Electronic Supplementary Information

Visible Light-Mediated Smiles Rearrangements and Annulations of Non-Activated Aromatics

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Contents

1 General Experimental

Methods and Materials: Catalysts (**PC2**, **PC3**, **PC4** and **PC5**) and reagents were supplied by commercial sources and used without further purification, unless otherwise stated. Reactions were monitored using Thin Layer Chromatography (TLC), High Performance Liquid Chromatography (HPLC) and Liquid Chromatography-Mass Spectrometry (LCMS). Yields refer to isolated yield of analytically pure material unless otherwise stated. IUPAC names generated using ChemBioDraw Ultra 12.0. Analytical methods used are detailed below. Nuclear magnetic resonance (NMR) spectra were recorded using a Bruker UltraShield™ 400 (^{1}H NMR at 400 MHz, ^{13}C NMR at 101 MHz and ^{19}F NMR at 376 MHz) and processed using ACD/Spectrus Processor 2017.2. Chemical shifts (δ) for protons are reported in parts per million (ppm) relative to tetramethylsilane and are referenced to residual protium in the NMR solvents (^{1}H NMR: $CDCl_3$ at 7.26 ppm, CD_3OD at 3.31 ppm, DMSO-d_6 at 2.50 ppm). Chemical shifts (δ) for carbon signals are reported in parts per million (ppm) relative to tetramethylsilane and are referenced to the carbon resonances of the NMR solvents (^{13}C NMR: $CDCl_3$ at 77.16 ppm, CD_3OD at 49.00 ppm and DMSO-d_6 at 39.52 ppm). The following abbreviations are used for multiplicities: s = singlet; br s = broad singlet; d = doublet; t = triplet; q = quartet; quin = quintet; app. = apparent; m = multiplet; dd = doublet of doublets; dt = doublet of triplets. Coupling constants (*J*) are reported in Hz. If not specifically stated, the NMR experiments were run at 30 °C; ^{13}C and ^{19}F were run in ^{1}H-decoupled mode. Infrared (IR) spectra were recorded using a PerkinElmer Spectrum Two FT-IR spectrometer fitted with a PerkinElmer Universal ATR (attenuated total reflectance) sampling accessory. The data were processed using PerkinElmer Spectrum software. Absorption frequencies (ν_{max}) are reported in wavenumbers (cm^{-1}) for the characteristic peaks away from the fingerprint region. Melting points were measured on a Stanford Research Systems OptiMelt melting point apparatus and monitored manually. Thin layer chromatography (TLC) was performed on POLYGRAM® SIL G/UV254 200 µm thick silica gel plates. Visualisation was carried out with short wave UV light (254 nm), or development with potassium permanganate solution followed by heating. Flash column chromatography was performed on a Biotage SP4, Isolera 1 or Isolera 4 purification system monitored by UV (λ = 254 nm and 220 nm) using, unless stated otherwise, Biotage® SNAP Ultra pre-packed cartridges. Chromatographic solvents were standard HPLC grade provided by Sigma-Aldrich/Merck KGaA, and when a modifier was required it was added in-house. Specific solvent systems and gradients employed are described for each procedure. High-resolution mass spectra (HRMS) were recorded on a Thermo Fisher Q Exactive™ Hybrid Quadrupole-Orbitrap™ Mass Spectrometer with electrospray ionisation in positive ion mode. Analytes were separated using an Acquity UPLC BEH C18 column (50 mm × 2.1 mm internal diameter, 1.7 µm particle size) at 35 °C using a 2-5 µL injection volume. Solvents employed:

A = 0.05% v/v solution of formic acid in water

B = 0.05% v/v solution of formic acid in acetonitrile

The gradient employed was:

Time / min	Flow Rate / mL min^{-1}	%A	%B
0	0.5	95	5
8	0.5	5	95

Photoreactor Configuration: Photoreactions were carried out in a HepatoChem EvoluChem™ PhotoRedOx Box (HCK1006-01-016) mirror box fitted with a 40 W polychromatic (380–520 nm) A160WE Tuna Blue Kessil® Saltwater Aquarium LED Lamp (YH33924). The lamp was set to 0% colour and 100% intensity (Setting: Colour 6). Reactions were run in crimp capped borosilicate glass microwave vials (2–5 mL) and were stirred using a PTFE coated magnetic stirrer bar on a magnetic stirrer plate. Reaction mixtures were sparged for 15 min by bubbling nitrogen through the mixture.

Lamp output spectrum was recorded using a BWTEK Inc, Exemplar LS (Low Straylight Smart CCD Spectrometer, http://bwtek.com/products/exemplar-ls/).

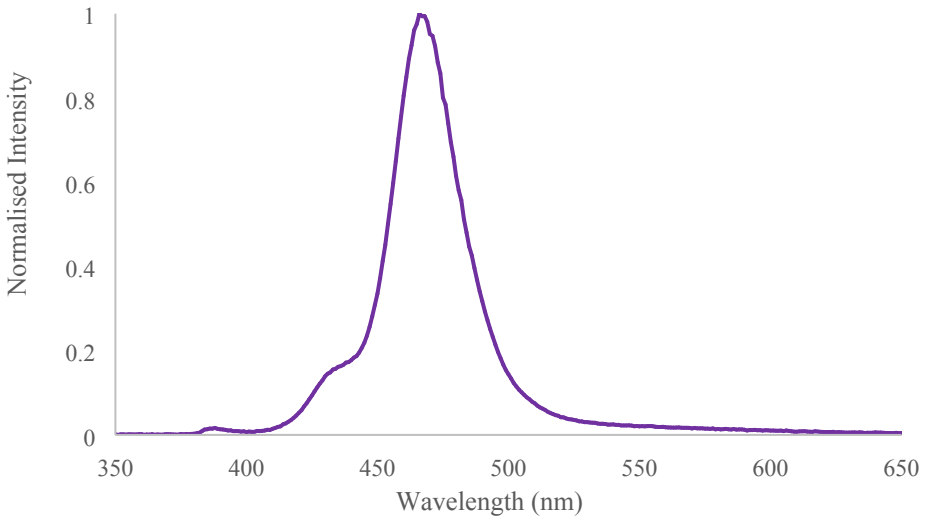


Figure 1. Output spectrum for single A160WE Tuna Blue Kessil® Saltwater Aquarium LED Lamp recorded using setting: 0% colour and 100% intensity (Colour 6) fitted in a HepatoChem EvoluChem™ PhotoRedOx Box.

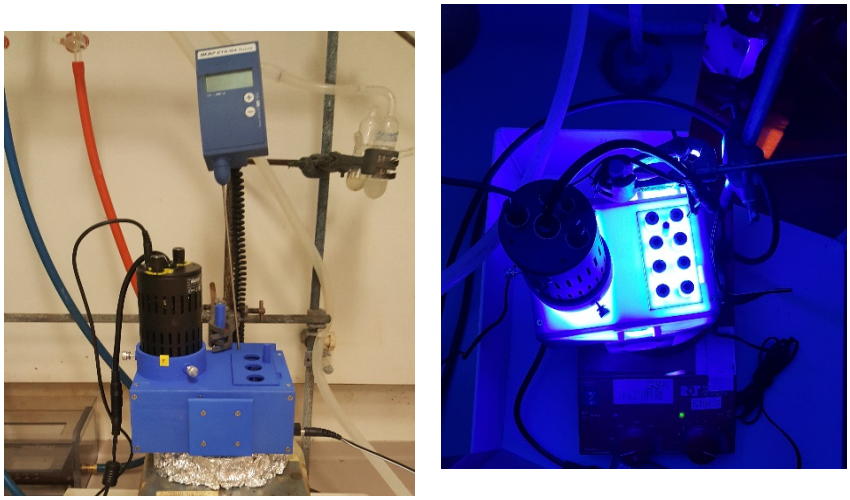
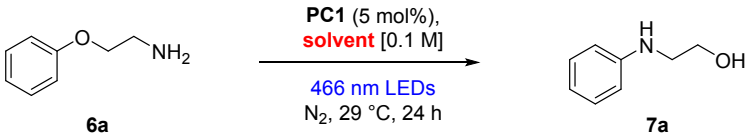
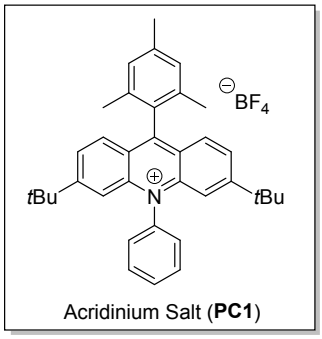


Figure 2. A160WE Tuna Blue Kessil® Saltwater Aquarium LED Lamp fitted into a HepatoChem EvoluChem™ PhotoRedOx Box mirror box.

2 Optimisation

Solvent Screen



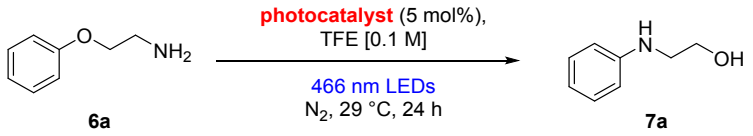


Acridinium Salt (**PC1**)

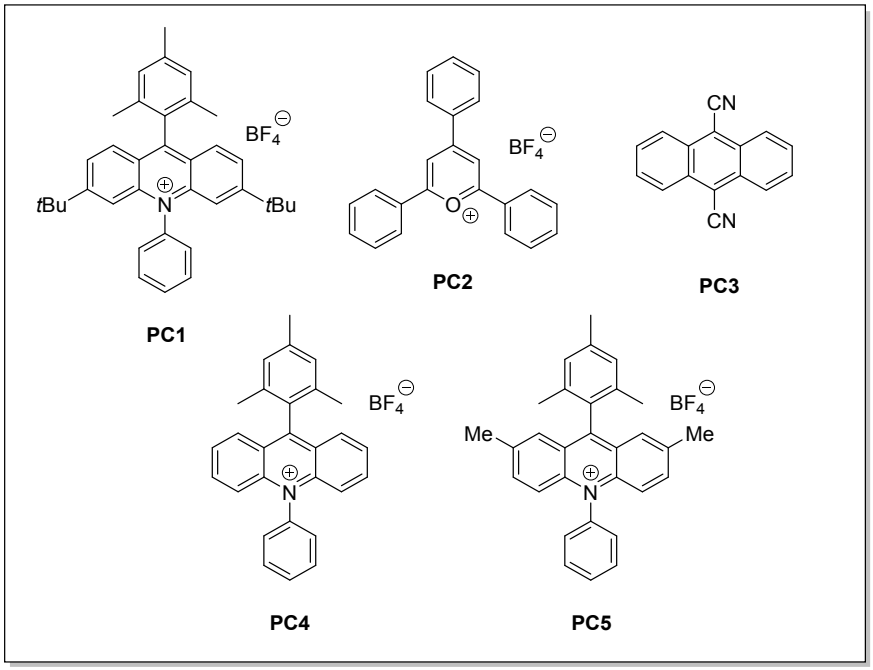
Entry[a]	Solvent	Yield (%)[b]
1	TFE:DCE (1:1)	87
2[c]	DCE	8
3	TFE	92
4	TFT	12
5	TFE:TFT (1:1)	86
6	MeCN	2
7	HFIP	42
8	THF (250 ppm BHT)	2
9	THF (inhibitor-free)	3
10	EtOH	11
11	EtOH (anhydrous)	10
12	EtOAc	2
13[d]	Hexane	4
14[d]	Toluene	7

[a] Unless otherwise stated, all reactions were conducted using 0.4 mmol of **6a** in degassed solvent [0.1 M] and irradiated with a Kessil lamp for 24 h. [b] Yields determined by ^{1}H NMR analysis of the crude reaction mixtures using 1,3,5-trimethoxybenzene as an internal standard. [c] White precipitate formed following irradiation. [d] Catalyst showed poor solubility in solvent. DCE = 1,2-dichloroethane; TFE = 2,2,2-trifluoroethanol; TFT = α,α,α-trifluorotoluene; HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol.

Photocatalyst Screen

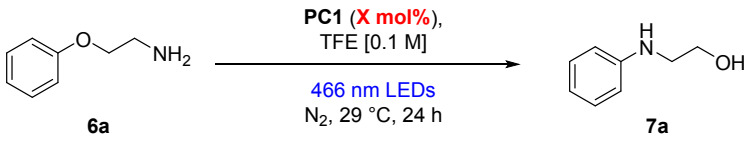


Entry[a]	Photocatalyst	Yield (%)[b]
1	9-Mesityl-3,6-di-tert-butyl-10-phenylacridinium tetrafluoroborate (**PC1**)	92
2[c]	2,4,6-Triphenylpyrylium tetrafluoroborate (**PC2**)	29
3[d]	9,10-Anthracenedicarbonitrile (**PC3**)	15
4	9-Mesityl-10-phenylacridinium tetrafluoroborate (**PC4**)	86
5	9-Mesityl-2,7-dimethyl-10-phenylacridinium tetrafluoroborate (**PC5**)	88

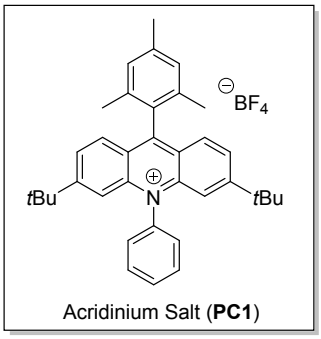


[a] Unless otherwise stated, all reactions were conducted using 0.4 mmol of **6a** in degassed solvent [0.1 M] and irradiated with a Kessil lamp for 24 h. [b] Yields determined by ^{1}H NMR analysis of the crude reaction mixtures using 1,3,5-trimethoxybenzene as an internal standard. [c] Catalyst chemically unstable in presence of starting material. [d] Catalyst showed poor solubility in solvent. TFE = 2,2,2-trifluoroethanol.

Catalyst Loading Screen



6a **7a**

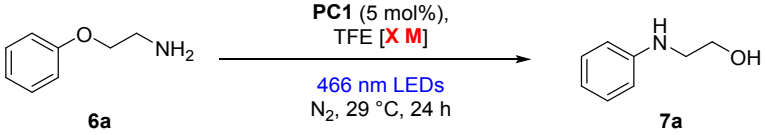


Acridinium Salt (**PC1**)

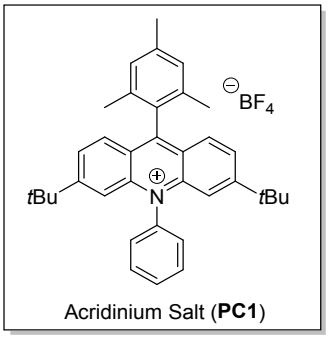
Entry[a]	X mol% photocatalyst	Yield (%)[b]
1	5	92
2	10	90
3	1	92

[a] Unless otherwise stated, all reactions were conducted using 0.4 mmol of **6a** in degassed solvent [0.1 M] and irradiated with a Kessil lamp for 24 h. [b] Yields determined by ^{1}H NMR analysis of the crude reaction mixtures using 1,3,5-trimethoxybenzene as an internal standard. TFE = 2,2,2-trifluoroethanol.

Reaction Concentration Screen



6a **7a**

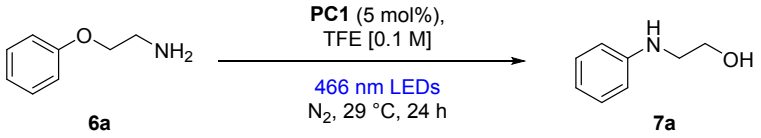


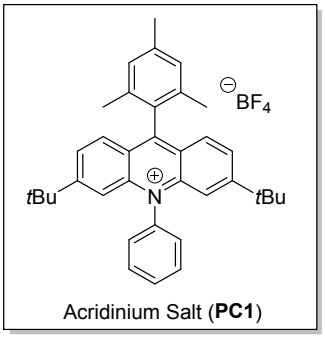
Acridinium Salt (**PC1**)

Entry[a]	Concentration (M)	Yield (%)[b]
1	[0.1 M]	92
2	[0.05 M]	96
3	[0.2 M]	82

[a] Unless otherwise stated, all reactions were conducted in degassed solvent and irradiated with a Kessil lamp for 24 h. [b] Yields determined by ^{1}H NMR analysis of the crude reaction mixtures using 1,3,5-trimethoxybenzene as an internal standard. TFE = 2,2,2-trifluoroethanol.

Control Reactions





Entry[a]	Conditions	Yield (%)[b]
1[c]	Standard conditions	92
2	No catalyst	<1
3	Dark (21 °C)	0
4	Dark (80 °C)	0
5	No catalyst/dark (21 °C)	0
6	No catalyst/dark (80 °C)	0

[a] Unless otherwise stated, all reactions were conducted using 0.4 mmol of **6a** in degassed solvent [0.1 M] and irradiated with a Kessil lamp for 24 h. [b] Yields determined by ^{1}H NMR analysis of the crude reaction mixtures using 1,3,5-trimethoxybenzene as an internal standard. [c] Internal temperature of reaction was measured at 29 °C using a thermocouple during irradiation. TFE = 2,2,2-trifluoroethanol.

UV-Vis:

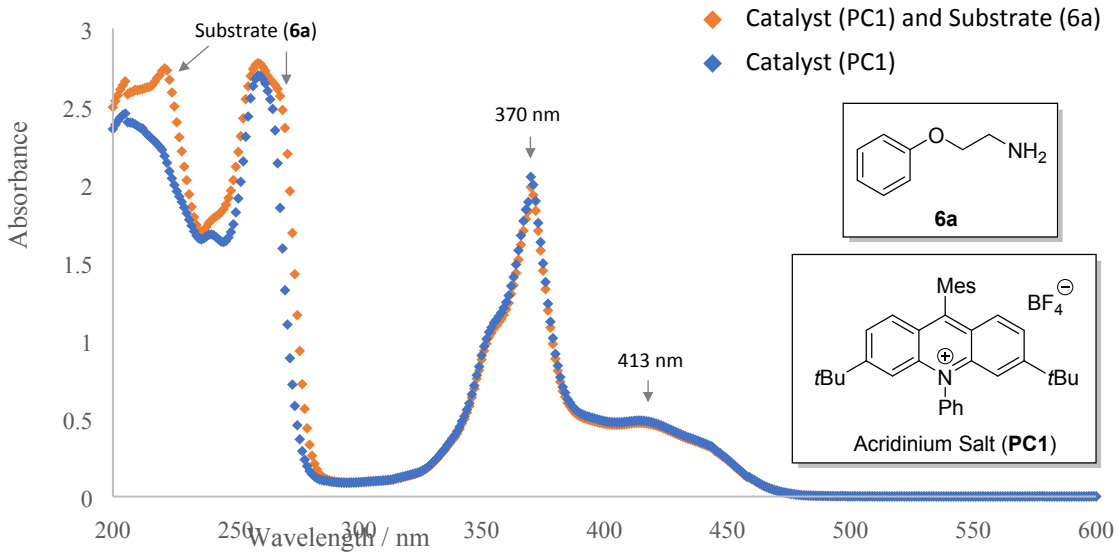


*Figure 3. UV-Vis spectra were collected on a SpectraMax M2 Spectrophotometer. Absorbance was measured every 1 nm between 200–600 nm. Samples were run in 2,2,2-trifluoroethanol (TFE). The ratio of catalyst to substrate was the same as the typical reaction mixture (0.4 mmol substrate (**6a**) and 5 mol% catalyst (**PC1**)). To obtain the spectra above, the reaction mixture stock solution was diluted 64-fold.*

*Note: Measured UV-Vis spectra show that if pre-association occurs (via π-π stacking) between the acridinium salt and the arene of the substrate, the complex is not present in measurable amounts. Success of para-isopropyl (**7c**) and para-tert-butyl (**7d**) substrates also suggests formation of such a complex may not be paramount to the reaction success.*

Time-Course:

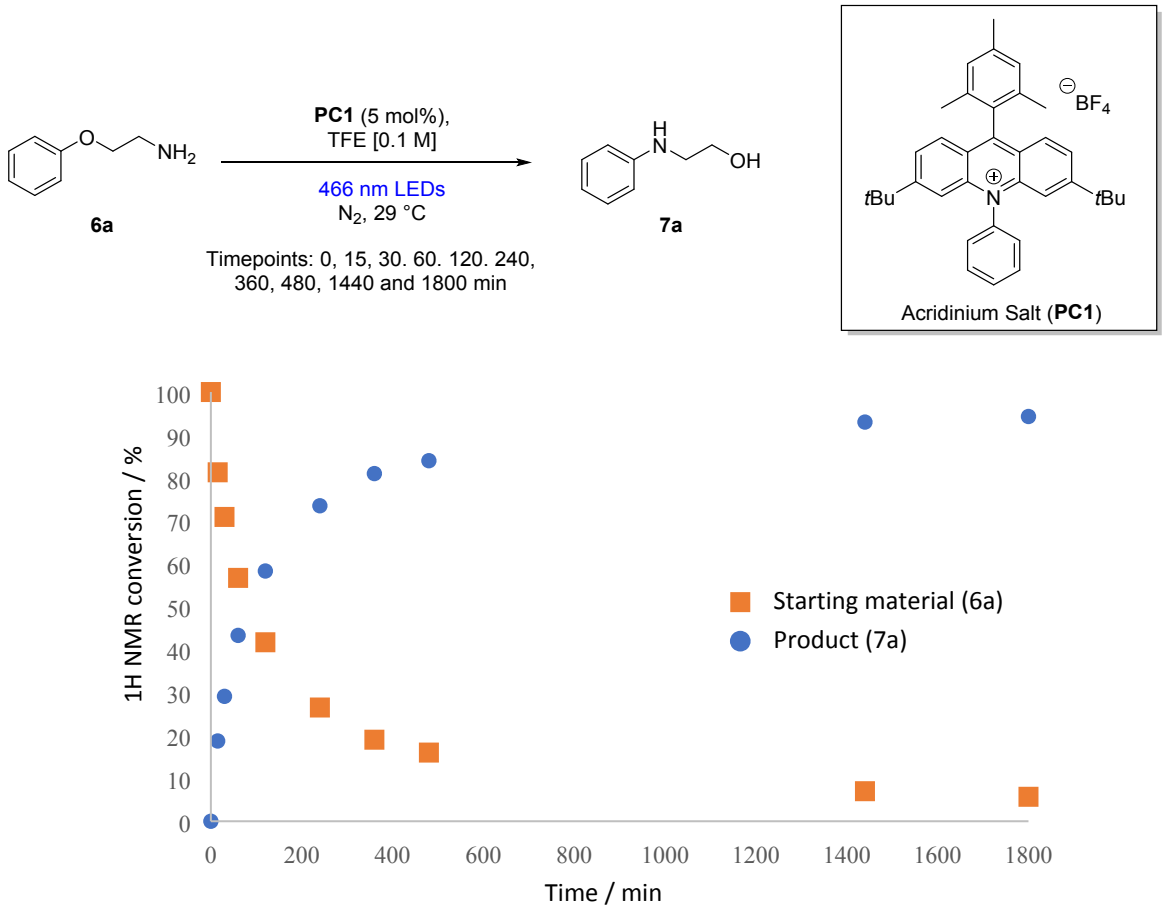


Figure 4. Reaction time-course over 30 h period. Conversion based on ratio of ^{1}H NMR integrals of starting material to product.

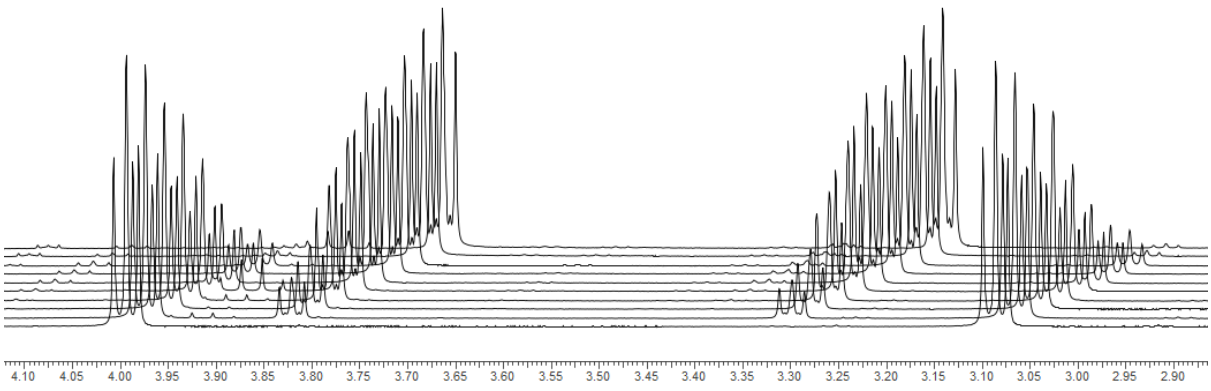
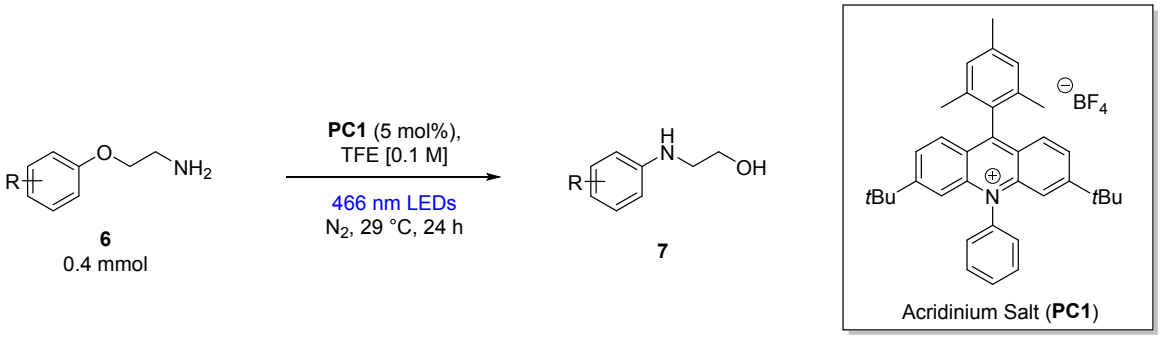


Figure 5. Overlay of ^{1}H NMR spectra at various time-points during the time-course.

3 General Procedures

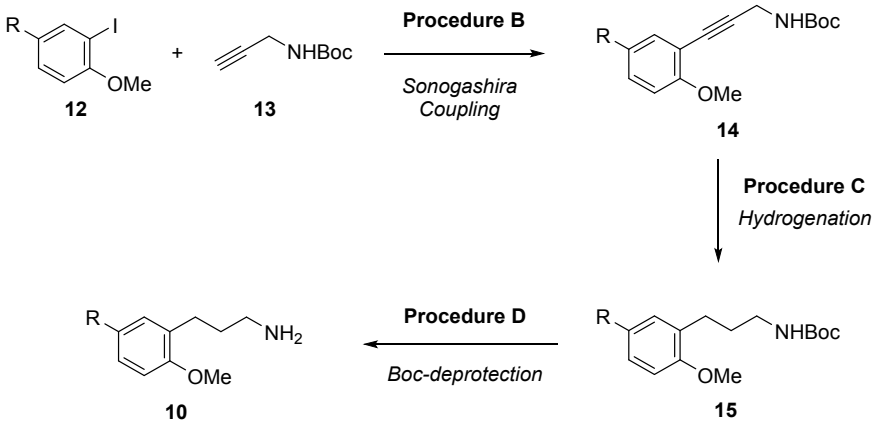
General Procedure for Photo-Smiles Rearrangement (Procedure A)



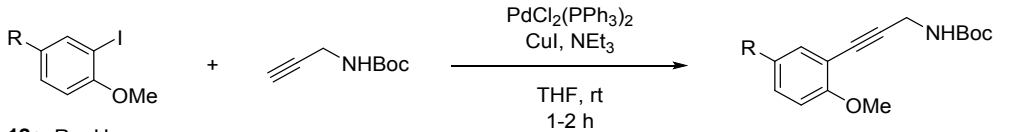
To a 2–5 mL microwave vial was added amine substrate (**6**) (0.40 mmol, 1 equiv) and a Teflon-coated magnetic stirrer bar. 9-Mesityl-3,6-di-tert-butyl-10-phenylacridinium tetrafluoroborate (**PC1**) (0.02 mmol, 0.05 equiv) dissolved in TFE (4 mL) was transferred to the reaction vial. The vial was then crimped shut and the mixture was sparged with N_2 for 15 min. The reaction was then stirred and irradiated with visible-light for 24 h. Following completion, the reaction mixture was concentrated *in vacuo* and purified *via* column chromatography on silica gel to yield the desired product (**7**).

General Procedures for Photo-Annulation (Procedures B, C, D & E)

Annulation precursors were prepared following the general scheme:



General Procedure for Sonogashira Coupling (Procedure B)



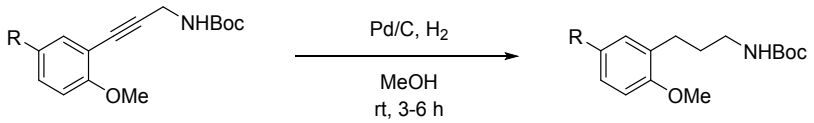
12a, R = H
12b, R = CH_2OH
12c, R = Ph
12d, R = OMe
12e, R = CO_2Me

13

14a, R = H; 83% yield
14b, R = CH_2OH; 81% yield
14c, R = Ph; 87% yield
14d, R = OMe; 76% yield
14e, R = CO_2Me; 92% yield

Based on a literature procedure,[1] copper(I) iodide (0.04 equiv) and bis(triphenylphosphine)palladium(II) chloride (0.02 equiv) were added to a degassed solution of *tert*-butyl prop-2-yn-1-ylcarbamate (**13**) (1 equiv), aryl iodide (**12**) (1.3–1.5 equiv) and triethylamine (2 equiv) in anhydrous THF [1.25 M] under a N_2 atmosphere. The suspension formed was stirred at rt. Upon consumption of limiting reagent (**13**), the reaction mixture was diluted with EtOAc and was filtered through a pad of celite. The organic layer was washed with sat. aq. sodium chloride and sat. aq. ammonium chloride. The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The resultant crude material was purified *via* column chromatography on silica gel to yield the desired product (**14**).

