Supporting Information

A Metal-free, Green Strategy for Intramolecular Aminoalkoxylation of Unfunctionalized Olefins via Recyclable NIS Catalysis with Water as the Sole Byproduct

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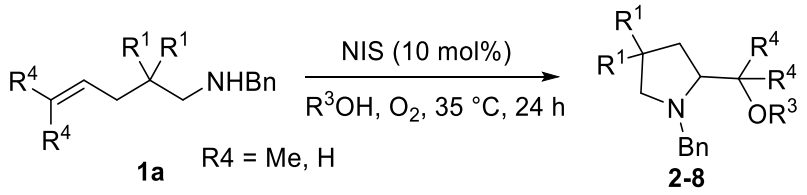
General experimental information

All reactions were carried out in sealed tube at 35°C under O_2 unless otherwise notified. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX 400 spectrometer at 298 K using deuterated chloroform as a solvent and TMS as an internal reference.

Reactions were monitored by thin-layer chromatography (TLC) on silica gel plates (GF 254) using a mixture of iodine and silica gel as the visualizing agent, unless otherwise noted. Flash column chromatography was performed using a silica gel (200 - 400 meshes). HRMS analyses were carried out with Varian FTICRMS 7.0T. Melting points were obtained on a Mettler Toledo MP50 apparatus.

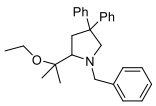
General procedure for intramolecular aminoalkoxylation reaction

Substrate (0.25 mmol) and NIS (10 mol%) were charged in a 50 mL sealed tube equipped with a stir bar in O_2 atmosphere. Solvent (2.5 mL) were added to the sealed tube by styinge and the mixture was stirred at 35 °C for 24 h. Upon completion, the mixture was extracted with CH_2Cl_2 (30 mL × 3). The combined organic mixture was dried with anhydrous magnesium sulfate, concentrated *in vacuo*, and purified over silica gel via flash column chromatography with PE and EA as the eluent to obtain desired product **2-8**.

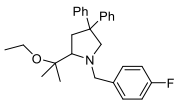


1a R4 = Me, H **2-8**

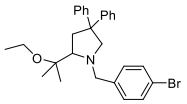
Compounds characterization.



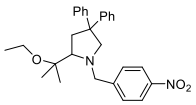
1-benzyl-2-(2-ethoxypropan-2-yl)-4,4-diphenylpyrrolidine 2a: yield: 93%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 250/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.09 (m, 15H), 4.27 (d, *J* = 13.7 Hz, 1H), 3.52 (d, *J* = 11.0 Hz, 1H), 3.45 – 3.23 (m, 2H), 3.19 – 3.05 (m, 3H), 2.95 – 2.89 (m, 1H), 2.13 – 2.05 (m, 1H), 1.11 – 1.02 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.3, 147.6, 141.7, 135.9, 130.1, 129.2, 128.3, 128.3, 128.2, 128.0, 127.8, 127.3, 127.1, 126.6, 126.0, 125.6, 78.7, 70.7, 65.1, 61.1, 56.4, 53.2, 41.6, 22.6, 21.4, 16.3. **HRMS** (ESI) calculated for $C_{28}H_{34}NO$ $[M+H]^+$: 400.2640, found: 400.2641.



2-(2-ethoxypropan-2-yl)-1-(4-fluorobenzyl)-4,4-diphenylpyrrolidine 2b: yield: 95%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 150/1); yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 6H), 7.15 – 7.02 (m, 6H), 6.91 (t, *J* = 8.7 Hz, 2H), 4.20 (d, *J* = 13.5 Hz, 1H), 3.49 (d, *J* = 10.9 Hz, 1H), 3.41 – 3.32 (m, 2H), 3.11 – 3.04 (m, 2H), 3.00 (d, *J* = 10.9 Hz, 1H), 2.95 – 2.85 (m, 1H), 2.17 – 2.07 (m, 1H), 1.14 – 1.04 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.6 (d, $J_{C–F}$ = 243.8 Hz), 149.1, 147.4, 137.2 (d, $J_{C–F}$ = 2.9 Hz), 129.6 (d, $J_{C–F}$ = 7.7 Hz), 128.3, 128.0, 127.2, 127.0, 125.8 (d, $J_{C–F}$ = 42.6 Hz), 114.9, 114.7, 78.6, 70.5, 64.9, 60.1, 56.3, 53.0, 41.5, 22.5, 21.1, 16.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.7. **HRMS** (ESI) calculated for $C_{28}H_{33}FNO$ $[M+H]^+$: 418.2546, found: 418.2541.

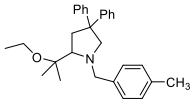


1-(4-bromobenzyl)-2-(2-ethoxypropan-2-yl)-4,4-diphenylpyrrolidine 2c: yield: 92%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 150/1); yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.3 Hz, 2H), 7.20 – 6.98 (m, 12H), 4.17 (d, *J* = 13.9 Hz, 1H), 3.48 (d, *J* = 10.9 Hz, 1H), 3.32 – 3.19 (m, 2H), 3.05 (t, *J* = 10.2 Hz, 2H), 2.98 (d, *J* = 11.1 Hz, 1H), 2.88 – 2.79 (m, 1H), 2.05 – 1.91(m= 1H), 1.11 (s, 3H), 1.10 (s, 3H), 1.07 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.0, 146.4, 139.7, 130.2, 128.9, 128.2, 127.3, 127.2, 127.0, 126.7, 126.2, 126.0, 125.0, 124.6, 119.1, 77.7, 69.7, 64.1, 59.4, 55.3, 52.1, 40.4, 21.5, 20.0, 15.2. **HRMS** (ESI) calculated for $C_{28}H_{33}BrNO$ $[M+H]^+$: 478.1746, found: 478.1749.

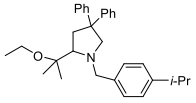


2-(2-ethoxypropan-2-yl)-1-(4-nitrobenzyl)-4,4-diphenylpyrrolidine 2d: yield: 91%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 100/1); yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 – 8.03 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 7.1 Hz, 1H), 7.21 – 7.15 (m, 4H), 7.08 – 7.03 (m, 4H), 6.98 (d, *J* = 9.3 Hz, 1H), 4.28 (d, *J* = 14.9 Hz, 1H), 3.51 (d, *J* = 10.9 Hz, 1H), 3.35 – 3.22 (m, 3H), 3.13 – 3.05 (m, 1H), 3.02 (d, *J* = 10.9 Hz, 1H), 2.88 (m, 1H), 2.05 (m, 1H), 1.03 (s, 6H), 0.94 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.9, 148.6, 147.2, 146.8, 128.7, 128.5, 128.4, 128.2, 127.6, 127.2, 126.9, 126.6, 126.2, 125.8, 123.5, 78.8, 71.1, 65.5, 60.8, 56.4, 53.5, 41.4,

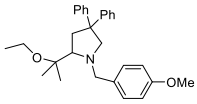
22.6, 20.6, 16.2. **HRMS** (ESI) calculated for $C_{28}H_{33}N_2O_3$ $[M+H]^+$: 445.2491; found: 445.2492.



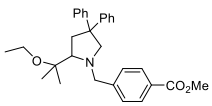
2-(2-ethoxypropan-2-yl)-1-(4-methylbenzyl)-4,4-diphenylpyrrolidine 2e: yield: 85%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 100/1); yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 – 7.03 (m, 14H), 4.22 (d, *J* = 13.4 Hz, 1H), 3.51 (d, *J* = 11.0 Hz, 1H), 3.38 – 3.11(m, 2H), 3.06 –2.99 (m, 3H), 2.95 – 2.88 (m, 1H), 2.26 (s, 3H), 2.08 – 1.96 (m, 1H), 1.17 – 1.06(m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.2, 146.5, 137.5, 134.9, 129.0, 127.8, 127.2, 126.9, 126.2, 126.1, 124.9, 124.4, 77.6, 69.5, 63.9, 59.6, 55.3, 52.0, 40.5, 21.5, 20.4, 20.1, 15.2. **HRMS** (ESI) calculated for $C_{29}H_{36}NO$ $[M+H]^+$: 414.2797, found: 414.2796.



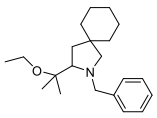
2-(2-ethoxypropan-2-yl)-1-(4-isopropylbenzyl)-4,4-diphenylpyrrolidine 2f: yield: 79%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 80/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.06 (m, 14H), 4.28 (d, *J* = 13.6 Hz, 1H), 3.60 (d, *J* = 11.0 Hz, 1H), 3.53 – 3.41(m, 2H), 3.15 (t, *J* = 10.1 Hz, 3H), 3.03 – 2.96 (m, 1H), 2.94 – 2.86 (m, 1H), 2.21 – 2.09 (m, 1H), 1.26 (d, *J* = 6.8 Hz, 6H), 1.16 (d, *J* = 14.7 Hz, 6H), 1.11 (t, *J* =6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.3, 147.5, 147.0, 138.9, 128.2, 128.2, 128.0, 127.3, 127.1, 126.1, 125.9, 125.5, 78.6, 70.6, 65.0, 60.7, 56.3, 53.2, 41.5, 33.7, 24.1, 24.1, 22.5, 21.5, 16.2. **HRMS** (ESI) calculated for $C_{31}H_{40}NO$ $[M+H]^+$: 442.3110, found: 442.3112.



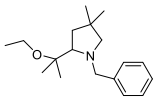
2-(2-ethoxypropan-2-yl)-1-(4-methoxybenzyl)-4,4–diphenylpyrrolidine 2g: yield: 83%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 100/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 – 7.05 (m, 12H), 6.78 (d, *J* = 8.1 Hz, 2H), 4.17 (d, *J* = 13.3 Hz, 1H), 3.71 (s, 3H), 3.49 (d, *J* = 10.9 Hz, 1H), 3.37 – 3.22 (m, 2H), 3.02 – 2.96 (m, 3H), 2.92 – 2.83(m, 1H), 2.11 – 2.02 (m, 1H), 1.09 – 1.01 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.4, 149.4, 147.7, 129.5, 128.6, 128.3, 128.1, 127.4, 127.2, 126.0, 125.6, 113.6, 78.7, 70.6, 64.9, 60.3, 56.4, 55.3, 53.1, 41.6, 22.6, 21.5, 16.3. **HRMS** (ESI) calculated for $C_{29}H_{36}NO_2$ $[M+H]^+$: 430.2746, found: 430.2748.



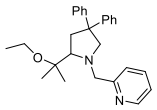
methyl 4-((2-(2-ethoxypropan-2-yl)-4,4-diphenylpyrrolidin-1-yl)methyl)benzoate 2h: yield: 54%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 60/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.02 (m, 12H), 4.32 (d, *J* = 14.3 Hz, 1H), 3.83 (d, *J* = 5.3 Hz, 2H), 3.53 (d, *J* = 10.9 Hz, 1H), 3.41 – 3.31 (m, 2H), 3.21 (d, *J* = 14.3 Hz, 1H), 3.08 (m, 1H), 3.02 (m, 1H), 2.91 (s, 1H), 2.19 – 2.00 (m, 1H), 1.10 – 1.05(m, 6H), 1.02 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.3, 149.0, 147.4, 147.3, 129.6, 128.3, 128.1, 128.1, 127.2, 127.0, 126.1, 125.6, 78.7, 70.9, 65.4, 61.0, 56.3, 53.2, 52.0, 41.5, 22.6, 21.0, 16.2. **HRMS** (ESI) calculated for $C_{30}H_{36}NO_3$ $[M+H]^+$: 458.2695, found: 458.2693.



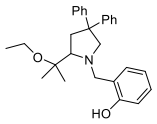
2-benzyl-3-(2-ethoxypropan-2-yl)-2-azaspiro [4.5] decane 2i: yield: 69%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 60/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.02 (m, 5H), 4.60 (d, *J* = 13.8 Hz, 1H), 3.45 –3.37 (m, 1H), 3.34 –3.30 (m, 1H), 3.12 (d, *J* = 13.9 Hz, 1H), 2.78 (t, *J* = 8.7 Hz, 1H), 2.67 (d, *J* = 9.7 Hz, 1H), 1.88 (d, *J* = 9.7 Hz, 1H), 1.58 –1.51 (m, 1H), 1.32 – 1.19 (m, 14H), 1.06 – 1.01(m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.9, 128.1, 128.1, 126.2, 78.5, 69.1, 60.5, 56.1, 39.4, 38.4, 38.0, 26.2, 23.6, 23.4, 20.4, 16.2. **HRMS** (ESI) calculated for $C_{21}H_{34}NO$ $[M+H]^+$: 316.2640, found: 316.2643.



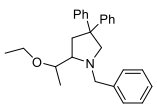
1-benzyl-2-(2-ethoxypropan-2-yl)-4,4-dimethylpyrrolidine 2j: yield: 65%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 100/1); colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.11 (m, 5H), 4.57 (d, *J* = 13.8 Hz, 1H), 3.45 – 3.36 (m, 2H), 3.21 – 3.16 (d, *J* = 13.8 Hz, 1H), 2.89 – 2.83 (m, 1H), 2.57 (d, *J* = 9.6 Hz, 1H), 1.94 (d, *J* = 9.6 Hz, 1H), 1.57 – 1.51(m, 1H), 1.25 – 1.18(m, 4H), 1.05 – 1.01 (m, 6H), 0.93 (t, *J* = 7.2 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.9, 128.1, 128.0, 126.2, 78.5, 70.2, 68.6, 60.7, 56.1, 43.9, 35.7, 29.7, 29.4, 28.7, 23.2, 20.5, 16.2. **HRMS** (ESI) calculated for $C_{18}H_{30}NO$ $[M+H]^+$: 276.2327, found: 276.2328.



2-((2-(2-ethoxypropan-2-yl)-4,4-diphenylpyrrolidin-1-yl)methyl) pyridine 2k: yield: 72%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 50/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 3.6 Hz, 1H), 7.62 – 7.06 (m, 13H), 4.47 (d, *J* = 15.4 Hz, 1H), 3.77 – 3.59 (m, 2H), 3.50 – 3.34 (m, 2H), 3.33 – 3.21 (m, 2H), 2.93 (m = 1H), 2.22 (m = 1H), 1.15 (d, *J* = 10.2 Hz, 6H), 1.07 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.1, 149.1, 148.8, 147.2, 128.4, 128.1, 127.3, 127.0, 126.1, 125.7, 122.4, 121.5, 78.6, 70.7, 66.0, 63.2, 56.3, 53.5, 41.6, 22.7, 21.2, 16.2. **HRMS** (ESI) calculated for $C_{27}H_{33}N_2O$ $[M+H]^+$:401.2593, found: 401.2593.

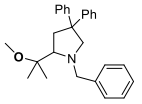


2-((2-(2-ethoxypropan-2-yl)-4, 4-diphenylpyrrolidin-1-yl)methyl) phenol 2l: yield: 65%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 80/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 3H), 7.40 – 7.13 (m, 11H), 4.08 (d, *J* = 13.7 Hz, 1H), 3.54 (m, 2H), 3.44 (m = 2H), 3.26 (d, *J* = 13.8 Hz, 1H), 3.15 (m = 1H), 2.88 (d, *J* = 13.7 Hz, 1H), 2.18 (m = 1H), 1.24 (s, 3H), 1.19 (s, 3H), 1.13 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.3, 145.9, 137.4, 136.9, 128.8, 128.5, 128.3, 128.1, 128.0, 127.0, 126.7, 126.6, 126.2, 118.5, 77.9, 73.0, 62.4, 60.3, 56.7, 54.4, 39.8, 23.1, 19.7, 16.1. **HRMS** (ESI) calculated for $C_{28}H_{34}NO_2$ $[M+H]^+$:416.2590, found: 416.2592.

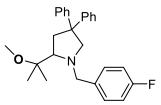


1-benzyl-2-(1-ethoxyethyl)-4,4-diphenylpyrrolidine 2m: yield 65%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 60/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.17 (m, 15H), 3.72 (d, *J* = 13.2 Hz, 1H), 3.55 (d, *J* = 13.1 Hz, 1H), 3.32 – 3.24 (m, 3H), 2.64 – 2.46

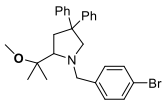
(m, 4H), 2.28 – 2.25 (m, 1H), 0.95 – 0.92 (t, *J* = 7.0 Hz, 3H), 0.82 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.7, 147.7, 138.5, 136.0, 129.4, 129.3, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.3, 127.2, 125.6, 73.6, 63.5, 63.0, 62.8, 56.0, 46.2, 45.6, 23.2, 16.0. **HRMS** (ESI) calculated for $C_{27}H_{32}NO$ $[M+H]^+$: 386.2484, found: 386.2482.



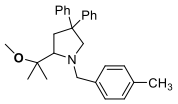
benzyl-2-(2-methoxypropan-2-yl)-4,4-diphenylpyrrolidine 3a: yield: 95%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 200/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23-6.98 (m, 15H), 4.19 (d, *J* = 13Hz, 1H), 3.52 (d, *J* = 11.0 Hz, 1H), 3.13 (s, 3H), 3.15-3.01 (m, 3H), 2.93 (m, 1H), 2.10 (m, 1H), 1.09-1.05 (s, 6H).; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.1, 147.4, 141.5, 128.2, 128.2 128.1,128.0, 127.2, 127.0, 126.5, 125.9, 125.5, 78.8, 70.6, 65.0, 61.1, 53.2, 49.0, 41.4, 21.6, 21.1. **HRMS** (ESI) calculated for $C_{27}H_{32}NO$ $[M+H]^+$: 386.2484, found: 386.2485.



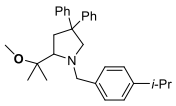
1-(4-fluorobenzyl)-2-(2-methoxypropan-2-yl)-4,4 -diphenylpyrrolidine 3b: yield: 93%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 150/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.15 (m, 6H), 7.08 (d, *J* = 6.6 Hz, 5H), 6.99 (t, *J* = 5.9 Hz, 1H), 6.90 (t, *J* = 8.7 Hz, 2H), 4.11 (d, *J* = 13.6 Hz, 1H), 3.49 (d, *J* = 11.0 Hz, 1H), 3.13 (s, 3H), 3.09 – 2.98 (m, 3H), 2.97 – 2.89 (m, 1H), 2.15 – 2.03 (m, 1H), 1.05 (d, *J* = 7.3 Hz, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.7 (d, $J_{C–F}$ = 243.8 Hz), 149.0, 147.4, 137.0 (d, $J_{C–F}$ = 2.9 Hz), 129.6 (d, $J_{C–F}$ = 7.8 Hz), 128.3, 128.0, 127.2,127.0, 125.8 (d, $J_{C–F}$ = 42.0 Hz), 115.0, 114.8, 78.8, 70.5, 64.8, 60.3, 53.1, 49.0, 41.3, 21.6, 20.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.6. **HRMS** (ESI) calculated for $C_{27}H_{31}FNO$ $[M+H]^+$: 404.2390, found 404.2389.



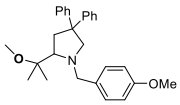
1-(4-bromobenzyl)-2-(2-methoxypropan-2-yl)-4,4 -diphenylpyrrolidine 3c: yield: 96%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 150/1); yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.9 Hz, 2H), 7.25 – 7.15 (m, 4H), 7.14 – 7.06 (m, 7H), 7.01 (d, *J* = 6.9 Hz, 1H), 4.10 (d, *J* = 13.9 Hz, 1H), 3.51 (d, J = 11.0 Hz, 1H), 3.12 (s, 3H), 3.09 – 2.98 (m, 3H), 2.98 – 2.87 (m, 1H), 2.14 – 2.04 (m, 1H), 1.05 (d, *J* = 4.9 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.9, 146.3, 139.5, 130.2, 128.9, 127.3, 127.0, 126.1, 125.9, 125.0, 124.6, 119.1, 77.8, 69.5, 63.9 59.4, 52.2, 48.0, 40.2, 20.6, 19.8. **HRMS** (ESI) calculated for $C_{27}H_{31}FNO$ $[M+H]^+$: 464.1589, found 464.1590.



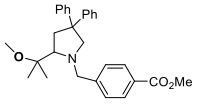
2-(2-methoxypropan-2-yl)-1-(4-methylbenzyl)-4,4 -diphenylpyrrolidine 3e: yield: 89%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 200/1); white solid, melting point: 56-58℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 –6.98 (m, 14H), 4.13 (d, *J* = 13.6 Hz, 1H), 3.51 (d, *J* = 11.0 Hz, 1H), 3.14 (s, 3H), 3.09 – 3.02 (m, 3H), 2.97 –2.86 (m, 1H), 2.26 (s, 3H), 2.14 –2.03 (m, 1H), 1.07 (d, *J* = 14.4 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.3, 147.6, 138.5, 136.1, 128.9, 128.3, 128.2, 128.1, 127.3, 127.1, 126.0, 125.6, 78.9, 70.7, 65.0, 60.9, 53.3, 49.1, 41.4, 21.7, 21.3, 21.2. **HRMS** (ESI) calculated for $C_{28}H_{34}NO$ $[M+H]^+$: 400.2640, found: 400.2643.



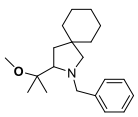
1-(4-isopropylbenzyl)-2-(2-methoxypropan-2-yl)-4,4 -diphenylpyrrolidine 3f： yield: 80%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 100/1); white solid, melting point: 75-77℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 9.0 Hz, 1H), 7.27 – 7.10 (m, 12H), 7.08 – 7.6.98 (m, 1H), 4.12 (d, *J* = 13.7 Hz, 1H), 3.53 (d, *J* = 11.1 Hz, 1H), 3.14 (s, 3H), 3.10 – 3.03 (m, 3H), 2.97 – 2.92 (m, 1H), 2.86 – 2.79 (m, 1H), 2.14 – 2.08 (m, 1H)1.26 (d, *J* = 6.9 Hz, 6H), 1.16 (d, *J* = 15.0 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.2, 147.5, 147.1, 138.9, 128.3, 128.2, 128.1, 128.1, 127.3, 127.1, 126.8, 126.3, 126.1, 126.0, 125.6, 118.5, 78.9, 70.7, 65.0, 60.9, 53.4, 49.2, 41.3, 33.8, 24.2, 24.2, 21.6, 21.3. **HRMS** (ESI) calculated for $C_{30}H_{38}NO$ $[M+H]^+$: 428.2953, found: 428.2953.



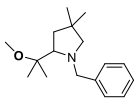
1-(4-methoxybenzyl)-2-(2-methoxypropan-2-yl)-4,4 -diphenylpyrrolidine 3g： yield: 85%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 200/1);colourless oil;**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 – 6.95 (m, 12H), 6.76 (d, *J* = 8.5 Hz, 2H), 4.06 (d, *J* = 13.3 Hz, 1H), 3.67 (s, 3H), 3.48 (d, *J* = 11.0 Hz, 1H), 3.11 (s, 3H), 3.04 – 2.99 (m, 3H), 2.95 – 2.90 (m, 1H), 2.11 – 2.07 (m, 1H), 1.05 (d, *J* = 13.6 Hz, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.2, 149.1, 147.4, 133.5, 129.2, 128.4, 128.2, 127.9, 127.4, 127.2, 127.0, 126.5, 125.9 125.4, 78.8, 76.0, 70.4, 64.6, 60.3, 53.1, 49.0,41.2, 21.5, 21.2. **HRMS** (ESI) calculated for $C_{28}H_{34}NO_2$ $[M+H]^+$: 416.2590, found: 416.2591.



methyl 4-((2-(2-methoxypropan-2-yl)-4,4-diphenylpyrrolidin-1-yl)methyl)benzoate 3h： yield: 65%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 80/1); white solid, melting point: 75-77℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.9 Hz, 2H), 7.44 – 6.99 (m, 12H), 4.22 (d, *J* = 14.1 Hz, 1H), 3.83 (s, 3H), 3.53 (d, *J* = 10.9 Hz, 1H), 3.20 (d, *J* = 14.4 Hz, 1H), 3.12 (s, 3H), 3.07 – 3.01(m, 2H), 2.94 – 2.91 (m, 1H), 2.14 – 2.10 (m, 1H), 1.05 (d, *J* = 5.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.2, 148.9, 147.3, 147.2, 131.0, 129.6, 128.5, 128.4, 128.1, 127.6, 127.2, 127.0, 126.6, 126.1, 125.7, 78.9, 70.8, 65.3, 61.1, 53.3, 52.1, 49.1, 41.4, 21.7, 20.8. **HRMS** (ESI) calculated for $C_{29}H_{34}NO_3$ $[M+H]^+$: 444.2539, found: 444.2541.

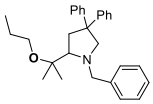


2-benzyl-3-(2-methoxypropan-2-yl)-2-azaspiro [4.5] decane 3i： yield: 73%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 50/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.09 (m, 5H), 4.53 (d, *J* = 13.9 Hz, 1H), 3.13 (s, 4H), 2.78 (t, *J* = 8.6 Hz, 1H), 2.68 (d, *J* = 9.5 Hz, 1H), 1.89 (d, *J* = 9.7 Hz, 1H), 1.65 – 1.51 (m, 1H), 1.34 – 1.19 (m, 14H), 1.03 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.8, 128.1, 128.0, 126.2, 78.8, 69.1, 60.5, 48.7, 39.5, 38.4, 38.0, 26.2, 23.6, 22.6, 19.9. **HRMS** (ESI) calculated for $C_{20}H_{32}NO$ $[M+H]^+$: 302.2484, found: 302.2484.

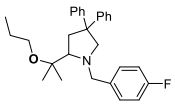


1-benzyl-2-(2-methoxypropan-2-yl)-4,4-dimethylpyrrolidine 3j: yield: 65%; (Flash column chromatography eluent, petroleum ether/ethyl acetate

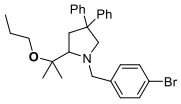
= 30/1); yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.10 (m, 5H), 4.51 (d, *J* = 14.4 Hz, 1H), 3.19 (d, *J* = 13.8 Hz, 1H), 3.14 (s, 3H), 2.88 – 2.82 (m, 1H), 2.58 (d, *J* = 9.7 Hz, 1H), 1.95 (d, *J* = 9.7 Hz, 1H), 1.61 – 1.50 (m, 1H), 1.31 – 1.24 (m, 1H), 1.22 (s, 3H), 1.03 (s, 3H), 0.94 (d, *J* = 10.4 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.9, 128.1, 126.2, 78.8, 70.1, 68.6, 60.8, 48.8, 43.9, 35.8, 29.4, 28.7, 22.5, 20.0. **HRMS** (ESI) calculated for $C_{17}H_{28}NO$ $[M+H]^+$: 262.2171, found: 262.2171.



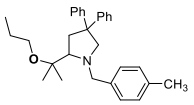
1-benzyl-4,4-diphenyl-2-(2-propoxypropan-2-yl) pyrrolidine 4a: yield: 80%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 200/1); yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.00 (m, 15H), 4.28 (d, *J* = 13.7 Hz, 1H), 3.52 (d, *J* = 11.0 Hz, 1H), 3.3 –3.20 (m, 2H), 3.12 – 3.01 (m, 3H), 2.95 – 2.89 (m, 1H), 2.12 – 2.05 (m, 1H), 1.49 – 1.33 (m, 2H), 1.07 (d, *J* = 12.2 Hz, 6H), 0.79 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.3, 147.7, 141.7, 128.4, 128.3, 128.2, 128.1, 127.4, 127.2, 126.5, 126.0, 125.6, 78.7, 71.1, 65.1, 62.9, 61.1, 53.2, 41.6, 23.9, 22.5, 21.1, 11.0. **HRMS** (ESI) calculated for $C_{29}H_{36}NO$ $[M+H]^+$: 414.2797, found: 414.2796.



1-(4-fluorobenzyl)-4,4-diphenyl-2-(2-propoxypropan-2-yl) pyrrolidine 4b: yield: 82%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 150/1); yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 – 6.90 (m, 14H), 4.21 (d, *J* = 13.5 Hz, 1H), 3.49 (d, *J* = 10.8 Hz, 1H), 3.29 – 3.19 (m, 2H), 3.07 – 2.96 (m, 3H), 2.95 – 2.88 (m, 1H), 2.13 (t, *J* = 10.9 Hz, 1H), 1.41 (d, *J* = 6.7 Hz, 2H), 1.06 (s, 6H), 0.79 (t, *J* = 8.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.9 (d, $J_{C–F}$ = 243.5 Hz), 149.2, 147.6, 137.3(d, $J_{C–F}$ = 2.6 Hz), 129.7(d, $J_{C–F}$ = 7.7 Hz), 128.3, 128.1 127.3, 127.1, 126.0(d, $J_{C–F}$ = 42.6 Hz), 115.0, 114.8, 78.6, 71.1, 65.0, 62.8, 60.2, 41.6, 23.9, 22.5, 20.8, 10.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.8. **HRMS** (ESI) calculated for $C_{29}H_{35}FNO$ $[M+H]^+$: 432.2703, found: 432.2704.

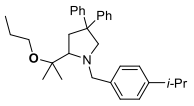


1-(4-bromobenzyl)-4,4-diphenyl-2-(2-propoxypropan-2-yl) pyrrolidine 4c: yield: 79%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 150/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 – 7.06 (m, 14H), 4.21 (d, *J* = 13.9 Hz, 1H), 3.50 (d, *J* = 10.9 Hz, 1H), 3.30 – 3.18 (m, 2H), 3.11 – 2.97 (m, 3H), 2.96 – 2.87 (m, 1H), 2.10 – 2.03(m, 1H), 1.44 – 1.33 (m, 2H), 1.05 (d, *J* = 2.9 Hz, 6H), 0.77 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.1, 147.5, 140.8, 131.2, 130.0, 129.2, 128.3, 128.3, 128.1, 127.8, 127.3, 127.0, 126.1, 125.6, 120.1, 78.7, 71.1, 65.1, 62.8, 60.4, 53.2, 41.5, 23.9, 22.5, 20.7, 11.0. **HRMS** (ESI) calculated for $C_{29}H_{35}BrNO$ $[M+H]^+$: 492.1902, found: 492.1904.

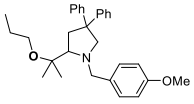


1-(4-methylbenzyl)-4,4-diphenyl-2-(2-propoxypropan-2-yl) pyrrolidine 4e: yield: 65%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 100/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 6.98 (m, 14H), 4.23 (d, *J* = 13.5 Hz, 1H), 3.51 (d, *J* = 10.7 Hz, 1H), 3.26 (d, *J* = 7.0 Hz, 2H), 3.04 (t, *J* = 13.3 Hz, 3H), 2.96 – 2.88 (m, 1H), 2.27 (s,

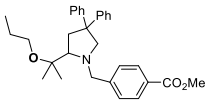
3H), 2.13 – 2.04 (m, 1H), 1.45 (d, *J* = 6.2 Hz, 2H), 1.07 (d, *J* = 12.8 Hz, 6H), 0.79 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.4, 147.7, 138.6, 136.0, 128.9, 128.3, 128.0, 127.3, 127.2, 126.0, 125.5, 78.6, 71.0, 65.0, 62.8, 60.8, 53.1, 41.6, 23.9, 22.5, 21.2, 21.2, 11.0. **HRMS** (ESI) calculated for $C_{30}H_{38}NO$ $[M+H]^+$: 428.2953, found: 428.2954.



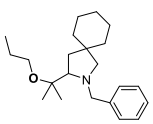
1-(4-isopropylbenzyl)-4,4-diphenyl-2-(2-propoxypropan-2-yl) pyrrolidine 4f: yield: 63%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 100/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 – 6.97 (m, 14H), 4.21 (d, *J* = 13.6 Hz, 1H), 3.52 (d, *J* = 11.0 Hz, 1H), 3.26 – 3.21 (m, 2H), 3.06 (t, *J* = 12.1 Hz, 3H), 2.95 – 2.88 (m, 1H), 2.86 – 2.78 (m, 1H), 2.11 – 2.05 (m, 1H), 1.44 – 1.36 (m, 2H), 1.18 (d, *J* = 6.8 Hz, 6H), 1.09 (s, 3H), 1.05 (s, 3H), 0.79 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.4, 147.7, 147.0, 139.0, 128.3, 128.3, 128.0, 127.4, 127.2, 126.2, 126.0, 125.5, 78.6, 71.1, 65.1, 62.3, 60.8, 53.2, 41.6, 33.8, 29.8, 24.2, 23.9, 22.5, 21.3, 11.0. **HRMS** (ESI) calculated for $C_{32}H_{42}NO$ $[M+H]^+$: 456.3266, found: 456.3266.



1-(4-methoxybenzyl)-4,4-diphenyl-2-(2-propoxypropan-2-yl) pyrrolidine 4g: yield: 68%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 100/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 6.72 (m, 14H), 4.19 (d, *J* = 13.1 Hz, 1H), 3.70 (s, 3H), 3.49 (d, *J* = 10.6 Hz, 1H), 3.34 (d, *J* = 6.4 Hz, 2H), 3.03 (d, *J* = 10.0 Hz, 3H), 2.93 (d, *J* = 10.3 Hz, 1H), 2.07 (t, *J* = 10.7 Hz, 1H), 1.48 (d, *J* = 6.1 Hz, 2H), 1.05 (d, *J* = 11.0 Hz, 6H), 0.79 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.4, 149.4, 147.8, 133.8, 129.5, 128.3, 128.1, 127.4, 127.2, 126.0, 125.6, 113.6, 78.7, 71.0, 64.9, 62.9, 60.4, 55.3, 53.1, 41.7, 24.0, 22.5, 21.2, 11.0. **HRMS** (ESI) calculated for $C_{30}H_{38}NO_2$ $[M+H]^+$: 444.2903, found: 444.2905.

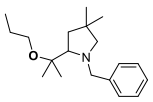


methyl 4-((4, 4-diphenyl-2-(2-propoxypropan-2-yl)pyrrolidin-1-yl)methyl)benzoate 4h: yield: 62%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 100/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.14 – 6.93 (m, 10H), 4.29 (d, *J* = 14.4 Hz, 1H), 3.72 (s, 3H), 3.50 (d, *J* = 10.9 Hz, 1H), 3.22 – 3.15 (m, 3H), 3.07 – 3.02 (m, 1H), 2.97 (d, *J* = 10.9 Hz, 1H), 2.96 – 2.85 (m, 1H), 2.08 – 2.02 (m, 1H), 1.37 – 1.32 (m, 2H), 1.02 (d, *J* = 6.0 Hz, 6H), 0.72 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.3, 149.1, 147.5, 144.2, 129.7, 128.6, 128.5, 128.4, 128.2, 128.2, 127.5, 127.3, 127.1, 126.7, 126.2, 125.8, 78.8, 71.4, 65.5, 62.9, 61.1, 53.4, 52.0, 41.6, 24.0, 22.6, 20.7, 11.1. **HRMS** (ESI) calculated for $C_{31}H_{38}NO_3$ $[M+H]^+$: 472.2852, found: 472.2854.

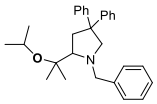


2-benzyl-3-(2-propoxypropan-2-yl)-2-azaspiro [4.5] decane 4i: yield: 65%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 80/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.12 (m, 5H), 4.60 (d, *J* = 13.9 Hz, 1H), 3.34 – 3.26 (m, 1H), 3.24 – 3.18 (m, 1H), 3.12 (d, *J* = 13.9 Hz, 1H), 2.79 (t, *J* = 8.4 Hz, 1H), 2.68 (t, *J* = 19.3 Hz, 1H), 1.90 (d, *J* =9.8 Hz,

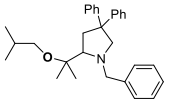
1H), 1.59 – 1.51 (m, 2H), 1.45 – 1.40 (m, 2H), 1.32 – 1.22 (m, 10H), 1.20 (s, 3H), 1.03 (s, 3H), 0.79 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.9, 128.1, 128.0, 126.1, 78.4, 69.5, 66.5, 62.6, 60.4, 41.7, 39.4, 38.4, 38.0, 26.2, 23.9, 23.5, 23.5, 23.3, 20.1, 10.9. **HRMS** (ESI) calculated for $C_{22}H_{36}NO$ $[M+H]^+$: 330.2797, found: 330.2797.



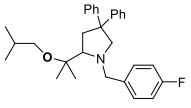
1-benzyl-4,4-dimethyl-2-(2-propoxypropan-2-yl) pyrrolidine 4j: yield: 67%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 80/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.10 (m, 5H), 4.58 (d, *J* = 13.8 Hz, 1H), 3.30 (d, *J* = 6.8 Hz, 1H), 3.23 (t, *J* = 11.1 Hz, 2H), 2.85 (t, *J* = 8.5 Hz, 1H), 2.57 (d, *J* = 9.4 Hz, 1H), 1.93 (d, *J* = 9.5 Hz, 1H), 1.58 – 1.50 (m, 1H), 1.45 – 1.37(m, 2H), 1.31 – 1.24 (m, 1H), 1.21 (s, 3H), 1.01 (s, 3H), 0.93 (d, *J* = 10.8 Hz, 6H), 0.79 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.0, 128.1, 128.0, 126.2, 78.5, 70.7, 68.6, 62.6, 60.8, 44.0, 35.8, 29.5, 28.7, 23.9, 23.2, 20.2, 11.0. **HRMS** (ESI) calculated for $C_{19}H_{32}NO$ $[M+H]^+$: 290.2484, found: 290.2483.



1-benzyl-2-(2-isopropoxypropan-2-yl)-4,4-diphenylpyrrolidine 5a: yield: 78%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 200/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 6.95 (m, 15H), 4.32 (d, *J* = 13.8 Hz, 1H), 3.80 – 3.71 (m, 1H), 3.51 (d, *J* = 11.0 Hz, 1H), 3.11 (d, *J* = 13.8 Hz, 1H), 3.05 – 2.90 (m, 3H), 2.11 – 2.01 (m, 1H), 1.05 (d, *J* = 17.5 Hz, 6H), 0.99 (d, *J* = 6.0 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.3, 147.7, 141.9, 128.4, 128.4, 128.3, 128.1, 127.4, 127.2, 126.6, 126.0, 125.6, 79.7, 72.3, 65.0, 63.3, 61.4, 53.3, 41.5, 25.5, 25.3, 23.3, 21.3. **HRMS** (ESI) calculated for $C_{29}H_{36}NO$ $[M+H]^+$: 414.2797, found: 414.2795.

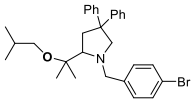


benzyl-2-(2-(isobutoxy) propan-2-yl)-4,4-diphenylpyrrolidine 6a: yield: 69%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 200/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.01 (m, 15H), 4.29 (d, *J* = 13.8 Hz, 1H), 3.52 (d, *J* = 11.0 Hz, 1H), 3.13 – 3.01 (m, 5H), 2.96 – 2.90 (m, 1H), 2.12 –2.04 (m, 1H), 1.63 (m, *J* = 15.5,7.8 Hz, 1H), 1.06 (d, *J* = 11.8 Hz, 6H), 0.78 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.2, 146.6, 140.7, 128.2, 127.2, 127.2, 127.1, 126.9, 126.7, 126.3, 126.0, 125.4, 124.9, 124.4, 77.5, 70.4, 66.9, 64.0, 60.1, 52.1, 41.6, 40.5, 28.1, 21.2, 19.7, 18.7. **HRMS** (ESI) calculated for $C_{30}H_{38}NO$ $[M+H]^+$: 428.2953, found: 428.2955.

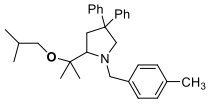


1-(4-fluorobenzyl)-2-(2-isobutoxypropan-2-yl)-4,4-diphenylpyrrolidine 6b: yield: 70%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 150/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 – 6.96 (m, 12H), 6.90 (t, *J* = 8.4 Hz, 2H), 4.22 (d, *J* = 13.6 Hz, 1H), 3.49 (d, *J* = 10.9 Hz, 1H), 3.09– 2.98 (m, 5H), 2.95 – 2.89 (m, 1H), 2.12 – 2.01 (m, 1H), 1.65 – 1.56 (m, 1H), 1.04 (d, *J* = 5.3 Hz, 6H), 0.77 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.7(d, $J_{C–F}$ = 243.8 Hz), , 149.2, 147.6, 137.4(d, $J_{C–F}$ = 2.9 Hz), 129.7(d, $J_{C–F}$ = 7.8 Hz), , 128.3, 128.1, 127.3, 127.1, 125.7(d, $J_{C–F}$ = 43.1 Hz), 115.0, 114.8, 78.6, 71.5, 68.0, 65.0, 60.3, 53.2, 41.6, 29.2, 22.4, 20.5, 19.8, 19.7, **^{19}F**

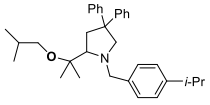
NMR (376 MHz, $CDCl_3$) δ -116.8. **HRMS** (ESI) calculated for $C_{30}H_{37}FNO$ $[M+H]^+$: 446.2859, found: 446.2857.



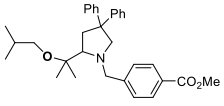
1-(4-bromobenzyl)-2-(2-isobutoxypropan-2-yl)-4,4-diphenylpyrrolidine 6c: yield: 68%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 150/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 2H), 7.22 – 7.18 (m, 3H), 7.13 – 6.99 (m, 9H), 4.22 (d, *J* = 14.0 Hz, 1H), 3.50 (d, *J* = 10.9 Hz, 1H), 3.08 – 2.99 (m, 5H), 2.95 – 2.89 (m, 1H), 2.10 – 2.02(m, 1H), 1.63 – 1.56 (m, 1H), 1.03 (d, *J* = 2.6 Hz, 6H), 0.77 – 0.73 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.1, 147.5, 140.8, 131.3, 130.0, 128.4, 128.1, 127.3, 127.1, 126.1, 125.7, 120.1, 78.6, 71.6, 68.0, 65.10, 60.5, 53.3, 41.5, 29.2, 22.4, 20.4, 19.8, 19.7. **HRMS** (ESI) calculated for $C_{30}H_{37}BrNO$ $[M+H]^+$: 506.2059, found: 506.2061.



