

PNP Type Ligands Enabled Copper-catalyzed *N*-Formylation of Amines with CO₂ in Presence of Silanes

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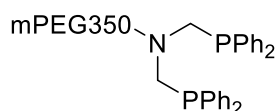
I. General information

General procedures. General Information Unless specifically stated, all reagents were commercially obtained and where appropriate, purified prior to use. For example, toluene, ether (Et₂O) was dried and distilled from metal sodium and benzophenone. Other commercially available reagents and solvents were used directly without purification. Reactions were monitored by GC. Flash column chromatography was performed over silica (200 – 300 mesh). ¹H, ¹³C, ³¹P NMR spectra were recorded on a Bruker 400 MHz or 500 MHz spectrometer in CDCl₃, *d*₆-DMSO or C₆D₆. Multiplicities were given as: s (singlet); d (doublet); dd (doublets of doublet); t (triplet); q (quartet); td (triplet of doublets); tt (triplet of triplets) ddd (doublet of doublet of doublets) or m (multiplets).

Reagents. The following chemicals were used as received: Formaldehyde (Aladdin), Diphenylphosphine (Meirui), Polyethylene glycol monomethylether, 350 (Alfa Aesar), Polyethylene glycol monomethylether, 750 (Alfa Aesar), Pyridine (J&K Scientific), Methylsulfonyl chloride (J&K Scientific), Ammonium hydroxide (Hannuo-Chemical), N-Butylamine (Alfa Aesar), 2-Aminopyridine (Yien-Chemical), 2,2'-Dipicolylamine (Aladdin), Aniline (Aladdin), Benzylamine (Aladdin), 4-Methoxyaniline (Yien-Chemical), Ethylenediamine (Meirui), 1,2-Diaminocyclohexane (J&K Scientific), N-Methylaniline (Macklin), N-Ethylaniline (Macklin), N-Ethylbenzylamine (Meirui), N-Methylcyclohexylamine (Energy-Chemical), Diethylamine (Aladdin), p-Toluidine (Aladdin), 4-Chloroaniline (Macklin), 4-Bromoaniline (Energy-Chemical), 4-Iodoaniline (Aladdin), 2,6-Dimethylaniline (Aladdin), 2,4,6-Trimethylaniline (Alfa Aesar), 2-Phenylethylamine (Aladdin), 2,6-Diethylaniline (Meirui), Octylamine (Aladdin), Dodecylamine (Alfa Aesar), Cupric acetate (Aladdin), Ferrous acetate (Energy-Chemical), Cobalt(II) acetate tetrahydrate (Aladdin), Nickel(II) acetate tetrahydrate (Macklin), Cupric acetylacetonate (Aladdin), Ferric acetylacetonate (Aladdin), Bis(acetylacetonato)cobalt (Macklin), Nickel(II) acetylacetonate (SCRC), Cupric bromide (SCRC), Cuprous bromide

(Meirui), Cuprous iodide (Macklin), Trimethoxysilane (Meirui), Phenylsilane (Energy-Chemical), Diphenylsilane (J&K Scientific), Triethoxysilane (Meirui), Triethylsilane (Macklin).

II. Synthesis of ligands



L1

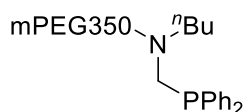
Synthesis of polyethylene glycol monomethyl ether-methanesulfonic ester: 17.5 g (0.0500 mol) mPEG350, 40.0 mL toluene resealed, 7.91 g (0.100 mol) pyridine were successively added into 250 mL three-necked flask the mixture was heated to 88 °C under argon, and then 11.45 g (0.100 mol) methyl sulfonyl chloride was added drop by drop. The reaction was kept at 88 °C for 30 h, cooled to room temperature, and then the mixture of 8.00 mL concentrated hydrochloric acid and 16.0 mL water was added. Solid precipitate appeared, and the precipitate disappeared after agitation. Placed without moving and the solution is stratified, the lower layer is pyridine salt. The lower layer was separated, extracted twice with toluene, and merged with the upper layer. Toluene was removed by vacuum distillation and 12.12 g product was obtained, with yield of 57.0%.

Synthesis of mPEG350-NH₂: polyethylene glycol monomethyl ether methyl sulfonate (7.00 mmol, 3.00 g) was added into ammonia (15.0 mmol, 0.530 g) drop by drop at 50 °C, and reacted for 5 h. The excess ammonia water was removed by vacuum at 50 °C, The product is 2.15 g, yield of 71.7%.

Synthesis of polyethylene glycol N,P ligand **mPEG350-C₂₆H₂₄NP₂ L1**: Argon gas was pumped into 30.0 mL of resealed toluene in a dried 100 mL two-necked flask for about 10 minutes. Under argon atmosphere, 2.15 g (5.00 mmol) MPEG350-NH₂ and 1.22 g (15.0 mmol, 50% excess) 37% formaldehyde solution were successively added into the toluene, heated up to 60 – 63 °C, and injected diphenylphosphine (10.0 mmol, 1.86g) in while stirring, and stirred for 6 h. After cooling to room temperature,

the upper layer was separated out by a separation funnel, anhydrous sodium sulfate was added and then filtrated. At last, toluene was removed by vacuum distillation. Vacuum drying at 60 °C, the compound was isolated as a light yellow oil (2.86 g, 3.835 mmol, 76.7% yield).

L1 : ^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.16 (20H, m), 3.66 (2H, t, J = 5.9 Hz), 3.56 (26H, q, J = 5.9, 5.1 Hz), 3.29 (3H, s); ^{13}C NMR (101 MHz, CDCl_3) δ 138.2, 133.2, 128.7, 71.9, 70.6, 70.6, 70.3, 62.6, 59.1; ^{31}P NMR (162 MHz, CDCl_3) δ – 12.6.



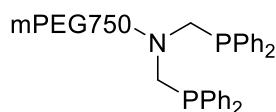
L2

Synthesis of mPEG350-NHC₄H₉: polyethylene glycol monomethyl ether methyl sulfonate (14.0 mmol, 6.00 g) was added into N-butyl amine (20.0 mmol, 1.46 g) drop by drop at 50 °C, and reacted for 5 h. Wash three times with anhydrous ether to remove excess N-butylamine. Anhydrous ether was removed by vacuum at 50 °C. The product is 4.26 g, yield of 75.0%.

Synthesis of polyethylene glycol N,P ligand **mPEG350-C₁₇H₂₁NP L2**: Argon gas was pumped into 30.0 mL of resteamed toluene in a dried 100 mL two-necked flask for about 10 minutes. Under argon atmosphere, 4.26g (10 mmol) MPEG350-NHC₄H₉ and 1.22 g (15.0 mmol, 50% excess) 37% formaldehyde solution were successively added into the toluene, heated up to 60 – 63 °C, and injected diphenylphosphine (10.0 mmol, 1.86g) in while stirring, and stirred for 6 h. After cooling to room temperature, the upper layer was separated out by a separation funnel, anhydrous sodium sulfate was added and then filtrated. At last, toluene was removed by vacuum distillation. Vacuum drying at 60 °C, the compound was isolated as a light yellow oil (5.30 g, 8.5 mmol, 85.0% yield).

L2 : ^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.30 (10H, m), 3.65 (2H, t, J = 5.9 Hz), 3.58 – 3.52 (26H, m), 3.28 (3H, s), 2.75 (2H, q, J = 8.2, 7.5 Hz), 2.33 (2H, s), 1.34 – 1.18 (2H, m), 1.08 (2H, dt, J = 15.0, 7.3 Hz), 0.74 (3H, dd, J = 16.8, 7.3 Hz); ^{13}C

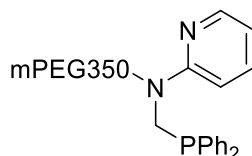
NMR (101 MHz, CDCl₃) δ 137.2, 132.0, 127.3, 70.9, 70.3, 69.6, 69.5, 69.5, 58.0, 57.8, 57.8, 55.1, 27.6, 19.3, 13.0; **³¹P NMR** (162 MHz, CDCl₃) δ – 28.6.



L3

Synthesis of polyethylene glycol N,P ligand **mPEG750-C₂₆H₂₄NP₂ L3**: Argon gas was pumped into 30 mL of resealed toluene in a dried 100 mL two-necked flask for about 10 minutes. Under argon atmosphere, 3.75 g (5.00 mmol) MPEG750-NH₂ and 1.22 g (15.0 mmol, 50% excess) 37% formaldehyde solution were successively added into the toluene, heated up to 60 – 63 °C, and injected diphenylphosphine (10.0 mmol, 1.86 g) in while stirring, and stirred for 6 h. After cooling to room temperature, the upper layer was separated out by a separation funnel, anhydrous sodium sulfate was added and then filtrated. At last, toluene was removed by vacuum distillation. Vacuum drying at 60 °C, the compound was isolated as a light yellow oil (4.61 g, 4.0 mmol, 80.0% yield).

L3 : **¹H NMR** (400 MHz, CDCl₃) δ 7.45 – 7.27 (20H, m), 3.68 (2H, t, J = 6.0 Hz), 3.64 – 3.48 (62H, m), 3.31 (3H, s), 2.15 – 1.98 (2H, s), 1.70 (2H, s); **¹³C NMR** (101 MHz, CDCl₃) δ 135.8, 133.0, 128.6, 128.5, 71.9, 71.3, 70.6, 70.5, 62.7, 59.0; **³¹P NMR** (162 MHz, CDCl₃) δ – 11.6.



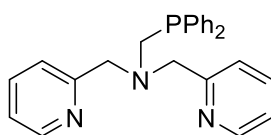
L4

Synthesis of mPEG350-NHC₅H₄: polyethylene glycol monomethyl ether methyl sulfonate (14.0 mmol, 6.00 g) was added into 2-aminopyridine (20.0 mmol, 1.88 g) drop by drop at 50 °C, and reacted for 5 h. Wash three times with anhydrous ether to remove excess 2-aminopyridine. Anhydrous ether was removed by vacuum at 50 °C. The product is 4.43 g, yield of 73.2%.

Synthesis of polyethylene glycol N,P ligand **mPEG350-C₁₈H₁₆N₂P L4**: Argon gas

was pumped into 30.0 mL of resteamed toluene in a dried 100 mL two-necked flask for about 10 minutes. Under argon atmosphere, 4.32g (10.0 mmol) MPEG350-NHC₅H₄ and 1.22 (15.0 mmol, 50% excess) 37% formaldehyde solution were successively added into the toluene, heated up to 60 – 63 °C, and injected diphenylphosphine (10.0 mmol, 1.86 g) in while stirring, and stirred for 6 h. After cooling to room temperature, the upper layer was separated out by a separation funnel, anhydrous sodium sulfate was added and then filtrated. At last, toluene was removed by vacuum distillation. Vacuum drying at 60 °C, the compound was isolated as a light yellow oil (5.20 g, 8.25 mmol, 82.5% yield).

L4 : ¹H NMR (400 MHz, CDCl₃) δ 7.82 (1H, d, *J* = 11.8 Hz), 7.77 (1H, d, *J* = 11.3 Hz), 7.51 – 7.27 (12H, m), 3.76 (2H, t, *J* = 5.9 Hz), 3.65 (26H, s), 3.38 (3H, s), 2.37 (2H, d, *J* = 10.2 Hz); ¹³C NMR (101 MHz, CDCl₃) δ 137.4, 137.1, 133.0, 132.8, 129.1, 128.7, 113.2, 107.6, 71.9, 71.4, 70.7, 70.6, 70.5, 59.1, 53.5; ³¹P NMR (162 MHz, CDCl₃) δ – 23.4.



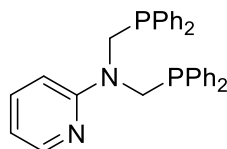
L5

Synthesis of 1-(diphenylphosphanyl)-*N,N*-bis(pyridin-2-ylmethyl)methanamine

L5: Argon gas was pumped into 30.0 mL of resteamed toluene in a dried 100 mL two-necked flask for about 10 minutes. Under argon atmosphere, 1.99 g (10.0 mmol) 2,2'-dimethylpyridine amine and 1.22 g (15.0 mmol, 50% excess) 37% formaldehyde solution were successively added into the toluene, heated up to 60 – 63 °C, and injected diphenylphosphine (10.0 mmol, 1.86 g) in while stirring, and stirred for 4 h. After cooling to room temperature, the upper layer was separated out by a separation funnel, anhydrous sodium sulfate was added and then filtrated, toluene was removed by vacuum distillation, attained the gooey substance. Vacuum drying at 60 °C, the compound was isolated as a white solid (3.23 g, 8.12 mmol, 81.2% yield).

1-(diphenylphosphanyl)-*N,N*-bis(pyridin-2-ylmethyl)methanamine L5 : ¹H NMR (400 MHz, CDCl₃) δ 8.41 (2H, d, *J* = 5.4 Hz), 7.43 (2H, td, *J* = 7.7, 1.8 Hz), 7.30 –

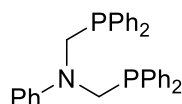
7.11 (14H, m), 3.94 (4H, s), 3.34 (2H, d, $J = 3.9$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 159.1, 148.8, 137.7, 136.4, 133.2, 133.0, 128.6, 128.4, 128.3, 123.2, 122.0, 61.3, 57.3; ^{31}P NMR (162 MHz, CDCl_3) δ -26.4.



L6

Synthesis of *N,N*-bis((diphenylphosphanyl)methyl)pyridin-2-amine **L6**: Argon gas was pumped into 30.0 mL of resealed toluene in a dried 100 mL two-necked flask for about 10 minutes. Under argon atmosphere, 0.940 g (10.0 mmol) 2-aminopyridine and 2.43 g (30.0 mmol, 50% excess) 37% formaldehyde solution were successively added into the toluene, heated up to 60–63 °C, and injected diphenylphosphine (20.0 mmol, 3.72 g) in while stirring, and stirred for 4 h. After cooling to room temperature, the upper layer was separated out by a separation funnel, anhydrous sodium sulfate was added and then filtrated, toluene was removed by vacuum distillation, attained the gooey substance. After cooling to room temperature, dichloromethane was added to dissolve all the viscous substances and then anhydrous ethanol was added, white substances appeared. Continue to standing for 2 – 5 h, white crystal appeared, filtered and washed with anhydrous ethanol, vacuum drying at 60 °C, the compound was isolated as a white solid (4.09 g, 8.34 mmol, 83.4% yield).

N,N-bis((diphenylphosphanyl)methyl)pyridin-2-amine **L6**: ^1H NMR (400 MHz, CDCl_3) δ 8.06 (1H, dd, $J = 4.8, 1.1$ Hz), 7.45 – 7.37 (1H, m), 7.33 – 7.21 (20H, m), 6.50 – 6.43 (2H, m), 4.13 (4H, d, $J = 3.3$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 147.7, 137.4, 136.9, 133.3, 128.8, 128.5, 112.2, 107.2, 50.8; ^{31}P NMR (162 MHz, CDCl_3) δ -23.5.

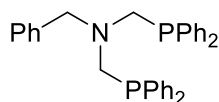


L7

Synthesis of *N,N*-bis((diphenylphosphanyl)methyl)aniline **L7**: Argon gas was

pumped into 30.0 mL of resealed toluene in a dried 100 mL two-necked flask for about 10 minutes. Under argon atmosphere, 0.930 g (10.0 mmol) phenylamine and 2.43 g (30.0 mmol, 50% excess) 37% formaldehyde solution were successively added into the toluene, heated up to 60 – 63 °C, and injected diphenylphosphine (20.0 mmol, 3.72 g) in while stirring, and stirred for 4 h. After cooling to room temperature, the upper layer was separated out by a separation funnel, anhydrous sodium sulfate was added and then filtrated, toluene was removed by vacuum distillation, attained the gooey substance. After cooling to room temperature, dichloromethane was added to dissolve all the viscous substances and then anhydrous ethanol was added, white substances appeared. Continue to standing for 2 – 5 h, white crystal appeared, filtered and washed with anhydrous ethanol, vacuum drying at 60 °C, the compound was isolated as a white solid (4.18 g, 8.54 mmol, 85.4% yield).

***N, N*-bis((diphenylphosphanyl)methyl)aniline L7:** ^1H NMR (400 MHz, CDCl_3) δ 7.55 – 7.41 (20H, m), 7.35 (2H, dd, $J = 8.7, 7.3$ Hz), 7.01 (2H, d, $J = 8.0$ Hz), 6.90 (1H, t, $J = 7.3$ Hz), 4.15 (4H, d, $J = 4.5$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 148.2, 137.6, 133.3, 129.1, 128.7, 117.8, 114.8, 54.2; ^{31}P NMR (162 MHz, CDCl_3) δ – 27.6.



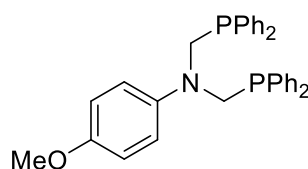
L8

Synthesis of *N*-benzyl-1-((diphenylphosphanyl)-*N*-((diphenylphosphanyl)methyl)-methanamine L8: Argon gas was pumped into 30.0 mL of resealed toluene in a dried 100 mL two-necked flask for about 10 minutes. Under argon atmosphere, 1.07 g (10.0 mmol) benzylamine and 2.43 g (30.0 mmol, 50% excess) 37% formaldehyde solution were successively added into the toluene, heated up to 60 – 63 °C, and injected diphenylphosphine (20.0 mmol, 3.72 g) in while stirring, and stirred for 4 h. After cooling to room temperature, the upper layer was separated out by a separation funnel, anhydrous sodium sulfate was added and then filtrated, toluene was removed by vacuum distillation, attained the gooey substance. After cooling to room temperature, dichloromethane was added to dissolve all the viscous substances and

then anhydrous ethanol was added, white substances appeared. Continue to standing for 2 – 5 h, white crystal appeared, filtered and washed with anhydrous ethanol, vacuum drying at 60 °C, the compound was isolated as a white solid (4.19 g, 8.32 mmol, 83.2% yield).

***N*-benzyl-1-(diphenylphosphanyl)-*N*-((diphenylphosphanyl)methyl)methanamine**

L8: ^1H NMR (400 MHz, CDCl_3) δ 7.54 (8H, td, $J = 7.4, 1.7$ Hz), 7.45 – 7.36 (15H, m), 7.30 (2H, dd, $J = 6.4, 2.7$ Hz), 4.22 (2H, d, $J = 8.6$ Hz), 3.79 (4H, d, $J = 3.0$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 138.6, 138.1, 133.3, 129.6, 128.6, 128.3, 127.2, 60.9, 58.5; ^{31}P NMR (162 MHz, CDCl_3) δ – 28.6.

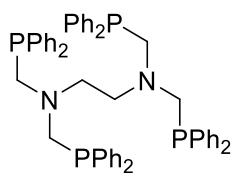


L9

Synthesis of *N,N*-bis((diphenylphosphanyl)methyl)-4-methoxyaniline L9: Argon gas was pumped into 30.0 mL of resteamed toluene in a dried 100 mL two-necked flask for about 10 minutes. Under argon atmosphere, 1.23 g (10.0 mmol) *p*-methoxyaniline and 2.43 g (30.0 mmol, 50% excess) 37% formaldehyde solution were successively added into the toluene, heated up to 60 – 63 °C, and injected diphenylphosphine (20.0 mmol, 3.72 g) in while stirring, and stirred for 4 h. After cooling to room temperature, the upper layer was separated out by a separation funnel, anhydrous sodium sulfate was added and then filtrated, toluene was removed by vacuum distillation, attained the gooey substance. After cooling to room temperature, dichloromethane was added to dissolve all the viscous substances and then anhydrous ethanol was added, white substances appeared. Continue to standing for 2 – 5 h, white crystal appeared, filtered and washed with anhydrous ethanol, vacuum drying at 60 °C, the compound was isolated as a white solid (4.53 g, 8.72 mmol, 87.2% yield).

***N,N*-bis((diphenylphosphanyl)methyl)-4-methoxyaniline L9:** ^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.37 (8H, m), 7.33 (12H, dd, $J = 9.6, 5.0$ Hz), 6.88 (2H, dd, $J = 9.6, 2.7$ Hz), 6.84 – 6.79 (2H, m), 4.08 (4H, t, $J = 6.9$ Hz), 3.78 (3H, d, $J = 6.4$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 153.2, 143.4, 137.9, 137.7, 133.4, 128.8, 118.7, 114.5,

55.7; ^{31}P NMR (162 MHz, CDCl_3) δ – 27.4.

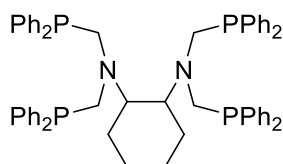


L10

Synthesis of N^1,N^1,N^2,N^2 -tetrakis((diphenylphosphanyl)methyl)ethane-

1,2-diamine L10: Argon gas was pumped into 30.0 mL of resteamed toluene in a dried 100 mL two-necked flask for about 10 minutes. Under argon atmosphere, 0.60 g (10.0 mmol) ethylenediamine and 4.87 g (60.0 mmol, 50% excess) 37% formaldehyde solution were successively added into the toluene, heated up to 60 – 63 °C, and injected diphenylphosphine (40.0 mmol, 7.45 g) in while stirring, and stirred for 4 h. After cooling to room temperature, the upper layer was separated out by a separation funnel, anhydrous sodium sulfate was added and then filtrated, toluene was removed by vacuum distillation, attained the gooey substance. After cooling to room temperature, dichloromethane was added to dissolve all the viscous substances and then anhydrous ethanol was added, white substances appeared. Continue to standing for 2 – 5 h, white crystal appeared, filtered and washed with anhydrous ethanol, vacuum drying at 60 °C, the compound was isolated as a white solid (7.72 g, 9.05 mmol, 90.5% yield).

N^1,N^1,N^2,N^2 -tetrakis((diphenylphosphanyl)methyl)ethane-1,2-diamine L10: ^1H NMR (400 MHz, CDCl_3) δ 7.31 – 7.23 (16H, m), 7.19 – 7.10 (24H, m), 3.42 (8H, d, J = 3.1 Hz), 2.80 (4H, s); ^{13}C NMR (101 MHz, CDCl_3) δ 138.2, 133.3, 133.1, 128.4, 58.9, 53.2; ^{31}P NMR (162 MHz, CDCl_3) δ – 28.4.



L11

Synthesis of N^1,N^1,N^2,N^2 -tetrakis((diphenylphosphanyl)methyl)cyclohexane-1,2-diamine L11: Argon gas was pumped into 30.0 mL of resteamed toluene in a dried

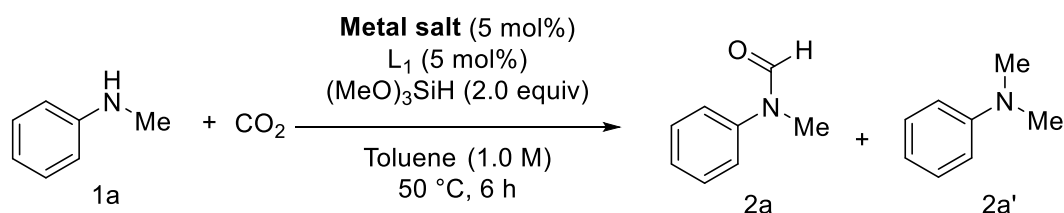
100 mL two-necked flask for about 10 minutes. Under argon atmosphere, 1.14 g (10.0 mmol) 1,2-cyclohexanediamine and 4.87 g (60.0 mmol, 50% excess) 37% formaldehyde solution were successively added into the toluene, heated up to 60 – 63 °C, and injected diphenylphosphine (40.0 mmol, 7.45 g) in while stirring, and stirred for 4 h. After cooling to room temperature, the upper layer was separated out by a separation funnel, anhydrous sodium sulfate was added and then filtrated, toluene was removed by vacuum distillation, attained the gooey substance. After cooling to room temperature, dichloromethane was added to dissolve all the viscous substances and then anhydrous ethanol was added, white substances appeared. Continue to standing for 2 – 5 h, white crystal appeared, filtered and washed with anhydrous ethanol, vacuum drying at 60 °C, the compound was isolated as a white solid (8.27 g, 9.12 mmol, 91.2% yield).

***N*¹,*N*¹,*N*²,*N*²-tetrakis((diphenylphosphanyl)methyl)cyclohexane-1,2-diamine L11:**

¹H NMR (400 MHz, CDCl₃) δ 7.53 – 7.43 (16H, m), 7.33 (24H, s), 3.92 – 3.74 (8H, m), 3.18 (2H, d, *J* = 9.2 Hz), 1.78 (2H, d, *J* = 12.3 Hz), 1.52 (2H, d, *J* = 7.4 Hz); ¹³C NMR (101 MHz, CDCl₃) δ 138.9, 133.9, 133.2, 128.7, 128.4, 61.8, 55.3, 28.0, 25.5; ³¹P NMR (162 MHz, CDCl₃) δ – 24.8.

III. Optimization of the reaction conditions

Table S1. Evaluation of different metal salts

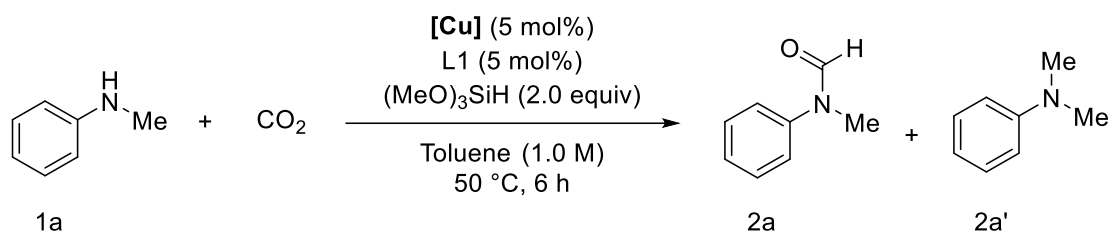


Entry	Catalyst	Yield (%)	Select.(%)	
			2a	2a'
1	Cu(OAc) ₂ /L1	98.6	95.4	4.6
2	Fe(OAc) ₂ /L1	-	-	-
3	Co(OAc) ₂ /L1	-	-	-
4	Ni(OAc) ₂ /L1	-	-	-
5	Cu(acac) ₂ /L1	81.8	97.7	2.3

6	Fe(acac) ₃ /L1	1.4	71.4	28.6
7	Co(acac) ₂ /L1	0.6	50.0	50.0
8	Ni(acac) ₂ /L1	2.1	9.5	90.5

Reaction conditions: **1a** (2.00 mmol), (MeO)₃SiH (4.00 mmol), **metal salt** (0.100 mmol), L1 (0.100 mmol), toluene (2.00 mL) at 50 °C for 6 h. Yield was determined by GC.

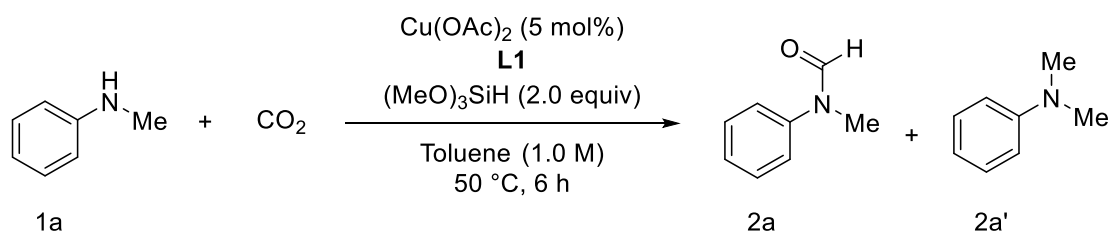
Table S2. Evaluation of different copper salts



Entry	Catalyst	Yield (%)	Select.(%)	
			2a	2a'
1	Cu(OAc) ₂	0.3	66.7	33.3
2	L1	0.4	75.0	25.0
3	Cu(OAc) ₂ /L1	98.6	95.4	4.6
4	Cu(acac) ₂ /L1	81.8	97.7	2.3
5	Cu(acac) ₂ /L1	81.8	97.7	2.3
6	CuBr ₂ /L1	1.4	35.7	64.3
7	CuI/L1	0.3	33.3	66.7
8	CuBr/L1	0.2	50.0	50.0

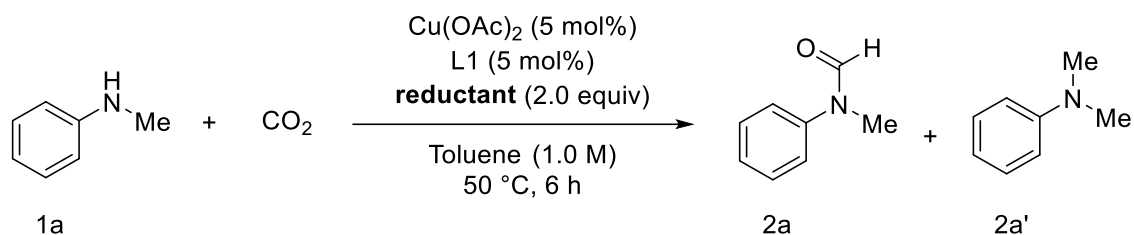
Reaction conditions: **1a** (2.00 mmol), (MeO)₃SiH (4.00 mmol), **[Cu]** (0.100 mmol), **L1** (0.100 mmol), toluene (2.00 mL) at 50 °C for 6 h. Yield was determined by GC.

