Supporting Information

Triphenylphosphine mediated Ir/Ni Dual Photoredox Catalyzed C(sp^2)-C(sp^3) coupling of alkyl alcohol and aryl bromide

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Materials and Methods

All reactions dealing with air- or moisture-sensitive compounds were carried out in an oven dried, sealed Borosil Glass under an atmosphere of nitrogen unless stated otherwise. Analytical thin-layer chromatography was performed on Aluminum plates coated with Silica gel 60 F254 (Merck). Flash silica gel column chromatography was performed on silica gel 230-400 mesh from Orochem .^{1}H NMR spectra were measured on a Bruker-400 MHz spectrometer and reported in parts per million. ^{1}H NMR spectra recorded at 400 MHz in $CDCl_3$, and ^{13}C NMR spectra were recorded at 100 MHz and referenced to the solvent resonance. were recorded on a Mass Spectrometer from Waters (Acquity QDa Mass Spectrometer) equipped with an electrospray source (Polarity: Positive and Negative Polarity Switch) (GC/GCMS data is not part of article or SI). High resolution mass spectra (HRMS) were recorded on the Exactive Mass Spectrometer (Thermo Scientific, USA) equipped with ESI ionization source. All reactions are performed using Penn photo reactor and Kessile photo reactor.

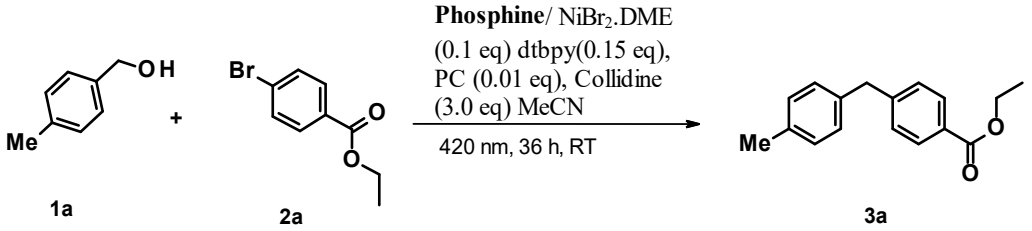
Materials: Unless otherwise noted, all materials were purchased from commercial suppliers and used as received. Solvents were used as commercial grade and bubbled with dry Nitrogen flow. Ir Catalyst, Collidine, dtbpy, triphenylphosphine, $NiBr_2$.dme were purchased from Aldrich Inc and BLD and used as received.

Optimization of Reaction conditions

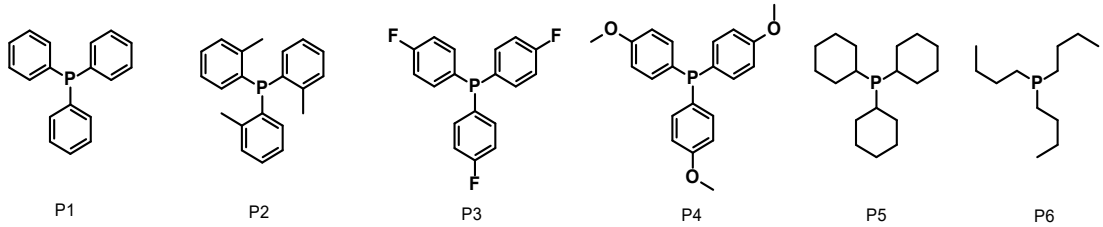
General procedure

To an oven dried Borosil glass vial charged with magnetic stir bar, **1a** (1.315 mmol), **2a** (0.438 mmol) collidine (1.315 mmol), followed by MeCN (10 ml). Reaction mixture stirred for 5 min with degassing by Nitrogen gas. In a separate vial, $NiBr_2$ DME complex (0.048 mmol) and dtbpy (0.065 mmol) dissolved in 1 ml of MeCN under nitrogen atmosphere. This green colored solution then transferred to reaction vial under nitrogen atmosphere followed by photocatalyst (PC) (0.006 mmol). Reaction was degassed for 5 min followed by addition of Triphenylphosphine (TPP) (0.877 mmol) under nitrogen. Vial was capped under nitrogen and sealed with Teflon tape. Reaction was stirred under 420 nm (blue light) in Penn photo reactor. Reaction conditions were optimized by following this general procedure for different parameters.

Table S1. Phosphine screening and Optimization.

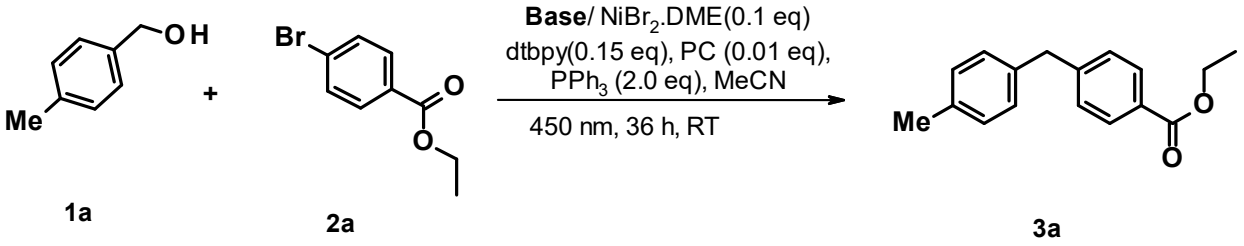


Entry[a]	Phosphine	Yield[b]
1	-	NP
2	P1 (1.5 eq)	71%
3	P2	12%
4	P3	NP
5	P4	traces
6	P5	NP
7	P6	NP
8	P1 (TBAB additive)	46%
9	P1 (open air)	25%
10	P1 (2.0 eq)	62%
11	P1 (3.0 eq)	55%



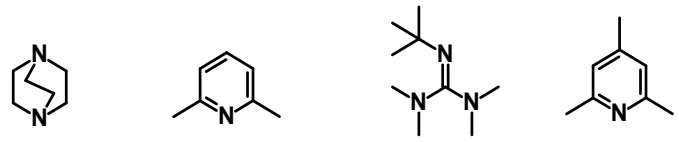
[a]Conditions: **1a** (1.315 mmol, 3.0 eq.), **2a** (0.438 mmol, 1.0 eq.), $NiBr_2$.DME (0.048 mmol, 0.1 eq.), dtbpy (0.065 mmol, 0.15 eq.), PC (0.006 mmol, 0.015eq.), collidine (1.315 mmol, 3.0 eq.), Phosphine, MeCN (10 ml), 420 nm, RT, 36h;[b]Isolated yields were given

Table S2. **Base screening and Optimization.**



1a 2a 3a

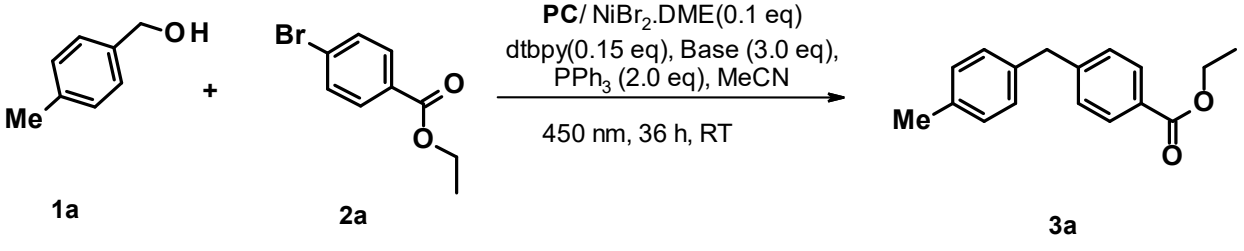
Entry[a]	Base	Yield[b]
1	DABCO	NP
2	Lutidine	traces
3	K_3PO_4	NP
4	Barton's Base	NP
5	Collidine	65%



DABCO Lutidine Barton's Base Collidine

[a]Conditions: **1a** (1.315 mmol), **2a** (0.438 mmol), $NiBr_2$.DME (0.048mmol), dtbpy (0.065 mmol), PC (0.006 mmol), Base (X mmol), Phosphine (0.877 mmol), MeCN (10 ml), 450 nm, RT, 36 h;[b]Isolated yields were given.

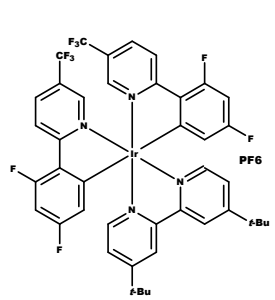
Table S3 Photocatalyst screening



1a 2a 3a

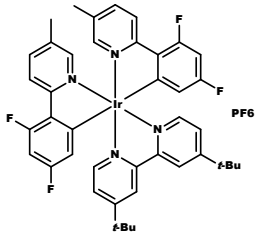
Entry[a]	PC	Yield[b]

1	-	NP
2	PC-1	67%
3	PC-2	Traces
4	PC-3	NP
5	PC-4	NP
6	PC-1 (2.5 mol%)	61%
7	PC-1 (1.5 mol%)	59%



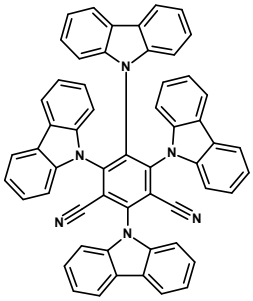
(Ir[dF(CF3)ppy]2(dtbpy))PF6

PC-1



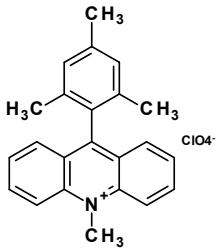
[Ir(dF(Meppy)2(dtbbpy)]PF6

PC-2



4CzIPN

PC-3

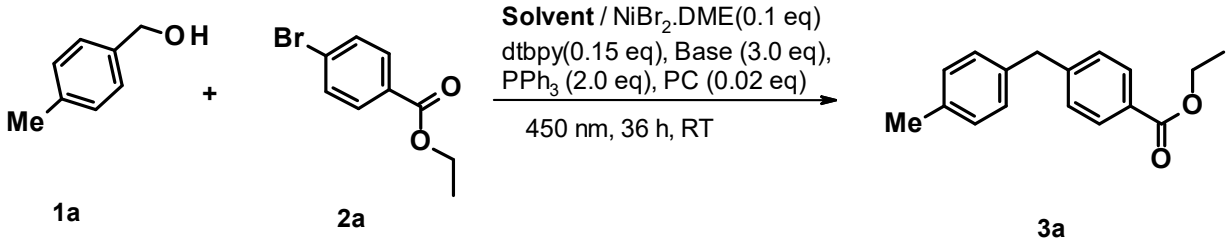


9-Mesityl-10-methylacridinium perchlorate

PC-4

[a]Conditions: **1a** (1.315 mmol), **2a** (0.4 mmol), $NiBr_2$.DME (0.048mmol), dtbpy (0.065 mmol), PC (0.009 mmol), Base (1.315 mmol), Phosphine (0.877 mmol), MeCN (10 ml), 450 nm, RT, 36h; [b]Isolated yields were given

Table S4 Solvent screening



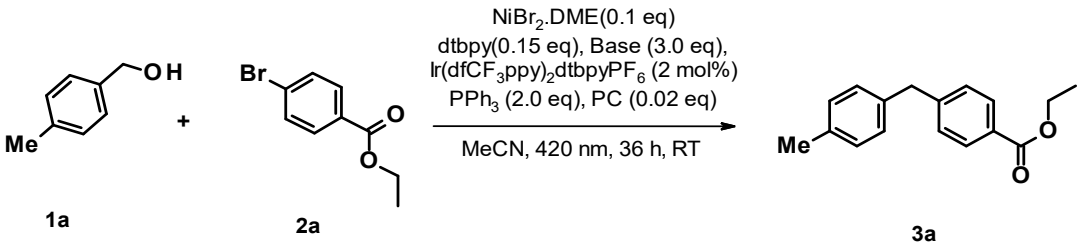
1a 2a 3a

Entry[a]	Solvent	Yield[b]
1	MeCN	65%
2	THF	Traces
3	DMF	7%
4	Toluene	NP
5	DCE	NP

6	2-Me-THF	Traces

[a]Conditions: **1a** (1.315 mmol), **2a** (0.438 mmol), $NiBr_2$.DME (0.048mmol), dtbpy (0.065 mmol), PC (0.009 mmol), collidine (1.315 mmol), Phosphine (0.877 mmol), Solvent (10 ml), 450 nm, RT, 36h; [b]Isolated yields were given.

Table S4 Control experiments

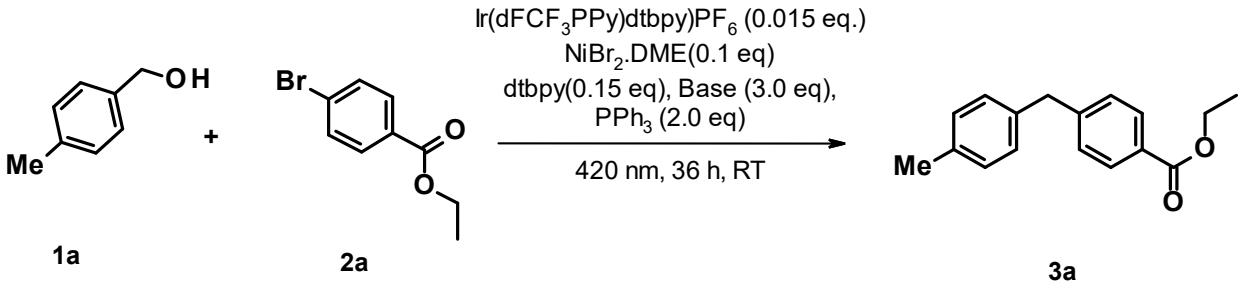


1a **2a** **3a**

Entry	Deviation from standard condition	Results[b]
1	none	71%
2	No PPh_3	0%
3	No light	0%
4	No PC	0%
5	No Base	traces
6	No Nickel	0%
7	No ligand	traces

[a]Conditions: **1a** (1.315 mmol), **2a** (0.438 mmol), $NiBr_2$.DME (0.048mmol), dtbpy (0.065 mmol), PC (0.006 mmol), collidine (1.315 mmol), Phosphine, MeCN (10 ml), 420 nm, RT, 36h;[b]Isolated yields were given.

General Procedure A Deoxygenative C(sp^2)-C(sp^3) Coupling with Alcohol and Aryl bromide.



A 20 mL oven-dried vial equipped with a magnetic stir bar was charged with Alcohol (2.631 mmol, 3.0 eq), Aryl bromide (0.87 mmol, 1.0 eq), and collidine (2.631 mmol, 3.0 eq), followed by the addition of MeCN (20 mL). The reaction mixture was stirred for 5 minutes while degassing with nitrogen. In a separate vial, $NiBr_2$.DME (0.087 mmol, 0.1 eq) and dtbpy (0.131 mmol 0.15 eq) were dissolved in 0.5 mL MeCN under a nitrogen atmosphere. The resulting, green-colored nickel complex solution was transferred *via* syringe to the reaction vial under nitrogen, followed by the addition of PC (0.0131 mmol, 0.015 eq) with stirring. The reaction vial was then degassed with nitrogen for 5 minutes, after which triphenyl phosphine (1.754 mmol, 2.0 eq) was added under a nitrogen atmosphere. The vial was capped under nitrogen gas and sealed with Teflon tape. Finally, the reaction vial was stirred at 250 rpm and irradiated with a 420 nm LED at 50% intensity in a Penn photoreactor for 36 hours, with the fan speed kept at 6000 rpm.

After this time, the reaction mixture was diluted with TBME (30 ml) and 2N HCl solution. The aqueous layer was extracted with TBME two times (20 ml X 2). The combined organic layer was washed with brine solution and dried over anhydrous Sodium sulphate. Organic was filtered out and the solution was evaporated, and the crude product was purified via silica gel column chromatography.

General Procedure B Deoxygenative C(sp2)-C(sp3) Coupling with Alcohol and Aryl bromide.

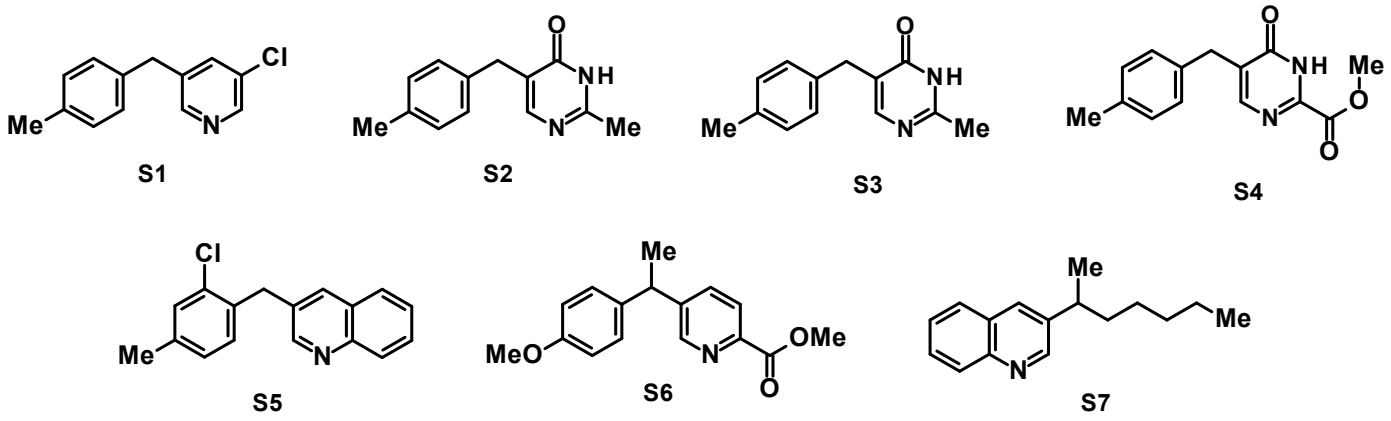
A 20 mL oven-dried vial equipped with a magnetic stir bar was charged with Alcohol (2.631 mmol, 3.0 eq), Aryl bromide (0.87 mmol, 1.0 eq), and collidine (2.631 mmol, 3.0 eq), followed by the addition of MeCN (20 mL). The reaction mixture was stirred for 5 minutes while degassing with nitrogen. In a separate vial, $NiBr_2$.DME (0.087 mmol, 0.1 eq) and dtbpy (0.131 mmol, 0.15 eq) were dissolved in 0.5 mL MeCN under a nitrogen atmosphere. The resulting, green-colored nickel complex solution was transferred via syringe to the reaction vial under nitrogen, followed by the addition of PC (0.0131 mmol, 0.015 eq) with stirring. The reaction vial was then degassed with nitrogen for 5 minutes, after which triphenylphosphine (1.754 mmol, 2.0 eq) was added under a nitrogen atmosphere. The vial was capped

under nitrogen gas and sealed with Teflon tape. Finally, the reaction vial was stirred at 250 rpm and irradiated with a 420 nm LED at 50% intensity in a Penn photoreactor for 36 hours, with the fan speed kept at 6000 rpm.

After this time, the reaction mixture was evaporated to get gummy crude product. Further to remove TPPO from crude product, $CaBr_2$ (15.41 mmol) was added to reaction followed by stirring in Toluene (20 ml) for 1h at rt. White precipitate was filtered through sintered funnel and triphenyl phosphine (TPPO) remains in solid cake along with $CaBr_2$.[1] Filtrate evaporated and adsorbed on silica and Crude product was purified by column chromatography.

General Procedure for chromatographic purification.

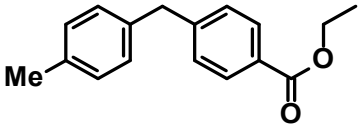
Crude obtained was adsorbed over silica gel (100-200 mesh size) and loaded over prepacked silica column (230-400 mesh 24 gm pack size) with flash chromatographic instrument (combi flash-Teledyne). Column eluted with Ethyl acetate and cyclohexane by gradient elution to get desired product. Column fraction collected according to UV absorption peaks, Pure fractions were concentrated and analyzed by ^{1}H & ^{13}C NMR and HR-MS.



Scheme 1 List of Unsuccessful Substrates

Compound Characterization Data

Ethyl 4-(p-tolylmethyl) benzoate (3a)[2]



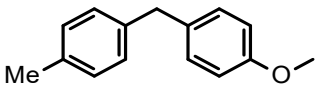
The general procedure A was applied to *p*-tolylmethanol (319.00 mg, 2.631 mmol), ethyl 4-bromobenzoate (200.00 mg, 0.873 mmol), $NiBr_2$.DME (26.00 mg, 0.087 mmol), dtbpy (35.00 mg, 0.131 mmol), PC-1 (14.68 mg, 0.01 mmol), collidine (317.00 mg, 2.63 mmol), Triphenylphosphine (457.00 mg, 1.75 mmol), MeCN (20 ml) at room temperature for 36 h under 420 nm irradiation. Crude product was purified by column chromatography on silica gel (EtOAc/Cyclohexane = 1/10) by gradient elution to afford the title compound as a gum (149 mg) 71% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ (ppm): 7.88 (d, *J*=8 Hz, 2H), 7.17 (d, *J*=8 Hz, 2H), 7.04-6.97 (m, 4H), 4.31-4.25 (q, *J*=8 Hz, 2H), 3.91 (s, 2H), 2.24 (s, 3H), 1.30 (t, *J*=8 Hz, 3H).

^{13}C NMR (100 MHz, CHLOROFORM-*d*) δ (ppm): 166.6, 146.7, 137.1, 135.9, 129.7, 129.3, 128.8, 128.8, 128.3, 60.8, 41.5, 21.0, 14.3.

HRMS (ESI+): Calcd for Molecular formula $[M+H]^+$ $C_{17}H_{18}O_2$: 255.1380; found: 255.1394

1-methoxy-4-(p-tolylmethyl) benzene (3b)[2]



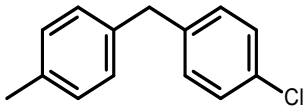
The general procedure A was applied to p-tolylmethanol (395 mg, 3.24 mmol), 1-bromo-4-methoxy-benzene (200 mg, 1.08 mmol), NiBr2.DME (33.29 mg, 0.10 mmol), dtbpy (43 mg, 0.16 mmol), PC (24.23 mg, 0.021 mmol), collidine (392.43 mg, 3.24 mmol), Triphenylphosphine (566 mg, 2.16 mmol), MeCN (20 ml), at room temperature for 36 h under 420 nm irradiation. Crude product was purified by column chromatography on silica gel (EtOAc/Cyclohexane = 1/10) to afford the title compound as a gum (145 mg, 63% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ (ppm): 7.07-7.16 (m, 6H), 6.85 (d, J=8 Hz, 2H), 3.91 (s, 2H), 3.81 (s, 3H), 2.34 (s, 3H)

^{13}C NMR (100 MHz, CHLOROFORM-*d*) δ (ppm): 157.8, 138.6, 135.5, 133.6, 129.8, 129.1, 128.7, 113.8, 55.3, 40.6, 21.0

HRMS (ESI+): Calcd for Molecular formula $[M+H]^{+}$ $C_{15}H_{16}O$: 213.1274; found: 213.1280.

1-chloro-4-(p-tolylmethyl) benzene (3c)[3]



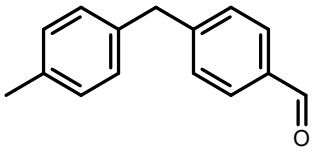
The general procedure A was applied to p-tolylmethanol (382 mg, 3.13 mmol), 1-bromo-4-chloro-benzene (200 mg, 1.04 mmol), NiBr2.DME (33.29 mg, 0.10 mmol), dtbpy (43 mg, 0.15 mmol), PC (24.23 mg, 0.015 mmol), collidine (392.43 mg, 3.13 mmol), Triphenylphosphine (566 mg, 2.89 mmol), MeCN (20 ml), at room temperature for 36 h under 420 nm irradiation. Crude product was purified by column chromatography on silica gel (EtOAc/Cyclohexane = 1/10) to afford the title compound as a gum (78 mg, 53% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ (ppm): 7.28-7.26 (d, *J* = 8.0 Hz, 2H), 7.14-7.05 (m, 6H), 3.93 (s, 2H), 2.35 (s, 3H)

^{13}C NMR (100 MHz, CHLOROFORM-*d*) δ (ppm): 139.9, 137.5, 135.8, 131.8, 130.2, 129.3, 128.7, 128.5, 40.8, 21.0

HRMS (ESI+): Calcd for Molecular formula $[M+H]^{+}$ $C_{14}H_{13}Cl$: 217.0779 ; found: 217.0785.

