Supporting Information

Electronically Tuneable Orthometalated Ru^{II}-NHC Complexes as Efficient Catalysts for the C-C and C-N Bond Formations *via* Borrowing Hydrogen Strategy

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General experimental procedures

All manipulations were performed under an argon/dinitrogen atmosphere using either standard Schlenk line or glovebox techniques. All glassware was oven-dried at 130 °C overnight prior to use. The solvents used were dried, distilled, and degassed by standard methods and stored over 4 Å molecular sieves. NMR measurements were carried out on Bruker 400 and 500 MHz FT-NMR spectrometers. ESI-MS was recorded using an Agilent 6545A Q-TOF Mass spectrometer. The chemical shifts in the ^{1}H NMR spectra were referenced to the residual proton signals of the deuterated solvents ($CDCl_3$, ^{1}H 7.26 ppm and $^{13}C\{^{1}H\}$ 77.16 ppm; CD_3CN, ^{1}H 1.96 ppm and $^{13}C\{^{1}H\}$ 1.79 and 118.26 ppm) and reported relative to tetramethylsilane. The coupling constants are expressed in hertz. $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$, the ligands (**1a-c**) and their ruthenium complexes (**2a-c**) were synthesized using reported procedures.[1] Primary and secondary alcohols were synthesized according to the literature procedures.[2,3] All the other chemicals were purchased from commercial sources and used as received without further purification.

General procedure for the β-alkylation reaction: The required amount of catalyst stock solution, synthesized in CH_3CN (0.01 mol%), was added to an oven dried Schlenk tube and the volatiles were removed in high vacuum. To this, secondary alcohol (1 mmol), primary alcohol (1.1 mmol), and KOH (0.2 mmol, 20 mol%) followed by toluene (1 mL) were added. The reaction tube was then kept in an oil bath (bath temperature 120 °C) and heated for the specified time. After the completion of reaction, the reaction mixture was cooled to room temperature and the pure products were isolated *via* column chromatography using hexane/ethyl acetate as eluent.

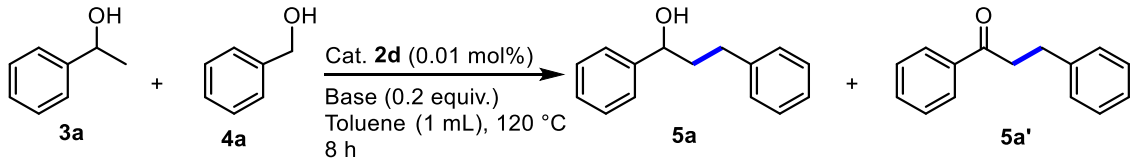
General procedure for one-pot sequential synthesis of α,α-disubstituted ketones: The required amount of catalyst stock solution, synthesized in CH_3CN (0.01 mol%), was added to an oven dried Schlenk tube and the volatiles were removed in high vacuum. To this, secondary alcohol (1 mmol), primary alcohol (1.1 mmol), and KOH (0.2 mmol, 20 mol%) followed by toluene (1 mL) were added. The reaction tube was then kept in an oil bath (bath temperature 120 °C) and heated for the specified time. Then 1 mol% catalyst, 1 equiv. of KO^{t}Bu and 1 equiv. of second primary alcohol were added to the reaction mixture and further heated at 150 °C for 24 h. After that, the reaction mixture was cooled to room temperature and the pure products were isolated *via* column chromatography using hexane/ethyl acetate as eluent.

General Procedure for the N-methylation of amines: An oven dried pressure tube, equipped with a magnetic stirring bar, was charged with KOH (0.5 mmol), catalyst (1 mol%), amine (0.5 mmol), and methanol (1 mL). The reaction mixture was then kept in a pre-heated oil bath (bath temperature 150 °C). After the specific reaction time, the pressure tube was cooled to room temperature. The residue obtained after removal of all the volatiles was purified *via* column chromatography using ethyl acetate and hexane as eluents to get the desired N-methylated products.

Procedure for the calculation of TON for β-alkylation reaction: The catalyst stock solution was synthesized by dissolving **2d** in CH_3CN. An oven dried Schlenk tube was charged with a required amount of **2d** (0.001 mol%) stock solution and all the volatiles were removed in vacuum. To this, secondary alcohol (10 mmol), primary alcohol (11 mmol), and KOH (2 mmol) followed by toluene (10 mL) were added. The reaction tube was then kept in an oil bath (bath temperature 120 °C) and heated for 36 h. After that the reaction mixture was cooled to room temperature and subjected to GC-MS analysis. The average data based on the GC-MS analysis shows the 68% formation of **4a** which provides TON of 68000.

Optimization studies

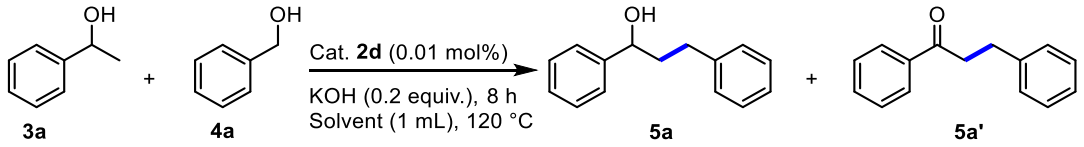
Table S1. Base screening[a]



Entry	Base	Conversion (%) (**5a**:**5a'**)
1	KO^{t}Bu	94 (85:15)
2	**KOH**	**99 (96:4)/92[b]**
3	Cs_2CO_3	Traces
4	K_3PO_4	Traces
5	-	Traces
6[c]	KOH	17%

[a]Reaction conditions: 1-phenylethanol (1.0 mmol), benzyl alcohol (1.1 mmol), cat. (0.01 mol%), base (0.2 mmol), and toluene (1 mL), 8 h. Conversion was determined by GC-MS analysis. [b]Isolated yield. [c]Without catalyst **2d**.

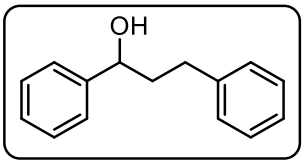
Table S2. Solvent screening[a]



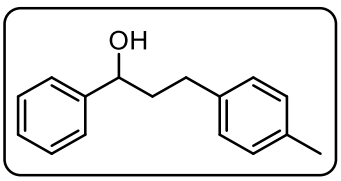
Entry	Solvent	Conversion (%) (**5a**:**5a'**)
1	^{t}AmOH	74
2	Dioxane	58
3	DMF	Traces
4	**Toluene**	**99 (96:4)/92**[b]
5	THF	Traces

[a]Reaction conditions: 1-phenylethanol (1.0 mmol), benzyl alcohol (1.1 mmol), cat. (0.01 mol%), KOH (0.2 mmol), and solvent (1 mL), 8 h. Conversion was determined by GC-MS analysis. [b]Isolated yield.

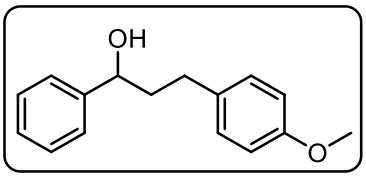
NMR characterization data of the isolated compounds



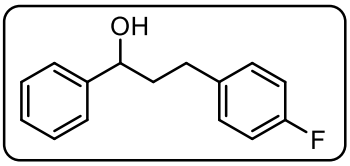
1,3-diphenylpropan-1-ol, **5a**.[4] The compound was synthesized following the general procedure and isolated as pale-yellow liquid (191 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.16 (m, 10H), 4.63 (t, J = 6.2 Hz, 1H), 2.76–2.60 (m, 2H), 2.15-1.95 (m, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 144.7, 141.9, 128.6, 128.5, 128.5, 127.7, 126.0, 125.9, 73.9, 40.5, 32.1 ppm.



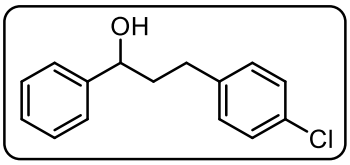
1-phenyl-3-(p-tolyl)propan-1-ol, 5b.[4] The compound was synthesized following the general procedure and isolated as pale-yellow liquid (192 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.25 (m, 5H), 7.07 (s, 4H), 4.63 (t, J = 6.7 Hz, 1H), 2.80–2.49 (m, 2H), 2.30 (s, 3H), 2.16 –1.84 (m, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 144.7, 138.8, 135.4, 129.2, 128.6, 128.4, 127.7, 126.0, 73.9, 40.6, 31.7, 21.1 ppm.



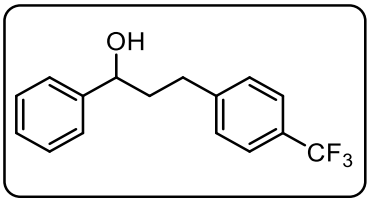
3-(4-methoxyphenyl)-1-phenylpropan-1-ol, **5c**.[4] The compound was synthesized following the general procedure and isolated as pale-yellow liquid (195 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.25 (m, 5H), 7.08 (d, J = 7.8 Hz, 2H), 6.80 (d, J = 7.8 Hz, 2H), 4.62 (t, J = 6.4 Hz, 1H), 3.74 (s, 3H), 2.69-2.54 (m, 2H), 2.12–1.91 (m, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 157.8, 144.7, 133.9, 129.4, 128.6, 127.7, 126.0, 113.9, 73.9, 55.3, 40.8, 31.2 ppm.



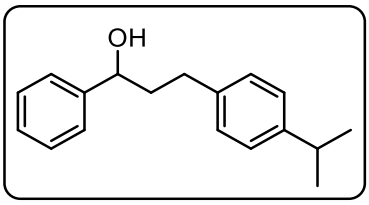
3-(4-fluorophenyl)-1-phenylpropan-1-ol, **5d**.[4] The compound was synthesized following the general procedure and isolated as pale-yellow liquid (173 mg, 75%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.34 (m, 4H), 7.31–7.28 (m, 1H), 7.16–7.12 (m, 2H), 6.96 (t, J = 8.6 Hz, 2H), 4.67 (t, J = 7.7 Hz, 1H), 2.77–2.61 (m, 2H), 2.16–1.95 (m, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.6, 160.2, 144.6, 137.5, 129.9, 129.8, 128.7, 127.9, 126.0, 115.3, 115.1, 73.9, 40.7, 31.4 ppm.



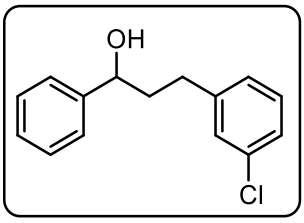
3-(4-chlorophenyl)-1-phenylpropan-1-ol, **5e**.[4] The compound was synthesized following the general procedure and isolated as pale-yellow liquid (215 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.26 (m, 5H), 7.21 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 8.1 Hz, 2H), 4.61 (t, J = 6.4 Hz, 1H), 2.71-2.56 (m, 2H), 2.21 (s, 1H), 2.10–1.92 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.5, 140.3, 131.6, 129.9, 128.6, 128.5, 127.8, 126.0, 73.7, 40.4, 31.4 ppm.



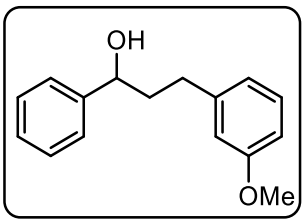
1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-ol, 5f.[4] The compound was synthesized following the general procedure and isolated as pale-yellow liquid (196 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.3 Hz, 2H), 7.27 (m, 4H), 7.20 (m, 3H), 4.59 (t, J =6 Hz, 1H), 2.78 – 2.56 (m, 2H), 2.09 – 1.84 (m, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.1, 144.4, 128.9, 128.7, 128.2, 127.9, 126.0, 125.4 (q, J =3.8 Hz), 127.4 (q, J =268.5 Hz) 73.8, 40.2, 32.0 ppm.



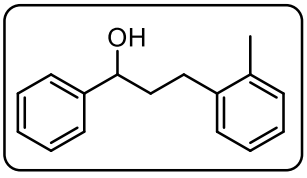
3-(4-isopropylphenyl)-1-phenylpropan-1-ol, **5g**.[4] The compound was synthesized following the general procedure and isolated as yellow liquid (221 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 4.3 Hz, 4H), 7.32 (q, J = 3.9 Hz, 1H), 7.18 (q, J = 7.9 Hz, 4H), 4.71 (t, J = 6.0 Hz, 1H), 2.93 (p, J = 6.8 Hz, 1H), 2.80–2.63 (m, 2H), 2.20–2.01 (m, 3H), 1.29 (d, J = 6.9 Hz, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.5, 144.7, 139.2, 128.6, 128.4, 127.7, 126.5, 126.1, 74.0, 40.6, 33.8, 31.7, 24.2 ppm.



3-(3-chlorophenyl)-1-phenylpropan-1-ol, **5h**.[4] The compound was synthesized following the general procedure and isolated as yellow liquid (202 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 4H), 7.32–7.30 (m, 1H), 7.21 (s, 3H), 7.10 (s, 1H), 4.70 (s, 1H), 2.79–2.64 (m, 2H), 2.15–2.09 (m, 1H), 2.07-1.99 (m, 1H), 1.87 (s, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.5, 144.0, 134.3, 129.7, 128.7, 127.9, 126.8, 126.2, 126.0, 73.8, 40.3, 31.9 ppm.

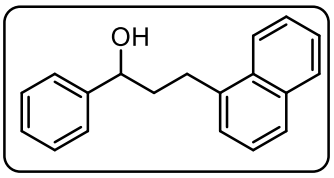


3-(3-methoxyphenyl)-1-phenylpropan-1-ol, **5i**.[4] The compound was synthesized following the general procedure and isolated as yellow liquid (189 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (m, 3H), 7.21–7.17 (m, 1H), 7.10 (t, J = 7.7 Hz, 1H), 6.69 (d, J = 7.6 Hz, 1H), 6.64 (d, J = 7.0 Hz, 2H), 4.58 (t, J = 6.8 Hz, 1H), 3.68 (s, 3H), 2.67–2.51 (m, 2H), 2.07–1.87 (m, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.8, 144.7, 143.6, 129.5, 128.6, 127.7, 126.0, 121.0, 114.3, 111.3, 73.9, 55.2, 40.4, 32.2 ppm.

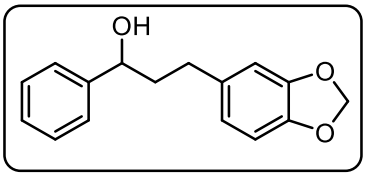


1-phenyl-3-(o-tolyl)propan-1-ol, **5j**.[4] The compound was synthesized following the general procedure and isolated as yellow liquid (163 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 3.9 Hz, 4H), 7.29–7.24 (m, 1H), 7.12–7.08 (m, 4H), 4.72 (s, 1H), 2.79–2.72 (m, 1H), 2.65 –2.58 (m, 1H), 2.26 (s, 3H), 2.12–2.05 (m, 1H), 2.02–1.94 (m, 1H), 1.91 (m, 1H) ppm. ^{13}C{^{1}H}

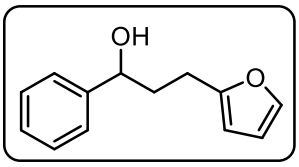
NMR (101 MHz, $CDCl_3$) δ 144.7, 140.1, 136.1, 130.3, 128.9, 128.7, 127.8, 126.1, 126.1, 126.0, 74.4, 39.4, 29.6, 19.4 ppm.



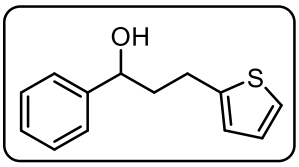
3-(naphthalen-1-yl)-1-phenylpropan-1-ol, **5k**.[4] The compound was synthesized following the general procedure and isolated as yellow liquid (236 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 6.1 Hz, 1H), 7.80 (d, J = 6.1 Hz, 1H), 7.66 (d, J = 7.2 Hz, 1H), 7.44–7.41 (m, 2H), 7.37–7.21 (m, 7H), 4.73–4.63 (t, J = 6.2 Hz, 1H), 3.21–3.14 (m, 1H), 3.07–3.00 (m, 1H), 2.33 –2.060 (m, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.6, 138.1, 134.0, 131.9, 128.8, 128.6, 127.7, 126.7, 126.0, 125.9, 125.6, 125.5, 123.9, 74.2, 39.9, 29.2 ppm.



3-(benzo[d][1,3]dioxol-5-yl)-1-phenylpropan-1-ol, **5l**.[4] The compound was synthesized following the general procedure and isolated as white solid (223 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.17 (m, 5H), 6.64 (d, J = 7.9 Hz, 1H), 6.60 (s, 1H), 6.55 (d, J = 7.9 Hz, 1H), 5.82 (s, 2H), 4.58 (t, J = 7.6 Hz, 1H), 2.62–2.47 (m, 2H), 2.04–1.84 (m, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.7, 145.7, 144.7, 135.7, 128.6, 127.8, 126.0, 121.3, 109.0, 108.3, 100.9, 73.8, 40.8, 31.9 ppm.

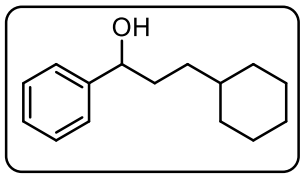


3-(furan-2-yl)-1-phenylpropan-1-ol, **5m**.[4] The compound was synthesized following the general procedure and isolated as brown oily liquid (129 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.17 (m, 6H), 6.19 (s, 1H), 5.91 (s, 1H), 4.59 (t, J = 6.6 Hz, 1H), 2.67–2.58 (m, 2H), 2.05–1.93 (m, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.7, 144.4, 141.1, 128.6, 127.8, 126.0, 110.2, 105.1, 73.8, 37.2, 24.5 ppm.

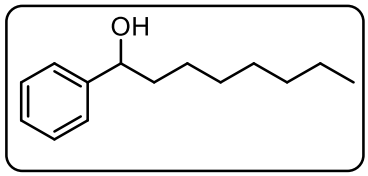


1-phenyl-3-(thiophen-2-yl)propan-1-ol, **5n**.[4] The compound was synthesized following the general procedure and isolated as brown oily liquid (131 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.36 (m, 4H), 7.31–7.29 (m, 1H), 7.14 (d, J = 5.0 Hz, 1H), 6.94 (m, 1H), 6.82 (s, 1H), 4.73 (t, J = 5.9 Hz, 1H), 3.01–2.88 (m, 2H), 2.24–2.04 (m, 3H) ppm. ^{13}C{^{1}H} NMR

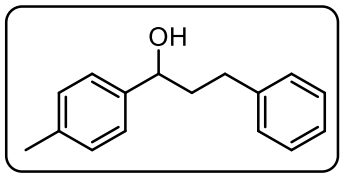
(101 MHz, $CDCl_3$) δ 144.7, 144.4, 128.7, 127.8, 126.9, 126.0, 124.4, 123.2, 73.6, 40.8, 26.3 ppm.



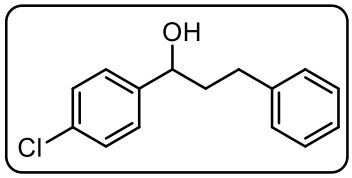
3-cyclohexyl-1-phenylpropan-1-ol, **5o**.[4] The compound was synthesized following the general procedure and isolated as colorless oily liquid (100 mg, 46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.13 (m, 5H), 4.44 (t, J = 6.4 Hz, 1H), 2.40 (s, 1H), 1.69–1.56 (m, 7H), 1.22–0.96 (m, 7H), 0.79–0.74 (m, 1H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.0, 128.4, 127.4, 126.0, 74.9, 37.7, 36.5, 33.5, 33.4, 33.3, 26.7 ppm.



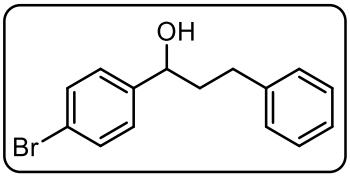
1-phenyloctan-1-ol, **5p**.[4] The compound was synthesized following the general procedure and isolated as colorless oily liquid (122 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29– 7.26 (m, 4H), 7.22–7.18 (m, 1H), 4.55 (t, J = 6.6 Hz, 1H), 2.15 (s, 1H), 1.77–1.52 (m, 2H), 1.37–1.30 (m, 1H), 1.26–1.21 (m, 8H), 0.83 (t, J = 6.7 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.1, 128.5, 127.5, 126.0, 74.7, 39.2, 31.9, 29.6, 29.3, 25.9, 22.7, 14.2 ppm.



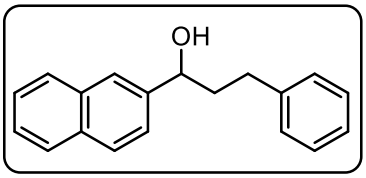
3-phenyl-1-(p-tolyl)propan-1-ol, **5q**.[4] The compound was synthesized following the general procedure and isolated as colorless oily liquid (199 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.12 (m, 9H), 4.60 (t, J = 6.5 Hz, 1H), 2.74–2.58 (m, 2H), 2.33 (s, 3H), 2.17–1.92 (m, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.0, 141.7, 137.4, 129.3, 128.6, 128.5, 126.0, 125.9, 73.8, 40.5, 32.2, 21.2 ppm.



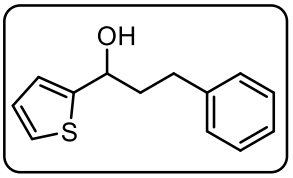
1-(4-chlorophenyl)-3-phenylpropan-1-ol, **5r**.[4] The compound was synthesized following the general procedure and isolated as colorless oily liquid (207 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.26 (m, 6H), 7.18 (t, J = 7.8 Hz, 3H), 4.65 (t, J = 7.1 Hz, 1H), 2.75–2.61 (m, 2H), 2.13–1.95 (m, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.2, 141.6, 133.4, 128.8, 128.6, 128.5, 127.4, 126.1, 73.3, 40.6, 32.0 ppm.



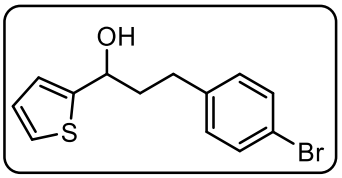
1-(4-bromophenyl)-3-phenylpropan-1-ol, **5s**.[4] The compound was synthesized following the general procedure and isolated as colorless oily liquid (253 mg, 87%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.3 Hz, 2H), 7.27 (t, J = 7.4 Hz, 2H), 7.17 (t, J = 8.8 Hz, 5H), 4.60 (t, J = 6.4 Hz, 1H), 2.73–2.59 (m, 2H), 2.13–1.92 (m, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.6, 141.6, 131.7, 128.6, 128.5, 127.8, 126.1, 121.4, 73.2, 40.5, 32.0 ppm.



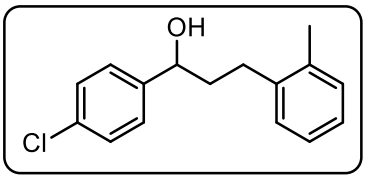
1-(naphthalen-2-yl)-3-phenylpropan-1-ol, **5t**.[4] The compound was synthesized following the general procedure and isolated as colorless oily liquid (233 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (m, 3H), 7.72 (s, 1H), 7.45–7.42 (m, 3H), 7.25 (t, J = 7.4 Hz, 2H), 7.16 (d, J = 7.4 Hz, 3H), 4.78 (t, J = 6.5 Hz, 1H), 2.77–2.61 (m, 2H), 2.21–2.04 (m, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.0, 141.9, 133.4, 133.1, 128.6, 128.0, 127.8, 126.3, 126.0, 124.8, 124.2, 74.0, 40.4, 32.1 ppm.



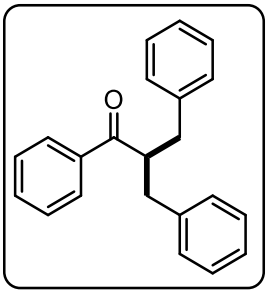
3-phenyl-1-(thiophen-2-yl)propan-1-ol, **5u**.[4] The compound was synthesized following the general procedure and isolated as yellow oily liquid (118 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.22 (m, 3H), 7.16–7.16 (m, 3H), 6.96–6.94 (m, 2H), 4.89 (t, J = 6.4 Hz, 1H), 2.79–2.65 (m, 2H), 2.24–2.07 (m, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.6, 141.6, 128.6, 128.5, 126.8, 126.1, 124.8, 124.0, 69.6, 40.8, 32.1 ppm.



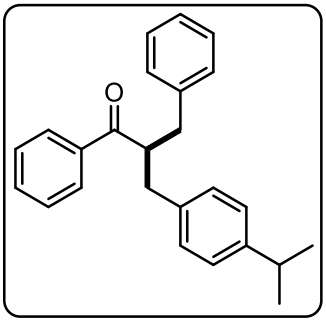
3-(4-bromophenyl)-1-(thiophen-2-yl)propan-1-ol, **5v**. The compound was synthesized following the general procedure and isolated as yellow oily liquid (155 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 7.9 Hz, 2H), 7.24 (s, 1H), 7.05 (d, J = 7.9 Hz, 2H), 6.95 (s, 2H), 4.87 (t, J = 5.6 Hz, 1H), 2.74–2.60 (m, 2H), 2.21–2.06 (m, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.4, 140.5, 131.6, 130.4, 126.8, 124.9, 124.1, 119.8, 69.4, 40.6, 31.5 ppm.



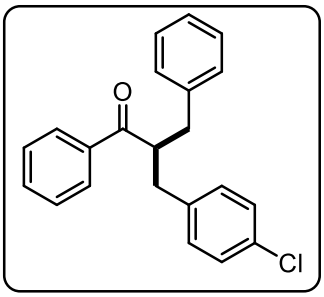
1-(4-chlorophenyl)-3-(o-tolyl)propan-1-ol, **5w**. The compound was synthesized following the general procedure and isolated as yellow oily liquid (156 mg, 60%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (q, J = 9.0 Hz, 4H), 7.10 (s, 4H), 4.67 (t, J = 6.4 Hz, 1H), 2.75–2.55 (m, 2H), 2.24 (s, 3H), 2.04–1.89 (m, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.2, 139.8, 136.0, 133.4, 130.4, 128.8, 128.8, 127.4, 126.2, 126.1, 73.6, 39.4, 29.4, 19.3 ppm.



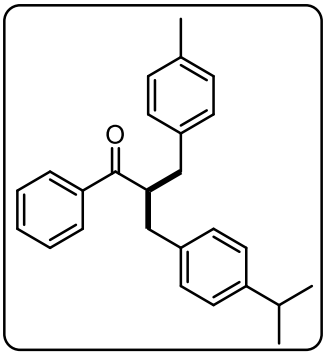
2-benzyl-1,3-diphenylpropan-1-one, **6a**. The compound was synthesized following the general procedure and isolated as yellow oily liquid (113 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 7.8 Hz, 2H), 7.30 (t, J = 7.4 Hz, 1H), 7.19 (t, J = 7.6 Hz, 2H), 7.12–7.06 (m, 4H), 7.01 (m, 6H), 3.92 (p, J = 7.1 Hz, 1H), 3.03 (dd, J = 13.7, 6.2 Hz, 2H), 2.70 (dd, J = 13.7, 6.2 Hz, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 203.4, 139.6, 137.4, 132.8, 129.1, 128.5, 128.2, 126.3, 50.6, 38.1 ppm. HRMS (ESI): $C_{22}H_{20}O$ calcd. for $[M+H]^+$: 301.1592 found: 301.1581.



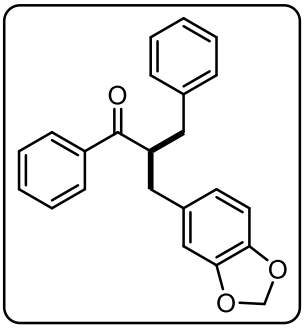
2-benzyl-3-(4-isopropylphenyl)-1-phenylpropan-1-one, **6b**. The compound was synthesized following the general procedure and isolated as yellow oily liquid (118 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.8 Hz, 2H), 7.36 (t, J = 7.2 Hz, 1H), 7.23 (t, J = 7.2 Hz, 2H), 7.12 (t, J = 7.1 Hz, 3H), 7.05 (d, J = 7.3 Hz, 3H), 6.98 (s, 3H), 3.93 (m, 1H), 3.03 (m, 2H), 2.71 (m, 3H), 1.10 (d, J = 6.9 Hz, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 203.6, 146.9, 139.8, 139.6, 137.6, 136.8, 132.8, 129.1, 129.0, 128.5, 128.3, 126.5, 126.3, 50.6, 38.2, 38.0, 33.8, 24.1 ppm. HRMS (ESI): $C_{23}H_{20}O_3$ calcd. for $[M+H]^+$: 344.1491 found: 344.1479.



2-benzyl-3-(4-chlorophenyl)-1-phenylpropan-1-one, **6c**. The compound was synthesized following the general procedure and isolated as yellow oily liquid (100 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 7.5 Hz, 2H), 7.40 (p, J = 7.4 Hz, 1H), 7.27 (p, J = 6.7 Hz, 2H), 7.10 (dt, J = 23.4, 7.3 Hz, 7H), 6.98 (d, J = 7.9 Hz, 2H), 3.90 (m, 1H), 3.03 (m, 2H), 2.70 (m, 2H) ppm. HRMS (ESI): $C_{22}H_{19}ClO$ calcd. for $[M+H]^+$: 335.1203 found: 335.1194.

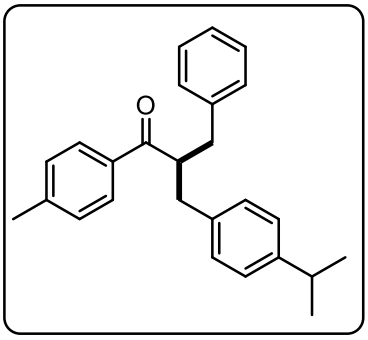


2-(4-isopropylbenzyl)-1-phenyl-3-(p-tolyl)propan-1-one, **6d**. The compound was synthesized following the general procedure and isolated as yellow oily liquid (116 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (q, J = 8.3, 7.8 Hz, 2H), 7.39–7.33 (m, 1H), 7.25 (q, J = 7.0 Hz, 2H), 6.95 (d, J = 13.9 Hz, 8H), 3.90 (p, J = 7.8 Hz, 1H), 3.01 (m, 2H), 2.76–2.61 (m, 3H), 2.17 (s, 3H), 1.10 (d, J = 6.9 Hz, 6H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 203.5, 146.9, 137.6, 136.9, 136.6, 135.8, 132.8, 129.2, 129.0, 128.5, 128.3, 127.8, 126.5, 50.6, 37.9, 37.8, 33.8, 24.1, 21.1 ppm. HRMS (ESI): $C_{26}H_{28}O$ calcd. for $[M+H]^+$: 357.2140 found: 357.2210.

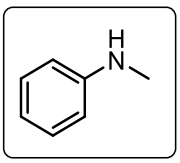


3-(benzo[d][1,3]dioxol-5-yl)-2-benzyl-1-phenylpropan-1-one, **6e**. The compound was synthesized following the general procedure and isolated as yellow oily liquid (124 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.8 Hz, 2H), 7.39 (t, J = 7.3 Hz, 1H), 7.27 (t, J = 7.5 Hz, 2H), 7.13 (d, J = 7.2 Hz, 2H), 7.06 (d, J = 7.3 Hz, 3H), 6.60–6.47 (m, 3H), 5.78 (s, 2H),

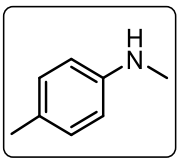
3.88 (p, J = 7.0 Hz, 1H), 3.00 (m, 2H), 2.68 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 203.4, 147.7, 146.1, 139.6, 137.6, 133.4, 132.9, 129.1, 128.6, 128.3, 126.4, 122.2, 109.5, 108.3, 100.9, 50.9, 38.4, 38.0 ppm. HRMS (ESI): $C_{23}H_{20}O_3$ calcd. for $[M+H]^+$: 345.1491 found: 345.1479.



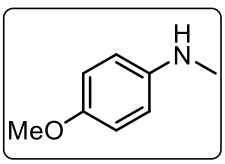
2-benzyl-3-(4-isopropylphenyl)-1-(p-tolyl)propan-1-one, **6f**. The compound was synthesized following the general procedure and isolated as yellow oily liquid (121 mg, 68%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 6.6 Hz, 2H), 7.09 (d, J = 7.1 Hz, 2H), 7.02 (t, J = 7.7 Hz, 5H), 6.96 (s, 4H), 3.89 (s, 1H), 3.09–2.93 (m, 2H), 2.70 (m, 3H), 2.22 (s, 3H), 1.08 (d, J = 7.0 Hz, 6H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 203.0, 146.8, 146.7, 143.6, 139.9, 139.7, 137.1, 136.9, 129.2, 129.1, 129.0, 128.4, 126.5, 126.2, 50.3, 38.1, 38.0, 33.8, 24.1, 21.6 ppm. HRMS (ESI): $C_{26}H_{28}O$ calcd. for $[M+H]^+$: 357.2218 found: 357.2212.



N-methylaniline, **8a**.[5] The compound was synthesized following the general procedure and isolated as yellow liquid (45 mg, 84%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, J = 7.8 Hz, 2H), 6.74 (t, J = 7.3 Hz, 1H), 6.64 (d, J = 8.0 Hz, 2H), 3.70 (s, 1H), 2.85 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 149.5, 129.3, 117.4, 112.5, 30.8 ppm.

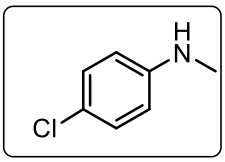


4-methyl-N-methylaniline, **8b**.[5] The compound was synthesized following the general procedure and isolated as yellow liquid (53 mg, 88%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, J = 7.9 Hz, 2H), 6.59 (d, J = 8.0 Hz, 2H), 3.58 (s, 1H), 2.85 (s, 3H), 2.30 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 147.3, 129.8, 126.5, 112.7, 31.2, 20.5 ppm.

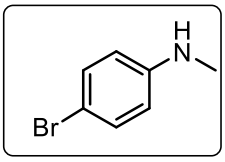


4-methoxy-N-methylaniline, **8c**.[5] The compound was synthesized following the general procedure and isolated as yellow liquid (63 mg, 92%). ^1H NMR (400 MHz, $CDCl_3$) δ 6.82 (d,

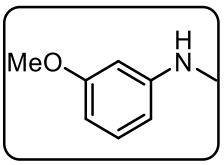
J = 8.6 Hz, 2H), 6.60 (d, J = 8.6 Hz, 2H), 3.77 (s, 3H), 3.16 (bs, 1H), 2.81 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 152.1, 143.8, 114.9, 113.7, 55.9, 31.6 ppm.



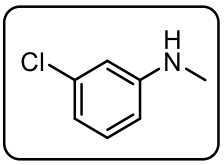
4-chloro-N-methylaniline, **8d**.[5] The compound was synthesized following the general procedure and isolated as yellow liquid (59 mg, 83%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, J = 8.6 Hz, 2H), 6.53 (d, J = 8.5 Hz, 2H), 3.72 (s, 1H), 2.81 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 148.0, 129.1, 121.9, 113.5, 30.9 ppm.



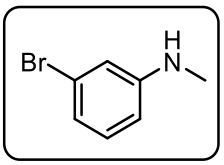
4-bromo-N-methylaniline, **8e**.[5] The compound was synthesized following the general procedure and isolated as yellow liquid (81 mg, 87%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 8.6 Hz, 2H), 6.45 (d, J = 8.7 Hz, 2H), 2.78 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 148.4, 131.9, 114.0, 108.8, 30.8 ppm.



3-methoxy-N-methylaniline, **8f**.[5] The compound was synthesized following the general procedure and isolated as yellow liquid (62 mg, 91%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, J = 8.1 Hz, 1H), 6.33 (d, J = 8.1 Hz, 1H), 6.27 (d, J = 9.2 Hz, 1H), 6.21 (s, 1H), 3.82 (s, 3H), 2.84 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.9, 150.8, 129.9, 105.7, 102.3, 98.3, 55.1, 30.7 ppm.

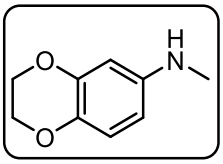


3-chloro-N-methylaniline, **8g**.[5] The compound was synthesized following the general procedure and isolated as yellow liquid (60 mg, 85%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.09 (t, J = 9.0 Hz, 1H), 6.68 (d, J = 7.8 Hz, 1H), 6.58 (d, J = 1.7 Hz, 1H), 6.48 (d, J = 8.2 Hz, 1H), 3.79 (s, 1H), 2.82 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 150.5, 135.1, 130.2, 117.1, 112.0, 110.9, 30.6 ppm.

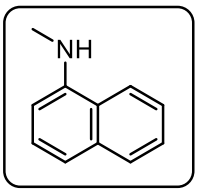


3-bromo-N-methylaniline, **8h**.[5] The compound was synthesized following the general procedure and isolated as yellow liquid (76 mg, 82%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.02 (t,

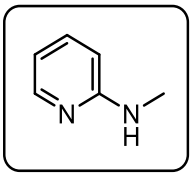
J = 8.0 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.74 (s, 1H), 6.51 (d, *J* = 8.1 Hz, 1H), 3.78 (s, 1H), 2.81 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) *δ* 150.7, 130.5, 123.4, 120.0, 114.9, 111.3, 30.6 ppm.



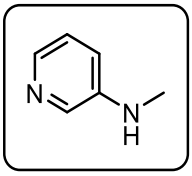
N-methyl-2,3-dihydrobenzo[b][1,4]dioxin-6-amine, **8i**.[5] The compound was synthesized following the general procedure and isolated as yellow liquid (74 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 6.72 (d, *J* = 8.5 Hz, 1H), 6.20–6.13 (m, 2H), 4.23 (dd, *J* = 5.6, 2.8 Hz, 2H), 4.18 (dd, *J* = 5.5, 2.9 Hz, 2H), 2.77 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) *δ* 144.6, 144.1, 135.6, 117.6, 106.5, 101.1, 64.8, 64.3, 31.5 ppm.



N-methylnaphthalen-1-amine, **8j**.[5] The compound was synthesized following the general procedure and isolated as yellow liquid (64 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.86 (d, *J* = 7.9 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.47 (dt, *J* = 17.3, 7.9 Hz, 3H), 7.31 (d, *J* = 8.2 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 4.43 (s, 1H), 3.04 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) *δ* 144.6, 134.3, 128.7, 126.8, 125.8, 124.8, 123.5, 119.9, 117.4, 31.1 ppm.



N-methylpyridin-2-amine, **8k**.[5] The compound was synthesized following the general procedure and isolated as yellow liquid (35 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.06 (d, *J* = 5.5 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 6.58–6.50 (m, 1H), 6.35 (d, *J* = 8.4 Hz, 1H), 4.73 (s, 1H), 2.88 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) *δ* 159.7, 148.1, 137.5, 112.7, 106.2, 29.1 ppm.



N-methylpyridin-3-amine, **8l**.[5] The compound was synthesized following the general procedure and isolated as yellow liquid (38 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.00 (s, 1H), 7.93 (s, 1H), 7.11–7.04 (m, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 3.88 (s, 1H), 2.83 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) *δ* 145.3, 138.6, 135.8, 123.8, 118.1, 30.3 ppm.

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2. S. N. R. Donthireddy, P. M. Illam and A. Rit, *Inorg. Chem.* 2020, **59**, 1835−1847.

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5. P. Piehl, R, Amuso, A. Spannenberg, B. Gabriele, H. Neumann and M. Beller, *Catal. Sci. Technol.*, 2021, **11**, 2512−2517.

