

Supporting Information

Ni-Catalyzed, Domino Synthesis of Tertiary Alcohols from Secondary Alcohols

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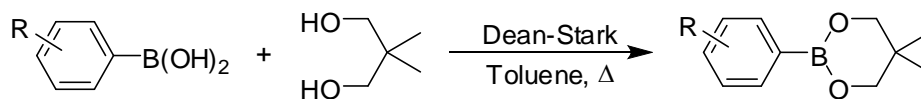
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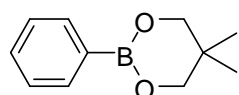
General Considerations

All reactions were carried out in oven dried glassware and set up in a nitrogen-filled glovebox or using standard Schlenk techniques. All reagent-grade chemicals and solvents were obtained from commercial suppliers and were used as received unless otherwise noted. Dry toluene was refluxed over sodium and then distilled. Chromatography purifications were performed by column chromatography using silica gel P60 (230-400 mesh). NMR Spectra were recorded on either 500 MHz or 300 MHz spectrometers. Chemical shifts are given in ppm (δ) and were referenced to the internal solvent signal or to TMS used as an internal standard. Multiplicities are declared as follows: s (singlet), br s (broad siglet), d (doublet), t (triplet), q (quadruplet), dd (doublet of doublet), m (multiplet). Coupling constants J are given in Hertz. High Resolution Mass Spectra (HRMS) were recorded on an on a Mass Spectrometer operating in positive EI (+) mode.

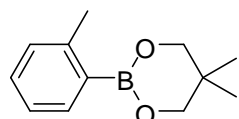
General Procedure for the Preparation of Boronic Esters



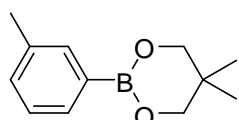
A solution of neopentylglycol (1 mol) and the corresponding phenylboronic acid (1 mol) in toluene (10 mL) was heated at reflux equipped with a Dean-Stark apparatus until no more water was distilled. Then the solvent was removed under vacuum and the mixture was purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate, 1/0 to 8/2) affording the corresponding boronic ester.



5,5-Dimethyl-2-phenyl-1,3,2-dioxaborinane. The title compound was prepared according to the above general procedure from phenylboronic acid (50 mmol, 6.1 g) as a white solid (9.5 g, 50 mmol, 99%). ¹H NMR matched that of a commercial sample. ¹H NMR (300 MHz, CDCl₃) δ 1.03 (s, 6H), 3.77 (s, 4H), 7.32-7.46 (m, 3H), 7.78-7.82 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 21.9, 31.9, 72.3, 127.6, 130.7, 133.8.



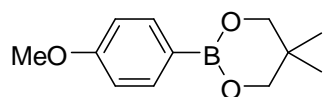
5,5-Dimethyl-2-(2-methylphenyl)-1,3,2-dioxaborinane. The title compound was prepared according to the above general procedure from 2-methylphenylboronic acid (20 mmol, 2.7 g) as a white solid (4.0 g, 19.6 mmol, 98%). ¹H NMR matched the reported literature values.¹ ¹H NMR (300 MHz, CDCl₃) δ 1.04 (s, 6H), 2.51 (s, 3H), 3.78 (s, 4H), 7.15 (t, *J* = 6.9 Hz, 2H), 7.25-7.31 (m, 2H), 7.72 (d, *J* = 6.6 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 21.9, 22.4, 31.6, 72.2, 124.6, 129.9, 130.0, 134.8, 143.9.



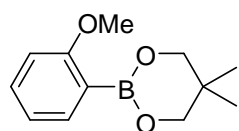
5,5-Dimethyl-2-(3-methylphenyl)-1,3,2-dioxaborinane. The title compound was prepared according to the above general procedure from 3-methylphenylboronic acid (20 mmol, 2.7 g) as a white solid (4.0 g, 19.6 mmol, 98%). ¹H NMR matched the reported literature values.¹ ¹H NMR (300 MHz,

¹ D.A. Wilson, C. J. Wilson, C. Moldoveanu, A.-M. Resmerita, P. Corcoran, L. M. Hoang, B. M. Rosen, V. Percec, *J. Am. Chem. Soc.* **2010**, *132*, 1800-1801.

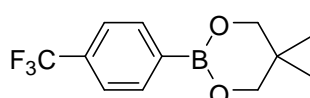
CDCl_3) δ 1.02 (s, 6H), 2.36 (s, 3H), 3.77 (s, 4H), 7.25 (s, 2H), 7.62 (br s, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 21.4, 21.9, 31.9, 72.3, 127.5, 130.8, 131.4, 134.4, 136.9.



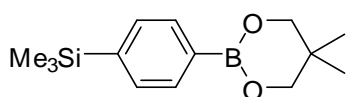
2-(4-Methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane. The title compound was prepared according to the above general procedure from 4-methoxyphenylboronic acid (20 mmol, 3.0 g) as a white solid (4.2 g, 19.1 mmol, 95%). ^1H NMR matched the reported literature values.¹ ^1H NMR (300 MHz, CDCl_3) δ 1.02 (s, 6H), 3.75 (s, 4H), 3.82 (s, 3H), 6.98 (d, $J = 7.9$ Hz, 2H), 7.74 (d, $J = 7.9$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 21.9, 31.9, 55.0, 72.2, 113.1, 135.5, 161.7.



2-(2-Methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane. The title compound was prepared according to the above general procedure from 2-methoxyphenylboronic acid (20 mmol, 3.2 g) as a colorless oil (4.3 g, 19.5 mmol, 98%). ^1H NMR matched the reported literature values.¹ ^1H NMR (300 MHz, CDCl_3) δ 1.04 (s, 6H), 3.79 (s, 4H), 3.83 (s, 3H), 6.86 (d, $J = 8.3$ Hz, 1H), 6.94 (t, $J = 7.3$ Hz, 1H), 7.32-7.41 (m, 1H), 7.65 (dd, $J = 7.3$ and 1.8 Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 21.9, 31.7, 55.7, 72.4, 110.3, 120.2, 131.6, 135.7, 163.6.



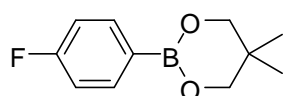
5,5-Dimethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborinane. The title compound was prepared according to the above general procedure from 4-(trifluoromethyl)phenylboronic acid (5.3 mmol, 1.0 g) as a white solid (1.3 g, 5.0 mmol, 95%). ^1H NMR matched the reported literature values.² ^1H NMR (300 MHz, CDCl_3) δ 1.03 (s, 6H), 3.79 (s, 4H), 7.59 (d, $J = 7.5$ Hz, 2H), 7.90 (d, $J = 7.5$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 21.8, 31.9, 72.4, 124.1 (d app, $J = 3.4$ Hz), 124.3 (q, $J = 272.1$ Hz), 132.2 (d, $J = 31.8$ Hz), 134.1.



2-(4-(Trimethylsilyl)phenyl)-5,5-dimethyl-1,3,2-dioxaborinane. The title compound was prepared according to the above general

² K. Ukai, M. Aoki, J. Takaya, N. Iwasawa, *J. Am. Chem. Soc.* **2006**, *128*, 8706-8707.

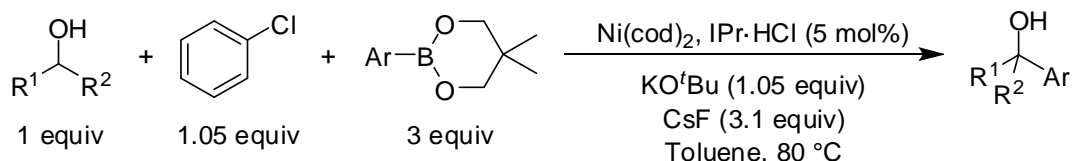
procedure from 4-(trimethylsilyl)phenylboronic acid (5.2 mmol, 1.0 g) as a white solid (1.3 g, 5.1 mmol, 99%). ^1H NMR matched the reported literature values.³ ^1H NMR (300 MHz, CDCl_3) δ 0.27 (s, 9H), 1.02 (s, 6H), 3.77 (s, 4H), 7.52 (d, $J = 7.6$ Hz, 2H), 7.78 (d, $J = 7.6$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ -1.2, 21.9, 31.9, 72.3, 132.5, 133.0, 143.3.



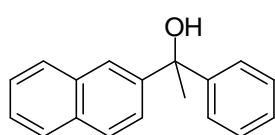
2-(4-Fluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane. The title compound was prepared according to the above general procedure from 4-fluorophenylboronic acid (20 mmol, 2.8 g) as a white solid (4.0 g, 19.2 mmol, 96%). ^1H NMR matched the reported literature values.¹ ^1H NMR (300 MHz, CDCl_3) δ 1.02 (s, 6H), 3.76 (s, 4H), 7.03 (d, $J = 8.2$ Hz, 2H), 7.78 (d, $J = 6.5$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 21.9, 31.9, 72.3, 114.6 (d, $J = 20.0$ Hz), 135.9 (d, $J = 8.3$ Hz), 164.8 (d, $J = 249.0$ Hz).

³ M. Tobisu, Y. Kita, Y. Ano, N. Chatani, *J. Am. Chem. Soc.*, 2008, **130**, 15982-15989.

General Procedure for Catalytic Domino Synthesis of Tertiary Alcohols

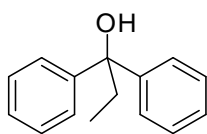


In the glovebox, bis(1,5-cyclooctadiene)nickel(0) [Ni(cod)₂] (5 mol%), 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride [IPr·HCl] (5 mol%), potassium *tert*-butoxide (1.05 mmol), cesium fluoride (3.1 mmol), the corresponding boronic ester (3.0 mmol) and dry toluene (2 mL) were charged to a screw top vial with a septum equipped with a magnetic bar. Outside the glovebox the corresponding alcohol (0.50 mmol) and chlorobenzene (0.53 mmol) were syringed in through the septum. When the alcohol was solid, it was loaded in the glovebox. Then the mixture was allowed to stir at 80 °C until the reaction reached completion or no further conversion was observed by gas chromatography. After cooling to room temperature, the combined mixtures from two vials were poured in a mixture of diethyl ether and water and stirred for 30 minutes. Then the aqueous layer was extracted three times with Et₂O. The combined organic layers were washed with brine, dried over anhydrous MgSO₄ and concentrated. The crude tertiary alcohol was purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate, 1/0 to 8/2).

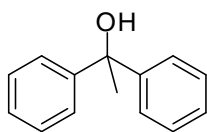


1-(Naphthalen-2-yl)-1-phenylethanol (Table 1, entry 1). The title compound was prepared according to the above general procedure from 1-(2-naphthyl)ethanol (0.50 mmol, 86 mg) as a light yellow oil after 1.5 hour stirring at 80 °C (245 mg, 0.98 mmol, 98%). NMRs matched the reported literature values.⁴ ¹H NMR (500 MHz, CDCl₃) δ 2.05 (s, 3H), 2.26 (s, 1H), 7.23-7.26 (m, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.41 (dd, *J* = 8.6 and 1.9 Hz, 1H), 7.45-7.49 (m, 4H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.79-7.85 (m, 2H), 7.97 (s, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 30.5, 76.4, 123.7, 124.9, 125.9, 126.1, 127.0, 127.5, 127.9, 128.2, 132.4, 133.0, 145.3, 147.7.

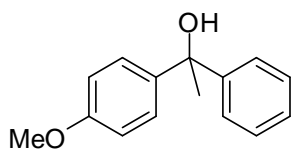
⁴ J. Bouffard, K. Itami, *Org. Lett.*, 2009, **11**, 4410-4413.



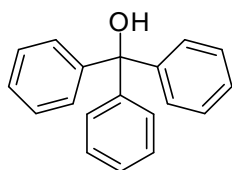
1,1-Diphenylpropanol (Table 1, entry 2). The title compound was prepared according to the above general procedure from 1-phenyl-1-propanol (0.50 mmol, 72 μ L) as a light yellow oil after 4 hours stirring at 80 $^{\circ}$ C (211 mg, 0.99 mmol, 99%). NMRs matched the reported literature values.⁵ 1 H NMR (500 MHz, CDCl_3) δ 0.88 (t, $J = 7.3$ Hz, 3H), 2.05 (s, 1H), 2.32 (q, $J = 7.3$ Hz, 2H), 7.21 (t, $J = 7.3$ Hz, 2H), 7.30 (t, $J = 7.7$ Hz, 4H), 7.41-7.42 (m, 4H). 13 C NMR (125 MHz, CDCl_3) δ 8.1, 34.4, 78.4, 126.1, 126.7, 128.1, 146.9.



1,1-Diphenylethanol (Table 1, entry 3). The title compound was prepared according to the above general procedure from 1-ethyl-1-propanol (0.50 mmol, 66 μ L) as a light yellow oil after 3 hours stirring at 80 $^{\circ}$ C (190 mg, 0.96 mmol, 96%). NMRs matched the reported literature values.⁶ 1 H NMR (500 MHz, CDCl_3) δ 1.95 (s, 3H), 2.16 (s, 1H), 7.23 (t, $J = 7.4$ Hz, 2H), 7.31 (t, $J = 7.6$ Hz, 4H), 7.41-7.42 (m, 4H). 13 C NMR (125 MHz, CDCl_3) δ 30.8, 76.2, 125.8, 126.9, 128.1, 148.0.



1-(4-Methoxyphenyl)-1-phenylethanol (Table 1, entry 4). The title compound was prepared according to the above general procedure from 4-methoxy- α -methylbenzyl alcohol (0.50 mmol, 71 μ L) as a light yellow oil after 5 hours stirring at 80 $^{\circ}$ C (204 mg, 0.89 mmol, 89%). NMRs matched the reported literature values.⁷ 1 H NMR (500 MHz, CDCl_3) δ 1.93 (s, 3H), 2.11 (s, 1H), 3.79 (s, 3H), 6.84 (d, $J = 8.6$ Hz, 2H), 7.23 (t, $J = 7.3$ Hz, 3H), 7.29-7.33 (m, 4H), 7.40-7.41 (m, 2H). 13 C NMR (125 MHz, CDCl_3) δ 31.0, 55.2, 75.9, 113.4, 125.7, 126.8, 127.1, 128.1, 140.3, 148.3, 158.5.



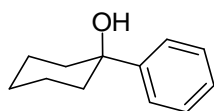
Triphenylmethanol (Table 1, entry 5). The title compound was prepared according to the above general procedure from diphenylmethanol (0.25 mmol, 46 mg) as a white solid 2 hours stirring at

⁵ M. Hatano, S. Suzuki, K. Ishihara, *J. Am. Chem. Soc.*, 2006, **128**, 9998-9999.

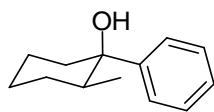
⁶ M. N. Alberti, M. Orfanopoulos, *Org. Lett.*, 2008, **10**, 2465-2468.

⁷ S. Zhou, K.-H. Wu, C.-A. Chen, H.-M. Gau, *J. Org. Chem.*, 2009, **74**, 3500-3505.

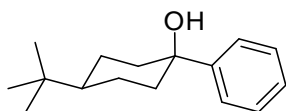
100 °C (111 mg, 0.43 mmol, 85%). NMRs matched that of a commercial sample. ^1H NMR (500 MHz, CDCl_3) δ 2.81 (s, 1H), 7.23-7.32 (m, 15H). ^{13}C NMR (125 MHz, CDCl_3) δ 82.0, 127.2, 127.9, 146.8.



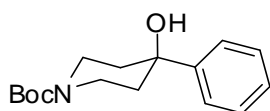
1-Phenylcyclohexanol (Table 1, entry 6). The title compound was prepared according to the above general procedure from cyclohexanol (0.50 mmol, 53 μL) as a colorless oil after 0.5 hour stirring at 80 °C (161 mg, 0.91 mmol, 91%). IR (thin film): 3390, 3080, 3050, 3020, 2930, 2850, 1440, 970, 750, 700 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 1.26-1.35 (m, 1H), 1.56 (s, 1H), 1.63-1.65 (m, 2H), 1.73-1.88 (m, 7H), 7.23 (t, $J = 7.4$ Hz, 1H), 7.35 (t, $J = 7.7$ Hz, 2H), 7.50-7.52 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 22.2, 25.5, 38.8, 73.1, 124.6, 126.7, 128.2, 149.4. HRMS (EI+) Calcd for $\text{C}_{12}\text{H}_{16}\text{O}$: 176.12012. Found: 176.12090 [(M) $^+$].



2-Methyl-1-phenylcyclohexanol (Table 1, entry 7). The title compound was prepared according to the above general procedure from 2-methylcyclohexanol (0.50 mmol, 62 μL) as a colorless oil after 6 hours stirring at 80 °C (93 mg, 0.48 mmol, 96%) as a single diastereoisomer. NMRs matched the reported literature values.⁴ ^1H NMR (300 MHz, CDCl_3) δ 0.62 (t, $J = 6.8$ Hz, 3H), 1.33-1.50 (m, 2H), 1.59-1.82 (m, 7H), 1.88-2.00 (m, 1H), 7.19-7.25 (m, 1H), 7.33 (t, $J = 7.8$ Hz, 2H), 7.43-7.46 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 15.5, 22.0, 26.1, 30.4, 39.8, 41.2, 75.8, 124.6, 126.2, 128.0, 148.4.



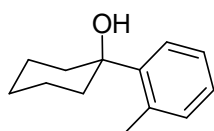
4-tert-Butyl-1-phenylcyclohexanol (Table 1, entry 8). The title compound was prepared according to the above general procedure from 4-tert-butylcyclohexanol (0.50 mmol, 80 mg) as a white solid after 0.5 hour stirring at 80 °C (228 mg, 0.98 mmol, 98%) as a single diastereoisomer. NMRs matched the reported literature values.⁴ ^1H NMR (500 MHz, CDCl_3) δ 0.92 (s, 9H), 1.10 (tt, $J = 12.1$ and 3.2 Hz, 1H), 1.49-1.57 (m, 3H), 1.71-1.73 (m, 2H), 1.79-1.89 (m, 4H), 7.23 (t, $J = 7.4$ Hz, 1H), 7.35 (t, $J = 7.7$ Hz, 2H), 7.50-7.52 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 22.9, 27.6, 32.5, 39.4, 47.5, 72.7, 124.5, 126.6, 128.2, 149.5.



tert-Butyl-4-hydroxy-4-phenyl-1-piperidinecarboxylate (Table 1,

entry 9). The title compound was prepared according to the above general procedure from 1-boc-4-hydroxypiperidine (0.50 mmol,

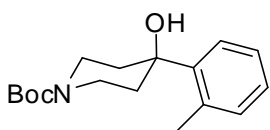
101 mg). as a colorless oil that slowly solidifies after 0.5 hour stirring at 80 °C (244 mg, 0.88 mmol, 88%). IR (thin film): 3430, 2970, 2930, 2870, 1690, 1660, 1480, 1430, 1360, 1280, 1250, 1160, 1020, 760, 700 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 1.48 (s, 9H), 1.57 (s, 1H), 1.72-1.75 (m, 2H), 2.01 (br s, 2H), 3.25 (br s, 2H), 4.03 (br s, 2H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 4.47-7.49 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 28.4, 38.0, 39.6, 71.4, 79.5, 124.4, 127.1, 128.4, 148.0, 154.8. HRMS (EI+) **Calcd for C₁₆H₂₃NO₃**: 277.16779. **Found**: 277.16849 [(M)⁺].



1-(2-Methylphenyl)cyclohexanol (Table 2, entry 1). The title compound

was prepared according to the above general procedure from cyclohexanol (0.25 mmol, 26 μL) as a colorless oil after 9 hours stirring at 80 °C (41 mg,

0.22 mmol, 44%). IR (thin film): 3460, 3100, 3060, 3010, 2920, 2860, 1450, 960, 750 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 1.21-1.35 (m, 1H), 1.50 (s, 1H), 1.61-1.99 (m, 9H), 2.62 (s, 3H), 7.14-7.15 (m, 3H), 7.41-7.44 (m, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 22.1, 22.4, 25.5, 37.3, 74.2, 125.2, 125.6, 126.8, 132.9, 136.5, 146.1. HRMS (EI+) **Calcd for C₁₃H₁₈O**: 190.13577. **Found**: 190.13610 [(M)⁺].

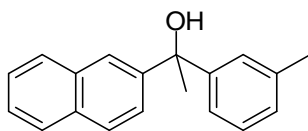


tert-Butyl-4-hydroxy-4-(2-methylphenyl)-1-piperidinecarboxylate

(Table 2, entry 2). The title compound was prepared according to the

above general procedure from 1-boc-4-hydroxypiperidine (0.25 mmol,

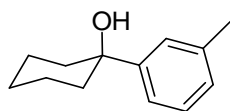
50 mg) as a light yellow oil after 1 hour stirring at 80 °C (97 mg, 0.33 mmol, 66%). IR (thin film): 3430, 3060, 3010, 2970, 2930, 2870, 1690, 1670, 1430, 1370, 1250, 1170, 1030, 750 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 1.48 (s, 9H), 1.53 (s, 1H), 1.90-1.95 (m, 2H), 2.01-2.09 (m, 2H), 2.61 (s, 3H), 3.28 (t, *J* = 11.4 Hz, 2H), 4.01 (br s, 2H), 7.15-7.18 (m, 3H), 7.34-7.38 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 22.1, 28.5, 36.8, 40.1, 72.6, 79.4, 125.1, 125.8, 127.4, 133.1, 136.5, 144.5, 154.9. HRMS (EI+) **Calcd for C₁₇H₂₅NO₃**: 291.18344. **Found**: 291.18386 [(M)⁺].



1-(3-Methylphenyl)-1-(naphthalen-2-yl)ethanol (Table 2, entry

3). The title compound was prepared according to the above general procedure from 1-(2-naphthyl)ethanol (0.25 mmol, 43 mg) as a

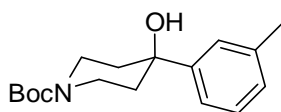
light yellow oil after 2 hours stirring at 80 °C (119 mg, 0.45 mmol, 91%). IR (thin film): 3430, 3050, 2980, 2930, 1590, 1370, 1310, 1130, 830, 750, 700 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 2.03 (s, 3H), 2.24 (s, 1H), 2.32 (s, 3H), 7.06 (d, $J = 7.1$ Hz, 1H), 7.19-7.26 (m, 3H), 7.41 (dd $J = 8.6$ and 1.9 Hz, 1H), 7.44-7.49 (m, 2H), 7.75 (d, $J = 8.6$ Hz, 1H), 7.79-7.85 (m, 2H), 7.97 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 21.6, 30.8, 76.3, 123.0, 123.7, 125.0, 125.9, 126.1, 126.6, 127.5, 127.8, 127.9, 128.1, 128.2, 132.4, 133.0, 137.8, 145.4, 147.7. HRMS (EI+) Calcd for $\text{C}_{19}\text{H}_{18}\text{O}$: 262.13577. Found: 262.13469 $[(\text{M})^+]$.



1-(3-Methylphenyl)cyclohexanol (Table 2, entry 4). The title compound

was prepared according to the above general procedure from cyclohexanol (0.25 mmol, 26 μL) as a colorless oil after 1 hour stirring at

80 °C (86 mg, 0.45 mmol, 90%). IR (thin film): 3400, 3020, 2930, 2840, 1600, 1440, 1300, 1130, 970, 790, 700 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 1.23-1.37 (m, 1H), 1.56 (s, 1H), 1.59-1.90 (m, 9H), 2.37 (s, 3H), 7.05-7.08 (m, 1H), 7.21-7.33 (m, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 21.6, 22.1, 25.5, 38.8, 73.1, 121.5, 125.3, 127.4, 128.1, 137.7, 149.4. HRMS (EI+) Calcd for $\text{C}_{13}\text{H}_{18}\text{O}$: 190.13577. Found: 190.13530 $[(\text{M})^+]$.

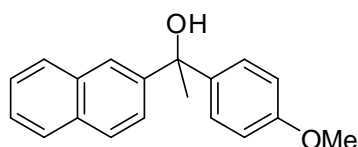


tert-Butyl-4-hydroxy-4-(3-methylphenyl)-1-piperidinecarboxylate

(Table 2, entry 5). The title compound was prepared according to the

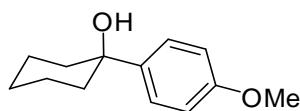
above general procedure from 1-boc-4-hydroxypiperidine

(0.25 mmol, 50 mg) as a light yellow oil after 0.5 hour stirring at 80 °C (120 mg, 0.41 mmol, 82%). IR (thin film): 3420, 2960, 2920, 2870, 1700, 1660, 1430, 1370, 1240, 1160, 780, 700 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 1.48 (s, 9H), 1.62 (s, 1H), 1.71-1.74 (m, 2H), 1.99 (br s, 2H), 2.37 (s, 3H), 3.24 (br s, 2H), 4.02 (br s, 2H), 7.08-7.10 (m, 1H), 7.23-7.19 (m, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 21.6, 28.4, 38.1, 39.9, 71.5, 79.5, 121.4, 125.2, 128.0, 128.4, 138.1, 148.0, 154.9. HRMS (EI+) Calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_3$: 291.18344. Found: 291.18234 $[(\text{M})^+]$.



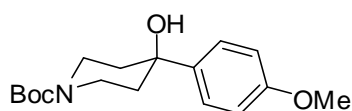
1-(4-Methoxyphenyl)-1-(naphthalen-2-yl)ethanol (Table 2, entry 6).

The title compound was prepared according to the above general procedure from 1-(2-naphthyl)ethanol (0.25 mmol, 43 mg) as a light yellow oil after 0.5 hour stirring at 80 °C (103 mg, 0.37 mmol, 74%). IR (thin film): 3440, 3050, 2980, 2930, 1620, 1510, 15.250, 1170, 1020, 840, 740 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 2.03 (s, 3H), 2.21 (s, 1H), 3.79 (s, 3H), 6.85 (d, $J = 8.8$ Hz, 2H), 7.34-7.50 (m, 5H), 7.75-7.86 (m, 3H), 7.97 (s, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 30.8, 55.2, 76.0, 113.4, 123.5, 124.9, 125.8, 126.0, 127.2, 127.4, 127.8, 128.2, 132.3, 132.9, 140.0, 145.5, 158.5. HRMS (EI+) **Calcd for $\text{C}_{19}\text{H}_{18}\text{O}_2$: 278.13068. Found: 278.12529 [(M) $^+$].**



1-(4-Methoxyphenyl)cyclohexanol (Table 2, entry 7).

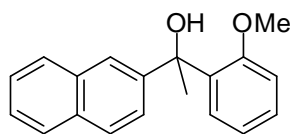
The title compound was prepared according to the above general procedure from cyclohexanol (0.25 mmol, 26 μL) as a colorless oil after 0.5 hour stirring at 80 °C (85 mg, 0.41 mmol, 82%). IR (thin film): 3400, 3010, 2930, 2850, 1640, 1620, 1510, 1250, 1180, 1030, 820 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 1.23-1.36 (m, 1H), 1.52 (s, 1H), 1.58-1.89 (m, 9H), 3.81 (s, 3H), 6.88 (d, $J = 8.8$ Hz, 2H), 7.43 (d, $J = 8.8$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 22.3, 25.5, 38.9, 55.2, 72.7, 113.5, 125.8, 141.6, 158.3. HRMS (EI+) **Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2$: 206.13068. Found: 206.13061 [(M) $^+$].**



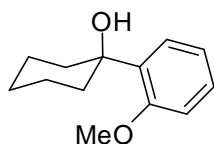
tert-Butyl-4-hydroxy-4-(4-methoxyphenyl)-

1-piperidinecarboxylate (Table 2, entry 8).