4-(p-tolylmethyl) benzaldehyde (3d)[4]



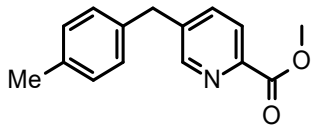
The general procedure A was applied to p-tolylmethanol **(**377 mg, 2.37 mmol), 4-bromo-benzaldehyde (200 mg, 0.79 mmol), $NiBr_2$.DME (31.29 mg, 0.07 mmol), dtbpy (41 mg, 0.11 mmol), PC (17.23 mg, 0.011 mmol), collidine (374.43 mg, 2.37 mmol), Triphenylphosphine (540 mg, 1.58 mmol), MeCN (20 ml) at room temperature for 36 h under 420 nm. Crude product was purified by column chromatography on silica gel (EtOAc/Cyclohexane = 1/10) to afford the title compound as gum (137 mg) 60% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ (ppm): 9.99 (s, 1H), 7.81-7.83 (d, *J*=8.25 Hz, 2H), 7.36-7.38 (d, *J*=8.00 Hz, 2H), 7.08 - 7.14 (m, 4H), 4.04 (s, 2 H), 2.35 (s, 3H)

^{13}C NMR (100 MHz, CHLOROFORM-*d*) δ (ppm): 192.0, 148.8, 136.7, 136.1, 134.6, 130.0, 129.5, 129.4, 128.9, 41.7, 21.0

HRMS (ESI+): Calcd for Molecular formula $[M+H]^+$ $C_{15}H_{14}O$: 211.1117; found: 211.1123

methyl 5-(p-tolylmethyl) pyridine-2-carboxylate (3e)



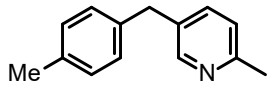
The general procedure B was applied to p-tolylmethanol (338.88 mg, 2.77 mmol), methyl 5-bromopyridine-2-carboxylate (200 mg, 0.92 mmol), $NiBr_2$.DME (28 mg, 0.092 mmol), dtbpy (37.2 mg, 0.138 mmol), PC (20.75 mg, 0.018 mmol), collidine (336 mg, 2.77 mmol), Triphenylphosphine (485 mg, 1.85 mmol), MeCN (20 ml) at room temperature for 36 h under 420 nm irradiation Crude product was purified by column chromatography on silica gel (EtOAc/Cyclohexane = 20/10) to afford the title compound as gum (140 mg, 61% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ (ppm): : 8.65 (s, 1H), 8.06 (d, J=8.0 Hz, 1H), 7.59-7.64 (m, 1H), 7.12-7.17 (m, 2H), 7.05-7.09 (m, 2H), 4.04 (s, 2H), 4.02 (s, 3H), 2.35 (s, 3H)

^{13}C NMR (100 MHz, CHLOROFORM-*d*) δ (ppm): 165.7, 150.2, 145.8, 140.9, 137.2, 136.4, 135.8, 129.5, 128.7, 125.1, 52.9, 38.6, 21.0

HRMS (ESI+): Calculated for Molecular formula $[M+H]^+$ $C_{15}H_{15}NO_2$ 242.1176 Found: 242.1184

2-methyl-5-(p-tolylmethyl) pyridine (3f)



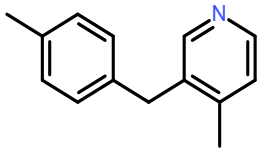
The general procedure B was applied to p-tolylmethanol (425.88 mg, 2.77 mmol), 2-methyl 5-bromopyridine (200 mg, 0.92 mmol), $NiBr_2$.DME (35 mg, 0.092 mmol), dtbpy (46.2 mg, 0.138 mmol), PC (26.75 mg, 0.018 mmol), collidine (422 mg, 2.77 mmol), Triphenylphosphine (609 mg, 1.85 mmol), MeCN (20 ml) at room temperature for 36 h under 420 nm irradiation. Crude product was purified by column chromatography on silica gel (EtOAc/Cyclohexane = 20/10) to afford the title compound as gum (180 mg, 78% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ (ppm): 8.39 (s, 1H), 7.33-7.38 (m, 1H), 7.11 (d, *J*=8 Hz, 2H), 7.06 (d, *J*=8 Hz, 3H), 3.90 (s, 2H), 2.52 (s, 3H), 2.32 (s, 3H)

^{13}C NMR (100 MHz, CHLOROFORM-*d*) δ (ppm): 156.0, 149.2, 137.1, 136.7, 135.9, 133.6, 129.3, 128.6, 123.0, 38.2, 23.9, 21.0

HRMS (ESI+): Calcd for Molecular formula $[M+H]^+$ $C_{14}H_{15}N$ 198.1277 Found: 198.1287

4-methyl-3-(p-tolylmethyl) pyridine (3g)[5]



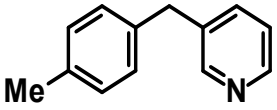
The general procedure B was applied to p-tolylmethanol (425.88 mg, 2.77 mmol), 3-bromo-4-methyl-pyridine(200 mg, 0.92 mmol), $NiBr_2$.DME (35 mg, 0.092 mmol), dtbpy (46.2 mg, 0.138 mmol), PC (26.75 mg, 0.018 mmol), collidine (422 mg, 2.77 mmol), Triphenylphosphine (609 mg, 1.85 mmol), MeCN (20 ml) at room temperature for 36 h under 420 nm irradiation. Crude product was purified by column chromatography on silica gel (EtOAc/Cyclohexane = 20/10) to afford the title compound as a Gummy liquid (105 mg) 58% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ (ppm): 8.37-8.38 (d, *J*=4 Hz, 1H, 2H), 7.08-7.13 (m, 3H), 7.02 (d, *J*=8 Hz, 2H), 3.97 (s, 2H), 2.33 (s, 3H), 2.23 (s, 3H)

^{13}C NMR (100 MHz, CHLOROFORM-*d*) δ (ppm): 157.3, 147.2 137.9, 137.3, 129.2, 128.5, 127.1, 126.0, 121.2, 65.2, 24.2, 21.1

HRMS (ESI+): Calcd for Molecular formula $[M+H]^+$ $C_{14}H_{15}N$ 198.1277 Found: 198.1283

3-(p-tolylmethyl) pyridine (3h)[6]



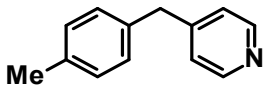
The general procedure B was applied to p-tolylmethanol (392 mg, 3.84 mmol), 3-bromopyridine (200 mg, 1.28 mmol), $NiBr_2$.DME (39.48 mg, 0.12 mmol), dtbpy (51.53 mg, 0.19 mmol), PC (28.74 mg, 0.025 mmol), collidine (465 mg, 3.84 mmol), Triphenylphosphine (671 mg, 2.56 mmol), MeCN (20 ml) at room temperature for 36 h under 420 nm irradiation. Crude product was purified by column chromatography on silica gel (EtOAc/Cyclohexane = 1/10) to afford the title compound as a Gummy (148 mg) 65% yield).

^{1}H NMR (400 MHz, CHLOROFORM-d) δ: 8.51 (d, *J*=2.1 Hz, 1H), 8.47-8.43 (m, 1H), 7.48-7.43 (m, 1H), 7.21-7.16 (m, 1H), 7.11 (d, *J*=8.1 Hz, 2H), 7.07 (d, *J*=8.1 Hz, 2H), 3.96 (s, 2H), 2.33 (s, 3H)

^{13}C NMR (100 MHz, CHLOROFORM-*d*) δ (ppm): 150.1, 147.6, 136.8, 136.7, 136.2, 136.0, 129.4, 128.7, 123.4, 38.7, 21.0

HRMS (ESI+): Calcd for Molecular formula $[M+H]^+$ $C_{13}H_{13}N$ 184.1121 Found: 184.1114

4-(p-tolylmethyl) pyridine (3i)[7]



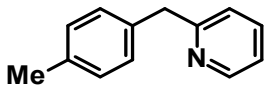
The general procedure B was applied to p-tolylmethanol (509 mg, 3.84 mmol), 4-bromopyridine (200 mg, 1.28 mmol), $NiBr_2$.DME (32.48 mg, 0.12 mmol), dtbpy (41.53 mg, 0.19 mmol), PC (17.74 mg, 0.025 mmol), collidine (378 mg, 3.84 mmol), Triphenylphosphine (545 mg, 2.56 mmol), MeCN (20 ml) at room temperature for 36 h under 420 nm irradiation Crude product was purified by column chromatography on silica gel (EtOAc/Cyclohexane = 1/10) to afford the title compound as a Gummy liquid (97 mg) 53% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ (ppm): 7.96 (d, *J*=8.19 Hz, 2H) 7.51 (d, *J*=7.95 Hz, 2H) 7.26 - 7.28 (m, 2H) 7.23 - 7.26 (m, 2H) 4.18 (s, 2 H) 2.49 (s, 3 H)

^{13}C NMR (100 MHz, CHLOROFORM-*d*) δ (ppm): 149.7, 147.1, 136.4, 135.9, 128.9, 128.3, 123.0, 38.2, 20.6

HRMS (ESI+): Calcd for Molecular formula $[M+H]^+$ $C_{13}H_{13}N$ 184.1121 Found: 184.1114

2-(p-tolylmethyl) pyridine (3j)[8]



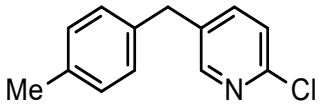
The general procedure B was applied to p-tolylmethanol (623 mg, 3.84 mmol), 2-bromopyridine (200 mg, 1.28 mmol), $NiBr_2$.DME (39.48 mg, 0.12 mmol), dtbpy (51.53 mg, 0.19 mmol), PC (21.74 mg, 0.025 mmol), collidine (462 mg, 3.84 mmol), Triphenylphosphine (667 mg, 2.56 mmol), MeCN (20 ml) at room temperature for 36 h under 420 nm irradiation Crude product was purified by column chromatography on silica gel (EtOAc/Cyclohexane = 1/10) to afford the title compound as a Gummy liquid (112 mg) 69% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ (ppm): 8.55 (d, *J*=8 Hz, 1H) 7.57-7.55 (m, 1H) 7.54-7.40 (m, 2H) 7.18-7.05 (m, 4H), 4.13 (s, 2H), 2.33 (s, 3H)

^{13}C NMR (100 MHz, CHLOROFORM-*d*) δ (ppm): 161.3, 149.3, 136.5, 136.4, 135.9, 129.3, 129.0, 123.0, 121.1, 44.3, 21.0

HRMS (ESI+): Calcd for Molecular formula $[M+H]^+$ $C_{13}H_{13}N$ 184.1121 Found: 184.1114

2-chloro-5-(p-tolylmethyl) pyridine (3k)[9]



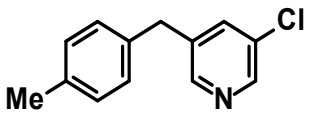
The general procedure B was applied to p-tolylmethanol (381 mg, 3.12 mmol), 5-bromo-2-chloro-pyridine (200 mg, 1.04 mmol), $NiBr_2$.DME (32 mg, 0.10 mmol), dtbpy (41.8 mg, 0.15 mmol), PC (23.35 mg, 0.020 mmol), collidine (378 mg, 3.12 mmol), Triphenylphosphine (545 mg, 2.08 mmol), MeCN (20 ml) at room temperature for 36 h under 420 nm irradiation . Crude product was purified by column chromatography on silica gel (EtOAc/Cyclohexane = 20/10) to afford the title compound as a Gummy liquid (130 mg) 57% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ (ppm): 8.29 (d, *J*=2.4 Hz, 1H), 7.41-7.47 (m, 1H), 7.25 (d, *J*=8.3 Hz, 1H), 7.12-7.17 (m, 2H), 7.04-7.10 (m, 2H), 3.94 (s, 2H), 2.35 (s, 3H)

^{13}C NMR (100 MHz, CHLOROFORM-*d*) δ (ppm): 149.7, 149.2, 139.3, 136.4, 136.2, 135.8, 129.5, 128.7, 124.1, 37.8, 21.0

HRMS (ESI+): Calcd for Molecular formula $[M+H]^+$ $C_{13}H_{12}ClN$: 218.0731, Found: 218.0739

(3n) 3-chloro-5-(p-tolylmethyl) pyridine (3l)



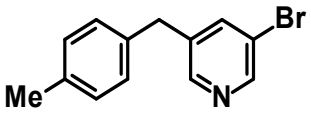
General procedure B was applied to p-tolylmethanol (381 mg, 3.12 mmol), 3-bromo-5-chloro-pyridine (200 mg, 1.04 mmol), $NiBr_2$.DME (32 mg, 0.10 mmol), dtbpy (41.8 mg, 0.15 mmol), PC (17.35 mg, 0.020 mmol), collidine (378 mg, 3.12 mmol), Triphenylphosphine (545 mg, 2.08 mmol), MeCN (20 ml) at room temperature for 36 h under 420 nm irradiation. Crude product was purified by column chromatography on silica gel (EtOAc/Cyclohexane = 20/10) to afford the title compound as a gum (82 mg, 52% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ (ppm): 8.44 (d, *J*=2.3 Hz, 1H), 8.40 (s, 1H), 7.47 (d, *J*=2.0 Hz, 1H),, 7.12-7.16 (m, 2H), 7.04-7.10 (m, 2H), 3.95 (s, 2H), 2.36 (s, 3H)

^{13}C NMR (100 MHz, CHLOROFORM-*d*) δ (ppm): 147.8, 146.5.2, 136.4, 136.0, 135.8, 129.5, 128.7, 128.5, 120.7, 38.1, 21.0

HRMS (ESI+): Calcd for Molecular formula $[M+H]^+$ $C_{13}H_{12}ClN$: 218.0731, Found: 218.0735

3-bromo-5-(p-tolylmethyl) pyridine (3m)



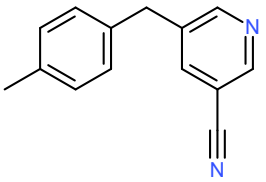
General procedure B was applied to p-tolylmethanol (261 mg, 3.12 mmol), 3,5-dibromopyridine (200 mg, 1.04 mmol), $NiBr_2$.DME (26 mg, 0.10 mmol), dtbpy (34.8 mg, 0.15 mmol), PC (14.35 mg, 0.020 mmol), collidine (310 mg, 3.12 mmol), Triphenylphosphine (447 mg, 2.08 mmol), MeCN (20 ml) at room temperature for 36 h under 420 nm irradiation. Crude product was purified by column chromatography on silica gel (EtOAc/Cyclohexane = 20/10) to afford the title compound as Gum(67 mg, 41% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ (ppm): 8.44 (s, 1H), 8.34 (s, 1H), 7.53 (s, 1H), 7.06 (m, *J*=8.00 Hz, 2H), 6.99 (m, *J*=8.00 Hz, 2H), 3.84 (s, 2H), 2.26 (s, 3H).

^{13}C NMR (100 MHz, CHLOROFORM-*d*) δ (ppm): 148.6, 148.2, 138.8, 138.7, 136.4, 135.8, 129.6, 128.7, 120.8, 38.2, 21.0

HRMS (ESI+): Calcd for Molecular formula $[M+H]^+$ $C_{13}H_{12}BrN$: 262.0226, Found: 262.0235

5-(p-tolylmethyl) pyridine-3-carbonitrile (3n)



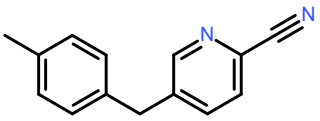
General procedure B was applied to p-tolylmethanol (402 mg, 2.89 mmol), 5-bromopyridine-3-carbonitrile (200 mg, 0.96 mmol), $NiBr_2$.DME (33.75 mg, 0.096 mmol), dtbpy (44.84 mg, 0.14 mmol), PC (18.66 mg, 0.019 mmol), collidine (399 mg, 2.89 mmol), Triphenylphosphine (575 mg, 1.93 mmol), MeCN (20 ml) at room temperature for 36 h under 420 nm irradiation . Crude product was purified by column chromatography on silica gel (EtOAc/Cyclohexane = 1/10) to afford the title compound as a gum (167 mg, 73% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ (ppm): 8.75 (s, 1H), 8.72 (d, 1H), 7.72 (s, 1H), 7.16-7.20 (m, 2H), 7.05-7.10 (m, 2H), 4.02 (s, 2H), 2.37 (s, 3H)

^{13}C NMR (100 MHz, CHLOROFORM-*d*) δ (ppm): 153.4, 150.1, 139.1, 137.5, 136.8, 134.9, 129.7, 128.7, 116.6, 109.8 , 38.1, 20.9

HRMS (ESI+): Calcd for Molecular formula $[M+H]^+$ $C_{14}H_{12}N_2$: 209.1073, Found: 209.1079

5-(p-tolylmethyl) pyridine-2-carbonitrile (3o)



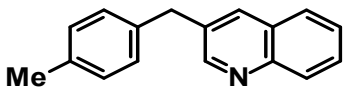
The general procedure B was applied to p-tolylmethanol (402 mg, 2.89 mmol), 5-bromopyridine-2-carbonitrile (200 mg, 0.96 mmol), $NiBr_2$.DME (33.75 mg, 0.096 mmol), dtbpy (43.84 mg, 0.14 mmol), PC (18.66 mg, 0.019 mmol), collidine (396 mg, 2.89 mmol), Triphenylphosphine (572 mg, 1.93 mmol), MeCN (20 ml) at room temperature for 36 h under 420 nm irradiation . Crude product was purified by column chromatography on silica gel (EtOAc/Cyclohexane = 1/10) to afford the title compound as a gum (102 mg,55% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ (ppm): 8.56 (s, 1H), 7.52 - 7.59 (m, 2H), 7.11 (d, *J*=7.82 Hz, 2H), 7.02 (d, *J*=7.95 Hz, 2H), 3.98 (s, 2 H), 2.30 (s, 3H)

^{13}C NMR (100 MHz, CHLOROFORM-*d*) δ (ppm): 151.6, 141.2, 137.0, 136.8, 135.0, 131.6, 129.7, 128.8, 128.3, 117.4, 38.7, 21.0

HRMS (ESI+): Calcd for Molecular formula $[M+H]^+$ $C_{14}H_{12}N_2$: 209.1073, Found: 209.1078

3-(p-tolylmethyl) quinoline (3p)[10]



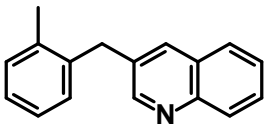
The general procedure B was applied to p-tolylmethanol (353 mg, 2.89 mmol), 3-bromoquinoline (200 mg, 0.96 mmol), $NiBr_2$.DME (29.75 mg, 0.096 mmol), dtbpy (38.84 mg, 0.14 mmol), PC (21.66 mg, 0.019 mmol), collidine (350 mg, 2.89 mmol), Triphenylphosphine (506 mg, 1.93 mmol), MeCN (20 ml) at room temperature for 36 h under 420 nm irradiation. The crude product was purified by column chromatography on silica gel (EtOAc/Cyclohexane = 1/10) to afford the title compound as a Gum (171 mg, 75% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ (ppm): 8.82 (s, 1H), 8.10 (d, *J*=8.4 Hz, 1H), 7.90 (s, 1H), 7.75 (d, *J*=8.1 Hz, 1H), 7.64-7.70 (m, 1H), 7.49-7.56 (m, 1H), 7.12-7.15 (m, 4H), , 4.14 (s, 2H), 2.34 (s, 3H)

^{13}C NMR (100 MHz, CHLOROFORM-*d*) δ (ppm): 152.0, 146.7, 136.6, 136.2, 134.9, 134.2, 129.5, 129.1, 128.9, 128.8, 128.0, 127.5, 126.7, 38.8, 21.0

HRMS (ESI+): Calcd for Molecular formula $[M+H]^+$ $C_{17}H_{15}N$: 234.1277, Found: 234.1289

3-(o-tolylmethyl) quinoline (4a)[11]



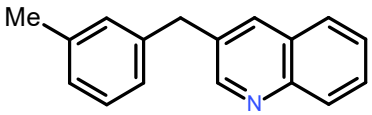
The general procedure B was applied to o-tolylmethanol (351 mg, 2.89 mmol), 3-bromoquinoline (200 mg, 0.96 mmol), $NiBr_2$.DME (29.75 mg, 0.096 mmol), dtbpy (38.84 mg, 0.14 mmol), PC (21.66 mg, 0.019 mmol), collidine (349 mg, 2.89 mmol), Triphenylphosphine (503 mg, 1.93 mmol), MeCN (20 ml) at room temperature for 36 h under 420 nm irradiation . Crude product was purified by column chromatography on silica gel (EtOAc/Cyclohexane = 1/10) to afford the title compound as a gum (97 mg, 51% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ (ppm): 8.83 (d, *J*=2.08 Hz, 1H), 8.09 (d, *J*=8.44 Hz, 1H), 7.75 (s, 1H), 7.71 (d, *J*=8.19 Hz, 1H), 7.67 (t, *J*=7.64 Hz, 1H), 7.48 - 7.55 (m, 1H),7.14 - 7.25 (m, 4H), 4.18 (s, 2H), 2.28 (s, 3H)

^{13}C NMR (100 MHz, CHLOROFORM-*d*) δ (ppm): 152.1, 146.8, 137.5, 136.5, 134.5, 133.2, 130.6, 129.9, 129.1, 128.8, 128.1, 127.4, 127.0, 126.6, 126.3, 36.8, 19.7

HRMS (ESI+): Calcd for Molecular formula $[M+H]^+$ $C_{17}H_{15}N$: 234.1277, Found: 234.1288

(3v)3-(m-tolylmethyl) quinoline (4b)



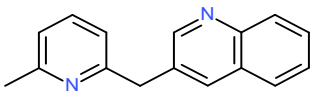
The general procedure B was applied to m-tolylmethanol (355 mg, 2.89 mmol), 3-bromoquinoline (200 mg, 0.96 mmol), $NiBr_2$.DME (29.75 mg, 0.096 mmol), dtbpy (38.84 mg, 0.14 mmol), PC (16.66 mg, 0.019 mmol), collidine (352 mg, 2.89 mmol), Triphenylphosphine (508 mg, 1.93 mmol), MeCN (20 ml) at room temperature for 36 h under 420 nm irradiation . Crude product was purified by column chromatography on silica gel (EtOAc/Cyclohexane = 1/10) to afford the title compound as a gum (106 mg, 64% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ (ppm): 8.84 (d, *J*=2.08 Hz, 1H) 8.11 (d, *J*=8.44 Hz, 1H) 7.77 (s, 1H) 7.71 - 7.75 (m, 1H) 7.66 - 7.70 (m, 1H) 7.51 - 7.57 (m, 1H) 7.16 - 7.27 (m, 4H) 4.19 (s, 2H) 2.30 (s, 3H)

^{13}C NMR (101 MHz, CHLOROFORM-*d*) δ (ppm): 152.2, 146.9, 136.8, 136.4, 135.2, 134.4, 129.7, 129.1, 129.4, 129.3, 128.4, 128.0, 127.8 127.7, 127.0,39.1, 21.3

HRMS (ESI+): Calcd for Molecular formula $[M+H]^+$ $C_{17}H_{15}N$: 234.1277, Found: 234.1288

3-[(6-methyl-2-pyridyl) methyl] quinoline (4c)



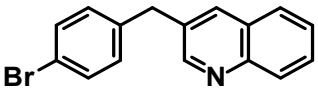
The general procedure B was applied to (6-methyl-2-pyridyl)methanol (354 mg, 2.89 mmol), 3-bromoquinoline (200 mg, 0.96 mmol), $NiBr_2$.DME (29.75 mg, 0.096 mmol), dtbpy (38.84 mg, 0.14 mmol), PC (16.66 mg, 0.019 mmol), collidine (352 mg, 2.89 mmol), Triphenylphosphine (503 mg, 1.93 mmol), MeCN (20 ml) at room temperature for 36 h under 420 nm irradiation . Crude product was purified by column chromatography on silica gel (EtOAc/Cyclohexane = 1/10) to afford the title compound as a gum(114 mg 64% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ (ppm): 8.91 (s, 1H) 8.10 (d, *J*=8 Hz, 1H) 8.02 (s, 1H) 7.80-7.77 (m, 1H) 7.60-7.70 (m, 1H) 7.50-7.55 (m, 2H) 7.04 (d, *J*=8 Hz, 1H) 6.96 (d, *J*=8 Hz, 1H) 4.34 (s, 2H) 2.59 (s, 3H)

^{13}C NMR (100 MHz, CHLOROFORM-*d*) δ (ppm): 158.9, 158.3, 152.2, 146.9, 137.0, 135.2, 132.5, 129.1, 128.9, 127.7, 127.5, 126.7, 121.2, 120.1, 41.9, 24.5

HRMS (ESI+): Calcd for Molecular formula $[M+H]^+$ $C_{17}H_{15}N$: 235.1230, Found: 235.1322

3-[(4-bromophenyl) methyl] quinoline (4d)[12]



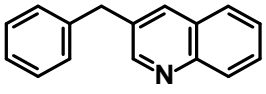
The general procedure B was applied to (4-bromophenyl)methanol (454 mg, 2.89 mmol), 3-bromoquinoline (200 mg, 0.96 mmol), $NiBr_2$.DME (29.75 mg, 0.096 mmol), dtbpy (38.84 mg, 0.14 mmol), PC (16.66 mg, 0.019 mmol), collidine (352 mg, 2.89 mmol), Triphenylphosphine (508 mg, 1.93 mmol), MeCN (20 ml) at room temperature for 36 h under 420 nm irradiation . Crude product was purified by column chromatography on silica gel (EtOAc/Cyclohexane = 1/10) to afford the title compound as a gum (64 mg,70% purity) 35% yield) and 3-benzylquinoline (Gum, 34 mg, 23% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ (ppm): 8.79 (d, *J*=2.25 Hz, 1H) 8.18 (d, *J*=7.96 Hz, 1H) 7.87 (s, 1H) 7.75 (d, *J*=8.25 Hz, 1H) 7.69 (ddd, *J*=8.41, 6.97, 1.50 Hz, 1H) 7.50 - 7.59 (m, 1H) 7.37 - 7.48 (m, 2H) 7.11 (d, *J*=8.38 Hz, 2H) 4.13 (s, 2H)

^{13}C NMR (100 MHz, CHLOROFORM-*d*) δ (ppm): 151.8, 146.9, 138.6, 134.9, 133.2, 131.8, 130.7, 129.1, 129.0, 128.1, 127.4, 126.8, 120.5, 38.6

HRMS (ESI+): Calcd for Molecular formula $[M+H]^+$ $C_{16}H_{12}BrN$: 298.0225, Found: 298.0232

3-benzylquinoline (4e)[12]

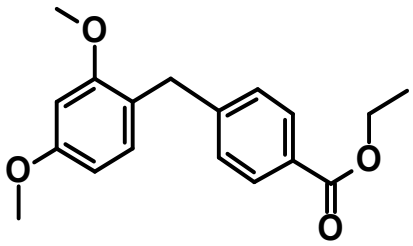


The compound was obtained from above protocol as a gum (34 mg, 23% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ (ppm): 8.85 (s, 1H), 8.11 (d, *J*=8Hz,1H), 7.59-7.77 (m, 3H), 7.53 (m, 1H), 7.17-7.24 (m, 5H), 4.19 (s, 2H)

HRMS (ESI+): Calcd for Molecular formula $[M+H]^+$ $C_{16}H_{13}N$: 220.1121, Found: 220.1127

Ethyl 4-[2,4-dimethoxyphenyl) methyl] benzoate (4f)



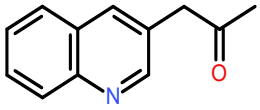
The general procedure A was applied to (2,4-dimethoxyphenyl)methanol (444 mg, 2.89 mmol), ethyl 4-bromobenzoate (200 mg, 0.96 mmol), $NiBr_2$.DME (27.75 mg, 0.096 mmol), dtbpy (35.84 mg, 0.14 mmol), PC (19.66 mg, 0.019 mmol), collidine (319 mg, 2.89 mmol), Triphenylphosphine (461 mg, 1.93 mmol), MeCN (20 ml) at room temperature for 36 h under 420 nm irradiation . Crude product was purified by column chromatography on silica gel (EtOAc/Cyclohexane = 1/10) to afford the title compound as a gum(79 mg, 56% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ (ppm): 7.95 (d, *J*=7.77 Hz, 2H), 7.25 - 7.30 (m, 2H), 6.99 (d, *J*=8.25 Hz, 1H), 6.48 (d, *J*=2.38 Hz, 1H), 6.45 (d, *J*=8.25 Hz, 1H), 4.37 (q, *J*=7.13 Hz, 2H), 3.96 (s, 2H), 3.82 (s, 3H), 3.79 (s, 3H),1.40 (t, *J*=7.13 Hz, 3H).

^{13}C NMR (100 MHz, CHLOROFORM-*d*) δ (ppm): 166.7, 159.6, 158.2, 147.0, 130.6, 129.5, 128.7, 128.0, 121.1, 103.9, 98.6, 77.2, 60.7, 55.3,, 35.4, 14.3.