NMR spectra of the isolated compounds

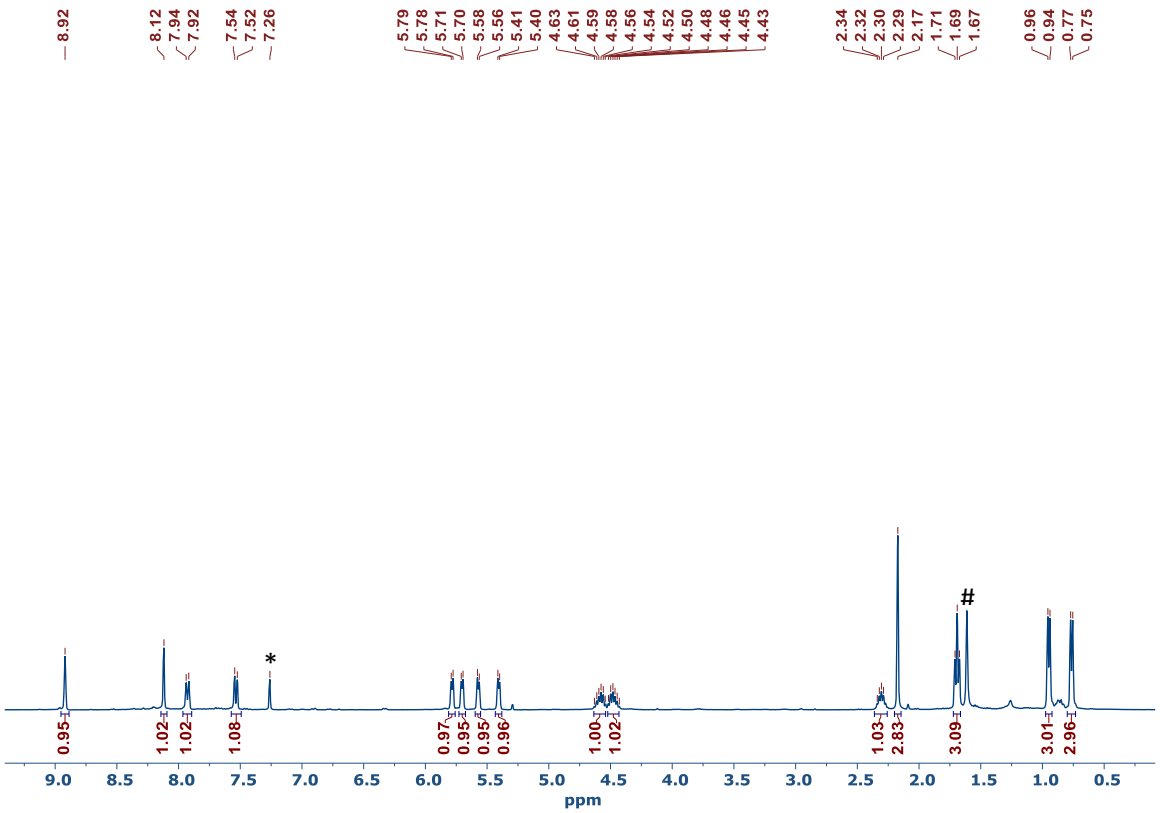


Figure S1. ^{1}H NMR spectrum of complex **2d** in $CDCl_3$. # represents solvent impurity of water in $CDCl_3$.

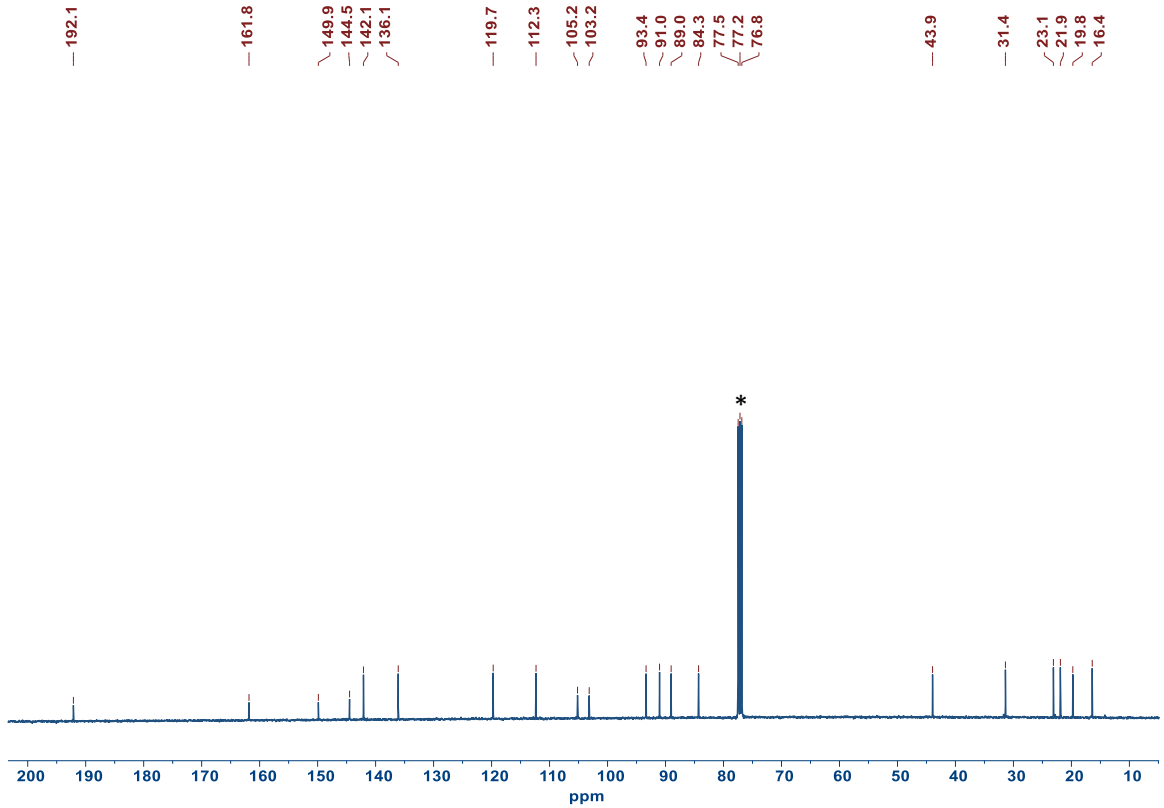


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of complex **2d** in $CDCl_3$.

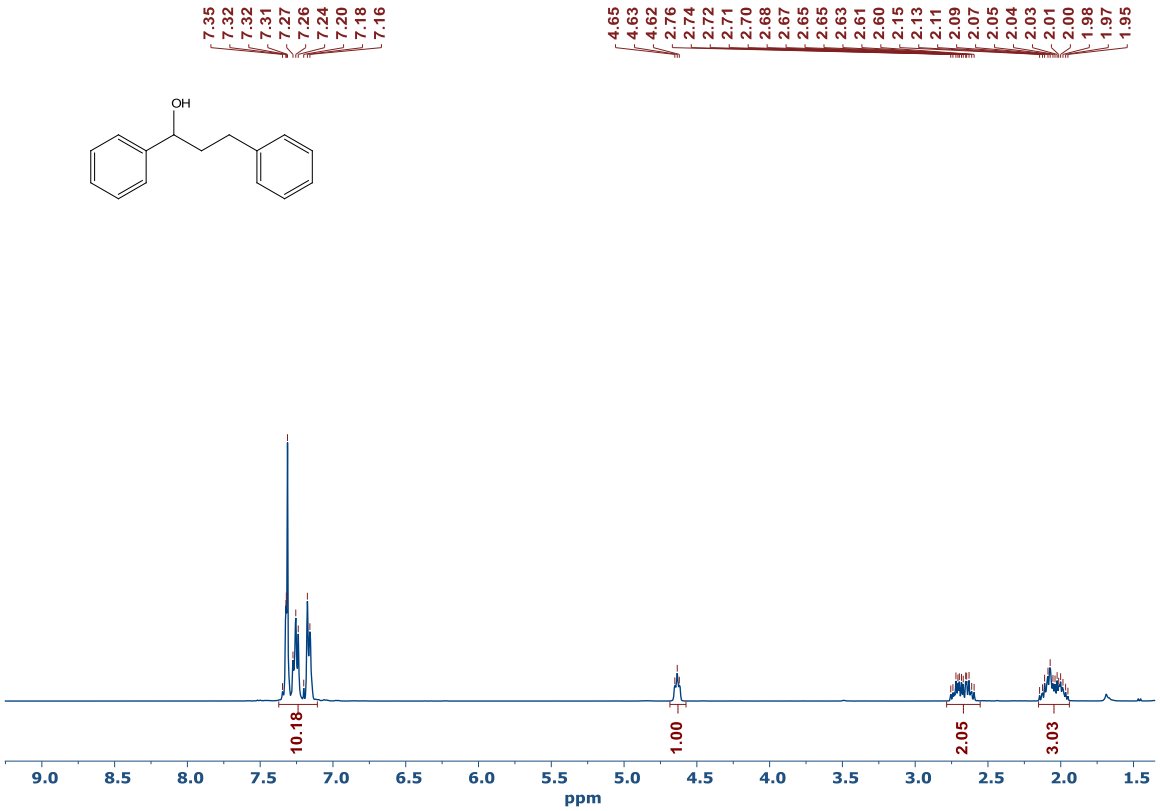


Figure S3. ^{1}H NMR spectrum of compound **5a** in $CDCl_3$.

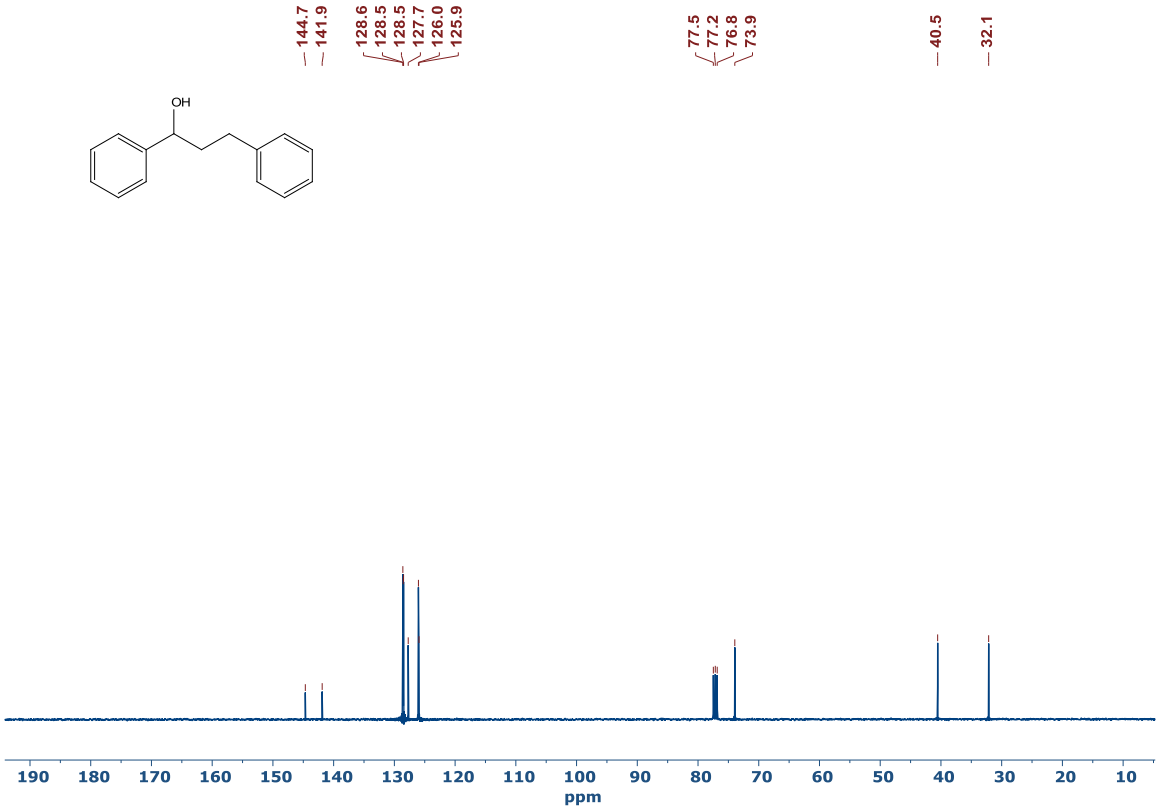


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5a** in $CDCl_3$.

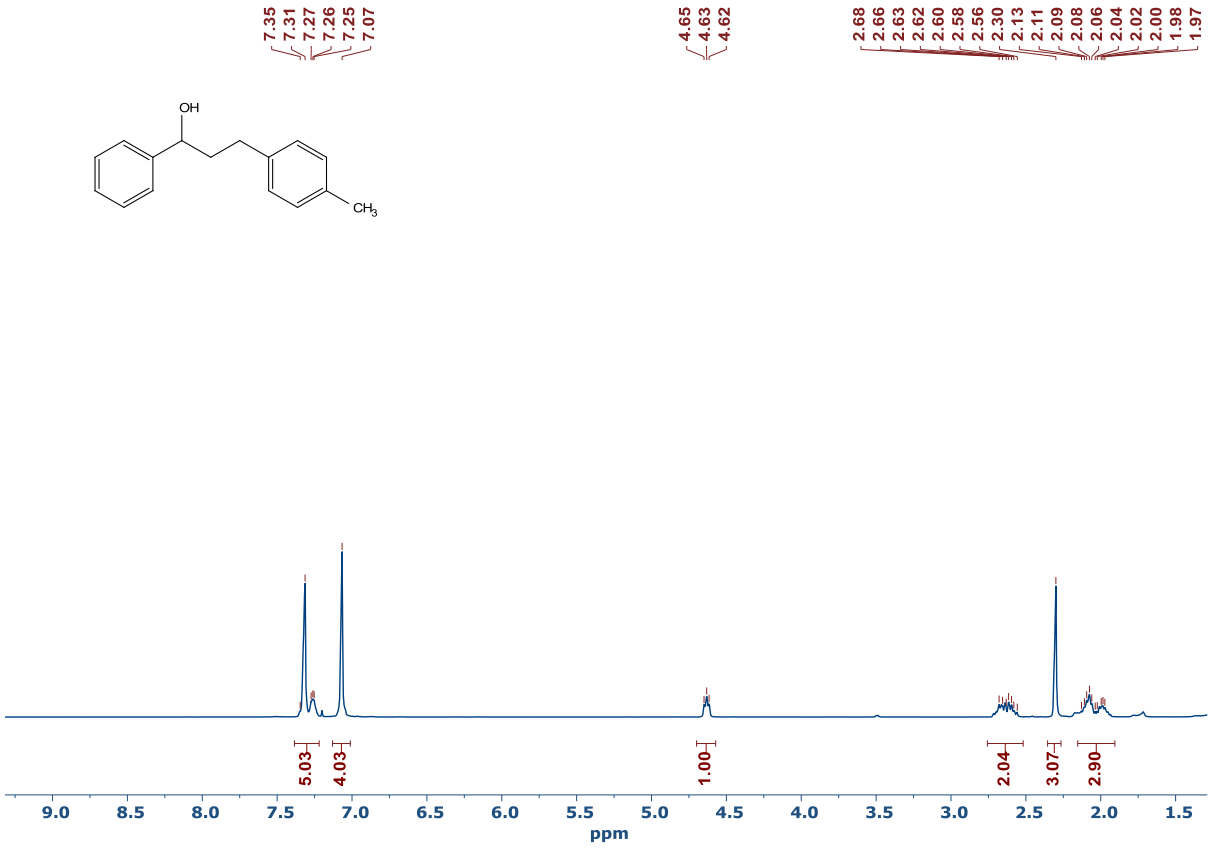


Figure S5. ^{1}H NMR spectrum of compound **5b** in $CDCl_3$.

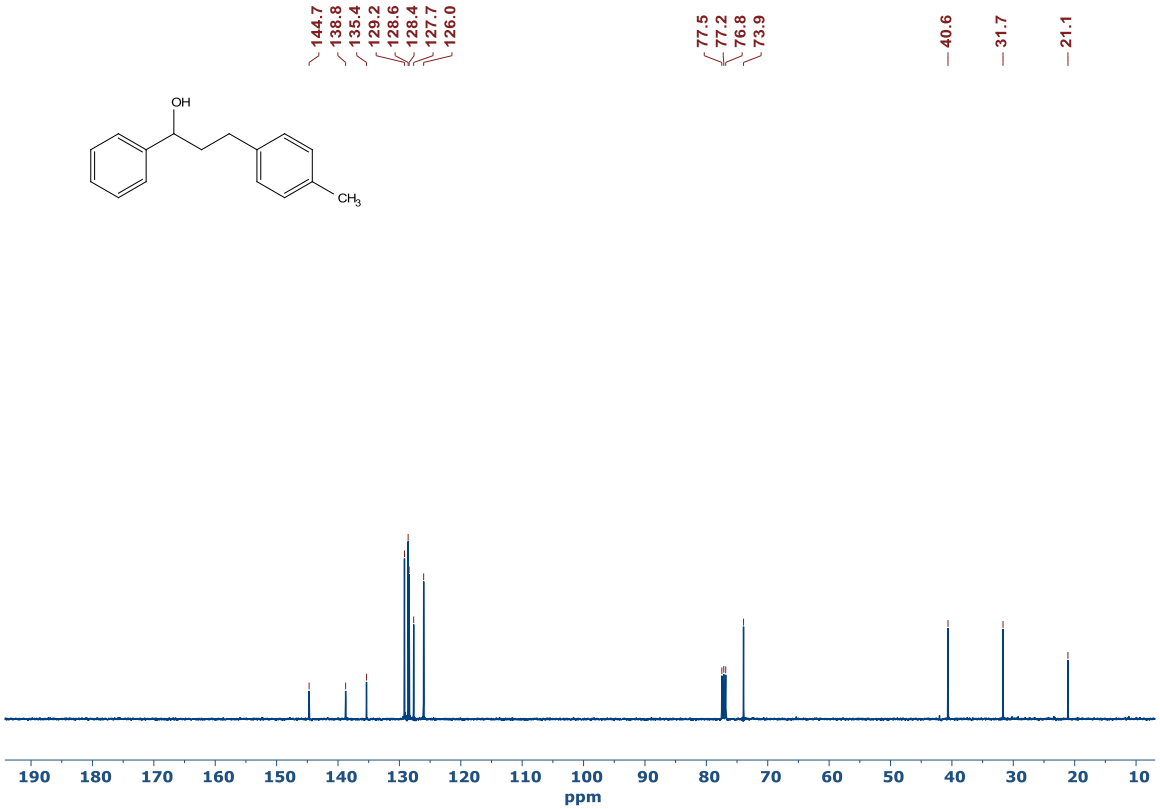


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5b** in $CDCl_3$.

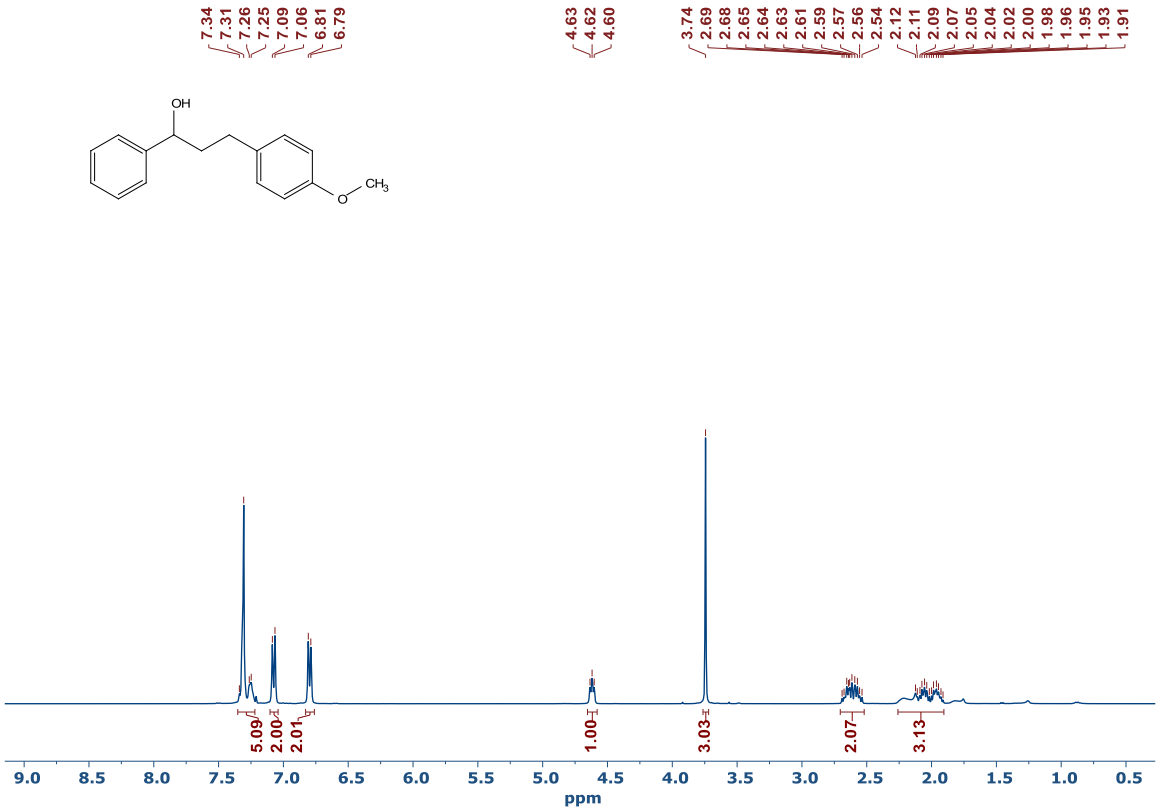


Figure S7. ^{1}H NMR spectrum of compound **5c** in $CDCl_3$.

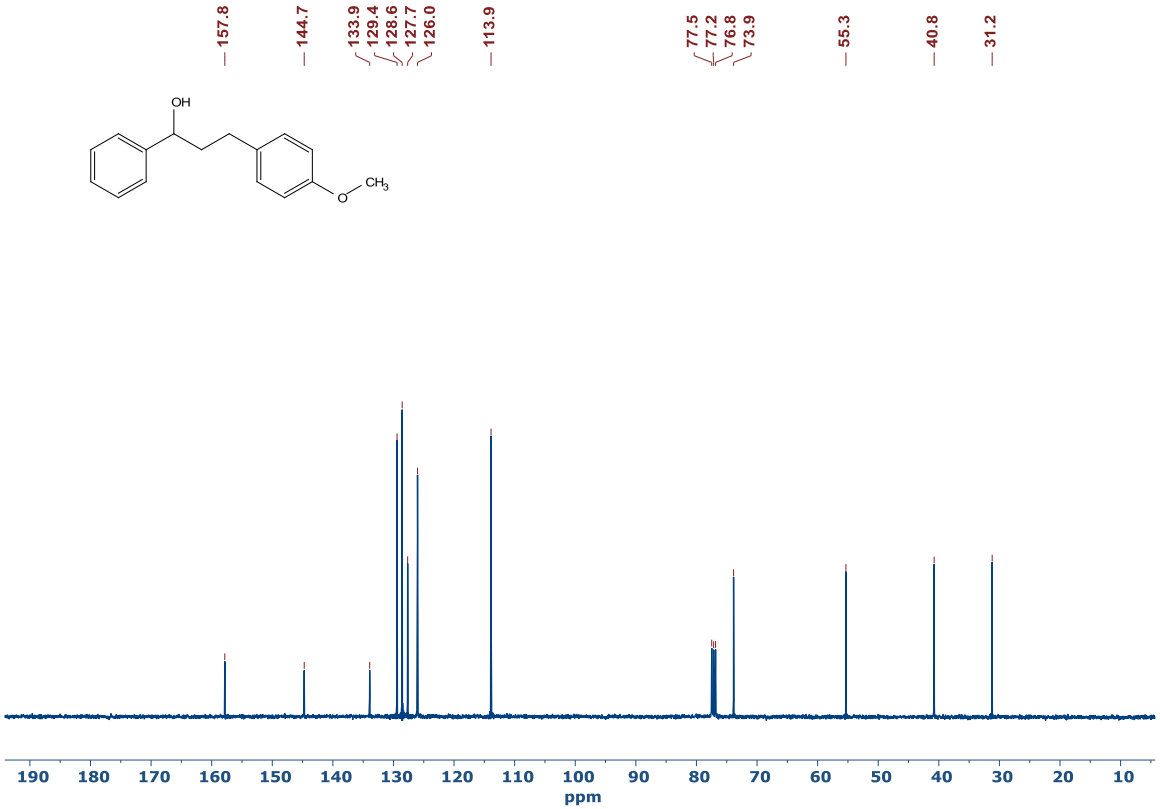


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5c** in $CDCl_3$.

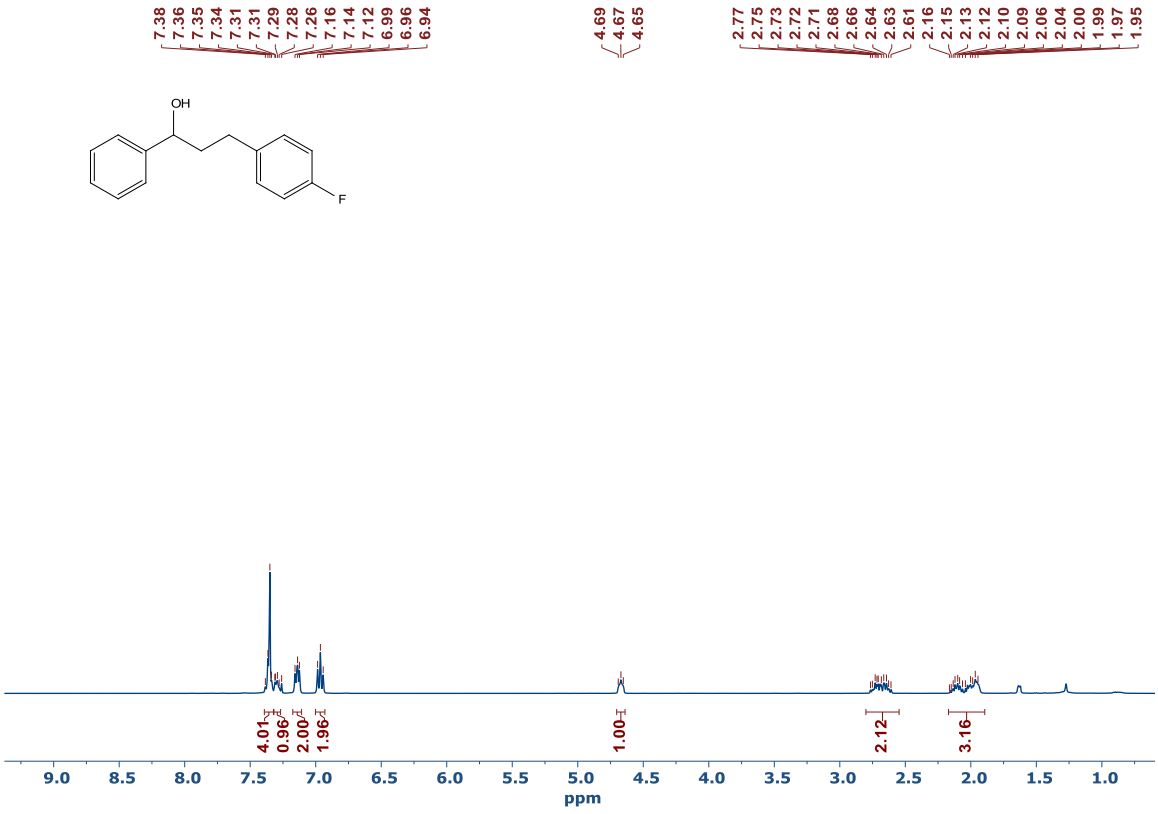


Figure S9. ^{1}H NMR spectrum of compound **5d** in $CDCl_3$.

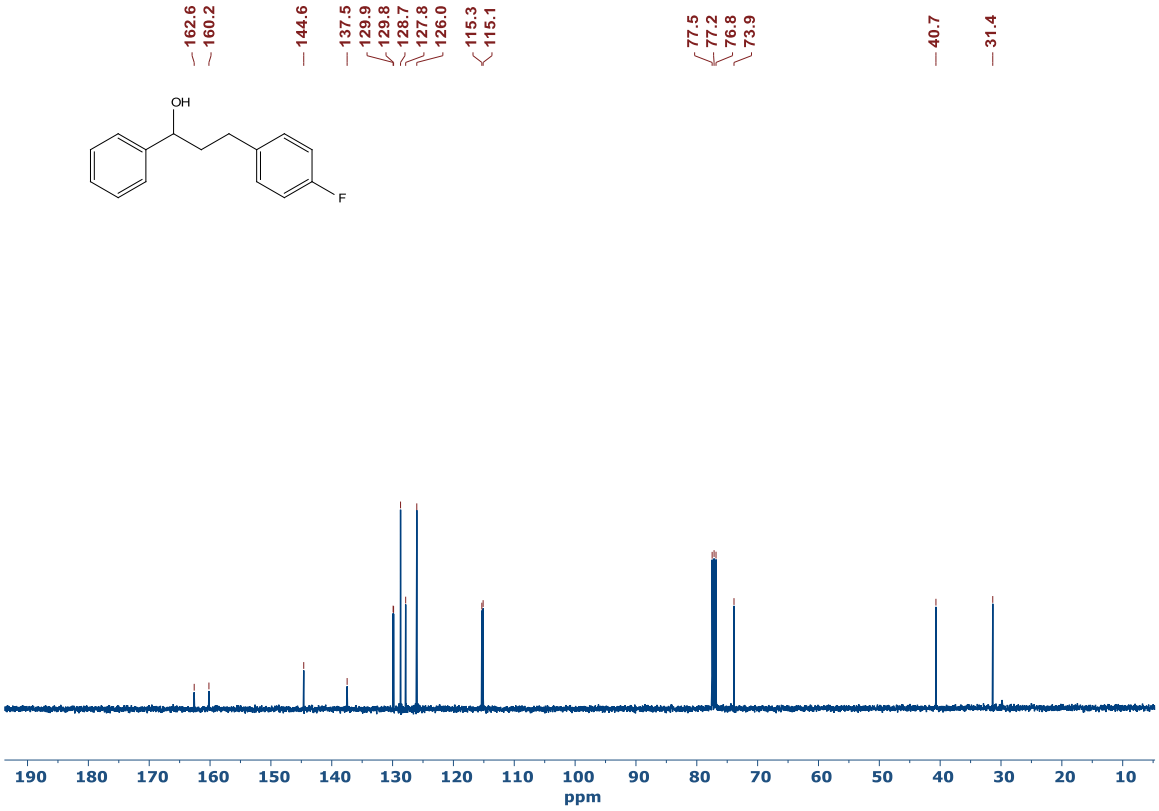


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5d** in $CDCl_3$.

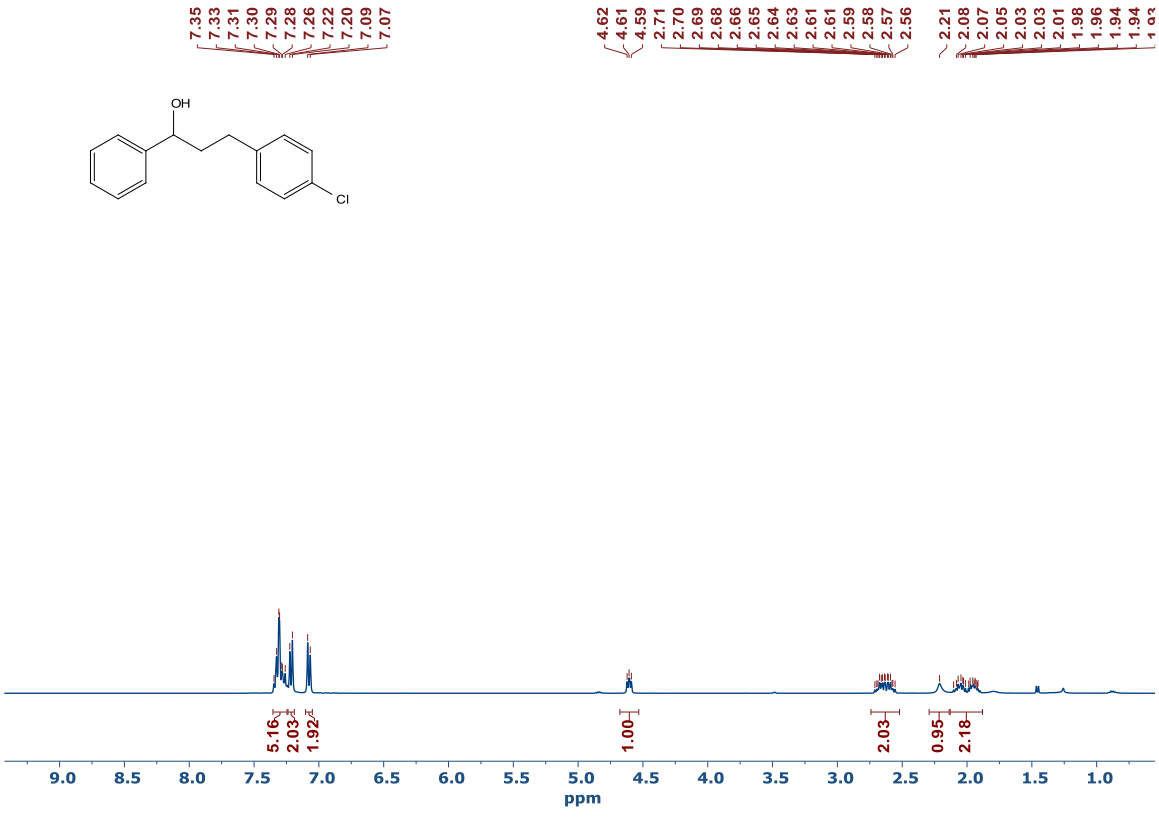


Figure S11. ^{1}H NMR spectrum of compound **5e** in $CDCl_3$.

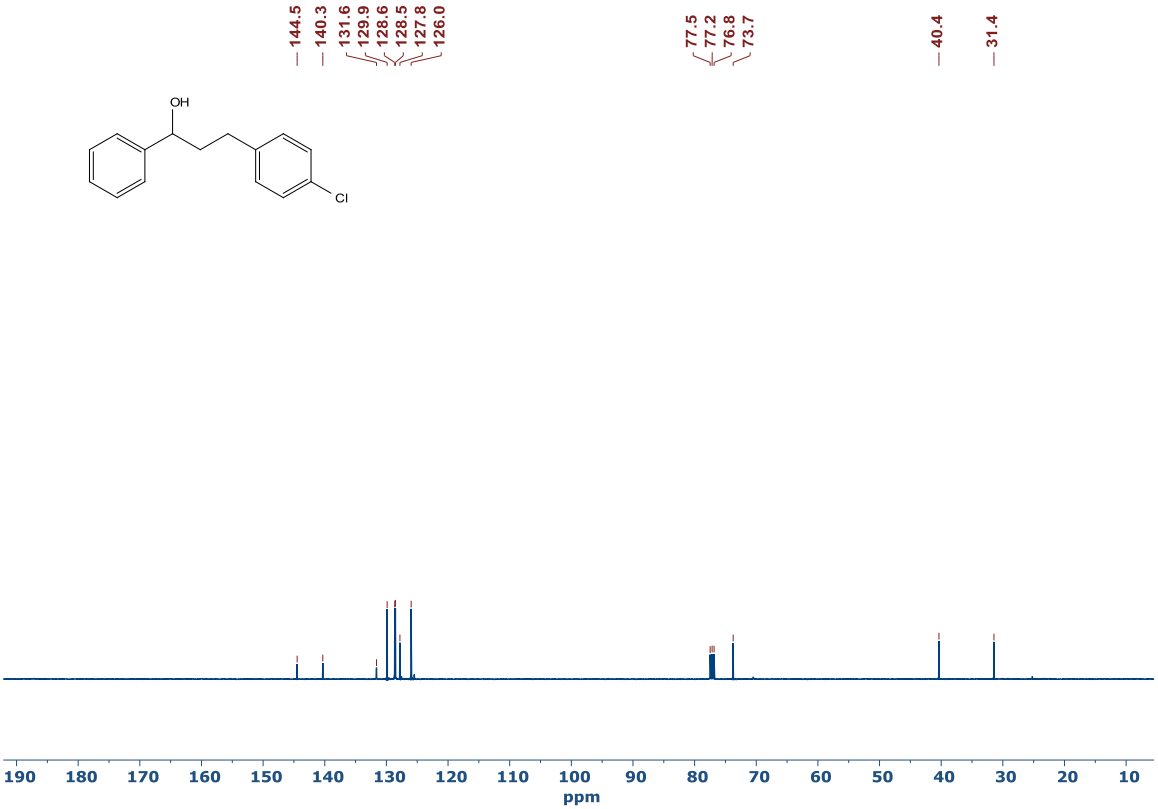


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5e** in $CDCl_3$.

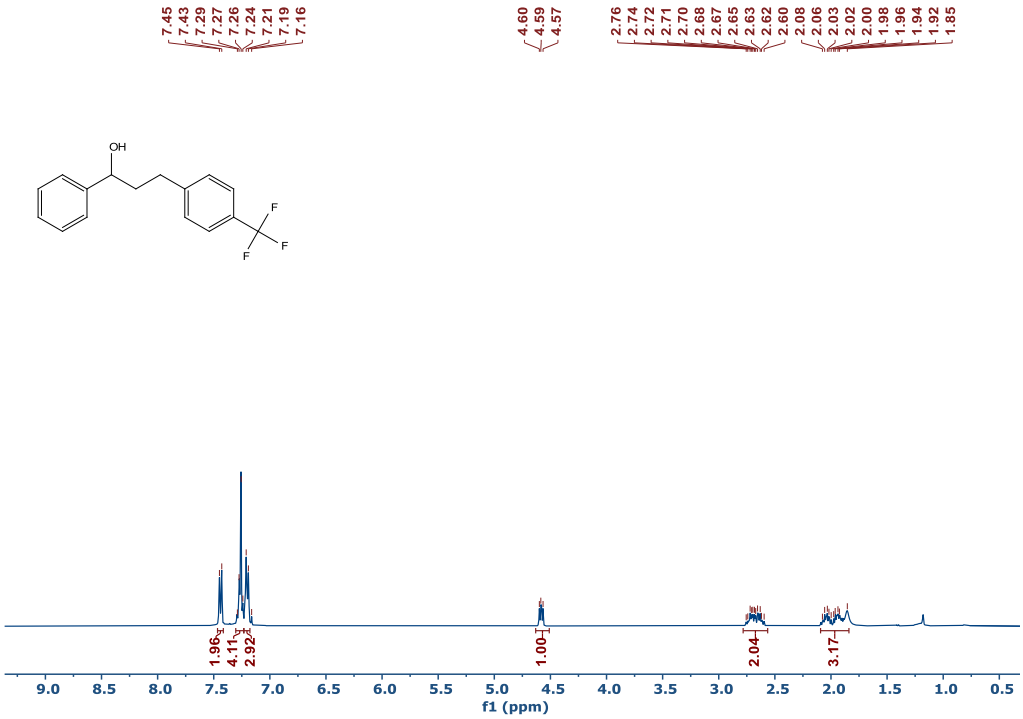


Figure S13. ^{1}H NMR spectrum of compound **5f** in $CDCl_3$.