General Procedure for Alkyne Hydrogenation (Procedure C)

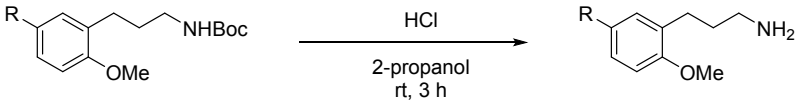


14a, R = H
14b, R = CH_2OH
14c, R = Ph
14d, R = OMe
14e, R = CO_2Me

15a, R = H; 96% yield
15b, R = Me; 82% yield
15c, R = Ph; 94% yield
15d, R = OMe; 81% yield
15e, R = CO_2Me; 95% yield

Alkyne (**14**) (1 equiv) and palladium on carbon (10% w/w, dry) (10–20 wt%) were suspended in MeOH [0.3 M] under a N_2 atmosphere to give a black suspension. The reaction mixture was subsequently subjected to a H_2 atmosphere (5 bar) at rt. Upon full consumption of starting material, the reaction mixture was filtered over a celite pad and rinsed with MeOH. The resultant solution was concentrated *in vacuo* to yield the desired product (**15**).

General Procedure for Boc-deprotection (Procedure D)

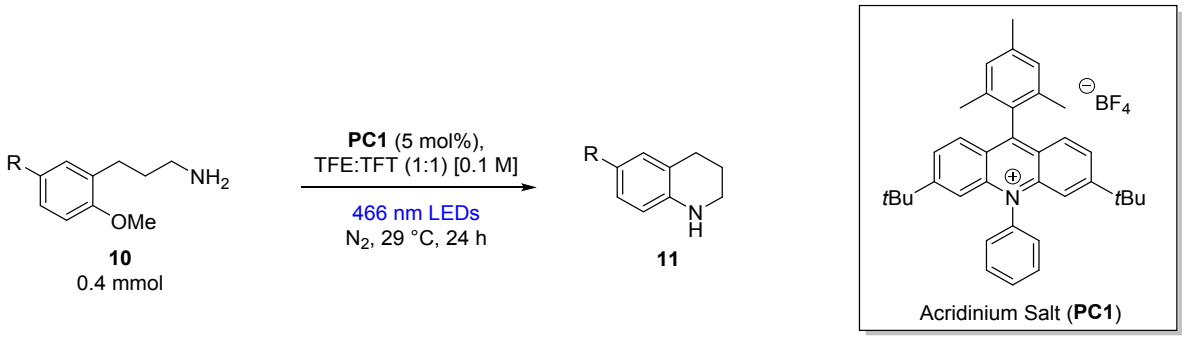


15a, R = H
15b, R = Me
15c, R = Ph
15d, R = OMe
15e, R = CO_2Me

10a, R = H; 100% yield
10b, R = Me; 84% yield
10c, R = Ph; 100% yield
10d, R = OMe; 88% yield
10e, R = CO_2Me; 67% yield

To a solution of Boc-protected amine (**15**) (1 equiv) in MeOH [0.3 M] was added HCl (5 to 6 M solution in 2-propanol) (15 equiv) dropwise at rt. After 3 h, solvent was removed *in vacuo* to give a white solid. The resultant material was dissolved in a minimum amount of water, then NaOH (2N) was added until pH 14. The aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo* to yield desired product (**10**).

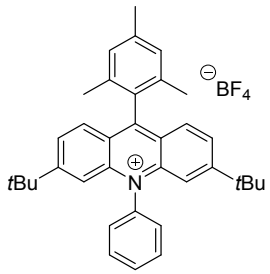
General Procedure for Photo-Annulation (Procedure E)



To a 2–5 mL microwave vial was added amine substrate (**10**) (0.4 mmol, 1 equiv) and a Teflon-coated magnetic stirrer bar. 9-Mesityl-3,6-di-tert-butyl-10-phenylacridinium tetrafluoroborate (**PC1**) (0.02 mmol, 0.05 equiv) dissolved in TFE (2 mL) and TFT (2 mL) was transferred to the reaction vial. The vial was then crimped shut and the mixture was sparged with N_2 for 15 min. The reaction was then stirred and irradiated with visible-light for 24 h. Following completion, the reaction mixture was concentrated *in vacuo* and purified *via* column chromatography on silica gel to yield the desired product (**11**).

4 Experimental Procedures and Characterisation Data

Synthesis of Catalyst



PC1

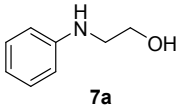
3,6-Di-*tert*-butyl-9-mesityl-10-phenylacridin-10-ium tetrafluoroborate (PC1): Acridinium salt was prepared following a reported literature procedure.[2] Analytical data matched those reported in the literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99–7.93 (2H, m), 7.92–7.86 (1H, m), 7.82–7.72 (6H, m), 7.42 (2H, br s), 7.16 (2H, br s), 2.49 (3H, s), 1.86 (6H, s), 1.29 (18H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.7, 162.4, 142.3, 140.3, 137.0, 136.3, 131.9, 131.7, 129.5, 129.1, 128.4, 128.2, 127.6, 124.2, 115.2, 36.8, 30.3, 21.4, 20.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ = −154.35, −154.40.

Photo-Smiles Rearrangement



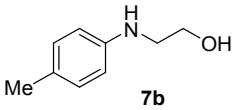
7a

2-(Phenylamino)ethan-1-ol (7a): 2-phenoxyethan-1-amine (**6a**) (56.0 mg, 0.40 mmol) was reacted following **General Procedure A**. Reaction mixture was irradiated for 24 h. The compound was isolated *via* column chromatography on silica gel (0–50% ethyl acetate in heptane) as a yellow oil (46.9 mg, 0.342 mmol, 85% yield). Analytical data matched those reported in the literature.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.20 (2H, dd, *J* = 8.6, 7.3 Hz), 6.75 (1H, tt, *J* = 7.3, 1.0 Hz), 6.67 (2H, dd, *J* = 8.6, 1.0 Hz), 3.87–3.78 (2H, m), 3.35–3.27 (2H, m), 2.78 (2H, br s).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 148.2, 129.4, 118.1, 113.4, 61.4, 46.3.

IR (neat) ν_{max} 3355, 3051, 2931, 2876, 1601, 1503, 1319, 1261, 1052, 747 cm^{-1}.



7b

2-(*p*-Tolylamino)ethan-1-ol (7b): 2-(*p*-tolyloxy)ethan-1-amine (**6b**) (61.7 mg, 0.40 mmol) was reacted following **General Procedure A**. Reaction mixture was irradiated for 24 h. The compound was isolated *via* column chromatography on silica gel (0–50% ethyl acetate in heptane) as an off-white solid (38.0 mg, 0.251 mmol, 63% yield). Analytical data matched those reported in the literature.[4]

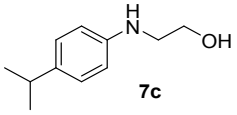
M.pt.: 39–41 °C (Lit.:[5] 41–42 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.00 (2H, d, *J* = 8.4 Hz), 6.59 (2H, d, *J* = 8.4 Hz), 3.84–3.79 (2H, m), 3.32– 3.26 (2H, m), 2.70 (2H, br s), 2.25 (3H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 146.0, 129.9, 127.4, 113.7, 61.5, 46.7, 20.5.

IR (neat) ν_{max} 3271, 3171, 2917, 2860, 1619, 1516, 1263, 1069, 819, 801 cm^{-1}.

HRMS (ESI+): ($C_9H_{14}NO$) $[M+H]^+$ requires 152.1075, found $[M+H]^+$ 152.1075 (Δ 0.0 ppm).



7c

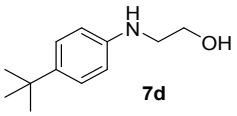
2-((4-Isopropylphenyl)amino)ethan-1-ol (7c): 2-(4-isopropylphenoxy)ethan-1-amine (**6c**) (71.7 mg, 0.40 mmol) was reacted following **General Procedure A**. Reaction mixture was irradiated for 24 h. The compound was isolated *via* column chromatography on silica gel (0–50% ethyl acetate in heptane) as a yellow oil (52.5 mg, 0.293 mmol, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.07 (2H, d, *J* = 8.5 Hz), 6.63 (2H, d, *J* = 8.5 Hz), 3.85–3.79 (2H, m), 3.33–3.27 (2H, m), 2.82 (1H, spt, *J* = 6.9 Hz), 2.71 (2H, br s), 1.22 (6H, d, *J* = 6.9 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 146.2, 138.8, 127.3, 113.6, 61.5, 46.7, 33.3, 24.4.

IR (neat) ν_{max} 3355, 2956, 2868, 1615, 1517, 1051, 819 cm^{-1}.

HRMS (ESI+): ($C_{11}H_{18}NO$) $[M+H]^+$ requires 180.1388, found $[M+H]^+$ 180.1389 (Δ 0.6 ppm).



7d

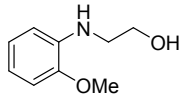
2-((4-(*tert*-Butyl)phenyl)amino)ethan-1-ol (7d): 2-(4-(*tert*-butyl)phenoxy)ethan-1-amine (**6d**) (77.0 mg, 0.40 mmol) was reacted following **General Procedure A**. Reaction mixture was irradiated for 24 h. The compound was isolated *via* column chromatography on silica gel (0–50% ethyl acetate in heptane) as a yellow oil (62.0 mg, 0.321 mmol, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.22 (2H, d, *J* = 8.7 Hz), 6.63 (2H, d, *J* = 8.7 Hz), 3.86–3.77 (2H, m), 3.35–3.27 (2H, m), 2.69 (2H, br s), 1.29 (9H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.8, 141.0, 126.2, 113.2, 61.5, 46.6, 34.0, 31.7.

IR (neat) ν_{max} 3355, 2955, 2866, 1614, 1518, 1193, 1059, 820 cm^{-1}.

HRMS (ESI+): ($C_{12}H_{20}NO$) $[M+H]^+$ requires 194.1545, found $[M+H]^+$ 194.1550 (Δ 2.6 ppm).



7e

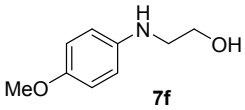
2-((2-Methoxyphenyl)amino)ethan-1-ol (7e): 2-(2-methoxyphenoxy)ethan-1-amine (**6e**) (45.0 µL, 0.29 mmol) was reacted following **General Procedure A** in a DCE:TFE (1:1) solvent system (2.5 mL). Reaction mixture was irradiated for 24 h. The compound was isolated *via* column chromatography on silica gel (15–100% ethyl acetate in heptane) as a yellow oil (36.0 mg, 0.215 mmol, 74% yield). Analytical data matched those reported in the literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.87 (1H, td, *J* = 7.6, 1.5 Hz), 6.79 (1H, dd, *J* = 7.9, 1.5 Hz), 6.70 (1H, td, *J* = 7.6, 1.5 Hz), 6.66 (1H, dd, *J* = 7.8, 1.5 Hz), 3.87–3.83 (5H, m), 3.36–3.31 (2H, m).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 147.3, 138.2, 121.4, 117.2, 110.4, 109.7, 61.6, 55.6, 46.1.

IR (neat) ν_{max} 3404, 2934, 1601, 1510, 1455, 1219, 1025, 732 cm^{-1}.

HRMS (ESI+): ($C_9H_{14}NO_2$) $[M+H]^+$ requires 168.1019, found $[M+H]^+$ 168.1013 (Δ −3.5 ppm).



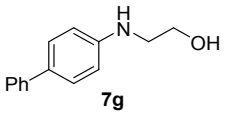
7f

2-((4-Methoxyphenyl)amino)ethan-1-ol (7f): 2-(4-methoxyphenoxy)ethan-1-amine (**6f**) (66.9 mg, 0.40 mmol) was reacted following **General Procedure A**. Reaction mixture was irradiated for 65 h. The compound was isolated *via* column chromatography on silica gel (0–50% ethyl acetate in heptane) as a dark yellow oil (2.8 mg, 0.017 mmol, 4% yield). Analytical data matched those reported in the literature.[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.82–6.76 (2H, m), 6.68–6.61 (2H, m), 3.85–3.80 (2H, m), 3.75 (3H, s), 3.29–3.23 (2H, m), 2.55 (2H, br s).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 152.7, 142.4, 115.1, 114.9, 61.5, 56.0, 47.3.

*Note: The poor conversion observed for substrate **6f** may be due to product inhibition. Supported by literature precedent, it is likely the arylamine product quenches the excited catalyst at a much faster rate than the starting material.[8]*



7g

2-([1,1'-Biphenyl]-4-ylamino)ethan-1-ol (7g): 2-([1,1'-biphenyl]-4-yloxy)ethan-1-amine (**6g**) (85.0 mg, 0.40 mmol) was reacted following **General Procedure A**. Reaction mixture was irradiated for 24 h. The compound was isolated *via* column chromatography on silica gel (0–50% ethyl acetate in heptane) as a white solid (27.1 mg, 0.127 mmol, 32% yield). Analytical data matched those reported in the literature.[9]

M.pt.: 112–114 °C (Lit.:[10] 112–113 °C (petroleum ether)).

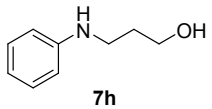
^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.59–7.49 (2H, m), 7.47–7.30 (4H, m), 7.26–7.14 (1H, m), 6.73–6.61 (2H, m), 5.67 (1H, t, *J* = 5.7 Hz), 4.68 (1H, t, *J* = 5.5 Hz), 3.57 (2H, app. q, *J* = 6.0 Hz), 3.13 (2H, app. q, *J* = 5.9 Hz).

^{13}C NMR (101 MHz, DMSO-d_6) δ = 148.5, 140.5, 128.6, 127.2, 127.1, 125.6, 125.3, 112.3, 59.6, 45.5.

IR (neat) ν_{max} 3315, 3030, 2922, 1610, 1488, 1206, 1055, 822, 760 cm^{-1}.

HRMS (ESI+): ($C_{14}H_{16}NO$) $[M+H]^+$ requires 214.1232, found $[M+H]^+$ 214.1230 (Δ −0.9 ppm).

Note: The starting material showed poor solubility in the reaction solvent.



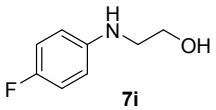
7h

3-(Phenylamino)propan-1-ol (7h): 3-phenoxypropan-1-amine (**6h**) (61.7 mg, 0.40 mmol) was reacted following **General Procedure A**. Reaction mixture was irradiated for 24 h. The compound was isolated *via* column chromatography on silica gel (0–50% ethyl acetate in heptane) as a yellow oil (51.3 mg, 0.339 mmol, 83% yield). Analytical data matched those reported in the literature.[11]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.21 (2H, dd, *J* = 8.6, 7.3 Hz), 6.75 (1H, tt, *J* = 7.3, 1.0 Hz), 6.67 (2H, dd, *J* = 8.6, 1.0 Hz), 3.84 (2H, t, *J* = 5.9 Hz), 3.31 (2H, t, *J* = 6.5 Hz), 2.71 (2H, br s), 1.91 (2H, app. quin, *J* = 6.2 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 148.4, 129.4, 117.9, 113.3, 61.8, 42.2, 32.1.

IR (neat) ν_{max} 3346, 2932, 2874, 1601, 1504, 747 cm^{-1}.



7i

2-((4-Fluorophenyl)amino)ethan-1-ol (7i): 2-(4-fluorophenoxy)ethan-1-amine (**6i**) (62.1 mg, 0.40 mmol) was reacted following **General Procedure A**. Reaction mixture was irradiated for 24 h. The compound was isolated *via* column chromatography on silica gel (0–50% ethyl acetate in heptane) as an off-white solid (50.4 mg, 0.325 mmol, 81% yield). Analytical data matched those reported in the literature.[6,12]

M.pt.: 40–42 °C.

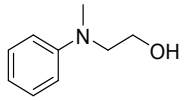
^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.94–6.86 (2H, m), 6.64–6.55 (2H, m), 3.86–3.80 (2H, m), 3.29–3.23 (2H, m), 2.68 (2H, br s).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.3 (d, $^1J_{CF}$ = 235 Hz), 144.5, 115.8 (d, $^2J_{CF}$ = 21 Hz), 114.4 (d, $^3J_{CF}$ = 8 Hz), 61.4, 47.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ = −127.3.

IR (neat) ν_{max} 3304, 3183, 2878, 1508, 1210, 1059, 824 cm^{-1}.

HRMS (ESI+): ($C_8H_{11}FNO$) $[M+H]^+$ requires 156.0825, found $[M+H]^+$ 156.0829 (Δ 2.6 ppm).



9

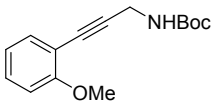
2-(Methyl(phenyl)amino)ethan-1-ol (9): *N*-methyl-2-phenoxyethan-1-amine (**8**) (62.4 mg, 0.4 mmol).was reacted following **General Procedure A**. Reaction mixture was irradiated for 24 h. The compound was isolated *via* column chromatography on silica gel (0–50% ethyl acetate in heptane) as a yellow oil (9.1 mg, 0.060 mmol, 15% yield). Analytical data matched those reported in the literature.[13]

^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.19–7.09 (2H, m), 6.71–6.64 (2H, m), 6.63–6.53 (1H, m), 4.63 (1H, t, *J* = 5.4 Hz), 3.53 (2H, app. q, *J* = 6.1 Hz), 3.37 (2H, t, *J* = 6.4 Hz), 2.90 (3H, s).

^{13}C NMR (101 MHz, DMSO-d_6) δ = 149.1, 128.8, 115.3, 111.6, 58.0, 54.2, 38.5.

*Note: 2-(Phenylamino)ethan-1-ol (**7a**) was also isolated in an 8% yield following 24 h irradiation of N-methyl-2-phenoxyethan-1-amine (**8**) (see above for analytical data). When irradiated for a longer time period (65 h), products **9** and **7a** were isolated in a 21% and 17% yield respectively. Unreacted starting material accounted for the remainder of the mass balance.*

Synthesis of Annulation Substrates



14a

***tert*-Butyl (3-(2-methoxyphenyl)prop-2-yn-1-yl)carbamate (14a):** 1-iodo-2-methoxybenzene (**12a**) (1.25 ml, 9.40 mmol) and *tert*-butyl prop-2-yn-1-ylcarbamate (**13**) (1.00 g, 6.25 mmol) were reacted following **General Procedure B**. The dark red suspension formed was stirred at rt for 2 h. The compound was isolated *via* column chromatography on silica gel (5–50% ethyl acetate in heptane) as a yellow solid (1.36 g, 5.20 mmol, 83% yield).

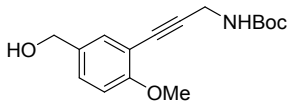
M.pt.: 62–63 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 (1H, dd, *J* = 7.6, 1.7 Hz), 7.31–7.26 (1H, m), 6.92–6.84 (2H, m), 4.79 (1H, br s), 4.21 (2H, br d, *J* = 4.2 Hz), 3.87 (3H, s), 1.46 (9H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.2, 155.4, 134.0, 130.0, 120.6, 112.0, 110.7, 89.5, 80.0, 79.6, 55.9, 31.5, 28.5.

IR (neat) ν_{max} 3366, 2968, 1683, 1510, 1167, 1027 cm^{-1}.

HRMS (ESI+):($C_{15}H_{20}NO_3$) [M+H]+ requires 262.1438, found [M+H]+ 262.1432 (Δ −2.2 ppm).



14b

***tert*-Butyl (3-(5-(hydroxymethyl)-2-methoxyphenyl)prop-2-yn-1-yl)carbamate (14b):** (3-iodo-4-methoxyphenyl)methanol (**12b**) (1.17 g, 4.30 mmol) and *tert*-butyl prop-2-yn-1-ylcarbamate (**13**) (0.5 g, 3.13 mmol) were reacted following **General Procedure B**. The dark red suspension formed was stirred at rt for 1 h. The compound was isolated *via* column chromatography on silica gel (0–60% ethyl acetate in heptane) as a yellow crystalline solid (0.74 g, 2.55 mmol, 81% yield).

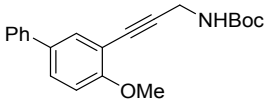
M.pt.: 94–95 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ =7.40 (1H, d, *J* = 2.2 Hz), 7.29 (1H, dd, *J* = 8.5, 2.2 Hz), 6.85 (1H, d, *J* = 8.5 Hz), 4.78 (1H, br s), 4.59 (2H, d, *J* = 5.8 Hz), 4.20 (2H, br d, *J* = 4.7 Hz), 3.88 (3H, s), 1.59 (1H, t, *J* = 5.8 Hz), 1.47 (9H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.6, 155.4, 133.2, 132.9, 128.9, 112.0, 110.8, 89.6, 80.1, 79.4, 64.7, 56.1, 31.7, 28.5.

IR (neat) ν_{max} 3356, 2977, 2926, 1678, 1519, 1266, 1166, 1017 cm^{-1}.

HRMS (ESI+): ($C_{16}H_{22}NO_4$) $[M+H]^+$ requires 292.1543, found $[M+H]^+$ 292.1548 (Δ 1.7 ppm).



14c

***tert*-Butyl (3-(4-methoxy-[1,1'-biphenyl]-3-yl)prop-2-yn-1-yl)carbamate (14c):** 3-iodo-4-methoxy-1,1'-biphenyl (**12c**) (1.48 g, 4.69 mmol) and *tert*-butyl prop-2-yn-1-ylcarbamate (**13**) (0.5 g, 3.13 mmol) were reacted following **General Procedure B**. The dark red suspension formed was stirred at rt for 1 h. The compound was isolated *via* column chromatography on silica gel (0–50% ethyl acetate in heptane) as an off-white fluffy solid (0.92 g, 2.73 mmol, 87% yield).

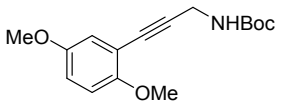
M.pt.: decomposition observed at 142 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 (1H, d, *J* = 2.5 Hz), 7.55–7.49 (3H, m), 7.44–7.38 (2H, m), 7.34–7.29 (1H, m), 6.94 (1H, d, *J* = 8.6 Hz), 4.80 (1H, br s), 4.23 (2H, br d, *J* = 4.4 Hz), 3.92 (3H, s), 1.47 (9H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.6, 155.4, 140.0, 133.8, 132.6, 128.9, 128.6, 127.2, 126.8, 112.3, 111.1, 89.6, 80.1, 79.6, 56.1, 31.7, 28.5.

IR (neat) ν_{max} 3371, 2980, 2940, 2844, 1685, 1508, 1488, 1246, 1157, 760 cm^{-1}.

HRMS (ESI+): ($C_{21}H_{23}NNaO_3$) $[M+Na]^+$ requires 360.1570, found $[M+Na]^+$ 360.1572 (Δ 0.4 ppm).



14d

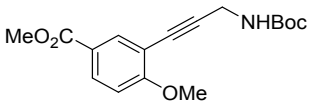
***tert*-Butyl (3-(2,5-dimethoxyphenyl)prop-2-yn-1-yl)carbamate (14d):** 2-iodo-1,4-dimethoxybenzene (**12d**) (1.26 g, 4.63 mmol) and *tert*-butyl prop-2-yn-1-ylcarbamate (**13**) (0.5 g, 3.13 mmol) were reacted following **General Procedure B**. The dark red suspension formed was stirred at rt for 2 h. The compound was isolated *via* column chromatography on silica gel (0–50% ethyl acetate in heptane) as a brown oil (0.69 g, 2.368 mmol, 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 (1H, d, *J* = 8.1 Hz), 6.46–6.40 (2H, m), 4.76 (1H, br s), 4.19 (2H, br d, *J* = 4.4 Hz), 3.85 (3H, s), 3.81 (3H, s), 1.46 (9H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 161.41, 161.37, 155.4, 134.7, 104.9, 104.5, 98.6, 87.9, 80.0, 79.6, 55.9, 55.6, 31.8, 28.5.

IR (neat) ν_{max} 3356, 2975, 2935, 2839, 2178, 1695, 1605, 1505, 1157, 1027 cm^{-1}.

HRMS (ESI+): ($C_{16}H_{21}NNaO_4$) $[M+Na]^+$ requires 314.1363, found $[M+Na]^+$ 314.1364 (Δ 0.4 ppm).



14e

Methyl 3-(3-((*tert*-butoxycarbonyl)amino)prop-1-yn-1-yl)-4-methoxybenzoate (14e): methyl 3-iodo-4-methoxybenzoate (**12e**) (1.4 g, 4.69 mmol) and *tert*-butyl prop-2-yn-1-ylcarbamate (**13**) (0.5 g, 3.13 mmol) were reacted following **General Procedure B**. The dark red suspension formed was stirred at rt for 1 h. The compound was isolated *via* column chromatography on silica gel (0–50% ethyl acetate in heptane) as an off-white solid (0.92 g, 2.87 mmol, 92% yield).

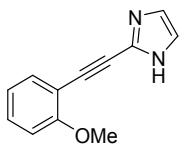
M.pt.: decomposition observed at 131 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 (1H, d, *J* = 2.2 Hz), 7.98 (1H, dd, *J* = 8.8, 2.2 Hz), 6.89 (1H, d, *J* = 8.9 Hz), 4.78 (1H, br s), 4.21 (2H, br d, *J* = 4.4 Hz), 3.93 (3H, s), 3.89 (3H, s), 1.47 (9H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.3, 163.5, 155.4, 135.6, 131.9, 122.7, 112.2, 110.3, 90.2, 80.1, 78.6, 56.2, 52.2, 31.6, 28.5.

IR (neat) ν_{max} 3355, 2980, 1707, 1683, 1515, 1268, 1130, 1020, 766 cm^{-1}.

HRMS (ESI+): ($C_{17}H_{21}NNaO_5$) $[M+Na]^+$ requires 342.1312, found $[M+Na]^+$ 342.1314 (Δ 0.7 ppm).



14f

2-((2-Methoxyphenyl)ethynyl)-1*H*-imidazole (14f): caesium carbonate (2.5 g, 7.60 mmol), copper(I) iodide (0.097 g, 0.50 mmol), bis(triphenylphosphine)palladium(II) chloride (0.355 g, 0.50 mmol) and

2-iodo-1*H*-imidazole (1.0 g, 5.00 mmol) were suspended in anhydrous DMF (15 mL) and heated to 80 °C under a N_2 atmosphere. To the reaction mixture was added 1-ethynyl-2-methoxybenzene (0.8 mL, 6.00 mmol) dropwise. After 17 h, the reaction mixture was cooled to rt, filtered through a pad of celite, diluted with MTBE (*ca.* 100 mL) and washed with sat. aq. ammonium chloride (2 × 100 mL) and water (100 mL). The aqueous layers were back-extracted with MTBE (*ca.* 100 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The compound was isolated *via* column chromatography on silica gel (0–100% ethyl acetate in heptane) as a yellow solid (0.5 g, 2.52 mmol, 50% yield).

M.pt.: 141–148 °C.

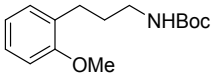
^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.02 (1H, br s), 7.49 (1H, dd, *J* = 7.6, 1.7 Hz), 7.36–7.29 (1H, m), 7.14 (2H, s), 6.96–6.86 (2H, m), 3.88 (3H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.4, 133.9, 130.8, 130.7, 120.7, 111.3, 110.9, 86.6, 83.5, 55.9.

IR (neat) ν_{max} 2459, 1880, 1494, 1425, 1249, 1107 cm^{-1}.

HRMS (ESI+): ($C_{12}H_{11}N_2O$) $[M+H]^+$ requires 199.0866, found $[M+H]^+$ 199.0859 (Δ −0.7 ppm).

*Note: Some peaks not observed in ^{13}C NMR spectrum, potentially due to broadening caused by tautomerism of the unprotected imidazole.[14] When substrate **14f** was methylated, all carbon environments were observed in ^{13}C NMR spectrum.*



15a

***tert*-Butyl (3-(2-methoxyphenyl)propyl)carbamate (15a):** *tert*-butyl (3-(2-methoxyphenyl)prop-2-yn-1-yl)carbamate (**14a**) (1.00 g, 3.83 mmol) was reacted following **General Procedure C** with palladium on carbon (10% w/w, dry) (0.1 g, 0.094 mmol). Subjected to H_2 atmosphere for 4 h. The compound was isolated following filtration and concentration as a yellow solid (0.97 g, 3.66 mmol, 96% yield).

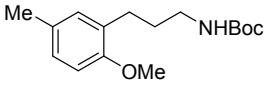
M.pt.: 39-41 °C.

^{1}H NMR (400 MHz, CD_3OD) δ = 7.19–7.06 (2H, m), 6.89 (1H, d, *J* = 8.1 Hz), 6.87–6.80 (1H, m), 3.81 (3H, s), 3.03 (2H, t, *J* = 7.2 Hz), 2.61 (2H, t, *J* = 7.2 Hz), 1.72 (2H, app. quin, *J* = 7.2 Hz), 1.44 (9H, s).

^{13}C NMR (101 MHz, CD_3OD) δ = 158.8, 158.5, 131.2, 130.8, 128.2, 121.4, 111.4, 79.8, 55.7, 41.2, 31.3, 28.8, 28.5.

IR (neat) ν_{max} 3366, 2965, 1681, 1518, 1239, 1165 cm^{-1}.

HRMS (ESI+): ($C_{15}H_{24}NO_3$) $[M+H]^+$ requires 266.1751, found $[M+H]^+$ 266.1748 (Δ −1.0 ppm).



15b

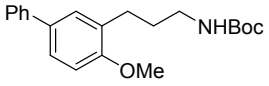
***tert*-Butyl (3-(2-methoxy-5-methylphenyl)propyl)carbamate (15b):** *tert*-butyl (3-(5-(hydroxymethyl)-2-methoxyphenyl)prop-2-yn-1-yl)carbamate (**14b**) (0.5 g, 1.716 mmol) was reacted following **General Procedure C** with palladium on carbon (10% w/w, dry) (0.1 g, 0.094 mmol). Subjected to H_2 atmosphere for 3 h. The compound was isolated *via* column chromatography on silica gel (0–40% ethyl acetate in heptane) as a colourless oil (0.39 g, 1.41 mmol, 82% yield).

