Electronic Supplementary Information

Selective Catalytic Hoffmann N-Alkylation of Poor Nucleophilic Amines and Amides with Catalytic Amounts of Alkyl Halides

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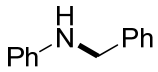
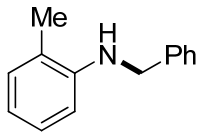
Experimental

General. Unless otherwise noted, all chemicals were purchased and used without further purification. The aniline hydrobromide salt $PhNH_2$•HBr was prepared from the reaction of aniline and HBr (33 wt% in HOAc) and dried under vacuum before use. All the reactions were carried out in sealed 20 mL Schlenk tubes under an air or under a nitrogen atmosphere, heated at the given temperatures as indicated in the tables, and then monitored by TLC and/or GC-MS. All the products were purified by column chromatography on silica gel using petroleum ether (PE) and ethyl acetate (EA) as the eluent. ^{1}H and ^{13}C NMR spectra of the products were recorded on a Bruker Avance III AV500 instrument (500 MHz for ^{1}H and 125 MHz for ^{13}C NMR spectroscopy) using $CDCl_3$ or DMSO-d_6 as the solvent. Chemical shifts for ^{1}H and ^{13}C NMR were referred to internal Me_4Si (0 ppm) as the standard. Mass spectra were measured on a Shimadzu GC-MS-QP2010 Plus spectrometer (EI). HRMS (ESI) analysis was measured on a Bruker micrOTOF-Q II instrument.

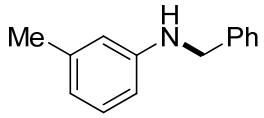
Typical Procedure for Alkyl Halides-Catalyzed Hoffmann N-Alkylation of Primary Amines with Primary Alcohols. The mixture of benzyl alcohol **1a** (0.21 mL, 2.0 mmol), aniline **2a** (0.26 mL, 3.0 mmol), and benzyl bromide (18 μL, 0.15 mmol, 7.5 mol%) was sealed under air in a 20 mL Schlenk tube, stirred at 160 ^{o}C for 24 h, and then monitored by TLC and/or GC-MS. After completion of the reaction, the mixture was directly purified, without any workup, through a silica gel column using ethyl acetate and petroleum ether as the eluent, giving *N*-benzylaniline **3a** in 82% isolated yield.



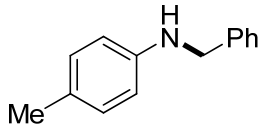
***N*-Benzyl aniline (3a).** Colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35-7.30 (m, 4H), 7.26-7.24 (m, 1H), 7.17-7.14 (m, 2H), 6.71-6.68 (m, 1H), 6.61-6.59 (m, 2H), 4.28 (s, 2H), 3.97 (b, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 148.1, 139.4, 129.2, 128.6, 127.4, 127.2, 117.5, 112.8, 48.2. MS (EI): *m/z* (%) 184 (7), 183 (47), 182 (18), 181 (4), 180 (6), 106 (18), 104 (10), 92 (9), 91 (100), 89 (3), 78 (4), 77 (23), 65 (20), 63 (4), 51 (11). This compound was known: Xu, Q.; Li, Q.; Zhu, X.; Chen, J. *Adv. Synth. Catal*. **2013**, *355*, 73-80.



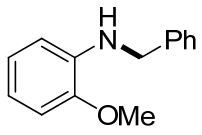
***N*-Benzyl 2-methylaniline (3b).** Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44-7.38 (m, 4H), 7.34-7.31 (m, 1H), 7.16-7.11 (m, 2H), 6.72 (t, J = 7.0 Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 4.42 (s, 2H), 3.90 (b, 1H), 2.21 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 146.1, 139.5, 130.1, 128.6, 127.5, 127.2, 127.1, 121.9, 117.2, 110.0, 48.3, 17.5. MS (EI): *m/z* (%) 198 (12), 197 (73), 196 (22), 120 (15), 118 (10), 106 (17), 92 (9), 91 (100), 77 (7), 65 (16). This compound was known: Kataoka, N.; Shelby, Q.; Stambuli, J. P.; Hartwig, J. F. *J. Org. Chem.* **2002**, *67*, 5553-5566



***N*-Benzyl 3-methylaniline (3c).** Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35-7.18 (m, 5H), 7.05 (t, J = 7.5 Hz, 1H), 6.53 (d, J = 7.5 Hz, 1H), 6.45-6.42 (m, 2H), 4.29 (s, 2H), 3.83 (b, 1H), 2.25 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 148.2, 139.6, 139.0, 129.1, 128.6, 127.5, 127.1, 118.5, 113.6, 110.0, 48.3, 21.6. MS (EI): *m/z* (%) 198 (16), 197 (100), 196 (49), 194 (5), 180 (3), 120 (26), 118 (8), 92 (9), 91 (99), 89 (3), 77 (6), 65 (15). This compound was known: Raghuvanshi, D. S.; Gupta, A. K.; Singh, K. N. *Org. Lett.* **2012**, *14*, 4326-4329.

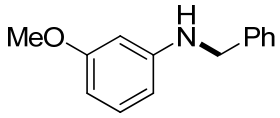


***N*-Benzyl 4-methylaniline (3d).** Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.22 (m, 5H), 6.98 (d, J = 8.0 Hz, 2H), 6.55 (d, J = 8.0 Hz, 2H), 4.29 (s, 2H), 3.88 (b, 1H), 2.23 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 145.9, 139.7, 129.7, 128.6, 127.5, 127.1, 126.7, 113.0, 48.7, 20.3. MS (EI): *m/z* (%) 198 (15), 197 (99), 196 (38), 195 (4), 194 (6), 120 (23), 118 (8), 106 (4), 92 (8), 91 (100), 89 (3), 79 (4), 77 (8), 65 (13). This compound was known: Xu, Q.; Li, Q.; Zhu, X.; Chen, J. *Adv. Synth. Catal*. **2013**, *355*, 73-80.

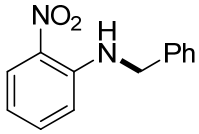


***N*-Benzyl 2-methoxyaniline (3e).** Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.18 (m, 5H), 6.84-6.80 (m, 1H), 6.77 (d, J = 8.0 Hz, 1H), 6.68-6.65 (m, 1H), 6.58 (d, J = 7.5 Hz, 1H), 4.60 (b,

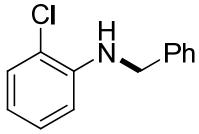
1H), 4.33 (s, 2H), 3.82 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 146.8, 139.6, 138.1, 128.5, 127.4, 127.0, 121.3, 116.6, 110.1, 109.4, 55.4, 48.0. MS (EI): *m/z* (%) 214 (14), 213 (86), 212 (15), 199 (5), 198 (30), 196 (5), 180 (3), 136 (10), 122 (5), 121 (5), 120 (15), 106 (8), 104 (3), 94 (11), 93 (5), 92 (17), 91 (100), 77 (10), 65 (19), 52 (4), 51 (4). This compound was known: Cano, R.; Yus, M.; Ramón, D. J. *Tetrahedron,* **2011**, *67*, 8079-8085.



***N*-Benzyl 3-methoxyaniline (3f).** Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.31 (m, 4H), 7.27-7.24 (m, 1H), 7.06 (t, J = 8.0 Hz, 1H), 6.28-6.23 (m, 2H), 6.18 (t, J = 2.5 Hz, 1H), 4.29 (s, 2H), 3.73 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 160.9, 149.6, 139.3, 130.0, 128.6, 127.5, 127.2, 106.0, 102.8, 98.9, 55.0, 48.3. MS (EI): *m/z* (%) 214 (15), 213 (100), 212 (55), 211 (7), 210 (6), 196 (5), 168 (5), 136 (26), 134 (5), 107 (5), 92 (11), 91 (89), 77 (7), 65 (13). This compound was known: Sydnes, M. O.; Kuse, M.; Isobe, M. *Tetrahedron,* **2008**, *64*, 6406-6414.

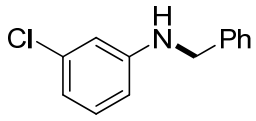


***N*-Benzyl 2-nitroaniline (3g).** Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.41 (brs, 1H), 8.17 (dd, J = 8.5, 1.5 Hz, 1H), 7.37-7.28 (m, 6H), 6.80 (d, J = 8.5 Hz, 1H), 6.65-6.62 (m, 1H), 4.52 (d, J = 5.5 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 145.2, 137.3, 136.1, 132.2, 128.8, 127.6, 127.0, 126.7, 115.6, 114.1, 47.0. MS (EI): *m/z* (%) 228 (23), 210 (9), 195 (9), 194 (15), 182 (6), 181 (28), 180 (31), 168 (11), 152 (7), 119 (6), 106 (7), 105 (66), 104 (7), 92 (13), 91 (100), 78 (5), 77 (12), 65 (19), 51 (5). This compound was known: Kommi, D. N.; Kumar, D.; Bansal, R.; Chebolu, R.; Chakraborti, Asit, K. *Green Chem.* **2012**, *14*, 3329-3335.

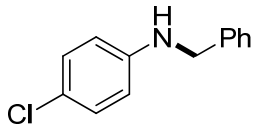


***N*-Benzyl 2-chloroaniline (3h).** Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.33 (m, 4H), 7.29-7.24 (m, 2H), 7.08 (d, J = 8.0 Hz, 1H), 6.64-6.61 (m, 2H), 4.73 (b, 1H), 4.40 (s, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 143.9, 138.8, 129.1, 128.7, 127.8, 127.3, 127.2, 119.1, 117.4, 111.5, 47.9. MS (EI): *m/z* (%) 219 (16), 218 (11), 217 (49), 216 (14), 180 (4), 140 (8), 138 (5), 111 (3), 92 (8), 91 (100), 77 (6), 65 (10). This compound was known: Zhang, M.; Yang, H.;

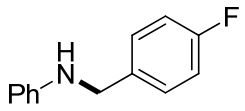
Zhang, Y.; Zhu, C.; Li, W.; Cheng, Y.; Hu, H. *Chem. Commun.* **2011,** *47*, 6605-6607.



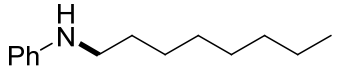
***N*-Benzyl 3-chloroaniline (3i).** Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35-7.24 (m, 5H), 7.05 (t, J = 8.0 Hz, 1H), 6.68-6.66(m, 1H), 6.61 (t, J = 2.0 Hz, 1H), 6.48 (dd, J = 8.0, 2.0 Hz, 1H), 4.30 (s, 2H), 4.10 (b, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 149.3, 138.8, 135.1, 130.2, 128.7, 127.5, 127.4, 117.4, 112.3, 111.1, 48.1. MS (EI): *m/z* (%) 219 (15), 218 (11), 217 (48), 216 (13), 140 (8), 92 (8), 91 (100), 77 (5), 65 (10). This compound was known: Yu, X.; Liu, C.; Jiang, L.; Xu, Q. *Org. Lett.* **2011**, *13*, 6184-6187.



***N*-Benzyl 4-chloroaniline (3j).** Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.22 (m, 5H), 7.09 (d, J = 8.5 Hz, 2H), 6.52 (d, J = 8.5 Hz, 2H), 4.27 (s, 2H), 4.07 (b, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 146.6, 138.9, 129.0, 128.7, 127.4, 127.3, 122.2, 114.0, 48.4. MS (EI): *m/z* (%) 219 (17), 218 (11), 217 (52), 216 (9), 140 (7), 138 (5), 111 (5), 92 (8), 91 (100), 77 (4), 75 (3), 65 (9), 52 (3), 51 (18), 50 (3). This compound was known: Xu, Q.; Li, Q.; Zhu, X.; Chen, J. *Adv. Synth. Catal*. **2013**, *355*, 73-80.



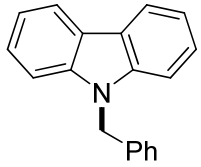
***N*-(4-Fluorobenzyl) aniline (3k).** Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.30 (m, 2H), 7.18-7.15 (m, 2H), 7.01 (t, J = 8.5 Hz, 2H), 6.73-6.70 (m, 1H), 6.61 (d, J = 8.5 Hz, 2H), 4.28 (s, 2H), 3.99 (b, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 162.1 (d, $J_{C\text{-}F}$ = 244.3 Hz), 147.9, 135.1 (d, $J_{C\text{-}F}$ = 3.1 Hz), 129.3, 128.9 (d, $J_{C\text{-}F}$ = 8.0 Hz), 117.8, 115.4 (d, $J_{C\text{-}F}$ = 21.3 Hz), 112.9, 47.6. MS (EI): *m/z* (%) 202 (8), 201 (55), 200 (10), 110 (8), 109 (100), 106 (7), 83 (10), 77 (9), 51 (4). This compound was known: Du, Y.; Oishi, S.; Saito, S. *Chem.- Eur. J.* **2011**, *17*, 12262-12267.



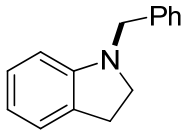
***N*-Octyl aniline (3l).** Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18-7.15 (m, 2H), 6.69-6.66 (m, 1H), 6.60-6.58 (m, 2H), 3.54 (b, 1H), 3.09 (t, J = 7.0 Hz, 2H), 1.63-1.57 (m, 2H), 1.41-1.27 (m, 10H), 0.88 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 148.5, 129.2, 117.1, 112.7, 44.0,

31.8, 29.6, 29.4, 29.2, 27.2, 22.6, 14.1. MS (EI): *m/z* (%) 105 (10), 107 (8), 106 (100), 93 (3), 79 (5), 77 (8). This compound was known:-Shimizu, K. I.; Imaiida, N.; Kon, K.; Hakim Siddiki, S. M. A.; Satsuma, A. *ACS Catal.* **2013**, *3*, 998-1005.

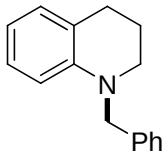
Typical Procedure for Alkyl Halides-Catalyzed Hoffmann N-Alkylation of Secondary Amines with Primary Alcohols. The mixture of benzyl alcohol **1a** (0.16 mL, 1.5 mmol) , 9H-carbazole (0.1670 g, 1 mmol), and benzyl bromide (12 μL, 0.1 mmol, 10 mol%) was sealed under air in a 20 mL Schlenk tube, stirred at 160 ^{o}C for 24 h, and then monitored by TLC and/or GC-MS. After completion of the reaction, the mixture was directly purified, without any workup, through a silica gel column using ethyl acetate and petroleum ether as the eluent, giving 9-benzyl carbazole **5a** in 76% isolated yield.



9-Benzyl carbazole (5a). White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (d, J = 8.0 Hz, 2H), 7.43-7.40 (m, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.26-7.21 (m, 5H), 7.14-7.12 (m, 2H), 5.50 (s, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 140.7, 137.2, 128.8, 127.4, 126.4, 125.8, 123.1, 120.4, 119.2, 108.9, 46.6. MS (EI): *m/z* (%) 158 (19), 257 (93), 256 (4), 254 (6), 180 (9), 166 (10), 152 (4), 140 (8), 139 (5), 128 (4), 92 (8), 91 (100), 65 (9). This compound was known: Sueki, S.; Kuninobu, Y. *Org. Lett.* **2013**, *15*, 1544-1547.

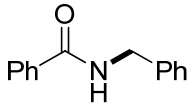


1-Benzyl indoline (5b). Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35-7.29 (m, 4H), 7.25-7.22 (m, 1H), 7.08-7.02 (m, 2H), 6.65 (t, J = 7.5 Hz, 1H), 6.48 (d, J = 7.5 Hz, 1H), 4.21 (s, 2H), 3.27 (t, J = 8.0 Hz, 2H), 2.93 (t, J = 8.0 Hz, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 152.5, 138.4, 128.4, 127.2, 127.0, 124.4, 117.6, 107.0, 53.6, 53.5, 28.5. MS (EI): *m/z* (%) 210 (7), 209 (46), 208 (11), 207 (8), 133 (3), 132 (31), 130 (4), 119 (3), 118 (29), 117 (12), 92 (13), 91 (100), 90 (5), 89 (7), 77 (6), 65 (21), 63 (4), 51 (4). This compound was known: Kubo, T.; Katoh, C.; Yamada, K.; Okano, K.; Tokuyama, H.; Fukuyama, T. *Tetrahedron,* **2008**, *64*, 11230-11236.

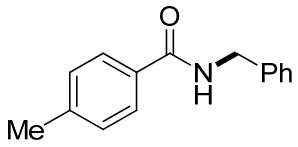


1-Benzyl 2,3,4-trihydroquinoline (5c). Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32-7.21 (m, 5H), 6.98-6.95 (m, 2H), 6.57 (t, J = 7.5 Hz, 1H), 6.50 (d, J = 8.5 Hz, 1H), 4.47 (s, 2H), 3.36 (t, J = 6.0 Hz, 2H), 2.82 (t, J = 6.0 Hz, 2H), 2.03-1.99 (m, 2H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 145.6, 139.0, 128.6, 127.2, 126.7, 126.6, 122.2, 115.8, 111.0, 55.2, 49.9, 28.2, 22.4. MS (EI): *m/z* (%) 224 (18), 223 (100), 222 (18), 147 (8), 133 (4), 132 (47), 131 (10), 130 (19), 118 (6), 117 (16), 115 (4), 111 (4), 105 (4), 92 (15), 91 (81), 89 (4), 77 (9), 70 (6), 65 (12), 61 (5). This compound was known: McGonagle, F. I.; MacMillan, D. S.; Murray, J.; Sneddon, H. F.; Jamiesona, C.; Watson, A. J. B. *Green Chem.* **2013**, *15*, 1159-1165.

Typical Procedure for Alkyl Halides-Catalyzed Hoffmann *N*-Alkylation of Amides and Sulfamides with Primary Alcohols. The mixture of benzamide (0.243 g, 2 mmol) , benzyl alcohol **1a** (0.25 mL, 2.4 mmol), and benzyl bromide (95 μL, 0.8 mmol, 40 mol%) was sealed under air in a 20 mL Schlenk tube, stirred at 170 ^{o}C for 24 h, and then monitored by TLC and/or GC-MS. After completion of the reaction, the mixture was directly purified, without any workup, through a silica gel column using ethyl acetate and petroleum ether as the eluent, giving *N*-benzyl benzamide **6a** in 63% isolated yield.

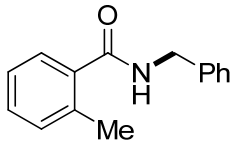


***N*-Benzyl benzamide (6a).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79-7.77 (m, 2H), 7.48-7.47(m, 1H), 7.42-7.39 (m, 2H), 7.34-7.33 (m, 4H), 7.30-7.28 (m, 1H), 6.59 (bs, 1H), 4.62 (d, J = 6.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.4, 138.3, 134.5, 131.5, 128.8, 128.6, 127.9, 127.6, 127.0, 44.1. MS (EI): *m/z* (%) 212 (11), 211 (70), 210 (27), 105 (100), 77 (54), 51 (14). This compound was known: Liu, C.; Liao, S.; Li, Q.; Feng, S.; Sun, Q.; Yu, X.; Xu, Q. *J. Org. Chem.* **2011**, *76*, 5759-5773.

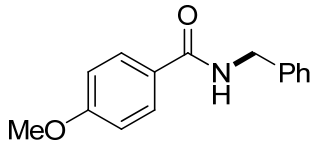


***N*-Benzyl 4-methylbenzamide (6b).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, J = 7.5

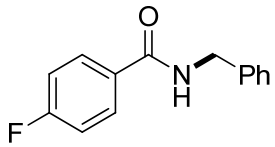
Hz, 2H), 7.31 (d, J = 4.0 Hz, 4H), 7.28-7.24 (m, 1H), 7.18 (d, J = 7.5 Hz, 2H), 6.67 (bs, 1H), 4.58 (d, J = 6.0 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.4, 141.9, 138.5, 131.6, 129.2, 128.7, 127.9, 127.5, 127.1, 44.0, 21.4. MS (EI): *m/z* (%) 226 (6), 225 (45), 194 (4), 119 (100), 91 (65), 77 (7), 65 (25), 51 (4). This compound was known: Soule, J. F.; Miyamura, H.; Kobayashi, S. *J. Am. Chem. Soc.* **2011**, *133*, 18550-18553.



***N*-Benzyl 2-methylbenzamide (6c).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.24 (m, 7H), 7.17-7.11 (m, 2H), 6.32 (bs, 1H), 4.53 (d, J = 4.0 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.0, 138.4, 136.3, 136.1, 131.0, 129.9, 128.7, 127.8, 127.5, 126.7, 125.7, 43.8, 19.8. MS (EI): *m/z* (%) 226 (9), 225 (51), 194 (6), 119 (100), 91 (73), 77 (7), 65 (26), 51 (5). This compound was known: Qu, G.-R.; Song, Y.-W.; Niu, H.-Y.; Guo, H. -M.; Fossey, J. S. *RSC Advances* **2012**, *2*, 6161.

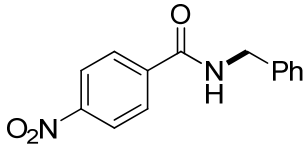


***N*-Benzyl 4-methoxybenzamide (6d).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, J = 9.0 Hz, 2H), 7.34-7.31 (m, 4H), 7.29-7.26 (m, 1H), 6.89 (d, J = 8.5 Hz, 2H), 6.50 (bs, 1H), 4.60 (d, J = 5.5 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.9, 162.3, 138.5, 128.8, 128.7, 127.9, 127.5, 126.7, 113.8, 55.4, 44.1. MS (EI): *m/z* (%) 242 (5), 241 (32), 135 (100), 107 (12), 92 (12), 77 (21), 64 (6), 51 (3). This compound was known: Soule, J. F.; Miyamura, H.; Kobayashi, S. *J. Am. Chem. Soc.* **2011**, *133*, 18550-18553.

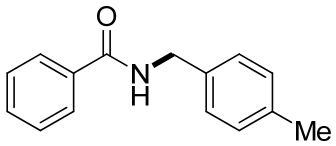


***N*-Benzyl 4-fluorobenzamide (6e).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (dd, J = 8.5, 5.5 Hz, 2H), 7.35-7.28 (m, 5H), 7.06 (t, J = 8.5 Hz, 2H), 6.62(bs, 1H), 4.60 (d, J = 5.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.4, 164.8 (d, $J_{C\text{-}F}$ = 251.3 Hz), 138.1, 130.6, 129.3 (d, $J_{C\text{-}F}$ = 8.8 Hz), 128.8, 127.9, 127.8, 115.6 (d, $J_{C\text{-}F}$ = 22.5 Hz), 44.2. MS (EI): *m/z* (%) 230 (8), 229 (51), 228 (14), 123 (100), 106 (22), 95 (40), 75 (11), 51 (5). This compound was known:

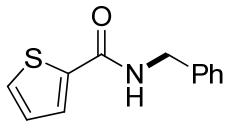
Allen, C. L.; Davulcu, S.; Williams, J. M. J. *Org. Lett.* **2010**, *12*, 5096-5099.



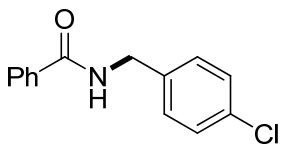
***N*-Benzyl 4-nitrobenzamide (6f).** Light yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (d, J = 8.5 Hz, 2H), 7.92 (d, J = 9.0 Hz, 2H), 7.34-7.29 (m, 5H), 6.91 (bs, 1H), 4.61 (d, J = 4.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.5, 149.6, 139.9, 137.5, 128.9, 128.2, 127.9, 123.8, 44.4. MS (EI): *m/z* (%) 257 (15), 256 (100), 255 (29), 209 (18), 150 (70), 120 (25), 106 (54), 91 (39), 79 (34), 65 (19), 51 (11). This compound was known: Soule, J. F.; Miyamura, H.; Kobayashi, S. *J. Am. Chem. Soc.* **2011**, *133*, 18550-18553.



***N*-(4-Methylbenzyl) benzamide (6g).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, J = 7.5 Hz, 2H), 7.47-7.45 (m, 1H), 7.39 (t, J = 7.5 Hz, 2H), 7.22 (d, J = 7.5 Hz, 2H), 7.13 (d, J = 7.5 Hz, 2H), 6.62 (bs, 1H), 4.57 (d, J = 5.5 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.5, 137.3, 135.2, 134.5, 131.5, 129.4, 128.6, 127.9, 127.0, 43.9, 21.1. This compound was known: Fan, W.; Yang, Y.; Lei, J.; Jiang, Q.; Zhou, W. *J. Org. Chem.* **2015**, *80*, 8782-8789.

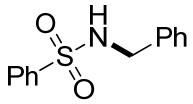


***N*-Benzyl thiophene-2-carboxamide (6h).** Brown solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (d, J = 3.5 Hz, 1H), 7.42 (d, J = 5.0 Hz, 1H), 7.29-7.23 (m, 5H), 7.00 (t, J = 4.5 Hz, 1H), 6.85 (bs, 1H), 4.53 (d, J = 5.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.0, 139.0, 138.2, 130.0, 128.7, 128.3, 127.8, 127.6, 127.5, 43.9. MS (EI): *m/z* (%) 218 (8), 217 (52), 111 (100), 106 (39), 91 (16), 83 (10), 77 (8), 65 (9), 51 (6). This compound was known: Wu, J.-W.; Wu, Y.-D.; Dai, J.-J; Xu, H.-J. *Adv. Synth. Catal.* **2014**, *356*, 2429-2436.



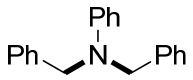
***N*-(4-Chlorobenzyl) benzamide (6i).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, J =

7.0 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.29-7.23 (m, 4H), 6.74 (bs, 1H), 4.56 (d, *J* = 5.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.5, 136.9, 134.2, 133.4, 131.7, 129.2, 128.9, 128.6, 127.0, 43.4. This compound was known: Fan, W.; Yang, Y.; Lei, J.; Jiang, Q.; Zhou, W. *J. Org. Chem.* **2015**, *80*, 8782-8789.

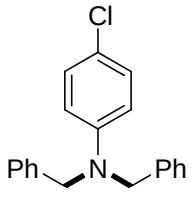


***N*-Benzyl benzenesulfonamide (6l).** Brown solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.26-7.21 (m, 3H), 7.18-7.16 (m, 2H), 5.07 (t, *J* = 6.0 Hz, 1H), 4.12 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.0, 136.3, 132.7, 129.1, 128.7, 127.9, 127.9, 127.1, 47.3. MS (EI): *m/z* (%) 247 (0.6), 143 (5), 141 (4), 106 (100), 91 (16), 77 (49), 51 (21). This compound was known: James, S. N.; Coster, M. J. *Tetrahedron Lett* **2015**, *56*, 2059-2061.

Typical Procedure for Alkyl Halides-Catalyzed Hoffmann *N,N-Di*-Alkylation of Amines with Primary Alcohols. The mixture of benzyl alcohol **1a** (0.42 mL, 4.0 mmol), aniline **2a** (90 μL, 1 mmol), and benzyl bromide (18 μL, 0.1 mmol, 15 mol%) was sealed under air in a 20 mL Schlenk tube, stirred at 150 ^{o}C for 24 h, and then monitored by TLC and/or GC-MS. After completion of the reaction, the mixture was directly purified, without any workup, through a silica gel column using ethyl acetate and petroleum ether as the eluent, giving *N,N*-dibenzyl aniline **4a** in 86% isolated yield.

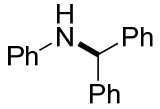


***N,N*-Dibenzyl aniline (4a).** Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.30 (m, 4H), 7.25-7.24 (m, 6H), 7.18-7.15 (m, 2H), 6.74-6.68 (m, 3H), 4.65 (s, 4H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 149.2, 138.6, 129.2, 128.6, 126.9, 126.7, 116.7, 112.5, 54.2. MS (EI): *m/z* (%) 274 (6), 273 (29), 196 (12), 182 (15), 181 (9), 180 (7), 104 (13), 92 (10), 91 (100), 77 (25), 65 (17), 51 (7). This compound was known: Nguyen, Q. P. B.; Kim, T. H. *Tetrahedron* **2013**, *69*, 4938-4943.

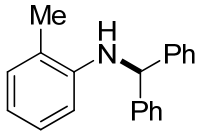


***N,N*-Dibenzyl 4-chloroaniline (4b).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32-7.20 (m, 10H), 7.08-7.06 (m, 2H), 6.63-6.61 (m, 2H), 4.61 (s, 4H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 147.7, 138.1, 129.0, 128.7, 128.2, 127.0, 126.6, 113.8, 54.5. MS (EI): *m/z* (%) 307 (23), 230 (6), 216 (9), 215 (6), 138 (8), 111 (10), 92 (12), 91 (100), 77 (7), 65 (17). This compound was known: Xiao, Q.; Tian, L.; Tan, R.; Xia, Y.; Qiu, D.; Zhang, Y.; Wang, J. *Org. Lett.* **2012**, *14*, 4230-4233.

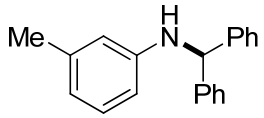
Typical Procedure for Alkyl Halides-Catalyzed Hoffmann *N*-Alkylation of Primary Amines with Secondary and Tertiary Alcohols. The mixture of benzohydrol **7a** (0.185 g, 1.0 mmol), aniline **2a** (0.13 mL, 1.5 mmol), and benzhydryl bromide (0.0247 g, 0.1 mmol, 10 mol%) was sealed under N_2 in a 20 mL Schlenk tube, stirred at 120 ^{o}C for 24 h, and then monitored by TLC and/or GC-MS. After completion of the reaction, the mixture was directly purified, without any workup, through a silica gel column using ethyl acetate and petroleum ether as the eluent, giving *N*-benzhydryl aniline **8a** in 85% isolated yield.



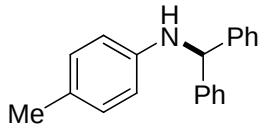
***N*-Benzhydryl aniline (8a).** Colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58-7.45 (m, 10H), 7.34-7.30 (m, 2H), 6.93-6.91 (m, 1H), 6.75-6.73 (m, 2H), 5.72 (s, 1H), 4.42 (br, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 147.2, 142.8, 129.0, 128.6, 127.4, 127.3, 117.6, 113.4, 62.9. MS (EI): *m/z* (%) 260 (4), 259 (20), 182 (4), 180 (3), 168 (14), 167 (100), 166 (10), 165 (27), 164 (2), 163 (2), 153 (3), 152 (17), 77 (8). This compound was known: Yu, A.; Wu, Y.; Cheng, B.; Wei, K.; Lia, J. *Adv. Synth. Catal*. **2009**, *351*, 767-771.



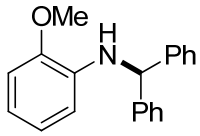
***N*-Benzhydryl 2-methylaniline (8b).** Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35-7.28 (m, 8H), 7.24-7.21 (m, 2H), 7.05 (d, J = 7.5 Hz, 1H), 6.97-6.94 (m, 1H), 6.65-6.62 (m, 1H), 6.41 (d, J = 8.0 Hz, 1H), 5.54 (s, 1H), 4.06 (b, 1H), 2.16 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 145.2, 143.1, 129.9, 128.7, 127.4, 127.3, 127.0, 122.0, 117.3, 111.3, 62.8, 17.6. MS (EI): *m/z* (%) 274 (4), 273 (20), 196 (2), 168 (15), 167 (100), 166 (9), 165 (23), 153 (2), 152 (15), 91 (5), 77 (2), 65 (3). HRMS calcd for $C_{20}H_{20}N$ ($[M+H]^+$): 274.1590; found: 274.1585.



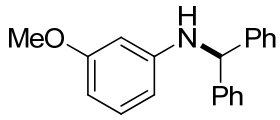
***N*-Benzhydryl 3-methylaniline (8c).** Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35-7.28 (m, 8H), 7.25-7.22 (m, 2H), 6.98 (t, J = 8.0 Hz, 1H), 6.51 (d, J = 7.5 Hz, 1H), 6.38 (s, 1H), 6.33 (d, J = 8.0 Hz, 1H), 5.48 (s, 1H), 4.15 (b, 1H), 2.20 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 147.4, 143.1, 138.8, 128.7, 127.4, 127.3, 118.6, 114.4, 110.5, 63.0, 21.6. MS (EI): *m/z* (%) 274 (5), 273 (22), 196 (4), 168 (15), 167 (100), 166 (8), 165 (22), 152 (14), 91 (5), 65 (3). This compound was known: Yu, A.; Wu, Y.; Cheng, B.; Wei, K.; Lia, J. *Adv. Synth. Catal*. **2009**, *351*, 767-771.



***N*-Benzhydryl 4-methylaniline (8d).** Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.29 (m, 8H), 7.25-7.21 (m, 2H), 6.91 (d, J = 8.0 Hz, 2H), 6.45 (d, J = 8.5 Hz, 2H), 5.45 (s, 1H), 4.10 (br, 1H), 2.20 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 145.1, 143.1, 129.6, 128.7, 127.4, 127.3, 126.8, 113.6, 63.3, 20.3. MS (EI): *m/z* (%) 274 (5), 273 (25), 196 (3), 194 (2), 168 (15), 167 (100), 166 (9), 165 (25), 153 (2), 152 (15), 91 (5), 77 (3), 65 (2). This compound was known: Yu, A.; Wu, Y.; Cheng, B.; Wei, K.; Lia, J. *Adv. Synth. Catal*. **2009**, *351*, 767-771.

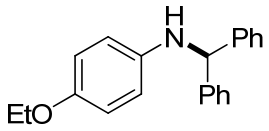


***N*-Benzhydryl 2-methoxyaniline (8e).** Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.20 (m, 10H), 6.77 (dd, J = 8.0, 1.0 Hz, 1H), 6.73-6.69 (m, 1H), 6.64 (td, J = 7.5, 1.5 Hz, 1H), 6.38 (dd, J = 8.0, 1.5 Hz, 1H), 5.48 (s, 1H), 4.86 (br, 1H), 3.81 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 146.8, 143.1, 137.3, 128.7, 127.4, 127.2, 121.1, 116.7, 111.2, 109.3, 62.9, 55.4. MS (EI): *m/z* (%) 290 (6), 289 (28), 212 (3), 196 (3), 168 (14), 167 (100), 166 (8), 165 (22). This compound was known: Singer, R. A.; Doré, M.; Sieser, J. E.; Berliner, M. A. *Tetrahedron Lett.* **2006**, *47*, 3727-3731.

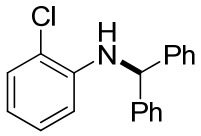


***N*-Benzhydryl 3-methoxyaniline (8f).** Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34-7.23 (m, 8H), 7.24-7.19 (m, 2H), 7.00 (t, J = 8.0 Hz, 1H), 6.26-6.24 (m, 1H), 6.16-6.14 (m, 1H), 6.09 (t, J

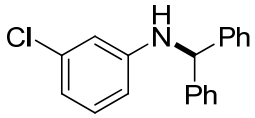
= 2.0 Hz, 1H), 5.48 (s, 1H), 4.24 (b, 1H), 3.65 (s, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 160.6, 148.7, 142.8, 129.8, 128.7, 127.4, 127.3, 106.6, 102.9, 99.6, 63.0, 54.9. MS (EI): *m/z* (%) 290 (6), 289 (26), 168 (15), 167 (100), 166 (8), 165 (21), 152 (14). This compound was known: Mukhopadhyay, P. P.; Miyata, O.; Naito, T. *Synlett* **2007**, 1403-1406.



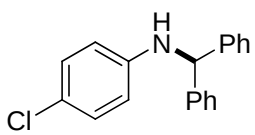
***N*-Benzhydryl 4-ethoxyaniline (8g).** Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.22 (m, 10H), 6.70 (d, J = 9.0 Hz, 2H), 6.49 (d, J = 9.0 Hz, 2H), 5.41 (s, 1H), 3.91 (q, J = 7.0 Hz, 2H), 1.33 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 151.5, 143.2, 141.6, 128.7, 127.4, 127.2, 115.6, 114.6, 64.0, 63.8, 15.0. MS (EI): *m/z* (%) 304 (8), 303 (32), 168 (16), 167 (100), 166 (7), 165 (20), 153 (3), 152 (14), 108 (5), 78 (3), 70 (3), 63 (3). HRMS calcd for $C_{21}H_{22}NO$ ($[M+H]^+$): 304.1696; found: 304.1702.



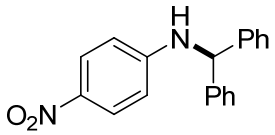
***N*-Benzhydryl 2-chloroaniline (8h).** Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35-7.23 (m, 11H), 6.98-6.95 (m, 1H), 6.61-6.58 (m, 1H), 6.46 (d, J = 8.0 Hz, 1H), 5.54 (s, 1H), 4.91 (b, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 143.1, 142.3, 129.0, 128.8, 127.6, 127.5, 127.3, 119.3, 117.6, 112.7, 62.6. MS (EI): *m/z* (%) 293 (10), 168 (14), 167 (100), 166 (9), 165 (22), 152 (15). HRMS calcd for $C_{19}H_{17}ClN$ ($[M+H]^+$): 294.1044; found: 294.1058.



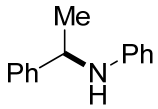
***N*-Benzhydryl 3-chloroaniline (8i).** Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.23 (m, 10H), 6.98 (t, J = 8.0 Hz, 1H), 6.64-6.63 (m, 1H), 6.52-6.50 (m, 1H), 6.39-6.37 (m, 1H), 5.47 (s, 1H), 4.29 (b, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 148.4, 142.3, 134.8, 130.1, 128.8, 127.5, 127.4, 117.6, 113.3, 111.6, 62.8. MS (EI): *m/z* (%) 293 (8), 168 (14), 167 (100), 166 (7), 165 (21), 152 (15). HRMS calcd for $C_{19}H_{17}ClN$ ($[M+H]^+$): 294.1044; found: 294.1050.



***N*-Benzhydryl 4-chloroaniline (8j).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32-7.22 (m, 10H), 7.04 (d, J = 8.5 Hz, 2H), 6.44 (d, J = 8.5 Hz, 2H), 5.44 (s, 1H), 4.24 (b, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 145.8, 142.5, 128.9, 128.8, 127.5, 127.4, 122.3, 114.6, 63.1. MS (EI): *m/z* (%) 293 (9), 168 (14), 167 (100), 166 (6), 165 (23), 152 (14), 111(3), 77(3). HRMS calcd for $C_{19}H_{17}ClN$ ($[M+H]^+$): 294.1044; found: 294.1050.This compound was known: Yu, A.; Wu, Y.; Cheng, B.; Wei, K.; Lia, J. *Adv. Synth. Catal*. **2009**, *351*, 767-771.



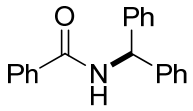
***N*-Benzhydryl 4-nitroaniline (8k).** Yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (d, J = 9.0 Hz, 2H), 7.38-7.29 (m, 10H), 6.51 (d, J = 9.0 Hz, 2H), 5.63 (d, J = 4.5 Hz, 1H), 5.00 (b, 1H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 152.1, 141.1, 138.6, 129.0, 128.0, 127.4, 126.2, 112.1, 62.4. MS (EI): *m/z* (%) 304 (4), 207 (5), 168 (17), 167 (100), 166 (9), 152 (16), 107 (4), 88 (5), 73 (4), 70 (6), 76 (6), 61 (6). This compound was known: Zhu, A.; Li, L.; Wang, J.; Zhuo, K.; *Green Chem.* **2011**, *13*, 1244-1250.



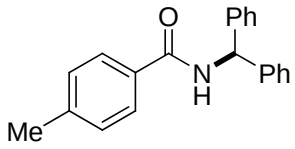
***N*-(1-Phenylethyl) aniline (8l).** Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.28 (m, 4H), 7.22-7.18 (m, 1H), 7.09-7.06 (m, 2H), 6.63 (t, J = 7.5 Hz, 1H), 6.50-6.49 (m, 2H), 4.47 (q, J = 6.5 Hz, 1H), 3.96 (br, 1H), 1.49 (d, J = 6.5 Hz, 3H). ^{13}C NMR (125.4 MHz, $CDCl_3$): δ 147.2, 145.2, 129.1, 128.6, 126.8, 125.8, 117.2, 113.3, 53.4, 24.9. MS (EI): *m/z* (%) 198 (7), 197 (45), 183 (14), 182 (100), 180 (6), 120 (8), 106 (6), 105 (71), 104 (18), 103 (10), 93 (46), 92 (7), 91 (13), 79 (13), 77 (32), 51 (7). This compound was known: Sato, S.; Sakamoto, T.; Miyazawa, E.; Kikugawa, Y. *Tetrahedron,* **2004**, *60*, 7899-7906.

Typical Procedure for Alkyl Halides-Catalyzed Hoffmann *N*-Alkylation of Amides with Secondary and Tertiary Aicohols. The mixture of benzamide (0.243 g, 2 mmol) , benzohydrol **7a** (0.443 g, 2.4 mmol), and benzhydryl bromide (0.0494 g, 0.2 mmol, 10 mol%) was sealed under air in a 20 mL Schlenk tube, stirred at 90 ^{o}C for 24 h, and then monitored by TLC and/or GC-MS. After completion of the reaction, the mixture was directly purified, without any workup,

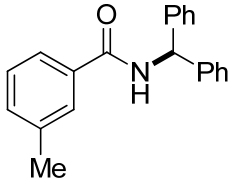
through a silica gel column using ethyl acetate and petroleum ether as the eluent, giving *N*-benzhydryl benzamide **10a** in 97% isolated yield.



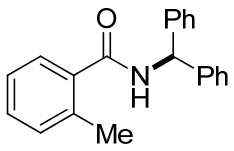
***N*-Benzhydryl benzamide (10a).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (d, J = 7.5 Hz, 2H), 7.50 (t, J = 7.5 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.36-7.27 (m, 10H), 6.73 (d, J = 7.0 Hz, 1H), 6.45 (d, J = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.5, 141.5, 134.3, 131.7, 128.8, 128.7, 127.6, 127.5, 127.1, 57.5. MS (EI): *m/z* (%) 289 (2), 288 (15), 287 (65), 210 (10), 182 (29), 152 (8), 105 (100), 77 (62), 51 (14). This compound was known: Li, L.; Zhu, A.; Zhang, Y.; Fan, X.; Zhang, G. *RSC Adv.* **2014**, *4*, 4286-4291.



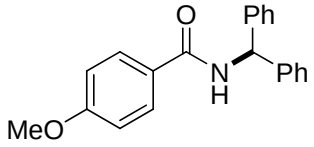
***N*-Benzhydryl 4-methylbenzamide (10b).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, J = 8.0 Hz, 2H), 7.35-7.28 (m, 10H), 7.22 (d, J = 7.5 Hz, 2H), 6.70 (d, J = 7.0 Hz, 1H), 6.44 (d, J = 8.0 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.5, 142.2, 141.6, 131.4, 129.3, 128.7, 127.5, 127.1, 57.4, 21.5. MS (EI): *m/z* (%) 302 (14), 301 (60), 182 (7), 167 (100), 119 (69), 91 (43), 77 (10), 65 (13), 51 (4). This compound was known: Yu, H.; Shen, J. *Org. Lett.* **2014**, *16*, 3204-3207.



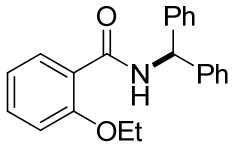
***N*-Benzhydryl 3-methylbenzamide (10c).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (s, 1H), 7.55 (d, J = 7.0 Hz, 1H), 7.33-7.20 (m, 12H), 6.93 (d, J = 7.5 Hz, 1H), 6.42 (d, J = 8.0 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.9, 141.6, 138.5, 134.3, 132.4, 128.7, 128.5, 127.9, 127.6, 127.5, 124.2, 57.4, 21.4. MS (EI): *m/z* (%) 302 (14), 301 (55), 182 (37), 165 (25), 119 (100), 104 (23), 91 (52), 65 (17), 51 (5). This compound was known: Yu, H.; Shen, J. *Org. Lett.* **2014**, *16*, 3204-3207.



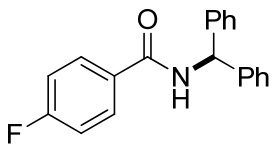
***N*-Benzhydryl 2-methylbenzamide (10d).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (d, J = 8.0 Hz, 1H), 7.34-7.23 (m, 11H), 7.17 (t, J = 8.0 Hz, 2H), 6.43 (s. 2H), 2.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.5, 141.5, 134.3, 131.7, 128.8, 128.7, 127.6, 127.5, 127.1, 57.5. MS (EI): *m/z* (%) 302 (15), 301 (62), 182 (8), 167 (100), 152 (11), 119 (77), 104 (13), 91 (43), 77 (10), 51 (4). This compound was known: Yu, H.; Shen, J. *Org. Lett.* **2014**, *16*, 3204-3207.



***N*-Benzhydryl 4-methoxybenzamide (10e).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, J = 8.5 Hz, 2H), 7.35-7.28 (m, 10H), 6.91 (d, J = 8.5 Hz, 2H), 6.62 (d, J = 7.5 Hz, 1H), 6.43 (d, J = 7.5 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.0, 162.4, 141.7, 128.9, 128.7, 127.5, 126.5, 113.8, 57.4, 55.4. MS (EI): *m/z* (%) 318 (8), 317 (36), 182 (33), 165 (14), 152 (5), 135 (100), 104 (10), 92 (10), 77 (24), 64 (4), 51 (4). This compound was known: Beisel, T.; Manolikakes, G. *Org. Lett.* **2013**, *15*, 6046-6049.

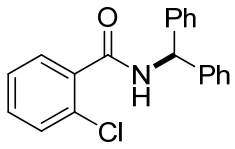


***N*-Benzhydryl 2-ethoxybenzamide (10f).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.78 (d, J = 7.0 Hz, 1H), 8.23 (dd, J = 7.5, 2.0 Hz, 1H), 7.40-7.37 (m, 1H), 7.33-7.29 (m, 8H), 7.25-7.23 (m, 2H), 7.04 (t, J = 7.5 Hz, 1H), 6.91 (d, J = 8.5 Hz, 1H), 6.45 (d, J = 7.5 Hz, 1H), 4.08 (q, J = 7.0 Hz, 2H), 1.27 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.4, 157.2, 142.3, 132.9, 132.5, 128.6, 127.5, 127.3, 121.34, 121.29, 112.3, 64.8, 57.6, 14.7. MS (EI): *m/z* (%) 332 (16), 331 (58), 182 (100), 149 (37), 121 (78), 104 (21), 77 (15), 65 (18), 51 (5). HRMS Calcd for $C_{22}H_{22}NO_2$ (M+H): 332.1645; found: 332.1649.

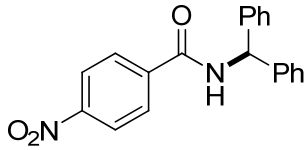


***N*-Benzhydryl 4-fluorobenzamide (10g).** White solid. ^{1}H NMR (500 MHz, DMSO): δ 9.32 (d,

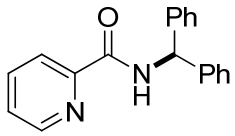
J = 9.0 Hz, 1H), 8.03 (dd, J = 8.0, 5.5 Hz, 2H), 7.38-7.24 (m, 12H), 6.42 (d, J = 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.9, 163.9(d, $J_{C\text{-}F}$ = 247.5 Hz), 142.2, 130.8, 130.3 (d, $J_{C\text{-}F}$ = 8.8 Hz), 128.3, 127.6, 127.0, 115.1 (d, $J_{C\text{-}F}$ = 22.5 Hz), 56.4. MS (EI): *m/z* (%) 306 (16), 305 (70), 228 (11), 182 (31), 165 (30), 152 (7), 123 (100), 104 (35), 77 (13), 51 (5). This compound was known: Wang, Z.; Zhang, Y.; Fu, H.; Jiang, Y.; Zhao, Y. *Org. Lett.* **2008**, *10*, 1863-1866.



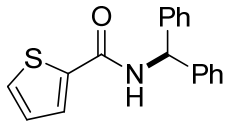
***N*-Benzhydryl 2-chlorobenzamide (10h).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, J = 7.5 Hz, 1H), 7.39-7.28 (m, 13H), 6.90 (d, J = 6.5 Hz, 1H), 6.45 (d, J = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.4, 141.2, 134.7, 131.5, 130.7, 130.6, 130.3, 128.7, 127.6, 127.5, 127.2, 57.9. HRMS Calcd for $C_{20}H_{17}ClNO$ (M+H): 322.0993; found: 322.0995.



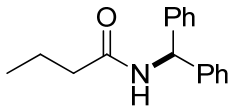
***N*-Benzhydryl 4-nitrobenzamide (10i).** Light yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.24 (d, J = 8.0 Hz, 2H), 7.94 (d, J = 8.5 Hz, 2H), 7.37-7.28 (m, 10H), 6.90 (d, J = 7.0 Hz, 1H), 6.42 (d, J = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.6, 149.7, 140.8, 139.8, 128.9, 128.3, 127.9, 127.5, 123.8, 57.9. This compound was known: Beisel, T.; Manolikakes, G. *Org. Lett.* **2013**, *15*, 6046-6049.



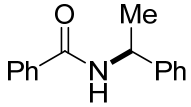
***N*-Benzhydryl picolinamide (10j).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.75 (d, J = 8.5 Hz, 1H), 8.50 (d, J = 4.5 Hz, 1H), 8.20 (d, J = 8.0 Hz, 1H), 7.77 (dd, J = 7.5, 1.5 Hz, 1H) 7.37-7.30 (m, 9H), 7.26-7.22 (m, 2H), 6.46 (d, J = 8.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.5, 149.8, 148.2, 141.7, 137.4, 128.7, 127.6, 127.5, 126.3, 122.5, 57.0. MS (EI): *m/z* (%) 288 (2), 211 (2), 182 (100), 165 (13), 152 (5), 106 (9), 78 (30), 51 (9). HRMS Calcd for $C_{19}H_{17}N_2O$ (M+H): 289.1335; found: 289.1340.



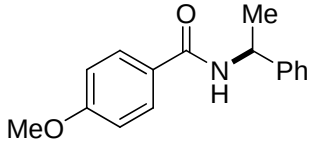
***N*-Benzhydryl thiophene-2-carboxamide (10k).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (s, 1H), 7.44 (d, J = 4.0 Hz, 1H), 7.33-7.25 (m, 10H), 7.01 (s, 1H), 6.72 (d, J = 7.0 Hz, 1H), 6.39 (d, J = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.1, 141.3, 138.7, 130.2, 128.8, 128.4, 127.7, 127.61, 127.58, 57.4. MS (EI): *m/z* (%) 294 (11), 293 (53), 182 (54), 165 (34), 111 (100), 83 (9), 77 (17), 51 (7). HRMS Calcd for $C_{18}H_{16}NOS$ (M+H): 294.0947; found: 294.0953.



***N*-Benzhydryl butyramide (10l).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29-7.18 (m, 10H), 6.56 (d, J = 6.5 Hz, 1H), 6.23 (d, J = 8.0 Hz, 1H), 2.16-2.12 (m, 2H), 1.66-1.58 (m, 2H), 0.91-0.87 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.2, 141.8, 128.6, 127.5, 127.4, 56.8, 38.6, 19.2, 13.8. MS (EI): *m/z* (%) 254 (19), 253 (94), 182 (93), 167 (100), 152 (24), 106 (63), 77 (31), 51 (10). This compound was known: Liu, X.; Zhang, Y.; Wang, L.; Fu, H.; Jiang, Y.; Zhao, Y. *J. Org. Chem.* **2008**, *73*, 6207-6212.

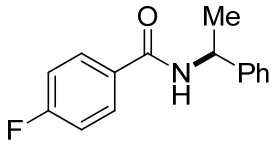


***N*-(1-Phenylethyl) benzamide (10m).** Light yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, J = 7.0 Hz, 2H), 7.45 (t, J = 7.5 Hz, 1H), 7.40-7.32 (m, 6H), 7.26 (t, J = 7.5 Hz, 1H), 6.51 (d, J = 6.5 Hz, 1H), 5.35-5.29 (m, 1H), 1.58 (d, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.6, 143.2, 134.7, 131.4, 128.7, 128.5, 127.4, 127.0, 126.3, 49.2, 21.8. MS (EI): *m/z* (%) 226 (5), 225 (29), 210 (8), 120 (8), 105 (100), 77 (45), 51 (11). This compound was known: Wang, Z.; Zhang, Y.; Fu, H.; Jiang, Y.; Zhao, Y. *Org. Lett.* **2008**, *10*, 1863-1866.

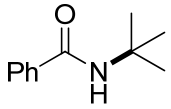


***N*-(1-Phenylethyl) 4-methoxybenzamide (10n).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, J = 8.5 Hz, 2H), 7.34-7.32 (m, 4H), 7.25 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 8.0 Hz, 2H), 6.46 (d, J = 7.0 Hz, 1H), 5.34-5.28 (m, 1H), 3.81 (s, 3H), 1.57 (d, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.2, 162.2, 143.4, 128.8, 128.7, 127.3, 126.9, 126.3, 113.7, 55.4, 49.1,

21.8. This compound was known: Vanjari, R.; Guntreddi, T.; Singh, K. N. *Green Chem.* **2014**, *16*, 351-356.

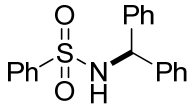


***N*-(1-Phenylethyl) 4-fluorobenzamide (10o).** Light yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (dd, J = 8.5, 5.5 Hz, 2H), 7.36-7.31 (m, 4H), 7.25 (t, J = 7.0 Hz, 1H), 7.02 (t, J = 8.5 Hz, 2H), 6.66 (d, J = 6.5 Hz, 1H), 5.31-5.25 (m, 1H), 1.56 (d, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.7, 164.7 (d, $J_{C\text{-}F}$ = 248.8 Hz), 143.2, 130.8, 129.4 (d, $J_{C\text{-}F}$ = 8.8 Hz), 128.7, 127.5, 126.2, 115.5 (d, $J_{C\text{-}F}$ = 21.3 Hz), 49.4, 21.7. MS (EI): *m/z* (%) 244 (5), 243 (29), 228 (11), 123 (100), 104 (23), 95 (31), 77 (9), 51 (4). This compound was known: Wang, Z.; Zhang, Y.; Fu, H.; Jiang, Y.; Zhao, Y. *Org. Lett.* **2008**, *10*, 1863-1866.



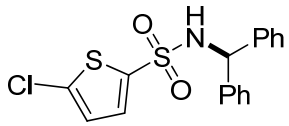
***N*-*t*-Butyl benzamide (10p).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72-7.69 (m, 2H), 7.46-7.43 (m, 1H), 7.40-7.37 (m, 2H), 5.99 (s, 1H), 1.47 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.9, 136.0, 131.0, 128.4, 126.7, 51.6, 28.9. MS (EI): *m/z* (%) 177 (20), 162 (25), 122 (18), 105 (100), 77 (32), 51 (8). This compound was known: Yaragorla, S.; Singh, G.; Lal Saini, P.; Reddy, M. K. *Tetrahedron Lett* **2014**, *55*, 4657-4660.

Typical Procedure for Alkyl Halides-Catalyzed Hoffmann *N*-Alkylation of Sulfamides with Secondary and Tertiary Aicohols. The mixture of benzenesulfonamide (0.314 g, 2 mmol), benzohydrol **7a** (0.443 g, 2.4 mmol), and benzhydryl bromide (0.0494 g, 0.2 mmol, 10 mol%) was sealed under air in a 20 mL Schlenk tube, stirred at 130 ^{o}C for 24 h, and then monitored by TLC and/or GC-MS. After completion of the reaction, the mixture was directly purified, without any workup, through a silica gel column using ethyl acetate and petroleum ether as the eluent, giving *N*-benzhydryl benzenesulfonamide **11a** in 98% isolated yield.

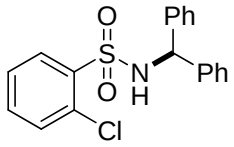


***N*-Benzhydryl benzenesulfonamide (11a).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d,

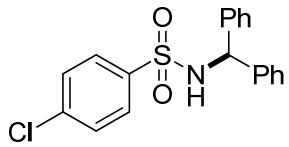
J = 7.0 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.21-7.15 (m, 6H), 7.10-7.08 (m, 4H), 5.60 (d, *J* = 7.5 Hz, 1H), 5.43 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 140.4, 132.4, 128.7, 128.6, 127.6, 127.4, 127.1, 61.4. MS (EI): *m/z* (%) 323 (0.5), 322 (0.6), 246 (7), 182 (100), 152 (12), 104 (32), 77 (63), 51 (15). This compound was known: Han, F.; Yang, L.; Li, Z.; Xia, C. *Adv. Synth. Catal.* **2012**, *354*, 1052-1060.



***N*-Benzhydryl 5-chlorothiophene-2-sulfonamide (11b).** Light yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.26-7.20 (m, 6H), 7.15 (d, *J* = 8.0 Hz, 4H), 7.06 (d, *J* = 4.0 Hz, 1H), 6.65 (d, *J* = 4.0 Hz, 1H), 5.75 (d, *J* = 8.0 Hz, 1H), 5.65 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 140.0, 139.5, 137.3, 131.8, 128.7, 127.8, 127.4, 126.4, 61.7. MS (EI): *m/z* (%) 364 (1), 328 (1), 285 (6), 182 (100), 180 (53), 152 (22), 117 (4), 104 (33), 82 (3), 51 (11). HRMS Calcd for $C_{17}H_{14}ClNNaO_2S_2$ (M+Na): 386.0047; found: 386.0054.

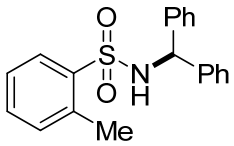


***N*-Benzhydryl 2-chlorobenzenesulfonamide (11c).** Light yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.88 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.35 (td, *J* = 8.0, 1.5 Hz, 1H), 7.25 (dd, *J* = 16.5, 8.5 Hz, 2H), 7.19-7.17 (m, 6H), 7.11-7.09 (m, 4H), 5.69 (d, *J* = 8.0 Hz, 1H), 5.56 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 139.9, 137.8, 133.4, 131.5, 131.3, 131.0, 128.5, 127.8, 127.3, 126.9, 61.8. MS (EI): *m/z* (%) 357 (0.4), 280 (9), 182 (100), 167 (24), 104 (30), 77 (25), 51 (10). HRMS Calced for $C_{19}H_{16}ClNNaO_2S$ (M+Na): 380.0482; found: 380.0464.

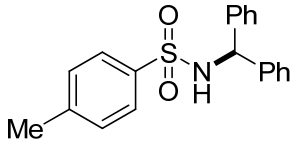


***N*-Benzhydryl 4-chlorobenzenesulfonamide (11d).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.51 (d, *J* = 8.5 Hz, 2H), 7.20-7.16 (m, 8H), 7.10-7.08 (m, 4H), 5.94 (d, *J* = 8.0 Hz, 1H), 5.60 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 140.2, 139.1, 138.7, 128.9, 128.62, 128.55, 127.7, 127.4, 61.5. MS (EI): *m/z* (%) 357 (0.3), 280 (6), 182 (100), 167 (34), 77 (29), 51 (10). This compound was known: Wang, Z.; Zhang, Y.; Fu, H.; Jiang, Y.; Zhao, Y. *Org. Lett.* **2008**, *10*,

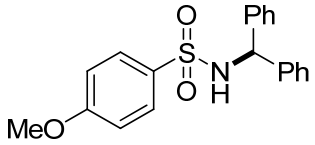
1863-1866.



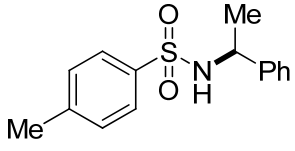
***N*-Benzhydryl 2-toluenesulfonamide (11e).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (t, J = 7.5 Hz, 1H), 7.37-7.33 (m, 1H), 7.18-7.07 (m, 12H), 5.50 (d, J = 7.5 Hz, 1H), 5.26 (d, J = 7.0 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.5, 138.2, 137.0, 132.6, 132.3, 129.7, 128.6, 127.7, 127.3, 126.0, 61.4, 20.1. MS (EI): *m/z* (%) 337 (0.5), 260 (5), 182 (100), 167 (23), 104 (25), 91 (35), 65 (10), 51 (70). This compound was known: Qureshi, Z. S.; Deshmukh, K. M.; Tambade, P. J. ; Dhake, K. P.; Bhanage, B. M. *Eur. J. Org. Chem.* **2010**, *2010*, 6233-6238.