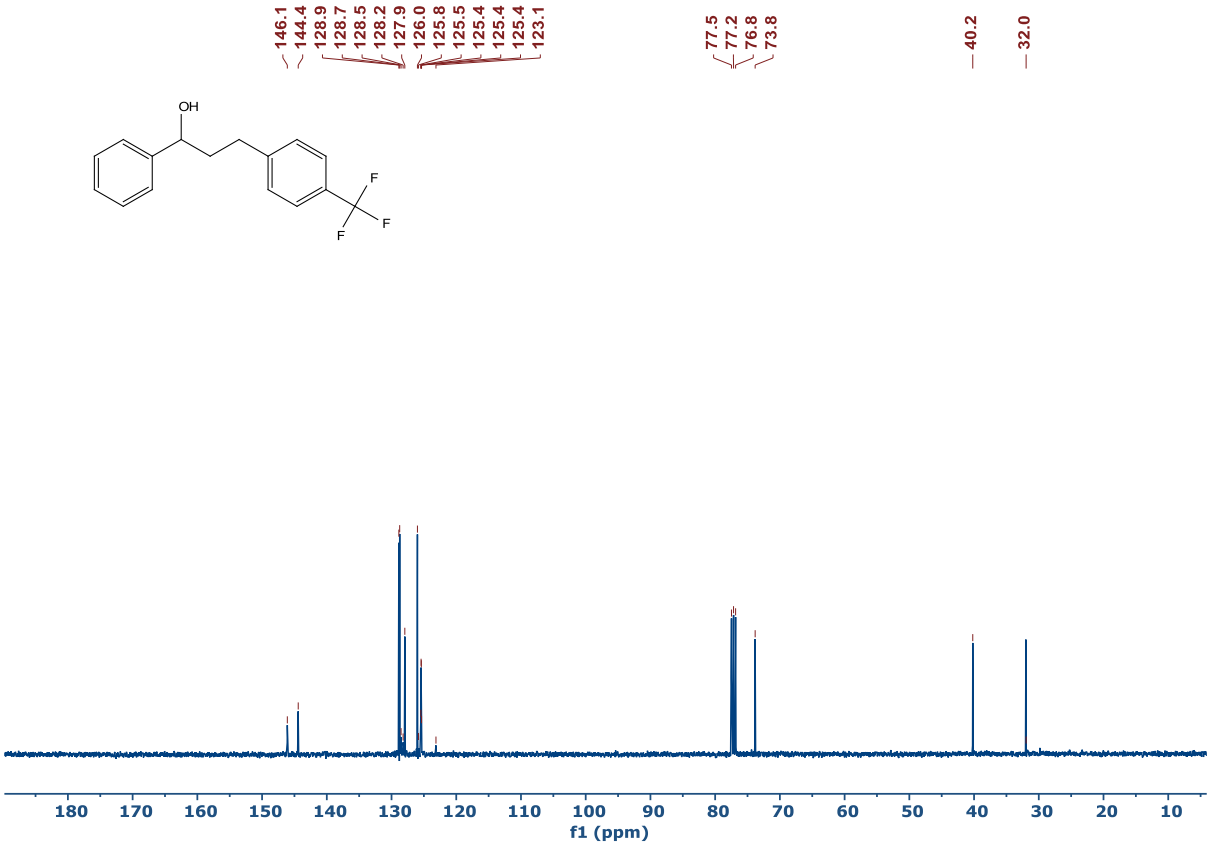


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5f** in $CDCl_3$.

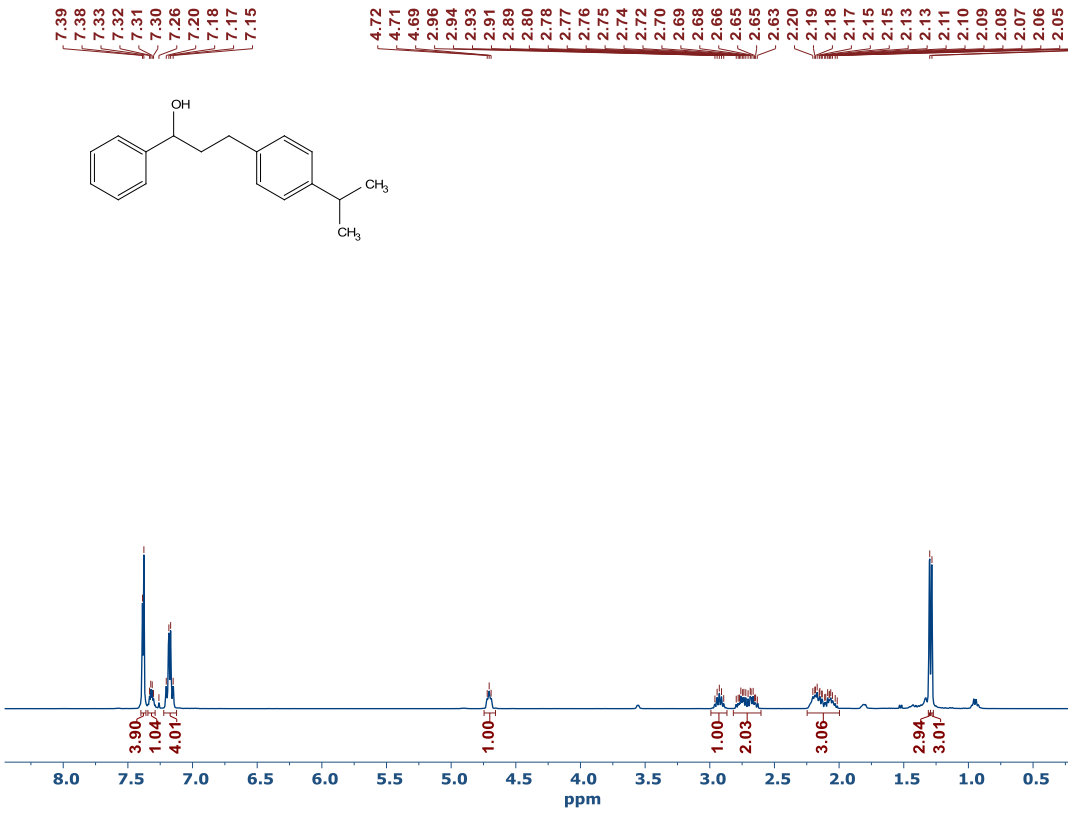


Figure S15. ^{1}H NMR spectrum of compound **5g** in $CDCl_3$.

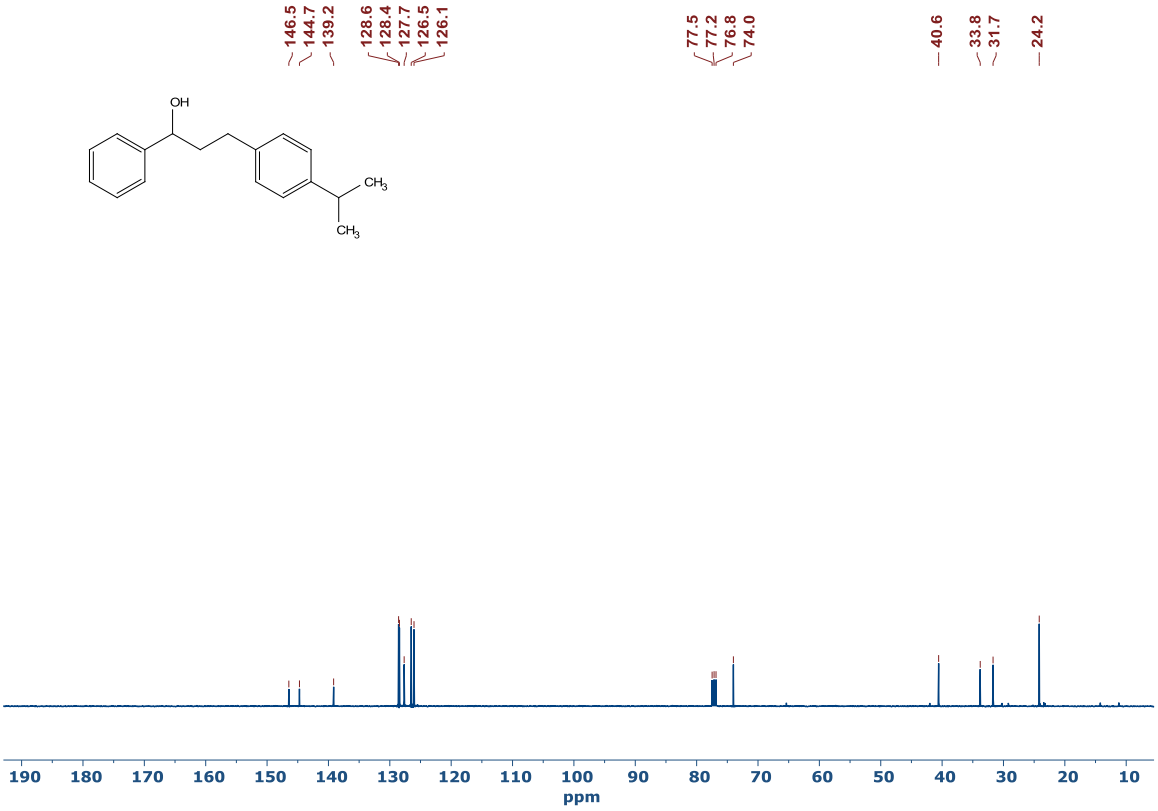


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5g** in $CDCl_3$.

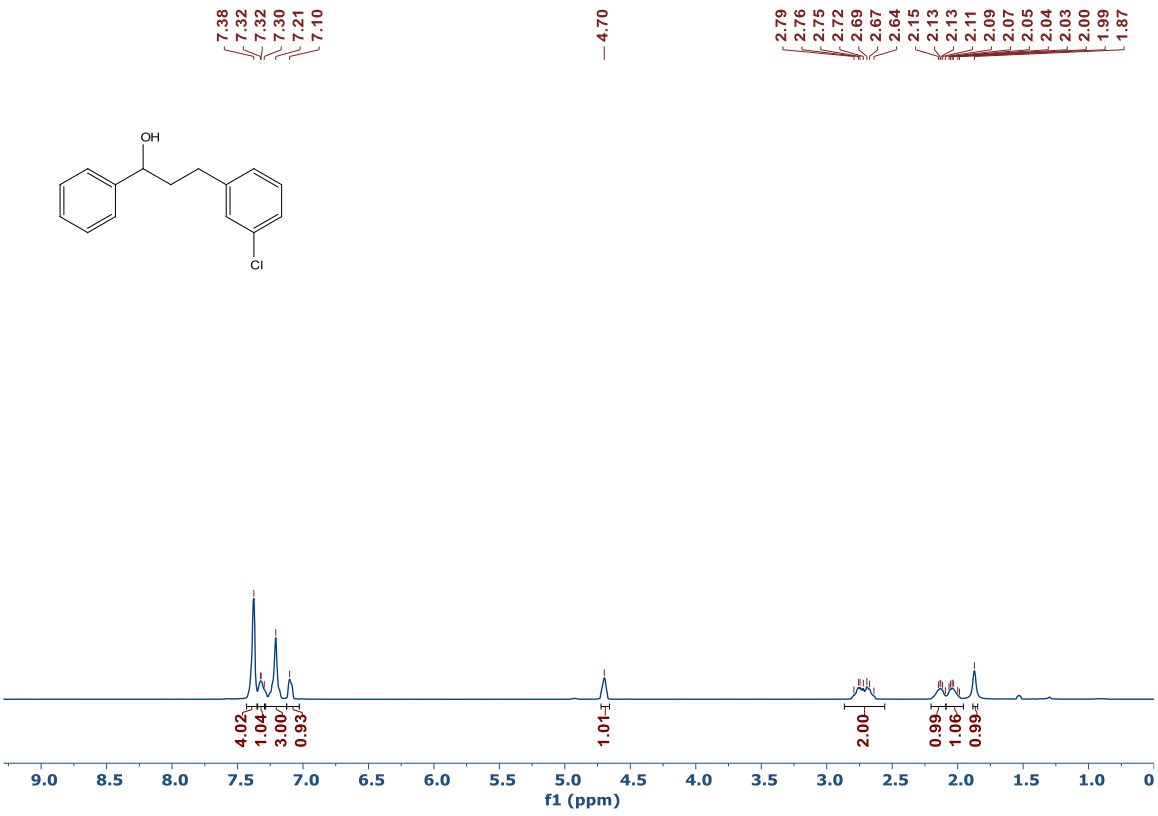


Figure S17. ^{1}H NMR spectrum of compound **5h** in $CDCl_3$.

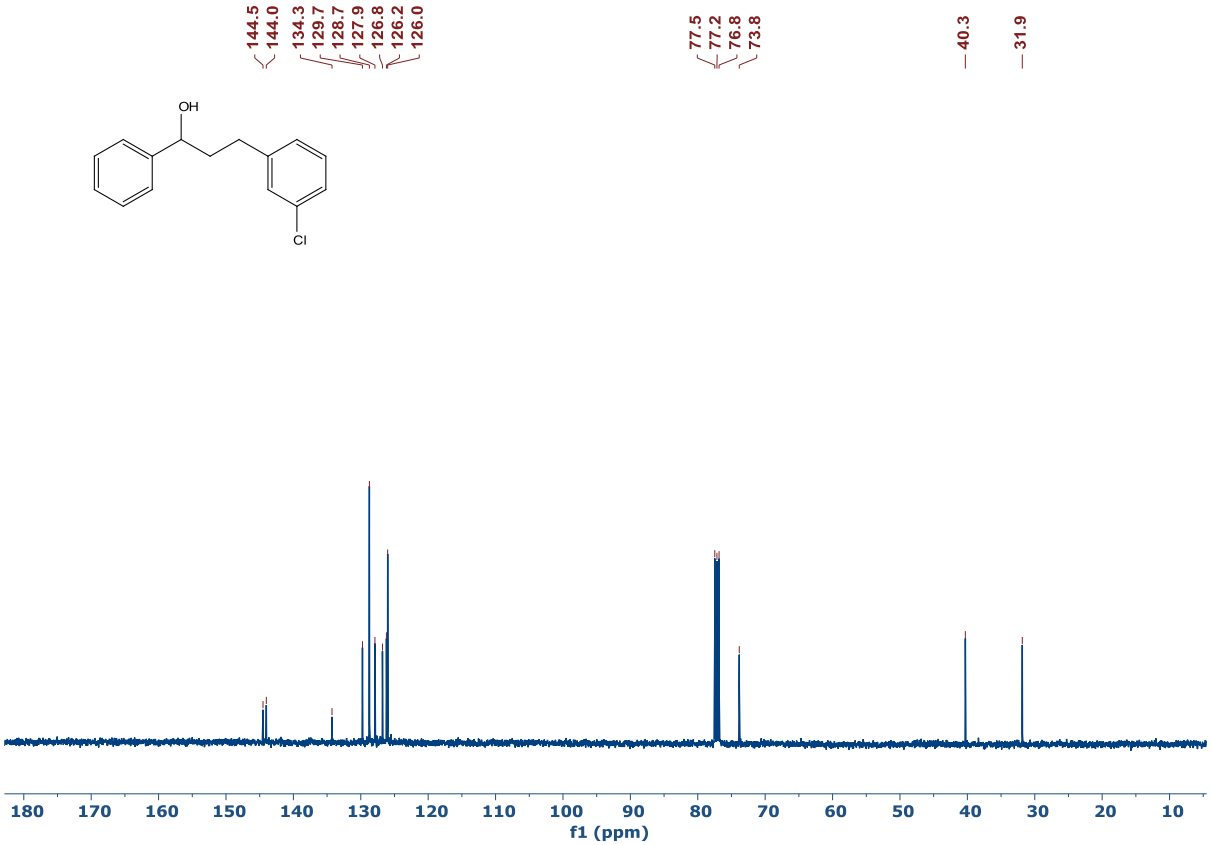


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5h** in $CDCl_3$.

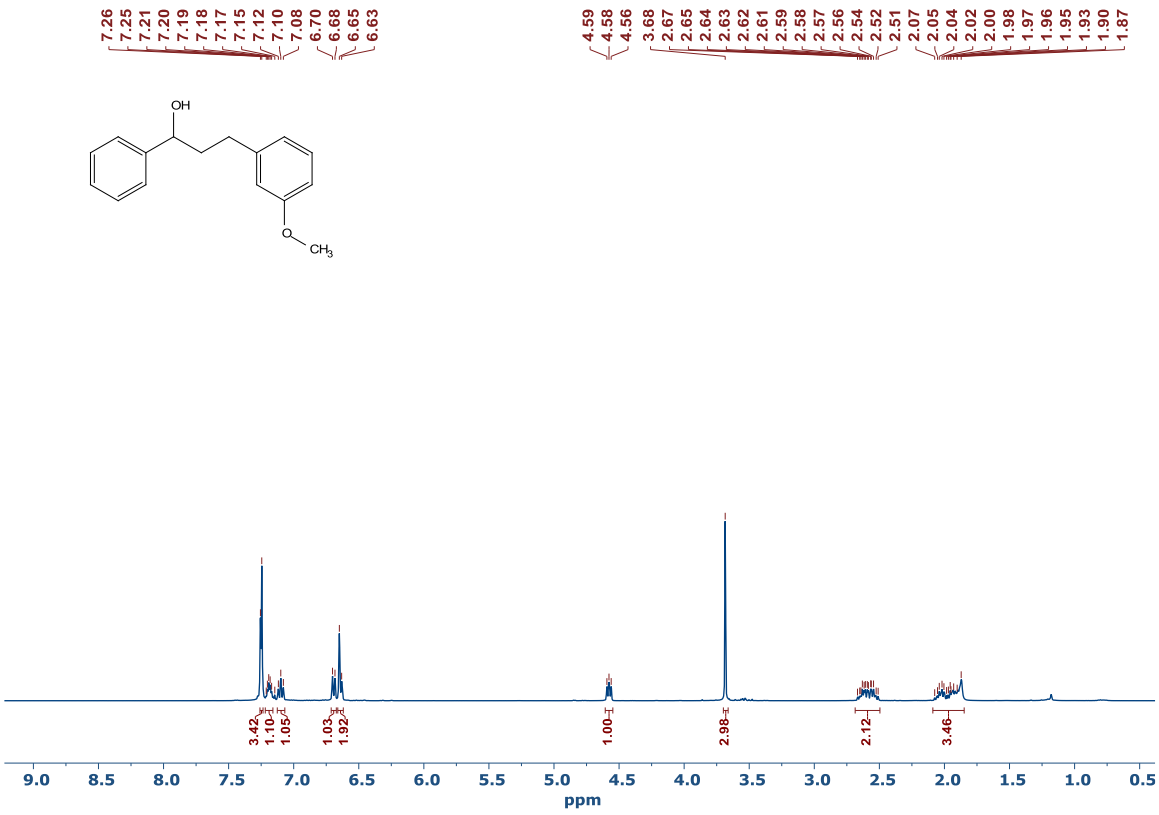


Figure S19. ^{1}H NMR spectrum of compound **5i** in $CDCl_3$.

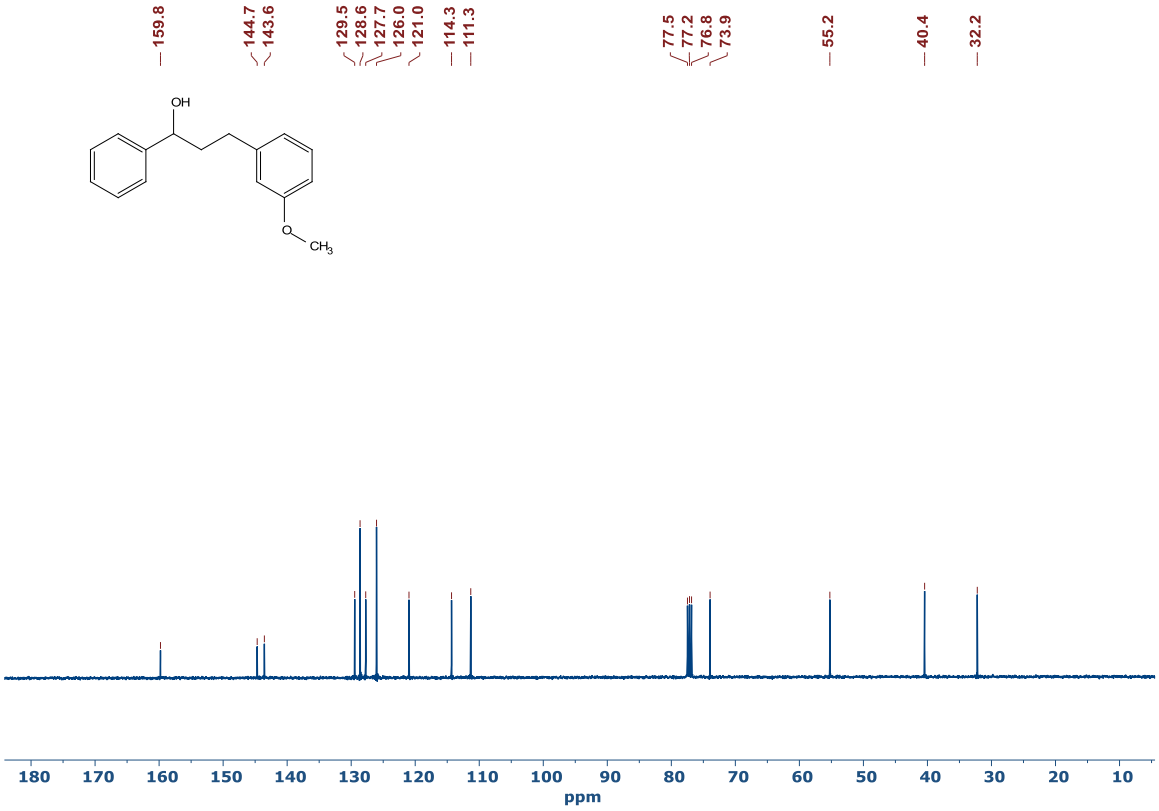


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5i** in $CDCl_3$.

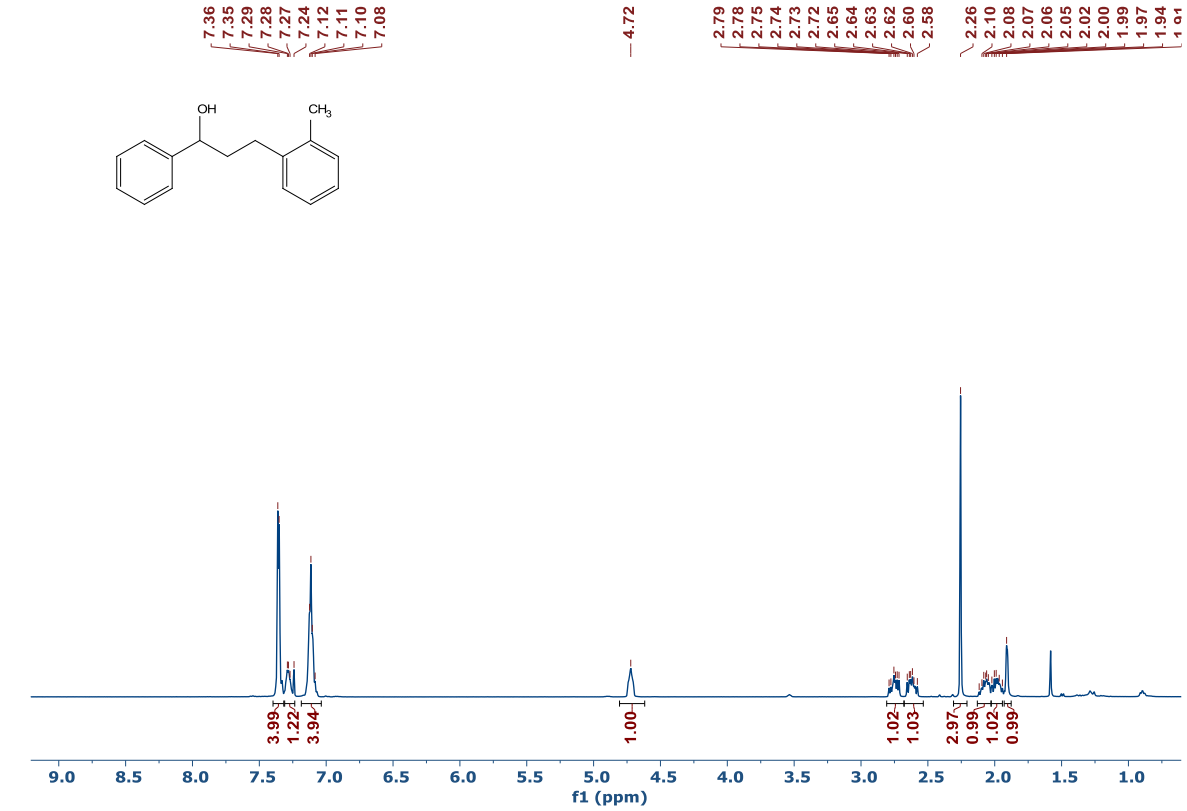


Figure S21. ^{1}H NMR spectrum of compound **5j** in $CDCl_3$.

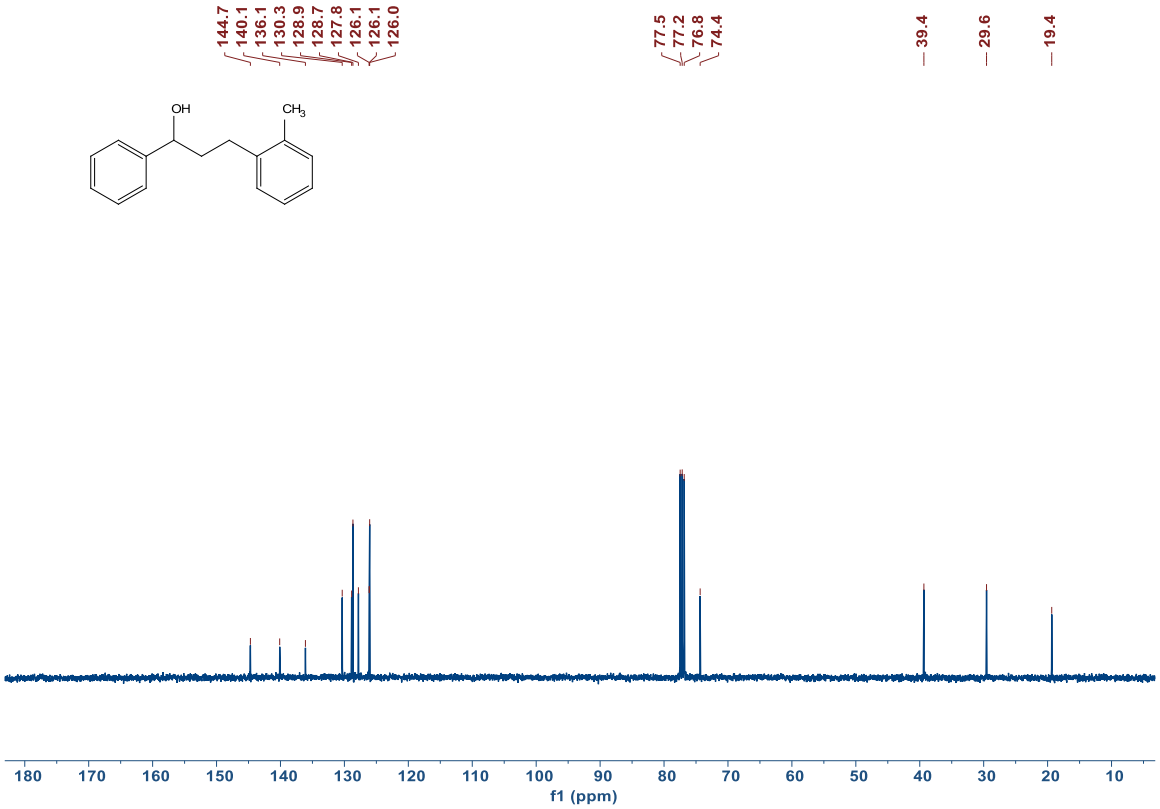


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5j** in $CDCl_3$.

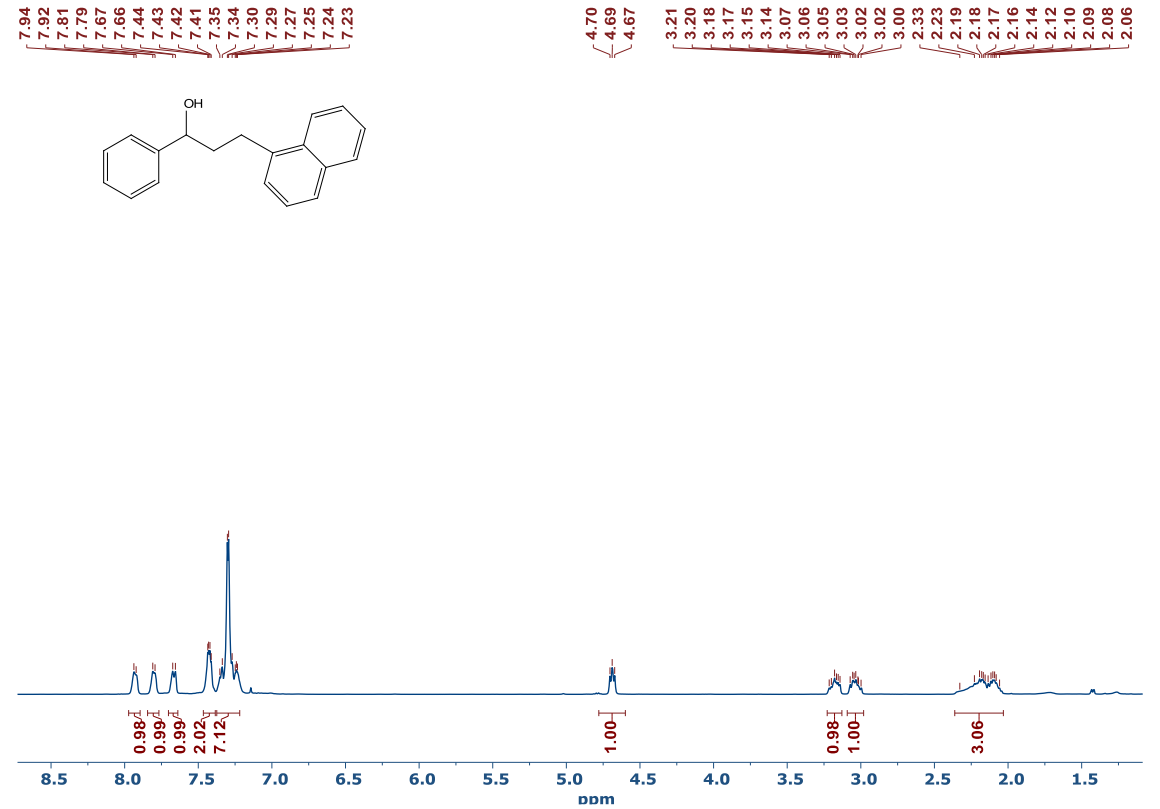


Figure S23. ^{1}H NMR spectrum of compound **5k** in $CDCl_3$.

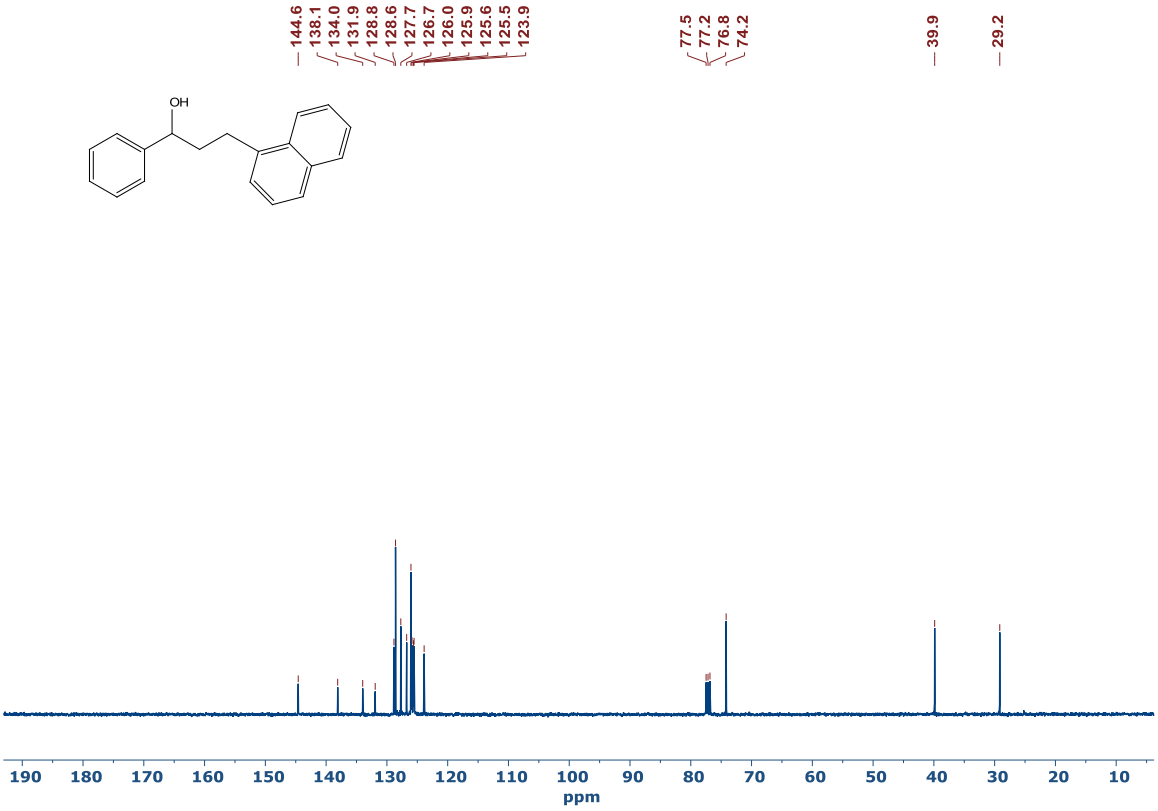


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5k** in $CDCl_3$.

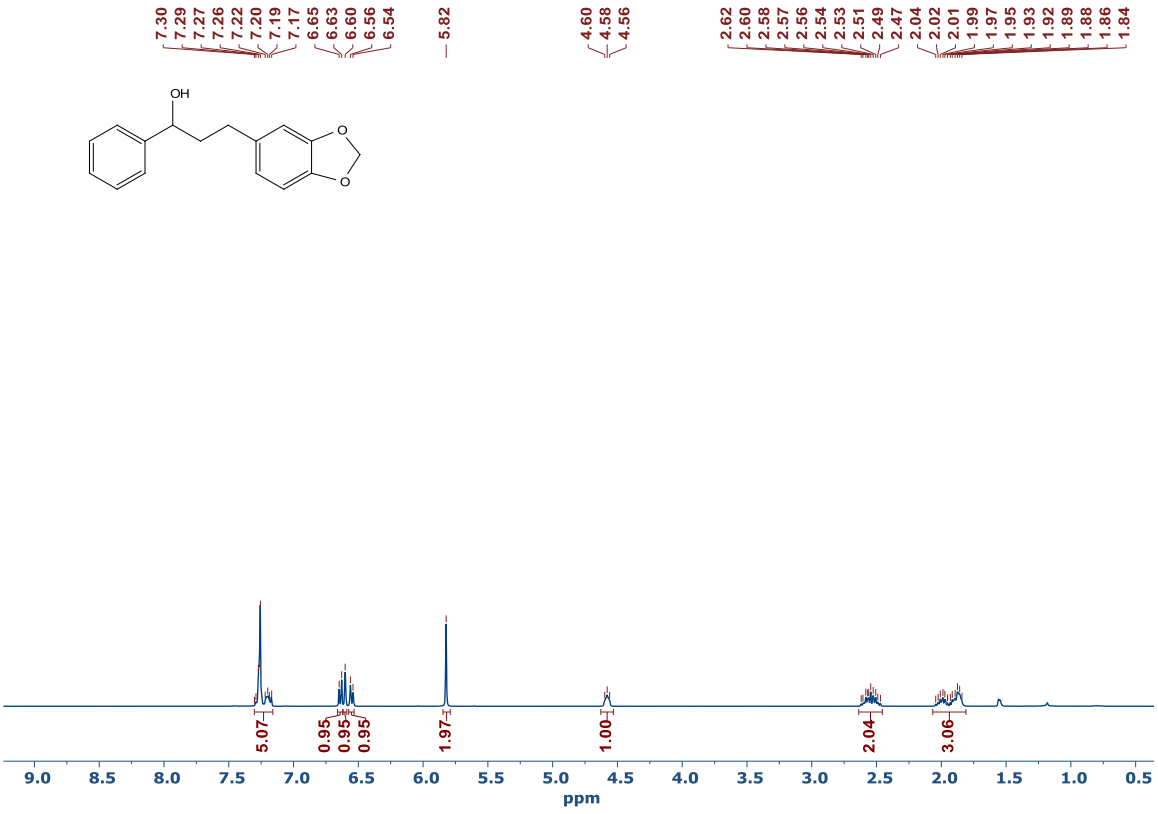


Figure S25. ^{1}H NMR spectrum of compound **5l** in $CDCl_3$.

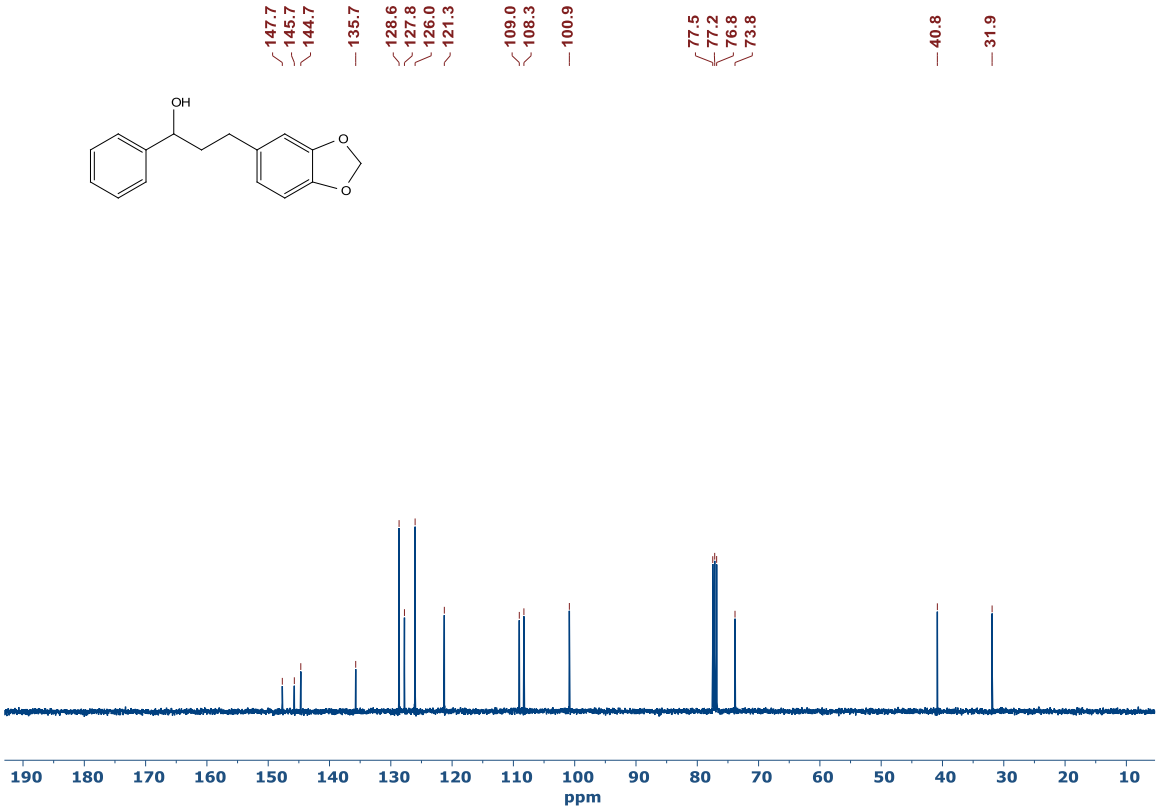


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5l** in $CDCl_3$.