^{1}H NMR (400 MHz, CD_3OD) δ = 6.97–6.90 (2H, m), 6.77 (1H, d, *J* = 8.1 Hz), 3.77 (3H, s), 3.02 (2H, t, *J* = 7.2 Hz), 2.57 (2H, t, *J* = 7.5 Hz), 2.23 (3H, s), 1.70 (2H, app. quin, *J* = 7.4 Hz), 1.44 (9H, s).

^{13}C NMR (101 MHz, CD_3OD) δ = 158.5, 156.8, 131.6, 130.9, 130.6, 128.4, 111.4, 79.8, 55.8, 41.2, 31.4, 28.8, 28.5, 20.6.

IR (neat) ν_{max} 3355, 2975, 2930, 1689, 1501,1230, 1166 cm^{-1}.

HRMS (ESI+): ($C_{16}H_{26}NO_3$) $[M+H]^+$ requires 280.1907, found $[M+H]^+$ 280.1917 (Δ 3.6 ppm).



15c

***tert*-Butyl (3-(4-methoxy-[1,1'-biphenyl]-3-yl)propyl)carbamate (15c):** *tert*-butyl (3-(4-methoxy-[1,1'-biphenyl]-3-yl)prop-2-yn-1-yl)carbamate (**14c**) (0.5 g, 1.482 mmol) was reacted following **General Procedure C** with palladium on carbon (10% w/w, dry) (0.1 g, 0.094 mmol). Subjected to H_2 atmosphere for 4 h. The compound was isolated following filtration and concentration as a white solid (0.48 g, 1.40 mmol, 94% yield).

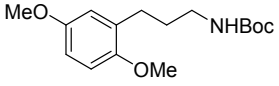
M.pt.: 96–98 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57–7.52 (2H, m), 7.44–7.35 (4H, m), 7.33–7.27 (1H, m), 6.92 (1H, d, *J* = 8.4 Hz), 4.67 (1H, br s), 3.87 (3H, s), 3.23–3.10 (2H, m), 2.71 (2H, t, *J* = 7.5 Hz), 1.82 (2H, app. quin, *J* = 7.2 Hz), 1.45 (9H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.1, 156.1, 141.1, 133.8, 130.4, 129.0, 128.8, 126.9, 126.7, 125.9, 110.7, 79.1, 55.6, 40.4, 30.4, 28.6, 27.6.

IR (neat) ν_{max} 3364, 2926, 1683, 1526, 1245, 1171, 1141, 766 cm^{-1}.

HRMS (ESI+): ($C_{21}H_{28}NO_3$) $[M+H]^+$ requires 342.2064, found $[M+H]^+$ 342.2066 (Δ 0.6 ppm).



15d

***tert*-Butyl (3-(2,5-dimethoxyphenyl)propyl)carbamate (15d):** *tert*-butyl (3-(2,5-dimethoxyphenyl)prop-2-yn-1-yl)carbamate (**14d**) (0.5 g, 1.716 mmol) was reacted following **General**

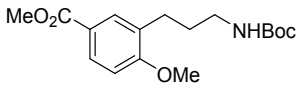
Procedure C with palladium on carbon (10% w/w, dry) (0.1 g, 0.094 mmol). Subjected to H_2 atmosphere for 3 h. The compound was isolated *via* column chromatography on silica gel (0–35% ethyl acetate in heptane) as a colourless oil (0.41 g, 1.385 mmol, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.01 (1H, d, *J* = 8.1 Hz), 6.45–6.39 (2H, m), 4.63 (1H, br s), 3.80 (3H, s), 3.79 (3H, s), 3.16–3.04 (2H, m), 2.57 (2H, t, *J* = 7.5 Hz), 1.72 (2H, app. quin, *J* = 7.2 Hz), 1.44 (9H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.4, 158.4, 156.1, 130.2, 122.4, 104.1, 98.7, 79.1, 55.5, 55.4, 40.3, 30.5, 28.6, 26.7.

IR (neat) ν_{max} 3361, 2934, 1692, 1505, 1155, 1036 cm^{-1}.

HRMS (ESI+): ($C_{16}H_{26}NO_4$) $[M+H]^+$ requires 296.1856, found $[M+H]^+$ 296.1855 (Δ −0.6 ppm).



15e

Methyl 3-(3-((*tert*-butoxycarbonyl)amino)propyl)-4-methoxybenzoate (15e): methyl 3-(3-((*tert*-butoxycarbonyl)amino)prop-1-yn-1-yl)-4-methoxybenzoate (**14e**) (0.5 g, 1.57 mmol) was reacted following **General Procedure C** with palladium on carbon (10% w/w, dry) (0.15 g, 0.141 mmol). Subjected to H_2 atmosphere for 6 h. The compound was isolated following filtration and concentration as a white solid (0.48 g, 1.487 mmol, 95% yield).

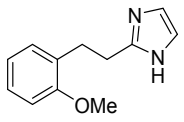
M.pt.: 97–99 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90 (1H, dd, *J* = 8.6, 2.2 Hz), 7.81 (1H, d, *J* = 2.2 Hz), 6.85 (1H, d, *J* = 8.6 Hz), 4.61 (1H, br s), 3.88 (3H, s), 3.88 (3H, s), 3.23–3.05 (2H, m), 2.69–2.62 (2H, m), 1.77 (2H, app. quin, *J* = 7.3 Hz), 1.44 (9H, s).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.2, 161.3, 156.1, 131.4, 130.1, 129.8, 122.5, 109.8, 79.2, 55.7, 52.0, 40.4, 30.1, 28.6, 27.4.

IR (neat) ν_{max} 3351, 2937, 1706, 1677, 1522, 1254, 1125, 1022, 768 cm^{-1}.

HRMS (ESI+): ($C_{17}H_{26}NO_5$) $[M+H]^+$ requires 324.1806, found $[M+H]^+$ 324.1806 (Δ 0.2 ppm).



15f

2-(2-Methoxyphenethyl)-1*H*-imidazole (15f): 2-((2-methoxyphenyl)ethynyl)-1*H*-imidazole (**14f**) (0.3 g, 1.513 mmol)was reacted following **General Procedure C** with palladium on carbon (10% w/w, dry) (45 mg, 0.042 mmol). Subjected to a H_2 atmosphere for 16 h. The compound was isolated following filtration and concentration as a green solid (0.29 g, 1.429 mmol, 94% yield).

M.pt.: 119–125 °C.

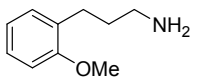
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 (1H, br s), 7.20 (1H, app. td, *J* = 7.8, 1.6 Hz), 7.10–7.06 (1H, m),

6.93 (2H, br s), 6.90–6.84 (2H, m), 3.81 (3H, s), 3.08–3.02 (4H, m).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.5, 148.4, 130.2, 129.2, 127.8, 121.4, 120.8, 110.6, 55.4, 29.3, 28.9.

IR (neat) ν_{max} 3148, 2837, 2710, 1601, 1494, 1462, 1438, 1240, 1090 cm^{-1}.

HRMS (ESI+): ($C_{12}H_{15}N_2O$) $[M+H]^+$ requires 203.1179, found $[M+H]^+$ 203.1172 (Δ −3.4 ppm).



10a

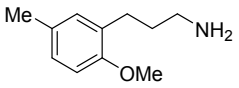
3-(2-Methoxyphenyl)propan-1-amine (10a): *tert*-butyl (3-(2-methoxyphenyl)propyl)carbamate (**15a**) (300 mg, 1.131 mmol) was reacted following **General Procedure D**. The compound was isolated as a yellow oil (188 mg, 1.130 mmol, 100% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.21–7.10 (2H, m), 6.91–6.81 (2H, m), 3.82 (3H, s), 3.06 (2H, br s), 2.76 (2H, t, *J* = 7.1 Hz), 2.67 (2H, t, *J* = 7.5 Hz), 1.81 (2H, app. quin, *J* = 7.3 Hz).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.6, 130.1, 130.0, 127.3, 120.6, 110.4, 55.4, 41.4, 32.8, 27.3.

IR (neat) ν_{max} 3360, 3284, 2932, 1600, 1492, 1240, 1028 cm^{-1}.

HRMS (ESI+): ($C_{10}H_{16}NO$) $[M+H]^+$ requires 166.1226, found $[M+H]^+$ 166.1227 (Δ 0.4 ppm).



10b

3-(2-Methoxy-5-methylphenyl)propan-1-amine (10b): *tert*-butyl (3-(2-methoxy-5-methylphenyl)propyl)carbamate (**15b**) (250 mg, 0.895 mmol) was reacted following **General Procedure D**. The compound was isolated as a white solid (135 mg, 0.753 mmol, 84% yield).

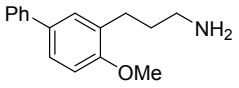
M.pt.: 98–99 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.99–6.92 (2H, m), 6.74 (1H, d, *J* = 8.1 Hz), 3.79 (3H, s), 2.70 (2H, t, *J* = 7.0 Hz), 2.61 (2H, t, *J* = 7.4 Hz), 2.26 (3H, s), 1.77–1.68 (2H, m), 1.54 (2H, br s).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.5, 130.8, 130.4, 129.7, 127.3, 110.4, 55.6, 42.0, 34.3, 27.4, 20.6.

IR (neat) ν_{max} 3376, 3326, 2919, 2836, 1577, 1488, 1314, 1239, 1032, 808 cm^{-1}.

HRMS (ESI+): ($C_{11}H_{18}NO$) $[M+H]^+$ requires 180.1383, found $[M+H]^+$ 180.1385 (Δ 1.2 ppm).



10c

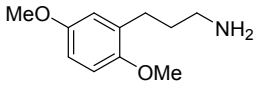
3-(4-Methoxy-[1,1'-biphenyl]-3-yl)propan-1-amine (10c): *tert*-butyl (3-(4-methoxy-[1,1'-biphenyl]-3-yl)propyl)carbamate (**15c**) (250 mg, 0.732 mmol) was reacted following **General Procedure D**. The compound was isolated as a yellow oil (177 mg, 0.733 mmol, 100% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58–7.53 (2H, m), 7.44–7.36 (4H, m), 7.32–7.27 (1H, m), 6.92 (1H, d, *J* = 8.4 Hz), 3.87 (3H, s), 2.79–2.69 (4H, m), 1.79 (2H, app. quin, *J* = 7.3 Hz), 1.49 (2H, br s).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.2, 141.2, 133.7, 130.9, 128.9, 128.8, 126.9, 126.7, 125.7, 110.7, 55.6, 42.0, 34.3, 27.7.

IR(neat) ν_{max} 3581, 3363, 2932, 2835, 1482, 1244, 763 cm^{-1}.

HRMS (ESI+): ($C_{16}H_{20}NO$**)** $[M+H]^+$ requires 242.1539, found $[M+H]^+$ 242.1545 (Δ 2.1 ppm).



10d

3-(2,5-Dimethoxyphenyl)propan-1-amine (10d): *tert*-butyl (3-(2,5-dimethoxyphenyl)propyl)carbamate (**15d**) (250 mg, 0.846 mmol) was reacted following **General Procedure D**. The compound was isolated as an off-white solid (146 mg, 0.748 mmol, 88% yield).

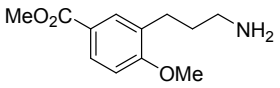
M.pt.: 96–99 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.02 (1H, d, *J* = 8.1 Hz), 6.46–6.39 (2H, m), 3.79 (3H, s), 3.79 (3H, s), 2.69 (2H, t, *J* = 7.0 Hz), 2.58 (2H, t, *J* = 7.6 Hz), 1.70 (2H, app. quin, *J* = 7.3 Hz), 1.49 (2H, br s).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.2, 158.4, 130.1, 123.0, 104.0, 98.6, 55.5, 55.4, 42.0, 34.4, 26.8.

IR(neat) ν_{max} 3356, 2998, 2940, 2857, 1611, 1493, 1207, 1035 cm^{-1}.

HRMS (ESI+): ($C_{11}H_{18}NO_2$) $[M+H]^+$ requires 196.1332, found $[M+H]^+$ 196.1338 (Δ 3.0 ppm).



10e

Methyl 3-(3-aminopropyl)-4-methoxybenzoate (10e): methyl 3-(3-((*tert*-butoxycarbonyl)amino)propyl)-4-methoxybenzoate (**15e**) (250 mg, 0.773 mmol) was reacted following **General Procedure D**. The compound was isolated as a yellow solid (116 mg, 0.520 mmol, 67% yield).

M.pt.: 96–101 °C.

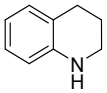
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 (1H, dd, *J* = 8.6, 2.2 Hz), 7.81 (1H, d, *J* = 2.2 Hz), 6.84 (1H, d, *J* = 8.6 Hz), 3.87 (3H, s), 3.87 (3H, s), 2.76–2.63 (4H, m), 1.78–1.68 (2H, m), 1.66 (2H, br s).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.2, 161.4, 131.4, 130.6, 129.6, 122.3, 109.7, 55.6, 52.0, 42.0, 33.9, 27.4.

IR (neat) ν_{max} 3313, 2925, 2851, 1714, 1605, 1435, 1251, 1131, 1027, 767 cm^{-1}.

HRMS (ESI+): ($C_{12}H_{18}NO_3$) $[M+H]^+$ requires 224.1281, found $[M+H]^+$ 224.1290 (Δ 3.7 ppm).

Photo-Annulation



11a

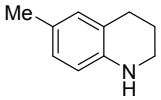
1,2,3,4-Tetrahydroquinoline (11a): 3-(2-methoxyphenyl)propan-1-amine (**10a**) (66 mg, 0.4 mmol) was reacted following **General Procedure E**. Reaction mixture was irradiated for 24 h. The compound was isolated *via* column chromatography on silica gel (0–50% ethyl acetate in heptane) as a colourless oil (34 mg, 0.257 mmol, 64% yield). Analytical data matched those reported in the literature.[15]

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.00–6.91 (2H, m), 6.64–6.57 (1H, m), 6.47 (1H, d, *J* = 7.9 Hz), 3.81 (1H, br s), 3.34–3.27 (2H, m), 2.77 (2H, t, *J* = 6.4 Hz), 2.00–1.90 (2H, m).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 144.9, 129.6, 126.9, 121.6, 117.1, 114.3, 42.1, 27.1, 22.3.

IR (neat) ν_{max} 3414, 2925, 2835, 1605, 1496, 1309, 742.5 cm^{-1}.

HRMS (ESI+): ($C_9H_{12}N$) $[M+H]^+$ requires 134.0964, found $[M+H]^+$ 134.0965 (Δ 0.2 ppm).



11b

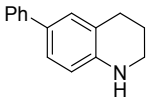
6-Methyl-1,2,3,4-tetrahydroquinoline (11b): 3-(2-methoxy-5-methylphenyl)propan-1-amine (**10b**) (72 mg, 0.4 mmol) was reacted following **General Procedure E**. Reaction mixture was irradiated for 24 h. The compound was isolated *via* column chromatography on silica gel (0–50% ethyl acetate in heptane) as a pale yellow oil (44 mg, 0.299 mmol, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.85–6.70 (2H, m), 6.46–6.36 (1H, m), 3.65 (1H, br s), 3.33–3.24 (2H, m), 2.74 (2H, t, *J* = 6.4 Hz), 2.21 (3H, s), 1.99–1.88 (2H, m).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 142.5, 130.2, 127.4, 126.4, 121.7, 114.6, 42.3, 27.1, 22.6, 20.5.

IR (neat) ν_{max} 3399, 3005, 2923, 2841, 1619, 1509, 1301, 805 cm^{-1}.

HRMS (ESI+): ($C_{10}H_{14}N$) $[M+H]^+$ requires 148.1121, found $[M+H]^+$ 148.1125 (Δ 2.7 ppm).



11c

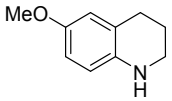
6-Phenyl-1,2,3,4-tetrahydroquinoline (11c): 3-(4-methoxy-[1,1'-biphenyl]-3-yl)propan-1-amine (**10c**) (97 mg, 0.4 mmol) was reacted following **General Procedure E**. Reaction mixture was irradiated for 72 h. The compound was isolated *via* column chromatography on silica gel (0–35% ethyl acetate in heptane) as a yellow oil (61 mg, 0.292 mmol, 73% yield).

^{1}H NMR (400 MHz, CD_3OD) δ = 7.51–7.46 (2H, m), 7.36–7.29 (2H, m), 7.21–7.14 (3H, m), 6.58–6.53 (1H, m), 3.29–3.24 (2H, m), 2.79 (2H, t, *J* = 6.4 Hz), 1.97–1.89 (2H, m).

^{13}C NMR (101 MHz, CD_3OD) δ = 146.0, 142.9, 130.9, 129.6, 128.6, 126.9, 126.7, 126.2, 122.9, 115.9, 42.8, 28.3, 23.4.

IR (neat) ν_{max} 3407, 3023, 2924, 2837, 1611, 1485, 1299, 761, 695 cm^{-1}.

HRMS (ESI+): ($C_{15}H_{16}N$) $[M+H]^+$ requires 210.1277, found $[M+H]^+$ 210.1285 (Δ 3.9 ppm).



11d

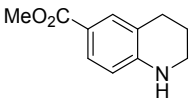
6-Methoxy-1,2,3,4-tetrahydroquinoline (11d): 3-(2,5-dimethoxyphenyl)propan-1-amine (**10d**) (78 mg, 0.4 mmol) was reacted following **General Procedure E**. Reaction mixture was irradiated for 40 h. The compound was isolated *via* column chromatography on silica gel (0–50% ethyl acetate in heptane) as a yellow oil (32 mg, 0.196 mmol, 49% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.84 (1H, br d, *J* = 8.1 Hz), 6.20 (1H, dd, *J* = 8.1, 2.5 Hz), 6.04 (1H, d, *J* = 2.5 Hz), 3.82 (1H, br s), 3.73 (3H, s), 3.31–3.25 (2H, m), 2.70 (2H, t, *J* = 6.4 Hz), 1.97–1.88 (2H, m).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.0, 145.7, 130.2, 114.2, 103.0, 99.6, 55.3, 42.1, 26.4, 22.6.

IR (neat) ν_{max} 3401, 2926, 2834, 1614, 1511, 1198, 1164 cm^{-1}.

HRMS (ESI+): ($C_{10}H_{14}NO$) $[M+H]^+$ requires 164.1070, found $[M+H]^+$ 164.1076 (Δ 3.9 ppm).



11e

Methyl 1,2,3,4-tetrahydroquinoline-6-carboxylate (11e): methyl 3-(3-aminopropyl)-4-methoxybenzoate (**10e**) (89 mg, 0.4 mmol) was reacted following **General Procedure E**. Reaction mixture was irradiated for 40 h. The compound was isolated *via* column chromatography on silica gel (0–50% ethyl acetate in heptane) as an off-white solid (29 mg, 0.152 mmol, 38% yield).

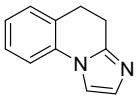
M.pt.: 67–70 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.49–7.42 (2H, m), 6.59 (1H, br s), 6.42 (1H, d, *J* = 8.6 Hz), 3.71 (3H, s), 3.26–3.19 (2H, m), 2.67 (2H, t, *J* = 6.3 Hz), 1.81–1.73 (2H, m).

^{13}C NMR (101 MHz, DMSO-d_6) δ = 166.4, 149.6, 130.5, 128.6, 118.7, 114.7, 112.0, 51.0, 40.5, 26.5, 20.7.

IR (neat) ν_{max} 3371, 2928, 2853, 1678, 1600, 1527, 1437, 1279, 766 cm^{-1}.

HRMS (ESI+): ($C_{11}H_{14}NO_2$) $[M+H]^+$ requires 192.1019, found $[M+H]^+$ 192.1027 (Δ 4.0 ppm).



11f

4,5-Dihydroimidazo[1,2-*a*]quinoline (**11f**): 2-(2-methoxyphenethyl)-1*H*-imidazole (**15f**) (81 mg, 0.4 mmol) was reacted following **General Procedure E** in a DCE:TFE (1:1) solvent system. Reaction mixture was irradiated for 24 h. The compound was isolated *via* column chromatography on silica gel (20–100% ethyl acetate in heptane) as a yellow oil (54 mg, 0.318 mmol, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 (1H, d, *J* = 1.5 Hz), 7.34–7.26 (3H, m), 7.19–7.12 (1H, m), 7.08 (1H, d, *J* = 1.2 Hz), 3.13–3.05 (2H, m), 3.05–2.98 (2H, m).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 145.6, 135.1, 129.2, 129.1, 127.9, 127.5, 125.5, 115.8, 113.5, 26.5,

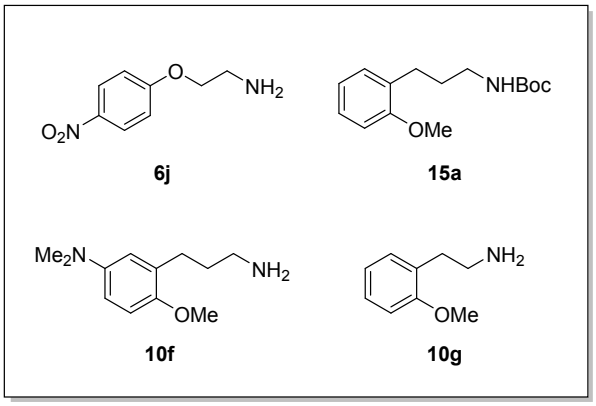
23.3.

IR (neat) ν_{max} 3101, 2904, 2835, 1533, 1501, 1308, 1275, 1175 cm^{-1}.

HRMS (ESI+): ($C_{11}H_{11}N_2$) $[M+H]^+$ requires 171.0917, found $[M+H]^+$ 171.0911 (Δ −3.4 ppm).

Incompatible Substrates

An example of substrates that were unsuccessfully rearranged or annulated under the described conditions (**Procedure A** or **E**).



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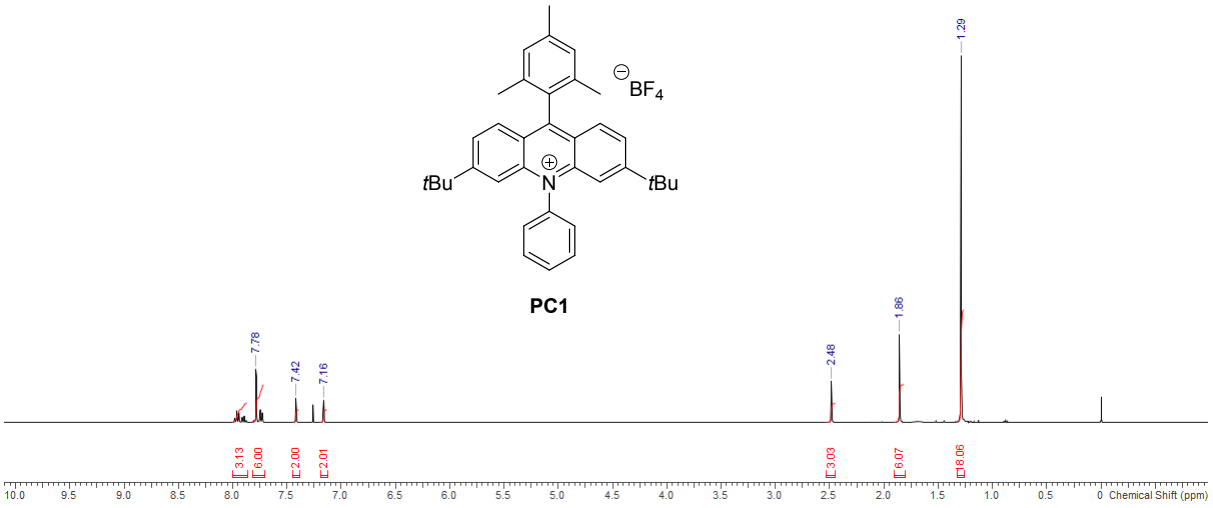
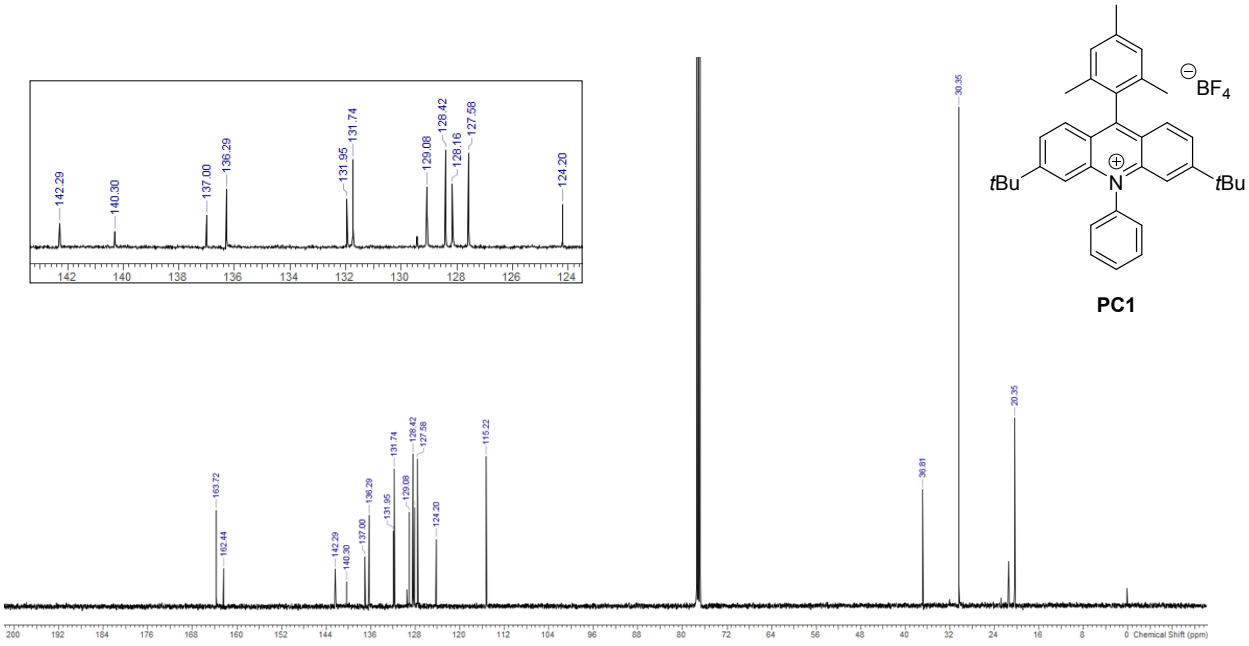
6 NMR Spectra

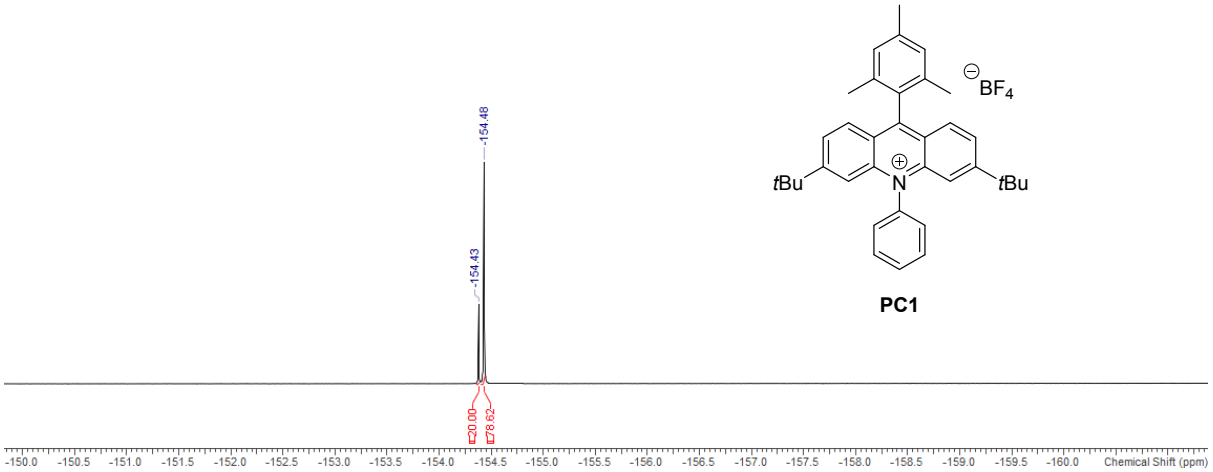
^{1}H NMR (400 MHz, $CDCl_3$), compound **PC1**



