

SUPPORTING INFORMATION

for

Neocuproine-KO^tBu Promoted Intramolecular Cross Coupling to Approach Fused Rings

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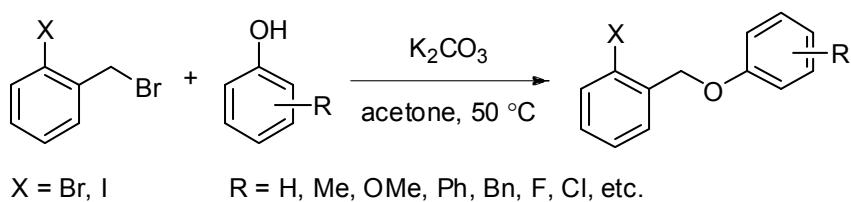
General Experimental Section:

Analytic methods. All the analytic methods, GC, MS, IR, and HRMS were performed by the State-Authorized Analytical Center at Peking University. The data GC-yields were obtained after amendment by standard curve, with the *n*-dodecane as the internal standard. ^1H NMR and ^{13}C NMR data were obtained on Varian 200 M, 300 M and Bruker 400 M nuclear resonance spectrometers with CDCl_3 as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^1H NMR spectrum as 0.00 ppm (chloroform, 7.26 ppm). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant (*J* values) in Hz and integration. Chemical shifts for ^{13}C NMR spectra were recorded in ppm from tetramethylsilane using the central peak of CDCl_3 (77.0 ppm) as the internal standard. Flash column chromatography was performed using 200-300 mesh silica with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm, 365 nm).

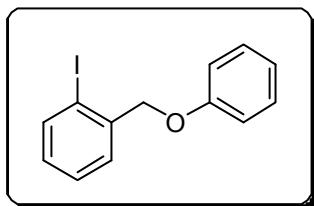
General preparation for chemicals. All the transition metal salts and all the substrates aryl iodides/bromides were purchased from Alfa Aesar China (Tianjin) Chemical Co., Ltd. and Acros Chemical Co. without any further purification. All the reagents and solvents were anhydrous.

General Experimental Procedures and Characterization Data:

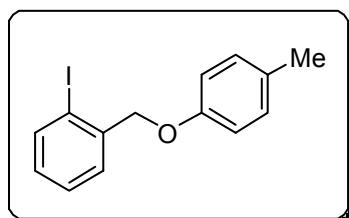
Synthesis of Ethers



The substituted ethers were synthesized according to the literature procedure.¹ The characterization data of new compounds are showed as belows.

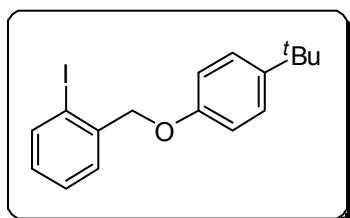


The titled compound was synthesized using the general procedure above and obtained as colorless oil in 97% isolated yield. ¹H NMR (CDCl_3 , 400 MHz): δ 5.09 (s, 2H), 7.02-7.04 (m, 4H), 7.33-7.42 (m, 3H), 7.55-7.57 (m, 1H), 7.90-7.91 (m, 1H). ¹³C NMR (CDCl_3 , 100 MHz): δ 73.9, 97.1, 115.0, 121.2, 128.4, 128.6, 129.4, 129.5, 139.2, 158.4. FTIR (cm^{-1}): 2955, 1598, 1494, 1240, 1013, 749. MS (EI): found: 310 (M^+), calcd for $\text{C}_{13}\text{H}_{11}\text{IO}$ (M^+): 310. HRMS (ESI Pos): $[\text{C}_{13}\text{H}_{11}\text{IO} + \text{H}]^+$: found: 310.99251, calc. 310.99328.



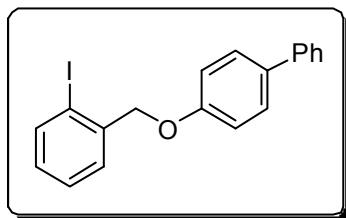
The titled compound was synthesized using the general procedure above and obtained as colorless oil in 100% isolated yield. ¹H NMR (CDCl_3 , 400 MHz): δ 2.28 (s, 3H), 5.00 (s, 2H), 6.86-6.88 (m, 2H), 6.98-7.01 (m, 1H), 7.08-7.10 (m, 2H), 7.32-7.36 (m, 1H), 7.49-7.51 (m, 1H), 7.83-7.85 (m, 1H). ¹³C NMR (CDCl_3 , 100 MHz): δ 20.5, 74.1, 97.1, 114.8, 128.3, 128.6, 129.3, 129.9, 130.4, 139.2, 139.4, 156.3. FTIR (cm^{-1}): 2916, 1505, 1234, 1010, 816, 740. MS (EI): found: 324 (M^+), calcd for $\text{C}_{14}\text{H}_{13}\text{IO}$ (M^+): 324. HRMS (ESI Pos): $[\text{C}_{14}\text{H}_{13}\text{IO} + \text{H}]^+$: found: 324.99251, calc. 324.99328.

$\text{H}]^+$: found: 325.00813, calc. 325.00839.



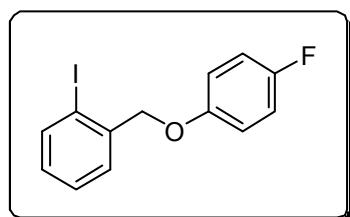
4-(2-iodobenzyloxy)-1-*tert*-butylbenzene.

The titled compound was synthesized using the general procedure above and obtained as colorless oil in 99% isolated yield. ^1H NMR (CDCl_3 , 400 MHz): δ 1.29 (s, 9H), 5.00 (s, 2H), 6.89-6.99 (m, 3H), 7.29-7.31 (m, 3H), 7.49-7.50 (m, 1H), 7.81-7.83 (m, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 31.5, 34.1, 74.0, 97.1, 114.4, 126.2, 128.3, 128.6, 129.3, 139.2, 139.4, 156.2. FTIR (cm^{-1}): 2956, 1510, 1242, 1184, 1013, 828, 746. MS (EI): found: 366 (M^+), calcd for $\text{C}_{17}\text{H}_{19}\text{IO}$ (M^+): 366. HRMS (ESI Pos): $[\text{C}_{17}\text{H}_{19}\text{IO} + \text{H}]^+$: found: 367.05512, calc. 367.05588.



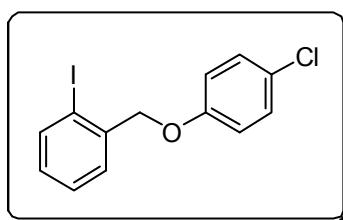
4-(2-iodobenzyloxy)-1-phenylbenzene.

The titled compound was synthesized using the general procedure above and obtained as white solid in 100% isolated yield. ^1H NMR (CDCl_3 , 400 MHz): δ 5.08 (s, 2H), 7.02-7.06 (m, 3H), 7.23-7.42 (m, 4H), 7.52-7.54 (m, 5H), 7.86-7.88 (m, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 74.1, 97.1, 115.2, 126.7, 128.2, 128.4, 128.6, 128.7, 129.5, 134.3, 139.1, 139.3, 140.7, 158.0. FTIR (cm^{-1}): 2923, 1518, 1485, 1265, 1244, 1008, 827, 738. MS (EI): found: 386 (M^+), calcd for $\text{C}_{19}\text{H}_{15}\text{IO}$ (M^+): 386. HRMS (ESI Pos): $[\text{C}_{19}\text{H}_{15}\text{IO} + \text{H}]^+$: found: 387.02389, calc. 387.02458.



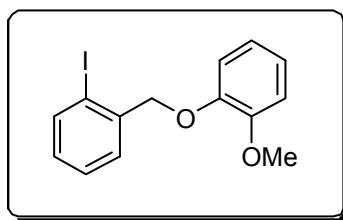
4-(2-iodobenzyl)-1-fluorobenzene.

The titled compound was synthesized using the general procedure above and obtained as colorless oil in 96% isolated yield. ^1H NMR (CDCl_3 , 400 MHz): δ 4.99 (s, 2H), 6.90-7.03 (m, 5H), 7.33-7.37 (m, 1H), 7.47-7.49 (m, 1H), 7.84-7.88 (m, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 74.6, 97.2, 115.9 (d, J = 23.1 Hz), 116.6 (d, J = 8.0 Hz), 128.4, 128.6, 129.5, 139.0, 139.3, 154.6, 157.6 (d, J = 237.4 Hz). FTIR (cm^{-1}): 2918, 1504, 1221, 1009, 828, 743. MS (EI): found: 328 (M^+), calcd for $\text{C}_{13}\text{H}_{10}\text{FIO}$ (M^+): 328. HRMS (ESI Pos): $[\text{C}_{13}\text{H}_{10}\text{FIO} + \text{H}]^+$: found: 328.98303, calc. 328.98386.



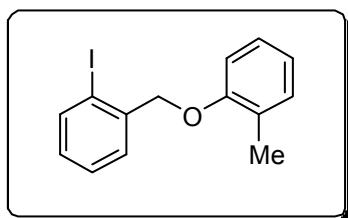
4-(2-iodobenzyl)-1-chlorobenzene.

The titled compound was synthesized using the general procedure above and obtained as white solid in 100% isolated yield. ^1H NMR (CDCl_3 , 400 MHz): δ 5.01 (s, 2H), 6.90 (d, J = 2.2 Hz, 2H), 7.00-7.04 (m, 1H), 7.24 (d, J = 2.2 Hz, 2H), 7.34-7.37 (m, 1H), 7.46-7.47 (m, 1H), 7.85-7.89 (m, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 74.2, 97.2, 116.3, 126.2, 128.4, 128.6, 129.4, 129.6, 138.8, 139.3, 157.0. FTIR (cm^{-1}): 2922, 1489, 1240, 1012, 818, 749. MS (EI): found: 344 (M^+), calcd for $\text{C}_{13}\text{H}_{10}\text{ClIO}$ (M^+): 344. HRMS (ESI Pos): $[\text{C}_{13}\text{H}_{10}\text{ClIO} + \text{H}]^+$: found: 344.95386, calc. 344.95431.



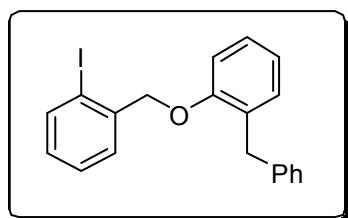
2-(2-iodobenzyl)-1-methoxybenzene.

The titled compound was synthesized using the general procedure above and obtained as white solid in 100% isolated yield. ^1H NMR (CDCl_3 , 400 MHz): δ 3.03 (s, 3H), 5.11 (s, 2H), 6.86-7.01 (m, 5H), 7.32-7.36 (m, 1H), 7.53-7.55 (m, 1H), 7.82-7.84 (m, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 56.1, 75.0, 96.6, 112.2, 114.5, 120.9, 121.8, 128.3, 128.4, 129.2, 139.1, 139.3, 147.9, 149.8. FTIR (cm^{-1}): 2923, 1506, 1251, 1223, 1122, 1006, 744. MS (EI): found: 340 (M^+), calcd for $\text{C}_{14}\text{H}_{13}\text{IO}_2$ (M^+): 340. HRMS (ESI Pos): $[\text{C}_{14}\text{H}_{13}\text{IO}_2 + \text{H}]^+$: found: 341.00342, calc. 341.00385.



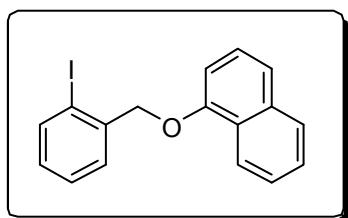
2-(2-iodobenzyloxy)-1-toluene.

The titled compound was synthesized using the general procedure above and obtained as white solid in 100% isolated yield. ^1H NMR (CDCl_3 , 400 MHz): δ 2.32 (s, 3H), 5.03 (s, 2H), 6.86-6.91 (m, 2H), 7.00-7.03 (m, 1H), 7.14-7.24 (m, 2H), 7.35-7.39 (m, 1H), 7.53-7.55 (m, 1H), 7.85-7.87 (m, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 16.4, 73.9, 96.9, 111.6, 120.9, 126.8, 127.1, 128.3, 129.3, 130.8, 139.2, 139.6, 156.5. FTIR (cm^{-1}): 2923, 1494, 1247, 1009, 741. MS (EI): found: 324 (M^+), calcd for $\text{C}_{14}\text{H}_{13}\text{IO}$ (M^+): 324. HRMS (ESI Pos): $[\text{C}_{14}\text{H}_{13}\text{IO} + \text{H}]^+$: found: 325.00900, calc. 325.00839.



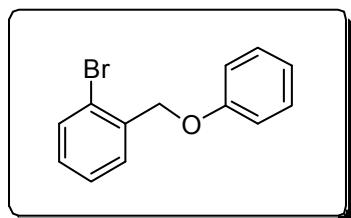
2-(2-iodobenzyloxy)-1-benzylbenzene.

The titled compound was synthesized using the general procedure above and obtained as white solid in 96% isolated yield. ^1H NMR (CDCl_3 , 400 MHz): δ 4.07 (s, 2H), 5.02 (s, 2H), 6.87-6.98 (m, 3H), 7.11-7.29 (m, 9H), 7.82-7.84 (m, 1H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 36.3, 73.8, 96.8, 111.8, 121.0, 125.8, 127.5, 128.3, 128.4, 129.0, 129.3, 129.9, 130.6, 139.1, 139.3, 140.9, 156.0. FTIR (cm^{-1}): 2926, 1495, 1447, 1238, 1011, 748. MS (EI): found: 400 (M^+), calcd for $\text{C}_{20}\text{H}_{17}\text{IO}$ (M^+): 400. HRMS (ESI Pos): $[\text{C}_{20}\text{H}_{17}\text{IO} + \text{H}]^+$: found: 401.03958, calc. 401.04023.



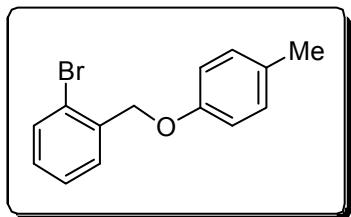
1-(2-iodobenzyloxy)-naphthalene.

The titled compound was synthesized using the general procedure above and obtained as light yellow solid in 98% isolated yield. ^1H NMR (CDCl_3 , 400 MHz): δ 5.24 (s, 2H), 6.87-6.89 (m, 1H), 7.04-7.05 (m, 1H), 7.36-7.51 (m, 4H), 7.62-7.65 (m, 1H), 7.81-7.82 (m, 1H), 7.89-7.91 (m, 1H), 8.37-8.38 (m, 1H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 74.1, 97.1, 105.5, 120.8, 122.2, 125.3, 125.8, 126.5, 127.5, 128.4, 128.6, 129.5, 134.6, 139.2, 139.3, 154.1. FTIR (cm^{-1}): 2923, 1467, 1400, 1277, 1100, 764. MS (EI): found: 360 (M^+), calcd for $\text{C}_{17}\text{H}_{13}\text{IO}$ (M^+): 360. HRMS (ESI Pos): $[\text{C}_{17}\text{H}_{13}\text{IO} + \text{H}]^+$: found: 361.00825, calc. 361.00893.



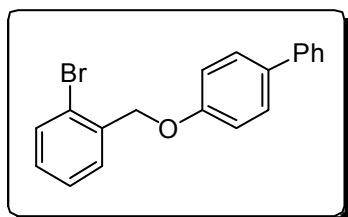
(2-bromobenzyl)benzene.

The titled compound was synthesized using the general procedure above and obtained as colorless oil in 92% isolated yield. ^1H NMR (CDCl_3 , 300 MHz): δ 5.13 (s, 2H), 6.95-7.00 (m, 3H), 7.14-7.19 (m, 1H), 7.27-7.34 (m, 3H), 7.54-7.58 (m, 2H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 69.3, 114.9, 121.2, 122.2, 127.5, 128.8, 129.2, 129.5, 132.6, 136.4, 158.4. FTIR (cm^{-1}): 3061, 1595, 1493, 1237, 1029, 748, 688. MS (EI): found: 263 (M^+), calcd for $\text{C}_{13}\text{H}_{11}\text{BrO}$ (M^+): 263. HRMS (ESI Pos): $[\text{C}_{13}\text{H}_{11}\text{BrO} + \text{H}]^+$: found: 263.00650, calc. 263.00715.



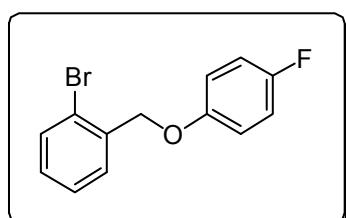
4-(2-bromobenzyl)-1-toluene.

The titled compound was synthesized using the general procedure above and obtained as colorless oil in 94% isolated yield. ^1H NMR (CDCl_3 , 300 MHz): δ 2.25 (s, 3H), 5.05 (s, 2H), 6.84-6.86 (m, 2H), 7.03-7.12 (m, 3H), 7.22-7.28 (m, 1H), 7.49-7.53 (m, 2H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 69.4, 114.7, 122.2, 127.4, 128.8, 129.0, 129.9, 130.3, 132.5, 136.5, 156.3. FTIR (cm^{-1}): 2919, 1510, 1240, 1026, 814, 744. MS (EI): found: 276 (M^+), calcd for $\text{C}_{14}\text{H}_{13}\text{BrO}$ (M^+): 276. HRMS (ESI Pos): $[\text{C}_{14}\text{H}_{13}\text{BrO} + \text{H}]^+$: found: 277.02227, calc. 277.02280.



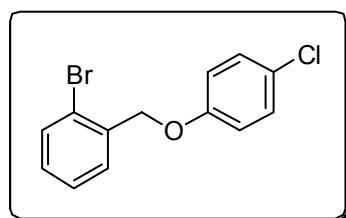
4-(2-bromobenzyl)phenylbenzene.

The titled compound was synthesized using the general procedure above and obtained as white solid in 90% isolated yield. ^1H NMR (CDCl_3 , 300 MHz): δ 5.17 (s, 2H), 7.03-7.07 (m, 2H), 7.15-7.21 (m, 1H), 7.27-7.30 (m, 2H), 7.32-7.38 (m, 2H), 7.41-7.60 (m, 6H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 69.5, 115.1, 122.3, 126.6, 127.6, 128.2, 128.7, 128.9, 129.2, 132.6, 134.3, 136.3, 140.7, 158.0. FTIR (cm^{-1}): 2918, 1516, 1483, 1240, 1026, 834, 763, 694. MS (EI): found: 338 (M^+), calcd for $\text{C}_{19}\text{H}_{15}\text{BrO}$ (M^+): 338. HRMS (ESI Pos): [$\text{C}_{19}\text{H}_{15}\text{BrO} + \text{H}]^+$: found: 339.03786, calc. 339.03845.



4-(2-bromobenzyl)1-fluorobenzene.

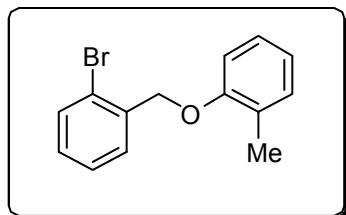
The titled compound was synthesized using the general procedure above and obtained as colorless oil in 88% isolated yield. ^1H NMR (CDCl_3 , 300 MHz): δ 5.08 (s, 2H), 6.88-7.01 (m, 4H), 7.14-7.20 (m, 1H), 7.29-7.34 (m, 1H), 7.51-7.59 (m, 2H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 70.0, 115.8 (d, $J = 11.2$ Hz), 115.8 (d, $J = 4.1$ Hz), 122.3, 127.6, 128.8, 129.3, 132.6, 136.1, 154.5, 157.5 (d, $J = 237.6$ Hz). FTIR (cm^{-1}): 1501, 1216, 1024, 825, 748. MS (EI): found: 328 (M^+), calcd for $\text{C}_{13}\text{H}_{10}\text{FBrO}$ (M^+): 328. HRMS (ESI Pos): [$\text{C}_{13}\text{H}_{10}\text{FBrO} + \text{H}]^+$: found: 328.98303, calc. 328.98386.



4-(2-bromobenzyl)1-chlorobenzene.

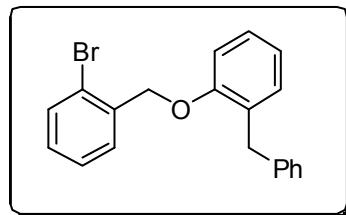
The titled compound was synthesized using the general procedure above and obtained

as white solid in 92% isolated yield. ^1H NMR (CDCl_3 , 300 MHz): δ 5.08 (s, 2H), 6.88-6.91 (m, 2H), 7.15-7.34 (m, 4H), 7.48-7.51 (m, 1H), 7.55-7.58 (m, 1H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 69.6, 116.2, 122.3, 126.1, 127.6, 128.8, 129.3, 129.4, 132.6, 135.8, 157.0. FTIR (cm^{-1}): 2925, 1487, 1237, 1029, 817, 745. MS (EI): found: 296 (M^+), calcd for $\text{C}_{13}\text{H}_{10}\text{FCIO}$ (M^+): 296. HRMS (ESI Pos): $[\text{C}_{13}\text{H}_{10}\text{FCIO} + \text{H}]^+$: found: 296.96312, calc. 296.96818.



2-(2-bromobenzyl)-1-toluene.

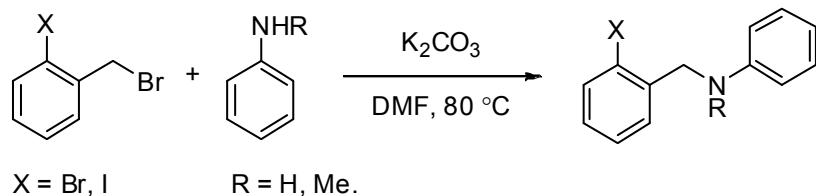
The titled compound was synthesized using the general procedure above and obtained as white solid in 95% isolated yield. ^1H NMR (CDCl_3 , 300 MHz): δ 2.32 (s, 3H), 5.12 (s, 2H), 6.86-6.91 (m, 2H), 7.13-7.19 (m, 3H), 7.30-7.36 (m, 1H), 7.56-7.59 (m, 2H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 69.2, 111.4, 120.8, 122.0, 126.8, 127.0, 127.5, 128.5, 129.0, 130.5, 132.5, 136.7, 156.5. FTIR (cm^{-1}): 2949, 1493, 1240, 1127, 1026, 749. MS (EI): found: 276 (M^+), calcd for $\text{C}_{14}\text{H}_{13}\text{BrO}$ (M^+): 276. HRMS (ESI Pos): $[\text{C}_{14}\text{H}_{13}\text{BrO} + \text{H}]^+$: found: 277.02232, calc. 277.02280.



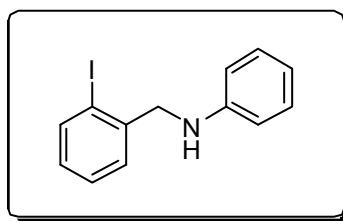
2-(2-bromobenzyl)-1-benzylbenzene.

The titled compound was synthesized using the general procedure above and obtained as white solid in 92% isolated yield. ^1H NMR (CDCl_3 , 300 MHz): δ 4.07 (s, 2H), 5.12 (s, 2H), 6.89-6.94 (m, 2H), 7.16-7.35 (m, 10H), 7.54-7.57 (m, 1H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 36.2, 69.2, 111.7, 121.0, 122.0, 125.8, 127.4, 127.5, 128.3, 128.6, 129.0, 129.9, 130.6, 132.4, 136.5, 140.9, 156.0. FTIR (cm^{-1}): 2921, 1496, 1451, 1251, 1025, 748. MS (EI): found: 352 (M^+), calcd for $\text{C}_{20}\text{H}_{17}\text{BrO}$ (M^+): 352. HRMS (ESI Pos): $[\text{C}_{20}\text{H}_{17}\text{BrO} + \text{H}]^+$: found: 353.05339, calc. 353.05410.

Synthesis of amines

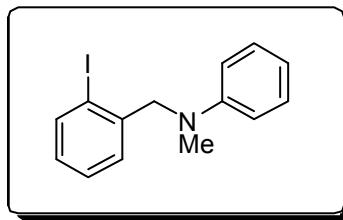


The synthesis of substituted amines were synthesized according to the literature procedure.²



N-(2-iodobenzyl)aniline.

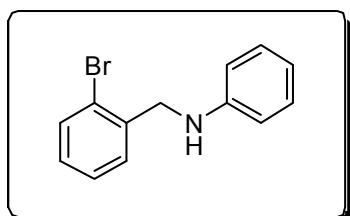
The titled compound was synthesized using the general procedure in the literature,² and obtained as white solid in 77% isolated yield. ¹H NMR (CDCl_3 , 300 MHz): δ 4.10 (s, 1H), 4.25 (s, 2H), 6.53-6.56 (m, 2H), 6.67-6.72 (m, 1H), 6.88-6.94 (m, 1H), 7.11-7.16 (m, 2H), 7.20-7.26 (m, 1H), 7.31-7.34 (m, 1H), 7.79-7.82 (m, 1H). ¹³C NMR (CDCl_3 , 75 MHz): δ 38.7, 62.4, 97.6, 111.9, 116.6, 122.8, 127.5, 128.3, 128.6, 129.2, 139.4, 139.8, 149.0. FTIR (cm^{-1}): 3414, 1597, 1496, 1436, 1010, 742, 692. MS (EI): found: 309 (M^+), calcd for $\text{C}_{13}\text{H}_{12}\text{IN}$ (M^+): 309. HRMS (ESI Pos): $[\text{C}_{13}\text{H}_{12}\text{IN} + \text{H}]^+$: found: 310.00873, calc. 310.00927.



N-(2-iodobenzyl)-*N*-methylaniline.

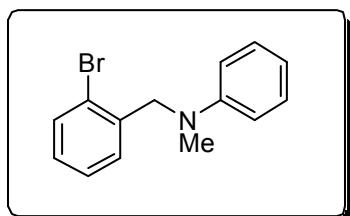
The titled compound was synthesized using the general procedure in the literature,² and obtained as orange liquid in 89% isolated yield. ¹H NMR (CDCl_3 , 300 MHz): δ 3.05 (s, 3H), 4.41 (s, 2H), 6.61-6.72 (m, 3H), 6.90-6.95 (m, 1H), 7.07-7.10 (m, 1H), 7.13-7.24 (m, 3H), 7.82-7.85 (m, 1H). ¹³C NMR (CDCl_3 , 75 MHz): δ 38.7, 62.4, 97.6, 111.9, 116.6, 122.8, 127.5, 128.3, 128.6, 129.2, 139.4, 139.8, 149.0. FTIR (cm^{-1}): 2924, 1596, 1504, 1012, 745, 694. MS (EI): found: 323 (M^+), calcd for $\text{C}_{14}\text{H}_{14}\text{IN}$ (M^+): 323. HRMS (ESI Pos): $[\text{C}_{14}\text{H}_{14}\text{IN} + \text{H}]^+$

$\text{H}]^+$: found: 324.02422, calc. 324.02492.