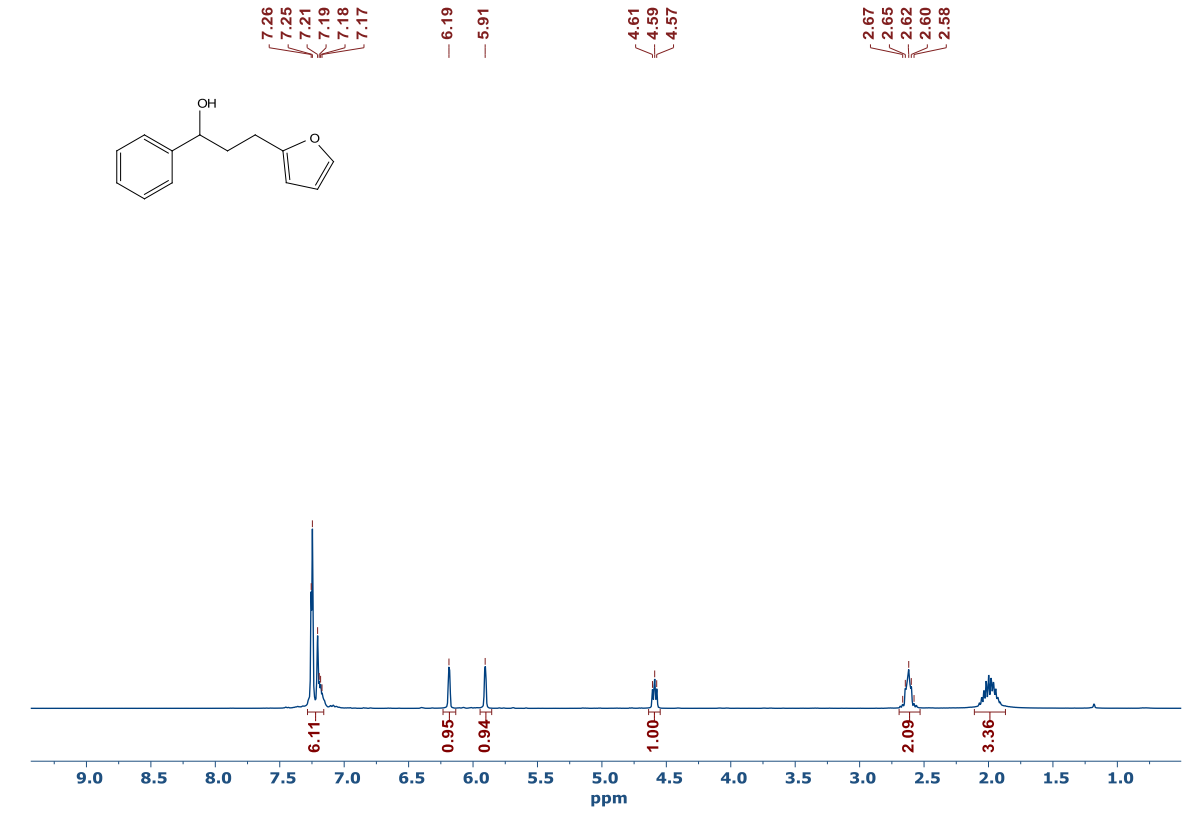


Figure S27. ^{1}H NMR spectrum of compound **5m** in $CDCl_3$.

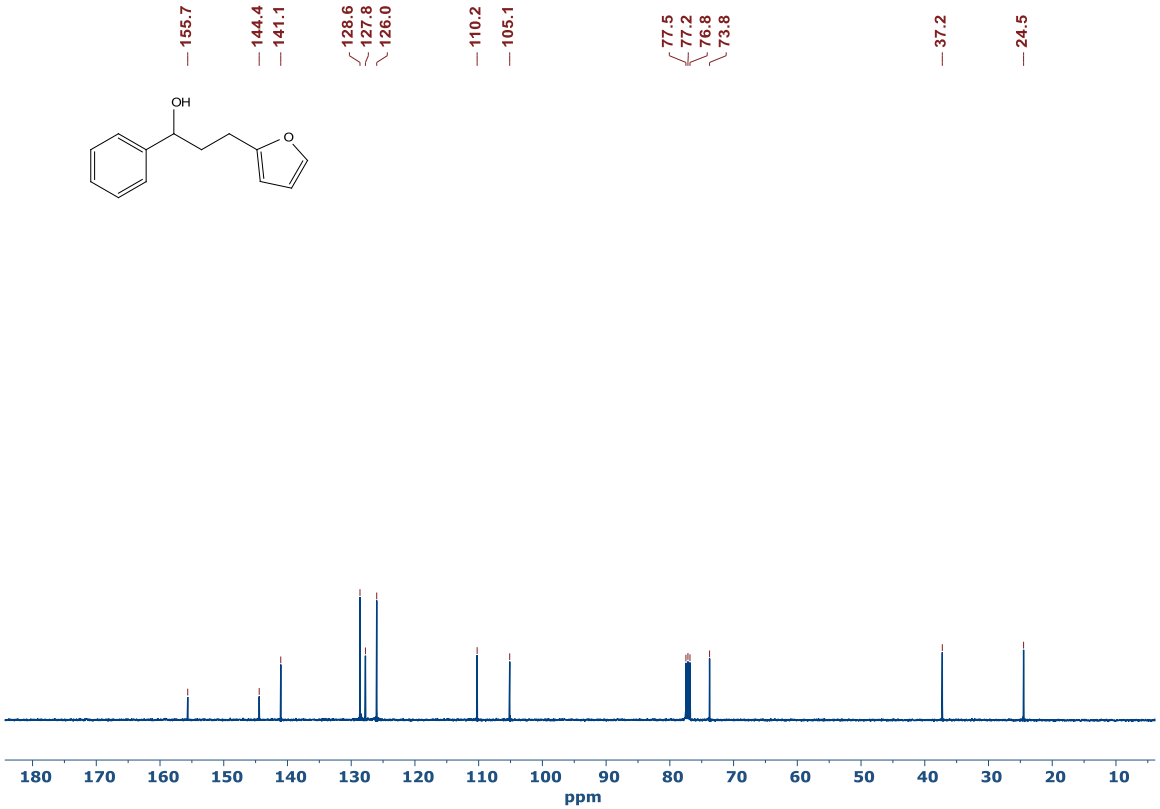


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5m** in $CDCl_3$.

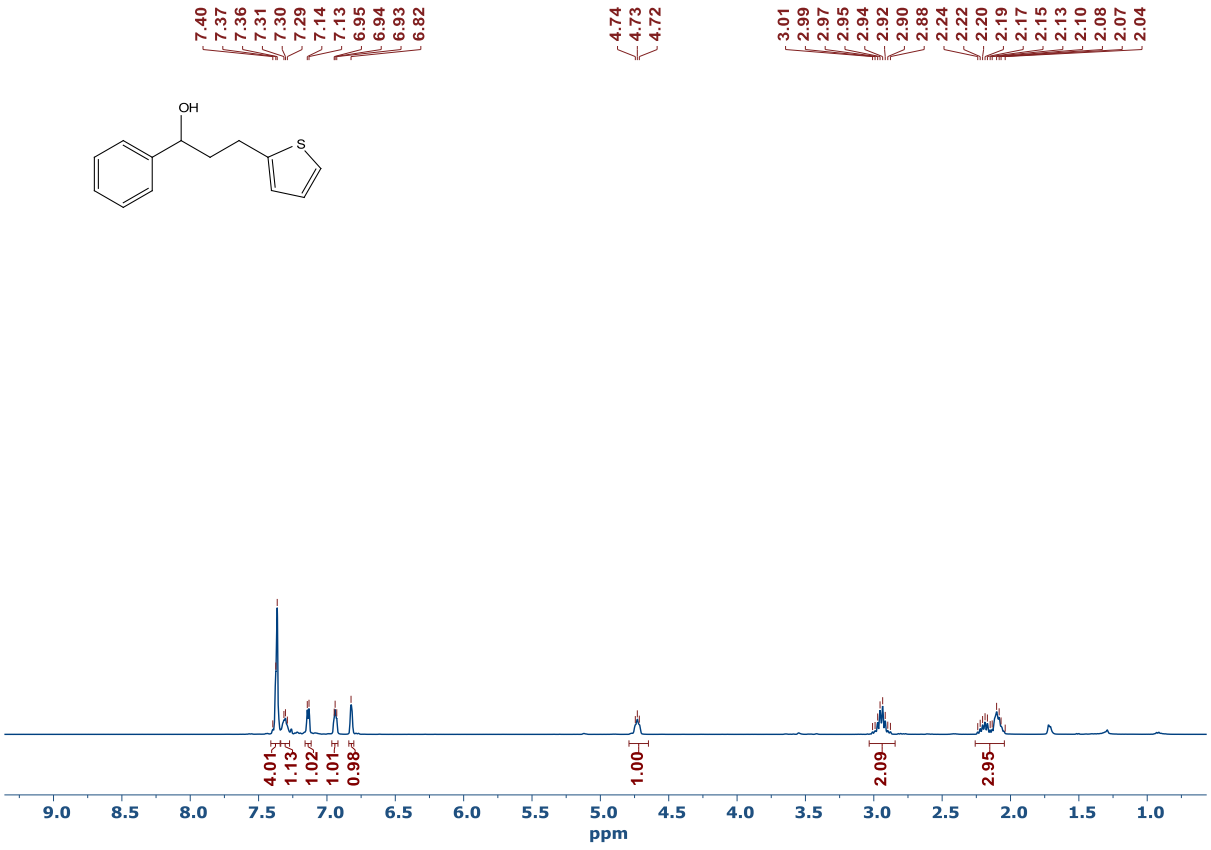


Figure S29. ^{1}H NMR spectrum of compound **5n** in $CDCl_3$.

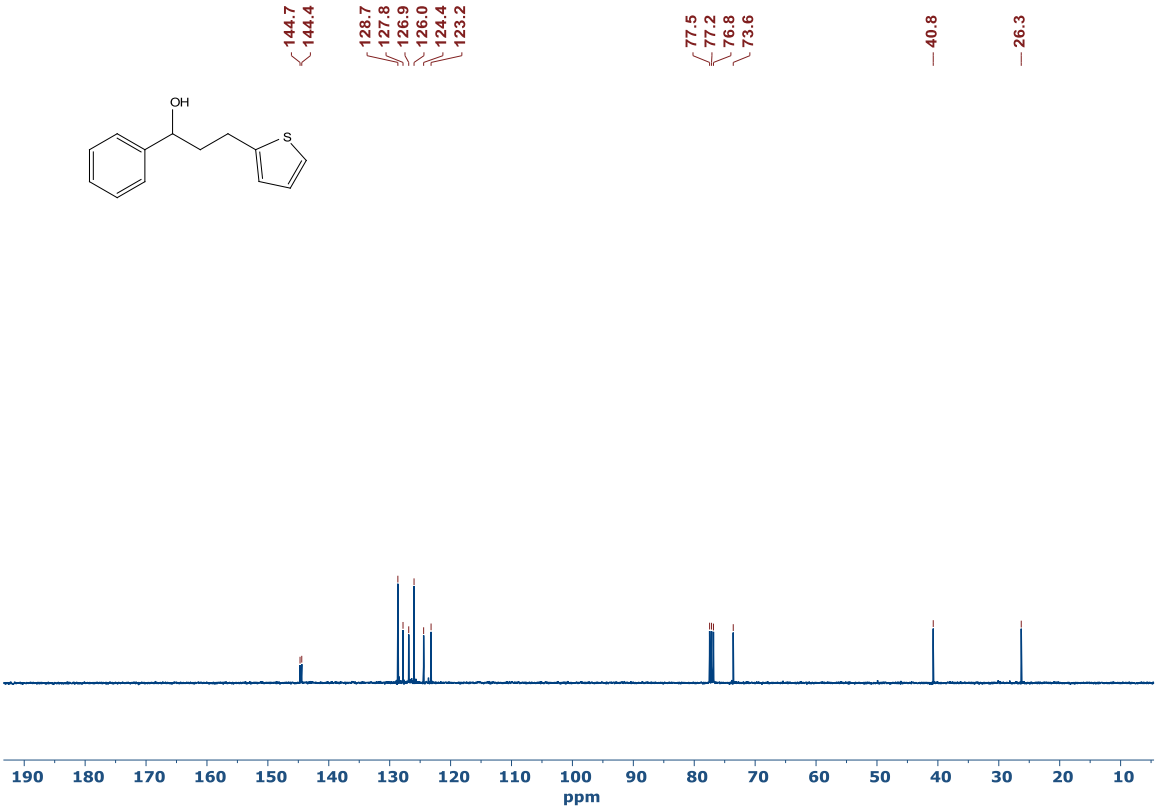


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5n** in $CDCl_3$.

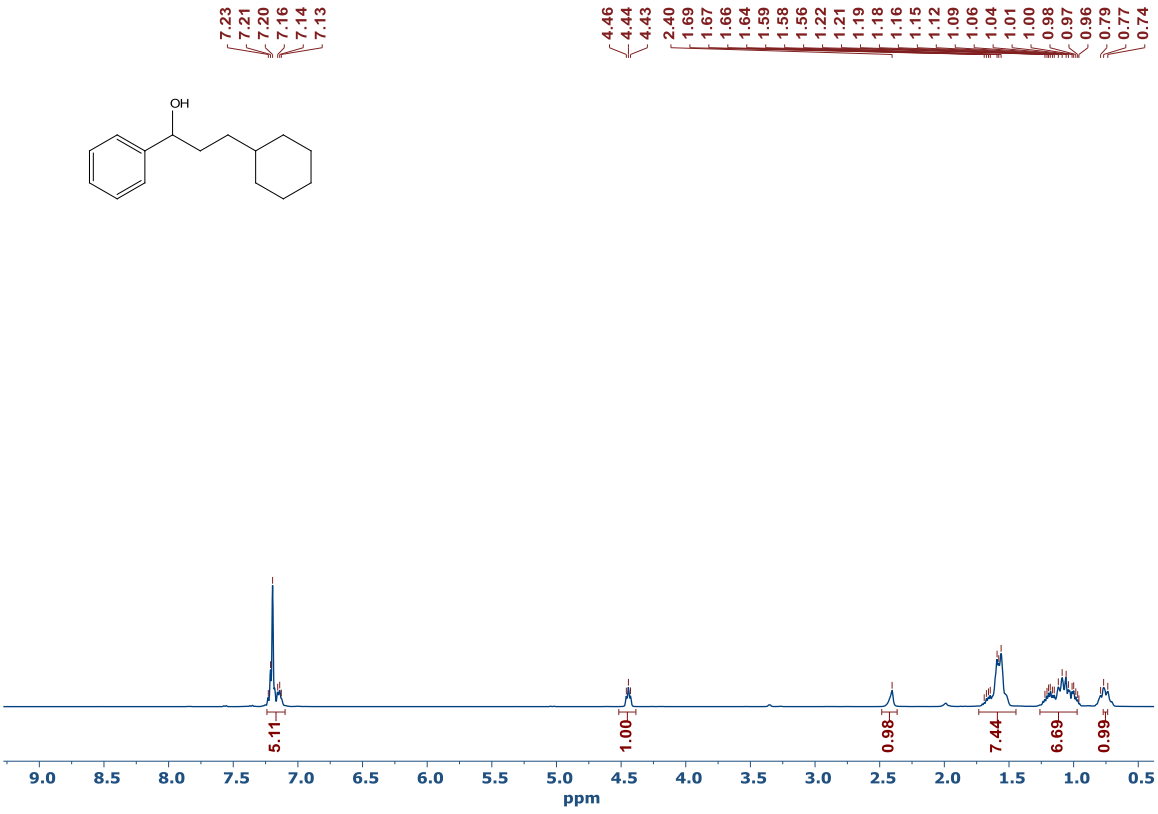


Figure S31. ^{1}H NMR spectrum of compound **5o** in $CDCl_3$.

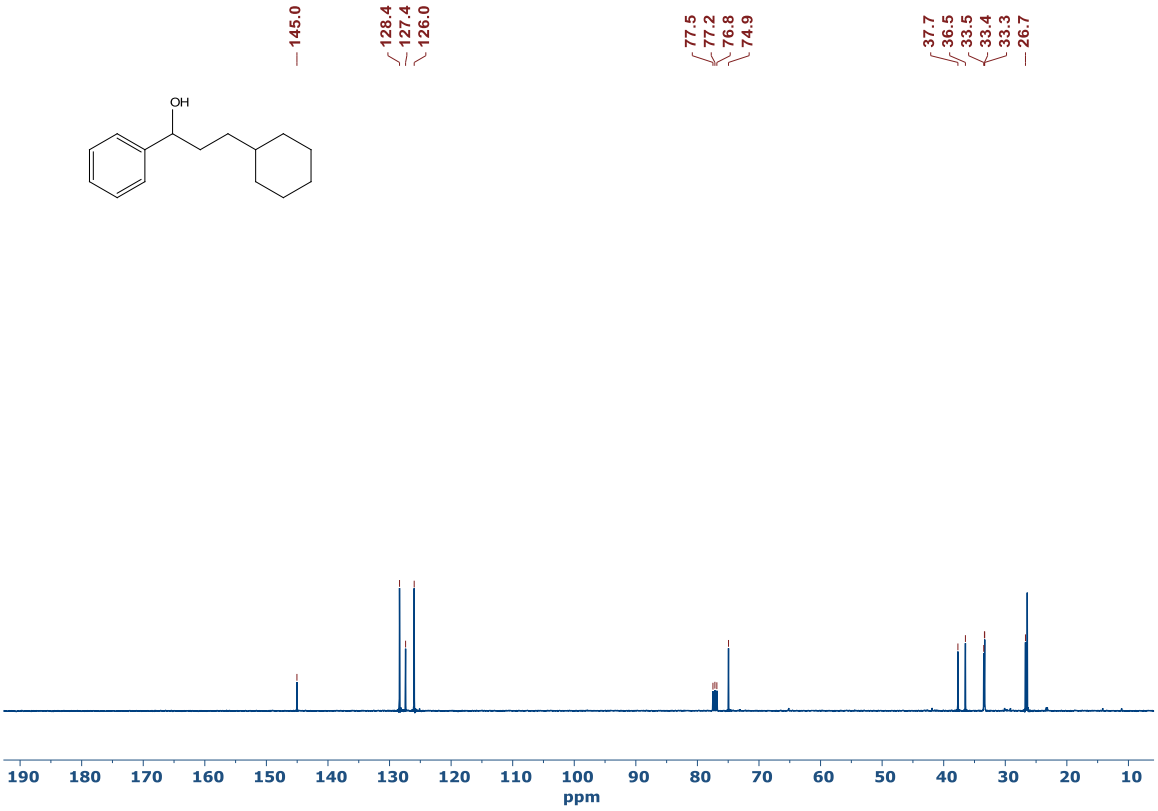


Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5o** in $CDCl_3$.

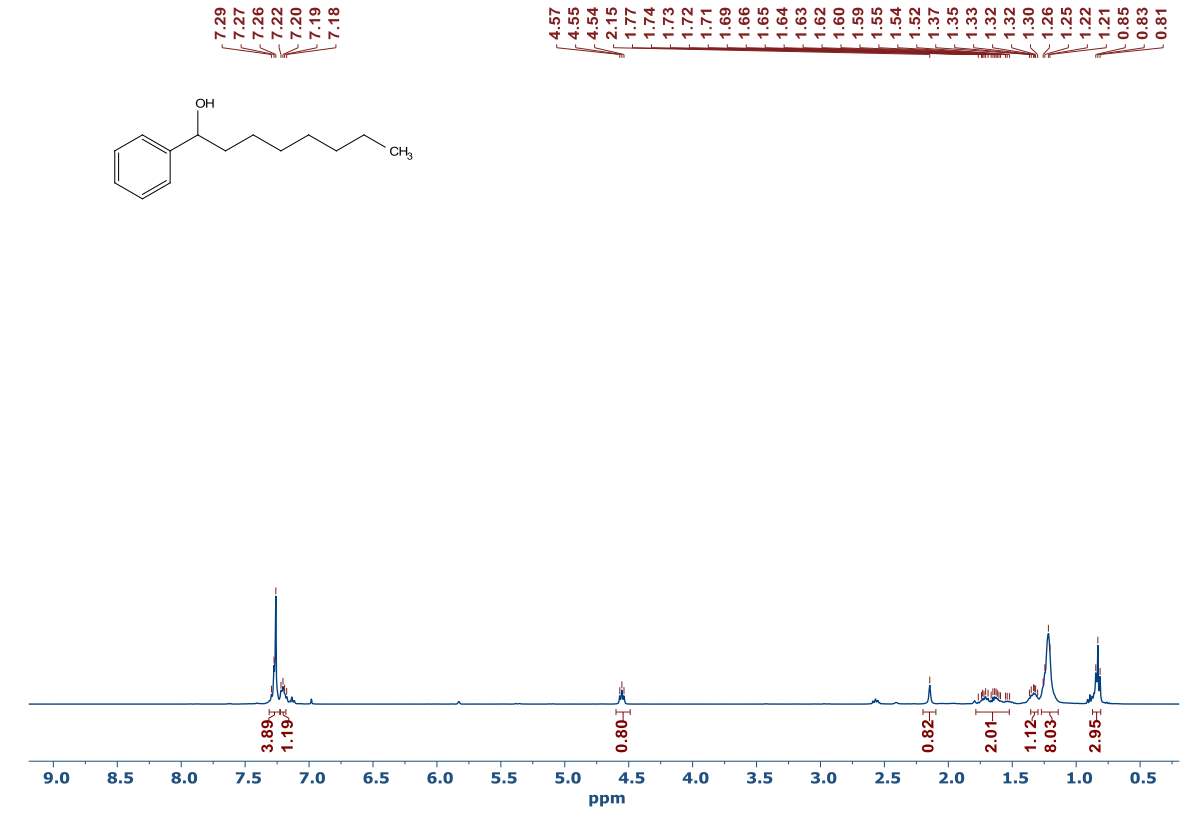


Figure S33. ^{1}H NMR spectrum of compound **5p** in $CDCl_3$.

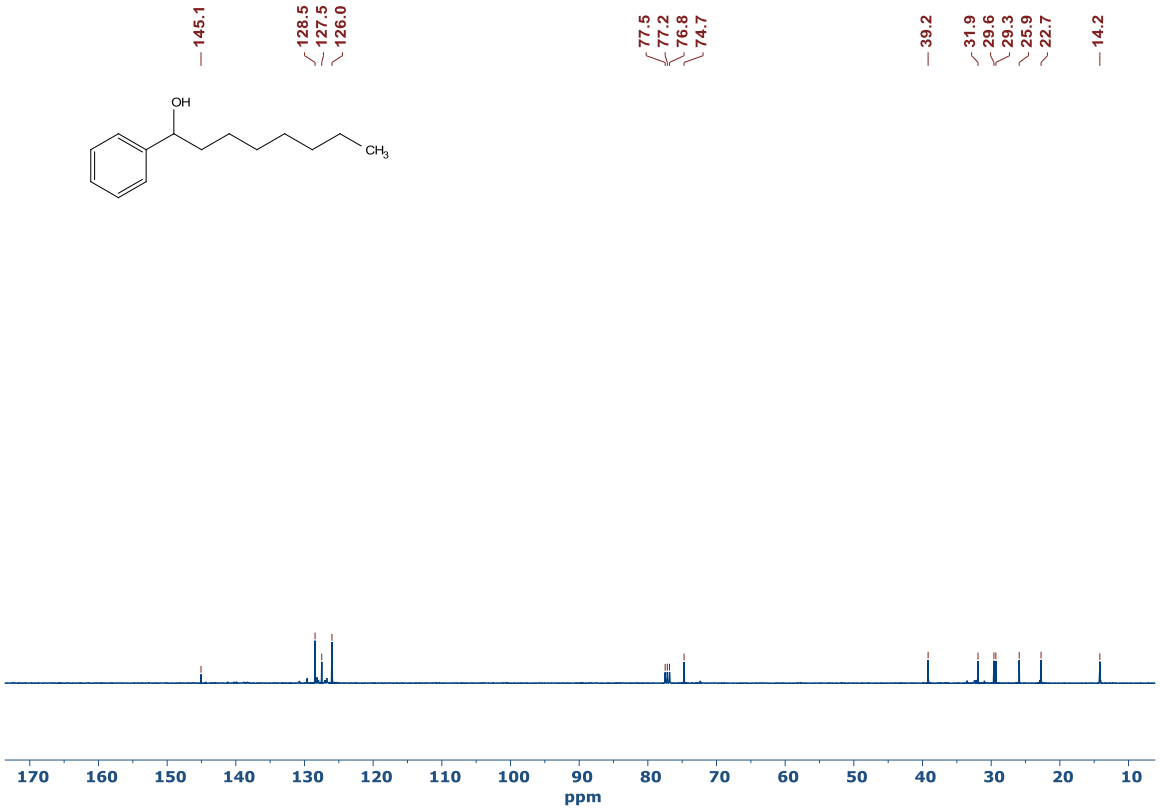


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5p** in $CDCl_3$.

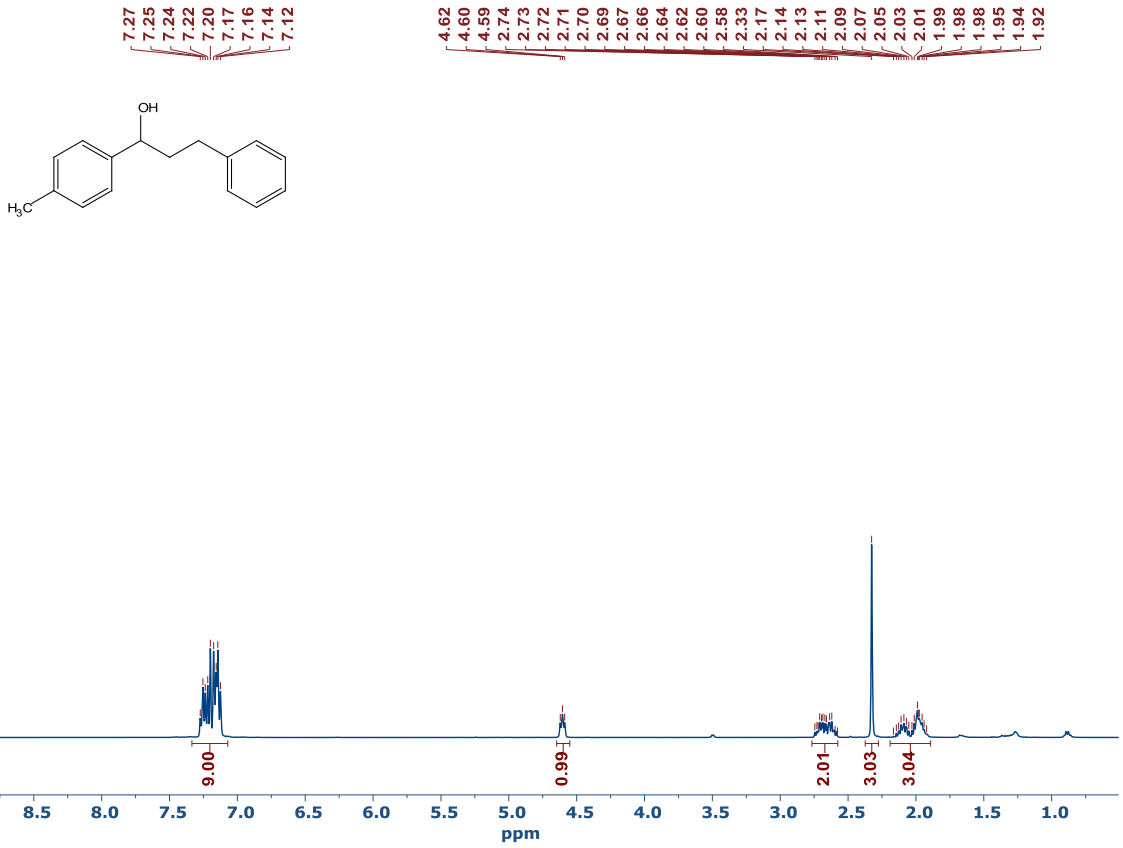


Figure S35. ^{1}H NMR spectrum of compound **5q** in $CDCl_3$.

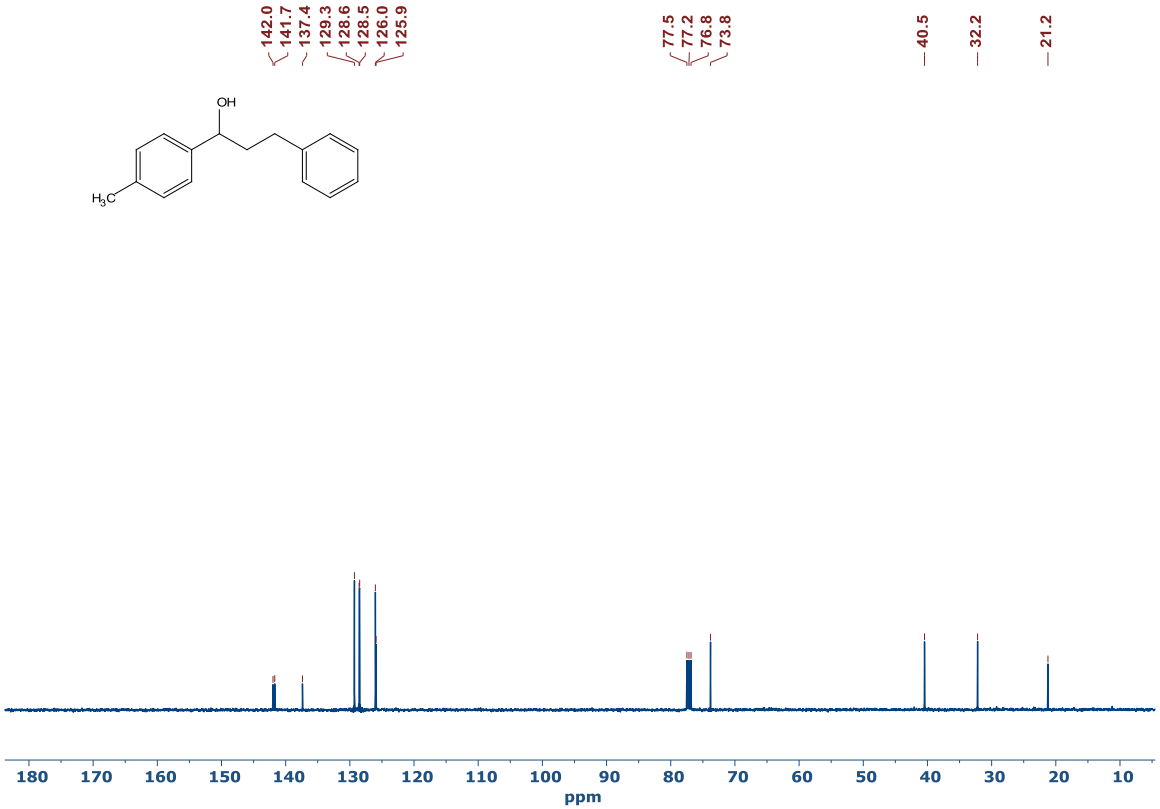


Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5q** in $CDCl_3$.

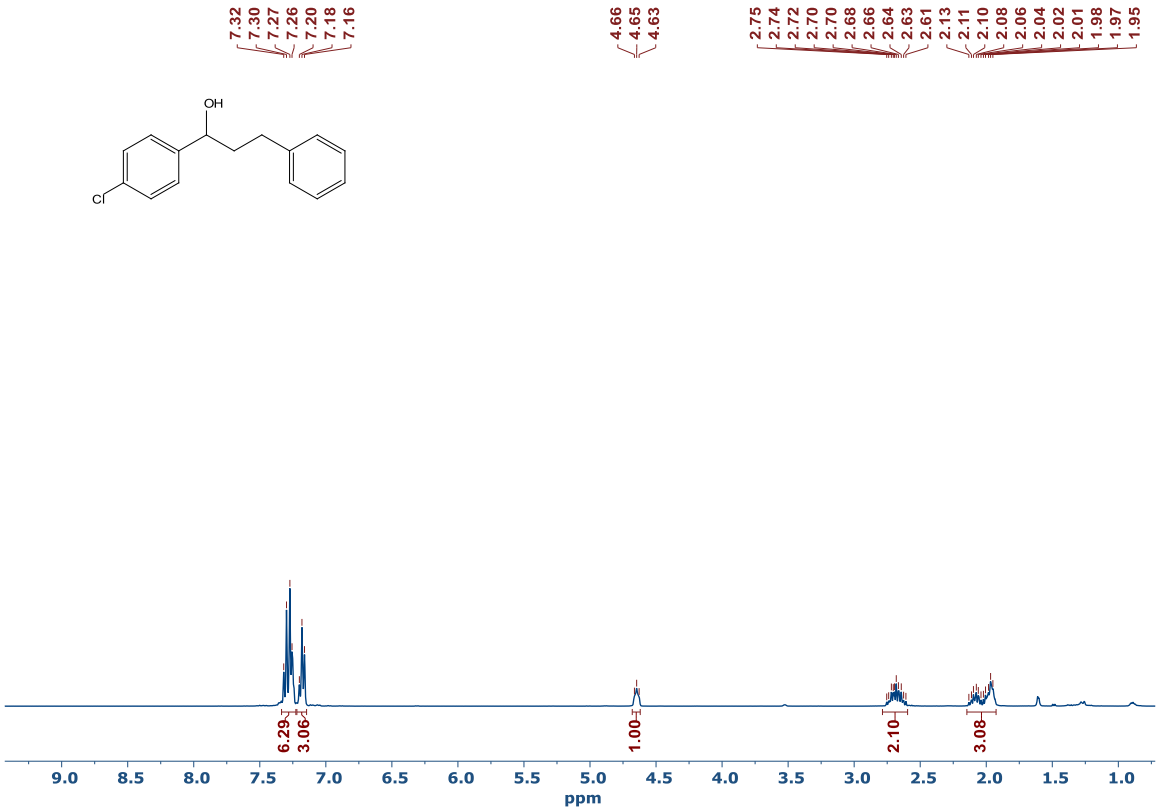


Figure S37. ^{1}H NMR spectrum of compound **5r** in $CDCl_3$.

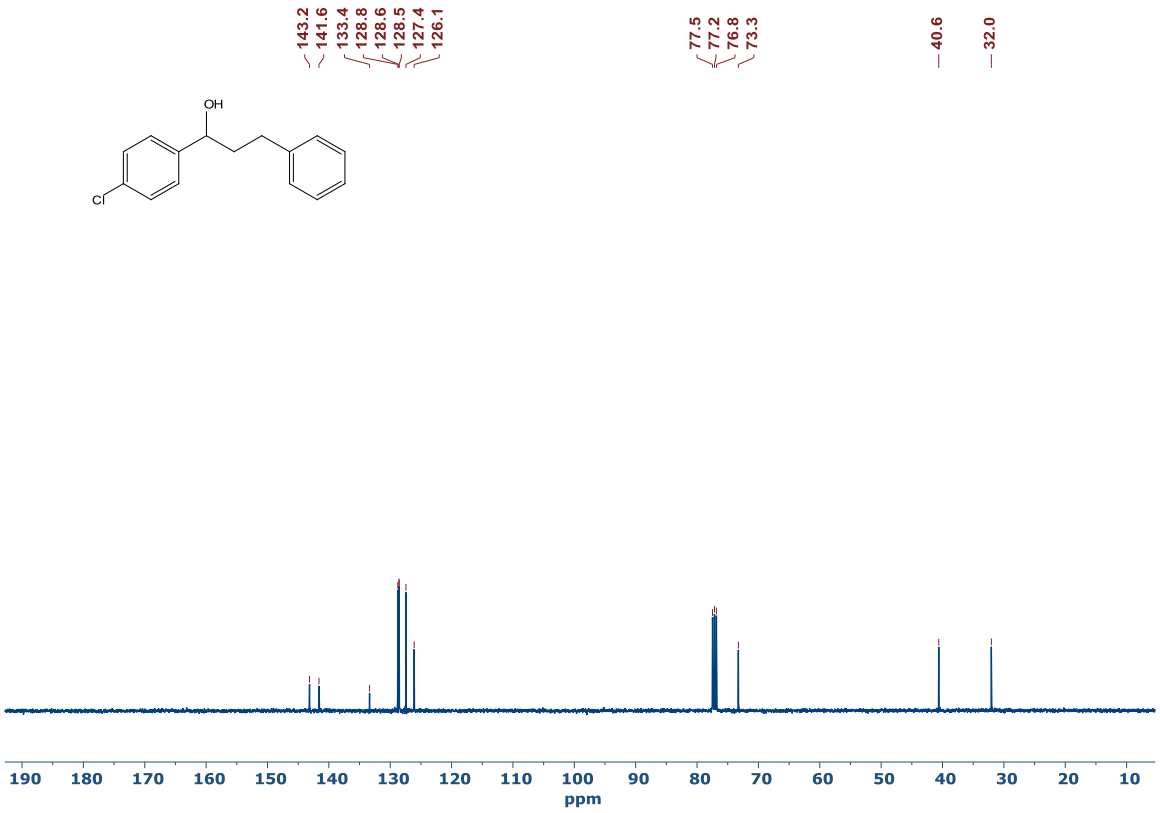


Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5r** in $CDCl_3$.

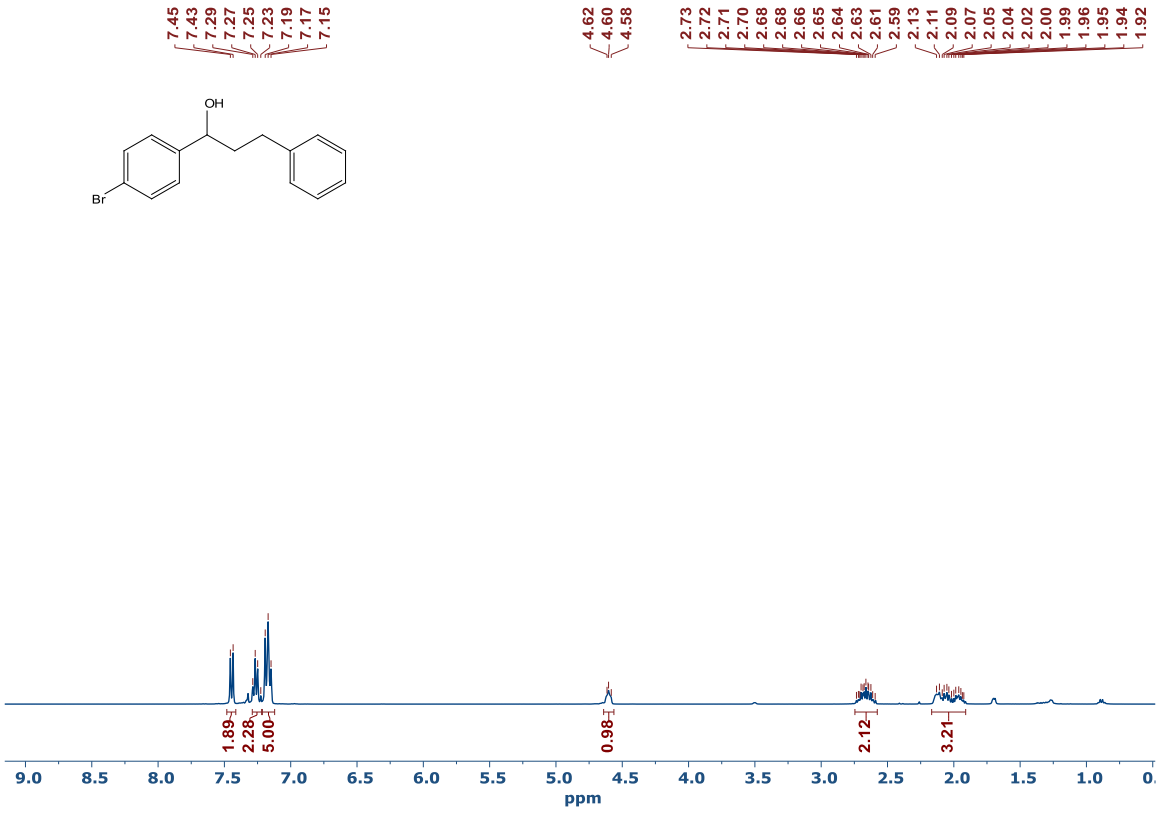


Figure S39. ^{1}H NMR spectrum of compound **5s** in $CDCl_3$.