HRMS (ESI+): Calcd for Molecular formula $[M+H]^+$ $C_{18}H_{20}O4$: 301.1434, Found: 301.1445

1-(3-quinolyl) propan-2-one (4g)[13]



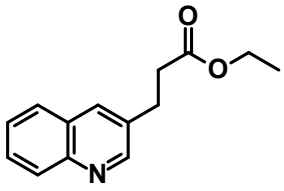
The general procedure B was applied to 1-hydroxypropan-2-one (213 mg, 2.89 mmol), 3-bromoquinoline (200 mg, 0.96 mmol), $NiBr_2$.DME (29.75 mg, 0.096 mmol), dtbpy (38.84 mg, 0.14 mmol), PC (16.66 mg, 0.019 mmol), collidine (349 mg, 2.89 mmol), Triphenylphosphine (503 mg, 1.93 mmol), MeCN (20 ml) at room temperature for 36 h under 420 nm irradiation . Crude product was purified by column chromatography on silica gel (EtOAc/Cyclohexane = 1/10) to afford the title compound as a gum (63 mg, 41% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ (ppm): 8.77 (s, 1H) 8.12 (d, *J*=8.50 Hz, 1H) 8.01-8.02 (d, *J*= 4 Hz, 1H) 7.81 (m, 1H) 7.79 (m, 1H) 7.58-7.72 (m, 1H) 3.93 (s, 2H) 2.28 (s, 3H)

^{13}C NMR (100 MHz, CHLOROFORM-*d*) δ (ppm): 203.8, 150.4, 145.9, 135.3, 128.4, 128.1 128.0, 126.5, 126.1 125.9, 46.6, 28.7.

HRMS (ESI+): Calcd for Molecular formula $[M+H]^+$ $C_{12}H_{11}NO$ 186.0913 Found: 186.0922

Ethyl 3-(3-quinolyl) propanoate(4h)[14]



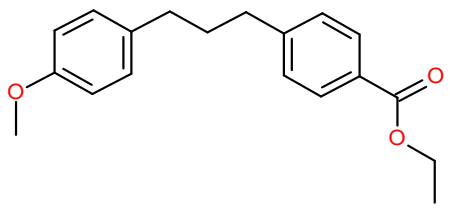
The general procedure B was applied to ethyl 3-hydroxypropanoate (342 mg, 2.89 mmol), 3-bromoquinoline (200 mg, 0.96 mmol), $NiBr_2$.DME (29.75 mg, 0.096 mmol), dtbpy (38.84 mg, 0.14 mmol), PC (16.66 mg, 0.019 mmol), collidine (349 mg, 2.89 mmol), Triphenylphosphine (506 mg, 1.93 mmol), MeCN (20 ml) at room temperature for 36 h under 420 nm irradiation . Crude product was purified by column chromatography on silica gel (EtOAc/Cyclohexane = 1/10) to afford the title compound as a gum (82 mg, 67% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ (ppm): 8.75 (br s, 1H), 8.04 (d, J=8.4 Hz, 1H), 7.93 (s, 1H), 7.72 (br d, *J*=8.1 Hz, 1H), 7.62 (t, *J*=7.2 Hz, 1H), 7.48 (t, *J*=7.2 Hz, 1H), 4.02-4.11 (m, 2H), 3.09 (t, *J*=7.6 Hz, 2H), 2.67 (t, *J*=7.6 Hz, 2H), 1.16 (t, *J*=7.2 Hz, 3H).

^{13}C NMR (100 MHz, CHLOROFORM-*d*) δ (ppm): 172.3, 151.4, 146.6, 134.9, 133.3, 129.1, 128.9, 127.5, 127.0, 126.9, 60.7, 35.4, 28.2, 14.2.

HRMS (ESI+): Calcd for Molecular formula $[M+H]^+$ $C_{14}H_{15}NO_2$ 230.1176 Found: 230.1186

Ethyl 4-[3-(4-methoxyphenyl) propyl] benzoate (4i)[15]



The general procedure A was applied to 3-(4-methoxyphenyl)propan-1-ol (436 mg, 2.89 mmol), ethyl 4-bromobenzoate (200 mg, 0.96 mmol), $NiBr_2$.DME (27.75 mg, 0.096 mmol), dtbpy (35.84 mg, 0.14 mmol), PC (14.66 mg, 0.019 mmol), collidine (318 mg, 2.89 mmol), Triphenylphosphine (459 mg, 1.93 mmol), MeCN (20 ml) at room temperature for 36 h under 420 nm irradiation . Crude product was

purified by column chromatography on silica gel (EtOAc/Cyclohexane = 1/10) to afford the title compound as a gum (41 mg, 23% yield).

^{1}H NMR (400 MHz, CHLOROFORM-*d*) δ (ppm): 7.97 (d, *J*=7.48 Hz, 2H), 7.23 - 7.28 (m, 2H), 7.10 (d, *J*=7.44 Hz, 2H), 6.84 (d, *J*=7.45 Hz, 2H), 4.37 (q, *J*=7.09 Hz, 2H), 3.80 (s, 3H), 2.65 - 2.74 (m, 2H), 2.60 (t, *J*=7.63 Hz, 2H), 1.94 (t, *J*=7.69 Hz, 2H), 1.40 (t, *J*=7.13 Hz, 3H).

^{13}C NMR (100 MHz, CHLOROFORM-*d*) δ (ppm): 165.6, 156.7, 146.7, 132.9, 128.6, 128.2, 127.3, 127.0, 112.7, 59.7, 54.2, 34.3, 33.3, 31.8, 13.3

HRMS (ESI+): Calcd for Molecular formula $[M+H]^{+}$ $C_{19}H_{22}O_3$ 299.1641 Found: 299.1643

Gram Scale synthesis

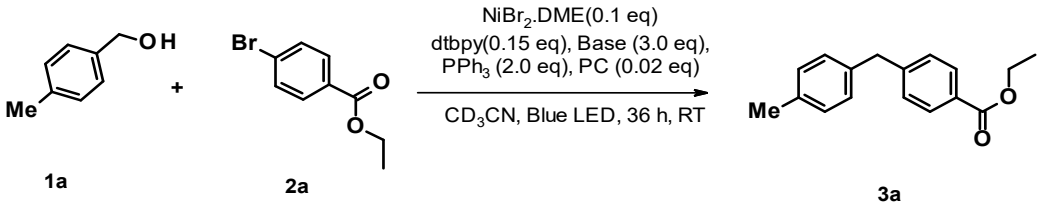
A 30 mL oven-dried vial equipped with a magnetic stir bar was charged with 1a (1.60 gm, 13.15 mmol), 2a (1.0 gm, 4.38 mmol), and collidine (1.68 gm 13.88 mmol), followed by the addition of MeCN (20 mL). The reaction mixture was stirred for 5 minutes while degassing with nitrogen. In a separate vial, $NiBr_2$.DME (0.142 gm 0.46 mmol) and dtbpy (0.186 gm, 0.69 mmol) were dissolved in 1 mL MeCN under a nitrogen atmosphere. The resulting, green-colored nickel complex solution was transferred via syringe to the reaction vial under nitrogen, followed by the addition of PC (0.051 gm, 0.046 mmol) with stirring. The reaction vial was then degassed with nitrogen for 5 minutes, after which triphenylphosphine (2.42 gm, 9.25mmol) was added under a nitrogen atmosphere. The vial was capped under nitrogen gas and sealed with Teflon tape. Finally, the reaction vial was stirred at 250 rpm and irradiated with a 420 nm LED at 50% intensity in a Penn photoreactor for 36 hours, with the fan speed kept at the default setting (6000 rpm).

As significant amount of side product forming in the reaction (TPPO), reaction mass volatiles was evaporated to get gummy crude product. further to remove TPPO from crude product $CaBr_2$ (3.0 gm, 15.41 mmol) was added to reaction followed by stirring in Toluene (20 ml) for 1h rt. White precipitate was filtered through sintered funnel to filtrate containing desired product along with soluble impurities.

TPPO remains in solid cake along with CaBr2. Filtrate evaporated and adsorbed on silica and Crude product was purified by column chromatography on silica gel (EtOAc/Cyclohexane = 1/10) to afford the title compound as a gum (0.85 gm, 77% yield).

Mechanistic study

^{1}H NMR Monitoring in CD_3CN



1a 2a 3a

A 5 mL oven-dried vial equipped with a magnetic stir bar was charged with 1a (48 mg), 2a (30 mg, mmol), and collidine (47 mg), followed by the addition of CD_3CN (2 mL). The reaction mixture was stirred for 5 minutes while degassing with nitrogen. In a separate vial, $NiBr_2$.DME (4.0 mg) and dtbpy (5.28 mg) were dissolved in 1 mL CD_3CN under a nitrogen atmosphere. The resulting, green-colored nickel complex solution was transferred via syringe to the reaction vial under nitrogen, followed by the addition of PC (2 mg) with stirring. The reaction vial was then degassed with nitrogen for 5 minutes, after which triphenylphosphine (68 mg) was added under a nitrogen atmosphere. The vial was capped under nitrogen gas and sealed with rubber septa cap. Finally, the reaction vial was stirred at 250 rpm and irradiated with a 420 nm LED at 50% intensity in a Penn photoreactor, with the fan speed kept at the default setting (6000 rpm).

To monitor reaction 0.5 ml reaction mass withdrawn from vial with syringe and needle under inert atmosphere at 0 h and submitted for analysis. Reaction was monitored by ^{1}H NMR every 6 h to study reaction progress.

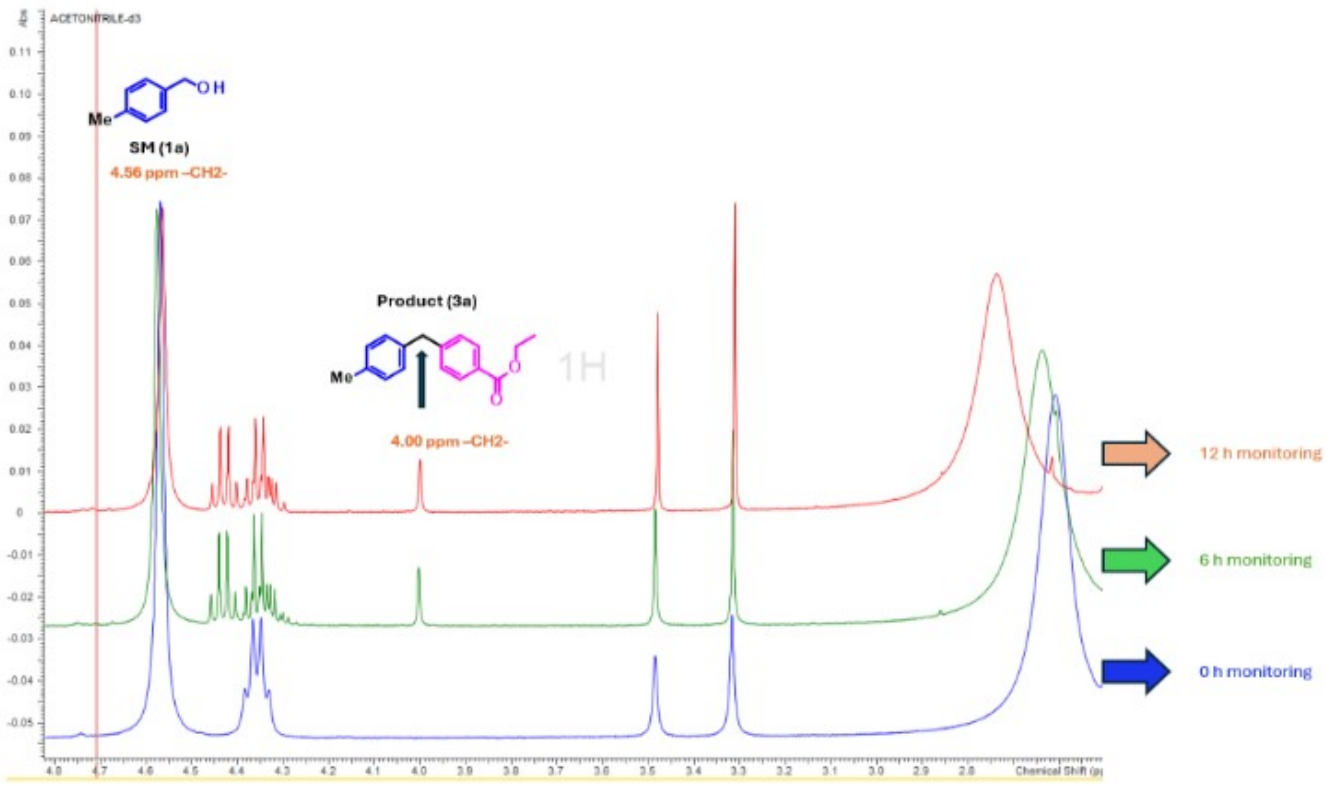
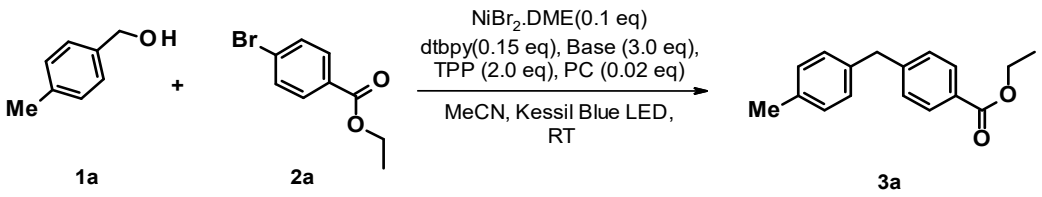


Figure 1: ^{1}H NMR Monitoring in CD_3CN

Figure 2 Pen Photoreactor Reaction Set up

React IR study



A 50 mL oven-dried 3- neck RBF equipped with a magnetic stir bar, Nitrogen inlet, React IR probe and rubber septa for addition via syringe. RBF placed on magnetic stirrer clamped with Kessile blue LED lamp 4 cm away from reaction vessel equipped with cooling Fan. Reaction was charged with 1a (0.7 mmol), 2a (0.4 mmol), and collidine (0.3 mmol), followed by the addition of MeCN (20 mL). The reaction mixture was stirred for 5 minutes while degassing with nitrogen. In a separate vial, $NiBr_2$.DME (0.01 mmol) and dtbpy (0.015 mmol) were dissolved in 0.5 mL MeCN under a nitrogen atmosphere. The resulting, green-colored nickel complex solution was transferred via syringe to the reaction vial under nitrogen, followed by the addition of PC (0.002 mmol) with stirring. The reaction vial was then degassed with nitrogen for 5 minutes, after which triphenylphosphine (0.2 mmol) was added under a nitrogen atmosphere. The vial was capped under nitrogen gas and sealed with Teflon tape. Finally, the reaction vial was stirred at 250 rpm and irradiated with a 420 nm LED at 50% intensity in a Penn photoreactor for 36 hours, with the fan speed kept at the default setting (6000 rpm).

IR stretching was measured for each component separately with substruction of background as well as Acetonitrile. Reaction continued for 27 h and reaction temperature was monitored by React IR probe.

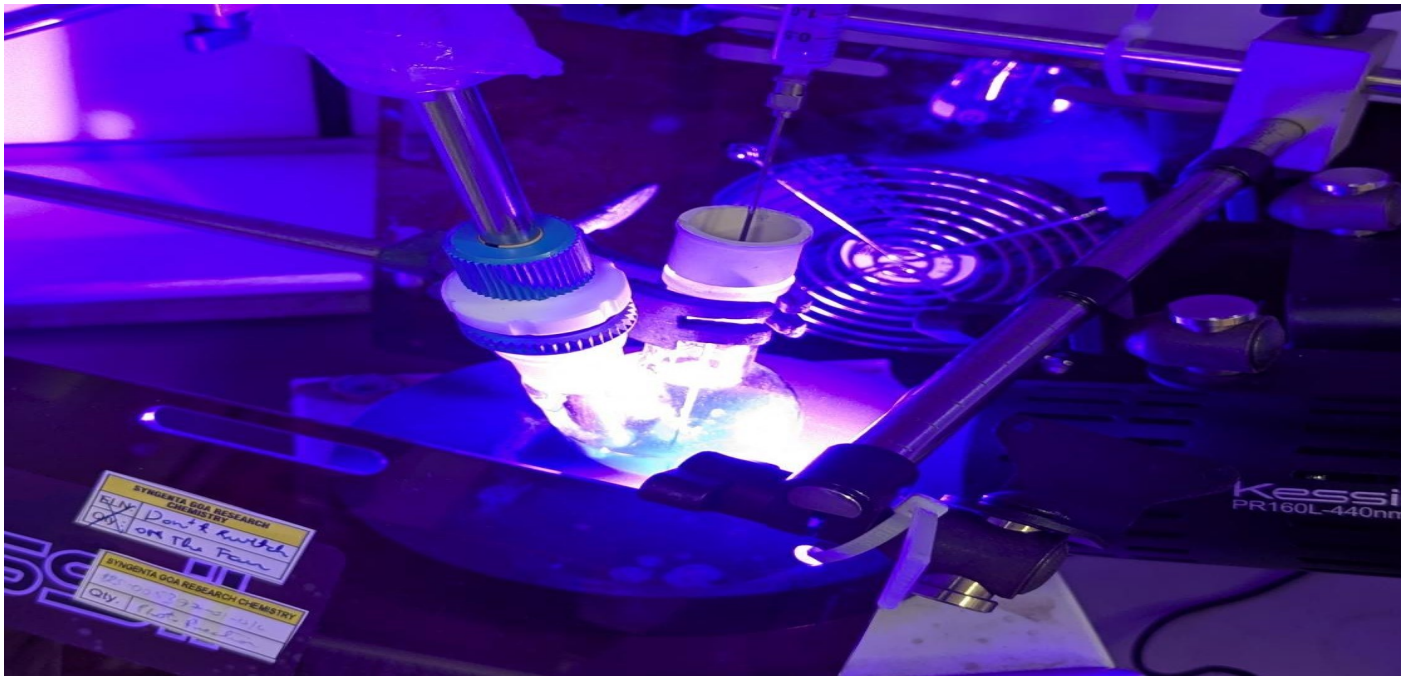


Figure 3 Reaction set up with Kessil lamp and React IR

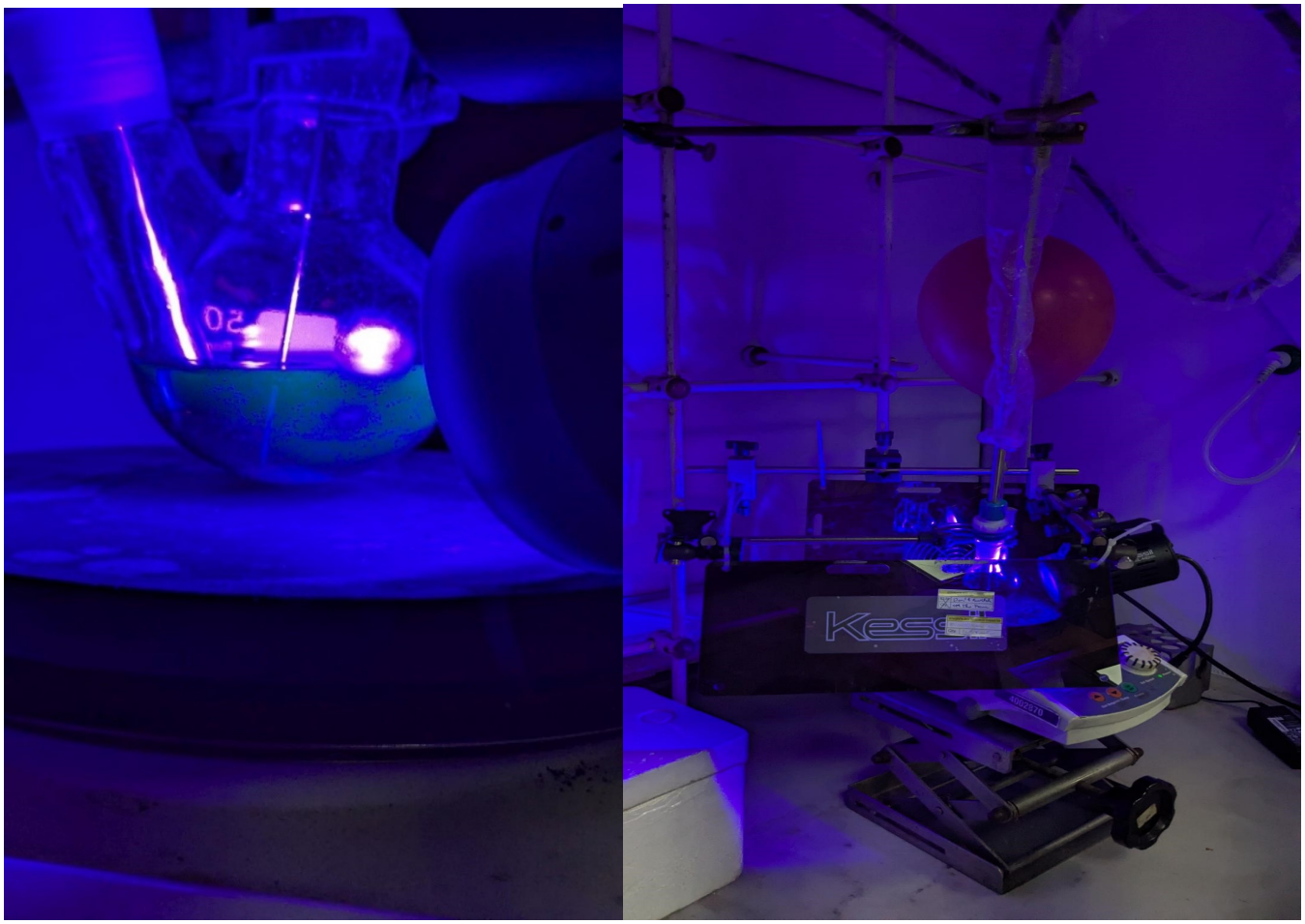


Figure 4 Reaction set up with Kessil lamp and React IR

Reaction Kinetics

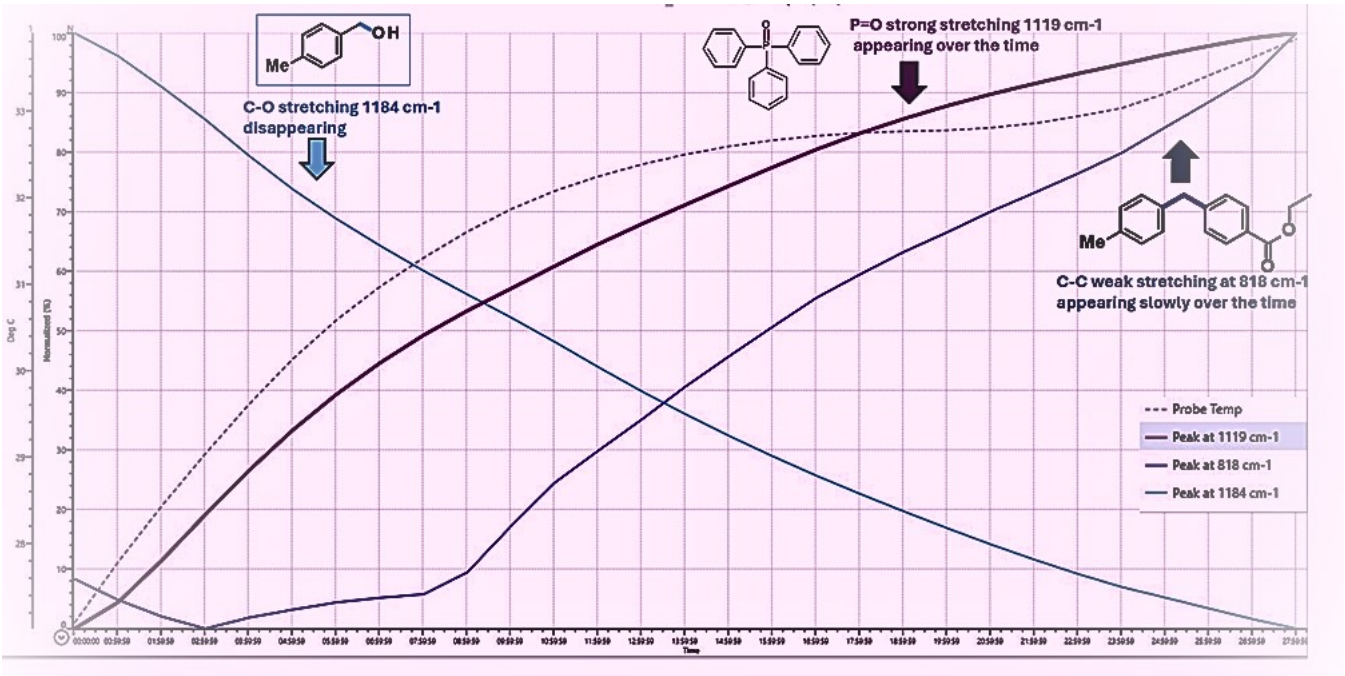


Figure 5 Reaction kinetics by React IR

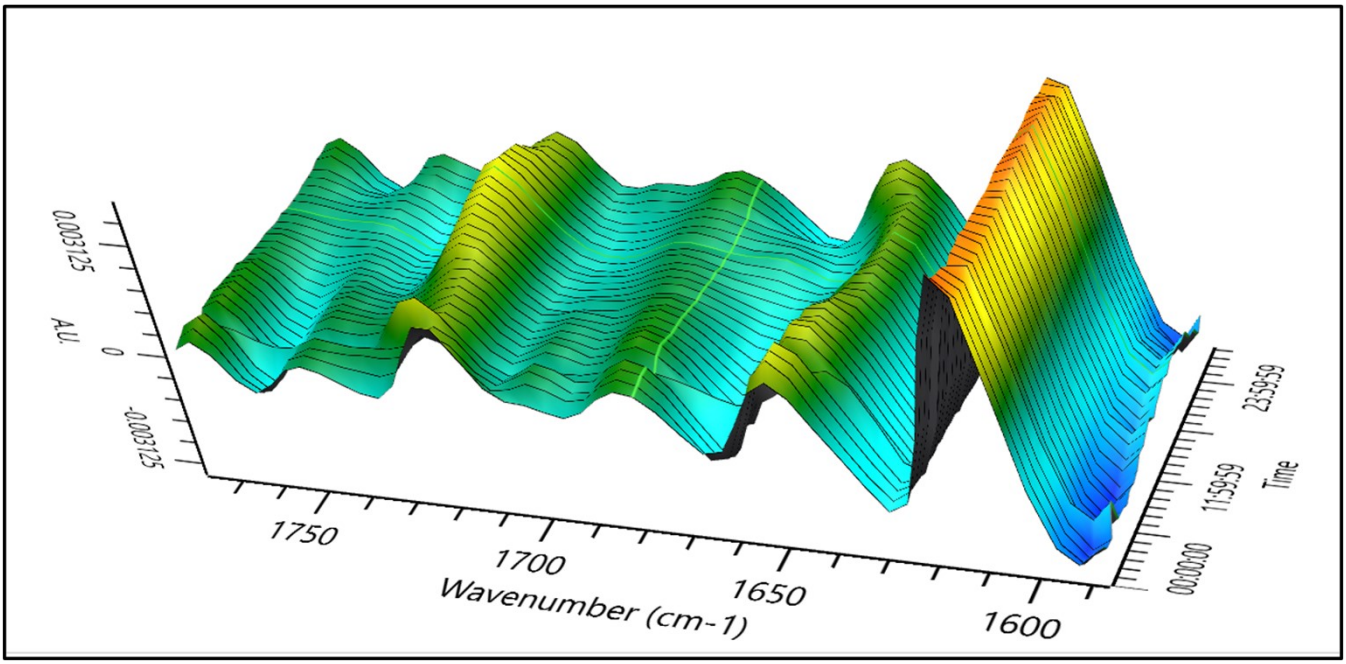


Figure 6 3D visualization for product formation with carbonyl Frequency 1740 cm^{-1}