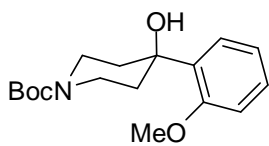
The title compound was prepared according to the above general procedure from 1-boc-4-hydroxypiperidine (0.25 mmol, 50 mg) as a light yellow oil after 0.5 hour stirring at 80 °C (150 mg, 0.49 mmol, 97%). IR (thin film): 3430, 2980, 2960, 2930, 2870, 2830, 1670, 1510, 1420, 1250, 1170, 1030, 760 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 1.48 (s, 9H), 1.60 (s, 1H), 1.72-1.75 (m, 2H), 1.97 (br s, 2H), 3.25 (t, $J = 12.8$ Hz, 2H), 3.81 (s, 3H), 4.00 (br s, 2H), 6.89 (d, $J = 8.8$ Hz, 2H), 7.39 (d, $J = 8.8$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 28.5, 38.2, 40.0, 55.3, 71.1, 79.5, 113.8, 125.7, 140.2, 154.9. HRMS (EI+) **Calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_4$: 307.17836. Found: 307.17796 [(M) $^+$].**



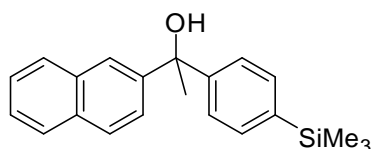
1-(2-Methoxyphenyl)-1-(naphthalen-2-yl)ethanol (Table 2, entry 9). The title compound was prepared according to the above general procedure from 1-(2-naphthyl)ethanol (0.25 mmol, 43 mg) as a light yellow oil after 9 hours stirring at 80 °C (57 mg, 0.20 mmol, 40%). IR (thin film): 3510, 2050, 2970, 2920, 1600, 1480, 1450, 1290, 2340, 1140, 1020, 820, 760 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 1.92 (s, 3H), 3.55 (s, 3H), 4.01 (s, 1H), 6.88-6.90 (m, 1H), 7.03-7.08 (m, 1H), 7.30-7.35 (m, 1H), 7.39-7.50 (m, 5H), 7.70-7.79 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3) δ 30.1, 55.6, 76.4, 112.1, 120.9, 123.0, 124.0, 125.4, 125.8, 127.2, 127.4, 127.4, 128.1, 128.9, 132.2, 133.1, 134.9, 147.0, 157.1. HRMS (EI+) **Calcd for $\text{C}_{19}\text{H}_{18}\text{O}_2$: 278.13068. Found: 278.13045 [(M) $^+$].**



1-(2-Methoxyphenyl)cyclohexanol (Table 2, entry 10). The title compound was prepared according to the above general procedure from cyclohexanol (0.25 mmol, 26 μL) as a colorless oil after 9 hours stirring at 80 °C (45 mg, 0.22 mmol, 44%). IR (thin film): 3540, 3450, 3060, 2930, 3850, 1600, 1580, 1490, 1450, 1440, 1230, 1030, 960, 740 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 1.21-1.1 (m, 1H), 1.56-1.94 (m, 7H), 2.02-2.05 (m, 9H), 3.89 (s, 3H), 3.95 (s, 1H), 6.91-6.98 (m, 2H), 7.20-7.23 (m, 1H), 7.31-7.33 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 21.9, 25.9, 36.7, 55.2, 73.0, 111.3, 121.0, 125.7, 127.9, 136.4, 157.2. HRMS (EI+) **Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2$: 206.13068. Found: 206.13110 [(M) $^+$].**

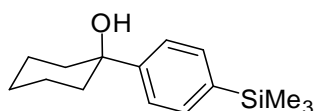


tert-Butyl-4-hydroxy-4-(2-methoxyphenyl)-1-piperidinecarboxylate (Table 2, entry 11). The title compound was prepared according to the above general procedure from 1-boc-4-hydroxypiperidine (0.25 mmol, 50 mg) as a light yellow oil after 9 hours stirring at 80 °C (45 mg, 0.15 mmol, 30%). IR (thin film): 3460, 3060, 2970, 2910, 2870, 2830, 1700, 1670, 1430, 1360, 1270, 1250, 1160, 1010, 750 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 1.47 (s, 9H), 1.89-2.02 (m, 4H), 3.31 (br s, 2H), 3.90 (s, 3H), 4.00 (br s, 2H), 4.08 (s, 1H), 6.93-6.99 (m, 2H), 7.24-7.27 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 28.4, 35.9, 39.8, 55.2, 71.2, 79.2, 111.3, 121.1, 125.4, 128.4, 134.5, 154.9, 157.0. HRMS (EI+) **Calcd for $\text{C}_{17}\text{H}_{25}\text{NO}_4$: 307.17836. Found: 307.17794 [(M) $^+$].**



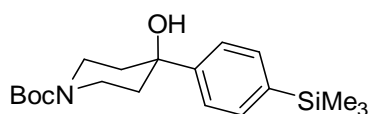
1-(Naphthalen-2-yl)-1-(4-(trimethylsilyl)phenyl)ethanol
(Table 2, entry 12).

The title compound was prepared according to the above general procedure from 1-(2-naphthyl)ethanol (0.25 mmol, 43 mg) as a light yellow oil after 0.5 hour stirring at 80 °C (154 mg, 0.48 mmol, 96%). IR (thin film): 3450, 3060, 3020, 2950, 2890, 1680, 1640, 1590, 1380, 1310, 1240, 1120, 1080, 1050, 850, 820, 740 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 0.25 (s, 9H), 2.05 (s, 3H), 2.25 (s, 1H), 7.42-7.50 (m, 7H), 7.75-7.77 (m, 1H), 7.79-7.81 (m, 1H), 7.84-7.85 (m, 1H), 7.98 (s, 1H). ¹³C NMR (125 MHz, CDCl₃) δ -1.1, 30.6, 76.3, 123.7, 124.9, 125.2, 125.9, 126.1, 127.5, 127.9, 128.2, 132.4, 133.0, 133.3, 139.1, 145.2, 148.2. HRMS (EI+) Calcd for C₂₁H₂₄OSi: 320.15964. Found: 320.16020 [(M)⁺].



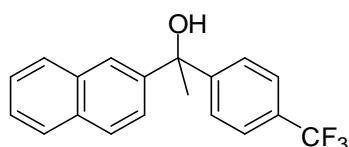
1-(4-(Trimethylsilyl)phenyl)cyclohexanol (Table 2, entry 13).

The title compound was prepared according to the above general procedure from cyclohexanol (0.25 mmol, 26 μL) as a colorless oil after 1 hour stirring at 80 °C (109 mg, 0.44 mmol, 88%). IR (thin film): 3390, 3070, 3020, 2340, 2840, 1450, 1370, 1270, 1240, 1120, 960, 830, 810, 750 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 0.26 (s, 9H), 1.23-1.37 (m, 1H), 1.59-1.90 (m, 10H), 7.48-7.53 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ -1.1, 22.1, 25.5, 38.7, 73.1, 123.9, 133.3, 138.5, 150.0. HRMS (EI+) Calcd for C₁₅H₂₄OSi: 248.15964. Found: 248.15910 [(M)⁺].



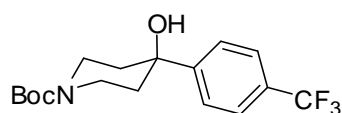
tert-Butyl-4-hydroxy-4-(4-(trimethylsilyl)phenyl)-1-piperidinecarboxylate (Table 2, entry 14).

The title compound was prepared according to the above general procedure from 1-boc-4-hydroxypiperidine (0.25 mmol, 50 mg) as a colorless oil that slowly solidifies after 5 hours stirring at 80 °C (127 mg, 0.36 mmol, 72%). IR (thin film): 3430, 3020, 2950, 2940, 1700, 1660, 1420, 1370, 1240, 1170, 1030, 840 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 0.27 (s, 9H), 1.48 (s, 9H), 1.52 (s, 1H), 1.72-1.74 (m, 2H), 2.01 (br s, 2H), 3.25 (br s, 2H), 4.03 (br s, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.53 (t, *J* = 8.1 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ -1.1, 28.5, 38.1, 40.1, 71.5, 79.5, 123.8, 133.6, 139.5, 148.4, 154.9. HRMS (EI+) Calcd for C₁₉H₃₁NO₃Si: 349.20732. Found: 349.20709 [(M)⁺].



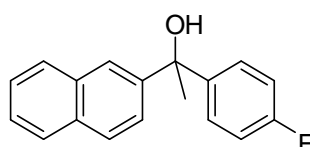
1-(Naphthalen-2-yl)-1-(4-(trifluoromethyl)phenyl)ethanol

(Table 2, entry 15). The title compound was prepared according to the above general procedure from 1-(2-naphthyl)ethanol (0.25 mmol, 43 mg) as a light yellow oil after 6 hours stirring at 80 °C (119 mg, 0.38 mmol, 75%). IR (thin film): 3420, 3060, 2980, 2930, 1610, 1420, 1320, 1170, 1120, 1100, 1070, 1010, 850 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 2.07 (s, 3H), 2.29 (s, 1H), 7.40 (dd, $J = 8.6$ and 1.9 Hz, 1H), 7.47-7.52 (m, 2H), 7.57-7.59 (m, 4H), 7.77-7.86 (m, 3H), 7.96 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 30.6, 76.1, 123.9, 124.1 (q, $J = 272.1$ Hz), 124.7, 125.1 (dd, $J = 7.2$ and 3.5 Hz), 126.2, 126.3, 126.4, 127.5, 128.2, 128.3, 129.1 (q, $J = 23.4$ Hz), 132.5, 132.9, 144.2, 151.6. HRMS (EI+) Calcd for $\text{C}_{19}\text{H}_{15}\text{F}_3\text{O}$: 316.10750. Found: 316.10840 $[(\text{M})^+]$.



tert-Butyl-4-hydroxy-4-(4-(trifluoromethyl)phenyl)-

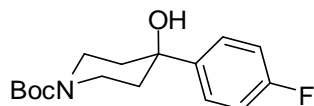
1-piperidinecarboxylate (Table 2, entry 16). The title compound was prepared according to the above general procedure from 1-boc-4-hydroxypiperidine (0.25 mmol, 50 mg) as a light yellow oil after 0.5 hour stirring at 80 °C (131 mg, 0.38 mmol, 76%). IR (thin film): 3440, 2980, 2940, 2890, 1660, 1490, 1440, 1370, 1330, 1280, 1250, 1170, 1070, 1040, 840 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 1.49 (s, 9H), 1.67 (s, 1H), 1.70-1.73 (m, 2H), 2.00 (br s, 2H), 3.23 (br s, 2H), 4.06 (br s, 2H), 7.61 (t, $J = 8.7$ Hz, 4H). ^{13}C NMR (75 MHz, CDCl_3) δ 28.4, 38.0, 39.8, 71.6, 79.8, 124.1 (q, $J = 271.8$ Hz), 125.0, 125.4, 125.4, 129.5 (q, $J = 64.9$ Hz), 134.1, 152.0, 154.8. HRMS (EI+) Calcd for $\text{C}_{17}\text{H}_{22}\text{F}_3\text{NO}_3$: 345.15518. Found: 345.15413 $[(\text{M})^+]$.



1-(4-Fluorophenyl)-1-(naphthalen-2-yl)ethanol (Table 2, entry

17). The title compound was prepared according to the above general procedure from 1-(2-naphthyl)ethanol (0.25 mmol, 43 mg) as a light yellow oil after 11 hours stirring at 80 °C (84 mg, 0.32 mmol, 63%). IR (thin film): 3430, 3050, 3980, 2930, 1600, 1500, 1230, 1160, 840, 820, 750 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 2.04 (s, 3H), 2.25 (s, 1H), 6.99 (d, $J = 8.8$ Hz, 2H), 7.37-7.45 (m, 3H), 7.47-7.52 (m, 2H), 7.76-7.86 (m, 3H), 7.95 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 30.9, 76.0, 114.9 (d, $J = 21.2$ Hz), 123.7, 124.8, 126.1, 126.2, 127.5, 127.7, 127.8, 128.1, 128.2, 132.4, 133.0,

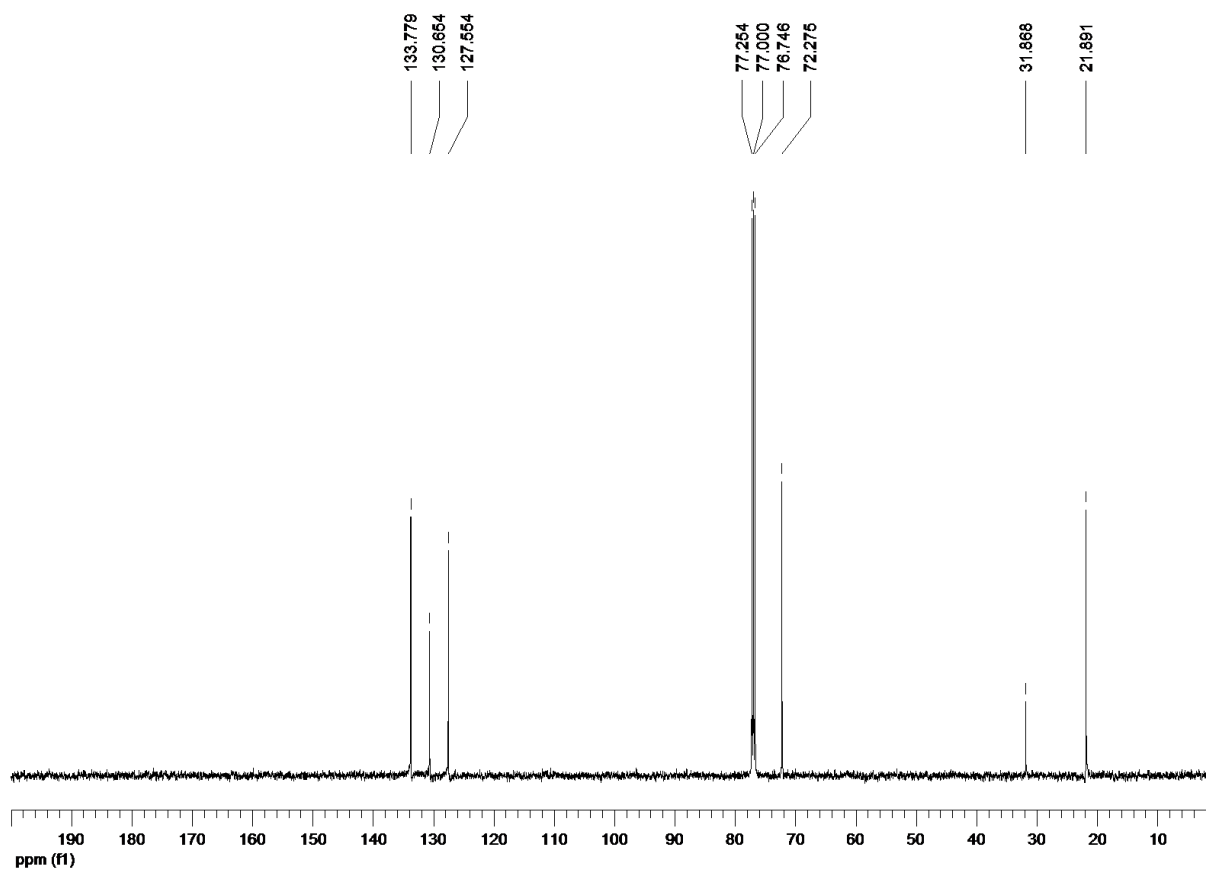
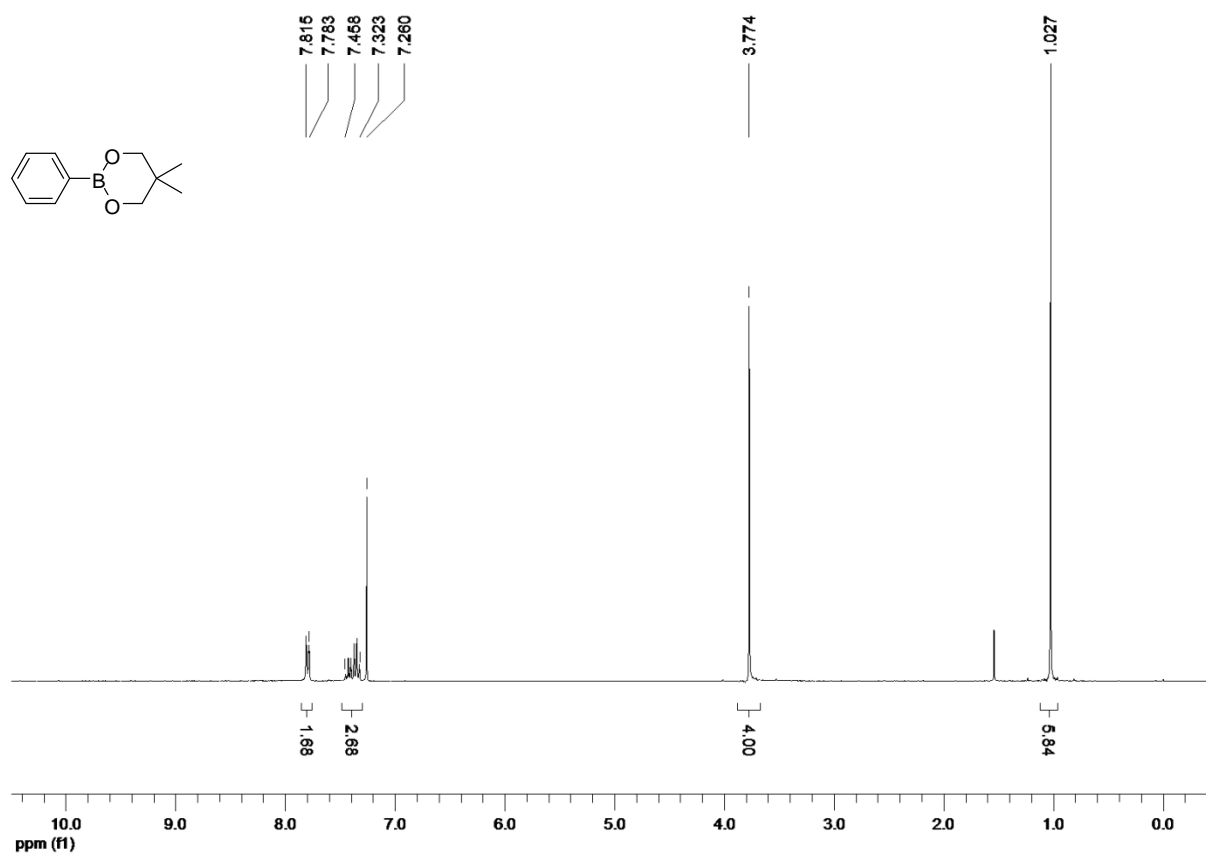
143.6 (d, $J = 143.6$ Hz), 145.0, 161.8 (d, $J = 245.7$ Hz). HRMS (EI+) **Calcd for C₁₈H₁₅FO**: 266.11069. **Found**: 266.11142 [(M)⁺].

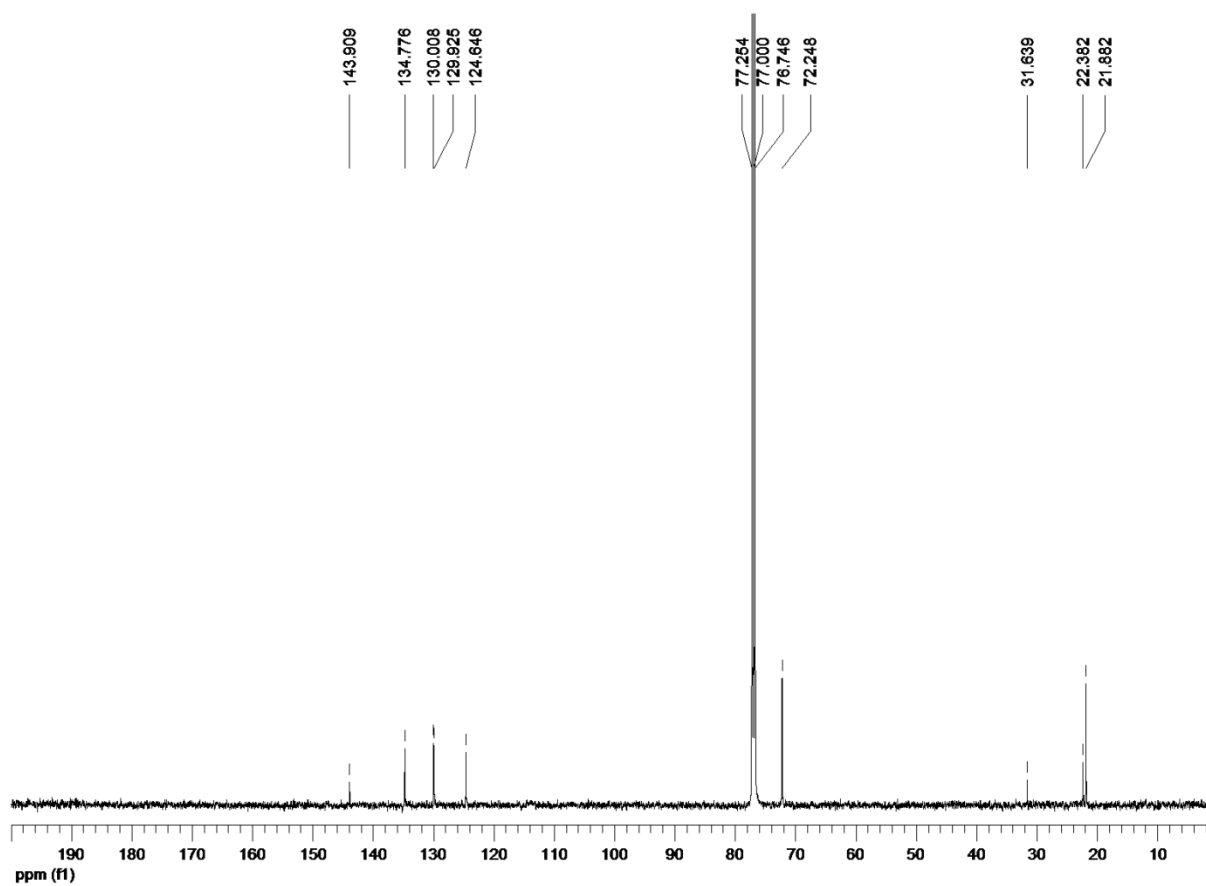
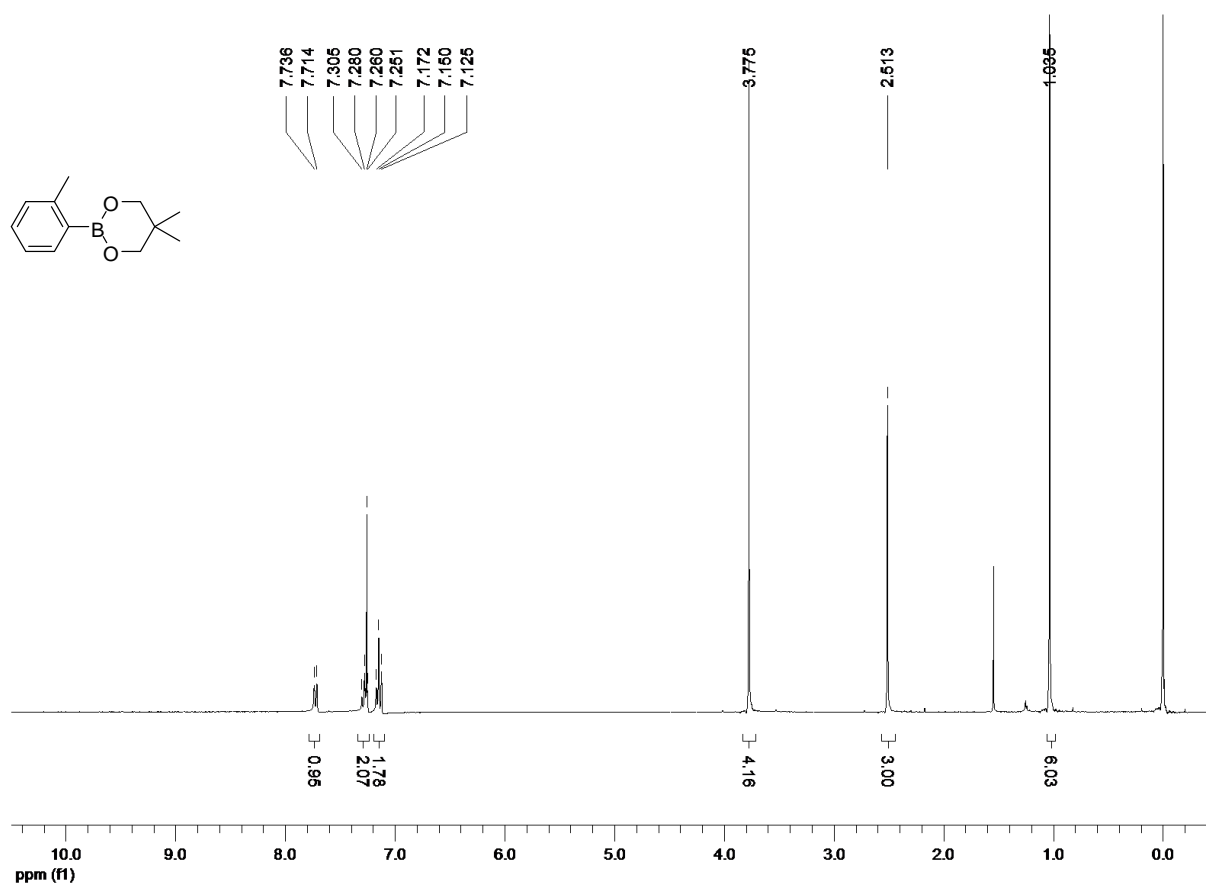