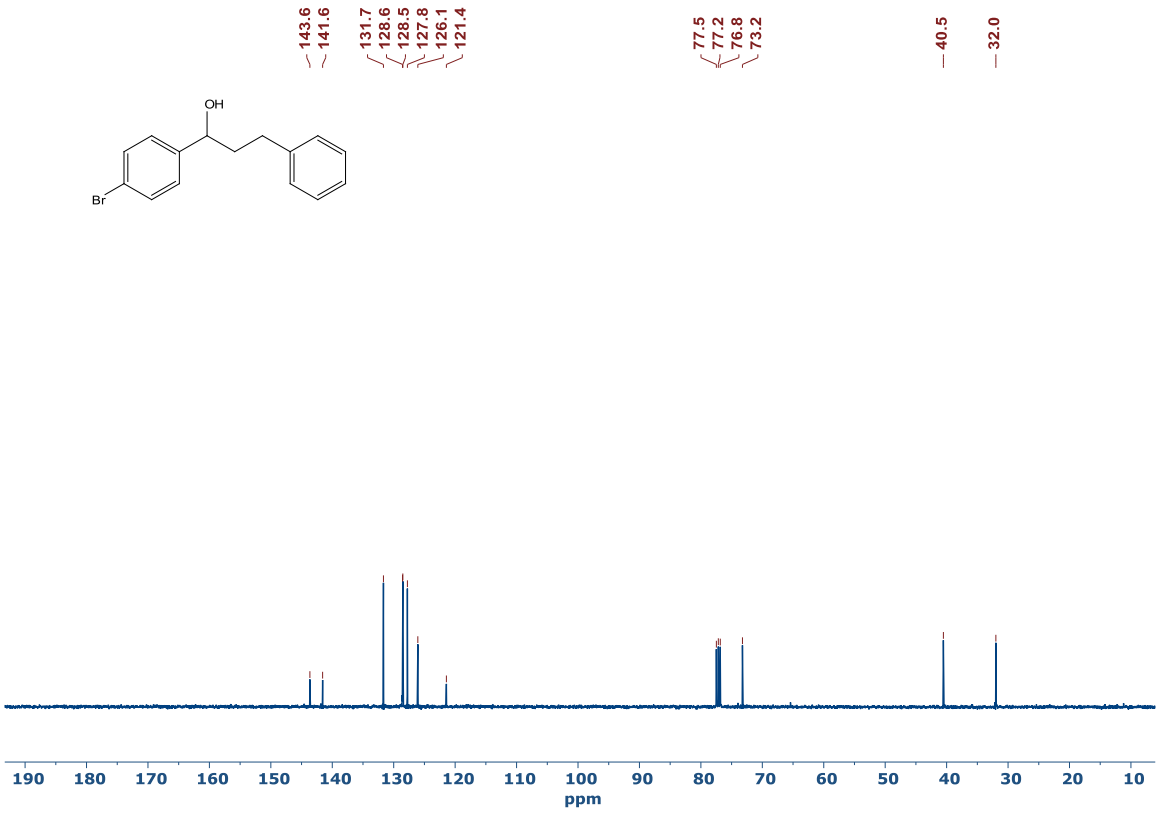


Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5s** in $CDCl_3$.

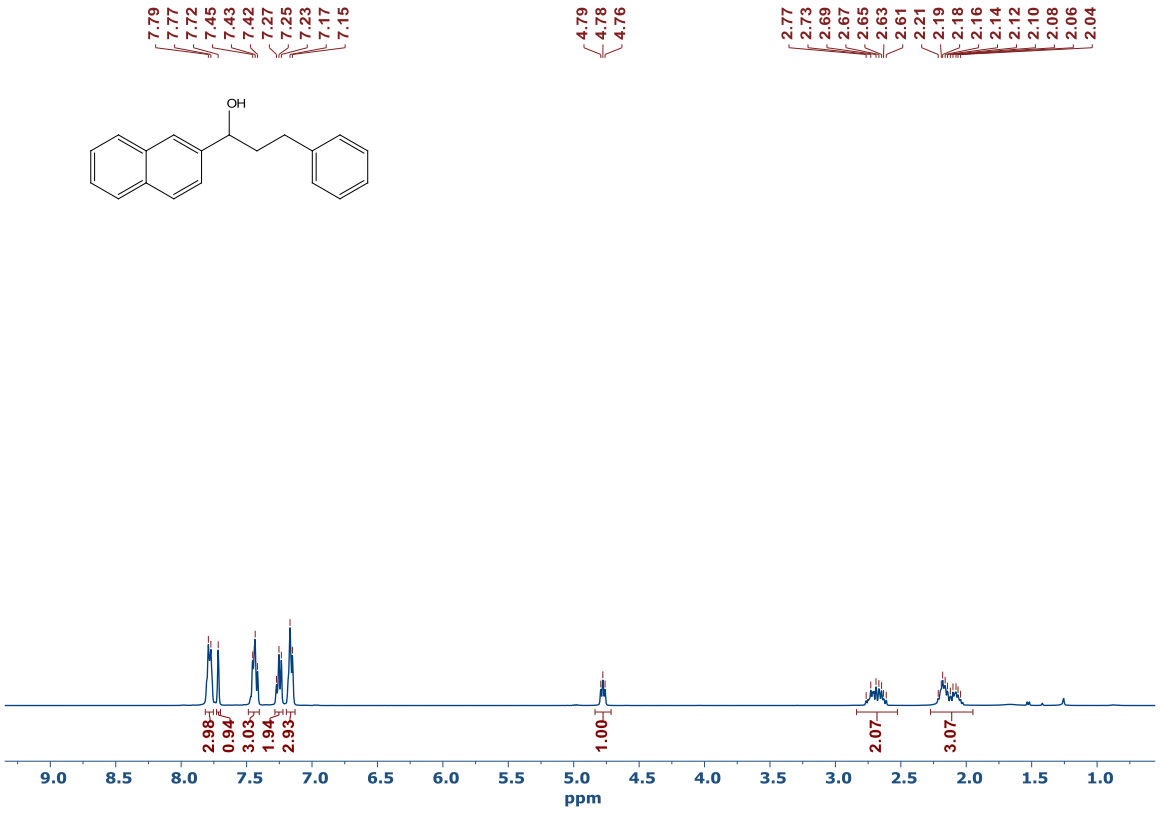


Figure S41. ^{1}H NMR spectrum of compound **5t** in $CDCl_3$.

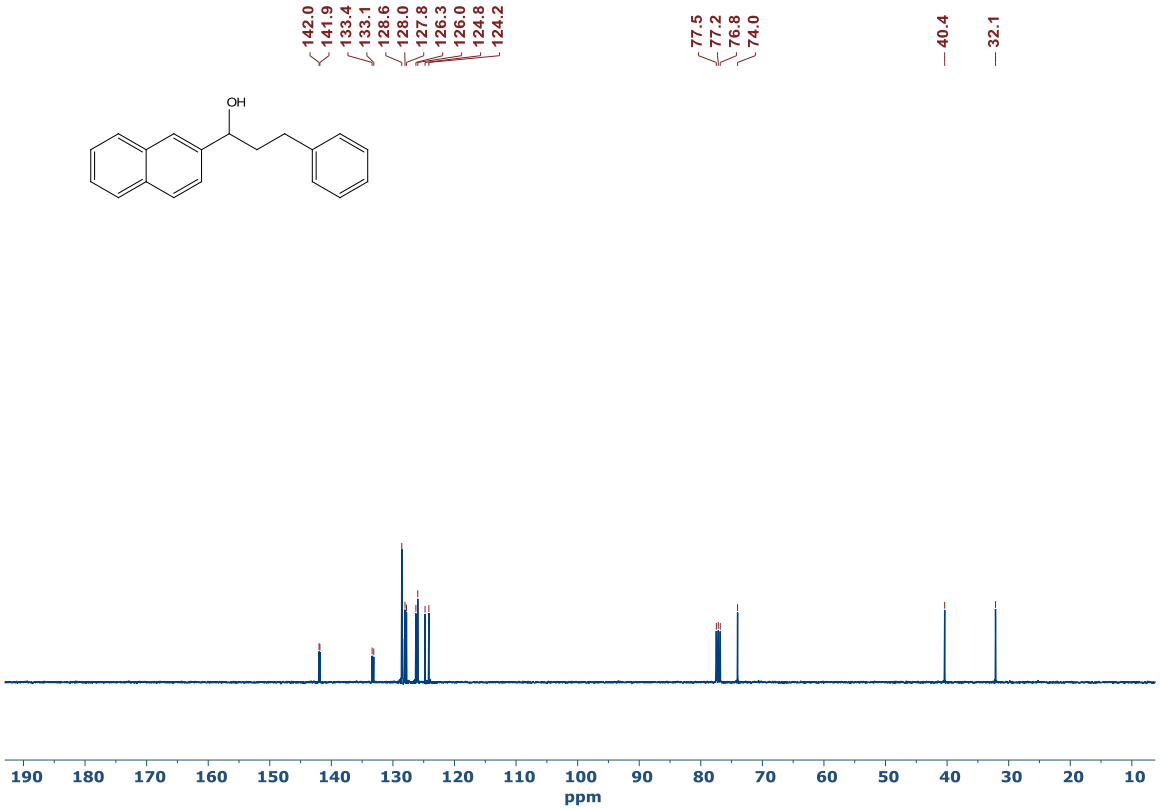


Figure S42. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5t** in $CDCl_3$.

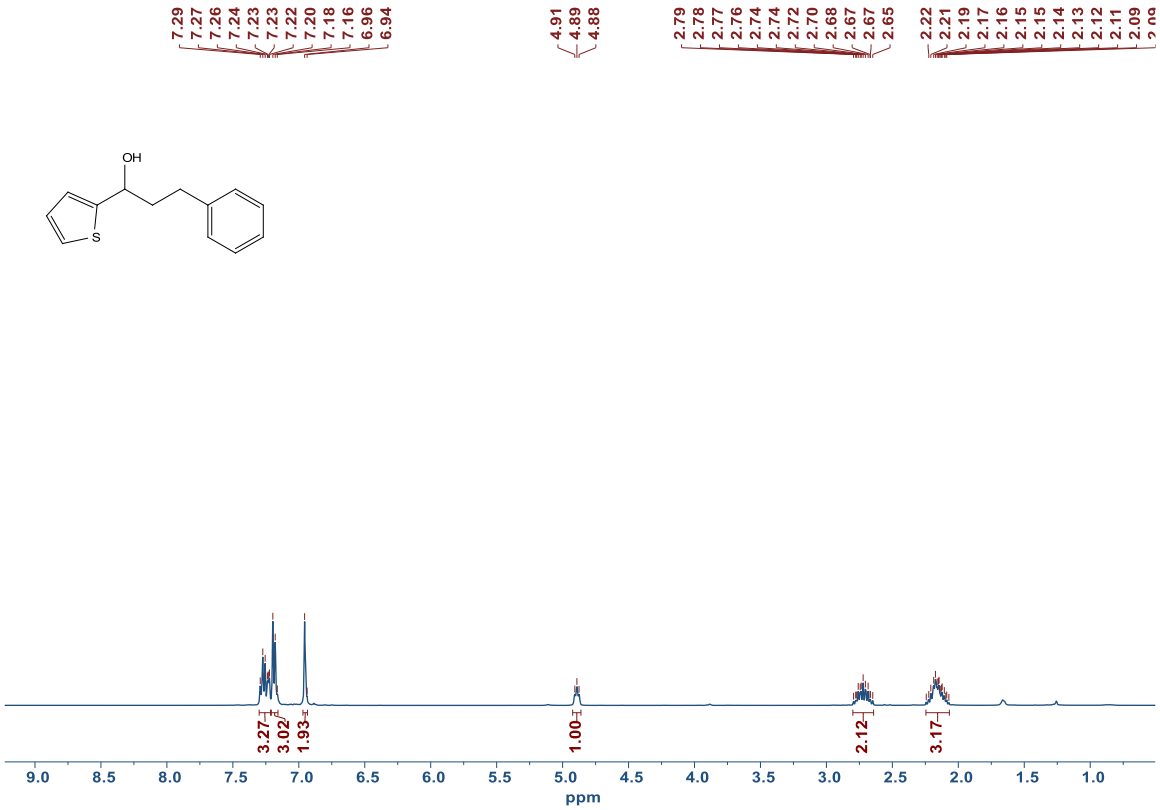


Figure S43. ^{1}H NMR spectrum of compound **5u** in $CDCl_3$.

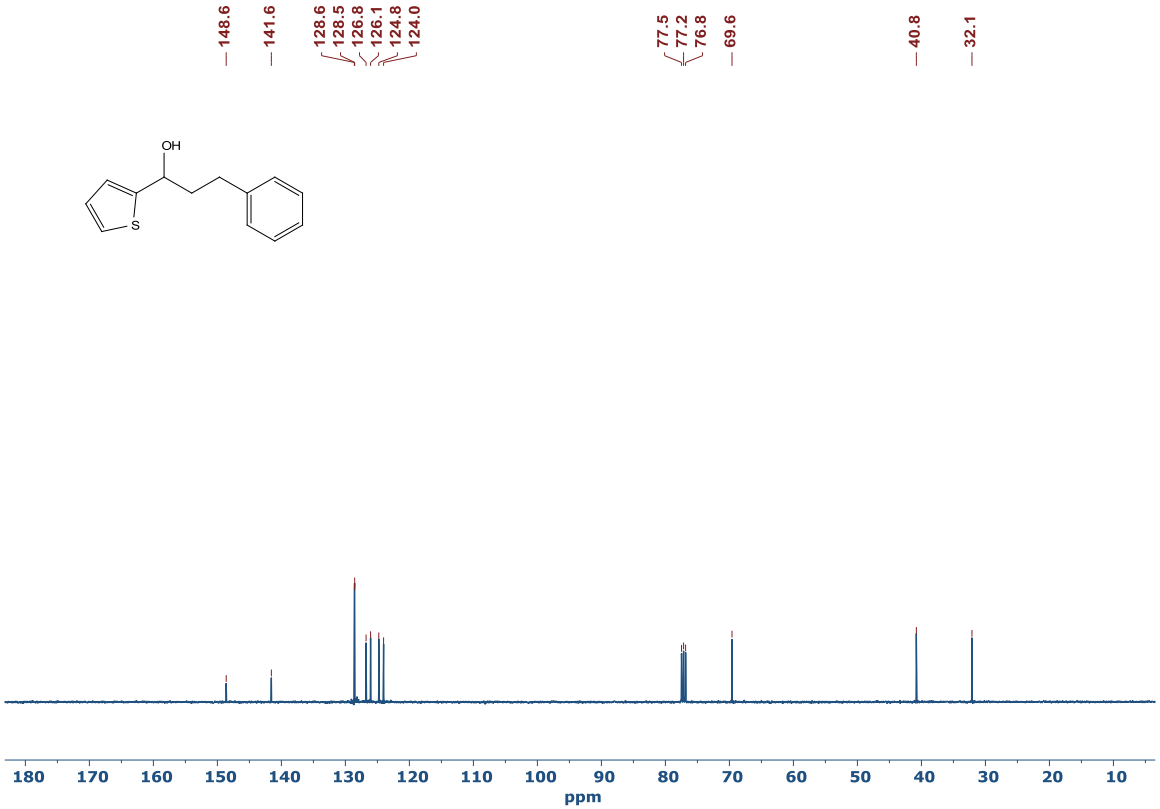


Figure S44. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5u** in $CDCl_3$.

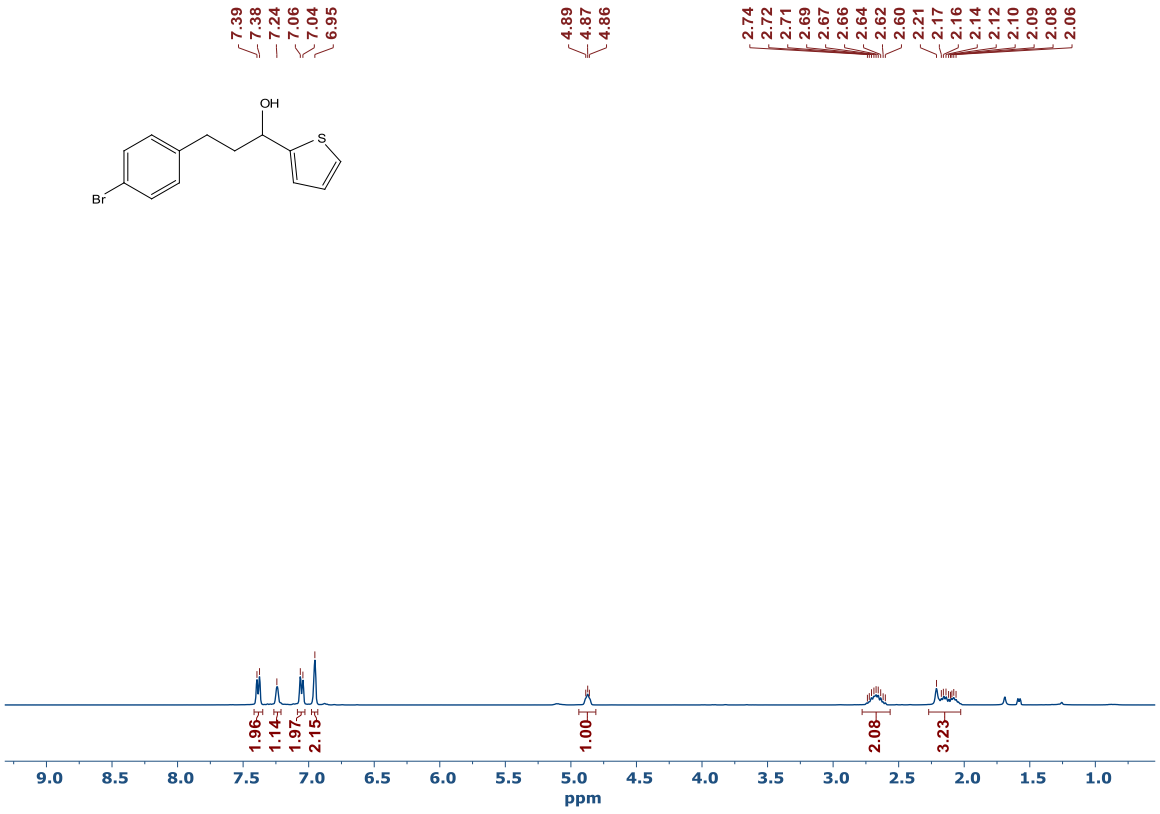


Figure S45. ^{1}H NMR spectrum of compound **5v** in $CDCl_3$.

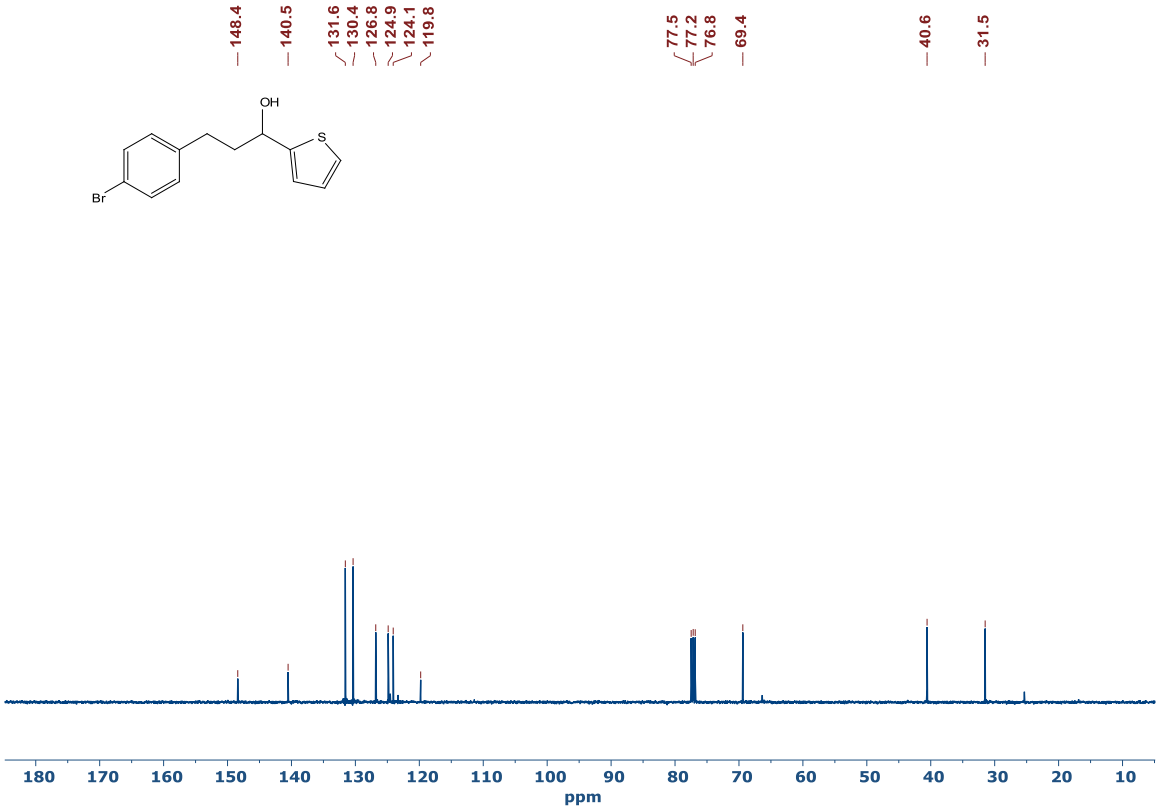


Figure S46. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5v** in $CDCl_3$.

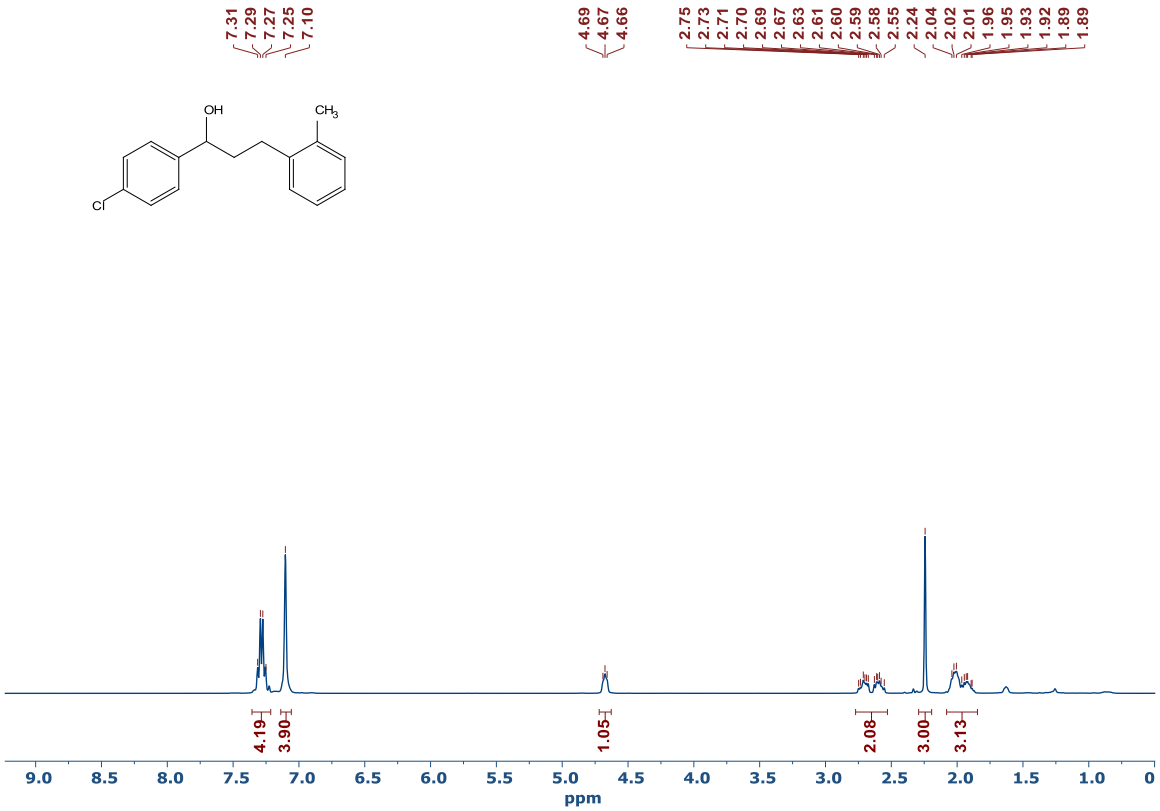


Figure S47. ^{1}H NMR spectrum of compound **5w** in $CDCl_3$.

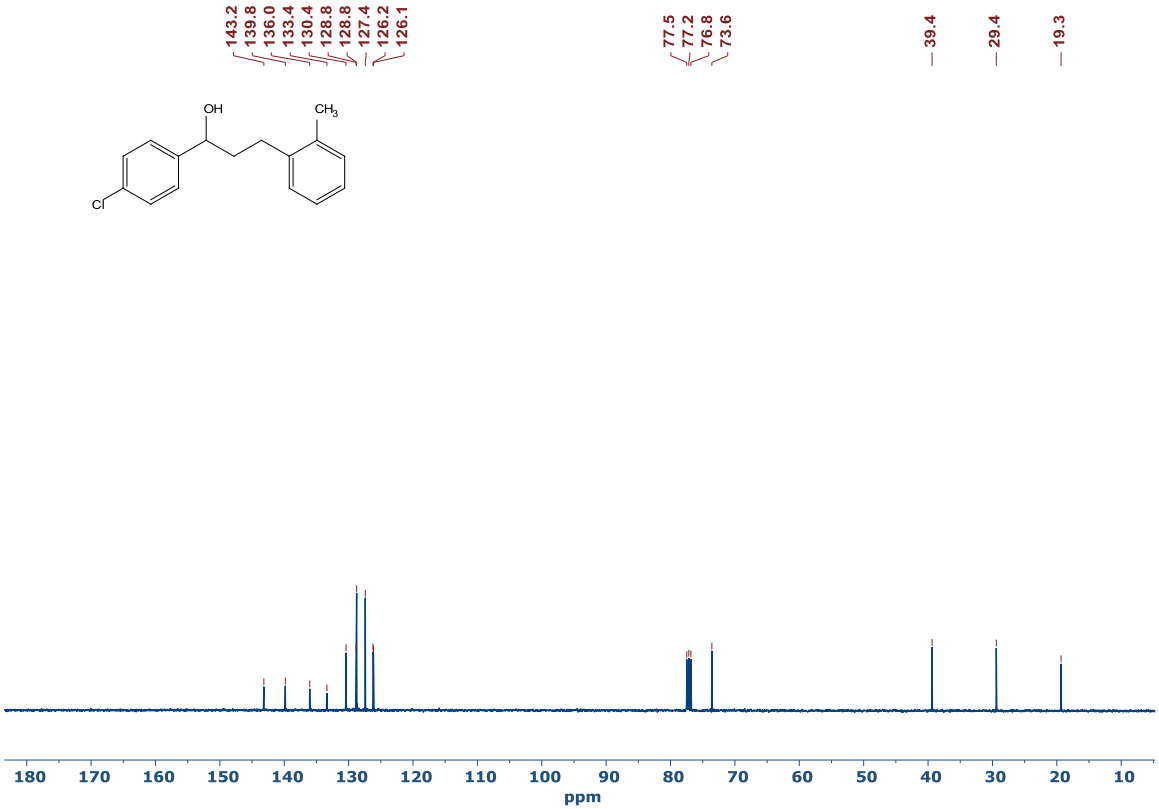


Figure S48. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5w** in $CDCl_3$.

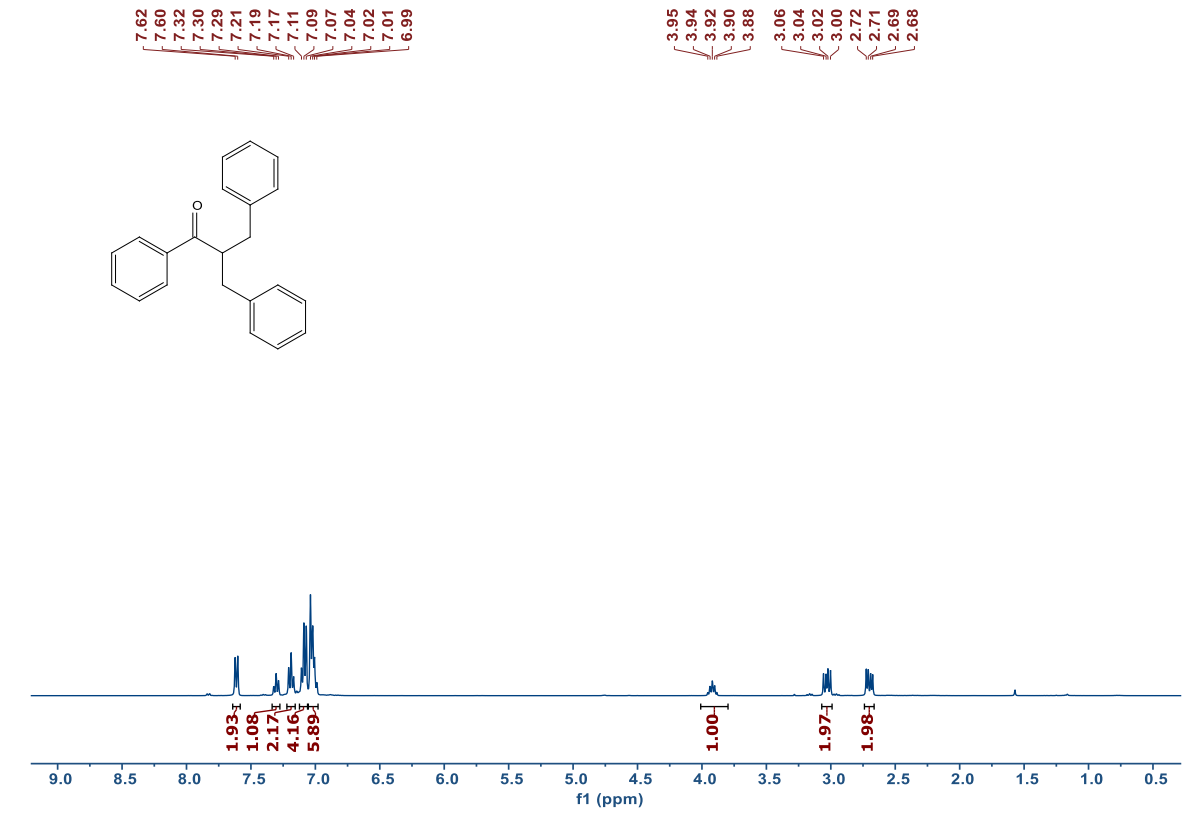


Figure S49. ^{1}H NMR spectrum of compound **6a** in $CDCl_3$.

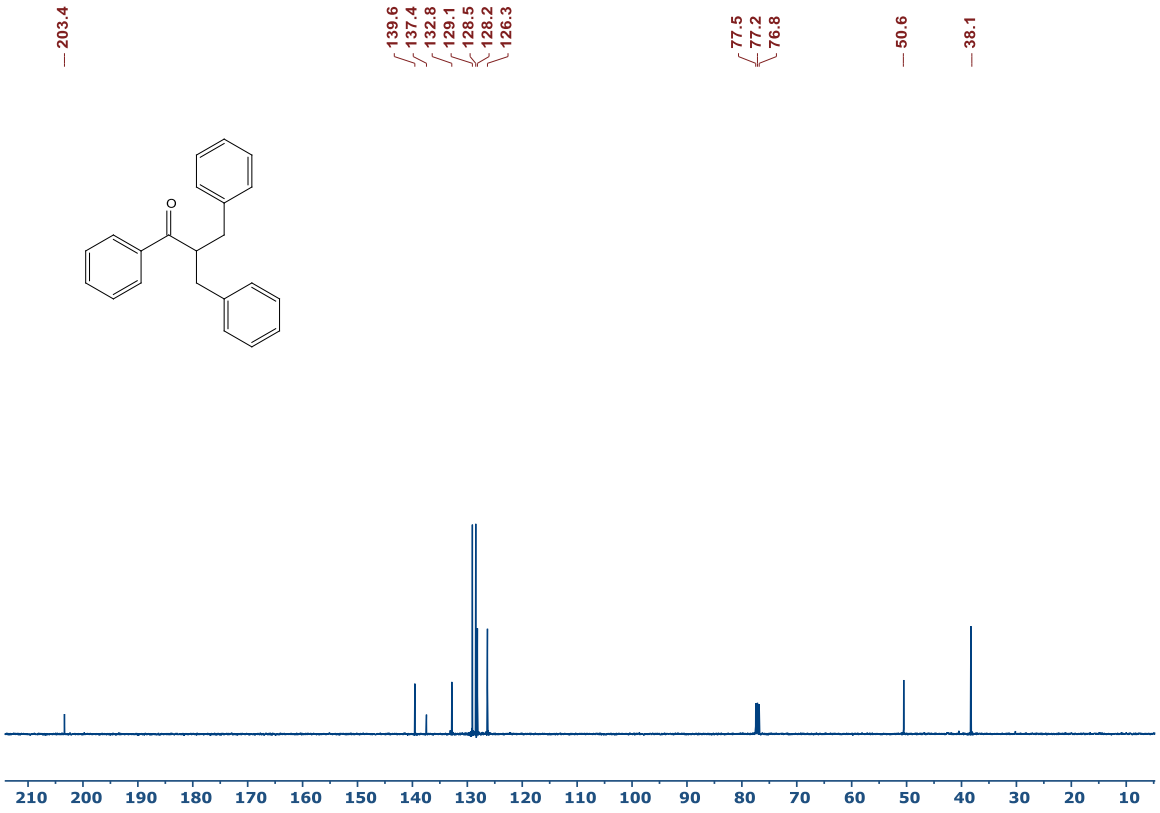


Figure S50. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6a** in $CDCl_3$.

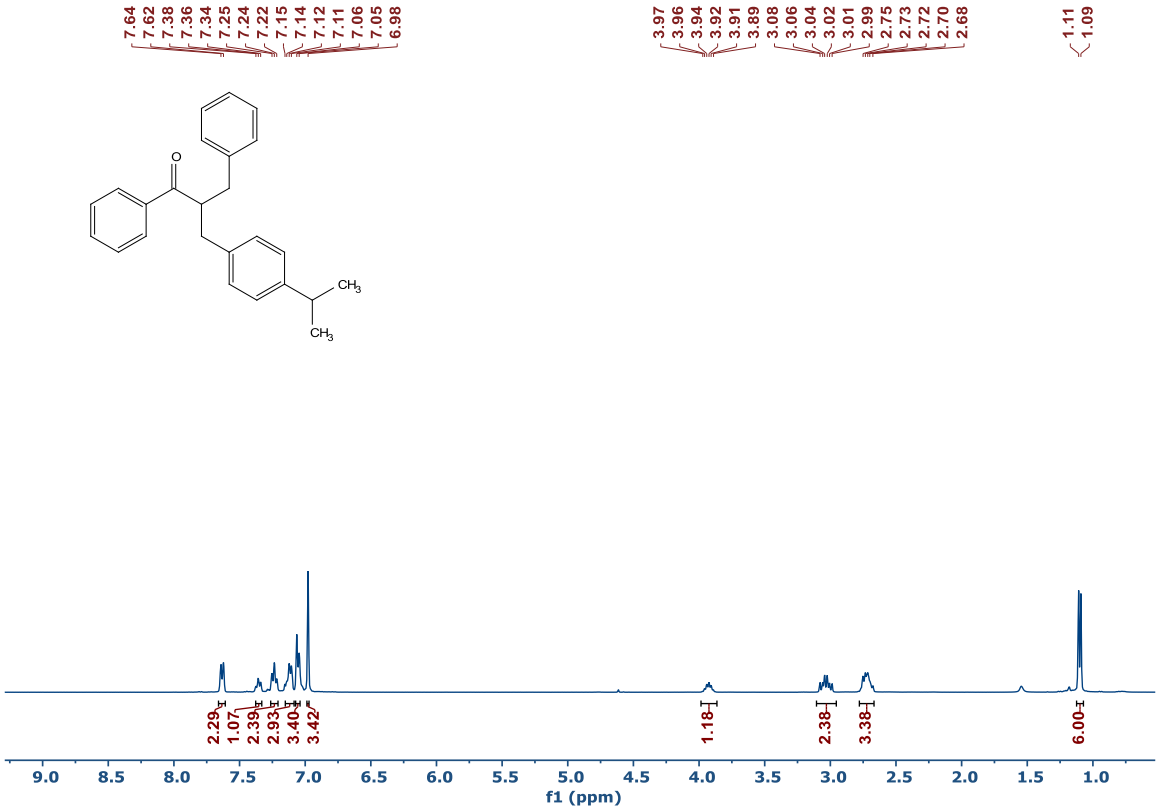


Figure S51. ^{1}H NMR spectrum of compound **6b** in $CDCl_3$.

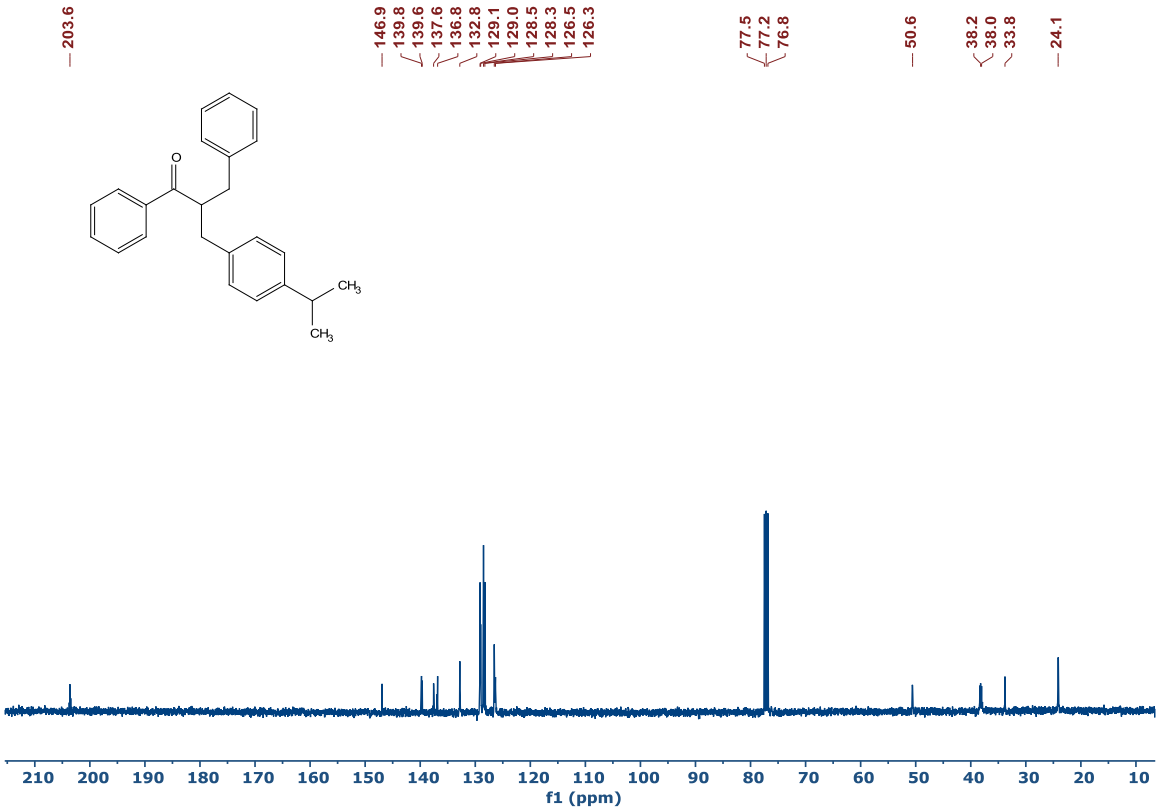


Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6b** in $CDCl_3$.