***N*-Benzhydryl 4-toluenesulfonamide (11f).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (d, J = 8.0 Hz, 2H), 7.19-7.14 (m, 6H), 7.10-7.07 (m, 6H), 5.76 (d, J = 7.0 Hz, 1H), 5.56 (d, J = 7.0 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.1, 140.7, 137.5, 129.3, 128.5, 127.5, 127.4, 127.2, 61.4, 21.4. MS (EI): *m/z* (%) 337 (0.2), 260 (5), 182 (100), 167 (20), 104 (26), 91 (37), 77 (21), 65 (10), 51 (7). This compound was known: Li, L.; Zhu, A.; Zhang, Y.; Fan, X.; Zhang, G. *RSC Adv.* **2014**, *4*, 4286-4291.



***N*-Benzhydryl 4-methoxybenzenesulfonamide (11g).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (d, J = 9.0 Hz, 2H), 7.14-7.09 (m, 6H), 7.03 (d, J = 5.5 Hz, 4H), 6.70 (d, J = 9.0 Hz, 2H), 5.48 (d, J = 7.0 Hz, 1H), 5.29 (d, J = 7.0 Hz, 1H), 3.73 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.7, 139.6, 131.1, 128.3, 127.5, 126.5, 126.4, 112.9, 60.4, 54.6. HRMS Calcd for $C_{20}H_{19}NNaO_3S$ (M+Na): 376.0978; found: 376.0986.



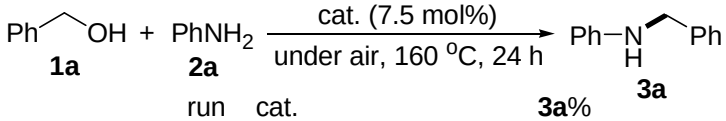
***N*-(1-Phenylethyl) 4-toluenesulfonamide (11h).** White solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ

7.54 (d, J = 8.5 Hz, 2H), 7.12-7.07 (m, 5H), 7.03-7.01 (m, 2H), 5.17 (d, J = 6.5 Hz, 1H), 4.40-4.35 (m, 1H), 2.29 (s, 3H), 1.33 (d, J = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.1, 142.2, 137.7, 129.4, 128.5, 127.4, 127.1, 126.1, 53.7, 23.6, 21.5. This compound was known: Cui, X.; Shi, F.; Tse, M. K.; Gordes, D.; Thurow, K.; Beller, M.; Deng, Y. *Adv. Synth. Catal.* **2009**, *351*, 2949-2958.

Control Experiments

Preparation of Aniline Hydrobromide Salt $PhNH_2$•HBr. To a solution of aniline **2a** (1.0 mL, 11.0 mmol) in ethyl acetate (10.0 mL) in a 50ml beaker was slowly added dropwise HBr (33 wt.% in acetic acid, 0.83 mL, 2.697 g, 11.0 mmol). Grey white solid precipitated from the mixture. The solid was then filtrated and dried under vacuum, giving 70% isolated yield of $PhNH_2$•HBr.

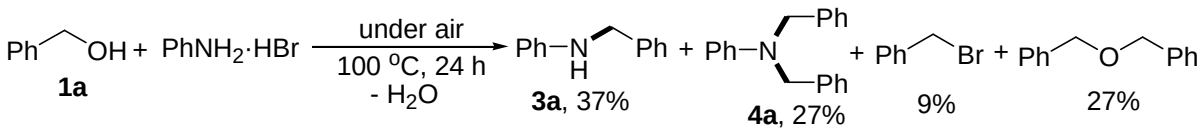
Typical Procedure for Ammonium Salts-Catalyzed N-Alkylation of Aniline with Benzyl Alcohol (eq. 6 in the text).



run	cat.	**3a**%
(1)	$PhNH_2$·HBr	39
(2)	$PhNH_2$·HCl	22
(3)	HBr (33 wt% in HOAc)	48

The mixture of benzyl alcohol **1a** (0.21 mL, 2.0 mmol), aniline **2a** (0.26 mL, 3.0 mmol), and $PhNH_2$•HBr (0.0259 g, 0.15 mmol, 7.5 mol%) in a 20 mL Schlenk tube was sealed under air and stirred at 160 °C for 24 h. The mixture was then directly purified, without any workup, through a silica gel column using ethyl acetate and petroleum ether as the eluent, giving *N*-benzylaniline **3a** in 39% isolated yield.

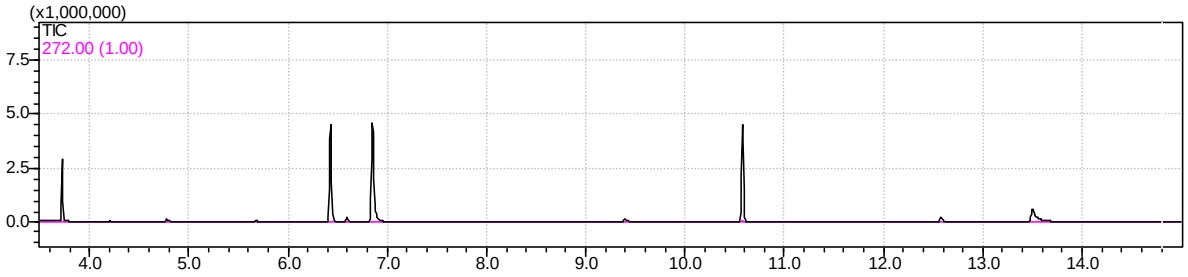
Procedure for the Reaction of Benzyl Alcohol and $PhNH_2$•HBr (eq. 7 in the text).



The mixture of benzyl alcohol **1a** (0.21 mL, 2.0 mmol, 1 equiv.) and $PhNH_2$•HBr (0.3460 g, 2.0

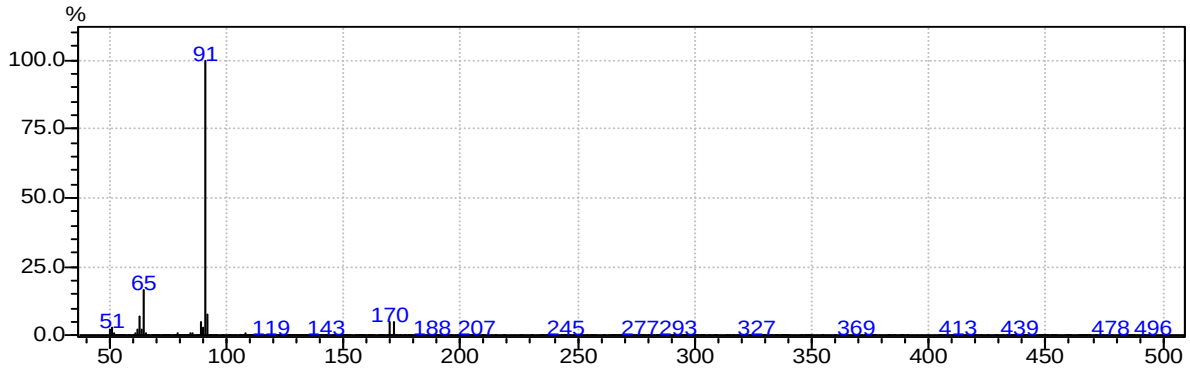
mmol) sealed in a 20 mL Schlenk tube under air was stirred at 100 °C for 24 h. The reaction was then monitored by TLC and/or GC-MS. GC-MS analysis of the mixture showed that the reaction is almost complete, giving 37% yield of **3a**, 27% yield of **4a** (**3a**/**4a** 59/41), 9% yield of benzyl bromide $PhCH_2Br$, as well as 27% yield of dibenzyl ether. For details see the GC-MS spectra below:

1. GC spectra:

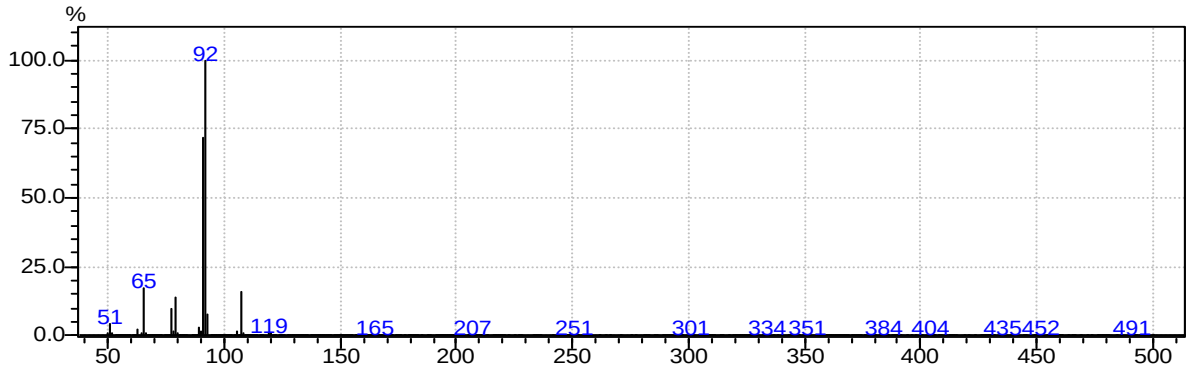


2. MS spectra of the peaks:

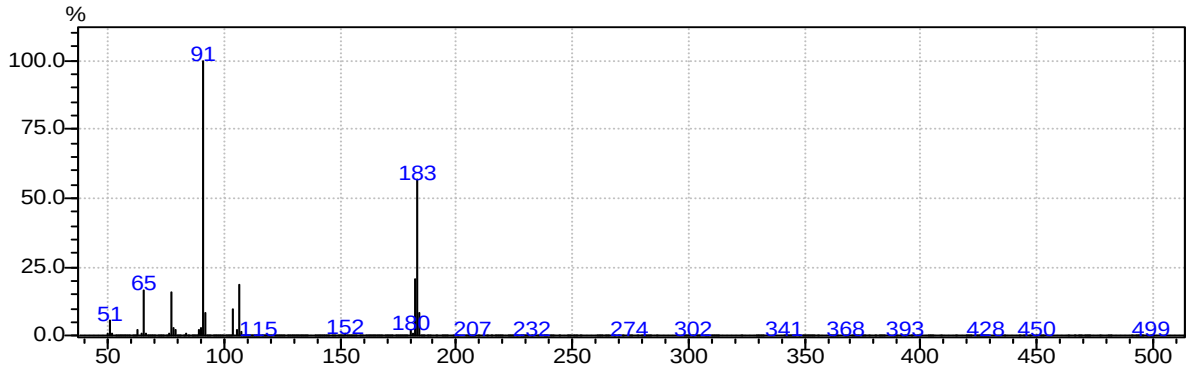
2.1 RT 3.73 min: MW 170/172, $PhCH_2Br$, 9% GC yield:



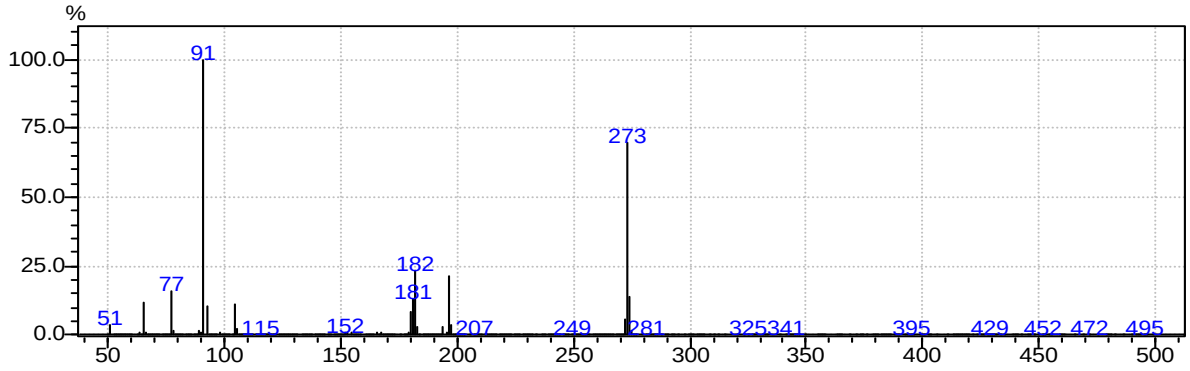
2.2 RT 6.43 min: MW 198 (by comparison with known compound), $(PhCH_2)O$, 27% GC yield:



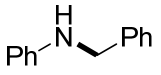
2.3 RT 6.86 min: MW 183, PhNHCH2Ph (**3a**), 37% GC yield:



2.4 RT 10.58 min: MW 273, PhN(CH2Ph)2, 27% GC yield:

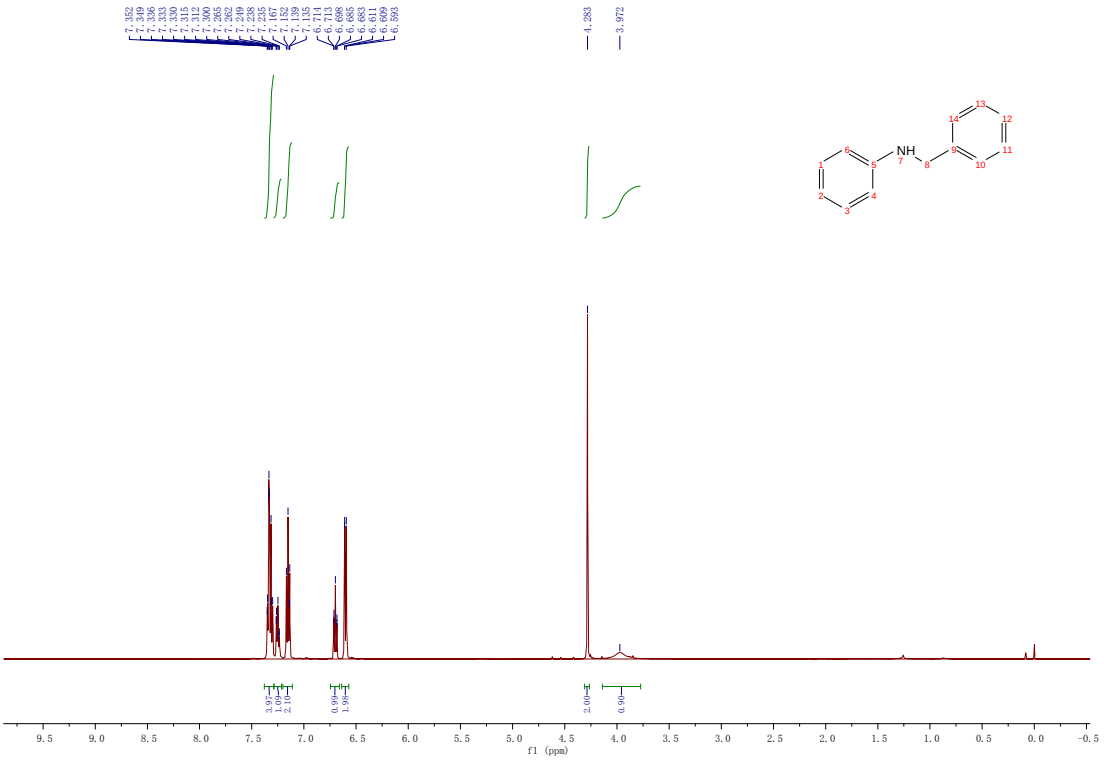


^{1}H and ^{13}C NMR Spectra of the Products

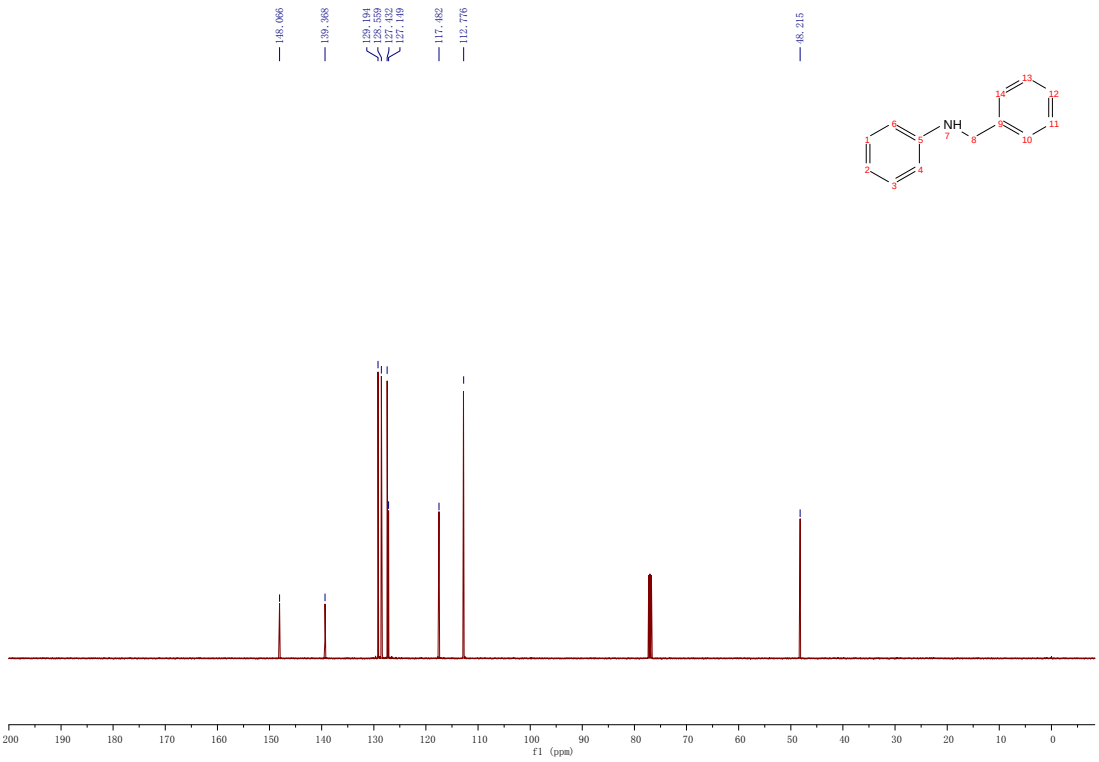


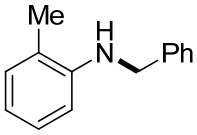
3a

^{1}H NMR



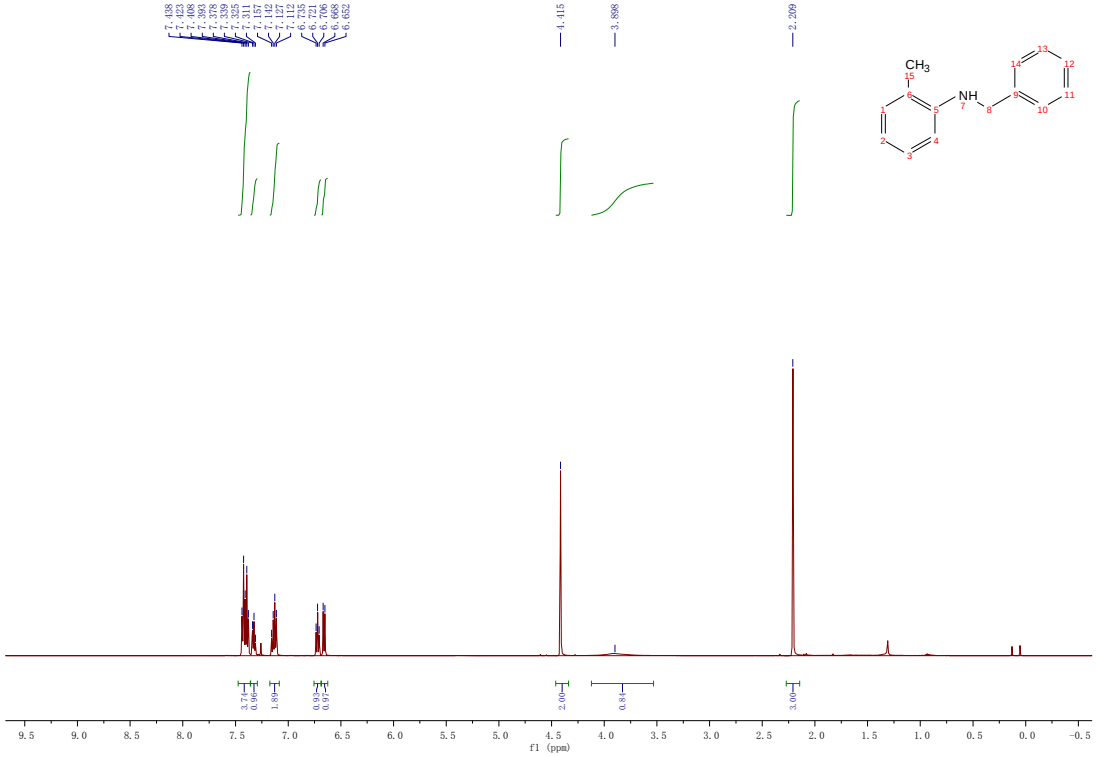
^{13}C NMR



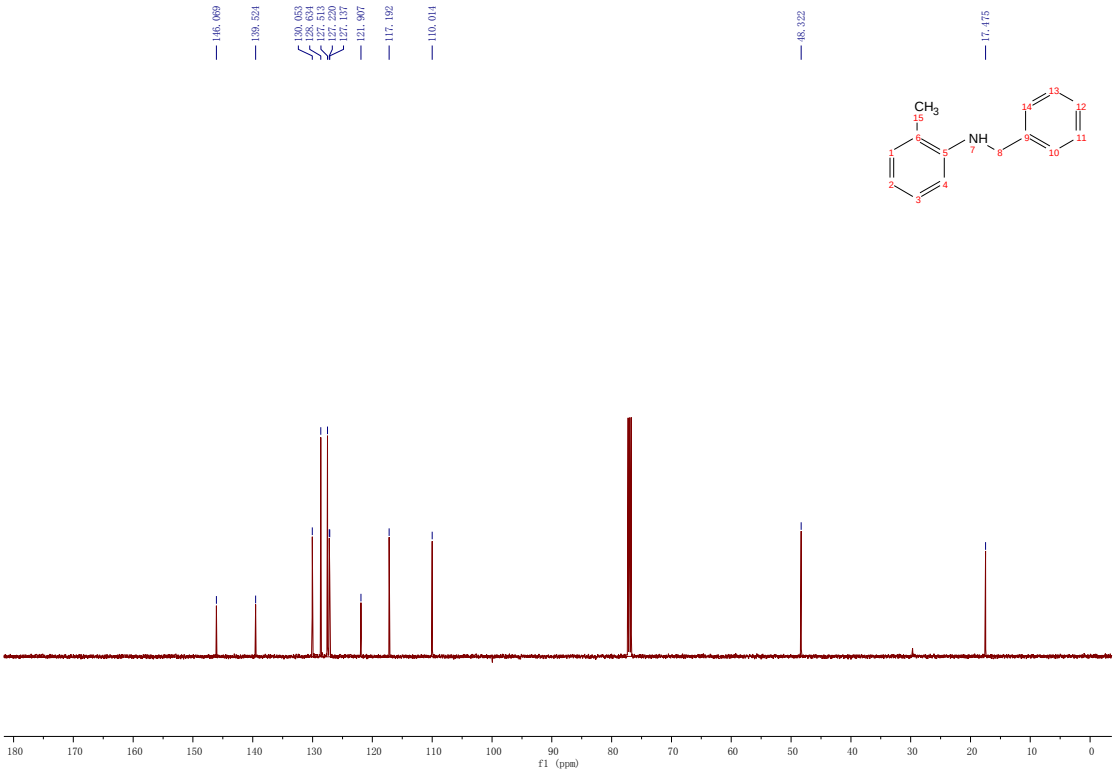


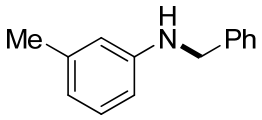
3b

^{1}H NMR



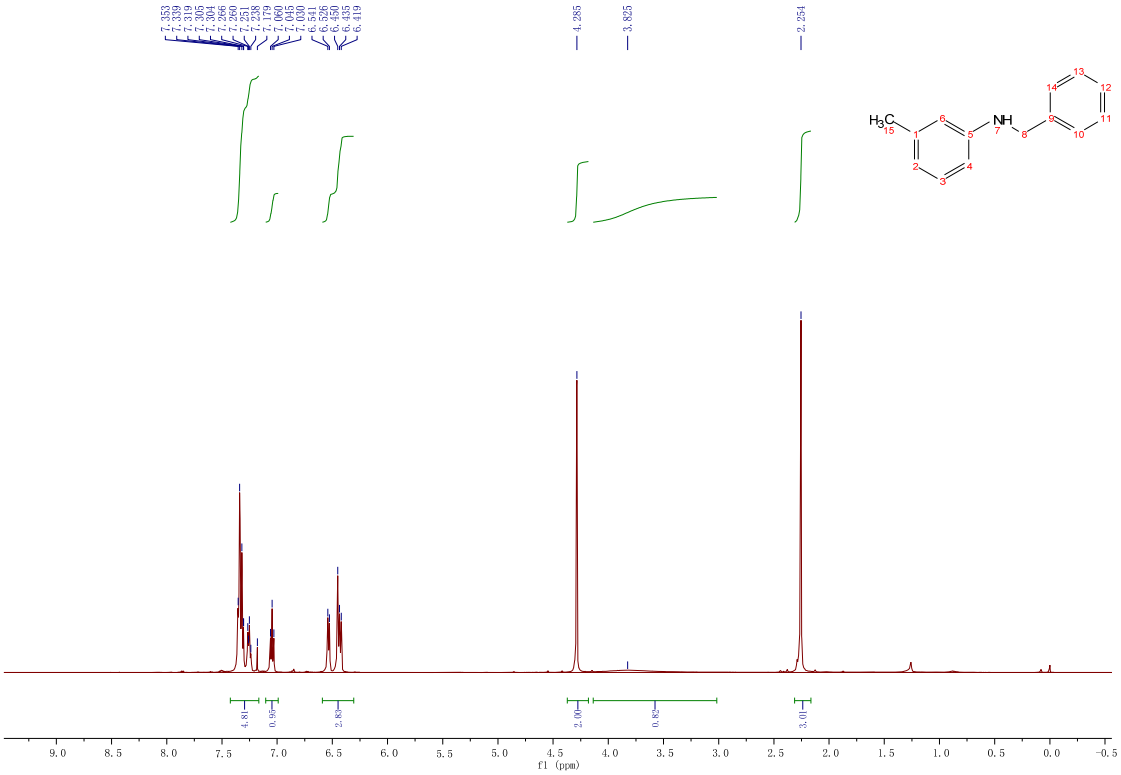
^{13}C NMR



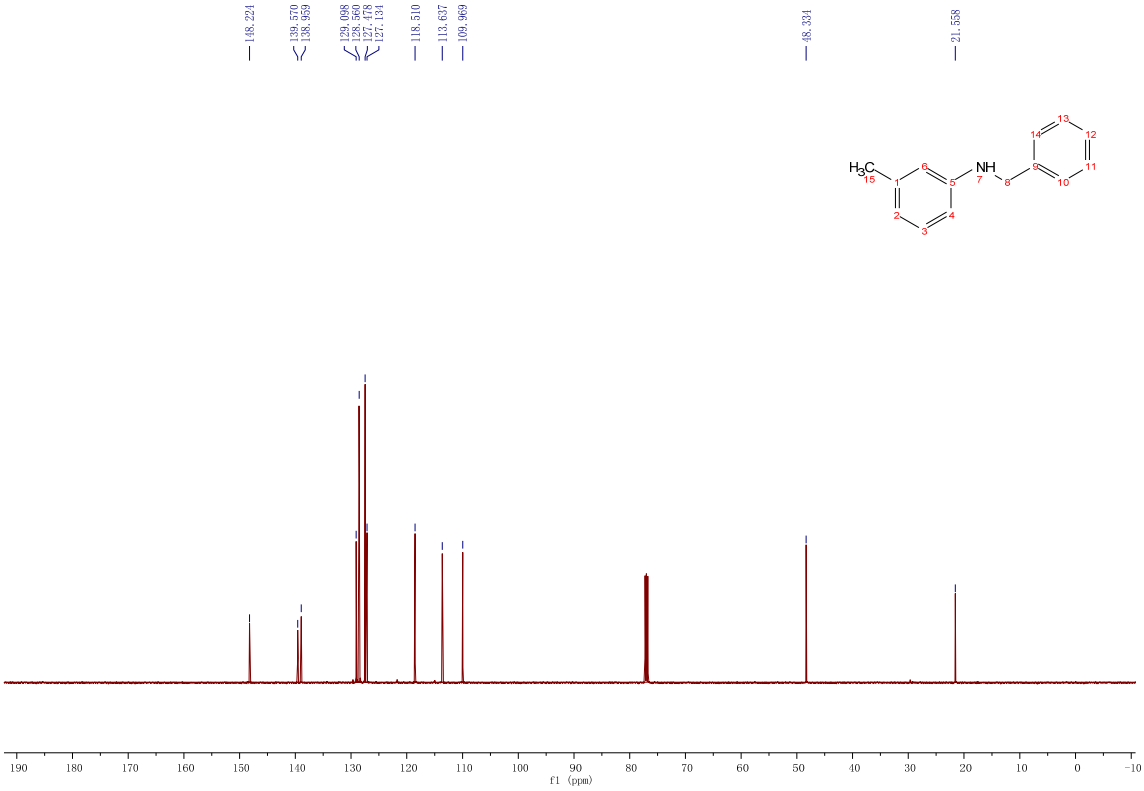


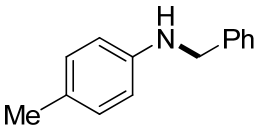
3c

^{1}H NMR



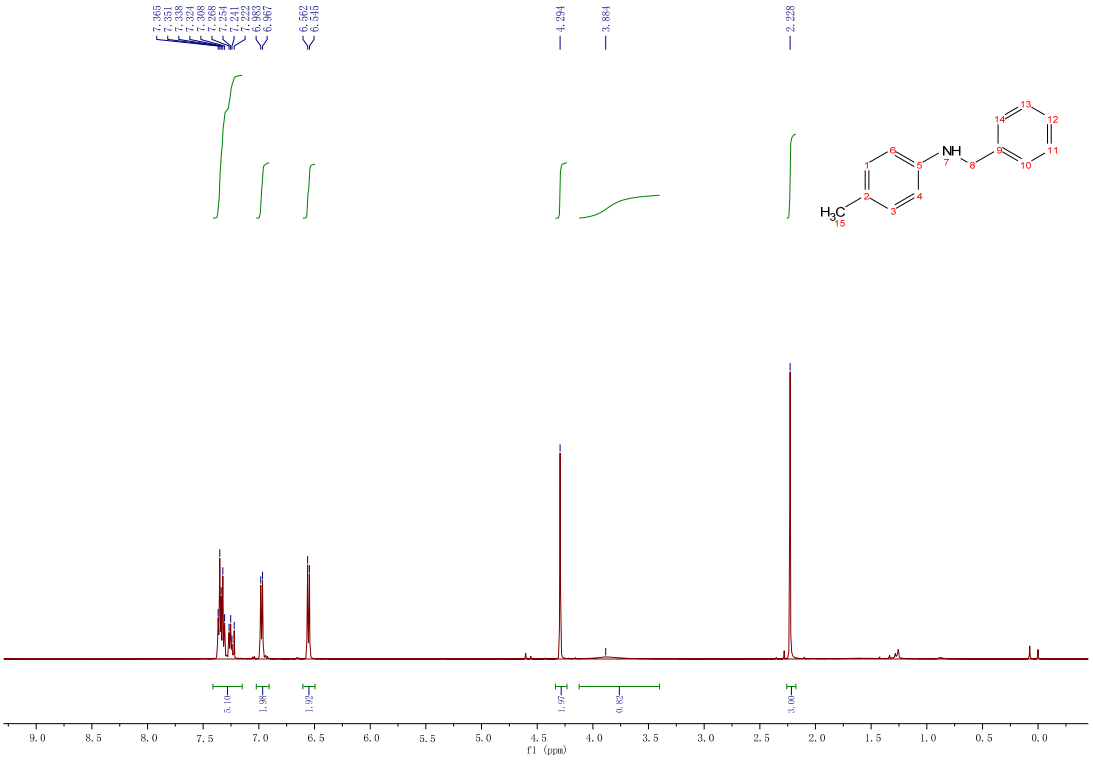
^{13}C NMR



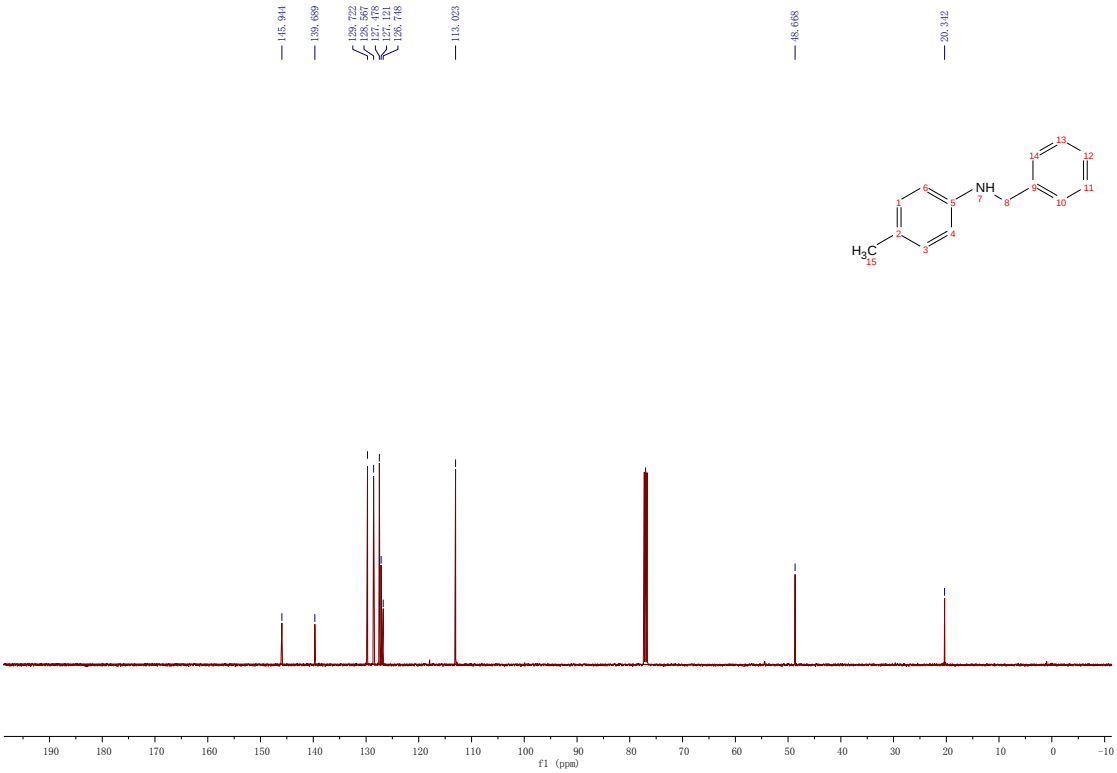


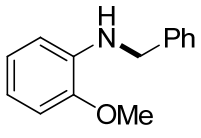
3d

^{1}H NMR



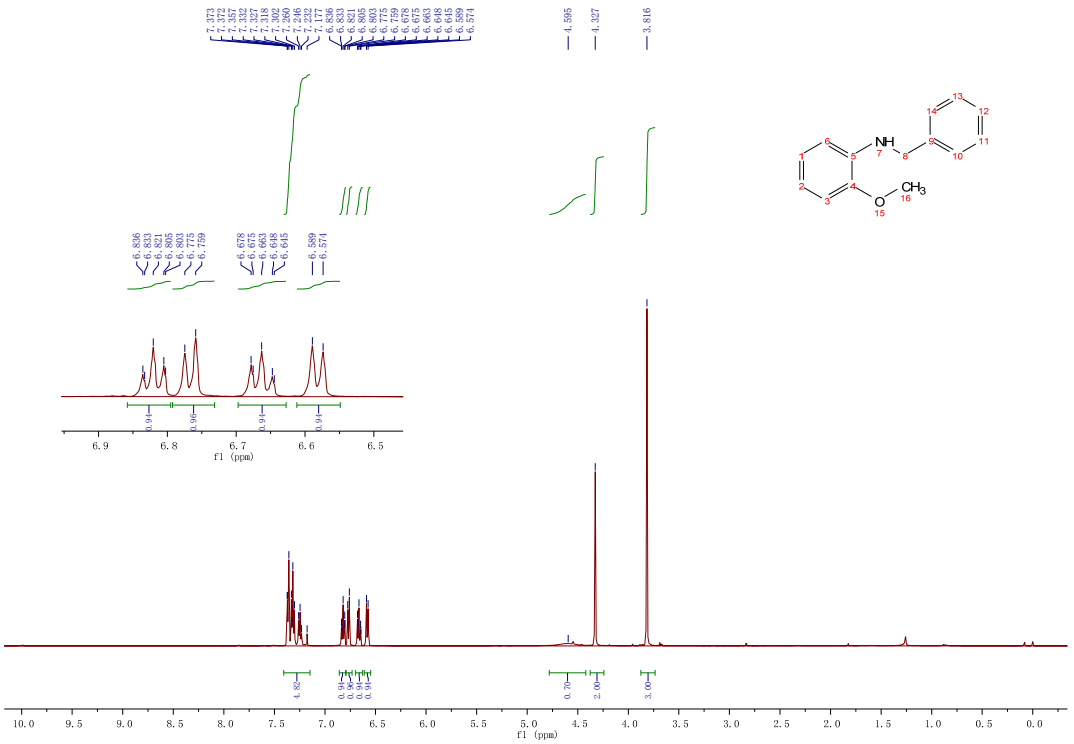
^{13}C NMR



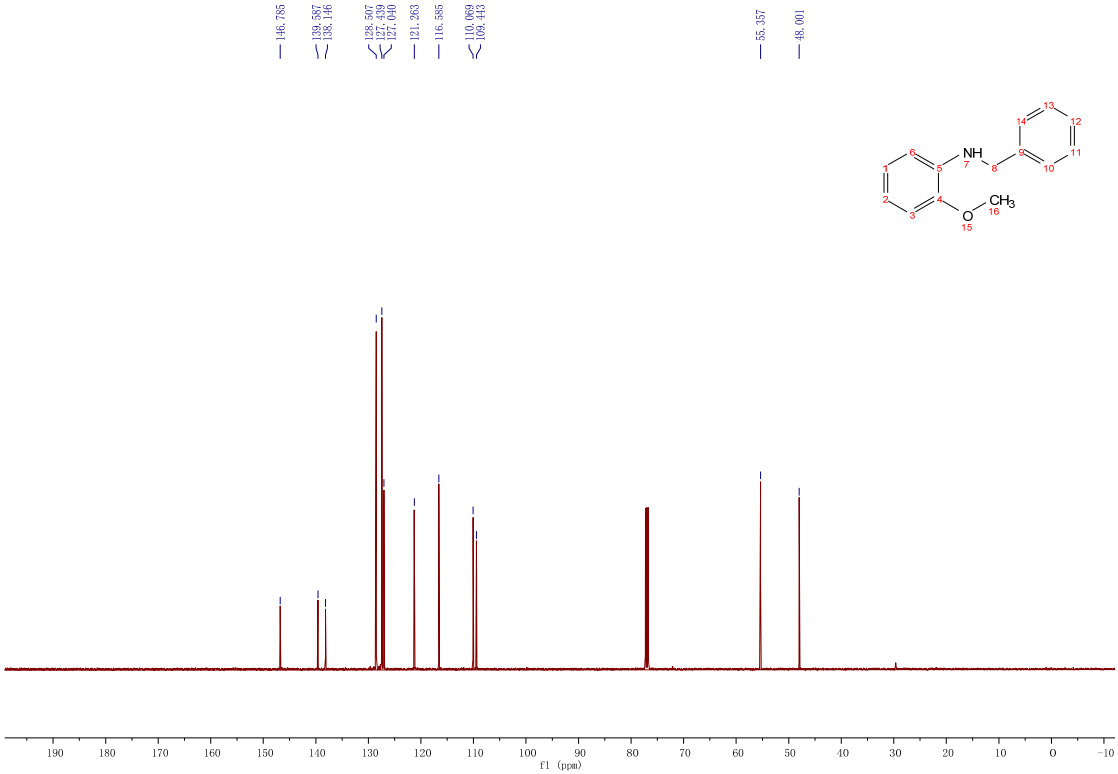


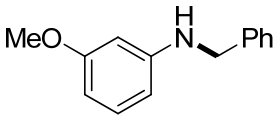
3e

^{1}H NMR



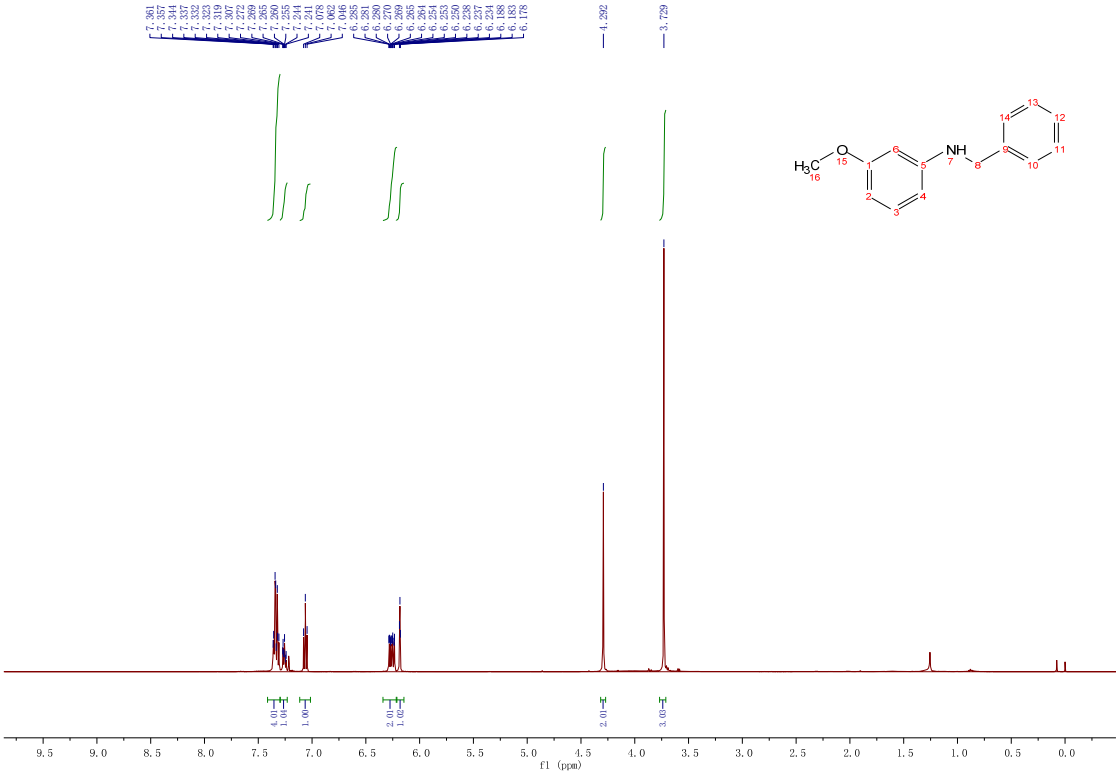
^{13}C NMR



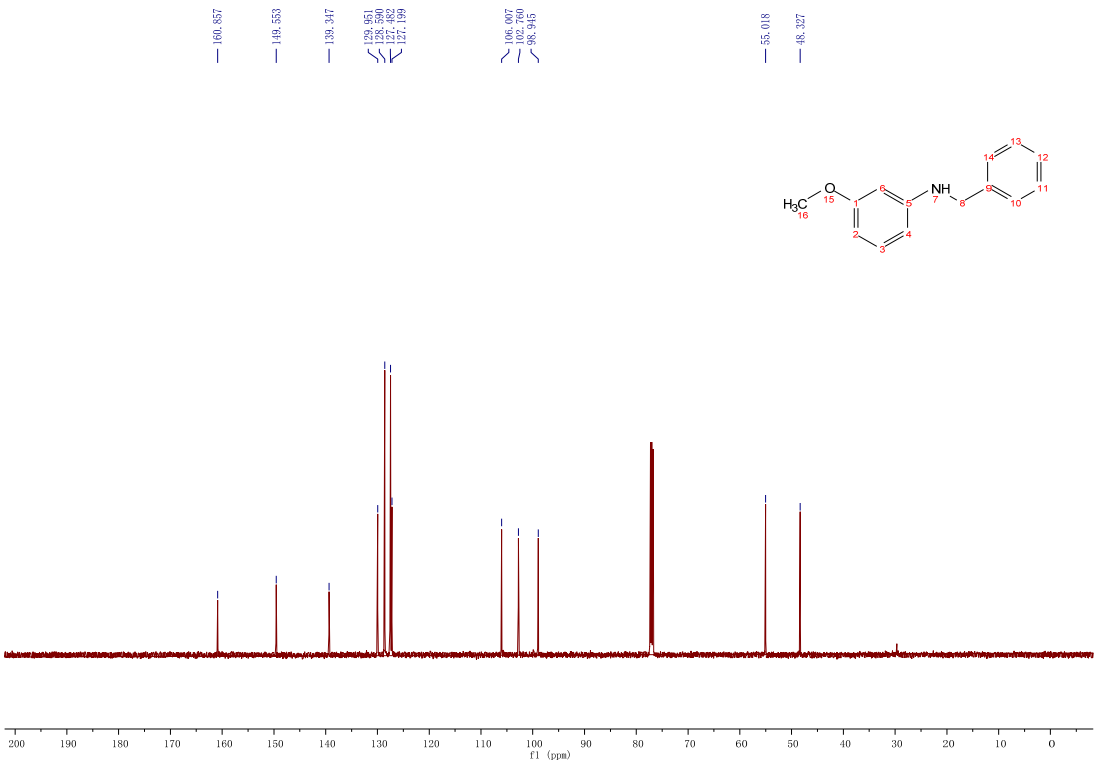


3f

^{1}H NMR

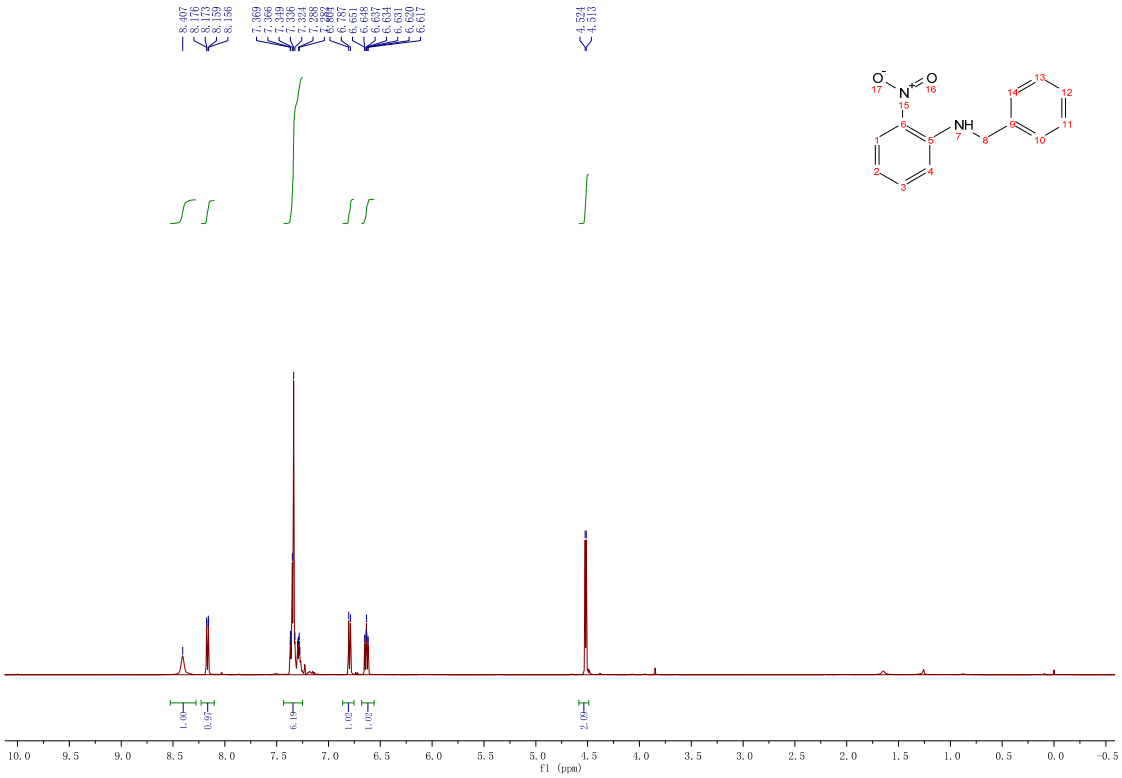


^{13}C NMR



3g

^{1}H NMR



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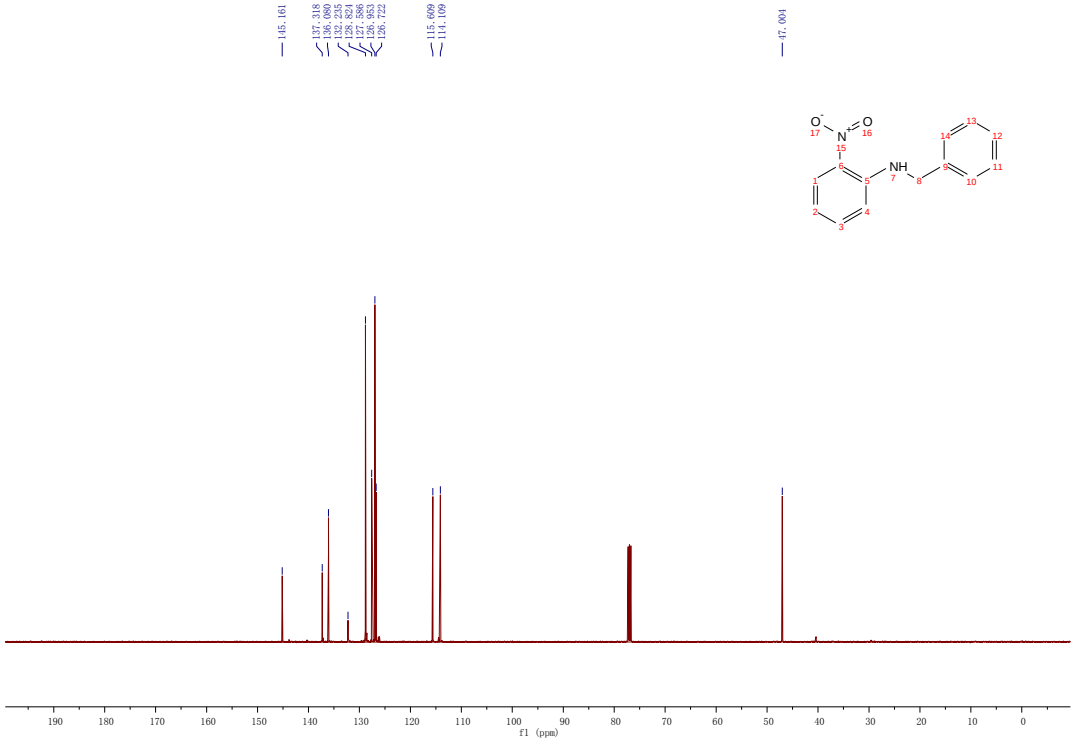

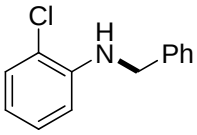

3h

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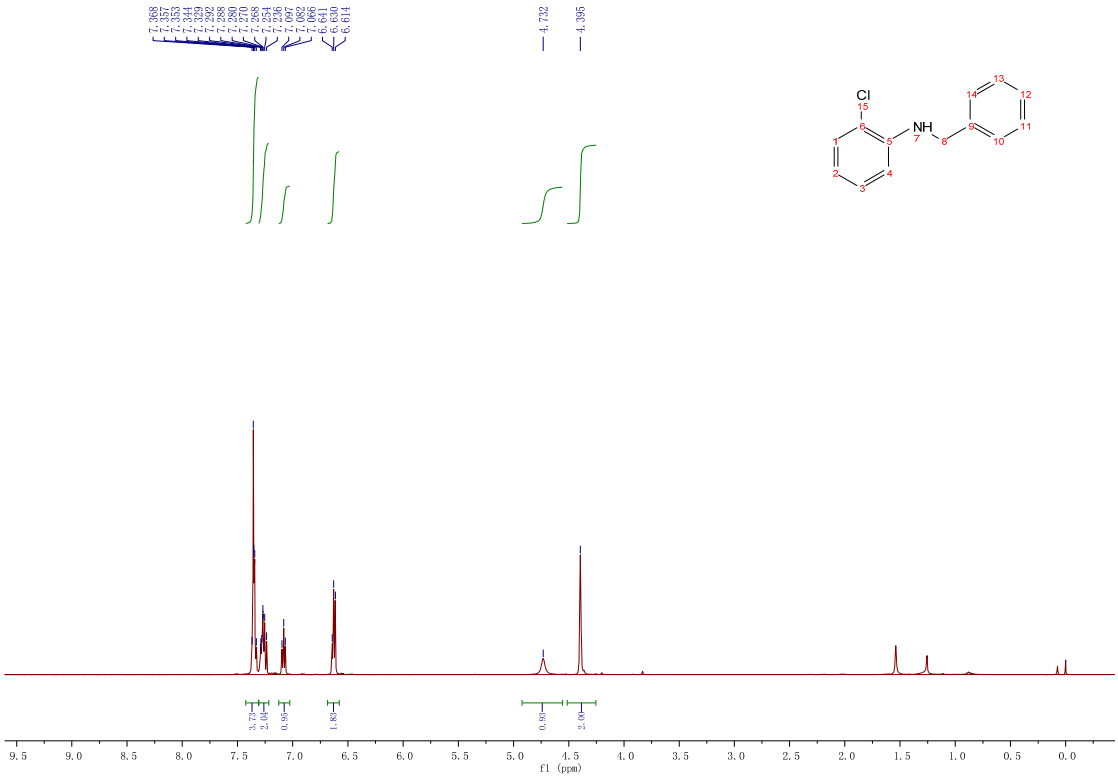

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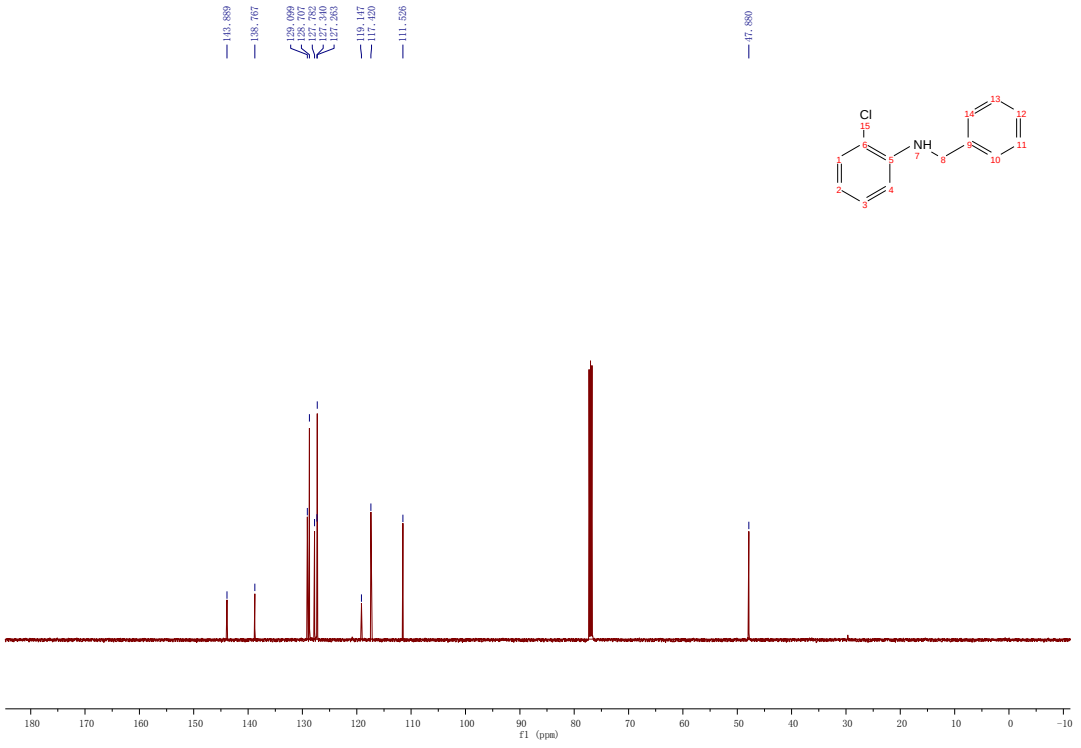

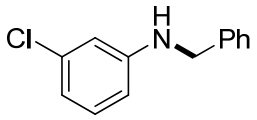

3l

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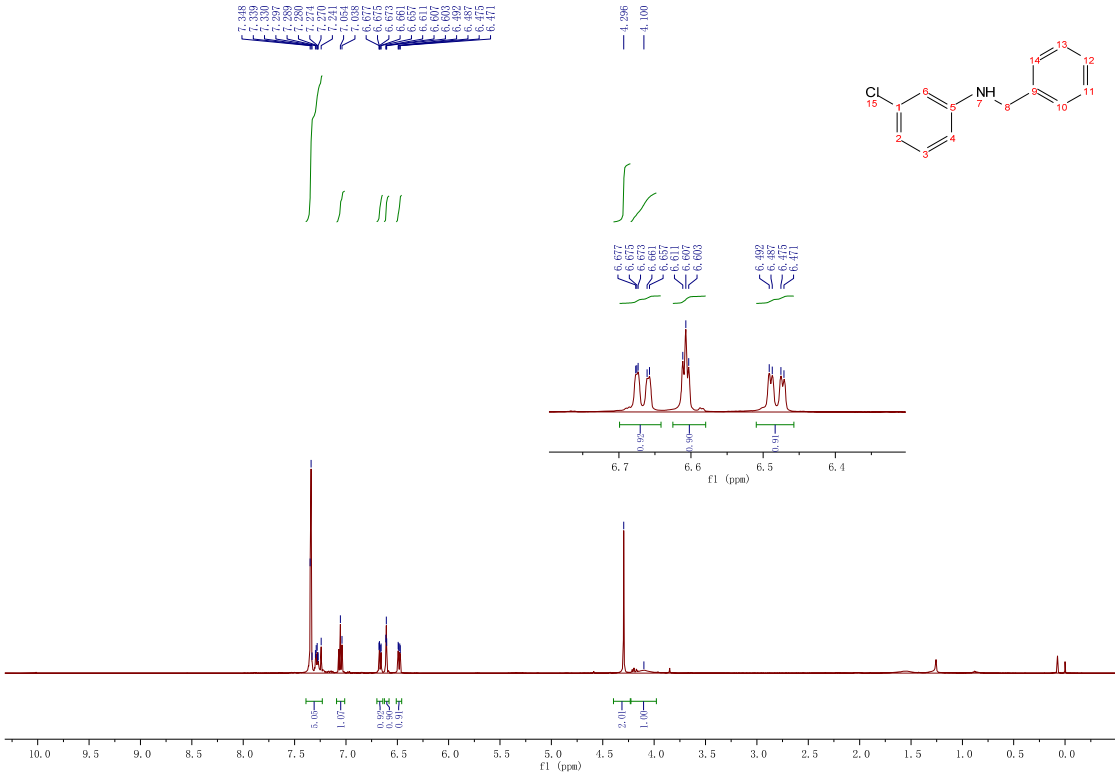

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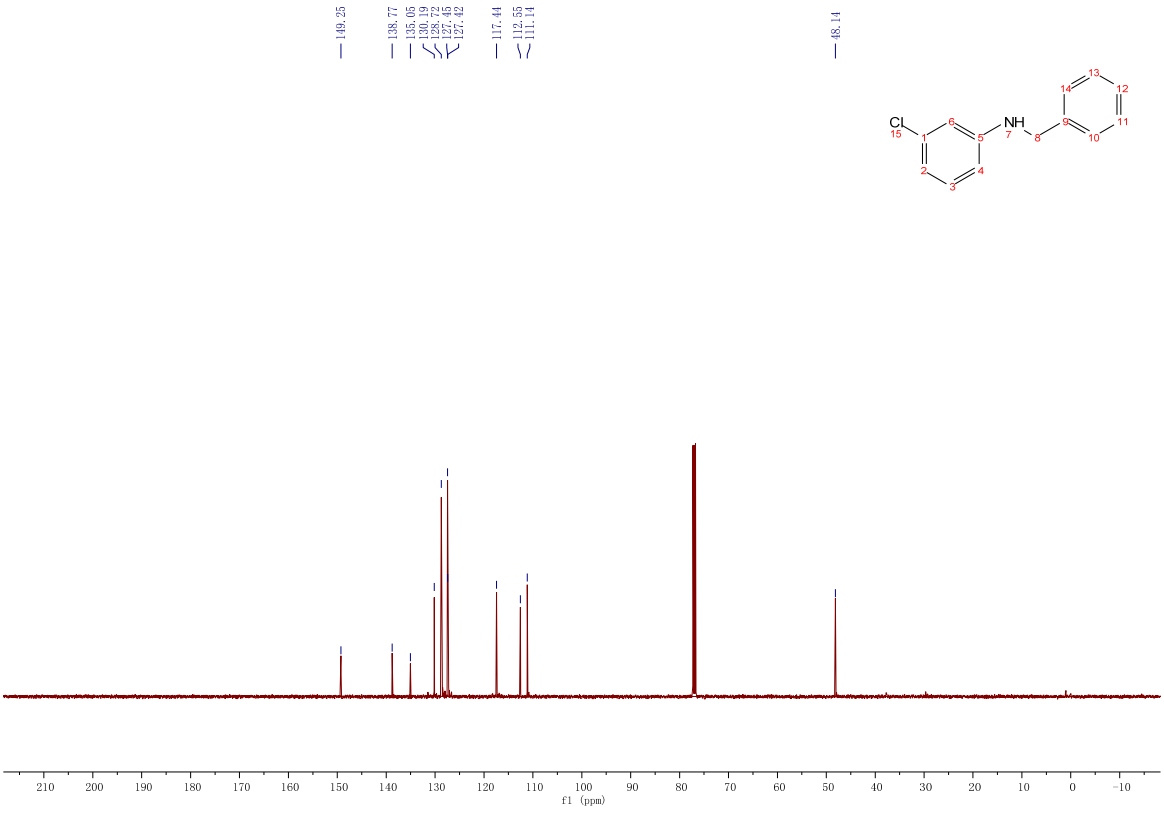

