Supporting Information

Iridium/*f*-diaphos Catalyzed Asymmetric Hydrogenation of 2-Imidazolyl Aryl/Alkyl Ketones

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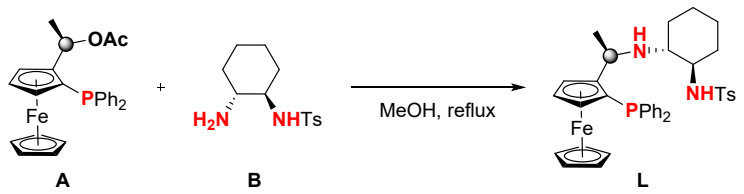
I. General experimental information

Commercial reagents were used without further purification, and solvents were dried before using. Melting points were recorded with a micro melting point apparatus and uncorrected. The ^{1}H NMR spectra were recorded at 400 or 600 MHz. The ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz. Chemical shifts were expressed in parts per million (δ) downfield from the internal standard tetramethylsilane, and were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet), br s (broad singlet), etc. The coupling constants J were given in Hz. HRMS spectra were recorded on an Agilent 1200HPLC-6210TOFMS using ESI as ion source. The conversion of starting materials was monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm). Optical rotations were determined using an AUTOPOL V polarimeter. HPLC analyses were performed using Agilent 1100 equipped with IA-H, IC-H, OD-H and AD-H.

II. General procedure for the preparation of ligands



After being flushed with Ar, A solution of (R_c, S_{FC})-**A** (1 mmol), (*R*, *R*)-1,2-diamine-**B** (1.5 mmol) in dry MeOH (1 mL) was stirred at reflux overnight. Upon completion, the reaction mixture was cooled to room temperature. Then, the resulting mixture was diluted with DCM (20 mL), and washed with water (10 mL) and brine (10 mL). The organic layer was dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as the eluent to give **L1** (90.9 mg, 78%). **L2-L12** were obtained in a similar manner.

The *f*-diaphos ligands **L1**, **L4-L6**, **L8** and **L12** have been reported in our previous work.[1,2]

***N*-((1*R*,2*R*)-2-(((*R*)-1-(2-(diphenylphosphanyl)ferrocenyl)ethyl)amino)cyclohexyl)-4-methylbenzenesulfonamide (L1)**

Orange solid, 65% yield, 431.7 mg, mp 153-154 °C, $[\alpha]^{20}_D$ = -129.1 (c = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 2H), 7.52 (s, 2H), 7.42 (s, 3H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.21 (s, 1H), 7.10 (s, 4H), 5.91 (s, 1H), 4.55 (s, 1H), 4.39 (s, 1H), 4.10-4.05 (m, 6H), 3.73 (s, 1H), 2.47 (s, 3H), 2.15 (s, 2H), 1.97-1.88 (m, 2H), 1.50 (s, 2H), 1.39 (d, *J* = 4.0 Hz, 3H), 1.11-0.99 (m, 2H), 0.90-0.83 (m, 1H), -0.26 to -0.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 139.9, 139.8, 137.2, 136.7, 136.6, 135.0, 134.8, 132.8, 132.6, 129.4, 129.1, 128.32, 128.27, 128.2, 128.1, 127.5, 98.2, 74.3, 74.2, 71.14, 71.10, 69.7, 69.5, 69.2, 57.7, 56.9, 32.1, 29.8, 24.8, 23.9, 21.5, 20.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ -24.85. HRMS (ESI) calcd for $C_{37}H_{42}FeN_2O_2PS$ $[M+H]^+$: 665.2049, found: 665.2053.

***N*-((1*S*,2*S*)-2-(((*R*)-1-(2-(diphenylphosphanyl)ferrocenyl)ethyl)amino)cyclohexyl)-4-methylbenzenesulfonamide (L2)**

Orange solid, 61% yield, 405.2 mg, mp 141-142 °C, $[\alpha]^{20}_D$ = -72.5 (c = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.64 (s, 2H), 7.42 (s, 3H), 7.31-7.30 (m, 7H), 5.15 (s, 1H), 4.46 (s, 2H), 4.07 (s, 2H), 3.96 (s, 5H), 2.47 (s, 3H), 2.41 (s, 1H), 1.99 (d, *J* = 8.4 Hz, 1H), 1.87-1.84 (m, 2H), 1.46-1.45 (m, 3H), 1.38-1.24 (m, 3H), 1.00-0.92 (m, 1H), 0.79-0.67 (m, 2H), 0.55-0.52 (m, 1H). ^{13}C NMR

(100 MHz, $CDCl_3$) δ 142.9, 140.24, 140.16, 137.84, 137.76, 137.6, 135.3, 135.1, 132.8, 132.6, 129.5, 129.2, 128.4, 128.3, 128.14, 128.11, 128.06, 127.3, 100.0, 74.0, 70.94, 70.90, 69.9, 69.7, 68.6, 68.5, 56.8, 47.5, 47.4, 31.9, 31.7, 24.8, 24.0, 23.8, 21.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ -24.83. HRMS (ESI) calcd for $C_{37}H_{42}FeN_2O_2PS$ $[M+H]^+$: 665.2049, found: 665.2044.

***N*-((1*R*,2*R*)-2-(((*S*)-1-(2-(diphenylphosphanyl)ferrocenyl)ethyl)amino)cyclohexyl)-4-methylbenzenesulfonamide (L3)**

Orange solid, 64% yield, 425.1 mg, mp 146-147 °C, $[\alpha]^{20}_D$ = +85.8 (c = 0.5, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 2H), 7.52-7.42 (m, 5H), 7.30-7.10 (m, 7H), 5.92 (s, 1H), 4.55 (s, 1H), 4.39 (s, 1H), 4.10 (s, 6H), 3.73 (s, 1H), 2.48 (s, 3H), 2.15 (s, 2H), 1.94-1.87 (m, 2H), 1.49-1.39 (m, 6H), 1.06-0.86 (m, 3H), -0.29 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 137.2, 136.6, 135.0, 134.8, 132.8, 132.6, 129.4, 129.2, 128.3, 127.5, 72.5, 71.1, 69.7, 69.2, 57.7, 56.9, 32.1, 29.8, 24.8, 23.9, 21.6, 20.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ -26.90. HRMS (ESI) calcd for $C_{37}H_{42}FeN_2O_2PS$ $[M+H]^+$: 665.2049, found: 665.2059.

***N*-((1*S*,2*S*)-2-(((*S*)-1-(2-(diphenylphosphanyl)ferrocenyl)ethyl)amino)cyclohexyl)-4-methylbenzenesulfonamide (L4)**

Orange solid, 65% yield, 431.7 mg, mp 146-147 °C, $[\alpha]^{20}_D$ = +60.1 (c = 0.5, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 2H), 7.57 (s, 2H), 7.47 (s, 3H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 4.0 Hz, 1H), 7.15 (s, 4H), 5.97 (s, 1H), 4.60 (s, 1H), 4.44 (s, 1H), 4.15 (s, 5H), 4.09 (d, *J* = 7.2 Hz, 1H), 3.78 (s, 1H), 2.53 (s, 3H), 2.20 (s, 2H), 2.01-1.91 (m, 2H), 1.54 (t, *J* = 11.6 Hz, 2H), 1.44 (s, 3H), 1.15-1.06 (m, 2H), 0.94-0.87 (m, 1H), -0.24 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 139.8, 137.1, 136.6, 135.0, 134.8, 132.8, 132.6, 129.4, 129.2, 128.4, 128.2, 128.1, 127.5, 74.2, 71.1, 69.7, 69.3, 57.7, 56.9, 32.1, 29.7, 24.7, 23.9, 21.6, 20.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ -25.03. HRMS (ESI) calcd for $C_{37}H_{42}FeN_2O_2PS$ $[M+H]^+$: 665.2049, found: 665.2056.

***N*-((1*R*,2*R*)-2-(((*R*)-1-(2-(diphenylphosphanyl)ferrocenyl)ethyl)amino)cyclohexyl)-2,4,6-trimethylbenzenesulfonamide (L5)**

Orange solid, 60% yield, 415.3 mg, mp 162-163 °C, $[\alpha]^{20}_D$ = -124.8 (c = 0.5, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 2H), 7.42 (s, 3H), 7.19 (s, 1H), 7.08 (s, 4H), 6.96 (s, 2H), 5.96 (s, 1H), 4.53 (s, 1H), 4.38 (s, 1H), 4.10 (s, 6H), 3.74 (s, 1H), 2.63 (s, 6H), 2.36 (s, 3H), 2.14-2.09 (m, 2H), 1.94-1.91 (m, 1H), 1.79 (s, 1H), 1.47-1.45 (m, 5H), 1.07-0.90 (m, 2H), 0.86-0.79 (m, 1H), -0.40 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 140.1, 140.0, 139.1, 136.5, 136.4, 135.1, 134.9, 134.2, 132.7, 132.5, 131.8, 129.2, 128.41, 128.35, 128.2, 128.1, 98.0, 74.12, 74.07, 71.1, 69.7, 69.4, 69.2, 57.7, 57.0, 46.2,

32.0, 29.8, 24.9, 23.9, 23.1, 20.9, 19.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ -25.07. HRMS (ESI) calcd for $C_{39}H_{46}FeN_2O_2PS$ $[M+H]^+$: 693.2362, found: 693.2355.

***N*-((1*R*,2*R*)-2-(((*R*)-1-(2-(diphenylphosphanyl)ferrocenyl)ethyl)amino)cyclohexyl)-2,4,6-triisopropylbenzenesulfonamide (L6)**

Orange solid, 48% yield, 372.6 mg, mp 148-149 °C, $[\alpha]^{20}_D$ = -56.1 (c = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.2 Hz, 2H), 7.41 (s, 3H), 7.19 (s, 2H), 7.14 (s, 3H), 7.03 (d, *J* = 6.4 Hz, 2H), 5.98 (s, 1H), 4.54 (s, 1H), 4.32 (s, 1H), 4.11 (t, *J* = 7.2 Hz, 1H), 4.08 (s, 5H), 3.70 (s, 1H), 3.00-2.93 (m, 1H), 2.19-2.04 (m, 4H), 1.56-1.43 (m, 5H), 1.34-1.31 (m, 7H), 1.27 (d, *J* = 6.8 Hz, 6H), 1.21 (d, *J* = 6.4 Hz, 6H), 1.10-1.00 (m, 2H), 0.92-0.86 (m, 2H), -0.13 (d, *J* = 12.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 150.3, 135.2, 135.0, 132.8, 132.6, 129.2, 128.3, 128.2, 128.1, 123.6, 97.5, 97.3, 71.2, 69.7, 69.1, 57.4, 57.3, 46.6, 34.1, 32.0, 29.9, 29.7, 25.2, 25.1, 23.9, 23.7, 23.6, 19.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ -25.02. HRMS (ESI) calcd for $C_{45}H_{58}FeN_2O_2PS$ $[M+H]^+$: 777.3301, found: 777.3310.

***N*-((1*R*,2*R*)-2-(((*R*)-1-(2-(diphenylphosphanyl)ferrocenyl)ethyl)amino)cyclohexyl)-3,5-bis(trifluoromethyl)benzenesulfonamide (L7)**

Orange solid, 52% yield, 408.8 mg, mp 106-108 °C, $[\alpha]^{20}_D$ = -138.6 (c = 0.6, MeOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 2H), 8.11 (s, 1H), 7.56-7.52 (m, 2H), 7.43 (s, 3H), 7.26-7.24 (m, 1H), 7.21-7.19 (m, 4H), 4.51 (s, 1H), 4.38 (s, 1H), 4.13-4.09 (m, 6H), 3.76 (s, 1H), 2.17 (t, *J* = 8.4 Hz, 1H), 2.04 (d, *J* = 6.8 Hz, 3H), 1.55 (d, *J* = 11.2 Hz, 2H), 1.41 (d, *J* = 6.8 Hz, 3H), 1.06-0.94 (m, 3H), -0.03 (d, *J* = 12.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.0, 139.9, 139.8, 136.4, 136.3, 135.1, 134.9, 132.9, 132.7, 132.6 (q, $^2J_{C\text{-}F}$ = 51.2 Hz), 129.2, 128.5, 128.4 (q, $^3J_{C\text{-}F}$ = 9.6 Hz), 128.2 (q, $^3J_{C\text{-}F}$ = 11.6 Hz), 127.4, 125.8, 122.5 (q, $^1J_{C\text{-}F}$ = 257.9 Hz), 97.5, 97.2, 74.3, 71.33, 71.29, 69.7, 69.5, 58.3, 57.1, 47.0, 46.9, 31.7, 30.0, 24.8, 23.8, 20.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.03. ^{31}P NMR (162 MHz, $CDCl_3$) δ -25.42. HRMS (ESI) calcd for $C_{38}H_{38}F_6FeN_2O_2PS$ $[M+H]^+$: 787.1640, found: 787.1648.

***N*-((1*R*,2*R*)-2-(((*R*)-1-(2-(bis(3,5-dimethylphenyl)phosphanyl)ferrocenyl)ethyl)amino)cyclohexyl)-2,4,6-trimethylbenzenesulfonamide (L8)**

Orange solid, 56% yield, 442.5 mg, mp 100-101 °C, $[\alpha]^{20}_D$ = -141.2 (c = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 2H), 7.43 (s, 6H), 7.33-7.28 (m, 2H), 7.12 (d, *J* = 6.8 Hz, 1H), 7.05 (t, *J* = 7.2 Hz, 2H), 6.94 (t, *J* = 7.2 Hz, 1H), 6.82 (t, *J* = 7.2 Hz, 3H), 6.75 (s, 2H), 6.67 (d, *J* = 7.2 Hz, 2H), 6.46 (d, *J* = 6.8 Hz, 2H), 4.52 (s, 1H), 4.39 (s, 1H), 4.03 (s, 6H), 3.93 (d, *J* = 8.4 Hz, 1H), 3.77 (s, 1H), 3.70-3.63 (m, 2H), 2.44 (s, 6H), 2.26 (s, 3H), 1.72 (s, 1H), 1.37 (d, *J* = 3.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 140.9, 140.8, 139.0, 138.4, 137.8, 137.4, 135.5, 135.3, 134.6, 132.6, 132.4, 131.3, 129.1, 128.5, 128.3,

128.14, 128.09, 128.0, 127.6, 127.5, 127.2, 126.9, 98.6, 74.0, 73.9, 71.4, 70.0, 69.7, 69.5, 65.0, 63.4, 47.5, 22.8, 20.8, 19.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ -24.43. HRMS (ESI) calcd for $C_{47}H_{48}FeN_2O_2PS$ $[M+H]^+$: 791.2518, found: 791.2510.

_N_-((1_R_,2_R_)-2-(((_R_)-1-(2-(dicyclohexylphosphanyl)ferrocenyl)ethyl)amino)cyclohexyl)-2,4,6-trimethylbenzenesulfonamide (L9)

Orange solid, 62% yield, 446.5 mg, mp 216-217 °C, $[\alpha]^{25}_D$ = -439.6 (c = 0.4, MeOH). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.53 (s, 1H), 7.82 (s, 2H), 7.64-7.60 (m, 2H), 7.47-7.44 (m, 5H), 7.04-7.03 (m, 4H), 6.70 (s, 1H), 5.49 (s, 1H), 4.79 (s, 1H), 4.50 (s, 1H), 4.15 (s, 5H), 3.71 (s, 1H), 1.72 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 184.0, 179.8, 167.8, 161.3, 141.6, 139.1, 136.7, 135.1, 134.9, 132.8, 132.6, 131.7 (q, $^2J_{C\text{-}F}$ = 32.8 Hz), 129.6, 128.6, 128.3, 127.6, 123.6 (q, $^1J_{C\text{-}F}$ = 271.2 Hz), 117.8, 114.6, 94.3, 94.0, 75.7, 72.2, 70.2, 69.7, 69.0, 55.3, 49.0, 22.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.10. ^{31}P NMR (162 MHz, $CDCl_3$) δ -21.36. HRMS (ESI) calcd for $C_{36}H_{28}F_6FeN_2O_2P$ $[M+H]^+$: 721.1137, found: 721.1149.

_N_-((1_R_,2_R_)-2-(((_R_)-1-(2-(diphenylphosphanyl)ferrocenyl)ethyl)amino)-1,2-diphenylethyl)-2,4,6-trimethylbenzenesulfonamide (L10)

Orange solid, 50% yield, 374.2 mg, mp 90-91 °C, $[\alpha]^{20}_D$ = -79.0 (c = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 1H), 7.17 (s, 1H), 7.06 (s, 1H), 6.93 (s, 2H), 6.89 (s, 1H), 6.79 (s, 1H), 6.77 (s, 1H), 6.01 (s, 1H), 4.51 (s, 1H), 4.36 (s, 1H), 4.10-4.06 (m, 6H), 3.76 (s, 1H), 2.65 (s, 6H), 2.36 (s, 6H), 2.31 (s, 3H), 2.15 (s, 6H), 2.09-2.06 (m, 2H), 1.95 (s, 1H), 1.86-1.83 (m, 1H), 1.48-1.42 (m, 4H), 1.34-1.31 (m, 1H), 1.03-0.97 (m, 2H), 0.93-0.87 (m, 2H), -0.34 (d, J = 9.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 139.5, 139.4, 138.9, 137.93, 137.86, 137.5, 137.4, 136.3, 136.2, 134.7, 132.8, 132.6, 131.8, 130.9, 130.7, 130.5, 130.0, 75.0, 74.9, 71.1, 69.6, 69.3, 69.0, 57.8, 57.3, 31.3, 29.8, 29.7, 26.9, 25.0, 23.9, 22.9, 21.4, 21.1, 20.9, 20.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ -25.06. HRMS (ESI) calcd for $C_{43}H_{54}FeN_2O_2PS$ $[M+H]^+$: 749.2988, found: 749.3001.

(_R_)-3-((3,5-bis(trifluoromethyl)phenyl)amino)-4-((1-(2-(diphenylphosphanyl)ferrocenyl)ethyl)amino)cyclobut-3-ene-1,2-dione (L11)

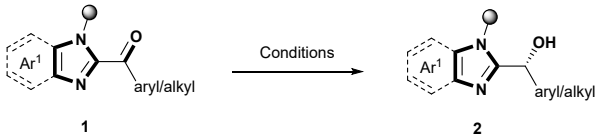
Orange solid, 47% yield, 331.0 mg, mp 86-87 °C, $[\alpha]^{25}_D$ = -89.4 (c = 0.5, MeOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (s, 2H), 6.11 (s, 1H), 4.42 (s, 1H), 4.35 (s, 1H), 4.20 (s, 5H), 4.15 (s, 1H), 3.97 (s, 1H), 2.63 (s, 6H), 2.35-2.29 (m, 4H), 2.26 (s, 3H), 2.18 (d, J = 9.6 Hz, 2H), 2.12-2.07 (m, 1H), 1.96-1.87 (m, 2H), 1.80-1.78 (m, 2H), 1.72-1.65 (m, 4H), 1.56-1.53 (m, 2H), 1.49 (d, J = 6.4 Hz, 3H), 1.44-1.30 (m, 4H), 1.19-1.10 (m, 8H), 0.92-0.75 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 138.9, 134.0, 131.8,

70.7, 69.4, 68.7, 67.3, 58.3, 57.5, 37.5, 37.3, 35.4, 35.3, 33.7, 33.4, 32.3, 31.7, 31.4, 31.3, 31.2, 31.0, 29.7, 29.5, 28.4, 28.3, 27.73, 27.68, 27.3, 27.2, 27.0, 26.9, 26.4, 25.2, 24.3, 23.1, 21.0, 20.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ -17.85. HRMS (ESI) calcd for $C_{39}H_{58}FeN_2O_2PS$ $[M+H]^+$: 705.3301, found: 705.3296.

***N*-((1*S*,2*S*)-2-(((*S*)-1-(2-(diphenylphosphanyl)ferrocenyl)ethyl)amino)cyclohexyl)-2,4,6-trimethylbenzenesulfonamide (L12)**

Orange solid, 60% yield, 415.3 mg, mp 159-160 °C, $[\alpha]^{20}_D$ = +67.9 (c = 0.63, EtOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.51 (m, 2H), 7.41 (d, *J* = 4.4 Hz, 3H), 7.19 (t, *J* = 4.4 Hz, 1H), 7.07 (s, 4H), 6.96 (s, 2H), 5.97 (s, 1H), 4.53 (s, 1H), 4.38 (s, 1H), 4.10 (s, 6H), 3.74 (s, 1H), 2.63 (s, 6H), 2.35 (s, 3H), 2.13 (d, *J* = 9.6 Hz, 2H), 1.93 (d, *J* = 12.4 Hz, 1H), 1.79 (s, 1H), 1.51-1.44 (m, 5H), 1.07-1.01 (m, 2H), 0.86-0.79 (m, 1H), -0.40 (d, *J* = 10.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 140.1, 140.0, 139.1, 136.5, 136.4, 135.1, 134.9, 134.2, 132.7, 132.5, 131.8, 129.2, 128.4, 128.3, 128.2, 128.1, 97.7, 74.1, 71.12, 71.09, 69.7, 69.4, 69.2, 57.7, 57.0, 46.2, 32.0, 29.8, 24.9, 24.0, 23.1, 21.0, 19.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ -24.91. HRMS (ESI) calcd for $C_{39}H_{46}FeN_2O_2PS$ $[M+H]^+$: 693.2362, found: 693.2357.

III. General procedure for the asymmetric hydrogenation of 2-imidazolyl aryl ketones



1 2

Condition A:

Under argon atomosphere, $[Ir(COD)Cl]_2$ (1.7 mg, 0.0025 mmol), **L5** (3.8 mg, 0.0055 mmol), and anhydrous ^{i}PrOH (1 mL) were added to an oven-dried vial (10 mL) and then stirred at 30 °C for 1.5 h to give a clear yellow solution. The mixture was concentrated to dryness, then 1 mL of dried Toluene was added to the crude Ir-**L5** complex. An aliquot of the catalyst solution (0.2 mL, 0.0005 mmol) was transferred into a 10 mL hydrogenation vessel, and then ketones (1.0 mmol), HCO_2Na (3.4 mg, 0.05 mmol) and anhydrous Toluene (2 mL) were added. The vial was placed in an alloy plate which was then placed into the autoclave. And the autoclave was purged five times with hydrogen, then pressurized to 45 atm of H_2 and stirred at 70 °C for 12 h. Upon completion, the reaction mixture was cooled to room temperature. After the hydrogen pressure was slowly released, the solvent was removed, and the mixture

was purifified by passing through a short column of silica gel to afford **2a**-**2r**. The *ee* values of all compounds were determined by HPLC with a chiral column.

Condition B:

Under argon atomosphere, $[Ir(COD)Cl]_2$ (1.7 mg, 0.0025 mmol), **L1** (3.7 mg, 0.0055 mmol), and anhydrous ^{i}PrOH (1 mL) were added to an oven-dried vial (10 mL) and then stirred at 30 °C for 1.5 h to give a clear yellow solution. The mixture was concentrated to dryness, then 1 mL of dried Toluene was added to the crude Ir-**L1** complex. An aliquot of the catalyst solution (0.2 mL, 0.0005 mmol) was transferred into a 10 mL hydrogenation vessel, and then ketones (1.0 mmol), ^{t}BuOLi (4 mg, 0.05 mmol) and anhydrous ^{i}PrOH (2 mL) were added. The vial was placed in an alloy plate which was then placed into the autoclave. And the autoclave was purged five times with hydrogen, then pressurized to 30 atm of H_2 and stirred at 40 °C for 12 h. Upon completion, the reaction mixture was cooled to room temperature. After the hydrogen pressure was slowly released, the solvent was removed, and the mixture was purifified by passing through a short column of silica gel to afford **2s**-**2v**. The *ee* values of all compounds were determined by HPLC with a chiral column.

Condition C:

Under argon atomosphere, $[Ir(COD)Cl]_2$ (1.7 mg, 0.0025 mmol), **L12** (3.8 mg, 0.0055 mmol), and anhydrous ^{i}PrOH (1 mL) were added to an oven-dried vial (10 mL) and then stirred at 30 °C for 1.5 h to give a clear yellow solution. The mixture was concentrated to dryness, then 1 mL of dried Toluene was added to the crude Ir-**L12** complex. An aliquot of the catalyst solution (0.2 mL, 0.0005 mmol) was transferred into a 10 mL hydrogenation vessel, and then ketones (1.0 mmol), HCO_2Na (3.4 mg, 0.05 mmol) and anhydrous Toluene (2 mL) were added. The vial was placed in an alloy plate which was then placed into the autoclave. And the autoclave was purged five times with hydrogen, then pressurized to 45 atm of H_2 and stirred at 70 °C for 12 h. Upon completion, the reaction mixture was cooled to room temperature. After the hydrogen pressure was slowly released, the solvent was removed, and the mixture was purifified by passing through a short column of silica gel to afford **3a** and **3h**. The *ee* values of all compounds were determined by HPLC with a chiral column.

(*R*)-phenyl(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2a)

White solid, 99% yield, 131.7 mg, mp 211-212 ^{o}C, $[\alpha]^{25}_{D}$ = +73.9 (c = 0.66, MeOH). The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; $t_R(S)$ = 9.83 min (minor), $t_R(R)$ = 13.98 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.2 Hz, 3H), 7.35-7.29 (m, 3H), 6.94 (s, 1H), 6.17 (s, 1H), 3.47 (s, 3H), 2.38 (s,

3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 140.2, 139.4, 134.8, 132.0, 130.9, 128.5, 127.7, 126.4, 119.1, 109.4, 69.6, 30.2, 20.5, 20.2. HRMS (ESI) calcd for $C_{17}H_{19}N_2O$ $[M+H]^+$: 267.1492, found: 267.1501.

(*R*)-(5,6-dimethyl-1*H*-benzo[*d*]imidazol-2-yl)(phenyl)methanol (2b)

White solid, 99% yield, 124.8 mg, mp 216-217 °C, $[\alpha]^{25}_D$ = -36.2 (c = 0.9, MeOH); lit. [3] mp 210-211 °C, $[\alpha]^{21}_D$ = -82.7 (*c*= 1.0, water, 99% *ee*). The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R(*S*) = 9.10 min (minor), t_R(*R*) = 19.44 min (major). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.16 (br, 1H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.29-7.26 (m, 3H), 6.50 (s, 1H), 5.91 (s, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 156.5, 143.1, 130.1, 128.5, 127.7, 126.9, 70.4, 20.4. HRMS (ESI) calcd for $C_{16}H_{17}N_2O$ $[M+H]^+$: 253.1335, found: 253.1342.

(*R*)-(1-benzyl-5,6-dimethyl-1*H*-benzo[*d*]imidazol-2-yl)(phenyl)methanol (2c)

White solid, 95% yield, 162.5 mg, mp 216-217 °C, $[\alpha]^{25}_D$ = +42.0 (c = 0.35, MeOH). The *ee* was determined by HPLC on Chiralpak IA-H column, hexane: isopropanol = 95:5; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R(*S*) = 25.72 min (minor), t_R(*R*) = 30.61 min (major). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.42 (t, *J* = 7.6 Hz, 3H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.27-7.23 (m, 4H), 7.01 (d, *J* = 4.8 Hz, 3H), 6.61 (d, *J* = 4.8 Hz, 1H), 6.13 (d, *J* = 4.8 Hz, 1H), 5.47 (s, 2H), 2.29 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 155.0, 142.0, 137.4, 134.5, 131.4, 130.5, 128.8, 128.5, 127.6, 127.0, 126.5, 119.7, 111.2, 69.4, 47.2, 20.6, 20.3. HRMS (ESI) calcd for $C_{23}H_{23}N_2O$ $[M+H]^+$: 343.1805, found: 343.1816.

(*R*)-(5,6-dimethyl-1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)(phenyl)methanol (2d)

White solid, 90% yield, 147.7 mg, mp 145-146 °C, $[\alpha]^{25}_D$ = +20.9 (c = 0.5, MeOH). The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R(*S*) = 8.79 min (minor), t_R(*R*) = 10.04 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.44 (m, 4H), 7.22-7.16 (m, 5H), 7.09 (s, 2H), 6.87 (s, 1H), 5.90 (s, 1H), 4.75 (br, 1H), 2.41 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 132.5, 131.6, 129.6, 128.9, 128.3, 127.9, 127.7, 119.6, 110.4, 69.7, 20.4, 20.2. HRMS (ESI) calcd for $C_{22}H_{21}N_2O$ $[M+H]^+$: 329.1648, found: 329.1655.

(*R*)-(1-isopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazol-2-yl)(phenyl)methanol (2e)

White solid, 99% yield, 145.6 mg, mp 201-202 °C, $[\alpha]^{25}_D$ = +66.4 (c = 0.7, MeOH). The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 85:15; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R(*R*) = 4.15 min (major), t_R(*S*) = 4.96 min (minor). ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.45 (s, 1H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.33-7.26 (m, 4H), 6.21 (s, 1H), 2.40 (s, 3H), 2.35 (s, 3H), 1.38 (d, *J* = 6.8 Hz, 3H), 1.22 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 140.8, 140.6, 132.3, 131.4, 130.7, 128.3, 127.5, 126.2, 119.7, 112.6, 69.7, 48.1, 20.7, 20.6, 20.2, 20.1. HRMS (ESI) calcd for $C_{19}H_{23}N_2O$ $[M+H]^+$: 295.1805, found: 295.1800.

(*R*)-(1-methyl-1*H*-benzo[*d*]imidazol-2-yl)(phenyl)methanol (2f)

White solid, 99% yield, 117.9 mg, mp 178-179 °C, $[\alpha]^{25}_D$ = +107.8 (c = 0.34, MeOH); lit. [4] $[\alpha]_D$ = +119.1 (*c*= 1.0, MeOH, 99% *ee*). The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R(*S*) = 9.64 min (minor), t_R(*R*) = 11.76 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (t, *J* = 4.0 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.37-7.30 (m, 3H), 7.28-7.24 (m, 2H), 7.17 (t, *J* = 4.0 Hz, 1H), 6.23 (s, 1H), 5.58 (br, 1H), 3.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 140.9, 140.0, 136.2, 128.5, 127.7, 126.2, 122.8, 122.1, 119.1, 109.2, 69.7, 30.3. HRMS (ESI) calcd for $C_{15}H_{15}N_2O$ $[M+H]^+$: 239.1179, found: 239.1188.

(*R*)-(5,6-difluoro-1-methyl-1*H*-benzo[*d*]imidazol-2-yl)(phenyl)methanol (2g)

White solid, 95% yield, 130.2 mg, mp 203-204 °C, $[\alpha]^{25}_D$ = +108.1 (c = 0.76, MeOH). The *ee* was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R(*S*) = 8.00 min (minor), t_R(*R*) = 13.44 min (major). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.72-7.65 (m, 2H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 6.60 (s, 1H), 6.11 (s, 1H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.7, 147.5 (dd, $^1J_{C\text{-}F}$ = 237.5 Hz, $^2J_{C\text{-}F}$ = 15.4 Hz), 147.0 (dd, $^1J_{C\text{-}F}$ = 235.4 Hz, $^2J_{C\text{-}F}$ = 14.9 Hz), 141.4, 137.2 (d, $^3J_{C\text{-}F}$ = 10.7 Hz), 132.3 (d, $^3J_{C\text{-}F}$ = 11.2 Hz), 128.6, 127.8, 126.6, 106.8 (d, $^2J_{C\text{-}F}$ = 19.2 Hz), 99.0 (d, $^2J_{C\text{-}F}$ = 22.8 Hz), 69.2, 31.1. HRMS (ESI) calcd for $C_{15}H_{13}F_2N_2O$ $[M+H]^+$: 275.0990, found: 275.0999.

(*R*)-(1-methyl-1*H*-imidazol-2-yl)(phenyl)methanol (2h)

White solid, 99% yield, 93.1 mg, mp 140-141 °C, $[\alpha]^{25}_D$ = +66.7 (c = 0.36, MeOH). The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R(*S*) = 6.49 min (minor), t_R(*R*) = 12.50 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.32 (m, 4H), 7.31-7.26 (m, 1H), 6.84 (s, 1H), 6.73 (m, 1H), 6.55 (s, 1H), 5.99 (s, 1H), 3.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 141.0, 128.3, 127.3, 126.1, 126.0, 122.1, 68.8, 33.2. HRMS (ESI) calcd for $C_{11}H_{13}N_2O$ $[M+H]^+$: 189.1022, found: 189.1030.

(*R*)-*p*-tolyl(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2i)

White solid, 99% yield, 138.7 mg, mp 187-188 °C, $[\alpha]^{25}_D$ = +82.4 (c = 0.6, MeOH). The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min;

UV detection at 254 nm; $t_R(S)$ = 8.00 min (minor), $t_R(R)$ = 10.57 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.89 (s, 1H), 6.15 (s, 1H), 3.46 (s, 3H), 2.36 (s, 3H), 2.344 (s, 3H), 2.337 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 139.5, 137.5, 137.1, 134.7, 131.7, 130.7, 129.1, 126.2, 119.1, 109.4, 69.5, 30.3, 21.2, 20.6, 20.2. HRMS (ESI) calcd for $C_{18}H_{21}N_2O$ $[M+H]^+$: 281.1648, found: 281.1655.

(*R*)-(4-fluorophenyl)(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2j)

White solid, 99% yield, 140.6 mg, mp 188-189 °C, $[\alpha]^{25}_D$ = +67.8 (c = 0.92, MeOH). The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; $t_R(S)$ = 7.79 min (minor), $t_R(R)$ = 10.32 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.31 (m, 3H), 6.99-6.92 (m, 3H), 6.13 (s, 1H), 3.48 (s, 3H), 2.38 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, $^1J_{C\text{-}F}$ = 244.4 Hz), 154.4, 139.4, 136.2, 134.7, 132.1, 131.0, 127.9 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 119.0, 115.2 (d, $^2J_{C\text{-}F}$ = 21.4 Hz), 109.4, 68.9, 30.2, 20.5, 20.1. HRMS (ESI) calcd for $C_{17}H_{18}FN_2O$ $[M+H]^+$: 285.1398, found: 285.1407.

(*R*)-(4-chlorophenyl)(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2k)

White solid, 95% yield, 142.6 mg, mp 191-192 °C, $[\alpha]^{25}_D$ = +43.0 (c = 0.86, MeOH). The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 80:20; flow rate = 1.0 mL/min; UV detection at 254 nm; $t_R(S)$ = 5.48 min (minor), $t_R(R)$ = 6.47 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 5H), 6.93 (s, 1H), 6.10 (s, 1H), 3.48 (s, 3H), 2.38 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 139.3, 138.9, 134.7, 133.3, 132.2, 131.1, 128.5, 127.5, 119.0, 109.5, 68.9, 30.3, 20.5, 20.1. HRMS (ESI) calcd for $C_{17}H_{18}ClN_2O$ $[M+H]^+$: 301.1102, found: 301.1111.

(*R*)-(4-(trifluoromethyl)phenyl)(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2l)

White solid, 92% yield, 153.7 mg, mp 222-223 °C, $[\alpha]^{25}_D$ = +67.1 (c = 0.8, MeOH). The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; $t_R(S)$ = 7.10 min (minor), $t_R(R)$ = 9.31 min (major). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.42 (s, 1H), 6.98 (s, 1H), 6.21 (s, 1H), 3.51 (s, 3H), 2.37 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 144.0, 138.6, 134.5, 132.7, 131.7, 130.1, 126.6, 125.4 (q, $^4J_{C\text{-}F}$ = 2.6 Hz), 124.0 (q, $^1J_{C\text{-}F}$ = 180.6 Hz), 118.8, 109.6, 68.9, 30.4, 20.5, 20.2. HRMS (ESI) calcd for $C_{18}H_{18}F_3N_2O$ $[M+H]^+$: 335.1366, found: 335.1374.

(*R*)-*m*-tolyl(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2m)

White solid, 99% yield, 138.7 mg, mp 189-190 °C, $[\alpha]^{25}_D$ = +104.8 (c = 0.6, MeOH). The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min;

UV detection at 254 nm; $t_R(S)$ = 7.45 min (minor), $t_R(R)$ = 10.83 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 5.2 Hz, 1H), 7.22-7.18 (m, 3H), 7.10 (d, *J* = 6.8 Hz, 1H), 6.93 (s, 1H), 6.13 (s, 1H), 3.47 (s, 3H), 2.38 (s, 3H), 2.37 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 140.2, 139.5, 138.2, 134.8, 131.8, 130.8, 128.4, 128.3, 127.0, 123.4, 119.2, 109.4, 69.7, 30.2, 21.4, 20.5, 20.2. HRMS (ESI) calcd for $C_{18}H_{21}N_2O$ $[M+H]^+$: 281.1648, found: 281.1655.

(*R*)-*o*-tolyl(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2n)

White solid, 97% yield, 135.9 mg, mp 193-194 °C, $[\alpha]^{25}_D$ = +71.9 (c = 0.8, MeOH). The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; $t_R(S)$ = 9.09 min (minor), $t_R(R)$ = 10.18 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 1H), 7.22-7.21 (m, 3H), 7.12-7.08 (m, 1H), 6.92 (s, 1H), 6.24 (s, 1H), 6.15 (br, 1H), 3.37 (s, 3H), 2.42 (s, 3H), 2.37 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 139.3, 138.2, 136.6, 134.4, 131.7, 130.7, 128.1, 127.0, 126.1, 119.1, 109.3, 67.5, 30.0, 20.6, 20.2, 19.4. HRMS (ESI) calcd for $C_{18}H_{21}N_2O$ $[M+H]^+$: 281.1648, found: 281.1659.

(*R*)-(3,5-dimethylphenyl)(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2o)

White solid, 99% yield, 145.6 mg, mp 197-198 °C, $[\alpha]^{25}_D$ = +77.0 (c = 0.96, MeOH). The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 80:20; flow rate = 1.0 mL/min; UV detection at 254 nm; $t_R(S)$ = 5.12 min (minor), $t_R(R)$ = 6.41 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.02 (s, 2H), 6.93 (d, *J* = 4.0 Hz, 2H), 6.11 (s, 1H), 3.49 (s, 3H), 2.39 (s, 3H), 2.38 (s, 3H), 2.29 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 140.1, 139.5, 138.0, 134.8, 131.8, 130.8, 129.3, 124.1, 119.2, 109.4, 69.7, 30.3, 21.3, 20.5, 20.2. HRMS (ESI) calcd for $C_{19}H_{23}N_2O$ $[M+H]^+$: 295.1805, found: 295.1813.

(*R*)-[1,1'-biphenyl]-4-yl(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2p)

White solid, 90% yield, 154.0 mg, mp 204-205 °C, $[\alpha]^{25}_D$ = +35.6 (c = 0.56, MeOH). The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; $t_R(S)$ = 11.24 min (minor), $t_R(R)$ = 13.73 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.48-7.43 (m, 5H), 7.38 (t, *J* = 7.6 Hz, 1H), 6.97 (s, 1H), 6.24 (s, 1H), 3.54 (s, 3H), 2.38 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 140.5, 139.3, 132.0, 131.0, 128.8, 127.3, 127.2, 127.1, 126.9, 119.2, 109.5, 69.5, 30.3, 20.5, 20.2. HRMS (ESI) calcd for $C_{23}H_{23}N_2O$ $[M+H]^+$: 343.1805, found: 343.1812.

(*R*)-pyridin-4-yl(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2q)

White solid, 85% yield, 113.5 mg, mp 212-213 °C, $[\alpha]^{25}_D$ = +43.7 (c = 0.3, MeOH). The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R(*S*) = 13.74 min (minor), t_R(*R*) = 18.43 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 6.4 Hz, 2H), 7.38 (s, 1H), 7.33 (t, *J* = 4.4 Hz, 2H), 6.96 (s, 1H), 6.16 (s, 1H), 3.53 (s, 3H), 2.38 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 149.8, 149.1, 134.5, 132.8, 131.7, 124.0, 120.9, 118.7, 109.7, 68.3, 30.4, 20.5, 20.2. HRMS (ESI) calcd for $C_{16}H_{18}N_3O$ $[M+H]^+$: 268.1444, found: 268.1450.

(*R*)-pyridin-3-yl(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2r)

White solid, 73% yield, 97.5 mg, mp 193-194 °C, $[\alpha]^{25}_D$ = +35.6 (c = 0.5, MeOH). The *ee* was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R(*S*) = 20.00 min (minor), t_R(*R*) = 25.78 min (major). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.65 (s, 1H), 8.53 (d, *J* = 4.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 2.8 Hz, 1H), 7.38 (s, 1H), 7.32 (s, 1H), 6.63 (d, *J* = 5.2 Hz, 1H), 6.18 (d, *J* = 5.2 Hz, 1H), 3.77 (s, 3H), 2.36 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.1, 148.9, 148.5, 140.6, 137.5, 135.2, 134.8, 131.4, 130.2, 123.7, 119.6, 110.5, 67.1, 30.5, 20.6, 20.3. HRMS (ESI) calcd for $C_{16}H_{18}N_3O$ $[M+H]^+$: 268.1444, found: 268.1453.

(*R*)-1-(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)ethan-1-ol (2s):

White solid, 99% yield, 204.0 mg, mp 197-198 °C, $[\alpha]^{25}_D$ = +87.8 (c = 0.61, MeOH). The *ee* was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R(*S*) = 10.96 min (minor), t_R(*R*) = 13.18 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 6.96 (d, *J* = 2.8 Hz, 1H), 5.14-5.10 (m, 1H), 4.61 (br, 1H), 3.75 (d, *J* = 1.2 Hz, 3H), 2.40 (s, 3H), 2.38 (s, 3H), 1.69 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 139.6, 134.5, 131.8, 130.8, 119.2, 109.4, 63.4, 30.0, 22.0, 20.5, 20.2. HRMS (ESI) calcd for $C_{18}H_{21}N_2O_2$ $[M+H]^+$: 205.1335, found: 205.1341.

(*R*)-1-(1,5,6-trimethyl-1*H*-benzo[d]imidazol-2-yl)propan-1-ol (2t):

White solid, 99% yield, 218 mg, mp 191-192 °C, $[\alpha]^{25}_D$ = +52.2 (c = 0.37, MeOH). The *ee* was determined by HPLC on Chiralpak IC-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R(*R*) = 11.27 min (major), t_R(*S*) = 12.78 min (minor). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (s, 1H), 6.92 (s, 1H), 4.81 (t, *J* = 6.6 Hz, 1H), 3.70 (s, 3H), 2.37 (s, 3H), 3.35 (s, 3H), 1.99 (t, *J* = 7.2 Hz, 2H), 0.98 (t, *J* = 7.8 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.1, 139.9, 134.5, 131.6,

130.7, 119.2, 109.4, 68.9, 30.0, 29.1, 20.5, 20.2, 10.1. HRMS (ESI) calcd for $C_{13}H_{19}N_2O$ $[M+H]^+$: 219.1492, found: 219.1499.

(*R*)-2-phenyl-1-(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)ethan-1-ol (2u):

White solid, 99% yield, 280 mg, mp 195-196 °C, $[\alpha]^{25}_D$ = +62.8 (c = 0.25, MeOH). The *ee* was determined by HPLC on Chiralpak IC-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R(*R*) = 12.73 min (major), t_R(*S*) = 16.13 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.23 (d, *J* = 3.6 Hz, 3H), 7.13 (t, *J* = 4.0 Hz, 2H), 6.93 (s, 1H), 5.60 (br, 1H), 5.14 (t, *J* = 7.2 Hz, 1H), 3.44-3.33 (m, 5H), 2.40 (s, 3H), 2.38m (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 139.9, 137.4, 134.1, 131.7, 130.9, 129.5, 128.4, 126.5, 119.2, 109.5, 68.4, 43.4, 29.6, 20.6, 20.2. HRMS (ESI) calcd for $C_{18}H_{21}N_2O_2$ $[M+H]^+$: 281.1648, found: 281.1652.

(*R*)-2-methyl-1-(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)propan-1-ol (2v):

White solid, 99% yield, 232 mg, mp 199-201 °C, $[\alpha]^{25}_D$ = +64.7 (c = 0.56, MeOH). The *ee* was determined by HPLC on Chiralpak IC-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R(*R*) = 7.00 min (major), t_R(*S*) = 9.46 min (minor). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.23 (d, *J* = 3.6 Hz, 3H), 7.13 (t, *J* = 4.0 Hz, 2H), 6.93 (s, 1H), 5.60 (br, 1H), 5.14 (t, *J* = 7.2 Hz, 1H), 3.44-3.33 (m, 5H), 2.40 (s, 3H), 2.38m (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.0, 139.8, 134.5, 131.7, 131.0, 119.3, 109.5, 72.8, 30.2, 29.7, 20.5, 20.2, 19.1, 18.0. HRMS (ESI) calcd for $C_{14}H_{21}N_2O$ $[M+H]^+$: 233.1648, found: 233.1652.

(*S*)-(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)(phenyl)methanol (3a)

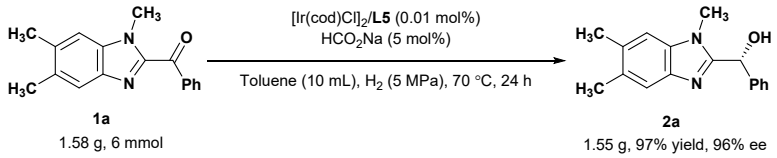
White solid, 98% yield, 130.4 mg, mp 207-208 °C, $[\alpha]^{25}_D$ = -105.1 (c = 0.74, MeOH). The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R(*S*) = 7.53 min (major), t_R(*R*) = 10.72 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.36 (d, *J* = 6.8 Hz, 2H), 7.32-7.27 (m, 2H), 7.25 (d, *J* = 6.8 Hz, 1H), 6.91 (s, 1H), 6.10 (s, 1H), 3.43 (s, 3H), 2.35 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 140.2, 139.7, 134.9, 131.9, 130.9, 128.5, 127.7, 126.5, 119.3, 109.4, 69.8, 30.1, 20.5, 20.1. HRMS (ESI) calcd for $C_{18}H_{21}N_2O_2$ $[M+H]^+$: 281.1648, found: 281.1655.

(*S*)-(1-methyl-1*H*-imidazol-2-yl)(phenyl)methanol (3h)

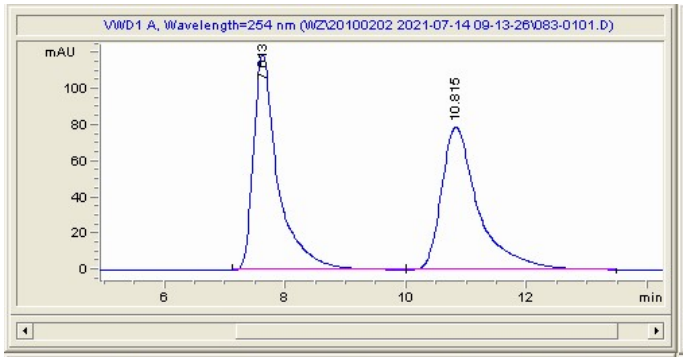
White solid, 84% yield, 79.0 mg, mp 144-145 °C, $[\alpha]^{25}_D$ = -68.0 (c = 0.43, MeOH). The *ee* was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10; flow rate = 1.0 mL/min; UV detection at 254 nm; t_R(*S*) = 8.60 min (major), t_R(*R*) = 14.99 min (minor). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.35 (d, *J* = 4.0 Hz, 4H), 7.27 (d, *J* = 4.0 Hz, 1H), 7.06 (s, 1H), 6.80 (m, 1H), 6.22 (s, 1H),

5.90 (s, 1H), 3.40 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.1, 142.6, 128.4, 127.3, 126.5, 122.8, 68.7, 33.2. HRMS (ESI) calcd for $C_{11}H_{13}N_2O$ $[M+H]^+$: 189.1022, found: 189.1031.

IV. Gram scale reaction



Under argon atomosphere, $[Ir(COD)Cl]_2$ (2.6 mg, 0.003 mmol), **L5** (4.7 mg, 0.0066 mmol), and anhydrous ^{i}PrOH (4 mL) were added to an oven-dried vial (25 mL) and then stirred at 30 °C for 1.5 h to give a clear yellow solution. The mixture was concentrated to dryness, and then **1a** (6 mmol), HCO_2Na (20.4 mg, 0.3 mmol) and anhydrous Toluene (10 mL) were added. The vial was placed in an alloy plate which was then placed into the autoclave. And the autoclave was purged five times with hydrogen, then pressurized to 50 atm of H_2 and stirred at 70 °C for 24 h. Upon completion, the reaction mixture was cooled to room temperature. After the hydrogen pressure was slowly released, the solvent was removed, and the mixture was purifified by passing through a short column of silica gel to afford **2a** in 1.55g, 97% yield with 96% *ee*. The *ee* values of all compounds were determined by HPLC with a chiral column.



#	Time	Area	Height	Width	Area%	Symmetry
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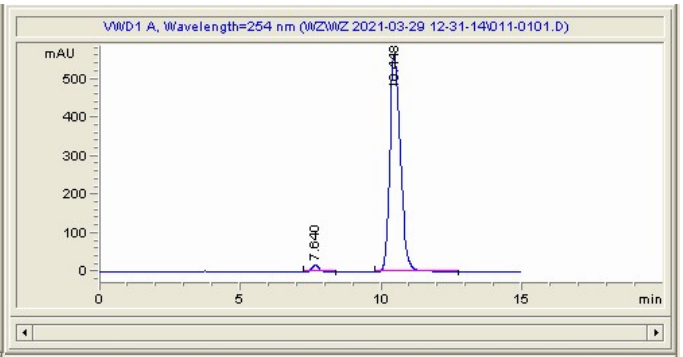
2	10.815	3357.3	79.1	0.6294	49.879	0.577



#	Time	Area	Height	Width	Area%	Symmetry
1	7.64	305.6	17.1	0.2721	2.008	0.846
2	10.448	14909.9	559.1	0.4101	97.992	0.736

V. References

(1) F. Ling, S. Nian, J. Chen, W. Luo, Z. Wang, Y. Lv and W. Zhong, *J. Org. Chem.,* 2018, **83**, 10749-10761.

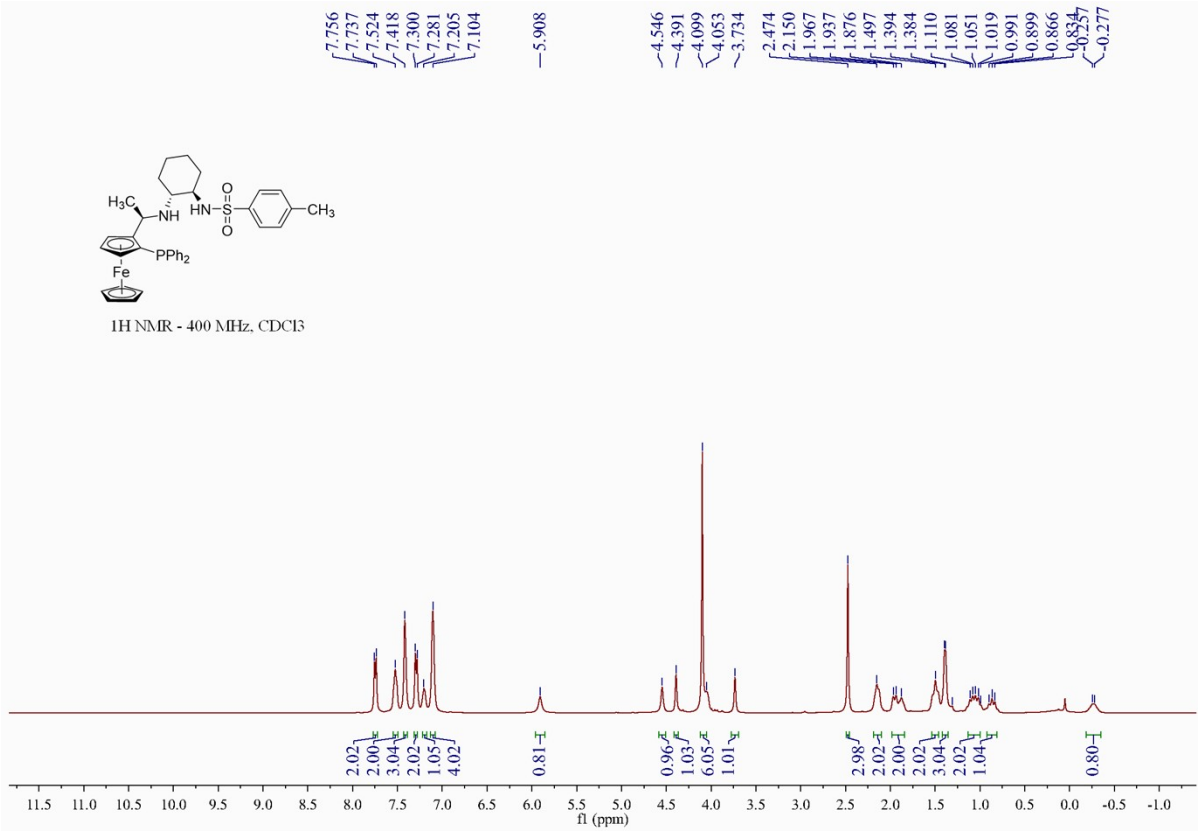
(2) S. Nian, F. Ling, J. Chen, Z. Wang, H. Shen, X. Yi, Y. F. Yang, Y. She and W. Zhong, *Org. Lett.*, 2019, **21**, 5392-5396.