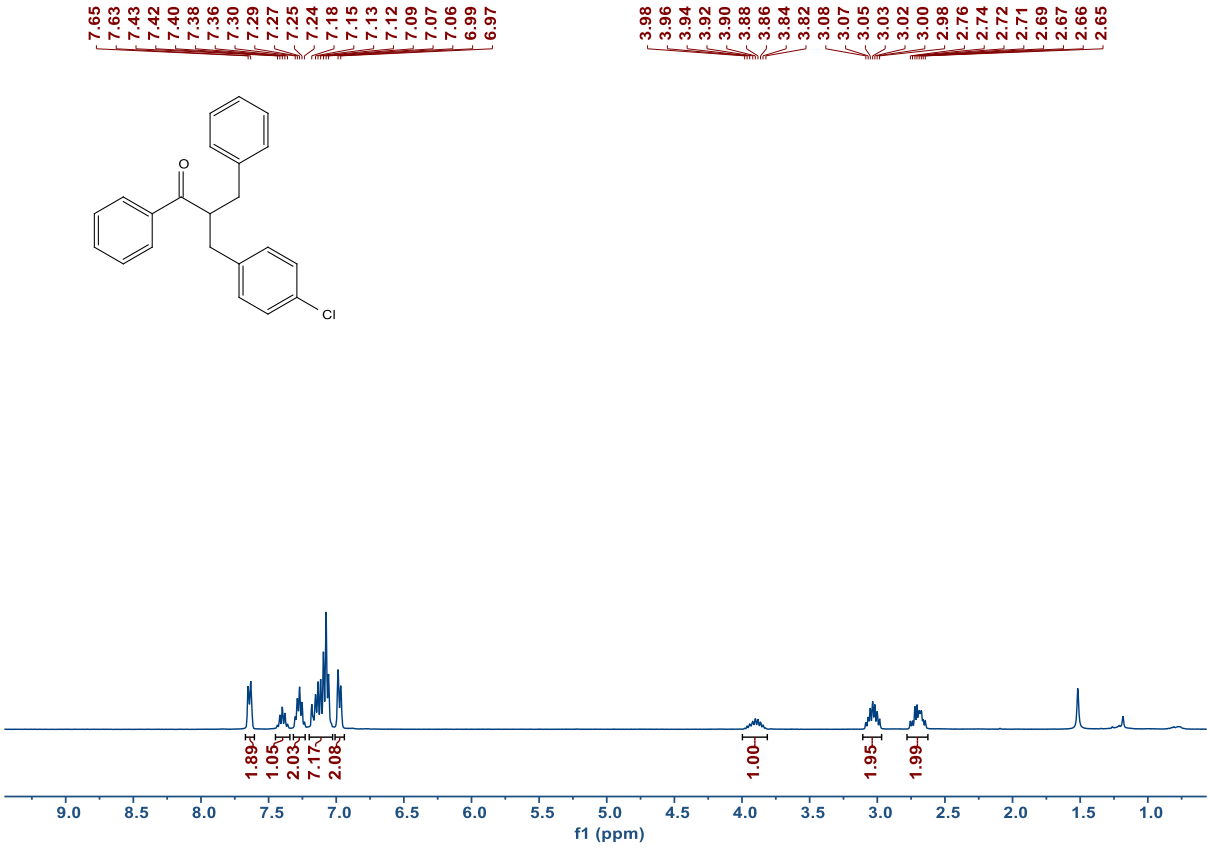


Figure S53. ^{1}H NMR spectrum of compound **6c** in $CDCl_3$.

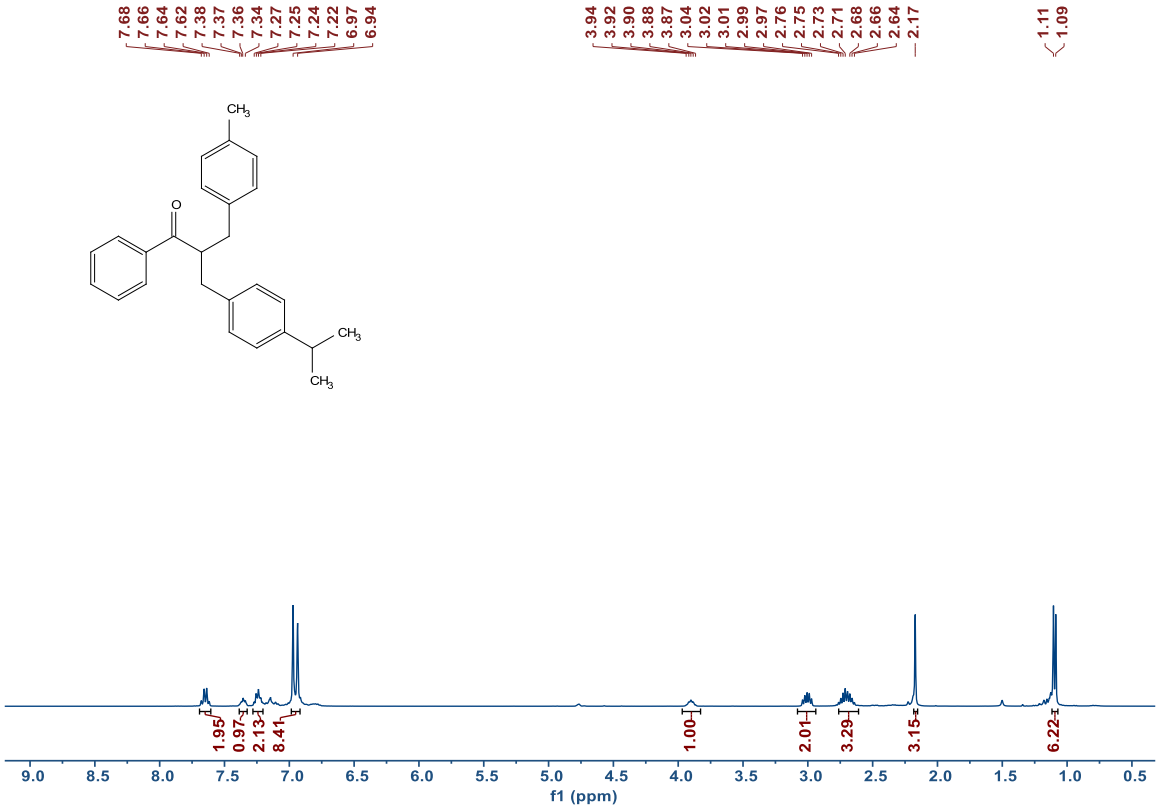


Figure S54. ^{1}H NMR spectrum of compound **6d** in $CDCl_3$.

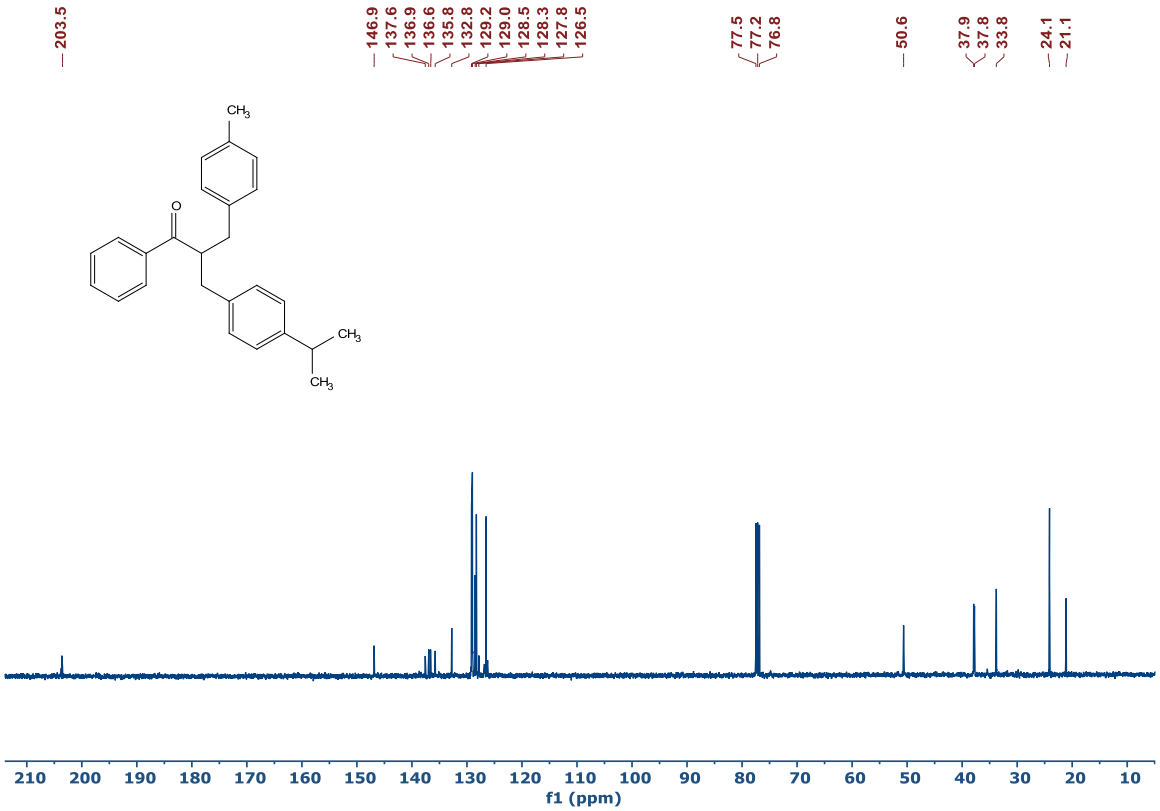


Figure S55. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6d** in $CDCl_3$.

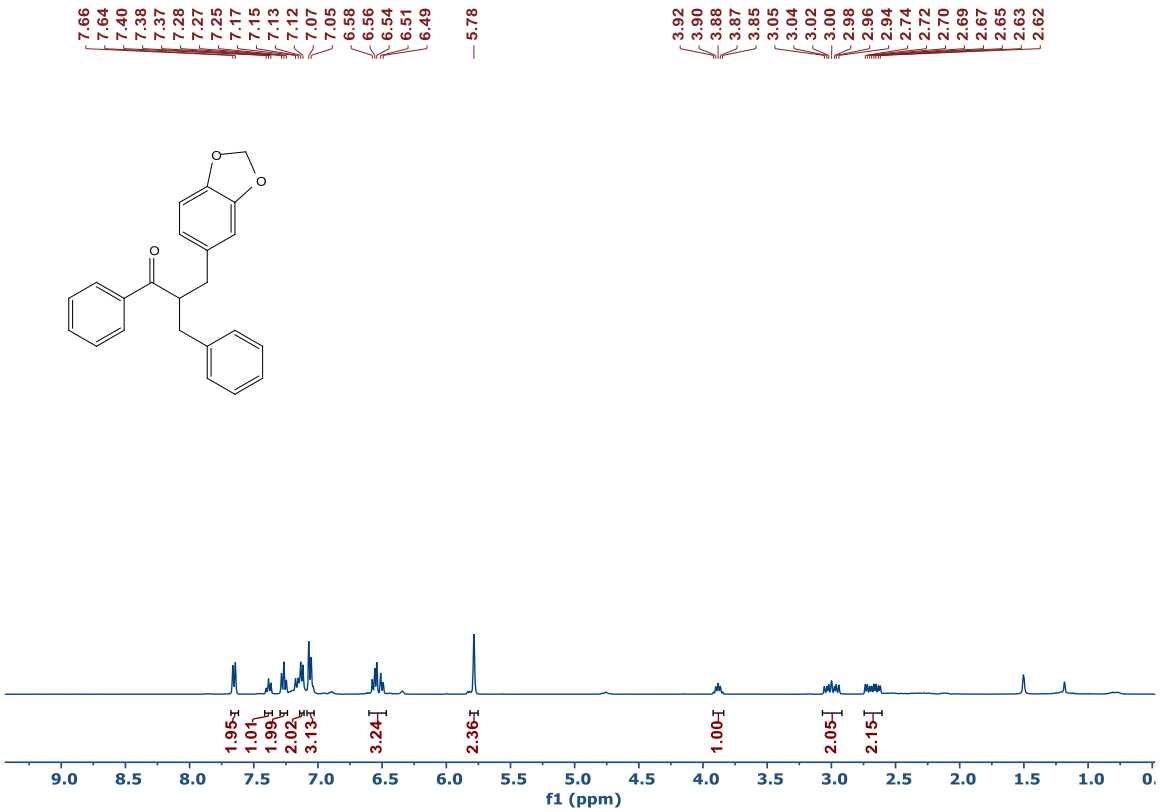


Figure S56. ^{1}H NMR spectrum of compound **6e** in $CDCl_3$.

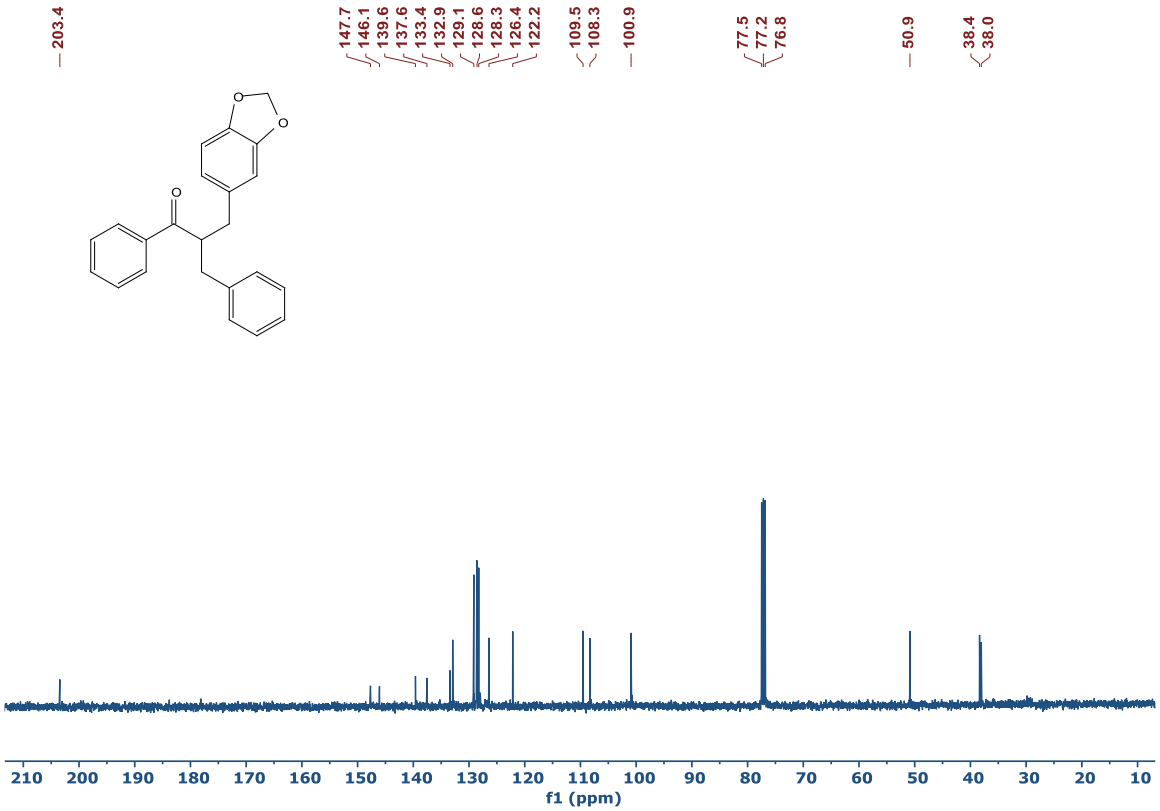


Figure S57. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6e** in $CDCl_3$.

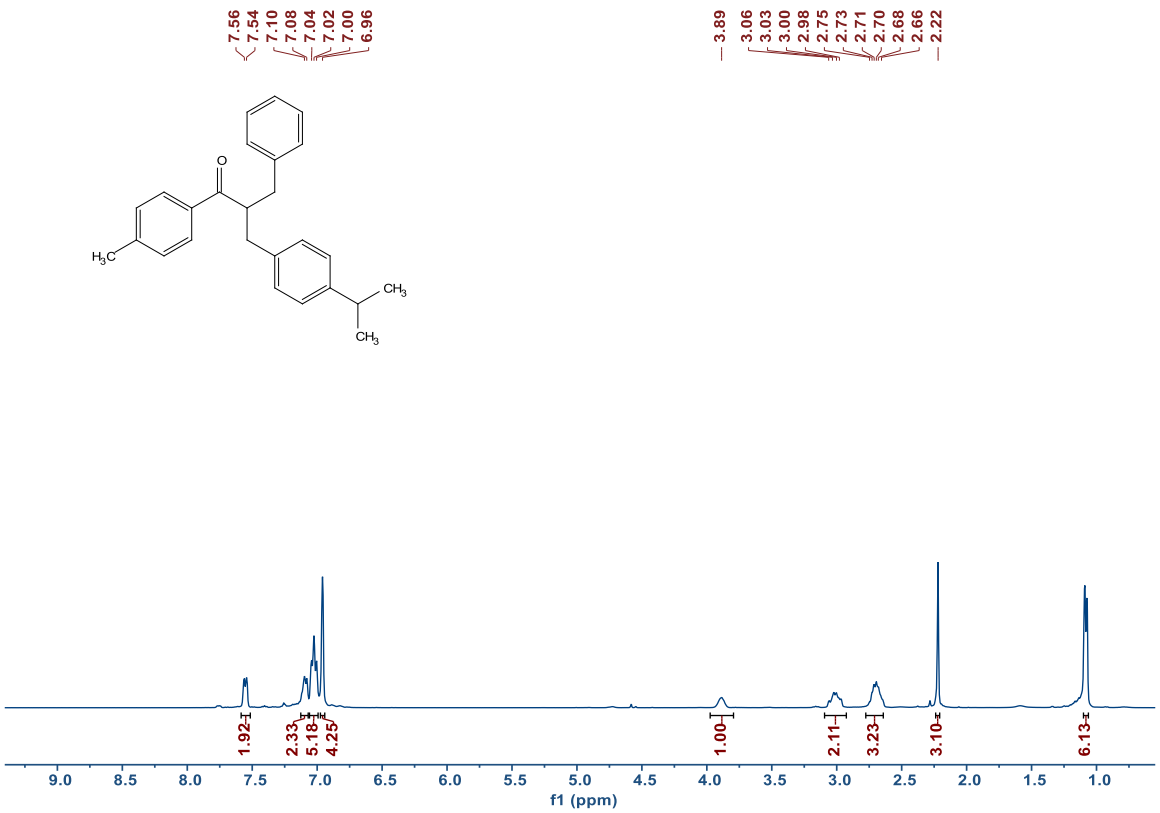


Figure S58. ^{1}H NMR spectrum of compound **6f** in $CDCl_3$.

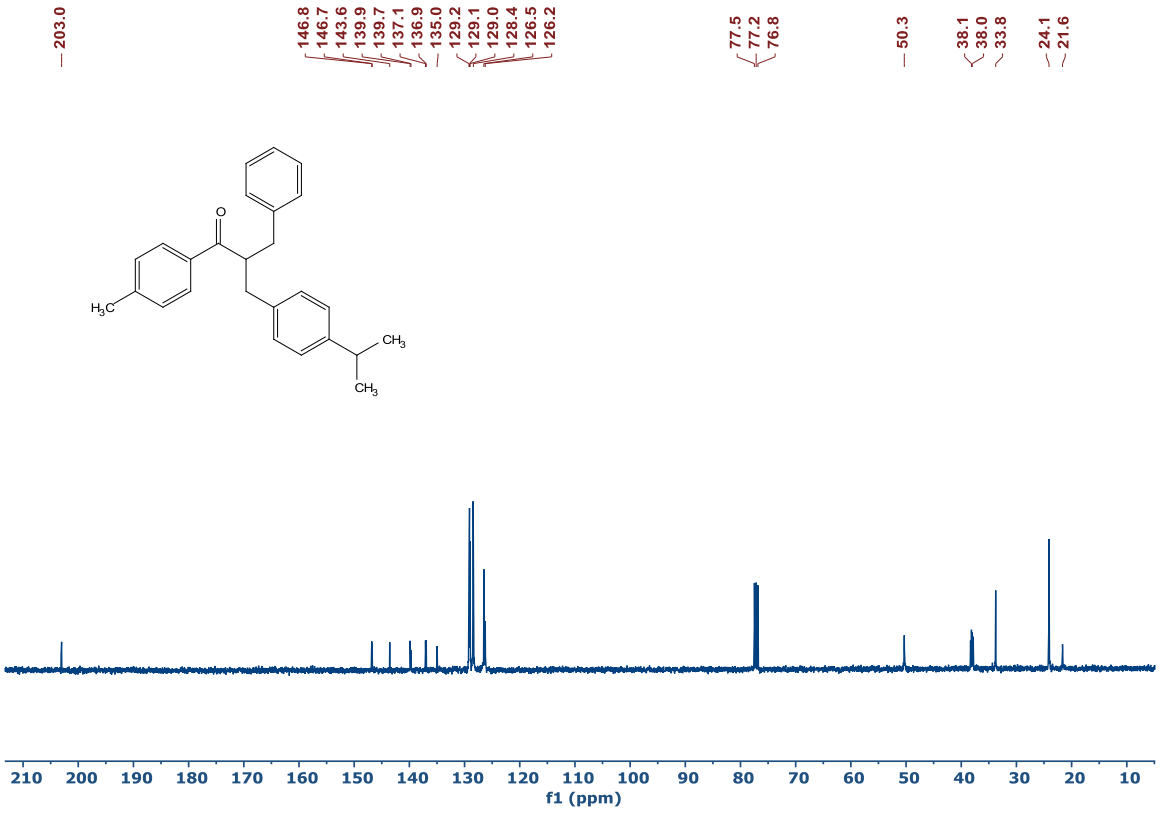


Figure S59. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6f** in $CDCl_3$.

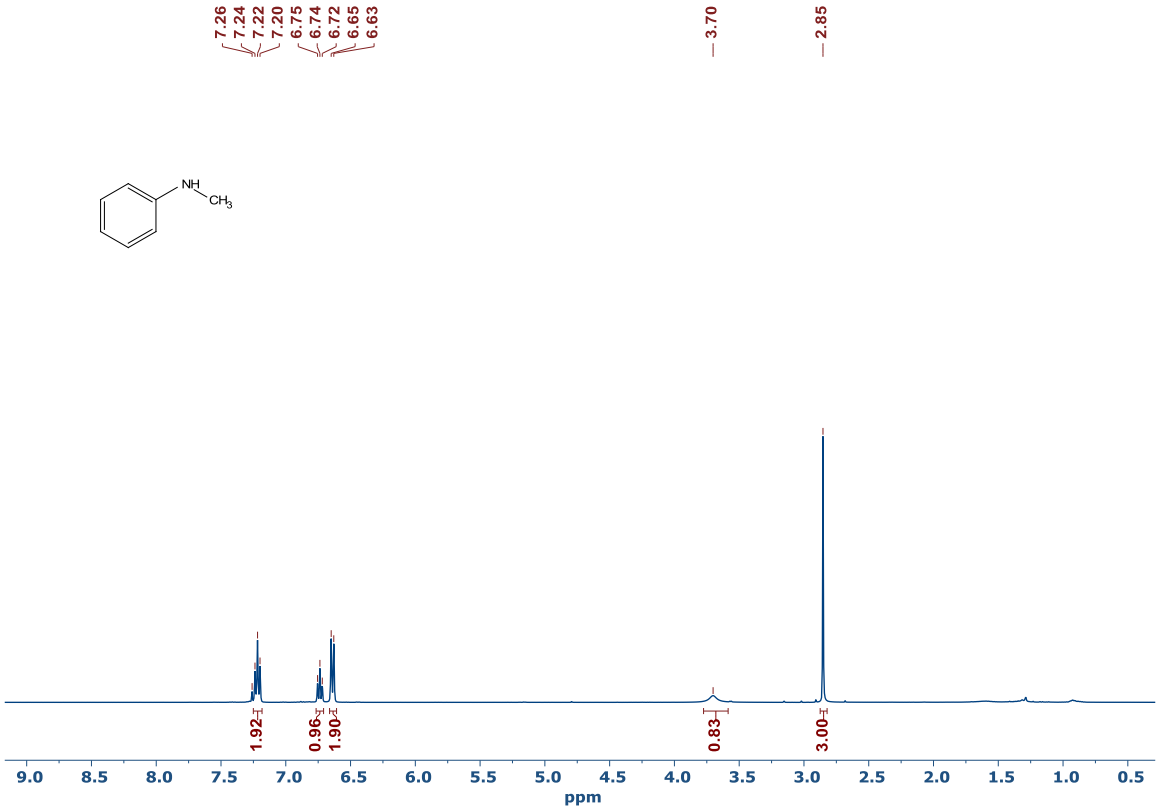


Figure S60. ^{1}H NMR spectrum of compound **8a** in $CDCl_3$.

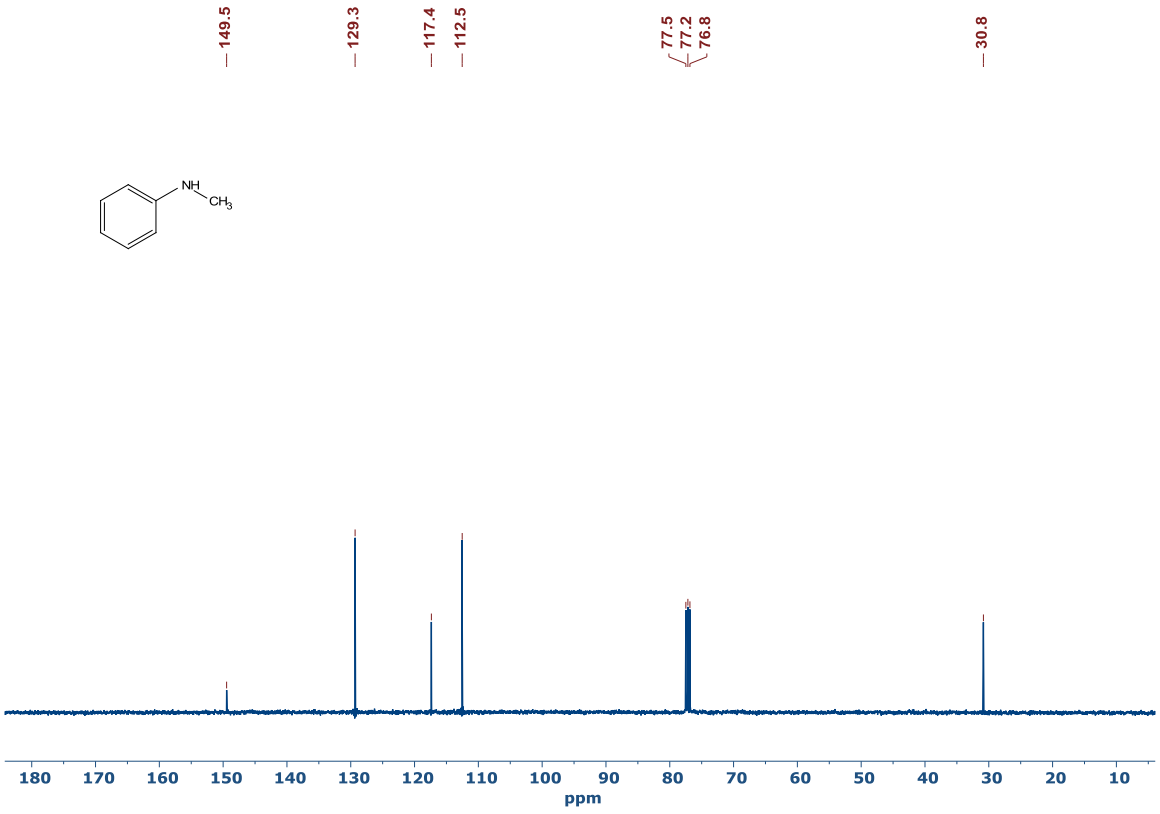


Figure S61. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8a** in $CDCl_3$.

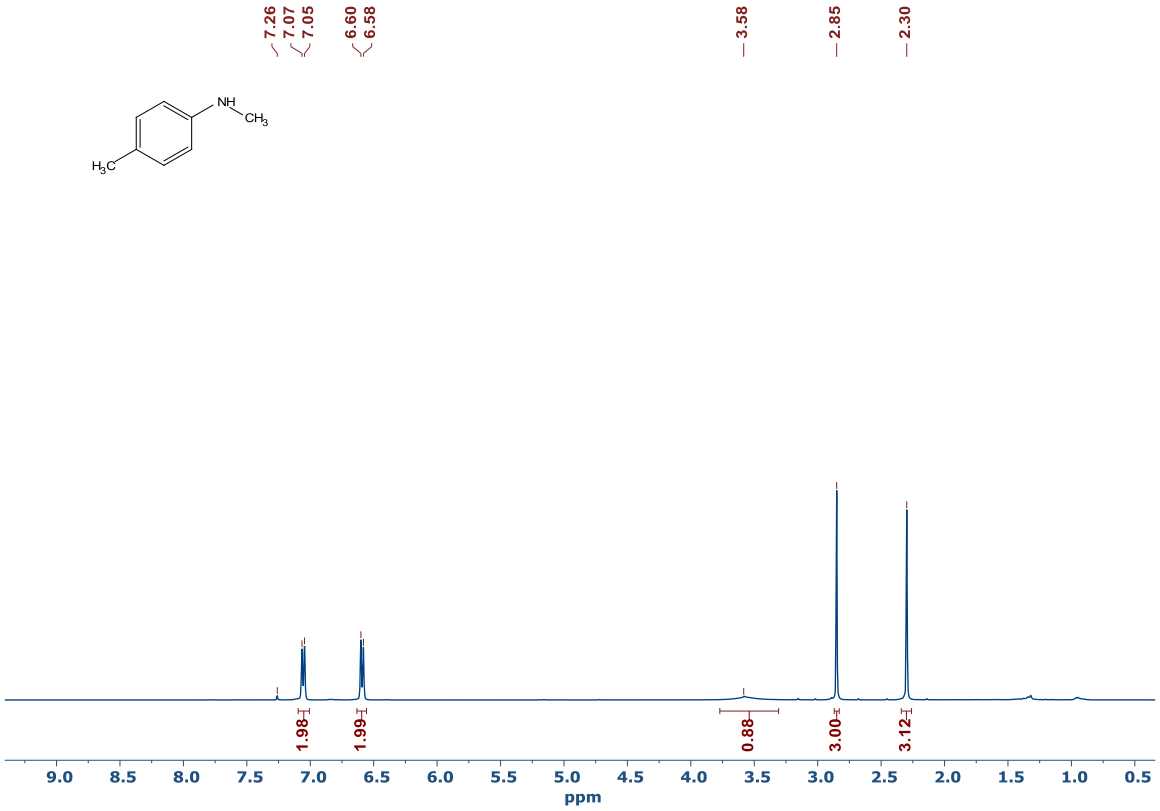


Figure S62. ^{1}H NMR spectrum of compound **8b** in $CDCl_3$.

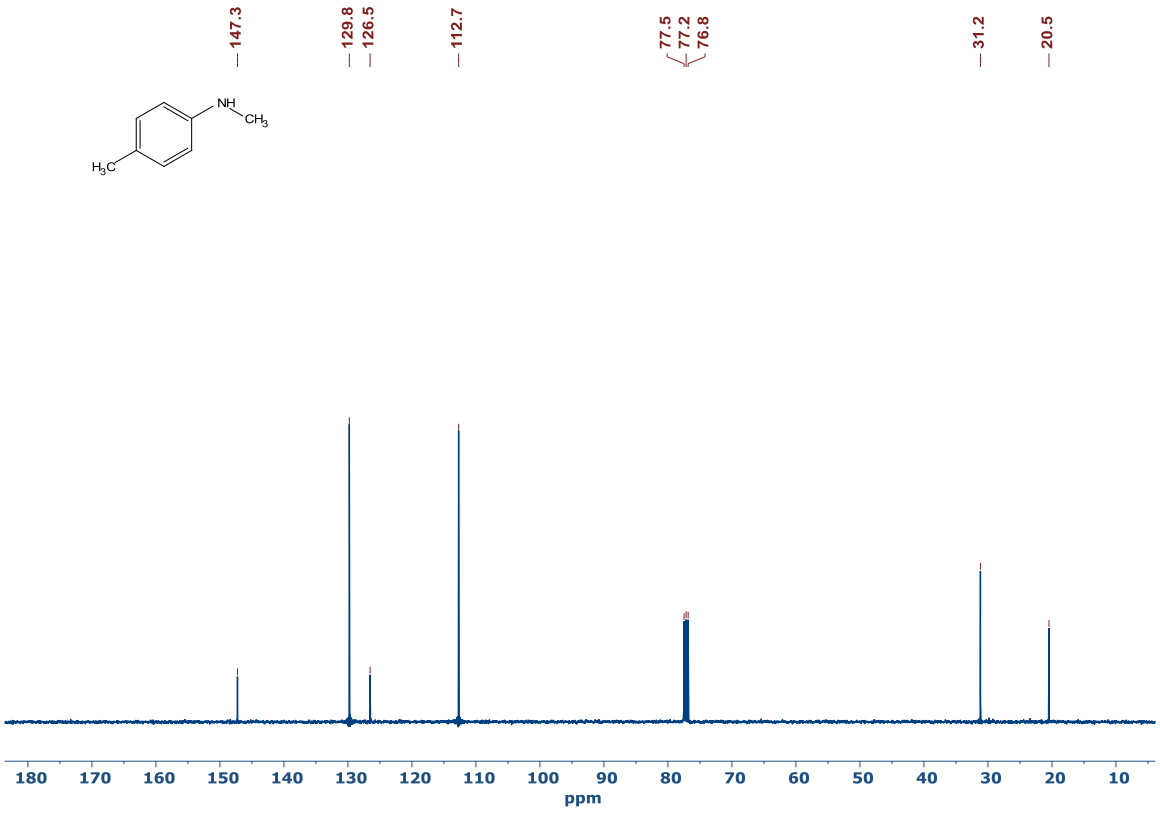


Figure S63. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8b** in $CDCl_3$.

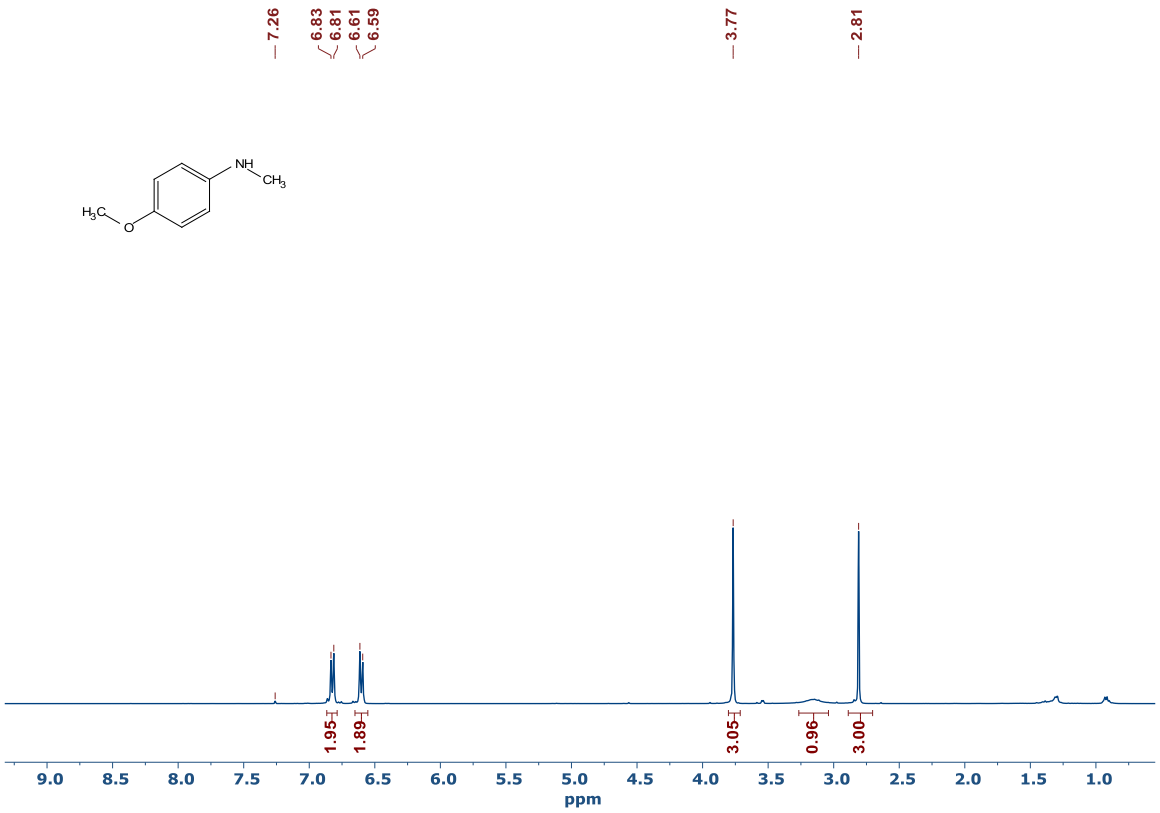


Figure S64. ^{1}H NMR spectrum of compound **8c** in $CDCl_3$.

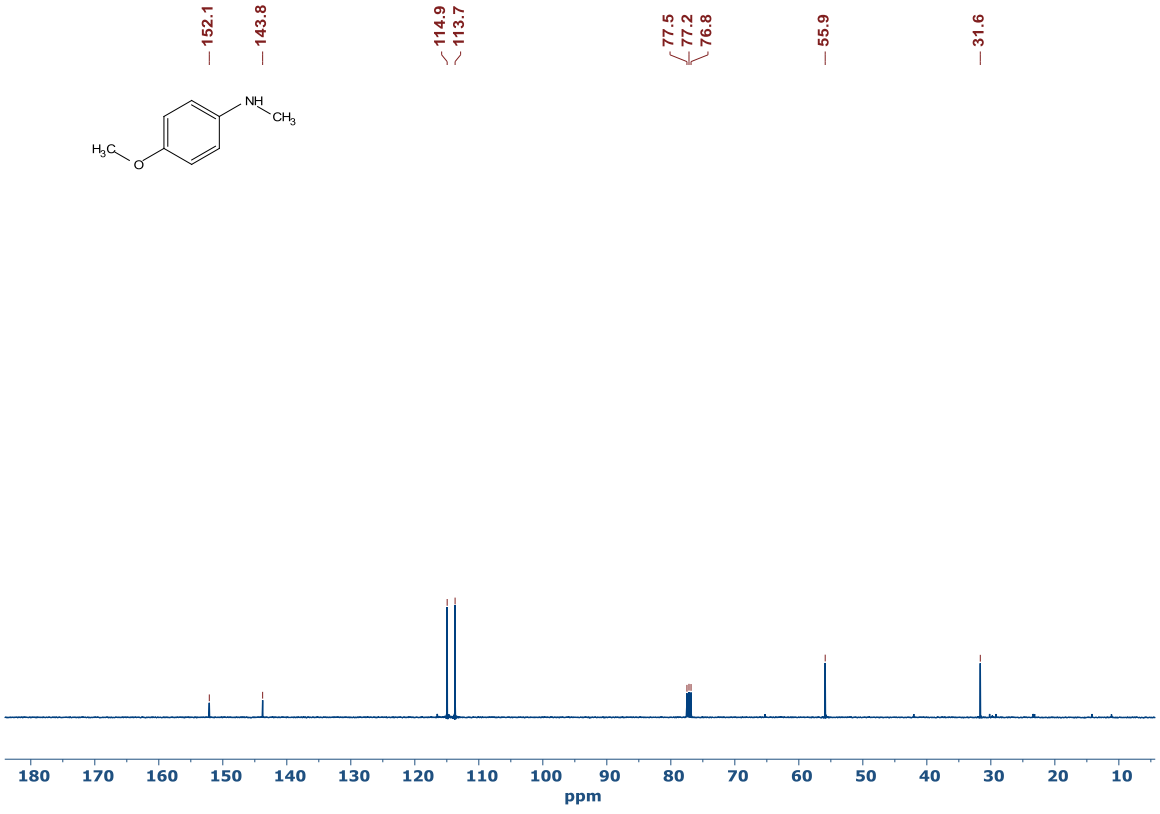


Figure S65. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8c** in $CDCl_3$.