Table S3. Evaluation of different proportions of L1 and Cu(OAc)₂



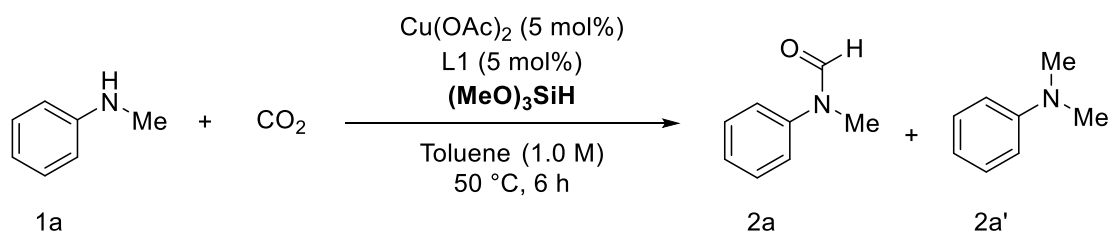
Entry	Cu(OAc) ₂ :L1	Yield (%)	Select.(%)	
			2a	2a'
1	1:1	98.6	95.4	4.6
2	1:2	93.7	97.0	3.0
3	1:3	86.3	95.7	4.3

Reaction conditions: **1a** (2.00 mmol), (MeO)₃SiH (4.00 mmol), Cu(OAc)₂ (0.100 mmol), **L1** (0.100 mmol), toluene (2.00 mL) at 50 °C for 6 h. Yield was determined by GC.

Table S4. Evaluation of different reductant

Entry	reductant	Yield (%)	Select.(%)	
			2a	2a'
1	$(\text{MeO})_3\text{SiH}$	98.6	95.4	4.6
2	PhSiH_3	98.5	90.7	9.3
3	Ph_2SiH_2	74.2	98.7	1.3
4	$(\text{EtO})_3\text{SiH}$	69.2	98.6	1.4
5	Et_3SiH	-	-	-
6	MeOH	-	-	-
7	H-bpin	-	-	-
8	PMHS	-	-	-
9	H_2	-	-	-

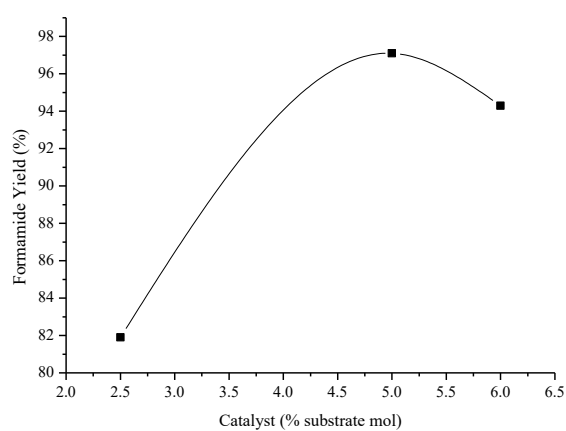
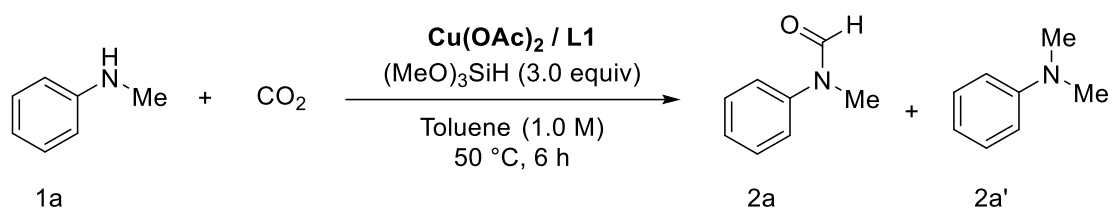
Reaction conditions: **1a** (2.00 mmol), **Hydrosilane** (4.00 mmol), $\text{Cu}(\text{OAc})_2$ (0.100 mmol), L1 (0.100 mmol), toluene (2.00 mL) at 50 °C for 6 h. Yield was determined by GC.

Table S5. Evaluation of different amounts of reducing agents

Entry	$(\text{MeO})_3\text{SiH}$ (equiv.)	Yield (%)	Select.(%)	
			2a	2a'
1	2.0	98.6	95.4	4.6
2	3.0	99.7	97.4	2.6
3	4.0	99.2	95.6	4.4

Reaction conditions: **1a** (2.00 mmol), $\text{Cu}(\text{OAc})_2$ (0.100 mmol), L1 (0.100 mmol), $(\text{MeO})_3\text{SiH}$ (equiv.) toluene (2.00 mL) at 50 °C for 6 h. Yield was determined by GC.

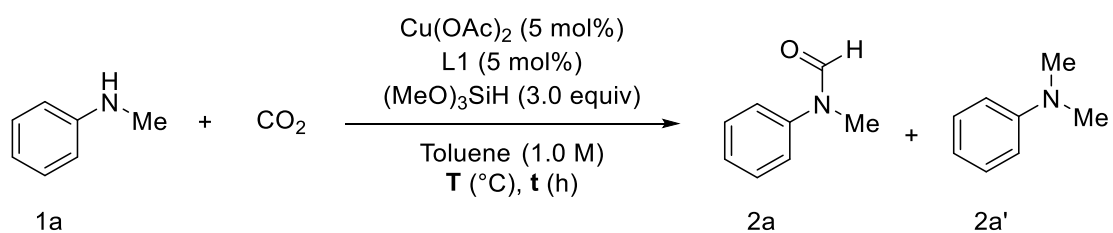
Table S6. Evaluation of different amounts of catalyst

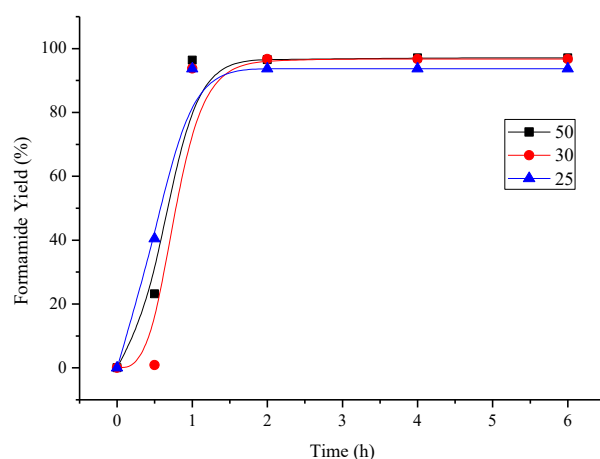


Reaction conditions: **1a** (2.00 mmol), $(\text{MeO})_3\text{SiH}$ (6.00 mmol), toluene (2.00 mL) at 50 °C for 6 h.

Yield was determined by GC.

Table S7. Evaluation of different reaction temperature and time

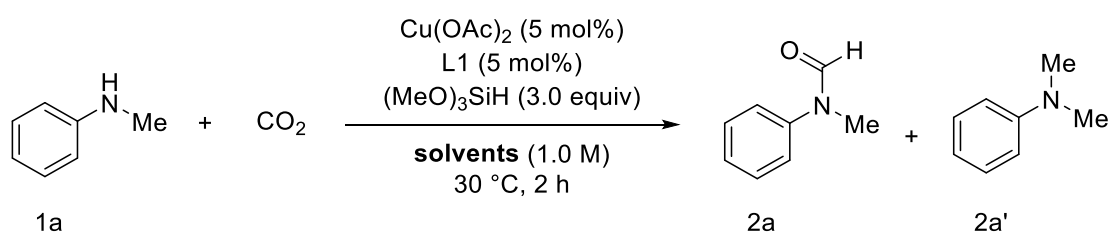




Reaction conditions: **1a** (2.00 mmol), (MeO)₃SiH (6.00 mmol), toluene (2.00 mL) at **T** °C for **t** h.

Yield was determined by GC.

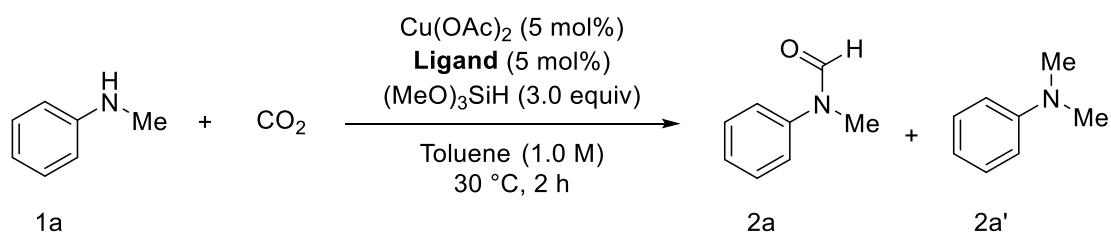
Table S8. Evaluation of different solvents



Entry	Solvent	Yield (%)	Select.(%)	
			2a	2a'
1	Toluene	99.7	97.4	2.6
2	THF	89.3	96.2	3.8
3	CH ₂ Cl ₂	79.2	93.2	6.8
4	CH ₃ CN	58.2	92.4	7.6
5	DMF	37.1	90.6	9.4
6	DMSO	20.2	84.7	15.3

Reaction conditions: **1a** (2.00 mmol), (MeO)₃SiH (6.00 mmol), Cu(OAc)₂ (0.100 mmol), L1 (0.100 mmol), **solvent** (2.00 mL) at 30 °C for 2 h. Yield was determined by GC.

Table S9. Evaluation of different ligands

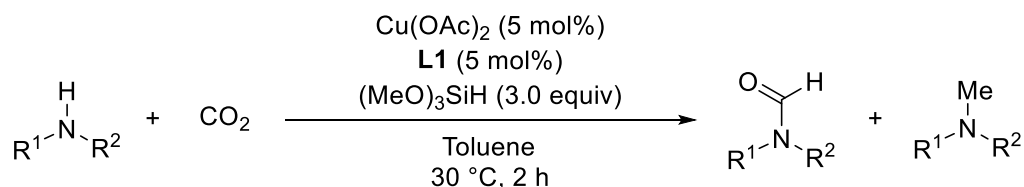


Entry	Ligand	Yield (%)	Select.(%)	
			2a	2a'
1	L1	99.7	97.4	2.6
2	L2	92.6	98.6	1.4
3	L3	99.8	97.0	3.0
4	L4	74.3	97.7	2.3
5	L5	12.4	97.6	2.4
6	L6	95.4	99.8	0.2
7	L7	99.6	97.4	2.6
8	L8	99.5	98.1	1.9
9	L9	99.5	97.4	2.6
10	L10	95.2	97.5	2.5
11	L11	95.9	94.3	5.7

Reaction conditions: **1a** (2.00 mmol), (MeO)₃SiH (6.00 mmol), Cu(OAc)₂ (0.100 mmol), **Ligand** (0.100 mmol), toluene (2.00 mL) at 30 °C for 2 h. Yield was determined by GC.

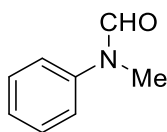
IV. Substrate scope

General Method C :

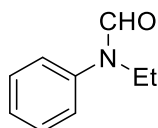


An 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with Cu(OAc)₂ (20.0 mg, 0.100 mmol, 0.0500 equiv), ligand L1 (74.5 mg, 0.100 mmol, 0.0500 equiv), amine (2.00 mmol, 1.00 equiv). The mixture was evacuated and backfilled with argon for three times. Then dry toluene (2.00 mL) was added under Ar. The schlenk tube was then connected to CO₂ gas and injected with (MeO)₃SiH (733.2 mg, 6.00 mmol, 3.00 equiv). And the mixture was allowed to stir for 2 h at 30 °C. After the addition was complete, the mixture was diluted with saturated NaCl aqueous solution (15.0 mL) and ethyl acetate (15.0 mL). And the organic layers were separated. The aqueous layer was extracted with ethyl acetate (10.0 mL x 3). The combined organic layers were washed with saturated NaCl aqueous solution (15.0 mL x 3), dried over Na₂SO₄ and filtered. The solvent was

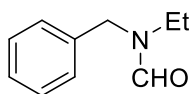
removed by rotary evaporation and the residue was purified by flash silica gel chromatography.



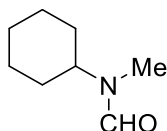
N-methyl-N-phenylformamide 2a: Prepared according to **General Method C** (Eluent: 100:1 to 10:1 petroleum ether: ethyl acetate) and the title compound was isolated as a light yellow liquid (210.9 mg, 1.560 mmol, 78.0%). **¹H NMR** (400 MHz, CDCl₃) δ 8.50 (1H, s), 7.44 (2H, t, J = 7.9 Hz), 7.34 – 7.26 (1H, m), 7.22 – 7.17 (2H, m), 3.34 (3H, s); **¹³C NMR** (101 MHz, CDCl₃) δ 162.4, 142.2, 129.6, 126.4, 122.4, 32.1.



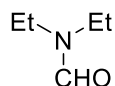
N-ethyl-N-phenylformamide 2b: Prepared according to **General Method C** (Eluent: 50:1 to 3:1 petroleum ether: ethyl acetate) and the title compound was isolated as a light yellow liquid (220.8 mg, 1.480 mmol, 74.0%). **¹H NMR** (400 MHz, CDCl₃) δ 8.32 (1H, s), 7.38 (2H, t, J = 7.8 Hz), 7.27 (1H, t, J = 7.4 Hz), 7.14 (2H, d, J = 7.4 Hz), 3.84 (2H, q, J = 7.2 Hz), 1.13 (3H, t, J = 7.2 Hz); **¹³C NMR** (101 MHz, CDCl₃) δ 162.0, 140.8, 129.6, 126.8, 124.2, 40.0, 13.0.



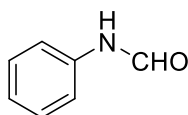
N-benzyl-N-ethylformamide 2c: Prepared according to **General Method C** (Eluent: 10:1 to 1:3 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (238.3 mg, 1.460 mmol, 73.0%). **¹H NMR** (400 MHz, CDCl₃) δ 8.18 (1H, d, J = 10.1 Hz), 7.34 – 7.11 (5H, m), 4.48 (1H, s), 4.32 (1H, s), 3.18 (2H, dq, J = 34.4, 7.2 Hz), 1.04 (3H, dt, J = 34.7, 7.2 Hz); **¹³C NMR** (101 MHz, CDCl₃) δ 136.6, 136.3, 128.8, 128.6, 128.1, 128.0, 127.5, 127.5, 50.8, 44.8, 41.5, 36.8, 14.4, 12.2.



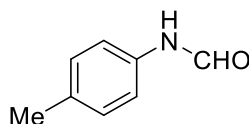
***N*-cyclohexyl-*N*-methylformamide (2d):** Prepared according to **General Method C** (Eluent: 5:1 to 1:5 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (223.1 mg, 1.580 mmol, 79.0%). **¹H NMR** (400 MHz, CDCl₃) δ 8.08 (0.7H, s), 7.95 (0.3H, s), 4.17 – 4.09 (0.3H, m) 3.26 – 3.16 (0.7H, m), 2.77, 2.73 (3H, s), 1.81 – 0.99 (10H, m); **¹³C NMR** (101 MHz, CDCl₃) δ 162.9, 162.5, 58.2, 50.8, 31.3, 30.2, 29.4, 25.9, 25.5, 25.4, 25.1.



***N,N*-diethylformamide 2e:** Prepared according to **General Method C** (Eluent: 5:1 to 1:1 petroleum ether: ethyl acetate) and the title compound was isolated as a light yellow oil (169.9 mg, 1.680 mmol, 84.0%). **¹H NMR** (400 MHz, CDCl₃) δ 7.98 (1H, s), 3.26 (4H, dq, J = 34.2, 7.2 Hz), 1.10 (6H, dt, J = 24.4, 7.2 Hz); **¹³C NMR** (101 MHz, CDCl₃) δ 161.3, 40.9, 35.6, 13.8, 11.7.

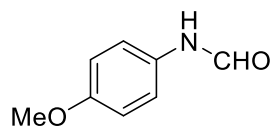


***N*-phenylformamide 2f:** Prepared according to **General Method C** (Eluent: 10:1 to 2:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (179.3 mg, 1.480 mmol, 74.0%). **¹H NMR** (400 MHz, CDCl₃) δ 9.30 (0.48H, s), 8.73 (1H, d, J = 11.3 Hz), 8.35 (0.52H, s), 7.63 – 7.56 (1H, m), 7.41 – 7.27 (2H, m), 7.25 – 7.09 (2H, m); **¹³C NMR** (101 MHz, CDCl₃) δ 163.3, 159.9, 137.1, 136.9, 129.8, 129.1, 125.3, 124.8, 120.2, 118.8.

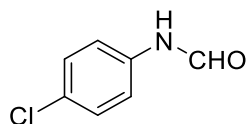


***N*-p-tolylformamide 2g:** Prepared according to **General Method C** (Eluent: 20:1 to 3:1 petroleum ether: ethyl acetate) and the title compound was isolated as a light yellow liquid (146.0 mg, 1.080 mmol, 54.0%). **¹H NMR** (400 MHz, CDCl₃) δ 8.85 (0.48H, d, J = 9.9 Hz), 8.55 (0.51H, d, J = 11.4 Hz), 8.21 (0.50H, d, J = 2.0 Hz), 8.07 (0.43H, s), 7.34 (1H, d, J = 8.4 Hz), 7.03 (2H, dd, J = 14.2, 8.2 Hz), 6.90 (1H, d, J = 8.4 Hz), 2.22 (3H, d, J = 9.7 Hz); **¹³C NMR** (101 MHz, CDCl₃) δ 163.3, 159.6, 135.1,

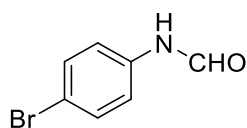
134.5, 134.4, 134.3, 130.2, 129.5, 120.2, 119.1, 20.9, 20.8.



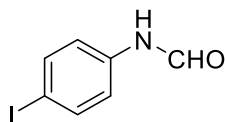
N-(4-methoxyphenyl)formamide 2h: Prepared according to **General Method C** (Eluent: 10:1 to 1:1 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (151.2 mg, 1.000 mmol, 50.0%). **¹H NMR** (400 MHz, CDCl₃) δ 8.45 (0.45H, d, J = 11.6), 8.27 – 8.12 (1H, m), 7.47 (0.44H, s), 7.38 (1H, d, J = 9.0 Hz), 6.97 (1H, d, J = 8.9 Hz), 6.80 (2H, dd, J = 12.5, 8.9 Hz), 3.72 (3H, d, J = 6.1 Hz); **¹³C NMR** (101 MHz, CDCl₃) δ 163.2, 159.1, 157.6, 156.7, 130.0, 129.6, 121.8, 121.6, 114.9, 114.2, 55.6, 55.5.



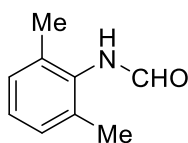
N-(4-chlorophenyl)formamide 2i: Prepared according to **General Method C** (Eluent: 10:1 to 3:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (205.4 mg, 1.320 mmol, 66.0%). **¹H NMR** (400 MHz, CDCl₃) δ 8.77 (0.43H, d, J = 11.6 Hz), 8.58 (0.5H, d, J = 11.3 Hz), 8.28 (0.66H, d, J = 1.8 Hz), 7.81 (0.61H, s), 7.43 (1H, d, J = 8.8 Hz), 7.23 (2H, dd, J = 17.2, 8.8 Hz), 6.97 (1H, d, J = 8.7 Hz); **¹³C NMR** (101 MHz, CDCl₃) δ 162.8, 159.3, 135.5, 135.4, 130.7, 129.9, 129.1, 121.3, 120.0.



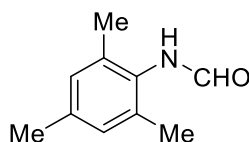
N-(4-bromophenyl)formamide 2j: Prepared according to **General Method C** (Eluent: 20:1 to 3:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (284.1 mg, 1.420 mmol, 71.0%). **¹H NMR** (400 MHz, CDCl₃) δ 8.73 – 8.54 (1H, m), 8.32 – 7.60 (1H, m), 7.43 – 7.33 (3H, m), 6.92 (1H, d, J = 8.8 Hz); **¹³C NMR** (101 MHz, CDCl₃) δ 162.6, 159.2, 135.9, 135.9, 132.8, 132.1, 121.6, 120.3, 118.3, 117.5.



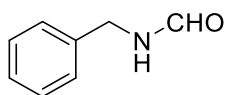
***N*-(4-iodophenyl)formamide 2k:** Prepared according to **General Method C** (Eluent: 20:1 to 3:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (281.6 mg, 1.140 mmol, 57.0%). **¹H NMR** (400 MHz, CDCl₃) δ 8.62 (1H, d, J = 10.6 Hz), 8.32 (1H, s), 7.58 (2H, dd, J = 12.0, 8.7 Hz), 7.26 (1H, d, J = 8.7 Hz), 6.80 (1H, d, J = 8.7 Hz); **¹³C NMR** (101 MHz, CDCl₃) δ 162.4, 159.1, 138.7, 138.1, 136.6, 136.5, 121.8, 120.5, 88.7, 88.2.



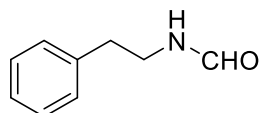
***N*-(2,6-dimethylphenyl)formamide 2l:** Prepared according to **General Method C** (Eluent: 20:1 to 1:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (217.8 mg, 1.460 mmol, 73.0%). **¹H NMR** (400 MHz, DMSO-*d*₆) δ 9.47 (0.79H, s), 9.30 (0.17H, d, J = 11.6 Hz), 8.25 (0.80H, s), 8.00 (0.15H, d, J = 11.6 Hz), 7.09 (3H, d, J = 15.8 Hz), 2.18 (6H, d, J = 25.6 Hz); **¹³C NMR** (101 MHz, DMSO-*d*₆) δ 164.7, 159.3, 134.7, 134.5, 134.0, 128.3, 127.7, 126.5, 18.3.



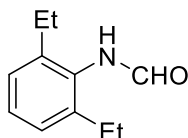
***N*-mesitylformamide 2m:** Prepared according to **General Method C** (Eluent: 20:1 to 1:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (274.2 mg, 1.680 mmol, 84.0%). **¹H NMR** (400 MHz, DMSO-*d*₆) δ 9.36 (0.75H, s), 9.19 (0.17H, d, J = 11.6 Hz), 8.23 (0.76H, s), 7.93 (0.16H, d, J = 11.5 Hz), 6.92 (0.34H, s), 6.87 (1.52H, s), 2.21 (3H, s), 2.17 (1H, s), 2.10 (5H, s); **¹³C NMR** (101 MHz, DMSO-*d*₆) δ 164.7, 159.4, 135.5, 134.7, 134.4, 131.3, 128.8, 128.3, 20.4, 18.3, 18.2.



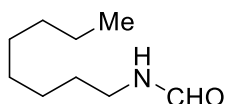
N-benzylformamide 2n: Prepared according to **General Method C** (Eluent: 10:1 to 1:3 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (205.5 mg, 1.520 mmol, 76.0%). **¹H NMR** (400 MHz, CDCl₃) δ 8.06 (0.83H, s), 7.97 (0.12H, d, J = 11.6), 7.20 (5H, dt, J = 23.6, 7.7 Hz), 6.56 (1H, s), 4.31 (1.7H, d, J = 6.1 Hz), 4.25 (0.28H, d, J = 6.4 Hz); **¹³C NMR** (101 MHz, CDCl₃) δ 164.9, 161.4, 137.7, 128.9, 128.7, 127.7, 127.6, 127.0, 45.7, 42.1.



N-phenethylformamide 2o: Prepared according to **General Method C** (Eluent: 20:1 to 1:5 petroleum ether: ethyl acetate) and the title compound was isolated as a light yellow liquid (191.0 mg, 1.280 mmol, 64.0%). **¹H NMR** (400 MHz, CDCl₃) δ 8.05 (0.90H, s), 7.80 (0.17H, d, J = 12.5 Hz), 7.31 (2H, t, J = 7.2 Hz), 7.21 (3H, m), 6.34 (1H, s), 3.48 (2H, dq, J = 39.3, 6.6 Hz), 2.83 (2H, t, J = 7.1 Hz); **¹³C NMR** (101 MHz, CDCl₃) δ 164.7, 161.5, 138.6, 128.9, 128.8, 128.8, 128.7, 126.9, 126.6, 43.3, 39.3, 37.7, 35.5.

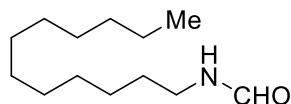


N-(2,6-diethylphenyl)formamide 2p: Prepared according to **General Method C** (Eluent: 20:1 to 1:1 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (251.7 mg, 1.420 mmol, 71.0%). **¹H NMR** (400 MHz, CDCl₃) δ 8.29 (0.42H, s), 7.99 (0.54H, d, J = 11.8 Hz), 7.56 (1H, s), 7.20 – 7.03 (3H, m), 2.59 (2H, q, J = 7.5 Hz), 2.52 (2H, q, J = 7.6 Hz), 1.12 (6H, q, J = 7.7 Hz); **¹³C NMR** (101 MHz, CDCl₃) δ 165.4, 160.3, 142.0, 141.4, 131.8, 131.2, 128.5, 128.4, 126.9, 126.4, 25.0, 24.9, 14.8, 14.5.



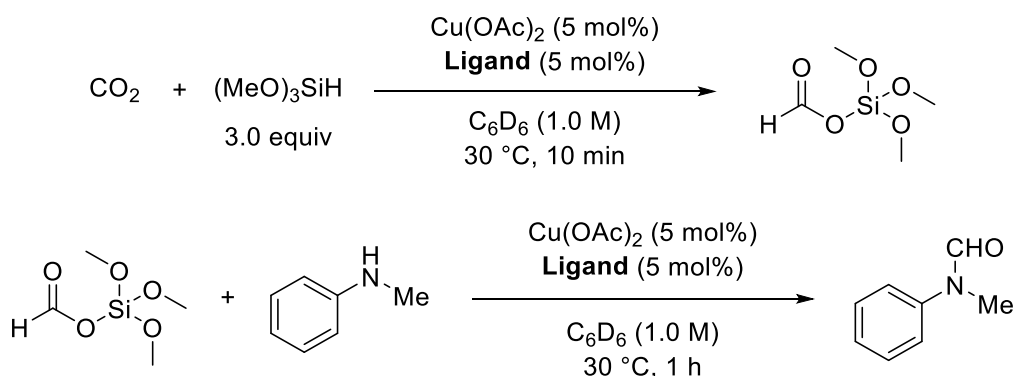
N-octylformamide 2q: Prepared according to **General Method C** (Eluent: 5:1 to 1:5 petroleum ether: ethyl acetate) and the title compound was isolated as a colorless liquid (257.9 mg, 1.640 mmol, 82.0%). **¹H NMR** (400 MHz, CDCl₃) δ 7.99 (0.82H, s),

7.89 (0.13H, d, $J = 12.3$), 6.94 (1H, s), 3.12 (2H, q, $J = 6.6$ Hz), 1.39 (2H, t, $J = 7.0$ Hz), 1.27 – 1.05 (10H, m), 0.75 (3H, t, $J = 6.4$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 161.6, 38.1, 31.7, 29.3, 29.1, 29.1, 26.8, 22.5, 14.0.

