Supporting Information

Nickel Catalysis Enables Convergent Paired Electrolysis for Direct Arylation of Benzylic C-H Bonds

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1. General Information

a. Materials

All manipulations were carried out under nitrogen. The following chemicals were purchased and used as received: Fluorine doped tin oxide (FTO) glass (~13 Ω/sq, Aldrich), carbon fibre (hydrophilic plain cloth 30x30 cm, Fuelcellsetc), Nickel(II) bromide ethylene glycol dimethyl ether complex ((DME)$NiBr_2$, Aldrich), 4-4'-Dimethoxy-2-2'-bipyridine (**L1**, Aldrich), lutidine (Aldrich), toluene and its derivatives (Aldrich or TCI), aryl bromide (Aldrich or TCI). [LutH]ClO_4[1] and substrates (4-bromophenyl 4-methylbenzenesulfonate,[2] 1-isopropoxy-4-methylbenzene,[3] 1-(2-chloroethoxy)-4-methylbenzene[3] and 2-(*p*-tolyloxy)ethyl acetate[4]) were prepared according to previously reported procedures. All other reagents and solvents were purchased from commercial sources and used without purification.

b. Analytical Methods

NMR spectra were recorded on Bruker Avance 400 MHz spectrometers. ^{1}H NMR chemical shifts were referenced to residual protio solvent peaks or tetramethylsilane signal (0 ppm), and ^{13}C NMR chemical shifts were referenced to the solvent resonance. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, coupling constant (s) in Hz, integration). Data for ^{13}C NMR, ^{11}B NMR and ^{19}F NMR are reported in terms of chemical shift (δ, ppm). GC measurements were conducted on an Agilent Technologies 7890A GC equipped with a FID detector. GC-MS measurements were conducted on an Agilent Technologies 7890A GC system equipped with a 5975C MS detector. HRMS-ESI measurements were conducted at the EPFL ISIC Mass Spectrometry Service with a Micro Mass QTOF. LSV and CV curves were recorded with a three-electrode configuration using VMP-3 instrument (Biologic Science Instrument). FTO glass or carbon fibre was used as a working electrode with a $Ag/AgNO_3$ reference electrode and a Pt counter electrode. LSV and CV curves were performed at a scan rate of 50 mV/s without stirring. All potentials (vs $Ag/AgNO_3$) were calibrated with ferrocene/ferrocenyl couple (Fc/Fc^+) by reducing 0.23 V.

2. Devices for the electrochemical reaction

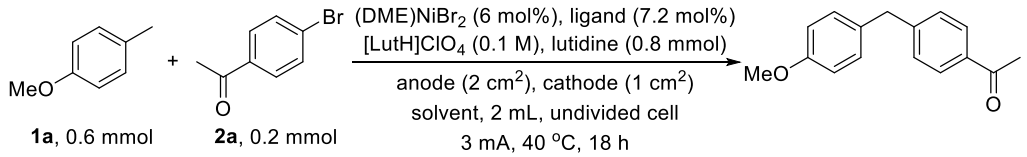
The reaction was performed in an undivided cell by a two-electrode configuration using VMP-3 instrument (Biologic Science Instrument). The distance between anode and cathode is 0.3~0.5 cm.

Figure S1. Undivided cell for the electrochemical reaction

3. Optimization of Reaction Conditions

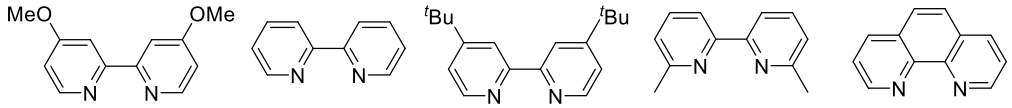
Table S1: Optimization of reaction conditions[a]

S1-1. The influence of ligand and nickel source



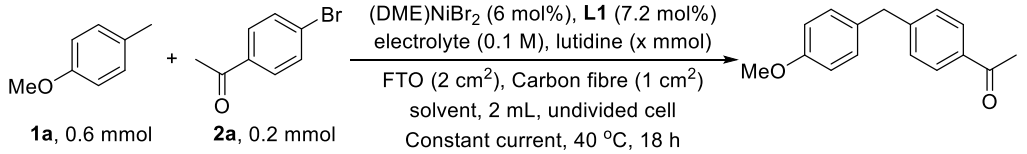
1a, 0.6 mmol **2a**, 0.2 mmol

Entry	Ligand	Anode	Cathode	Solvent	Yield (%)		
					1a	Acetophenone	Product
1-1	**L1**	FTO	Carbon fibre	THF/CH_3CN=4:1	39	6	50
1-2[b]	**L1**	FTO	Carbon fibre	THF/CH_3CN=4:1	--	--	76
1-3	**L2**	FTO	Carbon fibre	THF/CH_3CN=4:1	3	53	43
1-4	**L3**	FTO	Carbon fibre	THF/CH_3CN=4:1	6	30	46
1-5	**L4**	FTO	Carbon fibre	THF/CH_3CN=4:1	4	75	21
1-6	**L5**	FTO	Carbon fibre	THF/CH_3CN=4:1	31	18	48
1-7	no ligand	FTO	Carbon fibre	THF/CH_3CN=4:1	83	0	3
1-8[c]	**L1**	FTO	Carbon fibre	THF/CH_3CN=4:1	3	34	33



L1 **L2** **L3** **L4** **L5**

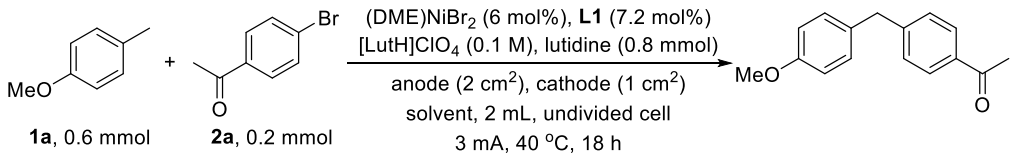
S1-2. The influence of base, solvent and electrolyte



1a, 0.6 mmol **2a**, 0.2 mmol

Entry	Lutidine	Electrolyte	Solvent	Yield (%)		
				1a	Acetophenone	Product
2-1	0 mmol	$[LutH]ClO_4$	THF/CH_3CN=4:1	8	73	19
2-2	0.4 mmol	$[LutH]ClO_4$	THF/CH_3CN=4:1	6	46	35
2-3	1.2 mmol	$[LutH]ClO_4$	THF/CH_3CN=4:1	53	0	40
2-4	0.8 mmol	$[LutH]ClO_4$	CH_3CN	90	0	4
2-5	0.8 mmol	$[LutH]ClO_4$	DMA	60	16	15
2-6	0.8 mmol	$[LutH]ClO_4$	DMF	82	3	6
2-7	0.8 mmol	$LiClO_4$	THF/CH_3CN=4:1	57	0	33
2-8	0.8 mmol	Bu_4NBF_6	THF/CH_3CN=4:1	23	38	8

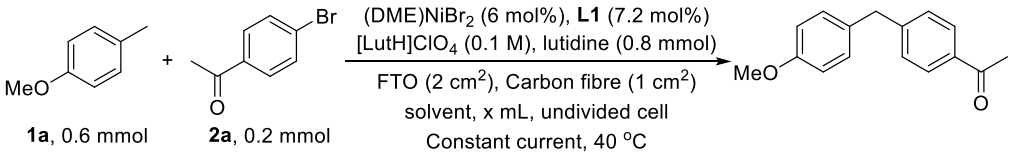
S1-3. The influence of the material of anode and cathode



1a, 0.6 mmol **2a**, 0.2 mmol

Entry	Anode	Cathode	Solvent	Yield (%)		
				1a	Acetophenone	Product
3-1	FTO	Ni foam	THF/CH_3CN=4:1	42	0	45
3-2	FTO	Pt foil	THF/CH_3CN=4:1	44	0	28
3-3	Carbon fibre (1 cm^2)	Carbon fibre	THF/CH_3CN=4:1	87	0	0
3-4	Pt foil (1 cm^2)	Carbon fibre	THF/CH_3CN=4:1	74	3	7
3-5	graphite (1 cm^2)	Carbon fibre	THF/CH_3CN=4:1	0	21	3

S1-4. The influence of current and concentration

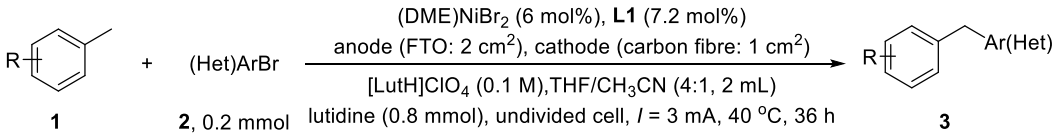


1a, 0.6 mmol **2a**, 0.2 mmol

Entry	Solvent	Current	Reaction time	Yield (%)		
				1a	Acetophenone	Product
4-1	THF/CH_3CN=4:1 (2 mL)	2 mA	36 h	15	23	54
4-2	THF/CH_3CN=4:1 (2 mL)	4 mA	27 h	33	3	52
4-3	THF/CH_3CN=4:1 (2 mL)	4 mA	36 h	13	4	62
4-4	THF/CH_3CN=4:1 (2 mL)	8 mA	18 h	7	4	25
4-5	THF/CH_3CN=4:1 (1.5 mL)	3 mA	18 h	34	13	44
4-6	THF/CH_3CN=4:1 (3 mL)	3 mA	18 h	38	23	24
4-7	THF/CH_3CN=4:1 (4 mL)	3 mA	18 h	13	17	13

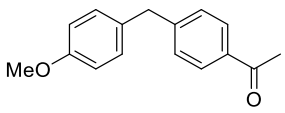
[a] Reaction conditions: **1a** (0.6 mmol), **2a** (0.2 mmol), (DME)$NiBr_2$ (6 mol%), ligand (7.2 mol mol%), $LutHClO_4$ (0.1 M), and lutidine (0.8 mmol) in solvent (2 mL) at 40 °C. GC yield. [b] Reaction time: 36 h. Isolated yield. [c] $Ni(acac)_2$ was used instead of (DME)$NiBr_2$.

4. Nickel-Catalyzed C−H Arylation *via* Convergent Paired Electrolysis



1 2, 0.2 mmol 3

General procedure for C−H Arylation *via* convergent paired electrolysis: In a nitrogen filled glovebox, aryl bromide (0.2 mmol), toluene derivatives (0.6 ~ 2 mmol, 3 ~ 10 equiv), lutidine (0.8mmol, 4 equiv), (DME)$NiBr_2$ or $Ni(acac)_2$ (0.01 or 0.012 mmol, 5 or 6 mol%), **L1** (0.012 or 0.0144 mmol, 6 or 7.2 mol%), $[LutH]ClO_4$ (41.5 mg, 0.1 M), and solvent (THF/CH_3CN = 4 : 1 or 3 : 1, 2 mL) were added to a 20 mL test tube equipped with a magnetic stir bar. FTO glass (2 cm^2) was used as the anode and carbon fibre (1 cm^2) was used as the cathode. The reaction tube was taken out of glovebox after it was sealed up. The electrolysis was performed with a constant current (3 mA) at 40 °C for 36 h. The voltage was normally between 3.5V~3.8V (the resistance of the solution we measured was around 300~400 Ohm. As the reaction current is 3 mA, the voltage consumed by the resistance is >0.9V. The cell voltage between anode and cathode matches the LSV measurements quite well). The resulting solution was concentrated under vacuum (Perchlorate salts should be handled with care. We did not encounter any problem in our reactions, which is conducted in a small scale. For a larger scle, we recommend to wash away [LutH]ClO4 with water before evaporation). The residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/hexane to give the corresponding products.

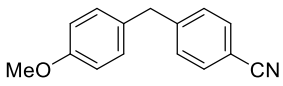


1-(4-(4-methoxybenzyl)phenyl)ethan-1-one (3a). 3a was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (10:1) to give the title compound as white solid (36.4 mg, 76%).

3a: ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 2H, aryl-*H*), 7.27 (d, *J* = 8.1 Hz, 2H, aryl-*H*), 7.09 (d, *J* = 8.6 Hz, 2H, aryl-*H*), 6.84 (d, *J* = 8.6 Hz, 2H, aryl-*H*), 3.98 (s,

2H, ArCH_2), 3.79 (s, 3H, ArOCH_3), 2.57 (s, 3H, COCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9 (C=O), 158.3 (aryl-*C*), 147.4 (aryl-*C*), 135.3 (aryl-*C*), 132.3 (aryl-*C*), 130.0 (aryl-*C*), 129.1 (aryl-*C*), 128.8 (aryl-*C*), 114.2 (aryl-*C*), 55.4 (Ar*C*H_2), 41.1 (ArO*C*H_3), 26.7 (CO*C*H_3).

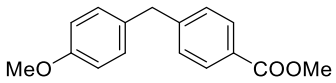
These spectroscopic data correspond to reported data.[5]



4-(4-methoxybenzyl)benzonitrile (3b). 3b was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (10:1) to give the title compound as colorless oil (26.6 mg, 60%).

3b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H, aryl-*H*), 7.27 (d, *J* = 8.4 Hz, 2H, aryl-*H*), 7.07 (d, *J* = 8.7 Hz, 2H, aryl-*H*), 6.85 (d, *J* = 8.7 Hz, 2H, aryl-*H*), 3.97 (s, 2H, ArCH_2), 3.79 (s, 3H, OCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5 (aryl-*C*), 147.4 (aryl-*C*), 132.4 (aryl-*C*), 131.5 (aryl-*C*), 130.1 (aryl-*C*), 129.6 (aryl-*C*), 119.1 (*C*N), 114.3 (aryl-*C*), 110.0 (aryl-*C*), 55.4 (Ar*C*H_2), 41.2 (O*C*H_3).

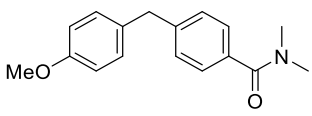
These spectroscopic data correspond to reported data.[6]



Methyl 4-(4-methoxybenzyl)benzoate (3c). 3c was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (10:1) to give the title compound as colorless oil (37.5mg, 73%).

3c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.3 Hz, 2H, aryl-*H*), 7.27 (d, *J* = 7.9 Hz, 2H, aryl-*H*), 7.12 (d, *J* = 8.0 Hz, 2H, aryl-*H*), 6.87 (d, *J* = 7.6 Hz, 2H, aryl-*H*), 4.00 (s, 2H, ArCH_2), 3.92 (s, 3H, COOCH_3), 3.81 (s, 3H, ArOCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2 (C=O), 158.3 (aryl-*C*), 147.1 (aryl-*C*), 132.3 (aryl-*C*), 130.0 (aryl-*C*), 129.9 (aryl-*C*), 128.9 (aryl-*C*), 128.1 (aryl-*C*), 114.1 (aryl-*C*), 55.3 (Ar*C*H_2), 52.1 (COO*C*H_3), 41.1 (ArO*C*H_3).

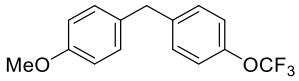
These spectroscopic data correspond to reported data.[7]



4-(4-methoxybenzyl)-N,N-dimethylbenzamide (3d). 3d was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (2:1) to give the title compound as pale yellow oil (35.6 mg, 66%).

3d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.8 Hz, 2H, aryl-*H*), 7.19 (d, *J* = 7.8 Hz, 2H, aryl-*H*), 7.09 (d, *J* = 8.3 Hz, 2H, aryl-*H*), 6.83 (d, *J* = 8.2 Hz, 2H, aryl-*H*), 3.93 (s, 2H, ArCH_2), 3.78 (s, 3H, ArOCH_3), 3.18 – 2.90 (br, 6H, NCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8 (C=O), 158.2 (aryl-*C*), 143.3 (aryl-*C*), 134.1 (aryl-*C*), 132.7 (aryl-*C*), 130.0 (aryl-*C*), 128.8 (aryl-*C*), 127.4 (aryl-*C*), 114.0 (aryl-*C*), 55.4 (Ar*C*H_2), 40.9 (ArO*C*H_3), 39.7 (N*C*H_3), 35.5 (N*C*H_3).

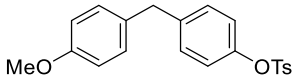
HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{20}NO_2^+$ 270.1489; Found 270.1495.



1-methoxy-4-(4-(trifluoromethoxy)benzyl)benzene (3e). 3e was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (100:1) to give the title compound as colorless oil (35.3 mg, 63%).

3e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.0 Hz, 2H, aryl-*H*), 7.15 – 7.07 (m, 4H, aryl-*H*), 6.85 (d, *J* = 7.9 Hz, 2H, aryl-*H*), 3.93 (s, 2H, ArCH_2), 3.79 (s, 3H, OCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3 (aryl-*C*), 147.7 (aryl-*C*), 140.5 (aryl-*C*), 132.7 (aryl-*C*), 130.1 (aryl-*C*), 130.0 (aryl-*C*), 121.1(aryl-*C*), 120.7 (q, *J* = 256.8 Hz, *C*F_3), 114.2 (aryl-*C*), 55.4 (Ar*C*H_2), 40.4 (O*C*H_3). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -57.9.

These spectroscopic data correspond to reported data.[8]

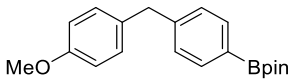


4-(4-methoxybenzyl)phenyl 4-methylbenzenesulfonate (3f). 3f was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (10:1) to give the title compound as colorless oil (51.7 mg, 70%).

3f: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.4 Hz, 2H, aryl-*H*), 7.30 (d, *J* = 7.6 Hz, 2H, aryl-*H*), 7.06 (t, *J* = 7.3 Hz, 4H, aryl-*H*), 6.88 (d, *J* = 7.3 Hz, 2H, aryl-*H*), 6.83 (d, *J* = 7.3 Hz, 2H, aryl-*H*), 3.87 (s, 2H, ArCH_2), 3.78 (s, 3H, OCH_3), 2.44 (s, 3H, ArCH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2 (aryl-*C*), 148.0 (aryl-*C*), 145.4 (aryl-*C*), 140.7 (aryl-*C*), 132.6 (aryl-*C*), 132.5 (aryl-*C*), 130.0 (aryl-*C*), 129.9 (aryl-*C*), 129.8 (aryl-*C*), 128.6 (aryl-*C*), 122.3 (aryl-*C*), 114.1 (aryl-*C*), 55.4 (Ar*C*H_2), 40.4 (O*C*H_3), 21.8 (Ar*C*H_3).

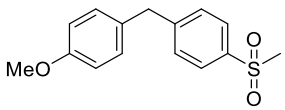
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{20}NaO_4S^+$ 391.0975; Found 391.0974.



2-(4-(4-methoxybenzyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g). 3g was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (10:1) to give the title compound as white solid (52.0 mg, 80%).

3g: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.0 Hz, 2H, aryl-*H*), 7.21 (d, *J* = 7.2 Hz, 2H, aryl-*H*), 7.10 (d, *J* = 7.8 Hz, 2H, aryl-*H*), 6.83 (d, *J* = 7.3 Hz, 2H, aryl-*H*), 3.95 (s, 2H, ArCH_2), 3.79 (s, 3H, OCH_3), 1.35 (s, 12H, C(CH_3)$_2$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1 (aryl-*C*), 145.0 (aryl-*C*), 135.1 (aryl-*C*), 133.1 (aryl-*C*), 130.0 (aryl-*C*), 128.4 (aryl-*C*), 114.0 (aryl-*C*), 55.4 (Ar*C*H_2), 41.3 (O*C*H_3), 25.0 (C(*C*H_3)$_2$). The resonances corresponding to the carbon attached to boron were not observed in the ^{13}C NMR spectrum. ^{11}B NMR ($CDCl_3$, 128 MHz): δ 31.1.

HRMS (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{20}H_{25}BO_3^+$ 324.1891; Found 324.1885.

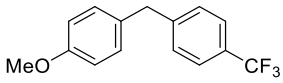


1-methoxy-4-(4-(methylsulfonyl)benzyl)benzene (3h). 3h was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as white solid (38.5 mg, 70%).

3h: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.8 Hz, 2H, aryl-*H*), 7.36 (d, *J* = 7.8 Hz, 2H, aryl-*H*), 7.09 (d, *J* = 8.0 Hz, 2H, aryl-*H*), 6.85 (d, *J* = 8.1 Hz, 2H, aryl-*H*), 4.00 (s, 2H, ArCH_2), 3.79 (s, 3H, OCH_3), 3.02 (s, 3H, SO_2C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5 (aryl-*C*), 148.3 (aryl-*C*), 138.4 (aryl-*C*), 131.6 (aryl-*C*), 130.1 (aryl-*C*), 129.8

(aryl-*C*), 127.7 (aryl-*C*), 114.3 (aryl-*C*), 55.4 (Ar*C*H_2), 44.7 (SO_2Me), 41.0 (O*C*H_3).

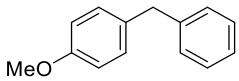
HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{17}O_3S^+$ 277.0893; Found 277.0892.



1-methoxy-4-(4-(trifluoromethyl)benzyl)benzene (3i). 3i was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (100:1) to give the title compound as colorless oil (31.2 mg, 59%).

3i: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.9 Hz, 2H, aryl-*H*), 7.29 (d, *J* = 7.9 Hz, 2H, aryl-*H*), 7.10 (d, *J* = 8.1 Hz, 2H, aryl-*H*), 6.86 (d, *J* = 8.1 Hz, 2H, aryl-*H*), 3.99 (s, 2H, ArCH_2), 3.80 (s, 3H, OCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4 (aryl-*C*), 145.8 (aryl-*C*), 132.2 (aryl-*C*), 130.0 (aryl-*C*), 129.2 (aryl-*C*), 128.5 (q, *J* = 32.4 Hz, aryl-*C*), 125.5 (q, *J* = 3.8 Hz, aryl-*C*), 124.5 (q, *J* = 271.8 Hz, *C*F_3), 114.2 (aryl-*C*), 55.4 (Ar*C*H_2), 41.0 (O*C*H_3). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.3.

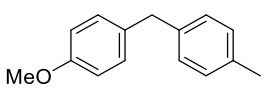
These spectroscopic data correspond to reported data.[5]



1-benzyl-4-methoxybenzene (3j). 3j was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (100:1) to give the title compound as pale yellow oil (22.0 mg, 56%).

3j: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.4 Hz, 2H, aryl-*H*), 7.24 – 7.17 (m, 3H, aryl-*H*), 7.12 (d, *J* = 8.2 Hz, 2H, aryl-*H*), 6.85 (d, *J* = 8.2 Hz, 2H, aryl-*H*), 3.95 (s, 2H, PhCH_2), 3.80 (s, 3H, OCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1 (aryl-*C*), 141.7 (aryl-*C*), 133.4 (aryl-*C*), 130.0 (aryl-*C*), 128.9 (aryl-*C*), 128.6 (aryl-*C*), 126.1 (aryl-*C*), 114.0 (aryl-*C*), 55.4 (Ph*C*H_2), 41.2 (O*C*H_3).

These spectroscopic data correspond to reported data.[6]

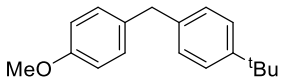


1-methoxy-4-(4-methylbenzyl)benzene (3k). 3k was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (100:1) to give the title compound as pale yellow oil (21.1

mg, 47%).

3k: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.07 (m, 6H, aryl-*H*), 6.86 (d, *J* = 8.5 Hz, 2H, aryl-*H*), 3.92 (s, 2H, ArCH_2), 3.80 (s, 3H, ArCH_3), 2.34 (s, 3H, OCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0 (aryl-*C*), 138.7 (aryl-*C*), 135.5 (aryl-*C*), 133.7 (aryl-*C*), 129.9 (aryl-*C*), 129.2 (aryl-*C*), 128.8 (aryl-*C*), 114.0 (aryl-*C*), 55.4 (Ar*C*H_2), 40.7 (O*C*H_3), 21.1 (Ar*C*H_3).

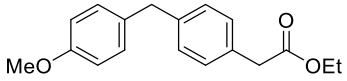
These spectroscopic data correspond to reported data.[8]



1-(tert-butyl)-4-(4-methoxybenzyl)benzene (3l). 3l was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (100:1) to give the title compound as pale yellow oil (31.8 mg, 60%).

3l: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.3 Hz, 2H, aryl-*H*), 7.15 (d, *J* = 8.6, Hz, 2H, aryl-*H*), 7.14 (d, *J* = 8.2, Hz, 2H, aryl-*H*), 6.86 (d, *J* = 8.6 Hz, 2H, aryl-*H*), 3.93 (s, 2H, ArCH_2), 3.81 (s, 3H, OCH_3), 1.33 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1 (aryl-*C*), 148.9 (aryl-*C*), 138.7 (aryl-*C*), 133.6 (aryl-*C*), 130.0 (aryl-*C*), 128.5 (aryl-*C*), 125.4 (aryl-*C*), 114.0 (aryl-*C*), 55.4 (Ar*C*H_2), 40.6 (O*C*H_3), 34.5 (C(*C*H_3)$_3$), 31.5 (*C*(CH$_3$)$_3$).

These spectroscopic data correspond to reported data.[8]

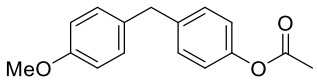


Ethyl 2-(4-(4-methoxybenzyl)phenyl)acetate (3m). 3m was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (10:1) to give the title compound as colorless oil (29.3 mg, 52%).

3m: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.9 Hz, 2H, aryl-*H*), 7.14 (d, *J* = 8.0 Hz, 2H, aryl-*H*), 7.11 (d, *J* = 8.5 Hz, 2H, aryl-*H*), 6.84 (d, *J* = 8.4 Hz, 2H, aryl-*H*), 4.16 (q, *J* = 7.1 Hz, 2H, OCH_2CH$_3$), 3.92 (s, 2H, ArCH_2), 3.79 (s, 3H, OCH_3), 3.59 (s, 2H, ArCH_2CO), 1.26 (t, *J* = 7.1 Hz, 3H, OCH$_2$CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8 (C=O), 158.1 (aryl-C), 140.5 (aryl-C), 133.2 (aryl-C), 131.9 (aryl-C), 130.0 (aryl-C), 129.4 (aryl-C), 129.1 (aryl-C), 114.0 (aryl-C), 60.9 (Ar*C*H$_2$O), 55.3 (Ar*C*H_2), 41.1, 40.7,

14.3 (CH_2CH_3).

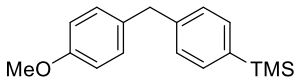
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{20}NaO_3^+$ 307.1305; Found 307.1308.



4-(4-methoxybenzyl)phenyl acetate (3n). 3n was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (10:1) to give the title compound as colorless oil (32.1 mg, 63%).

3n: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.3 Hz, 2H, aryl-*H*), 7.11 (d, *J* = 8.5 Hz, 2H, aryl-*H*), 7.00 (d, *J* = 8.3 Hz, 2H, aryl-*H*), 6.85 (d, *J* = 8.5 Hz, 2H, aryl-*H*), 3.92 (s, 2H, ArCH_2), 3.79 (s, 3H, ArOCH_3), 2.29 (s, 3H, COOCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7 (C=O), 158.2 (aryl-C), 149.0 (aryl-C), 139.3 (aryl-C), 133.0 (aryl-C), 130.0 (aryl-C), 129.8 (aryl-C), 121.5 (aryl-C), 114.0 (aryl-C), 55.4 (ArCH_2), 40.5 (OCH_3), 21.2 (COOCH_3).

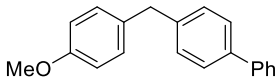
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{16}NaO_3^+$ 279.0992; Found 279.1000.



(4-(4-methoxybenzyl)phenyl)trimethylsilane (3o). 3o was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (10:1) to give the title compound as colorless oil (32.8mg, 61%).

3o: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.5 Hz, 2H, aryl-*H*), 7.20 (d, *J* = 7.5 Hz, 2H, aryl-*H*), 7.14 (d, *J* = 8.2 Hz, 2H, aryl-*H*), 6.86 (d, *J* = 8.2 Hz, 2H, aryl-*H*), 3.95 (s, 2H, ArCH_2), 3.80 (s, 3H, OCH_3), 0.28 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1 (aryl-*C*), 142.4 (aryl-*C*), 137.7 (aryl-*C*), 133.7 (aryl-*C*), 133.2 (aryl-*C*), 130.0 (aryl-*C*), 128.3 (aryl-*C*), 114.0 (aryl-*C*), 55.4 (ArCH_2), 41.2 (OCH_3), -0.9 (Si(CH_3)$_3$).

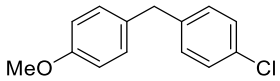
HRMS (nanochip-ESI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{17}H_{22}OSi^+$ 270.1434; Found 270.1430.



4-(4-methoxybenzyl)-1,1'-biphenyl (3p). 3p was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (100:1) to give the title compound as white solid (36.7 mg, 67%).

3p: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.5 Hz, 2H, aryl-*H*), 7.57 (d, *J* = 7.5 Hz, 2H, aryl-*H*), 7.48 (t, *J* = 7.3 Hz, 2H, aryl-*H*), 7.38 (t, *J* = 7.2 Hz, 1H, aryl-*H*), 7.30 (d, *J* = 7.7 Hz, 2H, aryl-*H*), 7.20 (d, *J* = 7.8 Hz, 2H, aryl-*H*), 6.91 (d, *J* = 7.8 Hz, 2H, aryl-*H*), 4.02 (s, 2H, ArCH_2), 3.84 (s, 3H, OCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2 (aryl-*C*), 141.2 (aryl-*C*), 140.9 (aryl-*C*), 139.1 (aryl-*C*), 133.3 (aryl-*C*), 130.0 (aryl-*C*), 129.3 (aryl-*C*), 128.8 (aryl-*C*), 127.3 (aryl-*C*), 127.2 (aryl-*C*), 127.1 (aryl-*C*), 114.1 (aryl-*C*), 55.4 (Ar*C*H_2), 40.8 (O*C*H_3).

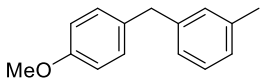
These spectroscopic data correspond to reported data.[8]



1-chloro-4-(4-methoxybenzyl)benzene (3q). 3q was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (100:1) to give the title compound as colorless oil (30.1 mg, 65%).

3q: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.5 Hz, 2H, aryl-*H*), 7.12 (t, *J* = 7.9 Hz, 4H, aryl-*H*), 6.87 (d, *J* = 7.4 Hz, 2H, aryl-*H*), 3.92 (s, 2H, ArCH_2), 3.82 (s, 3H, OCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2 (aryl-*C*), 140.2 (aryl-*C*), 132.8 (aryl-*C*), 131.9 (aryl-*C*), 130.3 (aryl-*C*), 129.9 (aryl-*C*), 128.7 (aryl-*C*), 114.1 (aryl-*C*), 55.4 (Ar*C*H_2), 40.5 (O*C*H_3).

These spectroscopic data correspond to reported data.[8]

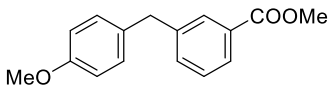


1-(4-methoxybenzyl)-3-methylbenzene (3r). 3r was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (100:1) to give the title compound as colorless oil (25.3 mg, 56%).

3r: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.8 Hz, 1H, aryl-*H*), 7.13 (d, *J* = 8.7 Hz, 2H, aryl-*H*), 7.06 – 6.98 (m, 3H, aryl-*H*), 6.86 (d, *J* = 8.6 Hz, 2H, aryl-*H*), 3.91 (s, 2H, ArCH_2), 3.80 (s, 3H, OCH_3), 2.34 (s, 3H, ArCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1

(aryl-*C*), 141.6 (aryl-*C*), 138.1 (aryl-*C*), 133.5 (aryl-*C*), 130.0 (aryl-*C*), 129.7 (aryl-*C*), 128.4 (aryl-*C*), 126.9 (aryl-*C*), 126.0 (aryl-*C*), 114.0 (aryl-*C*), 55.4 (Ar*C*H_2), 41.1 (O*C*H_3), 21.5(Ar*C*H_3).