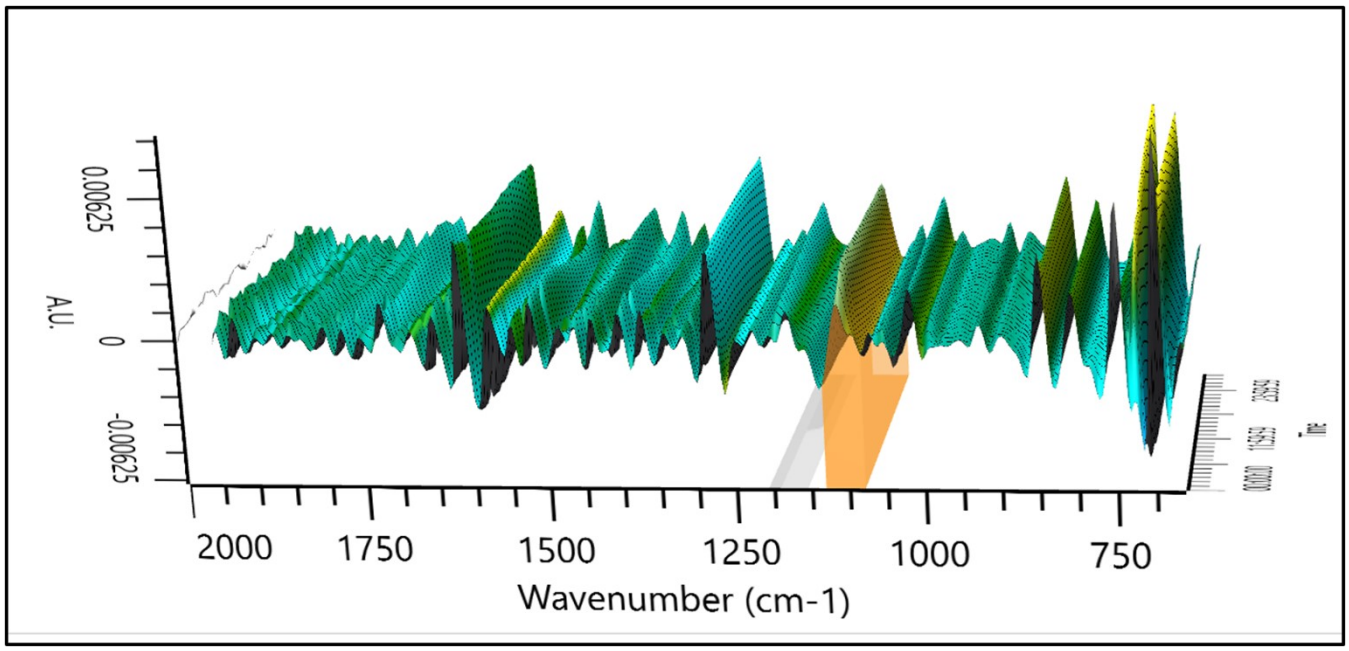


Figure 7 3D Visualization for PPh_3O formation PO at 1119 cm^{-1}

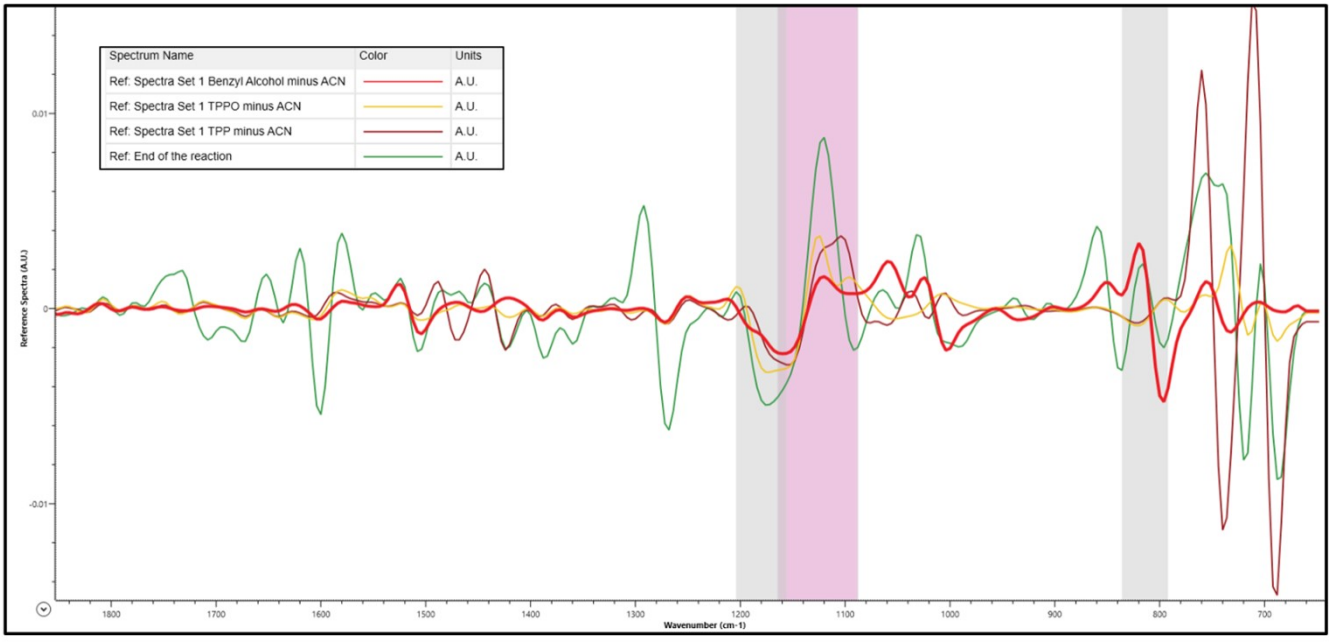


Figure 8 Overlapped spectra of 1a, PPh_3O, PPh_3 and Reaction mixture after completion

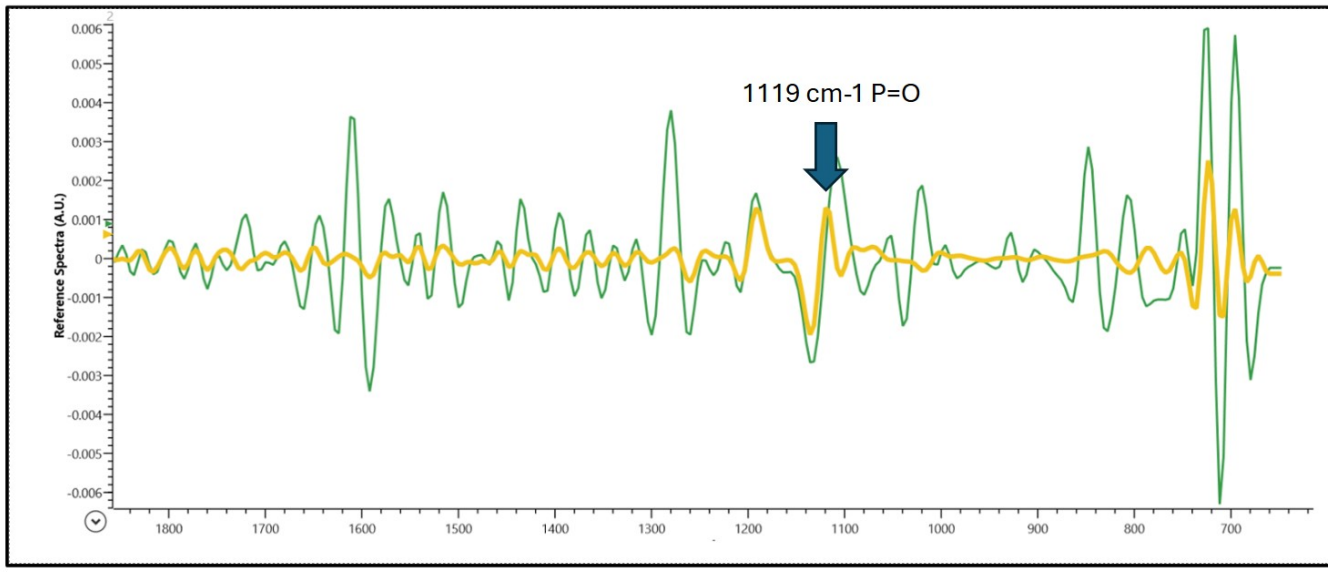


Figure 9 Overley of Reaction mixture (Green) and PPh_3O (yellow)

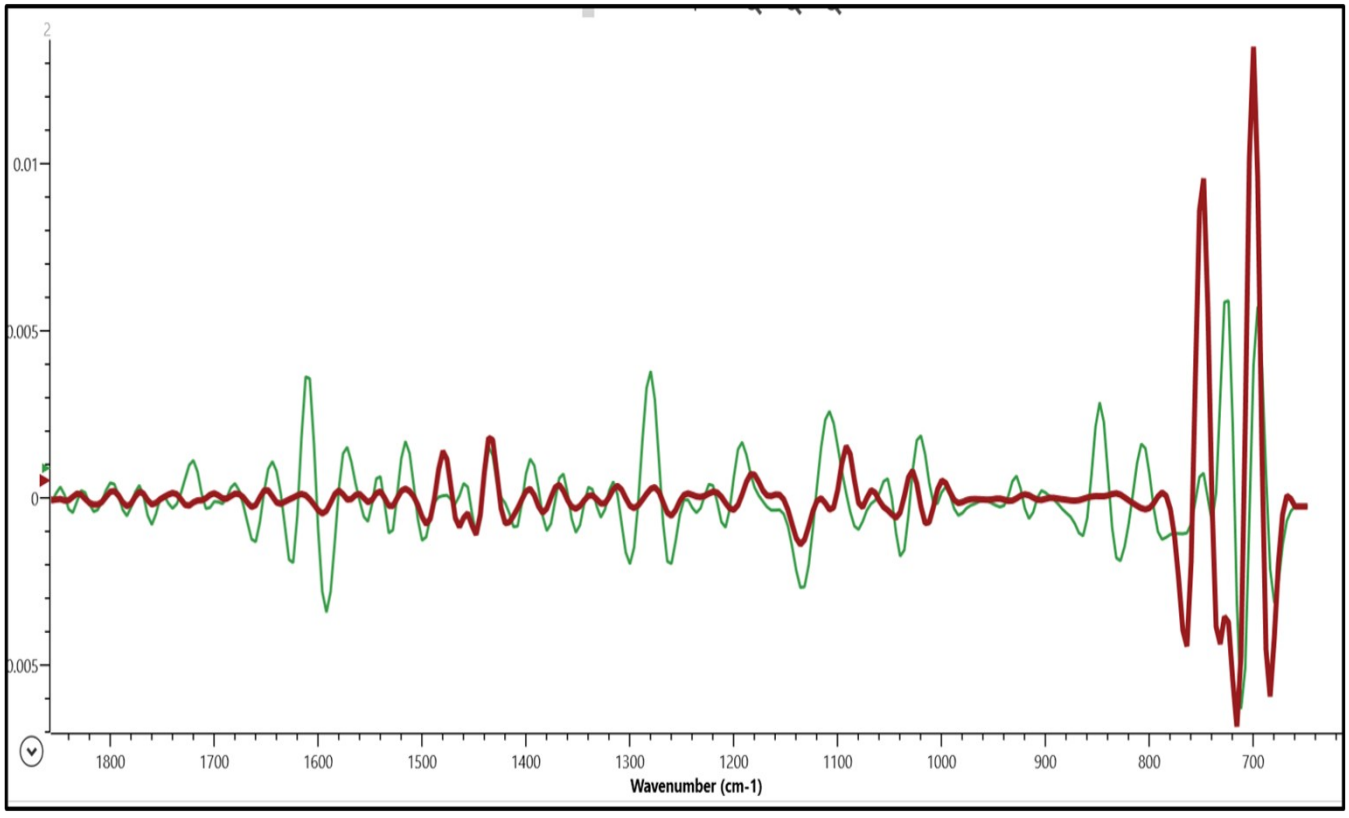


Figure 10 Overley of Reaction mixture (Green) and PPh_3 (Brown)

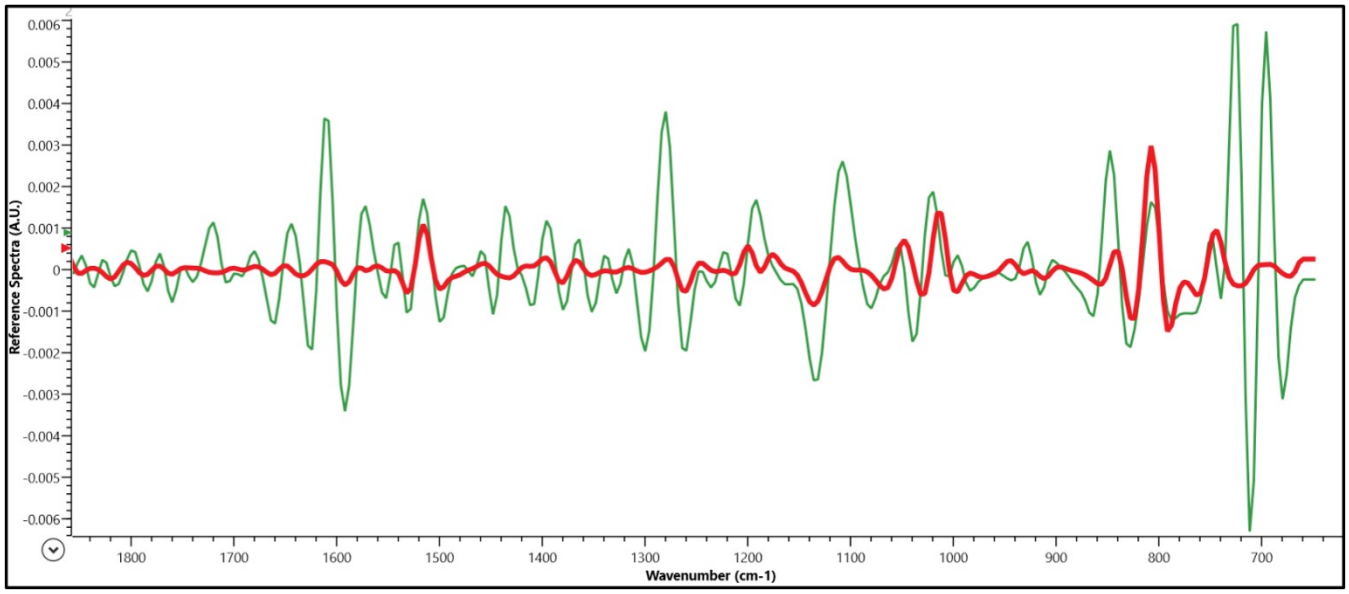


Figure 11 Overley of Reaction mixture (Green) and 1a (RED)

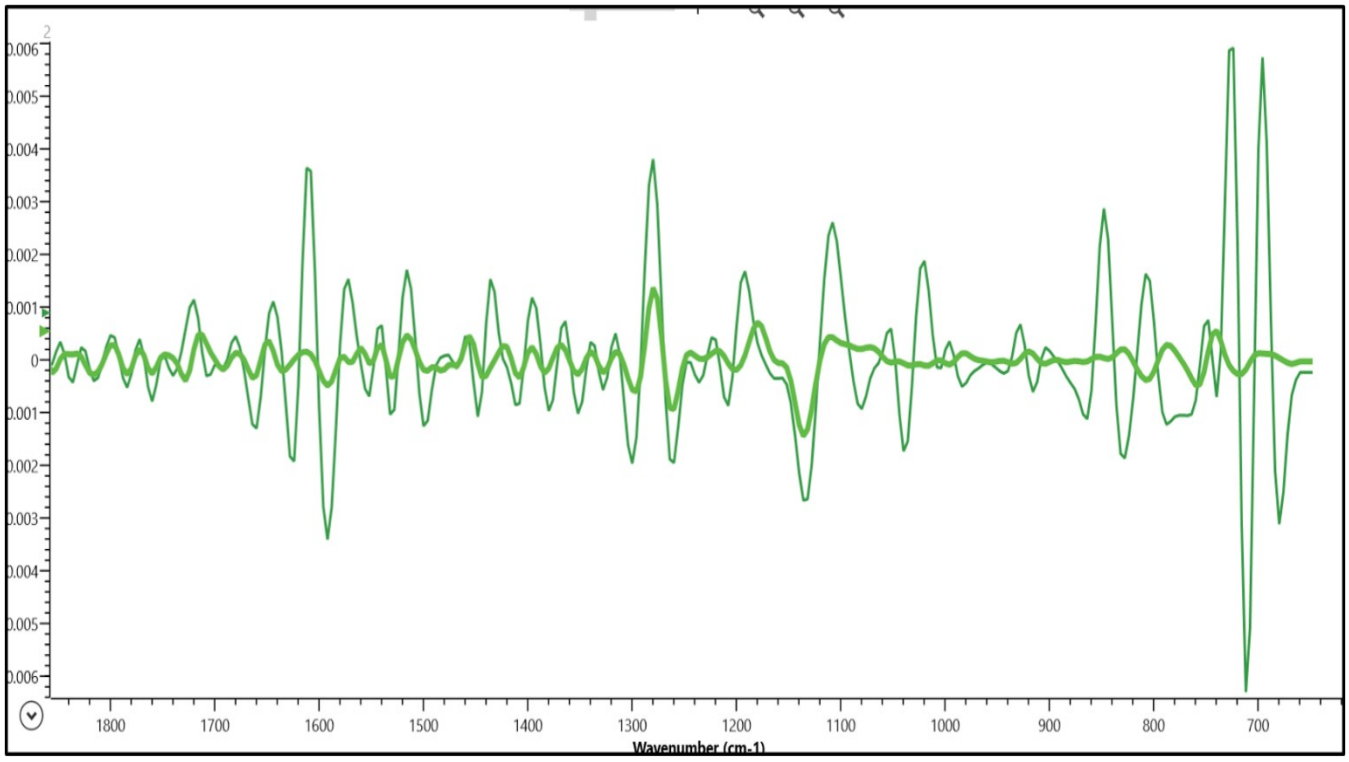


Figure 12 Overley of Reaction mixture (Green) and std product (dark Green)

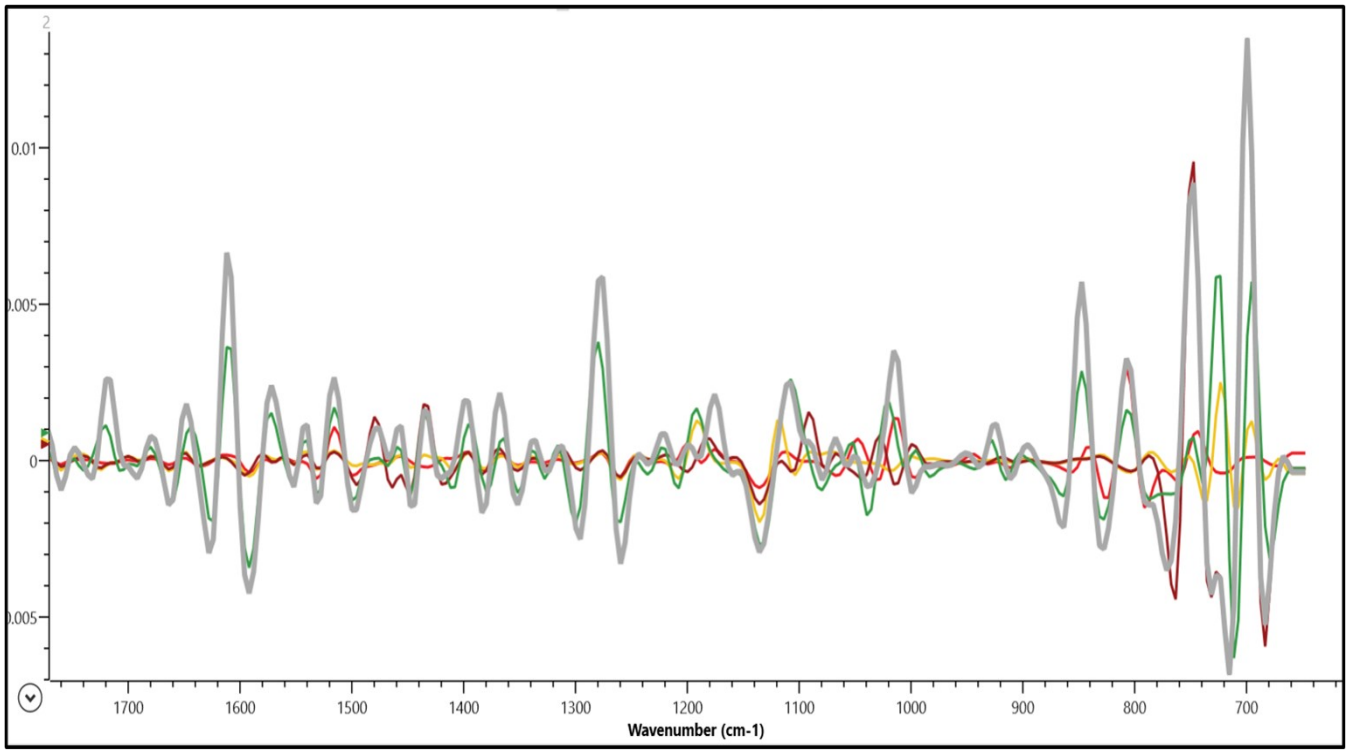
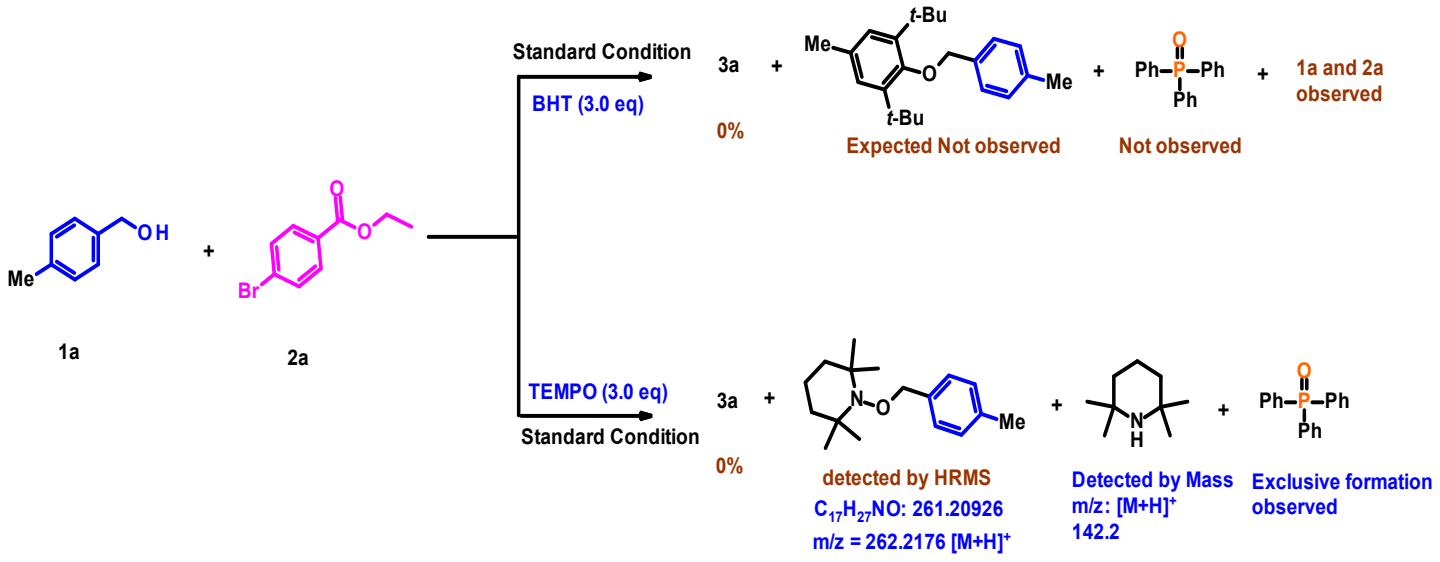


Figure 13 Overley of all components without Standard compound (3a)

Radical Scavenger Study



Radical scavenger- BHT (2,6-Di-*tert*-butyl-4-methylphenol)

Under standard reaction conditions, we conducted a radical scavenger experiment to investigate the involvement of radical intermediates in the reaction pathway. To this end, we introduced **BHT (1.76 mmol)**. The addition was performed under an inert nitrogen atmosphere Following the incorporation of BHT, the reaction was allowed to proceed under the standard. Upon completion, we carried out the standard work-up procedures. The crude product was then subjected to purification using column chromatography. In the presence of BHT, triphenylphosphine remained in its unoxidized state, and both starting materials 1a and 2a were recovered unchanged. These observations lead to the conclusion that the absence of triphenylphosphine oxide formation indicates that the oxidation of triphenylphosphine is impeded. The lack of conversion of starting materials implies that the initial steps of the reaction are blocked by radical scavenger

Radical Scavenger Study TEMPO (2,2,6,6-Tetramethylpiperidine 1-oxyl, free radical)

Similarly, to get more insights into the radical nature of reaction we carried out scavenger experiments by addition of TEMPO. Under standard conditions we introduced **TEMPO (1.75 mmol)**. Reaction was allowed to proceed under the standard. Upon completion, we carried out the standard work-up procedures. The crude product was then subjected to purification using column chromatography. The absence of product **3a**, coupled with the formation of TMP and TPPO, suggests that TEMPO intercepts a key radical intermediate early in the reaction pathway. Specifically, these observations are consistent with the initial formation of a phosphorus-centered radical species, which is rapidly trapped by TEMPO. The subsequent decomposition of the TEMPO-phosphorus adduct likely proceeds via homolytic cleavage of the N-O bond, resulting in the formation of TMP (tetramethyl piperidine) and oxidation of the phosphorus species to TPPO.

