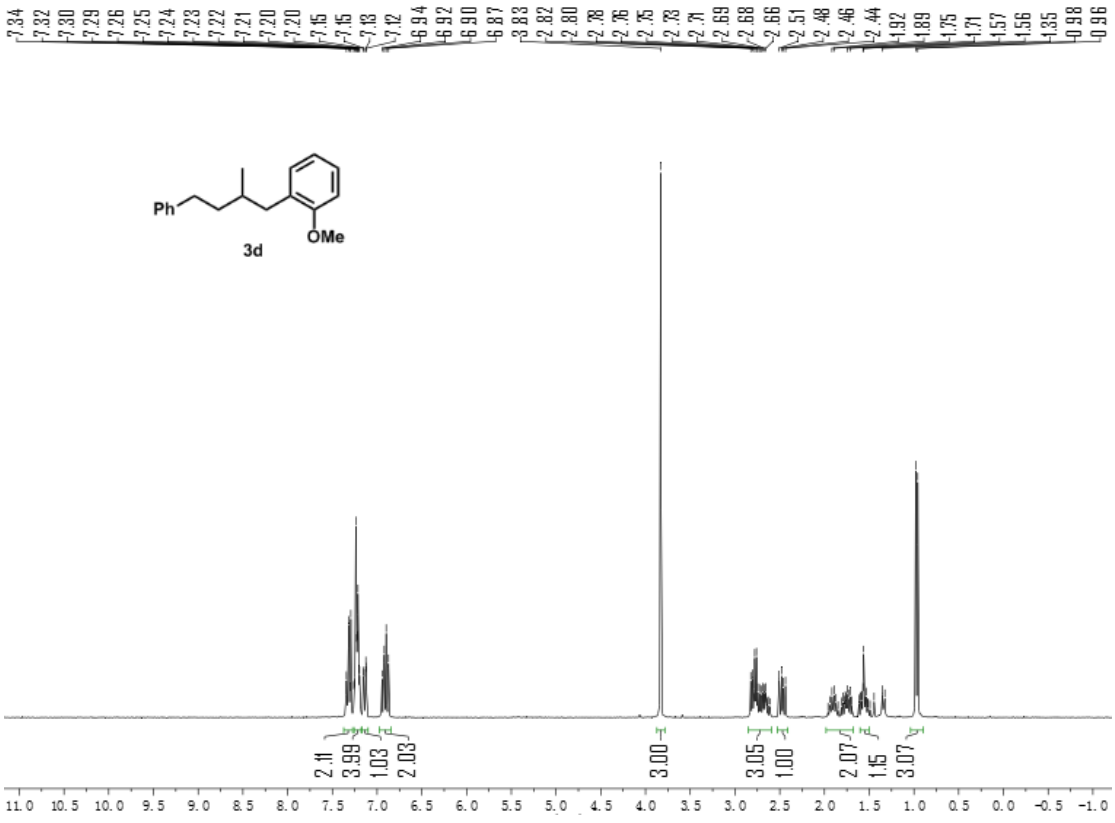
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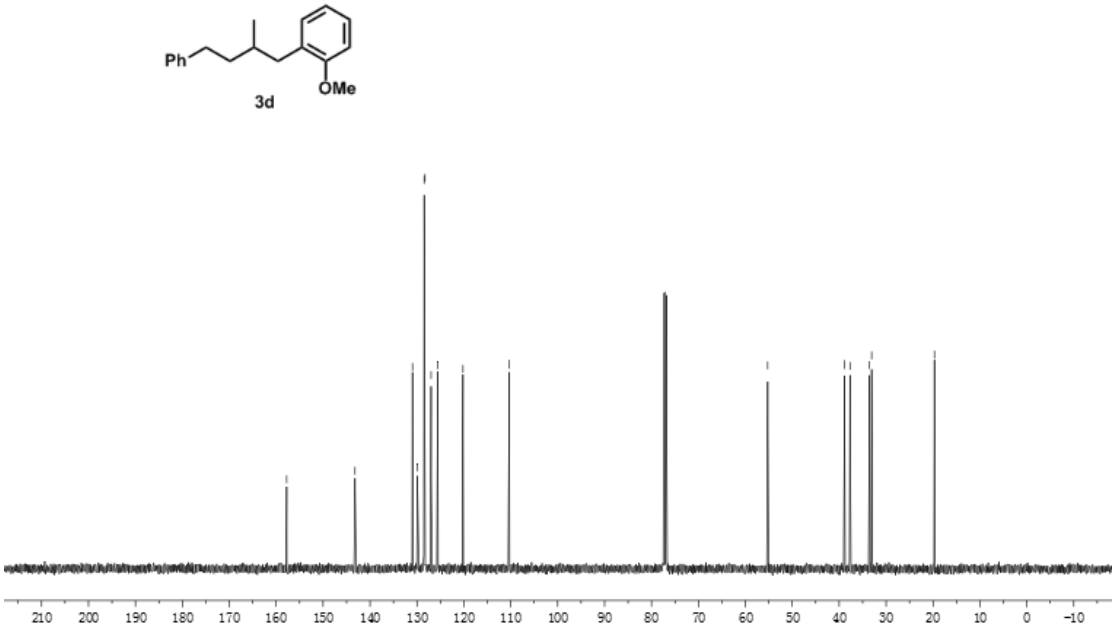
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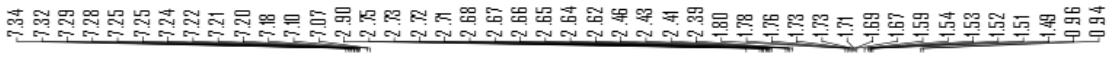
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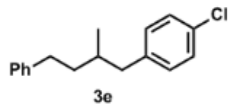
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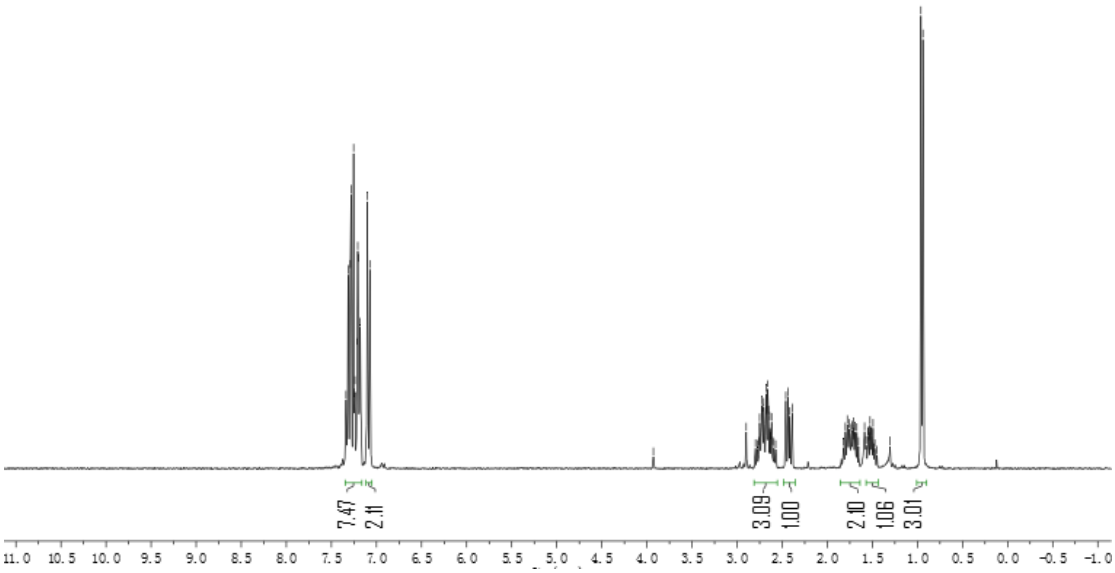
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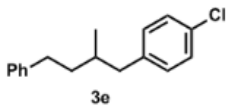
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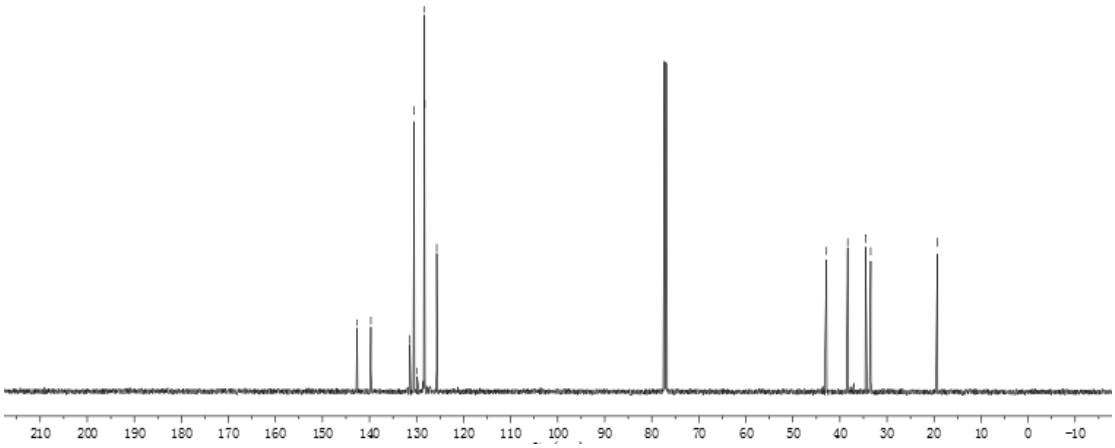
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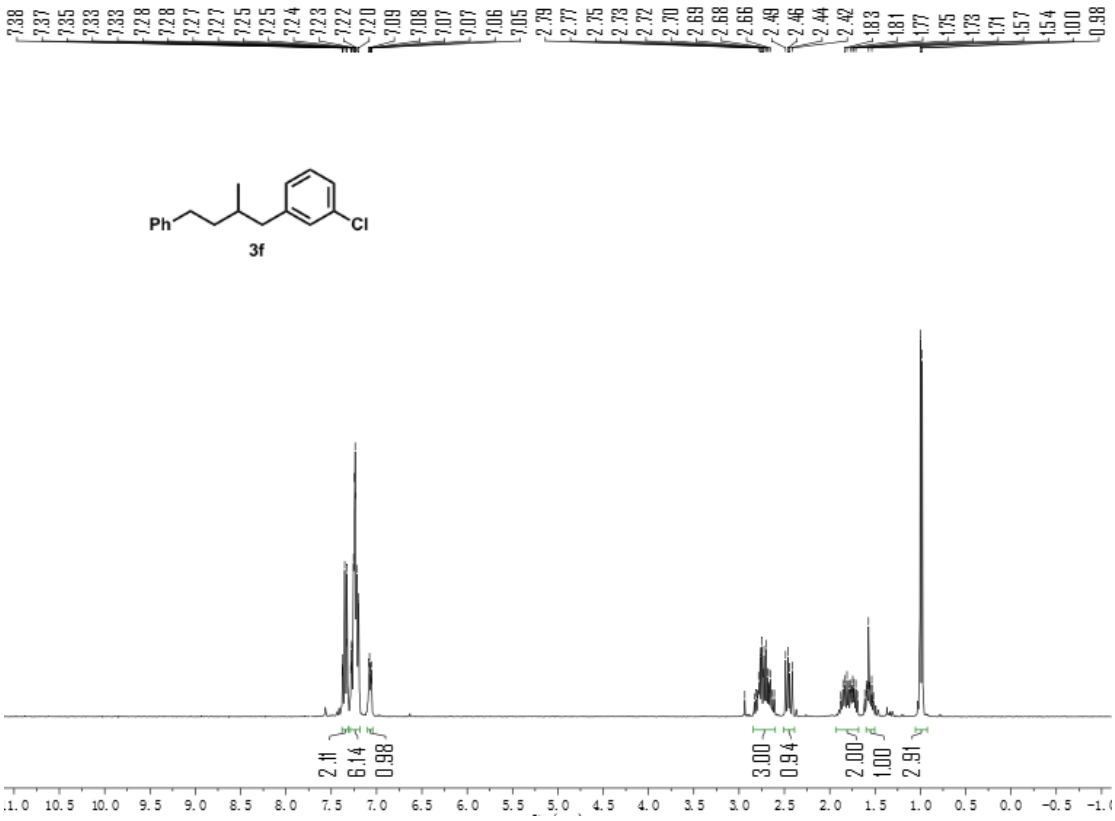
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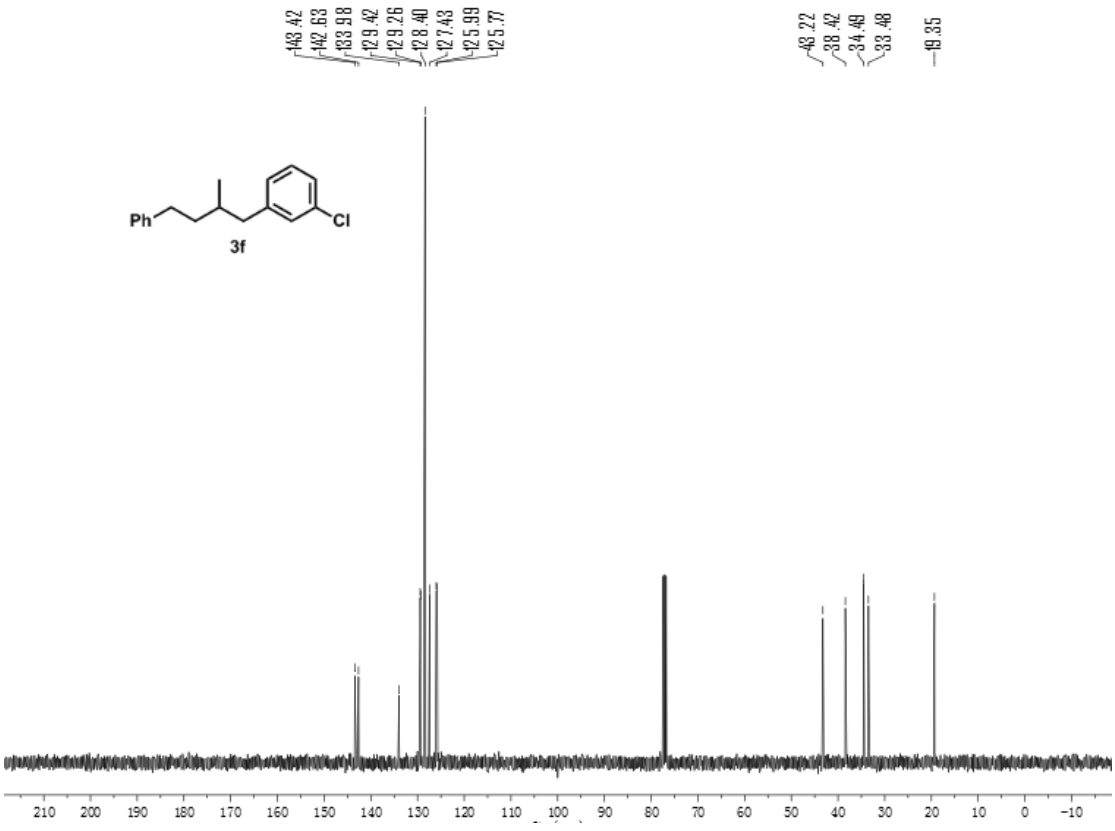