2-(2-isobutoxypropan-2-yl)-1-(4-methylbenzyl)-4,4-diphenylpyrrolidine 6e: yield: 59%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 100/1); yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.05 (m, 15H), 4.24 (d, *J* = 13.6 Hz, 1H), 3.51 (d, *J* = 11.0 Hz, 1H), 3.09 – 3.00 (m, 5H), 2.96 – 2.90 (m, 1H), 2.27 (s, 3H), 2.12 – 2.04 (m, 1H), 1.64 – 1.60 (m, 1H), 1.05 (d, *J* = 12.8 Hz, 6H), 0.78 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.4, 147.7, 138.7, 135.9, 132.4, 130.1, 129.2, 128.8, 128.3, 128.3, 128.0, 127.3, 127.1, 125.9, 125.5, 78.5, 71.5, 68.0, 65.0, 60.8, 53.2, 42.6, 41.6, 29.2, 22.3, 21.2, 20.8, 19.7. **HRMS** (ESI) calculated for $C_{31}H_{40}NO$ $[M+H]^+$: 442.3110, found: 442.3111.

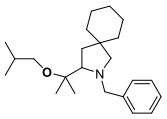


2-(2-isobutoxypropan-2-yl)-1-(4-isopropylbenzyl)-4,4-diphenylpyrrolidine 6f: yield: 54%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 100/1); yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.19 (m, 14H), 4.47 (d, *J* = 13.7 Hz, 1H), 3.77 (d, *J* = 11.0 Hz, 1H), 3.35 – 3.25(m, 5H), 3.20 – 3.12 (m, 1H), 3.09 – 3.02 (m, 1H), 2.36 – 2.28 (m, 1H), 1.90 – 1.82 (m, 1H), 1.42 (d, *J* = 6.9 Hz, 6H), 1.30 (d, *J* = 16.3 Hz, 6H), 1.02 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.5, 147.8, 147.1, 139.1, 128.4, 128.3, 128.1, 127.5, 127.3, 126.3, 126.1, 125.6, 78.6, 71.6, 68.1, 65.2, 60.9, 53.3, 41.7, 33.9, 29.3, 24.3, 24.2, 22.4, 21.1, 19.9. **HRMS** (ESI) calculated for $C_{33}H_{44}NO$ $[M+H]^+$: 470.3423, found: 470.3423.

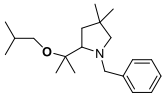


methyl 4-((2-(2-isobutoxypropan-2-yl)-4, 4-diphenylpyrrolidin-1-yl)methyl)benzoate 6h: yield: 66%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 60/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.23 – 7.14 (m, 4H), 7.12 – 6.97 (m, 6H), 4.34 (d, *J* = 14.4 Hz, 1H), 3.80 (s, 3H), 3.53 (d, *J* = 10.9 Hz, 1H), 3.19 (d, *J* = 14.4 Hz, 1H), 3.08 – 2.98 (m, 4H), 2.95 – 2.88 (m, 1H), 2.13 – 2.03 (m, 1H), 1.63 – 1.53 (m, 1H), 1.04 (d, *J* = 4.2 Hz, 6H), 0.74 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.3, 149.0, 147.5, 129.6, 128.5, 128.4, 128.1,

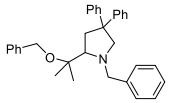
127.3, 127.1, 126.1, 125.7, 78.6, 71.7, 68.0, 65.4, 61.1, 53.3, 52.0, 41.5, 29.1, 22.4, 20.3, 19.7. **HRMS** (ESI) calculated for $C_{32}H_{40}NO_3$ $[M+H]^+$: 486.3008, found: 486.3008.



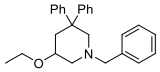
2-benzyl-3-(2-isobutoxypropan-2-yl)-2-azaspiro [4.5] decane 6i: yield: 59%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 80/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.10 (m, 5H), 4.61 (d, *J* = 14.0 Hz, 1H), 3.15 – 3.07 (m, 2H), 3.01 (t, *J* = 7.5 Hz, 1H), 2.76 (t, *J* = 8.6 Hz, 1H), 2.67 (d, *J* = 9.8 Hz, 1H), 1.89 (d, *J* = 9.7 Hz, 1H), 1.68 – 1.52 (m, 3H), 1.34 – 1.21 (m, 10H), 1.18 (s, 3H), 1.01 (s, 3H), 0.80 – 0.76 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.0, 128.1, 128.0, 126.1, 78.4, 70.0, 67.8, 66.6, 60.5, 41.8, 39.5, 38.4, 38.0, 29.2, 26.2, 23.6, 23.5, 23.2, 19.8, 19.8. **HRMS** (ESI) calculated for $C_{23}H_{38}NO$ $[M+H]^+$: 344.2953, found: 344.2952.



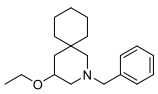
1-benzyl-2-(2-isobutoxypropan-2-yl)-4,4-dimethylpyrrolidine 6j: yield: 65%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 80/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.18 (m, 5H), 4.66 (d, *J* = 13.9 Hz, 1H), 3.27 (d, *J* = 13.9 Hz, 1H), 3.19 – 3.15 (m, 1H), 3.12 – 3.05 (m, 1H), 2.95 – 2.87 (m, 1H), 2.64 (d, *J* = 9.6 Hz, 1H), 2.01 (d, *J* = 9.7 Hz, 1H), 1.74 – 1.66 (m, 1H), 1.65 – 1.58 (m, 1H), 1.41 – 1.34 (m, 1H), 1.27 (s, 3H), 1.08 (s, 3H), 1.00 (d, *J* = 9.8 Hz, 6H), 0.85 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.0, 128.1, 128.0, 126.1, 78.3, 71.1, 68.5, 67.8, 60.8, 43.9, 35.8, 29.4, 29.1, 28.6, 23.0, 19.9, 19.7, 19.7. **HRMS** (ESI) calculated for $C_{20}H_{34}NO$ $[M+H]^+$: 304.2640, found: 304.2640.



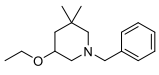
1-benzyl-2-(2-(benzyloxy)propan-2-yl)-4, 4-diphenylpyrrolidine 7a: yield: 74%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 150/1); white solid (m.p. = 104 – 105 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.01 (m, 20H), 4.45 (s, 2H), 4.22 (d, *J* = 13.8 Hz, 1H), 3.56 (d, *J* = 11.1 Hz, 1H), 3.19 (t, *J* = 8.5 Hz, 1H), 3.16 – 3.08 (m, 2H), 3.00 (m= 1H), 2.18 (m, 1H), 1.20 (d, *J* = 12.5 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.0, 146.3, 140.6, 138.9, 127.3, 127.2, 127.2, 127.1, 127.0, 126.2, 126.1, 126.0, 125.9, 125.4, 125.0, 124.5, 78.5, 70.3, 63.9, 62.6, 60.2, 52.4, 40.3, 21.4, 20.5. **HRMS** (ESI) calculated for $C_{33}H_{36}NO$ $[M+H]^+$: 462.2797, found: 462.2798.



1-benzyl-5-ethoxy-3, 3-diphenylpiperidine 8a: yield: 79%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 80/1); white solid (m.p. = 114 – 116 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.00 (m, 15H), 3.52 (s, 2H), 3.47 (d, *J* = 12.3 Hz, 1H), 3.35 (q, *J* = 6.8 Hz, 2H), 3.27 – 3.21 (m 1H), 3.14 – 3.11 (m, 1H), 2.76 (d, *J* = 10.2 Hz, 1H), 2.12 (d, *J* = 12.0 Hz, 1H), 1.95 (t, *J* = 11.7 Hz, 1H), 1.85 (t, *J* = 10.0 Hz, 1H), 1.05 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.0, 145.0, 137.0, 128.3, 127.4, 127.2, 127.2, 126.9, 126.2, 125.5, 125.0, 124.5, 71.5, 62.9, 61.9, 61.5, 57.5, 45.8, 40.8, 14.7. **HRMS** (ESI) calculated for $C_{26}H_{30}NO$ $[M+H]^+$: 372.2327, found: 372.2329.

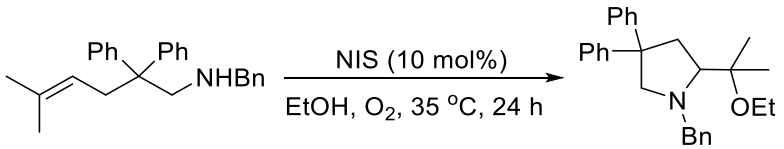


2-benzyl-4-ethoxy-2-azaspiro[5.5]undecane 8b: yield**:** 66%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 60/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.16 (m, 5H), 3.52 – 3.46 (m, 2H), 3.44 – 3.41 (m, 2H), 3.35 (d, *J* = 13.4 Hz, 1H), 3.05 (d, *J* = 6.0 Hz, 1H), 2.56 (d, *J* = 11.0 Hz, 1H), 1.93 (d, *J* = 9.7 Hz, 1H), 1.70 (t, *J* = 10.0 Hz, 1H), 1.53 – 1.48 (m, 2H), 1.45 – 1.14 (m, 10H), 1.10 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.2 127.6, 127.1, 125.8, 71.3, 62.7, 61.8, 58.7, 37.6, 33.4, 32.7, 25.8, 20.6, 14.7. **HRMS** (ESI) calculated for $C_{19}H_{30}NO$ $[M+H]^+$: 288.2327, found: 288.2326.



1-benzyl-5-ethoxy-3, 3-dimethylpiperidine 8c: yield**:** 69%; (Flash column chromatography eluent, petroleum ether/ethyl acetate = 80/1); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.13 (m, 5H), 3.52 – 3.34 (m, 5H), 3.05 – 3.01 (m, 1H), 2.26 (d, *J* = 10.9 Hz, 1H), 1.72 – 1.64 (m, 2H), 1.64 – 1.58 (t, J = 7.0 Hz, 1H), 1.09 (t, *J* = 7.0 Hz, 3H), 0.94 (d, *J* = 12.1 Hz, 4H), 0.80 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.0, 127.6, 127.1, 125.8, 71.9, 64.1, 62.7, 61.7, 58.0, 43.1, 30.7, 28.6, 24.8, 14.7. **HRMS** (ESI) calculated for $C_{16}H_{26}NO$ $[M+H]^+$: 248.2014, found: 248.2014.

The procedure for gram-scale reaction

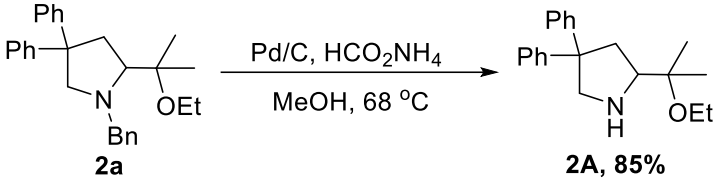


1a, 2.34 g **2a,** 2.37 g 90%

1a (6.5 mmol) and NIS (0.65 mmol) were charged in a 100 mL sealed tube equipped with a stir bar in O_2 atmosphere. Solvent (30 mL) were added to the sealed tube by syringe and the mixture was stirred at 35 ℃ for 24 h. Upon completion, the mixture was extracted with CH_2Cl_2 (50 mL × 3). The combined organic mixture was dried with anhydrous magnesium sulfate, concentrated *in vacuo*, and purified over silica gel via flash column chromatography with PE and EA as the eluent to obtain desired product **2a** (2.37 g, 97%).

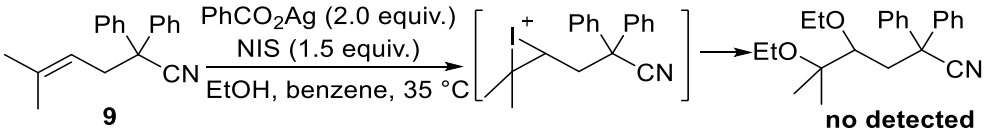
Procedure for debenzylation reaction: Substrate **2a** (1g), HCO_2NH_4 (0.25g), Pd/C (0.6g) and MeOH (20 mL) were charged in a 100 mL sealed reactor with a stir bar in H_2 atmosphere and then the mixture was stirred at 68 °C for 6 h. Upon completion, the mixture was extracted with CH_2Cl_2 (30 mL × 3). The combined organic mixture was dried with anhydrous magnesium sulfate, concentrated *in vacuo*, and

purified over silica gel via flash column chromatography with PE and EA as the eluent to obtain desired product **2A** (0.66 g, 85%).

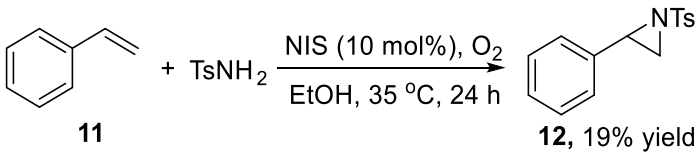


The procedure for control reactions

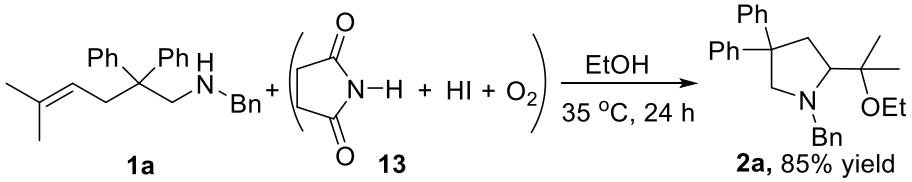
Substrate **9** (0.25 mmol), $PhCO_2Ag$ (2.0 equiv), NIS (1.5 equiv), benzene (10 mL) and EtOH (10mL) were added to a round-bottomed flask (100mL) with a magnetic stirrer. The mixture was stirring at 35 °C for 24 h. Finally, the mixture was extracted with CH_2Cl_2 (30 mL × 3) and the organic mixture was then dried with $MgSO_4$ and concentrated *in vacuo*. Reactions were monitored by thin-layer chromatography (TLC) on silica gel plates (GF 254) and NMR (Bruker DRX 400 spectrometer at 298 K using deuterated chloroform as a solvent and TMS as an internal reference), and it was found did not form the expected dialkoxylation product.



Styrene (0.25mmol), *p*-toluenesulfonamide (1.2 equiv) and NIS (1.5 equiv) were charged in a 50 mL sealed tube equipped with a stir bar in O_2 atmosphere. Solvent (20 mL) were added to the sealed tube by syringe and the mixture was stirred at 35 °C for 24 h. Upon completion, the mixture was extracted with CH_2Cl_2 (50 mL × 3). The combined organic mixture was dried with anhydrous magnesium sulfate, concentrated *in vacuo*, and purified over silica gel via flash column chromatography with PE and EA as the eluent to obtain desired product **12** (0.013 g, 19%).



Substrate **1a** (0.25 mmol) and **13** (1equiv) were charged in a 50 mL sealed tube equipped with a stir bar in O_2 and HI atmosphere. EtOH (10 mL) were added to the sealed tube by syringe and the mixture was stirred at 35 °C for 24 h. Upon completion, the mixture was extracted with CH_2Cl_2 (30 mL × 3). The combined organic mixture was dried with anhydrous magnesium sulfate, concentrated *in vacuo*, and purified over silica gel via flash column chromatography with PE and EA as the eluent to obtain desired product **2a** (0.085g, 85%).



Derivatization of the products.

Computational details

All DFT [1] calculations were carried out using Gaussian 16 ES64L-G16RevB.01 [2] suite of programs. Geometries of intermediates and transition states were optimized using the b3lyp[3] level of theory in combination with the DFT-D3 dispersion corrections with the Becke-Johnson damping scheme (D3BJ) [4, 5]. The def2-SVP basis set [6, 7] was used for all atoms and the solvent effects were computed with the SMD solvation model [8] (Solvent = EtOH). Vibrational frequency calculations were performed for all stationary points to confirm if each optimized structure is a local minimum or a transition state structure. All optimized transition state structures have only one imaginary (negative) frequency, and all minima (reactants, products, and intermediates) have no imaginary frequencies. The single-point energies and solvent effects were computed with the wB97XD [9]/def2-TZVPP [10, 11] basis sets. The corrections of free energies [12] were applied for entropy calculations with a frequency cut-off of 100 cm^{-1} using the Shermo [13] program. The relative Gibbs free energies are given in kcal/mol, which were calculated by adding the gas-phase thermal and non-thermal corrections at 308.15 K to the single-point energies.

1a

C	**4.4714930**	**-0.3649400**	**-0.7663200**
C	**3.5059360**	**0.5092060**	**-1.1082700**
C	**2.1683860**	**0.1936370**	**-1.7085780**
C	**0.9550810**	**0.2096400**	**-0.7137400**
C	**-0.3030720**	**-0.0739380**	**-1.5763950**
N	**-1.5278420**	**-0.1624530**	**-0.8075970**
C	**5.7498370**	**0.1075820**	**-0.1253280**
C	**4.3747710**	**-1.8567160**	**-0.9358920**
C	**1.2158100**	**-0.9039190**	**0.3088300**
C	**-2.7074770**	**-0.4251270**	**-1.6148460**
C	**-3.9694910**	**-0.4521590**	**-0.7816180**
C	**-4.1941380**	**0.5218660**	**0.2054470**
C	**-5.3682140**	**0.5128630**	**0.9620610**
C	**-6.3397630**	**-0.4712200**	**0.7446270**
C	**-6.1250320**	**-1.4464070**	**-0.2333320**
C	**-4.9462130**	**-1.4367800**	**-0.9870160**

C	2.0262850	-0.6654940	1.4323280	N	0.9603400	-0.0632630	-0.2821560
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C	1.9108610	-2.9963930	2.0880780	C	-0.3140010	-1.7637080	0.7085460
C	1.1070000	-3.2521770	0.9752950	C	2.1862860	-2.2511460	0.2358220
C	0.7686280	-2.2178000	0.0958070	C	2.0564060	-2.6788830	-1.2269450
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C	0.1792450	4.1017130	1.1088920	C	2.0958490	-3.4548010	1.1797360
C	0.8952990	4.0152920	-0.0866120	C	2.0294600	0.7889610	-0.7291060
C	1.1708650	2.7672400	-0.6570550	C	1.5935850	2.2388460	-0.8520730
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H	4.3746440	-2.3516560	0.0515410	C	-1.1695200	0.5273680	2.3241080
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H	-2.6359110	-1.3697890	-2.1960680	C	-4.4856280	-2.7288710	-0.1183390
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H	-5.5271890	1.2785760	1.7263710	C	-4.1557530	-1.6778160	-2.2658420
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H	0.1551340	-2.4565390	-0.7742930	H	1.0502580	-3.0748860	-1.4250540
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H	-2.5145220	3.5342390	3.2418050	H	-6.2868940	1.1670820	-0.6383510
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				H	6.8786920	1.0748000	-0.9921390
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C	3.6031220	1.2710060	-0.0474710	I	1.4678630	-1.9147240	-0.3019850
C	4.7754490	1.5396680	-0.7553760				
C	5.9607710	0.8649090	-0.4367530	B			
C	5.9633240	-0.0794810	0.5934120	C	1.2475820	-0.3505880	-0.3038390
C	4.7853100	-0.3510370	1.2982640	C	1.2492060	-1.3462740	-1.4989470
C	-2.7212560	-0.3254730	-1.3273030	C	-0.1952170	-1.3936220	-1.9557900
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C	-2.7837110	-2.9622450	-0.4460590	C	1.2397490	1.1250590	-0.7531560
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C	-0.1615870	1.3613240	-1.4082950	C	-2.4456880	-2.6116410	-2.1541830
C	0.4479540	2.3946540	-2.1211930	C	-0.8159240	-3.4533650	-0.4310800
C	0.4691740	3.6935790	-1.6019960	C	-2.0531360	0.1830440	-1.0434840

C	-2.8961050	0.4411090	0.1772790				
C	-3.7370530	-0.5501690	0.7059020	EtOH			
C	-4.4987300	-0.2936940	1.8477730	O	-1.2383300	-0.2577340	-0.1102300
C	-4.4334010	0.9577980	2.4707710	H	-1.2477010	-0.8985940	0.6167380
C	-3.6001970	1.9506170	1.9483790	C	-0.0832780	0.5540650	0.0469810
C	-2.8318760	1.6908910	0.8095310	H	-0.1160350	1.2941790	-0.7703940
C	1.0965780	2.1199320	0.2307260	H	-0.1254850	1.1252200	0.9961840
C	1.0451170	3.4706820	-0.1108310	C	1.2106040	-0.2407320	-0.0216440
C	1.1401470	3.8605410	-1.4522980	H	2.0859280	0.4261580	0.0503530
C	1.2924430	2.8844790	-2.4370000	H	1.2709280	-0.9667810	0.8075930
C	1.3427560	1.5278500	-2.0900930	H	1.2750460	-0.7983070	-0.9706530
C	3.7287190	-0.5839770	0.0796940				
C	4.8475350	-0.7731920	0.8914540	EtOI			
C	4.6932480	-0.9566120	2.2705070	O	0.8432520	0.9582390	-0.3770640
C	3.4120690	-0.9462570	2.8246470	C	1.9992540	0.5260150	0.3346270
C	2.2898300	-0.7594030	2.0086520	H	2.7289380	1.3306320	0.1250250
H	1.5848390	-2.3300050	-1.1472500	H	1.8165770	0.5269460	1.4253980
H	1.9163910	-1.0458740	-2.3127810	C	2.5493780	-0.8104630	-0.1226140
H	-0.4558760	-0.9506310	-2.9199490	H	3.4987640	-1.0250630	0.3948460
H	-0.5249880	0.1419580	0.9574150	H	1.8488680	-1.6306580	0.1054660
H	-0.0892170	-1.5707910	0.9585810	H	2.7370760	-0.8040340	-1.2083990
H	-2.7152250	-1.8106460	-2.8523590	I	-0.8805290	-0.0822080	0.0170210
H	-3.2968180	-2.8193240	-1.4896100				
H	-2.2535340	-3.5165720	-2.7501270	H2O			
H	-0.8183690	-4.3835800	-1.0180870	O	0.0000000	0.0000000	0.1215240
H	0.1732500	-3.3602880	0.0296390	H	0.0000000	0.7553680	-0.4860970
H	-1.5718310	-3.5540450	0.3624020	H	0.0000000	-0.7553680	-0.4860970
H	-1.4915170	1.0829860	-1.3227570				
H	-2.6644100	-0.1107540	-1.9027010	HI			
H	-3.7961050	-1.5284730	0.2249000	I	0.0000000	0.0000000	0.0301120
H	-5.1493970	-1.0732590	2.2519250	H	0.0000000	0.0000000	-1.5959210
H	-5.0313890	1.1573150	3.3635890				
H	-3.5424170	2.9294450	2.4309100	NHS			
H	-2.1698680	2.4624700	0.4078480	N	0.0000000	0.0000000	0.9577930
H	1.0238300	1.8331680	1.2823570	H	0.0000000	0.0000000	1.9775160
H	0.9312680	4.2232790	0.6735660	C	0.0000000	1.1648660	0.2094250
H	1.0981390	4.9182030	-1.7239970	O	0.0000000	2.2853940	0.6757890
H	1.3715340	3.1723760	-3.4884300	C	0.0000000	-1.1648660	0.2094250
H	1.4602380	0.7949900	-2.8882470	O	0.0000000	-2.2853940	0.6757890
H	3.8625790	-0.4278790	-0.9933510	C	0.0000000	0.7664430	-1.2551680
H	5.8458440	-0.7751100	0.4462440	H	0.8861990	1.2074290	-1.7364440
H	5.5686710	-1.1033660	2.9080760	H	-0.8861990	1.2074290	-1.7364440
H	3.2779790	-1.0833200	3.9007500	C	0.0000000	-0.7664430	-1.2551680
H	1.3015500	-0.7486730	2.4708560	H	-0.8861990	-1.2074290	-1.7364440

H	0.8861990	-1.2074290	-1.7364440

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O	0.0000280	2.2921480	-0.8577790
C	0.0000000	-1.1730550	-1.3188960
O	-0.0000280	-2.2921480	-0.8577790
C	-0.0000660	0.7661230	-2.7796310
H	0.8868390	1.2065790	-3.2597650
H	-0.8871750	1.2063780	-3.2595740
C	0.0000660	-0.7661230	-2.7796310
H	-0.8868390	-1.2065790	-3.2597650
H	0.8871750	-1.2063780	-3.2595740
I	0.0000000	0.0000000	1.5072660

O2

O	0.0000000	0.0000000	0.5992980
O	0.0000000	0.0000000	-0.5992980

TS1

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O	-0.9497430	1.8211310	-1.4427590
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O	-1.9541730	-1.2924840	1.7372040
C	-3.1569820	1.0860410	-0.6840180
H	-3.4992880	0.7965830	-1.6899460
H	-3.5465660	2.0959880	-0.4841030
C	-3.4954400	0.0618550	0.4005150
H	-4.0563920	0.4849020	1.2483630
H	-4.0625770	-0.8078060	0.0343910
I	0.9907400	-1.0945680	-0.4345180
C	1.9014260	1.9068700	0.6309600
H	1.4936260	2.1778390	-0.3564290
H	1.6337170	2.7094460	1.3409550
C	3.3954420	1.6878140	0.5991690
H	3.7674040	1.3833070	1.5901830
H	3.6683840	0.9122290	-0.1327270
H	3.8976390	2.6247970	0.3119130
O	1.2363790	0.7228070	1.1115680
H	0.2350990	0.8230500	1.0522350

TS2

C	-4.4600760	-2.0145500	-0.8825370
C	-3.1300150	-2.1939010	-0.7740020
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C	-0.9227200	-0.8682110	-0.4498580
C	0.0168040	-0.0518830	-1.3811690
C	0.1942690	2.9655850	-0.8402430
C	0.0758020	3.4900070	0.4554680
C	-0.9704820	4.3563050	0.7764090
C	-1.9161990	4.7054500	-0.1934210
C	-1.8084680	4.1858490	-1.4864720
C	-0.7571900	3.3218570	-1.8073900
H	-2.7932280	-3.0317180	-0.1549030
H	-1.5134160	-2.0373810	-2.1551500
H	-2.4443190	-0.5548860	-1.9932690
H	0.4090160	-0.6912140	-2.1872490
H	-0.6102300	0.7003460	-1.8770020
H	0.8131630	3.2180410	1.2136960
H	-1.0517230	4.7567130	1.7896120
H	-2.5416330	4.4572710	-2.2503210
H	-0.6654280	2.9293640	-2.8236450
H	1.2804360	0.5009750	0.2773270
O	2.3290450	-0.2818580	1.3422380
N	1.1389660	0.6484020	-0.7499460
H	-2.7370250	5.3812880	0.0597650
C	3.2854040	0.2187360	2.1994650
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H	4.3075120	-0.1175160	1.8921440
C	3.2880710	1.7413930	2.3187720
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H	3.4909420	2.2076120	1.3393600
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I	3.3243950	-0.3965870	-1.0553950
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H	2.2597820	2.3975280	-0.6870020
H	1.5237470	2.0380240	-2.2639720
C	-1.4855470	0.0878040	0.6156430
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C	-2.6847360	0.7884140	0.4141840
C	-1.2748500	1.2065120	2.7770670
H	0.1812700	-0.1575630	1.9755440
C	-3.1845650	1.6625840	1.3839490
H	-3.2487740	0.6616490	-0.5070650
C	-2.4905320	1.8650110	2.5786380
H	-0.7010960	1.3728600	3.6927950

H	-4.1234340	2.1902620	1.1973780
H	-2.8842800	2.5443620	3.3389400
C	-0.2514920	-2.1078310	0.1678480
C	0.7354150	-2.8160690	-0.5328250
C	-0.6960080	-2.6498490	1.3864180
C	1.2911560	-3.9925210	-0.0224260
H	1.0858850	-2.4545200	-1.4988500
C	-0.1474250	-3.8270630	1.9010120
H	-1.4862100	-2.1507870	1.9468720
C	0.8579950	-4.5022830	1.2032070
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H	-0.5123370	-4.2181710	2.8544560
H	1.2938270	-5.4192900	1.6080220
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H	-6.0988390	-3.4306860	-0.8622490
H	-4.8966480	-3.6885130	0.4357880
H	-6.0650610	-2.3398510	0.5275660
C	-5.1229190	-0.9357090	-1.6967610
H	-5.7132620	-0.2669550	-1.0450210
H	-4.4164790	-0.3198130	-2.2690650
H	-5.8385290	-1.3790780	-2.4116040

TS3

C	-1.3973950	-1.0091950	0.4540570
C	-1.5220510	-1.4182530	1.9610130
C	-1.3400650	-0.3027380	2.8630340
N	-0.1412480	1.0263400	1.2469900
C	-0.1177330	-0.1295590	0.3750230
C	-2.6155200	-0.1808130	0.0548770
C	-1.3009930	-2.2684130	-0.4050760
C	-0.2853680	0.7191770	2.6856420
C	-0.5949200	1.9476840	3.5502980
C	1.0158970	0.0558450	3.2389050
C	-0.6667180	2.2729240	0.6928030
C	0.0730970	2.6814670	-0.5653960
C	1.4750890	2.6466650	-0.6189480
C	2.1519120	3.0364500	-1.7758910
C	1.4363510	3.4731000	-2.8973680
C	0.0401510	3.5129990	-2.8520790
C	-0.6359770	3.1132180	-1.6938710
C	-2.7829590	0.1525490	-1.3014460
C	-3.7930600	1.0229020	-1.7031660
C	-4.6677770	1.5766950	-0.7578940
C	-4.5282360	1.2380500	0.5870600
C	-3.5193300	0.3511150	0.9853780
C	-2.4236910	-3.1096170	-0.4943230
C	-2.3860170	-4.2805100	-1.2516520
C	-1.2215510	-4.6296170	-1.9449750
C	-0.1026170	-3.7981380	-1.8686080
C	-0.1385610	-2.6270990	-1.1026370
H	-0.6413240	-2.0675890	2.1724610
H	-2.4244980	-1.9978480	2.1890910
H	-1.9609730	-0.2507170	3.7674110
H	0.0254990	0.2096420	-0.6571200
H	0.7480090	-0.7583050	0.6247360
H	-1.5626960	2.3998240	3.2936000
H	0.1973910	2.6998950	3.4360700
H	-0.6265710	1.6411050	4.6052120
H	1.7938920	0.8341810	3.2056750
H	0.8872120	-0.2799400	4.2788850
H	1.3332680	-0.7977530	2.6278260
H	-1.7472010	2.2419820	0.4726910
H	-0.5210350	3.0663280	1.4361480
H	2.0356900	2.2891130	0.2471110
H	3.2438360	2.9924970	-1.8044550
H	1.9665750	3.7748730	-3.8044570
H	-0.5281040	3.8457620	-3.7248290
H	-1.7283150	3.1282580	-1.6663520
H	-2.0926210	-0.2545870	-2.0429320
H	-3.8931520	1.2832210	-2.7597480
H	-5.4593220	2.2600810	-1.0746870
H	-5.2120880	1.6476230	1.3341680
H	-3.4772770	0.0744070	2.0422420
H	-3.3421900	-2.8400900	0.0327440
H	-3.2704020	-4.9206800	-1.3051440
H	-1.1897750	-5.5435330	-2.5435550
H	0.8119460	-4.0565790	-2.4084350
H	0.7555680	-2.0049220	-1.0627670
I	3.8859550	-0.7562640	0.0579420

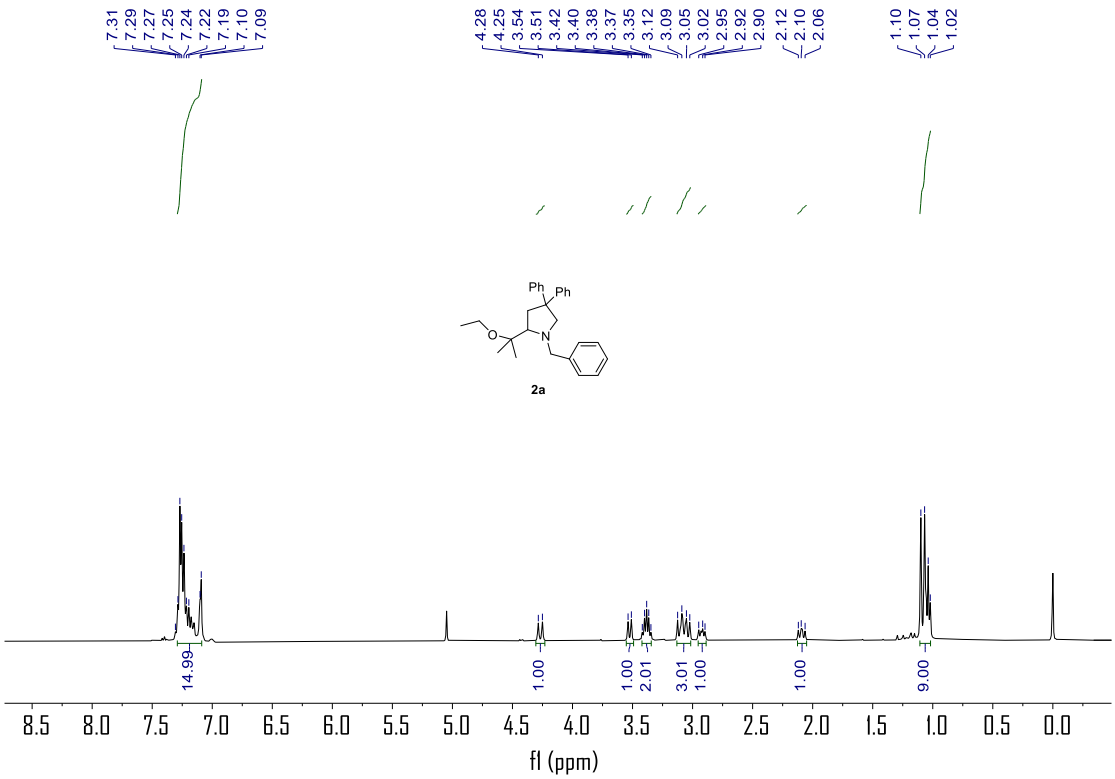
TS4

C	-1.8770770	-1.1508260	-0.1281960
C	-0.4318970	-1.4370250	0.3569060
C	0.1490100	-0.0510250	0.6640310
N	-0.7314230	0.9338210	0.0145280
C	-1.6490410	0.1980340	-0.8570330
C	-2.8695400	-0.9167500	1.0260510
C	-2.4072910	-2.2672800	-1.0195390

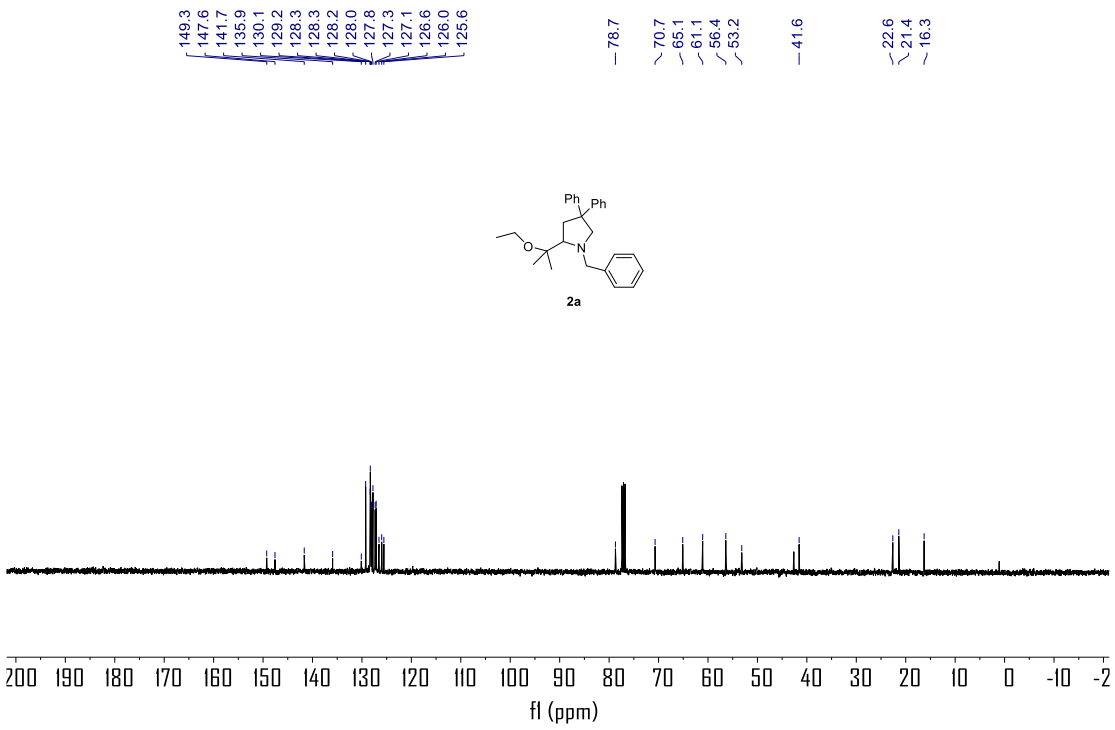
C	**1.3157210**	**0.4605400**	**-0.1076370**	**H**	**1.1460310**	**-0.8787540**	**-1.8129030**
C	**2.0424010**	**1.6577190**	**0.4033940**	**H**	**1.0880260**	**0.8722970**	**-2.1760730**
C	**1.5467490**	**0.1017700**	**-1.5356370**	**H**	**-1.9429280**	**1.6495220**	**1.6008870**
C	**-1.2482050**	**2.0320940**	**0.8326890**	**H**	**-0.3956280**	**2.4781180**	**1.3647100**
C	**-1.9337520**	**3.0859120**	**-0.0008480**	**H**	**-0.1483980**	**3.6103080**	**-1.1030390**
C	**-1.2153250**	**3.8071420**	**-0.9675220**	**H**	**-1.2818570**	**5.3258570**	**-2.5012450**
C	**-1.8524150**	**4.7692490**	**-1.7531410**	**H**	**-3.7176470**	**5.7765630**	**-2.1979880**
C	**-3.2190710**	**5.0232810**	**-1.5825040**	**H**	**-5.0096810**	**4.4993600**	**-0.4871060**
C	**-3.9419510**	**4.3089970**	**-0.6236510**	**H**	**-3.8694810**	**2.7745480**	**0.9018570**
C	**-3.3015150**	**3.3425250**	**0.1601120**	**H**	**-4.4716300**	**-0.3958440**	**-0.3337430**
C	**-4.1780390**	**-0.5076240**	**0.7126190**	**H**	**-6.1205300**	**0.0806430**	**1.4414790**
C	**-5.1110670**	**-0.2384810**	**1.7137210**	**H**	**-5.4841180**	**-0.1651080**	**3.8486320**
C	**-4.7563950**	**-0.3767330**	**3.0612000**	**H**	**-3.1720610**	**-0.9064290**	**4.4335910**
C	**-3.4644710**	**-0.7912980**	**3.3865820**	**H**	**-1.5279160**	**-1.3727050**	**2.6687860**
C	**-2.5304360**	**-1.0589850**	**2.3774530**	**H**	**-1.9480660**	**-3.8046240**	**0.4324460**
C	**-2.3654010**	**-3.5929460**	**-0.5549730**	**H**	**-2.8120210**	**-5.6662030**	**-0.9530580**
C	**-2.8575550**	**-4.6420350**	**-1.3326930**	**H**	**-3.7959940**	**-5.2044210**	**-3.2035670**
C	**-3.4092600**	**-4.3844470**	**-2.5930820**	**H**	**-3.8966150**	**-2.8550410**	**-4.0423550**
C	**-3.4639820**	**-3.0703060**	**-3.0617410**	**H**	**-3.0278240**	**-1.0012030**	**-2.6676030**
C	**-2.9673550**	**-2.0197390**	**-2.2808960**	**C**	**3.0598920**	**-0.5460260**	**2.9643760**
H	**0.1221640**	**-1.9273610**	**-0.4516080**	**H**	**3.1678480**	**-1.0188170**	**3.9543580**
H	**-0.3806340**	**-2.1016290**	**1.2253890**	**H**	**3.9941140**	**-0.0069950**	**2.7399200**
H	**0.2565630**	**0.1445040**	**1.7378060**	**H**	**2.2401010**	**0.1856670**	**3.0250090**
H	**-2.5612140**	**0.7800770**	**-1.0250760**	**C**	**2.7813530**	**-1.6103550**	**1.9192320**
H	**-1.1811160**	**0.0243120**	**-1.8383100**	**H**	**3.5715440**	**-2.3822150**	**1.9401600**
H	**1.8755420**	**1.8336070**	**1.4720490**	**H**	**1.8265240**	**-2.1181810**	**2.1228000**
H	**1.7191970**	**2.5430970**	**-0.1685420**	**O**	**2.6915440**	**-1.1054670**	**0.5849040**
H	**3.1193600**	**1.5426110**	**0.2112590**	**H**	**3.5815680**	**-0.7856760**	**0.3084350**
H	**2.6264210**	**0.1254780**	**-1.7426080**	**I**	**5.8666690**	**-0.0018990**	**-0.3883270**