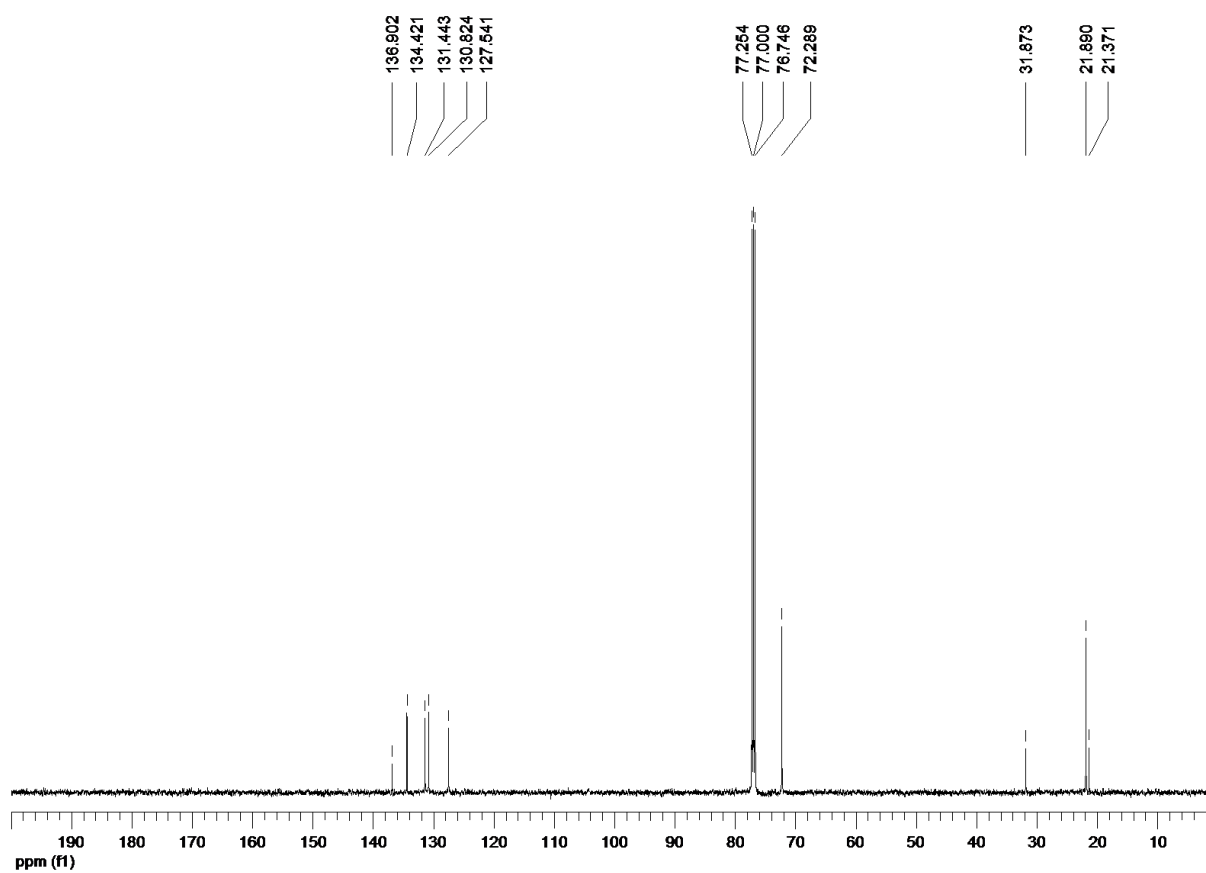
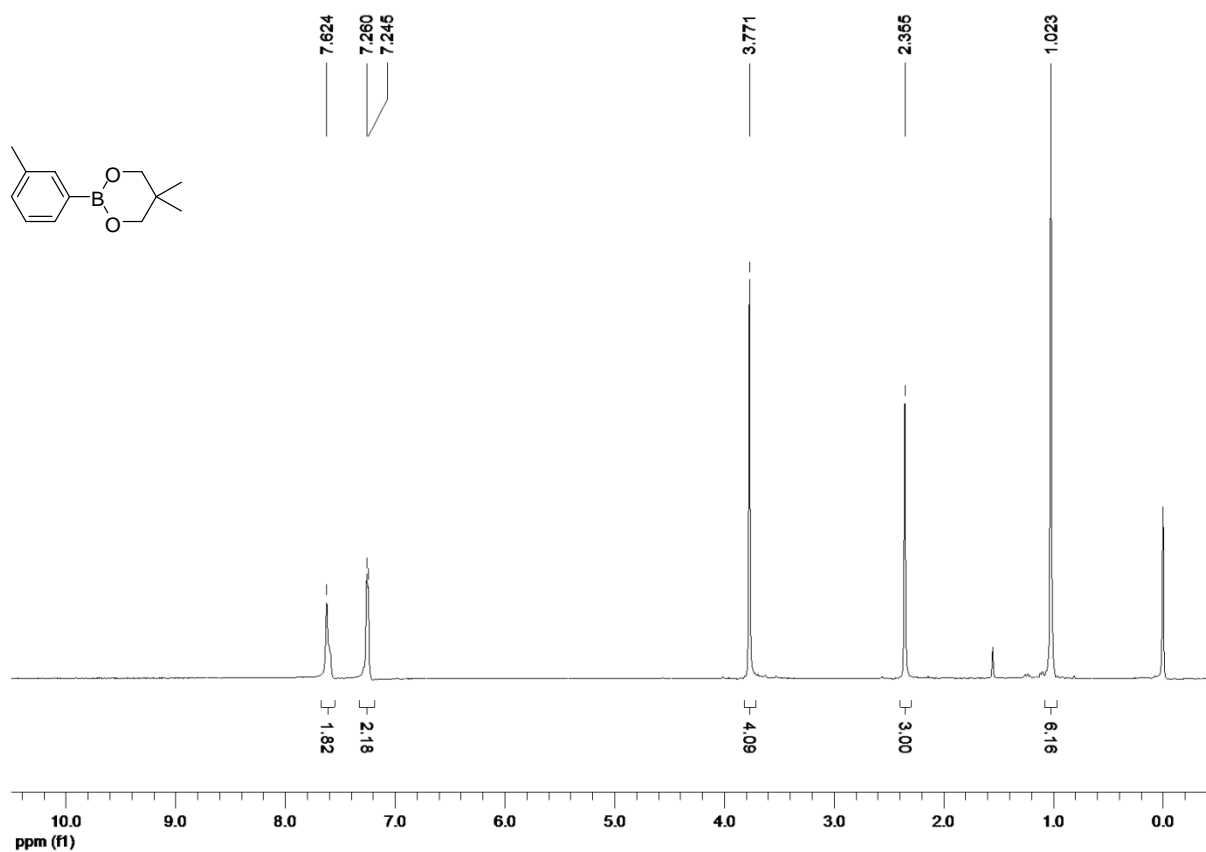
***tert*-Butyl-4-hydroxy-4-(4-fluorophenyl)-**

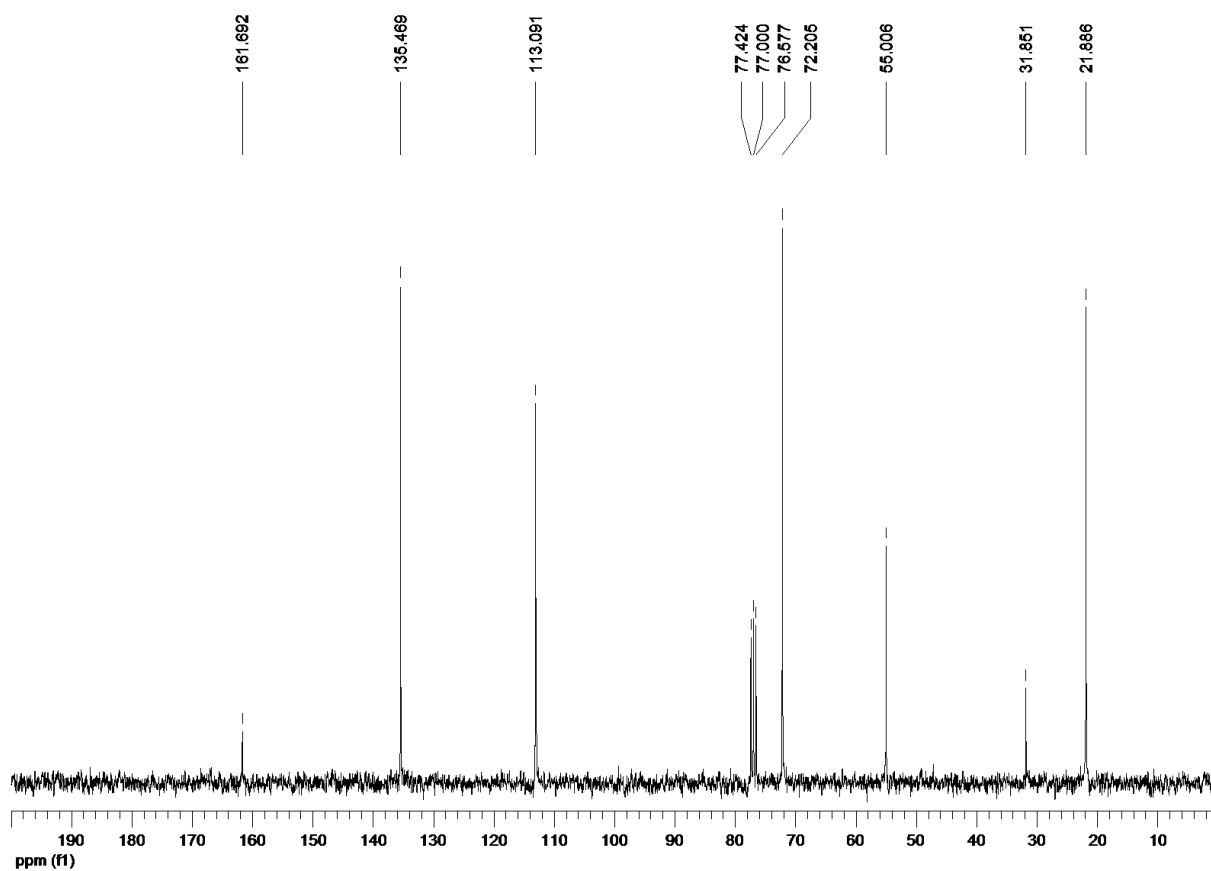
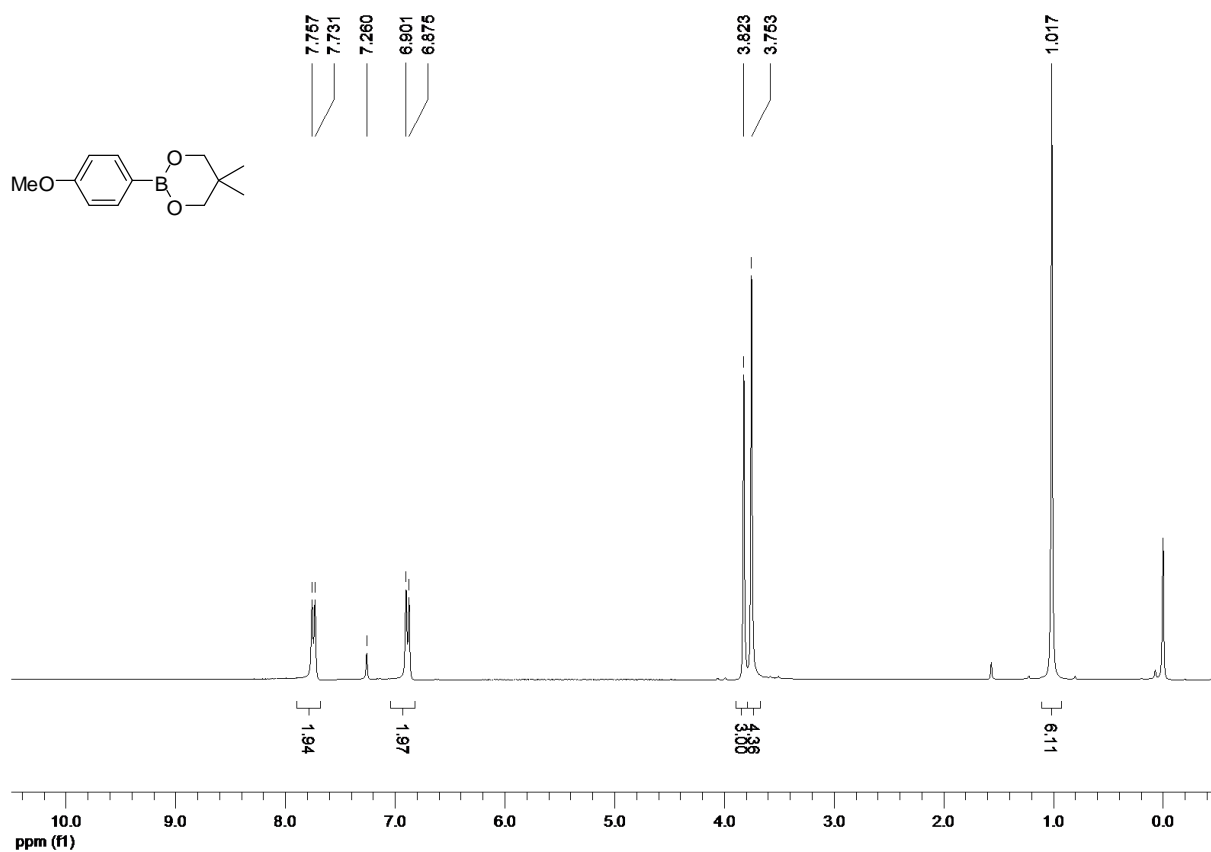
1-piperidinecarboxylate (Table 2, entry 18). The title compound

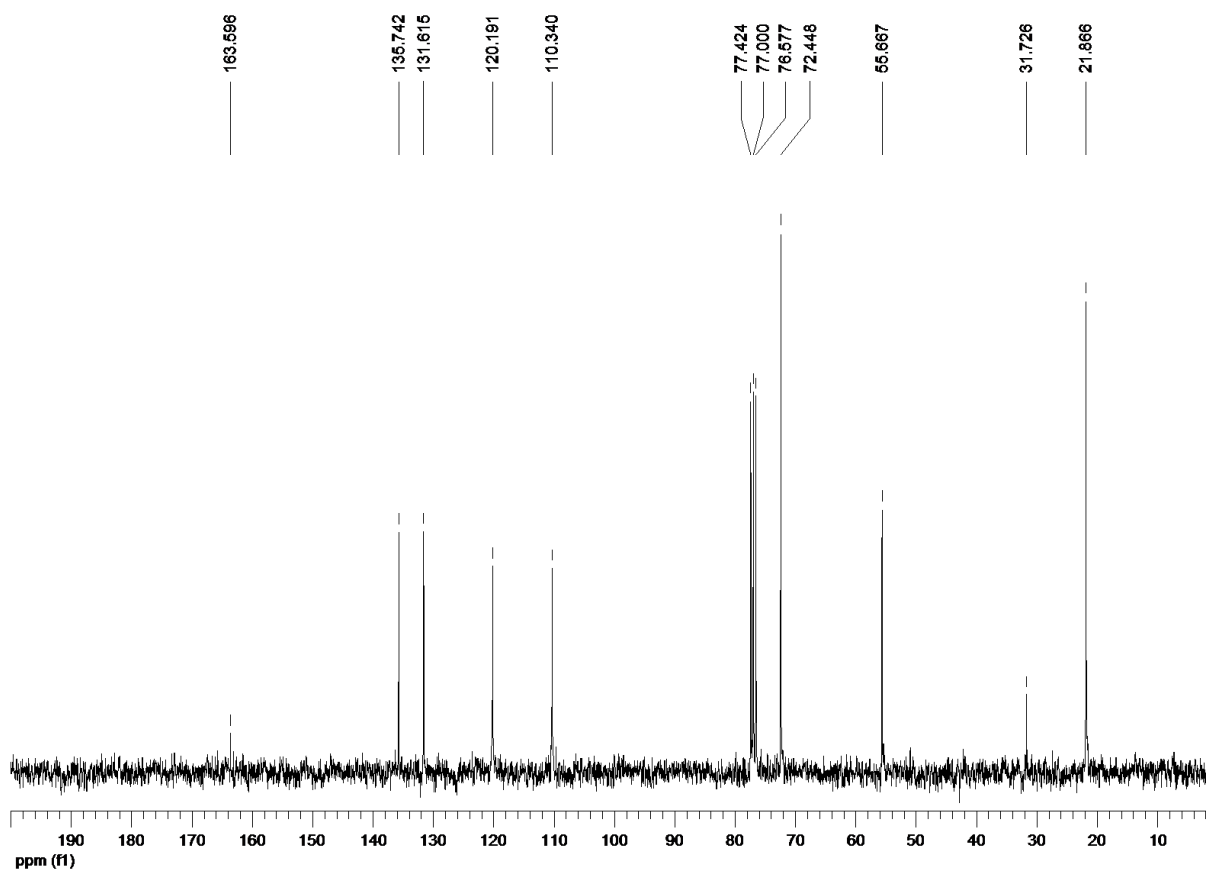
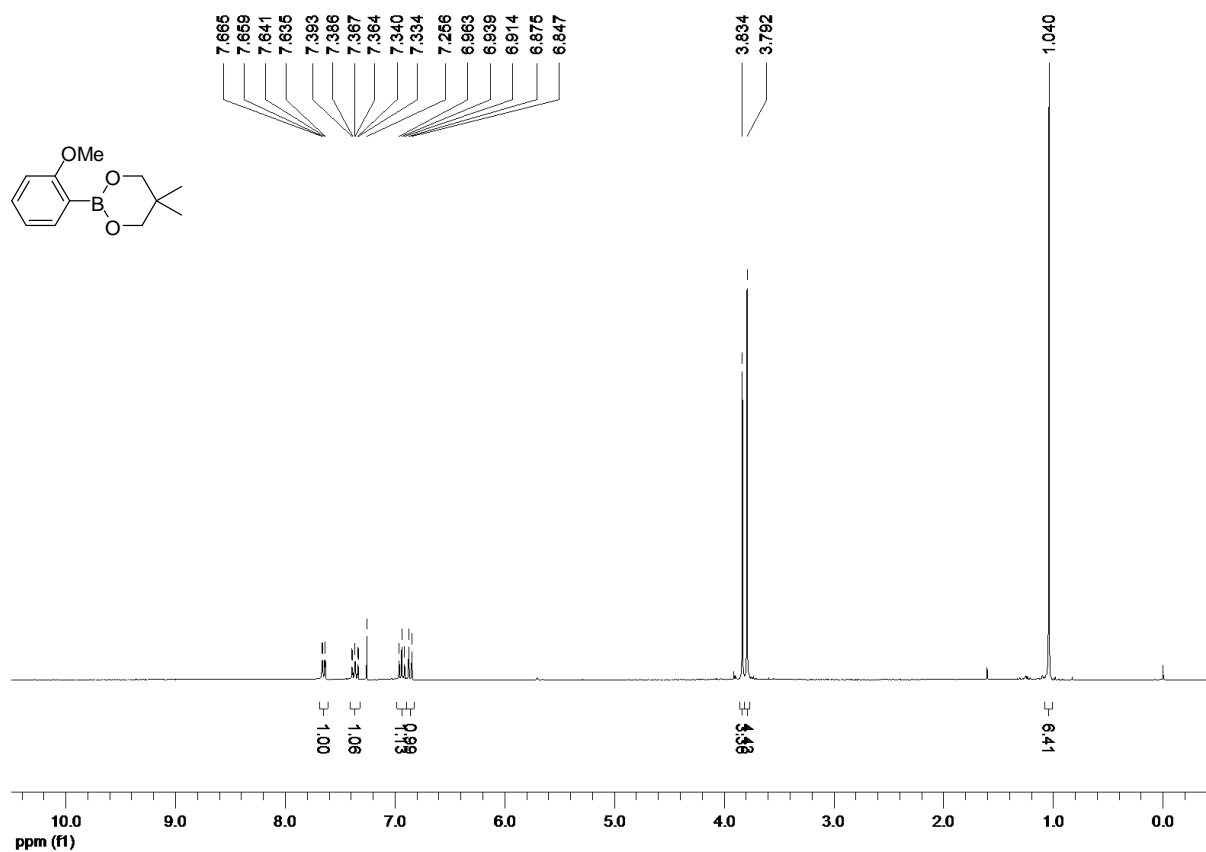
was prepared according to the above general procedure from 1-boc-4-hydroxypiperidine (0.25 mmol, 50 mg) as a light yellow oil after 2 hours stirring at 80 °C (121 mg, 0.41 mmol, 82%). IR (thin film): 3420, 2980, 2920, 2880, 1670, 1520, 1430, 1370, 1280, 1250, 1210, 1160. cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 1.47 (s, 9H), 1.57 (s, 1H), 1.70-1.73 (m, 2H), 1.96 (br s, 2H), 3.22 (br s, 2H), 4.02 (br s, 2H), 7.03 (t, $J = 8.7$ Hz, 2H), 7.43 (dd, $J = 8.9$ and 5.3 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 28.5, 38.3, 39.8, 71.3, 79.6, 115.2 (d, $J = 21.1$ Hz), 126.2 (d, $J = 7.8$ Hz), 143.9, 154.8, 162.0 (d, $J = 245.9$ Hz). HRMS (EI+) **Calcd for C₁₆H₂₂FNO₃**: 295.15837. **Found**: 295.15690 [(M)⁺].

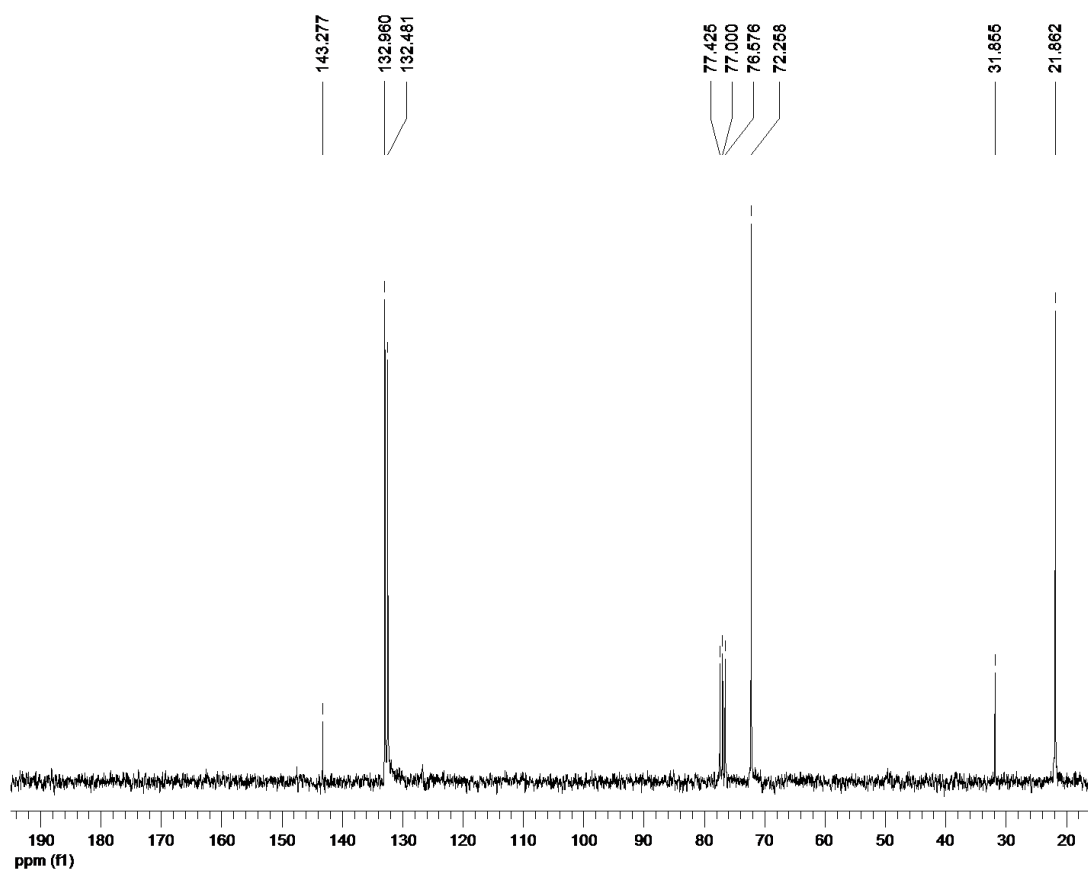
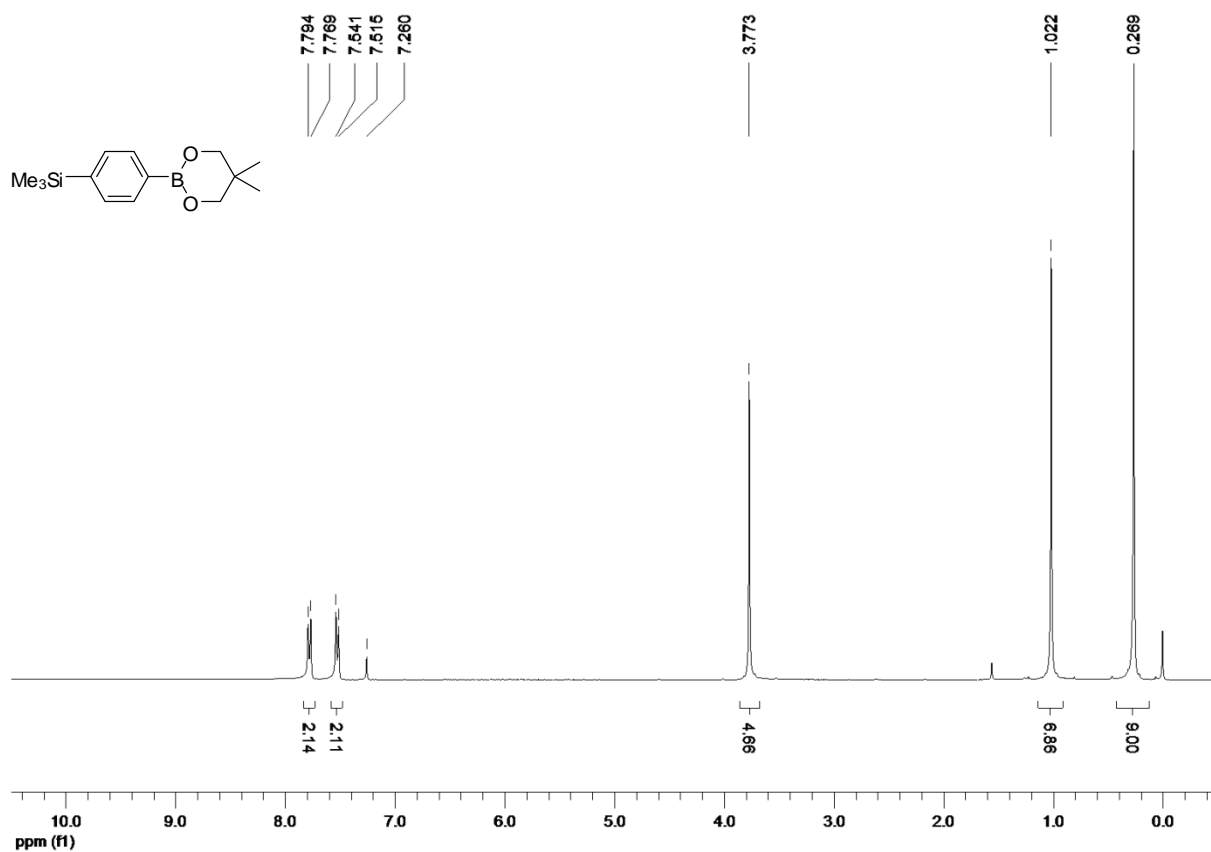