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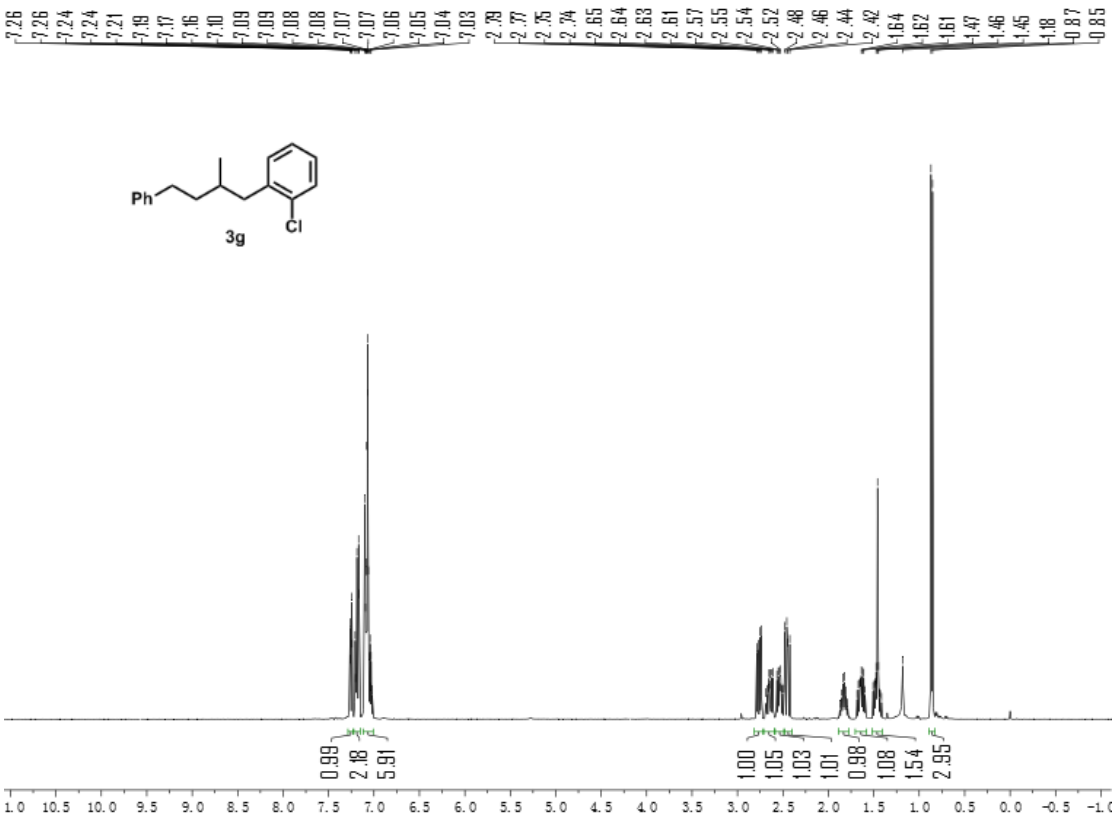
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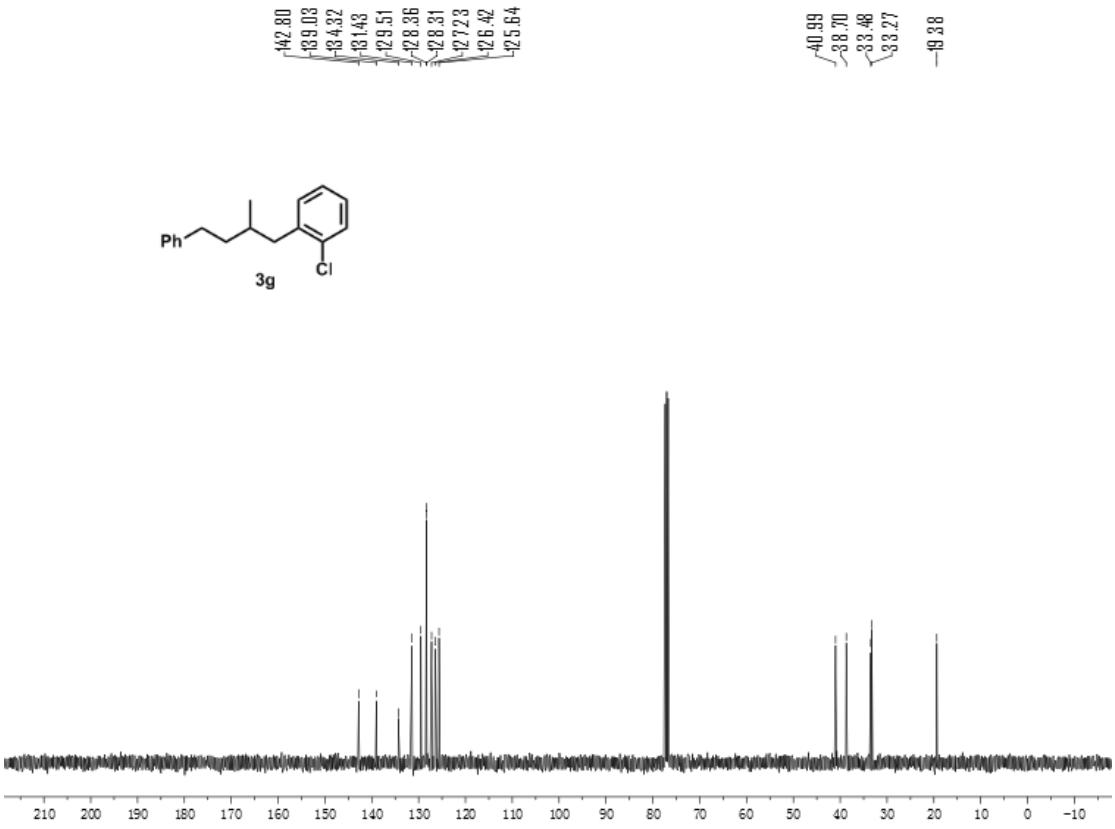
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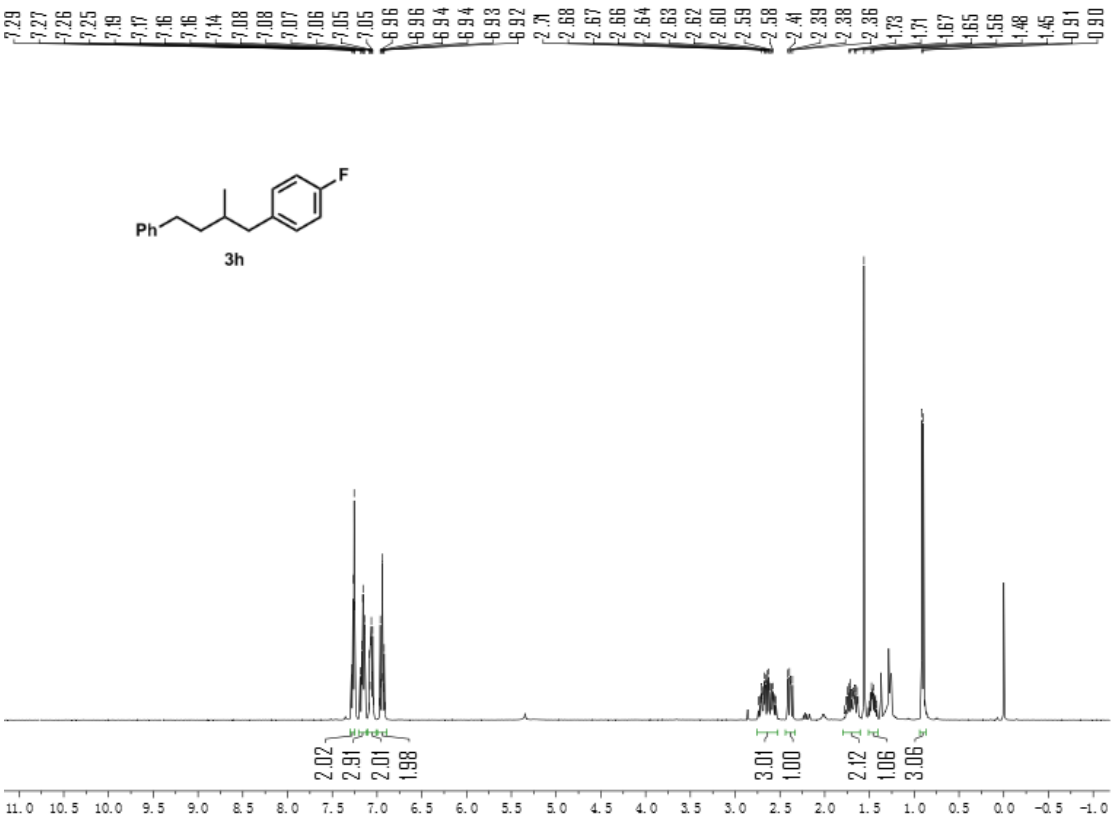
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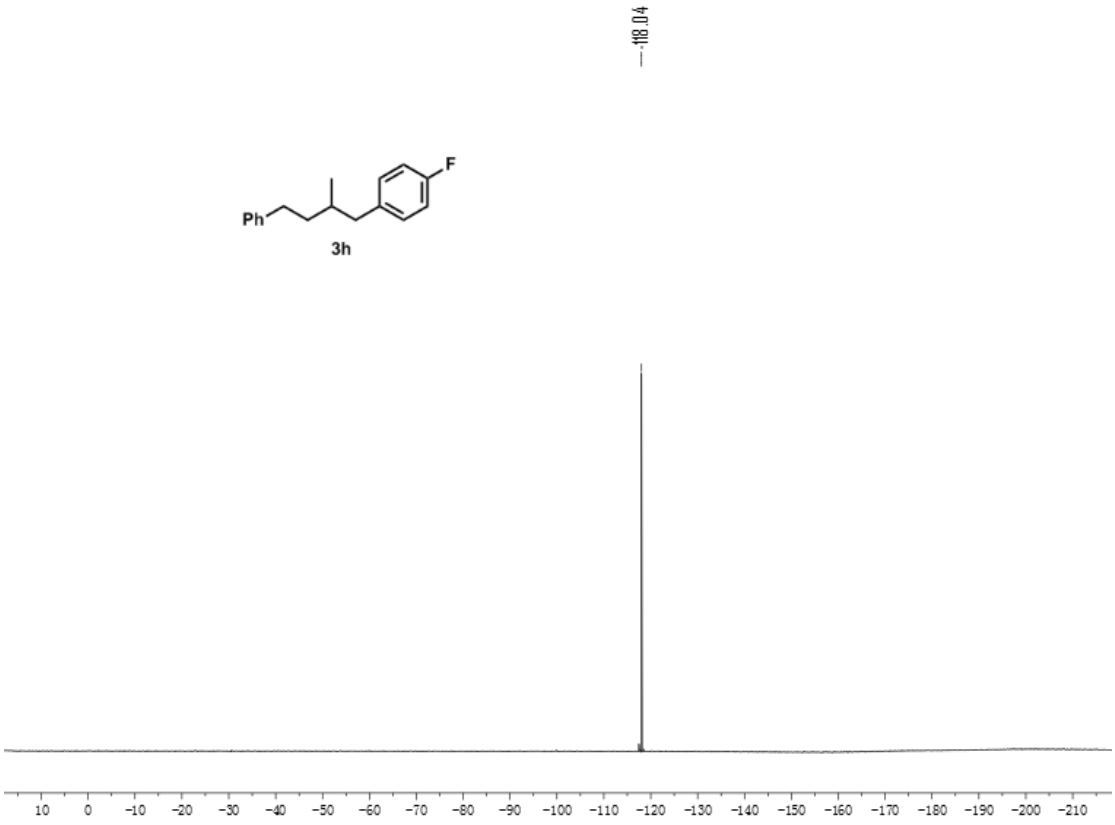
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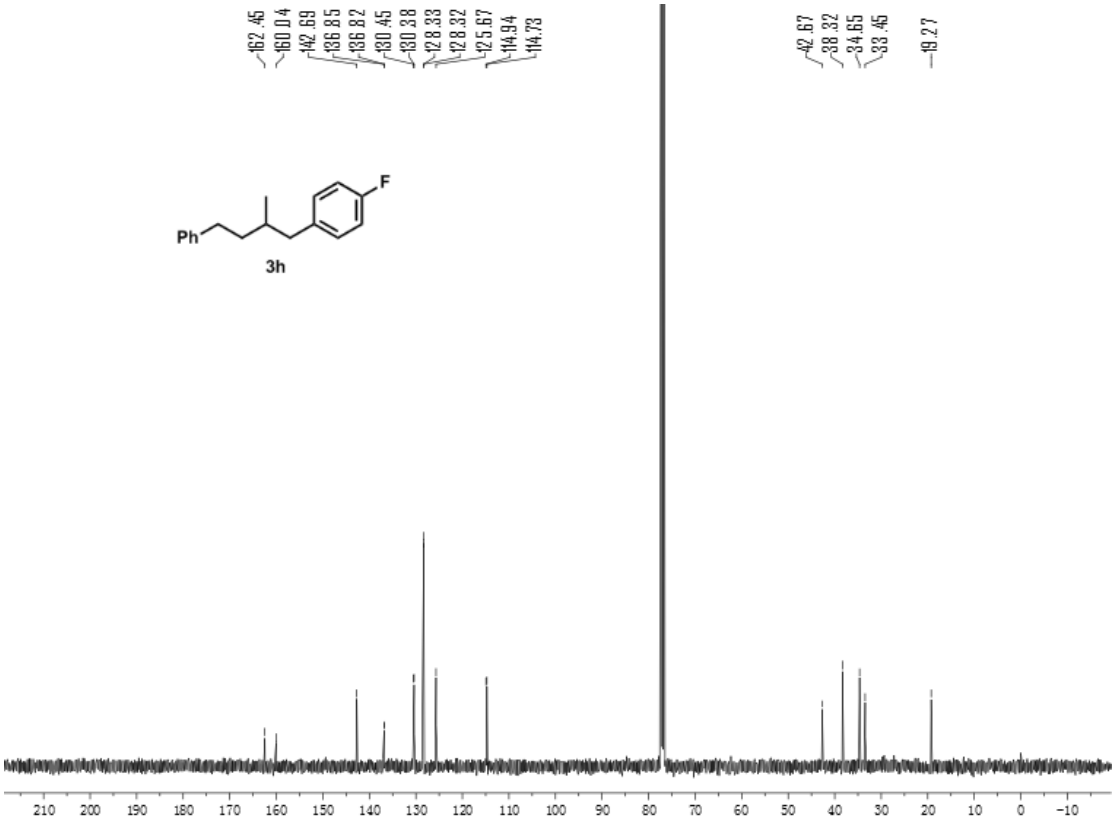
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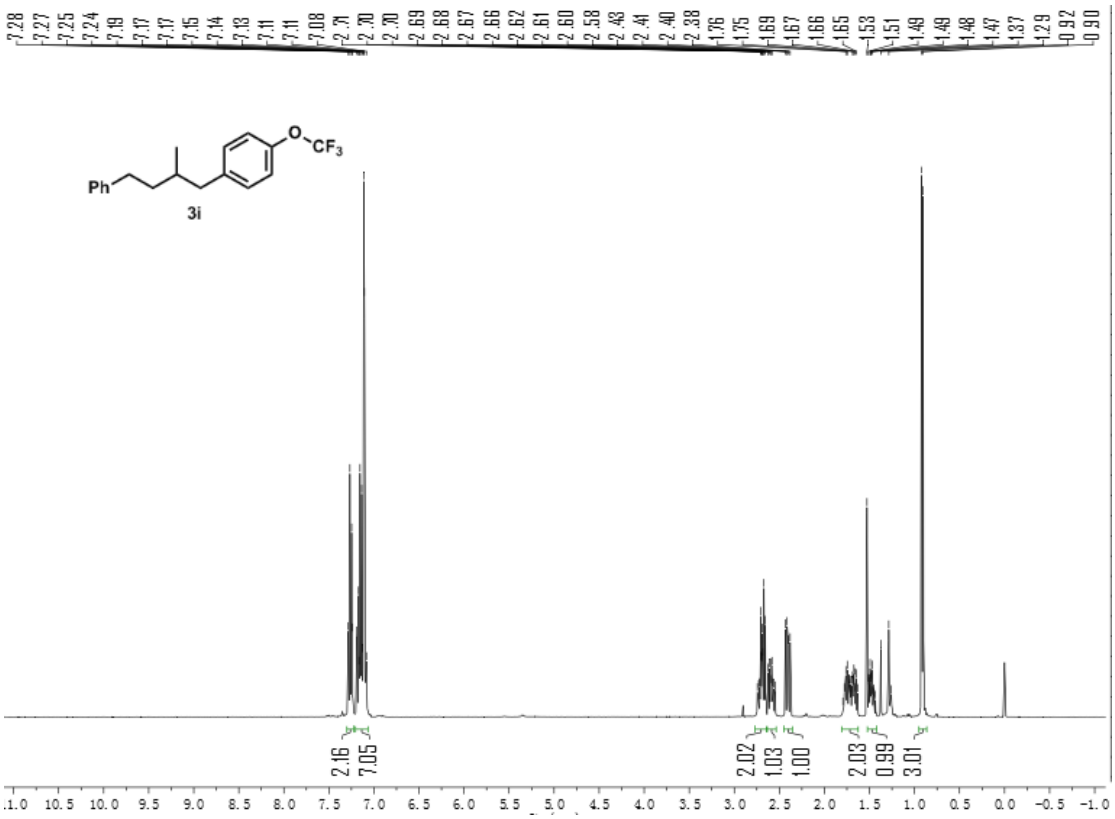
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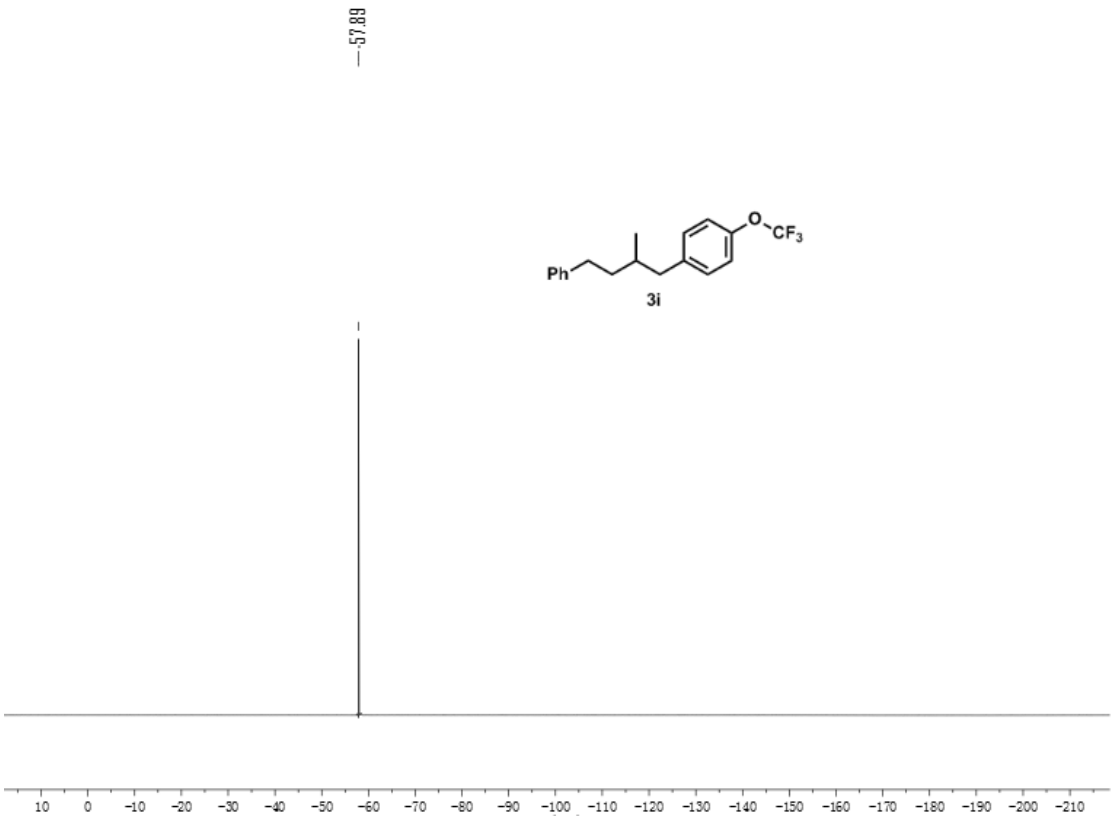
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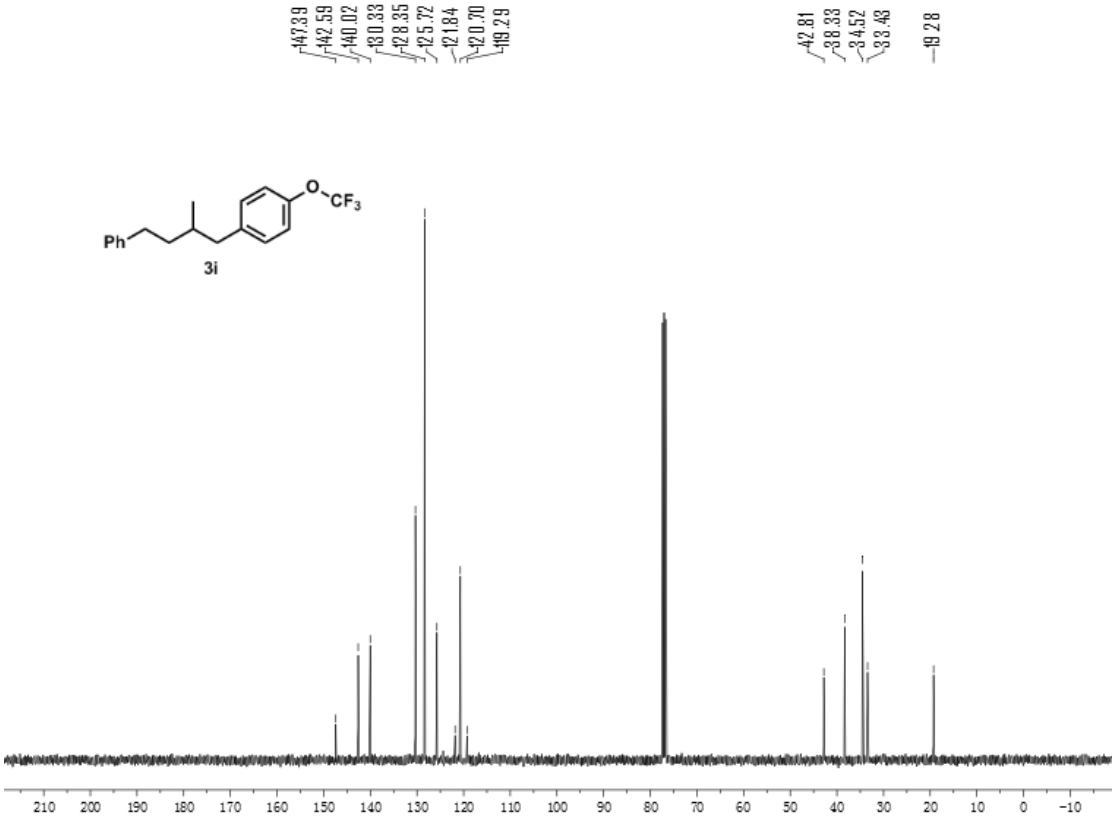