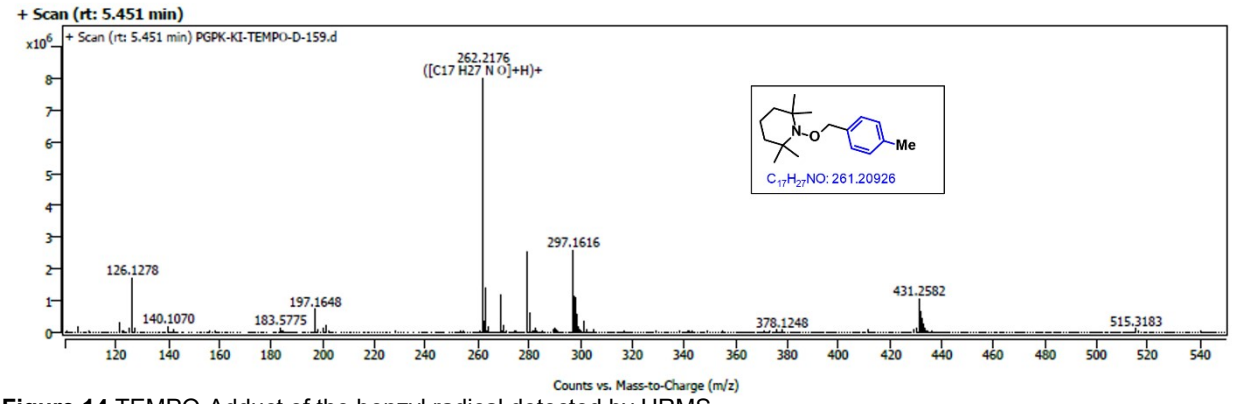


Figure 14 TEMPO-Adduct of the benzyl radical detected by HRMS

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^{1}H NMR and ^{13}C Spectra