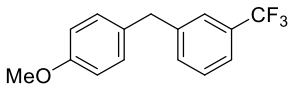
These spectroscopic data correspond to reported data.[8]



Methyl 3-(4-methoxybenzyl)benzoate (3s). 3s was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (10:1) to give the title compound as colorless oil (31.6 mg, 62%).

3s: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.91 (m, 2H, aryl-*H*), 7.39 – 7.32 (m, 2H, aryl-*H*), 7.10 (d, *J* = 8.6 Hz, 2H, aryl-*H*), 6.84 (d, *J* = 8.6 Hz, 2H, aryl-*H*), 3.97 (s, 2H, ArC*H*$_2$), 3.90 (s, 3H, COOC*H*$_3$), 3.78 (s, 3H, ArOC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3 (C=O), 158.2 (aryl-*C*), 142.1 (aryl-*C*), 133.5 (aryl-*C*), 132.7 (aryl-*C*), 130.4 (aryl-*C*), 130.0 (aryl-*C*), 129.9 (aryl-*C*), 128.6 (aryl-*C*), 127.5 (aryl-*C*), 114.1 (aryl-*C*), 55.4 (Ar*C*H_2), 52.2 (COO*C*H_3), 40.9 (O*C*H_3).

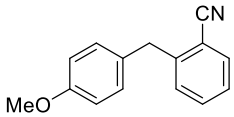
These spectroscopic data correspond to reported data.[9]



1-(4-methoxybenzyl)-3-(trifluoromethyl)benzene (3t). 3t was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (100:1) to give the title compound as colorless oil (32.8 mg, 62%).

3t: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H, aryl-*H*), 7.43 – 7.33 (m, 2H, aryl-*H*), 7.11 (d, *J* = 7.6 Hz, 2H, aryl-*H*), 6.87 (d, *J* = 7.4 Hz, 2H, aryl-*H*), 3.99 (s, 2H, ArC*H*$_2$), 3.80 (s, 3H, OC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4 (aryl-*C*), 142.6 (aryl-*C*), 132.3 (aryl-*C*), 132.2 (aryl-*C*), 130.9 (q, *J* = 31.9 Hz, aryl-*C*), 130.0 (aryl-*C*), 129.0 (aryl-*C*), 125.6 (q, *J* = 3.9 Hz, aryl-*C*), 124.4 (q, *J* = 272.4 Hz, *C*F_3), 123.1 (q, *J* = 3.6 Hz, aryl-*C*), 114.2 (aryl-*C*), 55.4 (Ar*C*H_2), 40.9 (O*C*H_3). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.5.

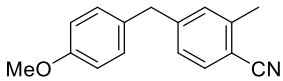
These spectroscopic data correspond to reported data.[8]



2-(4-methoxybenzyl)benzonitrile (3u). 3u was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (10:1) to give the title compound as colorless oil (24.5 mg, 55%).

3u: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.7 Hz, 1H, aryl-*H*), 7.49 (t, *J* = 8.2 Hz, 1H, aryl-*H*), 7.32 – 7.24 (m, 2H, aryl-*H*), 7.16 (d, *J* = 8.6 Hz, 2H, aryl-*H*), 6.85 (d, *J* = 8.6 Hz, 2H, aryl-*H*), 4.15 (s, 2H, ArCH_2), 3.79 (s, 3H, OCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5 (aryl-*C*), 145.6 (aryl-*C*), 133.0 (aryl-*C*), 133.0 (aryl-*C*), 131.0 (aryl-*C*), 130.1 (aryl-*C*), 130.0 (aryl-*C*), 126.8 (aryl-*C*), 118.3 (*C*N), 114.2 (aryl-*C*), 112.5 (aryl-*C*), 55.4 (Ar*C*H_2), 39.5 (O*C*H_3).

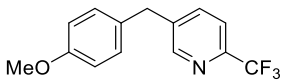
These spectroscopic data correspond to reported data.[10]



4-(4-methoxybenzyl)-2-methylbenzonitrile (3v). 3v was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (10:1) to give the title compound as colorless oil (24.3 mg, 51%).

3v: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.9 Hz, 1H, aryl-*H*), 7.14 – 7.05 (m, 4H, aryl-*H*), 6.85 (d, *J* = 8.1 Hz, 2H, aryl-*H*), 3.92 (s, 2H, ArCH_2), 3.79 (s, 3H, OCH_3), 2.50 (s, 3H, ArCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4 (aryl-*C*), 147.1 (aryl-*C*), 142.1 (aryl-*C*), 132.7 (aryl-*C*), 131.7 (aryl-*C*), 130.7 (aryl-*C*), 130.0 (aryl-*C*), 126.8 (aryl-*C*), 118.4 (*C*N), 114.2 (aryl-*C*), 110.4 (aryl-*C*), 55.3 (Ar*C*H_2), 41.1 (O*C*H_3), 20.5 (ArCH_3).

HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}NO^+$ 238.1226; Found 238.1231.

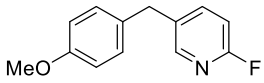


5-(4-methoxybenzyl)-2-(trifluoromethyl)pyridine (3w). 3w was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (10:1) to give the title compound as colorless oil (24.6 mg, 46%).

3w: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.64 – 7.55 (m, 2H, aryl-*H*), 7.09 (d, *J*

= 8.5 Hz, 2H, aryl-*H*), 6.86 (d, *J* = 8.5 Hz, 2H, aryl-*H*), 4.00 (s, 2H, ArC*H*$_2$), 3.79 (s, 3H, OC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7 (aryl-*C*), 150.4 (aryl-*C*), 146.4 (q, *J* = 34.6 Hz, aryl-*C*), 140.5 (aryl-*C*), 137.4 (aryl-*C*), 130.9 (aryl-*C*), 130.0 (aryl-*C*), 121.8 (q, *J* = 273.8 Hz, *C*F$_3$), 120.4 (q, *J* = 2.7 Hz, aryl-*C*), 114.5 (aryl-*C*), 55.4 (Ar*C*H$_2$), 38.1 (O*C*H$_3$). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -67.7.

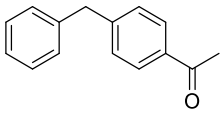
HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{13}F_3NO^+$ 268.0944; Found 268.0946.



2-fluoro-5-(4-methoxybenzyl)pyridine (3x). 3x was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (10:1) to give the title compound as pale yellow oil (24.3 mg, 56%).

3x: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H, aryl-*H*), 7.54 (td, *J* = 8.1, 2.5 Hz, 1H, aryl-*H*), 7.07 (d, *J* = 8.5 Hz, 2H, aryl-*H*), 6.87 – 6.80 (m, 3H, aryl-*H*), 3.90 (s, 2H, ArC*H*$_2$), 3.78 (s, 3H, OC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (d, *J* = 237.5 Hz, aryl-*C*), 158.4 (aryl-*C*), 147.2 (d, *J* = 14.5 Hz, aryl-*C*), 141.6 (d, *J* = 7.8 Hz, aryl-*C*), 134.7 (d, *J* = 4.5 Hz, aryl-*C*), 131.7 (aryl-*C*), 129.8 (aryl-*C*), 114.3 (aryl-*C*), 109.3 (d, *J* = 37.5 Hz, aryl-*C*), 55.4 (Ar*C*H$_2$), 37.2 (O*C*H$_3$). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -71.8.

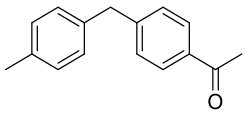
HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{13}FNO^+$ 218.0976; Found 218.0980.



1-(4-benzylphenyl)ethan-1-one (3aa). 3aa was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (10:1) to give the title compound as colorless oil (29.8 mg, 71%).

3aa: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H, aryl-*H*), 7.34 – 7.26 (m, 4H, aryl-*H*), 7.25 – 7.16 (m, 3H, aryl-*H*), 4.04 (s, 2H, ArC*H*$_2$), 2.58 (s, 3H, OC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9 (*C*=O), 146.9 (aryl-*C*), 140.2 (aryl-*C*), 135.4 (aryl-*C*), 129.2 (aryl-*C*), 129.1 (aryl-*C*), 128.8 (aryl-*C*), 126.5 (aryl-*C*), 42.0 (Ar*C*H$_2$), 26.7 (CO*C*H$_3$).

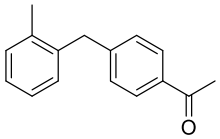
These spectroscopic data correspond to reported data.[11]



1-(4-(4-methylbenzyl)phenyl)ethan-1-one (3ab). 3ab was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (10:1) to give the title compound as white solid (25.6 mg, 57%).

3ab: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.9 Hz, 2H, aryl-*H*), 7.30 (d, *J* = 7.9 Hz, 2H, aryl-*H*), 7.14 (d, *J* = 7.8 Hz, 2H, aryl-*H*), 7.10 (d, *J* = 7.8 Hz, 2H, aryl-*H*), 4.02 (s, 2H, ArCH_2), 2.60 (s, 3H, OCH_3), 2.35 (s, 3H, ArCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9 (*C*=O), 147.3 (aryl-*C*), 137.1 (aryl-*C*), 136.1 (aryl-*C*), 135.3 (aryl-*C*), 129.4 (aryl-*C*), 129.2 (aryl-*C*), 128.9 (aryl-*C*), 128.7 (aryl-*C*), 41.6 (Ar*C*H_2), 26.7 (CO*C*H_3), 21.1 (Ar*C*H_3).

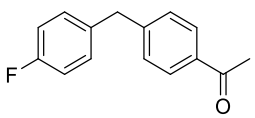
These spectroscopic data correspond to reported data.[11]



1-(4-(2-methylbenzyl)phenyl)ethan-1-one (3ac). 3ac was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (10:1) to give the title compound as colorless oil (25.4 mg, 57%).

3ac: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 2H, aryl-*H*), 7.22 (d, *J* = 8.0 Hz, 2H, aryl-*H*), 7.20 – 7.14 (m, 3H, aryl-*H*), 7.13 – 7.08 (m, 1H, aryl-*H*), 4.05 (s, 2H, ArCH_2), 2.58 (s, 3H, OCH_3), 2.23 (s, 3H, ArCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9 (*C*=O), 146.4 (aryl-*C*), 138.0 (aryl-*C*), 136.7 (aryl-*C*), 135.3 (aryl-*C*), 130.6 (aryl-*C*), 130.1 (aryl-*C*), 129.0 (aryl-*C*), 128.7 (aryl-*C*), 126.9 (aryl-*C*), 126.3 (aryl-*C*), 39.6 (Ar*C*H_2), 26.7 (CO*C*H_3), 19.8 (Ar*C*H_3).

HRMS (APCI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{17}O^+$ 225.1274; Found 225.1275.

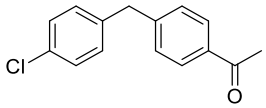


1-(4-(4-fluorobenzyl)phenyl)ethan-1-one (3ad). 3ad was synthesized following the

general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (10:1) to give the title compound as colorless oil (21.7 mg, 48%).

3ad: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.7 Hz, 2H, aryl-*H*), 7.28 (d, *J* = 7.3 Hz, 2H, aryl-*H*), 7.15 (t, *J* = 6.3 Hz, 2H, aryl-*H*), 7.01 (t, *J* = 8.3 Hz, 2H, aryl-*H*), 4.03 (s, 2H, ArCH_2), 2.60 (s, 3H, COCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9 (*C*=O), 161.7 (d, *J* = 244.6 Hz, aryl-*C*), 146.7 (aryl-*C*), 135.8 (d, *J* = 3.3 Hz, aryl-*C*), 135.5 (aryl-*C*), 130.5 (d, *J* = 7.8 Hz, aryl-*C*), 129.1 (aryl-*C*), 128.8 (aryl-*C*), 115.6 (d, *J* = 21.3 Hz, aryl-*C*), 41.1 (Ar*C*H_2), 26.7 (CO*C*H_3). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -116.7.

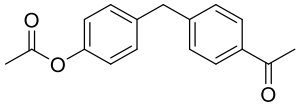
These spectroscopic data correspond to reported data.[11]



1-(4-(4-chlorobenzyl)phenyl)ethan-1-one (3ae). 3ae was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (10:1) to give the title compound as colorless oil (35.8 mg, 73%).

3ae: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H, aryl-*H*), 7.29 – 7.23 (m, 4H, aryl-*H*), 7.10 (d, *J* = 8.5 Hz, 2H, aryl-*H*), 4.00 (s, 2H, ArCH_2), 2.58 (s, 3H, COCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8 (*C*=O), 146.2 (aryl-*C*), 138.6 (aryl-*C*), 135.5 (aryl-*C*), 132.3 (aryl-*C*), 130.3 (aryl-*C*), 129.1 (aryl-*C*), 128.8 (aryl-*C*), 128.8 (aryl-*C*), 41.3 (Ar*C*H_2), 26.7 (CO*C*H_3).

These spectroscopic data correspond to reported data.[11]

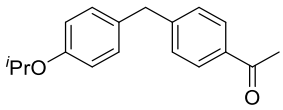


4-(4-acetylbenzyl)phenyl acetate (3af). 3af was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as colorless oil (28.2 mg, 53%).

3af: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 2H, aryl-*H*), 7.30 (d, *J* = 8.3 Hz, 2H, aryl-*H*), 7.19 (d, *J* = 8.5 Hz, 2H, aryl-*H*), 7.04 (d, *J* = 8.5 Hz, 2H, aryl-*H*), 4.05 (s, 2H, ArCH_2), 2.60 (s, 3H, ArCOCH_3), 2.31 (s, 2H, ArOCOCH_3). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 197.9 (Ar*C*=OCH_3), 169.7 (ArO*C*=OCH_3), 149.3 (aryl-*C*), 146.5 (aryl-*C*), 137.7 (aryl-*C*), 135.5 (aryl-*C*), 129.9 (aryl-*C*), 129.2 (aryl-*C*), 128.8 (aryl-*C*), 121.8 (aryl-*C*), 41.3 (Ar*C*H_2), 26.7 (ArCO*C*H_3), 21.2 (ArOCO*C*H_3).

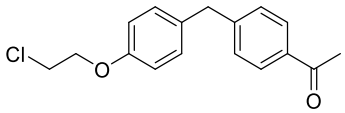
HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{17}O_3^+$ 269.1172; Found 269.1173.



1-(4-(4-isopropoxybenzyl)phenyl)ethan-1-one (3ag). 3ag was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (10:1) to give the title compound as colorless oil (27.8 mg, 52%).

3ag: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.7 Hz, 2H, aryl-*H*), 7.30 (d, *J* = 7.6 Hz, 2H, aryl-*H*), 7.09 (d, *J* = 7.9 Hz, 2H, aryl-*H*), 6.85 (d, *J* = 7.9 Hz, 2H, aryl-*H*), 4.53 (hept, *J* = 6.0 Hz, 1H, $(CH_3)_2CHO$), 3.99 (s, 2H, ArCH_2), 2.60 (s, 3H, COCH_3), 1.35 (d, *J* = 6.0 Hz, 6H, $(CH_3)_2CHO$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9 (*C*=O), 156.6 (aryl-*C*), 147.5 (aryl-*C*), 135.3 (aryl-*C*), 132.1 (aryl-*C*), 130.0 (aryl-*C*), 129.1 (aryl-*C*), 128.7 (aryl-*C*), 116.1 (aryl-*C*), 70.0 ($(CH_3)_2CHO$), 41.2 (ArCH_2), 26.7 (COCH_3), 22.2 ($(CH_3)_2$CHO).

These spectroscopic data correspond to reported data.[7]

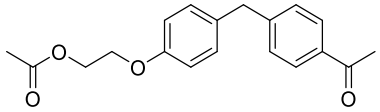


1-(4-(4-(2-chloroethoxy)benzyl)phenyl)ethan-1-one (3ah). 3ah was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (10:1) to give the title compound as colorless oil (23.8 mg, 41%).

3ah: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.5 Hz, 2H, aryl-*H*), 7.29 (d, *J* = 7.0 Hz, 2H, aryl-*H*), 7.12 (d, *J* = 7.5 Hz, 2H, aryl-*H*), 6.88 (d, *J* = 7.5 Hz, 2H, aryl-*H*), 4.23 (t, *J* = 5.5 Hz, 2H), 4.00 (s, 2H,, ArCH_2), 3.82 (t, *J* = 5.5 Hz, 2H), 2.60 (s, 2H, COCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9 (*C*=O), 157.0 (aryl-*C*), 147.2 (aryl-*C*), 135.4 (aryl-*C*), 133.1 (aryl-*C*), 130.2 (aryl-*C*), 129.1 (aryl-*C*), 128.8 (aryl-*C*), 115.0 (aryl-*C*),

68.2 (ArO*C*H_2), 42.0, 41.1, 26.7 (CO*C*H_3).

HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{18}ClO_2^+$ 289.0990; Found 289.0988.



2-(4-(4-acetylbenzyl)phenoxy)ethyl acetate (3ai). 3ai was synthesized following the general procedure. The residue was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (5:1) to give the title compound as colorless oil (31.0 mg, 50%).

3ai: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.4 Hz, 2H), 7.28 (d, *J* = 7.5 Hz, 2H), 7.11 (d, *J* = 7.7 Hz, 2H), 6.87 (d, *J* = 7.5 Hz, 2H), 4.43 (t, *J* = 3.7 Hz, 2H), 4.17 (t, *J* = 3.7 Hz, 2H), 3.99 (s, 2H, ArC*H*$_2$), 2.59 (s, 3H, ArCOC*H*$_3$), 2.11 (s, 3H, OCOC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9 (Ar*C*=OCH$_3$), 171.1 (O*C*=OCH$_3$), 157.2 (aryl-*C*), 147.3 (aryl-*C*), 135.3 (aryl-*C*), 132.8 (aryl-*C*), 130.1 (aryl-*C*), 129.1 (aryl-*C*), 128.7 (aryl-*C*), 114.9 (aryl-*C*), 66.1, 62.9, 41.1 (Ar*C*H$_2$), 26.7 (ArCO*C*H$_3$), 21.0 (OC=O*C*H$_3$).

HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{20}NaO_4^+$ 335.1254; Found 335.1254.

5. Electrochemical Measurements

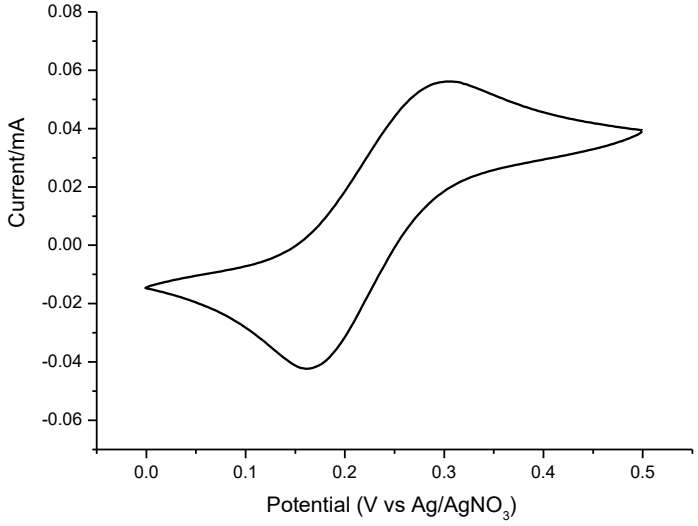
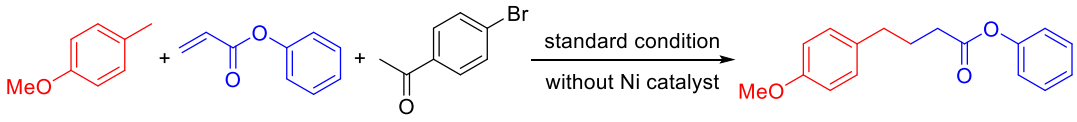


Figure S2: CV curve of ferrocene (5 x 10^{-3} M) in THF/CH_3CN (4:1, 2 mL) containing [LutH]ClO_4 (0.1 M) and lutidine (0.8 mmol). Glassy carbon electrode was used as a working electrode with a Ag/$AgNO_3$ reference electrode and a Pt counter electrode. Scan rate: 50 mV/s.

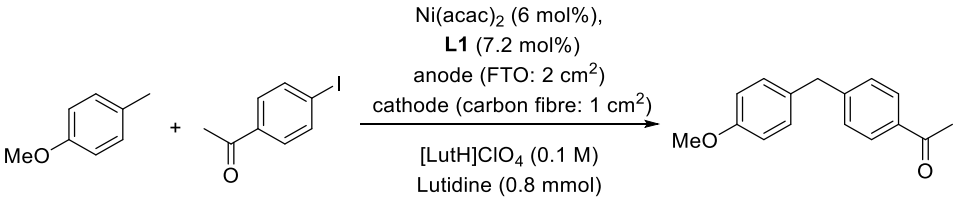
6. Mechanistic Study

Scheme S1. Benzyl radical trapping reaction



3.0 eq. 2.0 eq. **2a**, 0.2mmol ~12% based **2a**

Scheme S2. Control experiment under Br-free conditions.



0.6 mmol 0.2 mmol 24% GC yield

7. References

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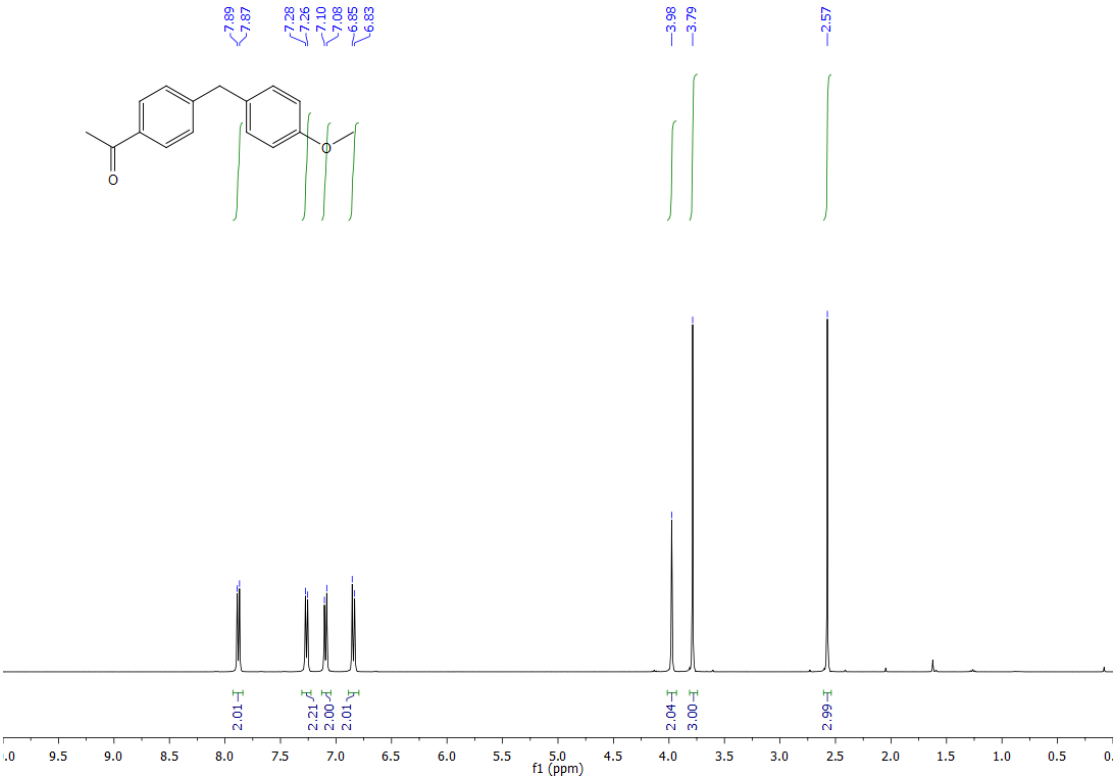
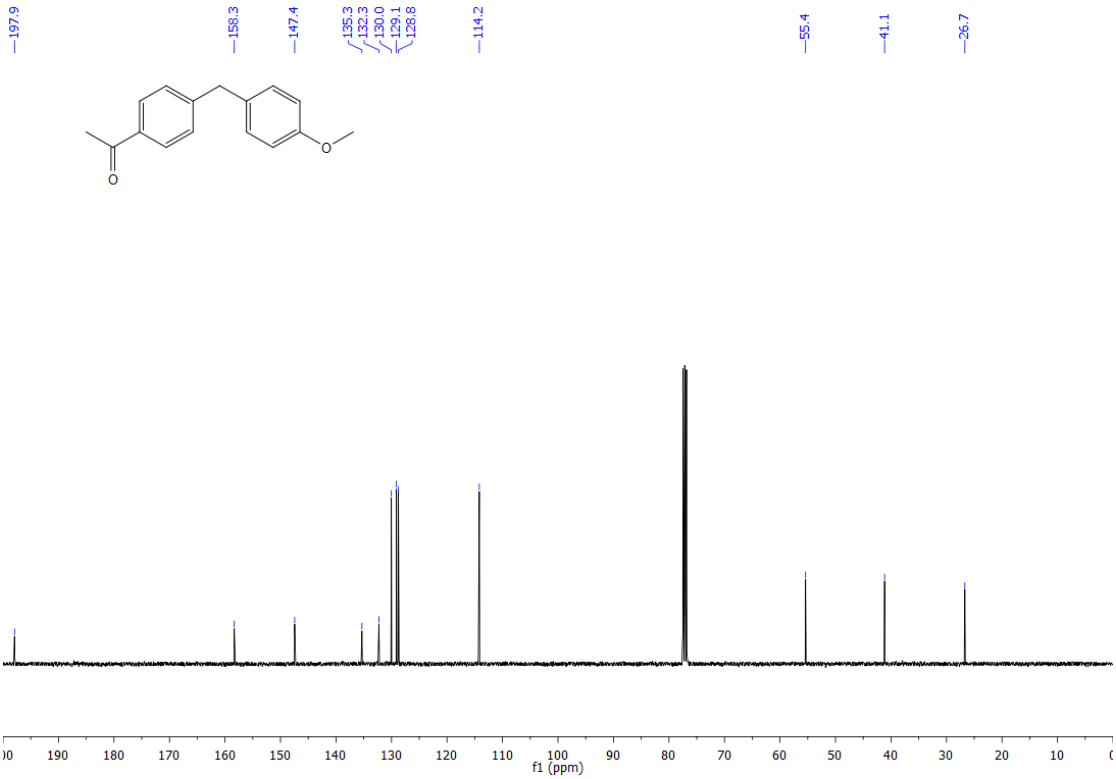
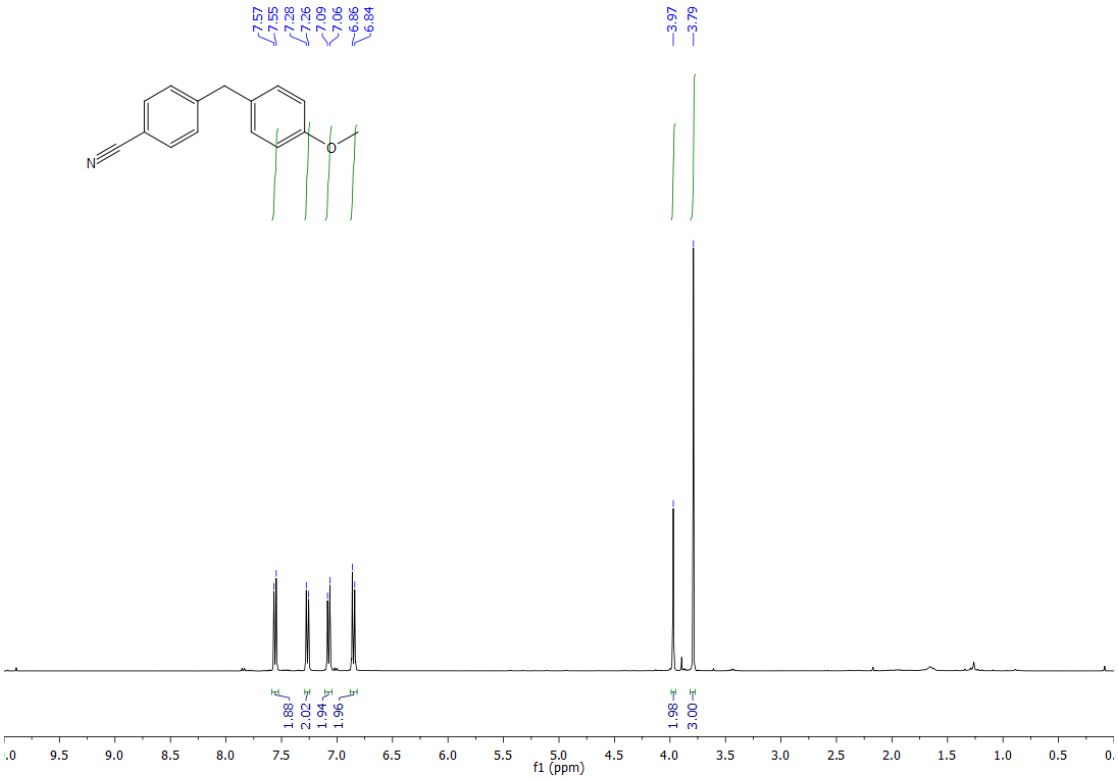
8. NMR Spectra