^{13}C NMR (101 MHz, $CDCl_3$), compound **PC1**

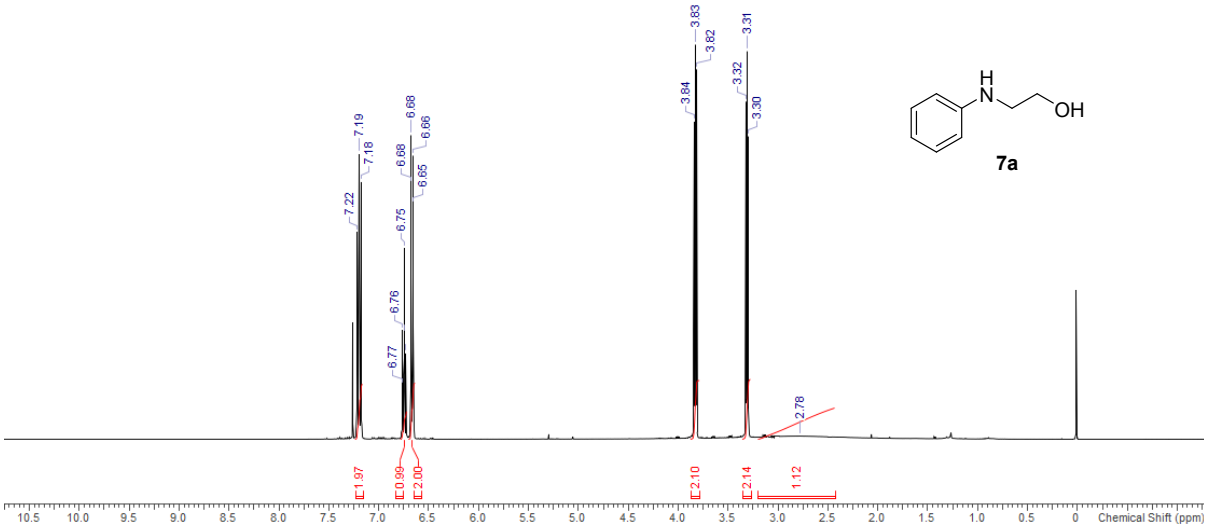


^{19}F NMR (376 MHz, $CDCl_3$), compound **PC1**



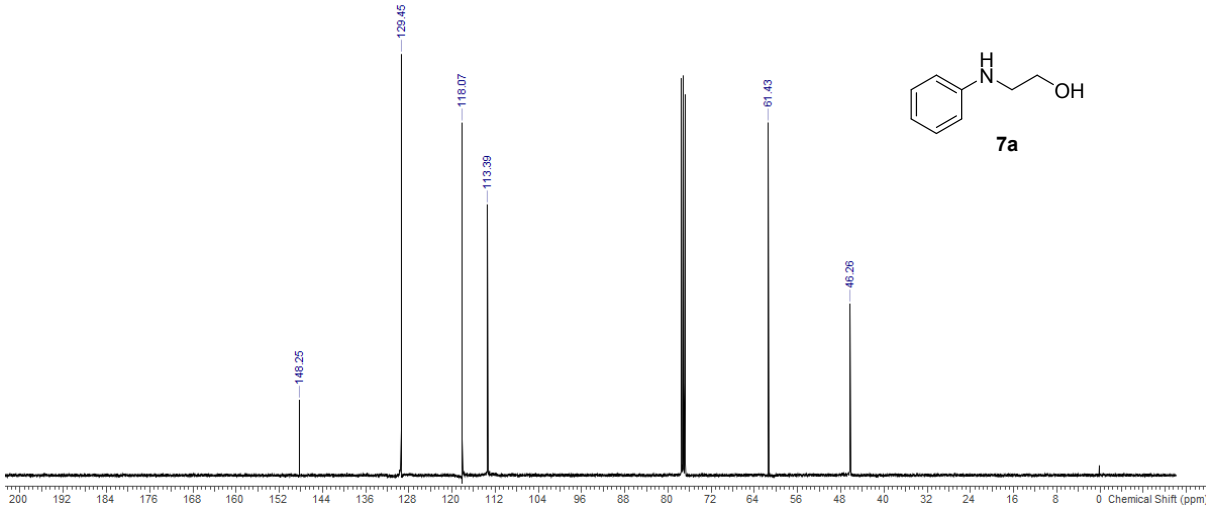
PC1

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

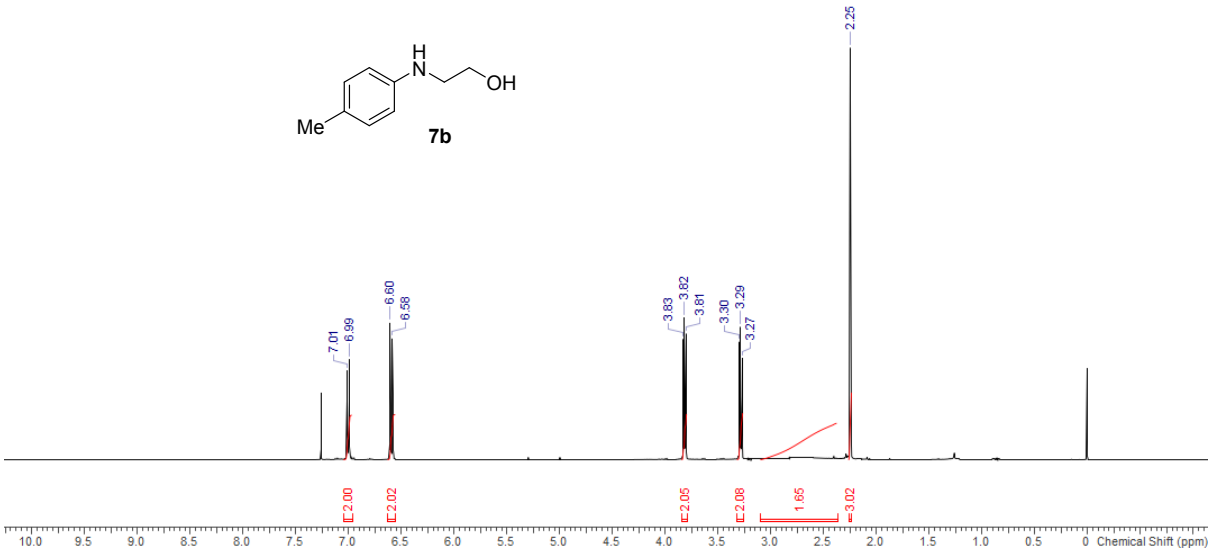


Note: ^{1}H NMR spectra of Photo-Smiles products appear to show triplets in the alkyl region, however, zoomed in shows a more complex pattern is present – potentially due to intramolecular hydrogen bonding resulting in differentiation of the protons attached to the same carbons.

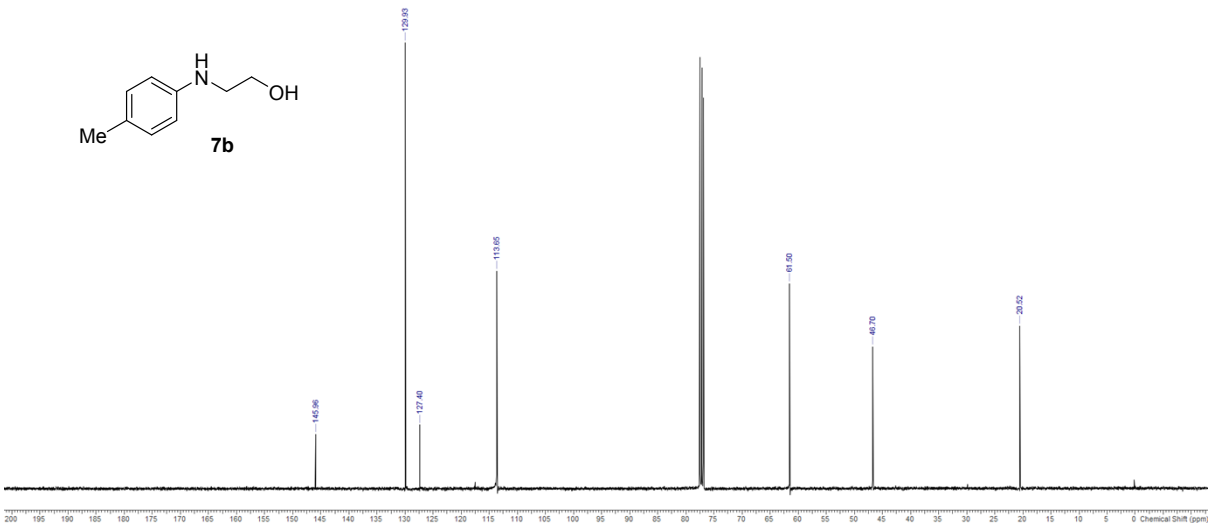
^{13}C NMR (101 MHz, $CDCl_3$), compound **7a**



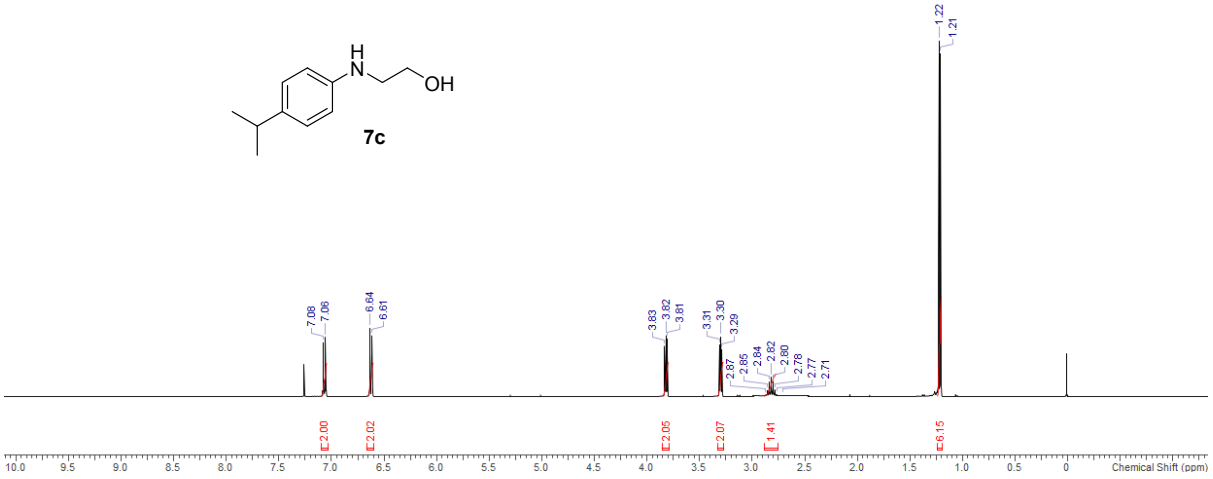
^{1}H NMR (400 MHz, $CDCl_3$), compound **7b**



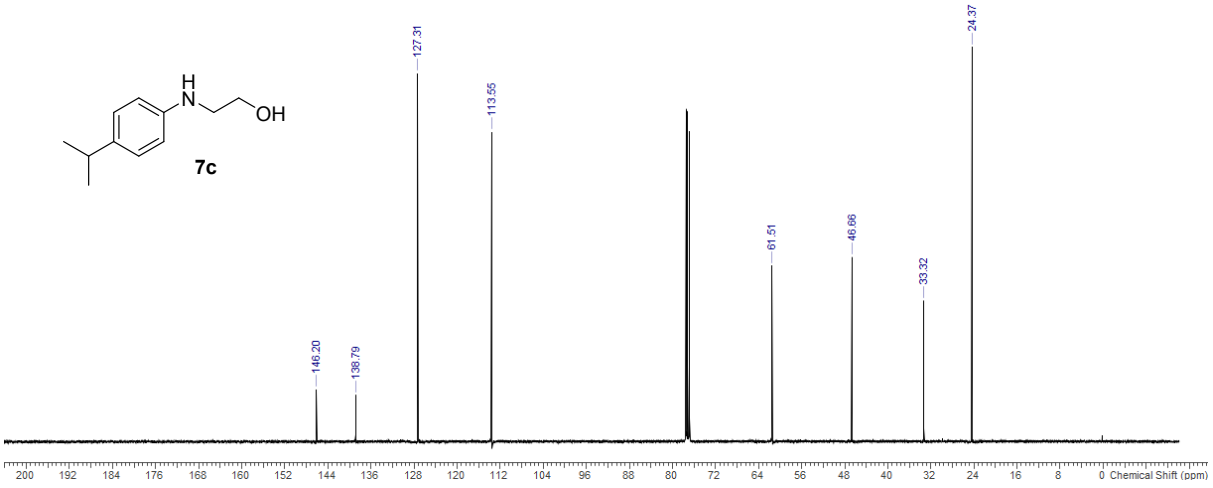
^{13}C NMR (101 MHz, $CDCl_3$), compound **7b**



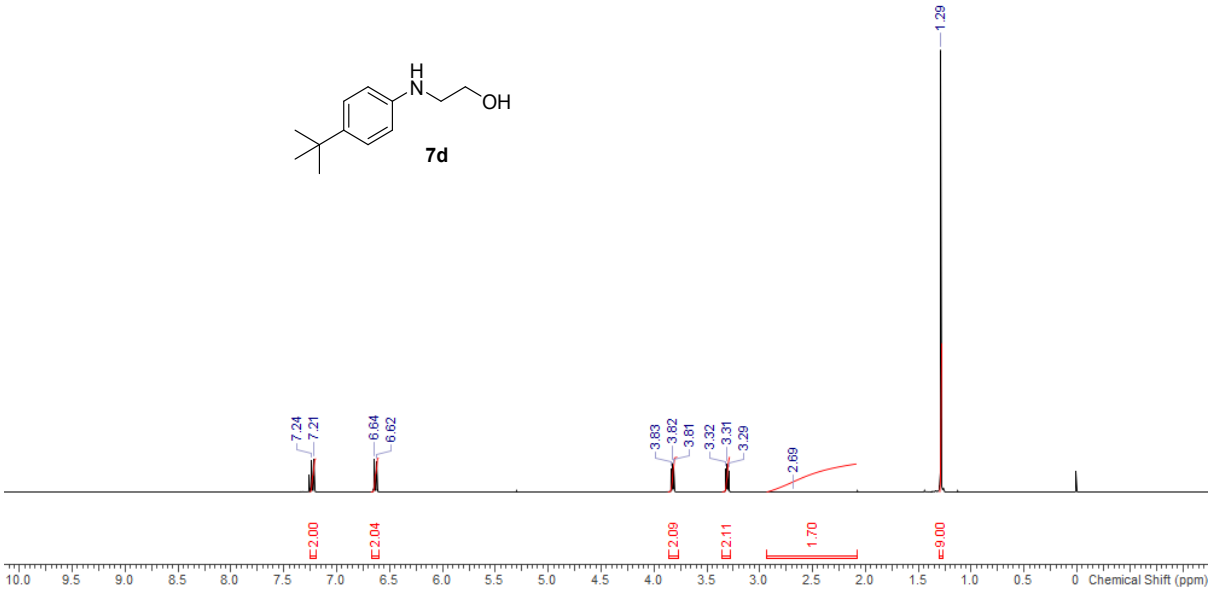
^{1}H NMR (400 MHz, $CDCl_3$), compound **7c**



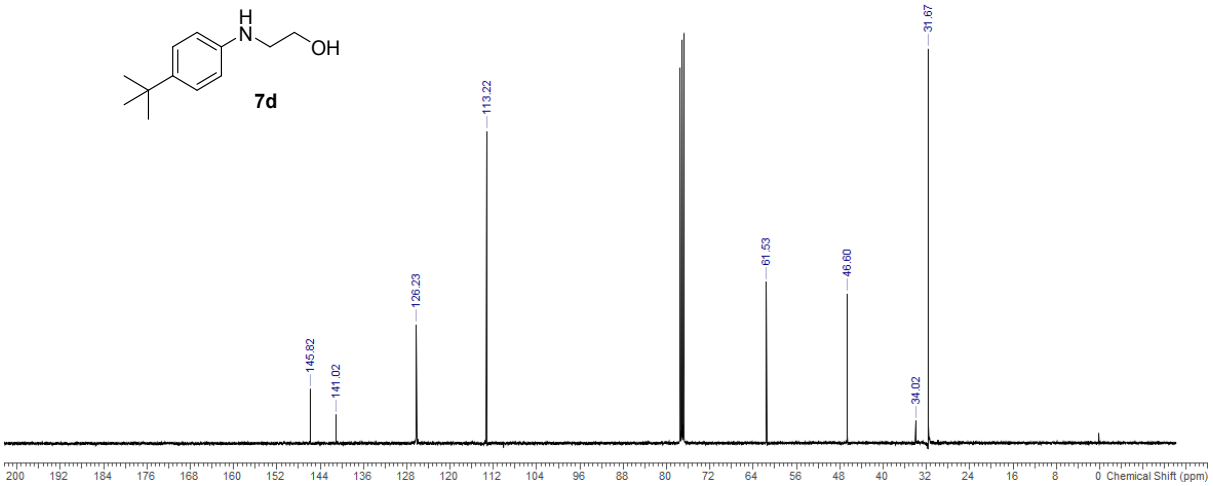
^{13}C NMR (101 MHz, $CDCl_3$), compound **7c**



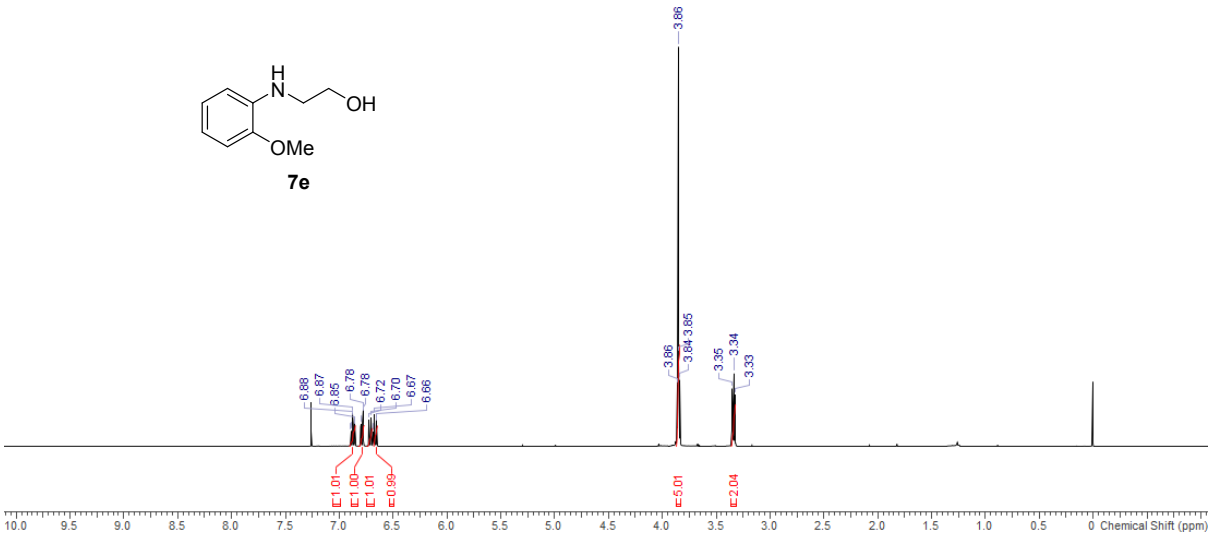
^{1}H NMR (400 MHz, $CDCl_3$), compound **7d**



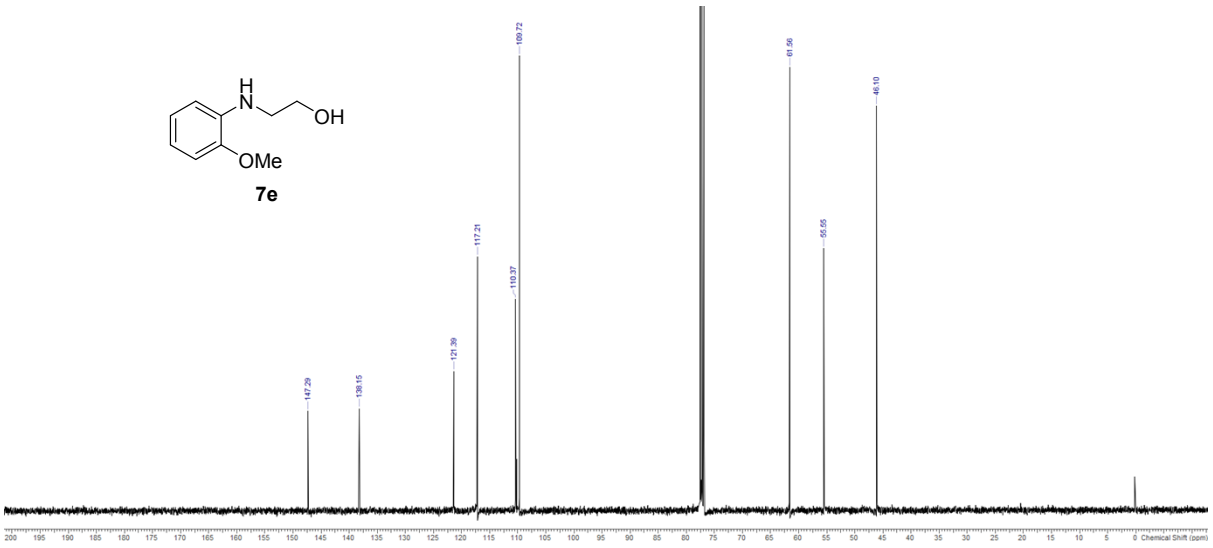
^{13}C NMR (101 MHz, $CDCl_3$), compound **7d**



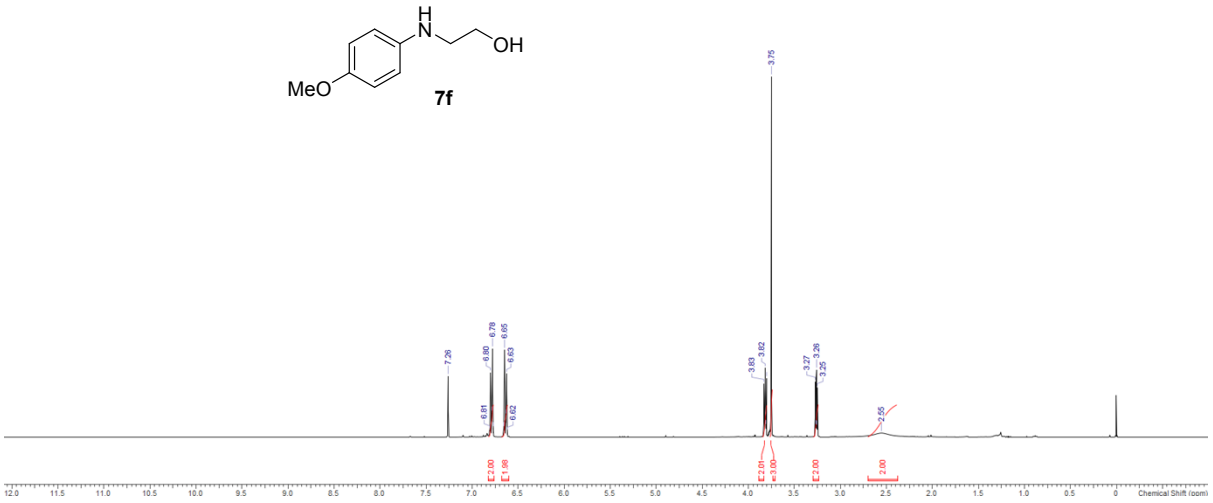
^{1}H NMR (400 MHz, $CDCl_3$), compound **7e**



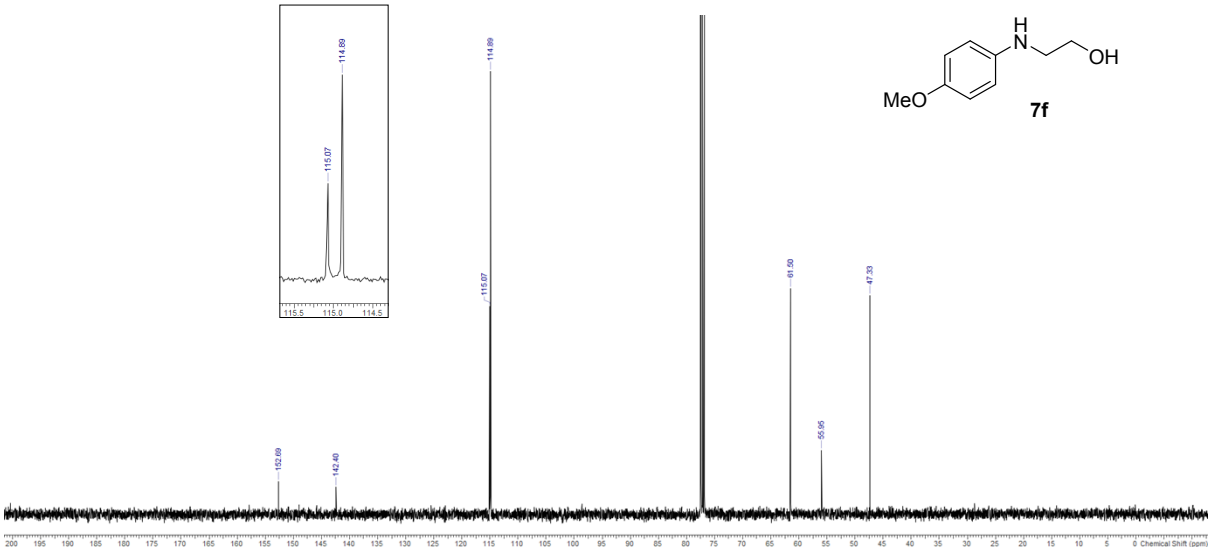
^{13}C NMR (101 MHz, $CDCl_3$), compound **7e**



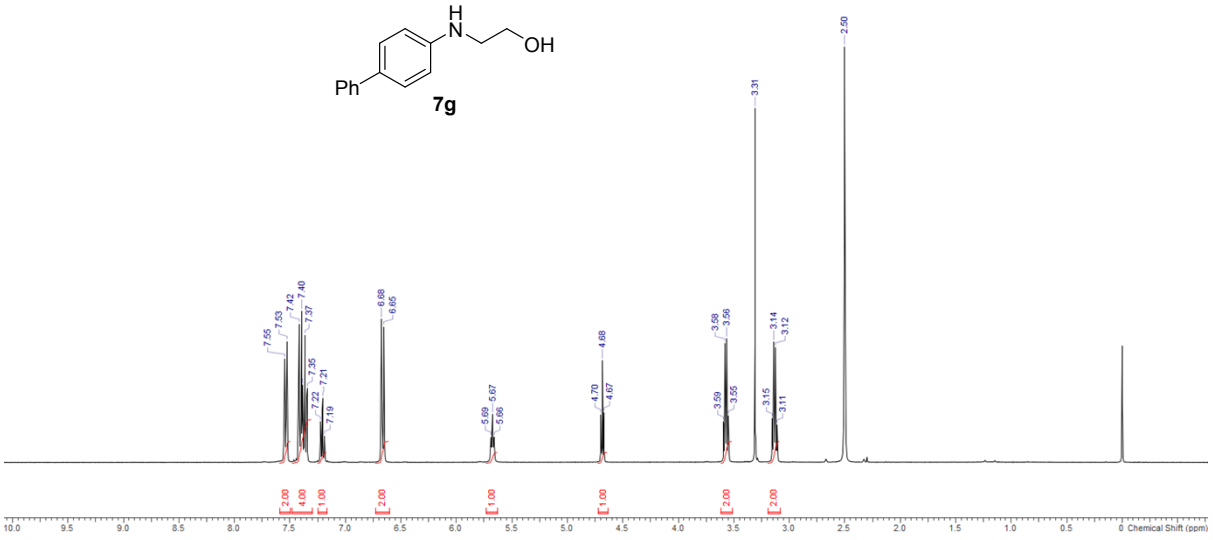
^{1}H NMR (400 MHz, $CDCl_3$), compound **7f**



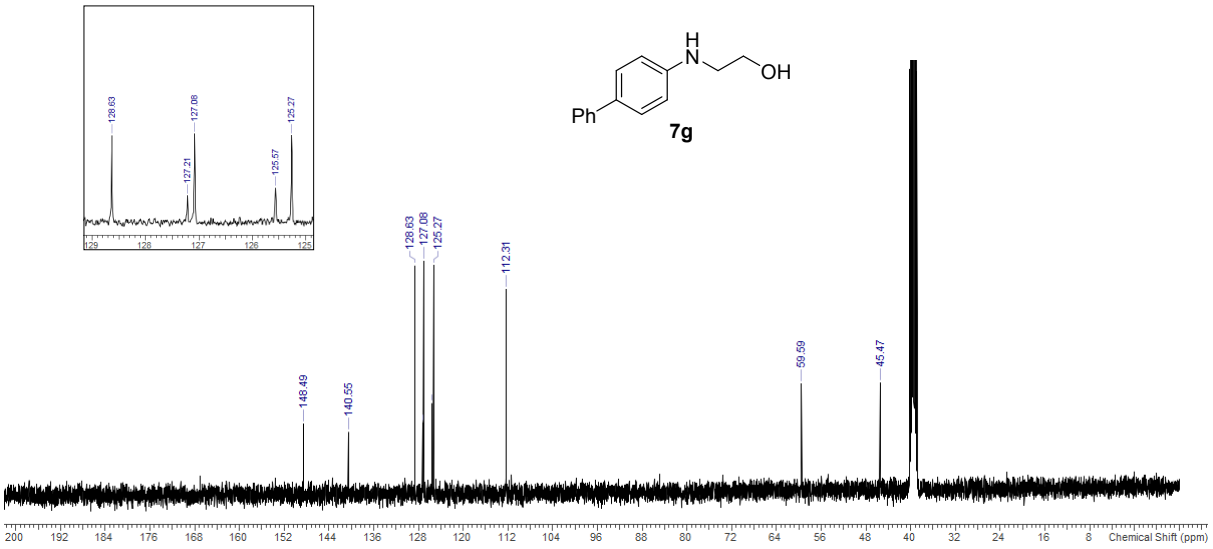
^{13}C NMR (101 MHz, $CDCl_3$), compound **7f**



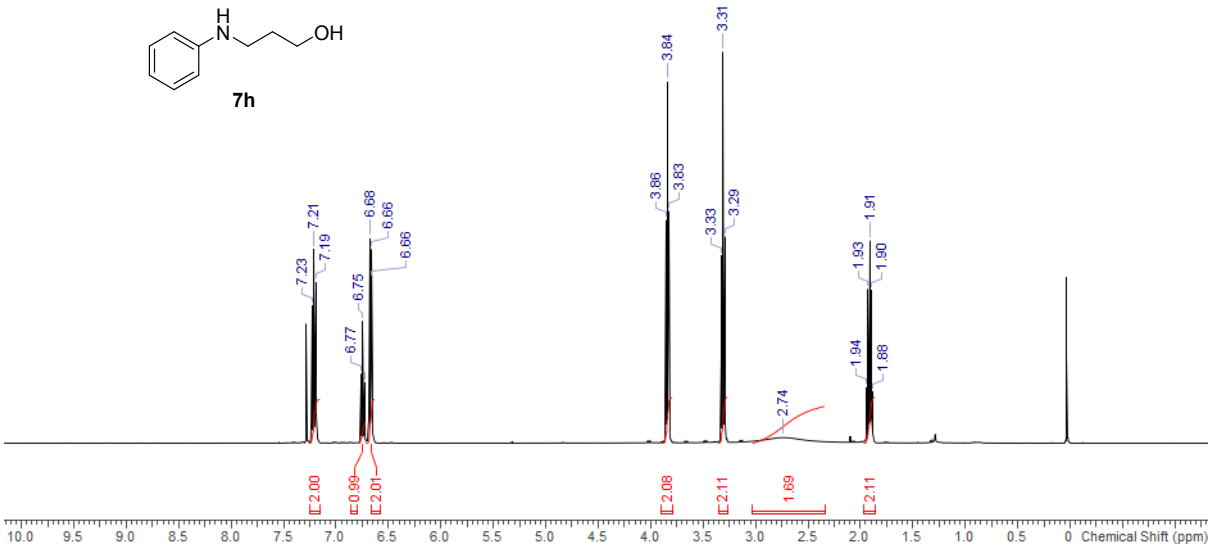
^{1}H NMR (400 MHz, DMSO-d_6), compound **7g**