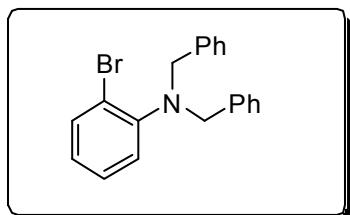
N-(2-bromobenzyl)aniline.

The titled compound was synthesized using the general procedure in the literature,² and obtained as yellow oil in 80% isolated yield. ¹H NMR (CDCl_3 , 300 MHz): δ 4.05 (s, 1H), 4.31 (s, 2H), 6.52-6.54 (m, 2H), 6.65-6.70 (m, 1H), 7.02-7.19 (m, 4H), 7.31-7.33 (m, 1H), 7.49-7.52 (m, 1H). ¹³C NMR (CDCl_3 , 75 MHz): δ 48.2, 112.8, 117.6, 123.1, 127.4, 128.5, 129.0, 129.2, 132.6, 138.1, 147.6. FTIR (cm^{-1}): 3416, 1603, 1501, 1024, 748, 692. MS (EI): found: 261 (M^+), calcd for $\text{C}_{13}\text{H}_{12}\text{BrN}$ (M^+): 261. HRMS (ESI Pos): $[\text{C}_{13}\text{H}_{12}\text{BrN} + \text{H}]^+$: found: 262.02259, calc. 262.02314.



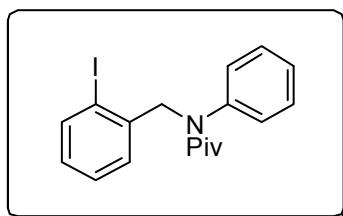
N-(2-bromobenzyl)-*N*-methylaniline.

The titled compound was synthesized using the general procedure in the literature,² and obtained as white solid in 96% isolated yield. ¹H NMR (CDCl_3 , 300 MHz): δ 3.03 (s, 3H), 4.50 (s, 2H), 6.62-6.71 (m, 3H), 7.05-7.20 (m, 5H), 7.52-7.54 (m, 1H). ¹³C NMR (CDCl_3 , 75 MHz): δ 38.6, 57.3, 111.9, 116.6, 122.6, 127.4, 127.8, 128.3, 129.2, 132.7, 137.3, 149.1. FTIR (cm^{-1}): 2920, 1599, 1502, 1440, 1025, 747, 687. MS (EI): found: 275 (M^+), calcd for $\text{C}_{14}\text{H}_{14}\text{BrN}$ (M^+): 275. HRMS (ESI Pos): $[\text{C}_{14}\text{H}_{14}\text{BrN} + \text{H}]^+$: found: 276.03800, calc. 276.03879.



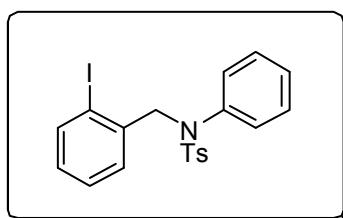
N,N-dibenzyl-2-bromoaniline.

The titled compound was synthesized using the general procedure in the literature,² and obtained as yellow oil in 82% isolated yield. ¹H NMR (CDCl₃, 300 MHz): δ 4.16 (s, 4H), 6.79-6.90 (m, 2H), 7.03-7.09 (m, 1H), 7.17-7.32 (m, 10H), 7.54-7.57 (m, 1H). ¹³C NMR (CDCl₃, 75 MHz): δ 56.4, 121.4, 124.4, 127.0, 127.5, 128.2, 128.5, 133.7, 137.9, 148.7. FTIR (cm⁻¹): 3025, 1584, 1474, 1026, 763, 697. MS (EI): found: 351 (M⁺), calcd for C₂₀H₁₈BrN (M⁺): 351. HRMS (ESI Pos): [C₂₀H₁₈BrN + H]⁺: found: 352.06917, calc. 352.07009.



N-(2-iodobenzyl)-*N*-phenylpivalamide.

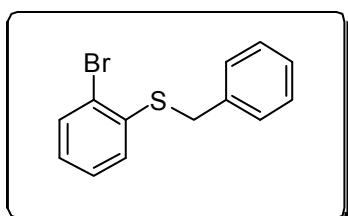
The titled compound was synthesized using the general procedure in the literature,³ and obtained as white solid in 86% isolated yield. ¹H NMR (CDCl₃, 300 MHz): δ 1.08 (s, 9H), 4.92 (s, 2H), 6.88-6.93 (m, 1H), 7.05-7.08 (m, 2H), 7.26-7.28 (m, 5H), 7.73-7.75 (m, 1H). ¹³C NMR (CDCl₃, 75 MHz): δ 21.5, 58.9, 98.4, 127.7, 127.8, 128.3, 128.7, 128.8, 129.2, 129.5, 129.8, 135.1, 138.1, 139.0, 139.2, 143.7. FTIR (cm⁻¹): 2961, 1634, 1288, 1191, 1015, 741, 706. MS (EI): found: 393 (M⁺), calcd for C₁₈H₂₀INO (M⁺): 393. HRMS (ESI Pos): [C₁₈H₂₀INO + H]⁺: found: 394.06635, calc. 394.06678.



N-(2-iodobenzyl)-4-methyl-*N*-phenylbenzenesulfonamide.

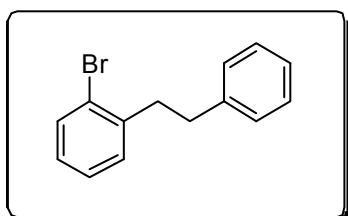
The titled compound was synthesized using the general procedure in the literature,⁴ and obtained as white solid in 72% isolated yield. ¹H NMR (CDCl₃, 300 MHz): δ 2.43 (s, 3H), 4.82 (s, 2H), 6.84-6.90 (m, 1H), 7.05-7.09 (m, 2H), 7.20-7.30 (m, 6H), 7.52-7.55 (m, 2H), 7.58-7.67 (m, 1H), 7.68-7.69 (m, 1H). ¹³C NMR (CDCl₃, 75 MHz): δ 21.5, 58.9, 98.4, 127.7, 127.8, 128.3, 128.7, 128.8, 129.2, 129.5, 129.8, 135.1, 138.1, 139.0, 139.2, 143.7. FTIR (cm⁻¹): 2919, 1347, 1161, 1090, 1016, 734, 694. MS (EI): found: 463 (M⁺), calcd for C₂₀H₁₈INO₂S (M⁺): 463. HRMS (ESI Pos): [C₂₀H₁₈INO₂S + H]⁺: found: 464.01754, calc.

464.01812.



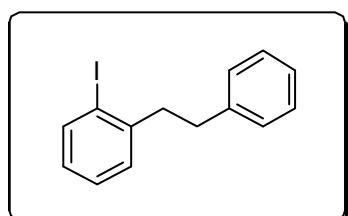
benzyl(2-bromophenyl)sulfane.

The titled compound was synthesized using the general procedure in the literature,⁵ and obtained as white solid in 72% isolated yield. ¹H NMR (CDCl_3 , 300 MHz): δ 4.14 (s, 2H), 6.99-7.04 (m, 1H), 7.17-7.36 (m, 7H), 7.53-7.55 (m, 1H). ¹³C NMR (CDCl_3 , 75 MHz): δ 37.9, 123.7, 126.9, 127.4, 127.7, 128.6, 128.8, 128.9, 132.9, 136.1, 137.8. FTIR (cm^{-1}): 2955, 2920, 1446, 1381, 1021, 744. MS (EI): found: 277 (M^+), calcd for $\text{C}_{13}\text{H}_{11}\text{BrS}$ (M^+): 277. HRMS (ESI Pos): $[\text{C}_{13}\text{H}_{11}\text{BrS} + \text{H}]^+$: found: 278.98381, calc. 278.98431.



1-bromo-2-phenethylbenzene.

The titled compound was synthesized using the general procedure in the literature,⁶ and obtained as colorless liquid in 80% isolated yield. ¹H NMR (CDCl_3 , 300 MHz): δ 2.94-2.98 (m, 2H), 3.06-3.10 (m, 2H), 7.12 (m, 1H), 7.20-7.37 (m, 7H), 7.60 (m, 1H). ¹³C NMR (CDCl_3 , 75 MHz): δ 37.2, 39.4, 125.4, 127.0, 128.4, 128.7, 129.3, 129.4, 131.4, 141.9, 142.4. FTIR (cm^{-1}): 3026, 1604, 1469, 1024. MS (EI): found: 260 (M^+), calcd for $\text{C}_{14}\text{H}_{13}\text{Br}$ (M^+): 260. HRMS (ESI Pos): $[\text{C}_{14}\text{H}_{13}\text{Br} + \text{H}]^+$: found: 261.02702, calc. 261.02789.



1-iodo-2-phenethylbenzene.

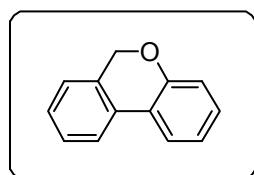
The titled compound was synthesized using the general procedure in the literature,⁷ and

obtained as white solid in 84% isolated yield. ^1H NMR (CDCl_3 , 300 MHz): δ 2.90-2.94 (m, 2H), 3.03-3.7 (m, 2H), 6.93 (m, 1H), 7.20-7.37 (m, 7H), 7.87 (m, 1H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 36.0, 42.8, 100.2, 125.8, 127.6, 128.1, 128.2, 129.3, 139.2, 141.0, 143.9. FTIR (cm^{-1}): 2926, 1563, 1454, 1011. MS (EI): found: 308 (M^+), calcd for $\text{C}_{14}\text{H}_{13}\text{I}$ (M^+): 308. HRMS (ESI Pos): $[\text{C}_{14}\text{H}_{13}\text{I} + \text{H}]^+$: found: 309.01345, calc. 309.01402.

General experimental procedures for direct arylation of alkenes with aryl bromides/iodides:

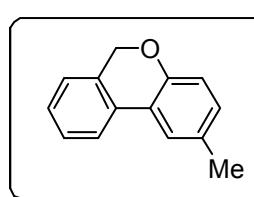
Catalysts, alkenes (if solid) and aryl bromides/iodides (if solid, 0.5 mmol) were added into Schlenk tubes. $\text{KO}^\ddagger\text{Bu}$ was added into Schlenk tubes in glove box. Aryl bromides/iodides (if liquid, 0.5 mmol) and alkenes (if liquid) were added into tubes by syringe. The solvent benzene was added by syringe. The tubes were degassed and refilled with N_2 . The mixture was stirred under N_2 atmosphere in sealed Schlenk tubes at corresponding temperature. The reaction was cooled down to room temperature. The mixture was filtered through a short plug of silica gel, washed with copious ethyl acetate. The combined organic phase was concentrated under vacuum. The product was purified through flash column chromatography on 200-300 mesh silica gel with petroleum ether/ethyl acetate as eluent.

Characterization of Products in details:



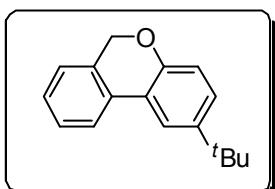
(2a) 6H-Benzo[c]chromene

The title compound was prepared according to the general procedure described above and purified by flash column chromatography as colorless oil (Isolated yield: 74%). $R_f = 0.40$ (petroleum ether/ethyl acetate = 100/1). ^1H NMR (300 MHz, CDCl_3): δ = 5.09 (s, 2H), 6.97-7.13 (m, 3H), 7.20-7.35 (m, 3H), 7.66-7.73 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ = 68.4, 117.3, 122.0, 122.1, 123.3, 124.6, 127.4, 127.6, 128.4, 129.4, 130.0, 131.4, 154.7. MS (EI): found: 182 (M^+), calcd for $\text{C}_{13}\text{H}_{10}\text{O}$ (M^+): 182.07.



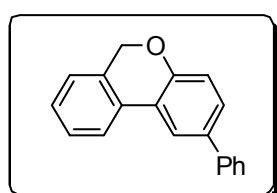
(2b) 2-Methyl-6H-benzo[c]chromene

The title compound was prepared according to the general procedure described above and purified by flash column chromatography as light yellow oil (Isolated yield: 75%). $R_f = 0.40$ (petroleum ether/ethyl acetate = 100/1). ^1H NMR (300 MHz, CDCl_3): δ = 2.35 (s, 3H), 5.06 (s, 2H), 6.87-6.90 (m, 1H), 7.01-7.04 (m, 1H), 7.11-7.13 (m, 3H), 7.23-7.28 (m, 1H), 7.32-7.37 (m, 1H), 7.52 (s, 1H), 7.66-7.68 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ = 20.9, 68.5, 117.0, 121.9, 122.6, 123.6, 124.6, 127.5, 128.3, 130.0, 130.2, 131.3, 131.5, 152.6. MS (EI): found: 196 (M^+), calcd for $\text{C}_{14}\text{H}_{12}\text{O}$ (M^+): 196.09.



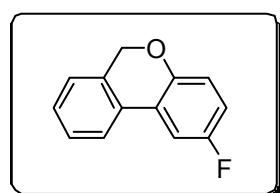
(2c) 2-tert-Bethyl-6H-benzo[c]chromene

The title compound was prepared according to the general procedure described above and purified by flash column chromatography as colorless oil (Isolated yield: 82%). $R_f = 0.40$ (petroleum ether/ethyl acetate = 100/1). ^1H NMR (300 MHz, CDCl_3): $\delta = 1.36$ (s, 9H), 5.08 (s, 2H), 6.91-6.94 (m, 1H), 7.11-7.13 (m, 1H), 7.25-7.38 (m, 4H), 7.71-7.75 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 31.5, 34.4, 68.5, 116.8, 119.9, 121.8, 122.1, 124.6, 126.6, 127.4, 128.3, 130.5, 131.6, 144.7, 152.5$. MS (EI): found: 238 (M^+), calcd for $\text{C}_{17}\text{H}_{18}\text{O}$ (M^+): 238.14.



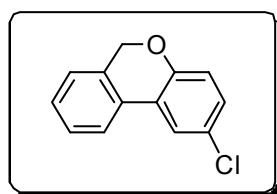
(2d) 2-Phenyl-6H-benzo[c]chromene

The title compound was prepared according to the general procedure described above and purified by flash column chromatography as white solid (Isolated yield: 63%). $R_f = 0.42$ (petroleum ether/ethyl acetate = 100/1). ^1H NMR (300 MHz, CDCl_3): $\delta = 5.11$ (s, 2H), 6.99-7.06 (m, 1H), 7.11-7.13 (m, 1H), 7.26-7.45 (m, 6H), 7.57-7.60 (m, 2H), 7.72-7.75 (m, 1H), 7.91-7.92 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3): $\delta = 68.5, 117.6, 121.9, 123.0, 124.7, 126.6, 126.8, 126.9, 127.8, 128.2, 128.4, 128.7, 129.9, 131.4, 135.3, 140.9, 154.3$. MS (EI): found: 258 (M^+), calcd for $\text{C}_{19}\text{H}_{14}\text{O}$ (M^+): 258.10.



(2e) 2-Fluoro-6H-benzo[c]chromene

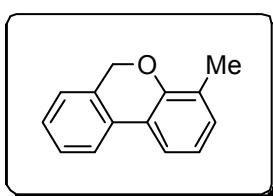
The title compound was prepared according to the general procedure described above and purified by flash column chromatography as colorless oil (Isolated yield: 66%). $R_f = 0.45$ (petroleum ether/ethyl acetate = 100/1). ^1H NMR (300 MHz, CDCl_3): $\delta = 5.11$ (s, 2H), 6.93-6.96 (m, 2H), 7.17-7.19 (m, 1H), 7.30-7.42 (m, 3H), 7.62-7.65 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 68.5, 109.6$ (d, $J = 23.5$ Hz), 115.8 (d, $J = 23.5$ Hz), 118.4 (d, $J = 5.6$ Hz), 122.2, 124.1 (d, $J = 8.5$ Hz), 124.7, 128.3, 128.5, 129.4 (d, $J = 3.2$ Hz), 131.5, 150.7, 158.2 (d, $J = 236.8$ Hz). MS (EI): found: 200 (M^+), calcd for $\text{C}_{13}\text{H}_9\text{FO}$ (M^+): 200.06.



(2f) 2-Chloro-6H-benzo[c]chromene

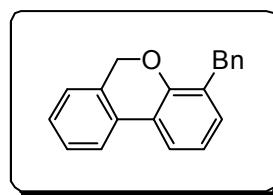
The title compound was prepared according to the general procedure described above and purified by flash column chromatography as colorless oil (Isolated yield: 71%). $R_f = 0.45$ (petroleum ether/ethyl acetate = 100/1). ^1H NMR (300 MHz, CDCl_3): $\delta = 5.11$ (s, 2H), 6.92-6.94 (m, 1H), 7.15-7.20 (m, 2H), 7.29-7.42 (m, 2H),

7.64-7.69 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ = 68.5, 118.7, 122.1, 123.1, 124.3, 124.7, 127.1, 128.3, 128.6, 129.0, 129.1, 131.2, 153.2. MS (EI): found: 216 (M^+), calcd for $\text{C}_{13}\text{H}_9\text{ClO}$ (M^+): 216.03.



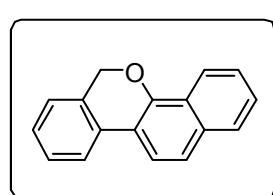
(2h) 4-Methyl-6*H*-benzo[*c*]chromene

The title compound was prepared according to the general procedure described above and purified by flash column chromatography as colorless oil (Isolated yield: 60%). R_f = 0.38 (petroleum ether/ethyl acetate = 100/1). ^1H NMR (300 MHz, CDCl_3): δ = 2.27 (s, 3H), 5.11 (s, 2H), 6.93-6.98 (m, 1H), 7.09-7.16 (m, 2H), 7.24-7.39 (m, 2H), 7.57-7.59 (m, 1H), 7.66-7.69 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ = 15.9, 68.4, 120.9, 121.4, 122.2, 122.4, 124.5, 126.7, 127.4, 128.4, 130.5, 130.8, 131.4, 152.9. MS (EI): found: 196 (M^+), calcd for $\text{C}_{14}\text{H}_{12}\text{O}$ (M^+): 196.09.



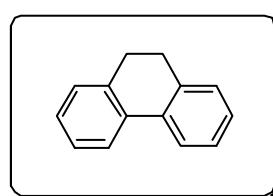
(2i) 4-Benzyl-6*H*-benzo[*c*]chromene

The title compound was prepared according to the general procedure described above and purified by flash column chromatography as colorless oil (Isolated yield: 62%). R_f = 0.40 (petroleum ether/ethyl acetate = 100/1). ^1H NMR (300 MHz, CDCl_3): δ = 4.01 (s, 2H), 5.04 (s, 2H), 6.93-6.97 (m, 1H), 7.03-7.34 (m, 10H), 7.57-7.66 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ = 35.7, 68.3, 121.5, 121.7, 122.2, 122.9, 124.5, 125.8, 127.5, 128.3, 128.2, 128.4, 128.8, 129.1, 129.9, 130.5, 131.5, 140.9, 152.6. MS (EI): found: 272 (M^+), calcd for $\text{C}_{20}\text{H}_{16}\text{O}$ (M^+): 272.12.



(2j) 5*H*-Dibenzo[*c,h*]chromene

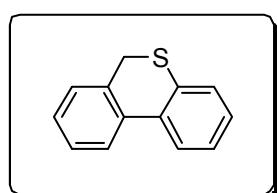
The title compound was prepared according to the general procedure described above and purified by flash column chromatography as light yellow solid (Isolated yield: 51%). R_f = 0.35 (petroleum ether/ethyl acetate = 100/1). ^1H NMR (300 MHz, CDCl_3): δ = 5.28 (s, 2H), 7.16-7.19 (m, 1H), 7.24-7.27 (m, 1H), 7.29-7.52 (m, 4H), 7.70-7.83 (m, 3H), 8.24-8.27 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ = 68.9, 117.1, 120.9, 121.5, 121.9, 122.2, 124.6, 125.3, 125.8, 126.6, 127.3, 128.5, 130.6, 130.7, 134.3, 150.3. MS (EI): found: 232 (M^+), calcd for $\text{C}_{17}\text{H}_{12}\text{O}$ (M^+): 232.09.



(6a) 9,10-Dihydrophenanthrene

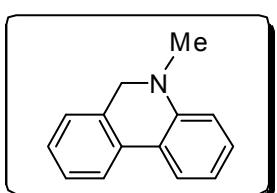
The title compound was prepared according to the general procedure described above and purified by flash column chromatography as colorless oil (Isolated yield: 77%). R_f = 0.45

(petroleum ether/ethyl acetate = 100/1). ^1H NMR (300 MHz, CDCl_3): δ = 2.94 (s, 4H), 7.26-7.38 (m, 6H), 7.82 (d, J = 7.5 Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ = 29.0, 123.7, 126.9, 127.4, 128.1, 134.4, 137.4. MS (EI): found: 180 (M^+), calcd for $\text{C}_{14}\text{H}_{12}$ (M^+): 180.09.



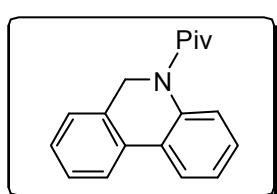
(6b) 6H-Benzo[c]thiochromene

The title compound was prepared according to the general procedure described above and purified by flash column chromatography as colorless oil (Isolated yield: 63%). R_f = 0.50 (petroleum ether/ethyl acetate = 100/1). ^1H NMR (300 MHz, CDCl_3): δ = 3.84 (s, 2H), 7.21-7.32 (m, 5H), 7.37-7.44 (m, 1H), 7.67-7.70 (m, 1H), 7.77-7.80 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ = 31.8, 125.7, 126.0, 126.4, 126.9, 127.7, 127.8, 127.9, 128.5, 133.6, 134.3, 134.5, 134.7. MS (EI): found: 198 (M^+), calcd for $\text{C}_{13}\text{H}_{10}\text{S}$ (M^+): 198.05.



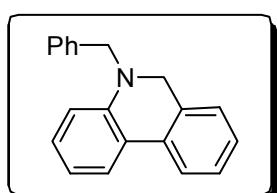
(6d) 5-Methyl-5,6-dihydrophenanthridine

The title compound was prepared according to the general procedure described above and purified by flash column chromatography as yellow oil (Isolated yield: 78%). R_f = 0.40 (petroleum ether/ethyl acetate = 20/1). ^1H NMR (300 MHz, CDCl_3): δ = 2.91 (s, 3H), 4.17 (s, 2H), 6.74-6.77 (m, 1H), 6.85-6.89 (m, 1H), 7.12-7.14 (m, 1H), 7.20-7.34 (m, 3H), 7.70-7.72 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ = 38.6, 55.0, 112.3, 118.6, 122.5, 123.4, 123.5, 125.6, 127.0, 127.7, 129.1, 132.1, 133.2, 147.2. MS (EI): found: 195 (M^+), calcd for $\text{C}_{14}\text{H}_{13}\text{N}$ (M^+): 195.10.



(6f) 5-Pivalyl-5,6-dihydrophenanthridine

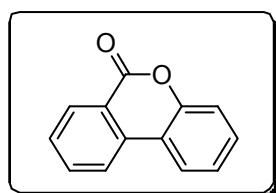
The title compound was prepared according to the general procedure described above and purified by flash column chromatography as white solid (Isolated yield: 27%). R_f = 0.30 (petroleum ether/ethyl acetate = 10/1). ^1H NMR (300 MHz, CDCl_3): δ = 1.07 (s, 9H), 3.33 (s, 2H), 7.61-7.81 (m, 4H), 8.14-8.17 (m, 1H), 8.30-8.33 (m, 1H), 8.52-8.55 (m, 1H), 8.60-8.63 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ = 30.4, 33.4, 46.9, 121.8, 122.2, 123.4, 126.2, 126.5, 126.8, 127.5, 128.4, 129.7, 130.0, 132.7, 143.4, 160.7. MS (EI): found: 265 (M^+), calcd for $\text{C}_{18}\text{H}_{19}\text{NO}$ (M^+): 265.15.



(6i) 5-Benzyl-5,6-dihydrophenanthridine

The title compound was prepared according to the general procedure described above and purified by flash column chromatography as light yellow oil (Isolated yield: 76%). R_f =

0.40 (petroleum ether/ethyl acetate = 20/1). ^1H NMR (300 MHz, CDCl_3): δ = 4.27 (s, 2H), 4.48 (s, 2H), 6.73-6.76 (m, 1H), 6.81-6.86 (m, 1H), 7.01-7.04 (m, 1H), 7.12-7.35 (m, 8H), 7.72-7.74 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ = 52.5, 54.6, 113.0, 118.4, 122.4, 123.1, 123.7, 125.6, 126.9, 127.0, 127.5, 127.6, 128.6, 129.0, 132.1, 133.0, 137.7, 146.3. MS (EI): found: 271 (M^+), calcd for $\text{C}_{20}\text{H}_{17}\text{N}$ (M^+): 271.14.