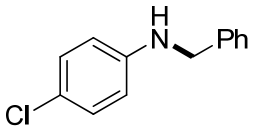

3j

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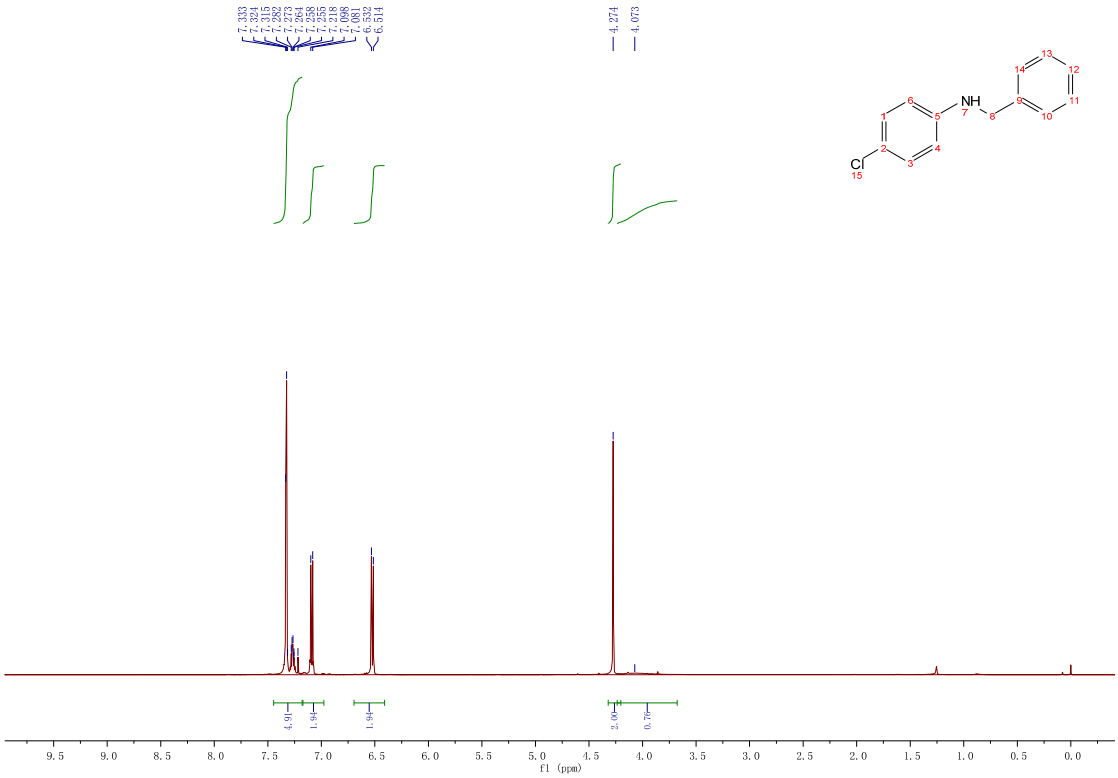

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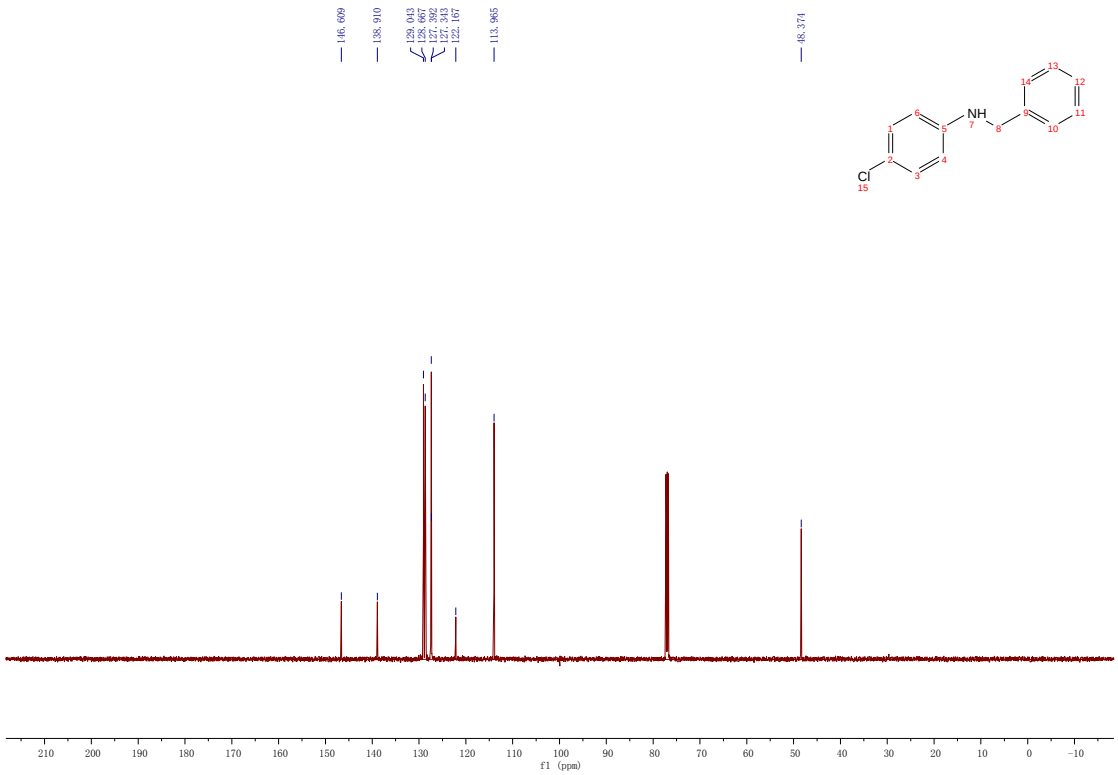

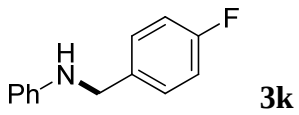

3k

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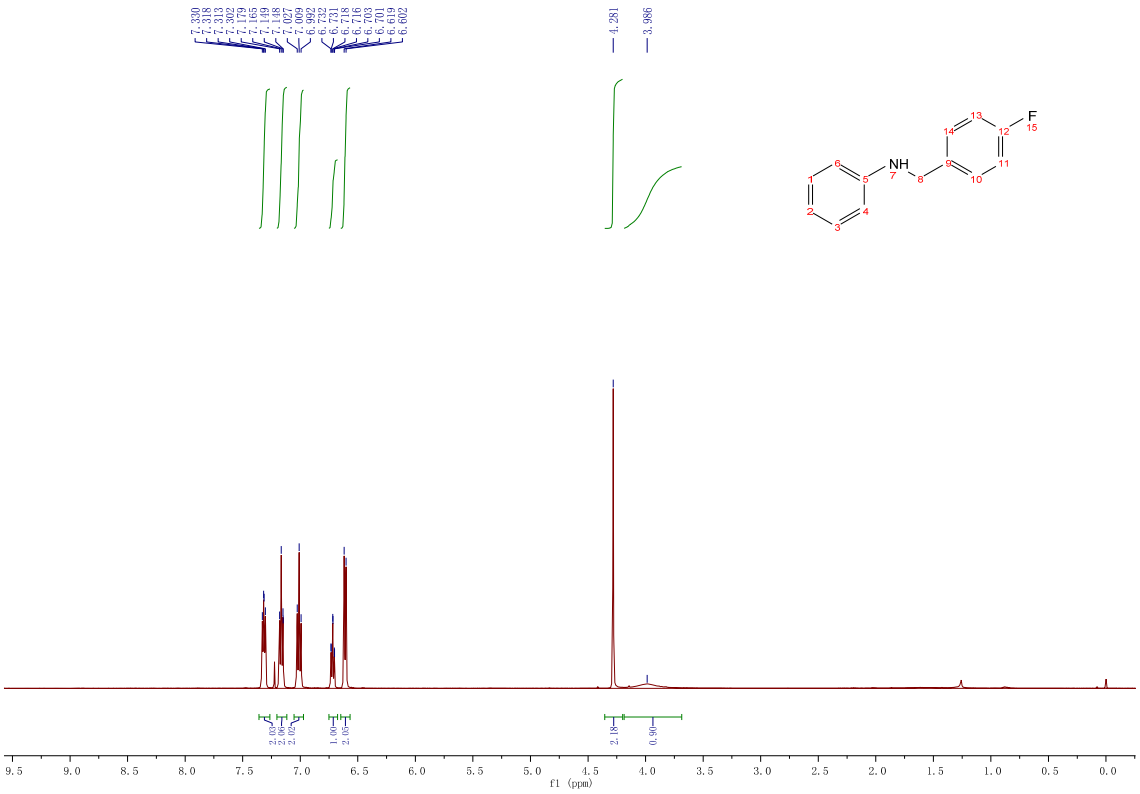

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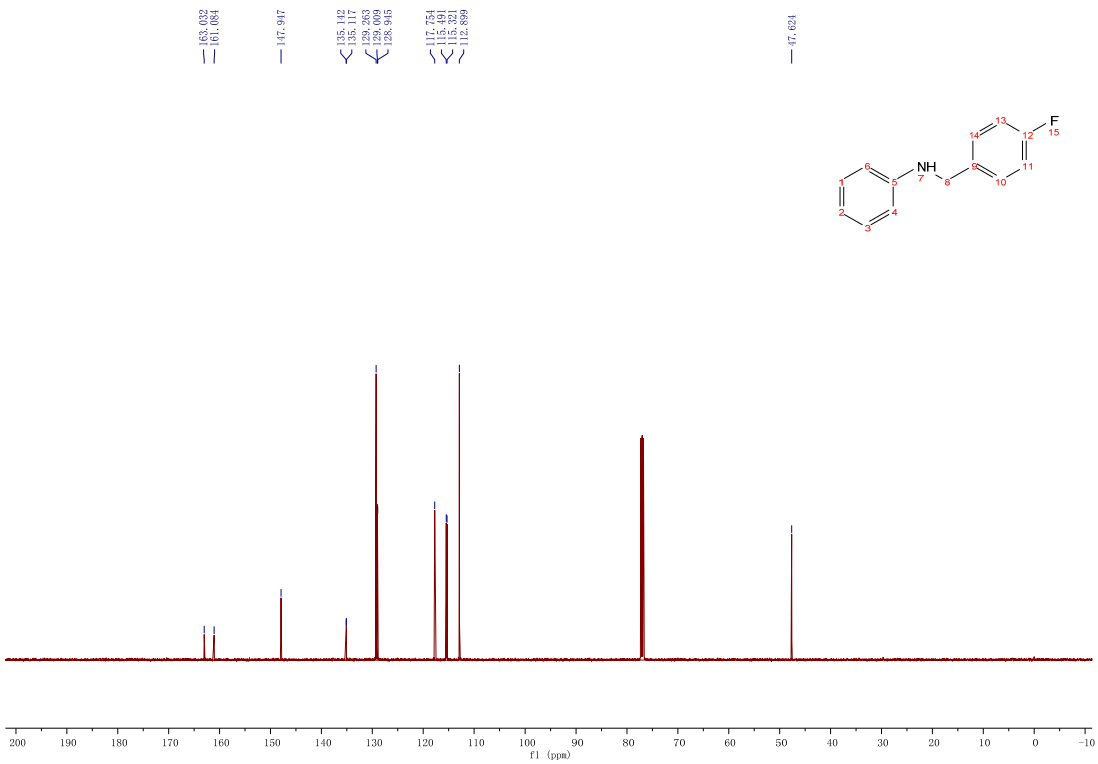
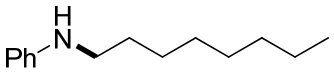
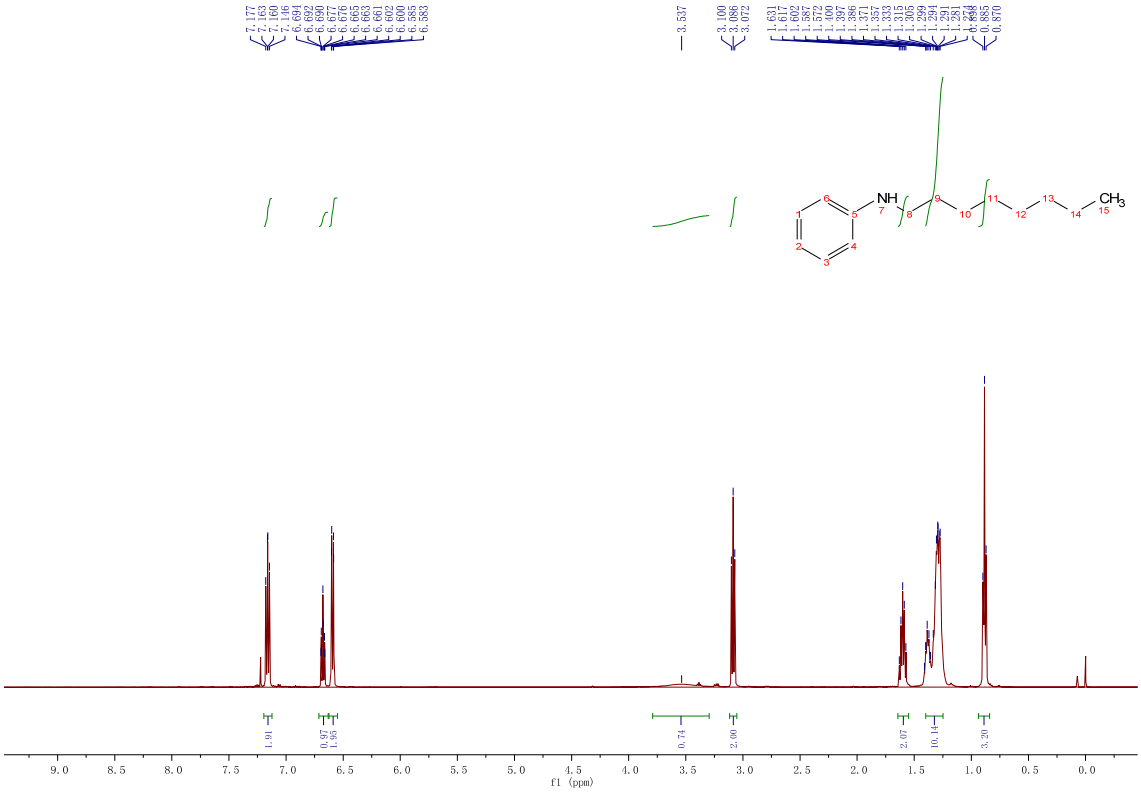




3l

^{1}H NMR



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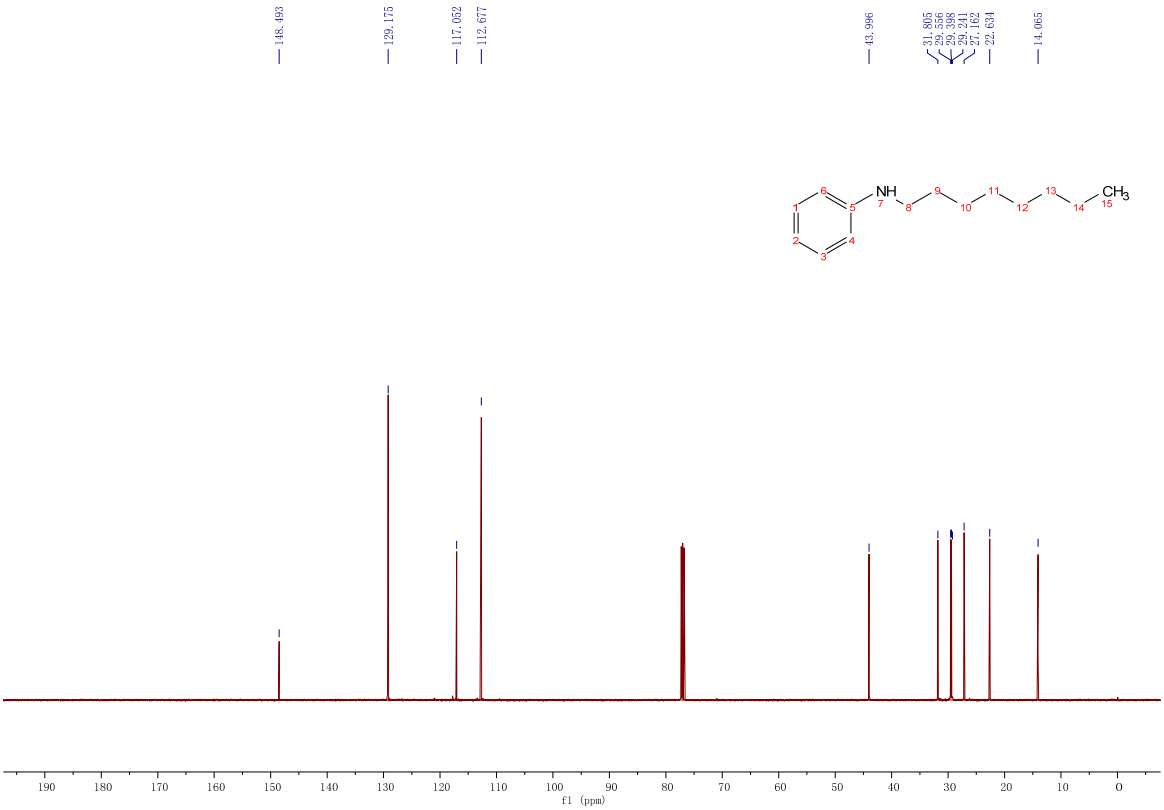
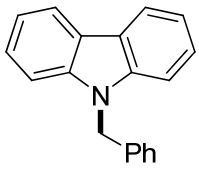
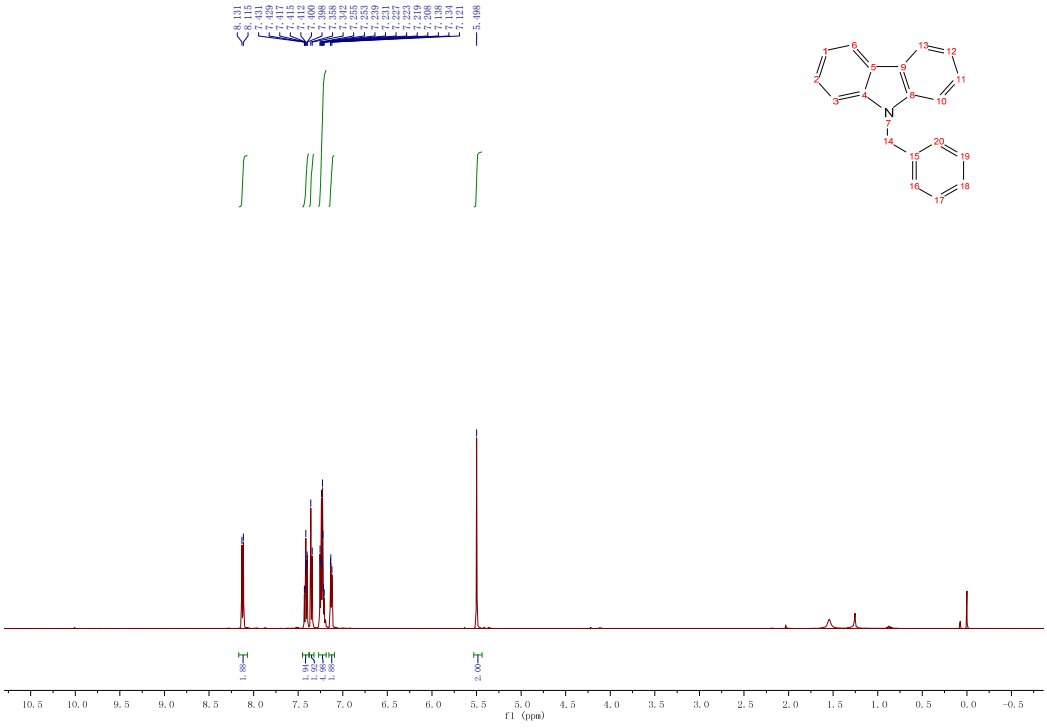




5a

^{1}H NMR



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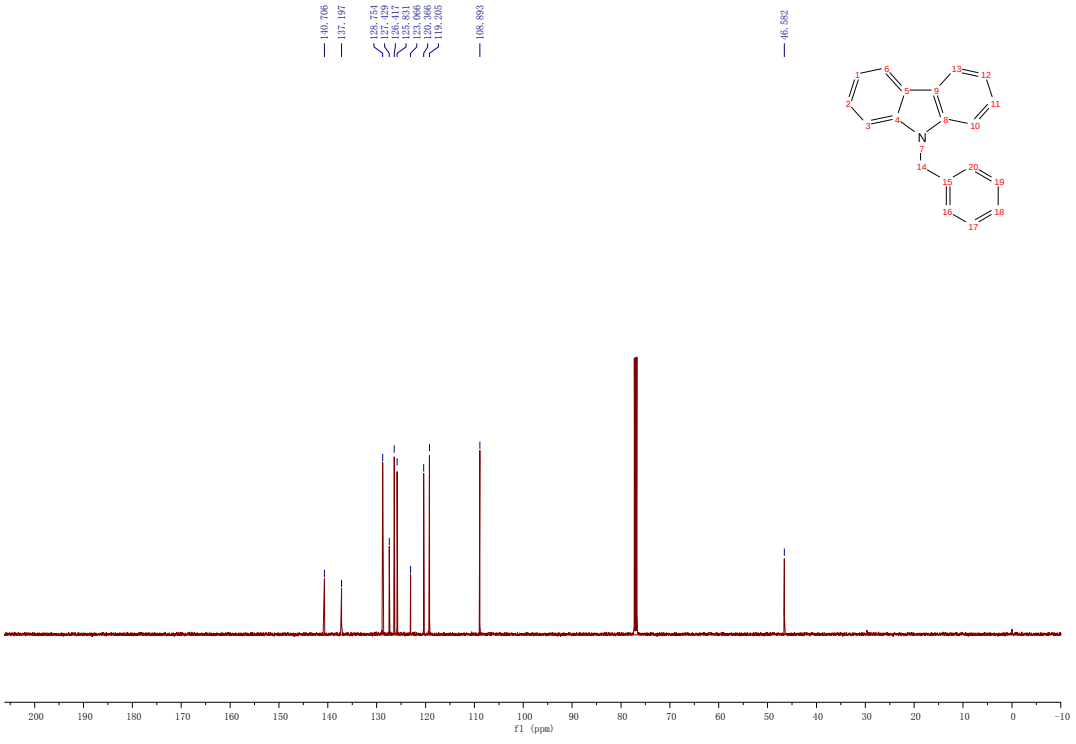
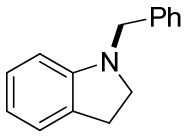
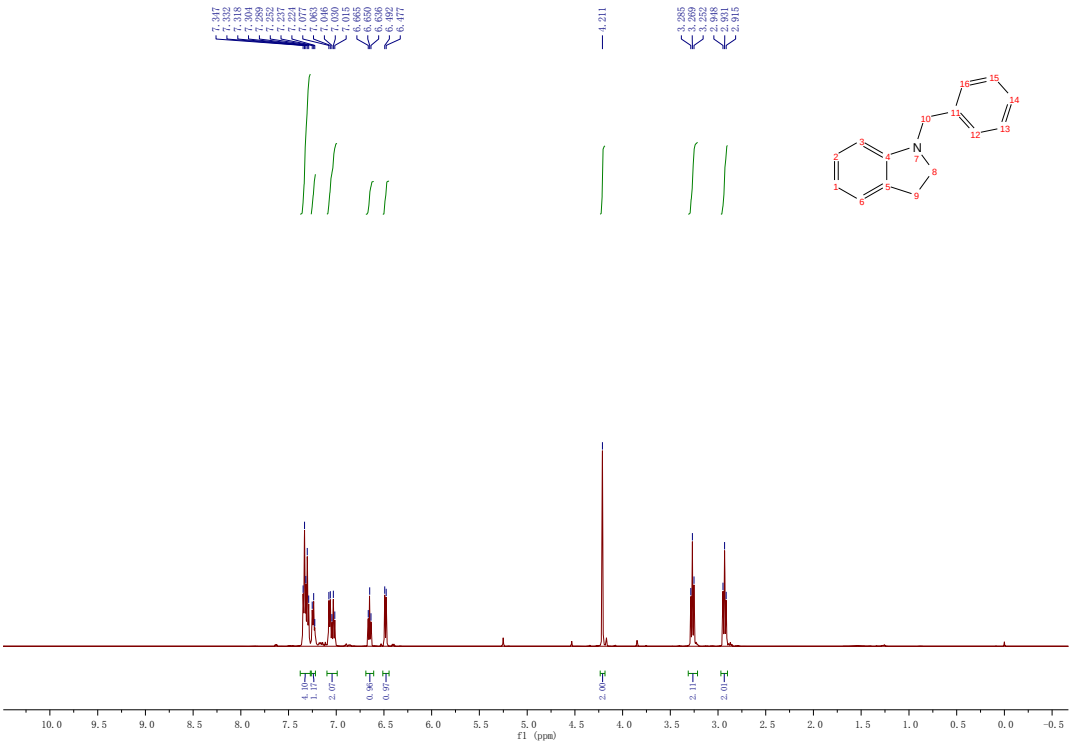




5b

^{1}H NMR



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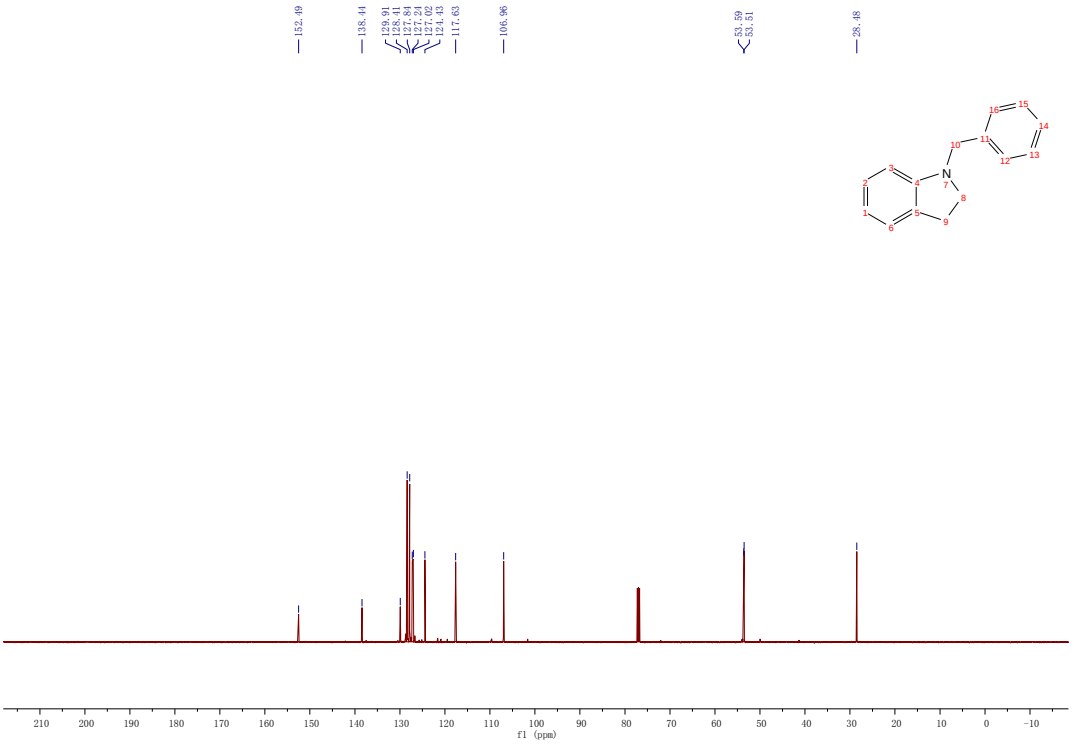
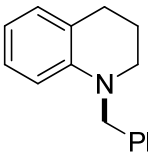
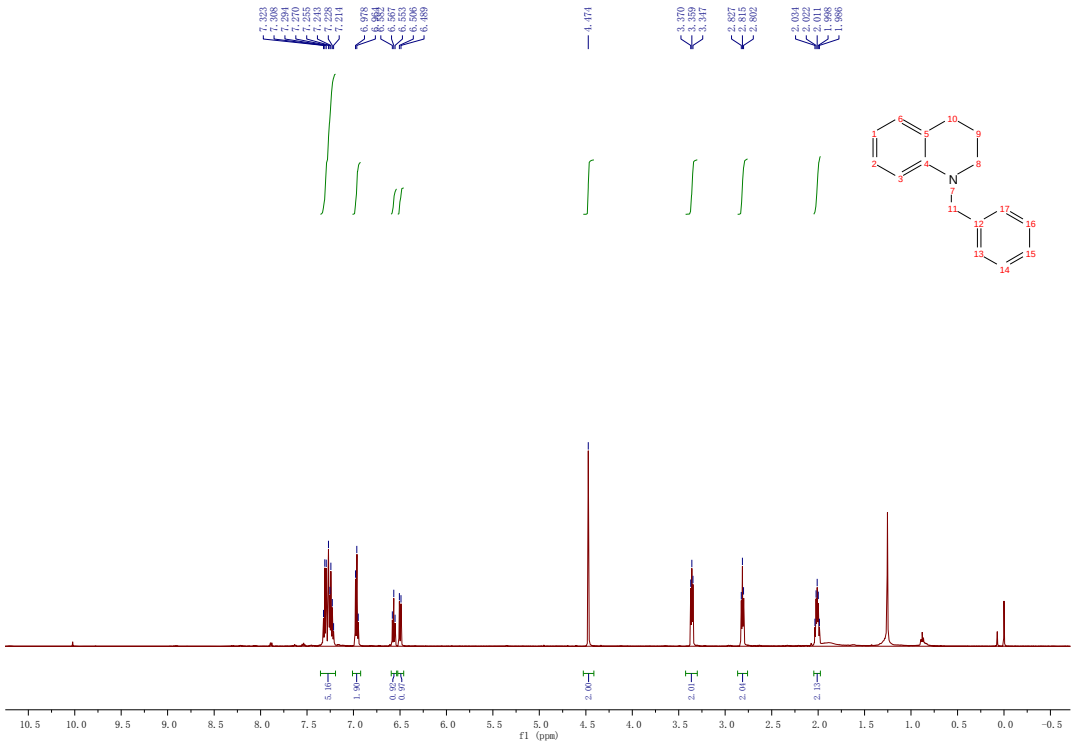




5c

^{1}H NMR



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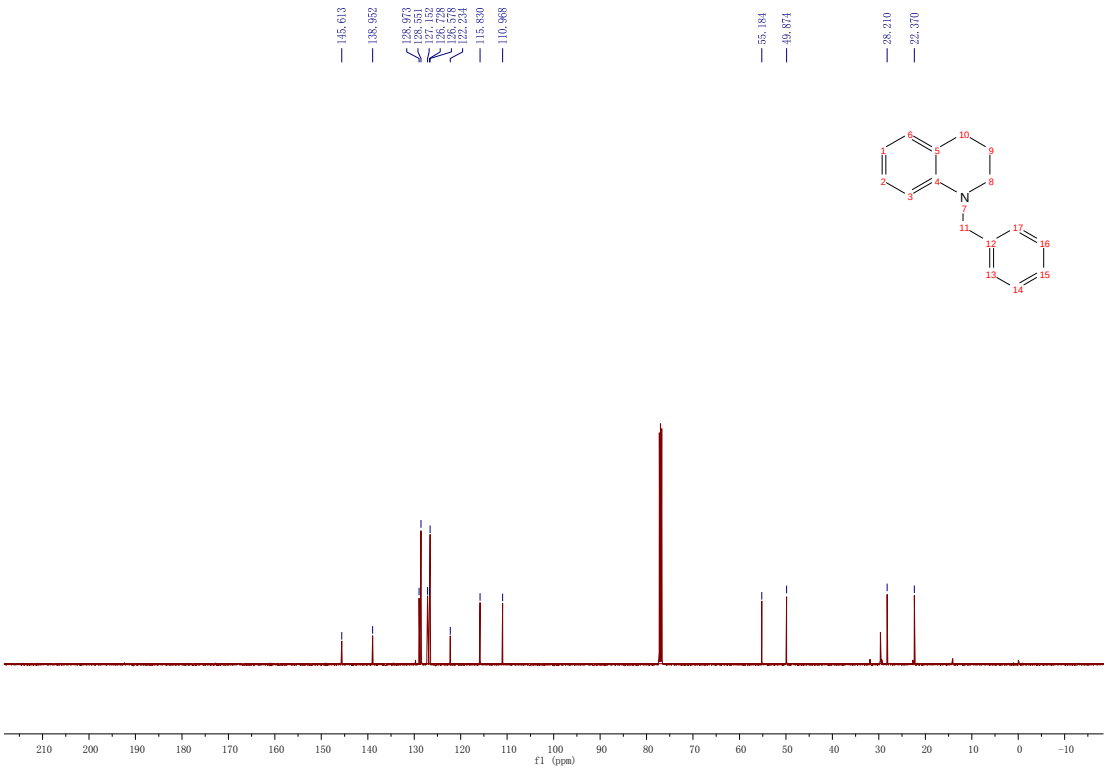
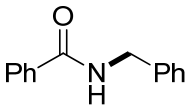
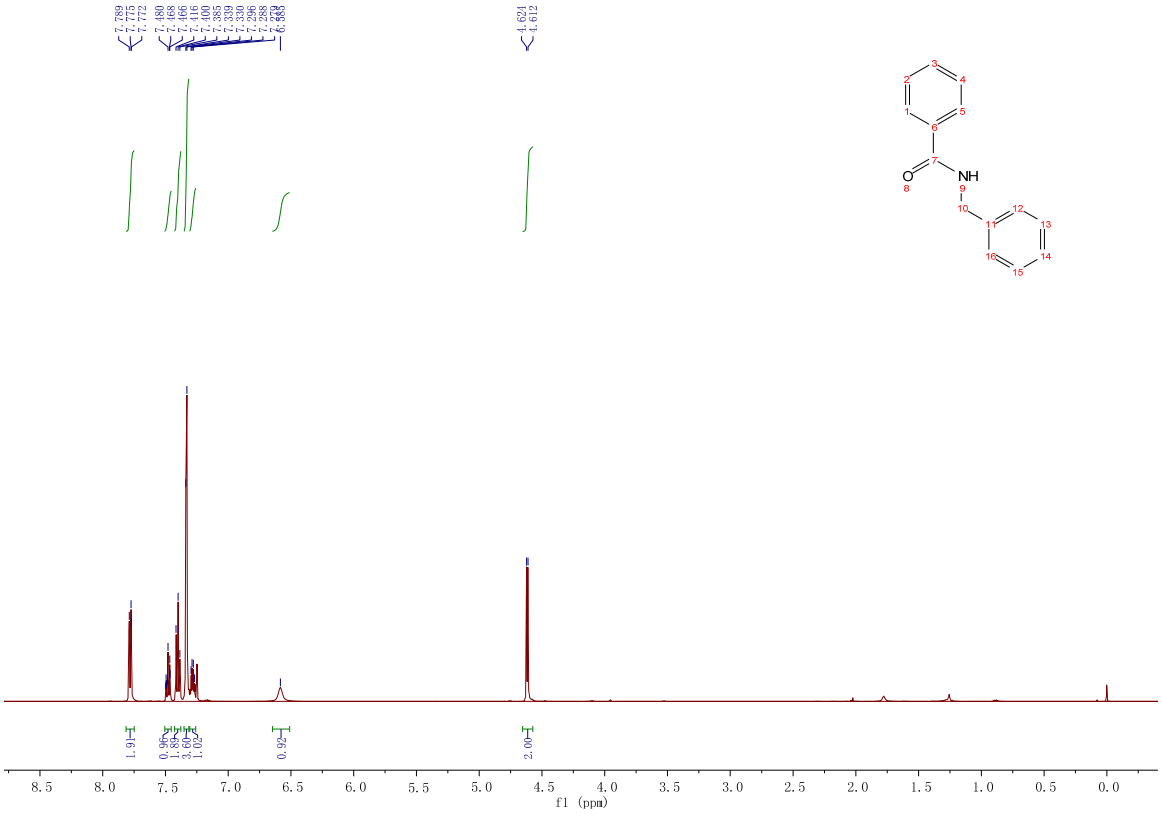




6a

^{1}H NMR



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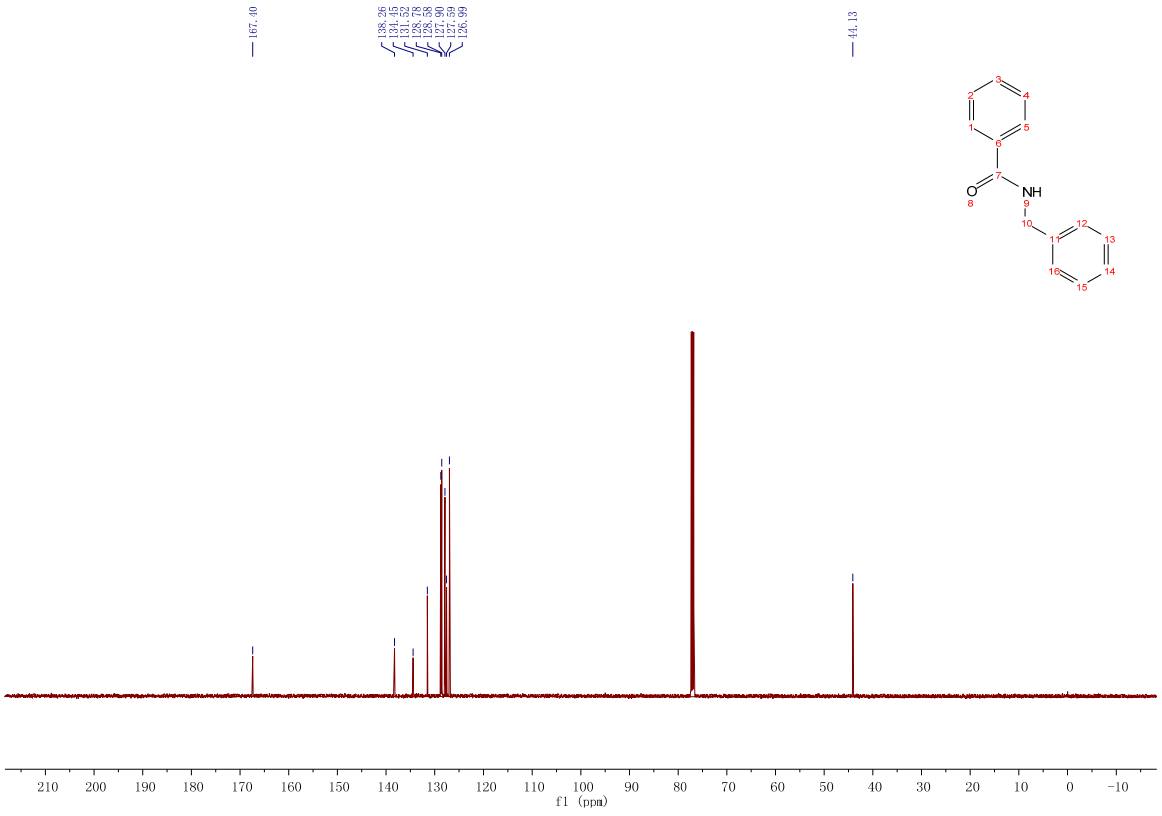
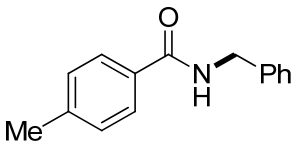
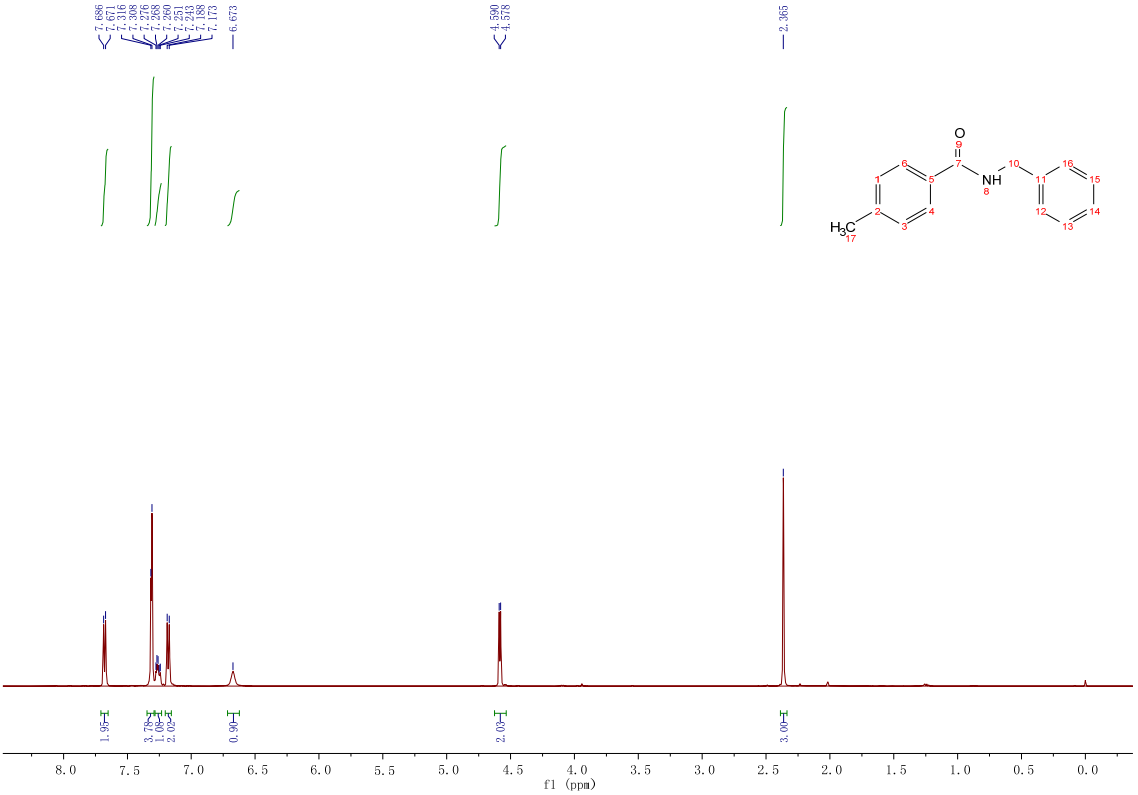




6b

^{1}H NMR



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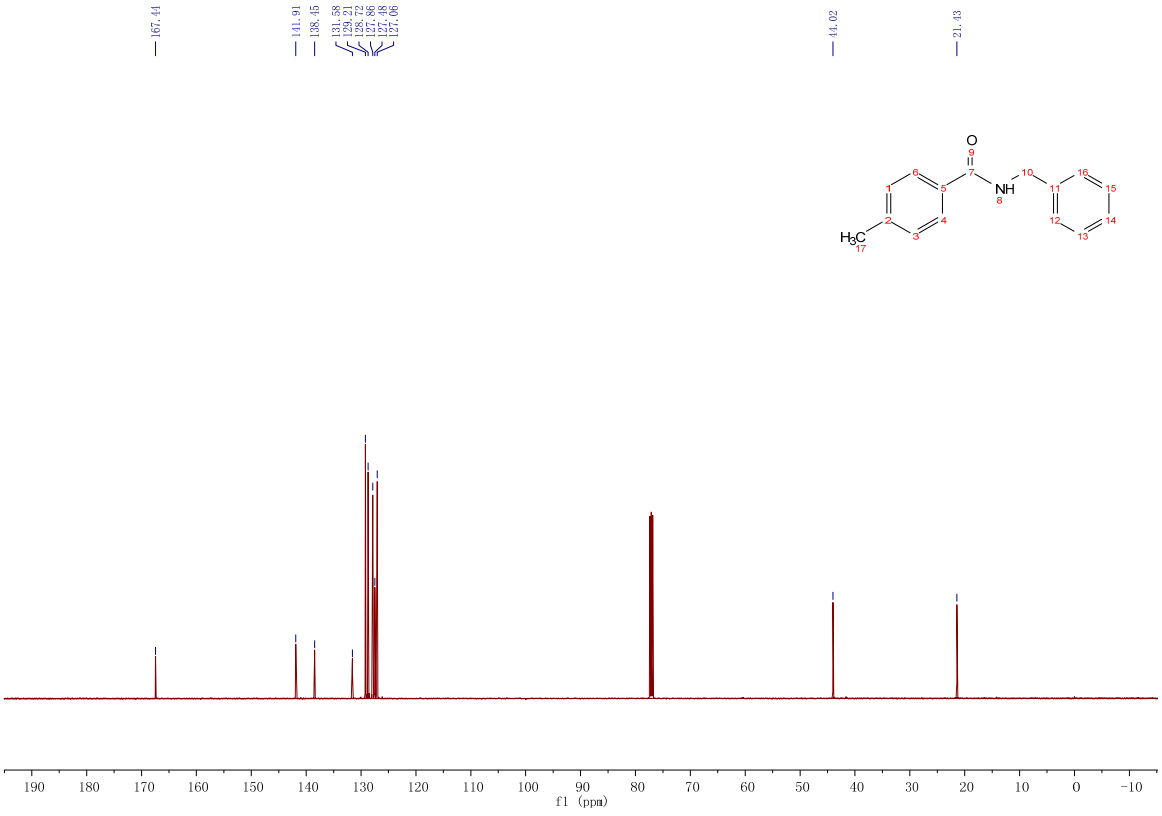
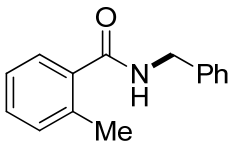
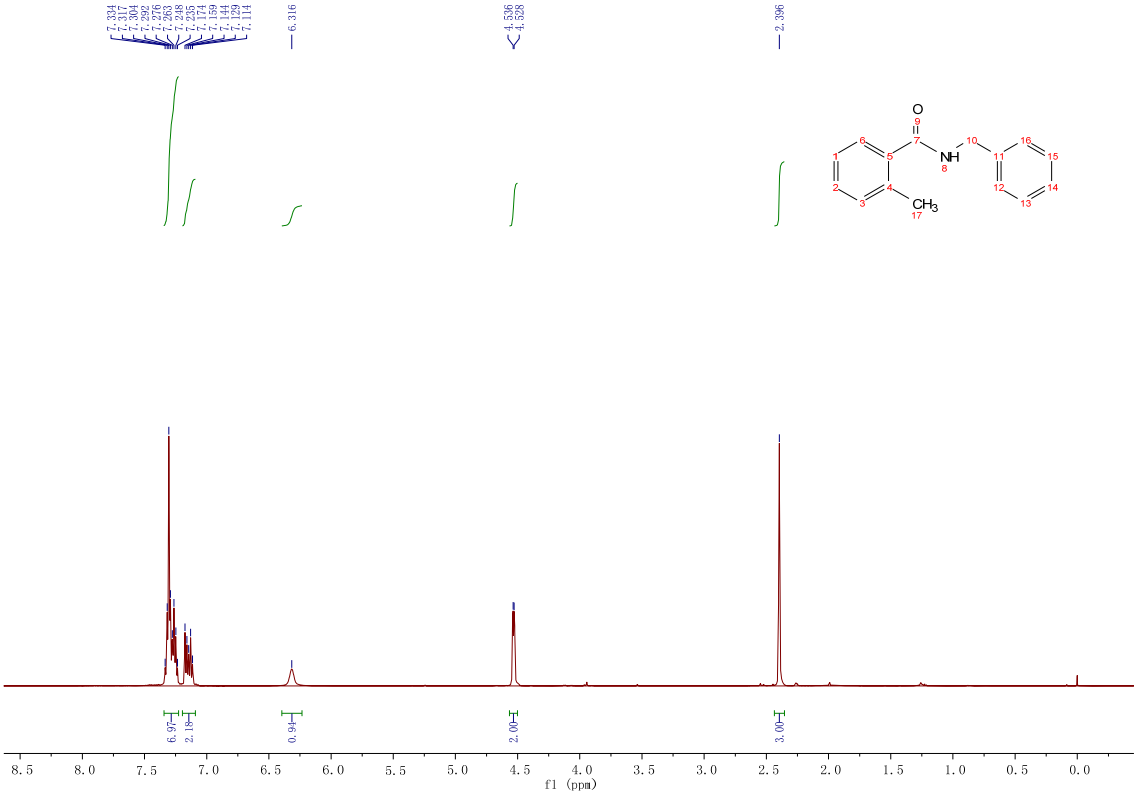




6c

^{1}H NMR



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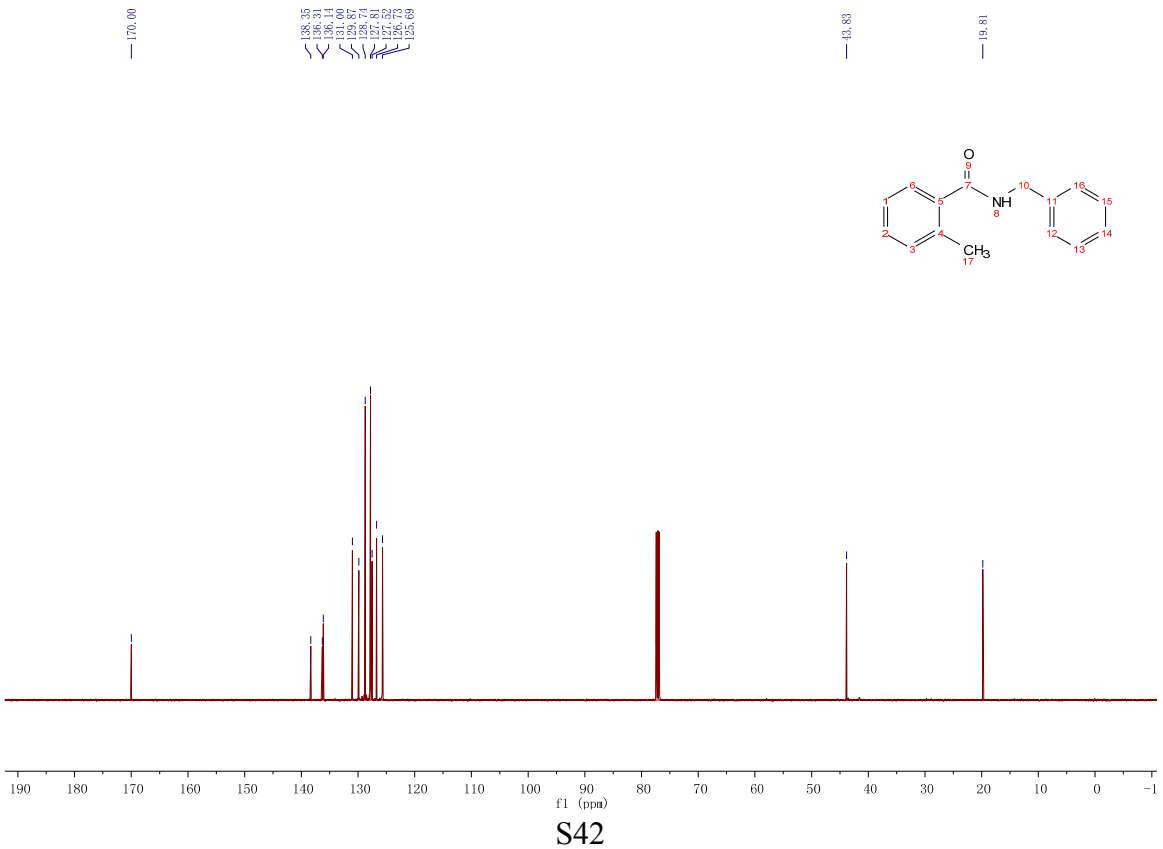

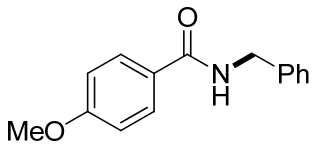

6d

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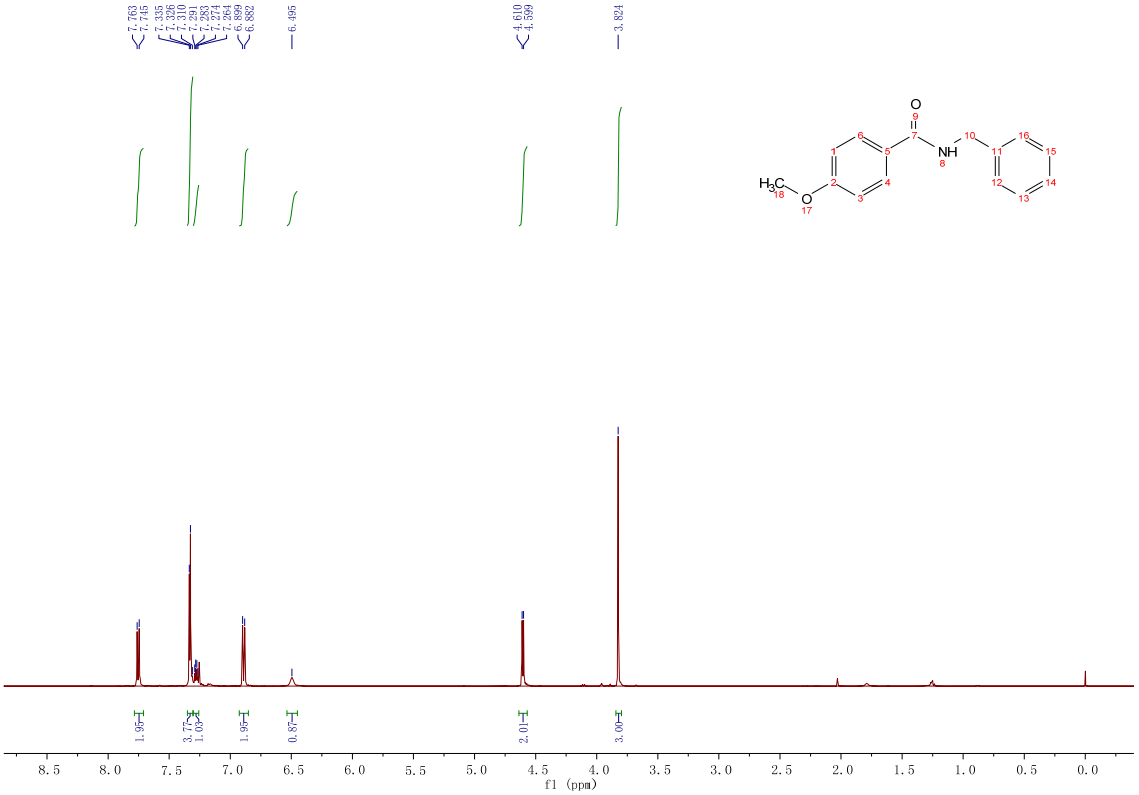

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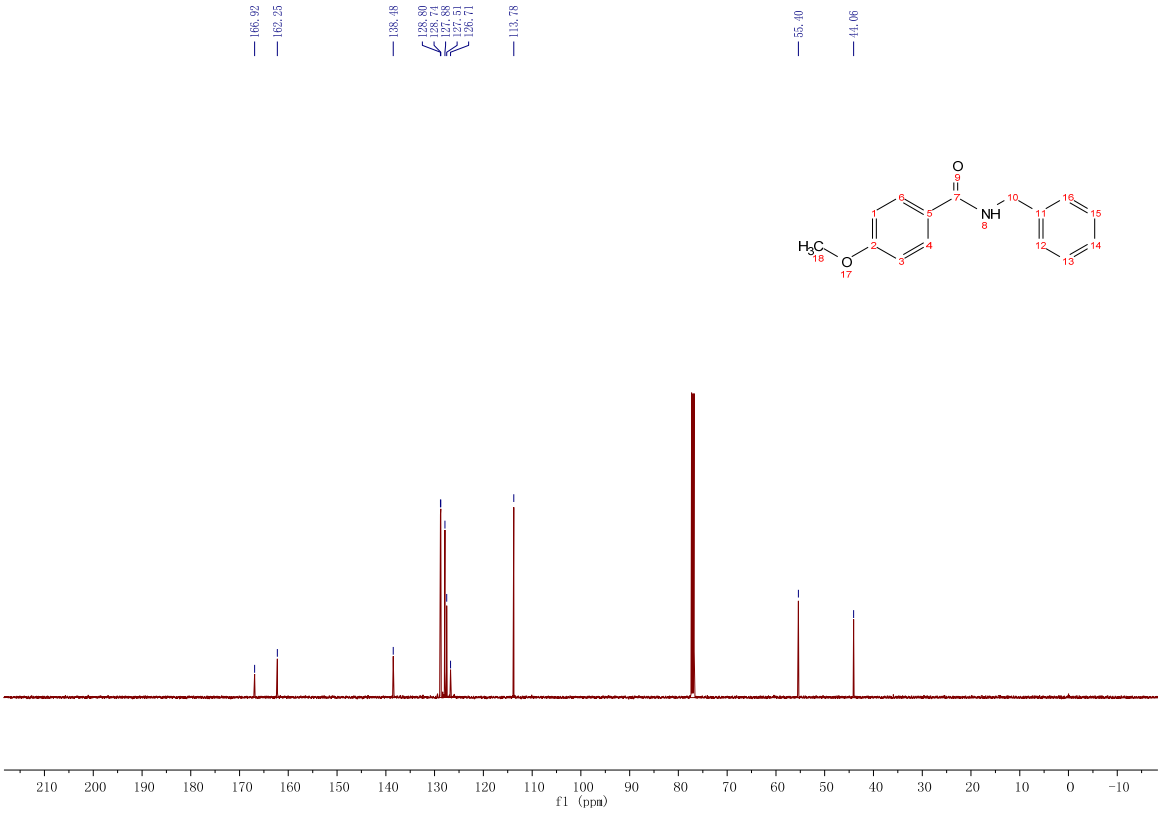

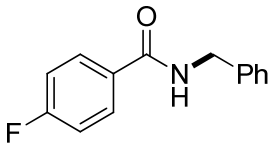

6e

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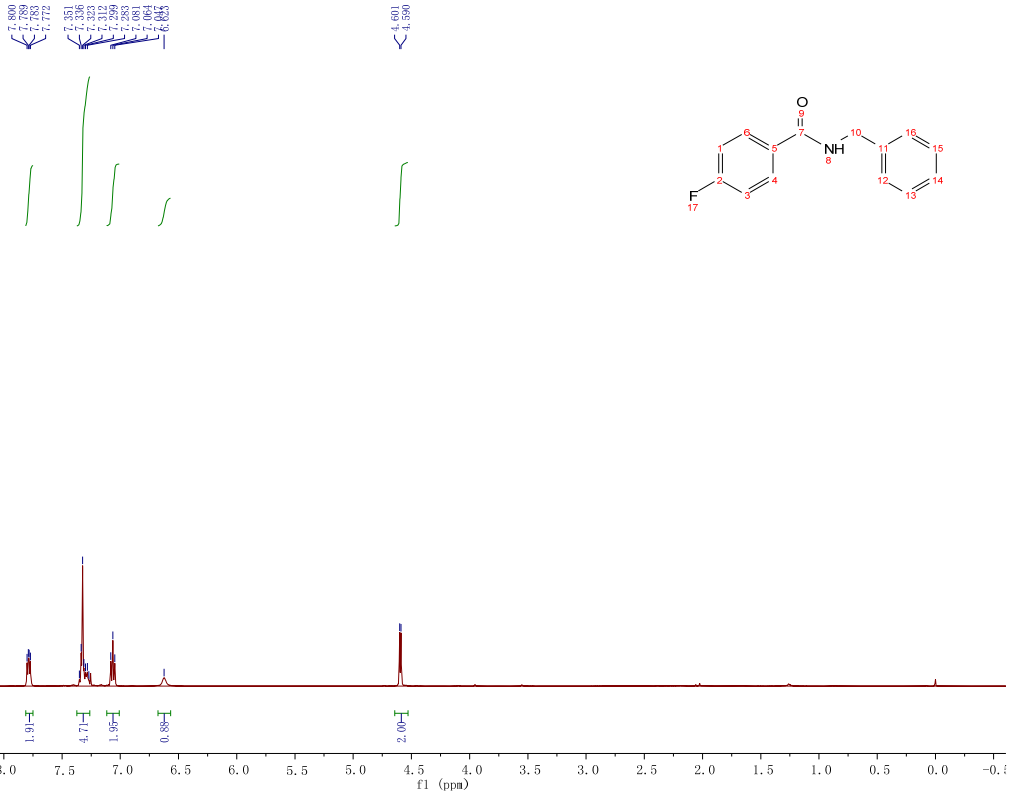

