Rhodium-Catalysed Selective C−C Bond Activation and Borylation of Cyclopropanes

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1. General Information

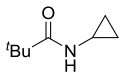
Unless otherwise mentioned, all reactions were performed under an argon atmosphere using flame-dried glasswares. Solvents were dried and purified by conventional methods prior to use. Tetrahydrofuran (THF), dichloromethane (DCM) and toluene were purified using Pure Solv MD-5 solvent purification system, from Innovative Technology, Inc., by passing the solvent through two activated alumina columns after purging with argon. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker AVANCE III 400 MHz or 500 MHz spectrometer. Chemical shifts (δ values) were reported in ppm with $CDCl_3$ (7.26 and 77.16 ppm for ^{1}H and ^{13}C respectively). Data are reported as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br.s = broad signal, coupling constant(s) in Hertz, integration. Mass spectra were conducted at Agilent 6540 Ultra-High-Definition (UHD) Accurate-Mass Quadrupole Time-of-Flight (Q-TOF) liquid chromatography/mass spectrometry (LC/MS) system and Thermo Scientific TRACE 1300 ISQ LT gas chromatography/mass spectrometry (GC/MS) system. IR spectra were recorded on a Bruker FT-IR spectrometer. All reactions were carried out in flame-dried schlenk tube (25 mL) with Teflon screw caps under argon. Unless otherwise noted, materials including cyclopropylamine, 1-methylcyclopropan-1-amine hydrochloride, 1-phenylcyclopropan-1-amine hydrochloride, 1-(p-tolyl)cyclopropan-1-amine hydrochloride, 1-(4-methoxyphenyl)cyclopropan-1-amine hydrochloride, 1-(4-methoxyphenyl)cyclopropan-1-amine hydrochloride, 1-(3-fluorophenyl)cyclopropan-1-amine hydrochloride, 1-(2,2-difluorobenzo[d][1,3]dioxol-5-yl)cyclopropan-1-amine hydrochloride, 1-(4-chlorophenyl)cyclopropan-1-amine hydrochloride, methyl 4-(1-aminocyclopropyl)benzoate hydrochloride, 4-(1-aminocyclopropyl)benzonitrile hydrochloride, 1-(thiophen-2-yl)cyclopropan-1-amine, (1-aminocyclopropyl)methanol hydrochloride, 2-(4-bromophenyl)cyclopropanamine hydrochloride , 2-(3,4-difluorophenyl)cyclopropan-1-amine hydrochloride, 2-phenylcyclopropan-1-amine hydrochloride were obtained from commercial suppliers and used without further purification.

2. Preparation of Starting Materials

2.1 General procedure:[1-2]

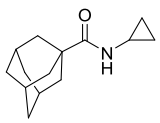
To a solution of cyclopropylamine (2.85 g, 5 mmol) and Et_3N (1.11 g, 11 mmol, 2.2 equiv) in dichloromethane (60 mL) was slowly added a solution of pivaloyl chloride (PivCl: 0.67 mL, 5.5 mmol, 1.1 equiv) in dichloromethane (40 mL) from a dropping funnel at 0 ℃. The reaction mixture was stirred at room temperature for 12 h. To the reaction mixture was added saturated aqueous $NaHCO_3$ (40 mL), which was then extracted with dichloromethane. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The obtained solid was crystallized from hexane to afford the corresponding products.

N-Cyclopropylpivalamide (**1a**) [1]



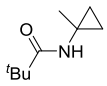
According to general procedure, compound **1a** was prepared from cyclopropylamine and pivaloyl chloride in 90% yield as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.73 (brs, 1H), 2.68 (tq, *J* = 7, 4 Hz, 1H), 1.15 (s, 9H), 0.77 – 0.71 (m, 2H), 0.46 – 0.41 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.8, 38.4, 27.5, 22.7, 6.6. **IR (cm^{-1}, neat):** 3302, 2962, 1632, 1514. **HRMS-ESI:** *m/z* calculated for $C_8H_{16}NO$ $[M + H]^+$ 142.1226, found 142.1227.

N-Cyclopropyladamantane-1-carboxamide (**4c**)



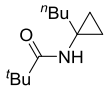
According to general procedure, compound **4c** was prepared from cyclopropylamine and 1-adamantanecarbonyl chloride in 91% yield as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.67 (brs, 1H), 2.68 (dq, *J* = 7, 3 Hz, 1H), 2.04 – 1.98 (m, 3H), 1.80 (d, *J* = 3 Hz, 6H), 1.74 – 1.64 (m, 6H), 0.78 – 0.71 (m, 2H), 0.46 – 0.39 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.3, 40.4, 39.2, 36.5, 28.1, 22.5, 6.6. **IR (cm^{-1}, neat):** 3300, 2974, 1631, 1468. **HRMS-ESI:** *m/z* calculated for $C_{14}H_{22}NO$ $[M + H]^+$ 220.1696, found 220.1696.

N-(1-Methylcyclopropyl)pivalamide (**1b**)



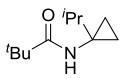
According to general procedure, compound **1b** was prepared from 1-methylcyclopropan-1-amine hydrochloride and pivaloyl chloride in 94% yield as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.90 (brs, 1H), 1.34 (s, 3H), 1.13 (s, 9H), 0.70 – 0.65 (m, 2H), 0.64 – 0.58 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.7, 38.5, 29.0, 27.5, 22.6, 14.5. **IR (cm^{-1}, neat):** 3301, 2964, 1640, 1525, 1265. **HRMS-ESI:** *m/z* calculated for $C_9H_{18}NO$ $[M + H]^+$ 156.1383, found 156.1383.

N-(1-Butylcyclopropyl)pivalamide (**1c**)



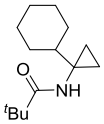
The preparation of corresponding cyclopropanamine was adapted from literature procedures[2]. According to general procedure, compound **1c** was prepared from 1-butylcyclopropan-1-amine and pivaloyl chloride in 85% yield as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.85 (brs, 1H), 1.61 – 1.48 (m, 2H), 1.29 (m, 4H), 1.12 (s, 9H), 0.90 – 0.79 (m, 3H), 0.67 – 0.51 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.5, 38.5, 35.3, 33.0, 28.6, 27.5, 22.6, 14.1, 13.5. **IR (cm^{-1}, neat):** 3331, 2958, 2930, 1639, 1518. **HRMS-ESI:** *m/z* calculated for $C_{12}H_{24}NO$ $[M + H]^+$ 198.1852, found 198.1853.

N-(1-Isopropylcyclopropyl)pivalamide (**1d**)



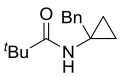
The preparation of corresponding cyclopropanamine was adapted from literature procedures[2]. According to general procedure, compound **1d** was prepared from 1-isopropylcyclopropan-1-amine and pivaloyl chloride in 83% yield as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.78 (brs, 1H), 1.58 – 1.46 (m, 1H), 1.15 (s, 9H), 0.90 (d, J = 7 Hz, 6H), 0.67 (dt, J = 6, 2 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.3, 38.7, 37.3, 34.3, 27.6, 19.1, 12.5. **IR (cm^{-1}, neat):** 3358, 2961, 2871, 1660, 1500, 1265. **HRMS-ESI:** *m/z* calculated for $C_{11}H_{22}NO$ $[M + H]^+$ 184.1696, found 184.1696.

N-(1-Cyclohexylcyclopropyl)pivalamide (**1e**)



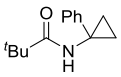
The preparation of corresponding cyclopropanamine was adapted from literature procedures[2]. According to general procedure, compound **1e** was prepared from 1-cyclohexylcyclopropan-1-amine and pivaloyl chloride in 82% yield as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.80 (brs, 1H), 1.74 (tt, *J* = 15, 3 Hz, 4H), 1.65 – 1.58 (m, 1H), 1.15 (s, 9H), 1.15 – 1.08 (m, 3H), 1.08 – 0.89 (m, 3H), 0.66 (dd, *J* = 2, 1 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.3, 44.3, 38.7, 36.8, 29.7, 27.6, 26.4, 26.3, 12.3. **IR (cm^{-1}, neat):** 3349, 2917, 2849, 1649, 1520. **HRMS-ESI:** *m/z* calculated for $C_{14}H_{26}NO$ $[M + H]^+$ 224.2009, found 224.2011.

N-(1-Benzylcyclopropyl)pivalamide (**1f**)



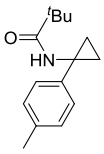
The preparation of corresponding cyclopropanamine was adapted from literature procedures[2]. According to general procedure, compound **1f** was prepared from 1-benzylcyclopropan-1-amine and pivaloyl chloride in 80% yield as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.26 – 7.20 (m, 1H), 7.20 – 7.13 (m, 2H), 5.66 (brs, 1H), 2.89 (s, 2H), 1.08 (s, 9H), 0.89 – 0.80 (m, 2H), 0.78 – 0.68 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.8, 139.4, 129.4, 128.2, 126.4, 41.0, 38.5, 34.1, 27.5, 13.4. **IR (cm^{-1}, neat):** 3298, 2962, 2920, 1634, 1522, 1302, 723, 698. **HRMS-ESI:** *m/z* calculated for $C_{15}H_{22}NO$ $[M + H]^+$ 232.1696, found 232.1697.

N-(1-Phenylcyclopropyl)pivalamide (**1g**)



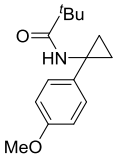
According to general procedure, compound **1g** was prepared from 1-phenylcyclopropan-1-amine hydrochloride and pivaloyl chloride in 89% yield as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.22 – 7.13 (m, 3H), 6.31 (brs, 1H), 1.29 – 1.24 (m, 2H), 1.23 – 1.18 (m, 2H), 1.20 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.4, 142.6, 128.3, 126.1, 125.1, 38.6, 34.7, 27.6, 18.1. **IR (cm^{-1}, neat):** 3268, 2963, 1644, 1529, 1120, 753, 694. **HRMS-ESI:** *m/z* calculated for $C_{14}H_{20}NO$ $[M + H]^+$ 218.1539, found 218.1540.

N-(1-(*p*-Tolyl)cyclopropyl)pivalamide (**1h**)



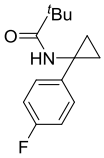
According to general procedure, compound **1h** was prepared from 1-(p-tolyl)cyclopropan-1-amine hydrochloride and pivaloyl chloride in 87% yield as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8 Hz, 2H), 7.08 (d, *J* = 8 Hz, 2H), 6.27 (brs, 1H), 2.29 (s, 3H), 1.25 – 1.21 (m, 2H), 1.19 (s, 9H), 1.16 – 1.14 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.4, 139.6, 135.8, 129.0, 125.3, 38.6, 34.6, 27.6, 20.9, 17.6. **IR (cm^{-1}, neat):** 3268, 2964, 1643, 1515, 1265, 734, 701. **HRMS-ESI:** *m/z* calculated for $C_{15}H_{22}NO$ $[M + H]^+$ 232.1696, found 232.1697.

N-(1-(4-Methoxyphenyl)cyclopropyl)pivalamide (**1i**)



According to general procedure, compound **1i** was prepared from 1-(4-methoxyphenyl)cyclopropan-1-amine hydrochloride and pivaloyl chloride in 86% yield as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.22 – 7.15 (m, 2H), 6.84 – 6.76 (m, 2H), 6.33 (brs, 1H), 3.76 (s, 3H), 1.20 – 1.15 (m, 2H), 1.17 (s, 9H), 1.14 – 1.11 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.4, 158.0, 134.8, 127.1, 113.6, 55.2, 38.5, 34.5, 27.5, 17.0. **IR (cm^{-1}, neat):** 3266, 2952, 1643, 1513, 1244, 824, 685. **HRMS-ESI:** *m/z* calculated for $C_{15}H_{22}NO_2$ $[M + H]^+$ 248.1645, found 248.1645.

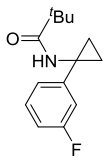
N-(1-(4-Fluorophenyl)cyclopropyl)pivalamide (**1j**)



According to general procedure, compound **1j** was prepared from 1-(4-fluorophenyl)cyclopropan-1-amine hydrochloride and pivaloyl chloride in 89% yield as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.19 – 7.14 (m, 2H), 6.91 (t, *J* = 9 Hz, 2H), 6.47 (brs, 1H), 1.18 – 1.12 (m, 4H), 1.15 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.5, 161.2 (d, *J* = 244.1 Hz), 138.4 (d, *J* = 3.2 Hz), 127.2 (d, *J* = 8.0 Hz), 114.8 (d, *J* = 21.4 Hz), 38.5, 34.3, 27.4, 17.5. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -117.14. **IR (cm^{-1}, neat):** 3263, 2972, 1643, 1530, 1229, 827,

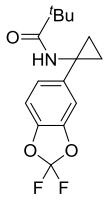
801. **HRMS-ESI:** *m/z* calculated for $C_{14}H_{19}FNO$ $[M + H]^+$ 236.1445, found 236.1444.

N-(1-(3-Fluorophenyl)cyclopropyl)pivalamide (**1k**)



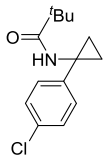
According to general procedure, compound **1k** was prepared from 1-(3-fluorophenyl)cyclopropan-1-amine hydrochloride and pivaloyl chloride in 87% yield as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 1H), 6.94 – 6.81 (m, 3H), 6.34 (brs, 1H), 1.27 – 1.24 (m, 2H), 1.23 – 1.22 (m, 2H), 1.21 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.5, 163.0 (d, *J* = 244.7 Hz), 145.6 (d, *J* = 7.2 Hz), 129.8 (d, *J* = 8.5 Hz), 120.4 (d, *J* = 2.7 Hz), 112.9 (d, *J* = 21.3 Hz), 112.1 (d, *J* = 22.7 Hz), 38.6, 34.4 (d, *J* = 2.3 Hz), 27.5, 18.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.55. **IR (cm^{-1}, neat):** 3276, 2962, 1644, 1525, 1207, 932, 778, 688. **HRMS-ESI:** *m/z* calculated for $C_{14}H_{19}FNO$ $[M + H]^+$ 236.1445, found 236.1447.

N-(1-(2,2-Difluorobenzo[d][1,3]dioxol-5-yl)cyclopropyl)pivalamide (**1l**)



According to general procedure, compound **1l** was prepared from 1-(2,2-difluorobenzo[d][1,3]dioxol-5-yl)cyclopropan-1-amine hydrochloride and pivaloyl chloride in 89% yield as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.02 (d, *J* = 2 Hz, 1H), 6.95 (dd, *J* = 8, 2 Hz, 1H), 6.91 (d, *J* = 8 Hz, 1H), 6.39 (brs, 1H), 1.18 (t, *J* = 2 Hz, 2H), 1.17 (d, *J* = 2 Hz, 2H), 1.16 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.6, 143.7, 142.2, 139.2, 131.6 (t, *J* = 254.6 Hz), 121.1, 108.9, 108.0, 38.5, 34.9, 27.4, 17.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -50.00. **IR (cm^{-1}, neat):** 3319, 2966, 1644, 1502, 1224, 1140, 941, 803, 701. **HRMS-ESI:** *m/z* calculated for $C_{15}H_{18}F_2NO_3$ $[M + H]^+$ 298.1249, found 298.1250.

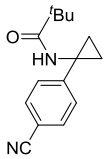
N-(1-(4-Chlorophenyl)cyclopropyl)pivalamide (**1m**)



According to general procedure, compound **1m** was prepared from 1-(4-chlorophenyl)cyclopropan-1-amine hydrochloride and pivaloyl

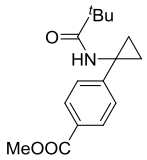
chloride in 84% yield as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2H), 7.16 – 7.11 (m, 2H), 6.29 (brs, 1H), 1.24 – 1.21 (m, 2H), 1.20 – 1.19 (m, 2H), 1.19 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.5, 141.2, 131.9, 128.4, 126.9, 38.6, 34.4, 27.5, 17.9. **IR (cm^{-1}, neat):** 3326, 2964, 1647, 1495, 1102, 819, 744. **HRMS-ESI:** *m/z* calculated for $C_{14}H_{19}ClNO$ $[M + H]^+$ 252.1150, found 252.1150.

N-(1-(4-Cyanophenyl)cyclopropyl)pivalamide (**1n**)



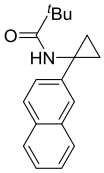
According to general procedure, compound **1m** was prepared from 4-(1-aminocyclopropyl)benzonitrile hydrochloride and pivaloyl chloride in 85% yield as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 2H), 7.23 – 7.20 (m, 2H), 6.32 (brs, 1H), 1.35 – 1.29 (m, 4H), 1.22 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.7, 148.5, 132.2, 125.4, 118.9, 109.7, 38.7, 34.7, 27.5, 19.5. **IR (cm^{-1}, neat):** 3331, 2965, 1651, 1505, 1190, 828. **HRMS-ESI:** *m/z* calculated for $C_{15}H_{19}N_2O$ $[M + H]^+$ 243.1492, found 243.1493.

Methyl 4-(1-pivalamidocyclopropyl)benzoate (**1o**)



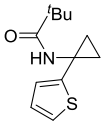
According to general procedure, compound **1o** was prepared from methyl 4-(1-aminocyclopropyl)benzoate hydrochloride and pivaloyl chloride in 85% yield as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 – 7.90 (m, 2H), 7.21 – 7.16 (m, 2H), 6.33 (brs, 1H), 3.88 (s, 3H), 1.36 – 1.31 (m, 2H), 1.29 – 1.25 (m, 2H), 1.22 (s, 9H). **^{13}C NMR** (101 MHz, ^c) δ 178.6, 166.9, 148.2, 129.7, 127.9, 124.6, 52.0, 38.7, 34.7, 27.5, 19.2. **IR (cm^{-1}, neat):** 3331, 2955, 1719, 1648, 1510, 1277, 1113. **HRMS-ESI:** *m/z* calculated for $C_{16}H_{22}NO_3$ $[M + H]^+$ 276.1594, found 276.1596.

N-(1-(Naphthalen-2-yl)cyclopropyl)pivalamide (**1p**)



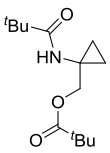
The preparation of corresponding cyclopropanamine was adapted from literature procedures[2]. According to the references, corresponding cyclopropylamine. According to general procedure, compound **1p** was prepared from 1-(naphthalen-2-yl)cyclopropan-1-amine and pivaloyl chloride in 84% yield as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 – 7.72 (m, 3H), 7.68 (d, *J* = 2 Hz, 1H), 7.48 – 7.38 (m, 2H), 7.34 (dd, *J* = 9, 2 Hz, 1H), 1.40 – 1.34 (m, 2H), 1.28 (dd, *J* = 4, 3 Hz, 2H), 1.23 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.5, 140.0, 133.2, 132.1, 128.1, 127.8, 127.4, 125.9, 125.4, 124.1, 124.0, 38.7, 35.0, 27.6, 17.7. **IR (cm^{-1}, neat):** 3281, 2960, 1642, 1477, 1196, 814, 741. **HRMS-ESI:** *m/z* calculated for $C_{18}H_{22}NO$ $[M + H]^+$ 268.1696, found 268.1696.

N-(1-(Thiophen-2-yl)cyclopropyl)pivalamide (**1q**)



According to general procedure, compound **1q** was prepared from 1-(thiophen-2-yl)cyclopropan-1-amine and pivaloyl chloride in 87% yield as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.07 (dd, *J* = 5, 1 Hz, 1H), 6.86 (dd, *J* = 5, 4 Hz, 1H), 6.80 (dd, *J* = 4, 1 Hz, 1H), 6.36 (brs, 1H), 1.31 – 1.28 (m, 2H), 1.26 – 1.23 (m, 2H), 1.18 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.4, 148.3, 126.5, 123.3, 122.7, 38.6, 31.9, 27.5, 18.8. **IR (cm^{-1}, neat):** 3279, 2959, 1639, 1519, 1300, 694. **HRMS-ESI:** *m/z* calculated for $C_{12}H_{18}NOS$ $[M + H]^+$ 224.1104, found 224.1106.

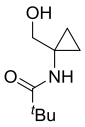
(1-Pivalamidocyclopropyl)methyl pivalate (**1r**)



According to general procedure, compound **1r** was prepared from (1-aminocyclopropyl)methanol hydrochloride, Et_3N (4.4 equiv) and pivaloyl chloride (2.2 equiv) in 79% yield as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.93 (brs, 1H), 4.12 (s, 2H), 1.20 (s, 9H), 1.15 (s, 9H), 0.87 – 0.83 (m, 2H), 0.82 – 0.78 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 178.8, 178.2, 67.8, 38.8, 38.6, 32.3, 27.4, 27.2, 12.1. **IR (cm^{-1}, neat):**3357, 2968, 1728, 1650, 1510 1155.

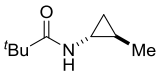
HRMS-ESI: *m/z* calculated for $C_{14}H_{26}NO_3$ $[M + H]^+$ 256.1907, found 256.1907.

N-(1-(Hydroxymethyl)cyclopropyl)pivalamide (**1s**)



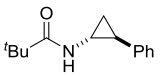
According to general procedure, compound **1s** was prepared from (1-aminocyclopropyl)methanol hydrochloride and pivaloyl chloride in 81% yield as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.37 (brs, 1H), 4.48 (brs, 1H), 3.53 (s, 2H), 1.12 (s, 9H), 0.89 – 0.82 (m, 2H), 0.76 – 0.69 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.7, 69.6, 38.4, 35.3, 27.3, 12.8. **IR (cm^{-1}, neat):** 3351, 2919, 1639, 1277, 1014. **HRMS-ESI:** *m/z* calculated for $C_9H_{18}NO_2$ $[M + H]^+$ 172.1332, found 172.1330.

Trans-N-(2-methylcyclopropyl)pivalamide (**Trans-1t**)



The preparation of corresponding cyclopropanamine was adapted from literature procedures[9]. According to general procedure, compound **1t** was prepared from 2-methylcyclopropan-1-amine trifluoromethanesulfonate and pivaloyl chloride in 86% yield as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.71 (brs, 1H), 2.34 (dq, *J* = 7, 3 Hz, 1H), 1.14 (s, 9H), 1.07 (d, *J* = 6 Hz, 3H), 0.79 (ddt, *J* = 12, 6, 3 Hz, 1H), 0.60 – 0.48 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.6, 38.4, 30.0, 27.5, 17.2, 14.8, 14.7. **IR (cm^{-1}, neat):** 3316, 2956, 1633, 1523, 1255. **HRMS-ESI:** *m/z* calculated for $C_9H_{18}NO$ $[M + H]^+$ 156.1383, found 156.1383.

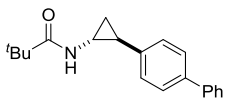
Trans-N-(2-phenylcyclopropyl)pivalamide (**Trans-1u**)



According to general procedure, compound **1u** was prepared from 2-phenylcyclopropan-1-amine hydrochloride and pivaloyl chloride in 84% yield as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (td, *J* = 7, 2 Hz, 2H), 7.22 – 7.13 (m, 3H), 5.89 (brs, 1H), 2.86 (ddt, *J* = 7, 4, 3 Hz, 1H), 2.02 (ddd, *J* = 10, 6, 3 Hz, 1H), 1.26 – 1.22 (m, 1H), 1.20 (s, 9H), 1.12 (ddd, *J* = 10, 6, 4 Hz, 1H).

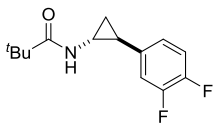
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.6, 140.5, 128.3, 126.6, 126.1, 38.5, 32.1, 27.5, 24.8, 16.1. **IR (cm^{-1}, neat):** 3321, 2964, 1636, 1519, 1225, 746, 696. **HRMS-ESI:** *m/z* calculated for $C_{14}H_{20}NO$ $[M + H]^+$ 218.1539, found 218.1542.

Trans-N-(2-([1,1'-biphenyl]-4-yl)cyclopropyl)pivalamide (**Trans-1v**)



According to general procedure, compound N-(2-(4-bromophenyl)cyclopropyl)pivalamide was prepared from 2-(4-bromophenyl)cyclopropan-1-amine hydrochloride and pivaloyl chloride. A 25.0 mL flame-dried schlenk tube with a magnetic stirring bar was charged with N-(2-(4-bromophenyl)cyclopropyl)pivalamide (189 mg, 0.6 mmol), $Pd(PPh_3)_4$ (138 mg, 0.12 mmol), phenylboronic acid (292.6 mg, 2.4 mmol), Na_2CO_3 (127 mg, 1.2 mmol), 0.04 mL H_2O, 0.5 mL MeOH and 2.16 mL toluene under nitrogen atmosphere. The tube was heated to 80 ℃ and held at that temperature for 12 h. The reaction mixture was then allowed to cool at room temperature and concentrated in vacuo. The resultant residue was purified by silica gel chromatography (PE : EA = 5:1) to afford **Trans-1v** in 53% yield as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 2H), 7.53 – 7.47 (m, 2H), 7.42 (t, *J* = 8 Hz, 2H), 7.35 – 7.29 (m, 1H), 7.27 (d, *J* = 2 Hz, 2H), 5.89 (brs, 1H), 2.90 (ddt, *J* = 8, 4, 3 Hz, 1H), 2.06 (ddd, *J* = 10, 6, 3 Hz, 1H), 1.32 – 1.12 (m, 2H), 1.21 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.7, 141.0, 139.7, 139.1, 128.7, 127.1, 127.1, 127.0, 127.0, 38.6, 32.2, 27.6, 24.7, 16.2. **IR (cm^{-1}, neat):** 3332, 2970, 1634, 1530, 750, 689. **HRMS-ESI:** *m/z* calculated for $C_{20}H_{24}NO$ $[M + H]^+$ 294.1852, found 294.1853.

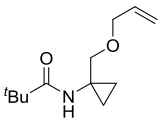
Trans-N-(2-(3,4-difluorophenyl)cyclopropyl)pivalamide (**Trans-1w**)



According to general procedure, compound **1w** was prepared from 2-(3,4-difluorophenyl)cyclopropan-1-amine hydrochloride and pivaloyl chloride in 83% yield as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.08 – 7.00 (m, 2H), 7.00 – 6.94 (m, 1H), 5.87 (brs, 1H), 2.78 –

2.71 (m, 1H), 1.97 (ddd, *J* = 10, 6, 3 Hz, 1H), 1.20 (s, 9H), 1.18 – 1.10 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 179.8, 150.1 (dd, *J* = 247.6, 12.2 Hz), 148.9 (dd, *J* = 246.1, 12.7 Hz), 137.5 (dd, *J* = 5.8, 3.9 Hz), 123.1 (dd, *J* = 6.2, 3.4 Hz), 116.9 (d, *J* = 17.1 Hz), 116.0 (d, *J* = 17.4 Hz), 38.5, 31.9, 27.5, 24.5 (d, *J* = 1.7 Hz), 15.3. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -138.33 (d, *J* = 21.41 Hz), -141.66 (d, *J* = 20.87 Hz). **IR (cm^{-1}, neat):** 3331, 2971, 1659, 1513, 1276, 750, 669. **HRMS-ESI:** *m/z* calculated for $C_{14}H_{18}F_2NO$ $[M + H]^+$ 254.1351, found 254.1347.

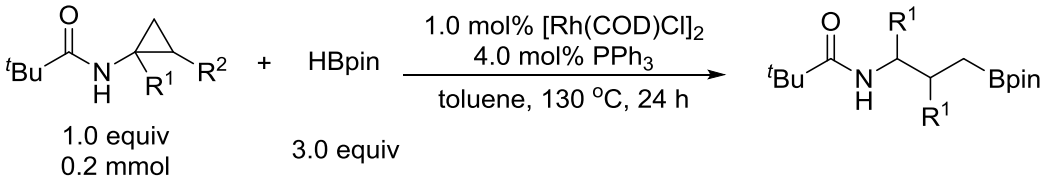
N-(1-((Allyloxy)methyl)cyclopropyl)pivalamide (1x')



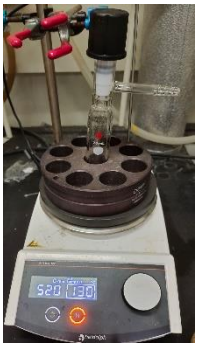
White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.11 (brs, 1H), 5.94 – 5.75 (m, 1H), 5.30 – 5.09 (m, 2H), 3.95 (dt, *J* = 6, 1 Hz, 2H), 3.45 (s, 2H), 1.14 (s, 9H), 0.77 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.1, 134.6, 117.1, 74.0, 72.0, 38.6, 33.0, 27.4, 11.8. **IR (cm^{-1}, neat):** 3343, 2959, 1644, 1513, 1089. **HRMS-ESI:** *m/z* calculated for $C_{12}H_{22}NO_2$ $[M + H]^+$ 212.1645, found 212.1645.

3. Experimental Procedures and Characterization of Products

3.1. General procedure:



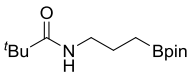
To a 25.0 mL flame-dried sealed Schlenk tube with a stirring bar was added substrate **1** (0.2 mmol, 1.0 equiv), PPh_3 (2.1 mg, 4.0 mol %), $[Rh(cod)Cl]_2$ (1.0 mg, 1.0 mol %), HBpin (76.8 mg, 0.6 mmol, 3.0 equiv) and toluene (1 mL) under argon. The reaction vessel was sealed and the resulting mixture was stirred at 130 °C



under Ar for 24 h. The solution was then cooled to room temperature, and 3 mL of ethyl acetate were added. The mixture was concentrated in vacuo and purified by flash column chromatography on silica gel. (Silica gel must be soaked in solvent (petroleum ether/Et_3N = 100:1) for 24h before column chromatography)

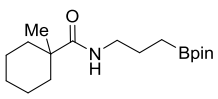
3.2. Characterization data

N-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)pivalamide (**2a**)



The general procedure was followed with **1a** (28.2 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (1.0 mg, 1.0 mol %), and PPh_3 (2.1 mg, 4 mol %) in toluene (1 mL) at 130 ℃ for 24 h. The resulting mixture was purified by flash column chromatography (dichloromethane/ethyl acetate = 5:1) to afford the product **2a** as a brown oil (49.0 mg, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.77 (brs, 1H), 3.17 (td, *J* =7, 6 Hz, 2H), 1.62 – 1.51 (m, 2H), 1.21 (s, 12H), 1.14 (s, 9H), 0.75 (t, *J* = 8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.2, 83.1, 41.5, 38.5, 27.6, 24.7, 23.7, 8.5. **^{11}B NMR** (128 MHz, Chloroform-d) δ 33.9. **IR (cm^{-1}, neat):** 3301, 2978, 2962, 1632, 1514. **HRMS-ESI:** *m/z* calculated for $C_{14}H_{29}BNO_3$ $[M + H]^+$ 270.2235, found 270.2239.

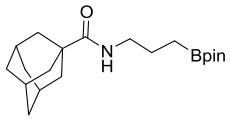
1-Methyl-N-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)cyclohexane-1-carboxamide (**5b**)



The general procedure was followed with **4b** (36.3 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (2.5 mg, 2.5 mol %), and PPh_3 (5.3 mg, 10.0 mol %) in toluene (1 mL) at 130 ℃ for 24 h. The resulting mixture was purified by flash column chromatography (dichloromethane/ ethyl acetate = 7:1) to afford the product **5b** as a brown oil (45.2 mg, 73% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.77 (brs, 1H), 3.22 (td, *J* =7, 6 Hz, 2H), 1.86 (ddd, *J* = 12, 7, 3 Hz, 2H), 1.64 – 1.55 (m, 2H), 1.54 – 1.27 (m, 8H), 1.23 (s, 12H), 1.11 (s, 3H), 0.78 (t, *J* =8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.5, 83.2, 42.5, 41.5, 35.6,

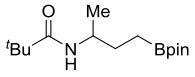
26.4, 25.8, 24.8, 23.8, 22.8, 8.6. **^{11}B NMR** (128 MHz, Chloroform-d) δ 34.0. **IR (cm^{-1}, neat):** 3350, 2926, 1632, 1530, 1370, 1144. **HRMS-ESI:** *m/z* calculated for $C_{17}H_{33}BNO_3$ $[M + H]^+$ 310.2548, found 310.2546.

(1s,3s)-N-(3-(4,4,5-Trimethyl-1,3,2-dioxaborolan-2-yl)propyl)adamantane-1-carboxamide (**5c**)



The general procedure was followed with **4c** (43.9 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (2.5 mg, 2.5 mol %), and PPh_3 (5.3 mg, 10.0 mol %) in toluene (1 mL) at 130 ℃ for 24 h. The resulting mixture was purified by flash column chromatography (dichloromethane/ethyl acetate = 7:1) to afford the product **5c** as a brown oil (24.7 mg, 36% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.70 (brs, 1H), 3.20 (td, *J* = 7, 6 Hz, 2H), 2.01 (dd, *J* = 6, 3 Hz, 3H), 1.82 (d, *J* = 3 Hz, 6H), 1.75 – 1.64 (m, 6H), 1.62 – 1.54 (m, 2H), 1.23 (s, 12H), 0.77 (t, *J* = 8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.8, 83.1, 41.3, 40.5, 39.3, 36.5, 28.1, 24.8, 23.8, 8.4. **^{11}B NMR** (128 MHz, Chloroform-d) δ 33.9. **IR (cm^{-1}, neat):** 3347, 2904, 1632, 1529, 1371, 1145. **HRMS-ESI:** *m/z* calculated for $C_{20}H_{35}BNO_3$ $[M + H]^+$ 348.2705, found 348.2702.

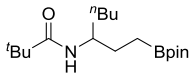
N-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)pivalamide (**2b**)



The general procedure was followed with **1b** (31.0 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (1.0 mg, 1.0 mol %), and PPh_3 (2.1 mg, 4 mol %) in toluene (1 mL) at 130 ℃ for 24 h. The resulting mixture was purified by flash column chromatography (dichloromethane/ethyl acetate = 5:1) to afford the product **2b** as a yellow oil (46.0 mg, 81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.42 (d, *J* = 8 Hz, 1H), 3.87 (dq, *J* = 8, 7 Hz, 1H), 1.58 – 1.44 (m, 2H), 1.23 (s, 12H), 1.16 (s, 9H), 1.08 (d, *J* = 7 Hz, 3H), 0.75 (t, *J* = 8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.6, 83.1, 46.7, 30.7, 27.6, 24.8, 24.7, 20.5, 7.4. **^{11}B NMR** (128 MHz, Chloroform-d) δ 34.0. **IR (cm^{-1}, neat):** 3343, 2974, 2930, 1633, 1370, 1143.

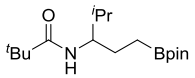
HRMS-ESI: *m/z* calculated for $C_{15}H_{31}BNO_3$ $[M + H]^+$ 284.2392, found 284.2397.

N-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)heptan-3-yl)pivalamide (**2c**)



The general procedure was followed with **1c** (39.5 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (1.0 mg, 1.0 mol %), and PPh_3 (2.1 mg, 4 mol %) in toluene (1 mL) at 130 ℃ for 24 h. The resulting mixture was purified by flash column chromatography (dichloromethane/ethyl acetate = 20:1) to afford the product **2c** as a white solid (53.5 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.32 (d, *J* = 9 Hz, 1H), 3.91 – 3.76 (m, 1H), 1.63 (ddd, *J* = 10, 5, 3 Hz, 2H), 1.53 – 1.39 (m, 2H), 1.38 – 1.27 (m, 4H), 1.24 (s, 12H), 1.18 (s, 9H), 0.94 – 0.84 (m, 3H), 0.83 – 0.69 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.8, 83.1, 50.5, 38.7, 34.6, 29.1, 28.0, 27.7, 24.9, 24.8, 22.6, 14.0. **^{11}B NMR** (128 MHz, Chloroform-d) δ 34.3. **IR (cm^{-1}, neat):** 3355, 2977, 2929, 1637, 1370, 1143. **HRMS-ESI:** *m/z* calculated for $C_{18}H_{37}BNO_3$ $[M + H]^+$ 326.2861, found 326.2858.

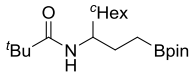
N-(4-Methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-3-yl)pivalamide (**2d**)



The general procedure was followed with **1d** (36.7 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (1.0 mg, 1.0 mol %), and PPh_3 (2.1 mg, 4 mol %) in toluene (1 mL) at 130 ℃ for 24 h. The resulting mixture was purified by flash column chromatography (dichloromethane/ethyl acetate = 20:1) to afford the product **2d** as a white solid (56.9 mg, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.32 (d, *J* = 9 Hz, 1H), 3.72 (tt, *J* = 10, 5 Hz, 1H), 1.73 (pd, *J* = 7, 5 Hz, 1H), 1.62 (dddd, *J* = 14, 10, 7, 5 Hz, 1H), 1.39 – 1.31 (m, 1H), 1.22 (s, 12H), 1.18 (s, 9H), 0.84 (dd, *J* = 10, 7 Hz, 6H), 0.78 – 0.61 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.0, 83.0, 55.4, 38.8, 31.6, 27.7, 26.1, 24.8, 24.7, 19.2, 17.6, 7.5. **^{11}B NMR** (128 MHz, Chloroform-d) δ 33.9. **IR (cm^{-1}, neat):** 3351, 2958, 1634, 1370, 1145. **HRMS-ESI:** *m/z* calculated for $C_{17}H_{35}BNO_3$ $[M + H]^+$ 312.2705, found 312.2705.

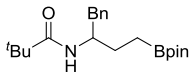
N-(1-Cyclohexyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)pivalamid

e (**2e**)



The general procedure was followed with **1e** (44.7 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (1.0 mg, 1.0 mol %), and PPh_3 (2.1 mg, 4 mol %) in toluene (1 mL) at 130 ℃ for 24 h. The resulting mixture was purified by flash column chromatography (dichloromethane/ethyl acetate = 20:1) to afford the product **2e** as a white solid (51.3 mg, 73% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.32 (d, *J* = 9 Hz, 1H), 3.72 (tdd, *J* = 10, 6, 4 Hz, 1H), 1.73 – 1.59 (m, 6H), 1.36 (dddd, *J* = 12, 6, 4, 2 Hz, 2H), 1.23 (s, 12H), 1.18 (s, 9H), 1.15 – 0.84 (m, 5H), 0.79 – 0.64 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.9, 83.0, 54.9, 41.8, 38.8, 29.8, 28.2, 27.8, 26.5, 26.3, 26.3, 26.0, 24.9, 24.7, 7.3. **^{11}B NMR** (128 MHz, Chloroform-d) δ 34.5. **IR (cm^{-1}, neat):** 3349, 2976, 2924, 1633, 1371, 1145. **HRMS-ESI:** *m/z* calculated for $C_{20}H_{39}BNO_3$ $[M + H]^+$ 352.3018, found 352.3013.

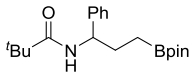
N-(1-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)pivalamid e (**2f**)



The general procedure was followed with **1f** (46.2 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (1.0 mg, 1.0 mol %), and PPh_3 (2.1 mg, 4 mol %) in toluene (1 mL) at 130 ℃ for 24 h. The resulting mixture was purified by flash column chromatography (dichloromethane/ethyl acetate = 20:1) to afford the product **2f** as a white solid (35.7 mg, 50% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 6 Hz, 2H), 7.21 – 7.12 (m, 3H), 5.36 (d, *J* = 9 Hz, 1H), 4.17 – 4.04 (m, 1H), 2.88 – 2.67 (m, 2H), 1.70 – 1.60 (m, 1H), 1.50 – 1.41 (m, 1H), 1.23 (s, 12H), 1.09 (s, 9H), 0.84 – 0.75 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.8, 138.2, 129.5, 128.2, 126.2, 83.2, 51.6, 40.4, 38.6, 28.0, 27.5, 24.9, 24.7. **^{11}B NMR** (128 MHz, Chloroform-d) δ 34.7. **IR (cm^{-1}, neat):** 3346, 2976, 1633, 1562, 1371, 1144, 967, 700. **HRMS-ESI:** *m/z* calculated for $C_{21}H_{35}BNO_3$ $[M + H]^+$ 360.2705, found 360.2704.

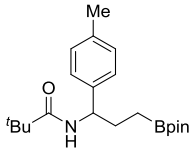
N-(1-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)pivalamide

(**2g**)



The general procedure was followed with **1g** (43.4 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (1.0 mg, 1.0 mol %), and PPh_3 (2.1 mg, 4 mol %) in toluene (1 mL) at 130 ℃ for 24 h. The resulting mixture was purified by flash column chromatography (dichloromethane/ethyl acetate = 10:1) to afford the product **2g** as a brown solid (53.0 mg, 77% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.25 – 7.19 (m, 3H), 5.99 (d, *J* = 8 Hz, 1H), 4.85 (q, *J* = 7 Hz, 1H), 1.91 – 1.82 (m, 2H), 1.23 (s, 12H), 1.19 (s, 9H), 0.84 – 0.66 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.6, 142.7, 128.5, 127.0, 126.3, 83.2, 55.1, 38.6, 30.7, 27.6, 24.9, 24.8, 7.8. **^{11}B NMR** (128 MHz, Chloroform-d) δ 33.8. **IR (cm^{-1}, neat):** 3334, 2973, 1634, 1537, 1372, 1146, 853, 701. **HRMS-ESI:** *m/z* calculated for $C_{20}H_{33}BNO_3$ $[M + H]^+$ 346.2548, found 346.2554.

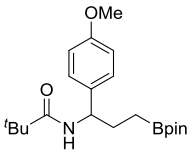
N-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(p-tolyl)propyl)pivalamide (**2h**)



The general procedure was followed with **1h** (46.2 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (1.0 mg, 1.0 mol %), and PPh_3 (2.1 mg, 4 mol %) in toluene (1 mL) at 130 ℃ for 24 h. The resulting mixture was purified by flash column chromatography (dichloromethane/ethyl acetate = 10:1) to afford the product **2h** as a brown solid (57.1 mg, 79% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 – 7.08 (m, 4H), 5.94 (d, *J* = 8 Hz, 1H), 4.81 (q, *J* = 7 Hz, 1H), 2.31 (s, 3H), 1.90 – 1.80 (m, 2H), 1.22 (s, 12H), 1.18 (s, 9H), 0.82 – 0.64 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.5, 139.7, 136.5, 129.2, 126.3, 83.2, 54.9, 38.6, 30.7, 27.6, 24.8, 24.8, 21.0, 7.8. **^{11}B NMR** (128 MHz, Chloroform-d) δ 34.0. **IR (cm^{-1}, neat):** 3349, 2976, 1639, 1515, 1371, 1145, 968, 814. **HRMS-ESI:** *m/z* calculated for $C_{21}H_{35}BNO_3$ $[M + H]^+$ 360.2705, found 360.2702.

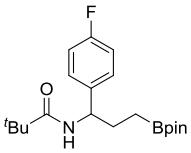
N-(1-(4-Methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)pi

valamide (**2i**)



The general procedure was followed with **1i** (49.4 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (1.0 mg, 1.0 mol %), and PPh_3 (2.1 mg, 4 mol %) in toluene (1 mL) at 130 ℃ for 24 h. The resulting mixture was purified by flash column chromatography (dichloromethane/ethyl acetate = 10:1) to afford the product **2i** as a brown solid (60.1 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 – 7.13 (m, 2H), 6.86 – 6.82 (m, 2H), 5.91 (d, *J* = 8 Hz, 1H), 4.79 (q, *J* = 7 Hz, 1H), 3.78 (s, 3H), 1.84 (dtd, *J* = 10, 7, 3 Hz, 2H), 1.23 (s, 12H), 1.18 (s, 9H), 0.82 – 0.64 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.5, 158.5, 134.8, 127.5, 113.9, 83.2, 55.2, 54.6, 38.6, 30.6, 27.6, 24.9, 24.8. **^{11}B NMR** (128 MHz, Chloroform-d) δ 33.8. **IR (cm^{-1}, neat):** 3348, 2976, 1639, 1512, 1371, 1246, 830. **HRMS-ESI:** *m/z* calculated for $C_{21}H_{35}BNO_4$ $[M + H]^+$ 376.2654, found 376.2663.

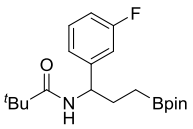
N-(1-(4-Fluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)piv alamide (**2j**)



The general procedure was followed with **1j** (47.0 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (1.0 mg, 1.0 mol %), and PPh_3 (2.1 mg, 4 mol %) in toluene (1 mL) at 130 ℃ for 24 h. The resulting mixture was purified by flash column chromatography (dichloromethane/ethyl acetate = 10:1) to afford the product **2j** as a white solid (55.3 mg, 76% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 – 7.15 (m, 2H), 7.01 – 6.93 (m, 2H), 5.98 (d, *J* = 8 Hz, 1H), 4.80 (q, *J* = 7 Hz, 1H), 1.86 – 1.80 (m, 2H), 1.22 (s, 12H), 1.17 (s, 9H), 0.73 (dq, *J* =28, 8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.6, 161.7 (d, *J* = 244.7 Hz), 138.6 (d, *J* = 3.1 Hz), 127.8 (d, *J* = 7.9 Hz), 115.2 (d, *J* = 21.3 Hz), 83.3, 54.5, 38.6, 30.6, 27.5, 24.8, 24.7, 7.8. **^{11}B NMR** (128 MHz, Chloroform-d) δ 33.9. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -116.06. **IR (cm^{-1}, neat):** 3333, 2979, 1632, 1511, 1372, 1144, 735. **HRMS-ESI:** *m/z* calculated for $C_{20}H_{32}BFNO_3$ $[M + H]^+$

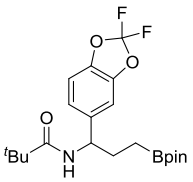
364.2454, found 364.2452.

N-(1-(3-Fluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)pivalamide (**2k**)



The general procedure was followed with **1k** (47.0 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (1.0 mg, 1.0 mol %), and PPh_3 (2.1 mg, 4 mol %) in toluene (1 mL) at 130 ℃ for 24 h. The resulting mixture was purified by flash column chromatography (dichloromethane/ethyl acetate = 10:1) to afford the product **2k** as a brown solid (53.9 mg, 74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 2H), 7.02 (dt, *J* = 8, 1.22 Hz, 1H), 6.94 – 6.87 (m, 2H), 6.02 (d, *J* = 7 Hz, 1H), 4.84 (q, *J* = 7 Hz, 1H), 1.89 – 1.79 (m, 2H), 1.24 (s, 12H), 1.20 (s, 9H), 0.84 – 0.67 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.7, 163.0 (d, *J* = 245.7 Hz), 145.6 (d, *J* = 6.7 Hz), 129.9 (d, *J* = 8.4 Hz), 122.1 (d, *J* = 2.8 Hz), 113.8 (d, *J* = 21.2 Hz), 113.1 (d, *J* = 21.7 Hz), 83.3, 54.7 (d, *J* = 1.8 Hz), 38.6, 30.5, 27.6, 24.9, 24.8. **^{11}B NMR** (128 MHz, Chloroform-d) δ 39.2. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -113.21. **IR (cm^{-1}, neat):** 3357, 2978, 1640, 1371, 1144, 784, 698. **HRMS-ESI:** *m/z* calculated for $C_{20}H_{32}BFNO_3$ $[M + H]^+$ 364.2454, found 364.2459.

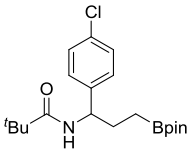
N-(1-(2,2-Difluorobenzo[d][1,3]dioxol-5-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)pivalamide (**2l**)



The general procedure was followed with **1l** (59.4 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (1.0 mg, 1.0 mol %), and PPh_3 (2.1 mg, 4 mol %) in toluene (1 mL) at 130 ℃ for 24 h. The resulting mixture was purified by flash column chromatography (dichloromethane/ethyl acetate = 10:1) to afford the product **2l** as a brown solid (58.2 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.99 – 6.92 (m, 3H), 6.03 (d, *J* = 7 Hz, 1H), 4.77 (q, *J* = 7 Hz, 1H), 1.82 (q, *J* = 8 Hz, 2H), 1.23 (s, 12H), 1.19 (s, 9H), 0.75

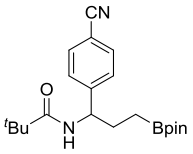
(tp, *J* = 16, 8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.8, 143.9, 142.6, 139.5, 131.6 (t, *J* = 254.7 Hz), 121.5, 109.2, 107.5, 83.4, 55.1, 38.6, 30.7, 27.6, 24.9, 24.7, 7.7. **^{11}B NMR** (128 MHz, Chloroform-d) δ 33.8. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -49.85 (d, *J* = 7.87 Hz). **IR (cm^{-1}, neat):** 3351, 2926, 1640, 1372, 1240, 1145, 848. **HRMS-ESI:** *m/z* calculated for $C_{21}H_{31}BF_2NO_5$ $[M + H]^+$ 426.2258, found 426.2261.

N-(1-(4-Chlorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)pivalamide (**2m**)



The general procedure was followed with **1m** (50.2 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (1.0 mg, 1.0 mol %), and PPh_3 (2.1 mg, 4 mol %) in toluene (1 mL) at 130 ℃ for 24 h. The resulting mixture was purified by flash column chromatography (dichloromethane/ethyl acetate = 10:1) to afford the product **2m** as a white solid (47.9 mg, 63% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 2 Hz, 2H), 7.20 – 7.13 (m, 2H), 5.99 (d, *J* = 7 Hz, 1H), 4.80 (q, *J* = 7 Hz, 1H), 1.87 – 1.79 (m, 2H), 1.23 (s, 12H), 1.18 (s, 9H), 0.82 – 0.67 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.7, 141.4, 132.6, 128.6, 127.7, 83.3, 54.6, 38.6, 30.5, 27.6, 27.6, 24.9, 24.8. **^{11}B NMR** (128 MHz, Chloroform-d) δ 33.9. **IR (cm^{-1}, neat):** 3343, 2921, 1632, 1535, 1147, 835. **HRMS-ESI:** *m/z* calculated for $C_{20}H_{32}BClNO_3$ $[M + H]^+$ 380.2158, found 380.2152.

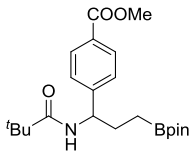
N-(1-(4-Cyanophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)pivalamide (**2n**)



The general procedure was followed with **1n** (48.4 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (1.0 mg, 1.0 mol %), and PPh_3 (2.1 mg, 4 mol %) in toluene (1 mL) at 130 ℃ for 24 h. The resulting mixture was purified by flash column chromatography (dichloromethane/ethyl acetate = 10:1) to afford the product **2n** as a white solid (48.7 mg, 66% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8 Hz, 2H), 7.33 (d, *J* = 8

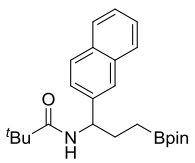
Hz, 2H), 6.14 (d, *J* = 7 Hz, 1H), 4.82 (q, *J* = 7 Hz, 1H), 1.84 (ddt, *J* = 9, 8, 6 Hz, 2H), 1.23 (s, 12H), 1.19 (s, 9H), 0.84 – 0.67 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.99, 148.67, 132.33, 126.97, 118.85, 110.72, 83.49, 55.17, 38.61, 30.32, 27.53, 24.87, 24.71, 7.7. **^{11}B NMR** (128 MHz, Chloroform-d) δ 33.7. **IR (cm^{-1}, neat):** 3351, 2976, 1640, 1512, 1371, 1144, 846. **HRMS-ESI:** *m/z* calculated for $C_{21}H_{32}BN_2O_3$ [M + H]$^+$ 371.2500, found 371.2500.

Methyl 4-(1-Pivalamido-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate (**2o**)



The general procedure was followed with **1o** (55.0 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (1.0 mg, 1.0 mol %), and PPh_3 (2.1 mg, 4 mol %) in toluene (1 mL) at 130 ℃ for 24 h. The resulting mixture was purified by flash column chromatography (dichloromethane/ethyl acetate = 10:1) to afford the product **2o** as a brown solid (57.0 mg, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8 Hz, 2H), 7.29 (d, *J* = 8 Hz, 2H), 6.09 (d, *J* = 7 Hz, 1H), 4.88 (q, *J* = 7 Hz, 1H), 3.88 (s, 3H), 1.92 – 1.78 (m, 2H), 1.23 (s, 12H), 1.19 (s, 9H), 0.83 – 0.67 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.8, 166.9, 148.2, 129.8, 126.3, 83.3, 55.0, 52.0, 38.6, 30.4, 27.6, 24.9, 24.7. **^{11}B NMR** (128 MHz, Chloroform-d) δ 33.7. **IR (cm^{-1}, neat):** 3350, 2976, 1722, 1640, 1371, 1277, 848. **HRMS-ESI:** *m/z* calculated for $C_{22}H_{35}BNO_5$ [M + H]$^+$ 404.2603, found 404.2600.

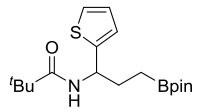
N-(1-(Naphthalen-2-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)pivalamide (**2p**)



The general procedure was followed with **1p** (53.5 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (1.0 mg, 1.0 mol %), and PPh_3 (2.1 mg, 4 mol %) in toluene (1 mL) at 130 ℃ for 24 h. The

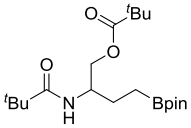
resulting mixture was purified by flash column chromatography (dichloromethane/ethyl acetate = 20:1) to afford the product **2p** as a brown solid (49.8 mg, 63% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.76 (m, 3H), 7.69 (d, *J* = 2 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.37 (dd, *J* = 8, 2 Hz, 1H), 6.08 (d, *J* = 8 Hz, 1H), 5.03 (q, *J* = 7 Hz, 1H), 1.96 (dt, *J* = 8, 7 Hz, 2H), 1.22 (d, *J* = 2 Hz, 12H), 1.21 (s, 9H), 0.86 – 0.71 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.7, 140.1, 133.4, 132.7, 128.3, 127.9, 127.6, 126.0, 125.6, 125.1, 124.7, 83.2, 55.2, 38.7, 30.5, 27.6, 24.9, 24.8. **^{11}B NMR** (128 MHz, Chloroform-d) δ 33.7. **IR (cm^{-1}, neat):** 3370, 3052, 2925, 1370, 1143, 967, 847. **HRMS-ESI:** *m/z* calculated for $C_{24}H_{35}BNO_3$ $[M + H]^+$ 396.2705, found 396.2706.

N-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(thiophen-2-yl)propyl)pival amide (**2q**)



The general procedure was followed with **1q** (44.6 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (1.0 mg, 1.0 mol %), and PPh_3 (2.1 mg, 4 mol %) in toluene (1 mL) at 130 ℃ for 24 h. The resulting mixture was purified by flash column chromatography (dichloromethane/ethyl acetate = 10:1) to afford the product **2q** as a brown solid (52.5 mg, 75% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.15 (dd, *J* = 5, 2 Hz, 1H), 6.94 – 6.90 (m, 2H), 5.91 (d, *J* = 8 Hz, 1H), 5.20 (td, *J* = 8, 6 Hz, 1H), 2.03 – 1.88 (m, 2H), 1.23 (s, 12H), 1.19 (s, 9H), 0.87 – 0.75 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.4, 146.8, 126.7, 123.9, 123.7, 83.2, 50.5, 38.6, 30.9, 27.5, 24.8, 24.7, 7.6. **^{11}B NMR** (128 MHz, Chloroform-d) δ 34.0. **IR (cm^{-1}, neat):** 3339, 2976, 1642, 1519, 1371, 1145, 694. **HRMS-ESI:** *m/z* calculated for $C_{18}H_{31}BNO_3S$ $[M + H]^+$ 352.2112, found 352.2113.

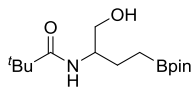
2-Pivalamido-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl pivalate (**2r**)



The general procedure was followed with **1r** (51.0 mg, 0.2 mmol),

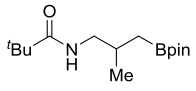
HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (1.0 mg, 1.0 mol %), and PPh_3 (2.1 mg, 4 mol %) in toluene (1 mL) at 130 ℃ for 24 h. The resulting mixture was purified by flash column chromatography (dichloromethane/ethyl acetate = 5:1) to afford the product **2r** as a brown oil (64.4 mg, 84% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.72 (d, *J* = 8 Hz, 1H), 4.16 – 4.08 (m, 2H), 4.08 – 4.00 (m, 1H), 1.69 – 1.50 (m, 2H), 1.23 (s, 12H), 1.18 (s, 9H), 1.16 (s, 9H), 0.79 (t, *J* = 8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.5, 177.9, 83.2, 65.4, 50.0, 38.8, 38.7, 27.6, 27.2, 25.8, 24.9, 24.7, 7.1. **^{11}B NMR** (128 MHz, Chloroform-d) δ 33.9. **IR (cm^{-1}, neat):** 3348, 2973, 1728, 1640, 1530, 1370, 1145. **HRMS-ESI:** *m/z* calculated for $C_{20}H_{39}BNO_5$ $[M + H]^+$ 384.2916, found 384.2918.

N-(1-Hydroxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)pivalamide (**2s**)



The general procedure was followed with **1s** (34.2 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (1.0 mg, 1.0 mol %), and PPh_3 (2.1 mg, 4 mol %) in toluene (1 mL) at 130 ℃ for 24 h. The resulting mixture was purified by flash column chromatography (dichloromethane/ethyl acetate = 5:1) to afford the product **2s** as a brown oil (31.5 mg, 53% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.22 (dd, *J* = 9, 8 Hz, 1H), 4.05 (dtd, *J* = 9, 7, 5 Hz, 1H), 3.89 (dd, *J* = 8, 7 Hz, 1H), 1.79 – 1.68 (m, 1H), 1.61 – 1.51 (m, 1H), 1.24 (s, 12H), 1.20 (s, 9H), 0.75 (dd, *J* = 9, 7 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 83.1, 71.7, 67.3, 33.1, 29.6, 27.9, 24.8, 24.8. **^{11}B NMR** (128 MHz, Chloroform-d) δ 34.4. **IR (cm^{-1}, neat):** 3348, 2975, 1640, 1444, 1320, 1145. **HRMS-ESI:** *m/z* calculated for $C_{15}H_{31}BNO_4$ $[M + H]^+$ 300.2341, found 300.2343.

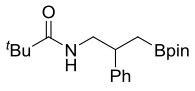
N-(2-Methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)pivalamide (**2t**)



The general modified was followed with **1t** (31.0 mg, 0.2 mmol),

HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (2.5 mg, 2.5 mol %), and PPh_3 (5.2 mg, 10 mol %) in toluene (1 mL) at 130 ℃ for 36 h. The resulting mixture was purified by flash column chromatography (dichloromethane/ethyl acetate = 5:1) to afford the product **2t** as a brown solid (38.1 mg, 55% yield). The resulting mixture was purified by flash column chromatography (dichloromethane/ethyl acetate = 5:1) to afford the product **2s** as a brown oil (28.9 mg, 51% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.84 (s, 1H), 3.17 – 3.07 (m, 2H), 1.96 – 1.85 (m, 1H), 1.25 (d, *J* = 2 Hz, 12H), 1.20 (s, 9H), 0.93 (d, *J* = 7 Hz, 3H), 0.85 – 0.68 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.3, 83.2, 47.0, 38.7, 29.7, 27.7, 24.9, 24.7, 20.2. **^{11}B NMR** (128 MHz, Chloroform-d) δ 34.1. **IR (cm^{-1}, neat):** 3407, 2976, 1642, 1370, 1144. **HRMS-ESI:** *m/z* calculated for $C_{15}H_{31}BNO_3$ $[M + H]^+$ 284.2392, found 284.2391.

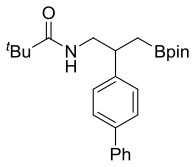
N-(2-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)pivalamide (2u)



The modified procedure was followed with **1u** (43.4 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (2.5 mg, 2.5 mol %), and PPh_3 (5.2 mg, 10 mol %) in toluene (1 mL) at 130 ℃ for 36 h. The resulting mixture was purified by flash column chromatography (dichloromethane/ethyl acetate = 10:1) to afford the product **2u** as a brown solid (38.1 mg, 55% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.19 (dd, *J* = 8, 2 Hz, 3H), 5.47 (s, 1H), 3.60 (dt, *J* = 13, 6 Hz, 1H), 3.24 (ddd, *J* = 13, 9, 5 Hz, 1H), 3.05 (tdd, *J* = 9, 7, 6 Hz, 1H), 1.17 (dd, *J* = 8, 3 Hz, 2H), 1.09 (d, *J* = 9 Hz, 12H), 1.04 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.0, 144.0, 128.4, 127.5, 126.6, 83.1, 46.4, 41.1, 38.5, 27.4, 24.7, 24.5, 16.3. **^{11}B NMR** (128 MHz, Chloroform-d) δ 33.4. **IR (cm^{-1}, neat):** 3347, 2975, 1640, 1530, 1367, 1144, 699. **HRMS-ESI:** *m/z* calculated for $C_{20}H_{33}BNO_3$ $[M + H]^+$ 346.2548, found 346.2553.

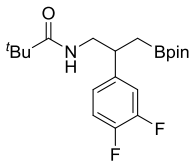
N-(2-([1,1'-Biphenyl]-4-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)

pivalamide (**2v**)



The modified procedure was followed with **1v** (58.7 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (2.5 mg, 2.5 mol %), and PPh_3 (5.2 mg, 10 mol %) in toluene (1 mL) at 150 ℃ for 48 h. The resulting mixture was purified by flash column chromatography (dichloromethane/ethyl acetate = 1:0) to afford the product **2v** as a brown oil (39.5 mg, 47% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.50 (m, 4H), 7.46 – 7.39 (m, 2H), 7.36 – 7.31 (m, 1H), 7.28 (d, *J* = 13 Hz, 4H), 5.53 (s, 1H), 3.68 – 3.60 (m, 1H), 3.30 (ddd, *J* = 13, 9, 5 Hz, 1H), 3.11 (tt, *J* = 9, 6 Hz, 1H), 1.21 (dd, *J* = 8, 4 Hz, 2H), 1.11 (d, *J* = 7 Hz, 12H), 1.06 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.1, 143.2, 140.9, 139.4, 128.7, 128.0, 127.1, 127.1, 126.9, 83.2, 46.4, 40.9, 38.6, 27.5, 24.7, 24.6. **^{11}B NMR** (128 MHz, Chloroform-d) δ 34.2. **IR (cm^{-1}, neat):** 3348, 2977, 1640, 1519, 1370, 1143, 967, 774. **HRMS-ESI:** *m/z* calculated for $C_{26}H_{37}BNO_3$ $[M + H]^+$ 422.2861, found 422.2860.

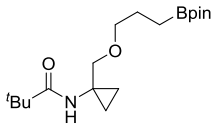
N-(2-(3,4-Difluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl) pivalamide (**2w**)



The modified procedure was followed with **1w** (50.7 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (2.5 mg, 2.5 mol %), and PPh_3 (5.2 mg, 10 mol %) in toluene (1 mL) at 150 ℃ for 48 h. The resulting mixture was purified by flash column chromatography (dichloromethane/ethyl acetate = 20:1) to afford the product **2w** as a brown solid (27.5 mg, 36% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 – 6.86 (m, 3H), 5.51 (s, 1H), 3.53 (dt, *J* = 13, 6 Hz, 1H), 3.25 (ddd, *J* = 13, 9, 6 Hz, 1H), 3.06 (tt, *J* = 9, 6 Hz, 1H), 1.34 – 1.24 (m, 2H), 1.11 (d, *J* = 11 Hz, 12H), 1.07 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.1, 123.5, 123.5, 123.4, 123.4, 117.0 (d, *J* = 17.0 Hz), 116.4 (d, *J* = 16.9 Hz), 83.4, 46.3, 40.6, 38.6, 27.5, 24.7, 24.6. **^{11}B NMR** (128 MHz, Chloroform-d) δ 33.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -137.90 (d, *J* = 20.07 Hz), -141.03 (d, *J* = 21.39

Hz). **IR (cm^{-1}, neat):** 2968, 1628, 1360, 1175, 998, 728, 697. **HRMS-ESI:** *m/z* calculated for $C_{20}H_{31}BF_2NO_3$ $[M + H]^+$ 382.2360, found 382.2360.

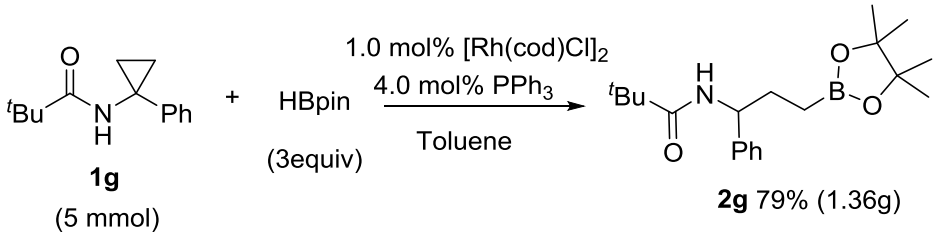
N-(1-((3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)methyl)cycloprop yl)pivalamide (**2x'**)



The general procedure was followed with **1x'** (42.3 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (1.0 mg, 1.0 mol %), and PPh_3 (2.1 mg, 4 mol %) in toluene (1 mL) at 130 ℃ for 24 h. The resulting mixture was purified by flash column chromatography (dichloromethane/ethyl acetate = 20:1) to afford the product **2x'** as a brown oil (36.4 mg, 54% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.86 (d, *J* = 9 Hz, 1H), 3.47 – 3.30 (m, 4H), 1.66 – 1.62 (m, 2H), 1.47 (t, *J* = 7 Hz, 2H), 1.23 (s, 12H), 1.17 (s, 9H), 0.76 (td, *J* = 8, 3 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.9, 83.0, 73.1, 71.5, 53.0, 50.5, 38.7, 27.6, 26.0, 24.8, 24.0. **^{11}B NMR** (128 MHz, Chloroform-d) δ 34.3. **IR (cm^{-1}, neat):** 3347, 2970, 1641, 1352, 1143. **HRMS-ESI:** *m/z* calculated for $C_{18}H_{35}BNO_4$ $[M + H]^+$ 340.2654, found 340.2649.

4. Synthetic Applications[3-6]

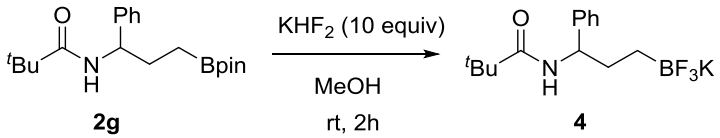
4.1. Gram-scale preparation of 2g



A 100.0 mL flame-dried schlenk tube with a stirring bar was added substrate **1g** (1.09g, 5 mmol), PPh_3 (0.053g, 4.0 mol %), $[Rh(cod)Cl]_2$ (25 mg, 1.0 mol %), HBpin (2.08mL, 3.0 equiv) and toluene (15 mL) under argon. The resulting mixture was stirred at 130 ^{o}C under Ar for 24 h. The solution was then cooled to room temperature and concentrated in vacuo. The collected fractions were purified by silica gel column

chromatography (dichloromethane/ethyl acetate = 20:1) to afford **2g** (1.36 g, 79% yield) as a white solid.

4.2. Preparation of 4

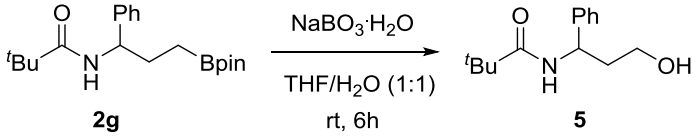


2g **4**

To a solution of **2g** (34.5 mg, 0.1 mmol) in MeOH (0.50 mL) was added KHF_2 (0.25 mL of saturated aqueous solution (4.0–4.5 M), 1.0 mmol) dropwise at room temperature. The solution was stirred at room temperature for 2 h, then concentrated in vacuo. To the residue was added 60% aqueous MeOH, which was then concentrated in vacuo. This procedure was repeated twice. The resultant white solid was dissolved in hot acetone, then ether was added. The precipitate was washed with ether, and the resultant precipitate was dissolved in acetone, and concentrated in vacuo overnight to afford potassium trifluoroborate **4** (29.1 mg, 89% yield) as a white solid.

N-(1-Phenyl-3-(trifluoroboranyl)propyl)pivalamide, potassium salt (**4**) **^{1}H NMR** (400 MHz, Acetone-d_6) δ 7.36 – 7.16 (m, 4H), 7.16 – 7.09 (m, 1H), 7.06 (d, J = 6 Hz, 1H), 4.81 (q, J = 7 Hz, 1H), 1.80 – 1.61 (m, 2H), 1.17 (s, 9H), 0.13 (tt, J = 14, 7 Hz, 2H). **^{13}C NMR** (101 MHz, Acetone-d_6) δ 177.5, 146.7, 128.5, 127.4, 126.6, 56.5, 39.0, 33.7, 33.7, 28.0. **^{11}B NMR** (128 MHz, Chloroform-d) δ 5.0. **^{19}F NMR** (376 MHz, Acetone-d_6) δ -140.14. **IR (cm^{-1}, neat):** 3370, 2974, 1640, 1372, 1146, 853, 701. **HRMS-ESI:** *m/z* calculated for $C_{14}H_{20}BF_3KNNaO$ $[M + Na]^+$ 348.1119, found 348.1114.

4.3. Preparation of 5

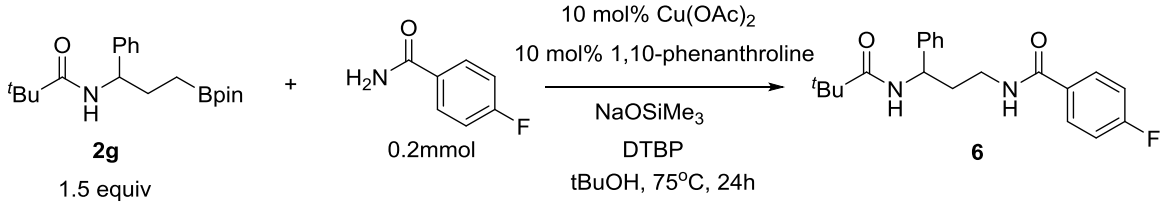


2g **5**

To a 25-mL flask containing a magnetic stirring bar were added **2g** (69.1 mg, 0.2 mmol), $NaBO_3 \cdot H_2O$ (79.8 mg, 0.8 mmol), THF (2 mL) and H_2O (2 mL). The mixture was stirred at room temperature for 6 h under air, upon which it was diluted with ethyl acetate. The mixture was extracted with ethyl acetate, the organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The resultant residue was purified by silica gel column chromatography (hexane/ethyl acetate = 3:1 to 2:1) to afford **5** (36.5 mg, 78% yield) as a colorless oil.

N-(3-Hydroxy-1-phenylpropyl)pivalamide (**5**) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 5H), 6.34 (d, *J* = 8 Hz, 1H), 5.19 (ddd, *J* = 10, 8, 4 Hz, 1H), 3.69 (dt, *J* = 9, 3 Hz, 1H), 3.61 – 3.54 (m, 1H), 2.14 (ddt, *J* = 15, 11, 4 Hz, 1H), 1.81 (ddt, *J* = 14, 10, 3 Hz, 1H), 1.22 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.1, 141.6, 128.8, 127.5, 126.4, 58.8, 50.4, 38.7, 38.4, 27.5. **IR (cm^{-1}, neat):** 3341, 2957, 1639, 1526, 1218, 1054, 699. **HRMS-ESI:** *m/z* calculated for $C_{14}H_{22}NO_2$ $[M + H]^+$ 236.1645, found 236.1643.

4.4. Preparation of 6

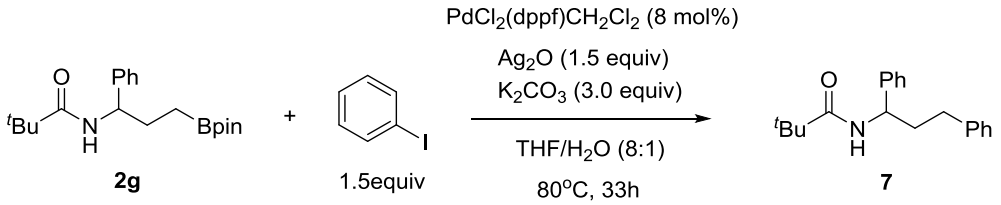


A 25.0 mL flame-dried schlenk tube was charged with a stir bar, 4-fluorobenzamide (27.8 mg, 0.2 mmol, 1.0 equiv), **2g** (103.6 mg, 0.3 mmol, 1.5 equiv), $Cu(OAc)_2$ (3.6 mg, 0.1 equiv), 1,10-phenanthroline (3.6 mg, 0.1 equiv), $NaOSiMe_3$ (26 mg, 1.1 equiv) and molecular sieves (0.7 g / mmol amide). The flask was evacuated and backfilled with nitrogen three times. *tert*-Butanol (1mL) and di-*tert*-butylperoxide (DTBP, 3.0 equiv) were added via syringe. The mixture was heated in an oil bath at 75 ℃ for 24 h with vigorous stirring. The reaction was then cooled to room temperature, diluted with

dichloromethane (10 mL) and concentrated in vacuo. The resultant residue was purified by flash silica gel chromatography (PE : EA = 5:1) to afford **6** (49.7 mg, 70% yield) as a white solid.

4-Fluoro-N-(3-phenyl-3-pivalamidopropyl)benzamide (**6**) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 – 7.84 (m, 2H), 7.71 (d, *J* =6 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.31 – 7.27 (m, 2H), 7.15 – 7.07 (m, 2H), 6.01 (d, *J* = 9 Hz, 1H), 5.15 (ddd, *J* = 11, 9, 4 Hz, 1H), 4.12 – 3.98 (m, 1H), 2.99 – 2.92 (m, 1H), 2.22 (dddd, *J* = 14, 11, 5, 4 Hz, 1H), 1.94 – 1.88 (m, 1H), 1.24 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.2, 166.1, 165.9, 163.4, 141.2, 130.6 (d, *J* = 3.1 Hz), 129.4 (d, *J* = 8.7 Hz), 127.8, 127.7 (d, *J* = 252.0 Hz), 115.4 (d, *J* = 21.8 Hz), 50.1, 38.9, 36.1, 35.4, 27.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -108.86. **IR (cm^{-1}, neat):** 3328, 2964, 1634, 1603, 1502, 1230, 1160, 801, 700. **HRMS-ESI:** *m/z* calculated for $C_{21}H_{26}FN_2O_2$ $[M + H]^+$ 357.1973, found 357.1970.

4.5. Preparation of 7

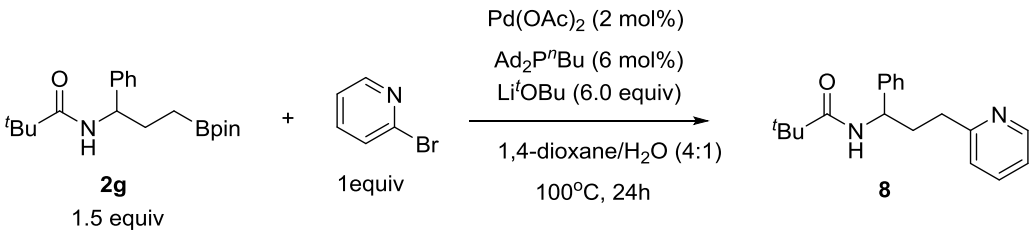


A 25.0 mL flame-dried schlenk tube was charged with a magnetic stirring bar, **2g** (69.1 mg, 0.2 mmol), iodobenzene (61.2 mg, 0.3 mmol), $PdCl_2$(dppf) CH_2Cl_2 (13.1 mg, 0.016 mmol), Ag_2O (69.5 mg, 0.3 mmol), K_2CO_3 (82.9 mg, 0.6 mmol) and water (0.20 mL) in THF (1.6 mL) under nitrogen atmosphere, then the tube was sealed and the mixture was stirred at 80 ℃ for 33 h. The reaction was then cooled to room temperature, diluted with dichloromethane and concentrated in vacuo. The resultant residue was purified by flash silica gel chromatography (PE : EA = 5:1) to afford **7** (40.0 mg, 69% yield) as a white solid.

N-(1,3-Diphenylpropyl)pivalamide (**7**) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.27 (dd, *J* = 7, 3 Hz, 5H), 7.22 – 7.10 (m, 3H), 5.83 (d, *J* = 8 Hz, 1H), 5.02

(q, *J* = 7 Hz, 1H), 2.69 – 2.50 (m, 2H), 2.23 – 2.05 (m, 2H), 1.16 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.5, 142.2, 141.5, 128.7, 128.5, 128.3, 127.4, 126.4, 126.0, 53.1, 38.6, 37.8, 32.5, 27.5. **IR (cm^{-1}, neat):** 3331, 2957, 1634, 1529, 1211, 750, 698. **HRMS-ESI:** *m/z* calculated for $C_{20}H_{26}NO$ $[M + H]^+$ 296.2009, found 296.2007.

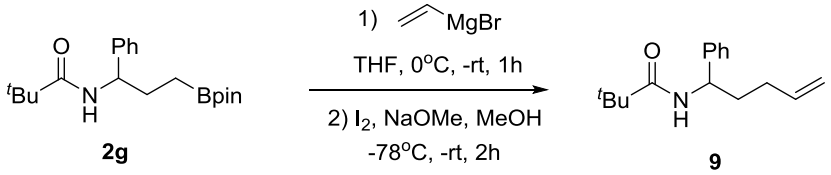
4.6. Preparation of 8



A 25.0 mL flame-dried schlenk tube with a magnetic stirring bar was charged with **2g** (103.5 mg, 0.3 mmol), $Pd(OAc)_2$ (1.4 mg, 0.006 mmol), Ad_2P^nBu (6.6 mg, 0.018 mmol), 2-bromopyridine (24 mg, 0.15 mmol, 1 equiv), and LiO^tBu (72.0 mg, 0.9 mmol, 6 equiv) under nitrogen atmosphere. 1,4-Dioxane (1.2 mL) and degassed water (0.8 mL) was added to the tube and the resulting mixture was stirred at room temperature for 5 minutes. The tube was heated to 100 ℃ and held at that temperature for 24 h. The reaction mixture was then allowed to cool at room temperature and concentrated in vacuo. The resultant residue was purified by flash silica gel chromatography (PE : EA = 5:1 to 3:1) to afford **8** (33.4 mg, 75% yield) as a white solid.

N-(1-Phenyl-3-(pyridin-2-yl)propyl)pivalamide (**8**) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (ddd, *J* = 5, 2, 1 Hz, 1H), 7.58 (td, *J* = 8, 2 Hz, 1H), 7.34 – 7.27 (m, 4H), 7.25 – 7.19 (m, 1H), 7.12 (ddd, *J* = 8, 6, 2 Hz, 2H), 6.79 (d, *J* = 7 Hz, 1H), 5.02 (td, *J* = 8, 6 Hz, 1H), 2.83 (td, *J* = 7, 1 Hz, 2H), 2.37 – 2.18 (m, 2H), 1.17 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.9, 161.3, 149.1, 142.8, 136.5, 128.6, 127.1, 126.3, 123.2, 121.2, 53.6, 38.6, 35.1, 34.6, 27.6. **IR (cm^{-1}, neat):** 3348, 2957, 2921, 1637, 1525, 1366, 751, 700. **HRMS-ESI:** *m/z* calculated for $C_{19}H_{25}N_2O$ $[M + H]^+$ 297.1961, found 297.1957.

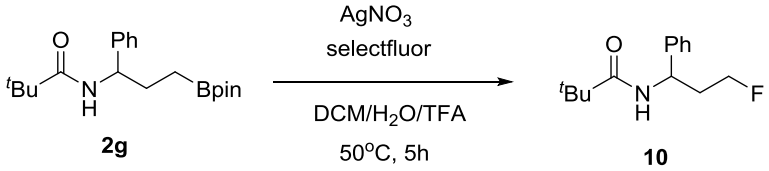
4.7. Preparation of 9



To a 25-mL flame-dried Schlenk tube charged with **2g** (69.1 mg, 0.20 mmol), THF (1.5 mL). Vinylmagnesium bromide (1.2 mL, 1.0 M in THF, 6.0 equiv) was then added dropwisely. The resulted mixture was allowed to stir as room tempereture for one hour. To the above solution at -78 ^{o}C, iodine (304.8 mg, 1.2 mmol, 6.0 equiv) was added dropwisely as a solution in methanol (2.0 mL). The reaction mixture was allowed to stir 30 min. at the same temperature followed by dropwise addition of a solution of NaOMe (64.8 mg, 1.2 mmol, 6.0 equiv) in methanol (2.5 mL). After warming to room temperature, the resultant mixture was allowed to stir for 1.5 h. Saturated aq. $Na_2S_2O_3$ (2 mL) was then added. The reaction mixture was diluted with Et_2O (15 mL) and water (15 mL). The combined ethereal solution was dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography on silica using PE/EtOAc (6:1) as the eluent to afford **9** as colorless oil (29.3 mg, 60% yield).

N-(1-Phenylpent-4-en-1-yl)pivalamide (**9**) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.26 (d, *J* = 3 Hz, 3H), 5.91 – 5.83 (m, 1H), 5.83 – 5.76 (m, 1H), 5.05 – 5.00 (m, 1H), 5.00 – 4.93 (m, 2H), 2.09 – 1.99 (m, 2H), 1.94 – 1.84 (m, 2H), 1.19 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.5, 142.3, 137.7, 128.7, 127.3, 126.4, 115.2, 52.8, 38.7, 35.4, 30.4, 27.6. **IR (cm^{-1}, neat):** 3321, 2968, 1632, 1536, 1451, 1217, 909, 699. **HRMS-ESI:** *m/z* calculated for $C_{16}H_{24}NO$ $[M + H]^+$ 246.1852, found 246.1854.

4.8. Preparation of 10

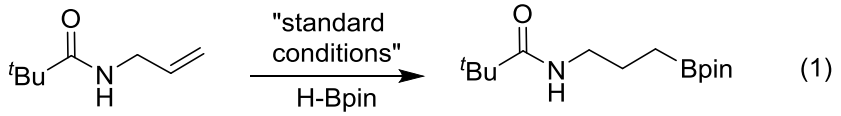


To a 25-mL flame-dried Schlenk tube charged with **2g** (69.1 mg, 0.20 mmol), $AgNO_3$ (6.8 mg, 0.04 mmol), Selectfluor (212.3 mg, 0.60 mmol, 3.0 equiv), DCM (1.0 mL), H_2O (1.0 mL) and TFA (62 μL, 0.8 mmol, 4.0 equiv) were then added. The reaction mixture was allowed to stir at 50 ^oC for 5 h. After cooling to room temperature, the reaction was quenched by slow addition of saturated aq. $NaHCO_3$ (5 mL), and the resulting mixture was extracted with EtOAc 3 times (3 × 10 mL). The combined ethereal solution was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by flash silica gel chromatography (PE : EA = 5:1) to afford **10** (33.7 mg, 71% yield) as a white solid.