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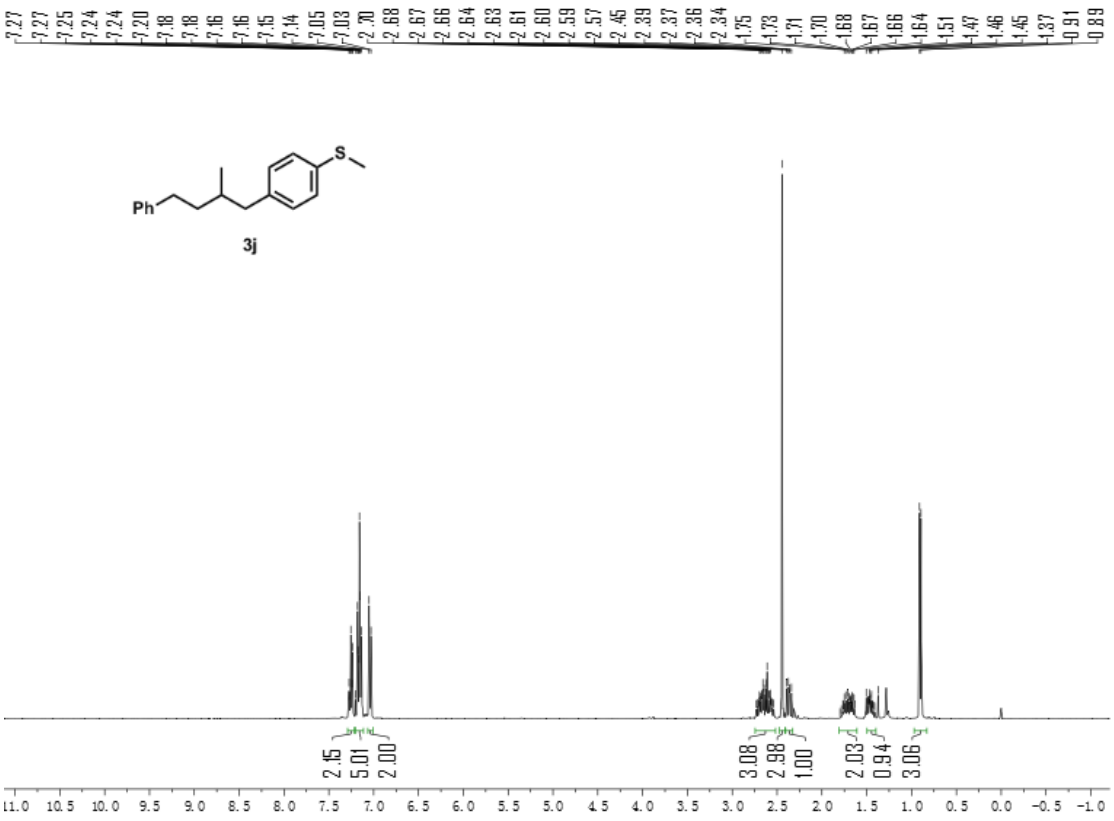
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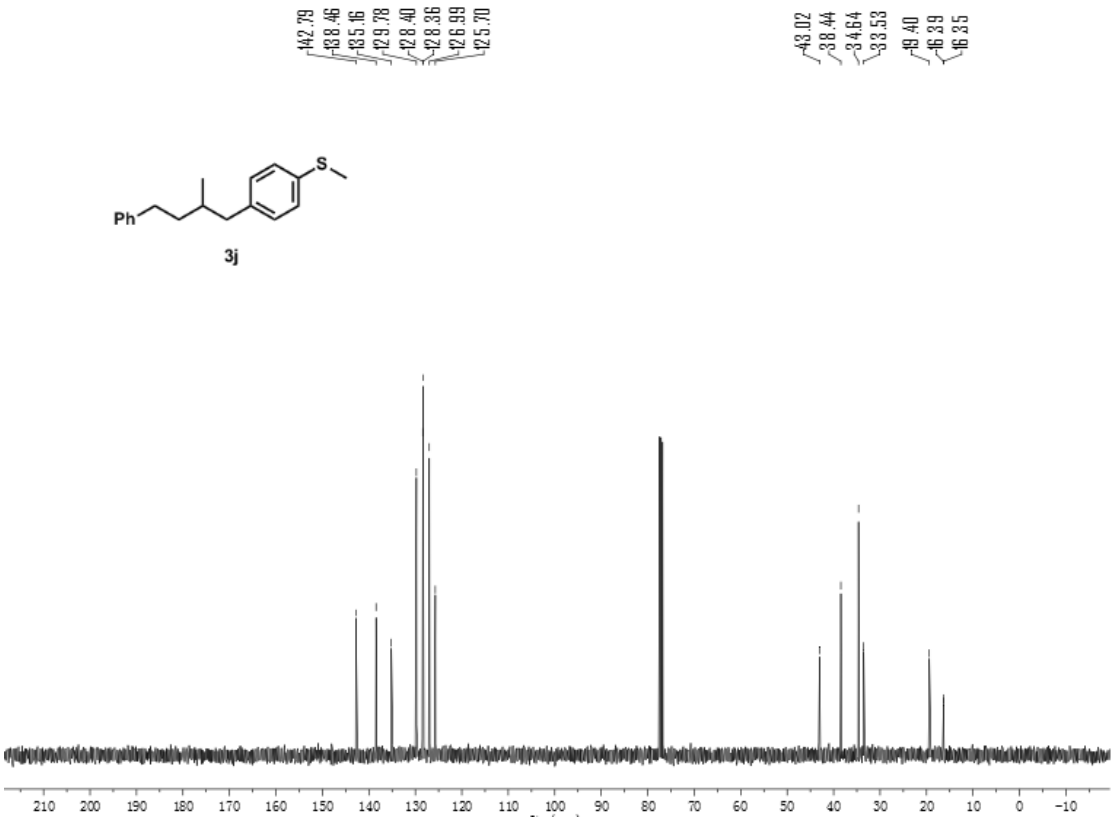
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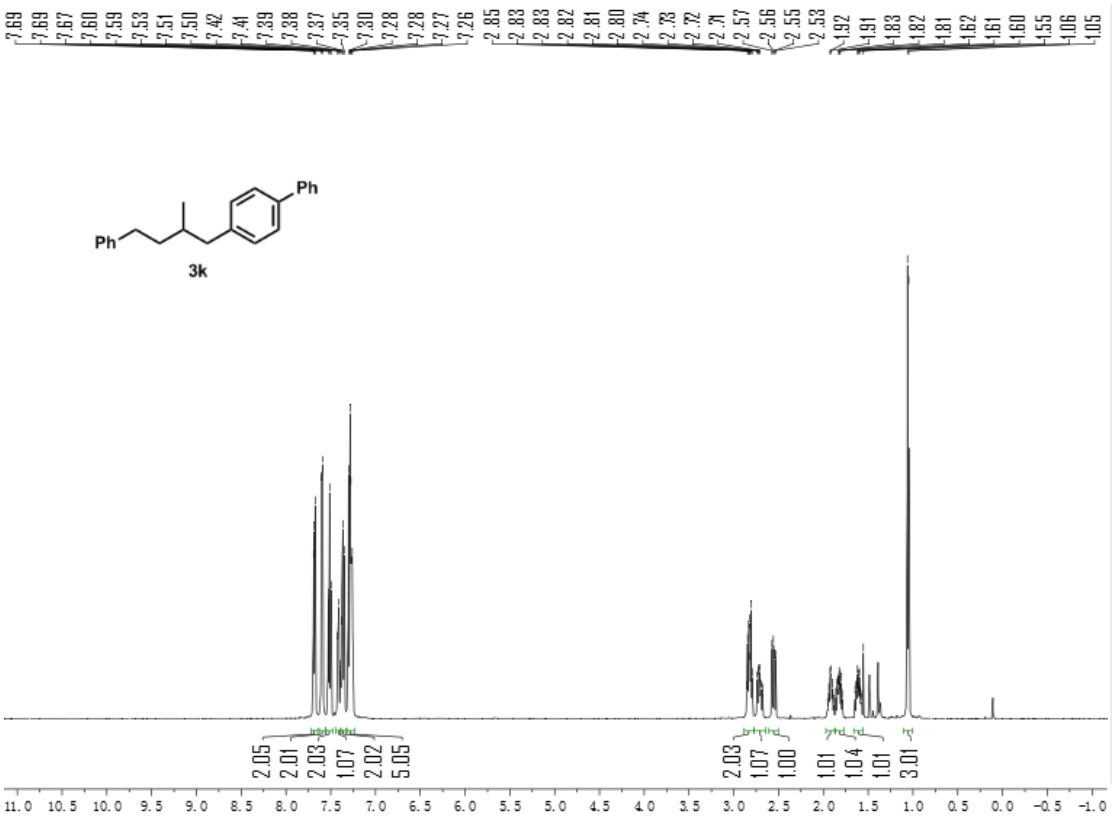
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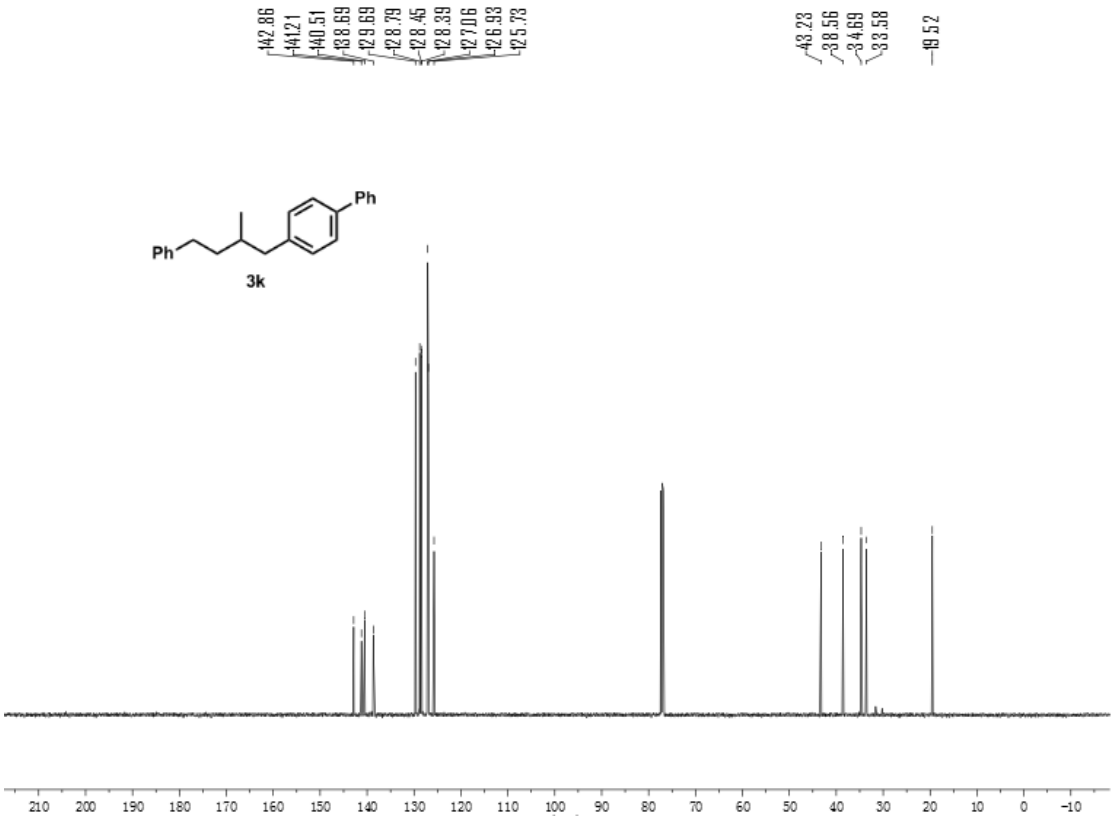
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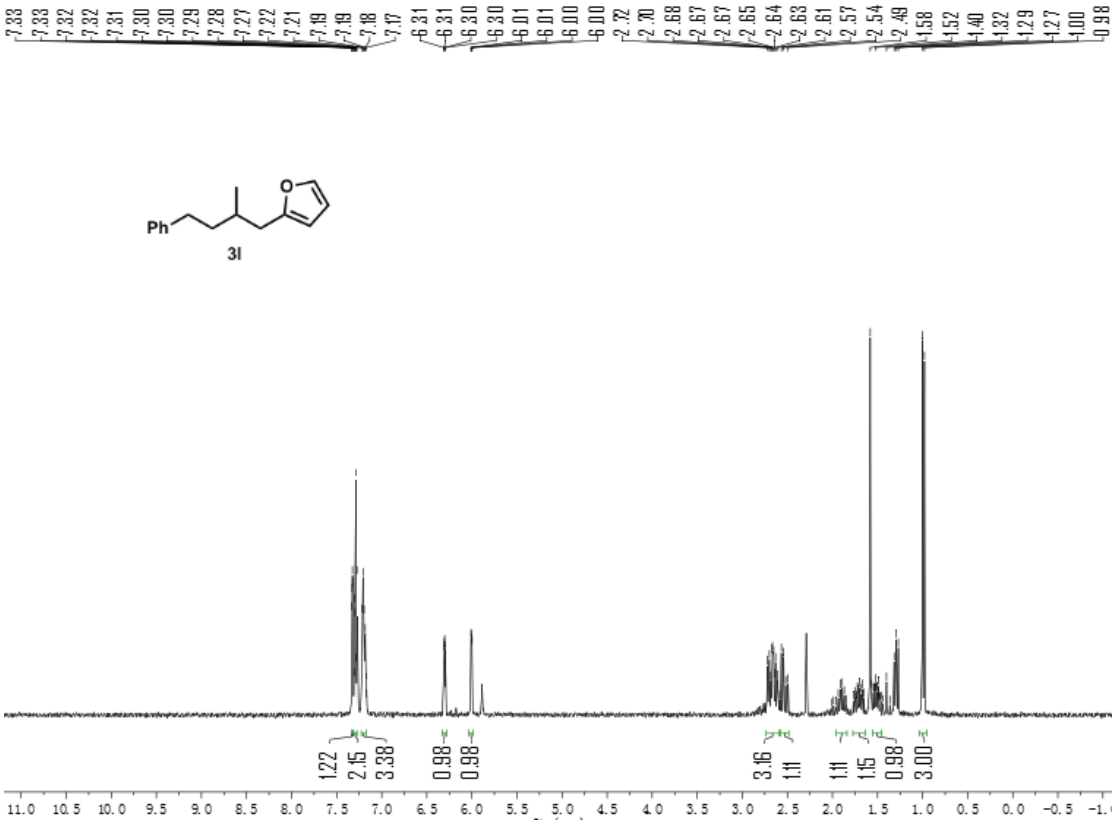
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Ph
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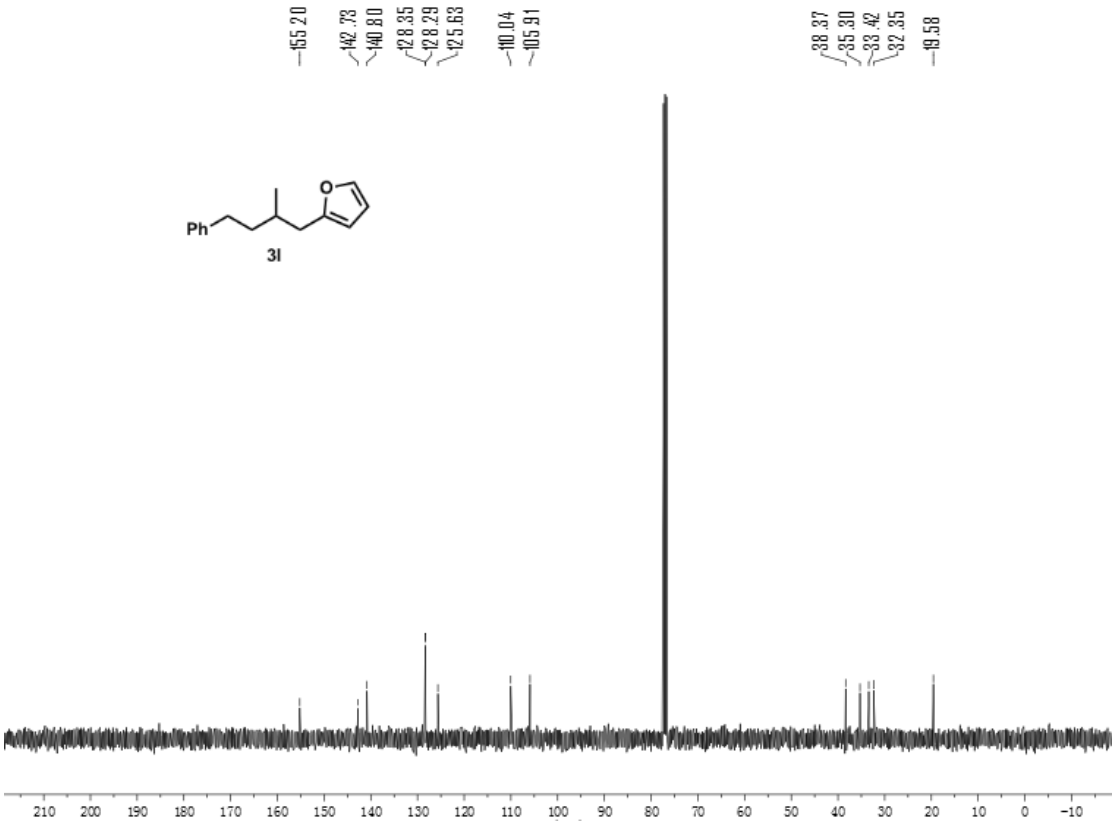
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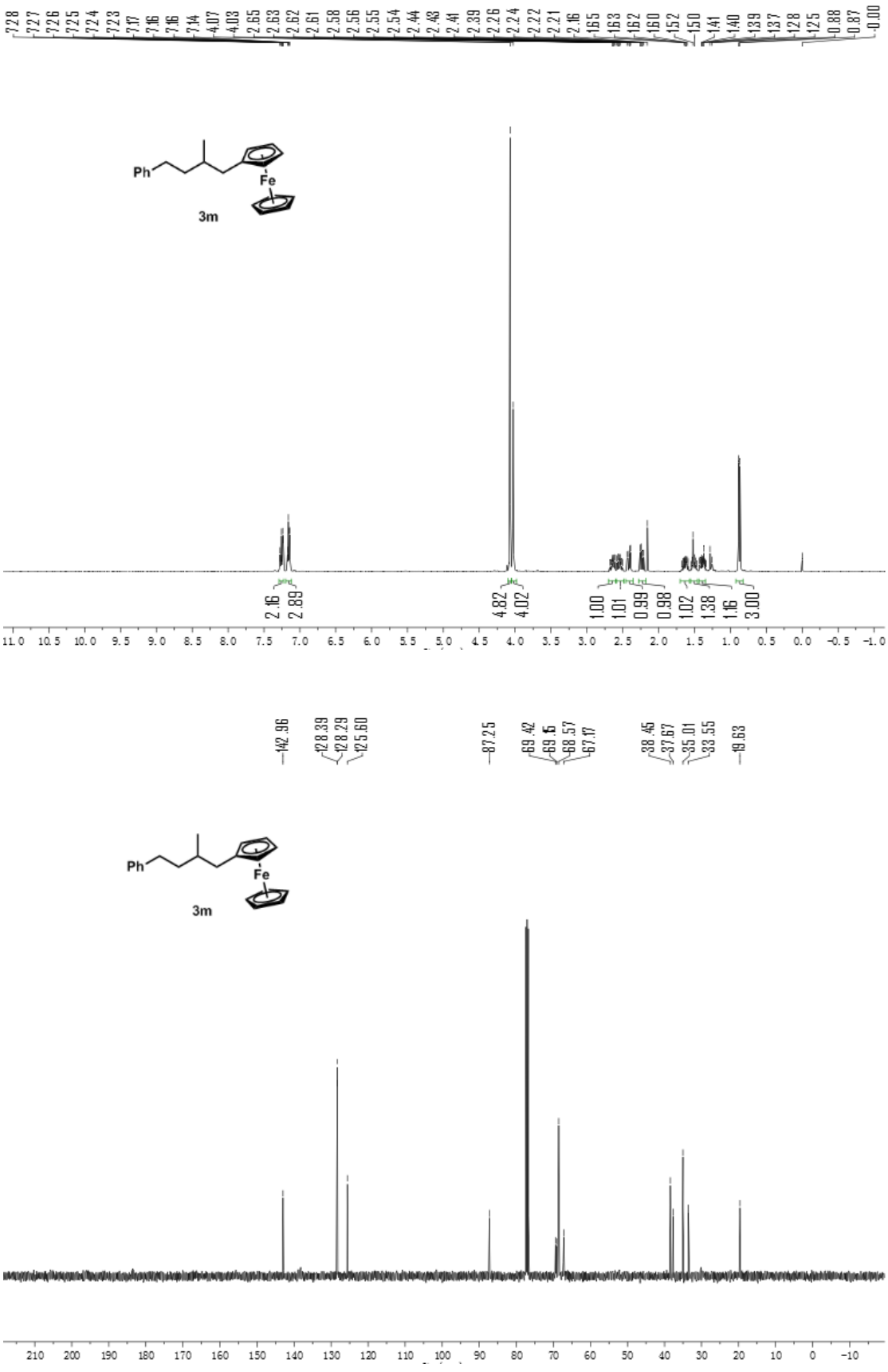
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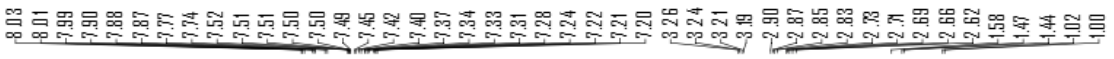