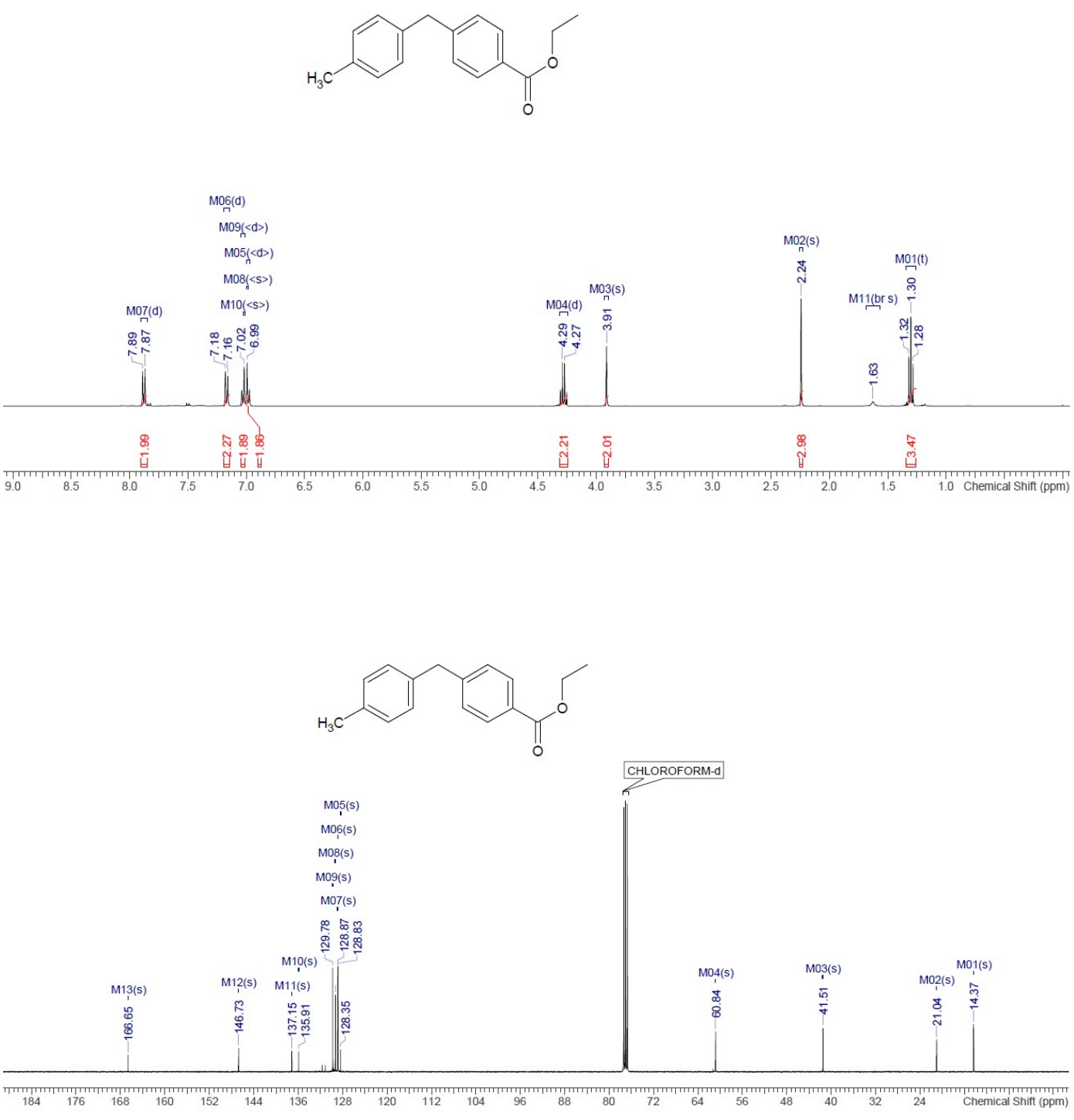


Figure 15 ^{1}H NMR and ^{13}C NMR of 3a

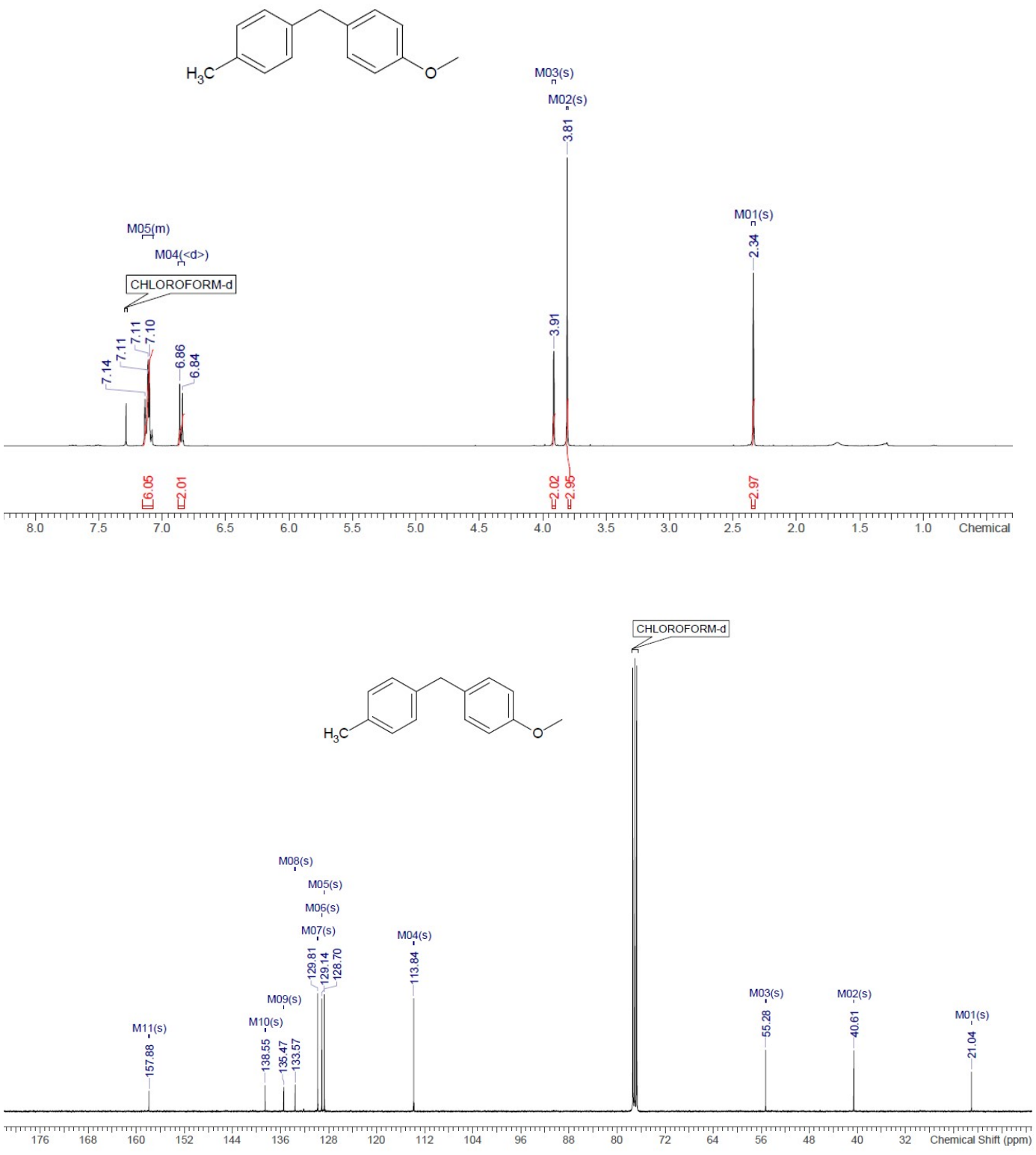


Figure 16 Figure 13 ^{1}H NMR and ^{13}C NMR of 3b

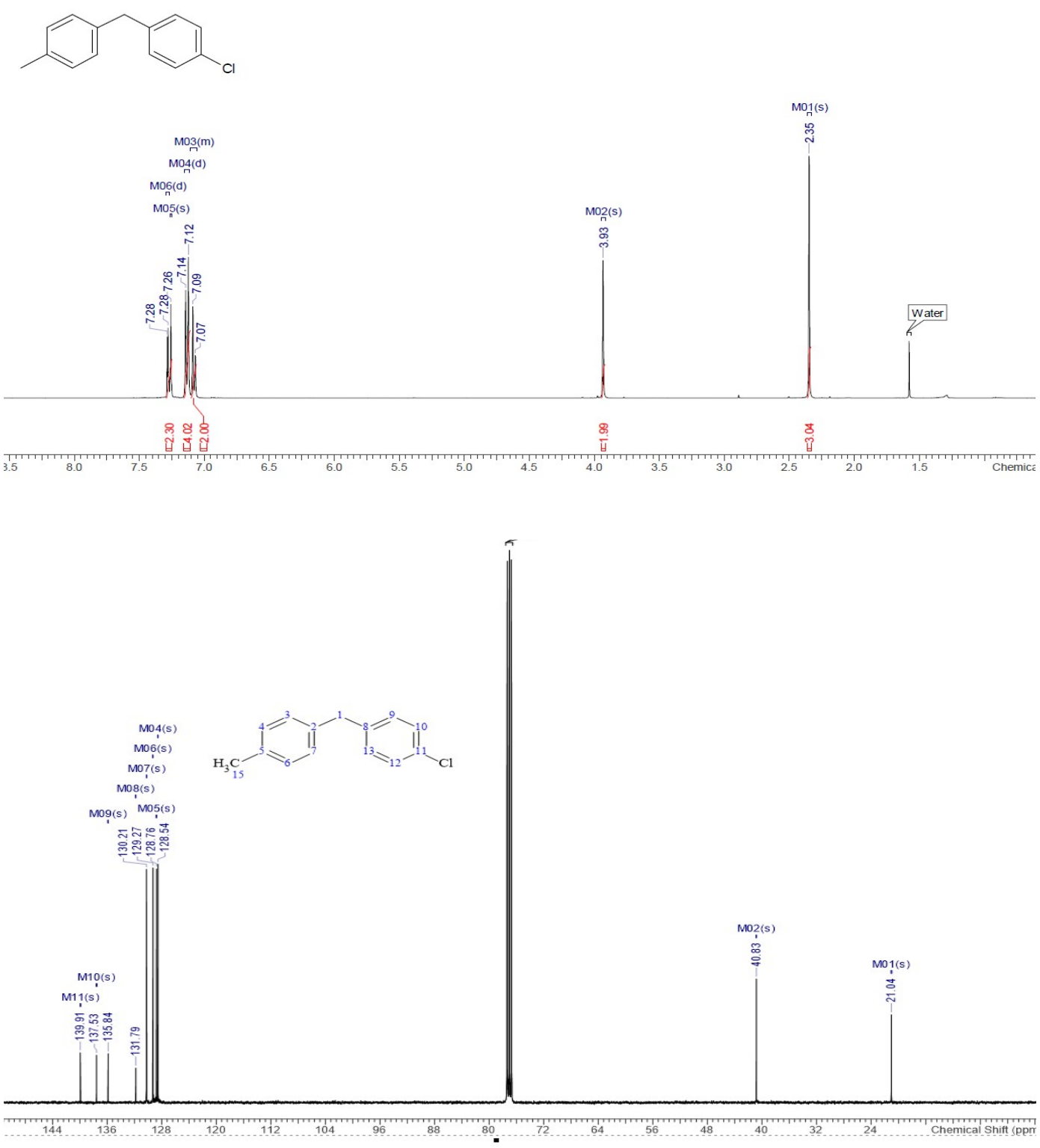


Figure 17 ^{1}H NMR and ^{13}C NMR of 3c

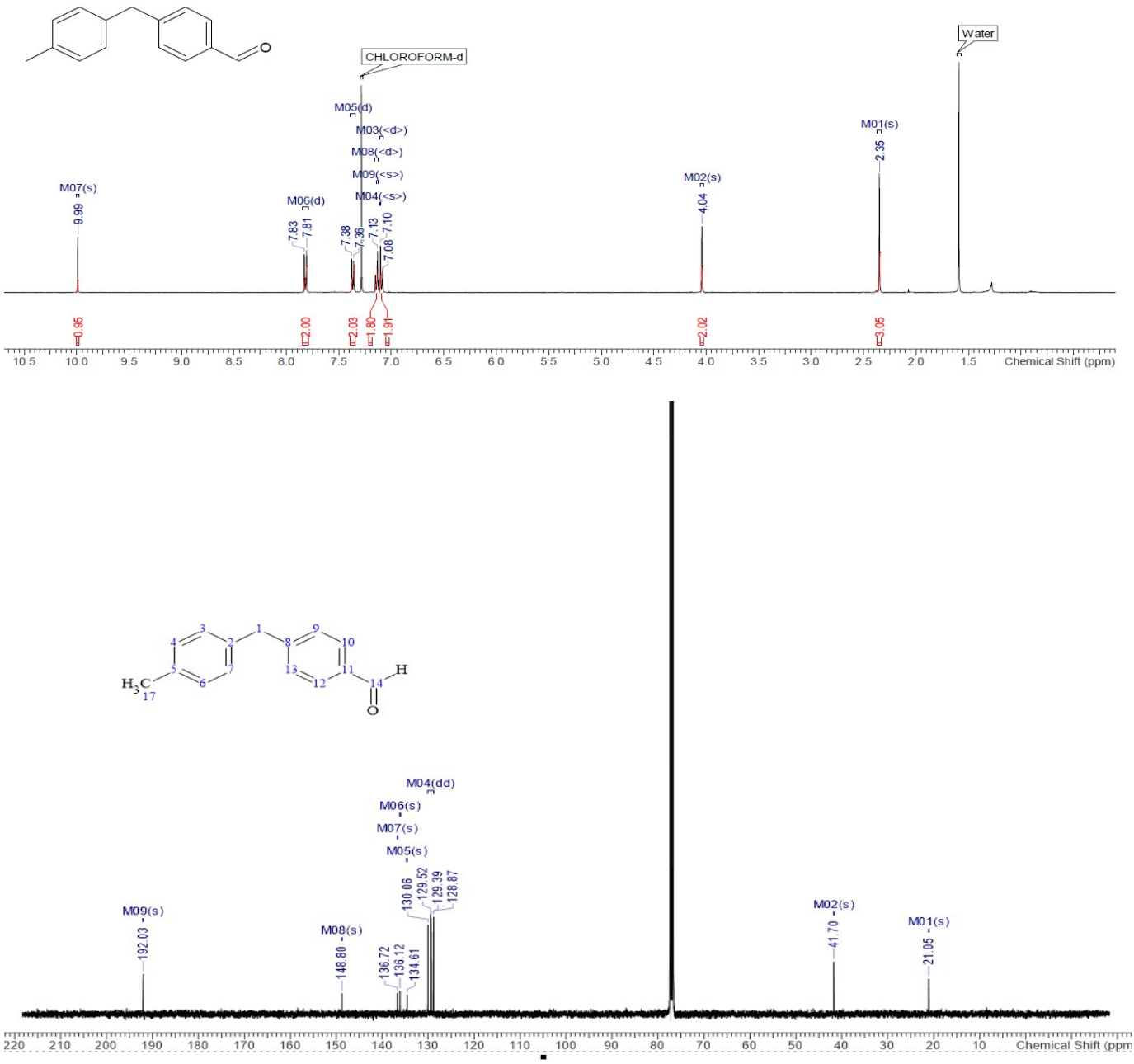


Figure 18 ^{1}H NMR and ^{13}C NMR of 3d

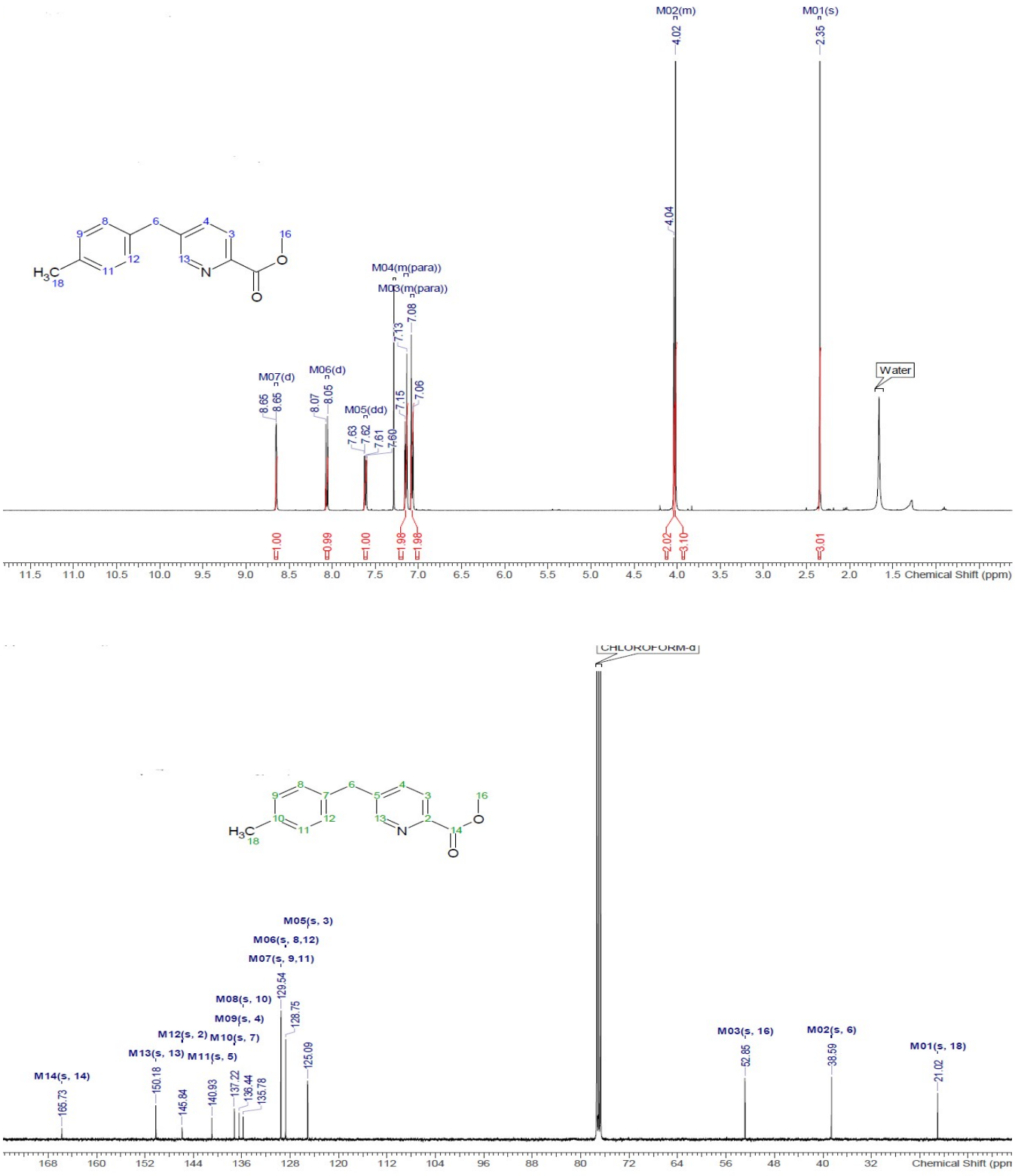


Figure 19 ^{1}H NMR and ^{13}C NMR of 3e

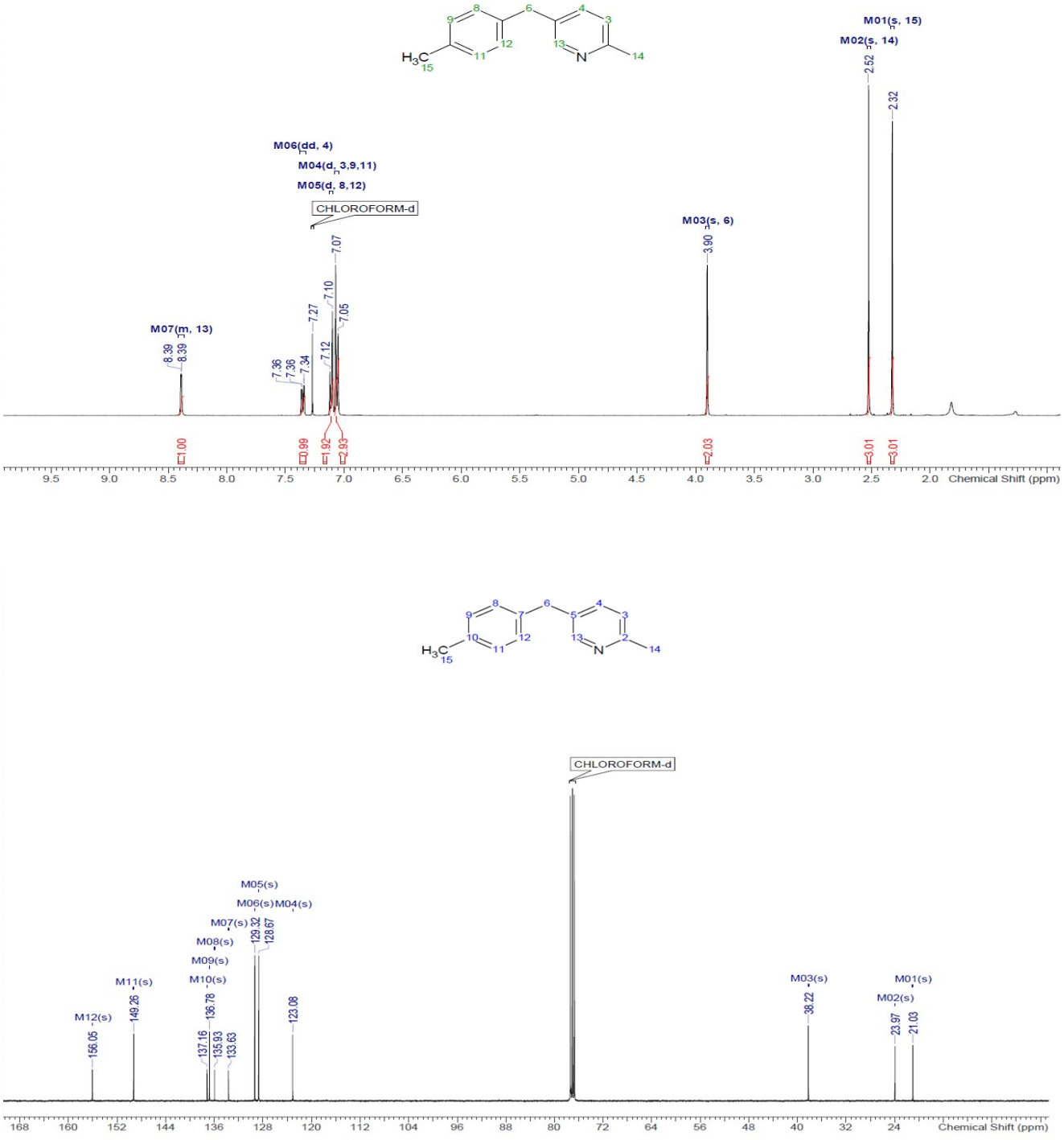


Figure 20 ^{1}H NMR and ^{13}C NMR of 3f

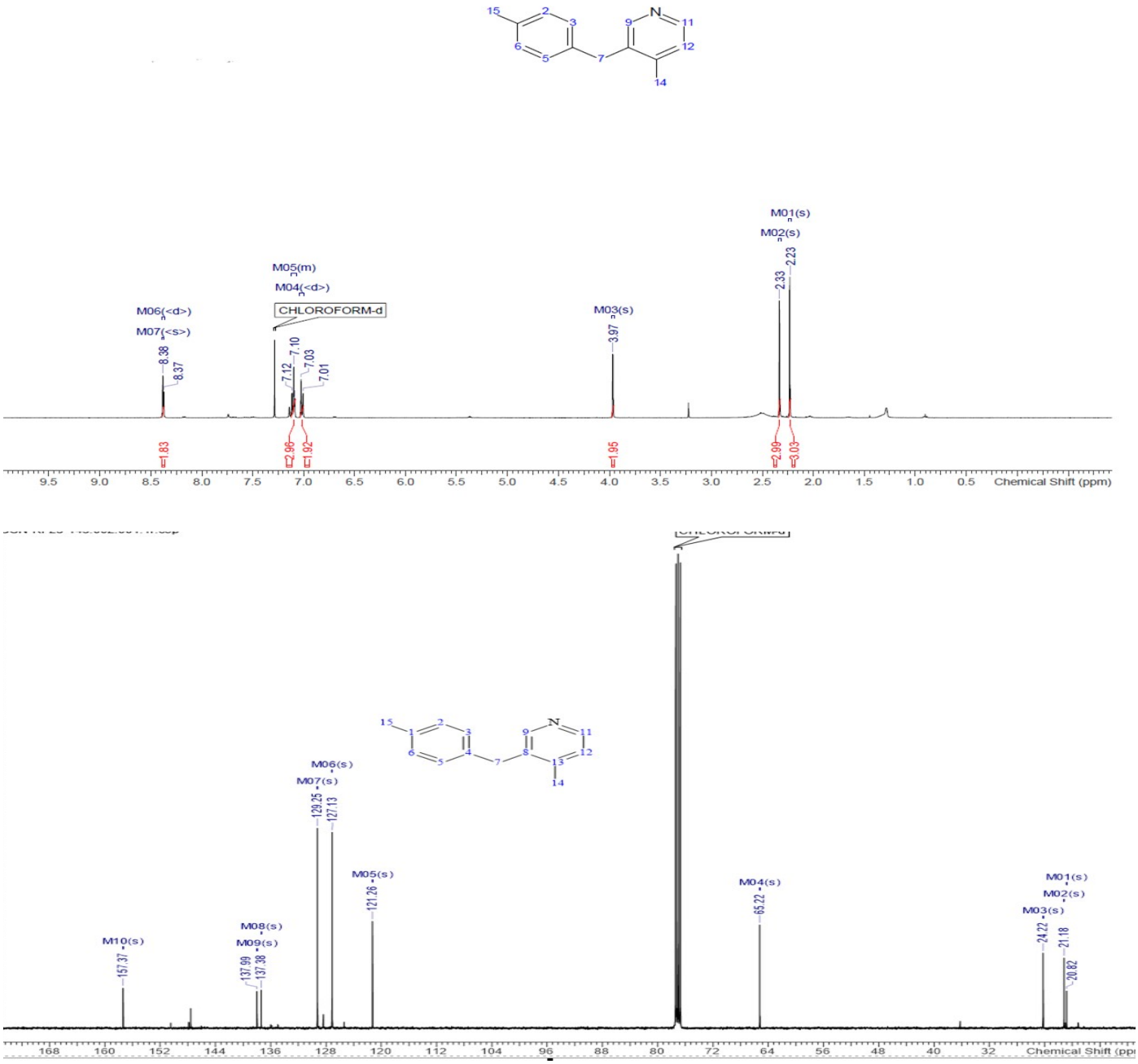


Figure 21 ^{1}H NMR and ^{13}C NMR of 3g

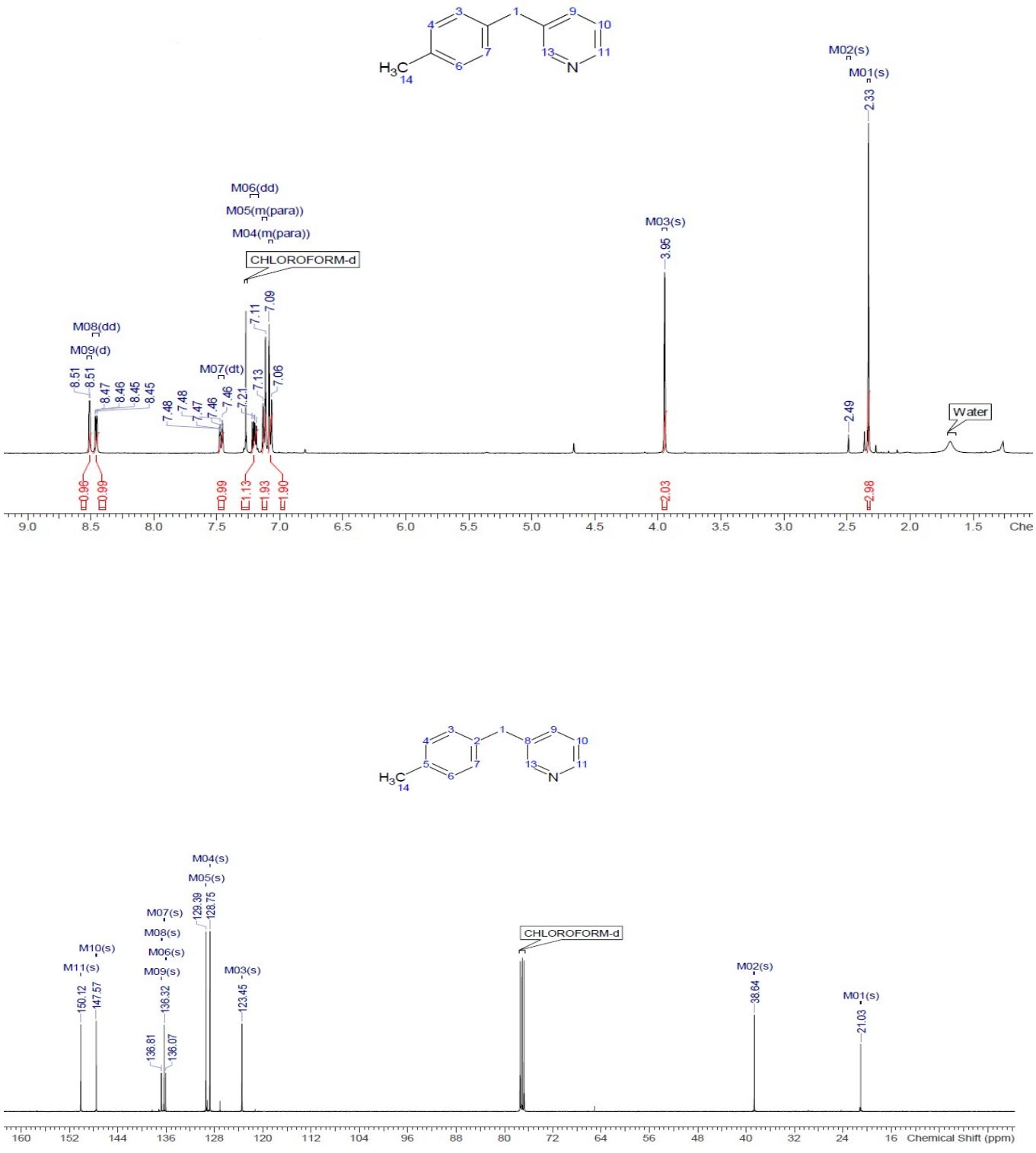


Figure 22 ^{1}H NMR and ^{13}C NMR of 3h

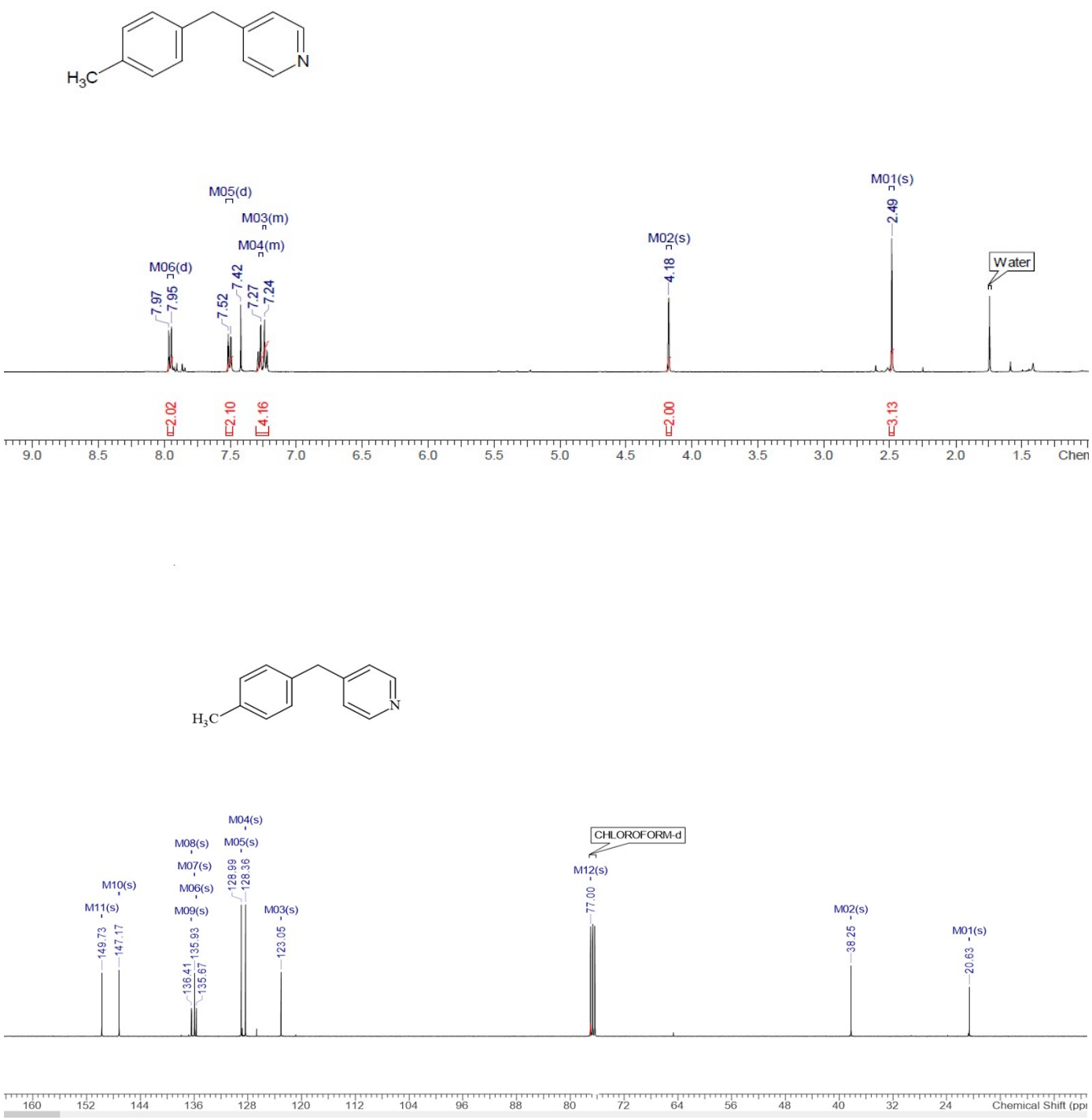


Figure 23 ^{1}H NMR and ^{13}C NMR of 3i

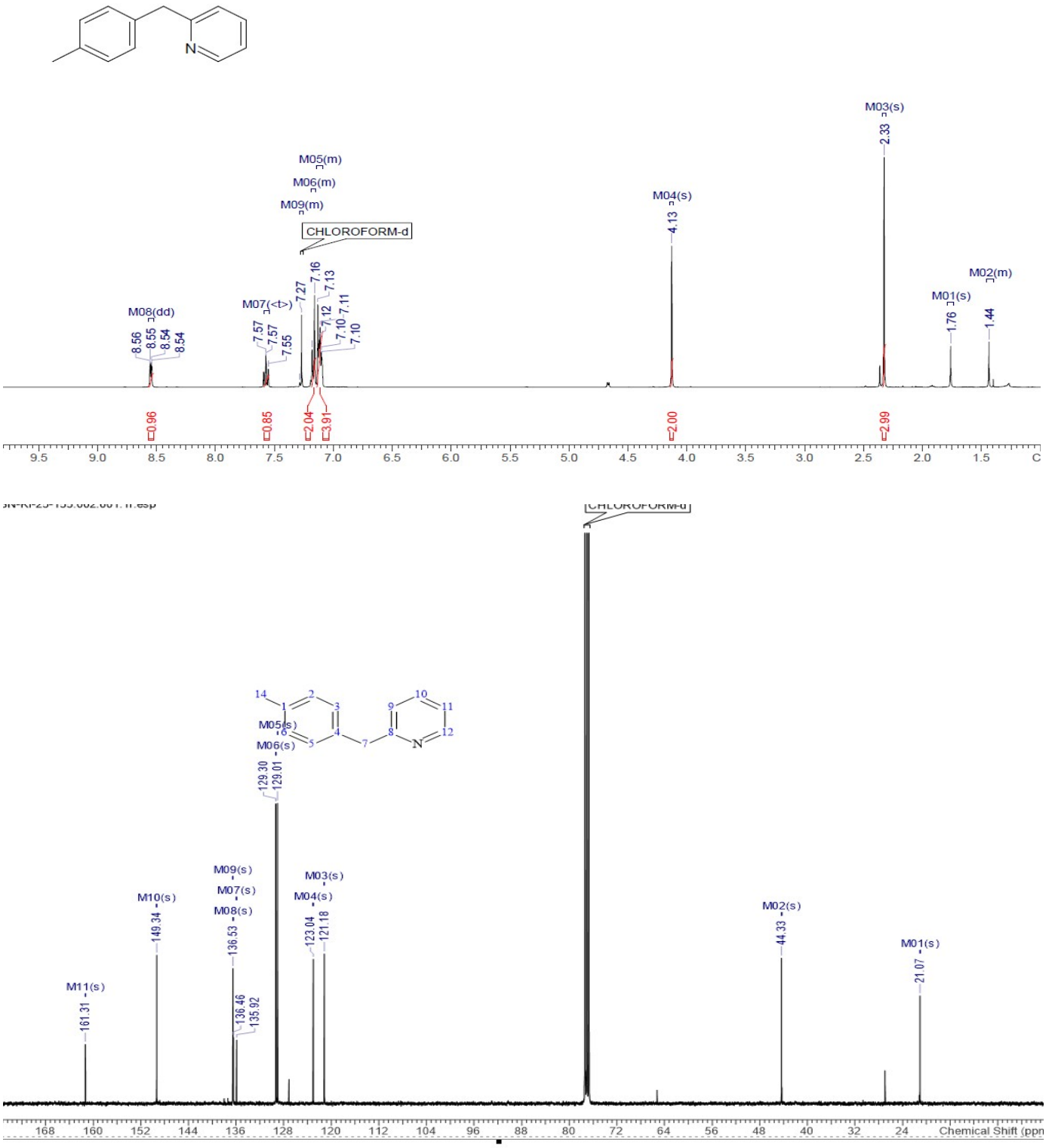


Figure 24 ^{1}H NMR and ^{13}C NMR of 3j

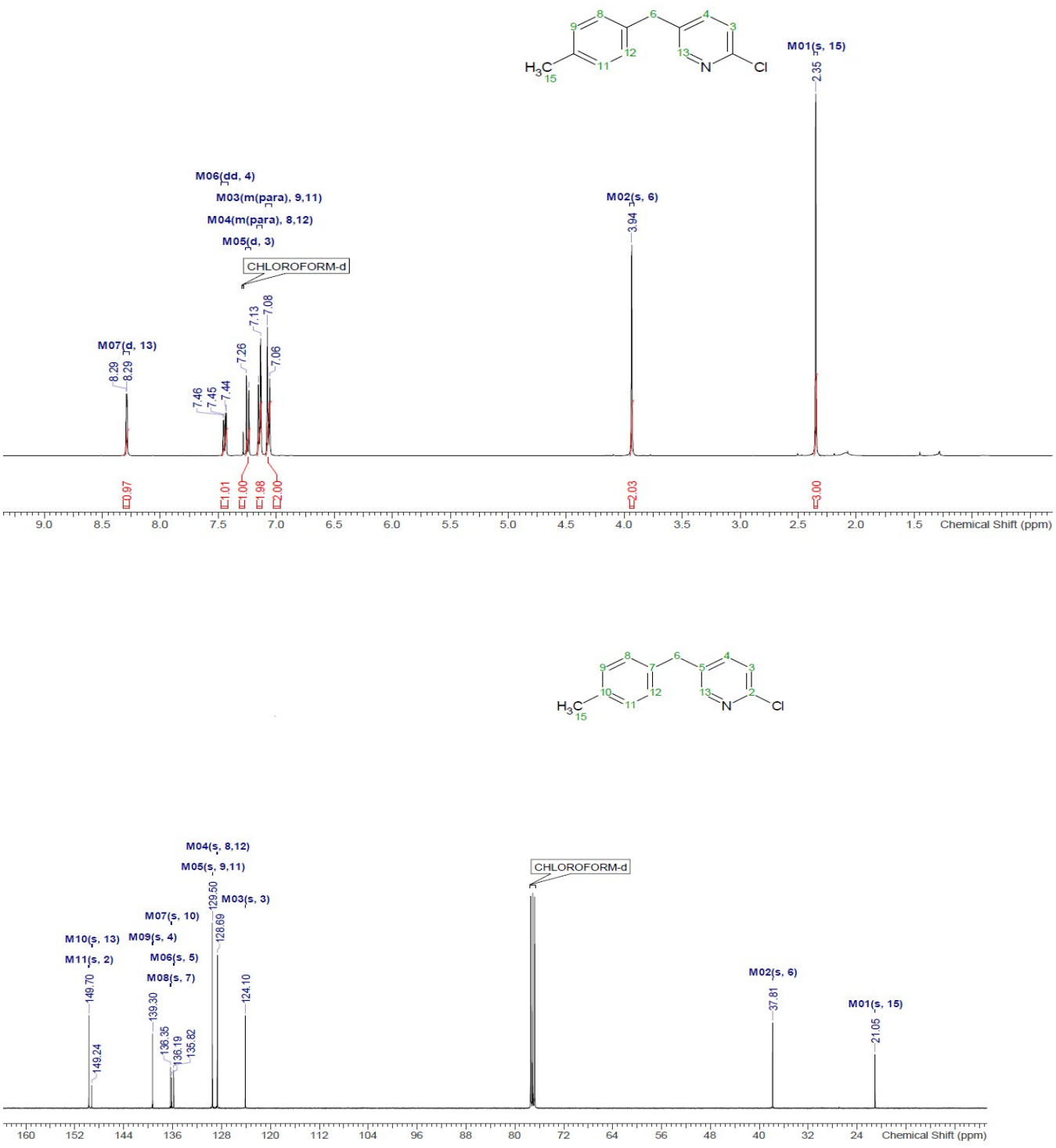
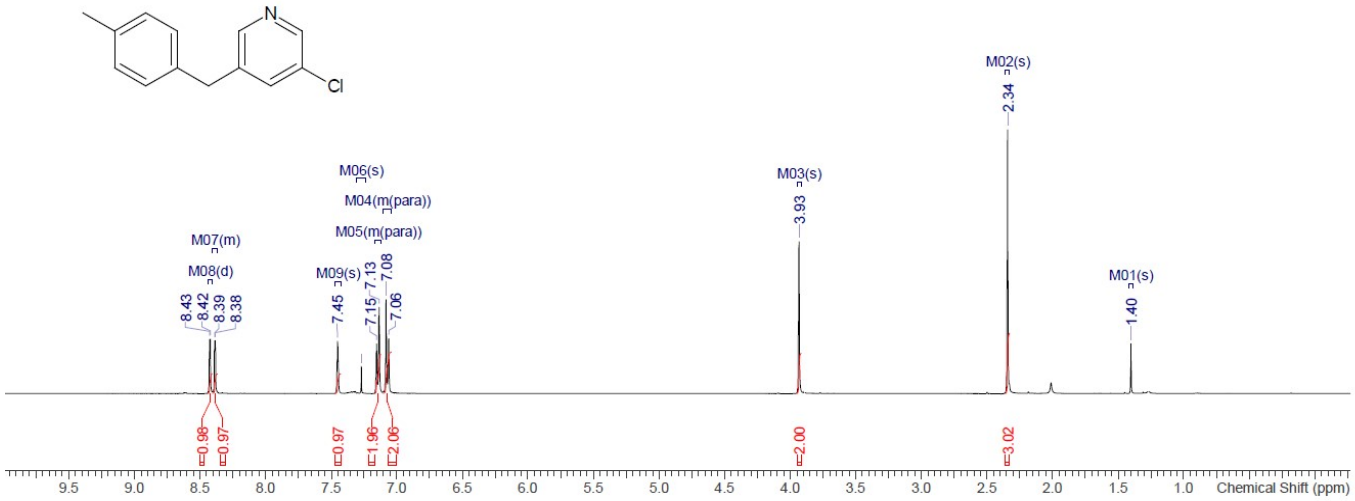