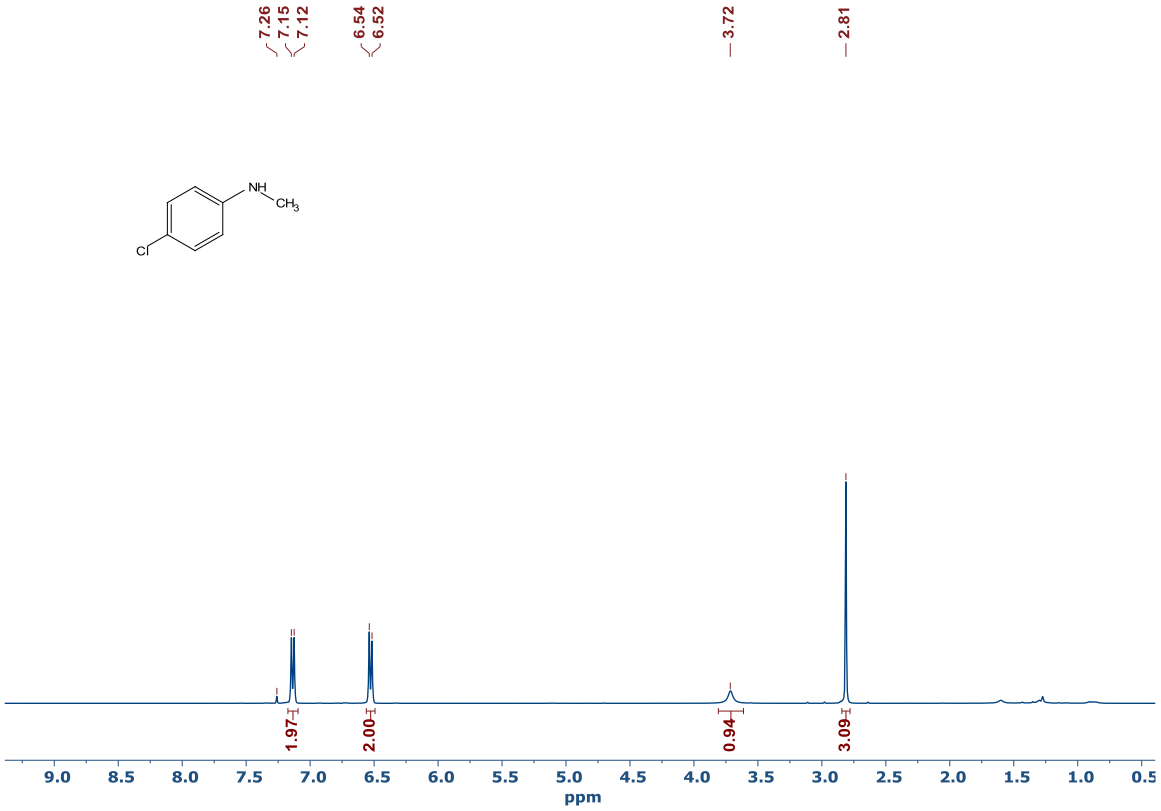


Figure S66. ^{1}H NMR spectrum of compound **8d** in $CDCl_3$.

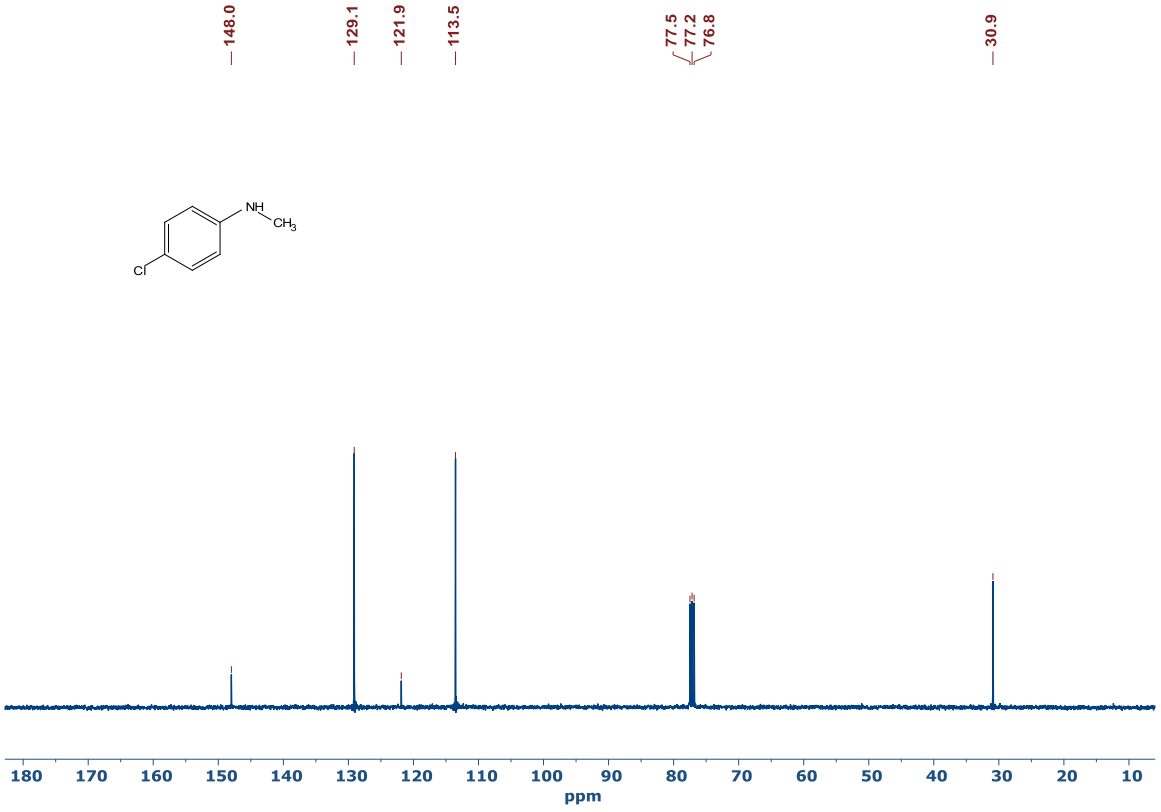


Figure S67. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8d** in $CDCl_3$.

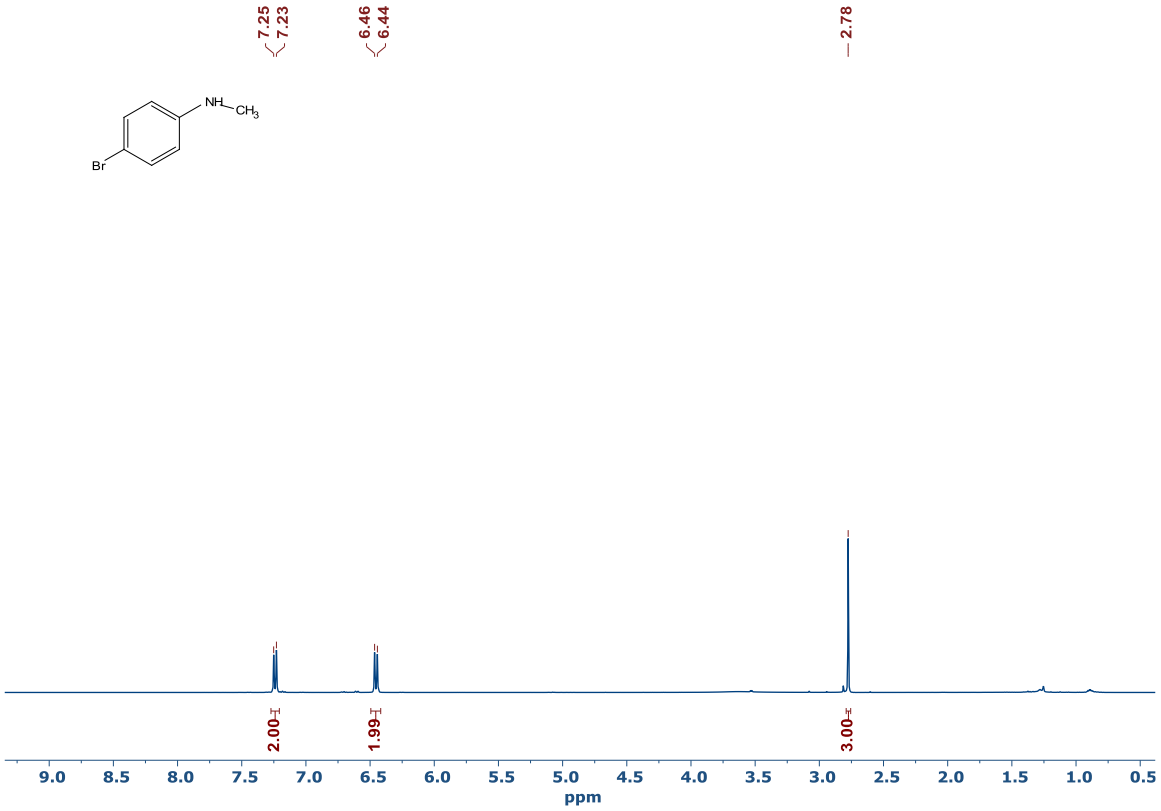


Figure S68. ^{1}H NMR spectrum of compound **8e** in $CDCl_3$.

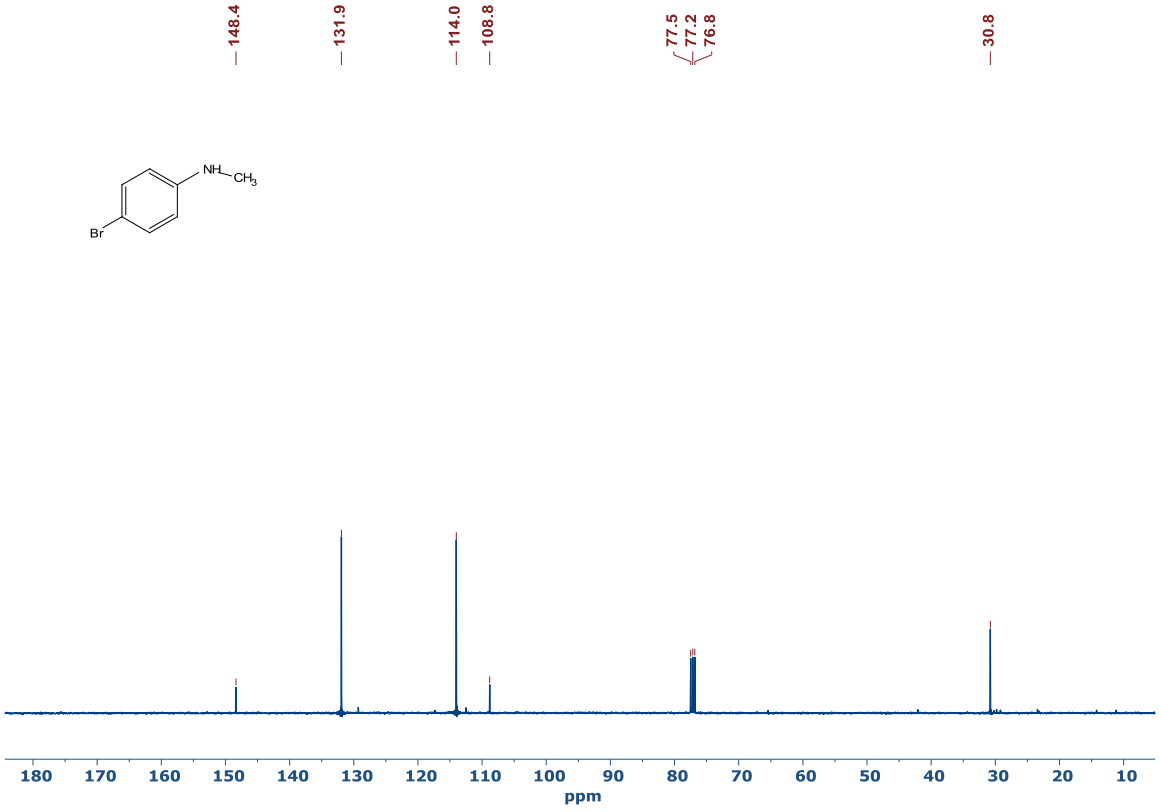


Figure S69. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8e** in $CDCl_3$.

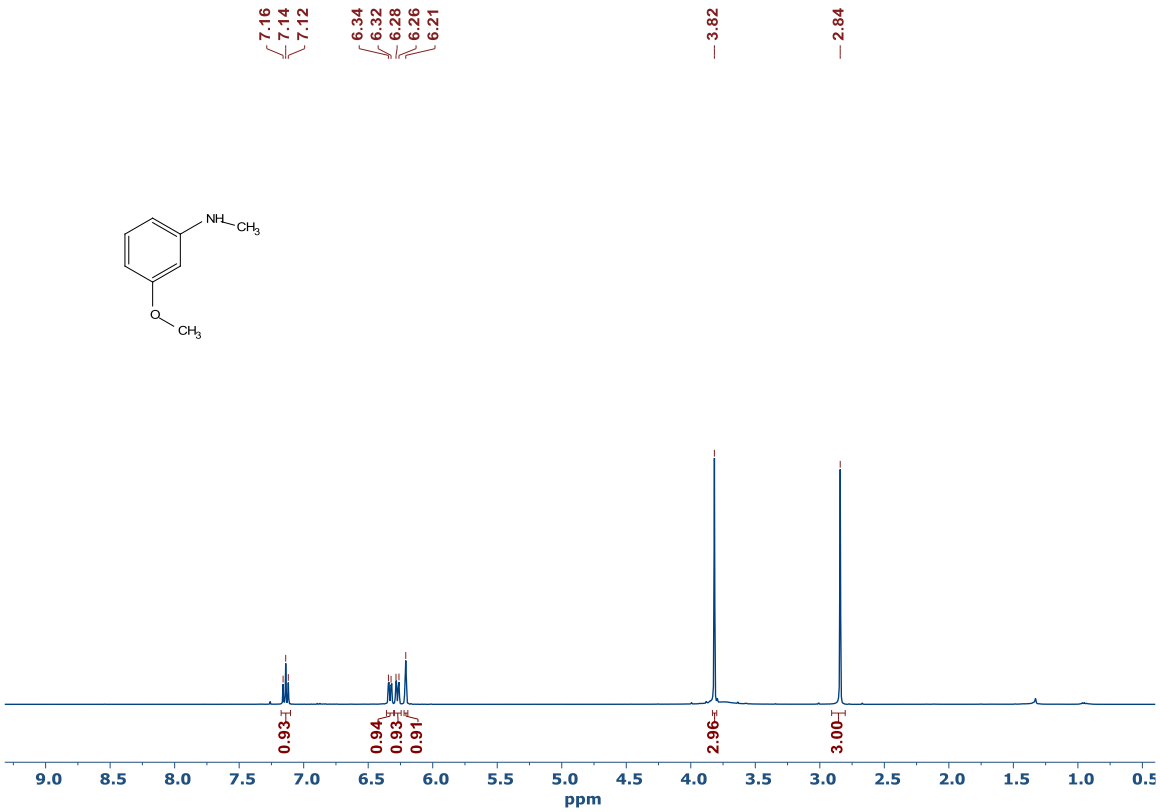


Figure S70. ^{1}H NMR spectrum of compound **8f** in $CDCl_3$.

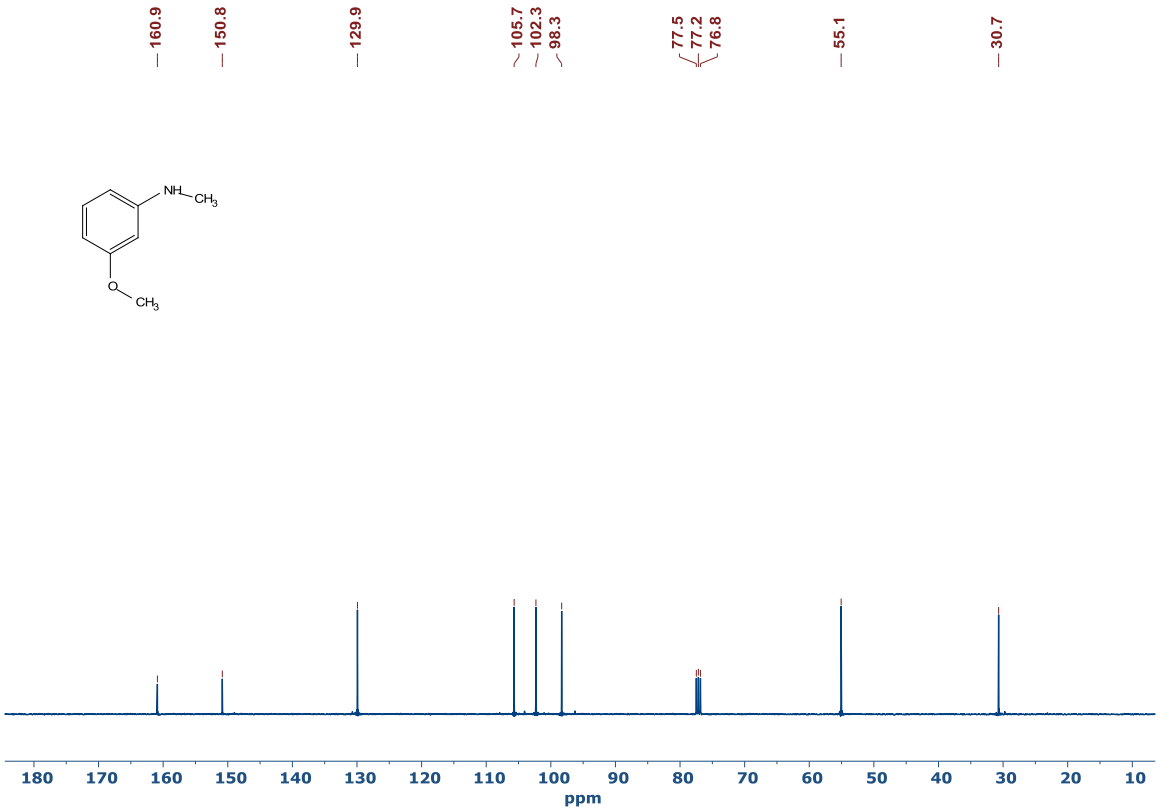


Figure S71. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8f** in $CDCl_3$.

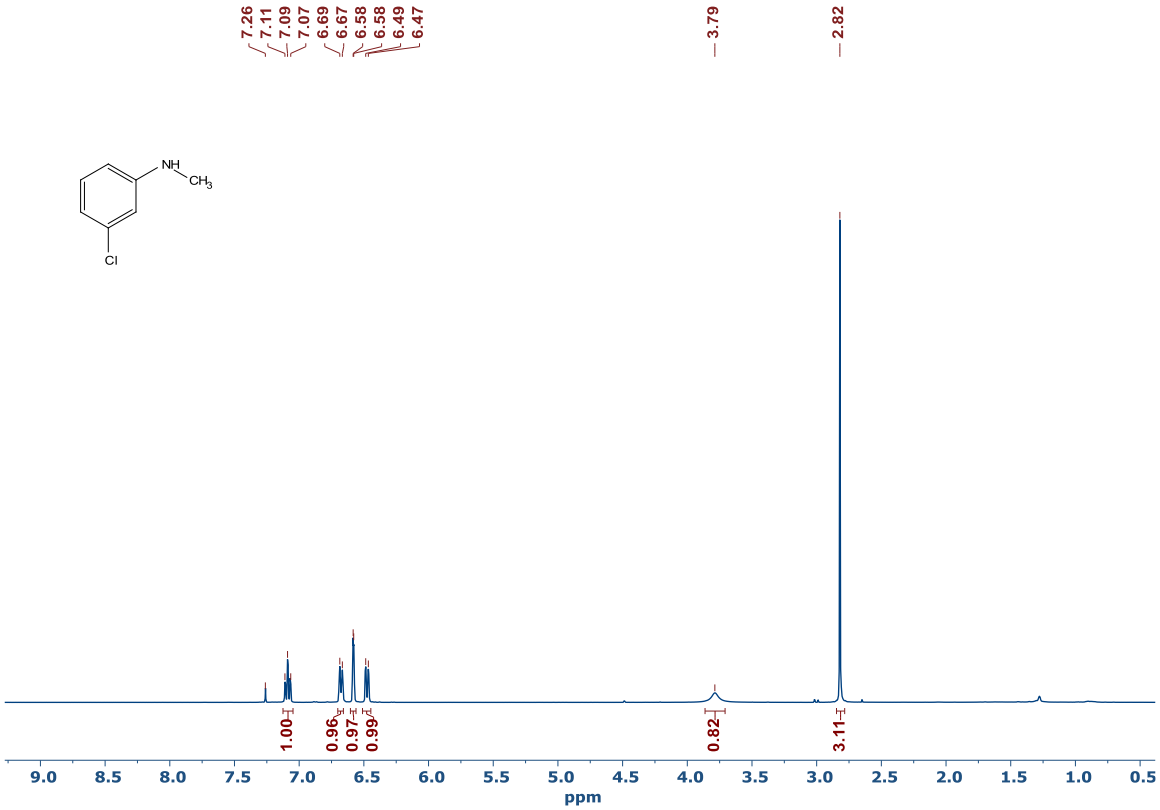


Figure S72. ^{1}H NMR spectrum of compound **8g** in $CDCl_3$.

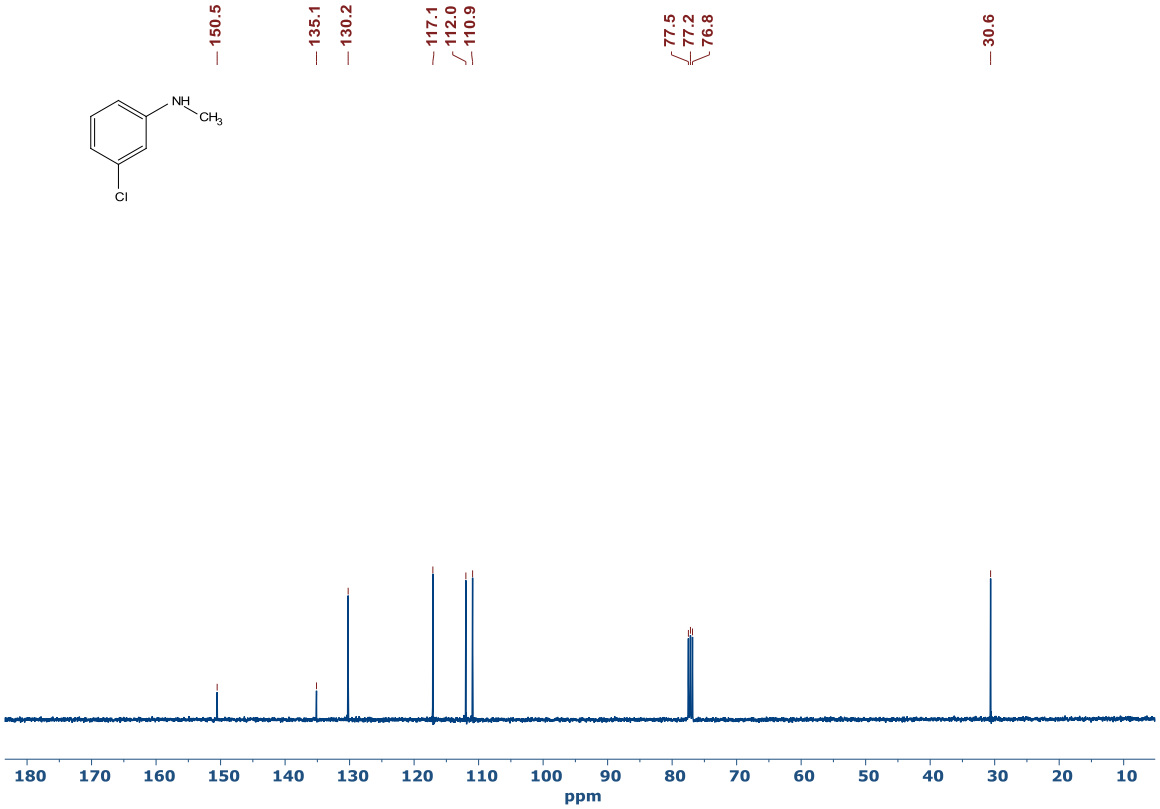


Figure S73. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8g** in $CDCl_3$.

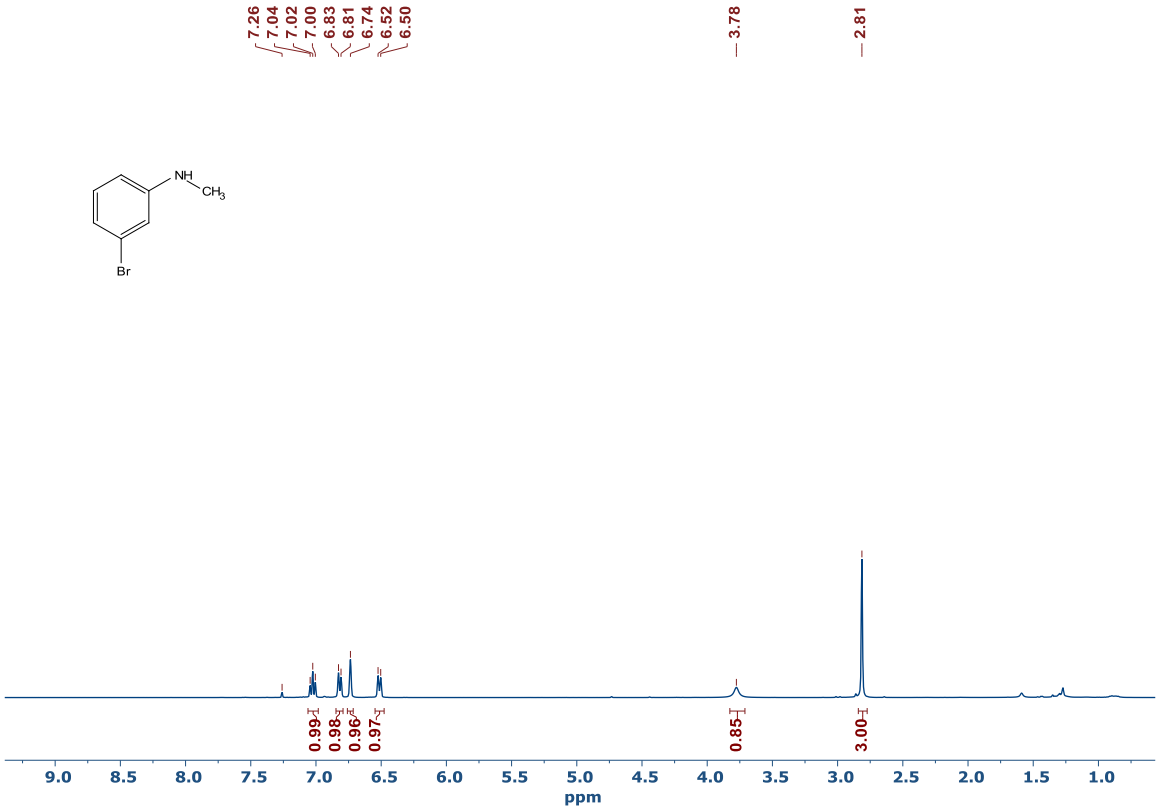


Figure S74. ^{1}H NMR spectrum of compound **8h** in $CDCl_3$.

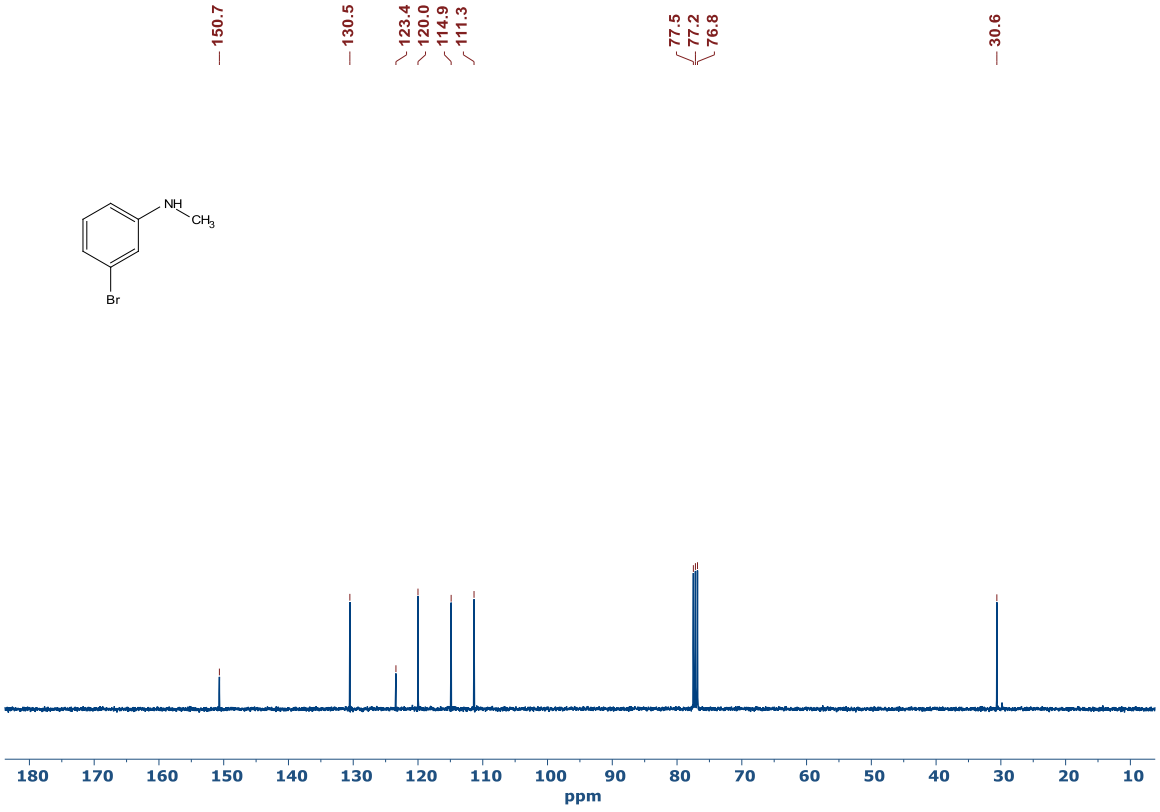


Figure S75. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8h** in $CDCl_3$.

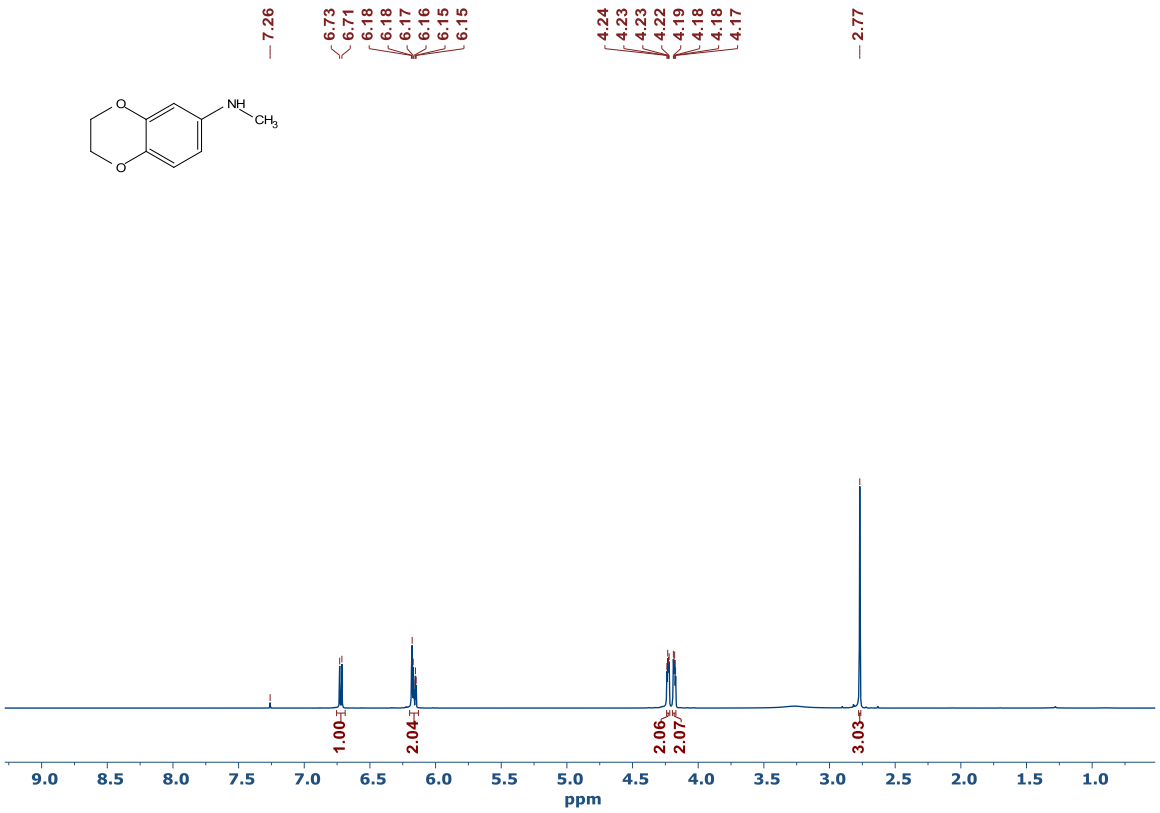


Figure S76. ^{1}H NMR spectrum of compound **8i** in $CDCl_3$.

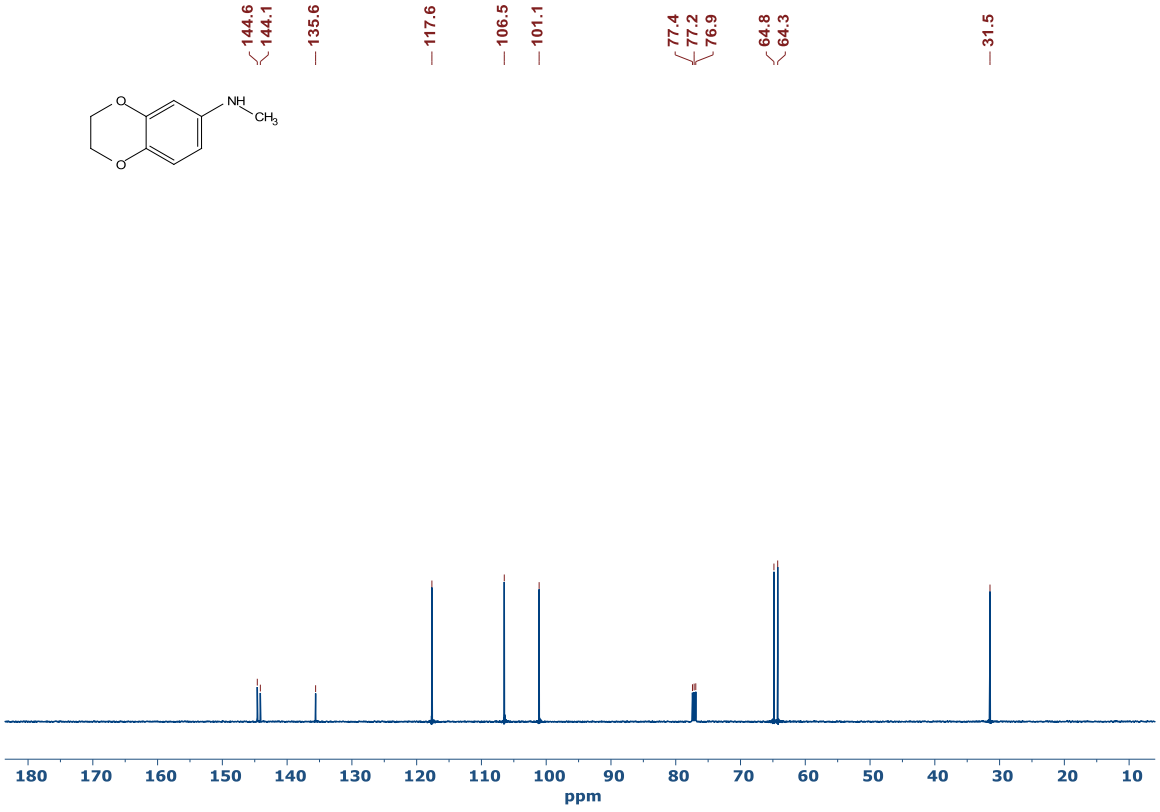


Figure S77. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8i** in $CDCl_3$.

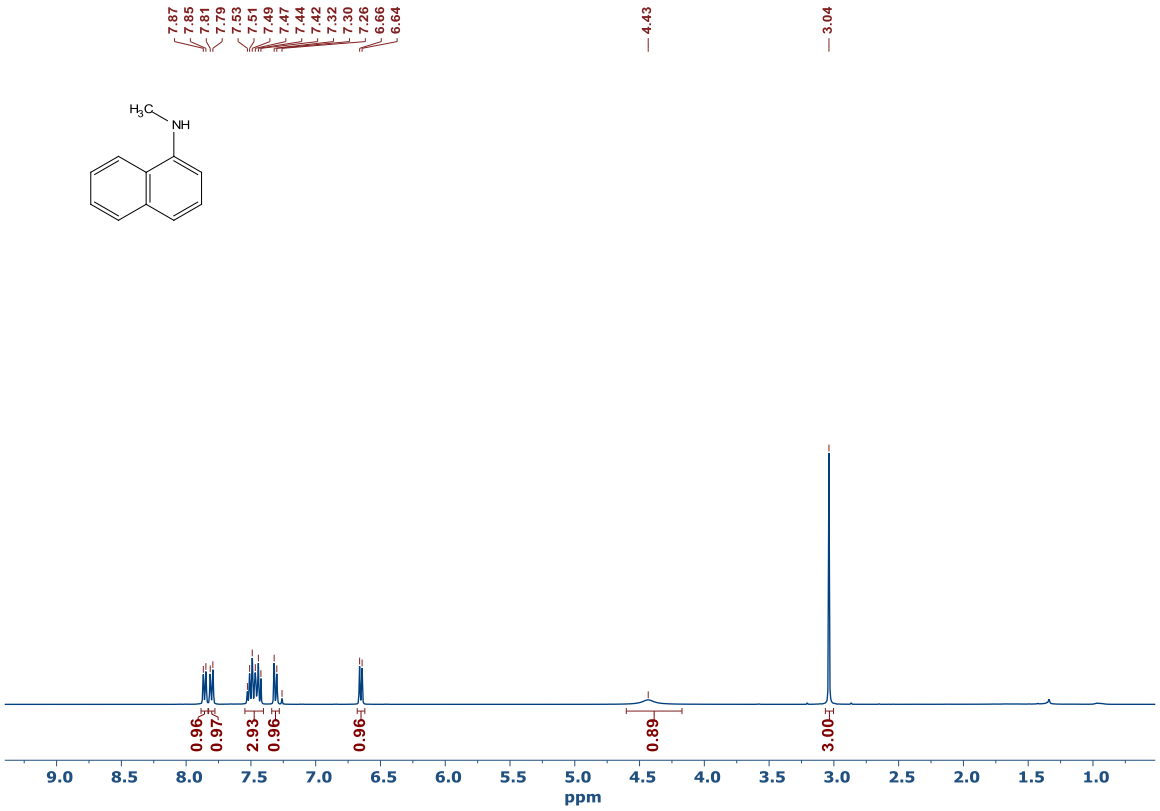


Figure S78. ^{1}H NMR spectrum of compound **8j** in $CDCl_3$.

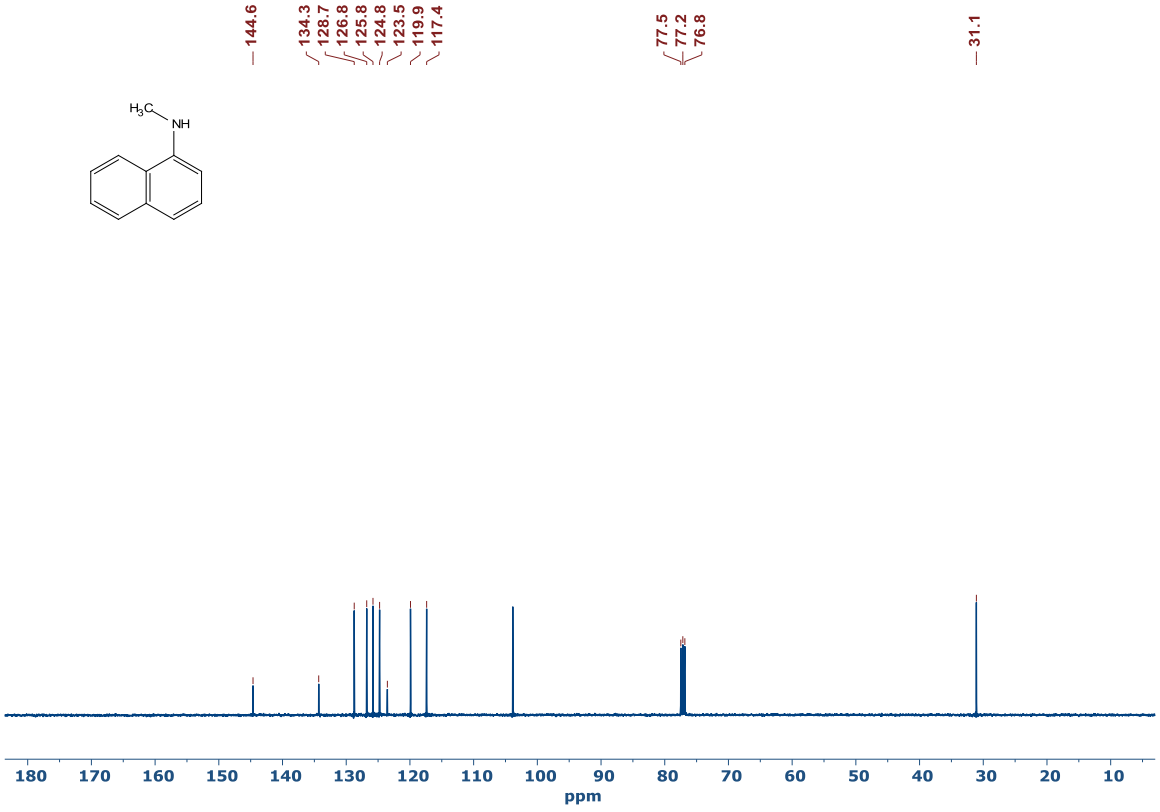


Figure S79. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8j** in $CDCl_3$.