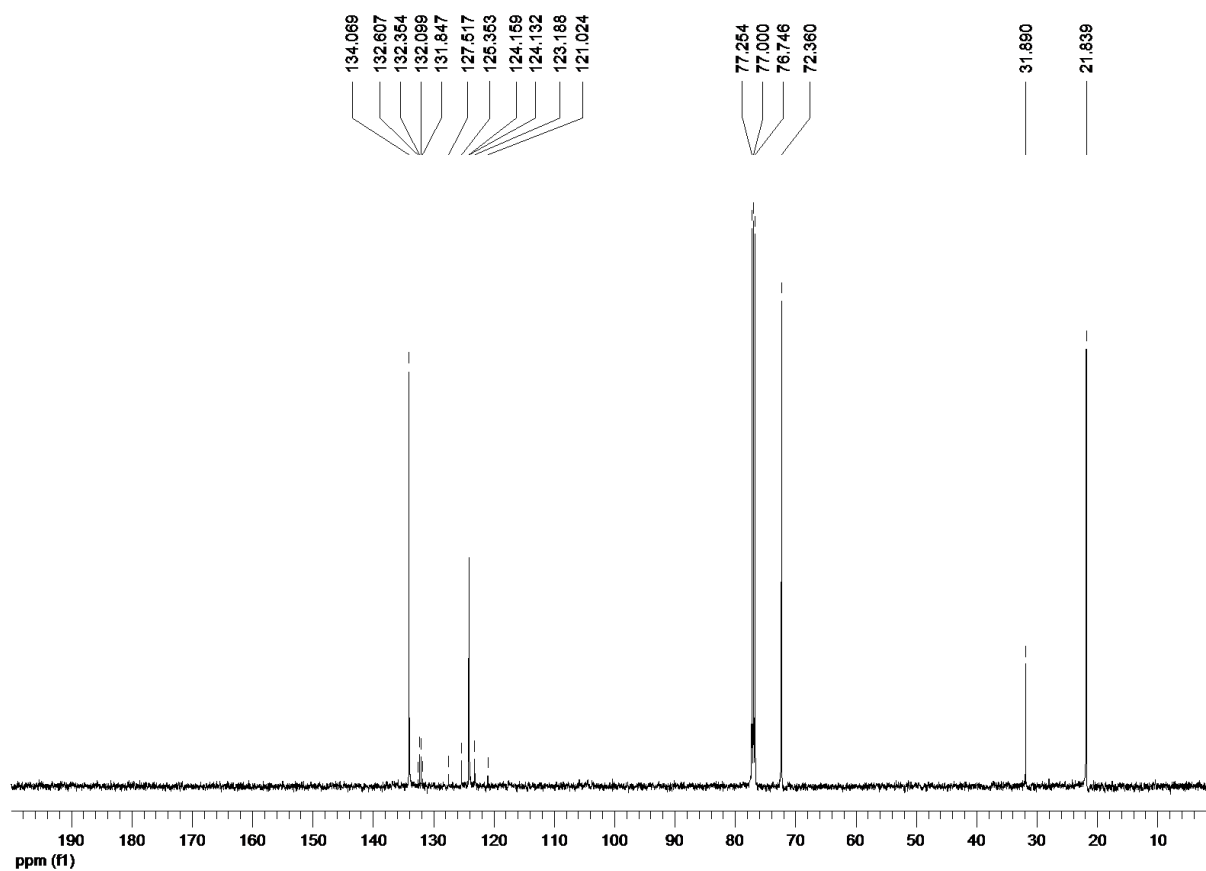
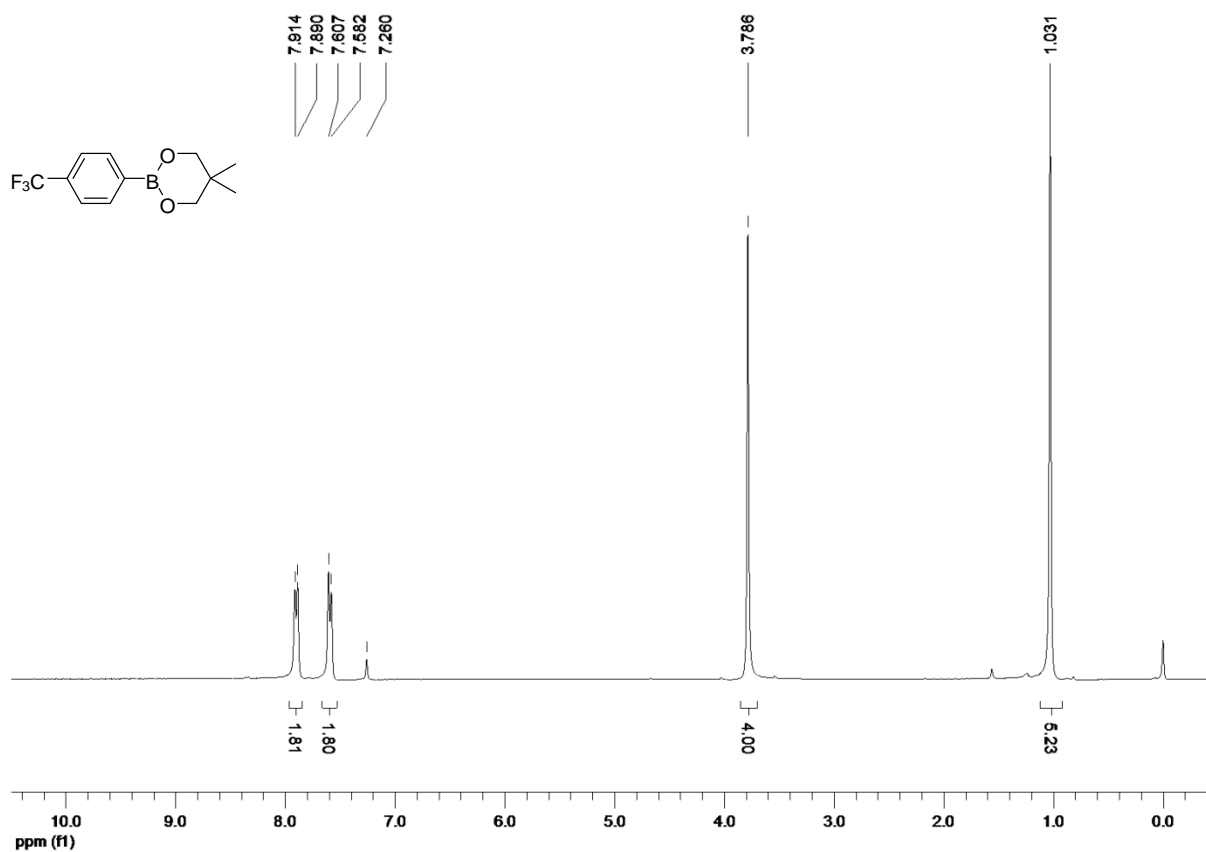


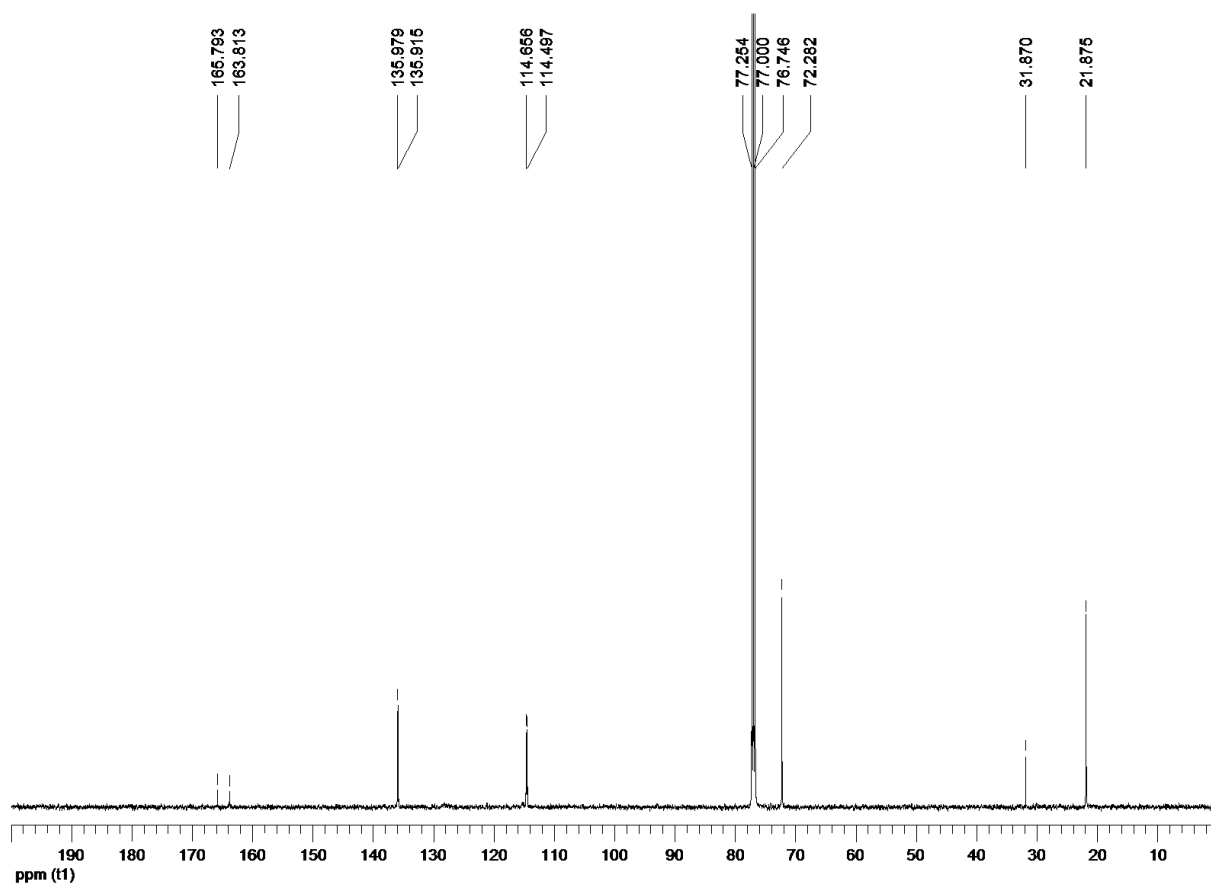
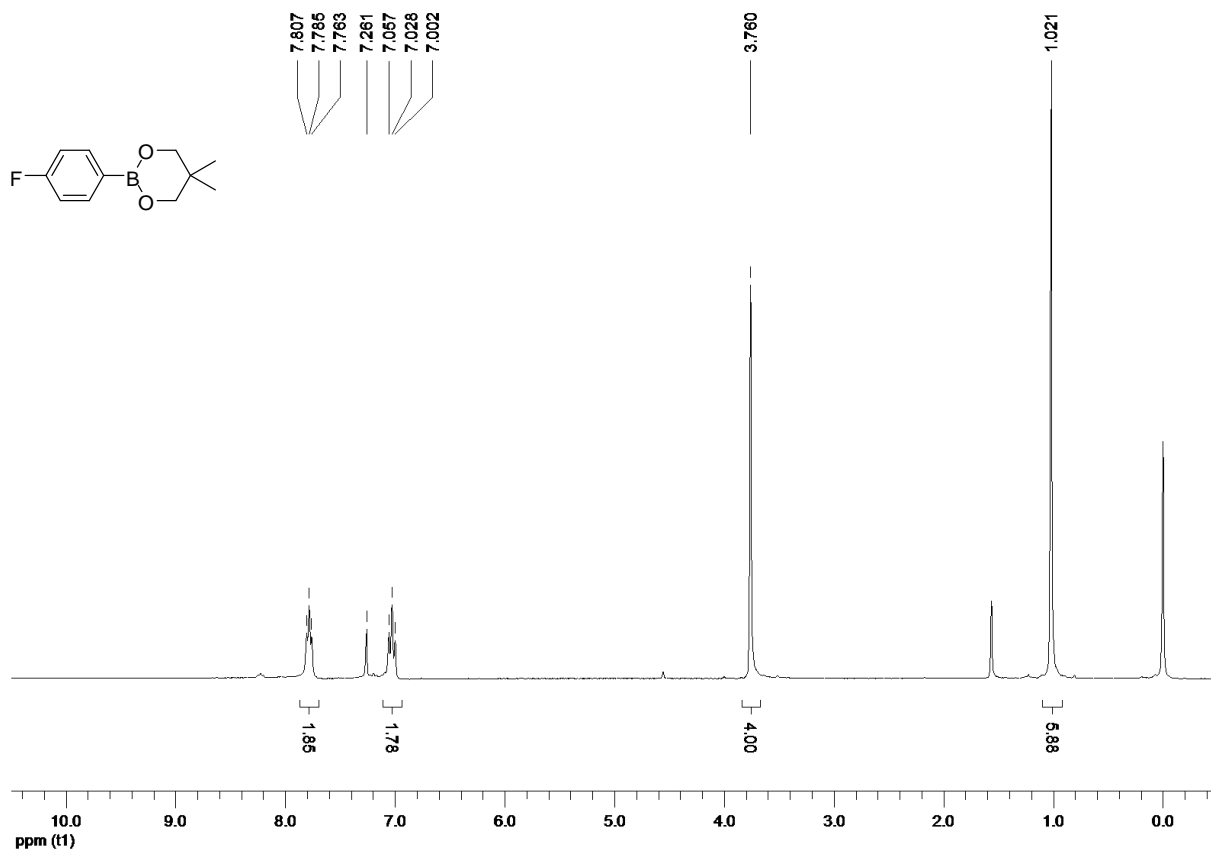


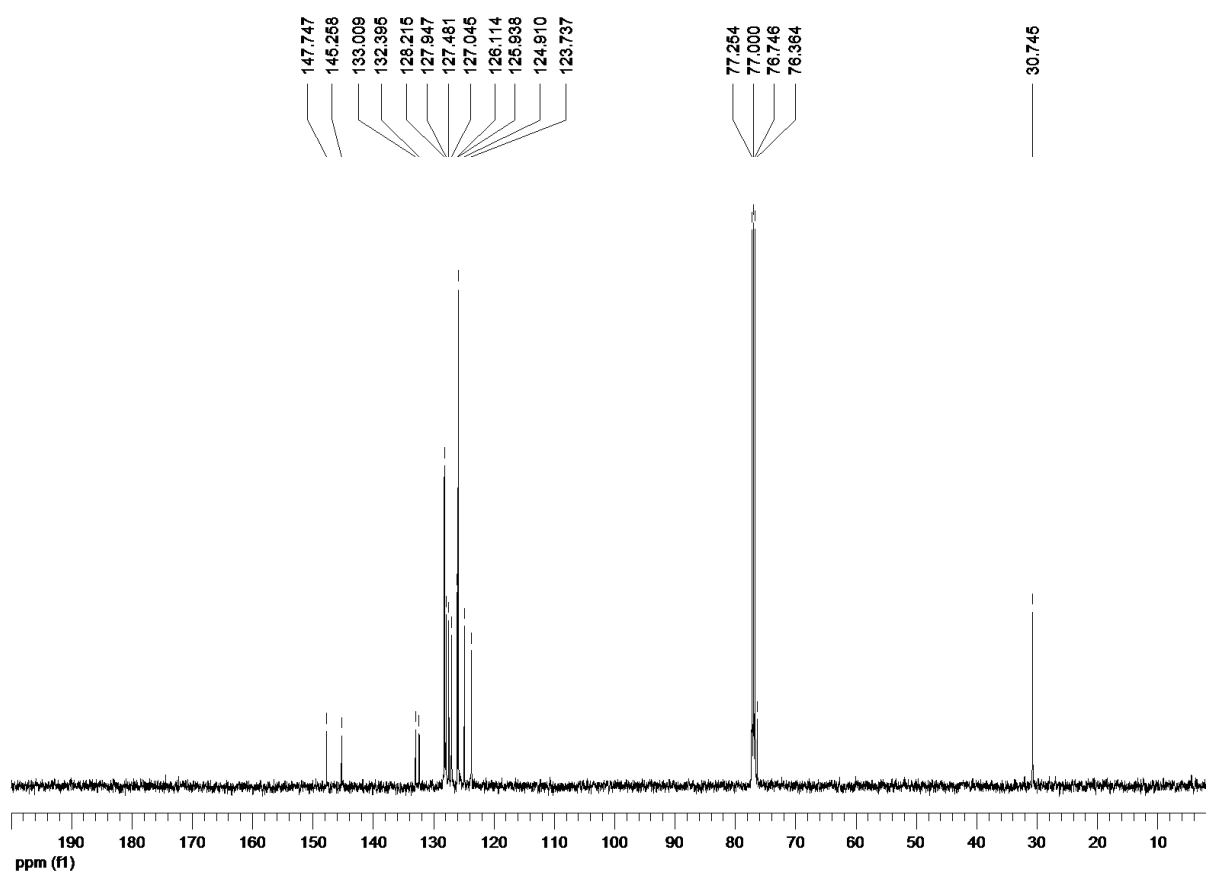
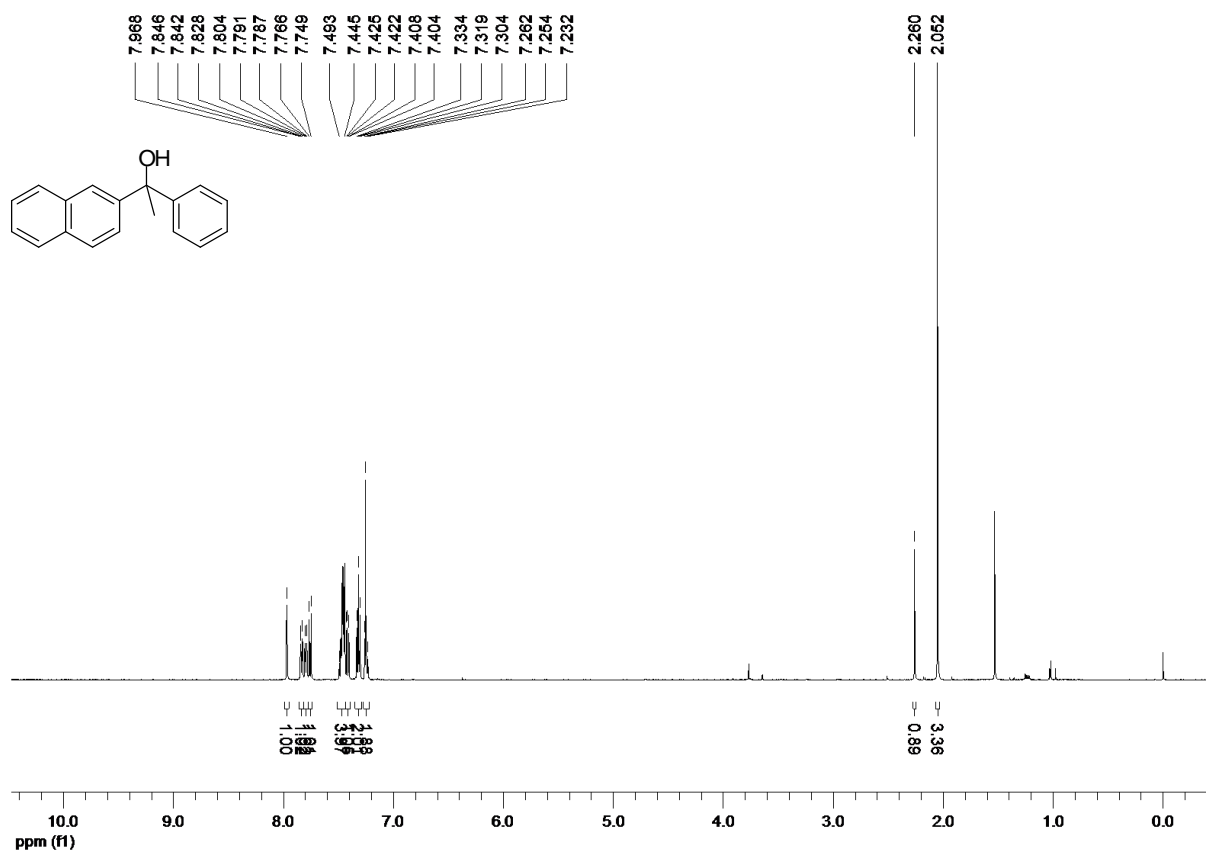


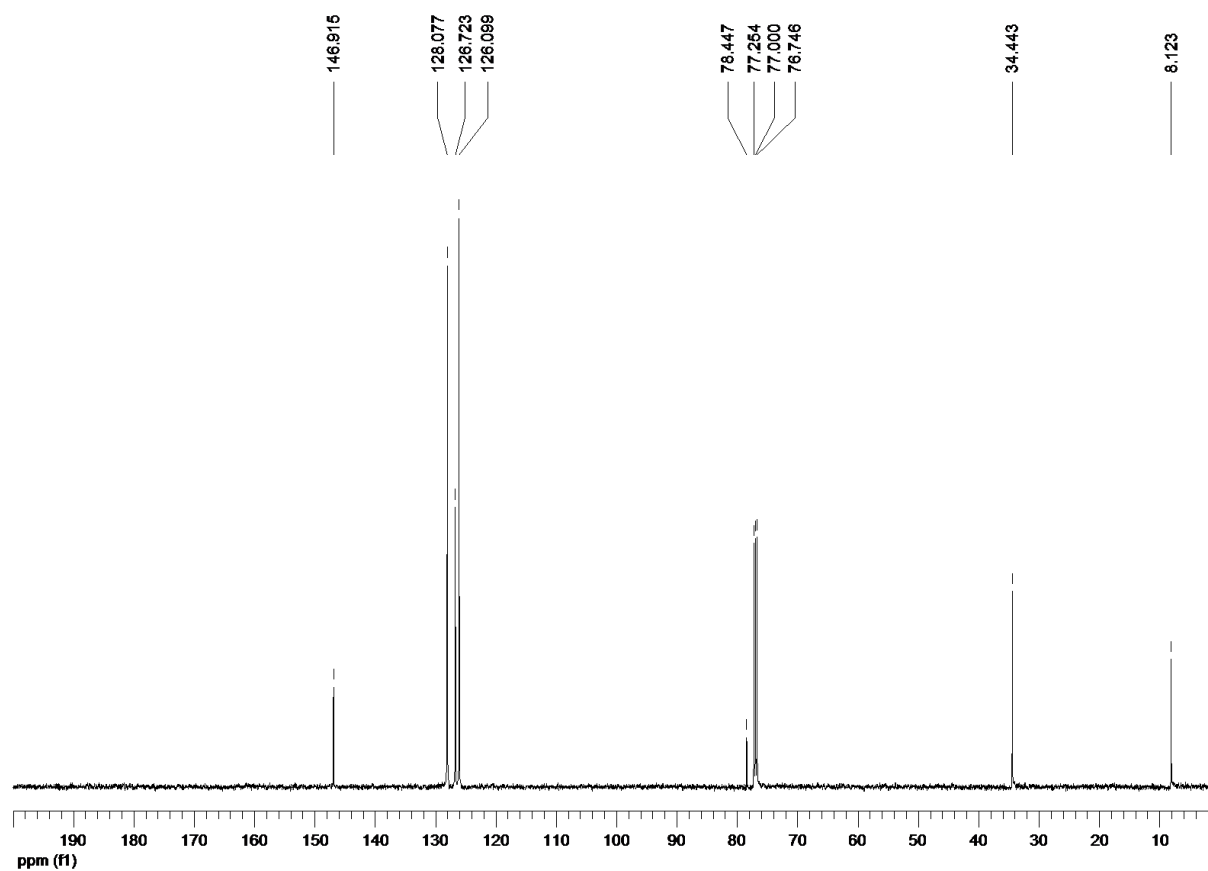
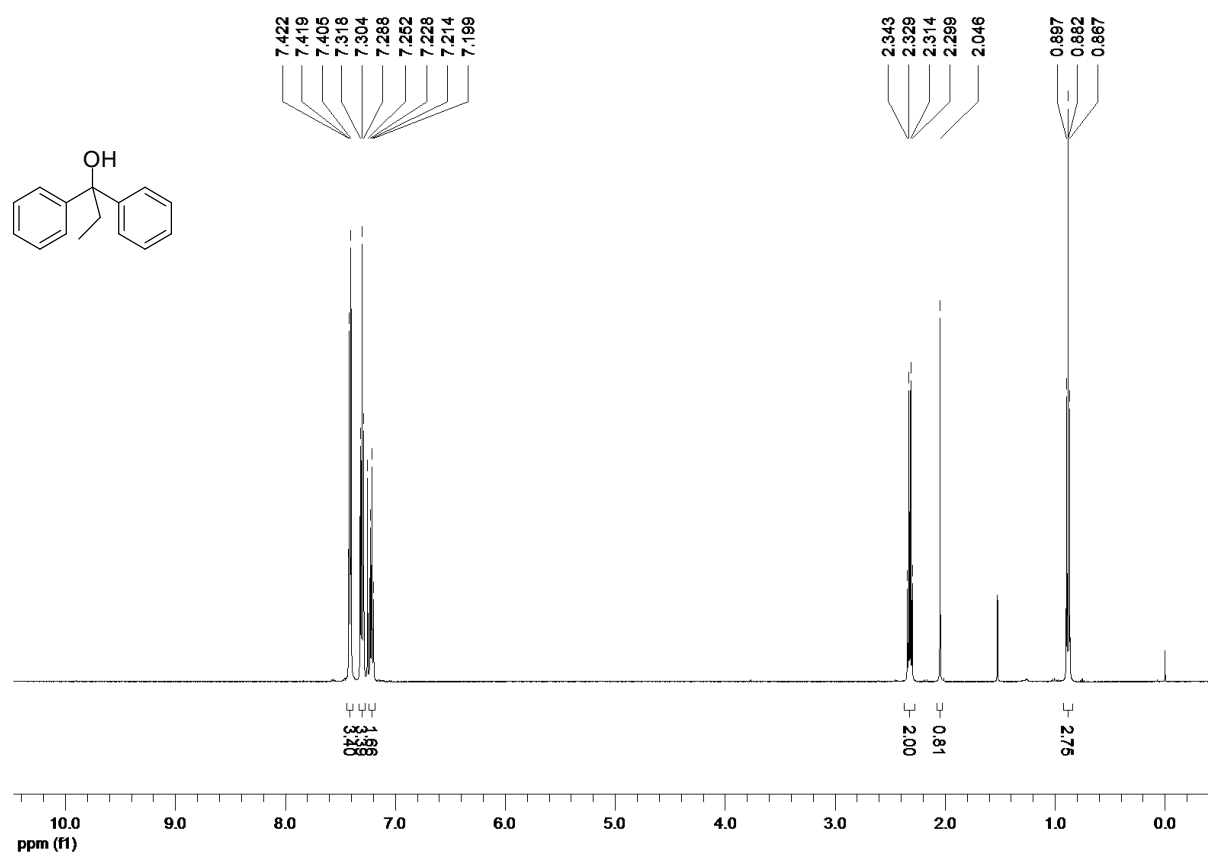


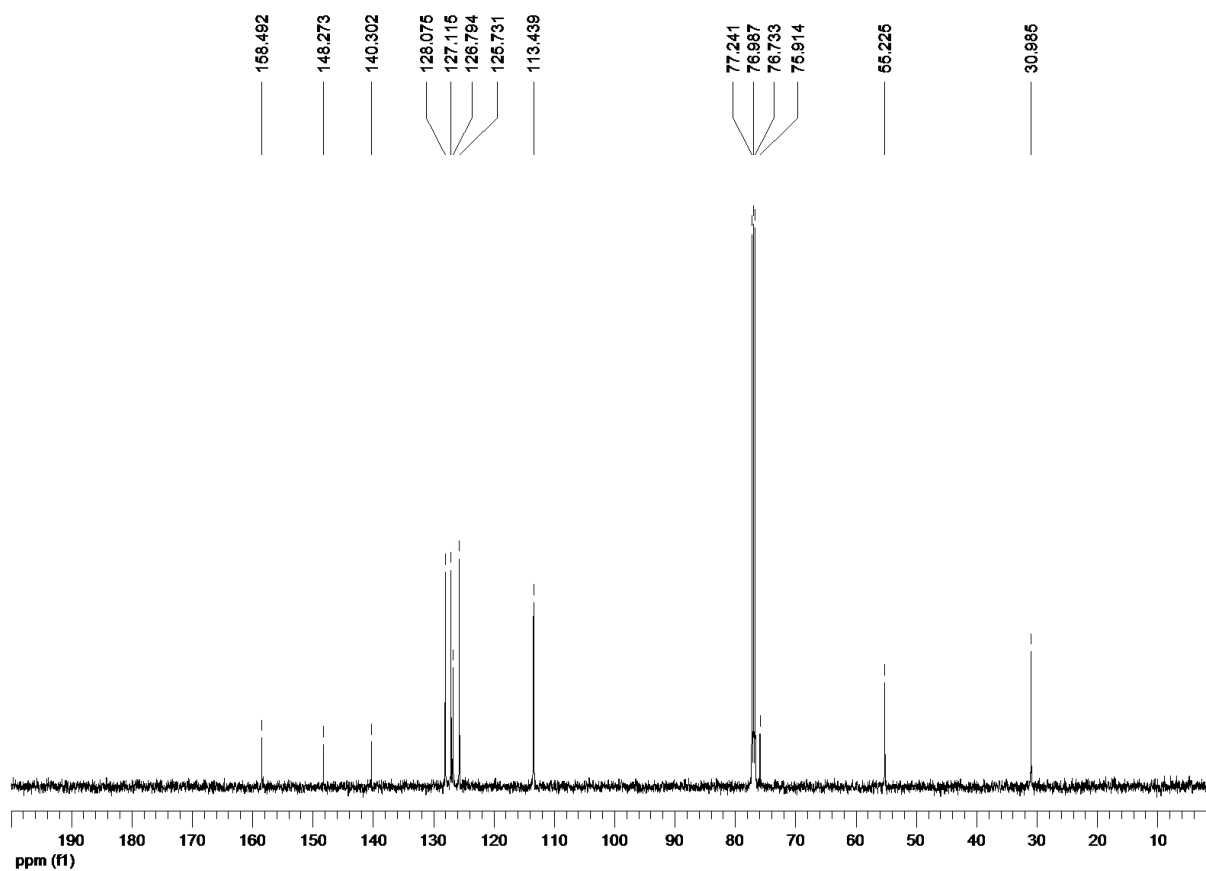
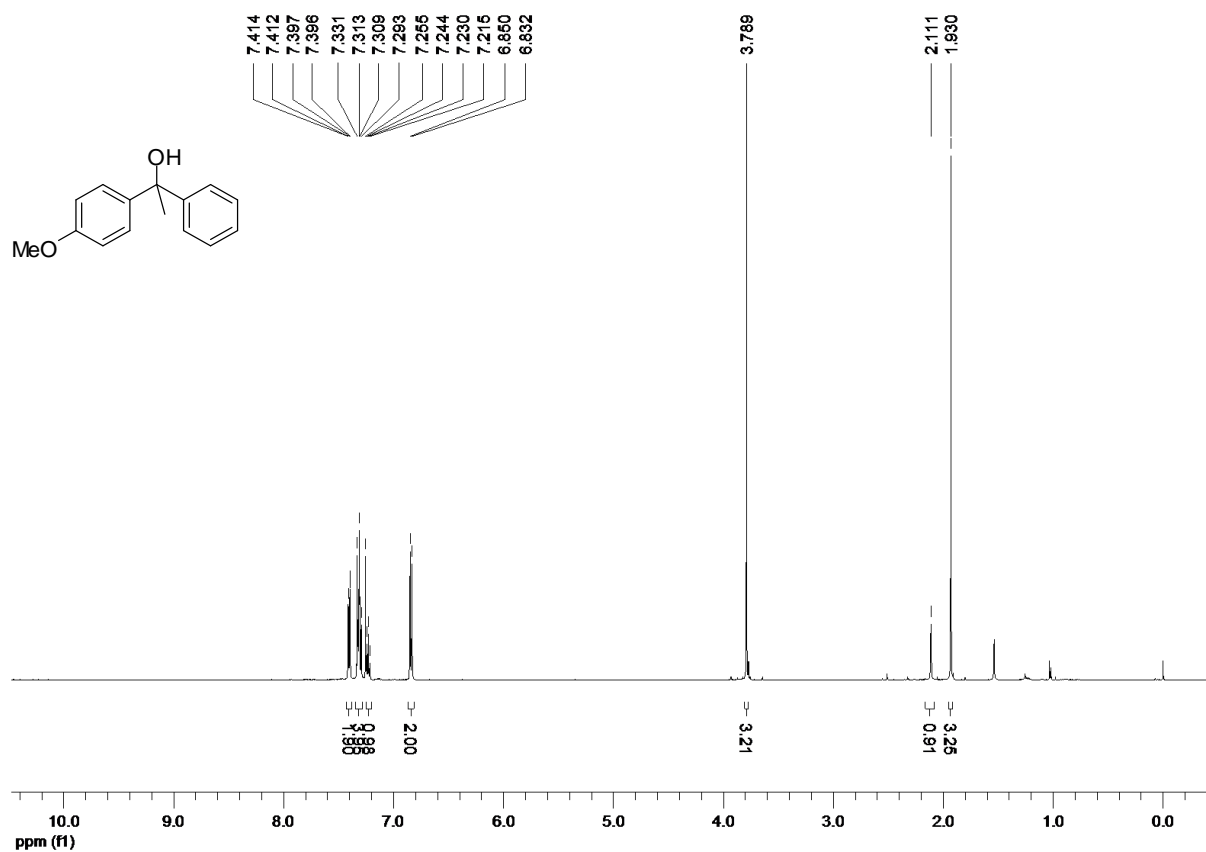