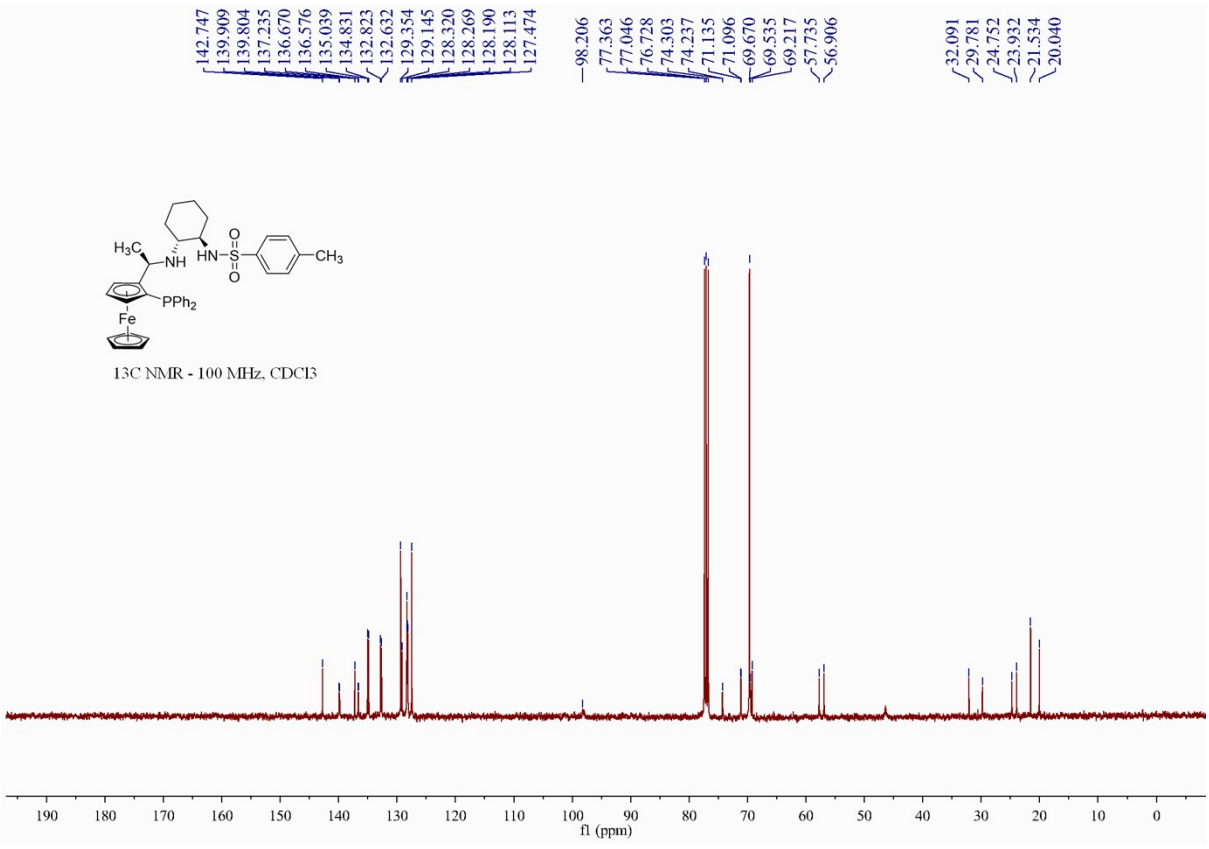
(3) S. B. Kadin, H. J. Eggers and I. Tamm, *Nature,* 1964, **201**, 639-640.

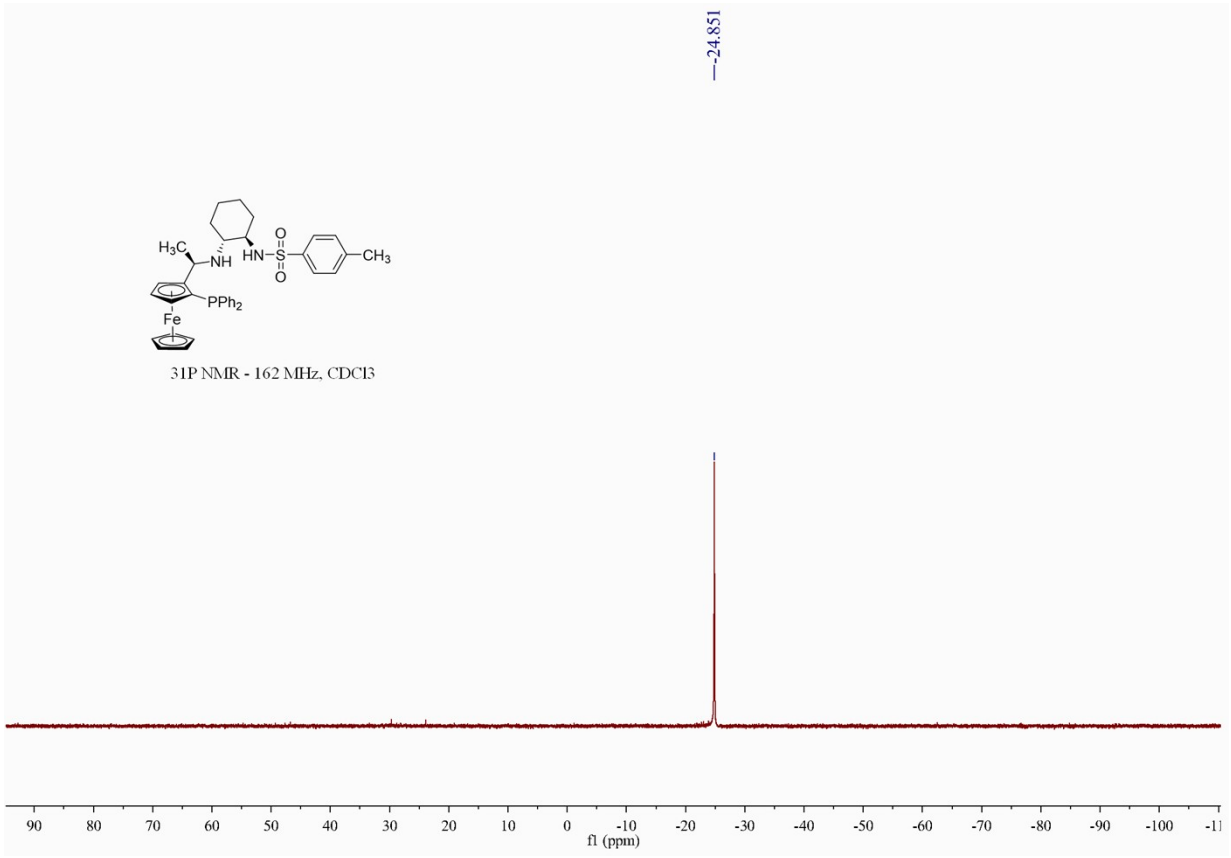
(4) A. Torrens, J. A. Castrillo, A. Claparols and J. Redondo, *Synlett*, 1999, **6**, 765-767.

VI. Copies of ^{1}H and ^{13}C NMR spectra

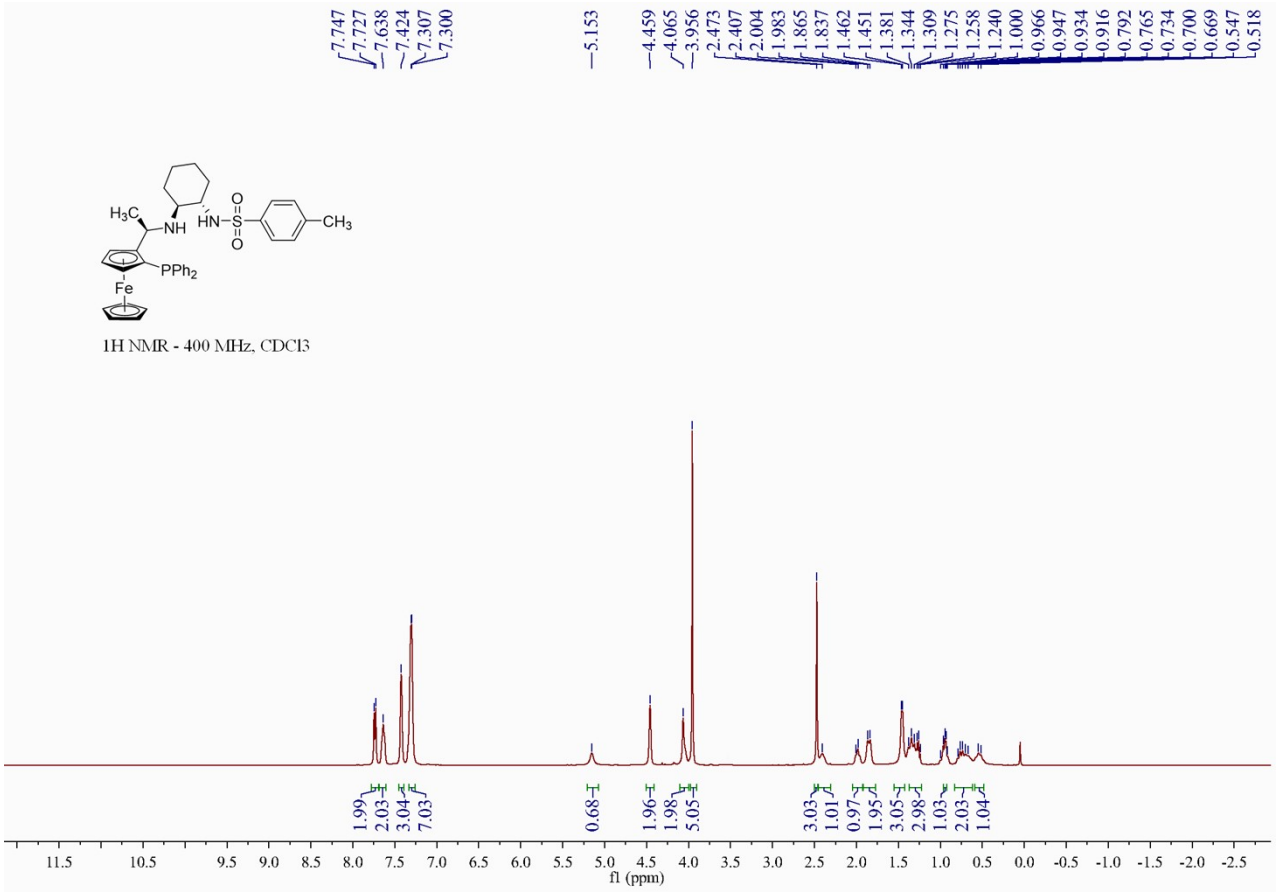
N-((1*R*,2*R*)-2-(((*R*)-1-(2-(diphenylphosphanyl)ferrocenyl)ethyl)amino)cyclohexyl)-4-methylbenzenesulfonamide (L1)

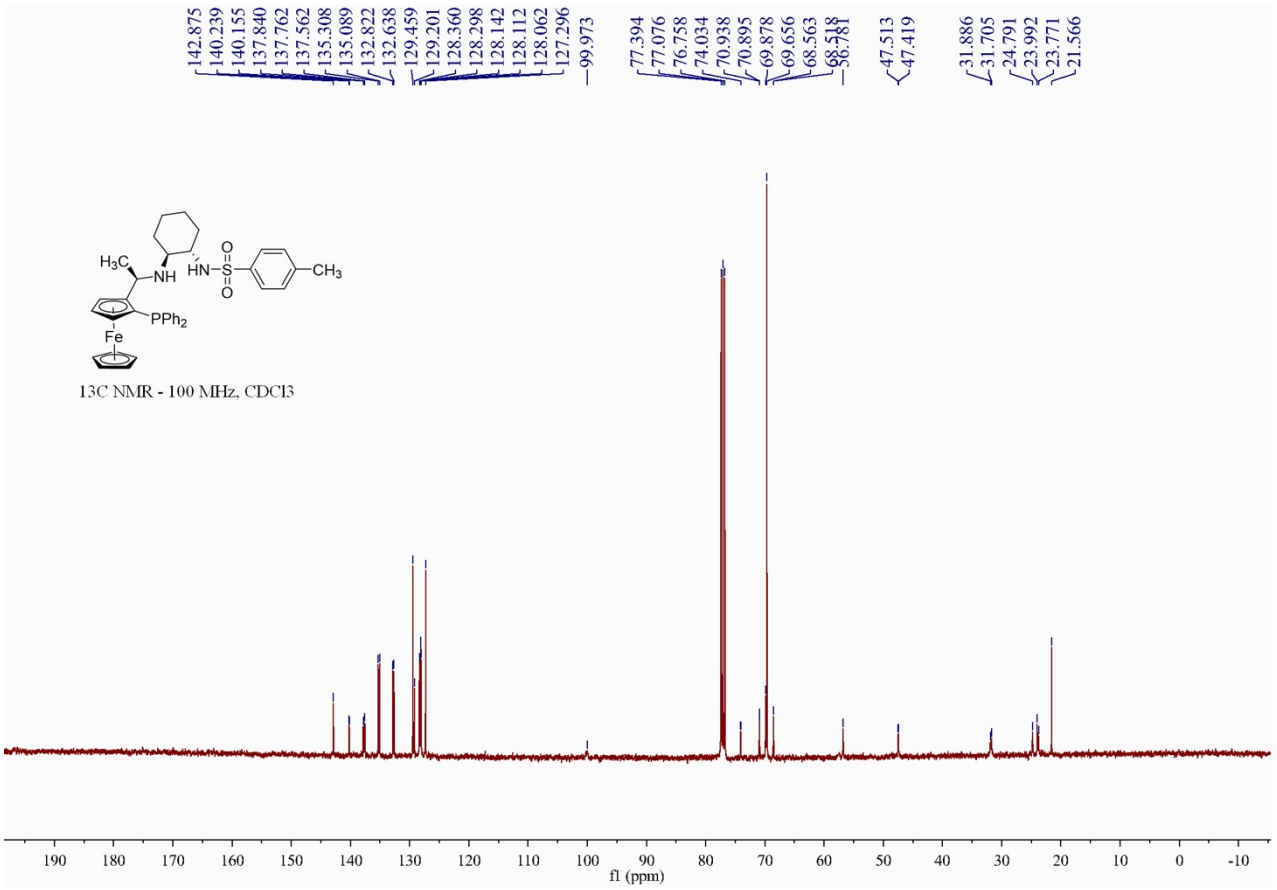






_N_-((1_S_,2_S_)-2-(((_R_)-1-(2-(diphenylphosphanyl)ferrocenyl)ethyl)amino)cyclohexyl)-4-methylbenzenesulfonamide (L2)

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137.762
137.562
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132.638
129.459
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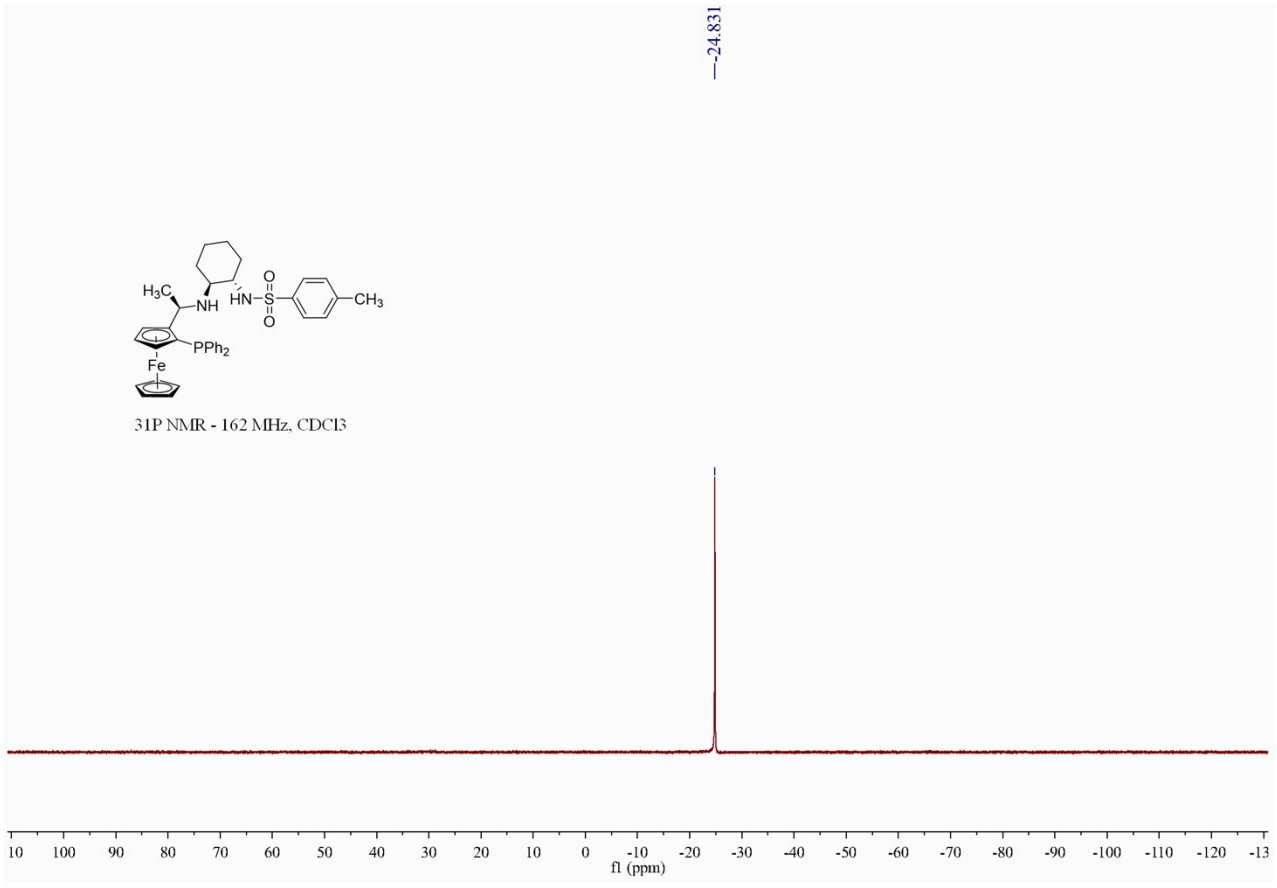
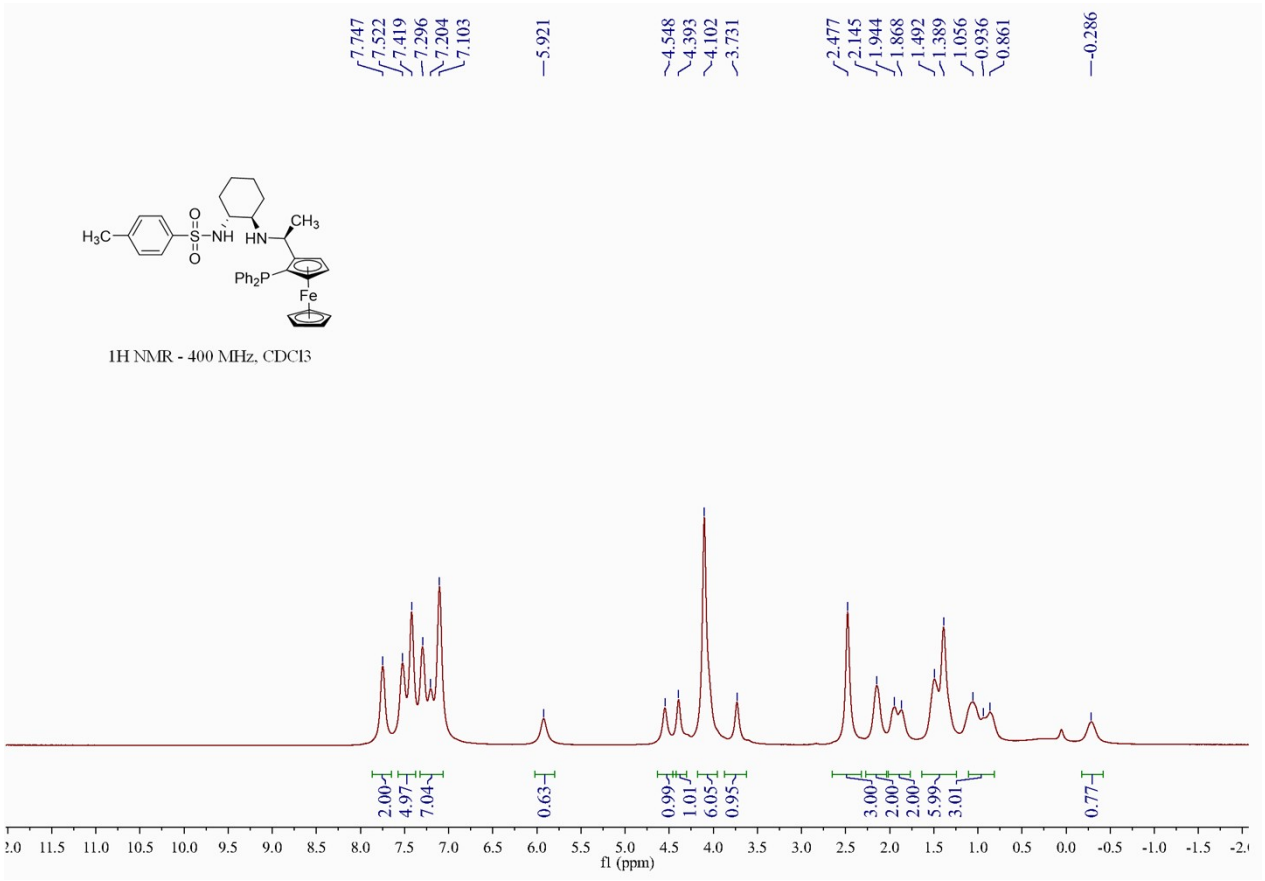
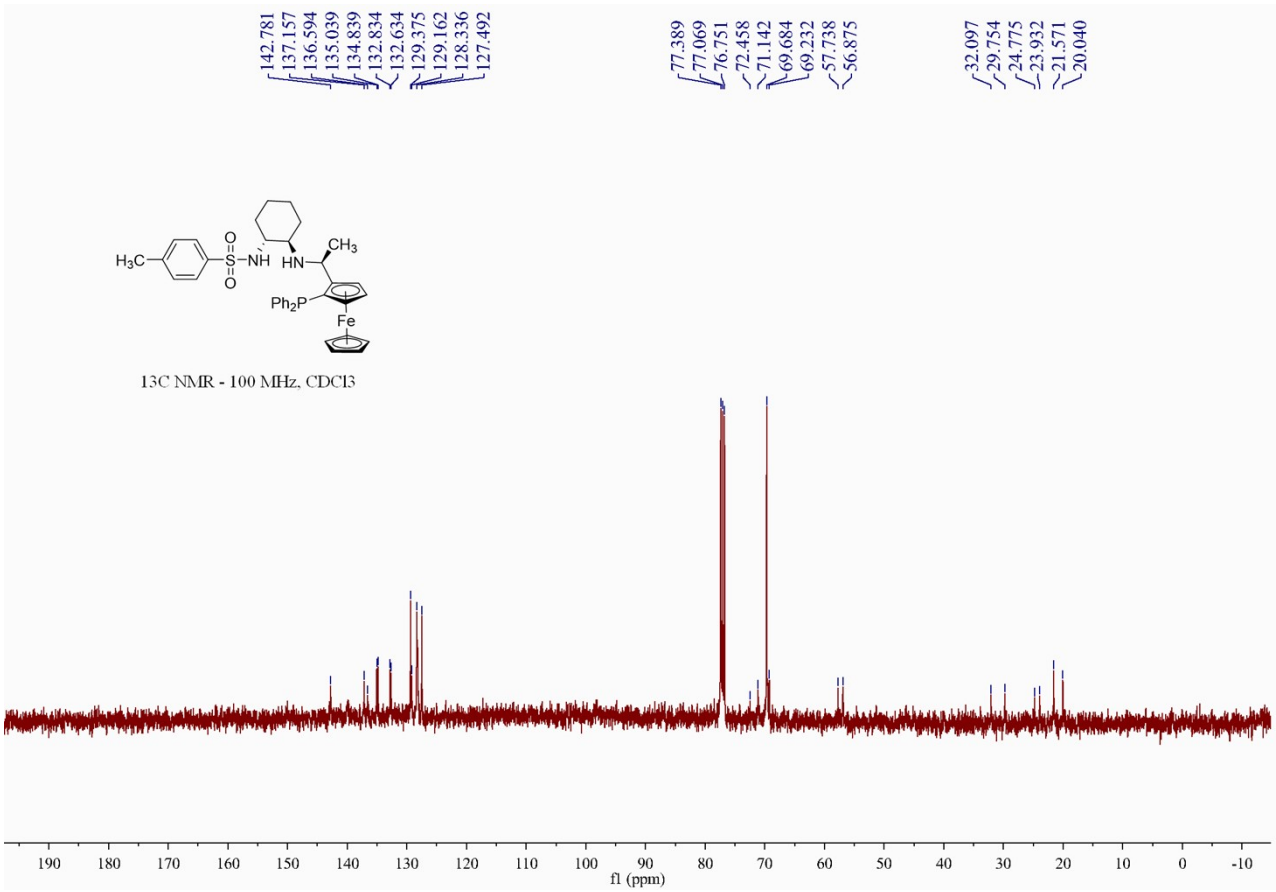
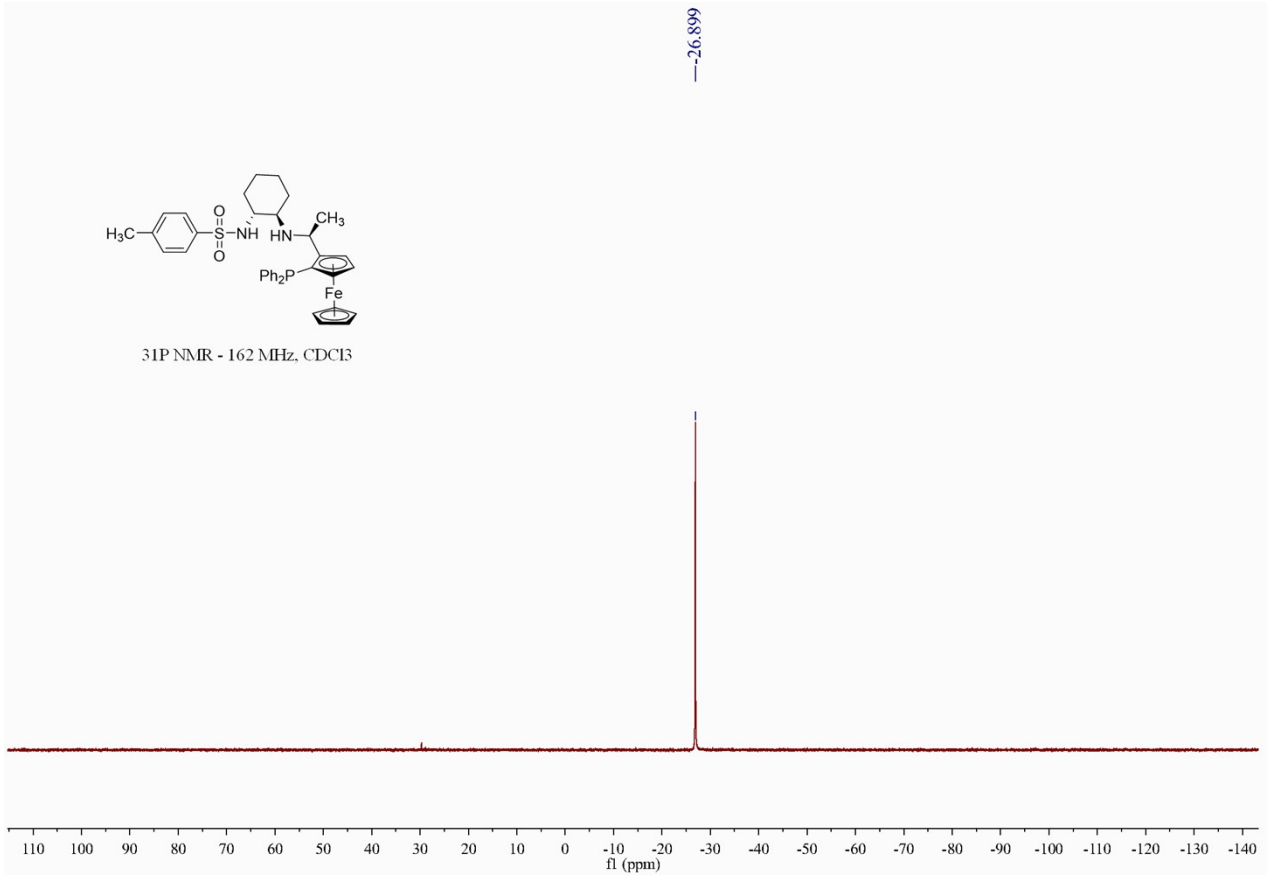
128.360
128.298
128.142
128.112
128.062
127.296
99.973
77.394
77.076
76.758
74.034
70.938
70.895
69.878
69.656
68.563
68.518
58.781
47.513
47.419
31.886
31.705
24.791
23.992
23.771
21.566
H3C
NH
HN
O
S
O
CH3
PPh2
Fe
13C NMR - 100 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


24.831
H3C
NH
HN
O
S
O
CH3
PPh2
Fe
31P NMR - 162 MHz, CDCl3
10 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -13
f1 (ppm)

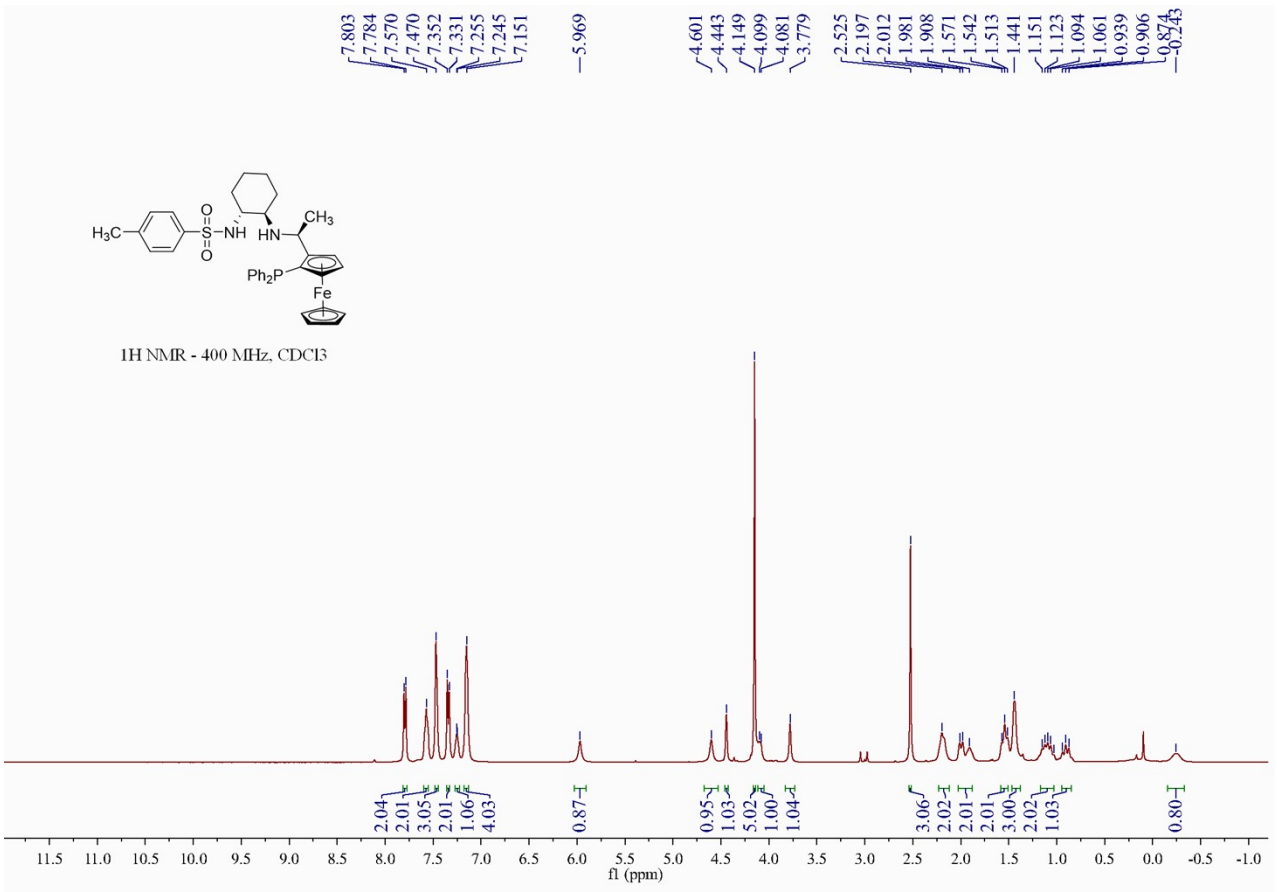
_N_-((1_R_,2_R_)-2-(((_S_)-1-(2-(diphenylphosphanyl)ferrocenyl)ethyl)amino)cyclohexyl)-4-methylbenzenesulfonamide (L3)

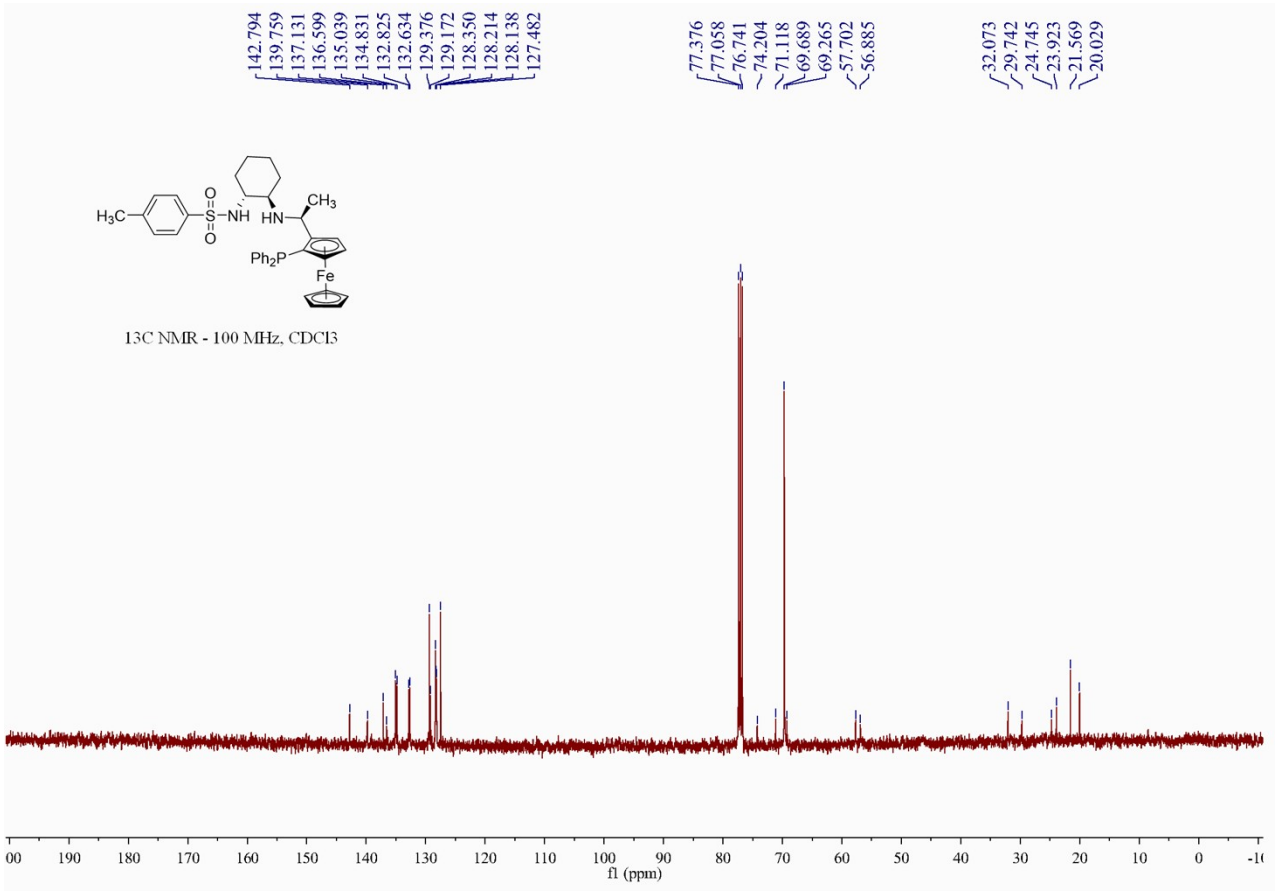




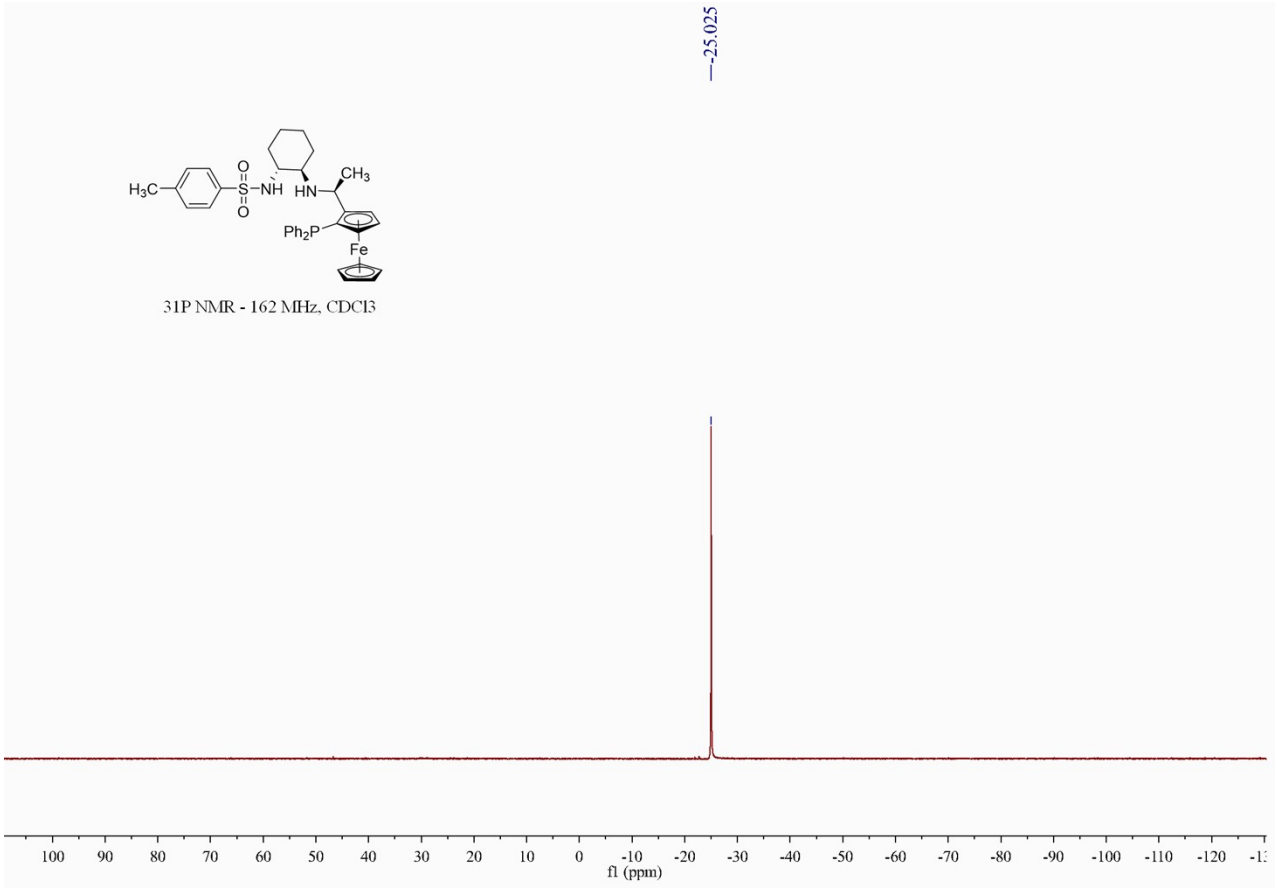


***N*-((1*S*,2*S*)-2-(((*S*)-1-(2-(diphenylphosphanyl)ferrocenyl)ethyl)amino)cyclohexyl)-4-methylbenzenesulfonamide (L4)**



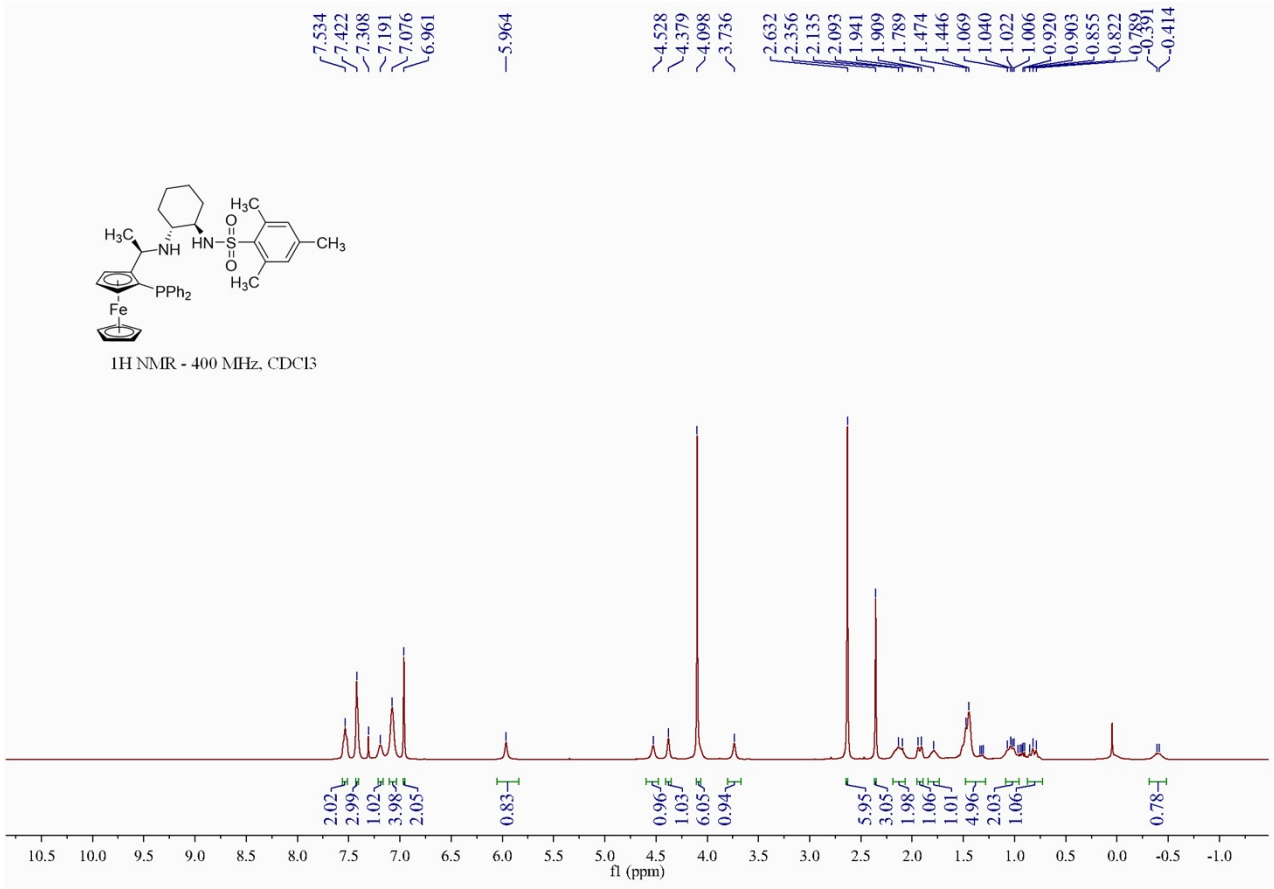


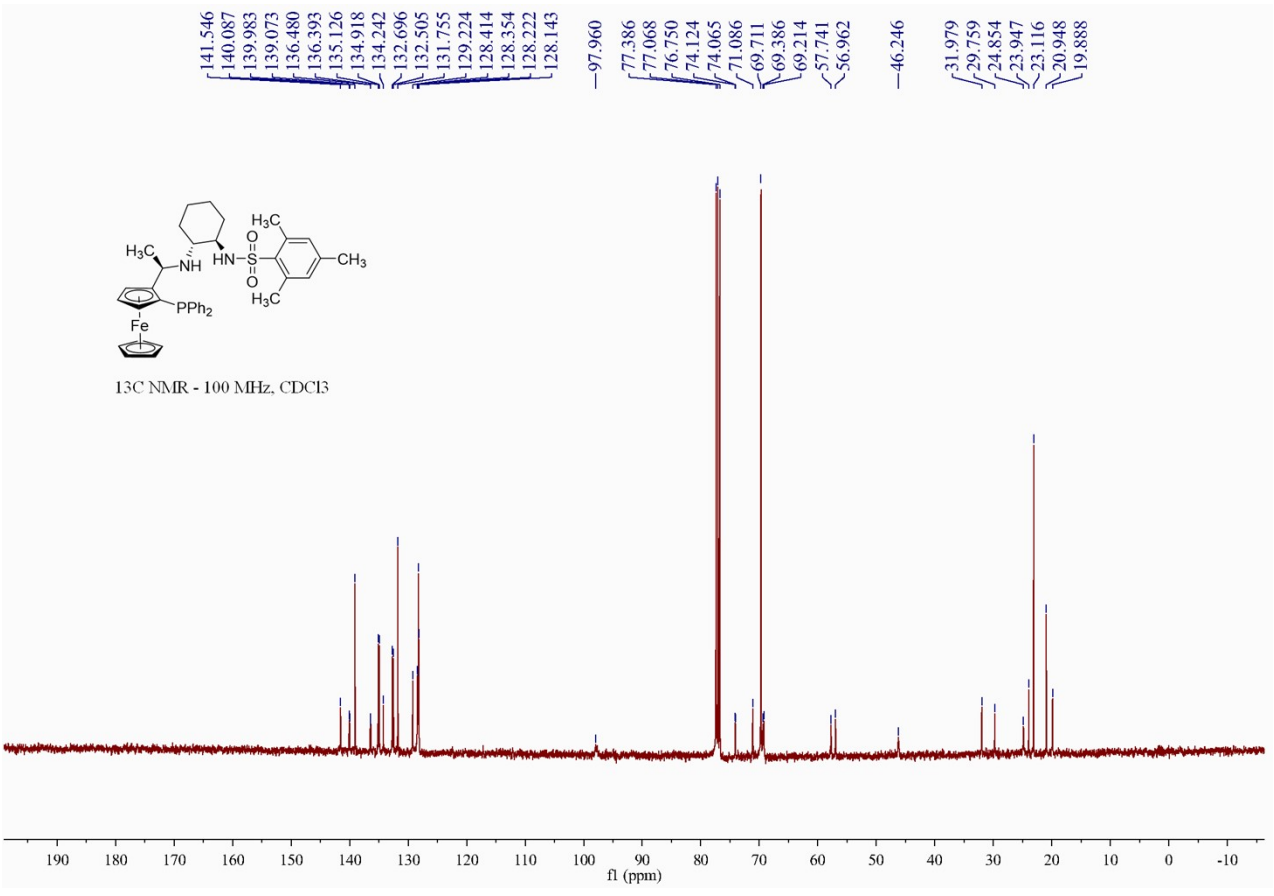
13C NMR - 100 MHz, CDCl3

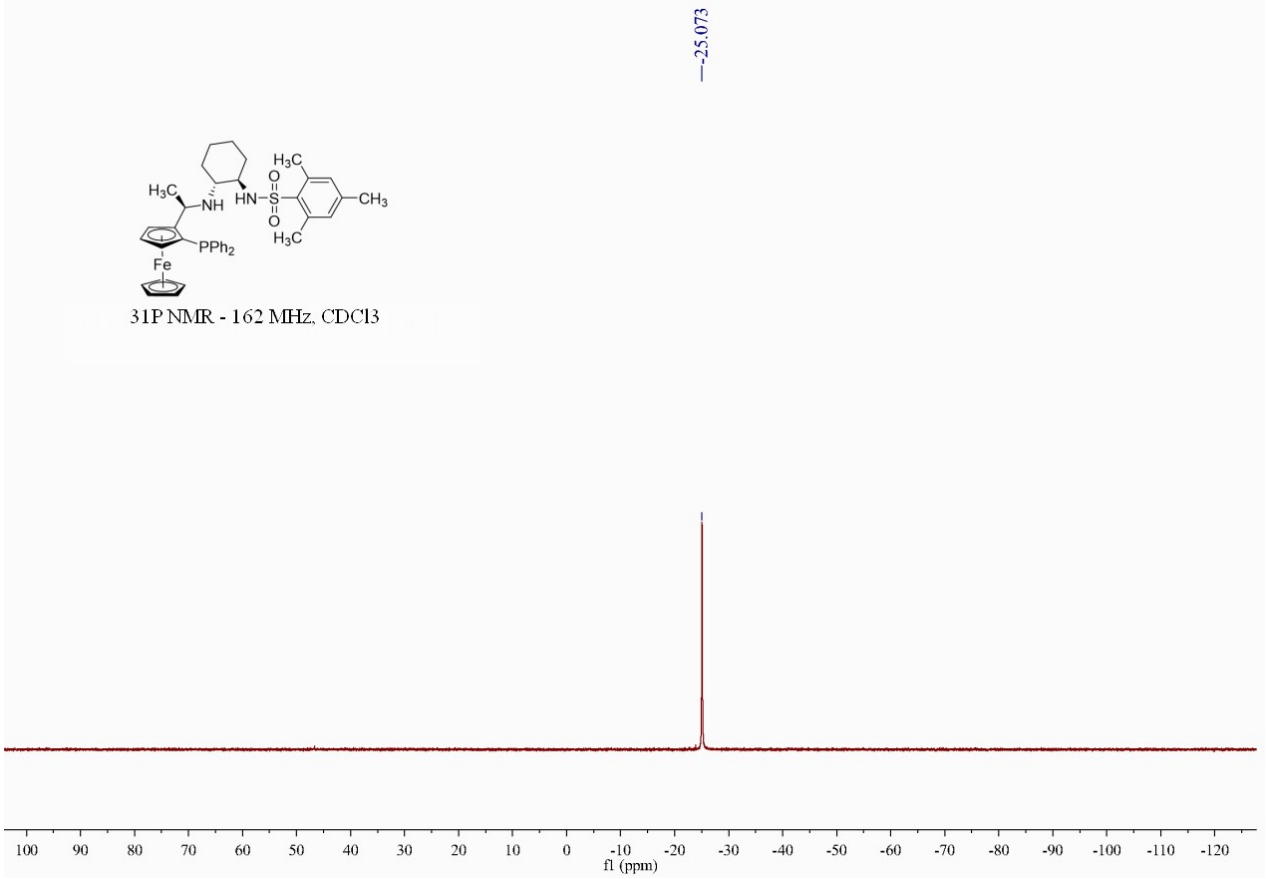


31P NMR - 162 MHz, CDCl3

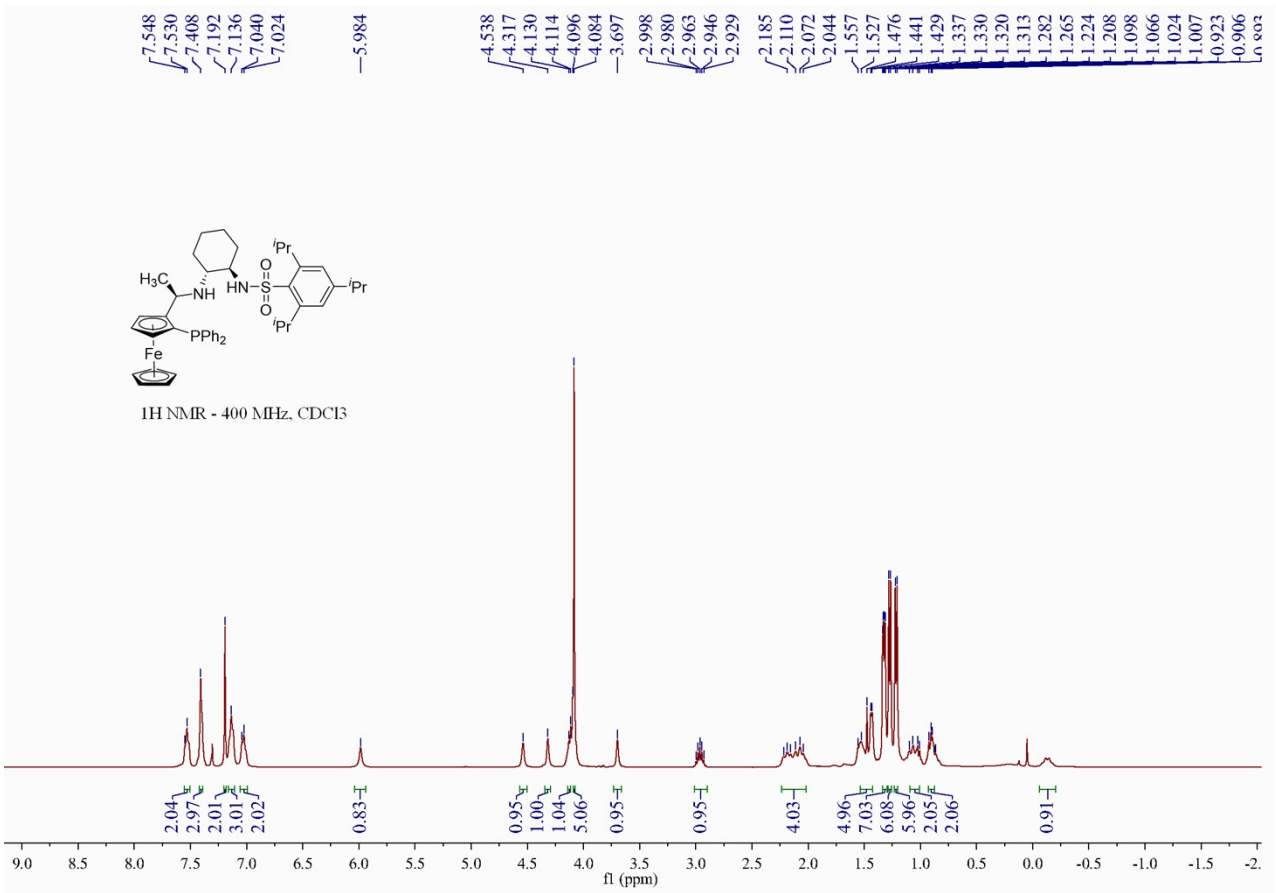
***N*-((1*R*,2*R*)-2-(((*R*)-1-(2-(diphenylphosphanyl)ferrocenyl)ethyl)amino)cyclohexyl)-2,4,6-trimethylbenzenesulfonamide (L5)**