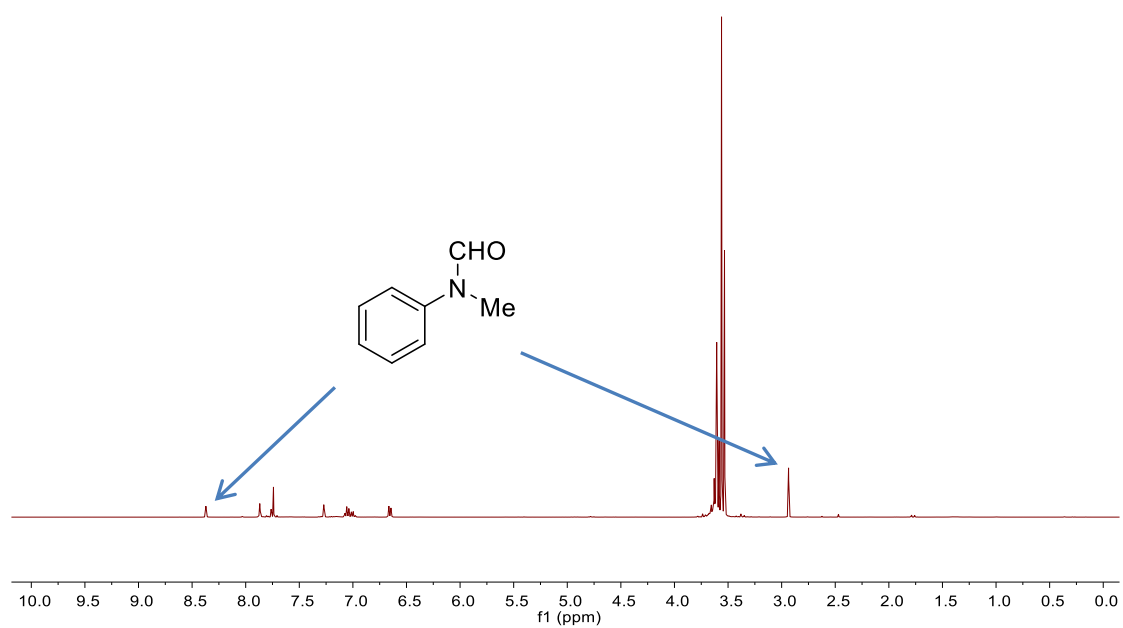
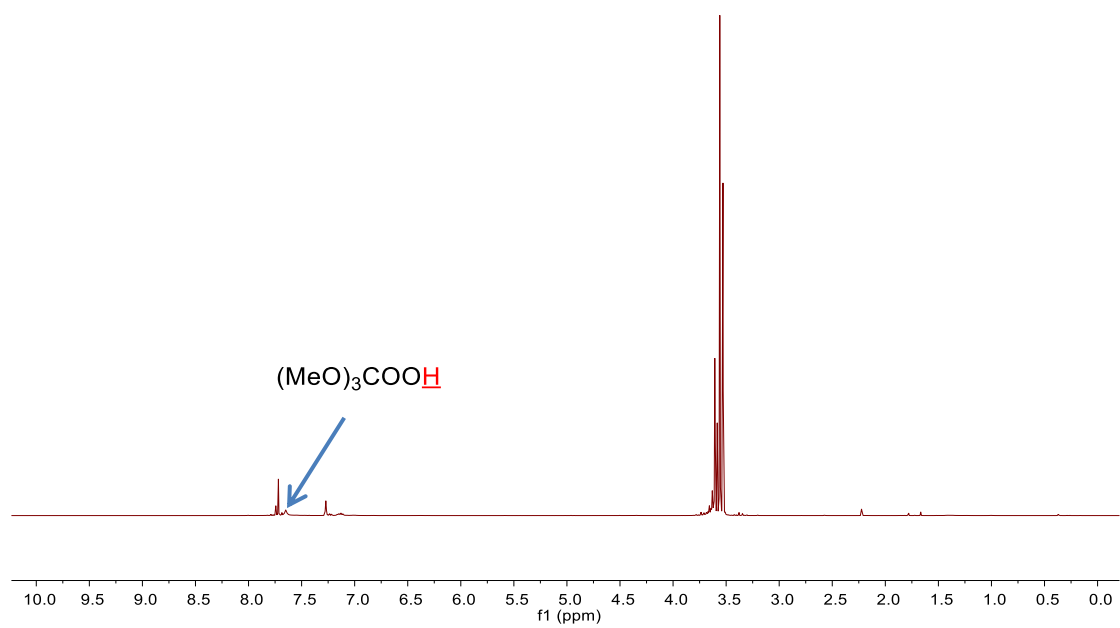


***N*-dodecylformamide 2r:** Prepared according to **General Method C** (Eluent: 1:1 to 1:2 petroleum ether: ethyl acetate) and the title compound was isolated as a white solid (341.4 mg, 1.600 mmol, 80.0%). ^1H NMR (400 MHz, CDCl_3) δ 8.04 (1H, s), 6.66 (1H, s), 3.23 – 3.06 (2H, m), 1.43 (2H, t, $J = 7.1$ Hz), 1.19 (18H, d, $J = 14.6$ Hz), 0.79 (3H, t, $J = 6.6$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 161.5, 38.2, 31.9, 29.6, 29.6, 29.6, 29.5, 29.5, 29.4, 29.3, 29.2, 26.9, 22.6, 14.1.

V. Mechanistic studies

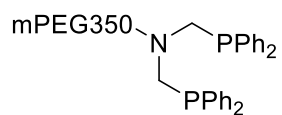


An 120 °C oven-dried 25-mL glass schlenck, equipped with a stirring bar, was charged with $\text{Cu}(\text{OAc})_2$ (20.0 mg, 0.100 mmol, 0.0500 equiv), ligand L1 (74.5 mg, 0.100 mmol, 0.0500 equiv). The mixture was evacuated and backfilled with argon for three times. Then C_6D_6 (2.00 mL) was added under Ar. The schlenk tube was then connected to CO_2 gas and injected with $(\text{MeO})_3\text{SiH}$ (733.2 mg, 6.00 mmol, 3.00 equiv). And the mixture was allowed to stir for 10 min at 30 °C. The mixture was analyzed by ^1H NMR. Then add *N*-methylaniline and stir for 1h at 30 °C. The mixture was analyzed by ^1H NMR.

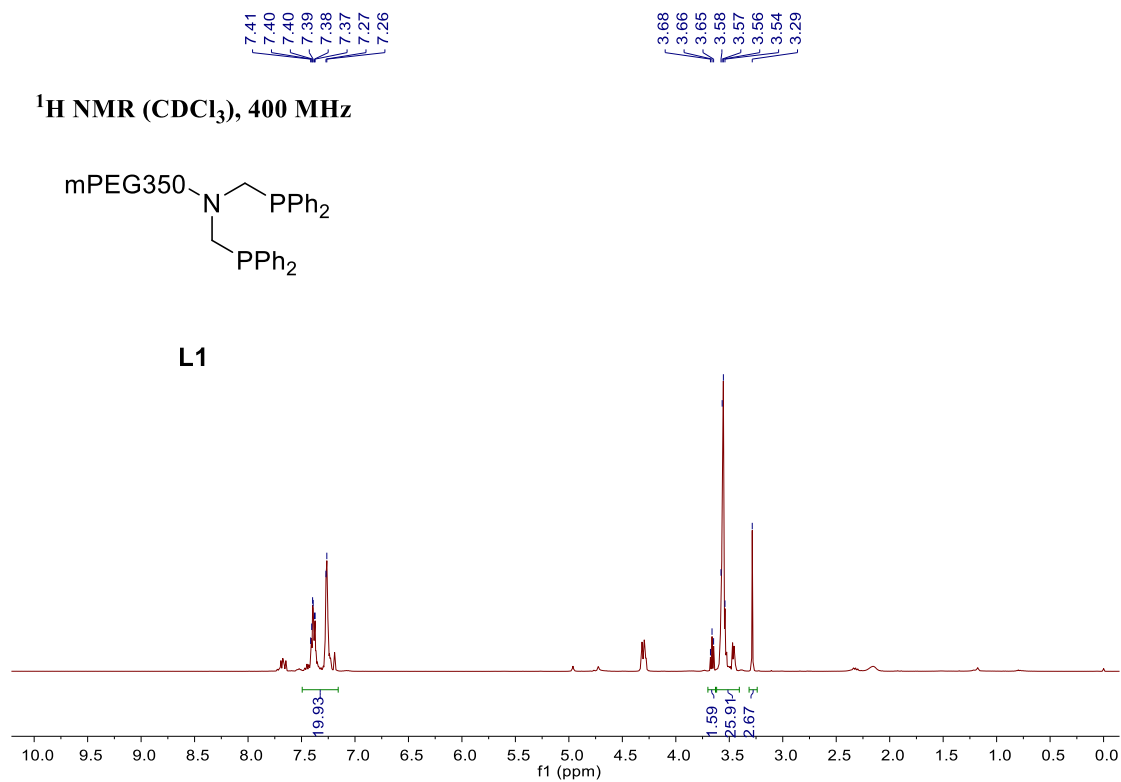


VI. NMR spectra

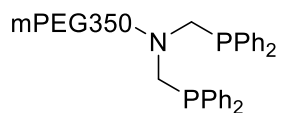
^1H NMR (CDCl_3), 400 MHz



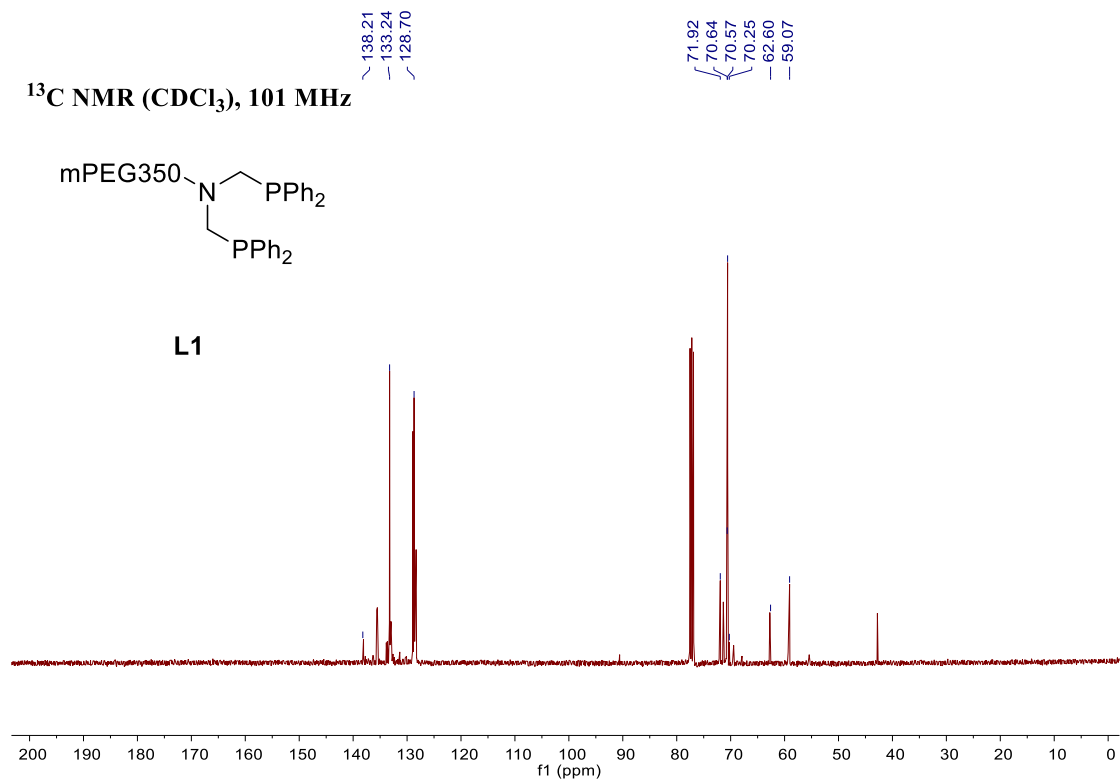
L1



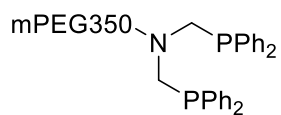
^{13}C NMR (CDCl_3), 101 MHz



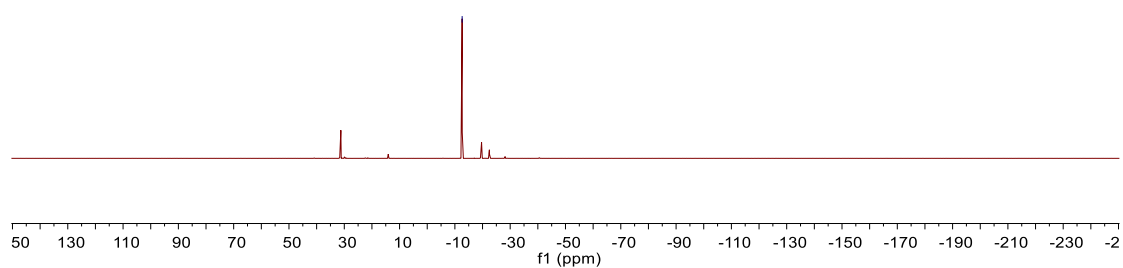
L1



^{31}P NMR (CDCl_3), 162 MHz



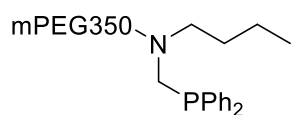
L1



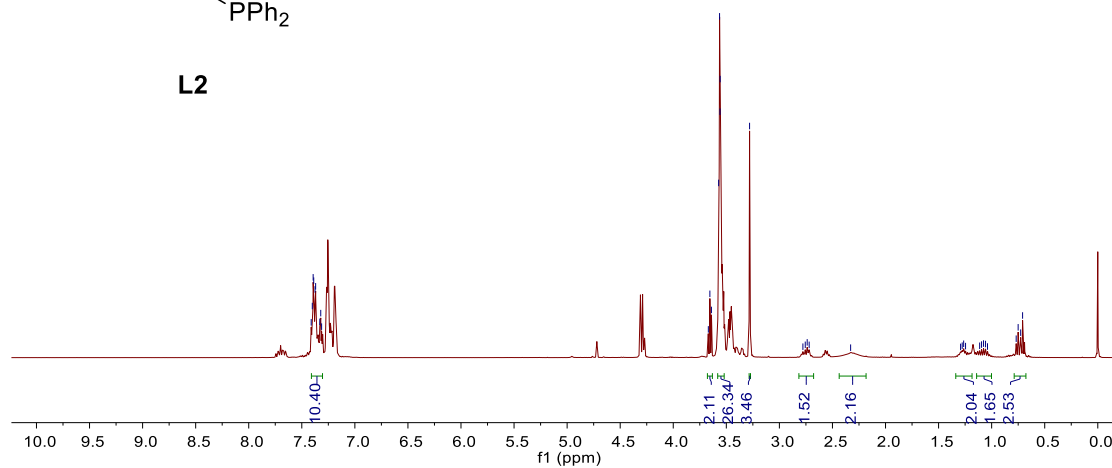
7.41
7.40
7.39
7.38
7.37
7.33
7.32
7.31

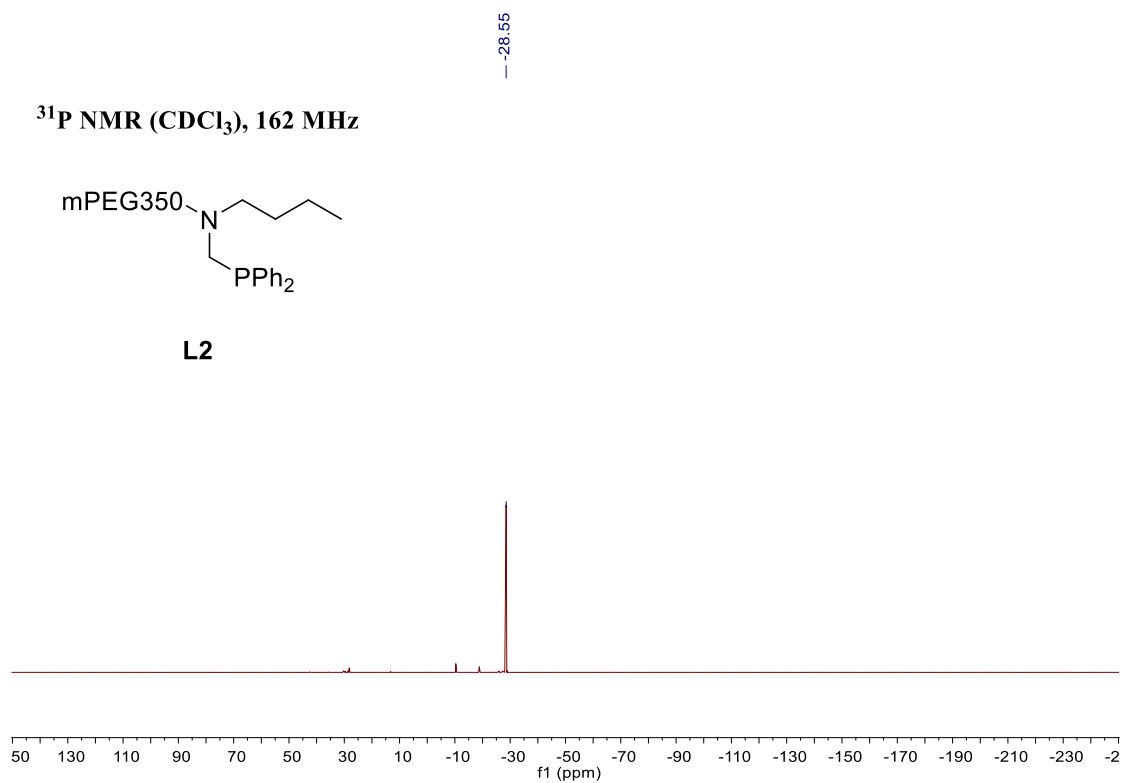
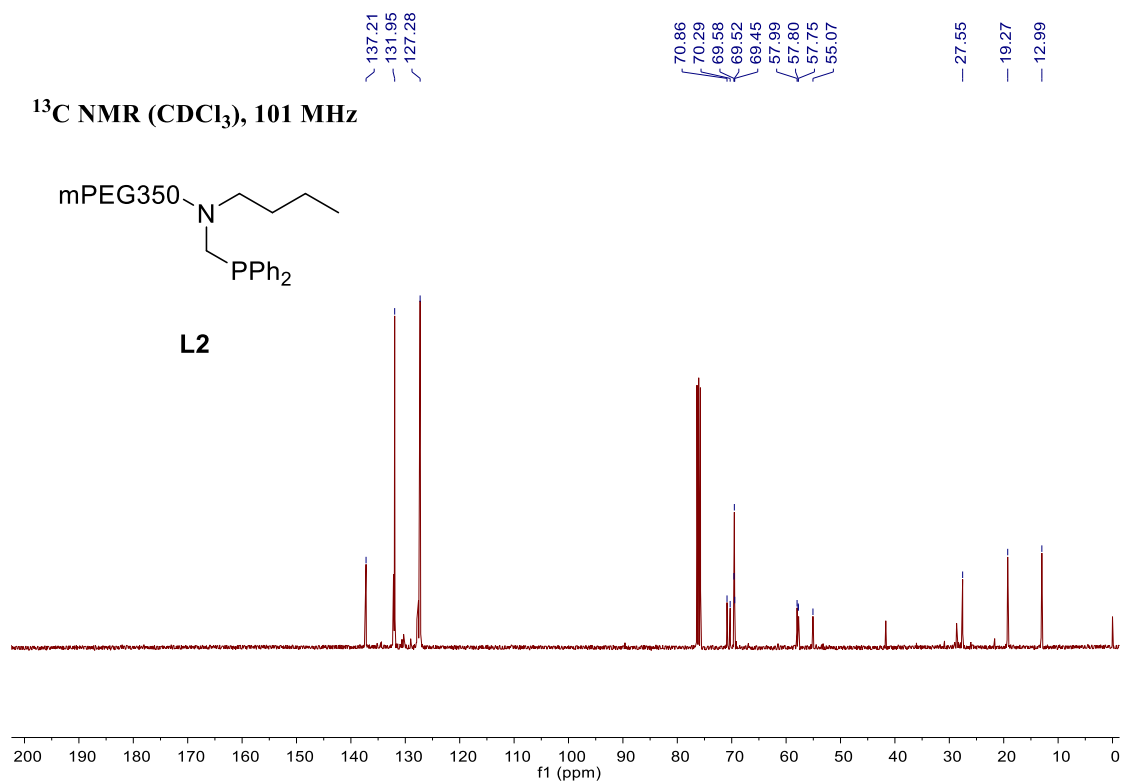
3.67
3.65
3.64
3.57
3.56
3.56
3.28
2.78
2.76
2.74
2.72
-2.33
1.29
1.28
1.26
1.25
1.11
1.10
1.08
1.06
1.04
0.77
0.75
0.73
0.71

^1H NMR (CDCl_3), 400 MHz

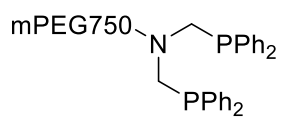


L2

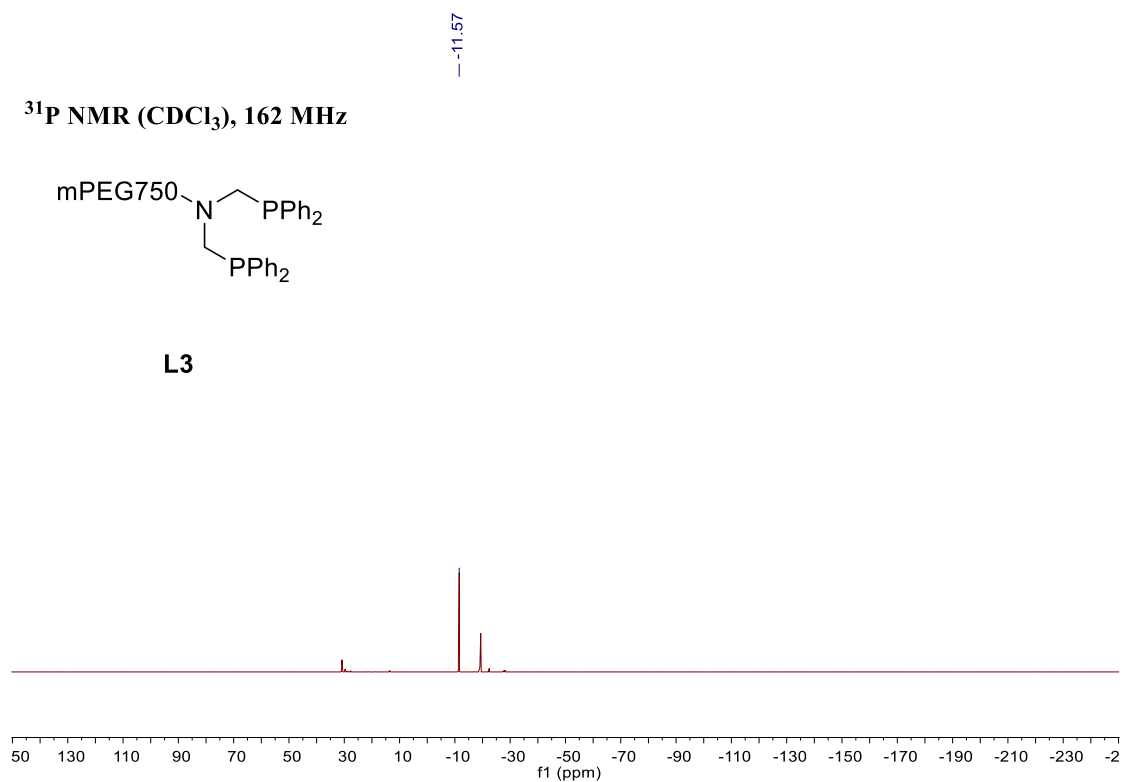




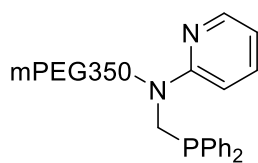
^{31}P NMR (CDCl_3), 162 MHz



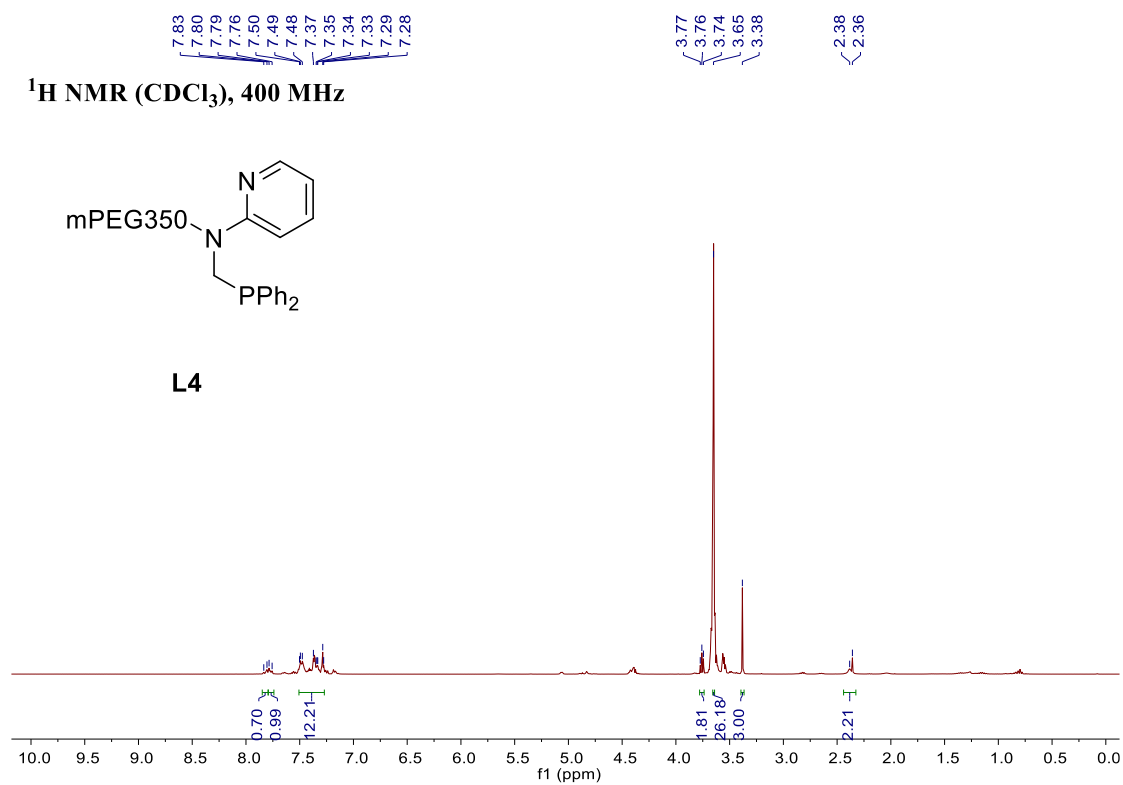
L3

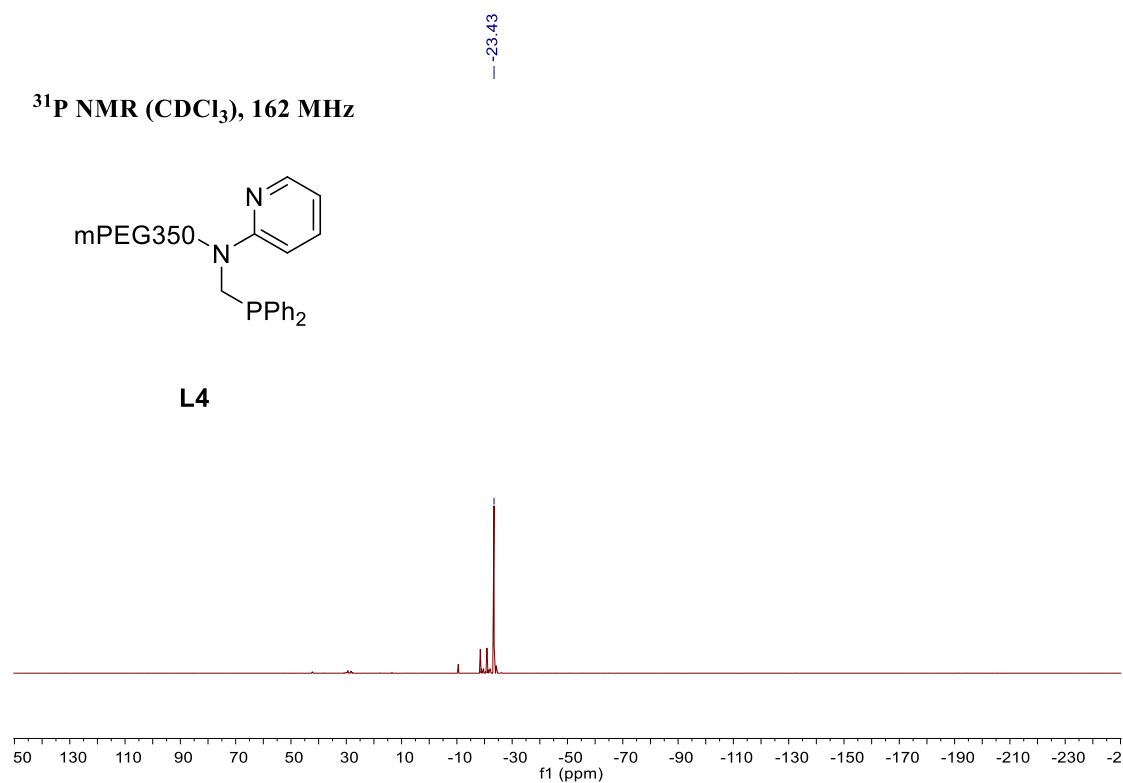
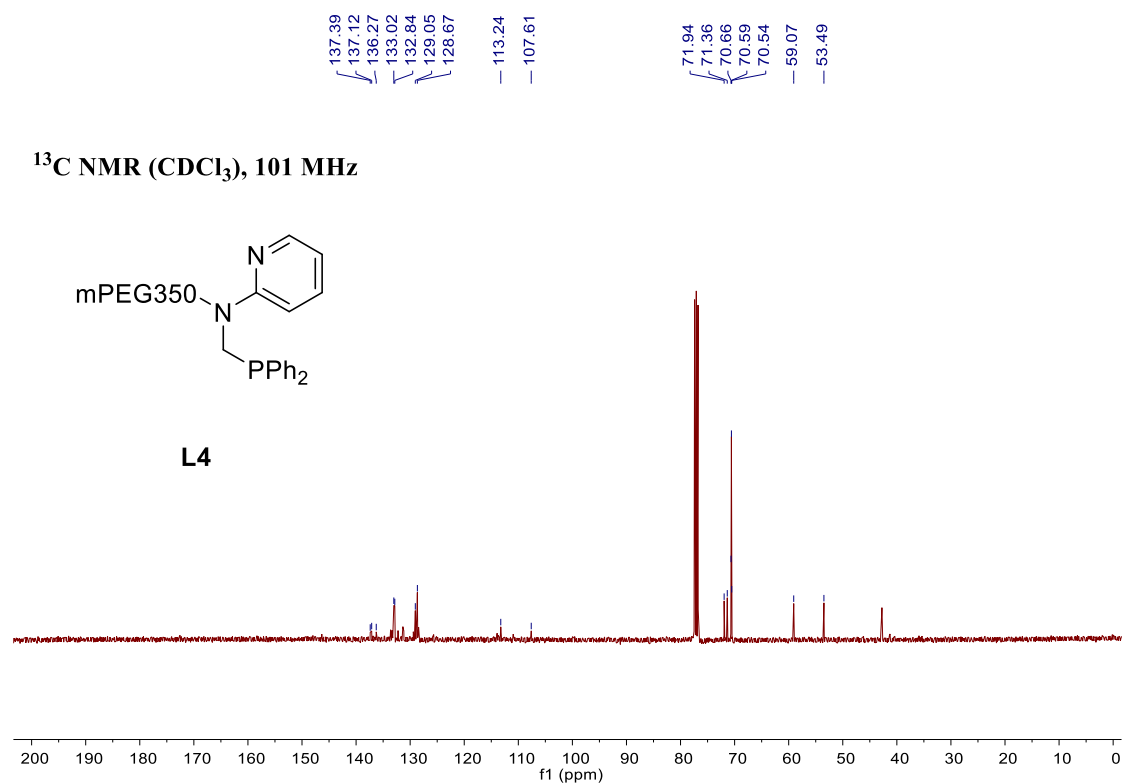