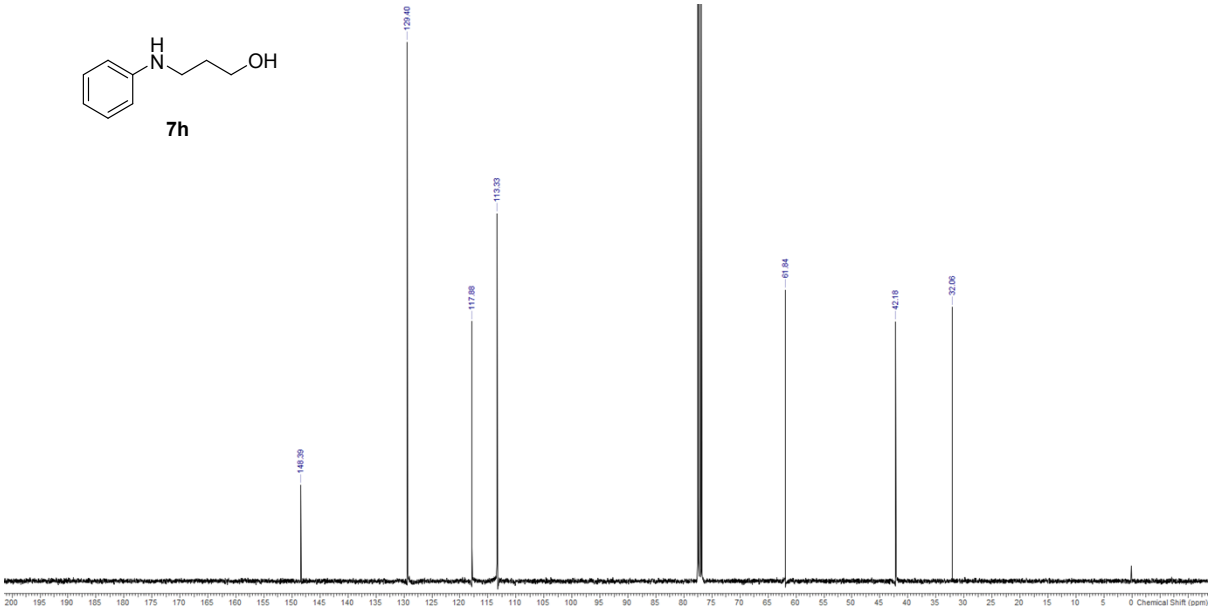
^{13}C NMR (101 MHz, DMSO-d_6), compound **7g**



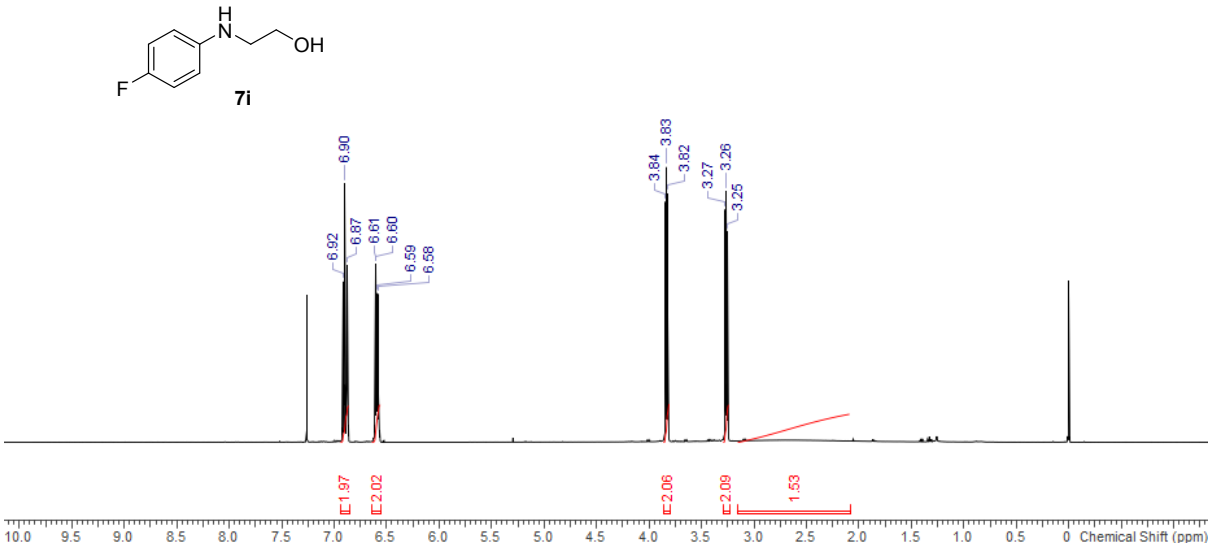
^{1}H NMR (400 MHz, $CDCl_3$), compound **7h**



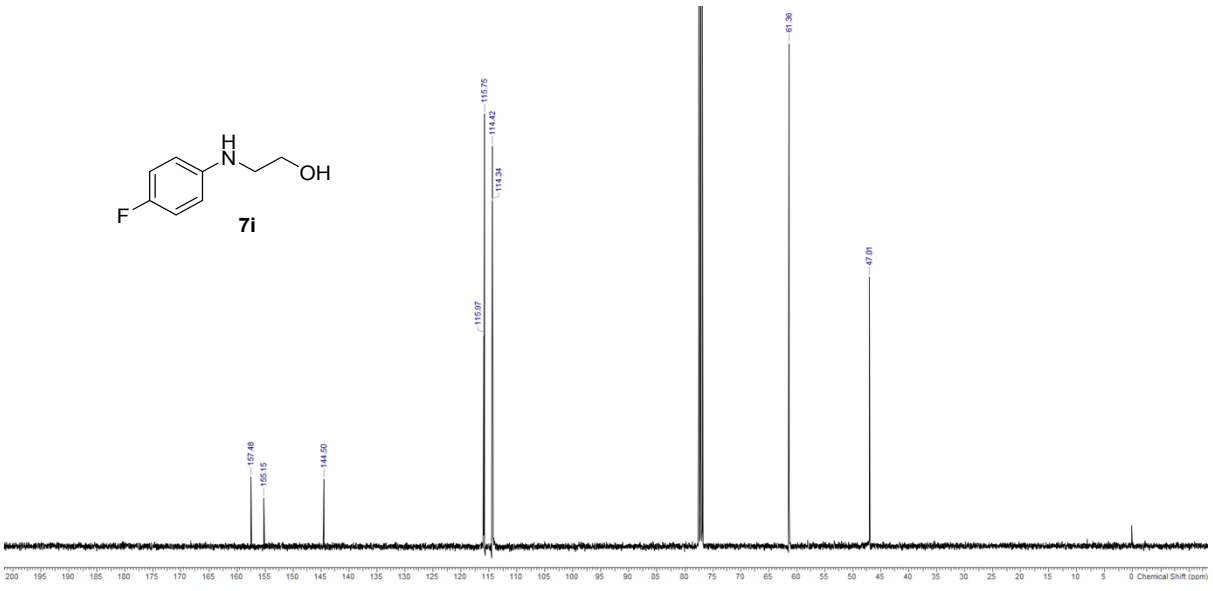
^{13}C NMR (101 MHz, $CDCl_3$), compound **7h**



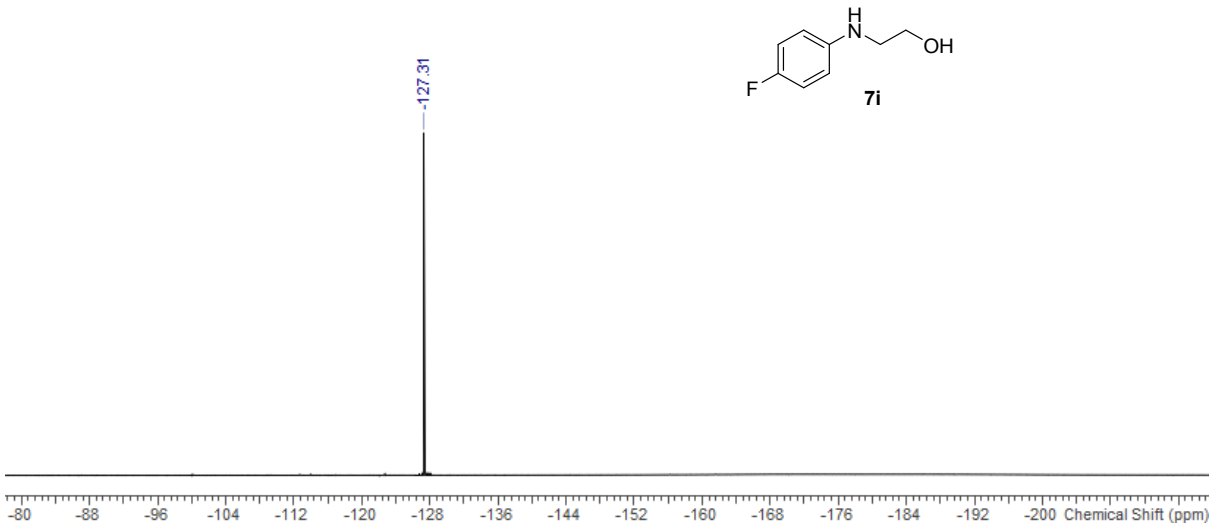
^{1}H NMR (400 MHz, $CDCl_3$), compound **7i**



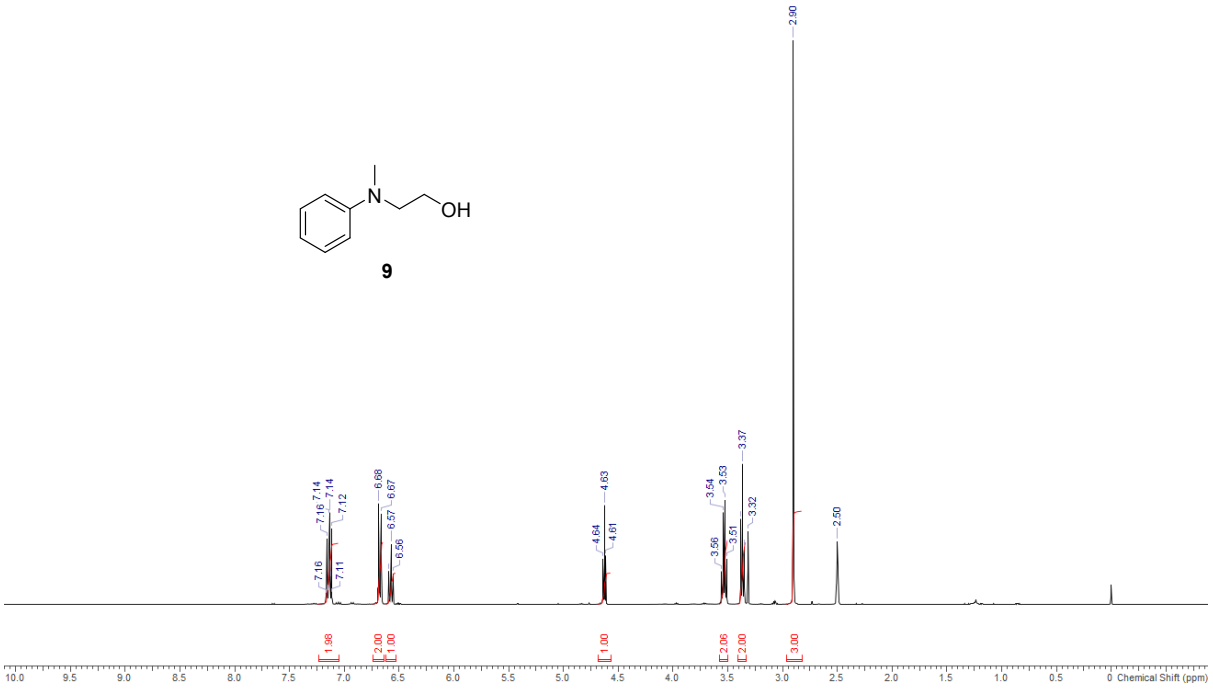
^{13}C NMR (101 MHz, $CDCl_3$), compound **7i**



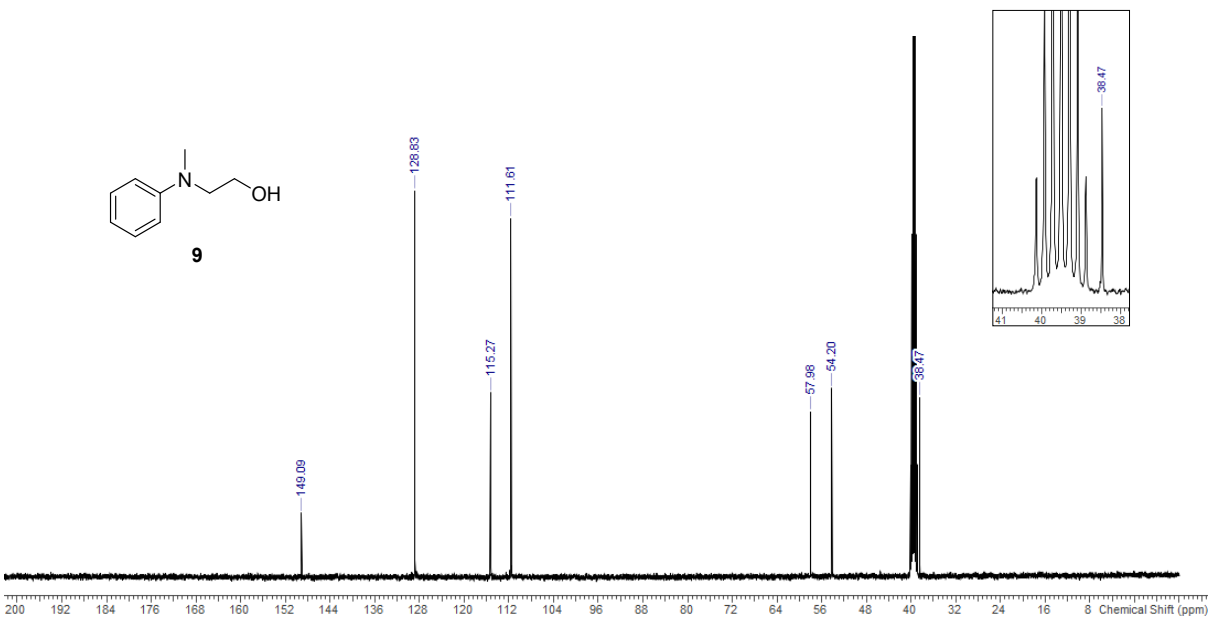
^{19}F NMR (376 MHz, $CDCl_3$), compound **7i**



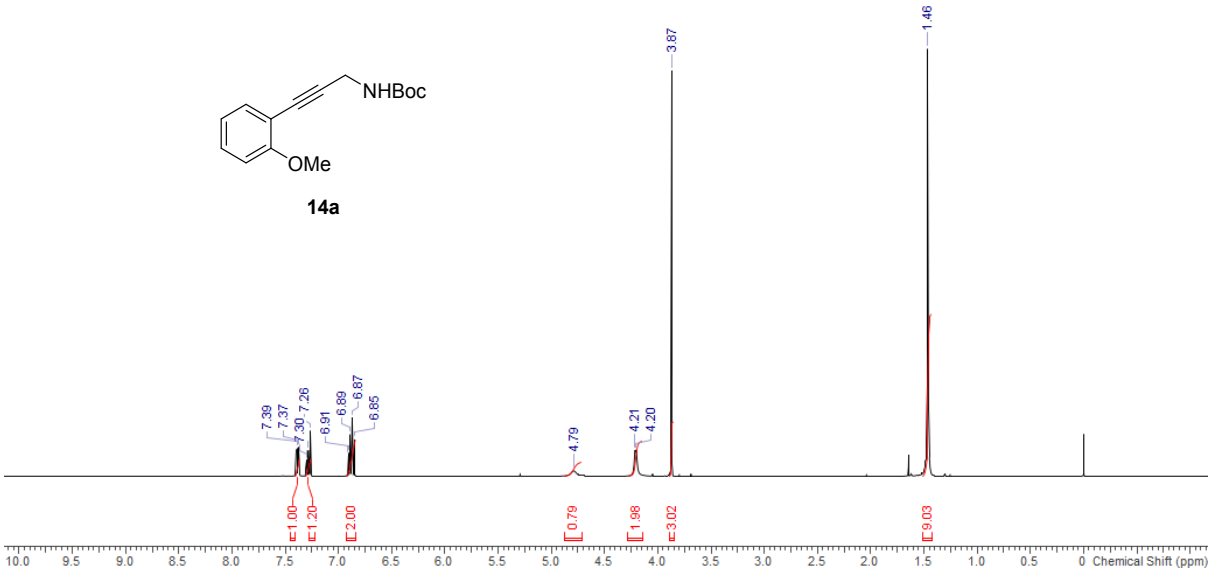
^{1}H NMR (400 MHz, DMSO-d_6), compound **9**



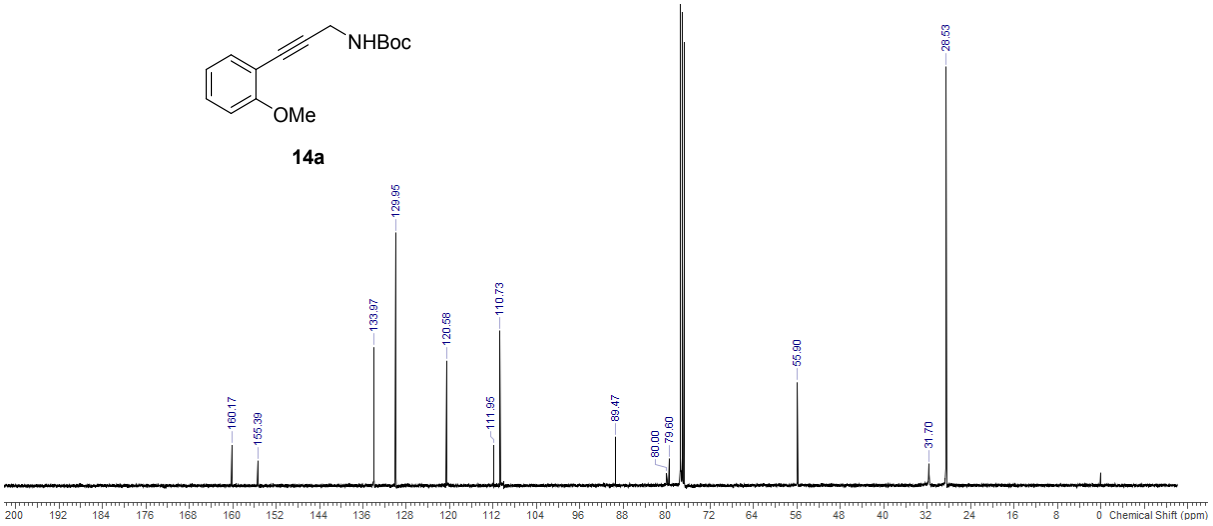
^{13}C NMR (101 MHz, DMSO-d_6), compound **9**



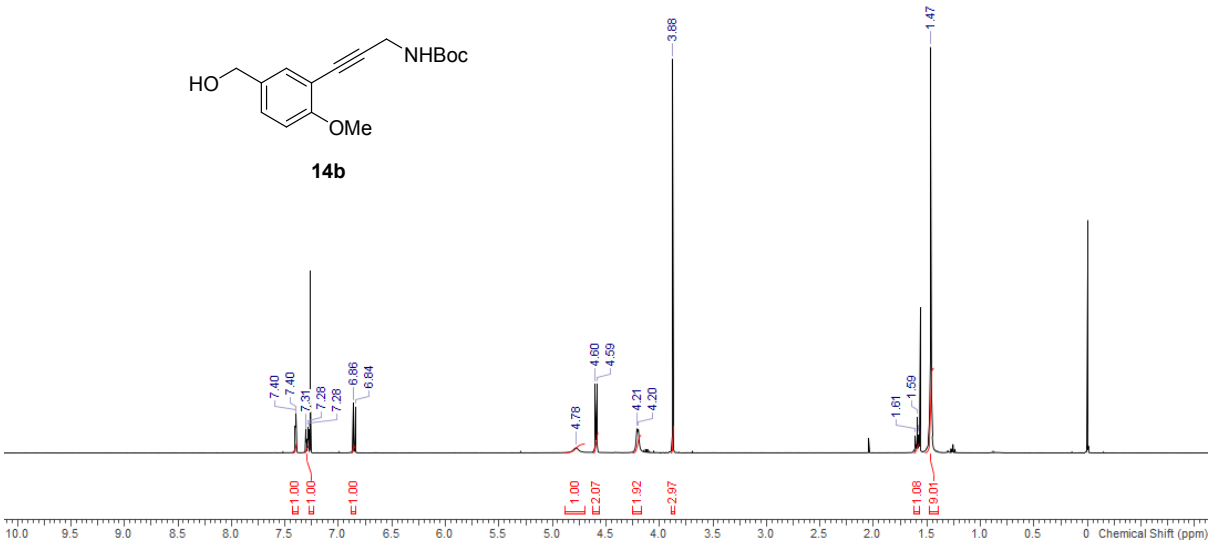
^{1}H NMR (400 MHz, $CDCl_3$), compound **14a**



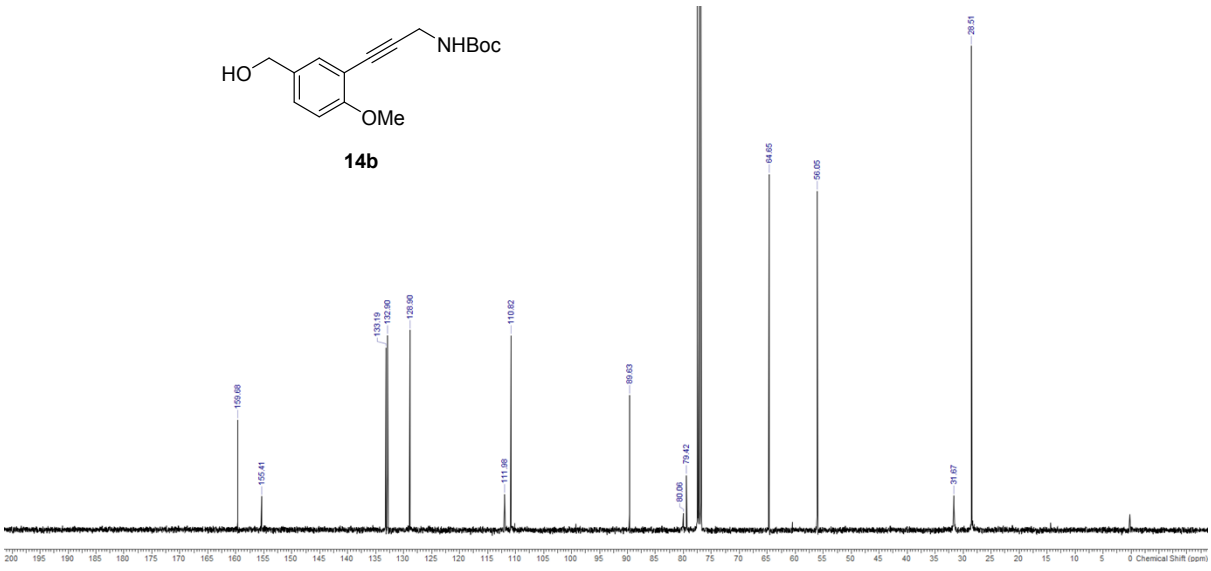
^{13}C NMR (101 MHz, $CDCl_3$), compound **14a**



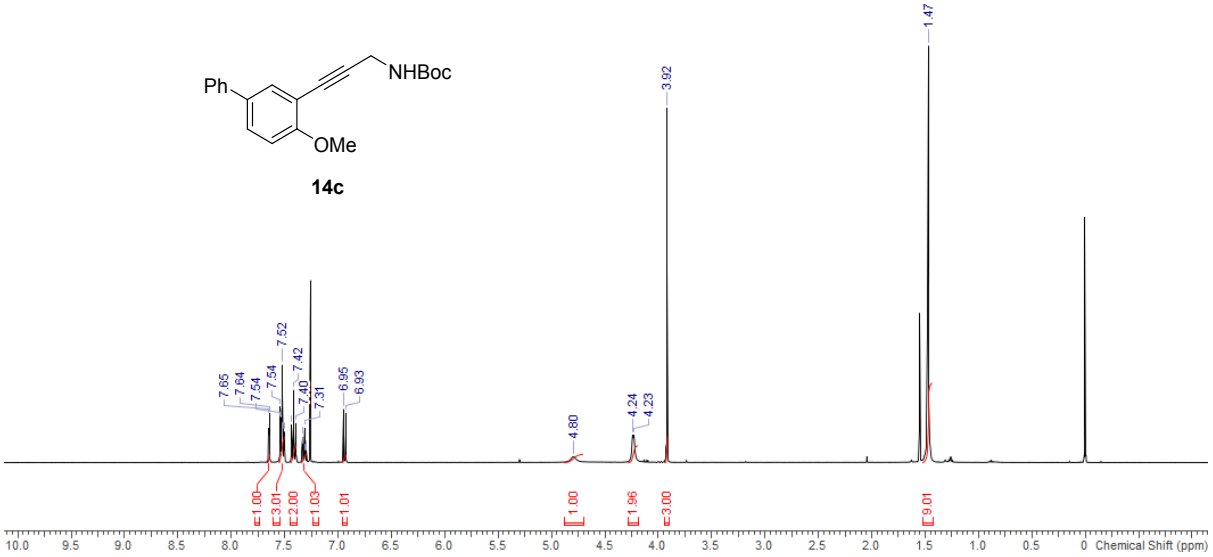
^{1}H NMR (400 MHz, $CDCl_3$), compound **14b**



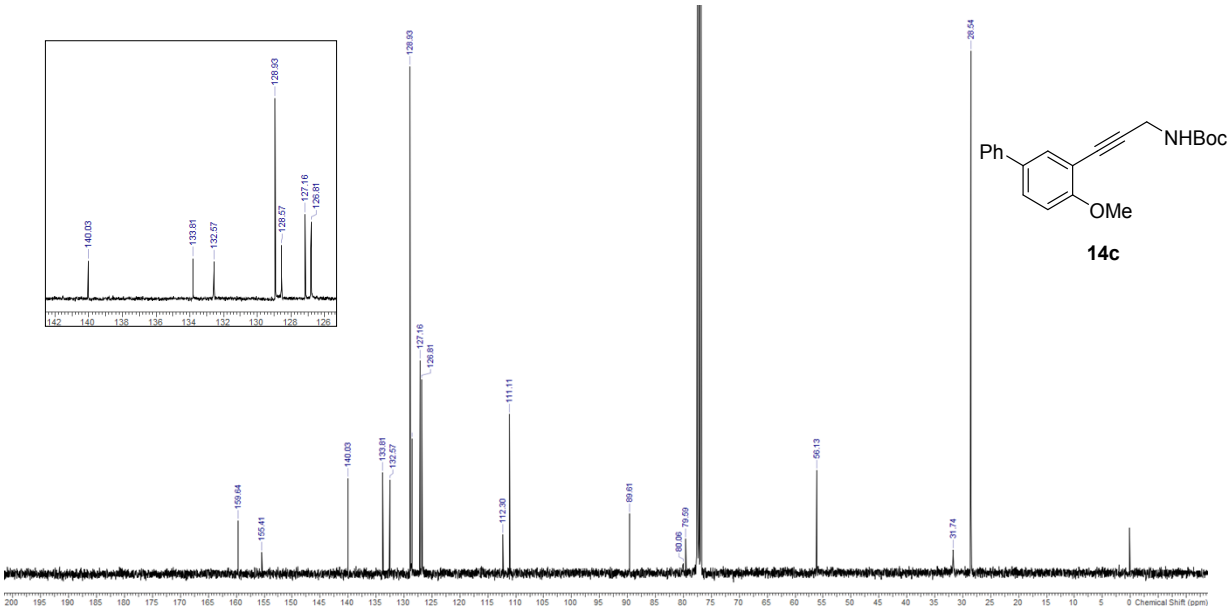
^{13}C NMR (101 MHz, $CDCl_3$), compound **14b**