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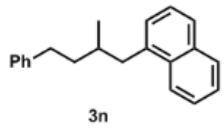
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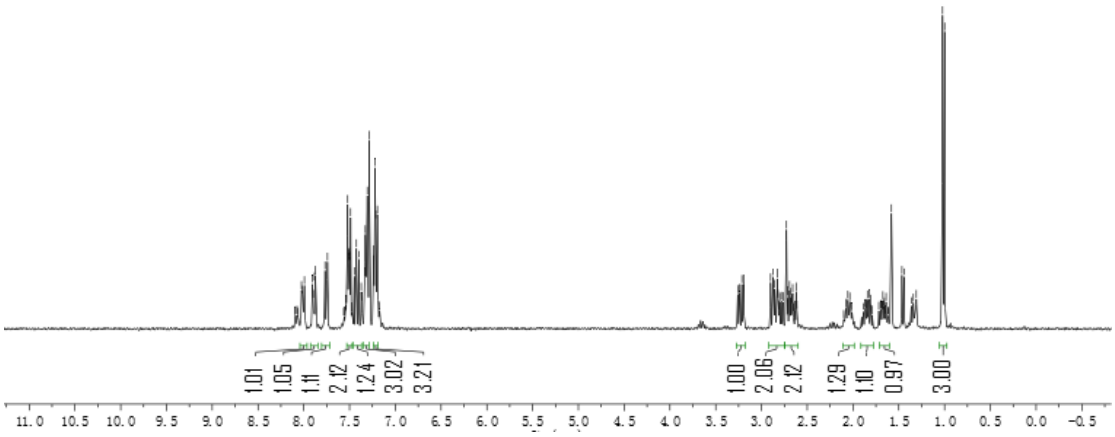
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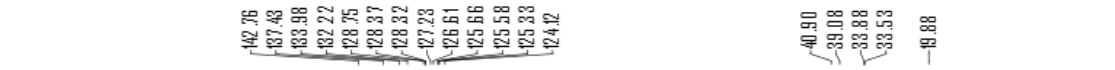
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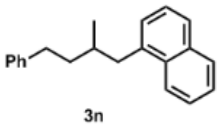
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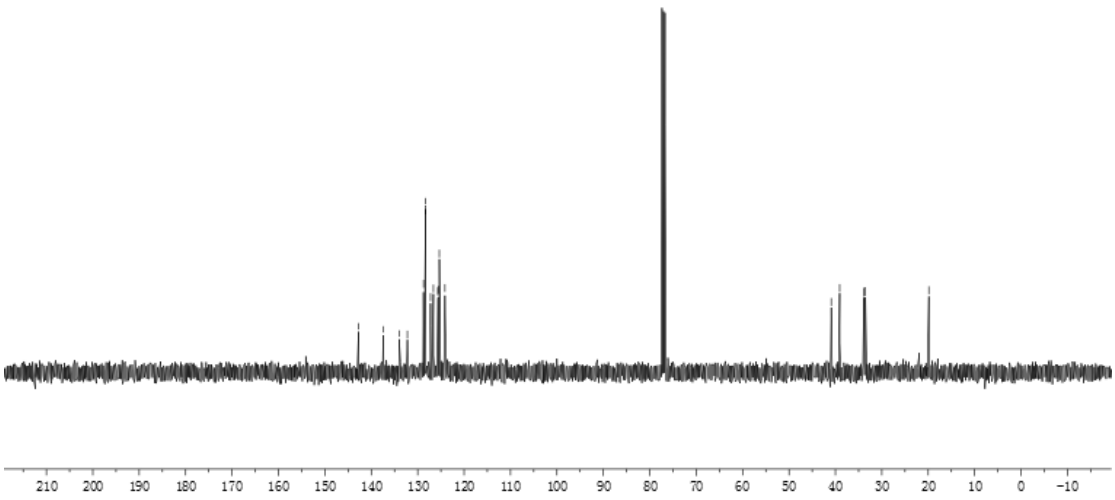
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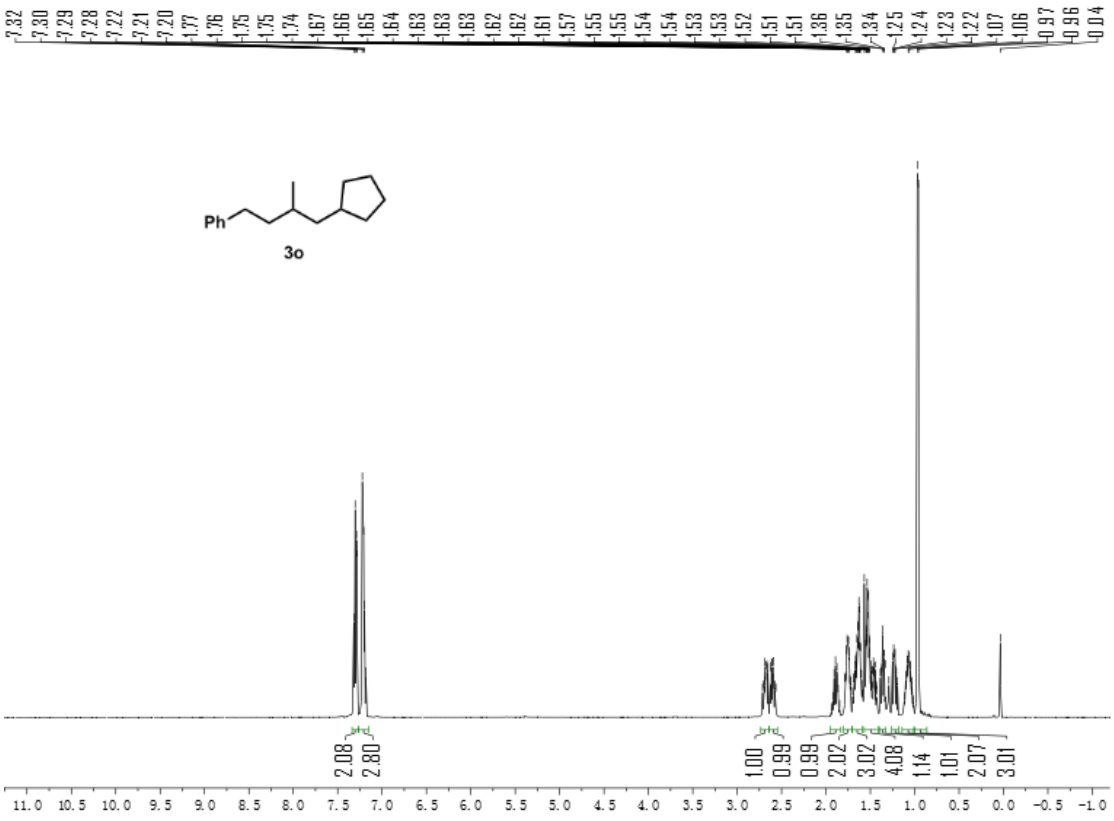
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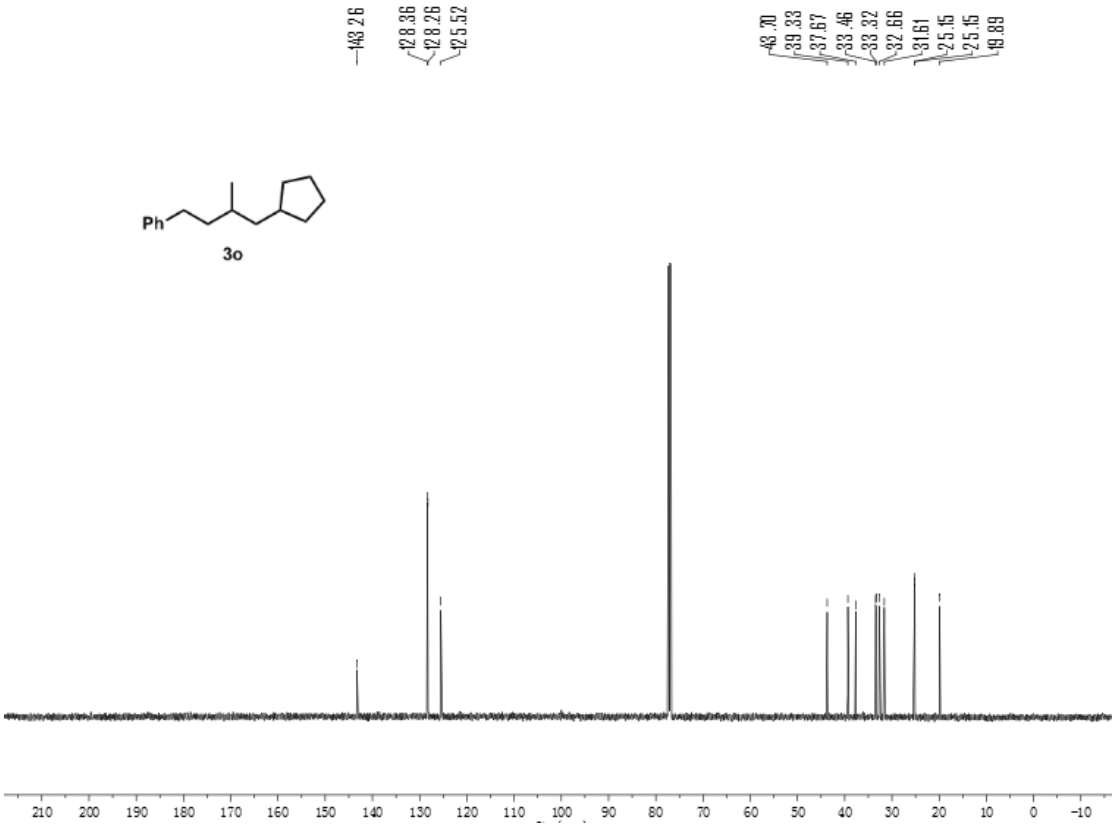
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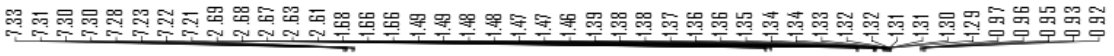