N-(3-Fluoro-1-phenylpropyl)pivalamide (**10**) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2H), 7.26 (d, *J* = 4 Hz, 3H), 6.23 (s, 1H), 5.18 (td, *J* = 8, 5 Hz, 1H), 4.60 – 4.38 (m, 2H), 2.31 – 2.11 (m, 2H), 1.21 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.7, 141.3, 128.7, 127.4, 126.1, 81.9 (d, *J* = 163.5 Hz), 50.8 (d, *J* = 3.3 Hz), 38.6, 36.5 (d, *J* = 18.9 Hz), 27.5. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -217.89. **IR (cm^{-1}, neat):** 3338, 2962, 1633, 1528, 1227, 701. **HRMS-ESI:** *m/z* calculated for $C_{14}H_{21}FNO$ $[M + H]^+$ 238.1602, found 238.1597.

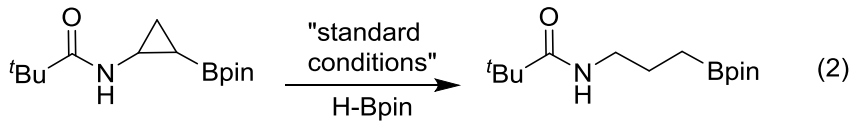
5. Mechanistic Experiments

5.1. Investigation of the plausible intermediates[7,8]



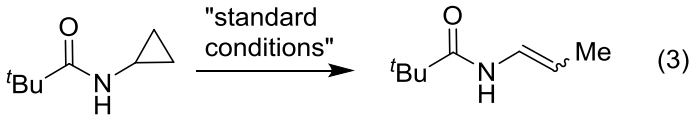
12 **2a**, 35%

12 (28.2 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (1.0 mg, 1 mol %), and PPh_3 (2.1 mg, 1 mol %) in toluene (1 mL) at 130 ℃ for 24 h. After cooling to room temperature, the solution was concentrated in vacuo. ^{1}H NMR yield of **2a** was 35% determined by using dibromomethane as an internal standard.



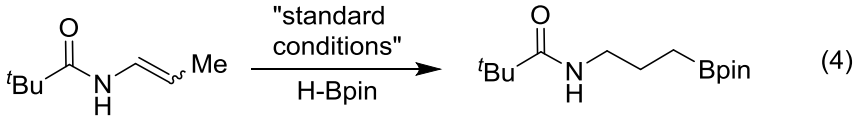
11 **2a**, n.d

11 (53.4 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (1.0 mg, 1 mol %), and PPh_3 (2.1 mg, 1 mol %) in toluene (1 mL) at 130 ℃ for 24 h. After cooling to room temperature, the solution was concentrated in vacuo.



1a **13**, 23%

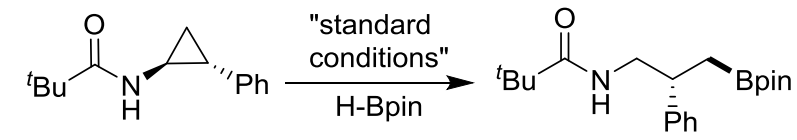
1a (28.2 mg, 0.2 mmol), $[Rh(cod)Cl]_2$ (1.0 mg, 1 mol %), and PPh_3 (2.1 mg, 1 mol %) in toluene (1 mL) at 130 ℃ for 24 h. After cooling to room temperature, the solution was concentrated in vacuo. ^{1}H NMR yield of **13** was 23% determined by using dibromomethane as an internal standard.



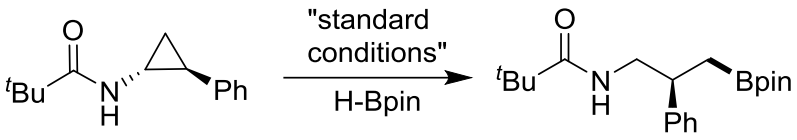
13 **2a**, 37%

13 (28.2 mg, 0.2 mmol), HBpin (87 uL, 0.6 mmol), $[Rh(cod)Cl]_2$ (1.0 mg, 1 mol %), and PPh_3 (2.1 mg, 1 mol %) in toluene (1 mL) at 130 ℃ for 24 h. After cooling to room temperature, the solution was concentrated in vacuo. ^{1}H NMR yield of **2a** was 37% determined by using dibromomethane as an internal standard.

5.2. Hydroboration of enantioenriched CPAs



(1*S*,2*R*)-**1v** (*R*)-**2v**, 49%, >99% ee



(1*R*,2*S*)-**1v** (*S*)-**2v**, 47%, >99% ee

The preparation of (R)-**2v** and (S)-**2v** followed the general procedure: A 25.0 mL flame-dried schlenk tube with a stirring bar was added substrate (1S,2R)-**1v** or (1R,2S)-**1v** (43.4 mg, 0.2 mmol, 1.0 equiv), PPh_3 (5.3 mg, 10.0 mol %), $[Rh(cod)Cl]_2$ (2.5 mg, 2.5 mol %), HBpin (76.8 mg, 0.6 mmol, 3.0 equiv) and toluene (1 mL) under argon. The resulting mixture was stirred at 130 ^oC under Ar for 36 h. The solution was then cooled to room temperature, and 3 mL of ethyl acetate were added. The mixture was concentrated in vacuo and purified by column chromatography on silica gel (DCM:EA = 10:1, 1% Et_3N) to afford (R)-**2v** (33.7 mg, 49% yield) in > 99% ee as a brown solid (Chiralcel OD-H column, Hexanes/ ^{i}PrOH = 90/10, flow: 1 mL/min, T = 25 ^oC). [α] 20 D -12.0 (c 0.3, CHCl3) and (S)-**2v** (32.3 mg, 47% yield) in > 99% ee as a brown solid (Chiralcel OD-H column, Hexanes/^{i}PrOH = 90/10, flow: 1 mL/min, T = 25 ^oC). [α] 20 D 45.6 (c 1.54, CHCl3).

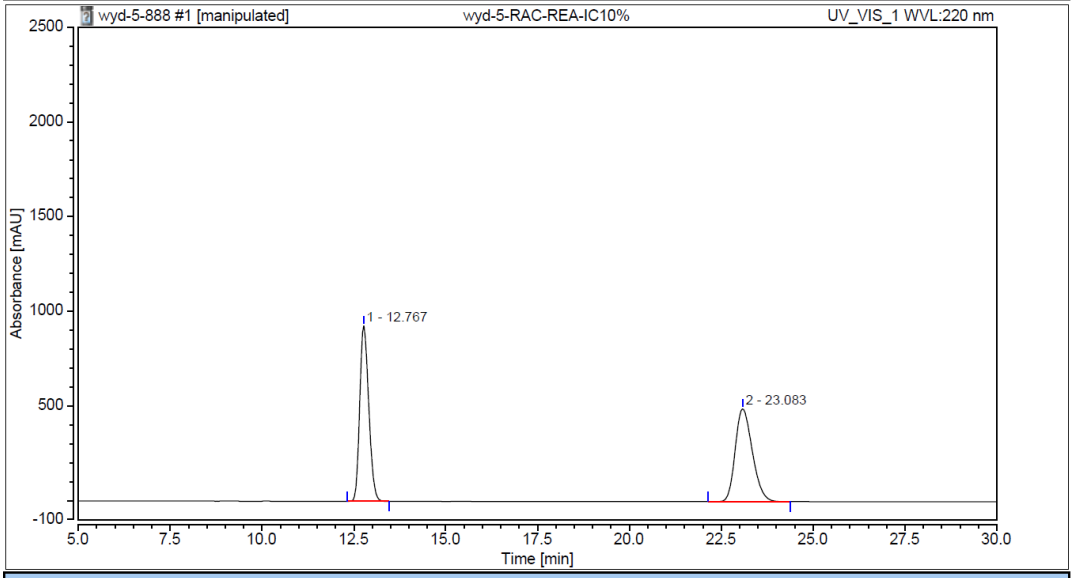
Supplementary Figure. HPLC of compound 1u

Chromatogram and Results

Injection Details

Injection Name:	**wyd-5-RAC-REA-IC10%**	*Run Time (min):*	**30.26**
Vial Number:	**RE1**	*Injection Volume:*	**20.00**
Injection Type:	**Unknown**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**220.0**
Instrument Method:	**atuto 90-10 1ml 60min**	*Bandwidth:*	**4**
Processing Method:	**New Processing Method**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**04/六月/20 14:22**	*Sample Weight:*	**1.0000**

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.767	263.045	926.292	49.80	65.40	n.a.
2		23.083	265.170	490.011	50.20	34.60	n.a.
Total:			**528.215**	**1416.303**	**100.00**	**100.00**	

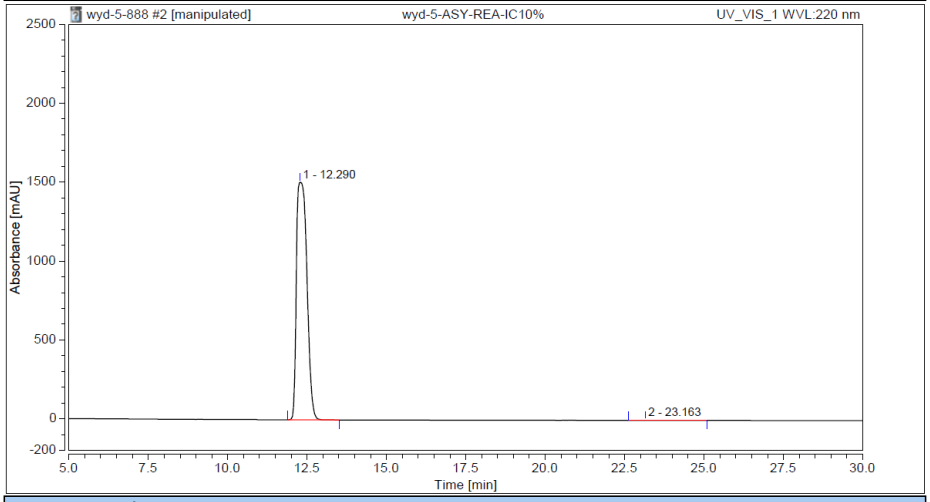
Supplementary Figure. HPLC of compound (1R,2S)-**1v**

Chromatogram and Results

Injection Details

Injection Name:	**wyd-5-ASY-REA-IC10%**	*Run Time (min):*	**46.06**
Vial Number:	**RC1**	*Injection Volume:*	**20.00**
Injection Type:	**Unknown**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**220.0**
Instrument Method:	**atuto 90-10 1ml 60min**	*Bandwidth:*	**4**
Processing Method:	**New Processing Method**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**17/六月/20 09:35**	*Sample Weight:*	**1.0000**

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.290	574.816	1506.440	99.98	99.99	n.a.
2		23.163	0.116	0.163	0.02	0.01	n.a.
Total:			**574.932**	**1506.604**	**100.00**	**100.00**	

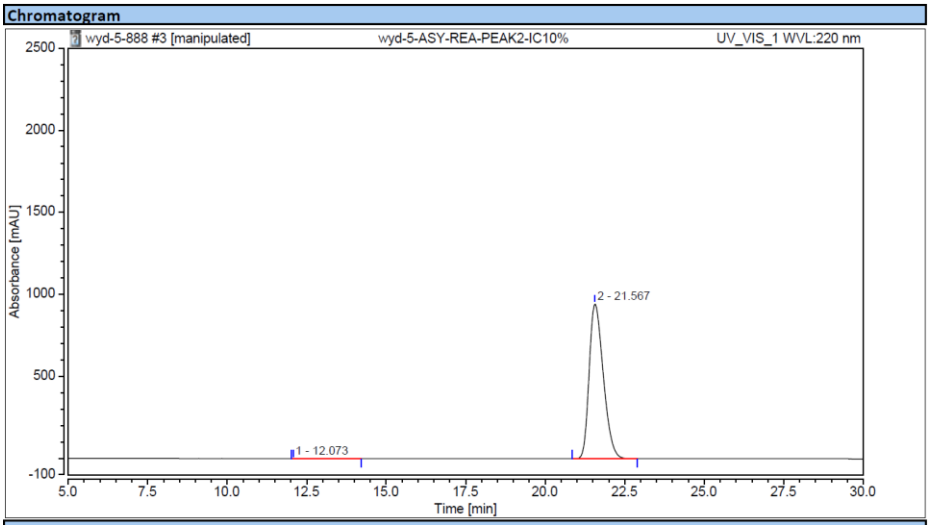
Supplementary Figure. HPLC of compound (1S,2R)-**1v**

Chromatogram and Results

Injection Details

Injection Name:	**wyd-5-ASY-REA-PEAK2-IC10%**	*Run Time (min):*	**36.48**
Vial Number:	**RC2**	*Injection Volume:*	**20.00**
Injection Type:	**Unknown**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**220.0**
Instrument Method:	**atuto 90-10 1ml 60min**	*Bandwidth:*	**4**
Processing Method:	**New Processing Method**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**17/六月/20 10:24**	*Sample Weight:*	**1.0000**

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.073	0.088	0.081	0.02	0.01	n.a.
2		21.567	485.671	944.599	99.98	99.99	n.a.
Total:			**485.759**	**944.680**	**100.00**	**100.00**	

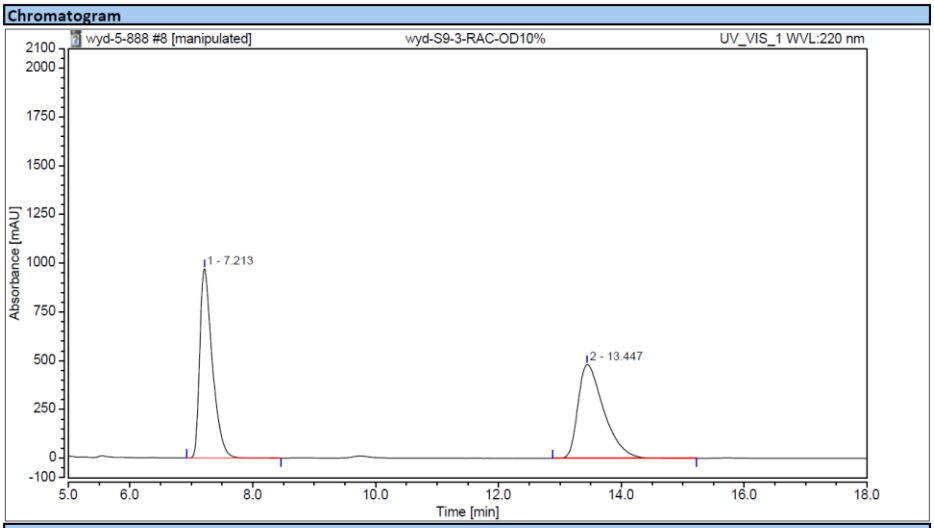
Supplementary Figure. HPLC of compound 2u

Chromatogram and Results

Injection Details

Injection Name:	**wyd-S9-3-RAC-OD10%**	*Run Time (min):*	**30.00**
Vial Number:	**RB2**	*Injection Volume:*	**5.00**
Injection Type:	**Unknown**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**220.0**
Instrument Method:	**atuto 90-10 1ml 30min**	*Bandwidth:*	**4**
Processing Method:	**New Processing Method**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**18/六月/20 11:39**	*Sample Weight:*	**1.0000**

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.213	229.903	971.228	49.60	66.88	n.a.
2		13.447	233.637	480.897	50.40	33.12	n.a.
Total:			**463.541**	**1452.126**	**100.00**	**100.00**	

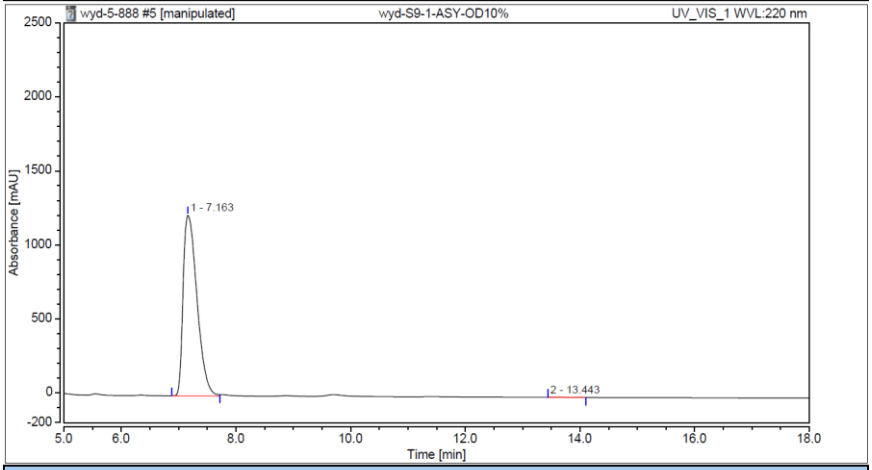
Supplementary Figure. HPLC of compound (S)-**2v**

Chromatogram and Results

Injection Details

Injection Name:	**wyd-S9-1-ASY-OD10%**	*Run Time (min):*	**22.76**
Vial Number:	**RB3**	*Injection Volume:*	**20.00**
Injection Type:	**Unknown**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**220.0**
Instrument Method:	**atuto 90-10 1ml 30min**	*Bandwidth:*	**4**
Processing Method:	**New Processing Method**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**18/六月/20 10:20**	*Sample Weight:*	**1.0000**

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.163	340.820	1220.754	99.99	100.00	n.a.
2		13.443	0.027	0.000	0.01	0.00	n.a.
Total:			**340.847**	**1220.754**	**100.00**	**100.00**	

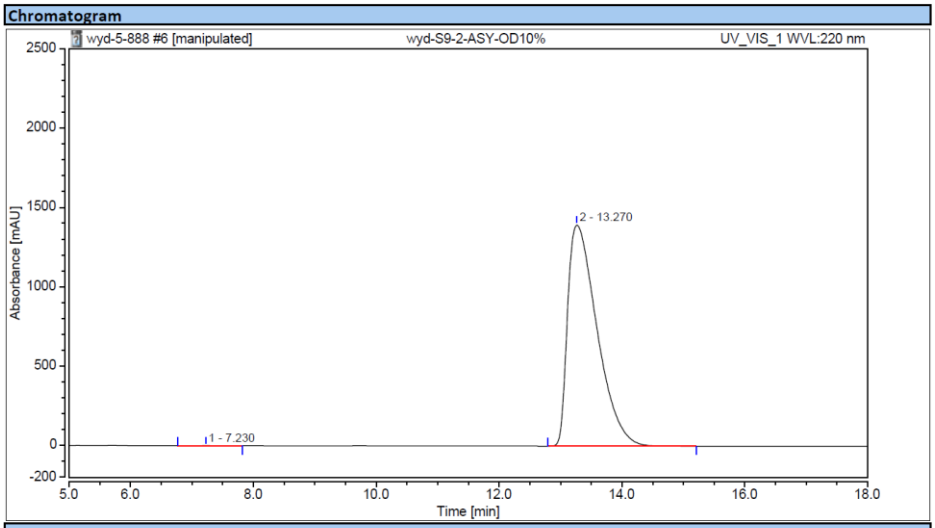
Supplementary Figure. HPLC of compound (R)-**2v**

Chromatogram and Results

Injection Details

Injection Name:	**wyd-S9-2-ASY-OD10%**	*Run Time (min):*	**21.75**
Vial Number:	**RB4**	*Injection Volume:*	**20.00**
Injection Type:	**Unknown**	*Channel:*	**UV_VIS_1**
Calibration Level:		*Wavelength:*	**220.0**
Instrument Method:	**atuto 90-10 1ml 30min**	*Bandwidth:*	**4**
Processing Method:	**New Processing Method**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**18/六月/20 10:45**	*Sample Weight:*	**1.0000**

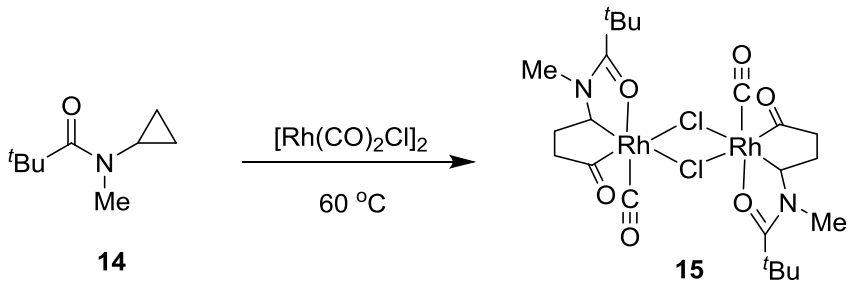
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.230	0.389	1.426	0.05	0.10	n.a.
2		13.270	771.464	1392.849	99.95	99.90	n.a.
Total:			**771.853**	**1394.275**	**100.00**	**100.00**	

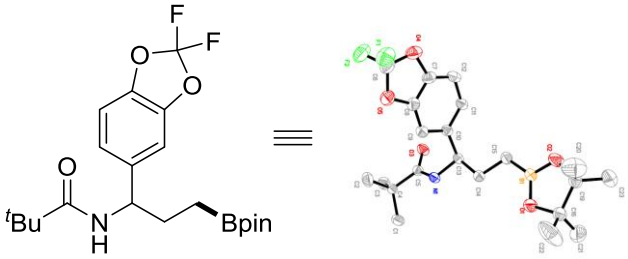
5.3. Synthesis of rhodacyclo complex 15[9]



Di-μ-chloro-tetracarbonyldirhodium (30 mg, 0.0773 mmol) and N-cyclopropyl-N-methylpivalamide (0.2 mL) were stirred at 60 ℃ for 24 h and then cooled to r.t. Hexane (1 mL) was added to complete precipitation of the metal complex and then the solvent was removed in vacuo. The precipitate was washed with Et_2O (3 × 1 mL) and then dried in vacuo to afford the metallacycle **15** (38 mg, 70 %) as a brown solid. The metallacycle was recrystallized by slow diffusion of hexane into CH_2Cl_2 to afford **15** as brown crystals.

6. Crystallographic Data

X-Ray crystal structure analysis of compound **2l**

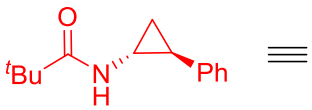


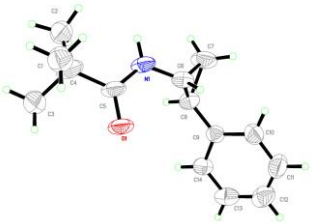
B(1)-O(2)	1.344(4)	C(10)-C(13)	1.517(4)
B(1)-O(1)	1.348(4)	C(11)-C(12)	1.396(4)
B(1)-C(15)	1.545(5)	C(11)-H(11)	0.9500
C(1)-C(4)	1.523(4)	C(12)-H(12)	0.9500
C(1)-H(1A)	0.9800	C(13)-N(1)	1.471(3)
C(1)-H(1B)	0.9800	C(13)-C(14)	1.528(4)
C(1)-H(1C)	0.9800	C(13)-H(13)	1.0000
C(2)-C(4)	1.533(4)	C(14)-C(15)	1.530(4)
C(2)-H(2A)	0.9800	C(14)-H(14A)	0.9900
C(2)-H(2B)	0.9800	C(14)-H(14B)	0.9900
C(2)-H(2C)	0.9800	C(15)-H(15A)	0.9900
C(3)-C(4)	1.520(4)	C(15)-H(15B)	0.9900
C(3)-H(3A)	0.9800	C(16)-O(1)	1.457(4)
C(3)-H(3B)	0.9800	C(16)-C(22)	1.496(7)
C(3)-H(3C)	0.9800	C(16)-C(21)	1.521(6)
C(4)-C(5)	1.530(4)	C(16)-C(19)	1.554(5)
C(5)-O(3)	1.239(3)	C(19)-O(2)	1.422(4)
C(5)-N(1)	1.338(4)	C(19)-C(23)	1.500(6)
C(6)-F(2)	1.328(5)	C(19)-C(20)	1.517(6)
C(6)-F(1)	1.337(4)	N(1)-H(1)	0.8800
C(6)-O(5)	1.365(5)	C(23)-H(23A)	0.9800
C(6)-O(4)	1.377(5)	C(23)-H(23B)	0.9800
C(7)-C(8)	1.361(4)	C(23)-H(23C)	0.9800
C(7)-C(12)	1.366(5)	C(21)-H(21A)	0.9800
C(7)-O(4)	1.399(4)	C(21)-H(21B)	0.9800
C(8)-C(9)	1.362(4)	C(21)-H(21C)	0.9800
C(8)-O(5)	1.403(4)	C(22)-H(22A)	0.9800
C(9)-C(10)	1.396(4)	C(22)-H(22B)	0.9800
C(9)-H(9)	0.9500	C(22)-H(22C)	0.9800
C(10)-C(11)	1.391(4)	C(20)-H(20A)	0.9800

C(20)-H(20B)	0.9800	O(5)-C(6)-O(4)	111.2(3)
C(20)-H(20C)	0.9800	C(8)-C(7)-C(12)	122.8(3)
		C(8)-C(7)-O(4)	108.7(3)
O(2)-B(1)-O(1)	111.7(3)	C(12)-C(7)-O(4)	128.5(3)
O(2)-B(1)-C(15)	122.0(3)	C(7)-C(8)-C(9)	123.3(3)
O(1)-B(1)-C(15)	126.3(3)	C(7)-C(8)-O(5)	108.9(3)
C(4)-C(1)-H(1A)	109.5	C(9)-C(8)-O(5)	127.8(3)
C(4)-C(1)-H(1B)	109.5	C(8)-C(9)-C(10)	116.1(3)
H(1A)-C(1)-H(1B)	109.5	C(8)-C(9)-H(9)	122.0
C(4)-C(1)-H(1C)	109.5	C(10)-C(9)-H(9)	122.0
H(1A)-C(1)-H(1C)	109.5	C(11)-C(10)-C(9)	120.1(3)
H(1B)-C(1)-H(1C)	109.5	C(11)-C(10)-C(13)	120.0(2)
C(4)-C(2)-H(2A)	109.5	C(9)-C(10)-C(13)	119.8(2)
C(4)-C(2)-H(2B)	109.5	C(10)-C(11)-C(12)	122.8(3)
H(2A)-C(2)-H(2B)	109.5	C(10)-C(11)-H(11)	118.6
C(4)-C(2)-H(2C)	109.5	C(12)-C(11)-H(11)	118.6
H(2A)-C(2)-H(2C)	109.5	C(7)-C(12)-C(11)	114.8(3)
H(2B)-C(2)-H(2C)	109.5	C(7)-C(12)-H(12)	122.6
C(4)-C(3)-H(3A)	109.5	C(11)-C(12)-H(12)	122.6
C(4)-C(3)-H(3B)	109.5	N(1)-C(13)-C(10)	112.0(2)
H(3A)-C(3)-H(3B)	109.5	N(1)-C(13)-C(14)	108.6(2)
C(4)-C(3)-H(3C)	109.5	C(10)-C(13)-C(14)	111.2(2)
H(3A)-C(3)-H(3C)	109.5	N(1)-C(13)-H(13)	108.3
H(3B)-C(3)-H(3C)	109.5	C(10)-C(13)-H(13)	108.3
C(3)-C(4)-C(1)	109.5(3)	C(14)-C(13)-H(13)	108.3
C(3)-C(4)-C(2)	109.4(3)	C(13)-C(14)-C(15)	114.0(2)
C(1)-C(4)-C(2)	109.9(3)	C(13)-C(14)-H(14A)	108.7
C(3)-C(4)-C(5)	109.5(2)	C(15)-C(14)-H(14A)	108.7
C(1)-C(4)-C(5)	112.1(2)	C(13)-C(14)-H(14B)	108.7
C(2)-C(4)-C(5)	106.4(2)	C(15)-C(14)-H(14B)	108.7
O(3)-C(5)-N(1)	121.2(2)	H(14A)-C(14)-H(14B)	107.6
O(3)-C(5)-C(4)	120.4(3)	C(14)-C(15)-B(1)	117.4(3)
N(1)-C(5)-C(4)	118.3(2)	C(14)-C(15)-H(15A)	108.0
F(2)-C(6)-F(1)	106.0(3)	B(1)-C(15)-H(15A)	108.0
F(2)-C(6)-O(5)	110.2(3)	C(14)-C(15)-H(15B)	108.0
F(1)-C(6)-O(5)	110.4(4)	B(1)-C(15)-H(15B)	108.0
F(2)-C(6)-O(4)	109.6(4)	H(15A)-C(15)-H(15B)	107.2
F(1)-C(6)-O(4)	109.3(3)	O(1)-C(16)-C(22)	106.9(4)

O(1)-C(16)-C(21)	105.9(4)	C(19)-C(23)-H(23C)	109.5
C(22)-C(16)-C(21)	112.0(5)	H(23A)-C(23)-H(23C)	109.5
O(1)-C(16)-C(19)	102.9(3)	H(23B)-C(23)-H(23C)	109.5
C(22)-C(16)-C(19)	115.1(4)	C(16)-C(21)-H(21A)	109.5
C(21)-C(16)-C(19)	113.0(4)	C(16)-C(21)-H(21B)	109.5
O(2)-C(19)-C(23)	108.8(4)	H(21A)-C(21)-H(21B)	109.5
O(2)-C(19)-C(20)	106.5(4)	C(16)-C(21)-H(21C)	109.5
C(23)-C(19)-C(20)	108.1(4)	H(21A)-C(21)-H(21C)	109.5
O(2)-C(19)-C(16)	103.5(3)	H(21B)-C(21)-H(21C)	109.5
C(23)-C(19)-C(16)	114.9(4)	C(16)-C(22)-H(22A)	109.5
C(20)-C(19)-C(16)	114.7(4)	C(16)-C(22)-H(22B)	109.5
C(5)-N(1)-C(13)	122.0(2)	H(22A)-C(22)-H(22B)	109.5
C(5)-N(1)-H(1)	119.0	C(16)-C(22)-H(22C)	109.5
C(13)-N(1)-H(1)	119.0	H(22A)-C(22)-H(22C)	109.5
B(1)-O(1)-C(16)	109.6(3)	H(22B)-C(22)-H(22C)	109.5
B(1)-O(2)-C(19)	110.9(3)	C(19)-C(20)-H(20A)	109.5
C(6)-O(4)-C(7)	105.5(3)	C(19)-C(20)-H(20B)	109.5
C(6)-O(5)-C(8)	105.5(3)	H(20A)-C(20)-H(20B)	109.5
C(19)-C(23)-H(23A)	109.5	C(19)-C(20)-H(20C)	109.5
C(19)-C(23)-H(23B)	109.5	H(20A)-C(20)-H(20C)	109.5
H(23A)-C(23)-H(23B)	109.5	H(20B)-C(20)-H(20C)	109.5

X-Ray crystal structure analysis of compound **(1R, 2S)-1v**





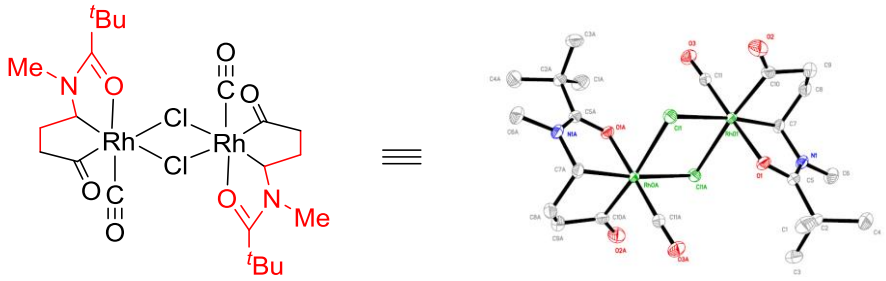
C(1)-C(4)	1.369(13)	C(3)-H(3B)	0.9800
C(1)-H(1A)	0.9800	C(3)-H(3C)	0.9800
C(1)-H(1B)	0.9800	C(4)-C(2')	1.29(2)
C(1)-H(1C)	0.9800	C(4)-C(5)	1.542(8)
C(2)-C(4)	1.585(13)	C(4)-C(3')	1.562(15)
C(2)-H(2A)	0.9800	C(4)-C(1')	1.757(18)
C(2)-H(2B)	0.9800	C(5)-O(1)	1.224(5)
C(2)-H(2C)	0.9800	C(5)-N(1)	1.343(6)
C(3)-C(4)	1.659(13)	C(6)-N(1)	1.423(6)
C(3)-H(3A)	0.9800	C(6)-C(7)	1.471(7)

C(6)-C(8)	1.507(6)	C(21)-H(21A)	0.9900
C(6)-H(6A)	1.0000	C(21)-H(21B)	0.9900
C(7)-C(8)	1.502(7)	C(22)-C(23)	1.485(7)
C(7)-H(7A)	0.9900	C(22)-H(22A)	1.0000
C(7)-H(7B)	0.9900	C(23)-C(28)	1.383(7)
C(8)-C(9)	1.470(6)	C(23)-C(24)	1.389(7)
C(8)-H(8A)	1.0000	C(24)-C(25)	1.387(8)
C(9)-C(10)	1.389(7)	C(24)-H(24A)	0.9500
C(9)-C(14)	1.386(6)	C(25)-C(26)	1.352(8)
C(10)-C(11)	1.387(8)	C(25)-H(25A)	0.9500
C(10)-H(10A)	0.9500	C(26)-C(27)	1.370(8)
C(11)-C(12)	1.342(10)	C(26)-H(26A)	0.9500
C(11)-H(11A)	0.9500	C(27)-C(28)	1.378(7)
C(12)-C(13)	1.353(9)	C(27)-H(27A)	0.9500
C(12)-H(12A)	0.9500	C(28)-H(28A)	0.9500
C(13)-C(14)	1.395(8)	N(1)-H(1D)	0.8800
C(13)-H(13A)	0.9500	N(2)-H(2D)	0.8800
C(14)-H(14A)	0.9500	C(1')-H(1'A)	0.9800
C(15)-C(17)	1.489(7)	C(1')-H(1'B)	0.9800
C(15)-H(15A)	0.9800	C(1')-H(1'C)	0.9800
C(15)-H(15B)	0.9800	C(3')-H(3'A)	0.9800
C(15)-H(15C)	0.9800	C(3')-H(3'B)	0.9800
C(16)-C(17)	1.557(8)	C(3')-H(3'C)	0.9800
C(16)-H(16A)	0.9800	C(2')-H(2'A)	0.9800
C(16)-H(16B)	0.9800	C(2')-H(2'B)	0.9800
C(16)-H(16C)	0.9800	C(2')-H(2'C)	0.9800
C(17)-C(19)	1.520(6)		
C(17)-C(18)	1.524(7)	C(4)-C(1)-H(1A)	109.5
C(18)-H(18A)	0.9800	C(4)-C(1)-H(1B)	109.5
C(18)-H(18B)	0.9800	H(1A)-C(1)-H(1B)	109.5
C(18)-H(18C)	0.9800	C(4)-C(1)-H(1C)	109.5
C(19)-O(2)	1.216(4)	H(1A)-C(1)-H(1C)	109.5
C(19)-N(2)	1.331(5)	H(1B)-C(1)-H(1C)	109.5
C(20)-N(2)	1.427(5)	C(4)-C(2)-H(2A)	109.5
C(20)-C(21)	1.480(6)	C(4)-C(2)-H(2B)	109.5
C(20)-C(22)	1.503(6)	H(2A)-C(2)-H(2B)	109.5
C(20)-H(20A)	1.0000	C(4)-C(2)-H(2C)	109.5
C(21)-C(22)	1.509(7)	H(2A)-C(2)-H(2C)	109.5

H(2B)-C(2)-H(2C)	109.5	C(7)-C(8)-H(8A)	114.5
C(4)-C(3)-H(3A)	109.5	C(6)-C(8)-H(8A)	114.5
C(4)-C(3)-H(3B)	109.5	C(10)-C(9)-C(14)	117.0(5)
H(3A)-C(3)-H(3B)	109.5	C(10)-C(9)-C(8)	122.6(4)
C(4)-C(3)-H(3C)	109.5	C(14)-C(9)-C(8)	120.3(4)
H(3A)-C(3)-H(3C)	109.5	C(9)-C(10)-C(11)	121.0(6)
H(3B)-C(3)-H(3C)	109.5	C(9)-C(10)-H(10A)	119.5
C(2')-C(4)-C(5)	108.9(11)	C(11)-C(10)-H(10A)	119.5
C(1)-C(4)-C(5)	111.1(8)	C(12)-C(11)-C(10)	120.5(6)
C(2')-C(4)-C(3')	130.5(14)	C(12)-C(11)-H(11A)	119.7
C(5)-C(4)-C(3')	102.1(7)	C(10)-C(11)-H(11A)	119.7
C(1)-C(4)-C(2)	114.4(8)	C(11)-C(12)-C(13)	120.5(6)
C(5)-C(4)-C(2)	113.6(6)	C(11)-C(12)-H(12A)	119.8
C(1)-C(4)-C(3)	110.0(8)	C(13)-C(12)-H(12A)	119.8
C(5)-C(4)-C(3)	109.1(5)	C(12)-C(13)-C(14)	120.1(6)
C(2)-C(4)-C(3)	97.8(8)	C(12)-C(13)-H(13A)	120.0
C(2')-C(4)-C(1')	113.0(13)	C(14)-C(13)-H(13A)	120.0
C(5)-C(4)-C(1')	101.3(8)	C(9)-C(14)-C(13)	120.9(5)
C(3')-C(4)-C(1')	96.9(9)	C(9)-C(14)-H(14A)	119.6
O(1)-C(5)-N(1)	120.3(5)	C(13)-C(14)-H(14A)	119.6
O(1)-C(5)-C(4)	121.8(5)	C(17)-C(15)-H(15A)	109.5
N(1)-C(5)-C(4)	117.9(4)	C(17)-C(15)-H(15B)	109.5
N(1)-C(6)-C(7)	118.2(4)	H(15A)-C(15)-H(15B)	109.5
N(1)-C(6)-C(8)	120.4(4)	C(17)-C(15)-H(15C)	109.5
C(7)-C(6)-C(8)	60.6(4)	H(15A)-C(15)-H(15C)	109.5
N(1)-C(6)-H(6A)	115.5	H(15B)-C(15)-H(15C)	109.5
C(7)-C(6)-H(6A)	115.5	C(17)-C(16)-H(16A)	109.5
C(8)-C(6)-H(6A)	115.5	C(17)-C(16)-H(16B)	109.5
C(6)-C(7)-C(8)	60.9(3)	H(16A)-C(16)-H(16B)	109.5
C(6)-C(7)-H(7A)	117.7	C(17)-C(16)-H(16C)	109.5
C(8)-C(7)-H(7A)	117.7	H(16A)-C(16)-H(16C)	109.5
C(6)-C(7)-H(7B)	117.7	H(16B)-C(16)-H(16C)	109.5
C(8)-C(7)-H(7B)	117.7	C(15)-C(17)-C(19)	110.0(4)
H(7A)-C(7)-H(7B)	114.8	C(15)-C(17)-C(18)	111.0(5)
C(9)-C(8)-C(7)	121.7(5)	C(19)-C(17)-C(18)	111.5(4)
C(9)-C(8)-C(6)	121.7(4)	C(15)-C(17)-C(16)	109.2(6)
C(7)-C(8)-C(6)	58.5(3)	C(19)-C(17)-C(16)	109.0(4)
C(9)-C(8)-H(8A)	114.5	C(18)-C(17)-C(16)	106.0(4)

C(17)-C(18)-H(18A)	109.5	C(24)-C(25)-H(25A)	120.2
C(17)-C(18)-H(18B)	109.5	C(25)-C(26)-C(27)	120.3(6)
H(18A)-C(18)-H(18B)	109.5	C(25)-C(26)-H(26A)	119.8
C(17)-C(18)-H(18C)	109.5	C(27)-C(26)-H(26A)	119.8
H(18A)-C(18)-H(18C)	109.5	C(26)-C(27)-C(28)	120.3(5)
H(18B)-C(18)-H(18C)	109.5	C(26)-C(27)-H(27A)	119.8
O(2)-C(19)-N(2)	120.6(4)	C(28)-C(27)-H(27A)	119.8
O(2)-C(19)-C(17)	121.7(3)	C(27)-C(28)-C(23)	120.9(5)
N(2)-C(19)-C(17)	117.7(3)	C(27)-C(28)-H(28A)	119.5
N(2)-C(20)-C(21)	119.3(4)	C(23)-C(28)-H(28A)	119.5
N(2)-C(20)-C(22)	120.4(4)	C(5)-N(1)-C(6)	121.8(4)
C(21)-C(20)-C(22)	60.8(3)	C(5)-N(1)-H(1D)	119.1
N(2)-C(20)-H(20A)	115.2	C(6)-N(1)-H(1D)	119.1
C(21)-C(20)-H(20A)	115.2	C(19)-N(2)-C(20)	121.1(3)
C(22)-C(20)-H(20A)	115.2	C(19)-N(2)-H(2D)	119.5
C(20)-C(21)-C(22)	60.4(3)	C(20)-N(2)-H(2D)	119.5
C(20)-C(21)-H(21A)	117.7	C(4)-C(1')-H(1'A)	109.5
C(22)-C(21)-H(21A)	117.7	C(4)-C(1')-H(1'B)	109.5
C(20)-C(21)-H(21B)	117.7	H(1'A)-C(1')-H(1'B)	109.5
C(22)-C(21)-H(21B)	117.7	C(4)-C(1')-H(1'C)	109.5
H(21A)-C(21)-H(21B)	114.9	H(1'A)-C(1')-H(1'C)	109.5
C(23)-C(22)-C(20)	119.8(4)	H(1'B)-C(1')-H(1'C)	109.5
C(23)-C(22)-C(21)	121.9(4)	C(4)-C(3')-H(3'A)	109.5
C(20)-C(22)-C(21)	58.8(3)	C(4)-C(3')-H(3'B)	109.5
C(23)-C(22)-H(22A)	114.9	H(3'A)-C(3')-H(3'B)	109.5
C(20)-C(22)-H(22A)	114.9	C(4)-C(3')-H(3'C)	109.5
C(21)-C(22)-H(22A)	114.9	H(3'A)-C(3')-H(3'C)	109.5
C(28)-C(23)-C(24)	117.3(5)	H(3'B)-C(3')-H(3'C)	109.5
C(28)-C(23)-C(22)	120.0(4)	C(4)-C(2')-H(2'A)	109.5
C(24)-C(23)-C(22)	122.6(4)	C(4)-C(2')-H(2'B)	109.5
C(25)-C(24)-C(23)	121.5(5)	H(2'A)-C(2')-H(2'B)	109.5
C(25)-C(24)-H(24A)	119.2	C(4)-C(2')-H(2'C)	109.5
C(23)-C(24)-H(24A)	119.2	H(2'A)-C(2')-H(2'C)	109.5
C(26)-C(25)-C(24)	119.6(5)	H(2'B)-C(2')-H(2'C)	109.5
C(26)-C(25)-H(25A)	120.2		

X-Ray crystal structure analysis of compound **15**



Rh(01)-C(11)	1.845(3)	C(9)-H(9A)	0.9700
Rh(01)-C(10)	2.006(3)	C(9)-H(9B)	0.9700
Rh(01)-C(7)	2.021(3)	C(4)-H(4A)	0.9600
Rh(01)-O(1)	2.0387(19)	C(4)-H(4B)	0.9600
Rh(01)-Cl(1)	2.4779(8)	C(4)-H(4C)	0.9600
Rh(01)-Cl(1)#1	2.5625(8)		
O(1)-C(5)	1.263(4)	C(11)-Rh(01)-C(10)	89.65(13)
O(3)-C(11)	1.128(3)	C(11)-Rh(01)-C(7)	98.06(13)
O(2)-C(10)	1.216(4)	C(10)-Rh(01)-C(7)	83.53(14)
N(1)-C(5)	1.311(4)	C(11)-Rh(01)-O(1)	178.87(11)
N(1)-C(6)	1.471(4)	C(10)-Rh(01)-O(1)	89.43(10)
N(1)-C(7)	1.495(4)	C(7)-Rh(01)-O(1)	81.19(10)
C(7)-C(8)	1.515(5)	C(11)-Rh(01)-Cl(1)	89.35(9)
C(7)-H(7)	0.9800	C(10)-Rh(01)-Cl(1)	98.49(10)
C(10)-C(9)	1.484(5)	C(7)-Rh(01)-Cl(1)	172.34(9)
C(5)-C(2)	1.545(4)	O(1)-Rh(01)-Cl(1)	91.43(6)
C(2)-C(4)	1.527(5)	C(11)-Rh(01)-Cl(1)#1	93.44(10)
C(2)-C(3)	1.528(5)	C(10)-Rh(01)-Cl(1)#1	173.77(10)
C(2)-C(1)	1.536(5)	C(7)-Rh(01)-Cl(1)#1	90.68(10)
C(6)-H(6A)	0.9600	O(1)-Rh(01)-Cl(1)#1	87.41(7)
C(6)-H(6B)	0.9600	Cl(1)-Rh(01)-Cl(1)#1	86.96(3)
C(6)-H(6C)	0.9600	Rh(01)-Cl(1)-Rh(01)#1	93.04(3)
C(3)-H(3A)	0.9600	C(5)-O(1)-Rh(01)	113.97(19)
C(3)-H(3B)	0.9600	C(5)-N(1)-C(6)	127.4(3)
C(3)-H(3C)	0.9600	C(5)-N(1)-C(7)	118.2(2)
C(8)-C(9)	1.470(6)	C(6)-N(1)-C(7)	114.4(3)
C(8)-H(8A)	0.9700	N(1)-C(7)-C(8)	111.9(3)
C(8)-H(8B)	0.9700	N(1)-C(7)-Rh(01)	106.10(19)
C(1)-H(1A)	0.9600	C(8)-C(7)-Rh(01)	109.3(2)
C(1)-H(1B)	0.9600	N(1)-C(7)-H(7)	109.8
C(1)-H(1C)	0.9600	C(8)-C(7)-H(7)	109.8

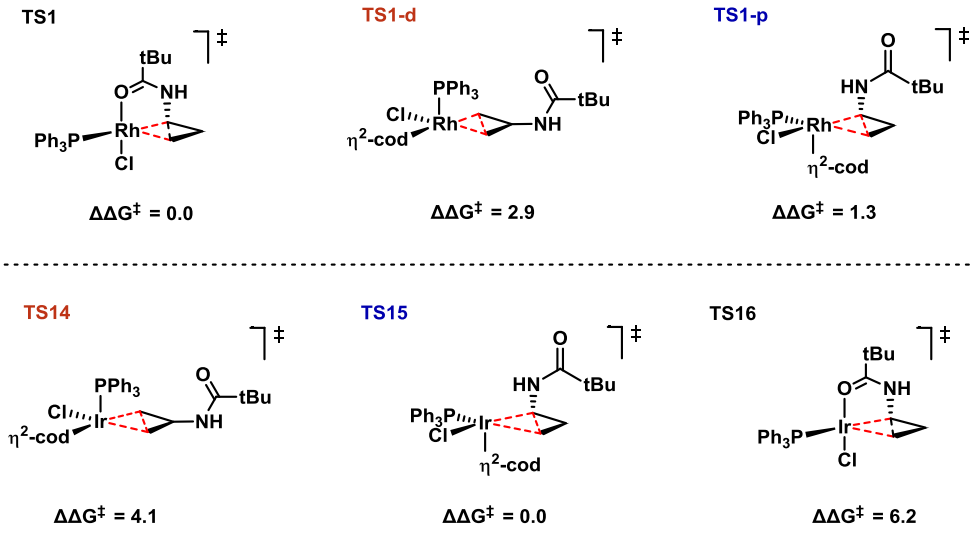
Rh(01)-C(7)-H(7)	109.8	H(3B)-C(3)-H(3C)	109.5
O(2)-C(10)-C(9)	124.5(3)	C(9)-C(8)-C(7)	109.3(3)
O(2)-C(10)-Rh(01)	122.9(3)	C(9)-C(8)-H(8A)	109.8
C(9)-C(10)-Rh(01)	112.6(3)	C(7)-C(8)-H(8A)	109.8
O(1)-C(5)-N(1)	119.1(3)	C(9)-C(8)-H(8B)	109.8
O(1)-C(5)-C(2)	115.3(3)	C(7)-C(8)-H(8B)	109.8
N(1)-C(5)-C(2)	125.5(3)	H(8A)-C(8)-H(8B)	108.3
O(3)-C(11)-Rh(01)	176.5(3)	C(2)-C(1)-H(1A)	109.5
C(4)-C(2)-C(3)	111.6(3)	C(2)-C(1)-H(1B)	109.5
C(4)-C(2)-C(1)	108.1(3)	H(1A)-C(1)-H(1B)	109.5
C(3)-C(2)-C(1)	108.1(3)	C(2)-C(1)-H(1C)	109.5
C(4)-C(2)-C(5)	114.2(3)	H(1A)-C(1)-H(1C)	109.5
C(3)-C(2)-C(5)	106.8(3)	H(1B)-C(1)-H(1C)	109.5
C(1)-C(2)-C(5)	107.7(3)	C(8)-C(9)-C(10)	111.3(3)
N(1)-C(6)-H(6A)	109.5	C(8)-C(9)-H(9A)	109.4
N(1)-C(6)-H(6B)	109.5	C(10)-C(9)-H(9A)	109.4
H(6A)-C(6)-H(6B)	109.5	C(8)-C(9)-H(9B)	109.4
N(1)-C(6)-H(6C)	109.5	C(10)-C(9)-H(9B)	109.4
H(6A)-C(6)-H(6C)	109.5	H(9A)-C(9)-H(9B)	108.0
H(6B)-C(6)-H(6C)	109.5	C(2)-C(4)-H(4A)	109.5
C(2)-C(3)-H(3A)	109.5	C(2)-C(4)-H(4B)	109.5
C(2)-C(3)-H(3B)	109.5	H(4A)-C(4)-H(4B)	109.5
H(3A)-C(3)-H(3B)	109.5	C(2)-C(4)-H(4C)	109.5
C(2)-C(3)-H(3C)	109.5	H(4A)-C(4)-H(4C)	109.5
H(3A)-C(3)-H(3C)	109.5	H(4B)-C(4)-H(4C)	109.5

7. Computational Details

All computations were performed in Gaussian 09[10]. When we explored mechanistic information of hydroboration of CPAs in the Rh catalytic systems, geometry optimizations of all the ground state and transition structures were carried out at the B3LYP-D3 level of theory[11] with the 6-31G(d) basis set [12] (LANL2DZ basis set[13] was used for Rh) in toluene using the CPCM model[14]. After geometry optimizations, vibrational frequencies were calculated at the same level to determine that optimized structures are local minimums or transition states, and to obtain thermal corrections at 298 K. Single-point energies were calculated at B3LYP-D3/6-311+G(d,p) level (SDD basis set for Rh) with the CPCM model in toluene.

In addition, when we investigated the opposite regioselectivity in two Ir catalytic systems, all of geometries were optimized at the B3LYP-D3 level of theory[11] with the 6-31G(d) basis set [12] (LANL2DZ basis set[13] for Ir) in gas. Vibrational frequencies were computed at the same level to determine that optimized structures are local minimums or transition states, and to evaluate thermal corrections at 298 K. Single-point energies were calculated at B3LYP-D3/6-311+G(d,p) level (SDD basis set for Ir) in gas. Molecular structures were visualized using CYLview[15].

As shown below, in the Rh catalytic system, non-directed transition states for both proximal and distal cleavages (**TS1-p** and **TS1-d**) are unfavorable. However, in the Ir catalytic system, the energy of directed transition state **TS16** is higher than that of non-directed transition states **TS14** and **TS15**.



DFT-Computed Energies and Cartesian Coordinate (unit:angstrom)

A

G_{sol}(toluene) = -1919.315143 Hartree

C	-0.931829	-0.489155	2.707776
C	-1.681778	-0.519003	1.522568
C	-3.027425	-0.902866	1.568612
C	-3.616402	-1.244929	2.786681
C	-2.869747	-1.199252	3.965644
C	-1.526081	-0.819563	3.924953
H	-3.613261	-0.947236	0.656944
H	-4.658531	-1.550029	2.813086
H	-3.330932	-1.466723	4.911989
H	-0.937699	-0.793711	4.837501
P	-0.848569	0.006104	-0.021022
C	-1.266972	1.792389	-0.137807
C	-1.574917	2.547363	1.002265
C	-1.178382	2.441235	-1.380392
C	-1.790424	3.923174	0.901050
H	-1.651484	2.060794	1.968861
C	-1.396615	3.814600	-1.479183
H	-0.957685	1.866978	-2.275358
C	-1.701024	4.560034	-0.337523
H	-2.033035	4.494909	1.792149
H	-1.330808	4.301385	-2.447882
H	-1.870727	5.629958	-0.414515
C	-1.809519	-0.715458	-1.404190
C	-3.057021	-0.185104	-1.774760
C	-1.295202	-1.814611	-2.105834
C	-3.779997	-0.753013	-2.822817
H	-3.457066	0.677878	-1.252530
C	-2.021679	-2.377691	-3.156476
H	-0.339765	-2.233760	-1.811880
C	-3.262714	-1.850238	-3.516149
H	-4.743883	-0.336166	-3.100179
H	-1.614465	-3.229513	-3.693308
H	-3.824938	-2.289319	-4.335327
Rh	1.429395	-0.506178	0.014667
C	3.446959	-1.196686	-0.701071
H	3.227681	-2.232299	-0.949126
C	3.594708	-0.893267	0.638830
H	3.450942	-1.705387	1.346856
C	4.212148	0.381362	1.180601
H	4.955509	0.762852	0.475422
H	4.756275	0.147598	2.101960
C	3.153567	1.462284	1.485560
H	2.722135	1.265082	2.474207
H	3.631048	2.452638	1.551857
C	2.008674	1.499004	0.495402
H	1.136410	2.034185	0.865622
C	2.100550	1.338337	-0.901926
H	1.277665	1.743925	-1.483700
C	3.403946	1.170711	-1.675207
H	4.205467	1.720482	-1.172070
H	3.292872	1.636315	-2.660356
C	3.801782	-0.307771	-1.871961
H	3.274482	-0.700604	-2.748180
H	4.876099	-0.385982	-2.099135
Cl	0.837388	-2.822787	0.479421
H	0.120218	-0.221731	2.664361

B

G_{sol}(toluene) = -2051.102649 Hartree

C	-2.925272	-2.288238	0.358235
C	-2.538367	-2.956313	-0.981644
Cl	0.829700	-3.229670	0.154654
Rh	-0.535774	-1.291553	-0.152959
O	-1.920109	0.257148	-0.387591
C	-3.115260	0.141349	-0.034712
N	-3.649140	-1.043485	0.317784
C	-3.979557	1.403247	0.003627
H	-4.606432	-1.058566	0.638534
C	-3.889001	2.070480	-1.383846
C	-5.450423	1.122969	0.347962
C	-3.357484	2.331789	1.069845
C	-3.655908	-3.501617	-0.138358
H	-2.271538	-2.415015	1.222166
H	-2.849217	2.283732	-1.638344
H	-4.315513	1.425826	-2.160960
H	-4.449286	3.011567	-1.374946
H	-5.565985	0.699426	1.353183
H	-6.008816	2.064073	0.332716
H	-5.921442	0.451462	-0.379535
H	-3.903715	3.281092	1.094091

H	-3.415849	1.879293	2.066589
H	-2.309923	2.535751	0.841293
H	-4.669837	-3.349030	-0.497506
H	-3.492154	-4.431864	0.395284
H	-1.614194	-3.523135	-1.031385
H	-2.808399	-2.413496	-1.881002
C	0.061781	2.443680	-1.082232
C	0.635135	1.858963	0.058018
C	0.732629	2.612874	1.233424
C	0.274656	3.932894	1.265810
C	-0.279747	4.512017	0.124115
C	-0.383845	3.763057	-1.052270
H	1.170134	2.173303	2.123422
H	0.358737	4.508073	2.183584
H	-0.630886	5.539664	0.148733
H	-0.817157	4.206449	-1.944388
P	1.157515	0.098921	-0.019808
C	2.215305	-0.092587	1.469240
C	3.543906	0.352256	1.506057
C	1.647622	-0.657299	2.619552
C	4.289781	0.239171	2.679681
H	3.999499	0.779284	0.618848
C	2.392700	-0.763355	3.794062
H	0.626189	-1.023017	2.572298
C	3.715167	-0.315599	3.825613
H	5.320674	0.581430	2.697890
H	1.944703	-1.204889	4.679720
H	4.298707	-0.404948	4.737620
C	2.349281	0.094640	-1.420974
C	3.051700	1.250408	-1.798199
C	2.580125	-1.103852	-2.111970
C	3.970038	1.206300	-2.847957
H	2.876394	2.186522	-1.278484
C	3.502275	-1.143976	-3.158356
H	2.038505	-1.997053	-1.818385
C	4.197138	0.009080	-3.529933
H	4.505629	2.107530	-3.133074
H	3.673928	-2.077629	-3.686568
H	4.910115	-0.023730	-4.349011
H	-0.032029	1.861528	-1.993704

TS1

G_{sol}(toluene) = -2051.09412 Hartree

C	-2.505776	-2.277005	0.488077
C	-1.975255	-2.823612	-1.186565
Cl	0.827575	-3.196826	0.396999
Rh	-0.616184	-1.328182	-0.135737
O	-1.939722	0.245026	-0.441362
C	-3.100840	0.039430	-0.006355
N	-3.438264	-1.173980	0.456486
C	-4.089423	1.199847	0.015030
H	-4.399919	-1.356607	0.713698
C	-4.107991	1.831603	-1.391269
C	-5.508150	0.769225	0.417010
C	-3.537699	2.222749	1.034771
C	-2.969342	-3.481729	-0.279967
H	-2.032008	-2.454959	1.455349
H	-3.103782	2.147521	-1.681818
H	-4.481780	1.122511	-2.138786
H	-4.766483	2.706728	-1.390949
H	-5.540711	0.361146	1.434162
H	-6.169385	1.641114	0.398448
H	-5.922732	0.029064	-0.277741
H	-4.188334	3.103789	1.057782
H	-3.506605	1.794651	2.043245
H	-2.528692	2.537890	0.759015
H	-4.013770	-3.490072	-0.592733
H	-2.652495	-4.432767	0.142814
H	-1.090611	-3.392590	-1.452037
H	-2.391936	-2.192042	-1.965920
C	-0.021797	2.386253	-1.237893
C	0.585533	1.907282	-0.066020
C	0.649297	2.741827	1.055867
C	0.120597	4.034827	1.006079
C	-0.470075	4.507561	-0.165864
C	-0.536700	3.679207	-1.290845
H	1.112326	2.385224	1.969743
H	0.177403	4.672197	1.884055
H	-0.877340	5.513862	-0.204912
H	-0.996290	4.039550	-2.206999
P	1.153754	0.160774	-0.022996
C	2.175061	0.087066	1.498346
C	3.472145	0.615387	1.556779
C	1.609303	-0.477056	2.649522
C	4.188474	0.586331	2.753229
H	3.924163	1.043545	0.667833
C	2.324770	-0.499538	3.847227

H	0.614783	-0.908426	2.588855
C	3.615032	0.031605	3.900341
H	5.194770	0.994071	2.789604
H	1.879418	-0.941187	4.734131
H	4.175585	0.007742	4.830643
C	2.378149	0.083188	-1.389443
C	3.037814	1.225299	-1.868616
C	2.674887	-1.168539	-1.949629
C	3.980351	1.116322	-2.892094
H	2.809332	2.199555	-1.449149
C	3.621748	-1.272621	-2.968961
H	2.166076	-2.051737	-1.575767
C	4.274136	-0.132395	-3.443696
H	4.483231	2.007088	-3.258184
H	3.846022	-2.246109	-3.395821
H	5.006428	-0.215747	-4.241857
H	-0.093324	1.740189	-2.107438

C

G_{sol}(toluene) = -2051.132415 Hartree

Cl	0.328880	-2.923724	0.024849
Rh	0.928166	-0.491930	-0.019177
O	3.010837	-0.909535	0.211379
C	3.713689	0.137949	0.123238
N	3.124649	1.315805	-0.070351
C	5.232110	0.018498	0.234665
H	3.699346	2.139593	-0.198766
C	1.677488	1.405444	-0.315617
C	5.700648	-0.872781	-0.935602
C	5.947417	1.376897	0.171394
C	5.545706	-0.673571	1.577110
C	1.357823	1.406549	-1.827296
C	1.197819	-0.095786	-2.010003
H	1.276756	2.256492	0.234245
H	5.202874	-1.845079	-0.903613
H	5.479359	-0.402501	-1.900720
H	6.782990	-1.028019	-0.871108
H	5.629490	2.043466	0.981545
H	7.025996	1.223565	0.277684
H	5.785246	1.881134	-0.788881
H	6.624860	-0.839395	1.663504
H	5.226099	-0.053902	2.422809
H	5.035164	-1.637227	1.643132
H	2.130708	1.878482	-2.453637
H	0.412741	1.932221	-1.998516
H	0.365303	-0.454520	-2.611963
H	2.119269	-0.624995	-2.265797
C	-1.460058	-1.284973	2.488084
C	-2.046716	-0.338372	1.637323
C	-3.233816	0.301255	2.031401
C	-3.821718	-0.001497	3.257518
C	-3.227663	-0.939710	4.106706
C	-2.050291	-1.579596	3.719523
H	-3.695559	1.036800	1.380837
H	-4.741106	0.496490	3.551758
H	-3.684493	-1.171182	5.064704
H	-1.588107	-2.314973	4.371579
P	-1.283518	0.064751	0.014959
C	-1.701200	1.853726	-0.118119
C	-2.556249	2.396237	-1.084354
C	-1.142926	2.706867	0.849592
C	-2.823479	3.768399	-1.101236
H	-3.029109	1.754769	-1.817860
C	-1.415568	4.072045	0.835895
H	-0.505477	2.293110	1.625290
C	-2.251732	4.609190	-0.147627
H	-3.487556	4.174103	-1.858955
H	-0.978553	4.716487	1.593100
H	-2.462160	5.674551	-0.162044
C	-2.337352	-0.779207	-1.219643
C	-3.198825	-1.812135	-0.828333
C	-2.229807	-0.460356	-2.583288
C	-3.944991	-2.505938	-1.781412
H	-3.279091	-2.081786	0.218198
C	-2.981648	-1.151262	-3.532737
H	-1.567496	0.334167	-2.910066
C	-3.840619	-2.177345	-3.133551
H	-4.605931	-3.307140	-1.464201
H	-2.892741	-0.889122	-4.582889
H	-4.422502	-2.719130	-3.873369
H	-0.569484	-1.815069	2.169772

TS2

G_{sol}(toluene) = -2462.981366 Hartree

C	1.302770	-2.947683	-0.519194
H	-0.741454	-1.312300	-1.269686

B	-1.424386	-1.710775	0.088160	H	-3.399303	-3.025616	-2.510678
Cl	1.528998	-0.308892	-2.486805	H	-4.816319	-2.069202	-2.030292
Rh	0.520039	-1.032594	-0.372002	H	-3.216919	-1.304045	-2.123950
O	2.499165	-0.748217	0.529336	C	-0.979151	0.981942	2.703735
C	3.264381	-1.688322	0.172809	C	-0.464326	1.884781	1.761311
N	2.754648	-2.774128	-0.402282	C	-0.176697	3.198196	2.165372
C	4.770313	-1.531620	0.365603	C	-0.405991	3.599808	3.481794
H	3.369947	-3.528162	-0.677148	C	-0.919417	2.694399	4.412801
C	5.020235	-1.060594	1.811420	C	-1.205717	1.385485	4.019869
C	5.545039	-2.832376	0.102520	H	0.228633	3.906111	1.450437
C	5.228146	-0.441435	-0.629639	H	-0.180442	4.619922	3.779675
C	0.661210	-3.508154	0.760111	H	-1.093275	3.007176	5.438536
C	0.005474	-2.259412	1.372716	H	-1.604663	0.674896	4.738566
H	1.081555	-3.492810	-1.435452	P	-0.174966	1.325743	0.032044
H	4.473853	-0.137885	2.019580	C	1.093799	2.524446	-0.532145
H	4.701920	-1.820070	2.534821	C	0.806225	3.587821	-1.394966
H	6.089805	-0.876523	1.958003	C	2.403534	2.361131	-0.053821
H	5.451258	-3.162095	-0.938985	C	1.814518	4.477771	-1.774865
H	6.610389	-2.664189	0.289561	H	-0.201585	3.723485	-1.772009
H	5.216122	-3.642810	0.763248	C	3.403859	3.255405	-0.427825
H	6.299009	-0.251428	-0.497987	H	2.637145	1.518042	0.586437
H	5.055097	-0.757091	-1.663677	C	3.112833	4.315804	-1.291438
H	4.680511	0.489834	-0.467956	H	1.581167	5.298030	-2.447987
H	1.386792	-3.988617	1.430176	H	4.414599	3.120560	-0.052202
H	-0.107155	-4.242221	0.505243	H	3.895289	5.009075	-1.586953
H	-0.909051	-2.470480	1.932807	C	-1.682084	1.832871	-0.878967
H	0.648268	-1.680819	2.037414	C	-2.663942	2.659857	-0.322341
C	-3.648226	-1.421327	0.600569	C	-1.847307	1.349407	-2.186470
C	-3.469180	-2.617136	-0.399290	C	-3.801645	2.994842	-1.059377
O	-2.347373	-0.779726	0.535947	H	-2.545905	3.035813	0.688391
O	-2.046514	-2.896538	-0.297417	C	-2.982972	1.689277	-2.920991
C	-3.861887	-1.866722	2.050592	H	-1.080785	0.715510	-2.623170
H	-3.755551	-0.997048	2.706325	C	-3.965611	2.508798	-2.357456
H	-4.861112	-2.288914	2.196333	H	-4.561407	3.632456	-0.615932
H	-3.126280	-2.617784	2.354759	H	-3.101926	1.311079	-3.932446
C	-4.705546	-0.399899	0.200248	H	-4.852725	2.767586	-2.928608
H	-5.694282	-0.869653	0.150620	H	-1.222987	-0.024972	2.395720
H	-4.743514	0.400223	0.945664	---			
H	-4.477294	0.055432	-0.764175	**D**			
C	-4.238920	-3.880683	-0.034832	G_{sol}(toluene) = -2463.022698 Hartree			
H	-5.316822	-3.685353	-0.023433	---			
H	-4.042747	-4.659027	-0.778976	C	-0.928868	0.681555	-0.939288
H	-3.942015	-4.262771	0.944438	H	1.189982	1.572167	-1.802054
C	-3.746867	-2.222174	-1.854140	B	-2.985760	-1.310054	-1.309044

Cl	2.432361	3.002058	0.951320	H	-2.396268	-1.231759	-3.445747
Rh	0.786589	1.644414	-0.333550	H	-3.245772	0.194860	-2.859812
O	-0.541487	3.332388	-0.421742	C	4.435757	0.820121	-0.674391
C	-1.740815	2.927163	-0.423374	C	3.775979	-0.140251	0.103289
N	-2.007333	1.642456	-0.617633	C	4.519492	-1.038849	0.879662
C	-2.864597	3.929185	-0.170261	C	5.912835	-0.977407	0.875447
H	-2.957108	1.289565	-0.567650	C	6.568743	-0.026061	0.090645
C	-2.740295	5.042343	-1.230590	C	5.829675	0.869826	-0.684884
C	-4.258481	3.287220	-0.249924	H	4.013084	-1.779891	1.490175
C	-2.638125	4.519230	1.237722	H	6.485023	-1.670871	1.484901
C	-1.117090	0.169336	-2.367877	H	7.653953	0.020784	0.088670
C	-2.485268	-0.550204	-2.592166	H	6.336555	1.617677	-1.287381
H	-1.048910	-0.152938	-0.240346	P	1.957218	-0.265817	0.010555
H	-1.750002	5.502529	-1.192721	C	1.405542	-0.936637	1.628055
H	-2.898173	4.643380	-2.239133	C	1.269843	-2.309908	1.883665
H	-3.495438	5.813966	-1.045810	C	1.077502	-0.016306	2.638696
H	-4.393232	2.503578	0.505060	C	0.783044	-2.753003	3.114619
H	-5.021016	4.051105	-0.067253	H	1.534025	-3.034559	1.122110
H	-4.451814	2.856552	-1.238989	C	0.591468	-0.464966	3.866966
H	-3.390488	5.288518	1.442607	H	1.224438	1.046863	2.469617
H	-2.724814	3.742666	2.006663	C	0.432339	-1.831966	4.103779
H	-1.644626	4.968212	1.312739	H	0.678645	-3.818435	3.298078
H	-0.306941	-0.526928	-2.588040	H	0.338560	0.256212	4.638472
H	-1.019992	1.005907	-3.068928	H	0.046211	-2.178806	5.057866
C	-3.813037	-1.535480	0.827330	C	1.710652	-1.640808	-1.179129
C	-3.448345	-2.945917	0.230587	C	2.663119	-1.886920	-2.178403
O	-3.761979	-0.680417	-0.356374	C	0.527967	-2.395433	-1.170741
O	-2.674794	-2.598950	-0.958416	C	2.434228	-2.868040	-3.144367
C	-2.776846	-1.004945	1.824186	H	3.584364	-1.315184	-2.203388
H	-2.972122	0.055004	2.012941	C	0.301234	-3.377048	-2.133506
H	-2.836937	-1.540384	2.776204	H	-0.235367	-2.215893	-0.425744
H	-1.753483	-1.096917	1.453404	C	1.255686	-3.616501	-3.123942
C	-5.209849	-1.431187	1.428467	H	3.181596	-3.047760	-3.911698
H	-5.317487	-2.117158	2.275300	H	-0.631520	-3.930402	-2.108467
H	-5.375221	-0.412801	1.794230	H	1.081286	-4.378875	-3.877680
H	-5.983505	-1.658545	0.692358	H	3.855974	1.533490	-1.248814
C	-2.582894	-3.818769	1.132204	---			
H	-3.119613	-4.066641	2.054228	**E**			
H	-2.344872	-4.754079	0.616123	G_{sol}(toluene) = -2775.035254 Hartree			
H	-1.644736	-3.328806	1.400532	---			
C	-4.665916	-3.731842	-0.261750	C	1.094964	0.439320	0.680855
H	-4.320865	-4.603879	-0.825092	H	-1.211752	0.434243	1.647094
H	-5.281622	-4.080773	0.572707	B	3.998867	-0.092089	1.301652
H	-5.288551	-3.123398	-0.924719	Cl	-0.093675	0.840775	-2.319177

Rh	-0.882212	0.533361	0.138031	H	-6.612670	3.457640	0.590037
O	-0.558295	2.626357	0.377640	C	-4.873347	3.890504	-0.444458
C	0.678615	2.851550	0.518139	H	-5.478364	4.479395	-1.134879
N	1.526903	1.853424	0.709322	C	-3.402654	3.836500	-0.788438
C	1.170182	4.295195	0.443742	H	-2.764028	3.903227	0.092095
H	2.528533	2.024286	0.723074	H	-3.160681	4.714069	-1.400762
C	0.396492	5.111168	1.498550	C	-3.014162	2.591804	-1.606553
C	2.681061	4.421690	0.692441	H	-3.622015	2.569949	-2.522817
C	0.826937	4.809566	-0.970791	H	-1.975546	2.680740	-1.942571
C	1.461645	-0.277133	1.982903	C	-3.177209	1.242750	-0.953020
C	2.933138	-0.083915	2.454353	H	-3.184358	0.417082	-1.660331
H	1.613824	-0.027929	-0.159919	C	-3.421574	0.917380	0.344544
H	-0.681264	5.026482	1.338342	H	-3.670036	-0.123921	0.537478
H	0.624353	4.760947	2.512029	C	-3.608355	1.827951	1.538502
H	0.679201	6.167303	1.430447	H	-2.873942	2.631933	1.537964
H	3.266295	3.886044	-0.063425	H	-3.408346	1.239049	2.441063
H	2.969888	5.476617	0.643943	C	-5.037943	2.388813	1.654064
H	2.963899	4.044229	1.681578	H	-5.738541	1.544811	1.741941
H	1.135320	5.856296	-1.068878	H	-5.122511	2.927363	2.611394
H	1.343231	4.221400	-1.737148	H	3.164439	-0.850662	3.202891
H	-0.247750	4.738243	-1.155918	H	3.011055	0.886448	2.963224
H	1.277446	-1.344591	1.826812	C	-3.698923	-2.313132	-1.030693
H	0.791926	0.046344	2.786486	C	-2.341109	-2.143694	-1.346837
C	5.729555	-0.667632	-0.071007	C	-1.953978	-2.153031	-2.694404
C	5.086160	0.676581	-0.566709	C	-2.902799	-2.335715	-3.699794
O	4.730406	-1.165083	0.872033	C	-4.251207	-2.500573	-3.377459
O	4.281596	1.059993	0.590536	C	-4.646354	-2.489296	-2.039147
C	7.018112	-0.459868	0.729517	H	-0.918775	-2.000636	-2.966108
H	7.293317	-1.403351	1.210102	H	-2.585073	-2.341597	-4.738288
H	7.843992	-0.147305	0.083134	H	-4.988191	-2.636688	-4.163557
H	6.882222	0.294287	1.510877	H	-5.692036	-2.618215	-1.775290
C	5.941034	-1.715190	-1.155861	P	-1.135026	-1.721582	-0.021073
H	6.632000	-1.342608	-1.919740	C	0.400235	-2.660504	-0.419105
H	6.374648	-2.618547	-0.715494	C	0.836501	-3.740286	0.363451
H	5.000393	-1.988507	-1.634712	C	1.187441	-2.249743	-1.508173
C	6.073432	1.798476	-0.860803	C	2.021061	-4.409353	0.049799
H	6.752014	1.510222	-1.670746	H	0.262837	-4.059798	1.224723
H	5.528446	2.692941	-1.179196	C	2.354375	-2.940774	-1.832626
H	6.666924	2.055113	0.019197	H	0.902126	-1.370432	-2.077477
C	4.119895	0.490756	-1.738720	C	2.778054	-4.020032	-1.054934
H	3.537929	1.406251	-1.878906	H	2.347963	-5.237301	0.672156
H	4.658982	0.279306	-2.667346	H	2.938134	-2.623005	-2.691773
H	3.417738	-0.324796	-1.551523	H	3.696142	-4.545236	-1.301421
C	-5.535850	3.285206	0.549079	C	-1.816115	-2.617460	1.431088

C	-2.268207	-3.941757	1.286119
C	-1.864996	-2.021256	2.695922
C	-2.759700	-4.646350	2.382483
H	-2.238319	-4.418953	0.311814
C	-2.357270	-2.728577	3.795241
H	-1.521513	-0.999992	2.814464
C	-2.805845	-4.039912	3.641282
H	-3.107823	-5.667094	2.254610
H	-2.391089	-2.250213	4.769712
H	-3.191549	-4.588734	4.495541
H	-4.021683	-2.316658	0.004284

TS3

G_{sol}(toluene) = -2775.004758 Hartree

C	-1.205931	0.150704	-1.061645
H	0.253485	0.461450	-1.506797
B	-3.900962	-0.899869	-1.238959
Cl	-0.621632	0.149815	2.338436
Rh	0.679845	0.631053	0.025737
O	-0.239119	2.562210	-0.060106
C	-1.361170	2.566367	-0.630768
N	-1.855264	1.461485	-1.186296
C	-2.129542	3.885950	-0.710634
H	-2.817684	1.472464	-1.502961
C	-1.239309	4.881379	-1.485227
C	-3.484020	3.749215	-1.423898
C	-2.333733	4.392394	0.732026
C	-1.503978	-0.738611	-2.270291
C	-3.024546	-0.917191	-2.548528
H	-1.582922	-0.344279	-0.163048
H	-0.277165	5.014146	-0.984173
H	-1.052995	4.531341	-2.507052
H	-1.739277	5.854182	-1.543008
H	-4.148327	3.036645	-0.923862
H	-3.987968	4.720845	-1.430735
H	-3.361426	3.435391	-2.467013
H	-2.831686	5.367755	0.712813
H	-2.953115	3.700998	1.312118
H	-1.372879	4.496508	1.241884
H	-1.060053	-1.713331	-2.056520
H	-1.008723	-0.351155	-3.169442
C	-4.963002	-1.535929	0.689356
C	-5.130342	0.020723	0.474241
O	-3.977192	-1.906158	-0.319655
O	-4.632546	0.211955	-0.887059
C	-6.223629	-2.342659	0.369254
H	-5.974674	-3.408014	0.384608
H	-7.013189	-2.161991	1.105059
H	-6.610086	-2.099635	-0.625246
C	-4.416322	-1.924277	2.059594
H	-5.094638	-1.591232	2.852337
H	-4.334530	-3.013723	2.127127
H	-3.429713	-1.489962	2.237032
C	-6.570267	0.522321	0.522062
H	-7.005927	0.349274	1.511761
H	-6.587019	1.599627	0.329162
H	-7.196722	0.032839	-0.226649
C	-4.253084	0.866088	1.398599
H	-4.329456	1.914278	1.095282
H	-4.595843	0.794700	2.435303
H	-3.200343	0.573530	1.370573
C	4.299596	4.259861	0.124791
H	5.341672	4.581803	0.160361
C	3.557529	4.516368	1.209348
H	4.070119	4.998797	2.042601
C	2.107138	4.186728	1.466051
H	1.492074	4.329512	0.578050
H	1.720067	4.886987	2.217261
C	1.892291	2.762317	2.016449
H	2.439016	2.677938	2.965691
H	0.835966	2.631412	2.268812
C	2.359353	1.606711	1.147120
H	2.788870	0.796187	1.725971
C	2.676963	1.595978	-0.218610
H	3.361790	0.809320	-0.531039
C	2.639830	2.741010	-1.205210
H	1.756845	3.359134	-1.060705
H	2.551731	2.314821	-2.212742
C	3.926317	3.589386	-1.174315
H	4.769403	2.947326	-1.469865
H	3.860162	4.352359	-1.966705
H	-3.171534	-1.852610	-3.101439
H	-3.375781	-0.111243	-3.205813
C	3.939400	-1.412724	1.573411
C	2.607501	-1.844297	1.460125
C	2.002875	-2.482572	2.550633
C	2.720515	-2.694639	3.727732

C	4.045049	-2.267123	3.832891
C	4.653348	-1.625547	2.752096
H	0.973240	-2.811131	2.486498
H	2.239825	-3.192890	4.564433
H	4.600498	-2.432435	4.751451
H	5.683591	-1.289298	2.823783
P	1.637337	-1.429498	-0.039745
C	0.457395	-2.821355	-0.249209
C	0.665563	-3.822489	-1.210500
C	-0.699879	-2.861787	0.545399
C	-0.263595	-4.851666	-1.366494
H	1.542622	-3.799256	-1.845491
C	-1.616324	-3.901169	0.391900
H	-0.886205	-2.068594	1.264347
C	-1.403661	-4.896235	-0.562940
H	-0.093928	-5.616739	-2.118819
H	-2.509675	-3.916454	1.004540
H	-2.127476	-5.696684	-0.687100
C	2.834703	-1.682883	-1.410327
C	3.808977	-2.692483	-1.349486
C	2.736871	-0.901344	-2.569364
C	4.670258	-2.907997	-2.424837
H	3.894153	-3.309549	-0.461261
C	3.597469	-1.119754	-3.645721
H	1.992396	-0.113422	-2.614041
C	4.566818	-2.121571	-3.574861
H	5.421407	-3.690054	-2.364047
H	3.513331	-0.502879	-4.535669
H	5.240445	-2.288617	-4.410332
H	4.424879	-0.916473	0.739464

F

G_{sol}(toluene) = -2775.046568 Hartree

C	-2.151986	1.682472	-1.155351
H	-2.625560	0.920767	-1.770555
C	-2.724469	1.820103	0.131994
H	-3.588985	1.184911	0.319314
C	-2.692721	3.017213	1.055388
H	-1.721701	3.506834	1.038415
H	-2.826807	2.648945	2.081298
C	-3.831010	4.016249	0.770185
H	-4.790036	3.506605	0.945671
H	-3.793844	4.817756	1.525232
C	-3.893467	4.637619	-0.602873
H	-4.861685	5.086568	-0.830745
C	-2.957754	4.722867	-1.556418
H	-3.257087	5.207645	-2.486636
C	-1.542306	4.199224	-1.547077
H	-1.067598	4.313699	-0.573512
H	-0.947292	4.800010	-2.247046
C	-1.436164	2.729095	-2.001172
H	-1.857596	2.657748	-3.014035
H	-0.374300	2.483724	-2.105019
Cl	0.781394	-0.513192	1.657967
Rh	-0.956127	0.647446	0.329114
O	0.299741	2.452419	0.500790
C	1.549682	2.515429	0.442454
N	2.303199	1.814732	-0.413363
C	2.263745	3.485563	1.396703
H	3.299237	1.798610	-0.231665
C	1.837898	0.770024	-1.319601
C	1.999085	2.975042	2.828532
C	3.778505	3.585374	1.155318
C	1.622785	4.875177	1.210680
H	2.014359	-0.201168	-0.847986
H	0.925077	2.920600	3.023360
H	2.417640	1.973706	2.970848
H	2.457779	3.655603	3.554663
H	4.007106	3.926459	0.139091
H	4.206825	4.312499	1.852800
H	4.290943	2.631864	1.326136
H	2.065423	5.584805	1.918224
H	1.790555	5.255156	0.196137
H	0.545607	4.831766	1.387934
C	2.511719	0.832141	-2.693252
H	2.160678	1.716459	-3.239165
H	2.161730	-0.046534	-3.248115
C	4.063555	0.822322	-2.647001
H	4.448368	0.538507	-3.632959
H	4.425136	1.838973	-2.447843
B	4.603714	-0.133332	-1.519886
O	4.802281	-1.479611	-1.630683
O	4.824445	0.343655	-0.248189
C	4.978597	-2.023046	-0.282990
C	5.357198	-0.746510	0.565149
C	3.643670	-2.654043	0.117775
C	6.063078	-3.093434	-0.343788