Selected NMR

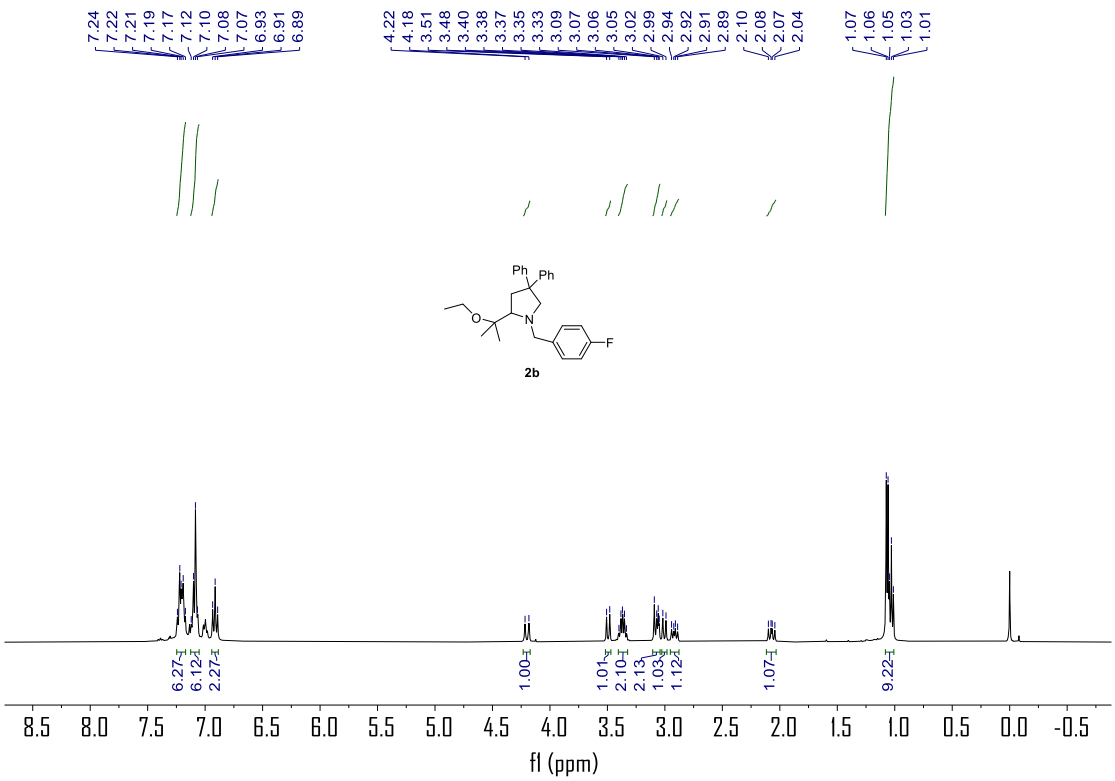
^{1}H NMR (400 MHz, $CDCl_3$) of 2a



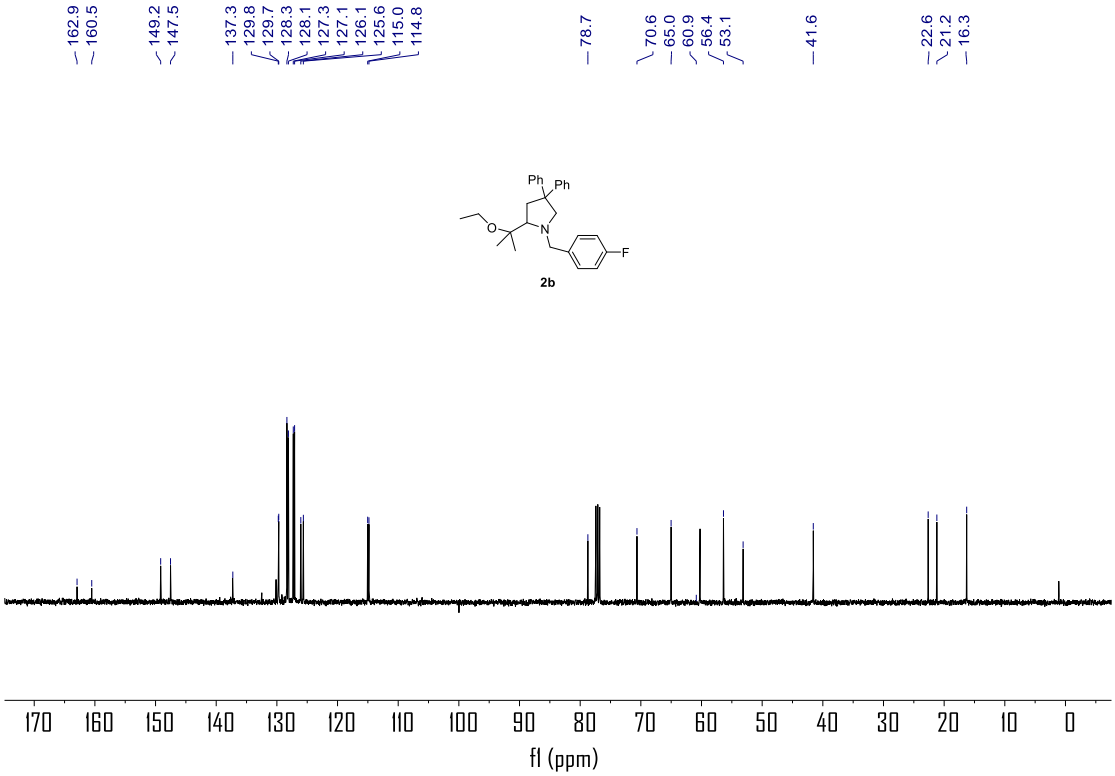
^{13}C NMR (101MHz, $CDCl_3$) of 2a



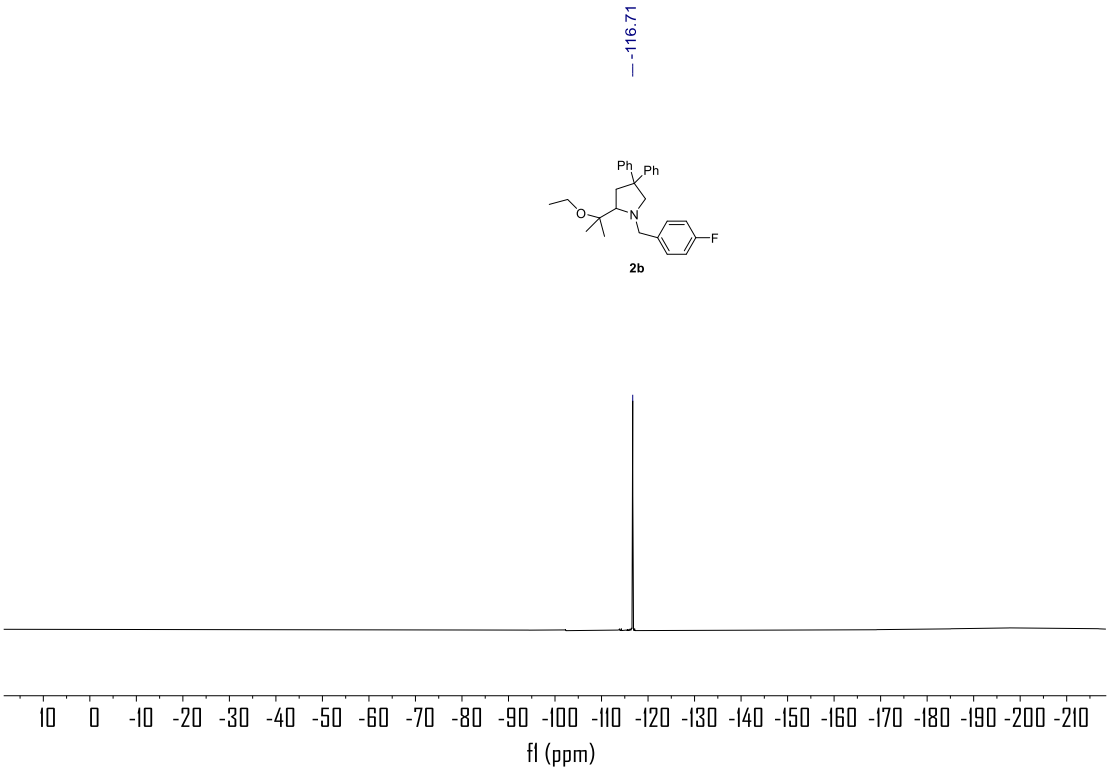
^{1}H NMR (400 MHz, $CDCl_3$) of 2b



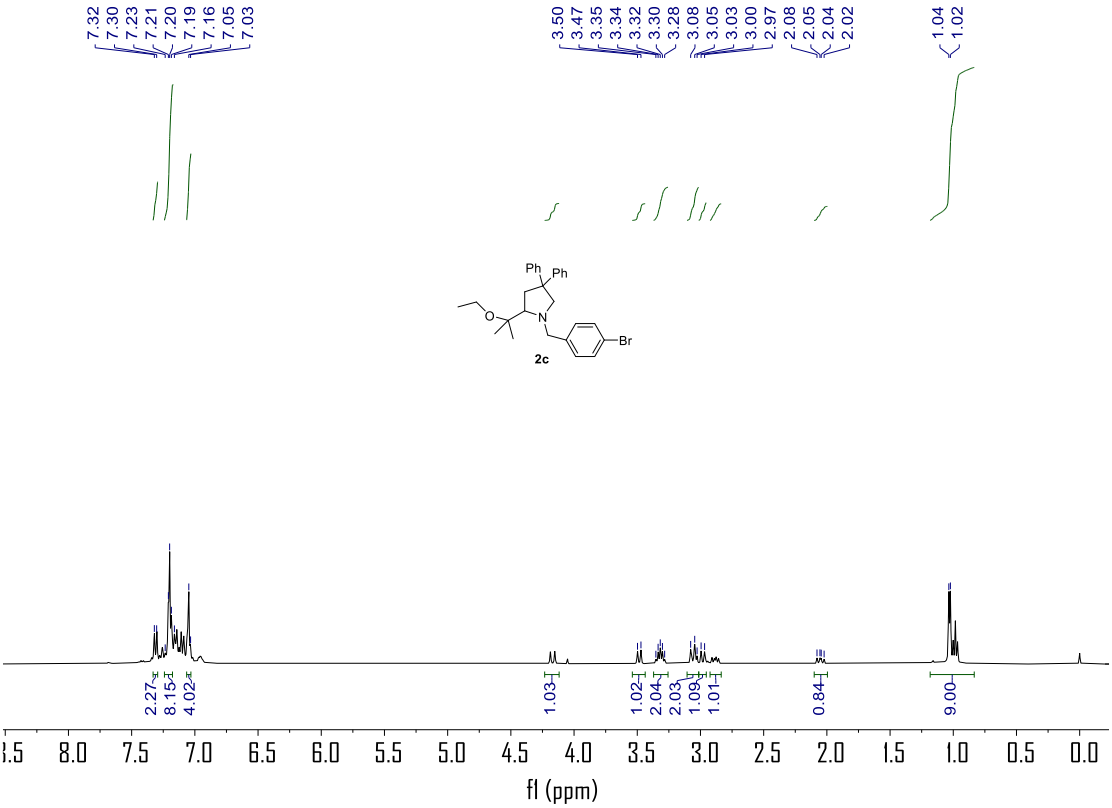
^{13}C NMR (101MHz, $CDCl_3$) of 2b



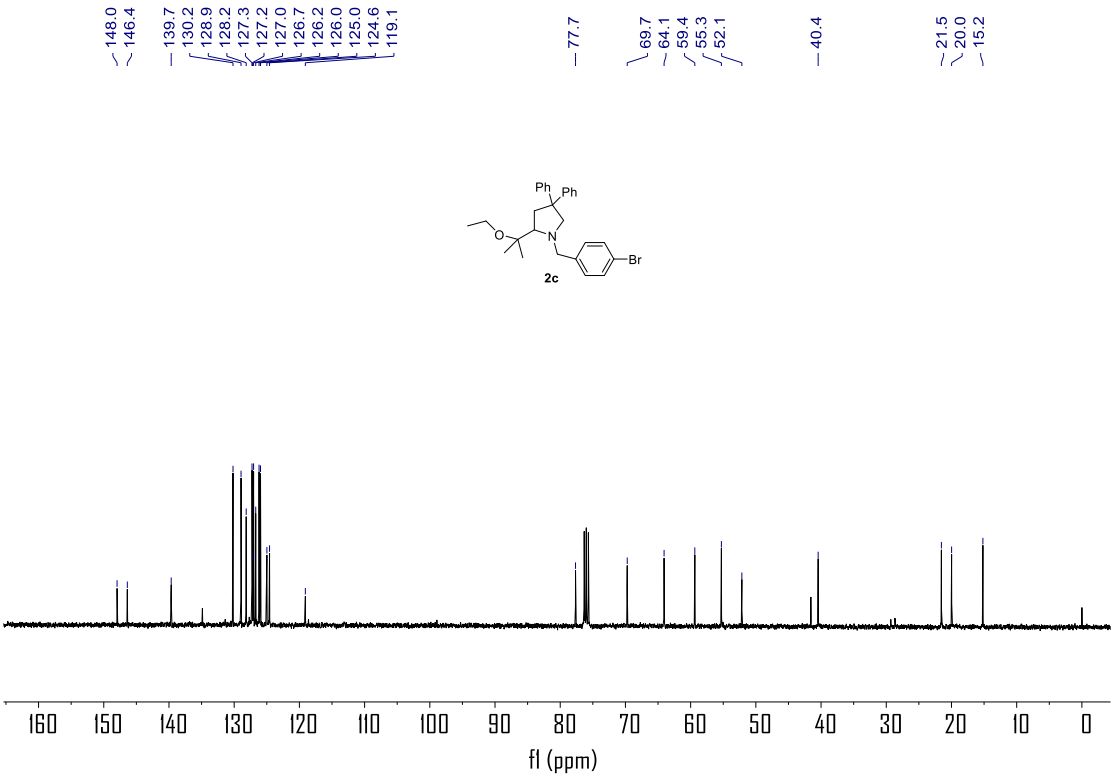
^{19}F NMR (376 MHz, $CDCl_3$) of 2b



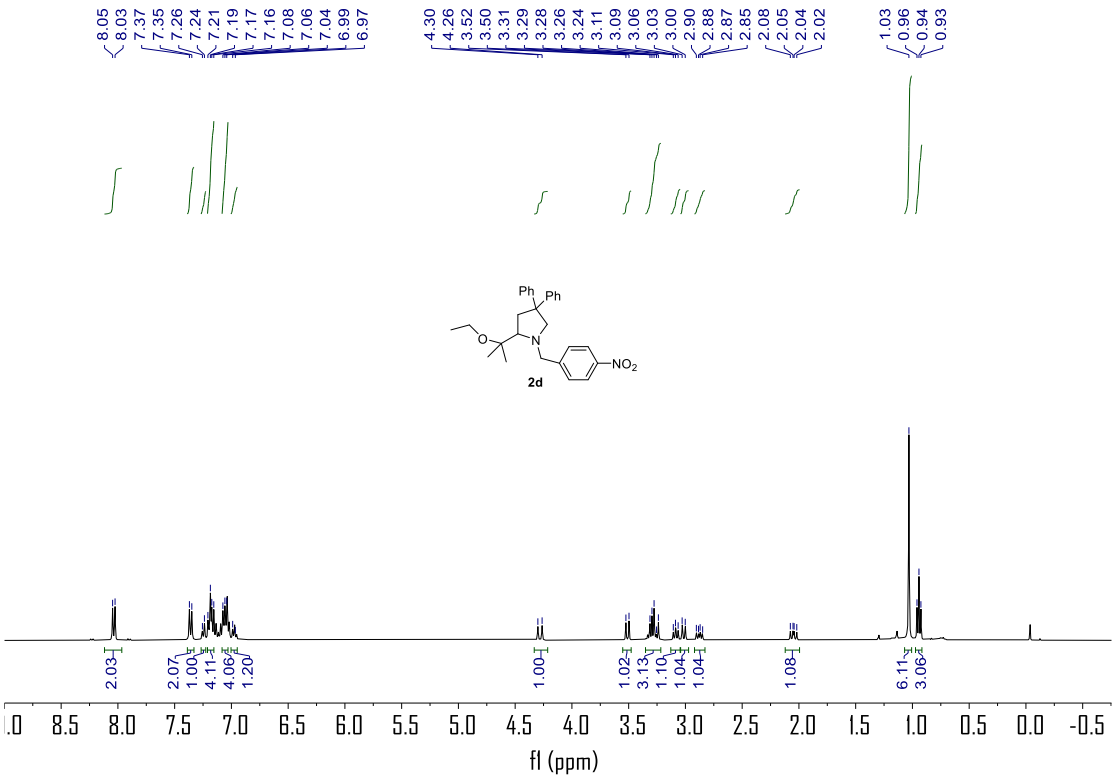
^{1}H NMR (400 MHz, $CDCl_3$) of 2c



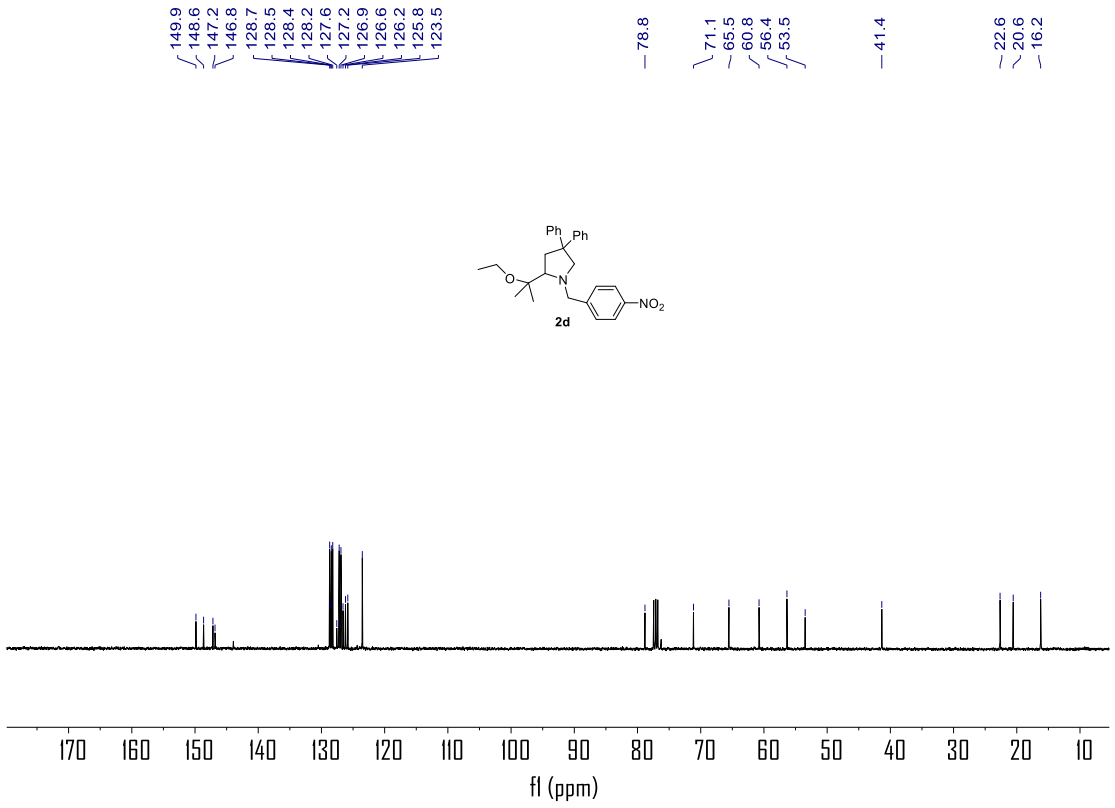
^{13}C NMR (101MHz, $CDCl_3$) of 2c



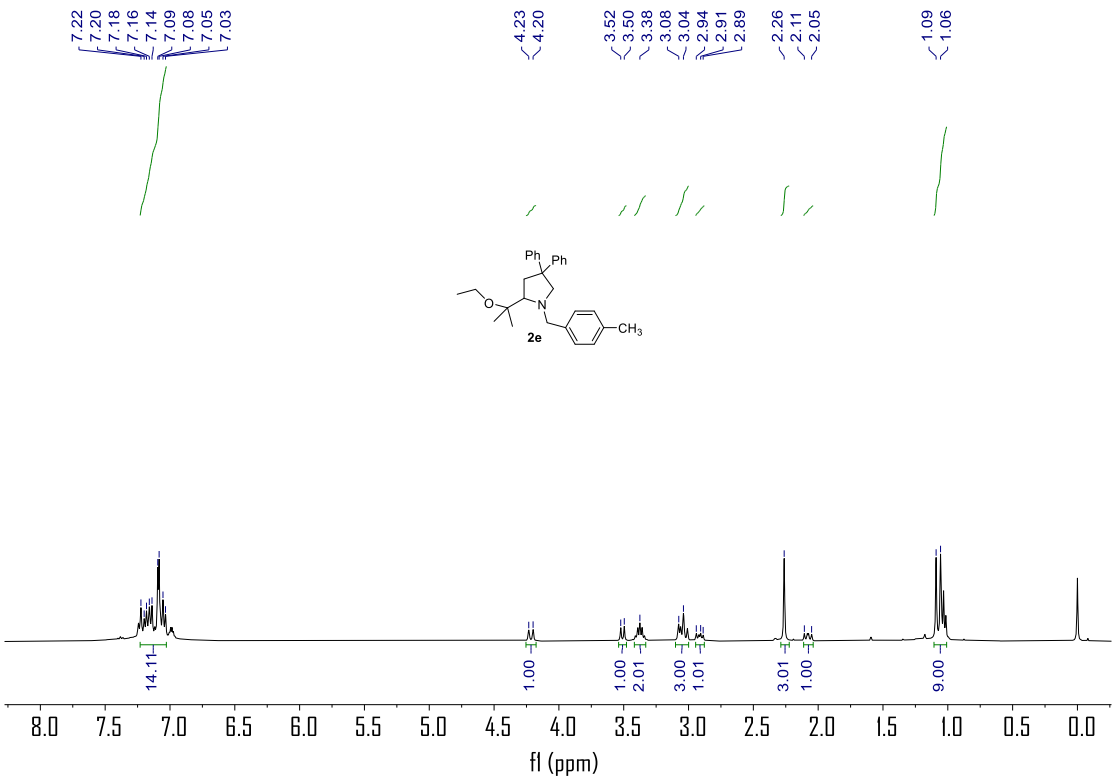
^{1}H NMR (400 MHz, $CDCl_3$) of 2d



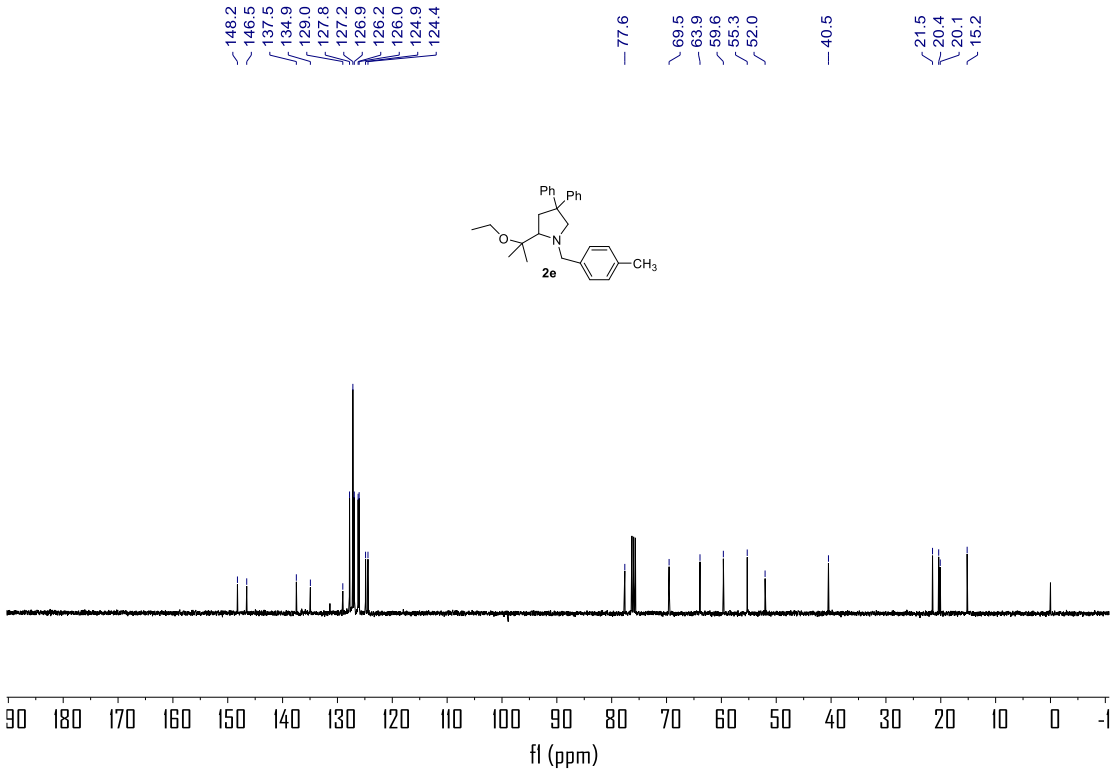
^{13}C NMR (101MHz, $CDCl_3$) of 2d



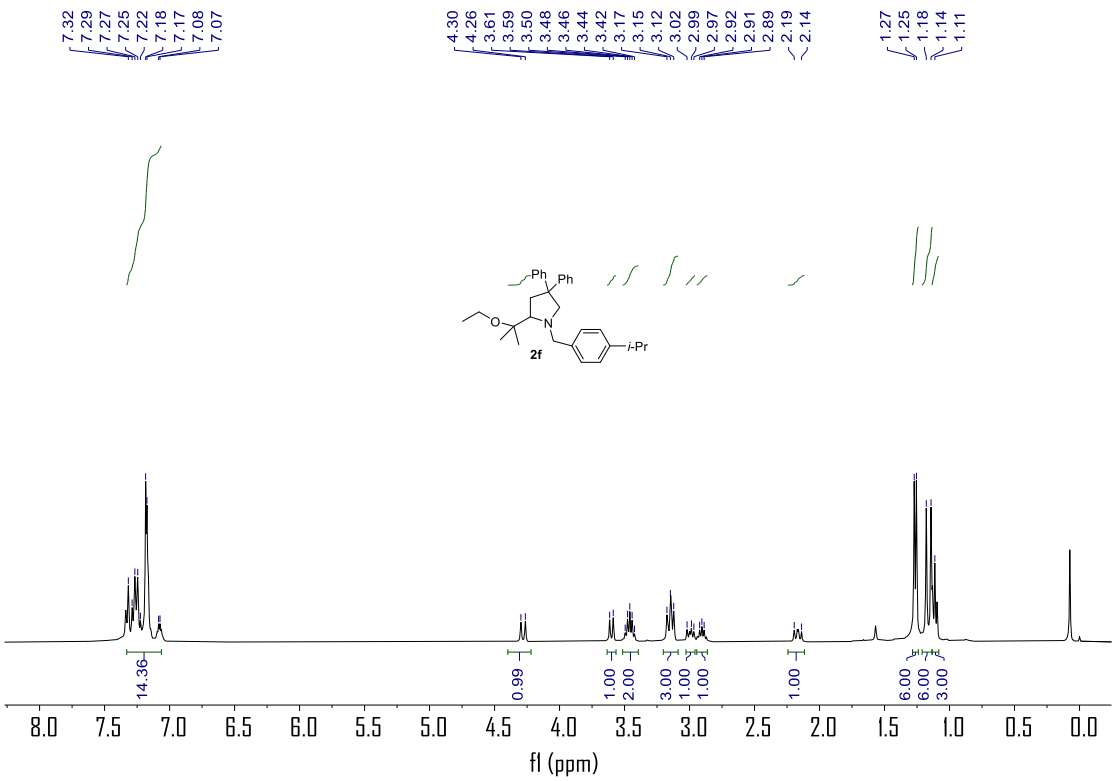
^{1}H NMR (400 MHz, $CDCl_3$) of 2e



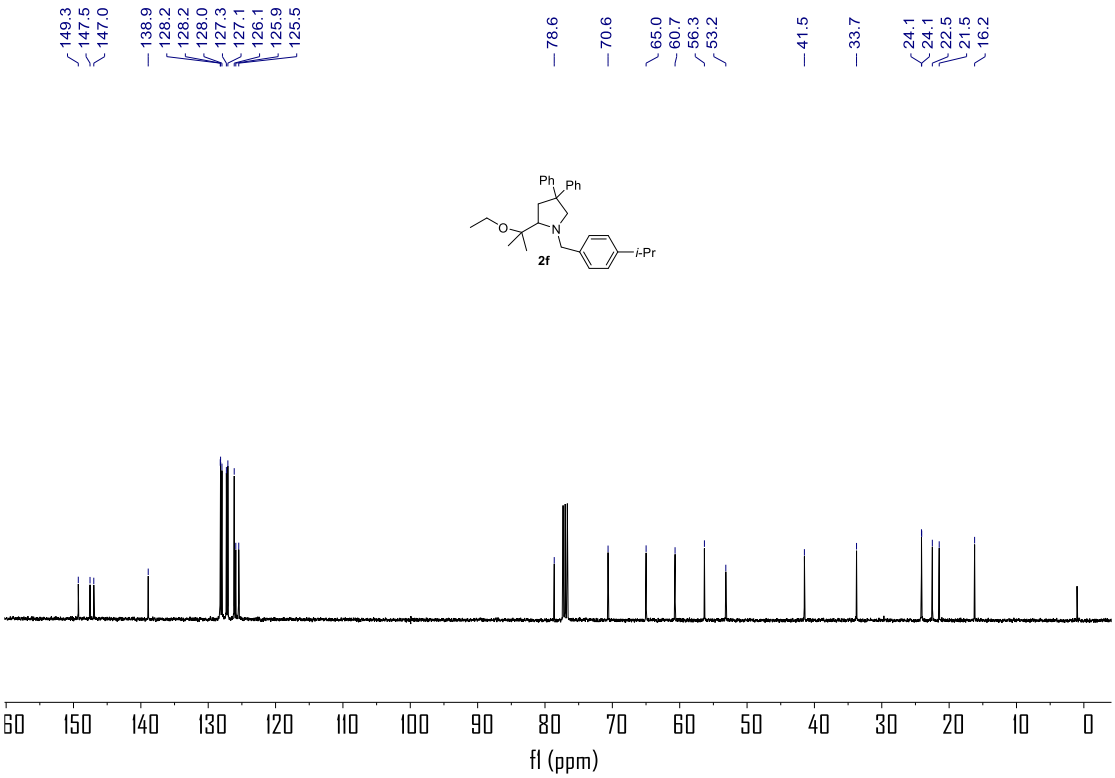
^{13}C NMR (101MHz, $CDCl_3$) of 2e



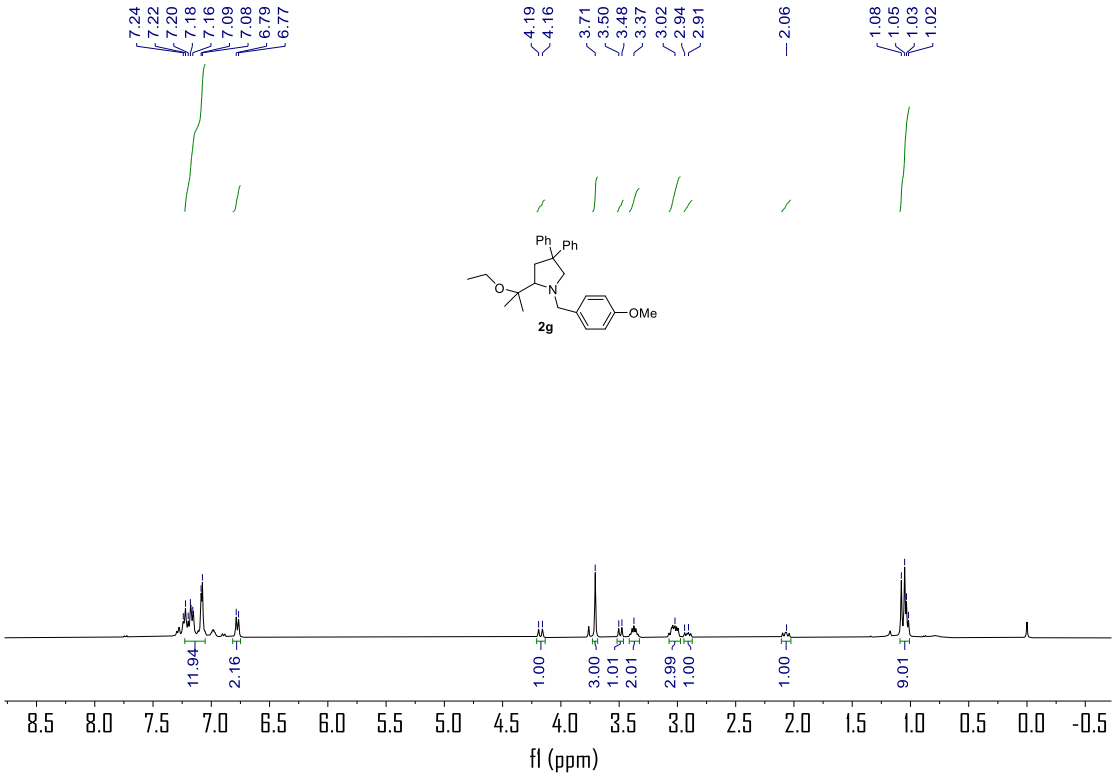
^{1}H NMR (400 MHz, $CDCl_3$) of 2f



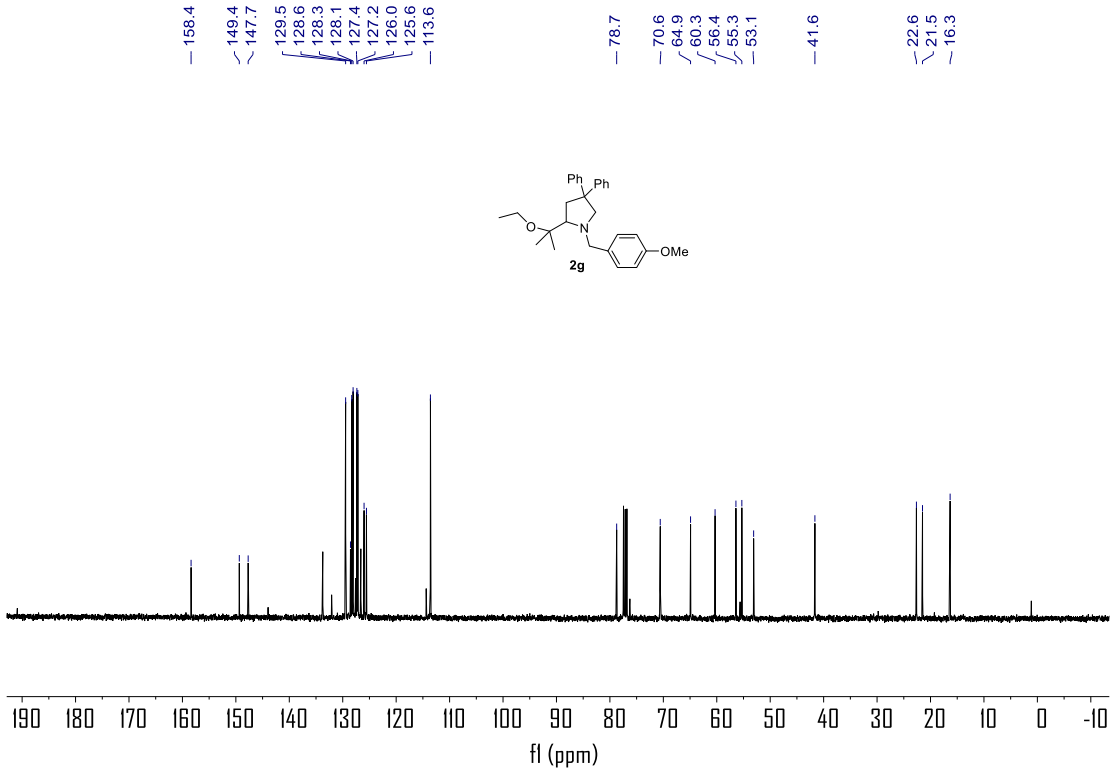
^{13}C NMR (101MHz, $CDCl_3$) of 2f



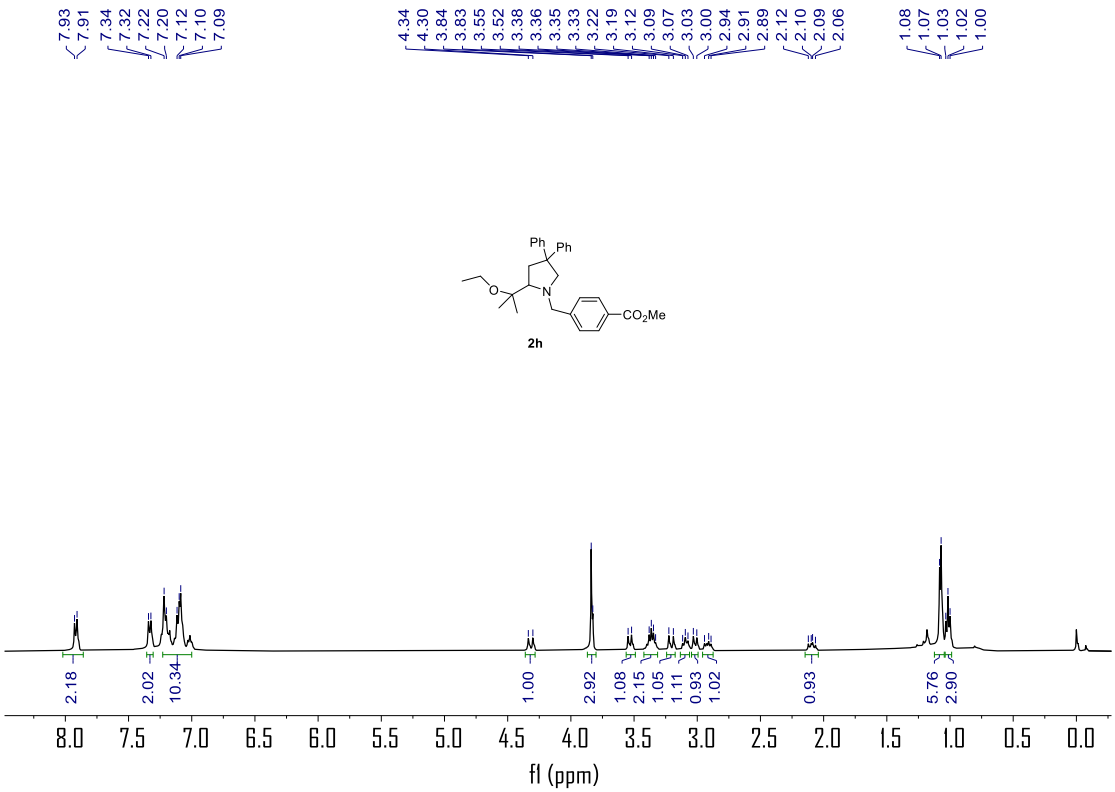
^{1}H NMR (400 MHz, $CDCl_3$) of 2g



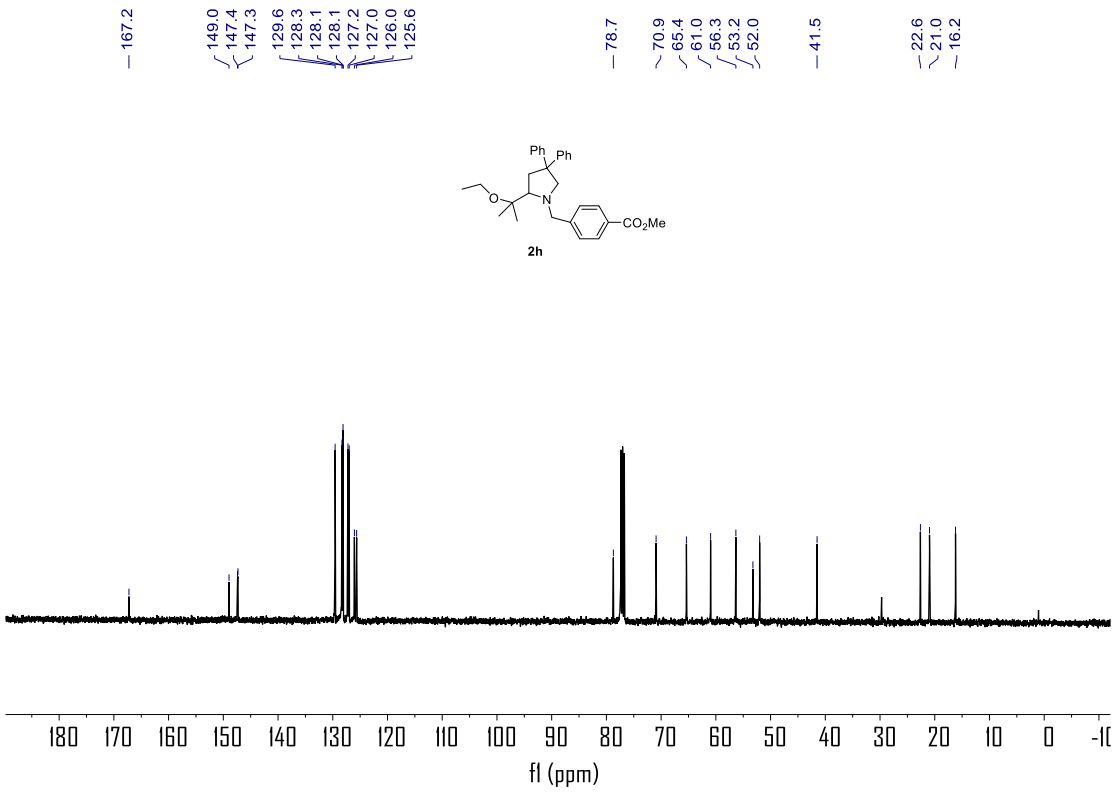
^{13}C NMR (101MHz, $CDCl_3$) of 2g