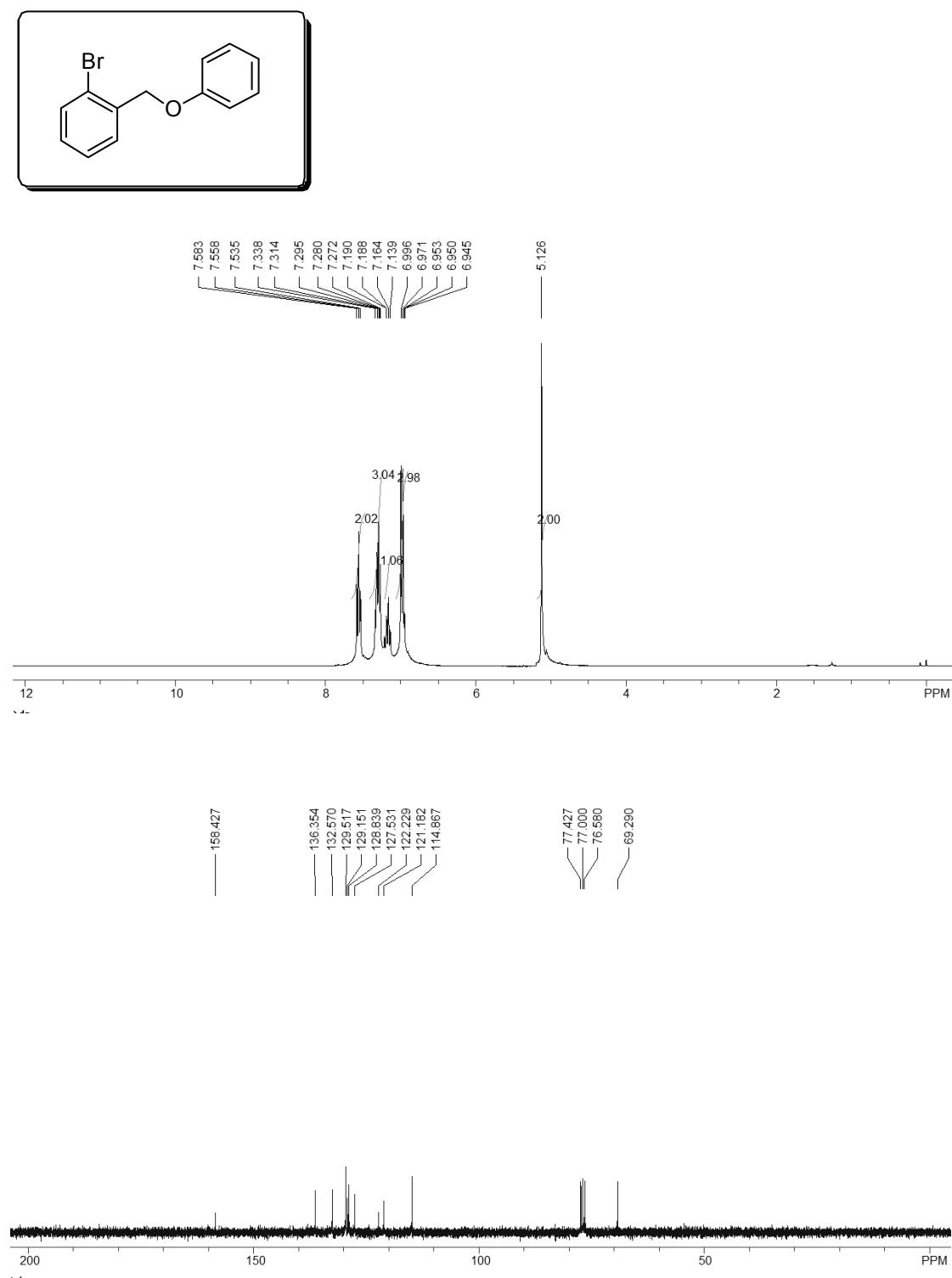
(6j) 6*H*-Benzo[*c*]chromen-6-one

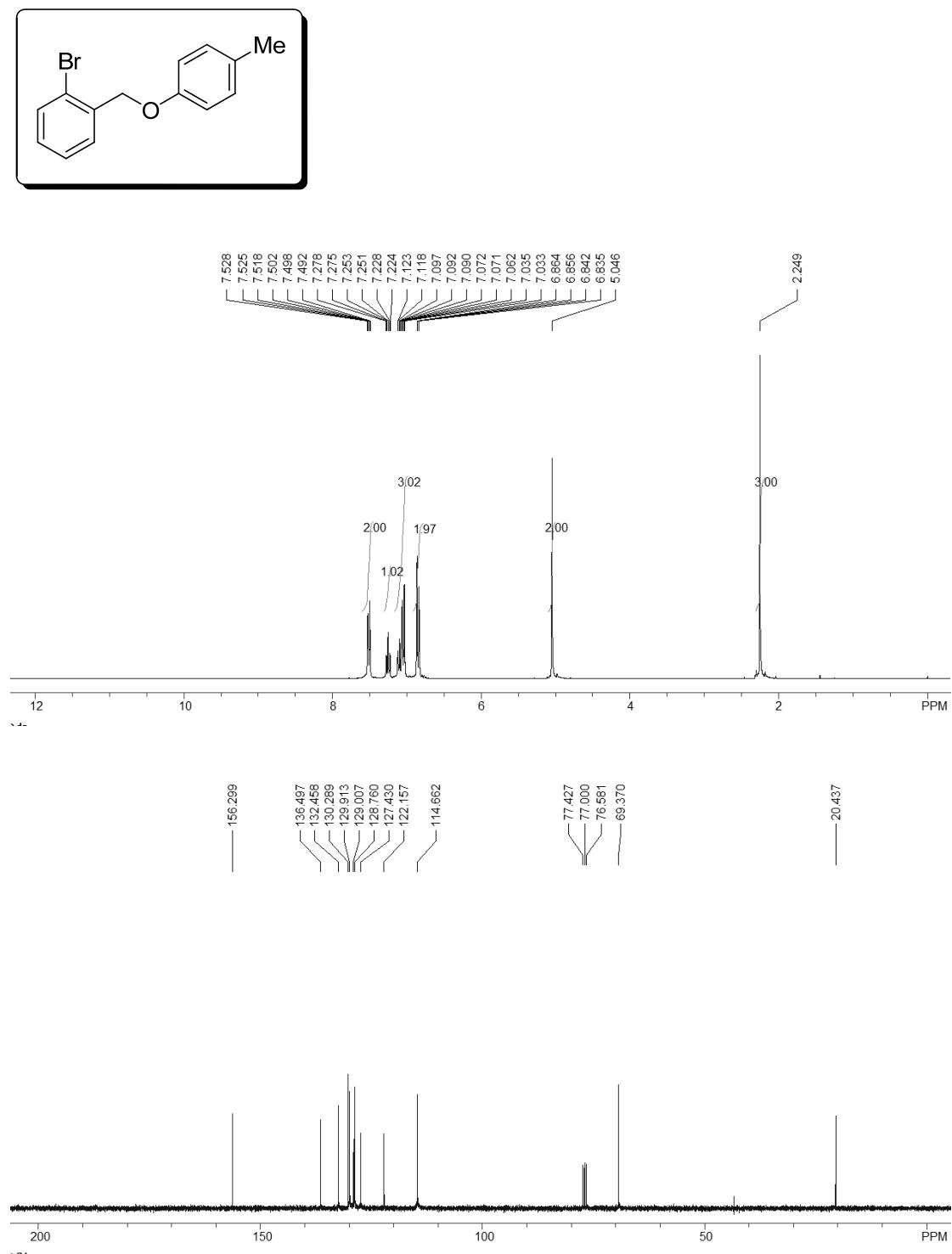
The title compound was prepared according to the general procedure described above and purified by flash column chromatography as white solid (Isolated yield: 92%). R_f = 0.30 (petroleum ether/ethyl acetate = 20/1). ^1H NMR (300 MHz, CDCl_3): δ = 7.25-7.29 (m, 2H), 7.39-7.44 (m, 1H), 7.48-7.53 (m, 1H), 7.72-7.77 (m, 1H), 7.91-8.00 (m, 2H), 8.29-8.31 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ = 117.4, 117.7, 120.9, 121.4, 122.5, 124.3, 128.6, 130.2, 134.4, 134.6, 150.9, 160.9. MS (EI): found: 196 (M^+), calcd for $\text{C}_{13}\text{H}_8\text{O}_2$ (M^+): 196.05.

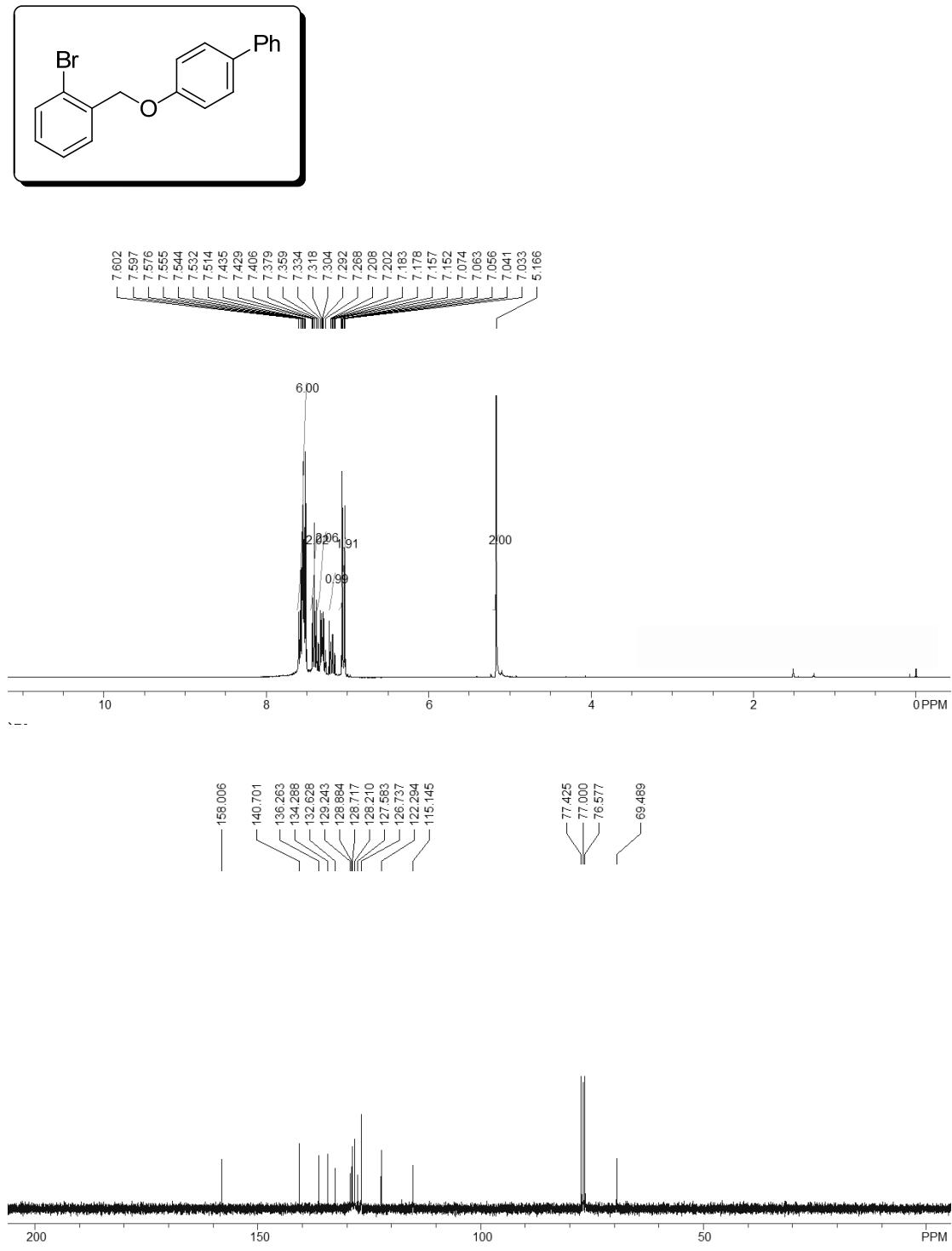
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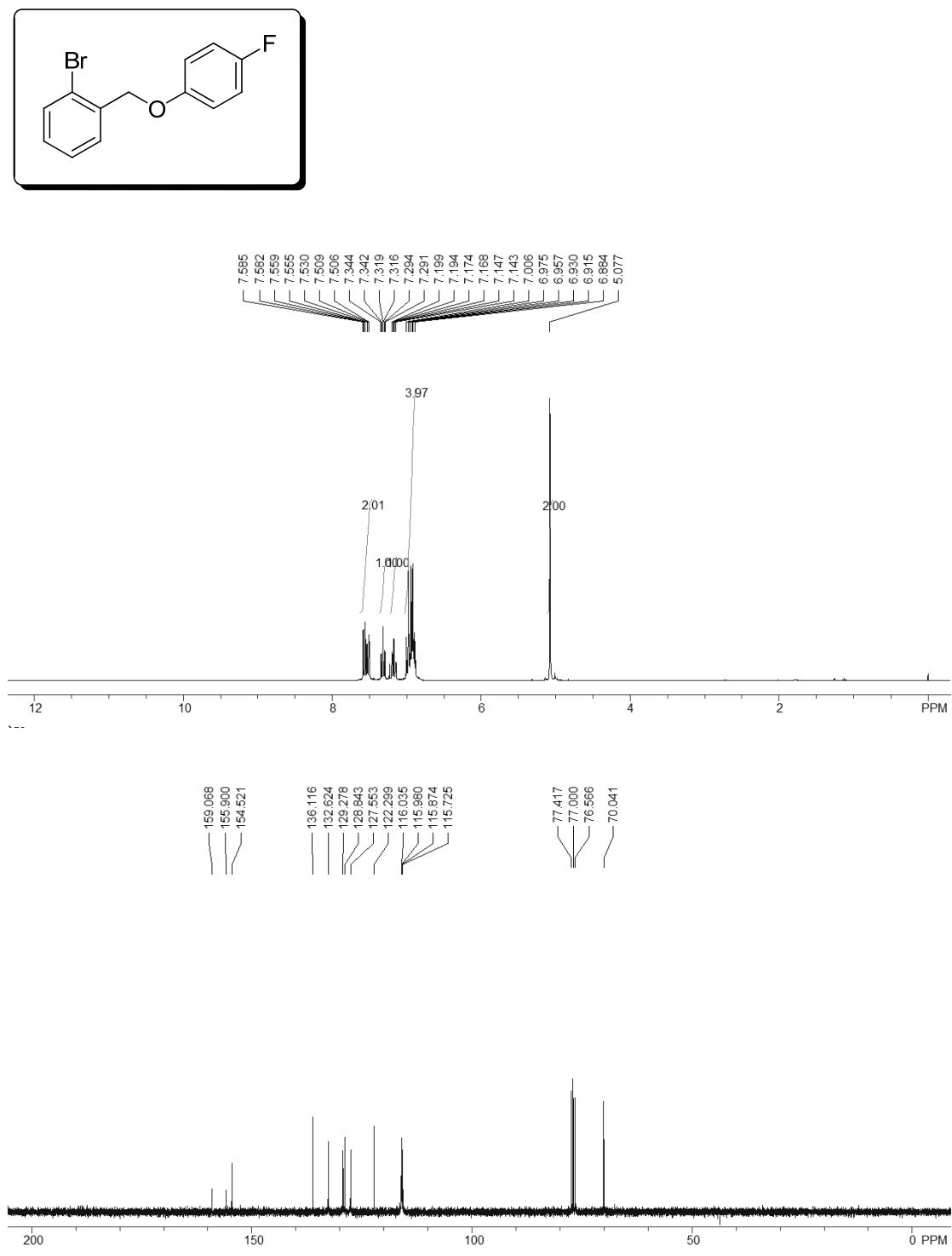
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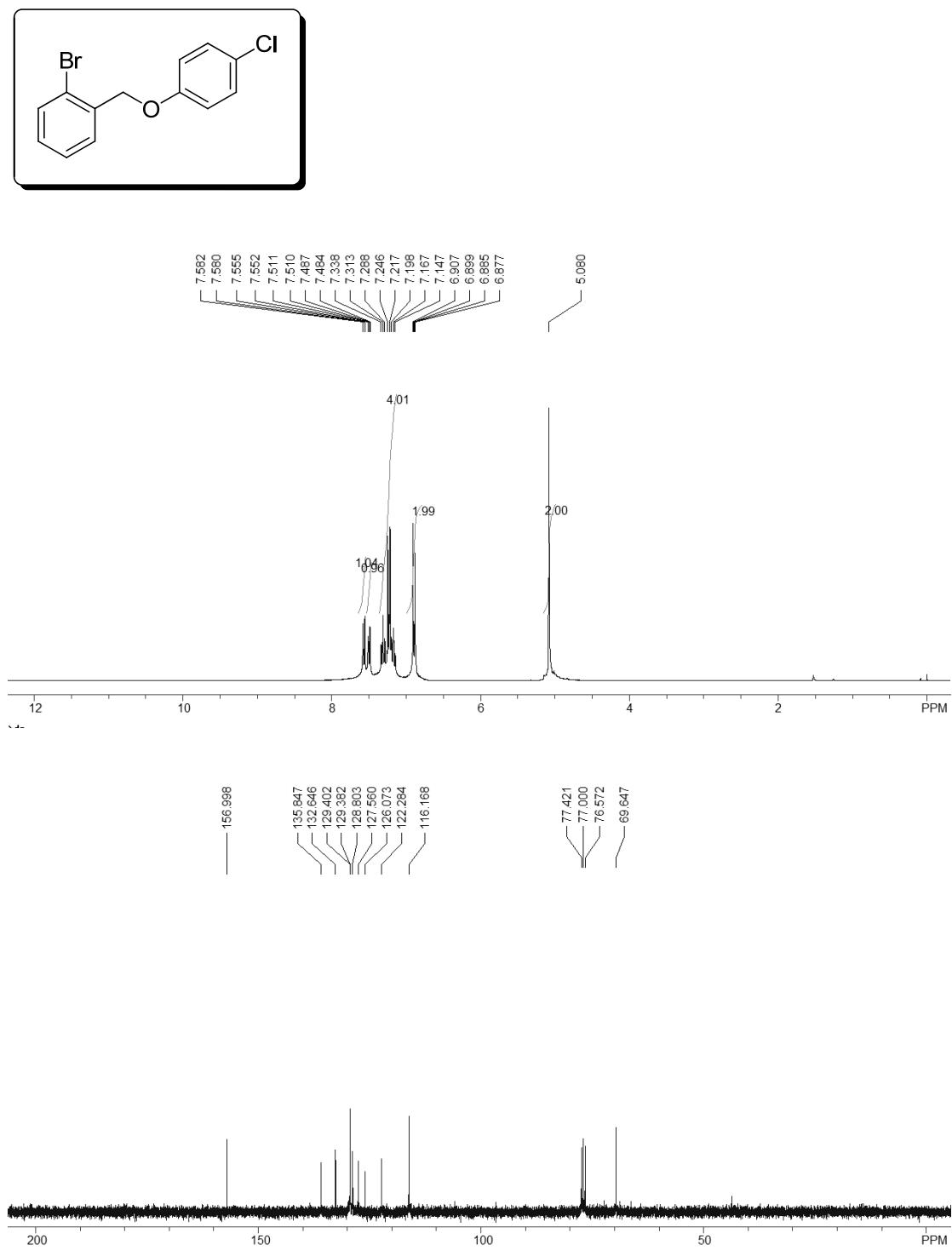
NMR Spectra of Substrates and Products:

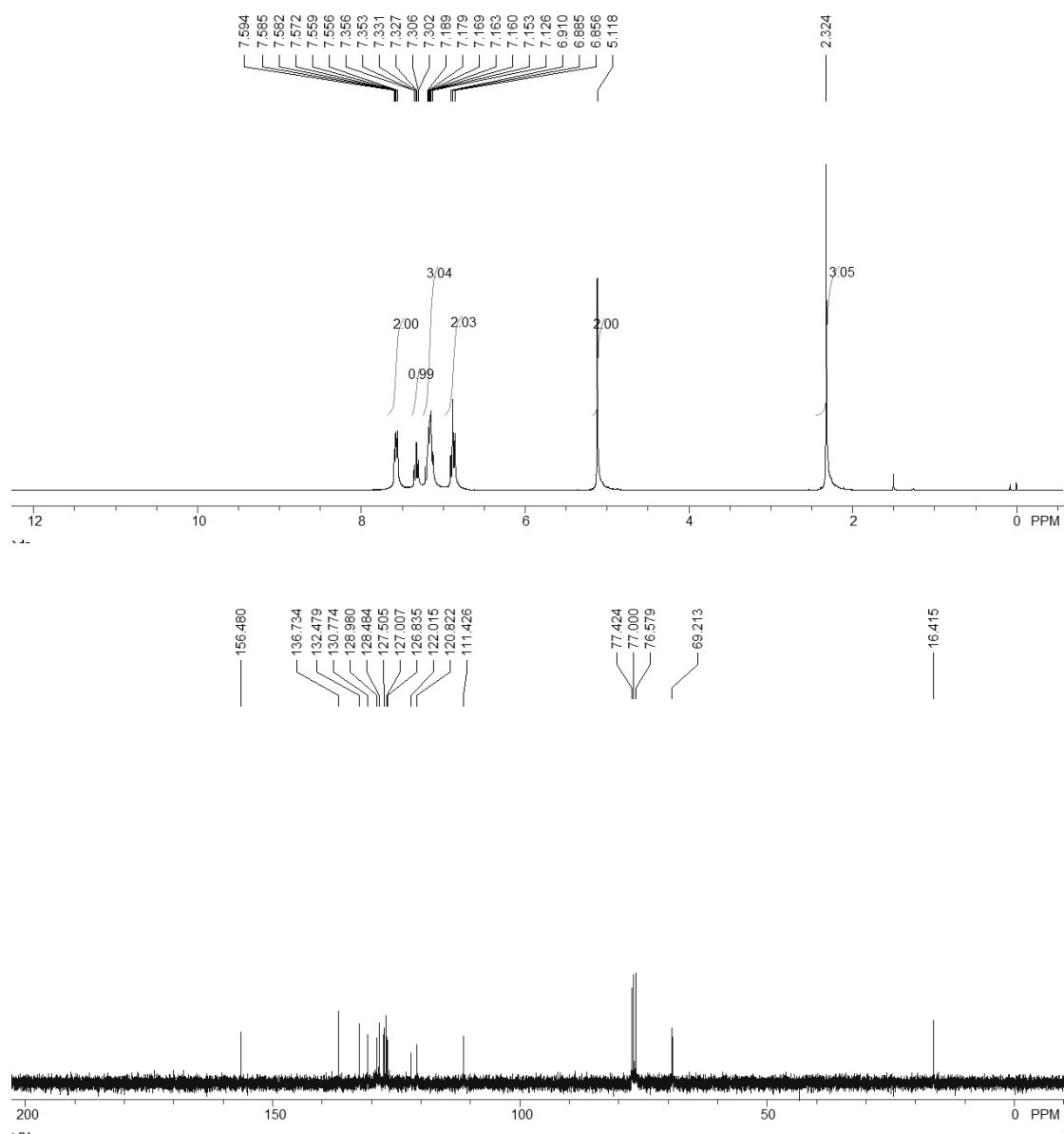
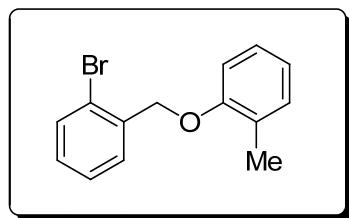