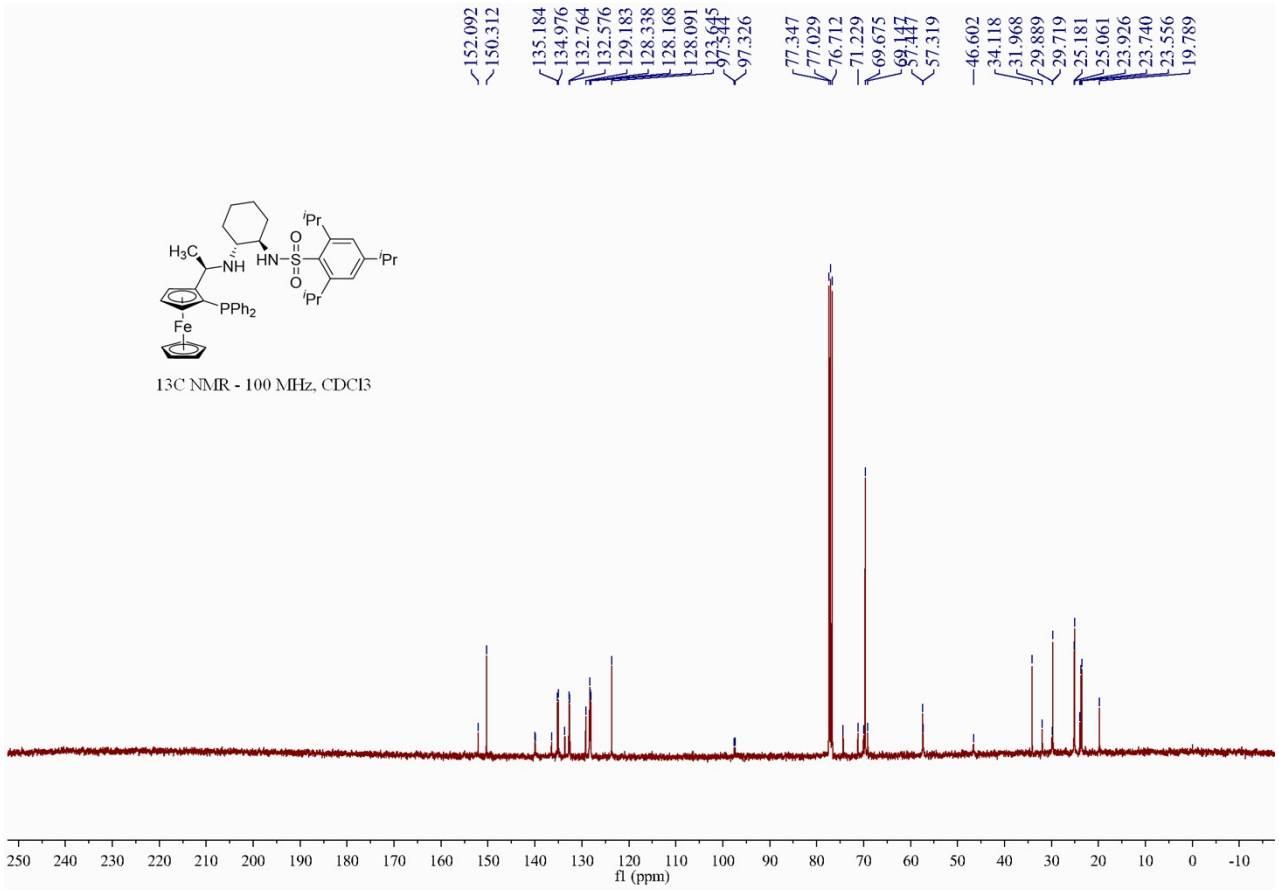






***N*-((1*R*,2*R*)-2-(((*R*)-1-(2-(diphenylphosphanyl)ferrocenyl)ethyl)amino)cyclohexyl)-2,4,6-triisopropylbenzenesulfonamide (L6)**

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134.976
132.764
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128.091
123.645
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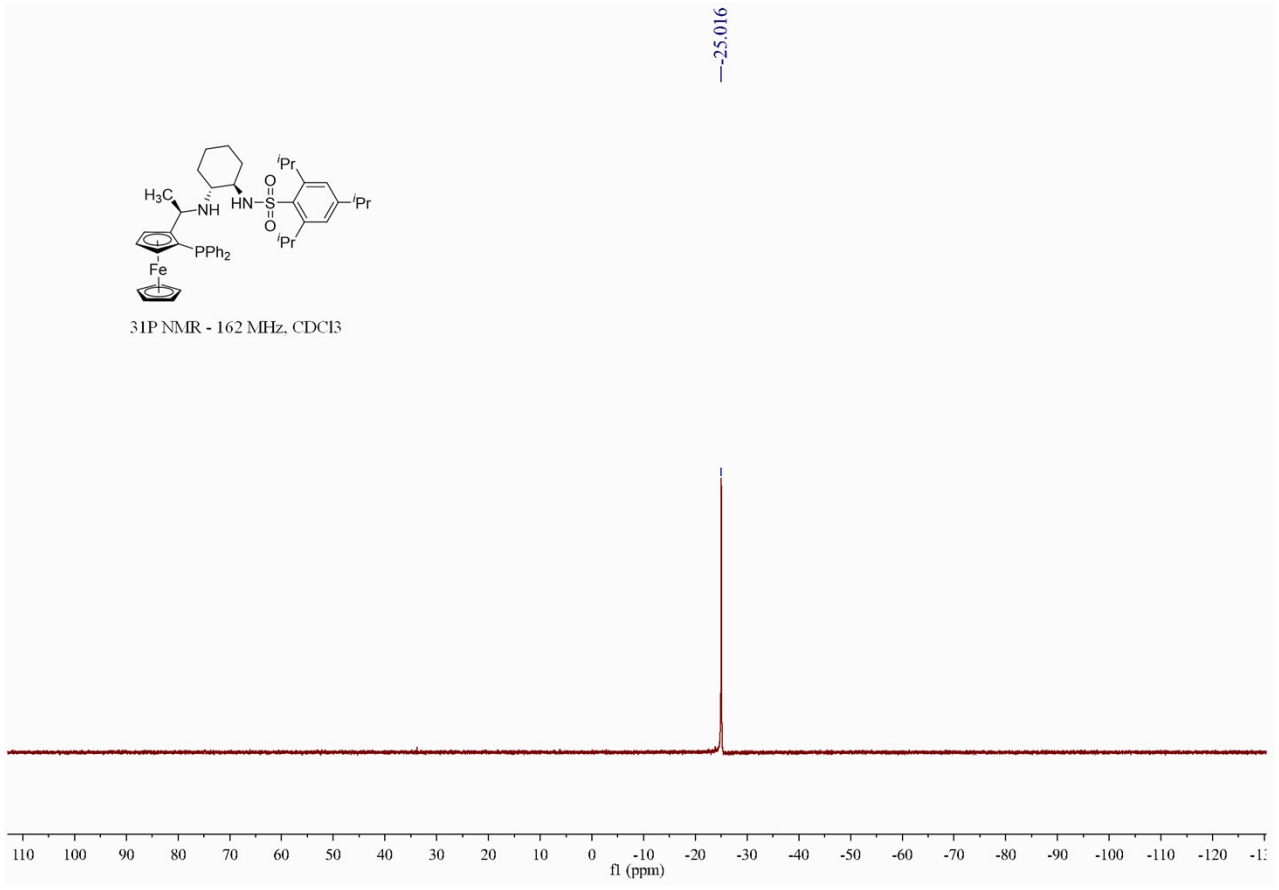
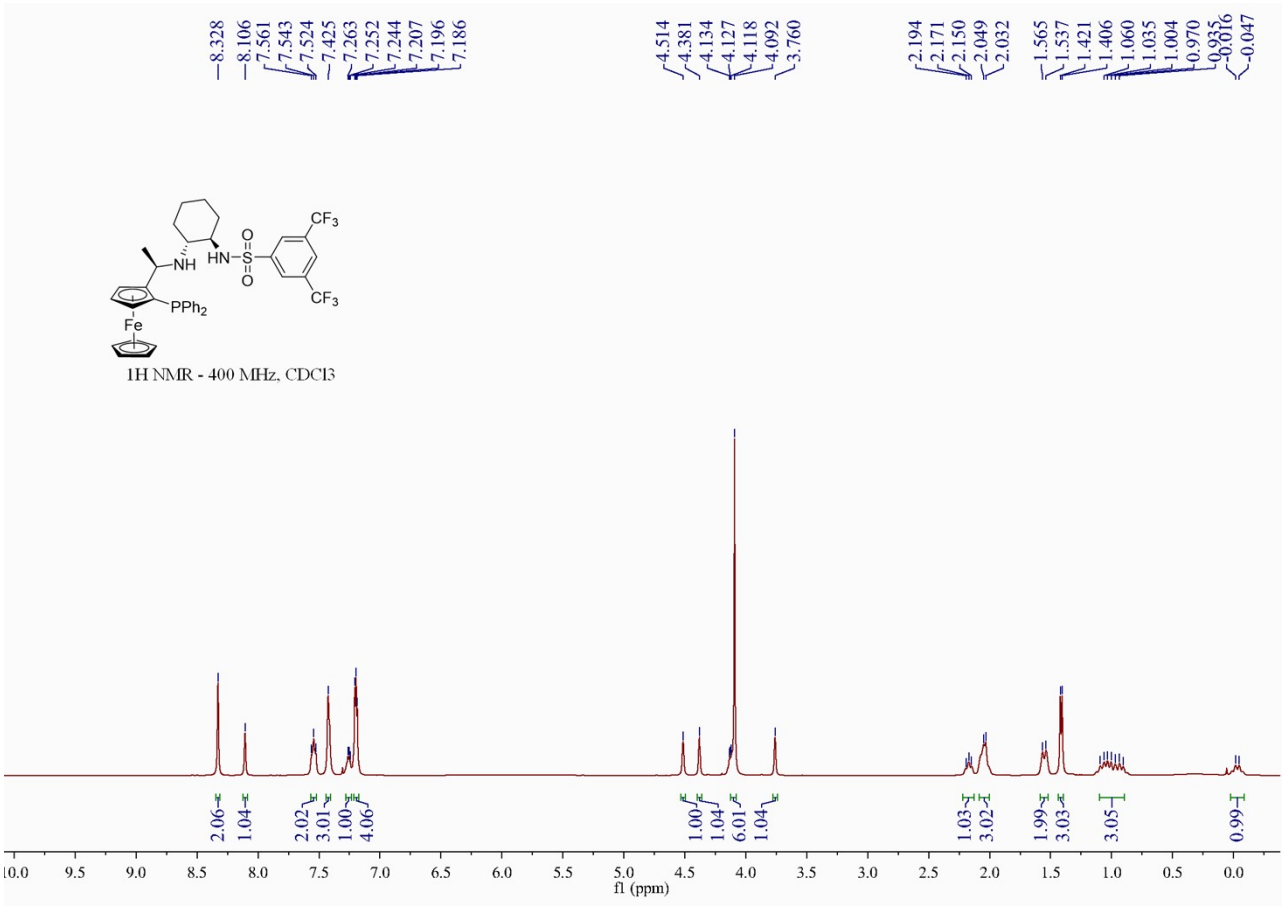
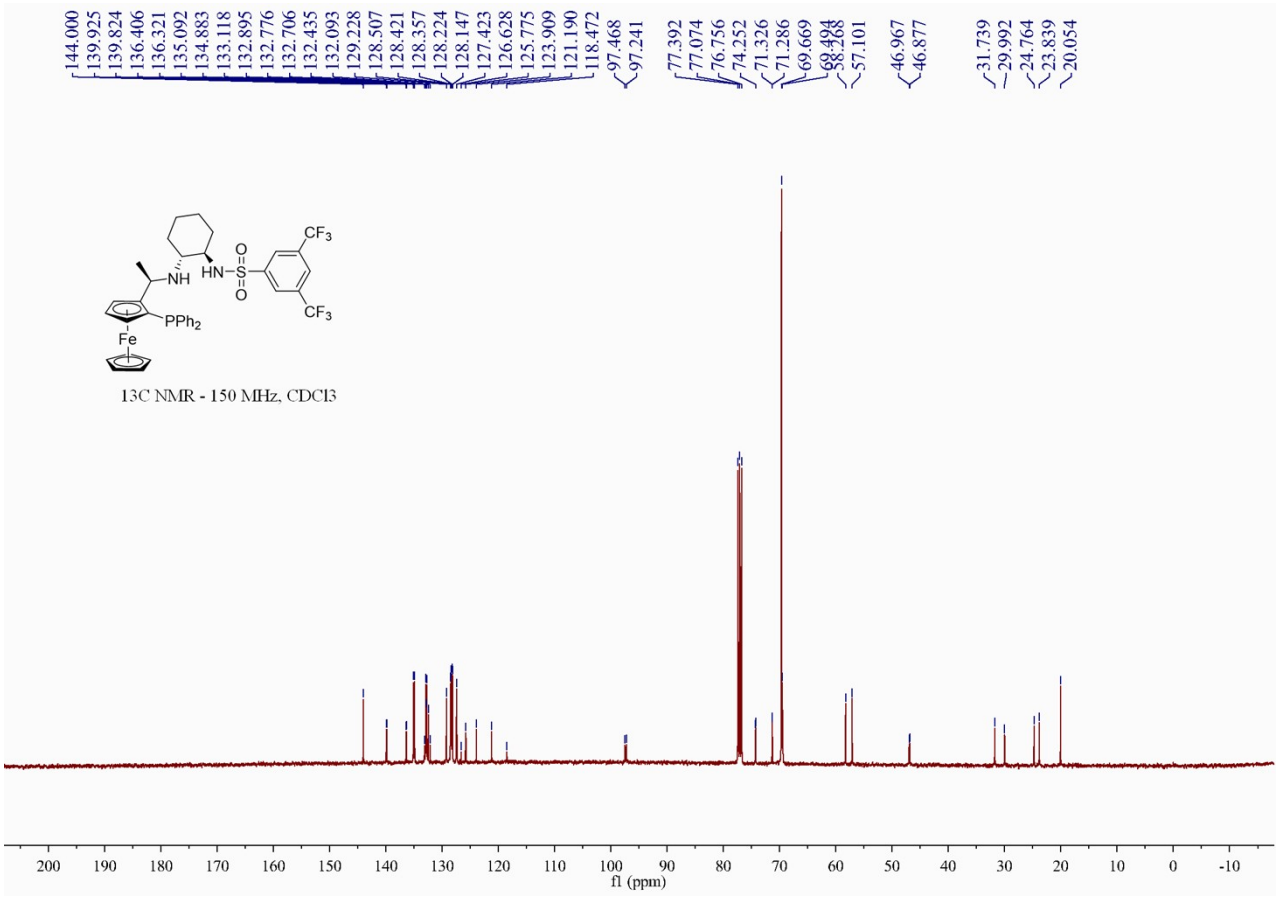
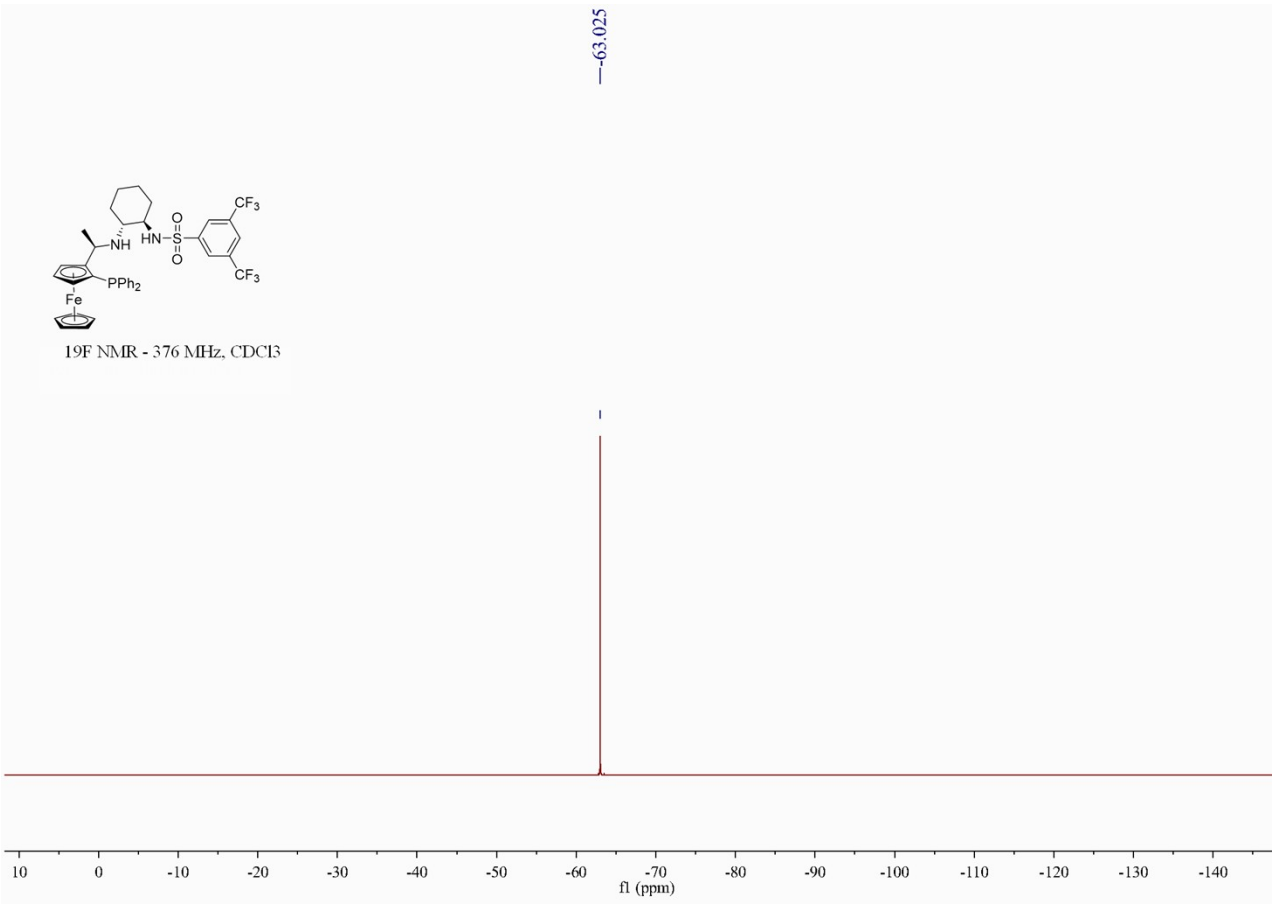
97.326
77.347
77.029
76.712
71.229
69.675
69.147
69.117
57.319
46.602
34.118
31.968
29.889
29.719
25.181
25.061
23.926
23.740
23.556
19.789
13C NMR - 100 MHz, CDCl3
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-25.016
31P NMR - 162 MHz, CDCl3
110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120
f1 (ppm)

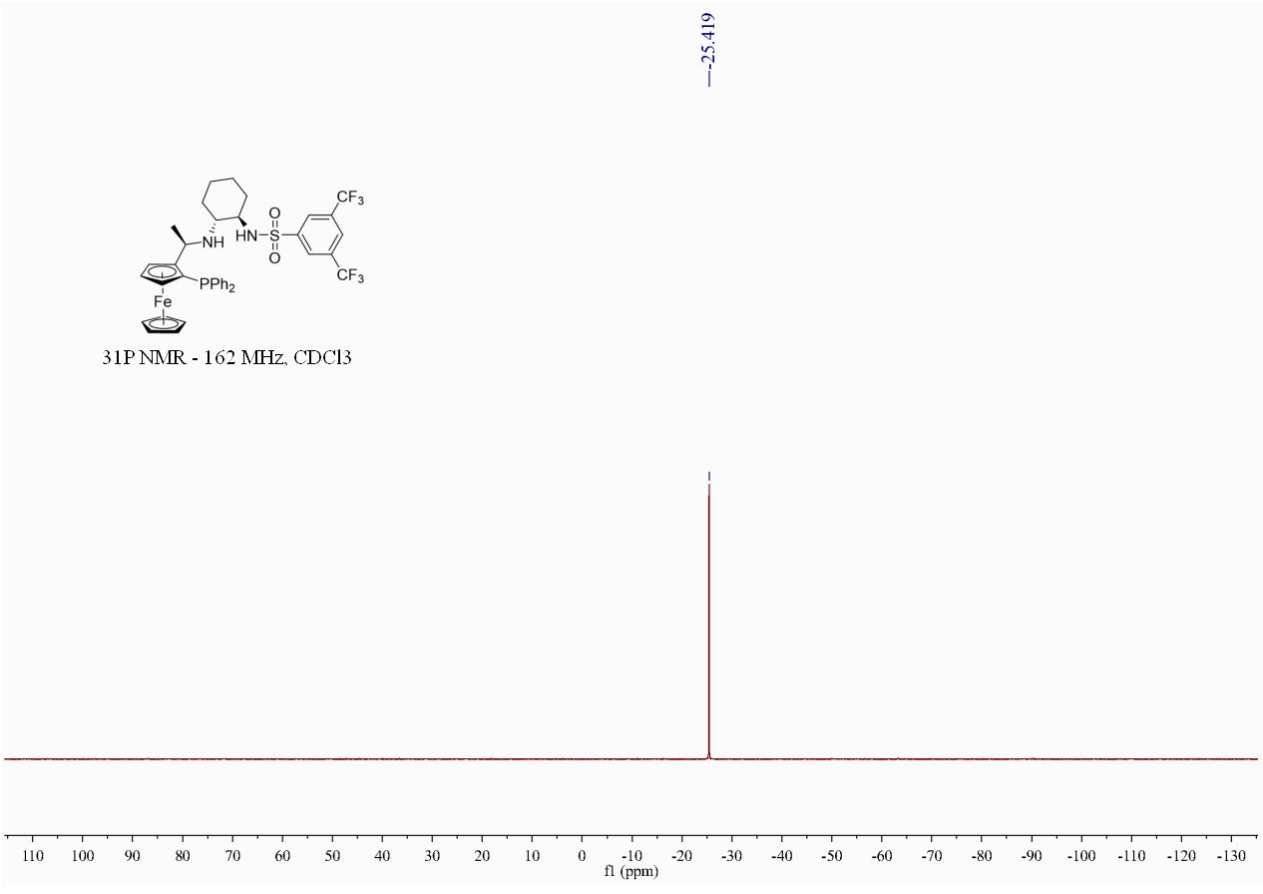
***N*-((1*R*,2*R*)-2-(((*R*)-1-(2-(diphenylphosphanyl)ferrocenyl)ethyl)amino)cyclohexyl)-3,5-bis(trifluoromethyl)benzenesulfonamide (L7)**





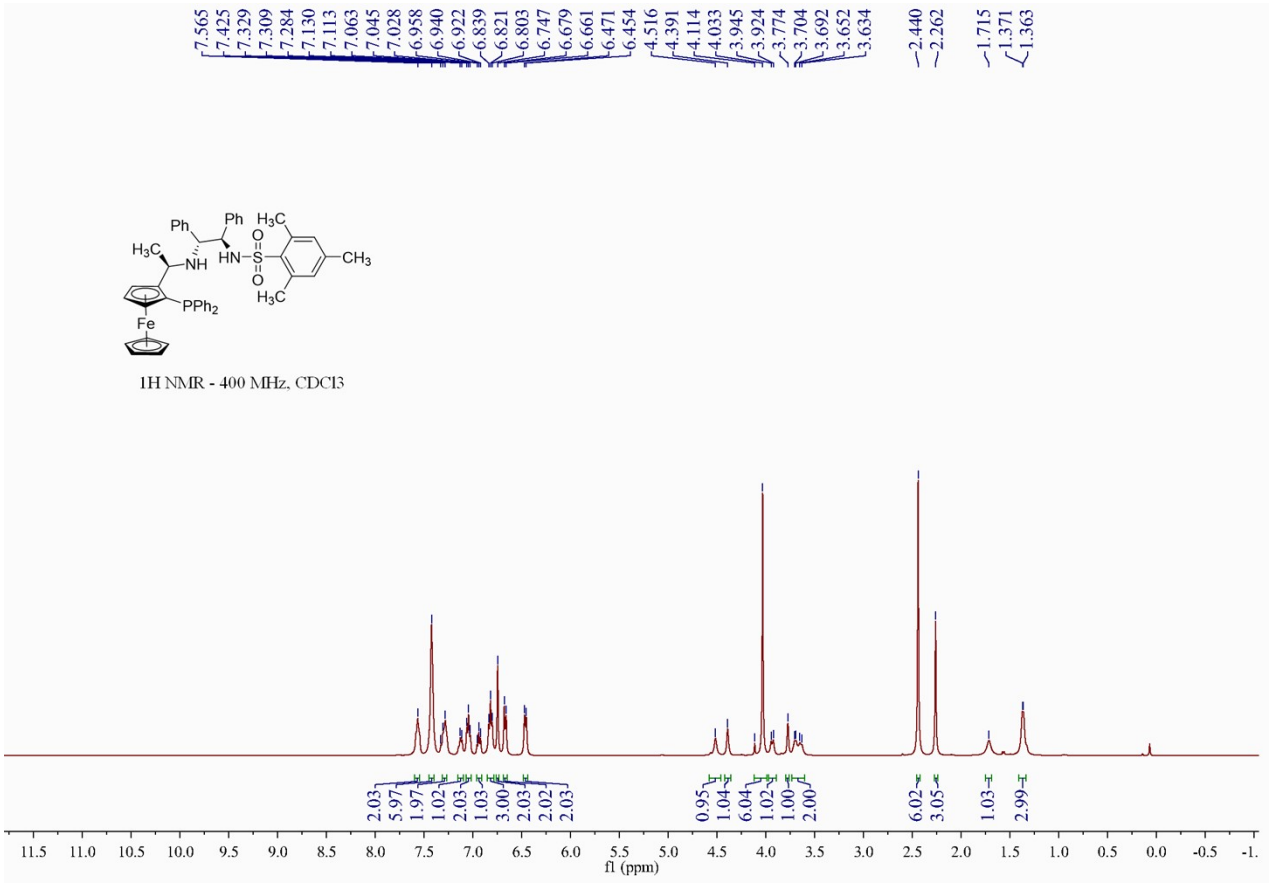


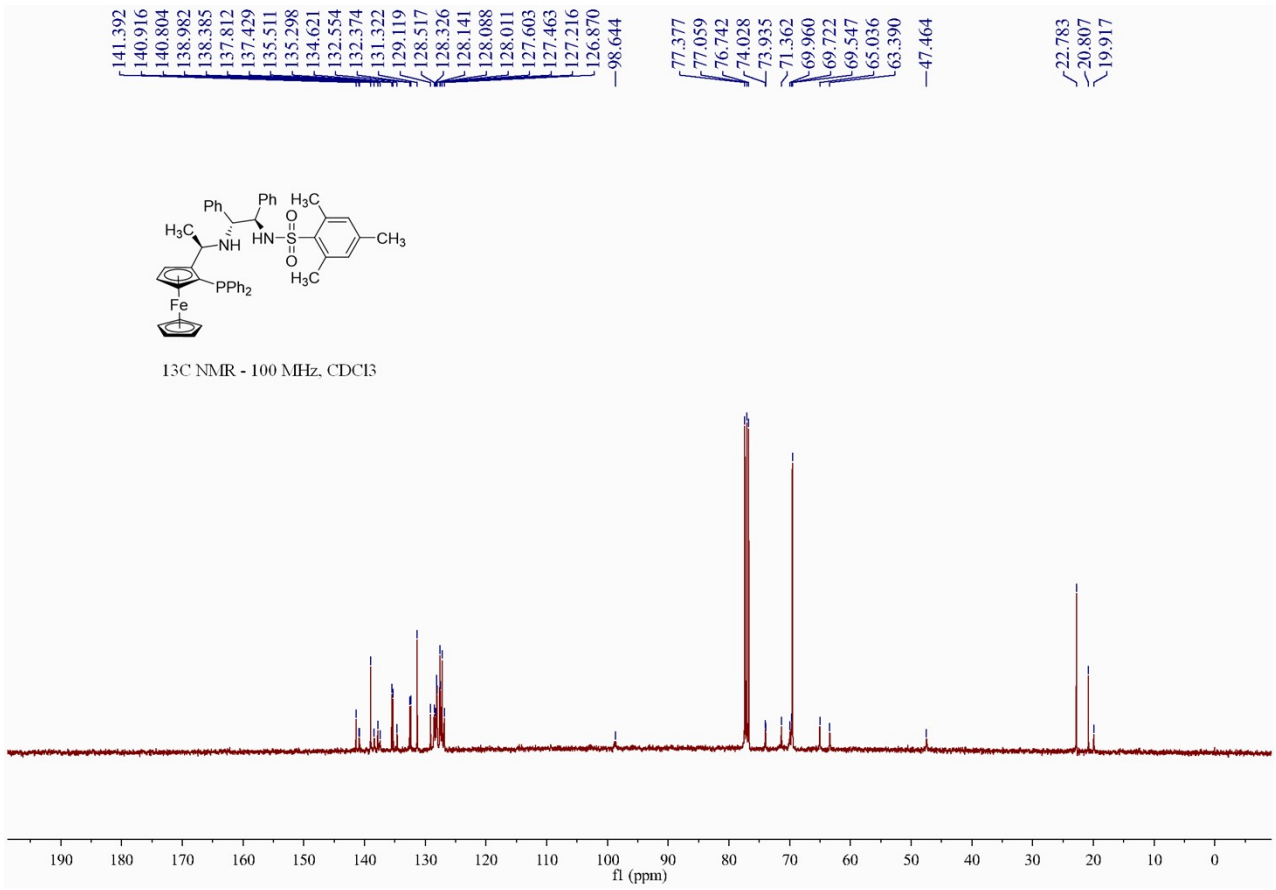
19F NMR - 376 MHz, CDCl3

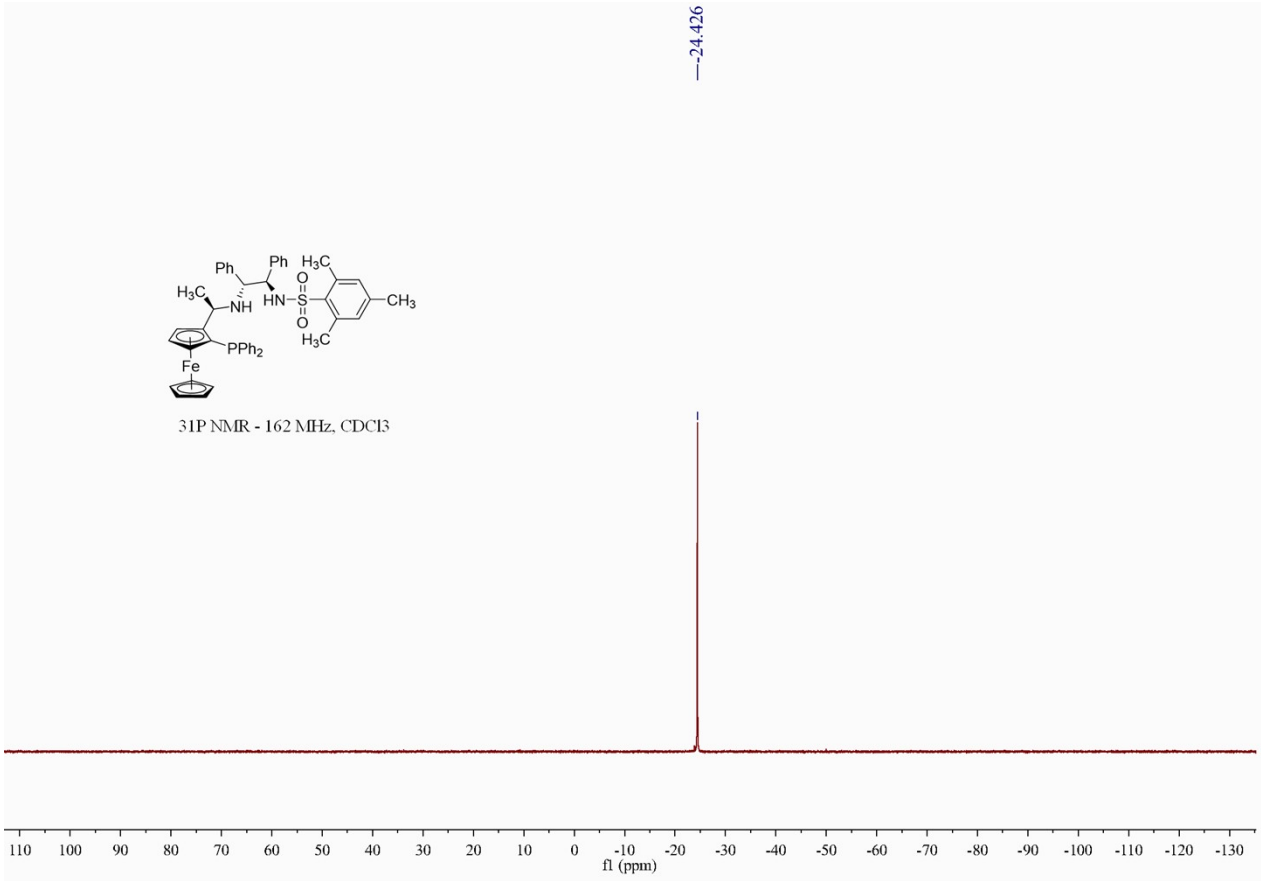


31P NMR - 162 MHz, CDCl3

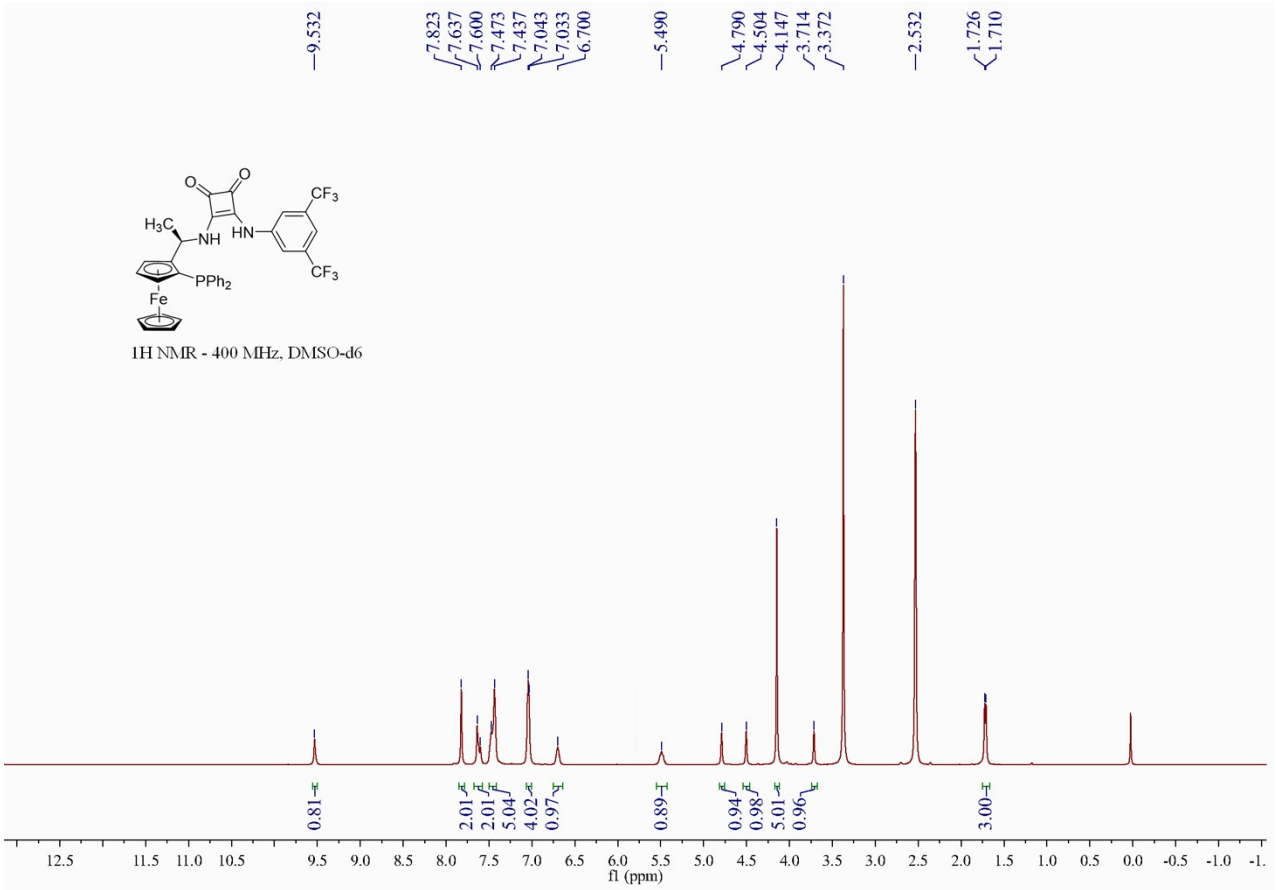
***N*-((1*R*,2*R*)-2-(((*R*)-1-(2-(bis(3,5-dimethylphenyl)phosphanyl)ferrocenyl)ethyl)amino)cyclohexyl)-2,4,6-trimethylbenzenesulfonamide (L8)**

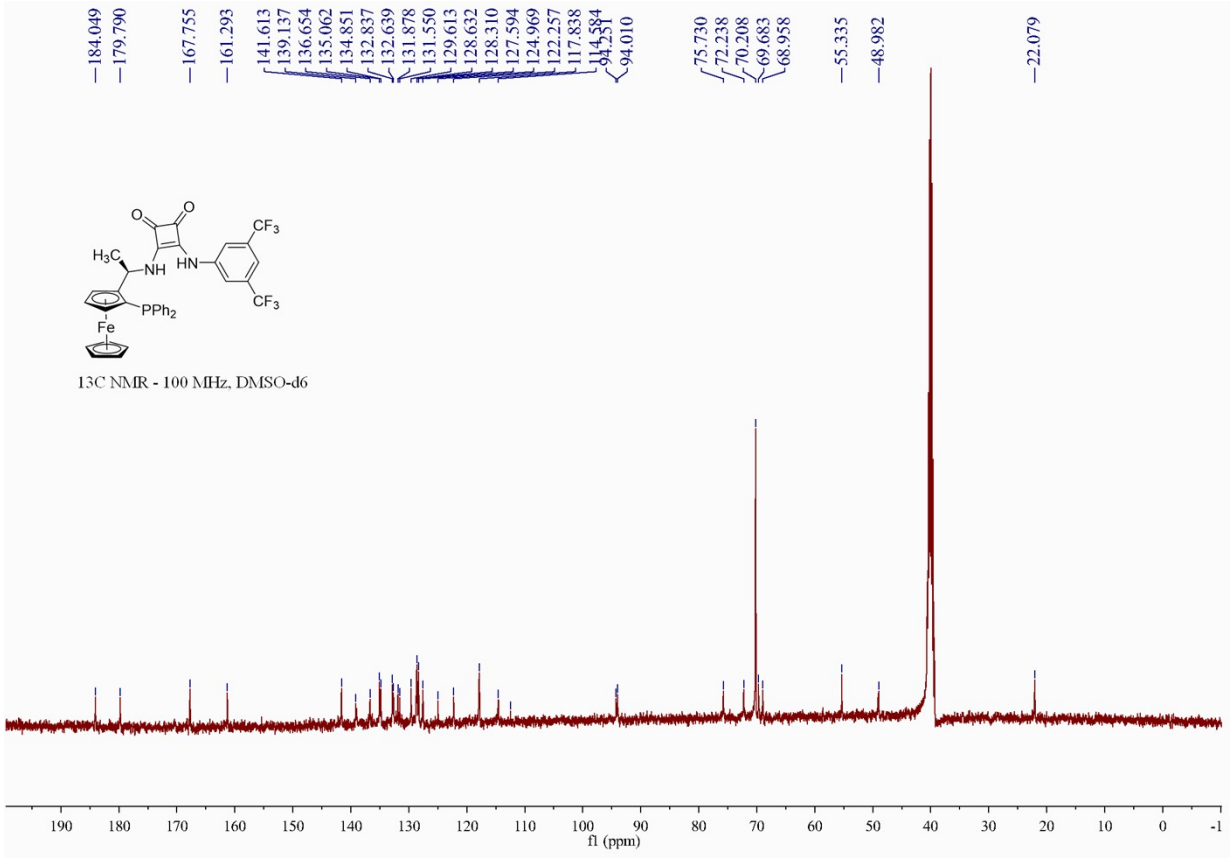


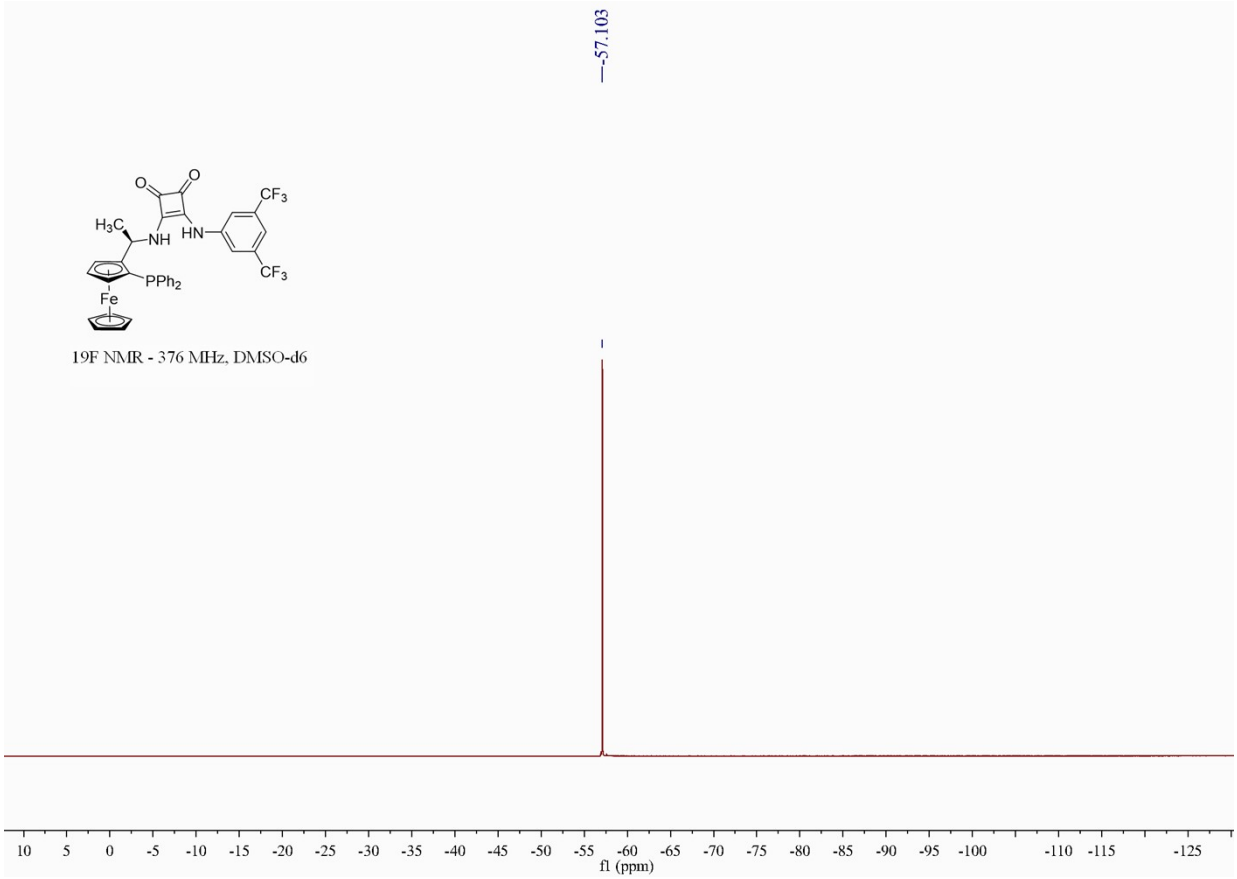


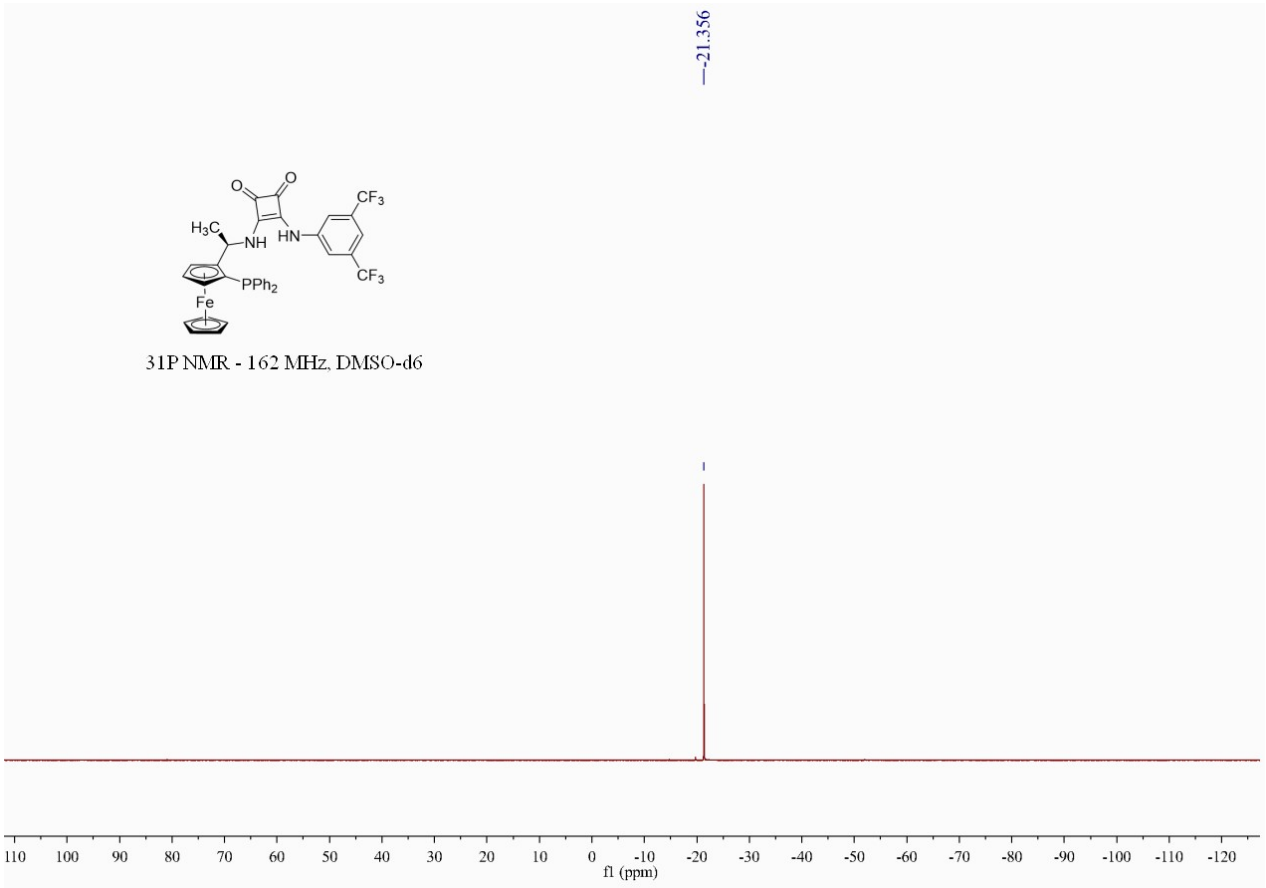


***N*-((1*R*,2*R*)-2-(((*R*)-1-(2-(dicyclohexylphosphanyl)ferrocenyl)ethyl)amino)cyclohexyl)-2,4,6-trimethylbenzenesulfonamide (L9)**