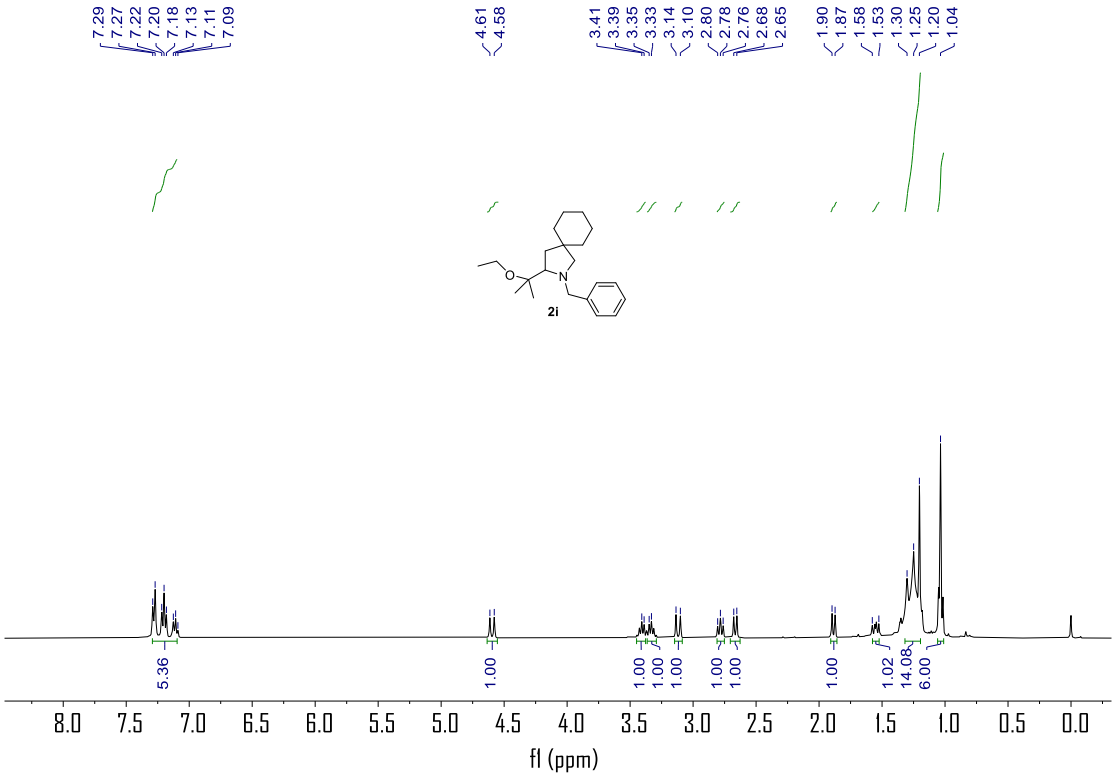
^{1}H NMR (400 MHz, $CDCl_3$) of 2h



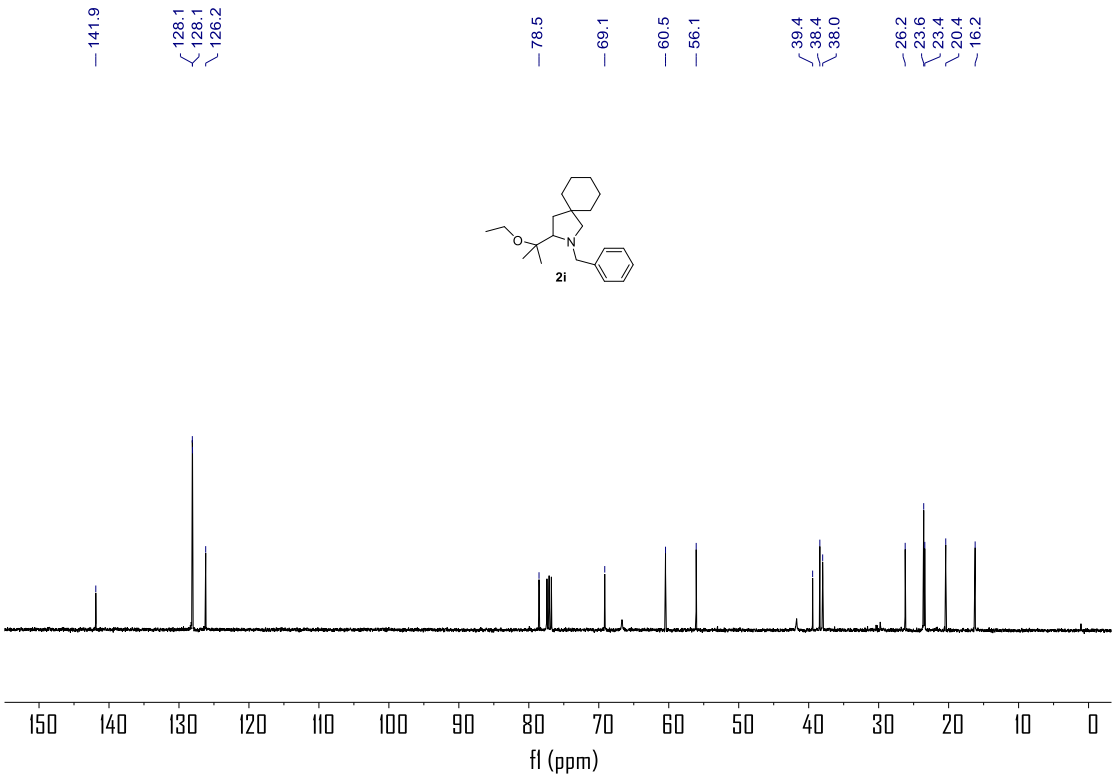
^{13}C NMR (101MHz, $CDCl_3$) of 2h



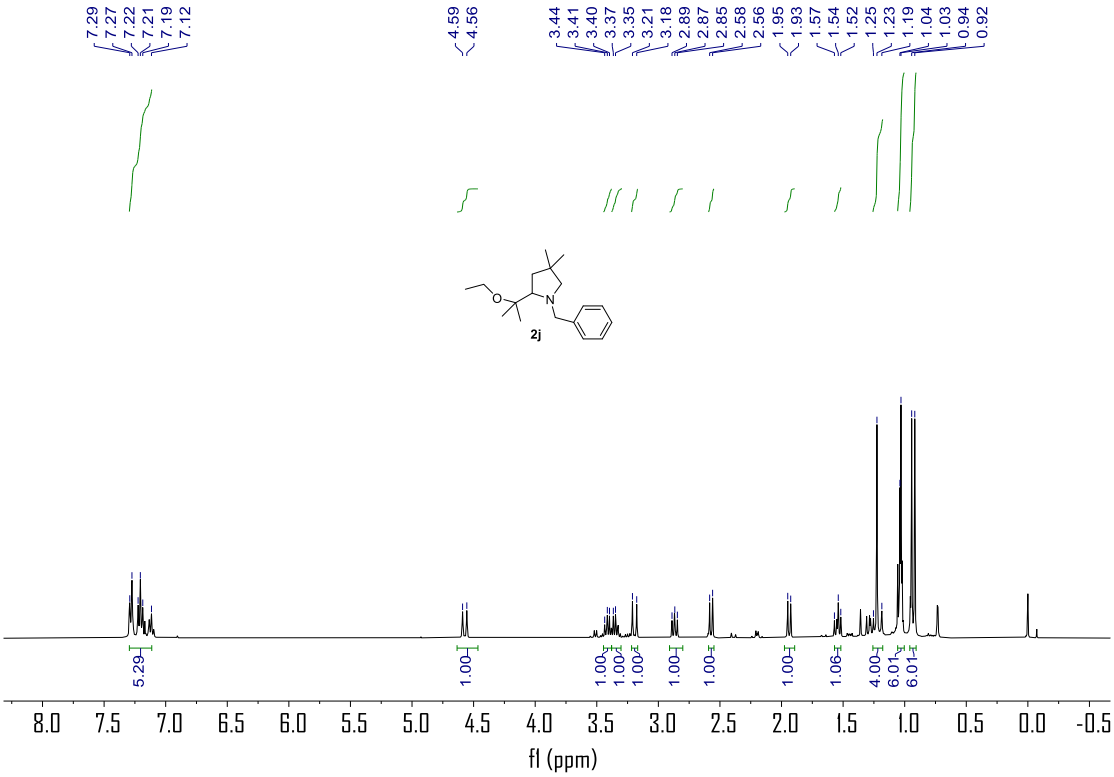
^{1}H NMR (400 MHz, $CDCl_3$) of 2i



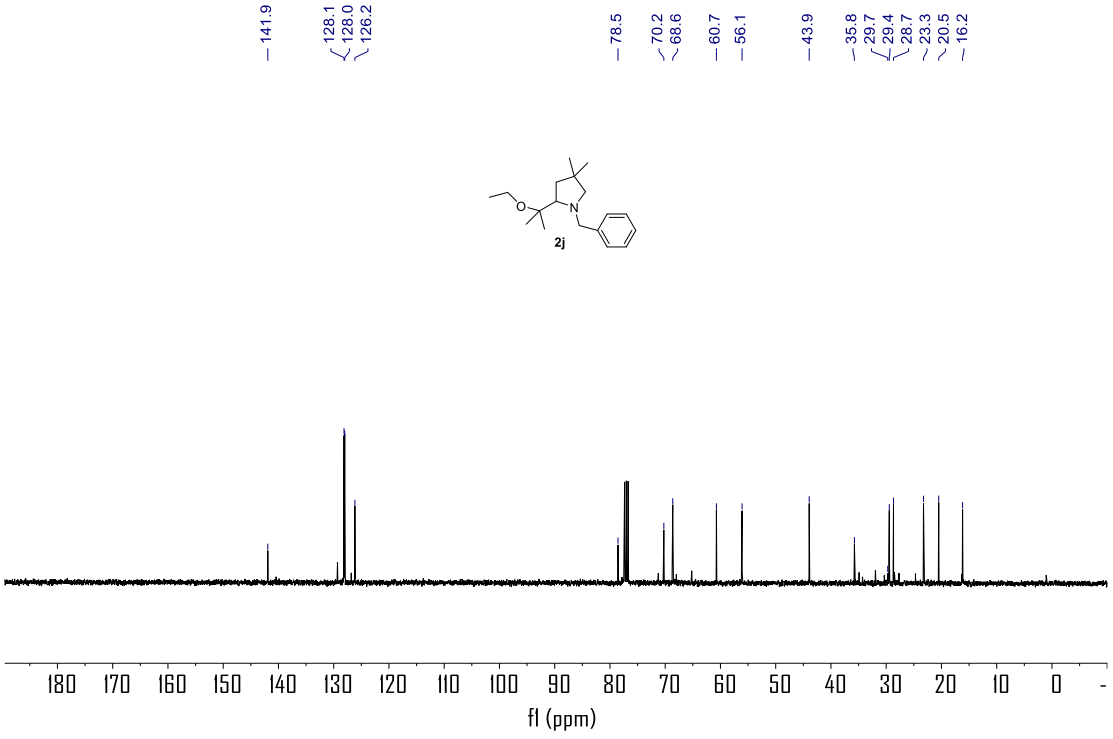
^{13}C NMR (101MHz, $CDCl_3$) of 2i



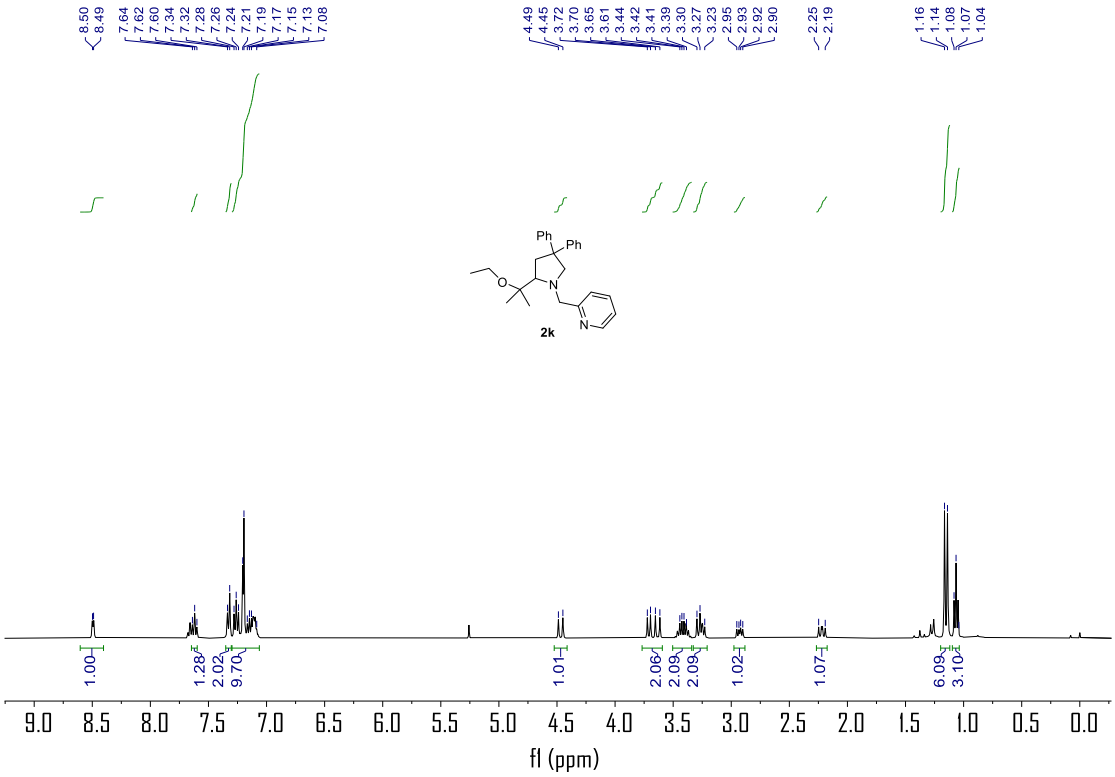
^{1}H NMR (400 MHz, $CDCl_3$) of 2j



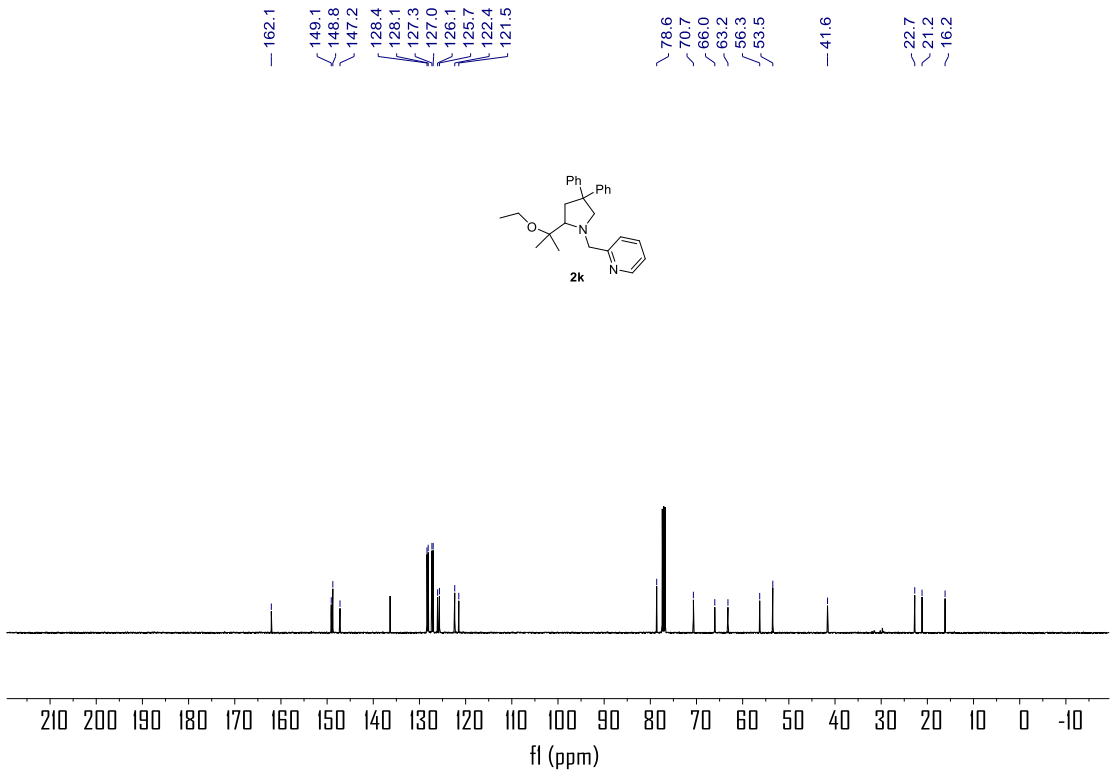
^{13}C NMR (101MHz, $CDCl_3$) of 2j



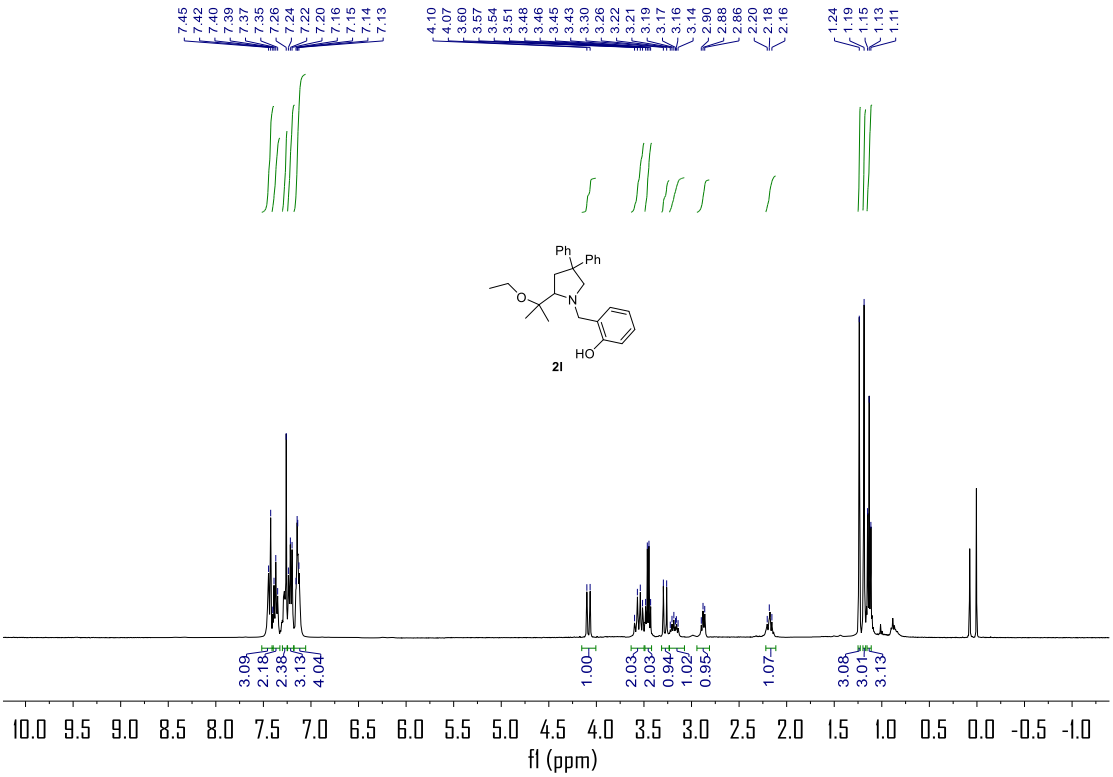
^{1}H NMR (400 MHz, $CDCl_3$) of 2k



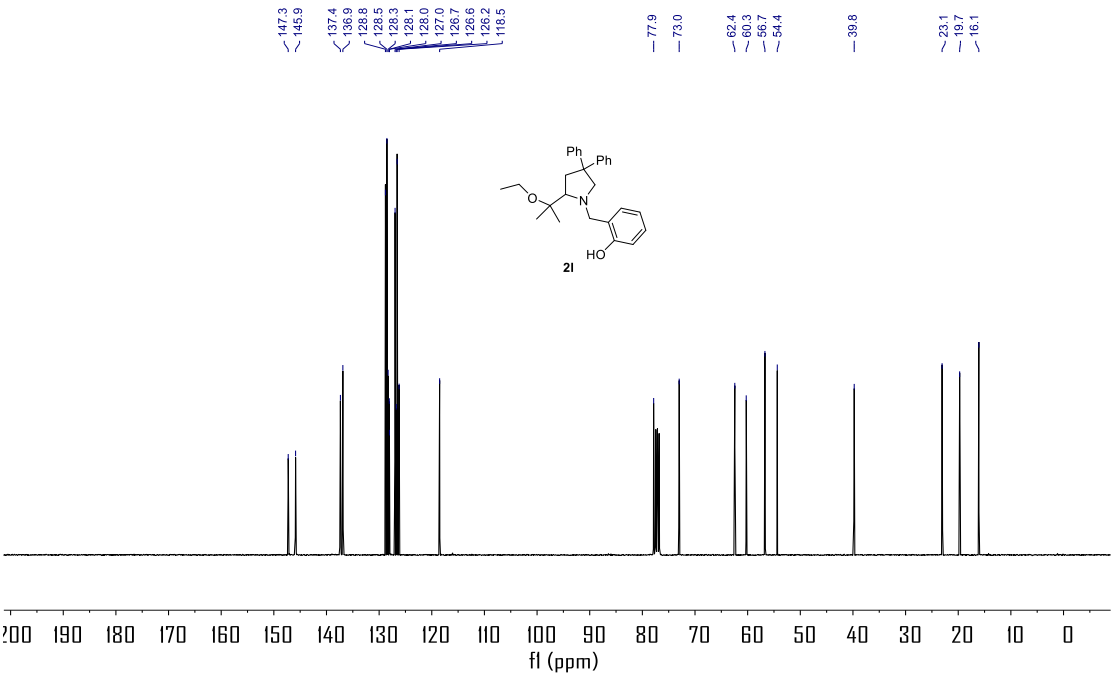
^{13}C NMR (101MHz, $CDCl_3$) of 2k



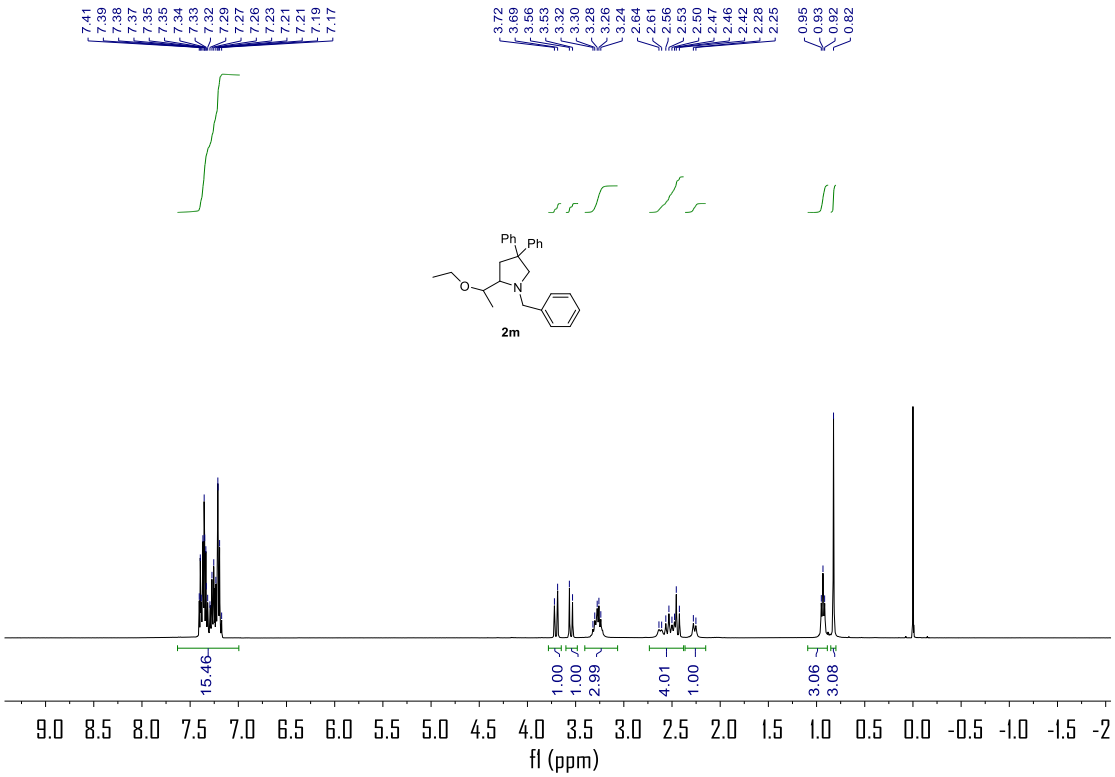
^{1}H NMR (400 MHz, $CDCl_3$) of 2l



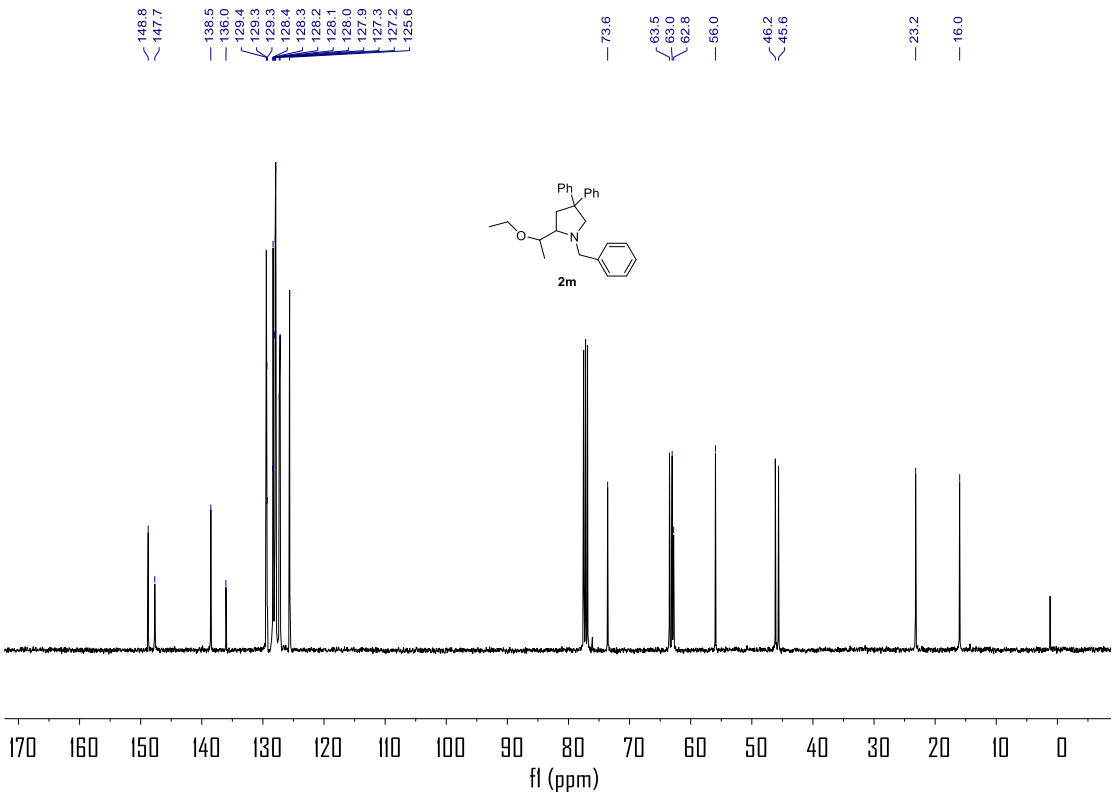
^{13}C NMR (101MHz, $CDCl_3$) of 2l



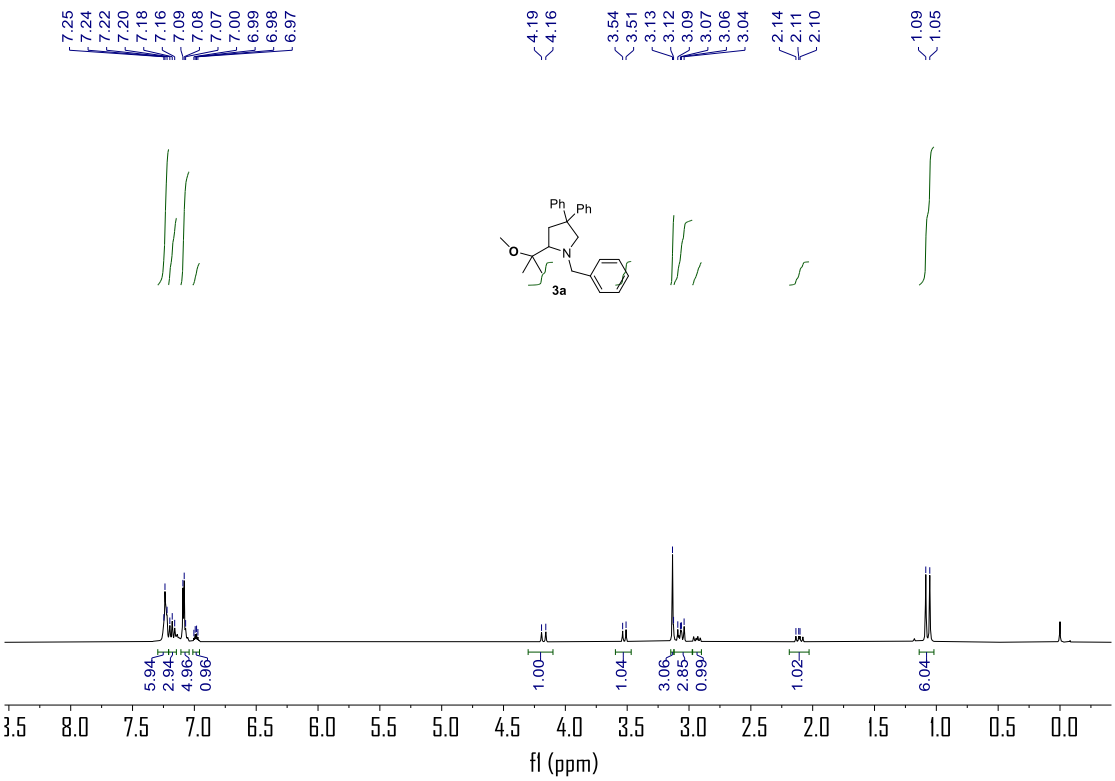
^{1}H NMR (400 MHz, $CDCl_3$) of 2m



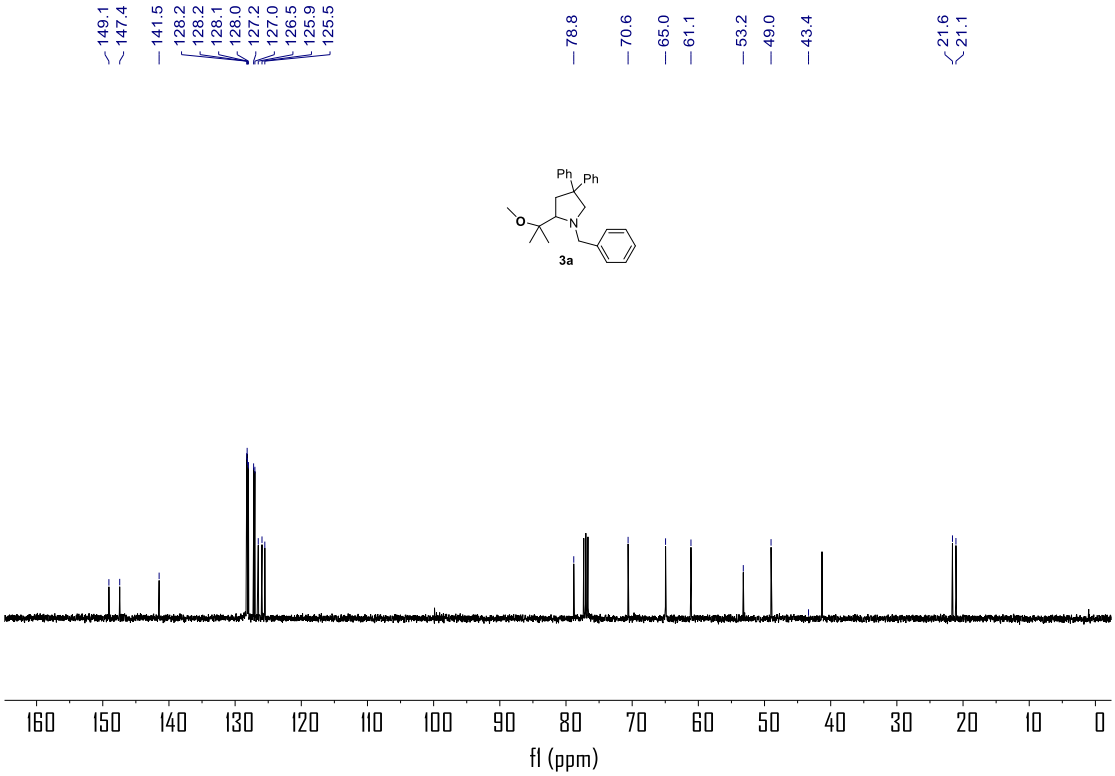
^{13}C NMR (101MHz, $CDCl_3$) of 2m



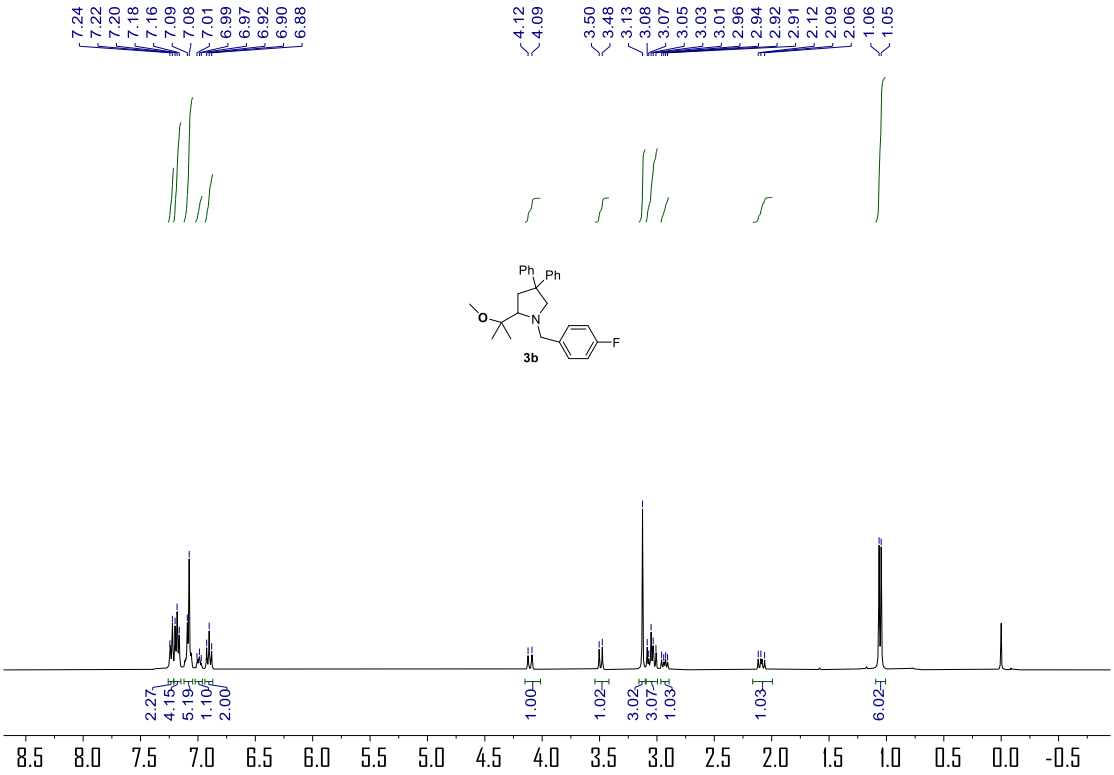
^{1}H NMR (400 MHz, $CDCl_3$) of 3a



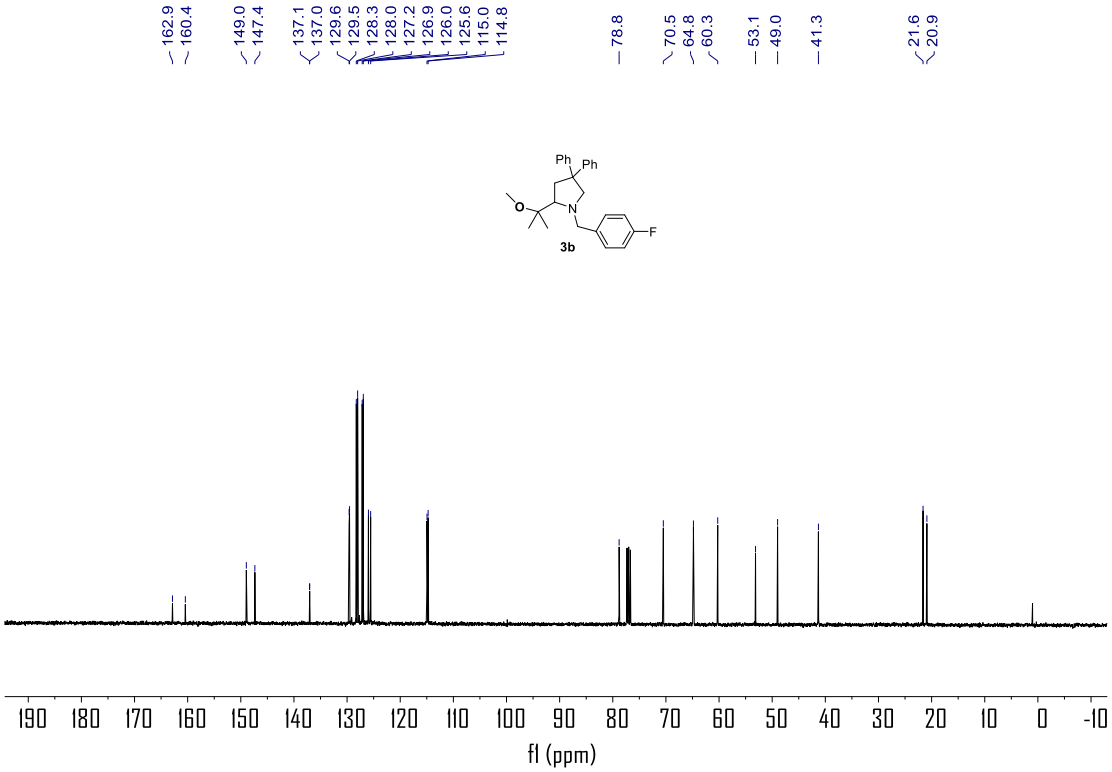
^{13}C NMR (101MHz, $CDCl_3$) of 3a



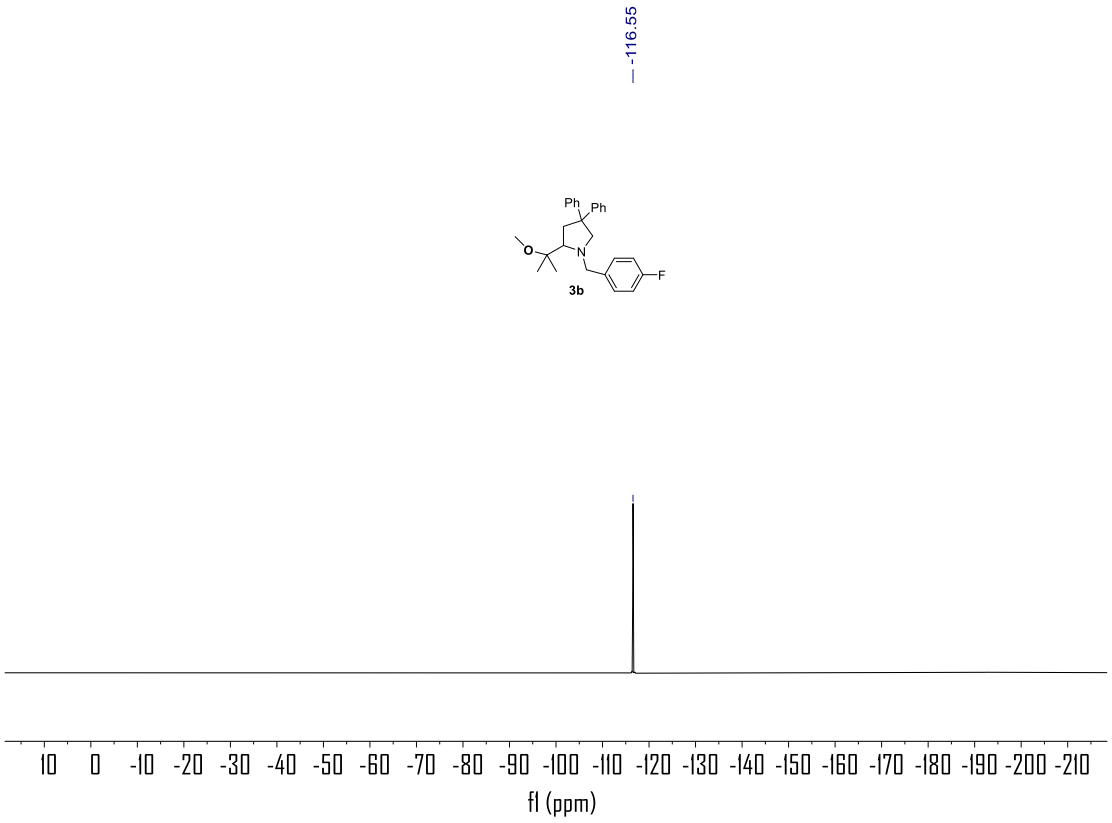
^{1}H NMR (400 MHz, $CDCl_3$) of 3b



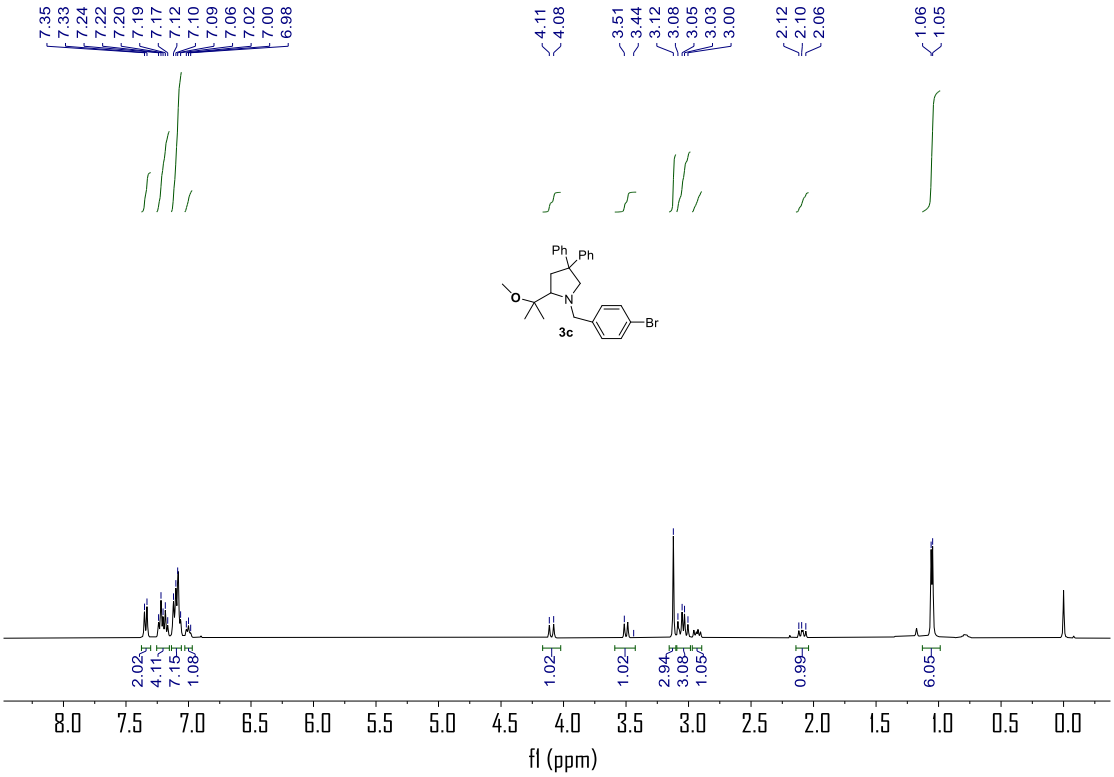