C	4.705275	-0.676273	1.941344	C	-3.483284	-3.435261	3.939171
C	6.863981	-0.501133	0.668989	H	-4.393029	-4.874525	2.611598
H	3.357522	-3.390915	-0.637115	H	-2.479424	-1.849367	5.000840
H	3.725510	-3.163084	1.083369	H	-3.840718	-3.923176	4.841589
H	2.838764	-1.919393	0.194773	H	-4.775730	-0.781807	0.714363
H	6.271679	-3.486726	0.656817	---			
H	5.720010	-3.923321	-0.969363	**G**			
H	6.991996	-2.707275	-0.768932	G_{soi}(toluene) = -2363.13388 Hartree			
H	5.019363	-1.524618	2.558917	---			
H	5.019326	0.242717	2.447773	Cl	-2.596291	0.180462	-2.107071
H	3.615318	-0.673848	1.872411	Rh	-0.353462	0.087828	-1.008826
H	7.032922	0.484304	1.113608	O	-0.862137	-3.365039	0.883125
H	7.348048	-1.251904	1.300951	C	-1.760166	-3.108298	0.073294
H	7.338976	-0.515343	-0.316775	N	-1.492639	-2.568832	-1.151724
H	0.755222	0.862280	-1.415855	C	-3.243681	-3.289046	0.436925
C	-4.730672	-0.997674	-0.348686	H	-2.274865	-2.196703	-1.678348
C	-3.509075	-1.367953	-0.935132	C	-0.243127	-1.941360	-1.428102
C	-3.481120	-1.671019	-2.302951	C	-3.643047	-1.989640	1.177492
C	-4.647082	-1.601126	-3.067833	C	-4.156282	-3.479564	-0.787493
C	-5.854556	-1.225247	-2.477867	C	-3.378849	-4.493685	1.379867
C	-5.893626	-0.926318	-1.114110	C	0.119682	-1.703266	-2.895460
H	-2.552380	-1.971965	-2.774293	C	0.547643	-0.232674	-2.825011
H	-4.609391	-1.845205	-4.125663	H	0.530453	-2.435433	-0.851611
H	-6.760333	-1.170541	-3.074663	H	-3.018712	-1.841545	2.065011
H	-6.830092	-0.640454	-0.643918	H	-3.530776	-1.117188	0.524115
P	-1.984117	-1.319234	0.099015	H	-4.689764	-2.049135	1.497288
C	-0.833421	-2.479646	-0.741566	H	-3.822045	-4.314913	-1.412603
C	-0.172109	-2.020592	-1.893149	H	-5.175146	-3.697752	-0.449203
C	-0.548697	-3.762594	-0.261210	H	-4.214858	-2.578661	-1.408560
C	0.735001	-2.837748	-2.564540	H	-4.408138	-4.567017	1.747905
H	-0.362640	-1.013357	-2.250372	H	-3.134138	-5.427963	0.861471
C	0.369127	-4.576695	-0.929081	H	-2.703266	-4.393374	2.232209
H	-1.029334	-4.124812	0.640319	H	-0.762440	-1.820561	-3.531302
C	1.007704	-4.120804	-2.082842	H	0.903610	-2.383209	-3.254619
H	1.237209	-2.470271	-3.454822	H	1.626672	-0.073719	-2.822139
H	0.586881	-5.567940	-0.541846	H	0.054701	0.435949	-3.533699
H	1.721310	-4.756161	-2.599420	C	-0.753931	2.535487	0.194574
C	-2.562124	-2.176549	1.612278	C	-0.840830	3.114096	-1.021606
C	-3.341369	-3.342414	1.527691	C	-2.043434	3.503949	-1.835703
C	-2.258285	-1.642247	2.870330	C	-3.390624	3.602024	-1.092893
C	-3.793992	-3.971464	2.686011	C	-3.382763	4.601208	0.041322
H	-3.600432	-3.751230	0.555699	C	-2.973691	4.440072	1.306304
C	-2.719323	-2.270940	4.028992	C	-2.402893	3.228076	1.998958
H	-1.651377	-0.746129	2.930001	C	-1.869354	2.087747	1.109785

H	0.238724	2.508106	0.638070	H	5.532237	3.972665	-0.872716
H	0.103583	3.415599	-1.472025	H	2.156359	1.996881	2.338855
H	-1.817189	4.479416	-2.289806	---			
H	-2.153487	2.794878	-2.665903	**TS4**			
H	-4.143363	3.915348	-1.826286	G_{soi}(toluene) = -2363.106246 Hartree			
H	-3.692605	2.607433	-0.765087	---			
H	-3.739467	5.596416	-0.226525	Cl	0.482284	-2.456136	0.879754
H	-3.058851	5.310390	1.958935	Rh	-0.140577	-0.830100	-0.988599
H	-1.584136	3.566165	2.650641	C	-4.272858	-3.965701	0.245310
H	-3.158774	2.812430	2.683678	C	-4.925231	-2.874169	0.664783
H	-1.479829	1.310646	1.774631	C	-4.385764	-1.580318	1.222954
H	-2.677997	1.626134	0.543219	C	-2.910212	-1.238508	0.931069
C	1.443674	1.273759	2.719462	C	-2.622102	-1.188334	-0.548534
C	1.064081	0.175789	1.935380	C	-2.278044	-2.216624	-1.378047
C	0.121088	-0.738785	2.439493	C	-2.098230	-3.688738	-1.068341
C	-0.409464	-0.563261	3.717394	C	-2.784317	-4.217270	0.209054
C	-0.032639	0.536303	4.491975	H	-4.885568	-4.778593	-0.145870
C	0.892298	1.453536	3.989375	H	-6.014103	-2.902659	0.604335
H	-0.205008	-1.582191	1.837038	H	-5.010372	-0.762642	0.835012
H	-1.130023	-1.280951	4.098733	H	-4.537389	-1.562404	2.313573
H	-0.460040	0.680302	5.479911	H	-2.718573	-0.248256	1.356214
H	1.187249	2.312696	4.584718	H	-2.232241	-1.922207	1.437564
P	1.572446	-0.009464	0.185858	H	-2.925570	-0.268320	-1.038235
C	2.592467	-1.533599	0.092511	H	-2.298451	-1.986222	-2.442419
C	2.539088	-2.548552	1.055110	H	-2.493171	-4.240203	-1.932616
C	3.397440	-1.709602	-1.045523	H	-1.032215	-3.928124	-1.003491
C	3.277459	-3.720751	0.880635	H	-2.611381	-5.299866	0.241671
H	1.922839	-2.434151	1.937814	H	-2.278653	-3.808096	1.083787
C	4.129357	-2.882165	-1.217972	C	1.024640	-1.069295	-2.773823
H	3.462715	-0.924058	-1.791712	C	-0.028540	-0.081806	-2.981653
C	4.069037	-3.892906	-0.254760	C	1.893329	-0.604522	-1.704649
H	3.228242	-4.499956	1.635398	H	-0.838762	-0.324940	-3.665898
H	4.748678	-3.005008	-2.101647	H	0.271266	0.963493	-2.983885
H	4.638767	-4.807687	-0.388942	H	2.200880	0.433734	-1.713125
C	2.833498	1.276741	-0.130618	N	2.834824	-1.455920	-1.103424
C	4.020193	1.316375	0.620066	C	3.941349	-0.940959	-0.462687
C	2.642242	2.201323	-1.163423	O	4.330997	0.204110	-0.680259
C	4.982788	2.288396	0.357323	C	4.622336	-1.841453	0.579609
H	4.188520	0.585087	1.405059	C	6.141237	-1.621601	0.488333
C	3.611753	3.170492	-1.430650	H	6.644005	-2.153398	1.303459
H	1.739738	2.147957	-1.760496	H	6.537869	-1.999765	-0.461231
C	4.778228	3.218519	-0.667224	H	6.381388	-0.558309	0.557987
H	5.895077	2.317723	0.945723	C	4.098167	-1.349805	1.950192
H	3.454921	3.882512	-2.235459	H	3.011357	-1.468013	2.016087

H	4.560659	-1.933864	2.754222
H	4.347598	-0.294445	2.100143
C	4.301032	-3.336794	0.413814
H	4.552239	-3.695582	-0.590979
H	4.894118	-3.913202	1.131950
H	3.247757	-3.557884	0.618861
H	2.457724	-2.325061	-0.740456
H	0.228970	-2.097512	-2.020247
H	1.282952	-1.879370	-3.456980
C	2.141283	2.419008	-0.300398
C	0.780281	2.537366	-0.624108
C	0.376376	3.560830	-1.491095
C	1.318037	4.443653	-2.027083
C	2.669188	4.313778	-1.705178
C	3.078606	3.297147	-0.838667
H	-0.670745	3.685521	-1.740837
H	0.989240	5.234991	-2.694830
H	3.399230	4.998125	-2.127592
H	4.127222	3.169722	-0.590439
P	-0.369069	1.279585	0.076872
C	-2.025683	2.046423	-0.164968
C	-2.790482	2.538455	0.899908
C	-2.569184	2.080374	-1.461166
C	-4.067987	3.057443	0.673635
H	-2.394975	2.512916	1.908704
C	-3.835652	2.615724	-1.688086
H	-2.002492	1.670663	-2.291450
C	-4.591798	3.102288	-0.618063
H	-4.651340	3.427225	1.511905
H	-4.237034	2.640400	-2.697032
H	-5.584088	3.508008	-0.791693
C	-0.062426	1.482005	1.873364
C	0.212072	2.749101	2.416170
C	-0.138693	0.371179	2.721824
C	0.400793	2.899020	3.788196
H	0.278420	3.614220	1.764205
C	0.053837	0.526337	4.096994
H	-0.312747	-0.612343	2.302922
C	0.321500	1.786318	4.631767
H	0.612751	3.881854	4.199352
H	0.001947	-0.343134	4.745929
H	0.473961	1.904146	5.700898
H	2.478591	1.629673	0.362029

H

G_{soi}(toluene) = -2363.137683 Hartree

C	-0.066084	-2.434418	1.037130
C	-2.404572	-1.919657	0.398830
Cl	-0.298238	-1.604512	-2.149120
Rh	-0.233305	-0.509061	0.182687
O	-4.401761	-1.335534	-1.424411
C	-4.651396	-1.234129	-0.231131
N	-3.679895	-1.493959	0.723044
C	-6.057987	-0.889834	0.288424
H	-3.896986	-1.334213	1.697200
C	-6.670008	0.156621	-0.658559
C	-6.875686	-2.199606	0.212867
C	-6.075380	-0.351771	1.729637
C	-1.421443	-2.081529	1.359746
H	-6.136153	1.110789	-0.589147
H	-6.620358	-0.186062	-1.694010
H	-7.717418	0.332025	-0.390939
H	-6.453799	-2.969630	0.868610
H	-7.908419	-2.011249	0.526525
H	-6.887190	-2.586442	-0.810389
H	-7.097037	-0.058526	1.992071
H	-5.769366	-1.106167	2.464933
H	-5.439573	0.533545	1.843776
H	0.608741	-2.558330	1.877877
H	0.129095	-3.096819	0.198391
C	-0.567402	1.680572	-0.896993
H	-0.252129	1.321810	-1.870939
C	-1.777081	1.202542	-0.460106
H	-2.320754	0.557656	-1.148420
C	-2.583843	1.714432	0.706925
H	-1.937806	2.044531	1.519267
H	-3.179511	0.890799	1.110404
C	-3.560173	2.831305	0.282701
H	-4.287679	2.398990	-0.418268
H	-4.152235	3.136652	1.160079
C	-2.968659	4.053050	-0.377267
H	-3.684881	4.618485	-0.974300
C	-1.716289	4.523631	-0.335299
H	-1.508541	5.417941	-0.922981
C	-0.528403	3.956320	0.404007

H	-0.817255	3.584317	1.389305
H	0.186223	4.766770	0.592698
C	0.233629	2.861596	-0.376376
H	0.701040	3.325625	-1.253511
H	1.069959	2.530829	0.245317
H	-2.270585	-2.221009	-0.633119
H	-1.652510	-1.790334	2.383251
H	-0.204578	0.170799	1.580971
C	3.199253	-2.649379	0.923846
C	2.918539	-1.819176	-0.173367
C	3.215513	-2.275703	-1.463558
C	3.787608	-3.534588	-1.651219
C	4.067665	-4.352795	-0.556255
C	3.773037	-3.905211	0.733607
H	3.001381	-1.655214	-2.324154
H	4.013058	-3.873777	-2.658032
H	4.513201	-5.332009	-0.705619
H	3.989598	-4.532641	1.593472
P	2.054244	-0.220364	0.096060
C	2.708608	0.882767	-1.229573
C	3.652821	1.884905	-0.962524
C	2.206737	0.751189	-2.535114
C	4.090107	2.733471	-1.980876
H	4.042369	2.018683	0.039118
C	2.653889	1.596154	-3.550302
H	1.452245	-0.000552	-2.745811
C	3.594166	2.591986	-3.277270
H	4.817464	3.508301	-1.755589
H	2.256518	1.479791	-4.554527
H	3.933860	3.255241	-4.067628
C	2.867630	0.439475	1.607871
C	4.238079	0.222339	1.832918
C	2.154555	1.241143	2.507966
C	4.872754	0.787430	2.937867
H	4.808483	-0.389696	1.142446
C	2.792350	1.813014	3.610361
H	1.095171	1.409054	2.347694
C	4.151172	1.585369	3.829455
H	5.931032	0.605809	3.101057
H	2.223801	2.431484	4.298744
H	4.646510	2.025149	4.690220
H	2.981227	-2.309587	1.930990

TS5

G_{soi}(toluene) = -2363.117791 Hartree

C	-0.322996	-0.718785	-2.703366
C	-2.461022	-0.799307	-1.607164
Cl	-1.239417	-1.586883	1.421645
Rh	-0.497203	-0.248841	-0.533931
O	-4.916993	0.344388	-1.188806
C	-4.604659	-0.644753	-0.528054
N	-3.455914	-1.354458	-0.800166
C	-5.430596	-1.113772	0.680198
H	-3.122643	-1.997182	-0.088126
C	-4.999671	-0.210280	1.859824
C	-6.918307	-0.890110	0.364739
C	-5.192488	-2.588217	1.051059
C	-1.320864	-1.518652	-2.029522
H	-3.934343	-0.339447	2.080501
H	-5.185118	0.843026	1.625747
H	-5.572692	-0.472203	2.756732
H	-7.252939	-1.550998	-0.443259
H	-7.523472	-1.103214	1.252657
H	-7.095360	0.142003	0.054320
H	-5.885022	-2.874781	1.849803
H	-5.368875	-3.252949	0.198176
H	-4.179618	-2.763112	1.431075
H	0.613992	-1.200550	-2.968151
H	-0.680510	-0.011363	-3.455196
C	-0.646131	5.112176	0.732535
H	-0.887689	6.027356	1.275497
C	-1.127776	5.019533	-0.513049
H	-1.734808	5.858053	-0.855217
C	-1.014626	3.890285	-1.513011
H	-0.003674	3.479403	-1.566190
H	-1.224865	4.295793	-2.509761
C	-2.028241	2.760602	-1.253250
H	-3.034755	3.198544	-1.196175
H	-2.056000	2.103526	-2.131724
C	-1.841007	1.925313	-0.007619
H	-2.724051	1.350130	0.258810
C	-0.824815	1.908947	0.900356
H	-1.023069	1.327641	1.798982
C	0.431137	2.750271	0.956326

H	0.922389	2.818848	-0.012275
H	1.149636	2.245732	1.609630
C	0.200823	4.158117	1.532129
H	-0.246824	4.063948	2.532816
H	1.183735	4.625045	1.703083
H	-2.790168	0.080808	-2.145918
H	-1.151252	-2.566089	-1.803041
H	0.027851	0.497537	-1.887171
C	2.736210	1.465440	-1.720161
C	2.874466	0.903756	-0.439958
C	3.794291	1.473770	0.449738
C	4.548659	2.587122	0.072176
C	4.403354	3.137685	-1.200918
C	3.498823	2.567393	-2.101199
H	3.915387	1.057795	1.443299
H	5.249716	3.023110	0.778083
H	4.987861	4.005634	-1.491421
H	3.379732	2.986878	-3.095965
P	1.762443	-0.477386	0.049724
C	2.286490	-0.848436	1.764759
C	3.437858	-1.608637	2.018898
C	1.562208	-0.318401	2.840199
C	3.861879	-1.825070	3.329928
H	4.002528	-2.028236	1.192494
C	1.991571	-0.531019	4.150237
H	0.651788	0.234481	2.650217
C	3.141147	-1.283853	4.397265
H	4.753658	-2.416277	3.517267
H	1.420447	-0.118846	4.976920
H	3.471183	-1.454457	5.417988
C	2.397124	-1.922042	-0.889718
C	3.517890	-1.875290	-1.726966
C	1.674205	-3.122334	-0.769995
C	3.908570	-3.011978	-2.441321
H	4.085223	-0.955697	-1.823684
C	2.074184	-4.255128	-1.474845
H	0.799754	-3.153888	-0.125149
C	3.190131	-4.201080	-2.316978
H	4.777378	-2.965166	-3.091828
H	1.512851	-5.179522	-1.372588
H	3.495462	-5.082654	-2.873169
H	2.025148	1.043486	-2.423050

TS6

G_{soi}(toluene) = -2363.114322 Hartree

C	-0.057348	-0.117080	-2.533947
C	-2.259698	-0.705945	-1.735676
Cl	-1.195688	-1.484530	1.411840
Rh	-0.391434	0.212248	-0.413819
O	-4.893269	-0.111773	-1.493892
C	-4.445768	-1.034848	-0.829182
N	-3.144057	-1.495661	-1.046031
C	-5.225180	-1.695116	0.311975
H	-2.719377	-2.072096	-0.319607
C	-4.995996	-0.788864	1.547042
C	-6.715894	-1.707822	-0.062745
C	-4.749556	-3.125175	0.624781
C	-0.926809	-1.125259	-2.027778
H	-3.933501	-0.744514	1.807953
H	-5.355132	0.226830	1.352076
H	-5.547641	-1.194230	2.402782
H	-6.902064	-2.367781	-0.917754
H	-7.305623	-2.072254	0.784998
H	-7.058884	-0.704736	-0.325948
H	-5.416061	-3.566279	1.373340
H	-4.774593	-3.763703	-0.265254
H	-3.739142	-3.144130	1.047121
H	0.939464	-0.419504	-2.837676
H	-0.471291	0.725580	-3.082675
C	-0.229653	2.074134	0.862990
H	0.729105	1.988188	1.370903
C	-0.121709	2.425699	-0.490347
H	0.899958	2.568054	-0.835422
C	-1.122620	3.121987	-1.392330
H	-2.122347	2.696466	-1.318632
H	-0.802348	2.957117	-2.428520
C	-1.185549	4.638394	-1.153560
H	-0.168965	5.055462	-1.222960
H	-1.739096	5.101284	-1.985703
C	-1.801256	5.109786	0.138099
H	-1.736826	6.191732	0.266759
C	-2.415294	4.436978	1.120370
H	-2.767551	5.042040	1.956592
C	-2.639645	2.951820	1.304497

H	-2.995247	2.458630	0.396502
H	-3.436406	2.816931	2.045208
C	-1.387451	2.228176	1.831632
H	-1.013694	2.787515	2.701852
H	-1.673573	1.238792	2.207742
H	-2.733023	0.068263	-2.329708
H	-0.608925	-2.144656	-1.844587
H	-1.967091	0.635347	-0.589054
C	3.042932	1.519829	-1.677767
C	3.073262	0.948505	-0.393354
C	3.988965	1.445667	0.544095
C	4.860598	2.482099	0.201867
C	4.834096	3.030337	-1.080104
C	3.922910	2.543991	-2.021504
H	4.023836	1.026407	1.542682
H	5.561270	2.858119	0.941708
H	5.514077	3.834730	-1.344727
H	3.890155	2.968476	-3.020683
P	1.857985	-0.363376	0.030887
C	2.320140	-0.816125	1.745871
C	3.461250	-1.599730	1.978889
C	1.581100	-0.338557	2.835354
C	3.860013	-1.892834	3.282348
H	4.037601	-1.979007	1.141051
C	1.985176	-0.630262	4.138642
H	0.677089	0.229318	2.663848
C	3.123339	-1.405837	4.364900
H	4.743162	-2.502064	3.451718
H	1.401184	-0.260270	4.976208
H	3.432499	-1.636144	5.380452
C	2.387094	-1.838483	-0.919348
C	3.445015	-1.841617	-1.835106
C	1.645699	-3.015357	-0.712289
C	3.755977	-3.007070	-2.541996
H	4.029720	-0.942108	-1.995083
C	1.965284	-4.175488	-1.413908
H	0.823157	-3.009081	-0.001036
C	3.019259	-4.172853	-2.333674
H	4.578521	-3.000897	-3.251476
H	1.390963	-5.081945	-1.245477
H	3.263939	-5.077092	-2.883340
H	2.322617	1.169060	-2.408003

I

G_{sol}(toluene) = -2363.156509 Hartree

Rh	0.421220	0.000827	0.293810
Cl	0.544565	-2.389469	0.840985
C	0.490353	1.871701	-0.769566
C	0.427486	2.125482	0.619987
C	1.528283	2.582490	1.566285
C	2.767170	3.243794	0.927260
C	2.436533	4.474940	0.119573
C	2.050653	4.558998	-1.159693
C	1.843837	3.476203	-2.190383
C	1.679424	2.026563	-1.691814
H	-0.450748	2.004161	-1.300626
H	-0.561241	2.396621	0.980251
H	1.075140	3.302030	2.261748
H	1.869141	1.740035	2.179261
H	3.442908	3.531985	1.742839
H	3.307202	2.504036	0.336923
H	2.491669	5.413389	0.672645
H	1.854009	5.561715	-1.542679
H	0.949154	3.742240	-2.772317
H	2.673471	3.507758	-2.914904
H	1.512043	1.396362	-2.575125
H	2.596682	1.664280	-1.232491
C	1.758064	-2.068315	-4.162847
C	2.610877	-1.492295	-1.886079
O	2.630721	0.004149	0.525974
C	3.469252	-0.896440	0.324186
N	3.508207	-1.619025	-0.815272
C	4.532729	-1.162226	1.395830
H	4.211745	-2.340729	-0.888965
C	5.370135	0.127200	1.532554
C	3.781650	-1.438387	2.714876
C	5.455954	-2.346642	1.070812
C	2.719304	-2.192609	-3.018612
H	5.912447	0.347900	0.605649
H	4.728504	0.979739	1.768468
H	6.103893	0.007505	2.337033
H	3.149896	-2.327499	2.627076
H	4.503882	-1.592795	3.524003
H	3.137416	-0.593878	2.970865
H	6.166978	-2.485300	1.891272
H	4.895977	-3.283193	0.964682
H	6.046343	-2.175364	0.162118

H	1.006284	-1.296217	-3.969686	Cl	-0.582128	-2.258670	1.087933
H	2.277323	-1.808504	-5.094587	C	-2.344586	4.530557	-0.328741
H	3.537882	-2.904016	-3.134817	C	-1.976094	4.484262	-1.615020
H	1.808900	-0.786583	-1.704959	C	-1.822043	3.303841	-2.543067
H	1.233033	-3.015408	-4.345616	C	-1.682896	1.902814	-1.913756
C	-4.046528	-0.348061	1.898854	C	-0.485521	1.807777	-0.994308
C	-2.658547	-0.522579	1.767177	C	-0.398329	2.189724	0.364105
C	-1.913955	-0.950263	2.874693	C	-1.483526	2.744909	1.275279
C	-2.548865	-1.206462	4.091342	C	-2.706319	3.388205	0.588056
C	-3.928911	-1.037687	4.213443	H	-2.359284	5.516113	0.138158
C	-4.677643	-0.608249	3.114575	H	-1.751169	5.440058	-2.091004
H	-0.844792	-1.094440	2.768754	H	-2.666859	3.290463	-3.250517
H	-1.962282	-1.537759	4.943385	H	-0.934565	3.489427	-3.165755
H	-4.420651	-1.236049	5.161587	H	-2.600481	1.605477	-1.410962
H	-5.751386	-0.471056	3.204903	H	-1.540906	1.189448	-2.735853
P	-1.801089	-0.191887	0.179215	H	0.449842	1.879198	-1.545770
C	-2.729991	1.262901	-0.463375	H	0.600180	2.472384	0.688592
C	-3.032351	2.331496	0.395703	H	-1.845837	1.960132	1.949527
C	-3.047613	1.377615	-1.824068	H	-1.009499	3.502185	1.914193
C	-3.636539	3.488239	-0.096099	H	-3.274094	2.617392	0.067856
H	-2.811868	2.252488	1.455632	H	-3.365766	3.768499	1.378817
C	-3.652481	2.535694	-2.314558	C	-2.018042	-3.640432	-3.305813
H	-2.825722	0.560437	-2.502060	C	-2.467903	-1.616682	-1.901709
C	-3.946026	3.594652	-1.453534	O	-2.630262	0.094776	0.445219
H	-3.866816	4.304452	0.582502	C	-3.496704	-0.775789	0.220161
H	-3.897052	2.607379	-3.370506	N	-3.493996	-1.570521	-0.860668
H	-4.416614	4.495423	-1.836662	C	-4.653467	-0.913916	1.222454
C	-2.306981	-1.538046	-0.961697	H	-4.229889	-2.257683	-0.935291
C	-3.418440	-2.358129	-0.737091	C	-4.018250	-1.189861	2.600821
C	-1.541540	-1.723709	-2.122680	C	-5.396742	0.437358	1.251022
C	-3.763534	-3.342318	-1.665501	C	-5.642239	-2.038385	0.877779
H	-4.008166	-2.242891	0.165362	C	-1.996467	-3.024864	-2.122584
C	-1.894834	-2.697295	-3.054942	H	-3.448263	-2.124152	2.590512
H	-0.659727	-1.109335	-2.274980	H	-3.334185	-0.383372	2.874732
C	-3.007796	-3.510489	-2.826755	H	-4.804094	-1.263017	3.360760
H	-4.622700	-3.979912	-1.477471	H	-5.850837	0.660677	0.278320
H	-1.295512	-2.829150	-3.950870	H	-6.195267	0.404854	2.000252
H	-3.279055	-4.277130	-3.546913	H	-4.711167	1.248843	1.505899
H	-4.631745	0.002738	1.054812	H	-6.424176	-2.078232	1.642733
				H	-6.141828	-1.869748	-0.084104
				H	-5.154987	-3.020465	0.861364
				H	-1.645701	-4.653943	-3.427272
				H	-2.402334	-3.150687	-4.198624
				H	-2.863712	-1.183452	-2.828495

J

G_{sol}(toluene) = -2363.14846 Hartree

H	-1.606756	-3.519508	-1.235130
H	-1.637257	-0.985059	-1.562968
C	1.505134	-2.197795	-1.764620
C	2.405958	-1.314931	-1.154961
C	3.747188	-1.309919	-1.573164
C	4.175947	-2.180495	-2.574861
C	3.269654	-3.057324	-3.177304
C	1.934180	-3.062692	-2.771592
H	4.452718	-0.615755	-1.127959
H	5.215478	-2.168533	-2.889788
H	3.604499	-3.728973	-3.962772
H	1.218093	-3.733151	-3.237913
P	1.795439	-0.178882	0.151124
C	2.779212	1.345078	-0.168795
C	3.286634	2.112010	0.889387
C	2.941609	1.811981	-1.483019
C	3.942789	3.318210	0.638549
H	3.174562	1.764712	1.911049
C	3.598708	3.016450	-1.732139
H	2.567807	1.223624	-2.315263
C	4.099357	3.774288	-0.671296
H	4.334451	3.898664	1.468946
H	3.720162	3.361203	-2.754987
H	4.610937	4.712559	-0.865119
C	2.501630	-0.784497	1.732702
C	3.636036	-1.601296	1.803348
C	1.880610	-0.365835	2.919035
C	4.146985	-1.986534	3.044029
H	4.115016	-1.950093	0.895187
C	2.400287	-0.740806	4.157087
H	0.979661	0.238028	2.858806
C	3.534820	-1.553460	4.221479
H	5.022527	-2.628029	3.089001
H	1.911967	-0.410937	5.069560
H	3.934675	-1.854904	5.185462
H	0.473880	-2.210238	-1.437436

TS7

G_{sol}(toluene) = -2462.978366 Hartree

C	0.009353	-3.061273	-1.808246
H	-1.284527	-1.862739	-1.589863
B	-2.029129	-0.969898	-0.494791
Cl	-0.310728	0.239987	-3.283537
Rh	-0.039028	-1.005125	-1.088743
O	2.231417	-1.050006	-1.153744
C	2.670081	-1.658336	-0.142927
N	1.825040	-2.239073	0.710033
C	4.180448	-1.761552	0.076800
H	2.190730	-2.691949	1.536869
C	4.802917	-0.370444	-0.143776
C	4.544335	-2.274448	1.479668
C	4.707498	-2.742058	-0.994734
C	0.040513	-3.606139	-0.378943
C	0.391259	-2.347528	0.426817
H	-0.738101	-3.497580	-2.472594
H	4.522412	0.034760	-1.117450
H	4.470744	0.336144	0.623023
H	5.894317	-0.444397	-0.089514
H	4.211880	-3.307108	1.640767
H	5.632663	-2.267214	1.597398
H	4.118897	-1.637919	2.263725
H	5.795460	-2.835321	-0.907980
H	4.266684	-3.737590	-0.868575
H	4.466199	-2.381442	-1.998534
H	0.745004	-4.438445	-0.231949
H	-0.957709	-3.948176	-0.086893
H	-0.159980	-2.227949	1.355140
C	-3.852045	-1.626169	0.729072
C	-4.267248	-0.500859	-0.285988
O	-2.397941	-1.542129	0.708784
O	-3.093371	-0.410084	-1.150396
C	-4.206279	-3.038854	0.254601
H	-3.720978	-3.766207	0.912687
H	-5.286117	-3.214095	0.281903
H	-3.851075	-3.213348	-0.765765
C	-4.325645	-1.414357	2.161631
H	-5.419709	-1.419487	2.212510
H	-3.952201	-2.225768	2.794554
H	-3.962827	-0.467897	2.568200
C	-5.468247	-0.839300	-1.162300
H	-6.363422	-0.987847	-0.548320
H	-5.661150	-0.011133	-1.850898
H	-5.295697	-1.740133	-1.754805
C	-4.466116	0.862804	0.372354
H	-4.580752	1.621497	-0.403697
H	-5.364622	0.866786	0.997774
H	-3.607646	1.144262	0.985481

C	-1.711666	2.606608	-0.897372	O	0.475028	2.475163	0.459351
C	-1.077606	2.224966	0.295593	C	-0.445064	3.313385	0.291666
C	-1.443412	2.833321	1.503107	N	-1.718796	2.945202	0.463845
C	-2.434452	3.817484	1.517648	C	-0.092563	4.742403	-0.111490
C	-3.049599	4.210088	0.327874	H	-2.454094	3.616489	0.298217
C	-2.684452	3.604158	-0.877245	C	0.710990	4.654948	-1.426482
H	-0.957325	2.544508	2.428902	C	-1.329746	5.629731	-0.318194
H	-2.716704	4.282467	2.458071	C	0.791300	5.330921	1.007999
H	-3.813309	4.982554	0.339926	C	-1.581998	1.405835	2.486736
H	-3.166678	3.900614	-1.804384	C	-2.077300	1.644765	1.030324
P	0.313550	1.041359	0.147895	H	-0.719736	-0.612229	2.737547
C	0.786203	0.642033	1.871947	H	1.610561	4.049966	-1.292698
C	2.082951	0.846389	2.360630	H	0.115946	4.190591	-2.218585
C	-0.152579	-0.016168	2.684925	H	1.003572	5.661887	-1.743689
C	2.438554	0.398823	3.634764	H	-1.919448	5.733060	0.600607
H	2.816148	1.357940	1.748681	H	-1.009786	6.633966	-0.613290
C	0.202515	-0.453269	3.960124	H	-1.974980	5.246252	-1.117180
H	-1.151361	-0.209992	2.308014	H	1.119248	6.337415	0.726829
C	1.500962	-0.252972	4.437210	H	0.239330	5.402390	1.952452
H	3.448292	0.565712	3.999257	H	1.674663	4.707899	1.170075
H	-0.534170	-0.958049	4.578689	H	-1.238962	2.351918	2.919617
H	1.777644	-0.599992	5.428561	H	-2.410471	1.036365	3.099044
C	1.636775	2.166937	-0.448393	H	-3.164149	1.605944	0.976239
C	1.933025	3.334265	0.275414	C	-4.301943	-0.939441	-0.817311
C	2.318021	1.904386	-1.642138	C	-4.024225	-1.726474	0.510613
C	2.921203	4.208075	-0.171971	O	-3.042490	-0.244145	-1.031895
H	1.388718	3.560116	1.187587	O	-3.070426	-0.858284	1.180968
C	3.301585	2.789062	-2.091806	C	-5.388311	0.129874	-0.670006
H	2.068216	1.024008	-2.216853	H	-5.369835	0.776319	-1.552382
C	3.610357	3.933843	-1.357468	H	-6.383781	-0.318073	-0.588869
H	3.147724	5.104791	0.397779	H	-5.220312	0.752494	0.214587
H	3.822690	2.579928	-3.021664	C	-4.578609	-1.811595	-2.035921
H	4.377687	4.617566	-1.709662	H	-5.474723	-2.422439	-1.879638
H	-1.437921	2.118487	-1.828662	H	-4.745554	-1.177526	-2.912140
H	0.971519	-2.996251	-2.316949	H	-3.735673	-2.471685	-2.251128
---				C	-5.235134	-1.912770	1.416197
TS8				H	-6.010828	-2.495460	0.907312
G_{sol}(toluene) = -2462.973541 Hartree				H	-4.940185	-2.455812	2.319729
---				H	-5.660445	-0.953383	1.718921
C	-0.460782	0.372113	2.349530	C	-3.321084	-3.069196	0.276410
H	-0.936499	-1.036696	0.223611	H	-2.972747	-3.456913	1.238782
B	-2.398026	-0.159641	0.180463	H	-3.998726	-3.805413	-0.167206
Cl	-0.301602	0.973177	-2.245881	H	-2.451975	-2.957037	-0.379121
Rh	-0.379137	0.424133	0.285867	C	0.214570	-2.474501	-1.855032

C	1.255643	-2.401658	-0.916814	C	3.343694	-1.486076	0.091093
C	2.041525	-3.536515	-0.665874	N	2.795619	-2.711563	0.068103
C	1.785387	-4.731289	-1.340037	C	4.856141	-1.309065	-0.044273
C	0.743748	-4.802246	-2.267206	H	3.389780	-3.512405	-0.096913
C	-0.036799	-3.672771	-2.524157	C	5.346640	-0.624983	1.249156
H	2.843471	-3.491725	0.063746	C	5.608220	-2.631708	-0.254405
H	2.396091	-5.605971	-1.135638	C	5.090598	-0.371508	-1.247859
H	0.541429	-5.734528	-2.786834	C	0.989182	-2.883192	1.852943
H	-0.845809	-3.721076	-3.247492	C	0.491346	-1.447541	2.010461
P	1.568478	-0.824593	-0.038027	H	1.142873	-3.919057	-0.095944
C	2.943280	-0.017435	-0.928989	H	4.820155	0.320282	1.402838
C	3.146795	1.358028	-0.742700	H	5.179858	-1.264200	2.124140
C	3.813172	-0.743242	-1.753100	H	6.420411	-0.421770	1.174305
C	4.221686	1.992692	-1.364820	H	5.290308	-3.138866	-1.173072
H	2.450980	1.927424	-0.138175	H	6.679635	-2.428835	-0.350658
C	4.881806	-0.100101	-2.378789	H	5.481498	-3.315206	0.593790
H	3.654461	-1.804164	-1.913184	H	6.163714	-0.182863	-1.362900
C	5.089824	1.266637	-2.183462	H	4.715184	-0.820316	-2.173642
H	4.372900	3.058618	-1.219204	H	4.576027	0.580448	-1.098150
H	5.549208	-0.667619	-3.020932	H	1.821191	-3.168500	2.512470
H	5.921509	1.765176	-2.673157	H	0.166979	-3.588243	2.017698
C	2.299172	-1.358963	1.552750	H	-0.463787	-1.358157	2.520581
C	3.520472	-0.857531	2.017837	H	1.226771	-0.760756	2.438183
C	1.567784	-2.246749	2.358913	C	-3.555328	-2.438235	0.468228
C	4.005803	-1.242114	3.270310	C	-3.704425	-1.547907	-0.814580
H	4.094104	-0.171963	1.403449	O	-2.238236	-2.049791	0.959154
C	2.058631	-2.634673	3.602828	O	-2.316798	-1.361123	-1.217052
H	0.617166	-2.635933	2.006453	C	-3.479999	-3.936375	0.161118
C	3.279196	-2.130742	4.062880	H	-3.175818	-4.470043	1.066797
H	4.955626	-0.849080	3.621321	H	-4.448631	-4.329420	-0.163075
H	1.487942	-3.326499	4.215535	H	-2.741886	-4.140618	-0.620663
H	3.659673	-2.430538	5.035027	C	-4.577647	-2.169390	1.565373
H	-0.379947	-1.590978	-2.064337	H	-5.590577	-2.388659	1.210582
H	0.513463	0.689437	2.727855	H	-4.372149	-2.813214	2.426518
---				H	-4.544179	-1.130161	1.899918
TS9				C	-4.451989	-2.200148	-1.971237
G_{sol}(toluene) = -2462.972647 Hartree				H	-5.484922	-2.427154	-1.684984
---				H	-4.476834	-1.511632	-2.821486
C	1.395438	-2.964512	0.366900	H	-3.966269	-3.122892	-2.295295
H	-0.055572	-2.500272	-0.409612	C	-4.287956	-0.161647	-0.527675
B	-1.524991	-1.539744	-0.111753	H	-4.175230	0.464430	-1.415408
Cl	1.019723	-0.988397	-2.554201	H	-5.351799	-0.227104	-0.277710
Rh	0.464984	-1.042199	-0.026138	H	-3.767004	0.333703	0.295537
O	2.625799	-0.470639	0.209707	C	-1.525389	1.358053	-2.362254

C	-1.451245	1.893578	-1.068718	N	-1.041750	1.806513	-1.101660
C	-2.326634	2.923414	-0.693659	C	-2.321189	3.253994	0.441382
C	-3.265902	3.411006	-1.602018	H	-1.820069	1.164382	-1.002748
C	-3.333175	2.881365	-2.892767	C	-2.504648	4.778871	0.494228
C	-2.459020	1.859906	-3.269946	C	-3.580237	2.602850	-0.157619
H	-2.283059	3.340701	0.306101	C	-2.083347	2.706562	1.867325
H	-3.943833	4.204438	-1.300423	C	-0.156429	0.280615	-2.834289
H	-4.064956	3.262571	-3.599645	C	0.174592	-1.083052	-2.195667
H	-2.508004	1.441111	-4.271069	H	-1.599824	5.261374	0.869720
P	-0.190889	1.251497	0.097605	H	-2.716718	5.182756	-0.502214
C	-0.823833	1.807205	1.726880	H	-3.343594	5.032731	1.151496
C	-0.463314	3.037602	2.295221	H	-3.556265	1.509166	-0.097668
C	-1.771497	1.004895	2.381521	H	-4.461517	2.933210	0.402747
C	-1.033767	3.452245	3.499917	H	-3.720450	2.888031	-1.205838
H	0.258772	3.673968	1.796073	H	-2.963514	2.891485	2.493550
C	-2.345761	1.426164	3.580356	H	-1.899517	1.626580	1.849800
H	-2.056204	0.048890	1.958870	H	-1.221031	3.195984	2.330933
C	-1.976013	2.648921	4.144727	H	0.503096	0.476912	-3.681334
H	-0.743978	4.406435	3.930529	H	-1.195936	0.340725	-3.177337
H	-3.077646	0.794160	4.075306	H	-0.644211	-1.796736	-2.283762
H	-2.419275	2.974055	5.081544	H	1.067077	-1.573676	-2.579877
C	1.287409	2.289402	-0.207295	C	-1.962599	-3.086029	0.163436
C	1.470520	2.950388	-1.427225	C	-2.826653	-1.776272	0.198890
C	2.305767	2.332547	0.757438	O	-0.606641	-2.557513	0.148082
C	2.653019	3.650290	-1.676120	O	-1.978951	-0.832033	-0.513302
H	0.695455	2.915972	-2.184646	C	-2.158555	-3.908202	-1.113965
C	3.477361	3.044302	0.512827	H	-1.371220	-4.665303	-1.172153
H	2.185568	1.800552	1.694988	H	-3.127794	-4.416353	-1.111510
C	3.656306	3.701606	-0.707997	H	-2.104262	-3.289128	-2.014005
H	2.785565	4.157080	-2.627538	C	-2.107740	-3.983584	1.386945
H	4.255550	3.076937	1.270130	H	-3.141633	-4.329729	1.492197
H	4.574056	4.249341	-0.902095	H	-1.465038	-4.862369	1.275577
H	-0.856940	0.552982	-2.647603	H	-1.817097	-3.463065	2.301867
---				C	-4.164927	-1.866899	-0.523349
TS10				H	-4.800716	-2.629806	-0.061423
G_{sol}(toluene) = -1738.598207 Hartree				H	-4.686700	-0.906779	-0.457621
---				H	-4.034458	-2.111845	-1.579393
C	0.122260	1.272252	-1.707876	C	-3.021409	-1.230940	1.617579
H	-0.076367	-0.278507	0.503409	H	-3.464150	-0.232606	1.562336
B	-0.651177	-1.272310	-0.368995	H	-3.689780	-1.868736	2.203667
Cl	3.026176	0.205904	-2.145312	H	-2.065551	-1.151814	2.145131
Rh	1.157819	-0.108181	-0.521154	C	2.970841	-1.713535	0.744883
O	-0.034724	3.660186	-0.257098	H	2.905512	-2.447485	-0.056746
C	-1.035172	2.946494	-0.348881	C	1.996369	-1.713205	1.677321

H	1.175222	-2.413155	1.560278
C	1.974583	-0.834650	2.903821
H	2.996052	-0.647555	3.243572
H	1.476594	-1.373927	3.717820
C	1.233436	0.511641	2.715447
H	0.152641	0.333838	2.746434
H	1.452740	1.156424	3.579848
C	1.542917	1.293940	1.458962
H	0.815969	2.056334	1.197833
C	2.721901	1.326319	0.765247
H	2.796181	2.075066	-0.016841
C	4.016359	0.636621	1.157365
H	4.132936	0.729167	2.241742
H	4.839033	1.206710	0.715437
C	4.205828	-0.845884	0.734151
H	4.605514	-0.859847	-0.280031
H	4.972571	-1.291366	1.385083
H	0.842998	2.060070	-1.904634

TS11

G_{sol}(toluene) = -1326.729979 Hartree

Cl	-0.444023	1.436393	-1.479742
Rh	0.950321	-0.396397	-0.387479
C	2.808103	1.145117	-0.999226
C	3.322540	-0.109939	-0.846418
C	3.993251	-0.653677	0.397805
C	3.328045	-0.260961	1.740532
C	1.808314	-0.177811	1.722654
C	1.081186	0.960782	1.423568
C	1.639241	2.297005	0.993592
C	2.864072	2.239397	0.046452
H	2.443865	1.429663	-1.981337
H	3.405480	-0.732923	-1.734943
H	4.005711	-1.744863	0.319588
H	5.047640	-0.339878	0.415202
H	3.623585	-1.000055	2.492465
H	3.727332	0.695578	2.089532
H	1.284510	-0.964072	2.259496
H	0.039134	0.979366	1.736597
H	0.833828	2.833819	0.488241
H	1.903260	2.882159	1.887717
H	2.935316	3.203389	-0.467809
H	3.785591	2.135291	0.626028
C	0.075135	-2.290698	-0.913141
C	1.351954	-2.499587	-0.232902
C	-0.791270	-1.584968	0.028166
H	2.188805	-2.882769	-0.810617
H	1.322615	-2.828634	0.801017
H	-0.765360	-1.881312	1.070147
N	-2.038528	-1.073355	-0.343228
C	-2.873648	-0.560122	0.631939
O	-2.669849	-0.783638	1.822156
C	-4.051252	0.309085	0.165628
C	-5.321575	-0.218038	0.859055
H	-6.165619	0.446662	0.644829
H	-5.579068	-1.221927	0.501223
H	-5.175814	-0.266338	1.940942
C	-3.743605	1.743177	0.651812
H	-2.828615	2.120321	0.182950
H	-4.572626	2.409613	0.387648
H	-3.614398	1.759209	1.737985
C	-4.254830	0.317793	-1.357923
H	-4.409155	-0.692631	-1.753864
H	-5.145626	0.907526	-1.598924
H	-3.410043	0.782340	-1.879378
H	-2.084418	-0.630825	-1.253481
H	0.487156	-1.274714	-1.780141
H	-0.284644	-2.861530	-1.773133

TS12

G_{gas} = -2587.38091116 Hartree

C	0.934821	-1.053987	2.095053
C	1.397520	0.820846	1.890064
Ir	-0.198664	0.111006	0.307121
B	-1.519598	0.158229	-1.287112
O	-1.770958	1.342056	-1.992616
O	-2.344992	-0.851026	-1.781128
C	-2.934700	1.152192	-2.824829
C	-2.952697	-0.400621	-3.011987
C	-2.755908	1.963750	-4.102453
C	-4.139067	1.667850	-2.027525
C	-2.061079	-0.876777	-4.163563
C	-4.341623	-1.020792	-3.129887
H	-3.586416	1.792852	-4.797361
H	-2.729093	3.031165	-3.858795
H	-1.819968	1.707565	-4.603425

H	-3.940433	2.696289	-1.710211	C	-4.087055	1.108584	4.368083
H	-5.060978	1.654668	-2.618493	C	0.250128	4.978077	-1.338932
H	-4.290503	1.055744	-1.132977	H	-1.626386	5.136590	-0.291761
H	-1.973813	-1.966165	-4.109599	C	1.315583	2.789776	-1.111191
H	-2.483200	-0.609525	-5.138545	H	-1.981888	-0.619909	3.656052
H	-1.055973	-0.460503	-4.071764	H	-0.723348	0.614882	3.738064
H	-4.872946	-0.626791	-4.004142	H	-1.683797	0.251657	5.179845
H	-4.252112	-2.105279	-3.249836	H	-2.940617	3.602556	3.928775
H	-4.943783	-0.829028	-2.238645	H	-2.029716	2.792552	5.205814
B	-1.233556	-1.610257	0.607458	H	-1.285299	3.042676	3.622026
O	-2.451004	-1.647763	1.296732	H	-3.970210	1.123870	5.457315
O	-0.840621	-2.905594	0.283835	H	-4.864920	1.837974	4.112340
C	-2.817879	-3.023137	1.550169	H	-4.449797	0.113884	4.082056
C	-1.945763	-3.811164	0.506073	C	1.339828	4.124465	-1.634133
C	-4.326211	-3.153343	1.359091	H	0.243059	5.990420	-1.733440
C	-2.445672	-3.338634	3.003196	C	2.407776	1.927861	-1.386655
C	-2.653686	-4.013920	-0.837942	C	2.445493	4.545042	-2.416110
C	-1.382769	-5.138585	1.006114	C	3.473209	2.374717	-2.134635
H	-4.651768	-4.193354	1.475775	H	2.381372	0.921190	-0.991888
H	-4.844152	-2.550240	2.112880	C	3.494786	3.689589	-2.658957
H	-4.629076	-2.798082	0.372050	H	2.448125	5.556708	-2.812869
H	-2.979047	-2.653669	3.669525	H	4.309884	1.710034	-2.324218
H	-2.719528	-4.362386	3.278414	H	4.342403	4.018731	-3.252377
H	-1.372095	-3.209237	3.170441	B	0.950243	-0.978319	-0.948629
H	-1.946996	-4.449497	-1.549603	O	0.680976	-1.226499	-2.293722
H	-3.507260	-4.693695	-0.742743	O	2.178725	-1.600685	-0.616510
H	-2.985163	-3.056191	-1.241676	C	1.495301	-2.317037	-2.762051
H	-2.188453	-5.839507	1.253360	C	2.725601	-2.265806	-1.785178
H	-0.770476	-5.592012	0.219971	C	1.827207	-2.079509	-4.233263
H	-0.752292	-5.003036	1.887731	C	0.662916	-3.595662	-2.617277
N	-1.718572	1.528810	1.380353	C	3.872788	-1.405534	-2.321251
C	-1.781136	2.663165	0.782977	C	3.253693	-3.632471	-1.356980
C	-2.972523	1.359838	2.146294	H	2.505031	-2.852057	-4.614420
C	-0.713126	3.193530	-0.066485	H	0.905127	-2.117929	-4.821389
O	-2.914852	3.388389	0.915871	H	2.285515	-1.100579	-4.390913
C	-3.855236	2.505699	1.594236	H	-0.260961	-3.473634	-3.190056
H	-3.372724	0.375831	1.895810	H	1.196402	-4.473416	-2.997927
C	-2.744175	1.419228	3.683474	H	0.384930	-3.755323	-1.574407
C	-0.775223	4.519424	-0.551670	H	4.623074	-1.264250	-1.539172
N	0.276309	2.346542	-0.342509	H	4.362254	-1.881781	-3.176999
H	-4.366778	3.094847	2.354597	H	3.510436	-0.424048	-2.635534
H	-4.576187	2.164367	0.847621	H	3.591712	-4.209640	-2.225247
C	-1.721614	0.348262	4.088556	H	4.107223	-3.512197	-0.682501
C	-2.225277	2.796730	4.127787	H	2.485754	-4.204288	-0.832553

H	1.184698	-1.916280	1.490075	H	-4.027253	1.393846	1.604721
H	2.043256	1.303257	1.164760	H	-0.727556	-0.649938	4.613032
C	6.995557	0.095042	2.564644	H	-2.238728	-1.555535	4.831866
C	5.772002	-0.283560	1.719945	H	-1.205163	-1.852480	3.406606
H	6.903380	1.114921	2.943871	H	-3.573716	0.735032	4.912474
H	7.095530	-0.569992	3.428741	H	-1.956219	1.458943	4.860974
H	7.907179	0.016926	1.960512	H	-3.183495	1.964272	3.689512
C	5.903192	-1.742702	1.249533	B	1.063640	0.831610	0.890931
C	5.669064	0.662254	0.503627	O	1.182783	2.218505	1.016263
H	5.079684	-2.048522	0.598382	O	1.919912	0.203702	1.789910
H	6.833110	-1.870216	0.682560	C	2.283108	2.522429	1.906140
H	5.927853	-2.430622	2.101494	C	2.424459	1.191256	2.723628
H	6.550720	0.555287	-0.140130	C	1.904400	3.747868	2.731707
H	4.780178	0.446086	-0.095953	C	3.501582	2.827887	1.029588
H	5.606578	1.705837	0.830284	C	1.523121	1.145351	3.960997
C	4.498371	-0.062681	2.564044	C	3.852620	0.820948	3.106771
O	4.500699	0.643051	3.569983	H	2.678770	3.977847	3.472450
N	3.361575	-0.668349	2.109363	H	1.801462	4.616293	2.071752
H	3.328255	-1.080559	1.181711	H	0.955208	3.599056	3.251161
C	2.076634	-0.279800	2.651334	H	3.264258	3.662032	0.362104
H	2.150128	-0.165873	3.730909	H	4.372661	3.108531	1.631191
H	0.119595	-1.205462	2.791907	H	3.759605	1.968983	0.407326
H	0.794116	1.504082	2.480975	H	1.546508	0.131292	4.371938
---				H	1.867419	1.839516	4.735281
TS13				H	0.490584	1.373936	3.692073
G_{gas} = -2587.37742249 Hartree				H	4.283108	1.577398	3.773109
---				H	3.852929	-0.136379	3.638402
C	1.673666	0.836227	-1.763672	H	4.493107	0.722246	2.230319
C	0.516296	-0.448651	-2.701597	N	-1.401382	2.091263	-0.959912
Ir	-0.202834	0.042591	-0.499935	C	-2.646681	1.805838	-1.084812
B	-1.443603	-0.085199	1.164513	C	-1.324992	3.453829	-0.369571
O	-2.621528	-0.831542	1.140781	C	-3.155626	0.511949	-1.548920
O	-1.341415	0.581462	2.385574	O	-3.555364	2.708585	-0.643980
C	-3.390707	-0.563025	2.329944	C	-2.774947	3.678318	0.114191
C	-2.305813	0.009605	3.304474	H	-0.623127	3.398186	0.462935
C	-4.044193	-1.865686	2.782674	C	-0.824424	4.536299	-1.368732
C	-4.470408	0.456675	1.950625	C	-4.522339	0.353285	-1.873608
C	-1.581739	-1.088411	4.090413	N	-2.269536	-0.480518	-1.565126
C	-2.789721	1.108522	4.243593	H	-3.186315	4.664473	-0.094431
H	-4.578385	-1.731821	3.730731	H	-2.901333	3.438662	1.174532
H	-4.766542	-2.192388	2.027360	C	0.576461	4.172823	-1.877055
H	-3.302243	-2.657303	2.902495	C	-1.773303	4.676490	-2.570488
H	-5.066689	0.049610	1.128234	C	-0.731241	5.870245	-0.604373
H	-5.139631	0.674295	2.789925	C	-4.970223	-0.891624	-2.237399

H	-5.180584	1.211565	-1.817988	C	5.199907	-0.555434	-1.574683
C	-2.696604	-1.728687	-1.922124	H	5.694053	0.206046	0.406138
H	1.258991	3.980509	-1.044674	H	4.439439	-1.040241	0.437269
H	0.545945	3.281395	-2.505319	H	6.128425	-1.492845	0.155753
H	0.986133	4.992062	-2.478920	C	4.824159	-1.899855	-2.233735
H	-2.783232	4.983365	-2.275975	C	6.509044	-0.031282	-2.176455
H	-1.389794	5.432053	-3.265177	H	4.711445	-1.778738	-3.317389
H	-1.850667	3.731007	-3.118243	H	5.612965	-2.641124	-2.056528
H	-0.338186	6.653596	-1.261725	H	3.885094	-2.294773	-1.837296
H	-1.703877	6.213786	-0.233599	H	7.321775	-0.740249	-1.978694
H	-0.054300	5.781144	0.253863	H	6.415559	0.106711	-3.256734
C	-4.063105	-1.977407	-2.273157	H	6.777571	0.937704	-1.745157
H	-6.012823	-1.057828	-2.494157	C	4.071995	0.452382	-1.881913
C	-1.776026	-2.805680	-1.943943	O	4.237617	1.434714	-2.600925
C	-4.459230	-3.291042	-2.632112	N	2.860551	0.162398	-1.317557
C	-2.191148	-4.066289	-2.304413	H	2.741065	-0.680937	-0.767376
H	-0.752470	-2.603534	-1.663311	C	1.394664	0.645514	-3.223496
C	-3.541973	-4.315773	-2.649882	H	0.834169	1.473806	-3.661384
H	-5.499465	-3.469840	-2.890591	H	1.534846	1.831173	-1.363233
H	-1.475679	-4.882901	-2.320003	H	-0.490645	-0.504387	-3.099110
H	-3.850418	-5.319811	-2.925300	H	2.247262	0.384033	-3.850354
B	0.553878	-1.680559	0.210228	---			
O	-0.006821	-2.481447	1.205261	**TS14**			
O	1.748884	-2.285528	-0.237492	G_{gas} = -2356.88624817 Hartree			
C	0.946089	-3.482501	1.619203	---			
C	1.875719	-3.599856	0.362291	C	1.373092	-1.713519	0.033158
C	0.183830	-4.755702	1.974623	C	1.302624	-0.814282	-1.558889
C	1.676609	-2.940232	2.853304	C	2.347818	-1.794698	-1.070922
C	1.370400	-4.610191	-0.673216	Cl	-0.940743	-3.052913	-1.665969
C	3.340683	-3.877119	0.681977	O	4.006842	-2.327039	1.118063
H	0.873438	-5.571899	2.219610	C	4.416333	-1.567635	0.246598
H	-0.445679	-4.570048	2.850815	N	3.651641	-1.231019	-0.837171
H	-0.465994	-5.075831	1.157050	C	5.842680	-0.976391	0.288936
H	0.941373	-2.732990	3.636087	H	4.048967	-0.654110	-1.563042
H	2.399260	-3.664296	3.244592	C	6.776430	-2.033124	-0.339502
H	2.183405	-2.002998	2.616527	C	5.971918	0.355737	-0.471090
H	1.924850	-4.470200	-1.606507	C	6.222045	-0.764405	1.762987
H	1.513886	-5.642066	-0.335956	H	2.357391	-2.748200	-1.598432
H	0.307701	-4.459905	-0.877535	H	6.701554	-2.981014	0.202212
H	3.440268	-4.826345	1.220871	H	6.519416	-2.217699	-1.389157
H	3.922308	-3.951088	-0.241334	H	7.817054	-1.690699	-0.299026
H	3.773639	-3.084195	1.293747	H	5.225493	1.082376	-0.133592
H	1.014896	-1.406900	-2.597435	H	6.965591	0.783337	-0.297021
C	5.366213	-0.732782	-0.053748	H	5.874085	0.232827	-1.557532

H	7.269492	-0.451518	1.840935	H	-2.932283	2.564000	-0.686800
H	5.594886	0.009178	2.217283	C	-3.867486	3.263930	2.503544
H	6.079097	-1.686704	2.329129	H	-2.671490	2.869447	4.253262
H	1.660853	-1.068356	0.847554	H	-4.805889	3.545201	0.581275
H	0.841113	-2.623842	0.274470	H	-4.689454	3.702076	3.062158
H	0.812871	-1.103889	-2.490494	C	1.102738	1.558561	1.032869
H	1.663798	0.208218	-1.502203	C	2.136984	2.415488	0.637022
C	-5.271075	-2.636166	0.436925	C	1.274964	0.786560	2.196050
C	-4.914094	-2.585004	1.725796	C	3.299905	2.523879	1.404014
C	-3.553976	-2.740645	2.362299	H	2.040037	3.002591	-0.268741
C	-2.317141	-2.511295	1.470182	C	2.432157	0.898766	2.963389
C	-2.331323	-1.135541	0.843446	H	0.506057	0.073968	2.482327
C	-2.924696	-0.742241	-0.387972	C	3.446673	1.775534	2.571459
C	-3.795318	-1.555845	-1.339337	H	4.090215	3.198675	1.086903
C	-4.403379	-2.857721	-0.776724	H	2.549613	0.290396	3.854813
H	-6.327074	-2.467332	0.221002	H	4.348805	1.866367	3.168816
H	-5.713559	-2.410431	2.447582	H	-0.513794	0.970351	-2.841655
H	-3.503961	-2.038270	3.207771	Ir	-0.741810	-0.826185	-0.612918
H	-3.476055	-3.740893	2.817107	---			
H	-1.426774	-2.586417	2.108609	**TS15**			
H	-2.213611	-3.288138	0.716576	G_{gas} = -2356.89283622 Hartree			
H	-2.272430	-0.349164	1.595627	---			
H	-3.199104	0.308882	-0.404121	C	-2.554665	-2.092126	0.488011
H	-4.621991	-0.898209	-1.643438	C	-2.058489	-2.705975	-1.072811
H	-3.241874	-1.805142	-2.248961	Cl	0.813522	-3.073495	0.377987
H	-5.019418	-3.299278	-1.570457	O	-1.856705	0.428693	-0.390526
H	-3.605339	-3.574670	-0.586165	C	-3.033878	0.264471	0.012670
C	-0.378525	2.031685	-2.659760	N	-3.429793	-0.945414	0.454843
C	-0.302649	2.490896	-1.339587	C	-3.973451	1.462964	0.027169
C	-0.184818	3.870483	-1.101666	H	-4.398010	-1.082841	0.709508
C	-0.113608	4.766213	-2.165857	C	-3.933263	2.114868	-1.369269
C	-0.173624	4.296570	-3.481600	C	-5.417759	1.082263	0.387209
C	-0.312427	2.930925	-3.726691	C	-3.408845	2.449600	1.075154
H	-0.159446	4.240511	-0.081008	C	-3.122553	-3.300814	-0.204969
H	-0.020074	5.830808	-1.970895	H	-2.042882	-2.273877	1.435313
H	-0.123624	4.996807	-4.310623	H	-2.909521	2.388972	-1.631132
H	-0.378053	2.562330	-4.746319	H	-4.319560	1.433824	-2.136442
P	-0.435854	1.292841	0.052071	H	-4.552220	3.018743	-1.371709
C	-1.740667	2.125302	1.060486	H	-5.493437	0.665095	1.398912
C	-1.680732	2.227507	2.456136	H	-6.046523	1.977741	0.363026
C	-2.878870	2.611831	0.396286	H	-5.842834	0.366240	-0.326942
C	-2.737201	2.793749	3.171590	H	-4.023126	3.356762	1.095961
H	-0.804669	1.882040	2.991869	H	-3.418805	2.006525	2.077581
C	-3.933553	3.174923	1.111963	H	-2.381060	2.726373	0.830358

H	-4.153425	-3.227039	-0.548010	B	-1.768112	-0.294748	0.859879
H	-2.885623	-4.255879	0.255987	O	-3.003411	0.084283	0.342498
H	-1.178252	-3.314057	-1.250896	O	-1.945813	-1.179480	1.904841
H	-2.403317	-2.100971	-1.904905	C	-4.057469	-0.505424	1.139879
C	0.107425	2.508928	-1.232566	C	-3.301227	-1.682930	1.845576
C	0.683306	2.007540	-0.054869	C	-5.188398	-0.921607	0.205647
C	0.751630	2.832759	1.072541	C	-4.536379	0.580162	2.107706
C	0.259154	4.139967	1.023090	C	-3.250025	-2.960835	0.999428
C	-0.300302	4.635274	-0.154545	C	-3.768589	-2.001623	3.260348
C	-0.372356	3.815424	-1.285222	H	-5.994026	-1.414820	0.761290
H	1.190796	2.455636	1.990061	H	-5.601941	-0.033715	-0.283630
H	0.319558	4.770878	1.905738	H	-4.834081	-1.598878	-0.574024
H	-0.677995	5.653295	-0.194075	H	-4.888491	1.440652	1.529803
H	-0.806151	4.194898	-2.206622	H	-5.358933	0.229532	2.739493
P	1.202108	0.242711	-0.012018	H	-3.717097	0.919631	2.746868
C	2.250436	0.151768	1.493406	H	-2.511959	-3.638728	1.435657
C	3.528144	0.725584	1.546662	H	-4.222213	-3.464110	0.963749
C	1.729735	-0.475912	2.631890	H	-2.926394	-2.742592	-0.021886
C	4.268431	0.682930	2.727201	H	-4.812218	-2.336561	3.259467
H	3.947833	1.197487	0.664029	H	-3.152800	-2.805484	3.675717
C	2.471775	-0.516124	3.812774	H	-3.679993	-1.135211	3.919010
H	0.751664	-0.941969	2.566089	B	-0.254787	0.967866	1.531507
C	3.740128	0.063882	3.862744	O	-0.892934	2.186527	1.791809
H	5.259599	1.127113	2.759613	O	0.439848	0.546974	2.661123
H	2.063497	-1.011064	4.689606	C	-0.422270	2.699072	3.063681
H	4.320337	0.027345	4.780884	C	0.105195	1.399058	3.776257
C	2.413300	0.136703	-1.391407	C	-1.591221	3.387481	3.760863
C	3.104229	1.261986	-1.864975	C	0.681226	3.719495	2.765301
C	2.670448	-1.118466	-1.961757	C	-0.968520	0.673823	4.594488
C	4.039692	1.133999	-2.892600	C	1.359838	1.596186	4.622028
H	2.903972	2.240226	-1.439836	H	-1.301332	3.735120	4.758804
C	3.610687	-1.241406	-2.984454	H	-1.906299	4.258804	3.177144
H	2.134863	-1.987670	-1.594005	H	-2.448731	2.718635	3.859924
C	4.295139	-0.118180	-3.453511	H	0.280420	4.491583	2.100169
H	4.565858	2.013032	-3.255170	H	1.037020	4.205710	3.679614
H	3.805021	-2.218324	-3.418545	H	1.531907	3.251458	2.264933
H	5.022355	-0.217329	-4.254909	H	-0.577205	-0.299228	4.904498
H	0.033492	1.866116	-2.104367	H	-1.248468	1.240311	5.488974
Ir	-0.549013	-1.148956	-0.098905	H	-1.859057	0.487657	3.991845
---				H	1.173116	2.294142	5.446253
L				H	1.662781	0.636212	5.052179
G_{gas} = -2587.408539 Hartree				H	2.190620	1.973642	4.022343
---				N	-1.330477	1.803531	-1.403995
Ir	-0.005176	0.135566	-0.396880	C	-2.344150	1.227020	-1.935472

C	-1.736076	3.192877	-1.086610	H	1.729078	-5.324919	2.281872
C	-2.339530	-0.169145	-2.374660	H	0.005107	-5.001718	2.021320
O	-3.488535	1.929684	-2.061516	H	1.101083	-5.077078	0.635700
C	-3.272113	3.123191	-1.252903	H	-0.167961	-2.996919	3.413493
H	-1.464305	3.378589	-0.046350	H	1.484418	-3.320464	3.997588
C	-1.035744	4.240799	-1.995347	H	1.037433	-1.717083	3.339876
C	-3.374358	-0.648266	-3.207861	H	4.108693	-3.084727	-0.214657
N	-1.336563	-0.926026	-1.921458	H	3.542999	-4.584320	0.543326
H	-3.719440	3.963500	-1.782119	H	2.505644	-3.719184	-0.610299
H	-3.781738	2.960450	-0.299537	H	3.851687	-3.536921	2.967175
C	0.484335	4.128543	-1.821389	H	4.635689	-2.251914	2.034776
C	-1.386592	4.021167	-3.476361	H	3.349390	-1.844178	3.181676
C	-1.485201	5.642383	-1.545513	H	2.238020	1.036128	0.949070
C	-3.355910	-1.963395	-3.594211	H	1.915604	-0.819976	-2.153350
H	-4.163086	0.032709	-3.502047	C	6.943405	1.549135	-0.014429
C	-1.253982	-2.224298	-2.366742	C	6.239044	0.547446	-0.950020
H	0.776460	4.279584	-0.776593	H	7.024398	2.523782	-0.502141
H	0.840639	3.146261	-2.134492	H	6.379479	1.678216	0.917500
H	0.995240	4.885821	-2.426578	H	7.948484	1.192894	0.242147
H	-2.462508	4.103953	-3.668020	C	6.095151	-0.804908	-0.240451
H	-0.882670	4.770527	-4.096628	C	7.067930	0.371180	-2.235743
H	-1.054043	3.033602	-3.812745	H	5.597441	-1.543224	-0.879436
H	-0.961422	6.410498	-2.125114	H	7.085147	-1.201305	0.012921
H	-2.560415	5.803833	-1.686174	H	5.529190	-0.715267	0.693550
H	-1.254147	5.806909	-0.485902	H	8.077896	0.017631	-1.995161
C	-2.279618	-2.790138	-3.194353	H	6.600888	-0.360895	-2.905624
H	-4.145467	-2.376731	-4.215568	H	7.138929	1.322596	-2.768029
C	-0.139286	-3.026285	-2.028102	C	4.896283	1.195600	-1.361153
C	-2.180762	-4.146081	-3.597819	O	4.902156	2.261281	-1.980571
C	-0.063819	-4.332893	-2.451681	N	3.755194	0.548540	-1.014230
H	0.645988	-2.583268	-1.441602	H	3.771605	-0.276238	-0.427992
C	-1.096397	-4.907649	-3.229496	C	2.433132	1.109022	-1.242506
H	-2.972810	-4.563325	-4.213568	H	2.605060	2.030085	-1.800886
H	0.803633	-4.929473	-2.185342	C	1.678806	1.363209	0.075140
H	-1.023062	-5.943998	-3.544909	H	1.379295	2.405556	0.191324
B	0.967161	-1.385410	0.508559	C	1.460609	0.153224	-1.950325
O	0.357033	-2.564492	0.923264	H	1.059924	0.559875	-2.886305
O	2.339584	-1.445507	0.791435	---			
C	1.246614	-3.254818	1.820350	**M**			
C	2.650805	-2.751042	1.338287	G_{gas} = -2587.41141 Hartree			
C	1.014563	-4.755514	1.676269	---			
C	0.892737	-2.794900	3.239948	Ir	-0.143017	-0.039007	-0.532274
C	3.232720	-3.592784	0.197534	B	-1.284703	0.221634	1.335170
C	3.680349	-2.585081	2.451148	O	-1.649231	-0.953155	1.989434

O	-1.373563	1.296818	2.192500	O	-0.961991	-3.898022	1.076532
C	-2.132161	-0.632916	3.313099	C	-2.295590	-3.882930	0.487195
C	-1.536803	0.802548	3.544727	H	-2.941244	-2.298775	-0.884279
C	-1.630872	-1.707503	4.273144	C	-2.015869	-3.854307	-2.096834
C	-3.661937	-0.657162	3.242087	C	1.699081	-3.283658	1.867145
C	-0.139807	0.784858	4.174303	N	1.189311	-1.082142	0.986647
C	-2.441804	1.765575	4.305126	H	-2.588997	-4.917301	0.314411
H	-1.926769	-1.484289	5.304450	H	-2.961212	-3.414380	1.216203
H	-2.060734	-2.675184	3.994973	C	-1.728943	-2.920214	-3.279335
H	-0.543656	-1.802489	4.232449	C	-0.886670	-4.895018	-2.004032
H	-3.986449	-1.648561	2.910350	C	-3.365633	-4.553607	-2.339665
H	-4.119241	-0.451406	4.215385	C	2.854298	-2.828760	2.446570
H	-4.029800	0.071720	2.515779	H	1.385670	-4.318139	1.931311
H	0.291253	1.787121	4.099399	C	2.301837	-0.590067	1.625332
H	-0.174458	0.493679	5.229585	H	-2.507409	-2.156073	-3.377887
H	0.523795	0.098703	3.642853	H	-0.768852	-2.416473	-3.156967
H	-2.632384	1.401910	5.321428	H	-1.697932	-3.493240	-4.213474
H	-1.954548	2.742770	4.377134	H	-1.044744	-5.612331	-1.191060
H	-3.398938	1.903696	3.797920	H	-0.826043	-5.464907	-2.937935
B	-2.106521	0.752006	-0.498025	H	0.082125	-4.409337	-1.847748
O	-3.270248	-0.026714	-0.564707	H	-3.340798	-5.103213	-3.287199
O	-2.413930	2.082188	-0.759966	H	-3.613435	-5.274201	-1.551808
C	-4.344975	0.787298	-1.093904	H	-4.181525	-3.822541	-2.397356
C	-3.846514	2.243650	-0.777527	C	3.175431	-1.455858	2.361259
C	-5.640901	0.383615	-0.398646	H	3.512330	-3.499712	2.991011
C	-4.442196	0.493476	-2.594801	C	2.573089	0.798357	1.620674
C	-4.254610	2.740267	0.613868	C	4.308222	-0.909801	3.016747
C	-4.206367	3.286692	-1.831249	C	3.674507	1.297786	2.279791
H	-6.471636	1.022207	-0.719902	H	1.866256	1.464959	1.152215
H	-5.890183	-0.651419	-0.655238	C	4.560681	0.441591	2.973965
H	-5.549968	0.449623	0.687420	H	4.966745	-1.583377	3.558016
H	-4.596033	-0.581486	-2.736162	H	3.852650	2.369301	2.278283
H	-5.281698	1.023659	-3.056612	H	5.427653	0.853414	3.481598
H	-3.522115	0.774335	-3.112740	B	0.523295	1.873159	-0.571766
H	-3.719642	3.671173	0.822330	O	1.197537	2.453743	-1.655221
H	-5.331120	2.929847	0.681943	O	0.397594	2.816034	0.445458
H	-3.965946	2.021215	1.383493	C	1.610888	3.794991	-1.313482
H	-5.293518	3.384087	-1.931934	C	0.708957	4.124574	-0.069587
H	-3.804050	4.260211	-1.534154	C	1.385998	4.690603	-2.528646
H	-3.785029	3.030450	-2.805762	C	3.105256	3.737663	-0.982160
N	-0.895010	-2.266106	-0.482018	C	-0.621234	4.788783	-0.441922
C	-0.337540	-2.841241	0.516153	C	1.396991	4.924548	1.033507
C	-2.131244	-3.023503	-0.786538	H	1.630478	5.734217	-2.299138
C	0.902923	-2.377024	1.139275	H	2.030685	4.362798	-3.350766

H	0.350424	4.640165	-2.870750	H	3.802852	-0.012452	-1.111610
H	3.649316	3.352148	-1.849563	C	1.400799	-0.323044	-2.025354
H	3.507163	4.726936	-0.739719	C	6.608204	-2.096600	0.585639
H	3.297808	3.066850	-0.140829	C	6.051804	0.182244	-0.310790
H	-1.257466	4.811323	0.447745	C	5.379702	-0.448661	2.036683
H	-0.475362	5.814297	-0.798728	C	2.167790	-1.364579	-1.187424
H	-1.146630	4.206621	-1.200643	C	1.136431	-1.622269	-0.085567
H	1.700606	5.914212	0.673136	H	1.376830	-0.547376	-3.092768
H	0.701428	5.062670	1.867101	H	6.248276	-2.941758	1.175980
H	2.280698	4.407119	1.415454	H	6.793547	-2.450512	-0.435204
C	5.657487	-1.272360	-2.763587	H	7.559070	-1.743982	1.002061
C	5.125838	-0.738336	-1.415453	H	5.381625	1.048849	-0.281553
H	5.545903	-2.360038	-2.811470	H	7.036666	0.527459	0.023889
H	5.106213	-0.834205	-3.603309	H	6.153360	-0.144509	-1.352212
H	6.719511	-1.024393	-2.881185	H	6.324517	-0.056714	2.431692
C	5.303709	0.785723	-1.357384	H	4.634517	0.354957	2.075961
C	5.908454	-1.389315	-0.265442	H	5.037289	-1.260505	2.684549
H	4.851091	1.205781	-0.453638	H	2.313457	-2.283937	-1.763357
H	6.371241	1.034586	-1.346057	H	0.896277	-2.674051	0.079435
H	4.870891	1.288246	-2.230159	H	1.378496	-1.131521	0.857753
H	6.984855	-1.231256	-0.403216	C	-2.910305	-1.324528	-0.528911
H	5.621351	-0.958029	0.697854	C	-2.258151	-2.451572	-0.124598
H	5.703346	-2.461291	-0.231892	C	-2.106278	-3.055247	1.249972
C	3.650689	-1.195899	-1.333102	C	-3.092666	-2.600759	2.345615
O	3.372258	-2.344585	-0.967043	C	-4.531215	-2.893327	1.991376
N	2.712553	-0.330095	-1.787052	C	-5.367821	-2.164856	1.244001
H	2.942211	0.642614	-1.930136	C	-5.157540	-0.846445	0.543031
C	0.644915	-0.054915	-3.163872	C	-3.712913	-0.357859	0.308719
H	0.574785	-0.722072	-4.037499	H	-3.073531	-1.240087	-1.604461
C	-0.709361	0.349199	-2.560056	H	-1.908423	-3.099243	-0.921170
H	-1.525187	-0.316105	-2.838795	H	-2.224561	-4.139255	1.118843
C	1.321921	-0.686307	-1.943956	H	-1.070001	-2.935276	1.596421
H	1.284708	-1.775488	-1.948899	H	-2.838921	-3.145609	3.263494
H	-0.991875	1.378199	-2.778147	H	-2.951107	-1.545351	2.578113
H	1.189162	0.839791	-3.475922	H	-4.915420	-3.838576	2.374318
---				H	-6.371348	-2.569244	1.106313
N				H	-5.655567	-0.911224	-0.435137
G_{gas} = -2356.920474 Hartree				H	-5.703443	-0.059868	1.087667
---				H	-3.780429	0.592082	-0.225174
Cl	-0.639312	-2.403497	-2.912226	H	-3.220607	-0.134514	1.256095
O	3.822366	-2.633141	0.656953	H	1.759356	0.692893	-1.855222
C	4.213771	-1.573216	0.169431	C	2.216900	1.968462	0.699271
N	3.457958	-0.872117	-0.714426	C	1.087158	2.221867	-0.093032
C	5.568748	-0.962116	0.594435	C	1.134129	3.257022	-1.034402

C	2.288318	4.029017	-1.179391	C	-5.465630	-0.375550	-0.661468
C	3.404020	3.779781	-0.380045	C	-5.426865	-1.957956	1.296031
C	3.363092	2.749816	0.563029	C	-1.004008	-1.189482	-2.868120
H	0.268497	3.465906	-1.653614	C	0.234788	-0.290312	-2.757126
H	2.310136	4.829977	-1.912775	H	-1.042554	-2.195131	-0.913840
H	4.298791	4.386295	-0.485960	H	-3.758405	-0.035846	2.345668
H	4.223069	2.556937	1.197224	H	-3.733423	1.068953	0.952033
P	-0.392812	1.133411	0.081355	H	-5.254591	0.770723	1.822563
C	-1.763323	2.198446	-0.523802	H	-5.609218	-1.161035	-1.411887
C	-2.575585	2.985068	0.300932	H	-6.455401	-0.058646	-0.314057
C	-2.037755	2.142676	-1.901080	H	-5.005009	0.493695	-1.145292
C	-3.642488	3.703072	-0.241363	H	-6.345229	-1.531263	1.715450
H	-2.399277	3.015907	1.369729	H	-5.707635	-2.782758	0.630483
C	-3.101539	2.863718	-2.441248	H	-4.820338	-2.368863	2.106147
H	-1.419806	1.521860	-2.546749	H	-1.793095	-0.683007	-3.432486
C	-3.908263	3.644371	-1.610265	H	-0.816968	-2.168198	-3.329873
H	-4.272716	4.301747	0.410152	H	1.183375	-0.826561	-2.831032
H	-3.304195	2.808129	-3.506743	H	0.239100	0.579017	-3.420860
H	-4.743328	4.199620	-2.027437	C	0.995782	2.351141	0.292647
C	-0.524584	1.111498	1.911189	C	1.198661	2.745978	-0.994741
C	-0.381680	2.280496	2.677866	C	0.520378	3.816263	-1.809542
C	-0.706330	-0.110486	2.561946	C	-0.312874	4.855891	-1.033780
C	-0.463000	2.222750	4.067267	C	0.490644	5.629191	-0.013965
H	-0.188950	3.229655	2.187616	C	0.790907	5.304336	1.249610
C	-0.777208	-0.171370	3.955192	C	0.425952	4.081719	2.053992
H	-0.773715	-1.008779	1.965302	C	-0.043492	2.836555	1.275739
C	-0.664078	0.996216	4.708416	H	1.797821	1.767990	0.738483
H	-0.357889	3.131994	4.652186	H	2.089313	2.342898	-1.469206
H	-0.915822	-1.130080	4.445922	H	1.321475	4.341752	-2.349593
H	-0.718820	0.953118	5.792335	H	-0.115245	3.352450	-2.571766
H	2.198814	1.167576	1.430858	H	-0.713266	5.563033	-1.770173
Ir	-0.431696	-0.760647	-1.142861	H	-1.180830	4.366128	-0.593920
----------				H	0.898998	6.572955	-0.377193
O				H	1.392566	6.024395	1.806235
G_{gas} = -2356.93645085 Hartree				H	1.302032	3.799466	2.656019
----------				H	-0.351508	4.346498	2.787512
Cl	-2.050632	1.810052	-1.632114	H	-0.225436	2.040331	2.005337
O	-2.624811	-2.146169	0.949386	H	-0.995292	3.020013	0.778909
C	-3.270153	-1.464329	0.143513	C	1.987011	0.044680	2.808358
N	-2.784753	-1.139931	-1.083775	C	0.996434	-0.552283	2.016489
C	-4.640358	-0.879460	0.534121	C	-0.309919	-0.676644	2.525051
H	-3.246259	-0.382718	-1.570712	C	-0.602635	-0.231877	3.814387
C	-1.382673	-1.276544	-1.378988	C	0.387437	0.364467	4.597583
C	-4.324292	0.307286	1.473590	C	1.680679	0.503349	4.090518

H	-1.098721	-1.114997	1.918373	C	-5.934296	0.277502	0.493439
H	-1.613229	-0.341515	4.197151	C	-6.078174	-0.850260	-1.747113
H	0.152636	0.723854	5.595416	H	-2.304279	-2.717454	1.641666
H	2.455114	0.971270	4.691778	H	-6.647173	-3.056161	-0.196358
P	1.245133	-0.947624	0.242335	H	-6.547012	-2.277510	1.395899
C	1.066805	-2.767895	0.066602	H	-7.780486	-1.754005	0.231663
C	0.357792	-3.557907	0.977793	H	-5.192564	1.013342	0.165194
C	1.597052	-3.361986	-1.090439	H	-6.929110	0.690861	0.294626
C	0.185898	-4.921894	0.736181	H	-5.855739	0.158134	1.581416
H	-0.074703	-3.116716	1.865861	H	-7.114728	-0.519591	-1.877367
C	1.419125	-4.722041	-1.330238	H	-5.417660	-0.090551	-2.177324
H	2.158365	-2.761340	-1.799679	H	-5.929652	-1.781277	-2.298283
C	0.711410	-5.505942	-0.415444	H	-1.537965	-1.076287	-0.804374
H	-0.369947	-5.523379	1.449230	H	-0.758536	-2.648741	-0.221621
H	1.834376	-5.170020	-2.228522	H	-0.762486	-1.098319	2.590613
H	0.570431	-6.566695	-0.602180	H	-1.555113	0.229384	1.583632
C	3.044545	-0.779346	-0.068974	C	5.325697	-2.853072	-0.289188
C	3.972830	-1.496255	0.703765	C	4.983055	-2.858562	-1.583704
C	3.502037	0.000137	-1.136030	C	3.624082	-2.981506	-2.229582
C	5.335592	-1.398963	0.434217	C	2.389137	-2.665545	-1.359559
H	3.623827	-2.133342	1.511100	C	2.447669	-1.265806	-0.799663
C	4.868244	0.089552	-1.412754	C	3.040719	-0.835945	0.382225
H	2.780999	0.517440	-1.756529	C	3.863672	-1.611695	1.394032
C	5.785790	-0.602310	-0.623400	C	4.436894	-2.965480	0.925749
H	6.047284	-1.950560	1.041760	H	6.386733	-2.725898	-0.070373
H	5.211418	0.696303	-2.245745	H	5.797376	-2.765007	-2.303894
H	6.848849	-0.531717	-0.835064	H	3.612310	-2.314287	-3.103781
H	2.993292	0.168083	2.423675	H	3.507795	-3.995604	-2.643011
Ir	-0.214764	0.375844	-0.843355	H	1.501543	-2.742436	-1.999934
---				H	2.258302	-3.400199	-0.568746
TS1-d				H	2.286181	-0.496320	-1.552072
G_{sol}(toluene) = -2363.091968 Hartree				H	3.231581	0.232365	0.422787
---				H	4.703314	-0.959509	1.673340
C	-1.267672	-1.723087	0.016441	H	3.285064	-1.782630	2.307186
C	-1.229390	-0.804416	1.652453	H	5.029787	-3.370814	1.755172
C	-2.258070	-1.764059	1.114736	H	3.617714	-3.667178	0.771923
Cl	0.966597	-3.111069	1.813254	C	0.578616	1.939983	2.678350
Rh	0.766653	-0.899540	0.671953	C	0.457691	2.418518	1.367854
O	-3.989399	-2.561953	-0.899585	C	0.374649	3.804491	1.149595
C	-4.359992	-1.664652	-0.142582	C	0.385337	4.688632	2.225772
N	-3.553641	-1.188558	0.846865	C	0.493394	4.200924	3.532233
C	-5.774039	-1.057215	-0.253213	C	0.595547	2.828180	3.756594
H	-3.910621	-0.508944	1.501606	H	0.309218	4.188835	0.136283
C	-6.746463	-2.103372	0.332092	H	0.316489	5.757617	2.046749