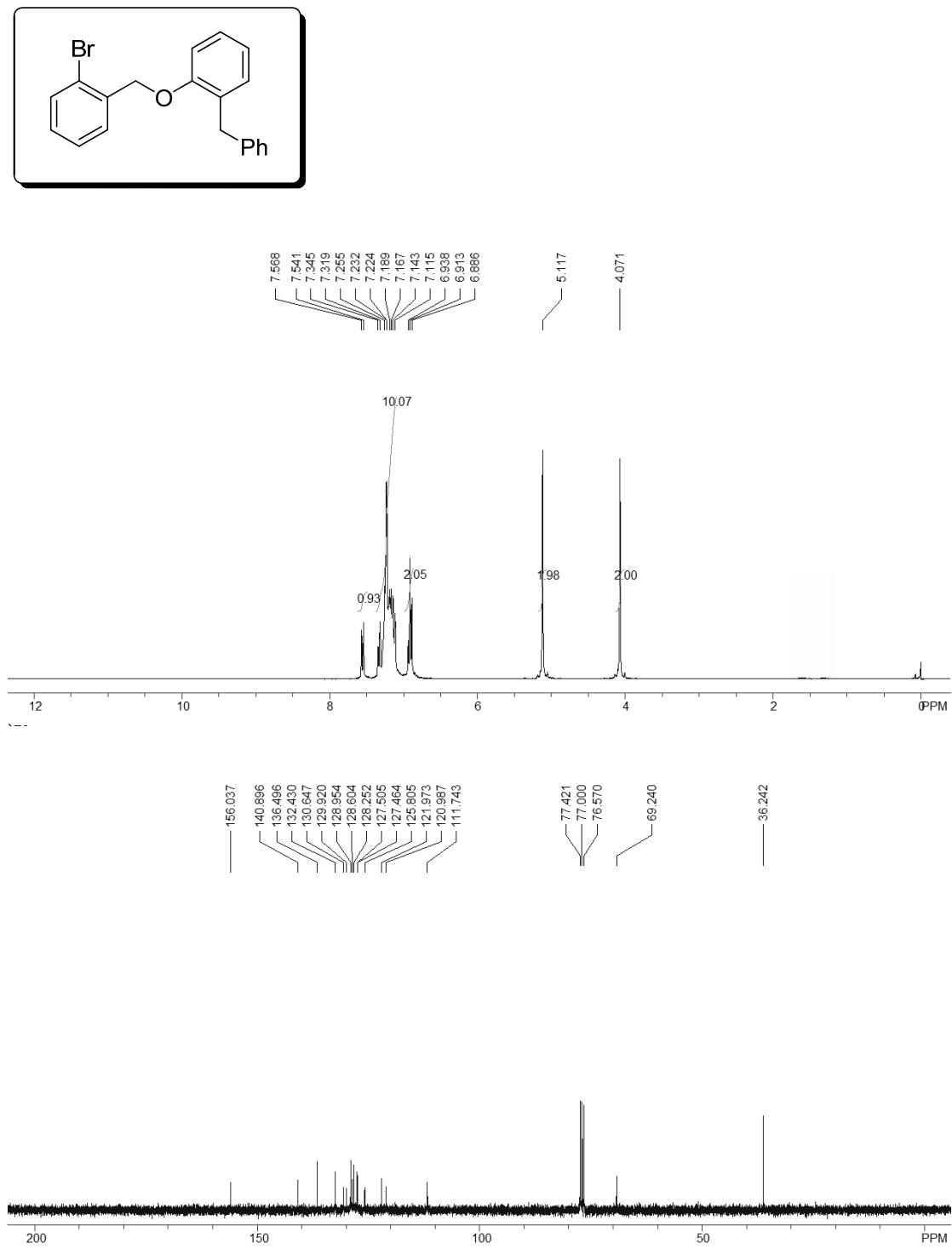


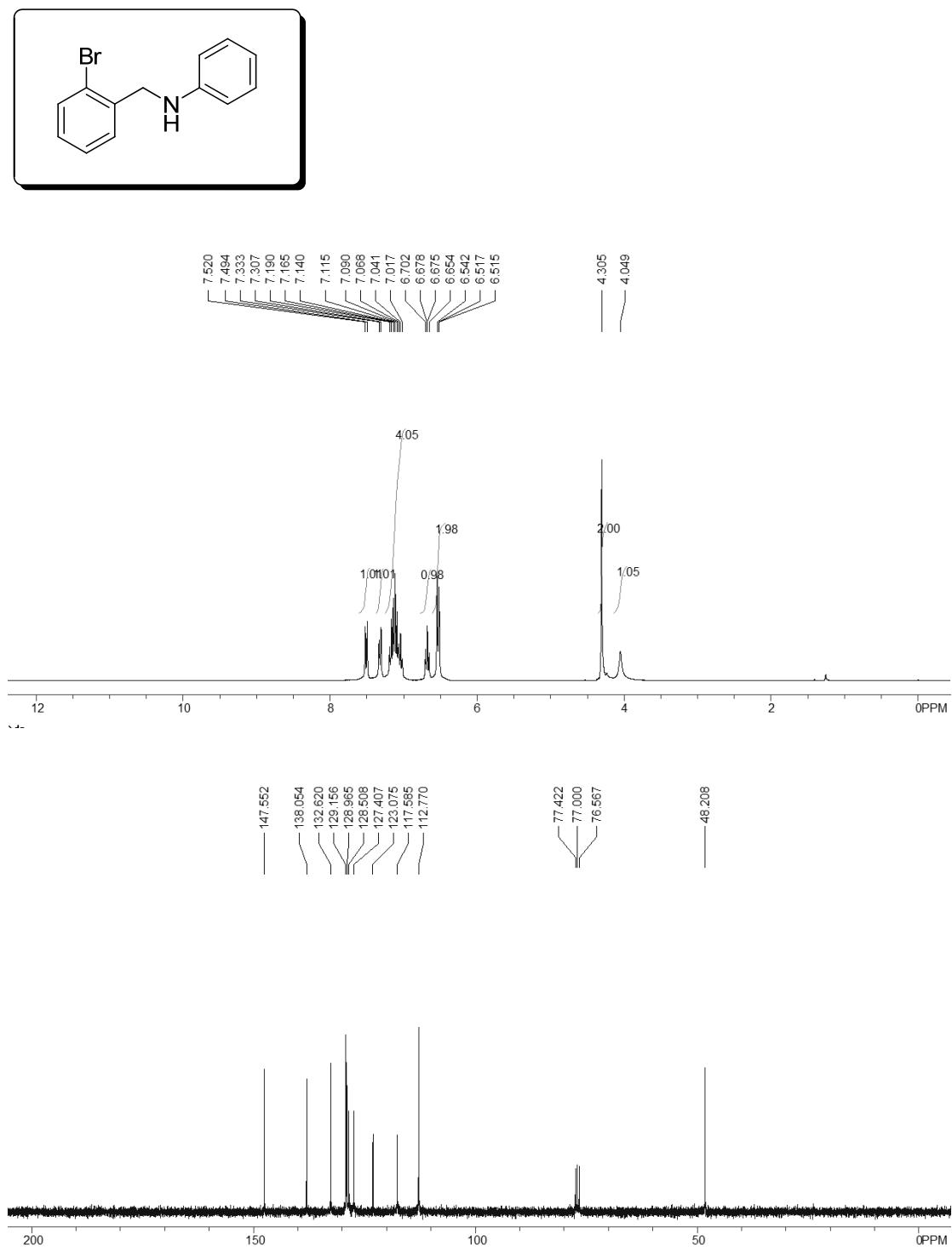


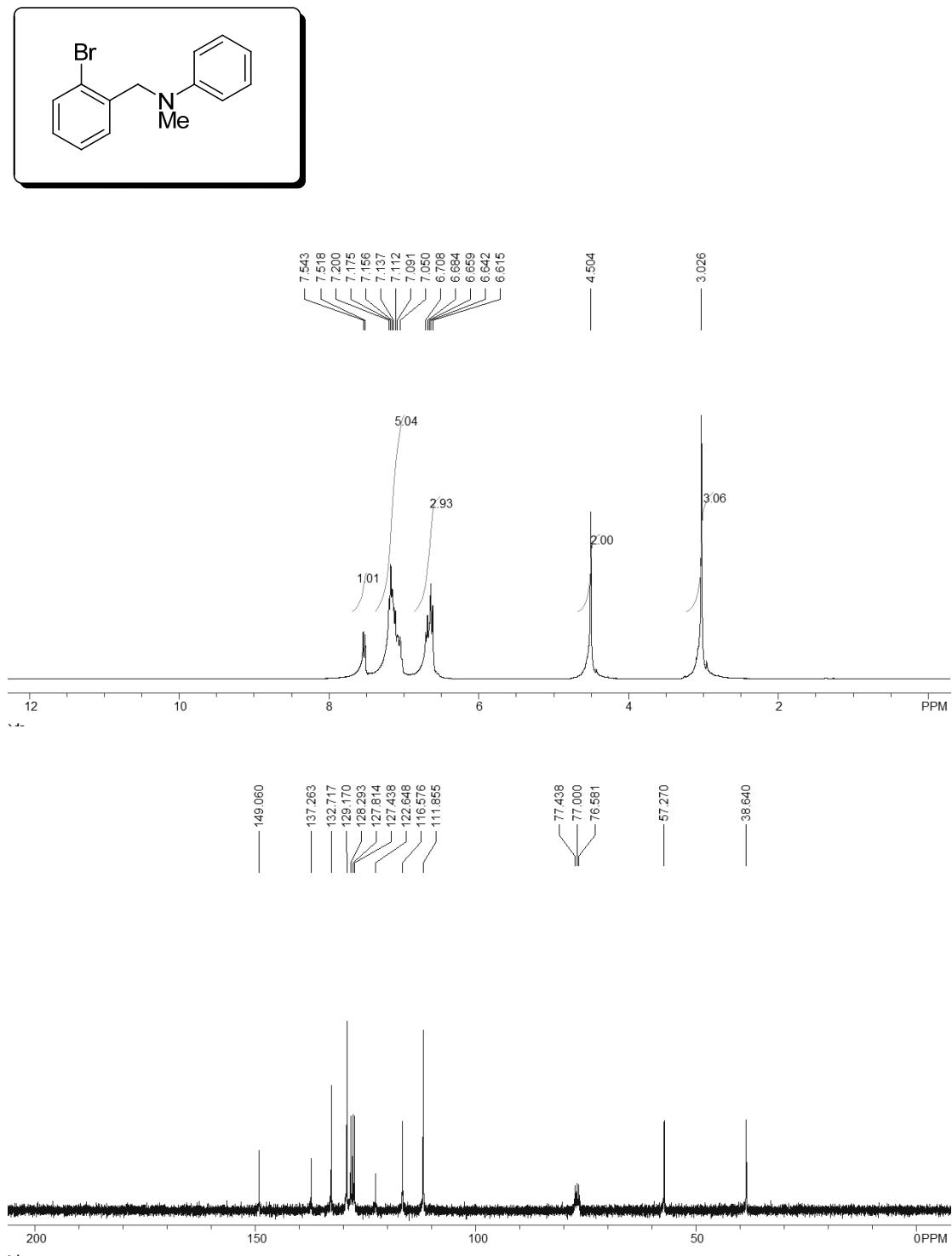


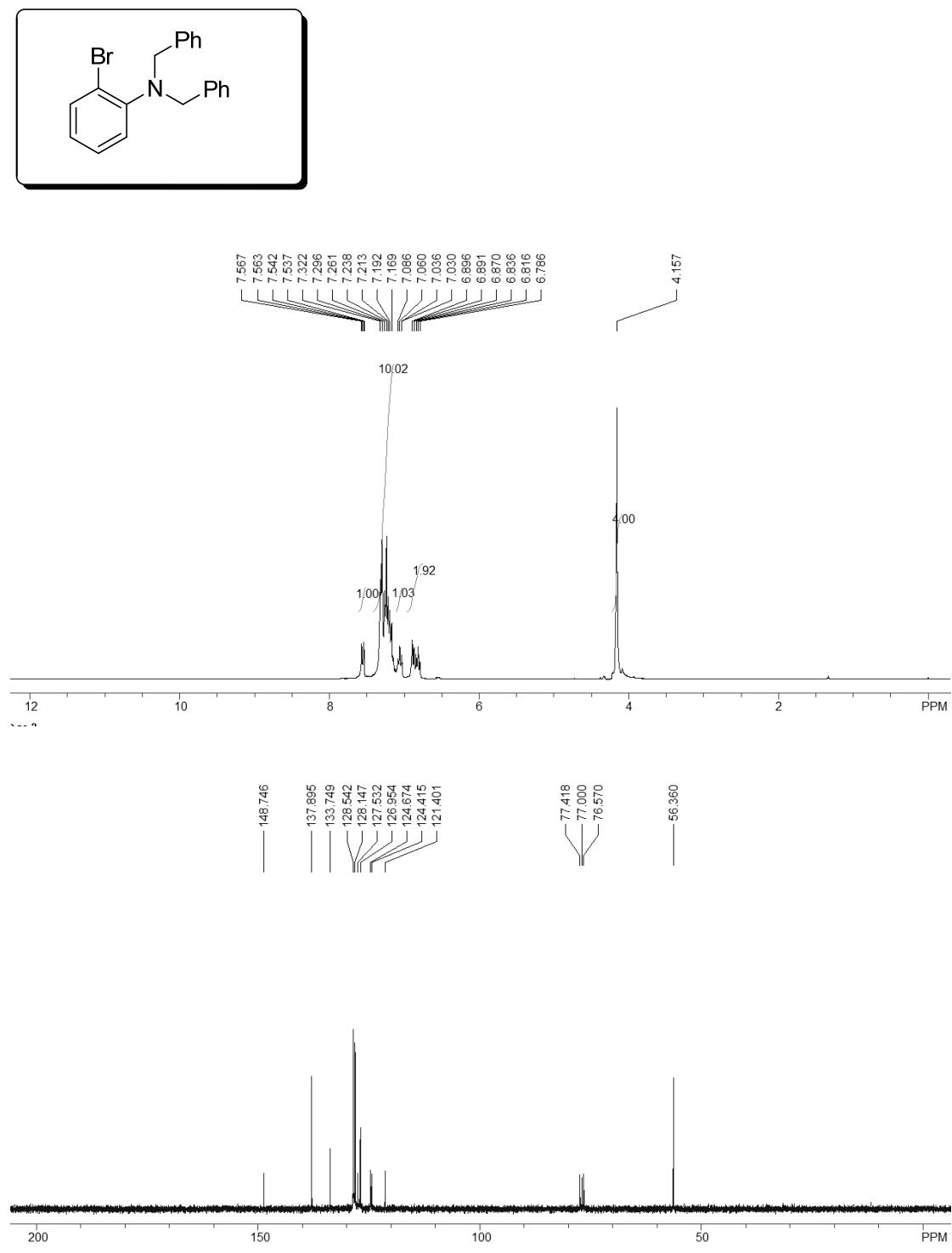


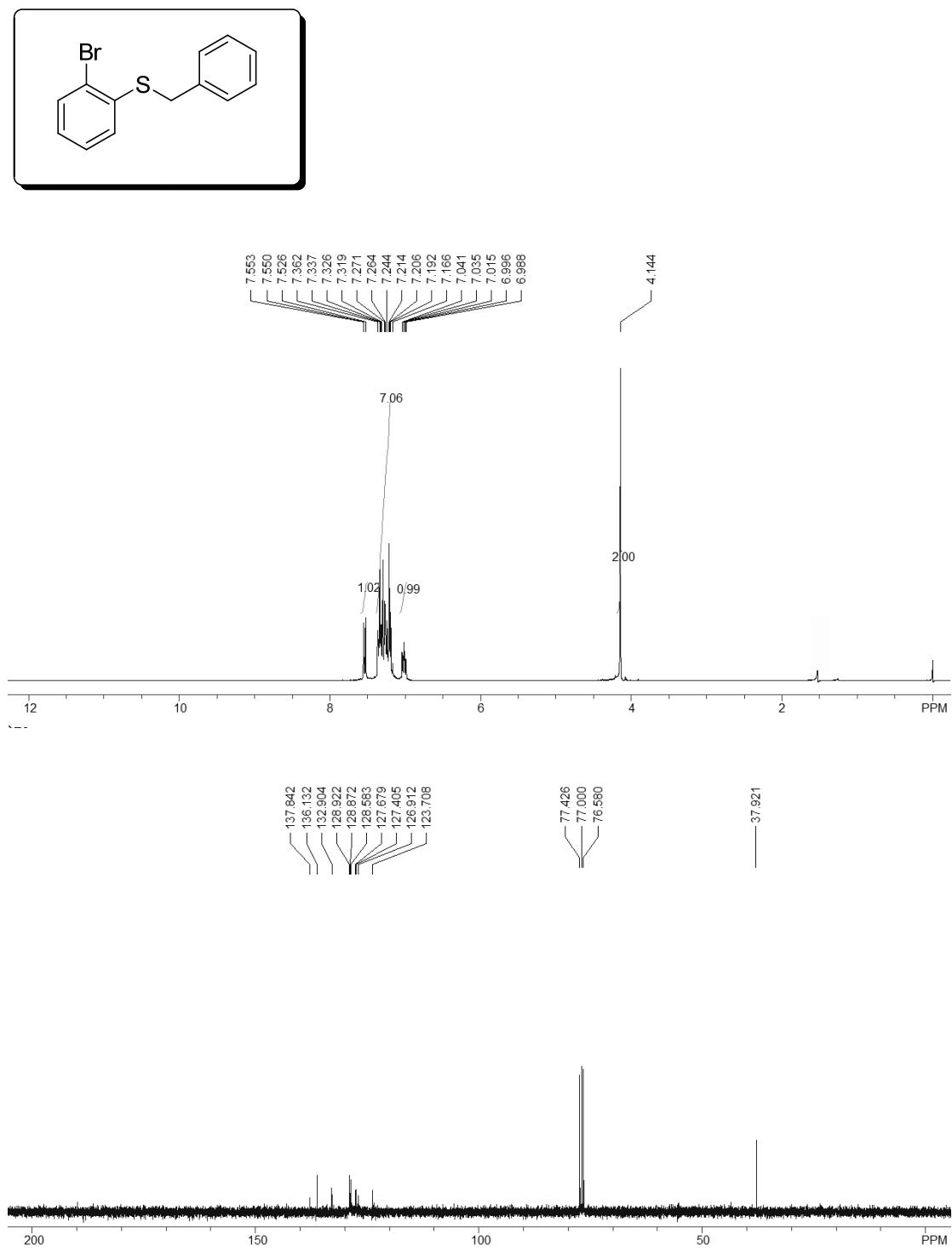


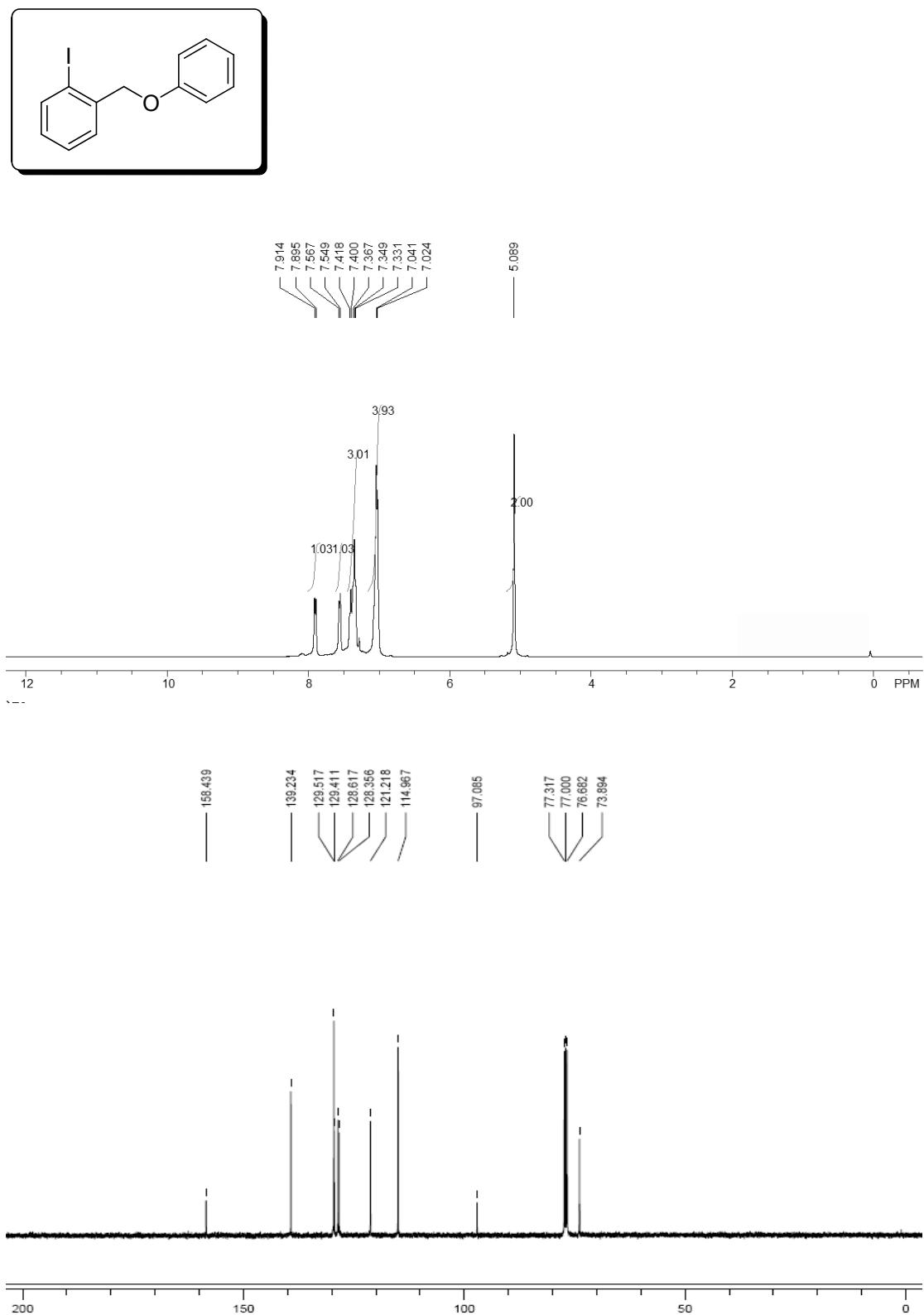


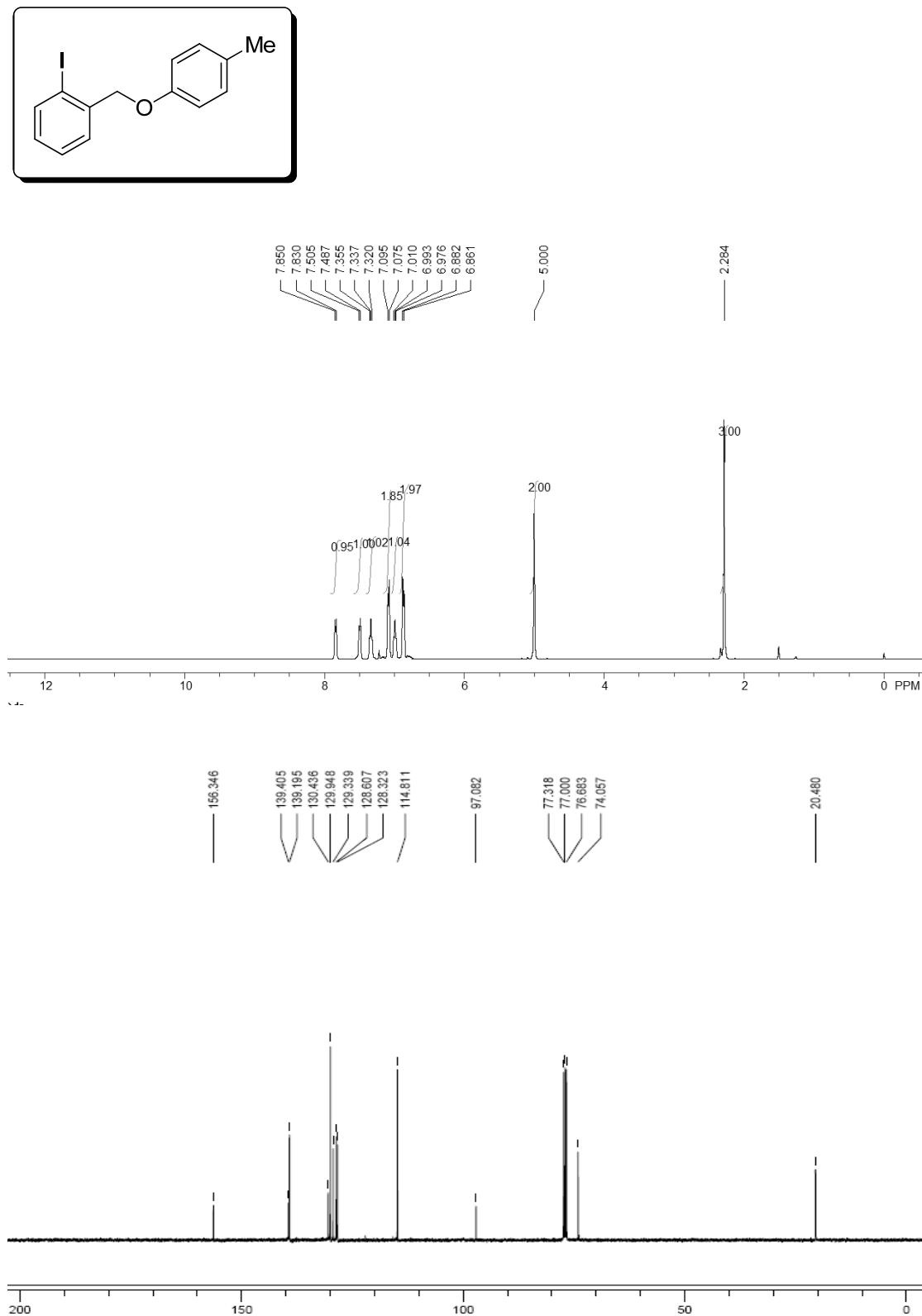