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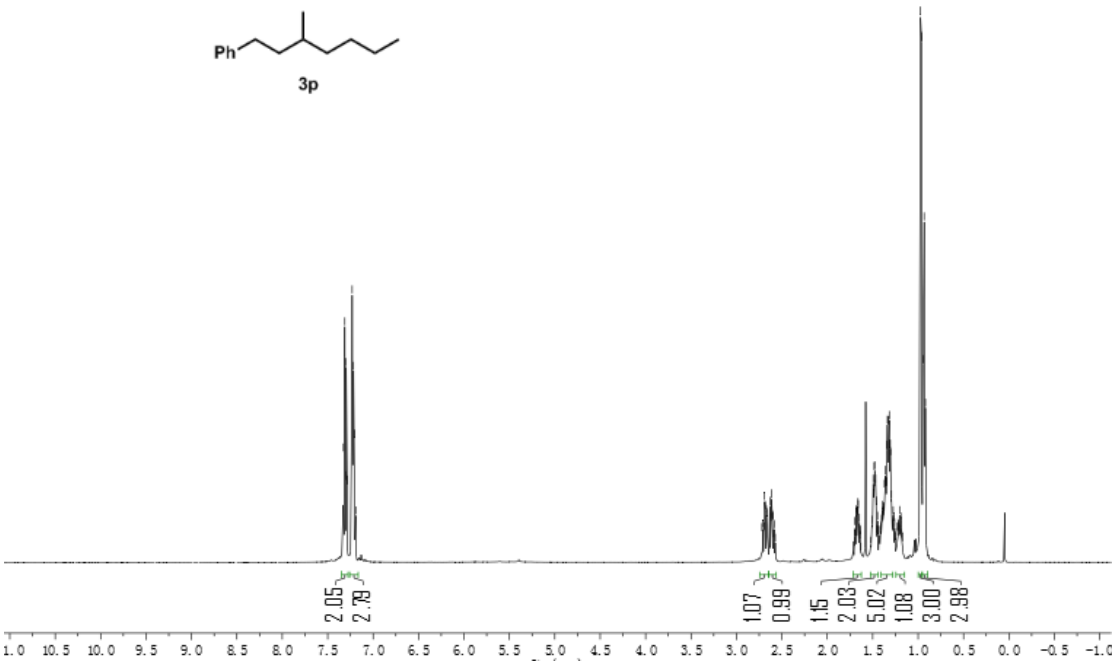
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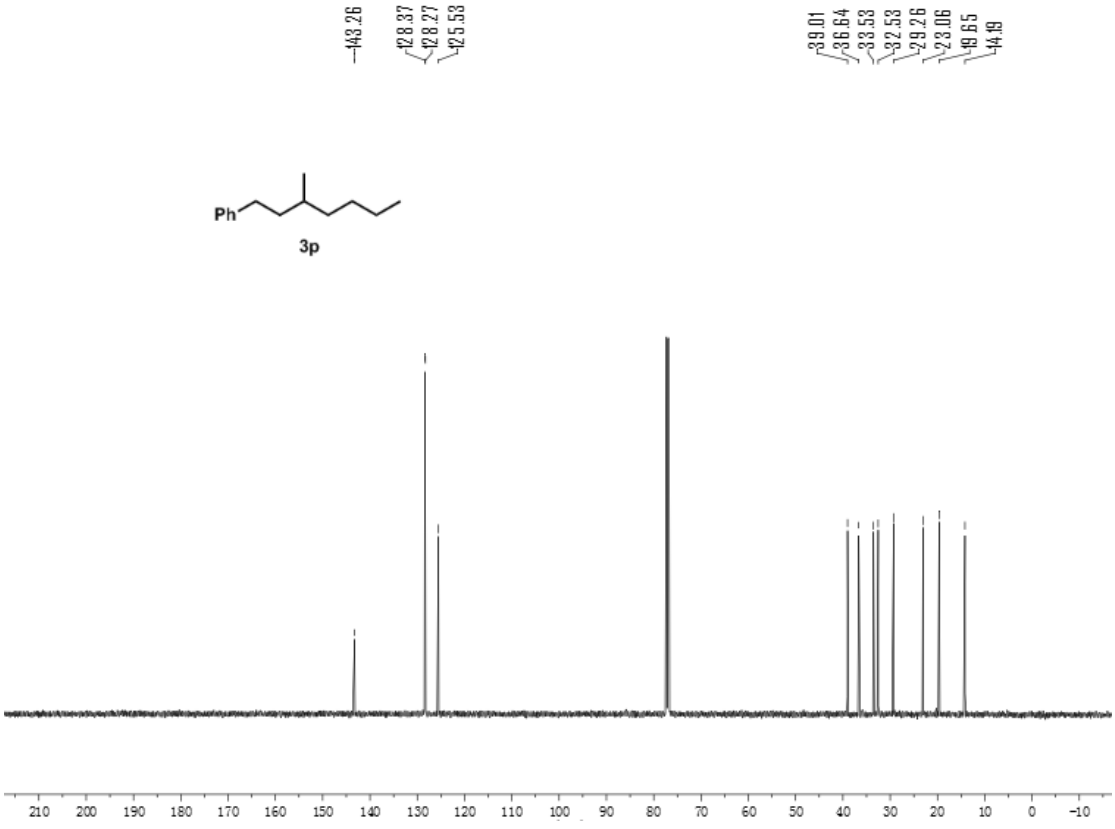
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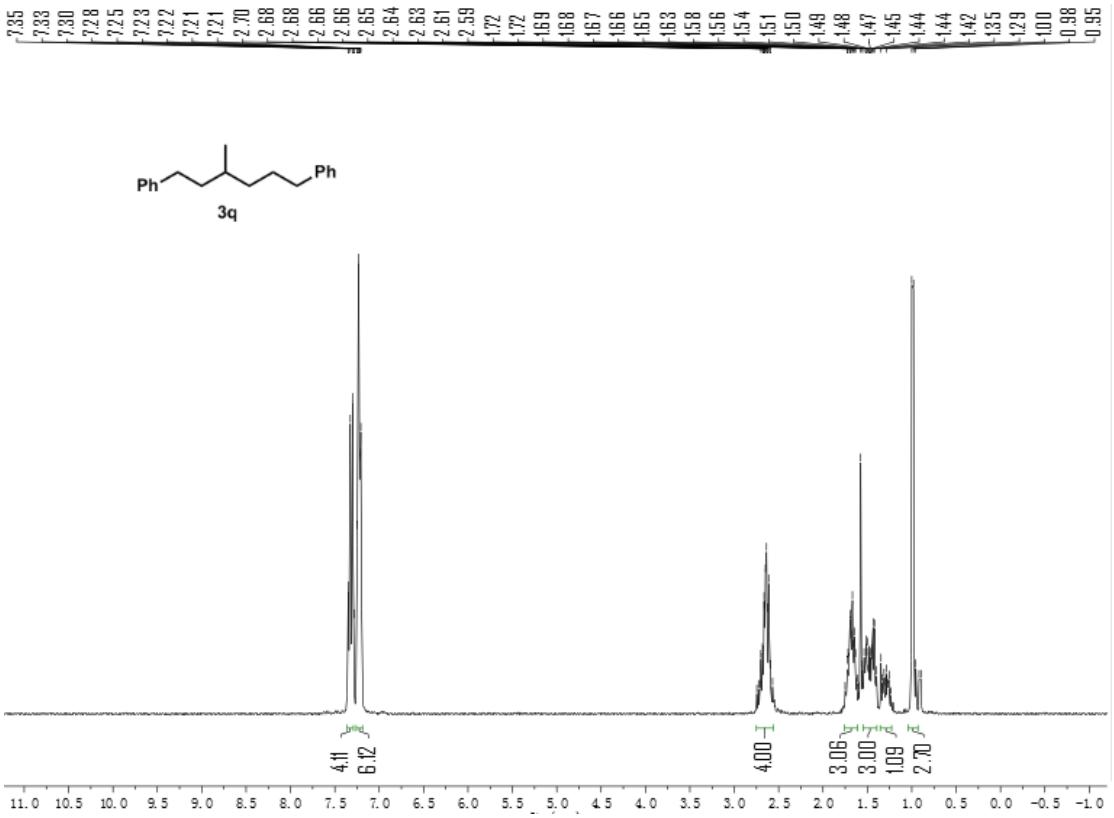
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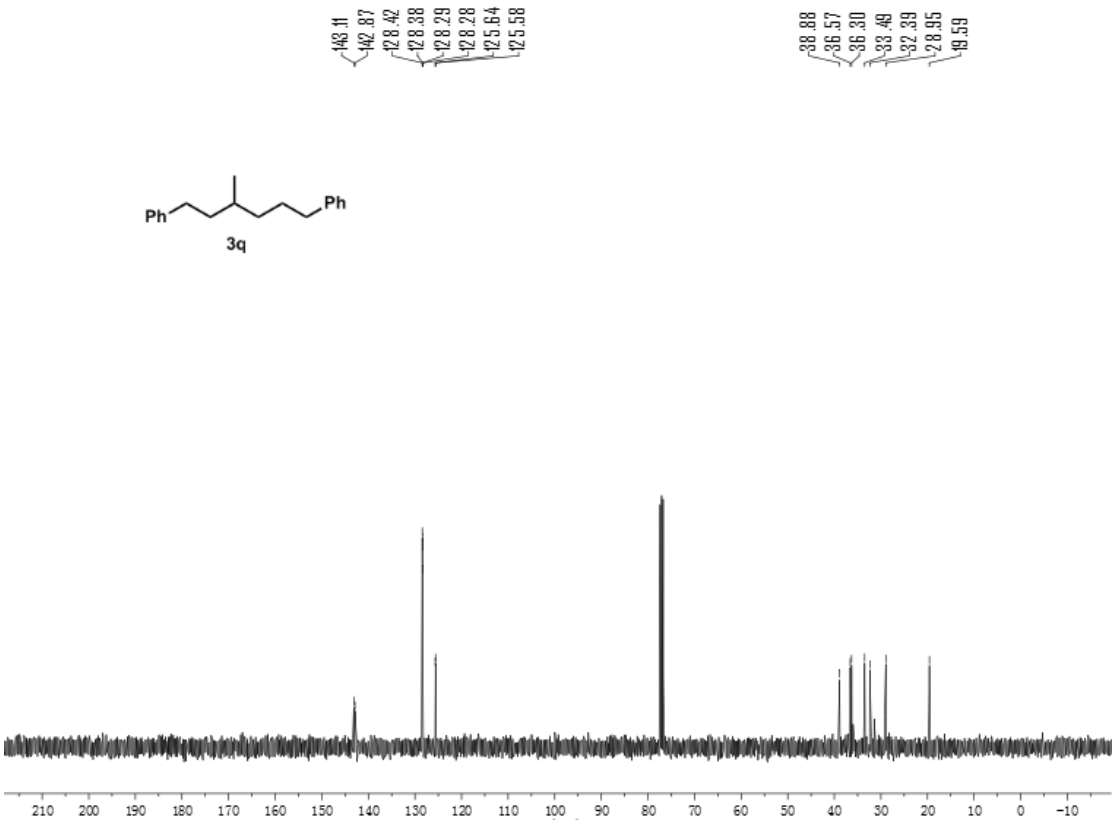
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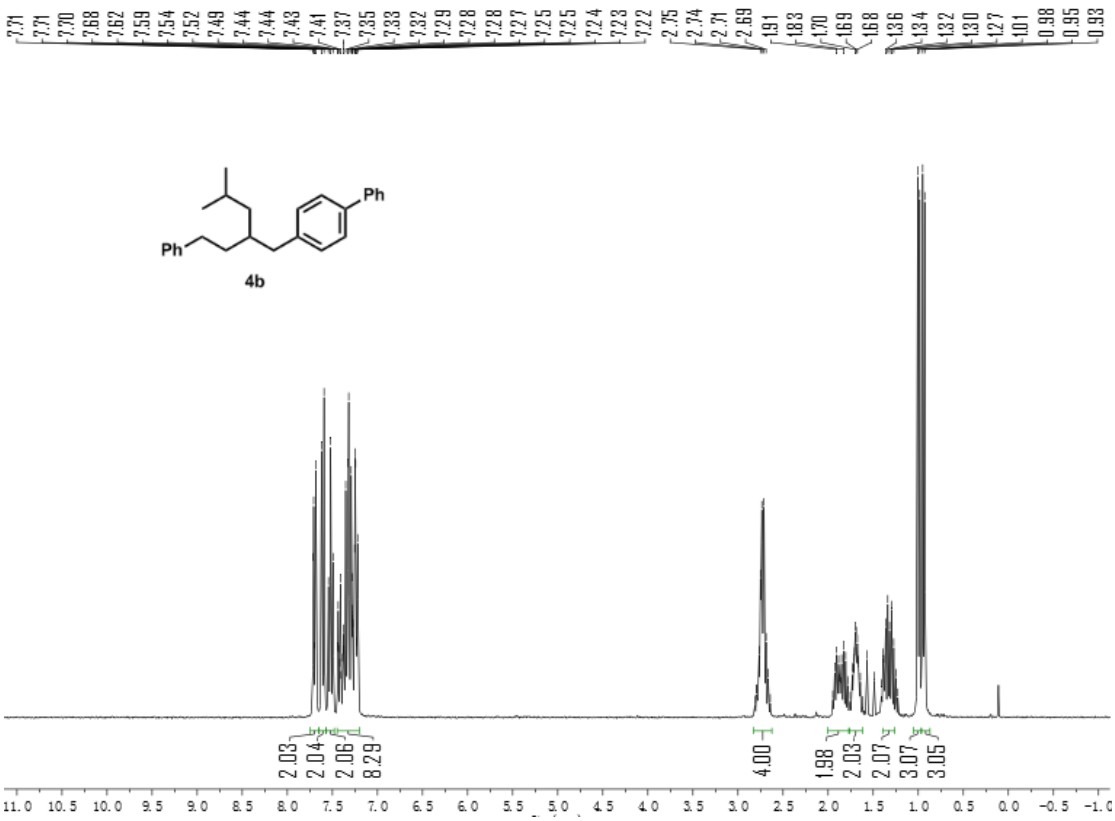
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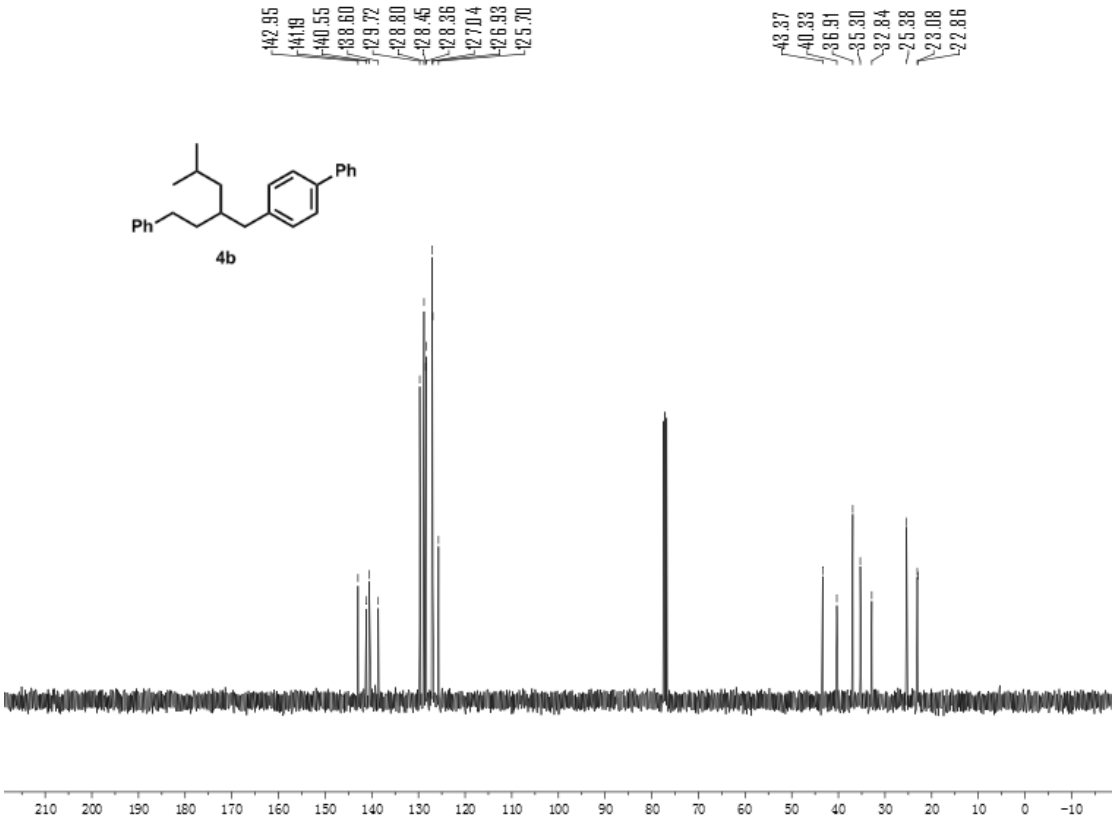
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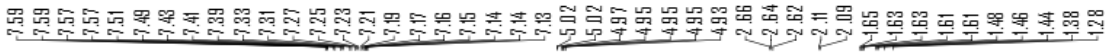

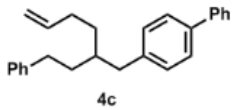

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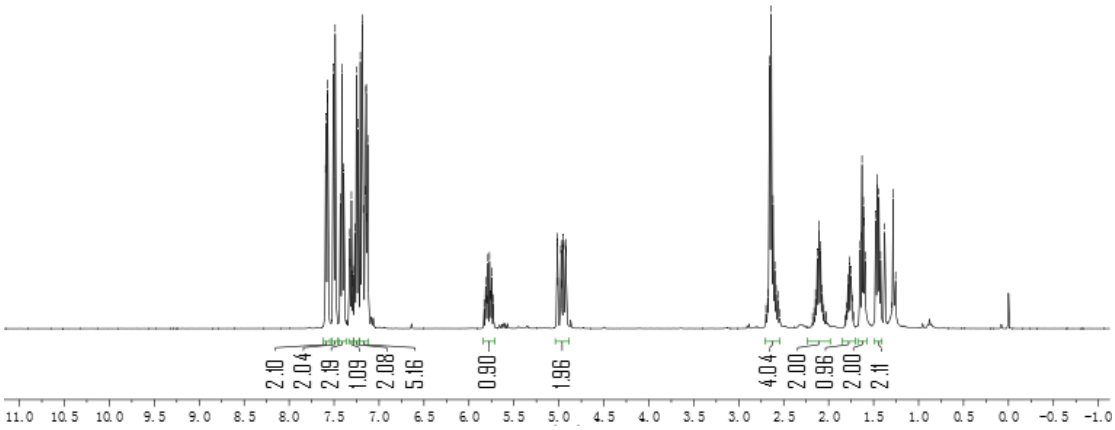

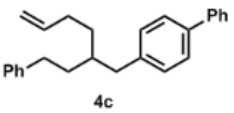