^1H NMR (CDCl_3), 400 MHz



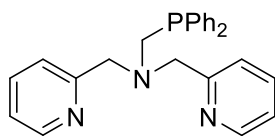
L4



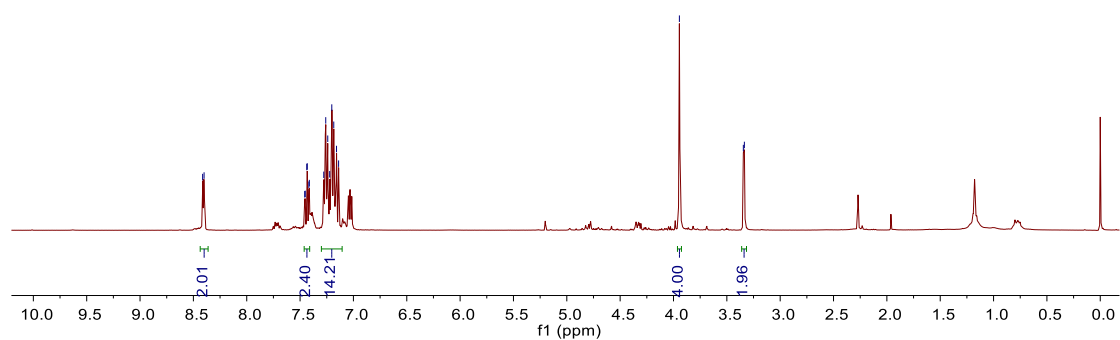




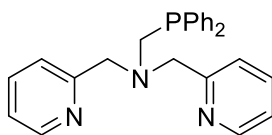
^1H NMR (CDCl_3), 400 MHz



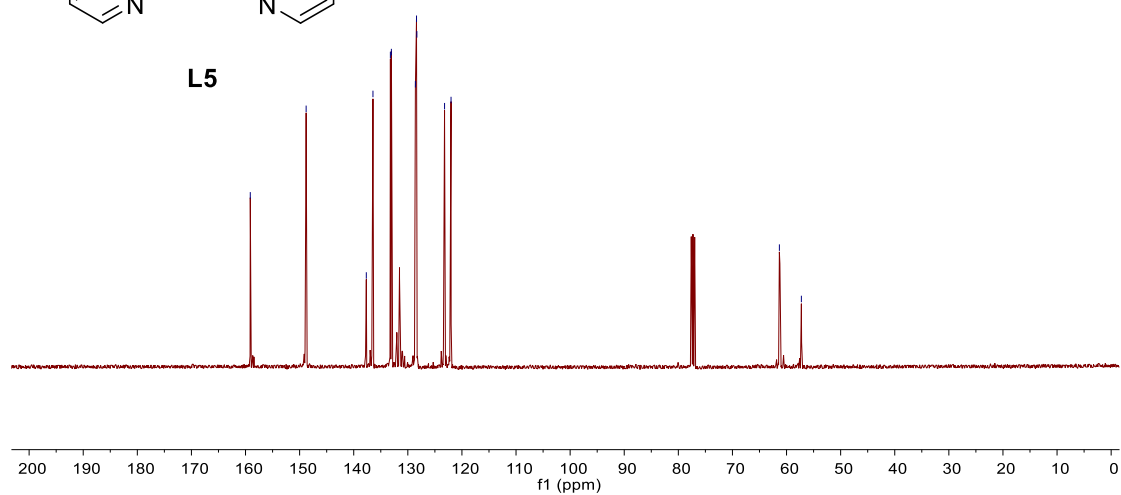
L5



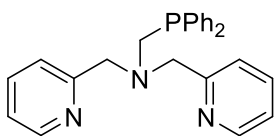
^{13}C NMR (CDCl_3), 101 MHz



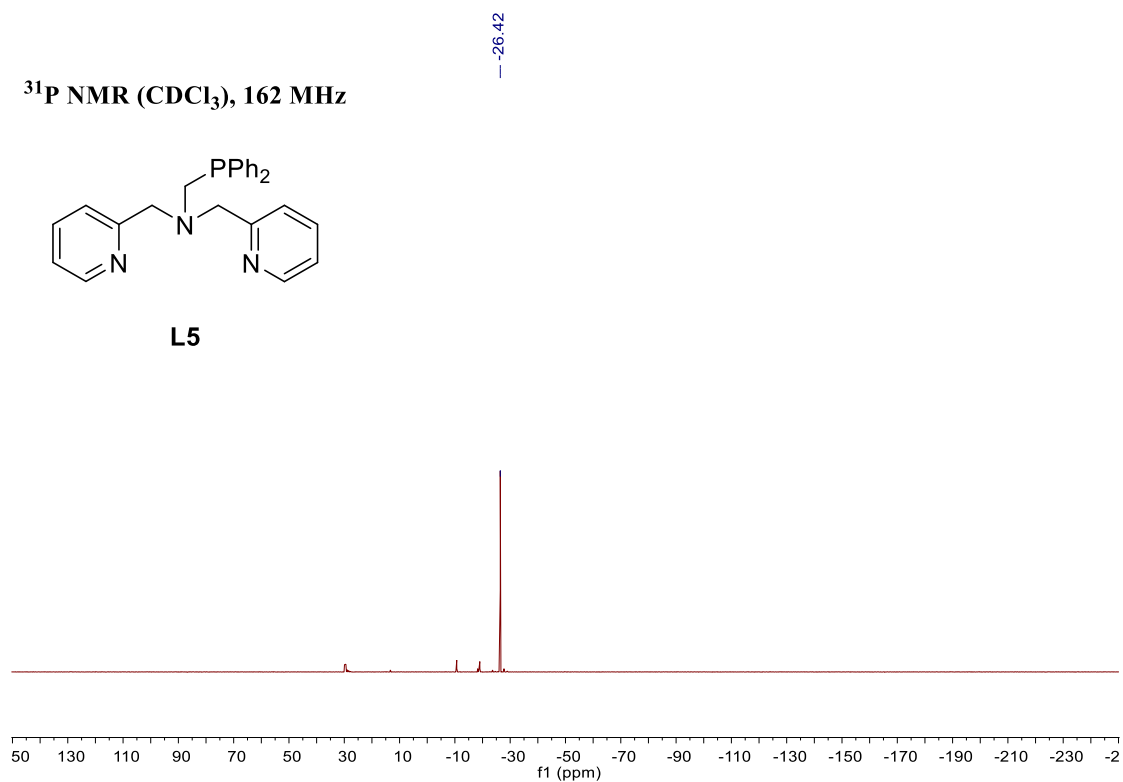
L5



^{31}P NMR (CDCl_3), 162 MHz



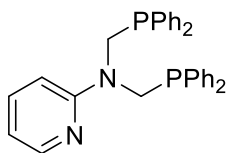
L5



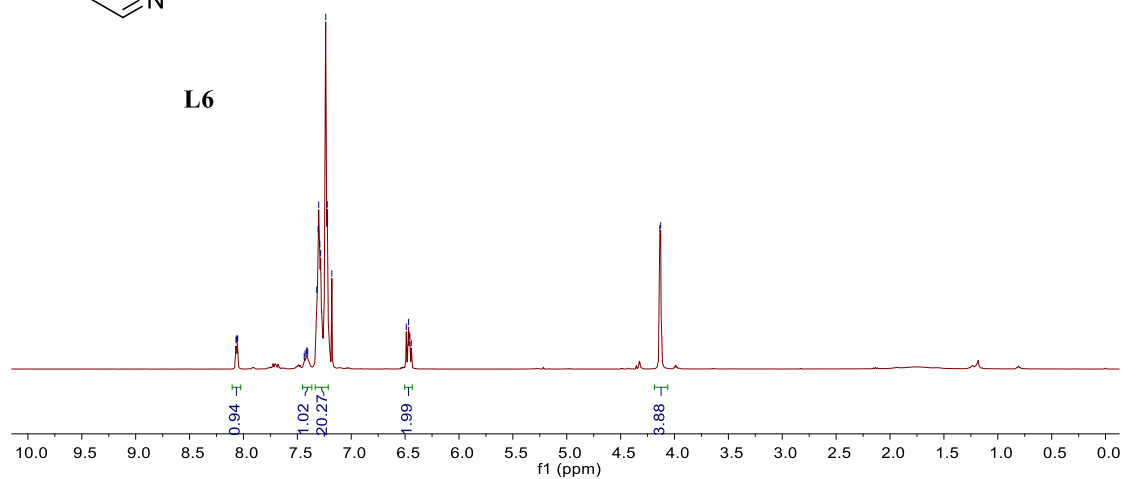
8.07
8.07
8.06
8.05
7.44
7.43
7.42
7.41
7.40
7.32
7.31
7.30
7.29
7.28
7.24
7.22
7.18
6.49
6.47
6.46
6.46
6.44

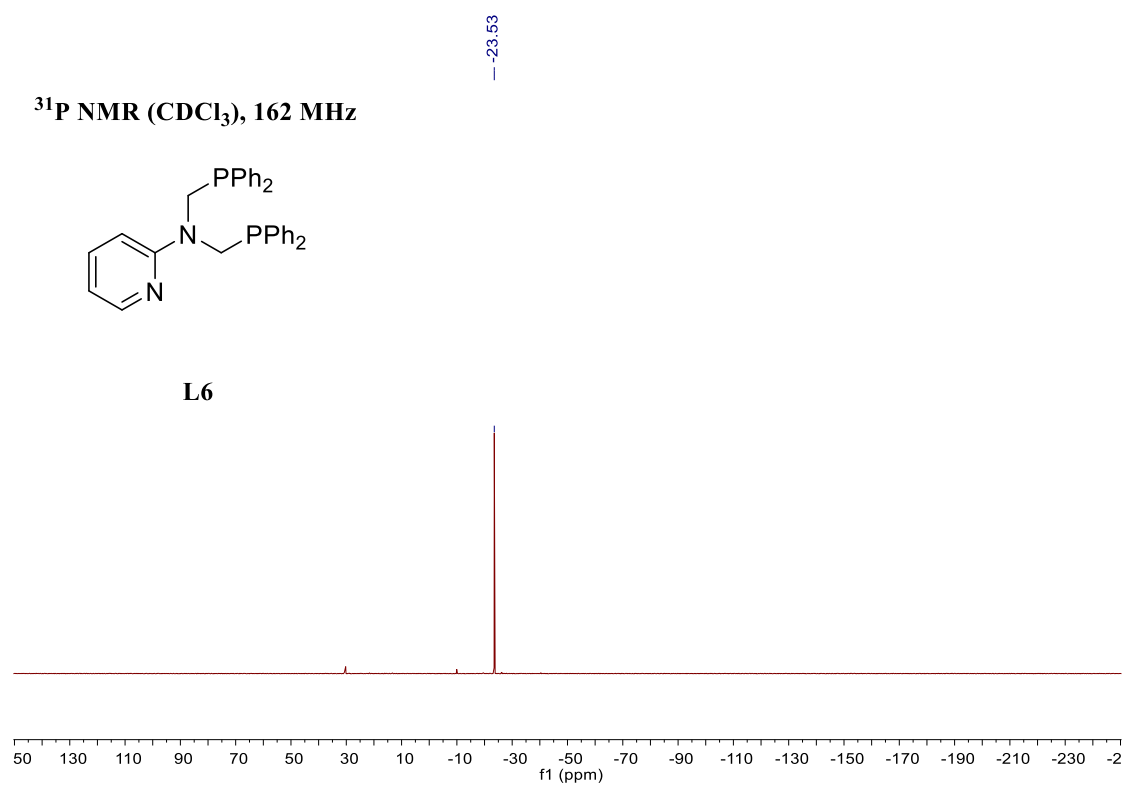
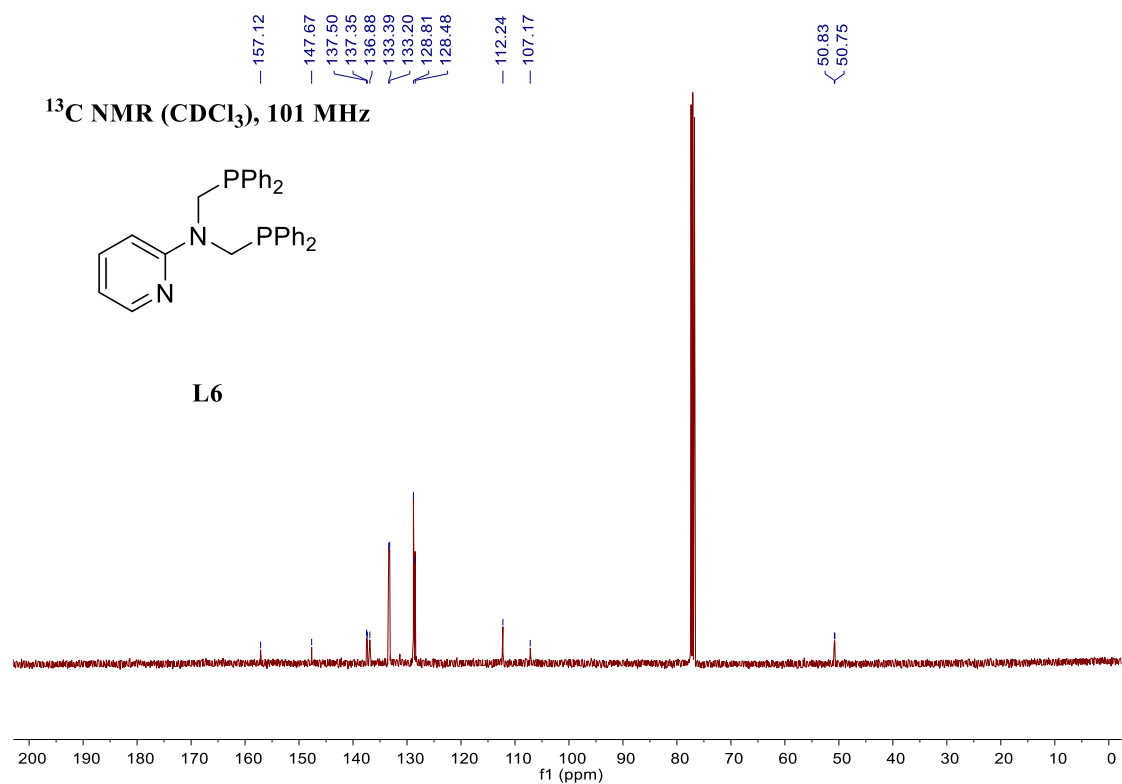
4.14
4.13

^1H NMR (CDCl_3), 400 MHz

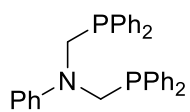


L6

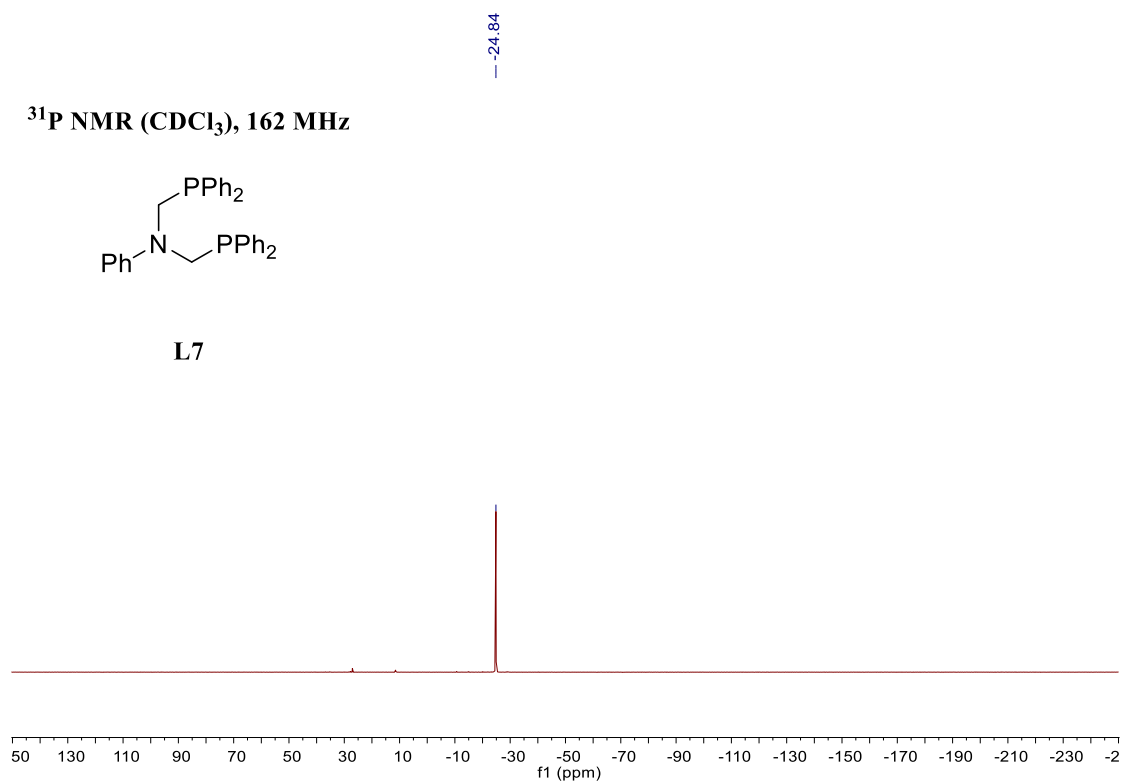




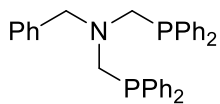
³¹P NMR (CDCl₃), 162 MHz



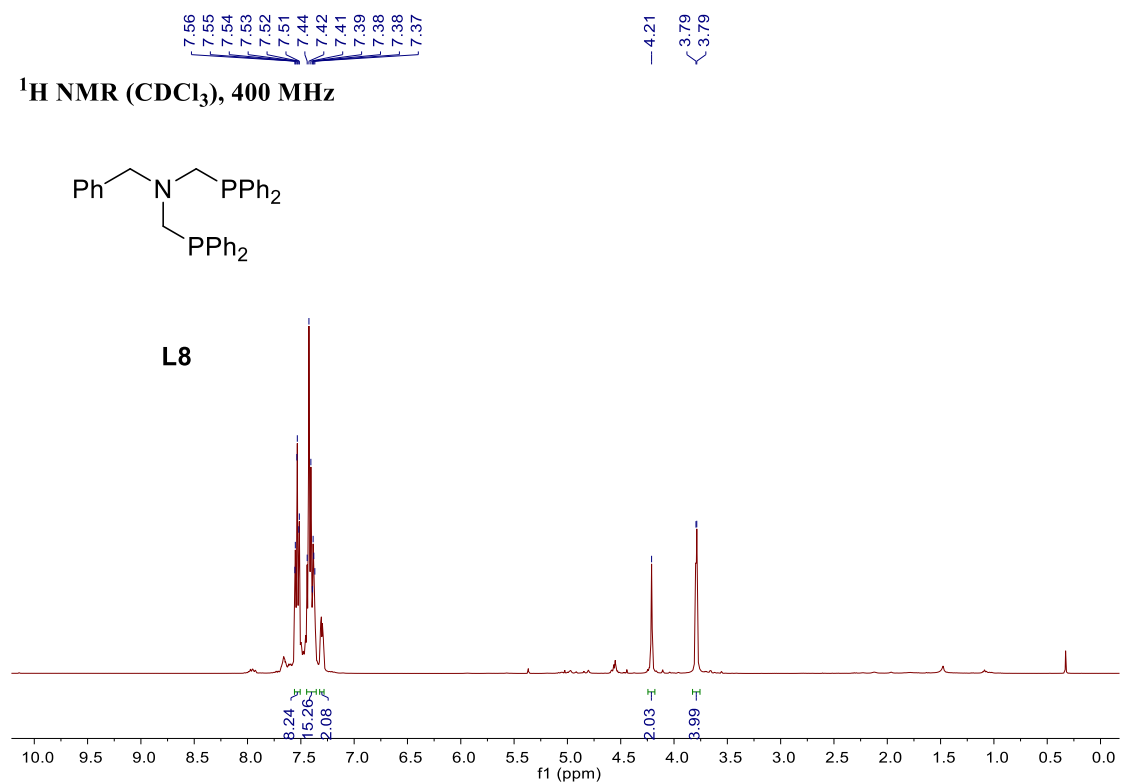
L7

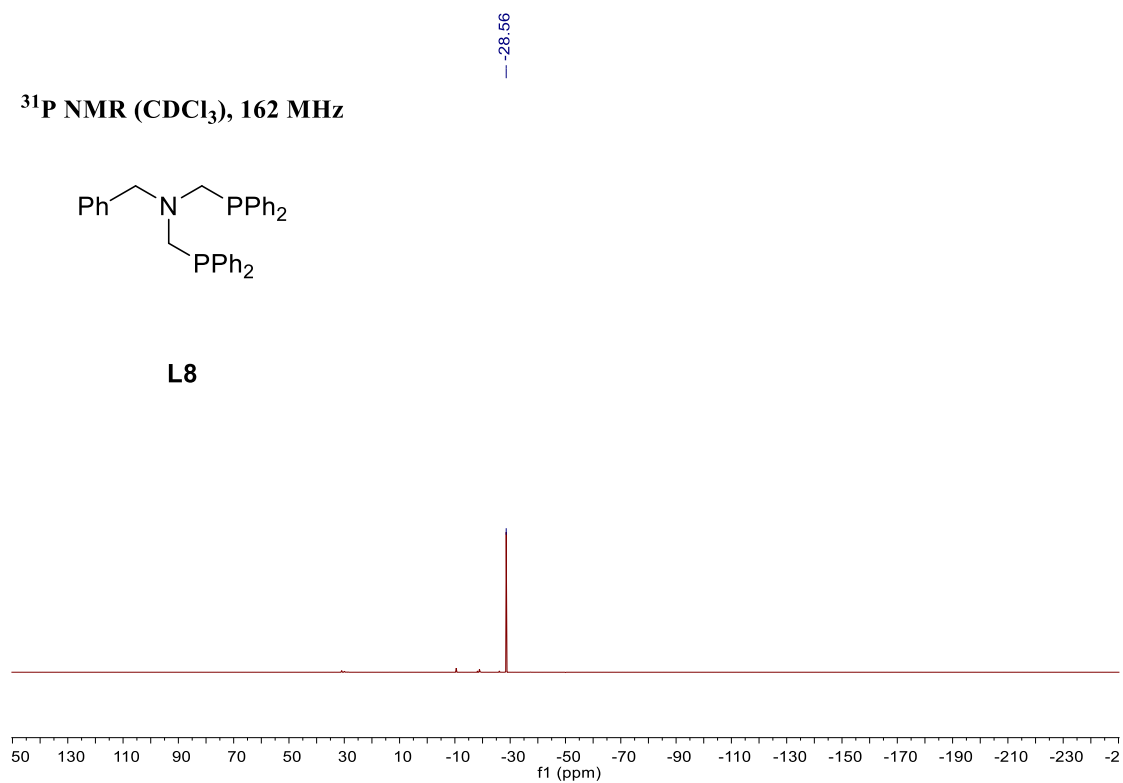
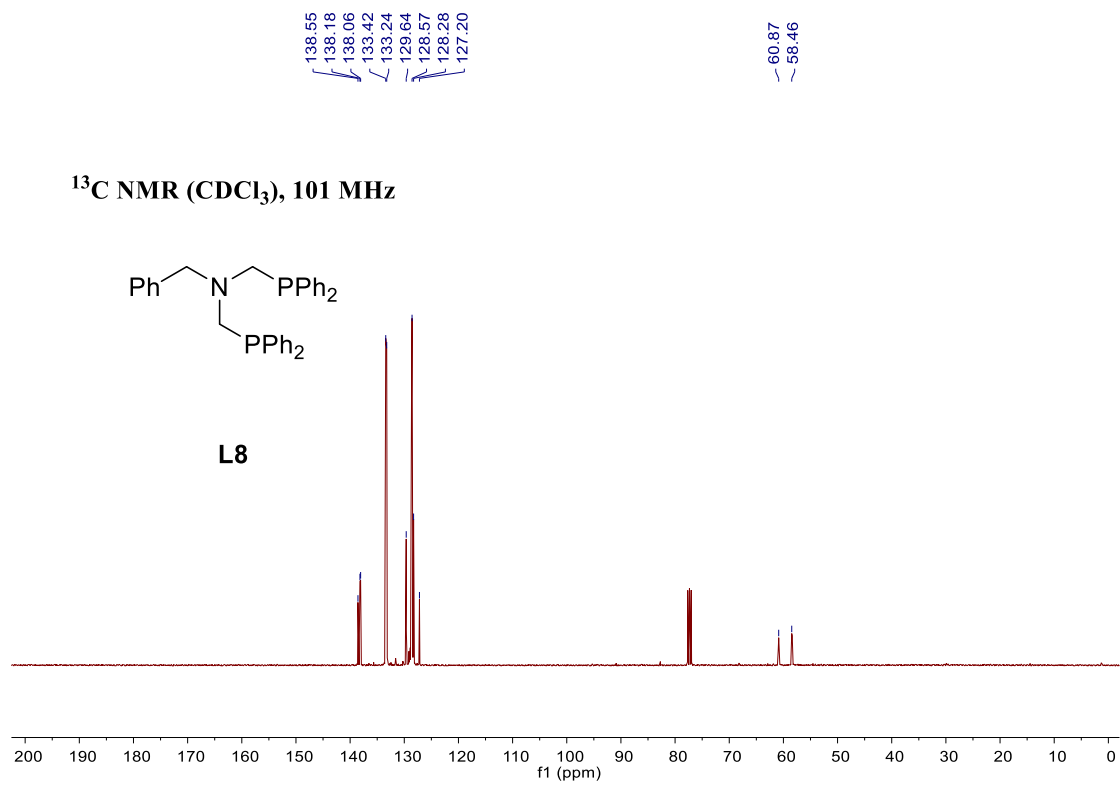