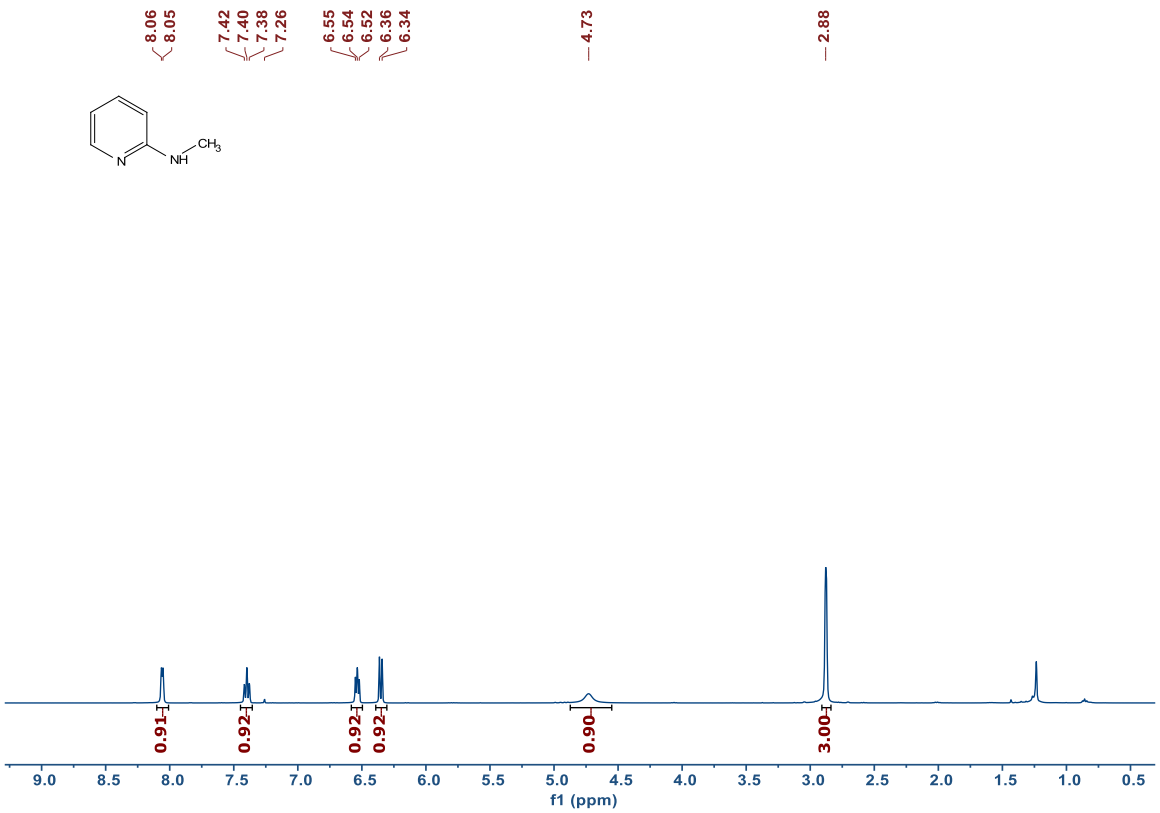


Figure S80. ^{1}H NMR spectrum of compound **8k** in $CDCl_3$.

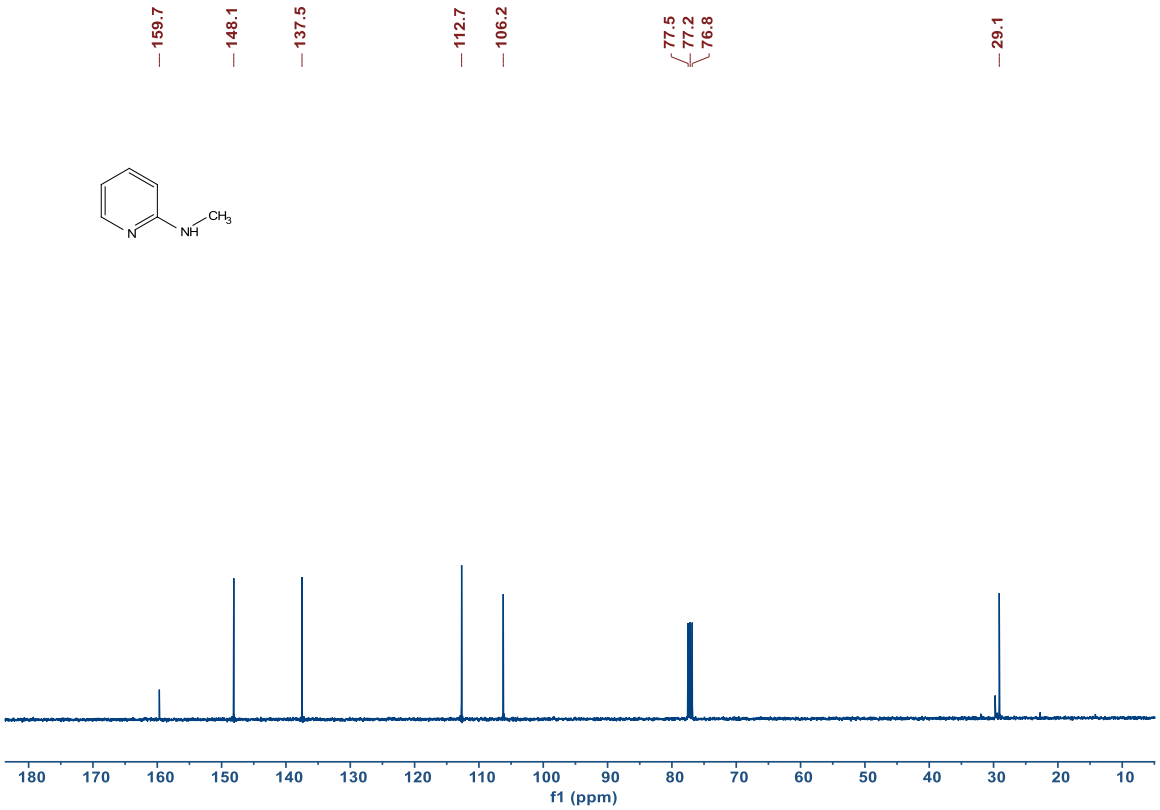


Figure S81. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8k** in $CDCl_3$.

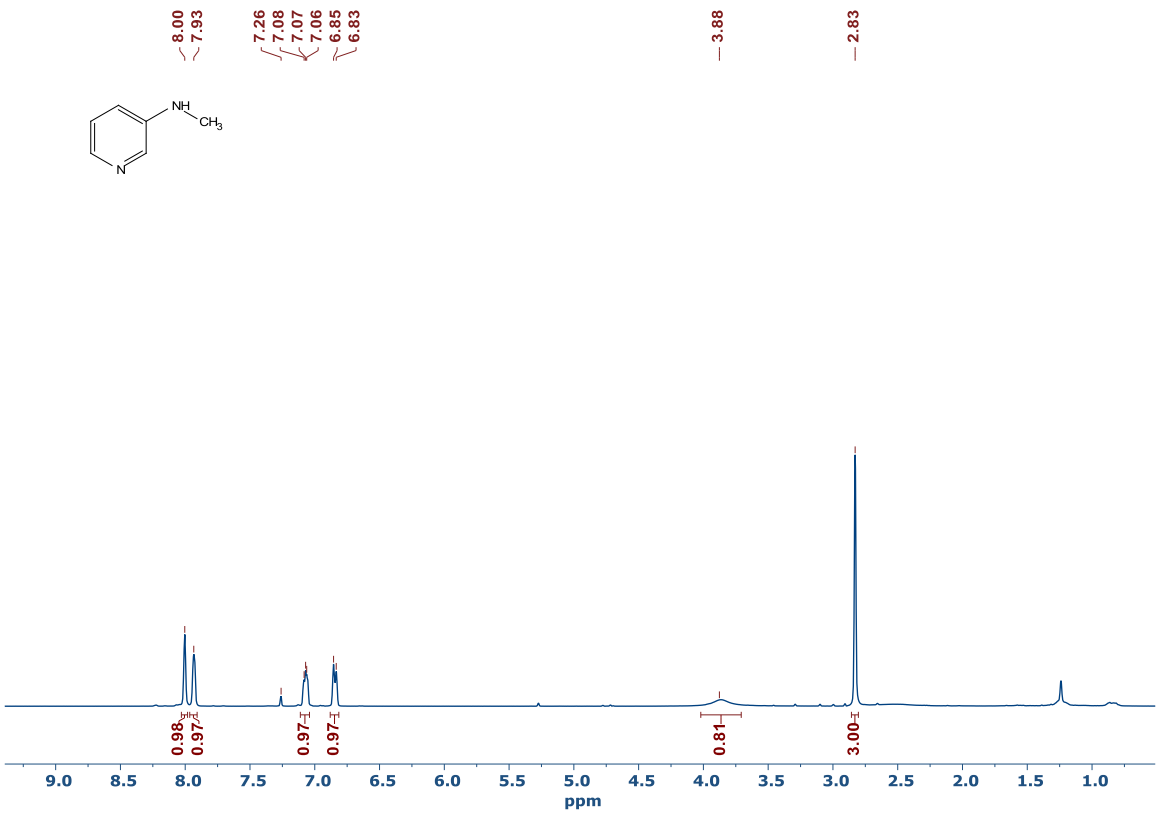


Figure S82. ^{1}H NMR spectrum of compound **8l** in $CDCl_3$.

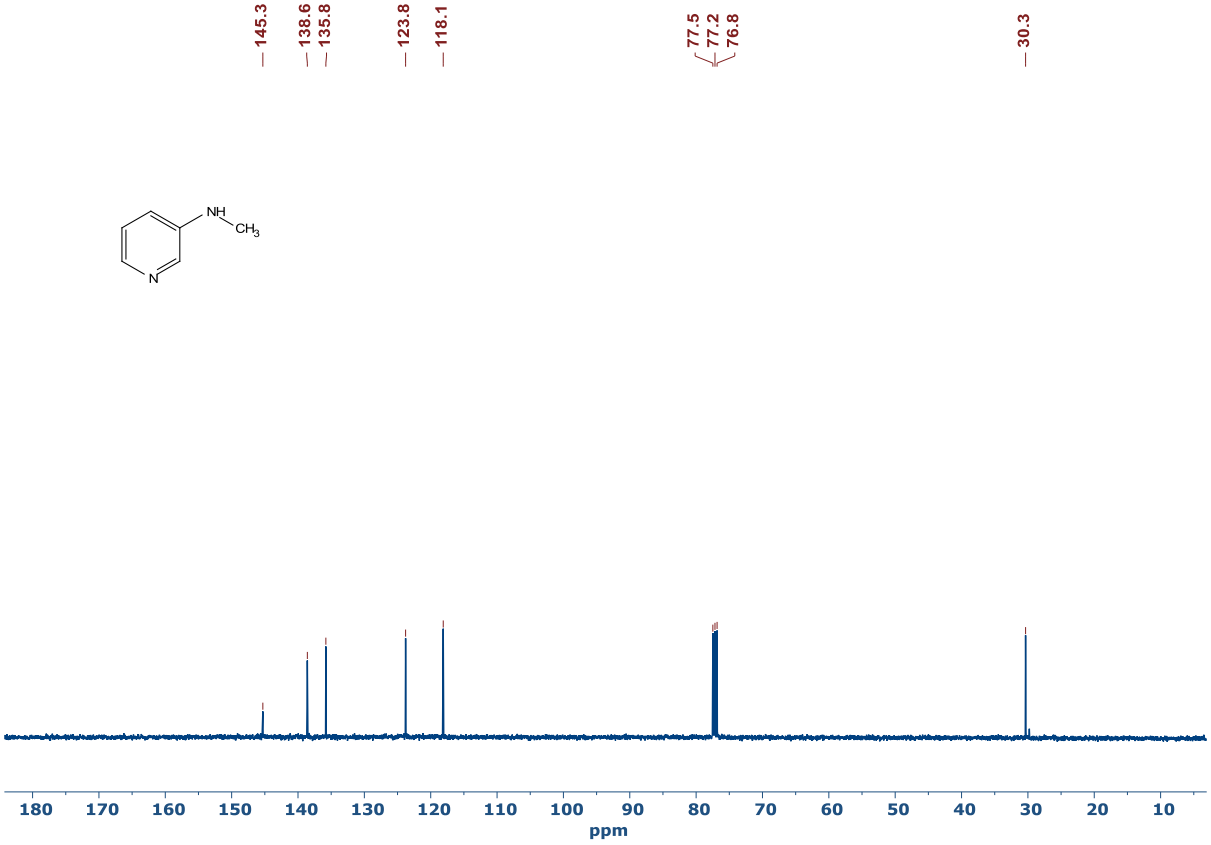


Figure S83. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8l** in $CDCl_3$.

Mechanistic studies

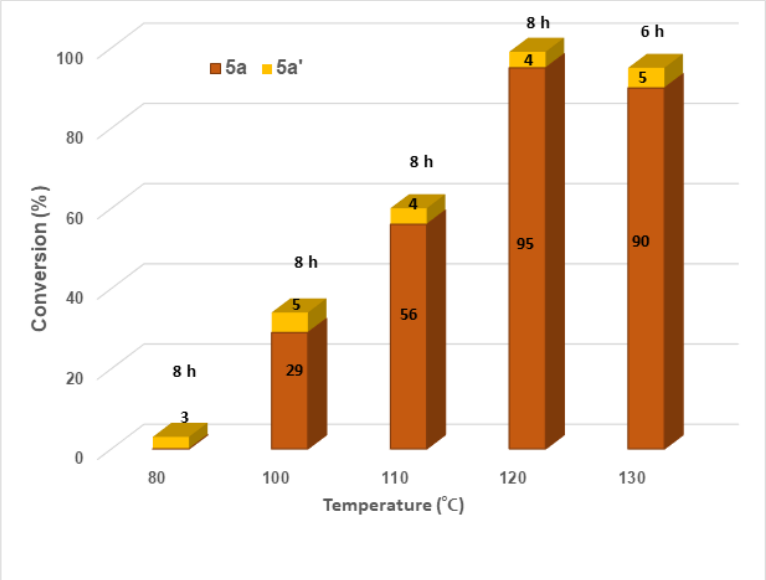


Figure S84. Effect of temperature on the reaction progress. Reaction conditions: 1-phenylethanol (1 mmol), benzyl alcohol (1.1 mmol), **2d** (0.01 mol%), KOH (0.20 mmol), and toluene (1 mL), 80-120 °C.

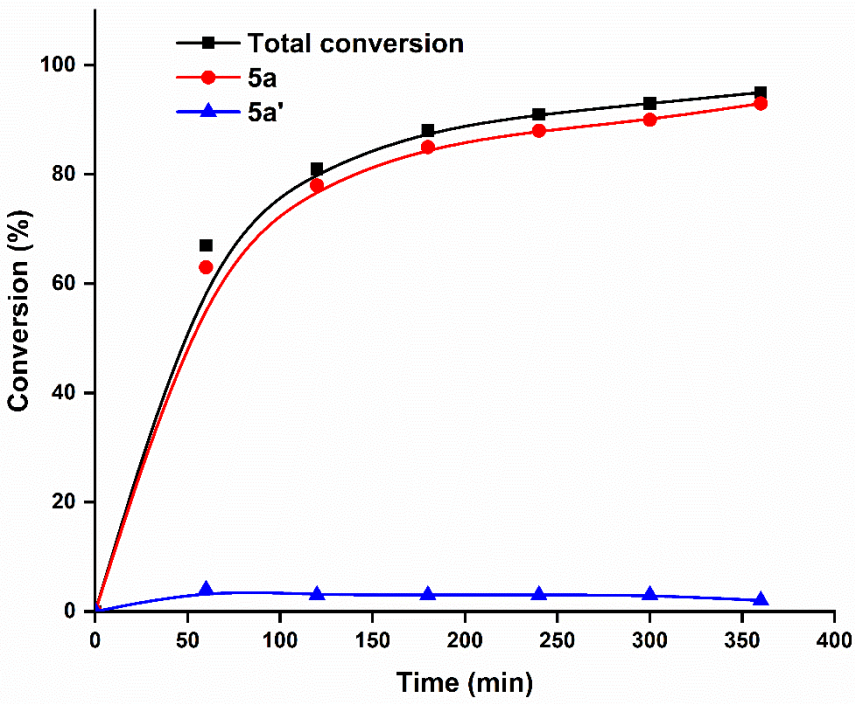
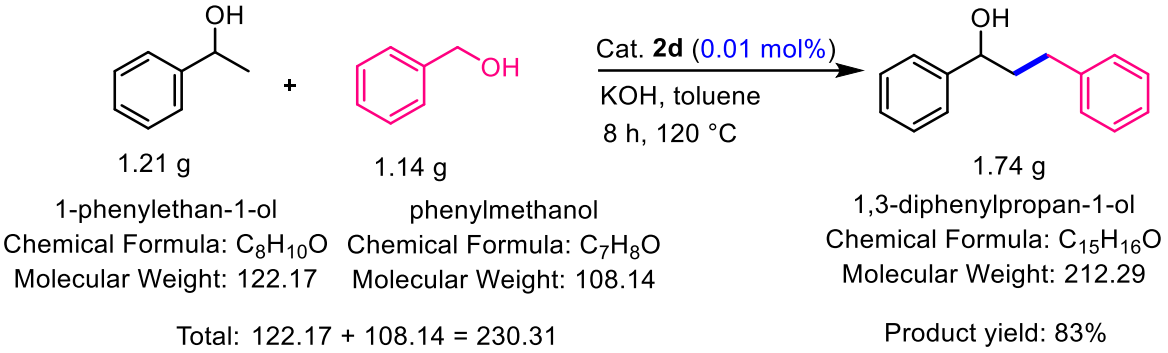


Figure S85. Plot of reaction progress with time. Reaction conditions: 1-phenylethanol (1 mmol), benzyl alcohol (1.1 mmol), cat. **2d** (0.02 mol%), KOH (0.20 mmol), and toluene (1 mL), 120 °C.

Calculation of Green metrics:



Reactant 1	1-phenylethan-1-ol	1.21 g	FW 122.17
Reactant 2	4-bromobenzyl alcohol	1.14 g	FW 108.14
Base	KOH	0.112 g	FW 56.11
Solvent	Toluene	0.867 g	-
Auxiliary	-	-	-
Product	1,3-diphenylpropan-1-ol	1.74 g	FW 212.19
Byproduct	Water	0.036 g	FW 18.01

Product yield = 83%

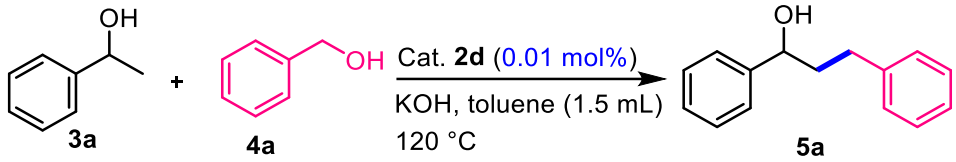
Atom economy: 212.29/230.31 = 92.2%

Atom efficiency: 83 X (92.2/100) = 76.5%

Carbon efficiency: (15/15) X 100 = 100%

Reaction mass efficiency: [1.74 g / (1.21 g + 1.14 g)] X 100 = 88.7%

Calculation of order of the reaction with respect to 1-phenylethanol:



3a: 0.5 mmol, **4a**: 0.55 mmol,
2d: 0.00005 mmol, KOH: 0.1 mmol

entry	Time (min)	Concentration of **3a** (mM)
1	120	160
2	150	140
3	180	117
4	210	103
5	240	83
6	270	73

3a: 0.55 mmol, **4a**: 0.605 mmol,
2d: 0.000055 mmol, KOH: 0.11 mmol

entry	Time (min)	Concentration of **3a** (mM)
1	120	231
2	150	205
3	180	180
4	210	167
5	240	150
6	270	128

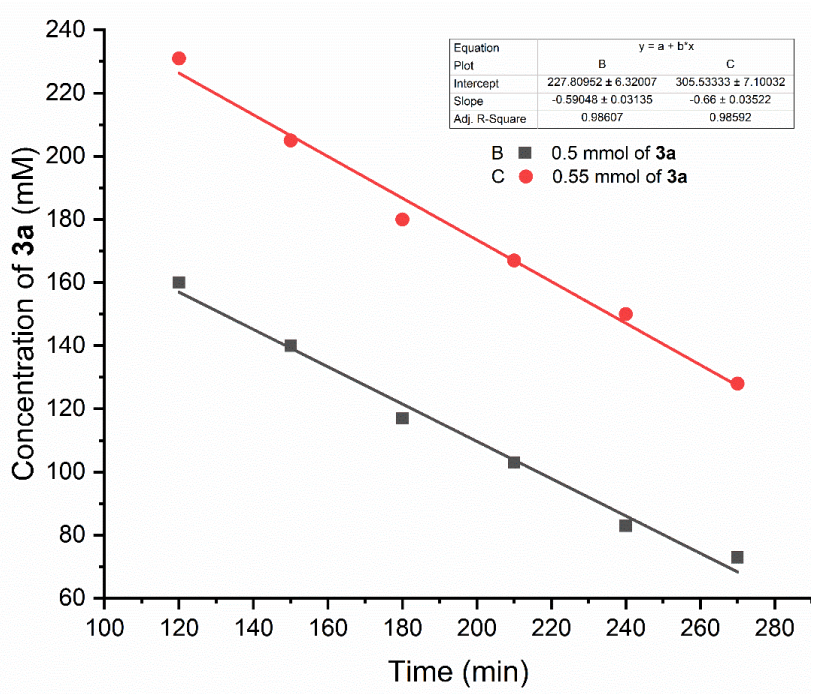


Figure S86. Plot of concentration variation of **3a** with time.

Considering steady state approximation for 1-phenylethanol, Slope = k[**3a**]^n

From 0.5 mmol scale reaction, -0.5905 = k × [0.5]^n

From 0.55 mmol scale reaction, -0.66 = k × [0.55]^n

$$-0.66/-0.5905 = [0.55/0.5]^n \Rightarrow 1.1176 = [1.1]^n$$

$$\log(1.1176) = n \log(1.1) \Rightarrow 0.0483 = n \times 0.0414$$

$$n = 1.17 \approx 1 \Rightarrow \text{Rate w.r.t. 1-phenylethanol} = k\,[\mathbf{3a}]^1$$

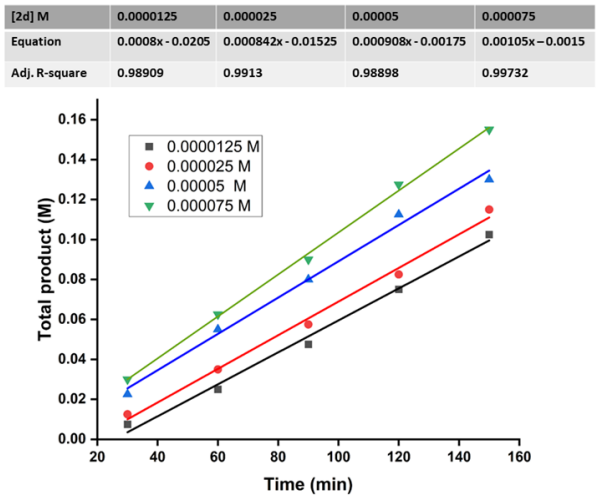
Calculation of order of the reaction with respect to 2d:

In order to find the order of the reaction with respect to catalyst concentration, initial rate method was used. For that, different sets of reactions were conducted by varying the catalyst concentration (0.005–0.02 mol%) keeping the other factors constant and the amount of product formed initially (upto 150 min) was calculated (from the conversions obtained from GC-MS analysis) in each case. Initial rates were calculated from the plots of product concentration vs time. Then, the initial rates were plotted against the catalyst concentration. The straight line nearly passing through origin indicated that the reaction is first order with respect to [**2d**].

Entry	3a (mmol)	4a (mmol)	2d (mol%)	2d (M)	KOH (mmol)	Toluene (mL)
1	0.5	0.55	0.005	0.0000125	0.10	2.0
2	0.5	0.55	0.01	0.000025	0.10	2.0
3	0.5	0.55	0.02	0.00005	0.10	2.0
4	0.5	0.55	0.03	0.000075	0.10	2.0

Entry	Time (min)	Concentration of product (M)			
		0.005 mol%	0.01 mol%	0.025 mol%	0.05 mol%
1	30	0.0075	0.0125	0.0225	0.03
2	60	0.025	0.035	0.055	0.0625
3	90	0.045	0.0575	0.08	0.09
4	120	0.075	0.0825	0.1125	0.1275
5	150	0.1075	0.115	0.13	0.155

a)



b)

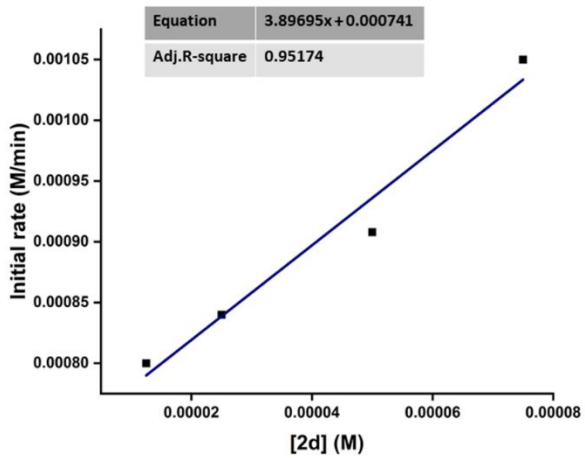


Figure S87. Plots to determine the rate of reaction w.r.to [**2d**]: a) Total product concentration (M) *vs* time with different concentrations of **2d**. b) Initial rate (M/min) *vs* [**2d**] (M).

Deuterium labelling studies

Procedure for the β-alkylation of 1-phenylethanol with benzyl alcohol-d_2: A catalyst stock solution (0.01 mol%) in acetonitrile was taken in a pre-dried Schlenk tube. After removing all the volatiles in vacuum, 1-phenylethanol (0.5 mmol), benzyl alcohol-d_2 (0.55 mmol), and KOH (0.10 mmol, 20 mol%) followed by toluene (1 mL) were added. The reaction tube was then heated in oil bath (bath temperature 120 °C) for 8 h. After the completion of reaction, the reaction mixture was cooled to room temperature and subjected to column chromatography using hexane/ethyl acetate as eluent. The obtained isolated product (70% yield) was analyzed by ^{1}H NMR to find out the deuterium incorporation percentage.

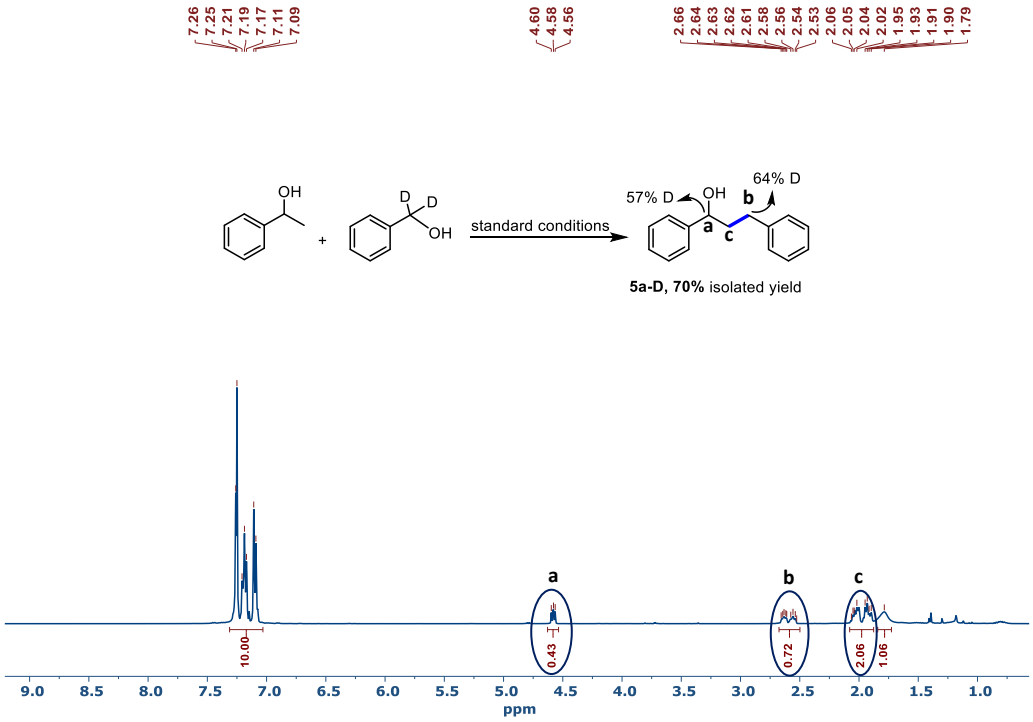


Figure S88. ^{1}H NMR spectrum of isolated product **5a-D**.

Procedure for detecting an in-situ generated Ru-H species: An oven dried pressure tube (25 mL) with a magnetic stirring bar was charged with **2c** (0.0565 mmol, 30 mg) and KOH (0.565 mmol, 32 mg). Then, 1-phenylethanol (0.565 mmol, 68 µL) and toluene (1 mL) were added and heated at 120 °C for 2 h. After the specified time, the reaction mixture was cooled, evaporated to dryness and the ^{1}H NMR spectrum was recorded in CD_3CN.

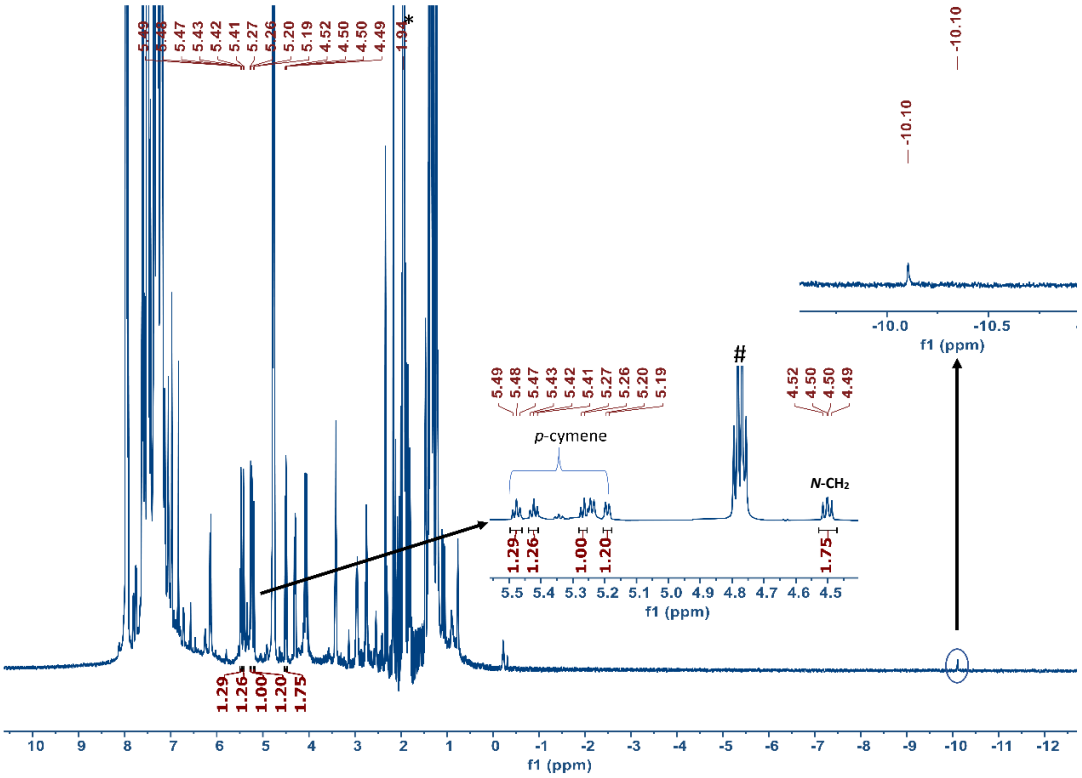


Figure S89. ^{1}H NMR spectrum of in-situ generated putative Ru-H species by reacting the complex **2c** with 1-phenylethanol in CD_3CN (*). # represents the quartet corresponds to CH proton of 1-phenylethanol.

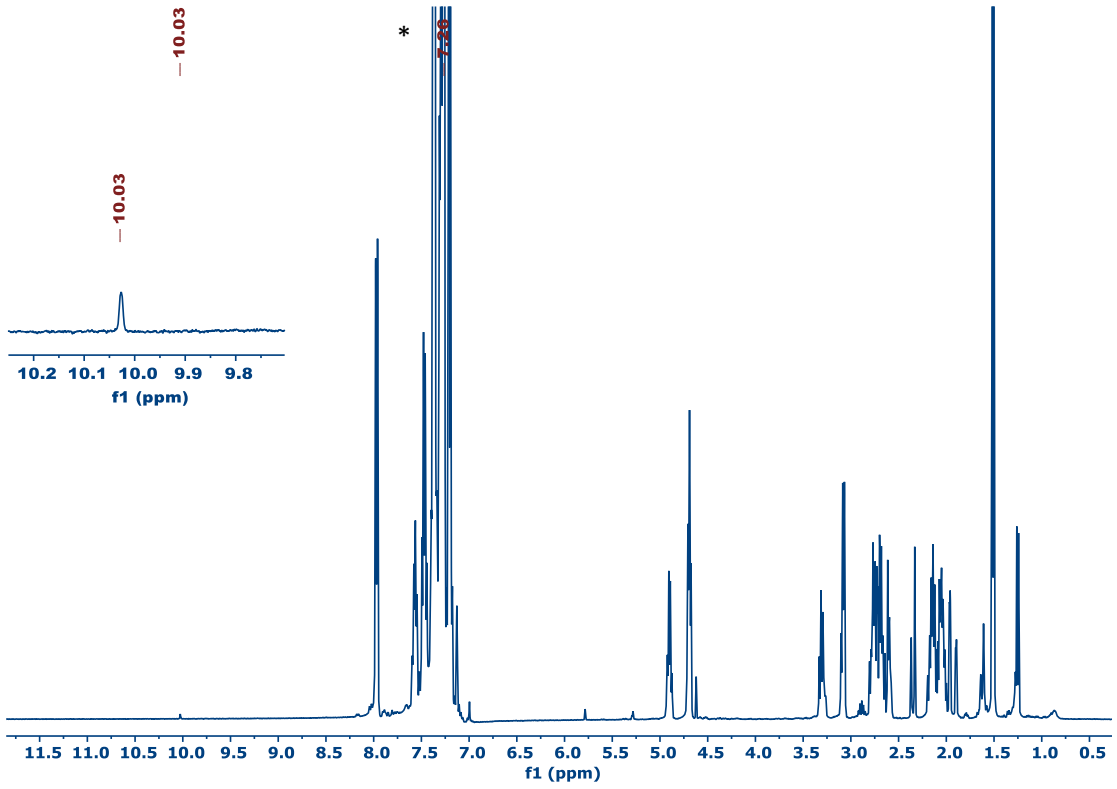


Figure S90. ^{1}H NMR spectrum of the reaction mixture of the standard reaction using the complex **2c** in $CDCl_3$ (*) after 2 h.

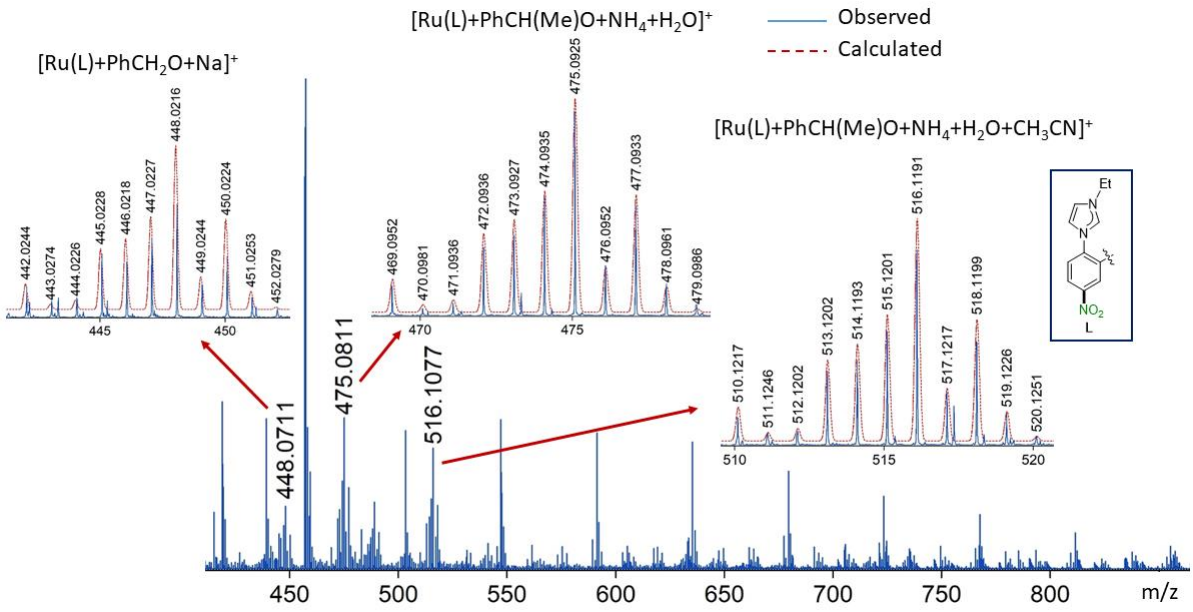


Figure S91. ESI-Mass spectrum of the reaction mixture containing **2c** (1 mol%), KOH (20 mol%), 1-phenylethanol (0.5 mmol), benzyl alcohol (0.55 mmol) in toluene (1 mL) stirred at 120 ℃ for 2 h.

Table S3. Crystallographic data for the compound **2d**

Compound	**2d**
CCDC No.	2102241
Empirical formula	$C_{20}H_{23}BrN_4O_2Ru$
Formula weight	532.40
Crystal system	Monoclinic
Space group	*P*21/*n*
a (Å)	7.9180(2)
b (Å)	17.8000(5)
c (Å)	14.7128(5)
α (°)	90°
β (°)	95.2089(14)°
γ (°)	90°
V ($Å^3$)	2065.06(11)
Z	4
D calc (Mg/m^3)	1.712
F (000)	1064
μ (mm^{-1})	2.717
θ Range (°)	2.68-26.02
Crystal size (mm)	0.150 x 0.120 x 0.100
No. of total reflns collected	3650
No. of unique reflns [I>2σ(I)]	2963
Data/restraints/parameters	3650 / 0 / 257
Goodness-of-fit on F^2	1.055
Final R indices (I > 2σ(I))	0.0600, 0.0561
R indices (all data)	0.0407, 0.0280