H	0.506534	4.892086	4.369932	H	-4.616748	-0.556450	1.984814
H	0.693795	2.444881	4.767886	H	-4.807042	0.214638	0.397299
P	0.487841	1.238918	-0.040656	H	-6.115049	-0.787245	1.054982
C	1.788876	2.016102	-1.096859	H	-4.666799	-2.967176	-1.622448
C	1.707298	2.068345	-2.495058	H	-6.054794	-2.004871	-1.125585
C	2.947501	2.506481	-0.470387	H	-4.610769	-1.185510	-1.743573
C	2.760603	2.590303	-3.248031	H	-5.946229	-3.284436	1.103224
H	0.818638	1.719754	-3.006450	H	-4.438618	-4.101518	0.644394
C	3.999065	3.025250	-1.224162	H	-4.502742	-3.132484	2.131718
H	3.021946	2.499252	0.612317	H	-0.807318	-3.564997	-2.496536
C	3.910625	3.065287	-2.616951	H	0.732190	-3.541512	-1.554504
H	2.676317	2.627926	-4.330181	H	1.153685	-1.279162	-2.408222
H	4.885320	3.400618	-0.721162	H	-0.553450	-1.210142	-3.088411
H	4.729331	3.469348	-3.204891	C	-2.060392	4.837152	-0.184382
C	-1.078526	1.554026	-0.953374	C	-2.451458	4.454874	1.038424
C	-2.071109	2.424610	-0.484332	C	-2.861343	3.095526	1.551817
C	-1.320456	0.827104	-2.133057	C	-2.458733	1.863130	0.715789
C	-3.259834	2.593367	-1.198277	C	-0.966331	1.790840	0.546180
H	-1.921168	2.976703	0.435839	C	-0.156180	2.397176	-0.404590
C	-2.503139	1.002685	-2.848985	C	-0.543559	3.305643	-1.558145
H	-0.588156	0.105165	-2.483231	C	-1.914632	4.004839	-1.435573
C	-3.474485	1.893459	-2.385668	H	-1.787089	5.887072	-0.298331
H	-4.016119	3.277558	-0.824611	H	-2.487579	5.233905	1.801892
H	-2.670785	0.434968	-3.758989	H	-2.439666	2.984210	2.561703
H	-4.395956	2.033084	-2.942441	H	-3.953384	3.076378	1.696228
H	0.674656	0.872585	2.847740	H	-2.770645	0.969550	1.262992
---				H	-2.978169	1.841405	-0.238040
TS1-p				H	-0.464603	1.510433	1.465579
G_{sol}(toluene) = -2363.094564 Hartree				H	0.878687	2.525710	-0.093641
---				H	0.237910	4.074575	-1.631926
C	-0.801829	-2.220944	-0.775293	H	-0.528221	2.753943	-2.504003
C	0.106577	-1.553738	-2.300289	H	-2.024283	4.662090	-2.307422
Cl	-2.289336	0.533466	-2.382719	H	-2.700799	3.255446	-1.521949
Rh	-0.264907	0.176865	-0.916252	C	2.911646	1.594820	-1.610781
O	-2.329239	-1.612713	1.463560	C	3.104617	0.776973	-0.489543
C	-2.900483	-1.865428	0.403284	C	4.402861	0.614699	0.023410
N	-2.200050	-2.212289	-0.724512	C	5.477931	1.287079	-0.554243
C	-4.436043	-1.935159	0.305891	C	5.272533	2.116460	-1.661112
H	-2.694549	-2.228508	-1.604941	C	3.991059	2.263261	-2.192567
C	-5.026875	-0.684588	0.980032	H	4.573534	-0.049609	0.864921
C	-4.960055	-2.028397	-1.136561	H	6.476532	1.158286	-0.147074
C	-4.854261	-3.194069	1.097635	H	6.112283	2.636995	-2.112296
C	-0.146664	-2.977317	-1.857876	H	3.828301	2.893826	-3.061668
H	-0.344401	-2.217695	0.200525	P	1.675443	-0.142427	0.208548

C	1.609531	0.275949	1.997536
C	0.539427	-0.258991	2.740503
C	2.514630	1.136842	2.629671
C	0.415906	0.025344	4.099013
H	-0.225819	-0.854513	2.248842
C	2.376247	1.431016	3.988610
H	3.321868	1.591126	2.067537
C	1.336063	0.868646	4.728000
H	-0.413039	-0.396091	4.660033
H	3.082610	2.104740	4.465036
H	1.231482	1.098556	5.784345
C	2.344756	-1.863600	0.192372
C	3.135310	-2.279799	-0.892002
C	1.986166	-2.806361	1.166357
C	3.544070	-3.607796	-1.005019
H	3.439320	-1.563207	-1.647747
C	2.393264	-4.136555	1.049854
H	1.396290	-2.506917	2.025343
C	3.167801	-4.542977	-0.037688
H	4.155781	-3.911271	-1.849612
H	2.106269	-4.852834	1.814093
H	3.482740	-5.578364	-0.127537
H	1.915143	1.690615	-2.029855

TS16

G_{gas} = -2044.88200391 Hartree

C	-2.561344	-2.077018	0.502585
C	-2.069631	-2.697872	-1.07328
Cl	0.823874	-3.087545	0.36651
O	-1.849926	0.427137	-0.390739
C	-3.031842	0.272835	0.014656
N	-3.430987	-0.92723	0.466095
C	-3.963695	1.476134	0.011719
H	-4.401268	-1.062749	0.71664
C	-3.928386	2.100591	-1.397757
C	-5.407209	1.108946	0.387831
C	-3.38797	2.479259	1.038025
C	-3.131443	-3.280724	-0.1945
H	-2.063088	-2.263972	1.455962
H	-2.906429	2.371604	-1.670708
H	-4.318837	1.404506	-2.148818
H	-4.547971	3.003545	-1.413086
H	-5.477174	0.707755	1.405909
H	-6.028797	2.008904	0.353227
H	-5.840485	0.384659	-0.312163
H	-4.000742	3.387273	1.045168
H	-3.393979	2.054566	2.048283
H	-2.361572	2.750061	0.780616
H	-4.163195	-3.202439	-0.532143
H	-2.897827	-4.236394	0.26704
H	-1.202729	-3.319798	-1.266809
H	-2.421335	-2.08976	-1.90038
C	0.113184	2.522476	-1.208063
C	0.694983	2.009549	-0.038158
C	0.789674	2.830209	1.090914
C	0.315414	4.144702	1.050909
C	-0.251635	4.650883	-0.118714
C	-0.349223	3.835605	-1.251103
H	1.234447	2.445875	2.002653
H	0.395565	4.771945	1.934345
H	-0.616516	5.673609	-0.150463
H	-0.790574	4.222836	-2.165287
P	1.201132	0.241617	-0.011741
C	2.247727	0.12873	1.494499
C	3.572925	0.583604	1.526081
C	1.67181	-0.389725	2.662423
C	4.307489	0.527081	2.7108
H	4.034632	0.97512	0.625634
C	2.405767	-0.440596	3.847793
H	0.652071	-0.760998	2.620141
C	3.724791	0.017373	3.873626
H	5.335784	0.877397	2.724836
H	1.951541	-0.846712	4.747209
H	4.299373	-0.028303	4.79457
C	2.40718	0.143826	-1.396567
C	3.12667	1.266614	-1.833461
C	2.627594	-1.095556	-2.014837
C	4.053589	1.150559	-2.870423
H	2.956439	2.233433	-1.371108
C	3.558418	-1.208034	-3.048021
H	2.069581	-1.962493	-1.676942
C	4.271531	-0.087047	-3.479133
H	4.602229	2.027277	-3.203234
H	3.722574	-2.17273	-3.519926
H	4.991206	-0.176266	-4.288116
H	0.020412	1.885976	-2.082645
Ir	-0.556858	-1.155333	-0.100504

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9. Copies of NMR Spectra

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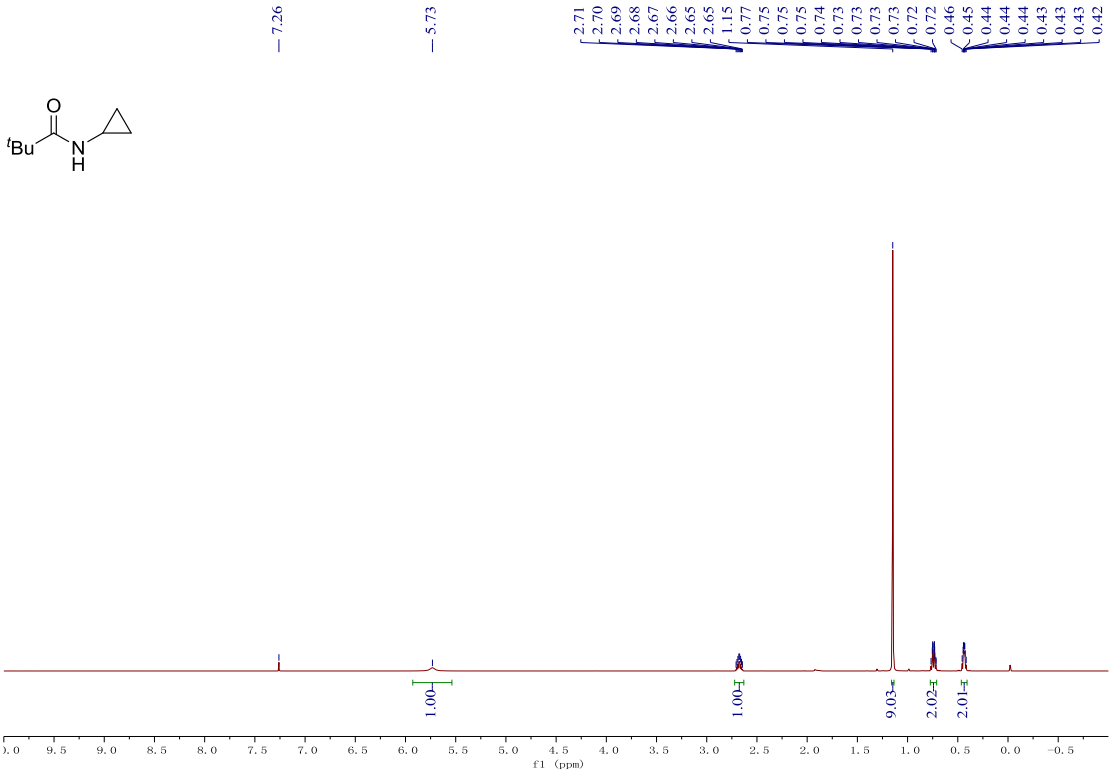

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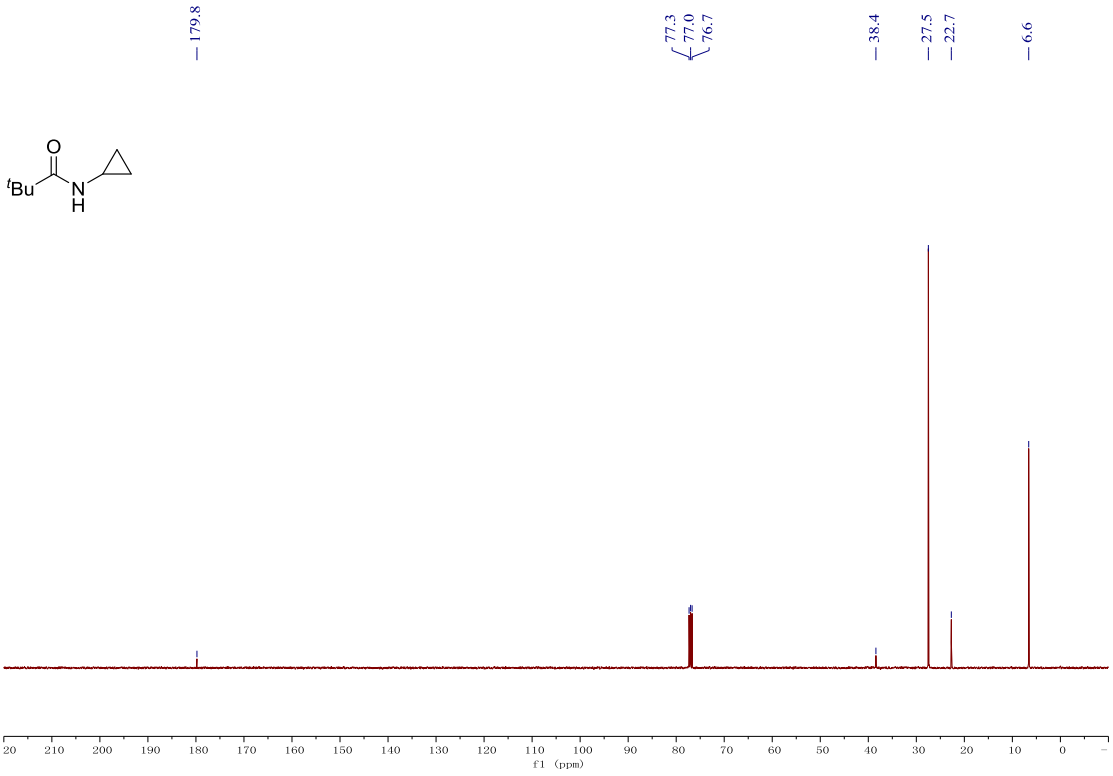

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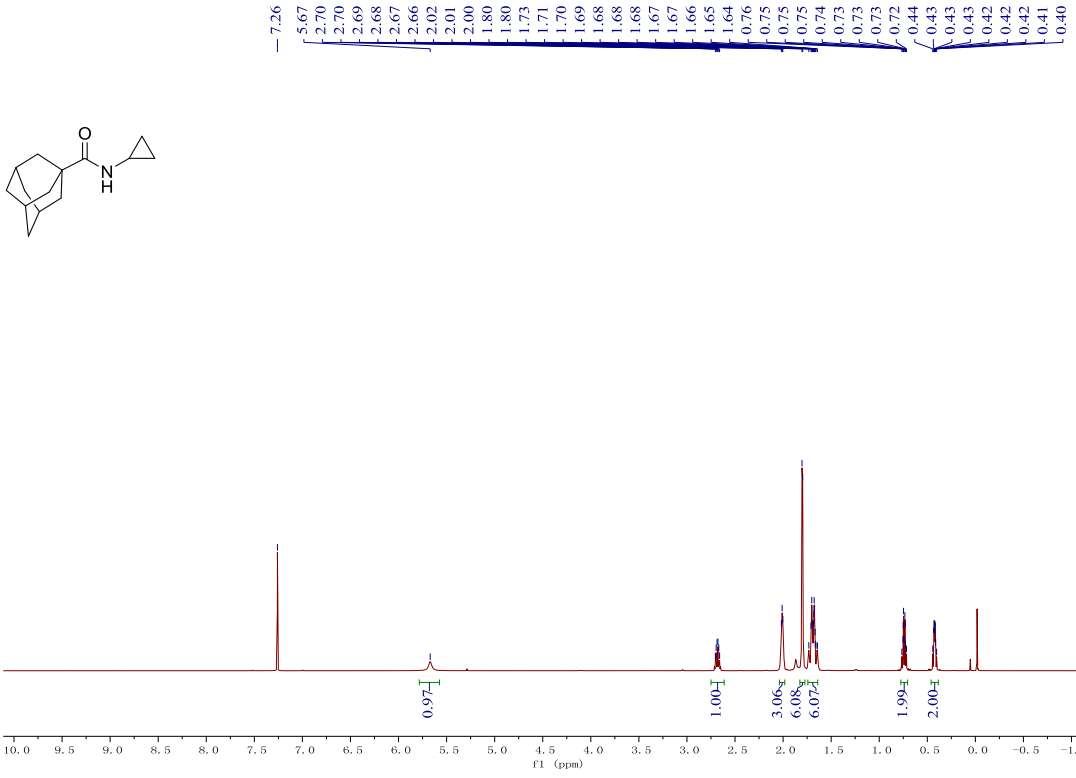

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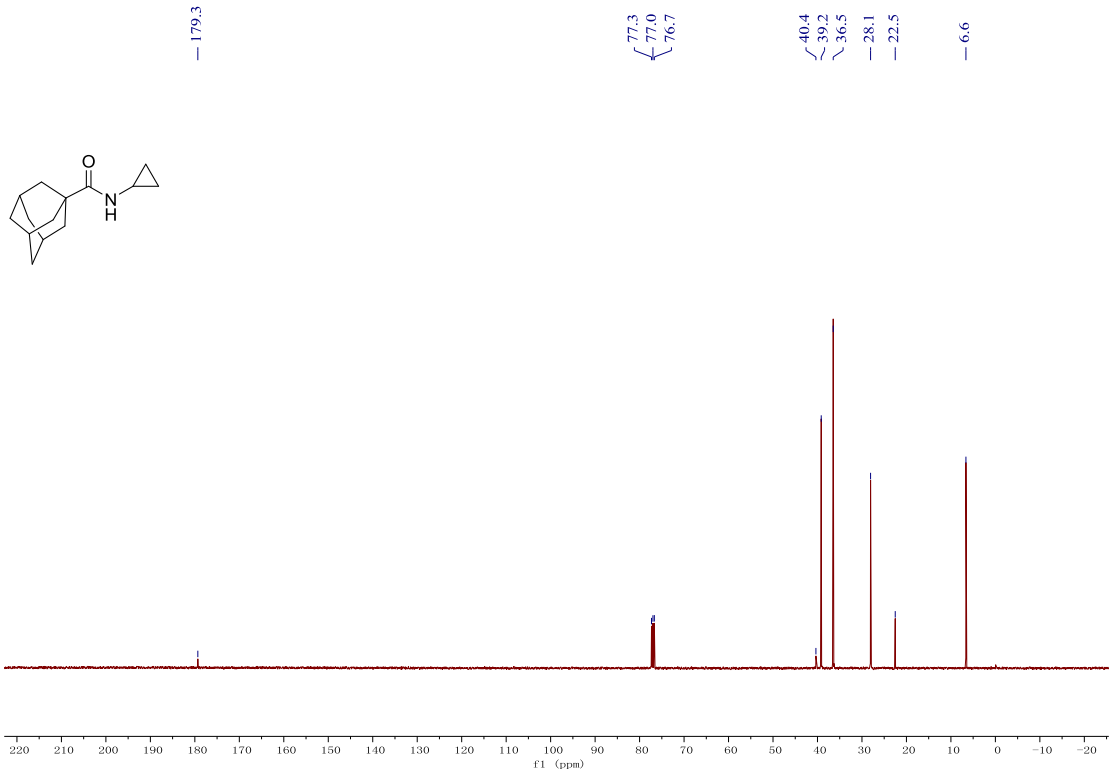

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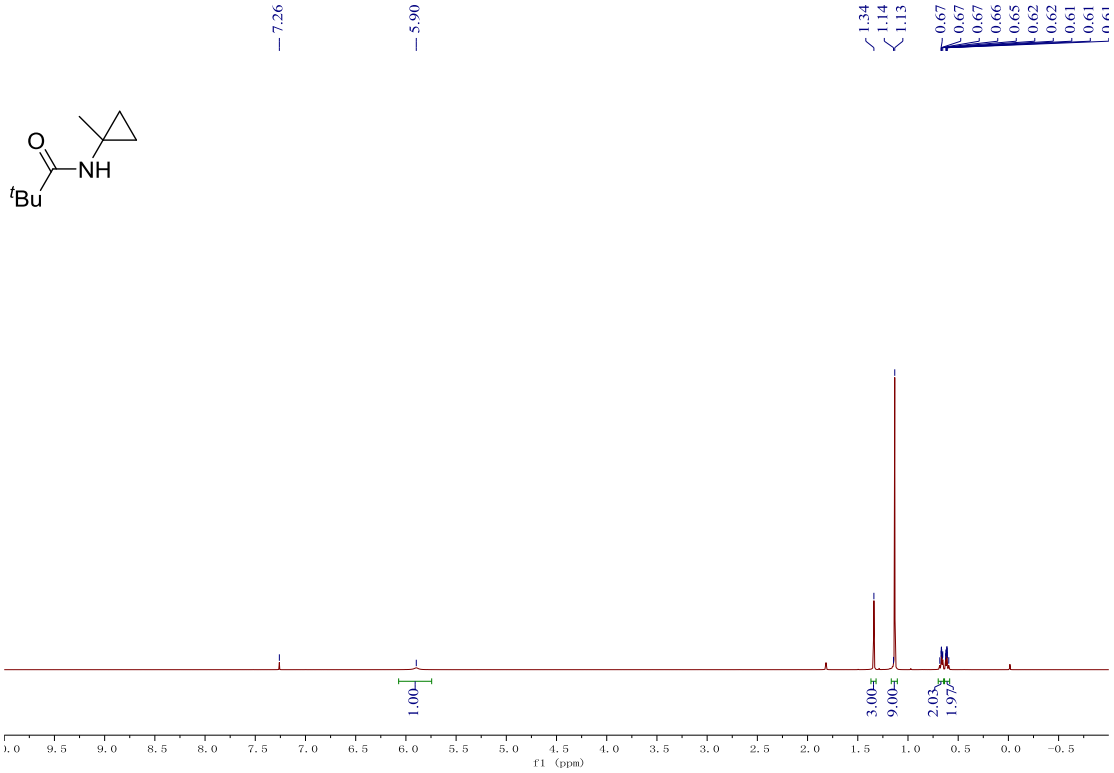

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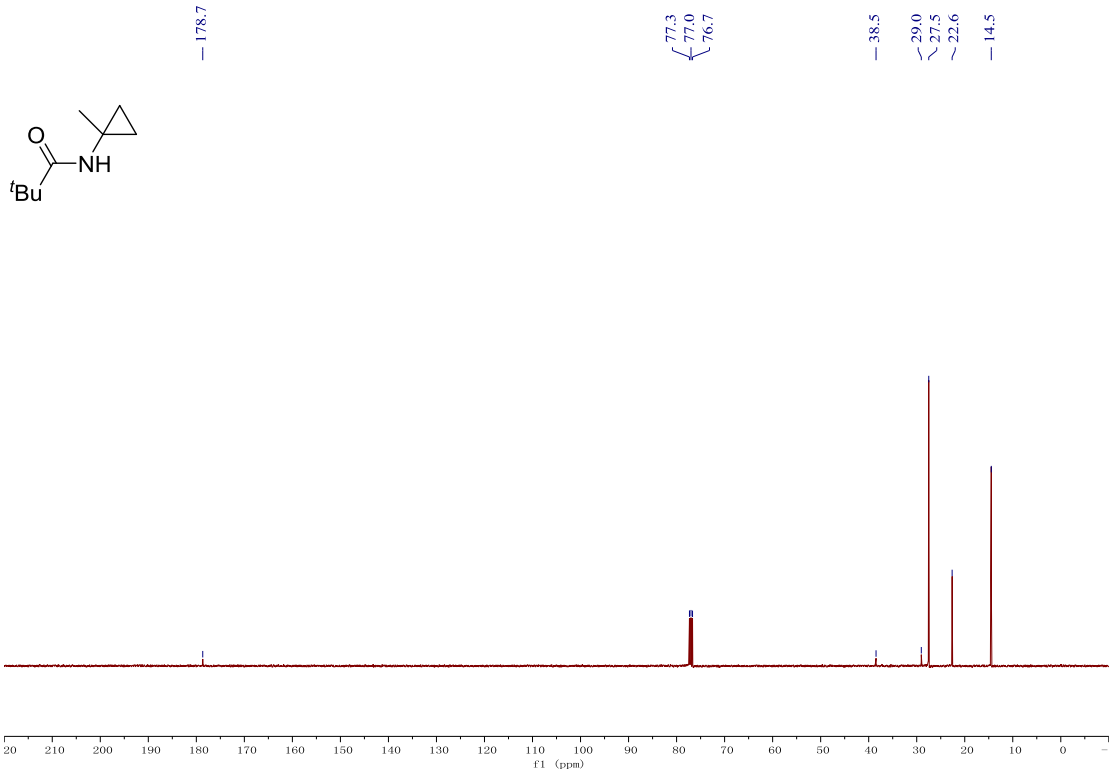

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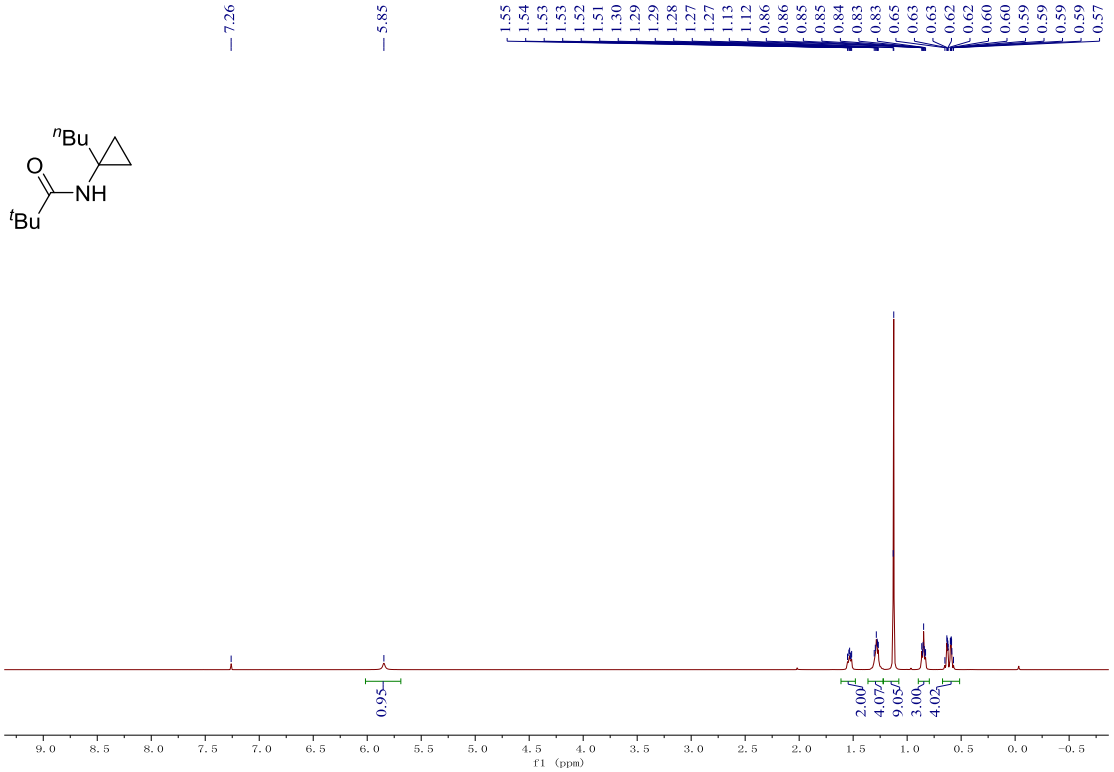

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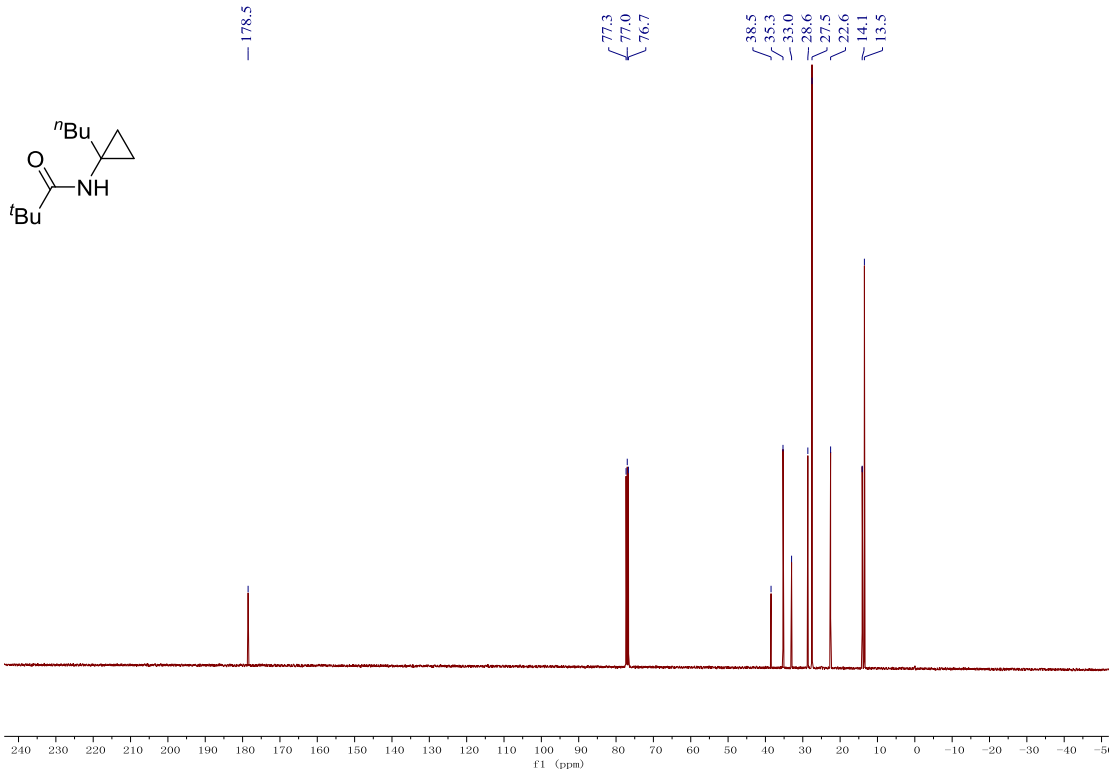

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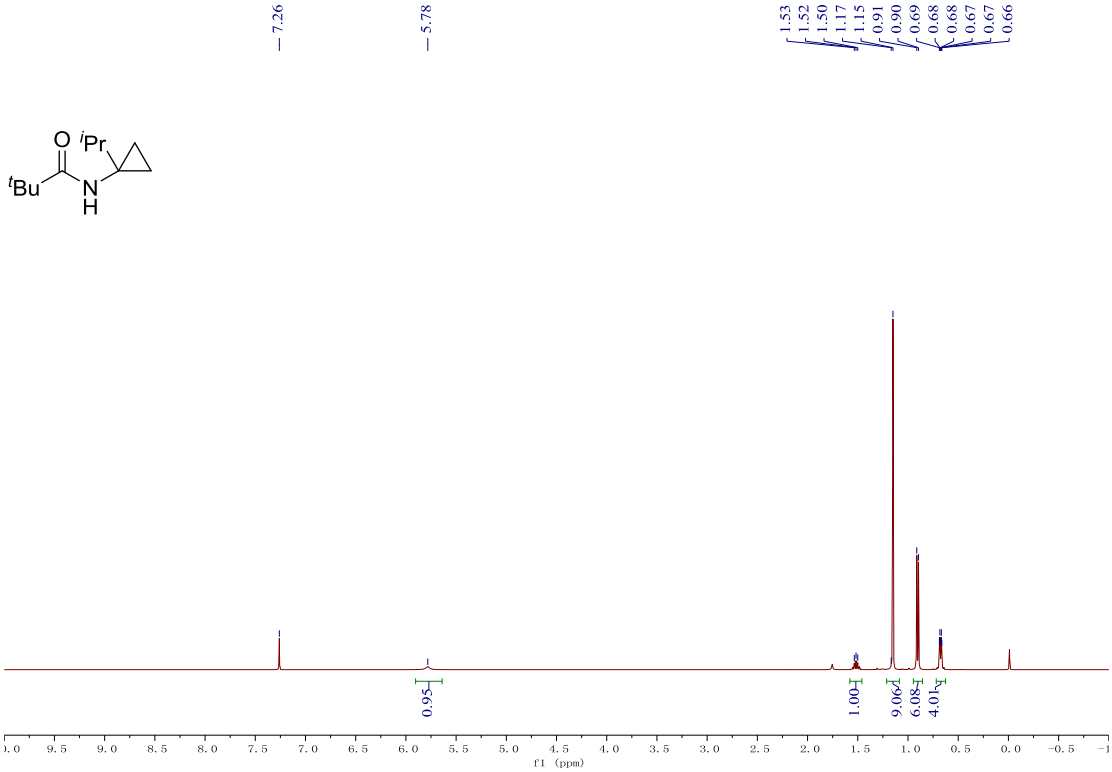

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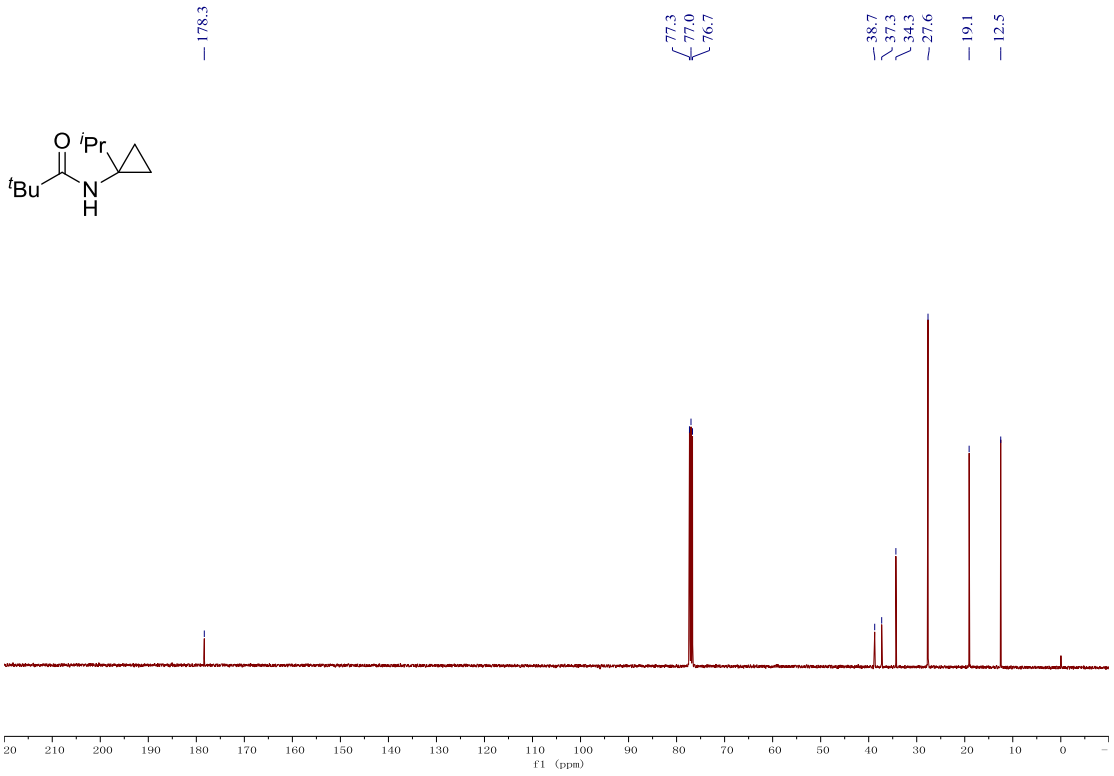

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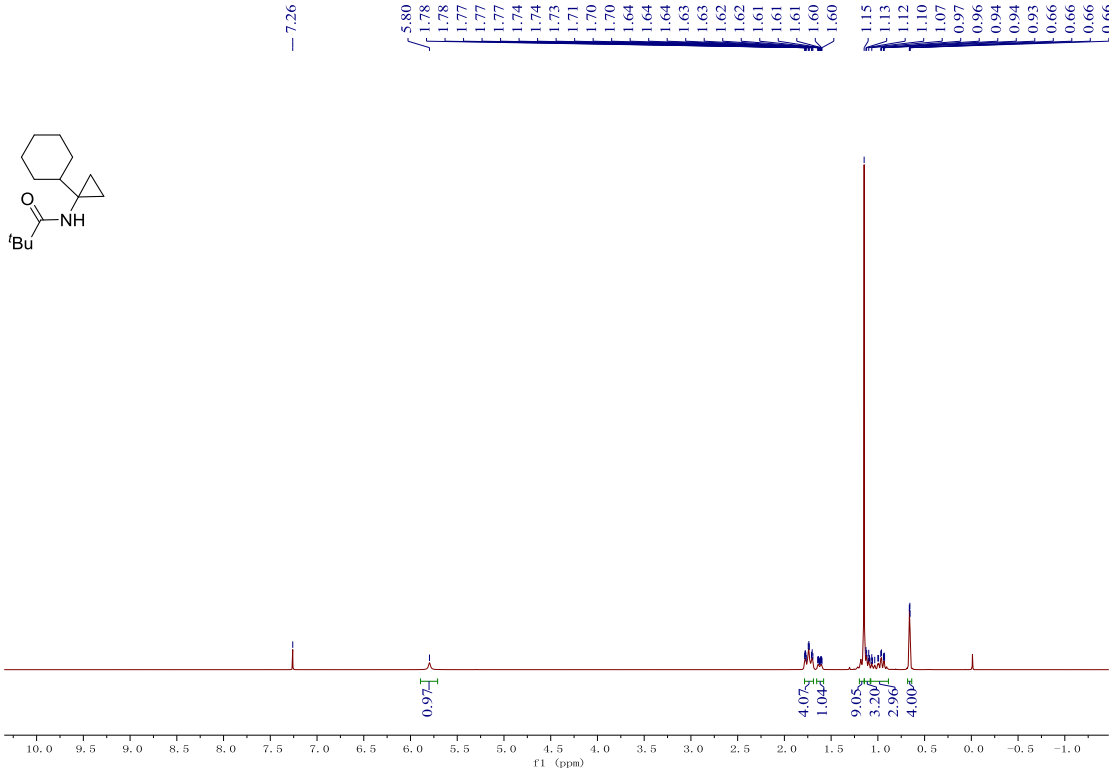

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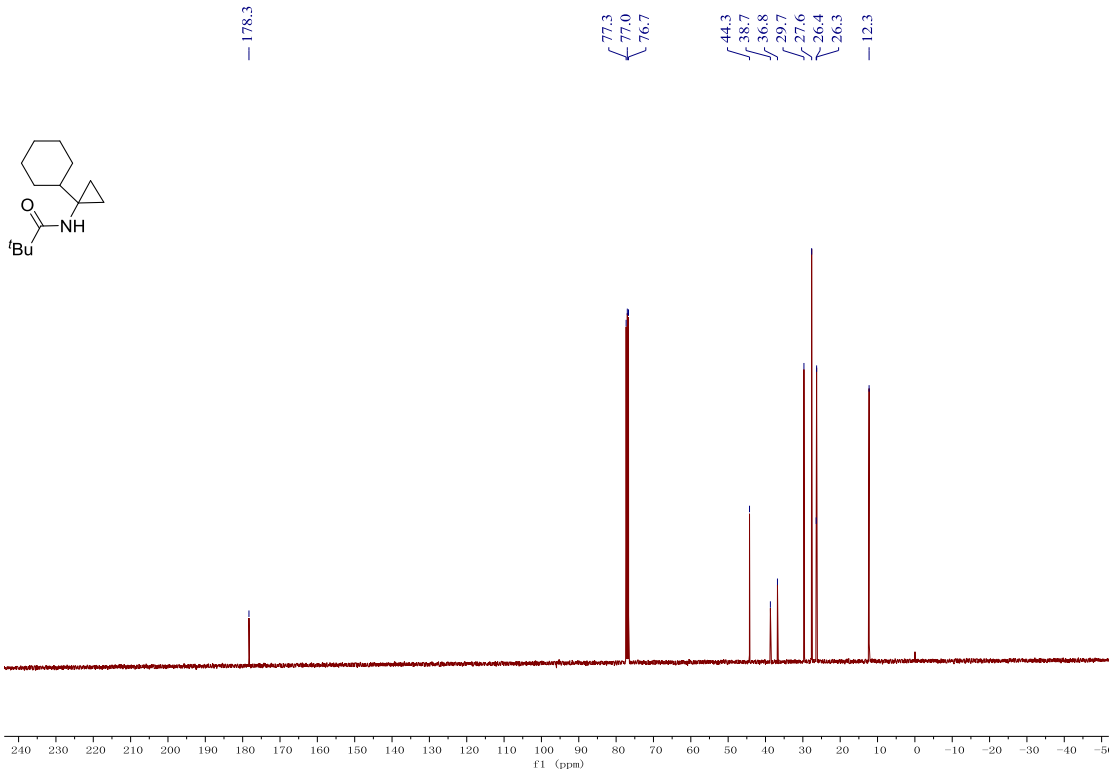

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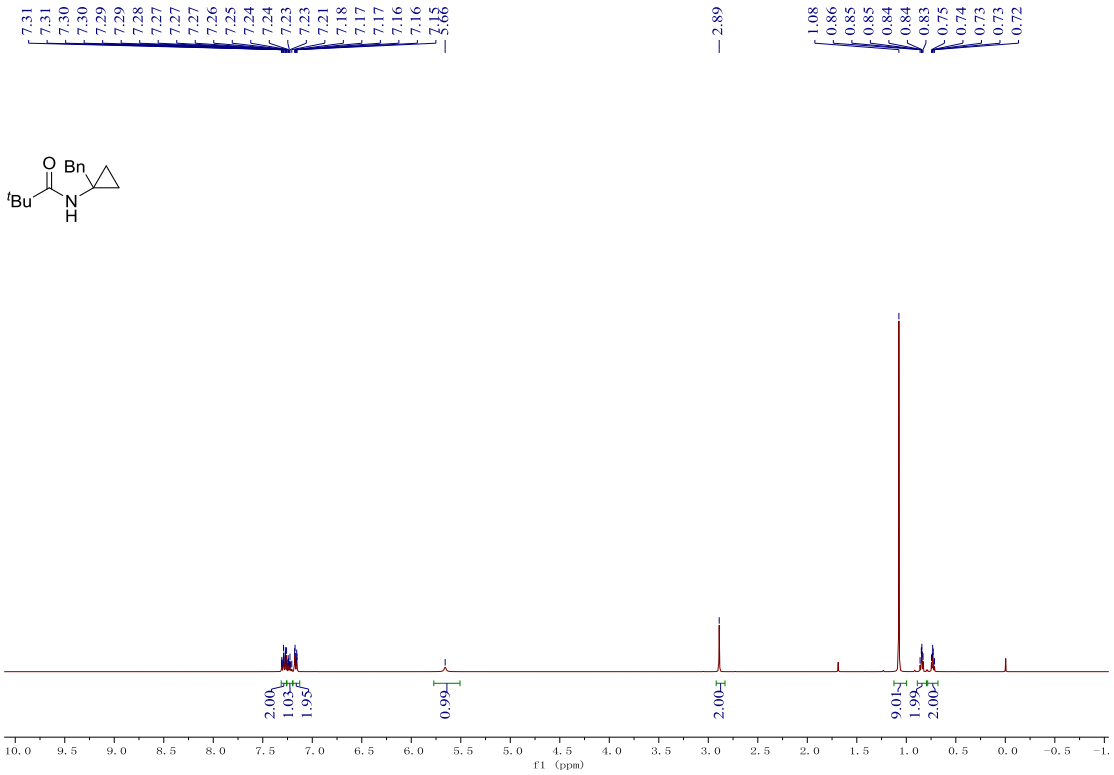

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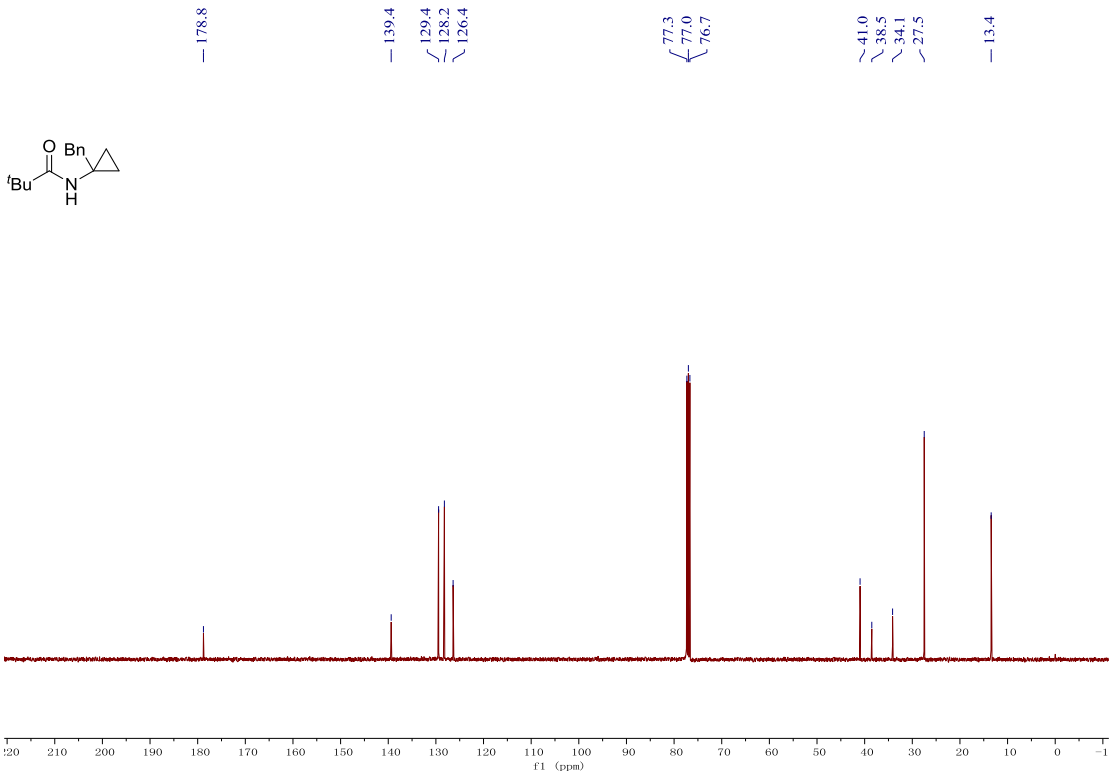

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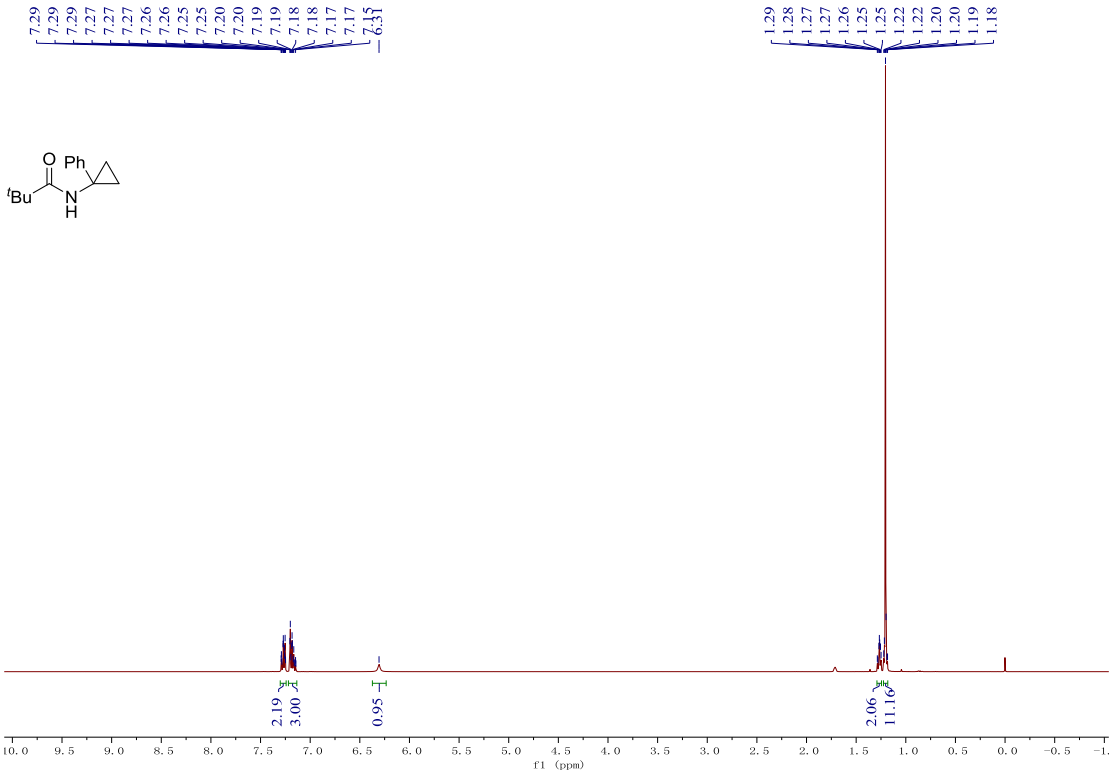

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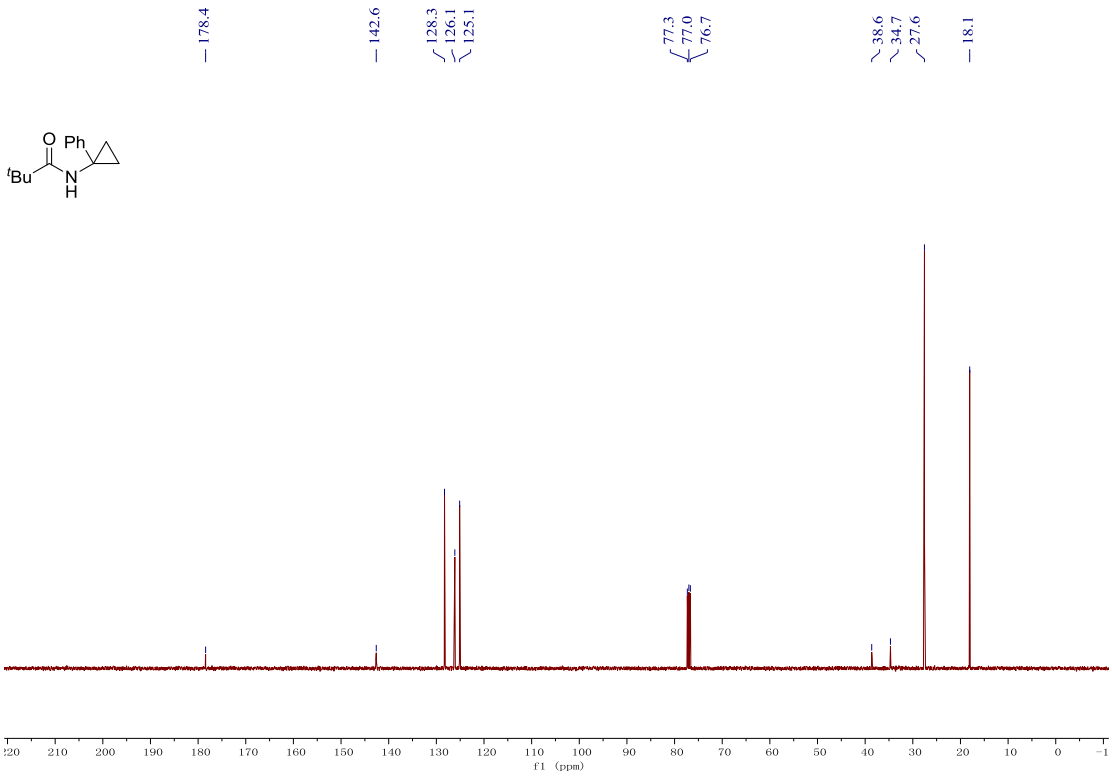

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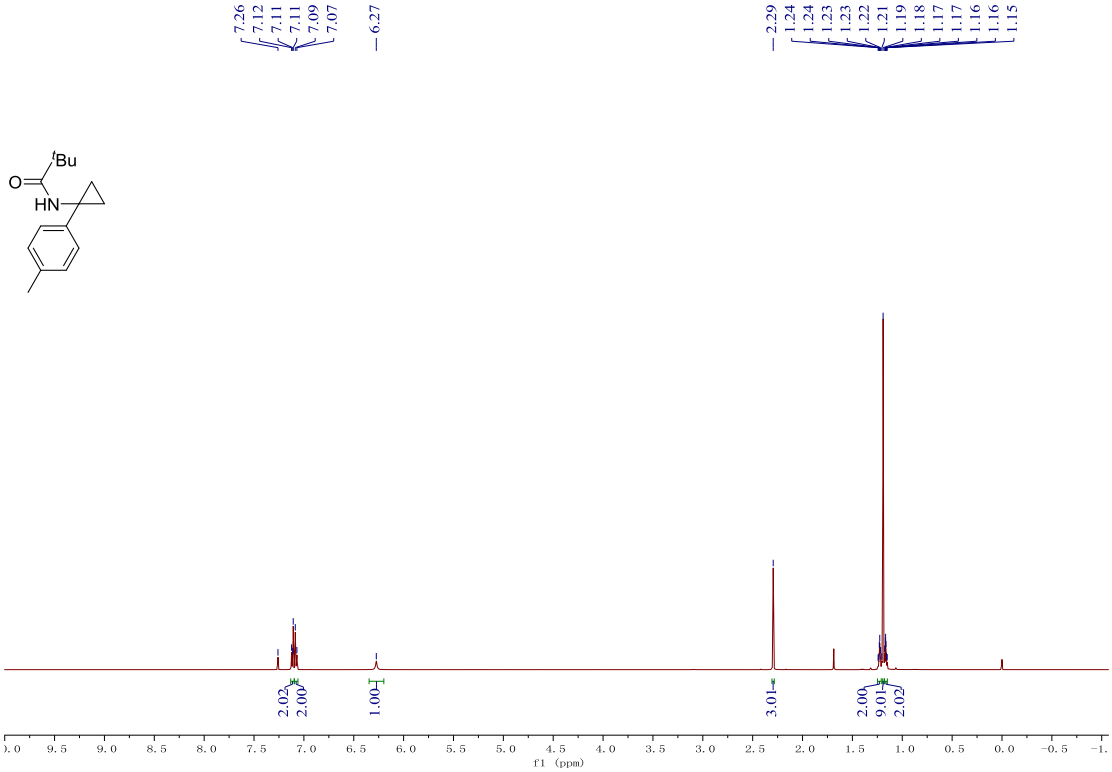

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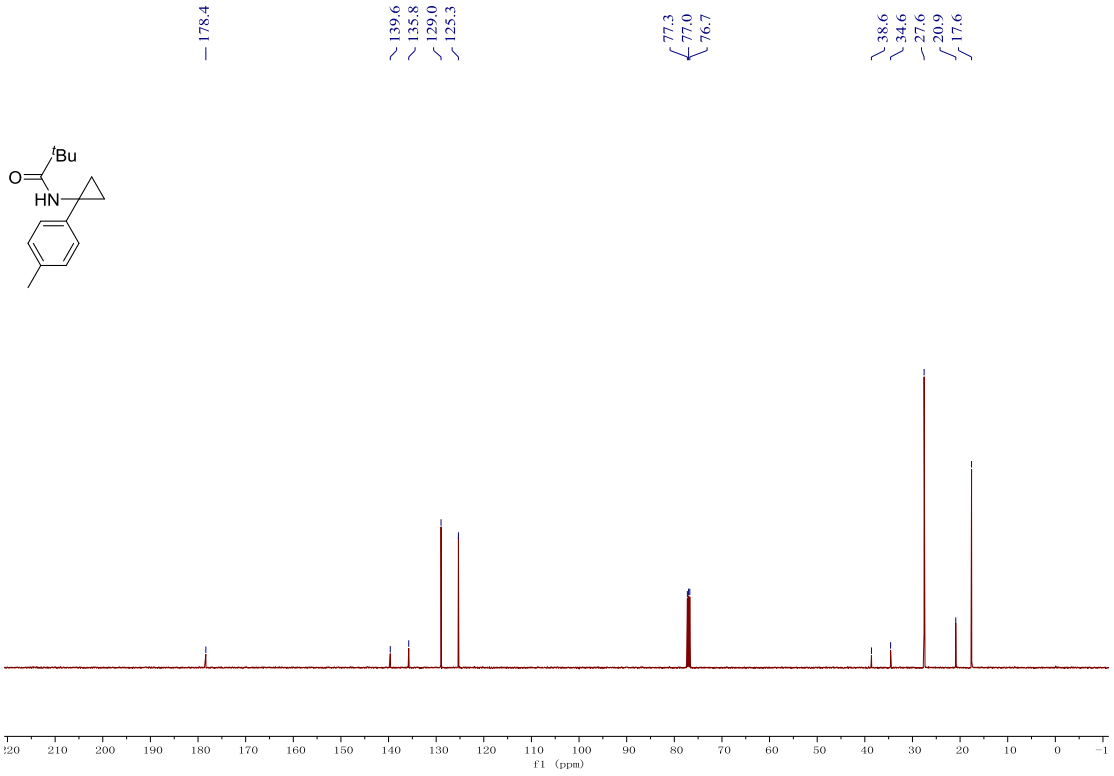

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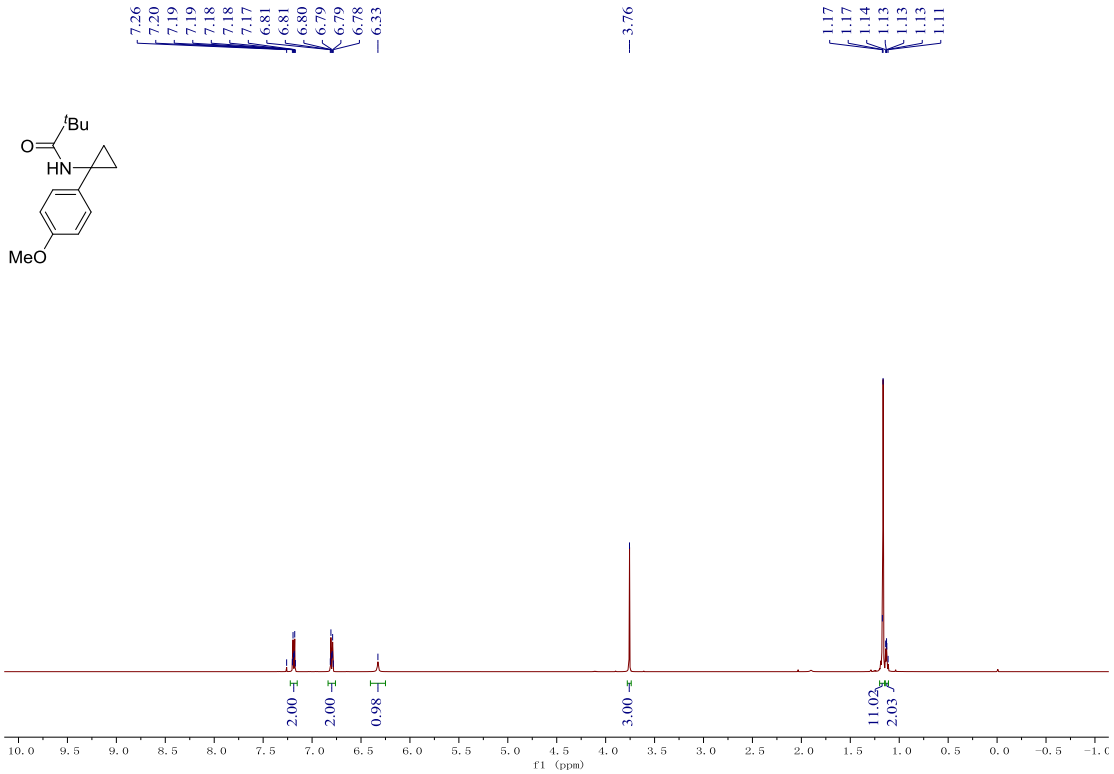

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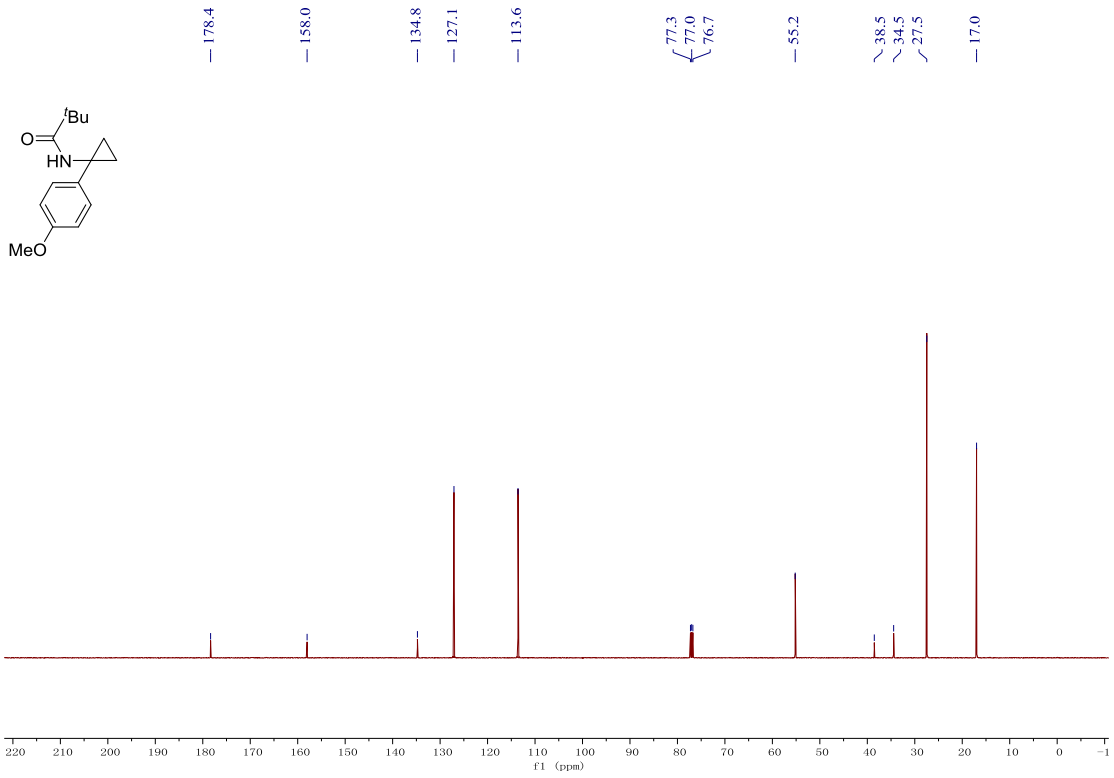

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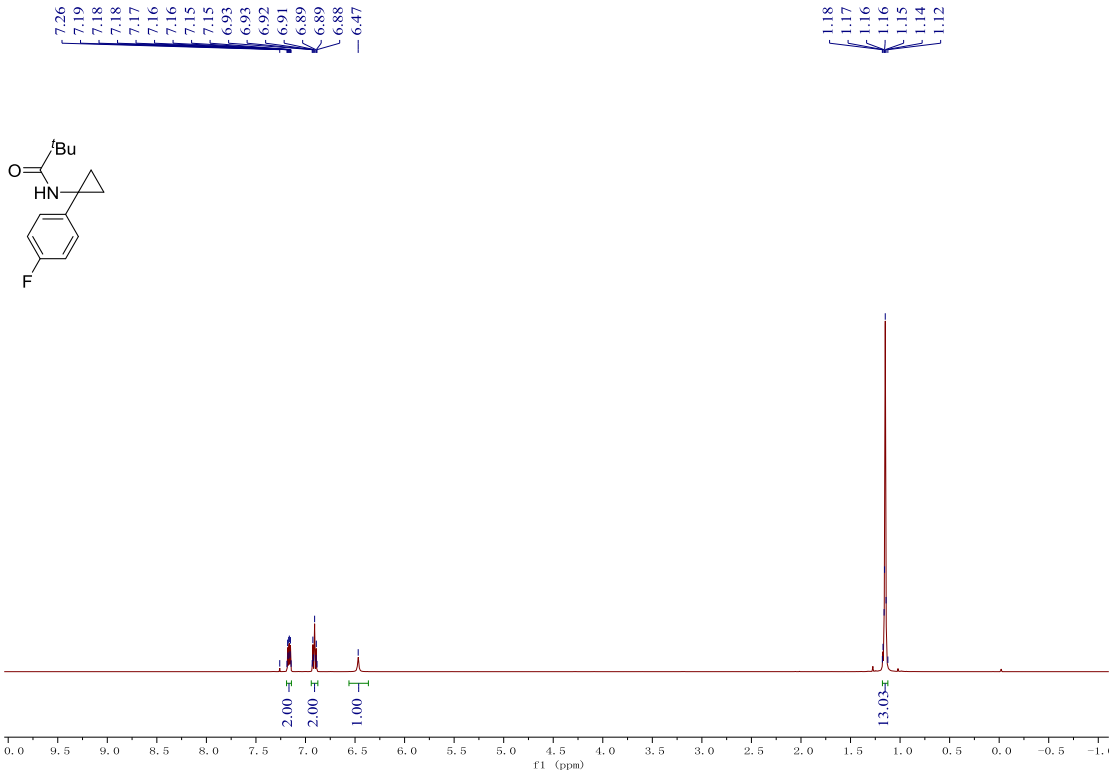

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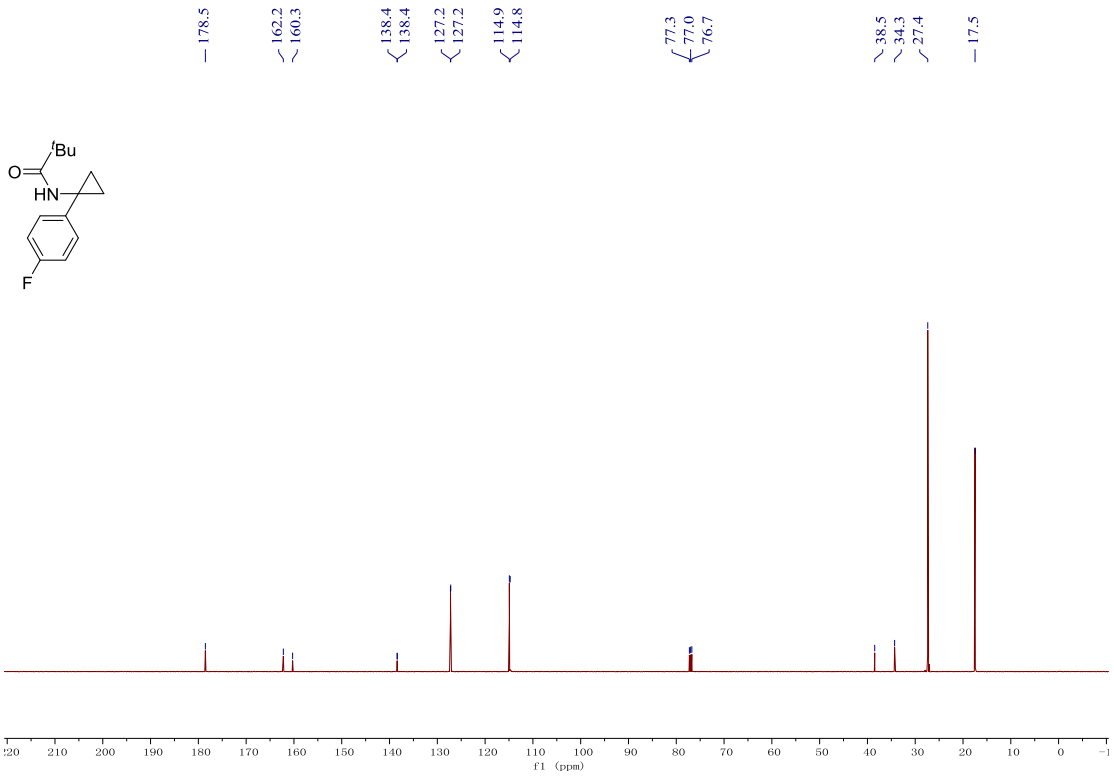
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138.4
127.2
127.2
114.9
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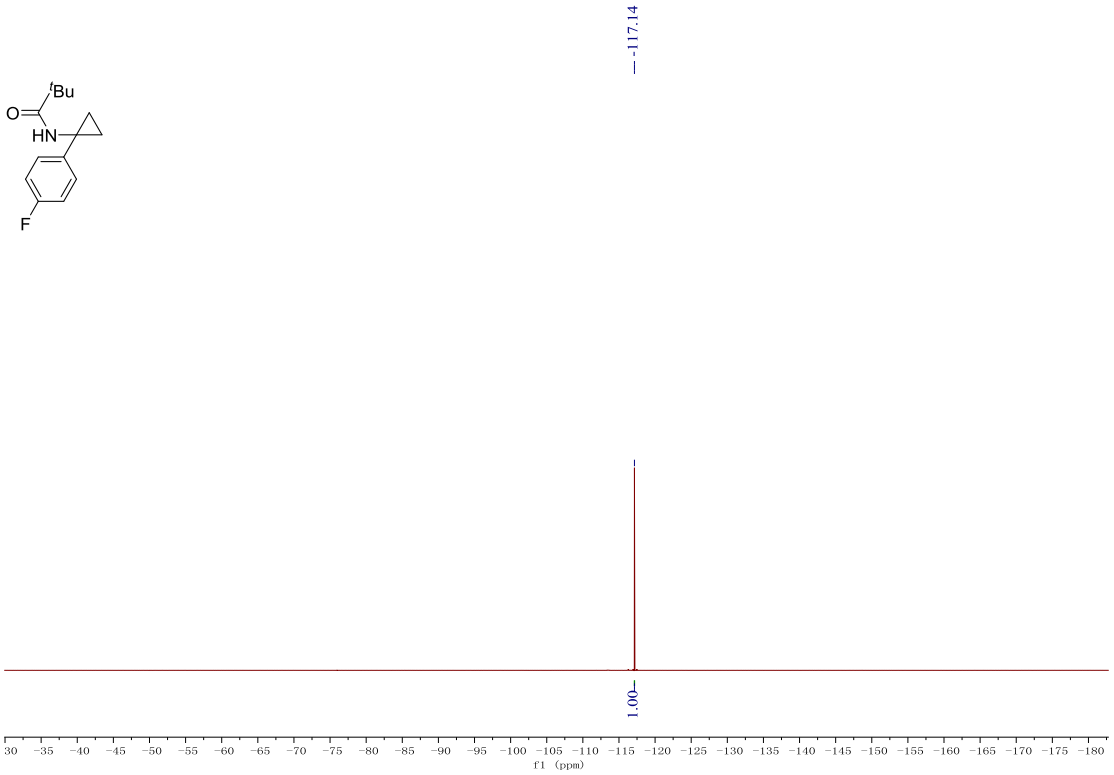
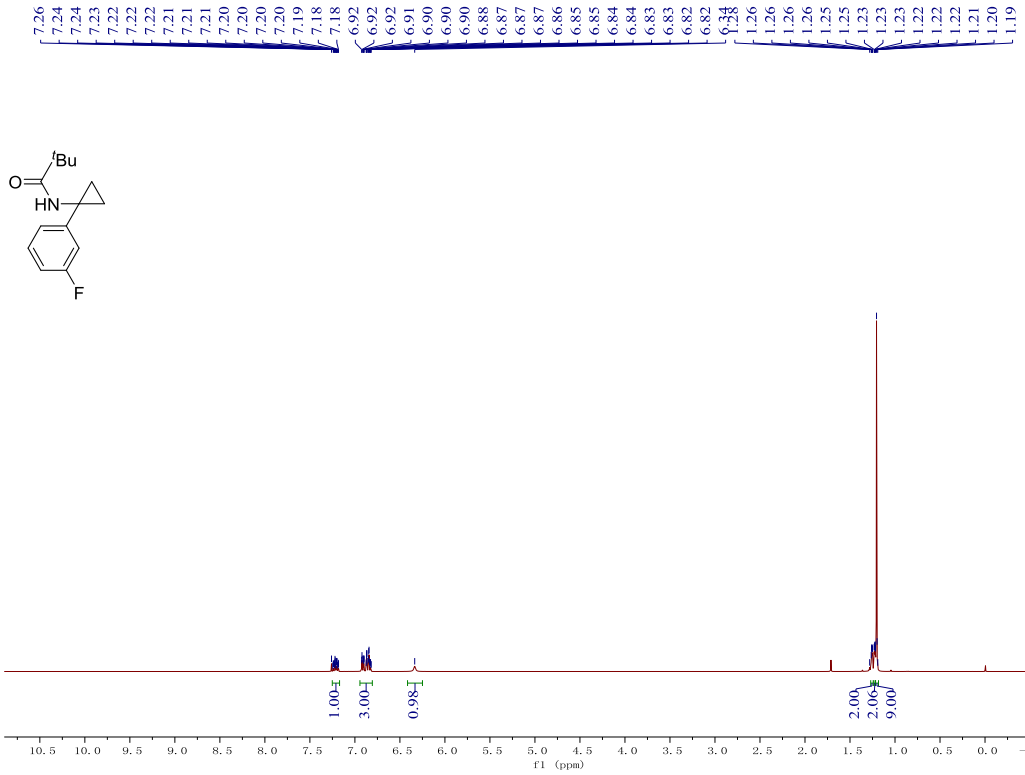
76.7
38.5
34.3
27.4
17.5
tBu
O
HN
F
f1 (ppm)

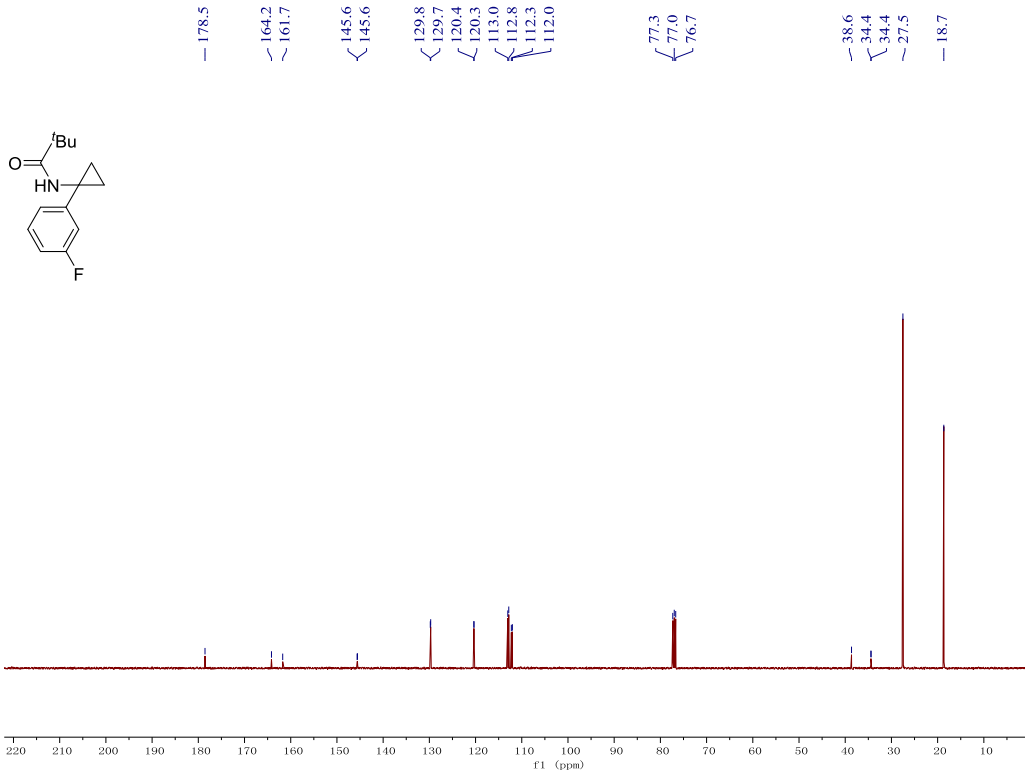
^{19}F NMR of 1j


-117.14
tBu
O
HN
F
1.00
f1 (ppm)

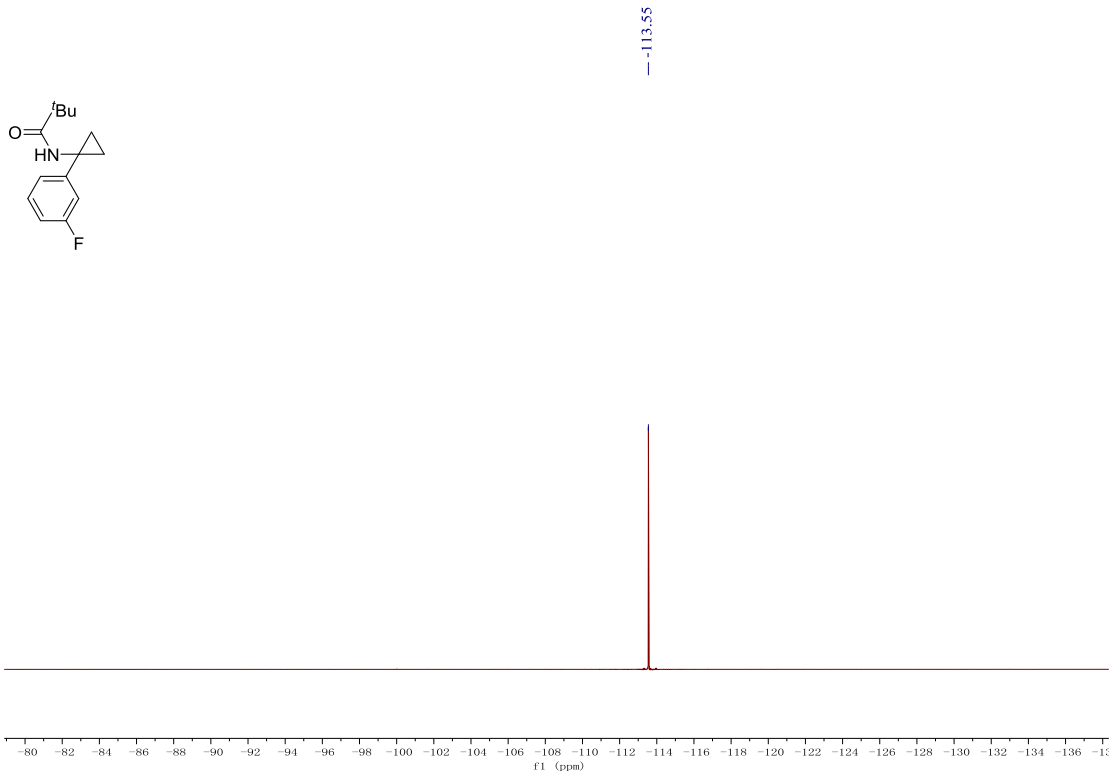
^{1}H NMR of 1k



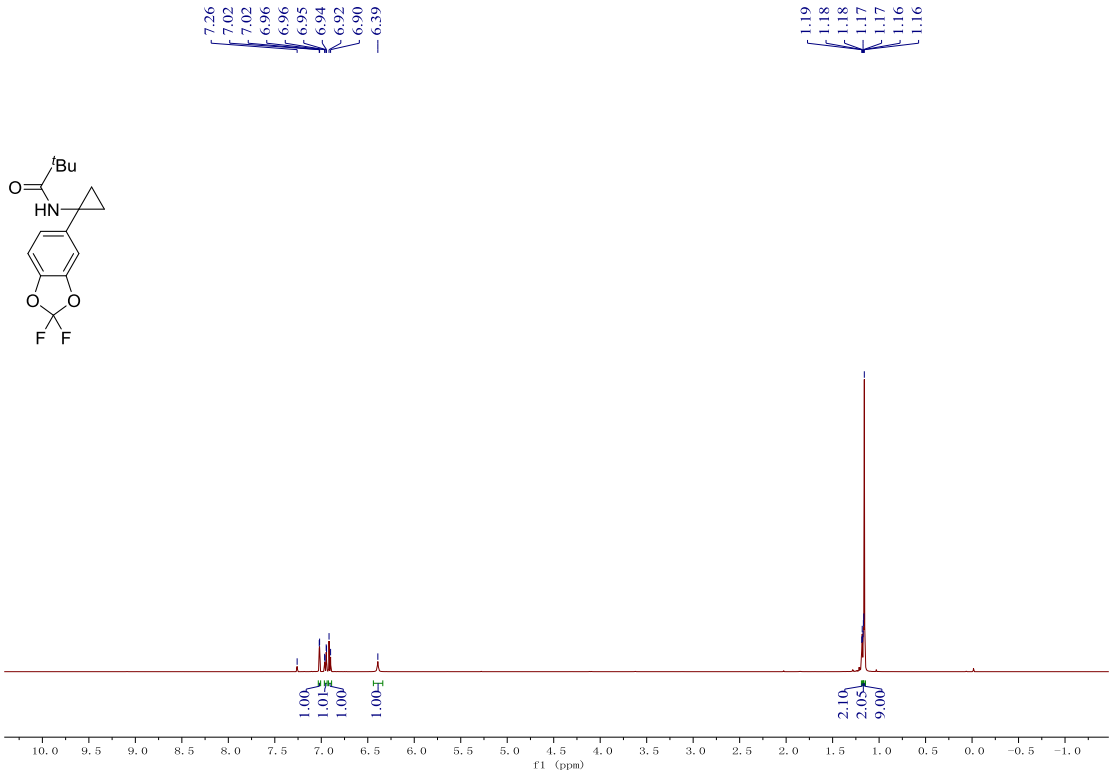
^{13}C NMR of 1k



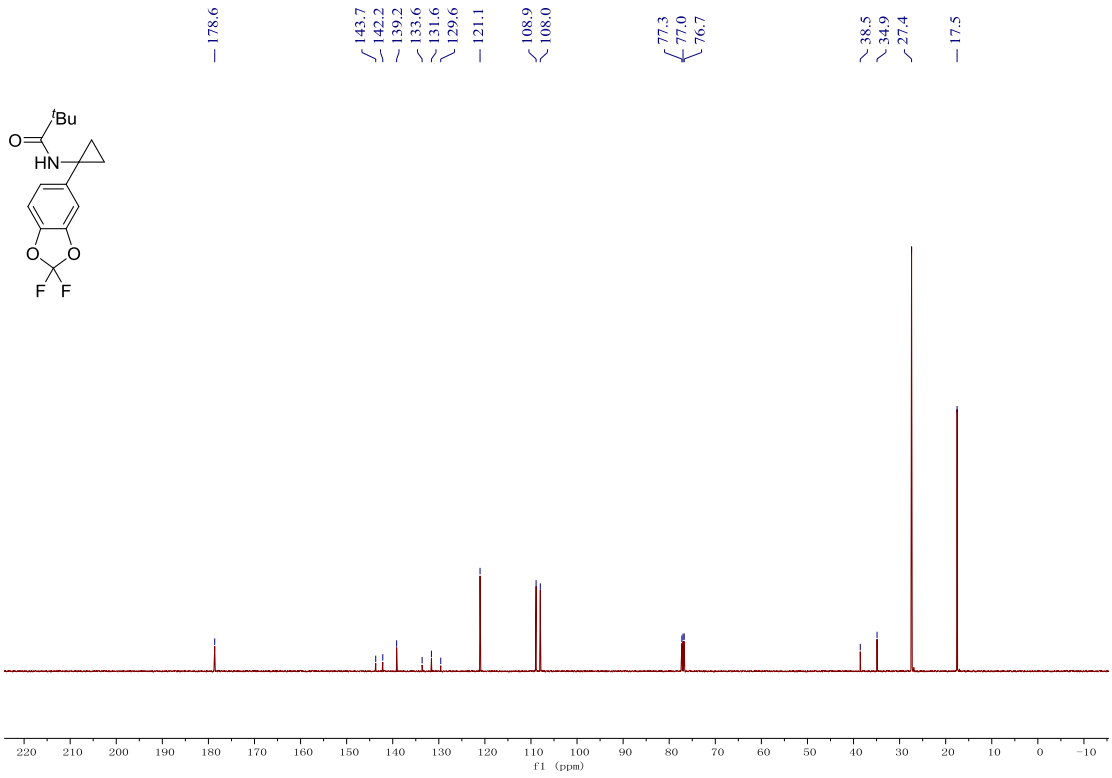
^{19}F NMR of 1k



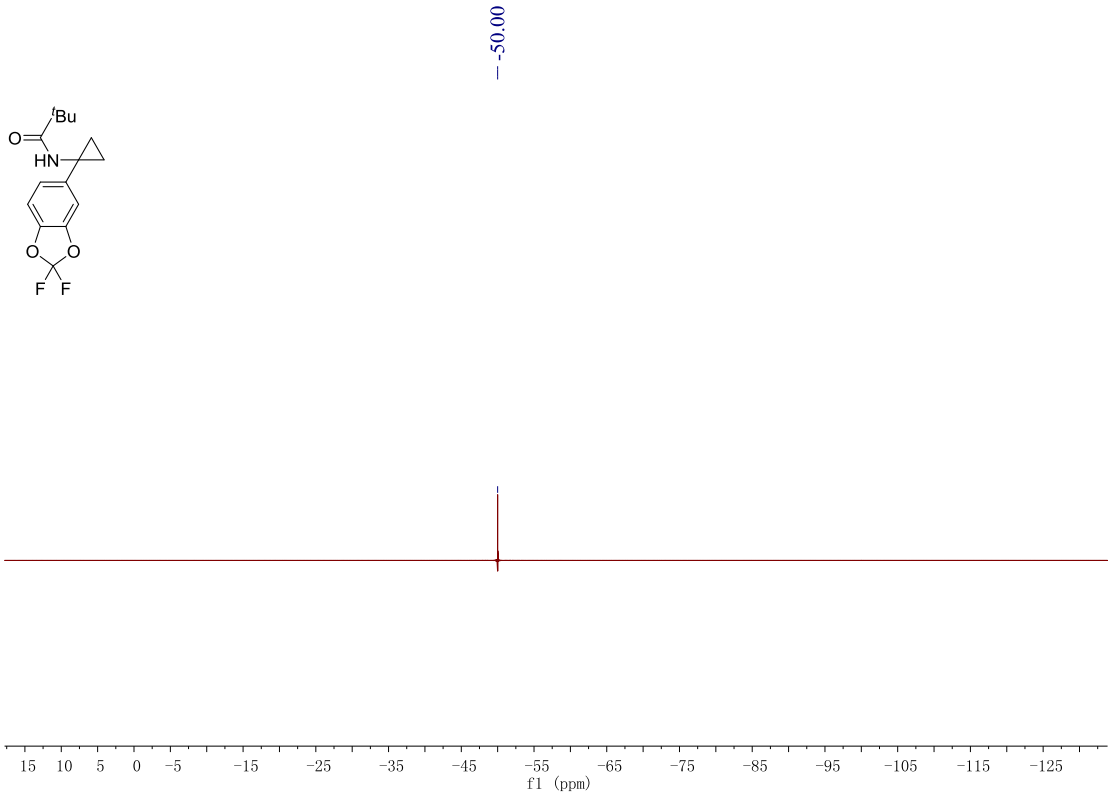
^{1}H NMR of 1l



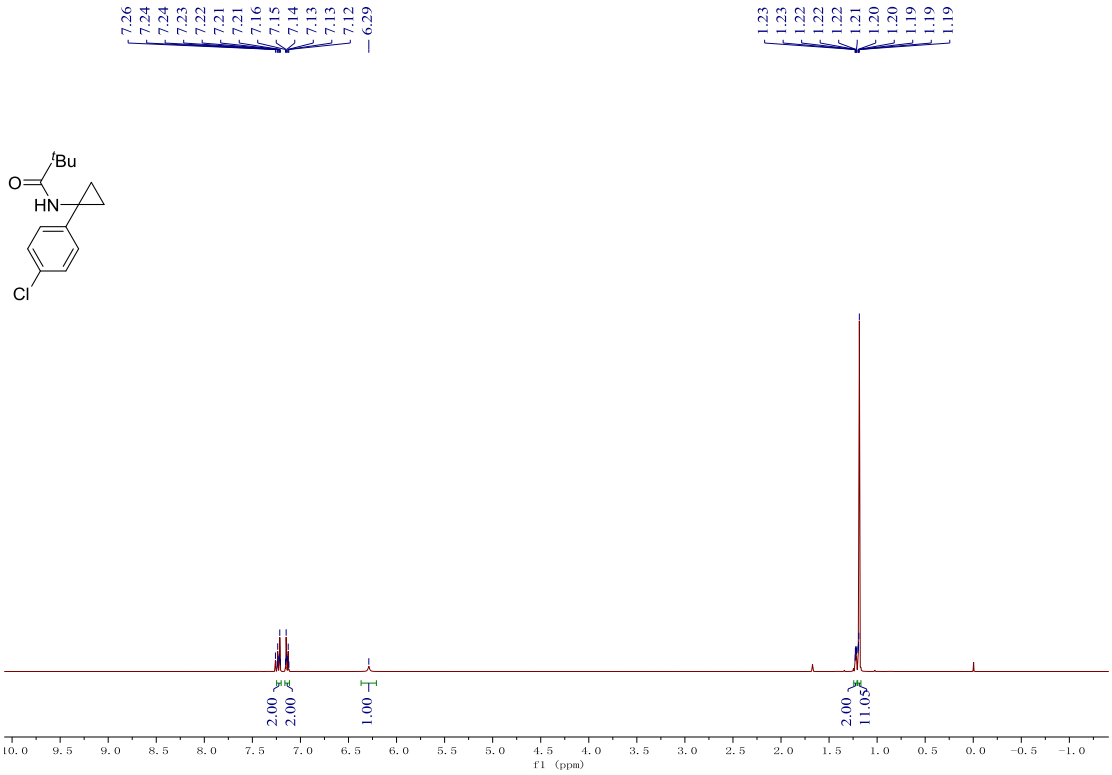
^{13}C NMR of 1l


178.6
143.7
142.2
139.2
133.6
131.6
129.6
121.1
108.9
108.0
77.3
77.0
76.7
38.5
34.9
27.4
17.5
tBu
O
HN
O
O
F F
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)