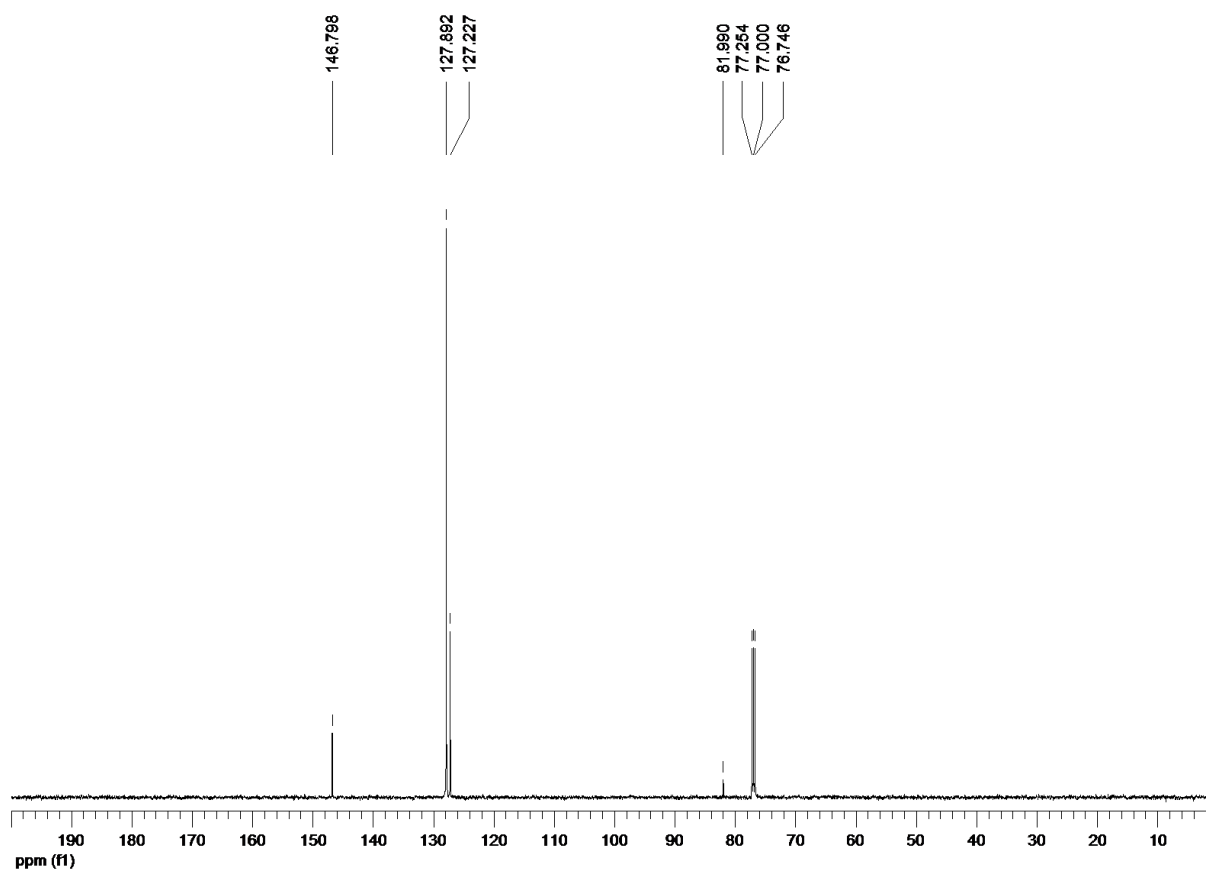
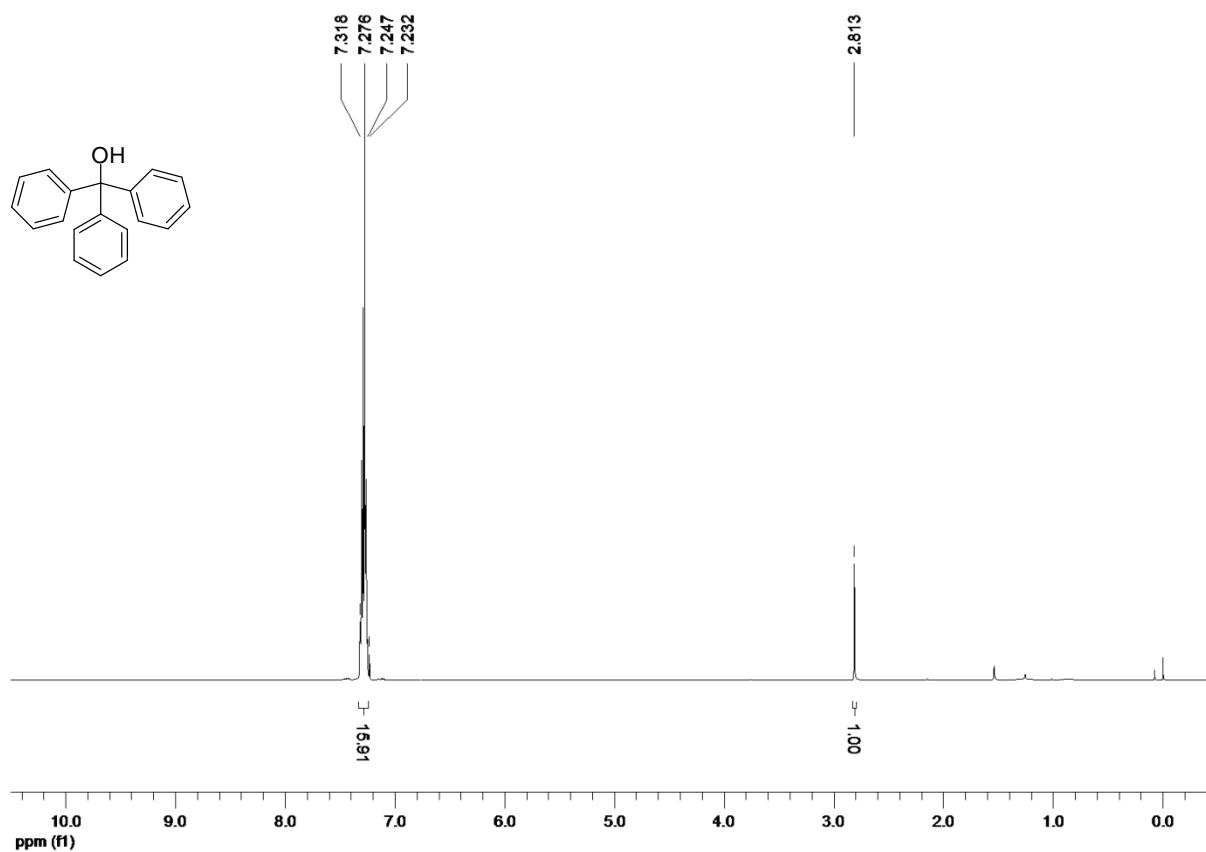


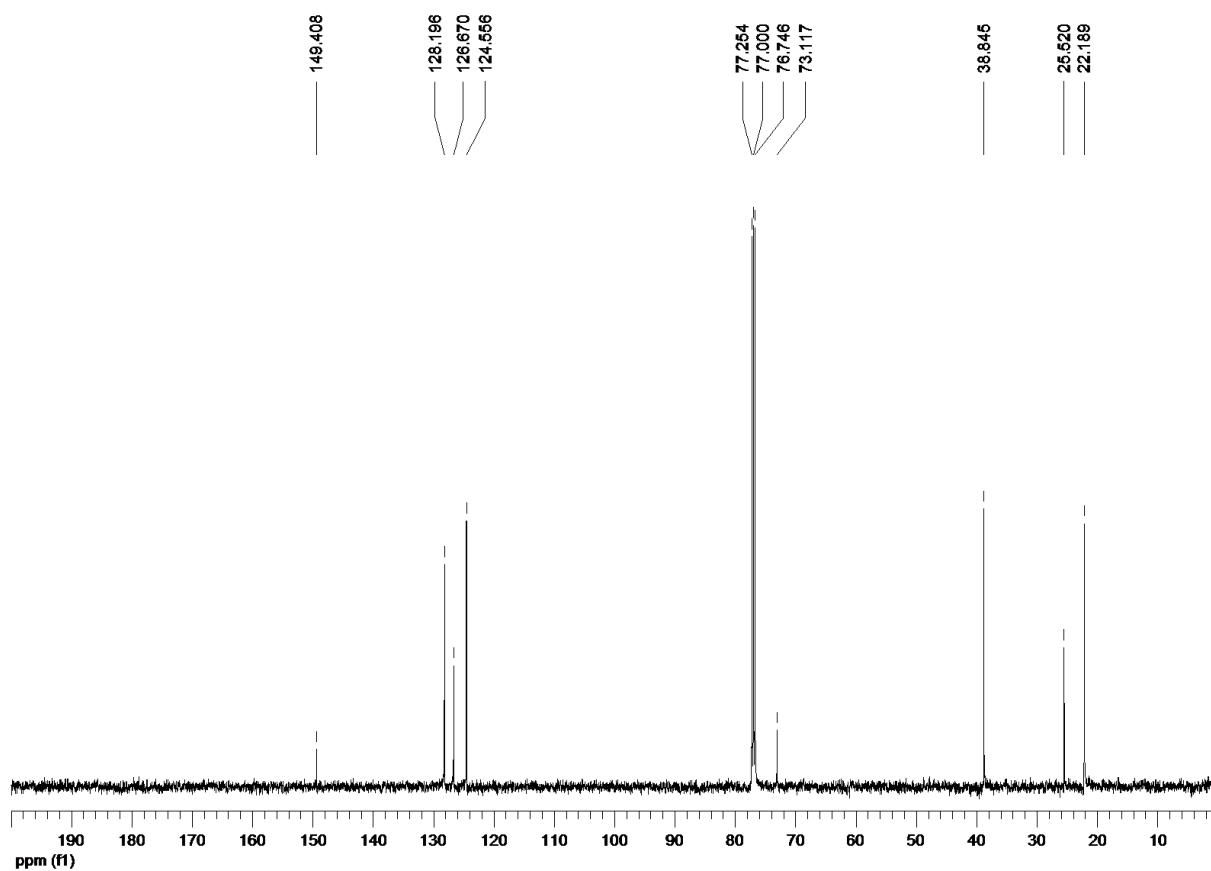
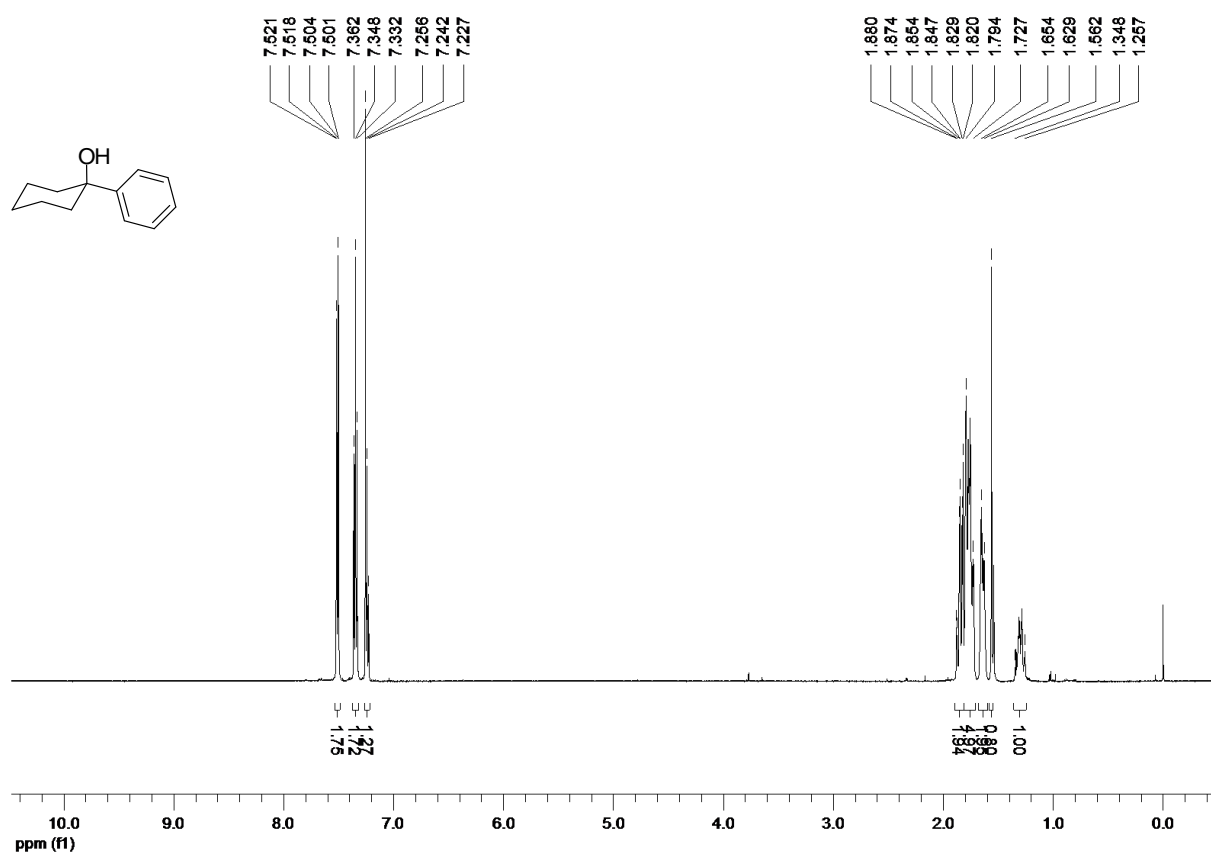


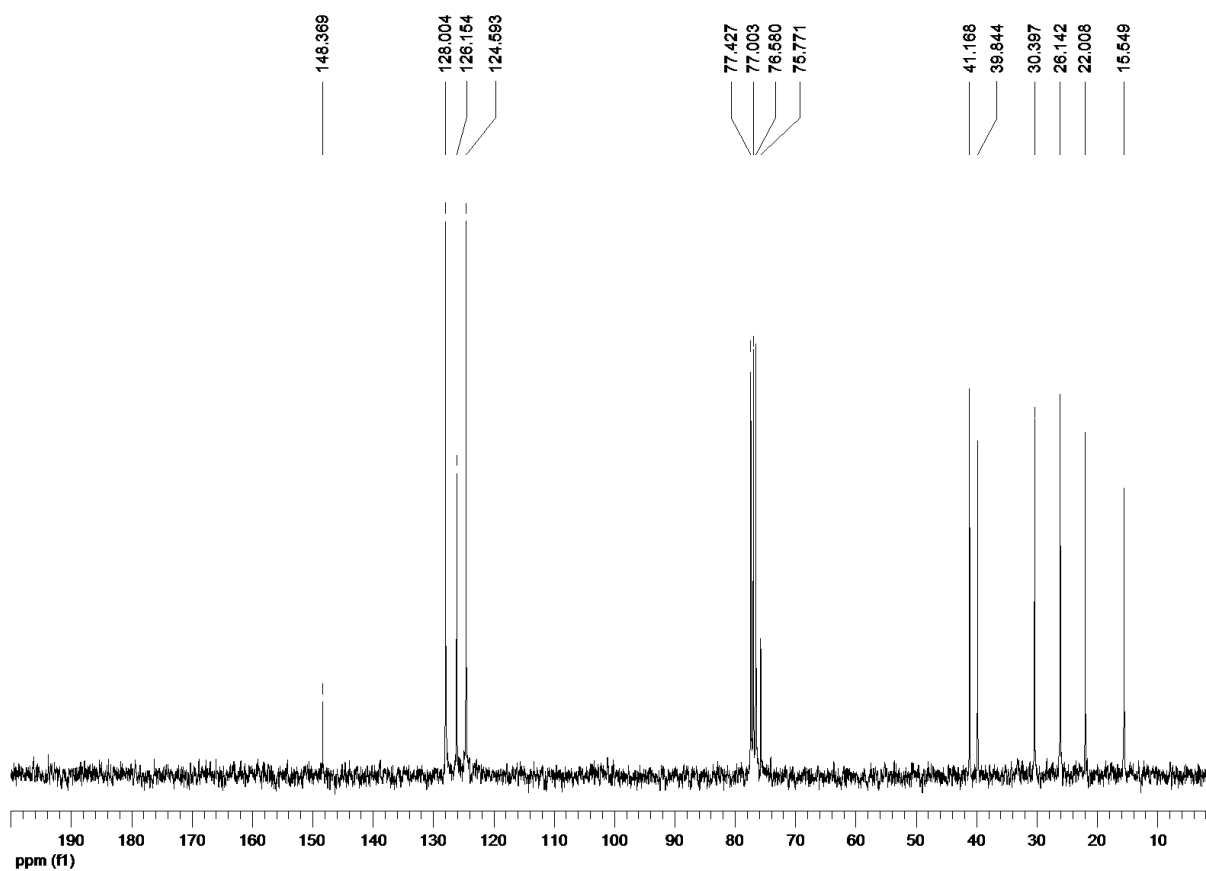
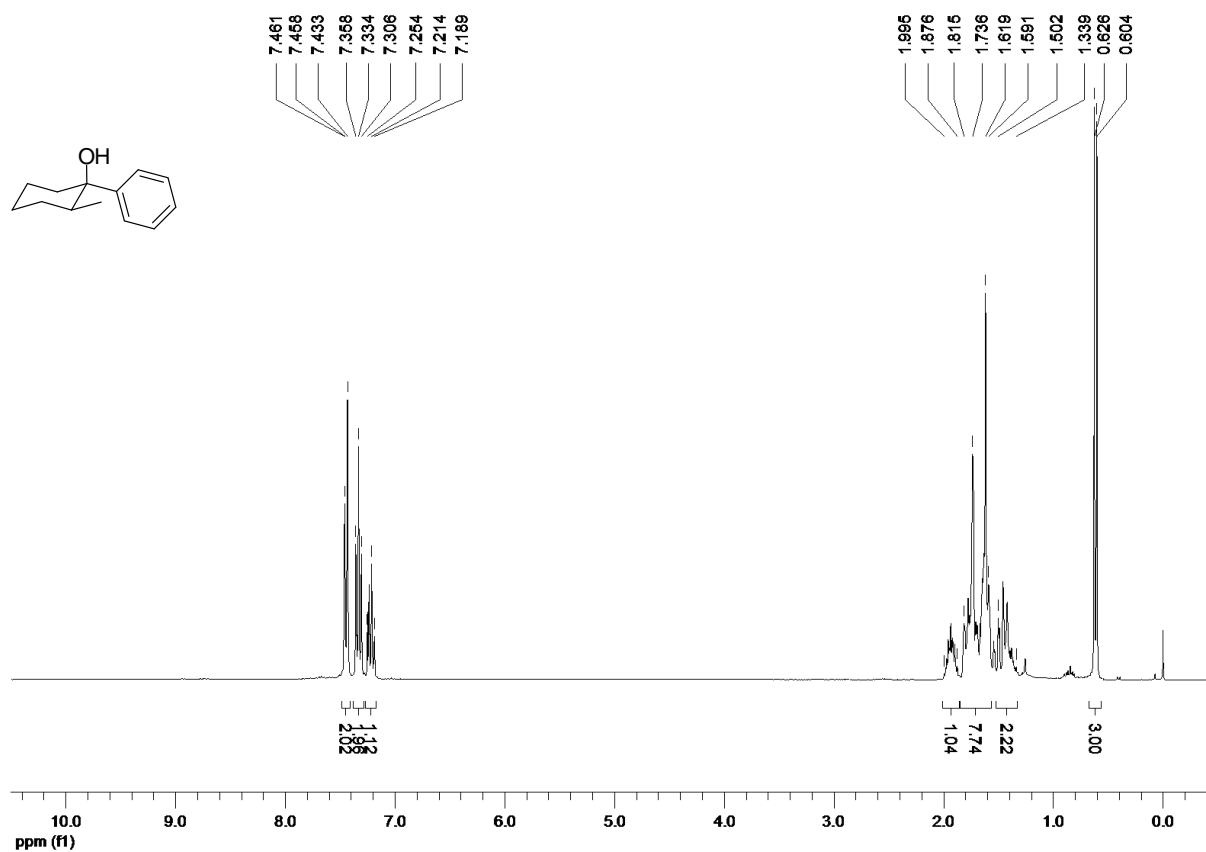


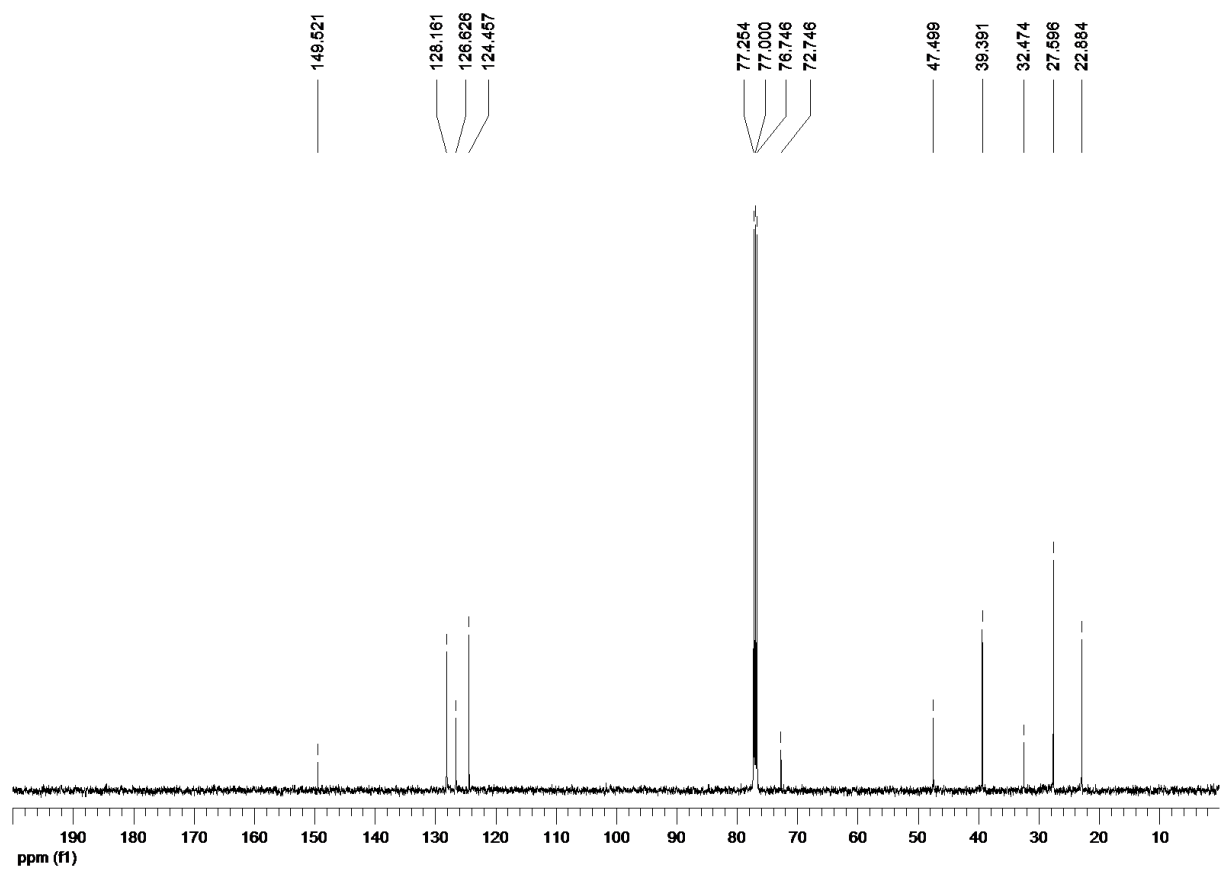
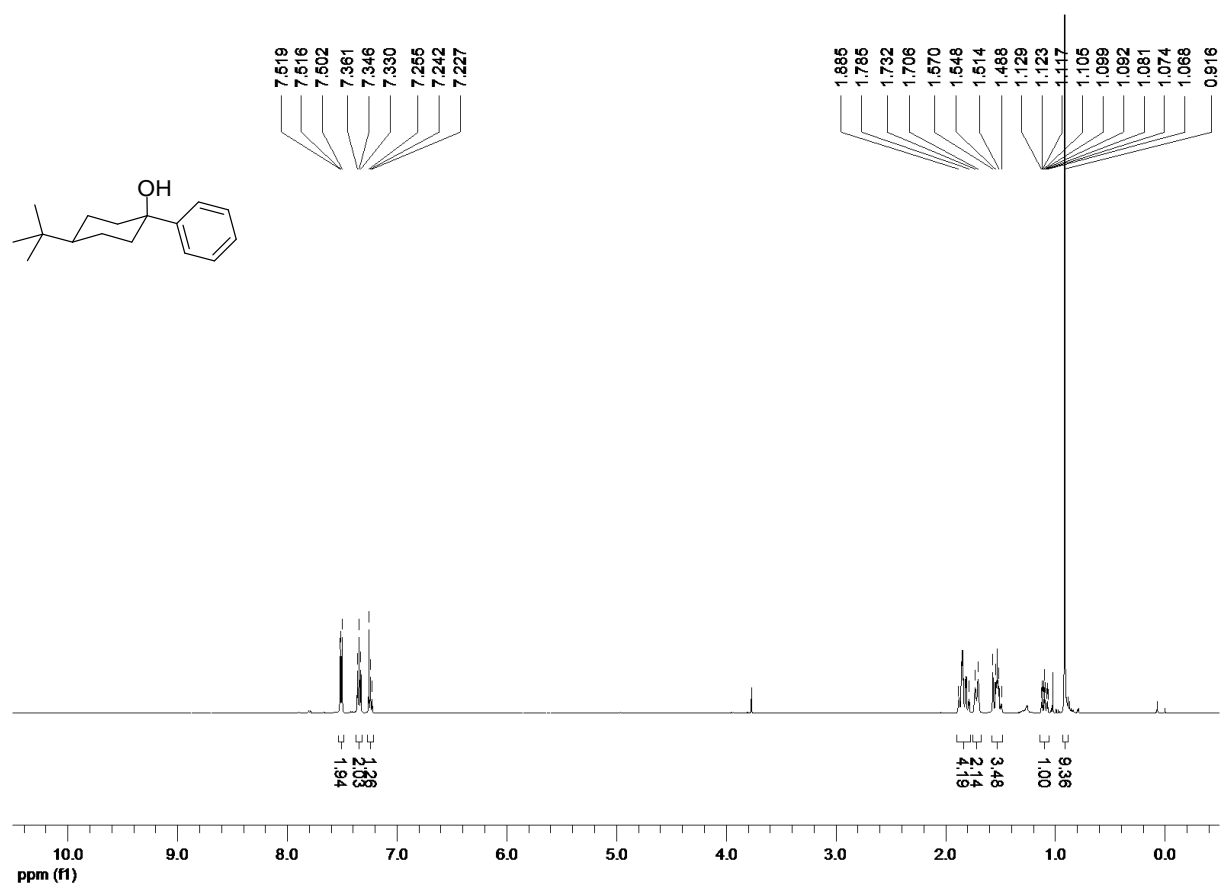