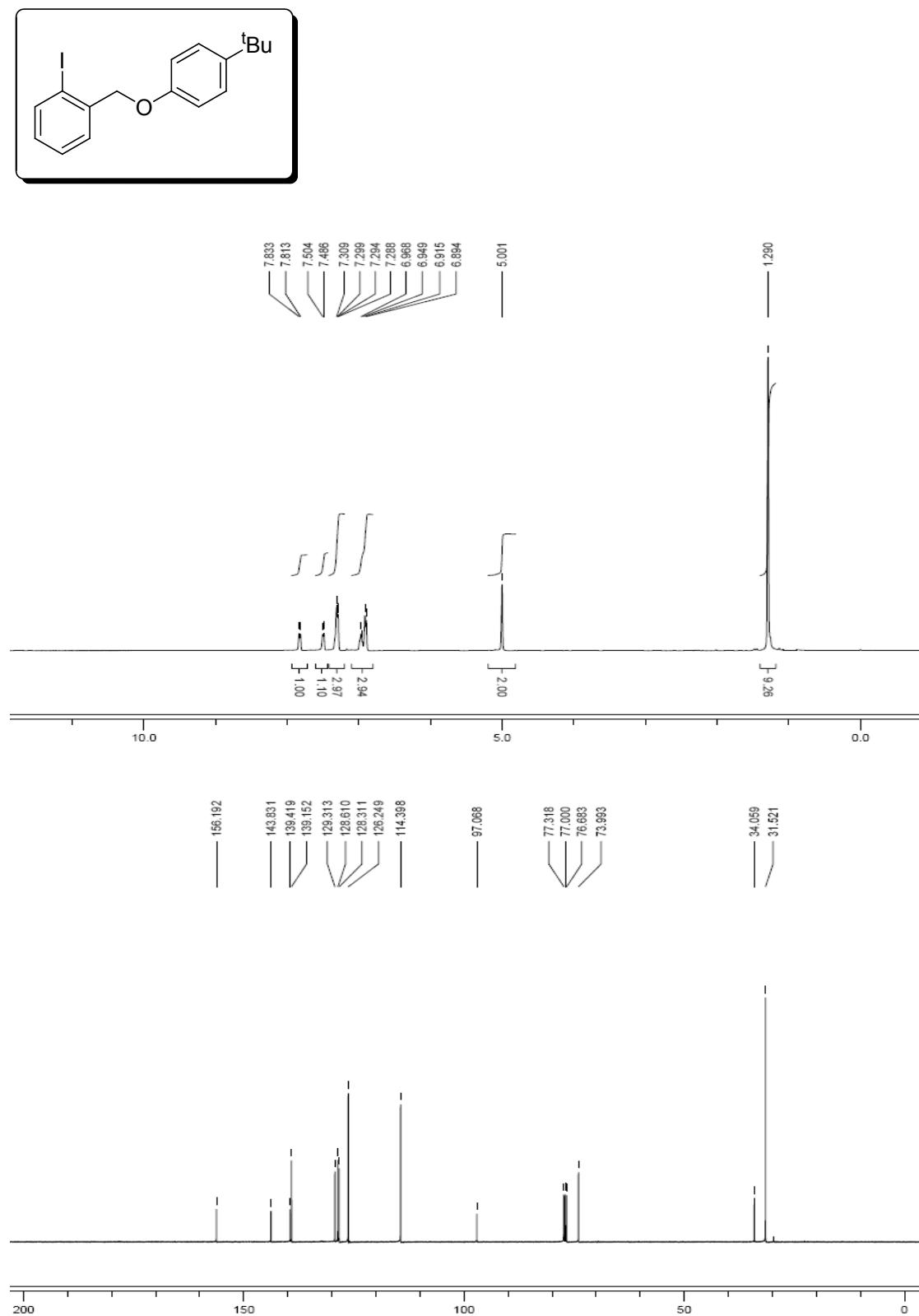


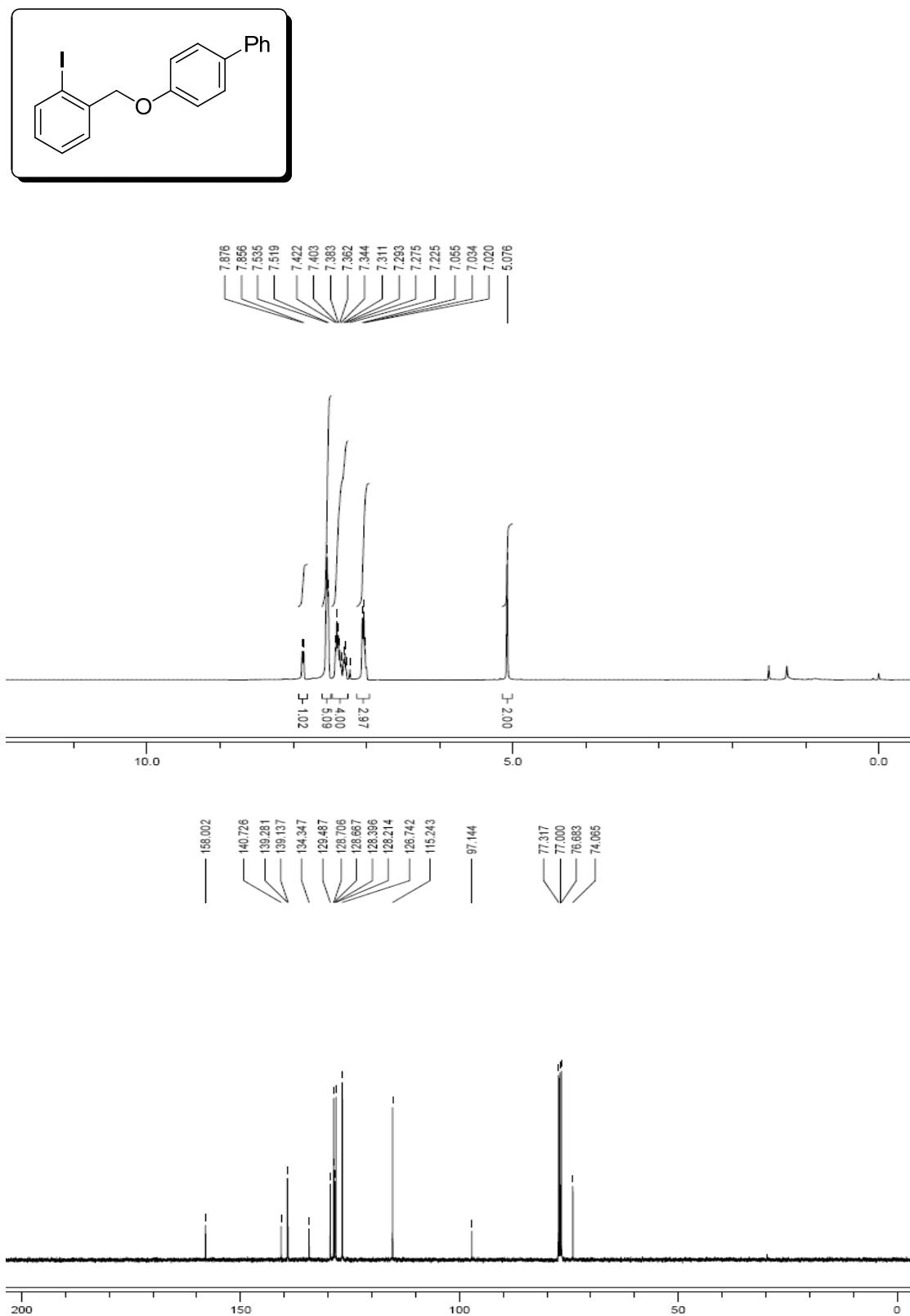


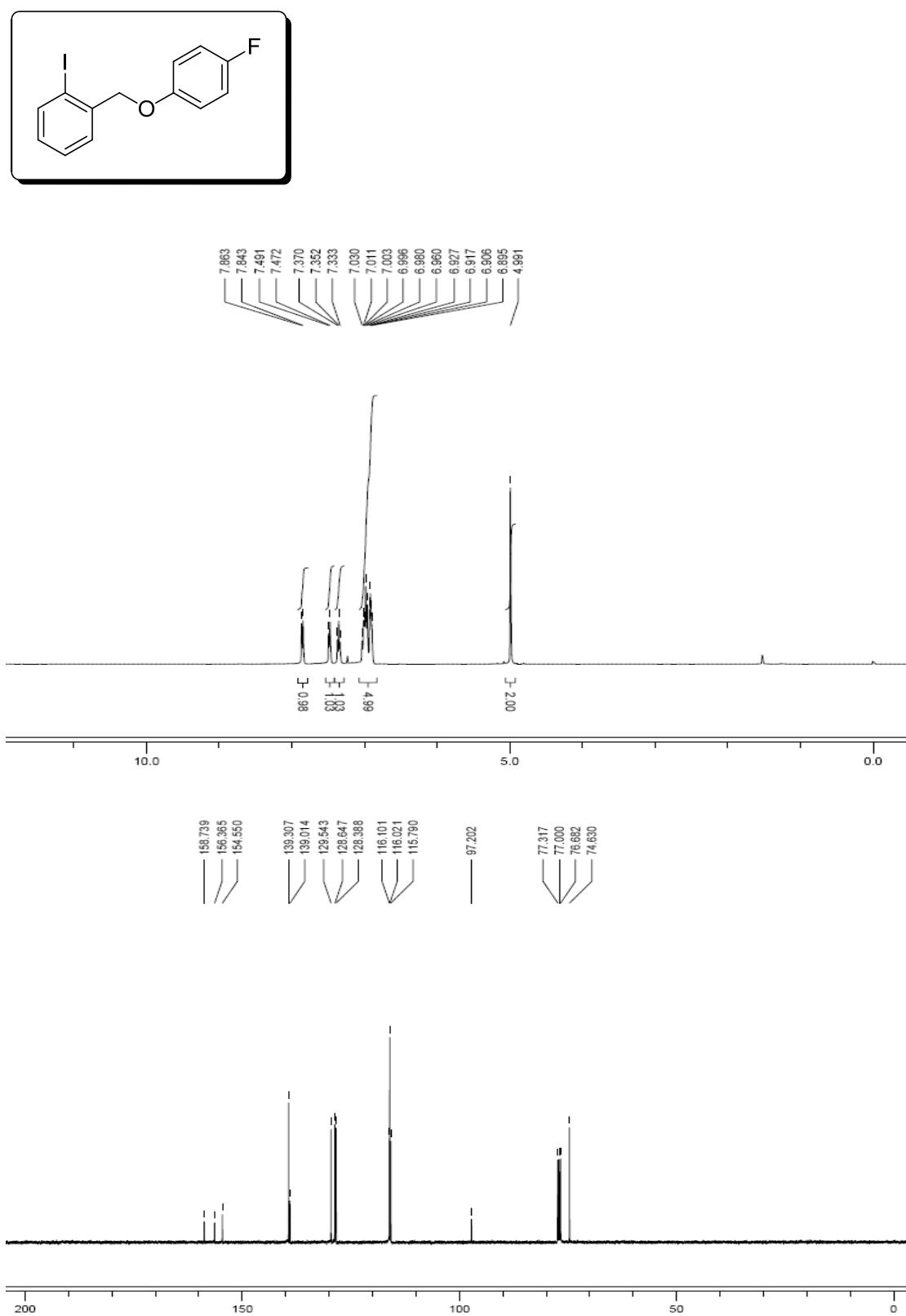


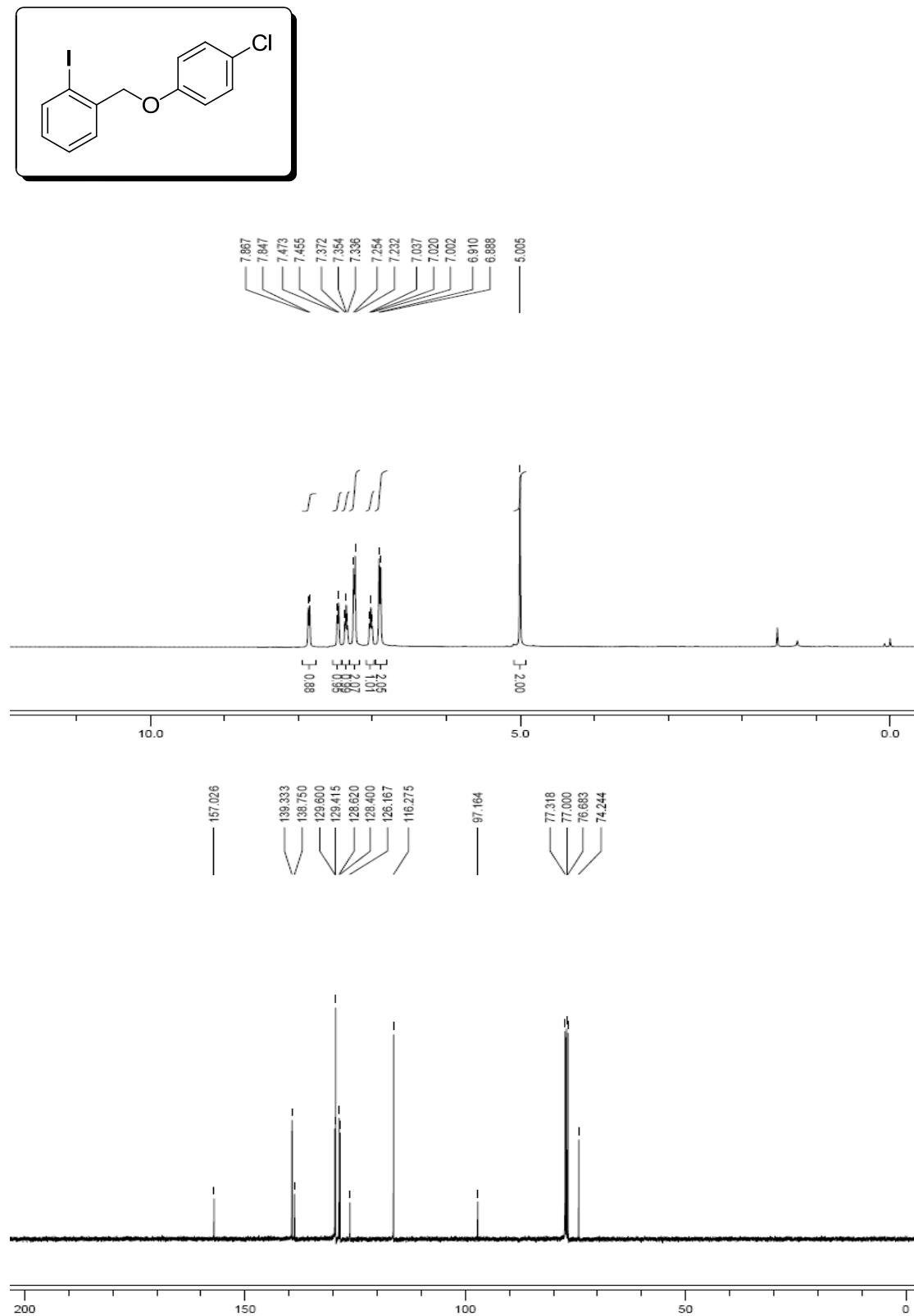


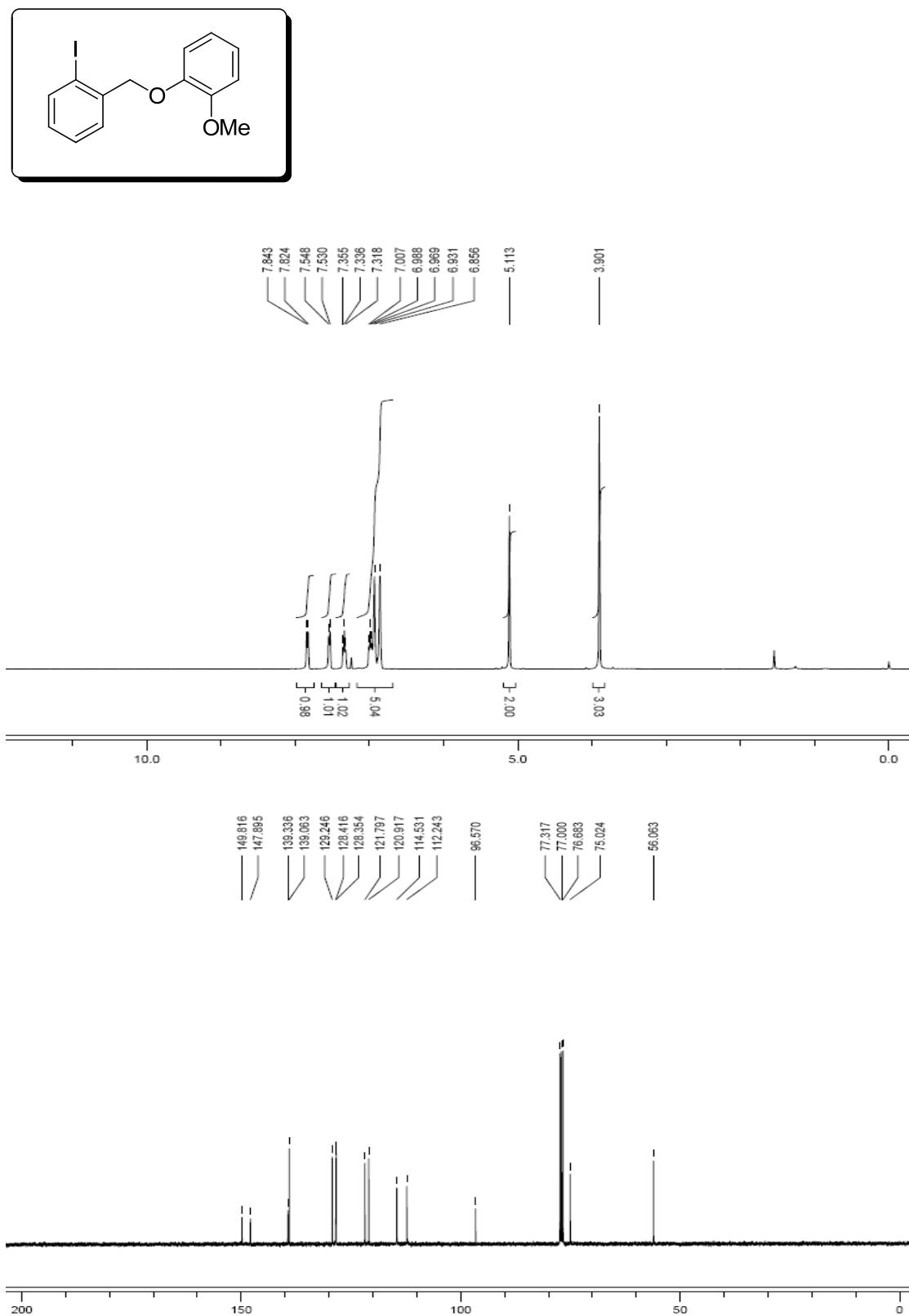


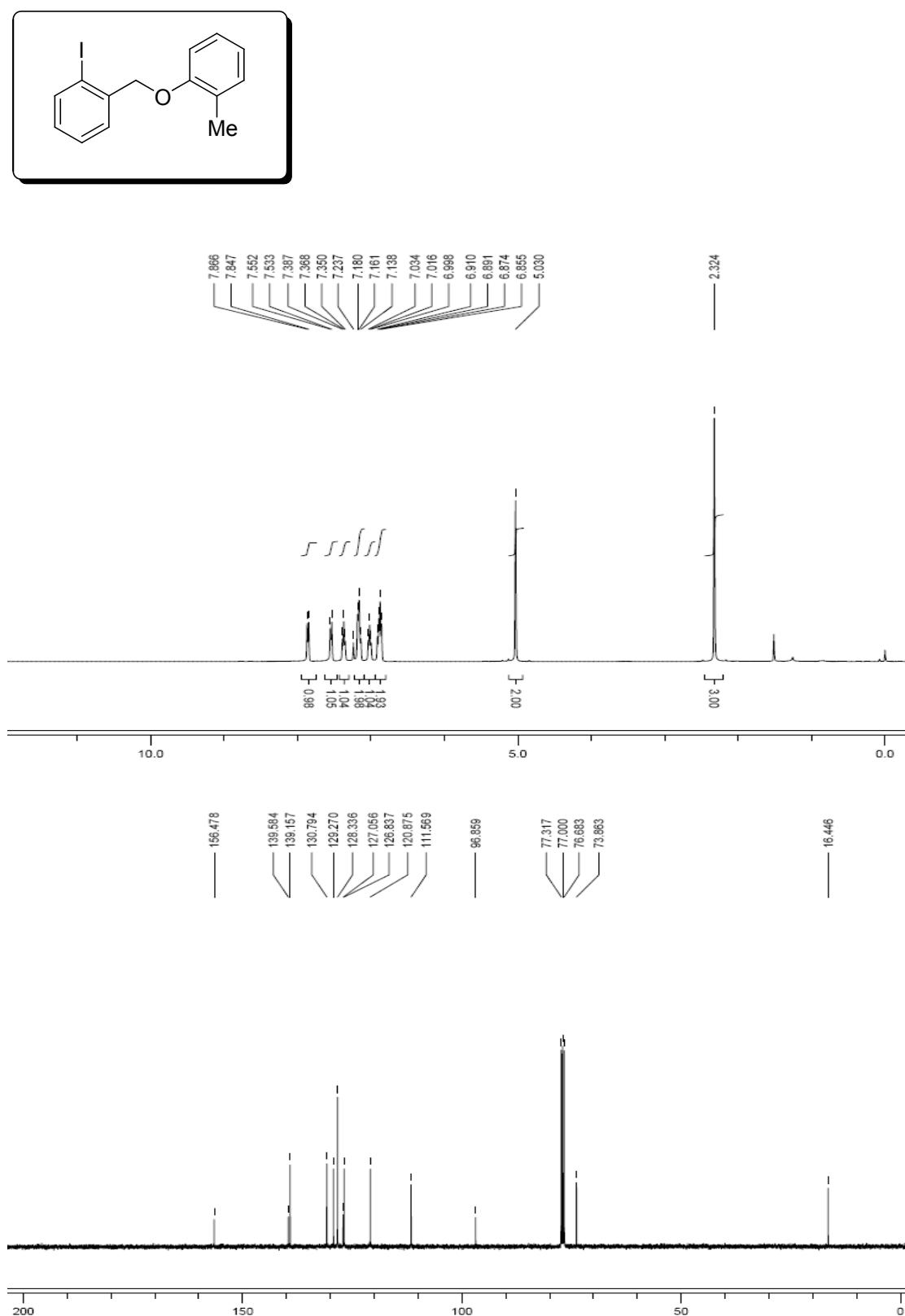


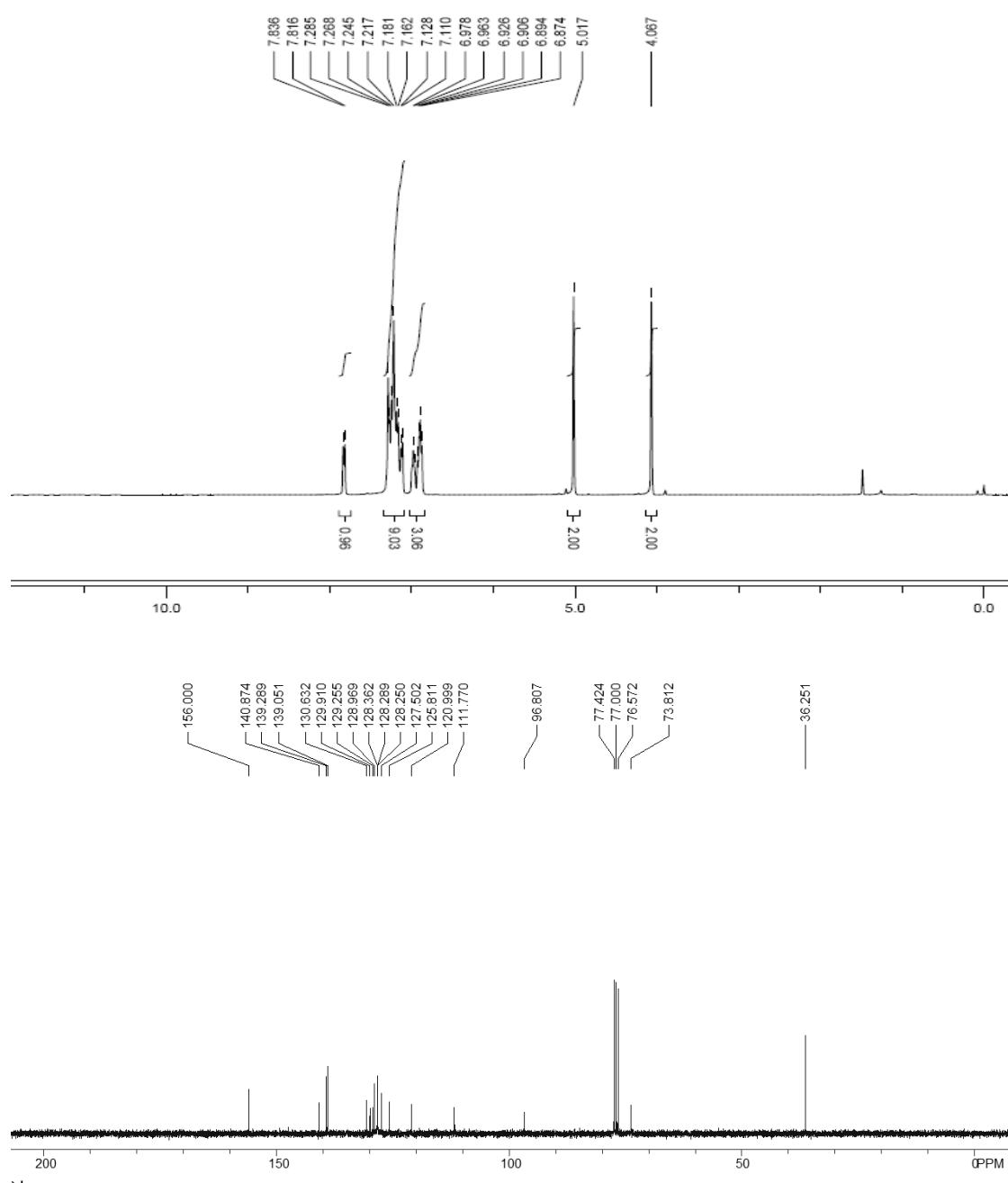
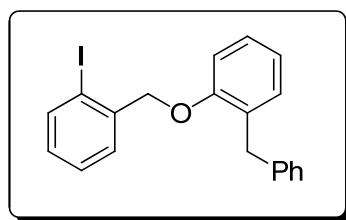


