Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Direct synthesis of indenes via a rhodium-catalyzed multicomponent C*sp*^{2}-H annulation reaction

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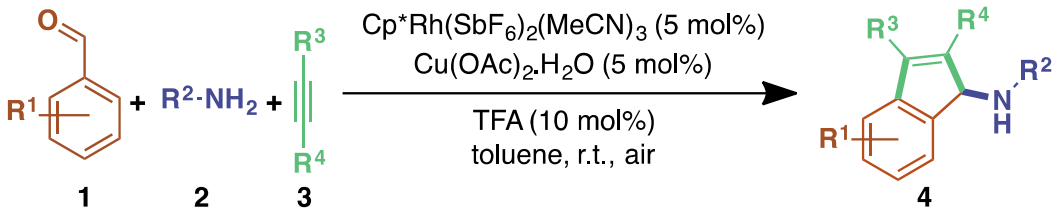
Supplementary Information



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1) General information

Solvents and reagents were purchased from Sigma-Aldrich chemical company and were used without further purification unless otherwise specified.

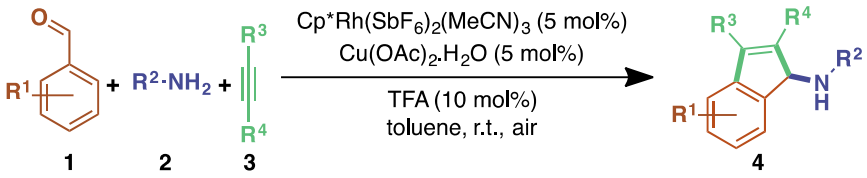
NMR Spectroscopy: Nuclear magnetic resonance spectra were recorded on a Bruker AV500 equipped with a 60-position SampleXpress sample changer (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{31}P, 202 MHz), a Varian MERCURY plus-500 spectrometer (^{1}H, 500 MHz; ^{13}C, 125 MHz) or Bruker AV400 spectrometer (^{1}H, 400 MHz; ^{13}C, 100 MHz). Chemical shifts for both ^{1}H NMR and ^{13}C NMR spectra were expressed in parts per million (ppm) units downfield from TMS, with the solvent residue peak as the chemical shift standard ($CDCl_3$: δ 7.28 ppm in ^{1}H NMR; δ 77.0 ppm in ^{13}C NMR; MeOD: δ S-4 3.31 ppm in ^{1}H NMR; δ 49.0 ppm in ^{13}C NMR; C_6D_6: δ 7.16 ppm in ^{1}H NMR; δ 128.1 ppm in ^{13}C NMR; DMSO-d6: δ 2.50 ppm in ^{1}H NMR; δ 39.5 ppm in ^{13}C NMR). Data were reported as following: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, td = triplet of doublets, q = quartet, quin = quintet, sep = septet, m = multiplet, br = broad singlet), coupling constants J (Hz), and integration.

Mass Spectrometry: Mass spectrometry (MS) was performed by the McGill Chemistry Department Mass Spectrometry Facility. High Resolution Mass spectra were recorded using electrospray ionization (ESI+) and/or atmospheric pressure chemical ionization APCI(+/-), performed either on "Exactive Plus Orbitrap" a ThermoScientific high resolution accurate mass (HR/AM) FT mass spectrometer, or a Bruker Daltonics Maxis Impact quadrupole-time of flight (QTOF) mass spectrometer. Protonated molecular ions $(M+H)^+$ or sodium adducts $(M+Na)^+$, were used for empirical formula confirmation.

All preparative chromatography were performed using gradient elution (hexanes and diethyl ether) on a Biotage IsoleraTM One automated chromatography system with SNAP ultra-silica gel cartridges and sample cartridges.

2) Experimental details and characterization data for all compounds

General procedure for optimization of reaction conditions

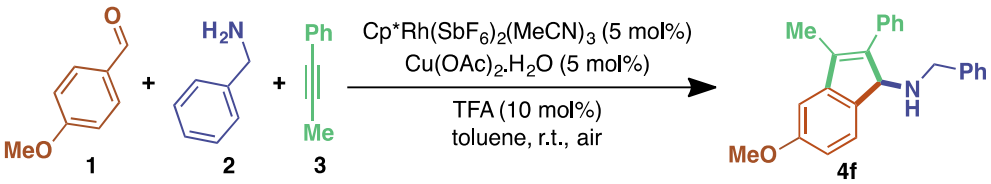


A V-shaped 10 mL Biotage reaction vial was charged with $Cp^*Rh(SbF_6)_2(MeCN)_3$ (5 mol%, 4.2 mg),[1] $Cu(OAc)_2$ (5 mol%, 2.0 mg), followed by solid reagents if present. Toluene-TFA (0.25 mL, 10%) stock solution was added, followed by subsequent slow additions of the corresponding benzaldehyde (0.1 mmol), the amine derivatives (0.12 mmol) and the internal alkyne (0.12 mmol). The reaction vessel was placed on a magnetic stir plate under vigorous stirring (approx. 1200 rpm) and held for 18 hours open to air. The mixture was diluted with ethyl acetate (2 mL), washed with saturated aqueous solution of $NaHCO_3$ (2 mL), filtered through a pad of silica, and rinsed with additional ethyl acetate. The combined organic phases were concentrated and purified by column chromatography or preparative thin layer chromatography to yield the corresponding indene compound **4**.