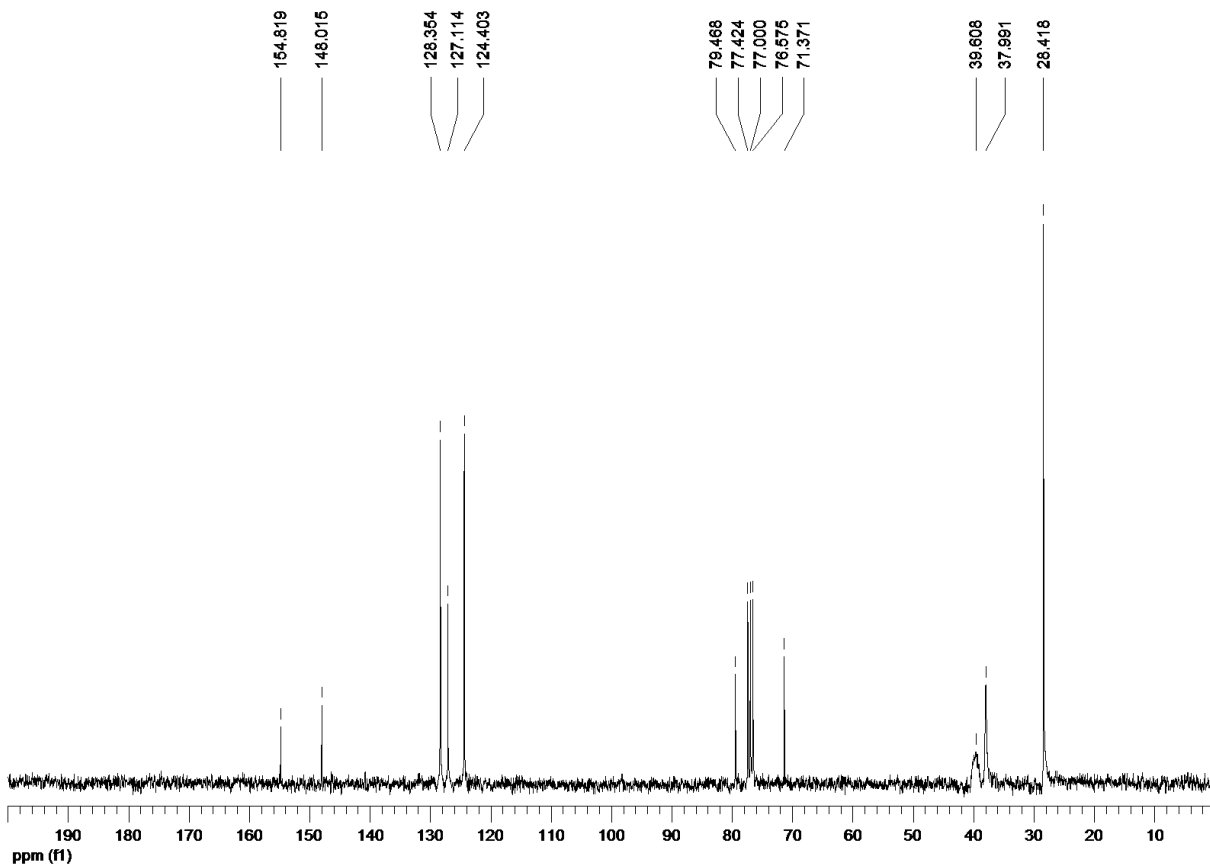
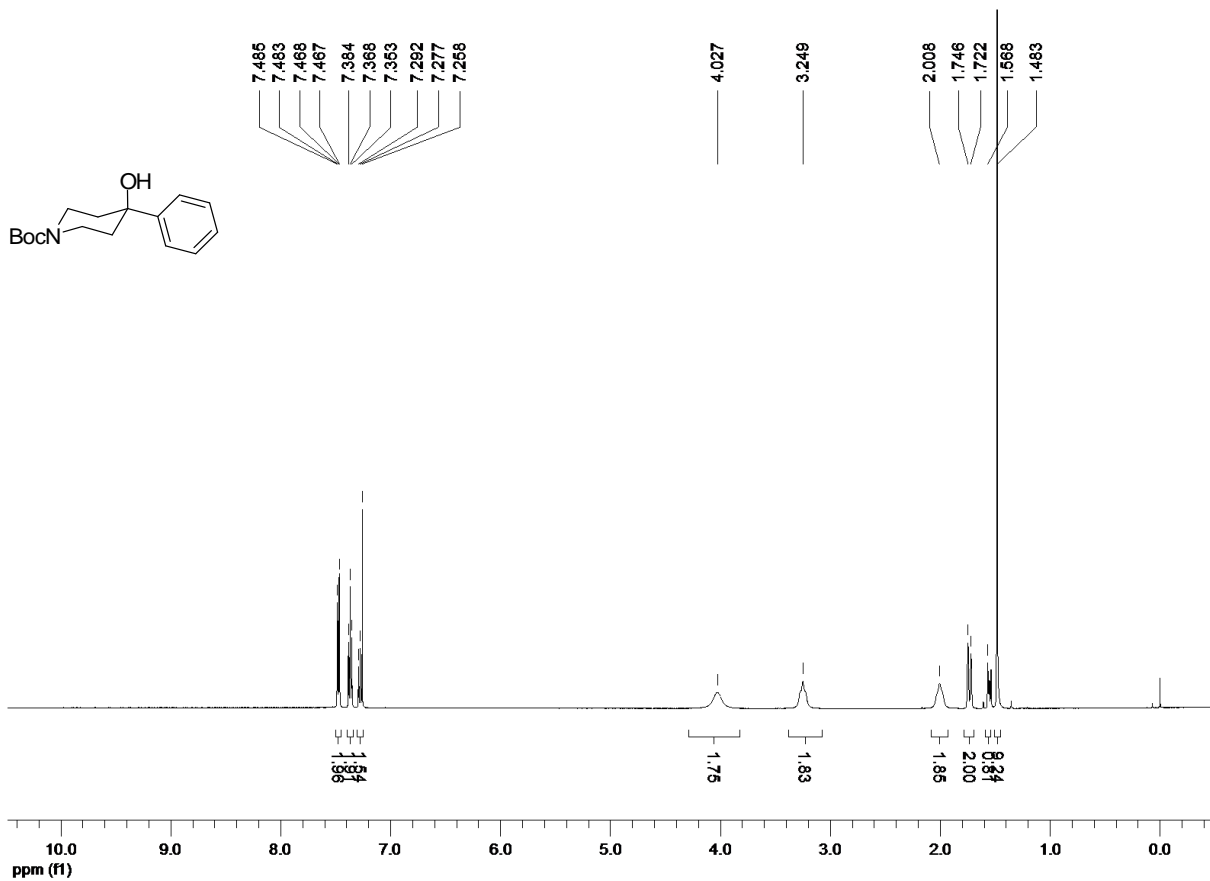


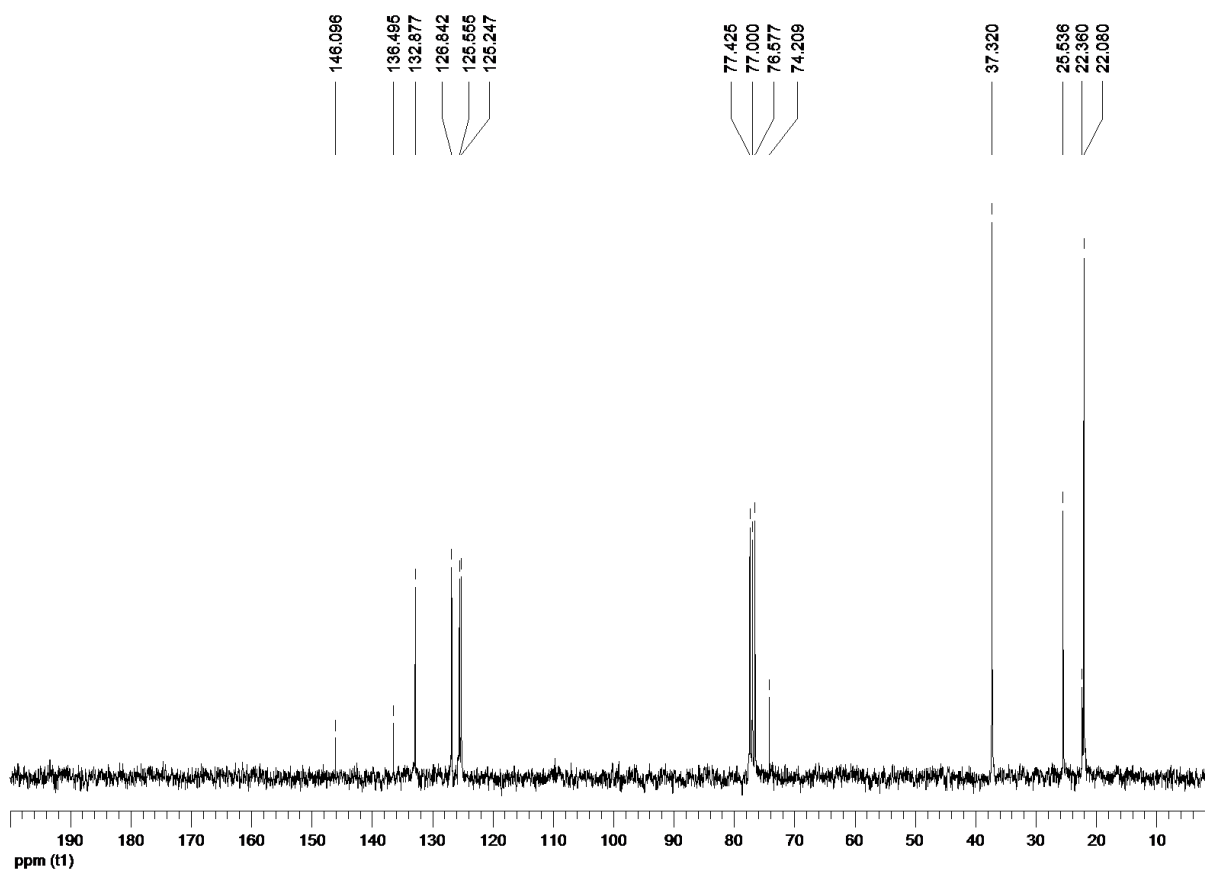
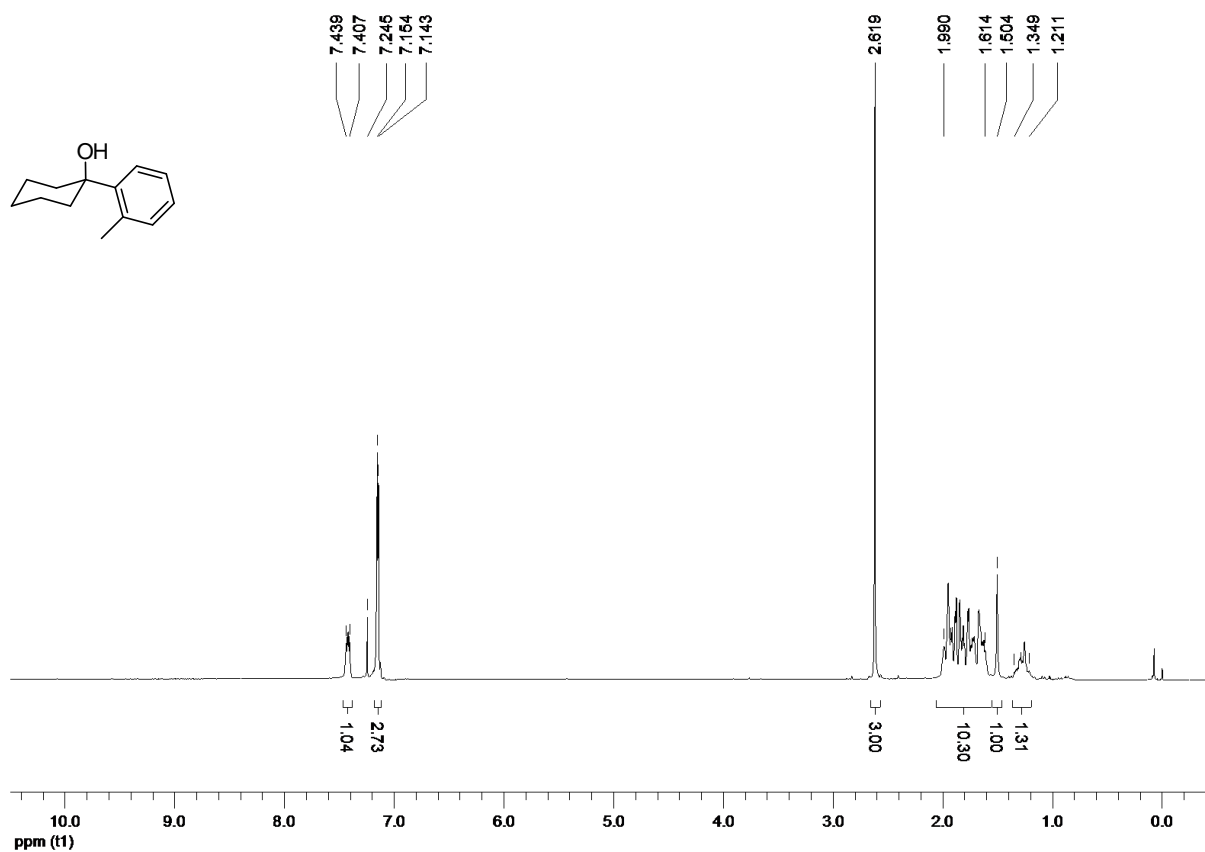




tert-Butyl-4-hydroxy-4-phenyl-1-piperidinecarboxylate (Table 1, entry 9)

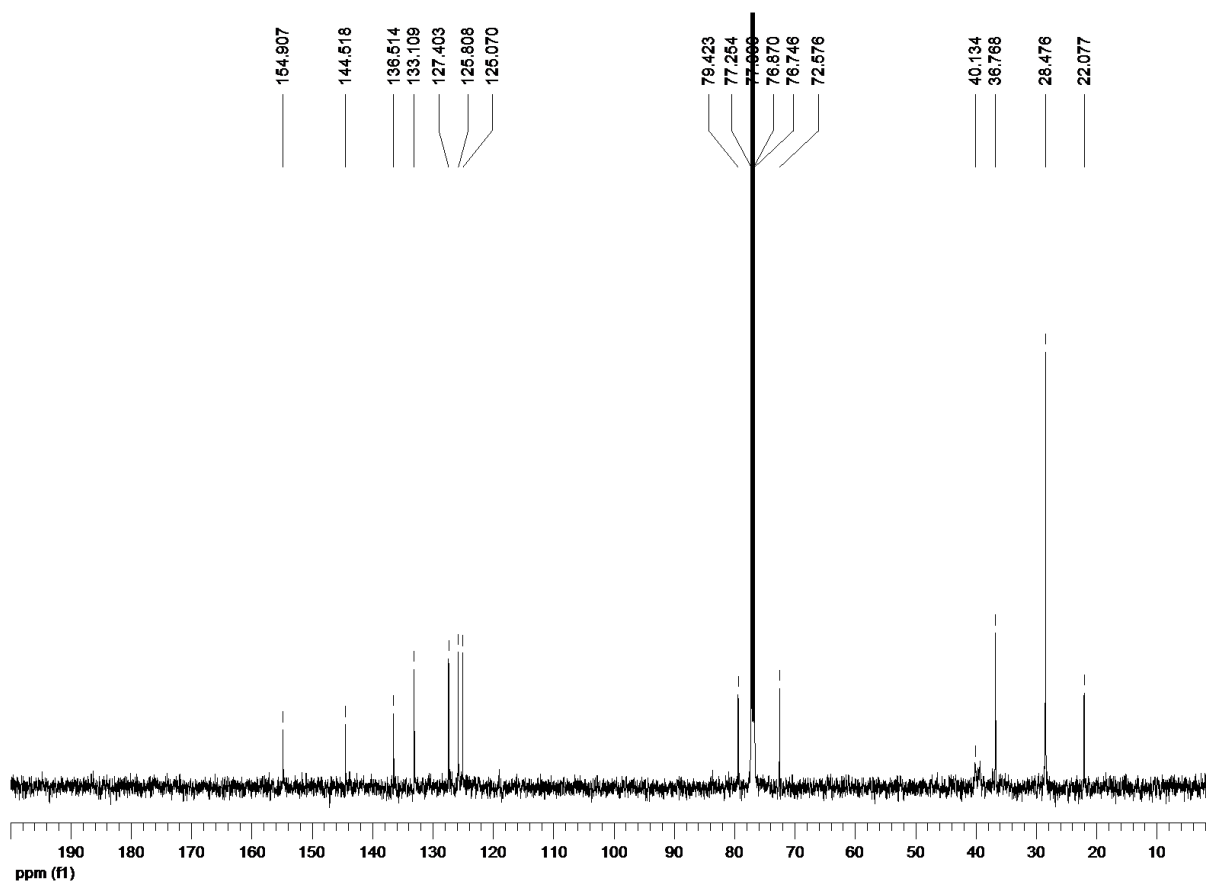
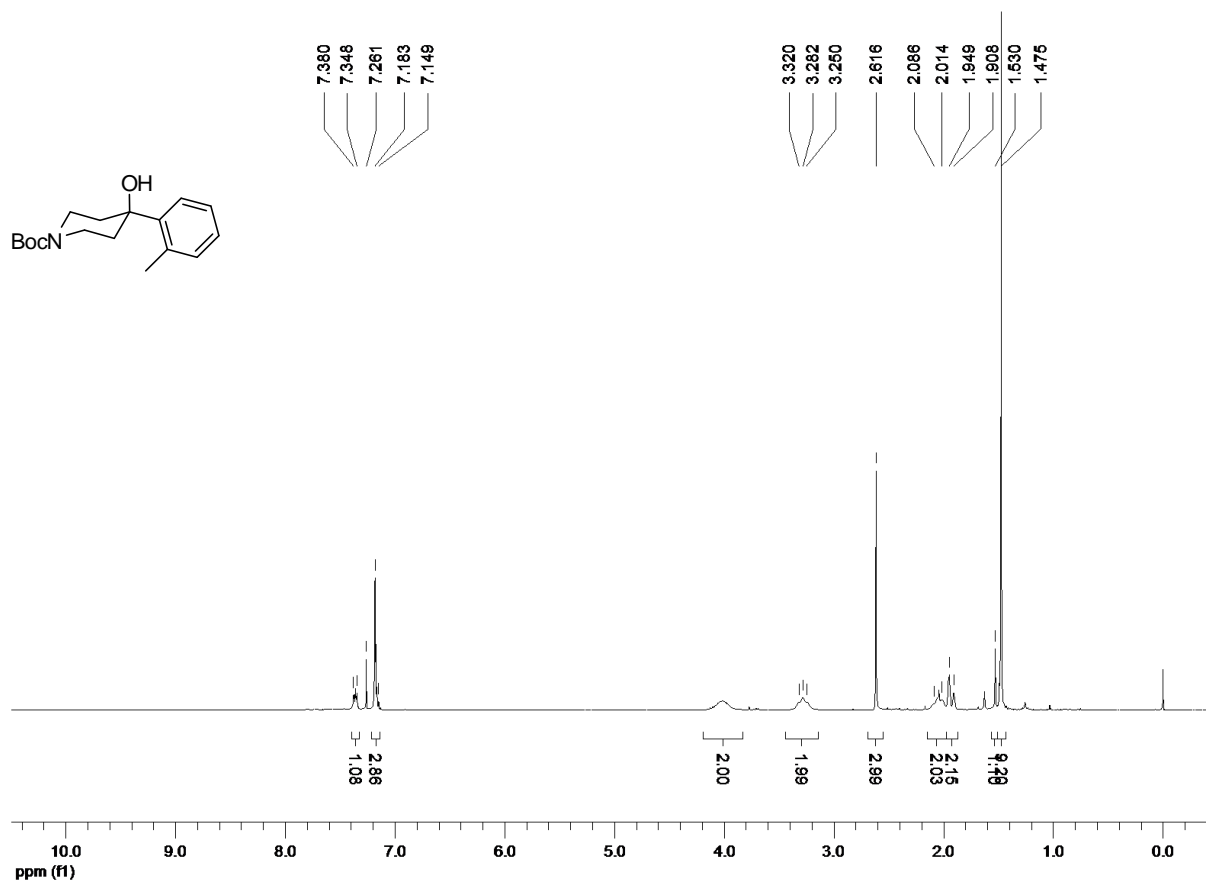
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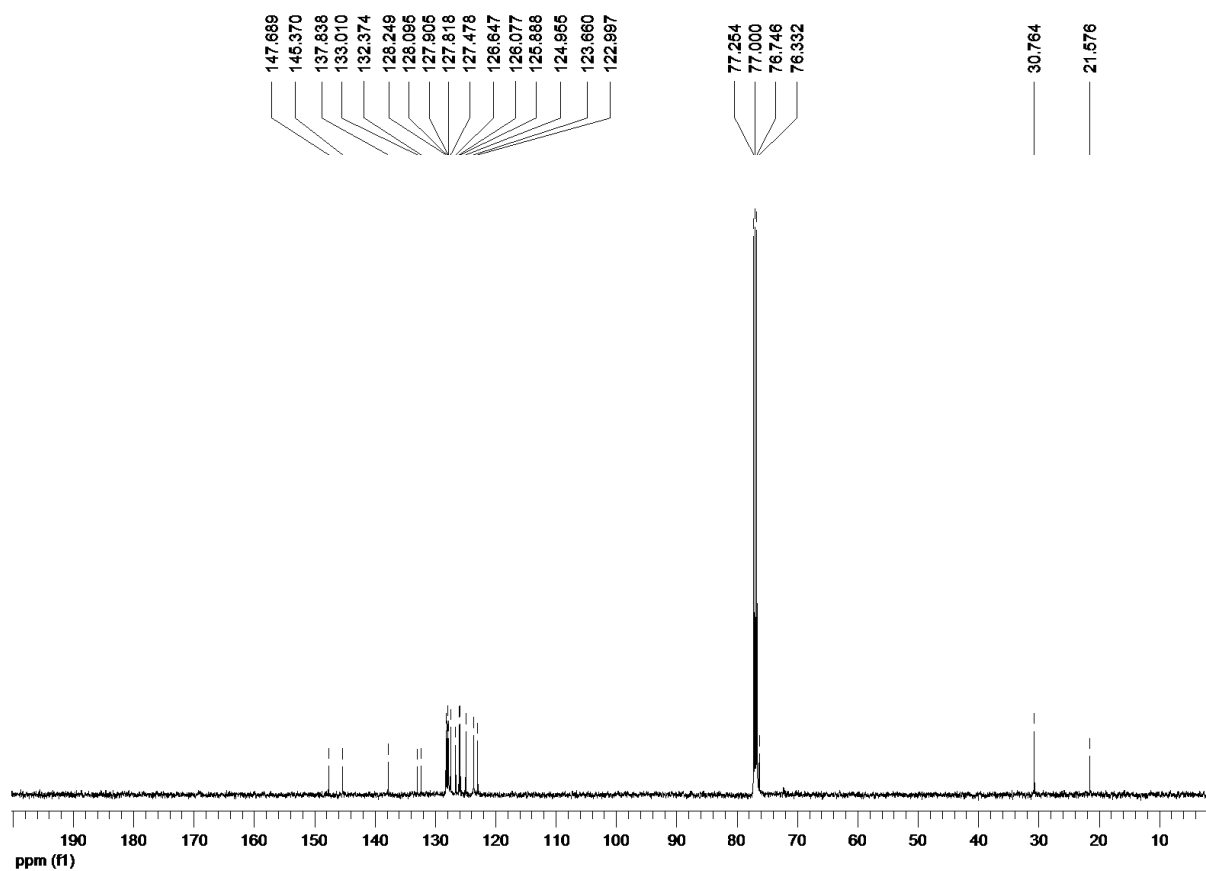
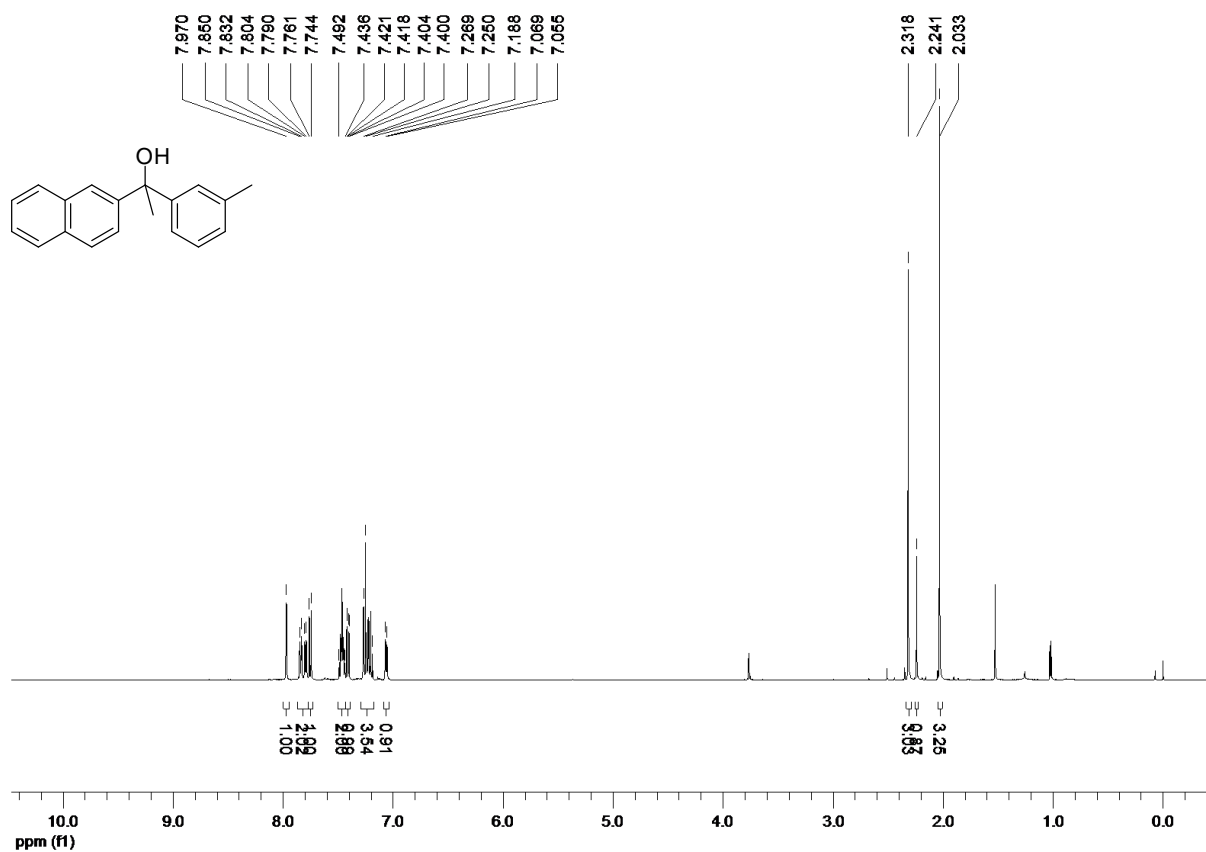