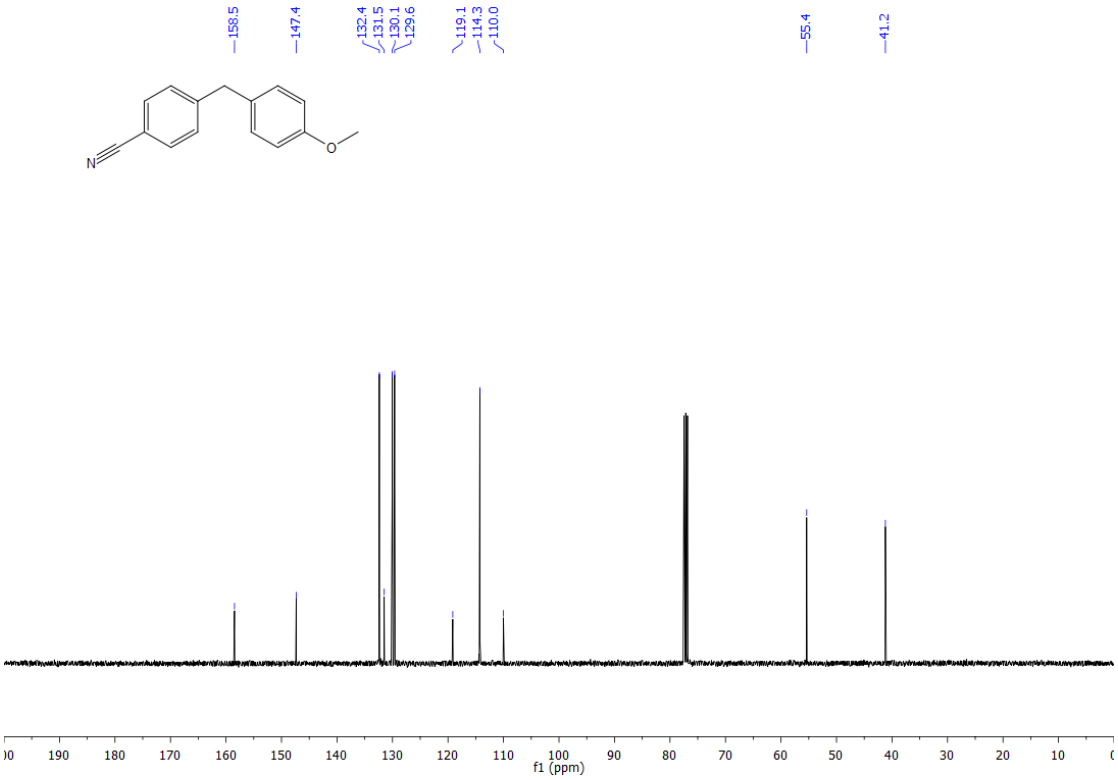
^{1}H NMR (400 MHz, $CDCl_3$) of 3**a**



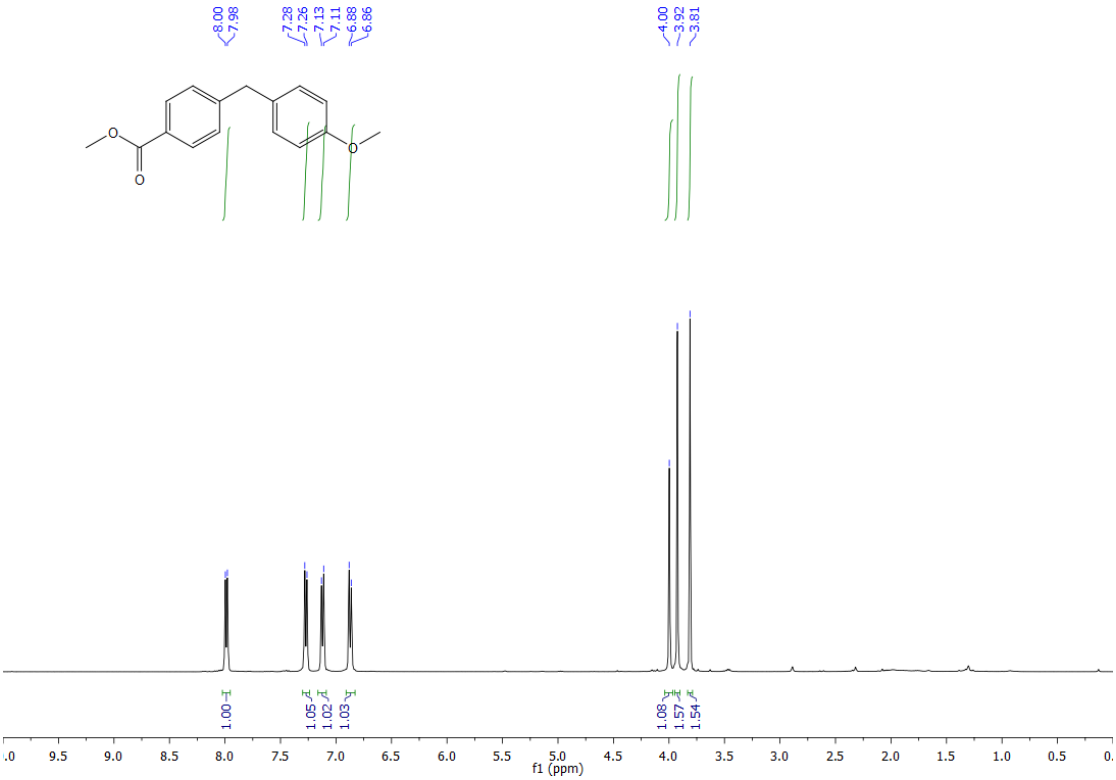
^{13}C NMR (101 MHz, $CDCl_3$) of **3a**



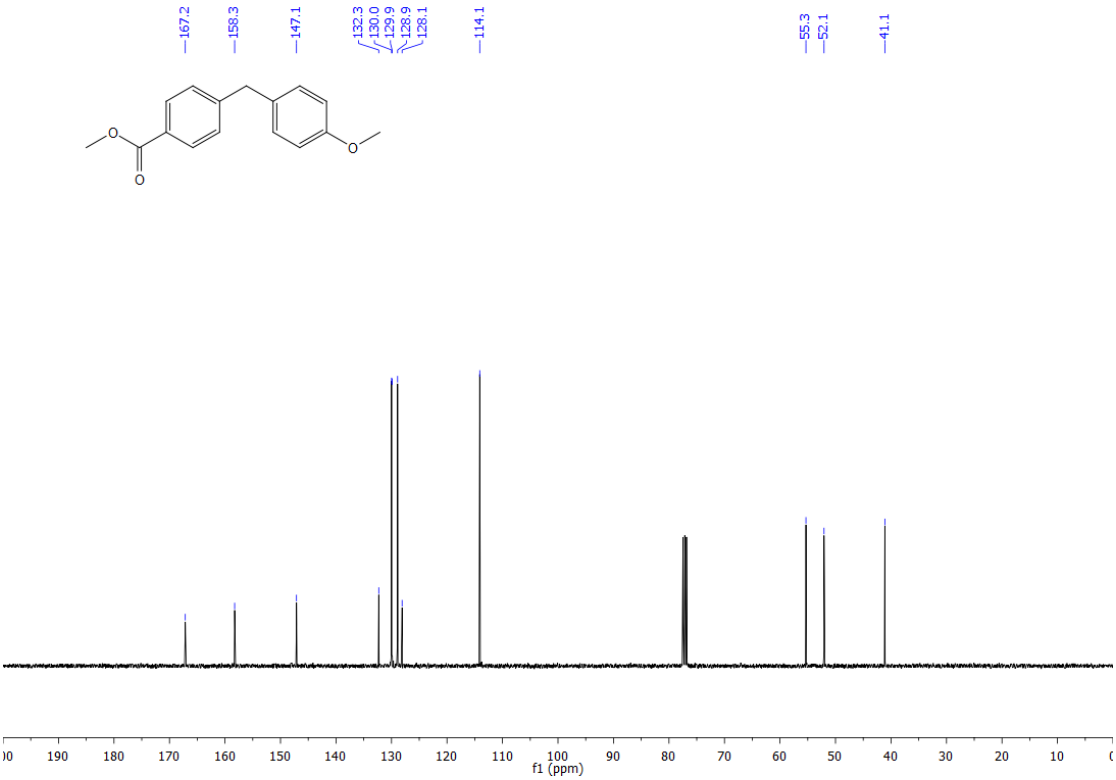
^{1}H NMR (400 MHz, $CDCl_3$) of **3b**



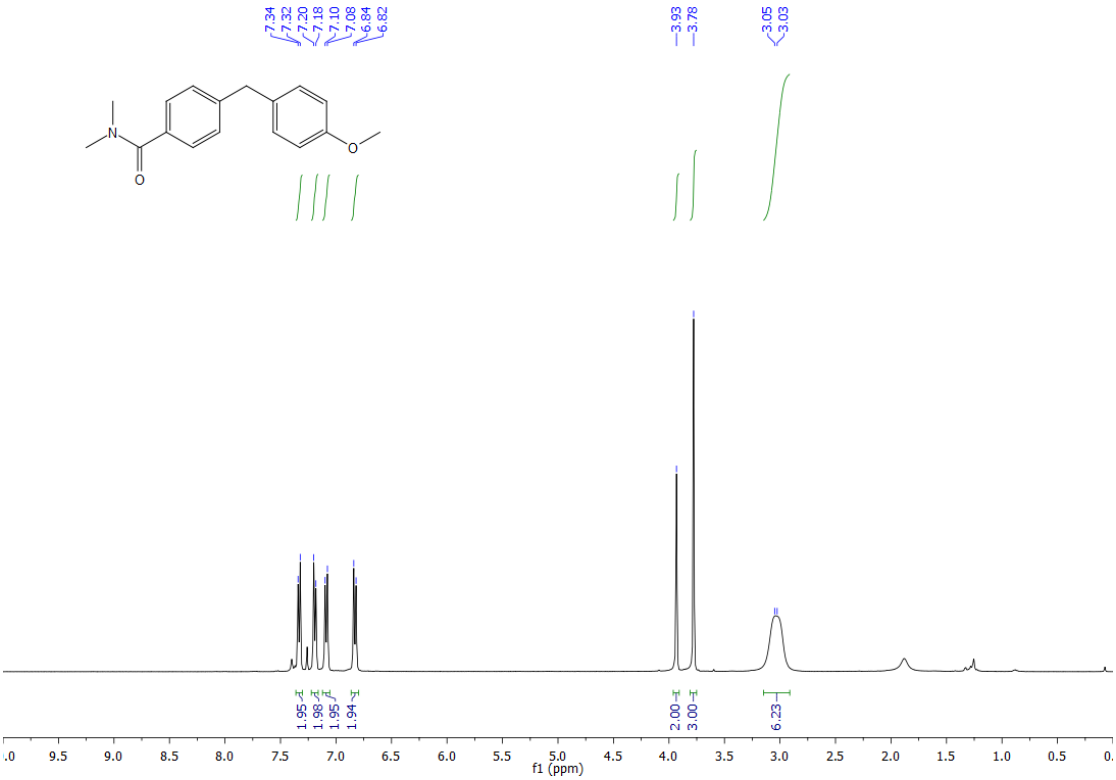
^{13}C NMR (101 MHz, $CDCl_3$) of **3b**



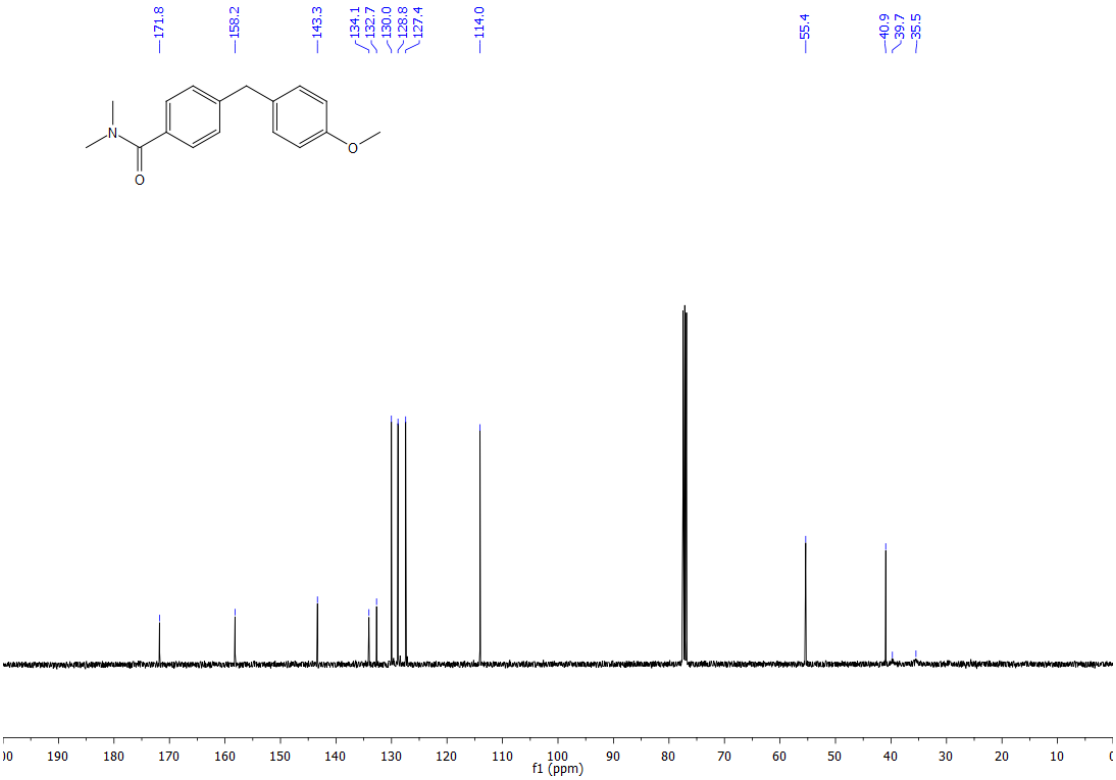
^{1}H NMR (400 MHz, $CDCl_3$) of **3c**



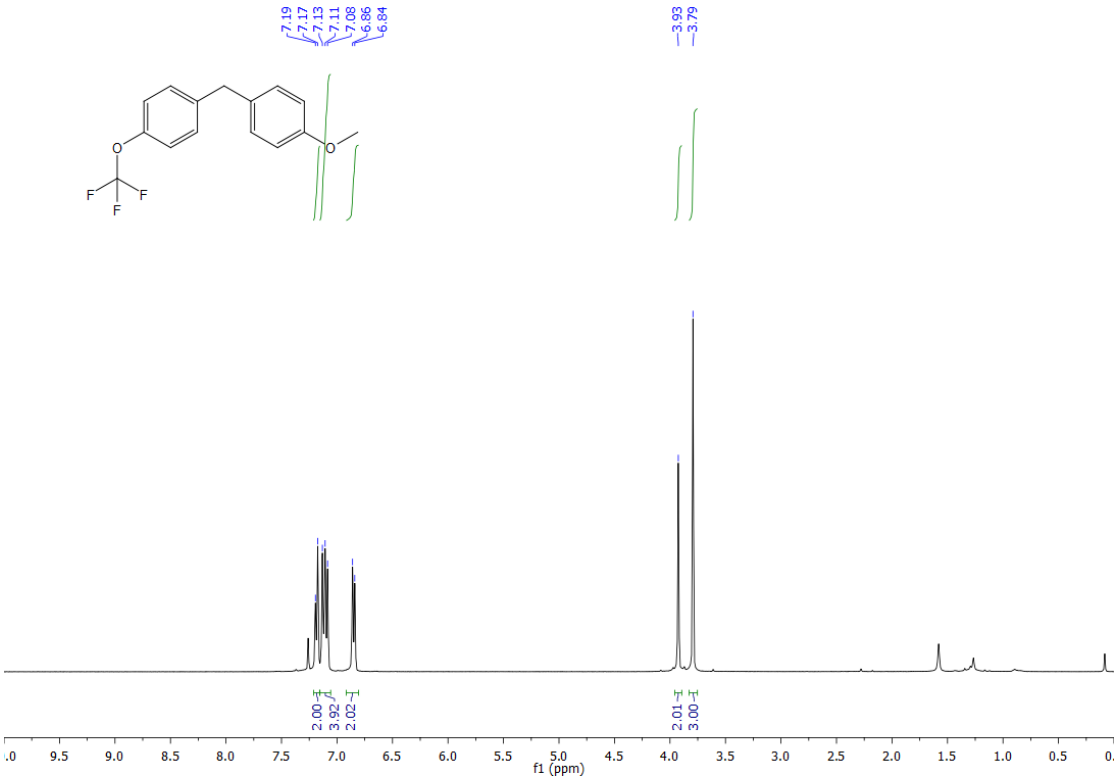
^{13}C NMR (101 MHz, $CDCl_3$) of **3c**



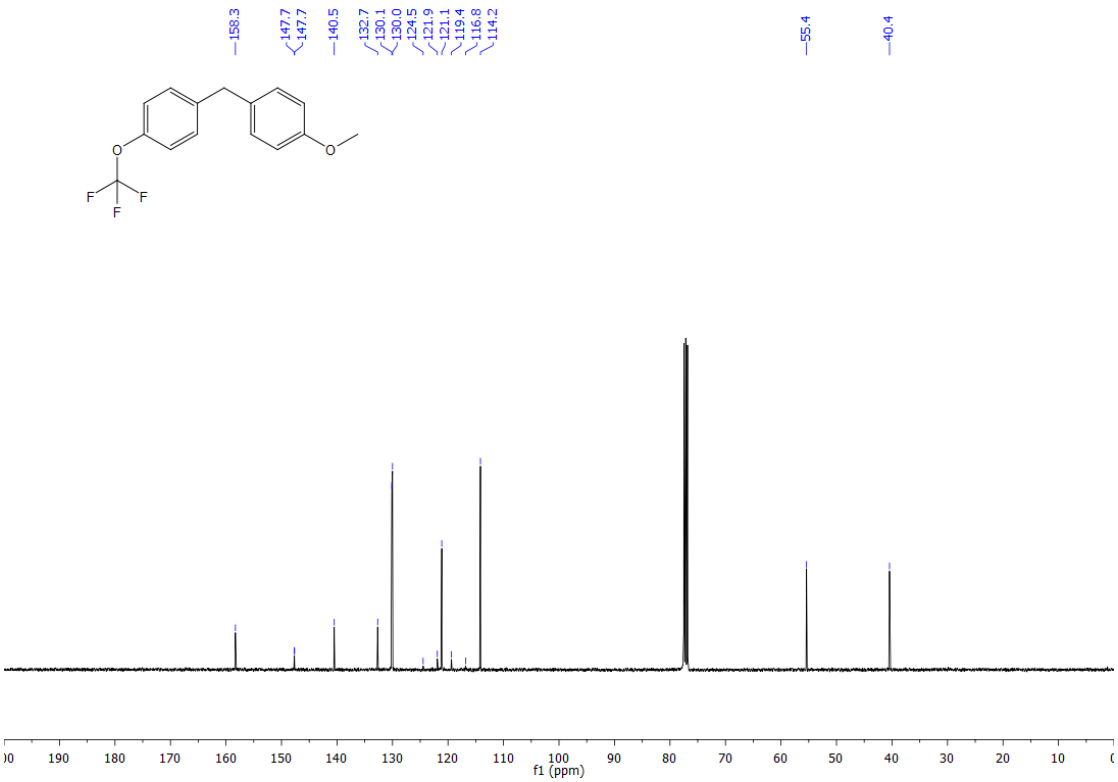
^{1}H NMR (400 MHz, $CDCl_3$) of **3d**



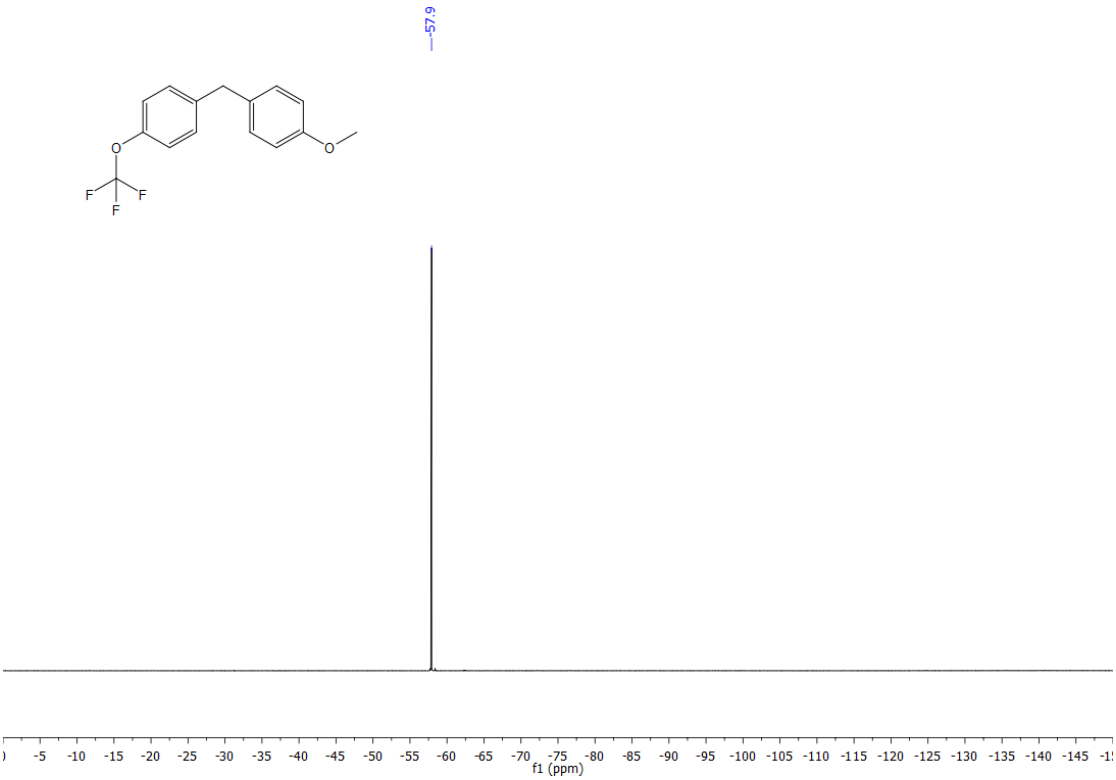
^{13}C NMR (101 MHz, $CDCl_3$) of **3d**



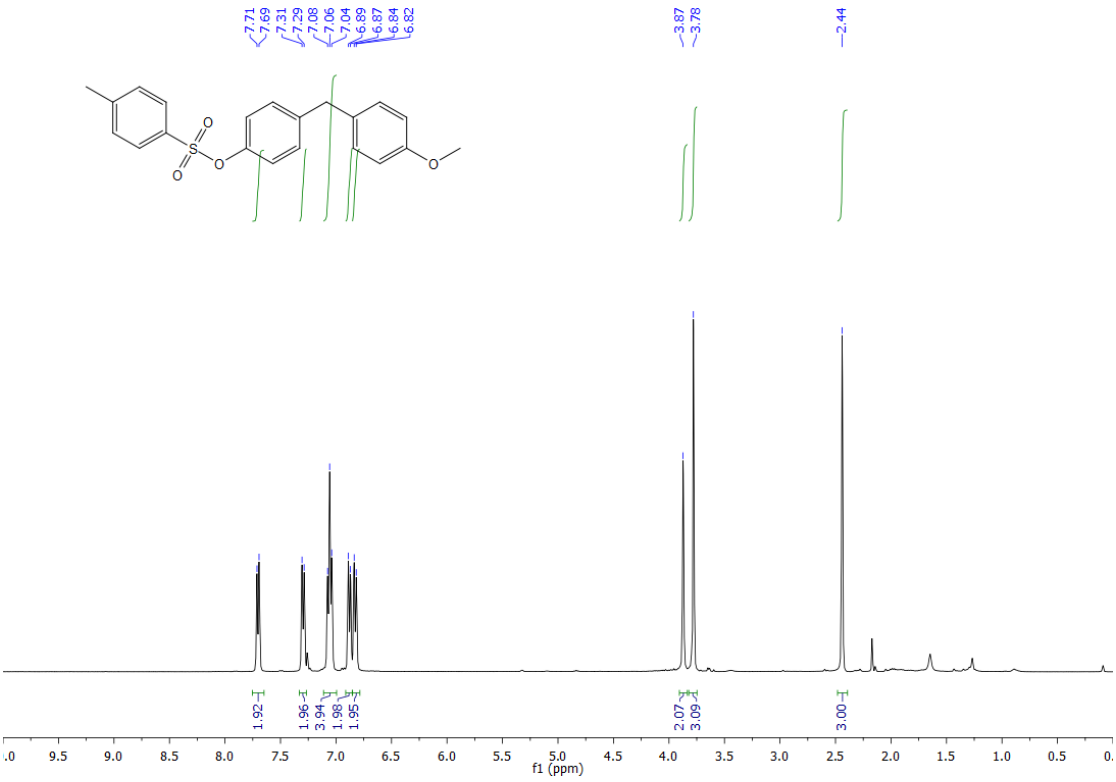
^{1}H NMR (400 MHz, $CDCl_3$) of **3e**



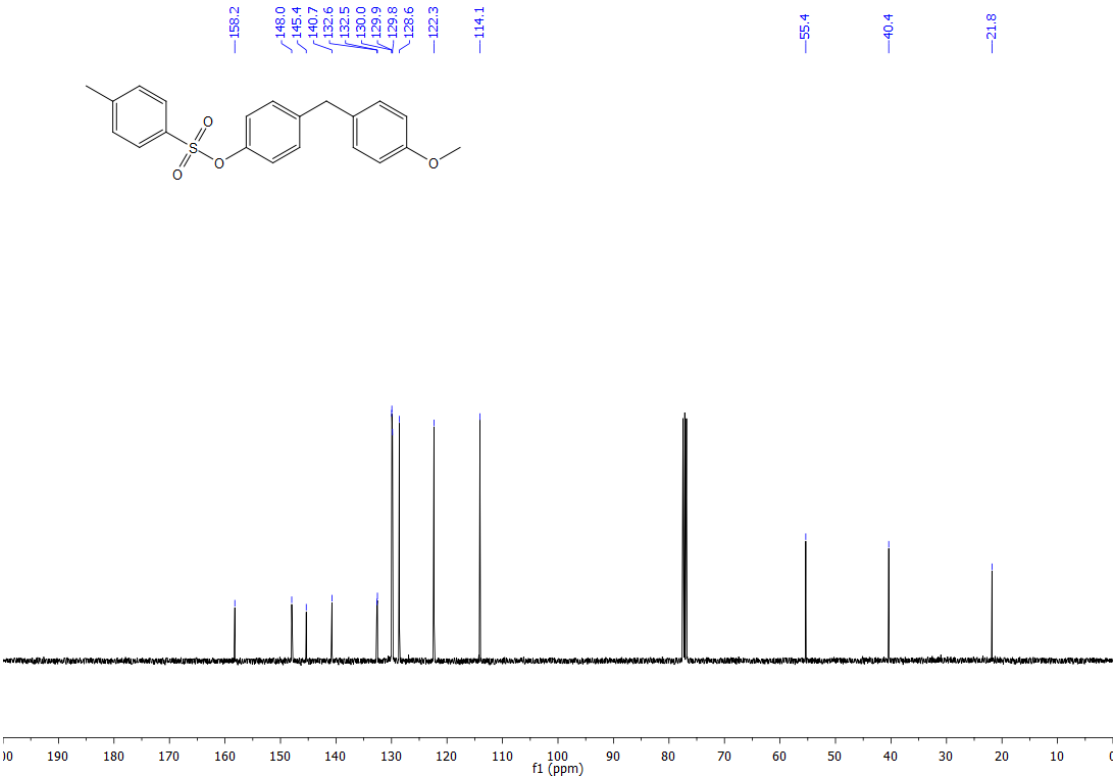
^{13}C NMR (101 MHz, $CDCl_3$) of **3e**



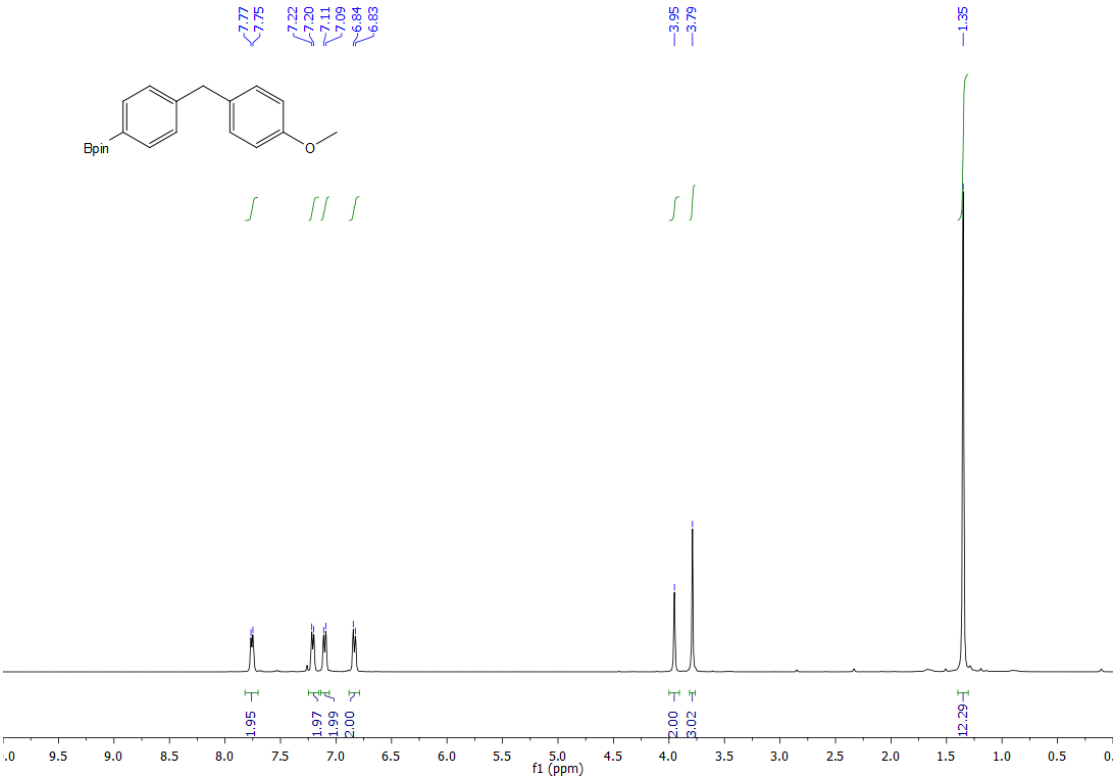
^{19}F NMR (376 MHz, $CDCl_3$) of **3e**



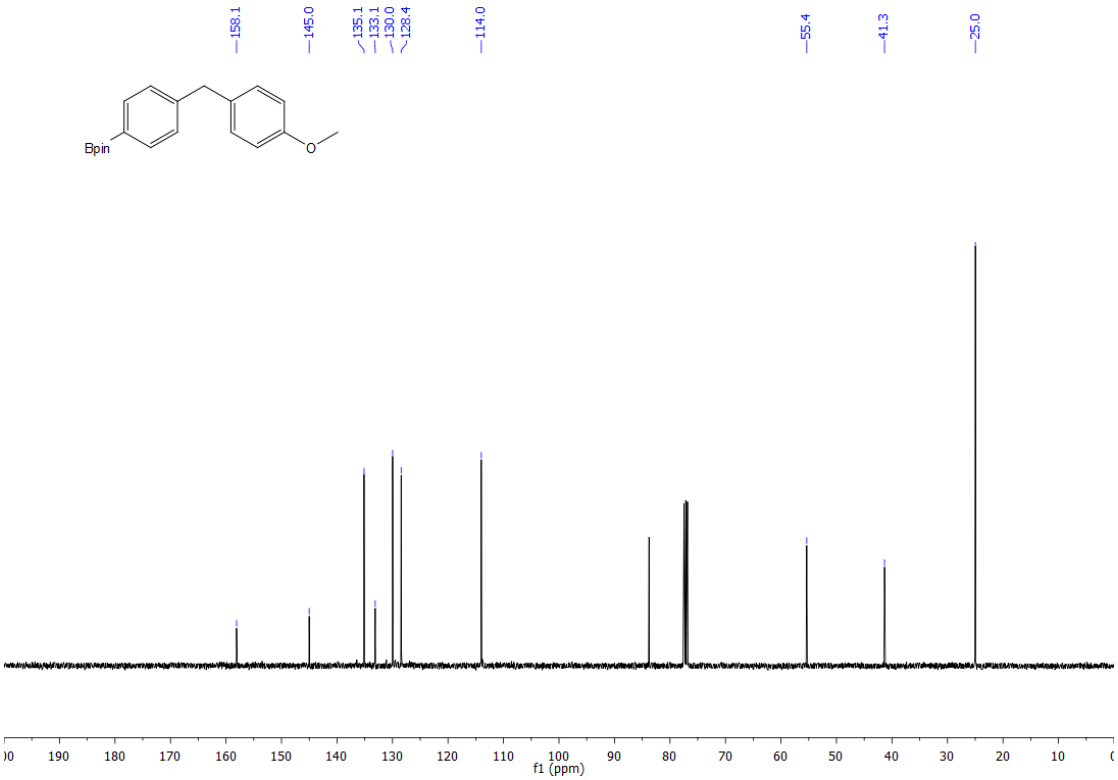
^{1}H NMR (400 MHz, $CDCl_3$) of 3**f**



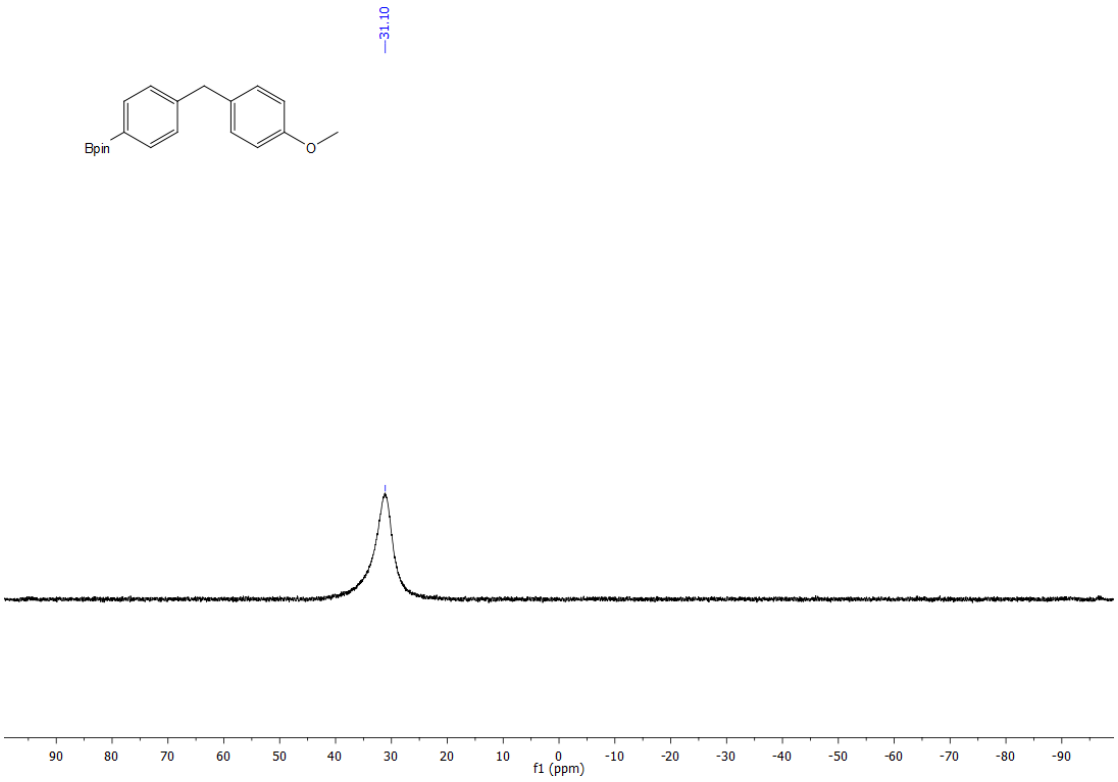
^{13}C NMR (101 MHz, $CDCl_3$) of **3f**