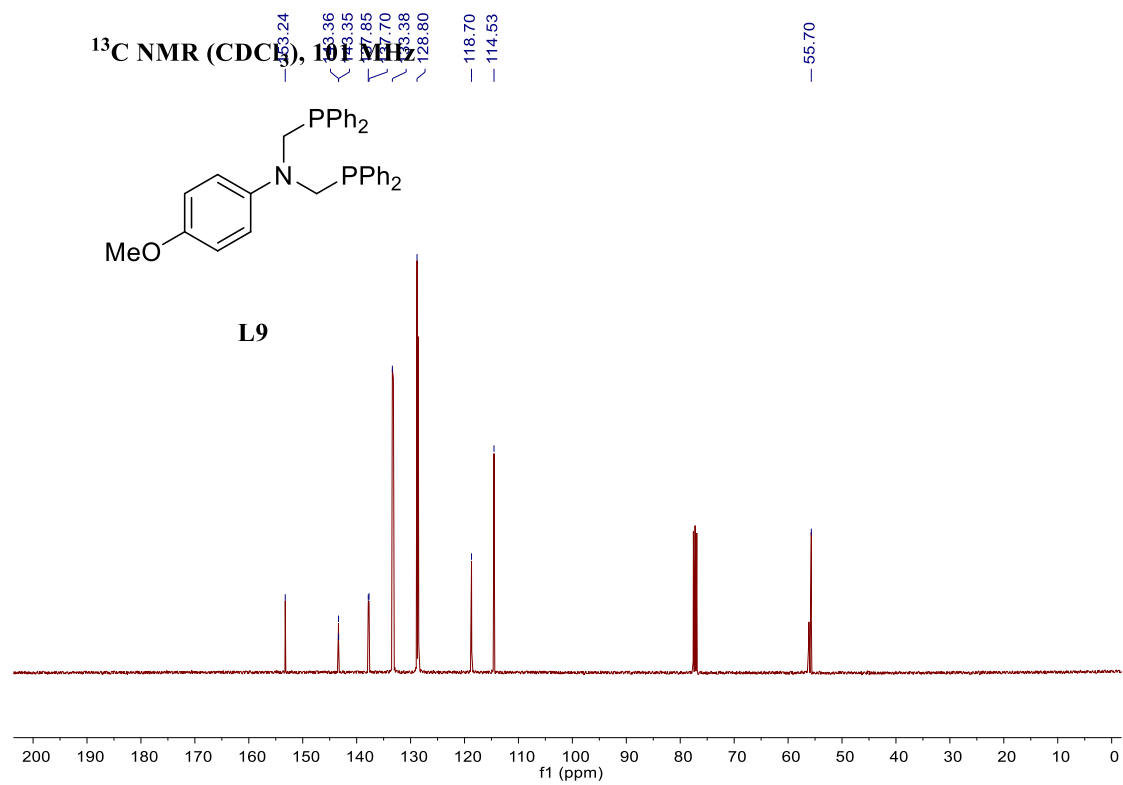
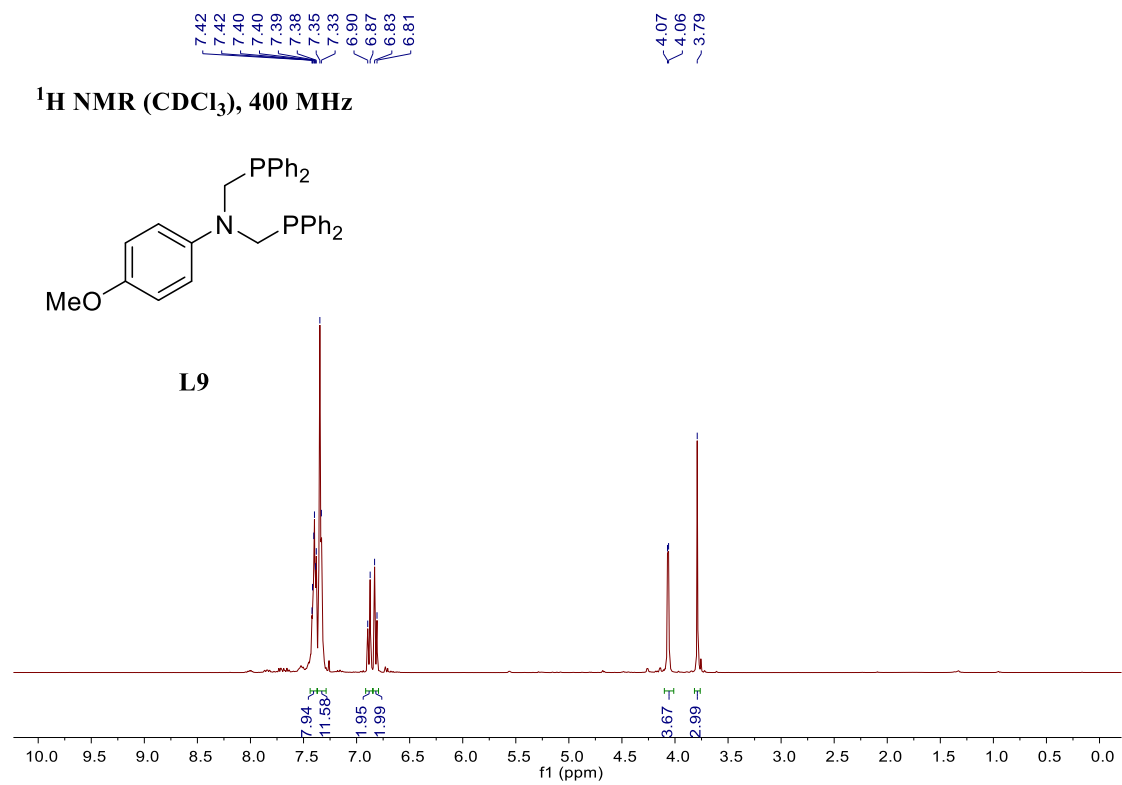
¹H NMR (CDCl₃), 400 MHz

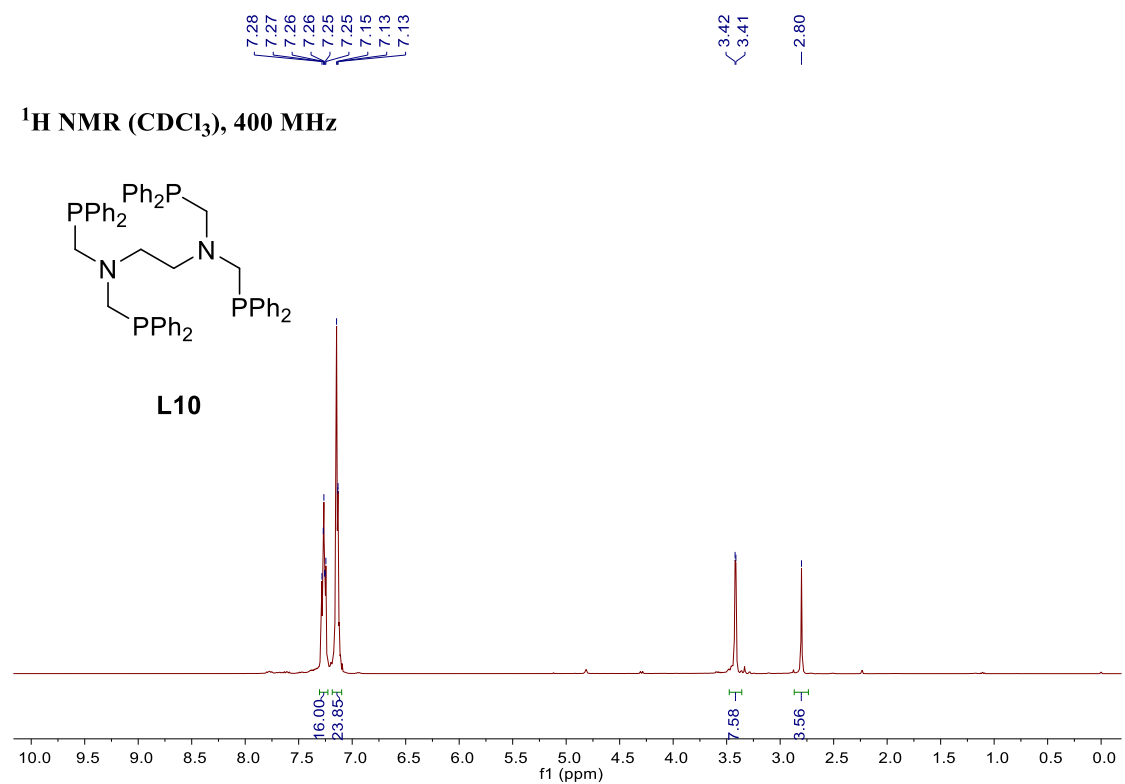
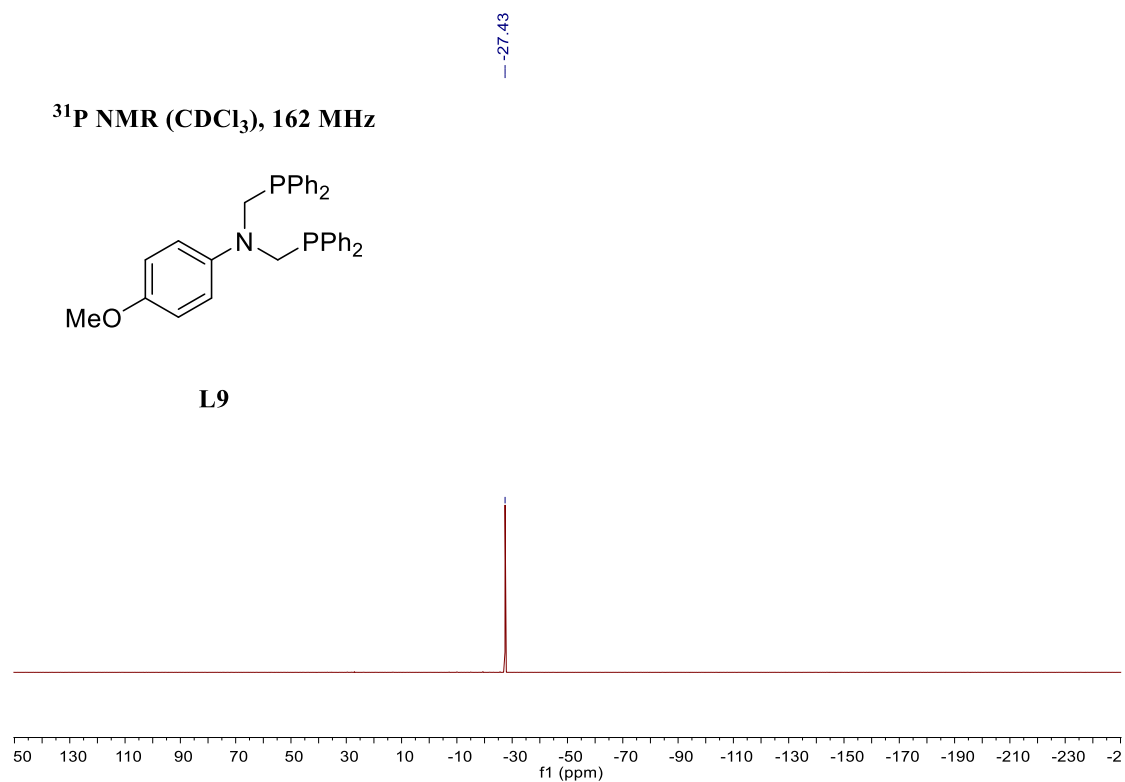


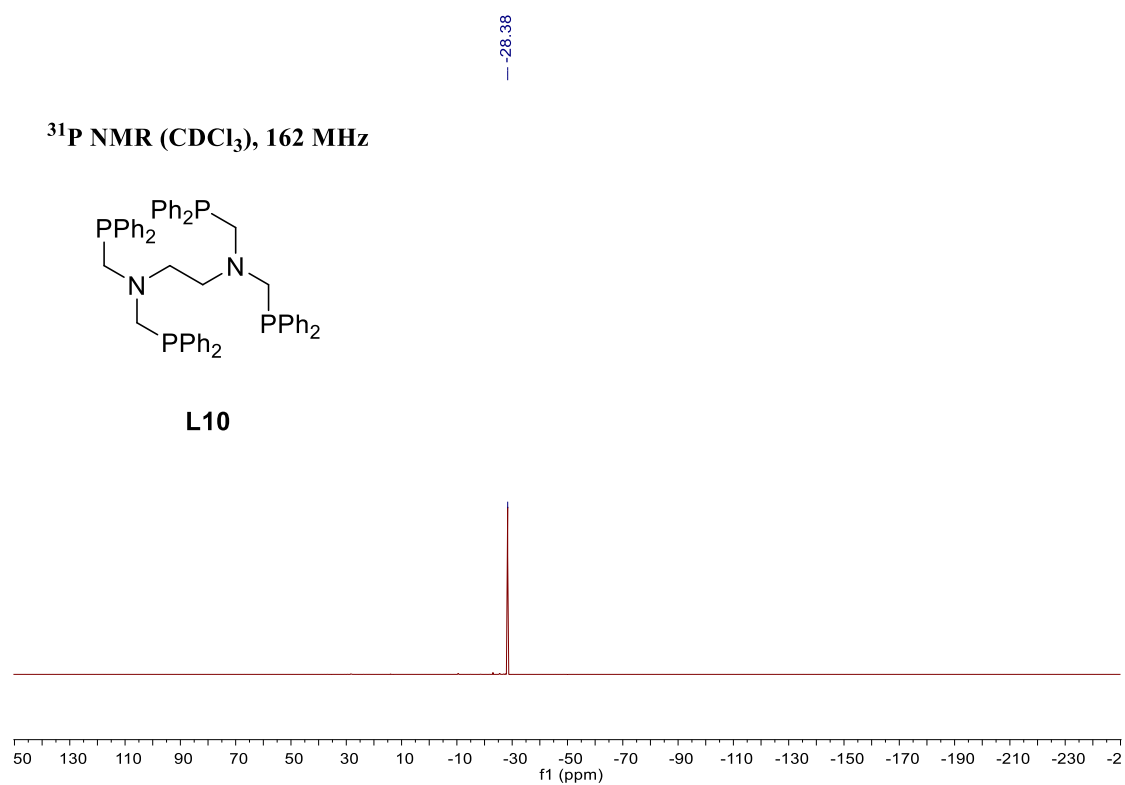
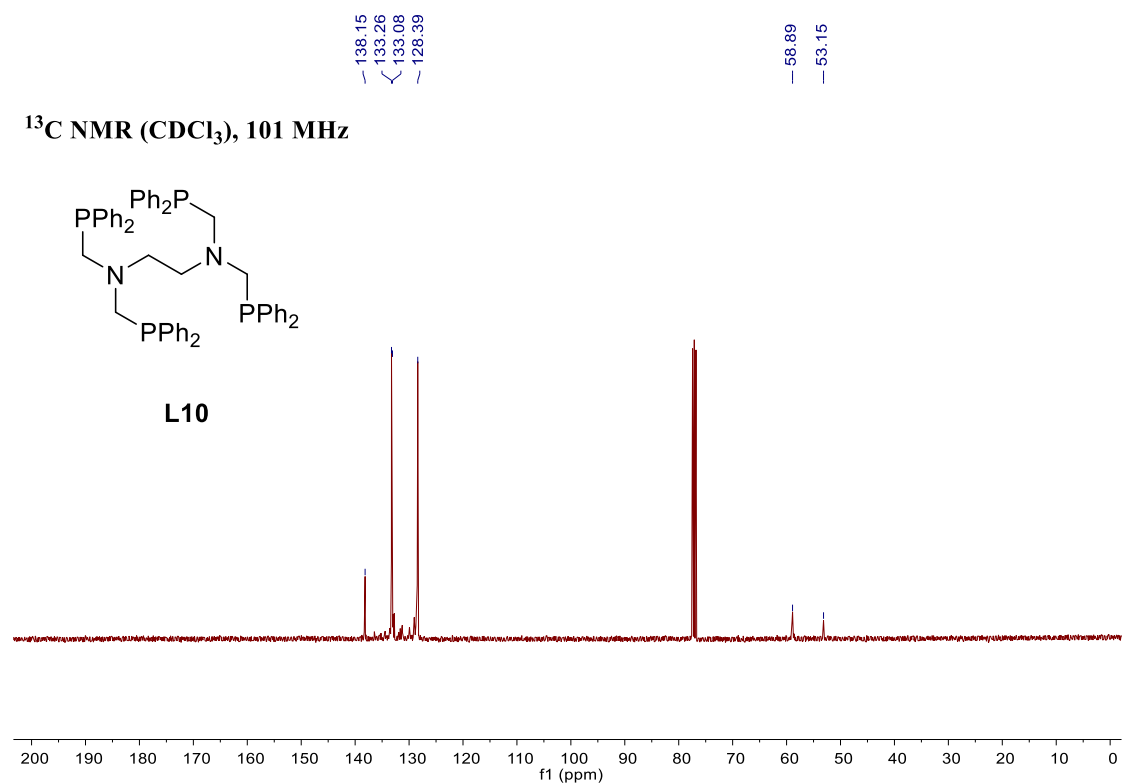
L8

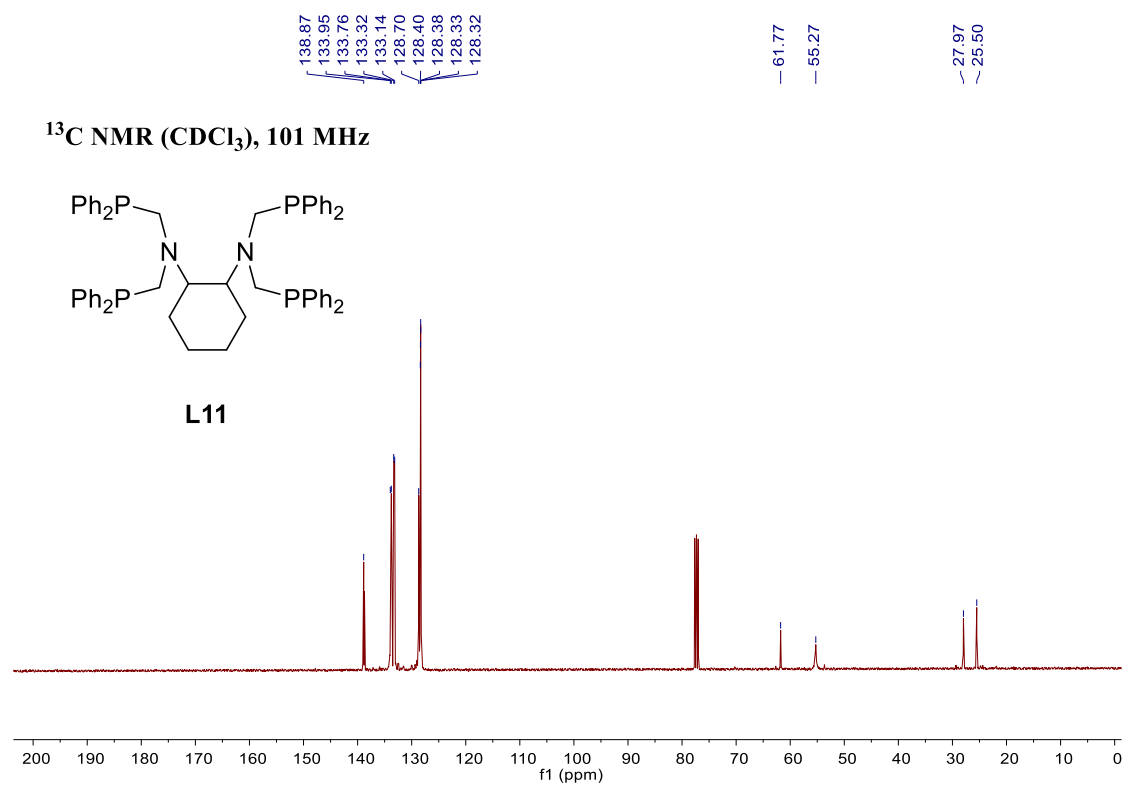
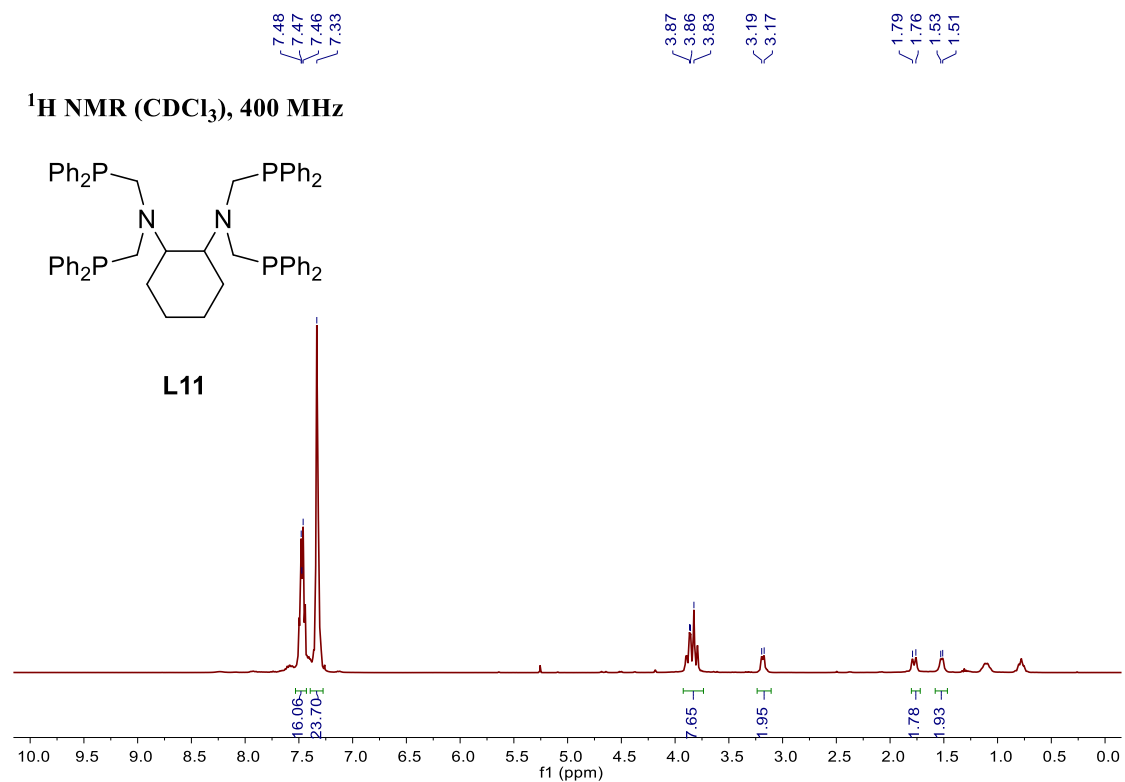












c1ccc(cc1)P(c2ccccc2)CN3C4C(C5C4C(C3)C5)C6C(C2)C(C1)C6

^{31}P NMR (CDCl_3), 162 MHz

L11

Chemical structure of L11: c1ccc(cc1)P(c2ccccc2)c3ccccc3N4CCCCC4N(c5ccccc5)P(c6ccccc6)c7ccccc7

Peak list (ppm):

Peak Label	Chemical Shift (ppm)
8.50	8.50
7.46	7.46
7.44	7.44
7.42	7.42
7.21	7.21
7.20	7.20
7.19	7.19
-24.84	-24.84
-3.34	-3.34

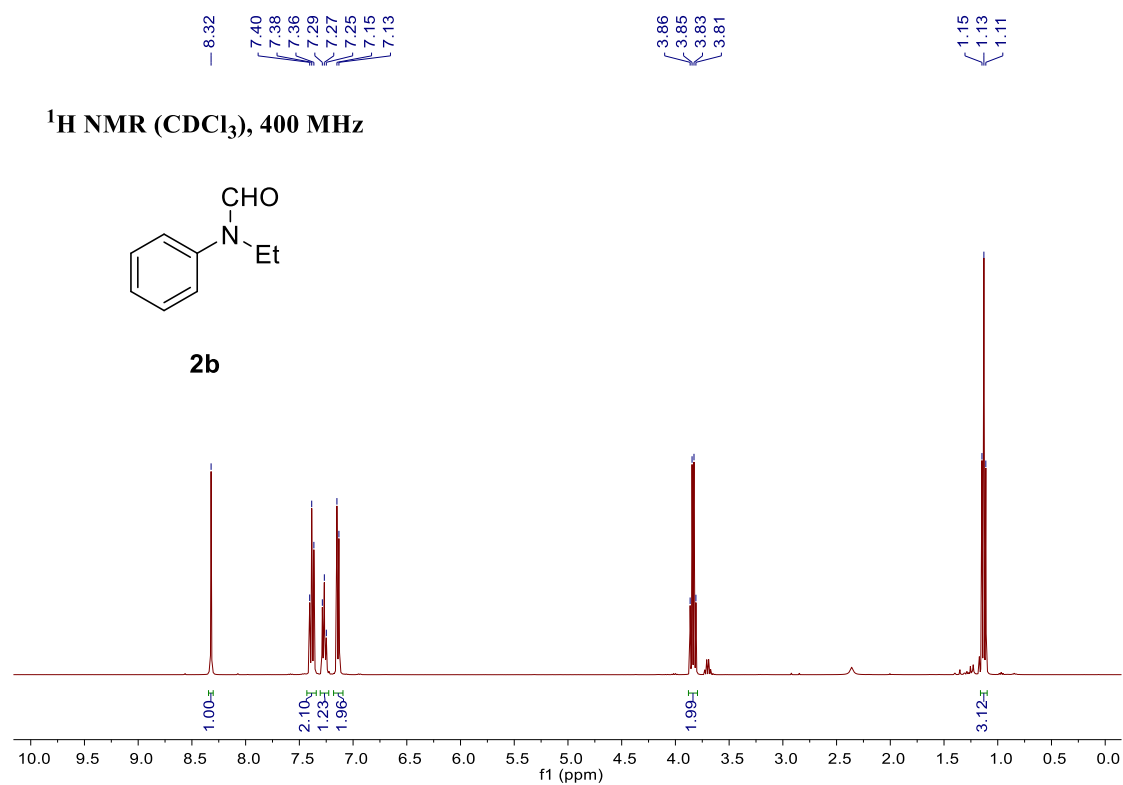
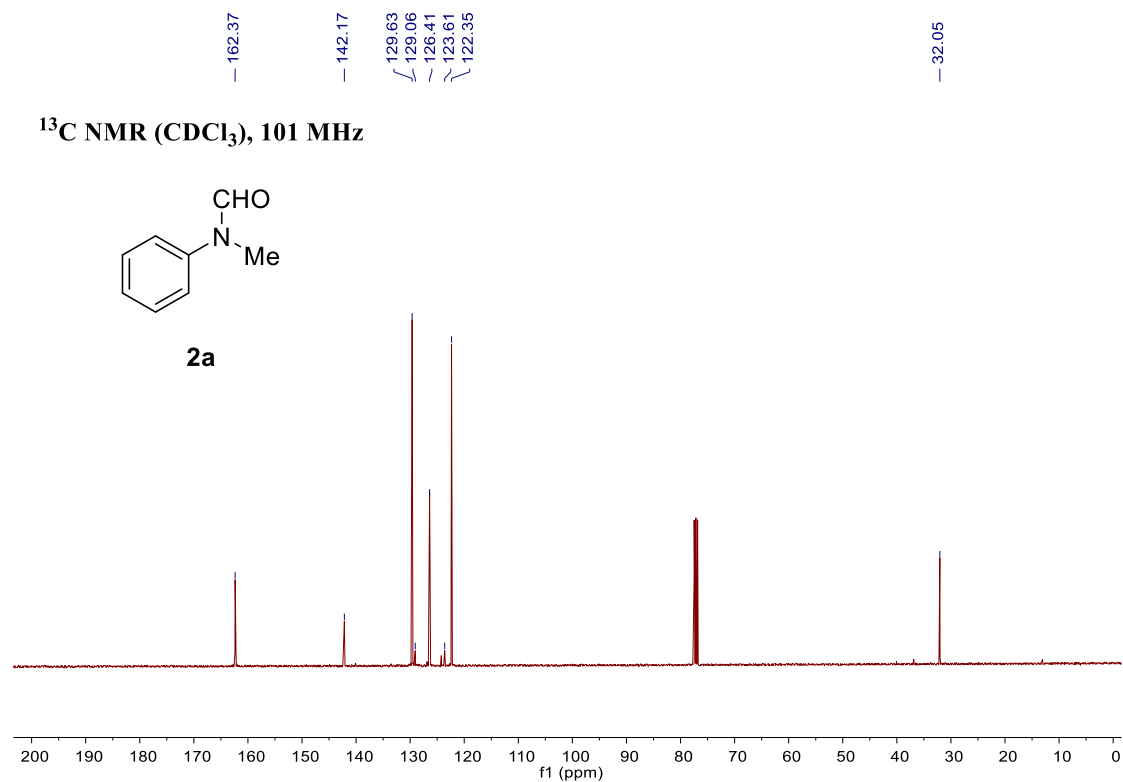
CN(C)Cc1ccccc1