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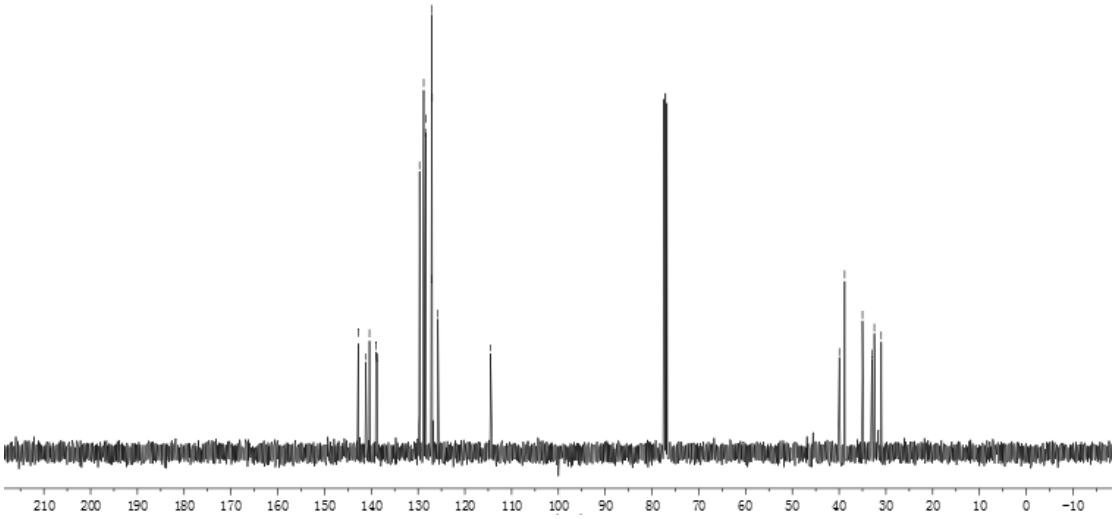

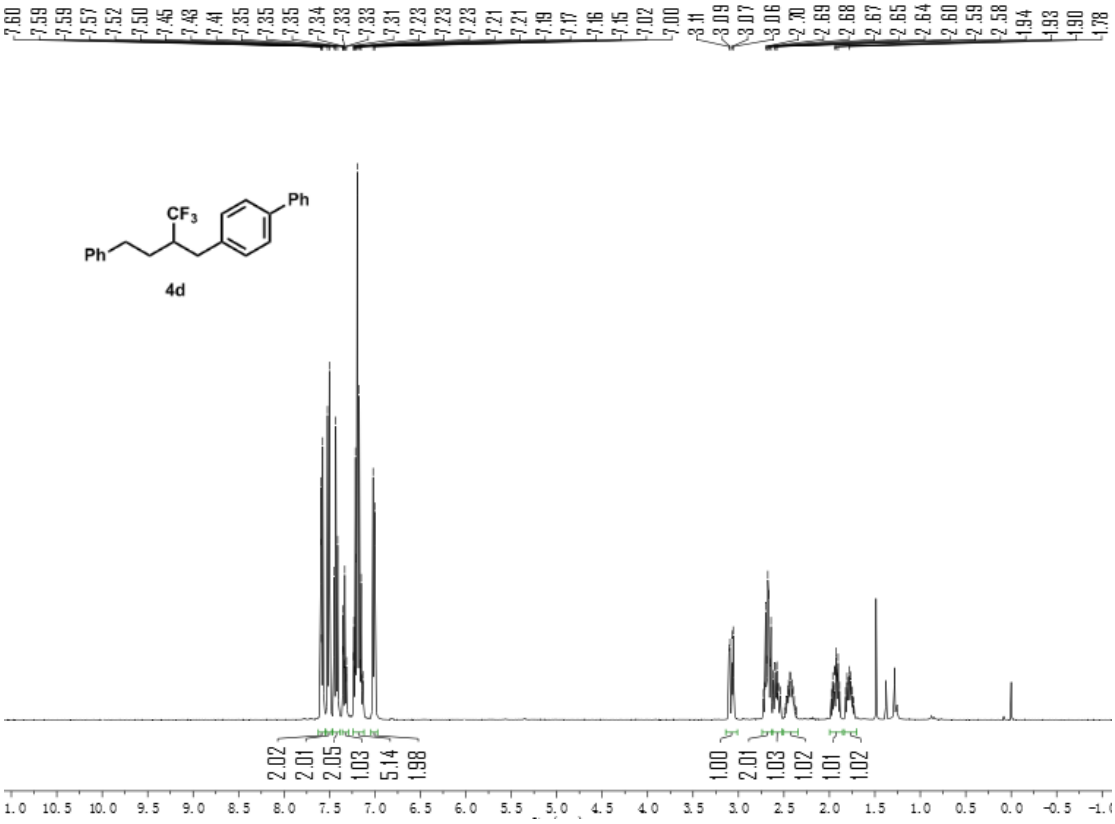
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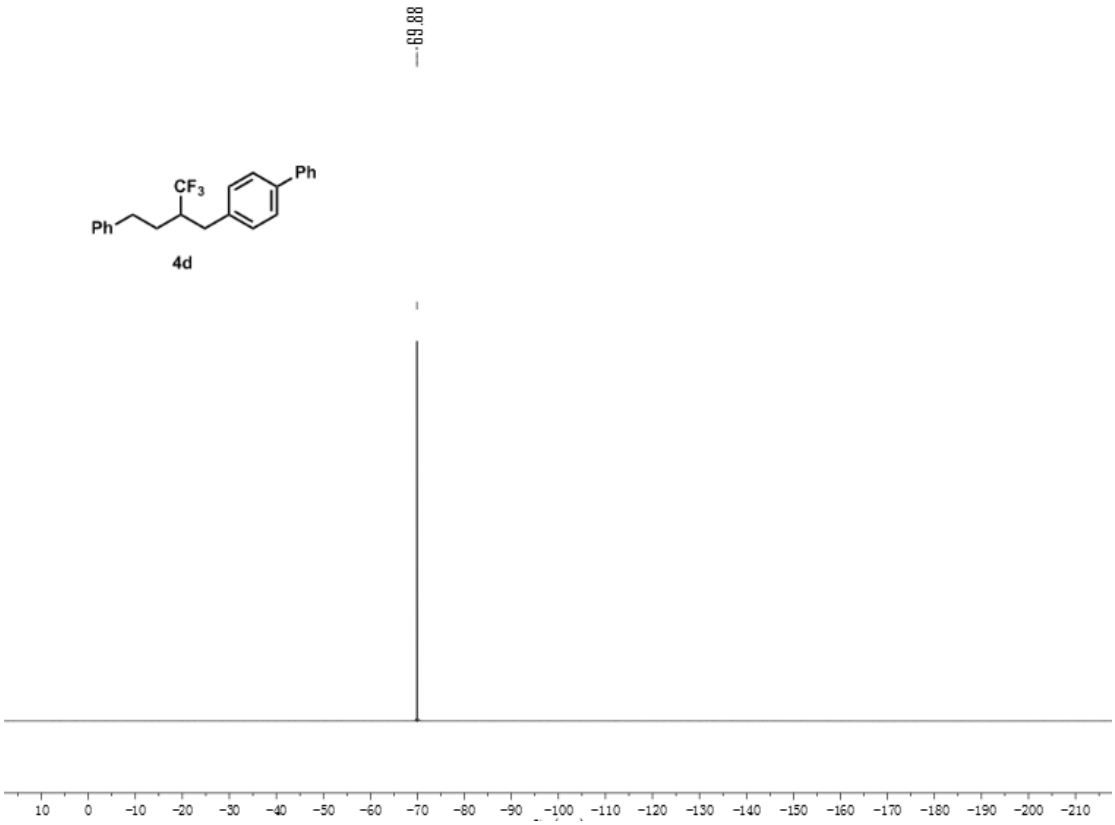
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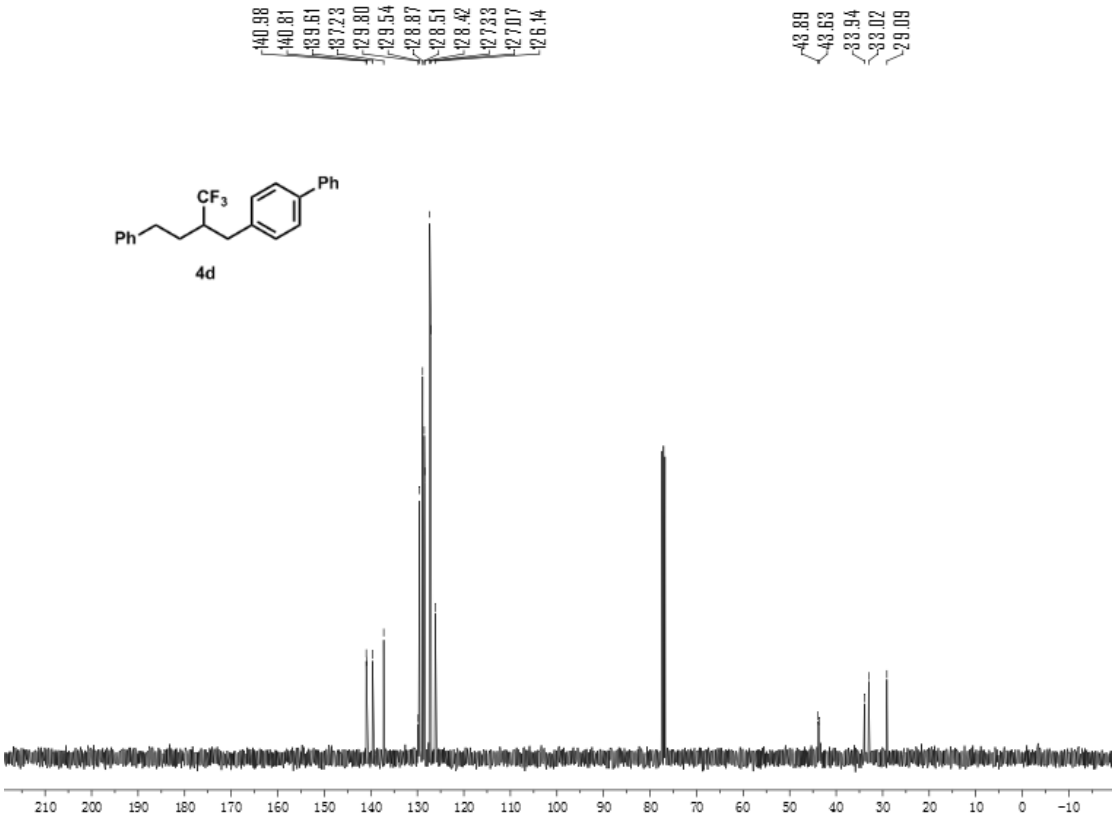
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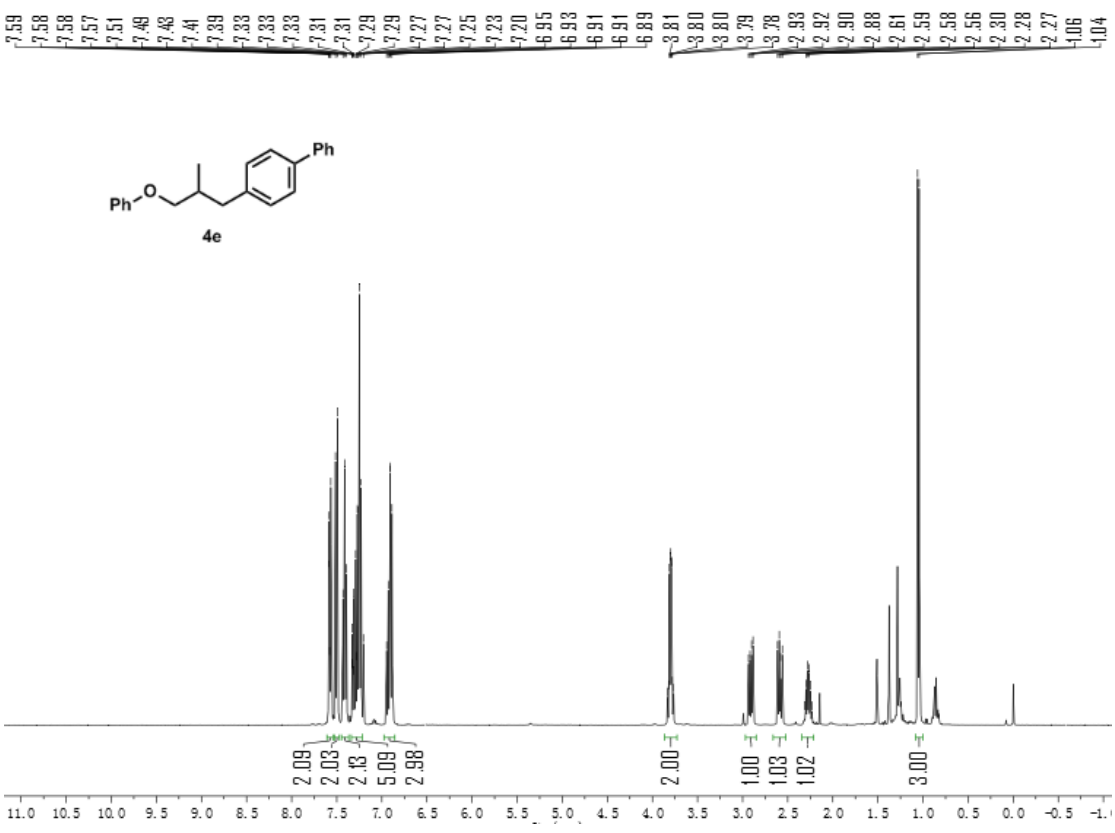
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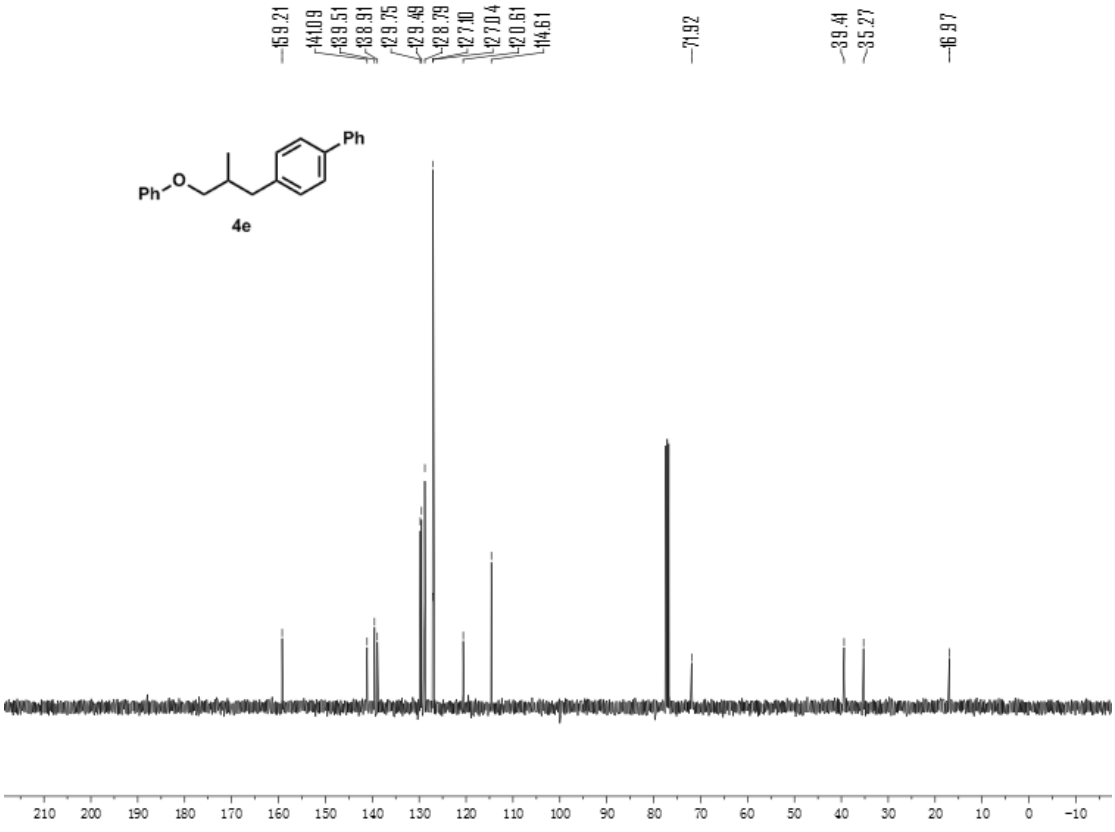
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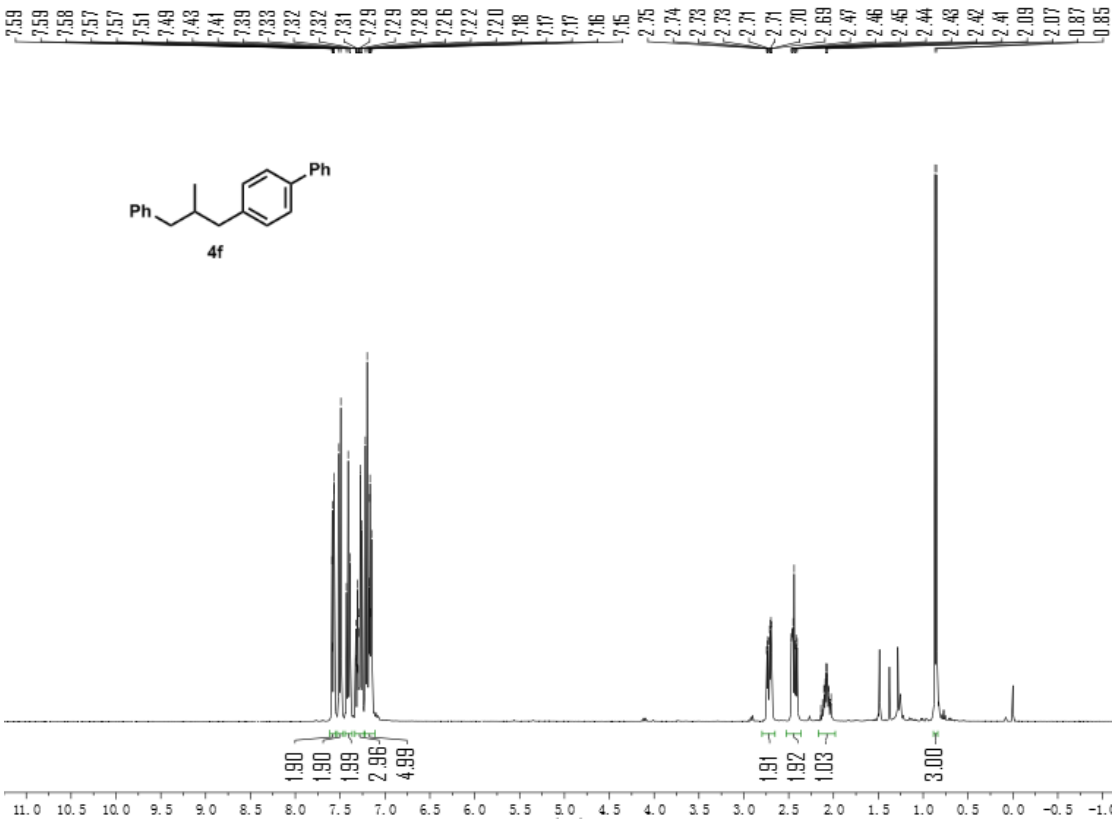
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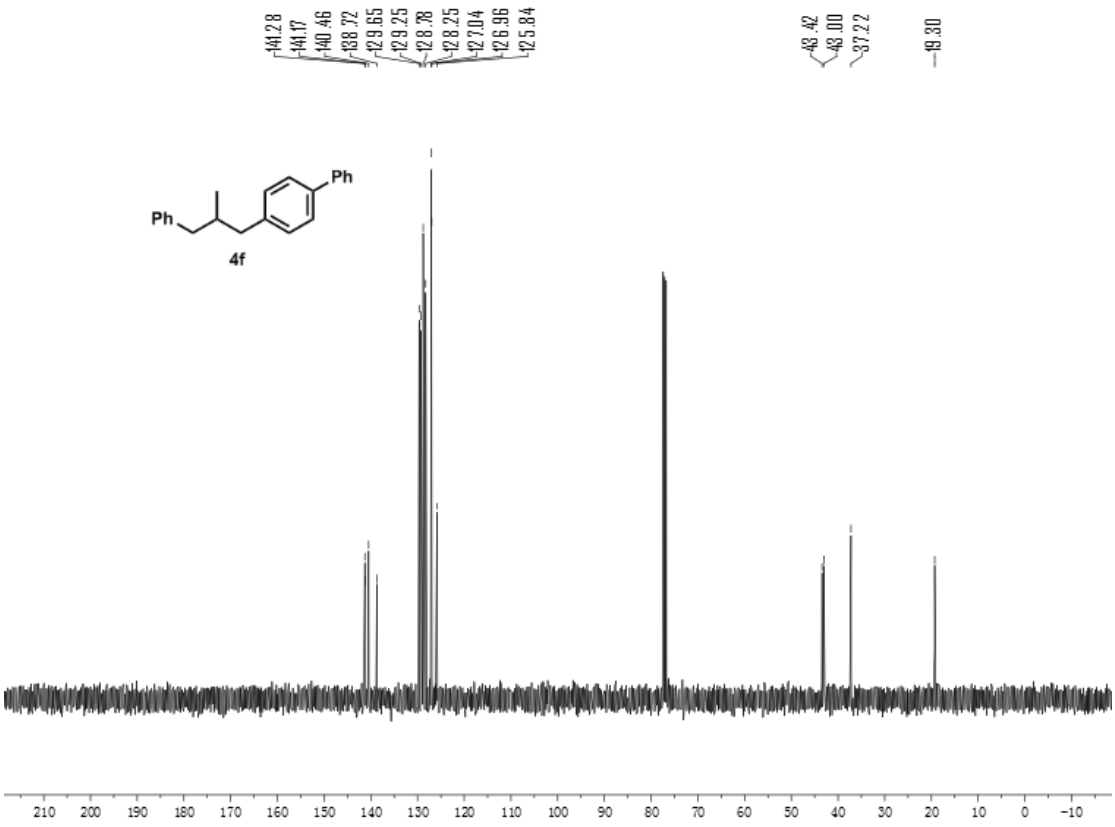
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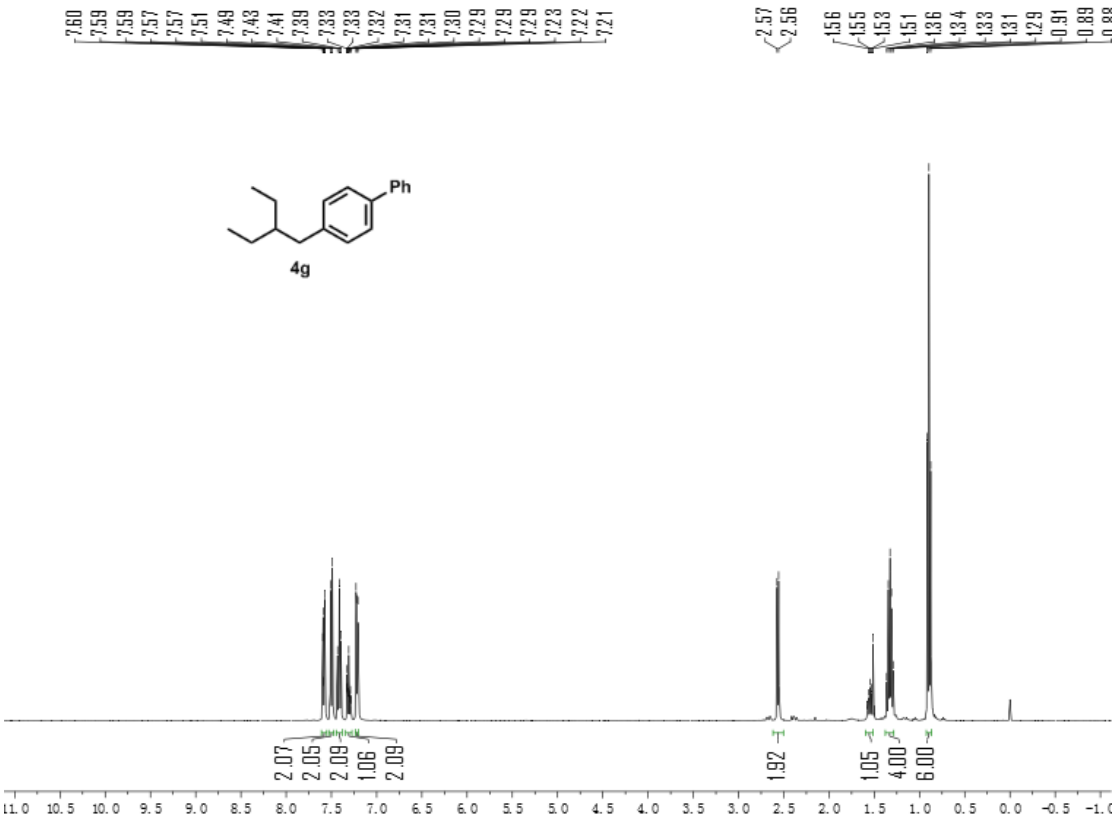