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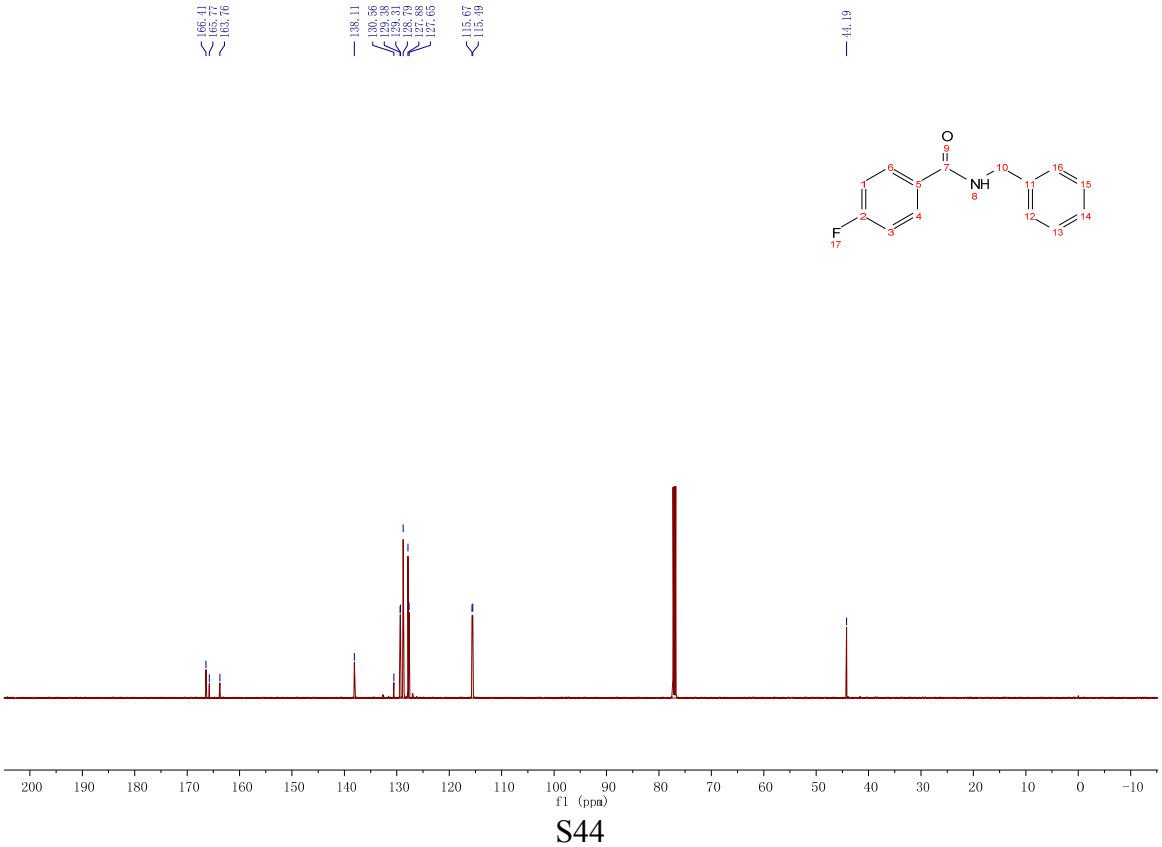
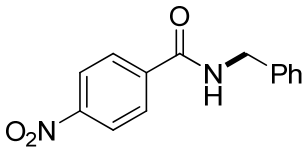
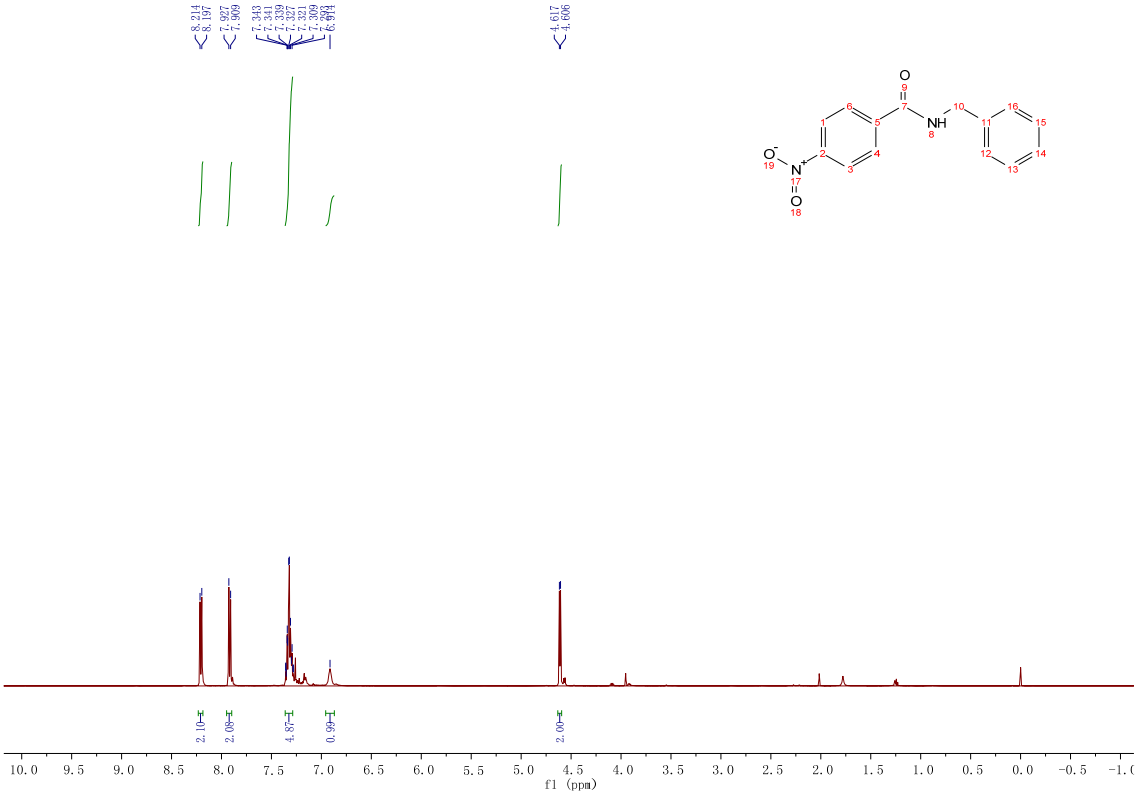


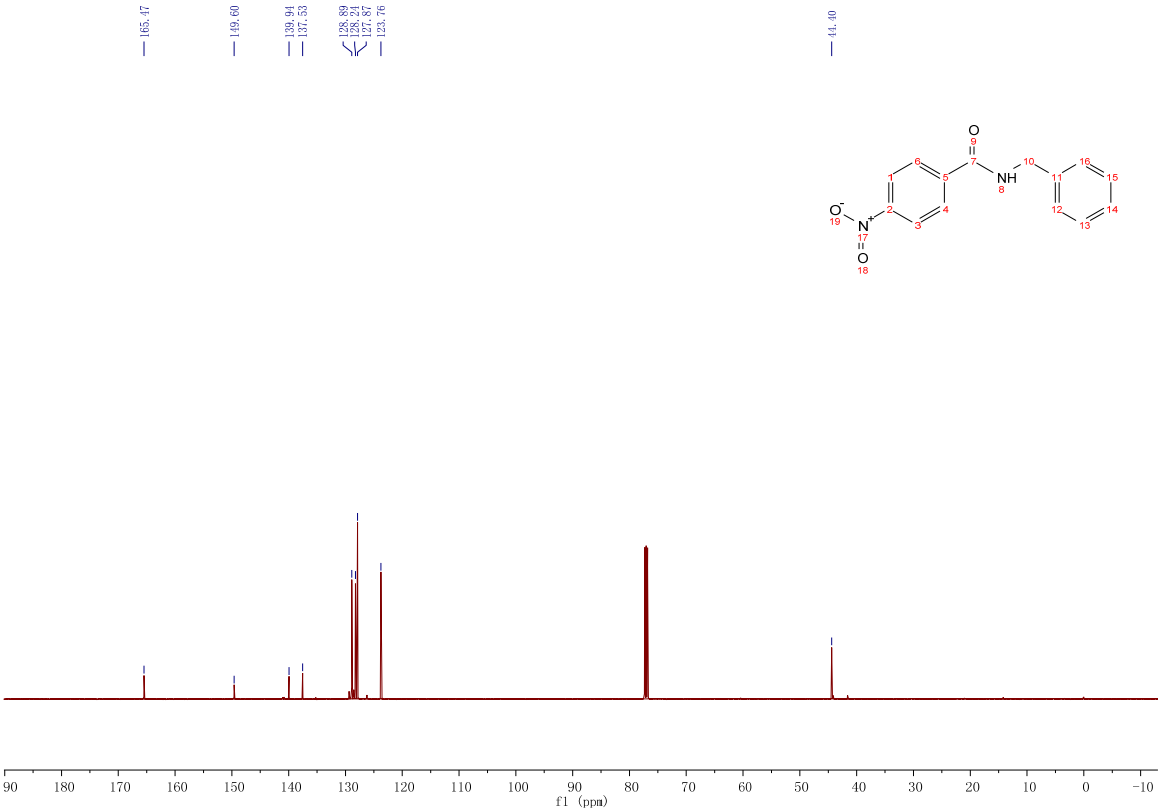


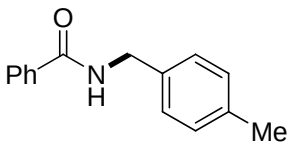
6f

^{1}H NMR



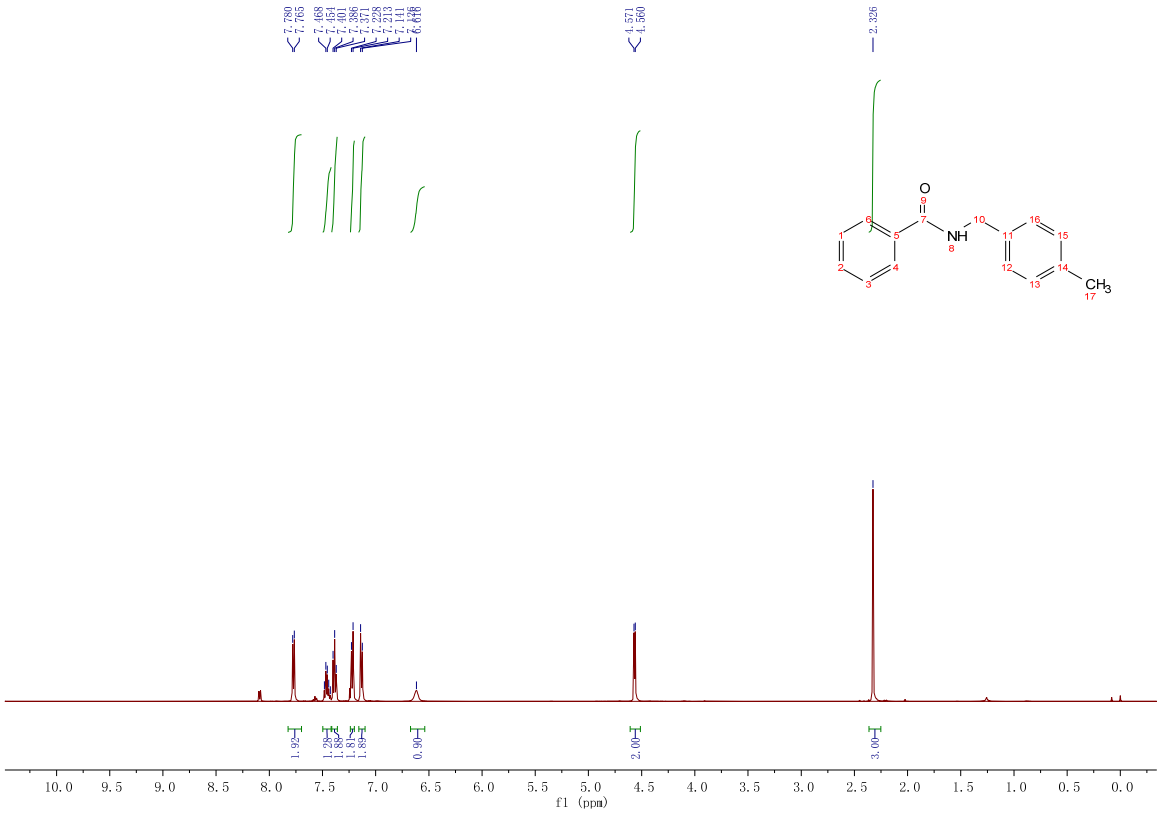
^{13}C NMR



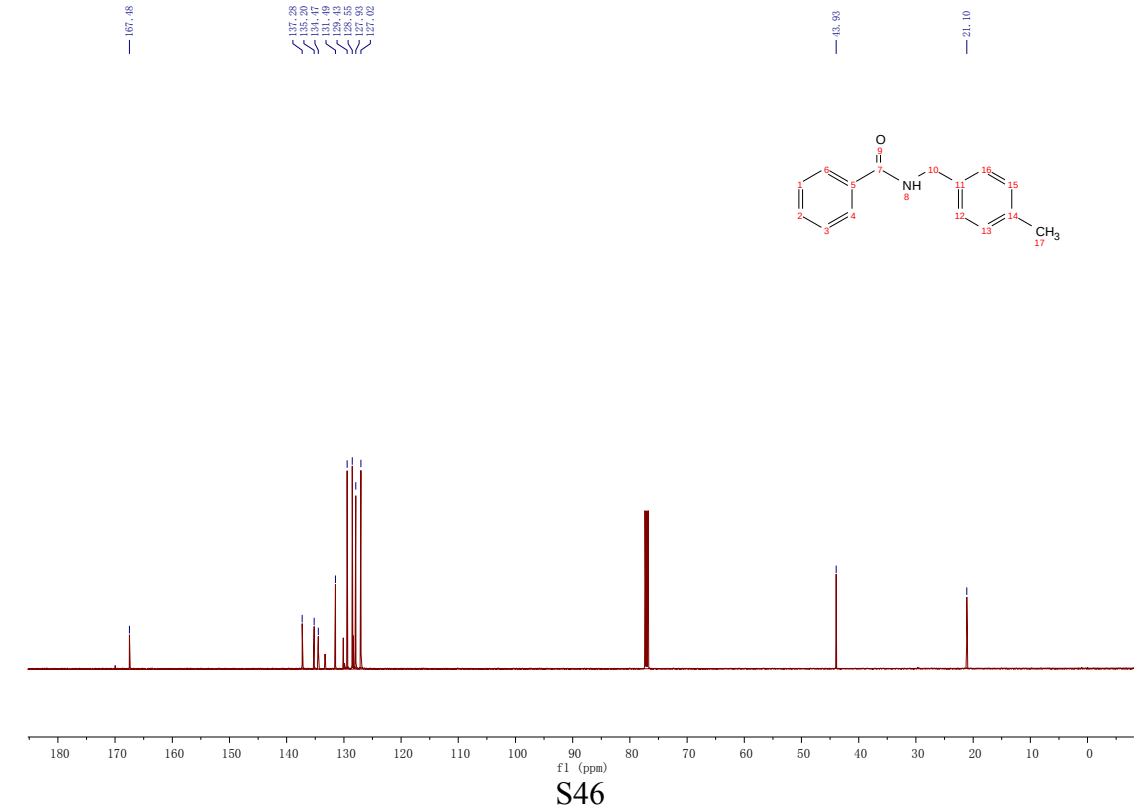


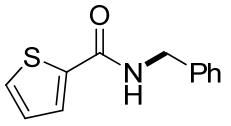
6g

^{1}H NMR



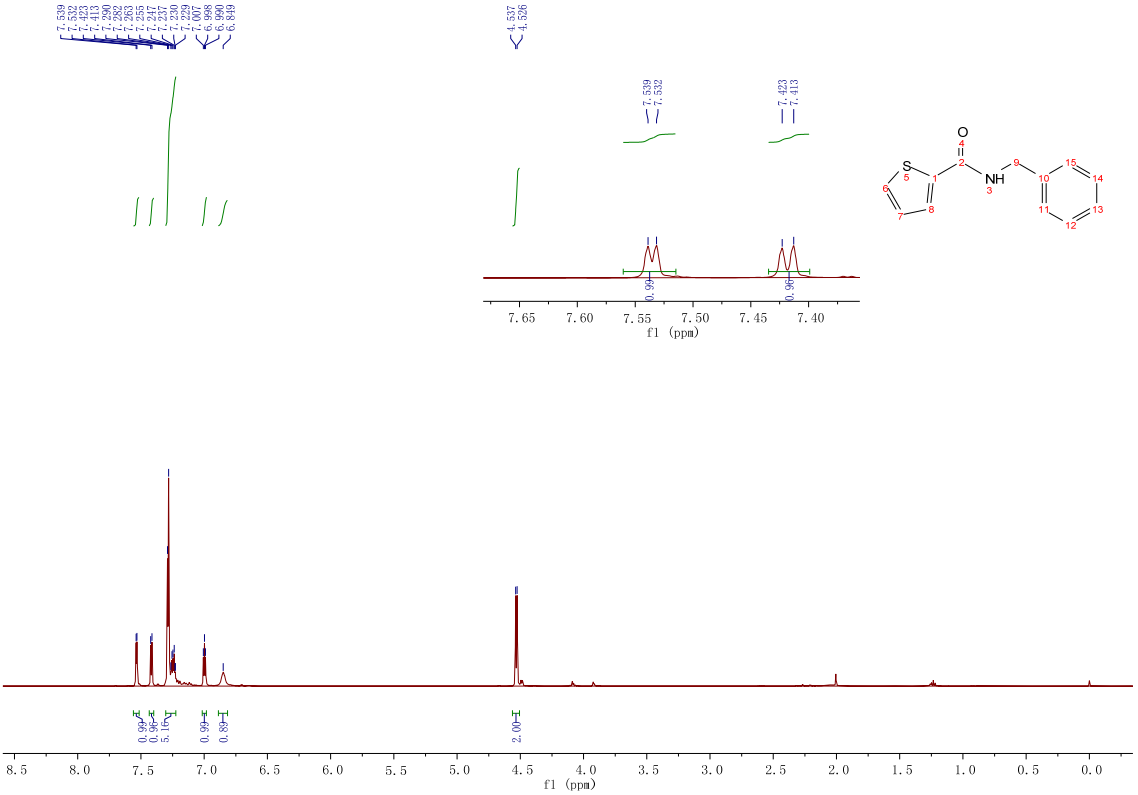
^{13}C NMR





6h

^{1}H NMR



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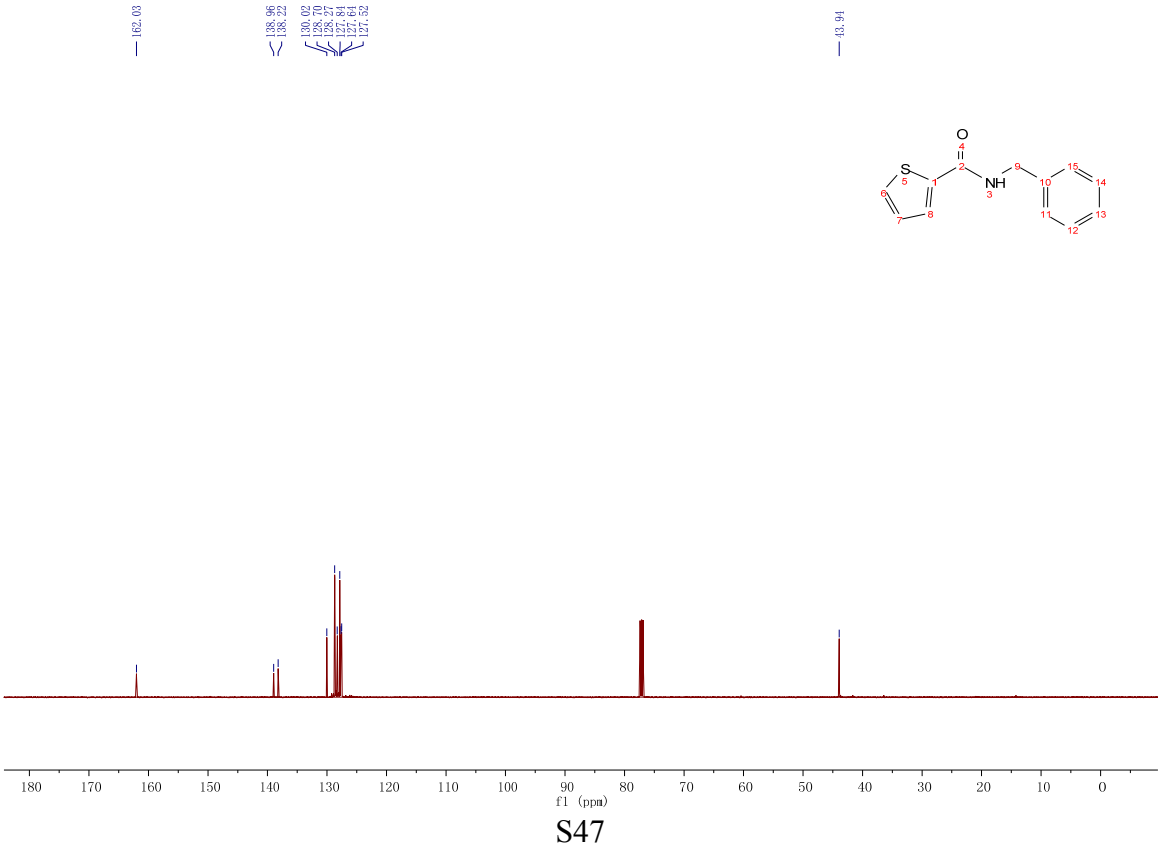
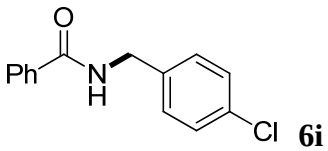
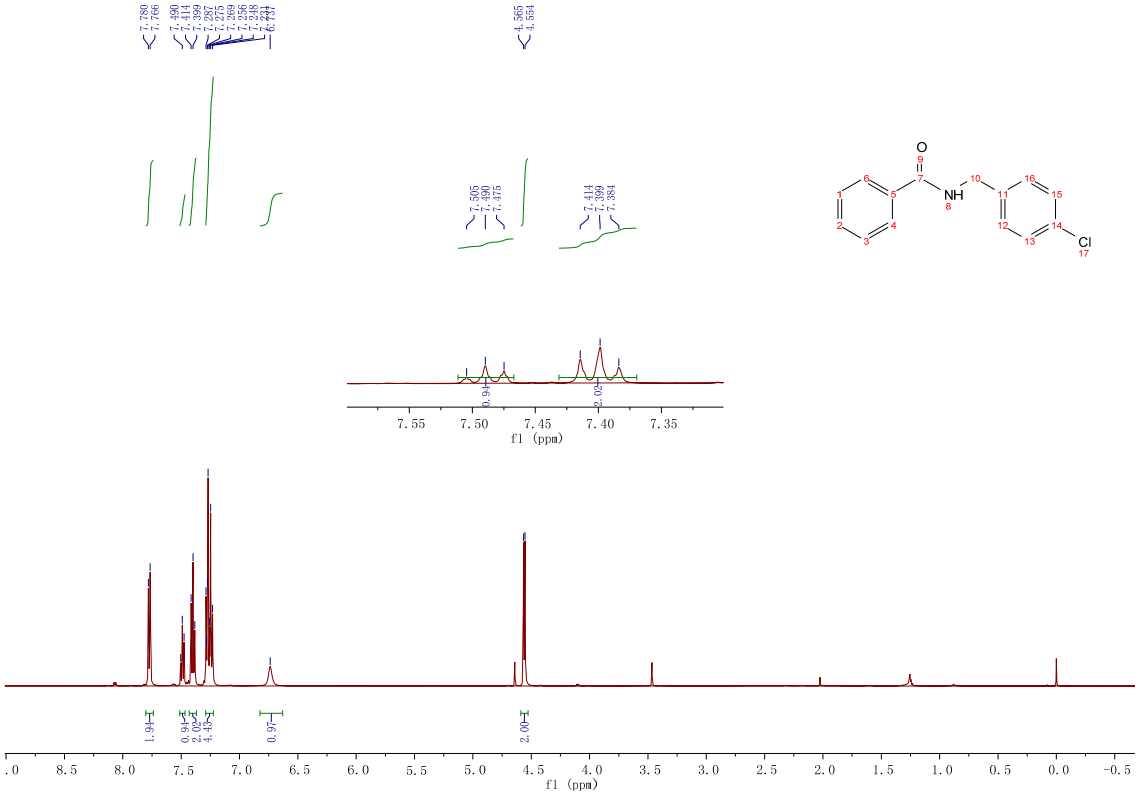


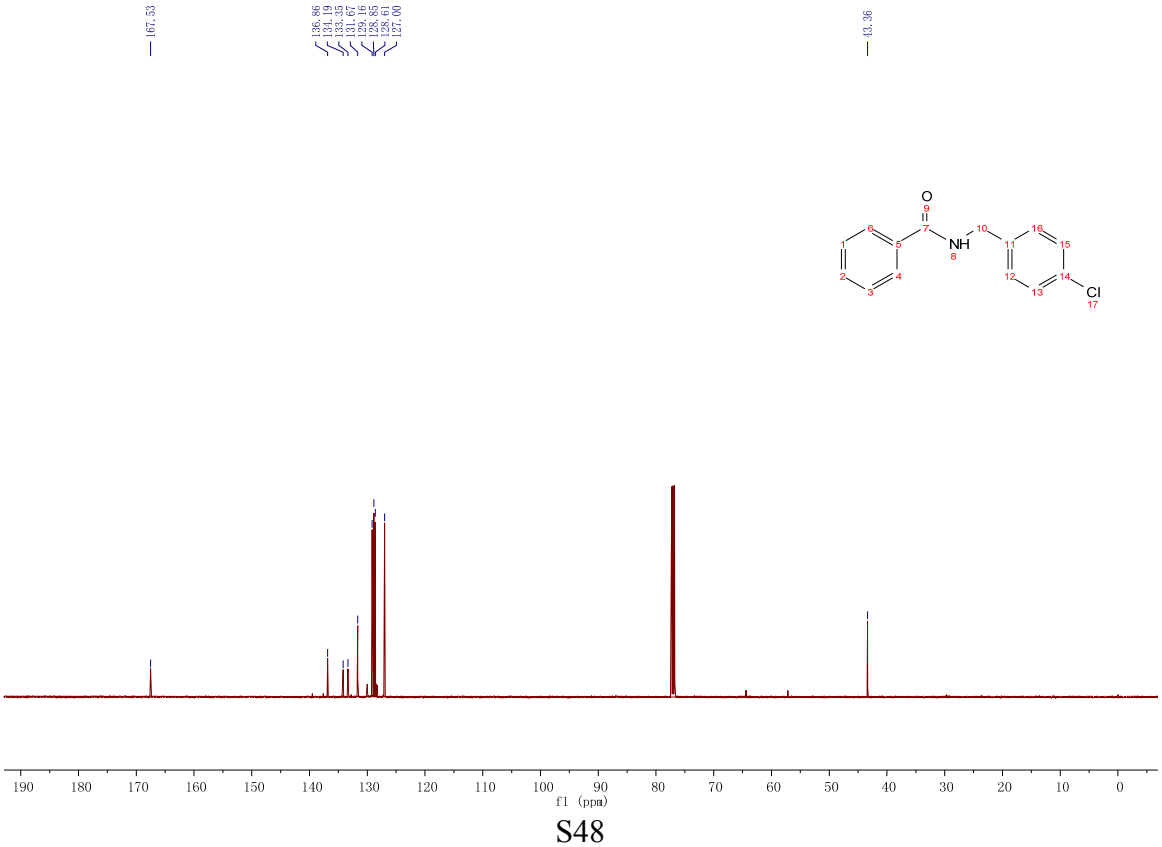


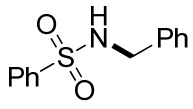
6i

^{1}H NMR



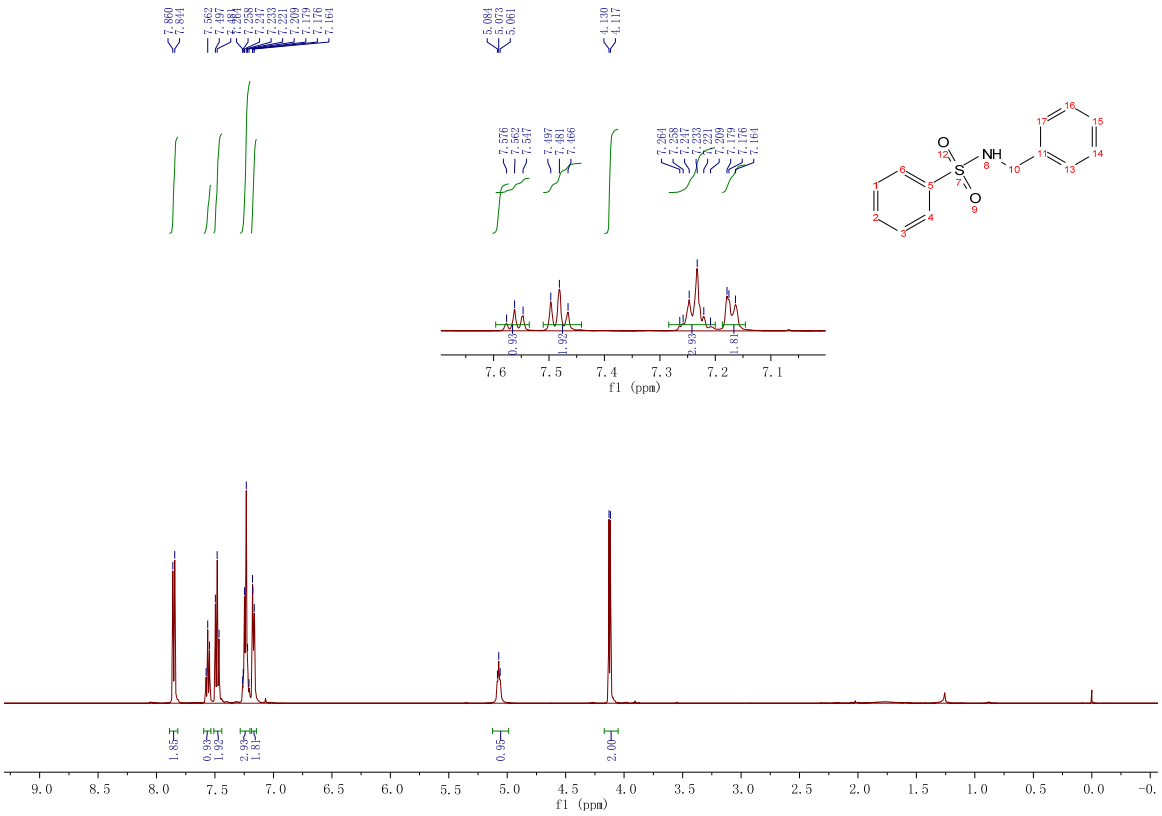
^{13}C NMR



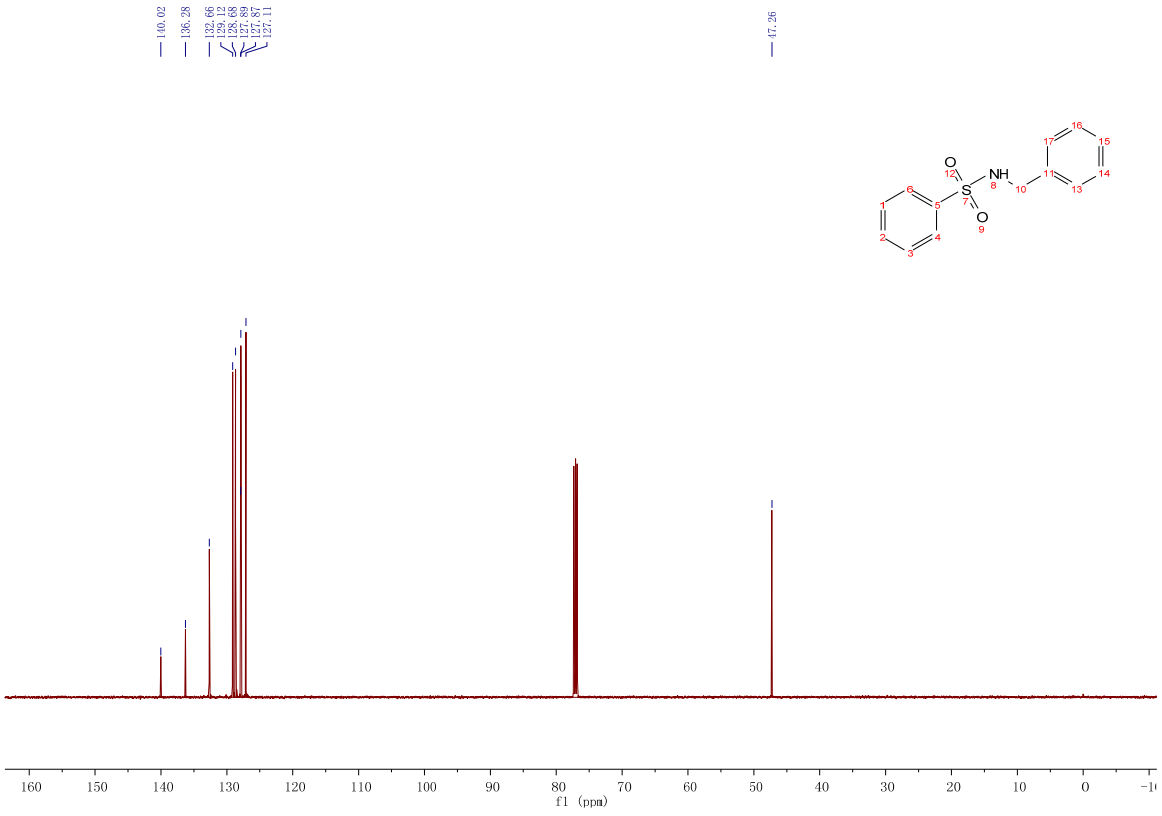


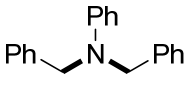
6l

^{1}H NMR



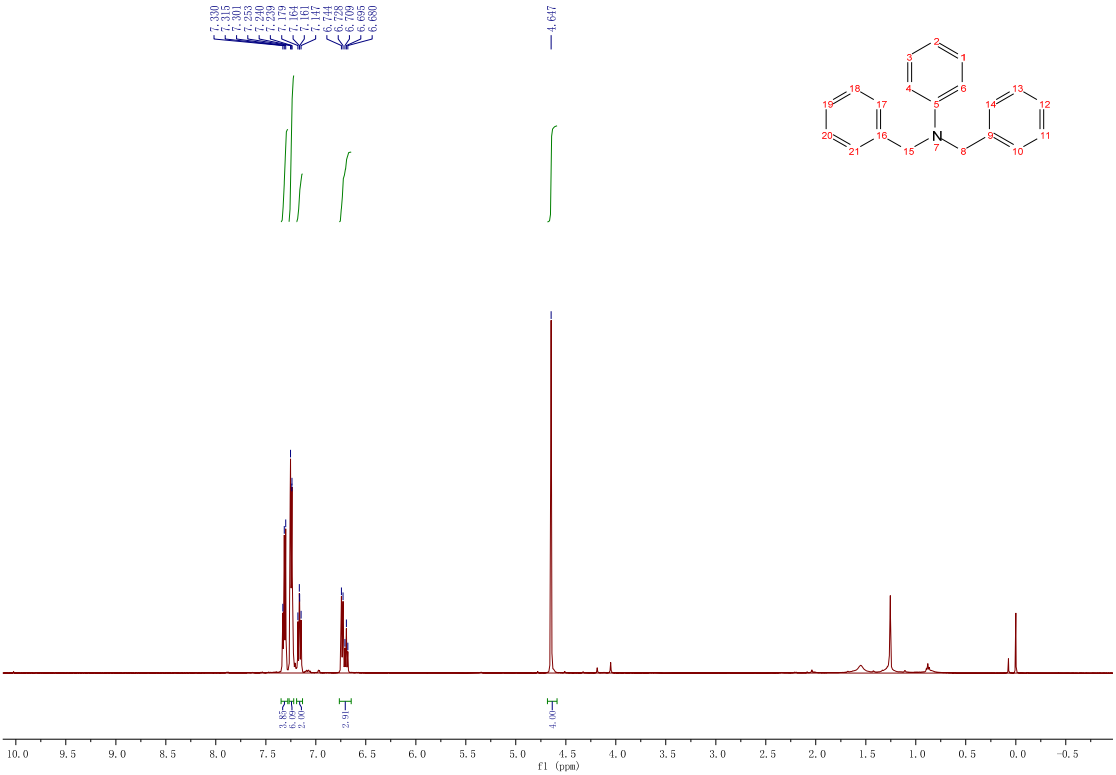
^{13}C NMR



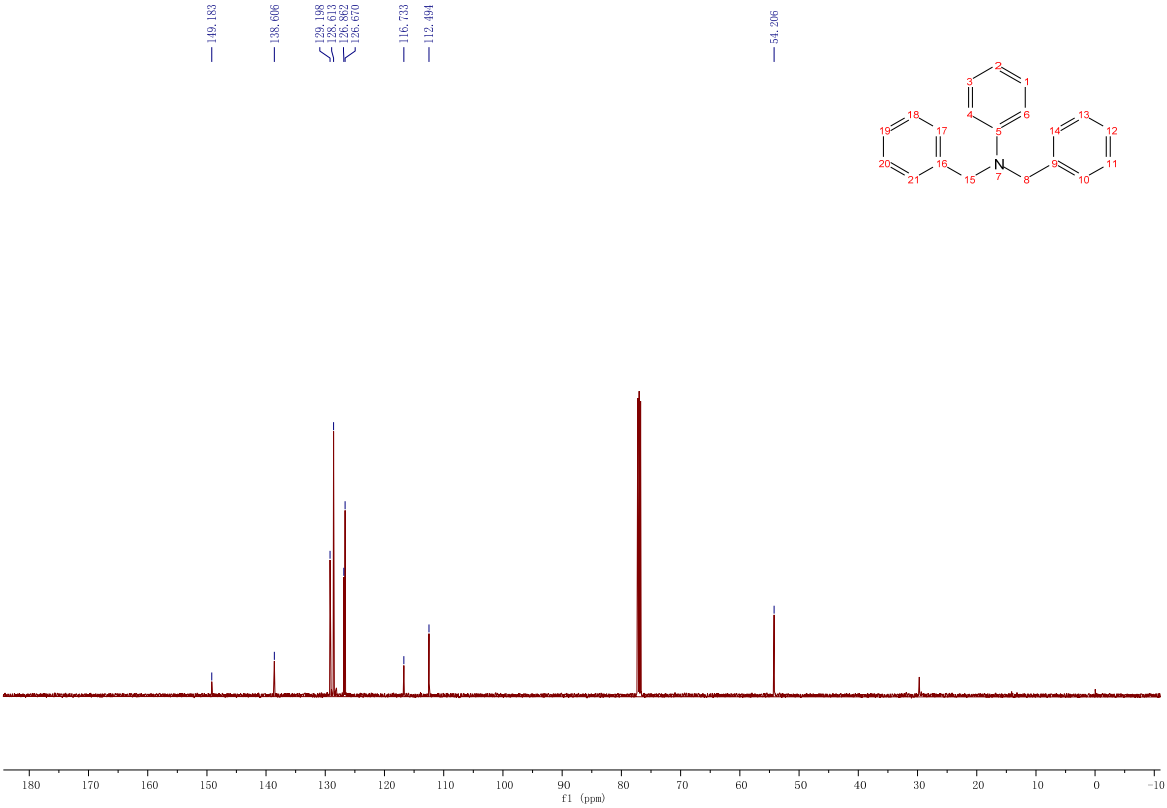


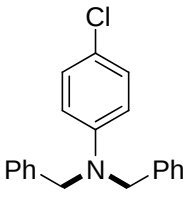
4a

^{1}H NMR



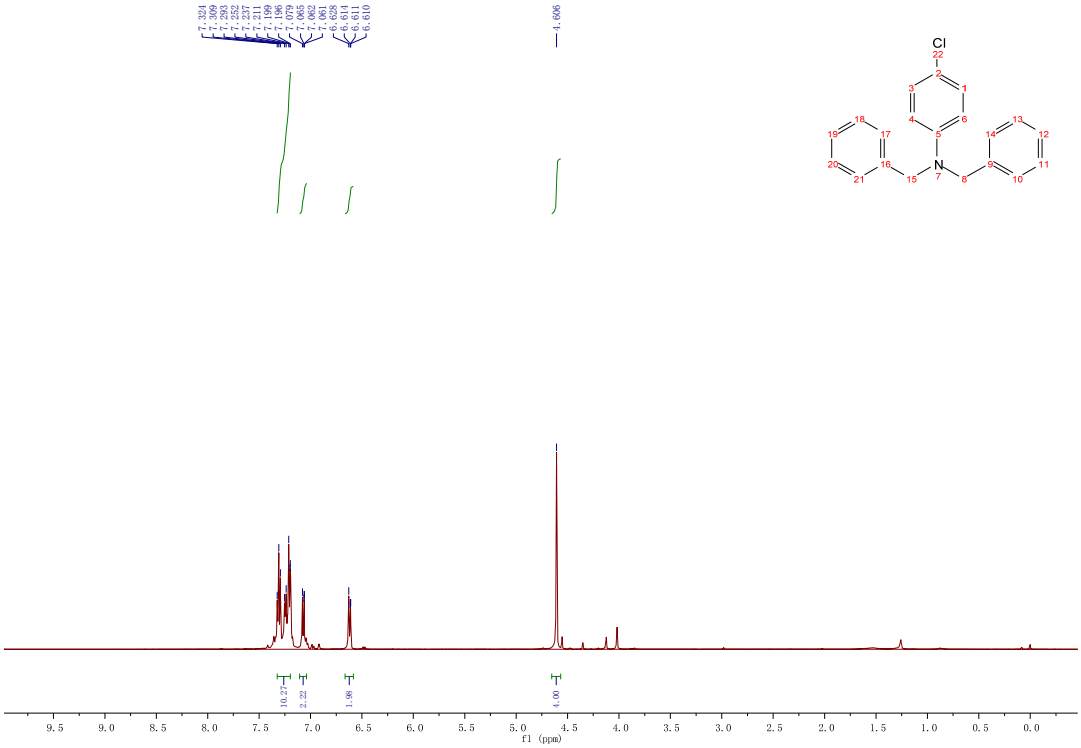
^{13}C NMR



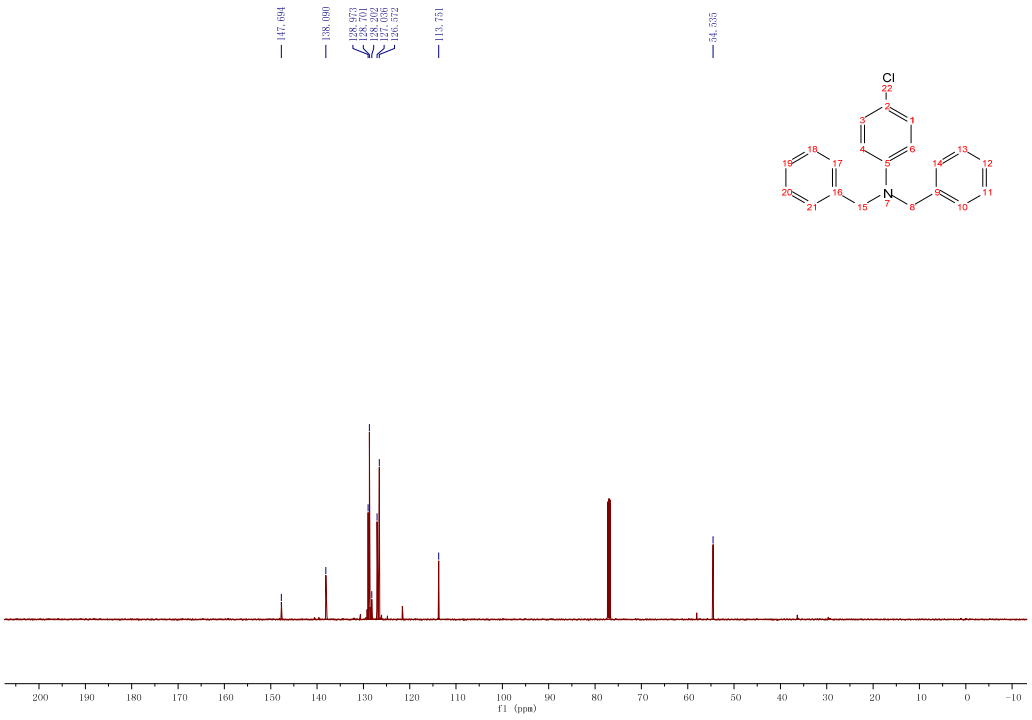


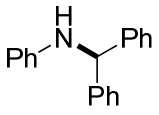
4b

^{1}H NMR



^{13}C NMR





8a

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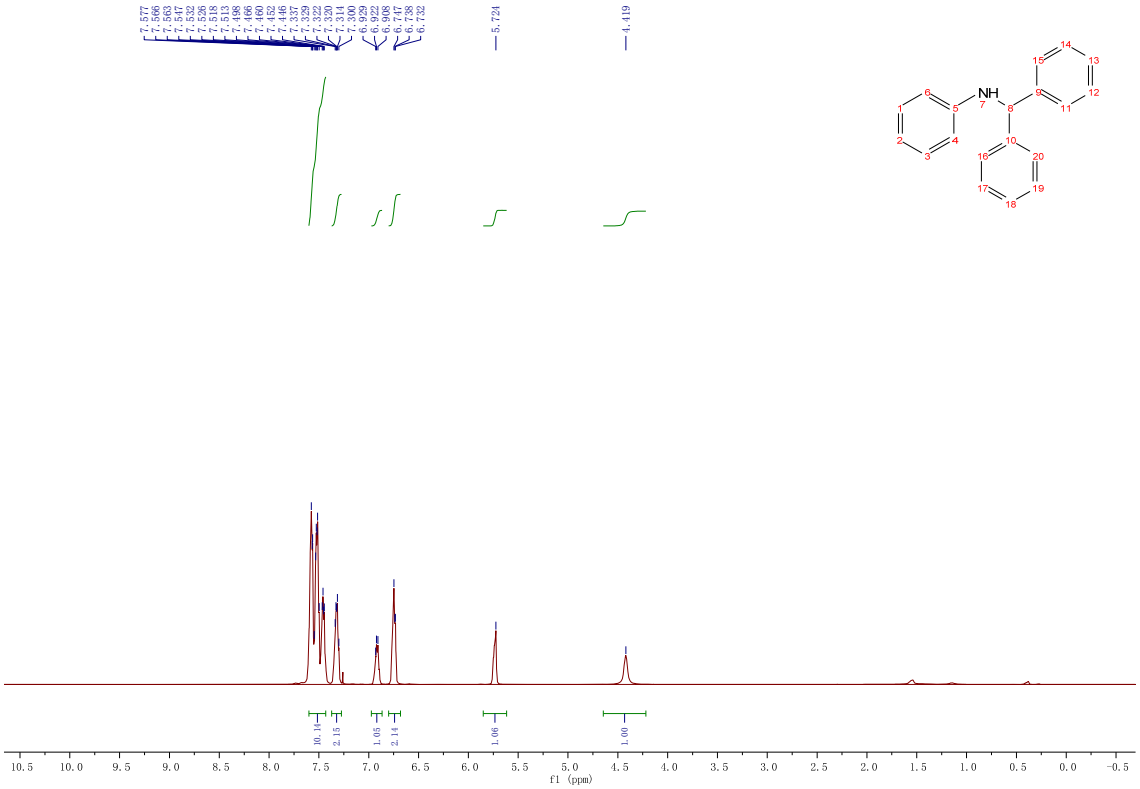
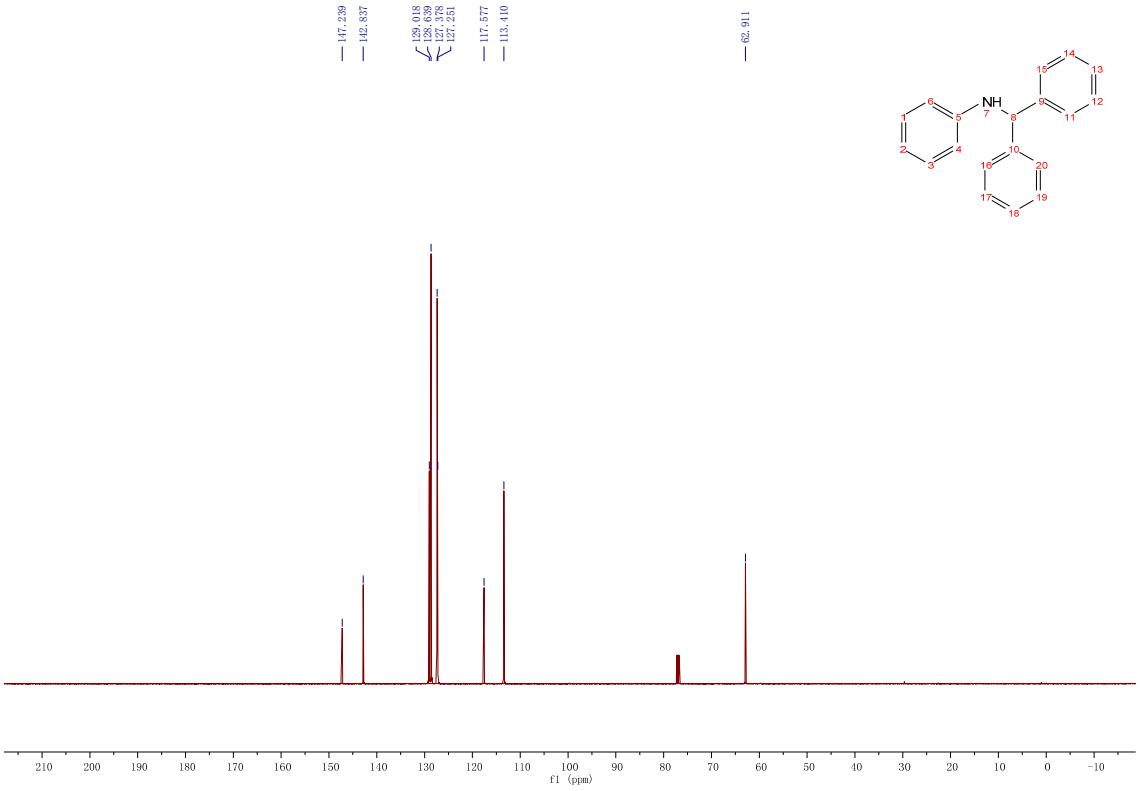
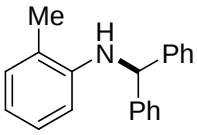


^{13}C NMR





8b

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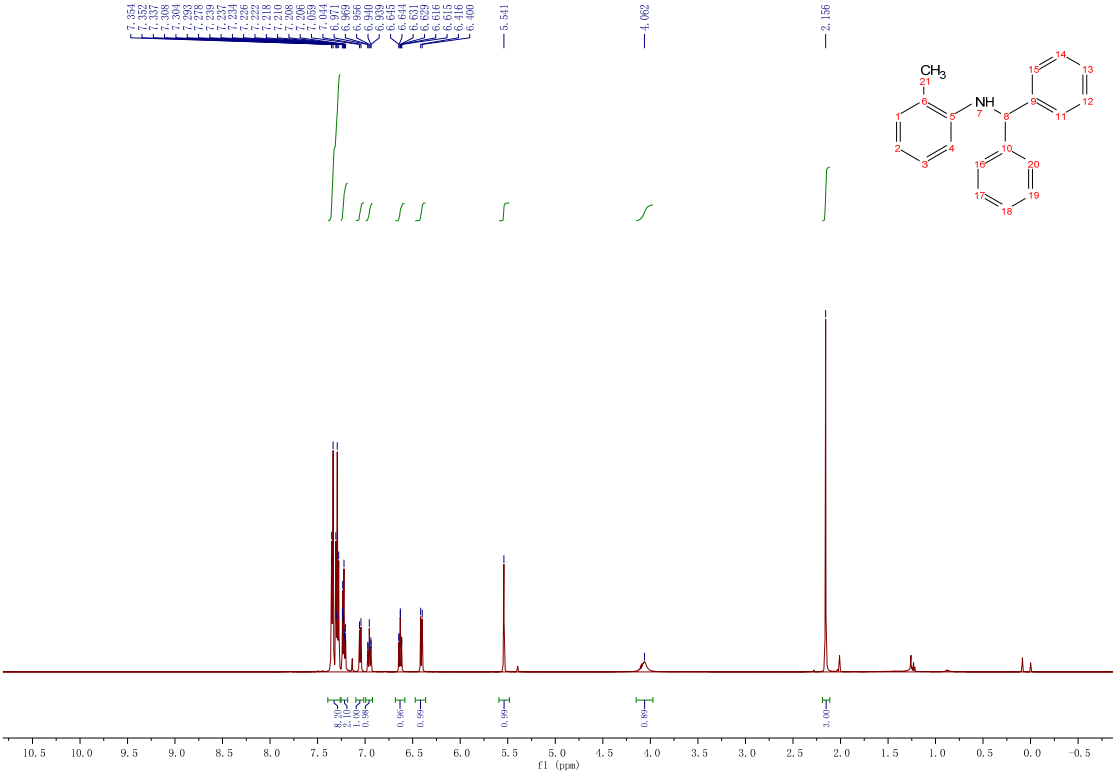

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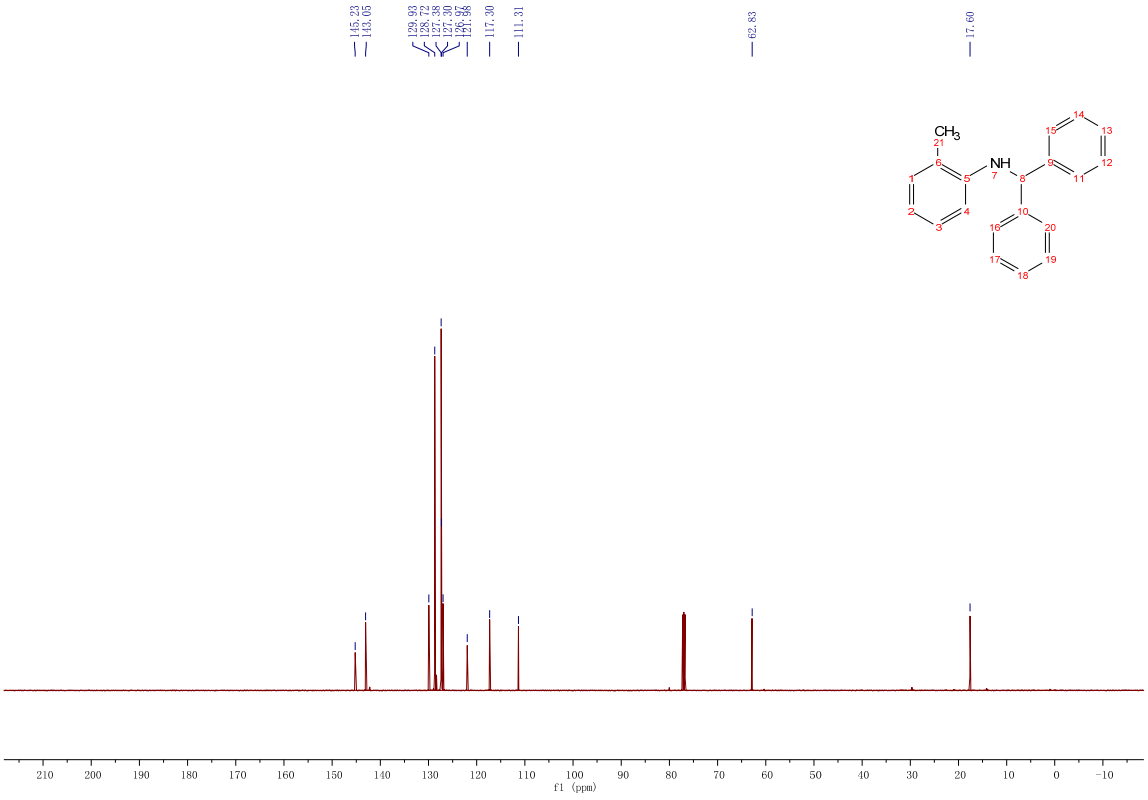

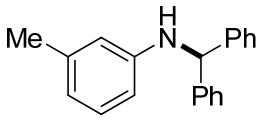

8c

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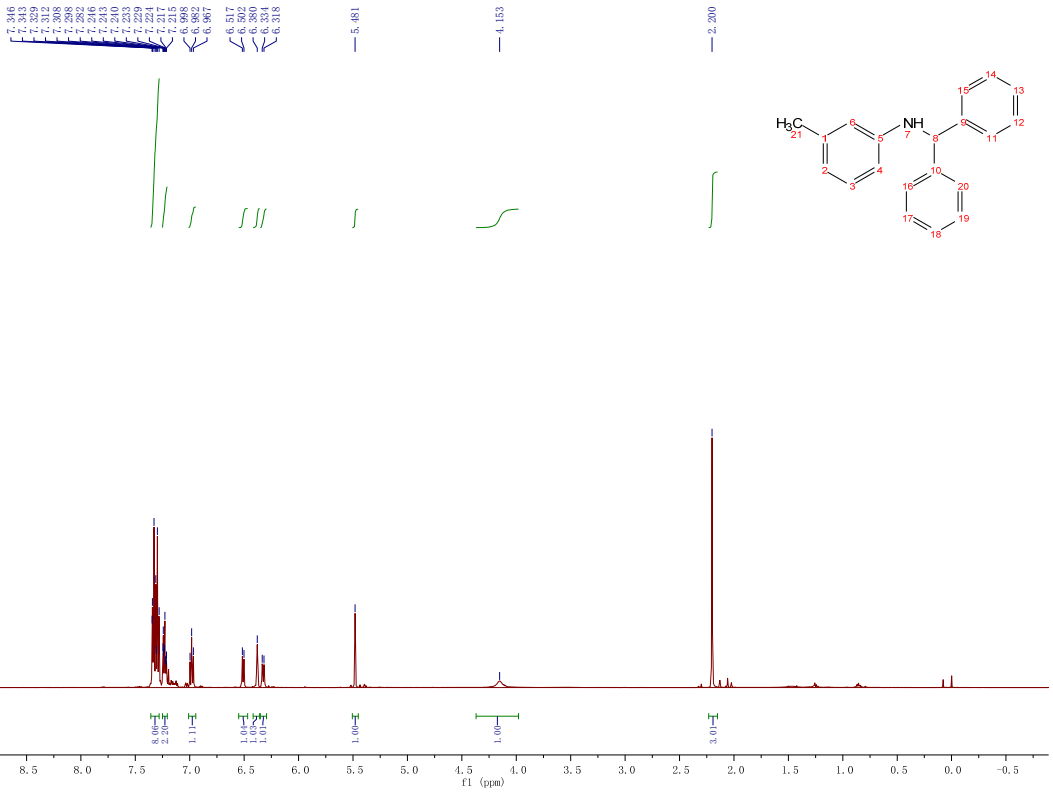