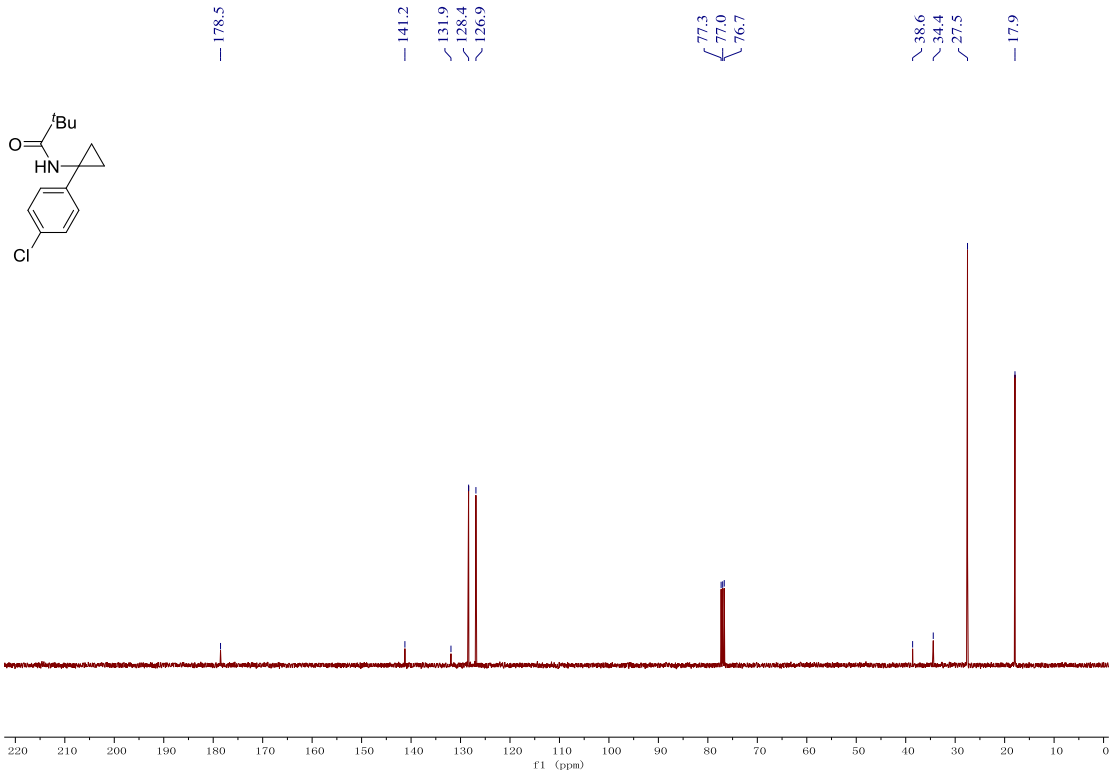
^{19}F NMR of 1l


-50.00
tBu
O
HN
O
O
F F
15 10 5 0 −5 −15 −25 −35 −45 −55 −65 −75 −85 −95 −105 −115 −125
f1 (ppm)

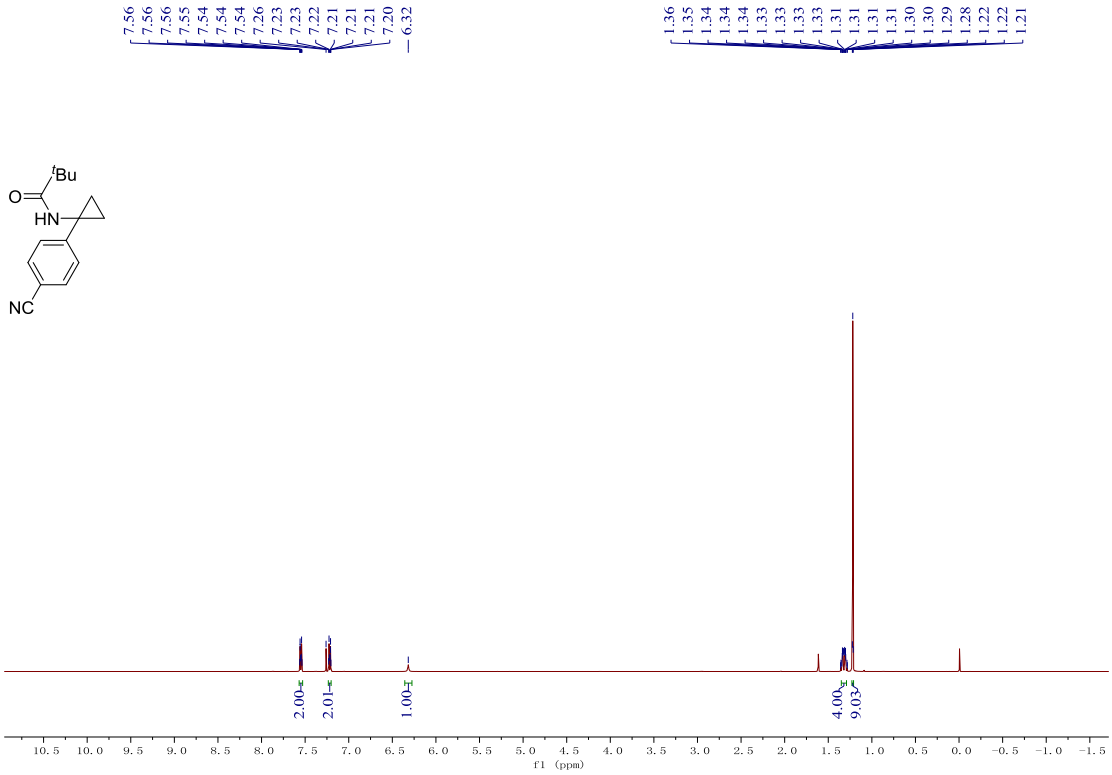
^{1}H NMR of 1m



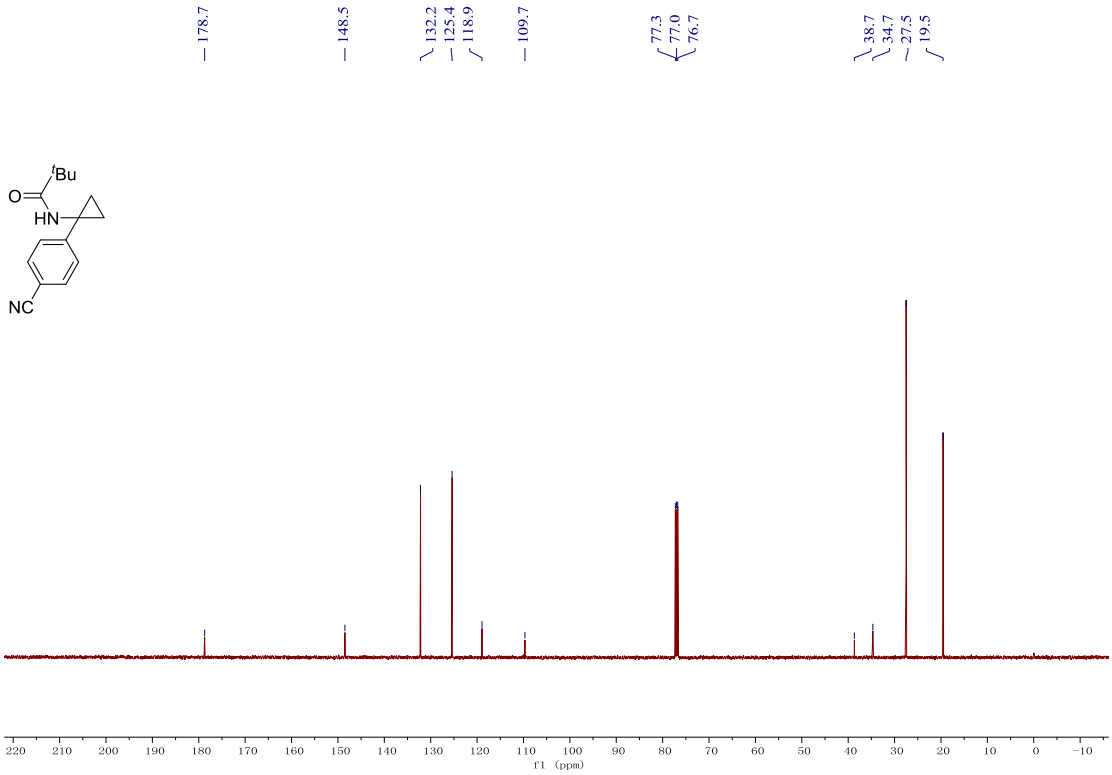
^{13}C NMR of 1m



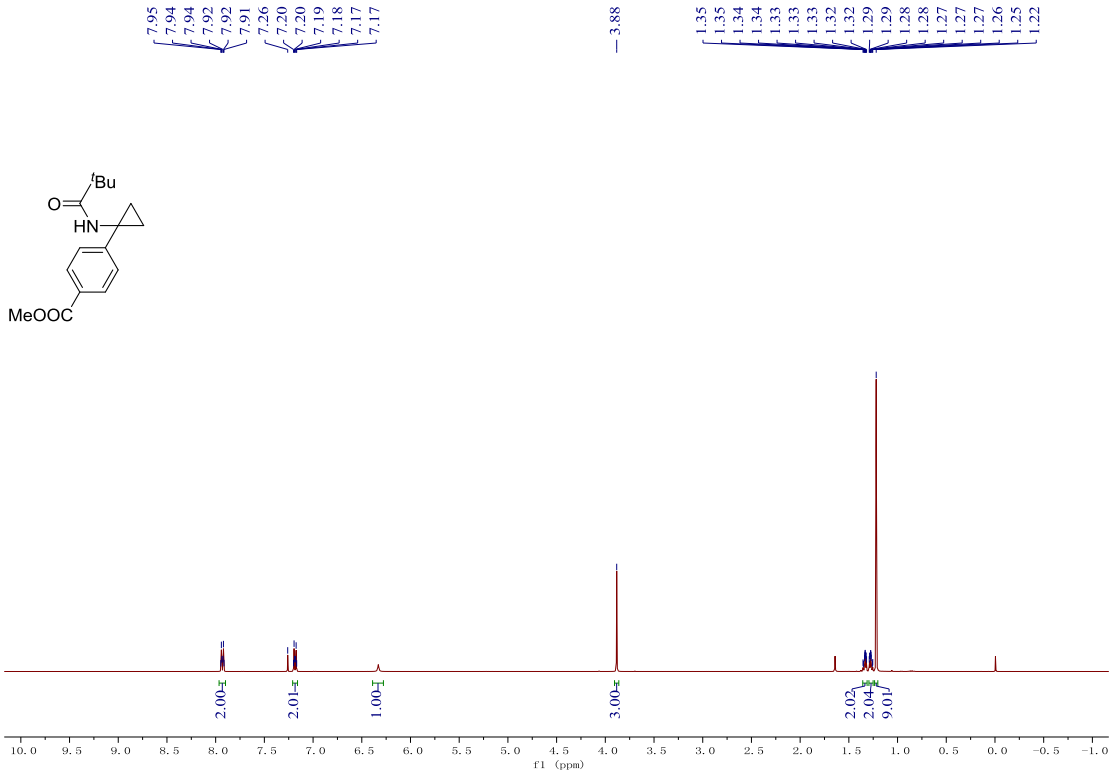
^{1}H NMR of 1n



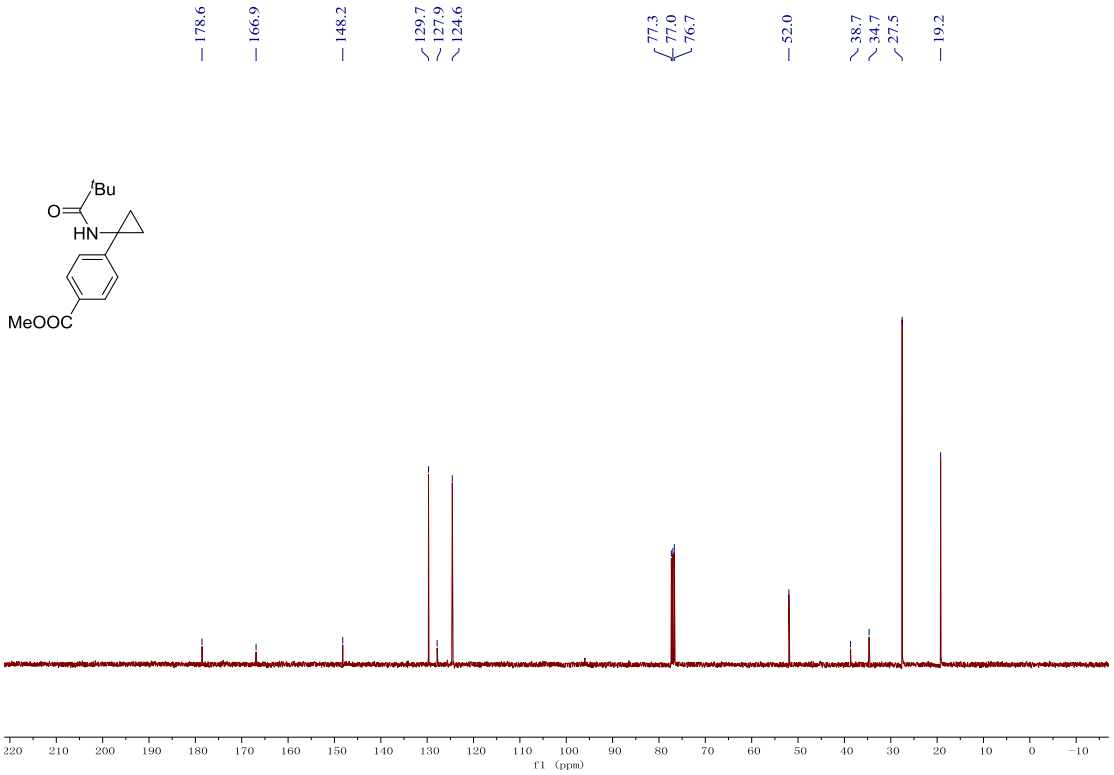
^{13}C NMR of 1n



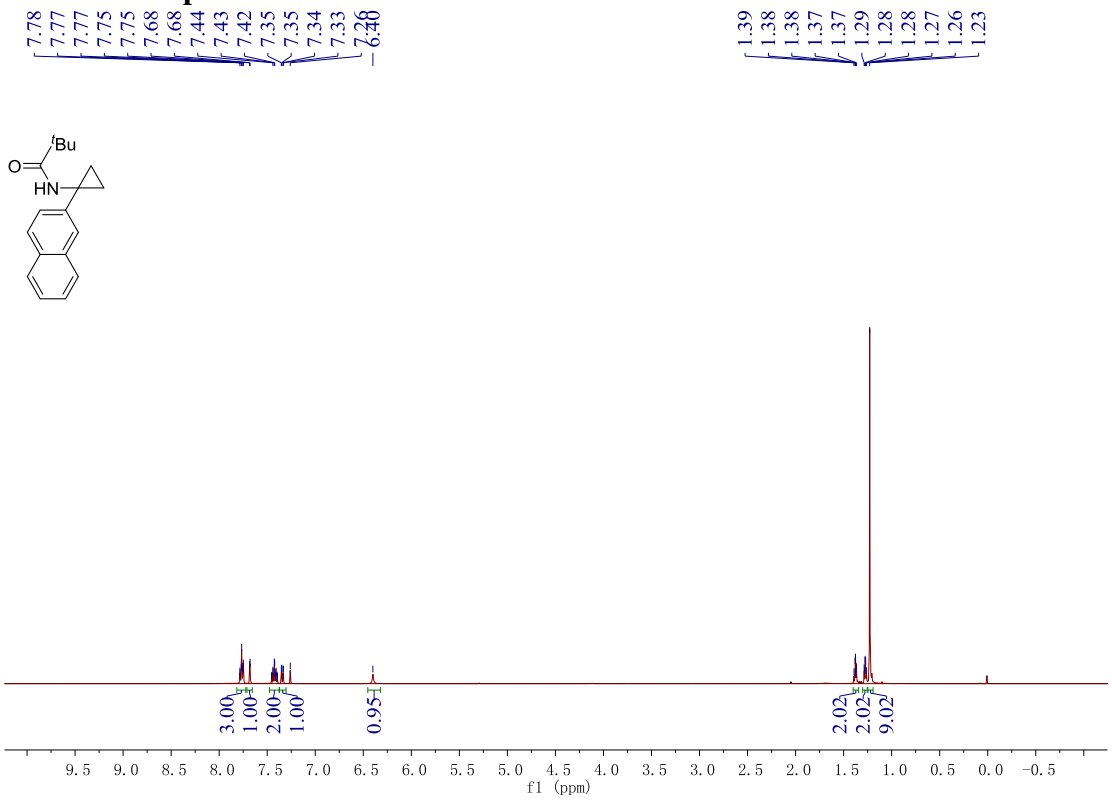
^{1}H NMR of 1o



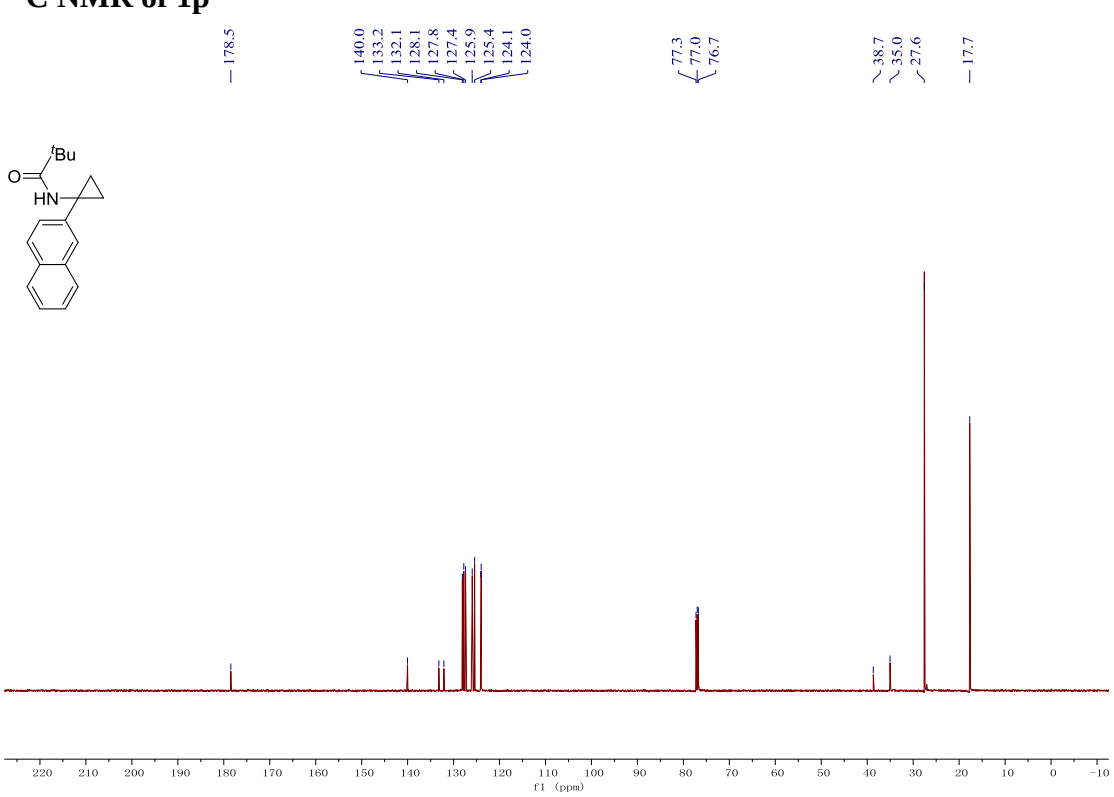
^{13}C NMR of 1o



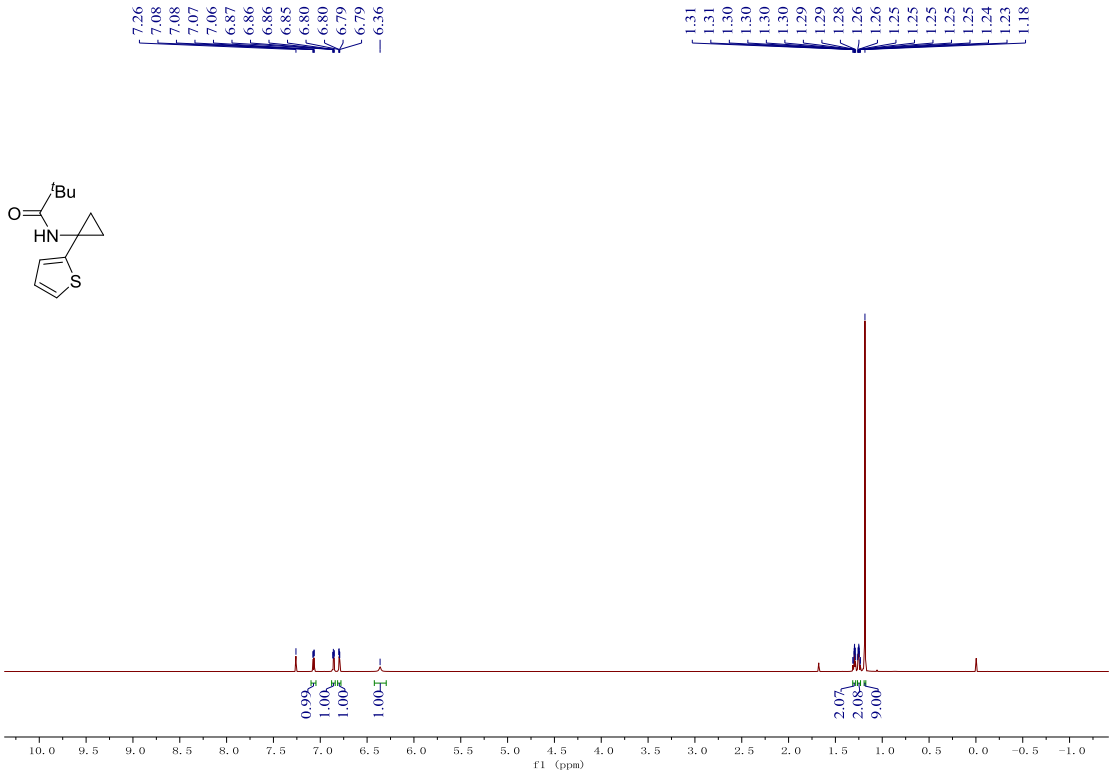
^{1}H NMR of 1p



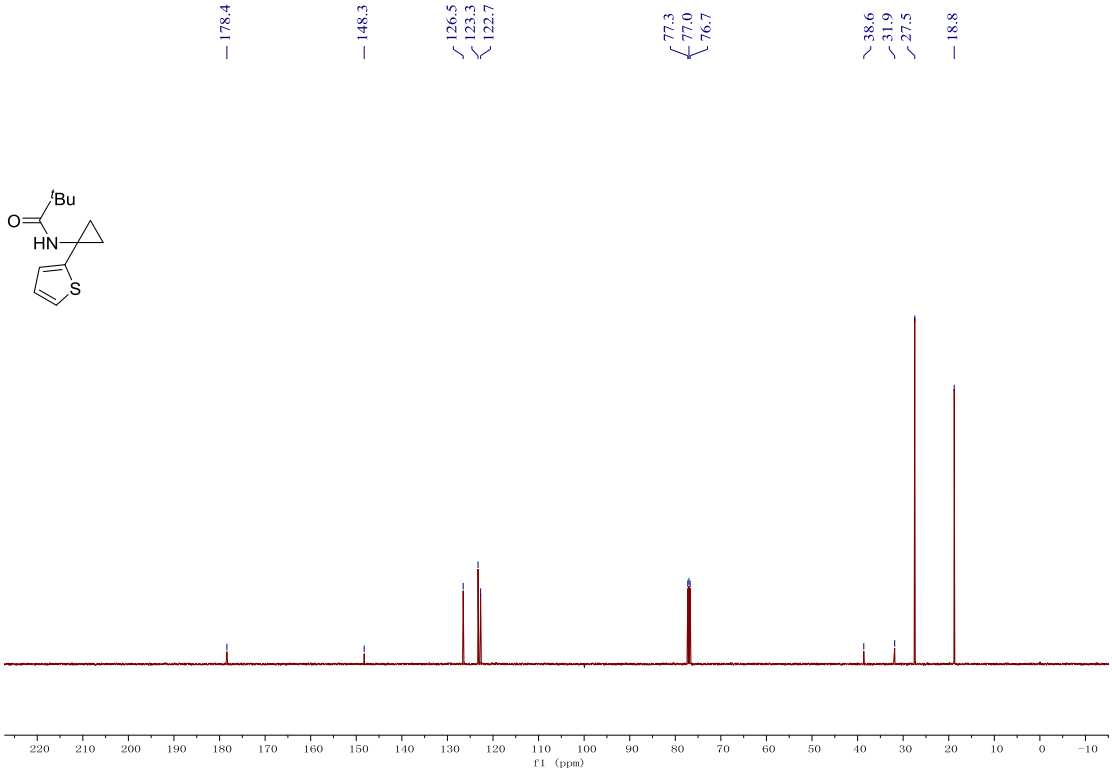
^{13}C NMR of 1p



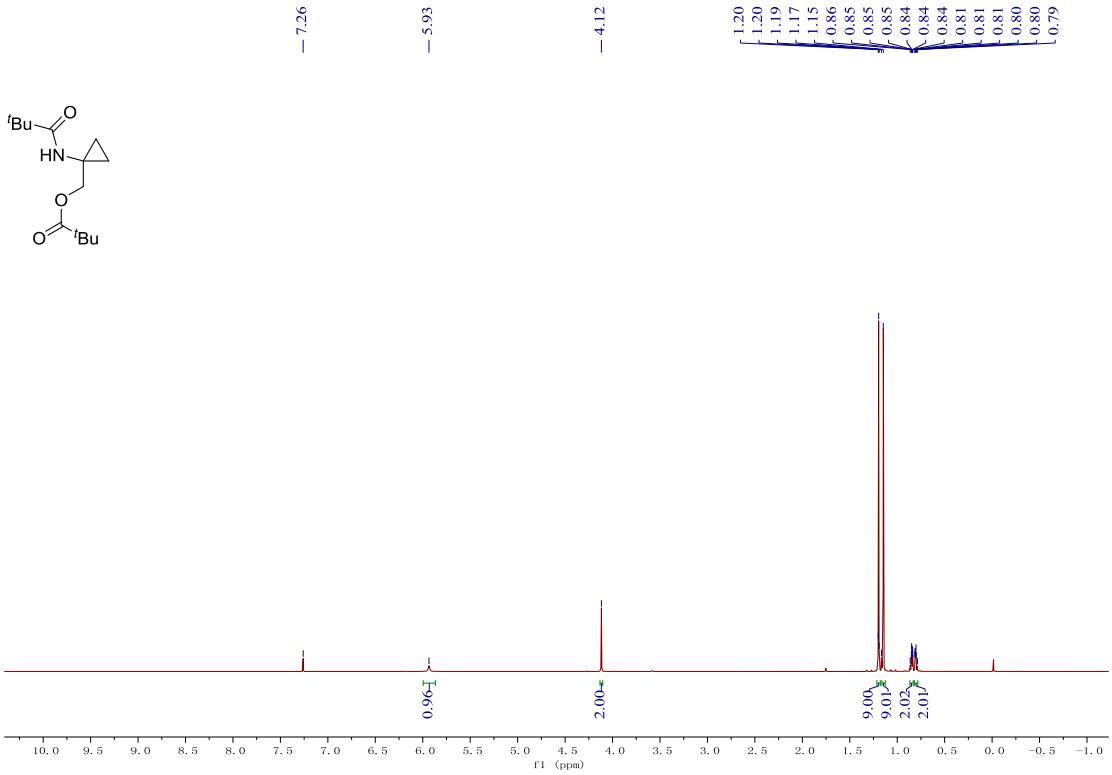
^{1}H NMR of 1q



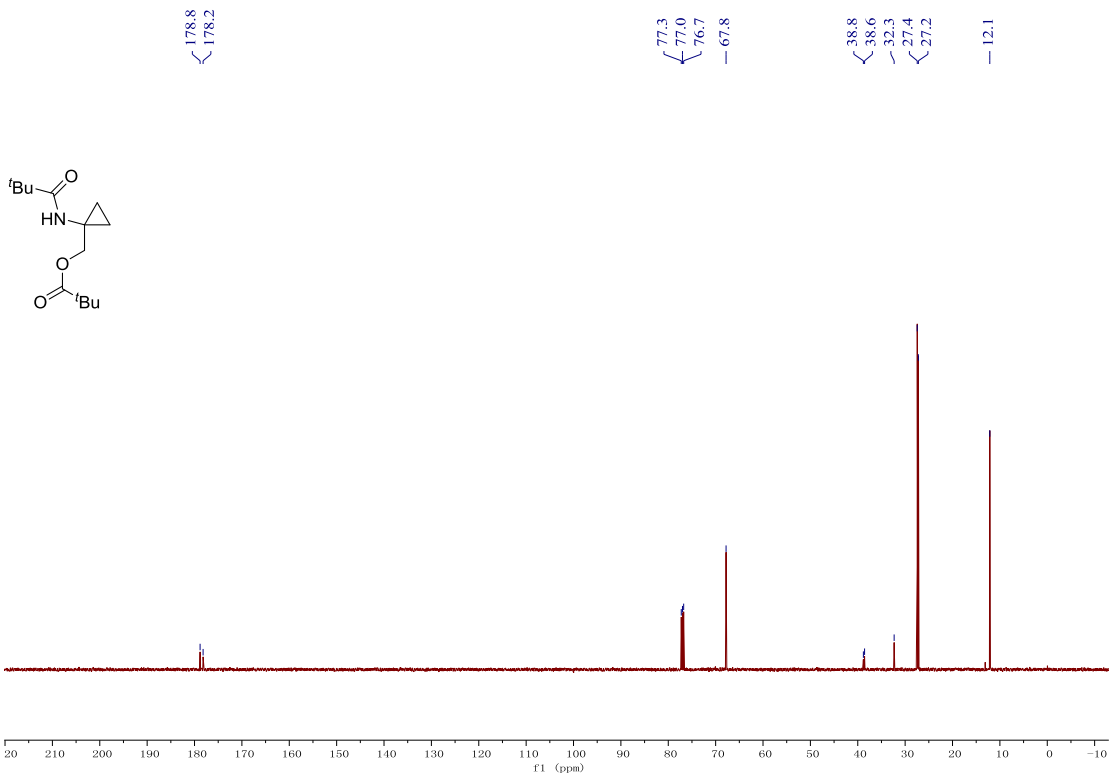
^{13}C NMR of 1q



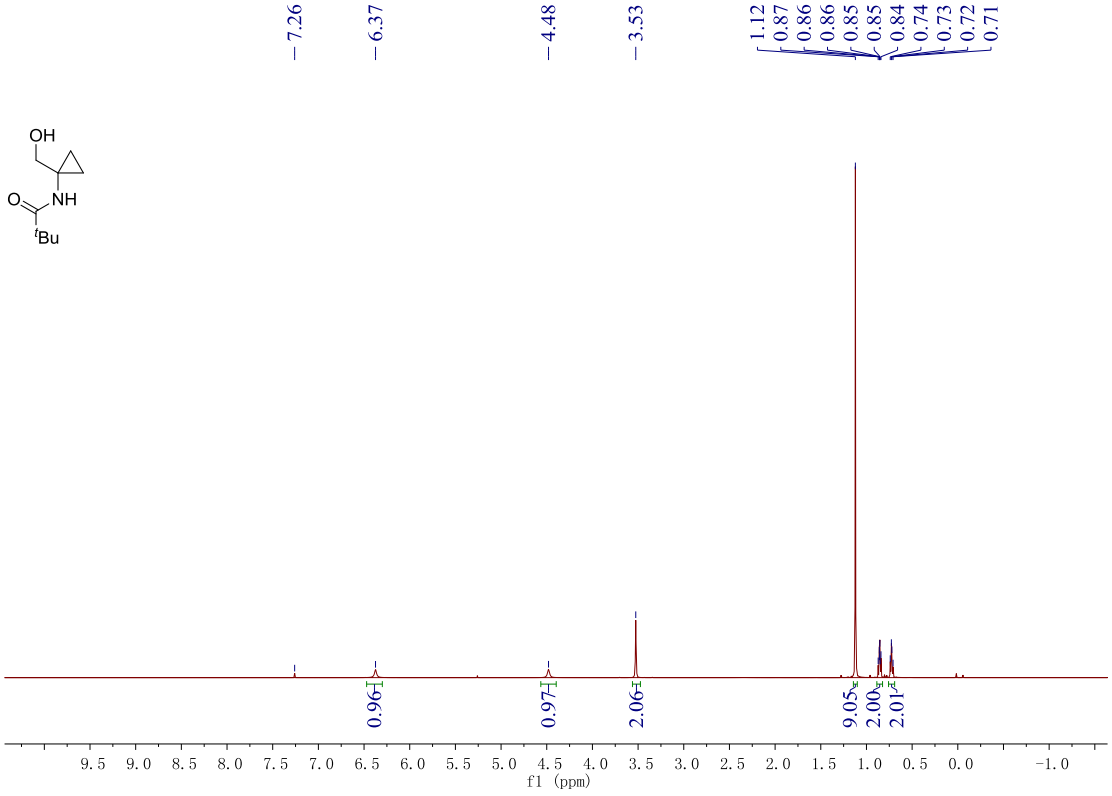
^{1}H NMR of 1r



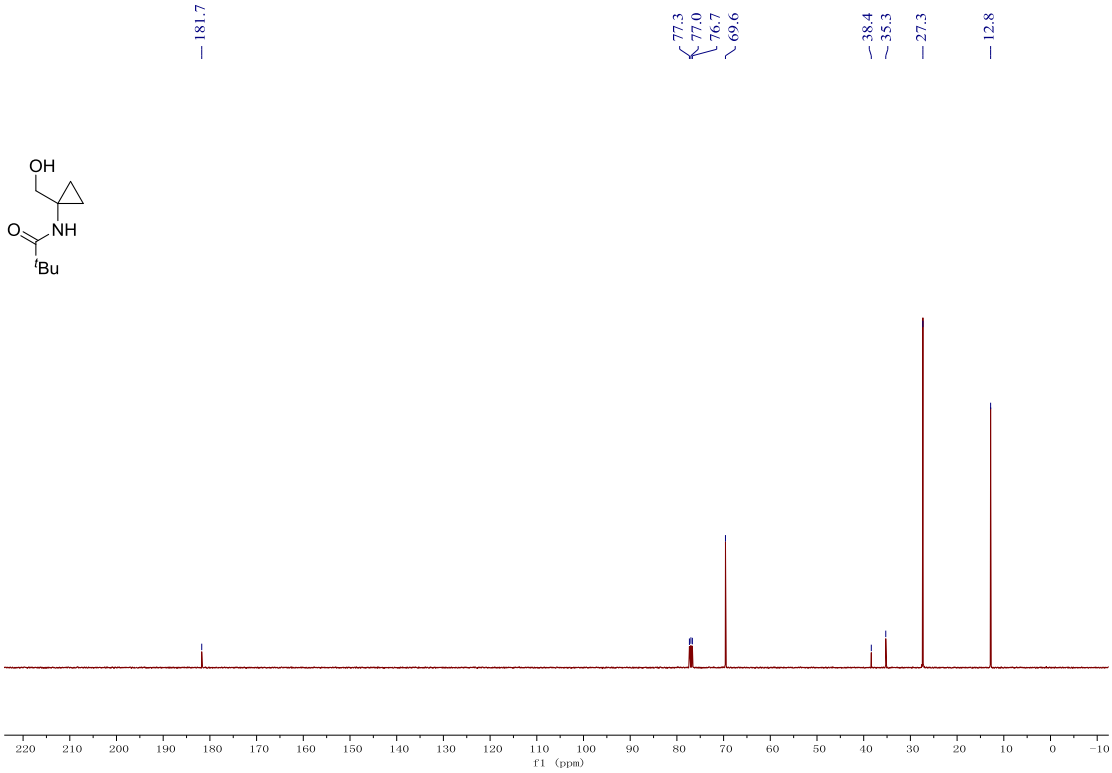
^{13}C NMR of 1r



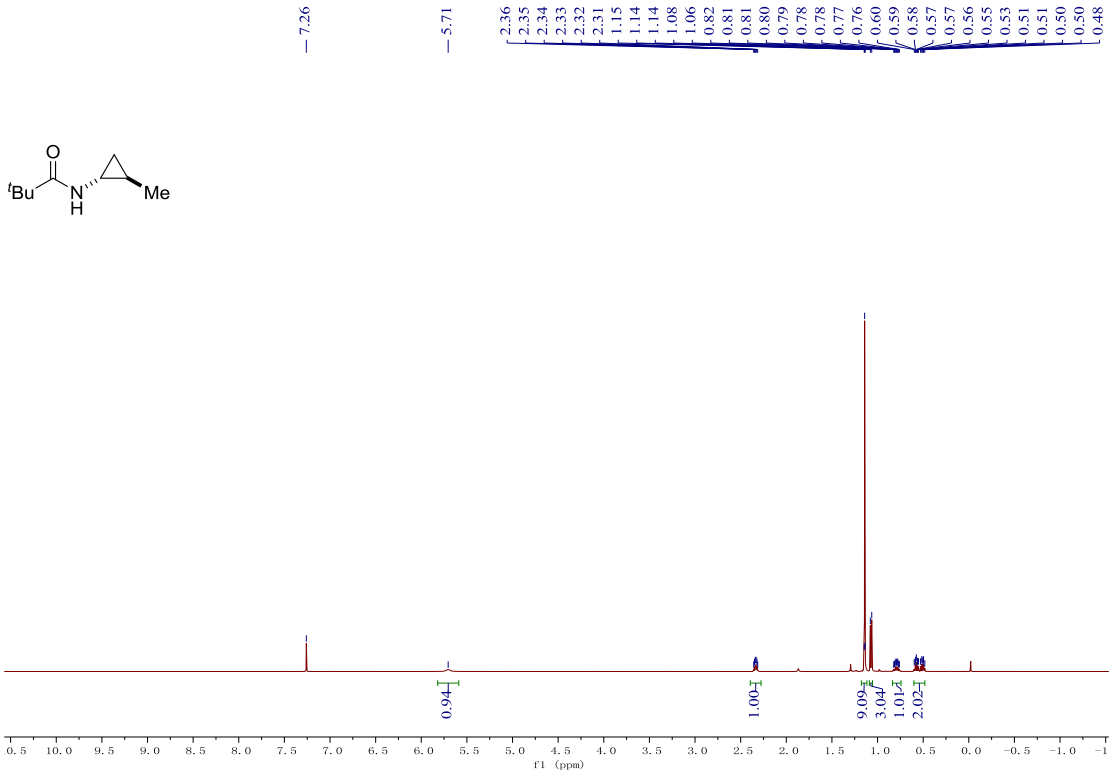
^{1}H NMR of 1s



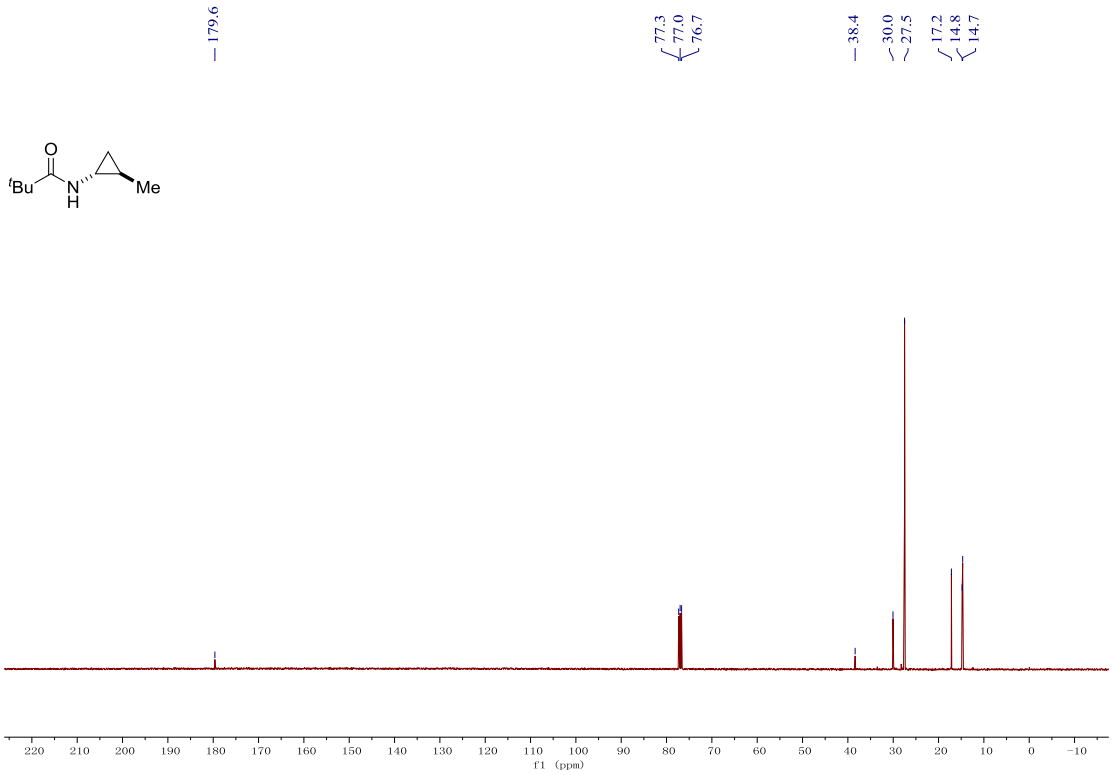
^{13}C NMR of 1s



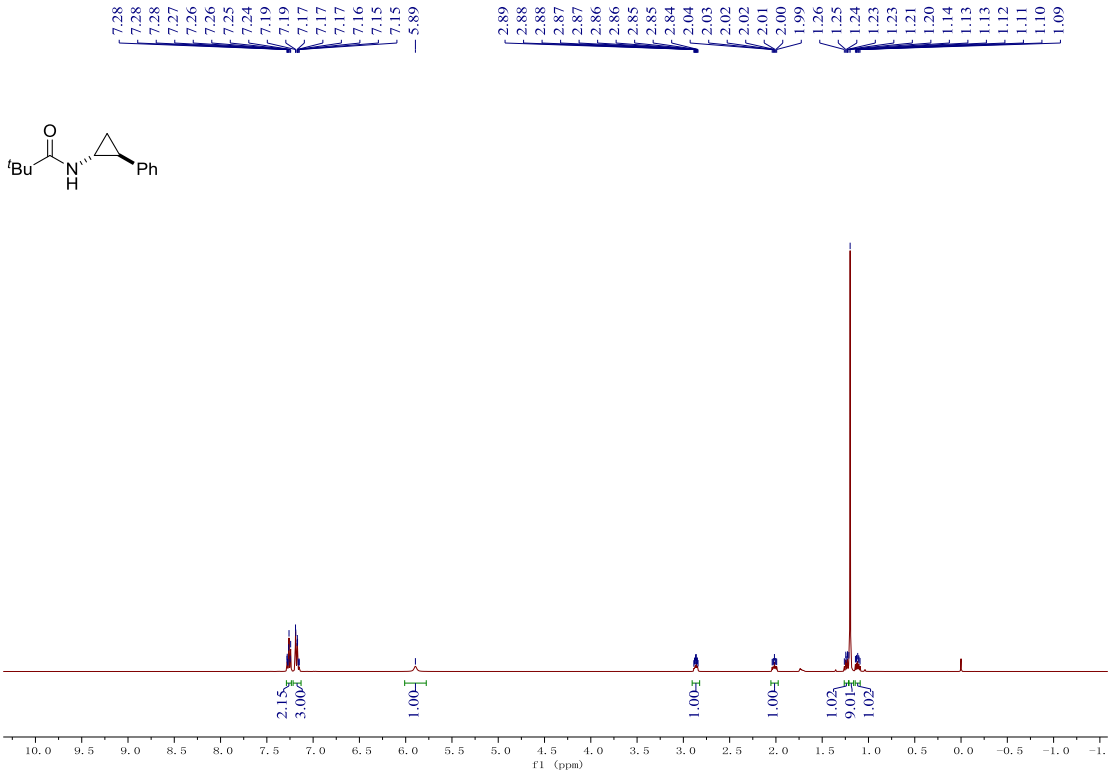
^{1}H NMR of Trans-1t



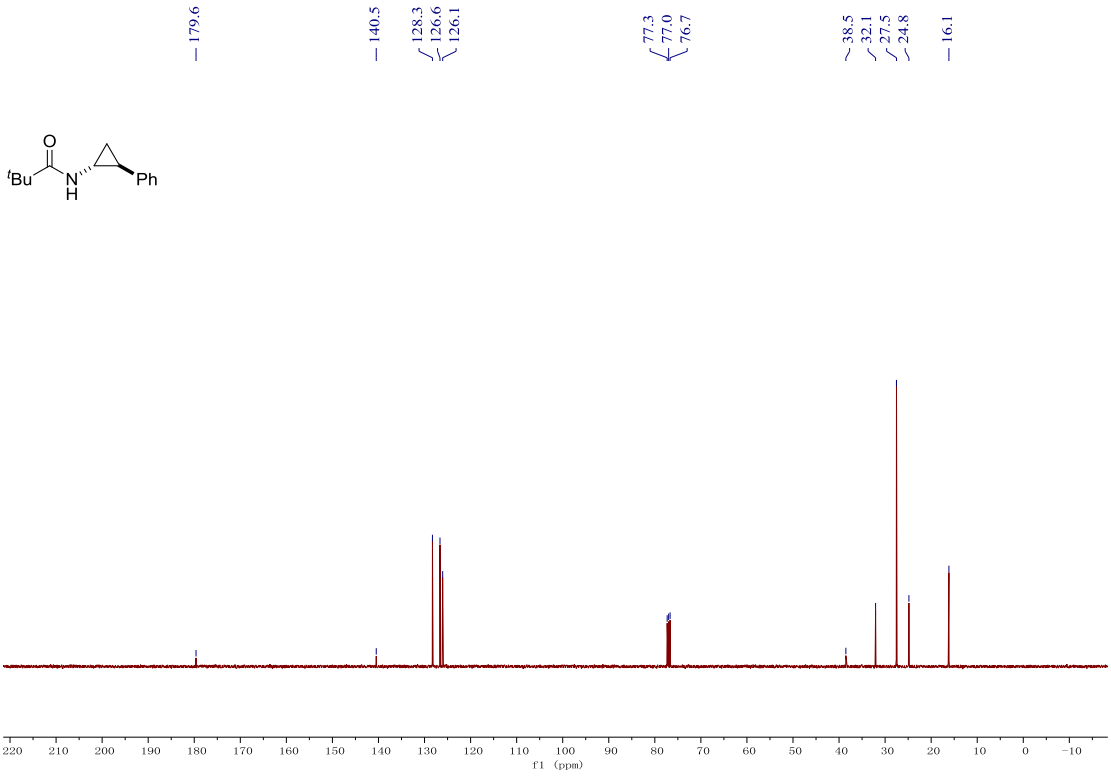
^{13}C NMR of Trans-1t



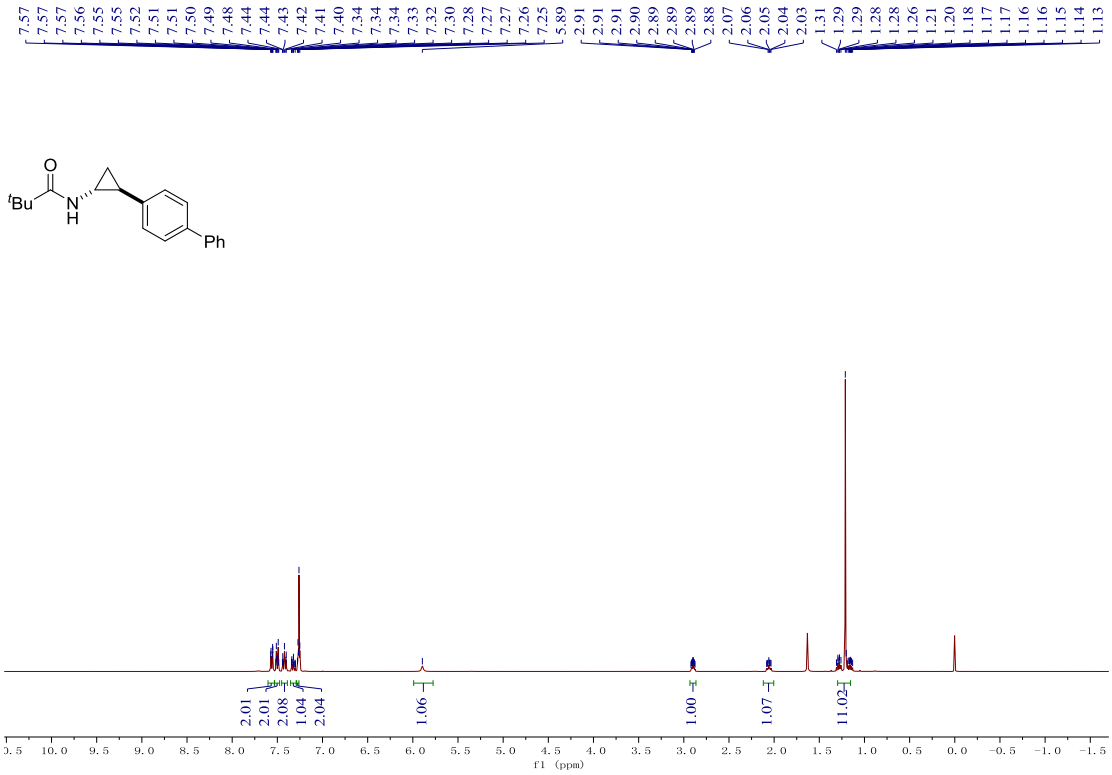
^{1}H NMR of Trans-1u



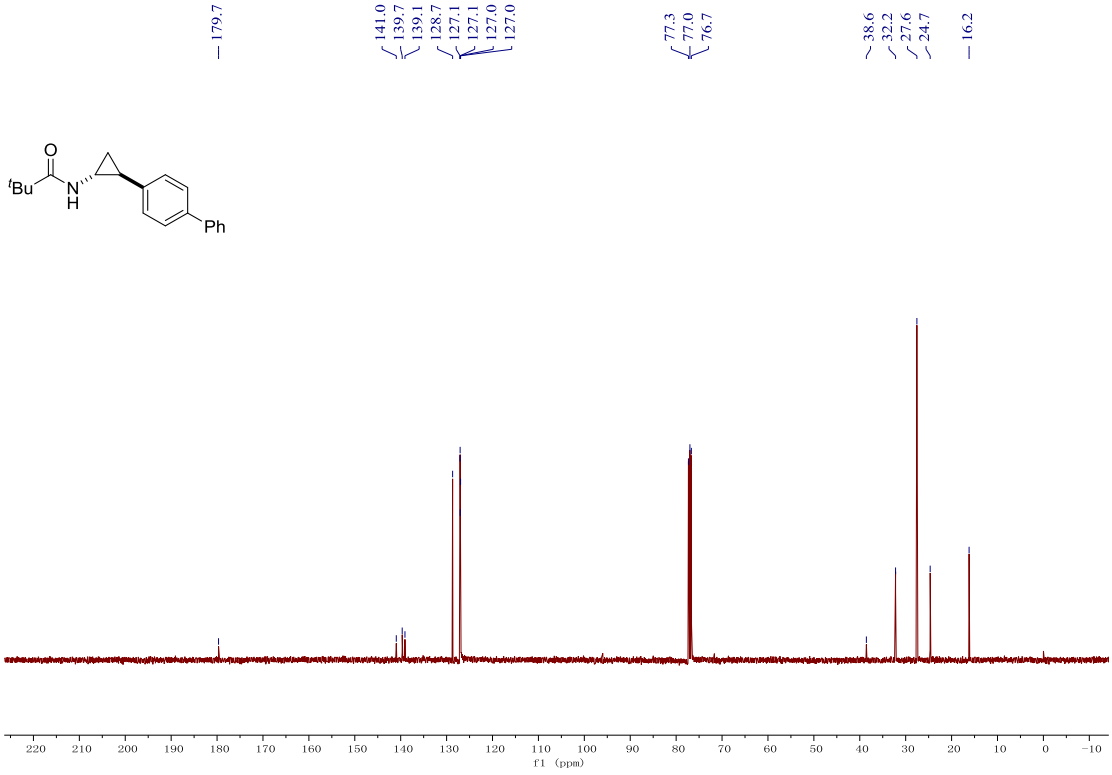
^{13}C NMR of Trans-1u



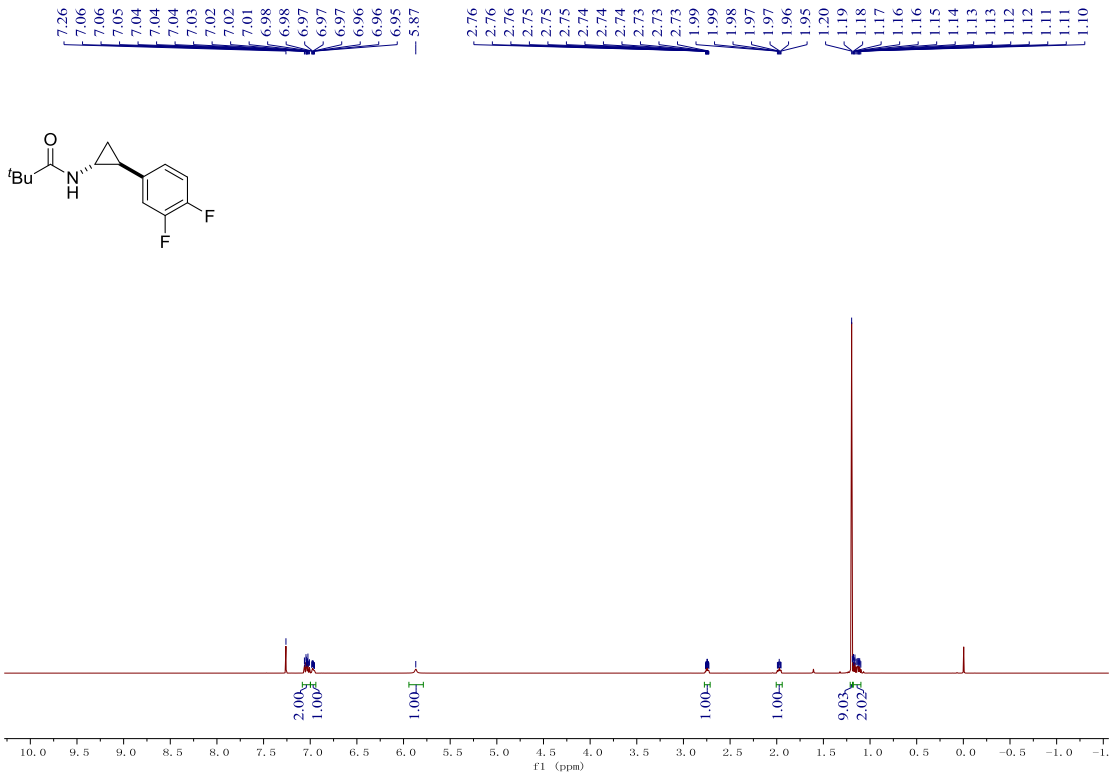
^{1}H NMR of Trans-1v



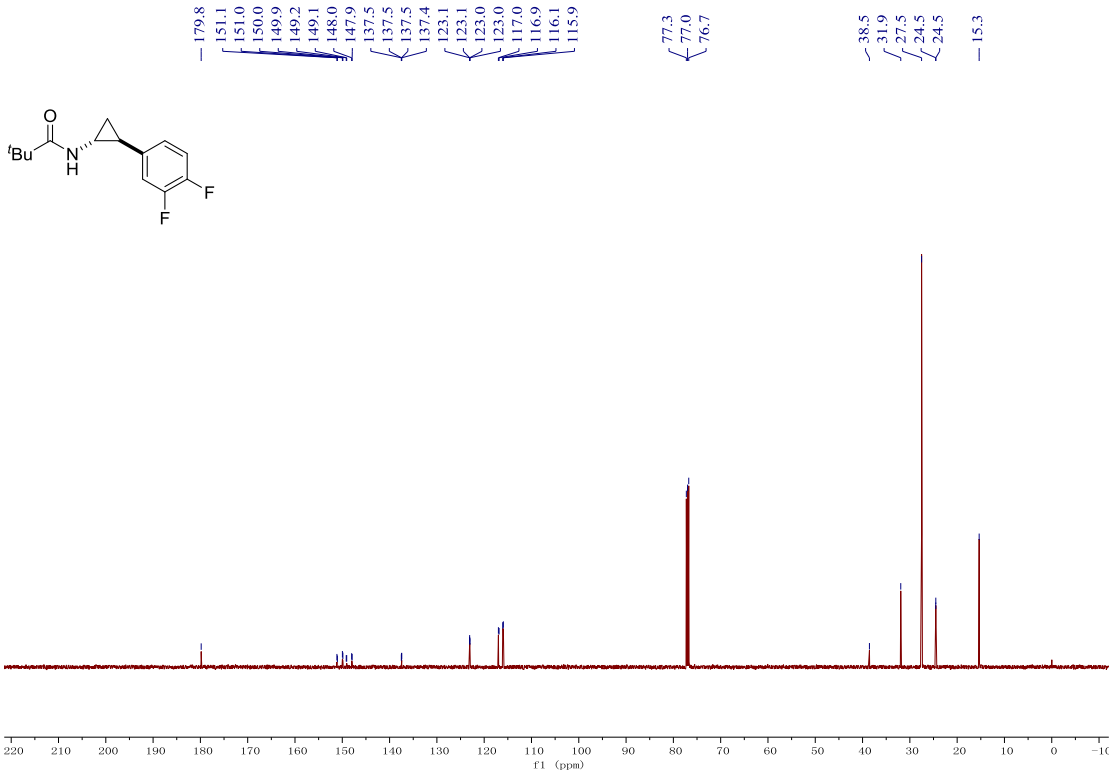
^{13}C NMR of Trans-1v



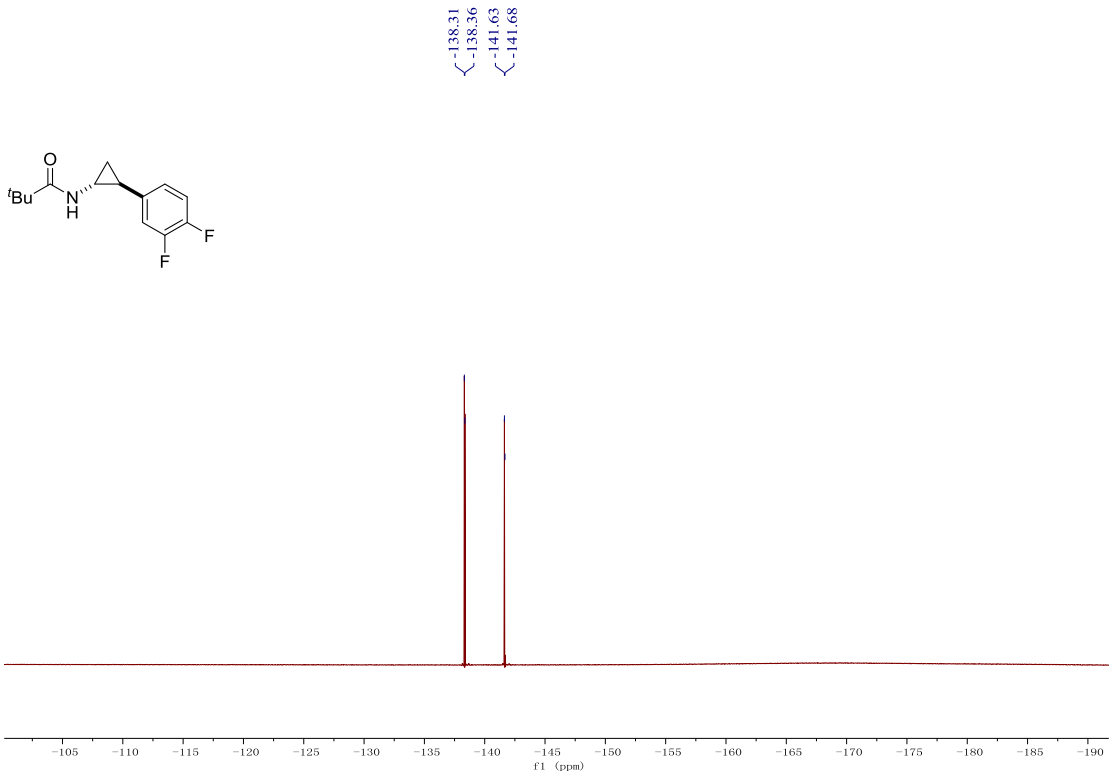
^{1}H NMR of Trans-1w



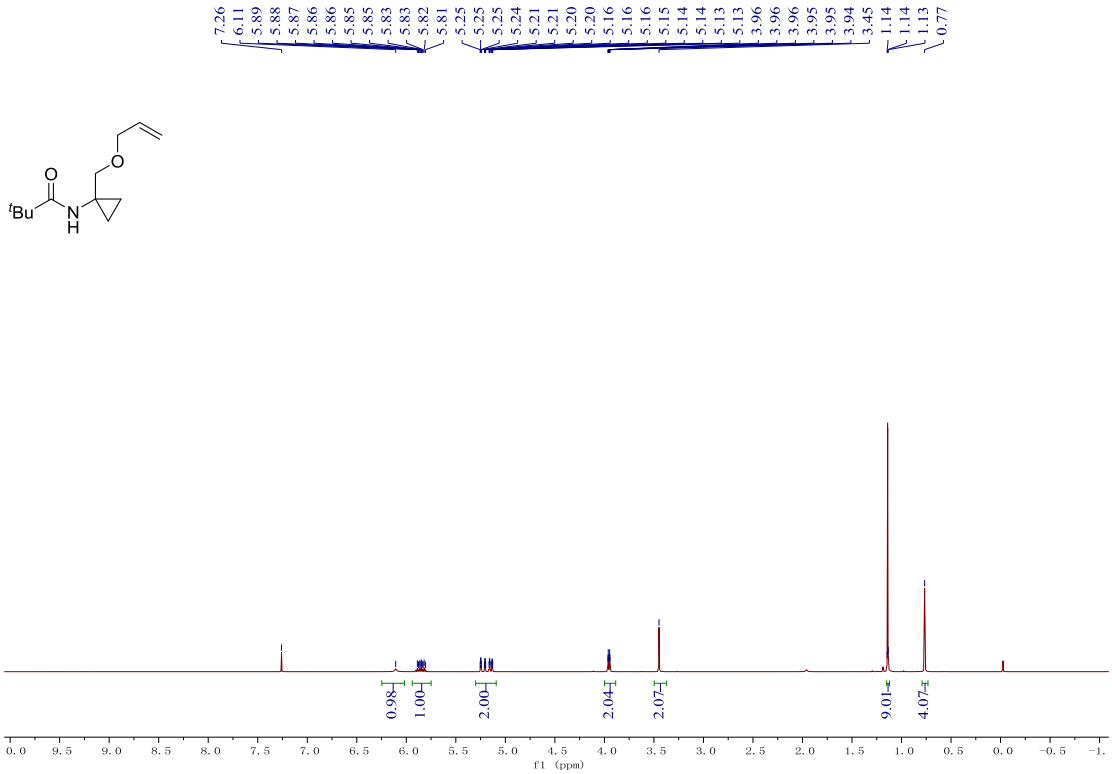
^{13}C NMR of Trans-1w



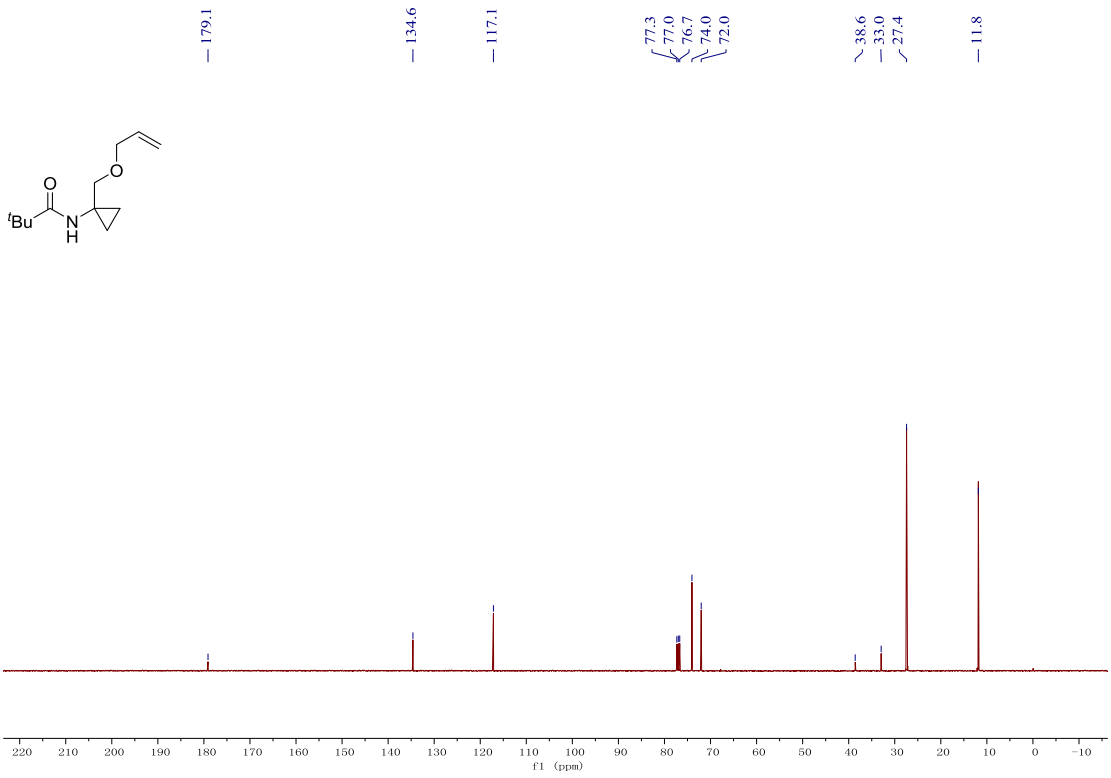
^{19}F NMR of Trans-1w



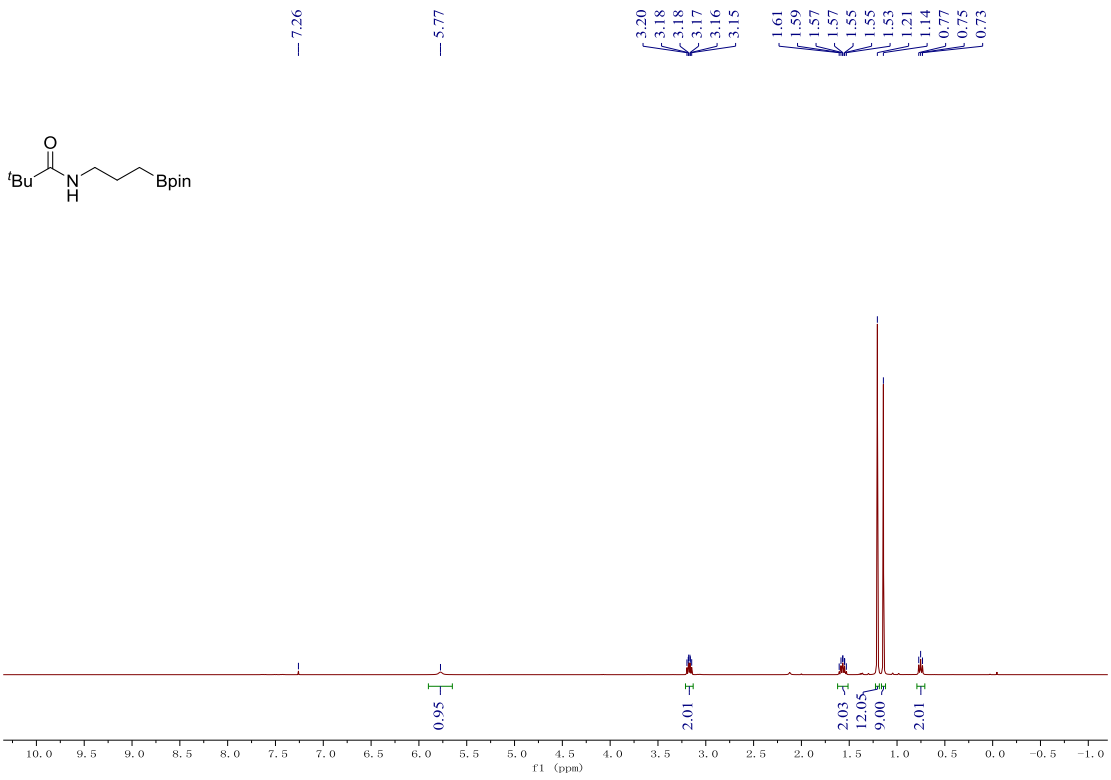
^{1}H NMR of 1x'



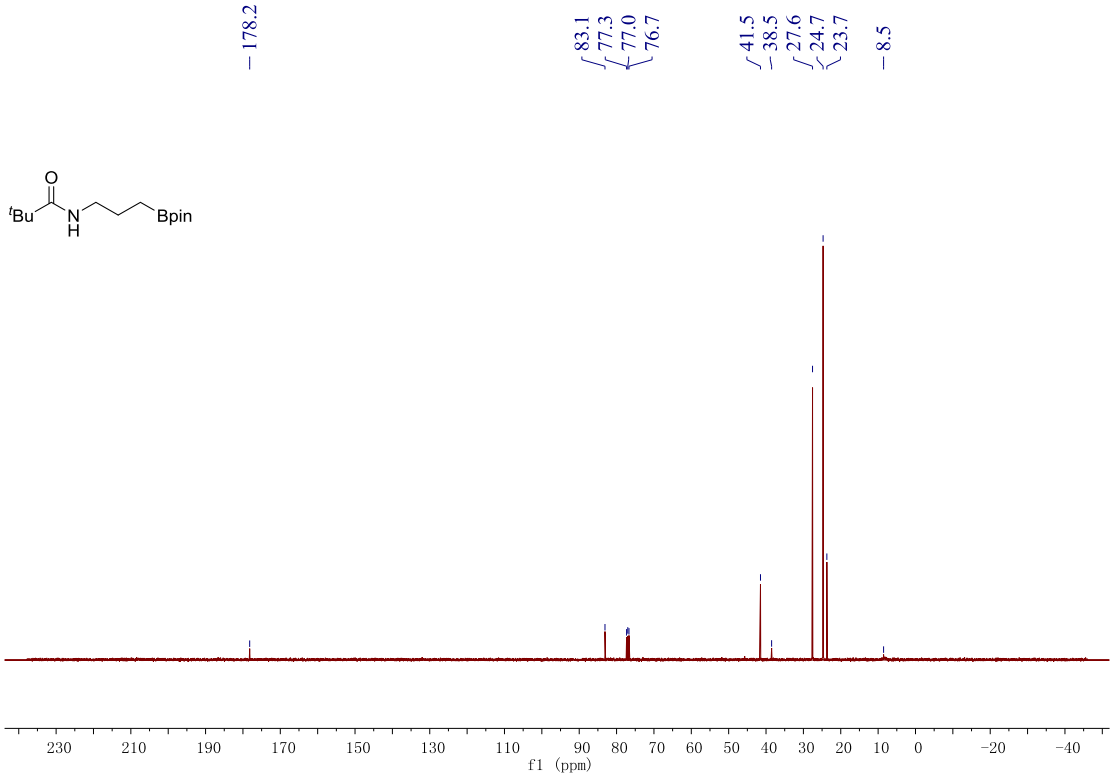
^{13}C NMR of 1x'


179.1
134.6
117.1
77.3
77.0
76.7
74.0
72.0
38.6
33.0
27.4
11.8
O
O
tBu
N
H
f1 (ppm)

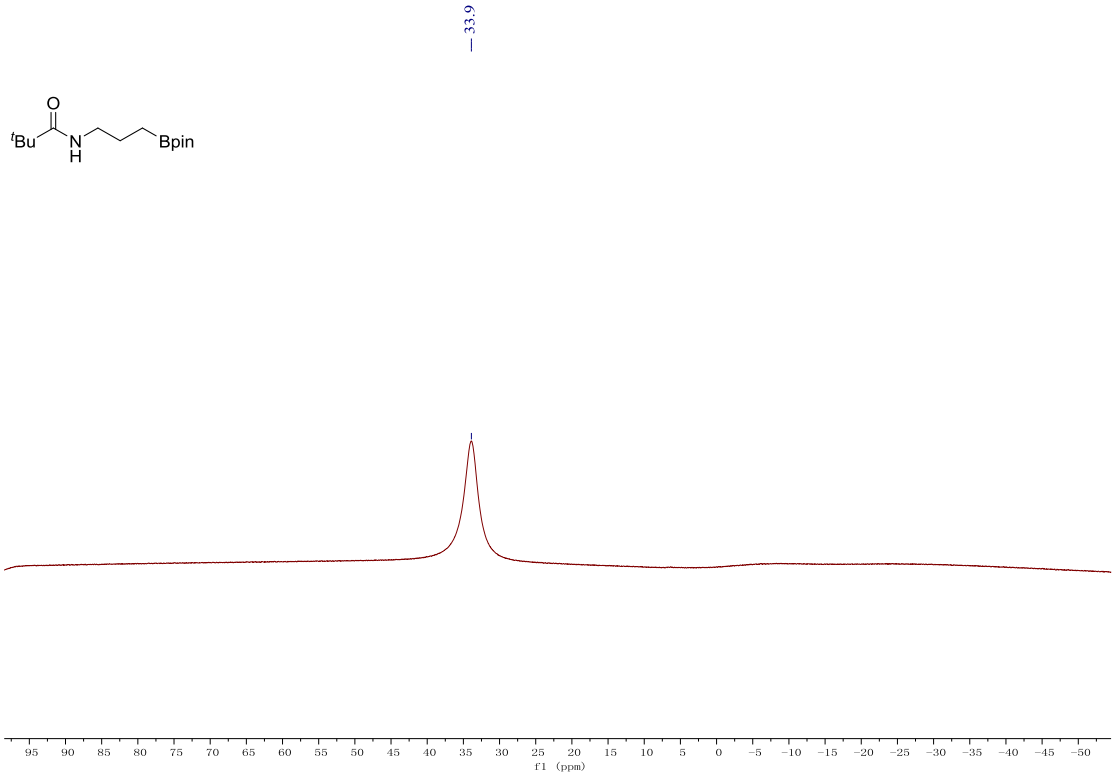
^{1}H NMR of 2a


7.26
5.77
3.20
3.18
3.18
3.17
3.16
3.15
1.61
1.59
1.57
1.57
1.55
1.55
1.53
1.21
1.14
0.77
0.75
0.73
O
tBu
N
H
Bpin
0.95
2.01
2.03
12.05
9.00
2.01
f1 (ppm)