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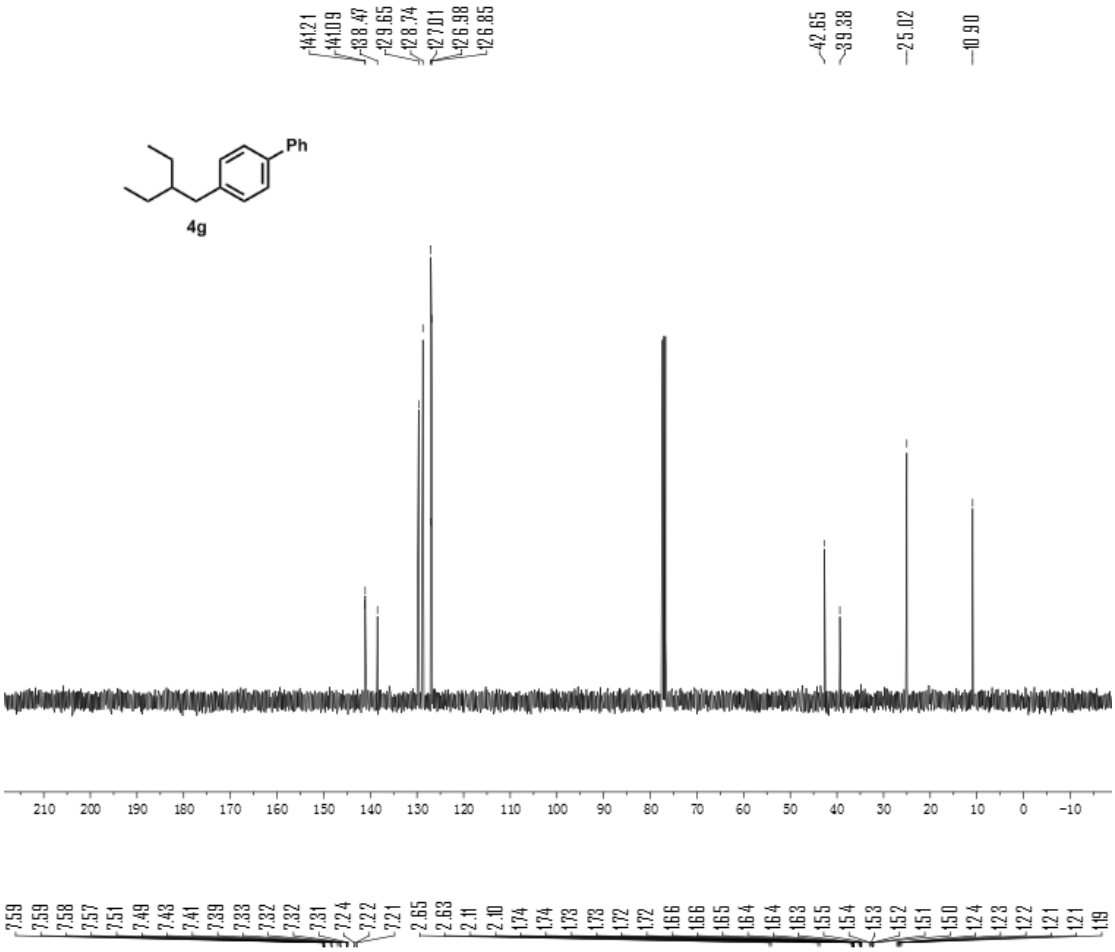
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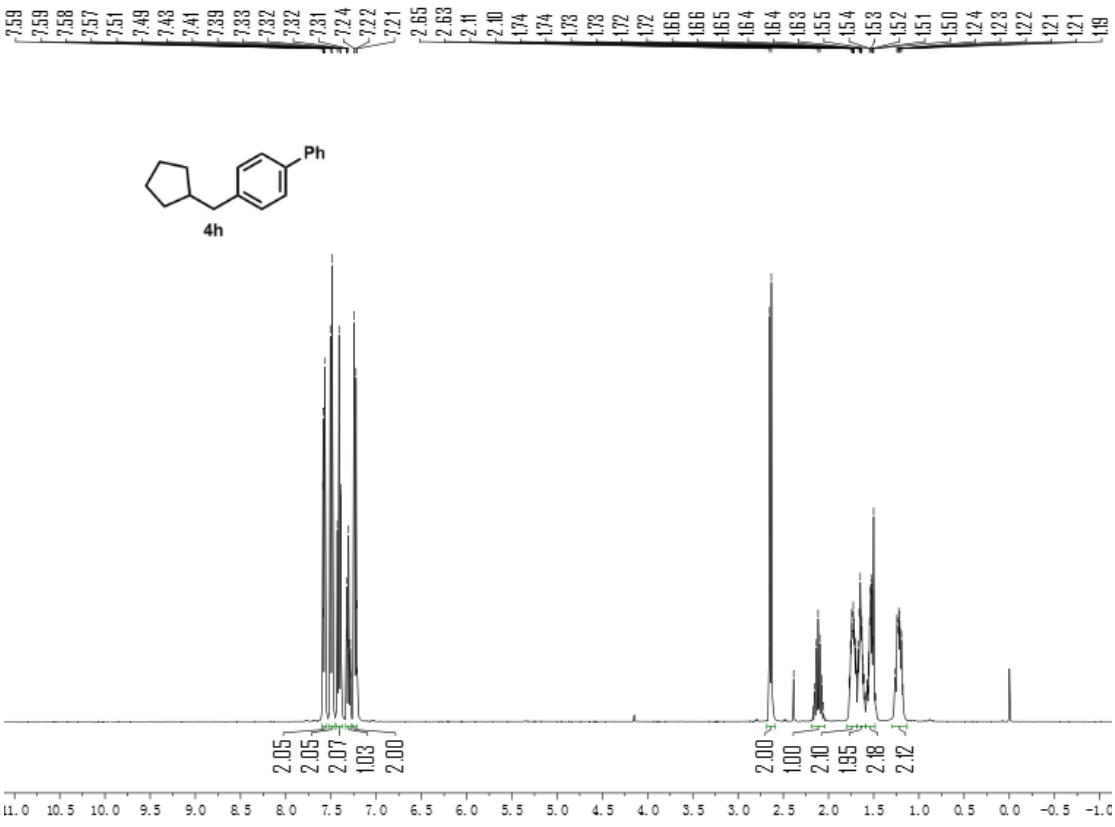
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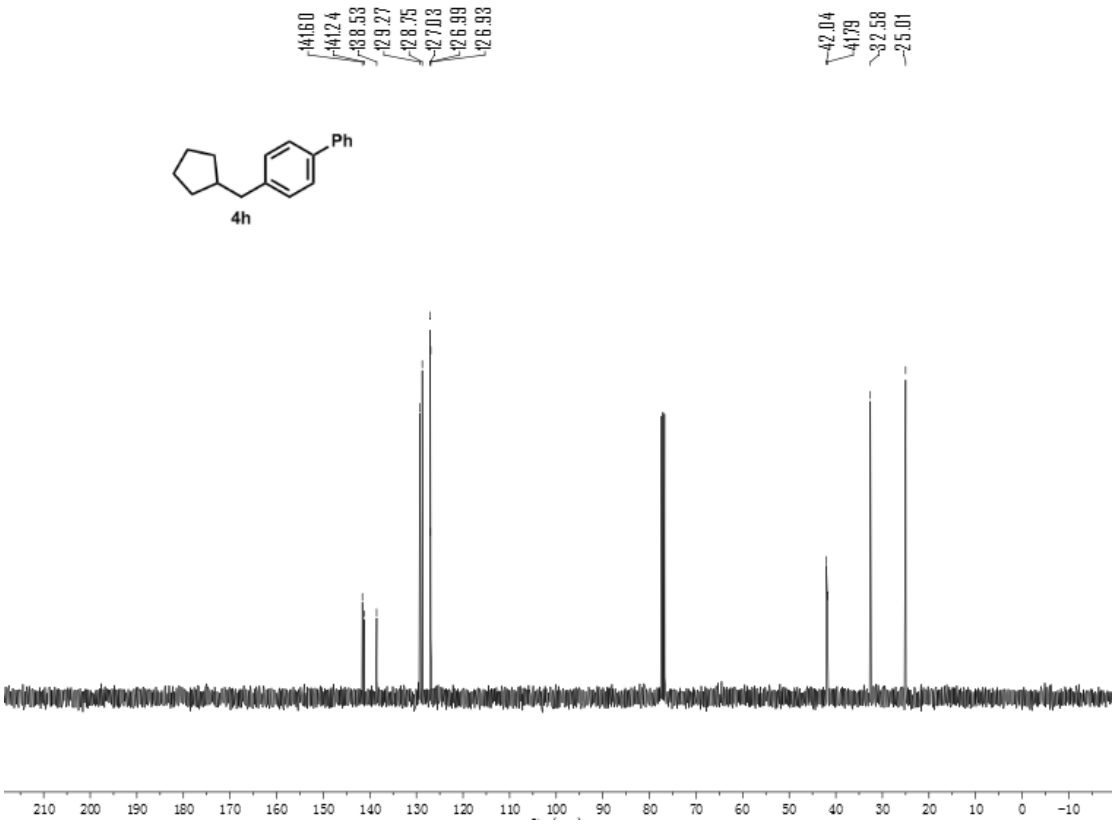
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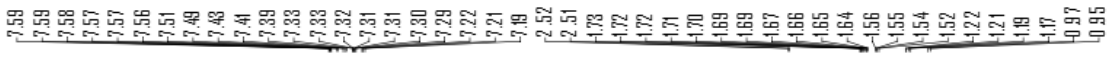
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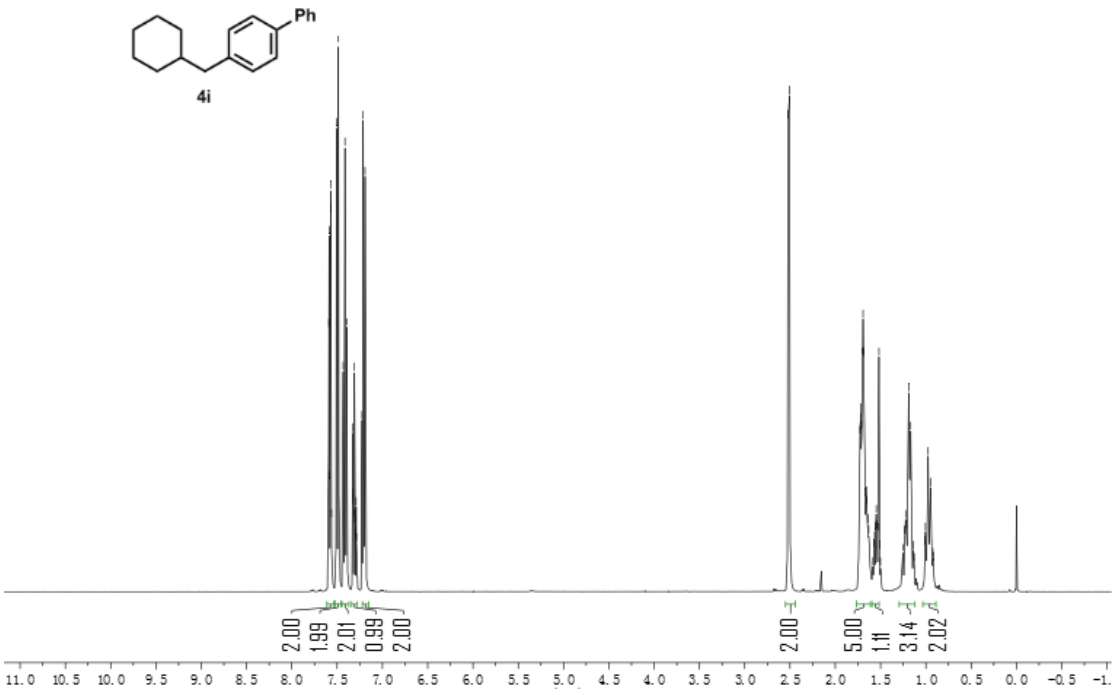
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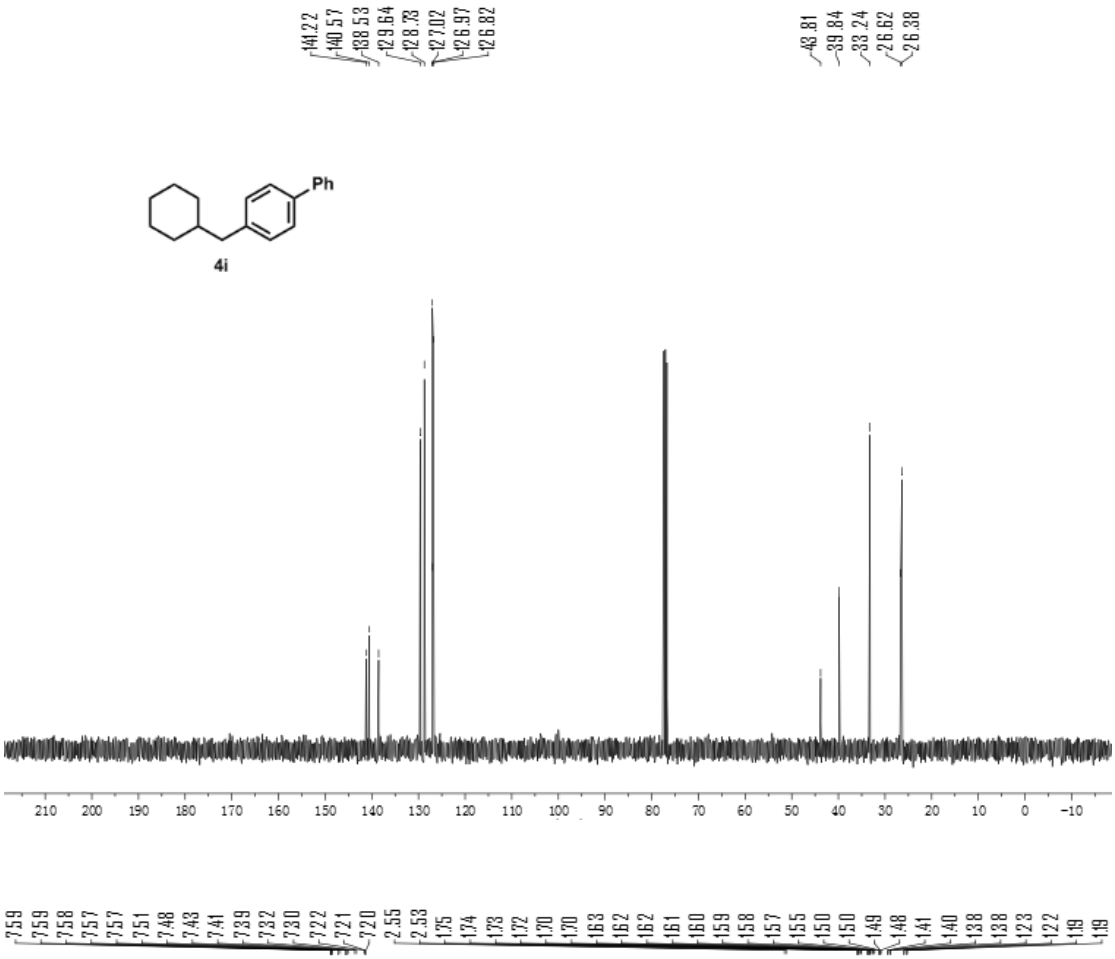
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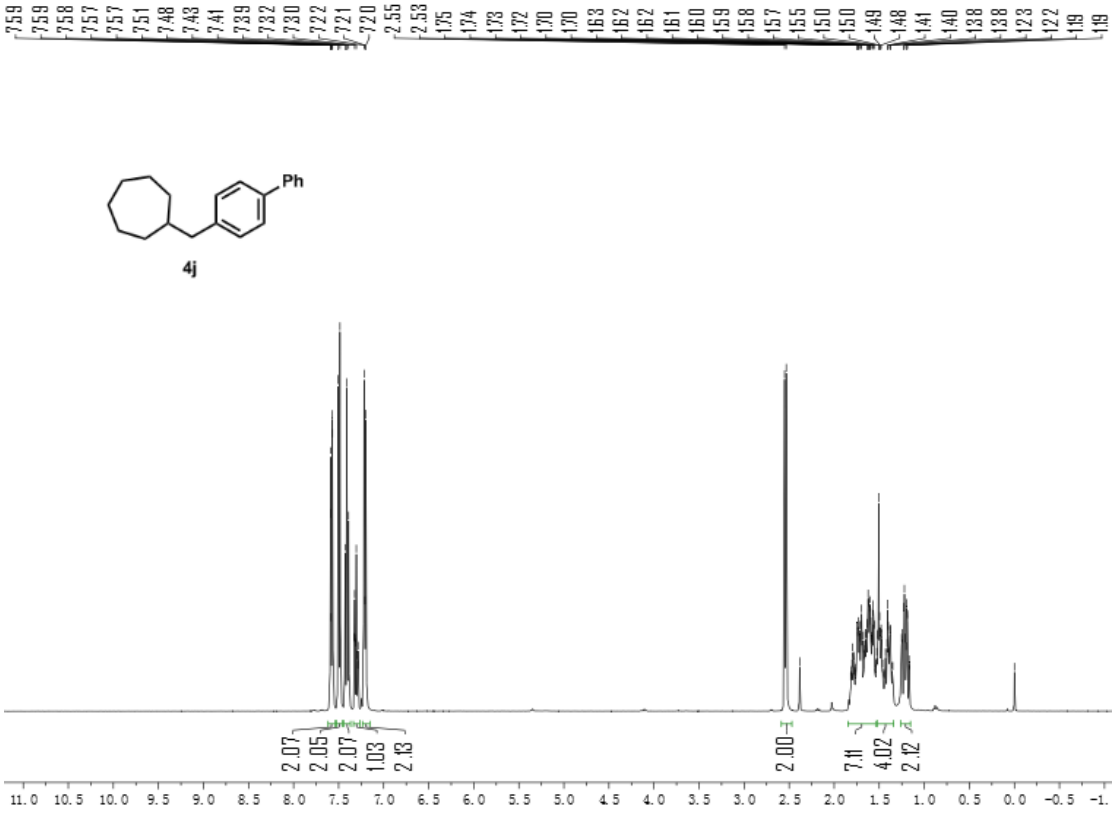
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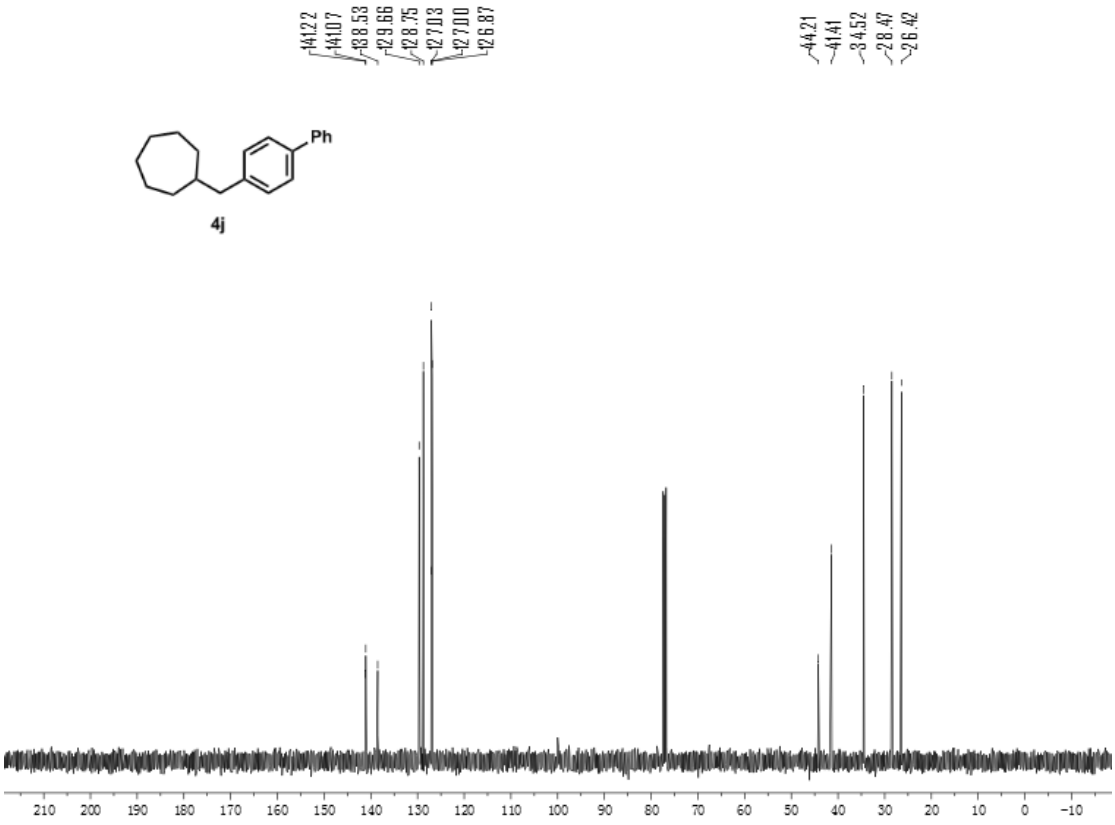