Figure 25 ^{1}H NMR and ^{13}C NMR of 3k



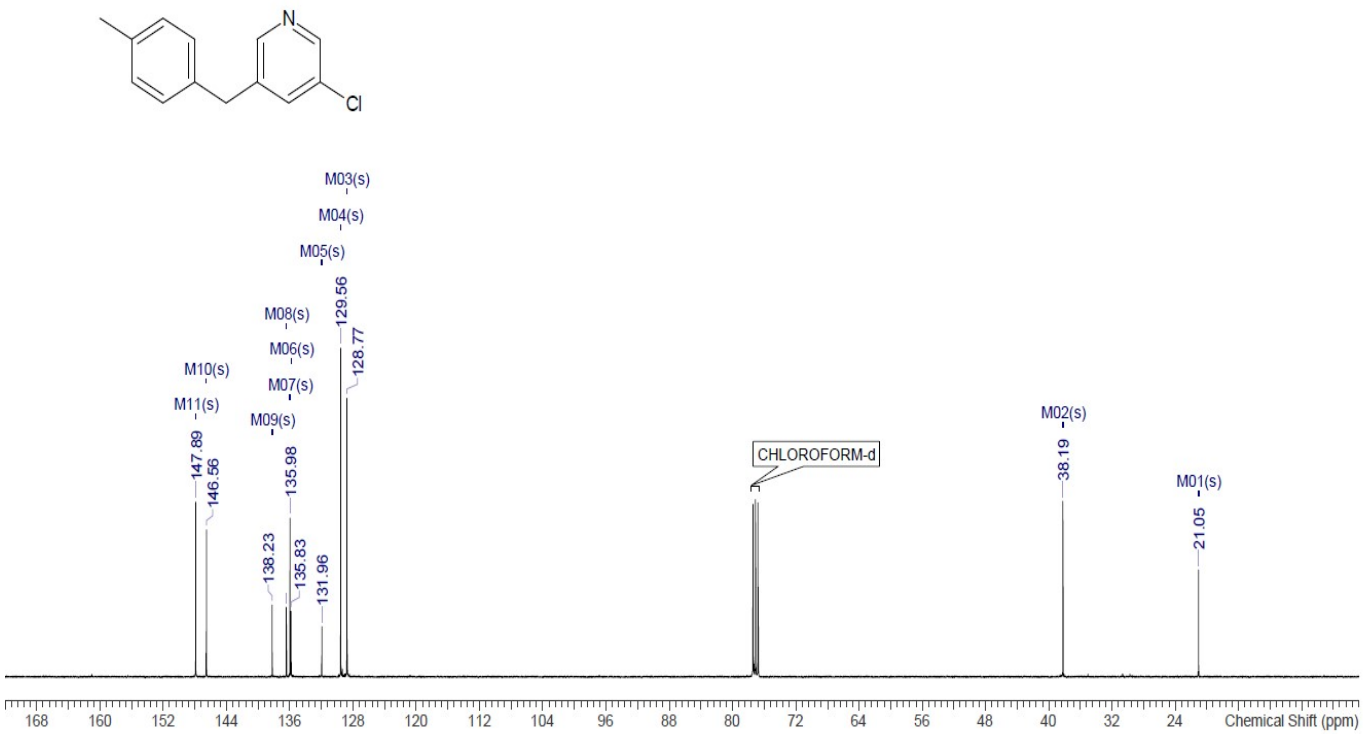


Figure 26 ^{1}H NMR and ^{13}C NMR of 3l

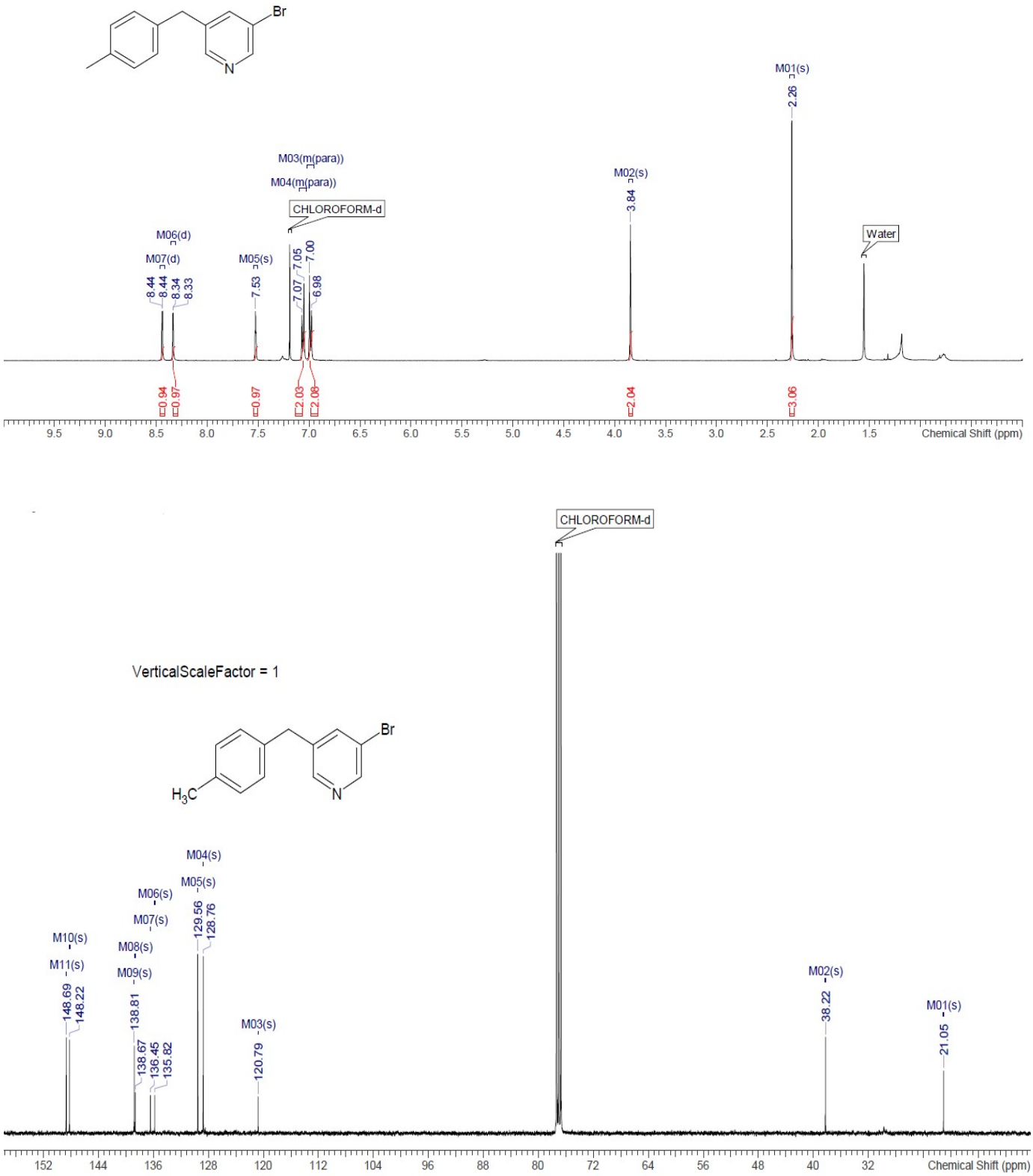


Figure 27 ^{1}H NMR and ^{13}C NMR of 3m

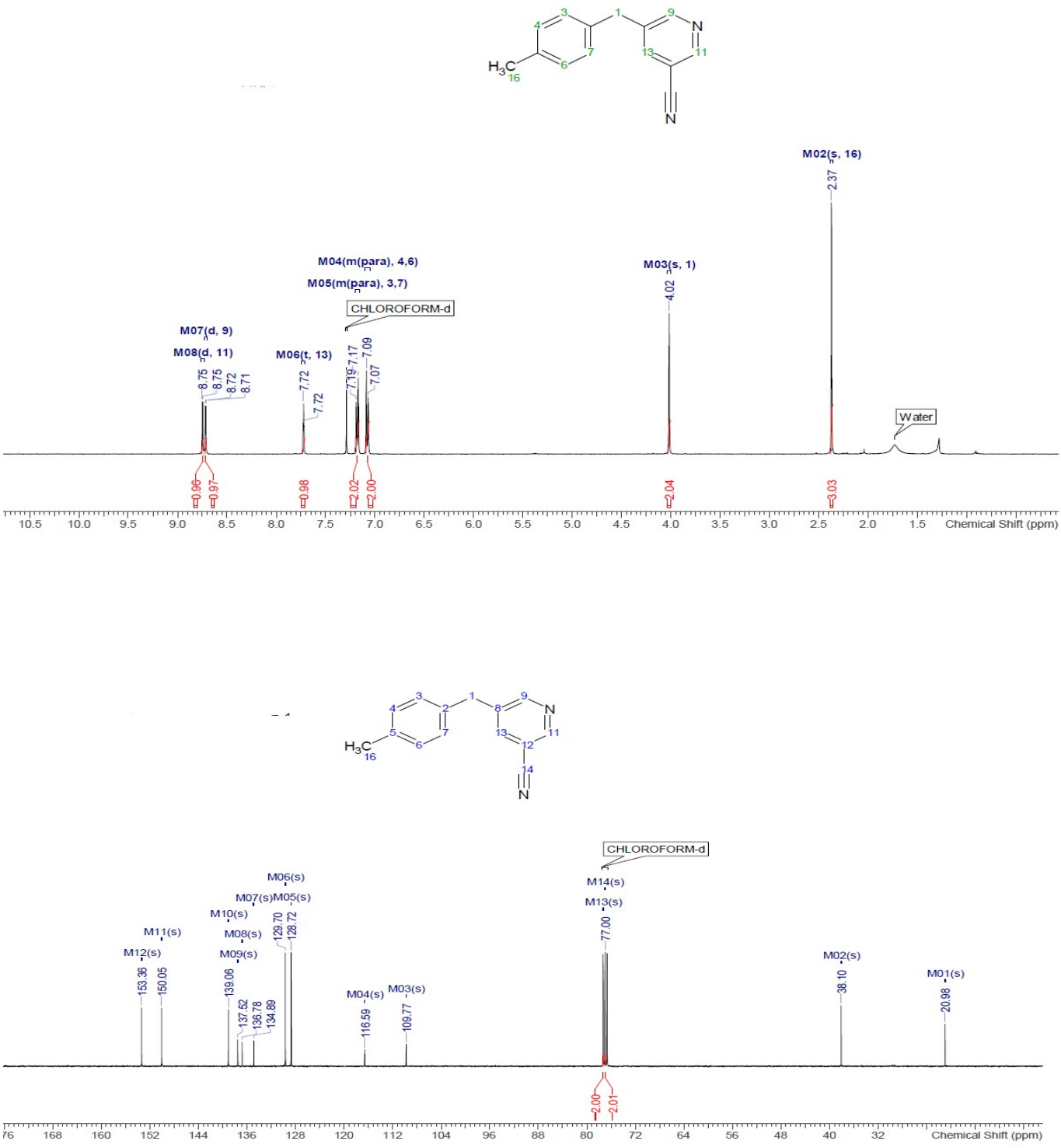


Figure 28 ^{1}H NMR and ^{13}C NMR of 3n

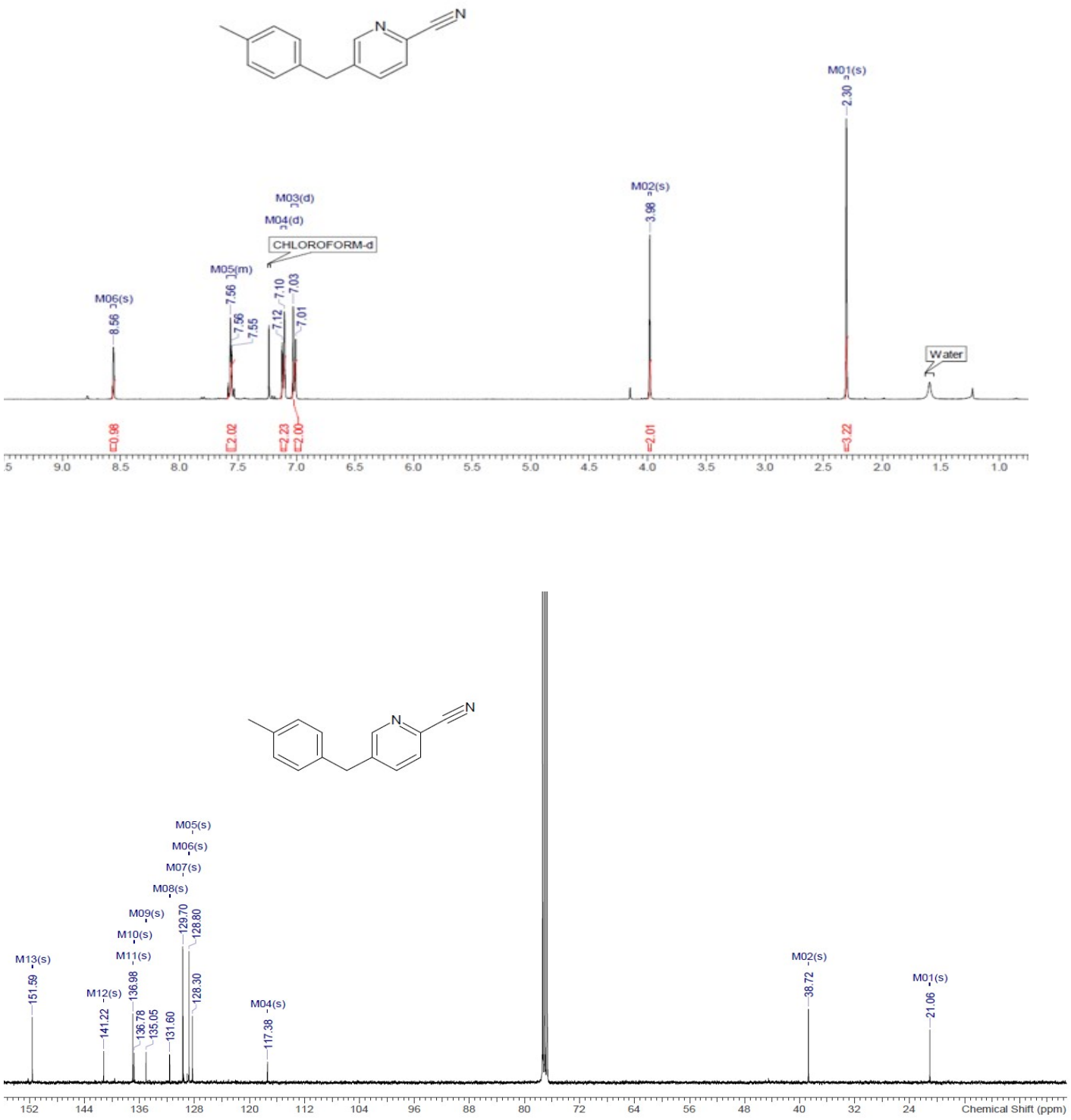


Figure 29 ^{1}H NMR and ^{13}C NMR of 3o

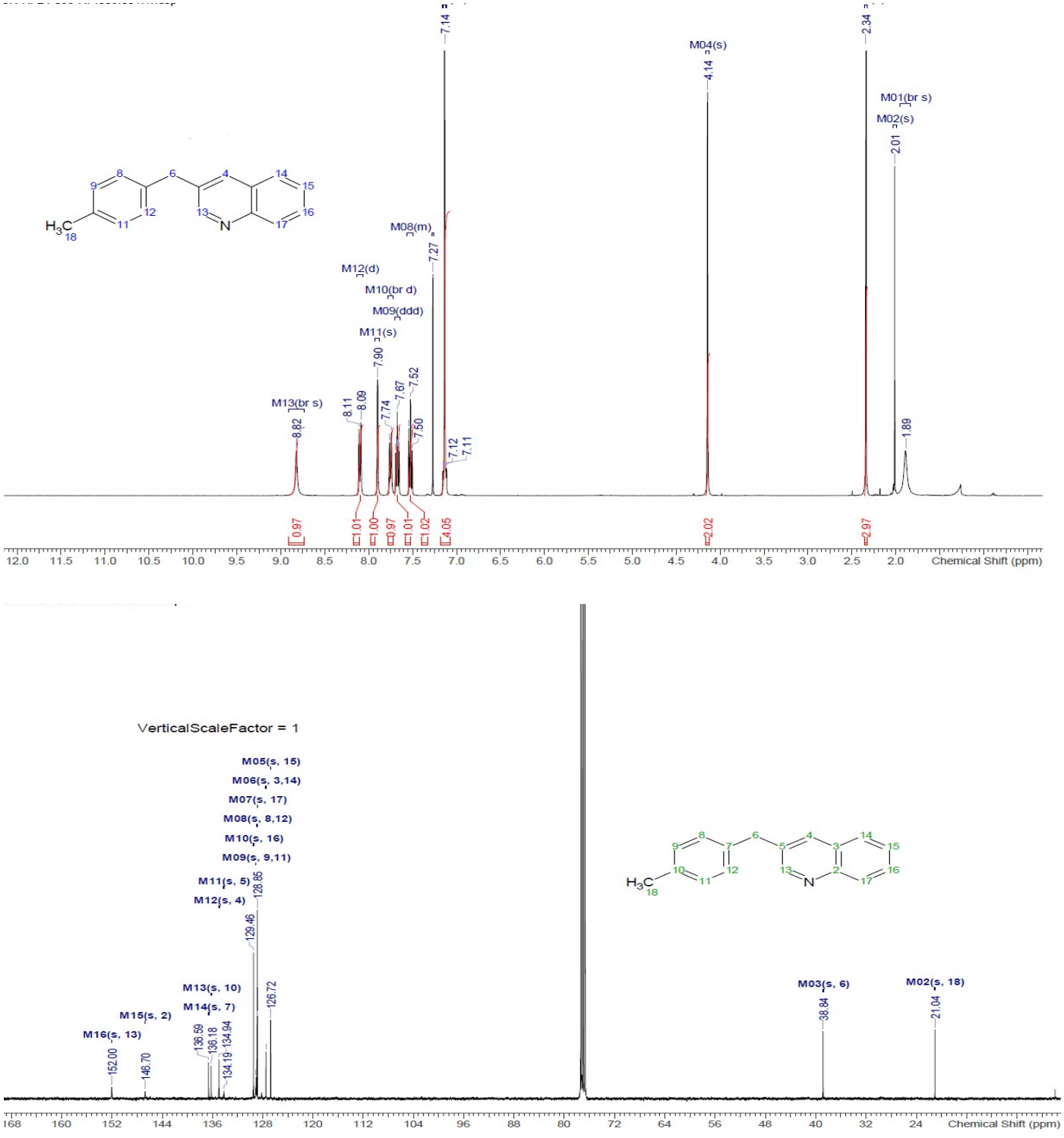


Figure 30 ^{1}H NMR and ^{13}C NMR of 3p

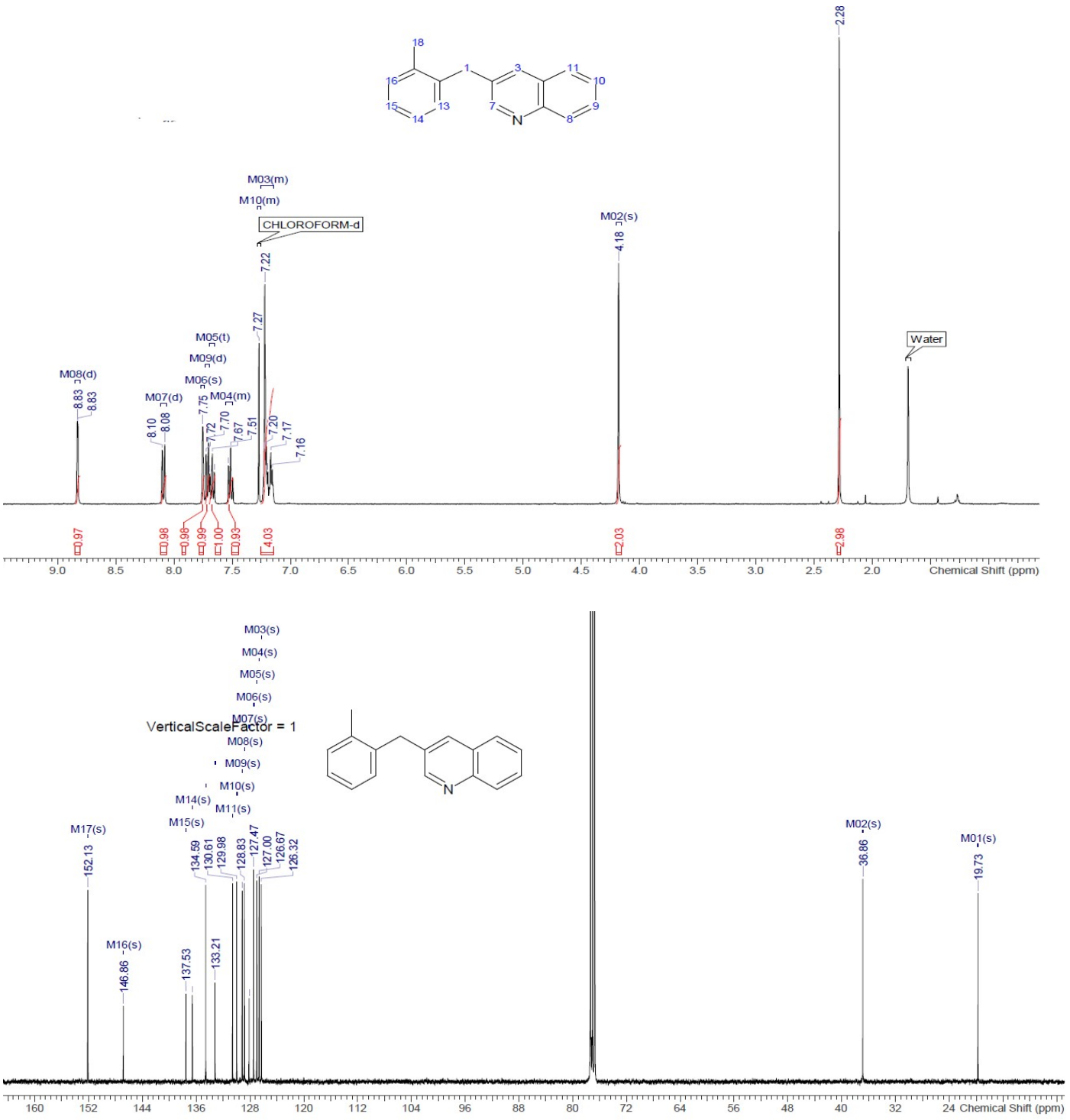


Figure 31 ^{1}H NMR and ^{13}C NMR of 4a

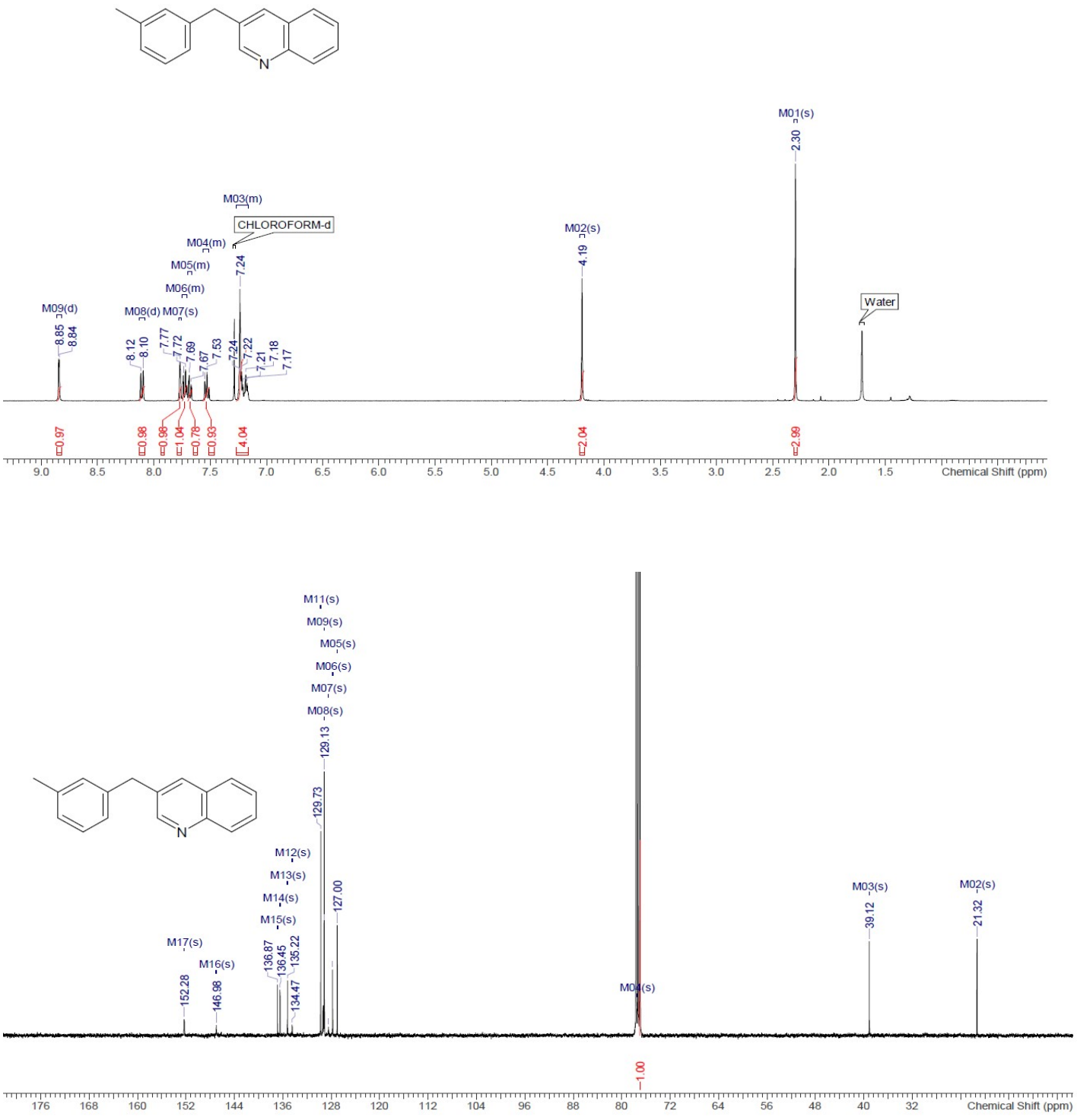


Figure 32 ^{1}H NMR and ^{13}C NMR of 4b

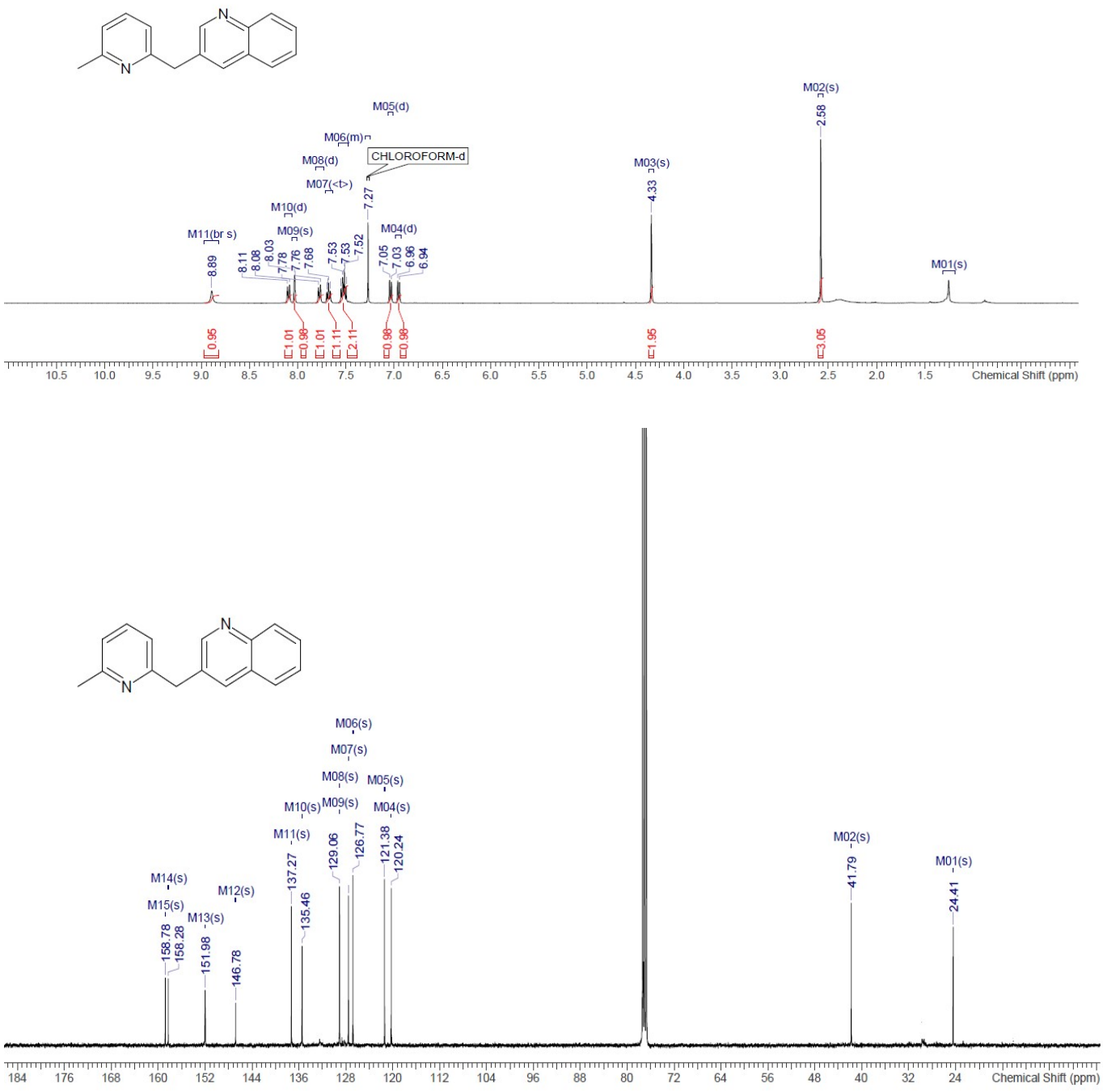