^{13}C NMR (101MHz, $CDCl_3$) of 3b



^{19}F NMR (376 MHz, $CDCl_3$) of 3b



^{1}H NMR (400 MHz, $CDCl_3$) of 3c



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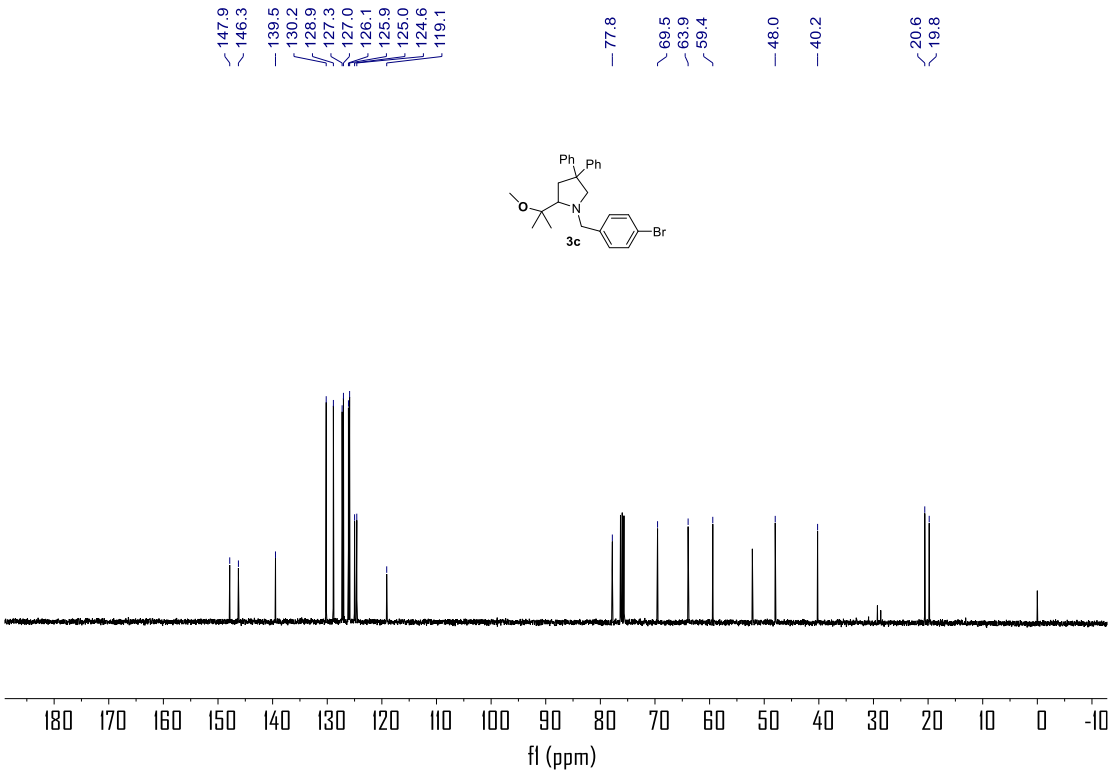
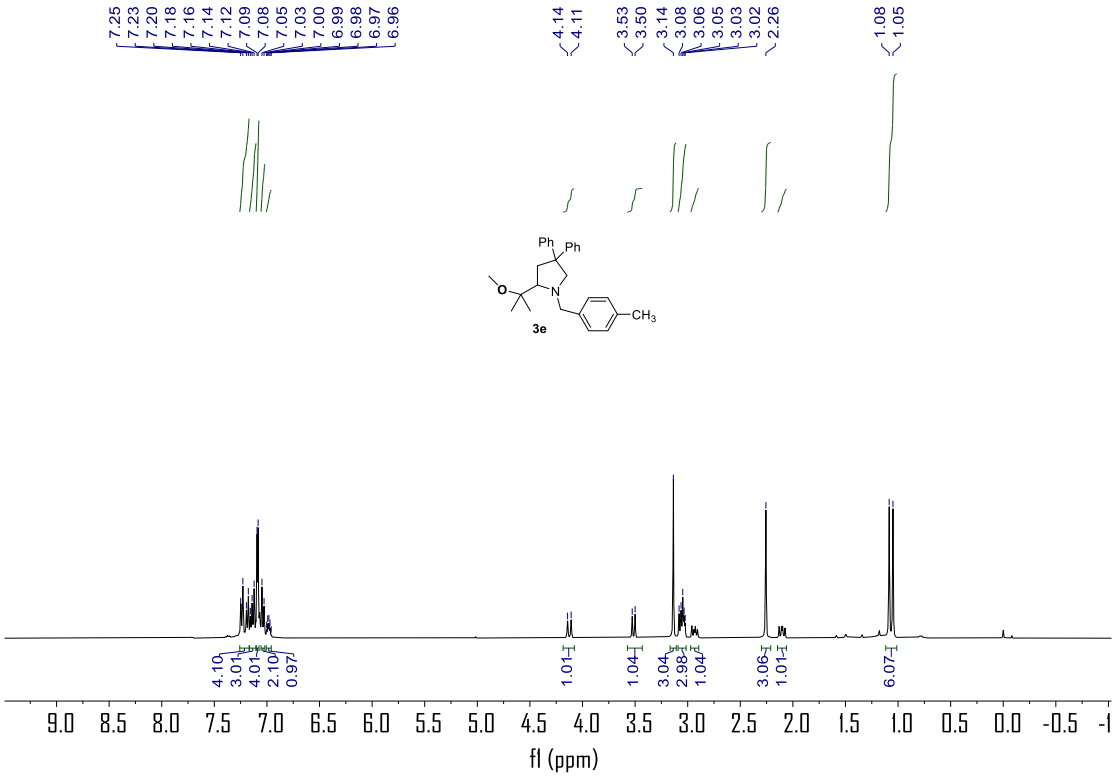
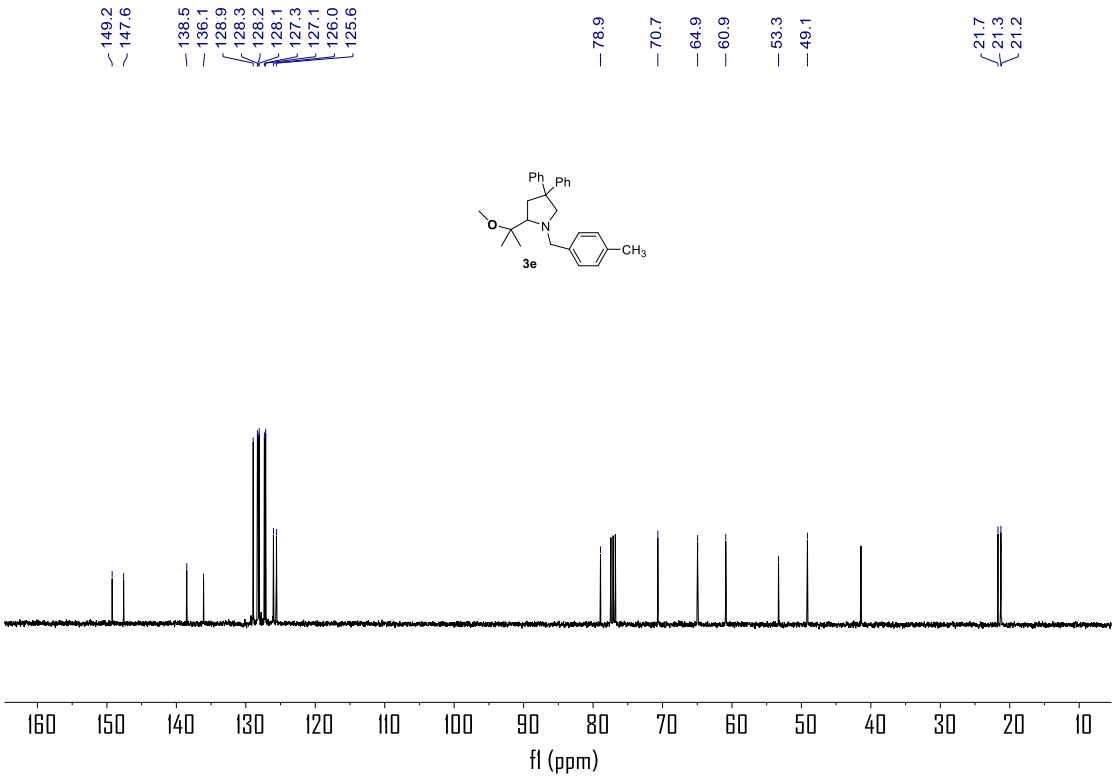


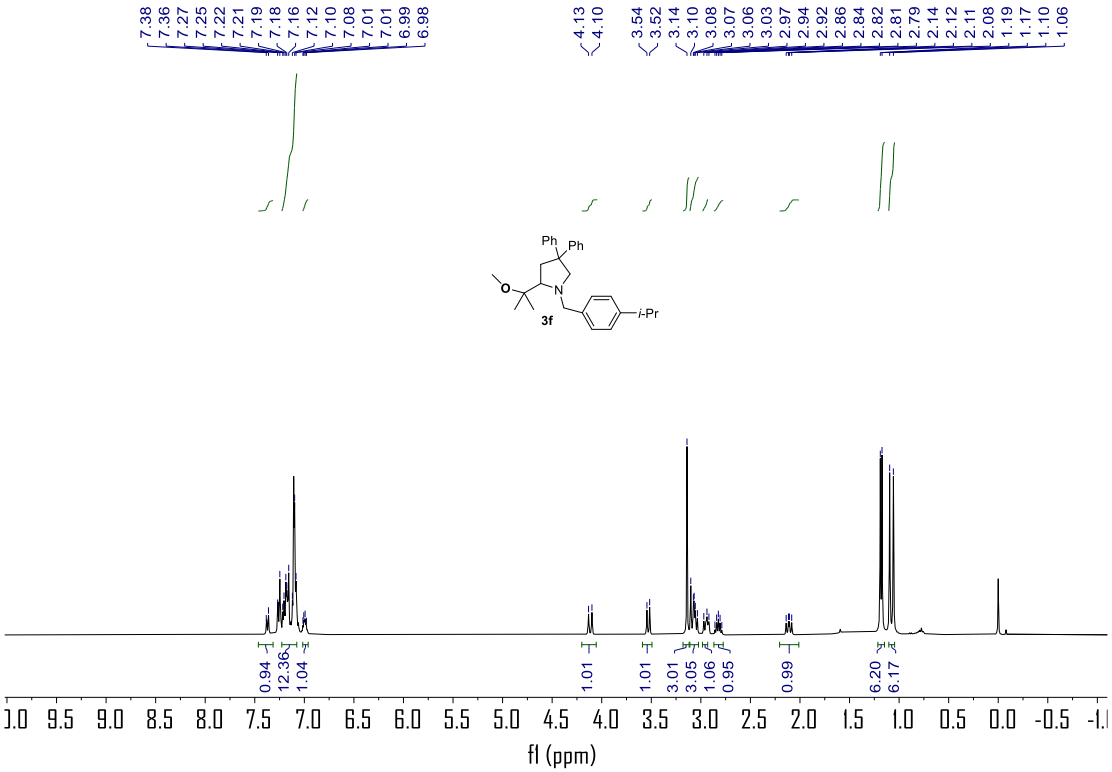
^{1}H NMR (400 MHz, $CDCl_3$) of 3e



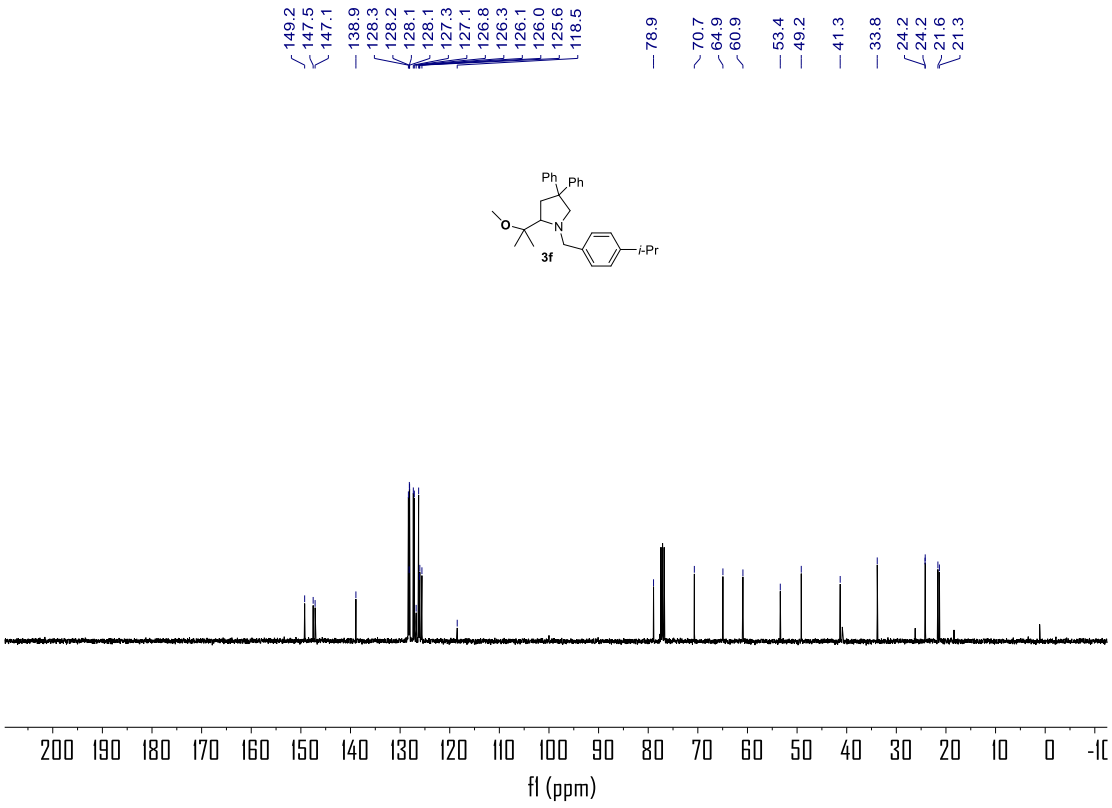
^{13}C NMR (101MHz, $CDCl_3$) of 3e



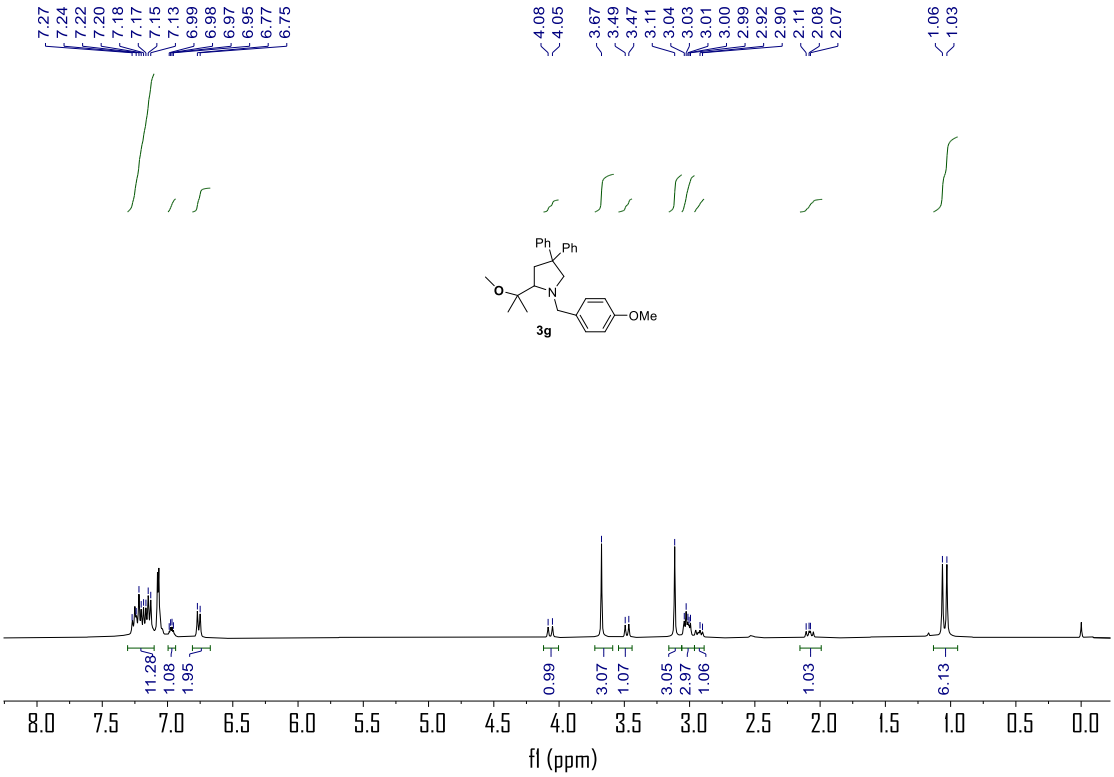
^{1}H NMR (400 MHz, $CDCl_3$) of 3f



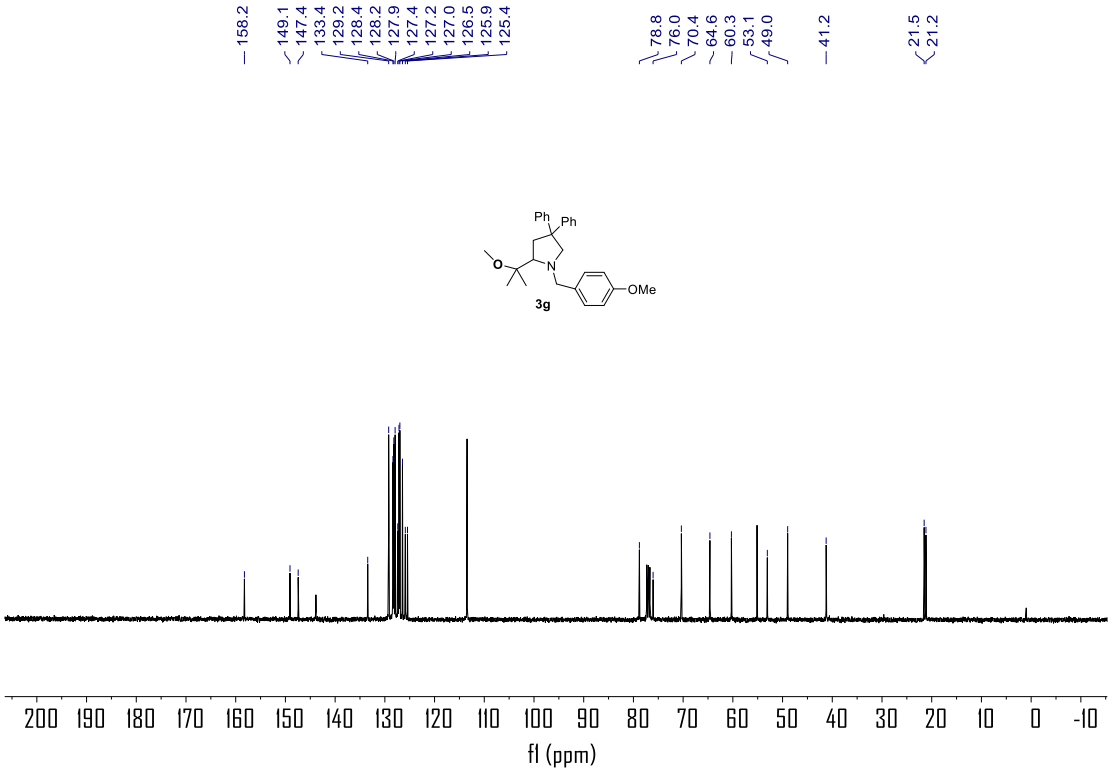
^{13}C NMR (101MHz, $CDCl_3$) of 3f



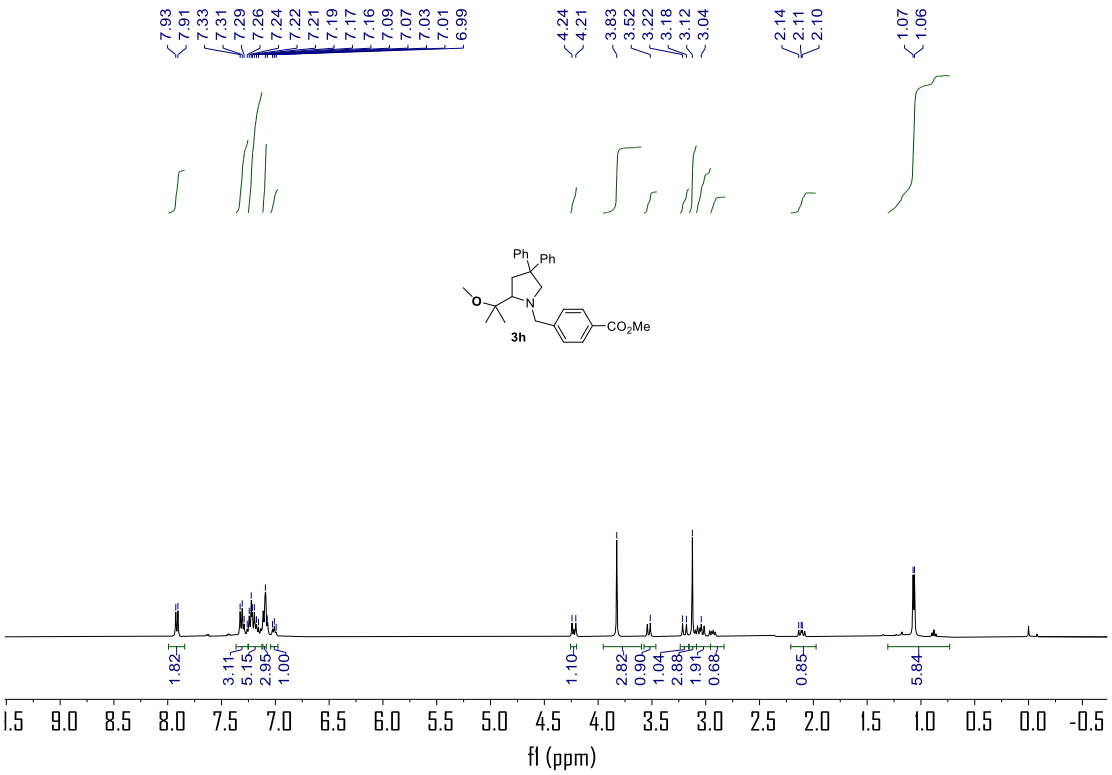
^{1}H NMR (400 MHz, $CDCl_3$) of 3g



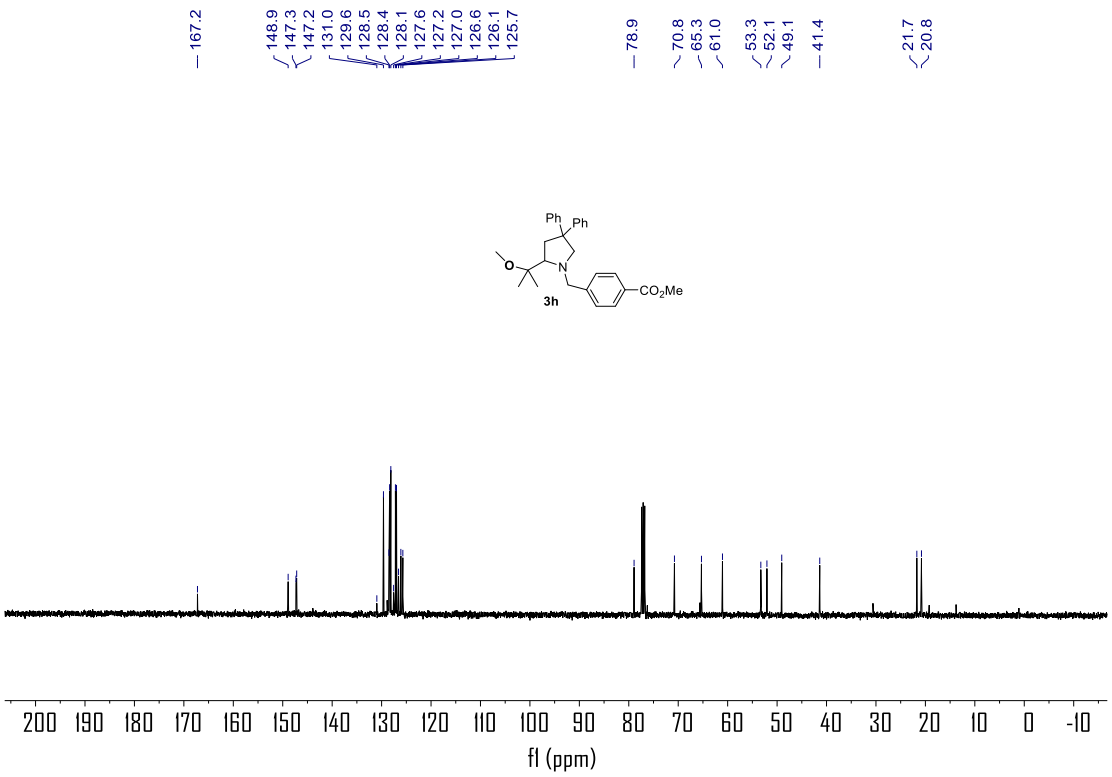
^{13}C NMR (101MHz, $CDCl_3$) of 3g



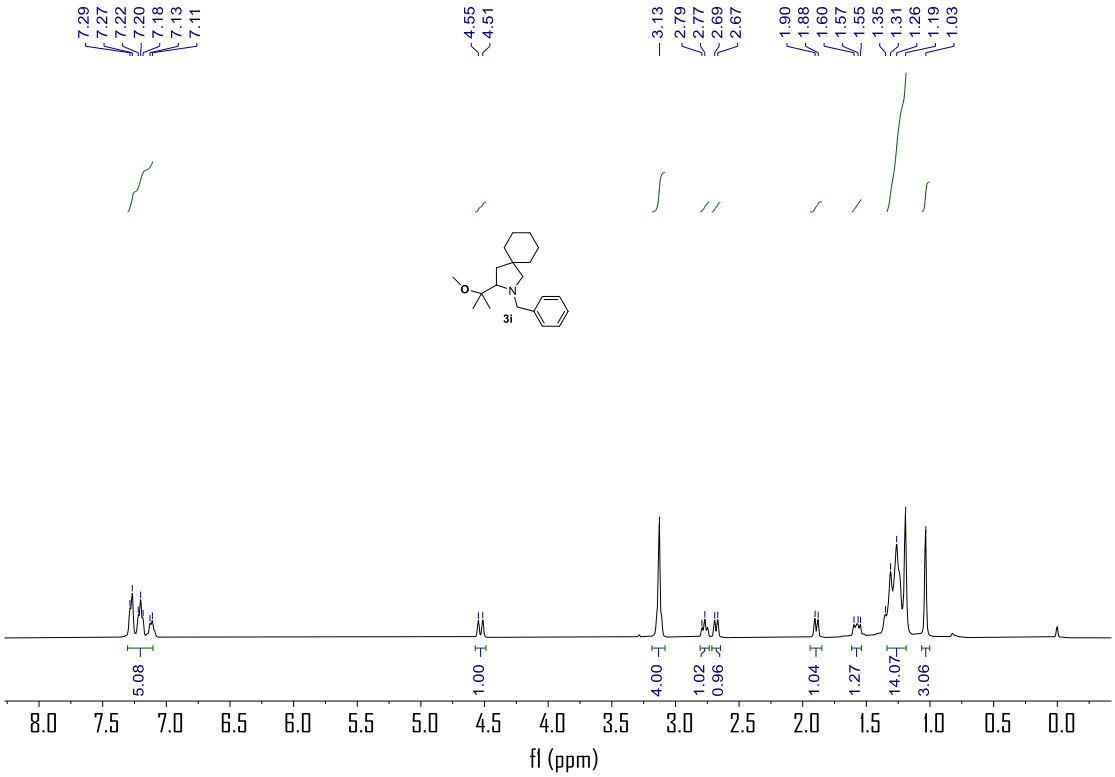
^{1}H NMR (400 MHz, $CDCl_3$) of 3h



^{13}C NMR (101MHz, $CDCl_3$) of 3h



^{1}H NMR (400 MHz, $CDCl_3$) of 3i



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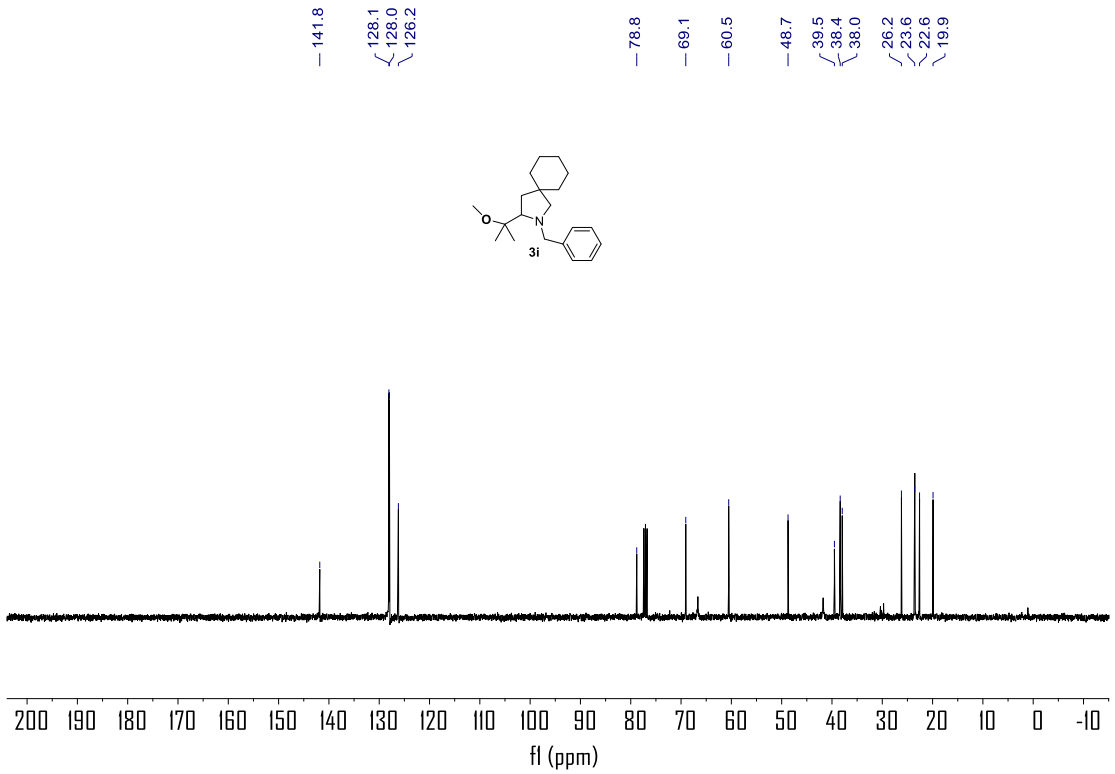
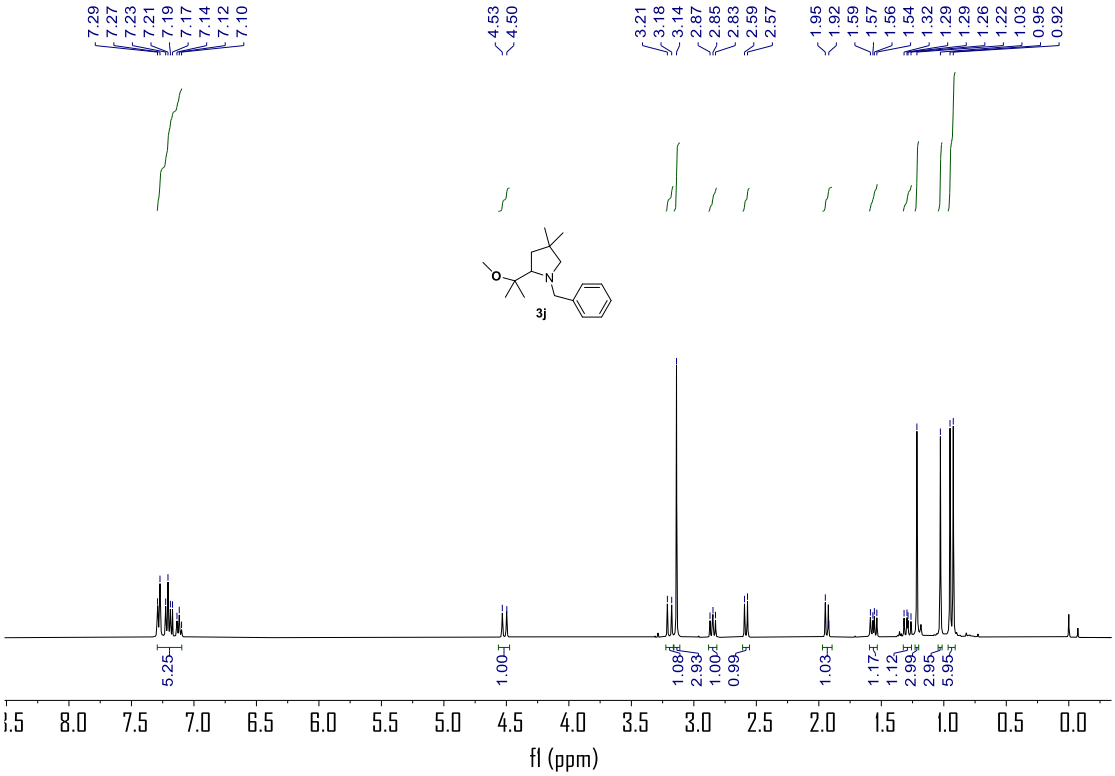


^{1}H NMR (400 MHz, $CDCl_3$) of 3j



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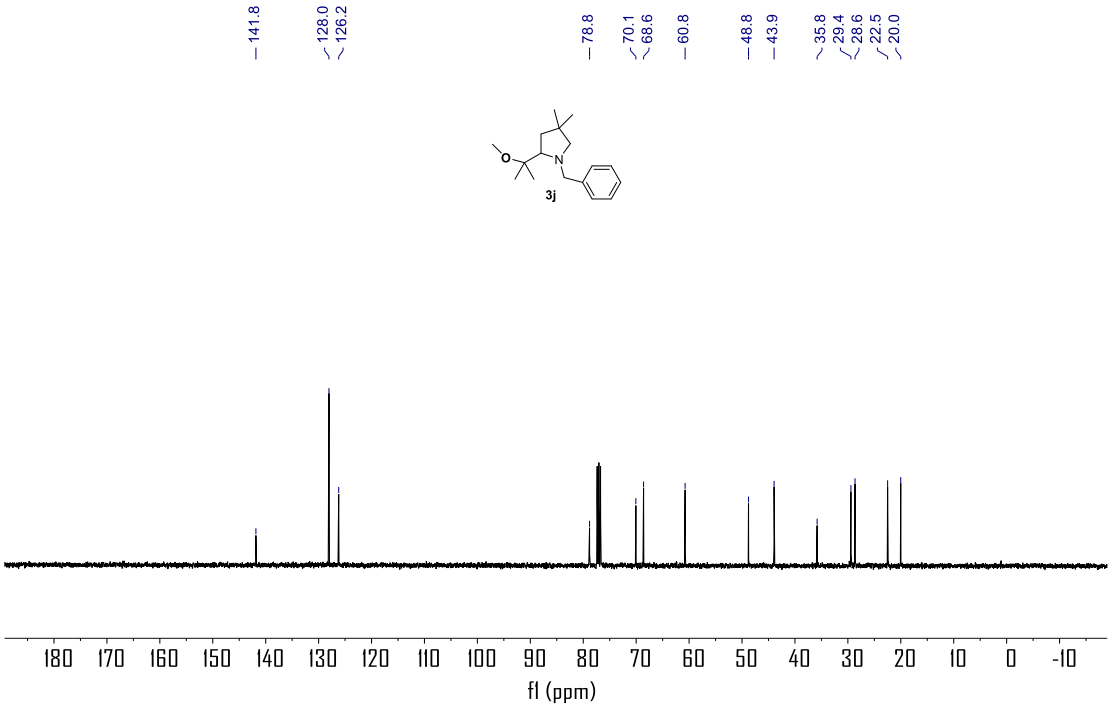
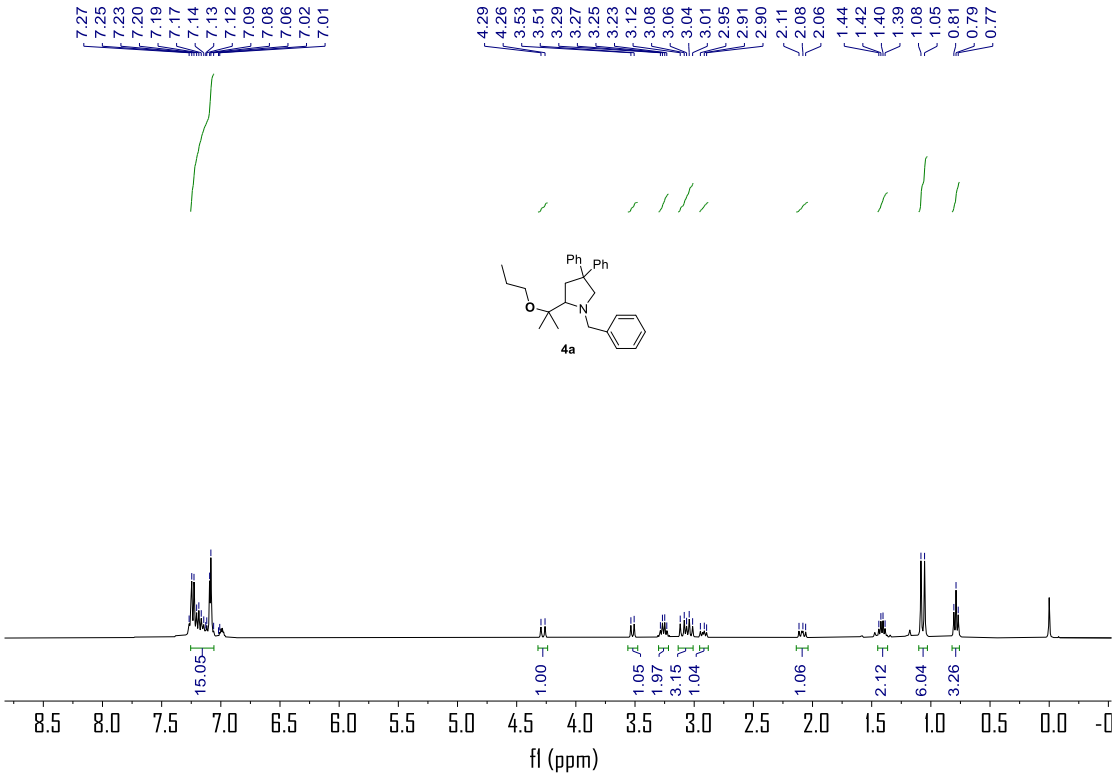