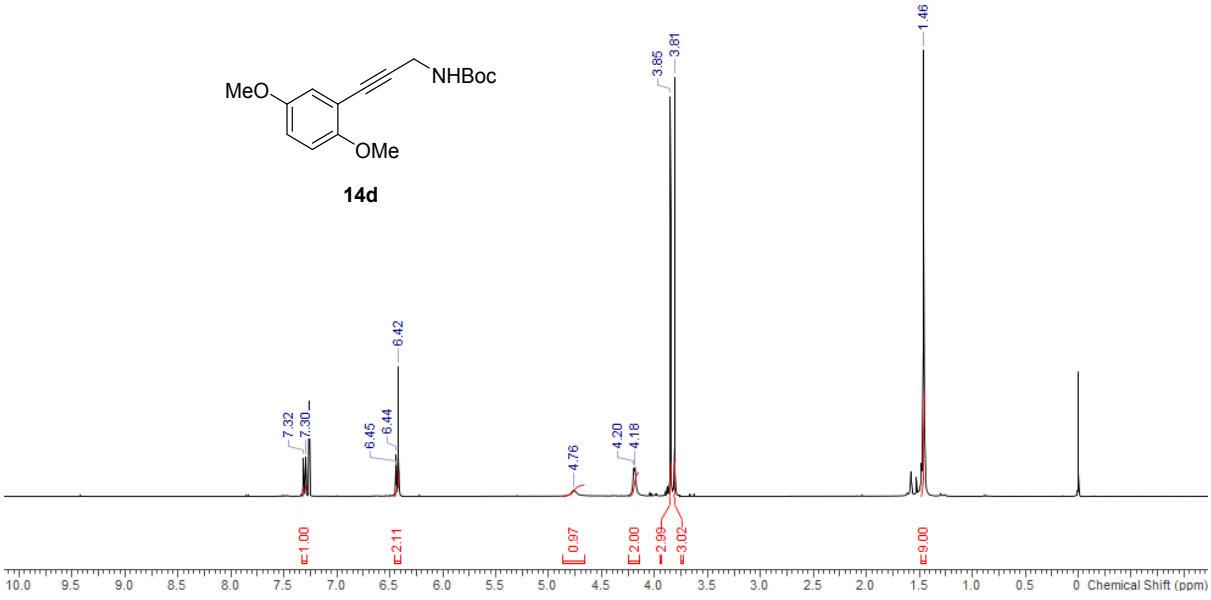
^{1}H NMR (400 MHz, $CDCl_3$), compound **14c**



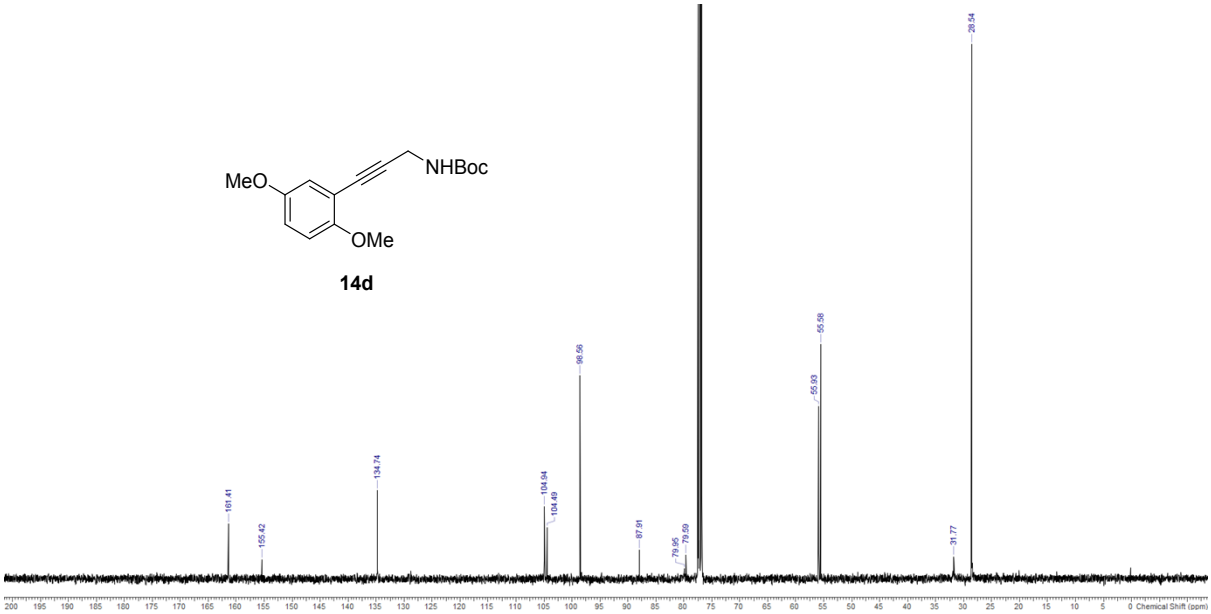
^{13}C NMR (101 MHz, $CDCl_3$), compound **14c**



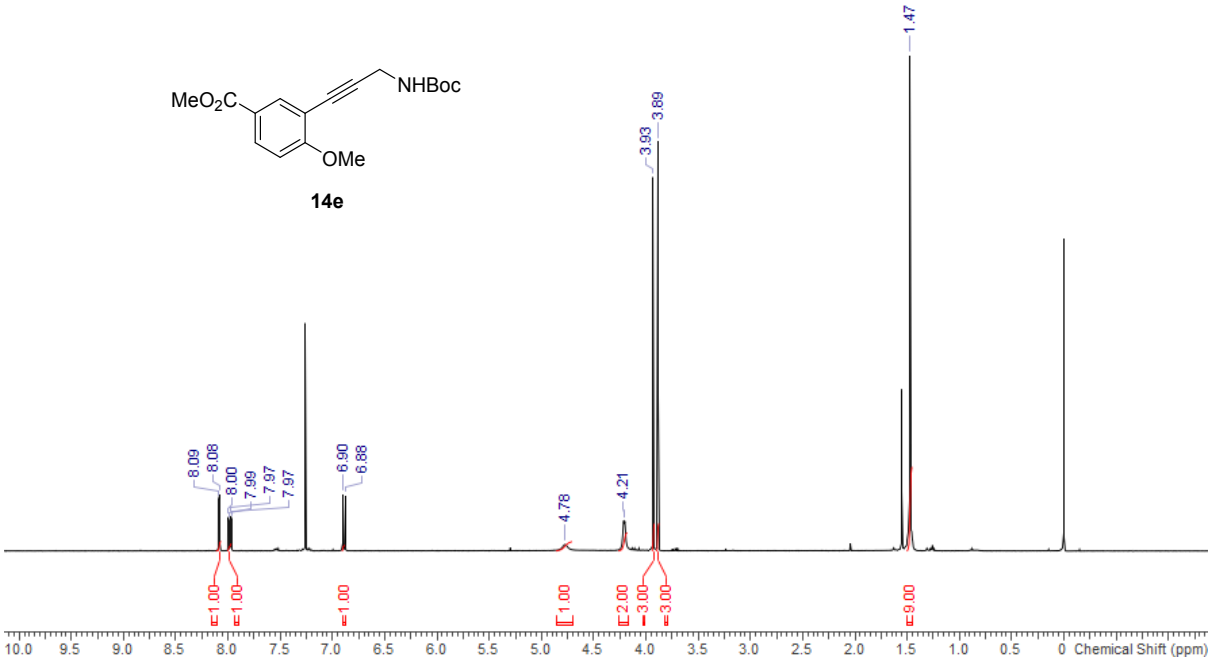
^{1}H NMR (400 MHz, $CDCl_3$), compound **14d**



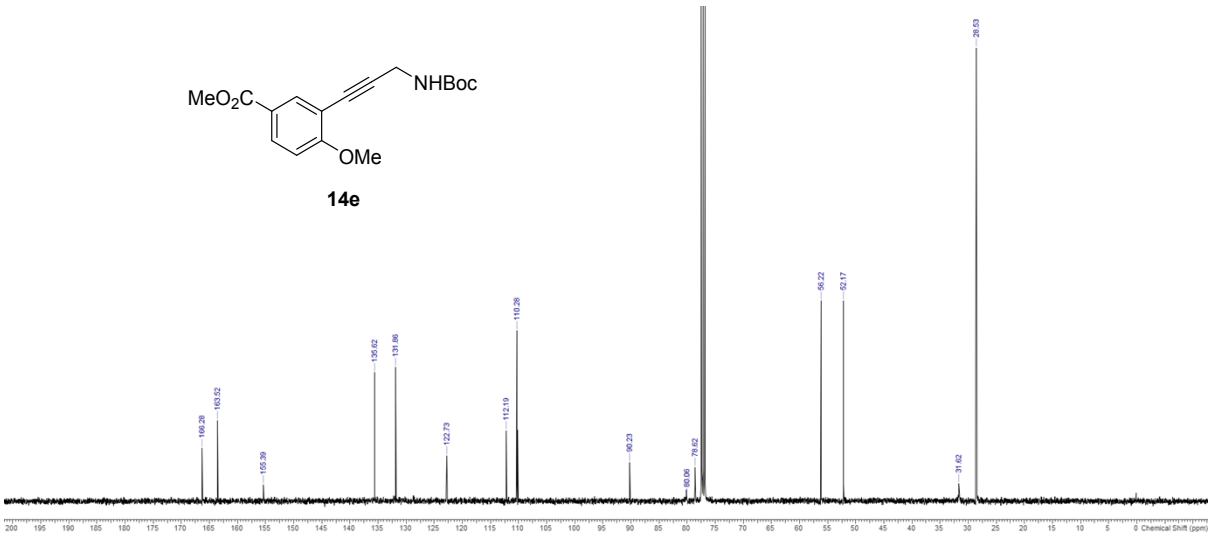
^{13}C NMR (101 MHz, $CDCl_3$), compound **14d**



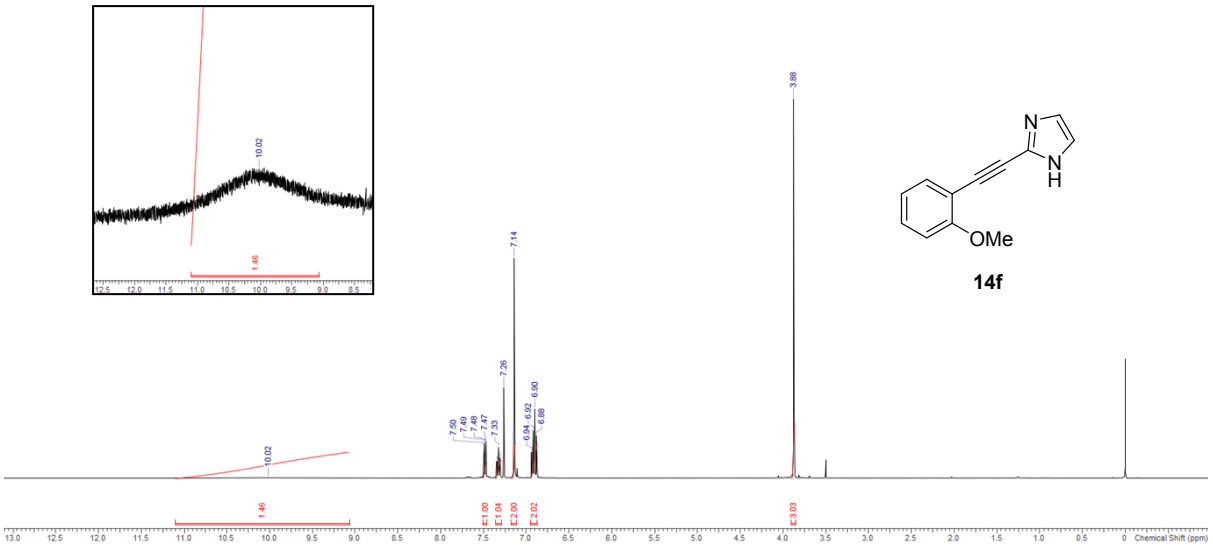
^{1}H NMR (400 MHz, $CDCl_3$), compound **14e**



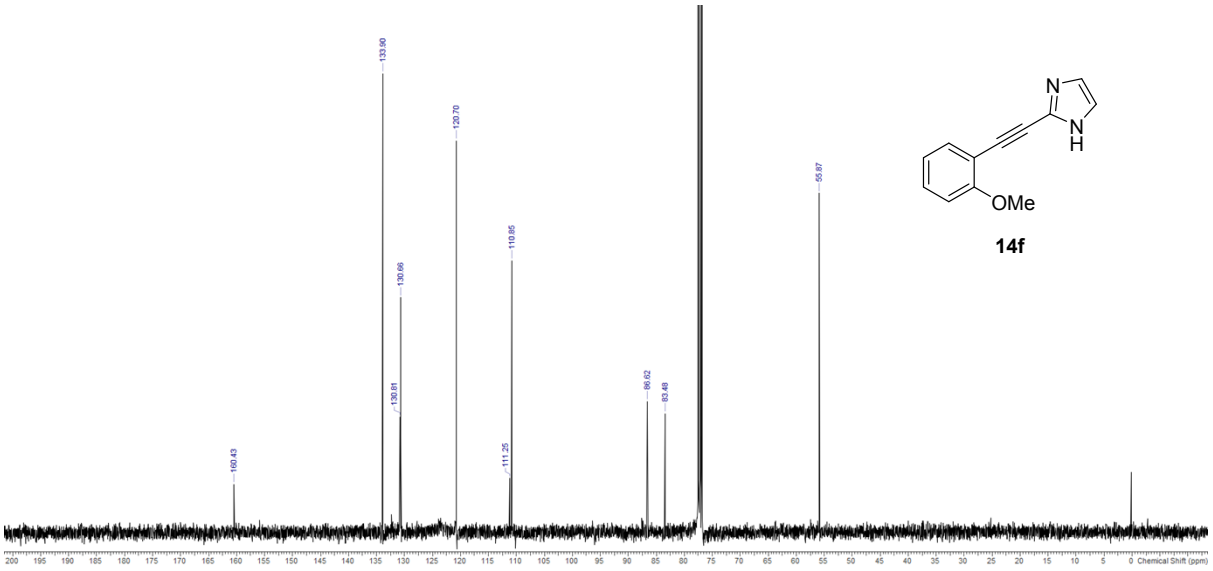
^{13}C NMR (101 MHz, $CDCl_3$), compound **14e**



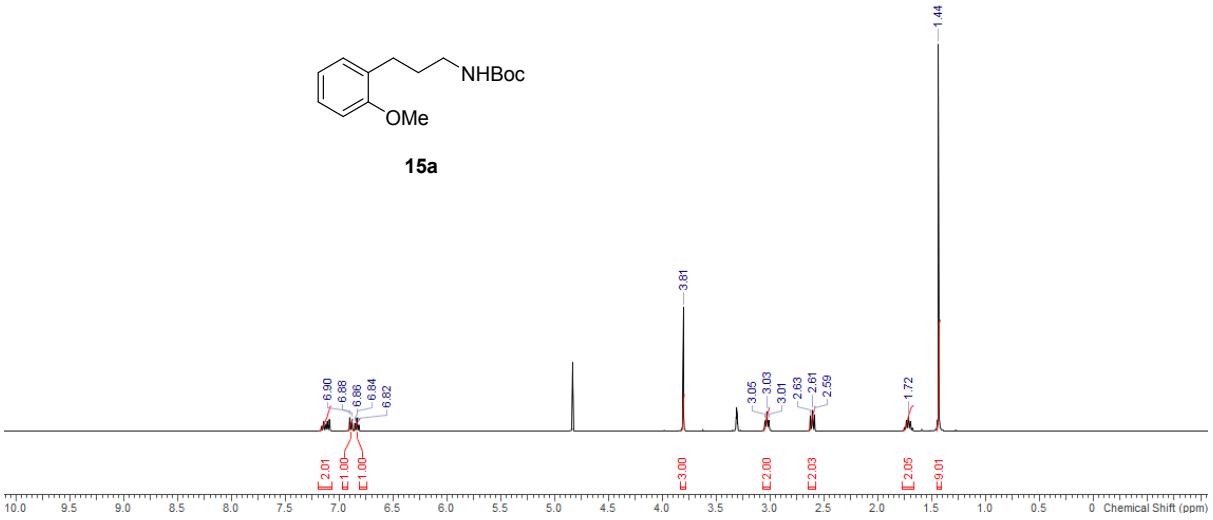
^{1}H NMR (400 MHz, $CDCl_3$), compound **14f**



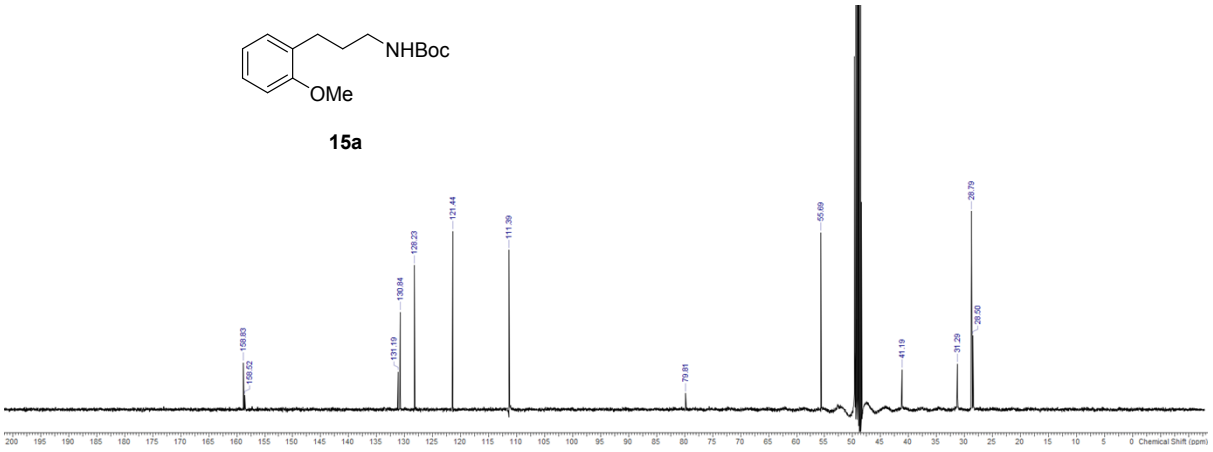
^{13}C NMR (101 MHz, $CDCl_3$), compound **14f**



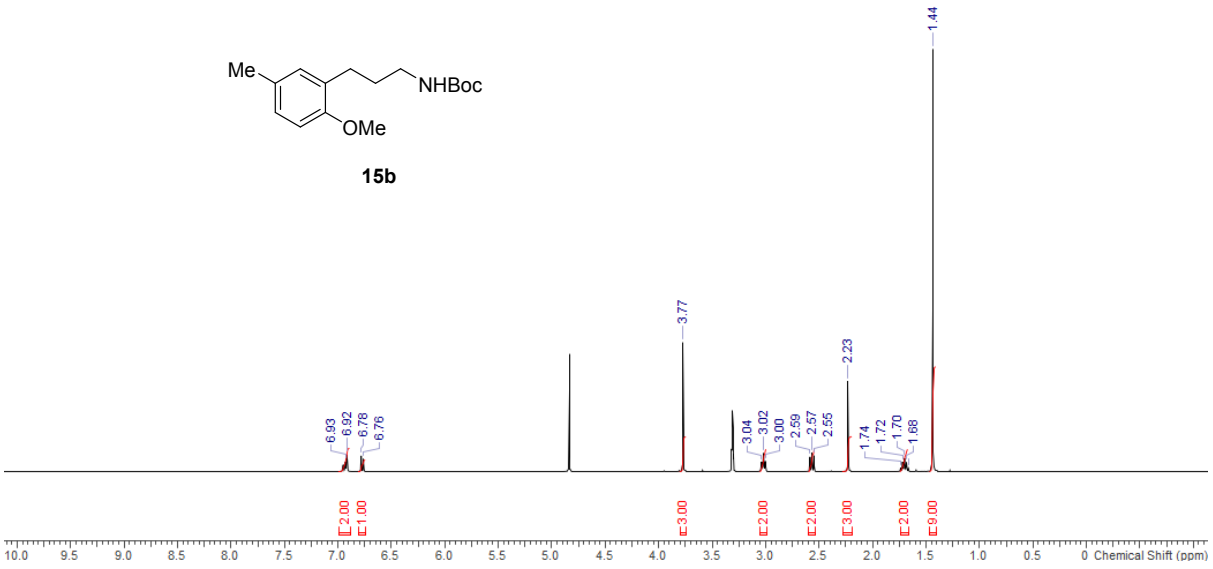
^{1}H NMR (400 MHz, CD_3OD), compound **15a**



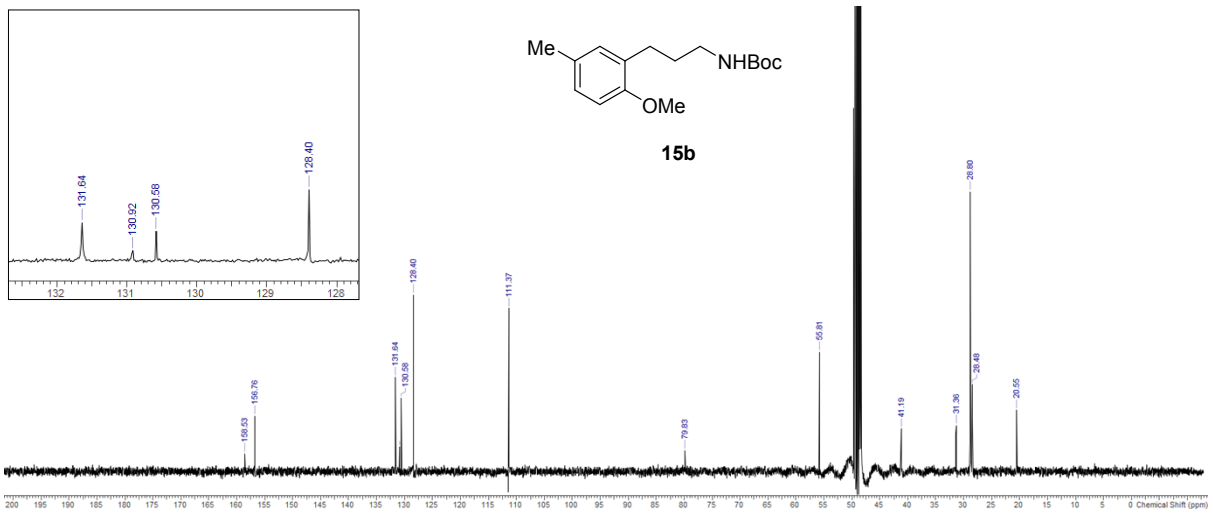
^{13}C NMR (101 MHz, CD_3OD), compound **15a**



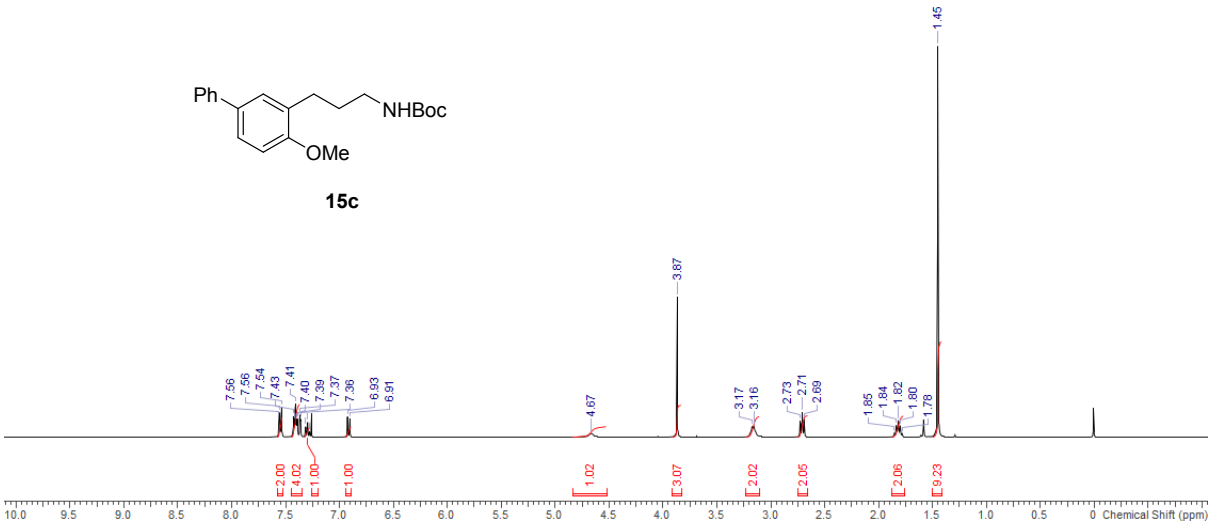
^{1}H NMR (400 MHz, CD_3OD), compound **15b**



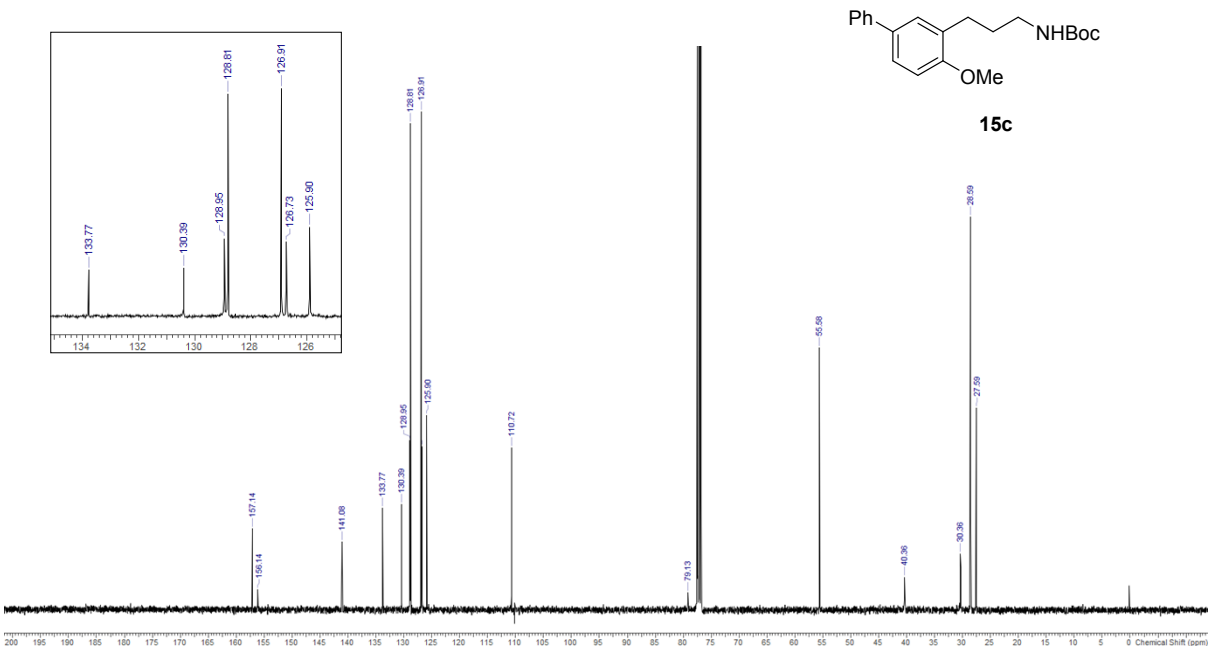
^{13}C NMR (101 MHz, CD_3OD), compound **15b**



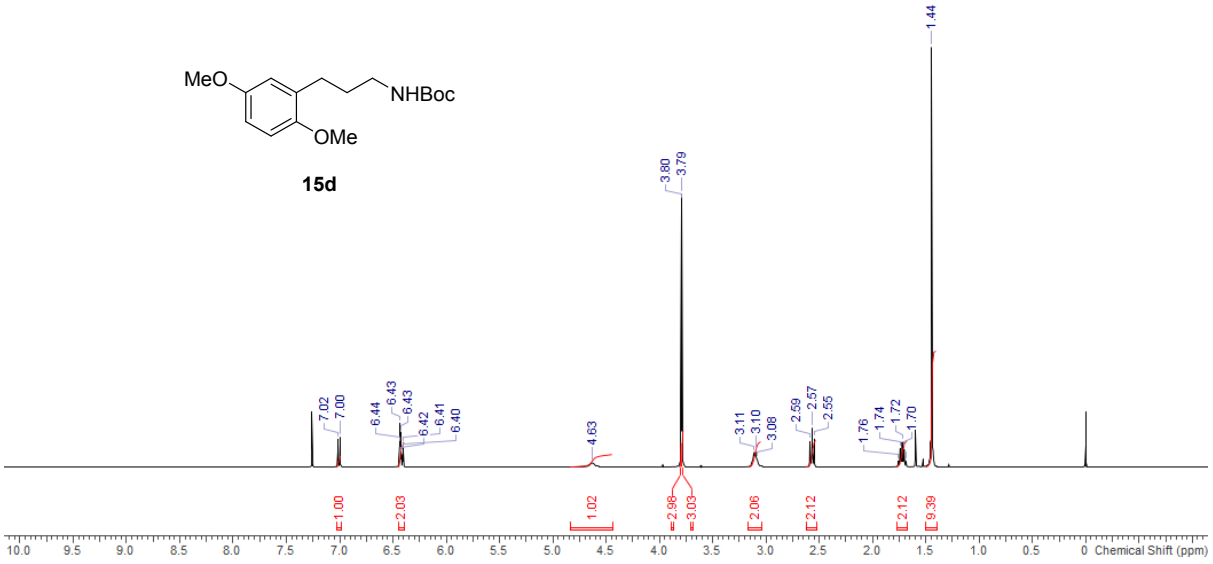
^{1}H NMR (400 MHz, $CDCl_3$), compound **15c**