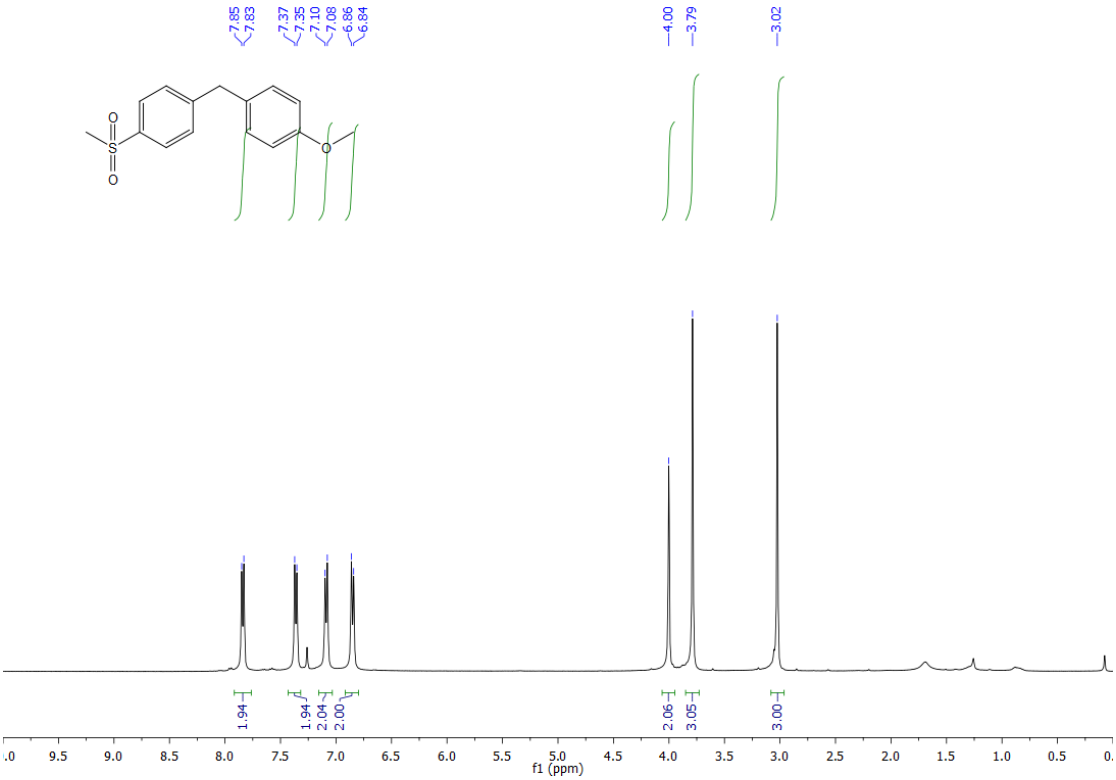
^{1}H NMR (400 MHz, $CDCl_3$) of 3**g**



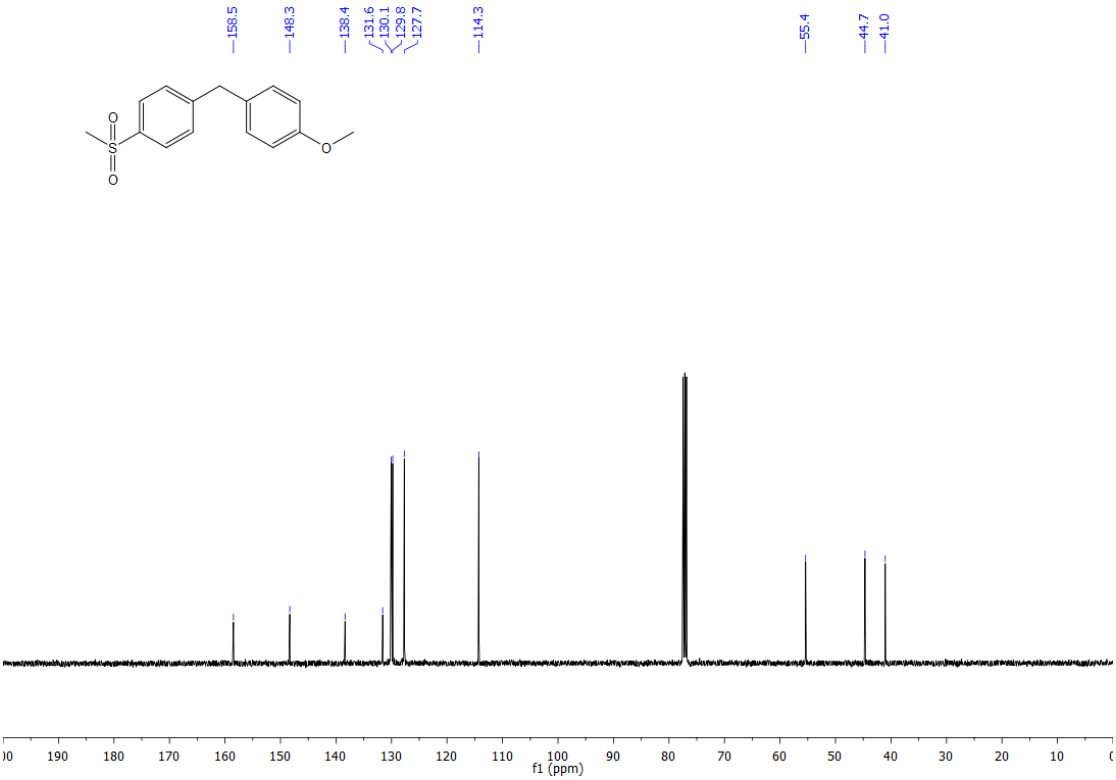
^{13}C NMR (101 MHz, $CDCl_3$) of **3g**



^{11}B NMR (128 MHz, $CDCl_3$) of **3g**

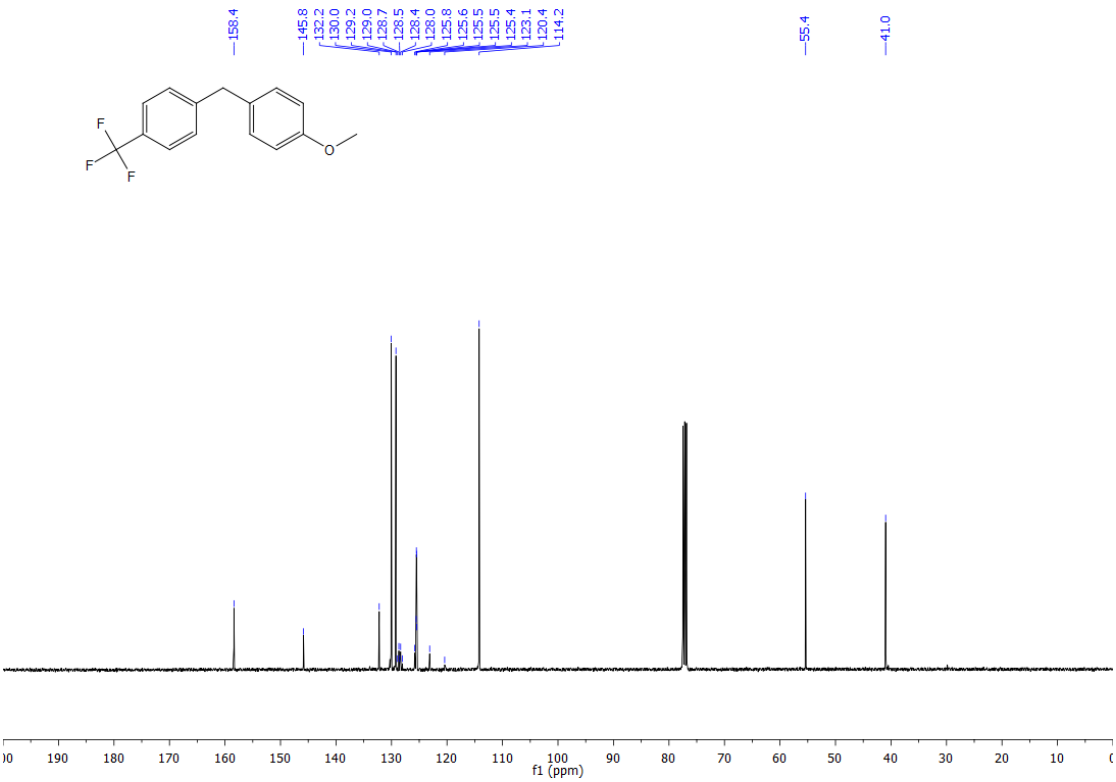


^{1}H NMR (400 MHz, $CDCl_3$) of 3**h**

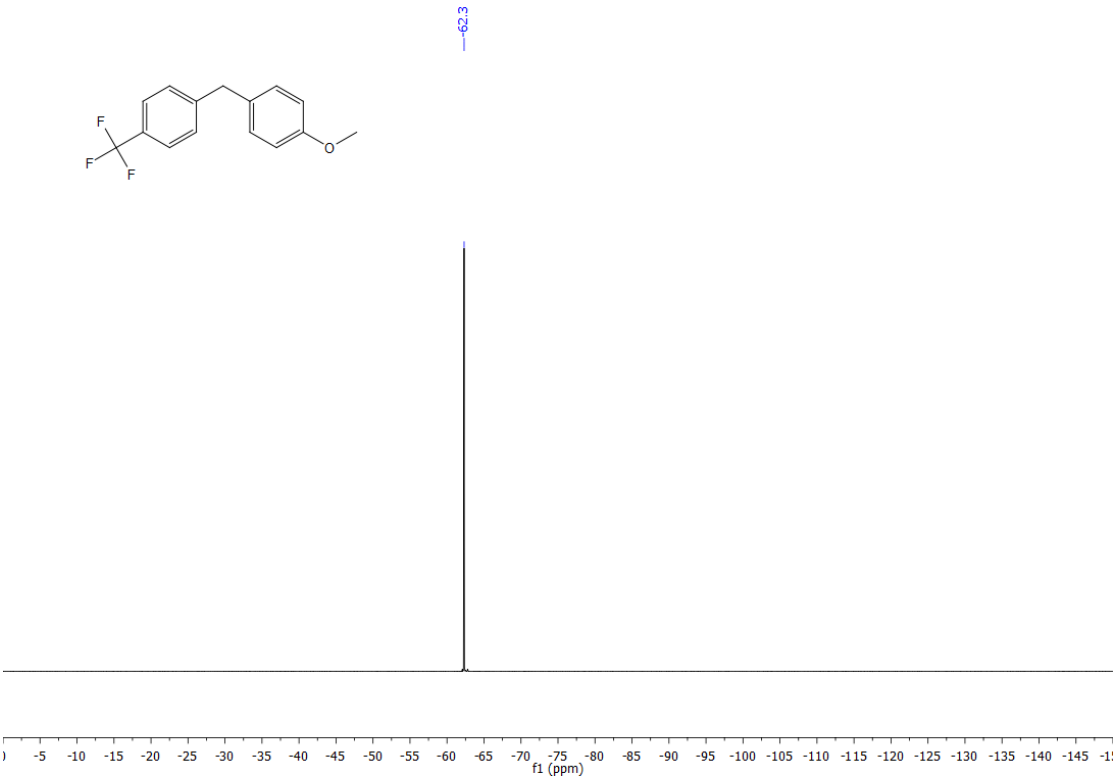


^{13}C NMR (101 MHz, $CDCl_3$) of **3h**

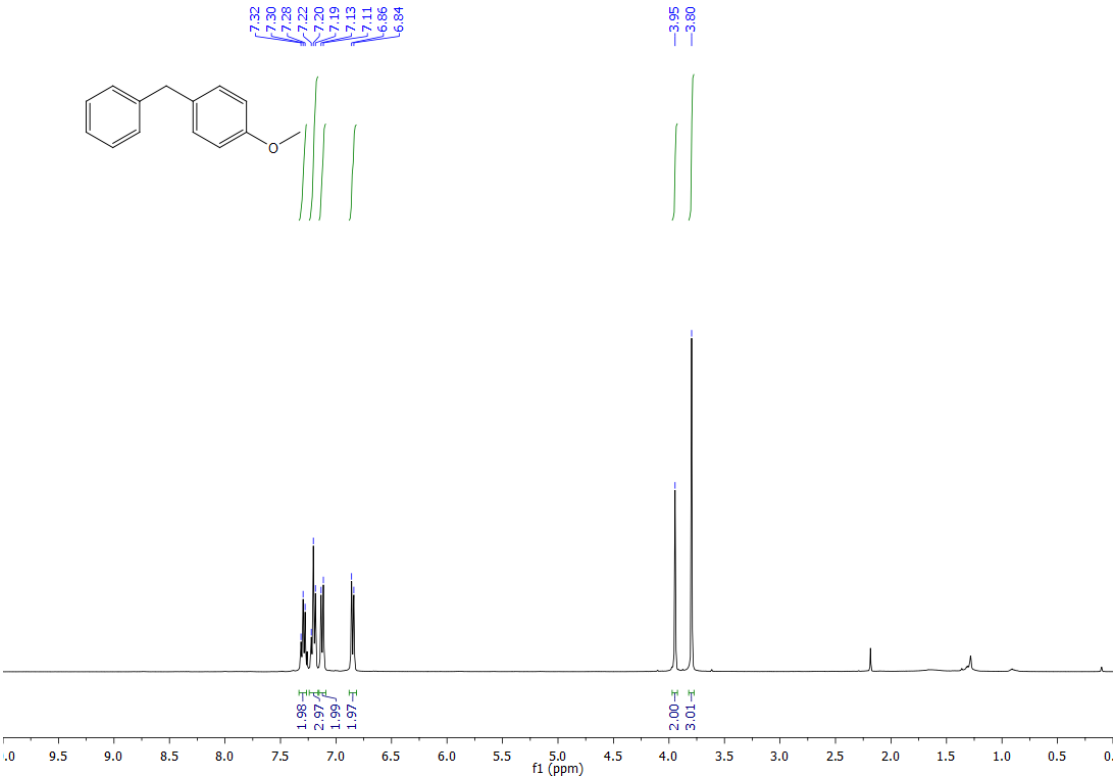
^{1}H NMR (400 MHz, $CDCl_3$) of **3i**



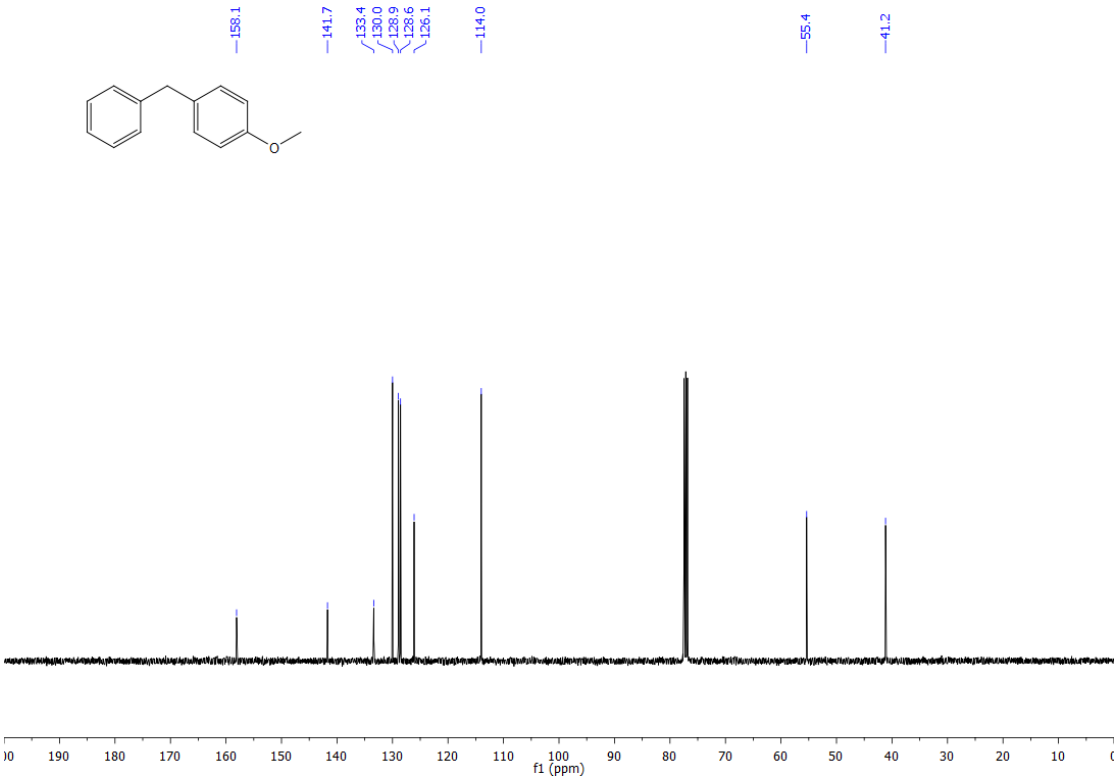
^{13}C NMR (101 MHz, $CDCl_3$) of **3i**



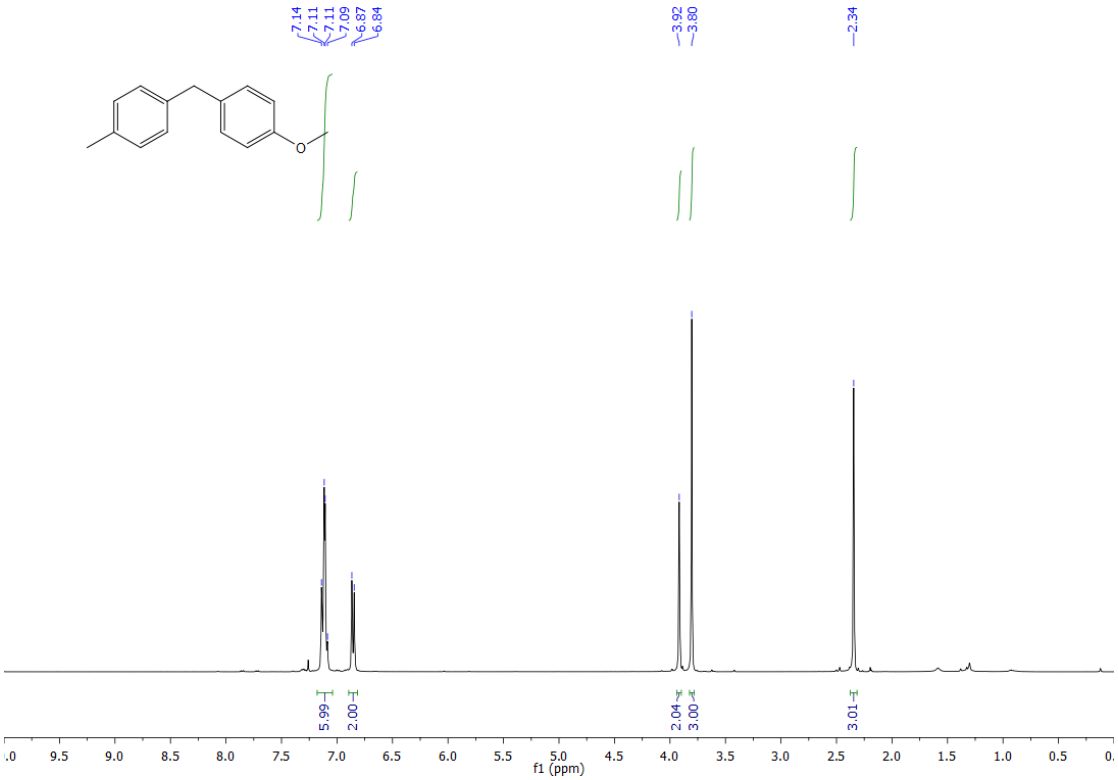
^{19}F NMR (376 MHz, $CDCl_3$) of **3i**



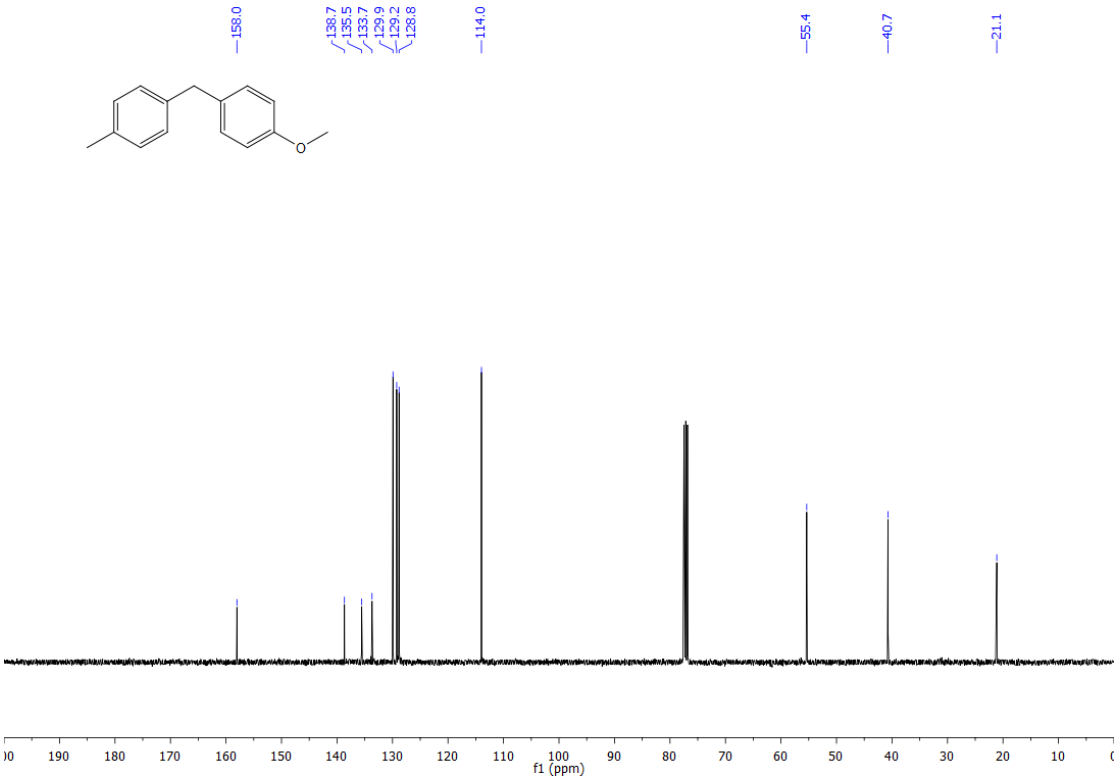
^{1}H NMR (400 MHz, $CDCl_3$) of 3**j**



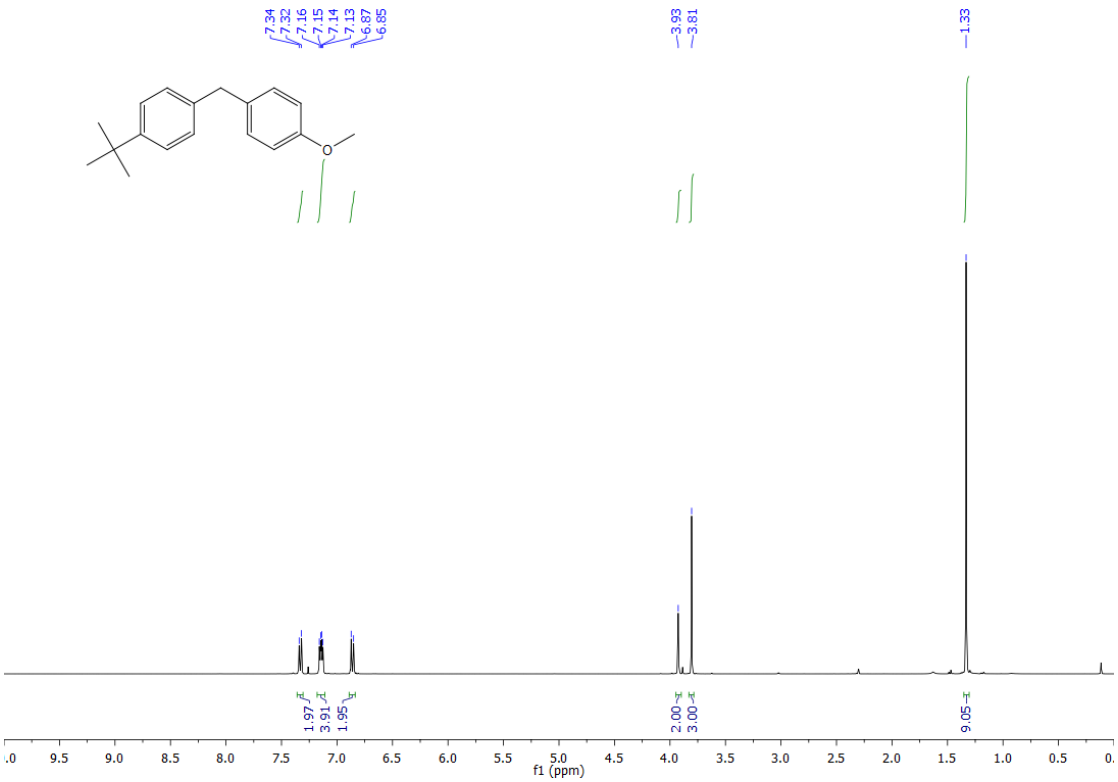
^{13}C NMR (101 MHz, $CDCl_3$) of **3j**



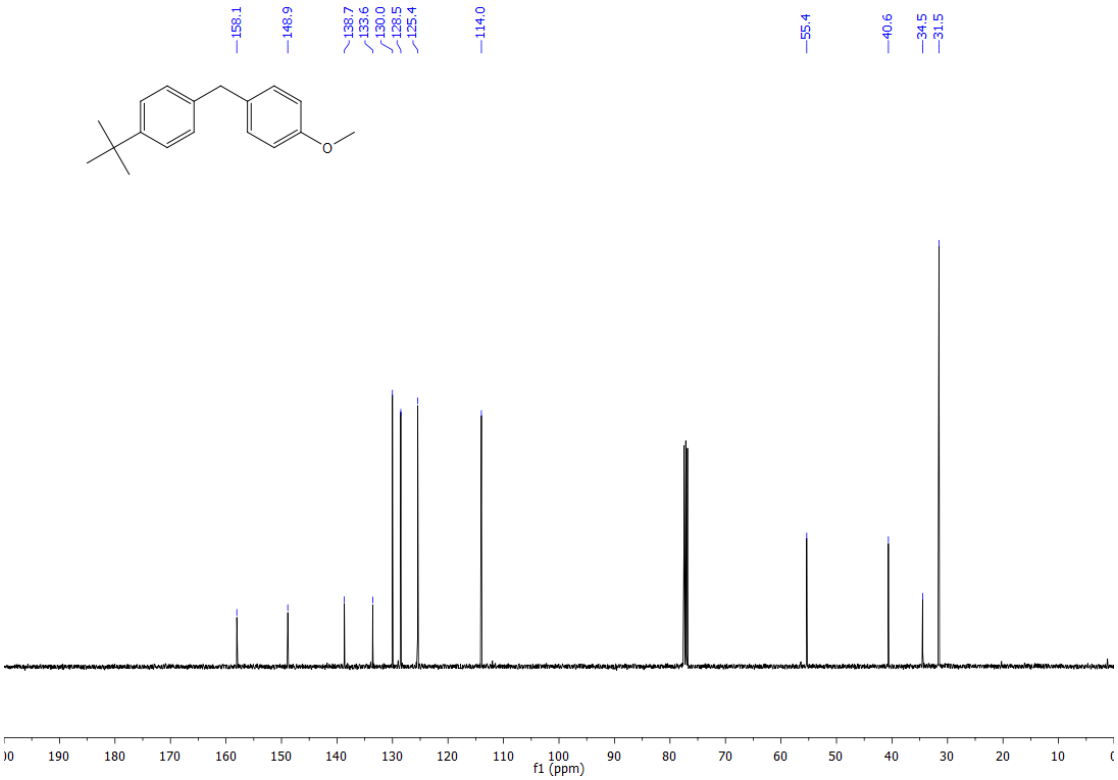
^{1}H NMR (400 MHz, $CDCl_3$) of 3**k**



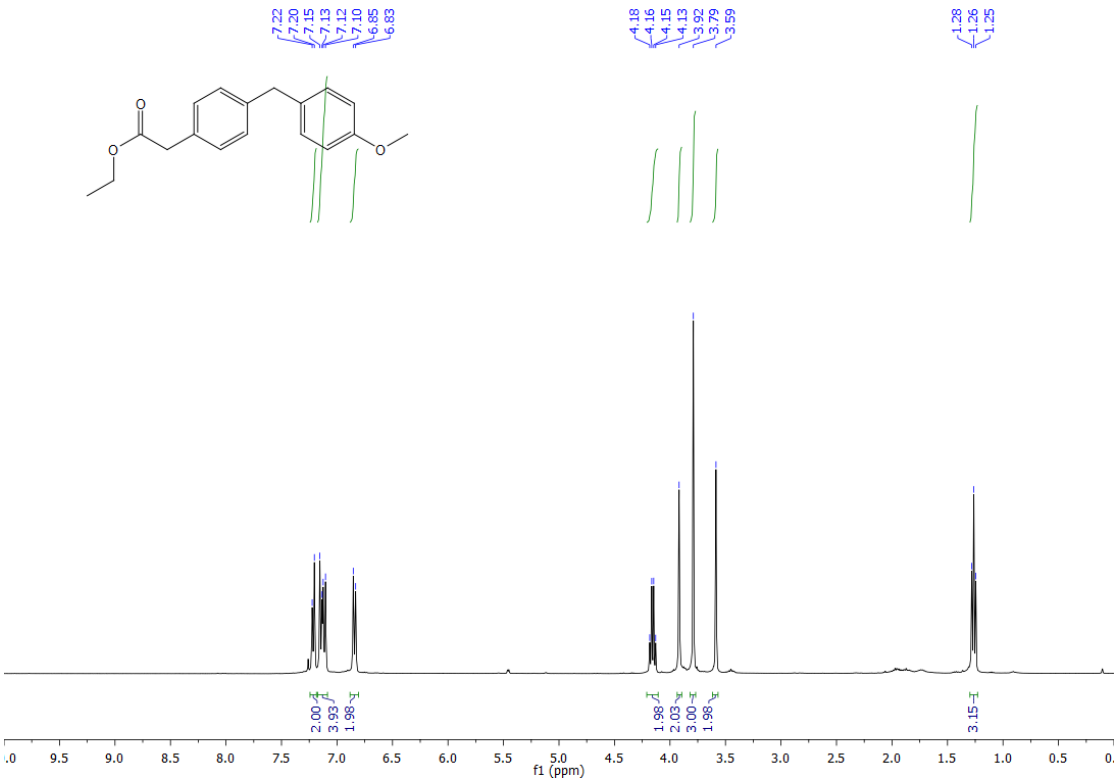
^{13}C NMR (101 MHz, $CDCl_3$) of **3k**