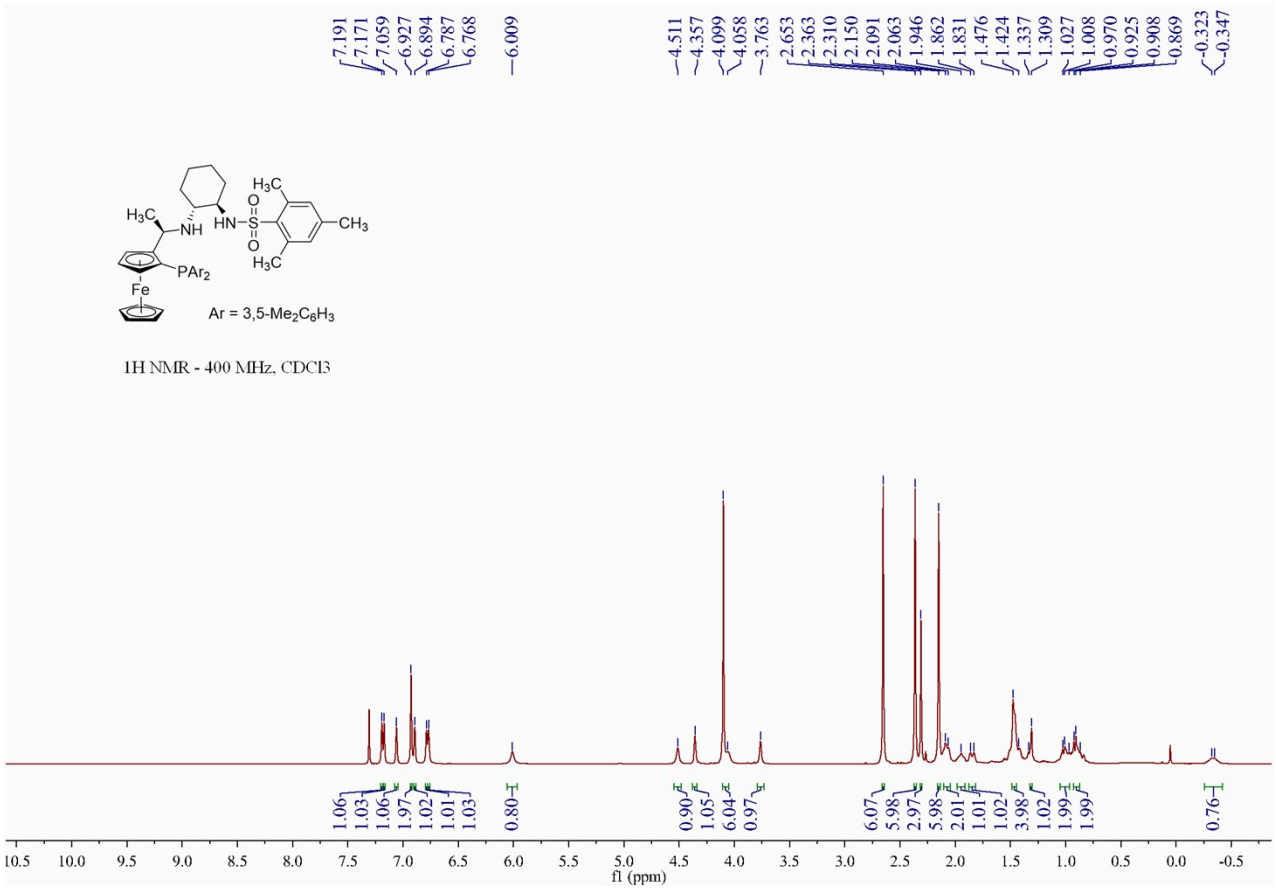


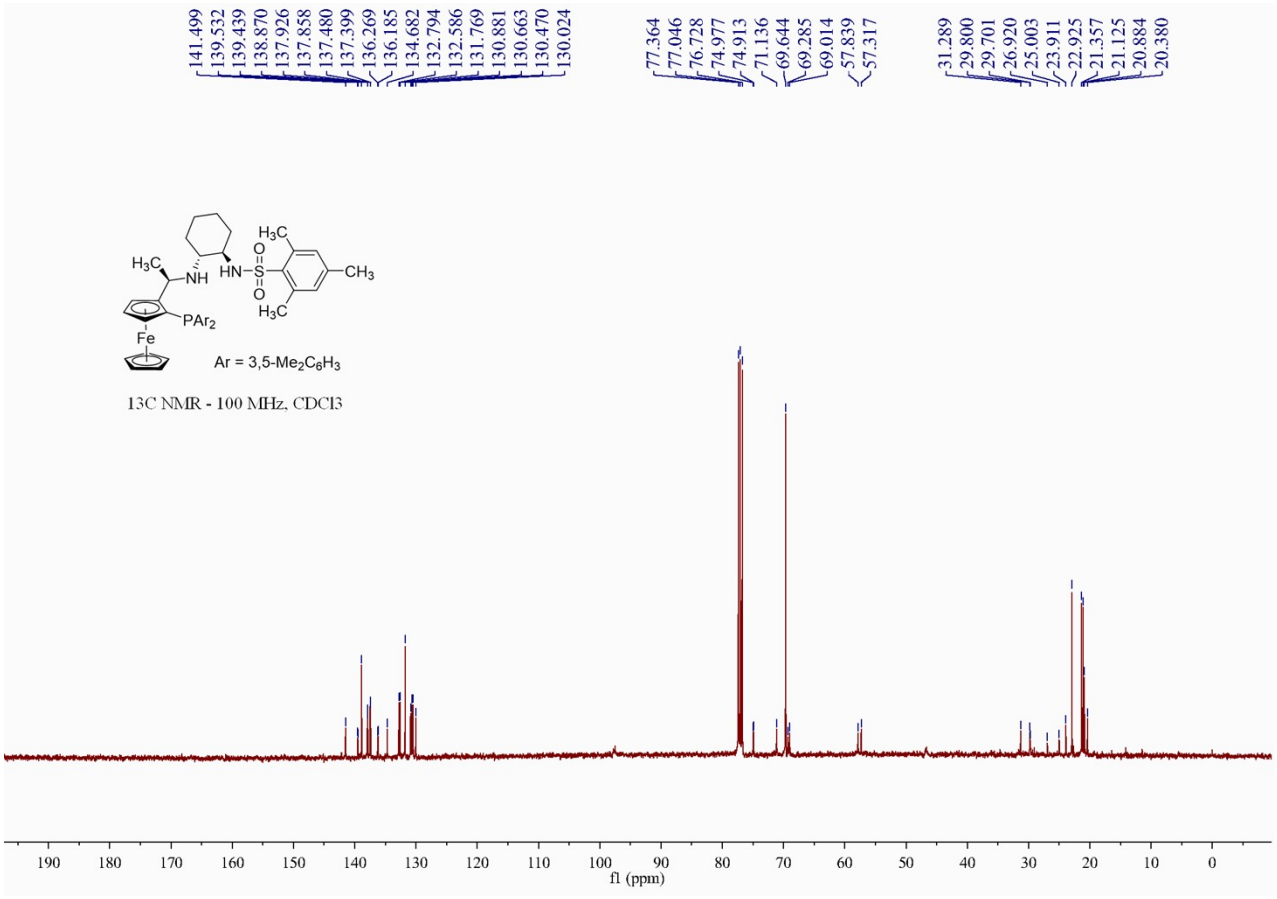

184.049
179.790
167.755
161.293
141.613
139.137
136.654
135.062
134.851
132.837
132.639
131.878
131.550
129.613
128.632
128.310
127.594
124.969
122.257
117.838
94.251
94.010
75.730
72.238
70.208
69.683
68.958
55.335
48.982
22.079
O
O
CF3
H3C
NH
HN
CF3
PPh2
Fe
13C NMR - 100 MHz, DMSO-d6
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

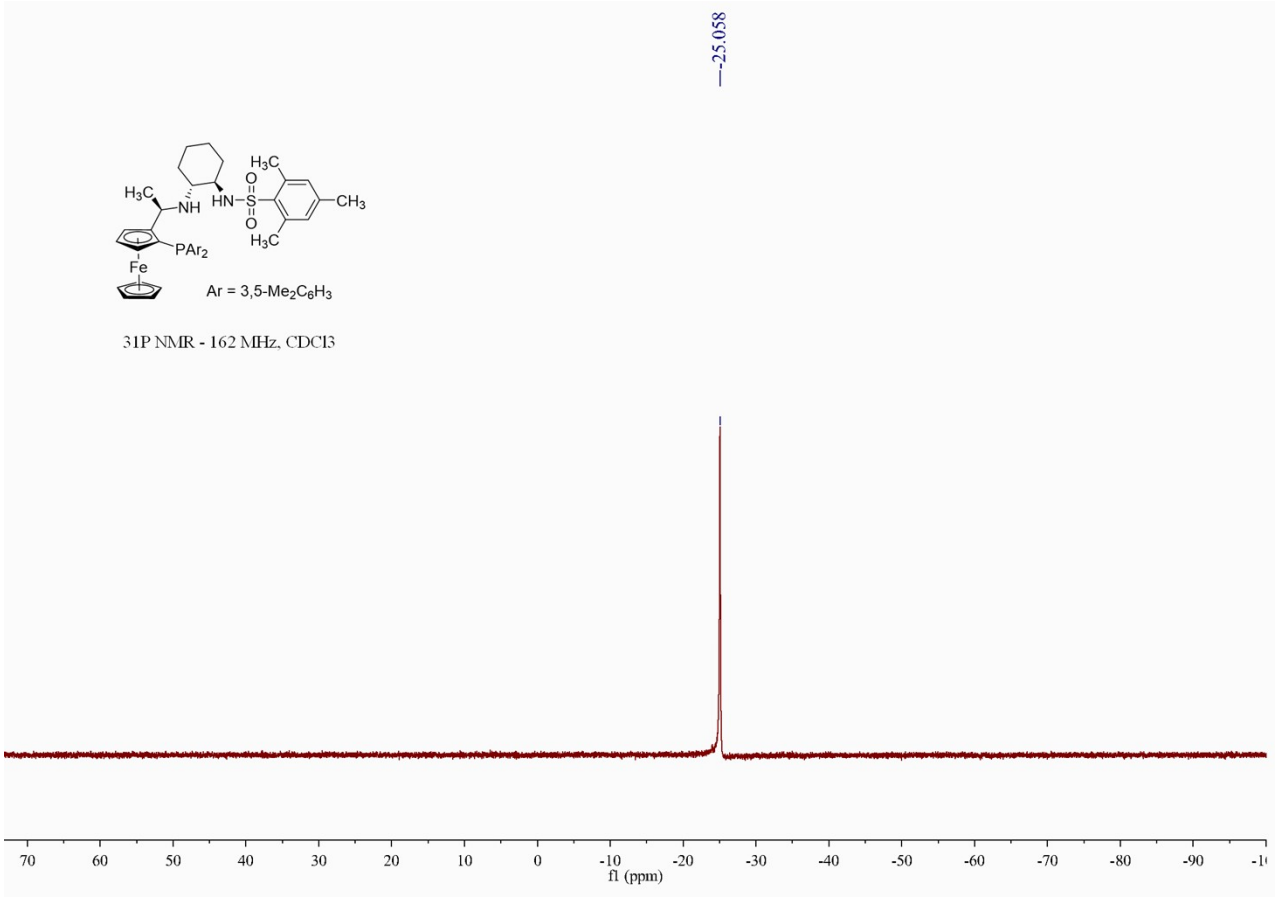

-57.103
O
O
CF3
H3C
NH
HN
CF3
PPh2
Fe
19F NMR - 376 MHz, DMSO-d6
10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -115 -125
f1 (ppm)



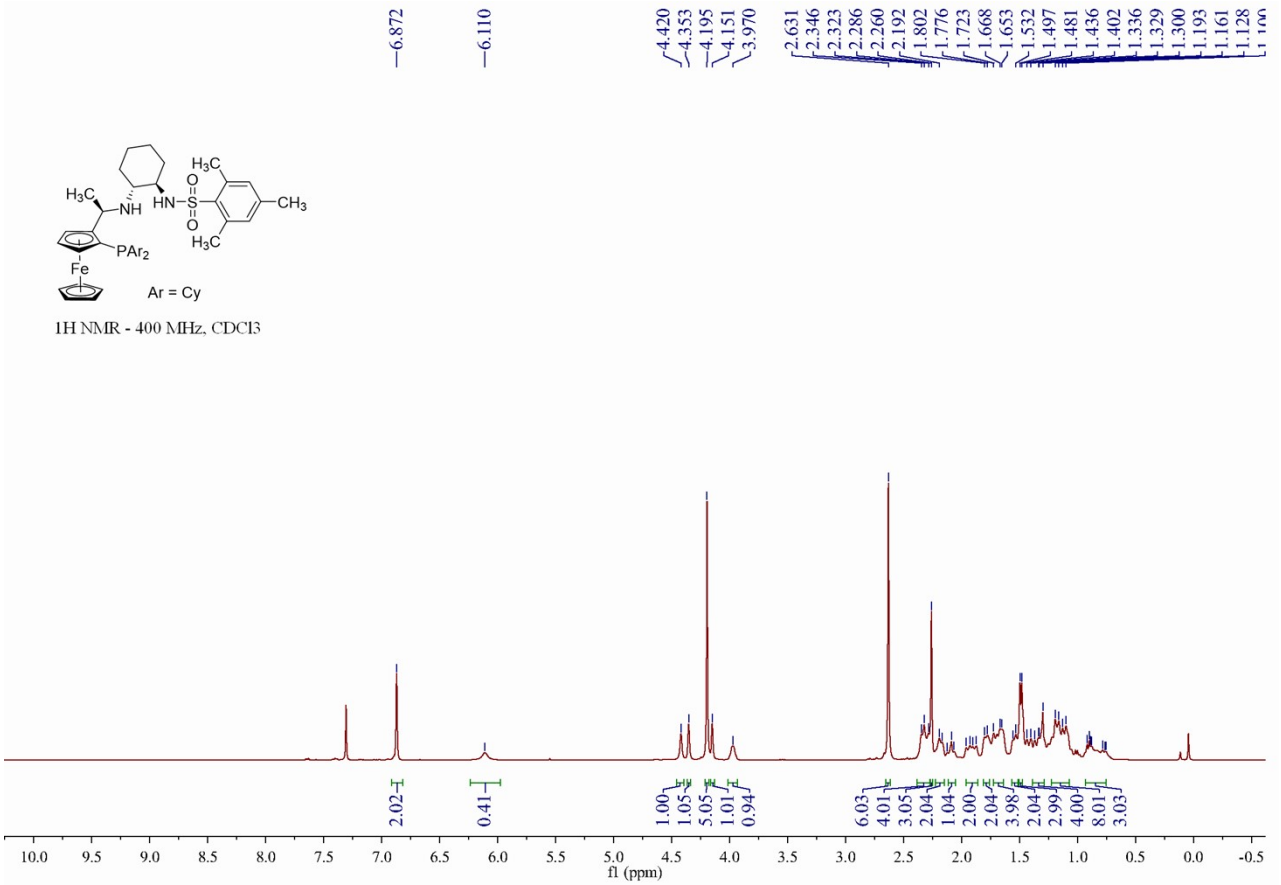
***N*-((1*R*,2*R*)-2-(((*R*)-1-(2-(diphenylphosphanyl)ferrocenyl)ethyl)amino)-1,2-diphenylethyl)-2,4,6-trimethylbenzenesulfonamide (L10)**

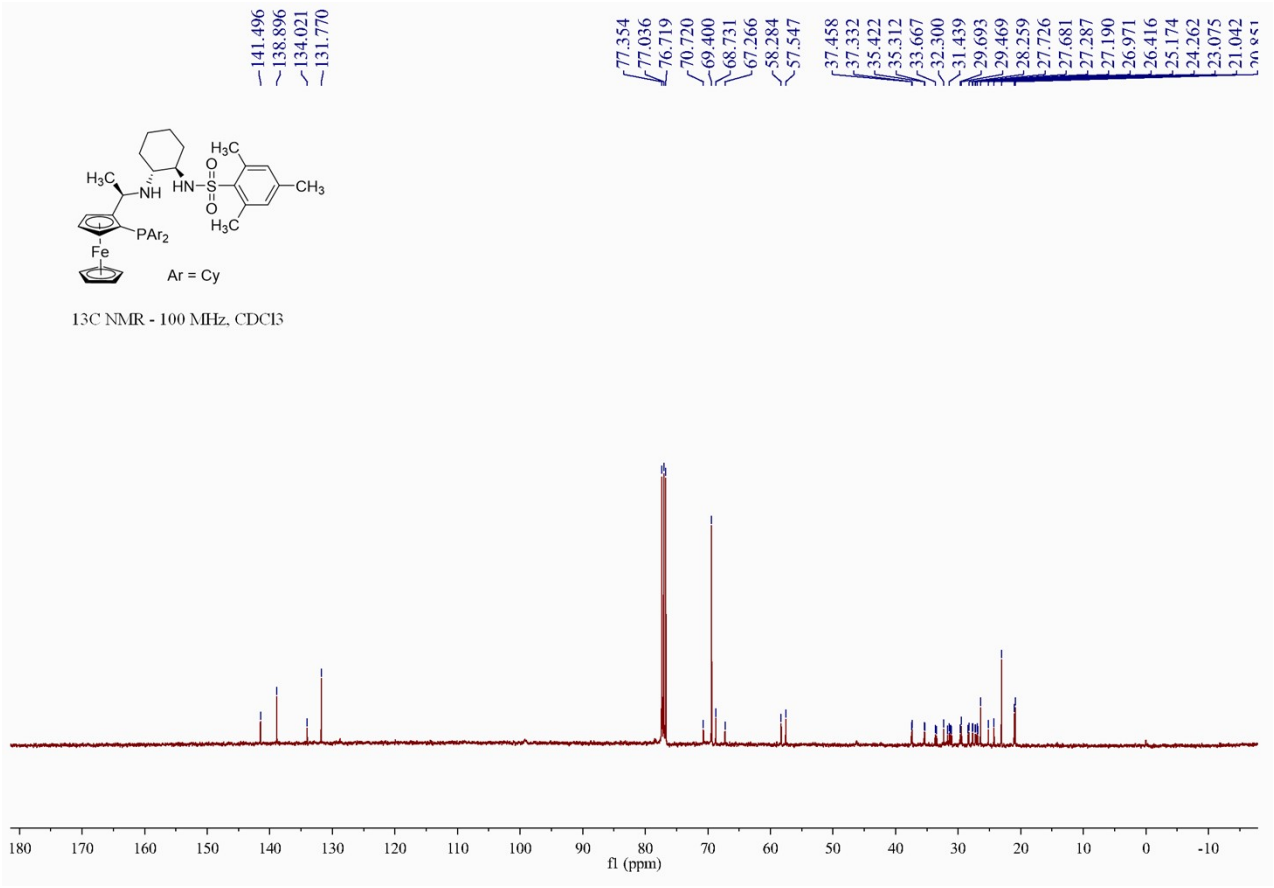


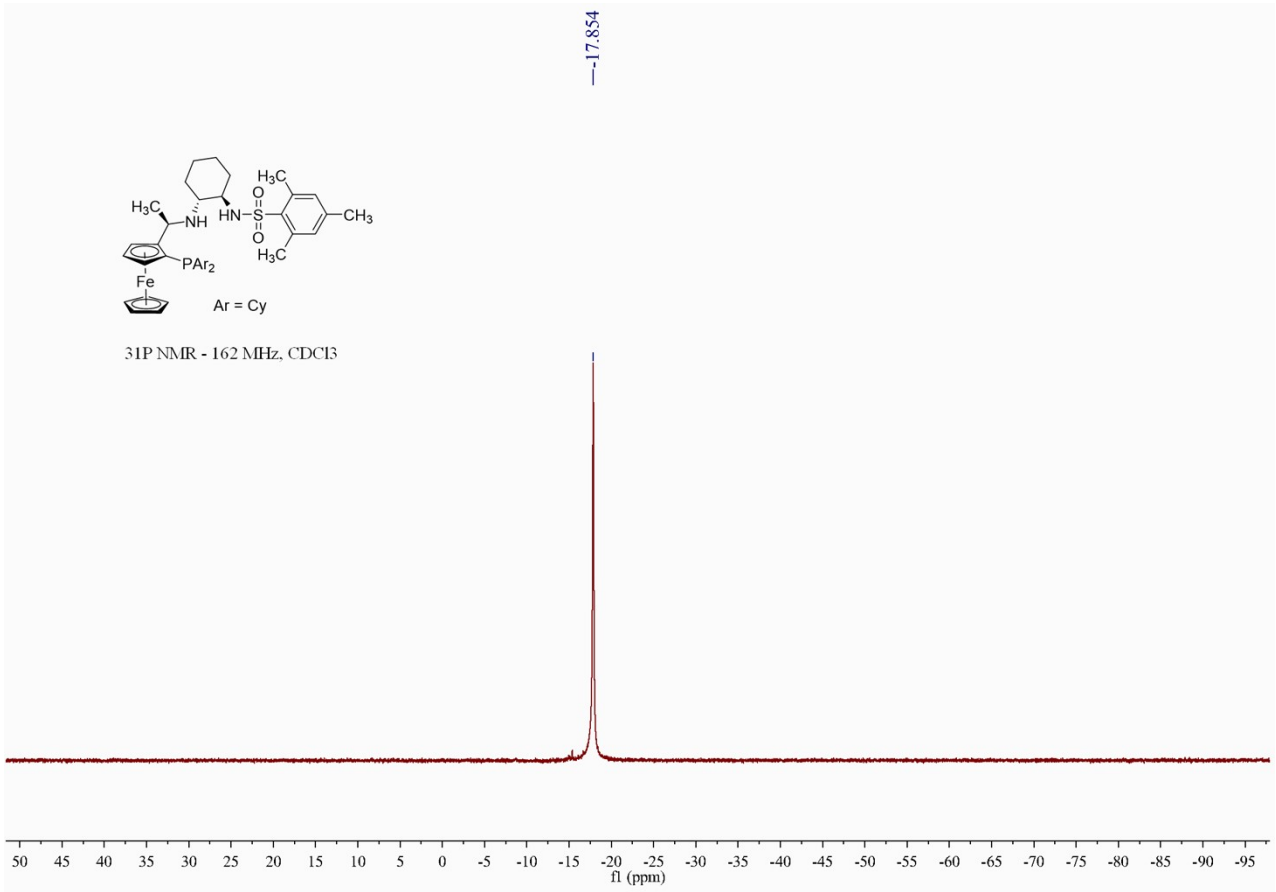

141.499
139.532
139.439
138.870
137.926
137.858
137.480
137.399
136.269
136.185
134.682
132.794
132.586
131.769
130.881
130.663
130.470
130.024
77.364
77.046
76.728
74.977
74.913
71.136
69.644
69.285
69.014
57.839
57.317
31.289
29.800
29.701
26.920
25.003
23.911
22.925
21.357
21.125
20.884
20.380
Ar = 3,5-Me2C6H3
13C NMR - 100 MHz, CDCl3
fl (ppm)


-25.058
Ar = 3,5-Me2C6H3
31P NMR - 162 MHz, CDCl3
fl (ppm)

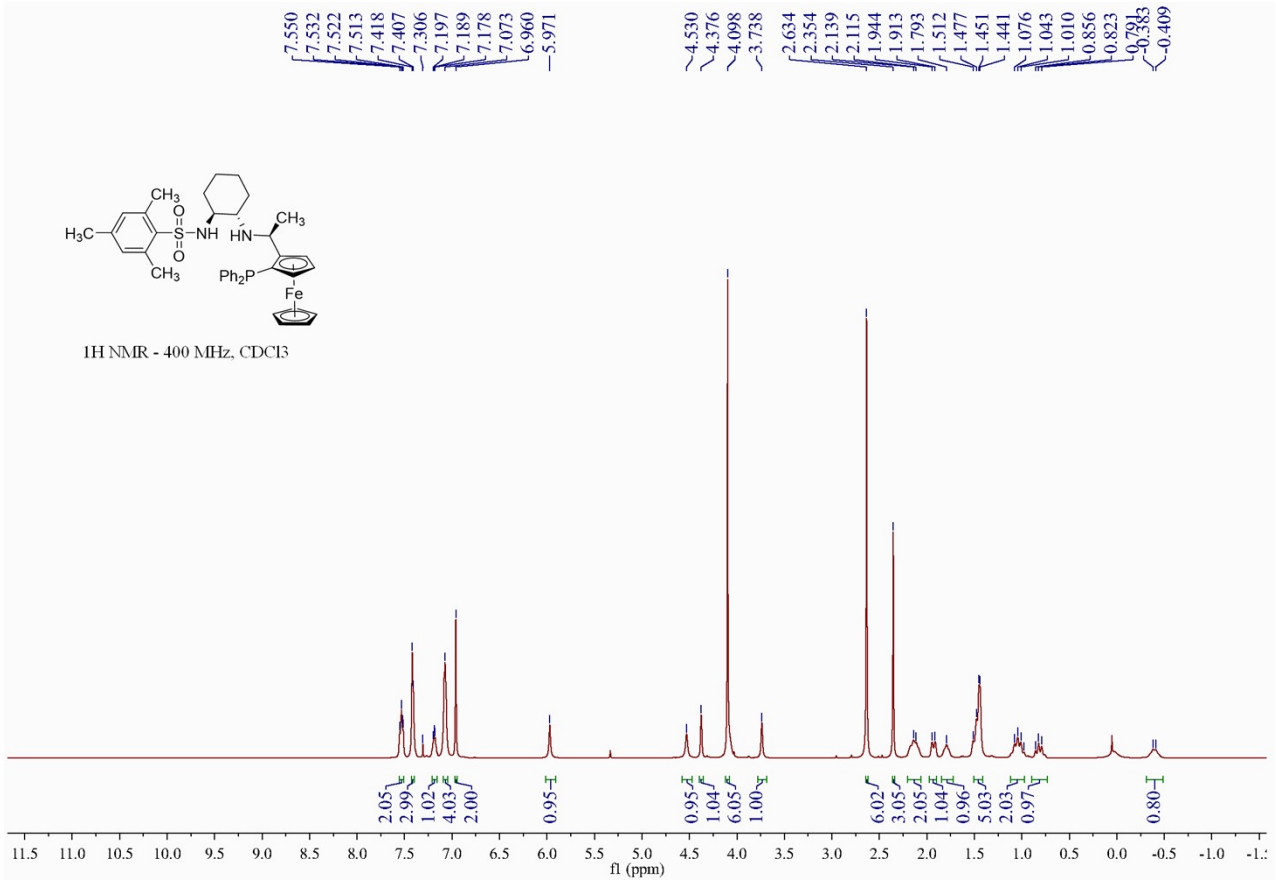
(*R*)-3-((3,5-bis(trifluoromethyl)phenyl)amino)-4-((1-(2-(diphenylphosphanyl)ferrocenyl)ethyl)amino)cyclobut-3-ene-1,2-dione (L11)

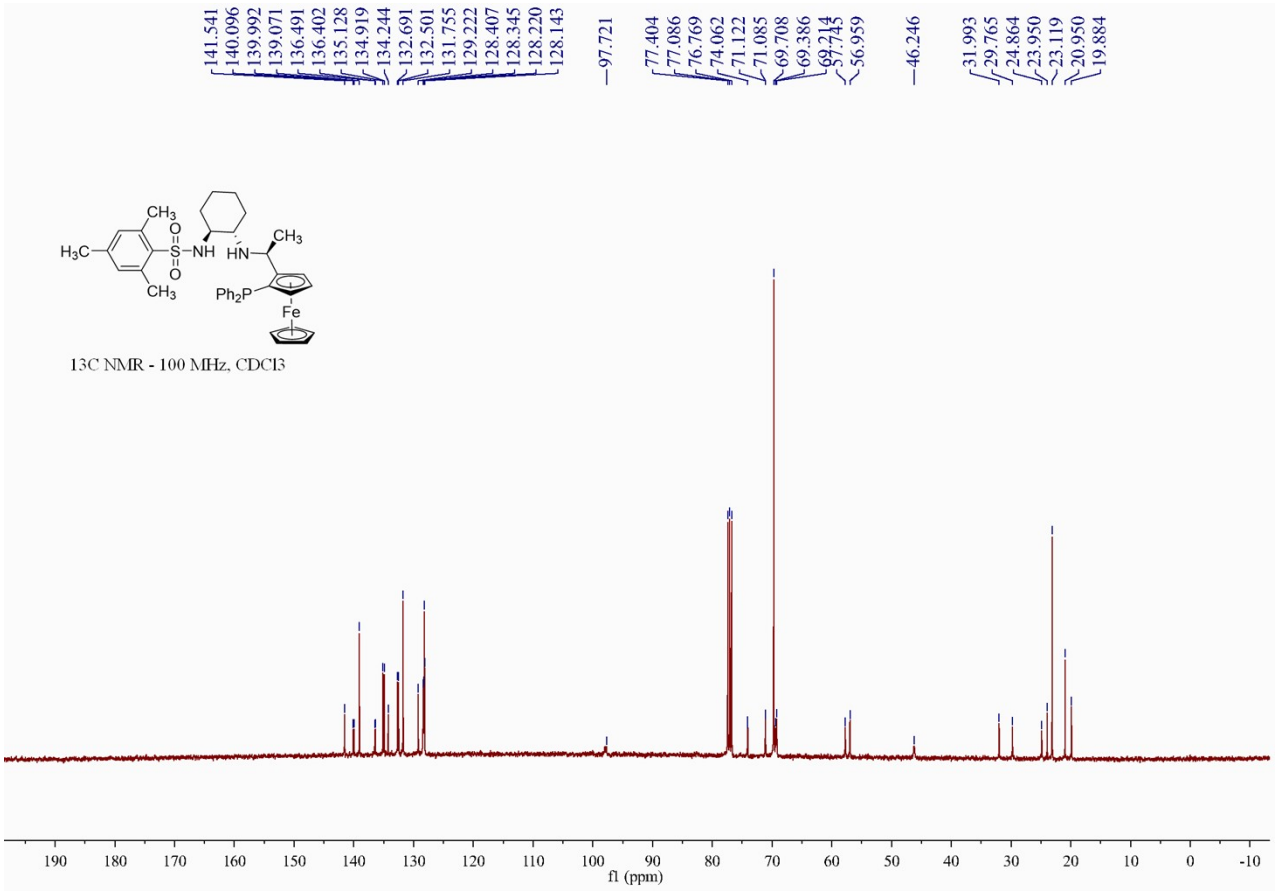


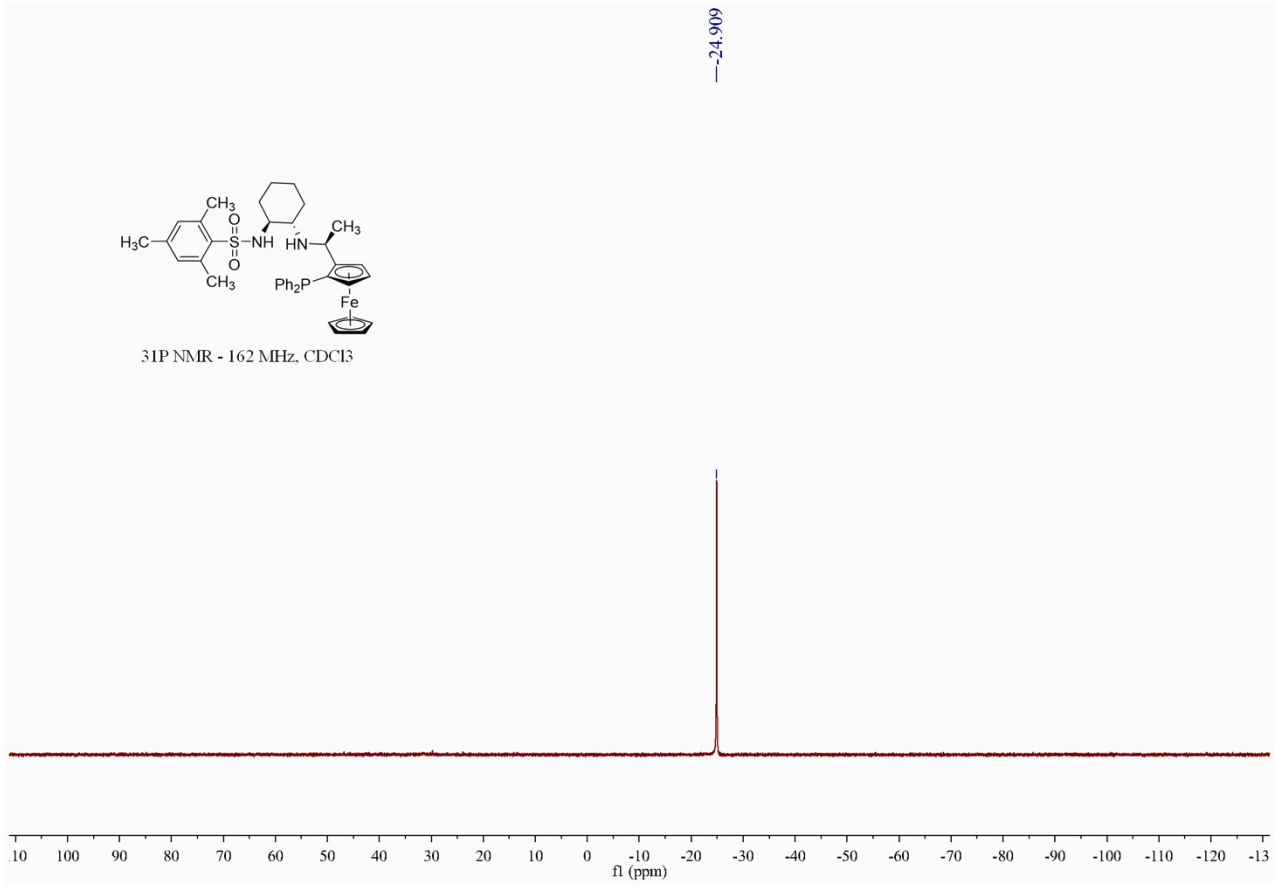




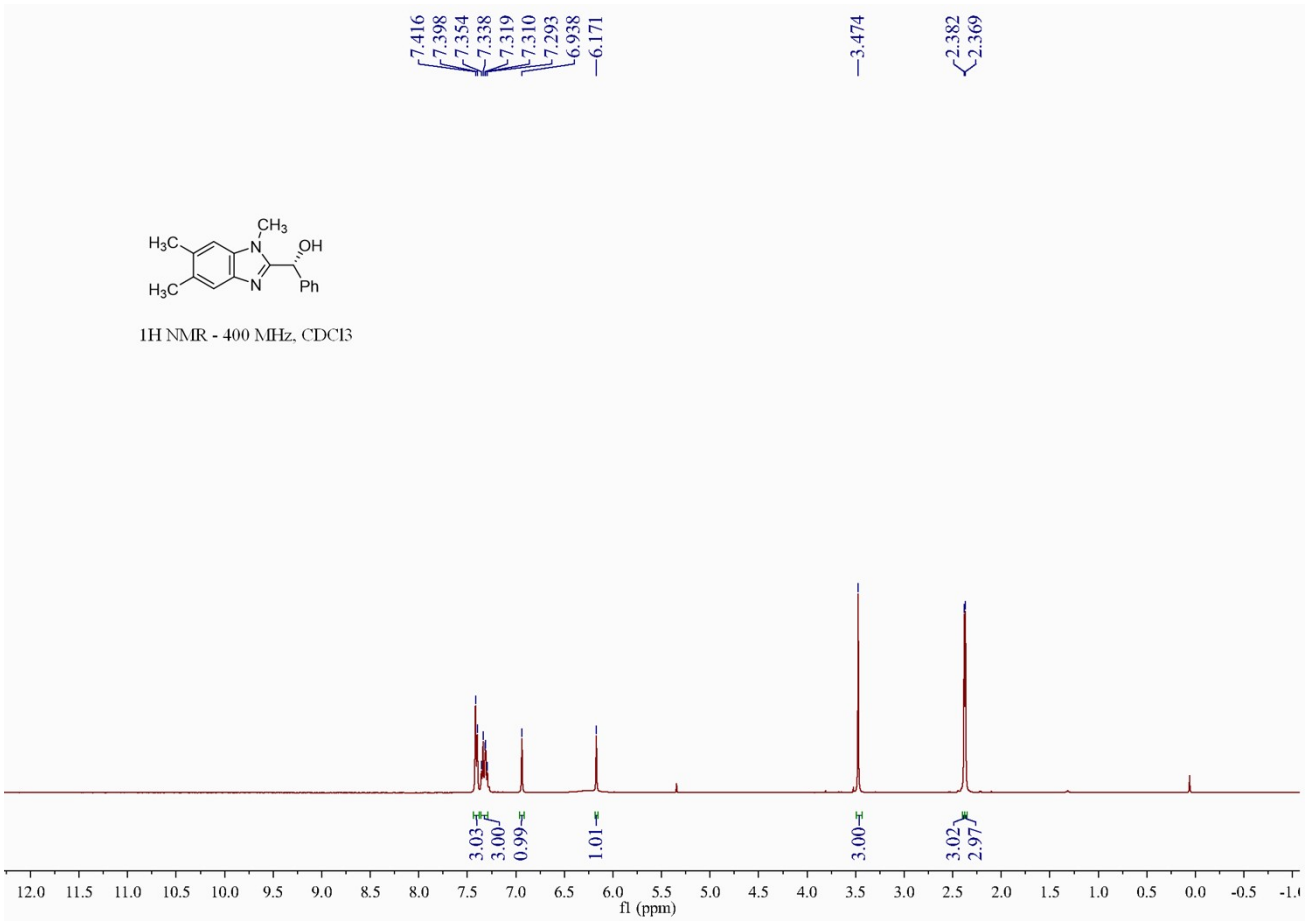
_N_-((1_S_,2_S_)-2-(((_S_)-1-(2-(diphenylphosphanyl)ferrocenyl)ethyl)amino)cyclohexyl)-2,4,6-trimethylbenzenesulfonamide (L12)

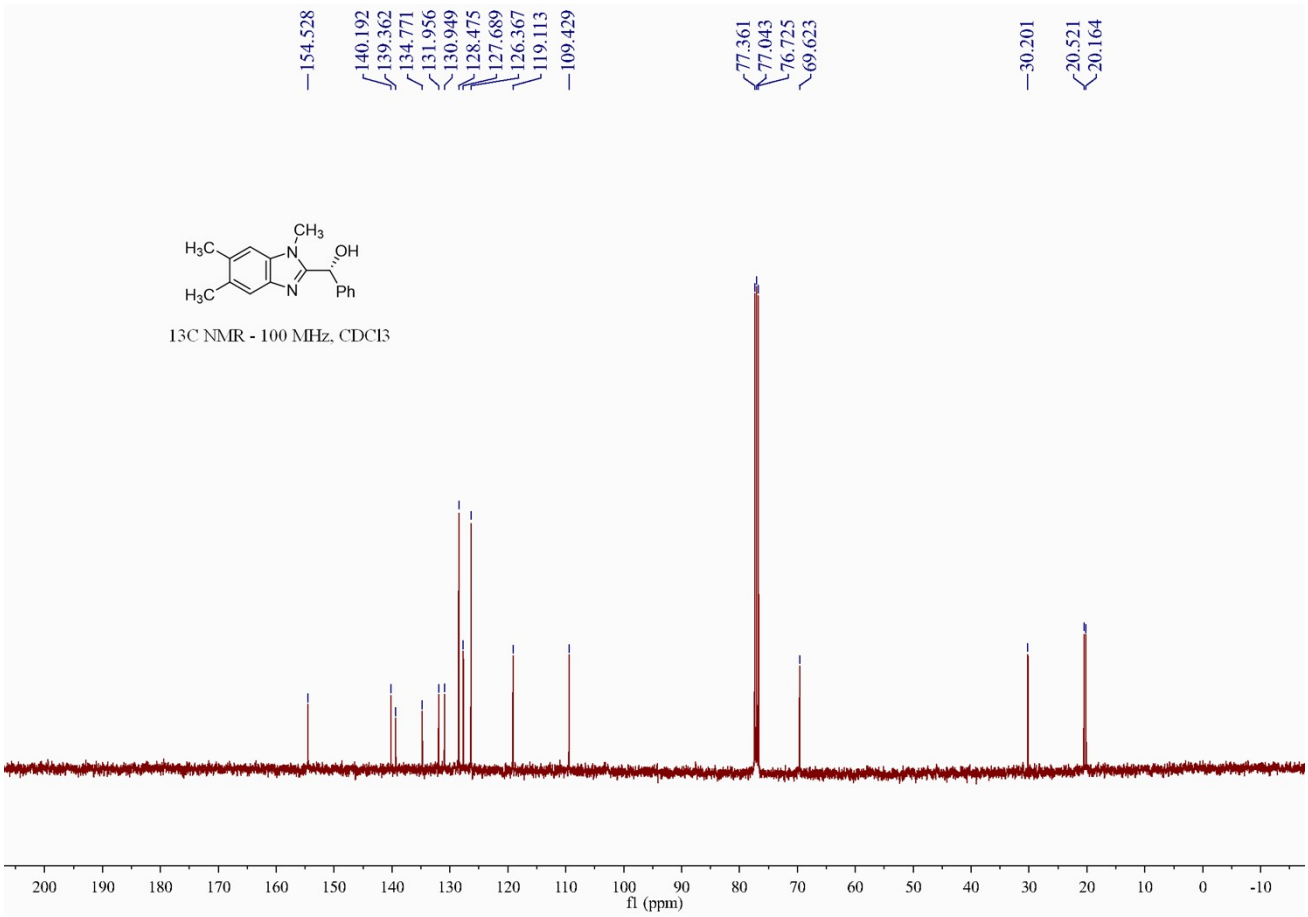



141.541
140.096
139.992
139.071
136.491
136.402
135.128
134.919
134.244
132.691
132.501
131.755
129.222
128.407
128.345
128.220
128.143
97.721
77.404
77.086
76.769
74.062
71.122
71.085
69.708
69.386
69.214
57.745
56.959
46.246
31.993
29.765
24.864
23.950
23.119
20.950
19.884
13C NMR - 100 MHz, CDCl3
f1 (ppm)

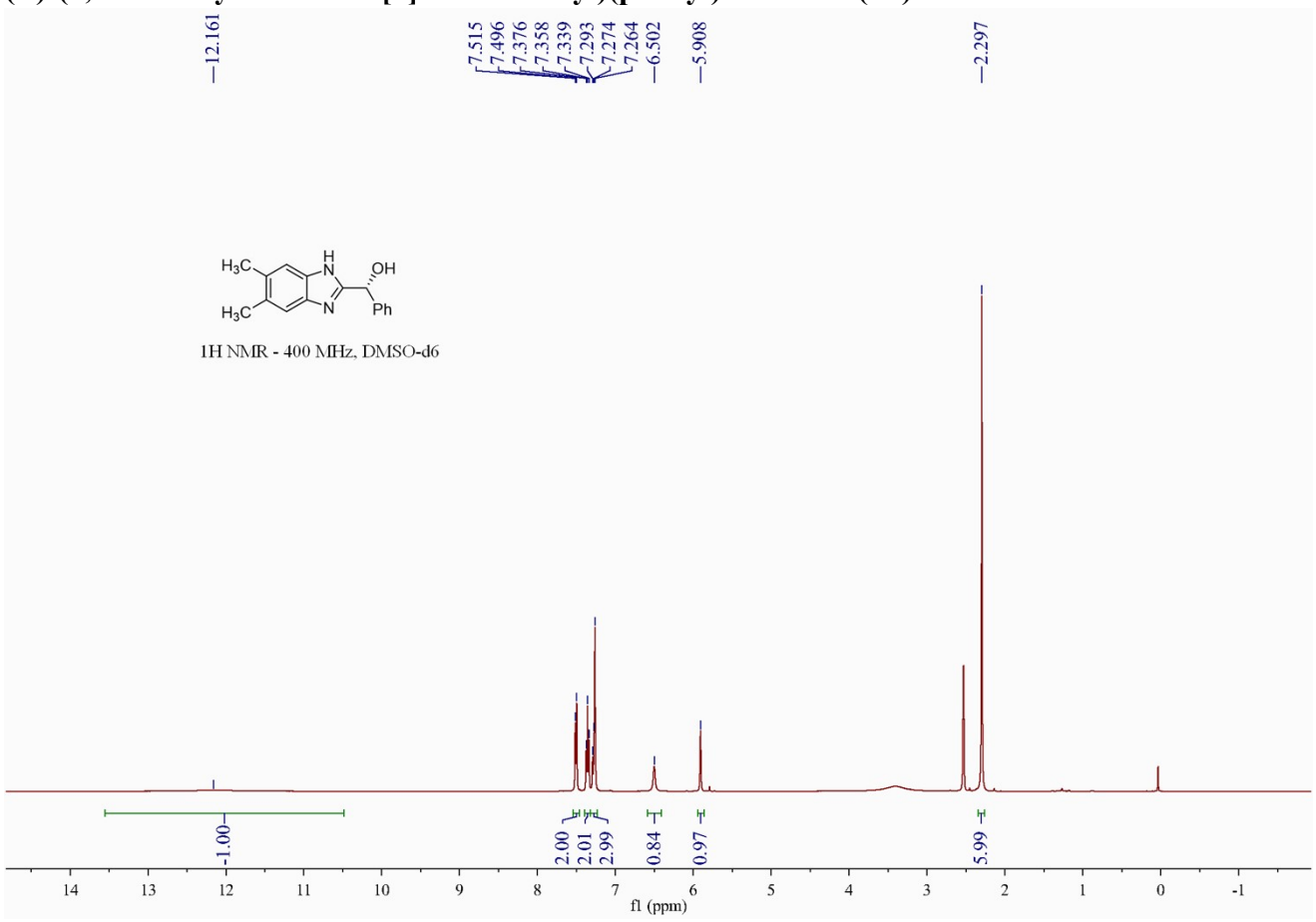

-24.909
31P NMR - 162 MHz, CDCl3
f1 (ppm)

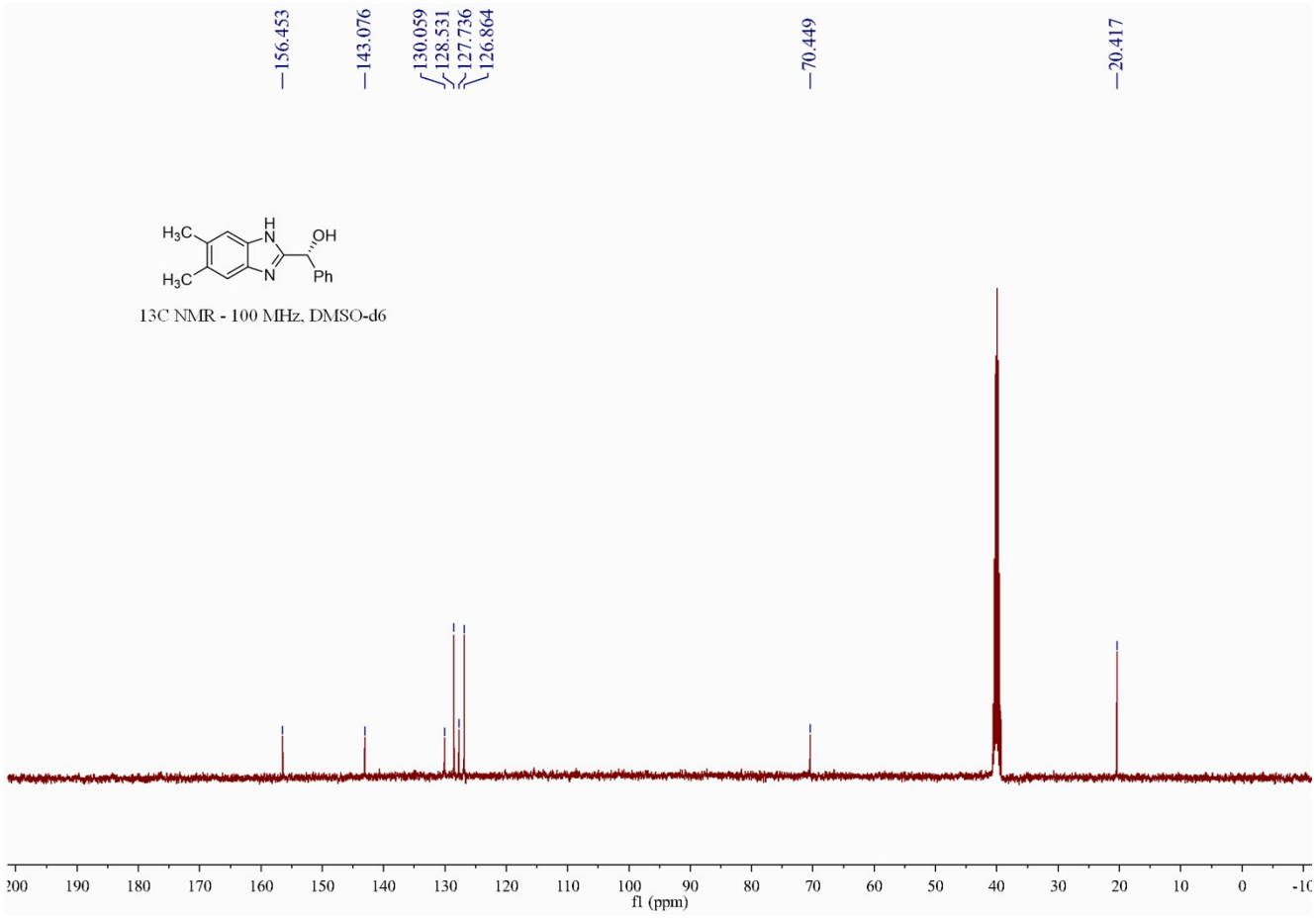
(*R*)-(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)(phenyl)methanol (2a)



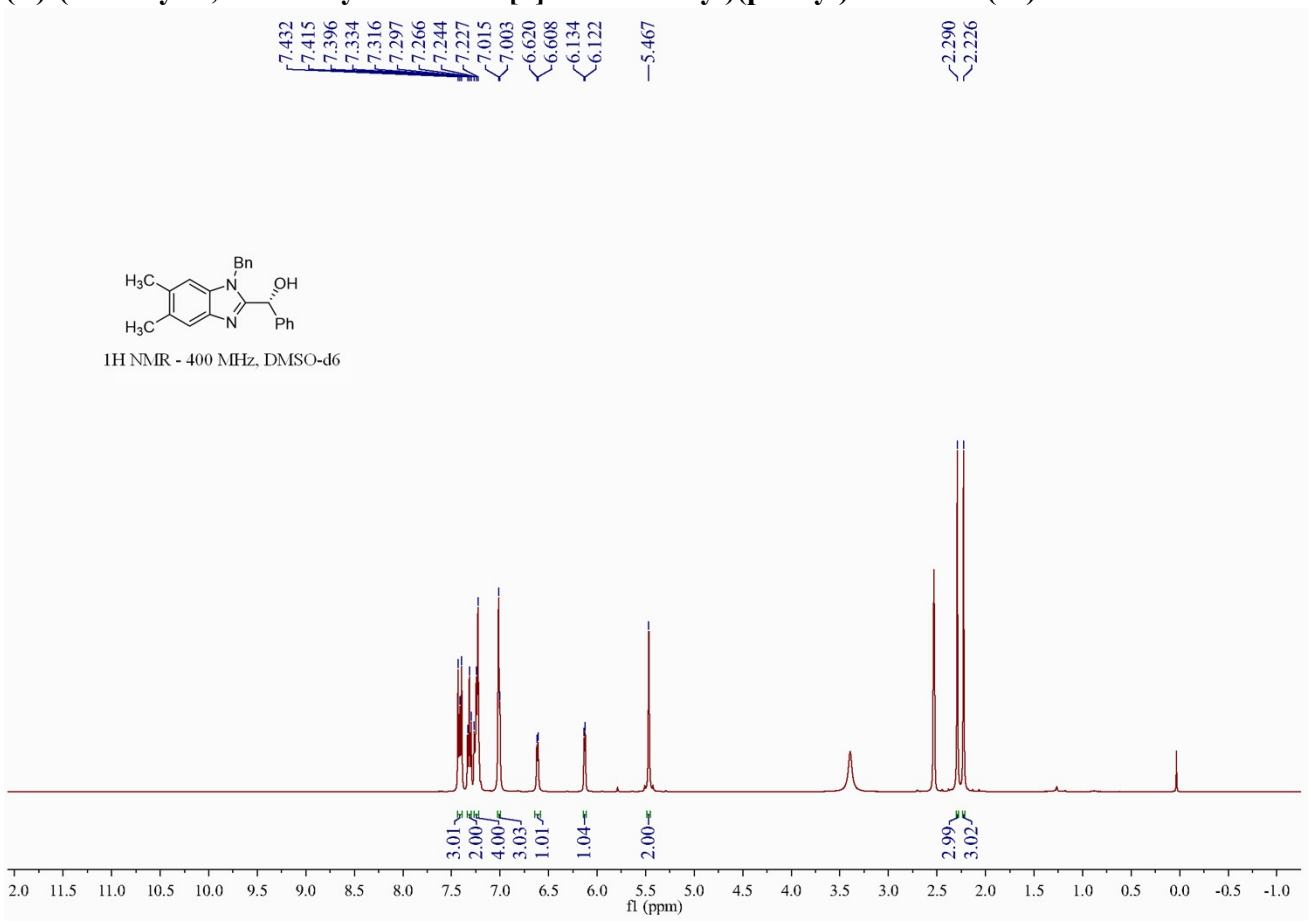


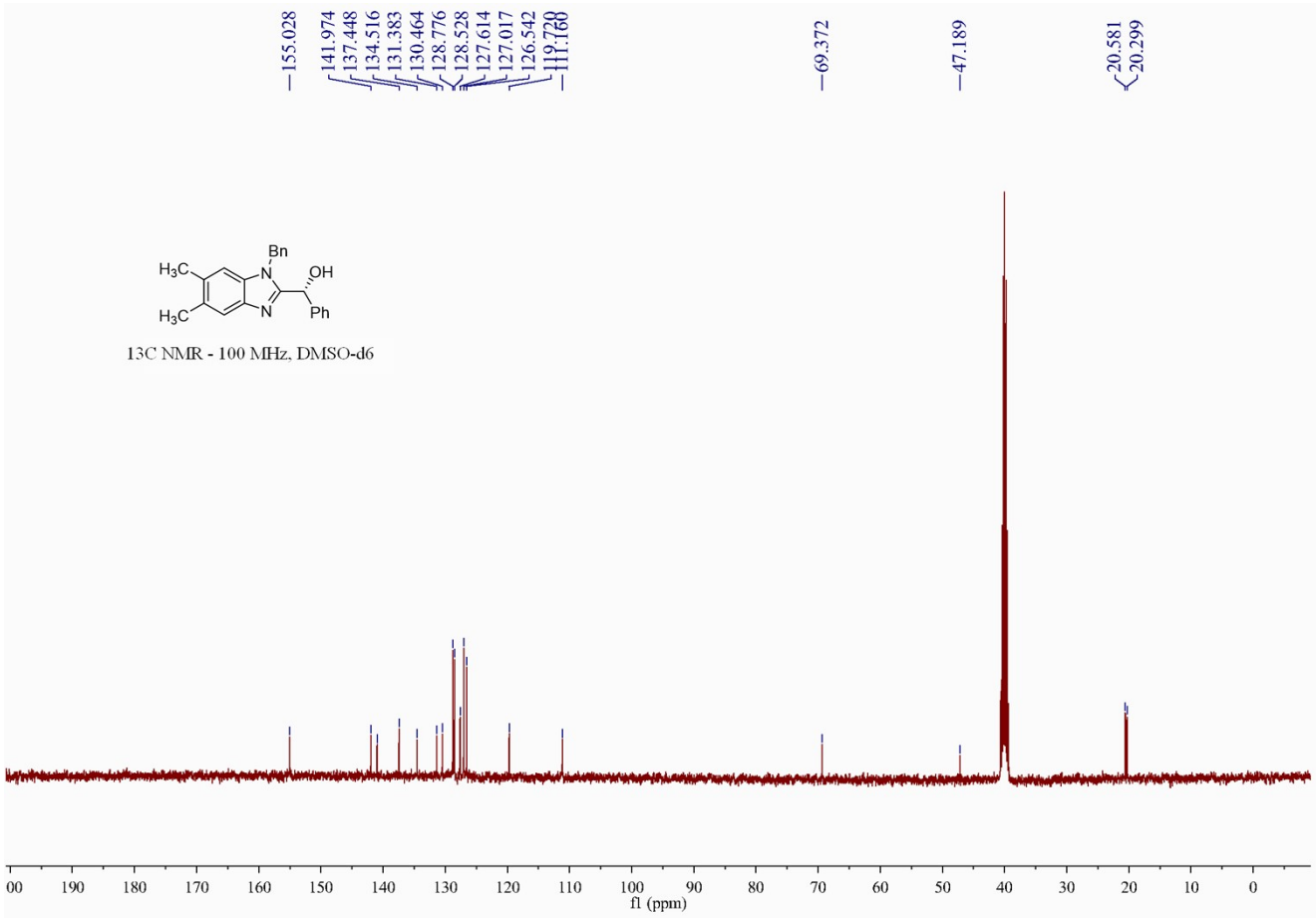
(*R*)-(5,6-dimethyl-1*H*-benzo[*d*]imidazol-2-yl)(phenyl)methanol (2b)