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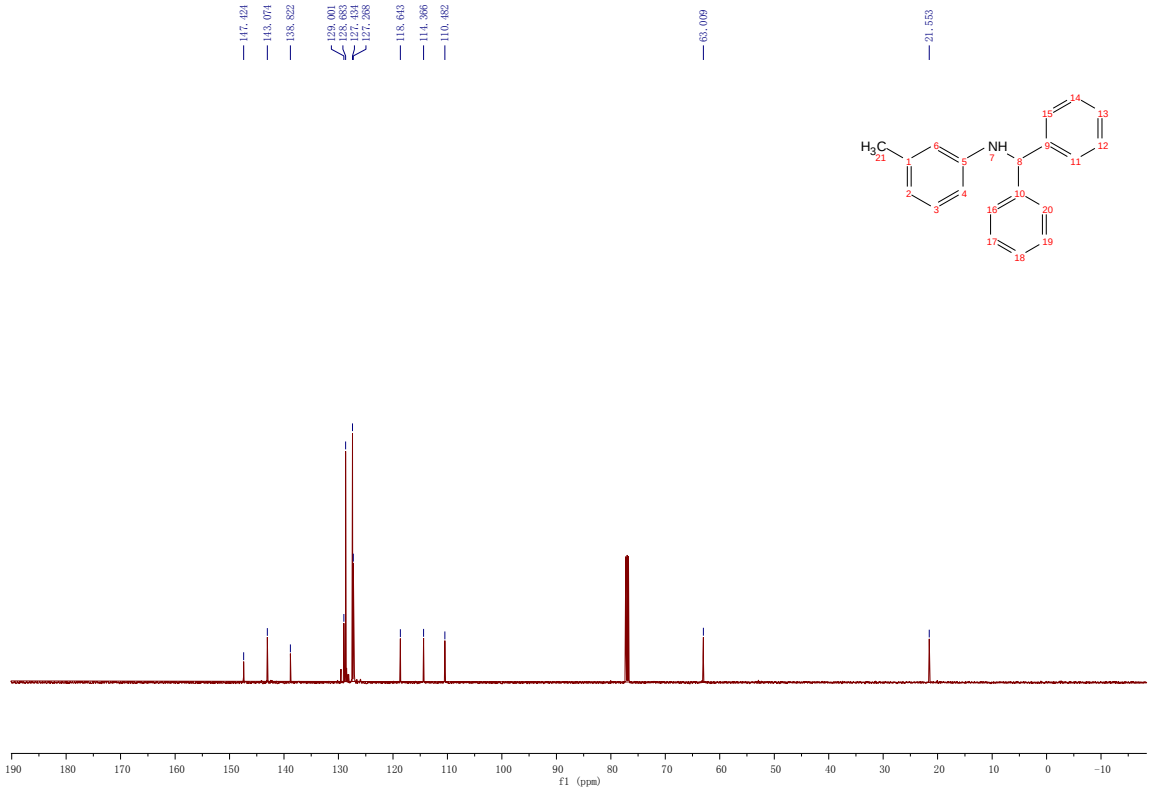

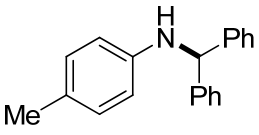

8d

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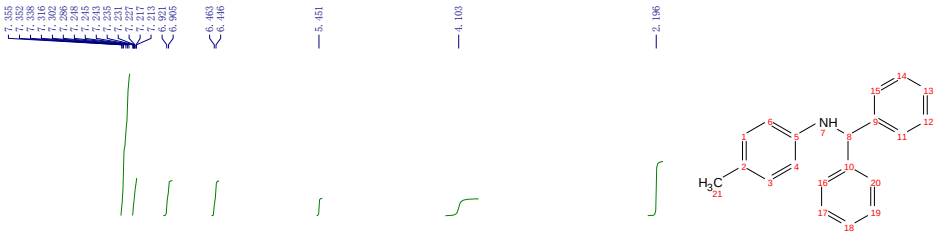

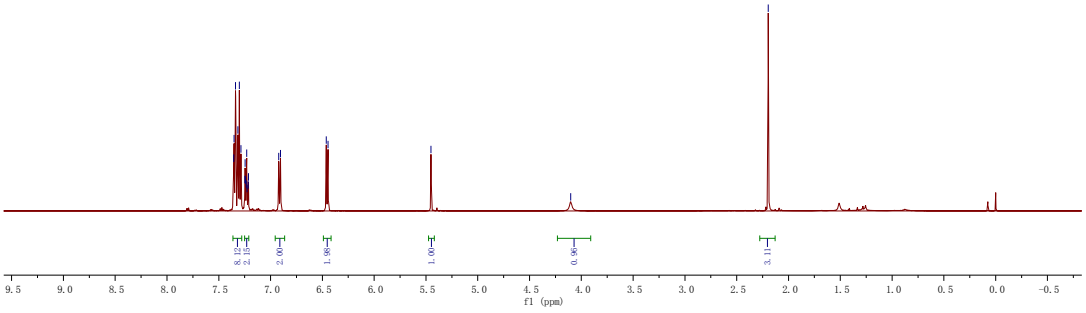

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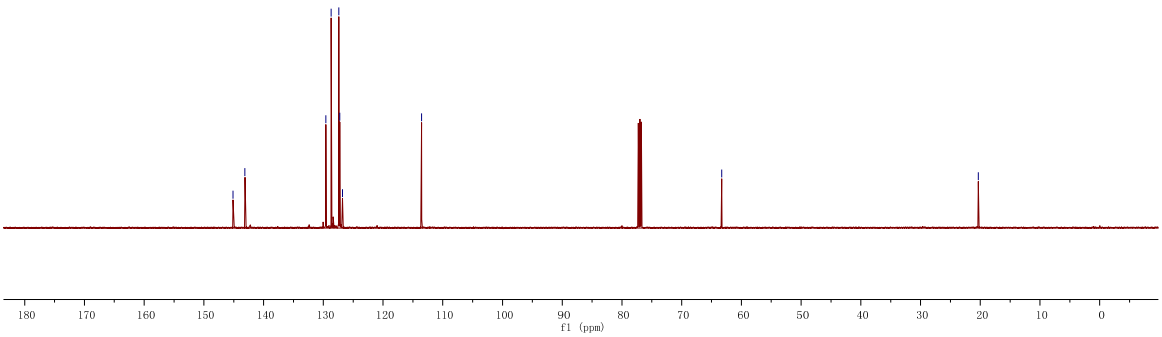
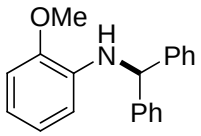
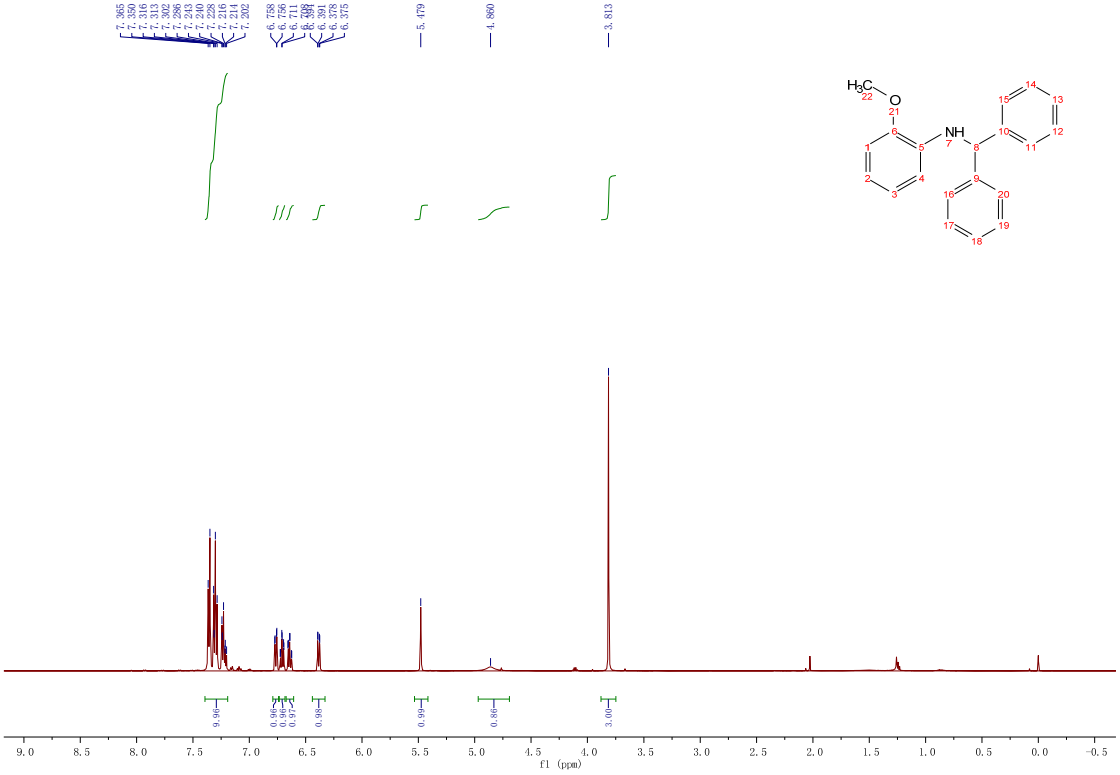




8e

^{1}H NMR



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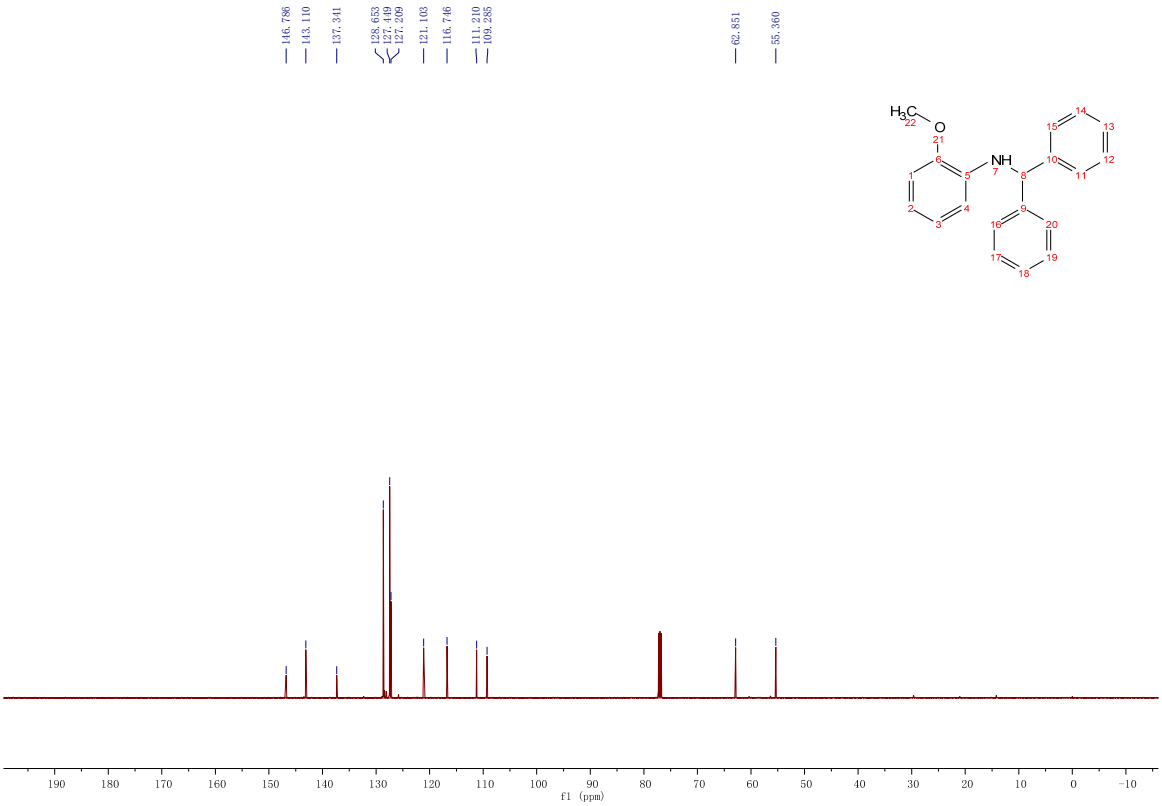
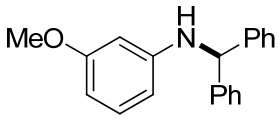
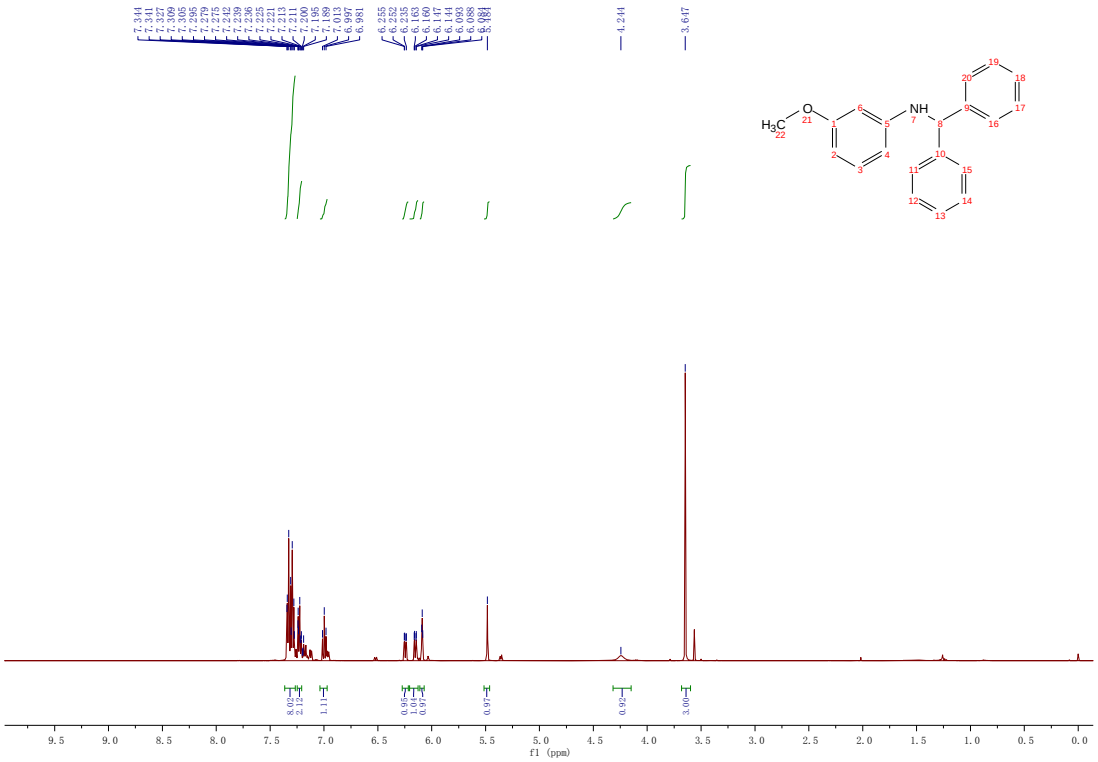




8f

^{1}H NMR



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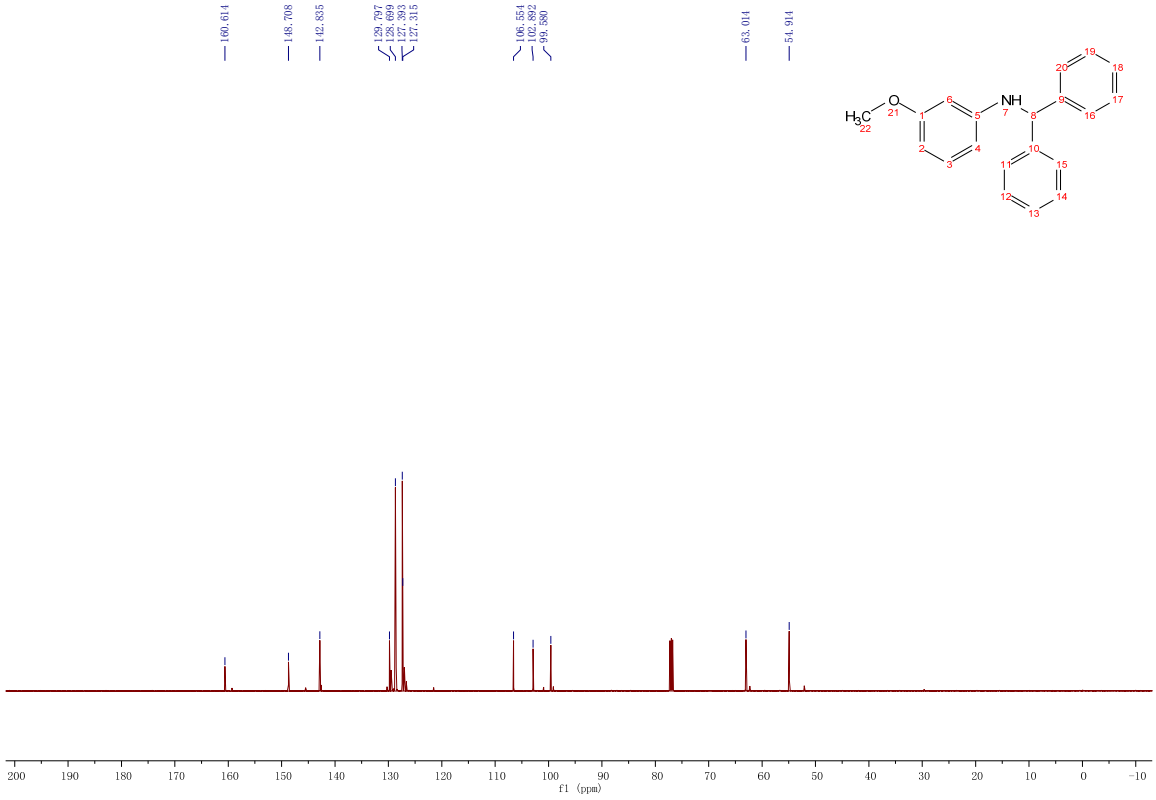

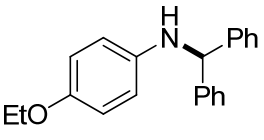

8g

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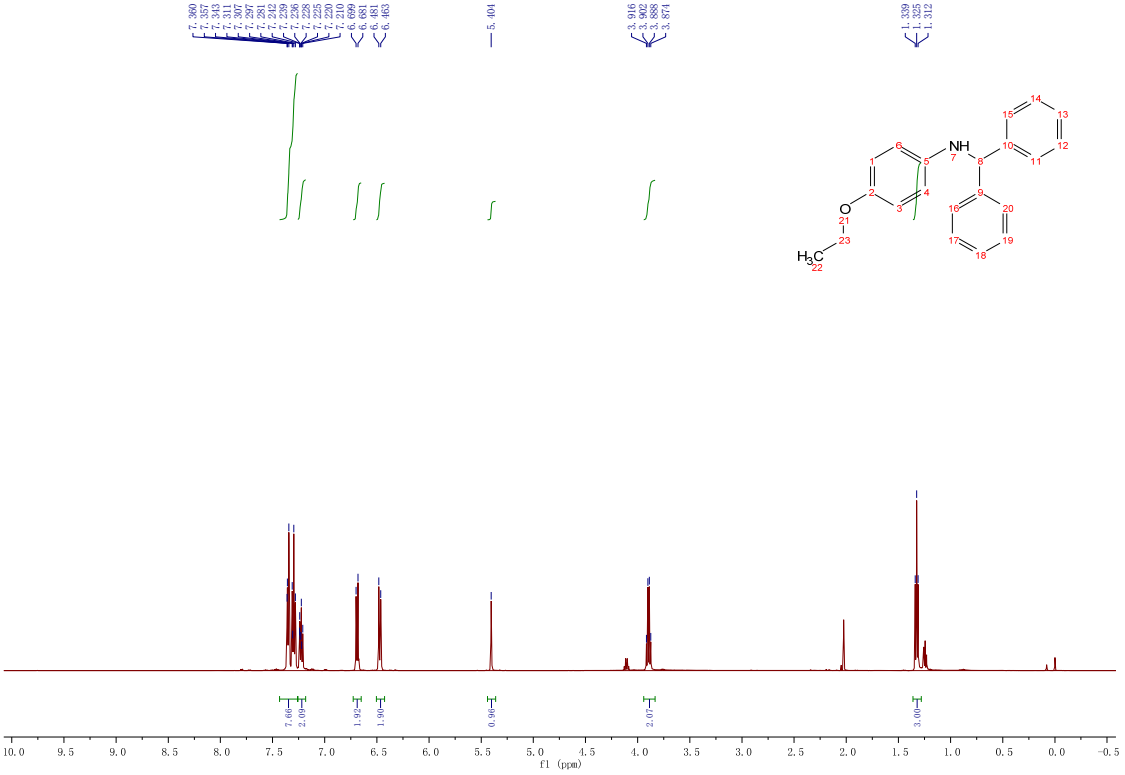

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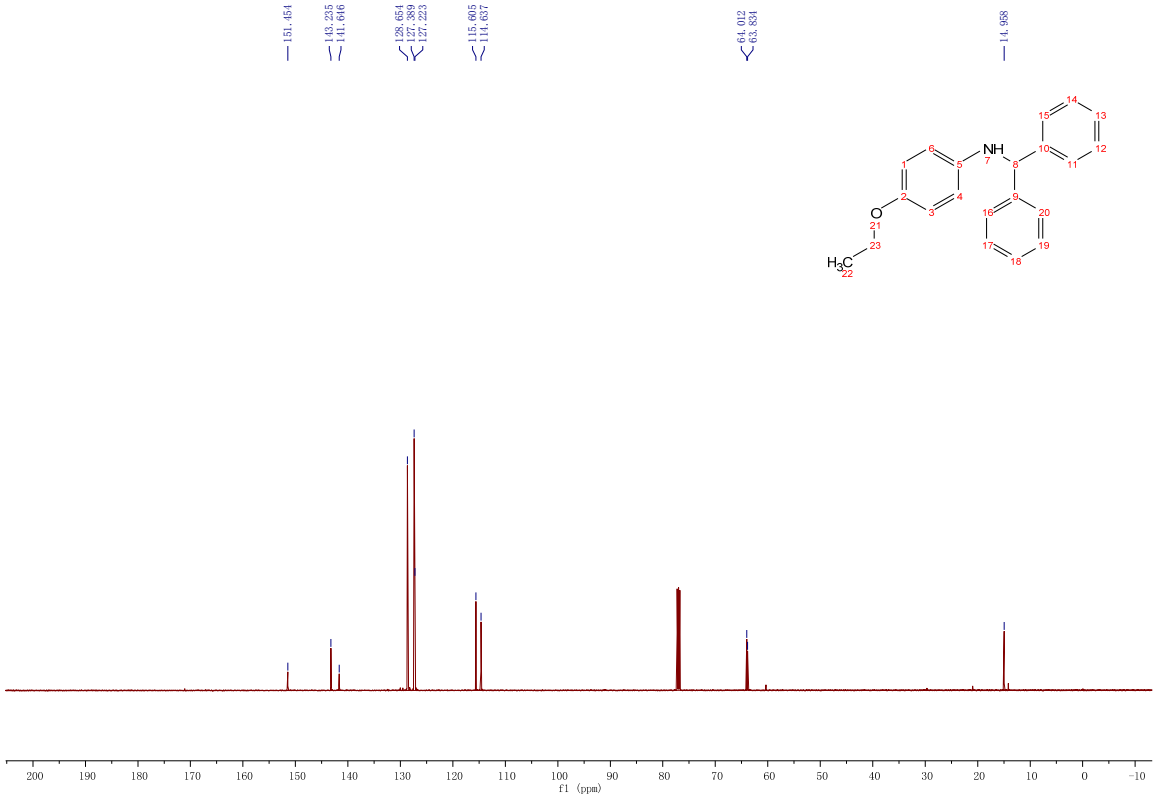
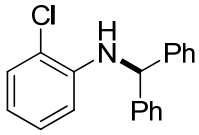
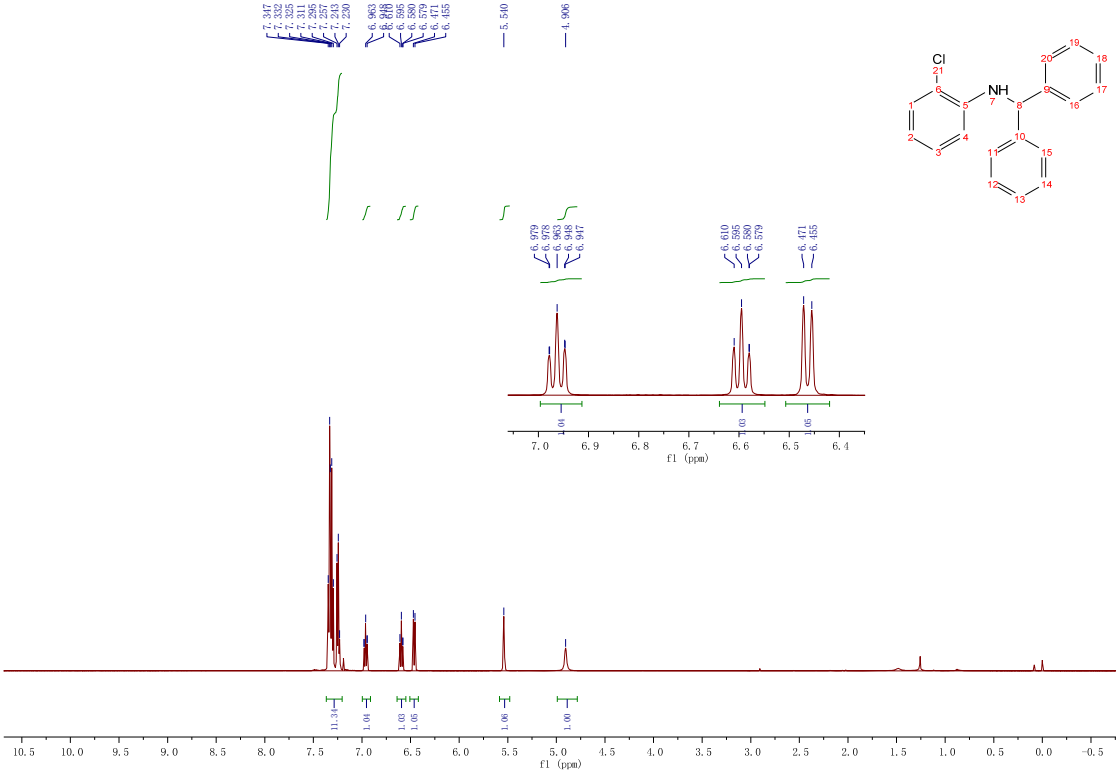




8h

^{1}H NMR



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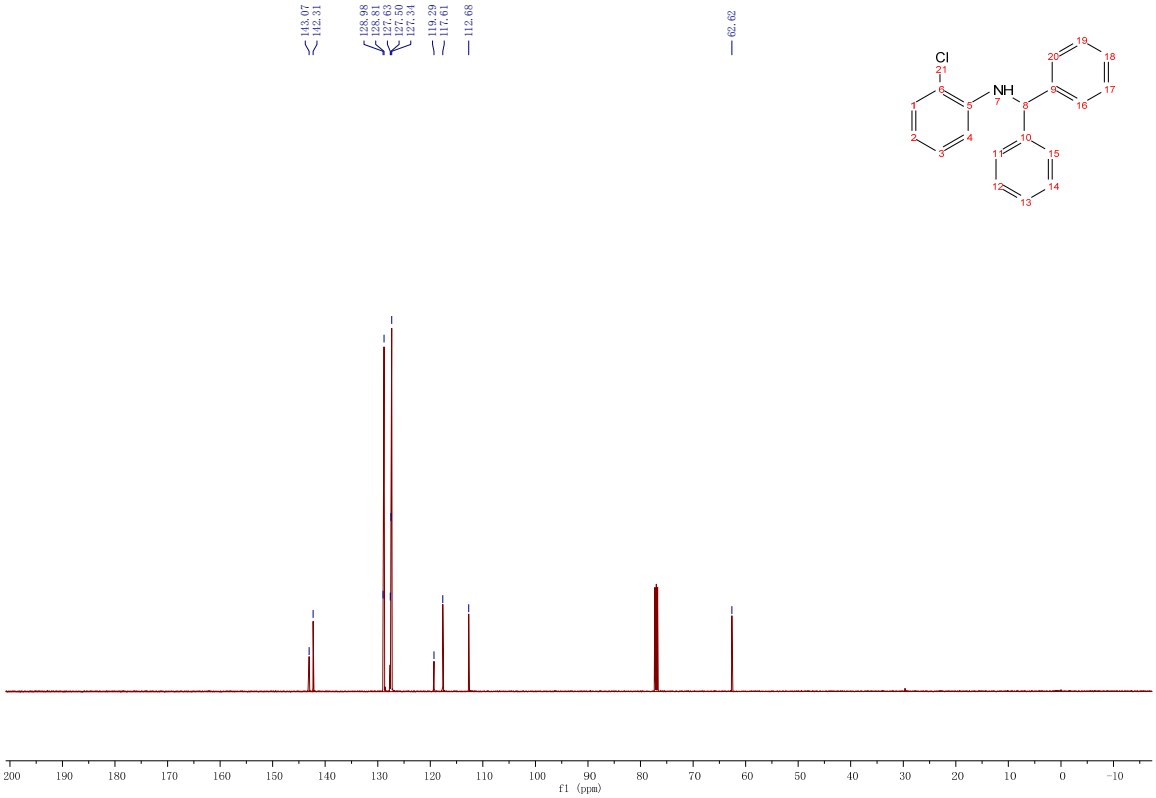
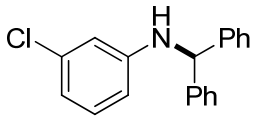
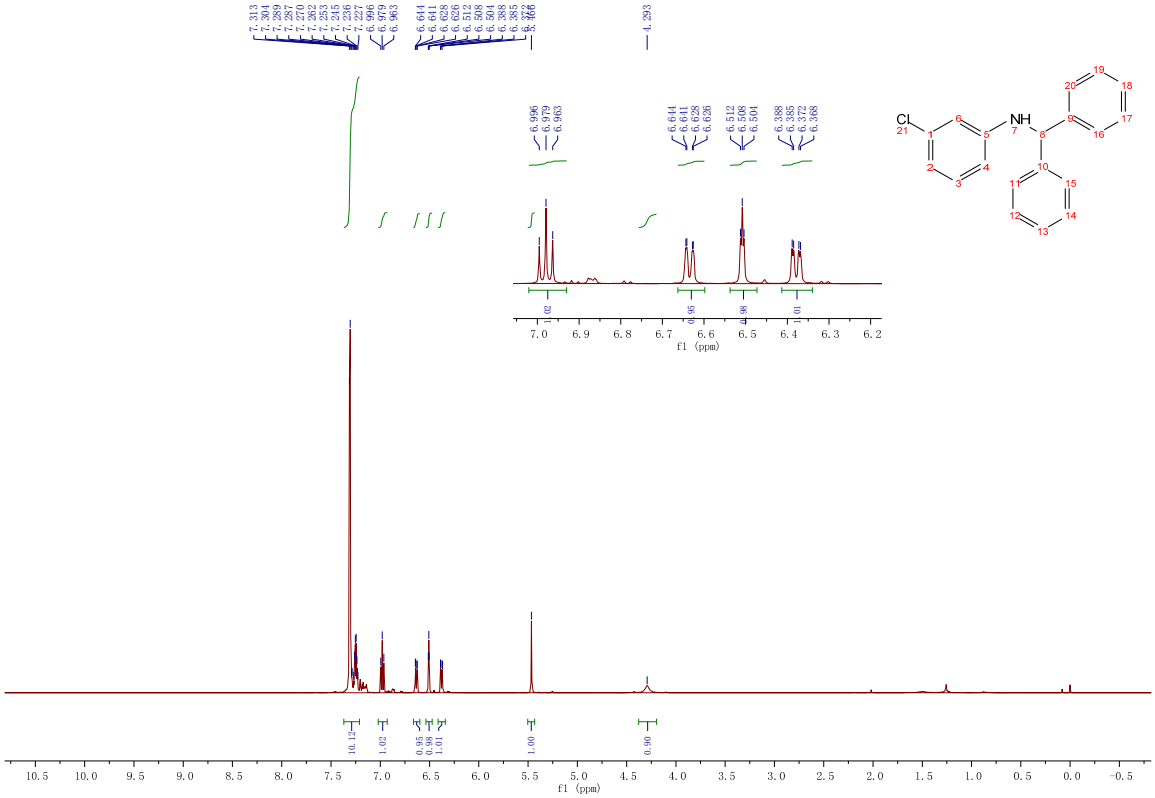




8i

^{1}H NMR



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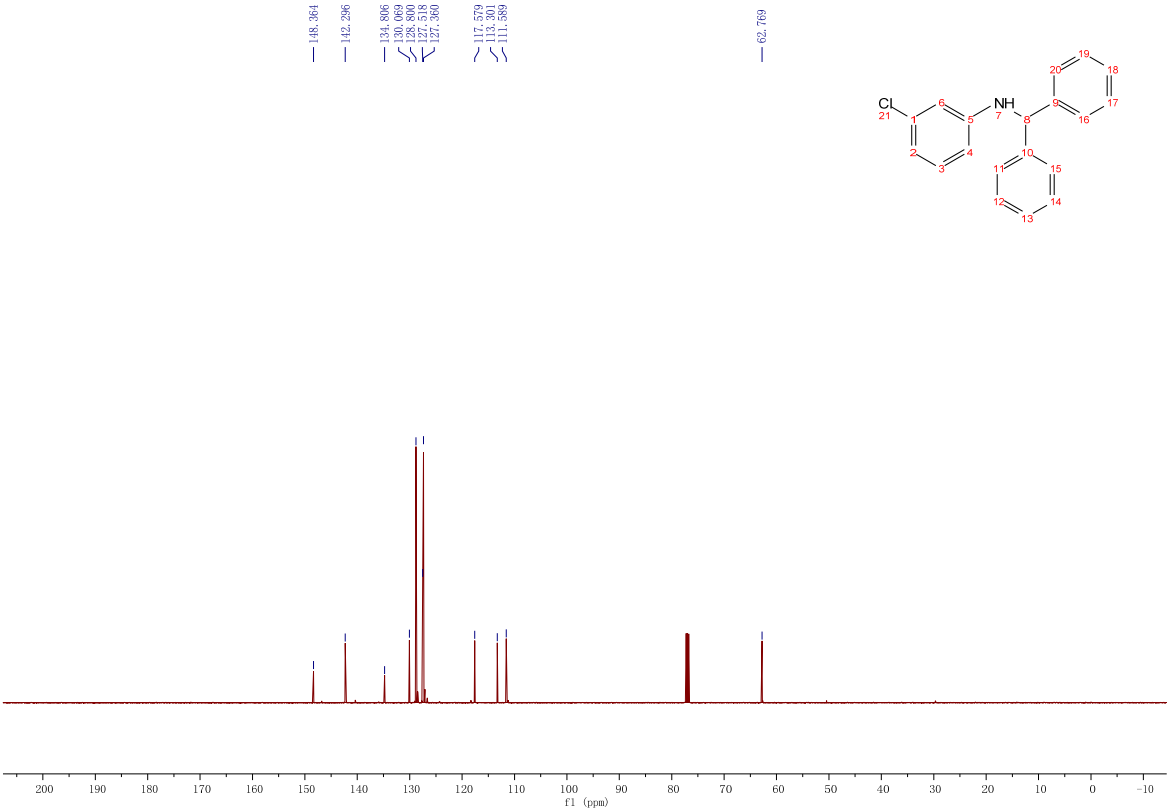
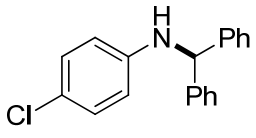
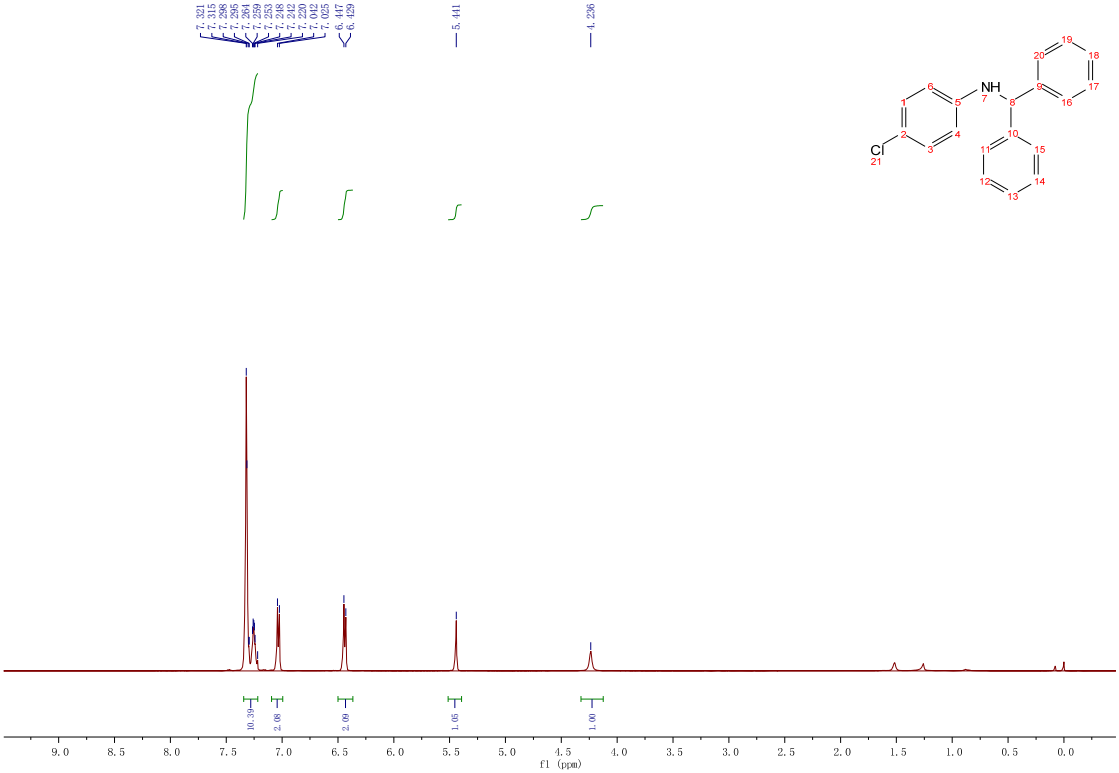




8j

^{1}H NMR



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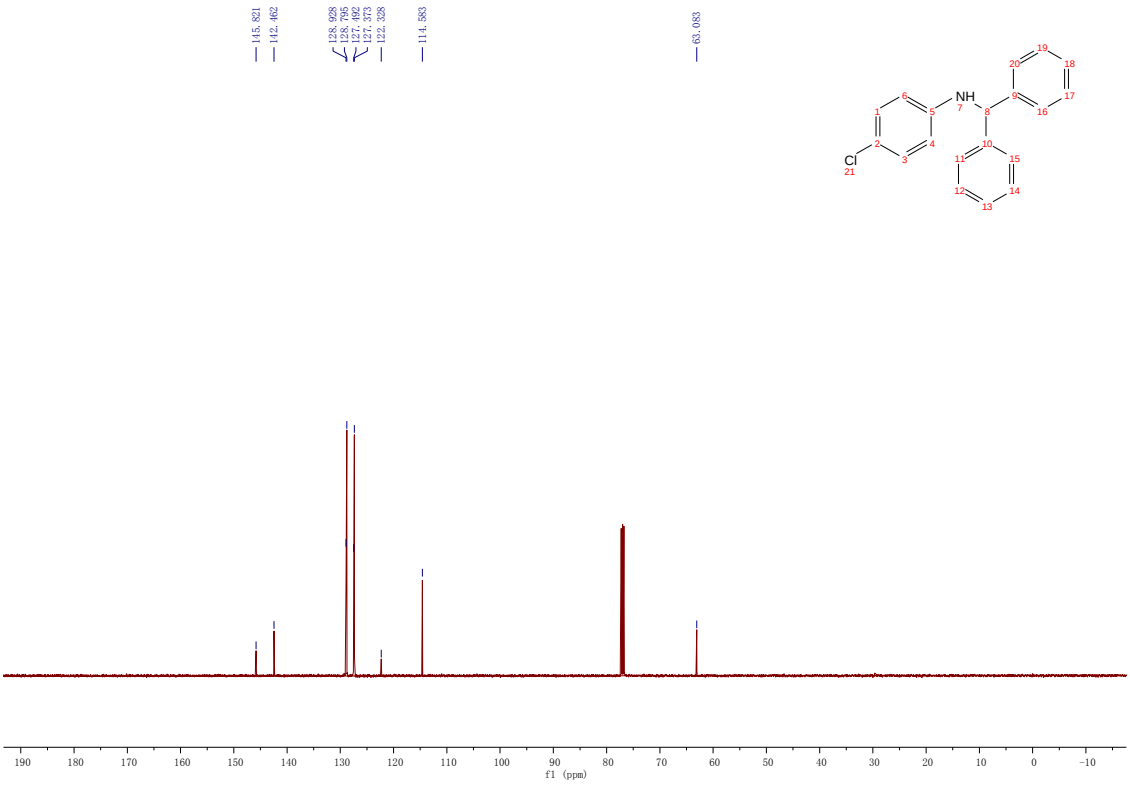
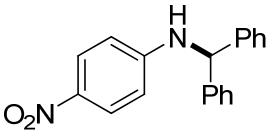
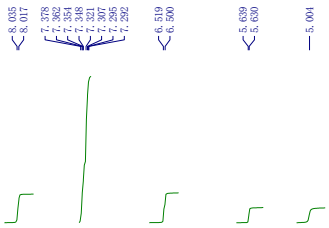
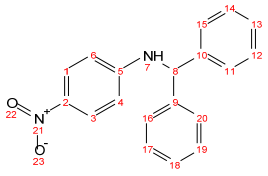


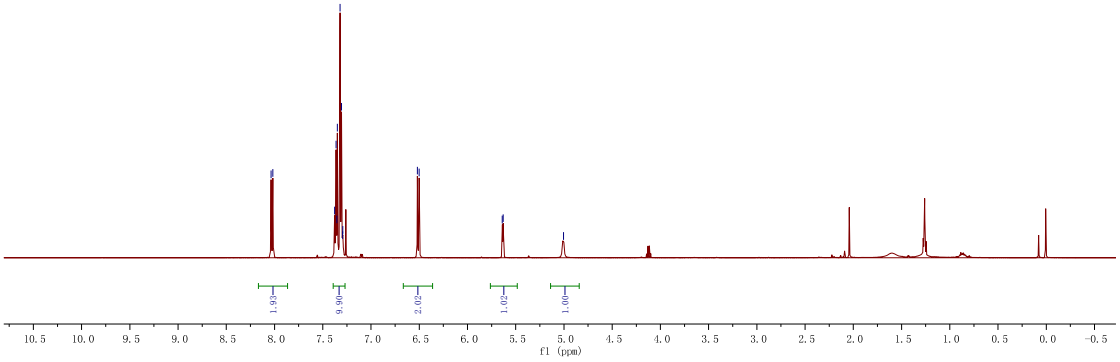


8k

^{1}H NMR







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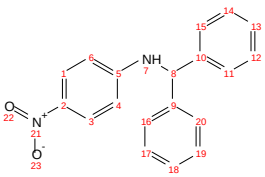
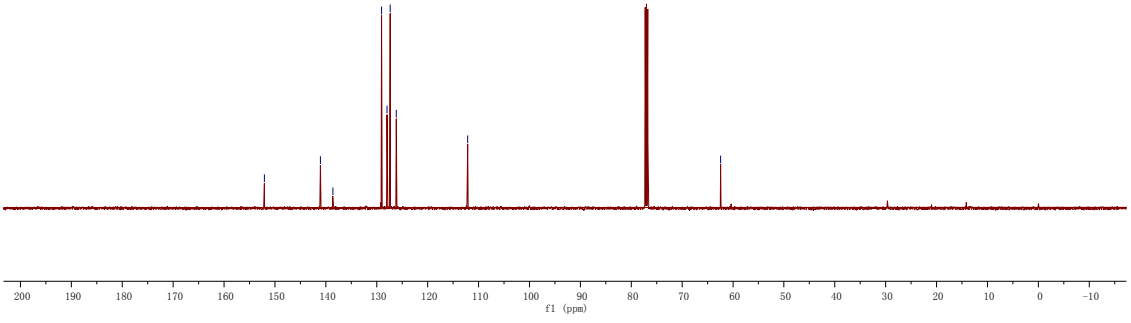
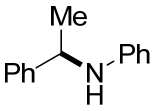
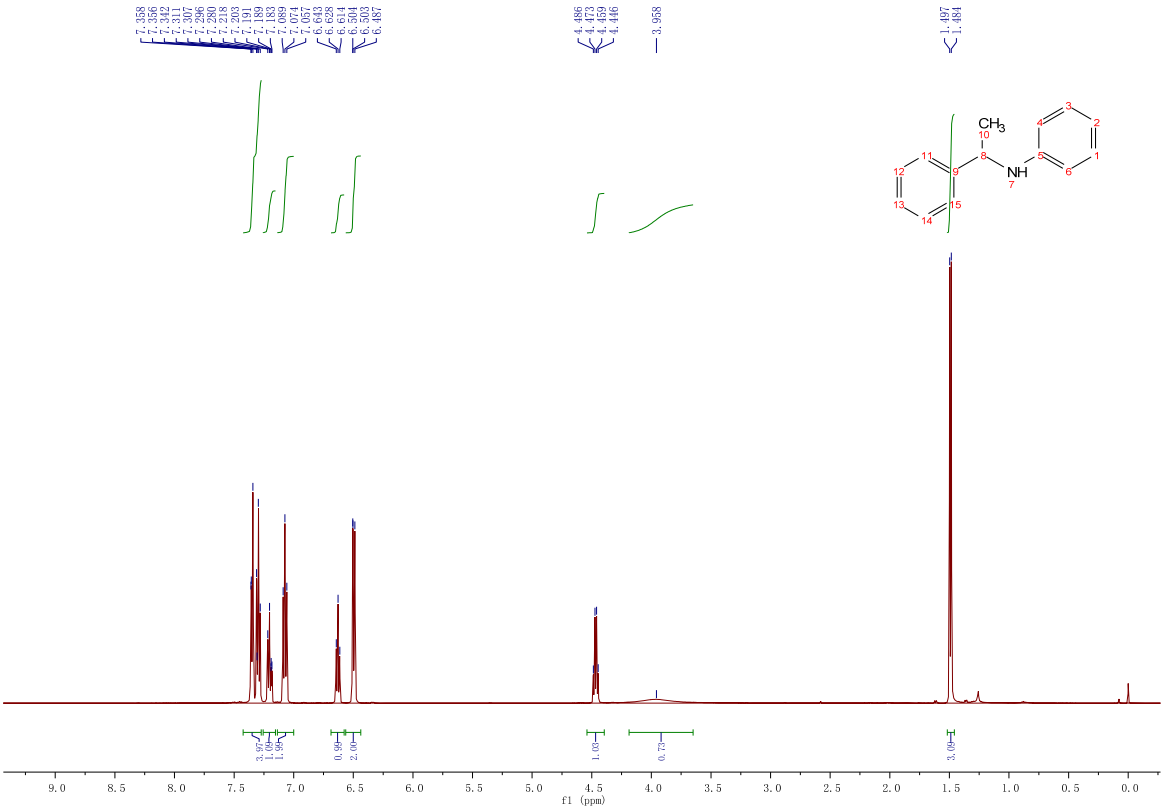




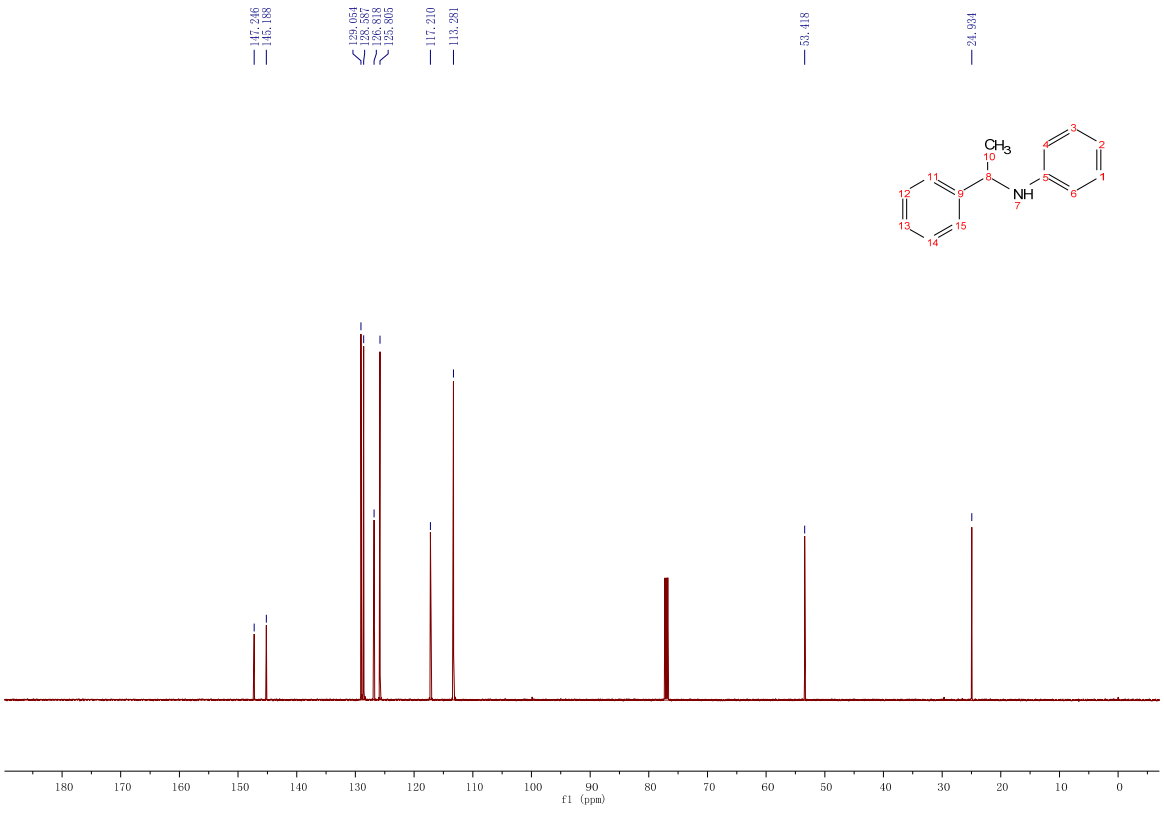


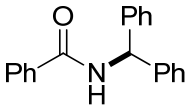
8l

^{1}H NMR



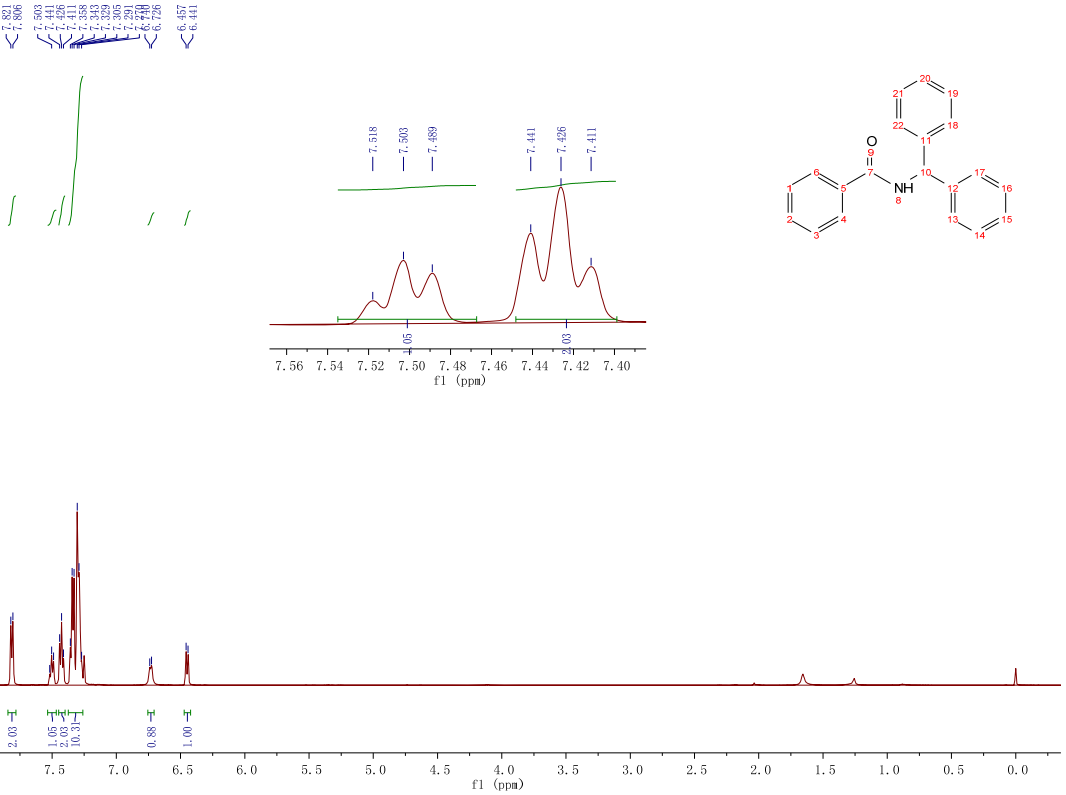
^{13}C NMR



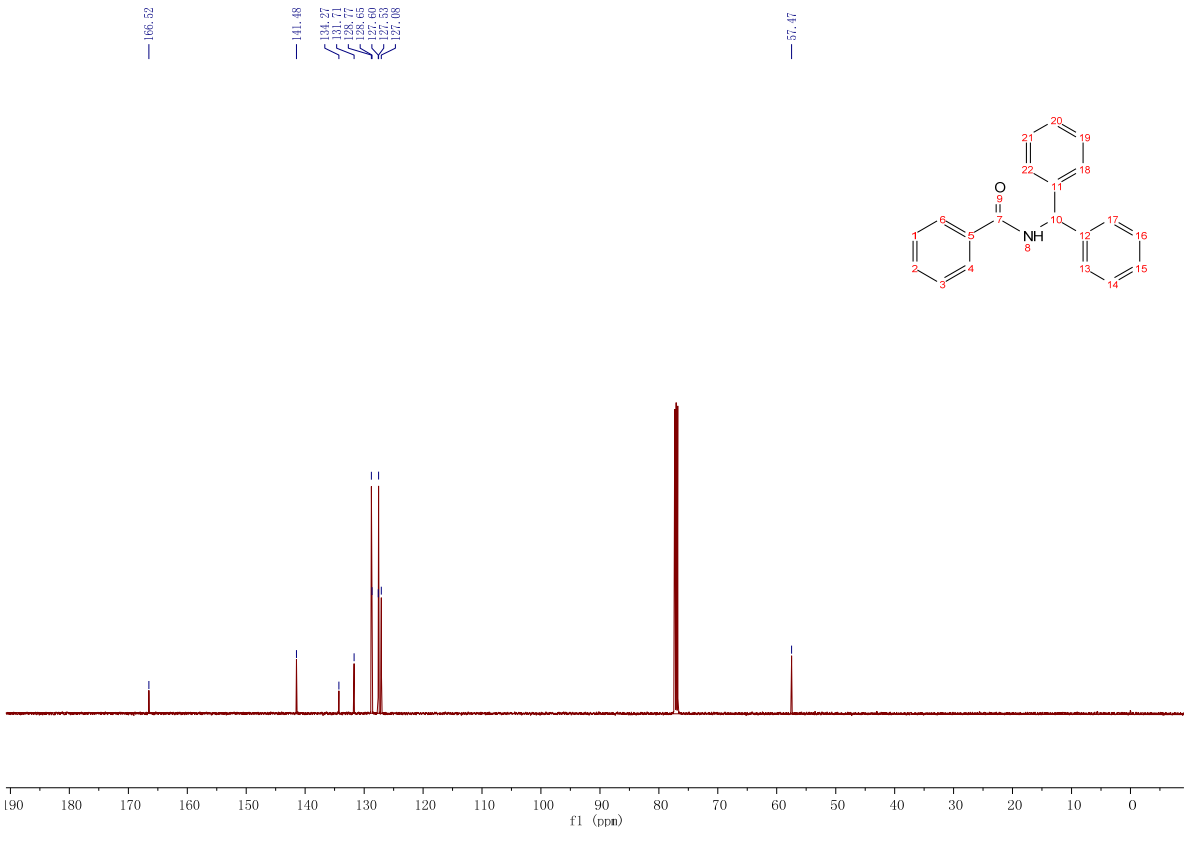


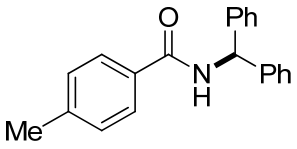
10a

^{1}H NMR



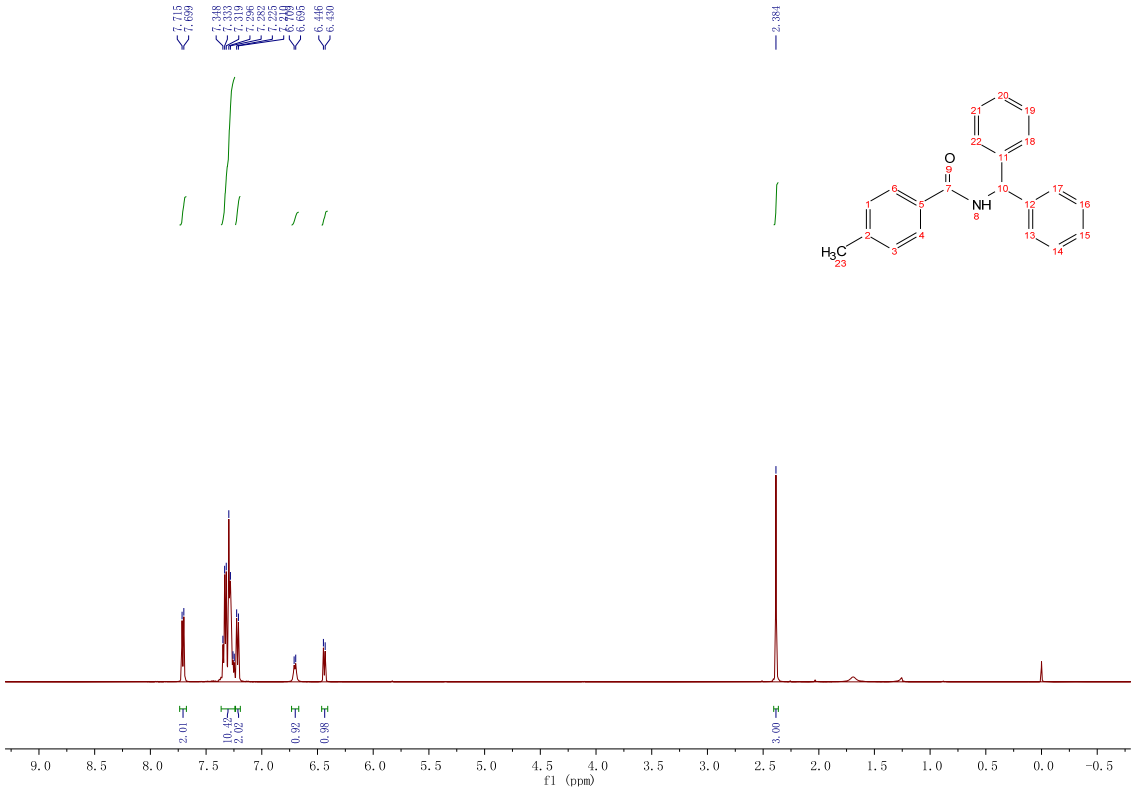
^{13}C NMR





10b

^{1}H NMR



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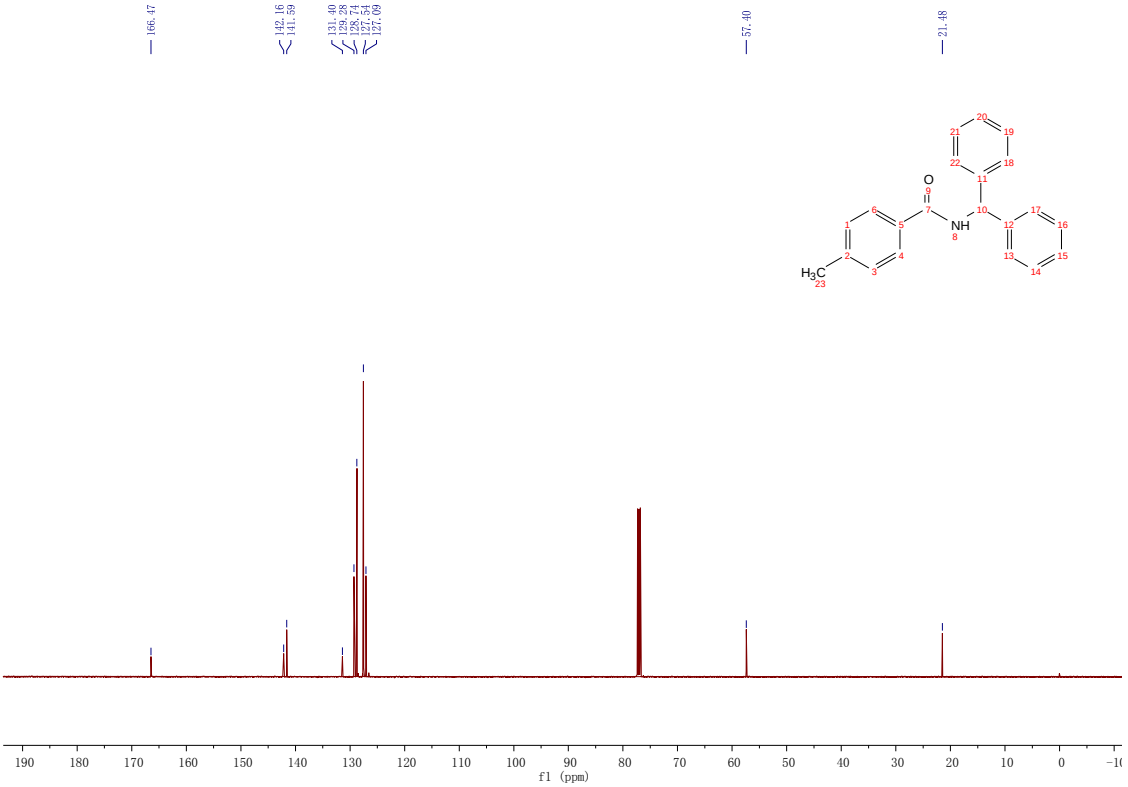
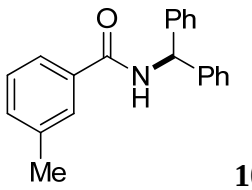
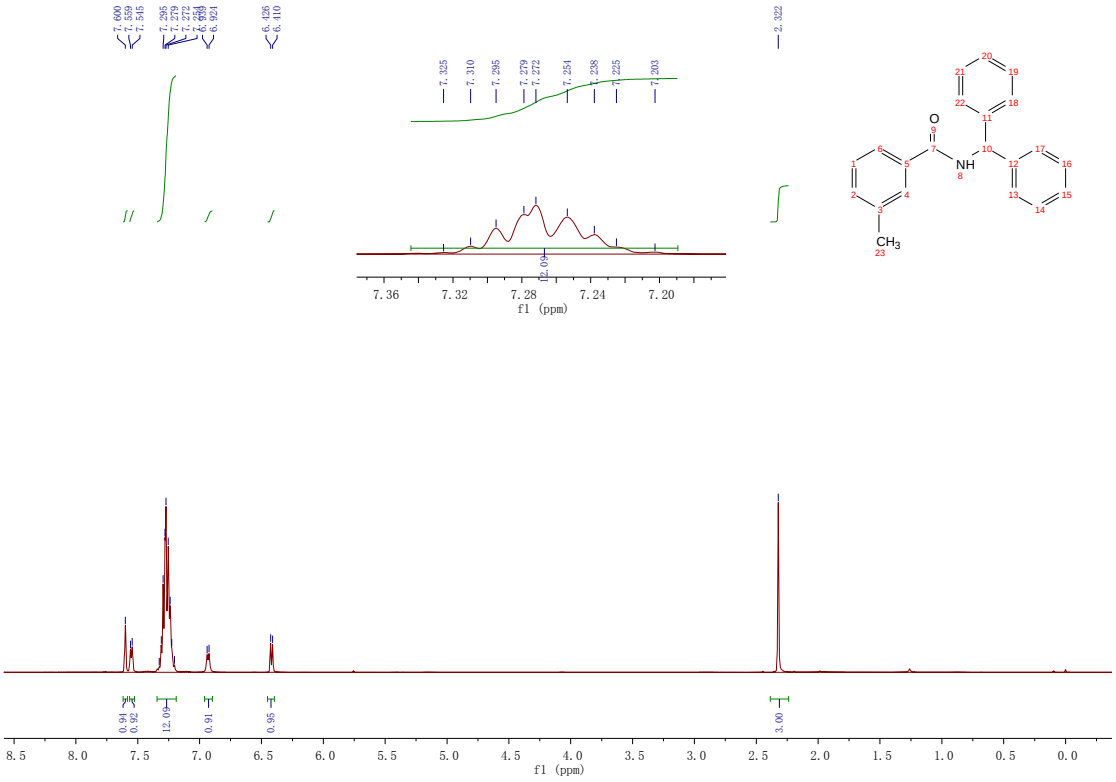