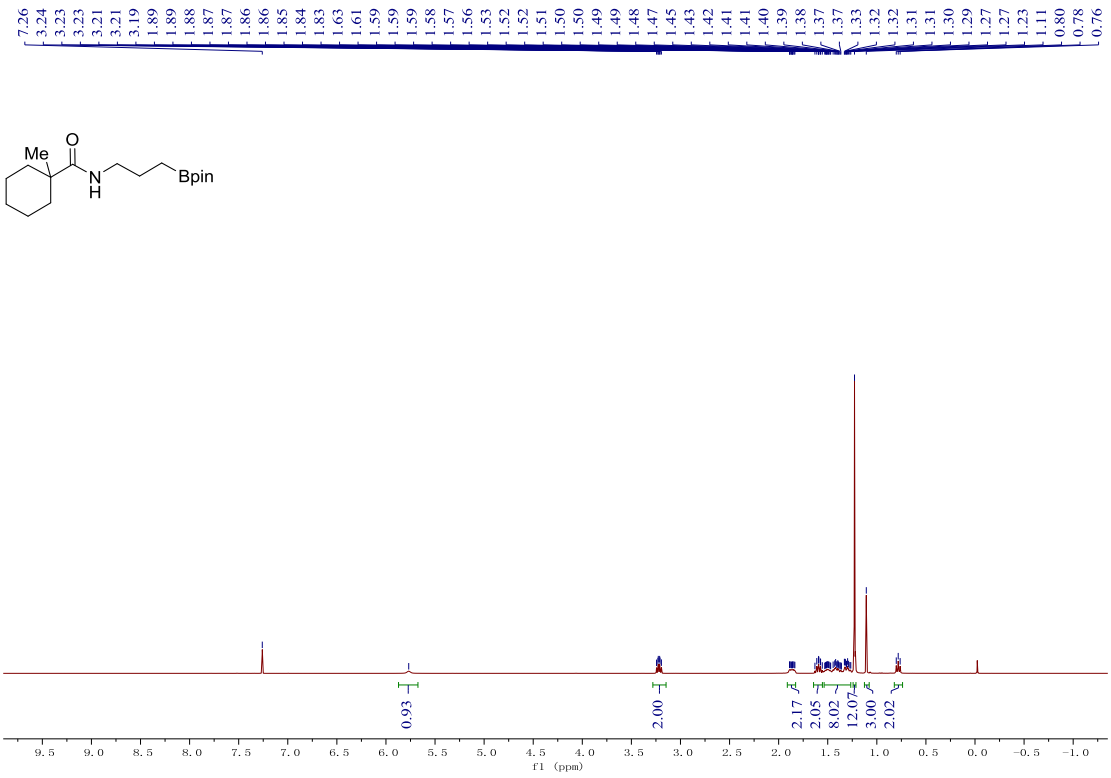
^{13}C NMR of 2a



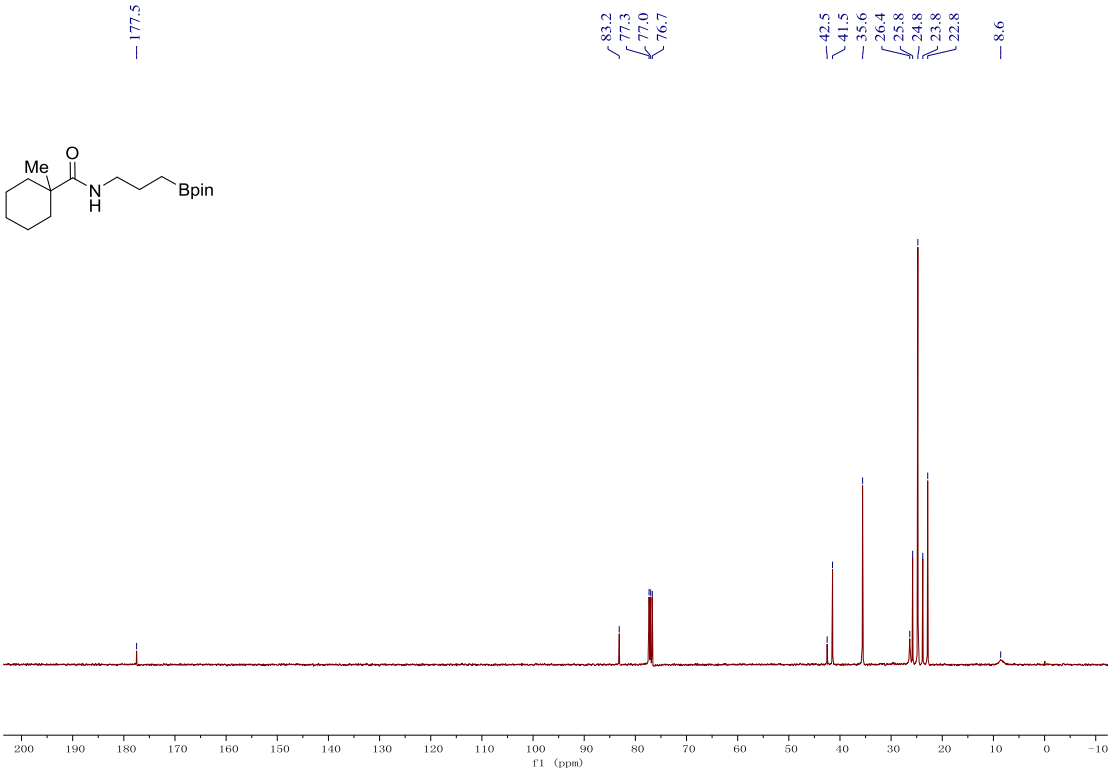
^{11}B NMR of 2a



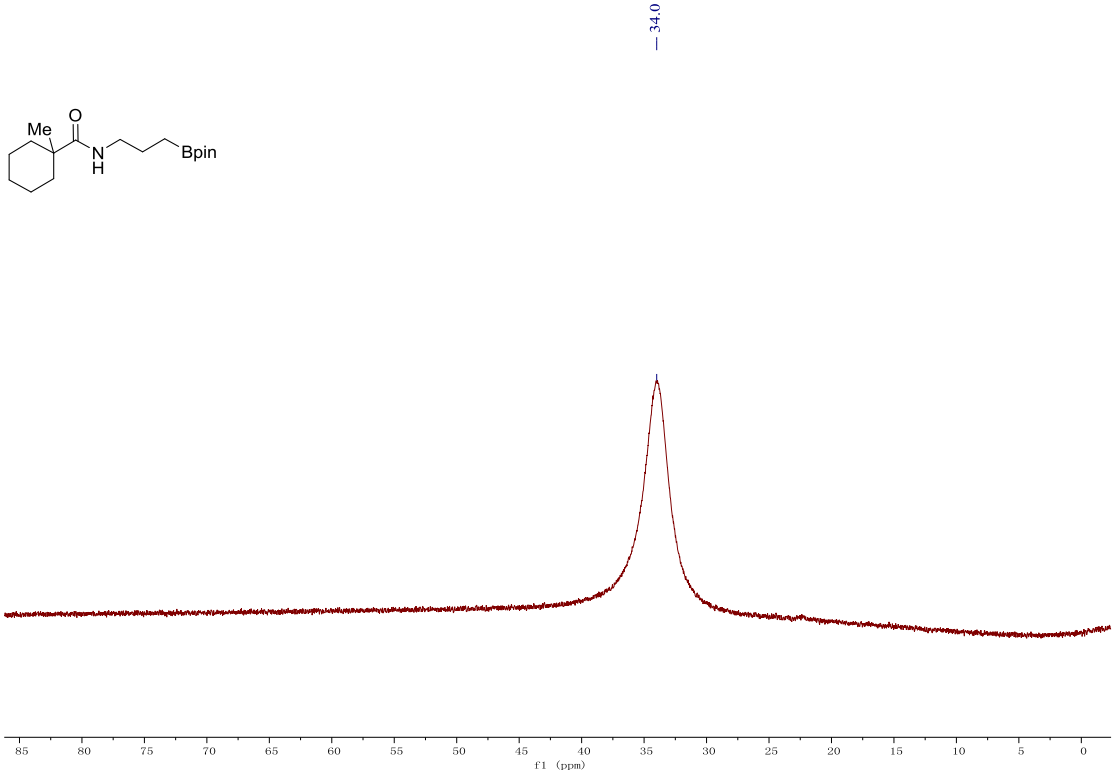
^{1}H NMR of 5b



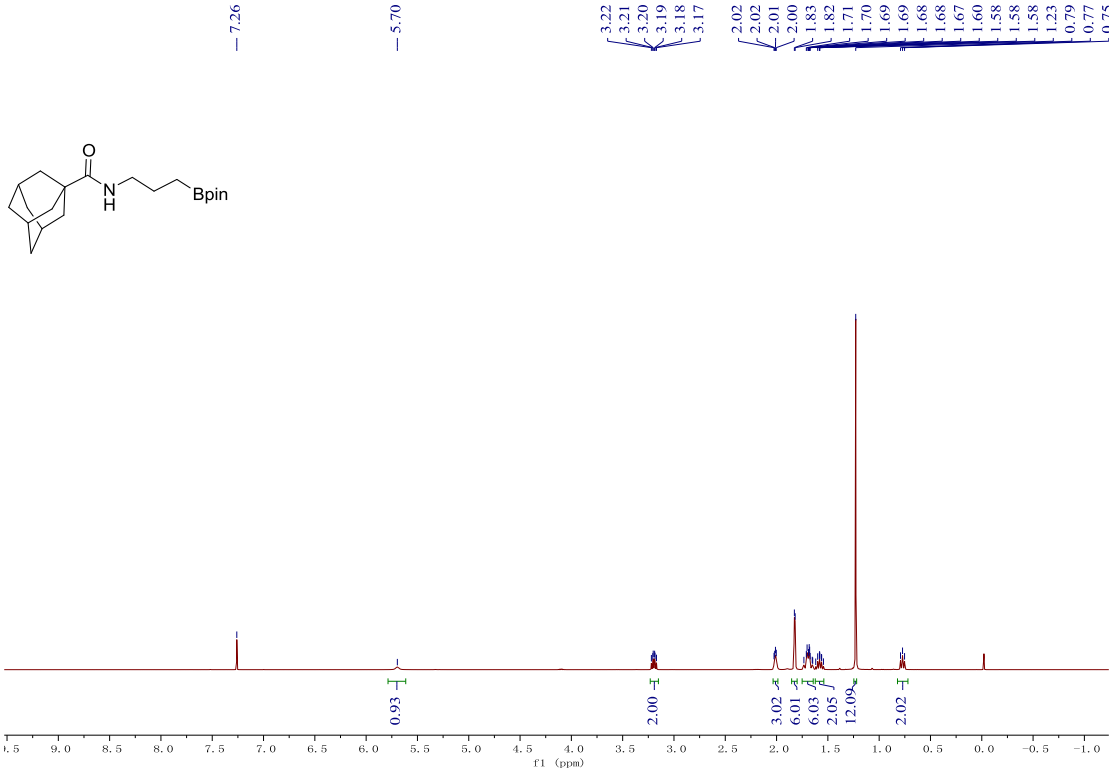
^{13}C NMR of 5b



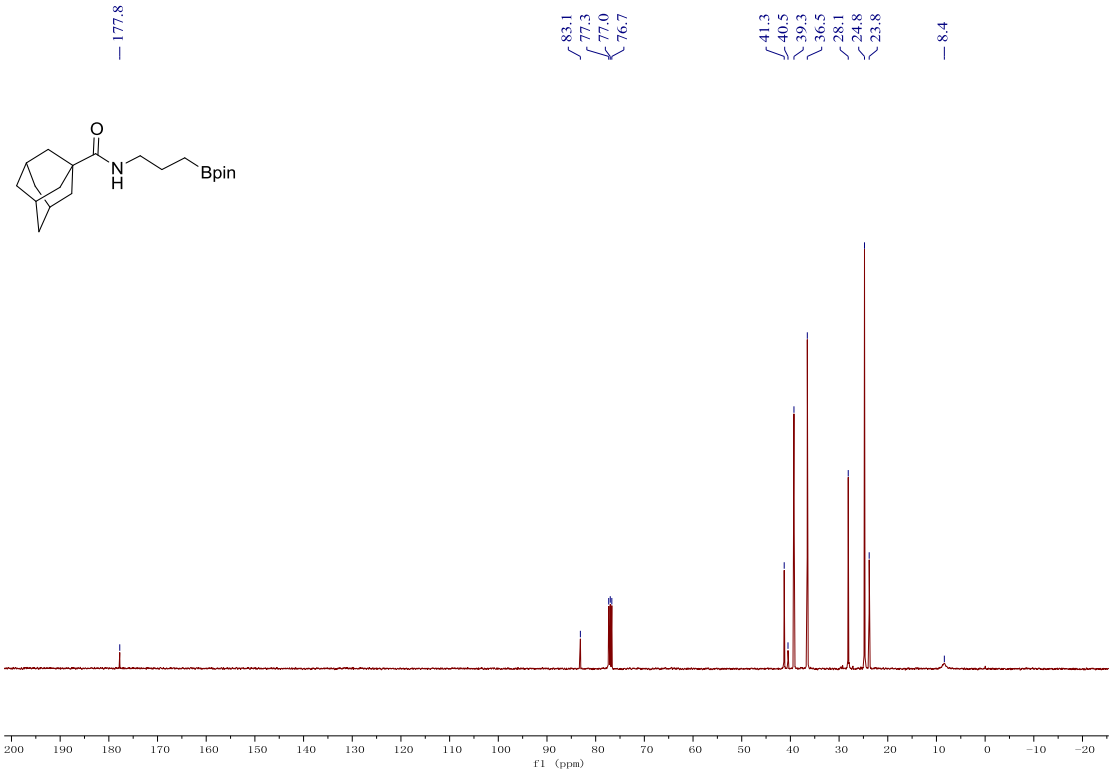
^{11}B NMR of 5b



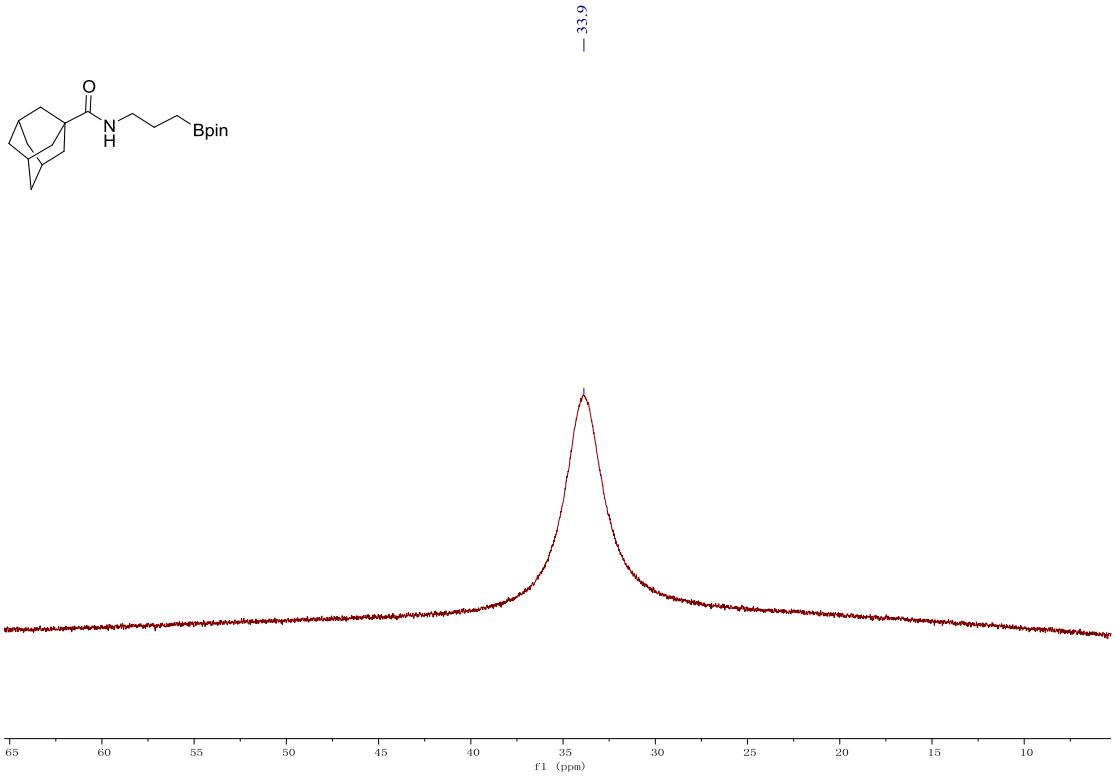
^{1}H NMR of 5c



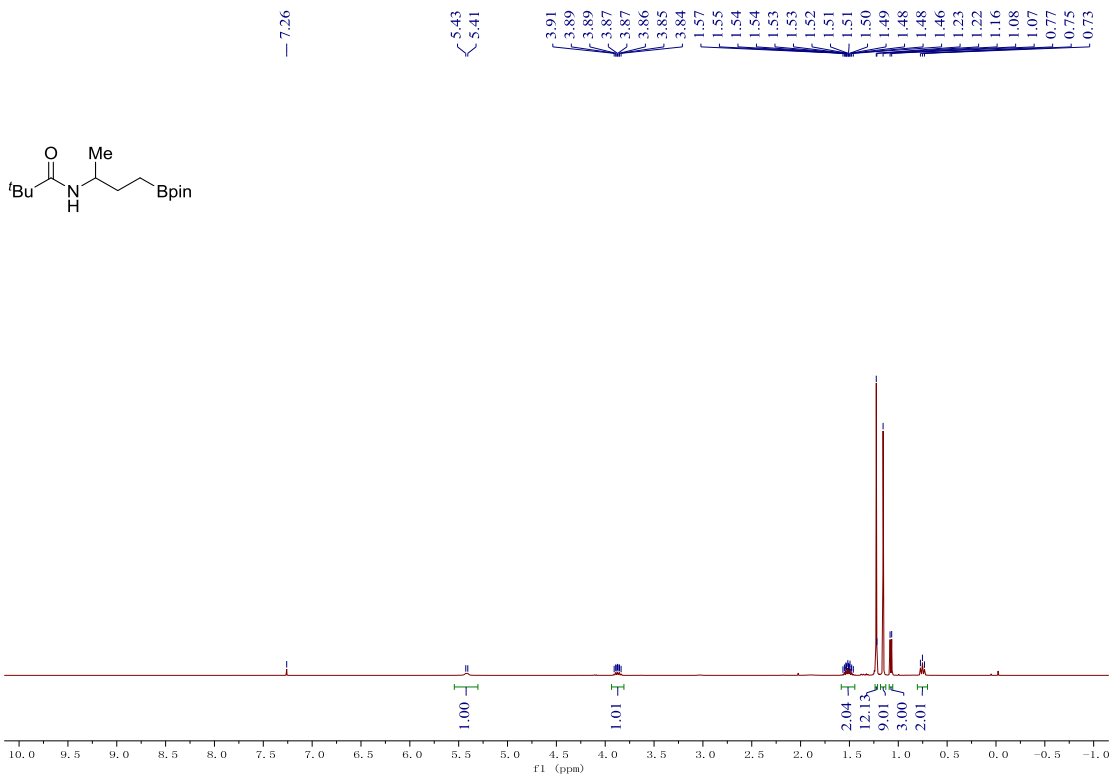
^{13}C NMR of 5c



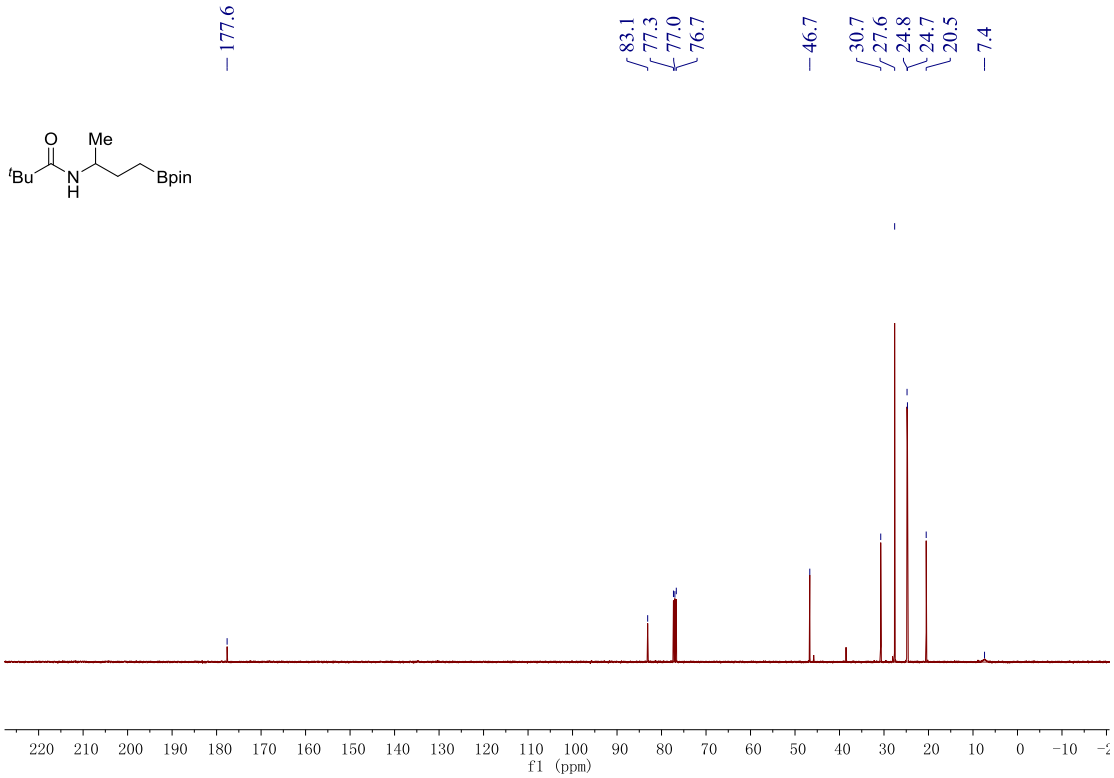
^{11}B NMR of 5c



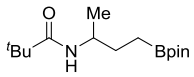
^{1}H NMR of 2b



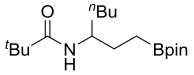
^{13}C NMR of 2b

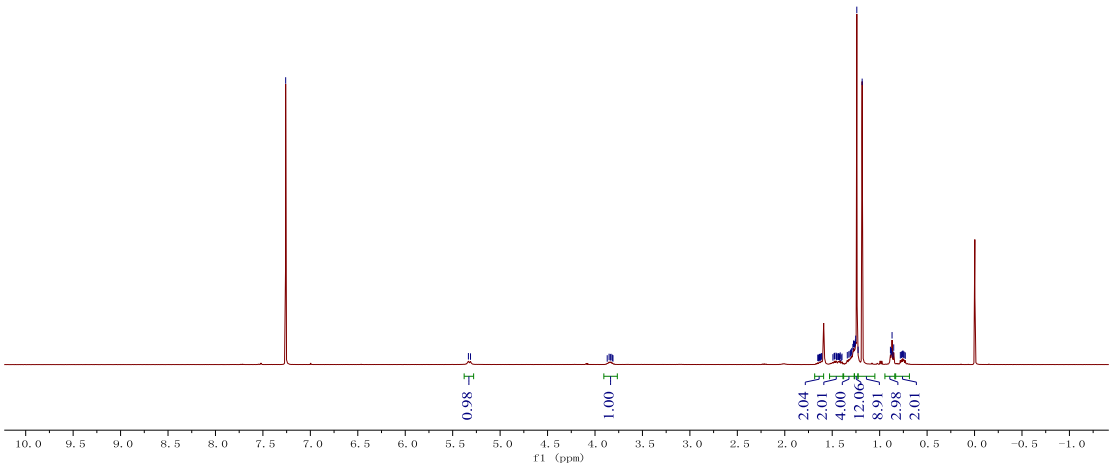


^{11}B NMR of 2b

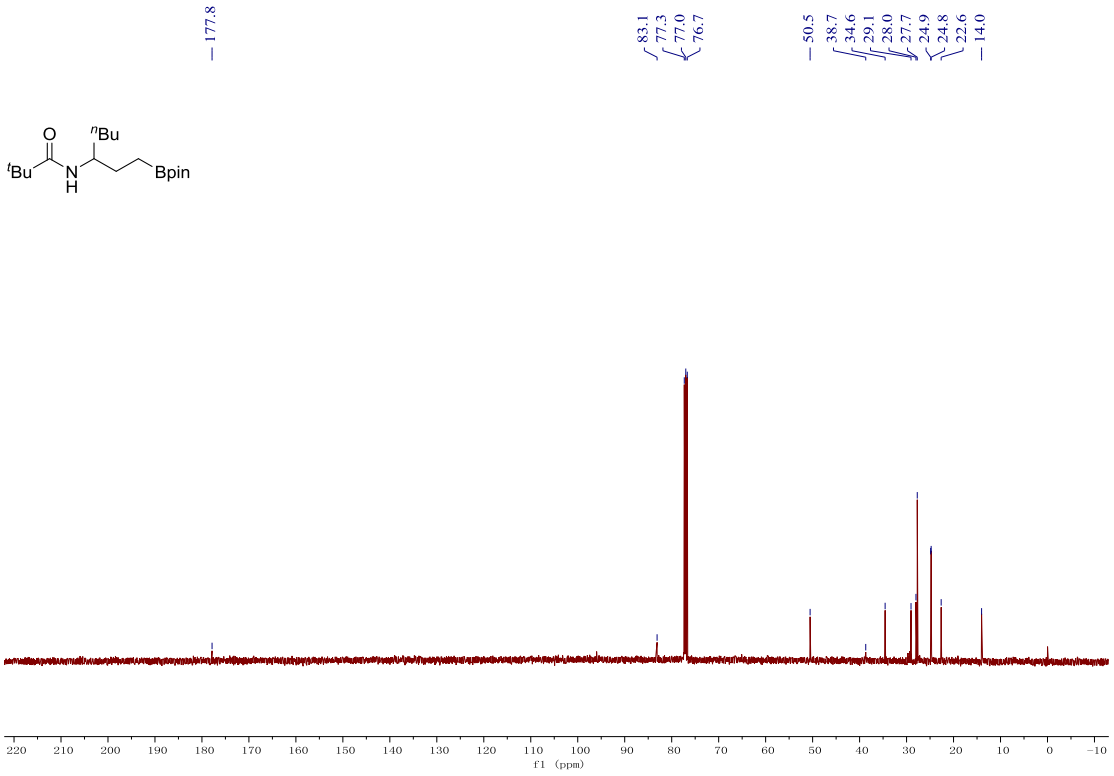


^{1}H NMR of 2c

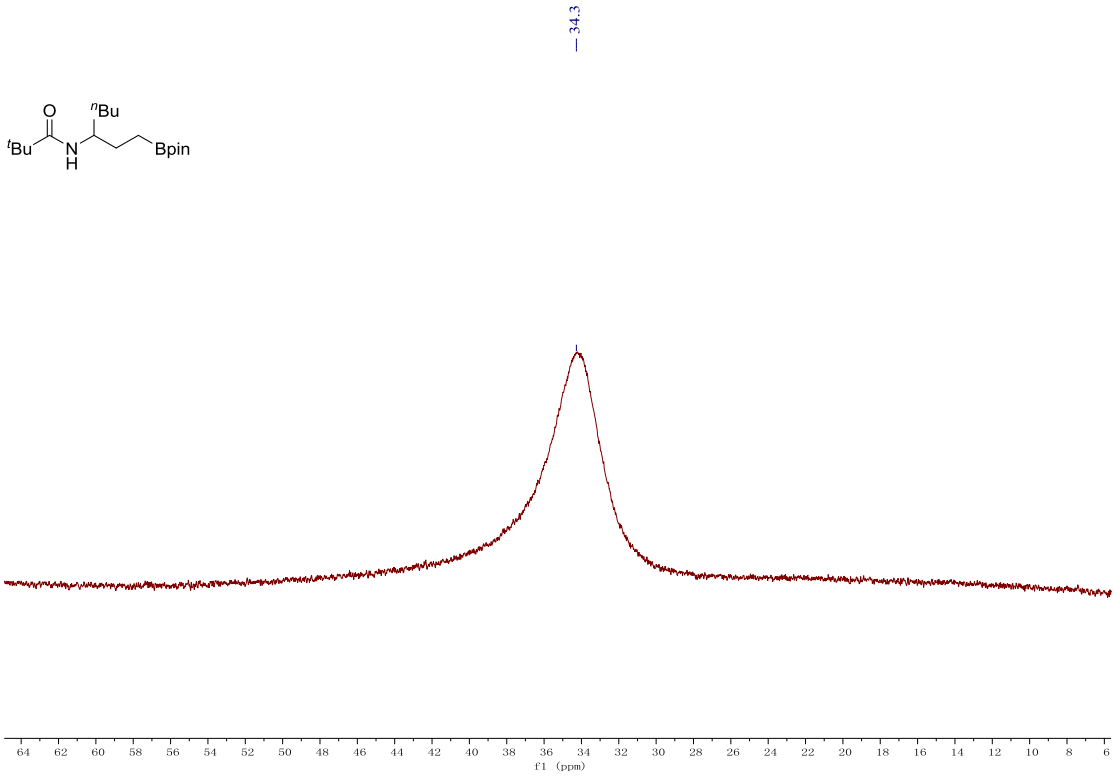




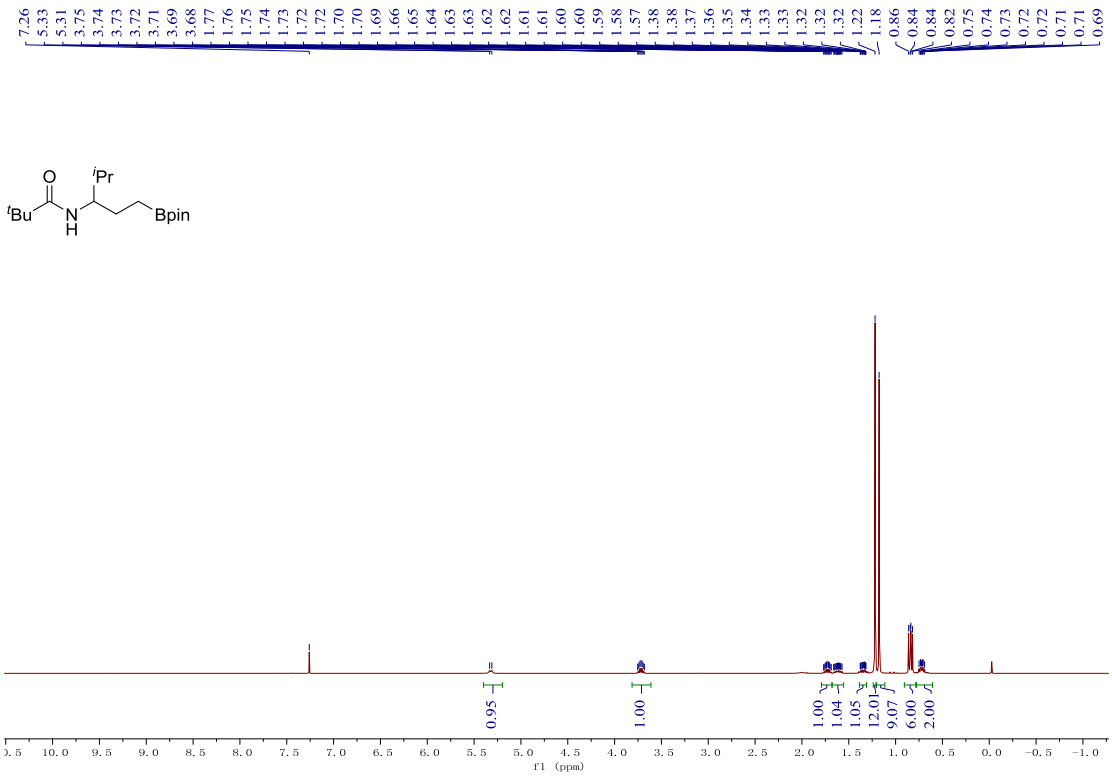
^{13}C NMR of 2c



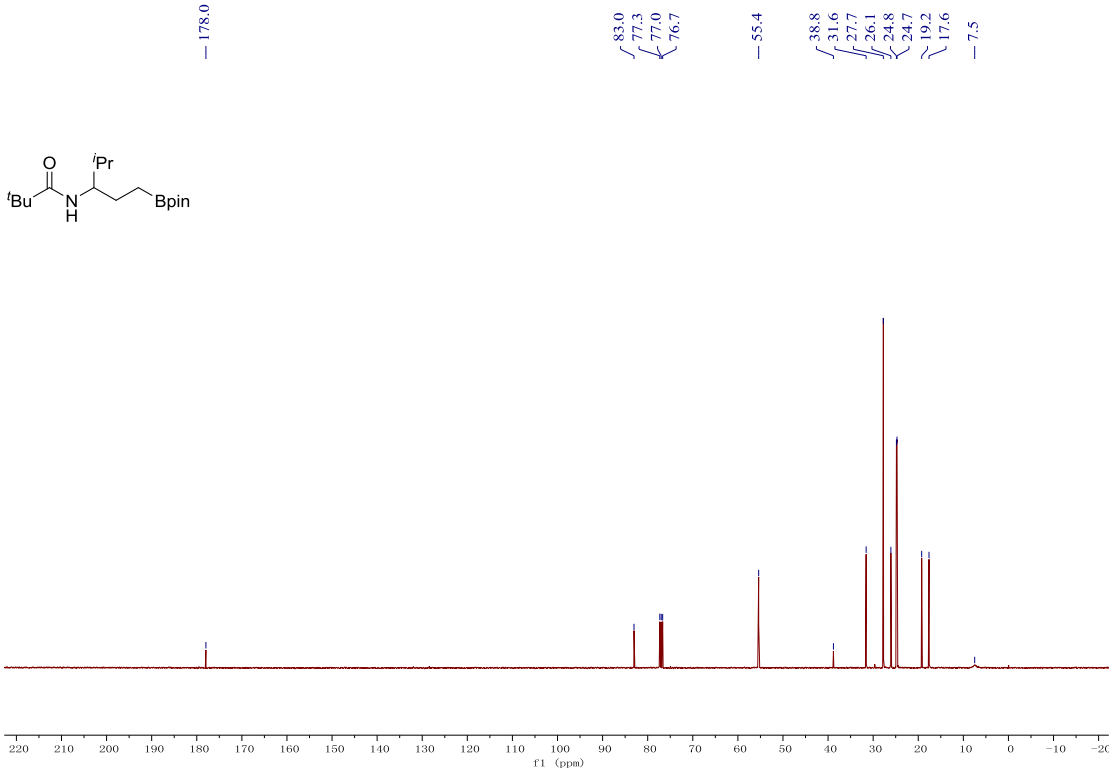
^{11}B NMR of 2c



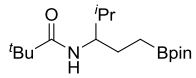
^{1}H NMR of 2d



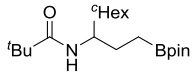
^{13}C NMR of 2d

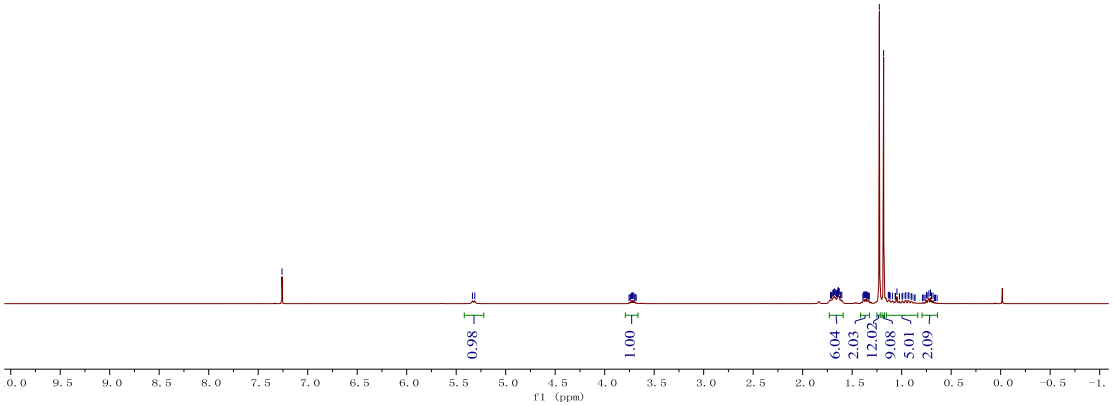


^{11}B NMR of 2d

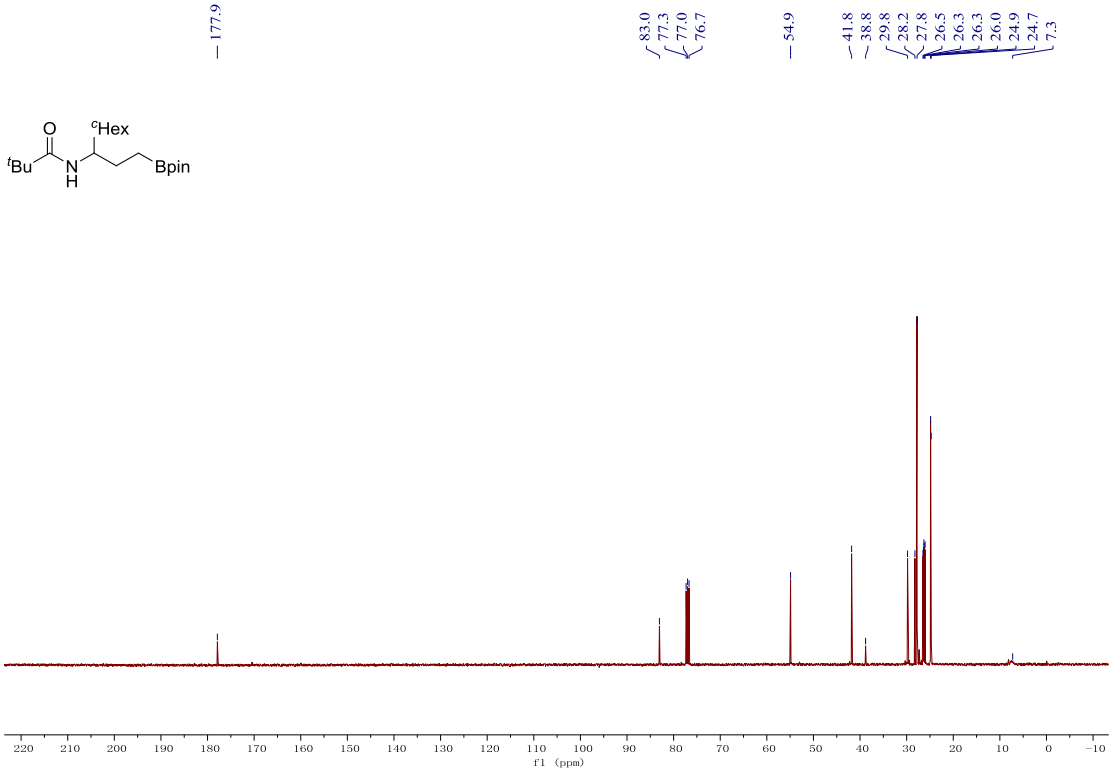


^{1}H NMR of 2e

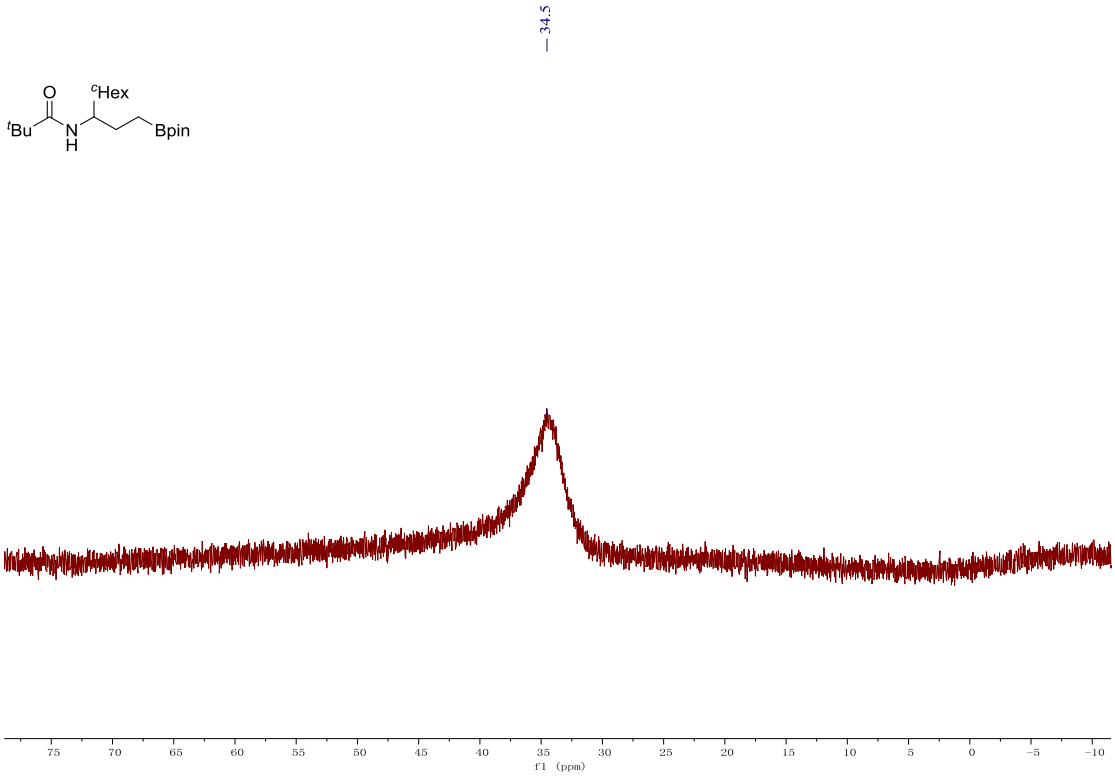




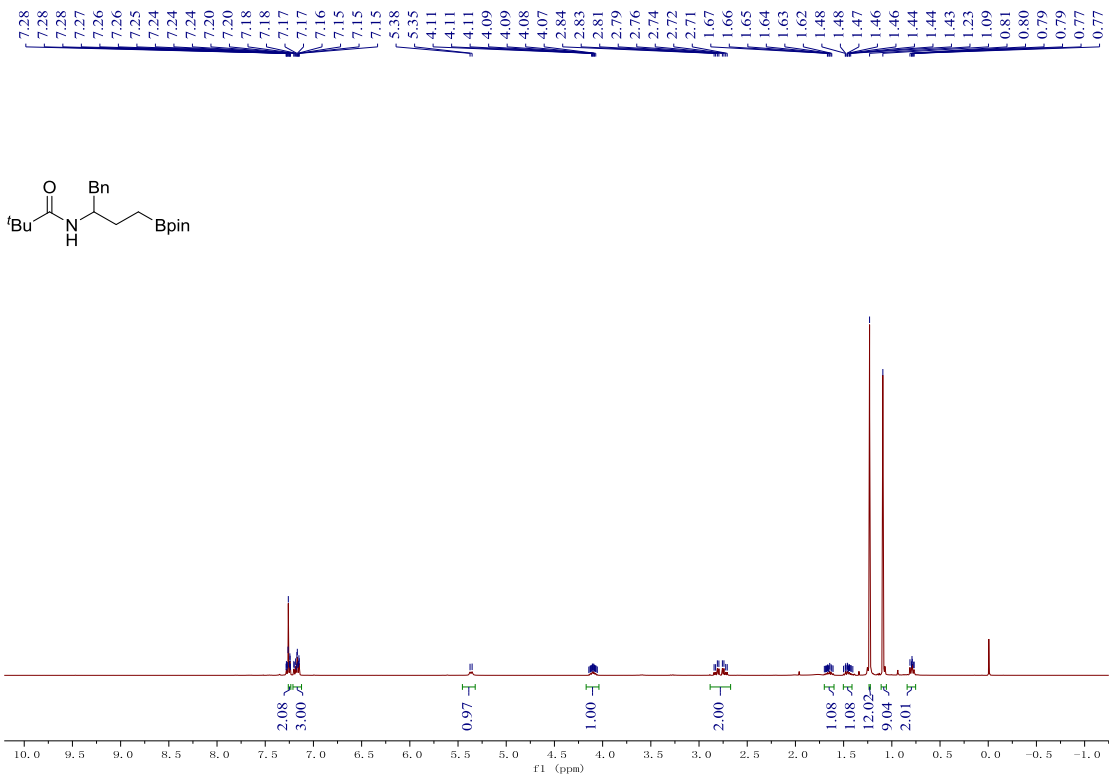
^{13}C NMR of 2e



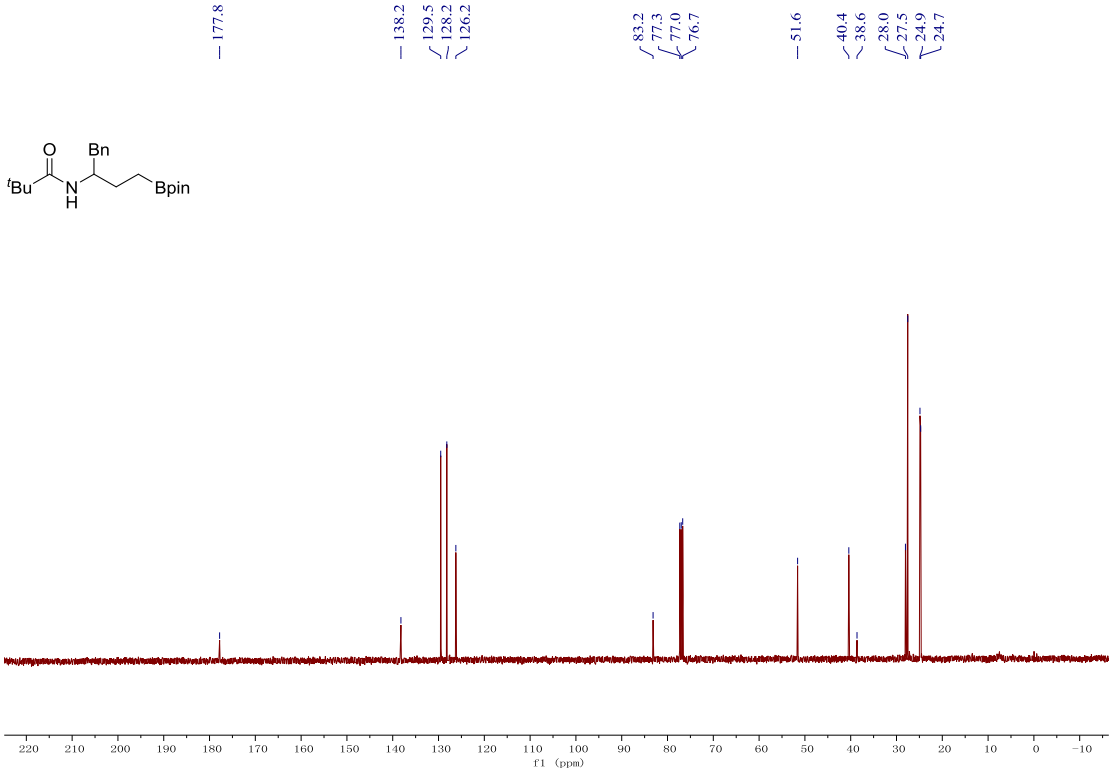
^{11}B NMR of 2e



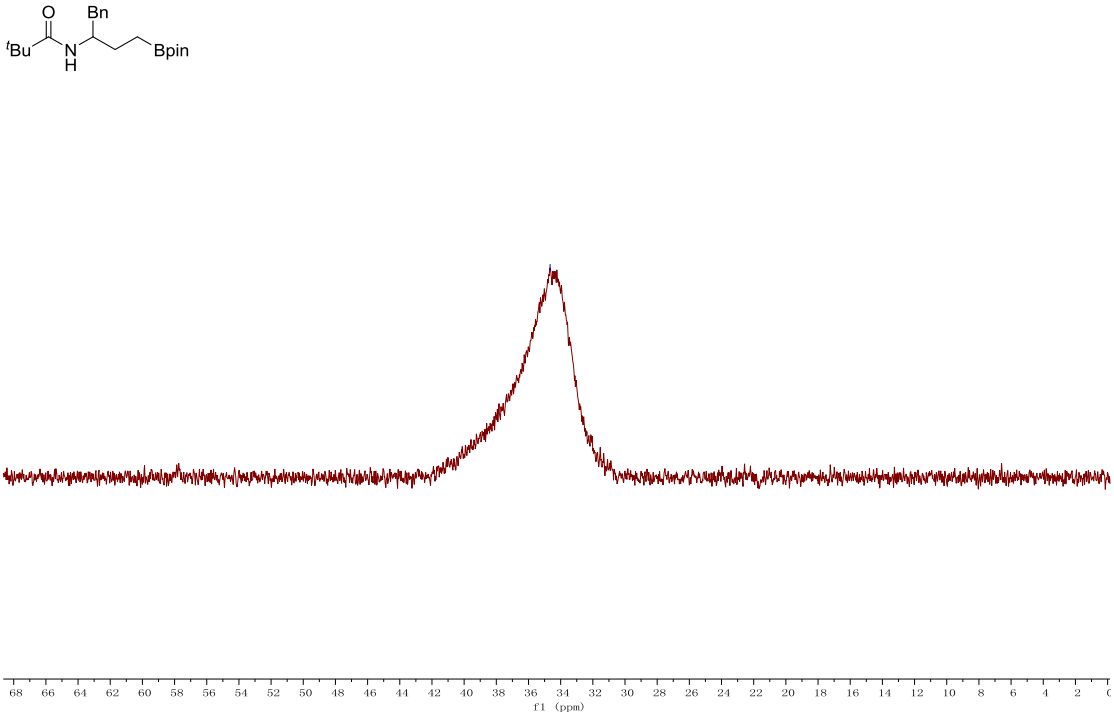
^{1}H NMR of 2f



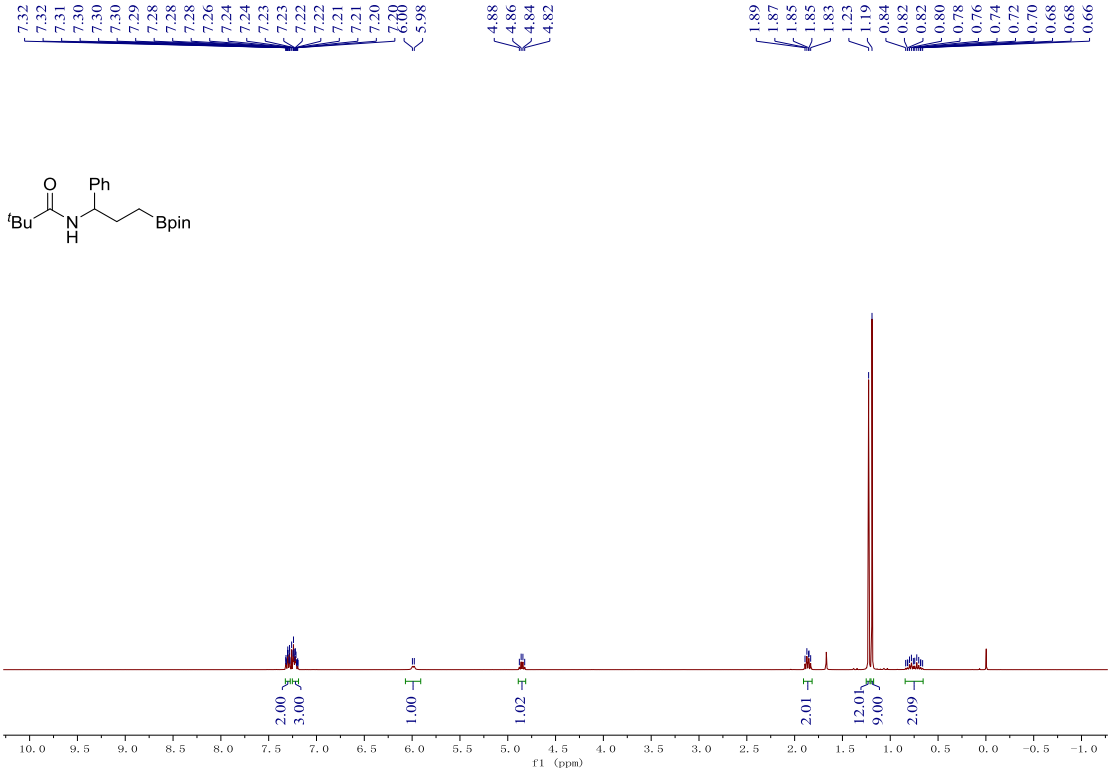
^{13}C NMR of 2f



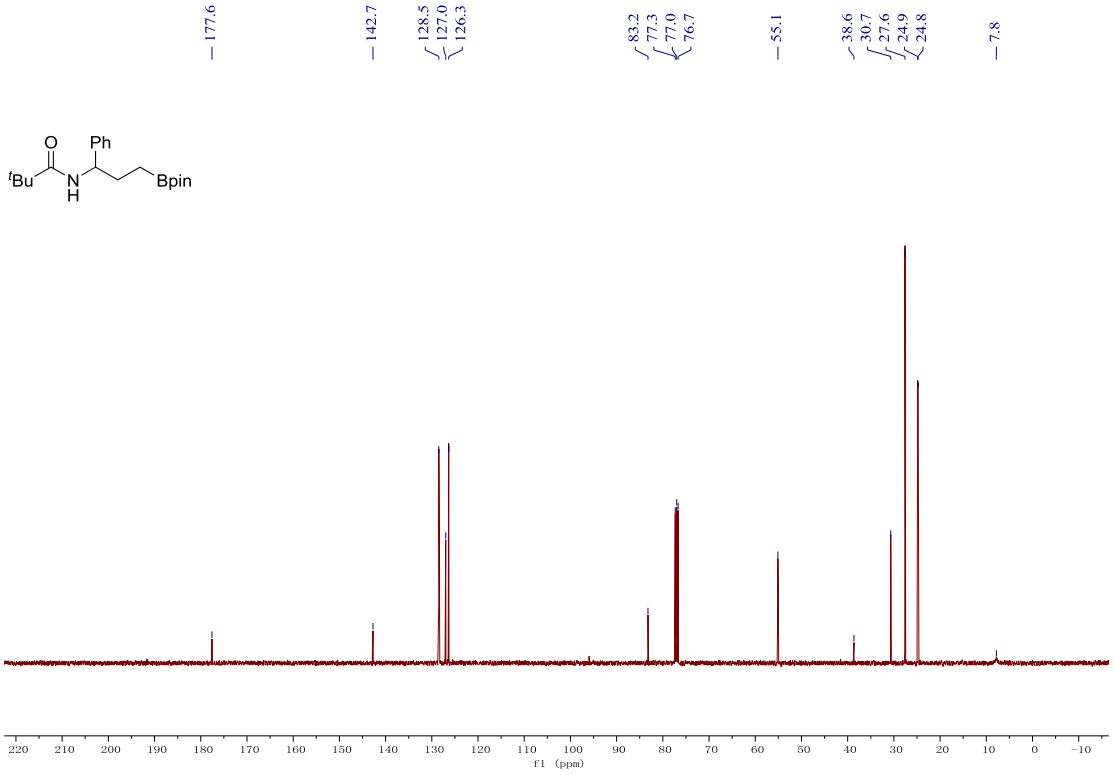
^{11}B NMR of 2f



^{1}H NMR of 2g



^{13}C NMR of 2g



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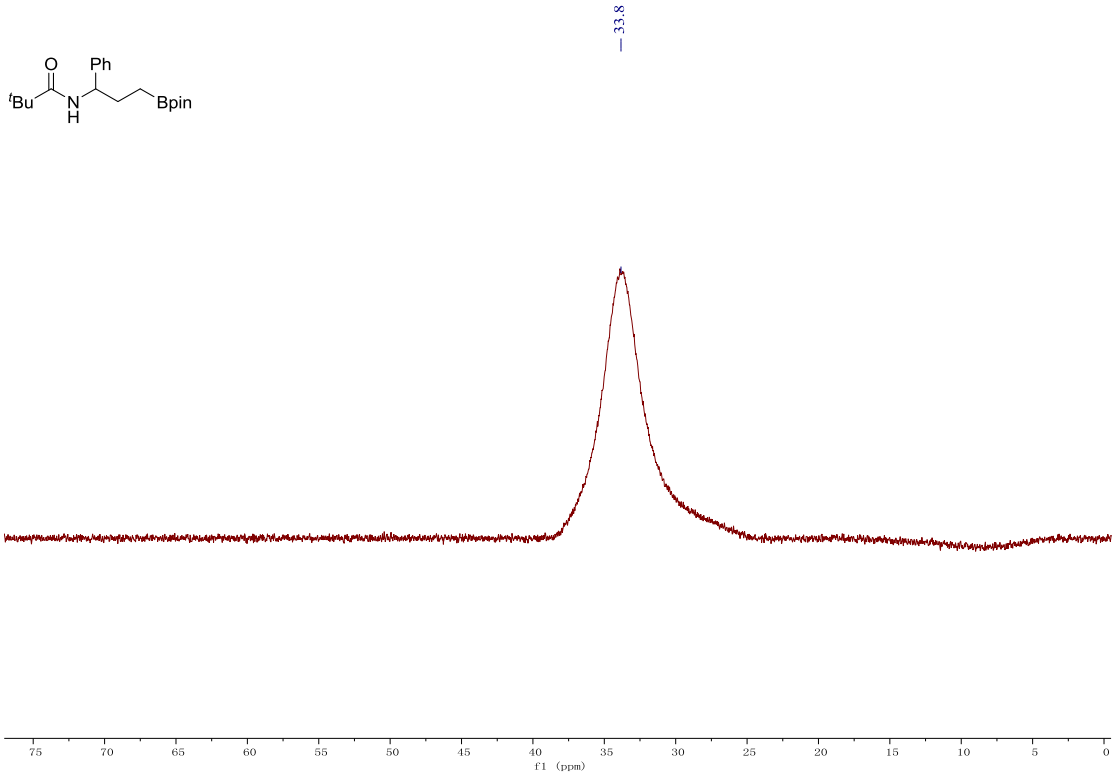
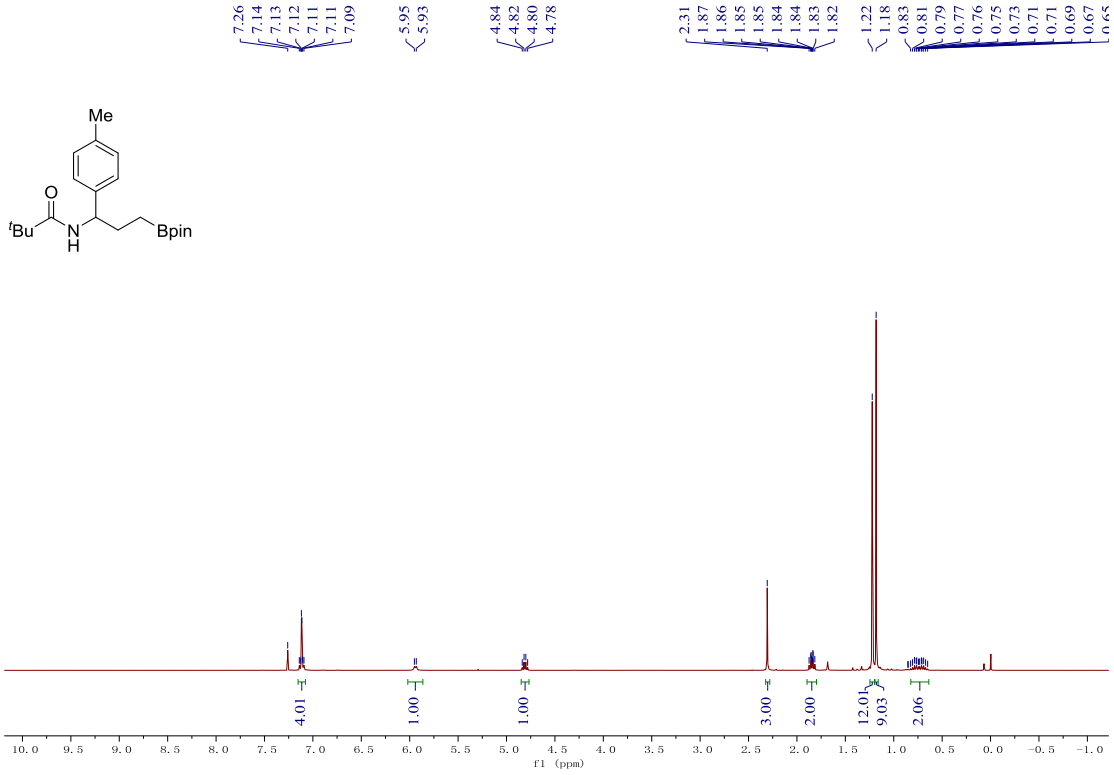
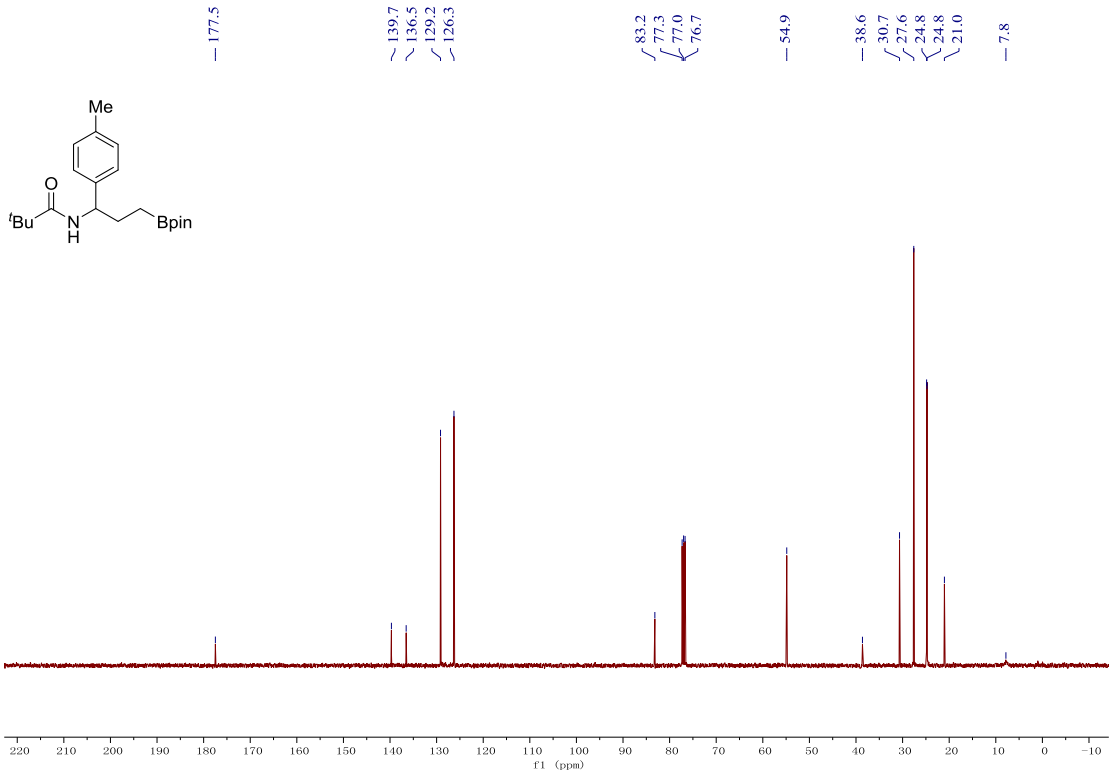


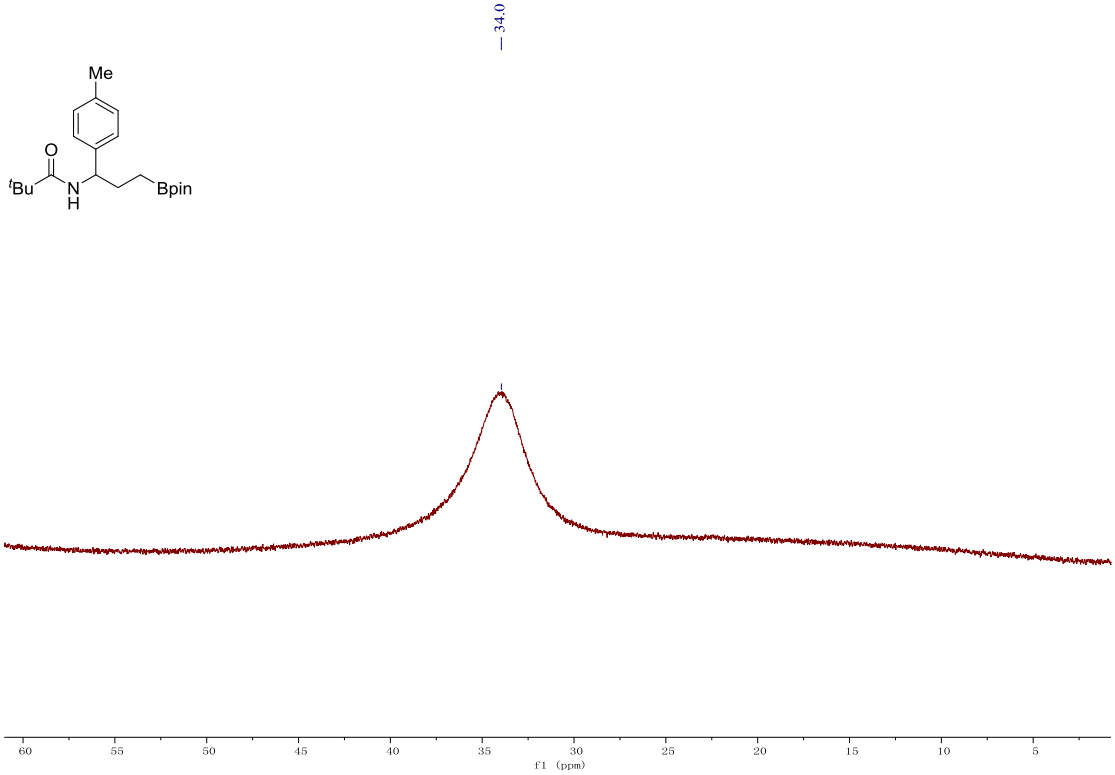
^{1}H NMR of 2h



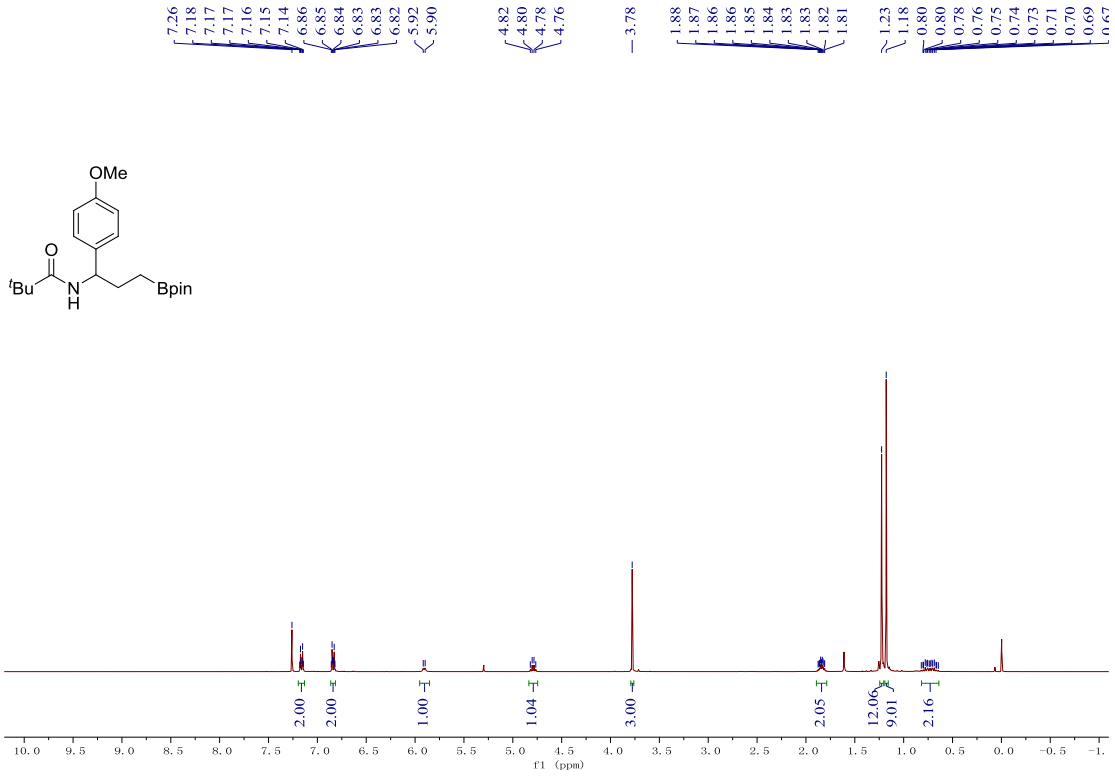
^{13}C NMR of 2h



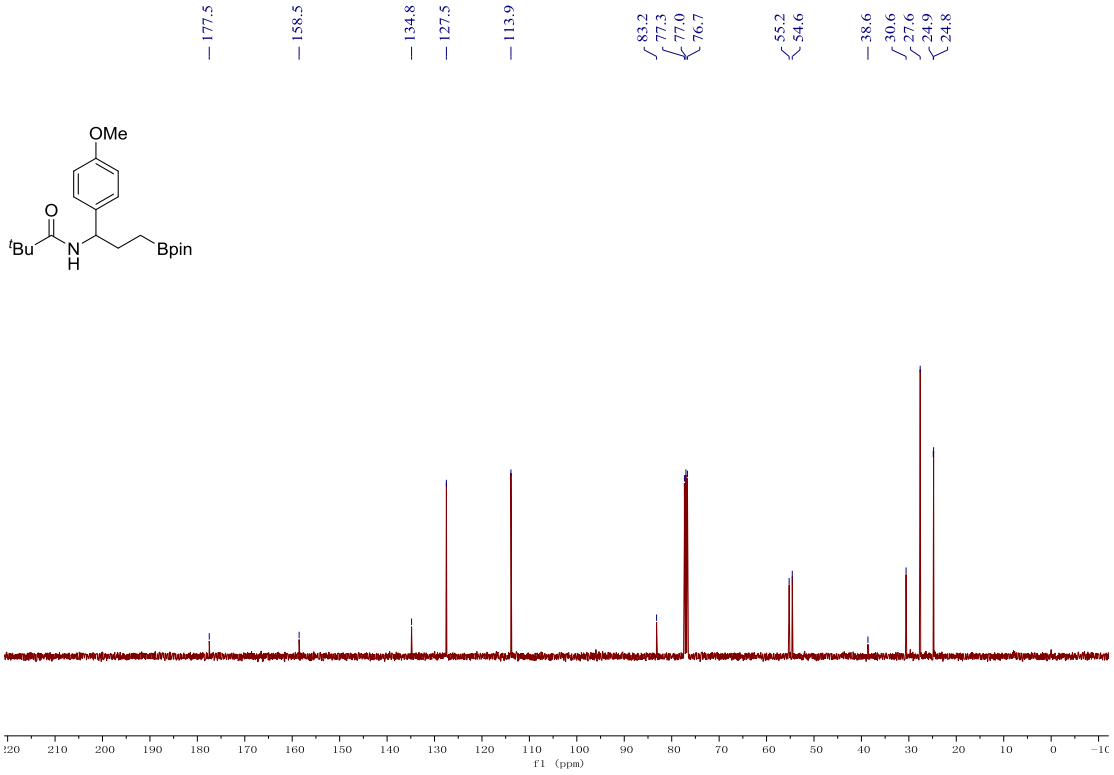
^{11}B NMR of 2h



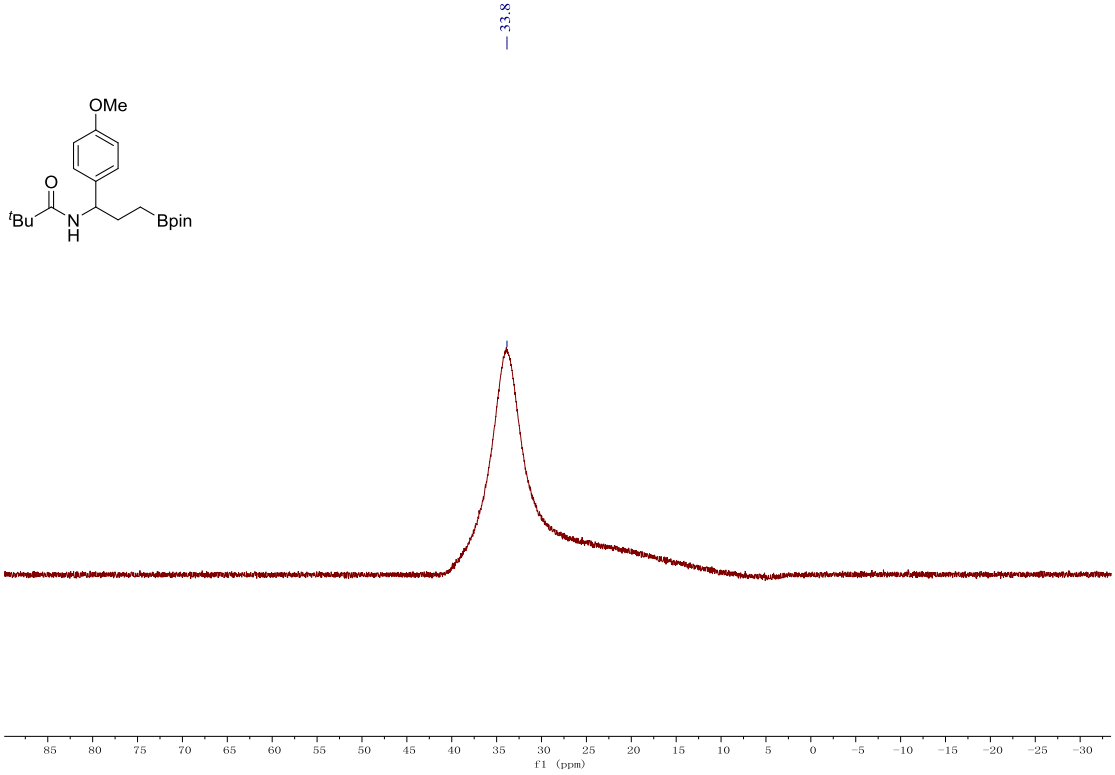
^{1}H NMR of 2i



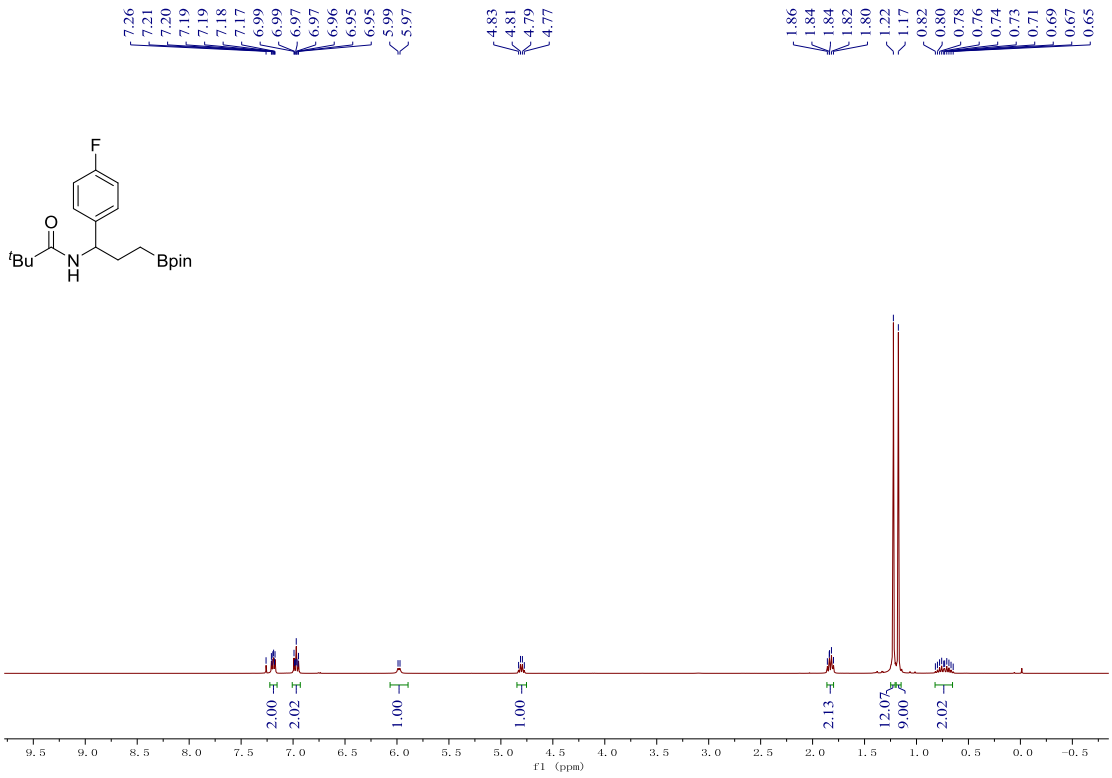
^{13}C NMR of 2i



^{11}B NMR of 2i



^{1}H NMR of 2j



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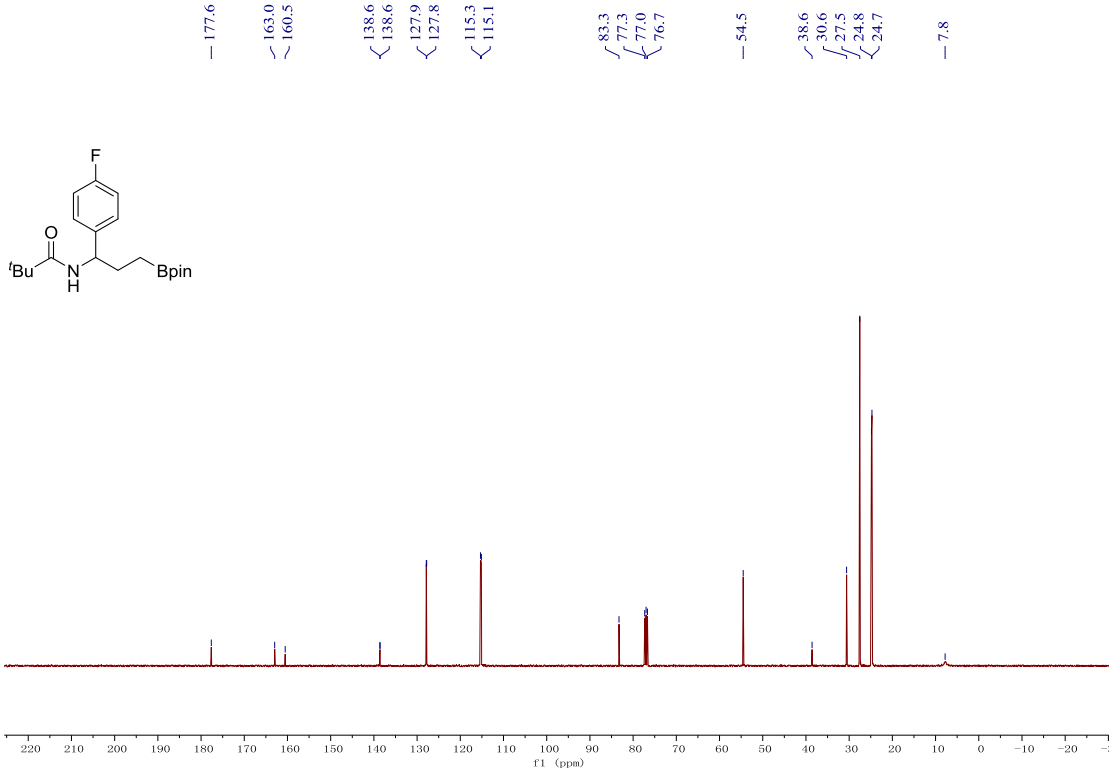
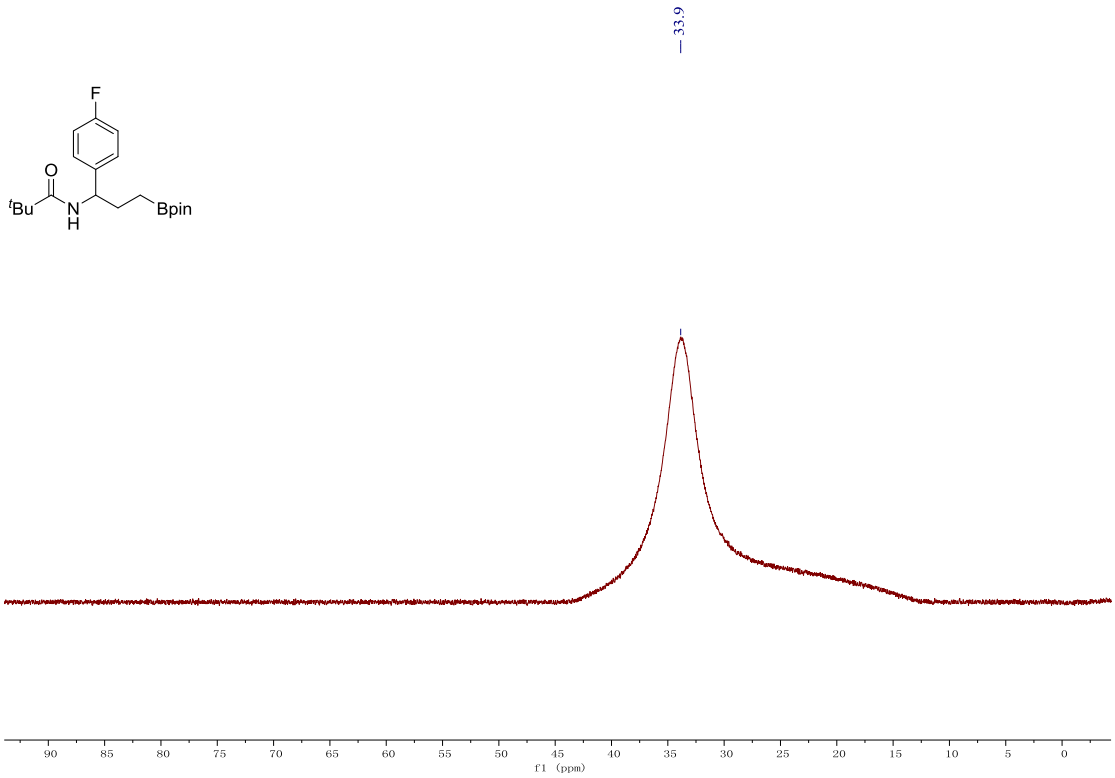
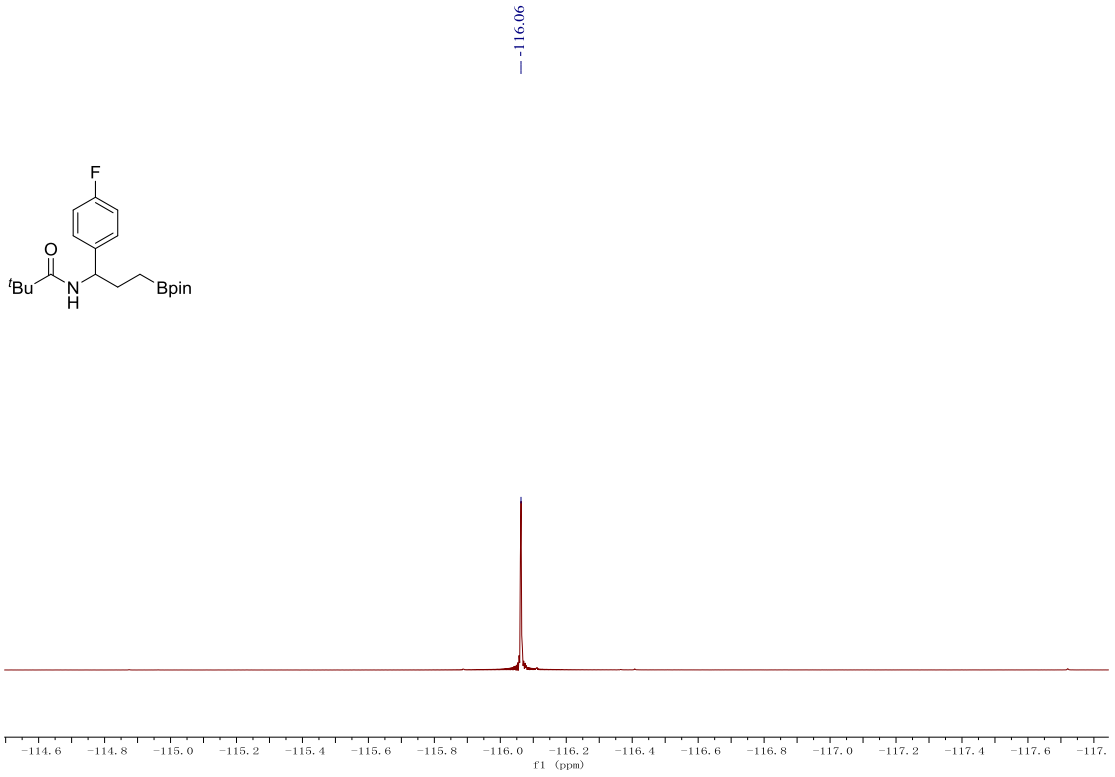