Nitromethane was used as internal standard for ^{1}H-NMR analysis.

a) Selected control experiments

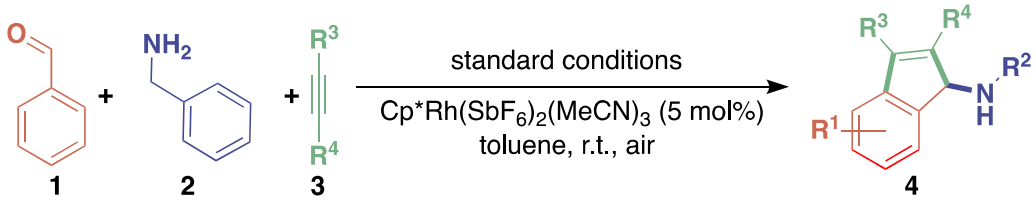
i) Table S1: Study of catalysts [a]



Entry	Modification from standard conditions	**4f** (%)[b]
1	No $Cp^*Rh(SbF_6)_2(MeCN)_3$	0
2	No $Cu(OAc)_2{\cdot}H_2O$	8
3	No $Cp^*Rh(SbF_6)_2(MeCN)_3$ / $Cu(OAc)_2{\cdot}H_2O$	0
4	Cp^*RhCl_2 (5 mol%) / AgOTf (10 mol%)	50
5	$Cp^*Rh(SbF_6)_2(MeCN)_3$ (1 mol%) / $Cu(OAc)_2{\cdot}H_2O$ (1 mol%)	22

[a]Reactions were performed on a 0.1 mmol scale using 5 mol% $Cp^*Rh(SbF_6)_2(MeCN)_3$, 5 mol% $Cu(OAc)_2{\cdot}H_2O$, **1** (0.1 mmol), **2** (1.2 equiv), **3** (1.2 equiv), in 0.25 mL of toluene and open air. [b]NMR yields of products are reported.

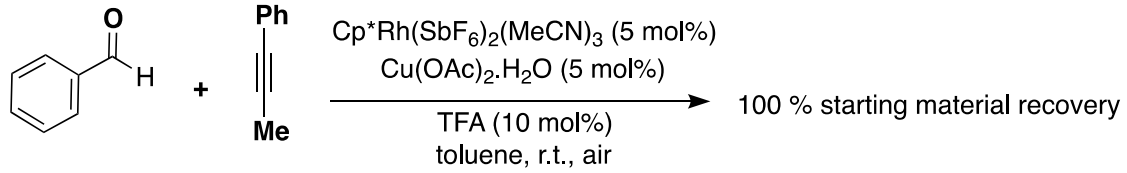
ii) Table S2: Study of additives [a]

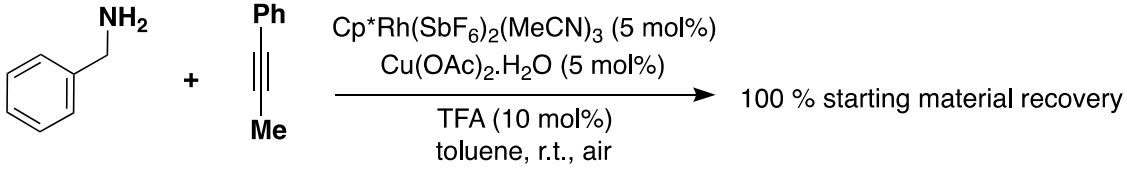


Entry	Change from standard conditions	**4a** (%)[b]
1	10 mol% TFA, 5 mol% $Cu(OAc)_2.H_2O$	>**99**
2	20 mol% TFA, 5 mol% $Cu(OAc)_2.H_2O$	>**99**
3	50 mol% TFA, 5 mol% $Cu(OAc)_2.H_2O$	>**99**
4	100 mol% TFA, 5 mol% $Cu(OAc)_2.H_2O$	>**99**
5	10 mol% AcOH, 5 mol% $Cu(OAc)_2.H_2O$	56
6	50 mol% AcOH, 5 mol% $Cu(OAc)_2.H_2O$	88
7	50 mol% PivOH, 5 mol% $Cu(OAc)_2.H_2O$	53
8	50 mol% TosOH, 5 mol% $Cu(OAc)_2.H_2O$	94
	10 mol% TFA, 5 mol% NaOAc	77
	10 mol% TFA, 5 mol% KOAc	90
	10 mol% TFA, 10 mol% KOAc	68
	10 mol% TFA, 20 mol% KOAc	69
	10 mol% TFA, 5 mol% NH_4OAc	60
	10 mol% TFA	80
	5 mol% KOAc	75
	5 mol% $Cu(OAc)_2.H_2O$	60

[a]Reactions were performed on a 0.1 mmol scale using 5 mol% $Cp^*Rh(SbF_6)_2(MeCN)_3$, 5 mol% $Cu(OAc)_2{\cdot}H_2O$, **1** (0.1 mmol), **2** (1.2 equiv), **3** (1.2 equiv), in 0.25 mL of toluene and open air. [b]NMR yields of products are reported.