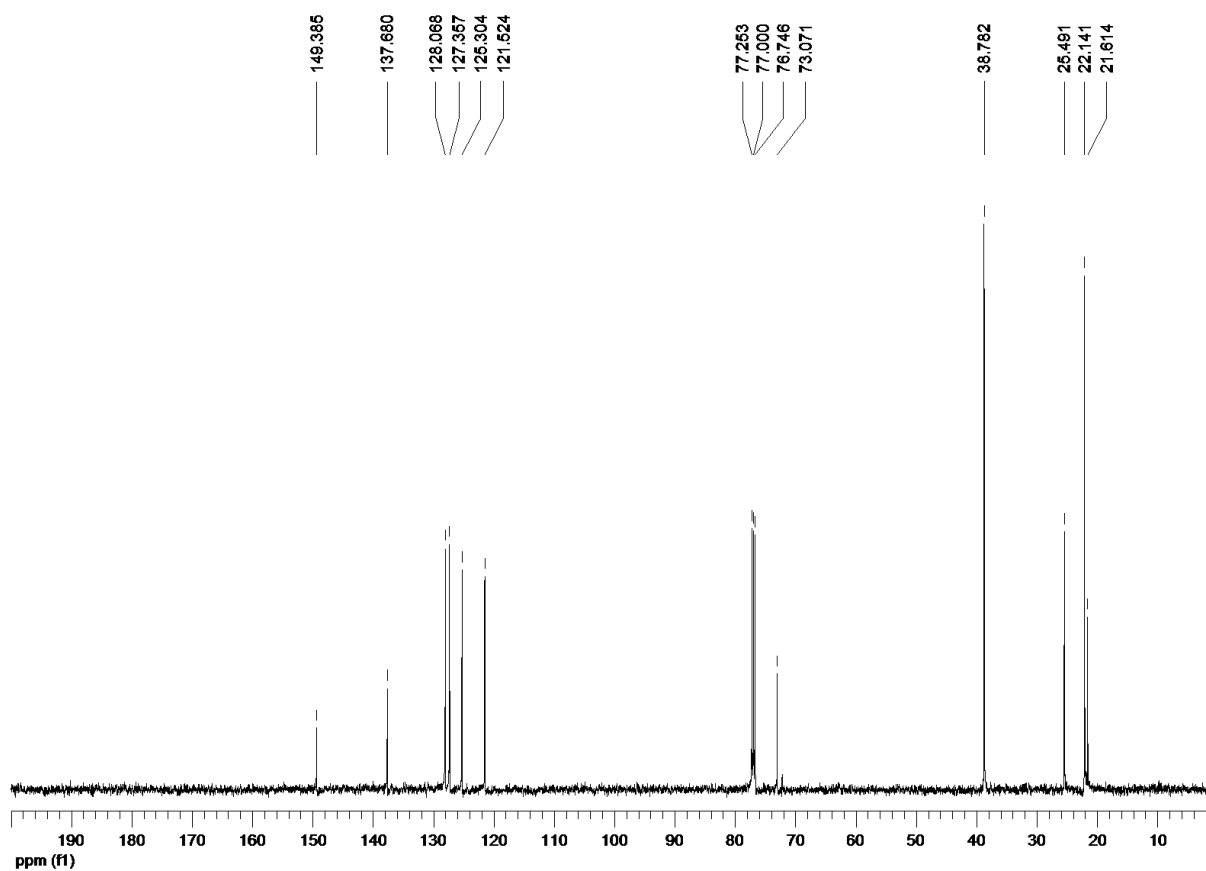
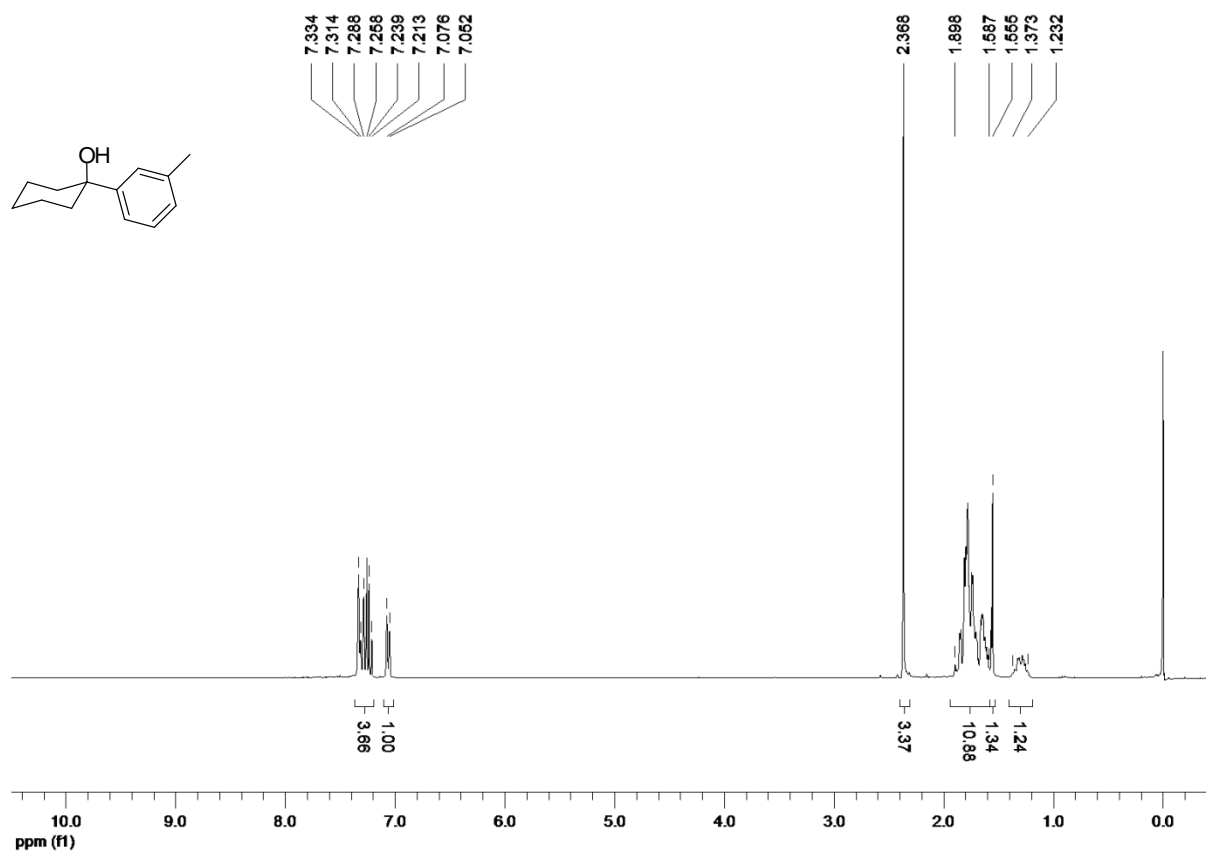


***tert*-Butyl-4-hydroxy-4-(2-methylphenyl)-1-piperidinecarboxylate (Table 2, entry 2)**

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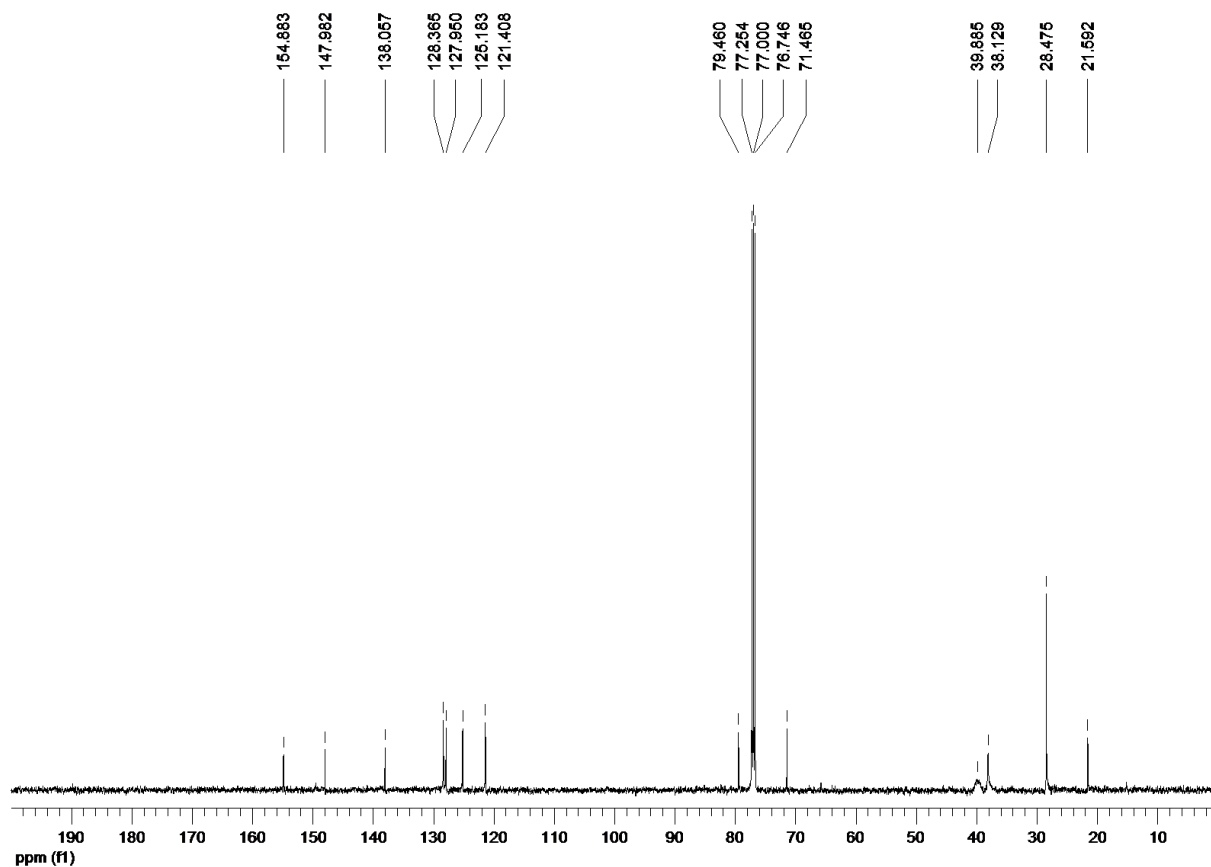
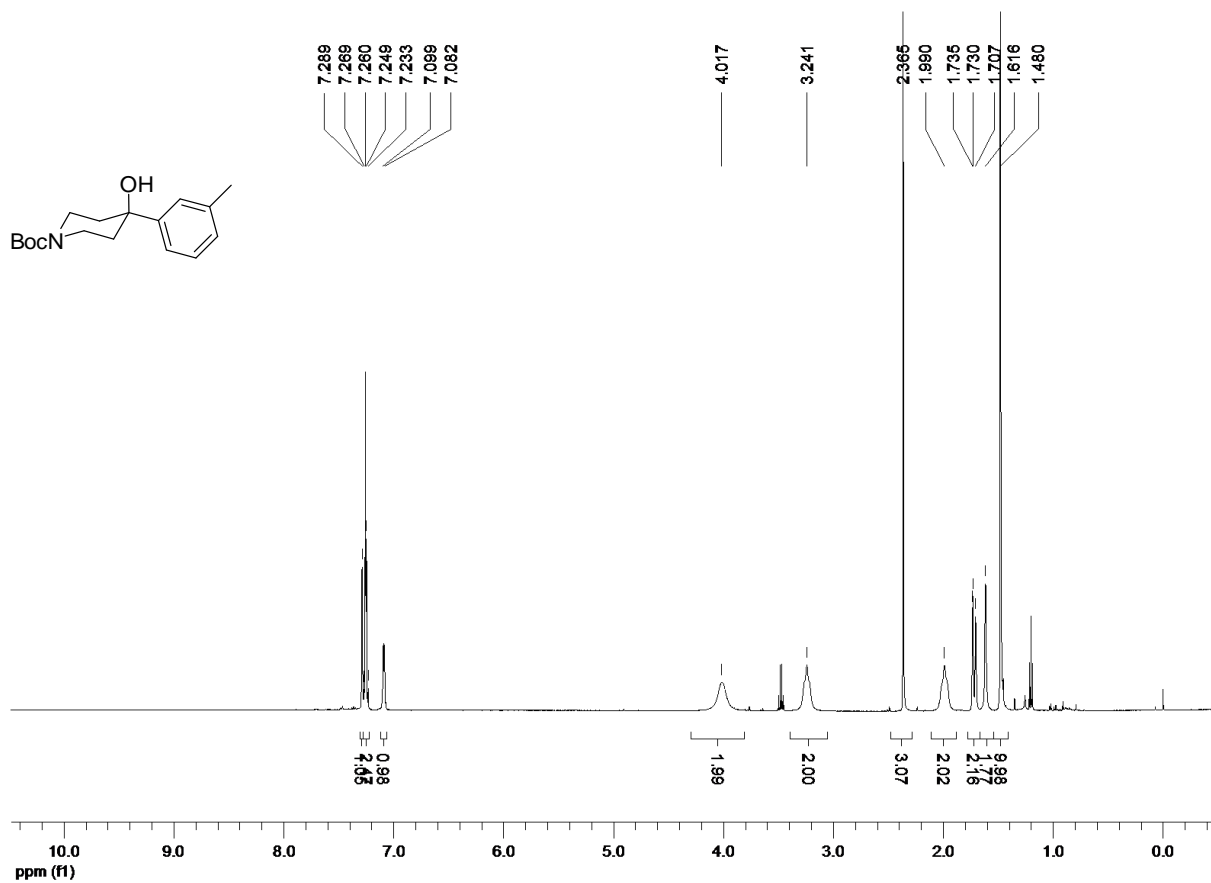






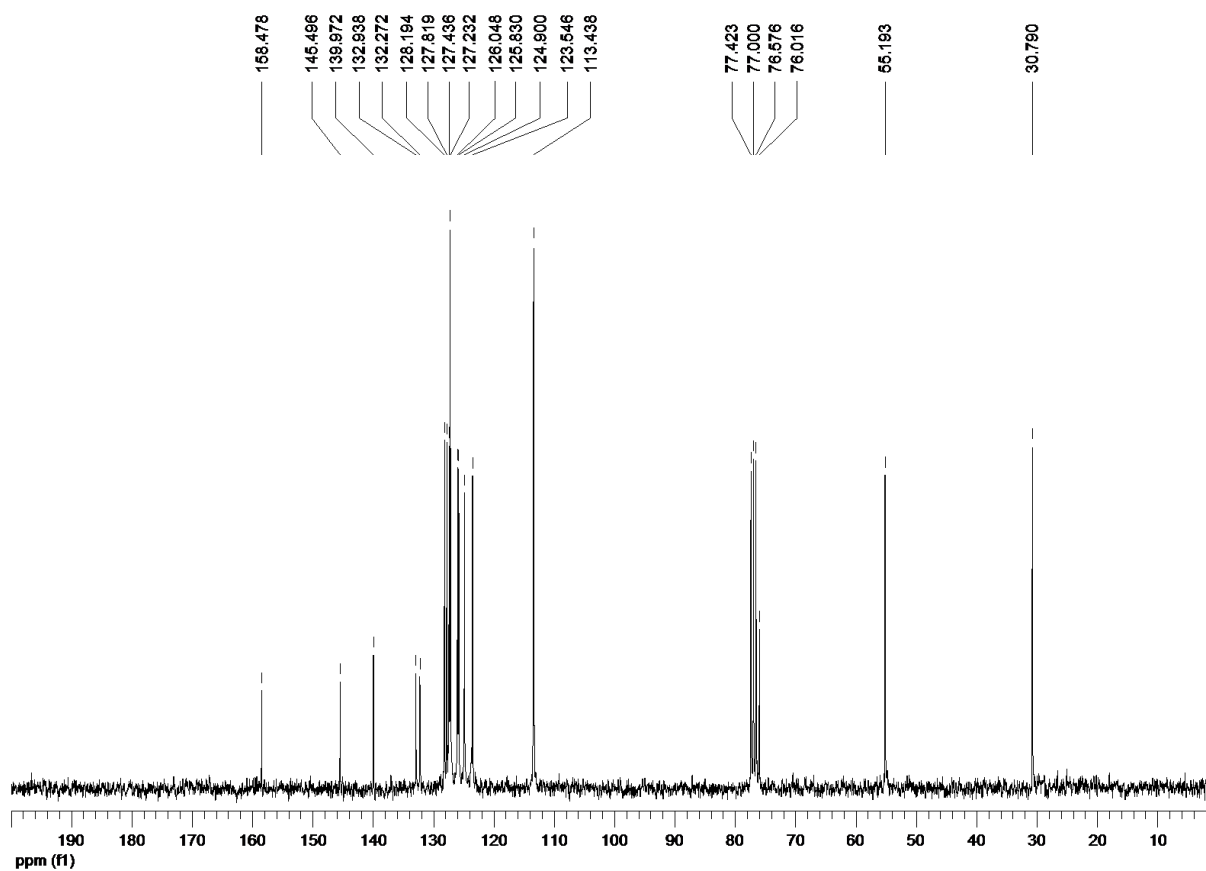
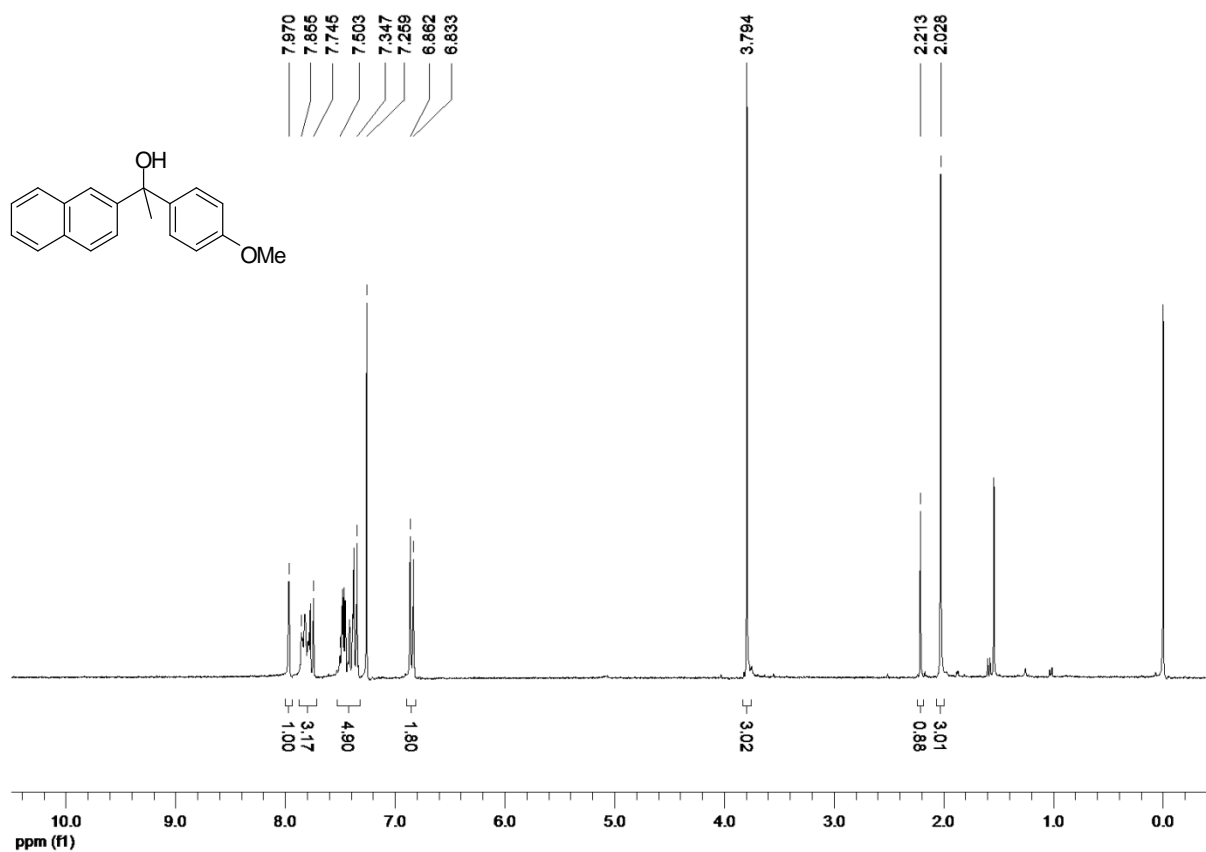
***tert*-Butyl-4-hydroxy-4-(3-methylphenyl)-1-piperidinecarboxylate (Table 2, entry 5)**