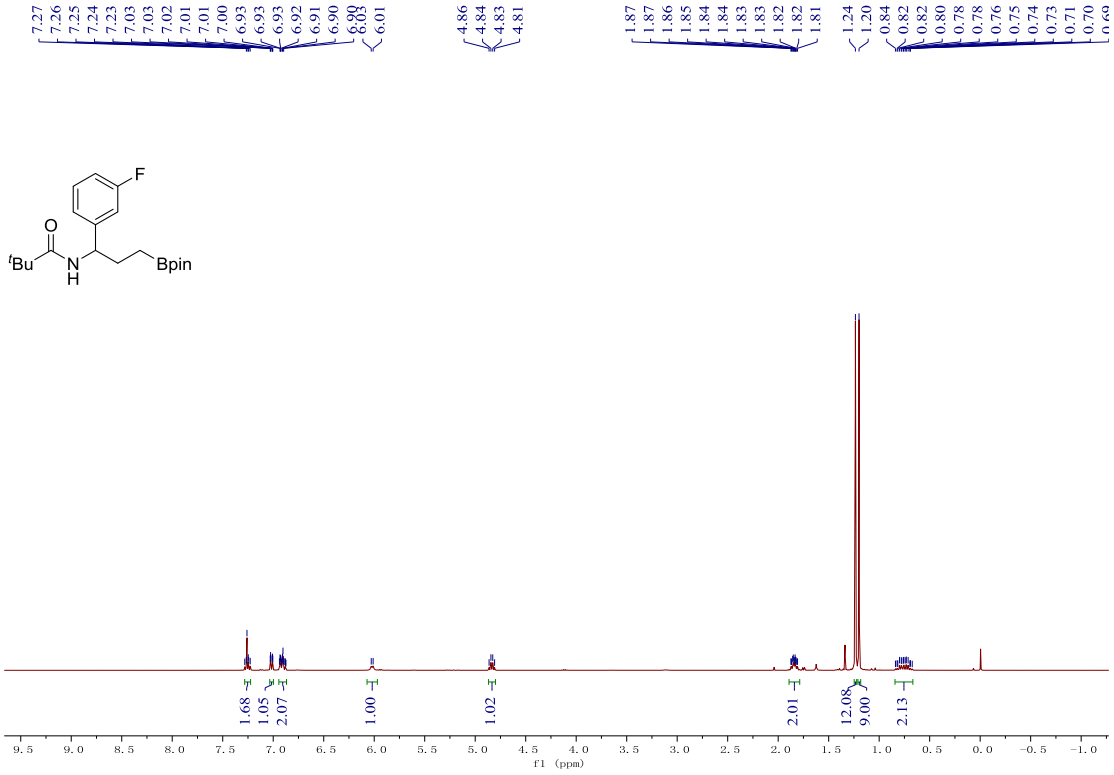
^{11}B NMR of 2j



^{19}F NMR of 2j



^{1}H NMR of 2k



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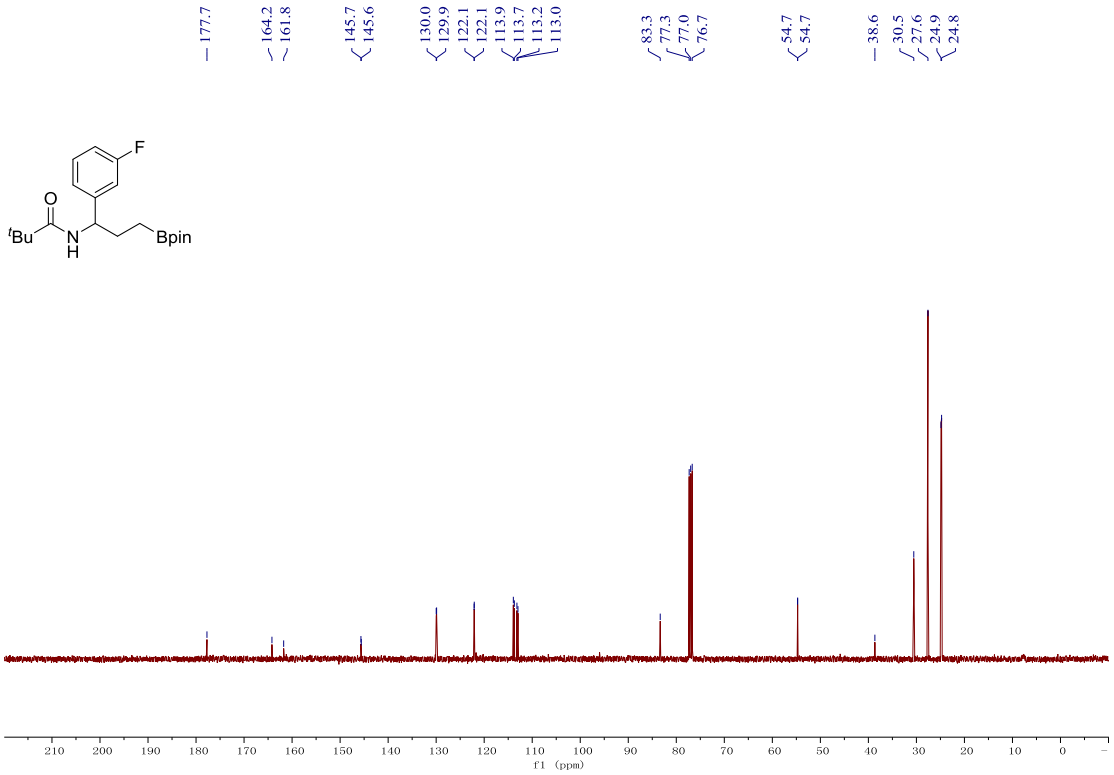

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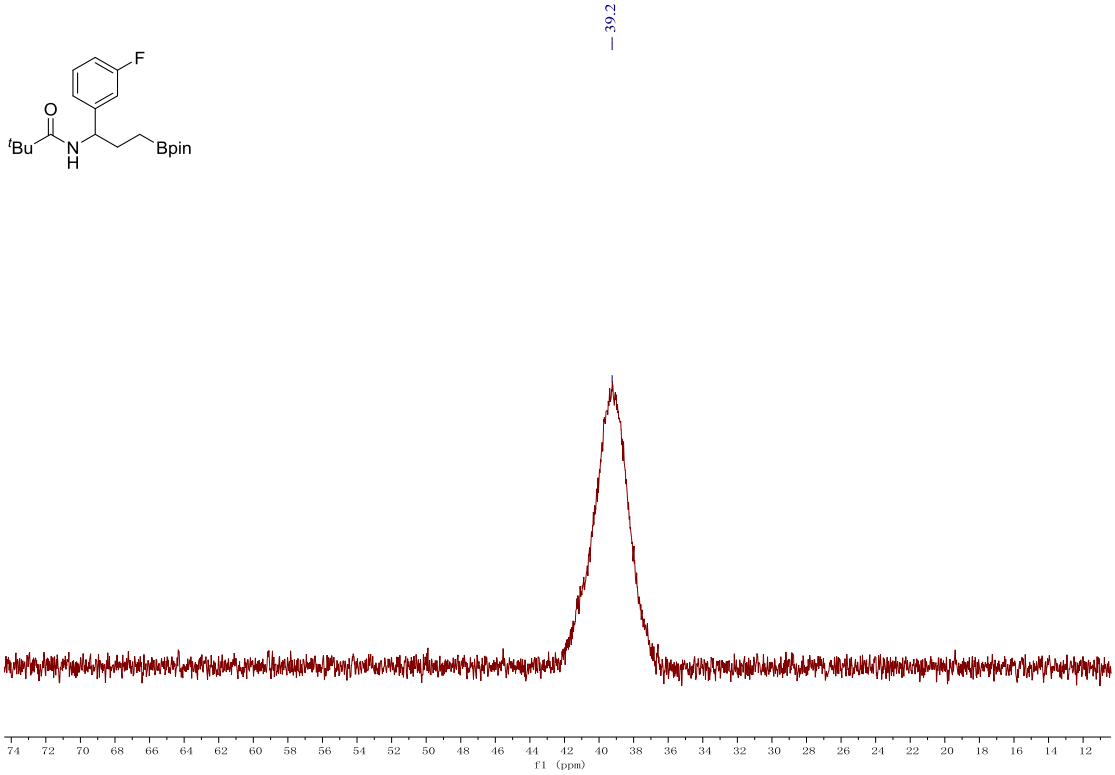

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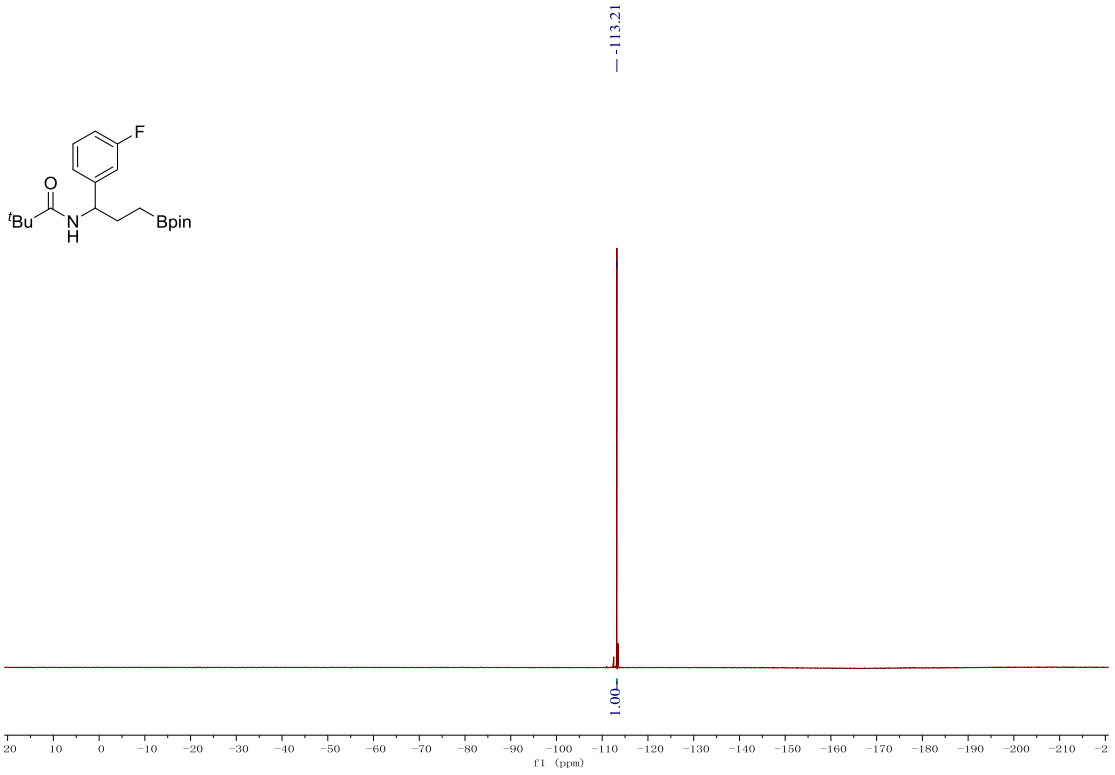
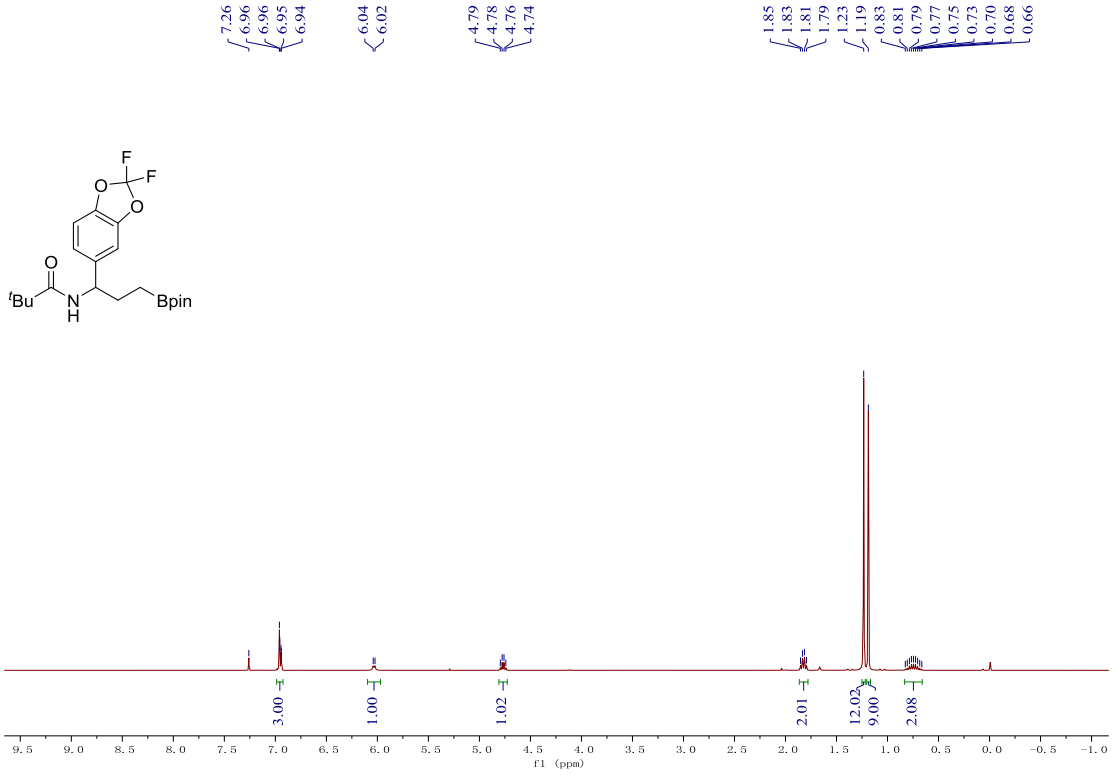


^{1}H NMR of 2l



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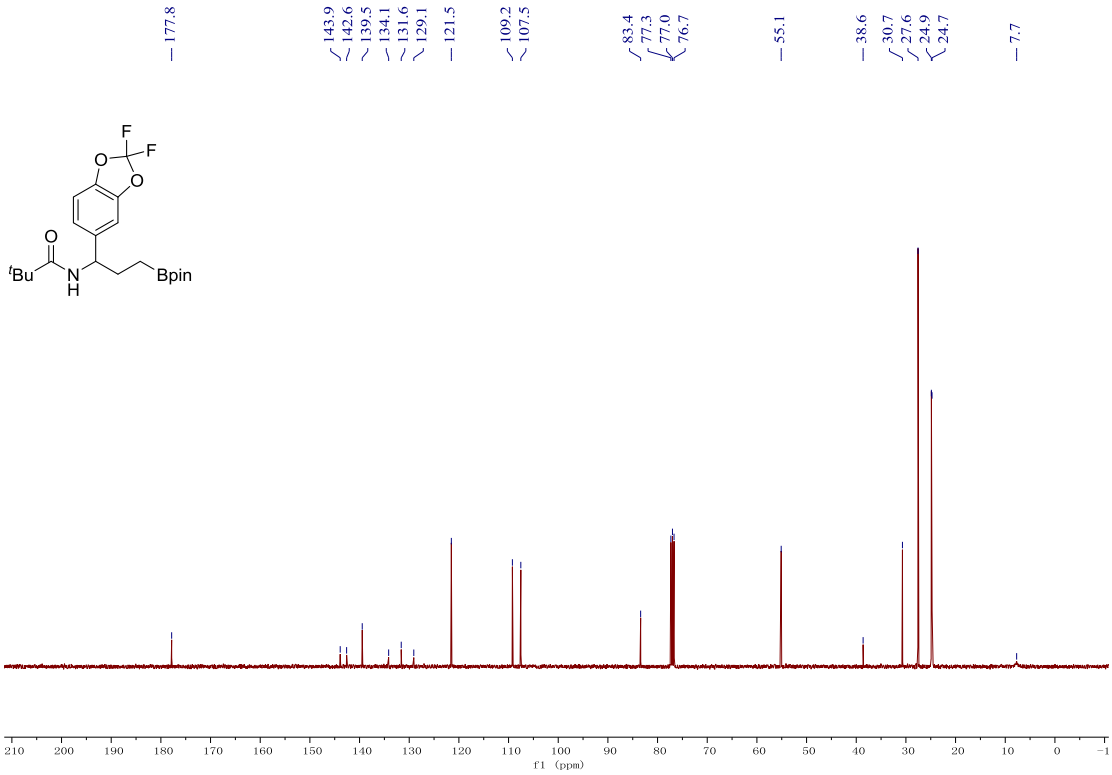

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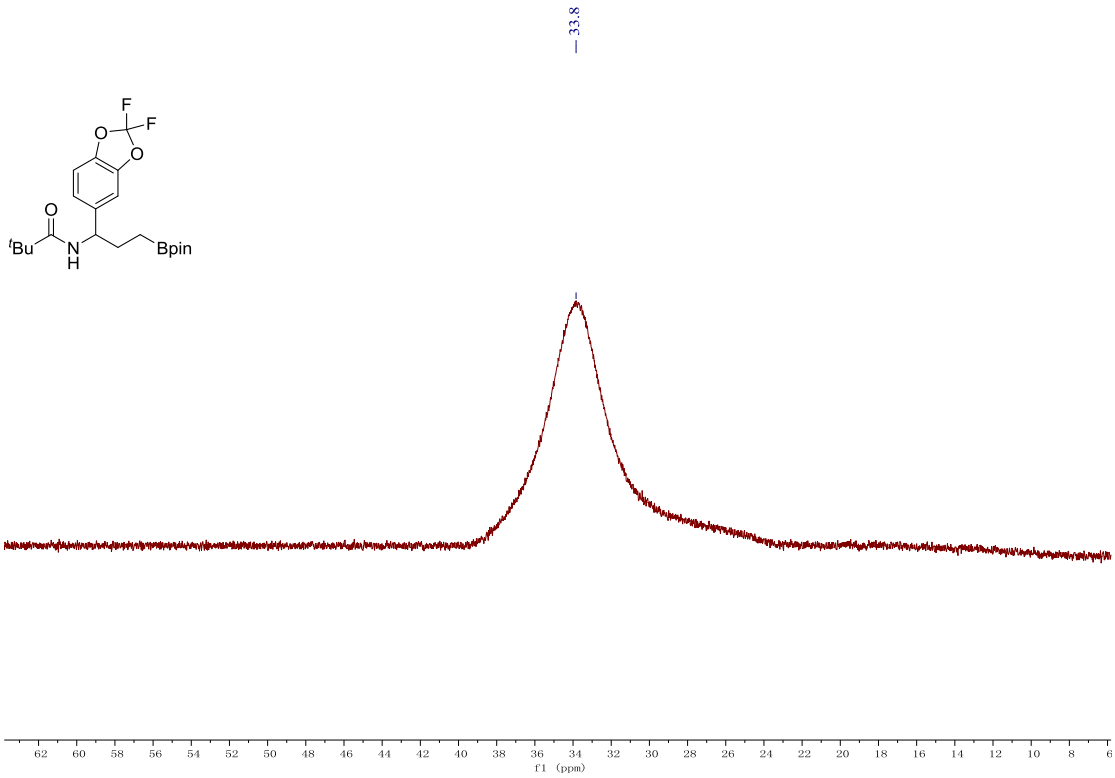

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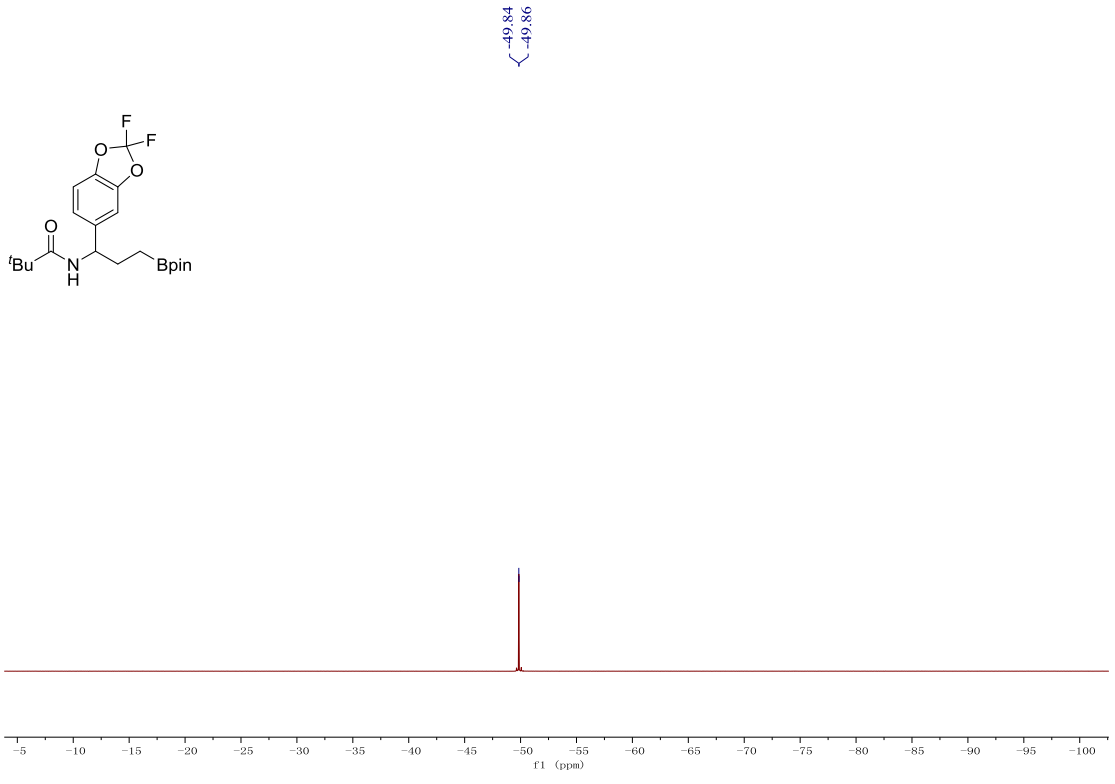
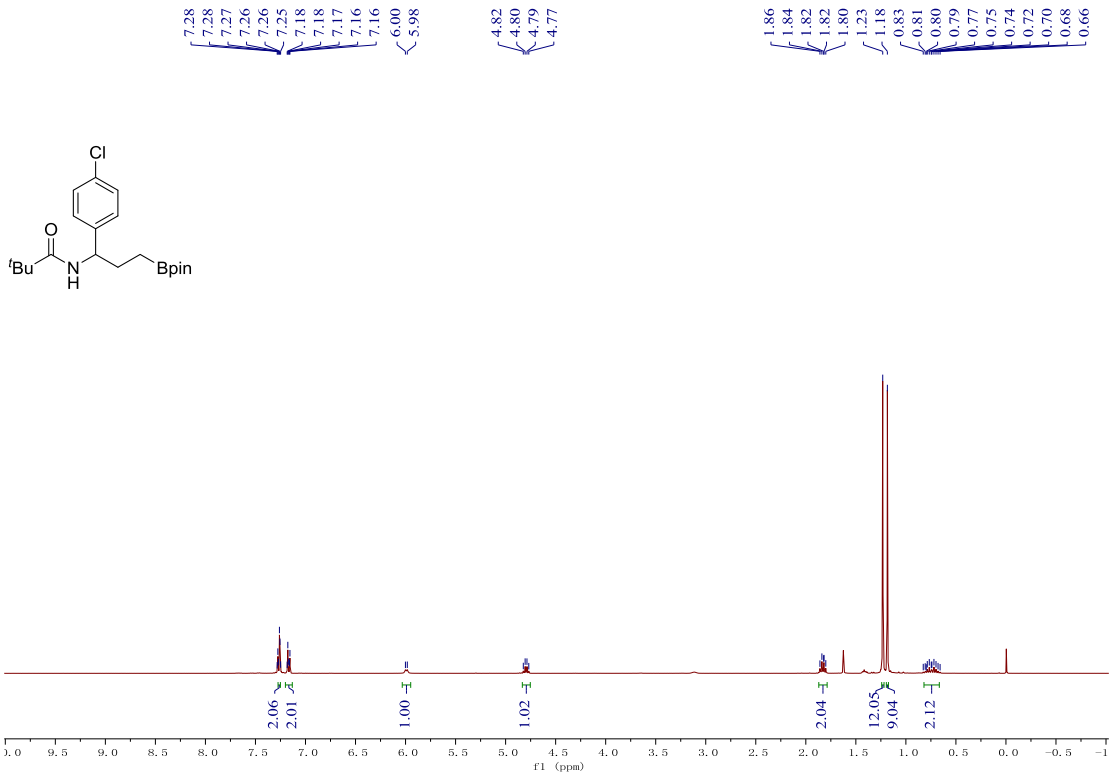
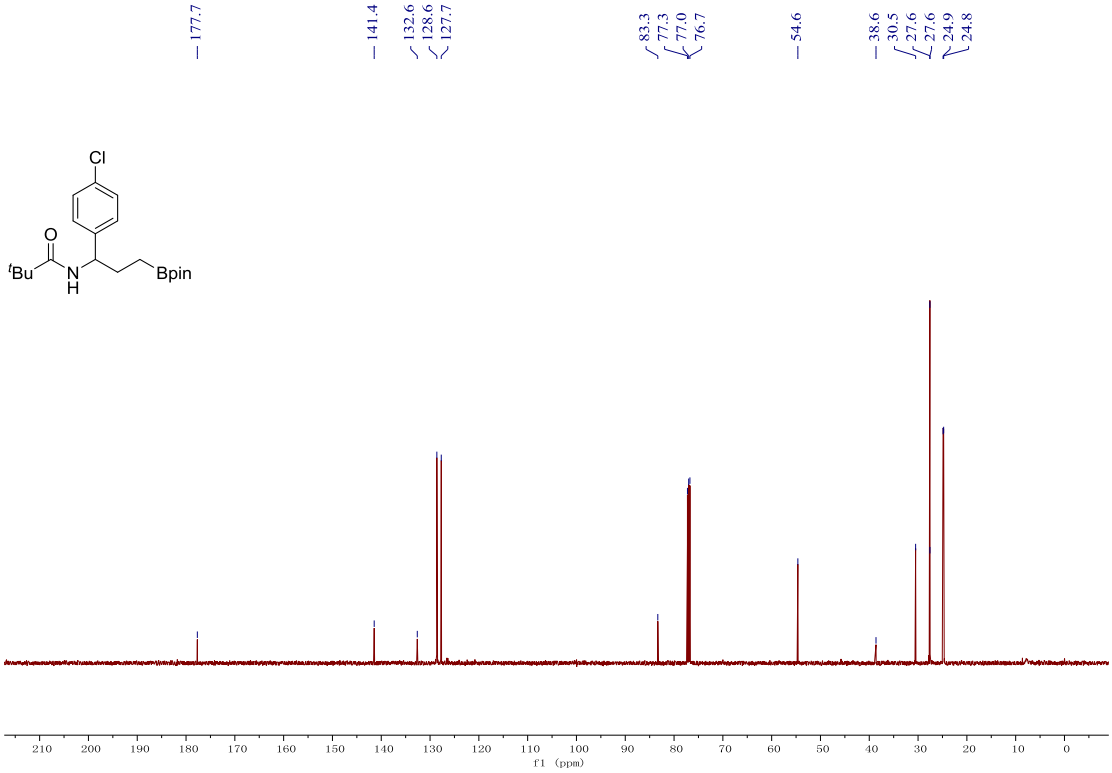


^{1}H NMR of 2m



^{13}C NMR of 2m



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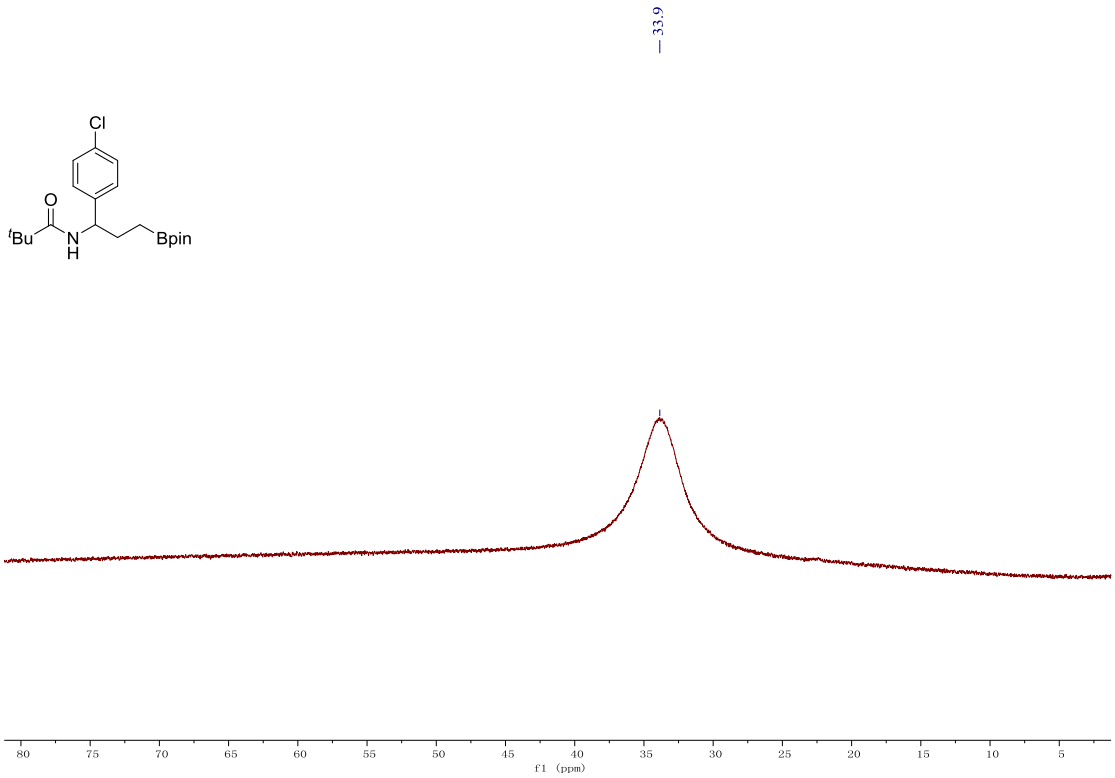

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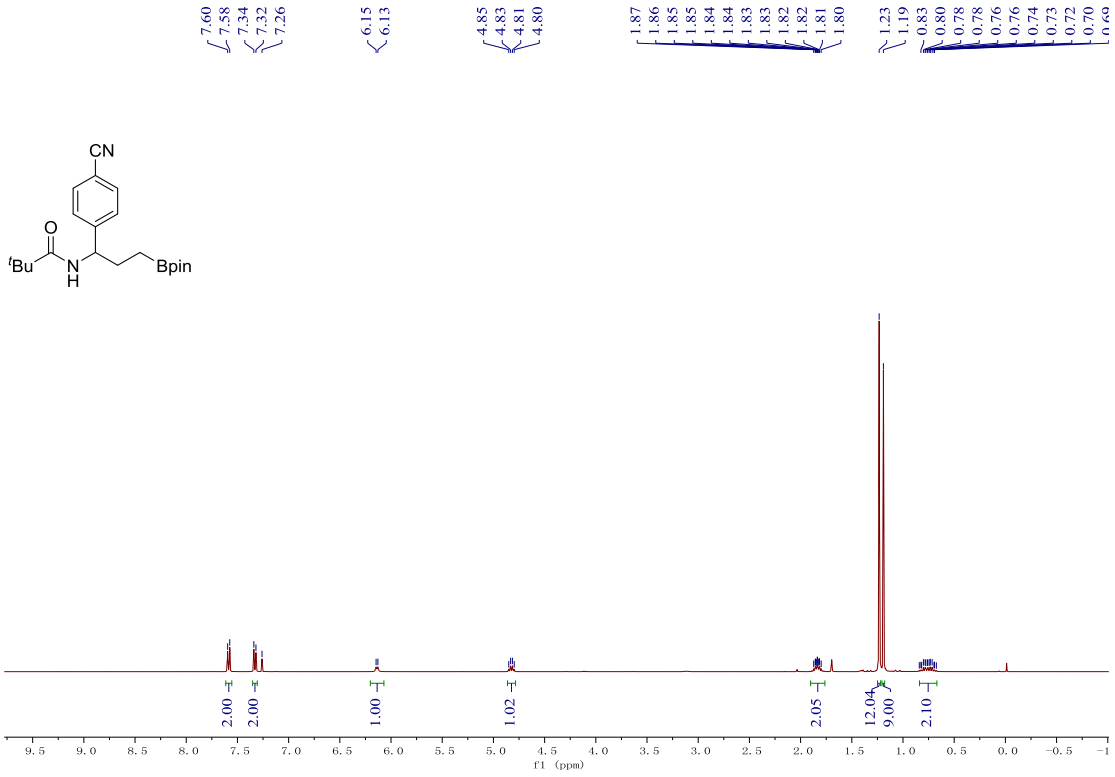

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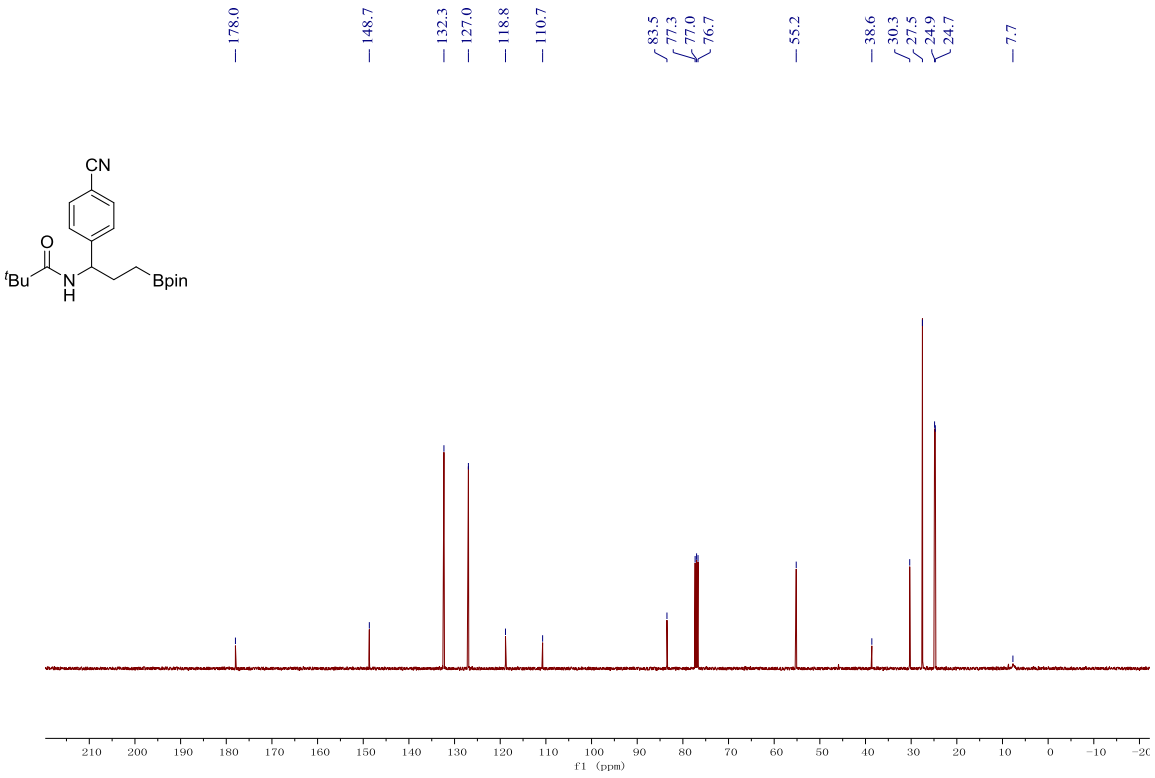

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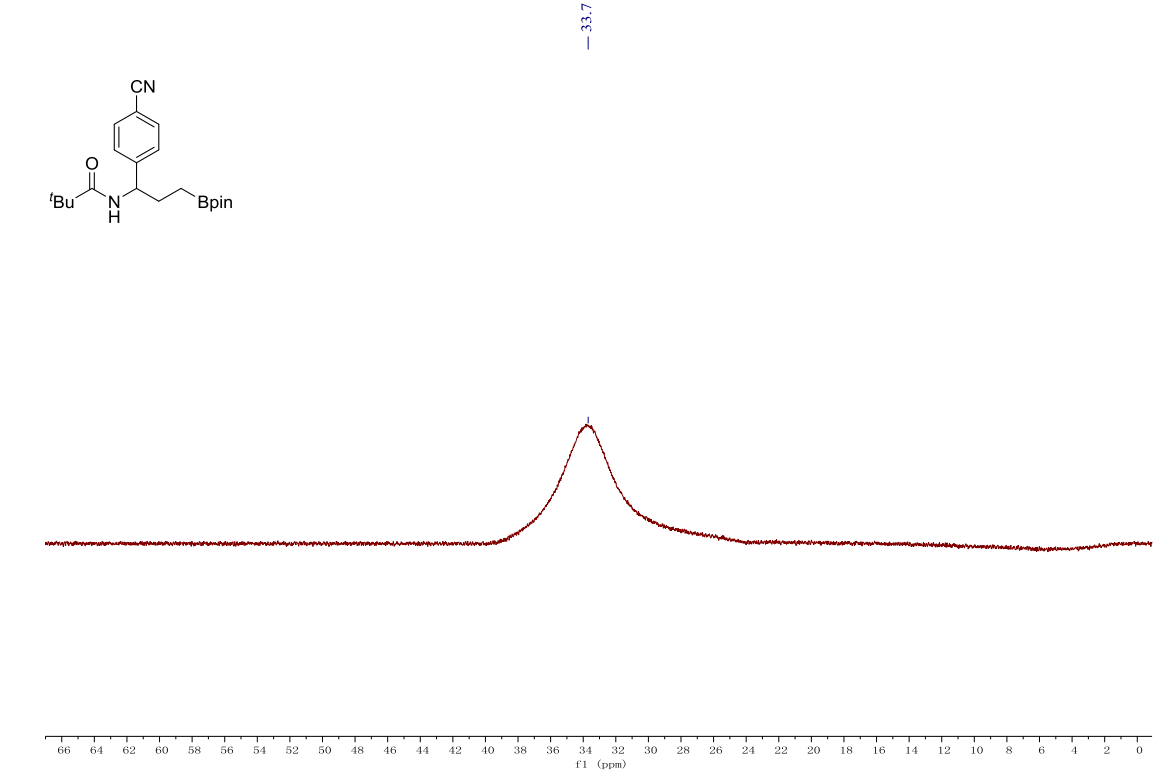
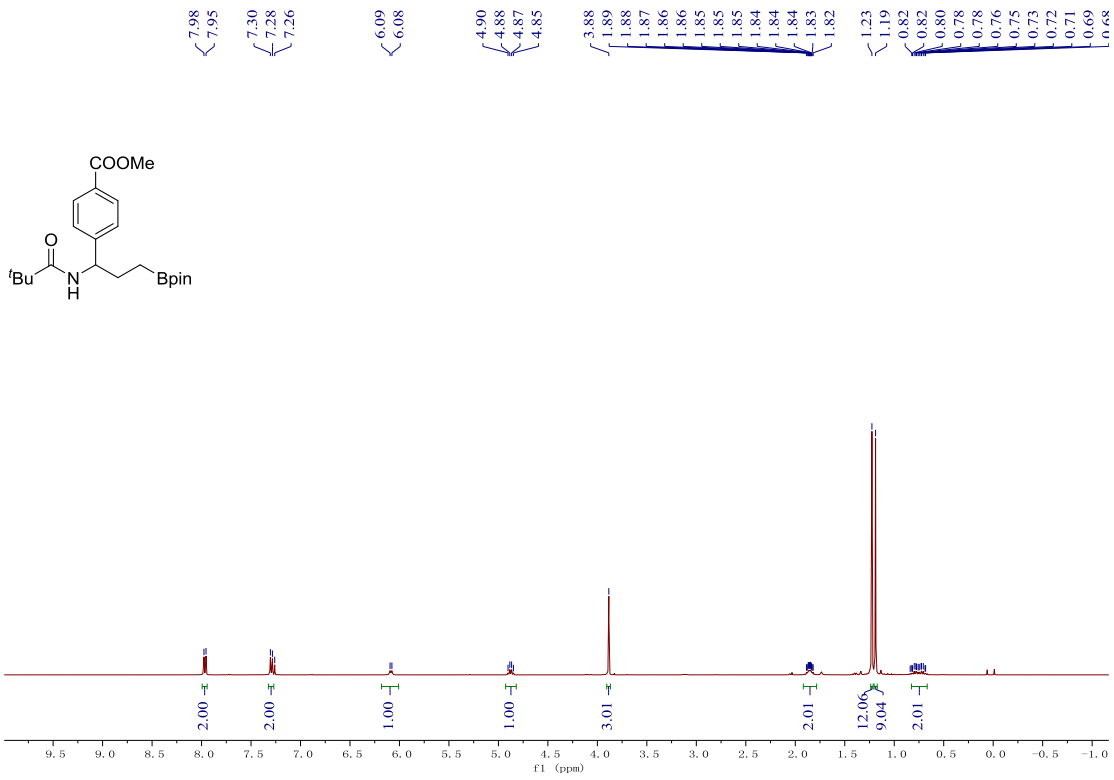
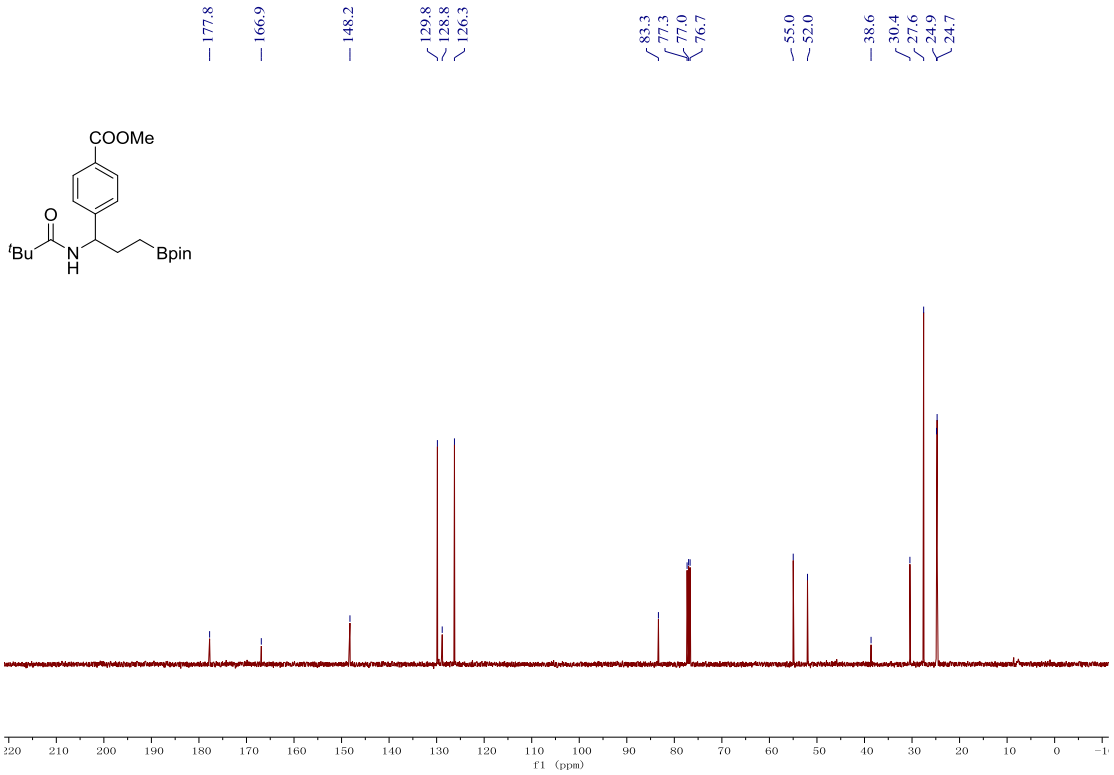


^{1}H NMR of 2o



^{13}C NMR of 2o



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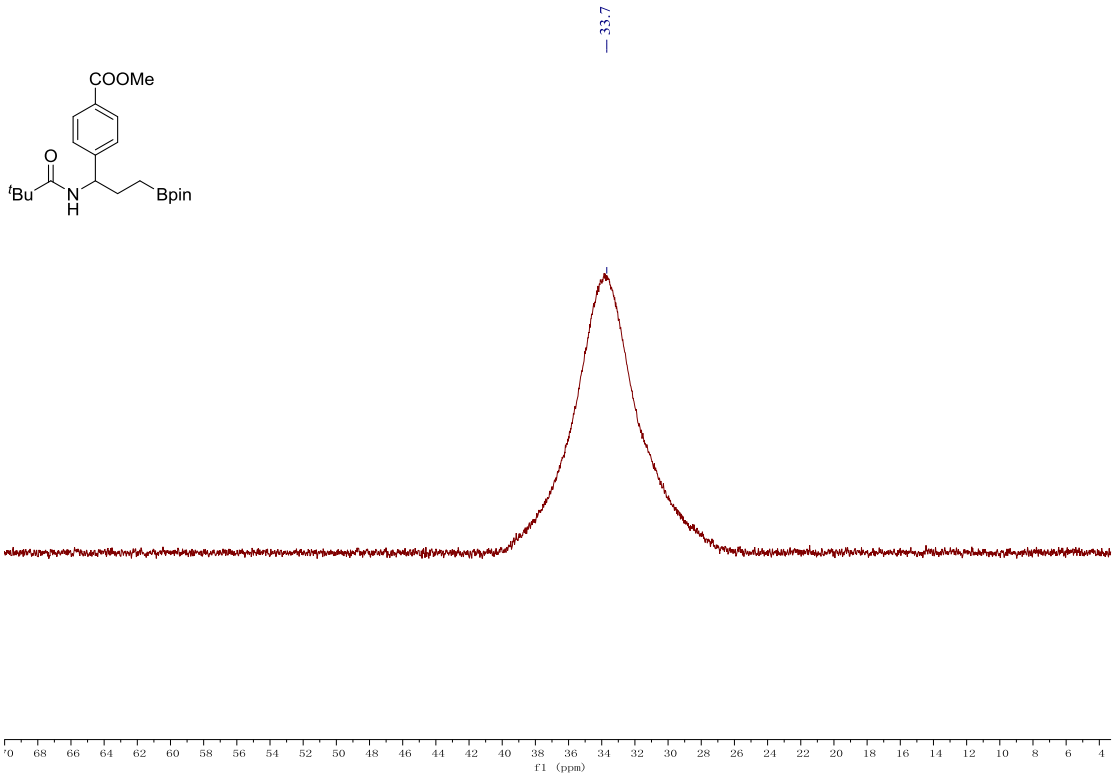
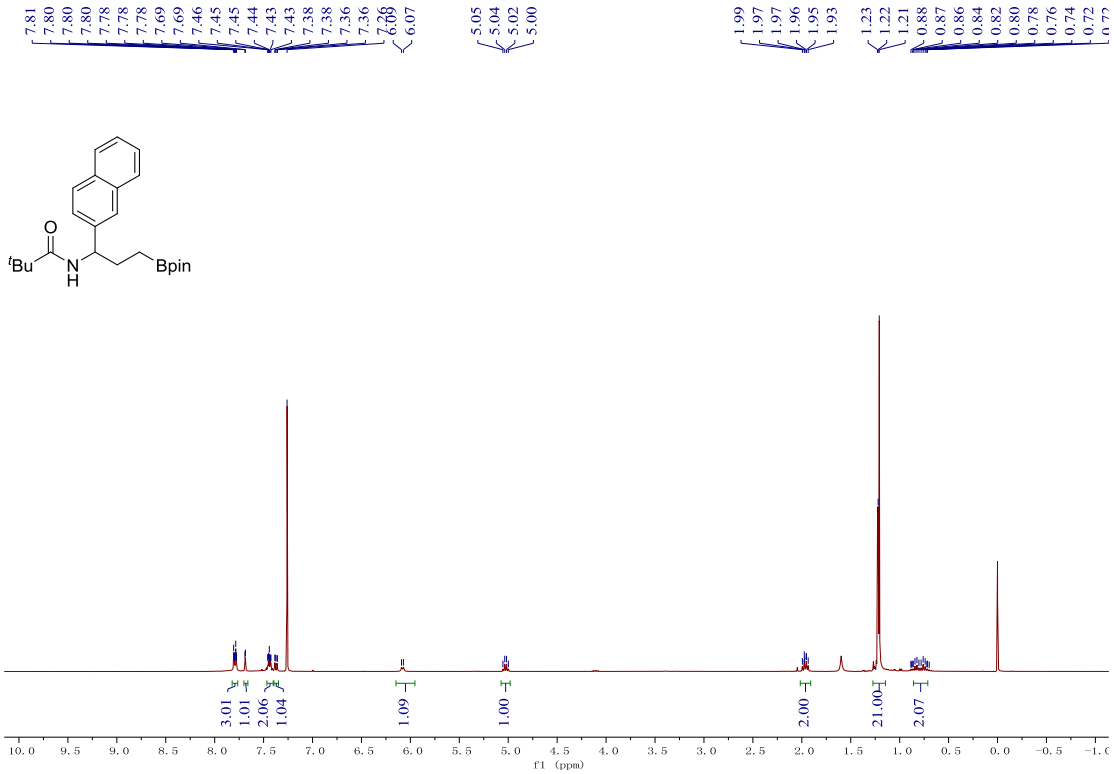
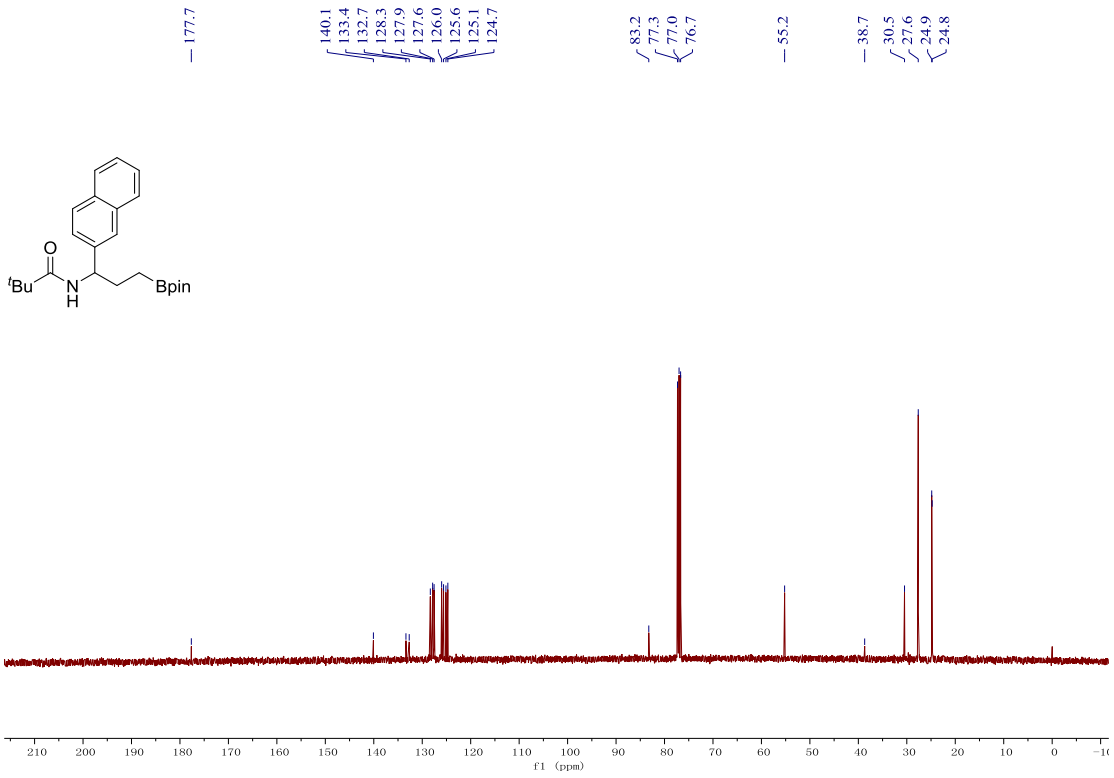


^{1}H NMR of 2p



^{13}C NMR of 2p



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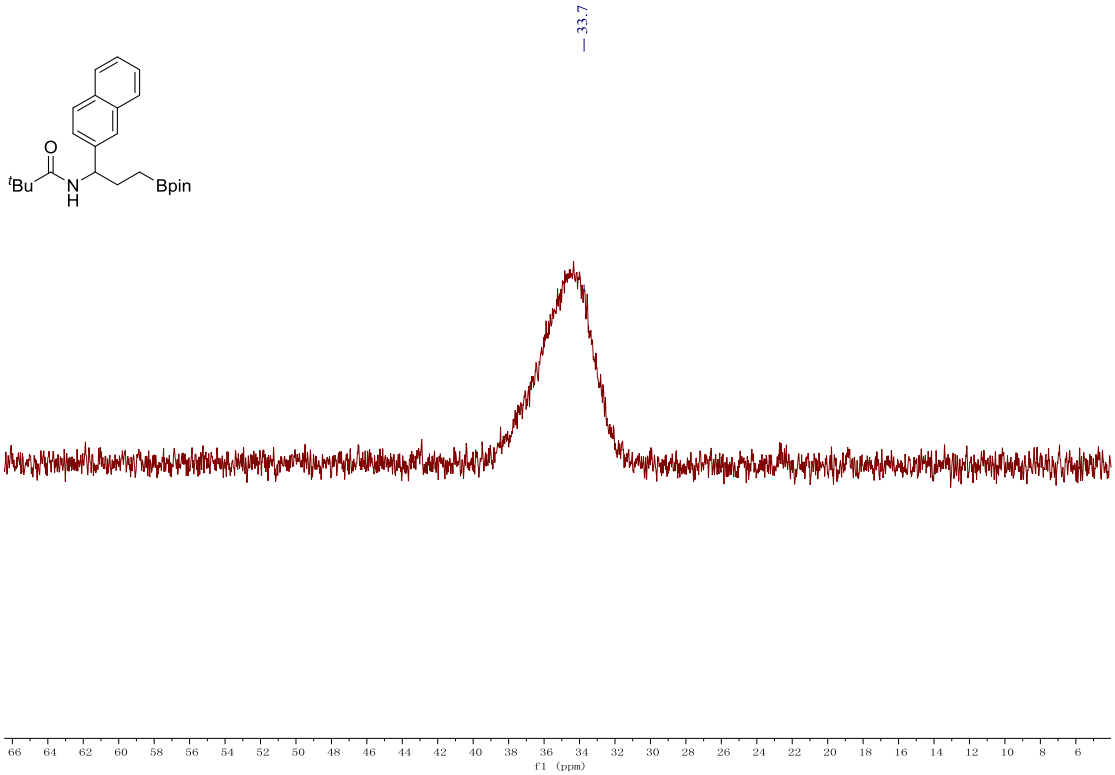

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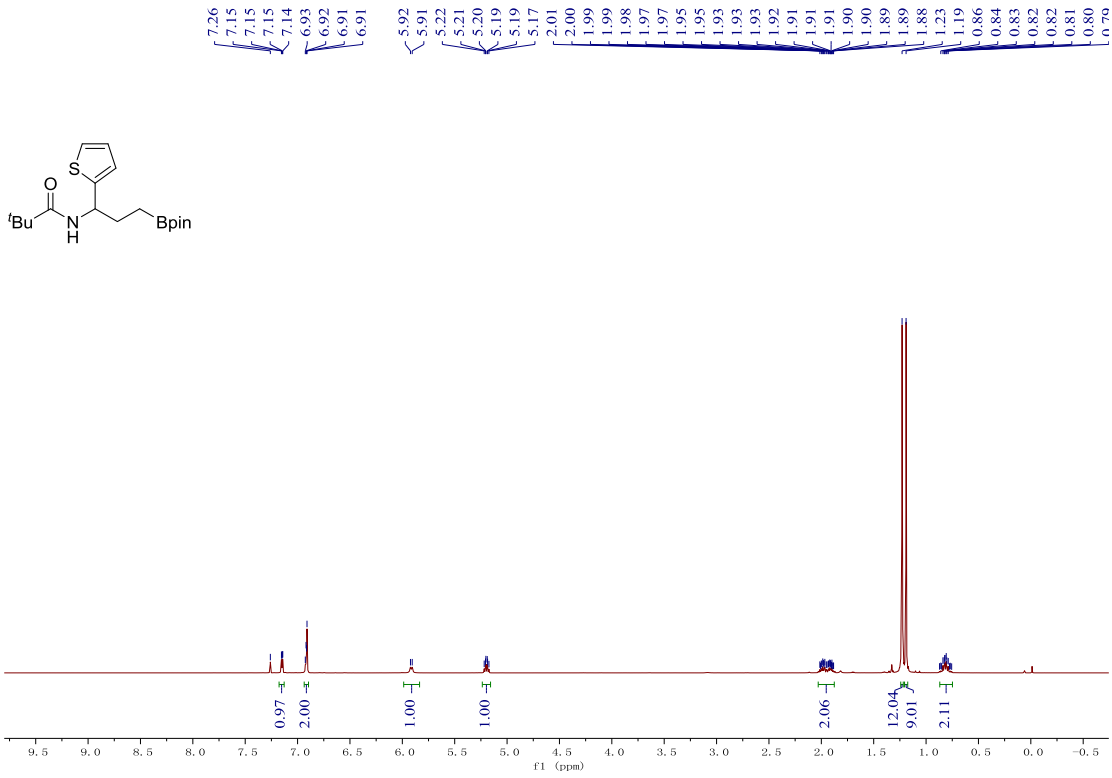
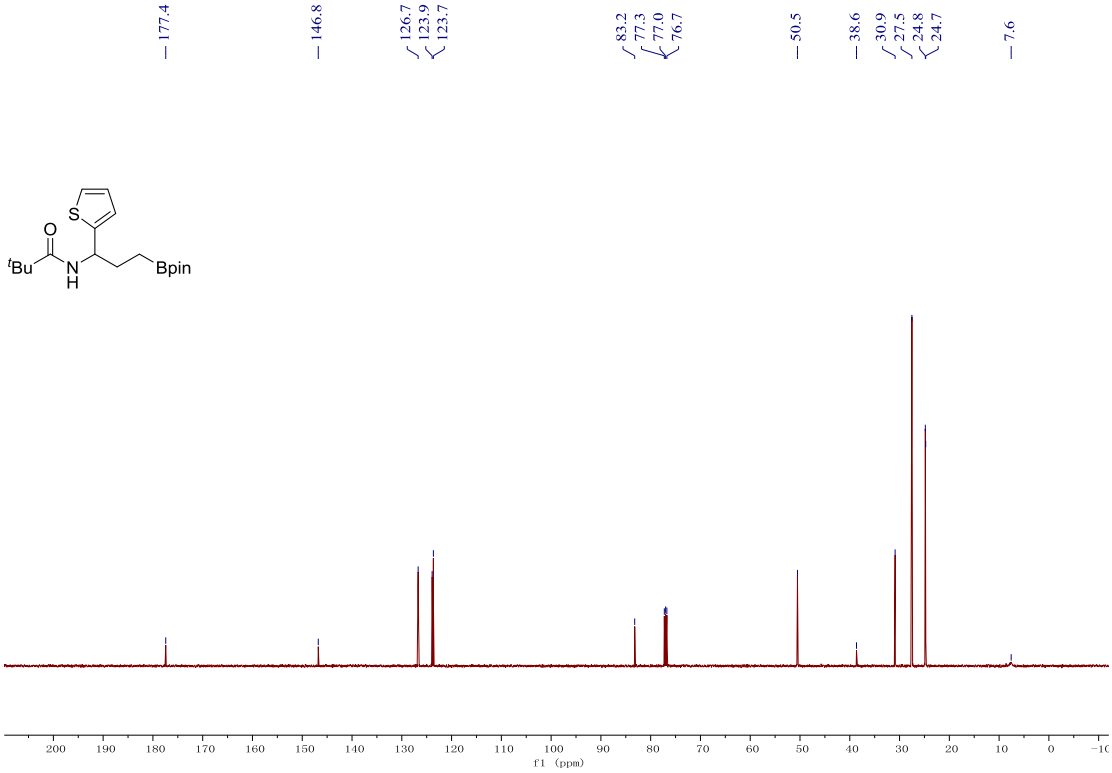
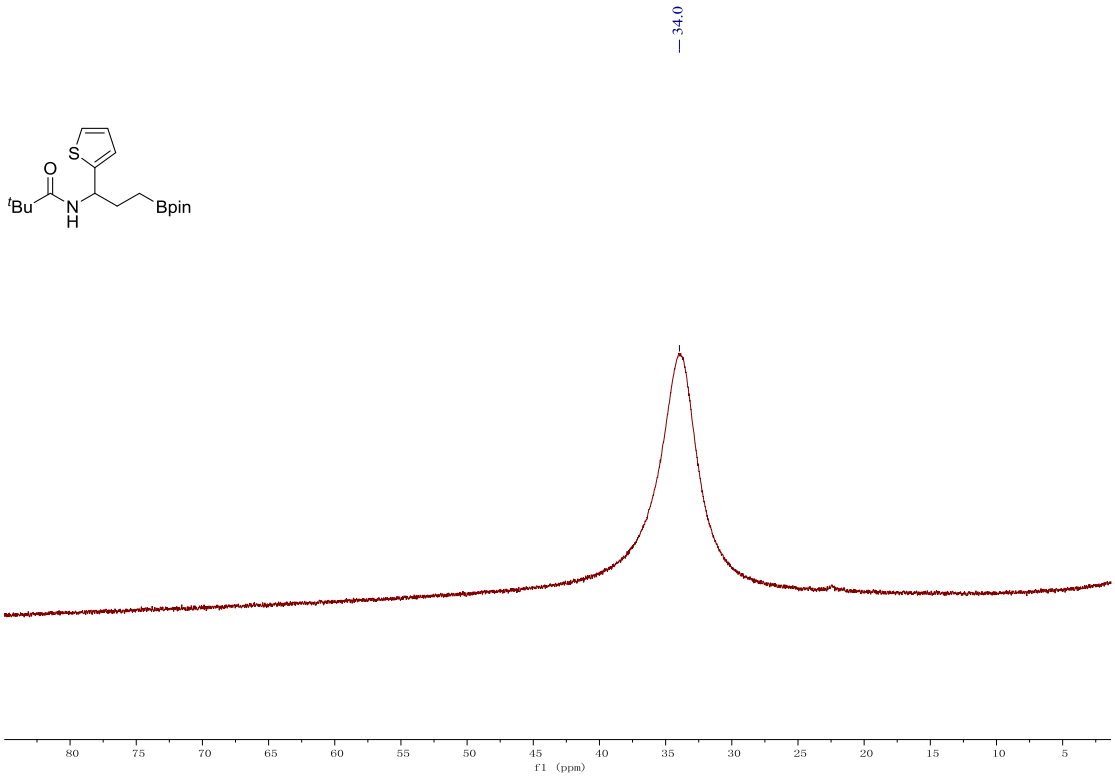


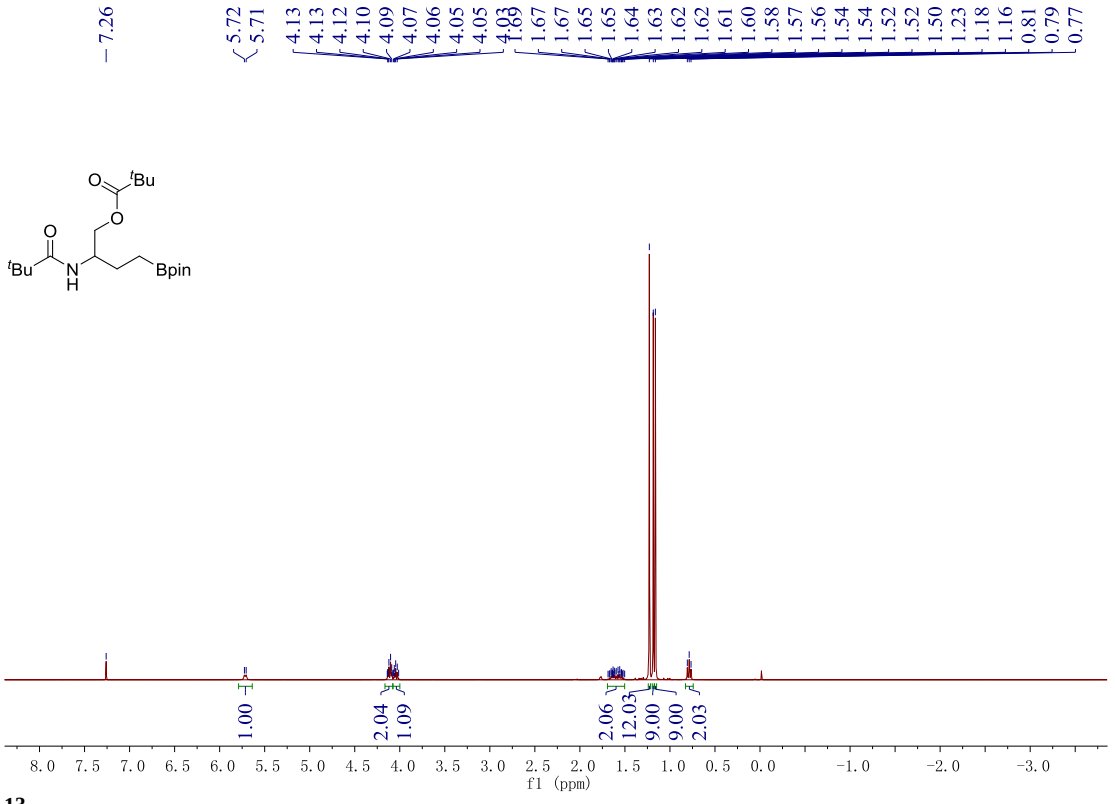
^{13}C NMR of 2q



^{11}B NMR of 2q



^{1}H NMR of 2r



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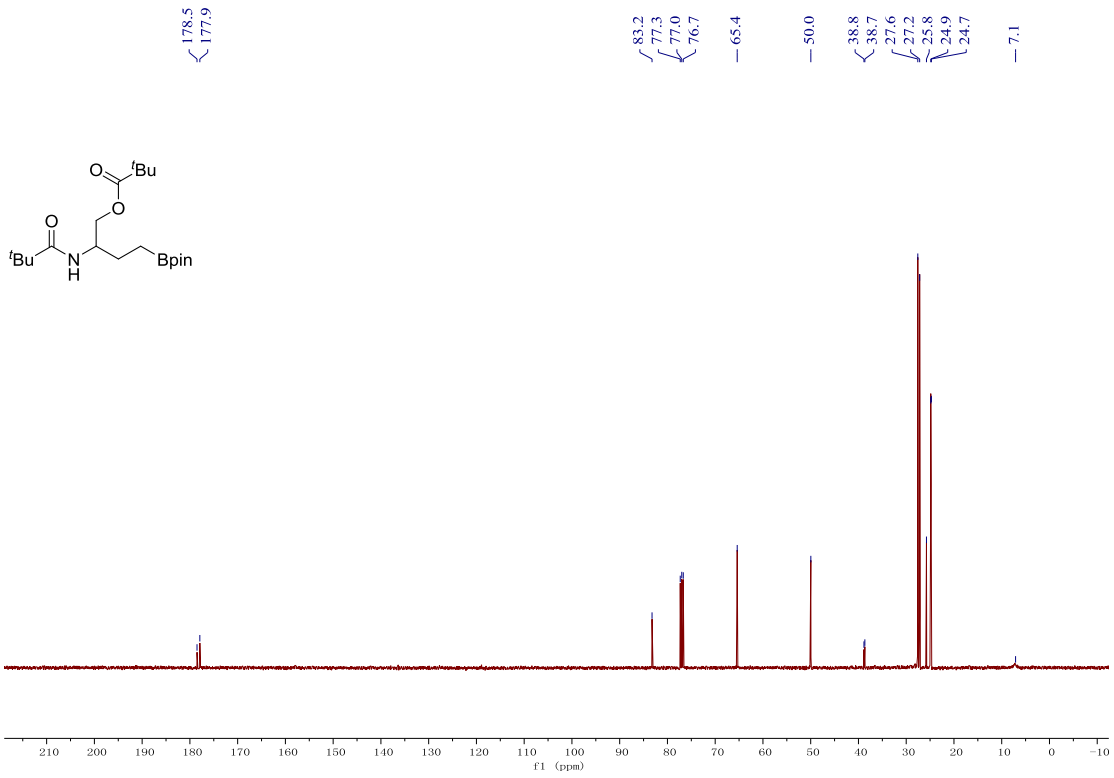
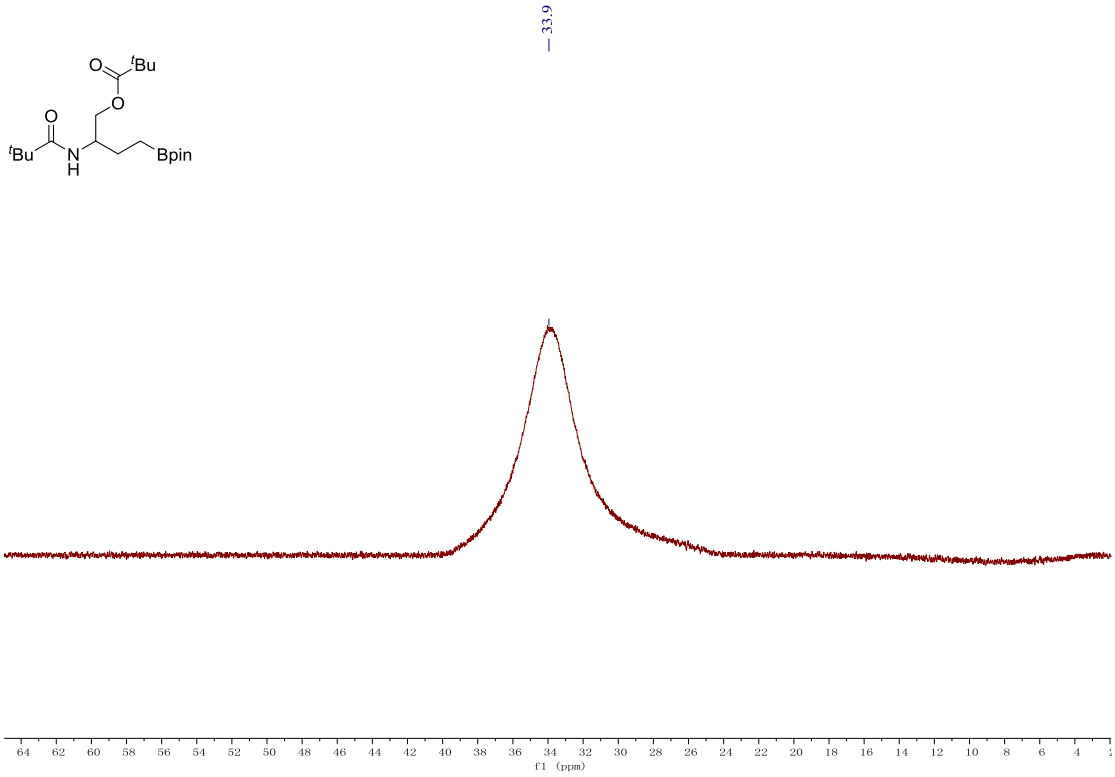
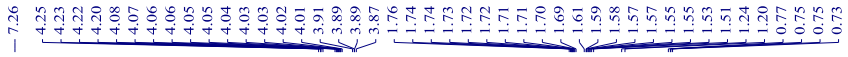
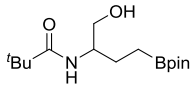


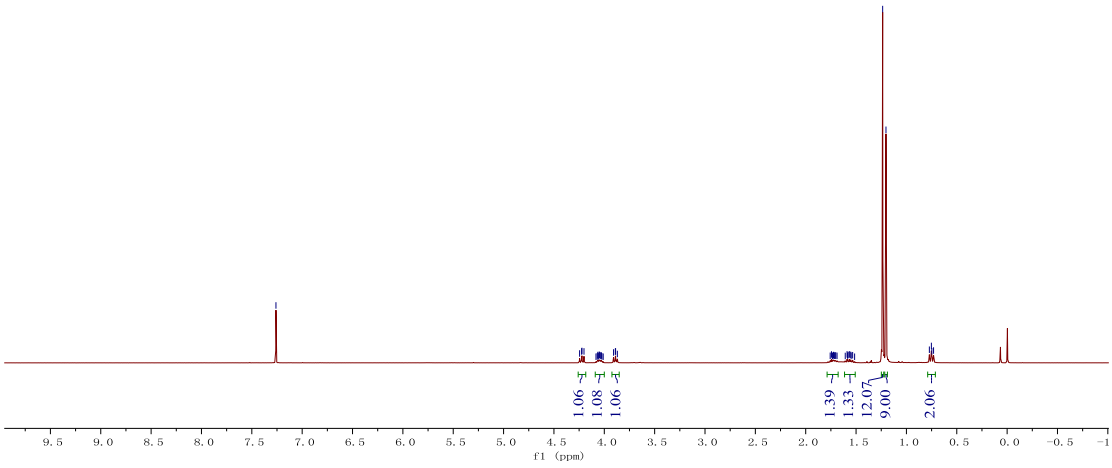
^{11}B NMR of 2r



^{1}H NMR of 2s







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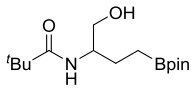

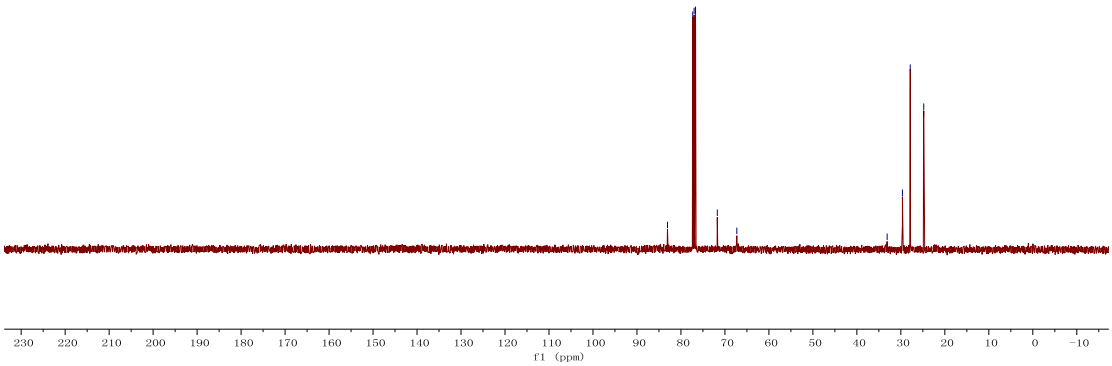

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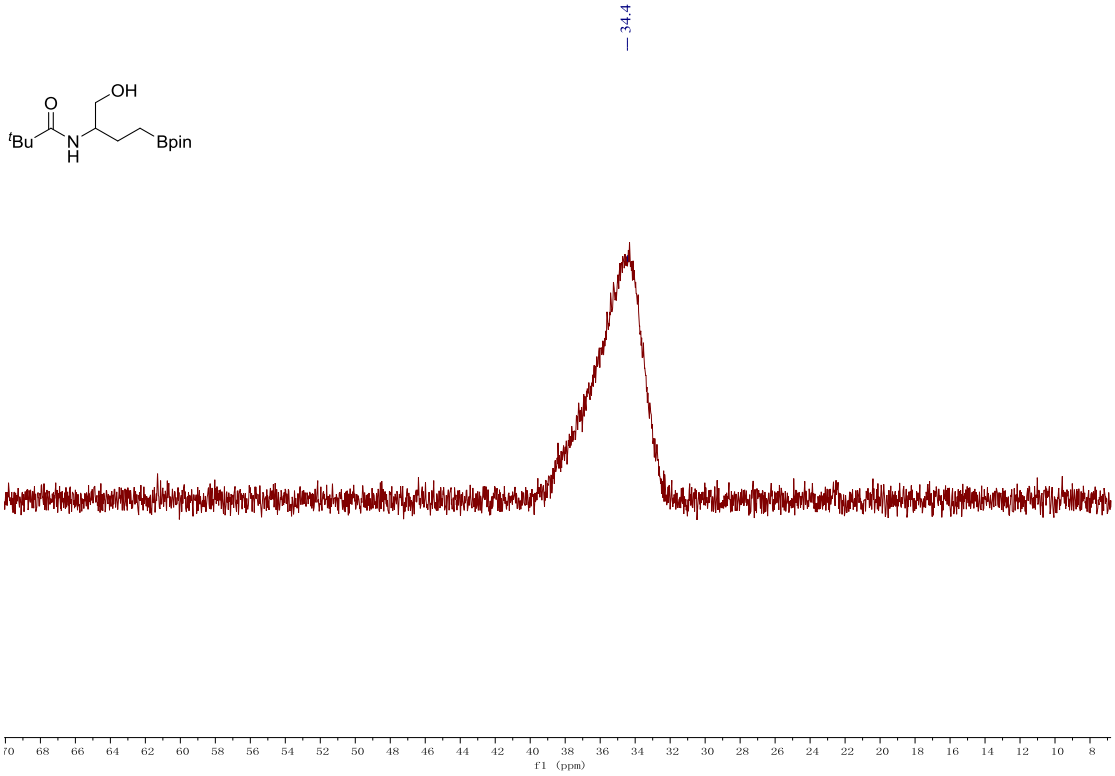

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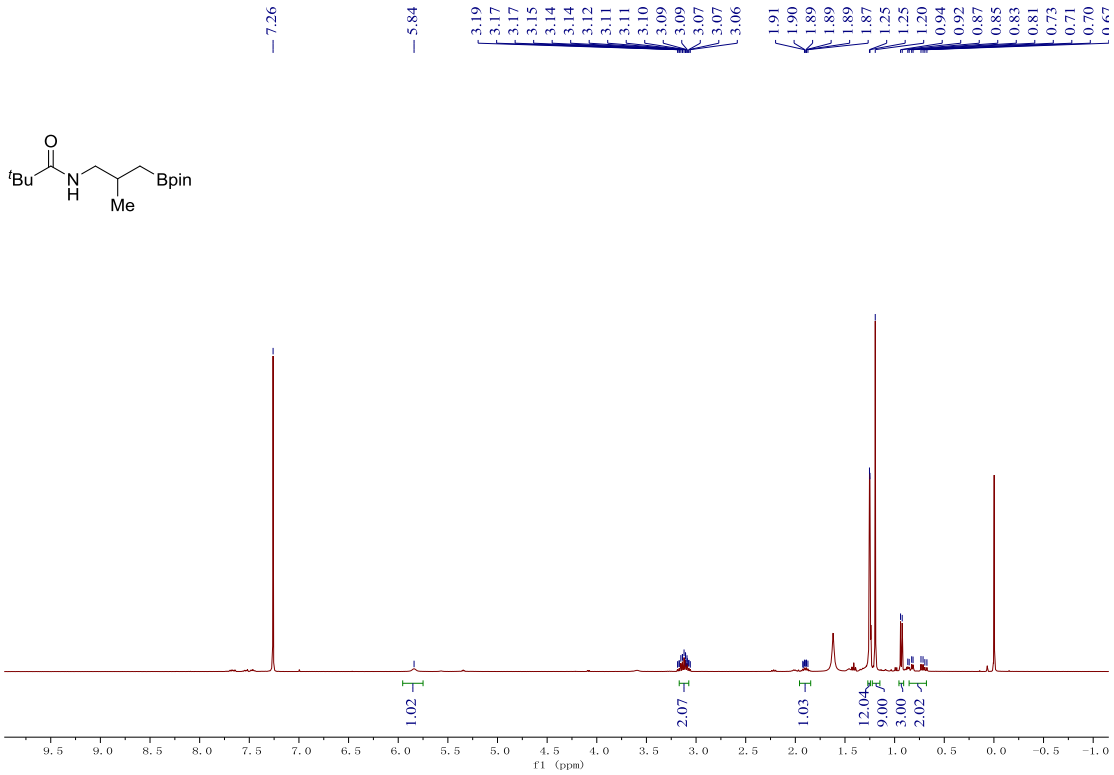