Figure 33 ^{1}H NMR and ^{13}C NMR of 4c

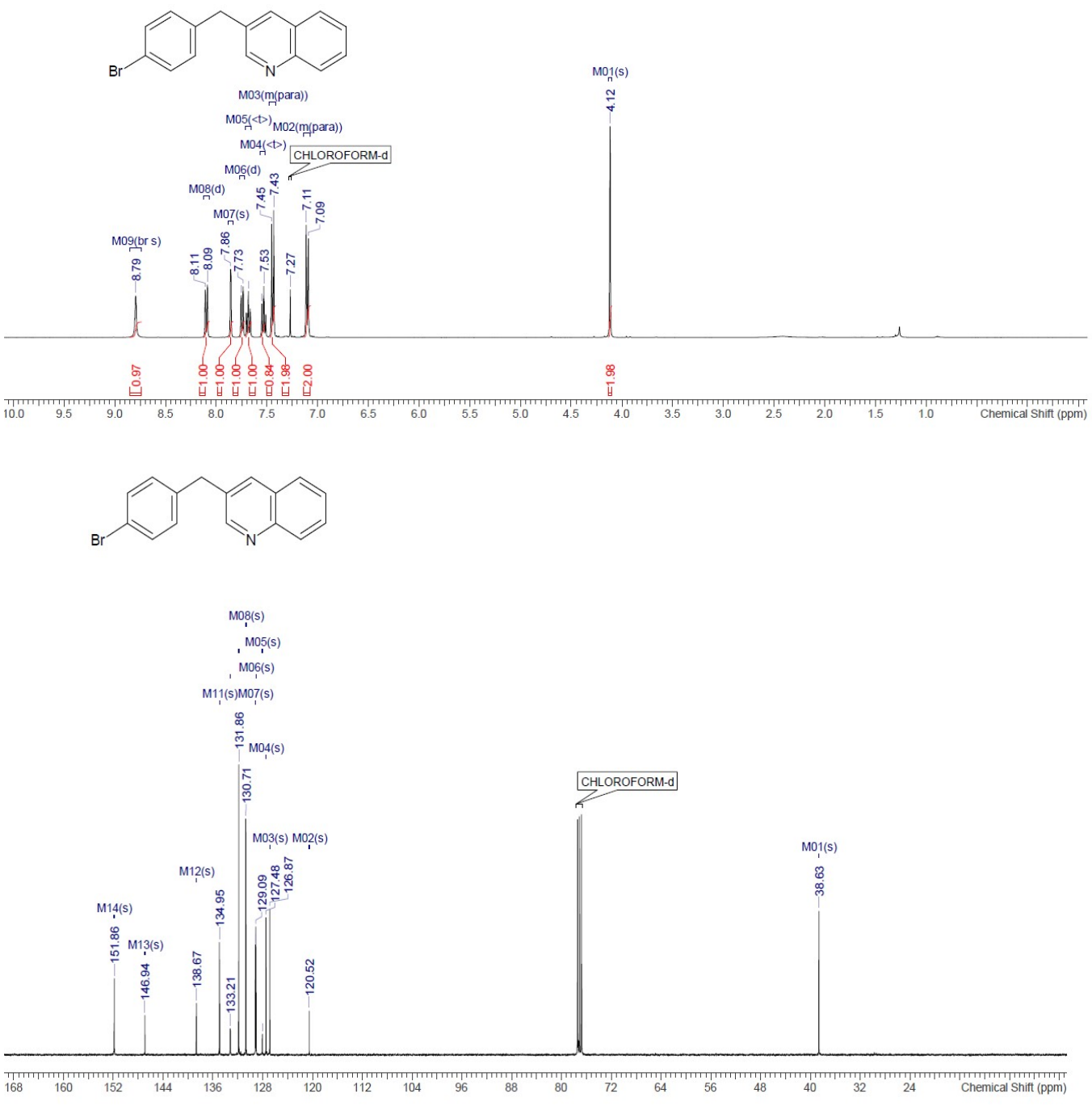


Figure 34 ^{1}H NMR and ^{13}C NMR of 4d

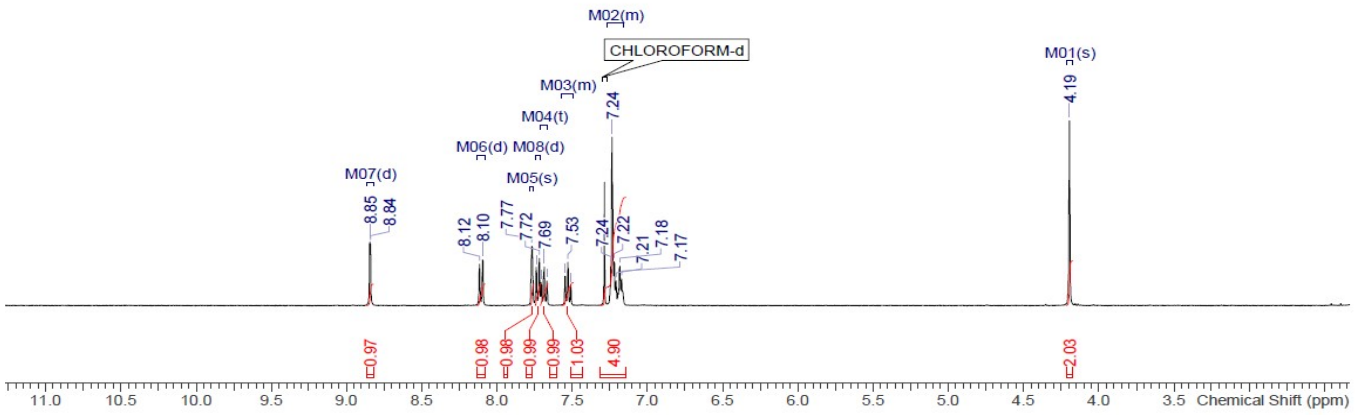
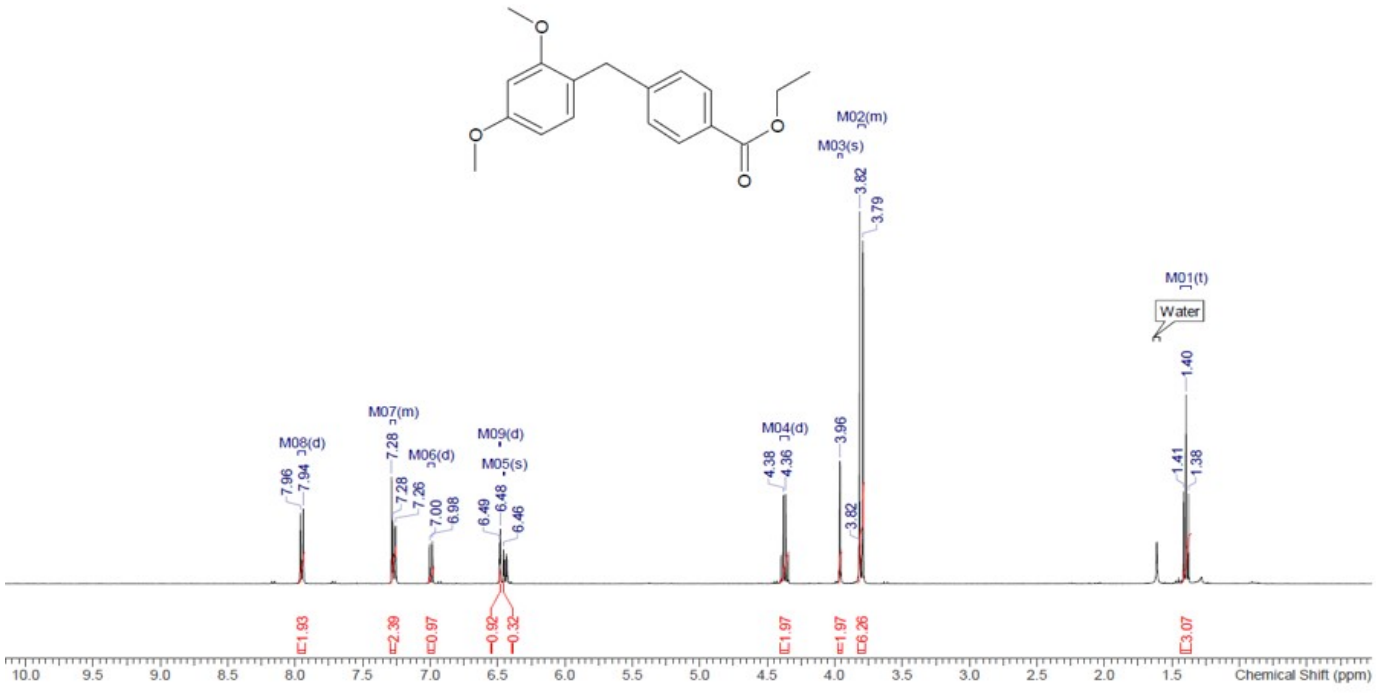


Figure 35 ^{1}H NMR of 4e



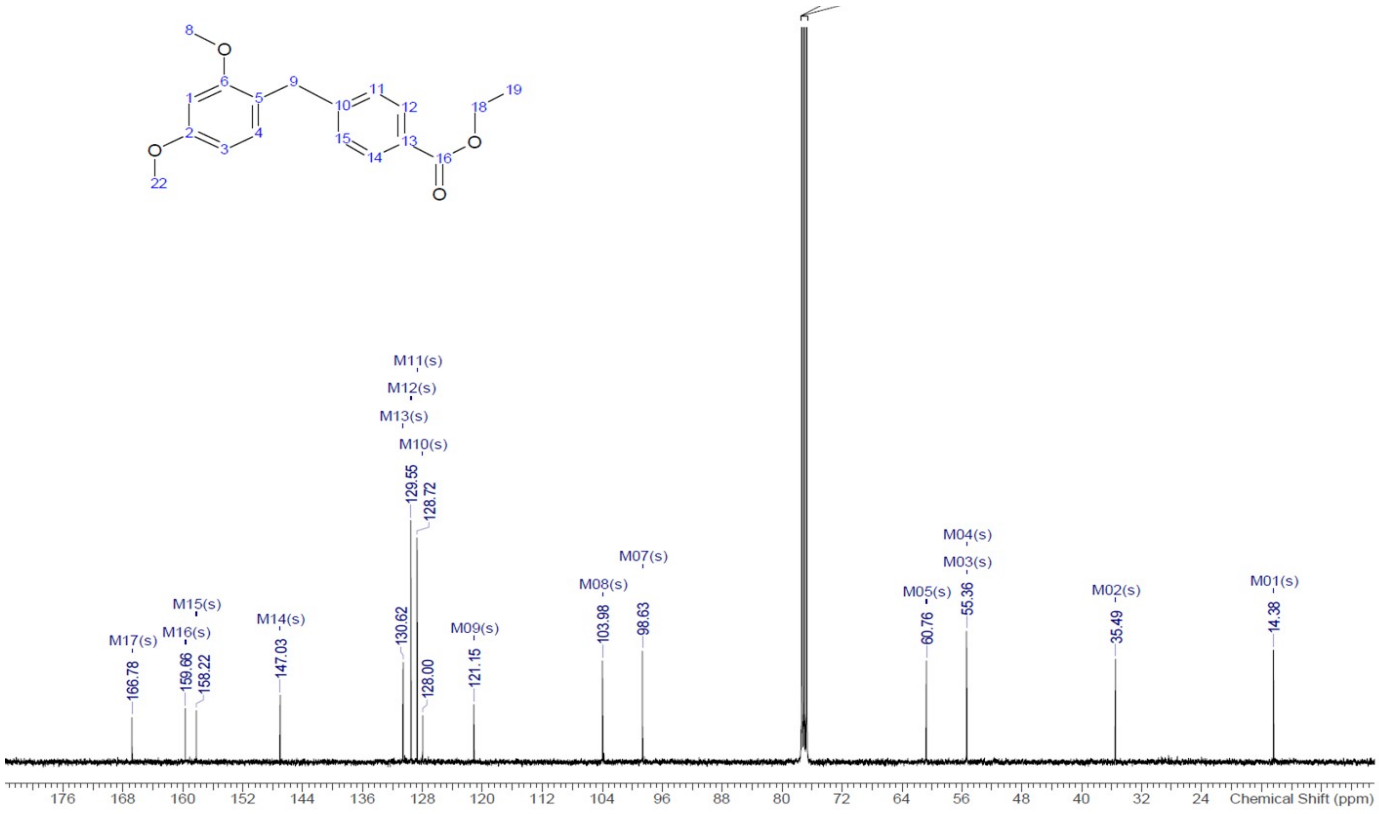
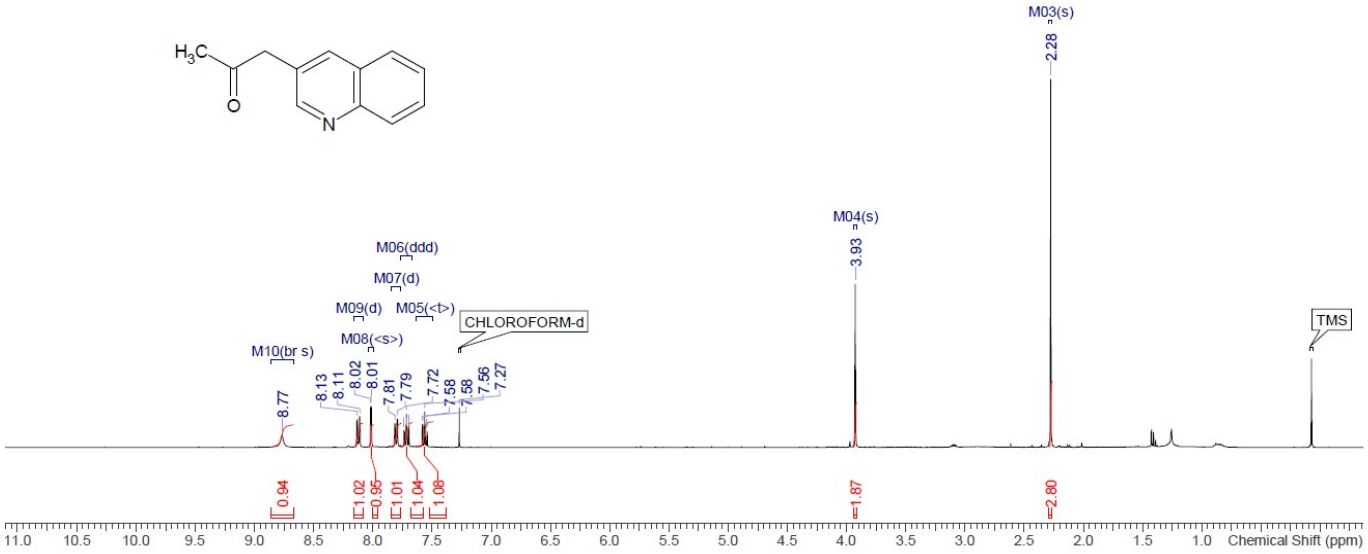


Figure 36 ^{1}H NMR and ^{13}C NMR of 4f



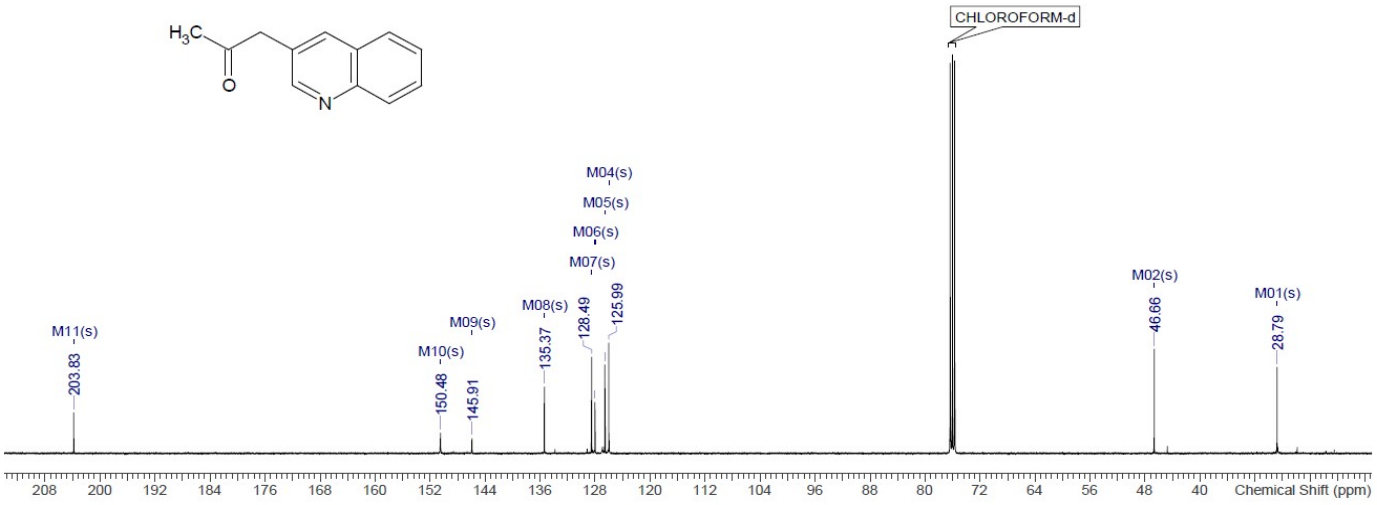
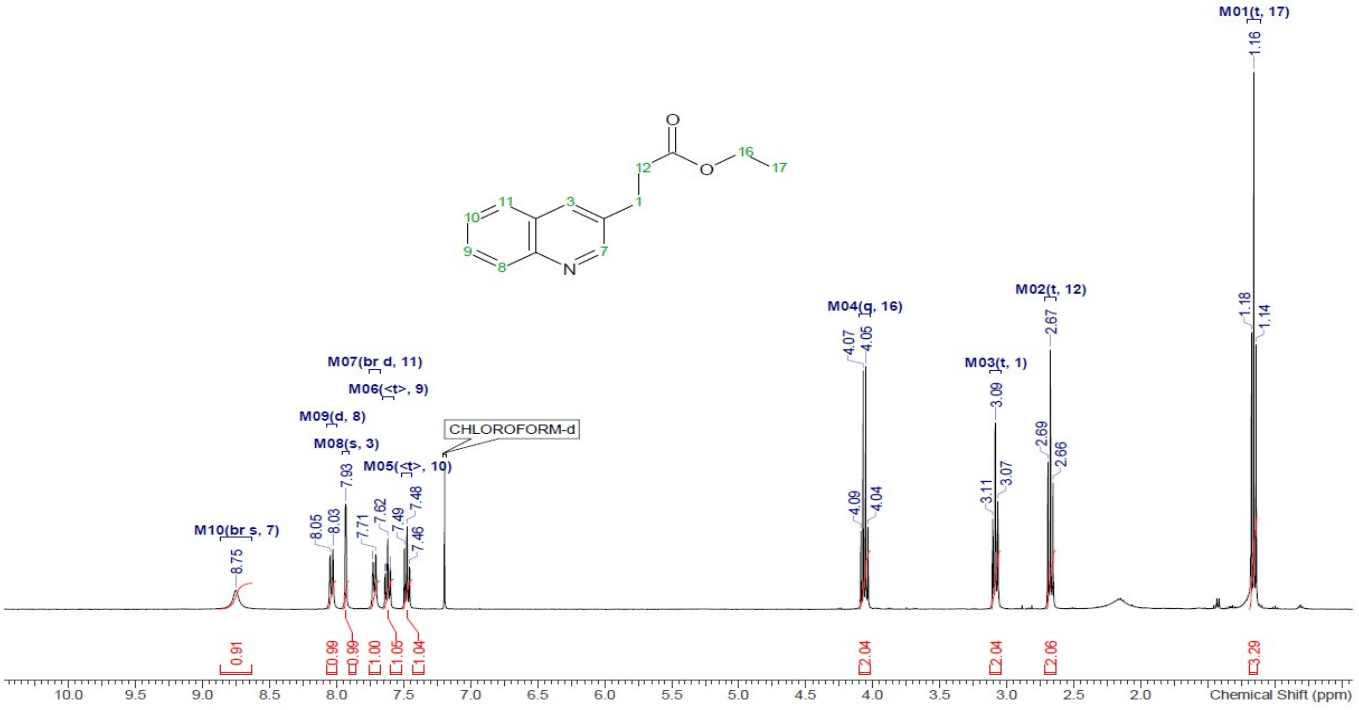


Figure 37 ^{1}H NMR and ^{13}C NMR of 4g



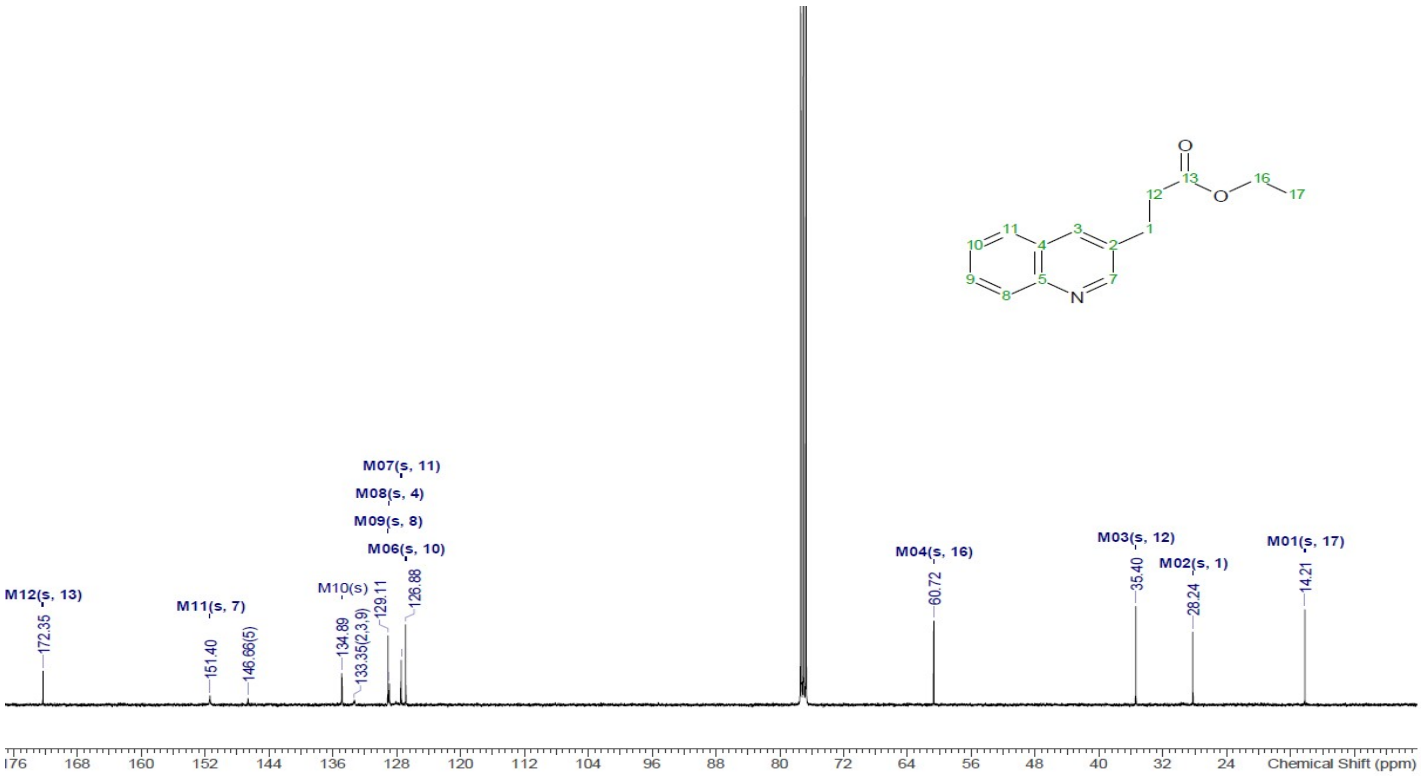
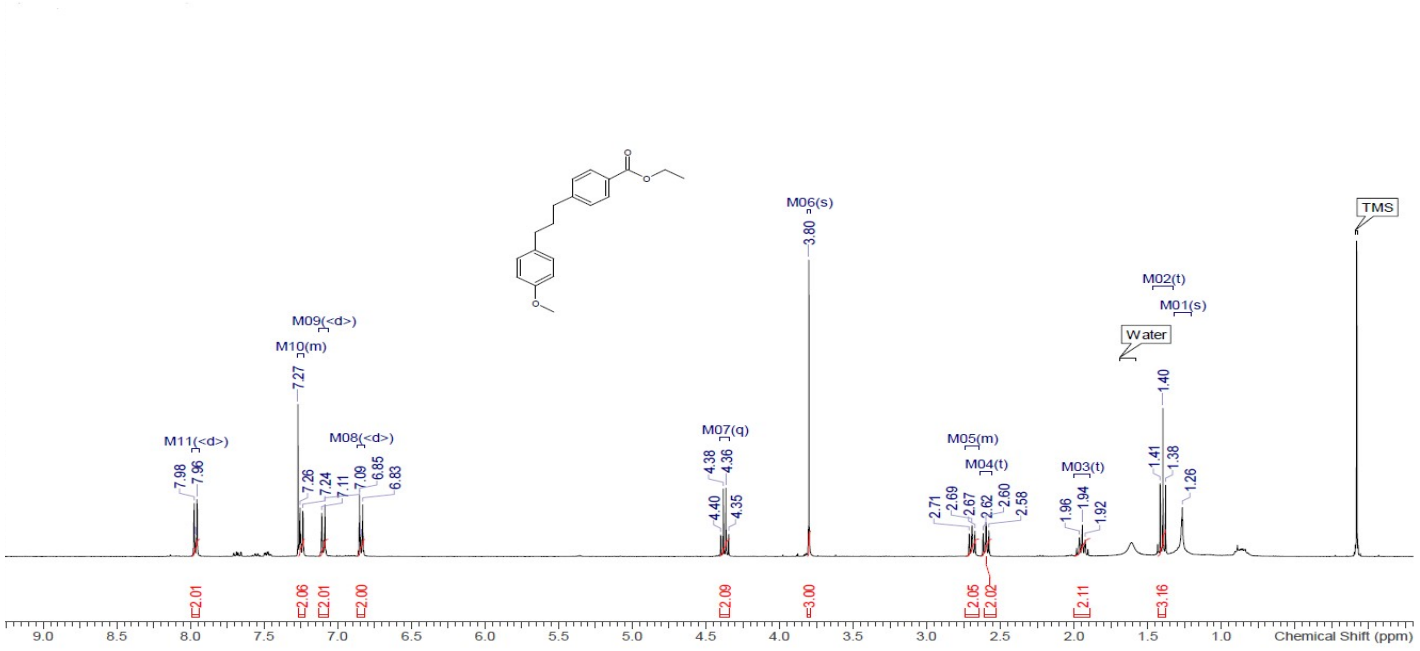


Figure 38 ^{1}H NMR and ^{13}C NMR of 4h



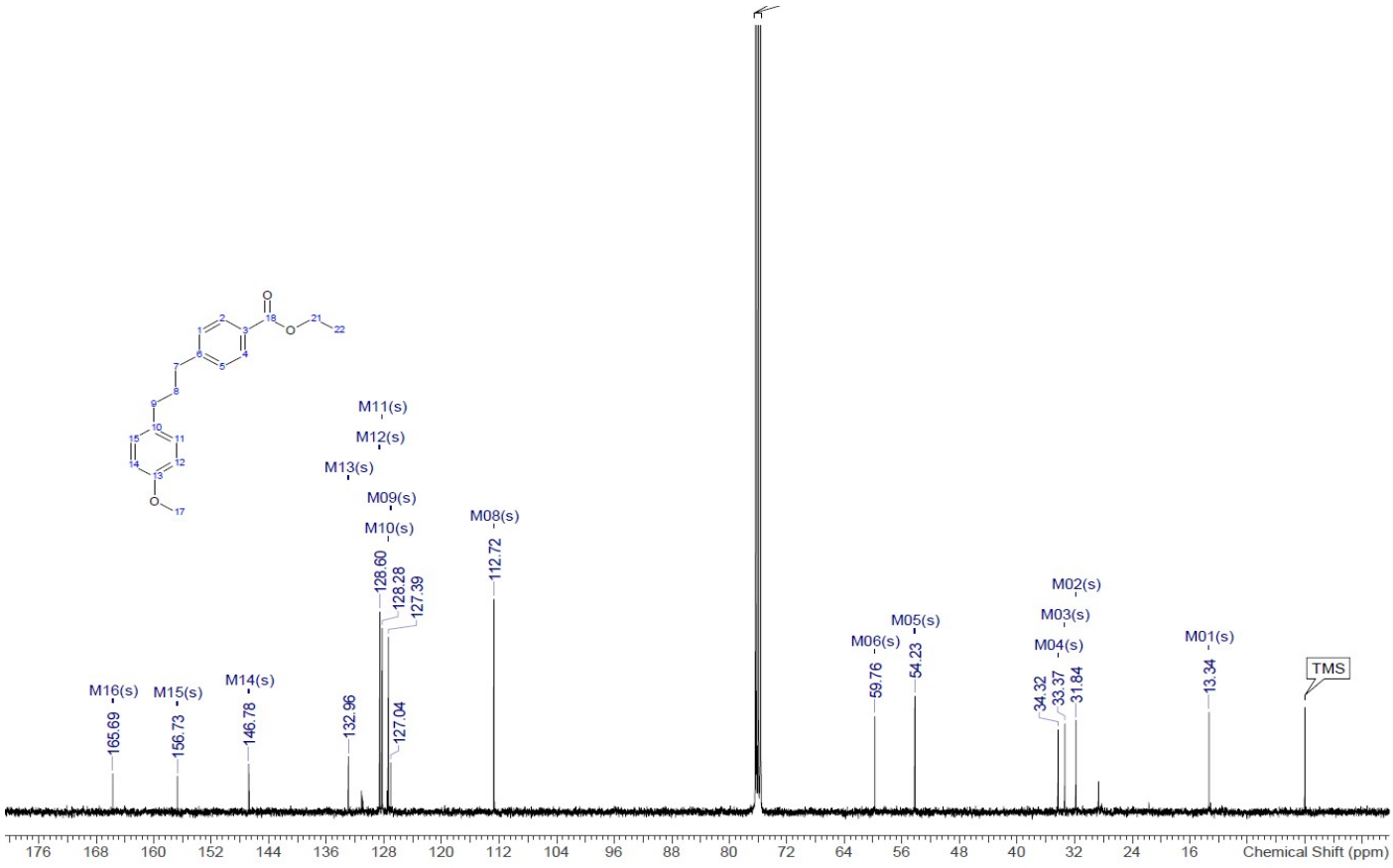


Figure 39 ^{1}H NMR and ^{13}C NMR of 4i