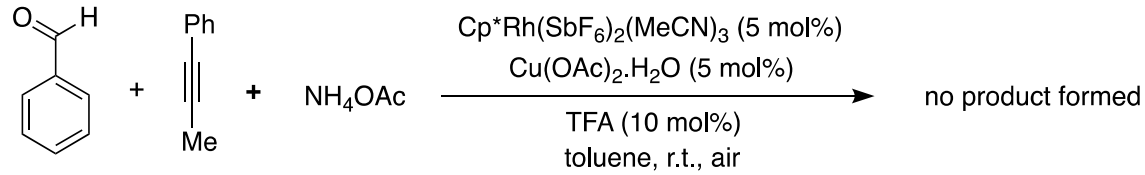
iii) Scheme S1: Study of potential side product formation





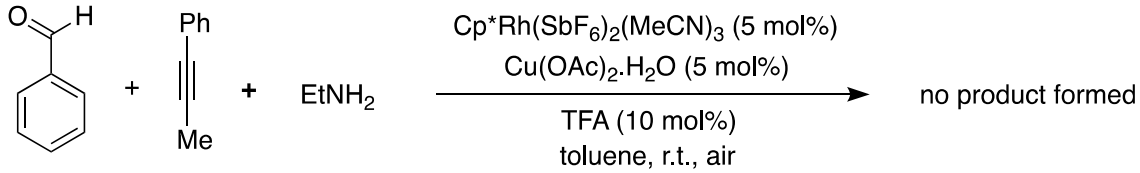
Under our optimized reaction conditions, we investigated the potential side product that could be generated. The reaction of benzaldehyde with internal alkyne resulted in the recovery of the starting material quantitatively. Similalrly, the reaction of benzyl amine with internal alkyne did not resulted in the formation of side product under our reaction conditions.

iv) Scheme S2: Reactivity of ammonia acetate.



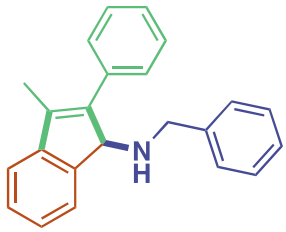
During our investigation, we found that the nucleophilicity of the amine is of high importance. Thus, we evaluated the ability of aniline and ammonia acetate under our reaction conditions, generating the corresponding indene in 35% yield and 0% yield, respectively. Low nucleophilic amine partner was not suitable for this reaction.

v) Scheme S3: Reactivity of ethyl amine (66% in water).



We evaluated the tolerance to ethyl amine in water towards our reaction conditions and no product was formed. The starting materials were recovered.

3) Spectroscopic data for indenes



4a

***N*-benzyl-3-methyl-2-phenyl-1*H*-inden-1-amine**

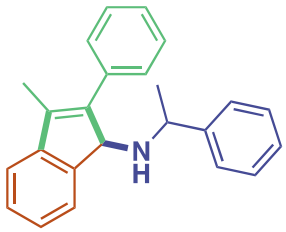
Use the general procedure described above, compound **4a** was obtained from benzaldehyde (0.1 mmol, 11 µL), benzylamine (0.12 mmol, 13.1 µL) and prop-1-yn-1-ylbenzene (0.12 mmol, 15 µL) as a light yellow solid (31.0 mg) in 99 % yield.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.68 (m, 1H), 7.48 (m, 4H), 7.44 – 7.34 (m, 3H), 7.32 (m, 1H), 7.24 – 7.15 (m, 3H), 7.10 – 7.03 (m, 2H), 5.10 – 4.88 (q, J = 1.9 Hz, 1H), 3.37 (d, J = 12.6, Hz, 1H), 3.29 (dd, J = 12.6, Hz, 1H), 2.32 (d, J = 1.9 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 145.7, 143.9, 143.7, 140.5, 135.7, 135.5, 128.9, 128.6, 128.2, 128.1, 127.8, 126.9, 126.7, 125.5, 123.3, 119.2, 65.7, 47.4, 11.7.

HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{23}H_{22}N$ 312.1752, found 312.1743.

Rf (Hexane/Et_2O 4:1): 0.4.



4b

3-methyl-2-phenyl-*N*-(1-phenylethyl)-1*H*-inden-1-amine

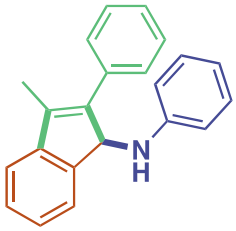
Use the general procedure described above, compound **4b** was obtained from benzaldehyde (0.1 mmol, 11.0 µL), 1-phenylethan-1-amine (0.12 mmol, 15.5 µL) and prop-1-yn-1-ylbenzene (0.12 mmol, 15.0 µL) as a light yellow solid (21.5 mg) in 66 % yield.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.62 – 7.58 (m, 1H), 7.50 – 7.46 (m, 2H), 7.40 – 7.31 (m, 9H), 7.23 – 7.19 (m, 1H), 4.64 (d, J = 2.0 Hz, 1H), 4.21 (q, J = 6.6 Hz, 1H), 2.26 (d, J = 2.0 Hz, 3H), 1.26 (d, J = 6.6 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 145.63, 145.60, 145.3, 143.9, 135.5, 134.8, 129.3, 128.33, 128.30, 127.5, 127.2, 127.0, 126.9, 125.2, 123.7, 119.3, 63.2, 55.8, 24.9, 11.6.

HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{24}H_{24}N$ 326.1909, found 326.1904.

Rf (Hexane/Et_2O 4:1): 0.6.



4c

3-methyl-*N*,2-diphenyl-1*H*-inden-1-amine

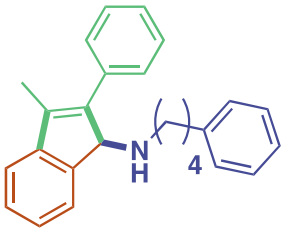
Use the general procedure described above, compound **4c** was obtained from benzaldehyde (0.1 mmol, 11.0 µL), aniline (0.12 mmol, 11.0 µL) and prop-1-yn-1-ylbenzene (0.12 mmol, 15.0 µL) as a yellow solid (10.4 mg) in 35 % yield.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55 – 7.51 (m, 1H), 7.46 – 7.35 (m, 6H), 7.32 – 7.27 (m, 1H), 7.22 – 7.09 (m, 3H), 6.74 – 6.70 (m, 1H), 6.68 – 6.66 (m, 2H), 5.54 (q, *J* = 2.2 Hz, 1H), 2.32 (d, *J* = 2.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 147.7, 145.1, 144.8, 142.2, 135.7, 135.1, 129.19, 129.10, 128.3, 127.9, 126.9, 125.9, 122.9, 119.4, 117.6, 113.7, 62.1, 11.9.

HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{22}H_{20}N$ 298.1596, found 398.1590.

Rf (Hexane/Et_2O 4:1): 0.4.



4d

***N*-benzyl-3-methyl-2-phenyl-1*H*-inden-1-amine**

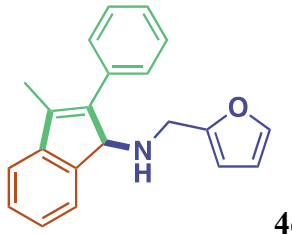
Use the general procedure described above, compound **4d** was obtained from benzaldehyde (0.1 mmol, 11.0 µL), 4-phenylbutan-1-amine (0.12 mmol, 18.9 µL) and prop-1-yn-1-ylbenzene (0.12 mmol, 15 µL) as a light yellow solid (35.2 mg) in 99 % yield.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.57 -7.55 (m, 1H), 7.48 – 7.40 (m, 4H), 7.38 – 7.29 (m, 3H), 7.28 – 7.26 (m, 1H), 7.25 -7.20 (m, 2H), 7.16 – 7.12 (m, 1H), 7.04 – 7.01 (m, 2H), 4.87 (q, *J* = 1.9 Hz, 1H), 3.50 (d, *J* = 7.0 Hz, 1H), 3.47 (d, *J* = 7.0 Hz, 1H), 2.40 (dd, *J* = 8.7, 6.7 Hz, 2H), 2.27 – 2.22 (m, 3H), 2.11 (ddd, *J* = 11.2, 7.6, 6.3 Hz, 1H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 145.6, 144.2, 143.9, 142.4, 135.8, 135.2, 128.8, 128.5, 128.3, 128.1, 127.6, 126.8, 125.5, 125.4, 123.2, 119.1, 65.9, 42.8, 35.4, 29.8, 28.7, 11.6.

HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{26}H_{27}N$ 353,2143, found 353.2140.

Rf (Hexane/Et_2O 4:1): 0.5.



4e

***N*-(furan-2-ylmethyl)-3-methyl-2-phenyl-1*H*-inden-1-amine**

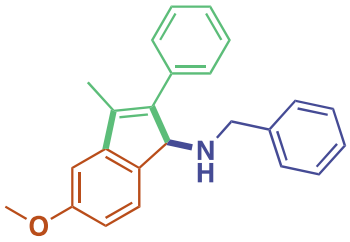
Use the general procedure described above, compound **4e** was obtained from benzaldehyde (0.1 mmol, 11.0 µL), furan-2-ylmethanamine (0.12 mmol, 10.7 µL) and prop-1-yn-1-ylbenzene (0.12 mmol, 15.0 µL) as a light yellow solid (16.6 mg) in 55 % yield.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.66 – 7.63 (m, 1H), 7.51 – 7.47 (m, 2H), 7.46 – 7.41 (m, 2H), 7.40 – 7.38 (m, 1H), 7.37 – 7.34 (m, 2H), 7.32 – 7.26 (m, 2H), 6.23 (dd, *J* = 3.2, 1.8 Hz, 1H), 5.96 (d, *J* = 3.2 Hz, 1H), 4.96 (t, *J* = 2.0 Hz, 1H), 3.45 (d, *J* = 14.1 Hz, 1H), 3.36 (d, *J* = 14.1 Hz, 1H), 2.29 (d, *J* = 2.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 153.8, 145.6, 143.5, 143.1, 141.6, 135.8, 135.5, 128.8, 128.6, 127.9, 127.0, 125.6, 123.4, 119.2, 110.0, 106.7, 65.1, 40.5, 11.6.

HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{21}H_{20}NO$ 302.1545, found 302.1534.

Rf (Hexane/Et_2O 4:1): 0.5.



4f

***N*-benzyl-5-methoxy-3-methyl-2-phenyl-1*H*-inden-1-amine**

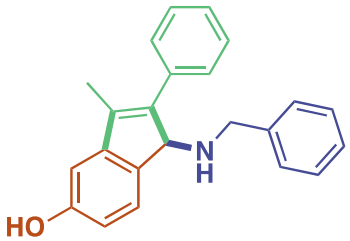
Use the general procedure described above, compound **4f** was obtained from 4-methoxybenzaldehyde (0.1 mmol, 12.1 µL), benzylamine (0.12 mmol, 13.1 µL) and prop-1-yn-1-ylbenzene (0.12 mmol, 15 µL) as a light yellow solid (20.5 mg) in 60 % yield.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55 – 7.53 (m, 1H), 7.51 – 7.43 (m, 4H), 7.38 – 7.32 (m, 1H), 7.23 – 7.13 (m, 3H), 7.08 – 7.00 (m, 2H), 6.94 – 6.92 (m, 1H), 6.85 – 6.83 (m, 1H), 4.94 (q, J = 1.8 Hz, 1H), 3.91 (s, 3H), 3.34 (d, J = 12.7 Hz, 1H), 3.28 (d, J = 12.7 Hz, 1H), 2.28 (d, J = 1.8 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 160.1, 147.3, 145.2, 140.7, 136.0, 135.7, 135.1, 128.8, 128.5, 128.2, 128.1, 126.9, 126.6, 123.8, 110.5, 105.5, 65.1, 55.5, 47.3, 11.6.

HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{24}H_{24}NO$ 342.1858, found 342.1850.

Rf (Hexane/Et_2O 4:1): 0.3.



4g

1-(benzylamino)-3-methyl-2-phenyl-1*H*-inden-5-ol

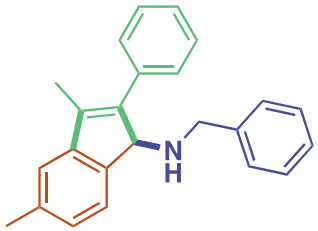
Use the general procedure described above, compound **4g** was obtained from 4-hydroxybenzaldehyde (0.1 mmol, 12.2 mg), benzylamine (0.12 mmol, 11.8 µL) and prop-1-yn-1-ylbenzene (0.12 mmol, 15.0 µL) as a light yellow solid (13.1 mg) in 40 % yield.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.58 – 7.55 (m, 1H), 7.50 – 7.46 (m, 2H), 7.44 – 7.39 (m, 2H), 7.38 – 7.34 (m, 1H), 7.22 – 7.16 (m, 3H), 7.05 – 6.99 (m, 2H), 6.84 – 7.81 (m, 1H), 6.73 – 6.70 (m, 1H), 4.99 (d, J = 2.1 Hz, 1H), 3.38 (d, J = 2.9 Hz, 2H), 2.23 (d, J = 1.8 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 156.6, 147.5, 143.8, 139.1, 136.0, 135.1, 134.1, 128.8, 128.7, 128.5, 128.3, 127.2, 127.1, 124.4, 112.6, 107.2, 64.4, 47.3, 11.6.

HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{23}H_{21}NO$ 328.1695, found 328.1692.

Rf (Hexane/Et_2O 4:1): 0.3.



4h

***N*-benzyl-3,5-dimethyl-2-phenyl-1*H*-inden-1-amine**

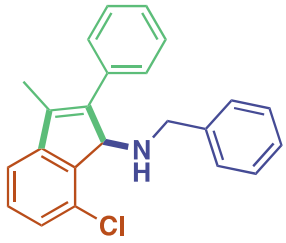
Use the general procedure described above, compound **4h** was obtained from 4-methylbenzaldehyde (0.1 mmol, 11.8 µL), benzylamine (0.12 mmol, 11.8 µL) and prop-1-yn-1-ylbenzene (0.12 mmol, 15.0 µL) as a light yellow solid (27.7 mg) in 85 % yield.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.59 – 7.56 (m, 1H), 7.52 – 7.44 (m, 4H), 7.39 – 7.34 (m, 1H), 7.24 – 7.16 (m, 4H), 7.15 – 7.12 (m, 1H), 7.08 – 7.04 (m, 2H), 4.98 (d, *J* = 2.0 Hz, 1H), 3.35 (d, *J* = 12.6 Hz, 1H), 3.30 (d, *J* = 12.6 Hz, 1H), 2.49 (s, 3H), 2.30 (d, *J* = 2.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 145.9, 143.8, 140.9, 140.5, 137.5, 135.7, 135.5, 128.9, 128.6, 128.2, 128.1, 126.9, 126.7, 126.2, 123.1, 120.0, 65.4, 47.3, 21.7, 11.7.

HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{24}H_{24}N$ 326.1909, found 326.1903.

Rf (Hexane/Et_2O 4:1): 0.5.



4i

***N*-benzyl-7-chloro-3-methyl-2-phenyl-1*H*-inden-1-amine**

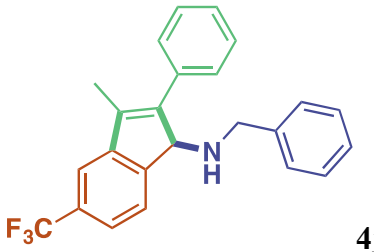
Use the general procedure described above, compound **4i** was obtained from 2-chlorobenzaldehyde (0.1 mmol, 11.2 µL), benzylamine (0.12 mmol, 11.8 µL) and prop-1-yn-1-ylbenzene (0.12 mmol, 15.0 µL) as a light yellow solid (19.4 mg) in 56 % yield.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.56 – 7.52 (m, 2H), 7.52 – 7.46 (m, 2H), 7.41 – 7.33 (m, 2H), 7.30 – 7.26 (m, 1H), 7.24 – 7.20 (m, 1H), 7.19 – 7.13 (m, 3H), 7.00 – 6.95 (m, 2H), 5.19 (q, *J* = 2.0 Hz, 1H), 3.20 (m, 2H), 2.29 (d, *J* = 2.0 Hz, 2H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 173.1, 148.2, 143.7, 139.8, 135.2, 134.9, 130.0, 129.6, 129.2, 128.4, 128.3, 128.0, 127.2, 126.7, 126.1, 117.7, 66.2, 46.7, 11.8.

HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{23}H_{21}ClN$ 346.1363, found 346.1357.

Rf (Hexane/Et_2O 4:1): 0.4.



4j

***N*-benzyl-3-methyl-2-phenyl-5-(trifluoromethyl)-1*H*-inden-1-amine**

Use the general procedure described above, compound **4j** was obtained from 4-(trifluoromethyl)benzaldehyde (0.1 mmol, 11.5 µL), benzylamine (0.12 mmol, 13.1 µL) and prop-1-yn-1-ylbenzene (0.12 mmol, 15.0 µL) as a light yellow solid (31.8 mg) in 84 % yield.