^{1}H NMR (400 MHz, $CDCl_3$) of 4a



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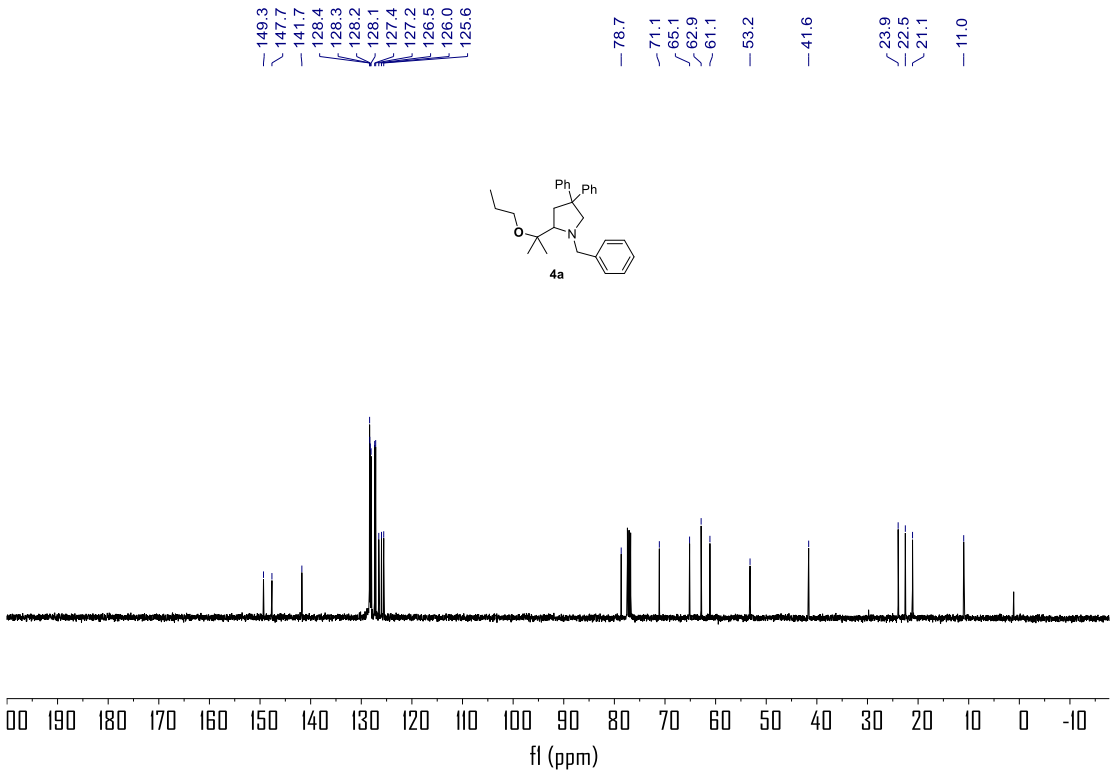
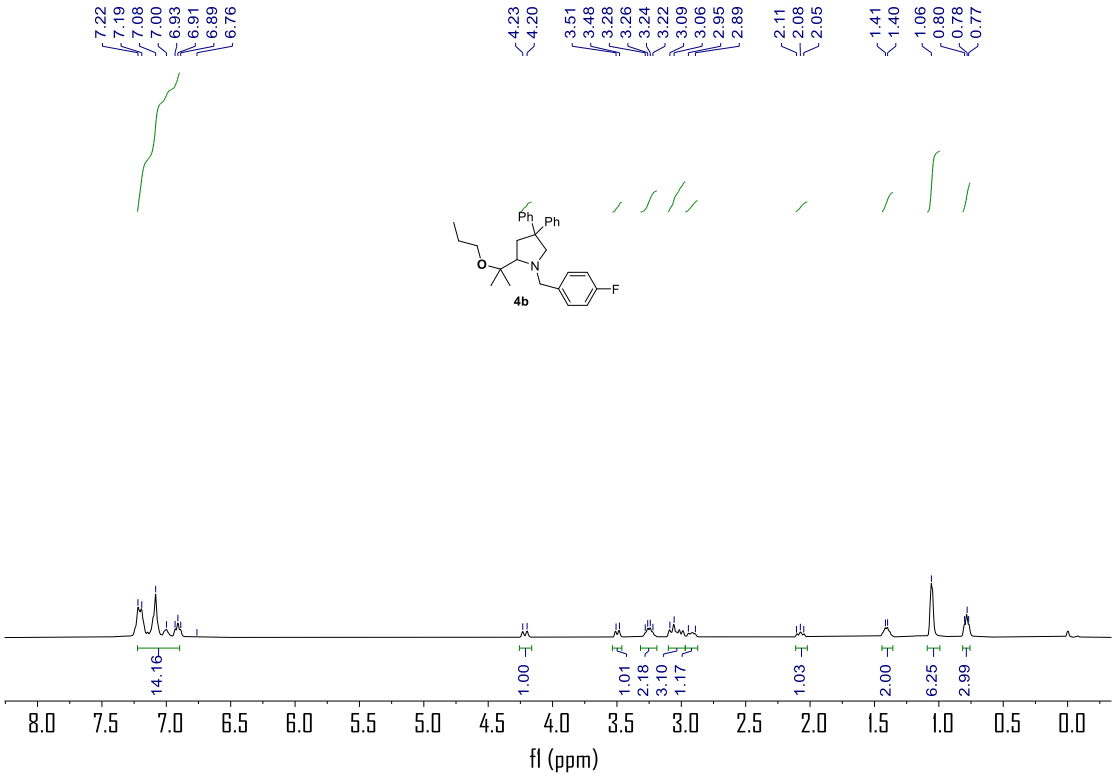
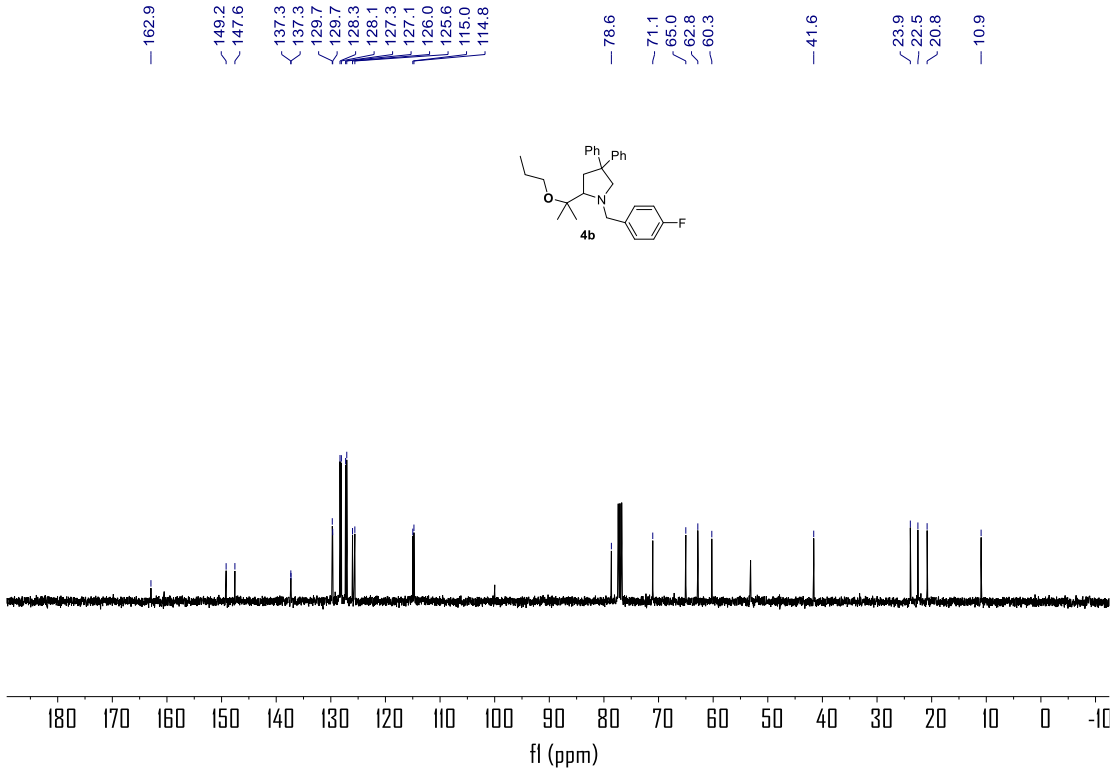


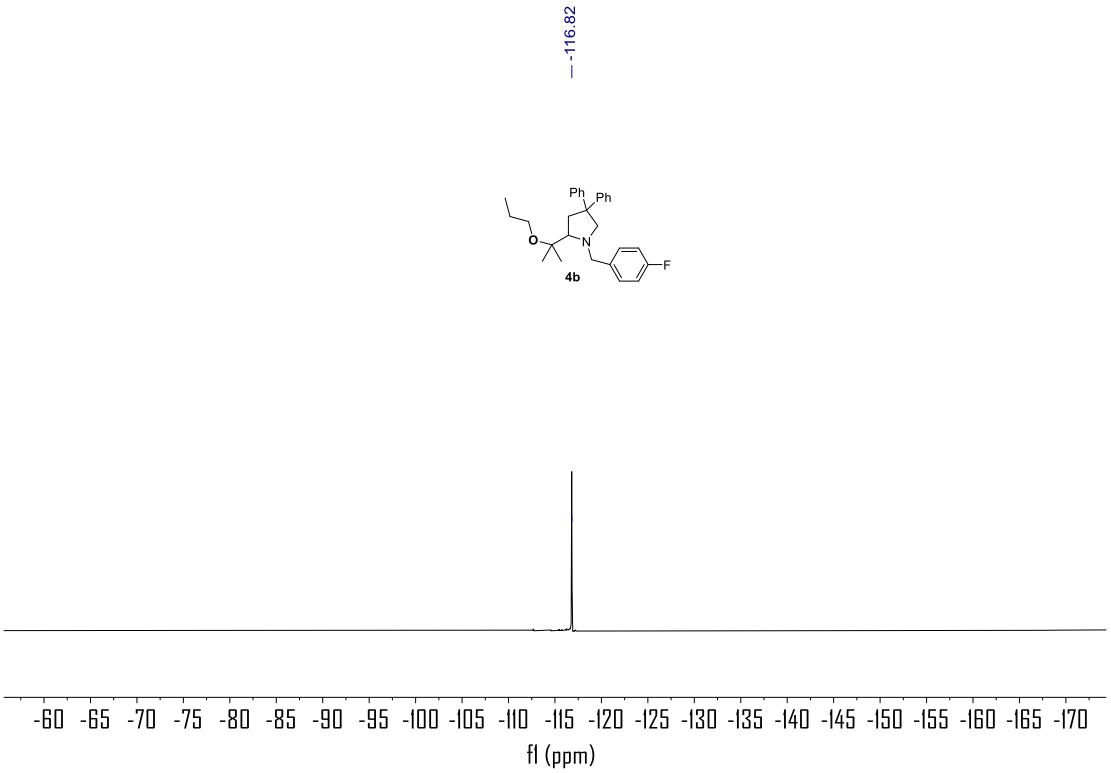
^{1}H NMR (400 MHz, $CDCl_3$) of 4b



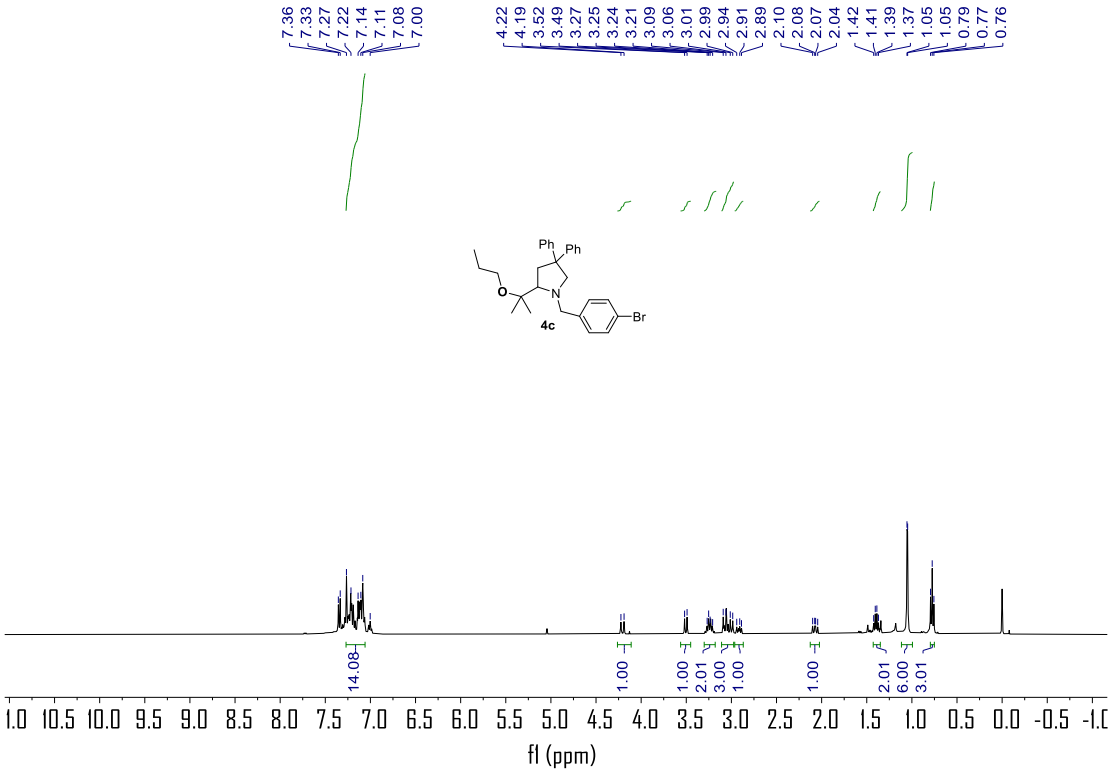
^{13}C NMR (101MHz, $CDCl_3$) of 4b



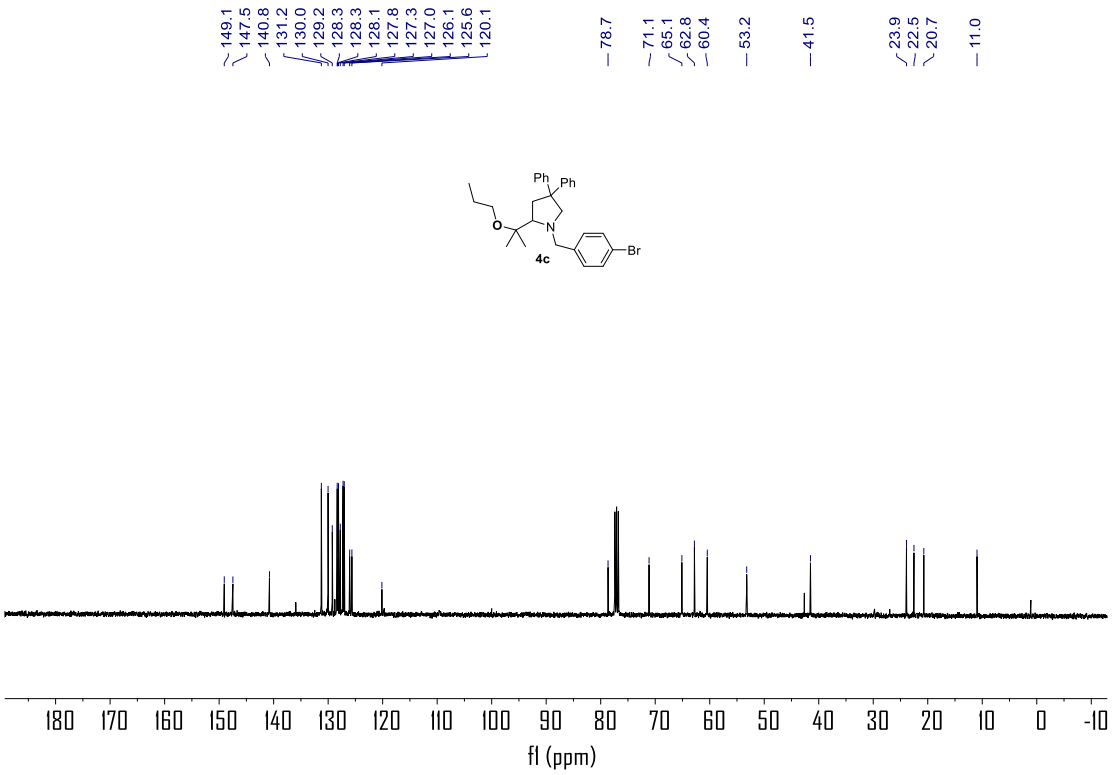
^{19}F NMR (376 MHz, $CDCl_3$) of 4b



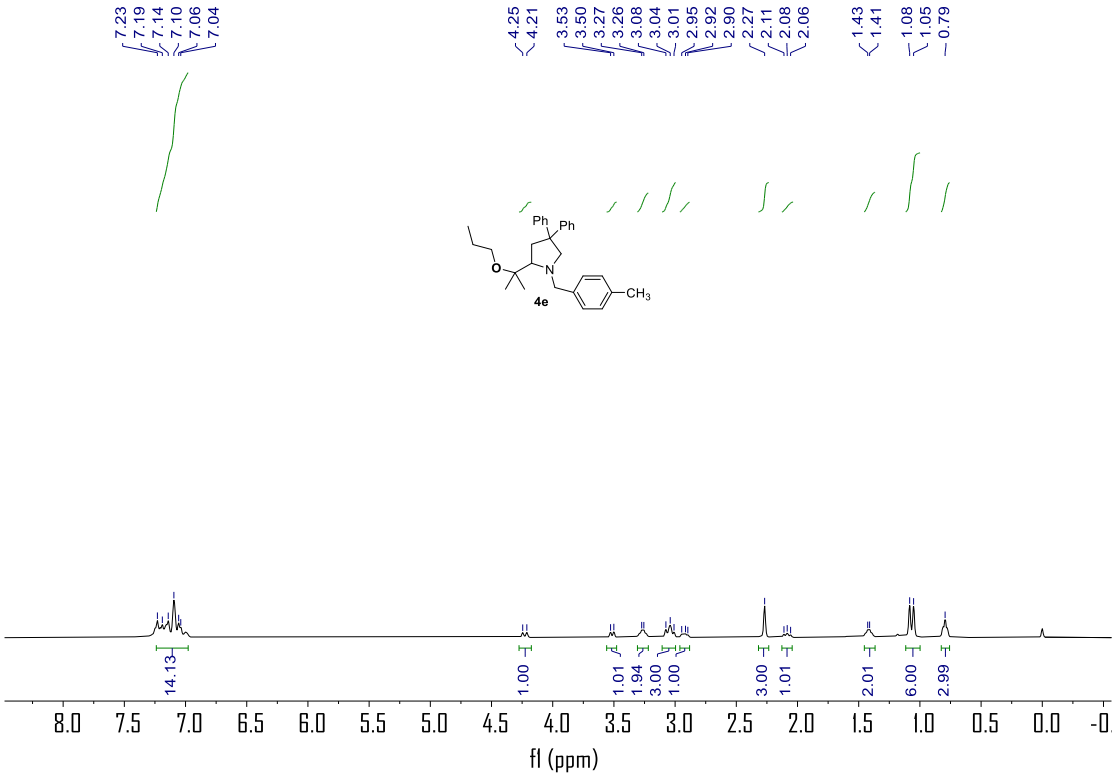
^{1}H NMR (400 MHz, $CDCl_3$) of 4c



^{13}C NMR (101MHz, $CDCl_3$) of 4c



^{1}H NMR (400 MHz, $CDCl_3$) of 4e



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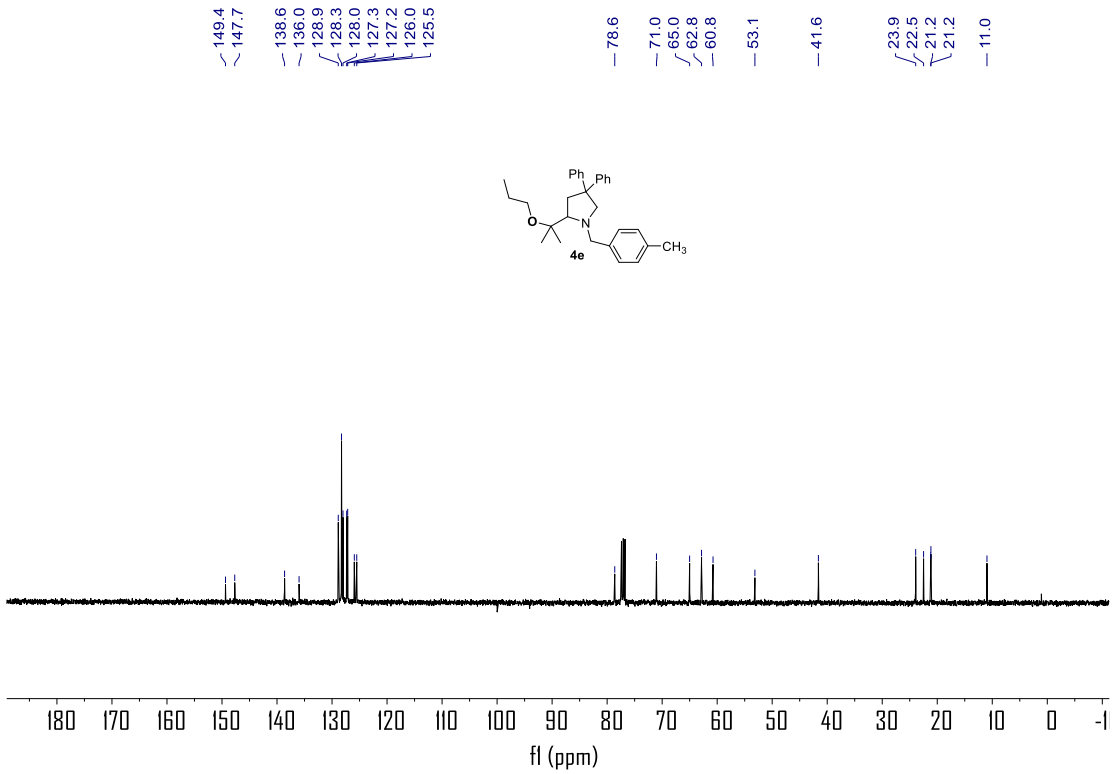
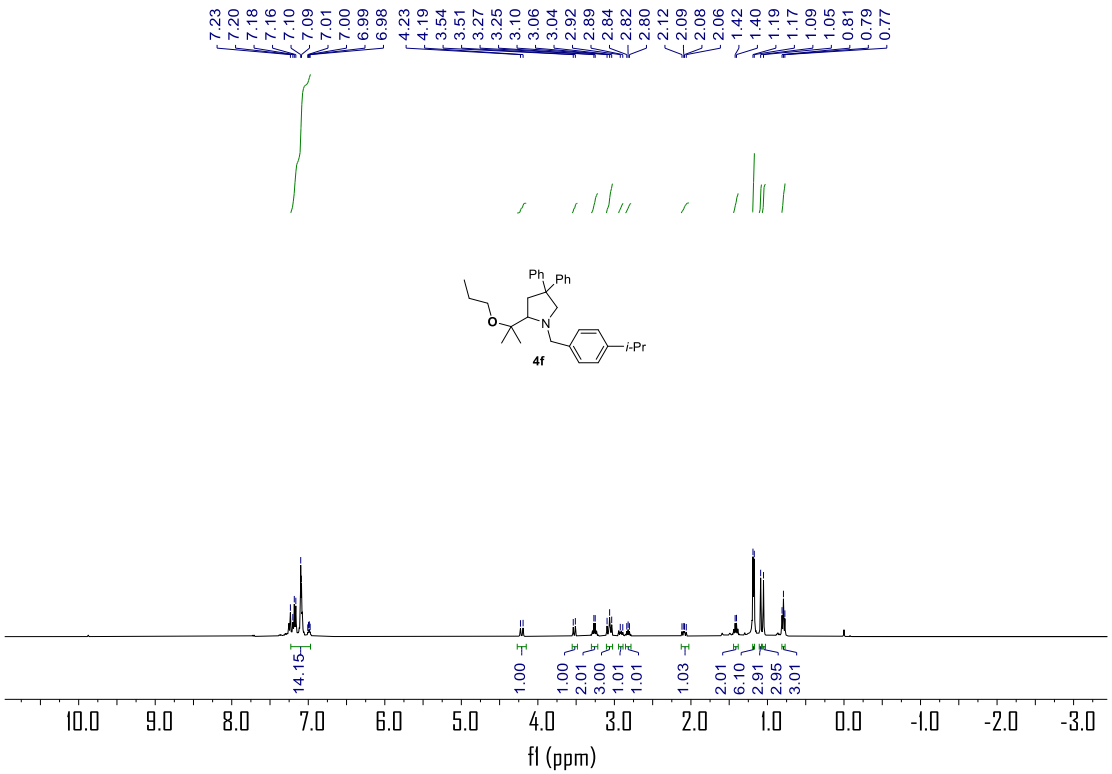


^{1}H NMR (400 MHz, $CDCl_3$) of 4f



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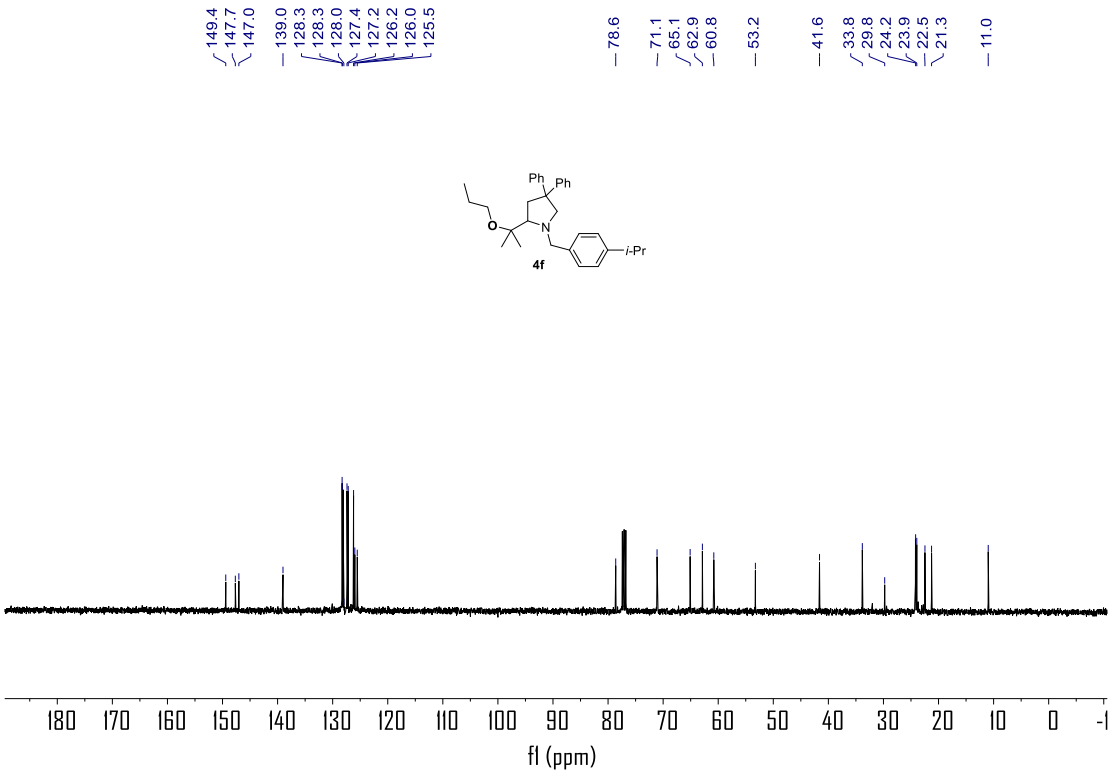
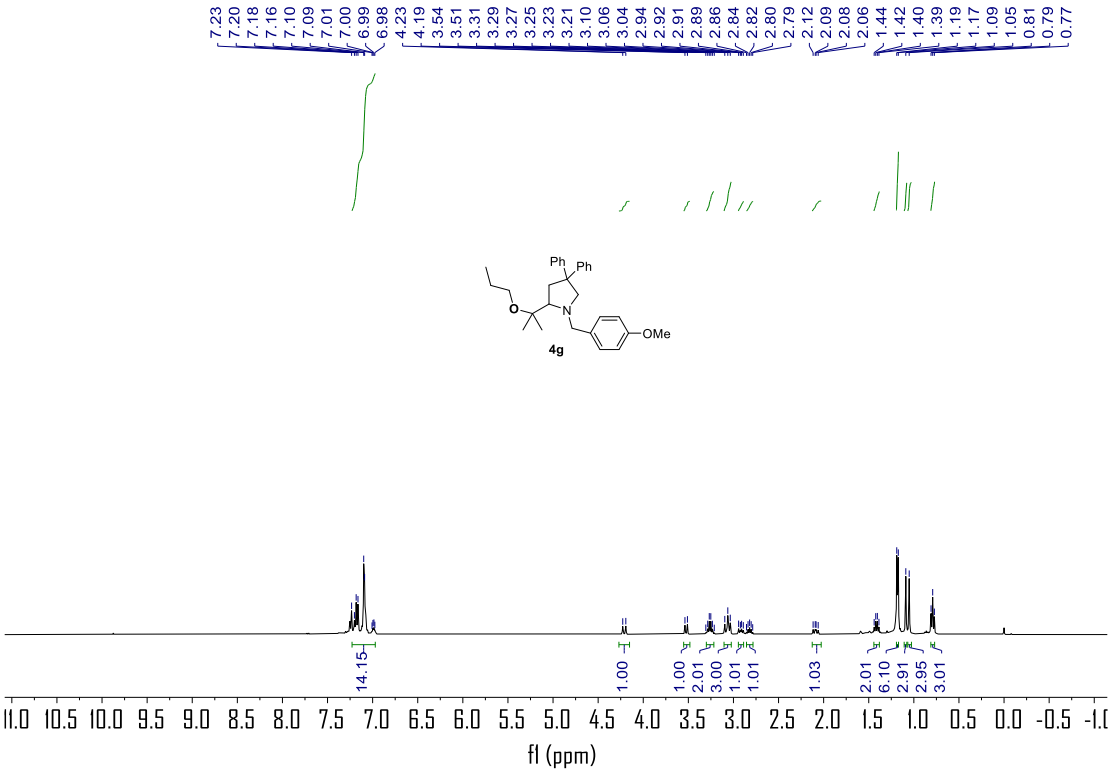


^{1}H NMR (400 MHz, $CDCl_3$) of 4g



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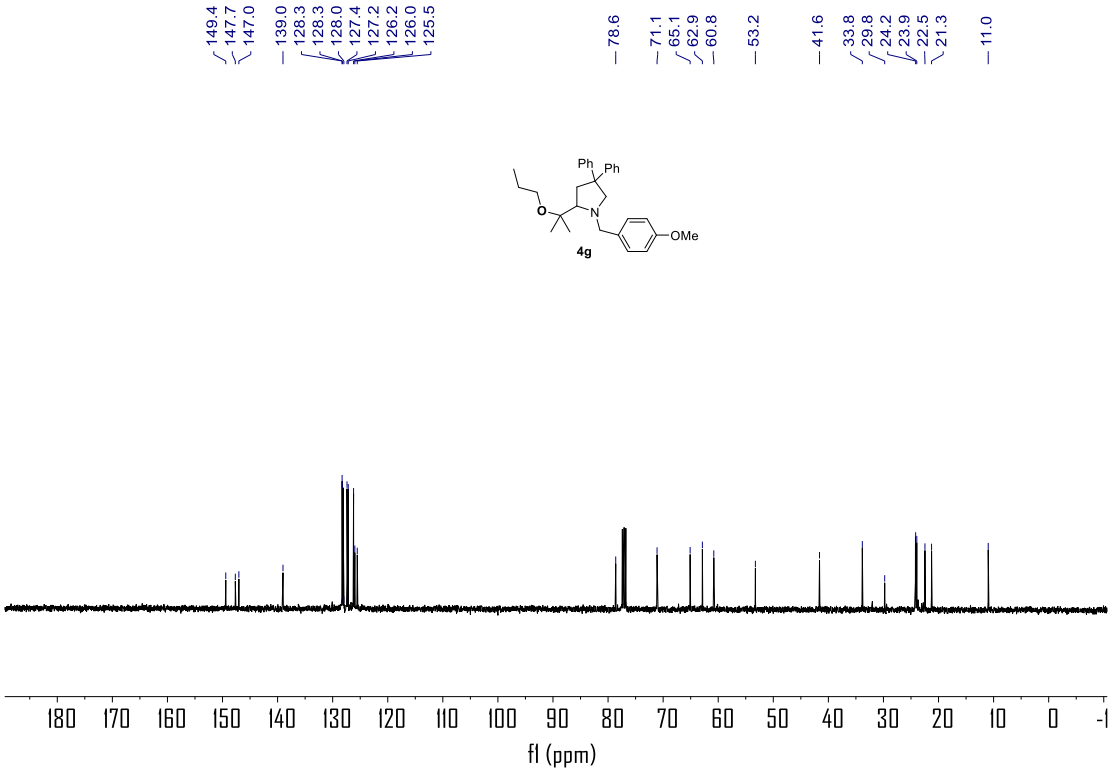

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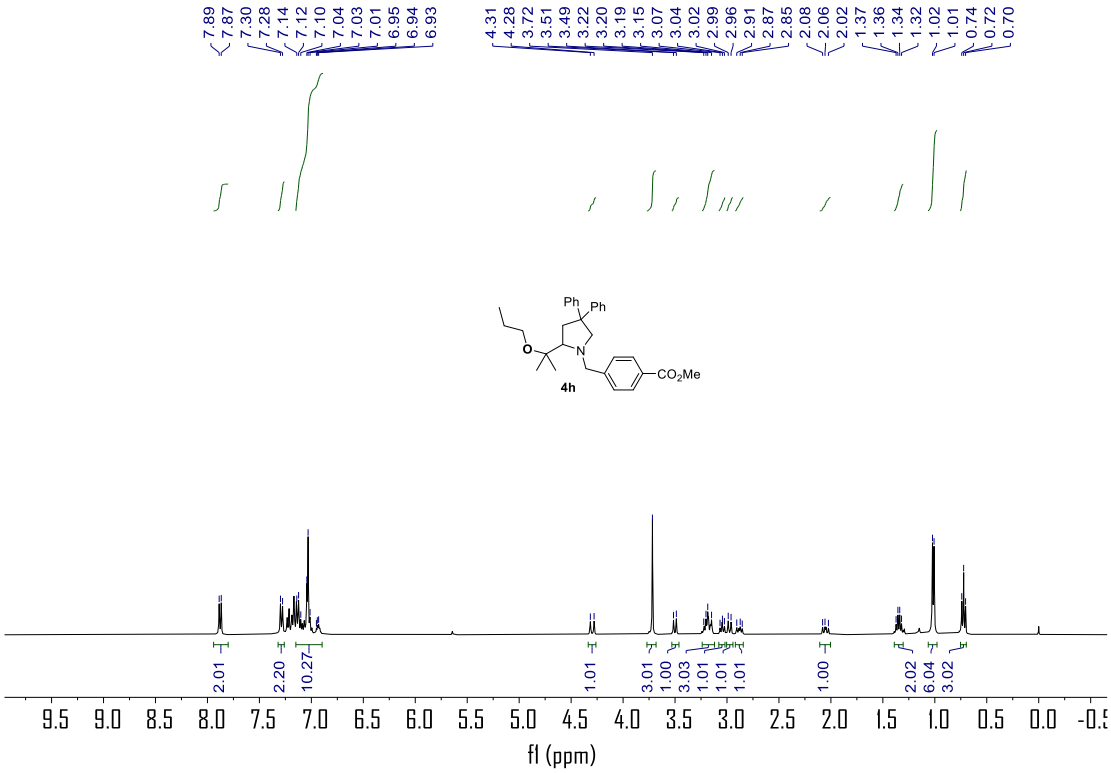

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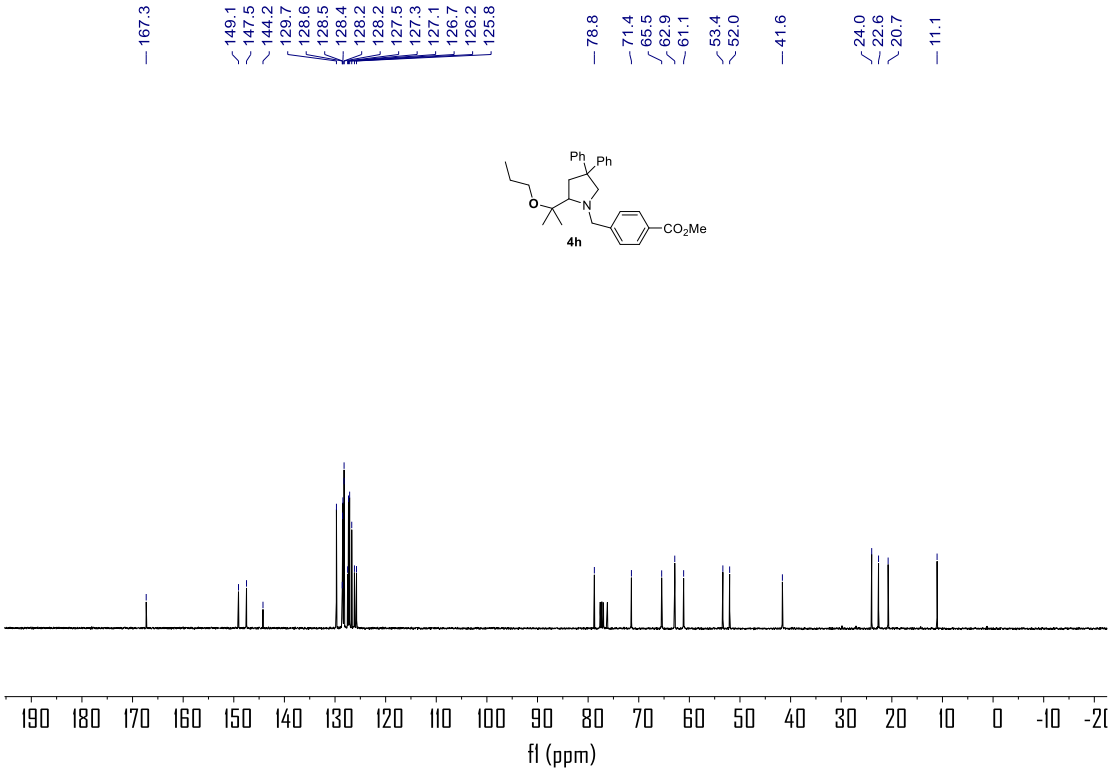
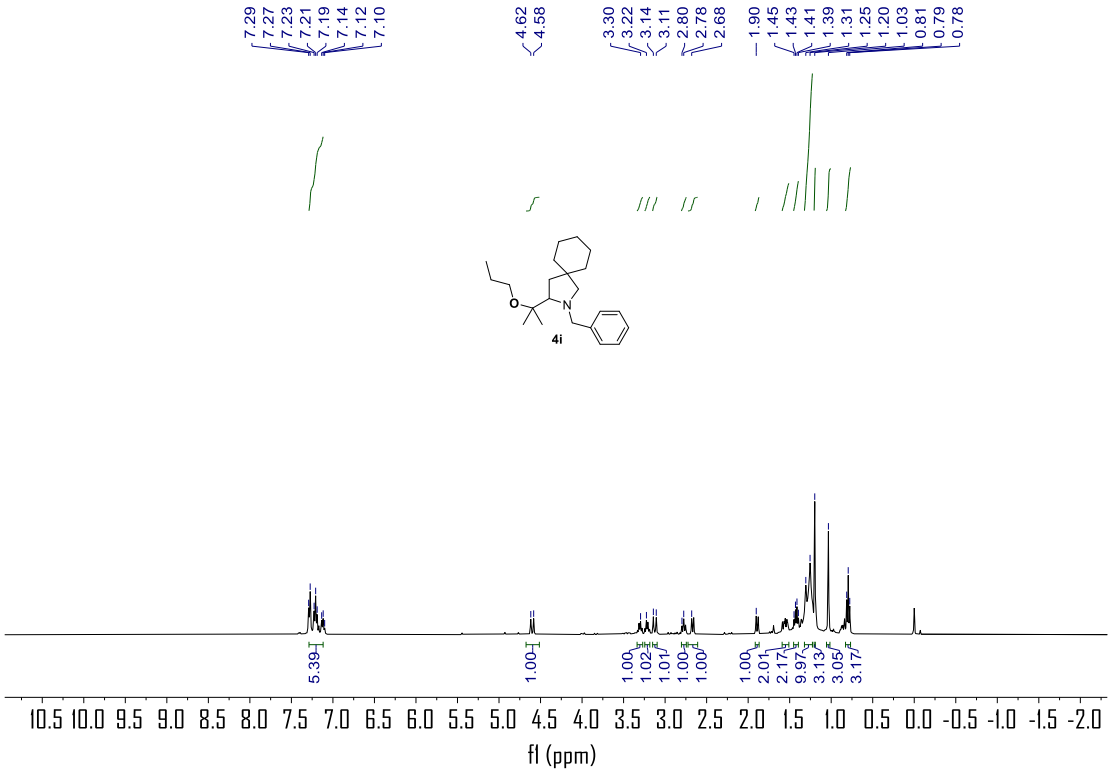