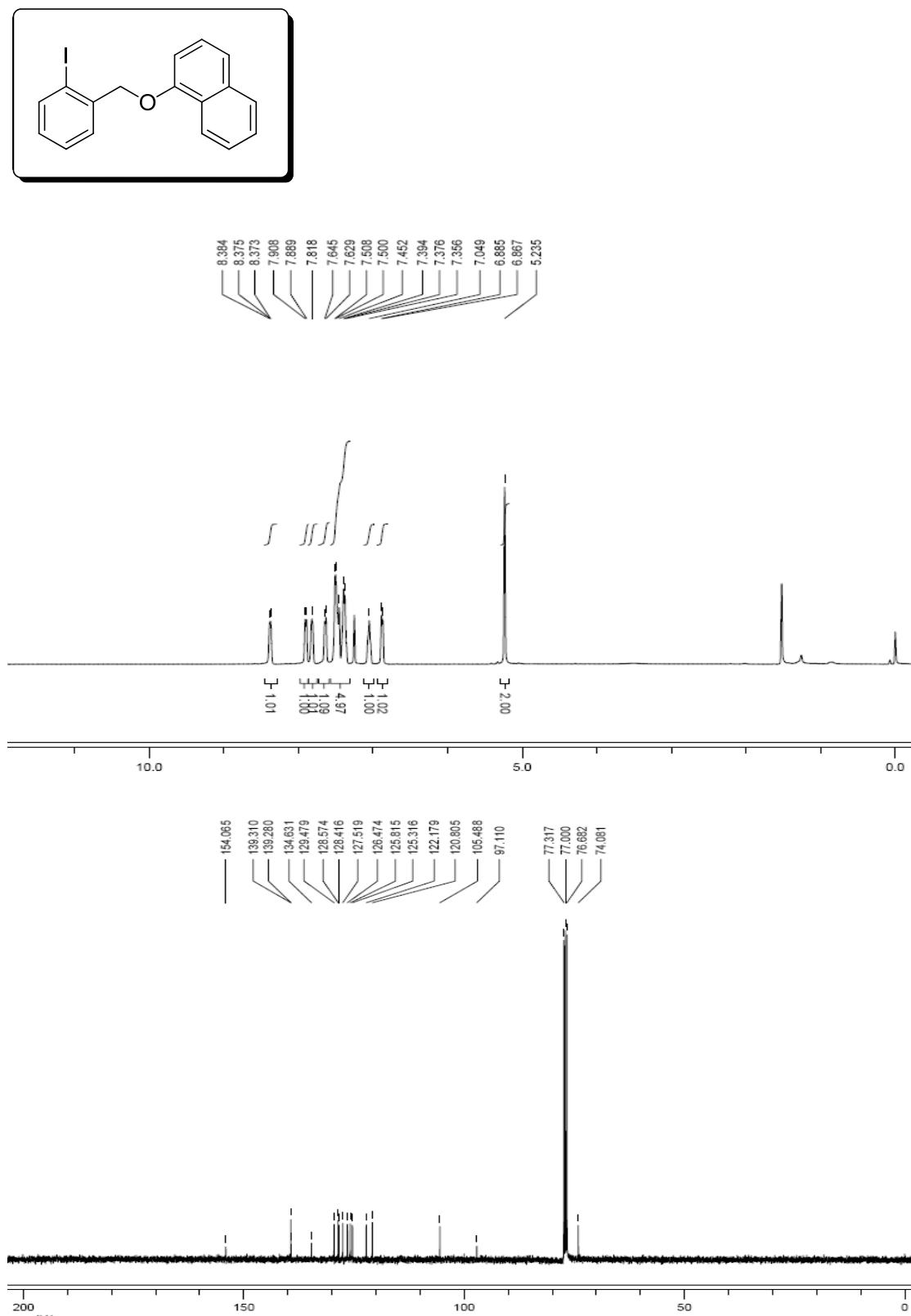


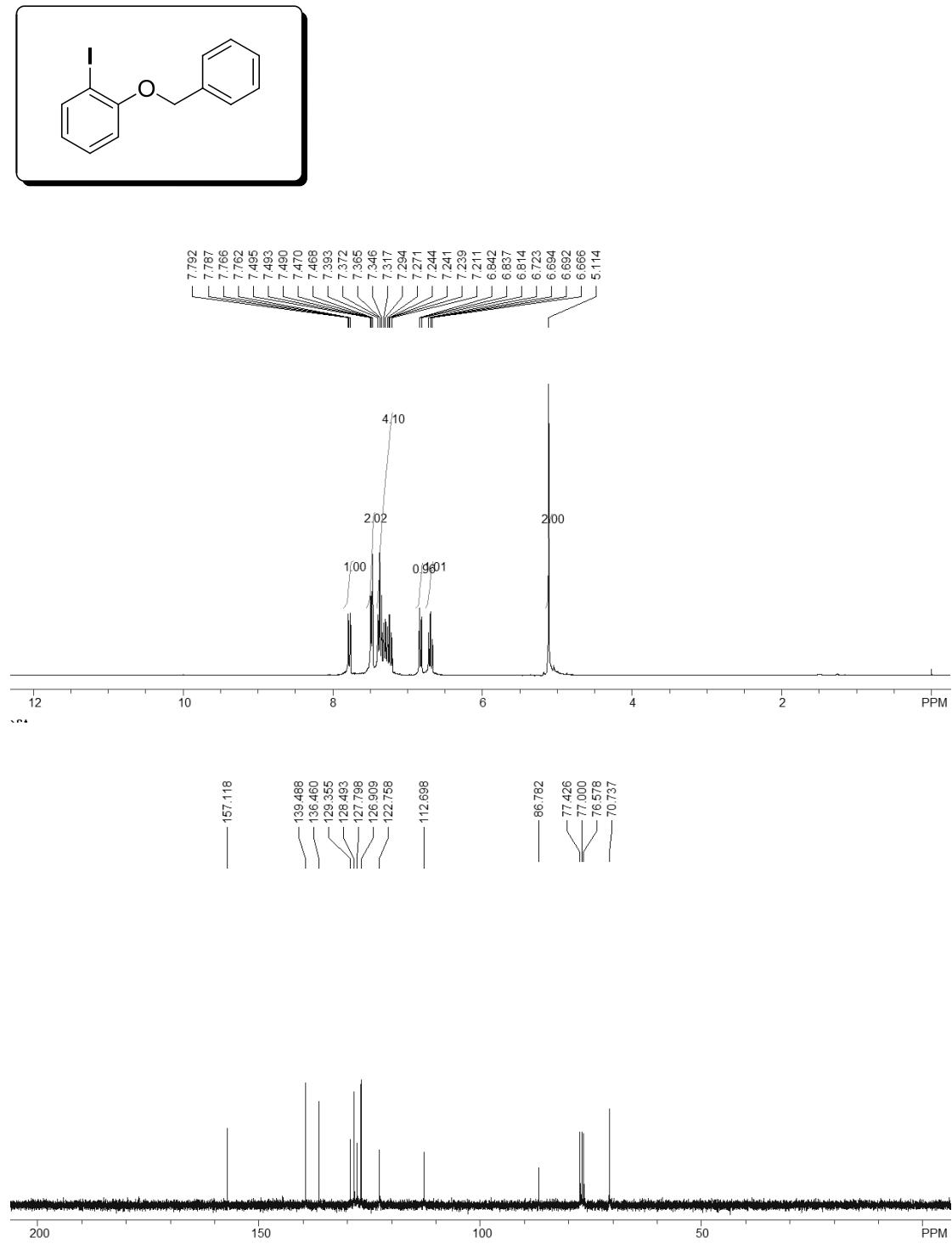


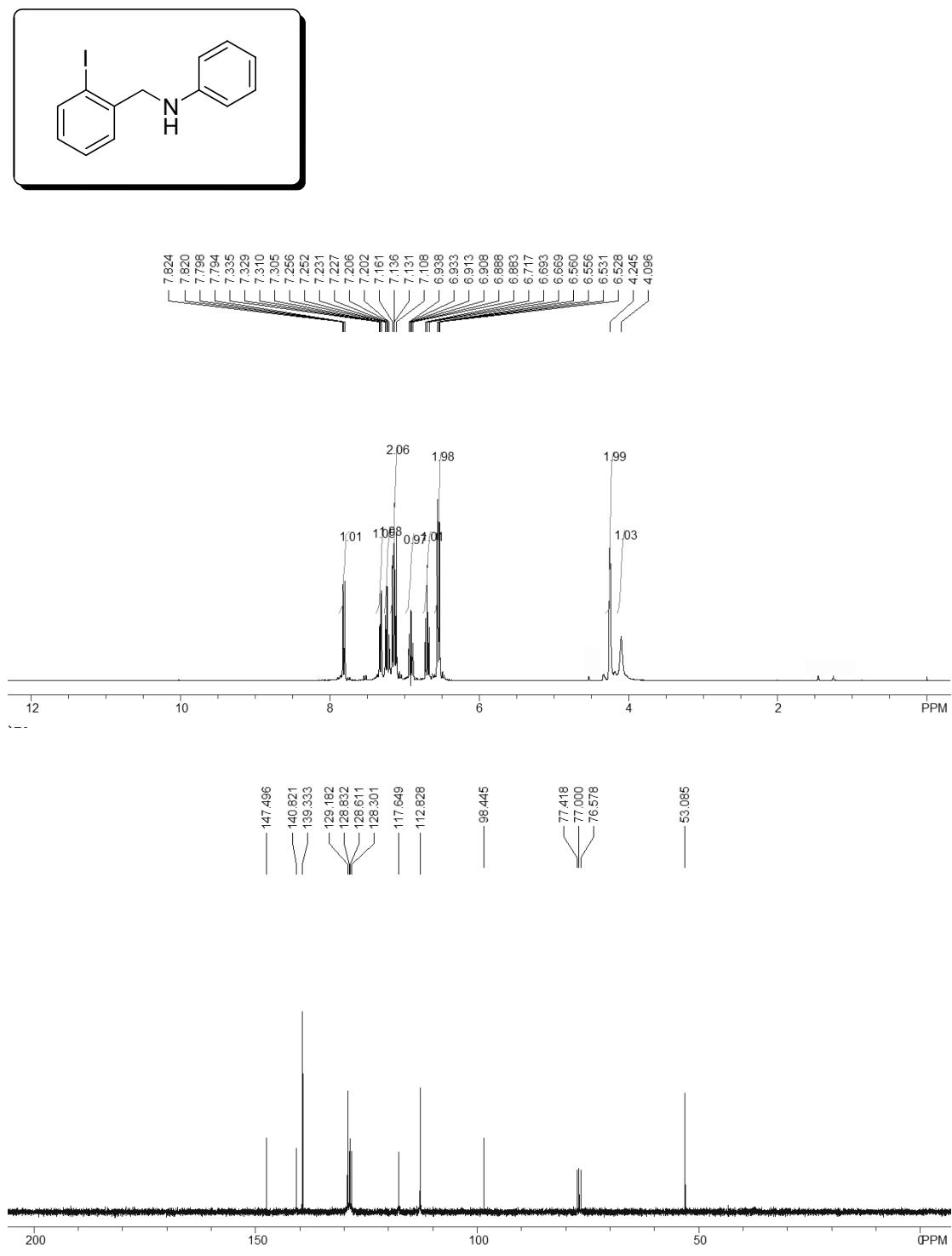


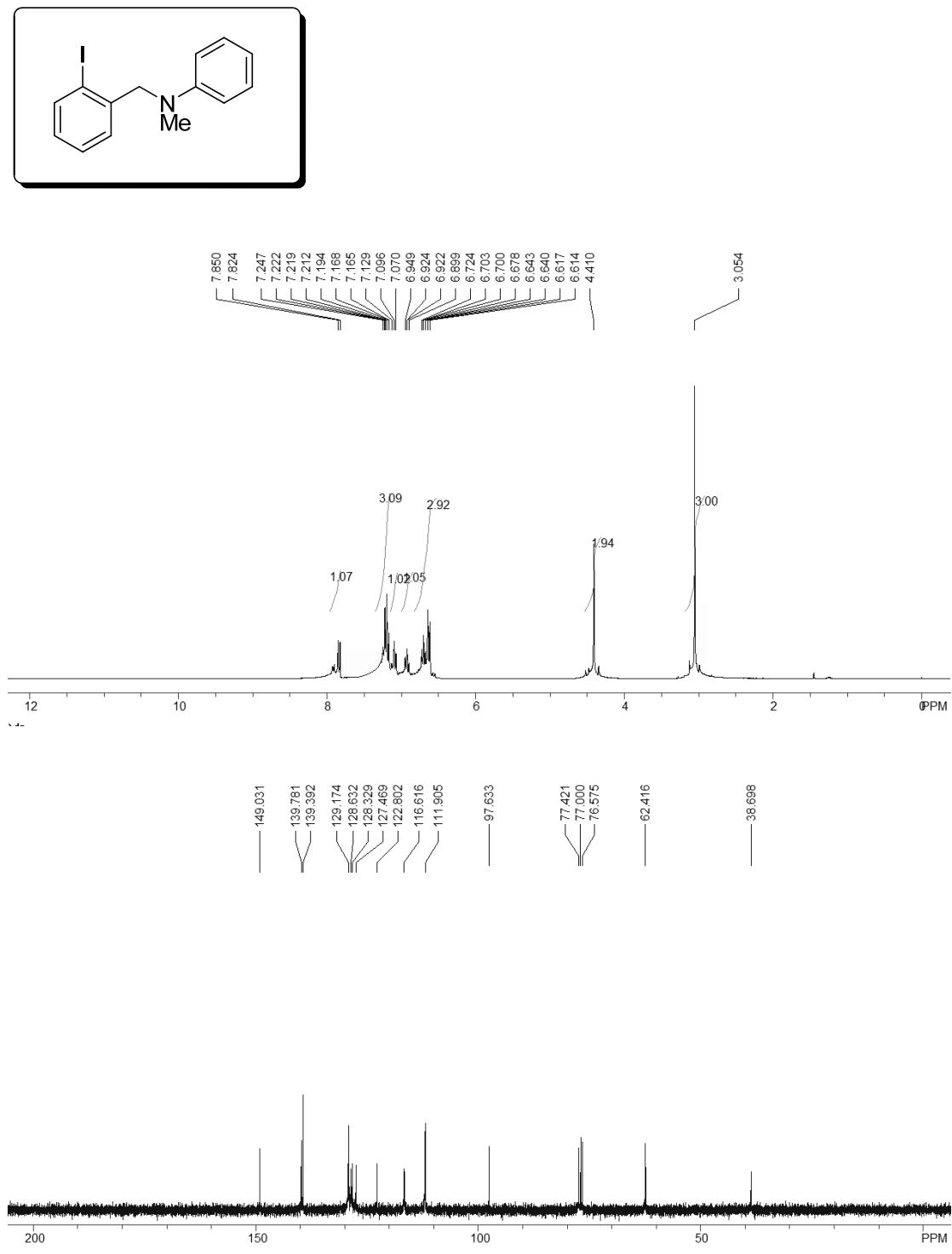


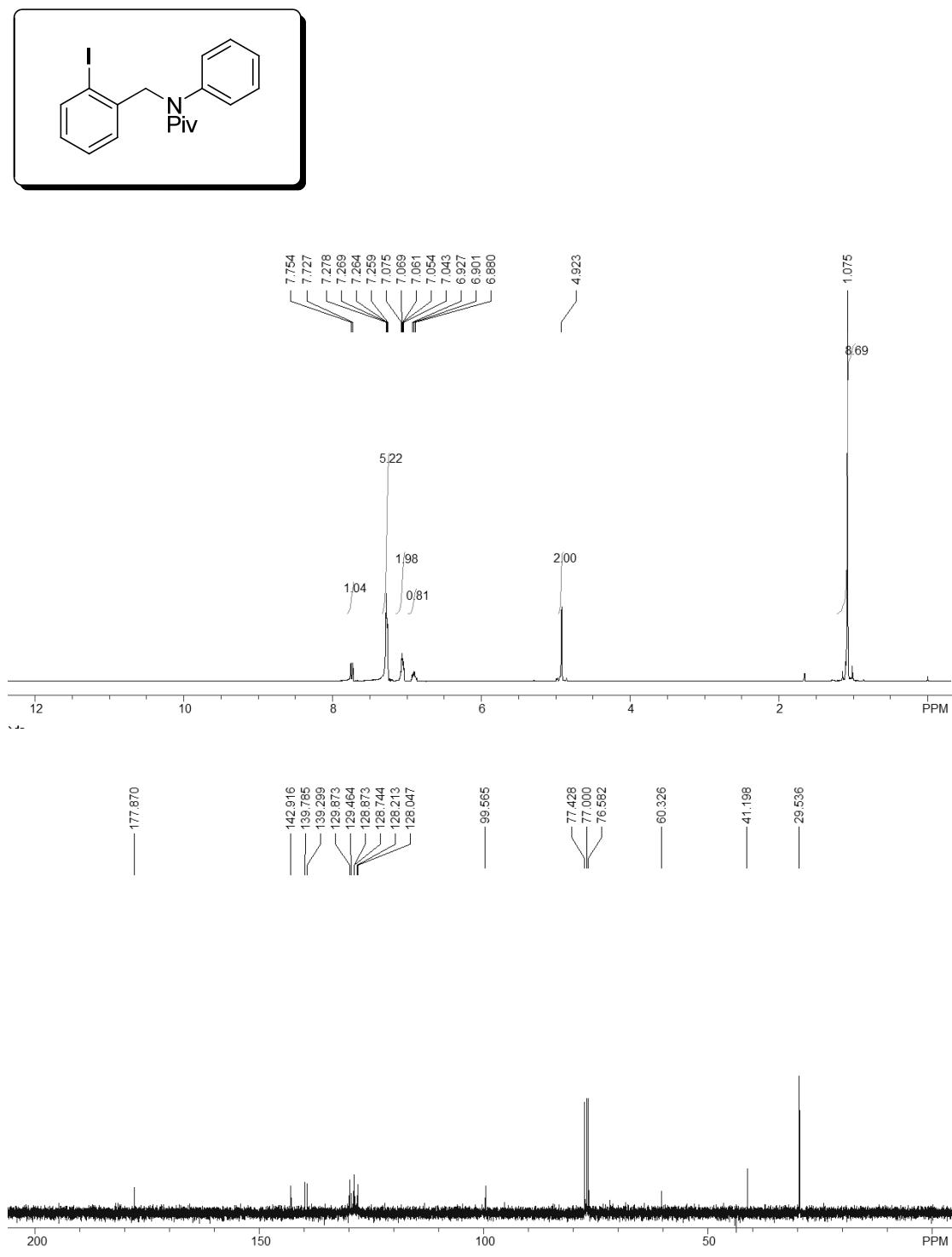


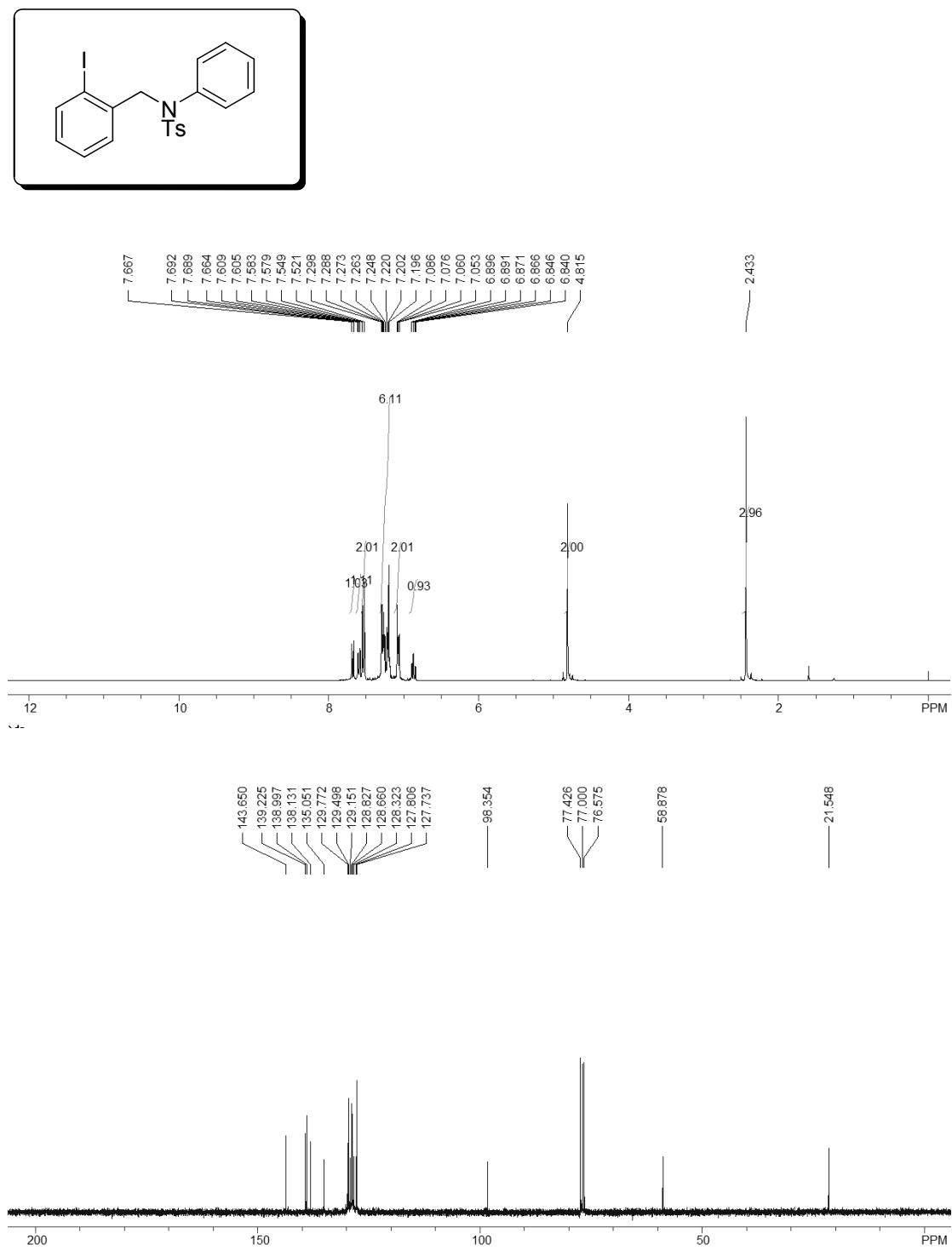




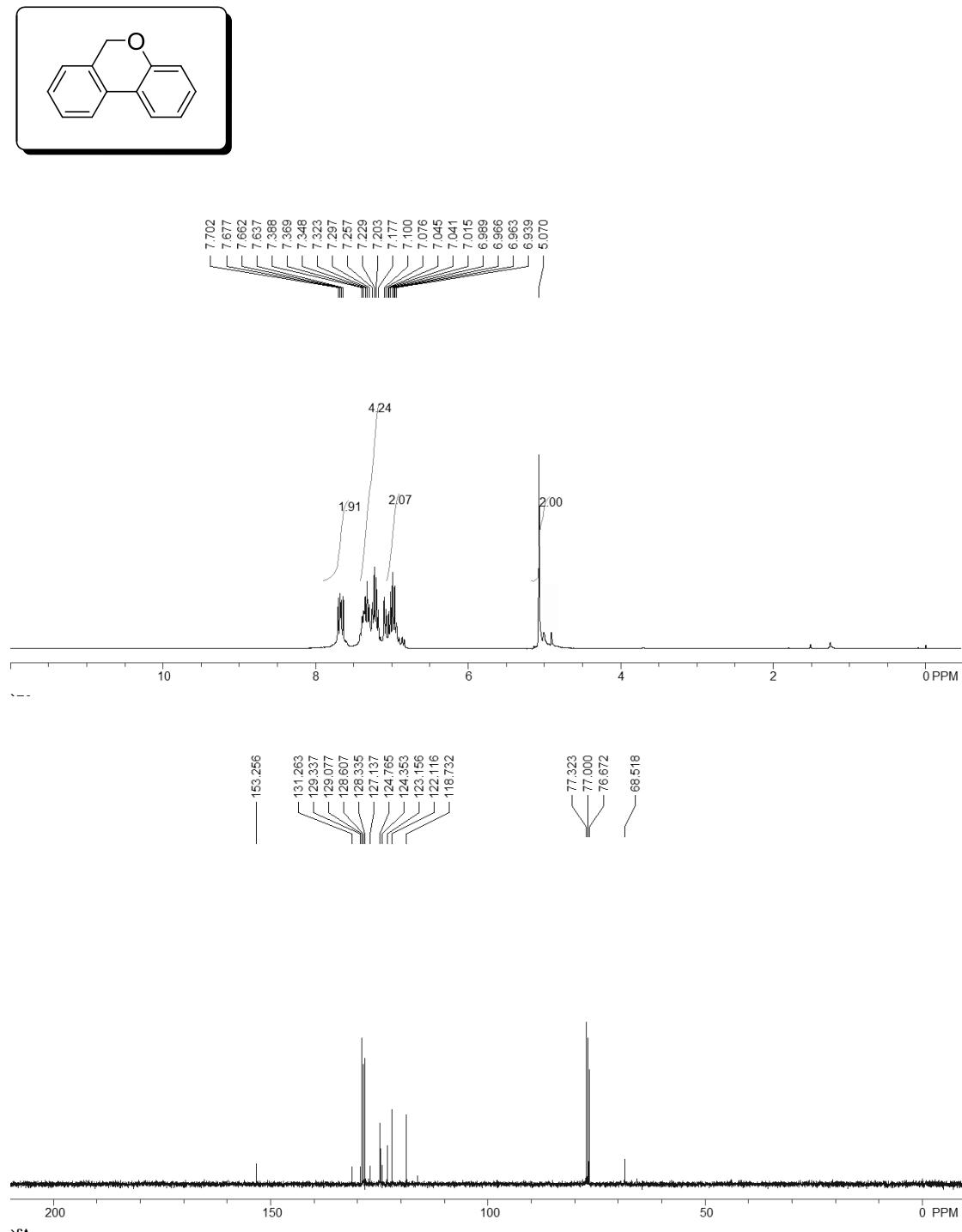




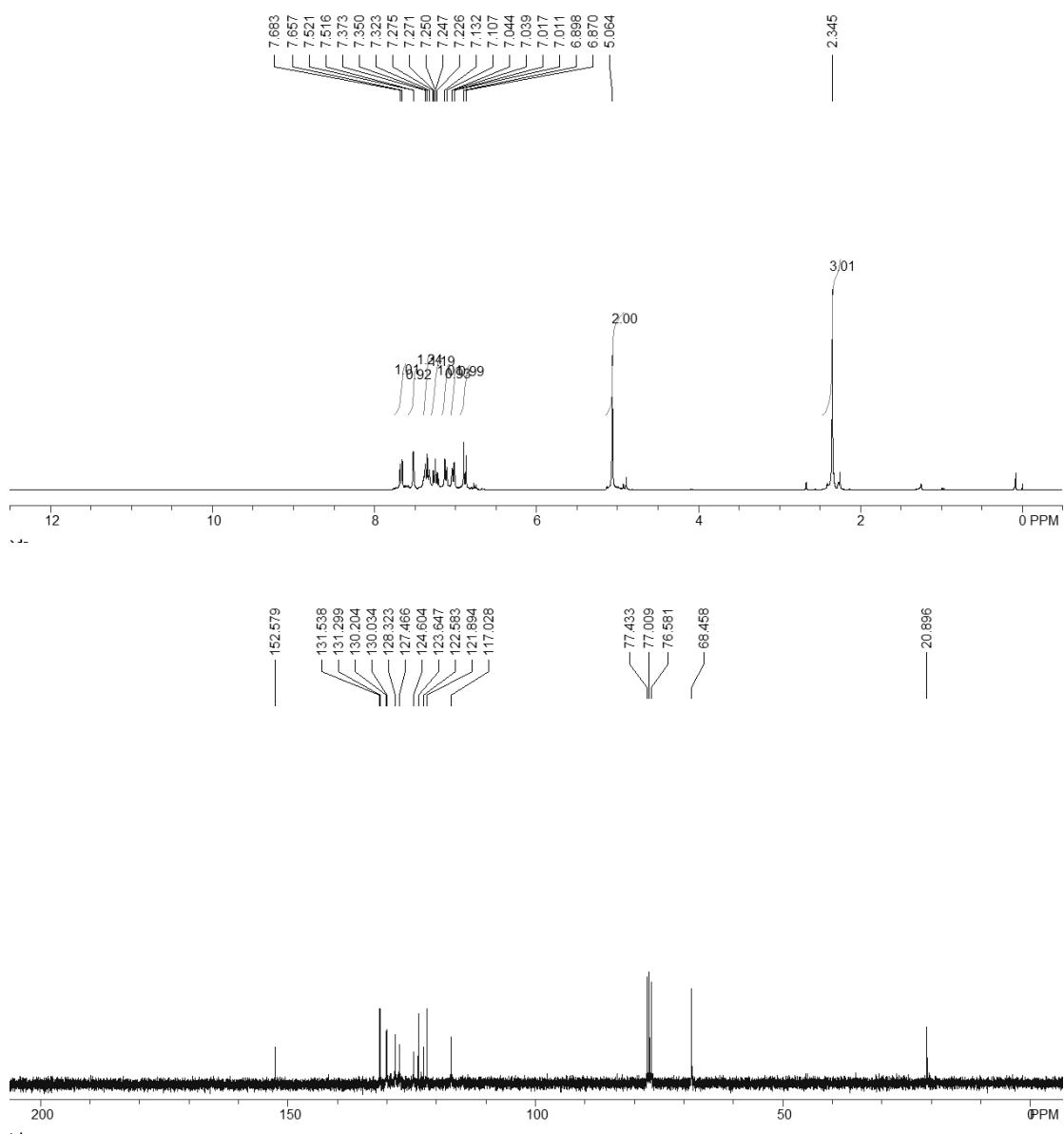
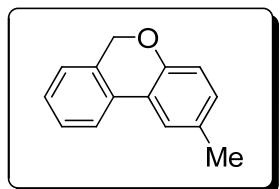