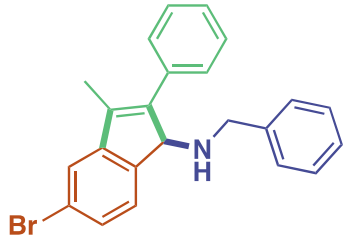
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.80 – 7.74 (m, 1H), 7.61 – 7.52 (m, 2H), 7.55 – 7.46 (m, 2H), 7.49 – 7.41 (m, 2H), 7.44 – 7.36 (m, 1H), 7.25 – 7.14 (m, 3H), 7.08 – 7.00 (m, 2H), 5.04 (s, 1H), 3.35 (d, J = 12.5 Hz, 1H), 3.23 (d, J = 12.5 Hz, 1H), 2.33 (d, J = 2.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 147.4, 146.3, 145.4, 139.8, 134.9, 134.8, 130.4 (q, J_{C-F}= 31.7 Hz), 128.9, 128.7, 128.2, 127.4, 126.9, 125.6, 123.58, 123.52 (q, J_{C-F}= 274 Hz), 122.6 (q, J_{C-F}= 4.0 Hz), 115.96 (q, J_{C-F}= 3.8 Hz), 65.6, 47.4, 11.6.

^{19}F NMR ($CDCl_3$, 471 MHz): δ = -61.9.

HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{24}H_{21}F_3N$ 380.1621, found 380.1626.

Rf (Hexane/Et_2O 4:1): 0.5.



4k

***N*-benzyl-5-bromo-3-methyl-2-phenyl-1*H*-inden-1-amine**

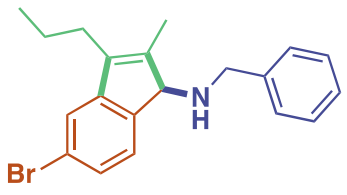
Use the general procedure described above, compound **4k** was obtained from 4-bromobenzaldehyde (0.1 mmol, 18.5 mg), benzylamine (0.12 mmol, 13.1 μL) and prop-1-yn-1-ylbenzene (0.12 mmol, 15.0 μL) as a light yellow solid (32.8 mg) in 84 % yield.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.55 – 7.54 (m, 1H), 7.53 – 7.47 (m, 3H), 7.46 – 7.43 (m, 3H), 7.42 – 7.37 (m, 1H), 7.24 – 7.18 (m, 3H), 7.06 – 7.02 (m, 2H), 4.96 (d, J = 2.0 Hz, 1H), 3.33 (d, J = 12.7 Hz, 1H), 3.25 (d, J = 12.6 Hz, 1H), 2.28 (d, J = 2.0 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 147.8, 145.3, 142.5, 140.1, 135.1, 134.6, 128.9, 128.7, 128.27, 128.24, 128.23, 127.3, 126.9, 124.8, 122.5, 121.9, 65.3, 47.3, 11.6.

HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{23}H_{21}NBr$ 390.0851, found 390.0858.

Rf (Hexane/Et_2O 4:1): 0.4.



4l

***N*-benzyl-5-bromo-2-methyl-3-propyl-1*H*-inden-1-amine**

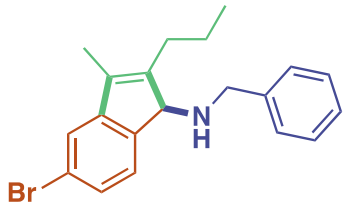
Use the general procedure described above, compound **4l** was obtained from 4-bromobenzaldehyde (0.1 mmol, 18.5 mg), benzylamine (0.12 mmol, 13.1 μL) and 2-hexyne (0.12 mmol, 13.5 μL) as a light yellow solid (19.4 mg) in 24 % yield.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.44 – 7.35 (m, 1H), 7.35 – 7.33 (m, 1H), 7.35 – 7.26 (m, 5H), 7.25 – 7.22 (m, 1H), 4.26 (s, 1H), 3.46 – 3.30 (m, 2H), 2.48 (t, J = 7.4 Hz, 2H), 2.05 (s, 3H), 1.62 (q, J = 7.4 Hz, 2H), 0.99 (t, J = 7.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 147.6, 142.8, 142.1, 138.3, 137.6, 128.9, 128.7, 128.4, 128.36, 128.35, 128.32, 127.0, 126.9, 124.2, 121.7, 121.6, 66.4, 47.3, 27.1, 21.5, 14.1, 11.9.

HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{20}H_{23}NBr$ 356.1008, found 356.1015.

Rf (Hexane/Et_2O 4:1): 0.4.



4l'

***N*-benzyl-5-bromo-3-methyl-2-propyl-1*H*-inden-1-amine**

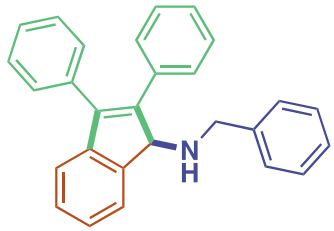
Use the general procedure described above, compound **4l'** was obtained from 4-bromobenzaldehyde (0.1 mmol, 18.5 mg), benzylamine (0.12 mmol, 13.1 μL) and 2-hexyne (0.12 mmol, 13.5 μL) as a light yellow solid (19.4 mg) in 44 % yield.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.41 – 7,39 (m, 1H), 7.38 – 7.31 (m, 2H), 7.32 – 7.30 (m, 4H), 7.26 – 7.22 (m, 1H), 4.38 (s, 1H), 3.50 – 3.34 (m, 2H), 2.50 – 2.38 (m, 2H), 2.03 (d, J = 1.9 Hz, 3H), 1.69 – 1.62 (m, 1H), 1.54 – 1.47 (m, 1H), 0.98 (t, J = 7.3 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 148.2, 142.9, 142.5, 140.4, 139.9, 128.4, 128.35, 128.32, 128.2, 127.9, 127.3, 127.15, 127.10, 124.2, 124.1, 121.6, 64.2, 47.6, 27.9, 22.9, 14.1, 10.3.

HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{20}H_{23}NBr$ 356.1008, found 356.1014.

Rf (Hexane/Et_2O 4:1): 0.5.



4m

***N*-benzyl-2,3-diphenyl-1*H*-inden-1-amine**

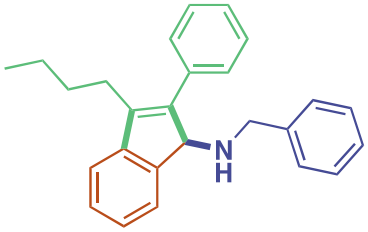
Use the general procedure described above, compound **4m** was obtained from benzaldehyde (0.1 mmol, 11.0 μL), benzylamine (0.12 mmol, 13.1 μL) and 1,2-diphenylethyne (0.12 mmol, 17.9 mg) as a light yellow solid (14.9 mg) in 40 % yield.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.78 – 7.74 (m, 1H), 7.45 – 7.37 (m, 5H), 7.37 – 7.33 (m, 2H), 7.33 – 7.24 (m, 6H), 7.24 – 7.16 (m, 3H), 7.09 – 7.04 (m, 2H), 5.15 (s, 1H), 3.42 (m, 2H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 144.8, 144.6, 144.1, 140.3, 140.2, 135.00, 134.9, 129.4, 129.2, 128.6, 128.39, 128.33, 128.2, 127.8, 127.5, 127.1, 126.8, 125.7, 123.8, 120.5, 65.8, 47.5.

HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{28}H_{24}N$ 374.1909, found 374.1900.

Rf (Hexane/Et_2O 4:1): 0.4.



4n

***N*-benzyl-3-butyl-2-phenyl-1*H*-inden-1-amine**

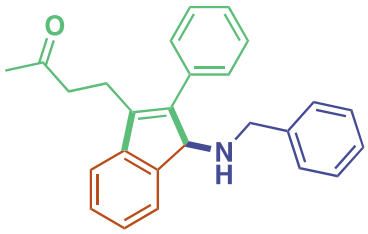
Use the general procedure described above, compound **4n** was obtained from benzaldehyde (0.1 mmol, 11.0 μL), benzylamine (0.12 mmol, 11.8 μL) and hex-1-yn-1-ylbenzene (0.12 mmol, 21.0 μL) as a light yellow solid (23.0 mg) in 82 % yield.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.73 – 7.68 (m, 1H), 7.53 – 7.48 (m, 2H), 7.46 – 7.35 (m, 5H), 7.34 – 7.28 (m, 1H), 7.24 – 7.15 (m, 3H), 7.09 – 7.04 (m, 2H), 4.99 (br, 1H), 3.38 (d, *J* = 12.7 Hz, 1H), 3.30 (d, *J* = 12.7 Hz, 1H), 2.73 (t, *J* = 7.8 Hz, 2H), 1.82 – 1.71 (m, 1H), 1.71 – 1.61 (m, 1H), 1.52 – 1.40 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 144.9, 144.1, 143.5, 140.4, 140.3, 135.9, 128.8, 128.6, 128.3, 128.3, 128.1, 127.7, 127.0, 126.8, 125.4, 123.6, 119.6, 65.9, 47.29, 31.29, 25.90, 23.08, 13.95.

HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{26}H_{28}N$ 354.2222, found 354.2216.

Rf (Hexane/Et_2O 4:1): 0.5.



4o

4-(1-(benzylamino)-2-phenyl-1*H*-inden-3-yl)butan-2-one

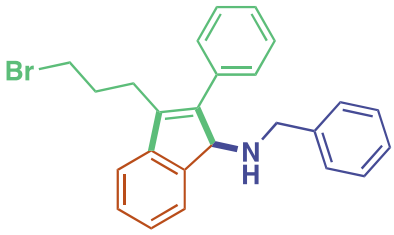
Use the general procedure described above, compound **4o** was obtained from benzaldehyde (0.1 mmol, 11 µL), benzylamine (0.12 mmol, 13.1 µL) and 7-phenylhept-6-yn-3-one (0.12 mmol, 22.3 µL) as a light yellow solid (26.7 mg) in 70 % yield.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.74 – 7.69 (m, 1H), 7.52 – 7.44 (m, 2H), 7.43 – 7.36 (m, 4H), 7.37 – 7.33 (m, 1H), 7.34 – 7.30 (m, 1H), 7.26 – 7.14 (m, 3H), 7.08 – 7.02 (m, 2H), 4.98 (s, 1H), 3.37 (d, *J* = 12.7 Hz, 1H), 3.30 (d, *J* = 12.7 Hz, 1H), 3.11 – 2.93 (m, 2H), 2.81 – 2.70 (m, 2H), 2.44 (q, *J* = 7.3 Hz, 2H), 1.08 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 210.4, 144.5, 144.1, 143.9, 140.0, 138.6, 135.3, 128.8, 128.7, 128.3, 128.2, 127.9, 127.3, 126.9, 125.7, 123.8, 119.3, 66.0, 47.3, 41.1, 35.9, 20.1, 7.8.