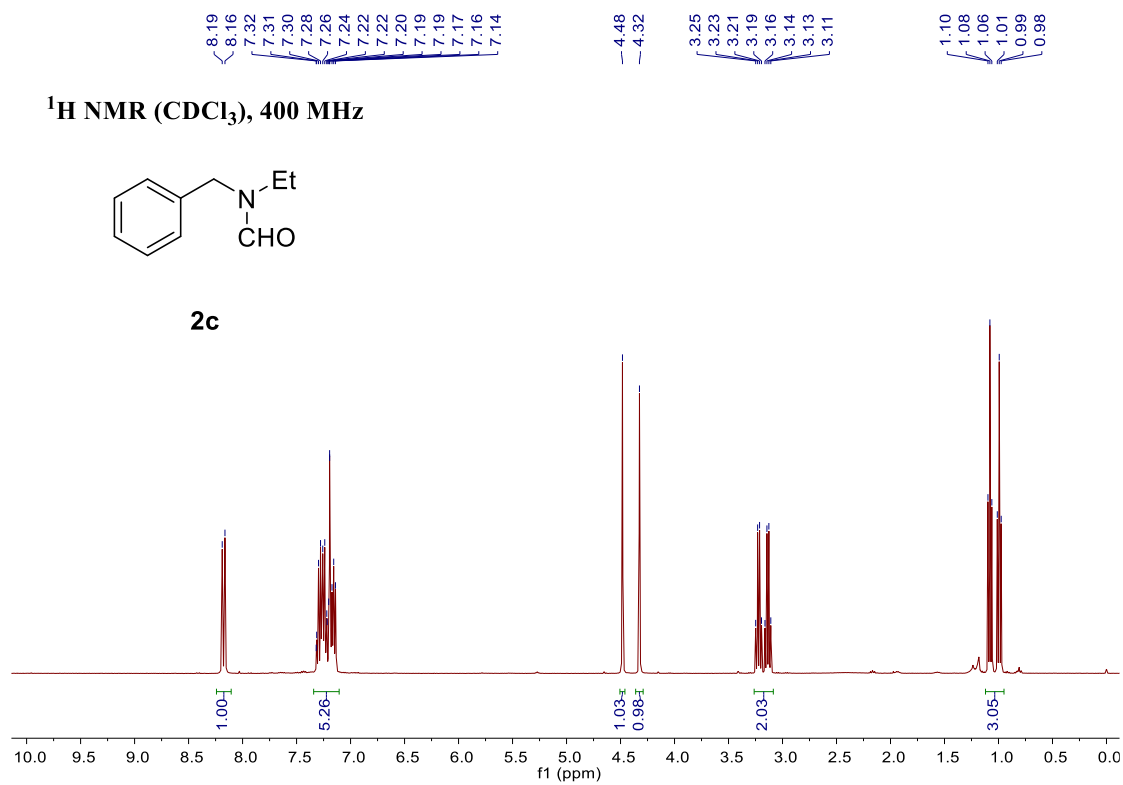
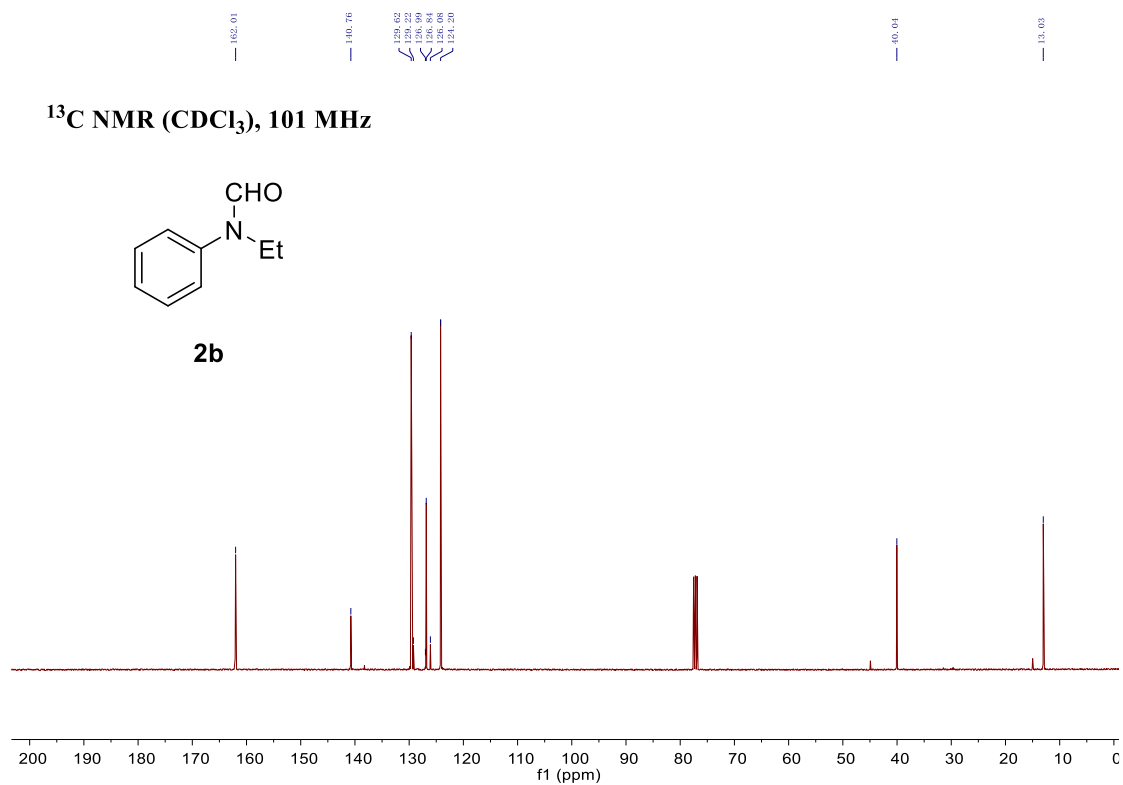
2a

CNc1ccccc1

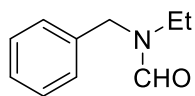
0.99
2.24
1.28
2.07
3.12

f1 (ppm)

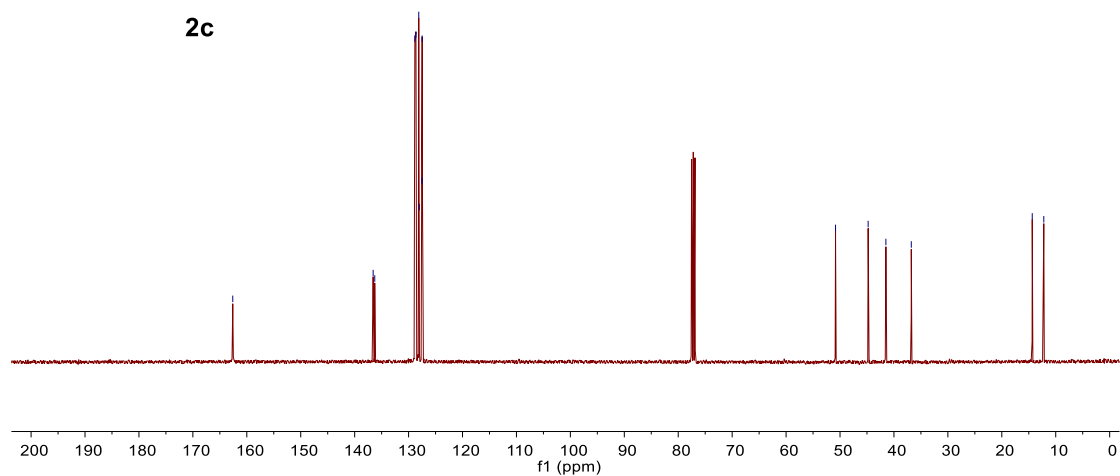




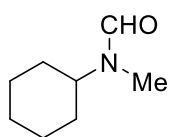
^{13}C NMR (CDCl_3), 101 MHz



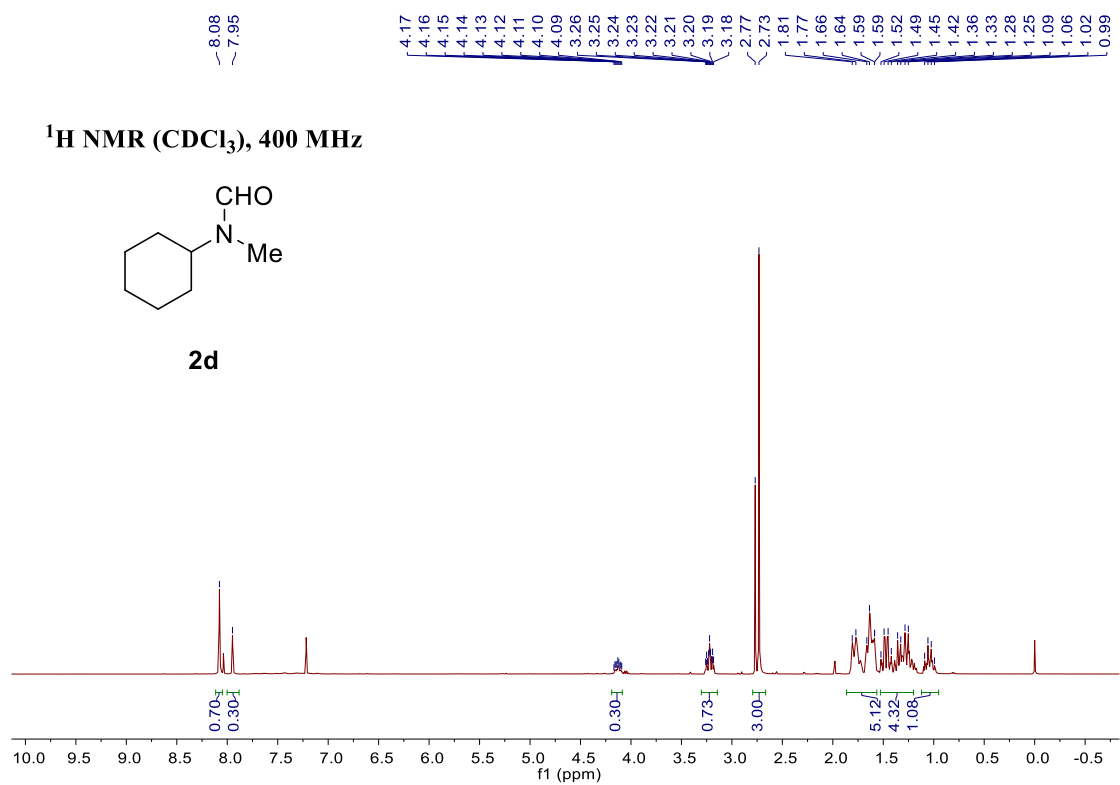
2c

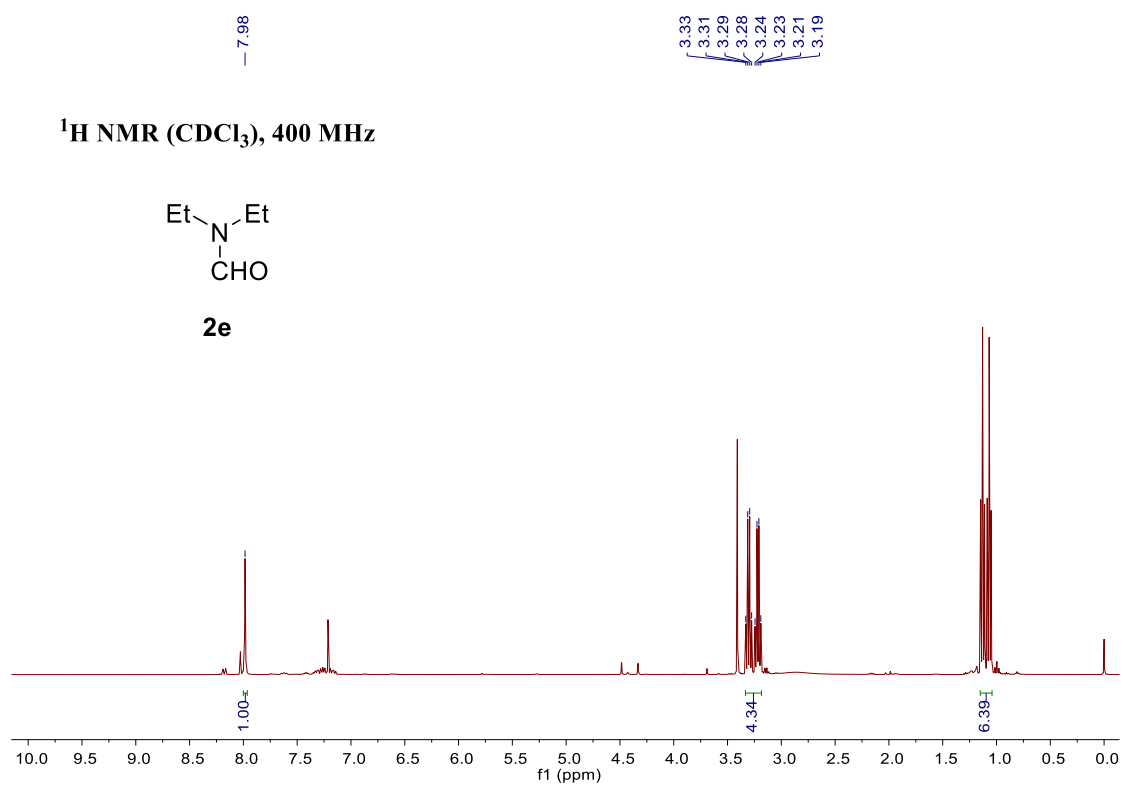
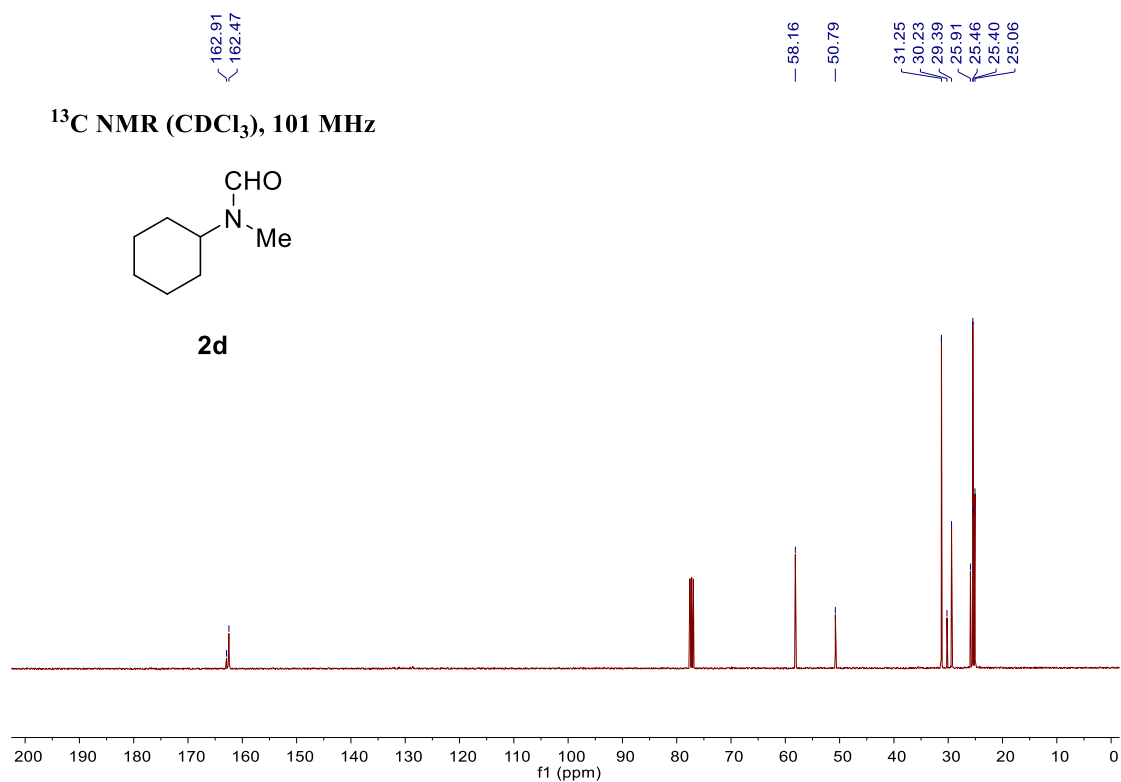


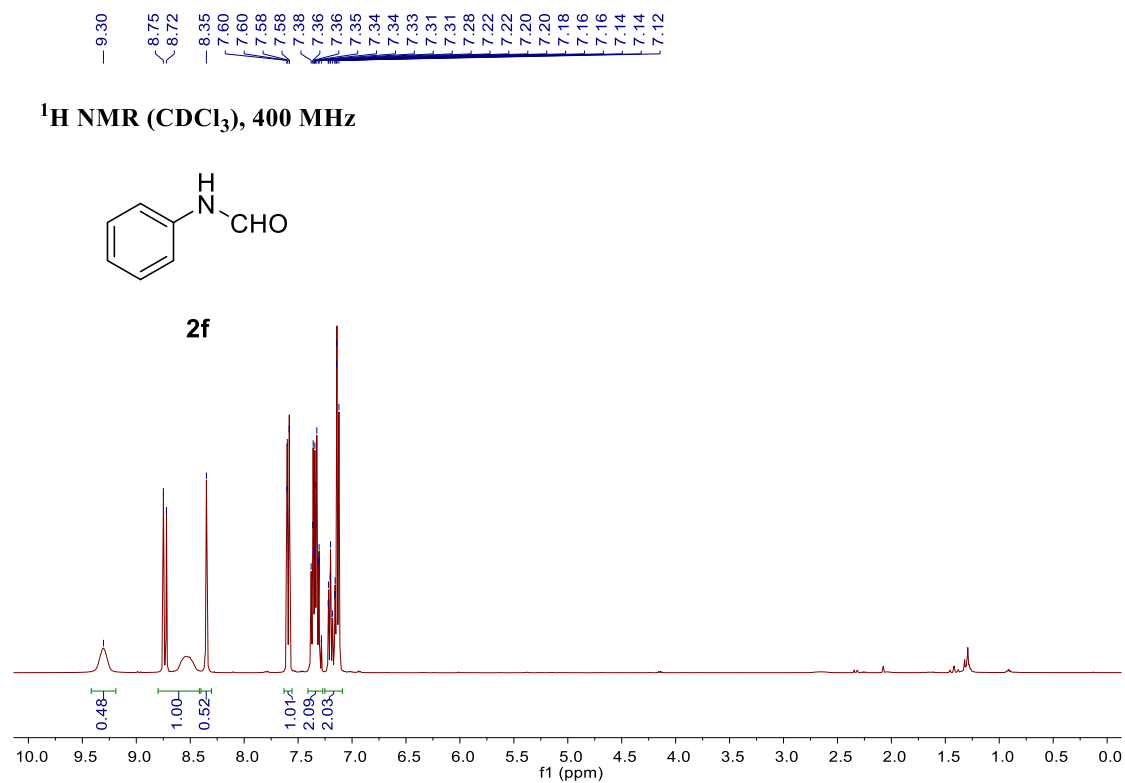
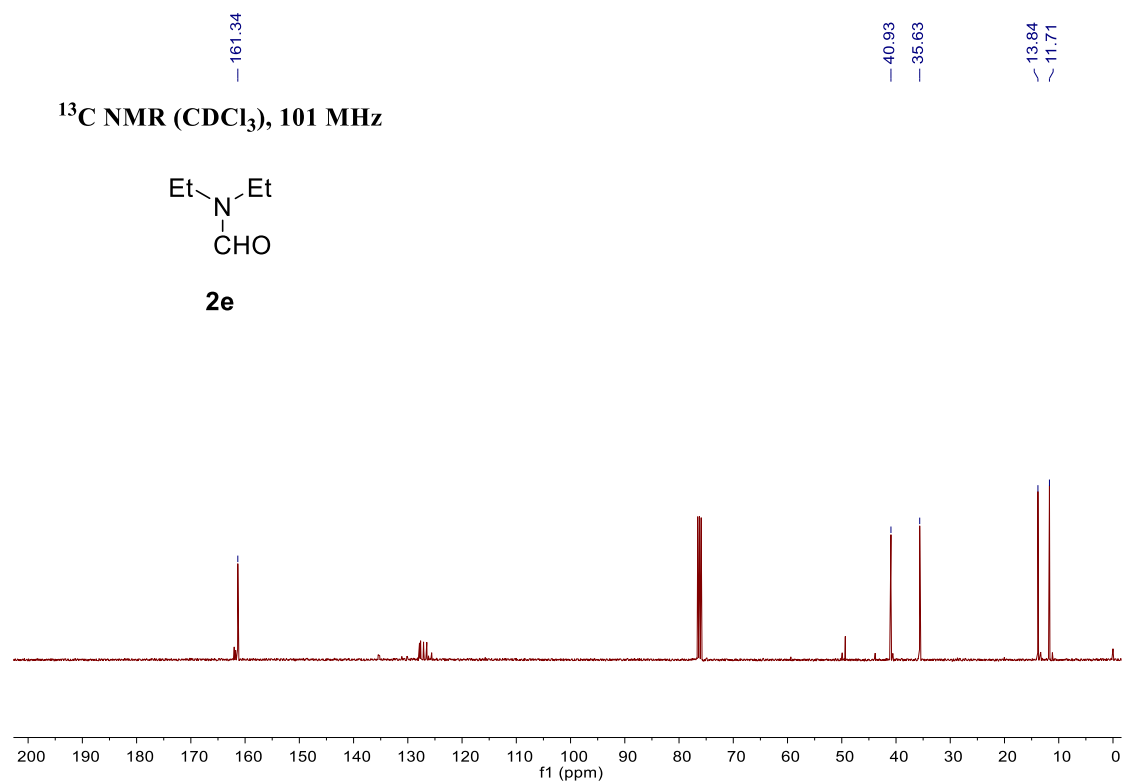
^1H NMR (CDCl_3), 400 MHz

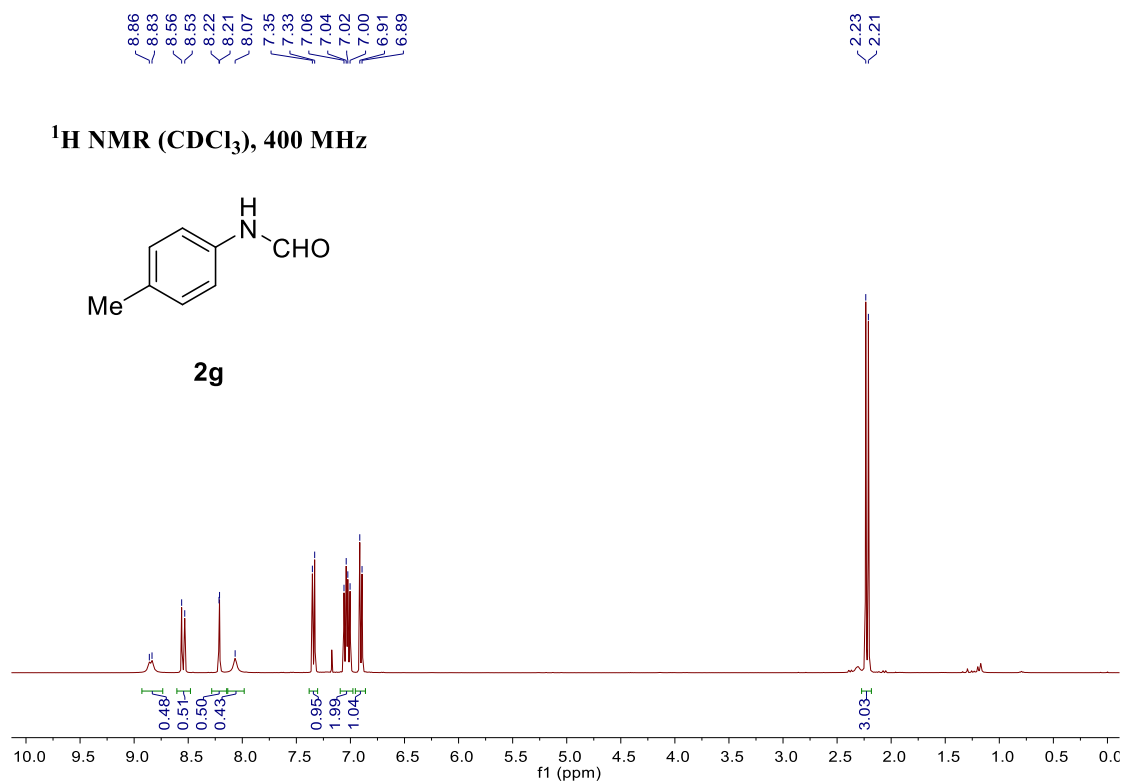
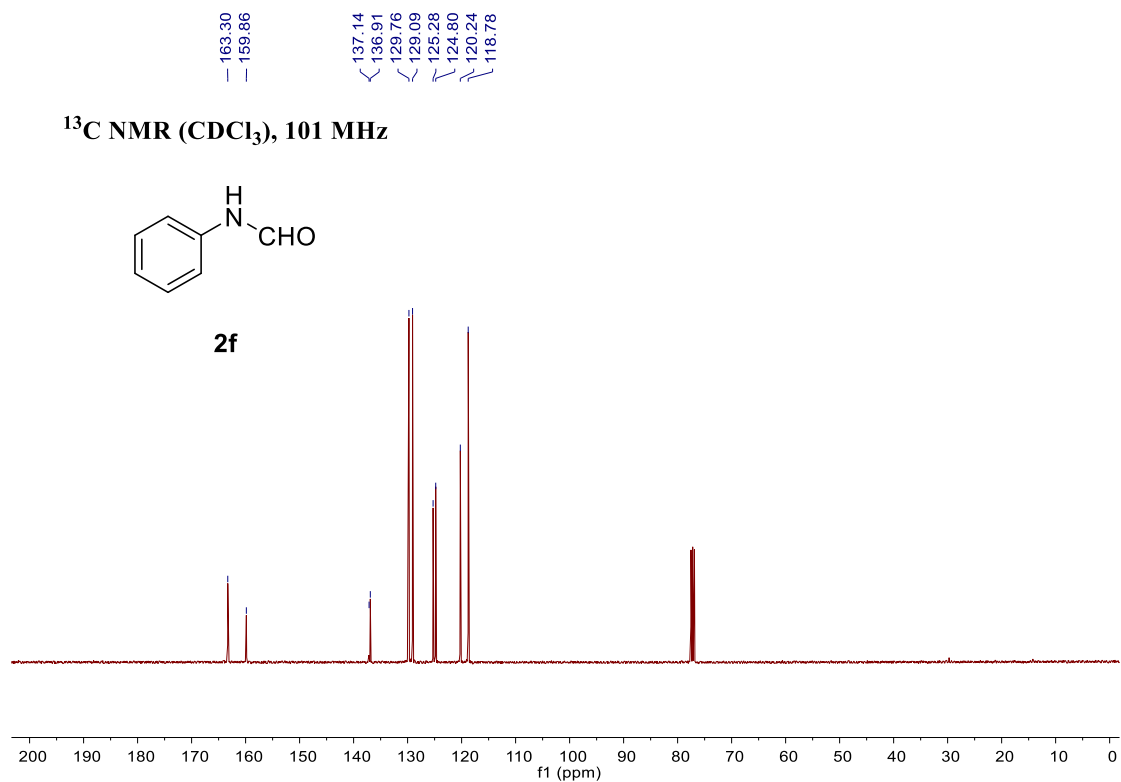


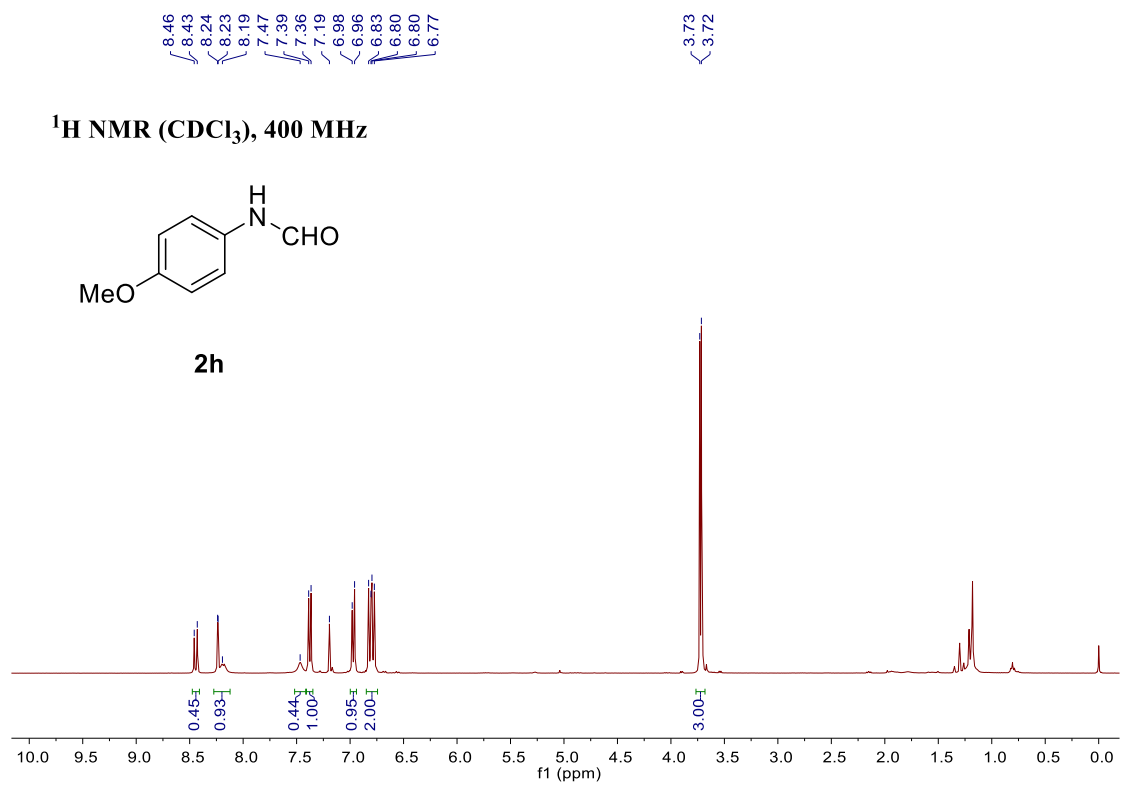
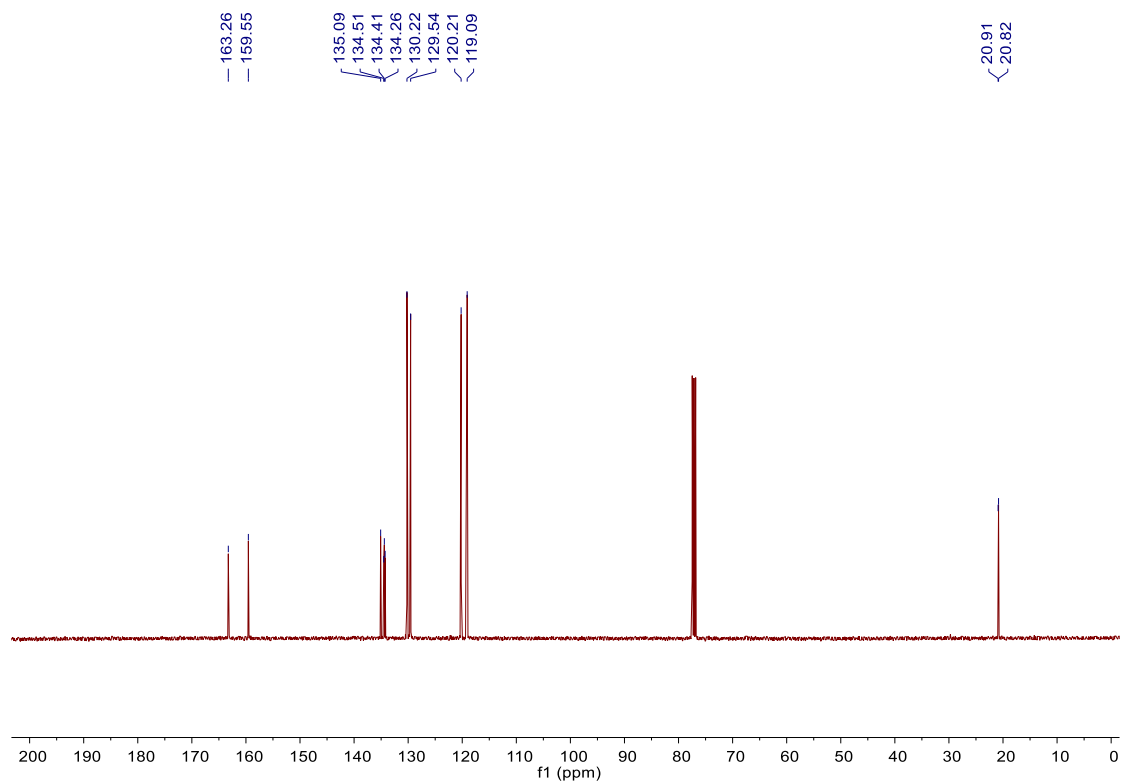
2d