10c

^{1}H NMR



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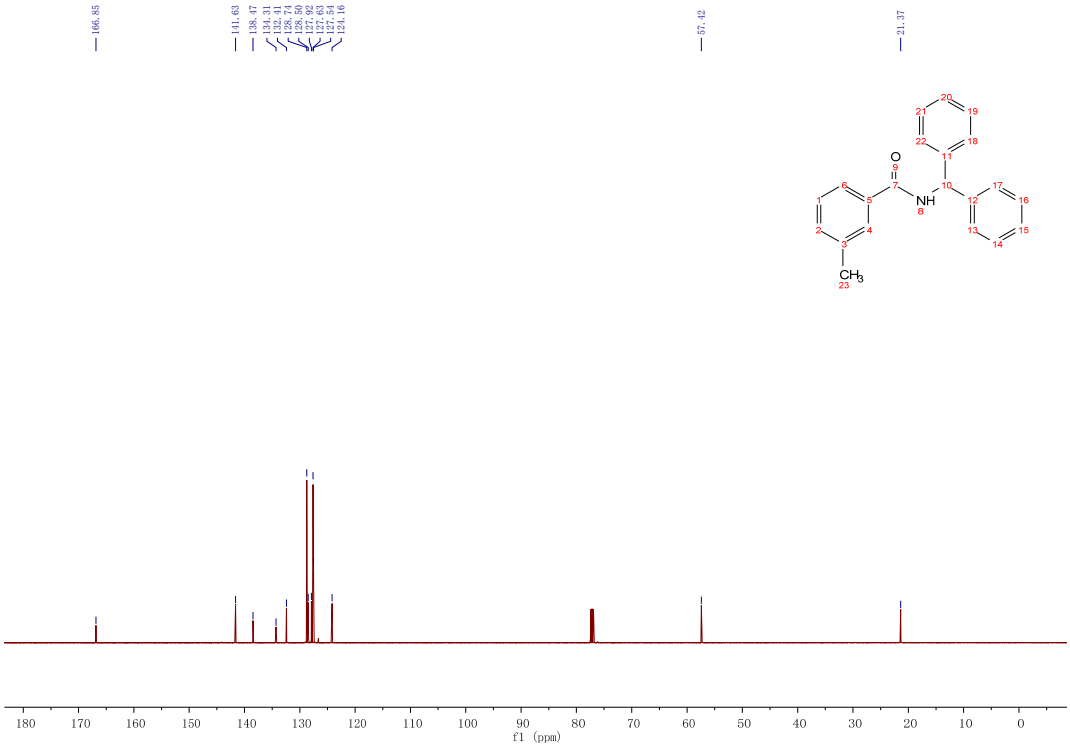
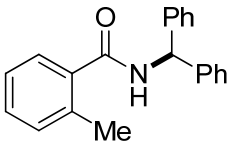
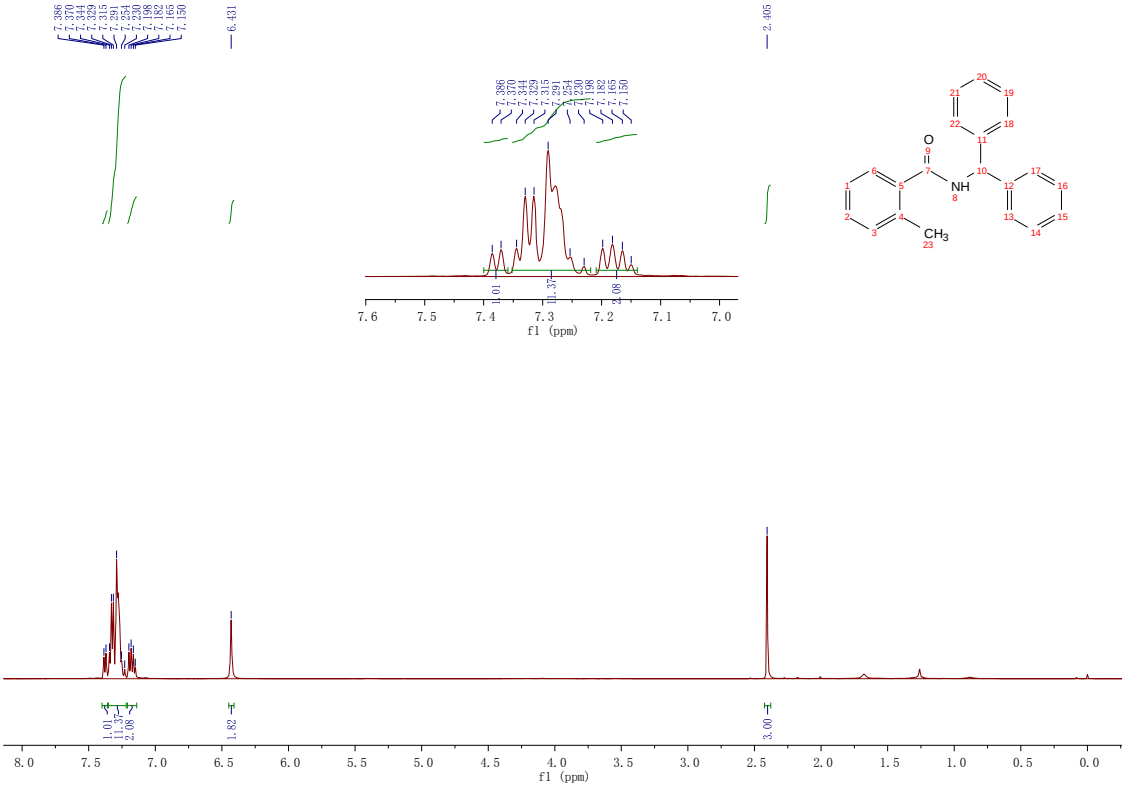




10d

^{1}H NMR



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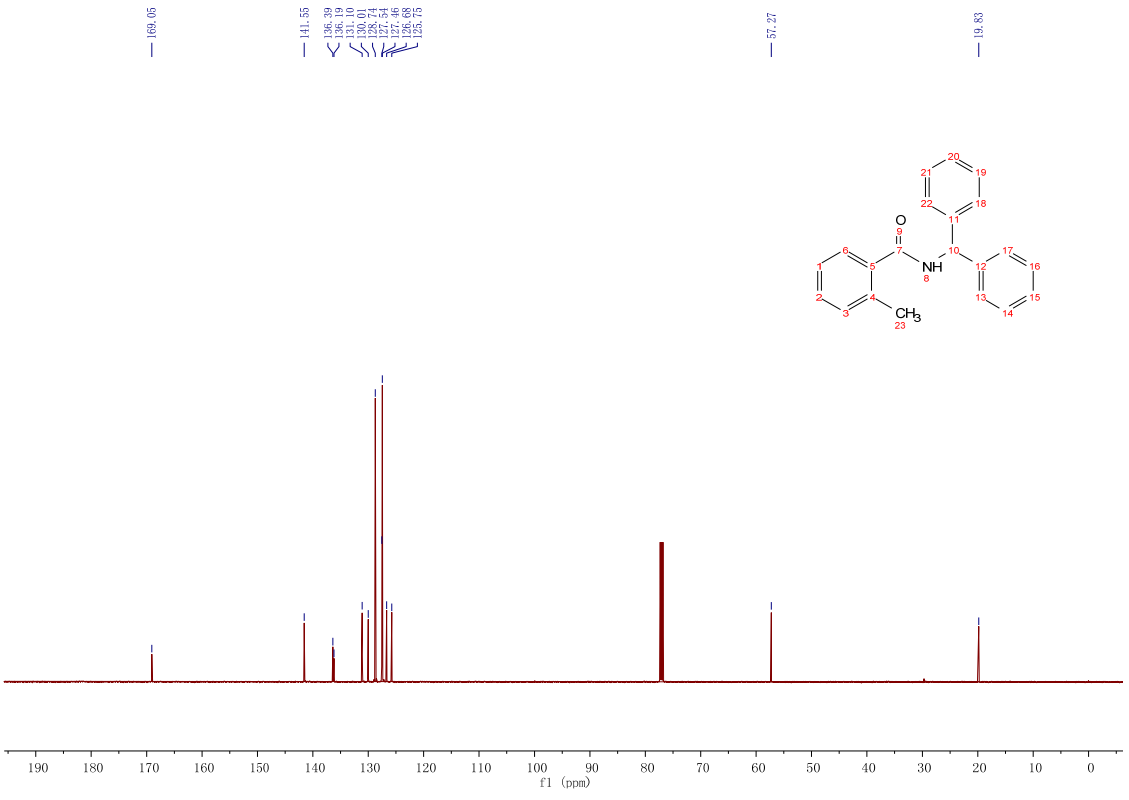
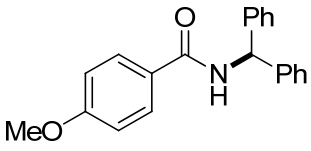
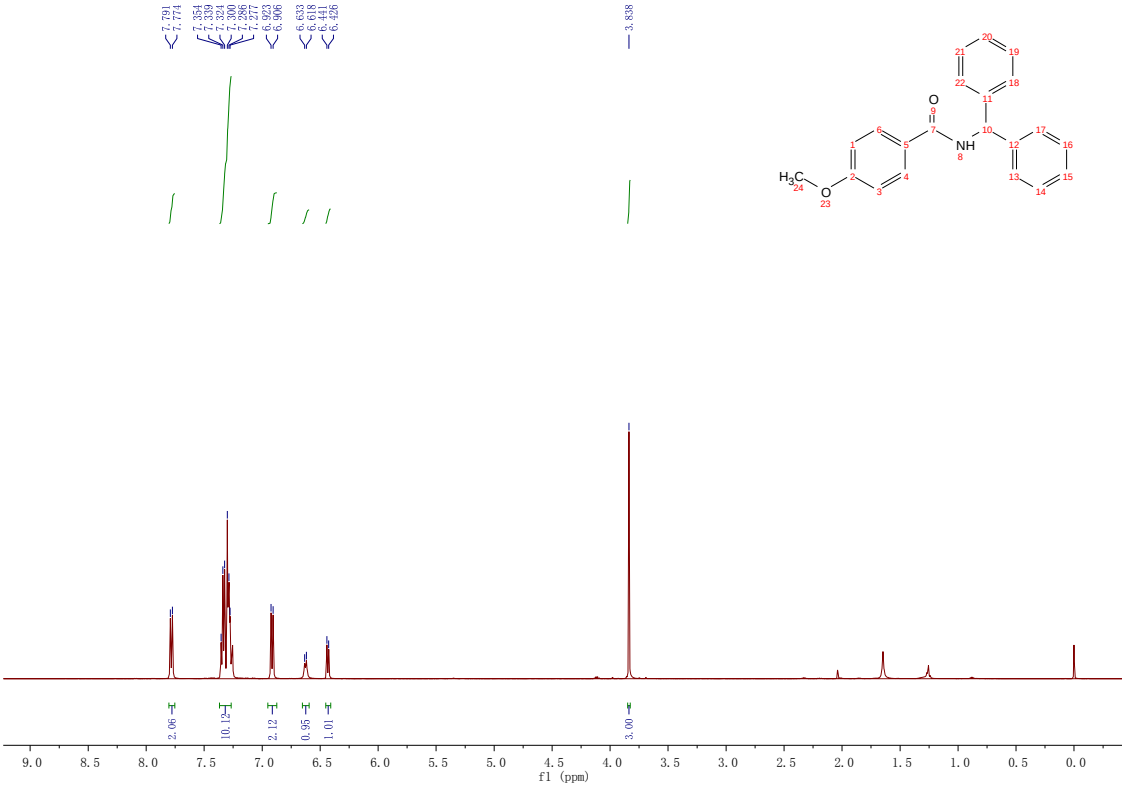