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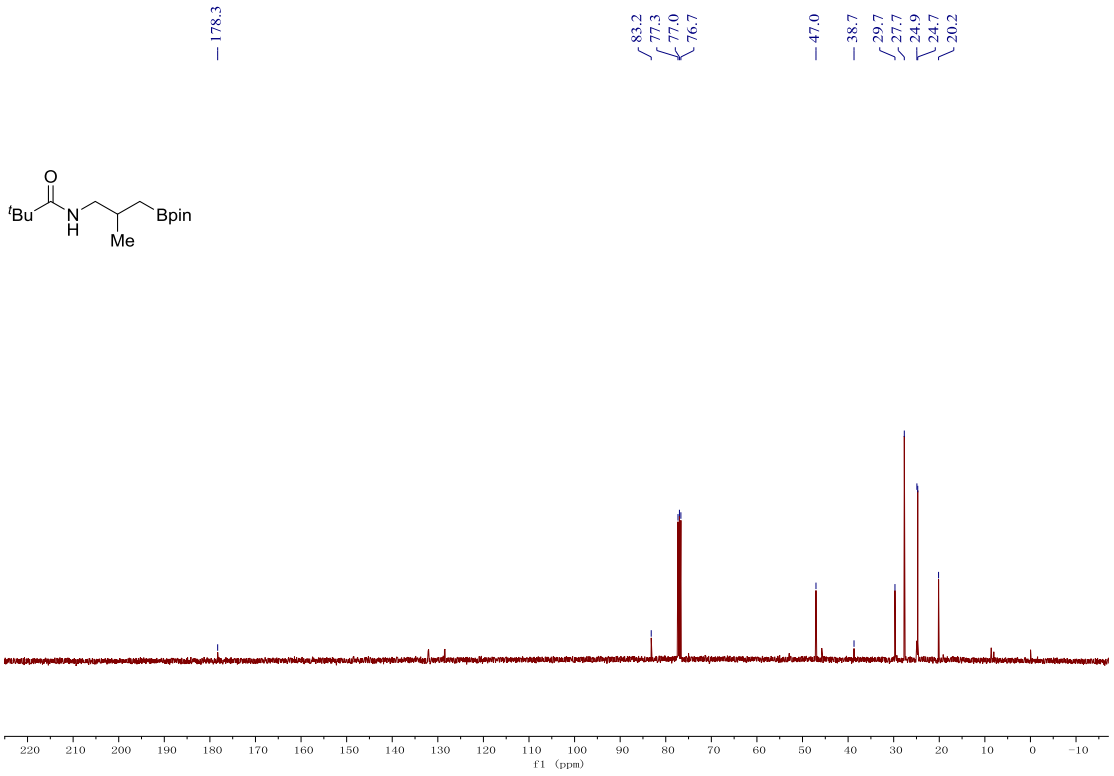

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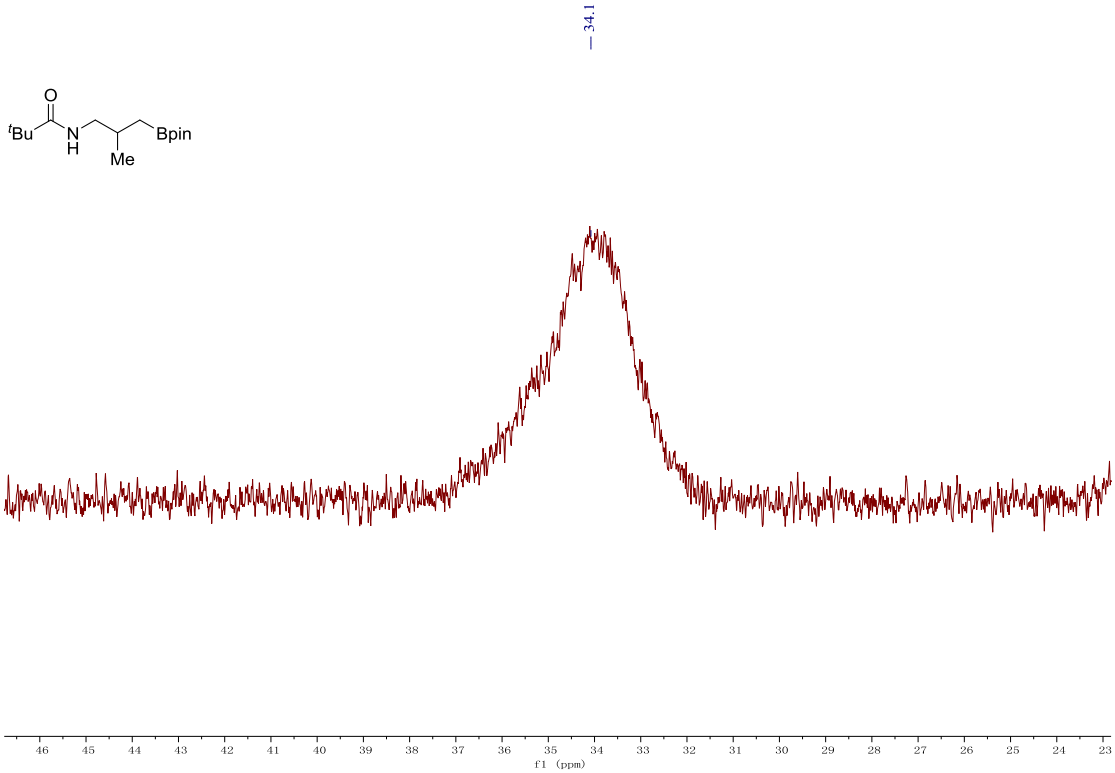
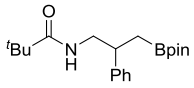
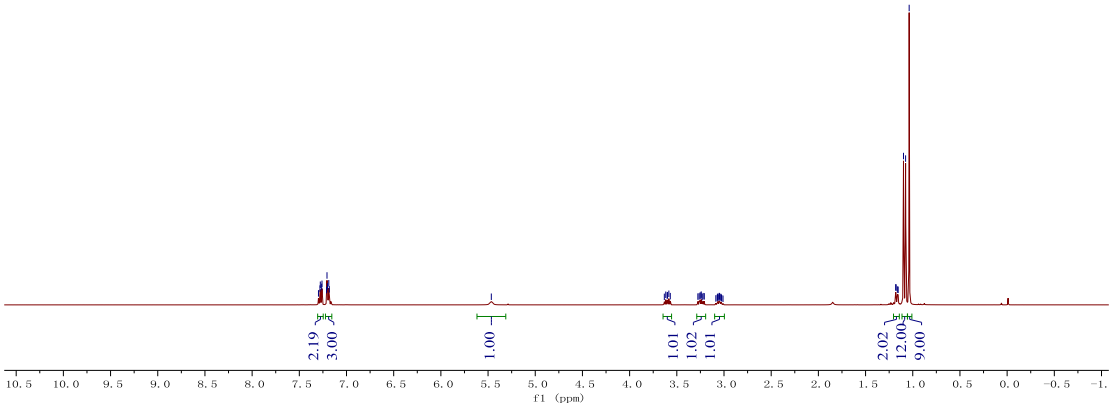


^{1}H NMR of 2u





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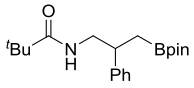

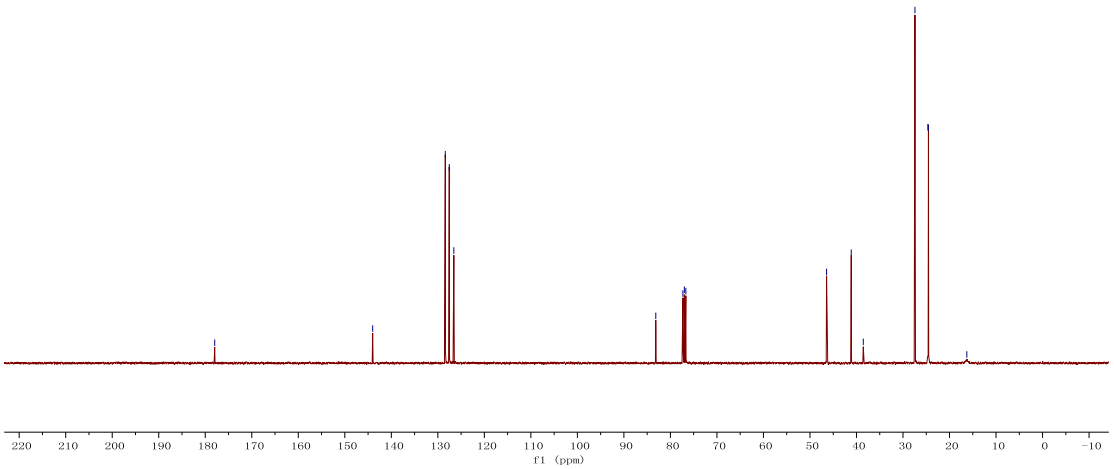

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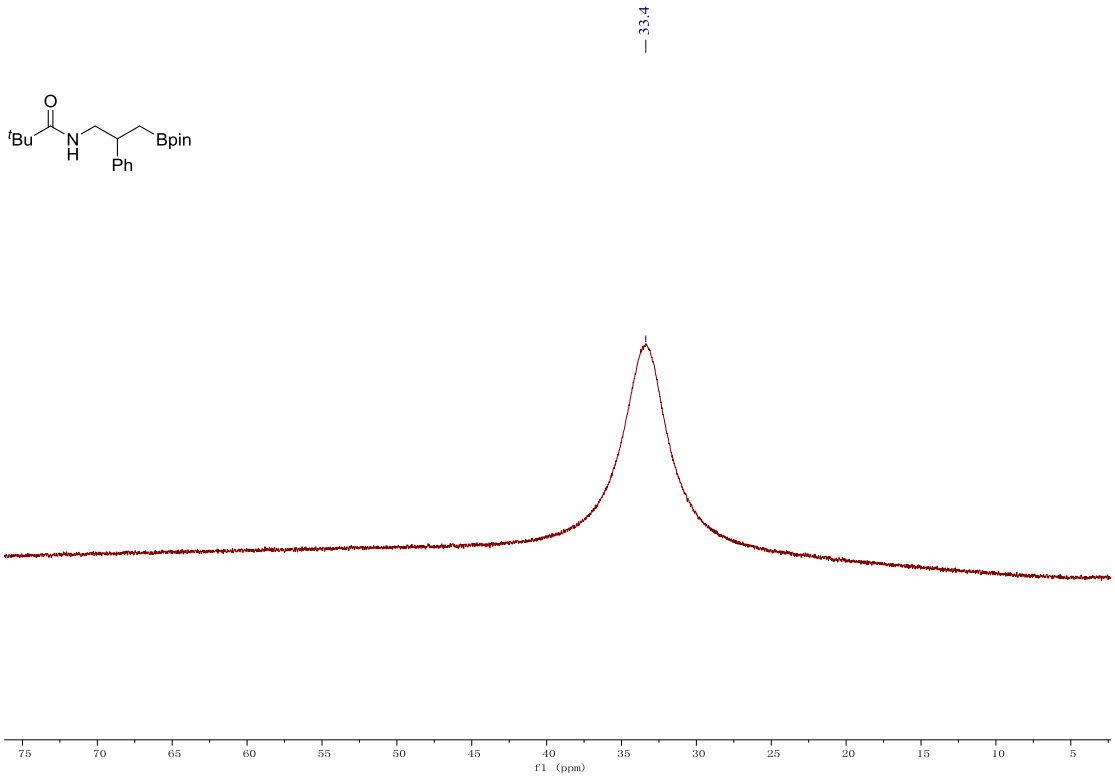
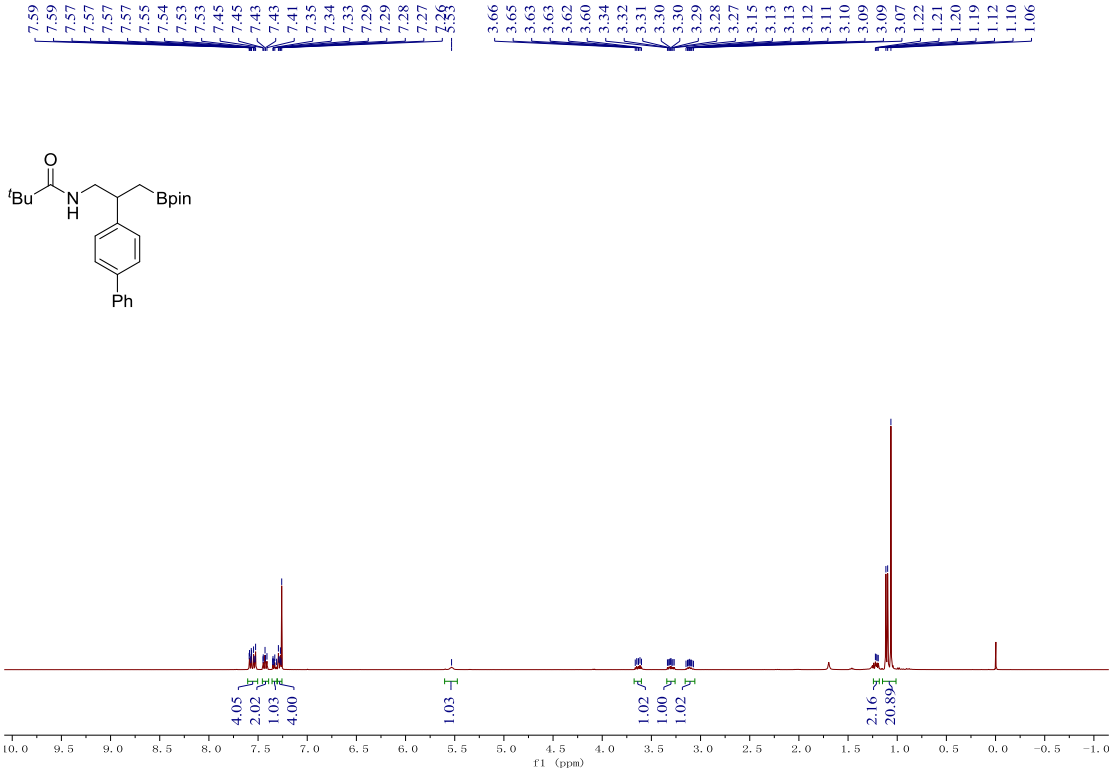
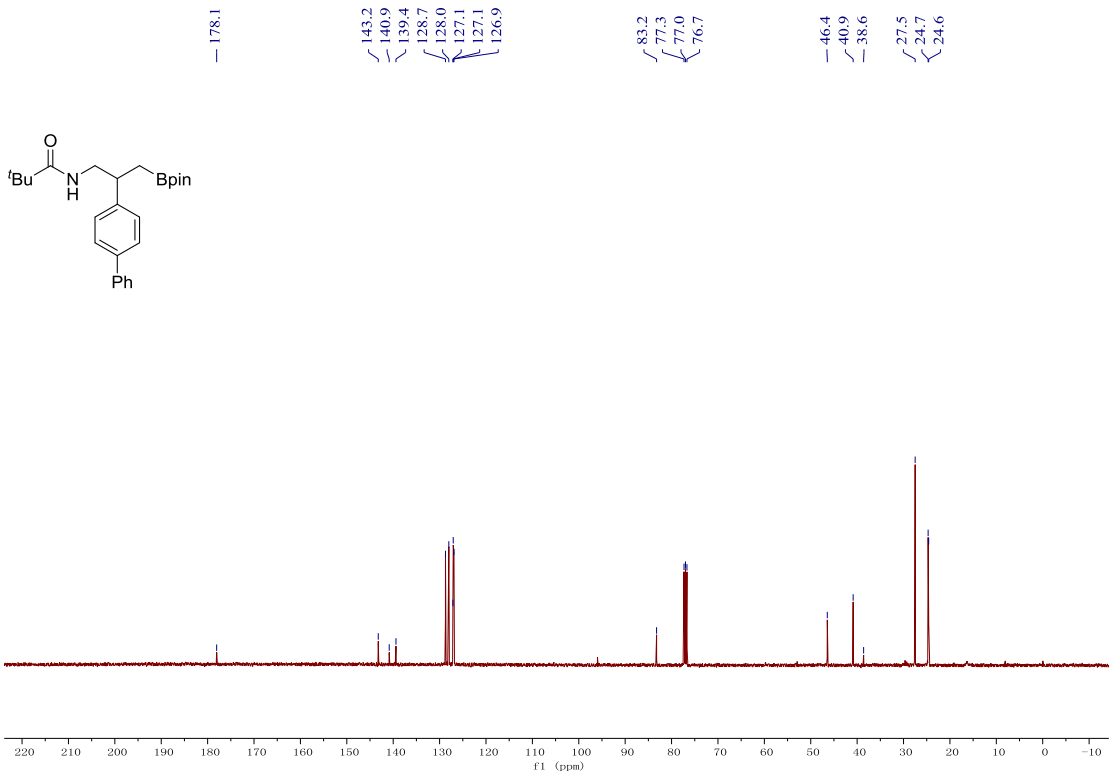


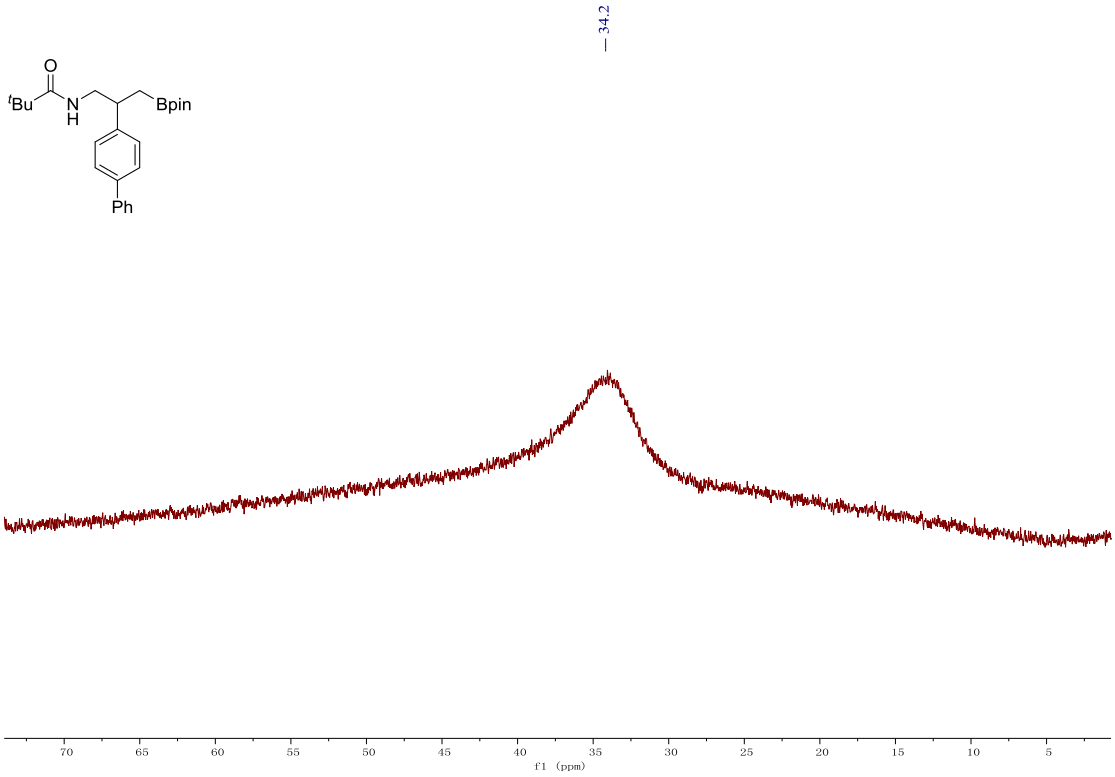
^{1}H NMR of 2v



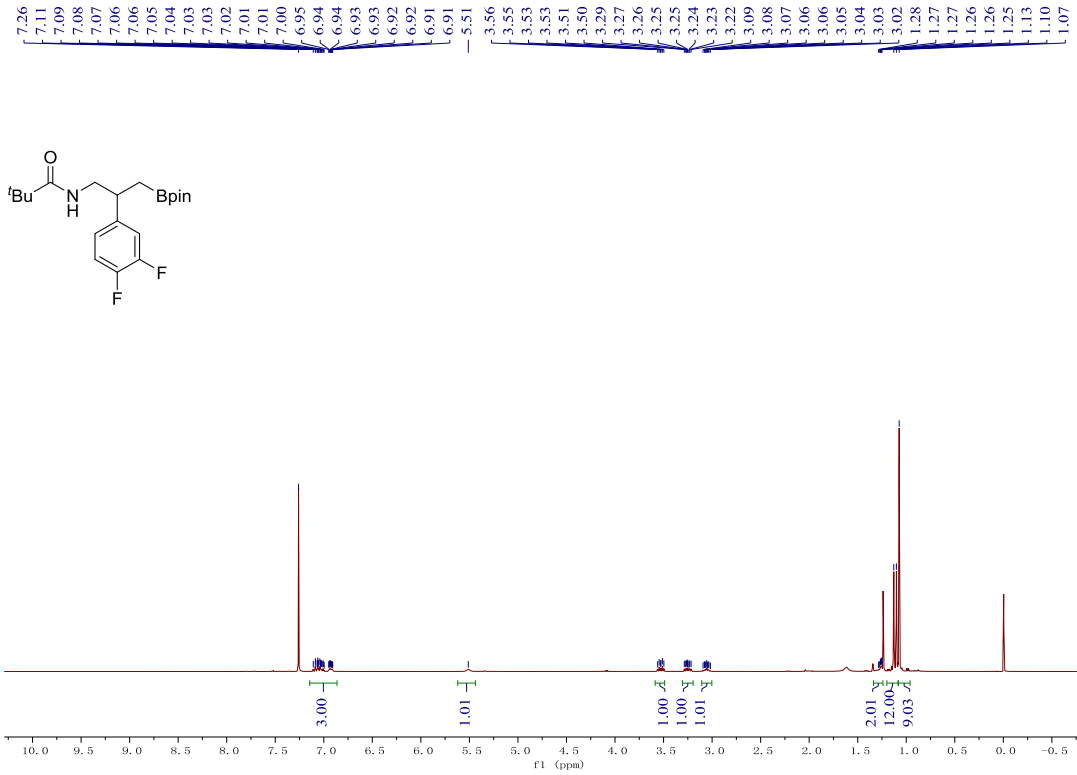
^{13}C NMR of 2v


178.1
143.2
140.9
139.4
128.7
128.0
127.1
127.1
126.9
83.2
77.3
77.0
76.7
46.4
40.9
38.6
27.5
24.7
24.6
tBu
N
H
O
Bpin
Ph
f1 (ppm)

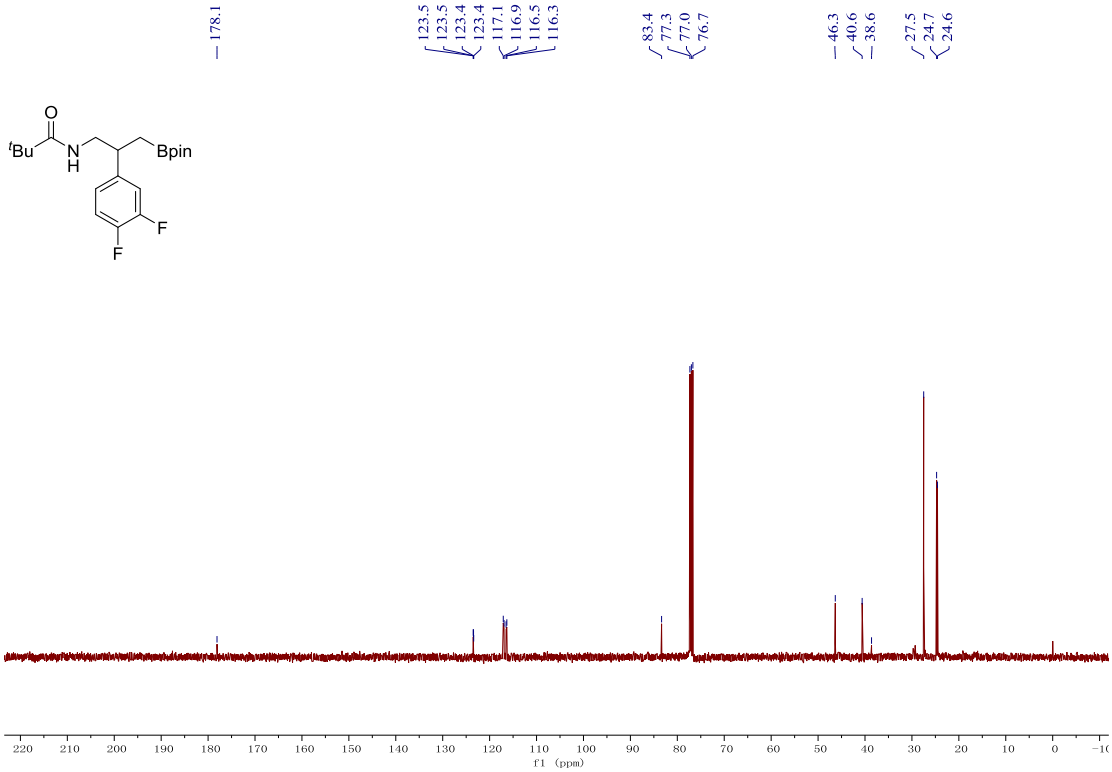
^{11}B NMR of 2v


34.2
tBu
N
H
O
Bpin
Ph
f1 (ppm)

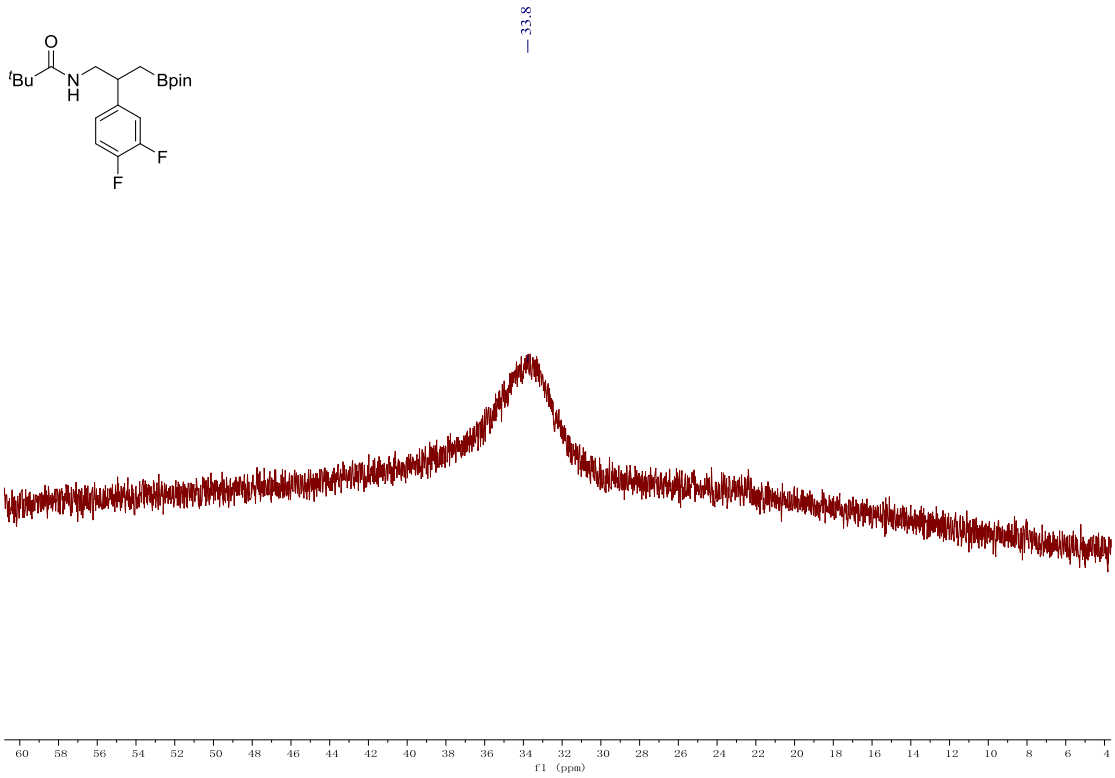
^{1}H NMR of 2w



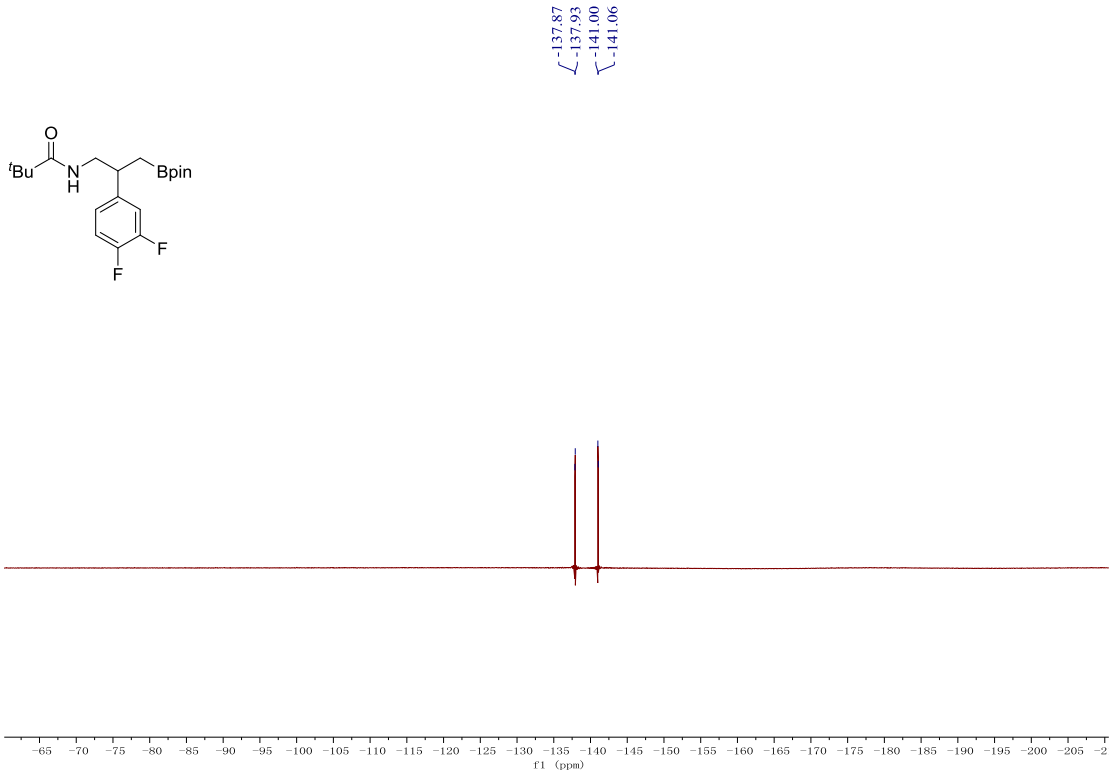
^{13}C NMR of 2w



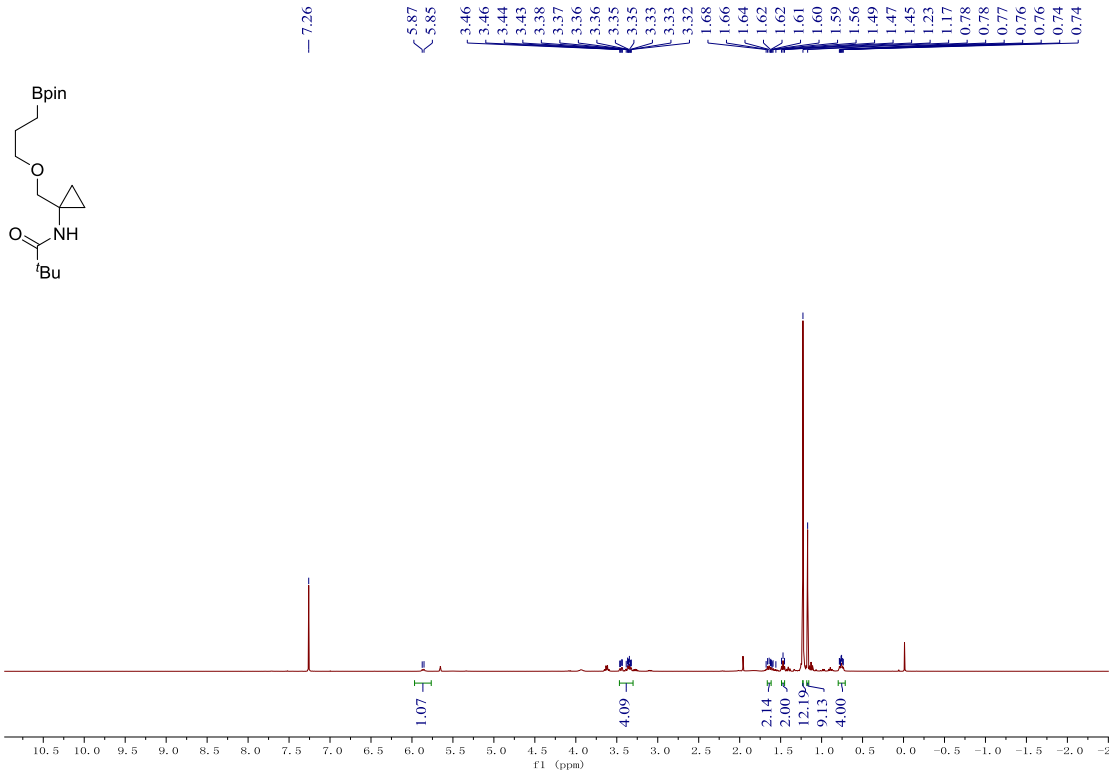
^{11}B NMR of 2w


33.8
tBu
O
N
H
Bpin
F
F
60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4
f1 (ppm)

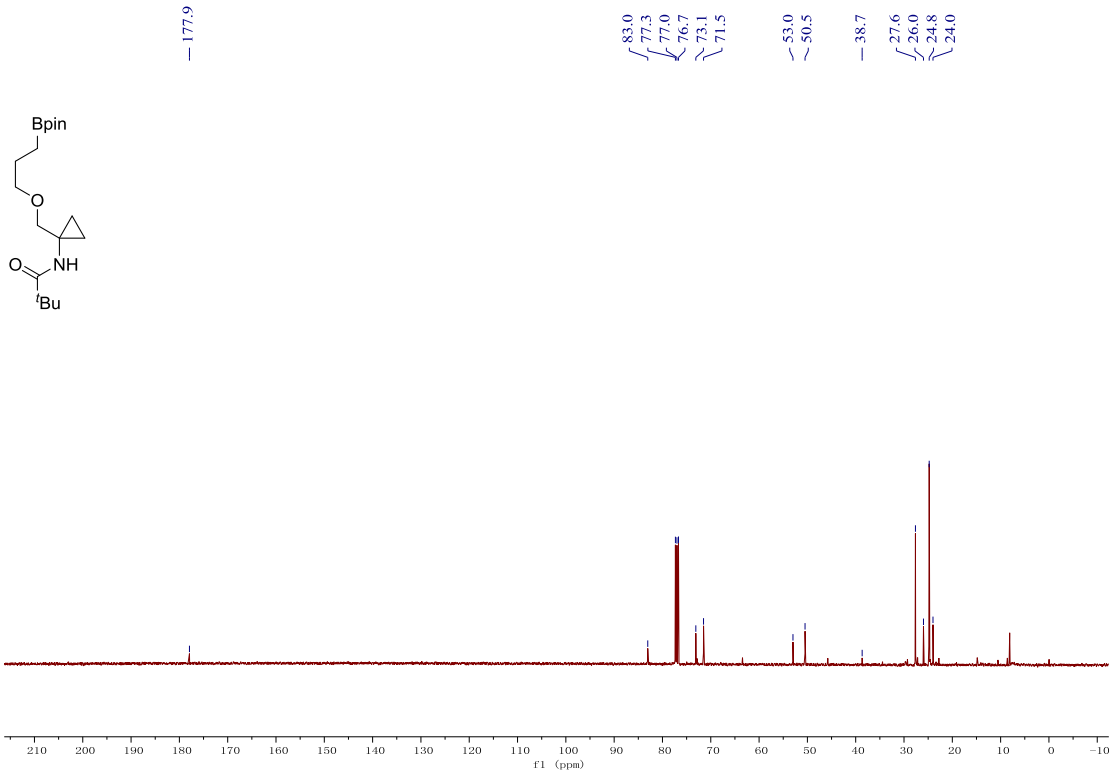
^{19}F NMR of 2w


-137.87
-137.93
-141.00
-141.06
tBu
O
N
H
Bpin
F
F
−65 −70 −75 −80 −85 −90 −95 −100 −105 −110 −115 −120 −125 −130 −135 −140 −145 −150 −155 −160 −165 −170 −175 −180 −185 −190 −195 −200 −205 −2
f1 (ppm)

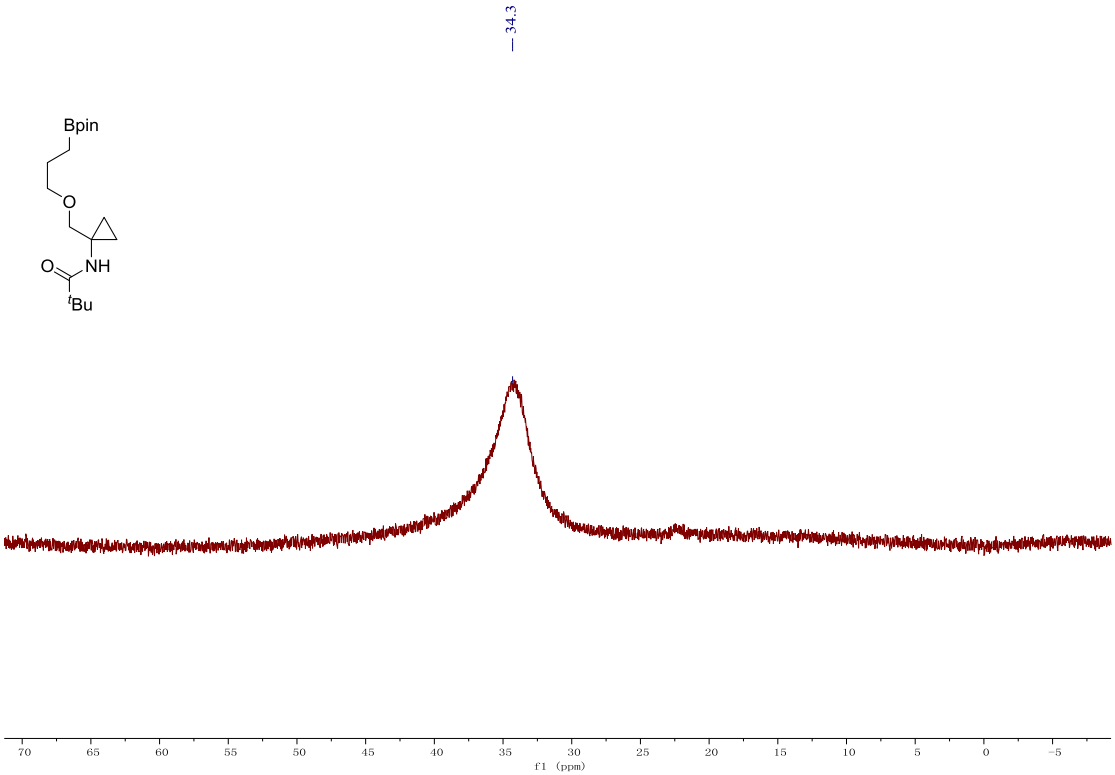
^{1}H NMR of 2x'



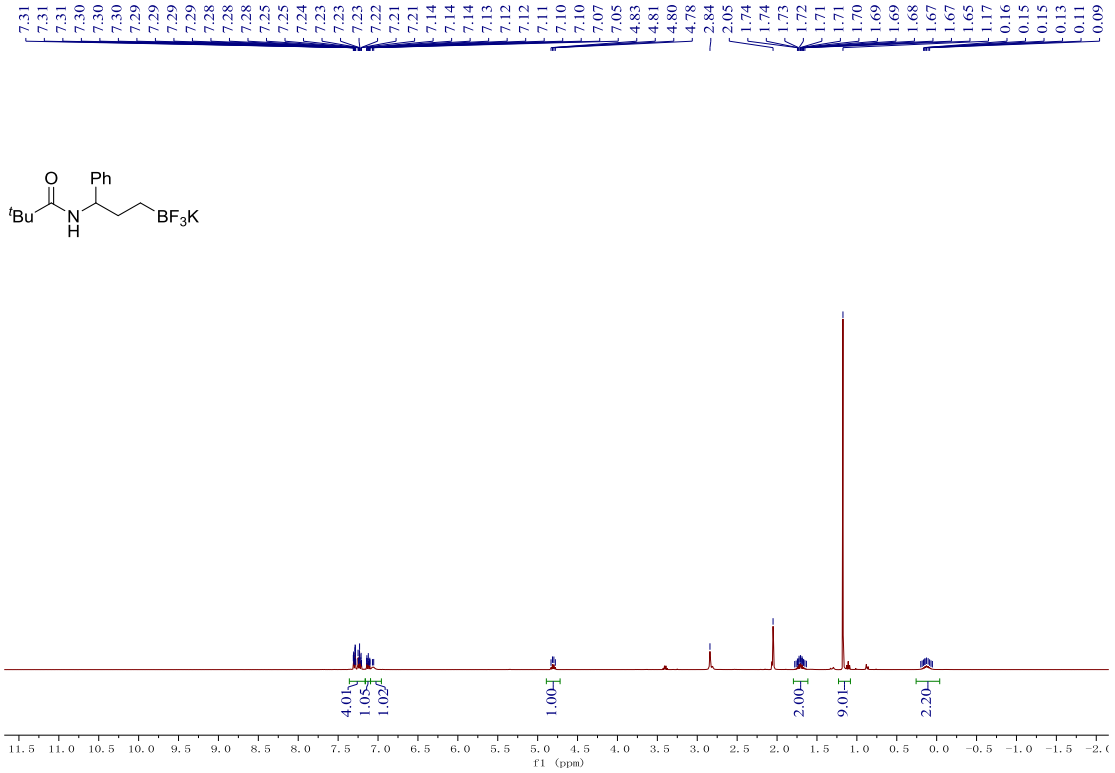
^{13}C NMR of 2x'



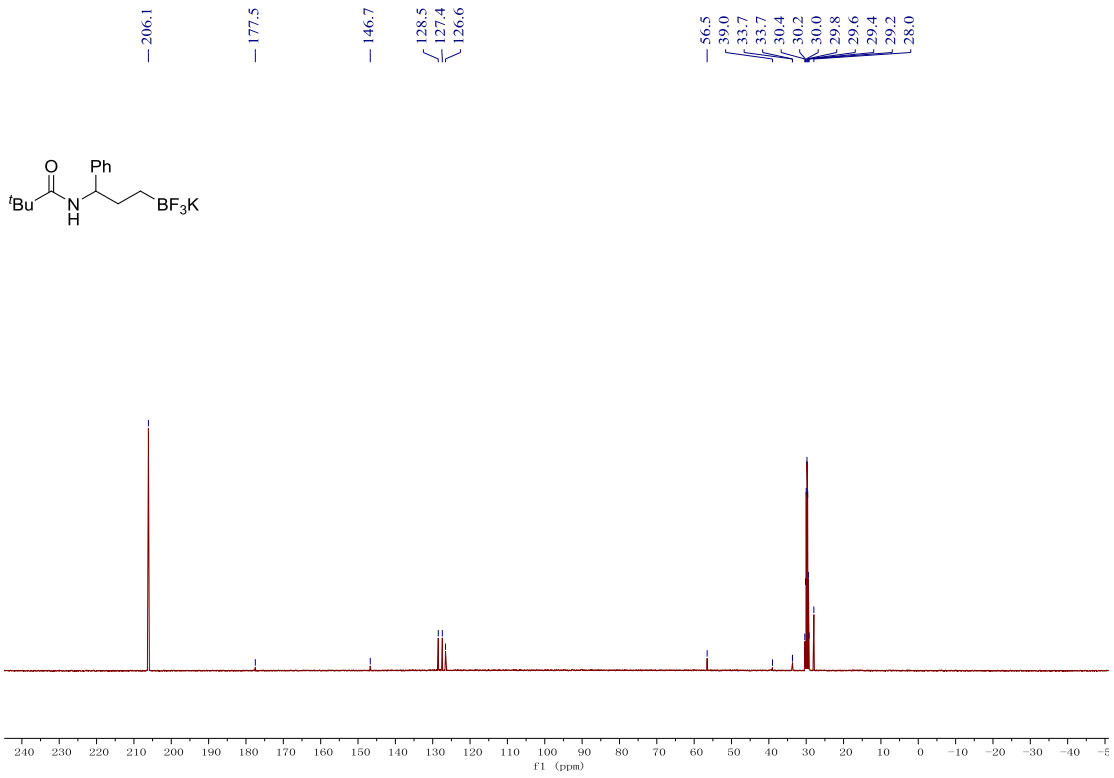
^{11}B NMR of 2x'



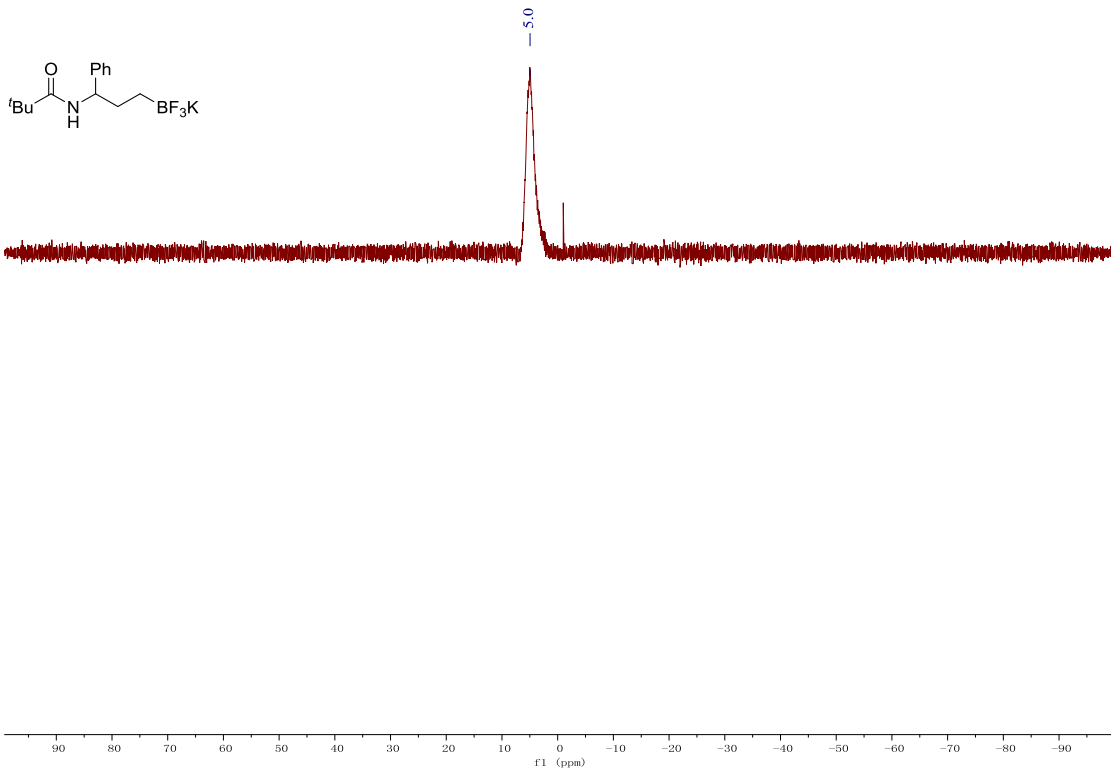
^{1}H NMR of 4



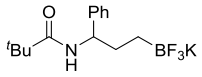
^{13}C NMR of 4



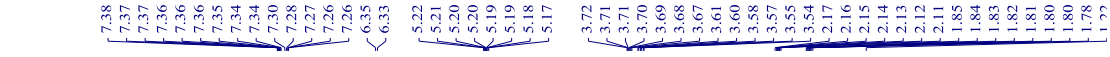
^{11}B NMR of 4

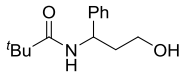


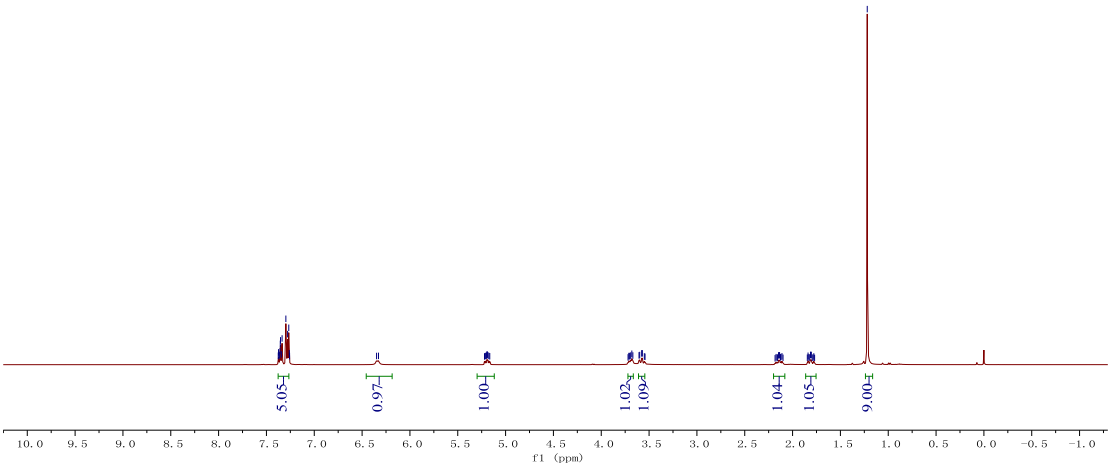
^{19}F NMR of 4



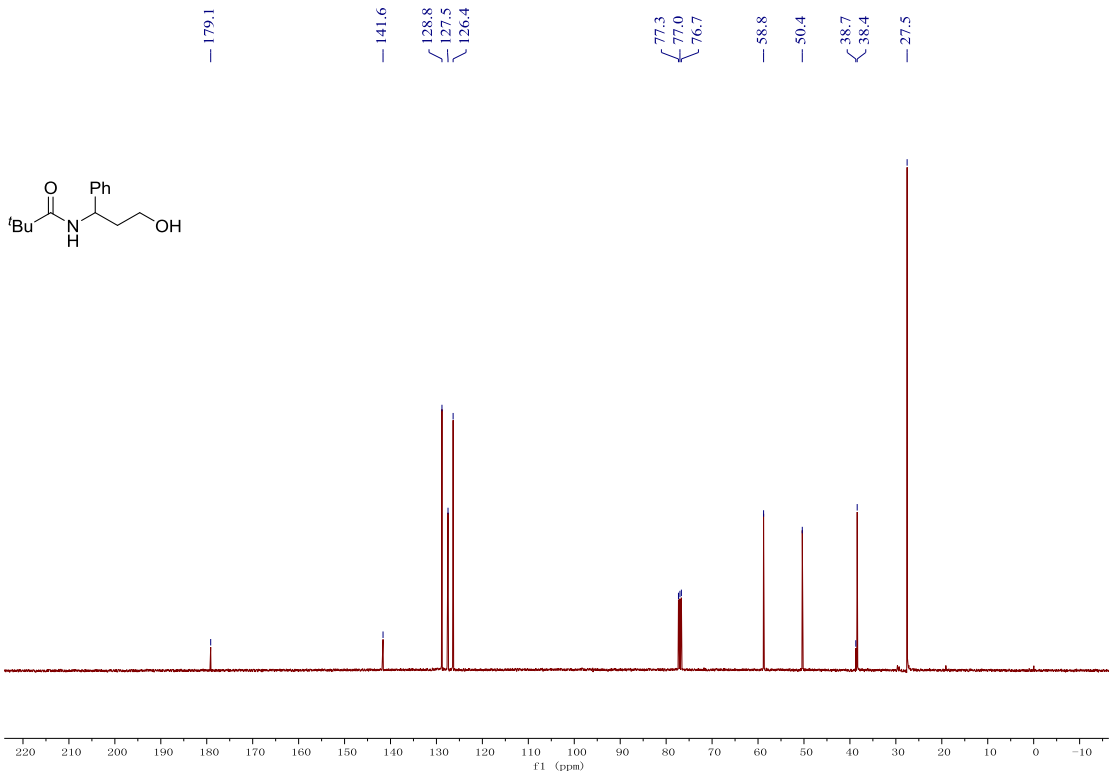
^{1}H NMR of 5



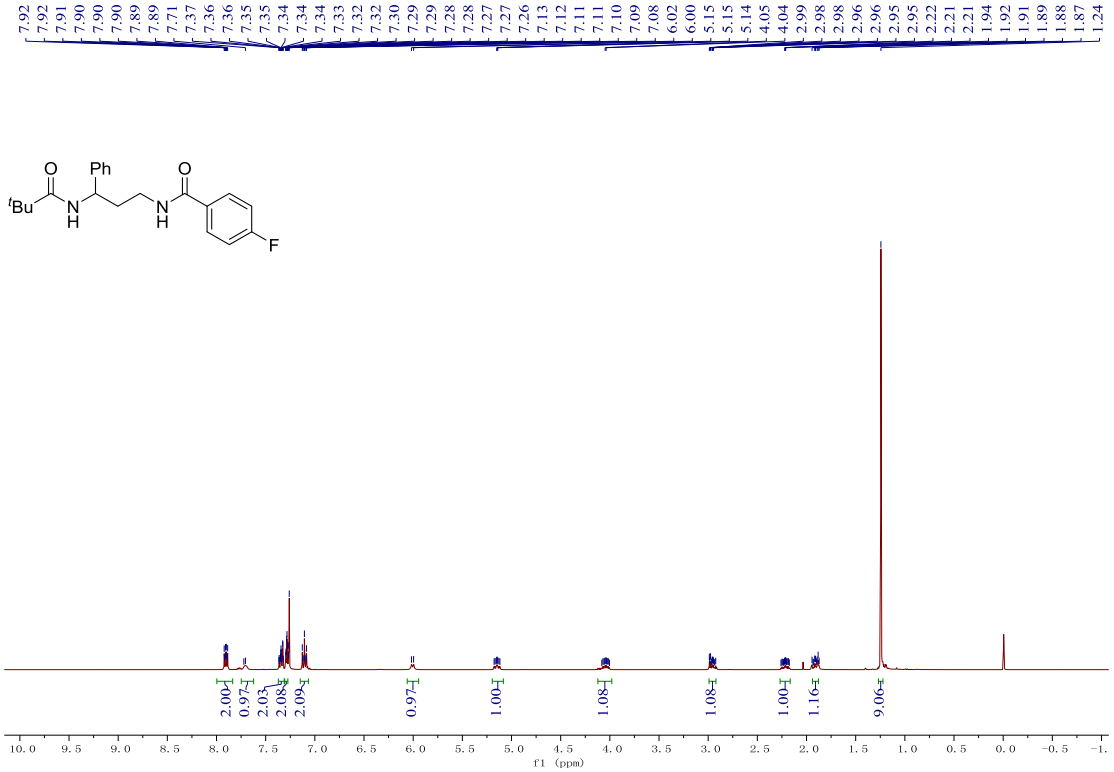




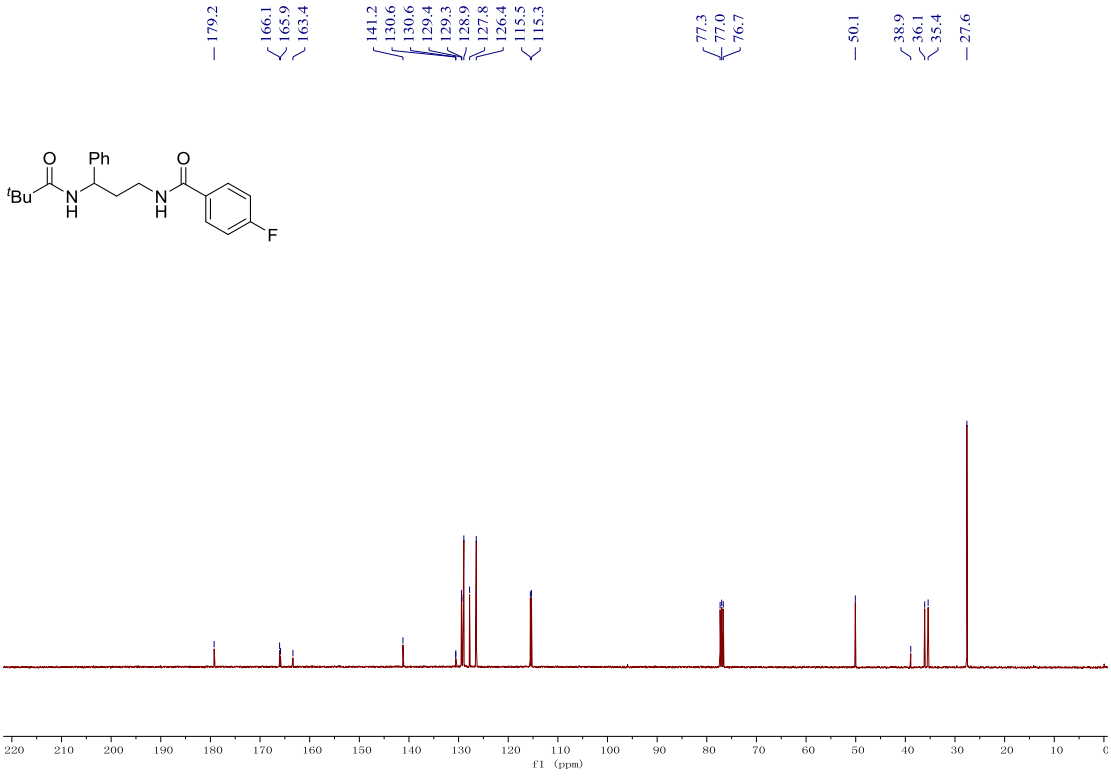
^{13}C NMR of 5



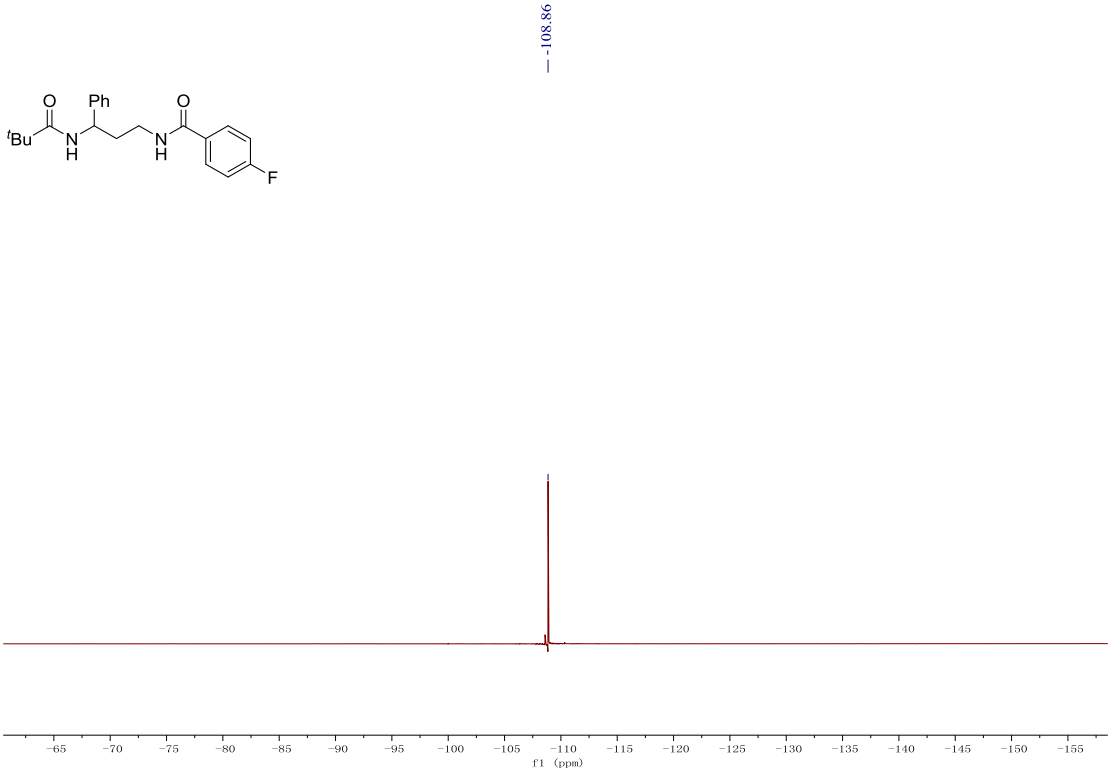
^{1}H NMR of 6



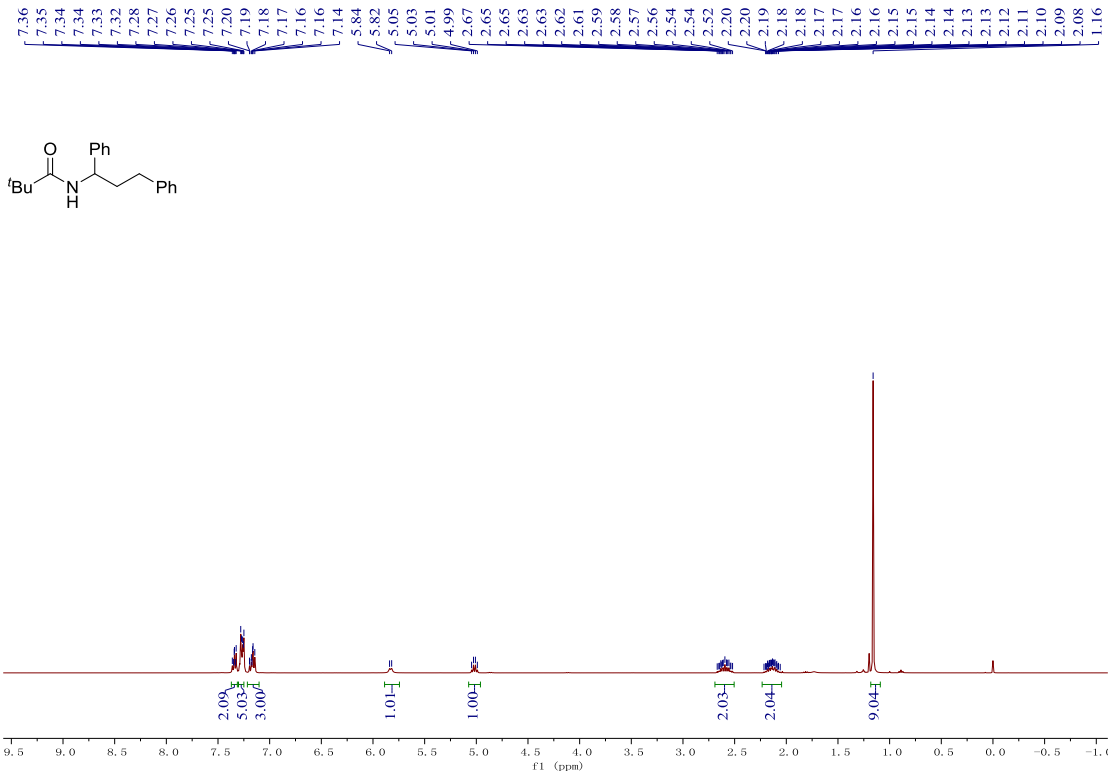
^{13}C NMR of 6



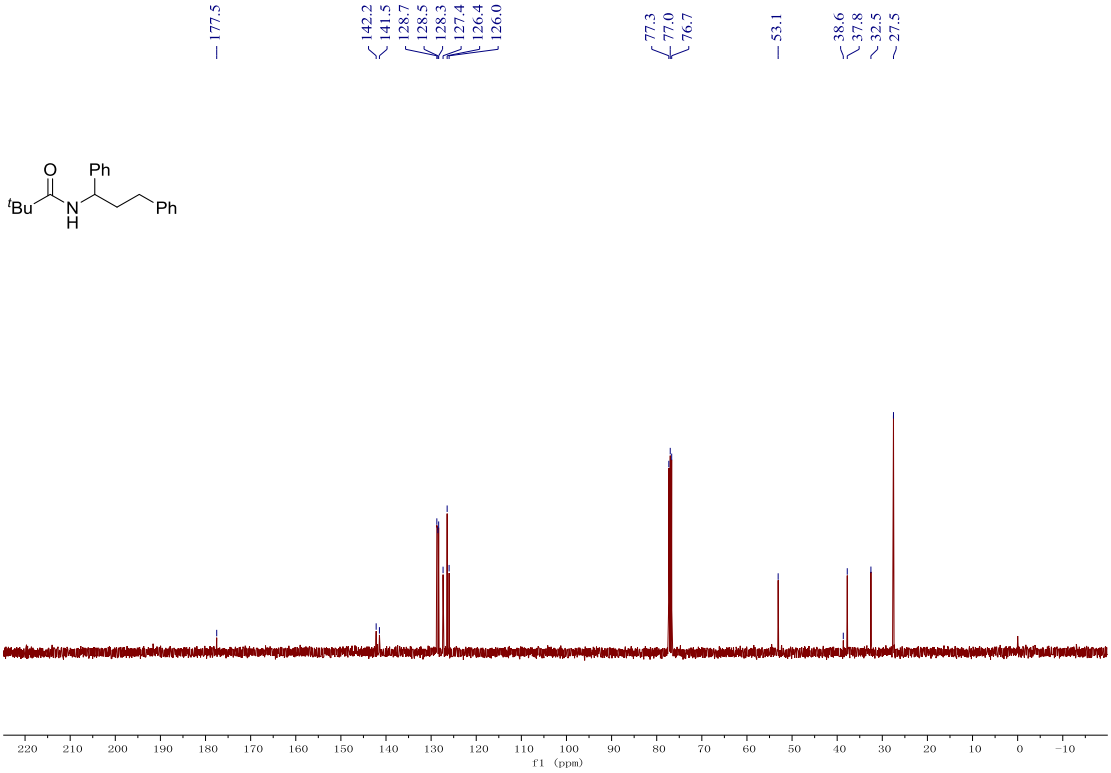
^{19}F NMR of 6



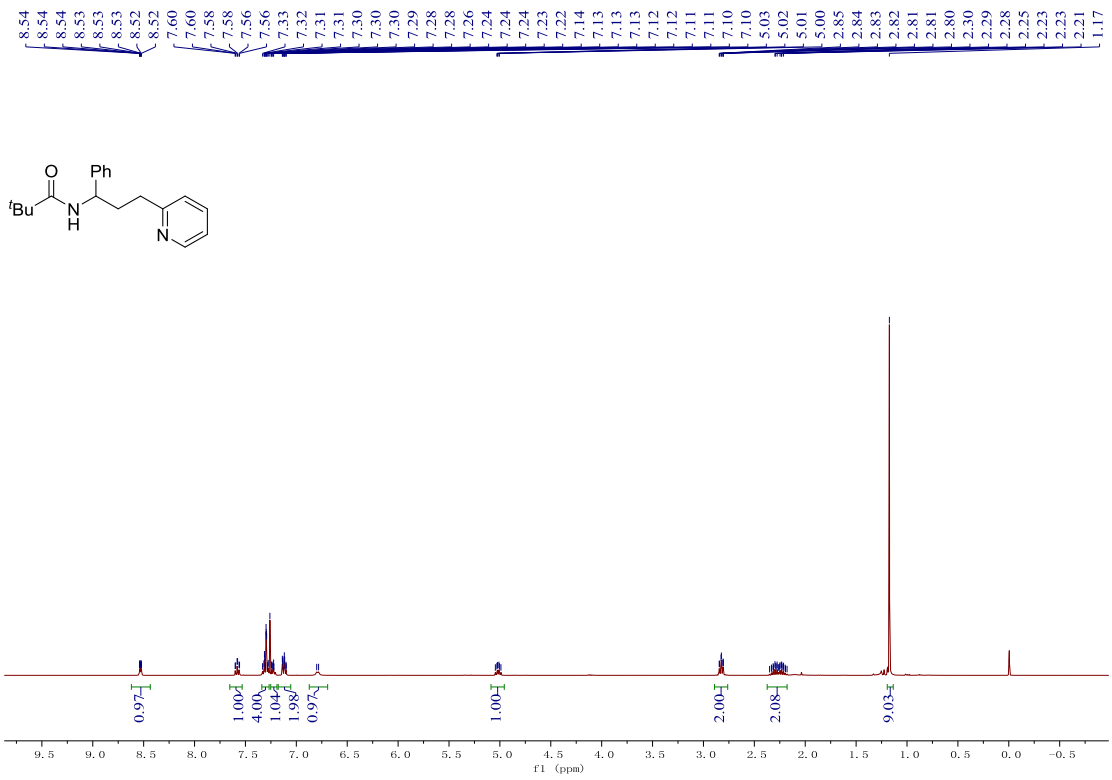
^{1}H NMR of 7


7.36
7.35
7.34
7.34
7.33
7.32
7.28
7.27
7.26
7.25
7.25
7.20
7.19
7.18
7.17
7.16
7.16
7.14
5.84
5.82
5.05
5.03
5.01
4.99
2.67
2.65
2.65
2.63
2.63
2.62
2.61
2.59
2.58
2.57
2.56
2.54
2.54
2.52
2.20
2.20
2.19
2.18
2.18
2.17
2.17
2.16
2.16
2.15
2.15
2.14
2.14
2.13
2.13
2.12
2.11
2.10
2.09
2.08
1.16
O
Ph
tBu
N
H
Ph
2.09
5.03
3.00
1.01
1.00
2.03
2.04
9.04
f1 (ppm)

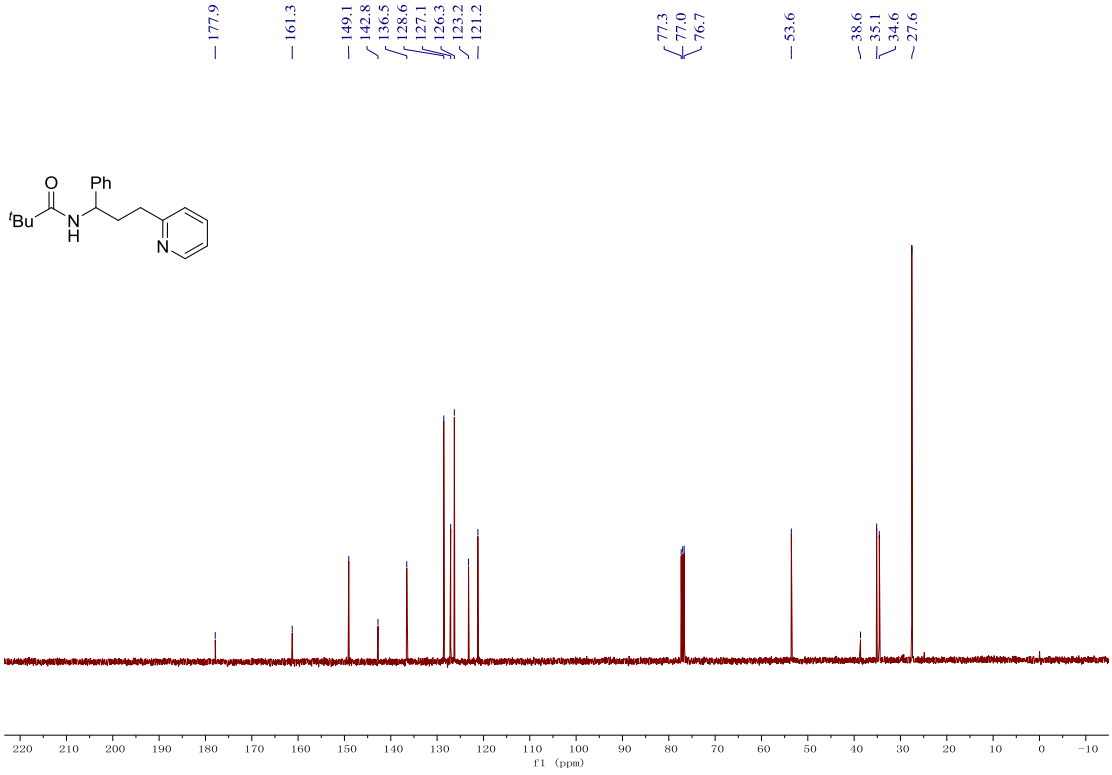
^{13}C NMR of 7


177.5
142.2
141.5
128.7
128.5
128.3
127.4
126.4
126.0
77.3
77.0
76.7
53.1
38.6
37.8
32.5
27.5
O
Ph
tBu
N
H
Ph
f1 (ppm)

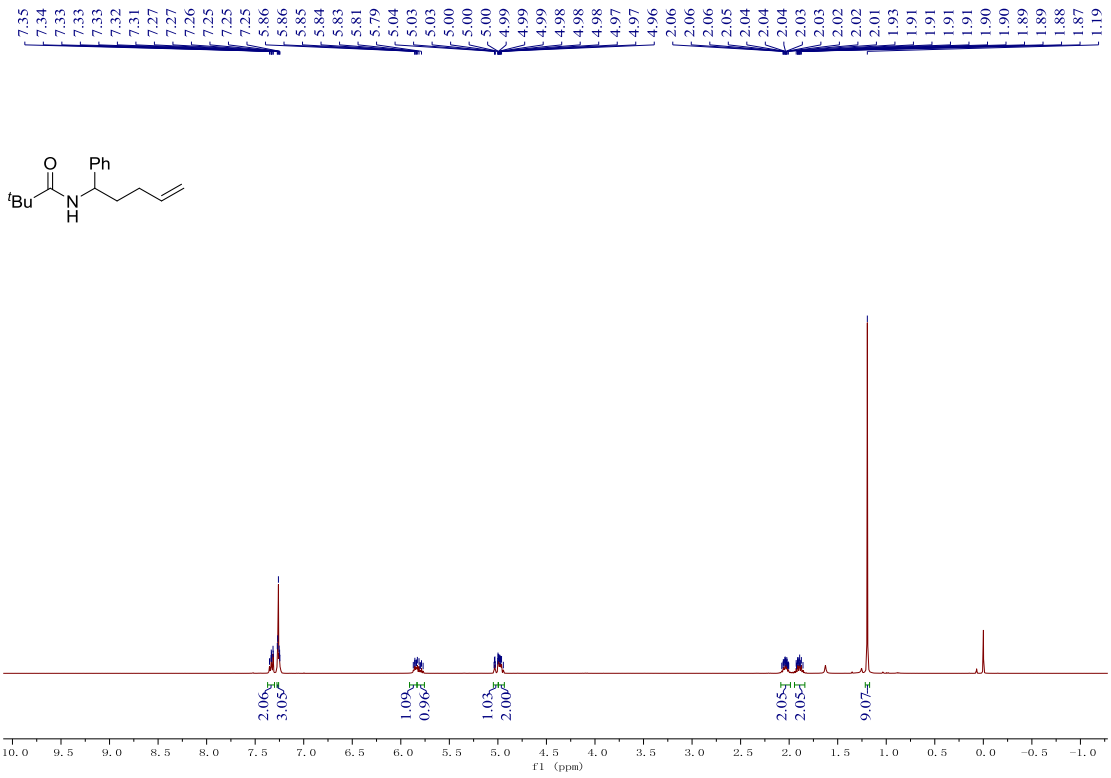
^{1}H NMR of 8



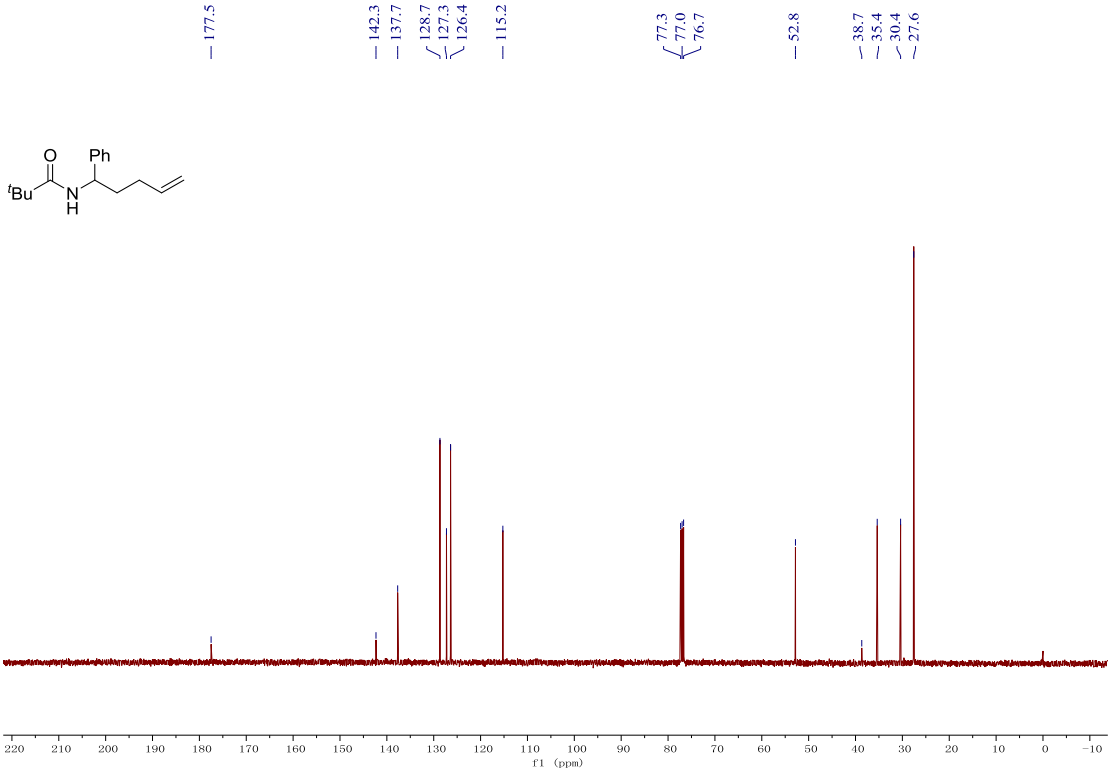
^{13}C NMR of 8



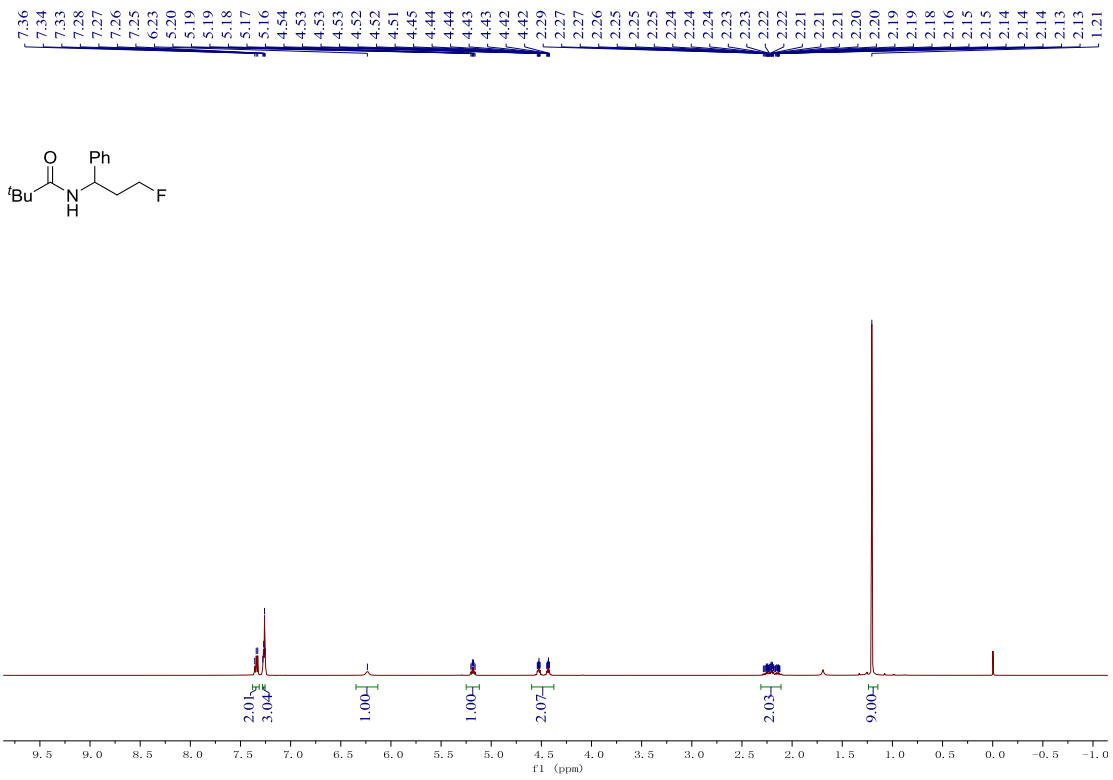
^{1}H NMR of 9



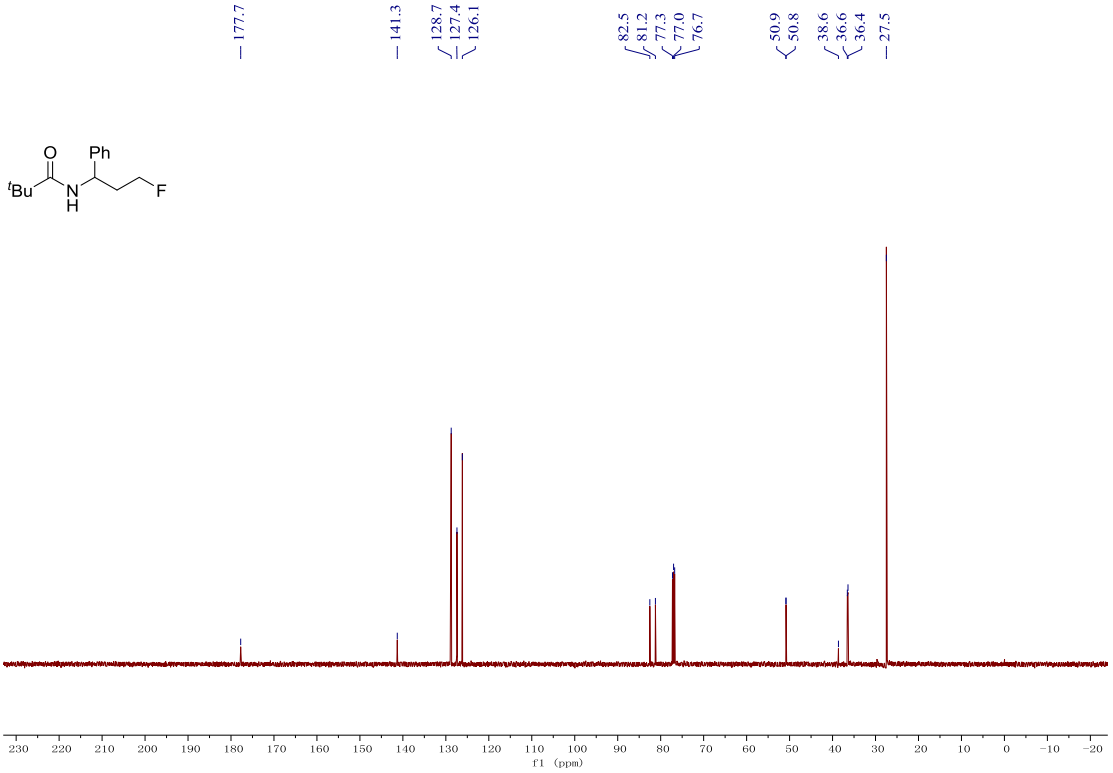
^{13}C NMR of 9



^{1}H NMR of 10



^{13}C NMR of 10



^{19}F NMR of 10