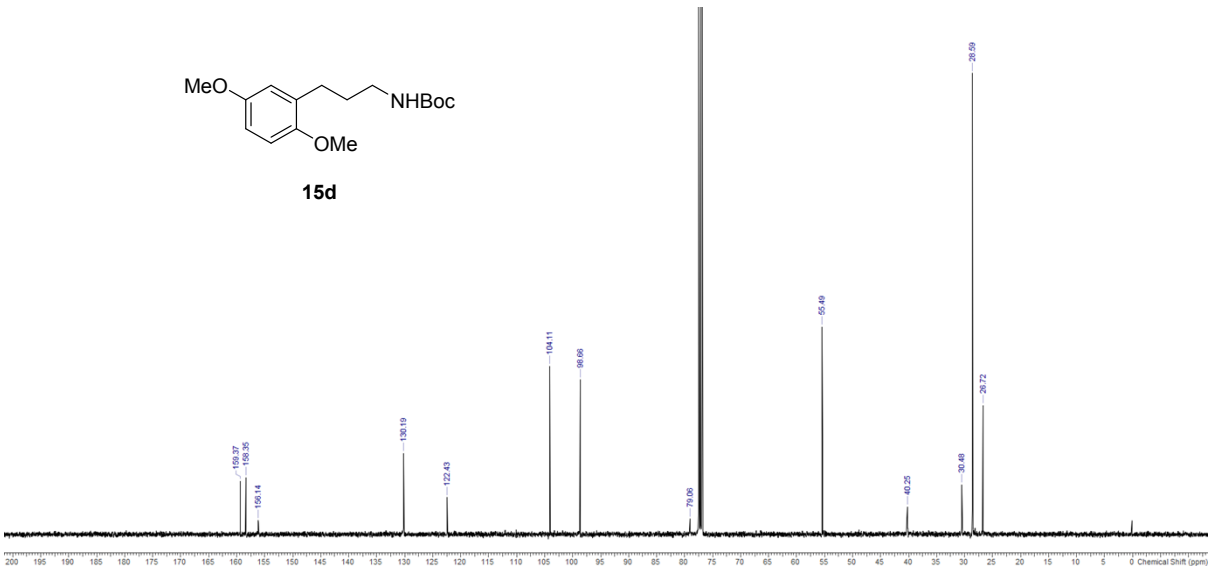
^{13}C NMR (101 MHz, $CDCl_3$), compound **15c**



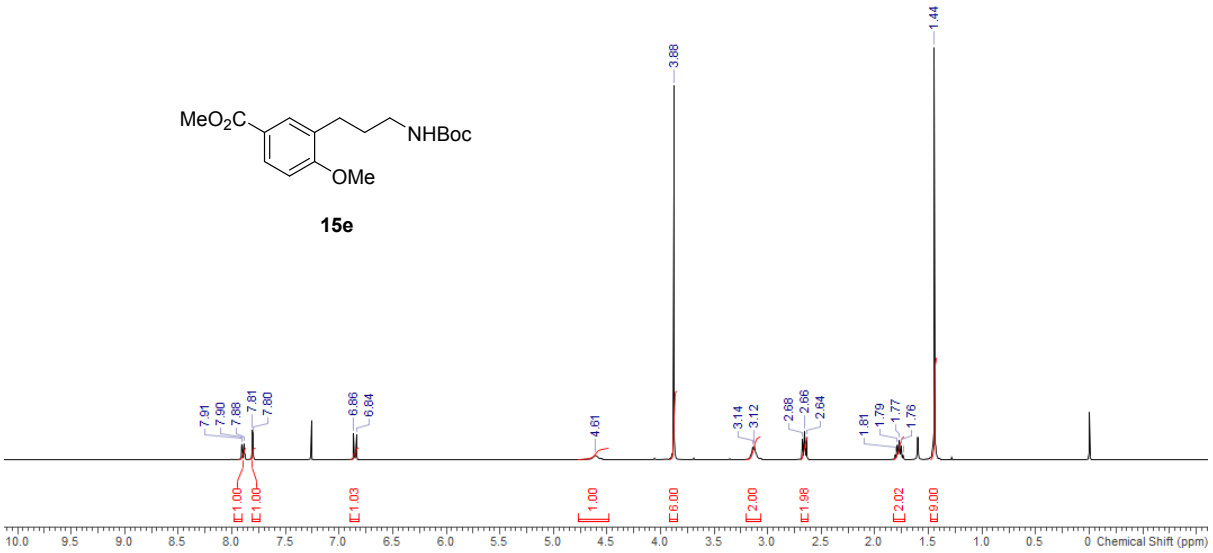
^{1}H NMR (400 MHz, $CDCl_3$), compound **15d**



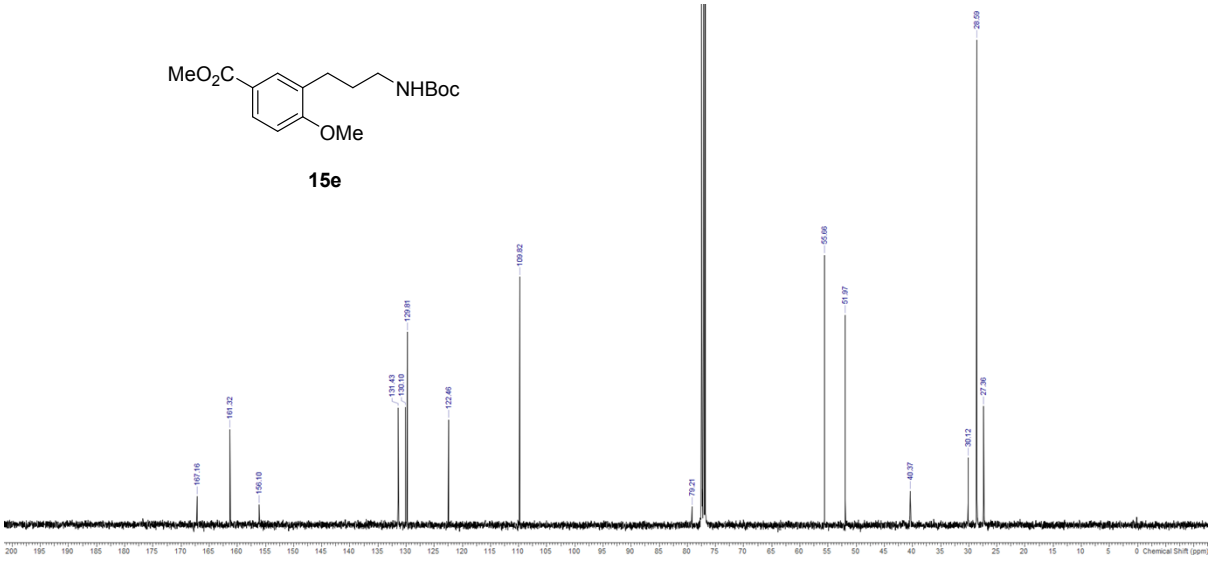
^{13}C NMR (101 MHz, $CDCl_3$), compound **15d**



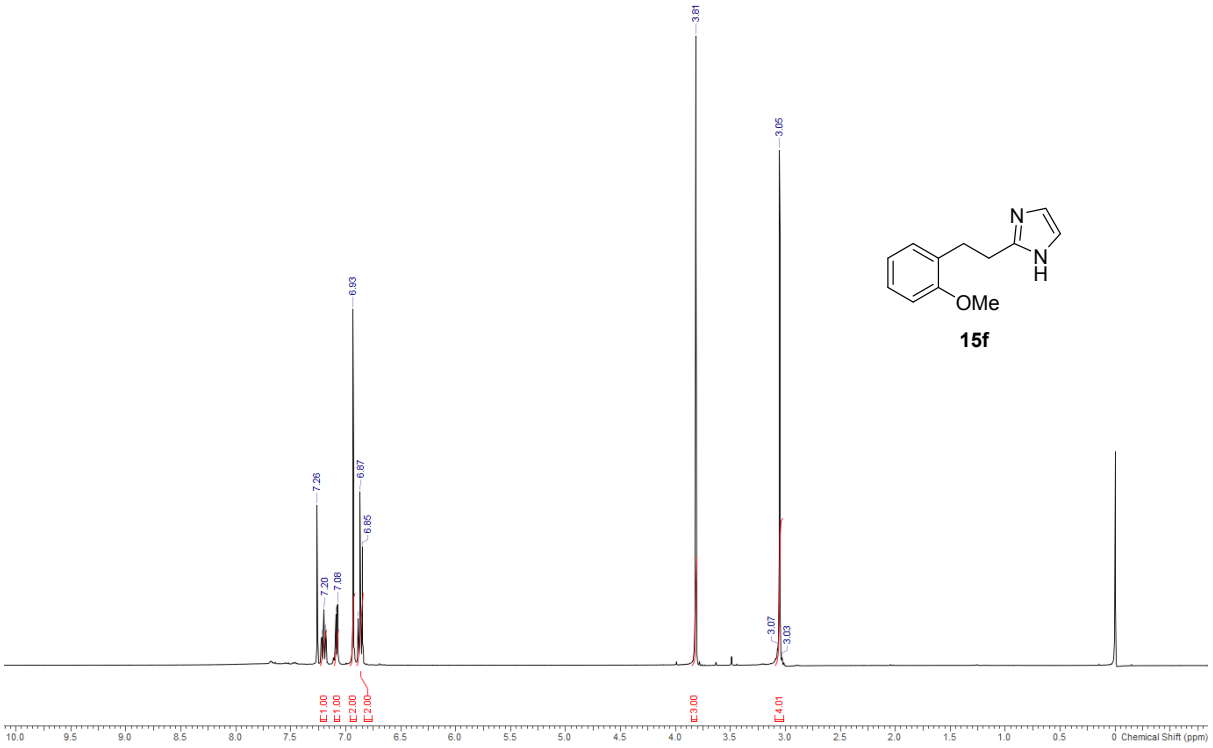
^{1}H NMR (400 MHz, $CDCl_3$), compound **15e**



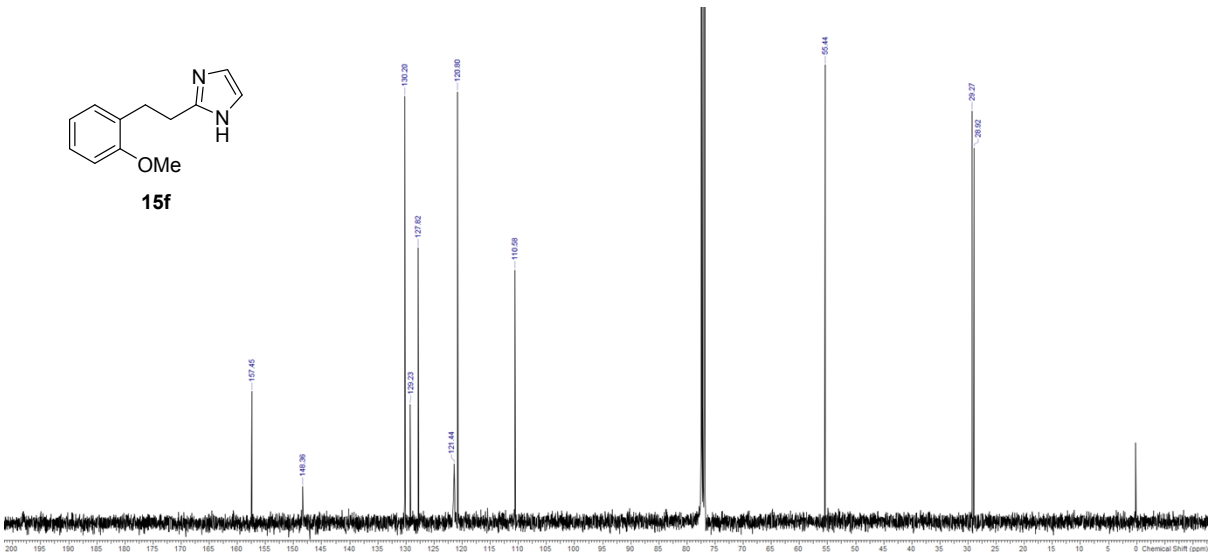
^{13}C NMR (101 MHz, $CDCl_3$), compound **15e**



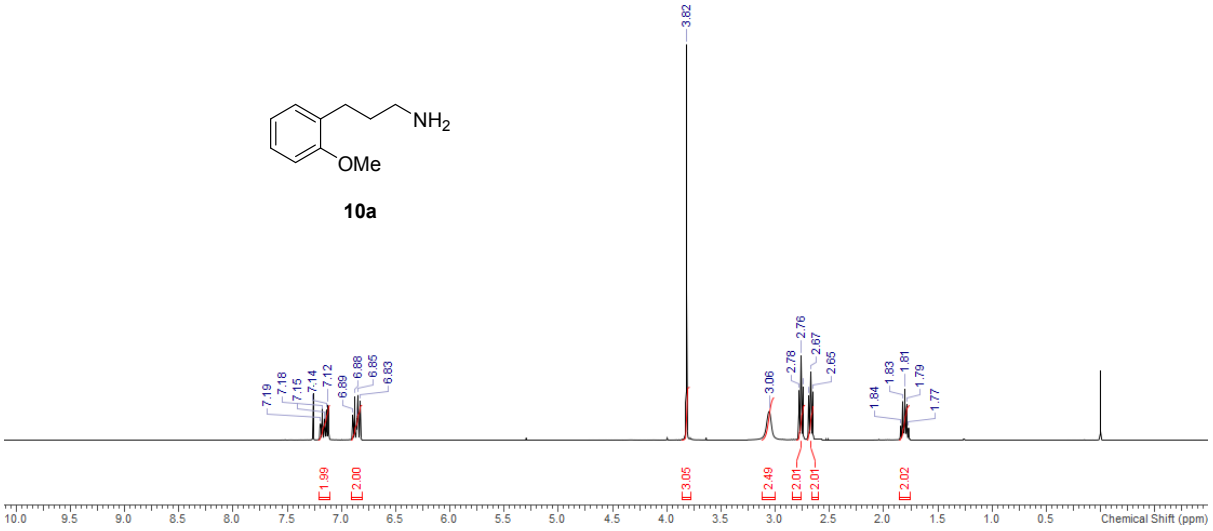
^{1}H NMR (400 MHz, $CDCl_3$), compound **15f**



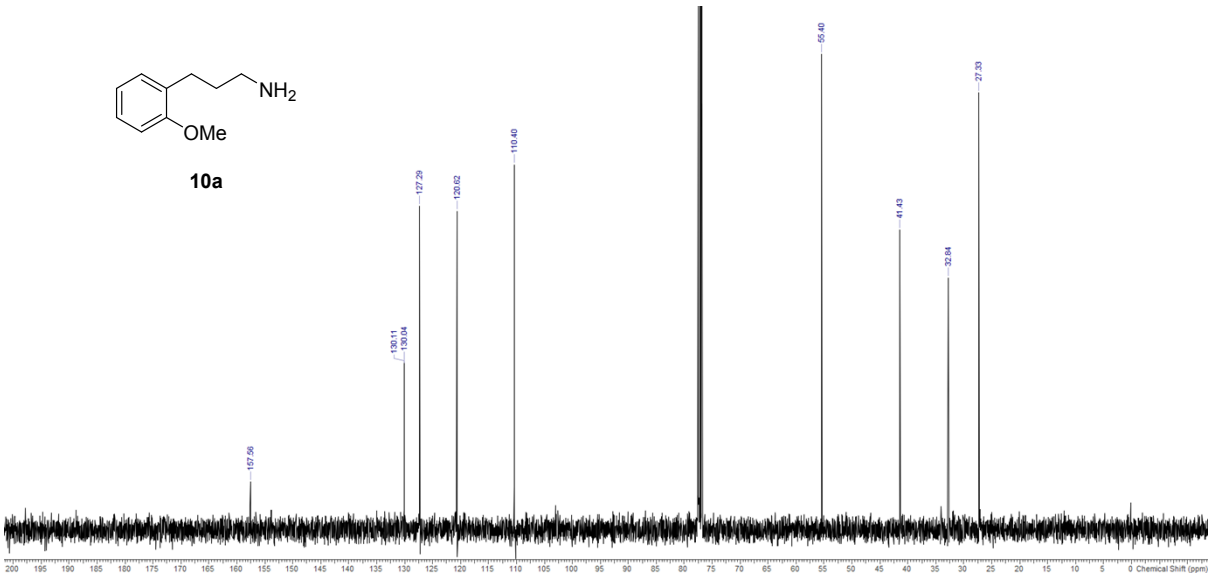
^{13}C NMR (101 MHz, $CDCl_3$), compound **15f**



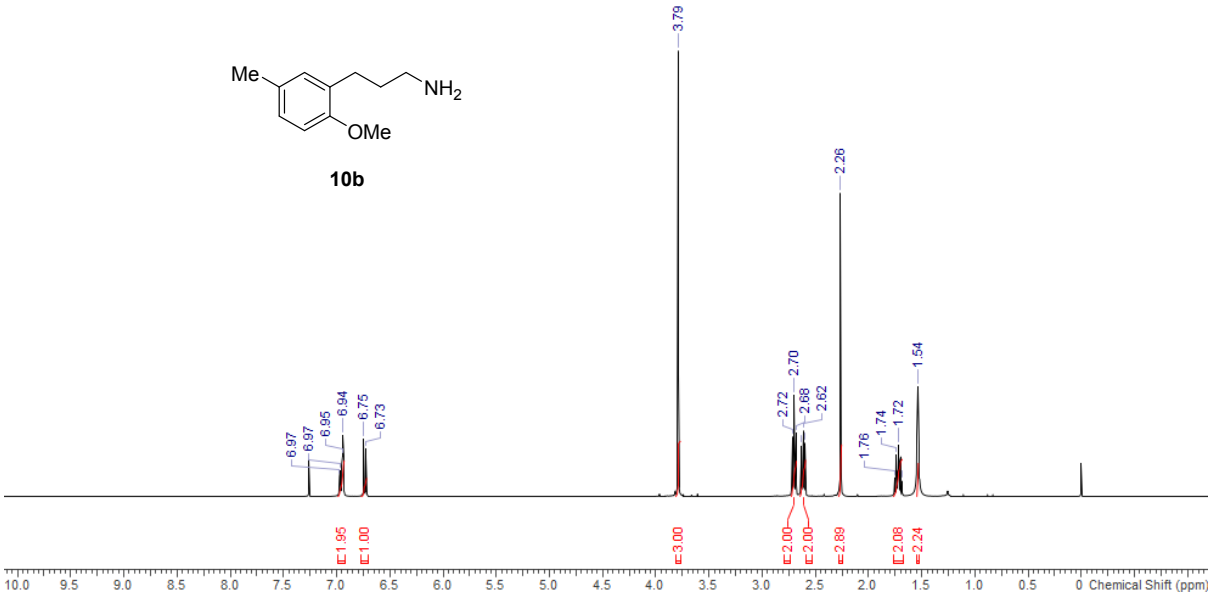
^{1}H NMR (400 MHz, $CDCl_3$), compound **10a**



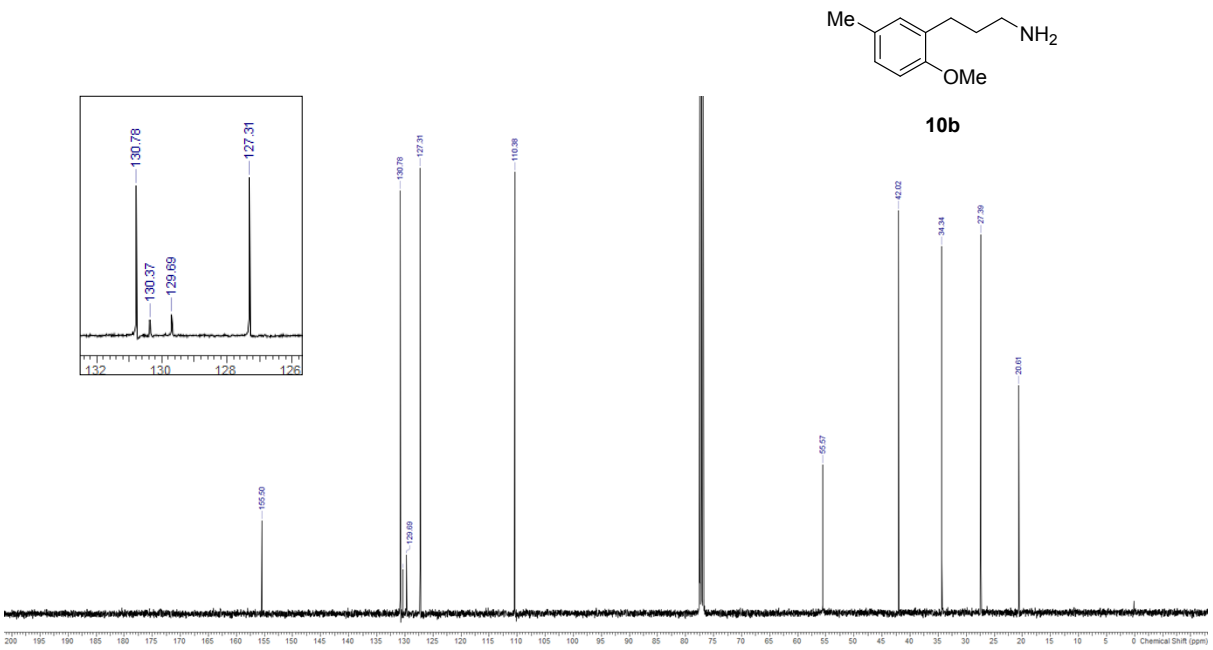
^{13}C NMR (101 MHz, $CDCl_3$), compound **10a**



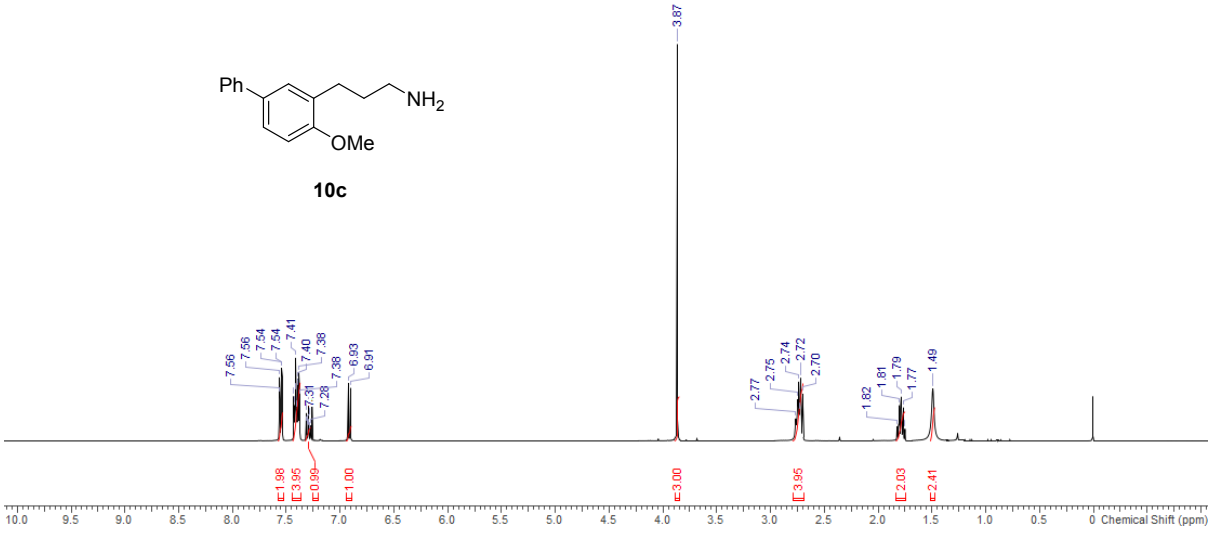
^{1}H NMR (400 MHz, $CDCl_3$), compound **10b**



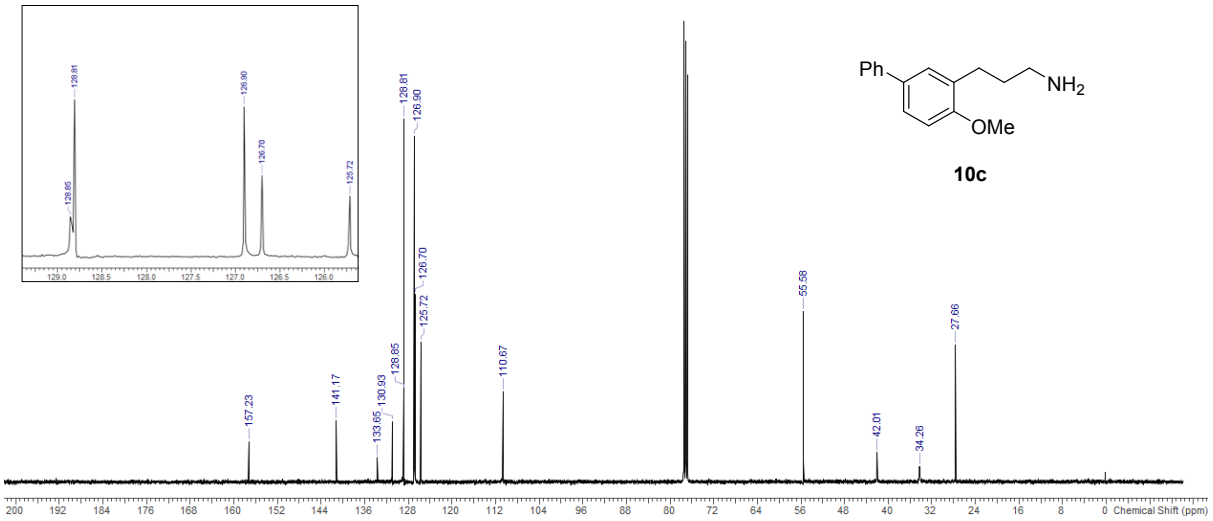
^{13}C NMR (101 MHz, $CDCl_3$), compound **10b**



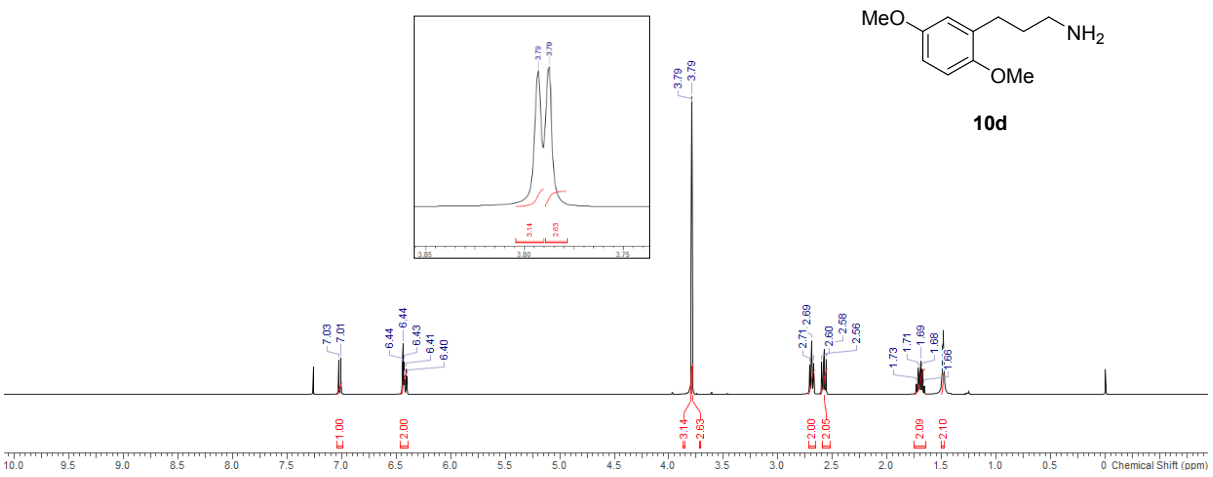
^{1}H NMR (400 MHz, $CDCl_3$), compound **10c**



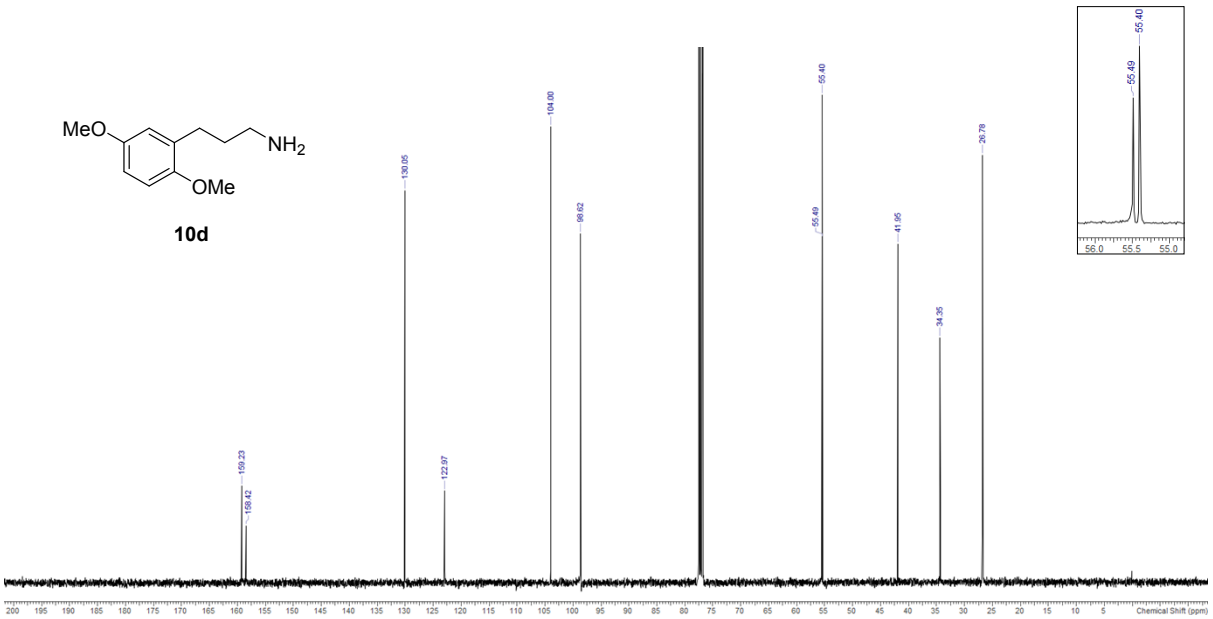
^{13}C NMR (101 MHz, $CDCl_3$), compound **10c**