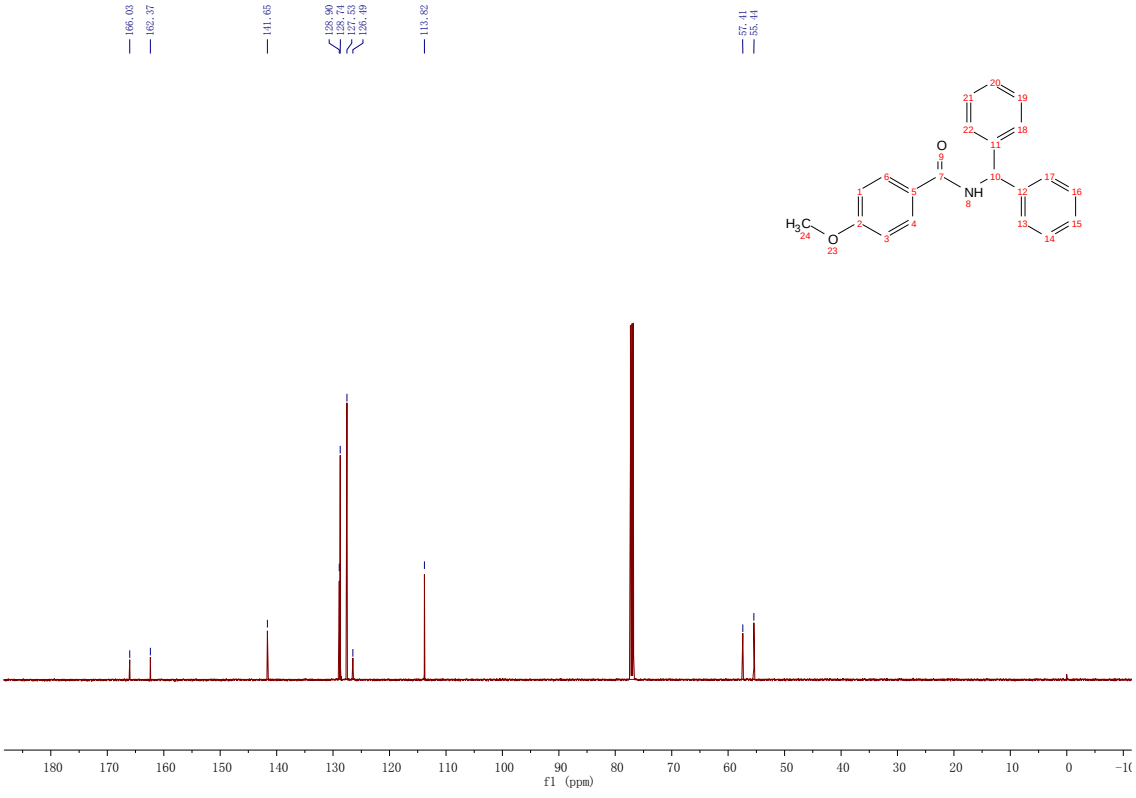


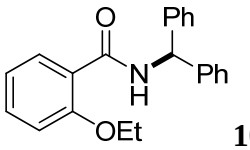
10e

^{1}H NMR



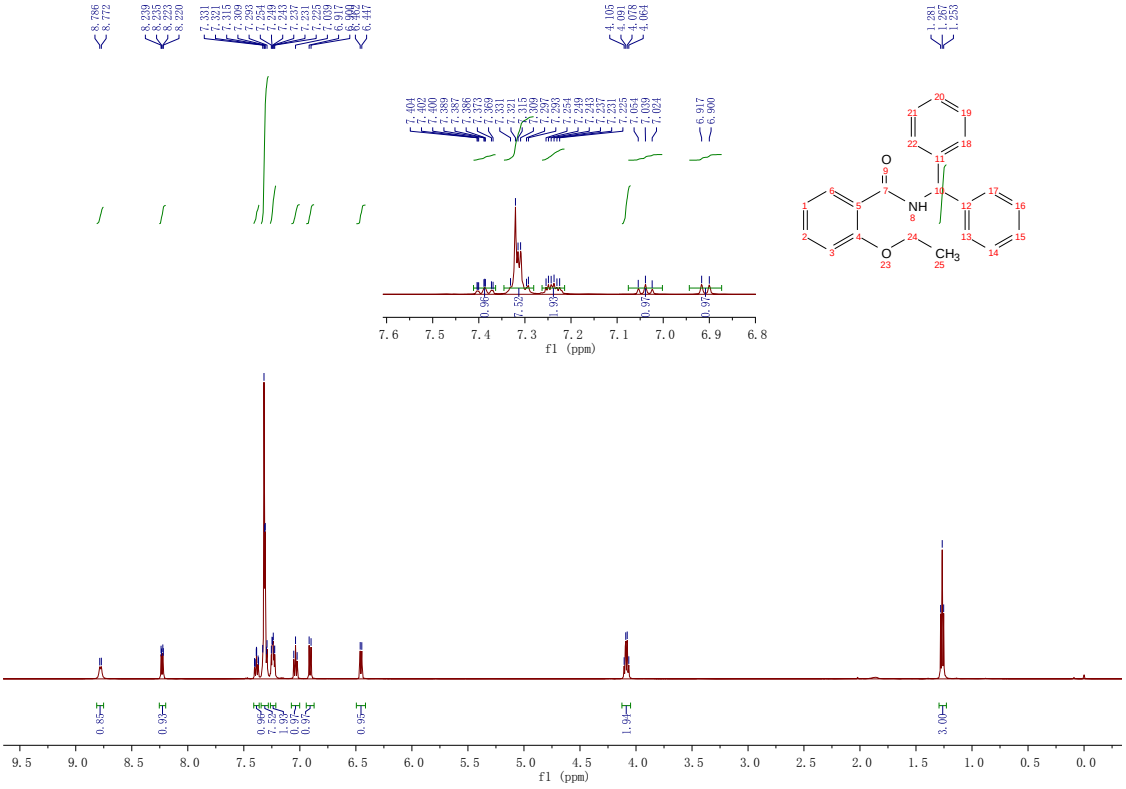
^{13}C NMR



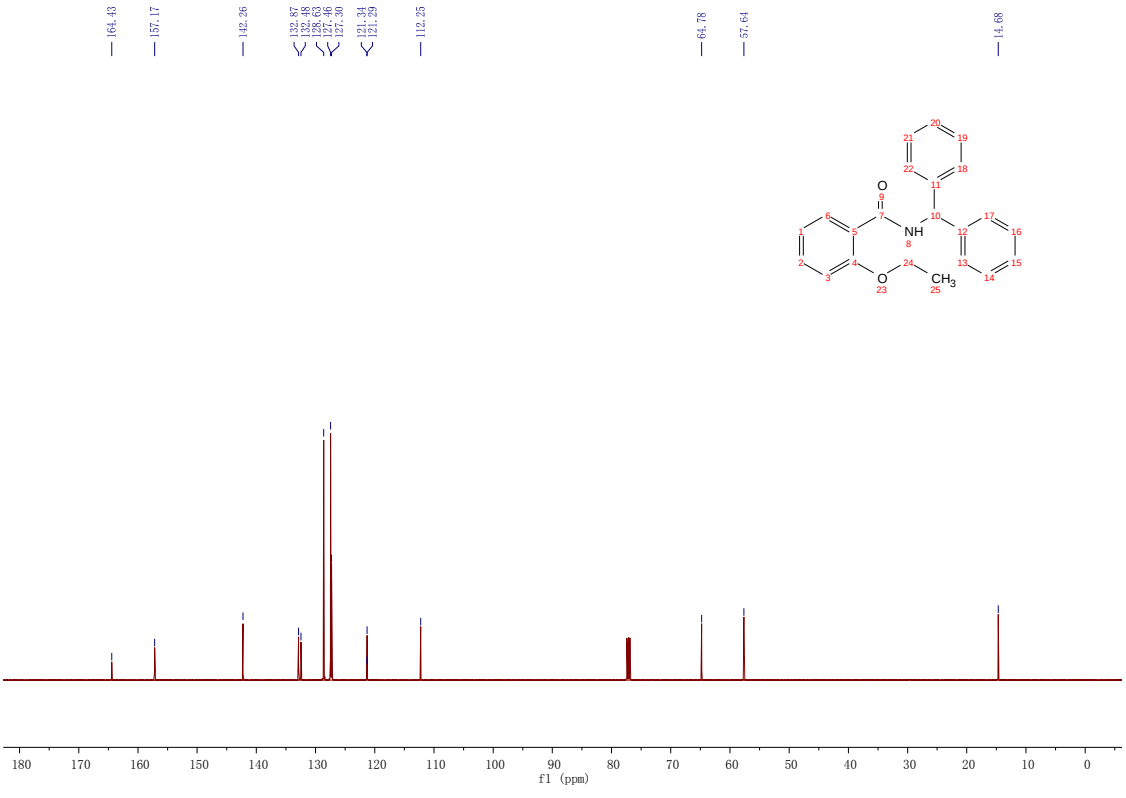


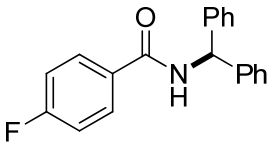
10f

^{1}H NMR



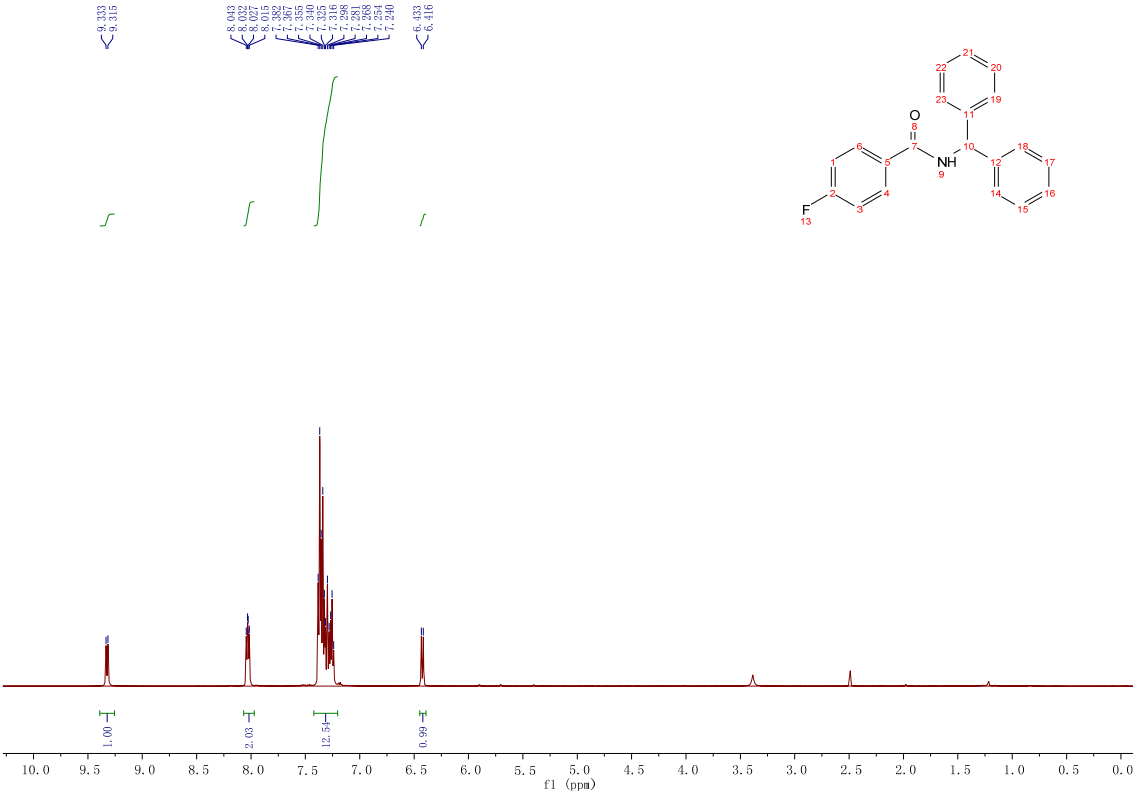
^{13}C NMR



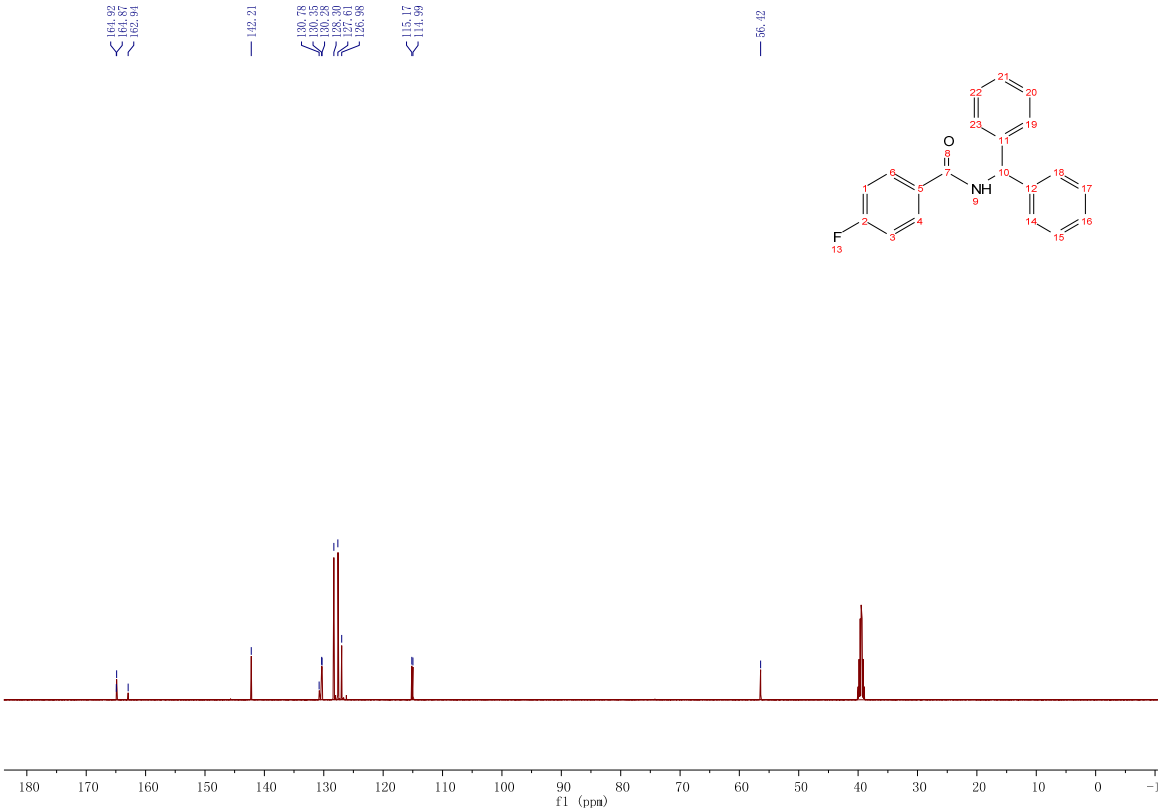


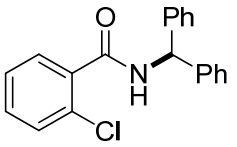
10g

^{1}H NMR



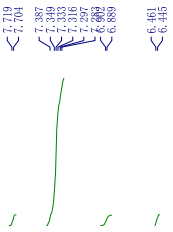
^{13}C NMR

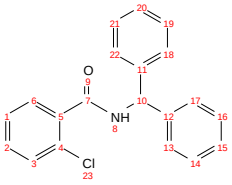


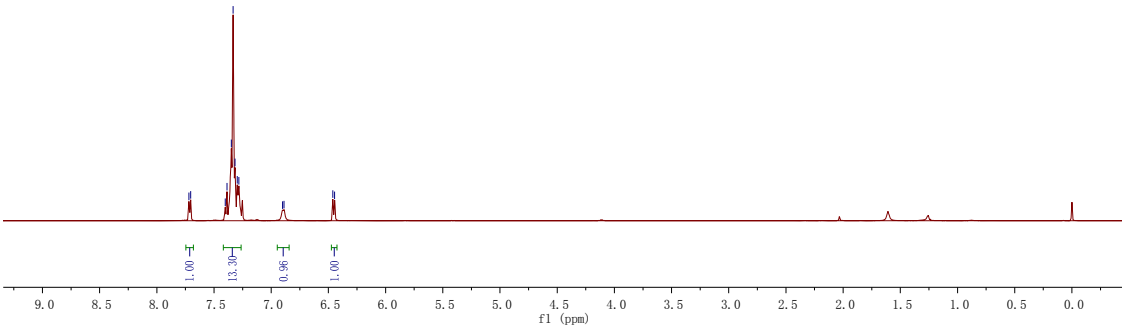


10h

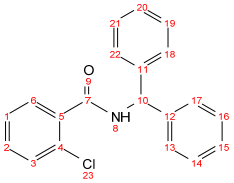
^{1}H NMR

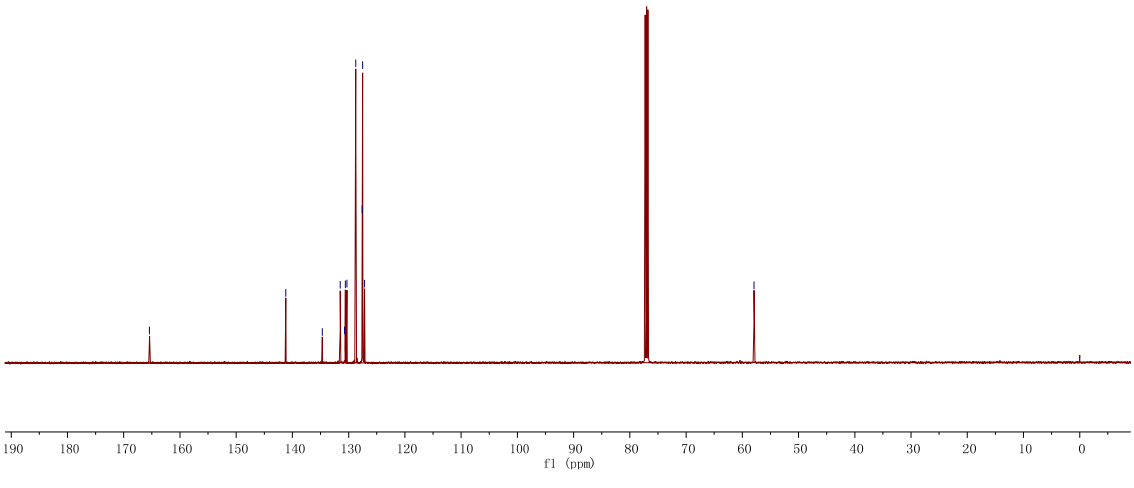


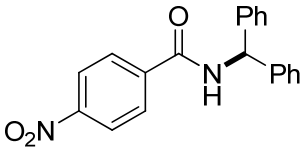




^{13}C NMR

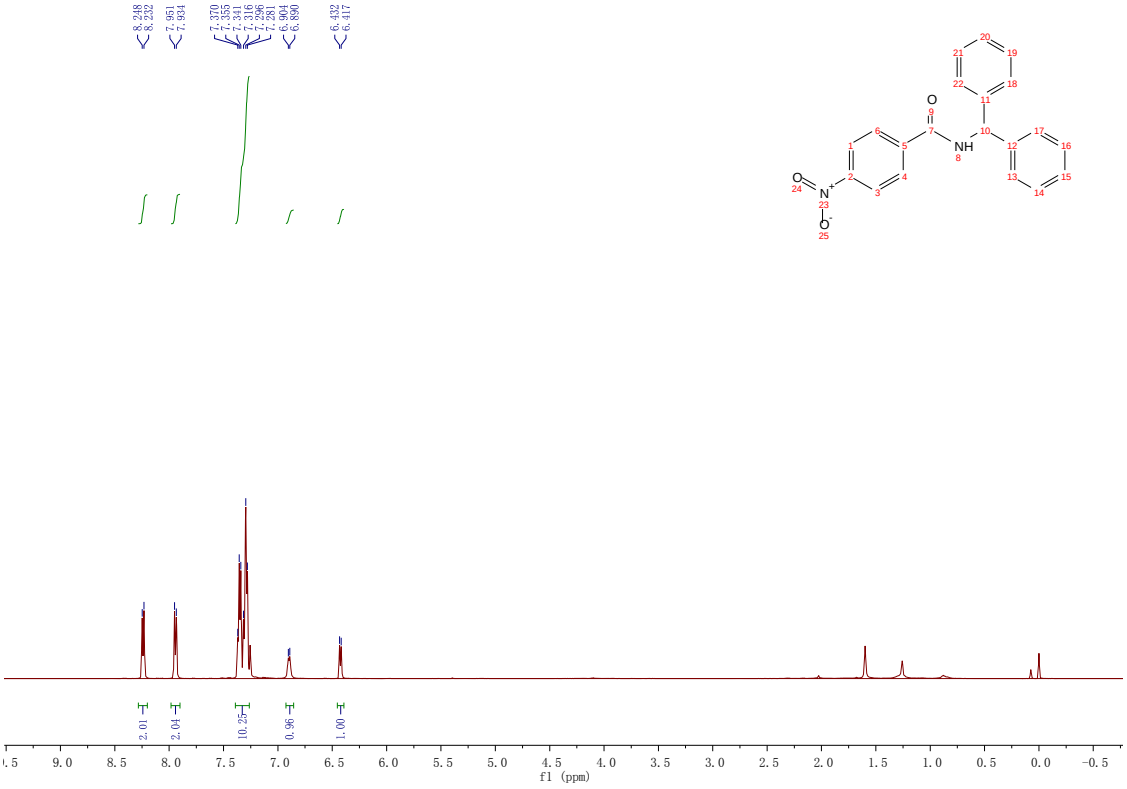




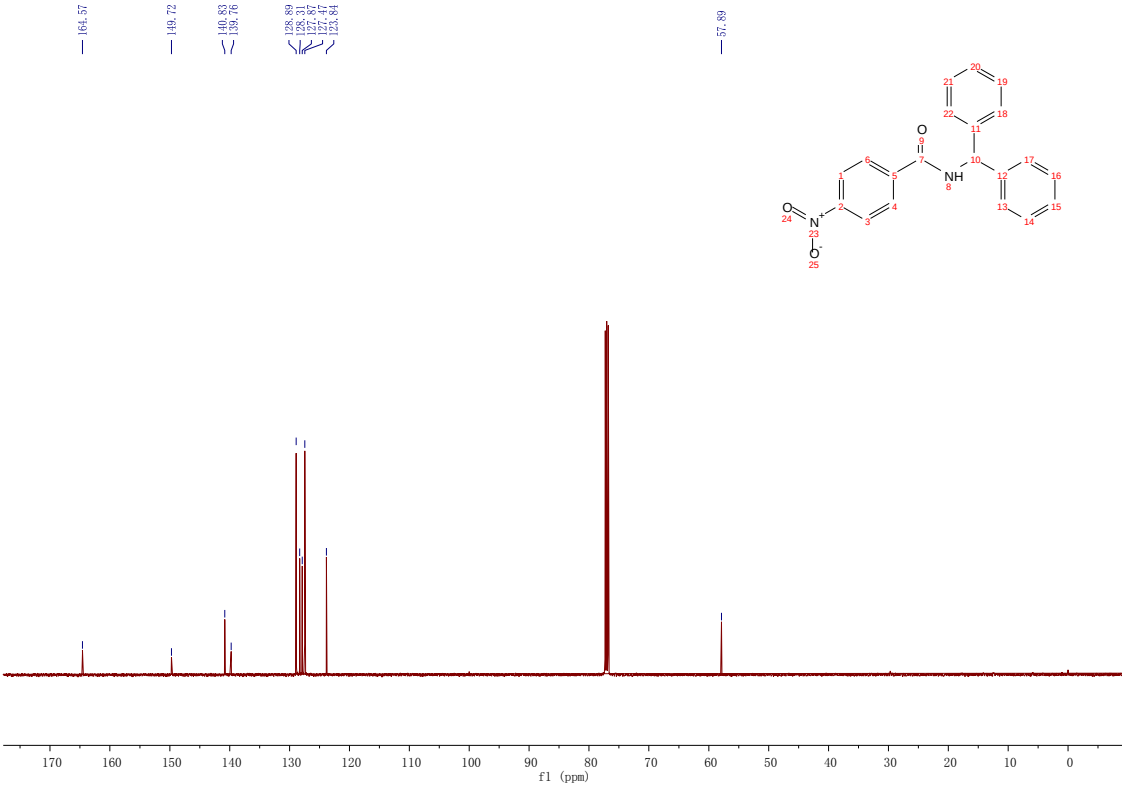


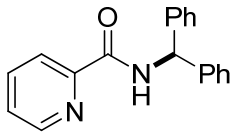
10i

^{1}H NMR



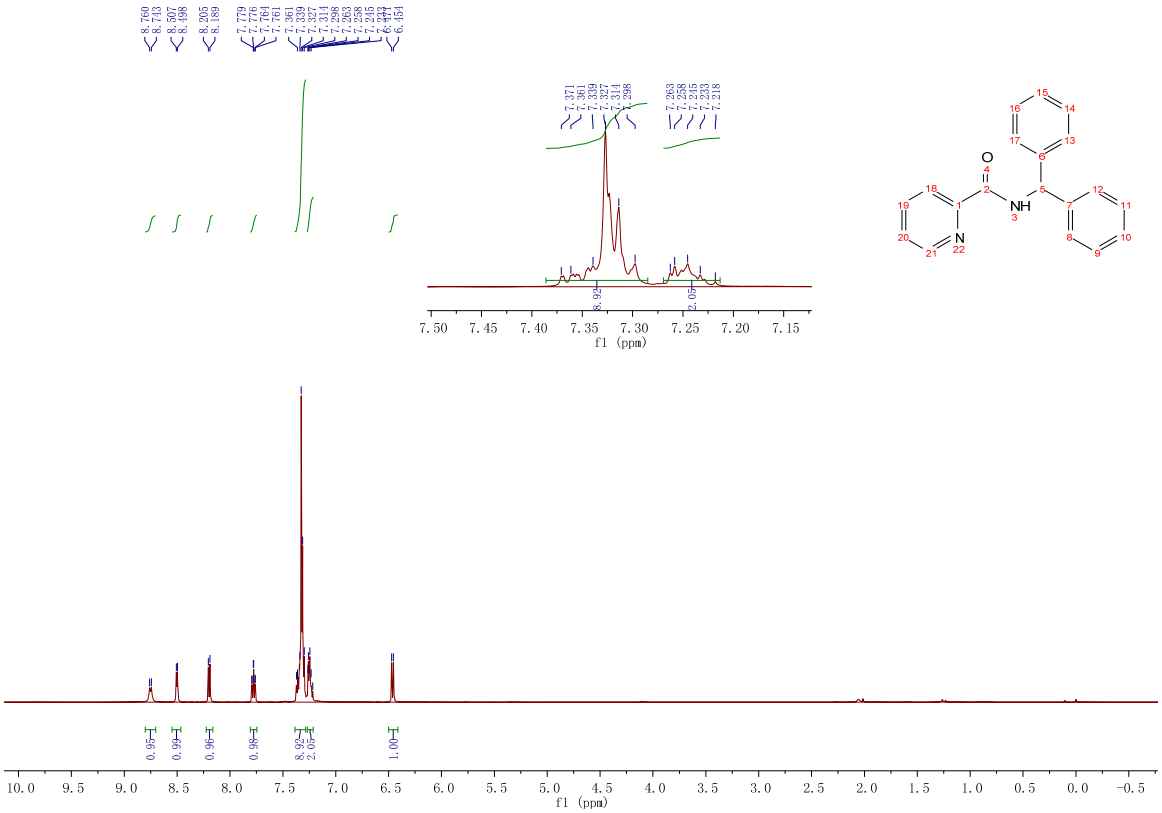
^{13}C NMR



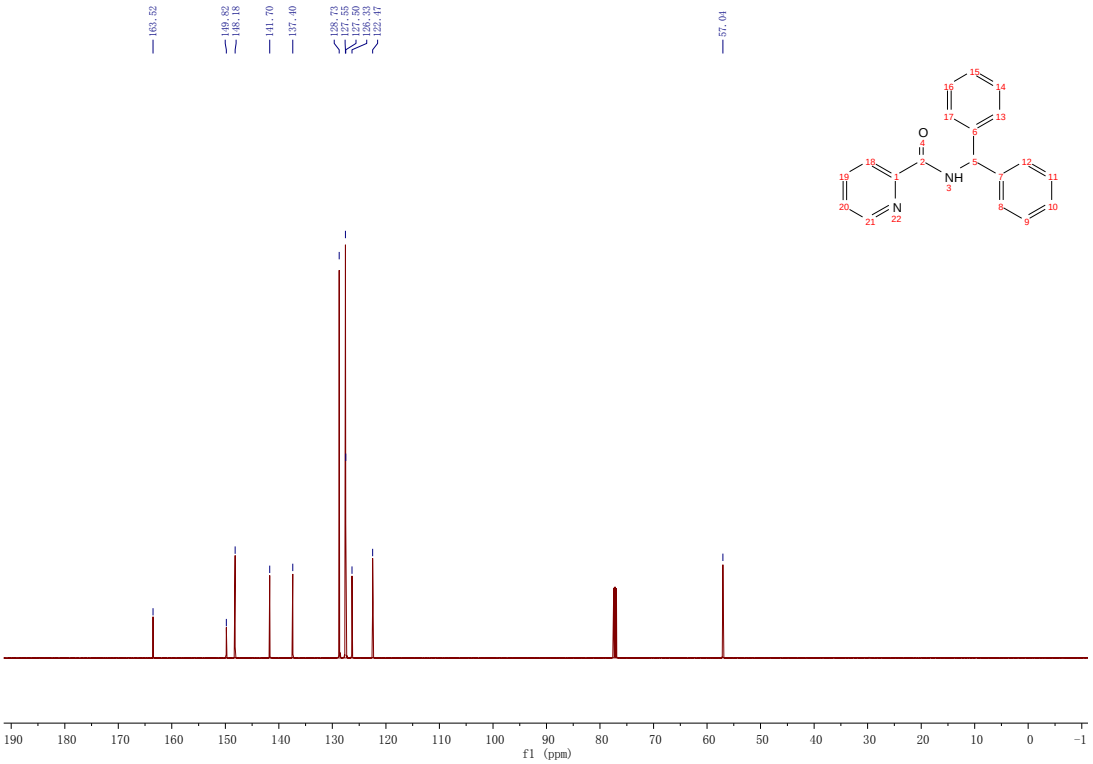


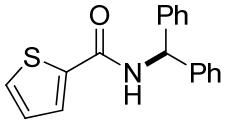
10j

^{1}H NMR



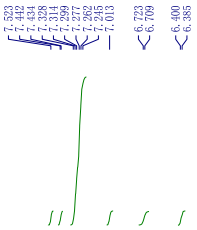
^{13}C NMR

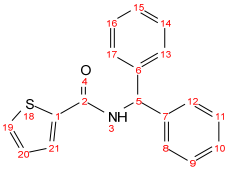


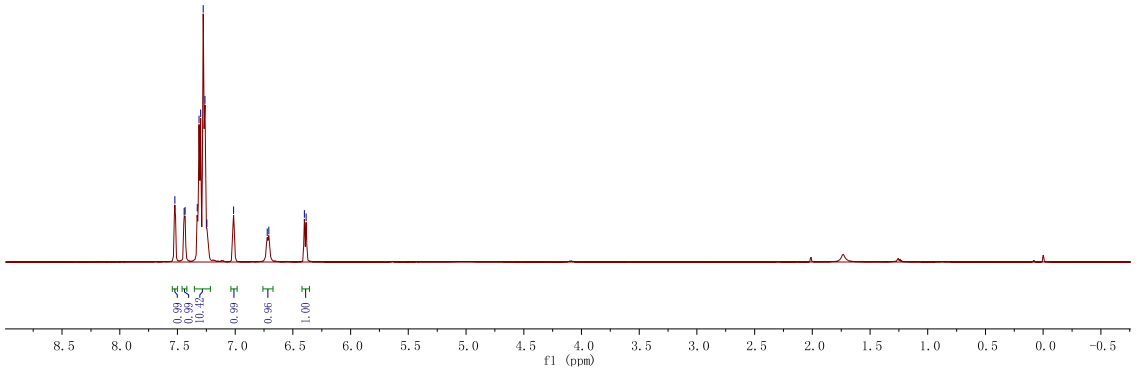


10k

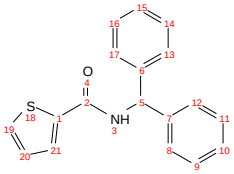
^{1}H NMR

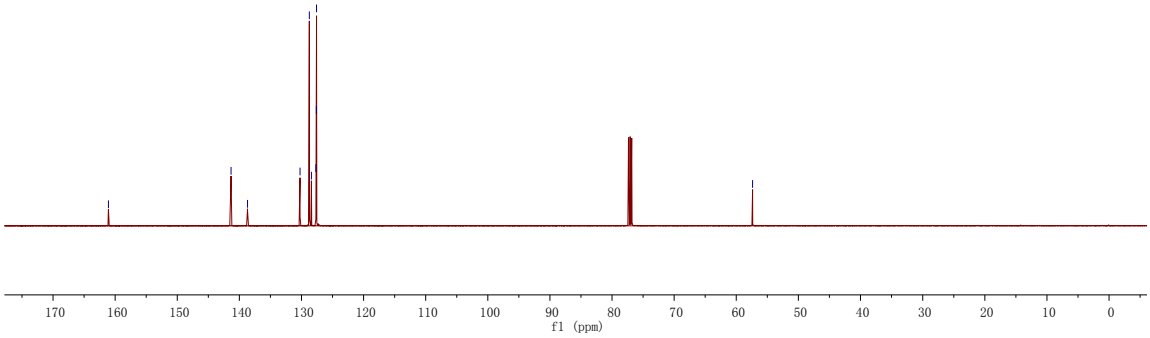


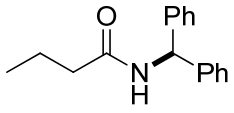




^{13}C NMR

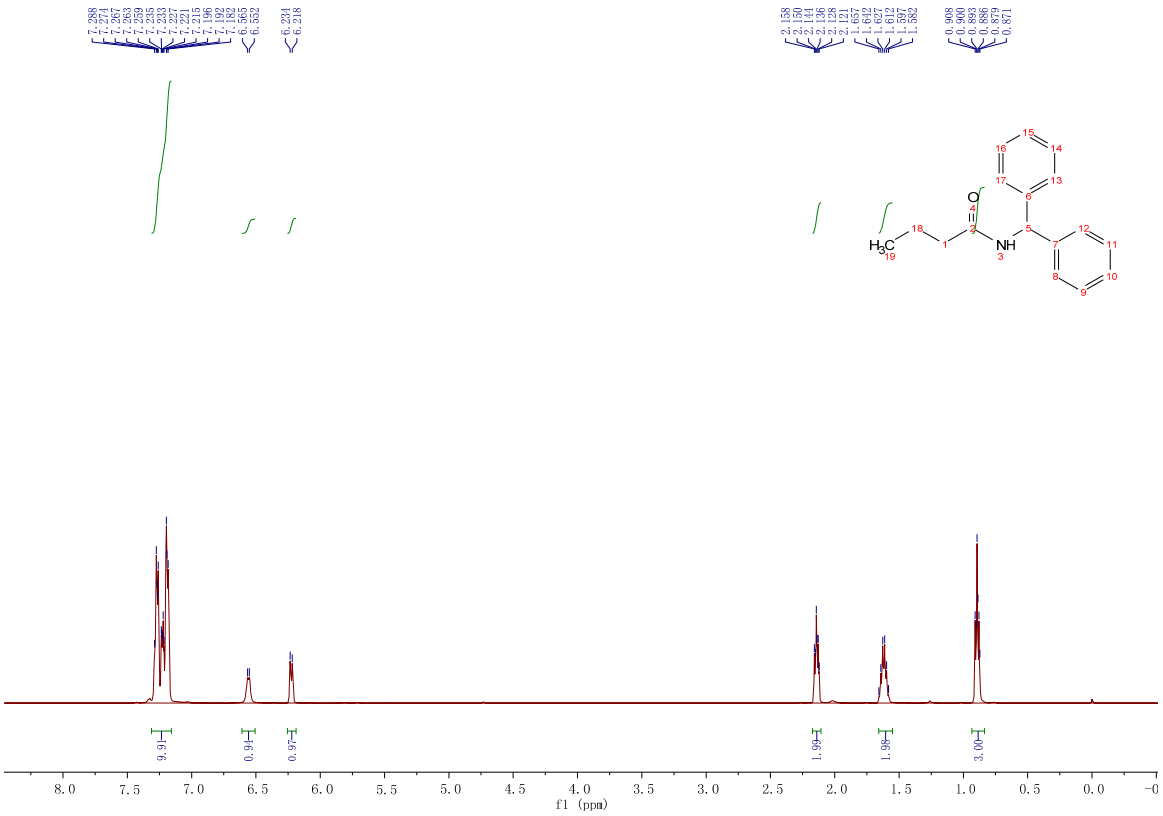




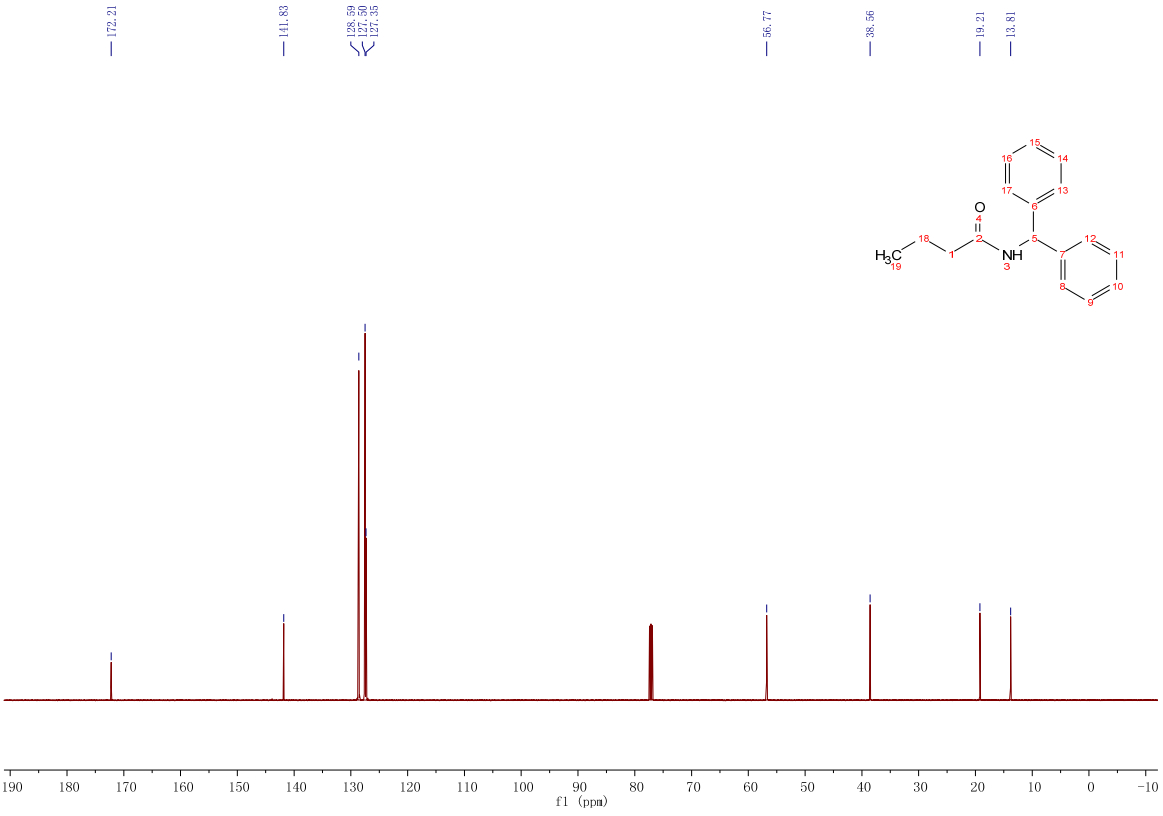


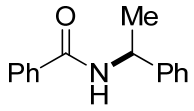
10l

^{1}H NMR



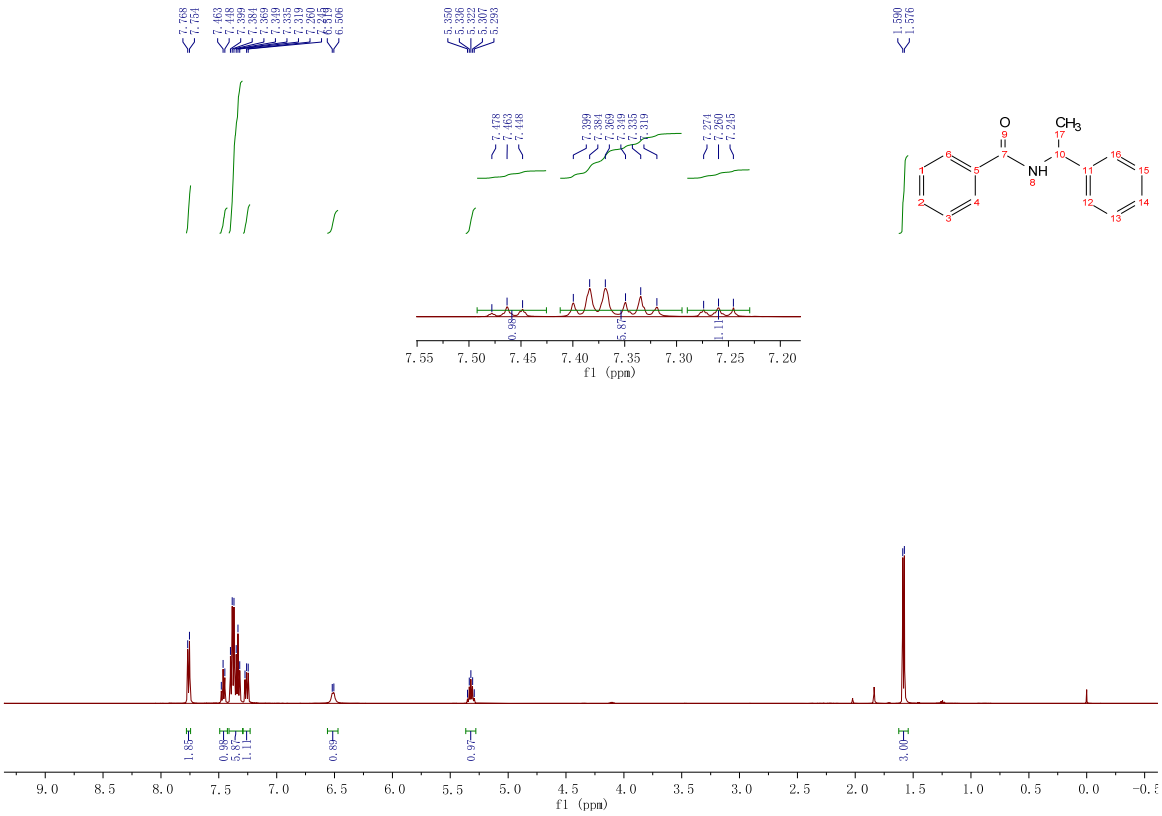
^{13}C NMR



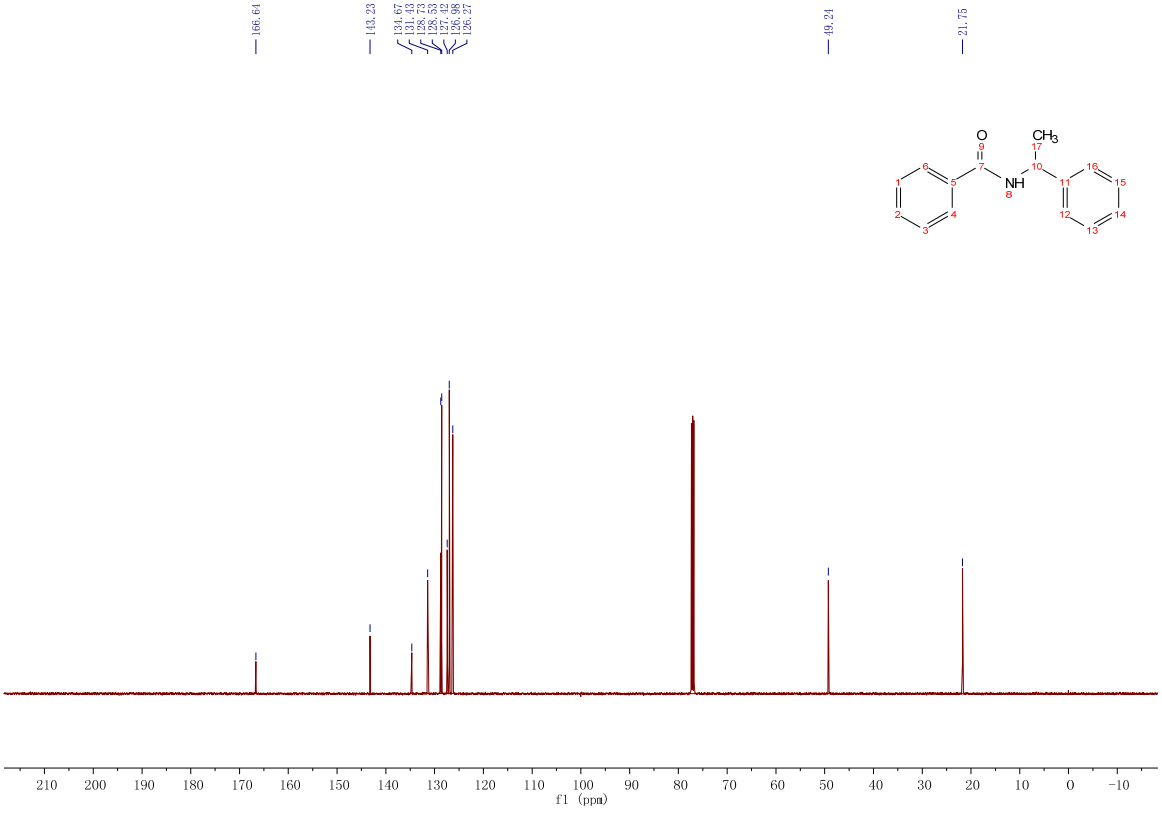


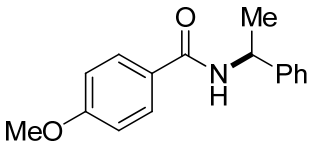
10m

^{1}H NMR



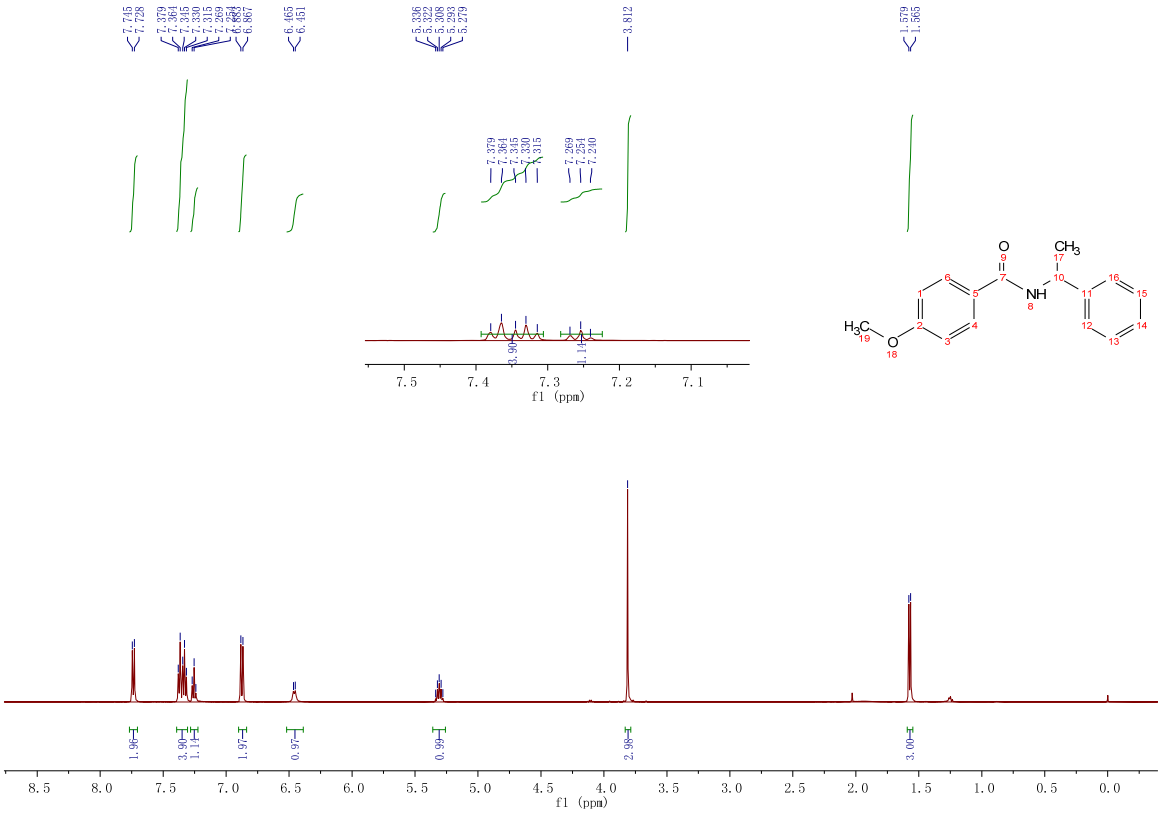
^{13}C NMR





10n

^{1}H NMR



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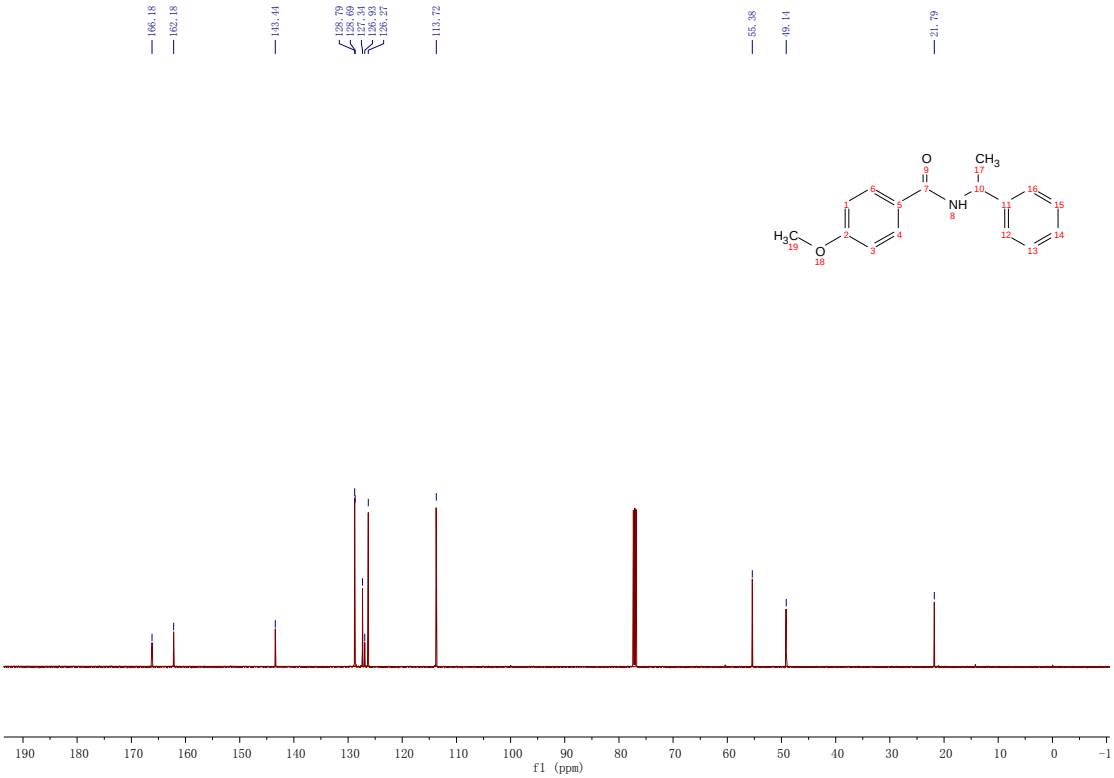
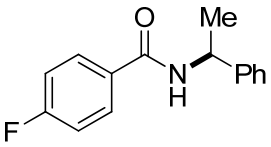
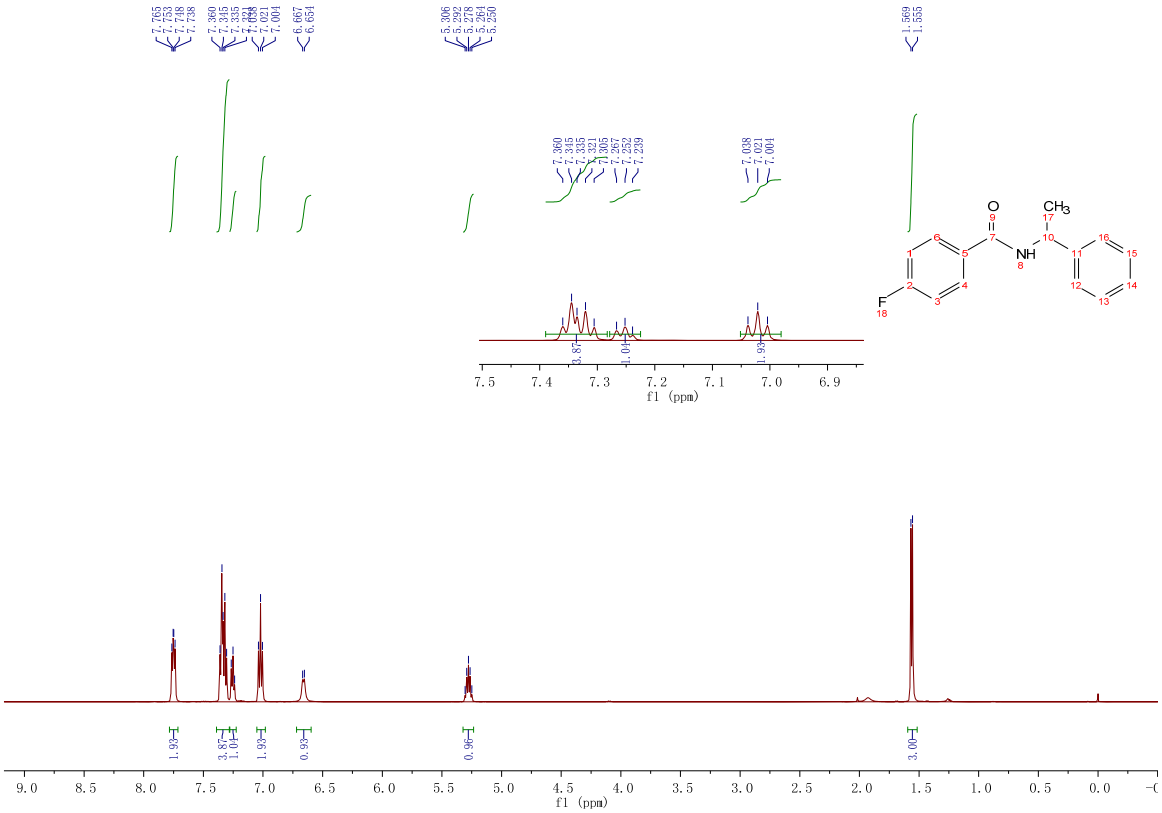