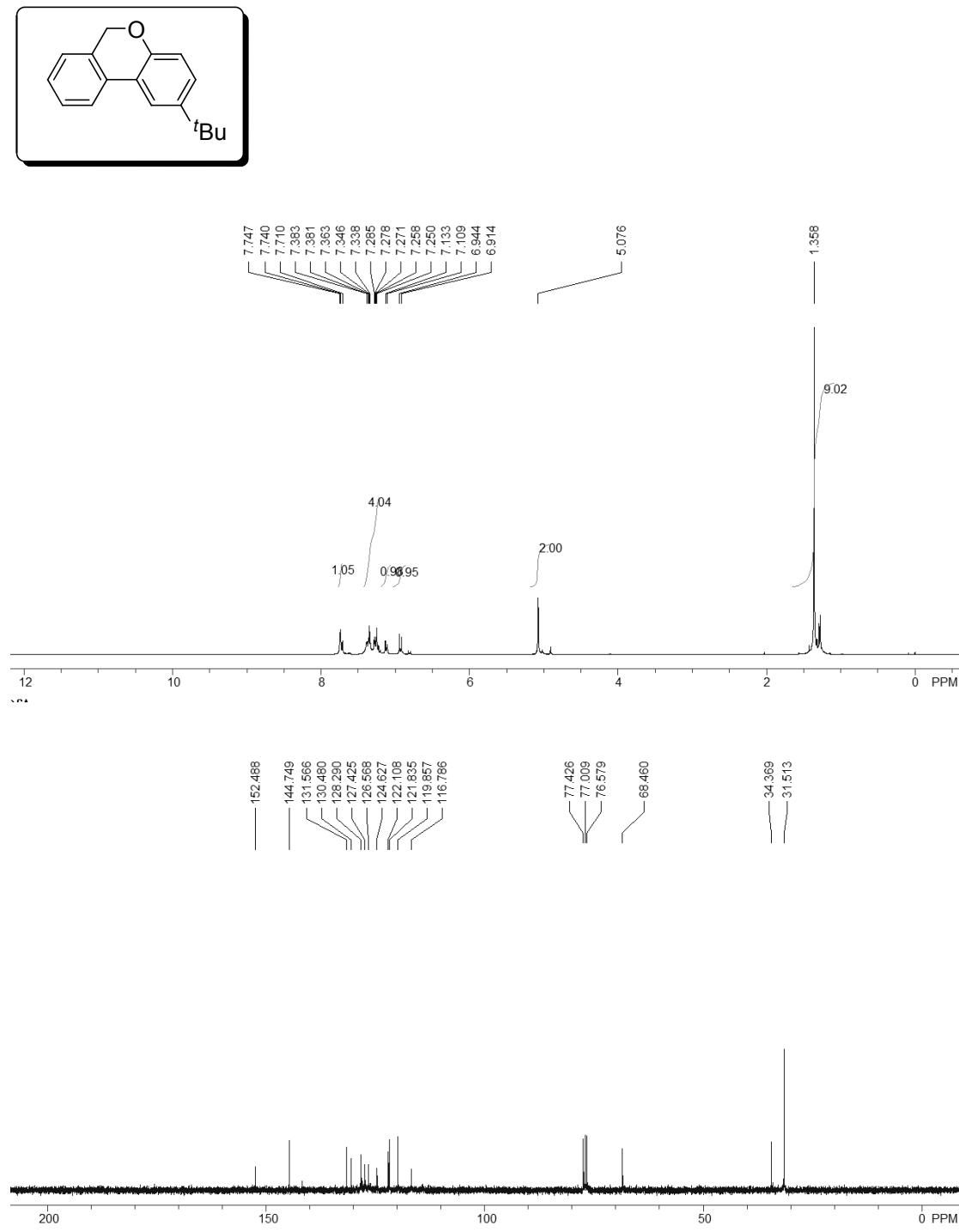
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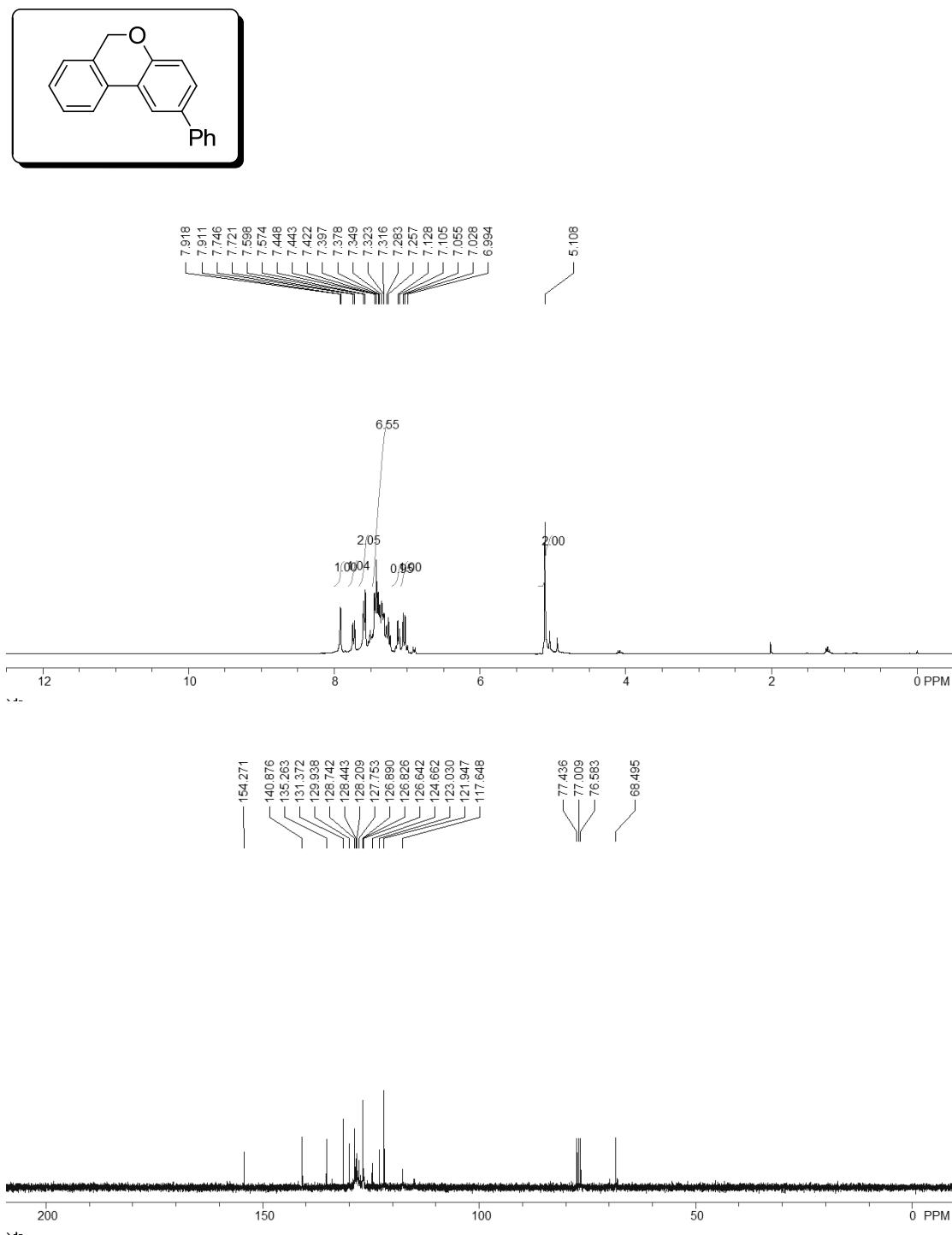
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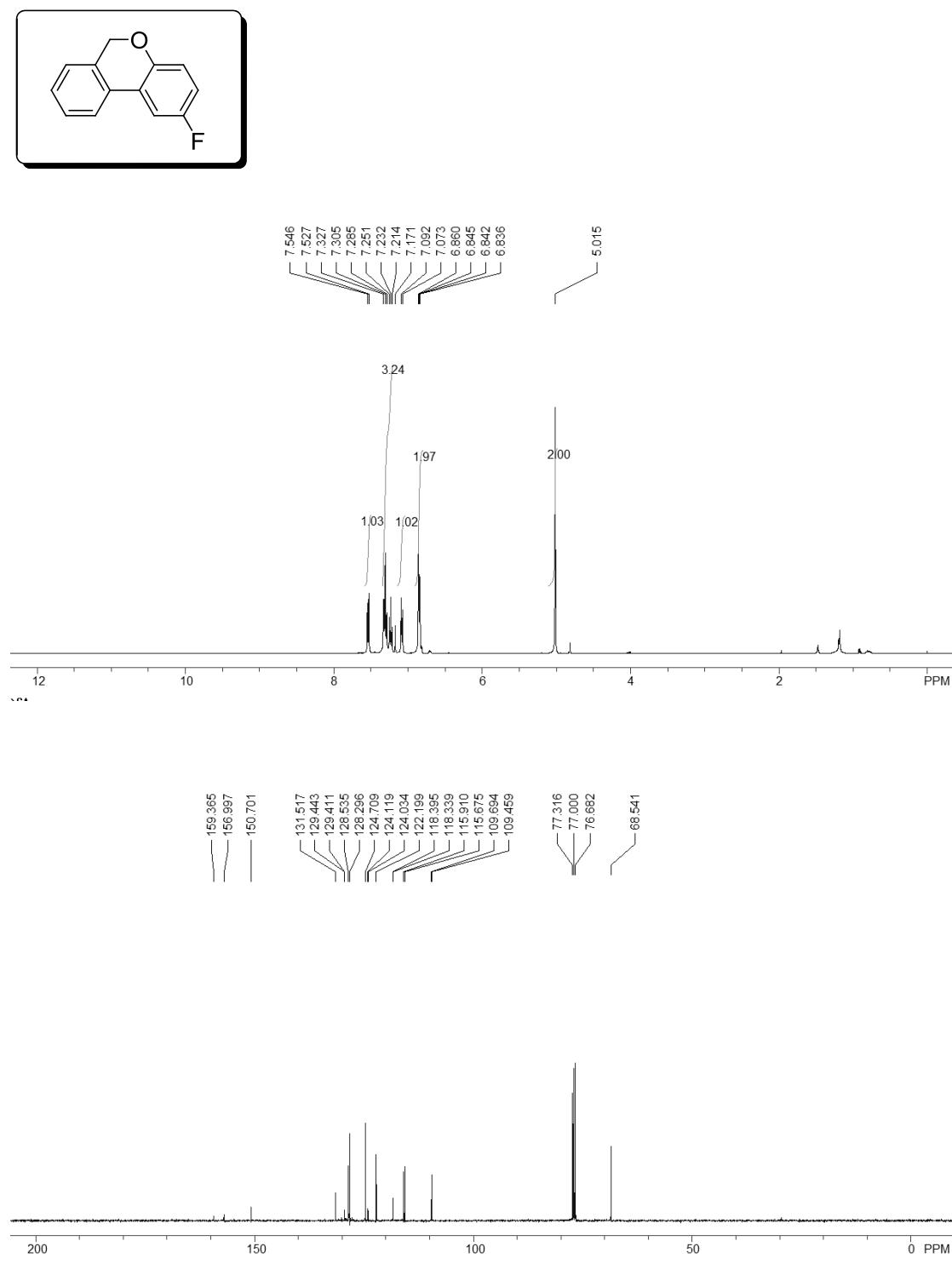
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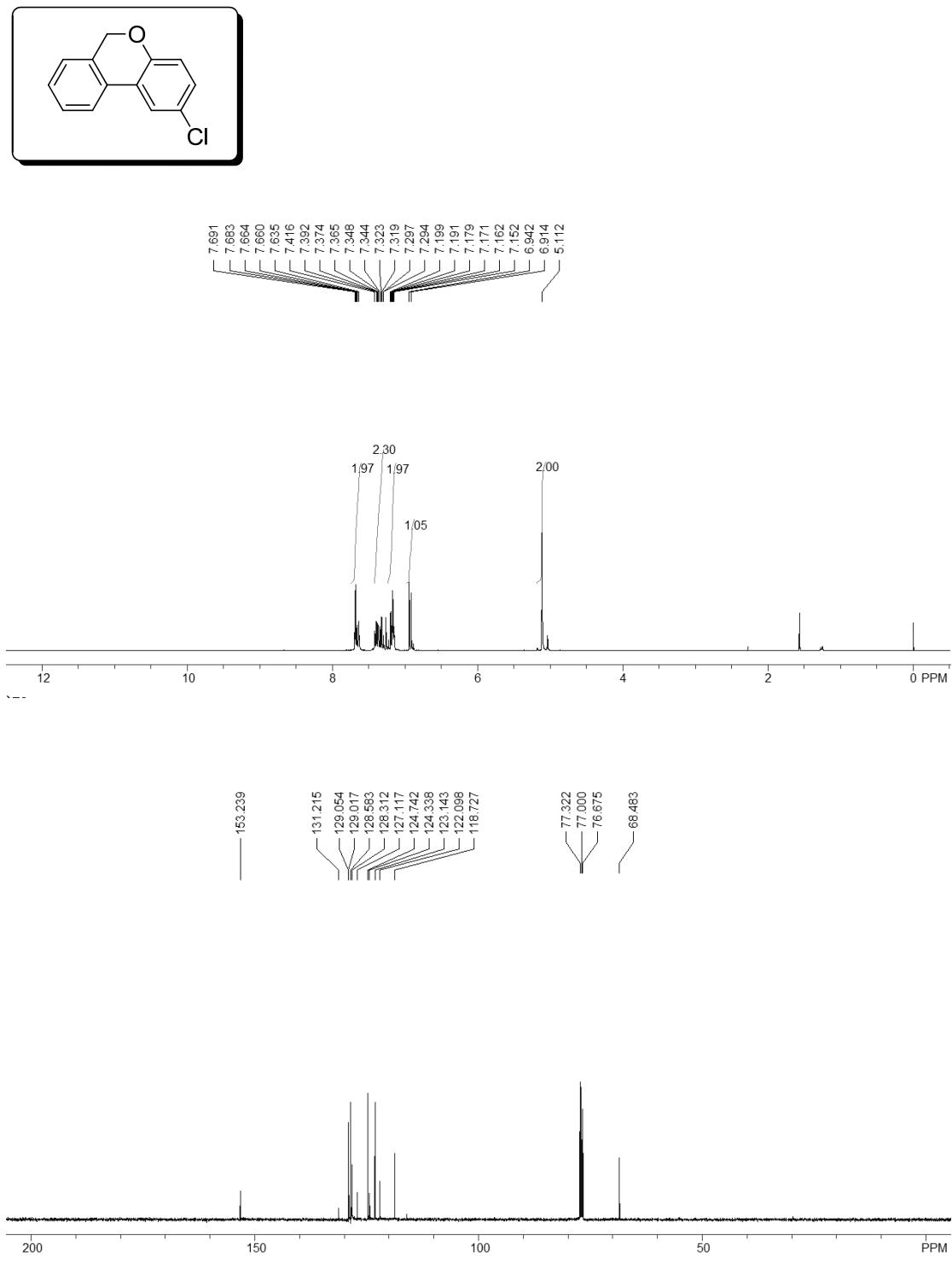
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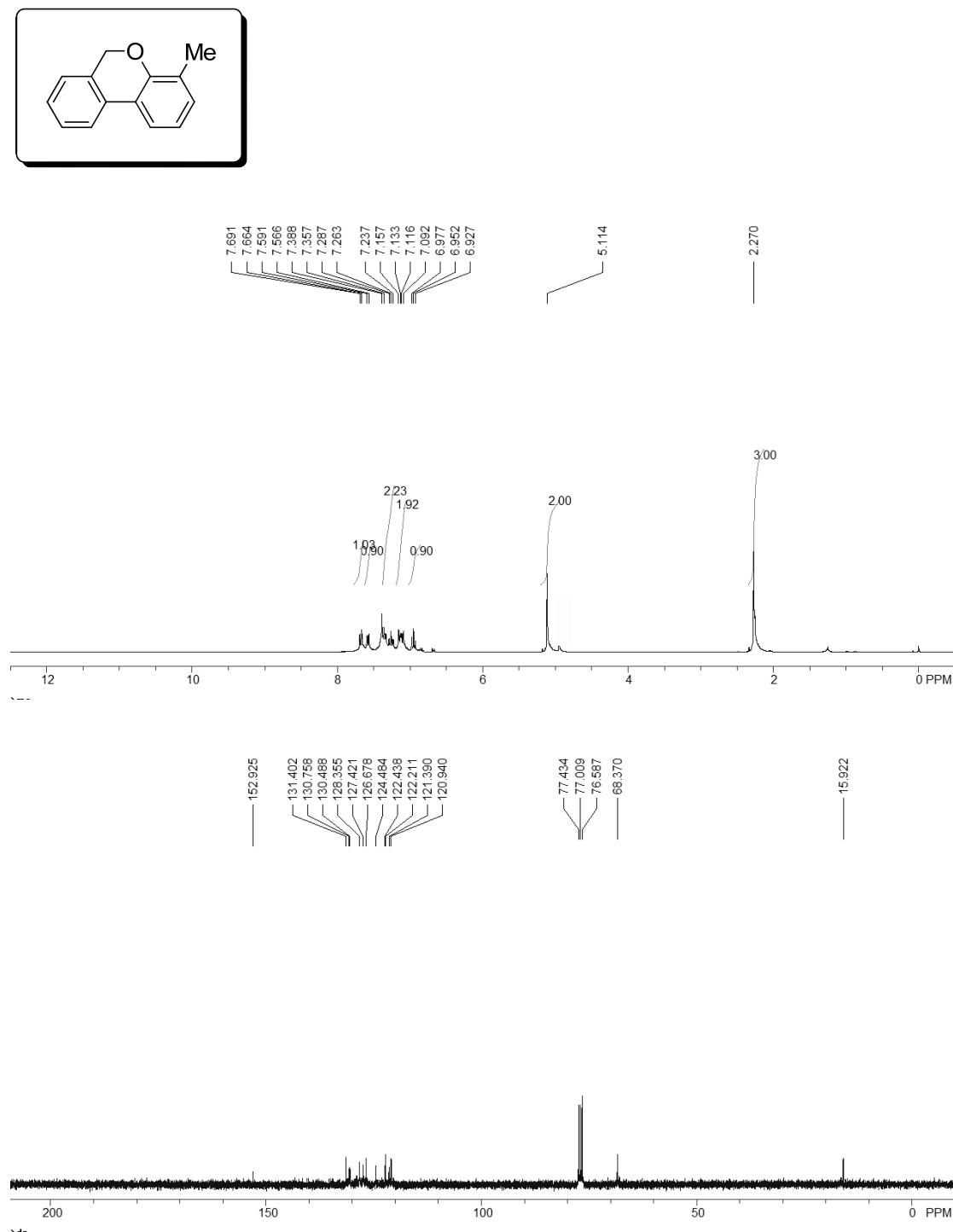
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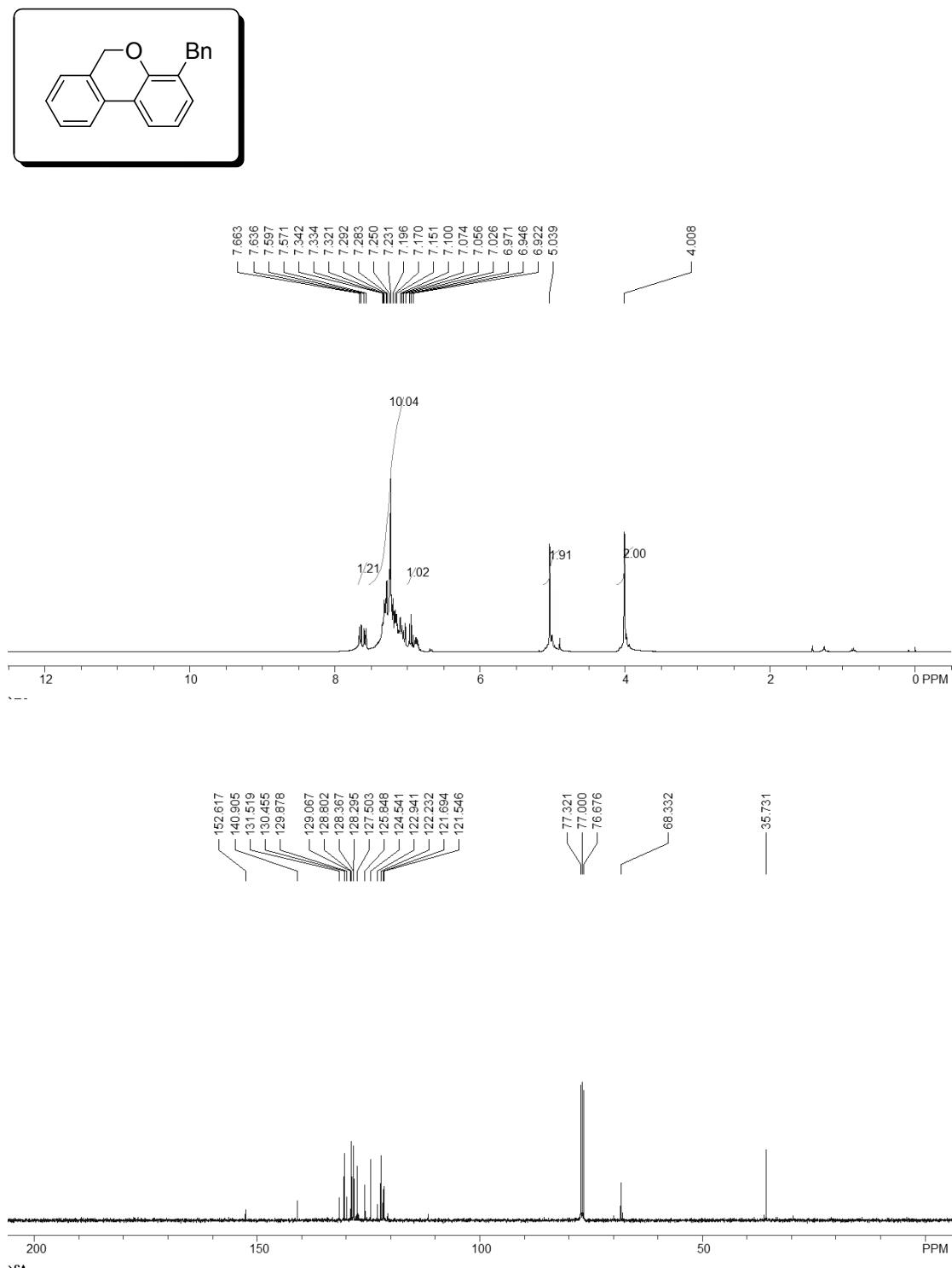
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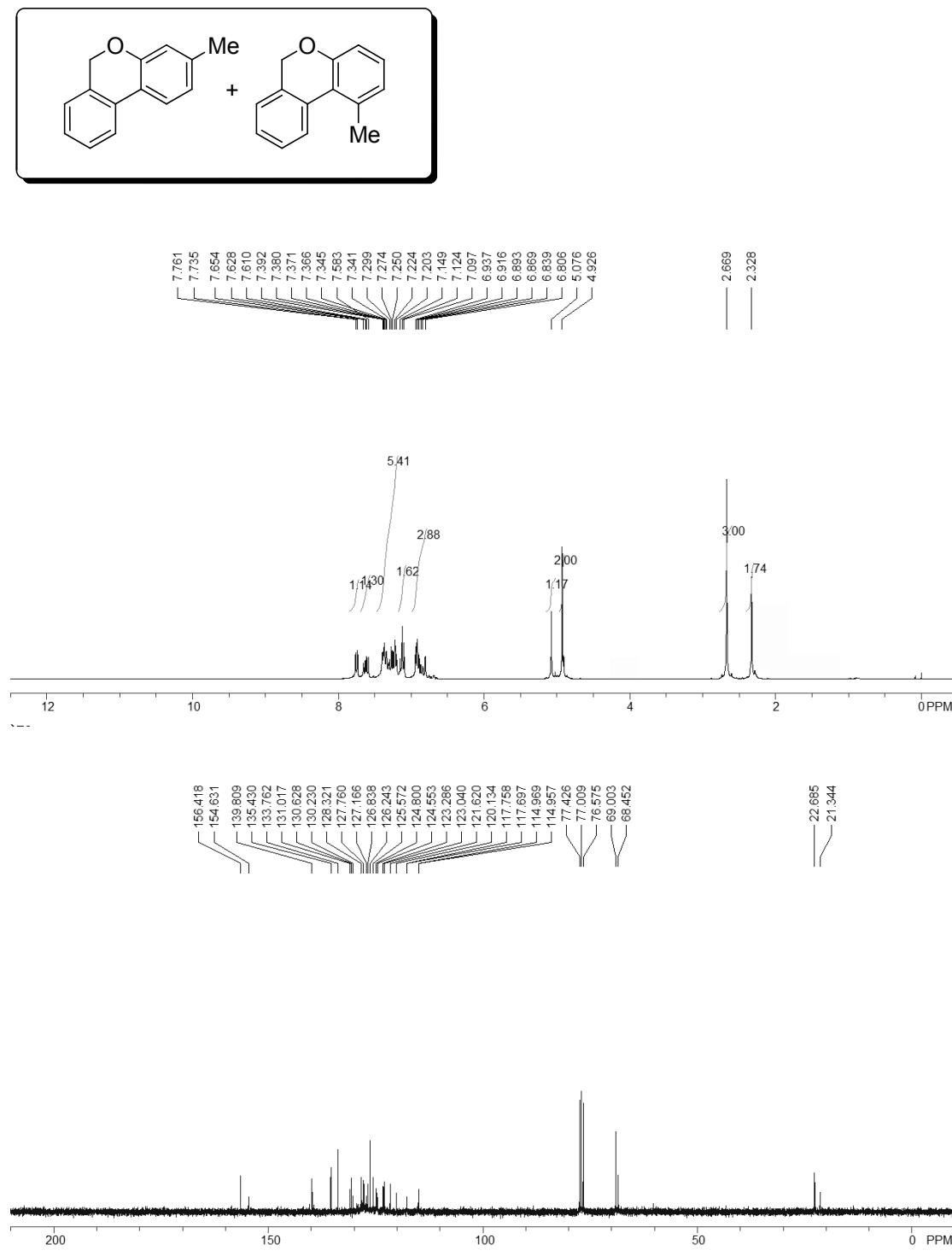
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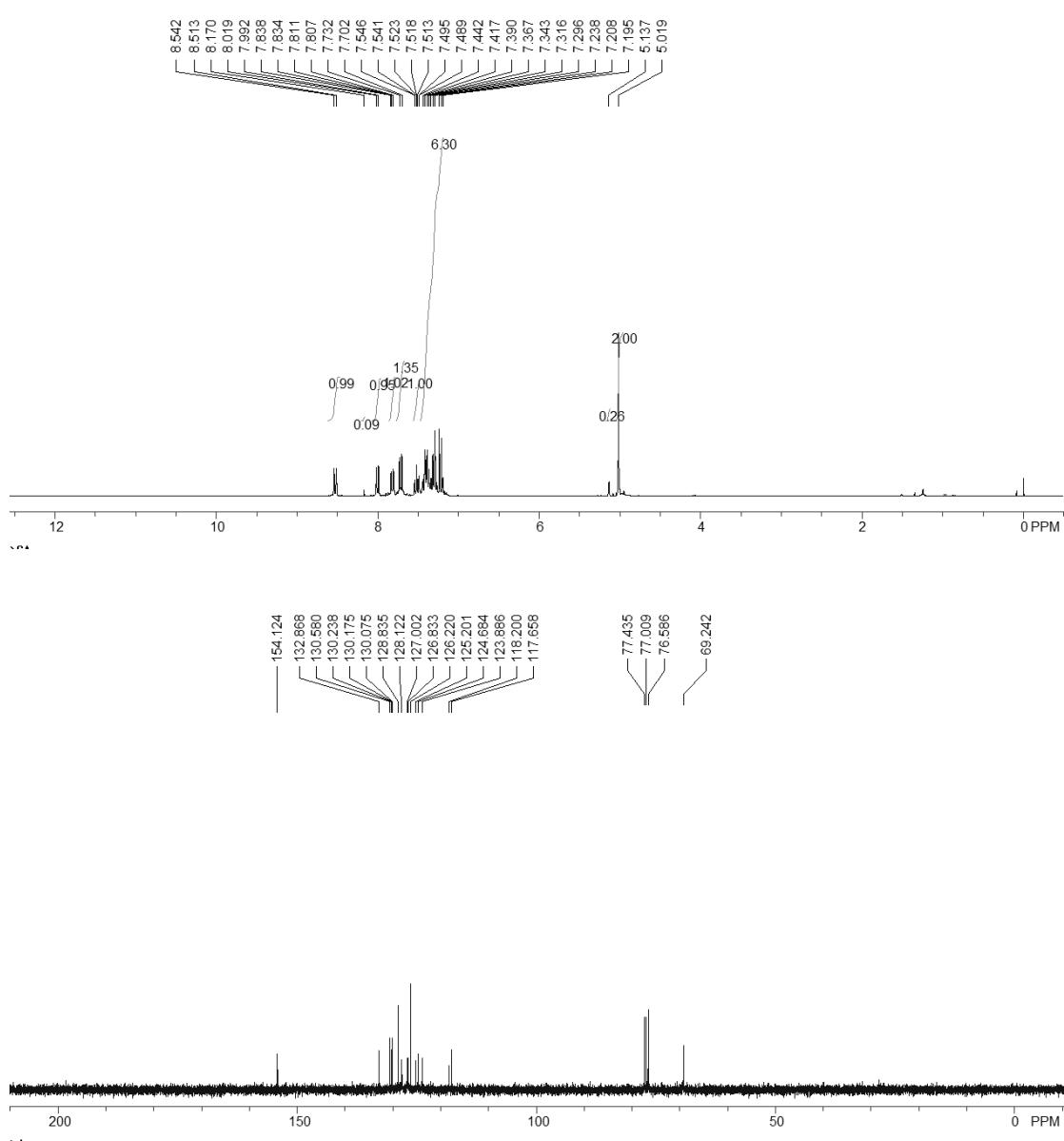
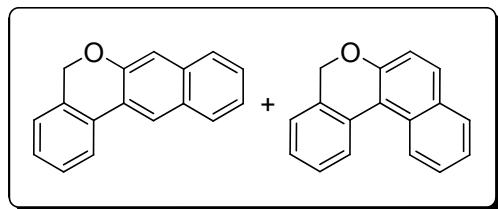