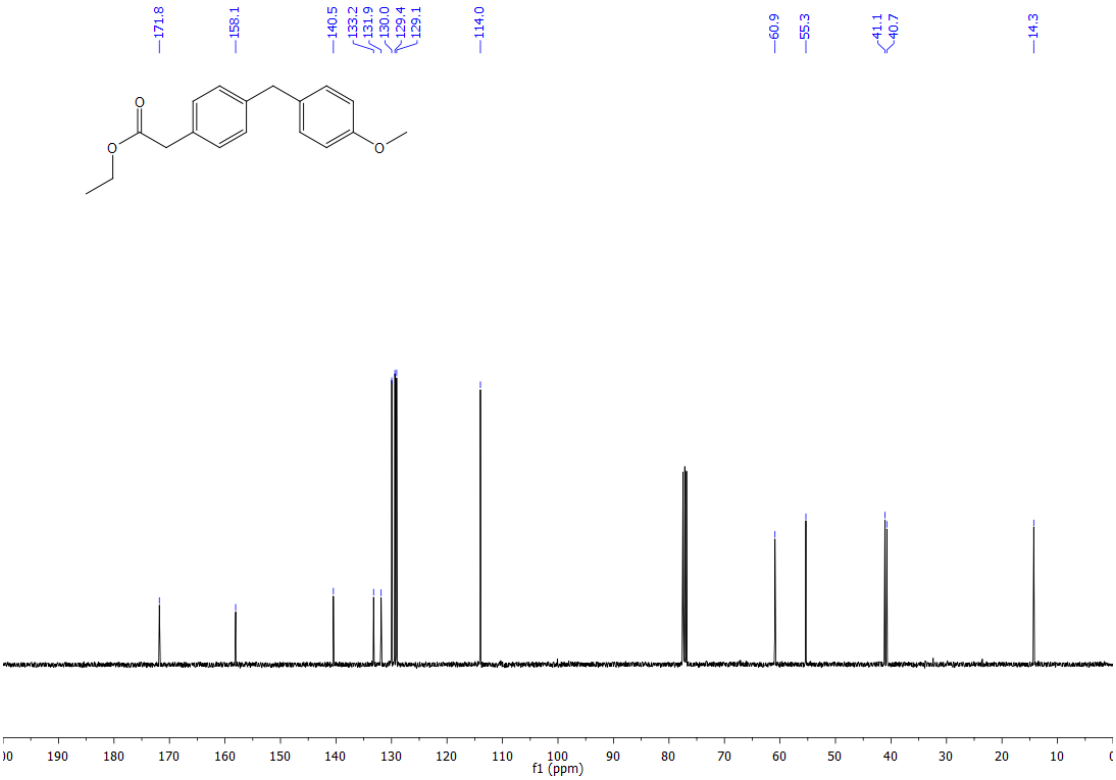
^{1}H NMR (400 MHz, $CDCl_3$) of **3l**



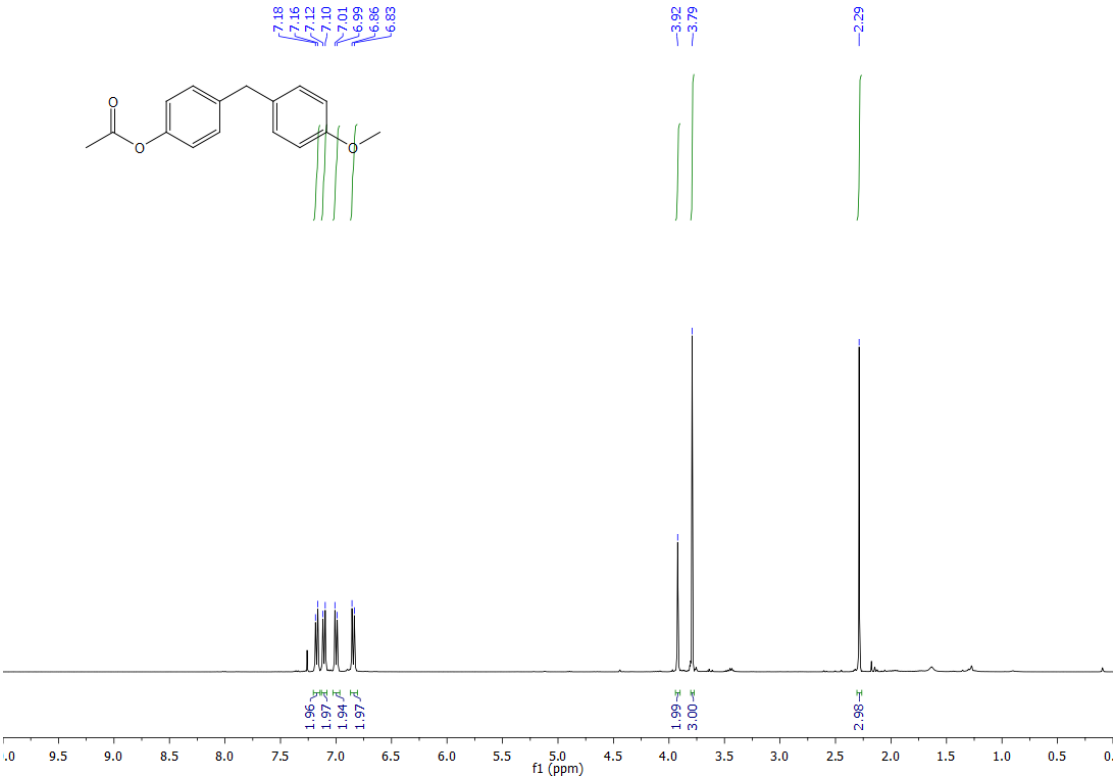
^{13}C NMR (101 MHz, $CDCl_3$) of **3l**



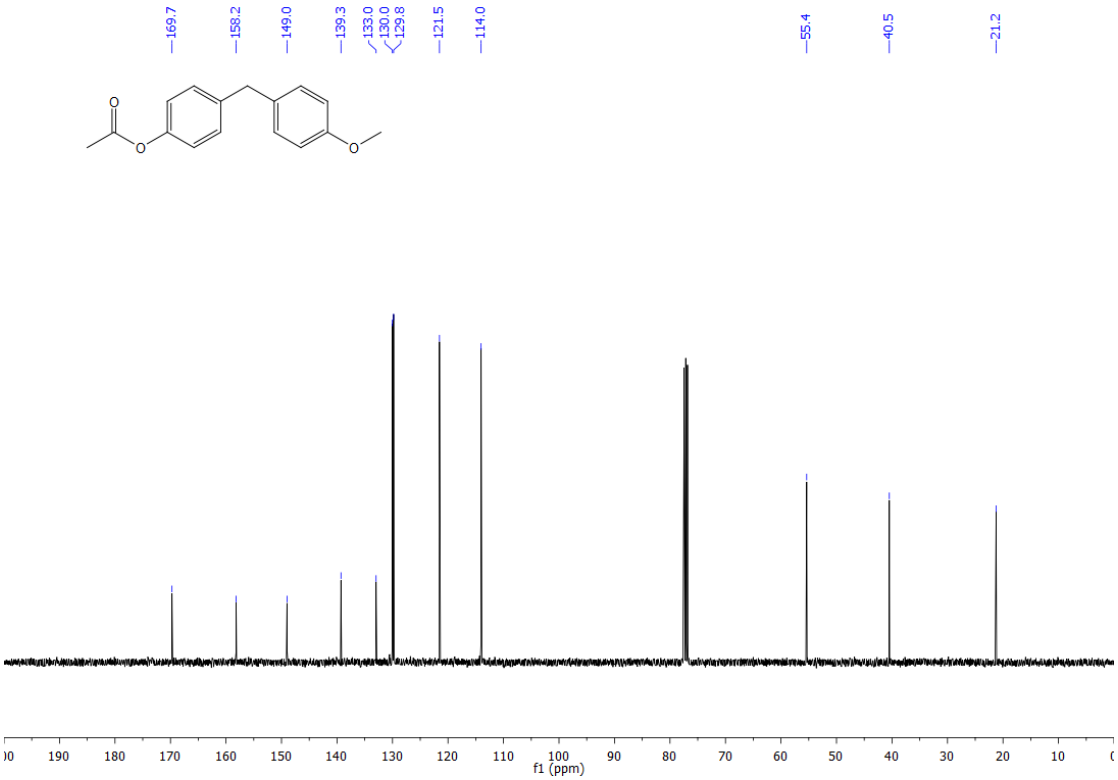
^{1}H NMR (400 MHz, $CDCl_3$) of 3**m**



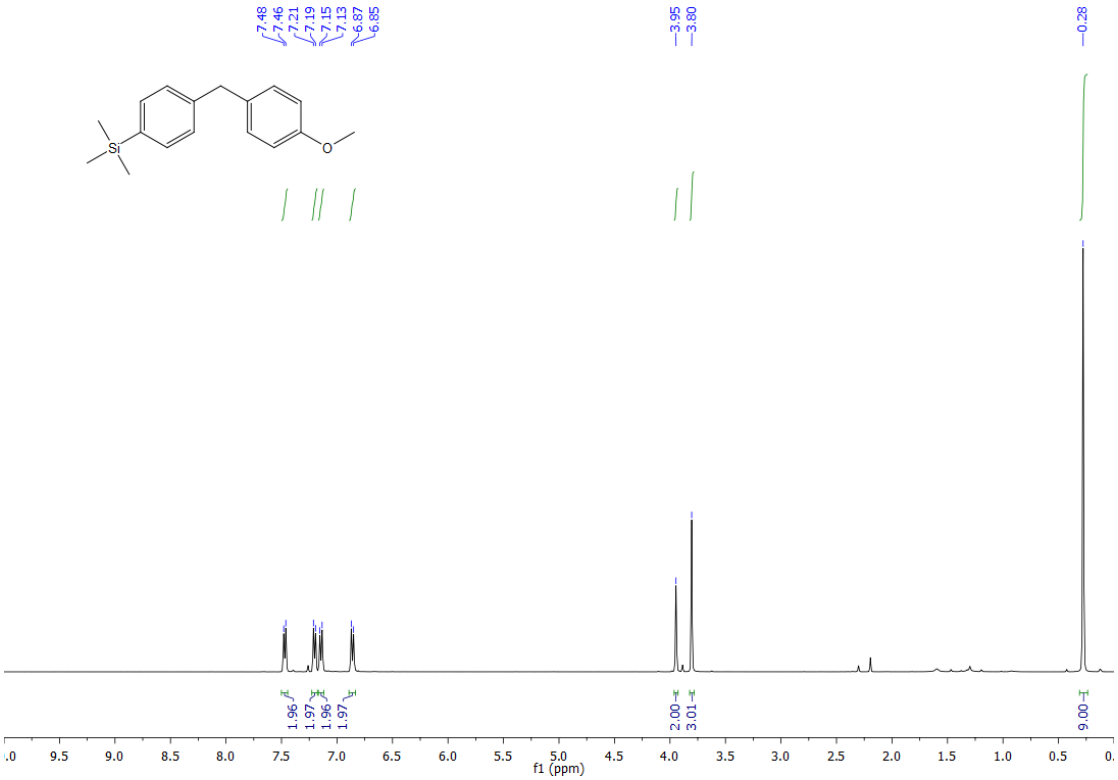
^{13}C NMR (101 MHz, $CDCl_3$) of **3m**



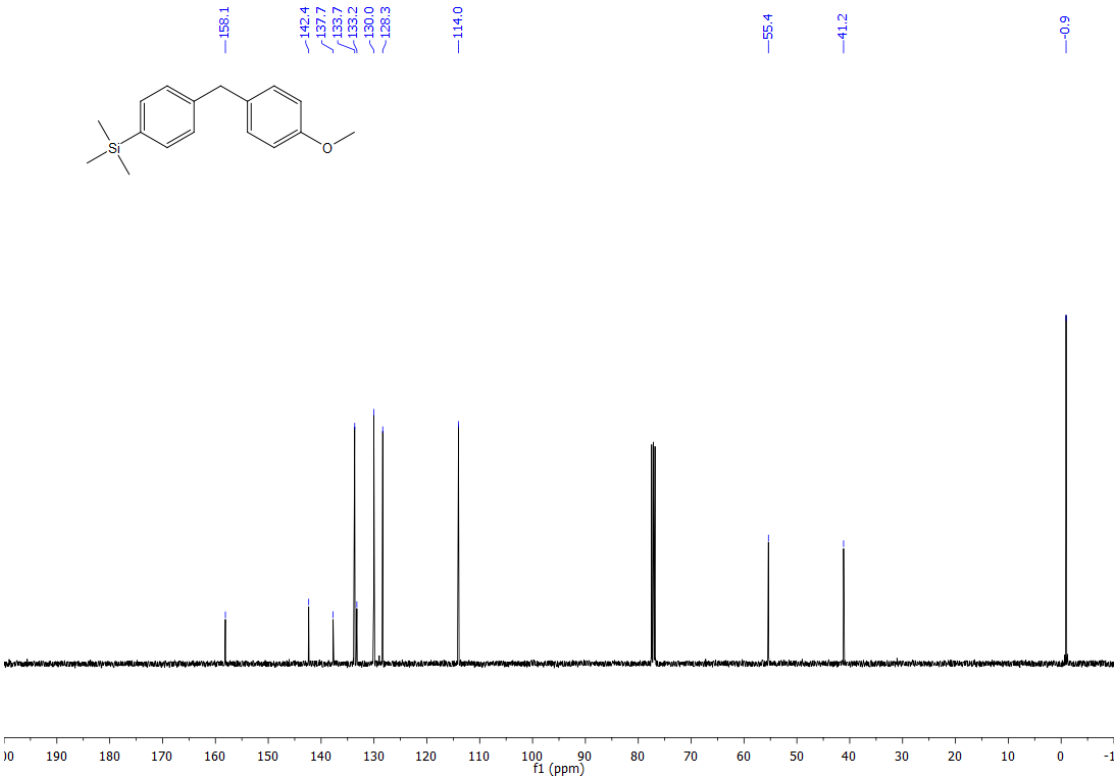
^{1}H NMR (400 MHz, $CDCl_3$) of 3**n**



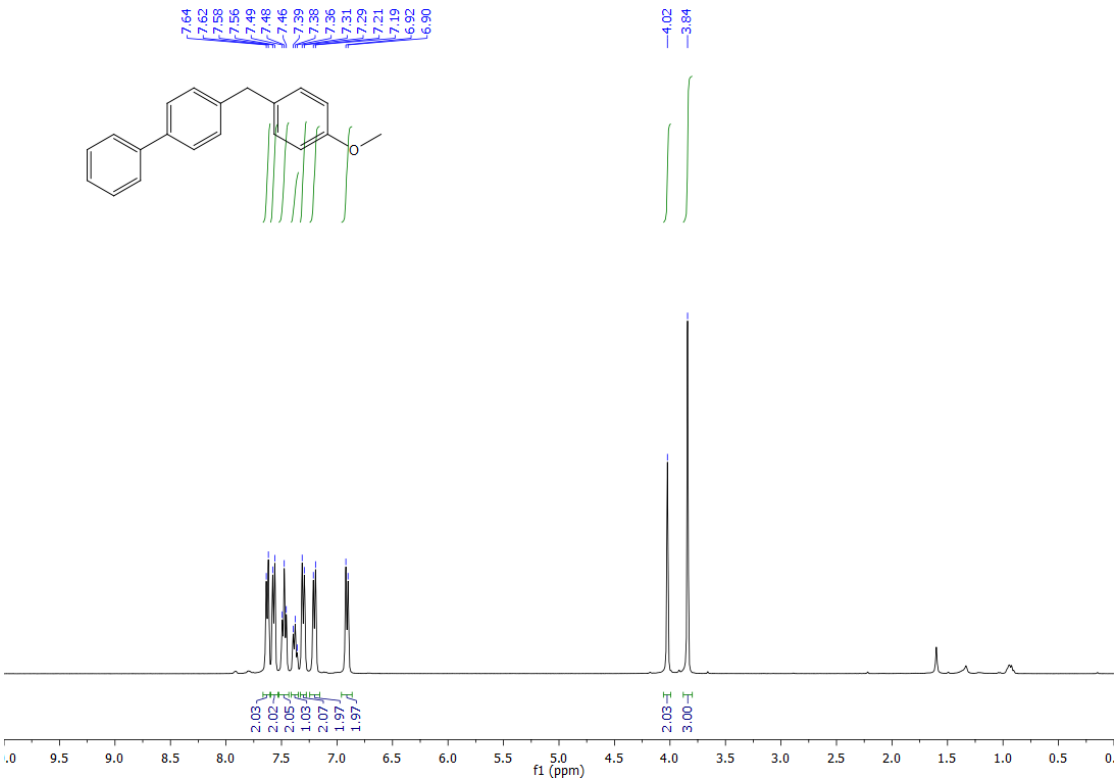
^{13}C NMR (101 MHz, $CDCl_3$) of **3n**



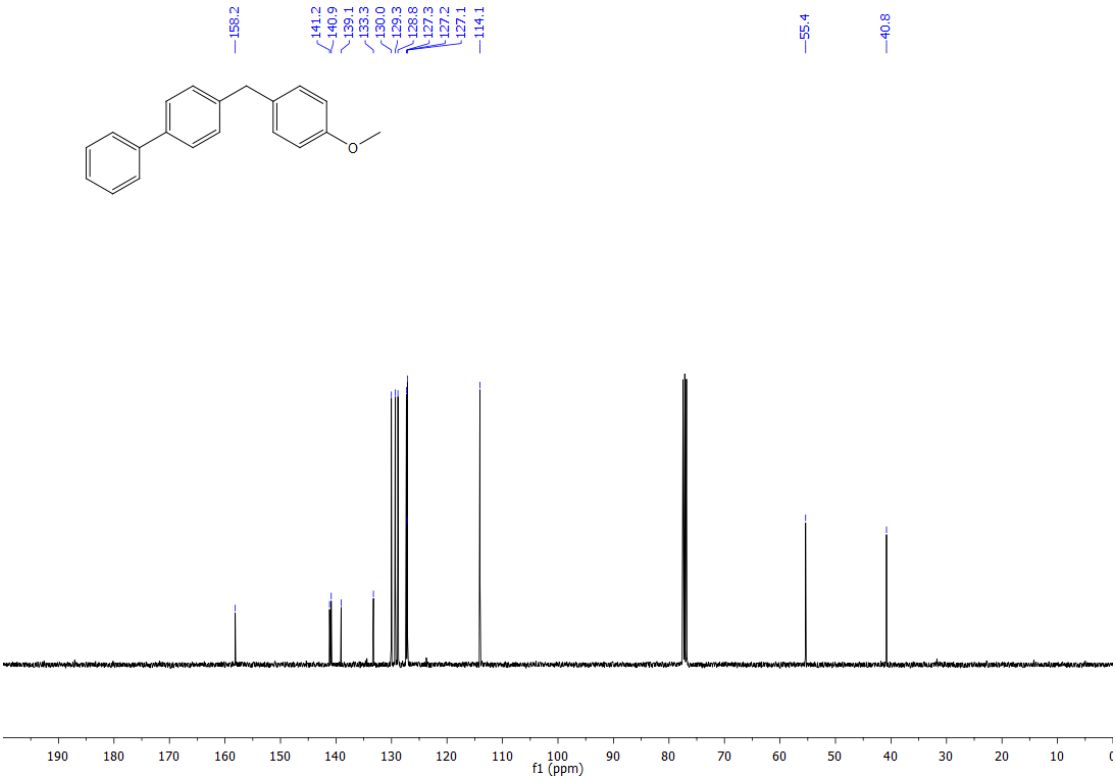
^{1}H NMR (400 MHz, $CDCl_3$) of 3**o**



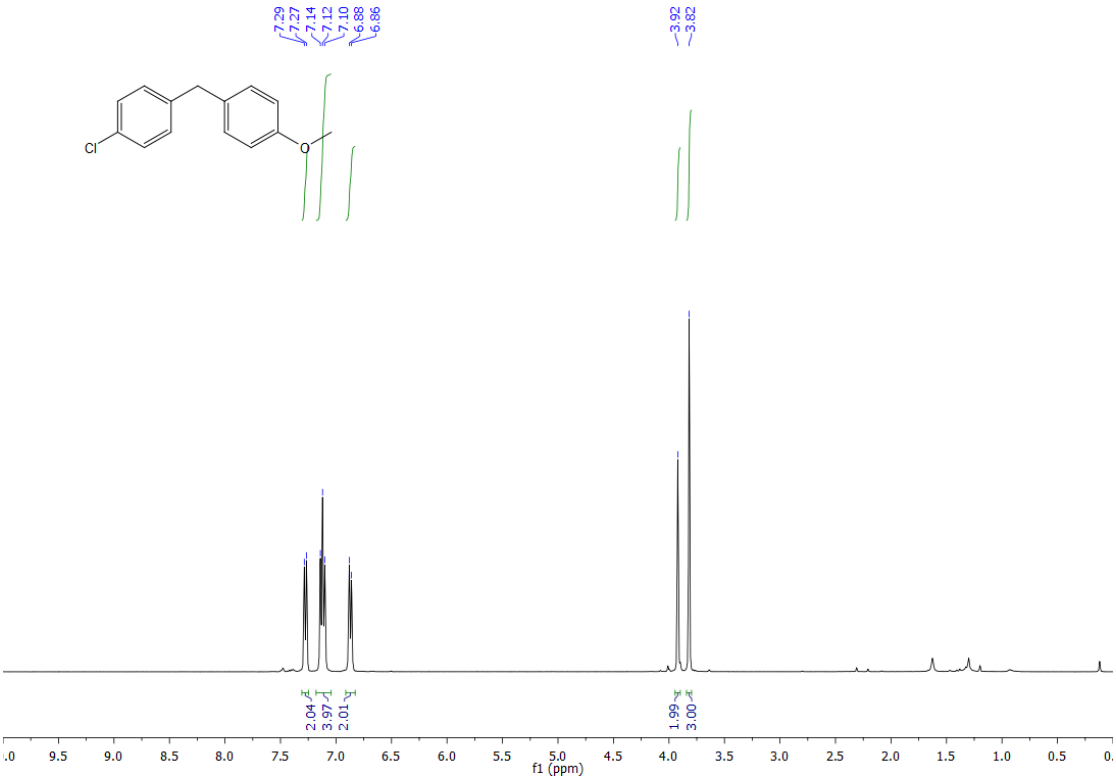
^{13}C NMR (101 MHz, $CDCl_3$) of **3o**



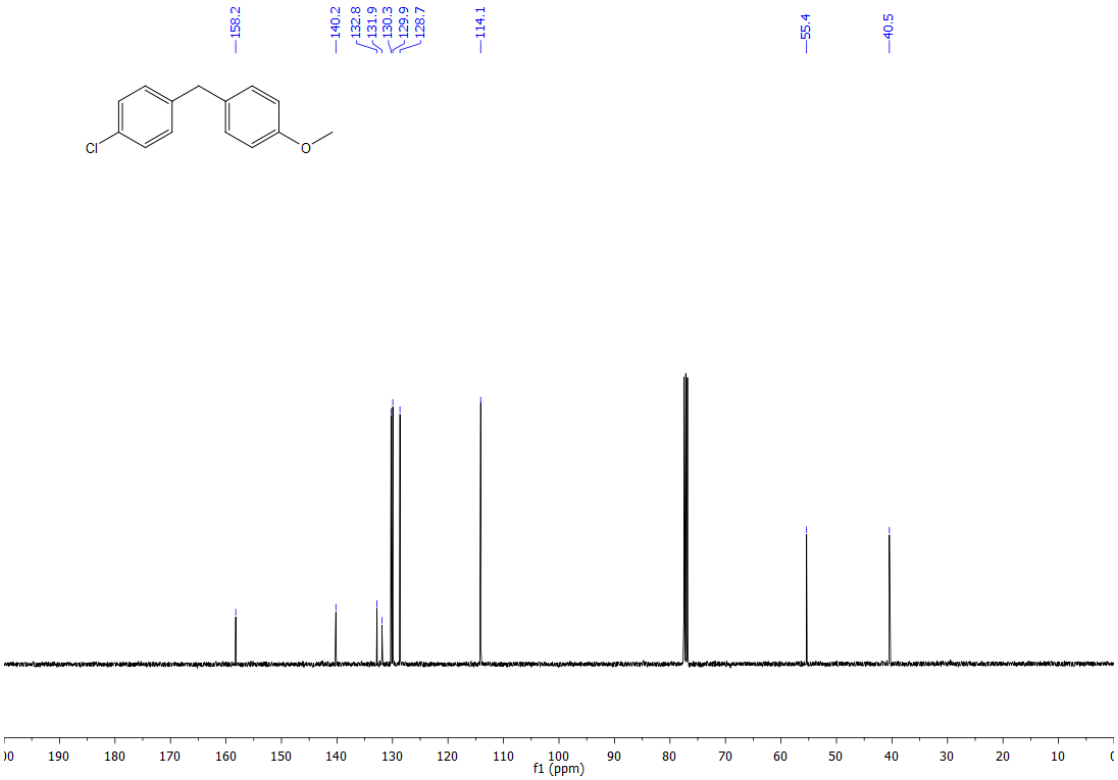
^{1}H NMR (400 MHz, $CDCl_3$) of 3**p**



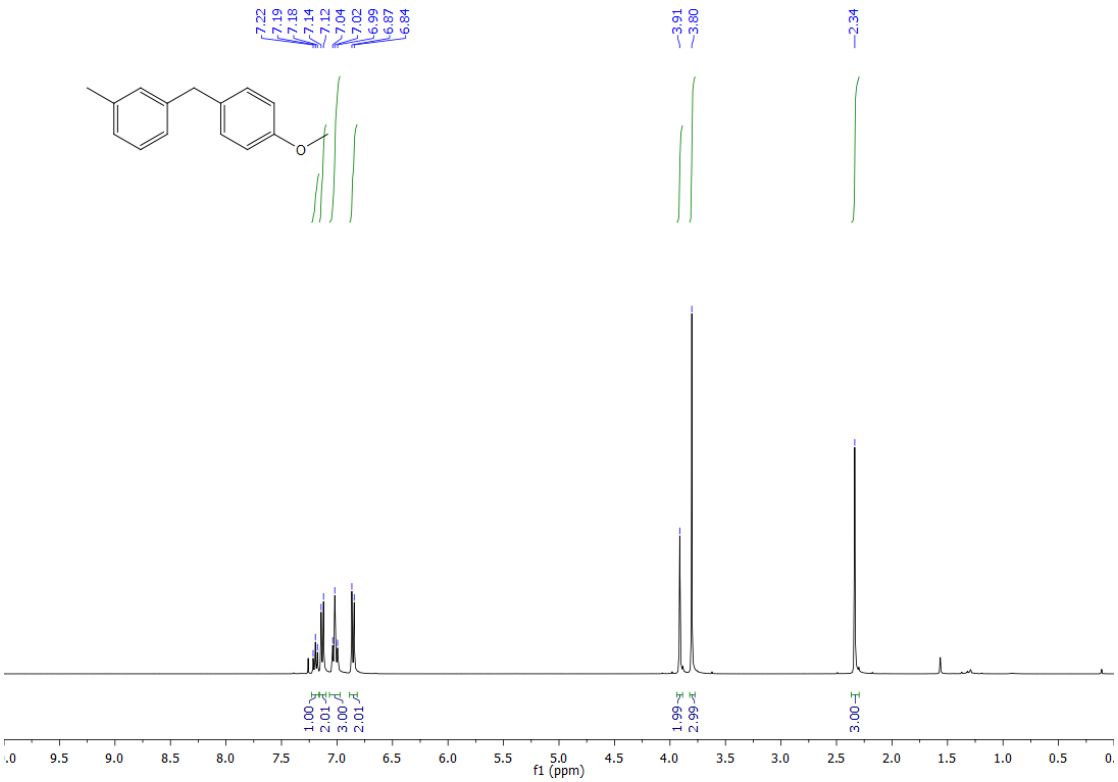
^{13}C NMR (101 MHz, $CDCl_3$) of **3p**