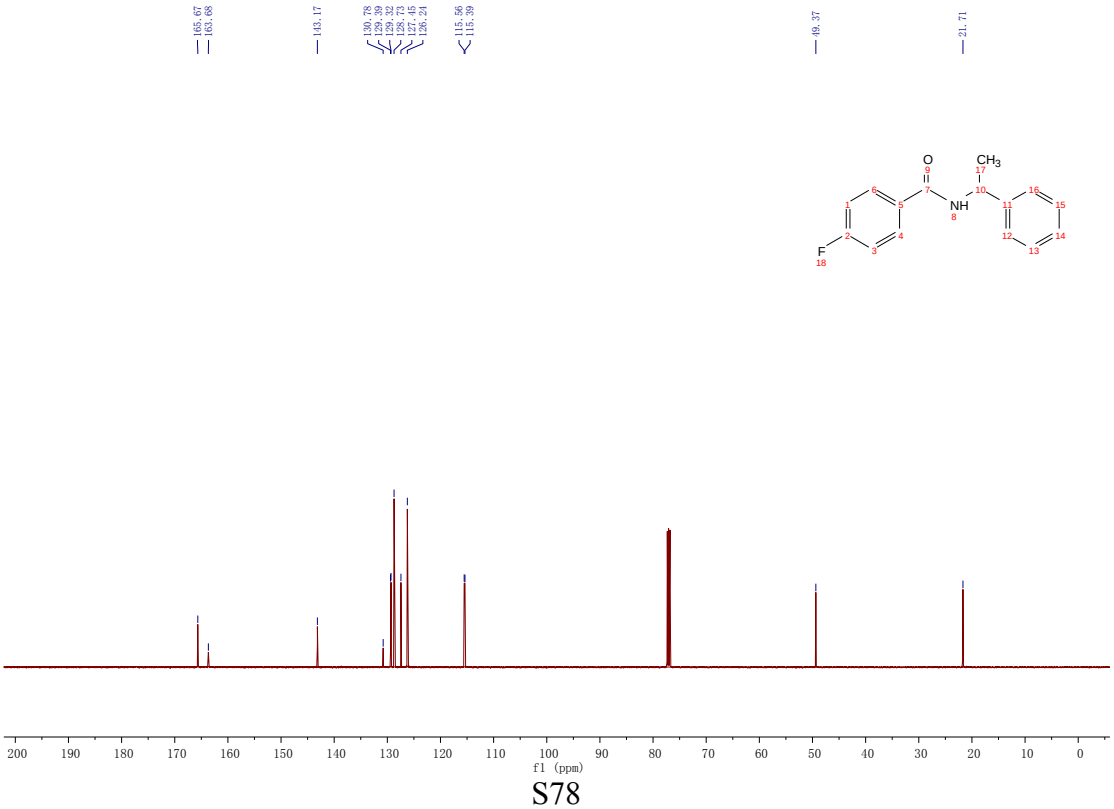


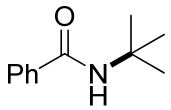
10o

^{1}H NMR



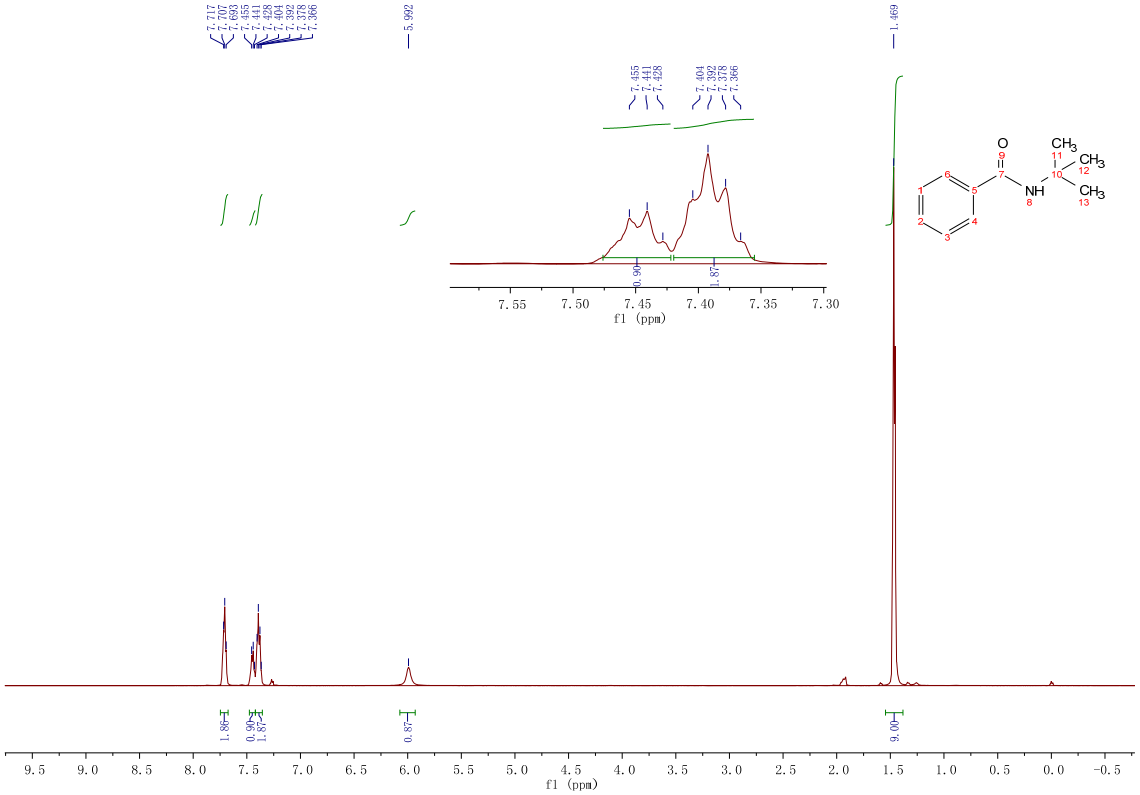
^{13}C NMR



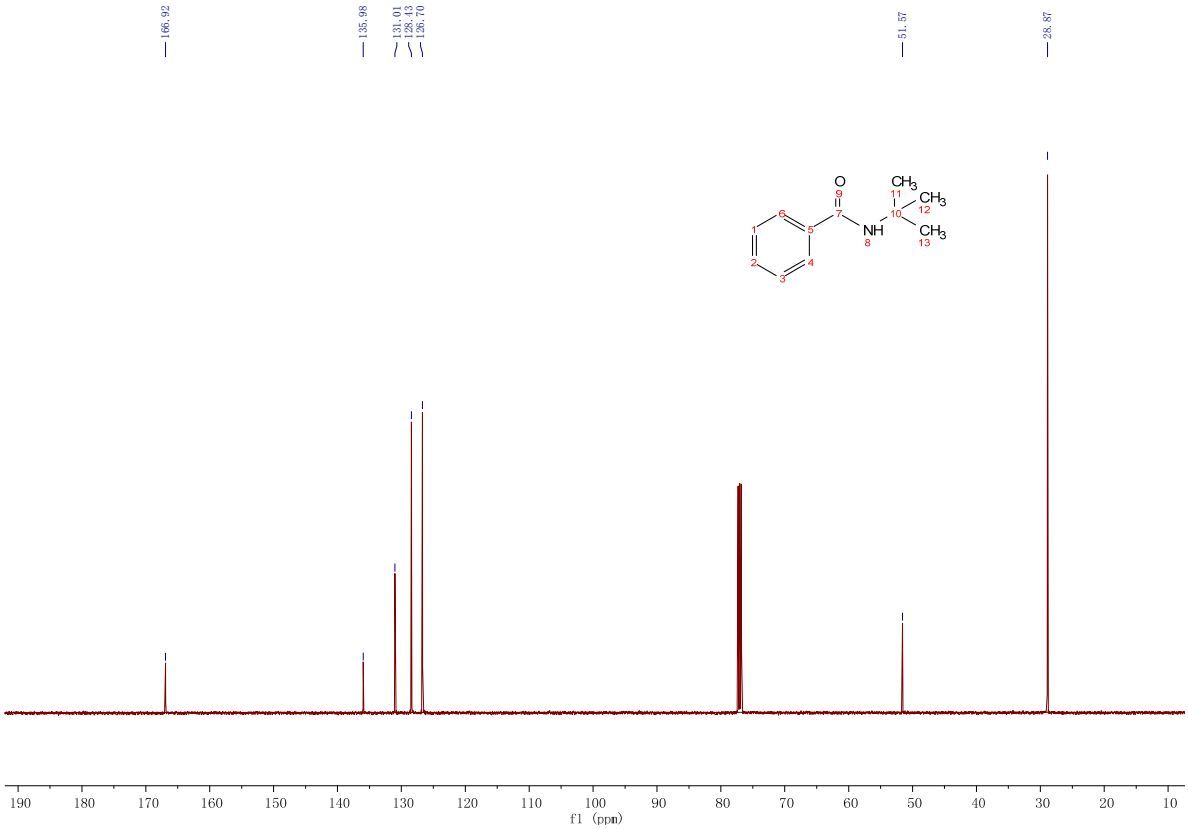


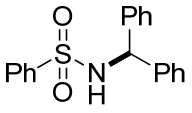
10p

^{1}H NMR



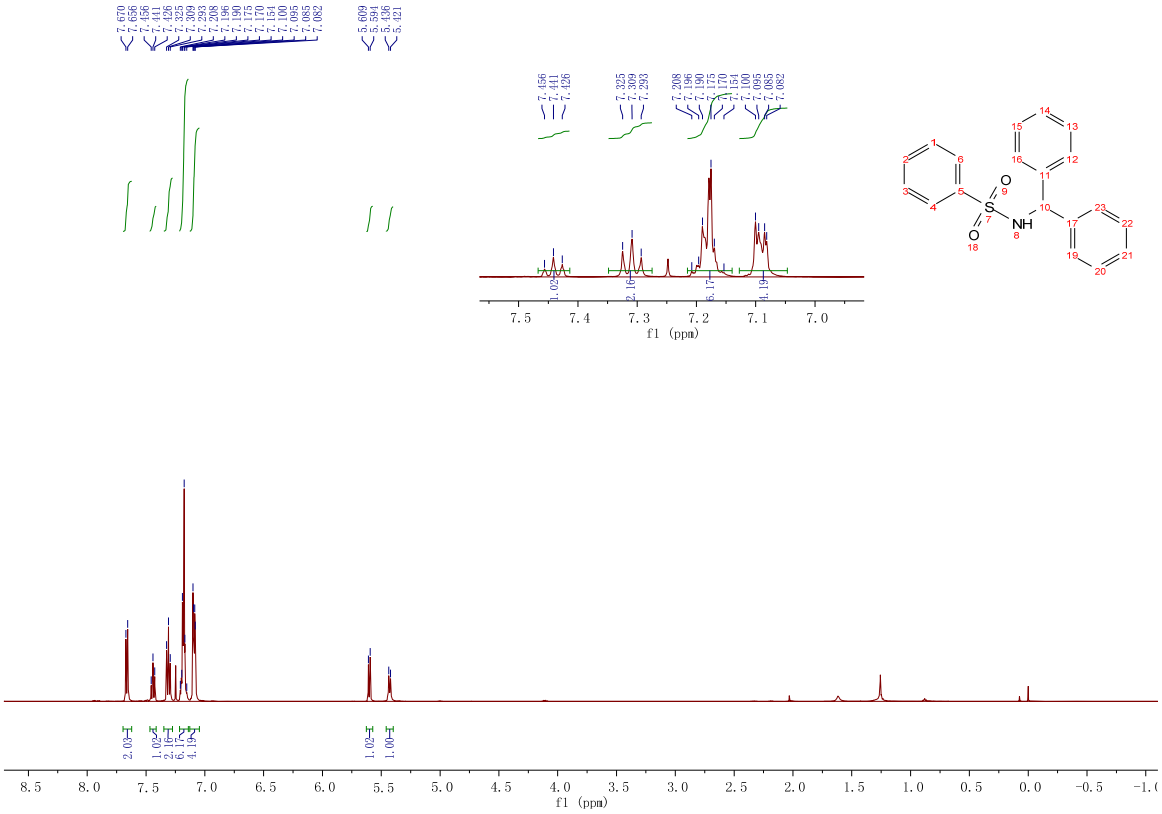
^{13}C NMR



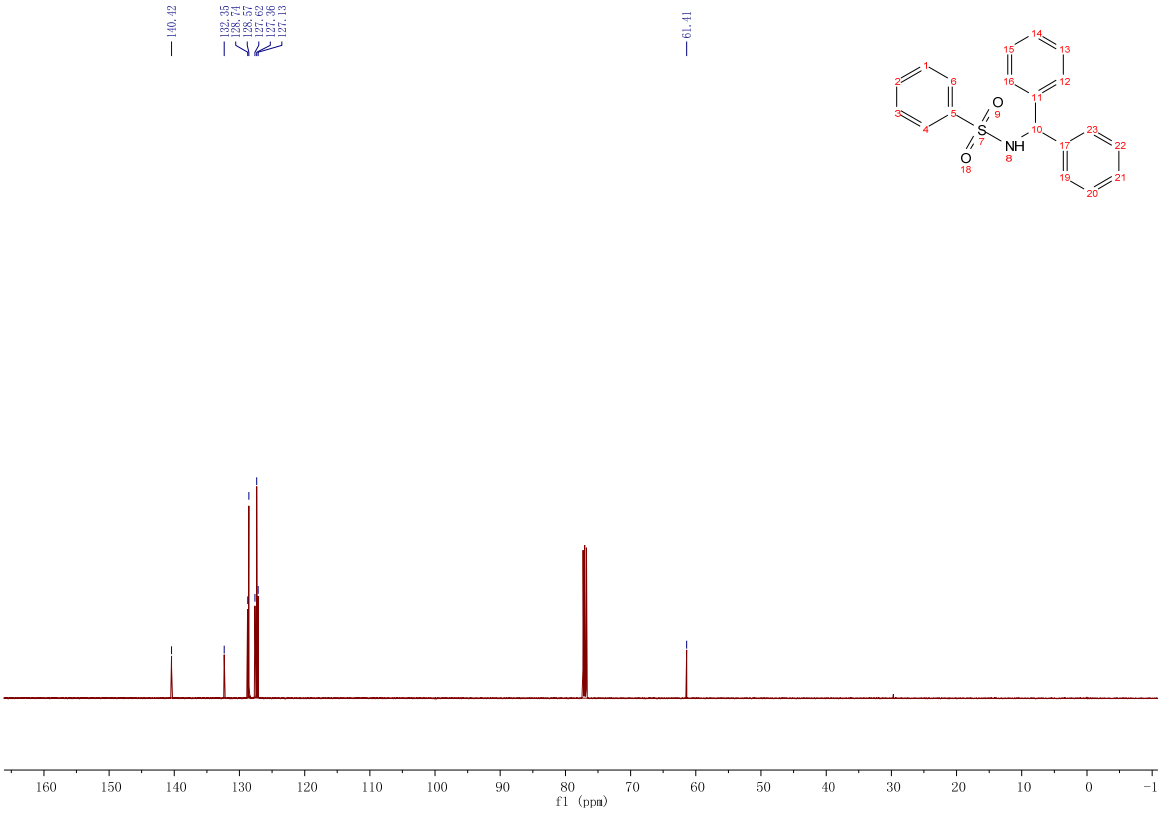


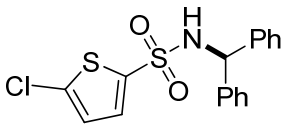
11a

^{1}H NMR



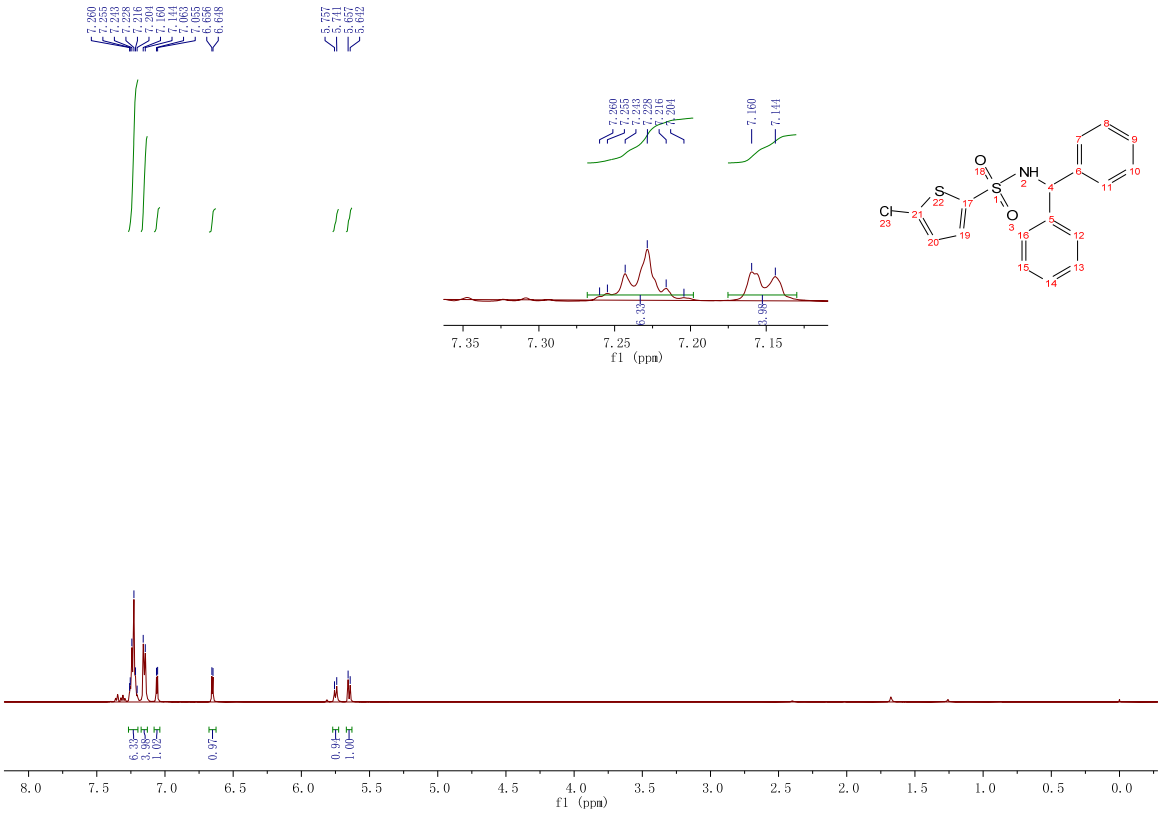
^{13}C NMR



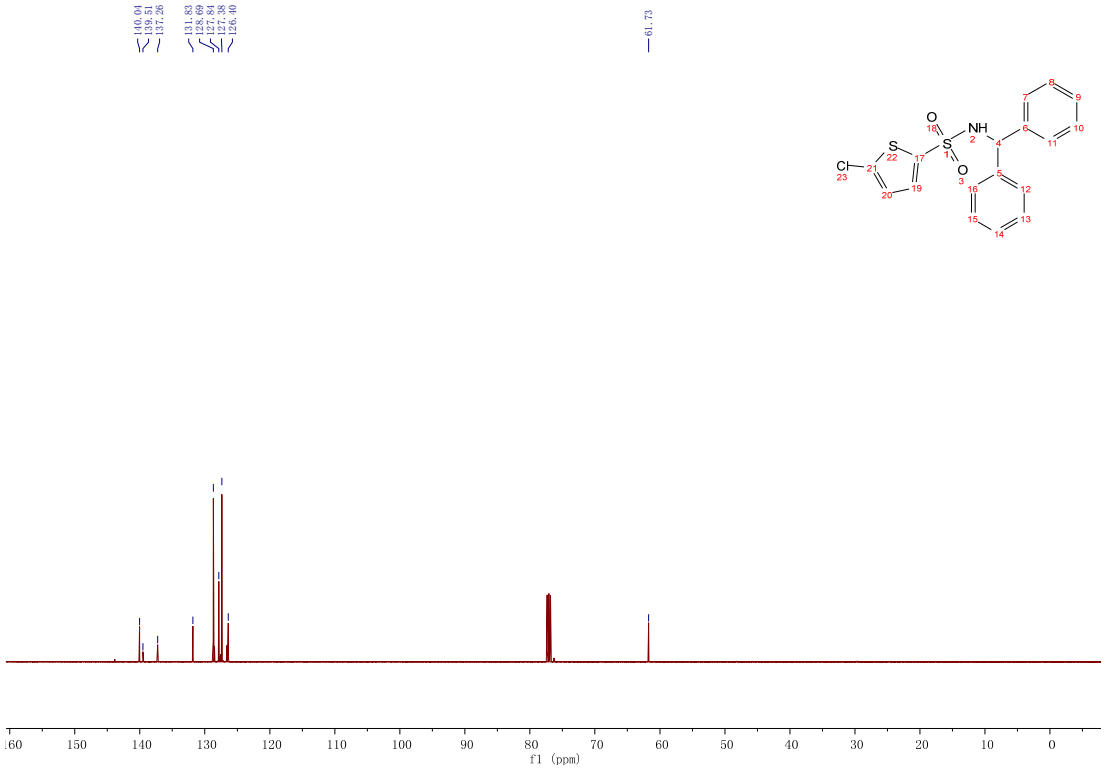


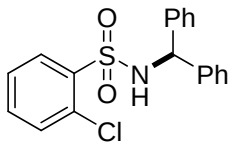
11b

^{1}H NMR



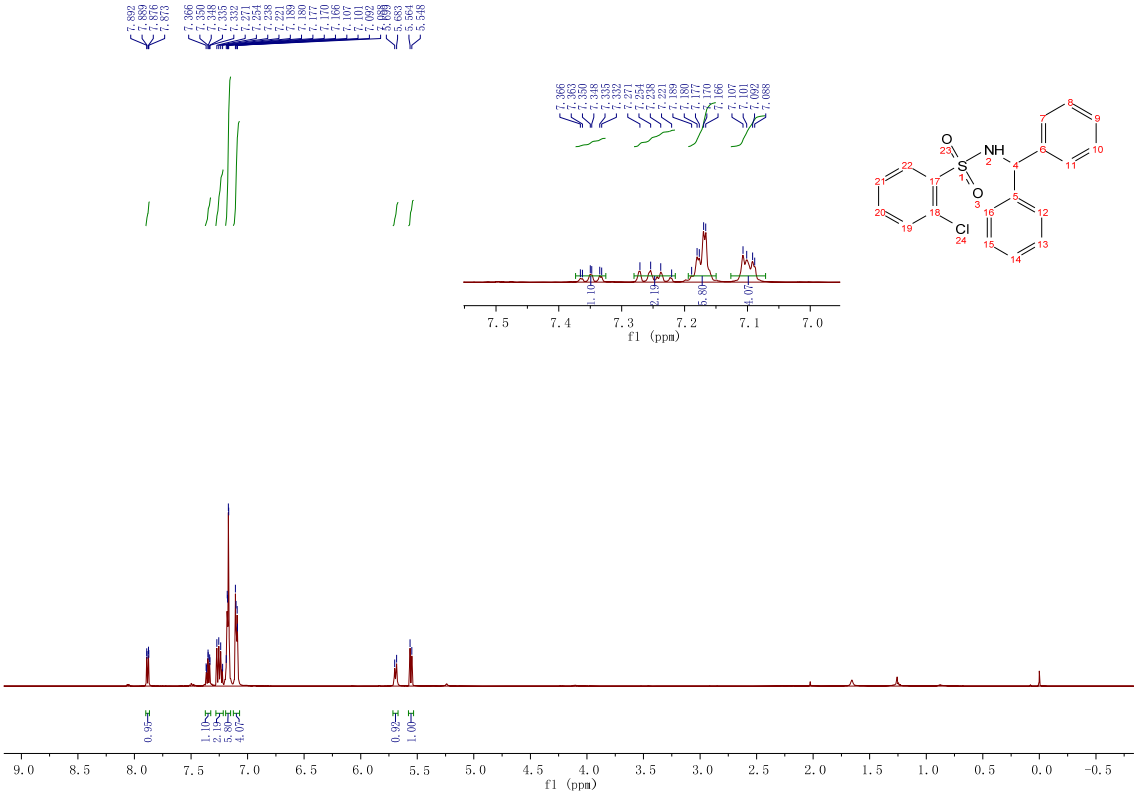
^{13}C NMR



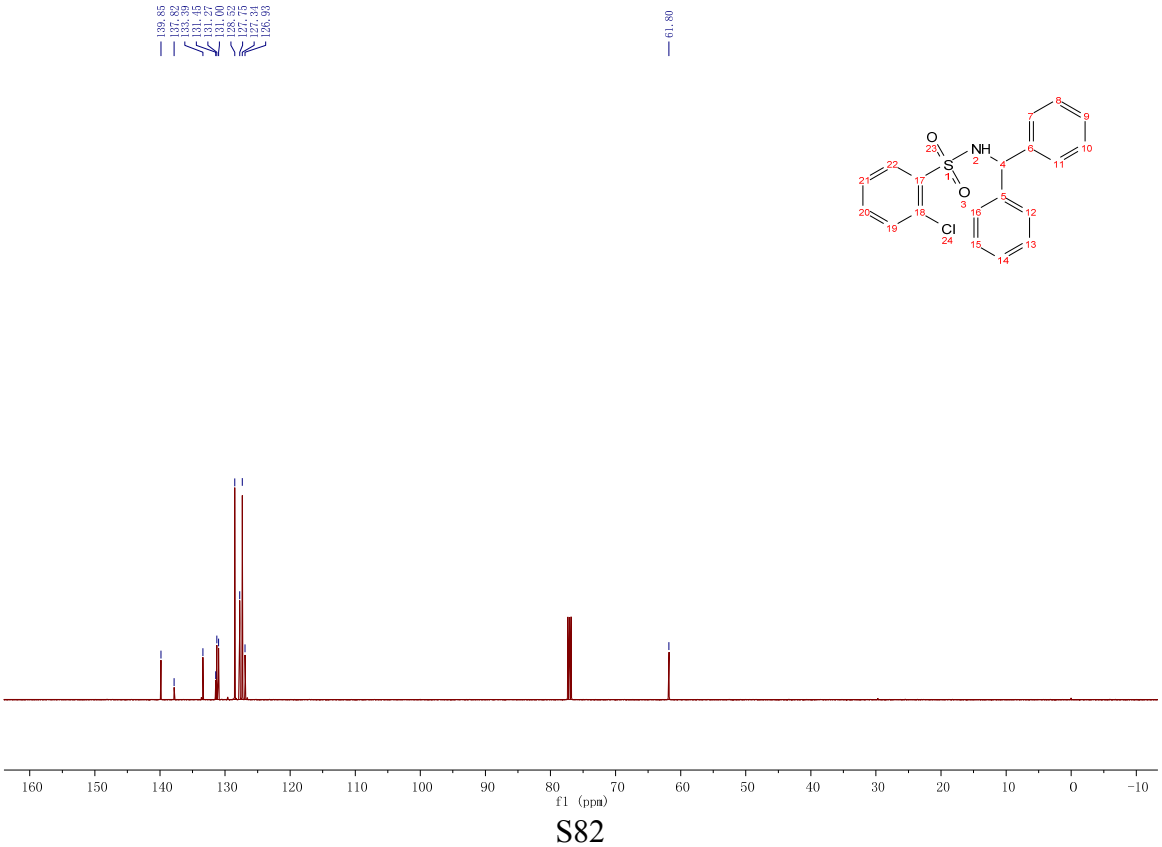


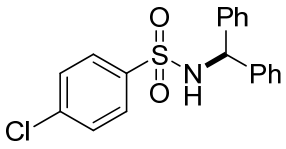
11c

^{1}H NMR



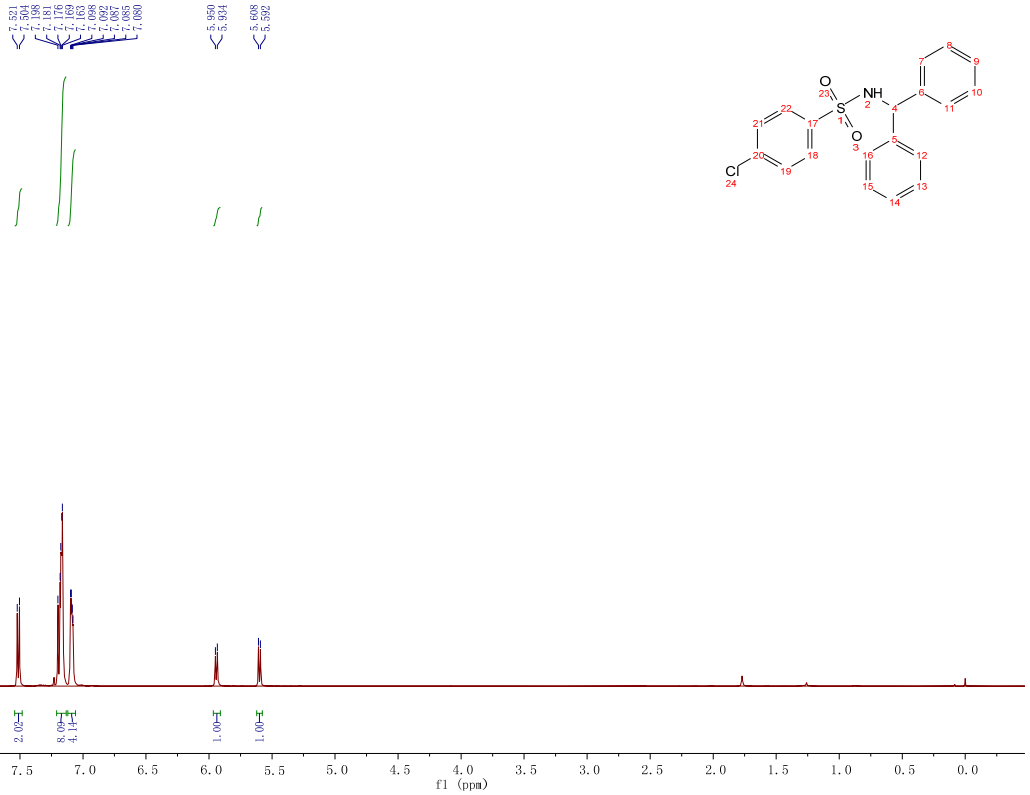
^{13}C NMR



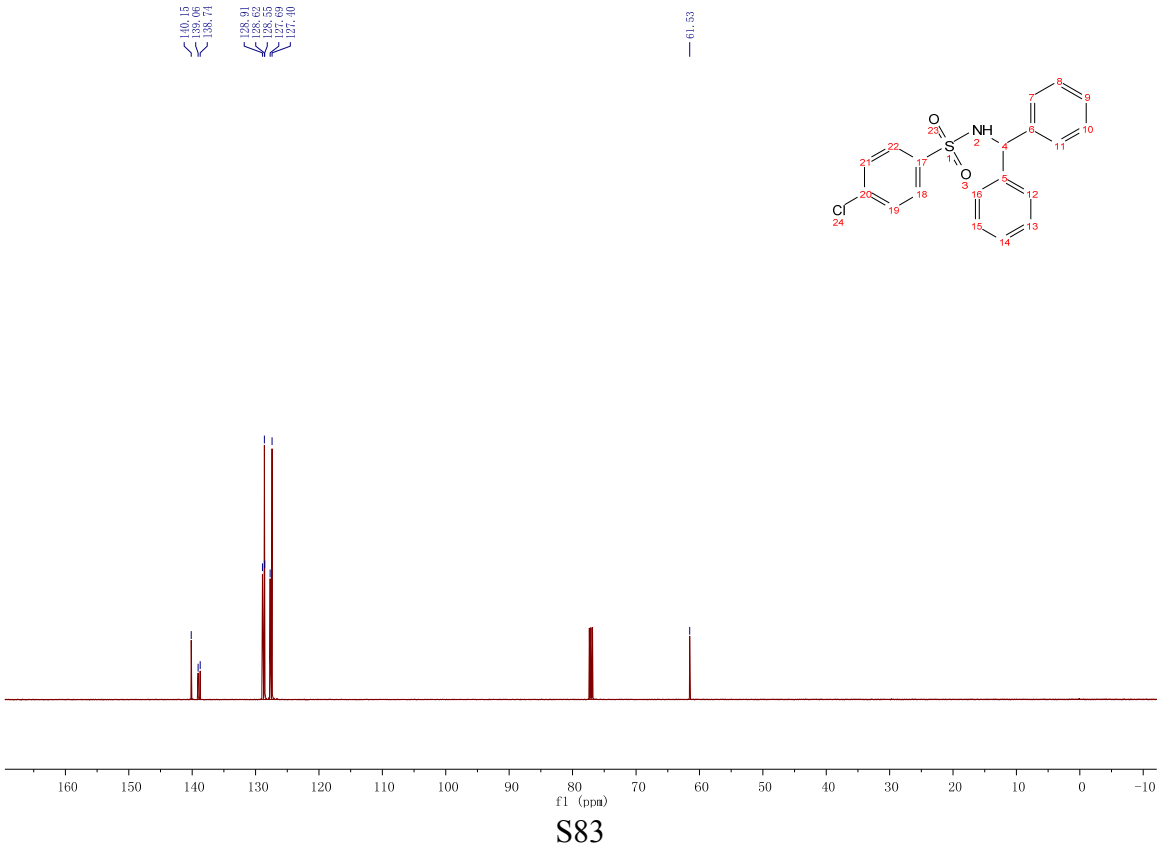


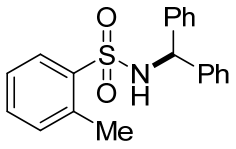
10d

^{1}H NMR



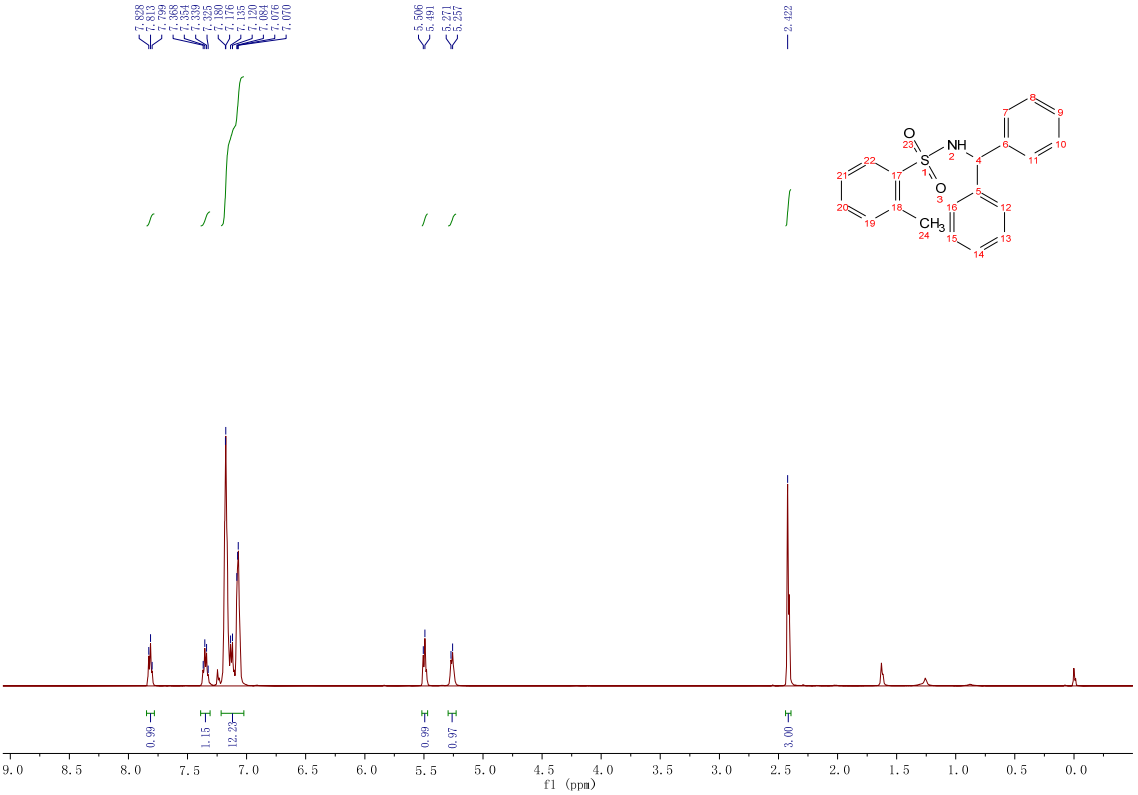
^{13}C NMR



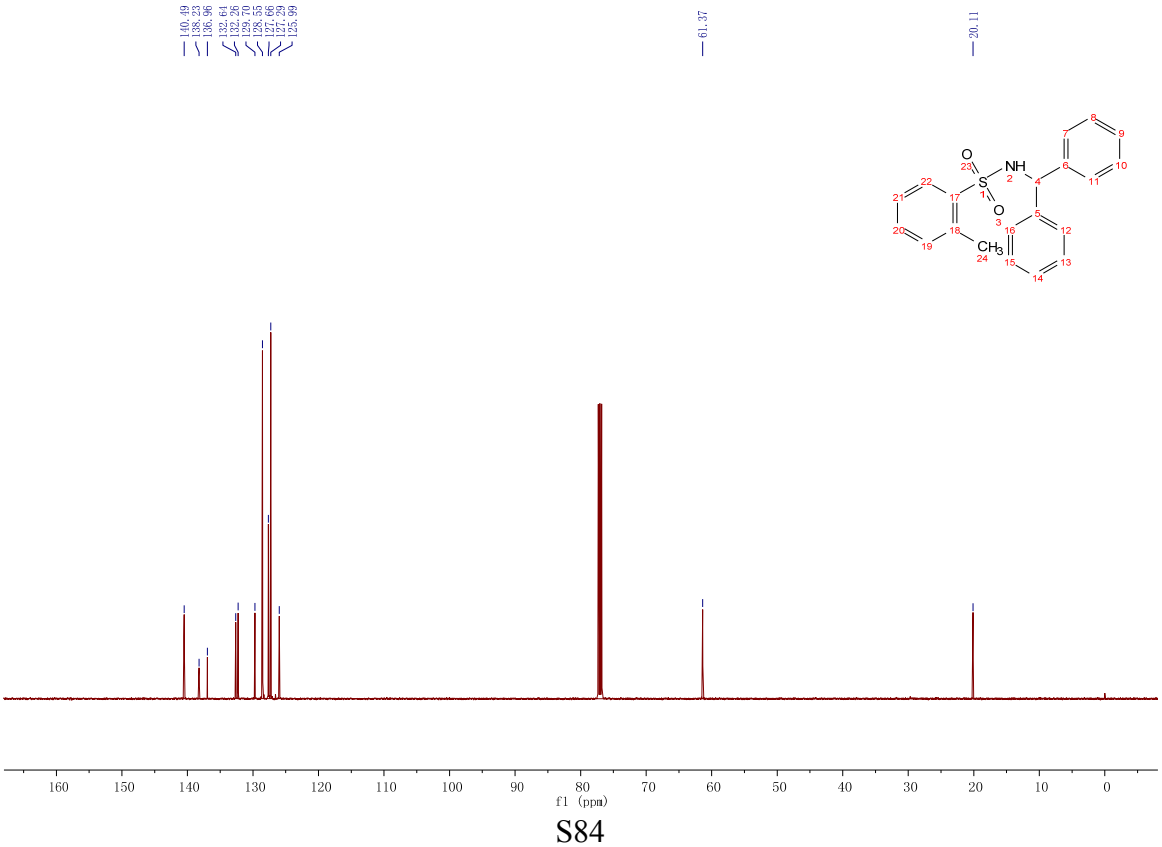


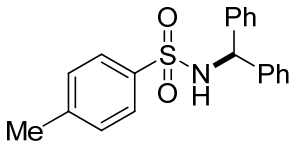
11e

^{1}H NMR



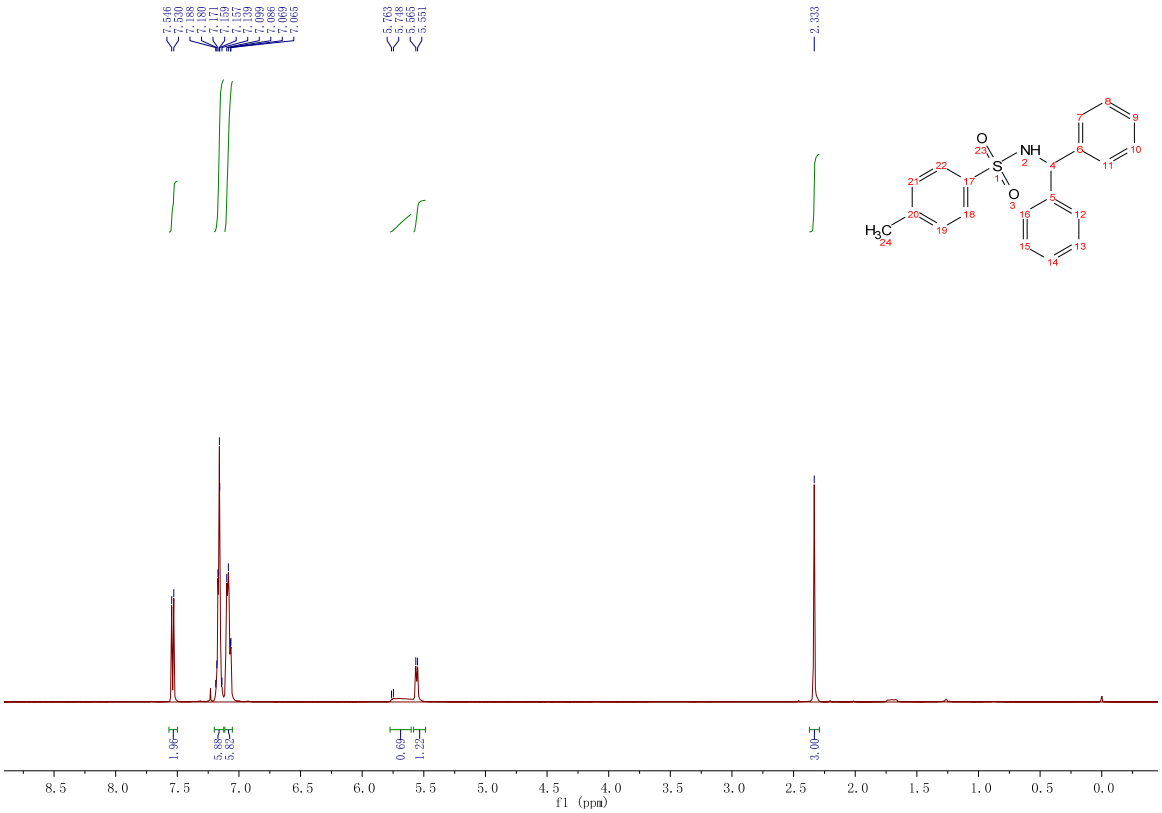
^{13}C NMR



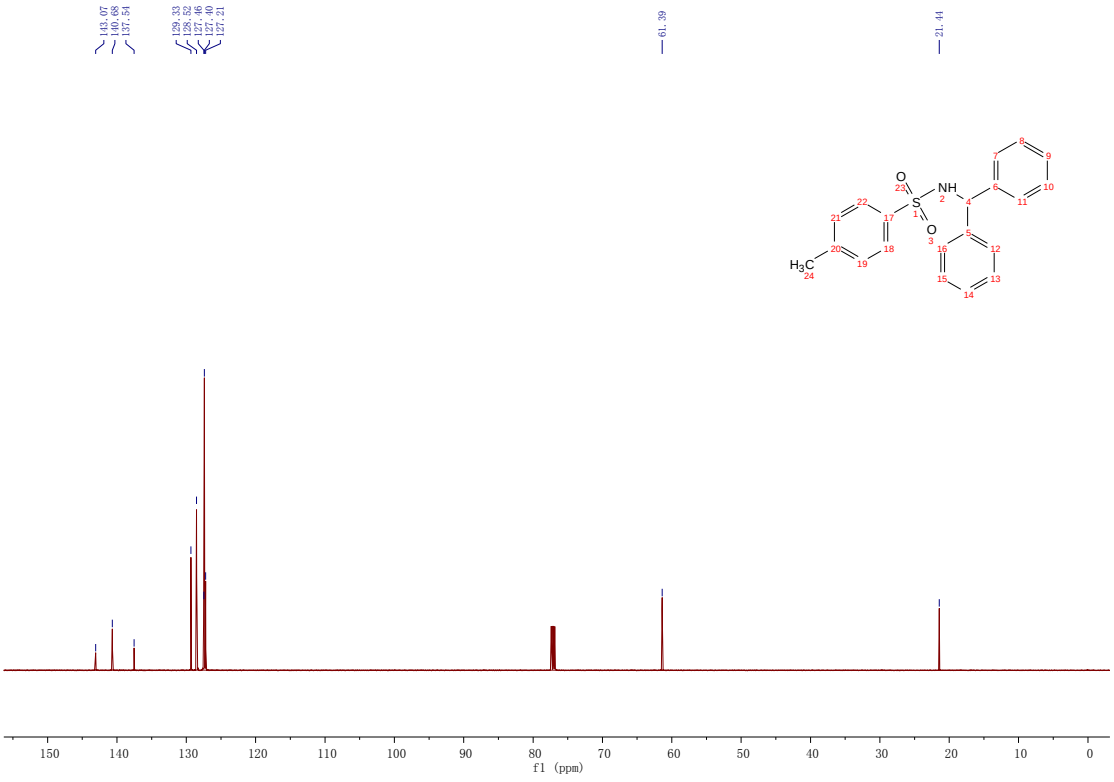


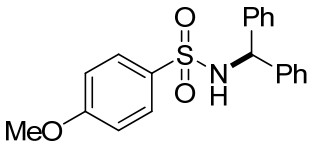
11f

^{1}H NMR



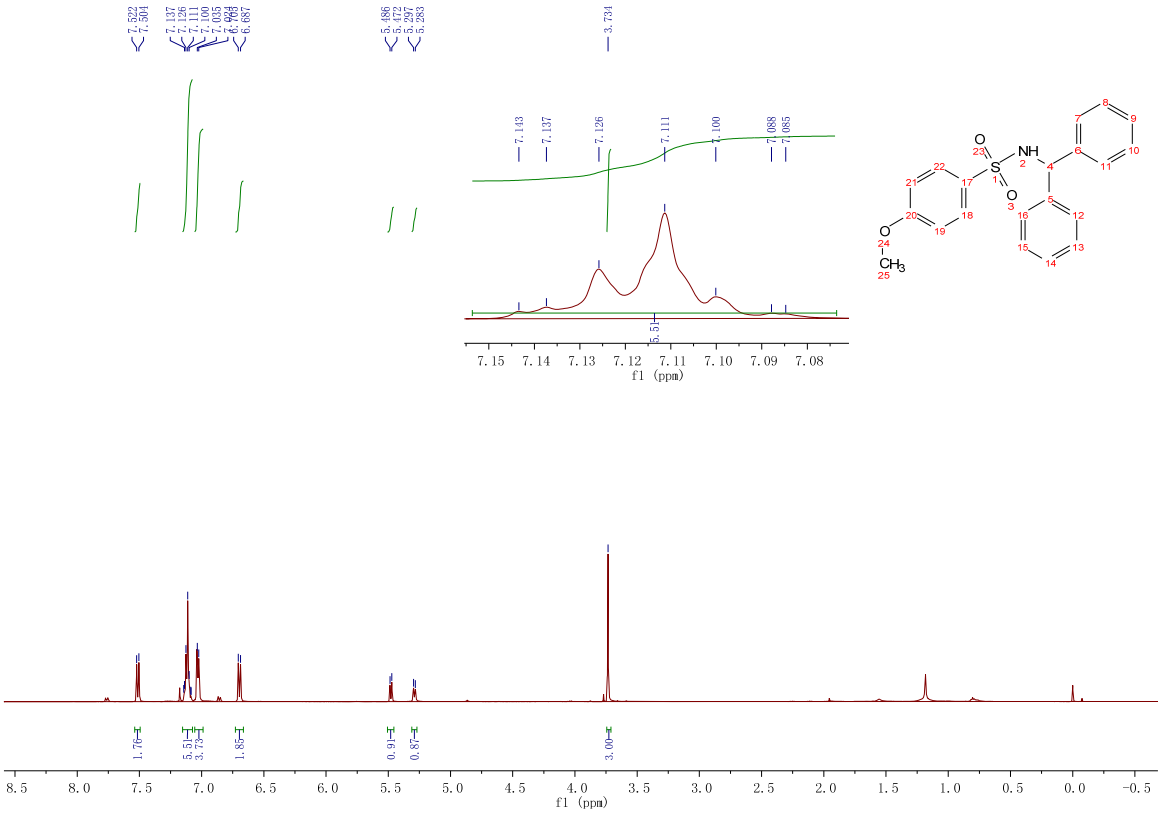
^{13}C NMR



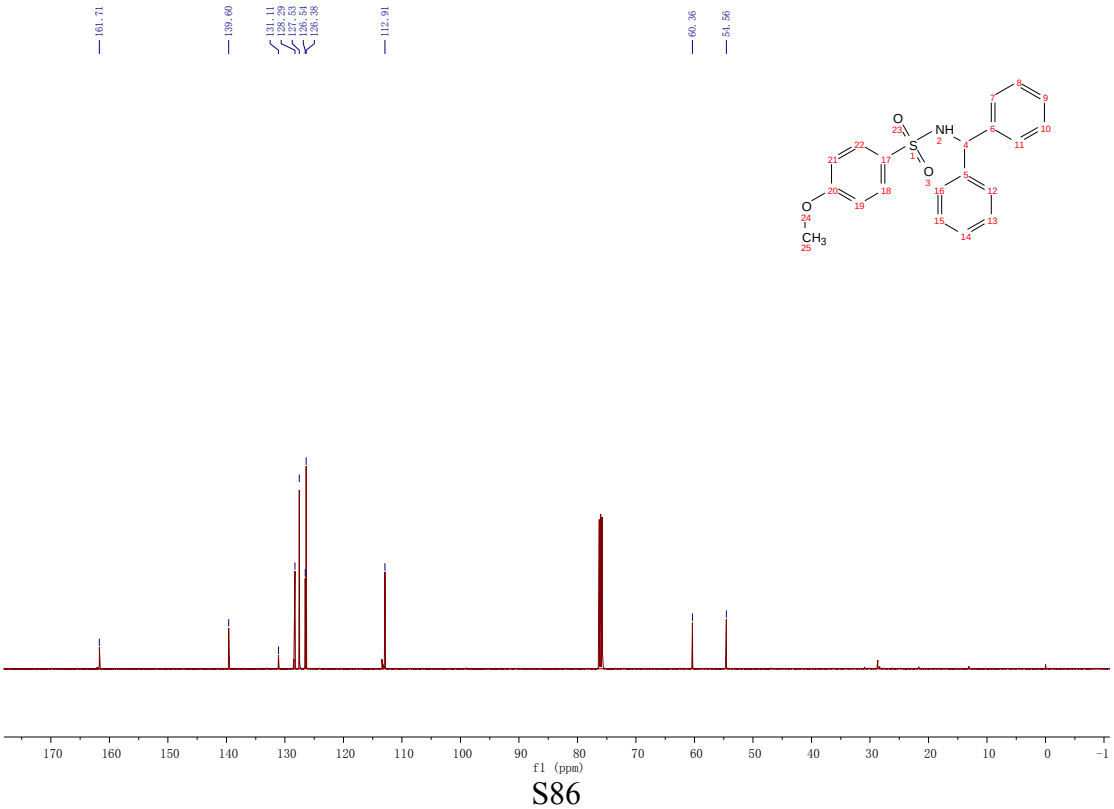


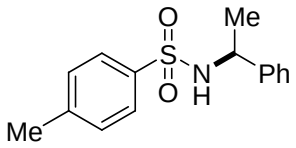
11g

^{1}H NMR

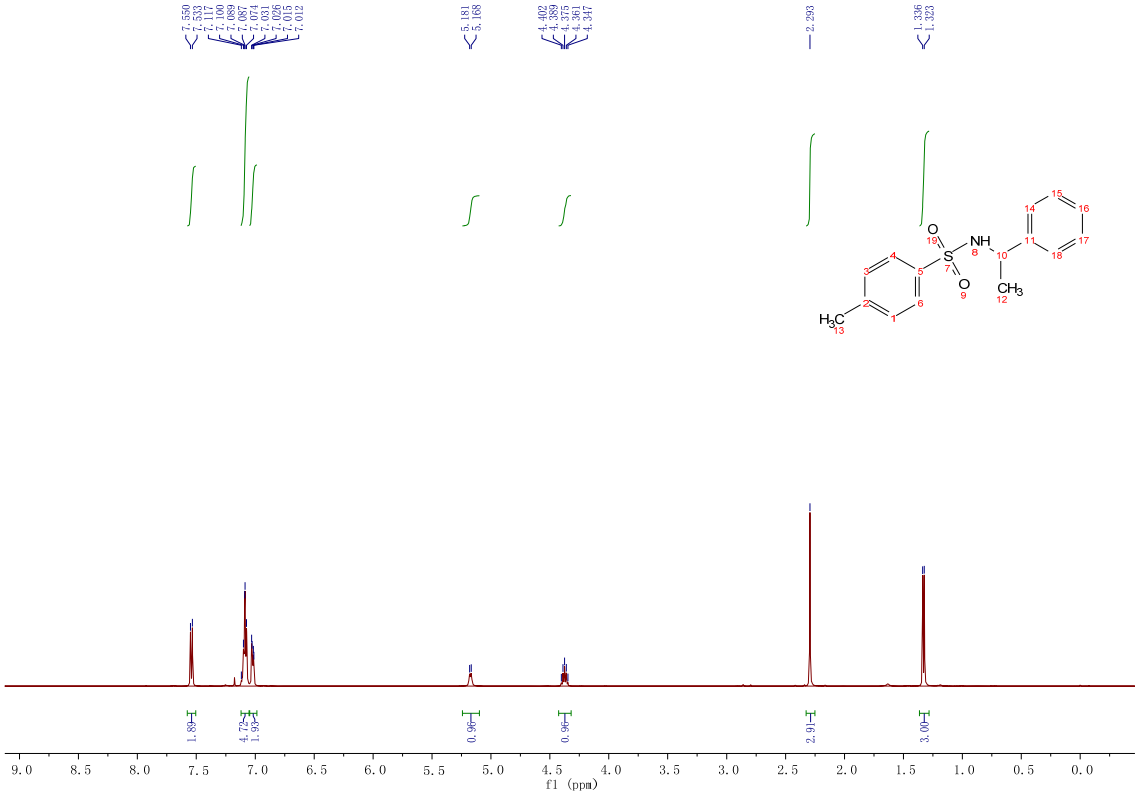


^{13}C NMR

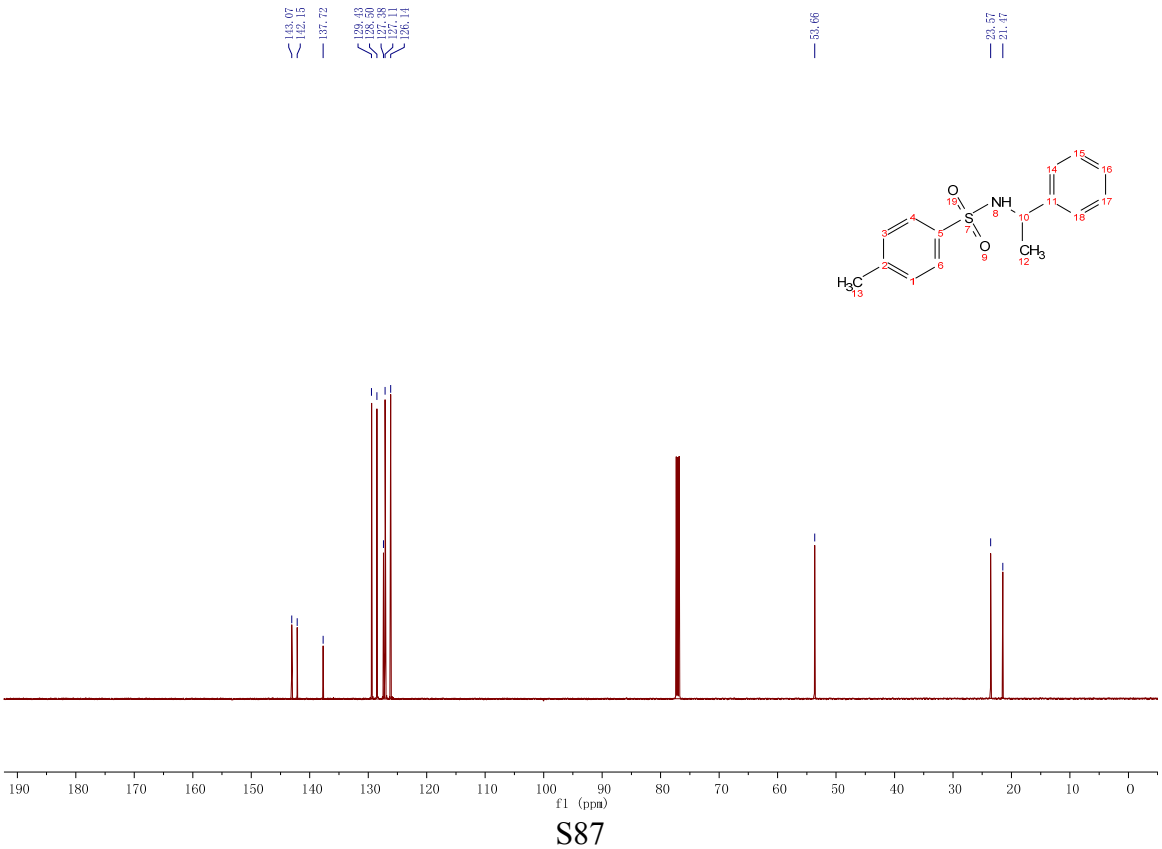




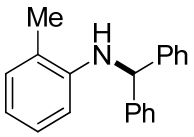
^{1}H NMR



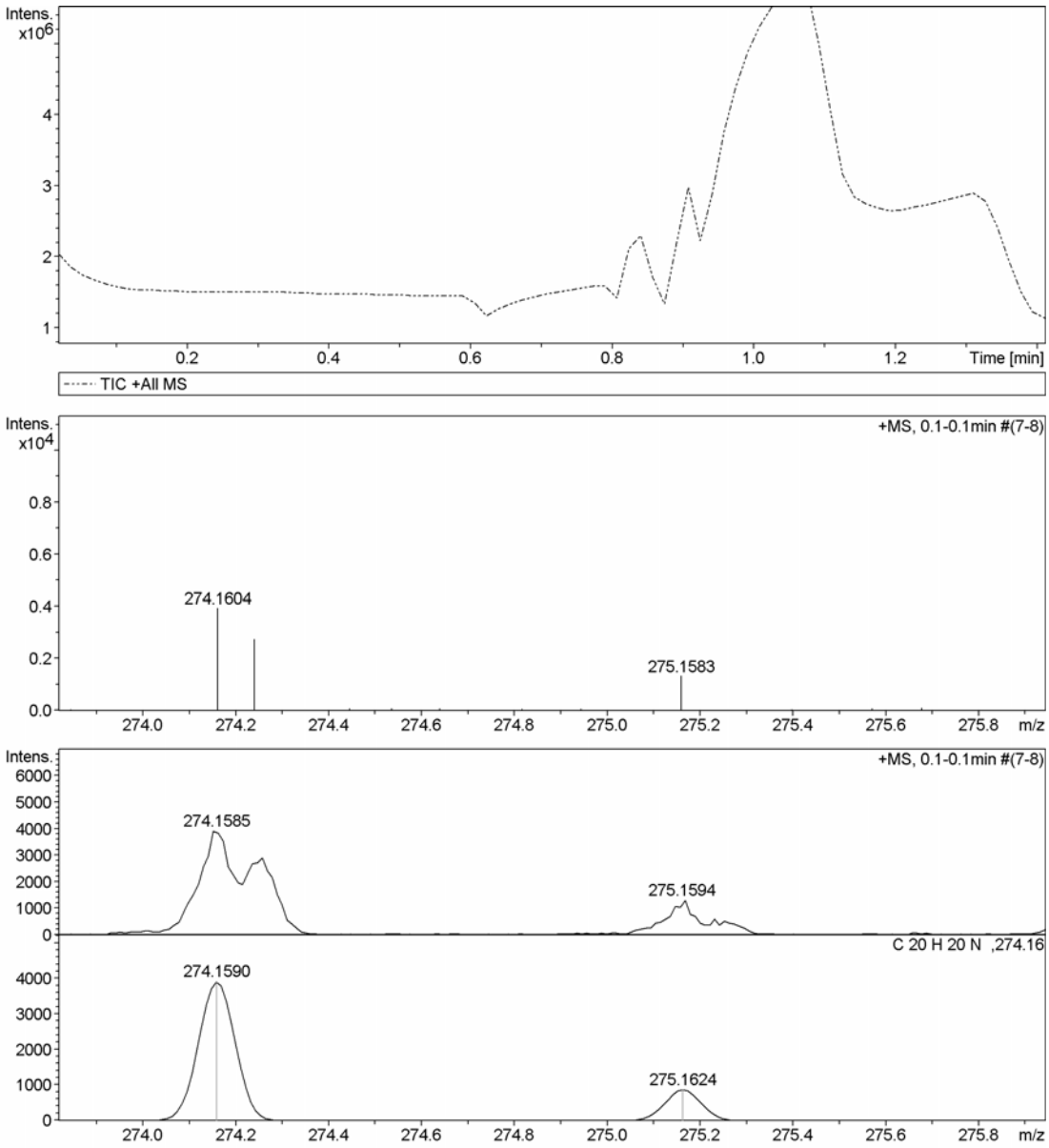
^{13}C NMR

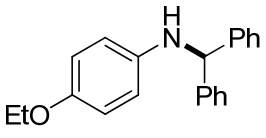


HRMS Spectra of the Unknown Products

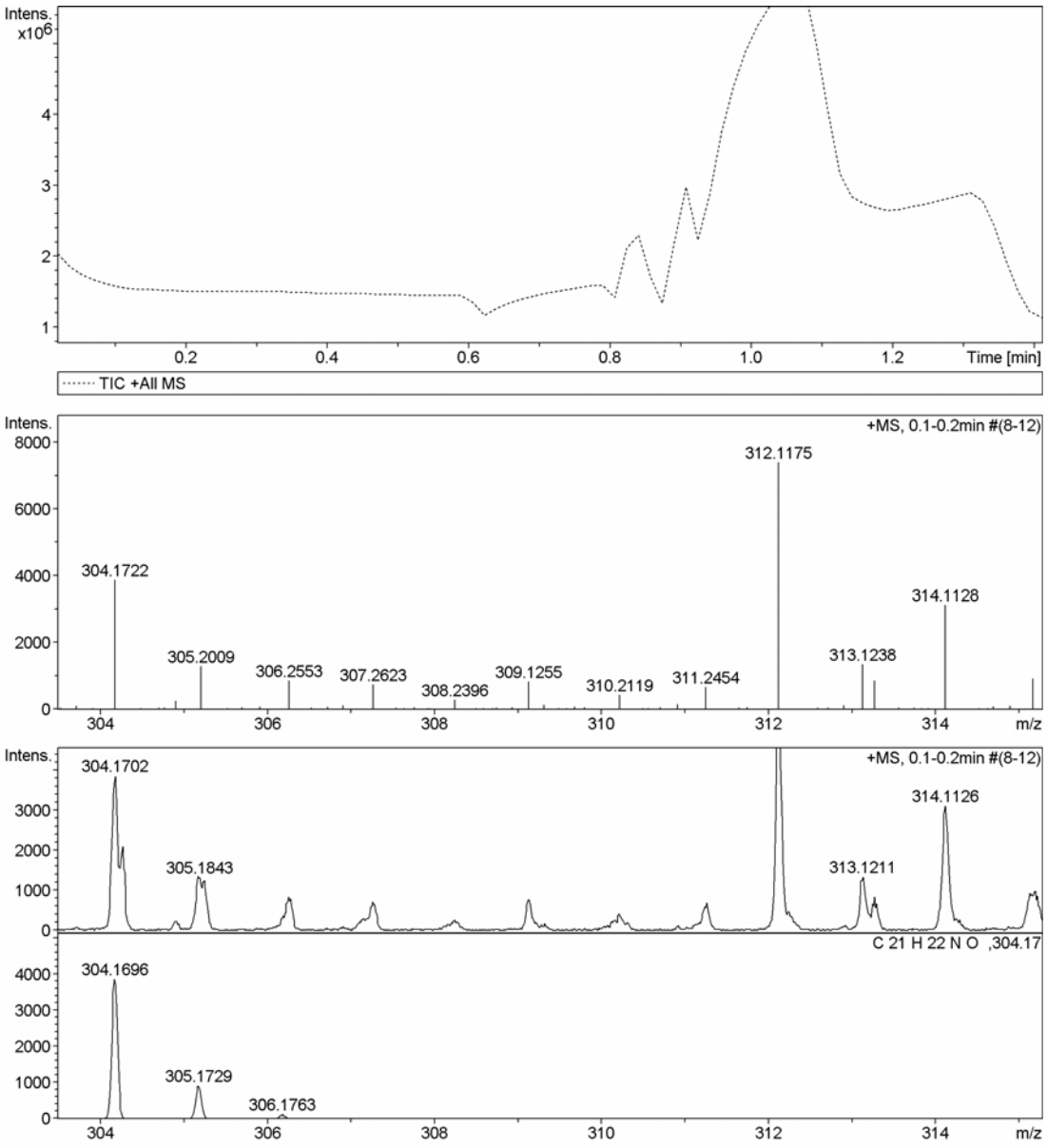


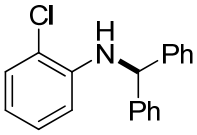
8b



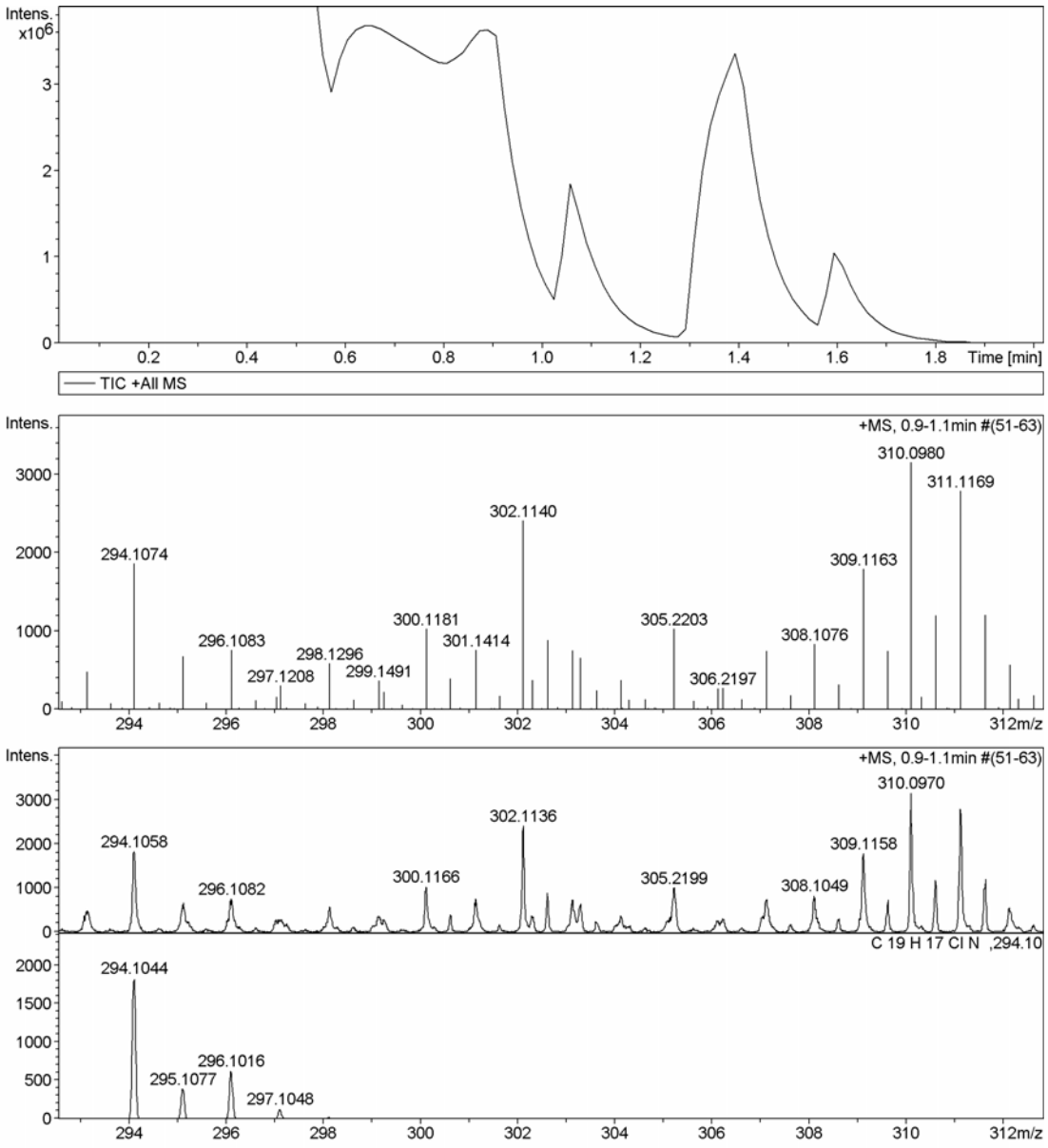

H
N
Ph
Ph
EtO

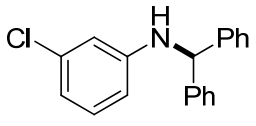
8g


Intens.
x10^6
4
3
2
1
0.2
0.4
0.6
0.8
1.0
1.2
Time [min]
TIC +All MS
Intens.
+MS, 0.1-0.2min #(8-12)
8000
6000
4000
2000
0
312.1175
304.1722
314.1128
305.2009
313.1238
306.2553
307.2623
309.1255
308.2396
310.2119
311.2454
304
306
308
310
312
314
m/z
Intens.
+MS, 0.1-0.2min #(8-12)
304.1702
314.1126
3000
2000
1000
0
305.1843
313.1211
C 21 H 22 N O ,304.17
4000
3000
2000
1000
0
304.1696
305.1729
306.1763
304
306
308
310
312
314
m/z

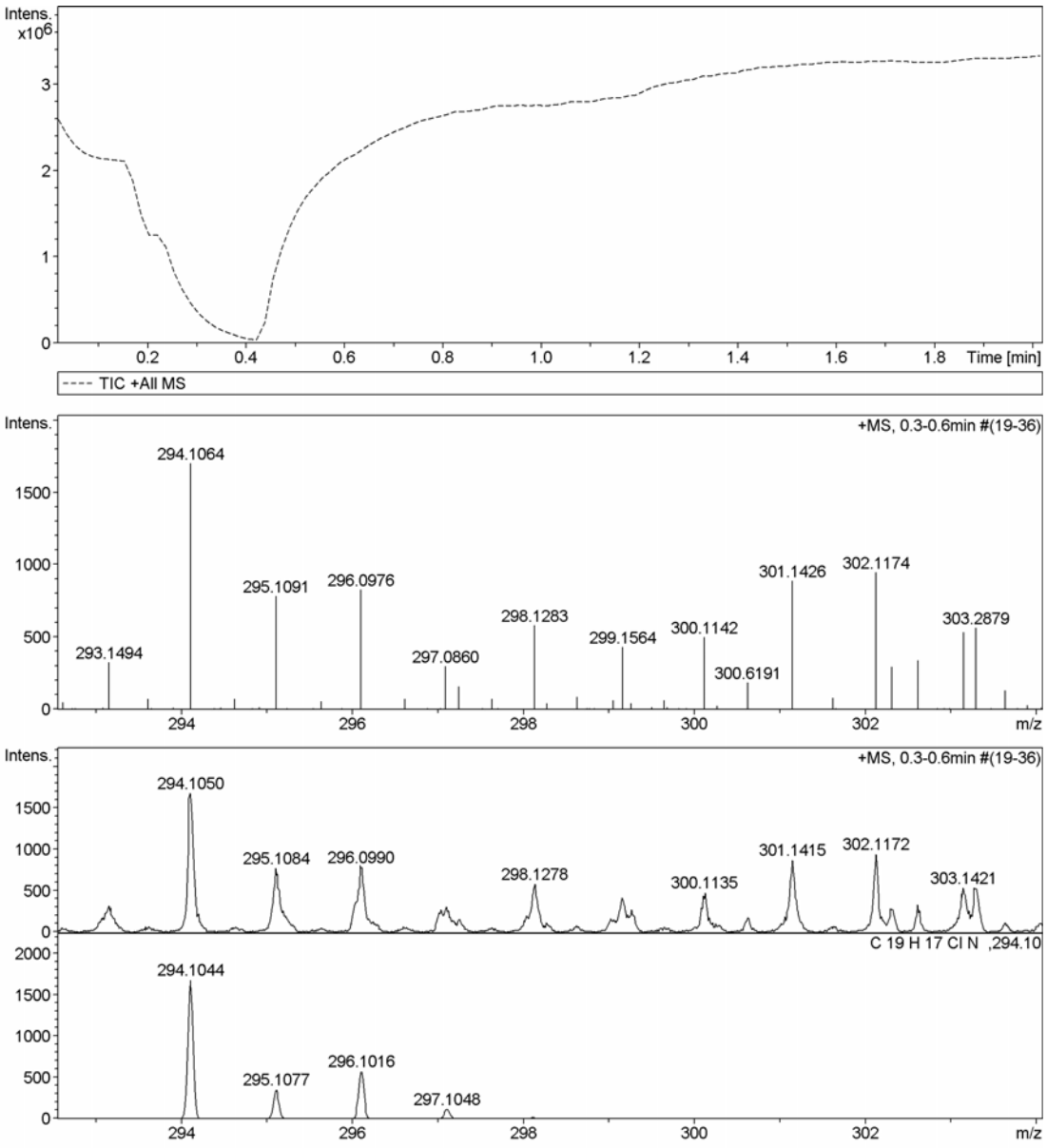

Cl
H
N
Ph
Ph

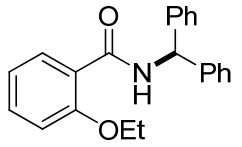
8h


Intens.
x10^6
3
2
1
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
Time [min]
TIC +All MS
Intens.
+MS, 0.9-1.1min #(51-63)
3000
2000
1000
0
310.0980
311.1169
302.1140
294.1074
309.1163
300.1181
305.2203
296.1083
301.1414
308.1076
298.1296
297.1208
299.1491
306.2197
294
296
298
300
302
304
306
308
310
312m/z
Intens.
+MS, 0.9-1.1min #(51-63)
3000
2000
1000
0
310.0970
302.1136
294.1058
309.1158
296.1082
300.1166
305.2199
308.1049
C 19 H 17 Cl N ,294.10
2000
1500
1000
500
0
294.1044
296.1016
295.1077
297.1048
294
296
298
300
302
304
306
308
310
312m/z

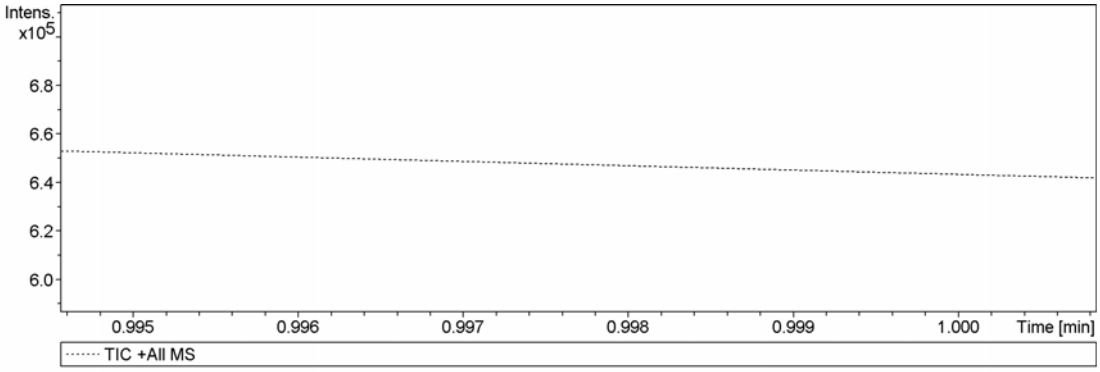

Cl
H
N
Ph
Ph

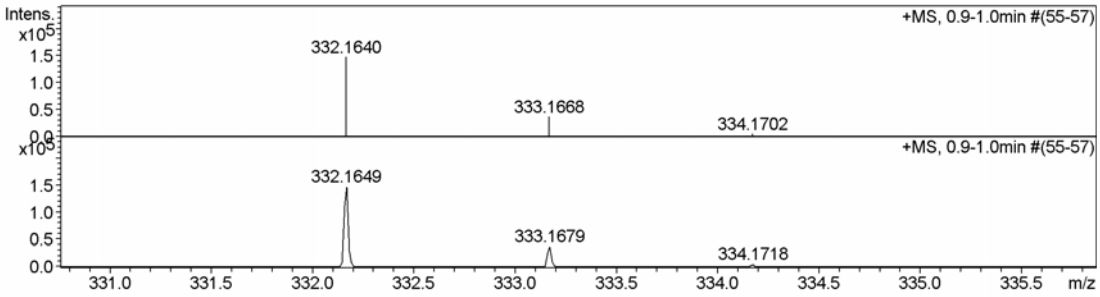
8i

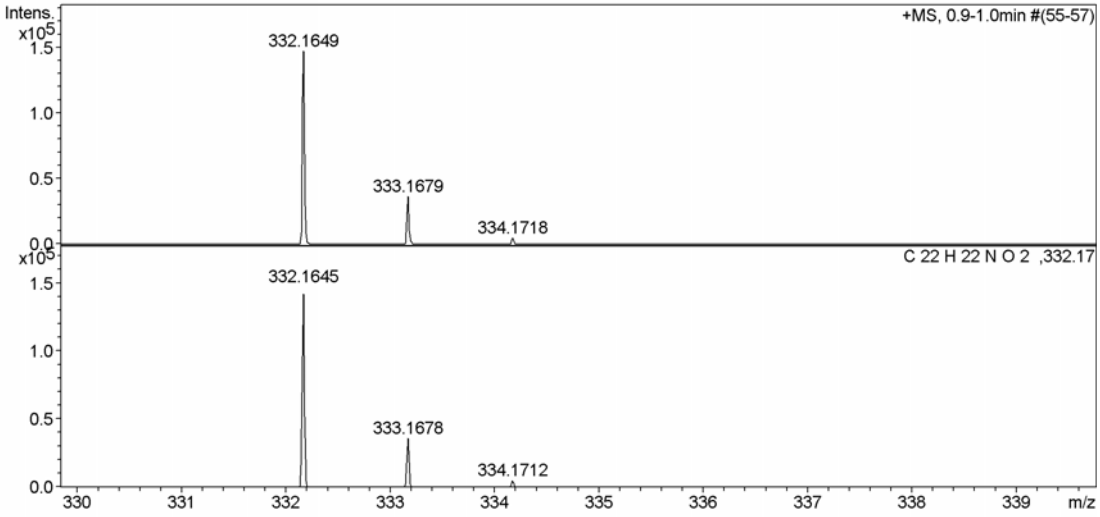

Intens.
x10^6
3
2
1
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
Time [min]
TIC +All MS
Intens.
+MS, 0.3-0.6min #(19-36)
294.1064
295.1091
296.0976
293.1494
297.0860
298.1283
299.1564
300.1142
300.6191
301.1426
302.1174
303.2879
1500
1000
500
0
294
296
298
300
302
m/z
Intens.
+MS, 0.3-0.6min #(19-36)
294.1050
295.1084
296.0990
298.1278
300.1135
301.1415
302.1172
303.1421
C 19 H 17 Cl N ,294.10
2000
1500
1000
500
0
294.1044
295.1077
296.1016
297.1048
294
296
298
300
302
m/z

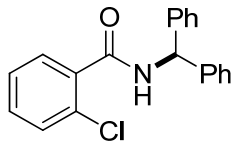

O
Ph
N
H
Ph
OEt

10f

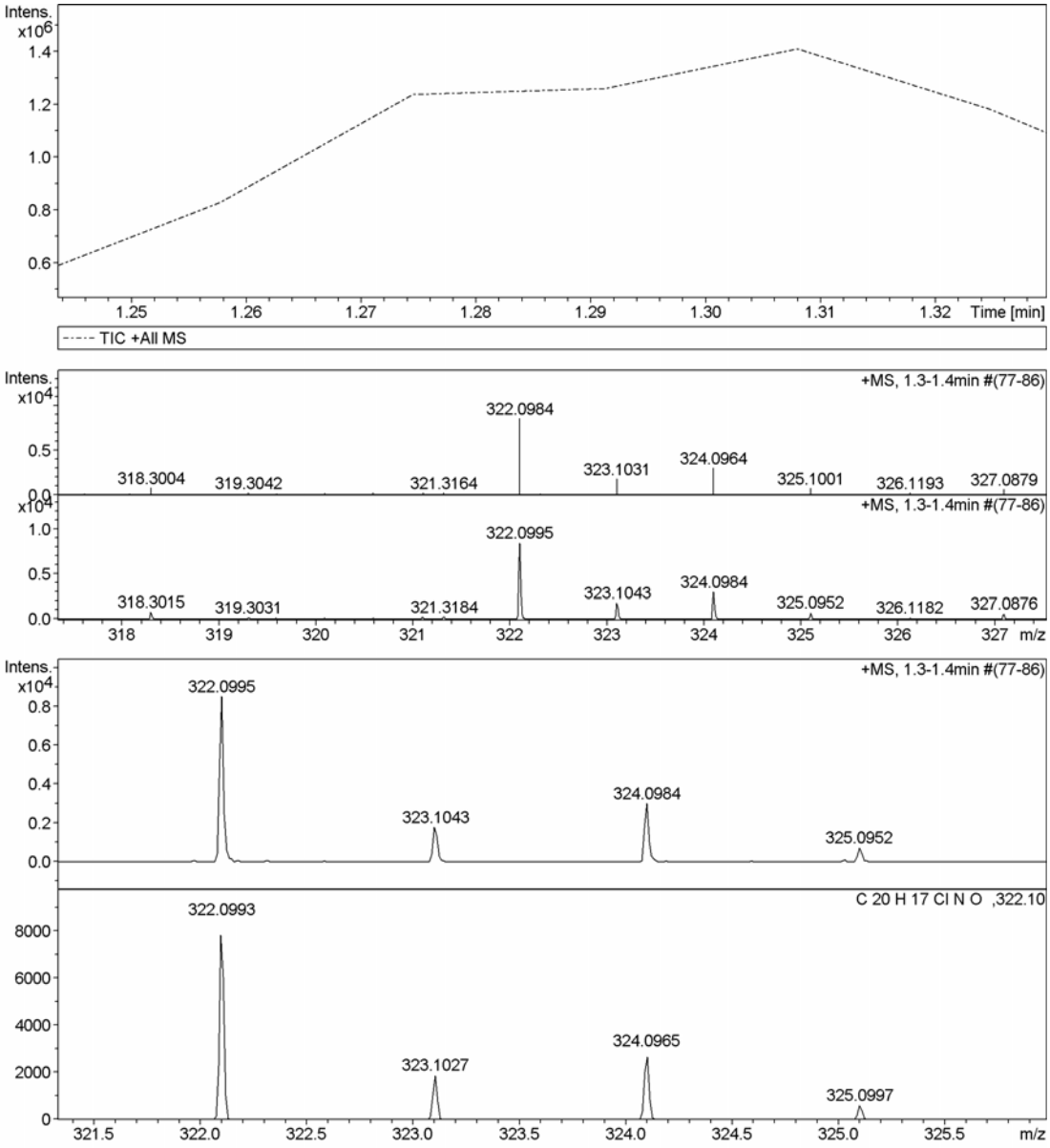

Intens.
x10^5
6.8
6.6
6.4
6.2
6.0
0.995
0.996
0.997
0.998
0.999
1.000
Time [min]
TIC +All MS

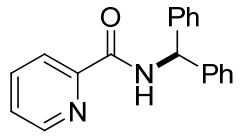

Intens.
x10^5
+MS, 0.9-1.0min #(55-57)
332.1640
333.1668
334.1702
+MS, 0.9-1.0min #(55-57)
332.1649
333.1679
334.1718
331.0
331.5
332.0
332.5
333.0
333.5
334.0
334.5
335.0
335.5
m/z


Intens.
x10^5
+MS, 0.9-1.0min #(55-57)
332.1649
333.1679
334.1718
C 22 H 22 N O 2 ,332.17
332.1645
333.1678
334.1712
330
331
332
333
334
335
336
337
338
339
m/z

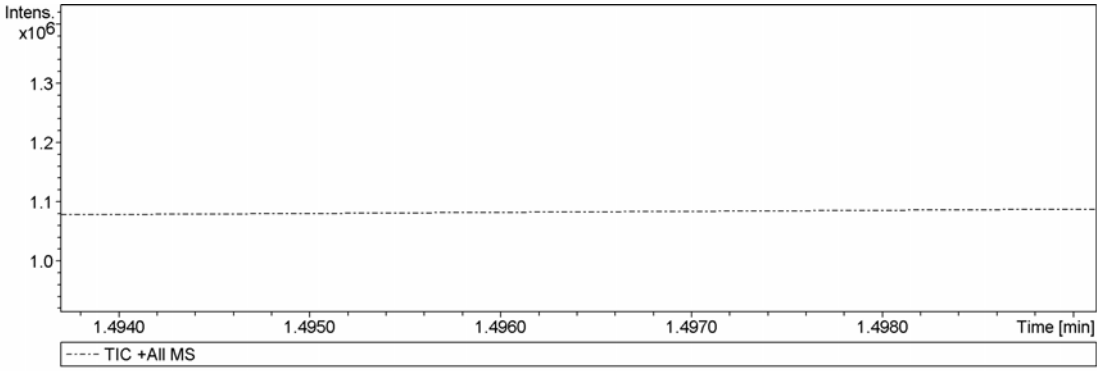

O
Ph
N
H
Ph
Cl

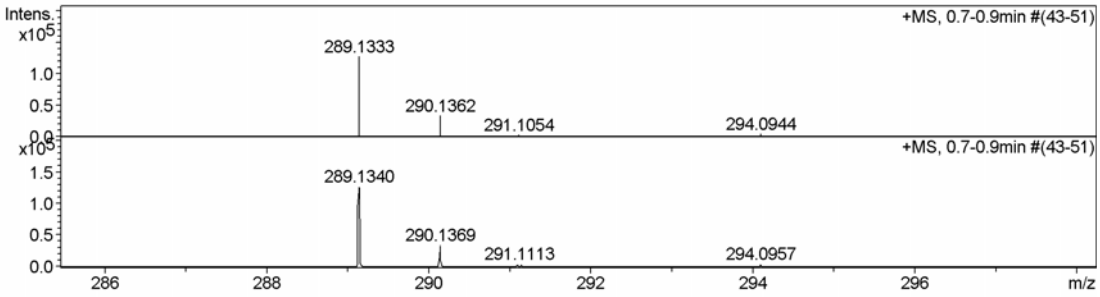
10h

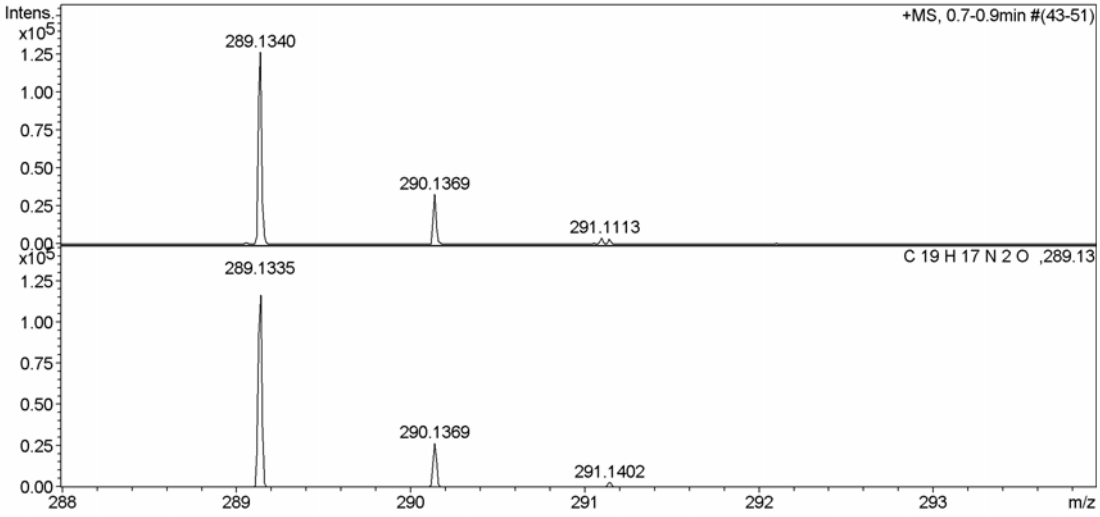

Intens.
x10^6
1.4
1.2
1.0
0.8
0.6
1.25
1.26
1.27
1.28
1.29
1.30
1.31
1.32
Time [min]
TIC +All MS
Intens.
x10^4
+MS, 1.3-1.4min #(77-86)
322.0984
318.3004
319.3042
321.3164
323.1031
324.0964
325.1001
326.1193
327.0879
x10^4
+MS, 1.3-1.4min #(77-86)
322.0995
318.3015
319.3031
321.3184
323.1043
324.0984
325.0952
326.1182
327.0876
318
319
320
321
322
323
324
325
326
327
m/z
Intens.
x10^4
+MS, 1.3-1.4min #(77-86)
322.0995
323.1043
324.0984
325.0952
C 20 H 17 Cl N O ,322.10
322.0993
323.1027
324.0965
325.0997
8000
6000
4000
2000
0
321.5
322.0
322.5
323.0
323.5
324.0
324.5
325.0
325.5
m/z

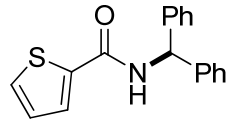


10j

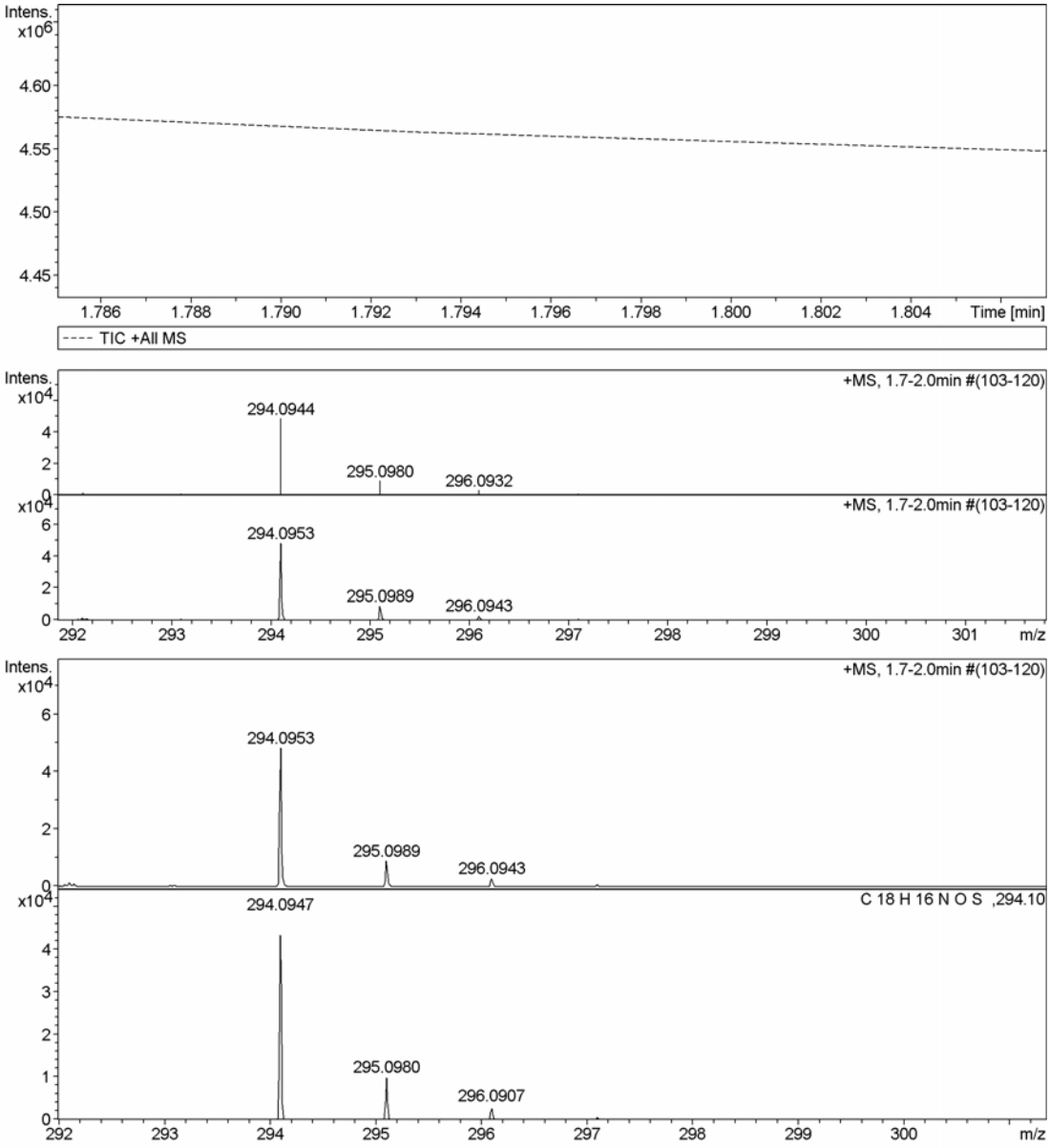

Intens.
x10^6
1.3
1.2
1.1
1.0
1.4940
1.4950
1.4960
1.4970
1.4980
Time [min]
----- TIC +All MS

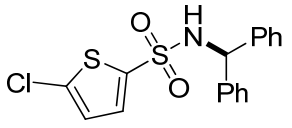

Intens.
x10^5
+MS, 0.7-0.9min #(43-51)
289.1333
290.1362
291.1054
294.0944
x10^5
+MS, 0.7-0.9min #(43-51)
289.1340
290.1369
291.1113
294.0957
286
288
290
292
294
296
m/z


Intens.
x10^5
+MS, 0.7-0.9min #(43-51)
289.1340
290.1369
291.1113
x10^5
C 19 H 17 N 2 O ,289.13
289.1335
290.1369
291.1402
288
289
290
291
292
293
m/z

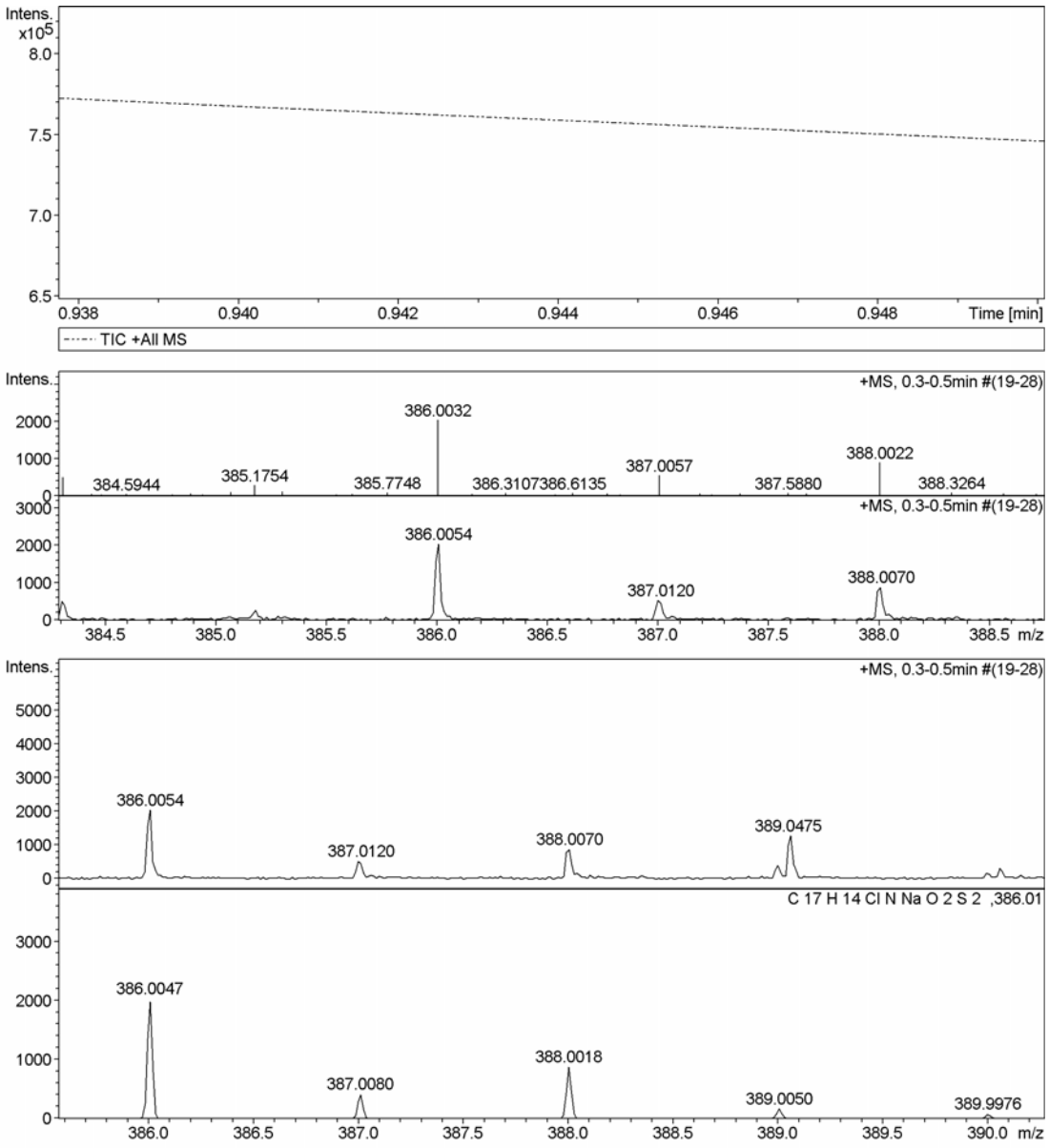

O
Ph
S
N
H
Ph

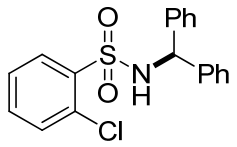
10k


Intens.
x10^6
4.60
4.55
4.50
4.45
1.786
1.788
1.790
1.792
1.794
1.796
1.798
1.800
1.802
1.804
Time [min]
---- TIC +All MS
Intens.
x10^4
+MS, 1.7-2.0min #(103-120)
294.0944
295.0980
296.0932
x10^4
+MS, 1.7-2.0min #(103-120)
294.0953
295.0989
296.0943
292
293
294
295
296
297
298
299
300
301
m/z
Intens.
x10^4
+MS, 1.7-2.0min #(103-120)
294.0953
295.0989
296.0943
x10^4
C 18 H 16 N O S ,294.10
294.0947
295.0980
296.0907
292
293
294
295
296
297
298
299
300
m/z

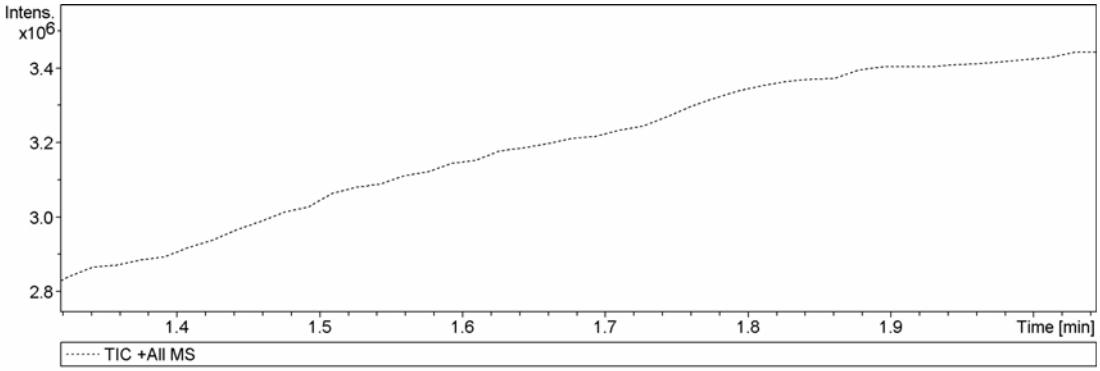

O
H
N
Ph
S
S
Cl
O
Ph

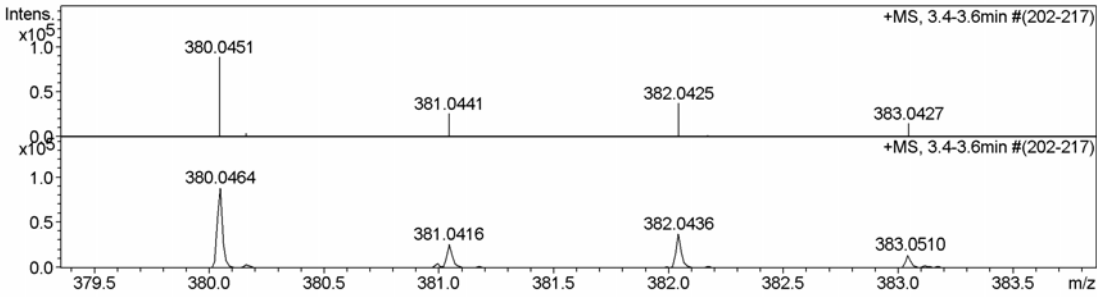
11b

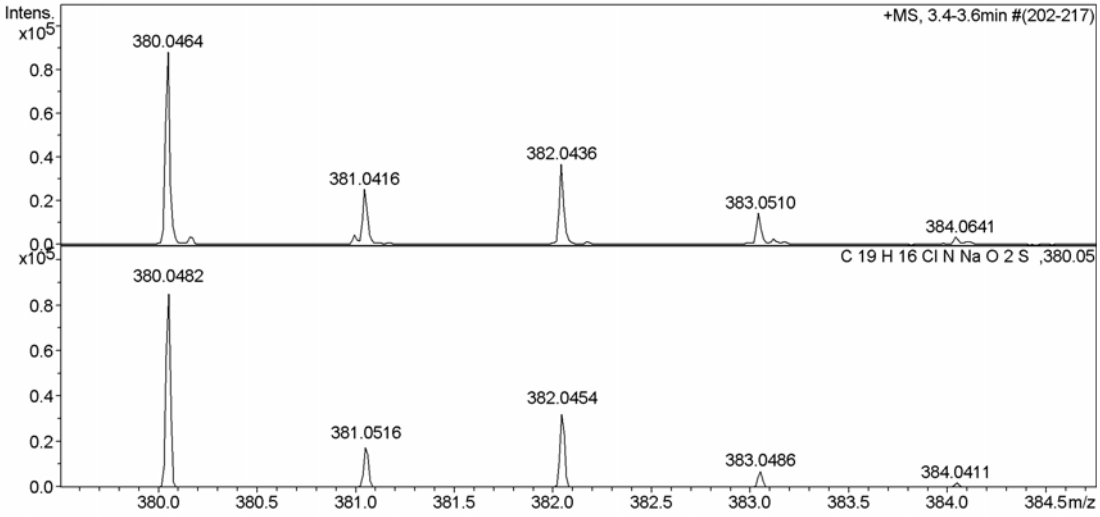

Intens.
x10^5
8.0
7.5
7.0
6.5
0.938
0.940
0.942
0.944
0.946
0.948
Time [min]
TIC +All MS
Intens.
+MS, 0.3-0.5min #(19-28)
386.0032
388.0022
387.0057
384.5944
385.1754
385.7748
386.3107386.6135
387.5880
388.3264
+MS, 0.3-0.5min #(19-28)
386.0054
388.0070
387.0120
384.5
385.0
385.5
386.0
386.5
387.0
387.5
388.0
388.5 m/z
Intens.
+MS, 0.3-0.5min #(19-28)
386.0054
387.0120
388.0070
389.0475
C 17 H 14 Cl N Na O 2 S 2 ,386.01
386.0047
388.0018
387.0080
389.0050
389.9976
386.0
386.5
387.0
387.5
388.0
388.5
389.0
389.5
390.0 m/z

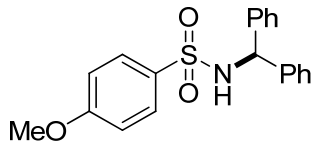


11c

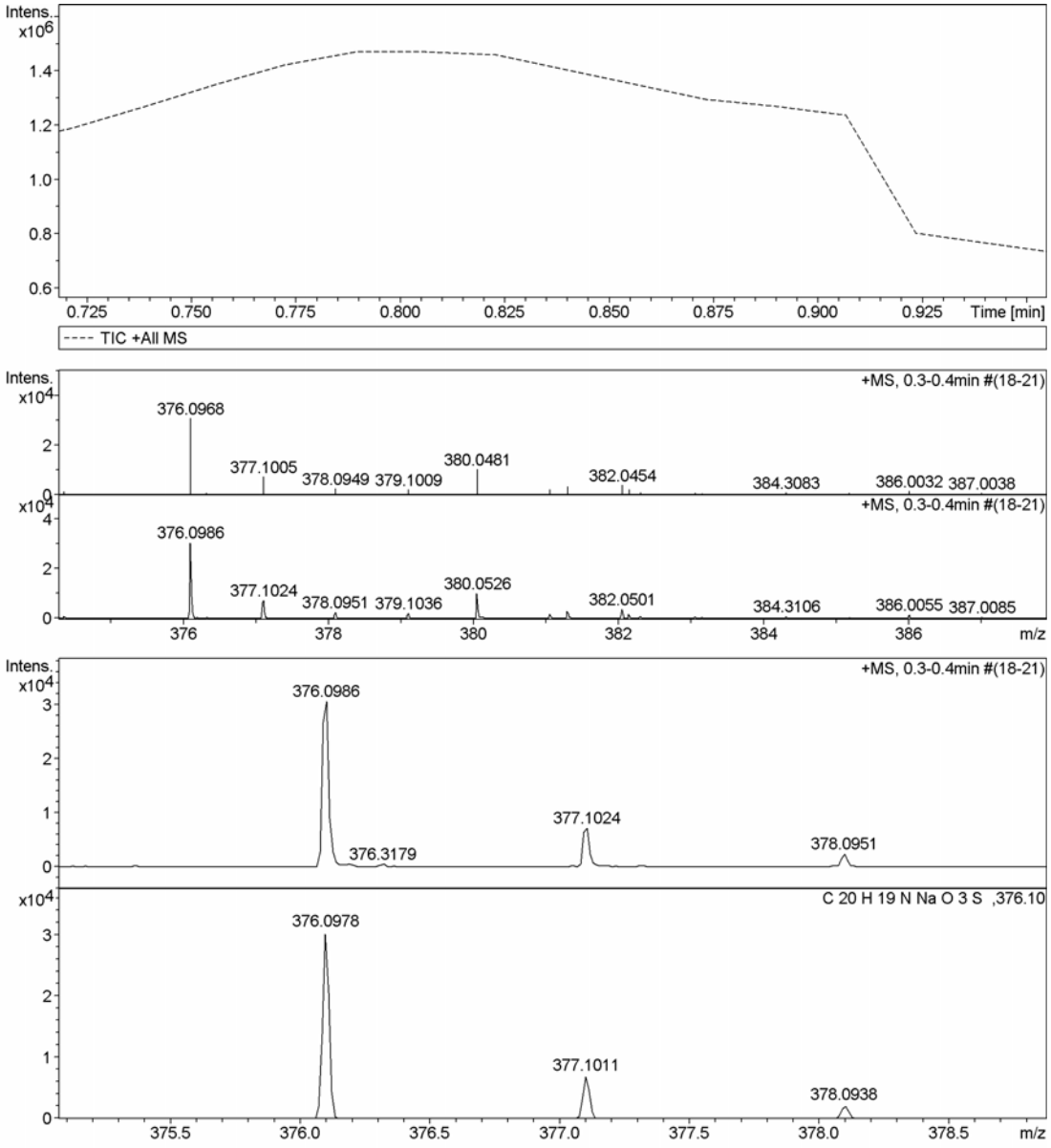

Intens.
x10^6
3.4
3.2
3.0
2.8
1.4
1.5
1.6
1.7
1.8
1.9
Time [min]
TIC +All MS


Intens.
x10^5
+MS, 3.4-3.6min #(202-217)
380.0451
381.0441
382.0425
383.0427
+MS, 3.4-3.6min #(202-217)
380.0464
381.0416
382.0436
383.0510
379.5
380.0
380.5
381.0
381.5
382.0
382.5
383.0
383.5
m/z


Intens.
x10^5
+MS, 3.4-3.6min #(202-217)
380.0464
381.0416
382.0436
383.0510
384.0641
C 19 H 16 Cl N Na O 2 S ,380.05
380.0482
381.0516
382.0454
383.0486
384.0411
380.0
380.5
381.0
381.5
382.0
382.5
383.0
383.5
384.0
384.5m/z


O
Ph
S
N
Ph
O
H
MeO

11g


Intens.
x10^6
1.4
1.2
1.0
0.8
0.6
0.725
0.750
0.775
0.800
0.825
0.850
0.875
0.900
0.925
Time [min]
---- TIC +All MS
Intens.
x10^4
+MS, 0.3-0.4min #(18-21)
376.0968
377.1005
378.0949
379.1009
380.0481
382.0454
384.3083
386.0032
387.0038
x10^4
+MS, 0.3-0.4min #(18-21)
376.0986
377.1024
378.0951
379.1036
380.0526
382.0501
384.3106
386.0055
387.0085
376
378
380
382
384
386
m/z
Intens.
x10^4
+MS, 0.3-0.4min #(18-21)
376.0986
376.3179
377.1024
378.0951
x10^4
C 20 H 19 N Na O 3 S ,376.10
376.0978
377.1011
378.0938
375.5
376.0
376.5
377.0
377.5
378.0
378.5
m/z