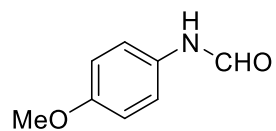




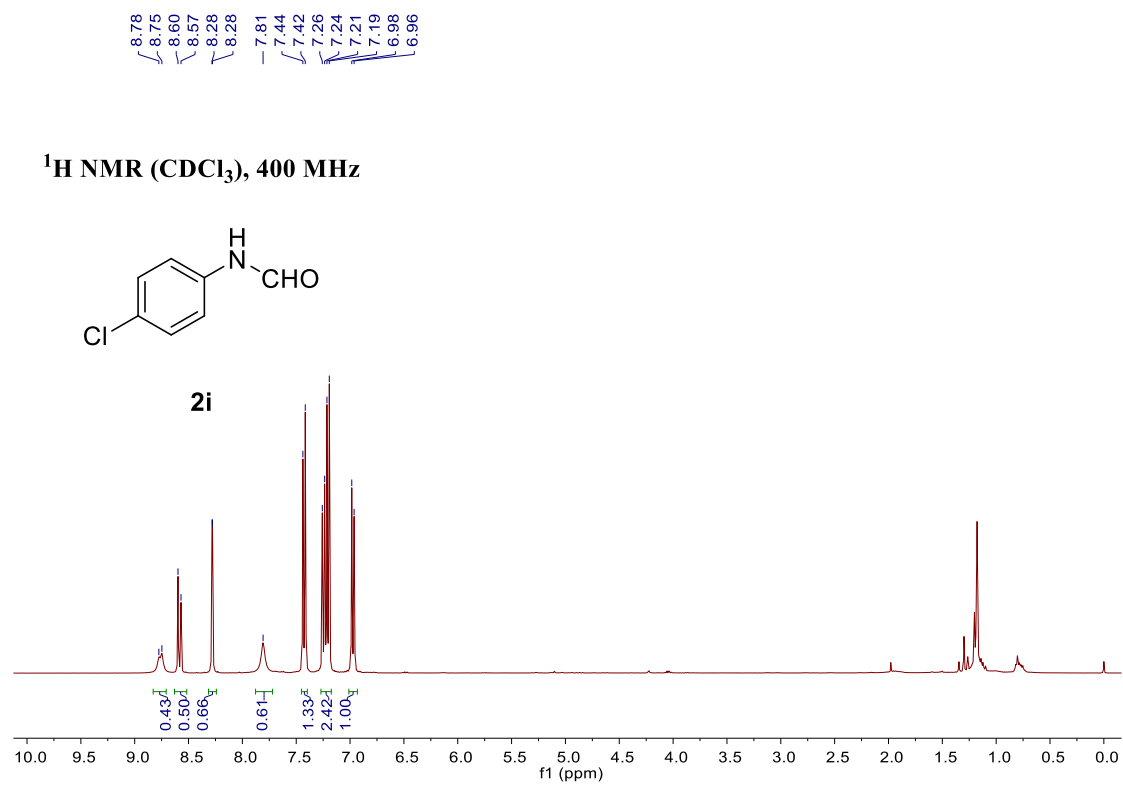
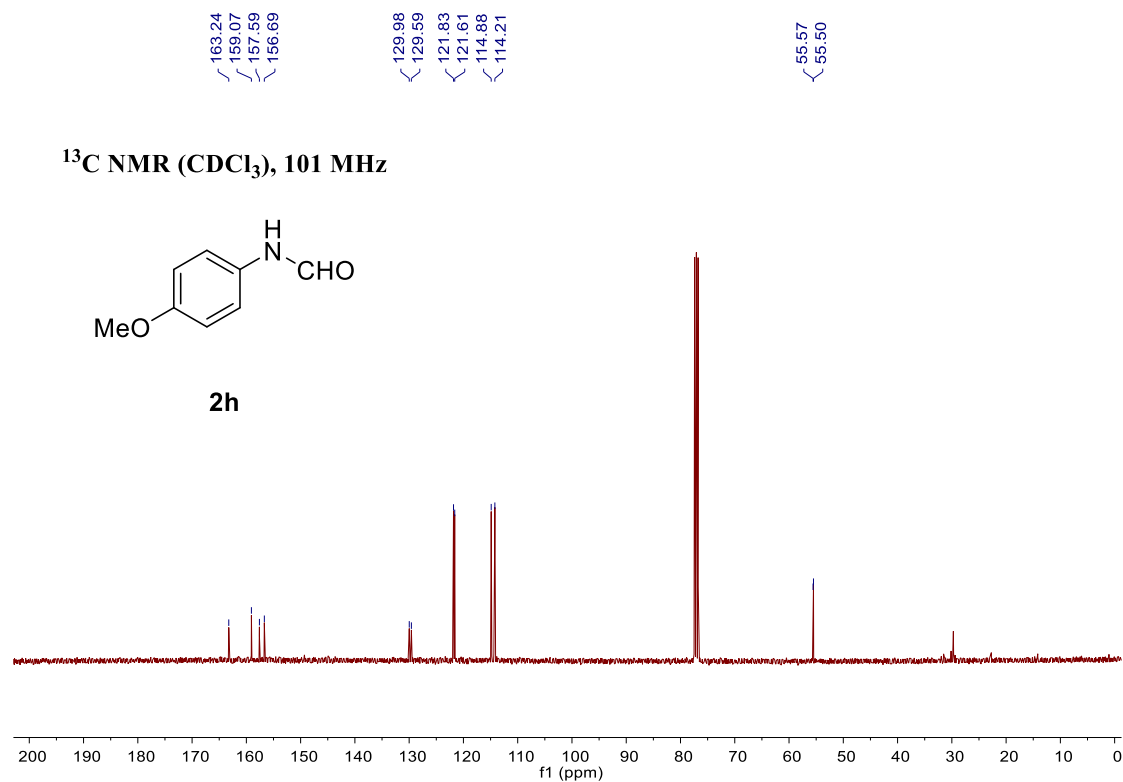




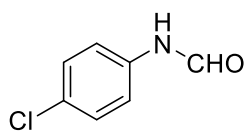
¹H NMR (CDCl₃), 400 MHz



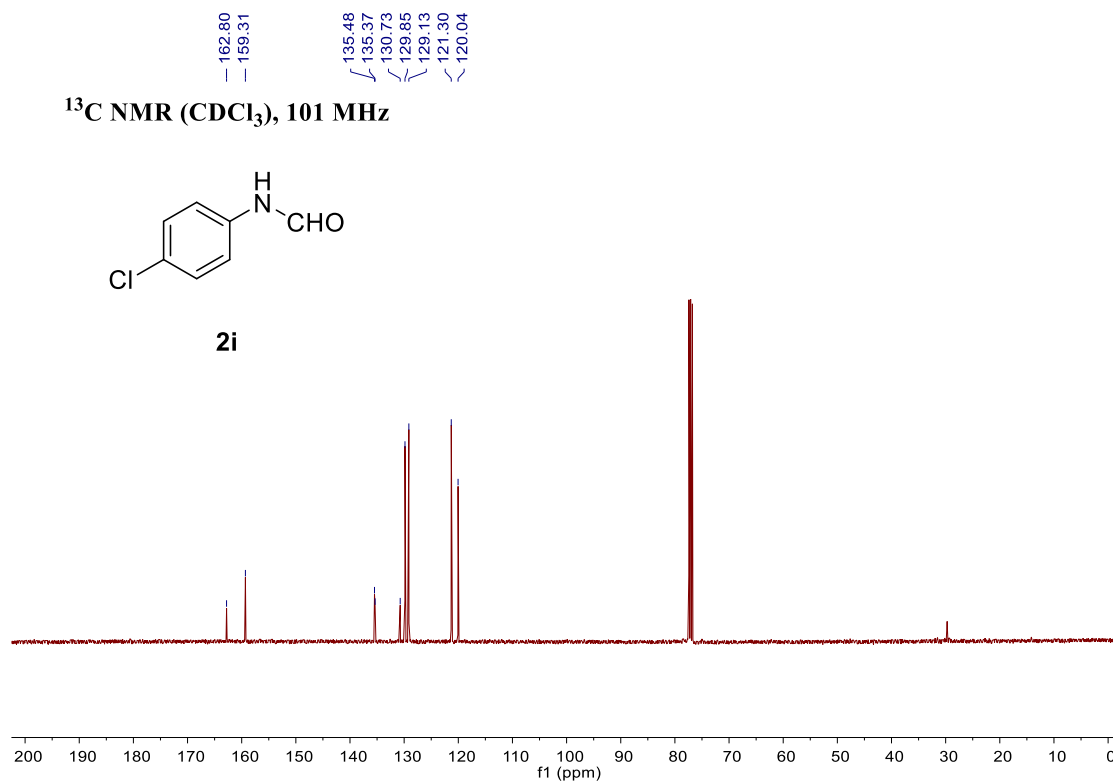
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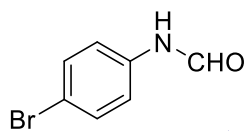
^{13}C NMR (CDCl_3), 101 MHz



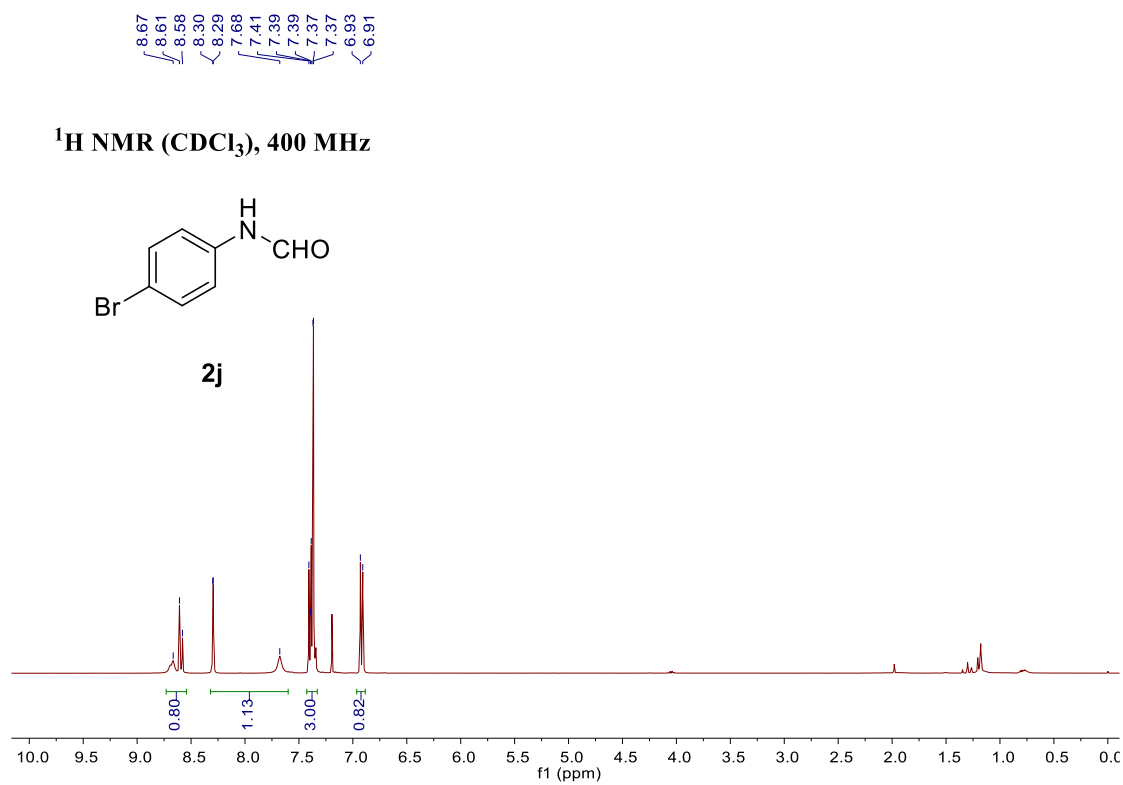
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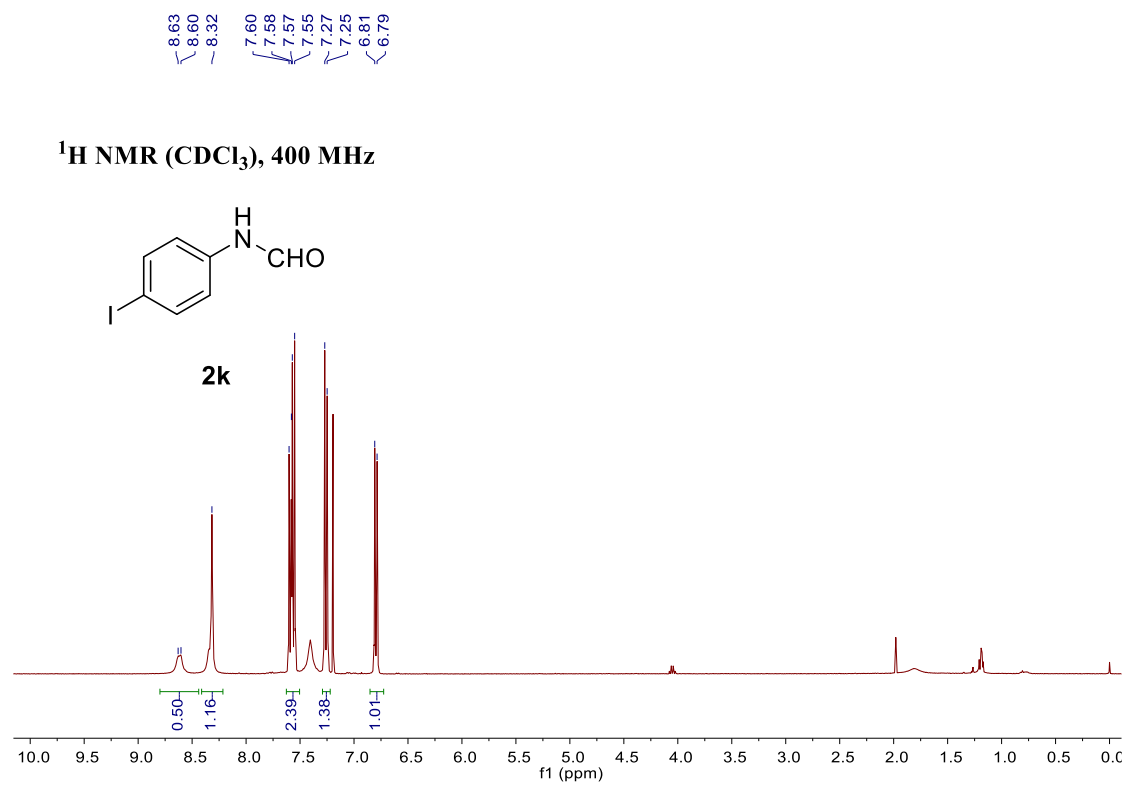
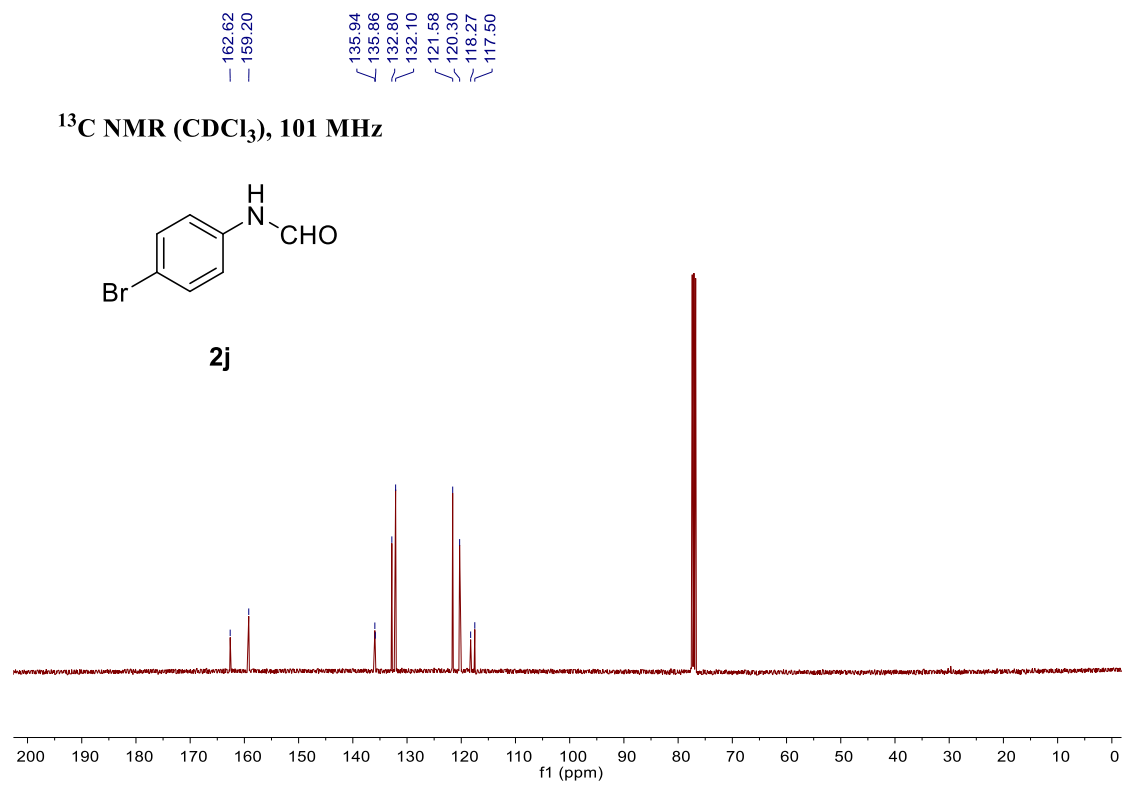


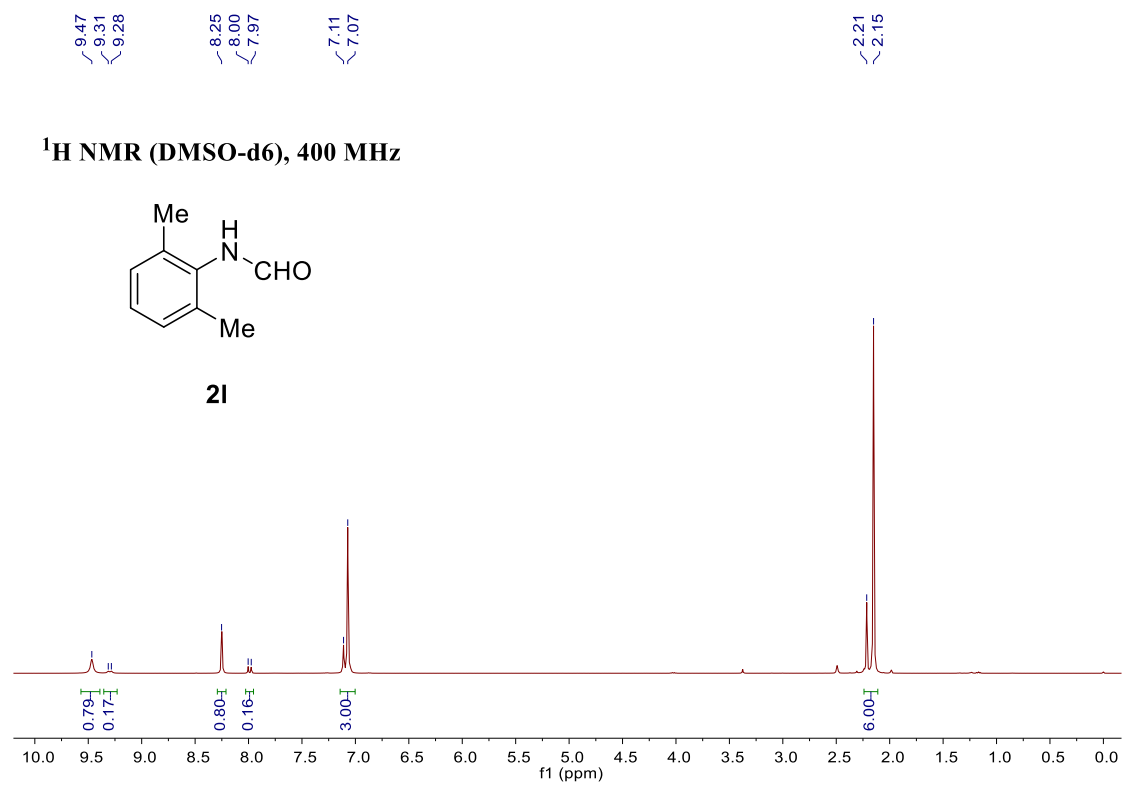
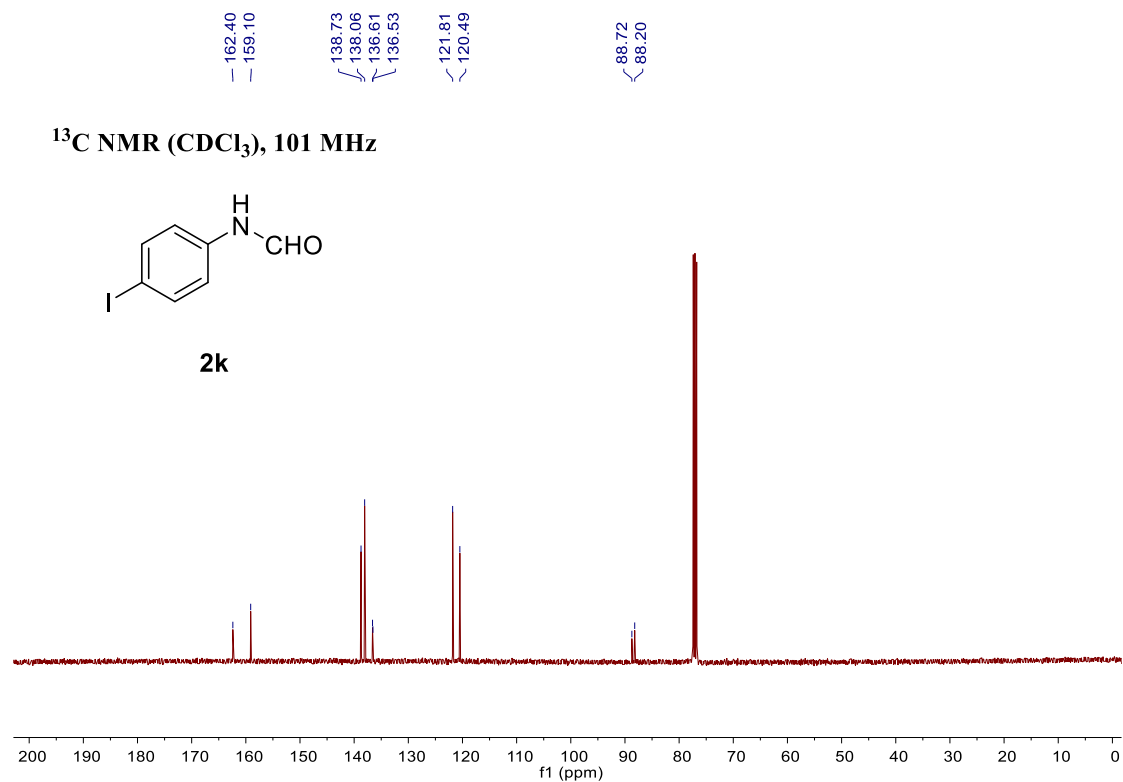
^1H NMR (CDCl_3), 400 MHz

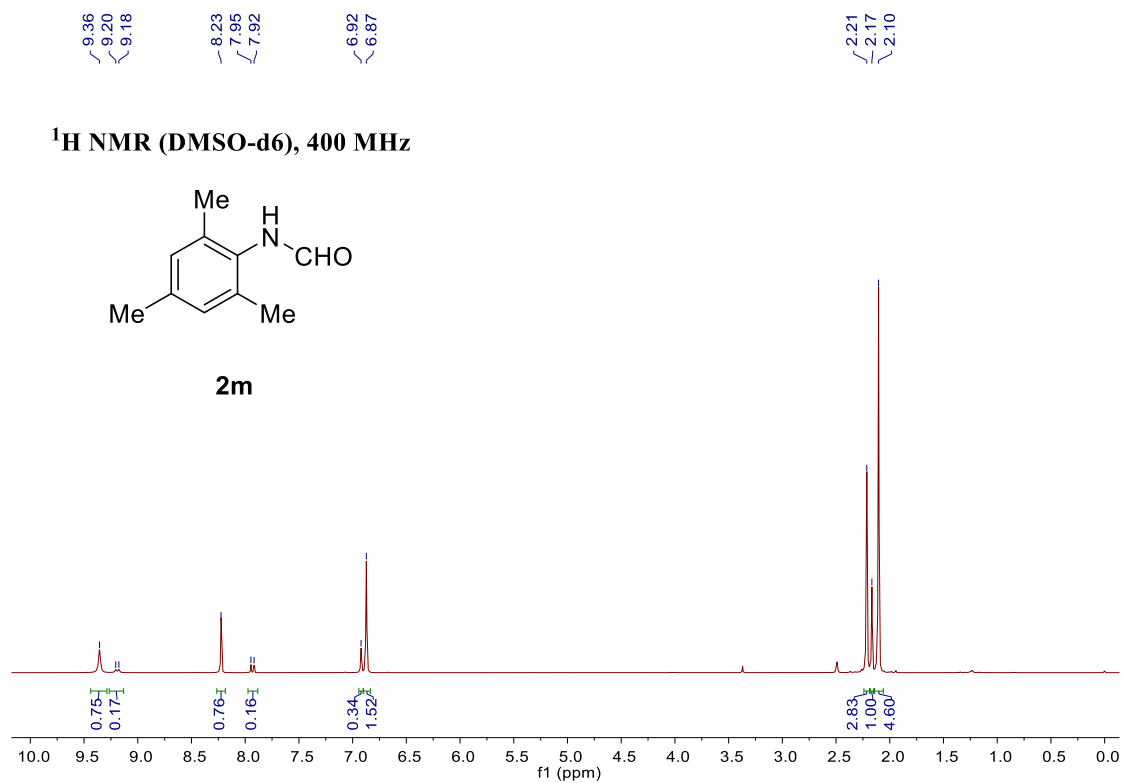
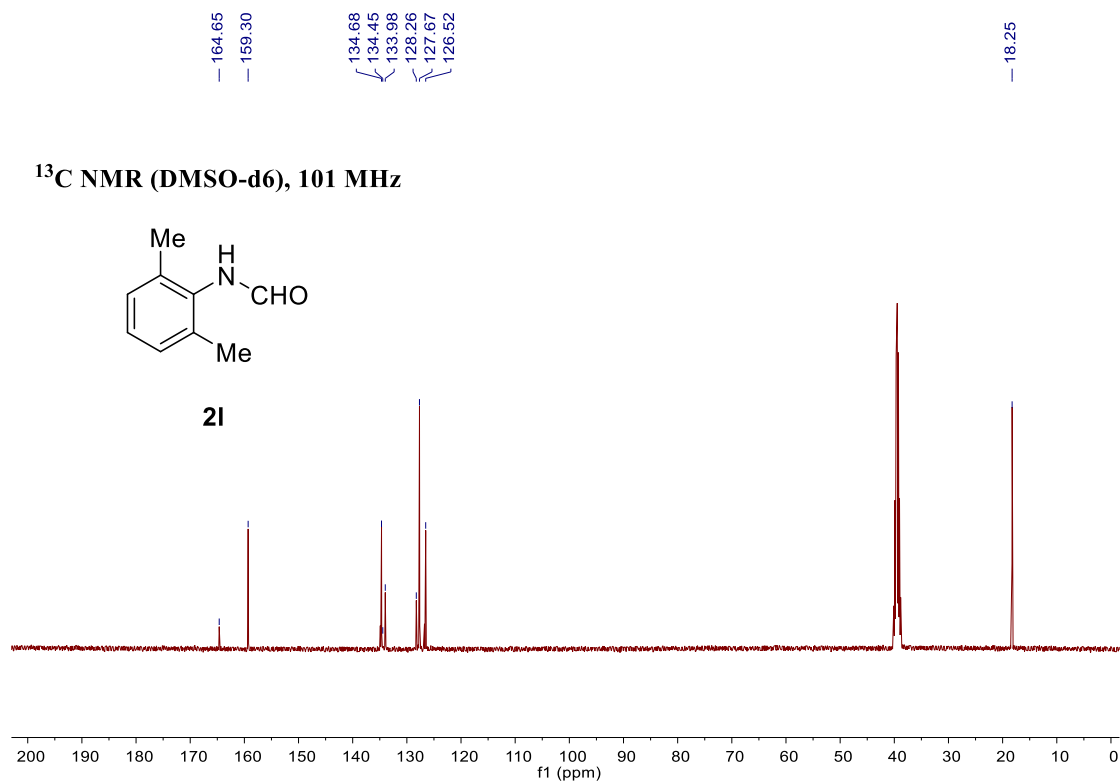