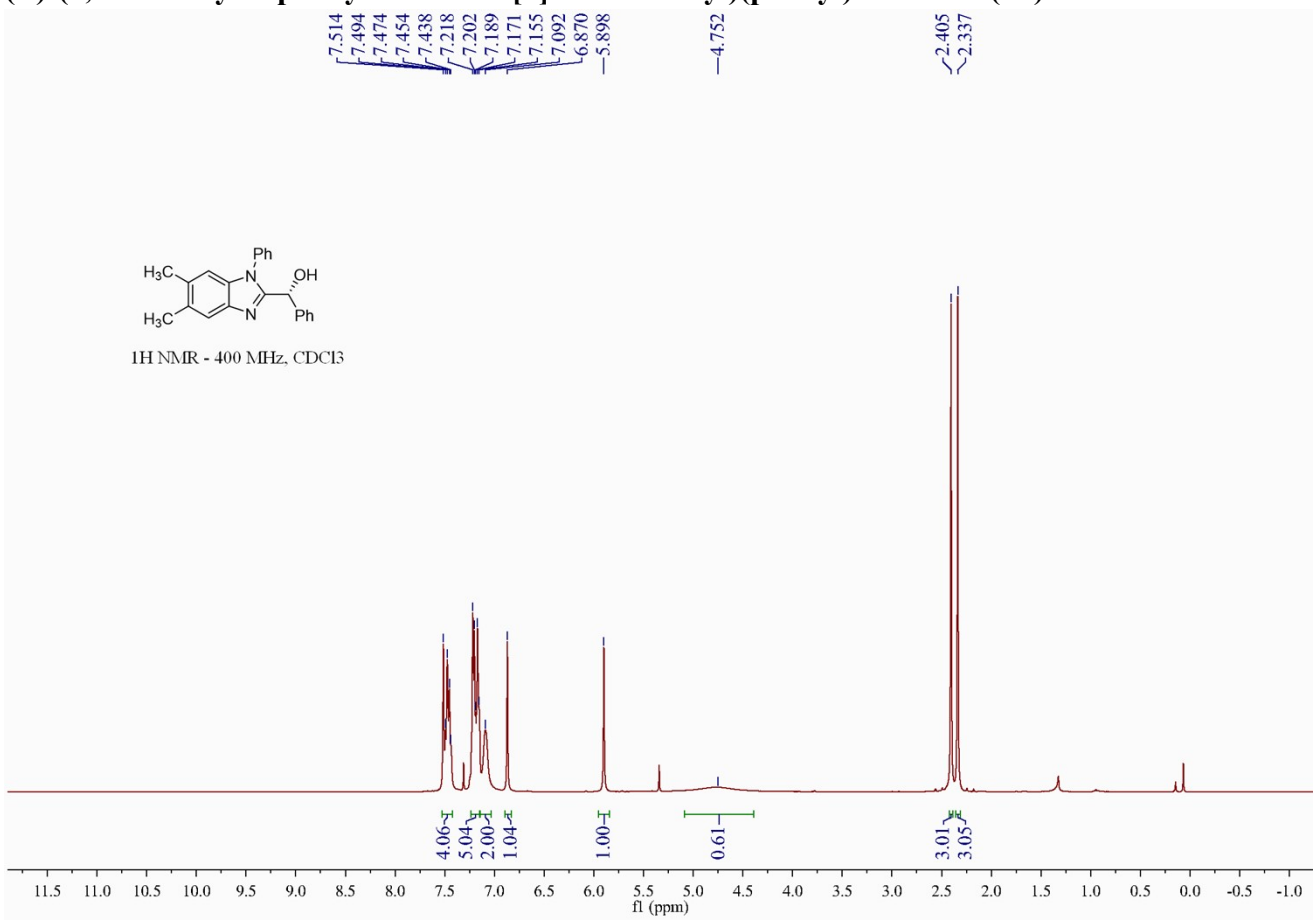


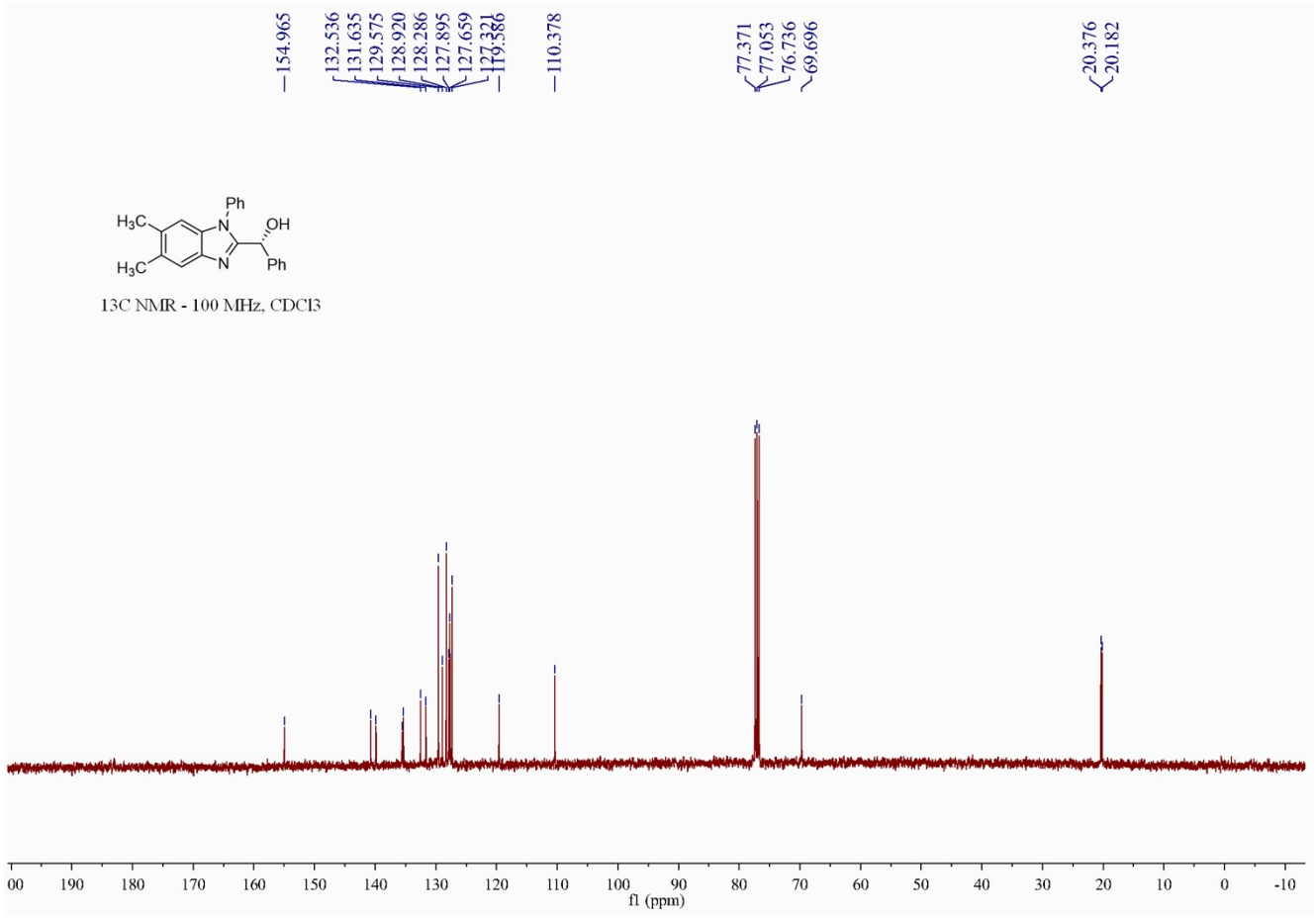
(*R*)-(1-benzyl-5,6-dimethyl-1*H*-benzo[*d*]imidazol-2-yl)(phenyl)methanol (2c)



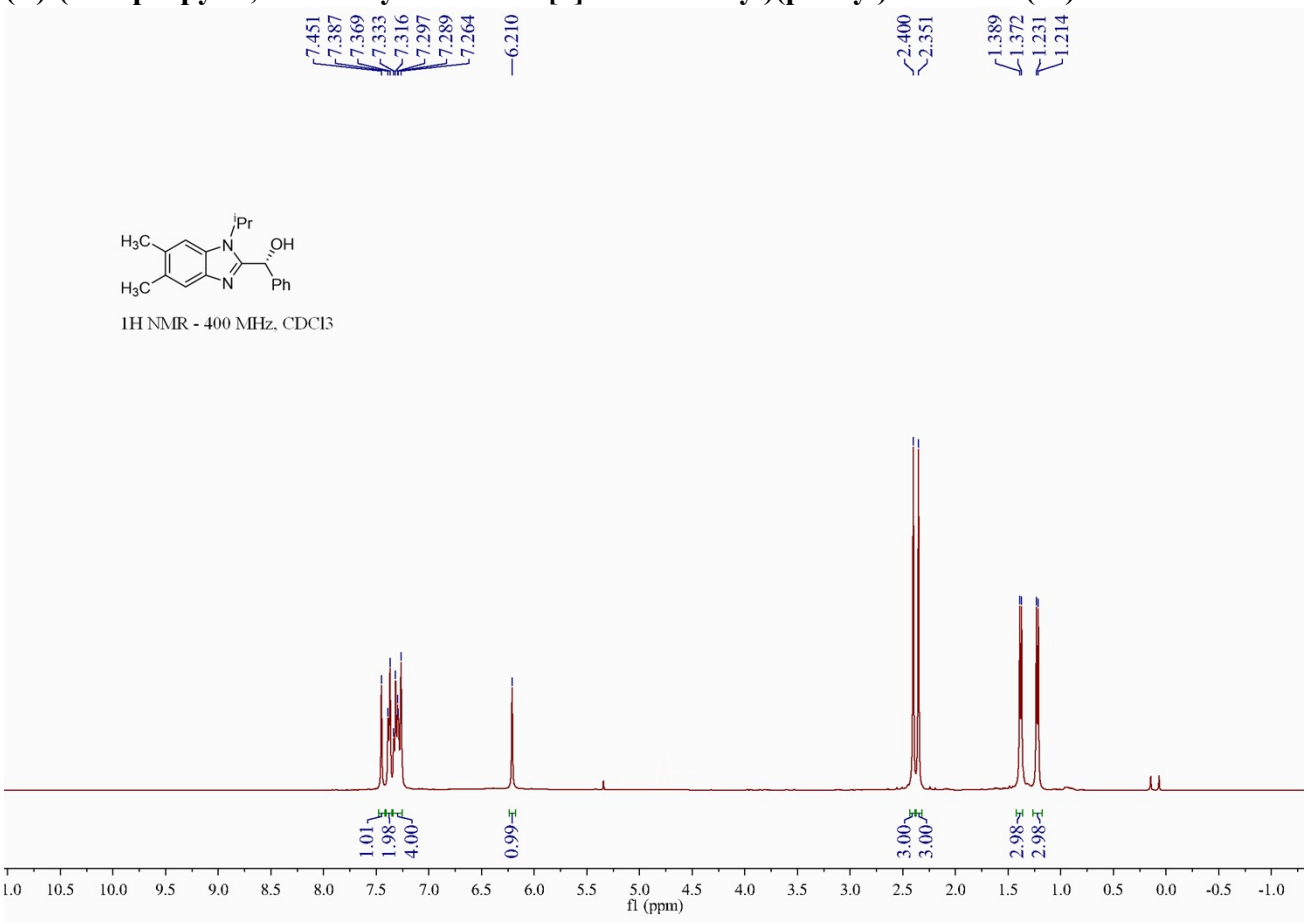


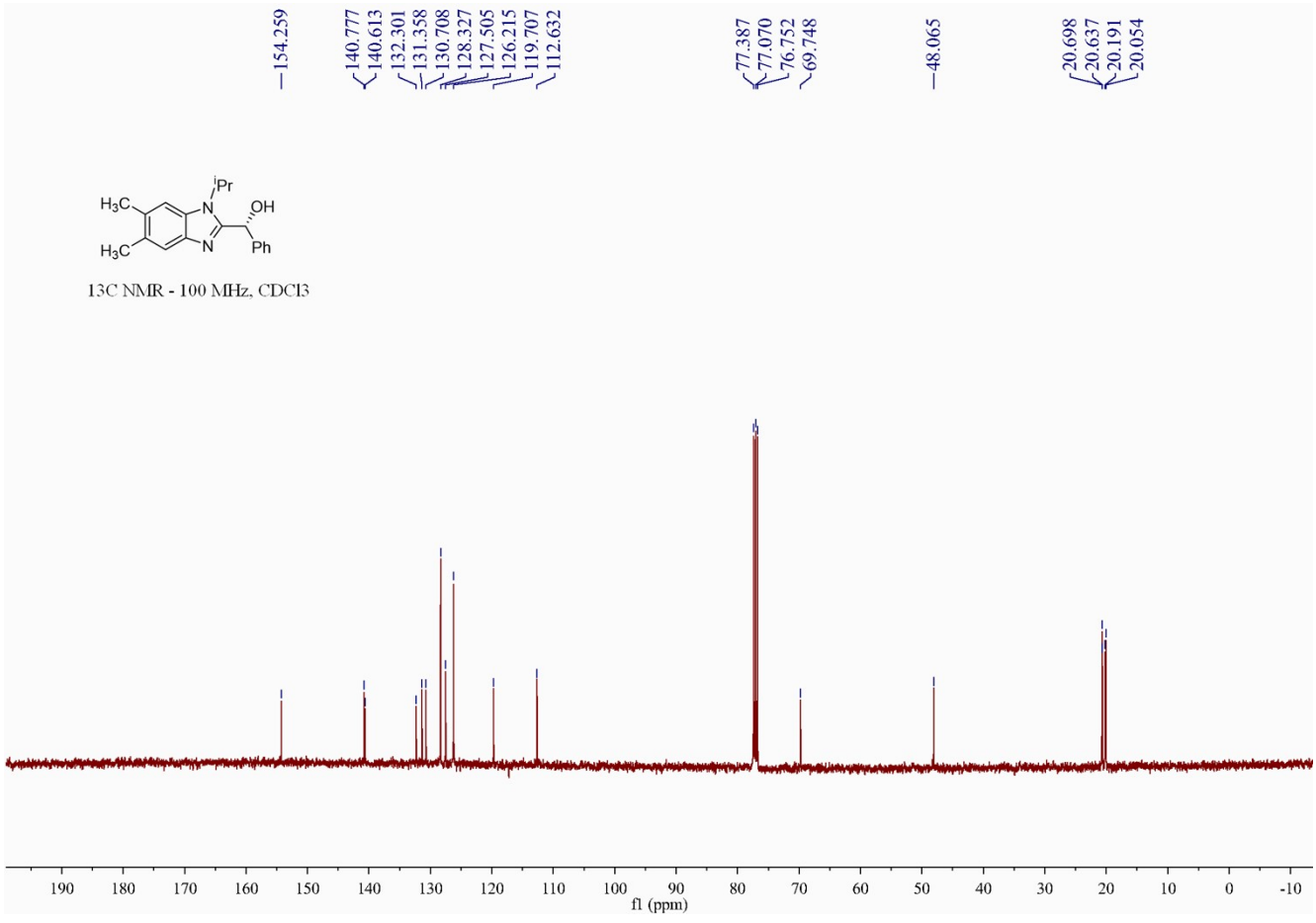
(*R*)-(5,6-dimethyl-1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)(phenyl)methanol (2d)



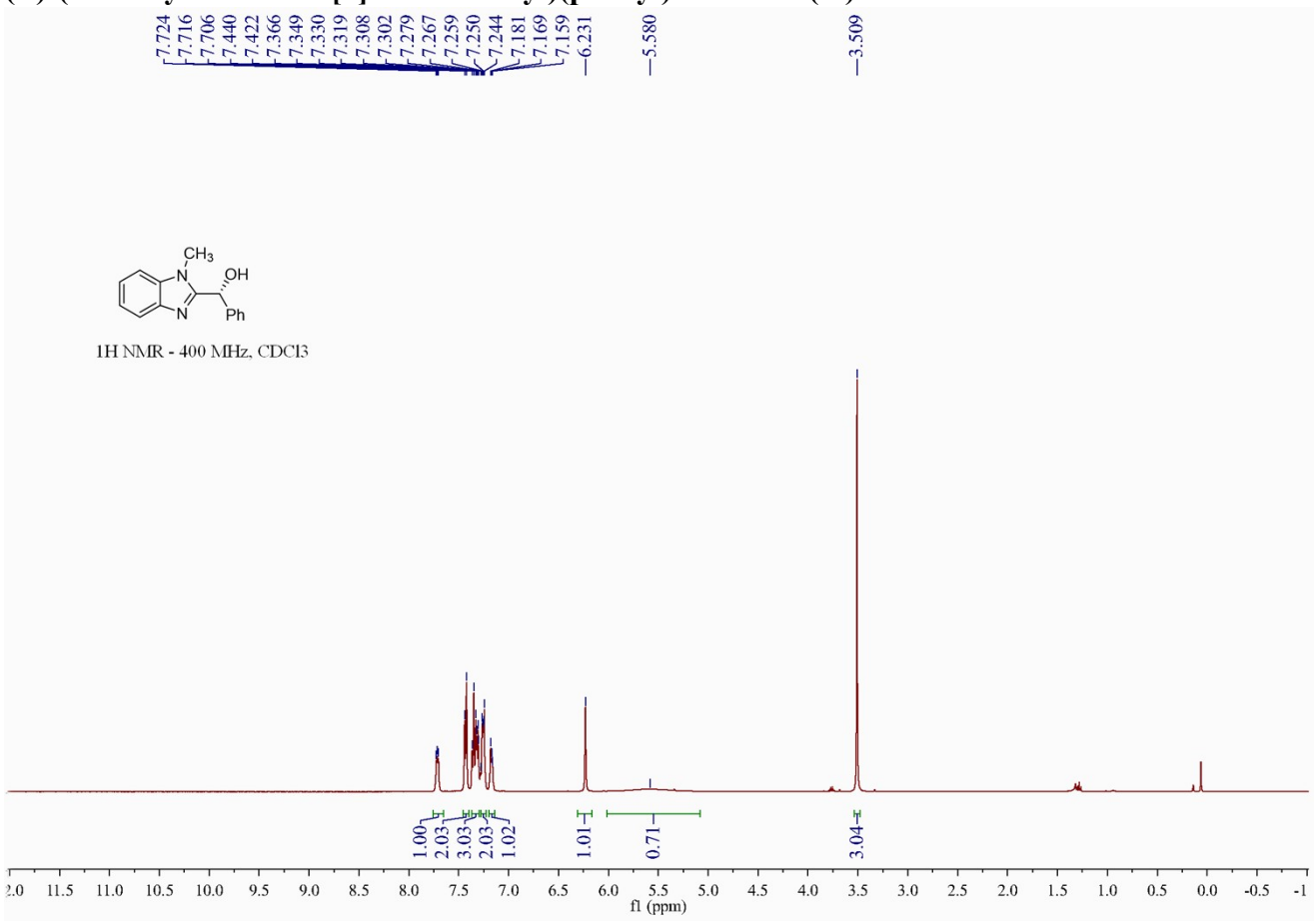


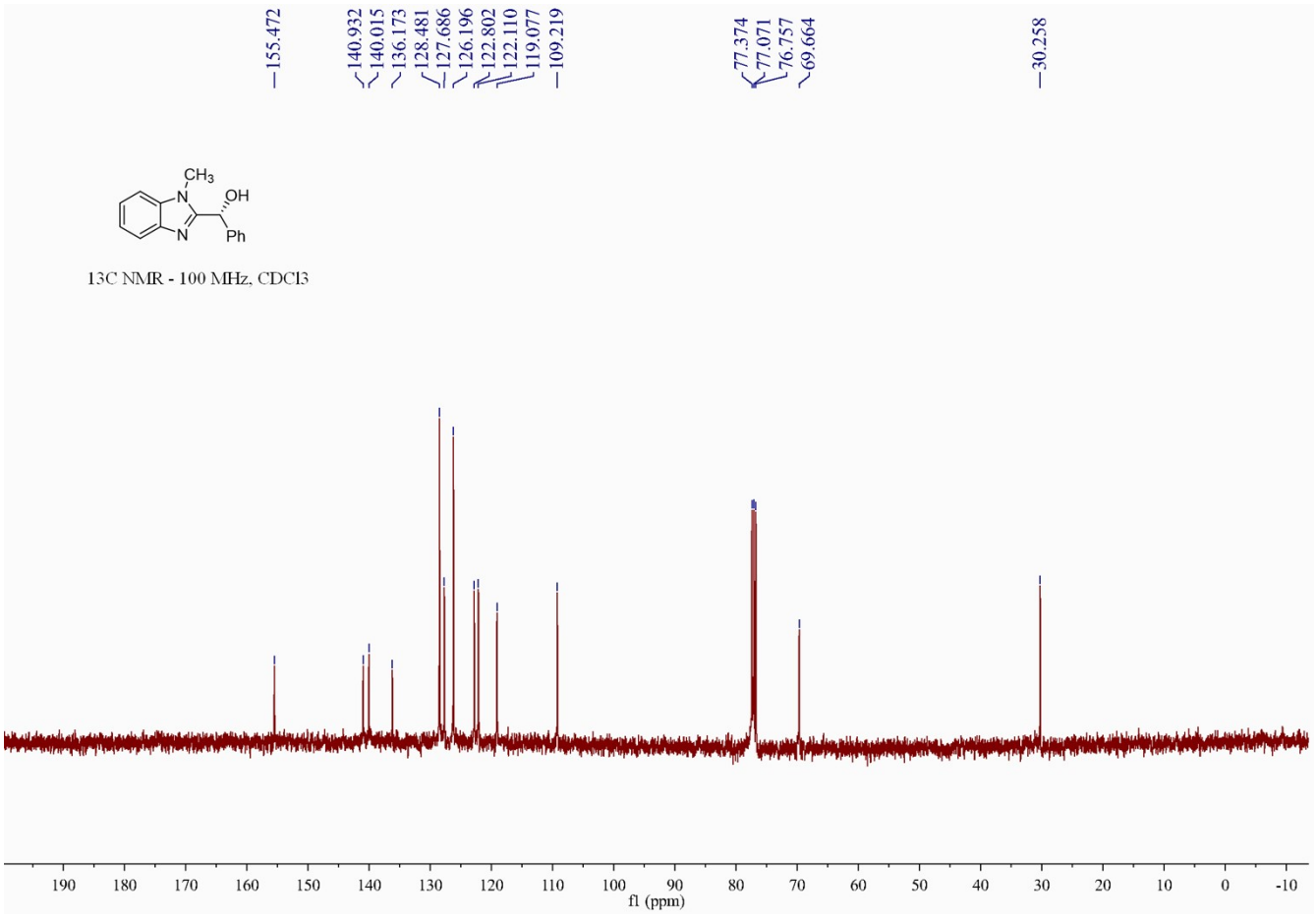
(*R*)-(1-isopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazol-2-yl)(phenyl)methanol (2e)



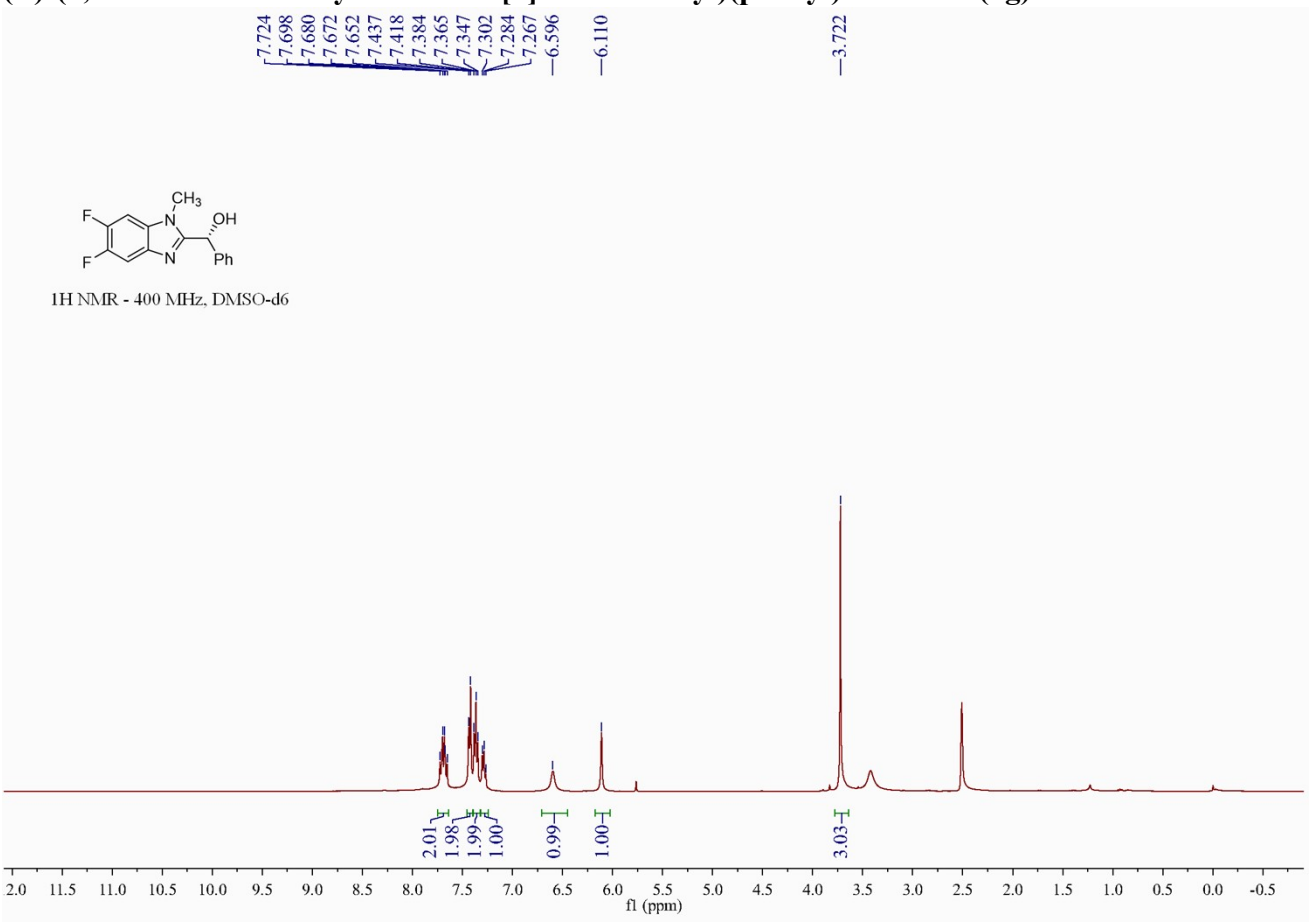


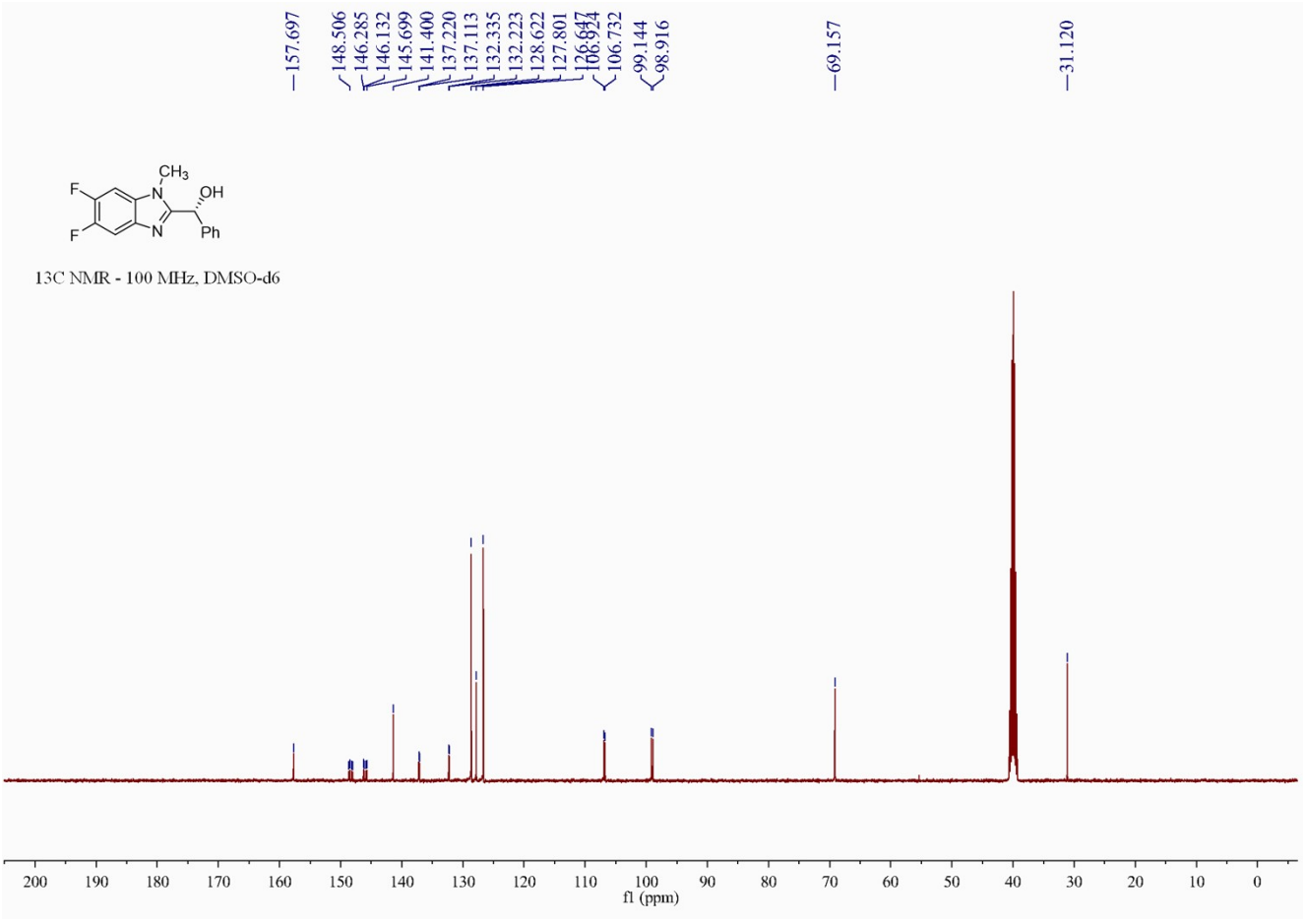
(*R*)-(1-methyl-1*H*-benzo[*d*]imidazol-2-yl)(phenyl)methanol (2f)



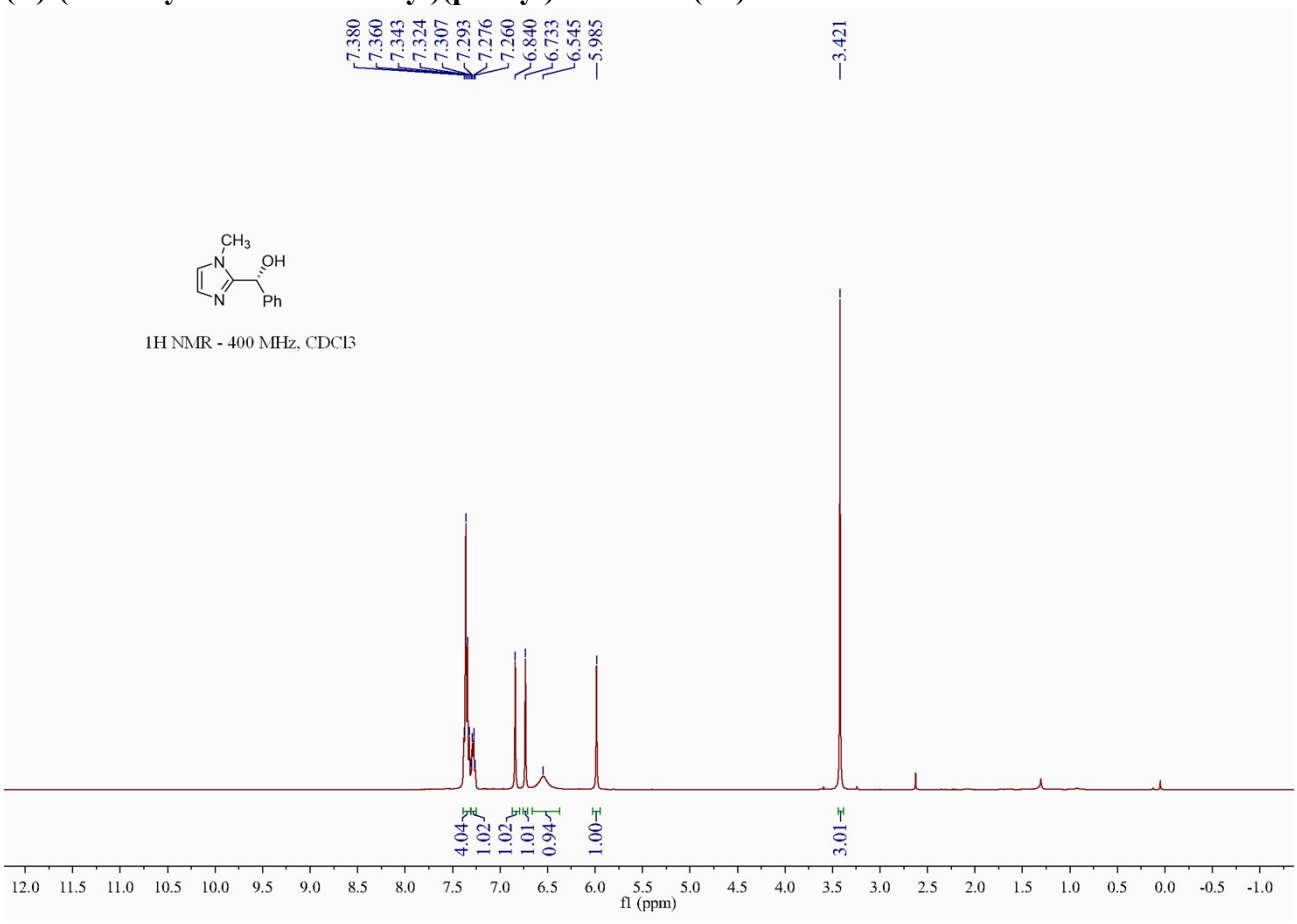


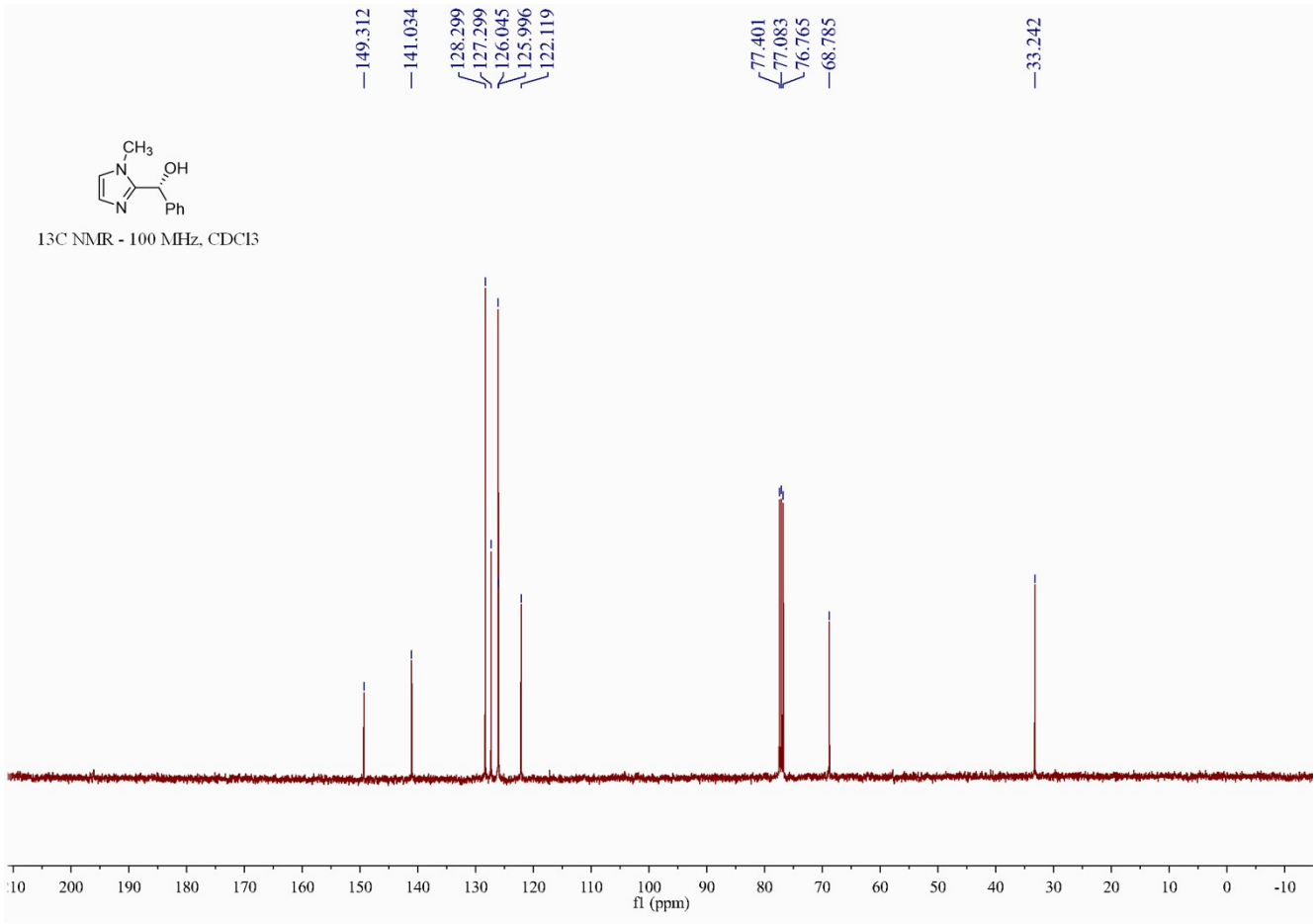
(*R*)-(5,6-difluoro-1-methyl-1*H*-benzo[*d*]imidazol-2-yl)(phenyl)methanol (2g)



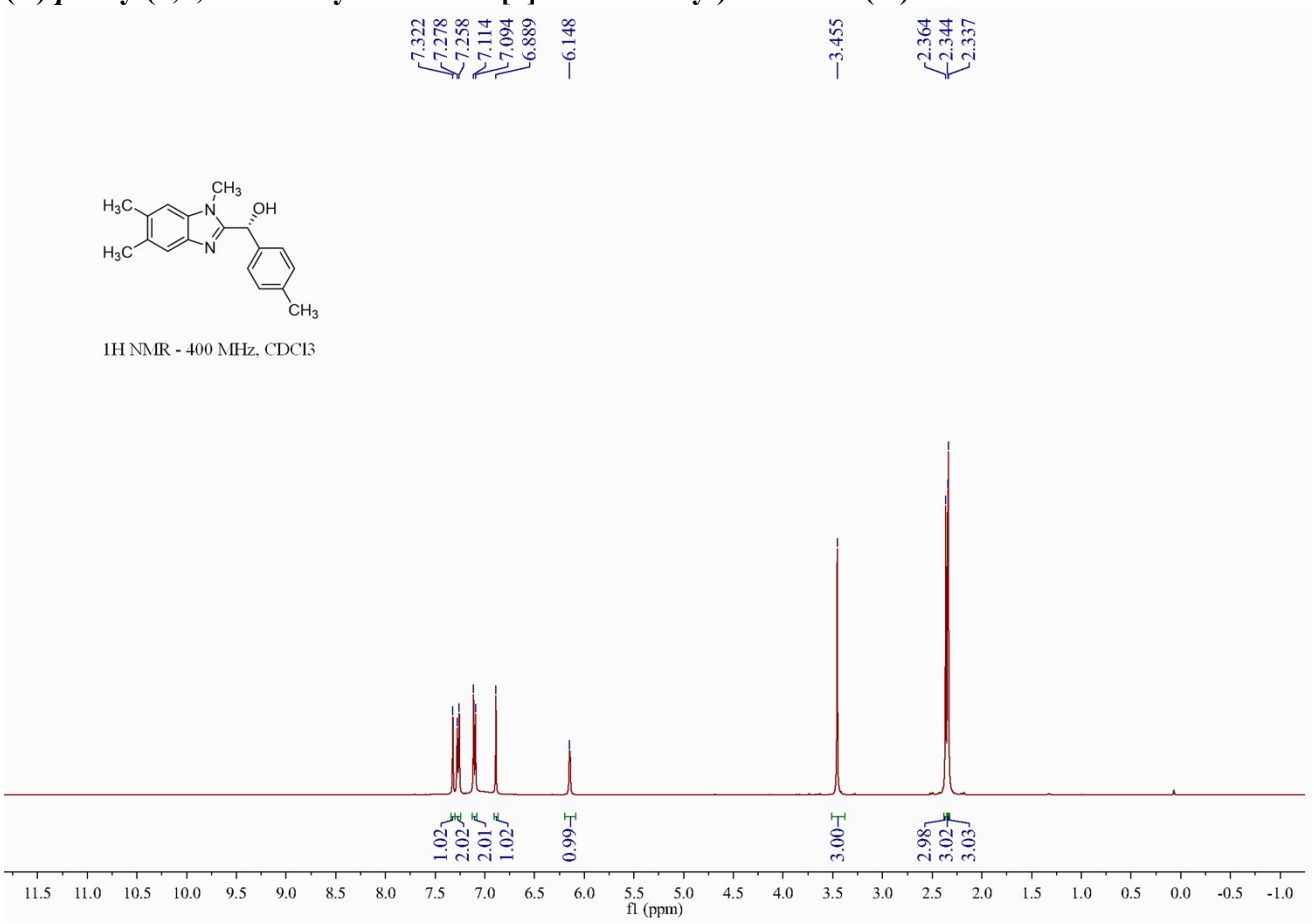


(*R*)-(1-methyl-1*H*-imidazol-2-yl)(phenyl)methanol (2h)

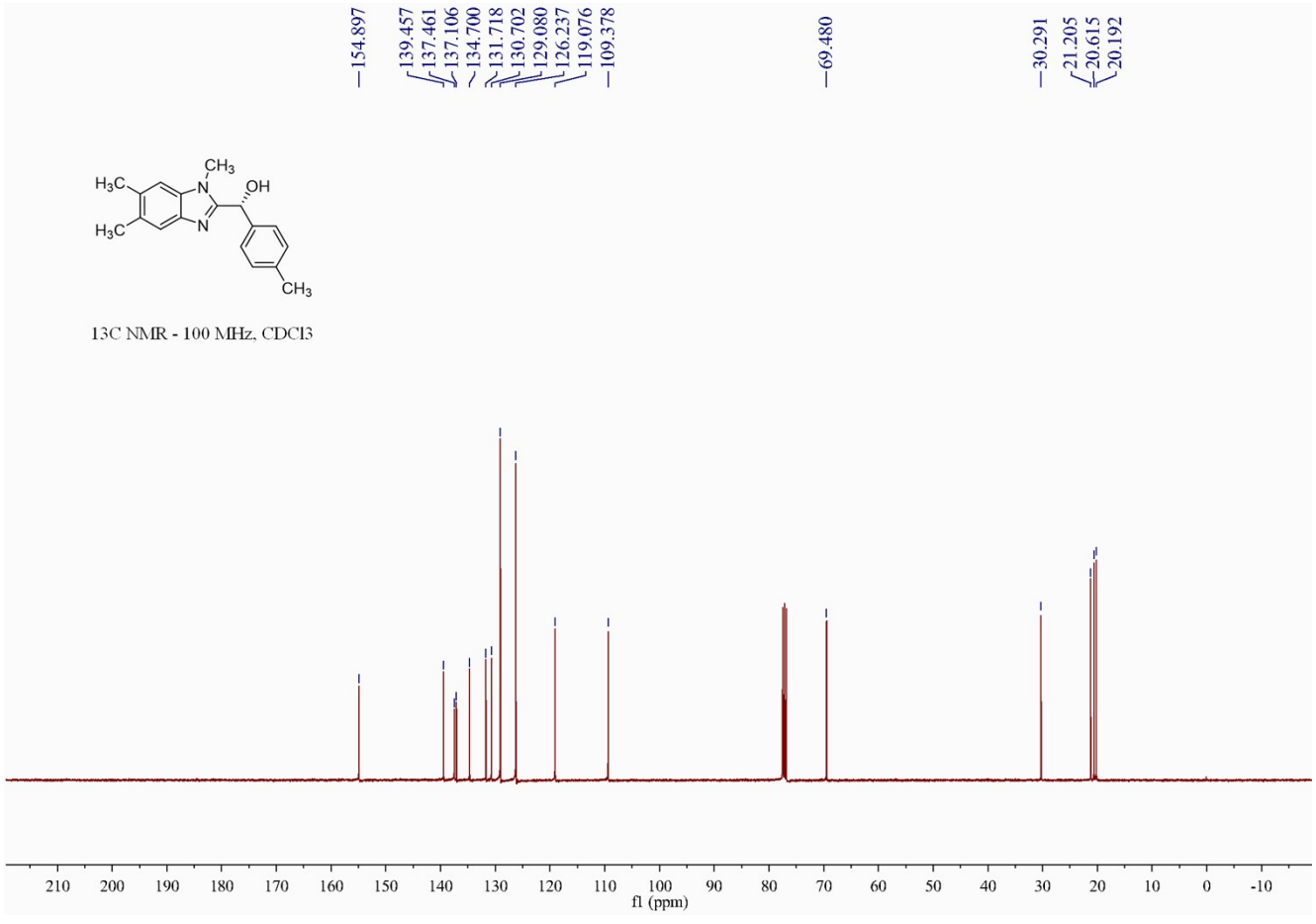




(*R*)-*p*-tolyl(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2i)