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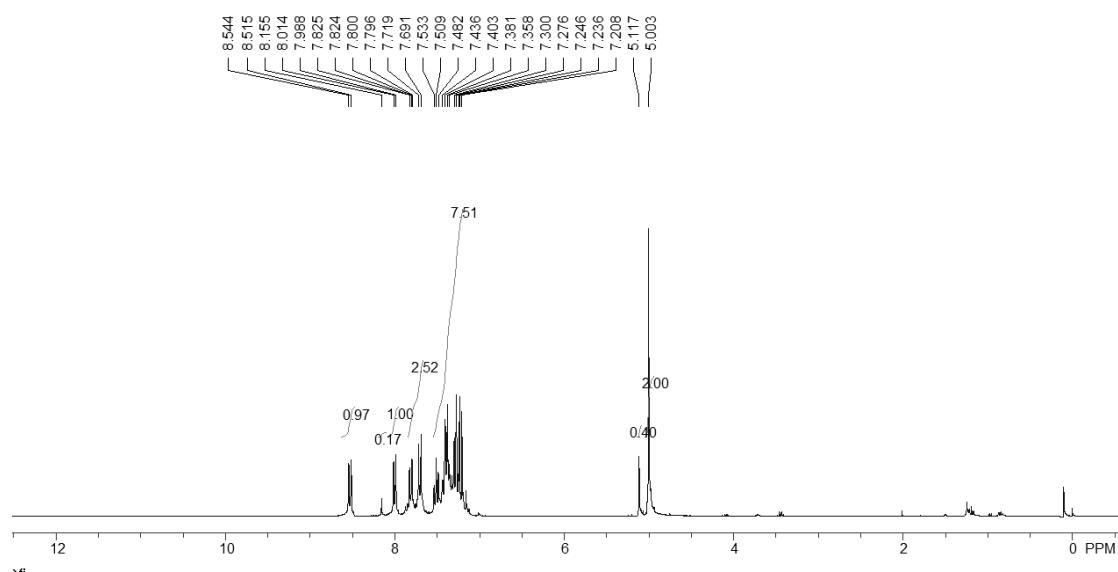
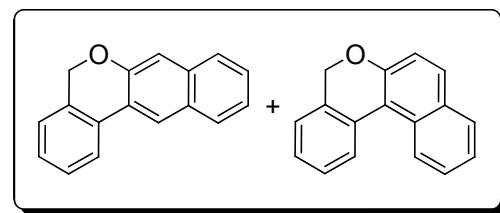
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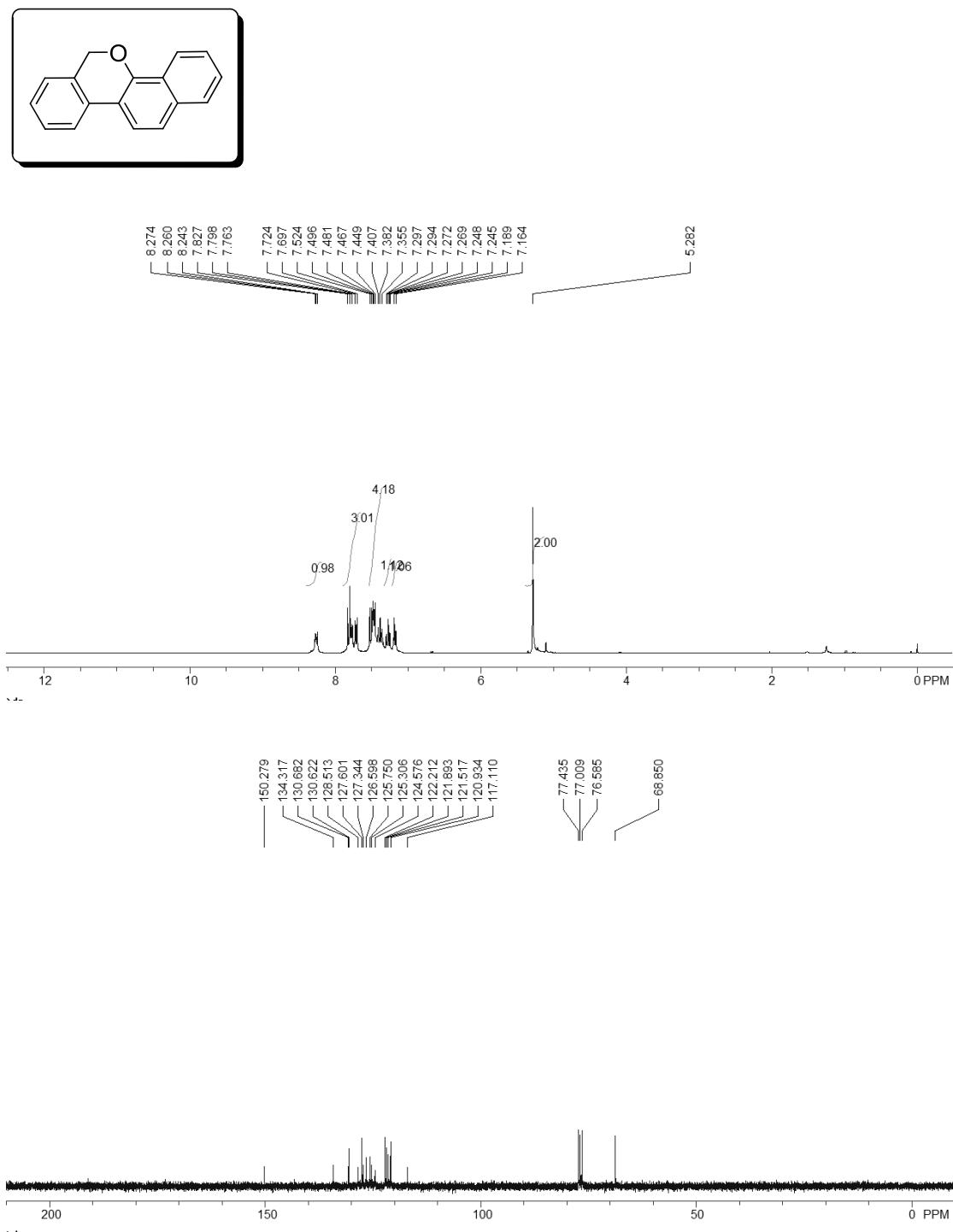
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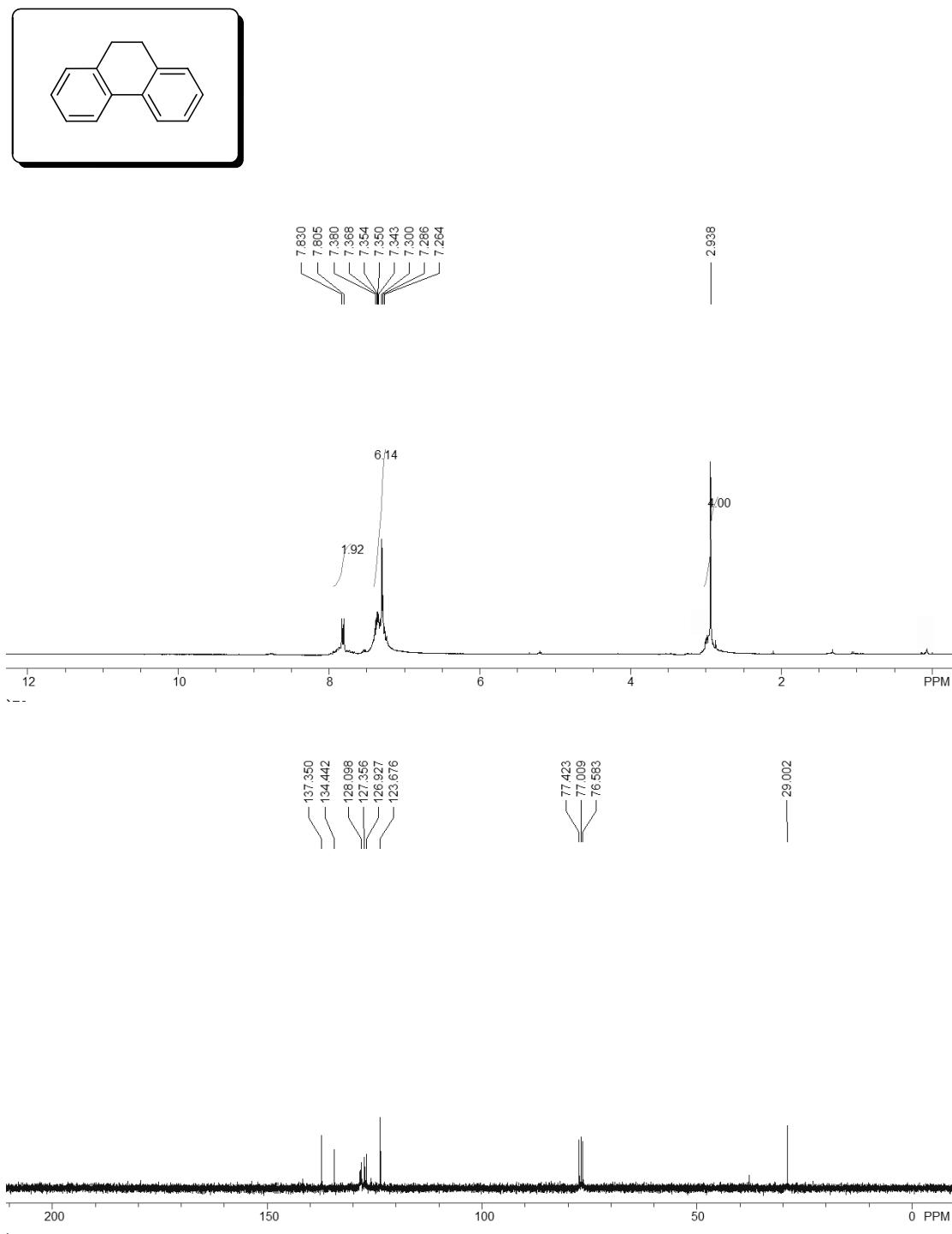
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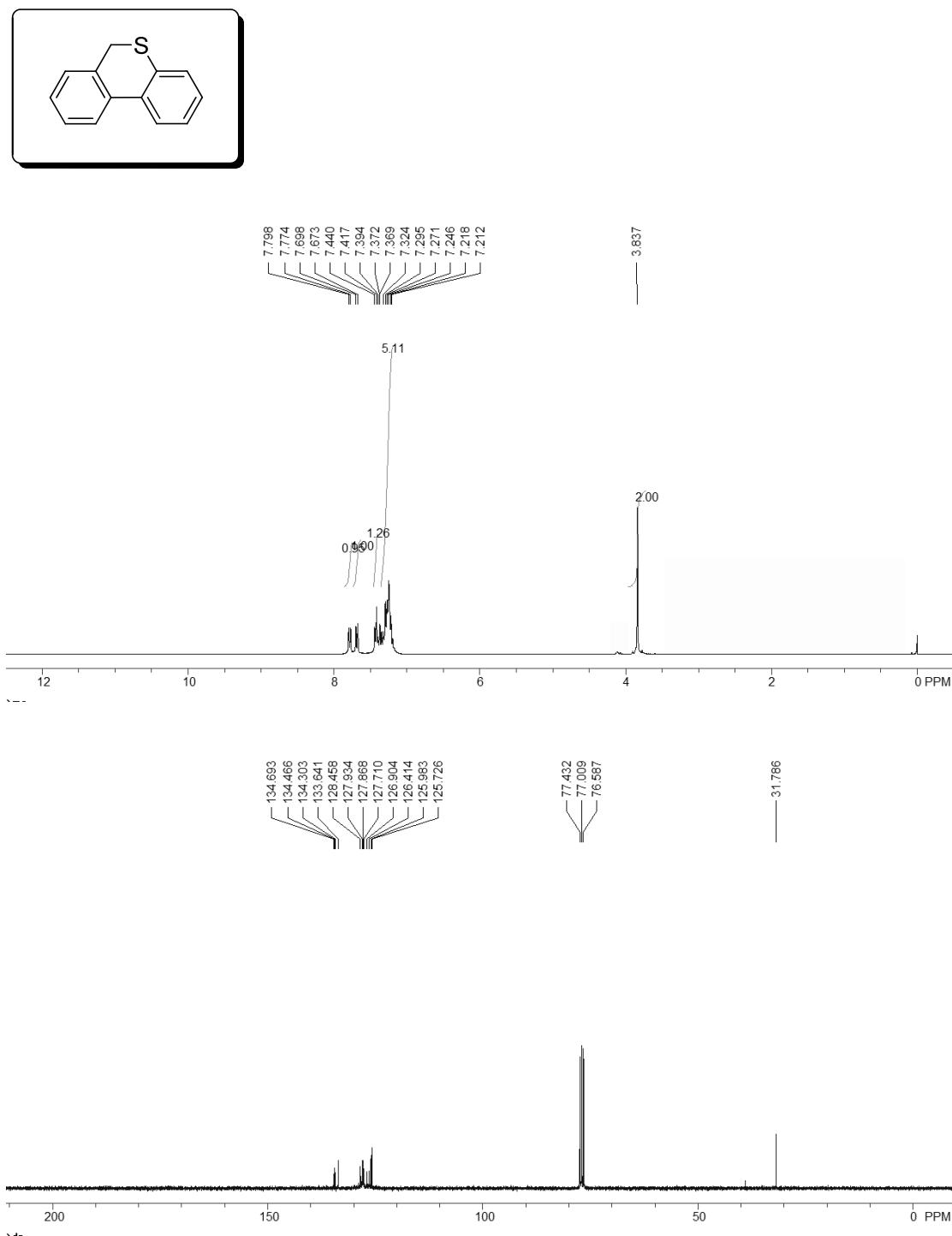
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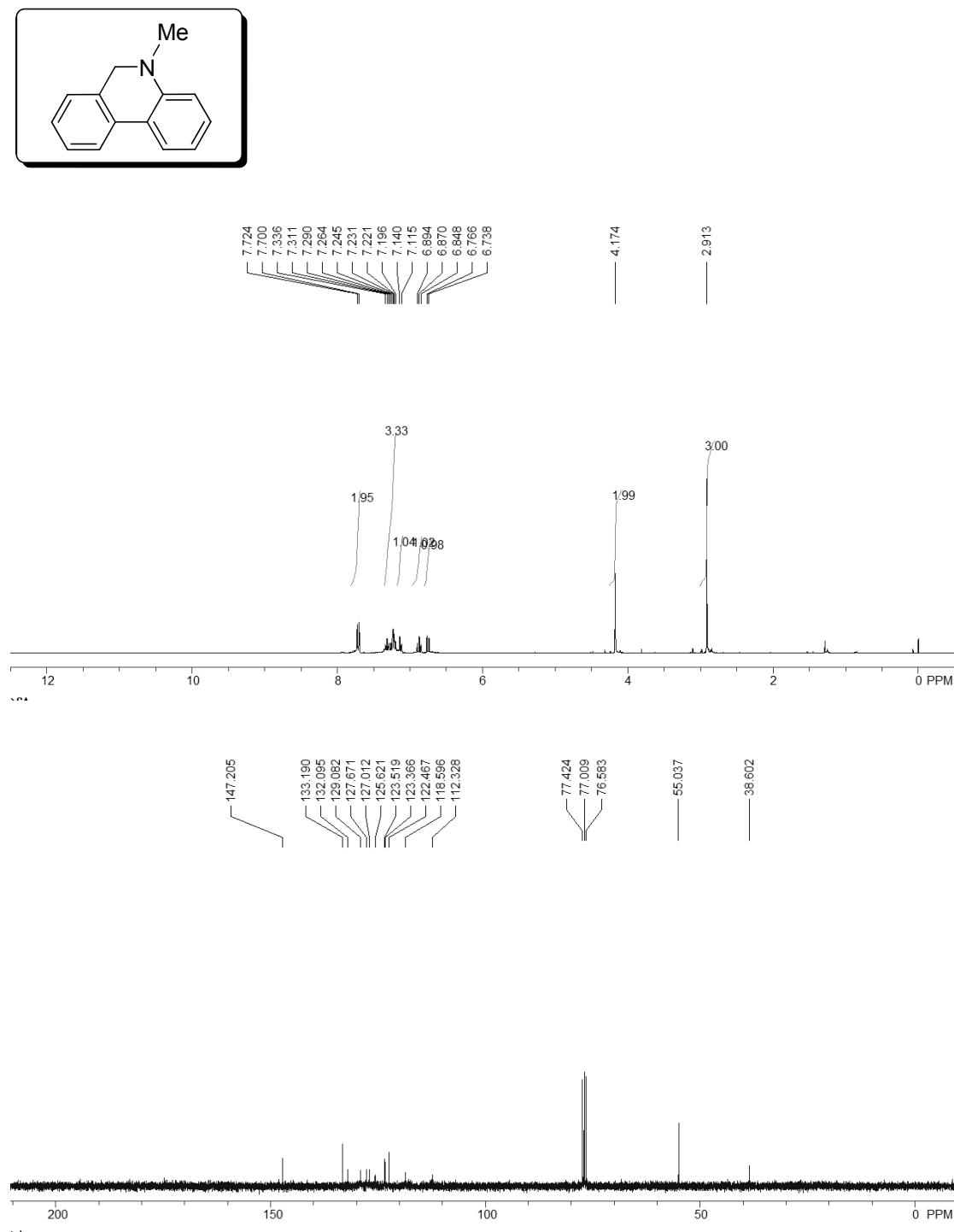
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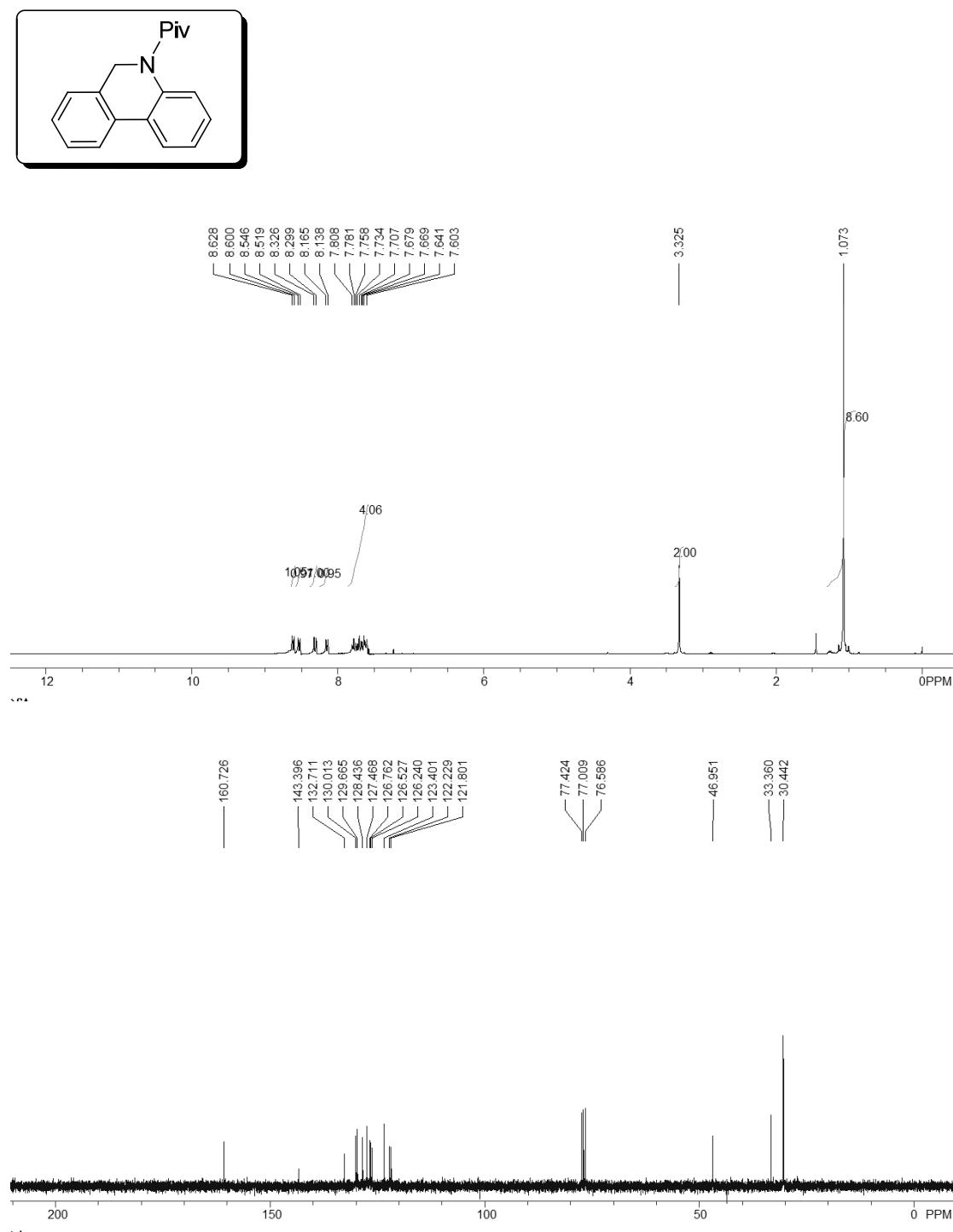
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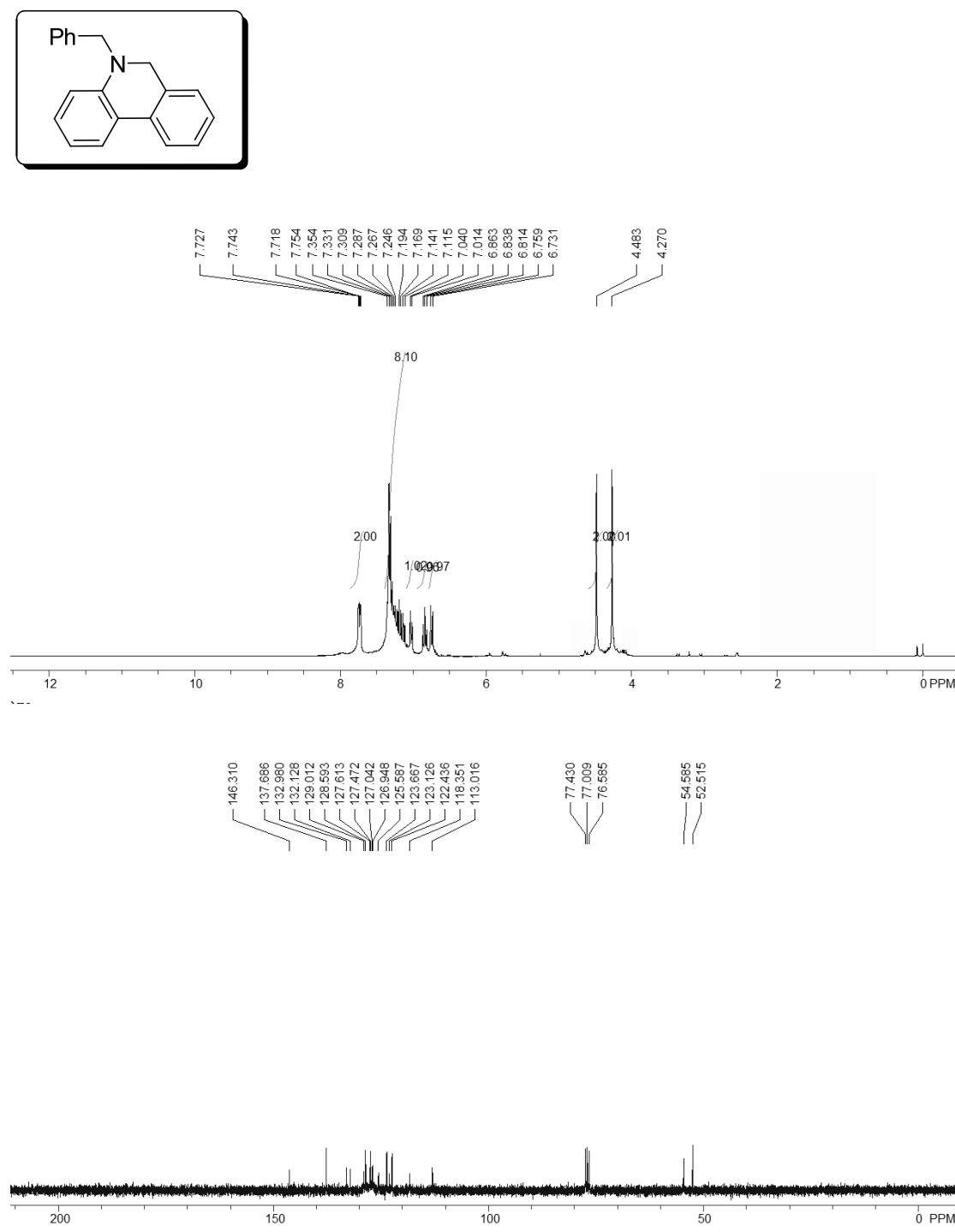
(6d)



(6f)



(6i)



(6j)