^{1}H NMR (400 MHz, $CDCl_3$) of 4i



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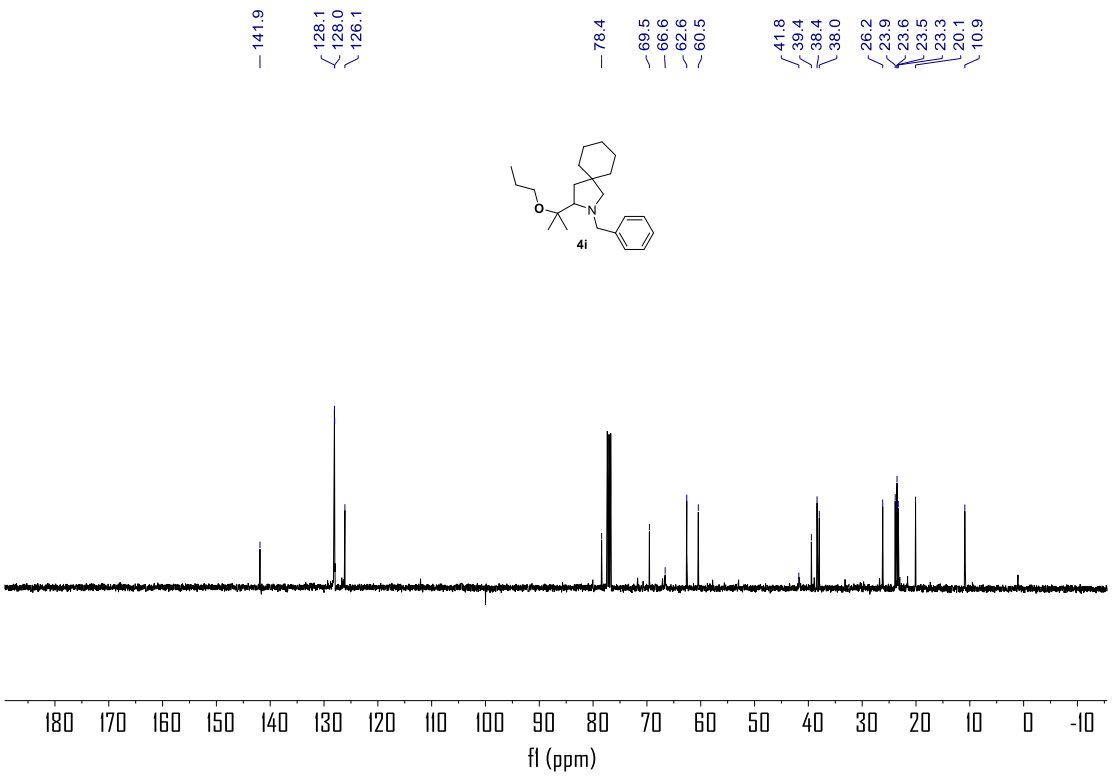

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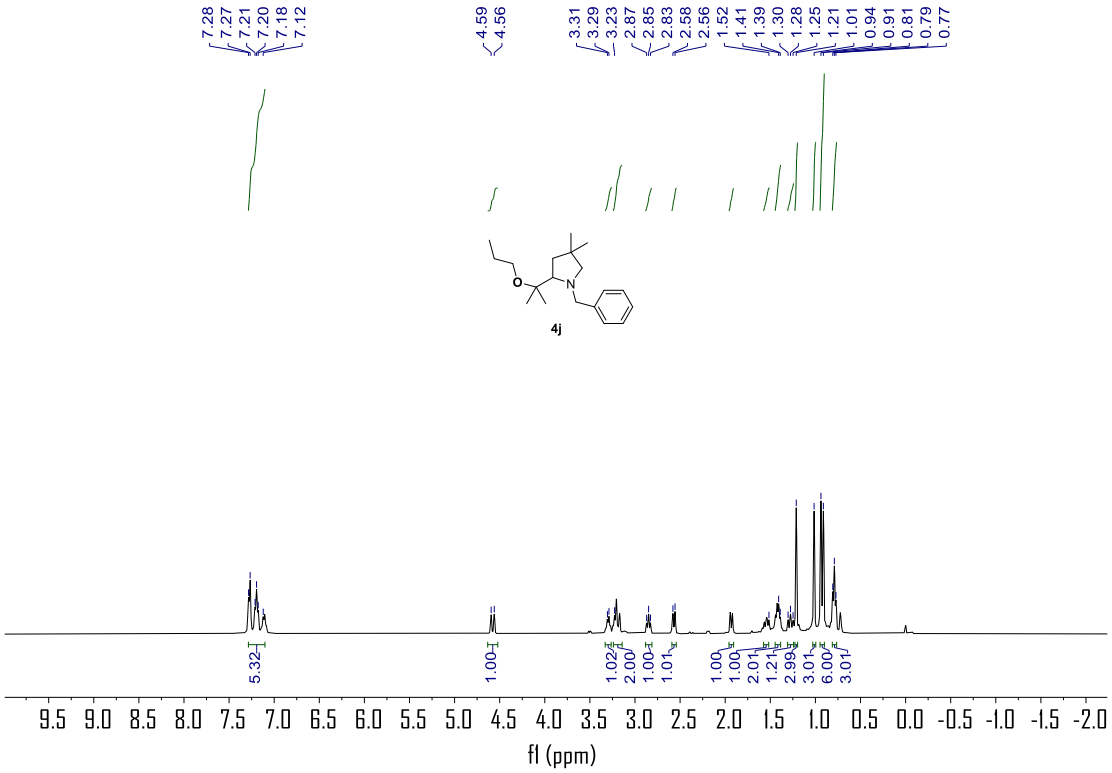

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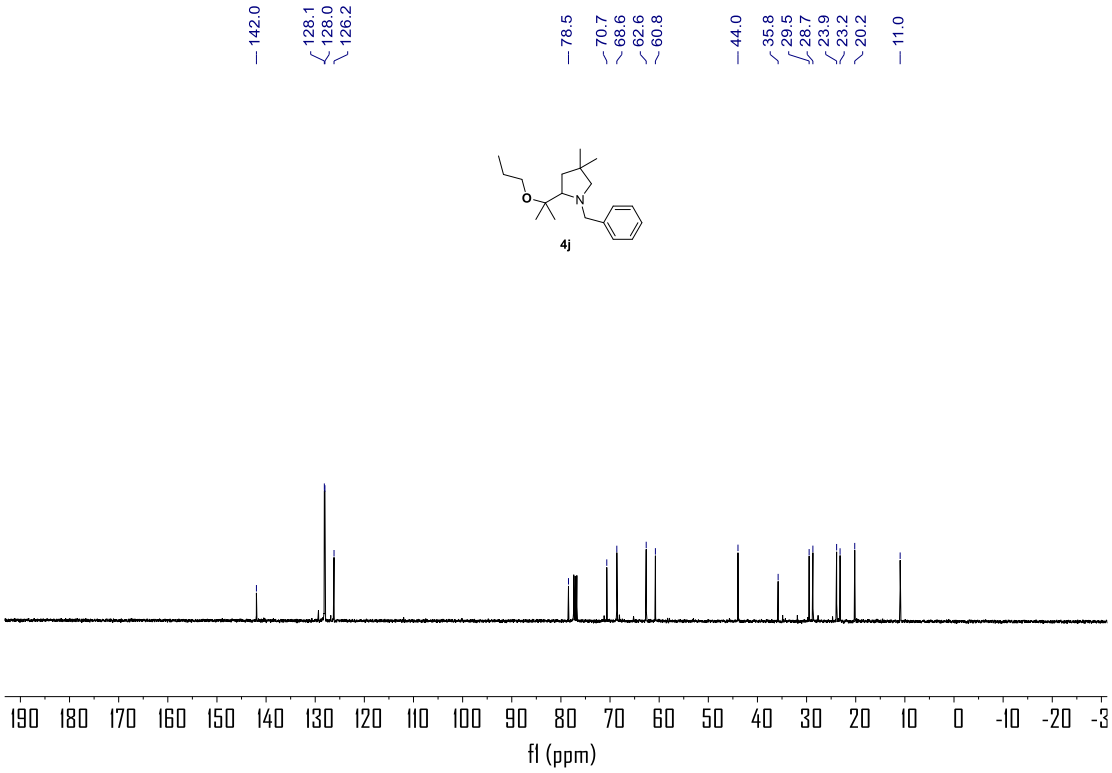
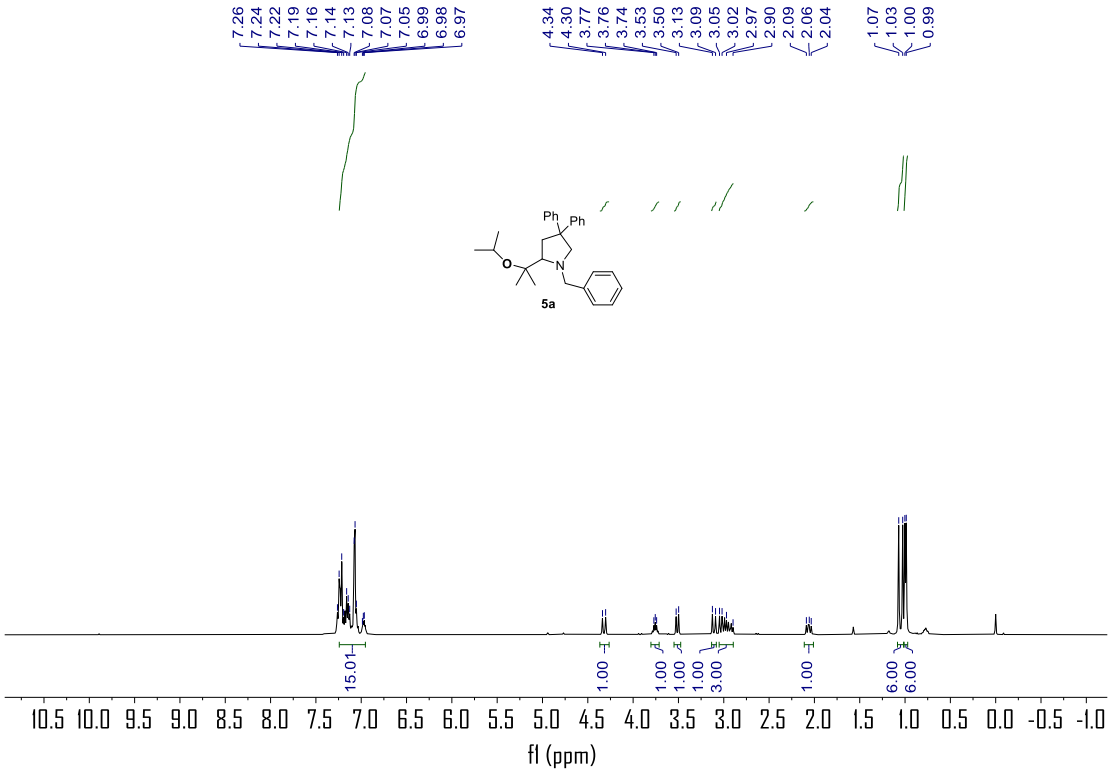
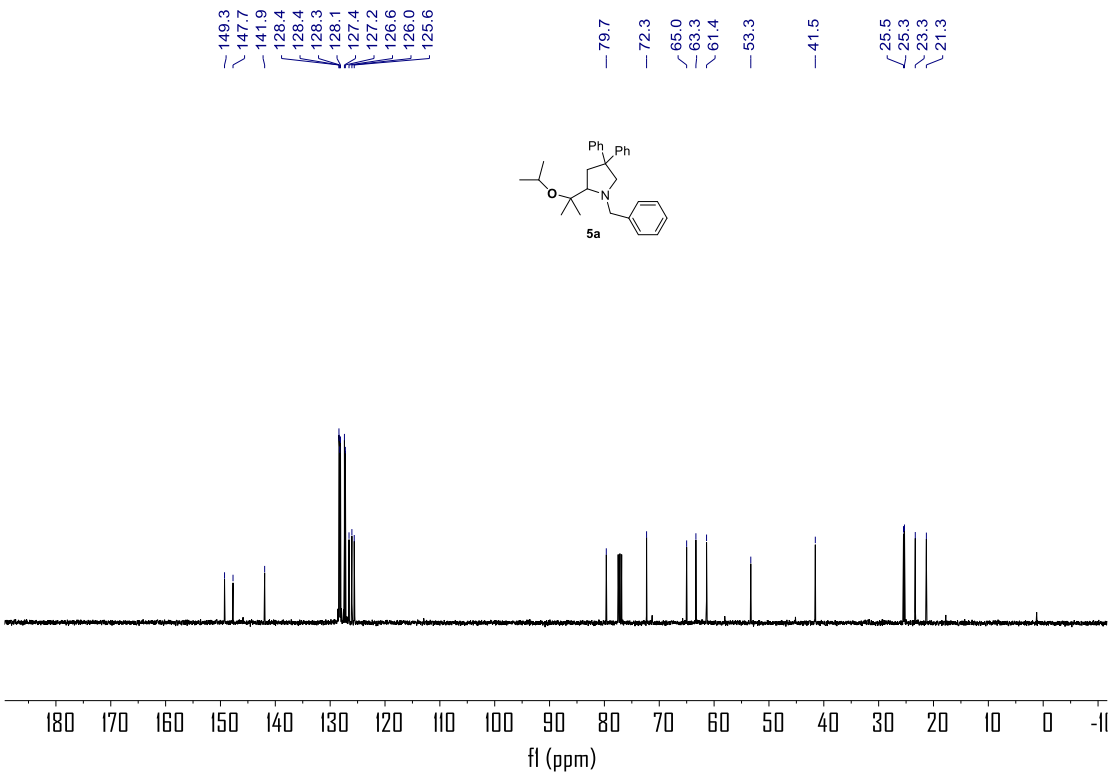


^{1}H NMR (400 MHz, $CDCl_3$) of 5a



^{13}C NMR (101MHz, $CDCl_3$) of 5a



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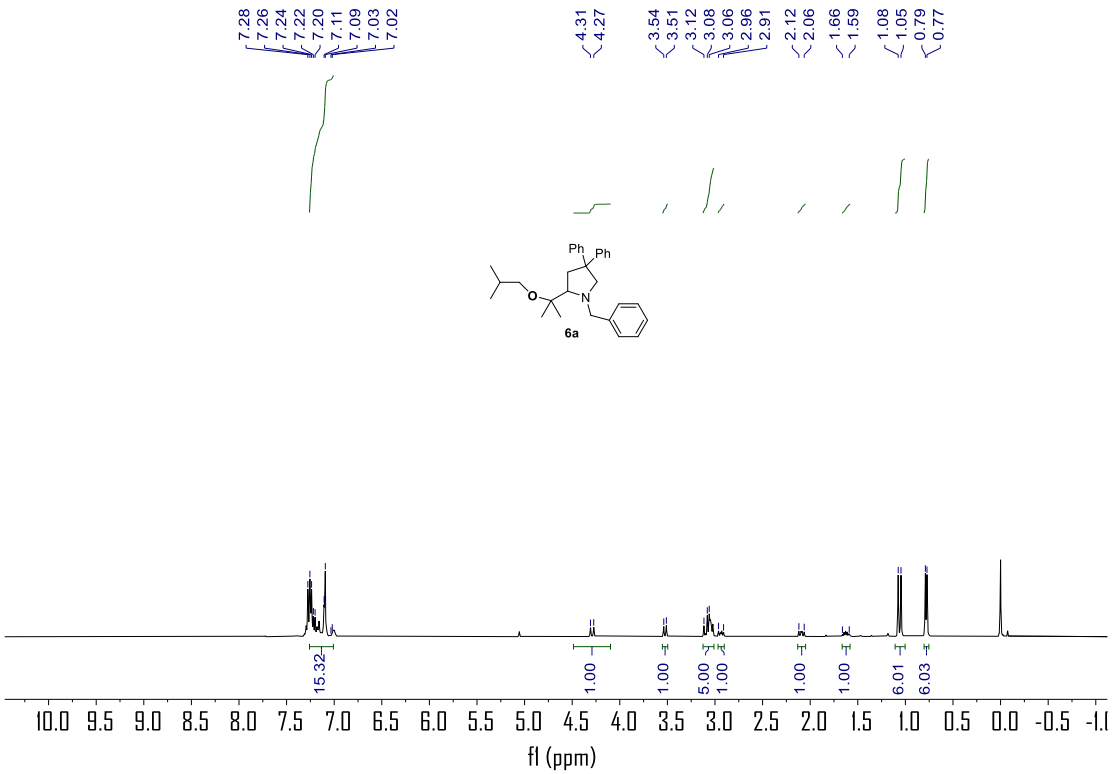
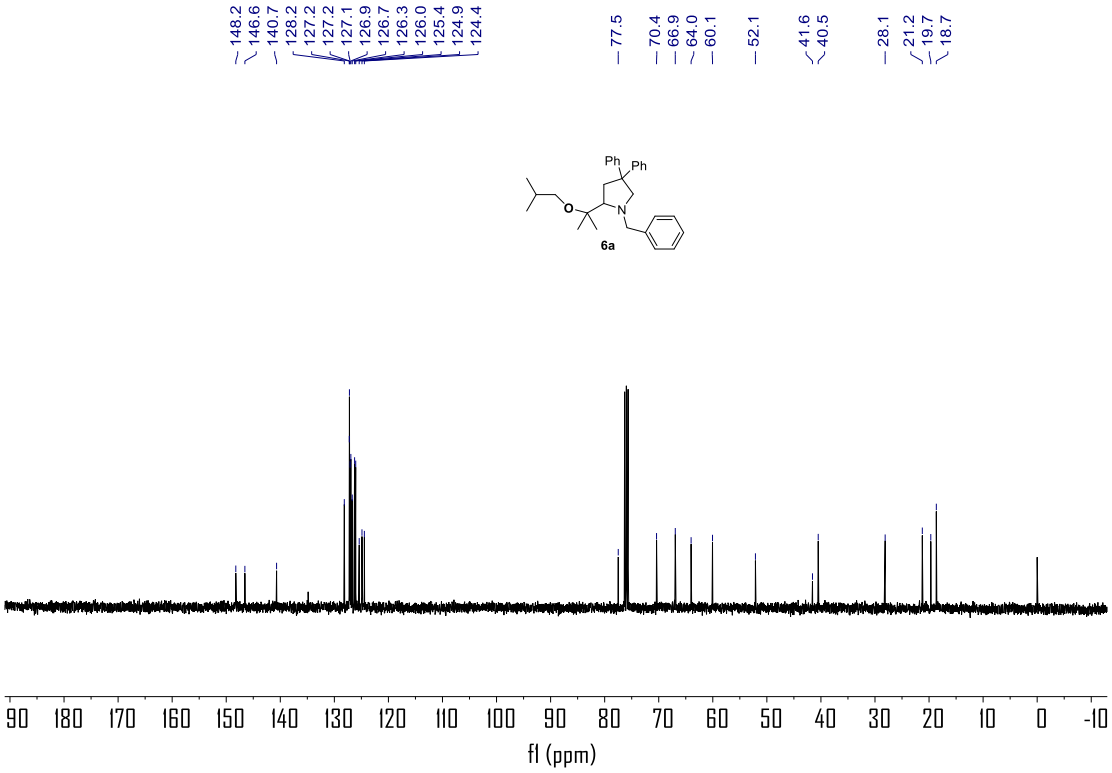
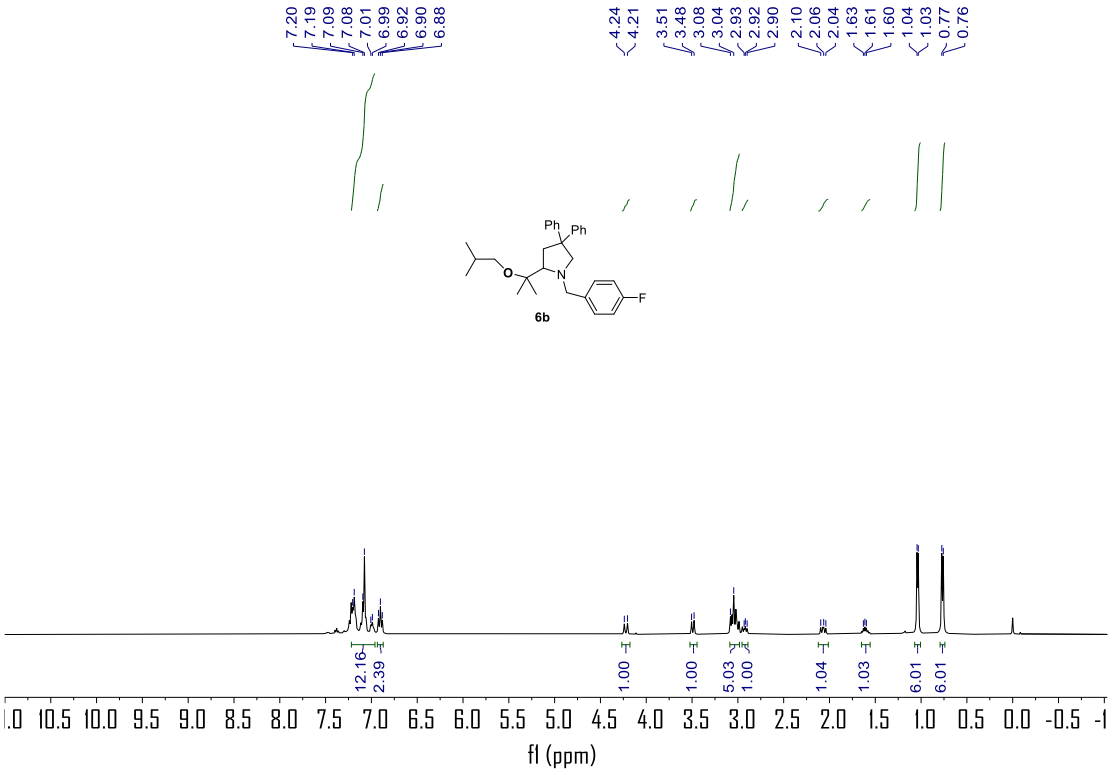