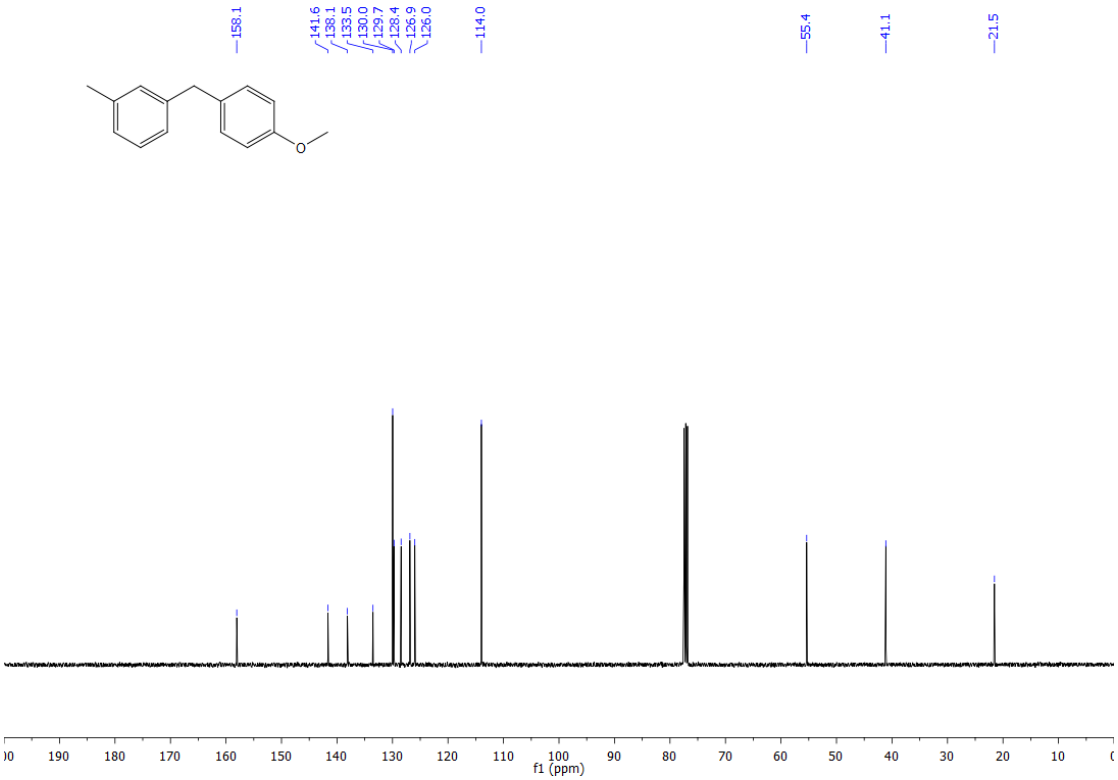
^{1}H NMR (400 MHz, $CDCl_3$) of 3**q**



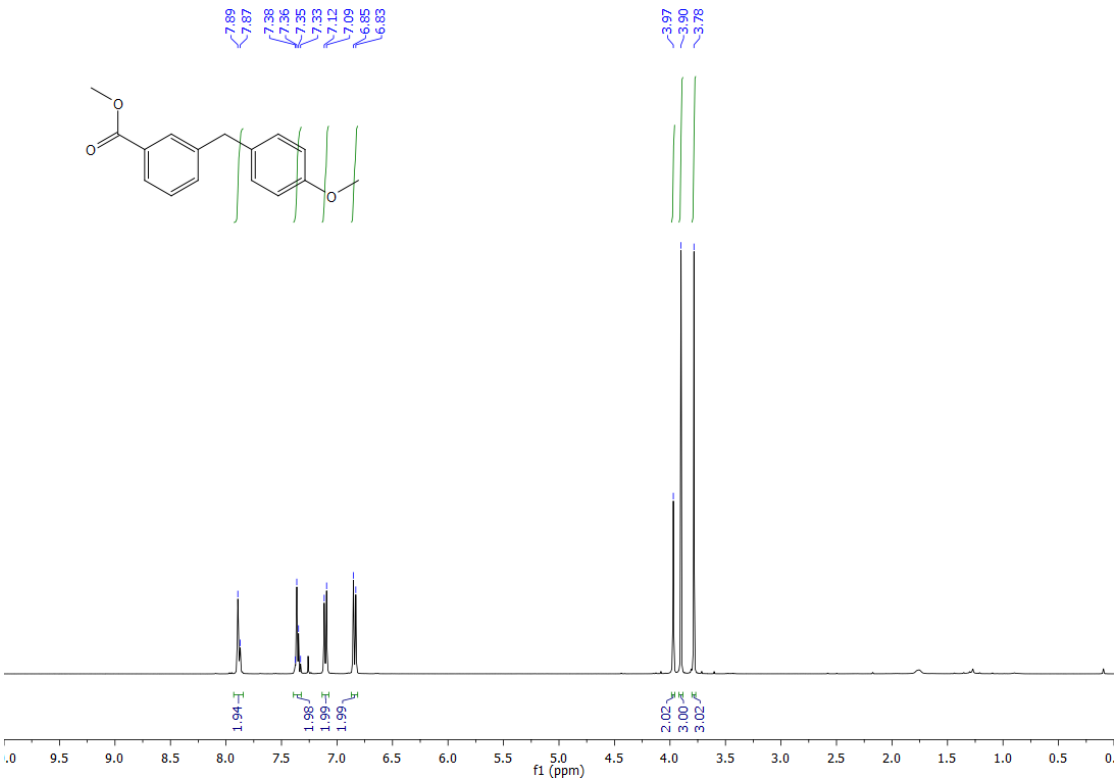
^{13}C NMR (101 MHz, $CDCl_3$) of **3q**



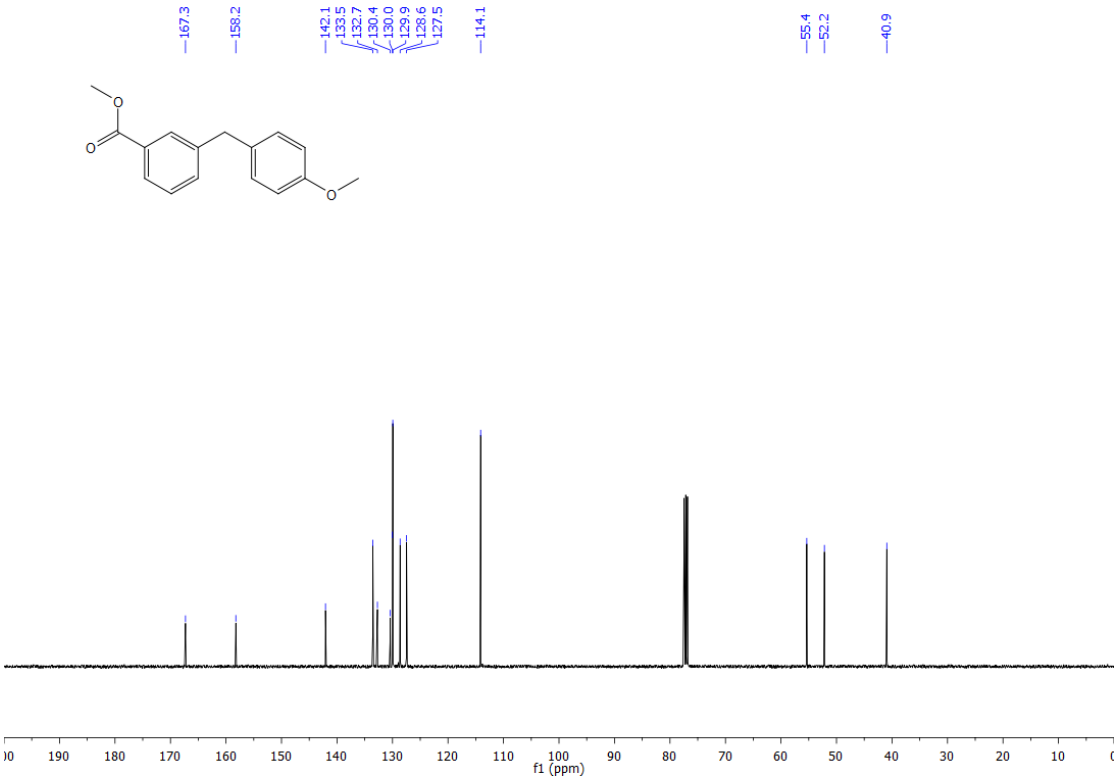
^{1}H NMR (400 MHz, $CDCl_3$) of 3**r**



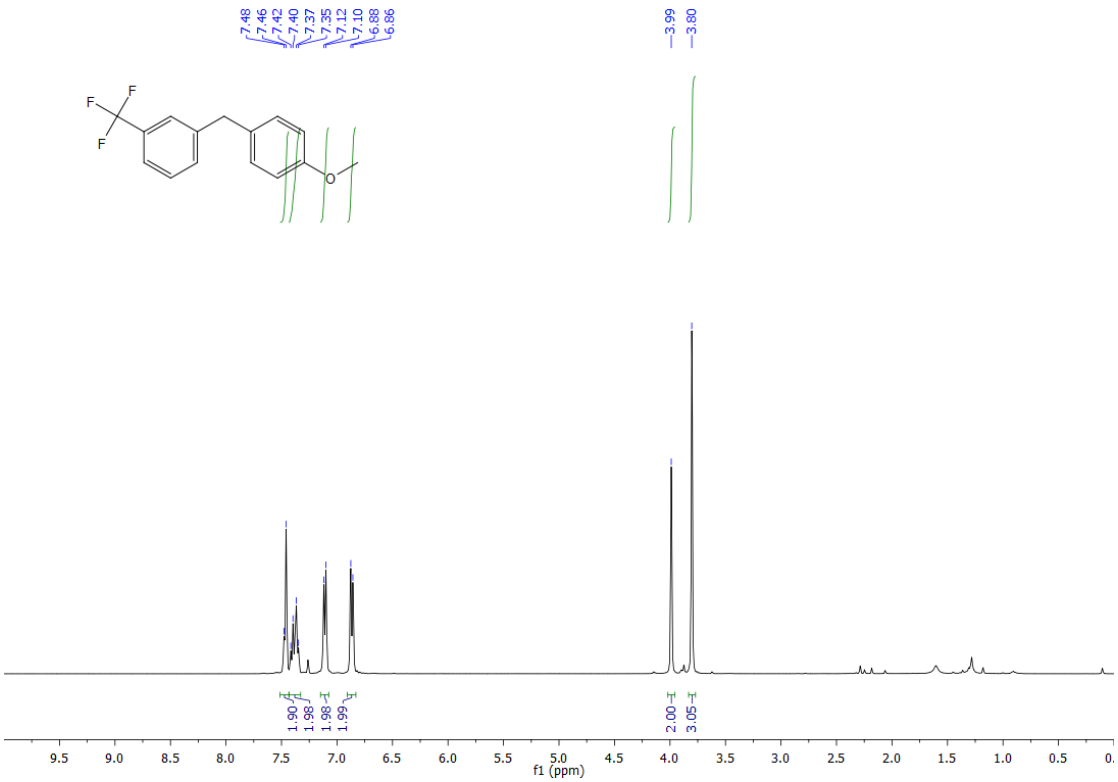
^{13}C NMR (101 MHz, $CDCl_3$) of **3r**



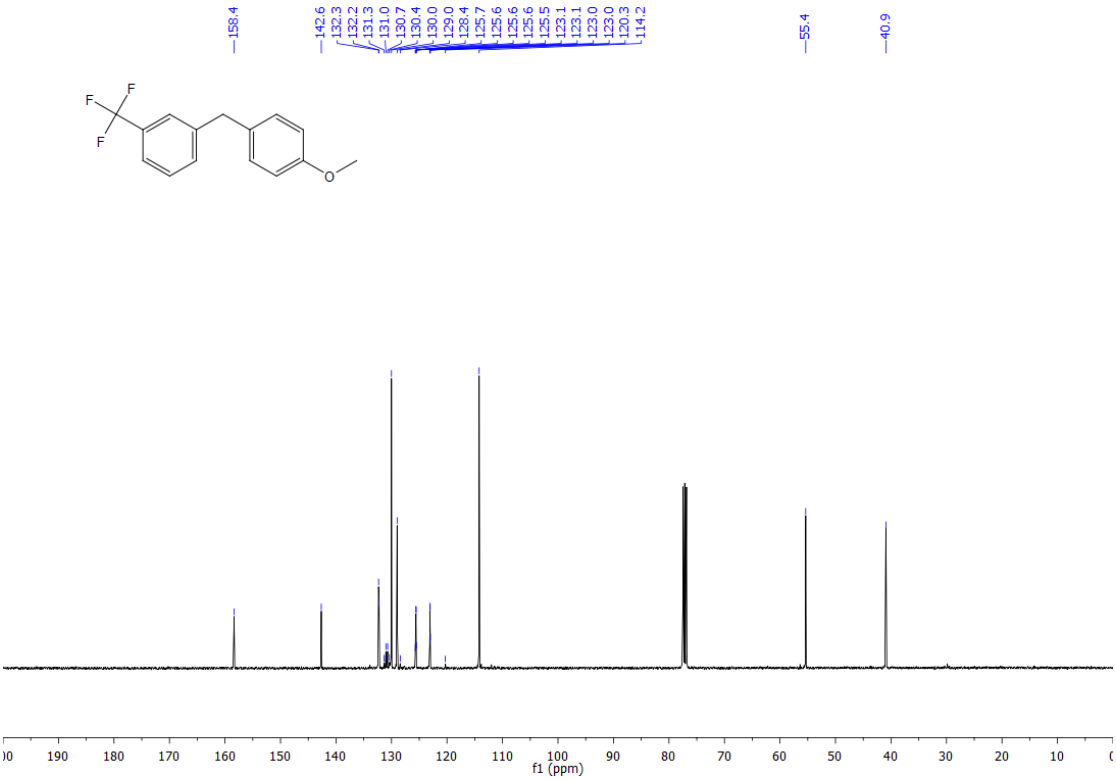
^{1}H NMR (400 MHz, $CDCl_3$) of 3**s**



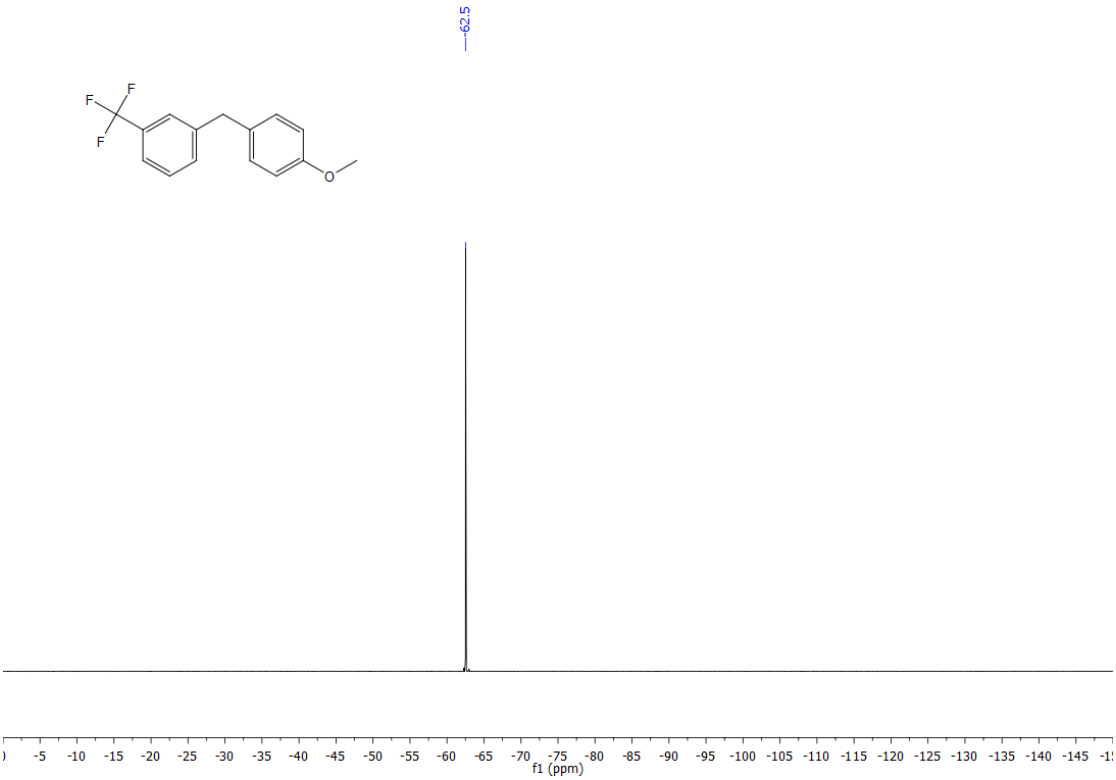
^{13}C NMR (101 MHz, $CDCl_3$) of **3s**



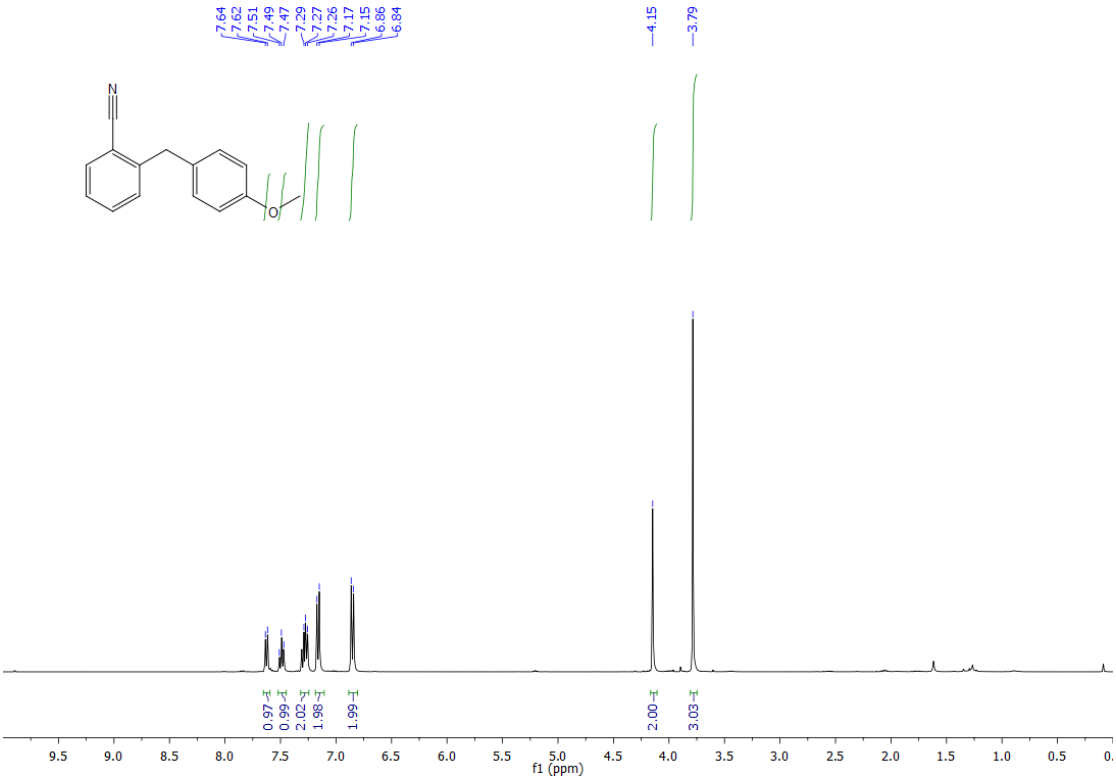
^{1}H NMR (400 MHz, $CDCl_3$) of 3**t**



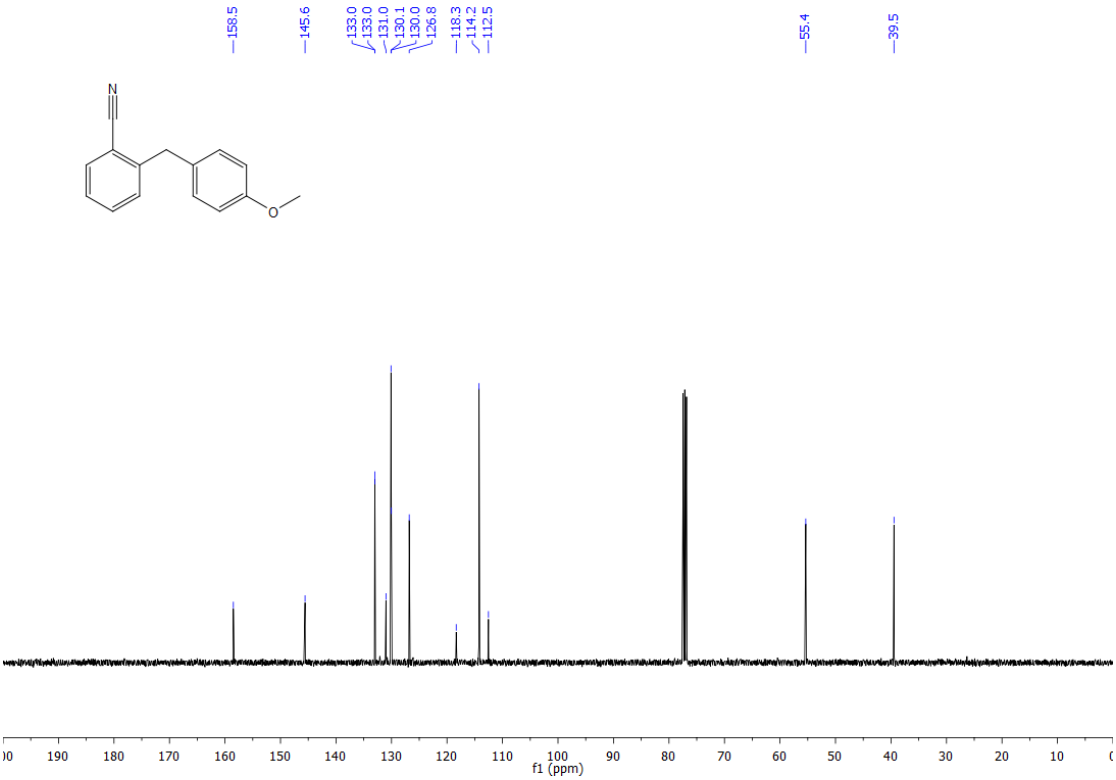
^{13}C NMR (101 MHz, $CDCl_3$) of **3t**



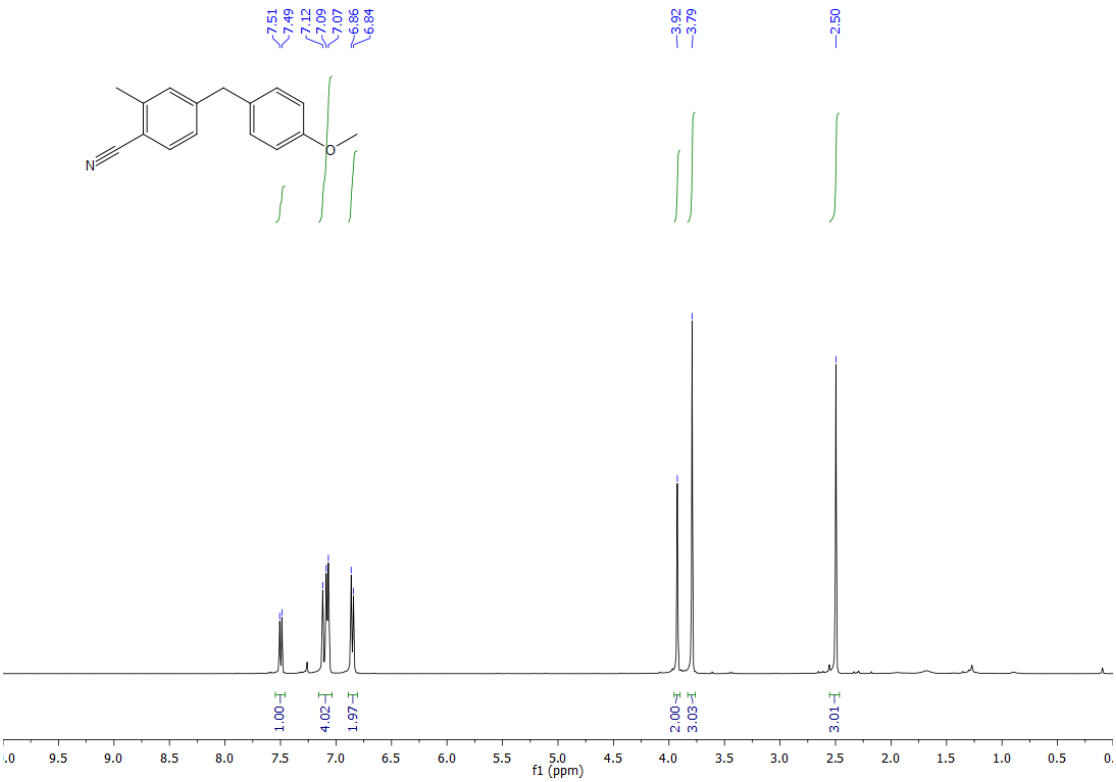
^{19}F NMR (376 MHz, $CDCl_3$) of **3t**



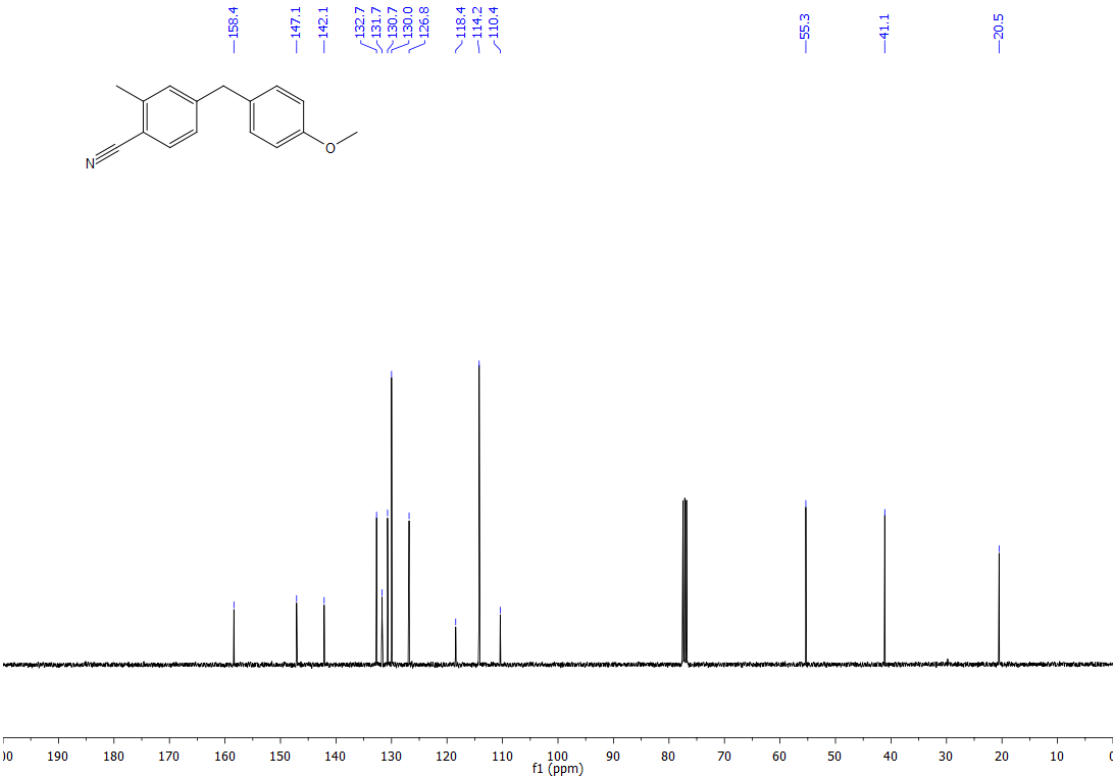
^{1}H NMR (400 MHz, $CDCl_3$) of **3u**



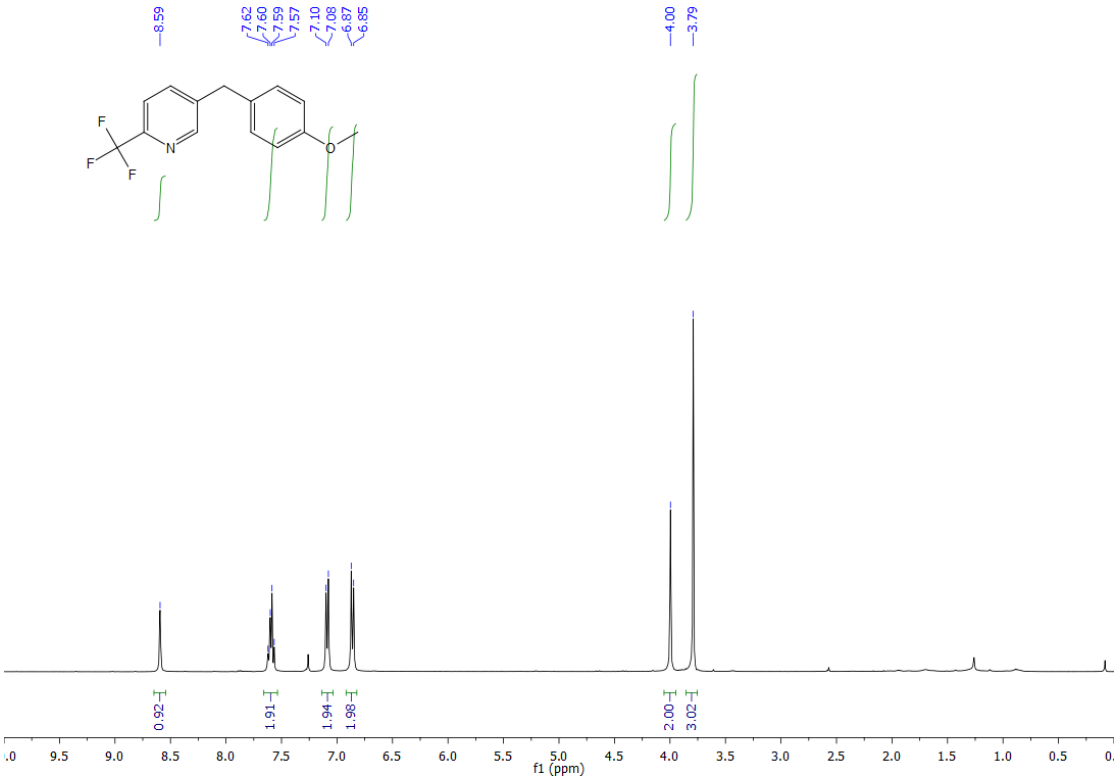
^{13}C NMR (101 MHz, $CDCl_3$) of **3u**



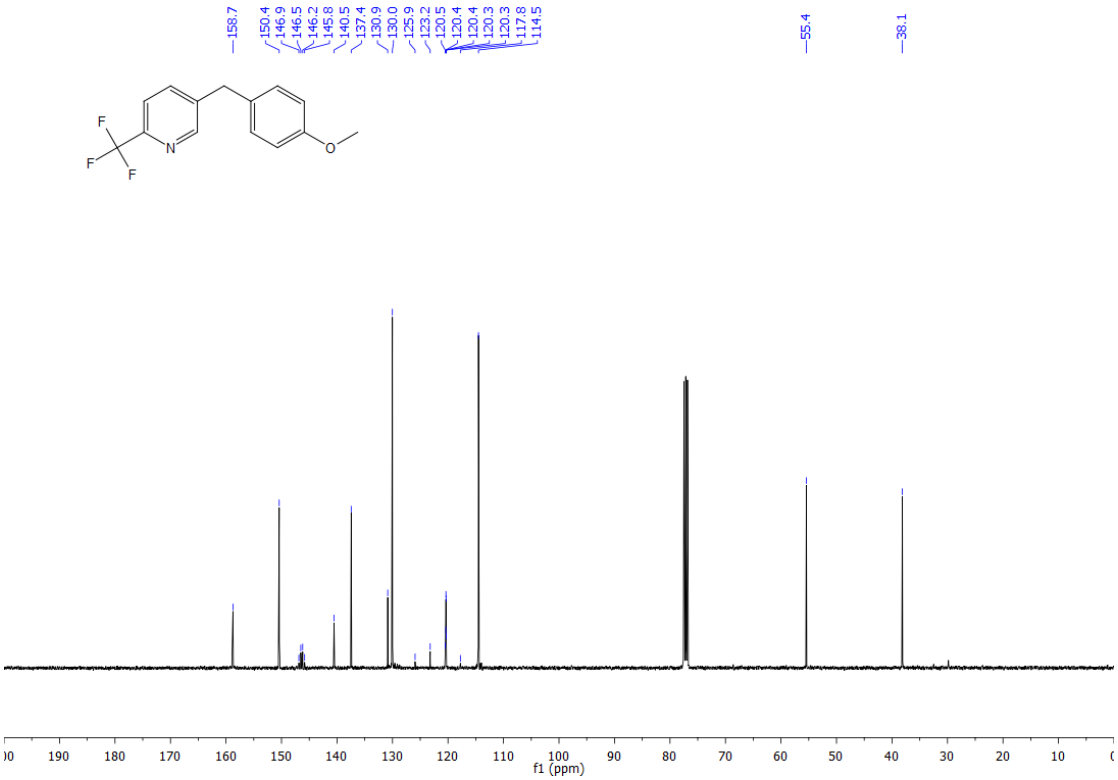
^{1}H NMR (400 MHz, $CDCl_3$) of **3v**



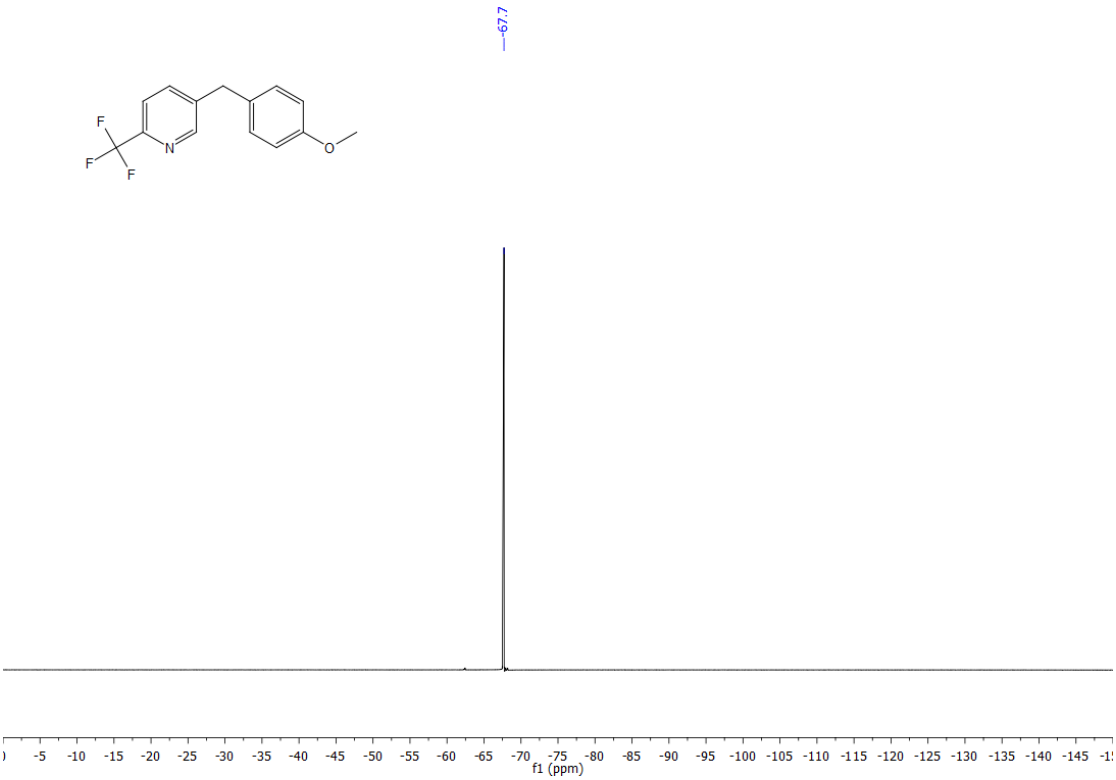
^{13}C NMR (101 MHz, $CDCl_3$) of **3v**