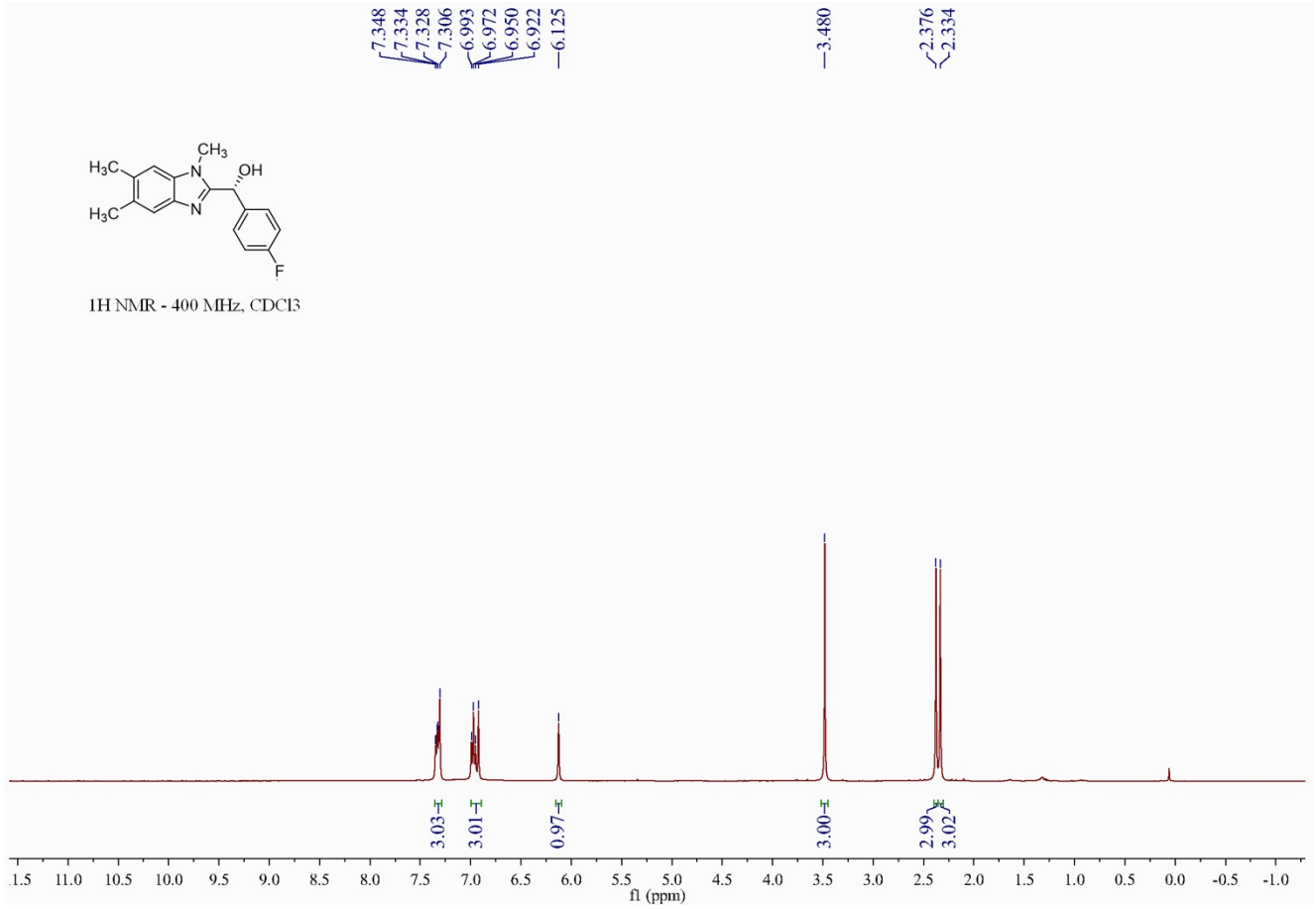


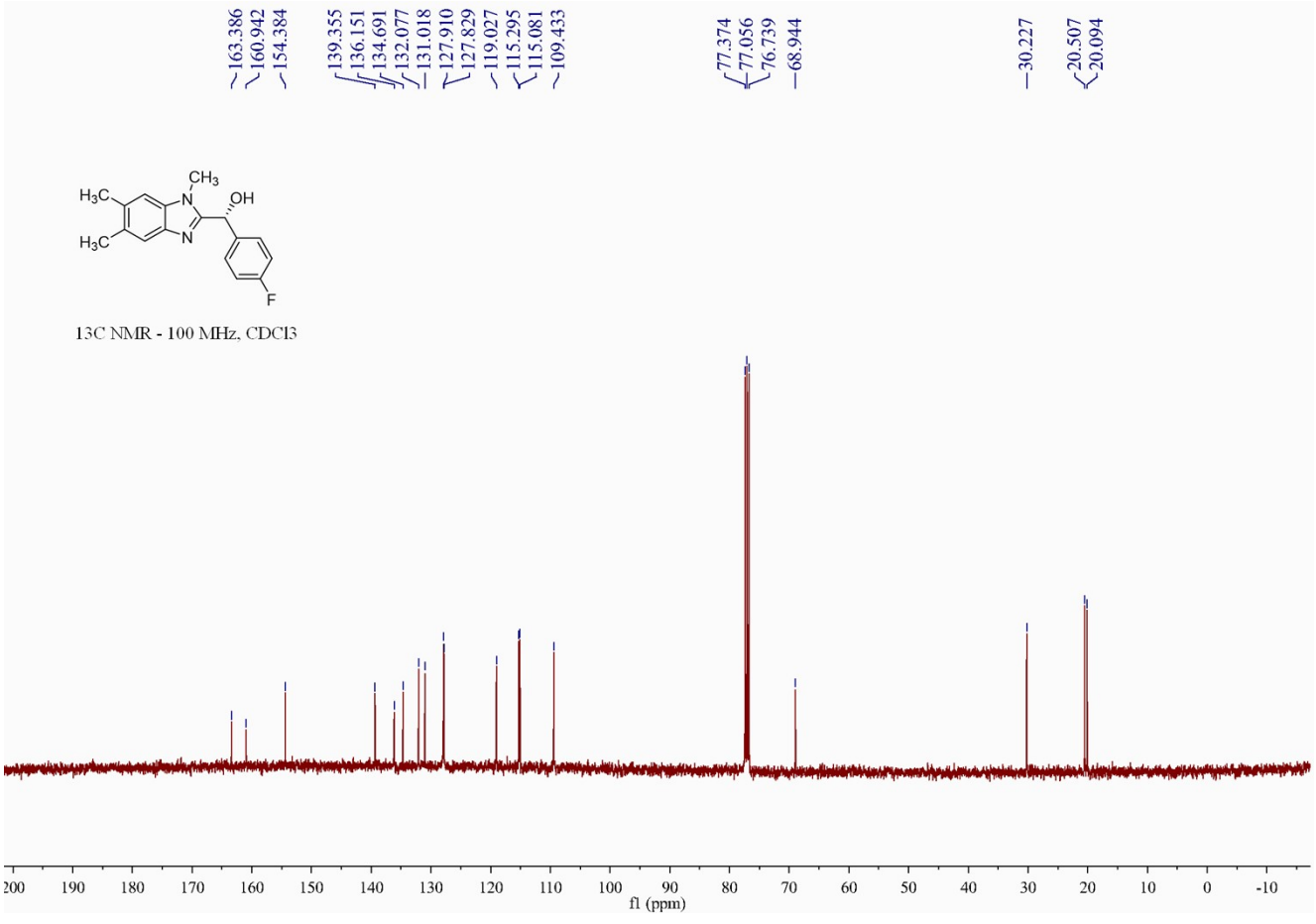
1H NMR - 400 MHz, CDCl3



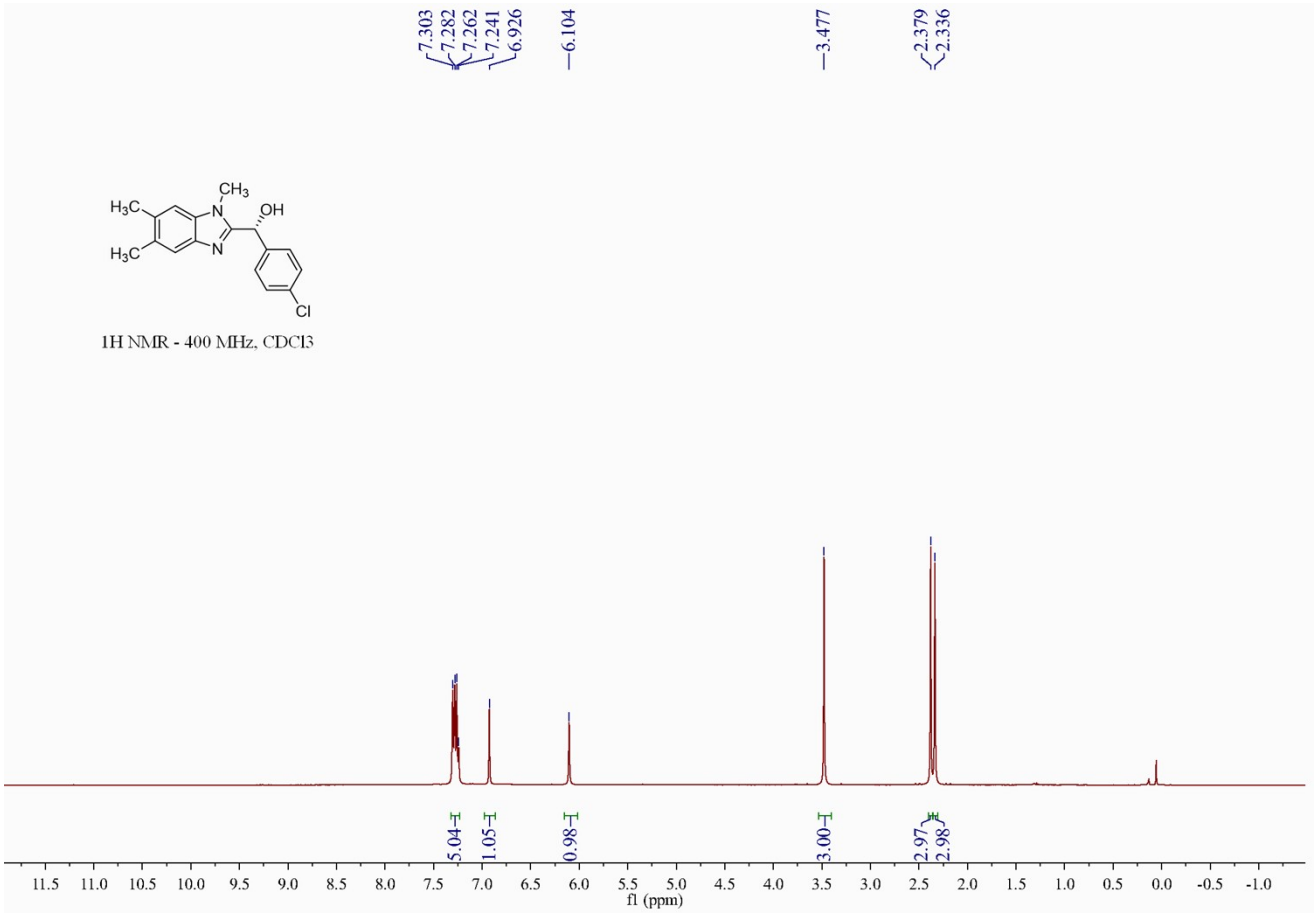
13C NMR - 100 MHz, CDCl3

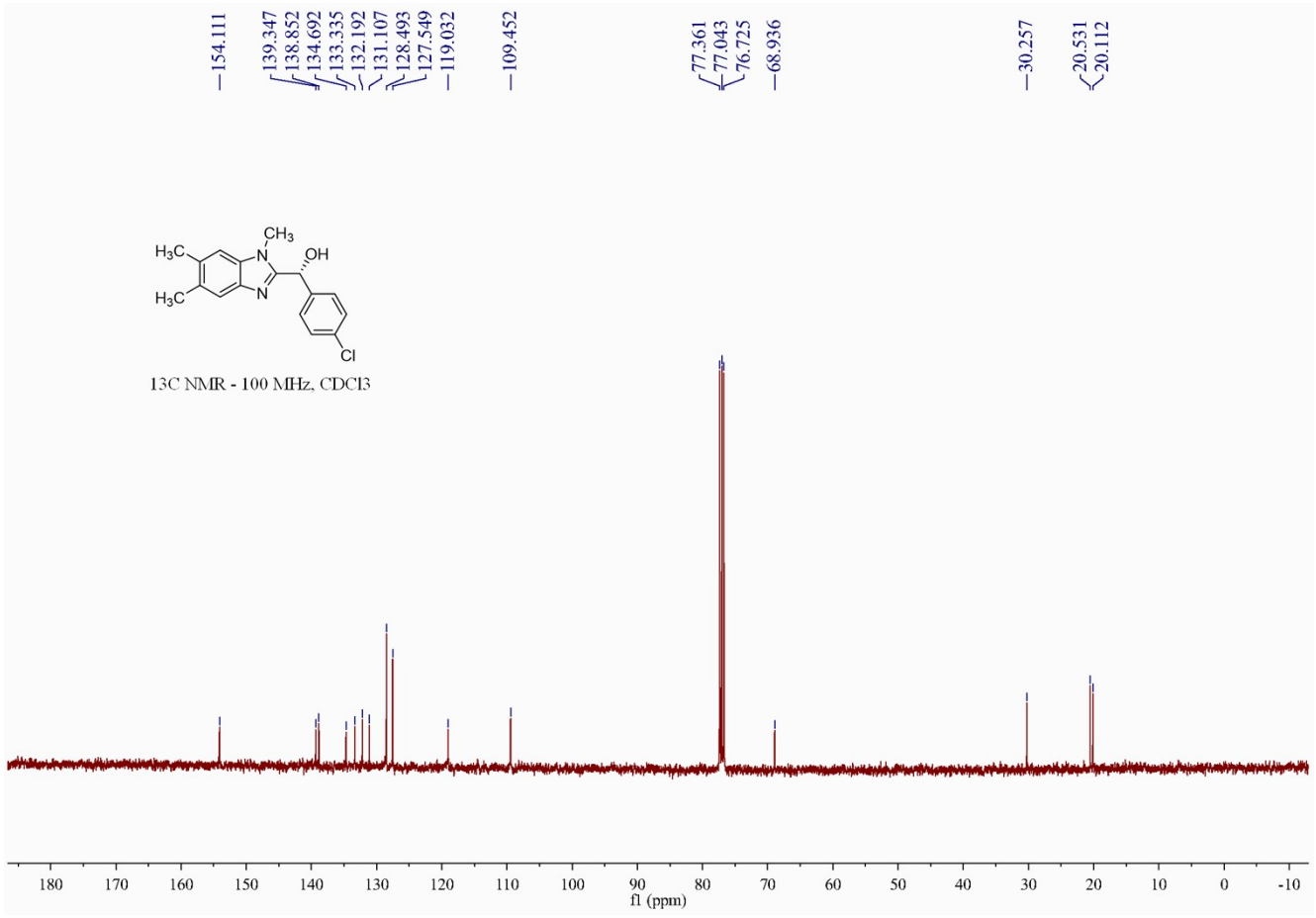
(*R*)-(4-fluorophenyl)(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2j)



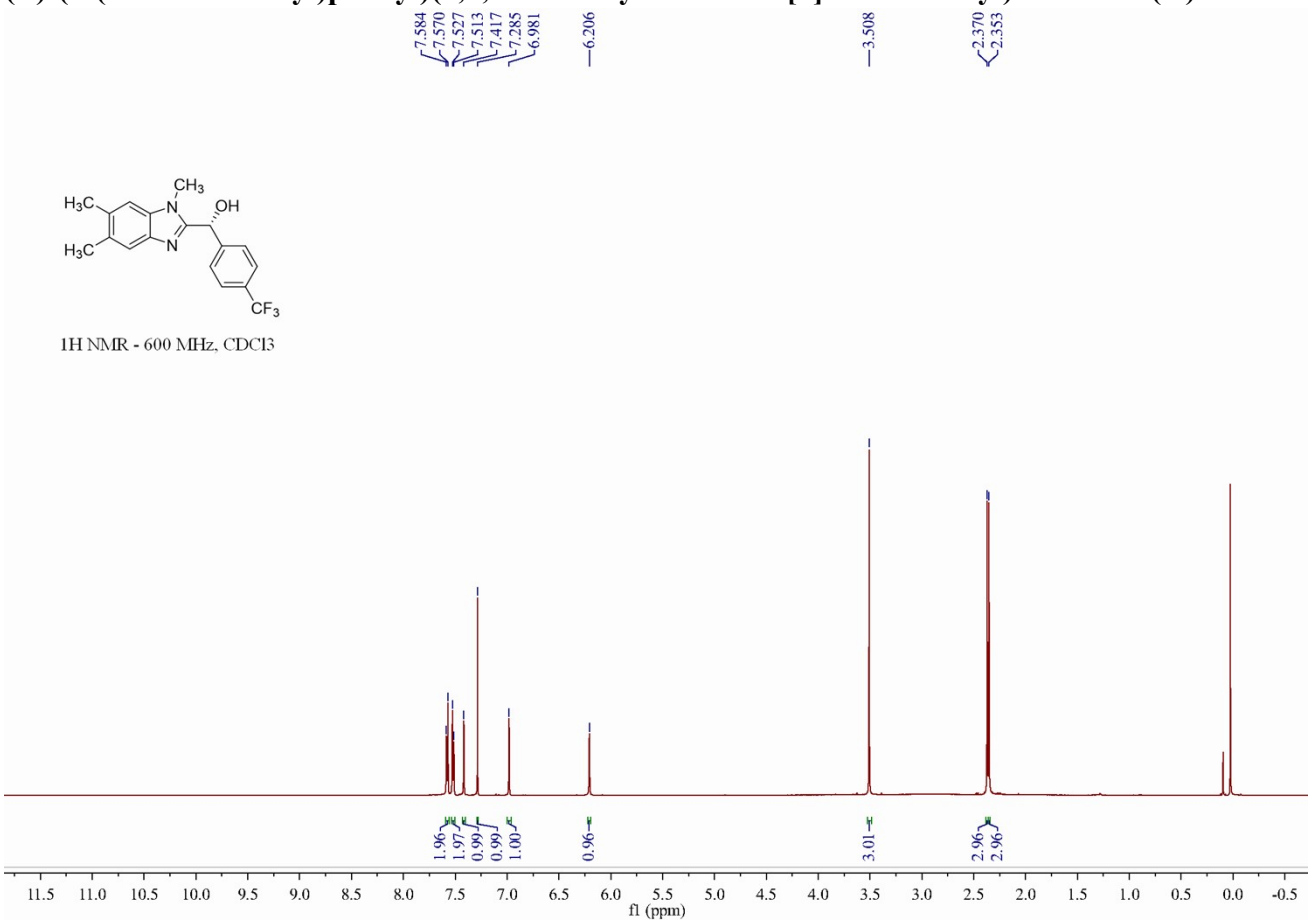


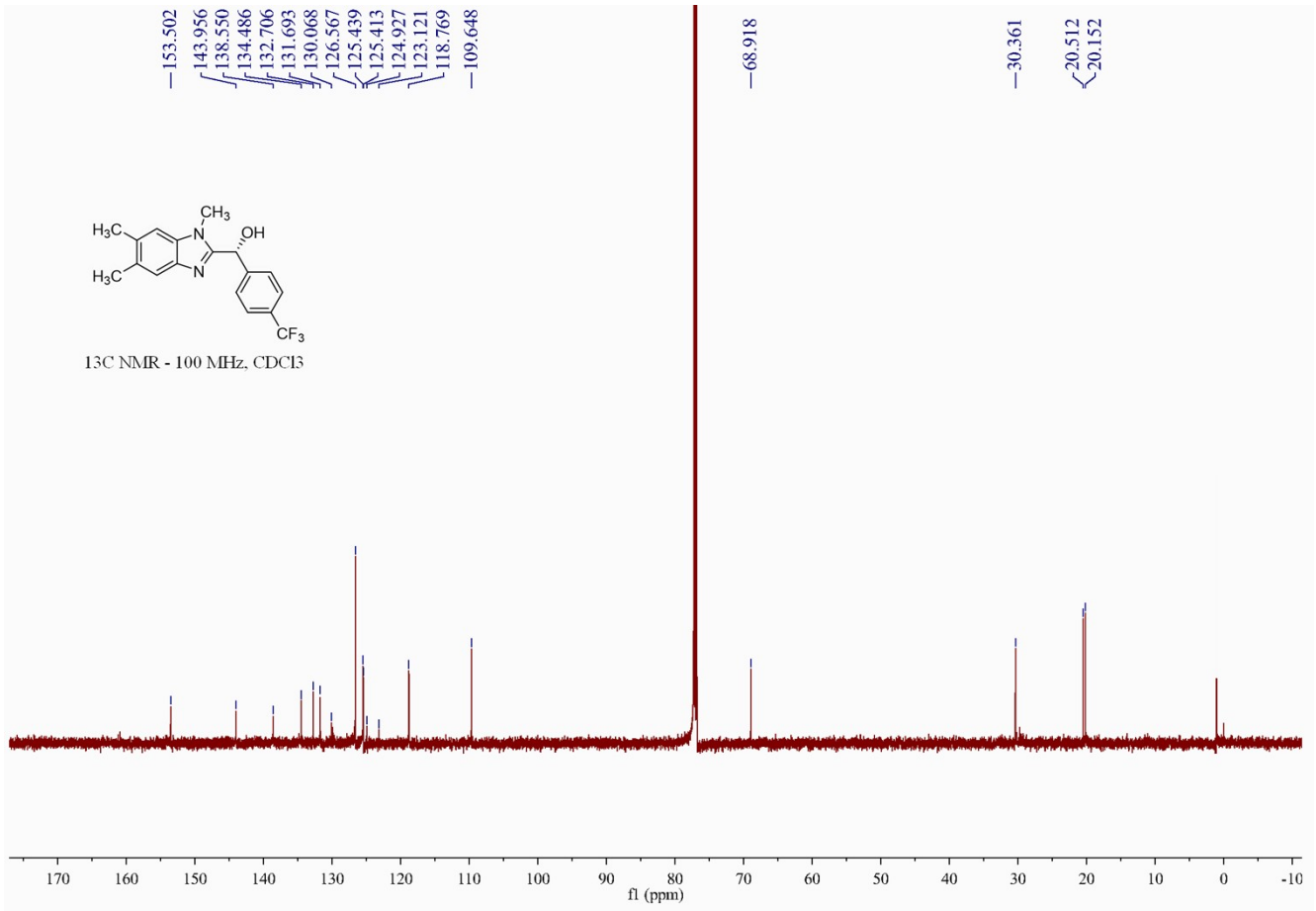
(*R*)-(4-chlorophenyl)(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2k)



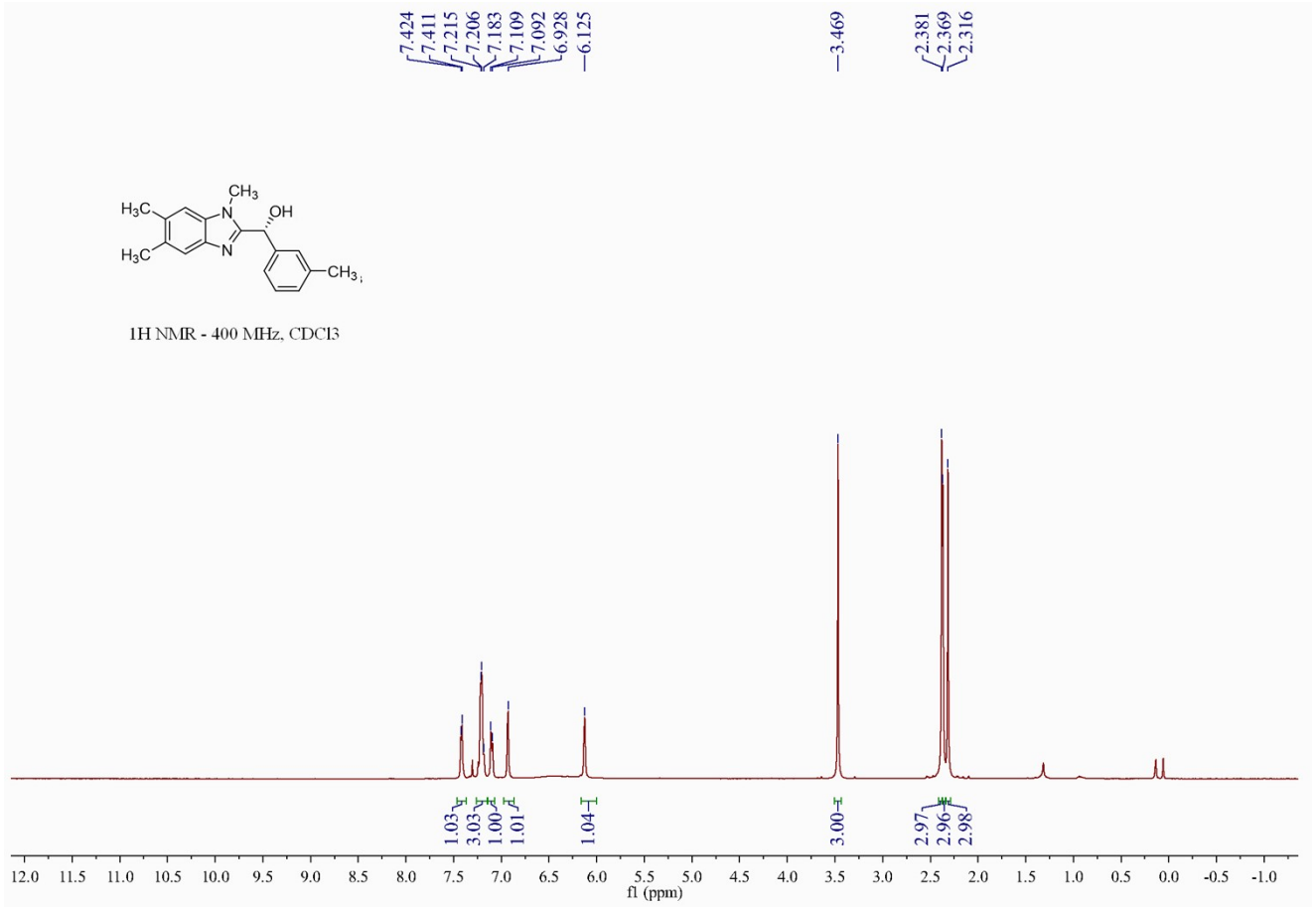


(*R*)-(4-(trifluoromethyl)phenyl)(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2l)

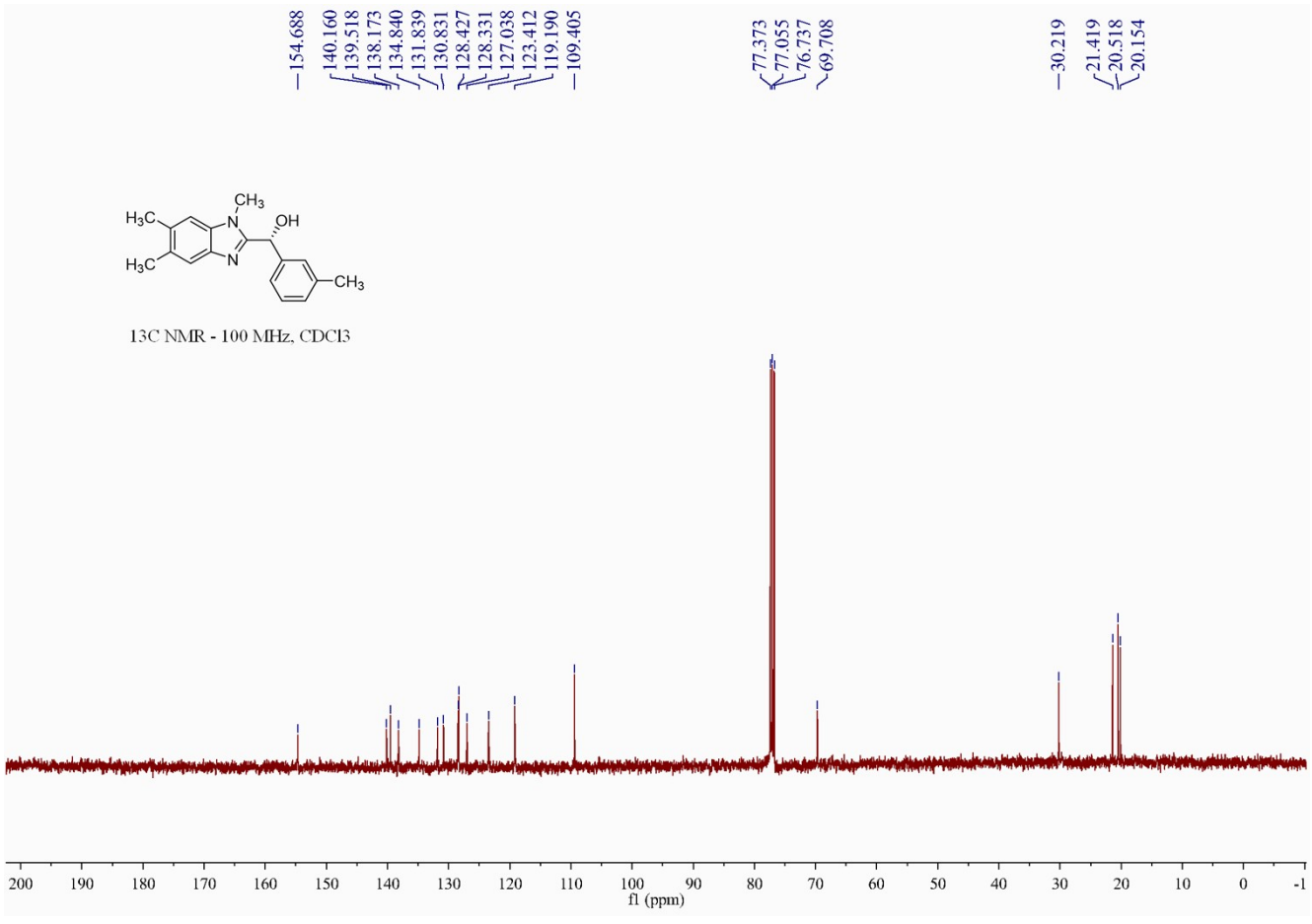




(*R*)-[1,1'-biphenyl]-4-yl(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2m)

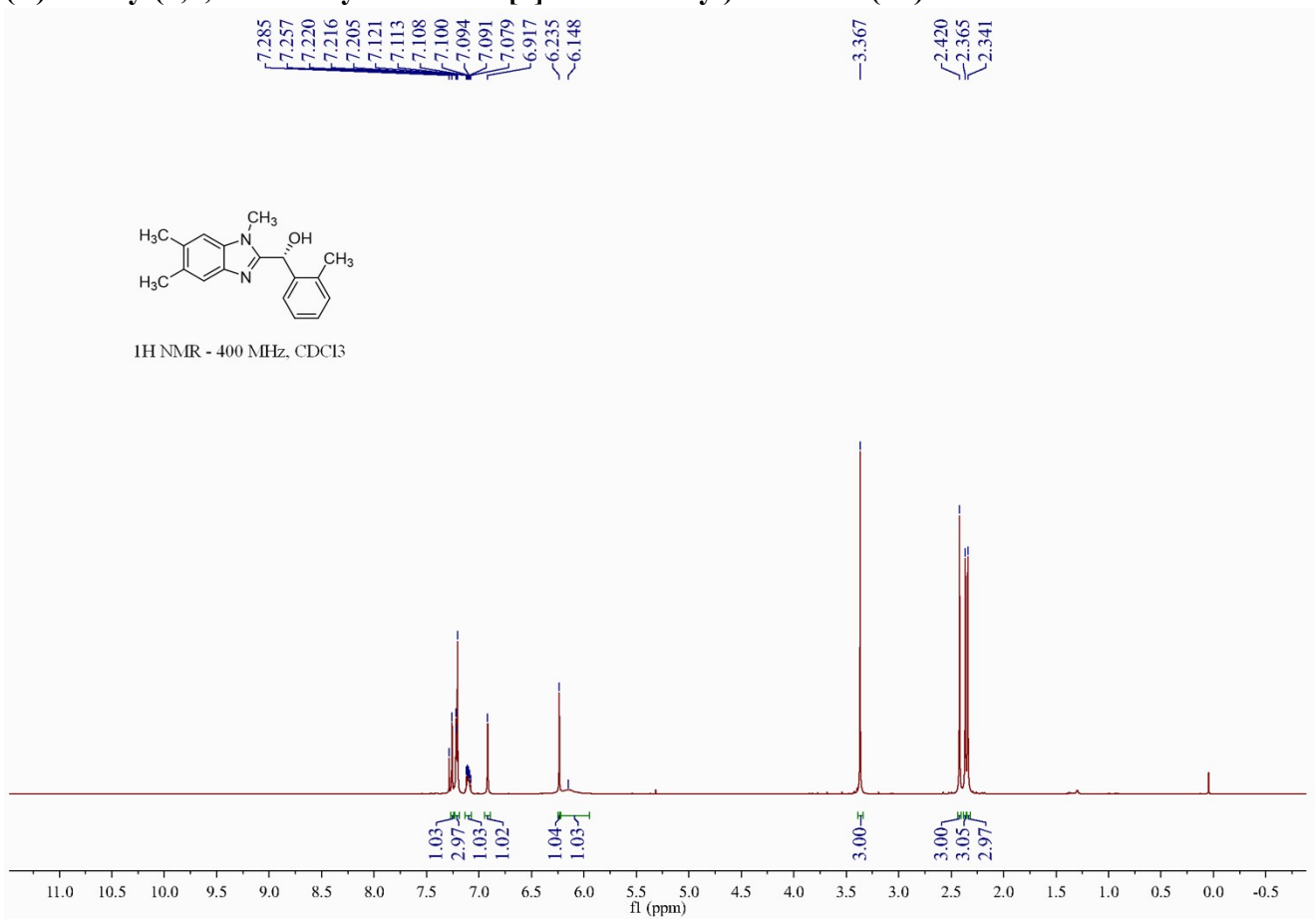


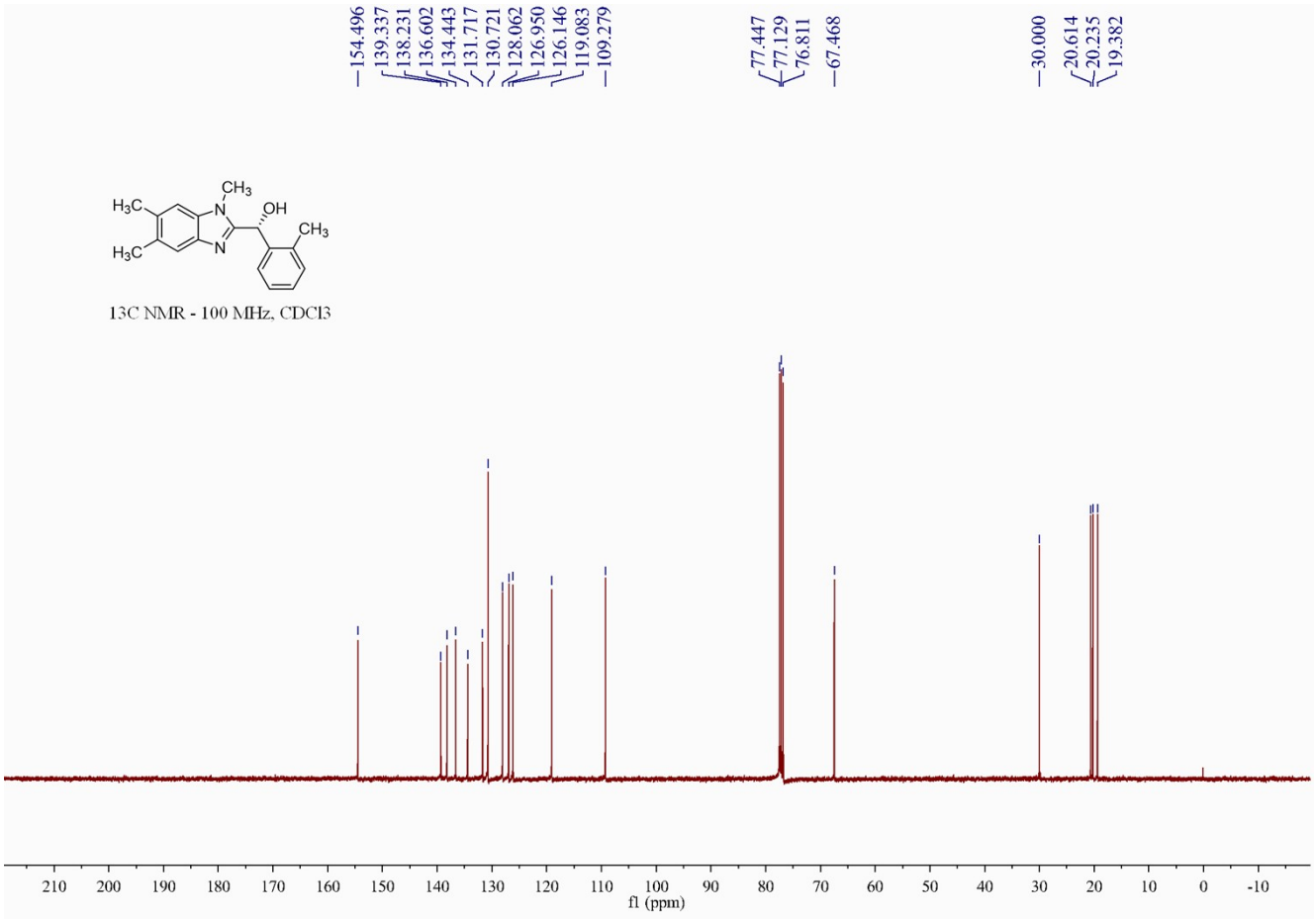
1H NMR - 400 MHz, CDCl3



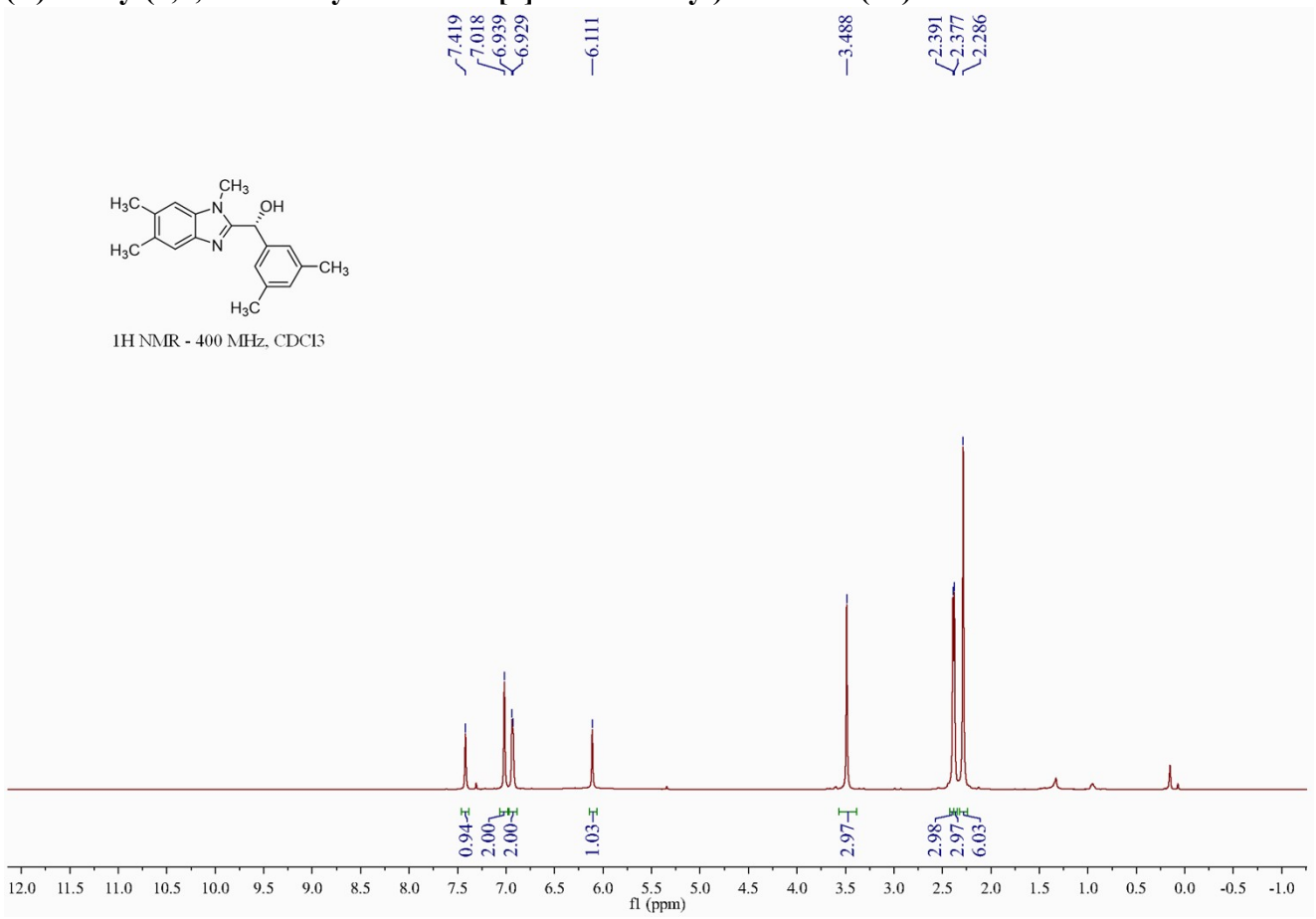
13C NMR - 100 MHz, CDCl3

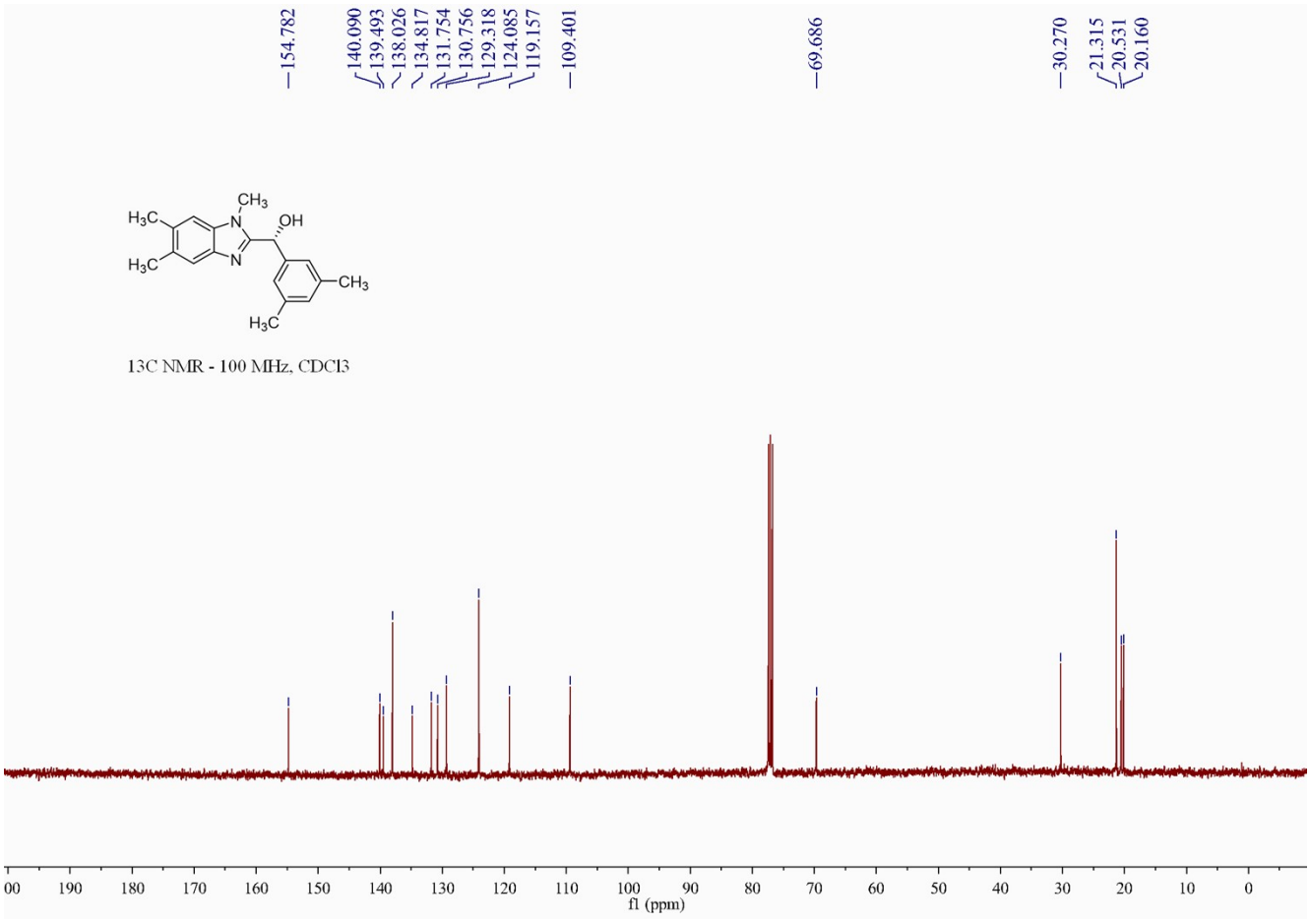
(*R*)-*m*-tolyl(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2n)



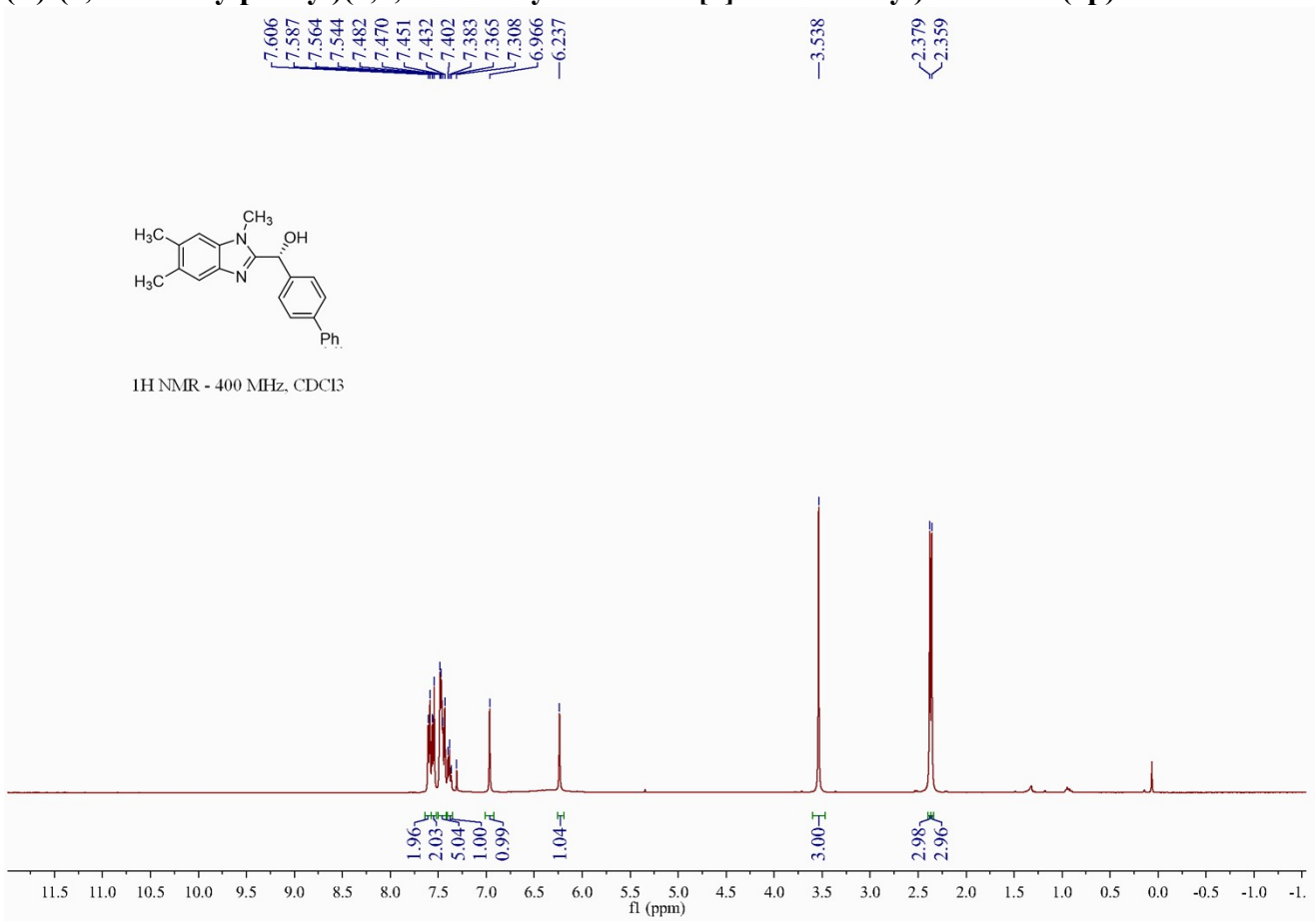


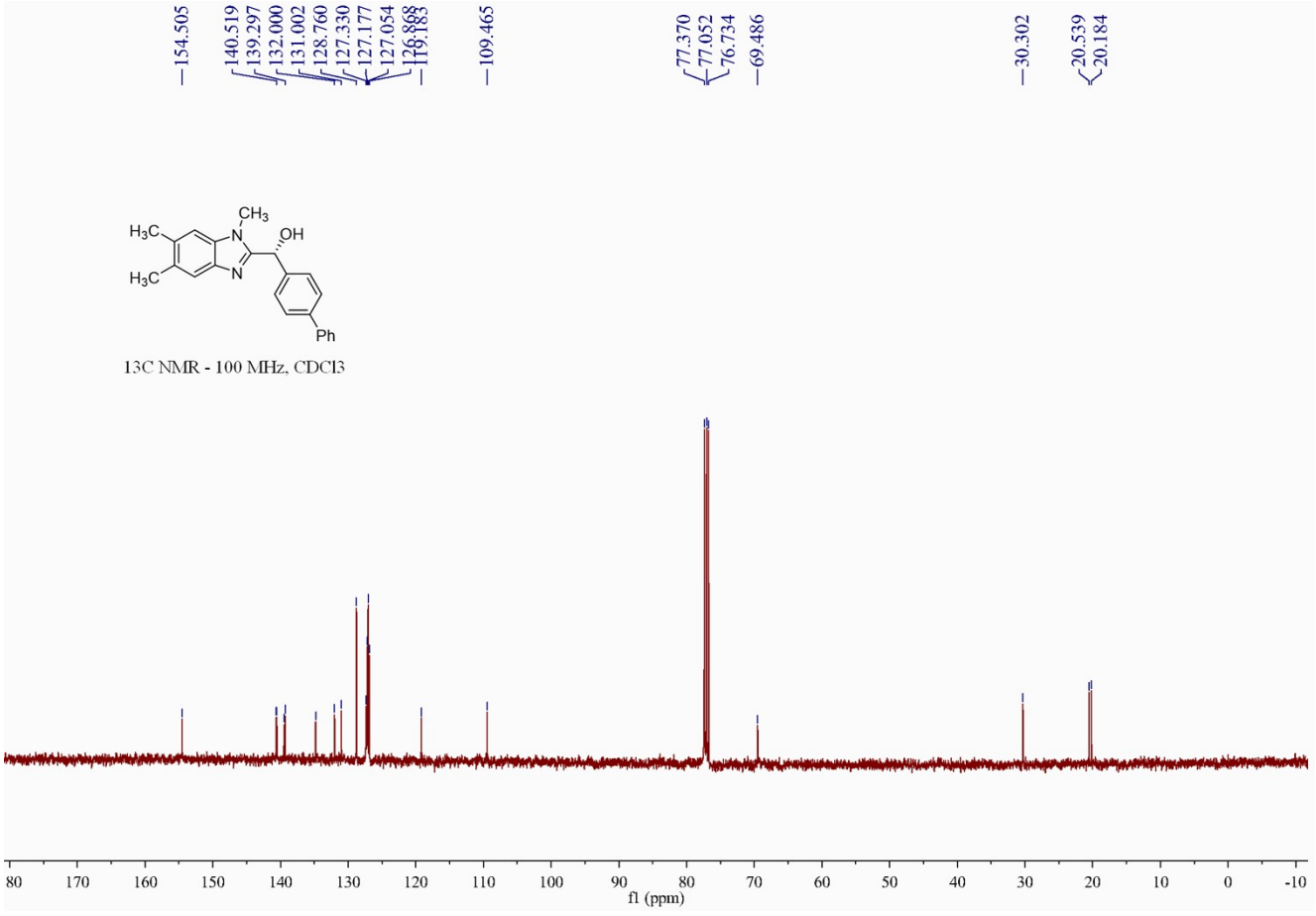
(*R*)-*o*-tolyl(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2o)



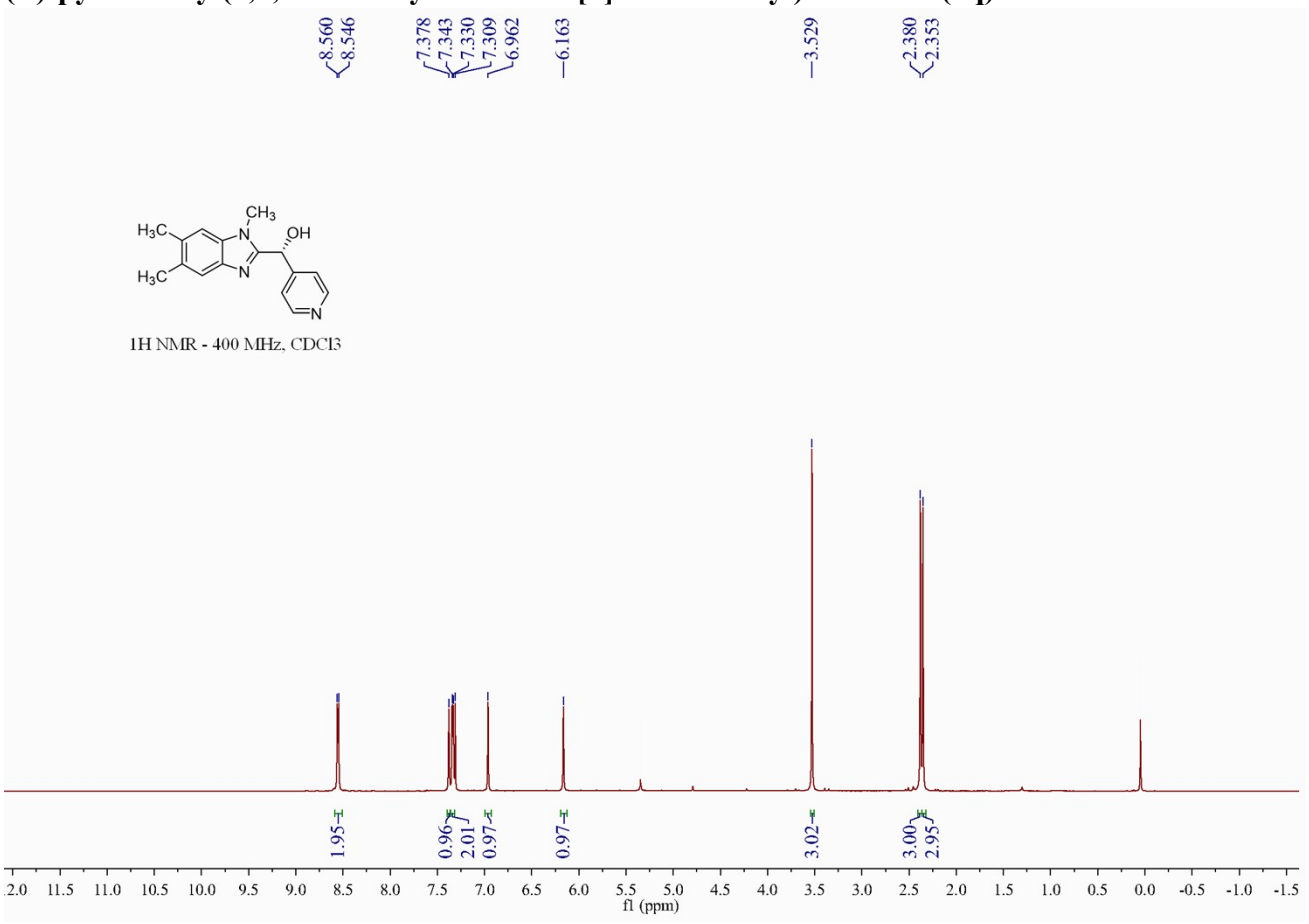


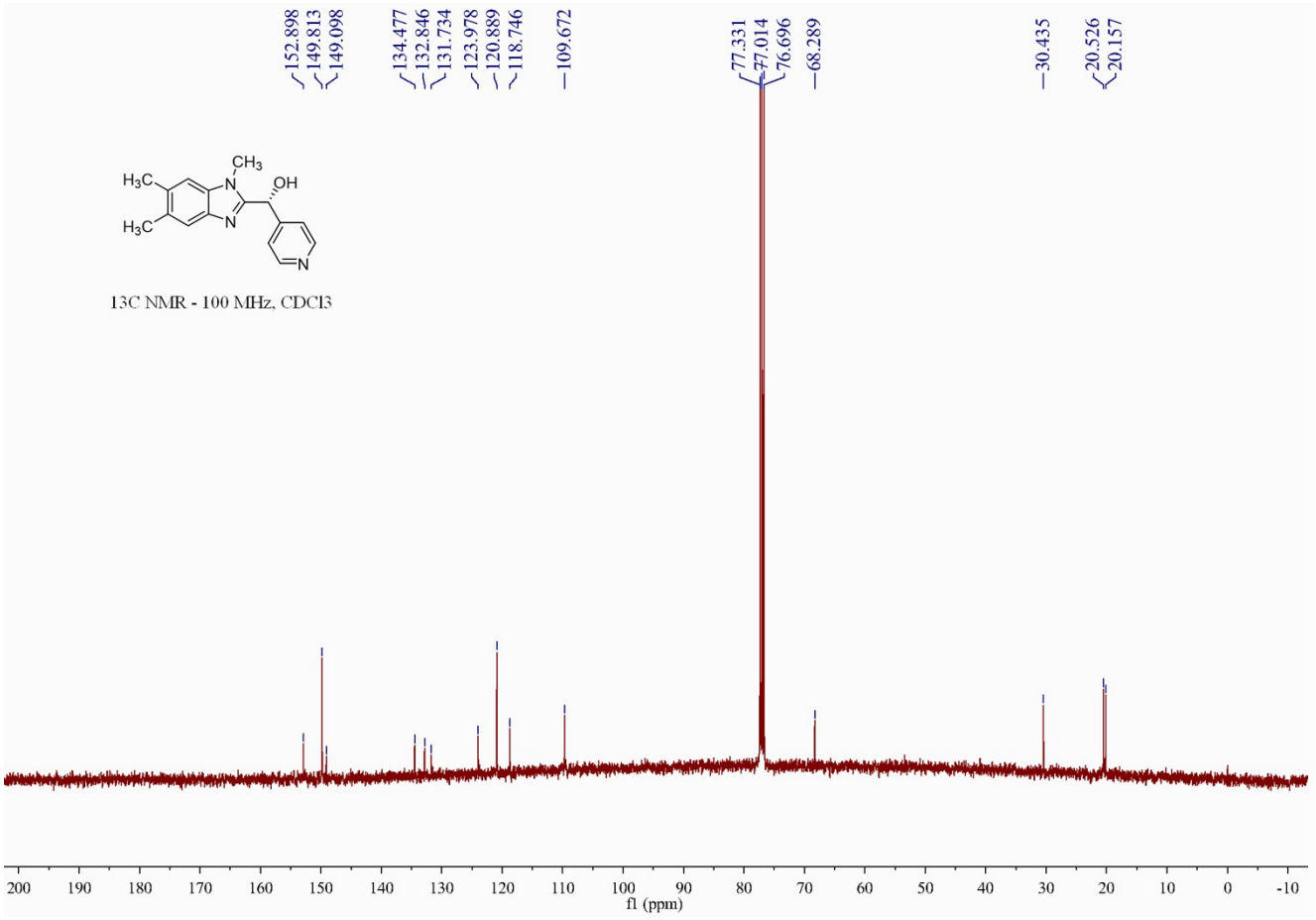
(*R*)-(3,5-dimethylphenyl)(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2p)