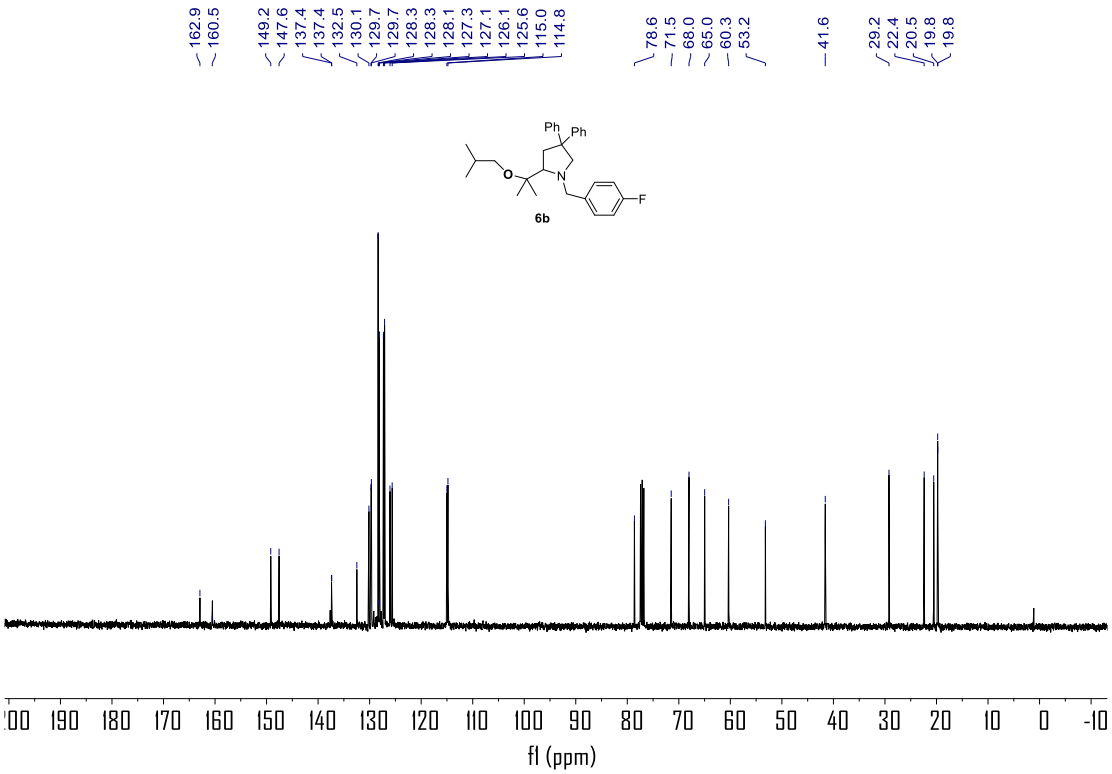
^{13}C NMR (101MHz, $CDCl_3$) of 6a



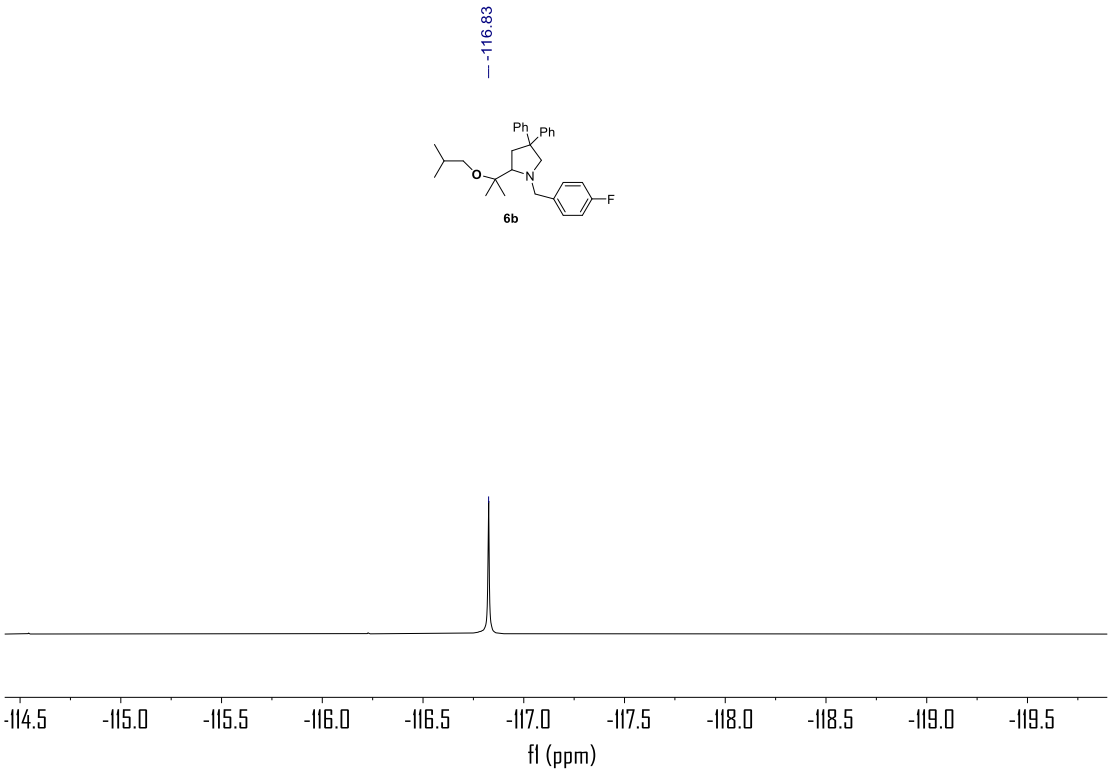
^{1}H NMR (400 MHz, $CDCl_3$) of 6b



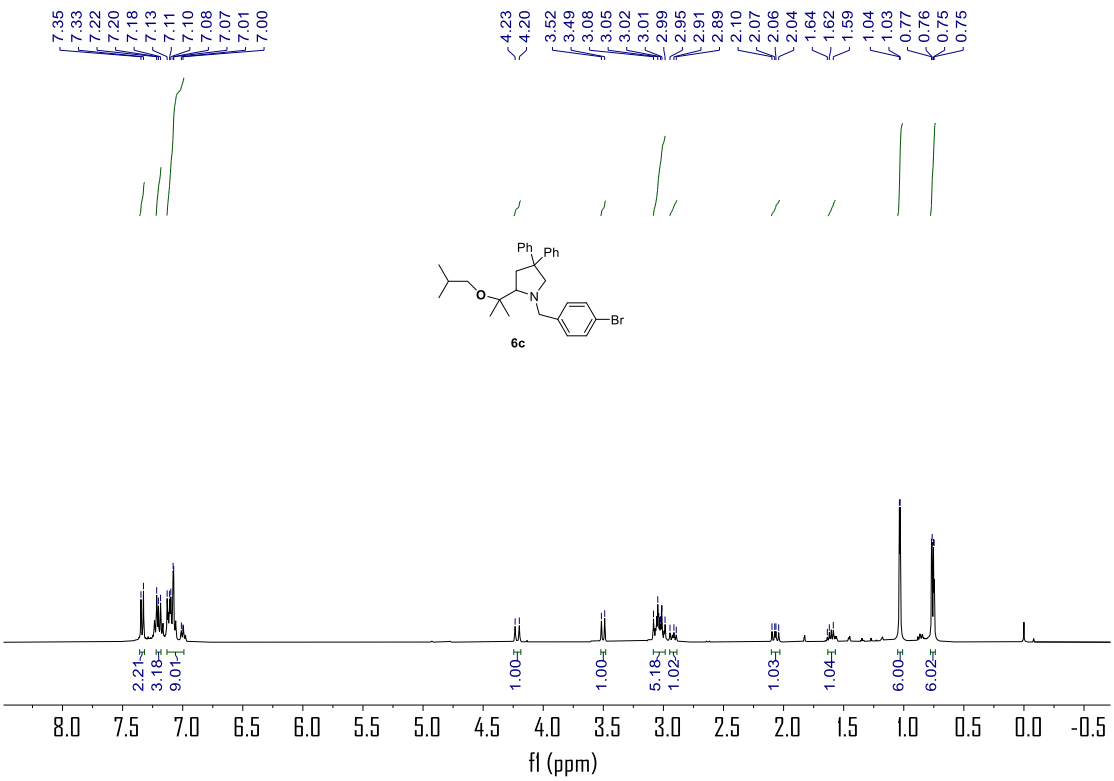
^{13}C NMR (101MHz, $CDCl_3$) of 6b



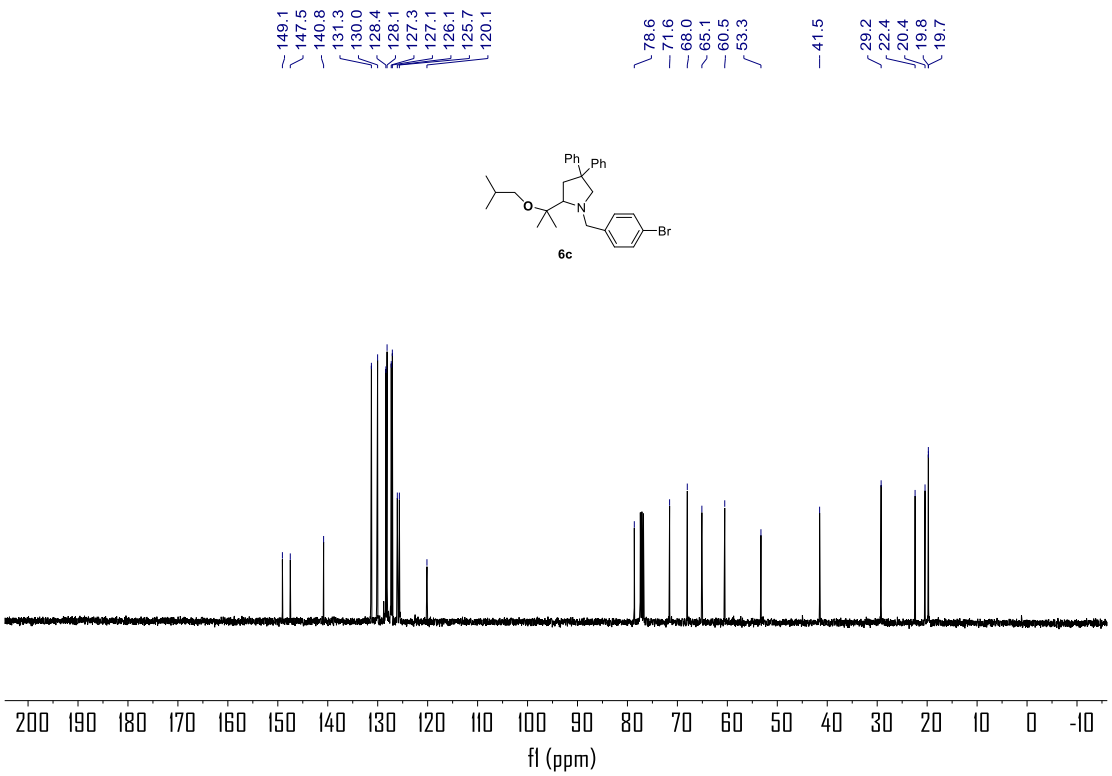
^{19}F NMR (376 MHz, $CDCl_3$) of 6b



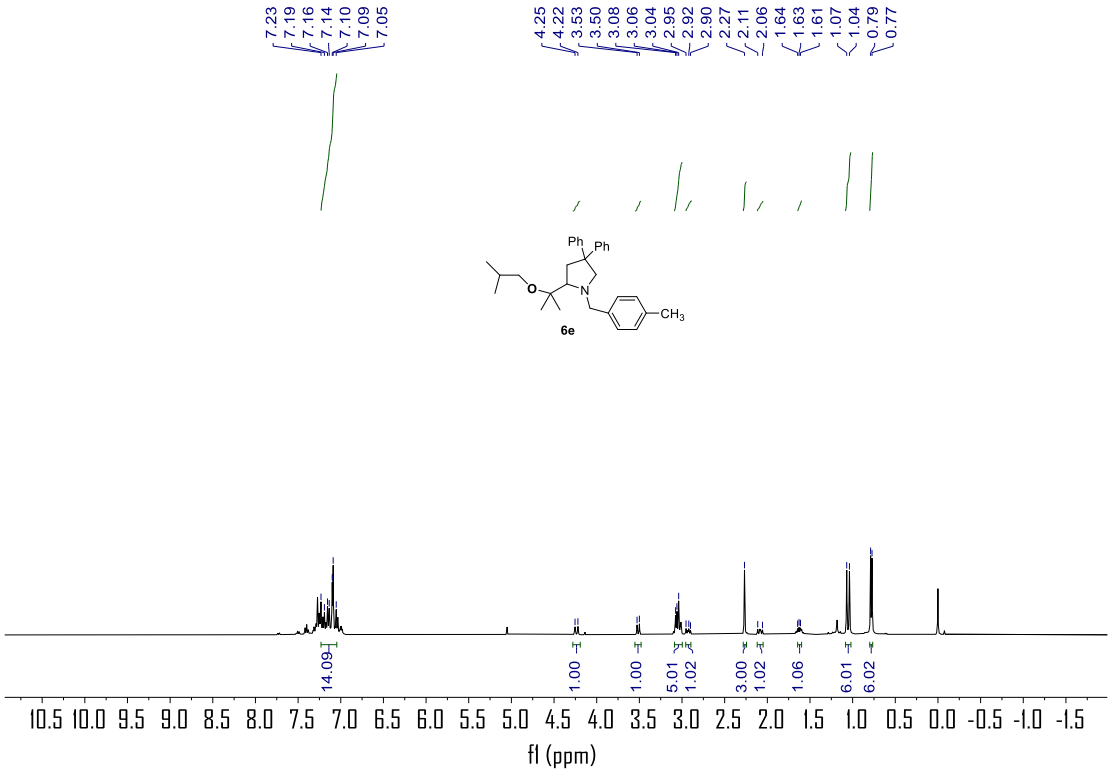
^{1}H NMR (400 MHz, $CDCl_3$) of 6c



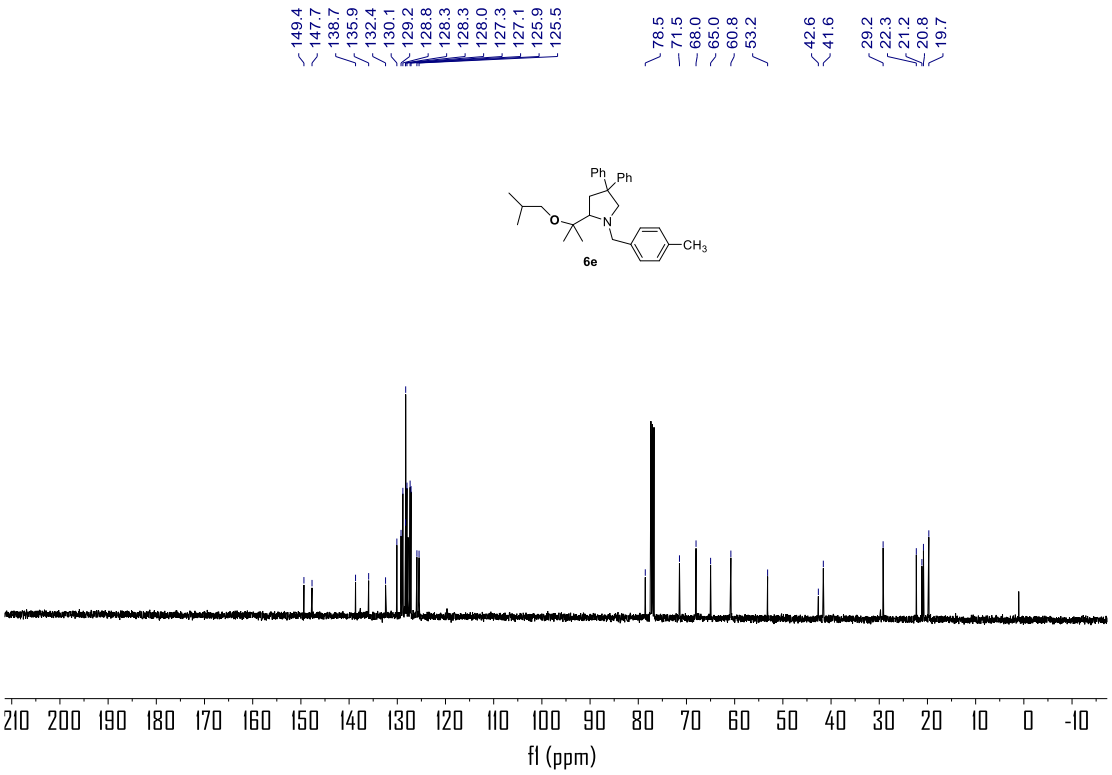
^{13}C NMR (101MHz, $CDCl_3$) of 6c



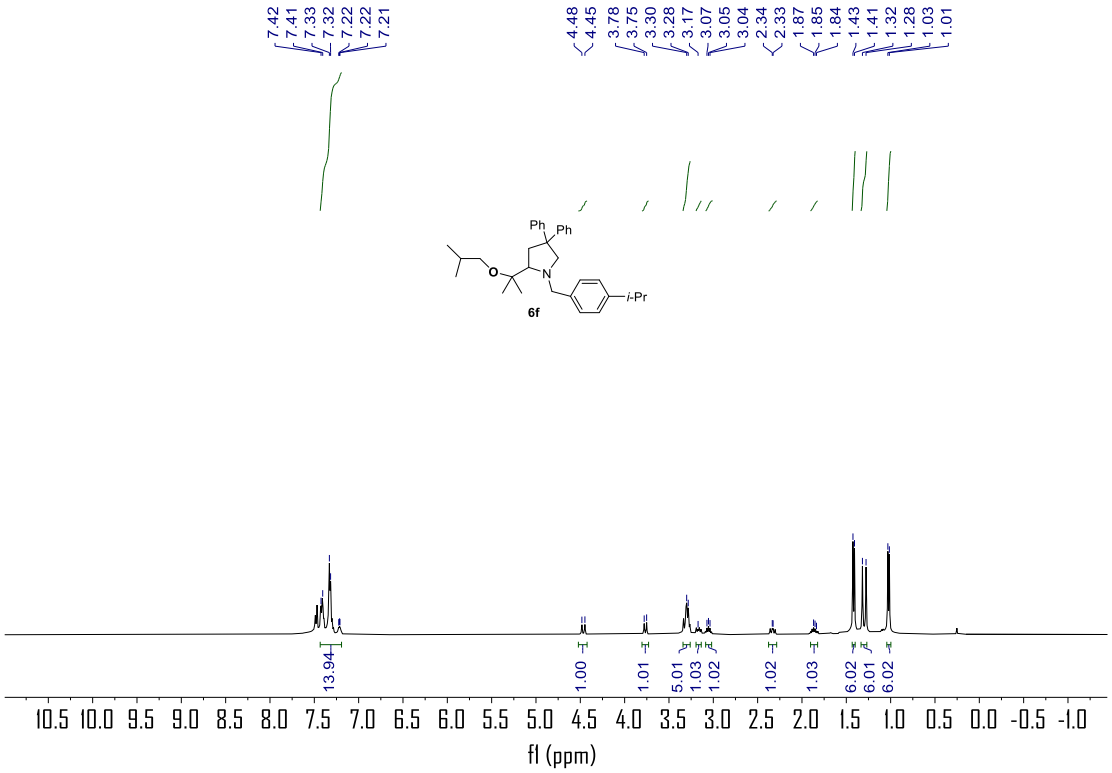
^{1}H NMR (400 MHz, $CDCl_3$) of 6e



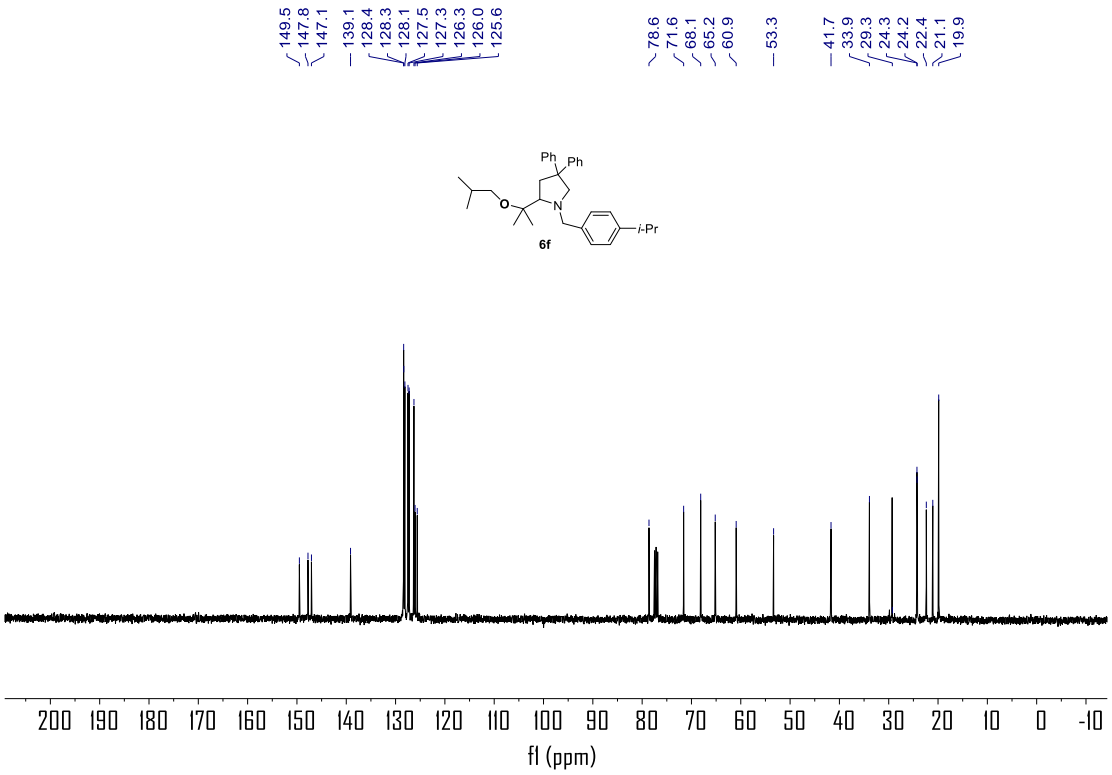
^{13}C NMR (101MHz, $CDCl_3$) of 6e



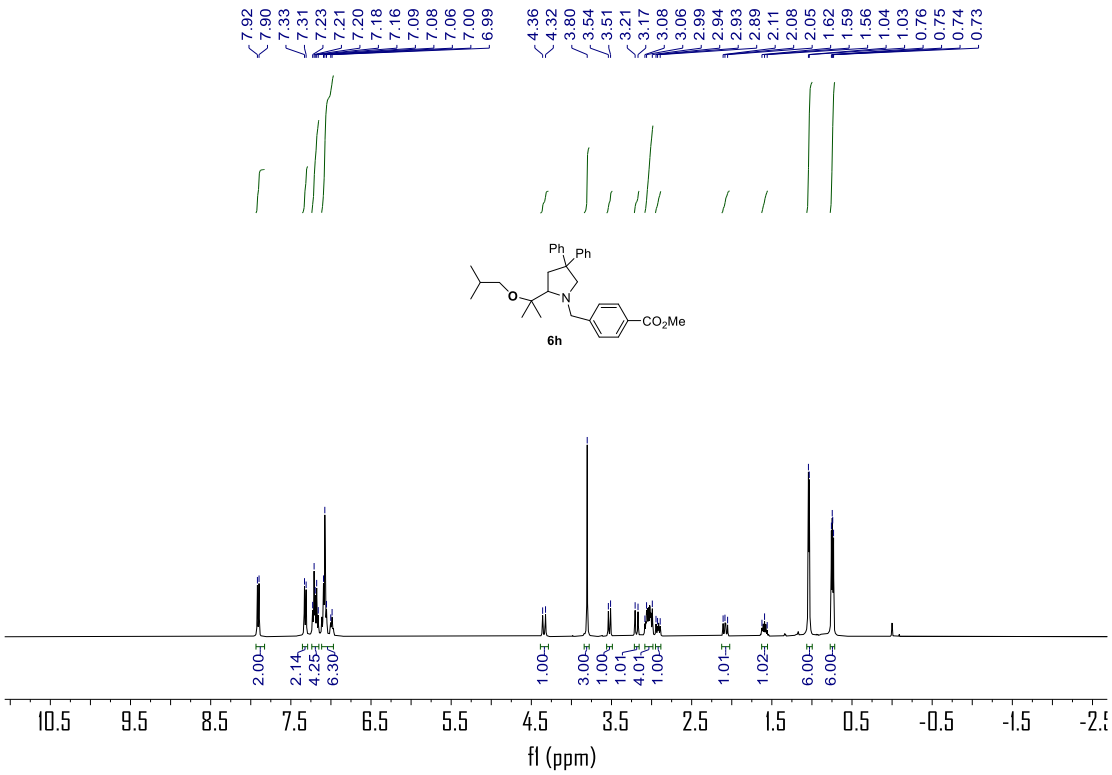
^{1}H NMR (400 MHz, $CDCl_3$) of 6f



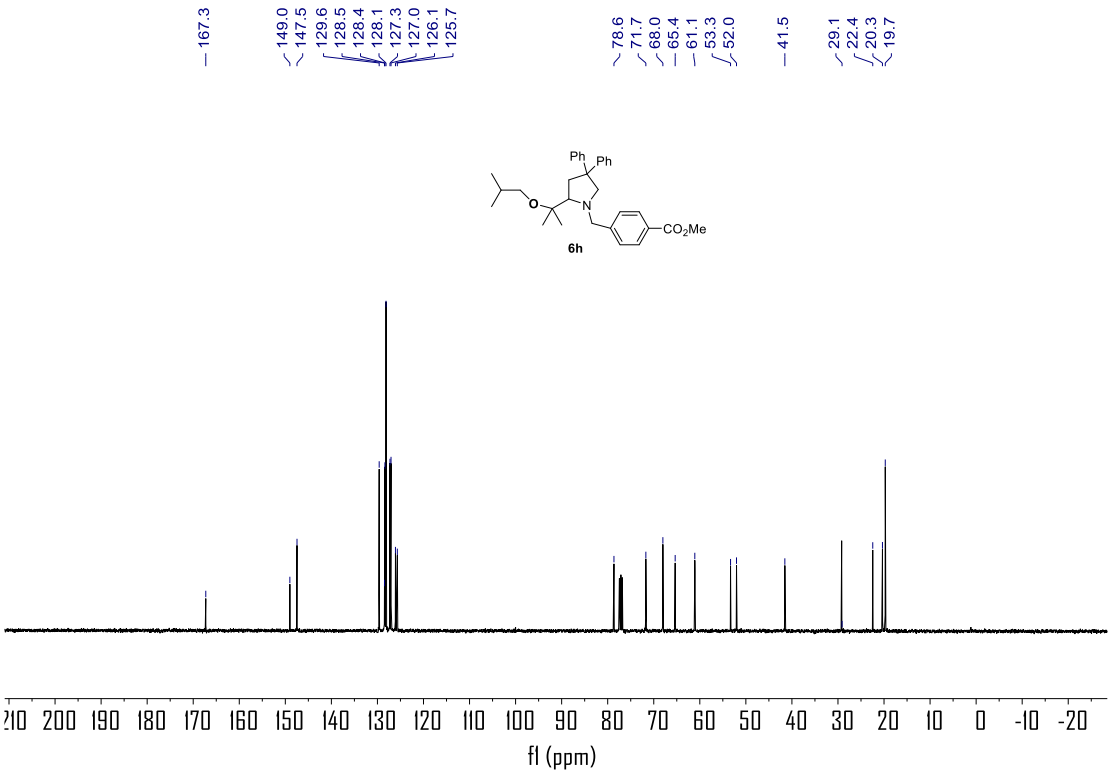
^{13}C NMR (101MHz, $CDCl_3$) of 6f



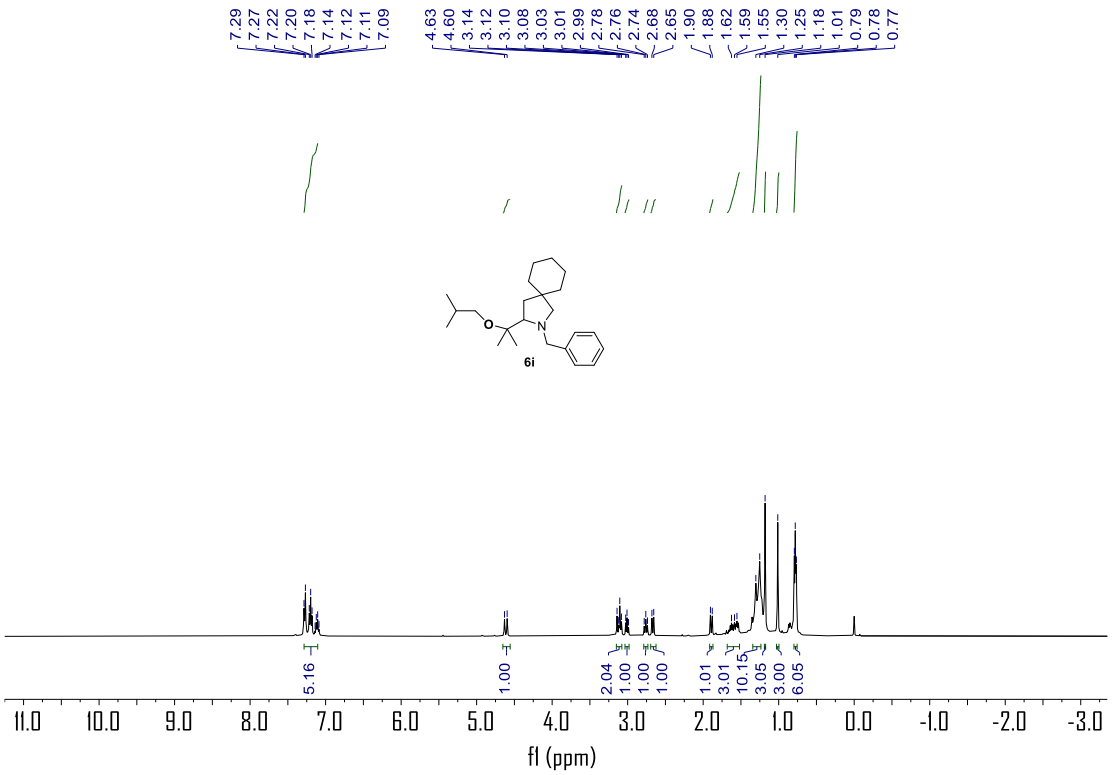
^{1}H NMR (400 MHz, $CDCl_3$) of 6h



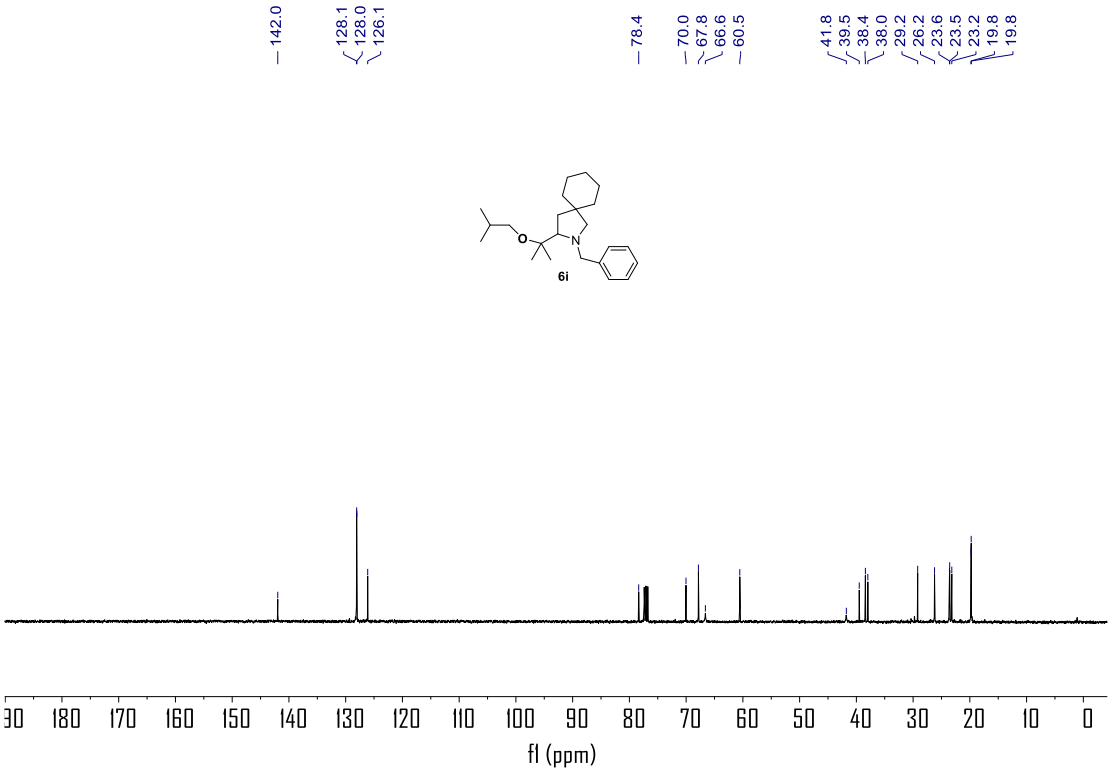
^{13}C NMR (101MHz, $CDCl_3$) of 6h



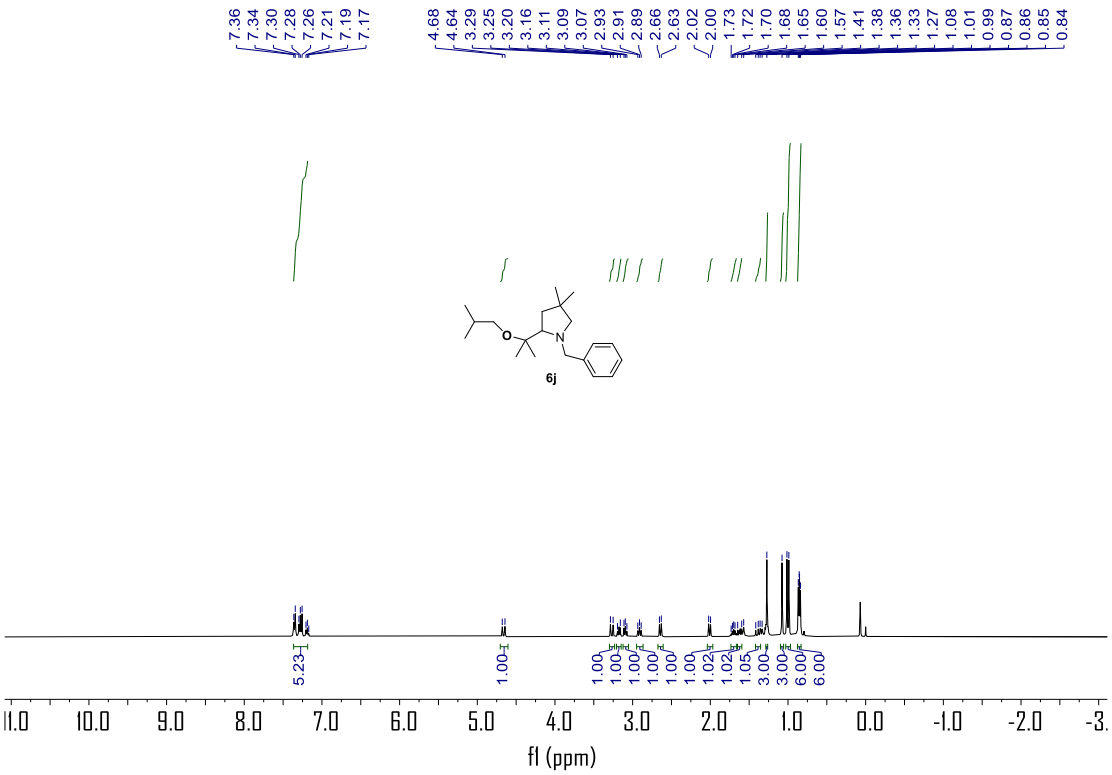
^{1}H NMR (400 MHz, $CDCl_3$) of 6i



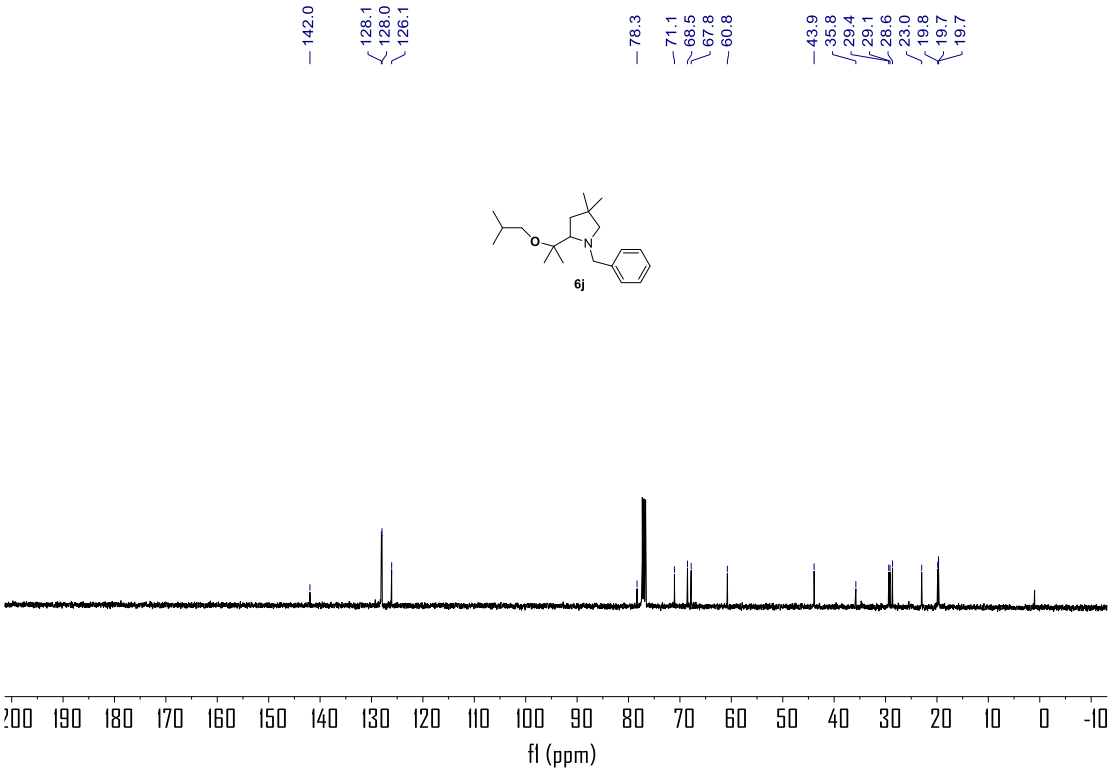
^{13}C NMR (101MHz, $CDCl_3$) of 6i



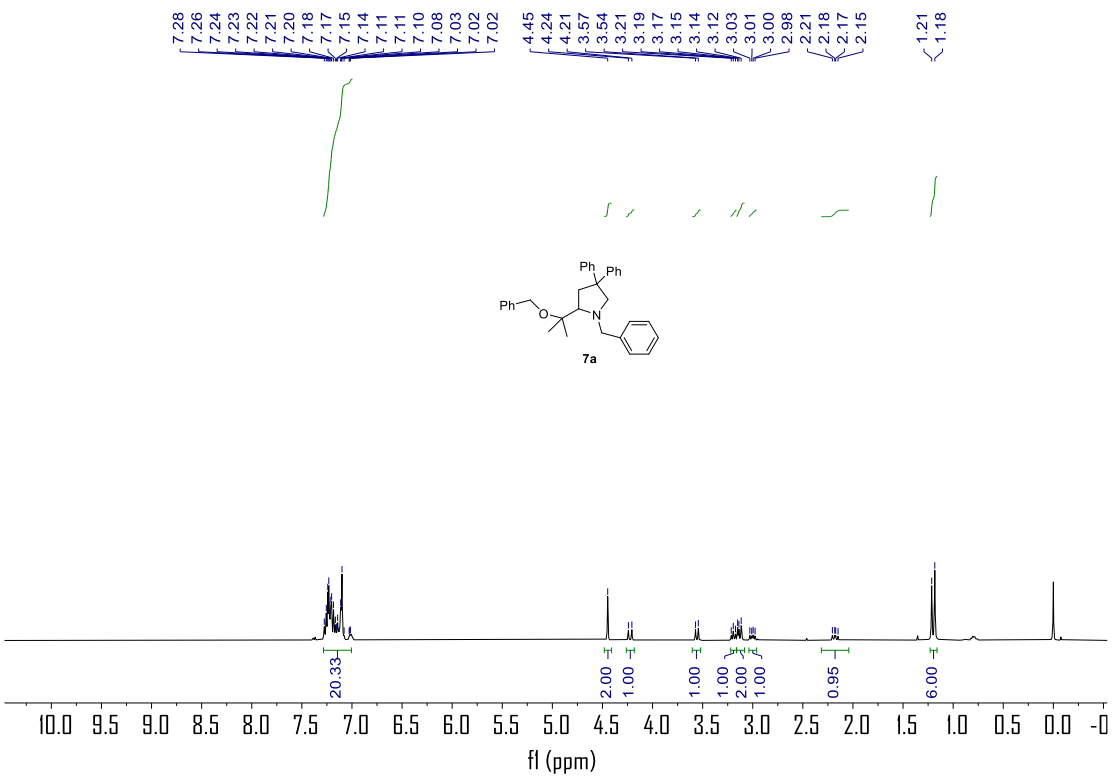
^{1}H NMR (400 MHz, $CDCl_3$) of 6j



^{13}C NMR (101MHz, $CDCl_3$) of 6j



^{1}H NMR (400 MHz, $CDCl_3$) of 7a



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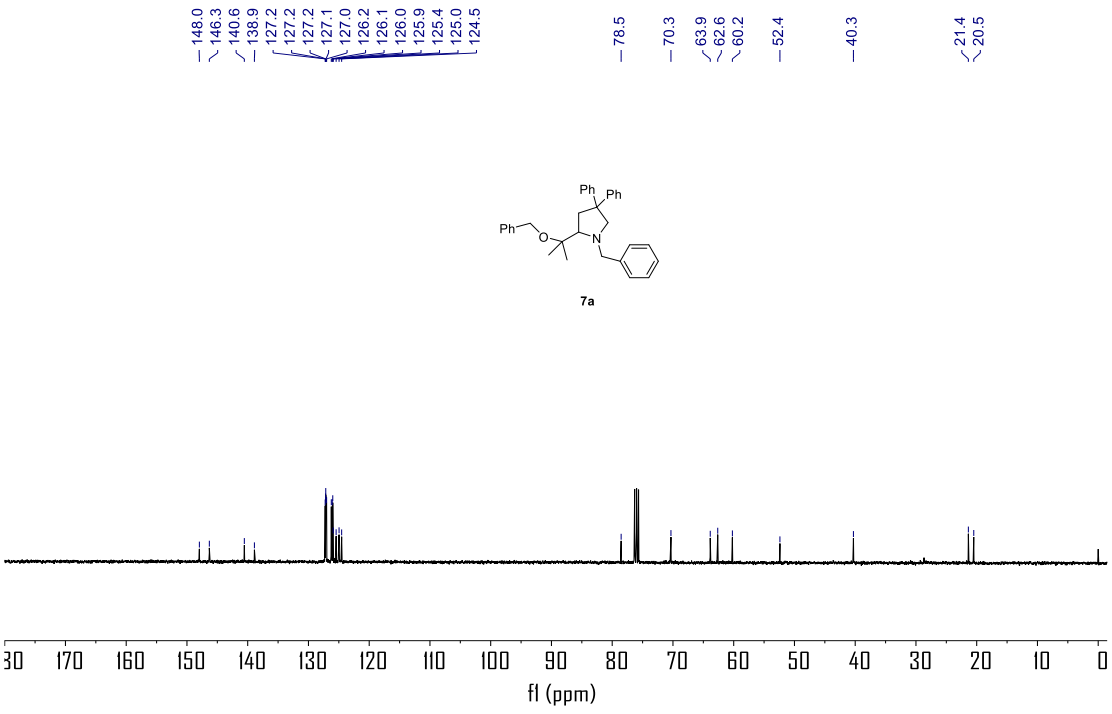

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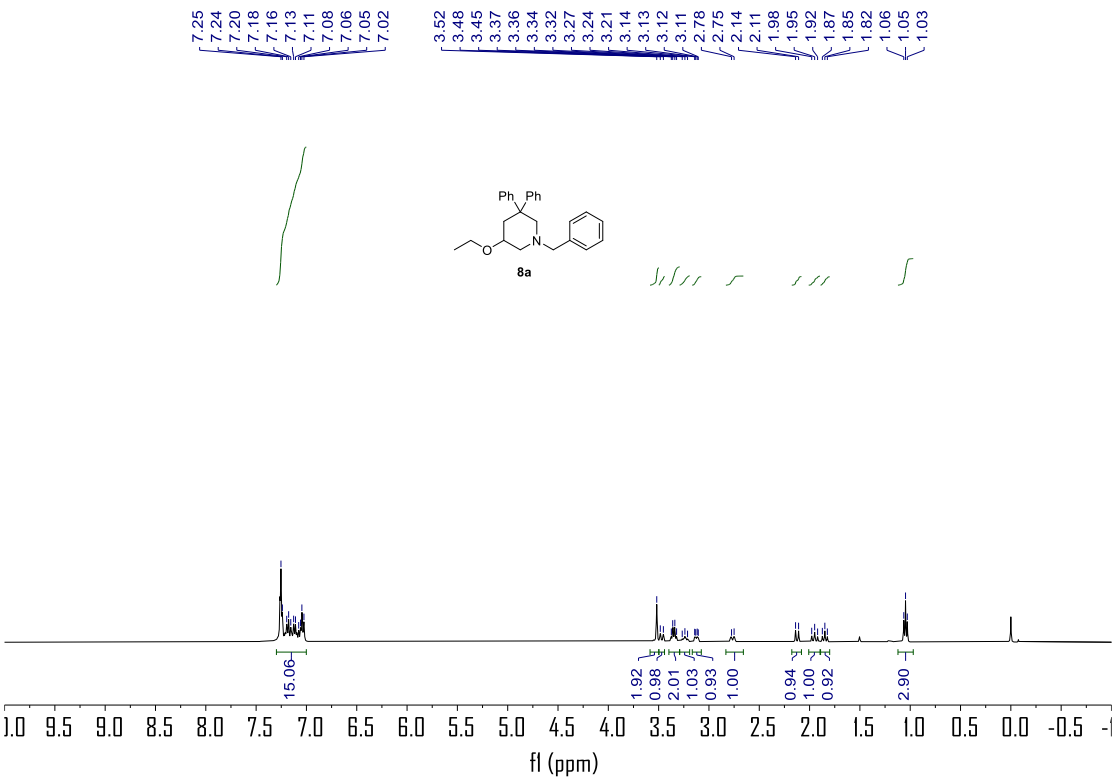
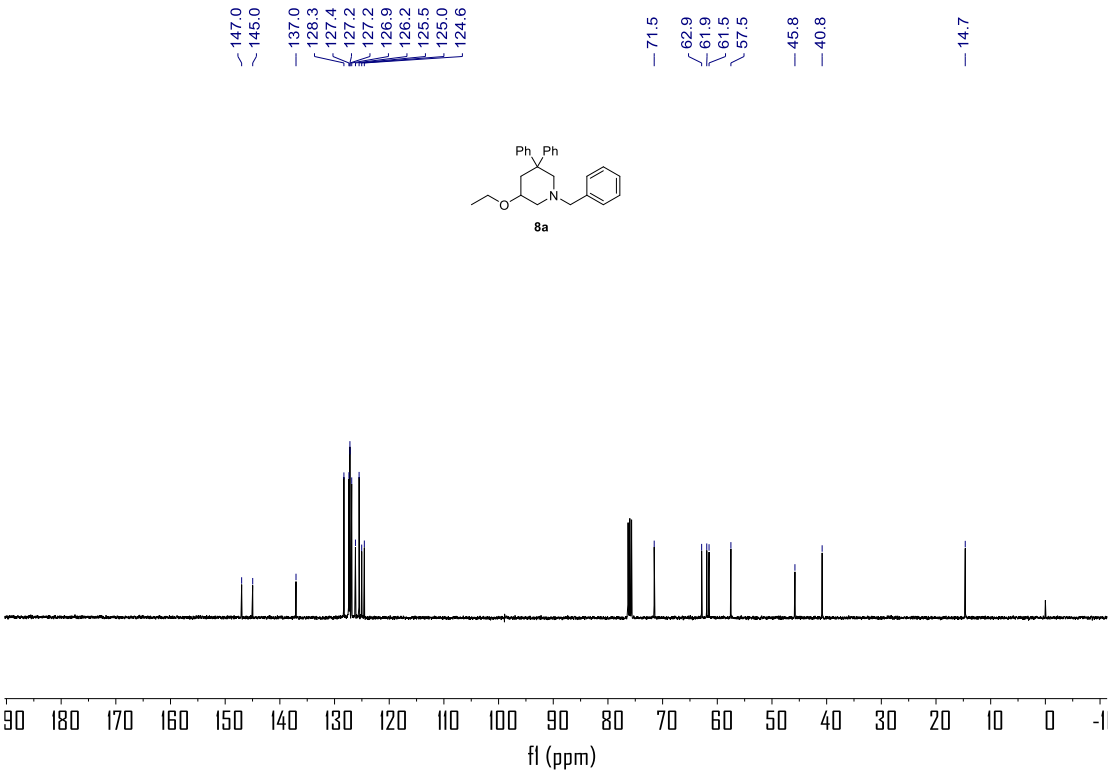
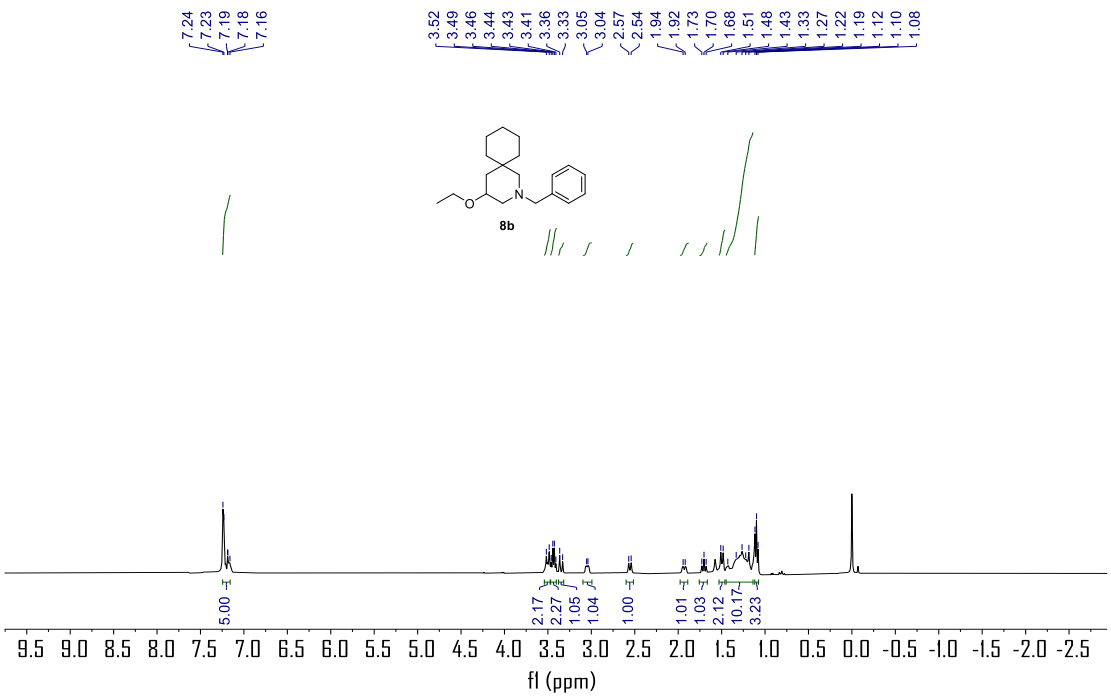


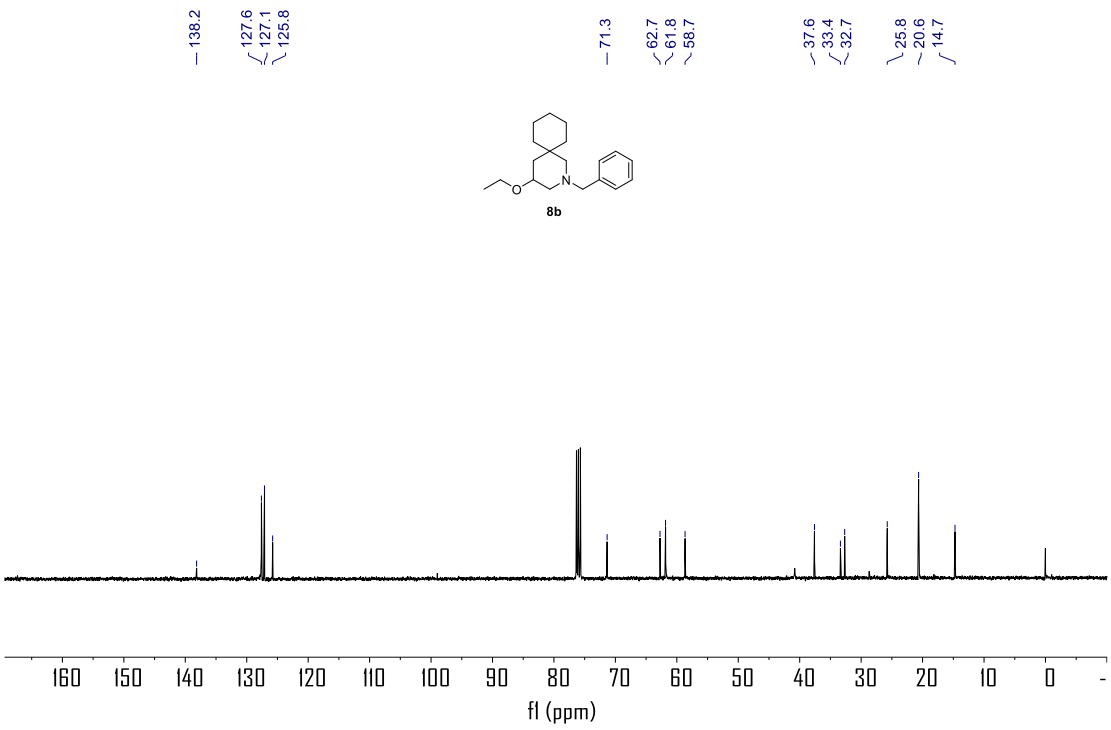
^{13}C NMR (101MHz, $CDCl_3$) of 8a



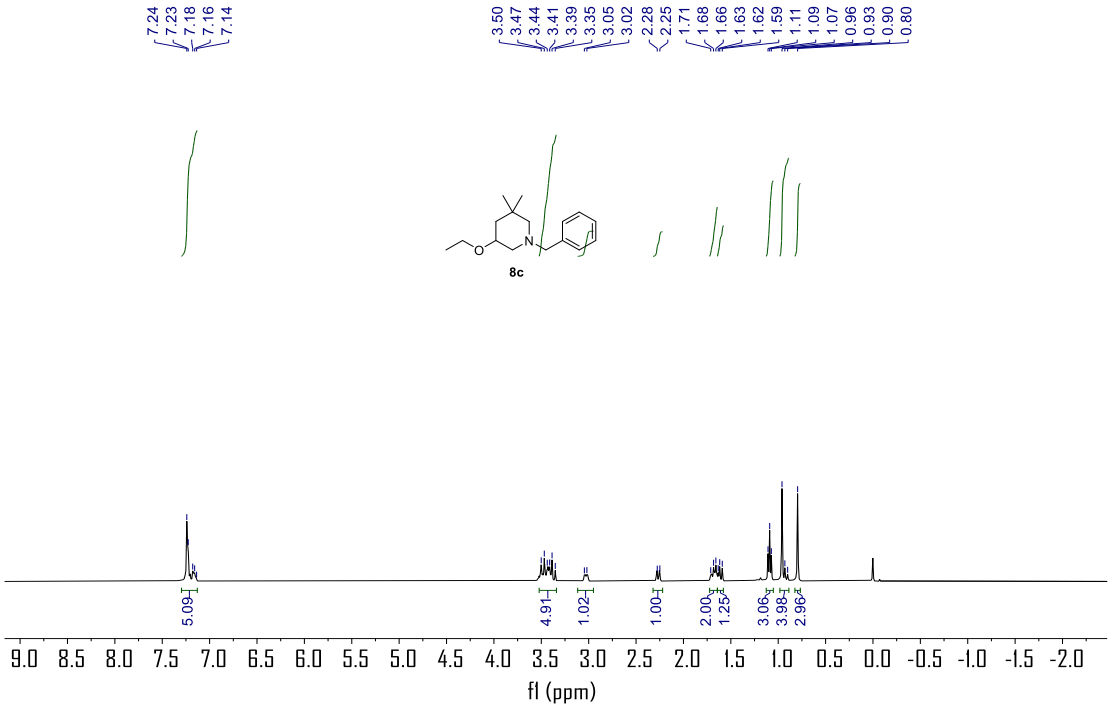
^{1}H NMR (400 MHz, $CDCl_3$) of 8b



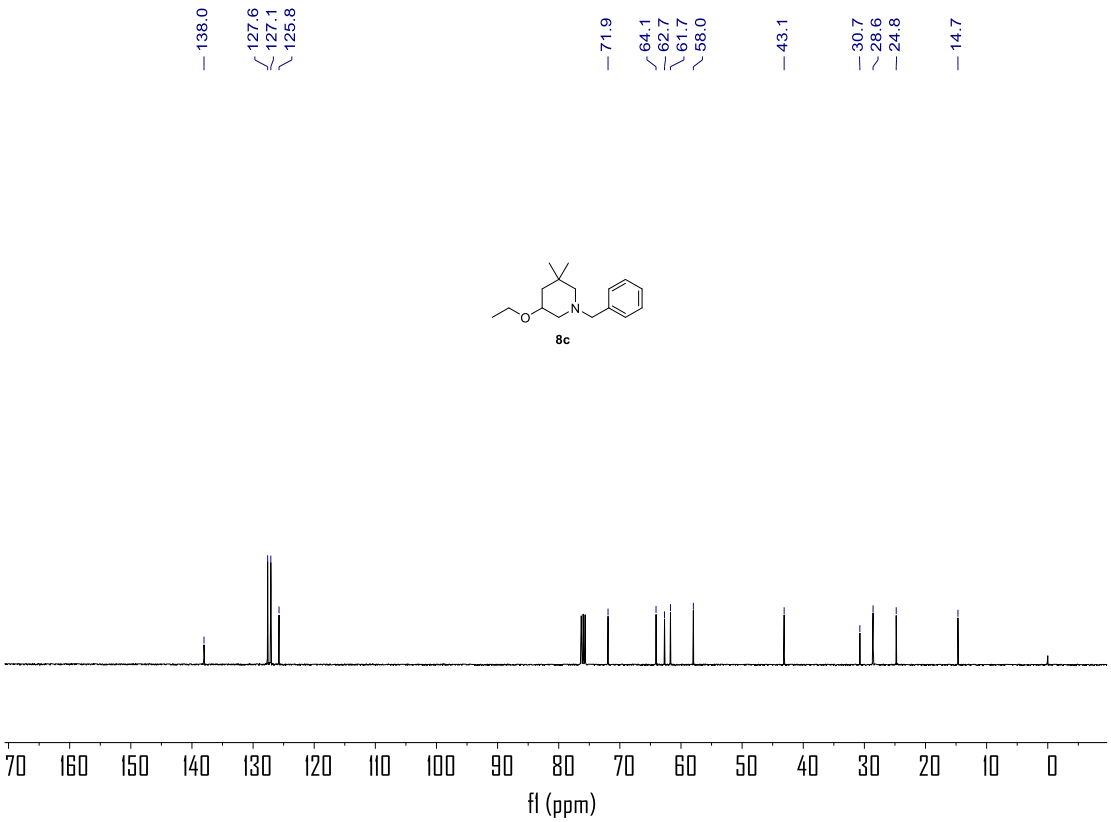
^{13}C NMR (101MHz, $CDCl_3$) of 8b



^{1}H NMR (400 MHz, $CDCl_3$) of 8c



^{13}C NMR (101MHz, $CDCl_3$) of 8c



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