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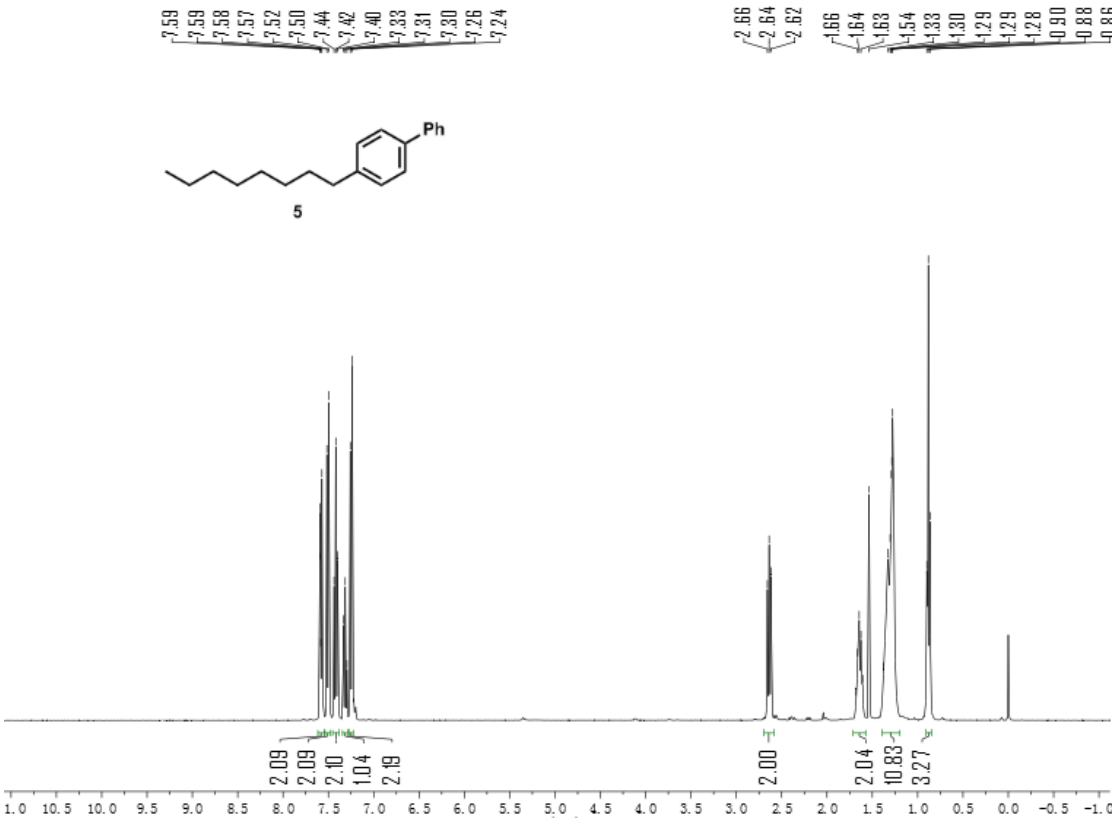
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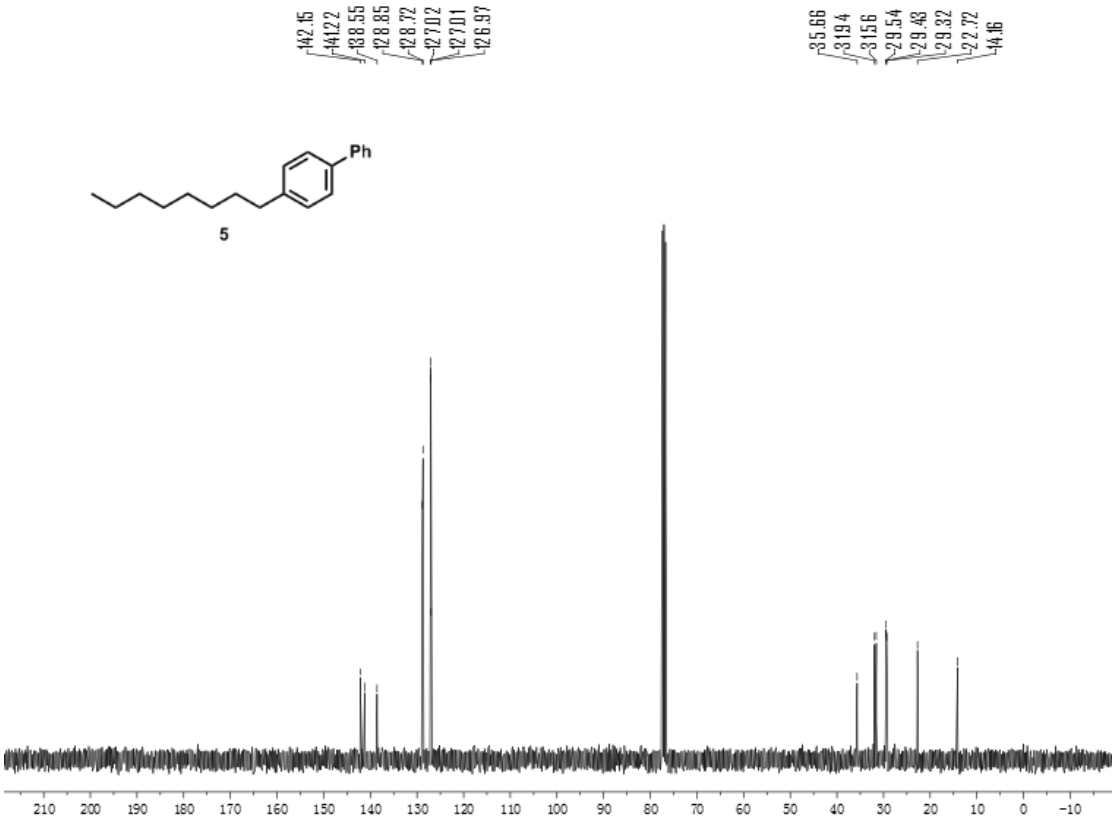
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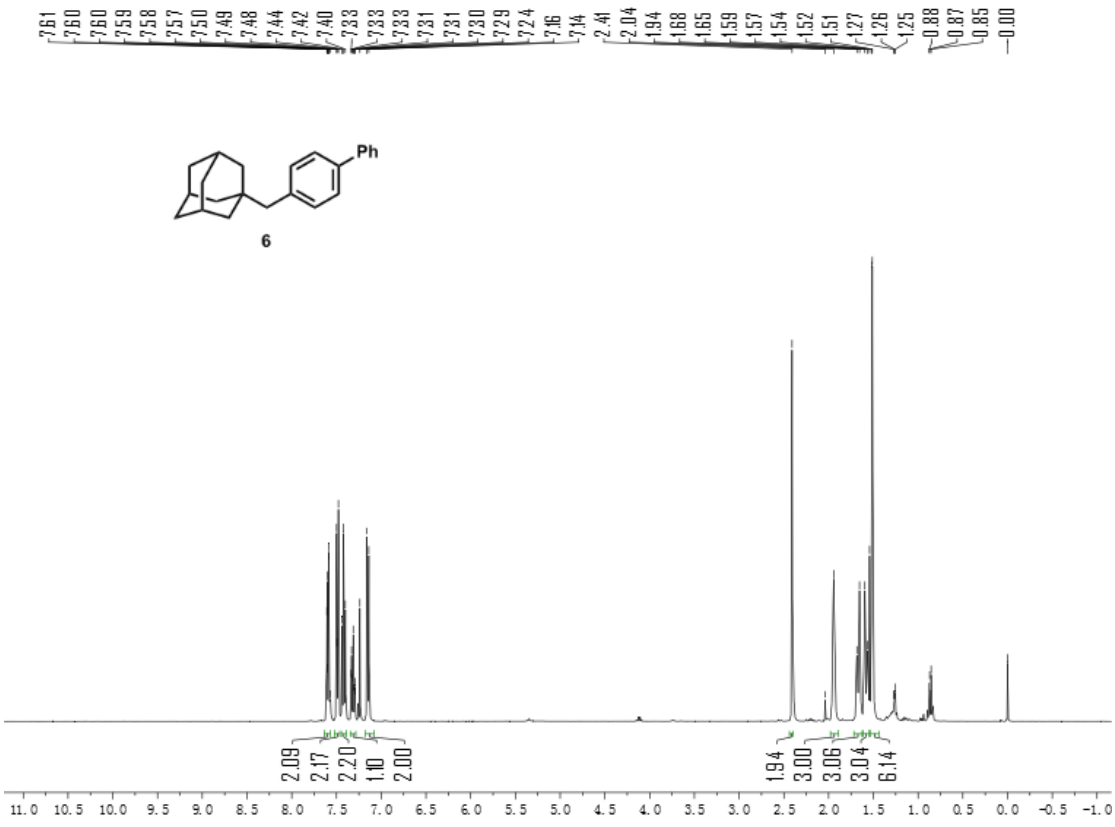
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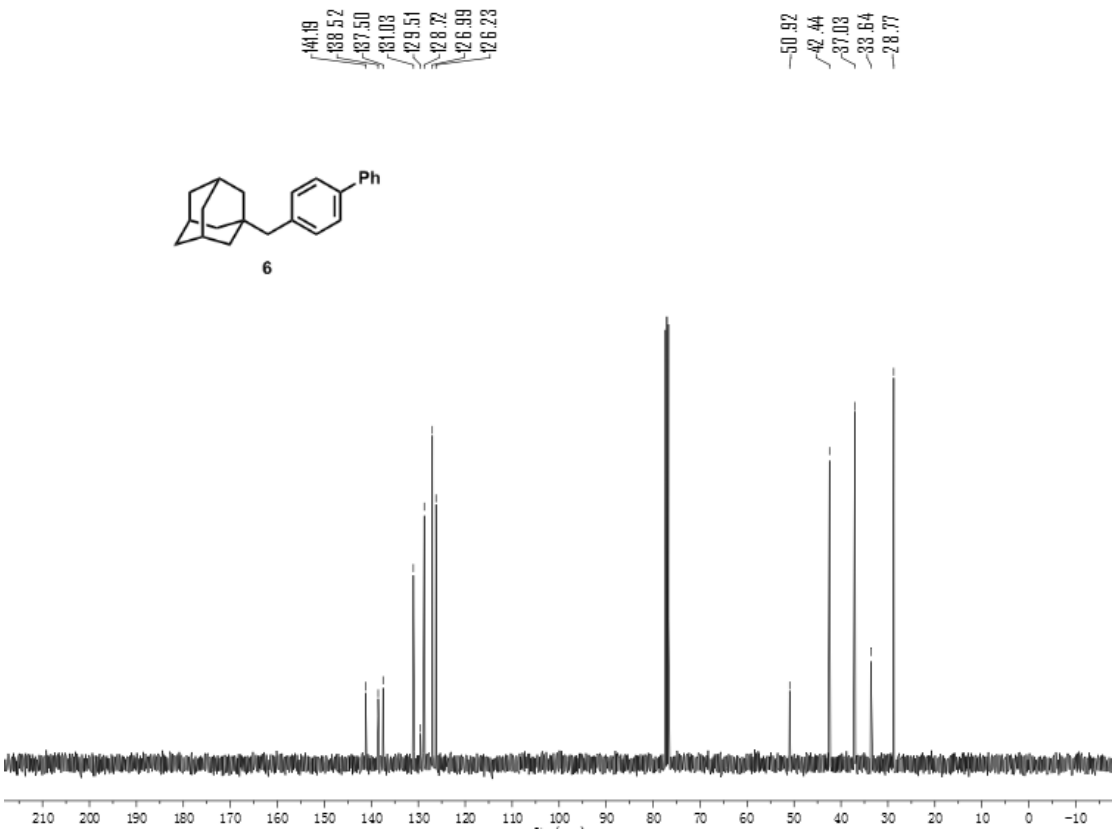
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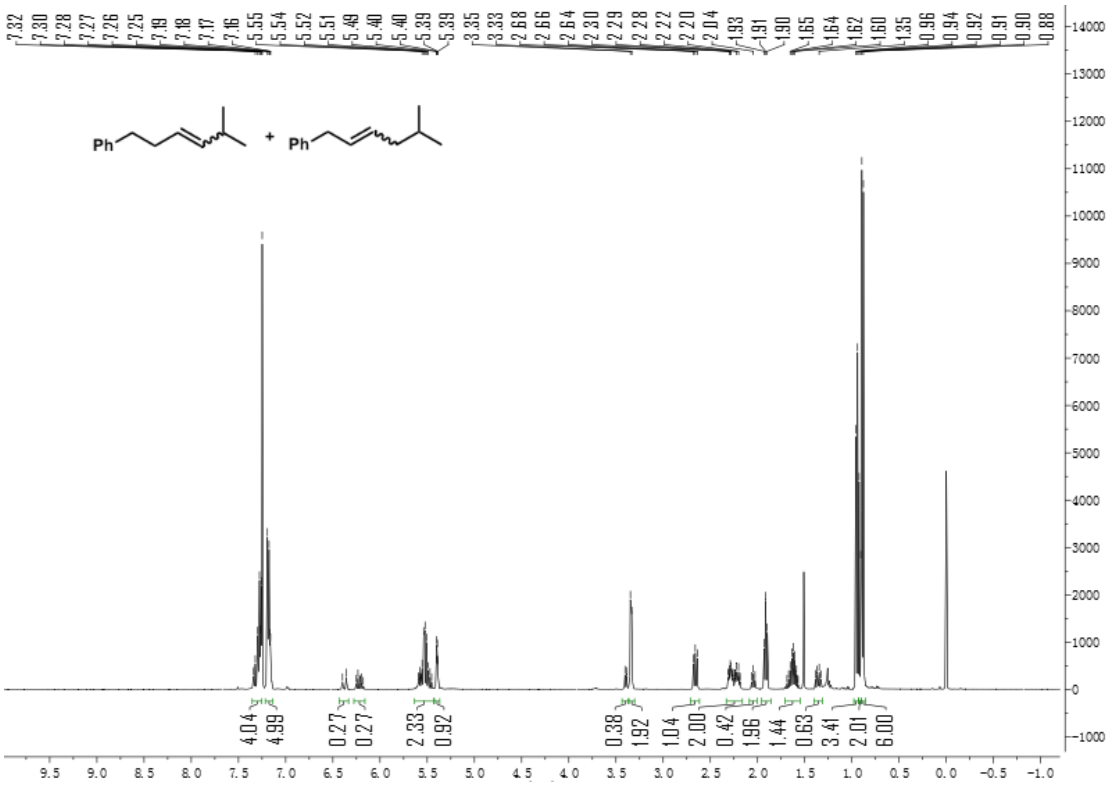
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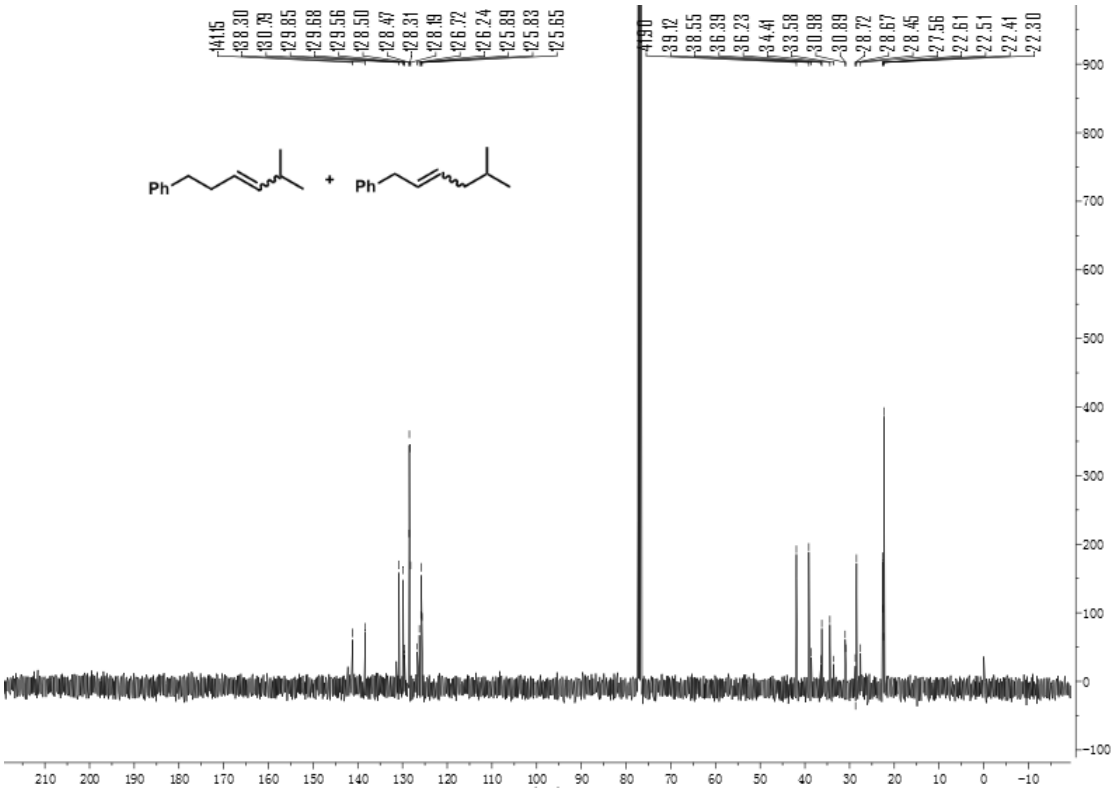
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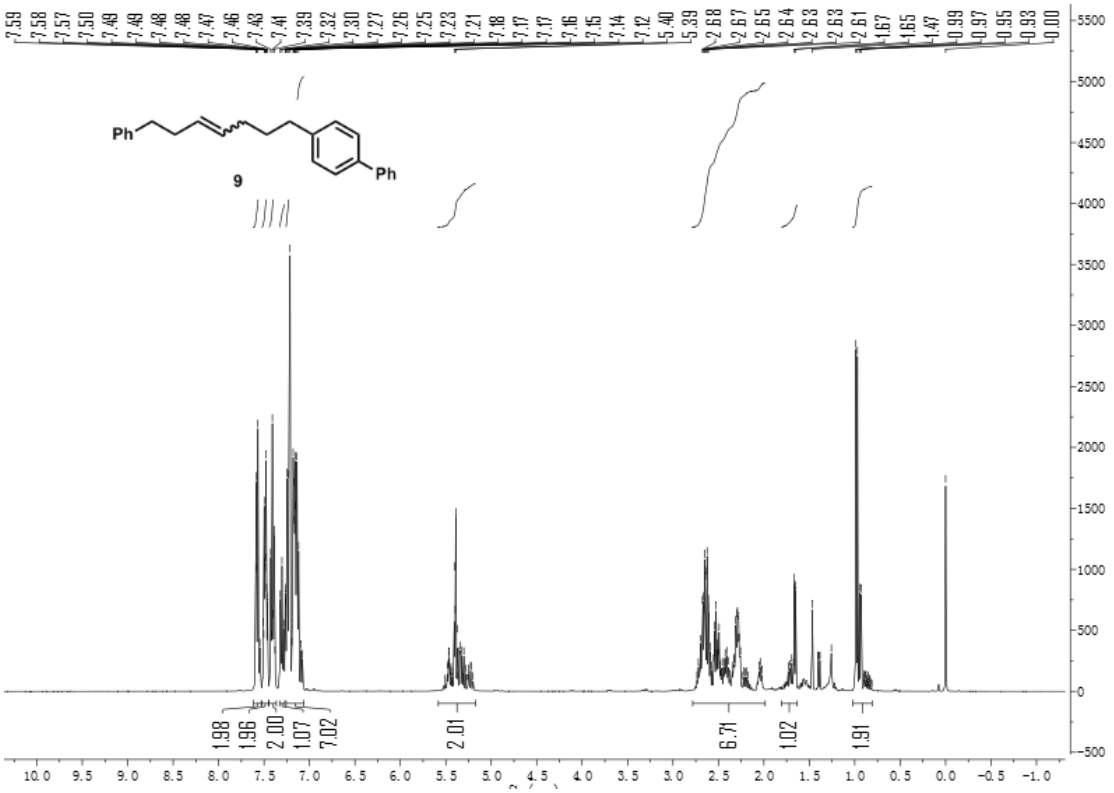
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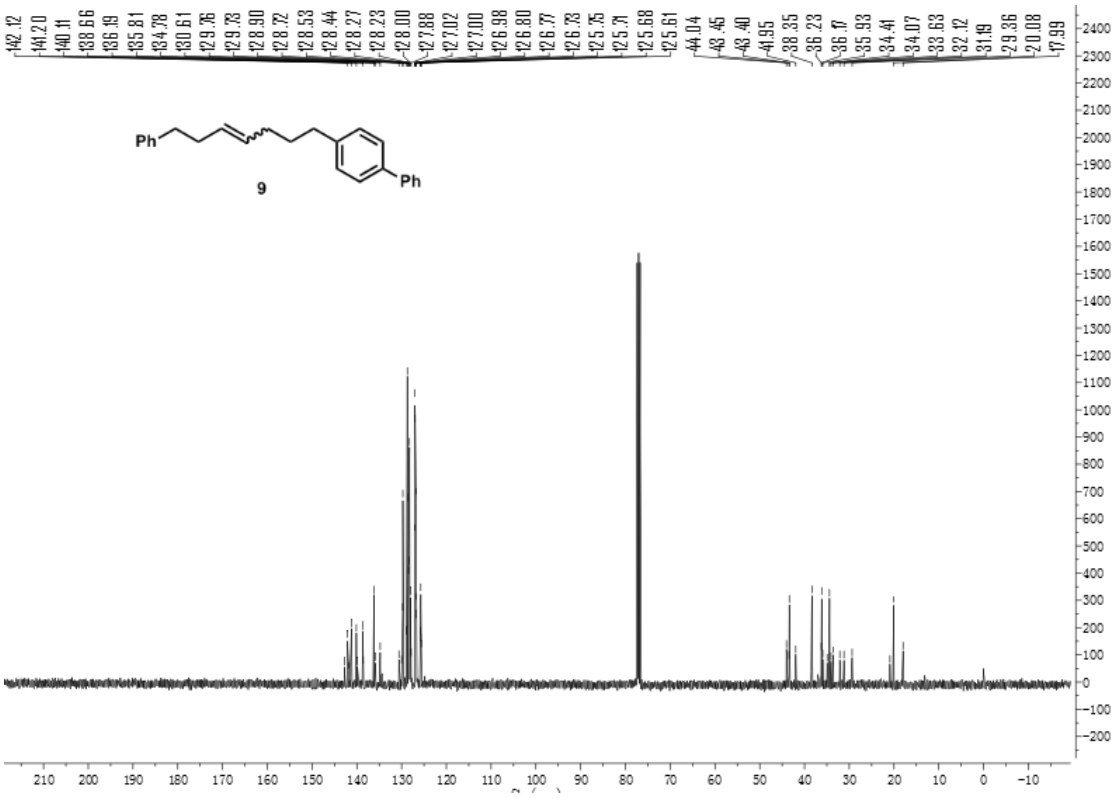
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