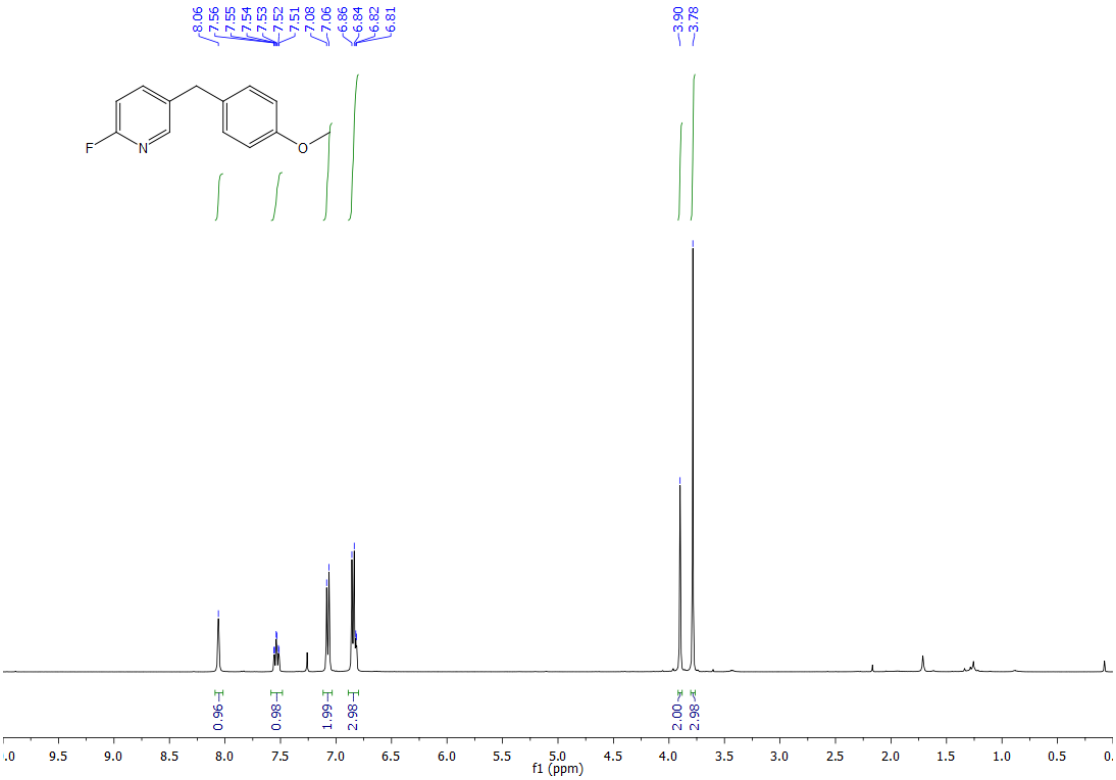
^{1}H NMR (400 MHz, $CDCl_3$) of **3w**



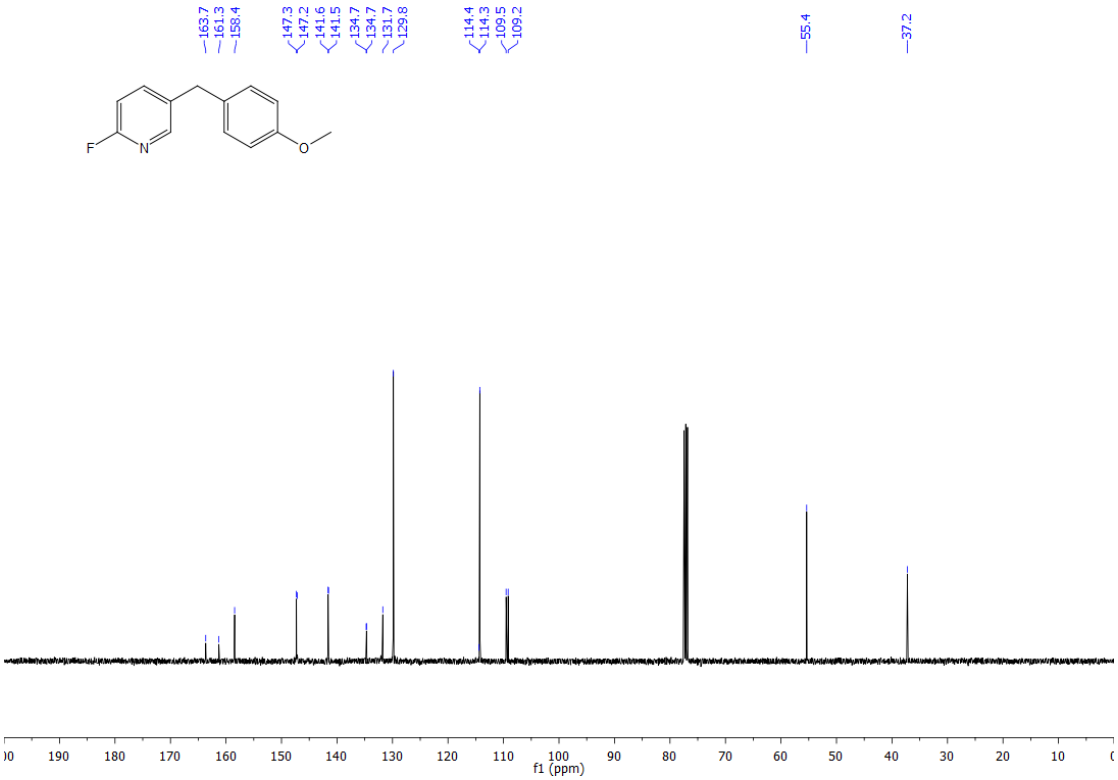
^{13}C NMR (101 MHz, $CDCl_3$) of **3w**



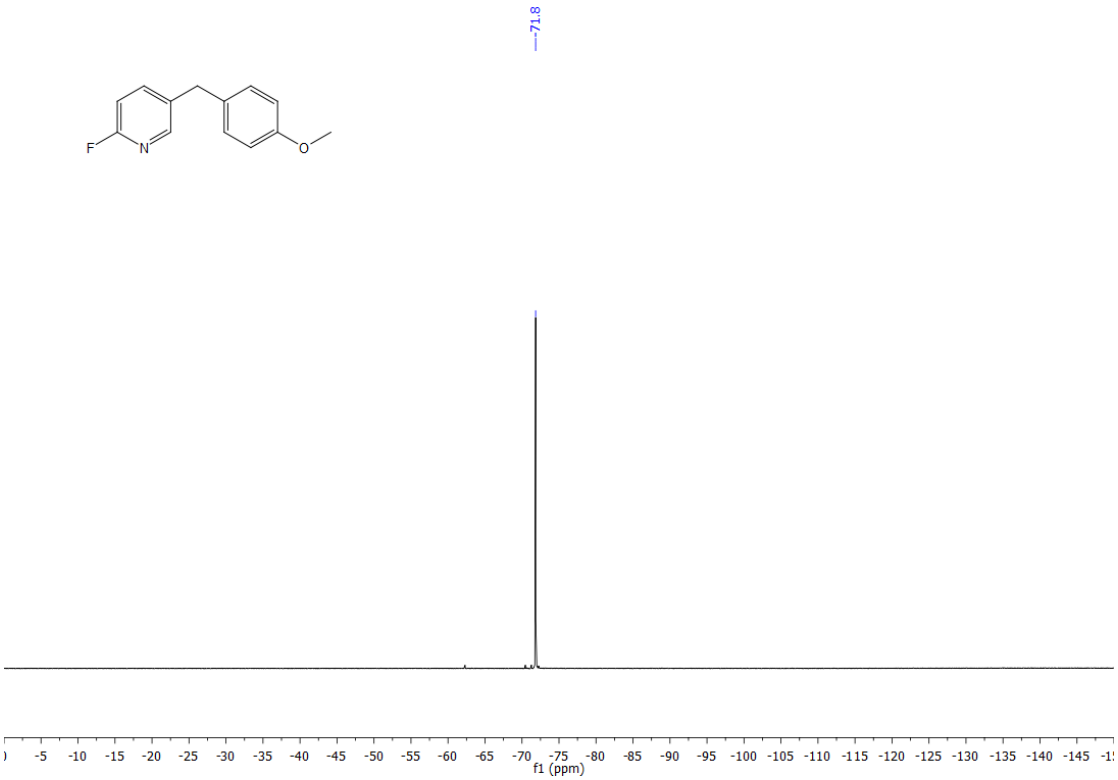
^{19}F NMR (376 MHz, $CDCl_3$) of **3w**



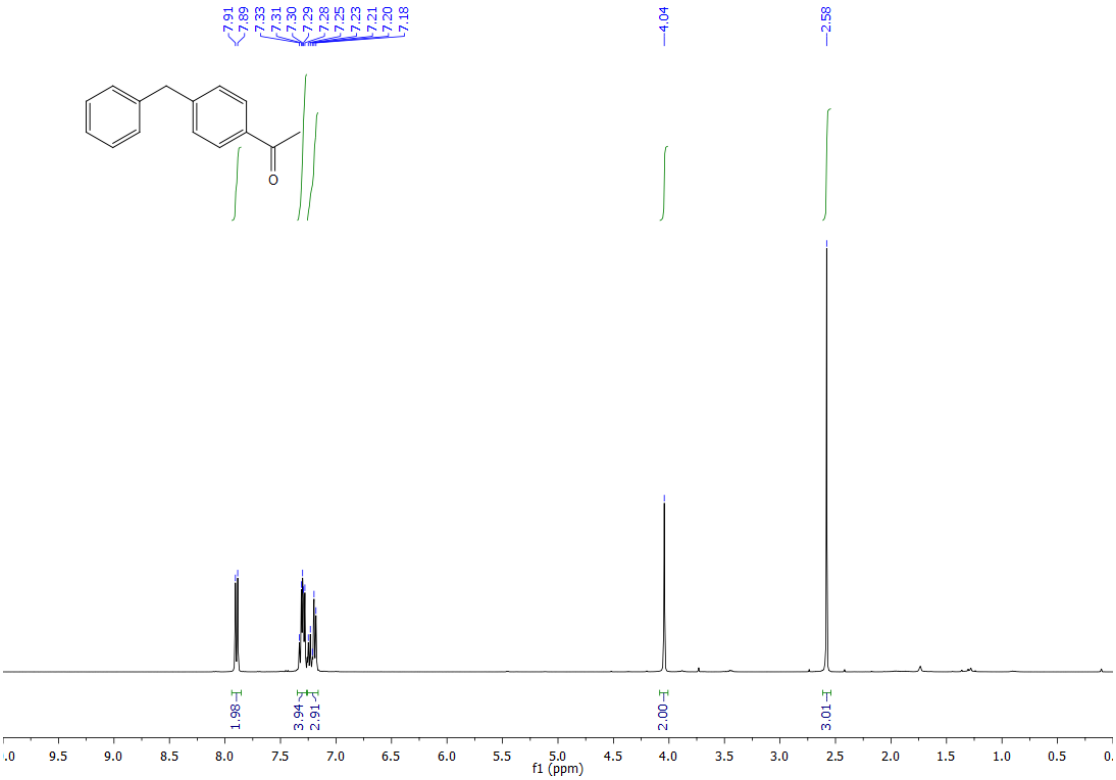
^{1}H NMR (400 MHz, $CDCl_3$) of 3**x**



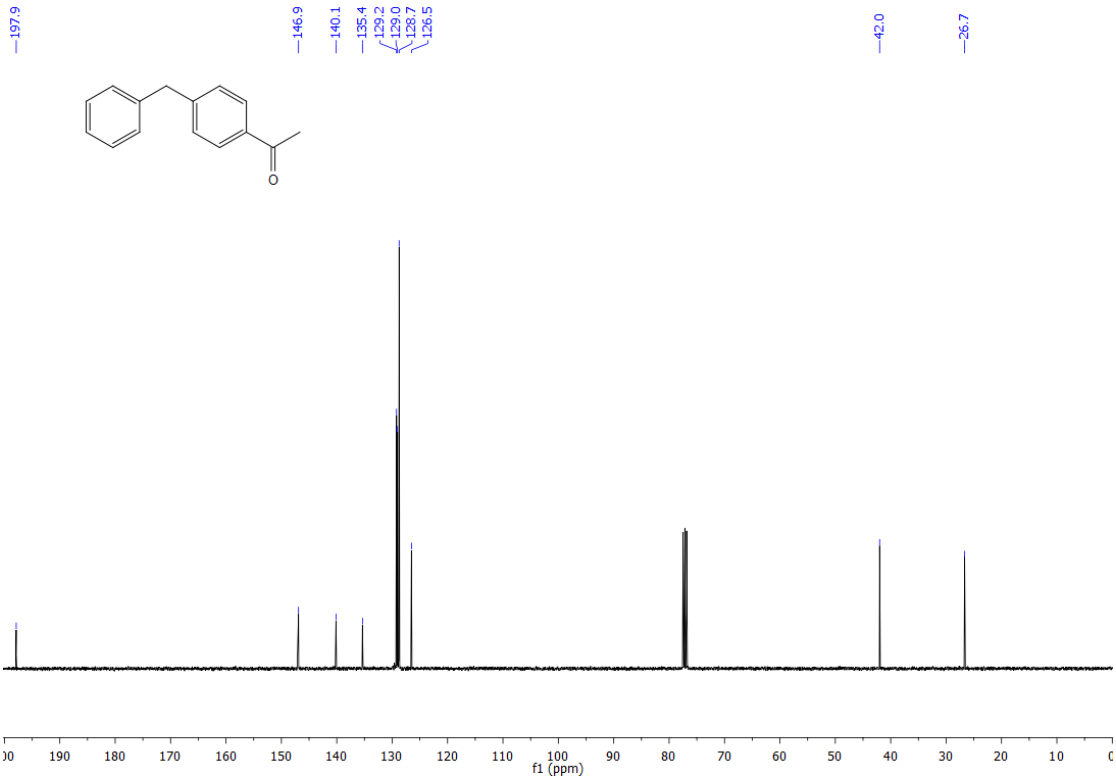
^{13}C NMR (101 MHz, $CDCl_3$) of **3x**



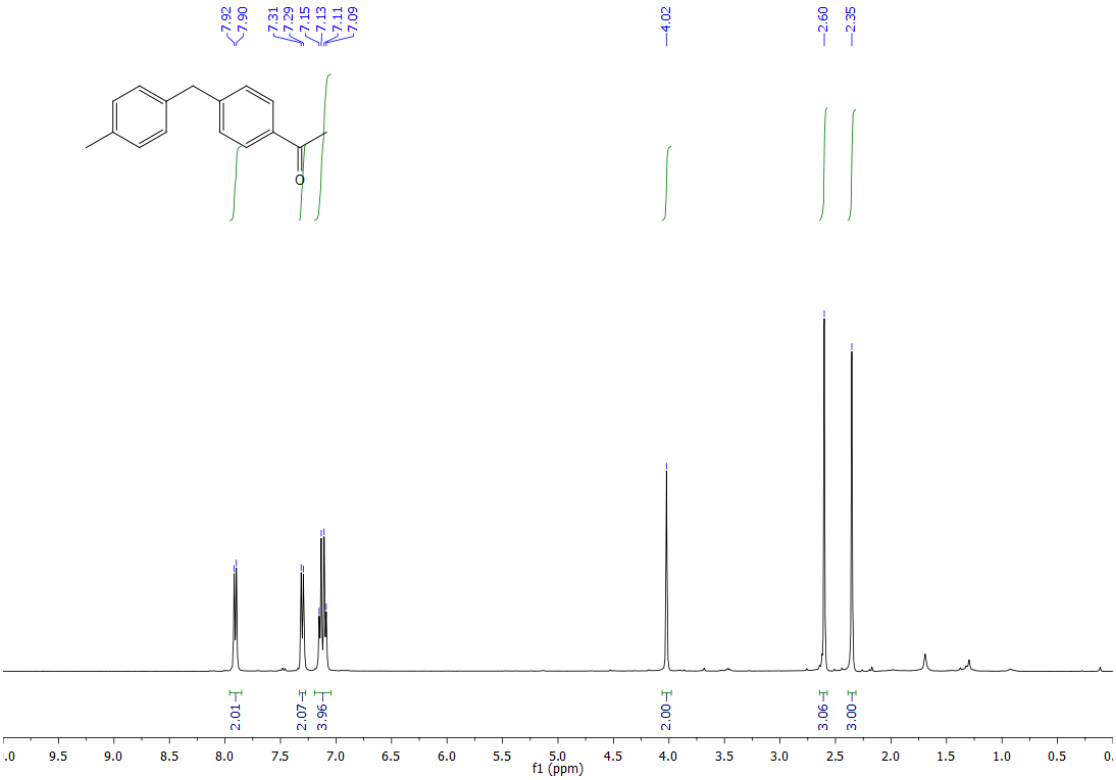
^{19}F NMR (376 MHz, $CDCl_3$) of **3x**



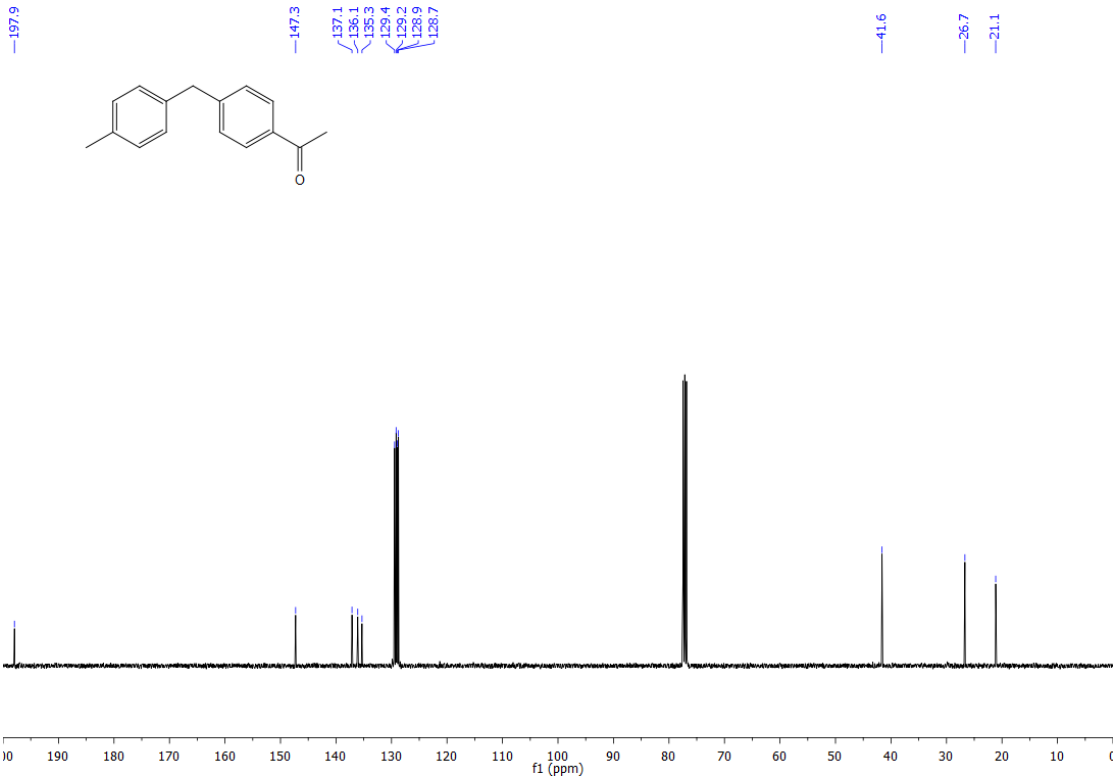
^{1}H NMR (400 MHz, $CDCl_3$) of 3**aa**



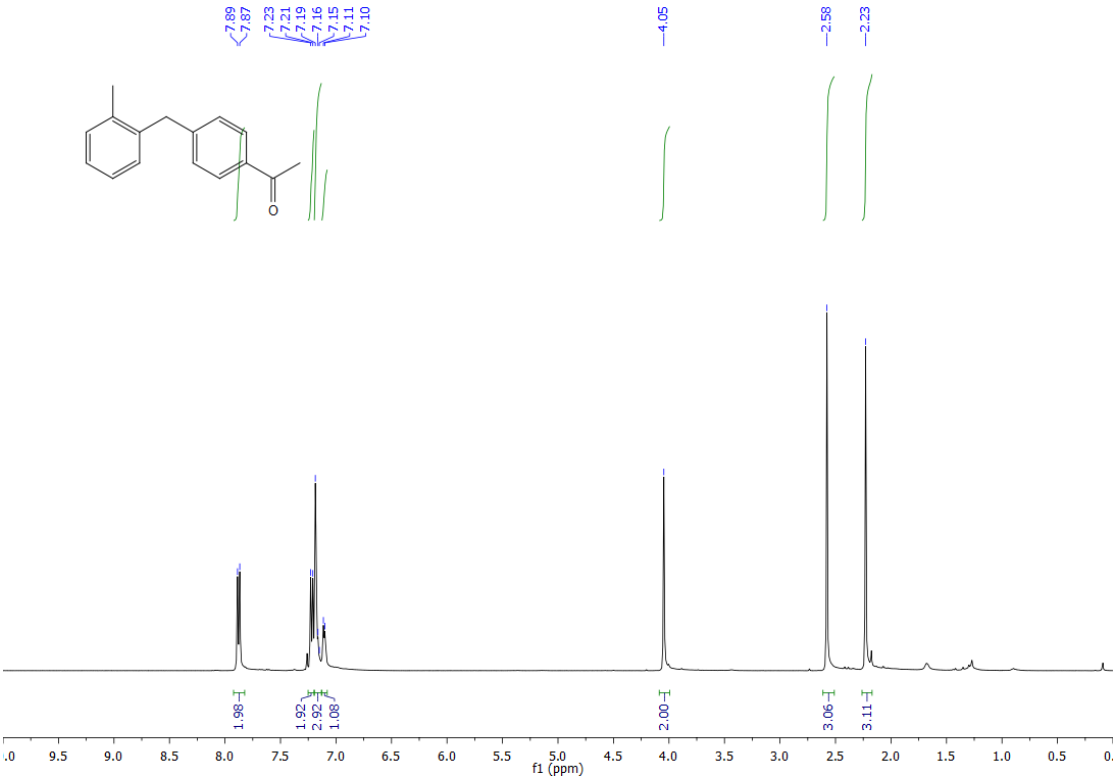
^{13}C NMR (101 MHz, $CDCl_3$) of **3aa**



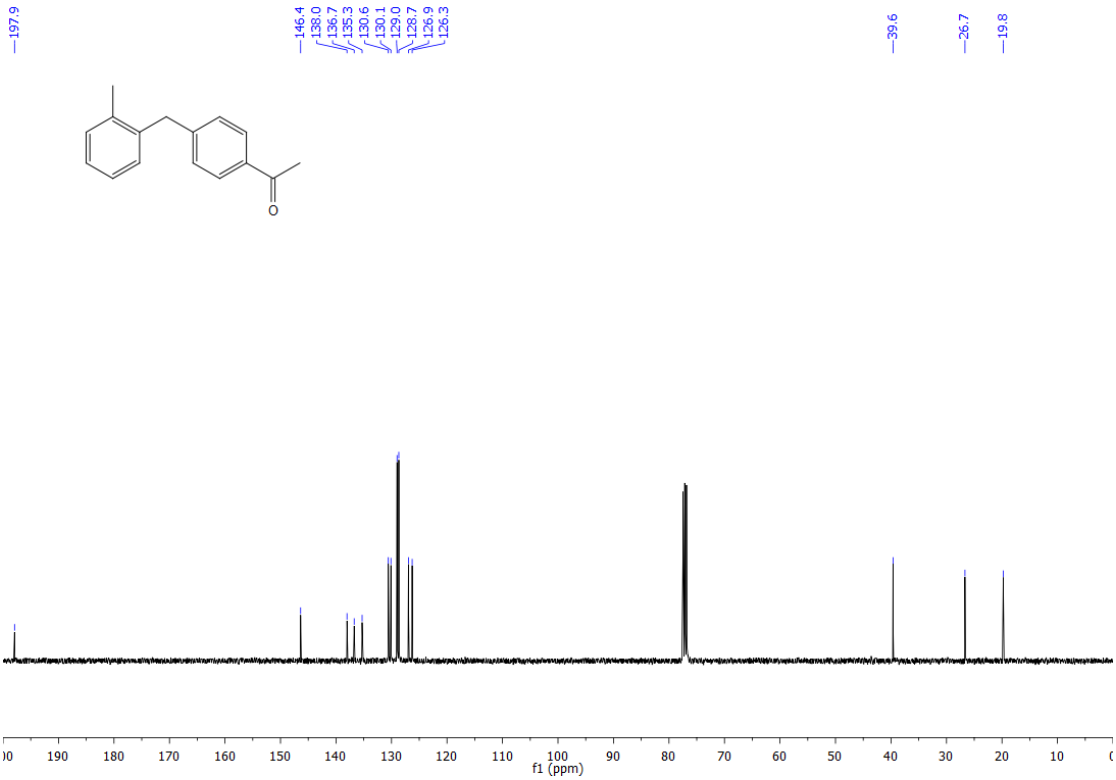
^{1}H NMR (400 MHz, $CDCl_3$) of 3**ab**



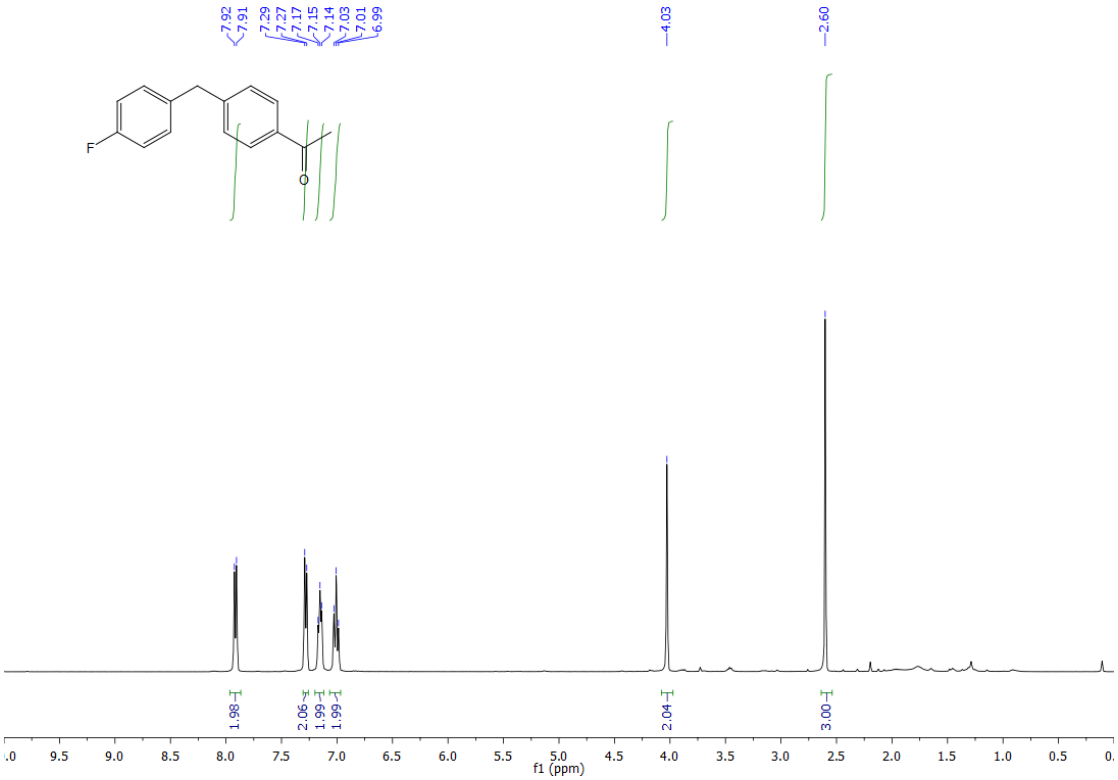
^{13}C NMR (101 MHz, $CDCl_3$) of **3ab**



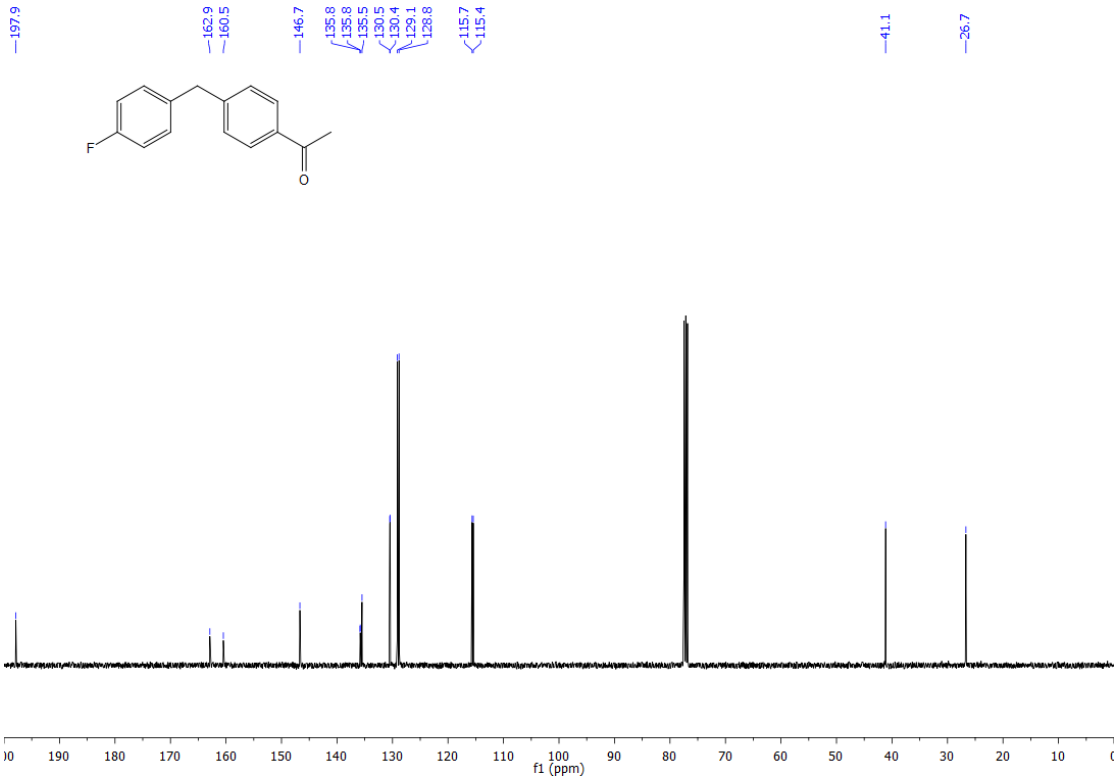
^{1}H NMR (400 MHz, $CDCl_3$) of 3**ac**