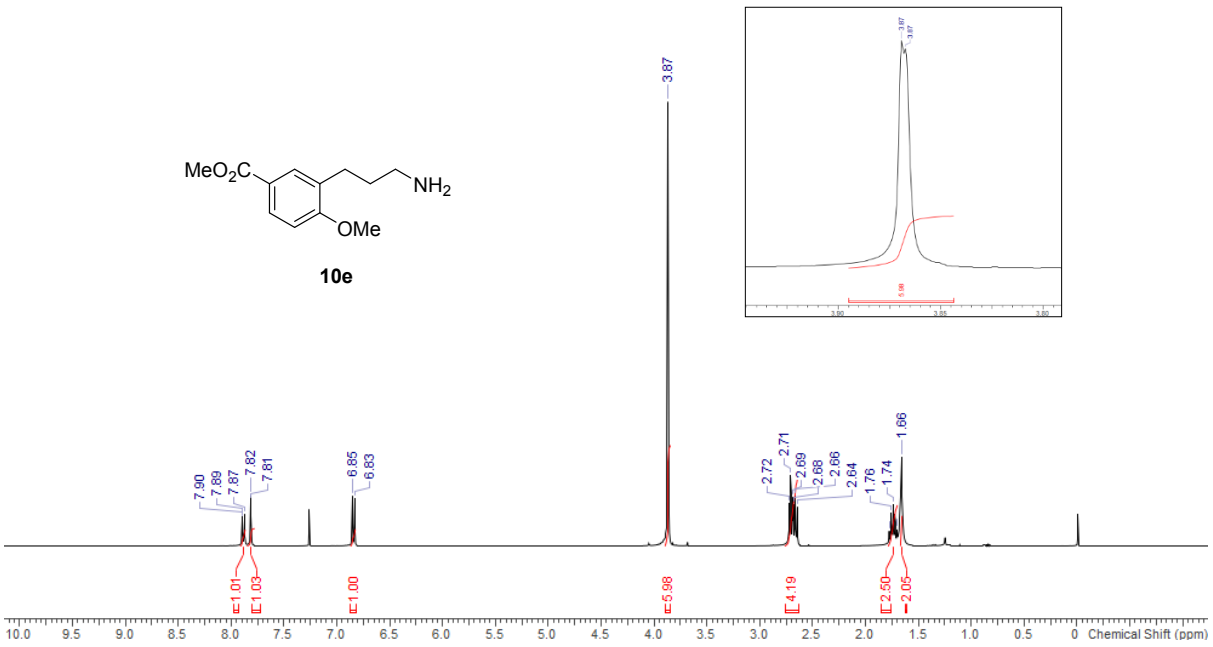
^{1}H NMR (400 MHz, $CDCl_3$), compound **10d**



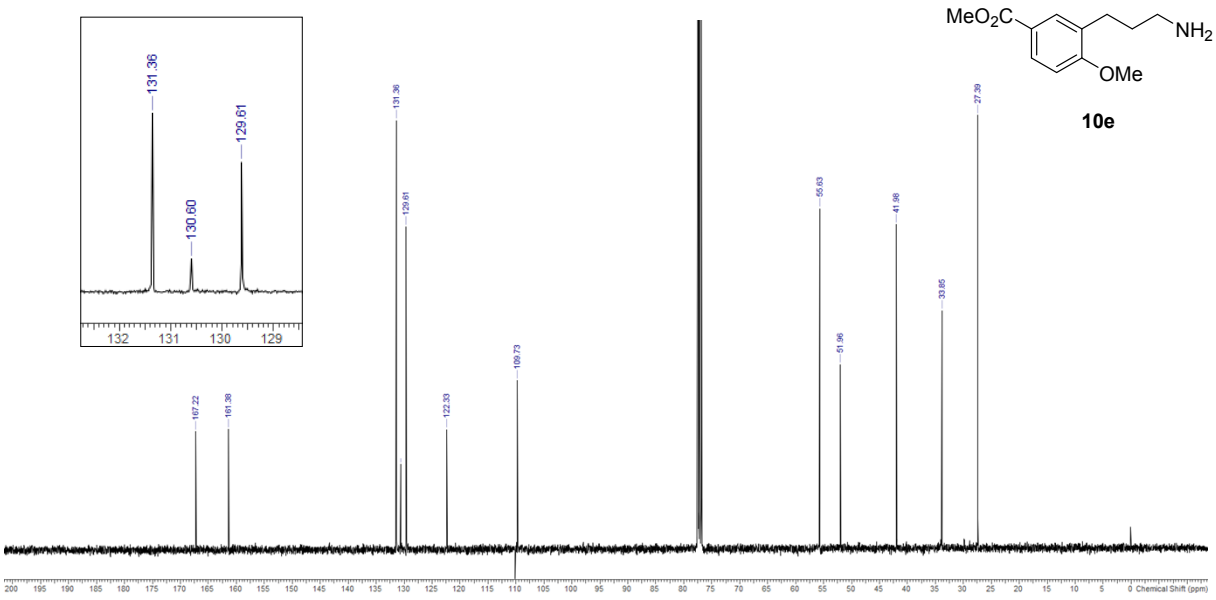
^{13}C NMR (101 MHz, $CDCl_3$), compound **10d**



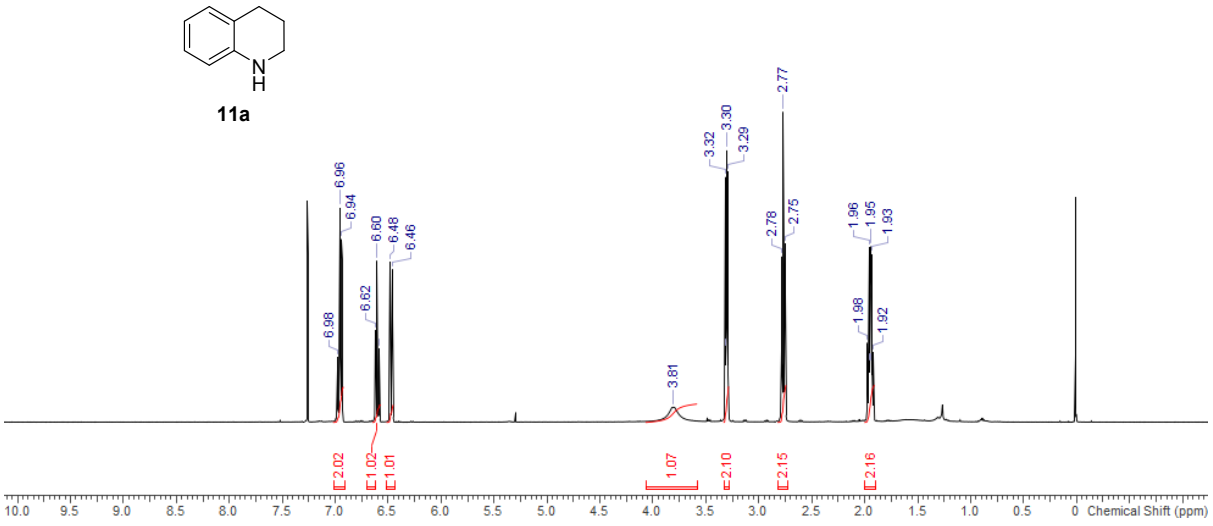
^{1}H NMR (400 MHz, $CDCl_3$), compound **10e**



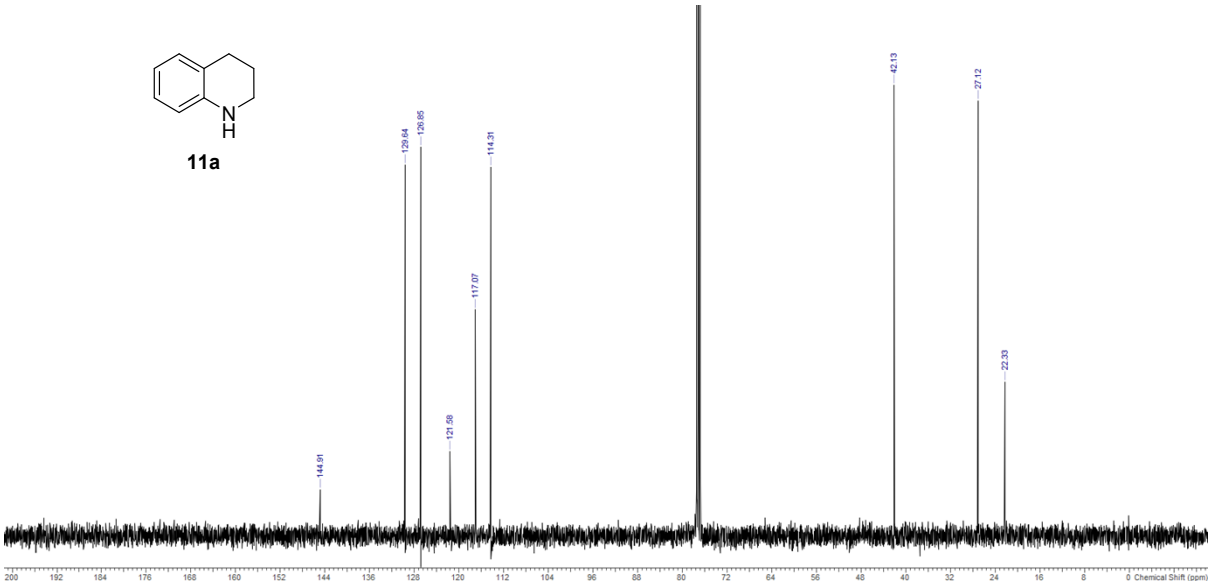
^{13}C NMR (101 MHz, $CDCl_3$), compound **10e**



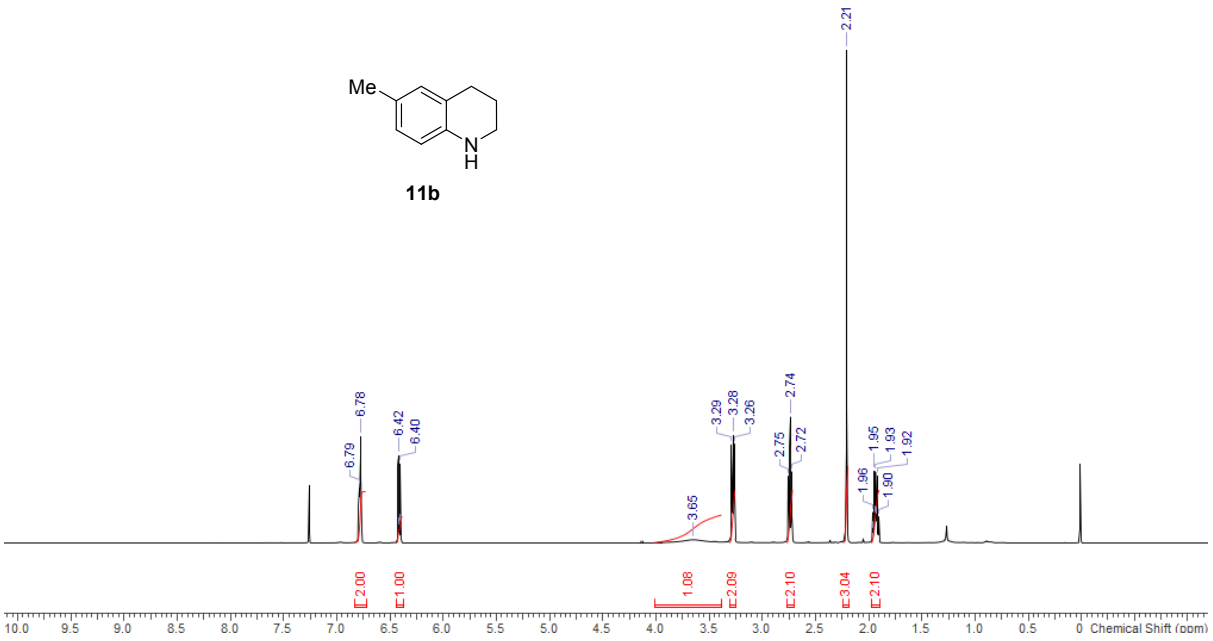
^{1}H NMR (400 MHz, $CDCl_3$), compound **11a**



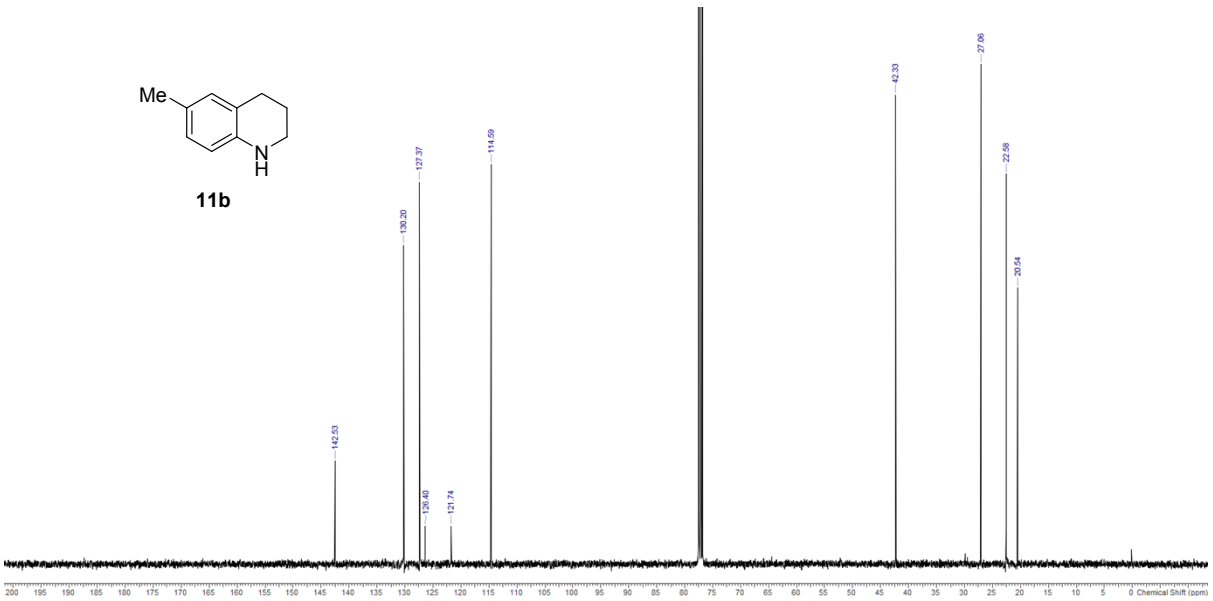
^{13}C NMR (101 MHz, $CDCl_3$), compound **11a**



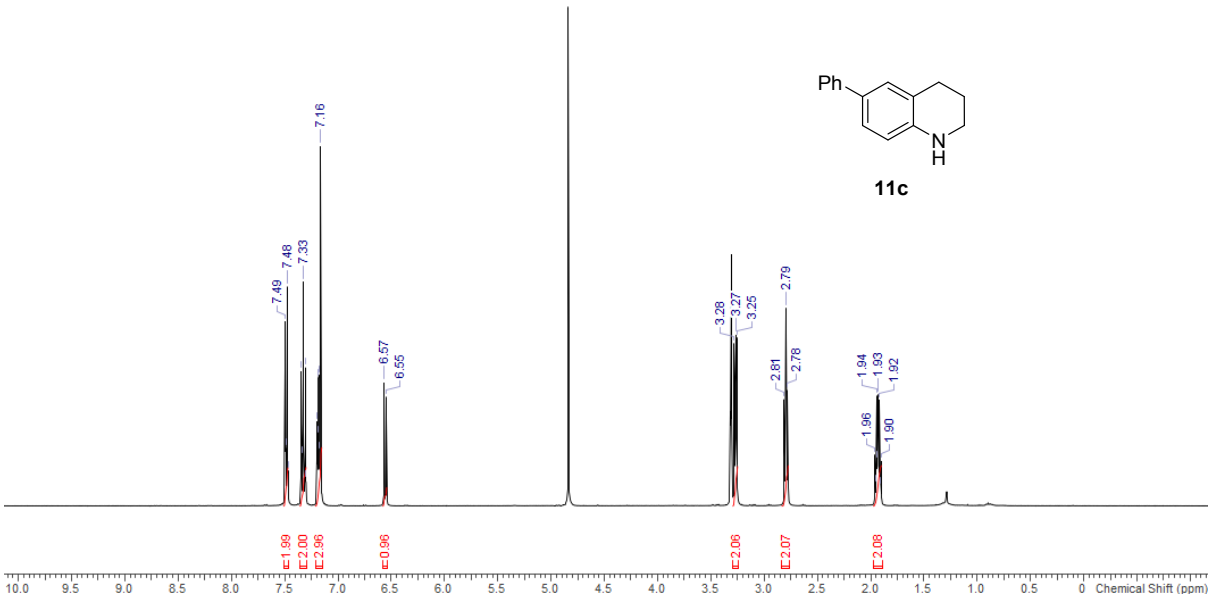
^{1}H NMR (400 MHz, $CDCl_3$), compound **11b**



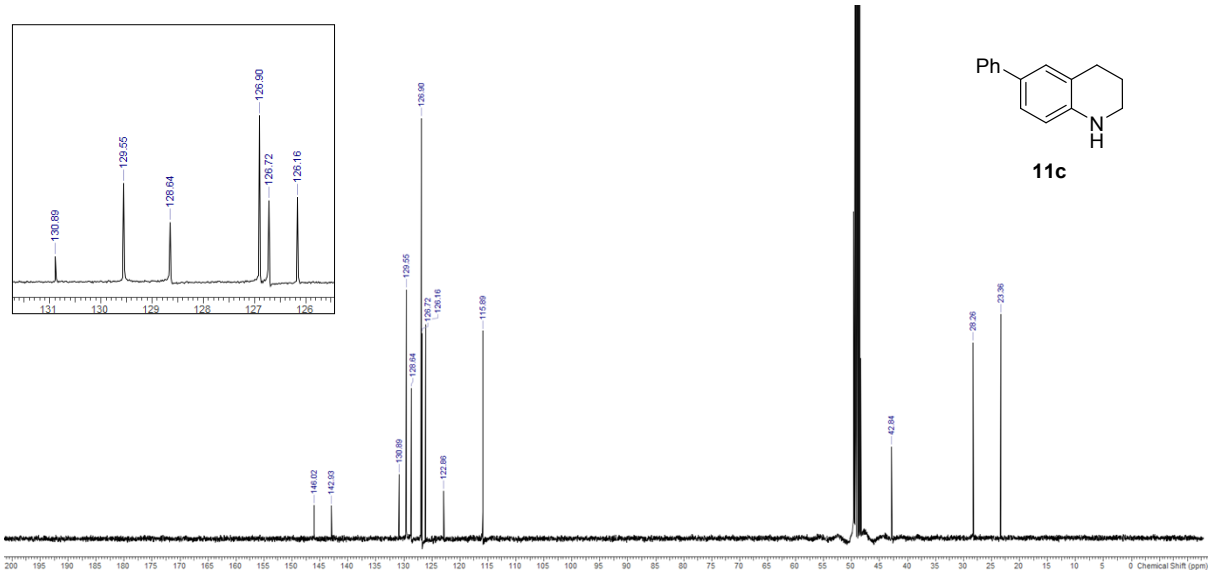
^{13}C NMR (101 MHz, $CDCl_3$), compound **11b**



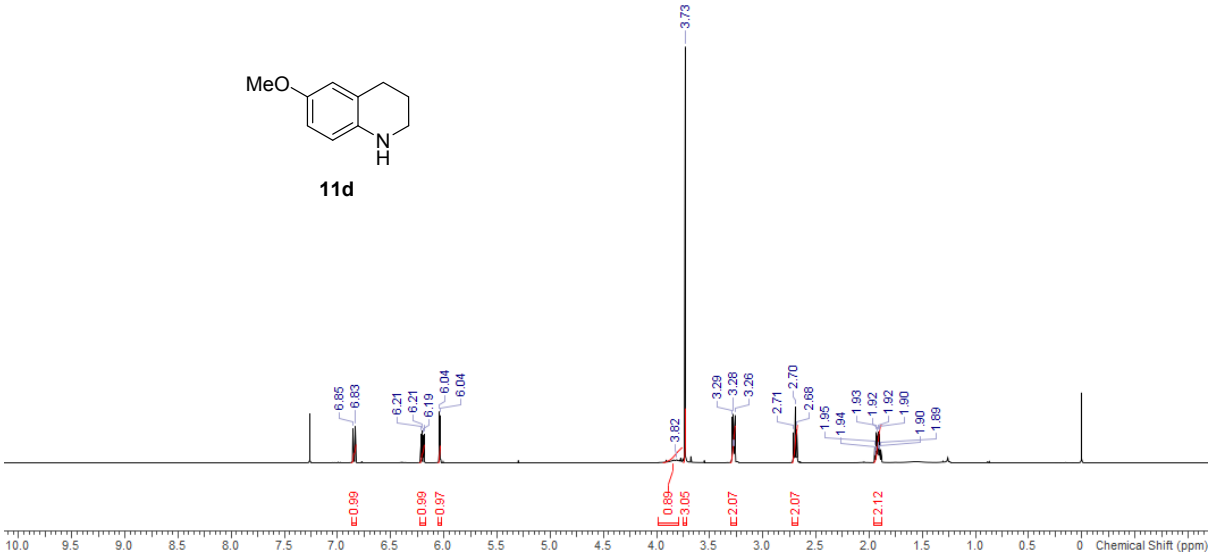
^{1}H NMR (400 MHz, CD_3OD), compound **11c**



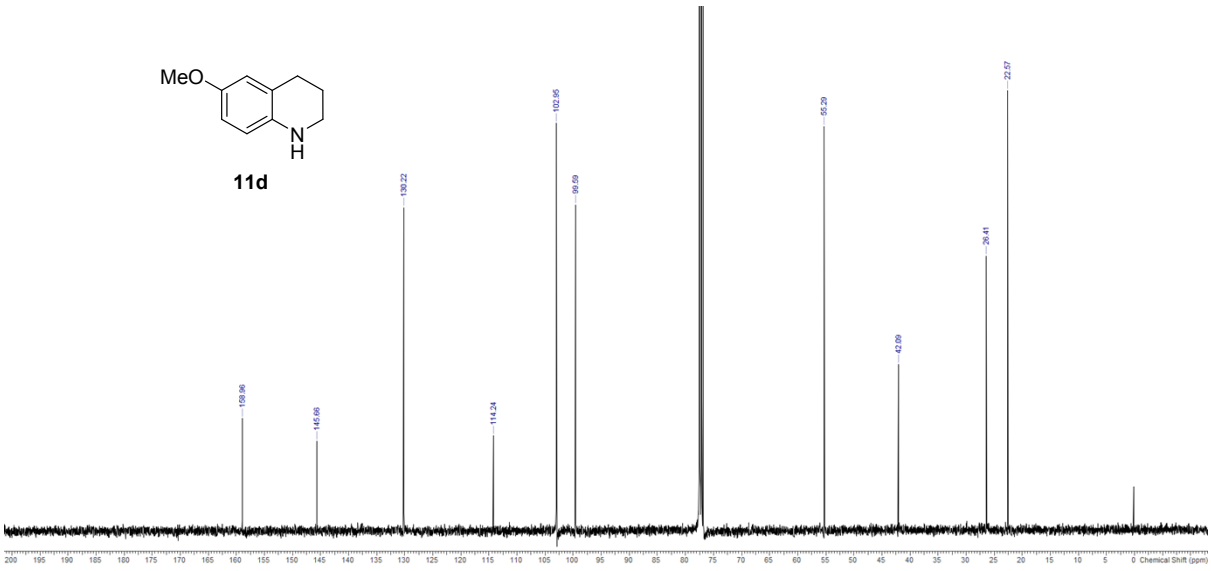
^{13}C NMR (101 MHz, CD_3OD), compound **11c**



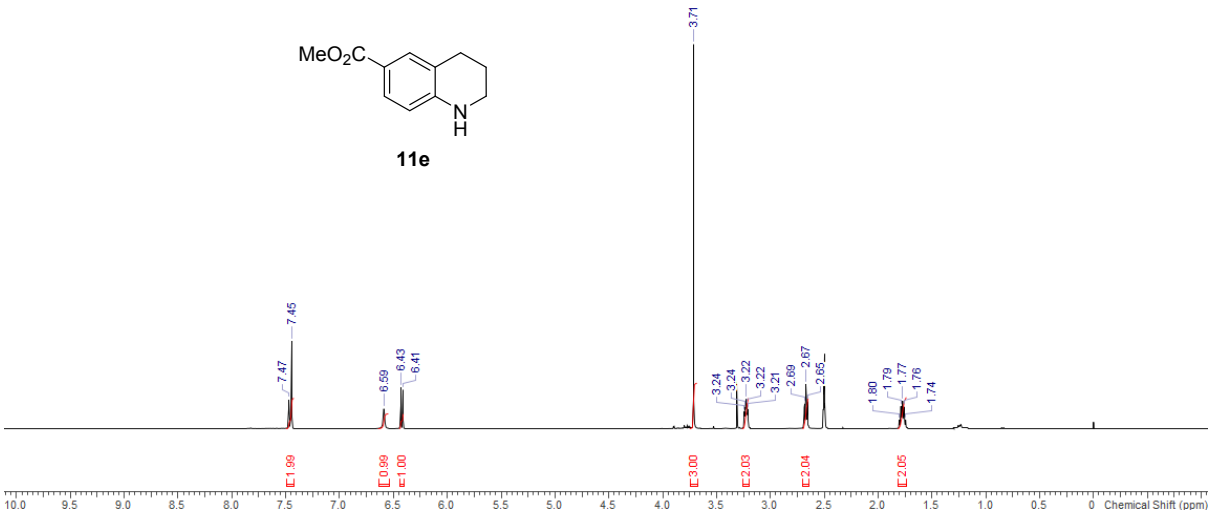
^{1}H NMR (400 MHz, $CDCl_3$), compound **11d**



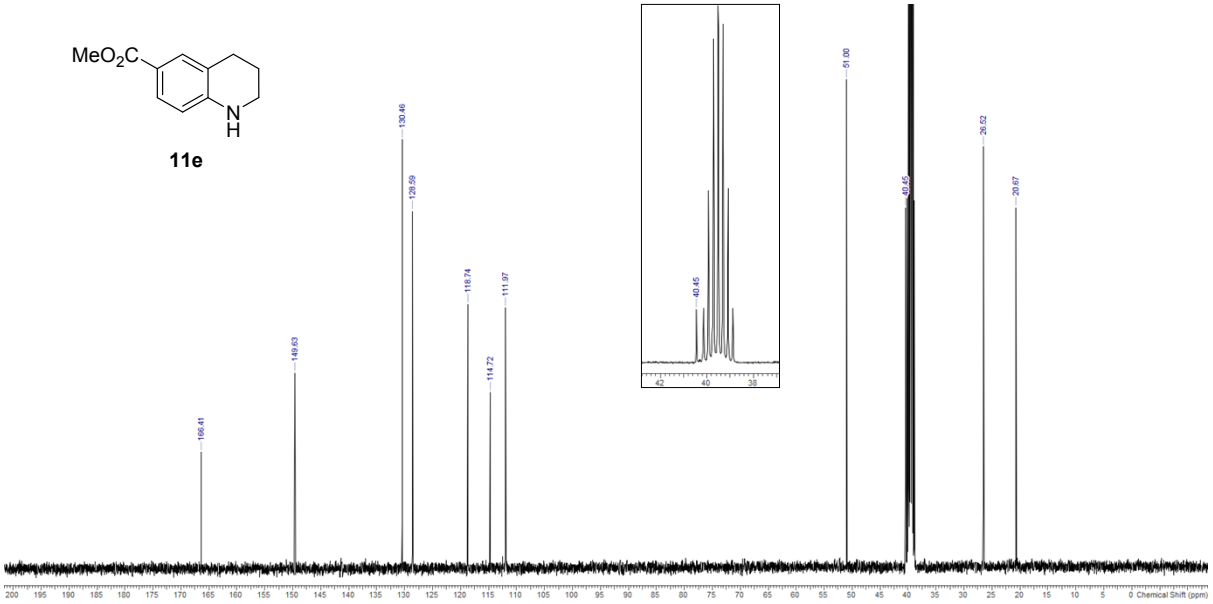
^{13}C NMR (101 MHz, $CDCl_3$), compound **11d**



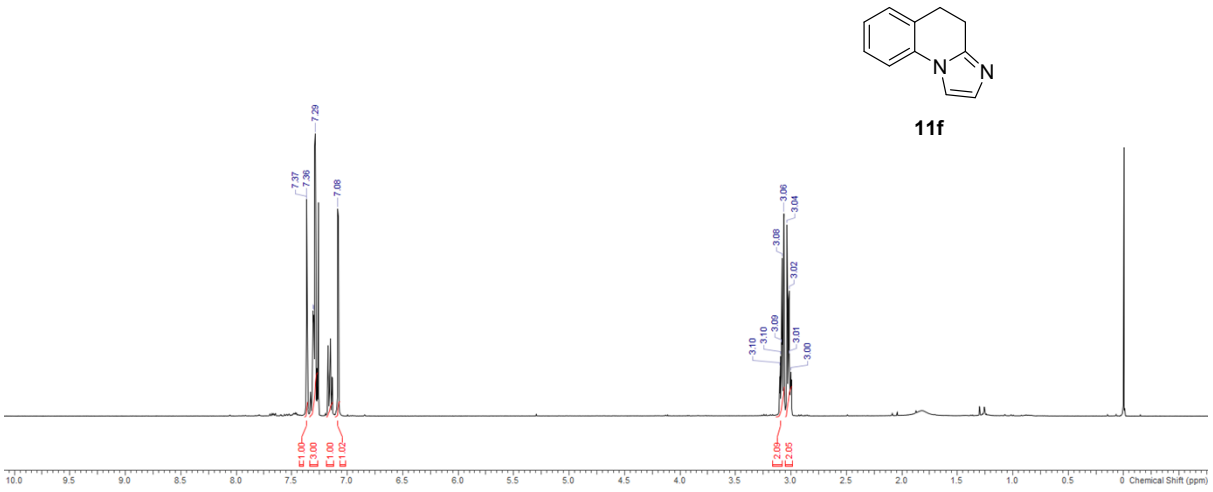
^{1}H NMR (400 MHz, DMSO-d_6), compound **11e**



^{13}C NMR (101 MHz, DMSO-d_6), compound **11e**



^{1}H NMR (400 MHz, $CDCl_3$), compound **11f**



^{13}C NMR (101 MHz, $CDCl_3$), compound **11f**