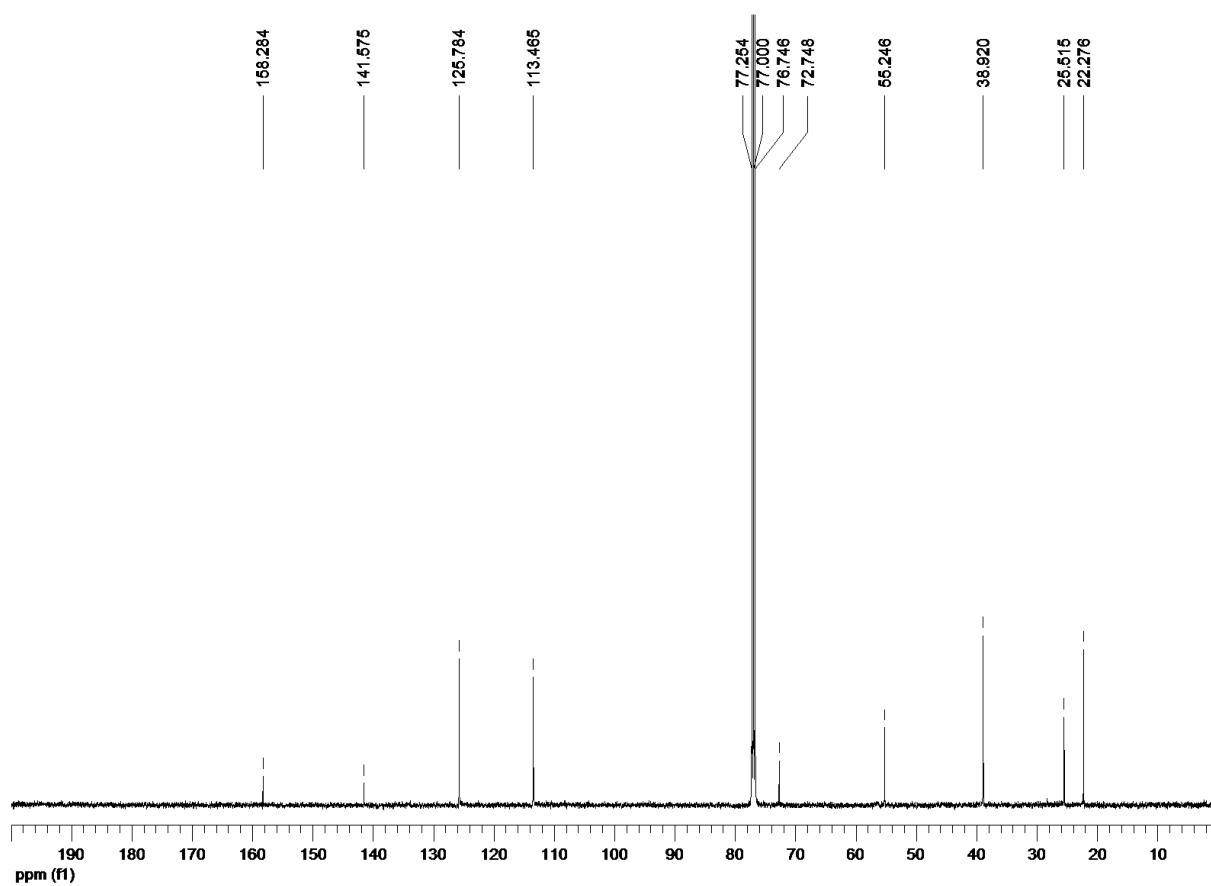
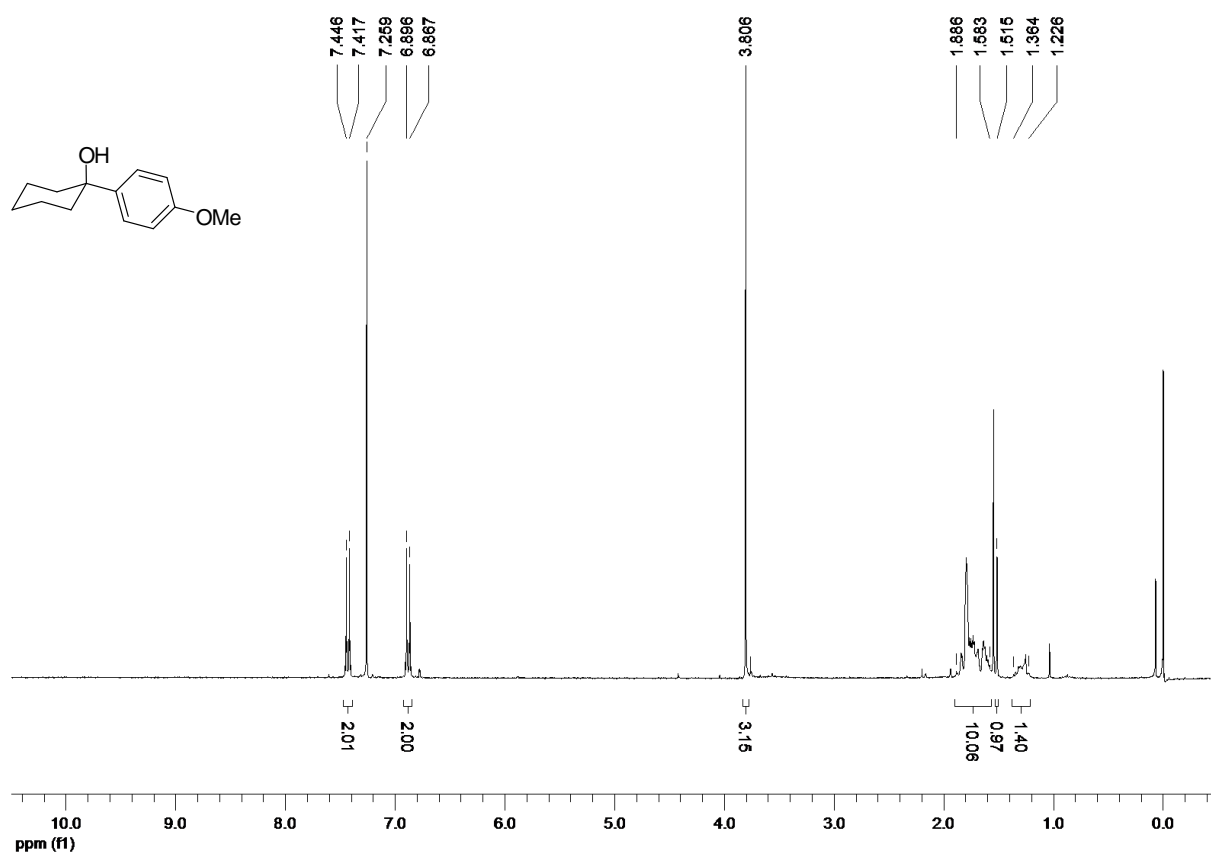
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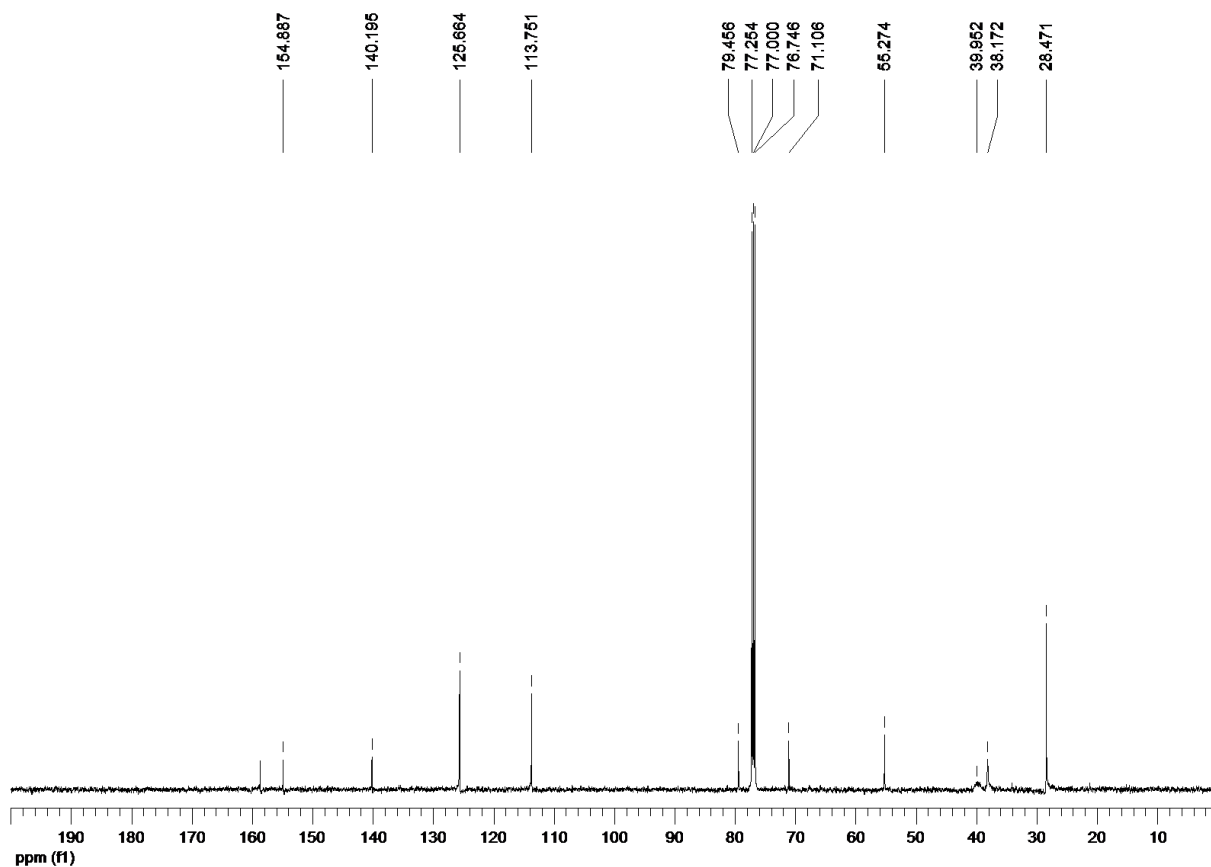
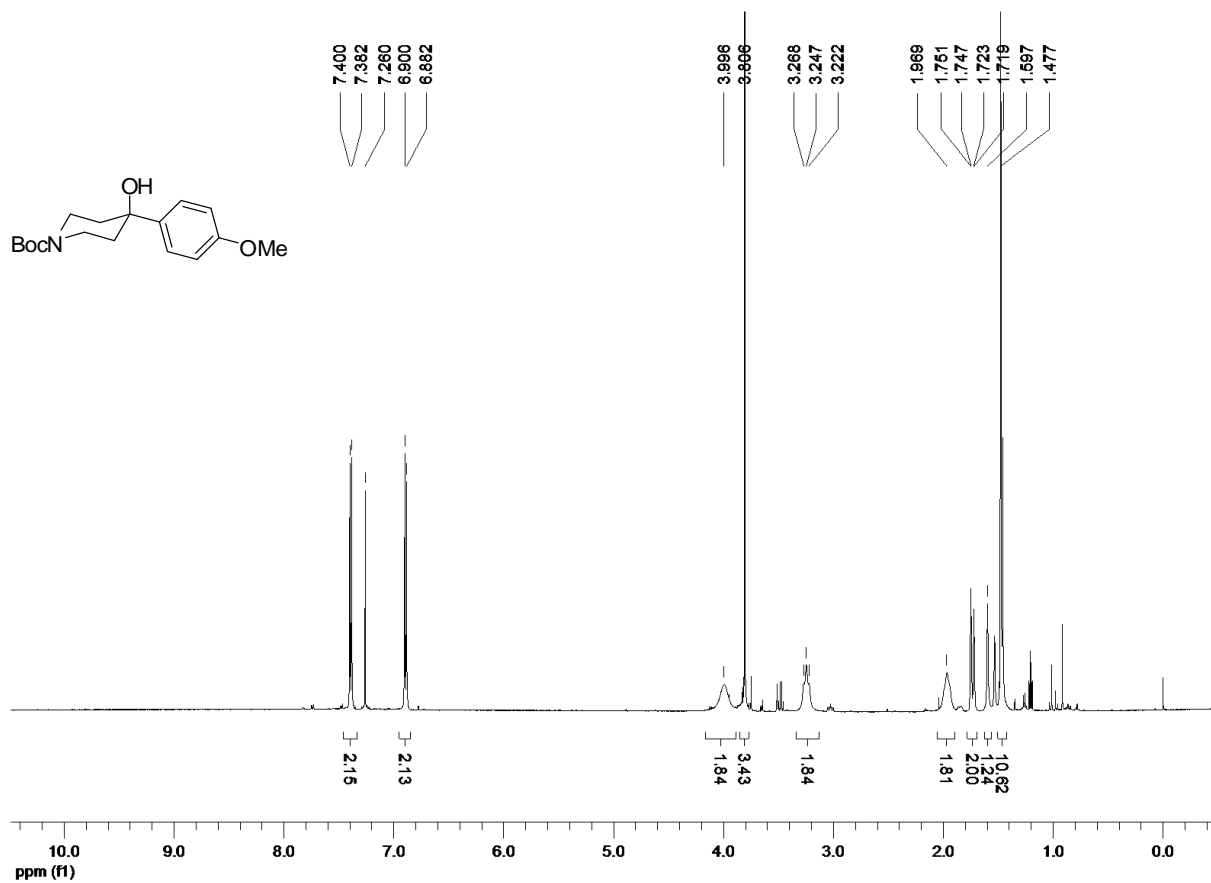


1-(4-Methoxyphenyl)-1-(naphthalen-2-yl)ethanol (Table 2, entry 6)

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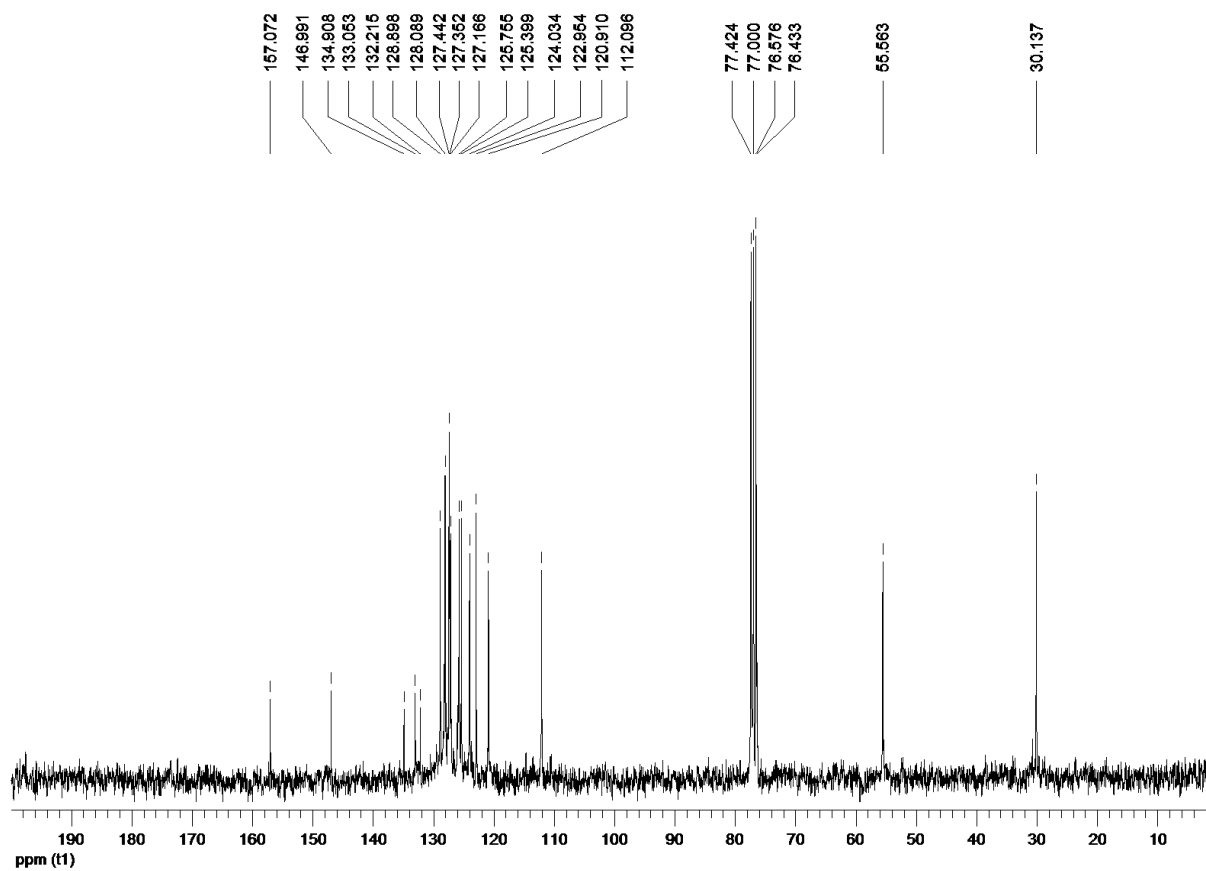
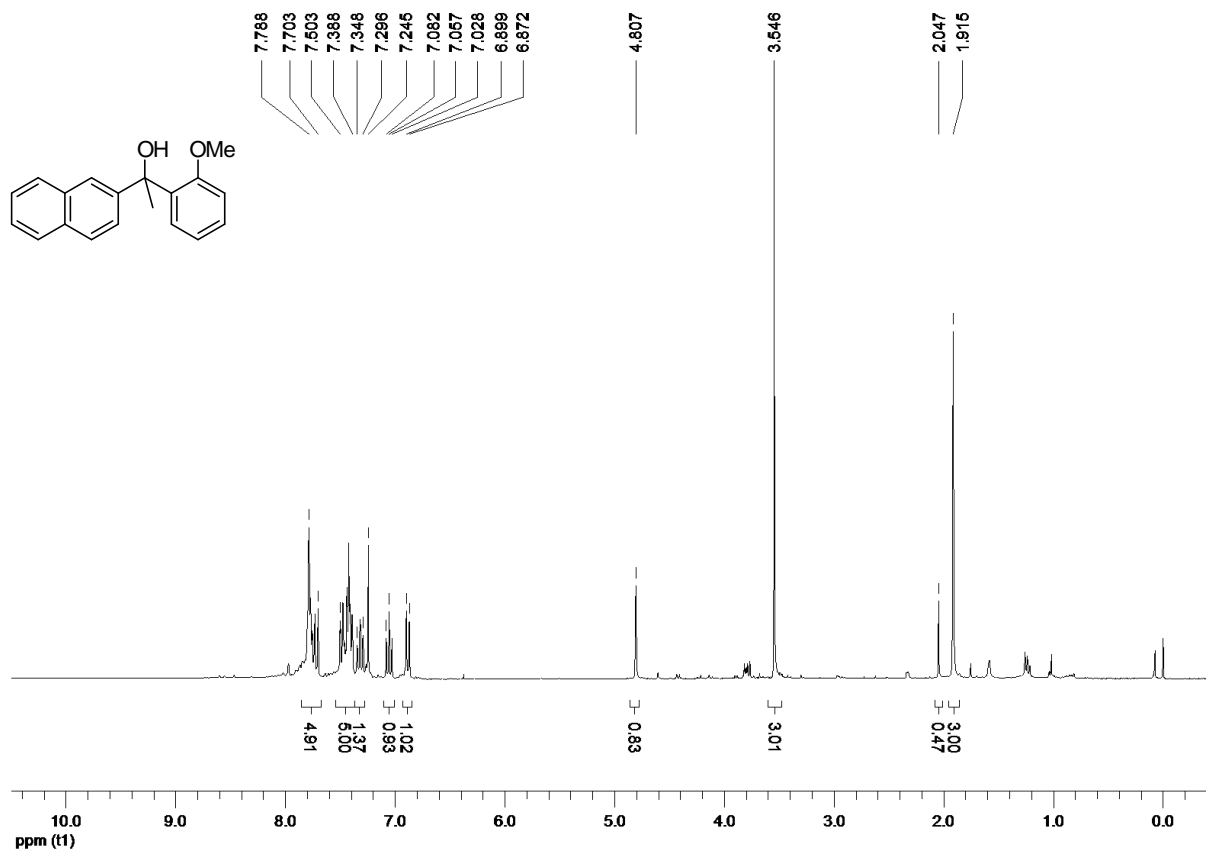


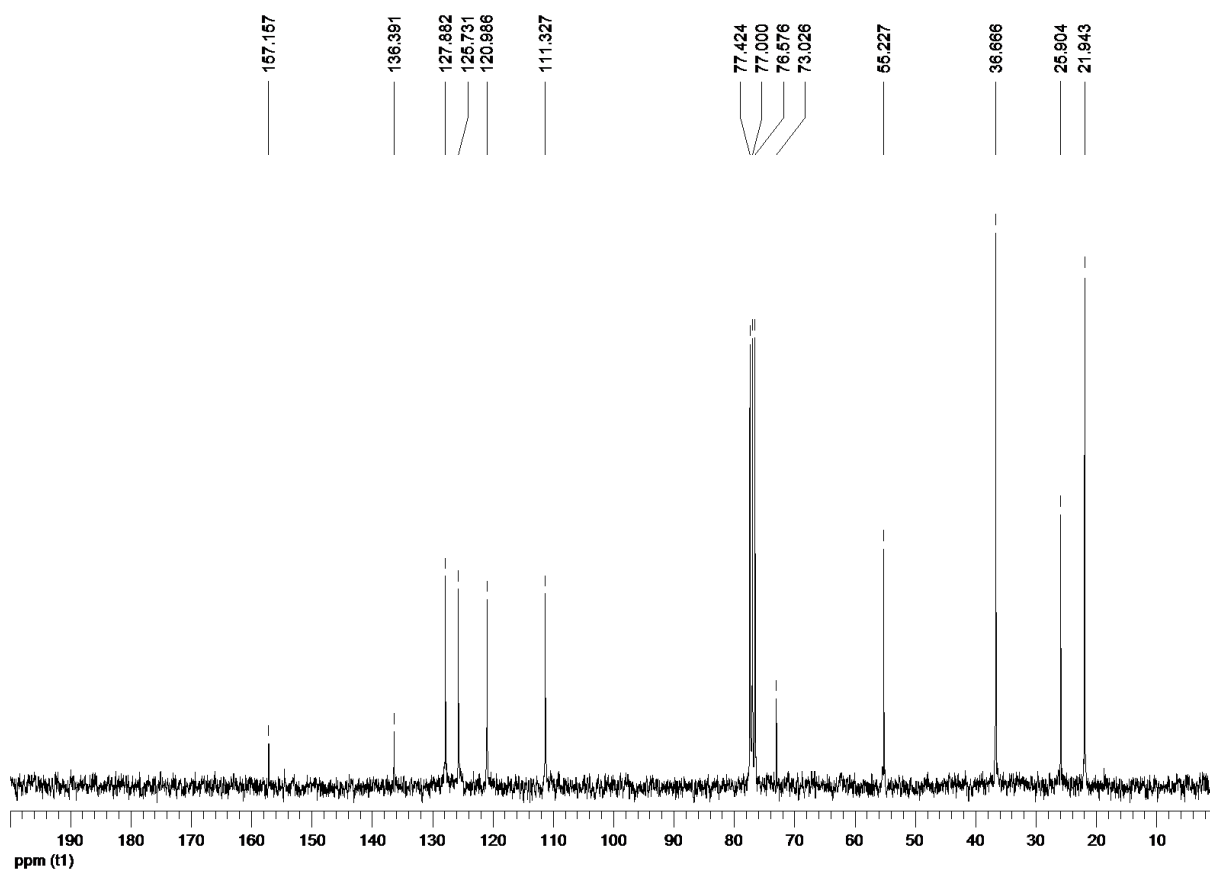
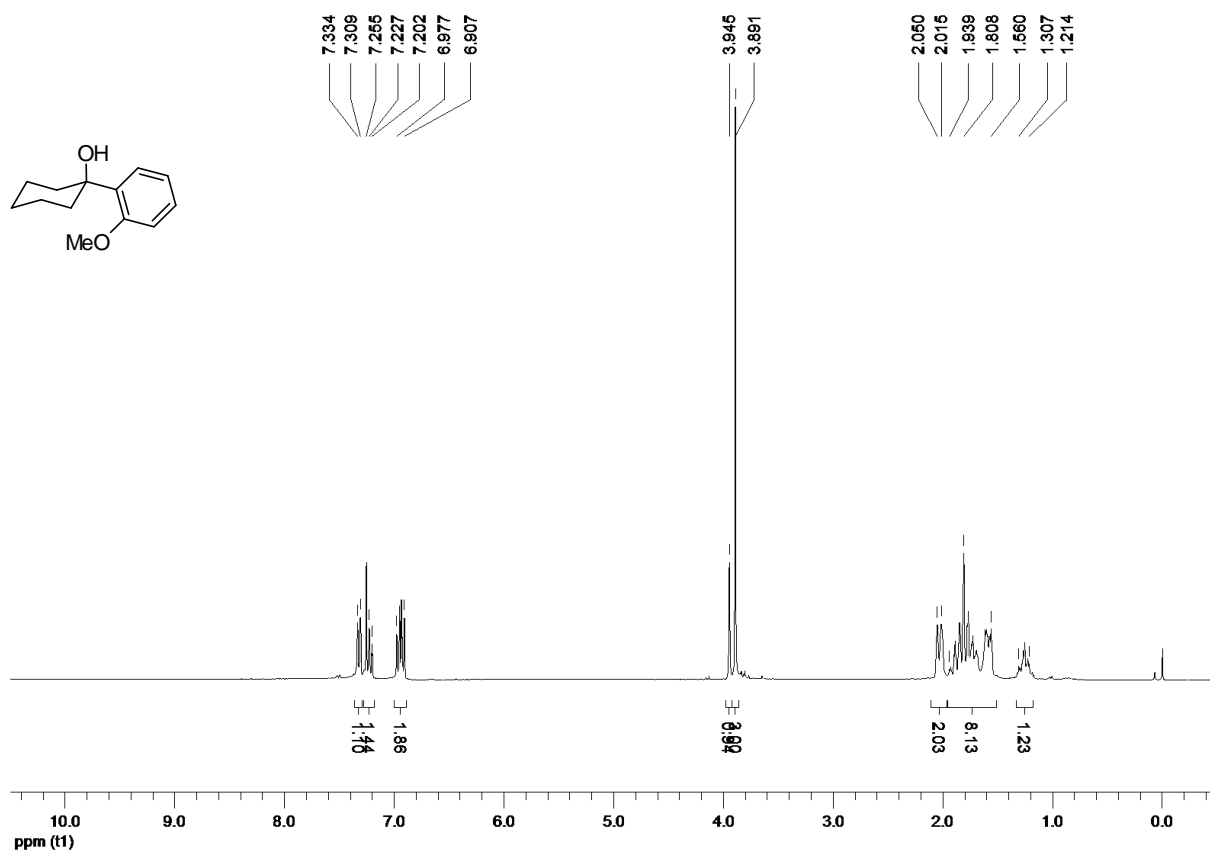




1-(2-Methoxyphenyl)-1-(naphthalen-2-yl)ethanol (Table 2, entry 9)
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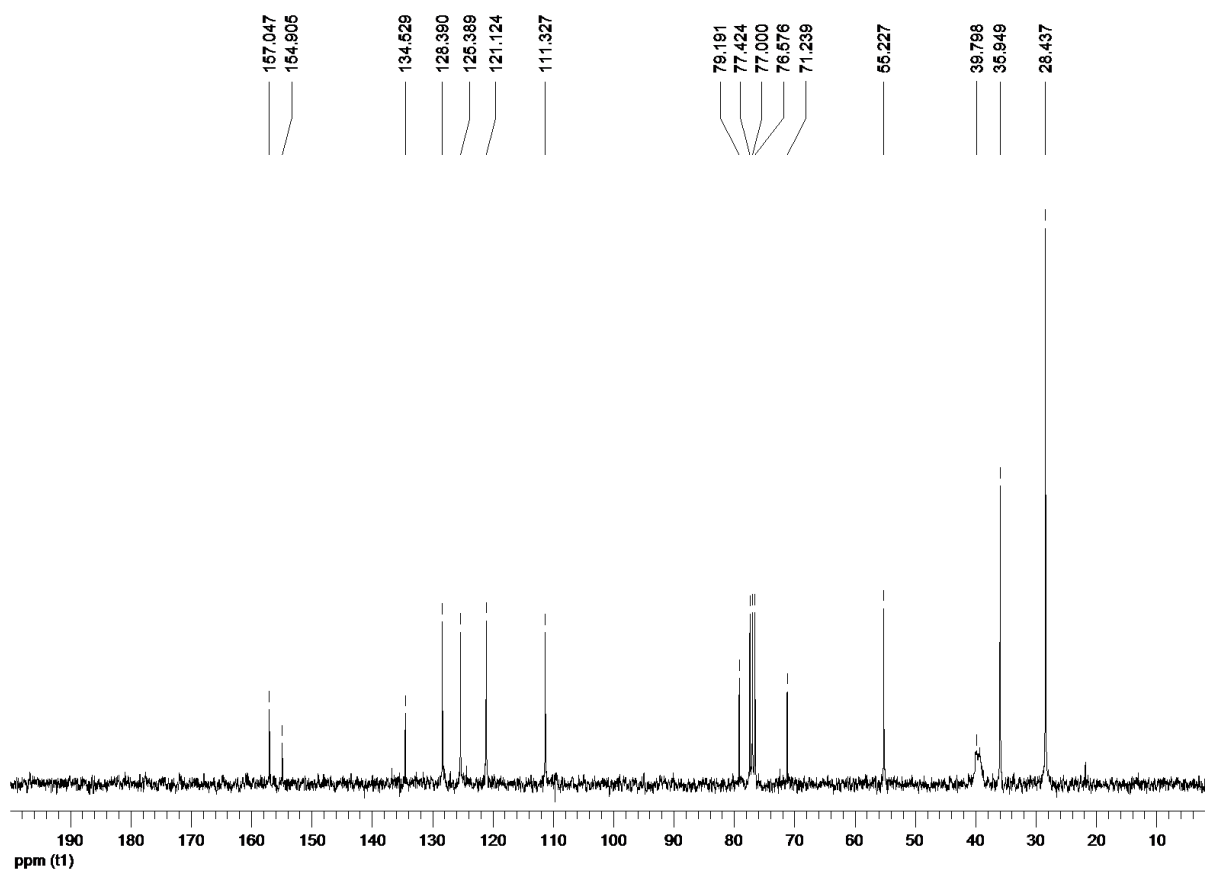
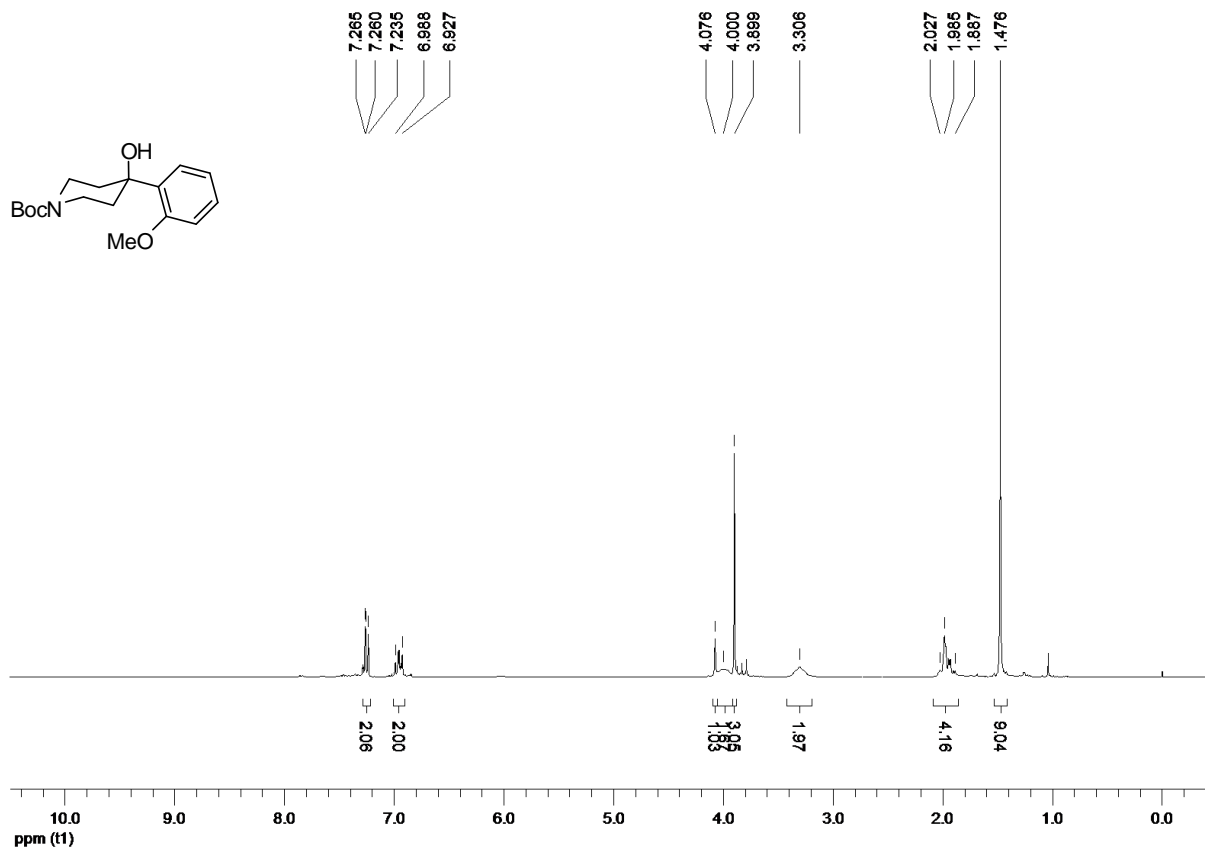
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***tert*-Butyl-4-hydroxy-4-(2-methoxyphenyl)-1-piperidinecarboxylate (Table 2, entry 11)**

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1-(Naphthalen-2-yl)-1-(4-(trimethylsilyl)phenyl)ethanol (Table 2, entry 12)

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