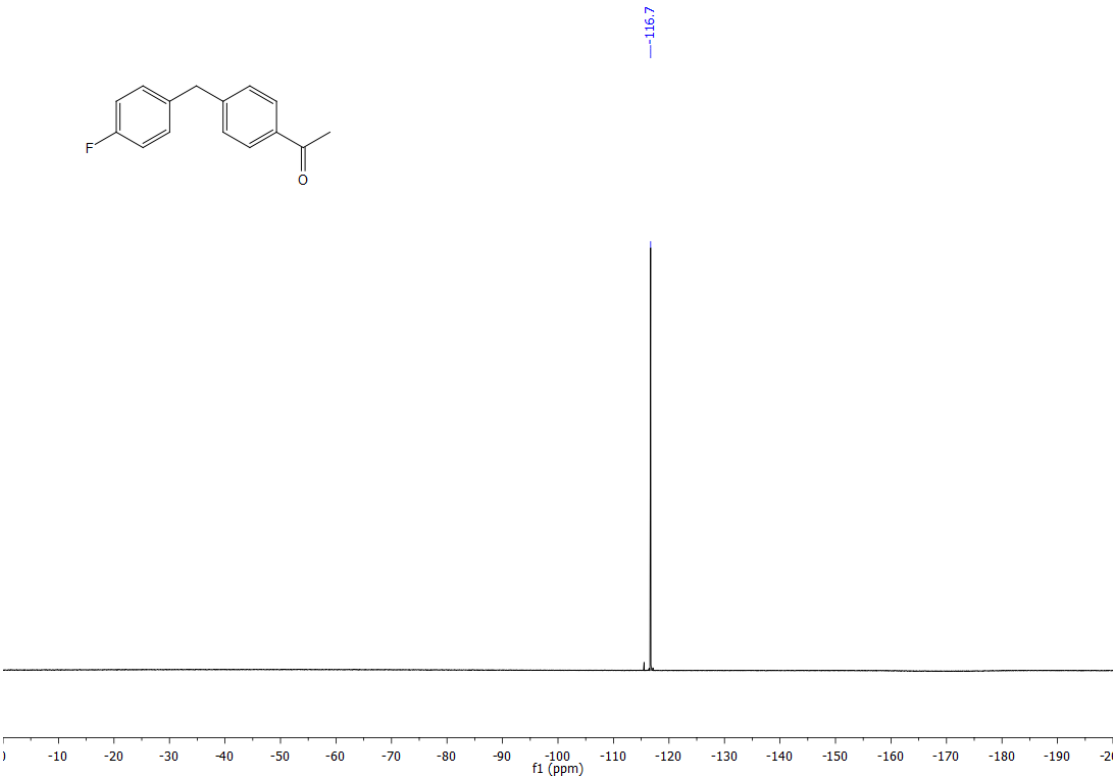
^{13}C NMR (101 MHz, $CDCl_3$) of **3ac**



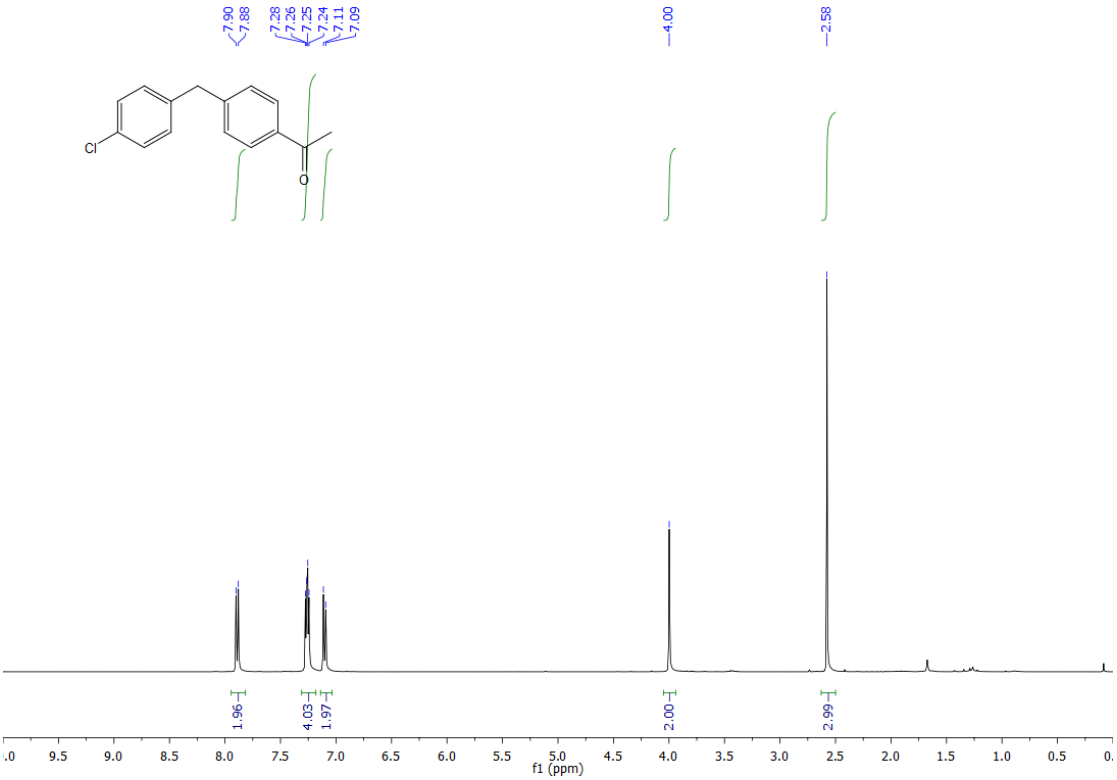
^{1}H NMR (400 MHz, $CDCl_3$) of 3**ad**



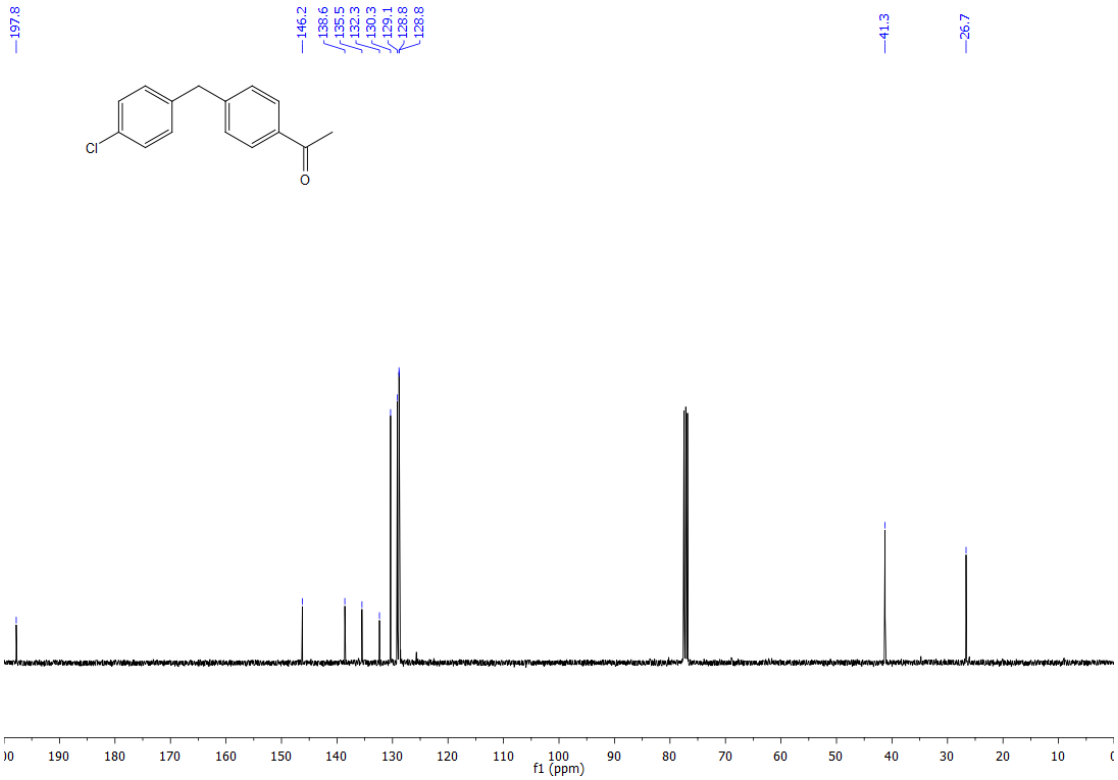
^{13}C NMR (101 MHz, $CDCl_3$) of **3ad**



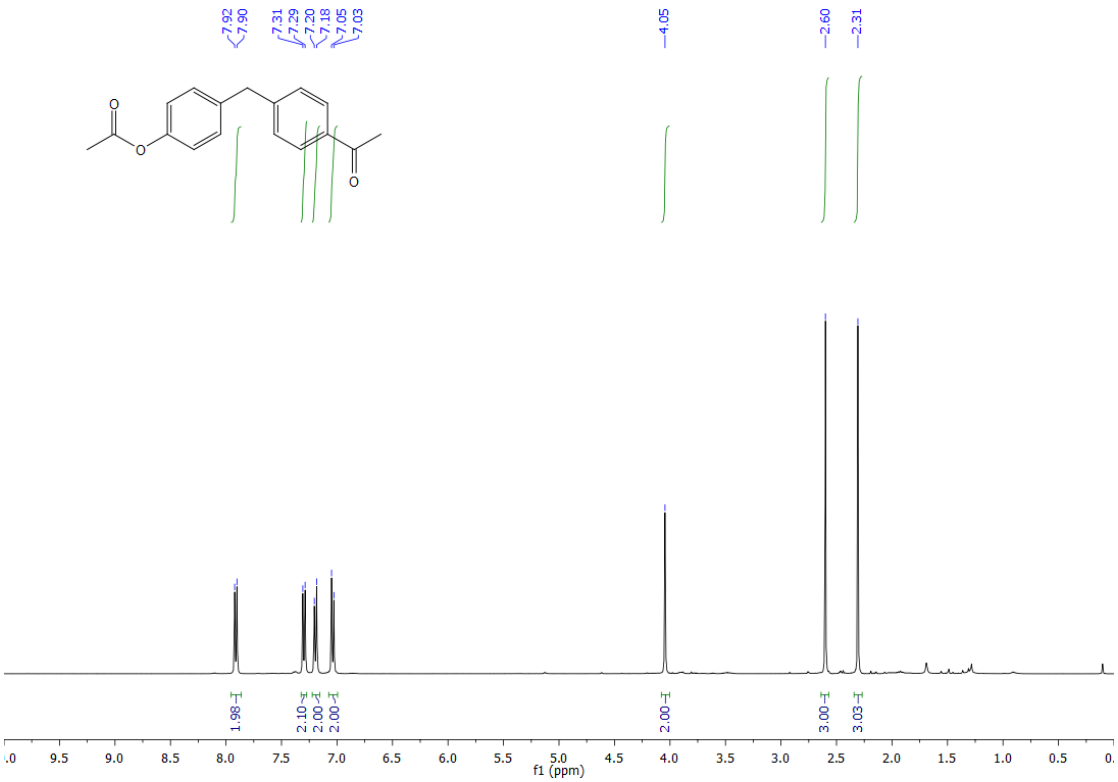
^{19}F NMR (376 MHz, $CDCl_3$) of **3ad**



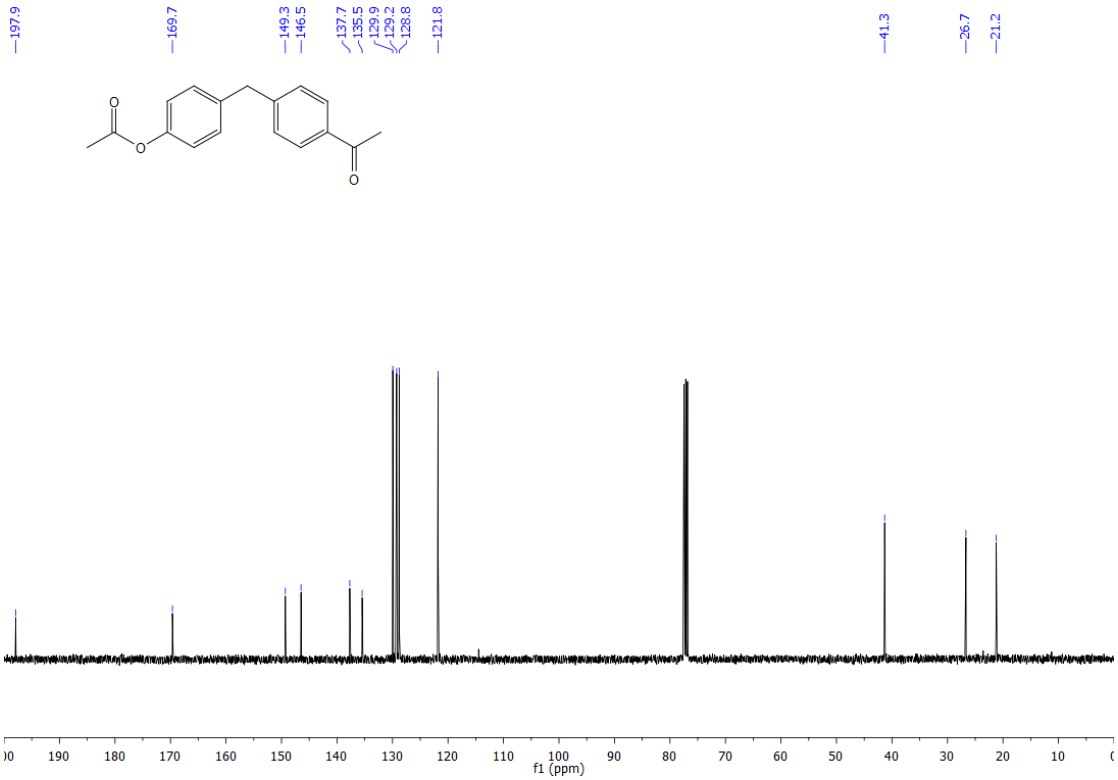
^{1}H NMR (400 MHz, $CDCl_3$) of 3**ae**



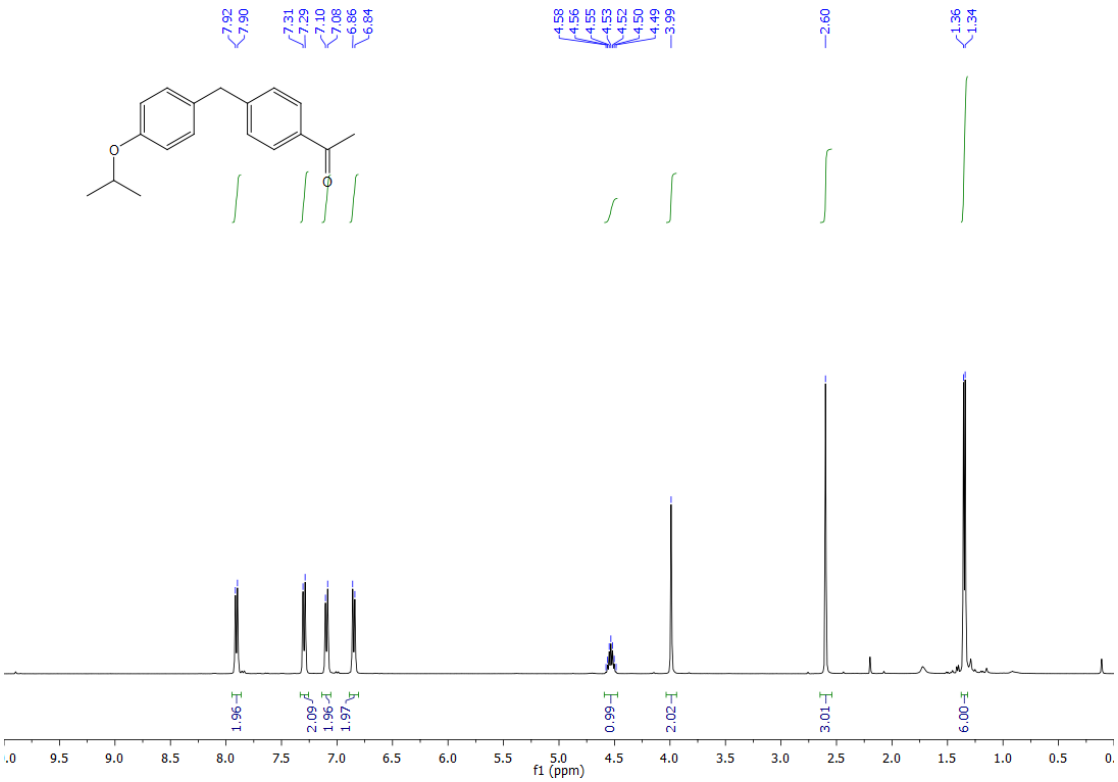
^{13}C NMR (101 MHz, $CDCl_3$) of **3ae**



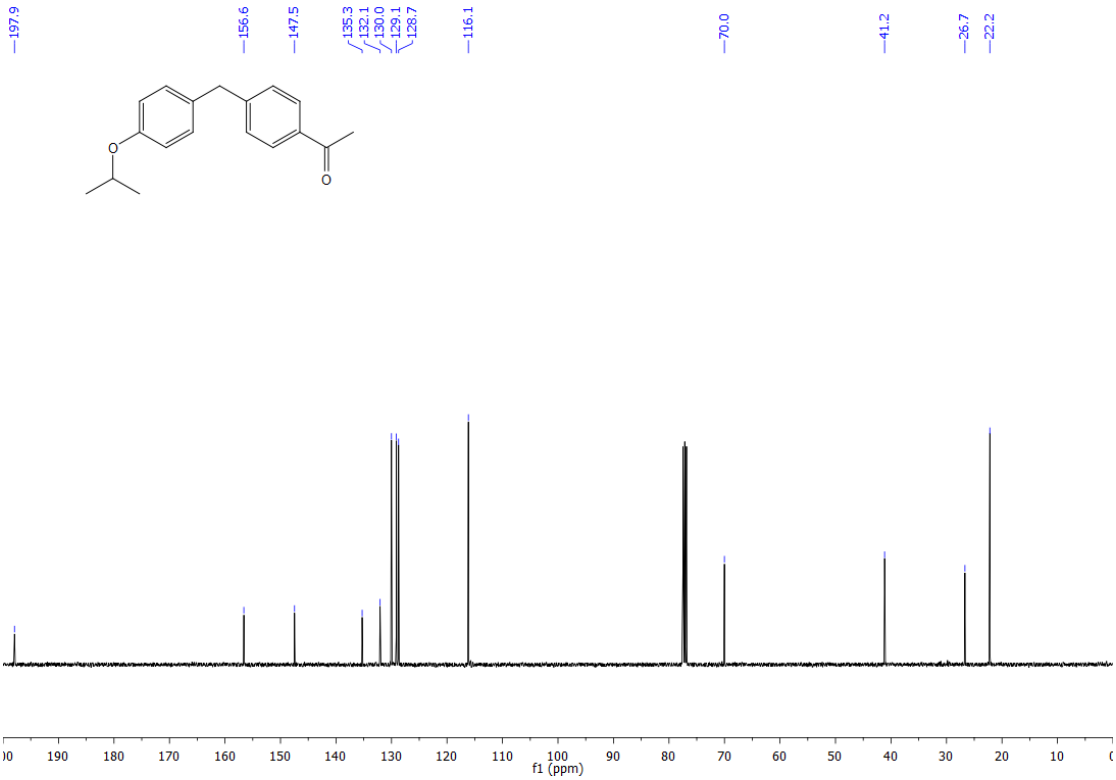
^{1}H NMR (400 MHz, $CDCl_3$) of 3**af**



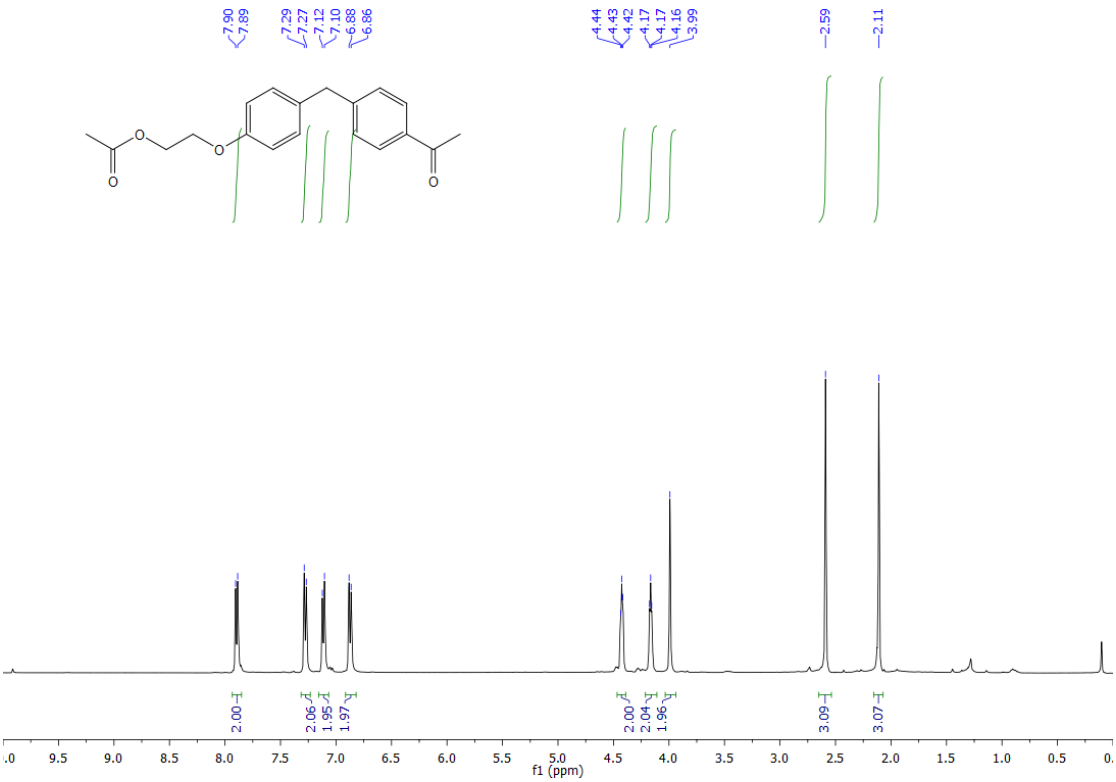
^{13}C NMR (101 MHz, $CDCl_3$) of **3af**



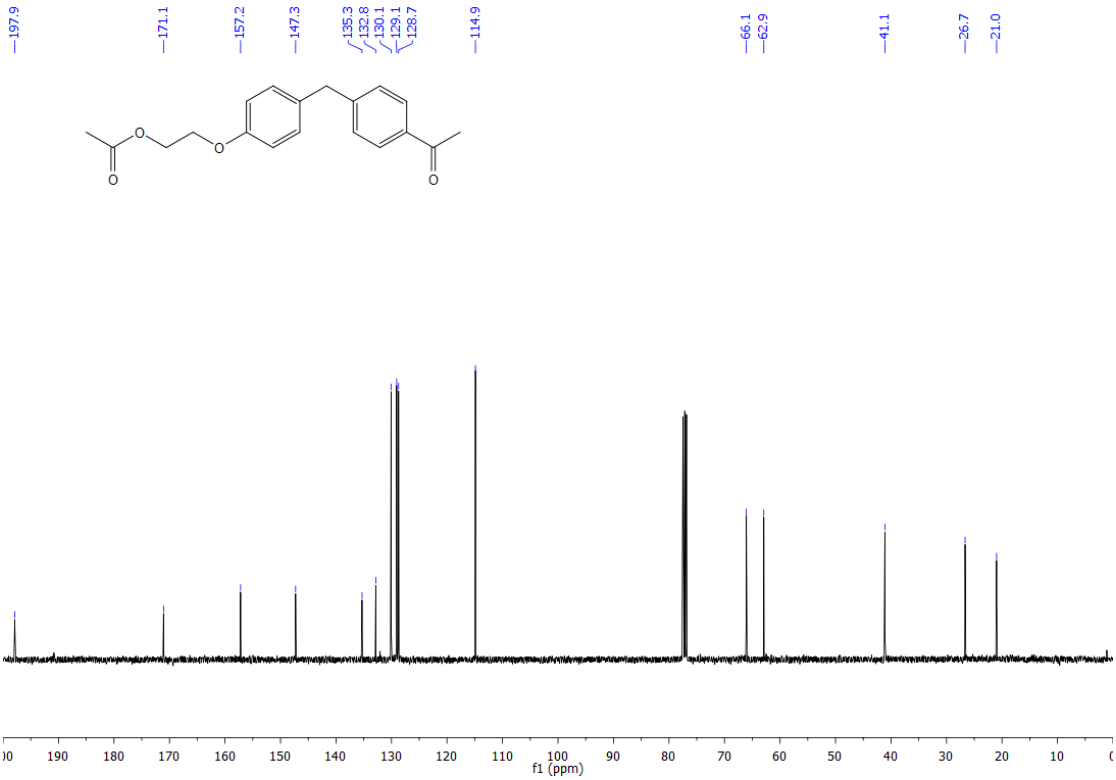
^{1}H NMR (400 MHz, $CDCl_3$) of 3**ag**



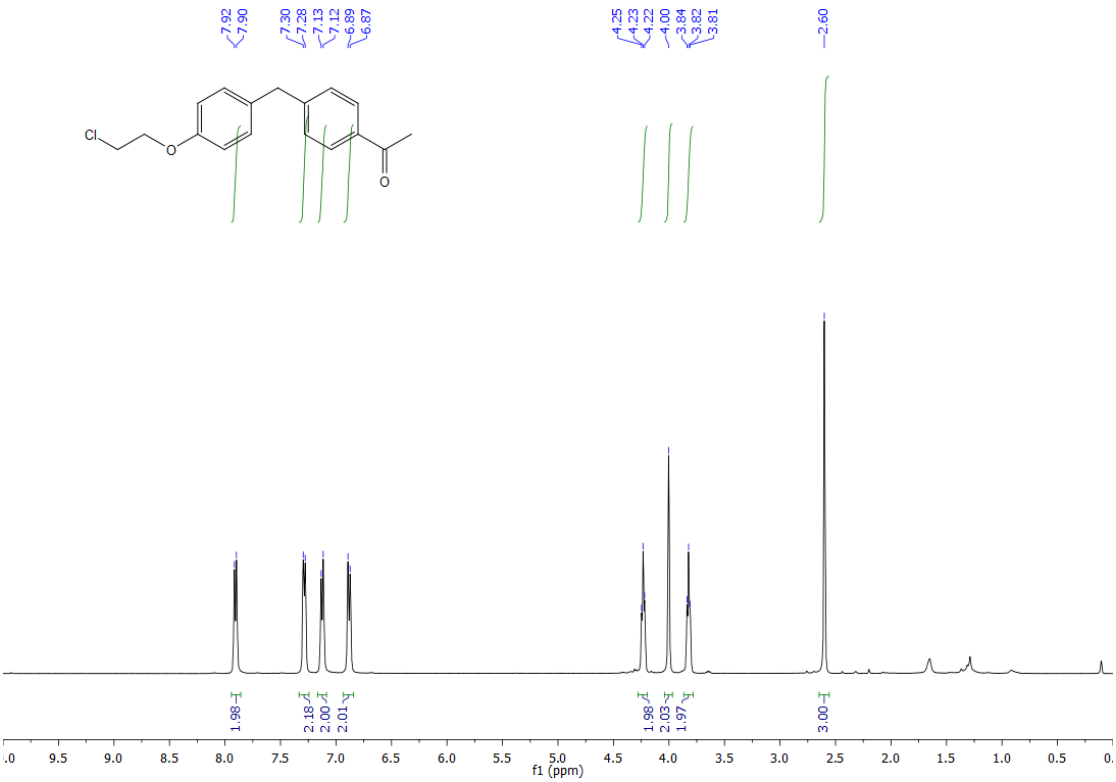
^{13}C NMR (101 MHz, $CDCl_3$) of **3ag**



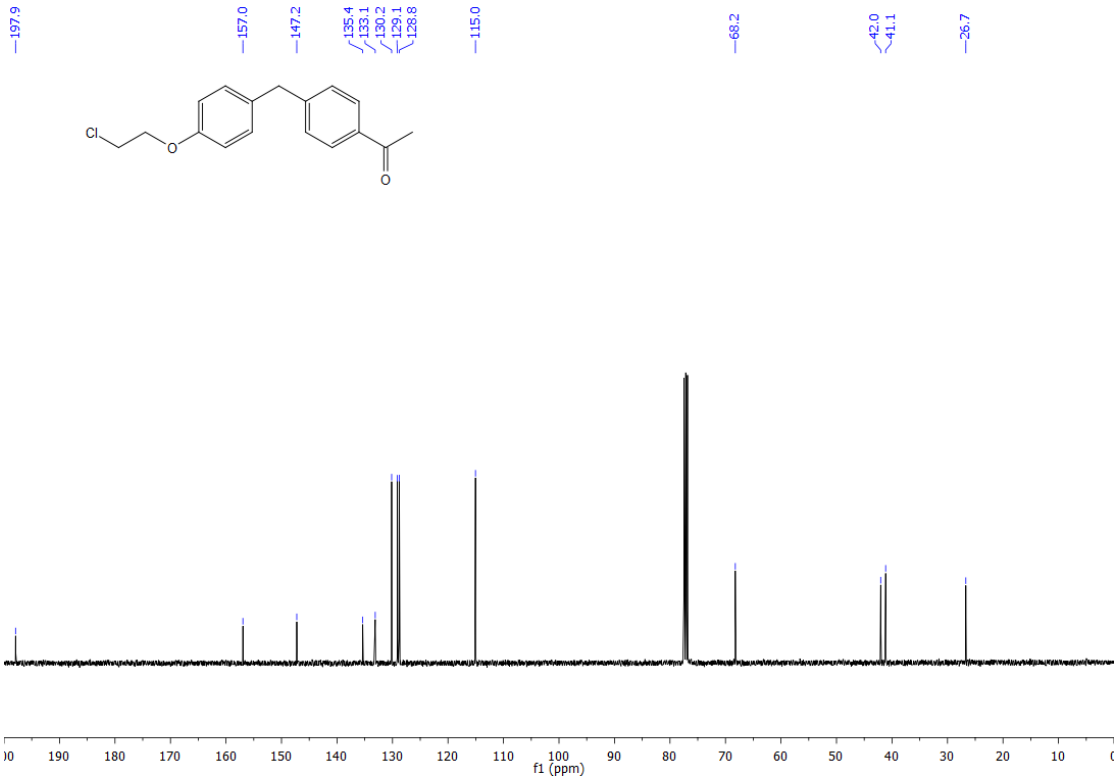
^{1}H NMR (400 MHz, $CDCl_3$) of 3**ah**



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



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



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