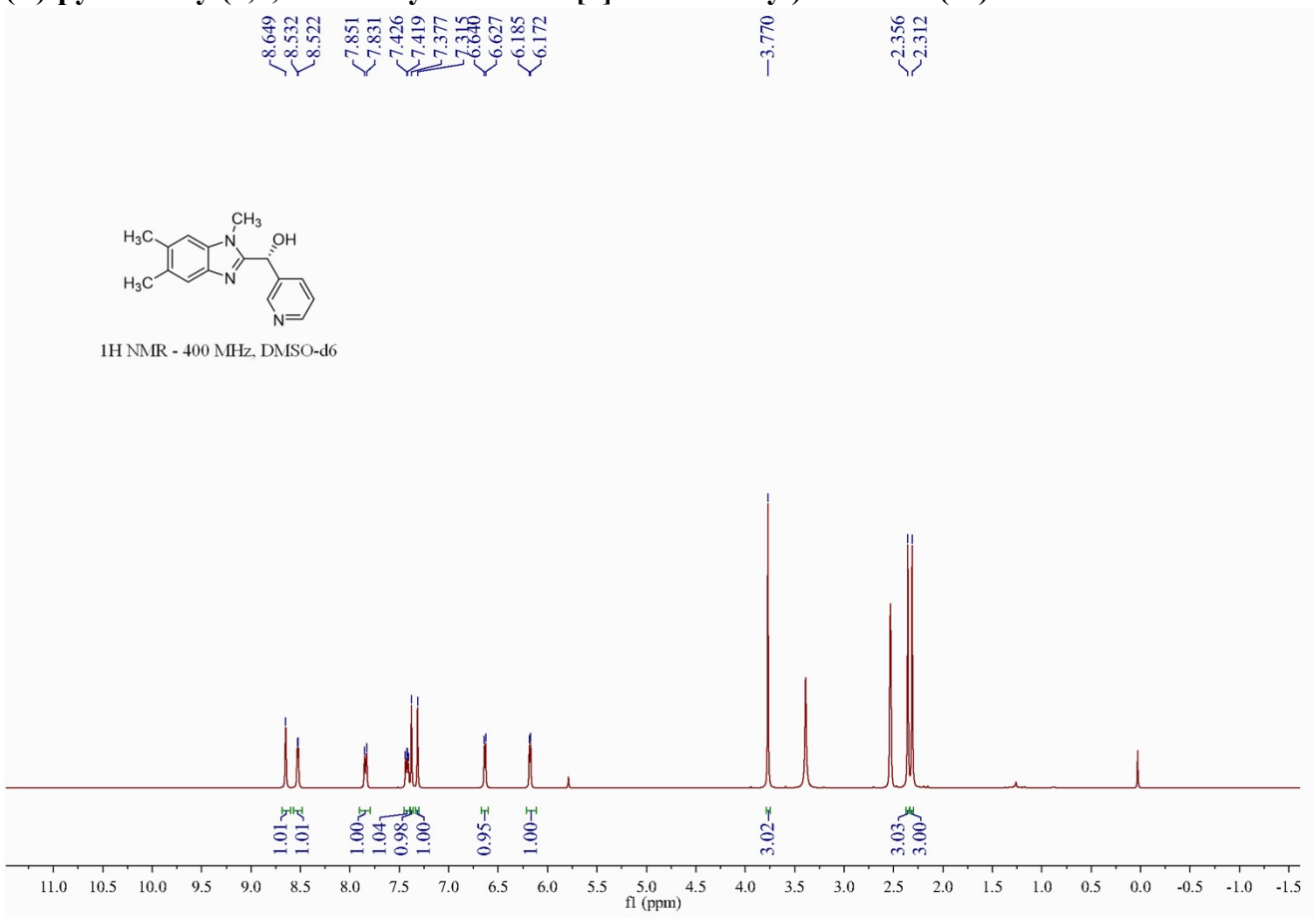


(*R*)-pyridin-4-yl(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2q)

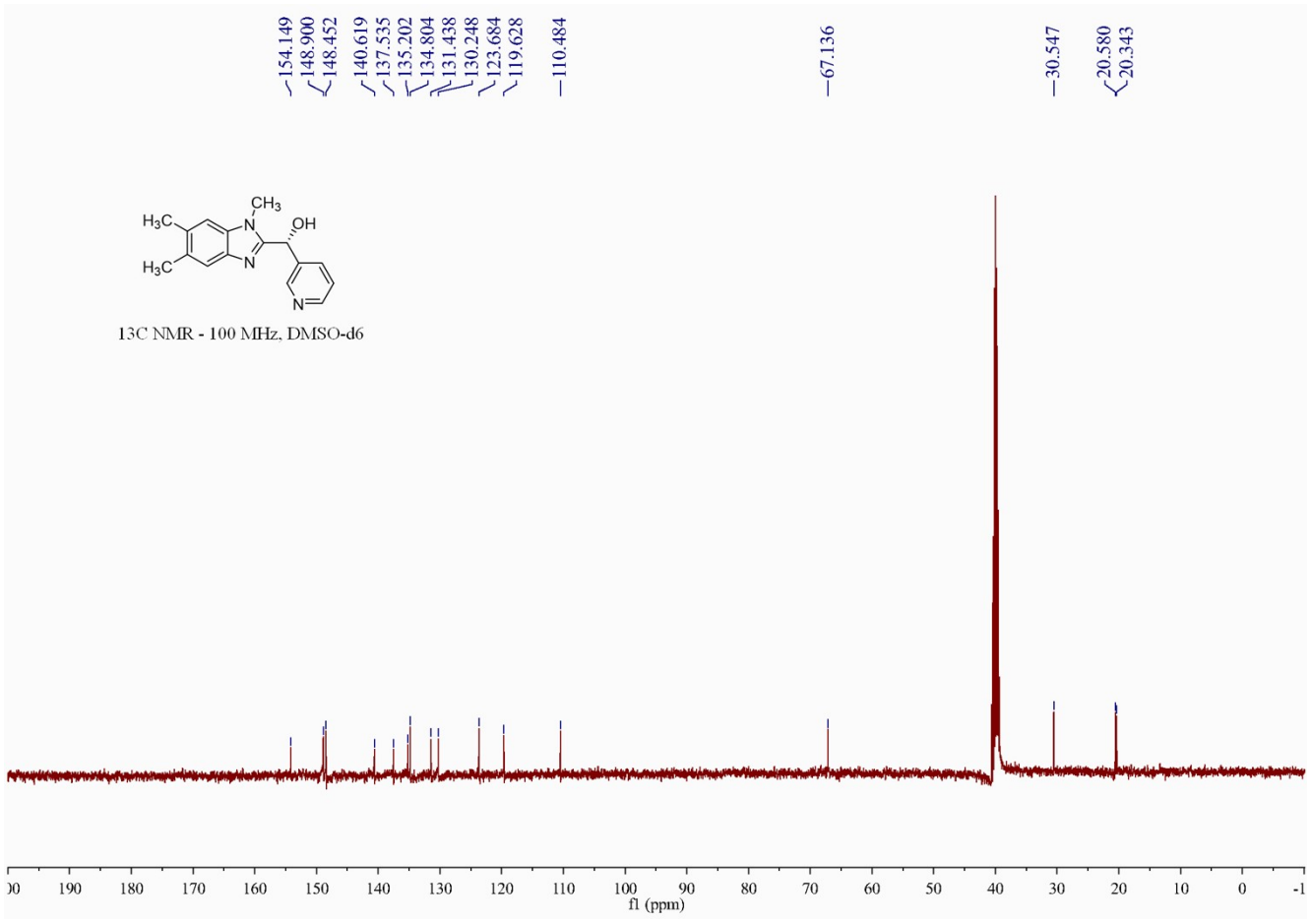




(*R*)-pyridin-3-yl(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2r)

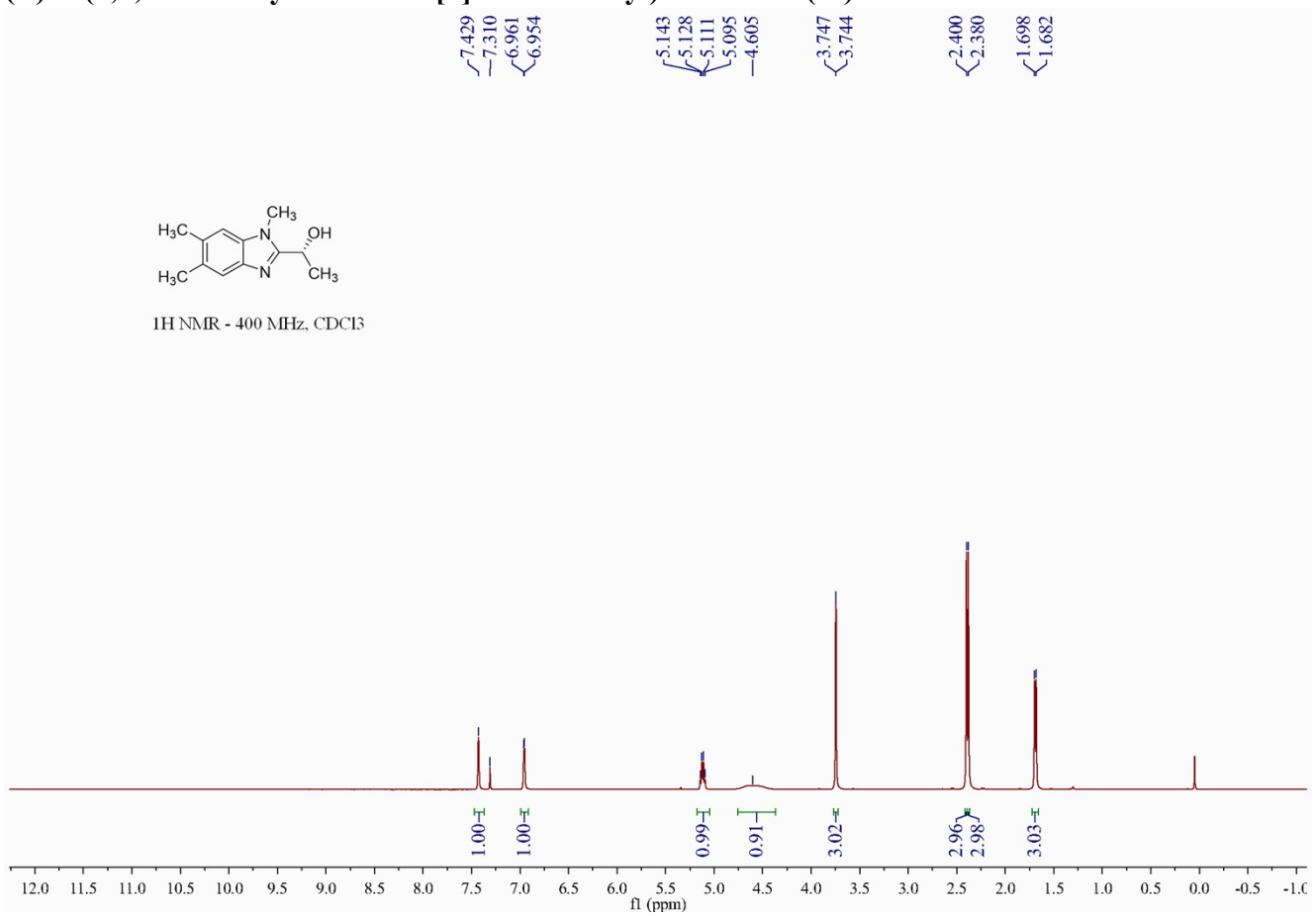


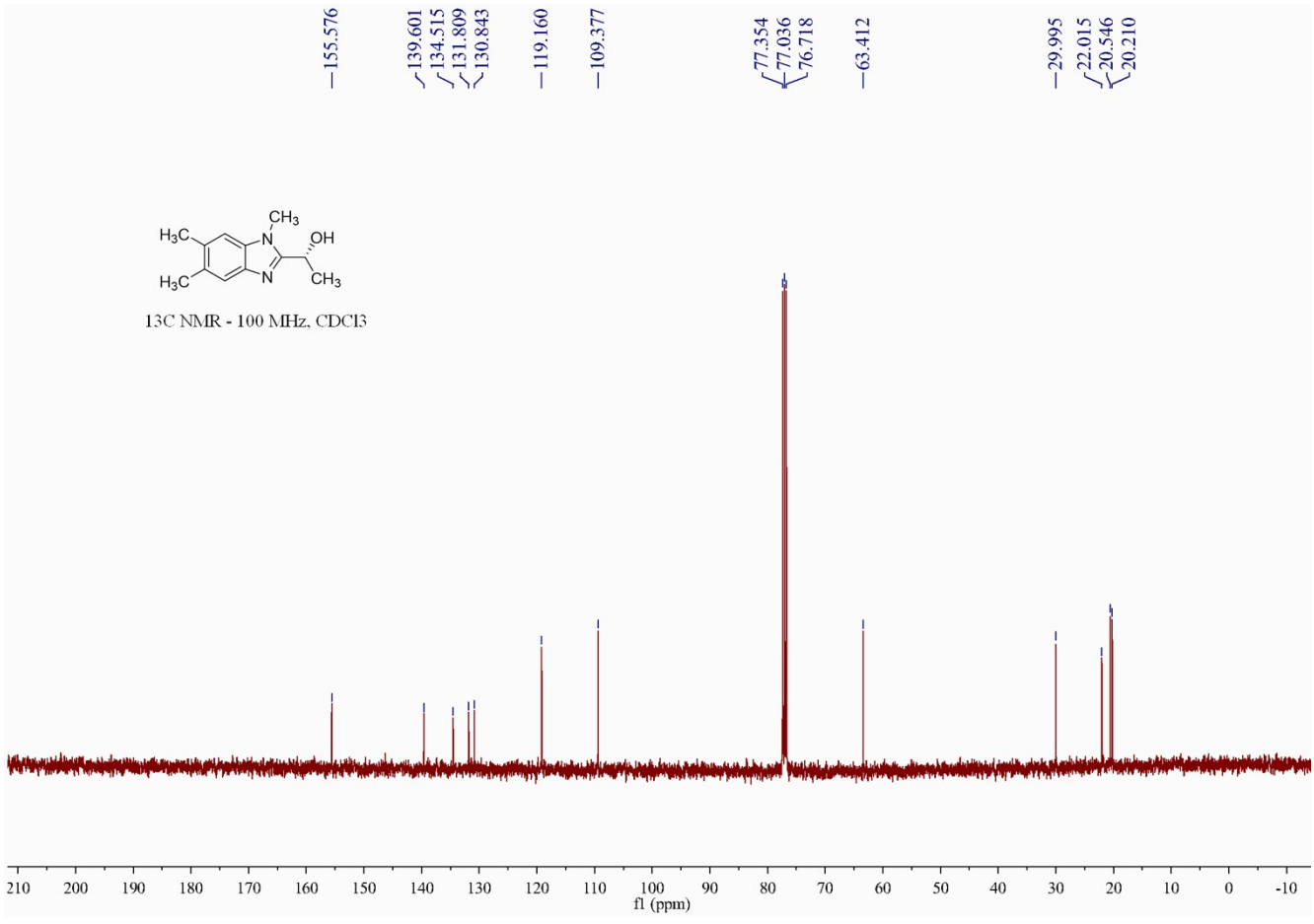
1H NMR - 400 MHz, DMSO-d6



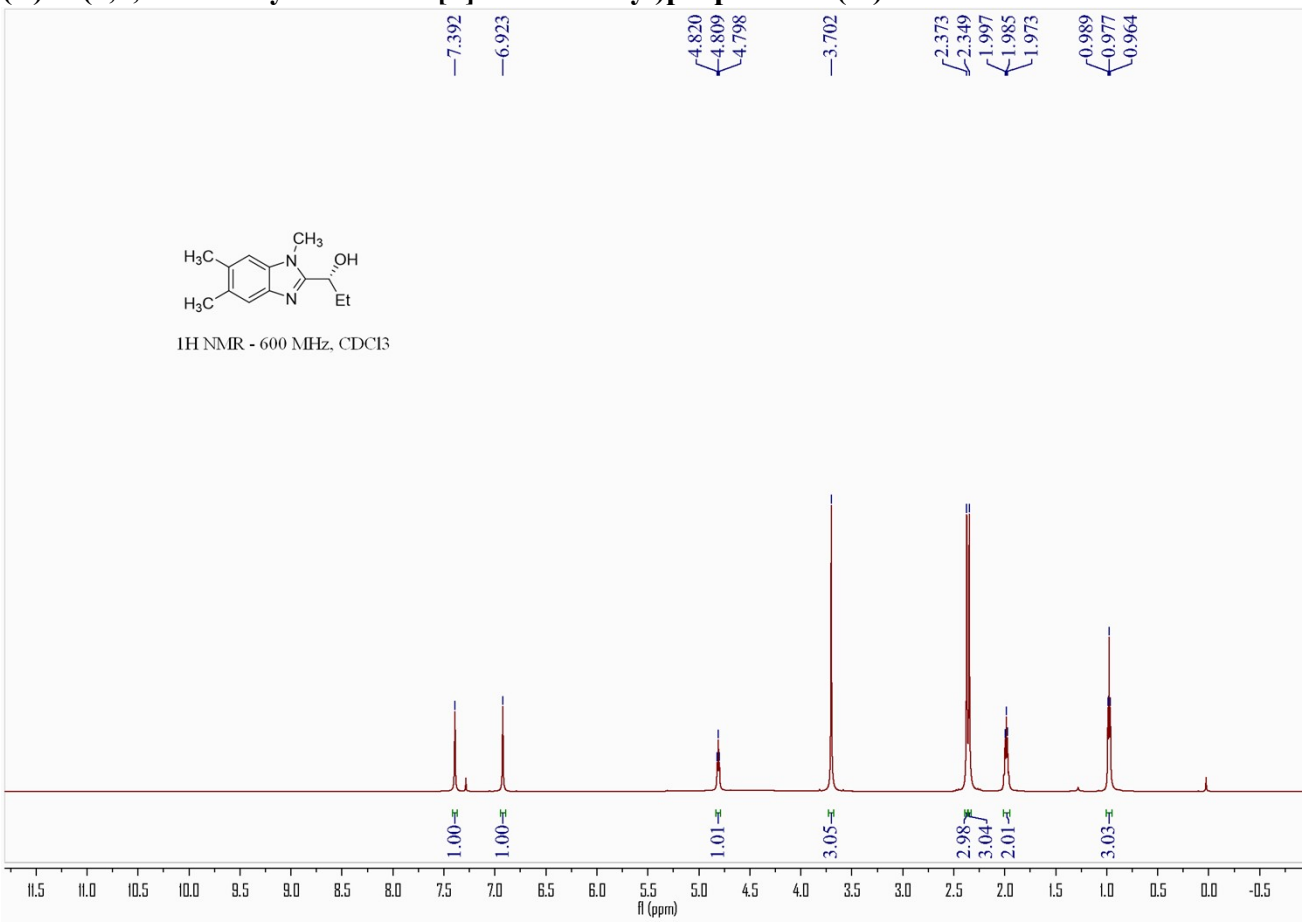
13C NMR - 100 MHz, DMSO-d6

(*R*)-1-(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)ethan-1-ol (2s)

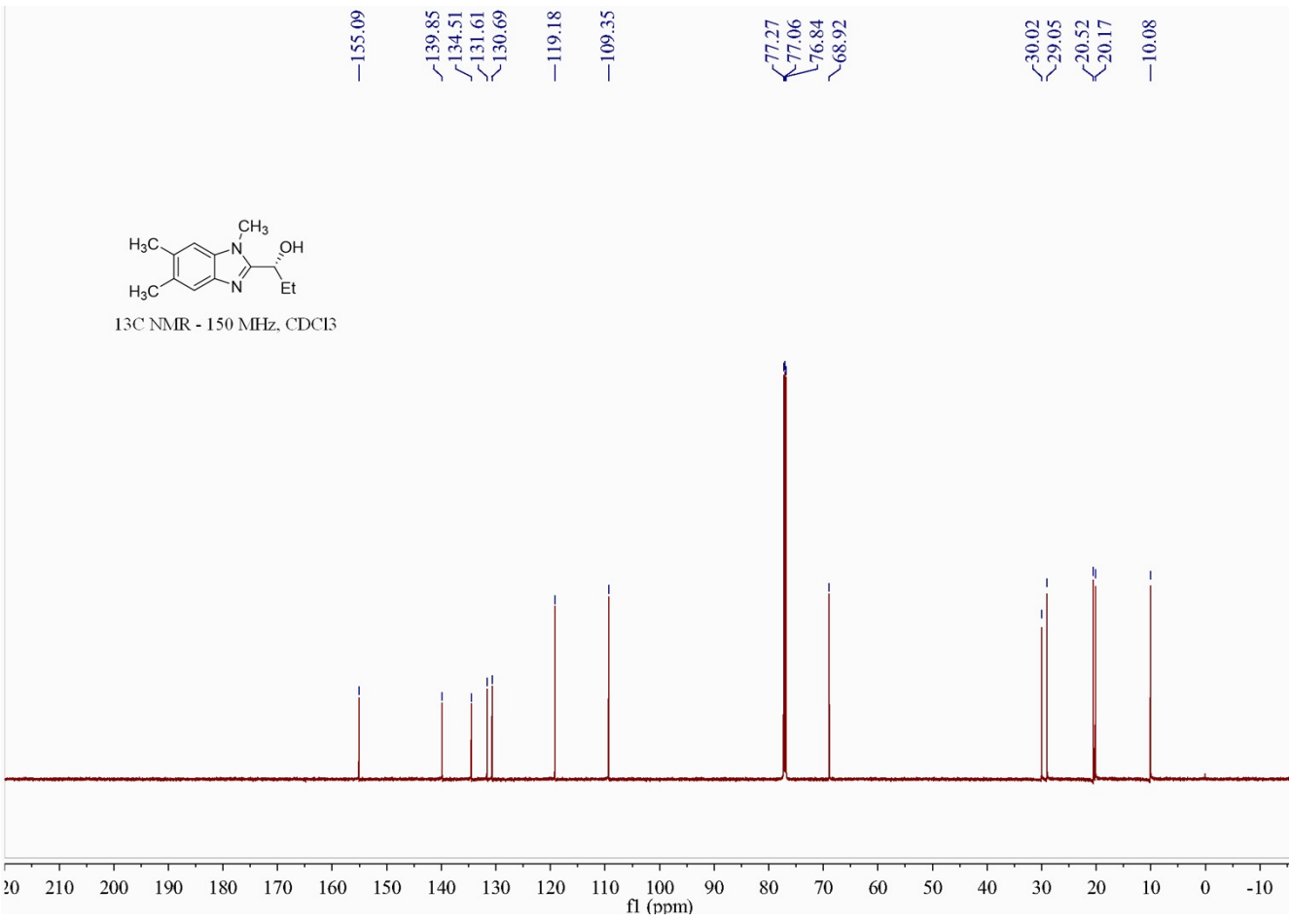




(*R*)-1-(1,5,6-trimethyl-1*H*-benzo[d]imidazol-2-yl)propan-1-ol (2t)

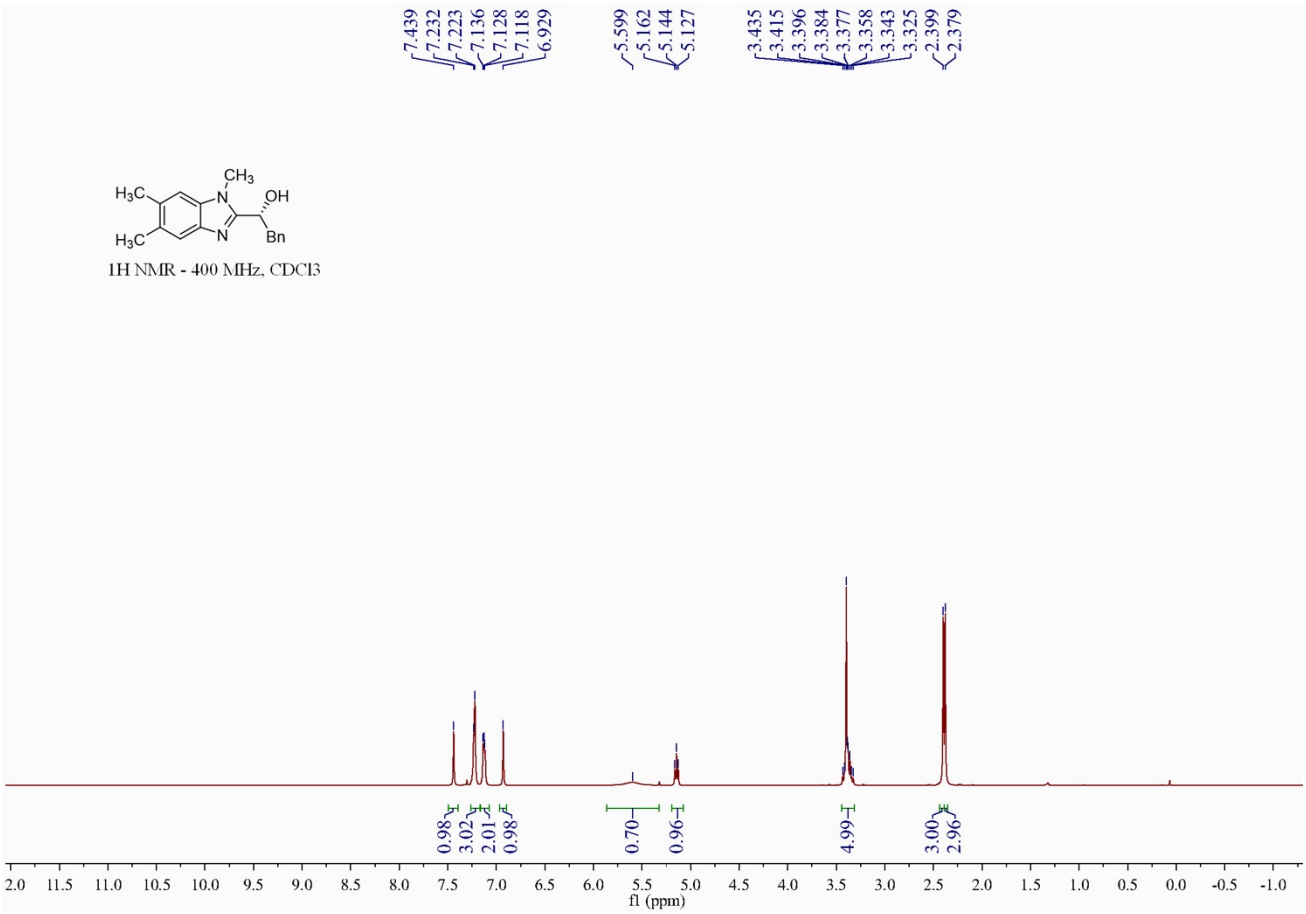


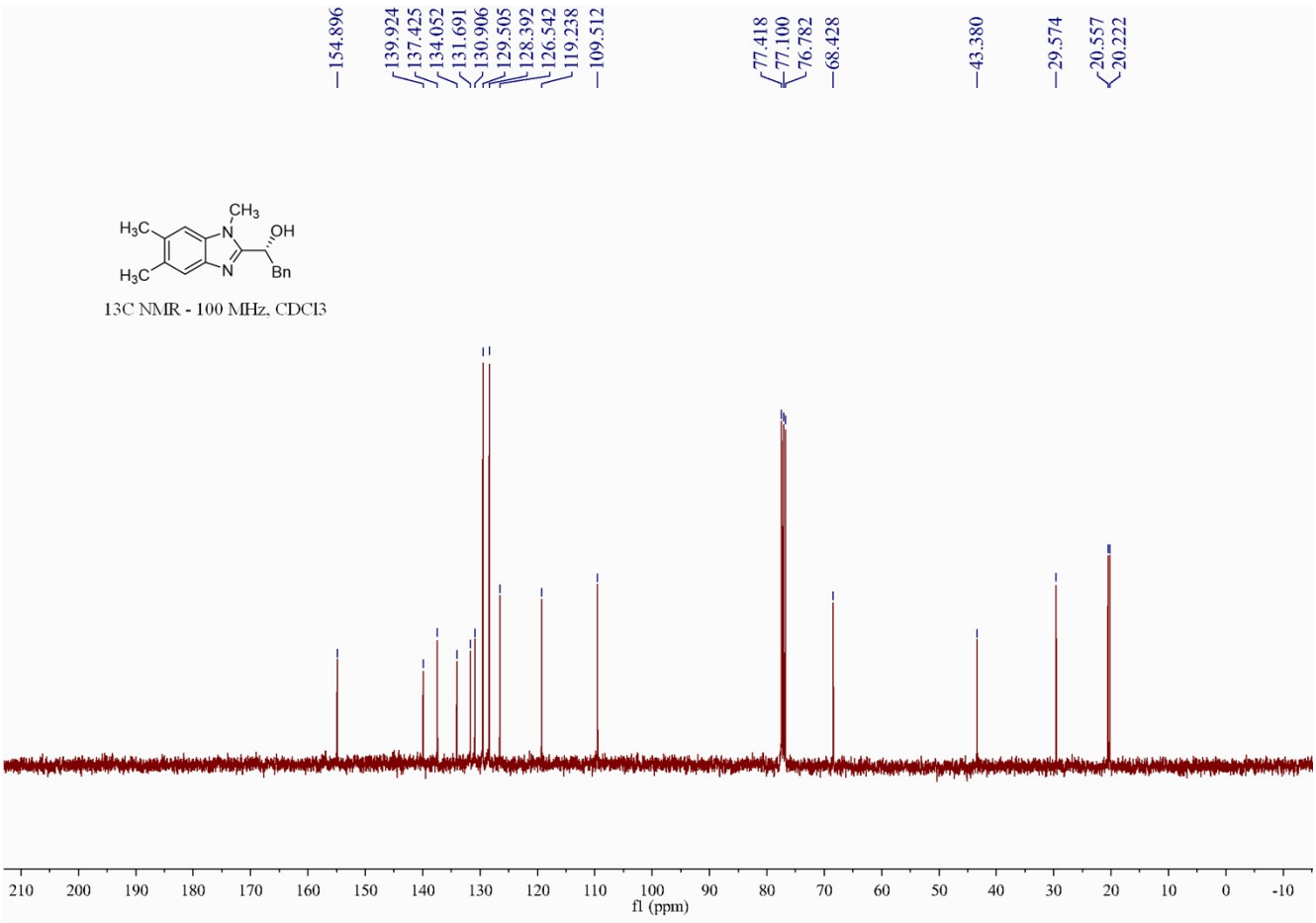
1H NMR - 600 MHz, CDCl3



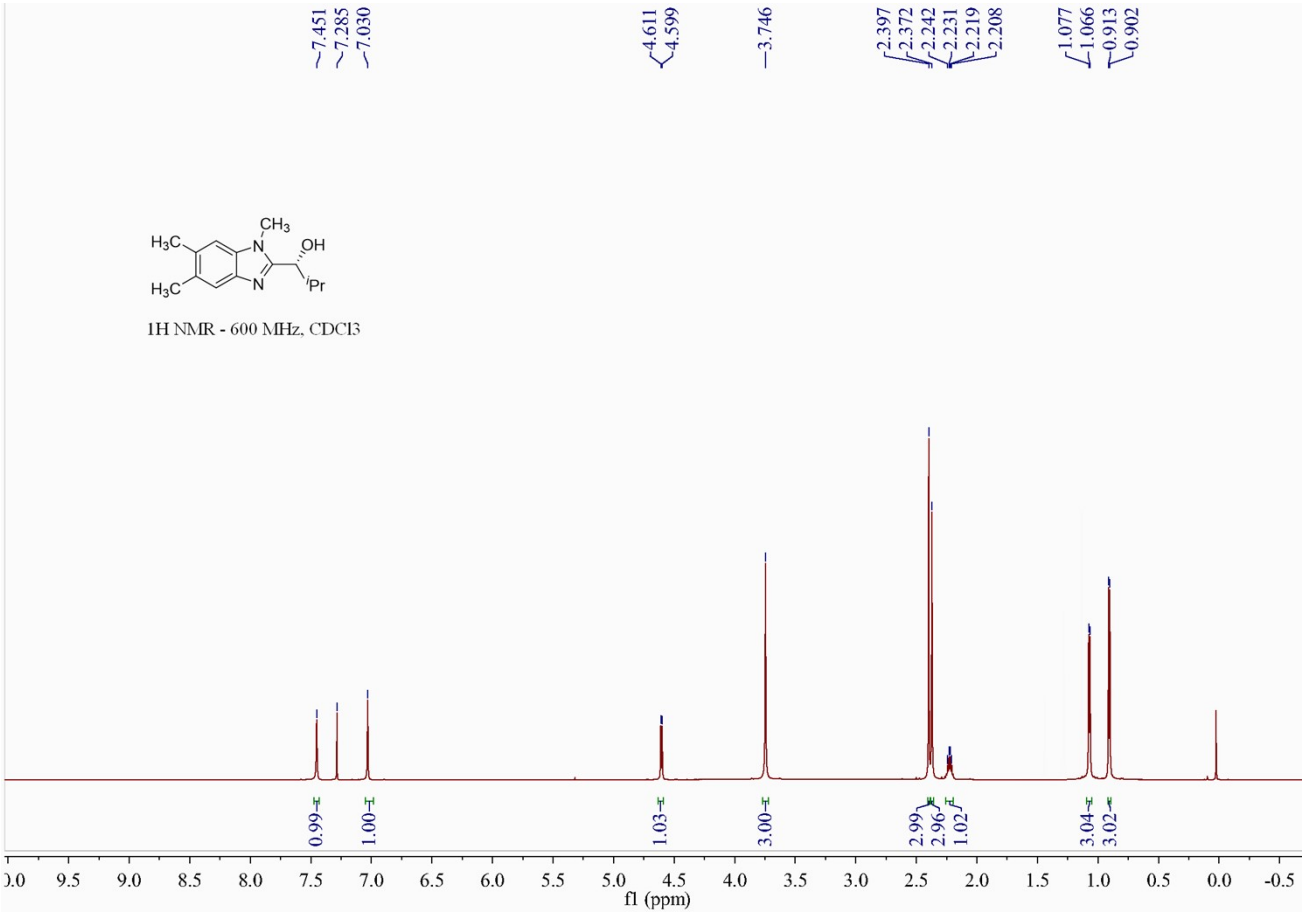
13C NMR - 150 MHz, CDCl3

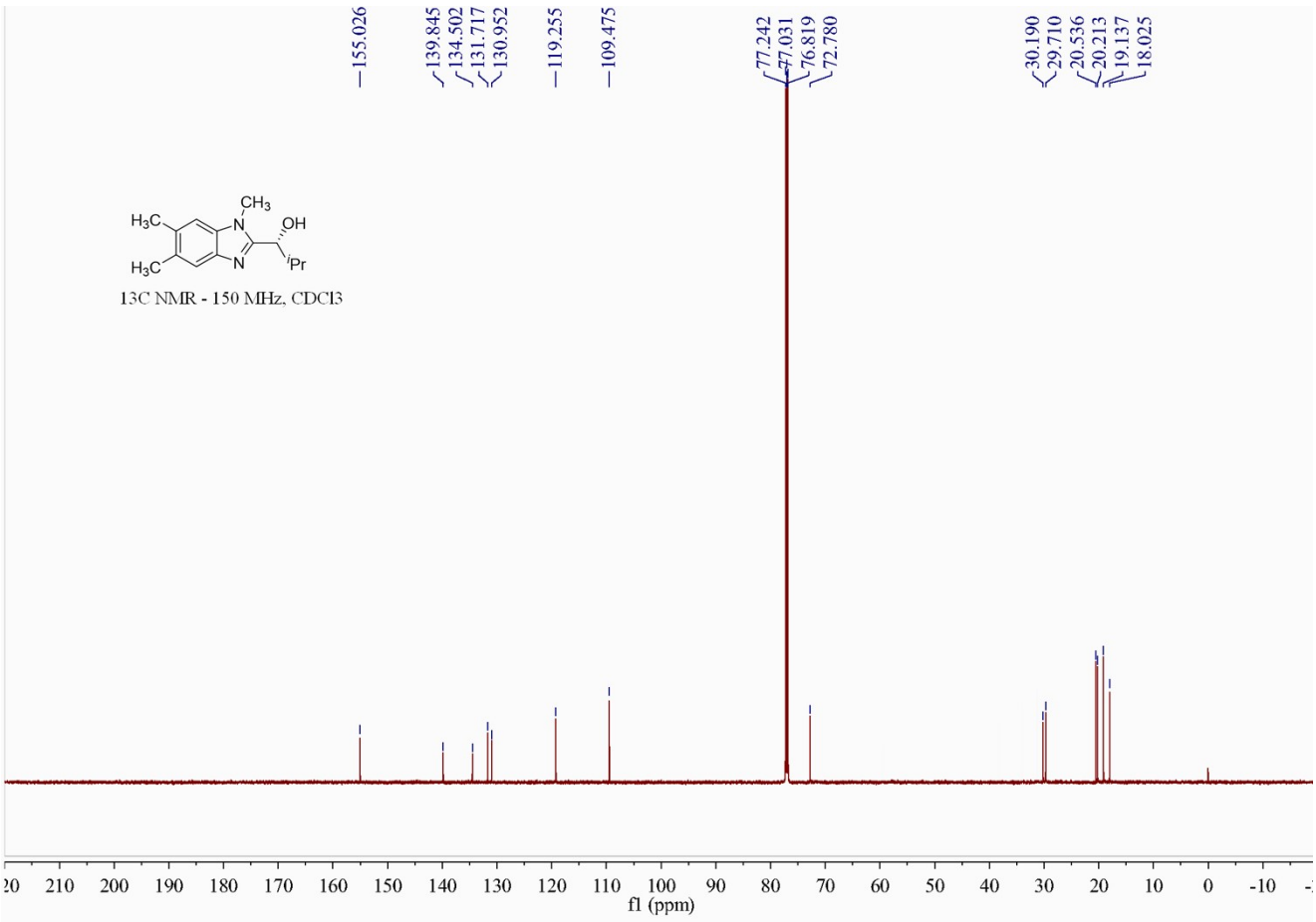
(*R*)-2-phenyl-1-(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)ethan-1-ol (2u)



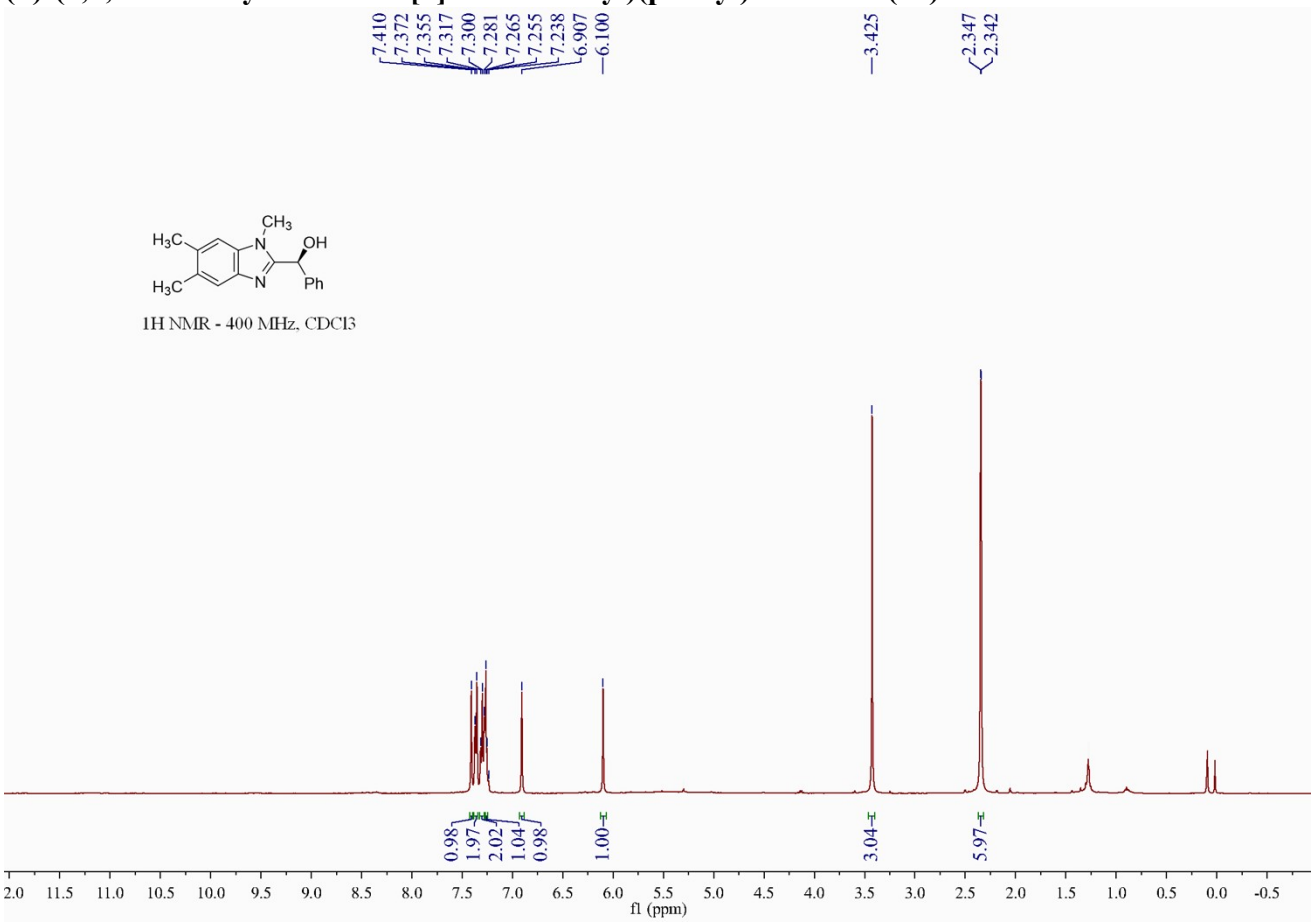


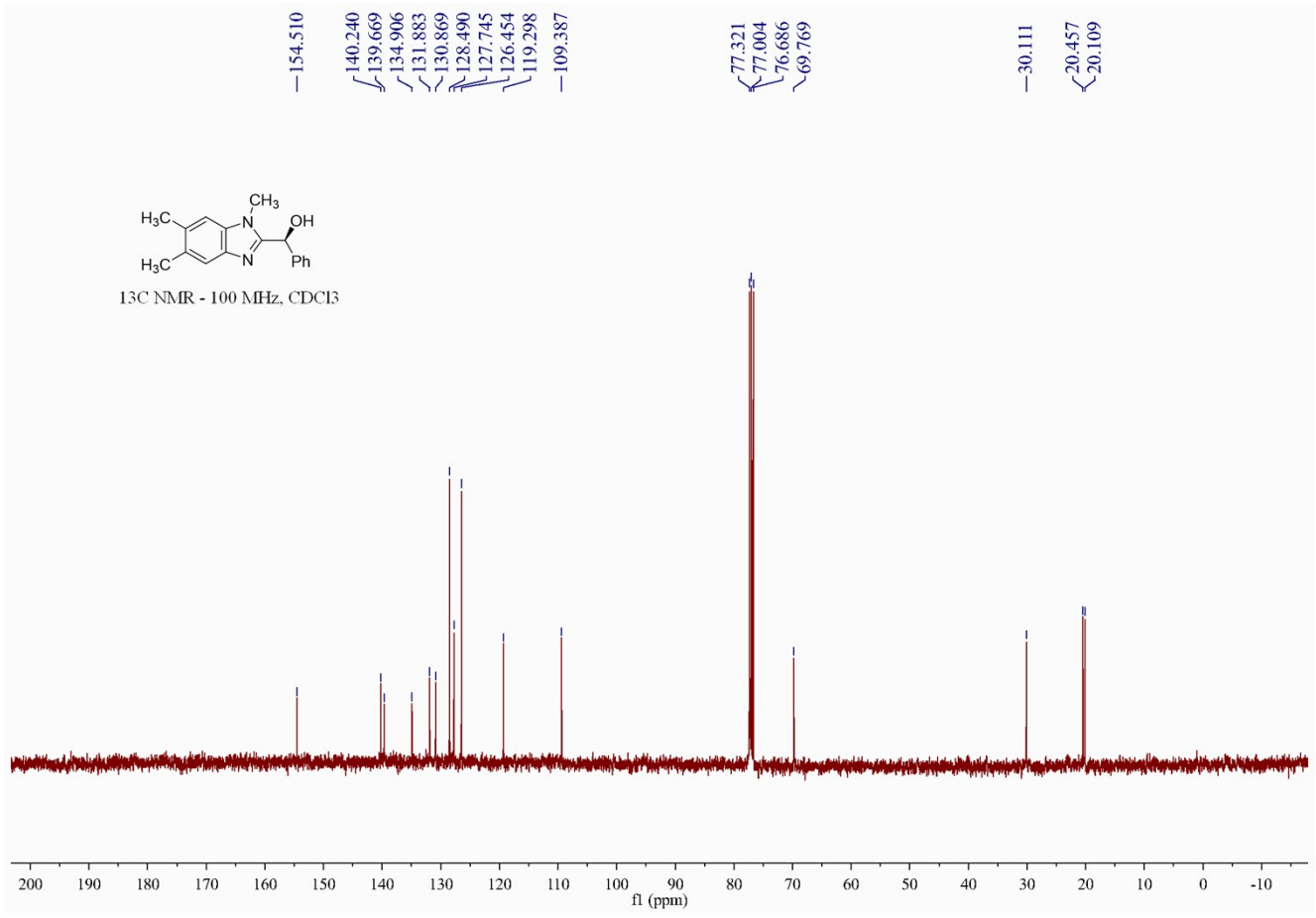
(*R*)-2-methyl-1-(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)propan-1-ol (2v)



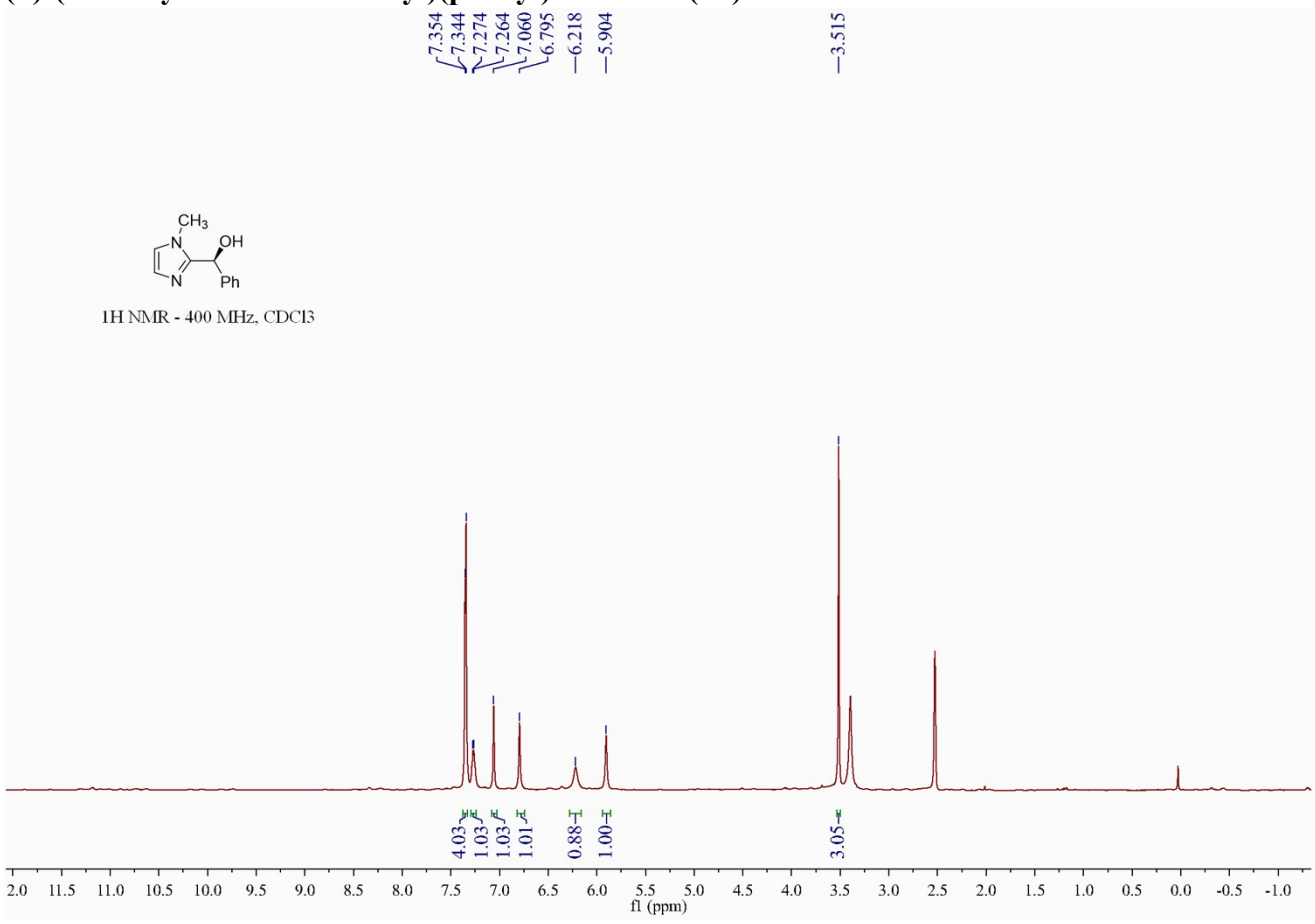


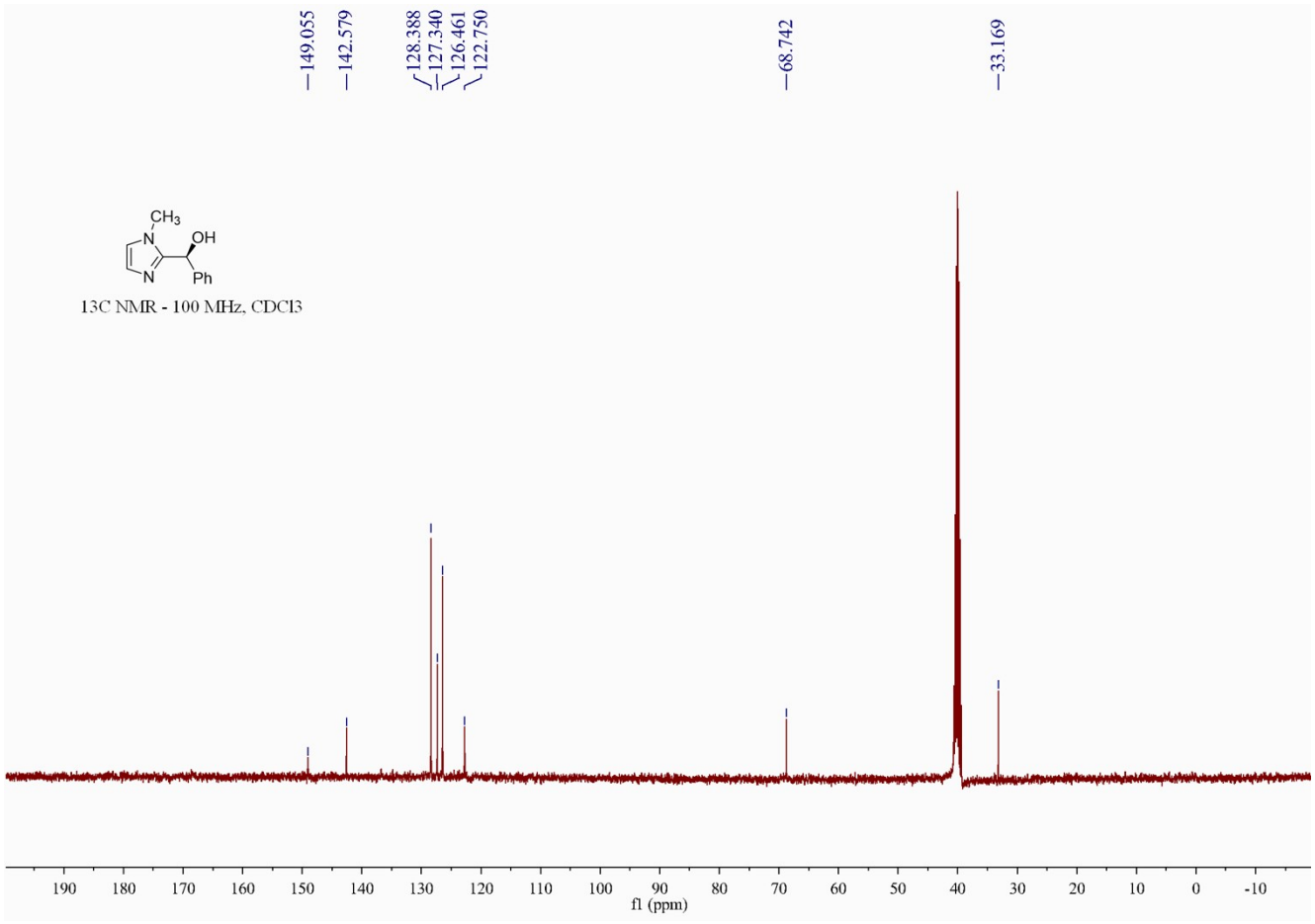
(*S*)-(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)(phenyl)methanol (3a)