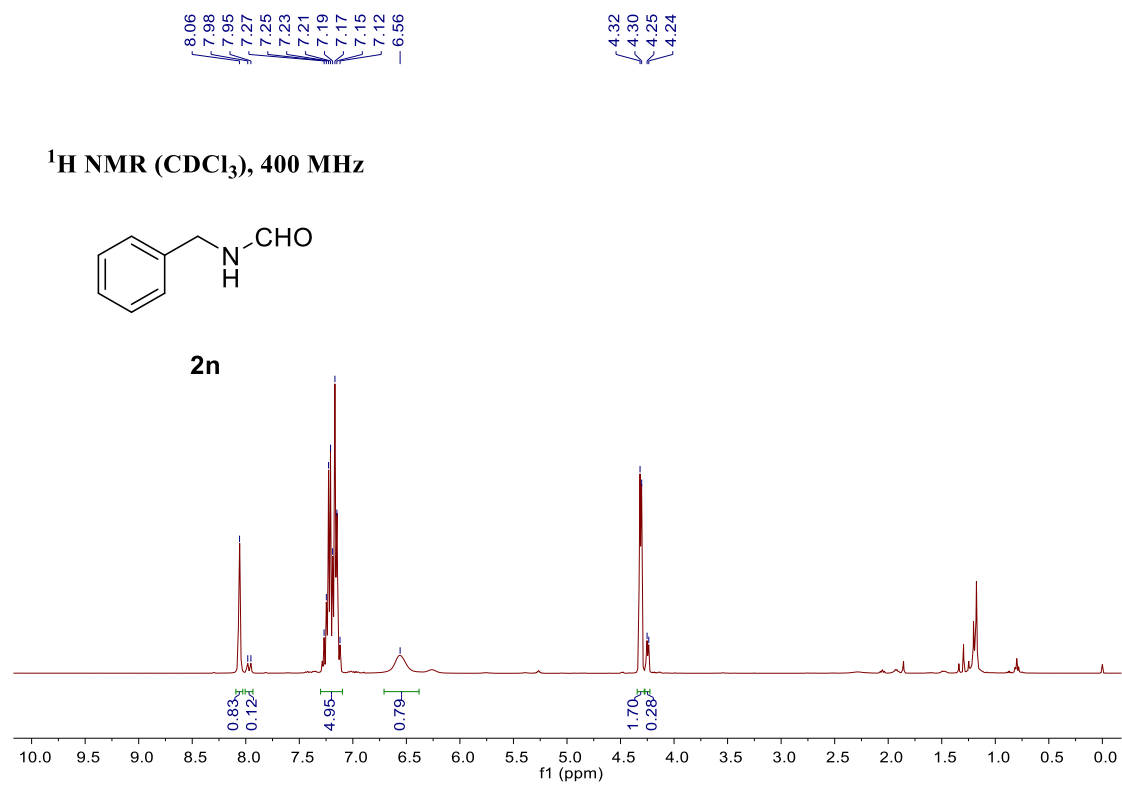
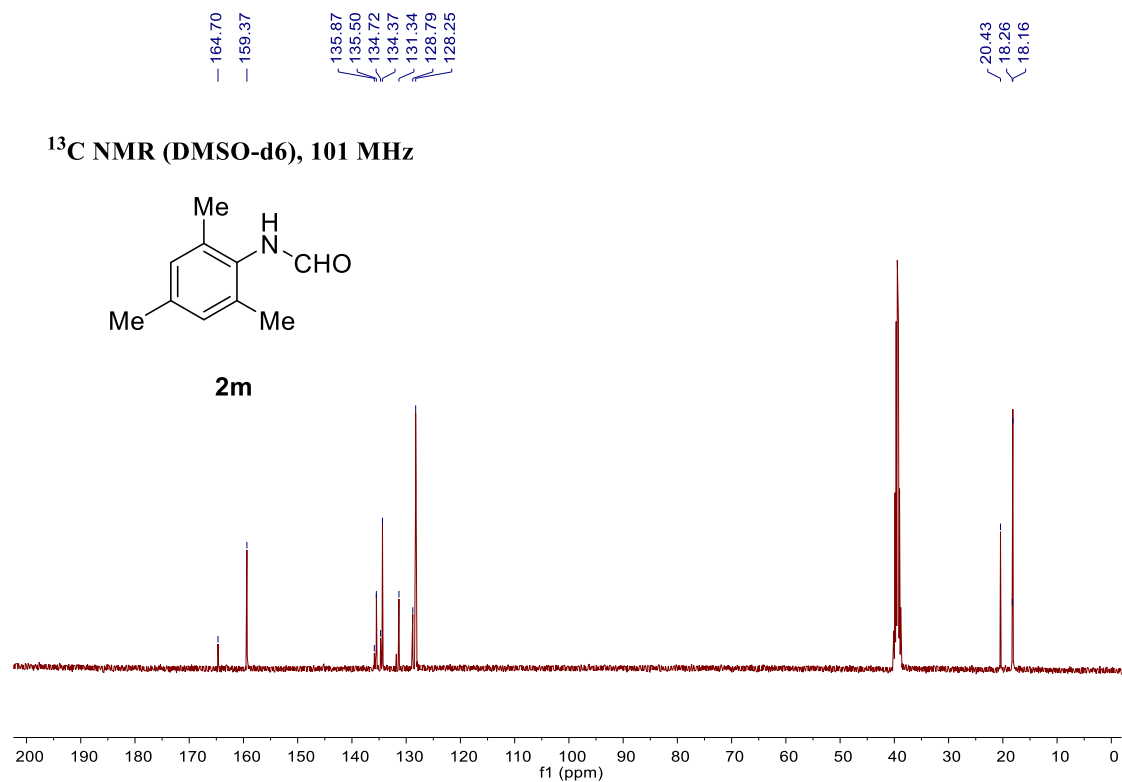
2j

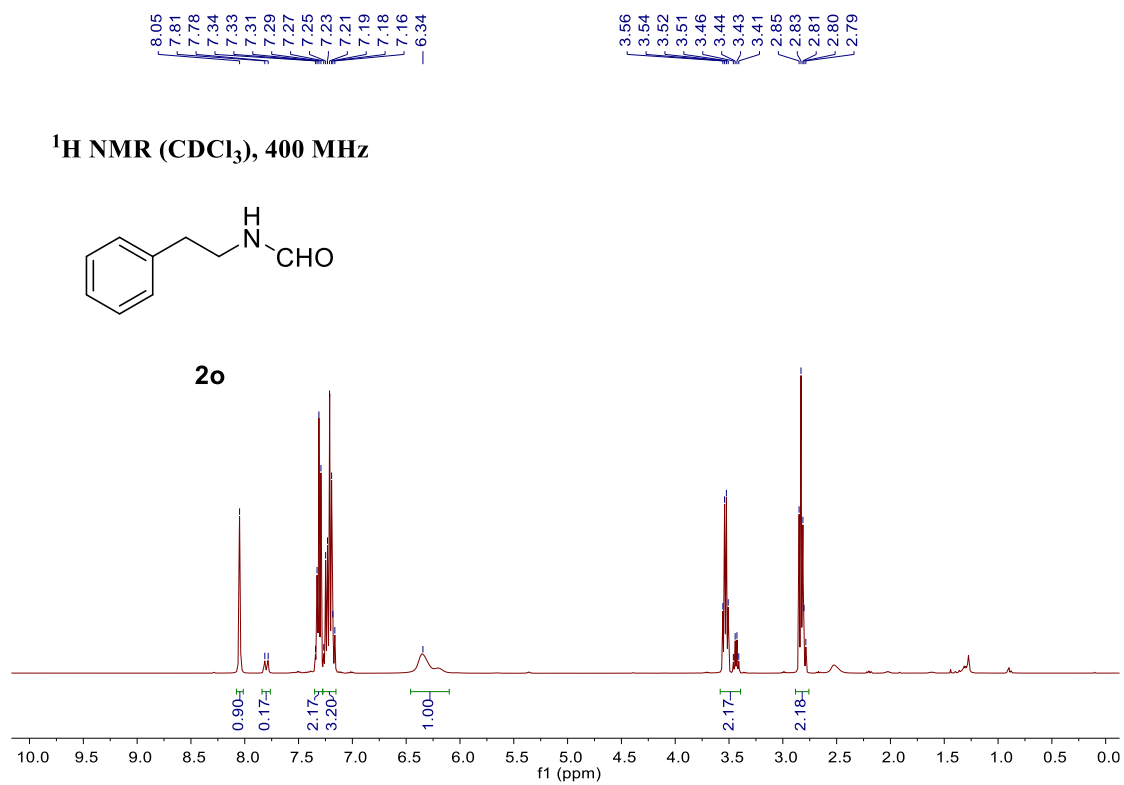
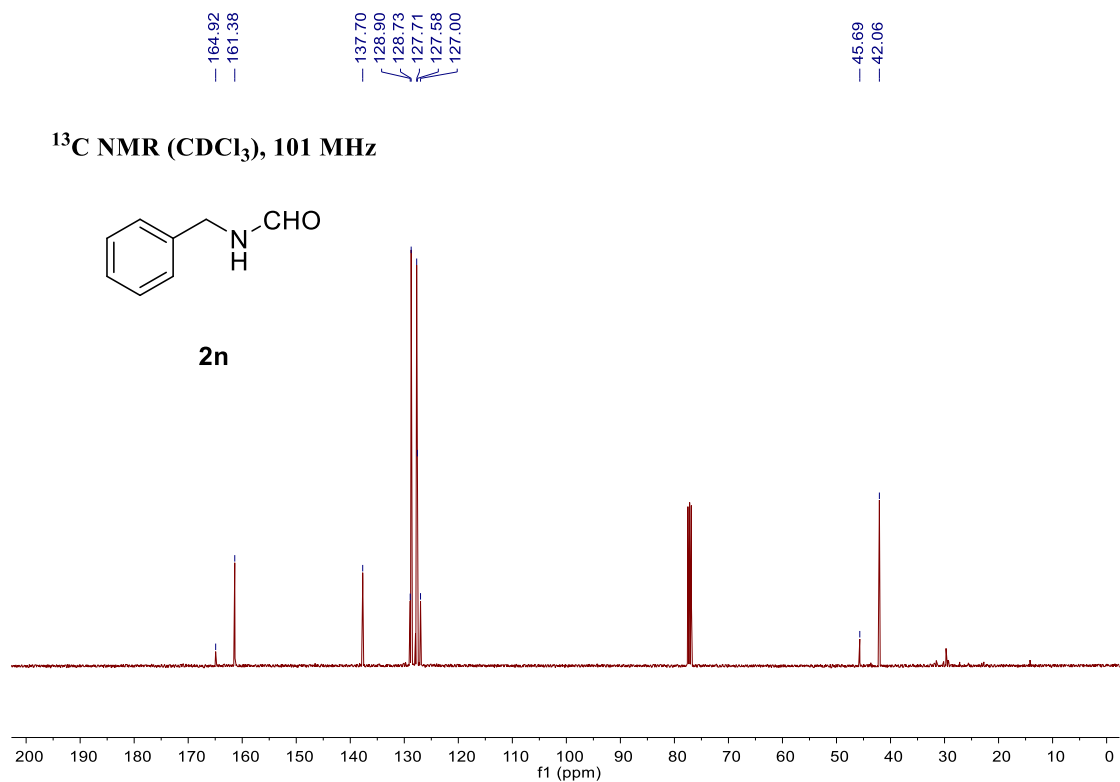


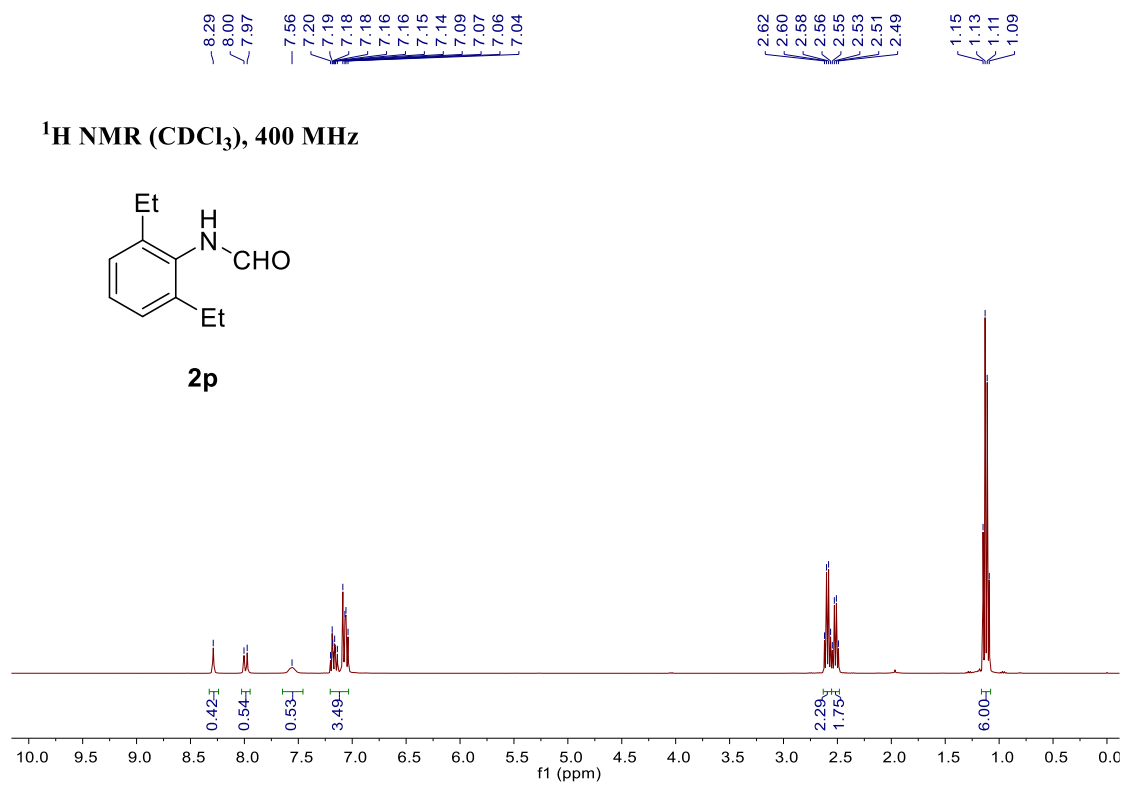
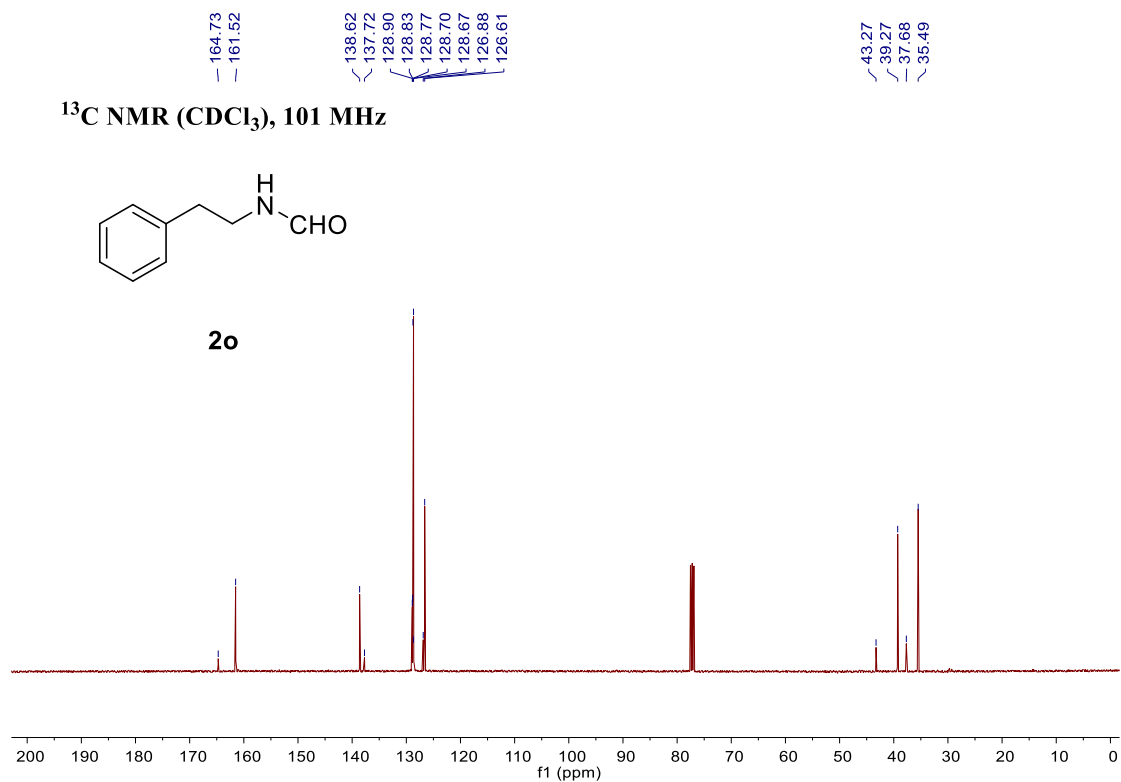


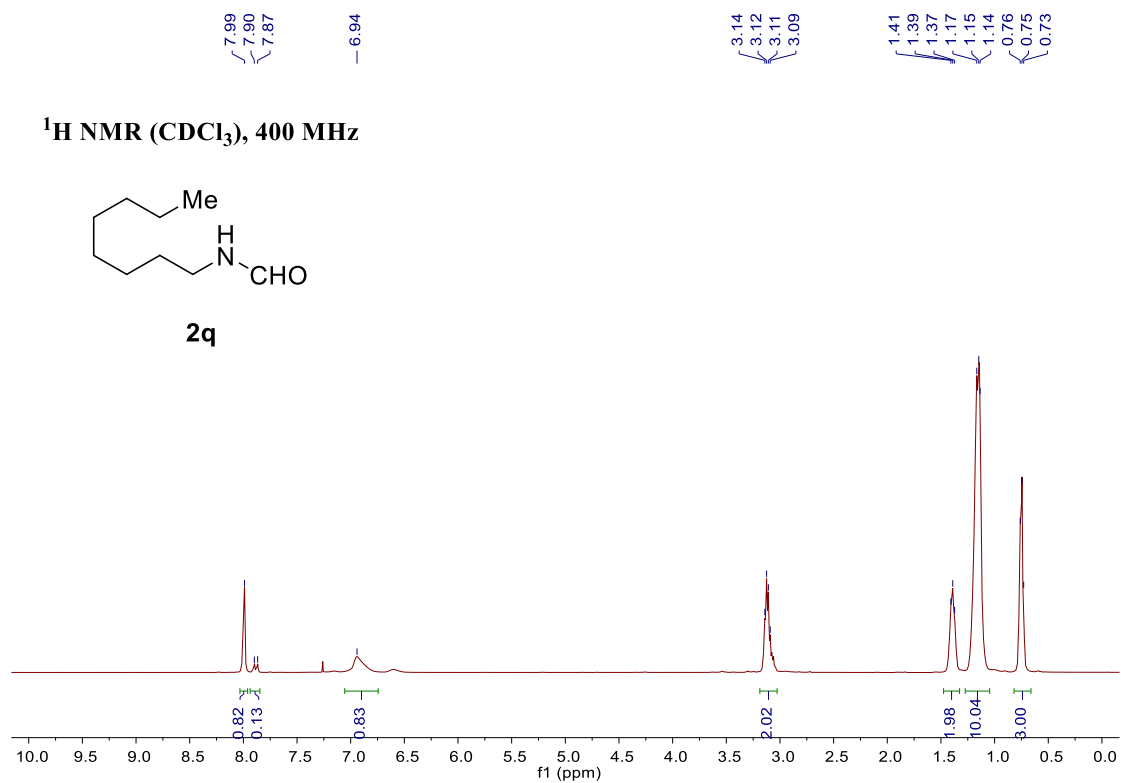
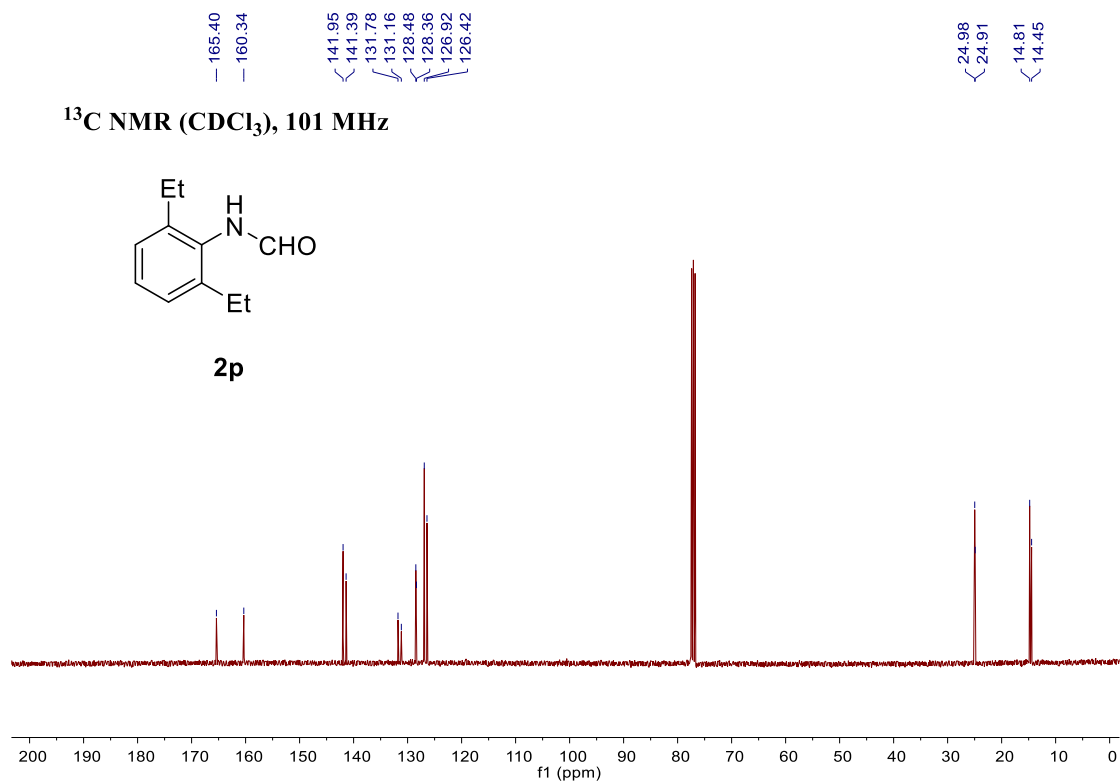


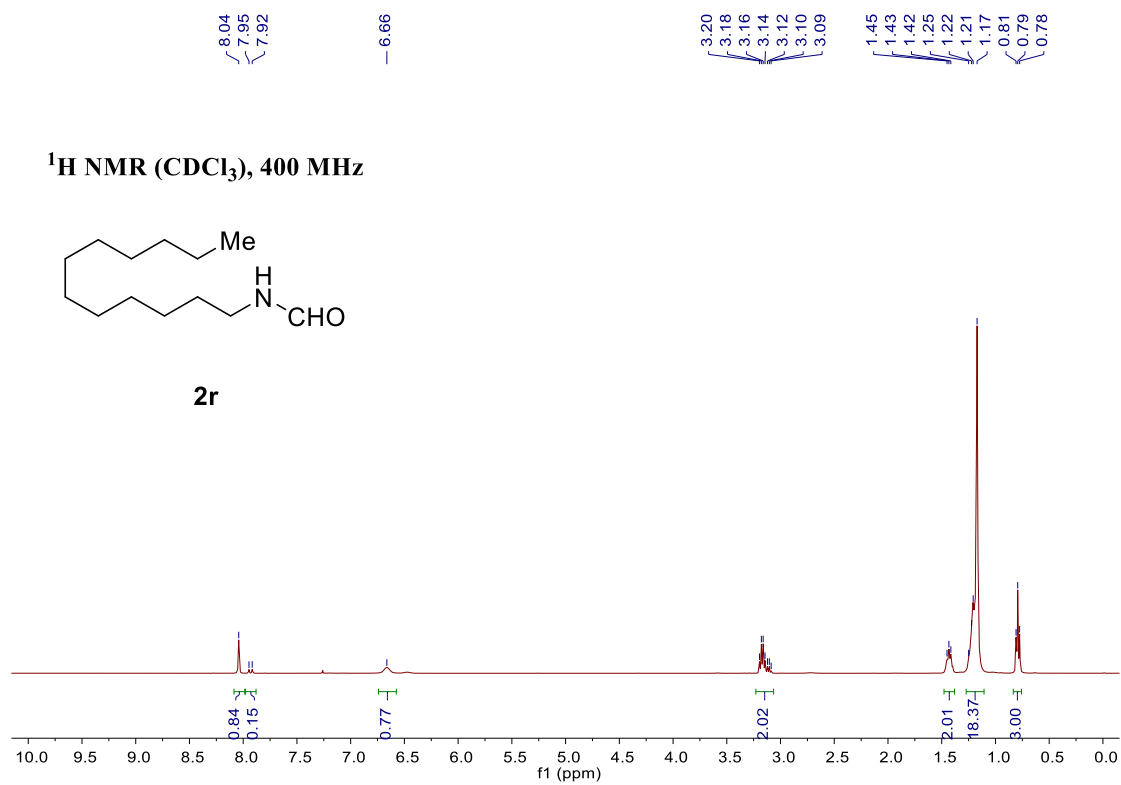
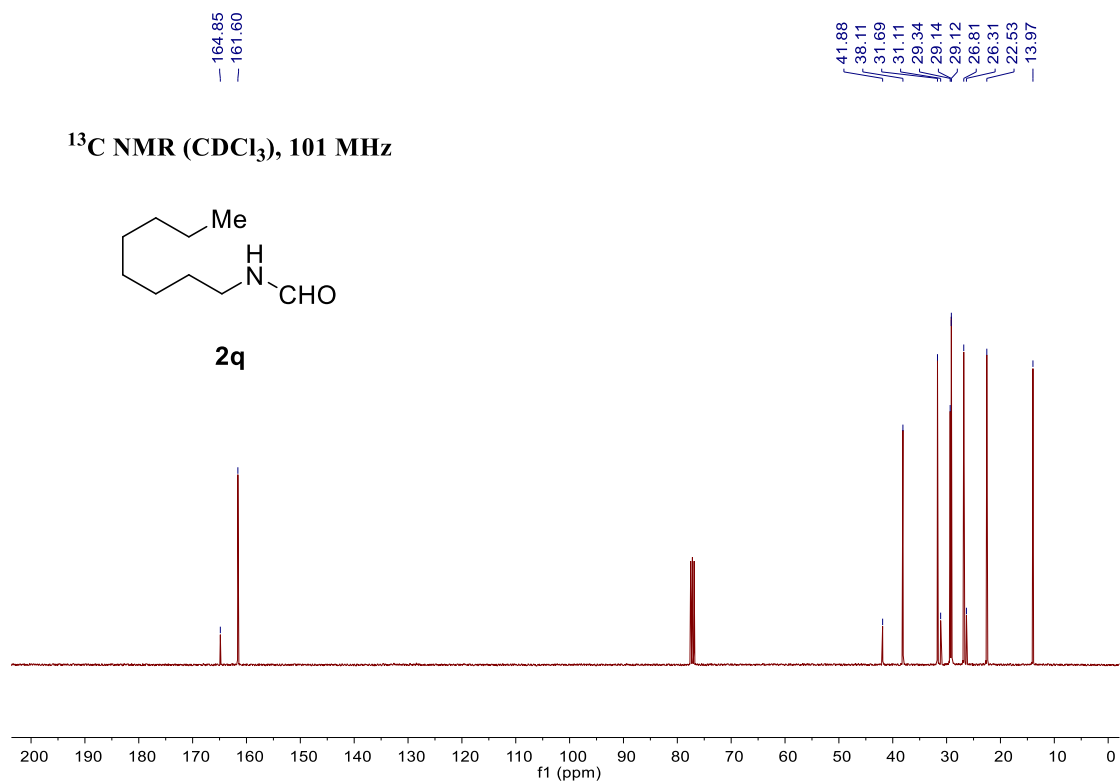




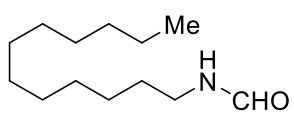








¹³C NMR (CDCl₃), 101 MHz



2r