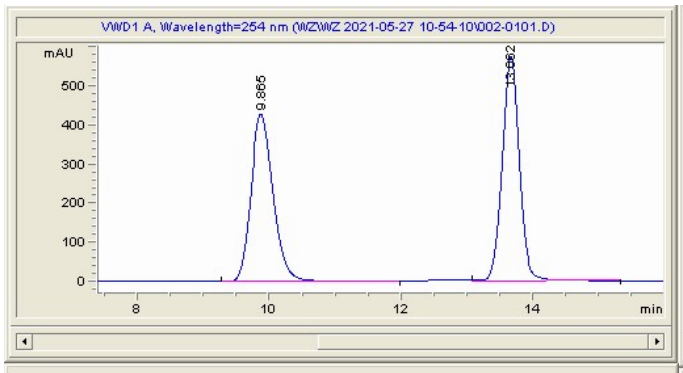
(*S*)-(1-methyl-1*H*-imidazol-2-yl)(phenyl)methanol (3h)



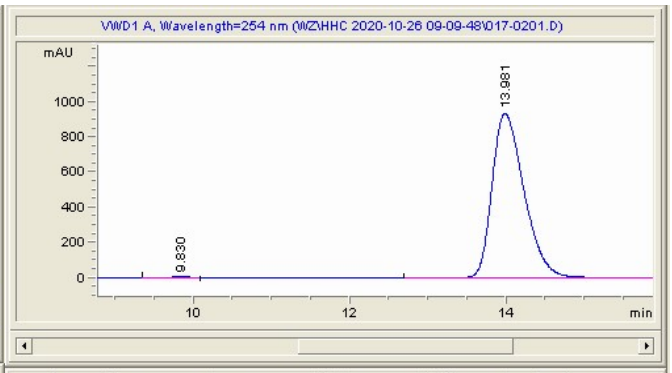


VII. Copies of HPLC charts of chiral alcohols 2a-2v, 3a, 3h

(*R*)-phenyl(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2a)

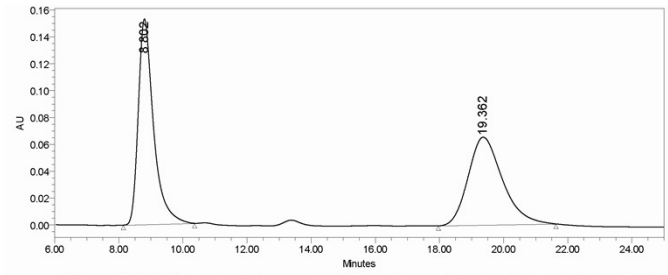


#	Time	Area	Height	Width	Area%	Symmetry
1	9.865	10094.3	427.6	0.3628	49.624	0.801
2	13.662	10247.4	575.4	0.2718	50.376	0.955



#	Time	Area	Height	Width	Area%	Symmetry
1	9.83	121.8	5.9	0.3125	0.455	1.04
2	13.981	26650	935.3	0.4373	99.545	0.639

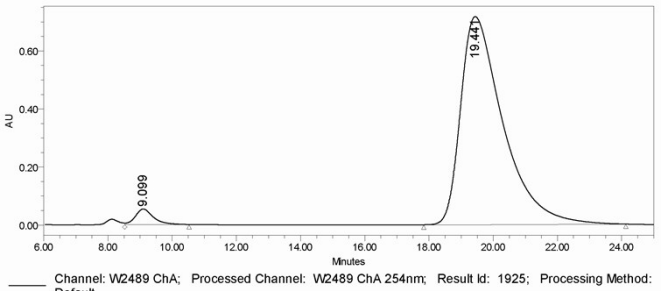
(*R*)-(5,6-dimethyl-1*H*-benzo[*d*]imidazol-2-yl)(phenyl)methanol (2b)



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2021; Processing Method: wz

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.802	5085861	51.04	153058
2	W2489 ChA 254nm	19.362	4878018	48.96	65422

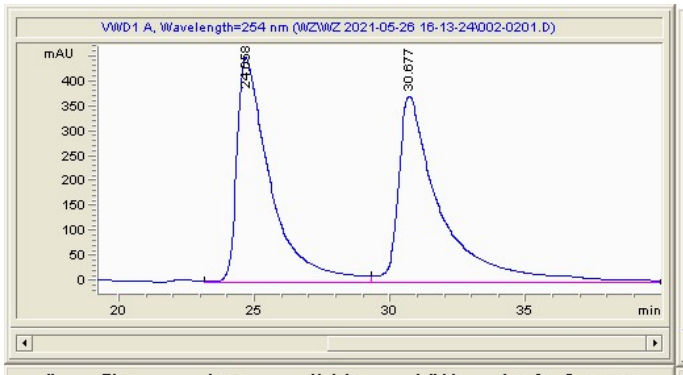


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1925; Processing Method: Default

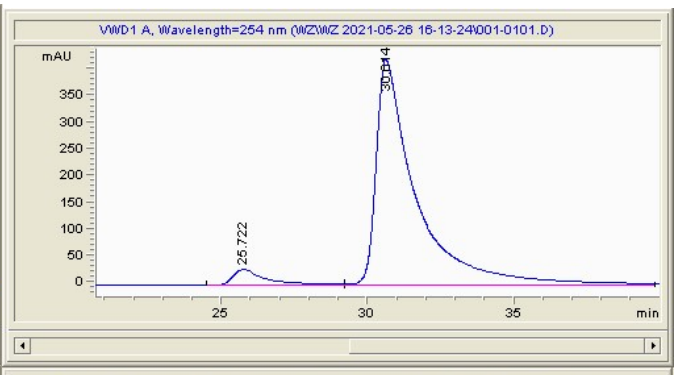
Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	9.099	2099800	3.10	53827
2	W2489 ChA 254nm	19.441	65737065	96.90	716690

(*R*)-(1-benzyl-5,6-dimethyl-1*H*-benzo[*d*]imidazol-2-yl)(phenyl)methanol (2c)

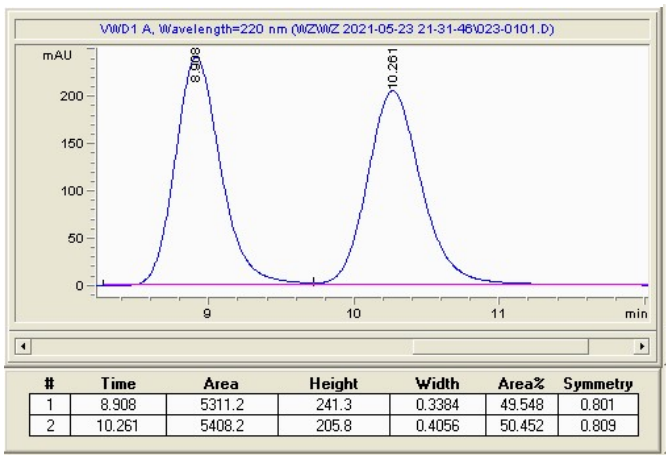


#	Time	Area	Height	Width	Area%	Symmetry
1	24.658	38863.1	452	1.2128	48.739	0.336
2	30.677	40874.6	372.7	1.5125	51.261	0.308

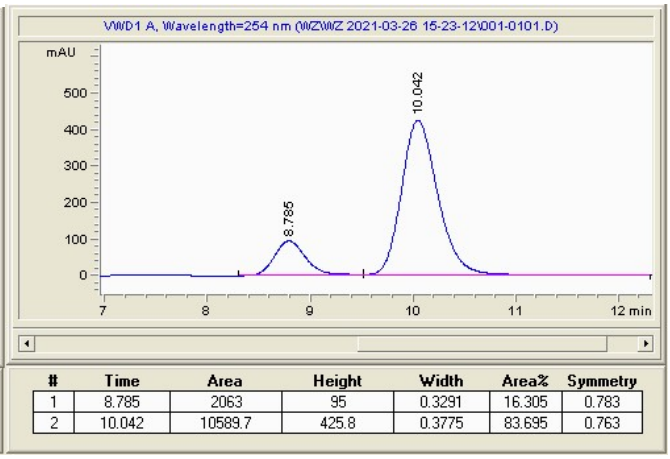


#	Time	Area	Height	Width	Area%	Symmetry
1	25.722	2610.3	30	1.2136	5.939	0.373
2	30.614	41339.9	423.7	1.342	94.061	0.302

(*R*)-(5,6-dimethyl-1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)(phenyl)methanol (2d)

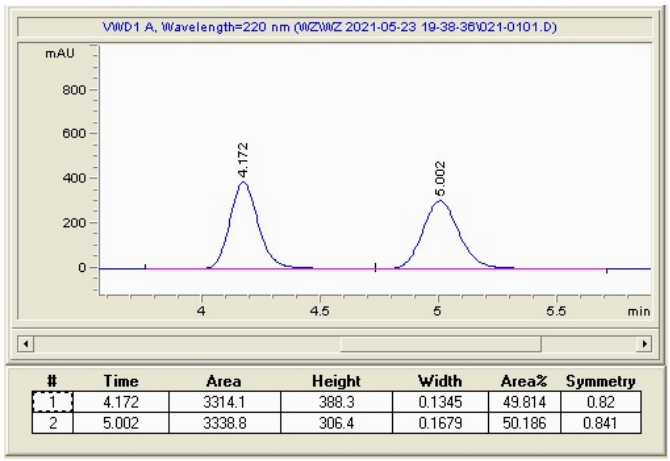


#	Time	Area	Height	Width	Area%	Symmetry
1	8.908	5311.2	241.3	0.3384	49.548	0.801
2	10.261	5408.2	205.8	0.4056	50.452	0.809

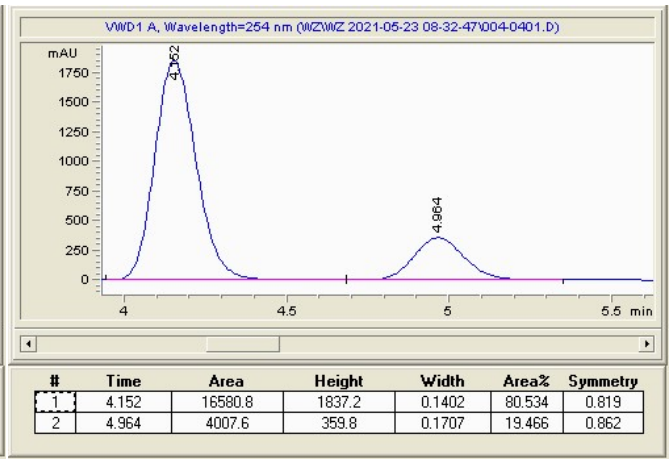


#	Time	Area	Height	Width	Area%	Symmetry
1	8.785	2063	95	0.3291	16.305	0.783
2	10.042	10589.7	425.8	0.3775	83.695	0.763

(*R*)-(1-isopropyl-5,6-dimethyl-1*H*-benzo[*d*]imidazol-2-yl)(phenyl)methanol (2e)

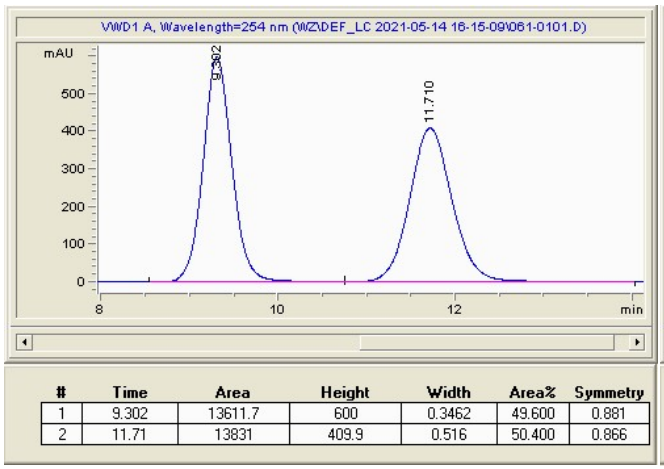


#	Time	Area	Height	Width	Area%	Symmetry
1	4.172	3314.1	388.3	0.1345	49.814	0.82
2	5.002	3338.8	306.4	0.1679	50.186	0.841

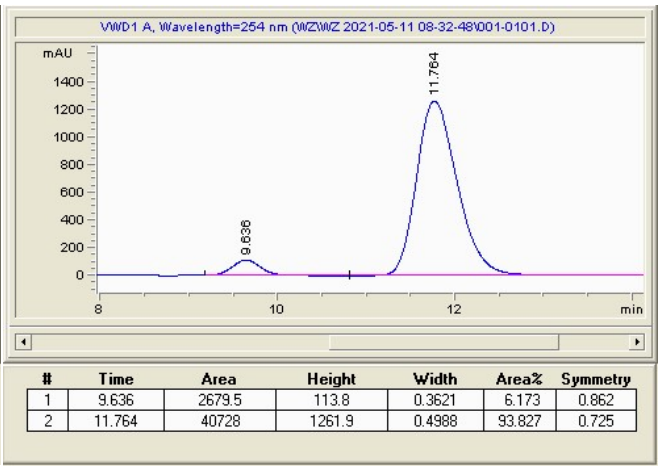


#	Time	Area	Height	Width	Area%	Symmetry
1	4.152	16580.8	1837.2	0.1402	80.534	0.819
2	4.964	4007.6	359.8	0.1707	19.466	0.862

(*R*)-(1-methyl-1*H*-benzo[*d*]imidazol-2-yl)(phenyl)methanol (2f)

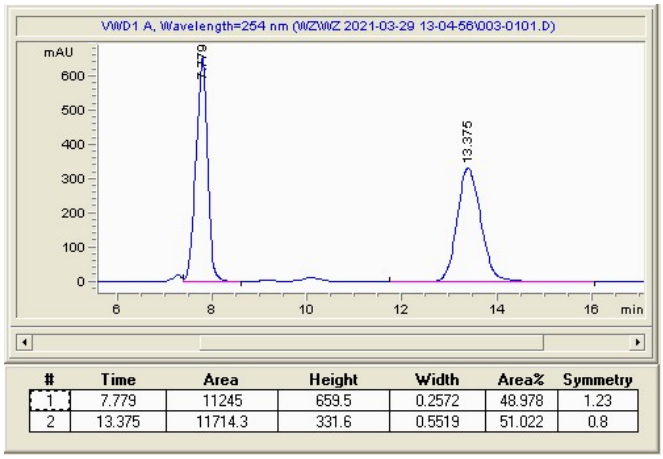


#	Time	Area	Height	Width	Area%	Symmetry
1	9.302	13611.7	600	0.3462	49.600	0.881
2	11.71	13831	409.9	0.516	50.400	0.866

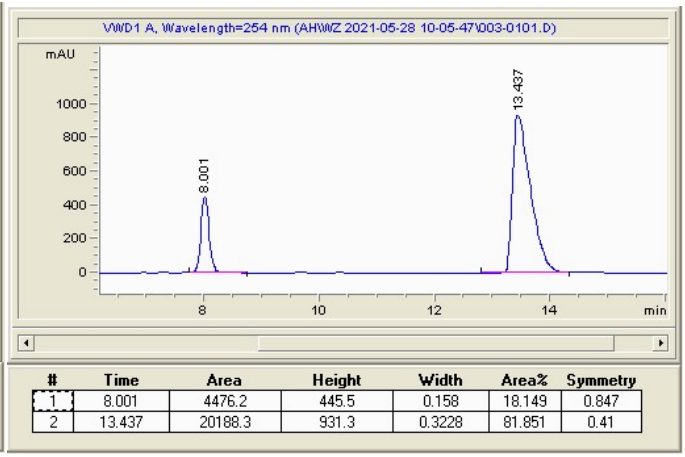


#	Time	Area	Height	Width	Area%	Symmetry
1	9.636	2679.5	113.8	0.3621	6.173	0.862
2	11.764	40728	1261.9	0.4988	93.827	0.725

(*R*)-(5,6-difluoro-1-methyl-1*H*-benzo[*d*]imidazol-2-yl)(phenyl)methanol (2g)

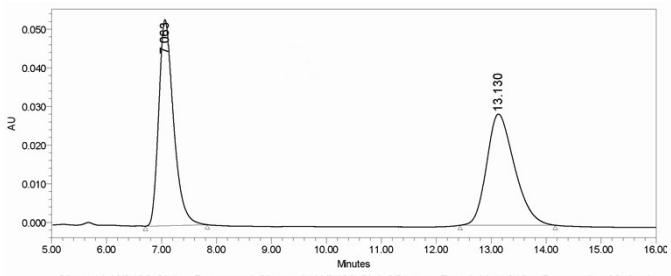


#	Time	Area	Height	Width	Area%	Symmetry
1	7.779	11245	659.5	0.2572	48.978	1.23
2	13.375	11714.3	331.6	0.5519	51.022	0.8



#	Time	Area	Height	Width	Area%	Symmetry
1	8.001	4476.2	445.5	0.158	18.149	0.847
2	13.437	20188.3	931.3	0.3228	81.851	0.41

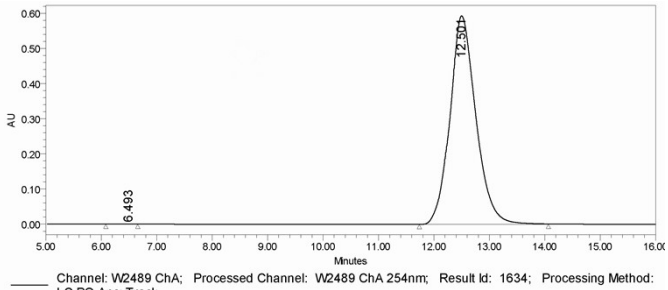
(*R*)-(1-methyl-1*H*-imidazol-2-yl)(phenyl)methanol (2h)



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1619; Processing Method: LC PQ ApexTrack

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.063	1007188	49.80	53306
2	W2489 ChA 254nm	13.130	1015164	50.20	28774

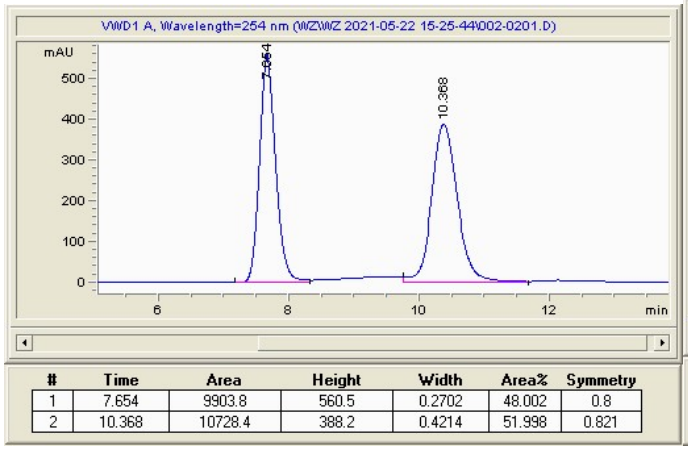


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1634; Processing Method: LC PQ ApexTrack

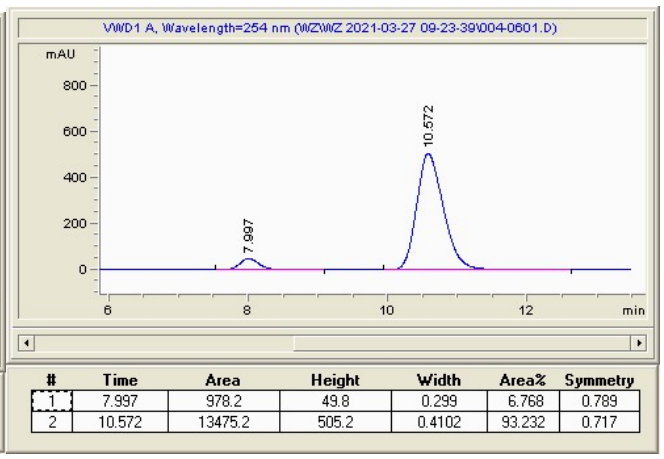
Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.493	3642	0.02	228
2	W2489 ChA 254nm	12.501	19248847	99.98	593014

(*R*)-*p*-tolyl(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2i)

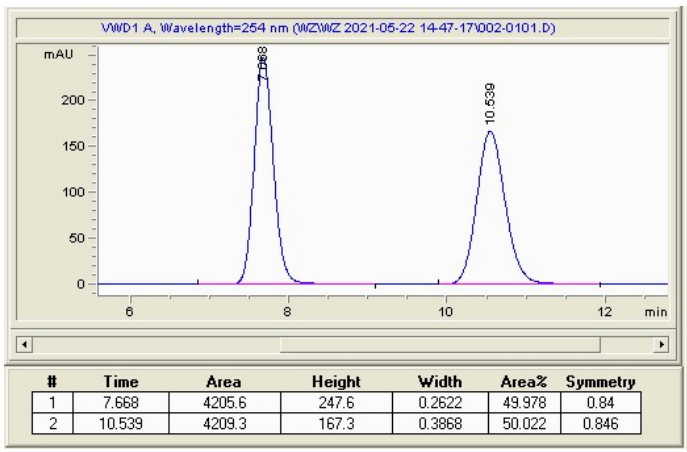


#	Time	Area	Height	Width	Area%	Symmetry
1	7.654	9903.8	560.5	0.2702	48.002	0.8
2	10.368	10728.4	388.2	0.4214	51.998	0.821

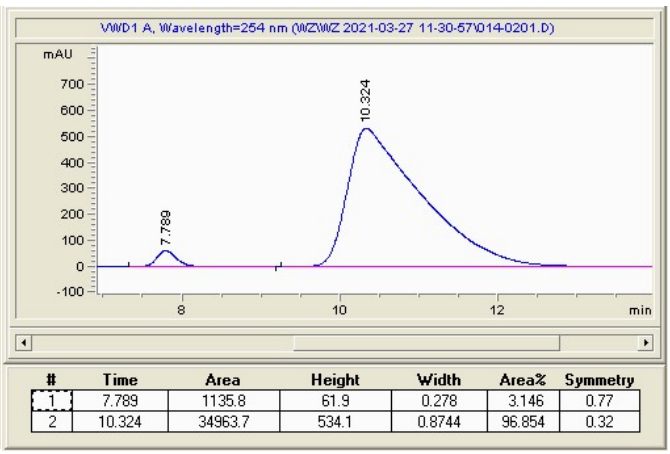


#	Time	Area	Height	Width	Area%	Symmetry
1	7.997	978.2	49.8	0.299	6.768	0.789
2	10.572	13475.2	505.2	0.4102	93.232	0.717

(*R*)-(4-fluorophenyl)(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2j)

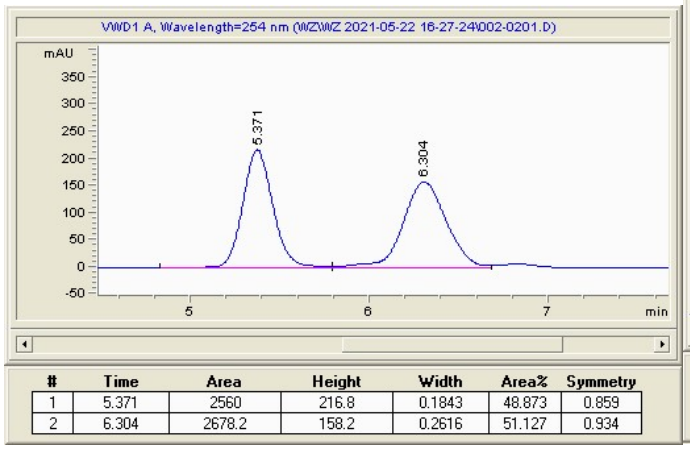


#	Time	Area	Height	Width	Area%	Symmetry
1	7.668	4205.6	247.6	0.2622	49.978	0.84
2	10.539	4209.3	167.3	0.3868	50.022	0.846

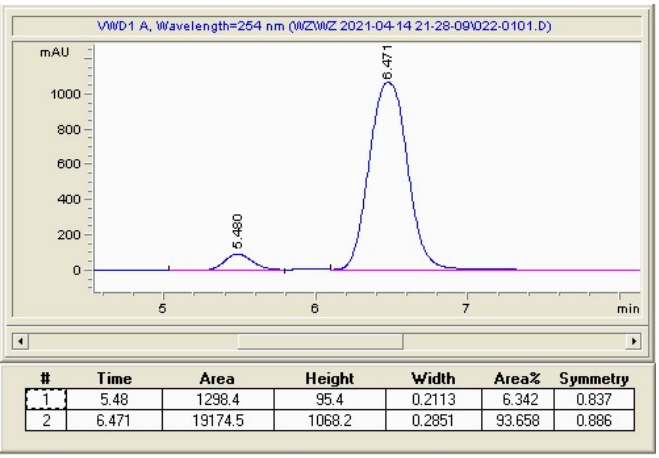


#	Time	Area	Height	Width	Area%	Symmetry
1	7.789	1135.8	61.9	0.278	3.146	0.77
2	10.324	34963.7	534.1	0.8744	96.854	0.32

(*R*)-(4-chlorophenyl)(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2k)

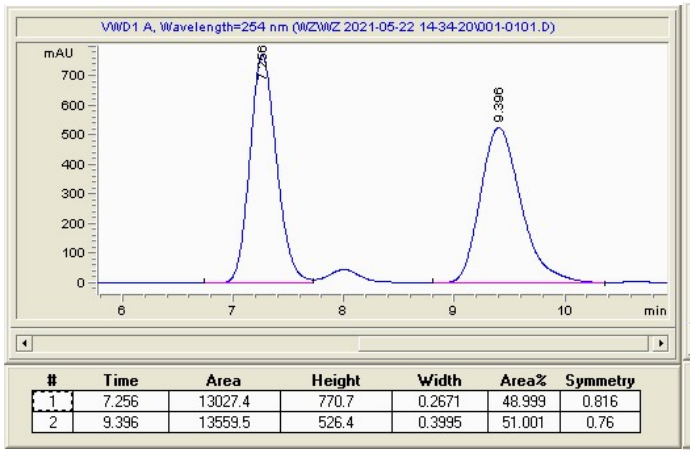


#	Time	Area	Height	Width	Area%	Symmetry
1	5.371	2560	216.8	0.1843	48.873	0.859
2	6.304	2678.2	158.2	0.2616	51.127	0.934

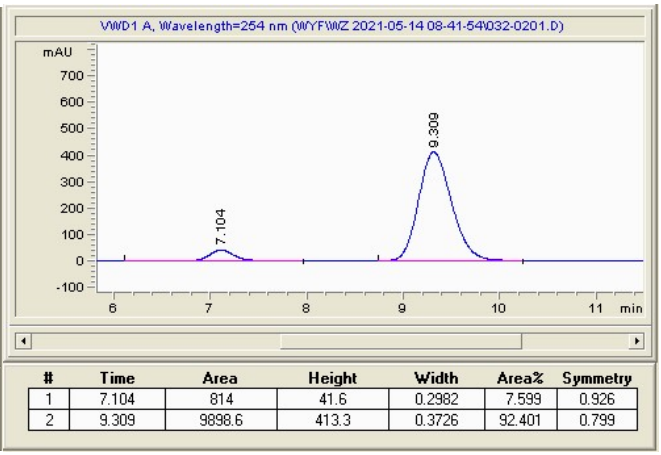


#	Time	Area	Height	Width	Area%	Symmetry
1	5.48	1298.4	95.4	0.2113	6.342	0.837
2	6.471	19174.5	1068.2	0.2851	93.658	0.886

(*R*)-(4-(trifluoromethyl)phenyl)(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2l)

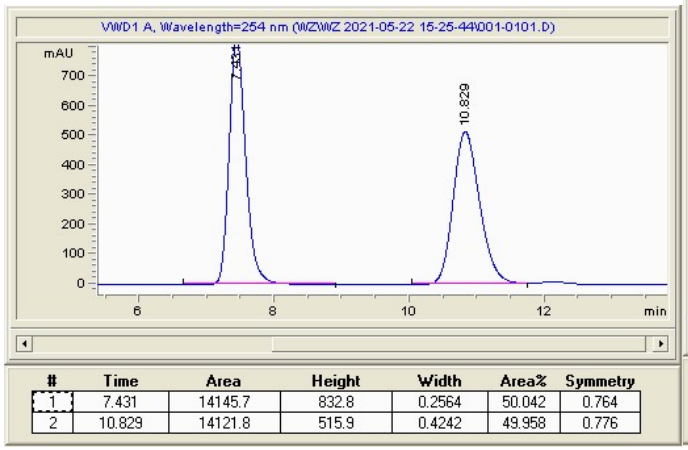


#	Time	Area	Height	Width	Area%	Symmetry
1	7.256	13027.4	770.7	0.2671	48.999	0.816
2	9.396	13559.5	526.4	0.3995	51.001	0.76

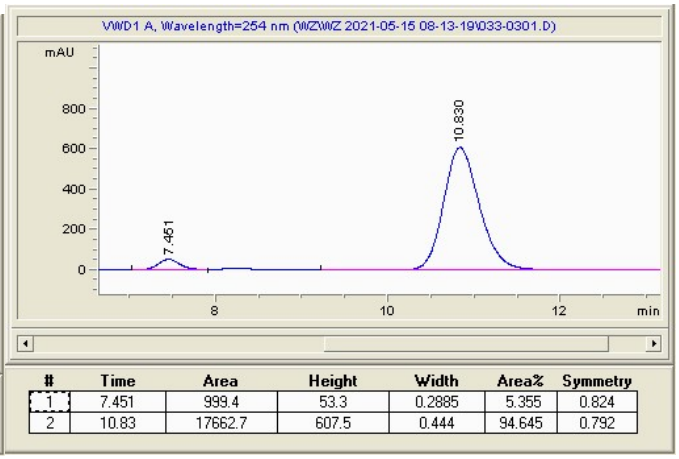


#	Time	Area	Height	Width	Area%	Symmetry
1	7.104	814	41.6	0.2982	7.599	0.926
2	9.309	9898.6	413.3	0.3726	92.401	0.799

(*R*)-*m*-tolyl(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2m)

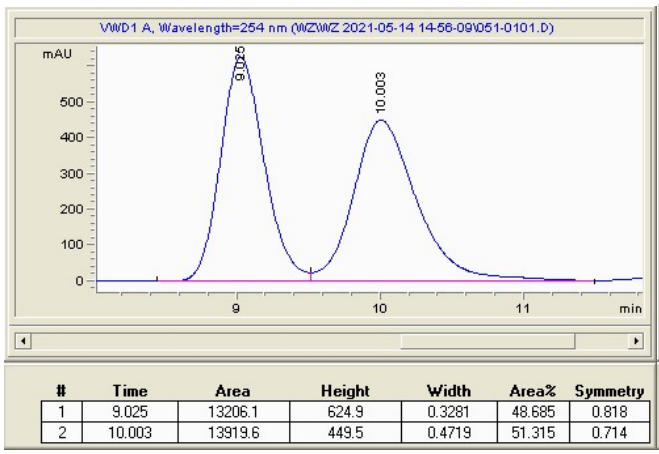


#	Time	Area	Height	Width	Area%	Symmetry
1	7.431	14145.7	832.8	0.2564	50.042	0.764
2	10.829	14121.8	515.9	0.4242	49.958	0.776

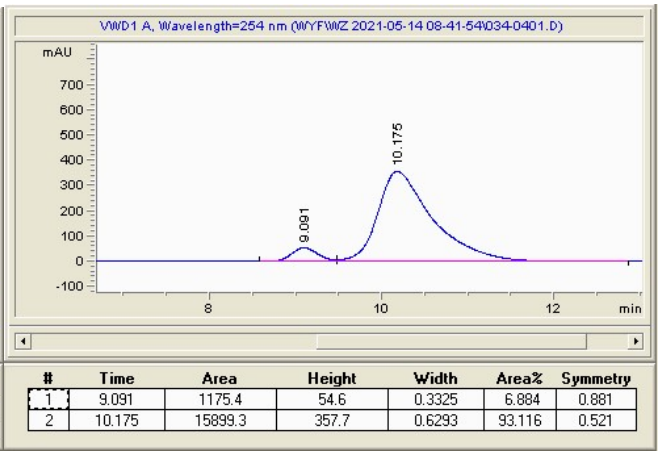


#	Time	Area	Height	Width	Area%	Symmetry
1	7.451	999.4	53.3	0.2885	5.355	0.824
2	10.83	17662.7	607.5	0.444	94.645	0.792

(*R*)-*o*-tolyl(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2n)

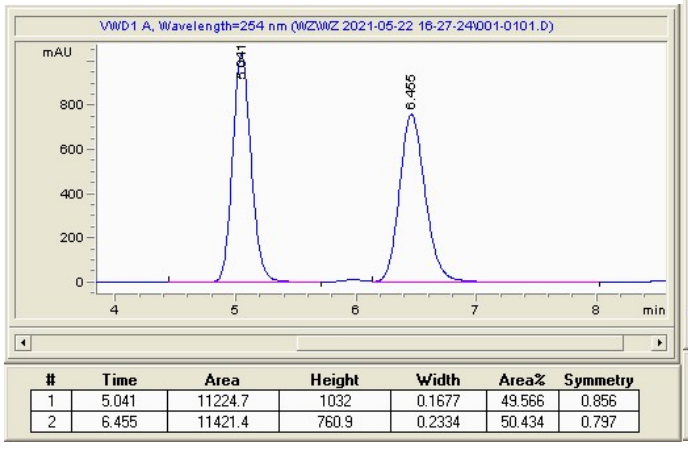


#	Time	Area	Height	Width	Area%	Symmetry
1	9.025	13206.1	624.9	0.3281	48.685	0.818
2	10.003	13919.6	449.5	0.4719	51.315	0.714

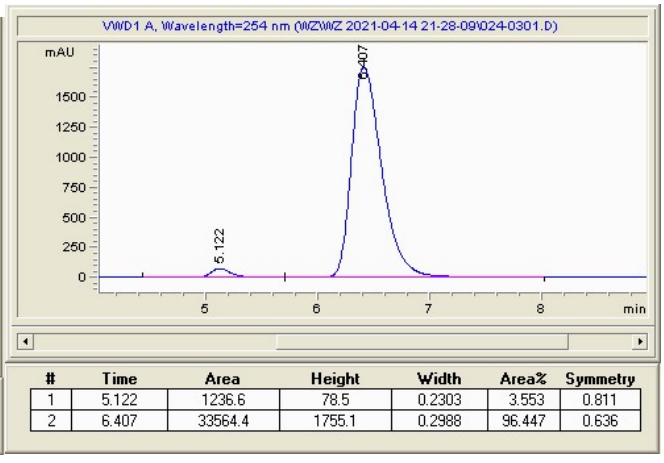


#	Time	Area	Height	Width	Area%	Symmetry
1	9.091	1175.4	54.6	0.3325	6.884	0.881
2	10.175	15899.3	357.7	0.6293	93.116	0.521

(*R*)-(3,5-dimethylphenyl)(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2o)

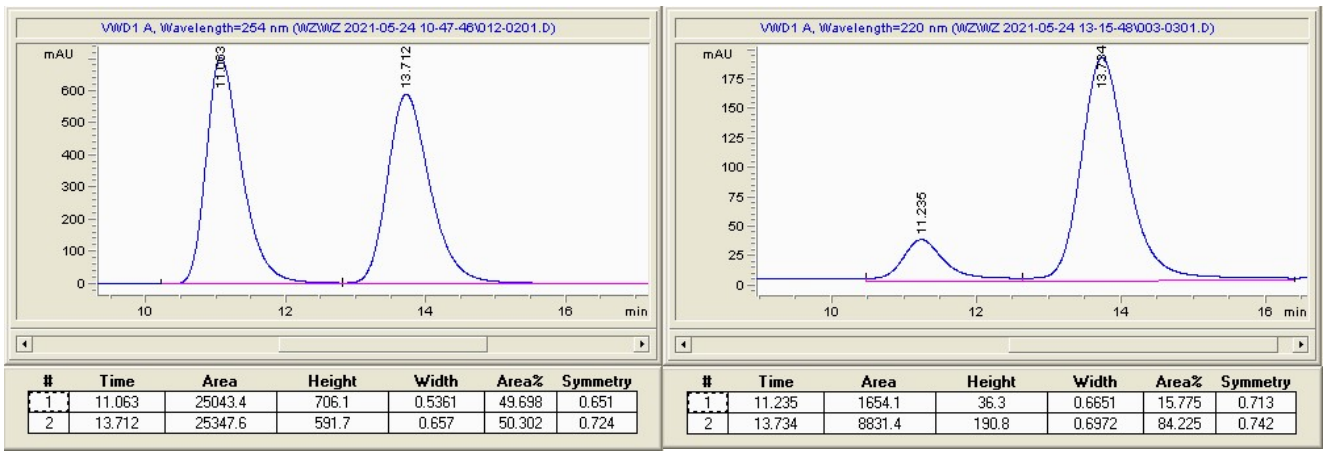


#	Time	Area	Height	Width	Area%	Symmetry
1	5.041	11224.7	1032	0.1677	49.566	0.856
2	6.455	11421.4	760.9	0.2334	50.434	0.797



#	Time	Area	Height	Width	Area%	Symmetry
1	5.122	1236.6	78.5	0.2303	3.553	0.811
2	6.407	33564.4	1755.1	0.2988	96.447	0.636

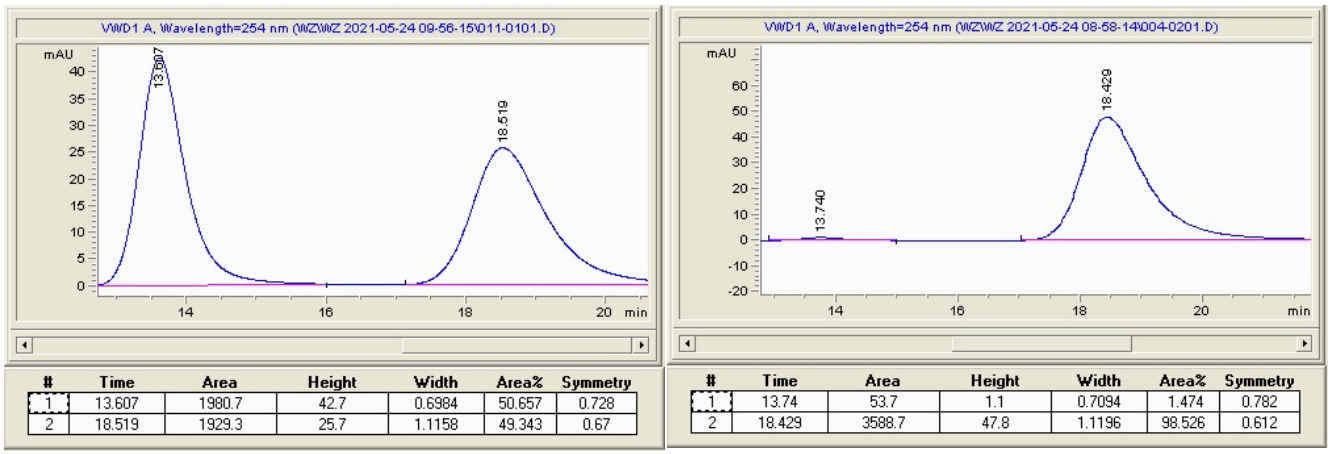
(*R*)-[1,1'-biphenyl]-4-yl(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2p)



#	Time	Area	Height	Width	Area%	Symmetry
1	11.063	25043.4	706.1	0.5361	49.698	0.651
2	13.712	25347.6	591.7	0.657	50.302	0.724

#	Time	Area	Height	Width	Area%	Symmetry
1	11.235	1654.1	36.3	0.6651	15.775	0.713
2	13.734	8831.4	190.8	0.6972	84.225	0.742

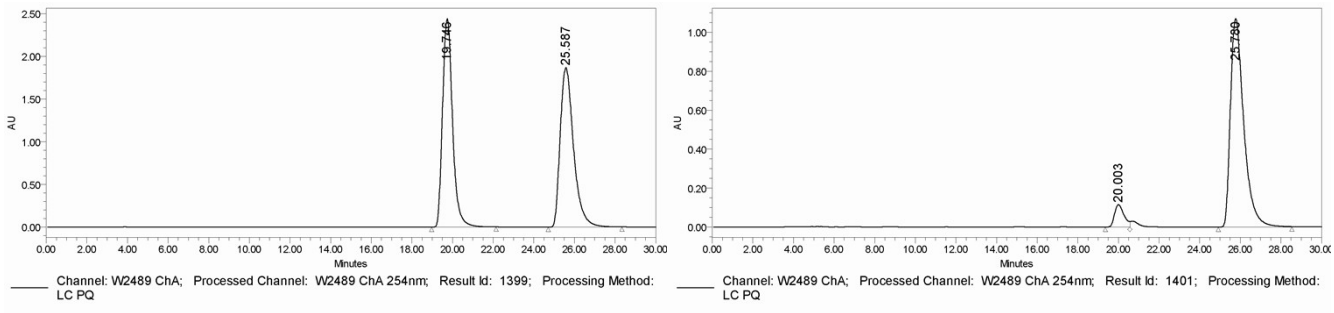
(*R*)-pyridin-4-yl(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2q)



#	Time	Area	Height	Width	Area%	Symmetry
1	13.607	1980.7	42.7	0.6984	50.657	0.728
2	18.519	1929.3	25.7	1.1158	49.343	0.67

#	Time	Area	Height	Width	Area%	Symmetry
1	13.74	53.7	1.1	0.7094	1.474	0.782
2	18.429	3588.7	47.8	1.1196	98.526	0.612

(*R*)-pyridin-3-yl(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)methanol (2r)



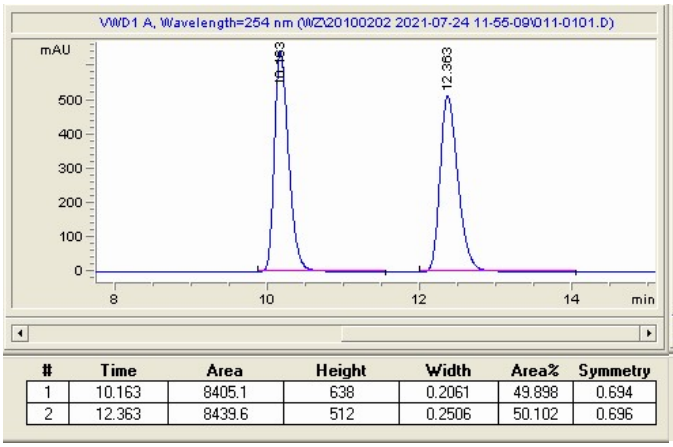
Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	19.746	83714060	49.50	2440608
2	W2489 ChA 254nm	25.587	85415159	50.50	1867632

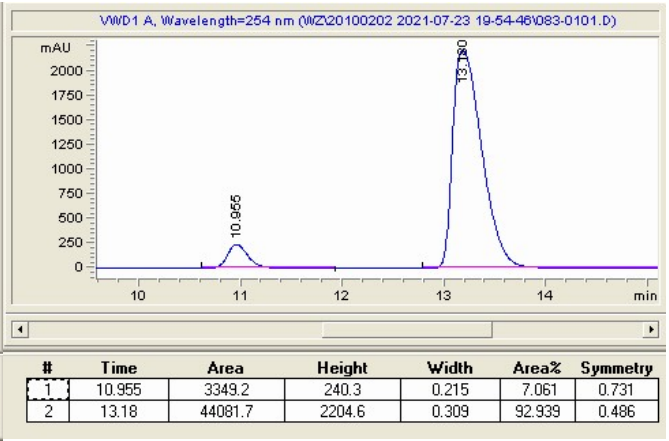
Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	20.003	3744816	7.12	115140
2	W2489 ChA 254nm	25.780	48815984	92.88	1069426

(*R*)-1-(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)ethan-1-ol (2s)

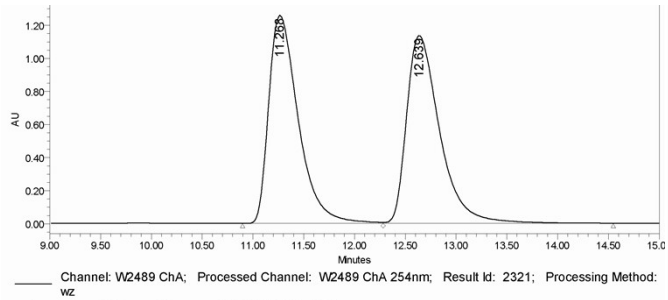


#	Time	Area	Height	Width	Area%	Symmetry
1	10.163	8405.1	638	0.2061	49.898	0.694
2	12.363	8439.6	512	0.2506	50.102	0.696



#	Time	Area	Height	Width	Area%	Symmetry
1	10.955	3349.2	240.3	0.215	7.061	0.731
2	13.18	44081.7	2204.6	0.309	92.939	0.486

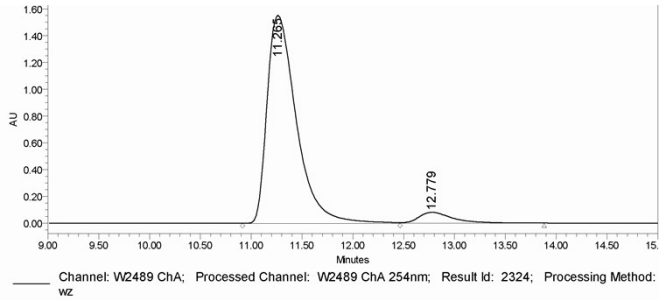
(*R*)-1-(1,5,6-trimethyl-1*H*-benzo[d]imidazol-2-yl)propan-1-ol (2t)



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2321; Processing Method: wz

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	11.268	25455101	49.73	1258080
2	W2489 ChA 254nm	12.639	25735497	50.27	1136345

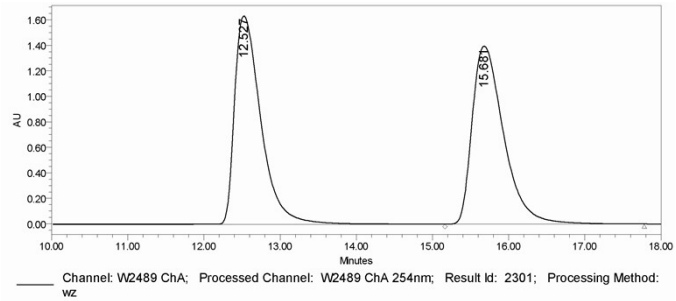


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2324; Processing Method: wz

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	11.265	31221563	94.13	1554852
2	W2489 ChA 254nm	12.779	1948132	5.87	82710

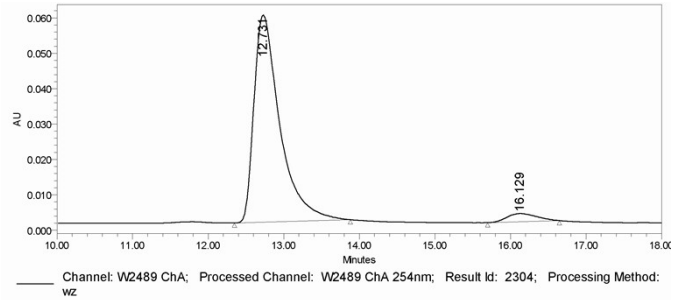
(*R*)-2-phenyl-1-(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)ethan-1-ol (2u)



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2301; Processing Method: wz

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	12.527	40117306	49.97	1635880
2	W2489 ChA 254nm	15.681	40160999	50.03	1397627

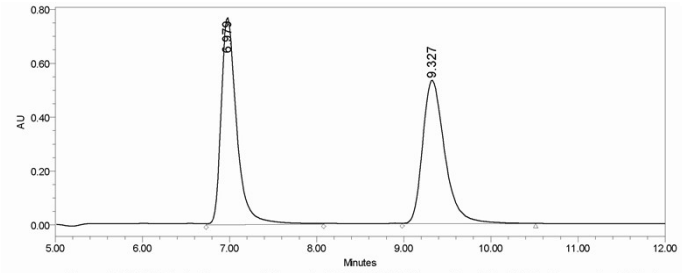


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2304; Processing Method: wz

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	12.731	1396336	95.66	58509
2	W2489 ChA 254nm	16.129	63385	4.34	2318

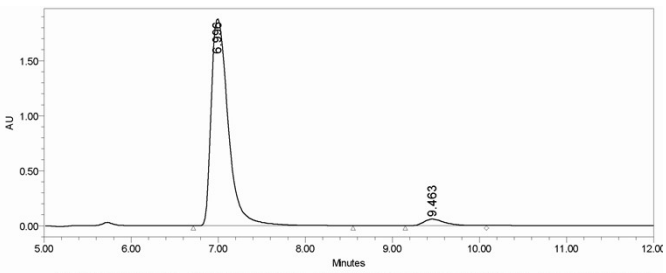
(*R*)-2-phenyl-1-(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)ethan-1-ol (2v)



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2306; Processing Method: wz

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.979	9614130	50.56	768682
2	W2489 ChA 254nm	9.327	9399472	49.44	532324

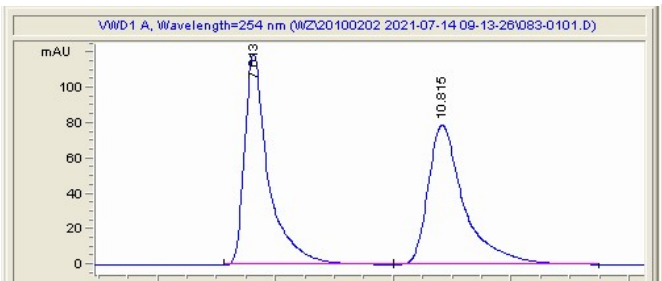


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2309; Processing Method: wz

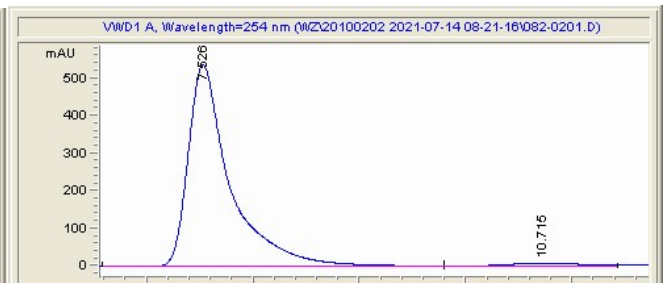
Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.996	25568569	96.12	1880402
2	W2489 ChA 254nm	9.463	1033075	3.88	60072

(*S*)-(1,5,6-trimethyl-1*H*-benzo[*d*]imidazol-2-yl)(phenyl)methanol (3a)

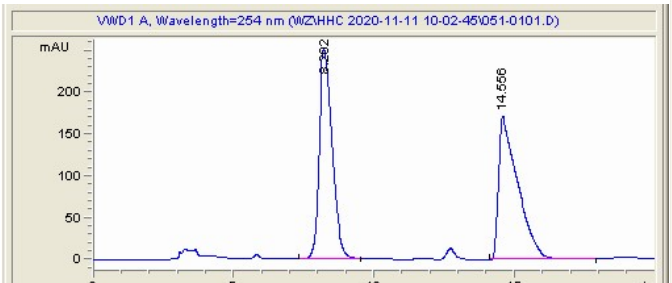


#	Time	Area	Height	Width	Area%	Symmetry
1	7.613	3373.6	119.1	0.4119	50.121	0.521
2	10.815	3357.3	79.1	0.6294	49.879	0.577

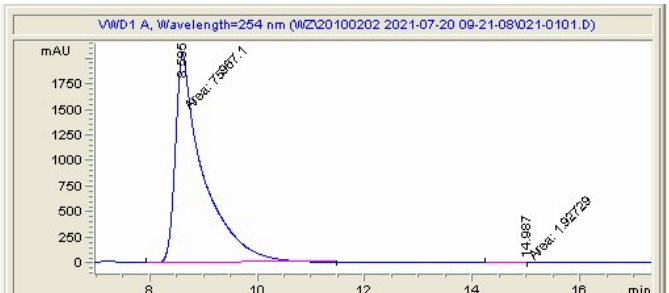


#	Time	Area	Height	Width	Area%	Symmetry
1	7.526	14895.2	535.9	0.4	96.449	0.481
2	10.715	548.3	9.8	0.7937	3.551	0.899

(*S*)-(1-methyl-1*H*-imidazol-2-yl)(phenyl)methanol (3h)



#	Time	Area	Height	Width	Area%	Symmetry
1	8.202	8229.8	251.5	0.5099	49.607	0.599
2	14.556	8360.3	172	0.6426	50.393	0.247



#	Time	Area	Height	Width	Area%	Symmetry
1	8.595	75967.1	2052.6	0.6566	99.997	5.57E-3
2	14.987	1.9	9.4E-2	0.3415	0.003	0