HRMS (ESI) m/z: $[M + Na]^+$ calculated for $C_{27}H_{27}NONa$ 404.1985, found 404.2003.

Rf (Hexane/Et_2O 4:1): 0.3.



4p

***N*-benzyl-3-(3-bromopropyl)-2-phenyl-1*H*-inden-1-amine**

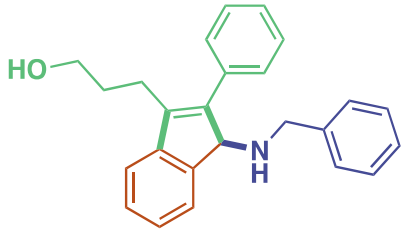
Use the general procedure described above, compound **4p** was obtained from benzaldehyde (0.1 mmol, 11 µL), benzylamine (0.12 mmol, 13.1 µL) and (5-bromopent-1-yn-1-yl)benzene (0.12 mmol, 20.4 µL) as a light white solid (25.1 mg) in 60 % yield.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.75 – 7.71 (m, 1H), 7.51 – 7.47 (m, 2H), 7.45 – 7.35 (m, 6H), 7.34 – 7.30 (m, 1H), 7.26 – 7.14 (m, 3H), 7.09 – 7.01 (m, 2H), 5.00 (s, 1H), 3.52 – 3.40 (m, 2H), 3.37 (d, *J* = 12.7 Hz, 1H), 3.31 (d, *J* = 12.7 Hz, 1H), 2.95 – 2.83 (m, 2H), 2.32 – 2.13 (m, 2H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 144.6, 144.3, 143.7, 139.8, 138.5, 135.3, 128.82, 128.80, 128.3, 128.2, 128.0, 127.4, 126.9, 125.7, 123.8, 119.5, 65.9, 47.3, 33.5, 31.9, 24.7.

HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{25}H_{25}BrN$ 418.1165, found 418.1163.

Rf (Hexane/Et_2O 4:1): 0.3.



4q

3-(1-(benzylamino)-2-phenyl-1*H*-inden-3-yl)propan-1-ol

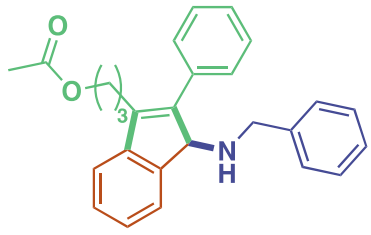
Use the general procedure described above, compound **4q** was obtained from benzaldehyde (0.1 mmol, 11 μL), benzylamine (0.12 mmol, 13.1 μL) and 5-phenylpent-4-yn-1-ol (0.12 mmol, 18.5 μL) as a light yellow solid (30.2 mg) in 85 % yield.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.74 – 7.69 (m, 1H), 7.51 – 7.46 (m, 2H), 7.46 – 7.40 (m, 3H), 7.40 – 7.35 (m, 2H), 7.32 – 7.29 (m, 1H), 7.24 – 7.15 (m, 3H), 7.08 – 7.02 (m, 2H), 4.99 (s, 1H), 3.75 – 3.63 (m, 2H), 3.37 (d, *J* = 12.7 Hz, 1H), 3.31 (d, *J* = 12.7 Hz, 1H), 2.90 – 2.73 (m, 2H), 1.99 – 1.88 (m, 2H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 144.5, 144.1, 143.8, 140.0, 139.5, 135.6, 128.8, 128.7, 128.3, 128.2, 127.9, 127.3, 126.9, 125.6, 123.7, 119.6, 65.9, 62.4, 47.3, 31.7, 22.1.

HRMS (ESI) m/z: $[M + H]^+$ calculated for $C_{25}H_{26}NO$ 356.2009, found 356.2007.

Rf (Hexane/Et_2O 4:1): 0.1.



4r

3-(1-(benzylamino)-2-phenyl-1*H*-inden-3-yl)propyl acetate

Use the general procedure described above, compound **4r** was obtained from benzaldehyde (0.1 mmol, 11 μL), benzylamine (0.12 mmol, 13.1 μL) and 5-phenylpent-4-yn-1-yl acetate (0.12 mmol, 23.1 μL) as a light yellow solid (32.6 mg) in 82 % yield.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.73 – 7.69 (m, 1H), 7.53 – 7.47 (m, 2H), 7.46 – 7.37 (m, 6H), 7.35 – 7.32 (m, 1H), 7.25 – 7.17 (m, 3H), 7.10 – 7.05 (m, 2H), 5.00 (s, 1H), 4.17 – 4.05 (m, 2H), 3.39 (d, *J* = 12.6 Hz, 1H), 3.31 (d, *J* = 12.6 Hz, 1H), 2.93 – 2.77 (m, 2H), 2.13 – 2.01 (m, 2H), 2.00 (s, 3H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 171.1, 144.9, 144.3, 144.2, 140.3, 138.6, 135.6, 128.8, 128.7, 128.29, 128.22, 127.8, 127.2, 126.8, 125.6, 123.7, 119.4, 66.1, 63.9, 47.4, 27.7, 22.3, 20.8.

HRMS (ESI) m/z: $[M + Na]^+$ calculated for $C_{27}H_{27}NO_2Na$ 420.1934, found 420.1942.

Rf (Hexane/Et_2O 4:1): 0.4.

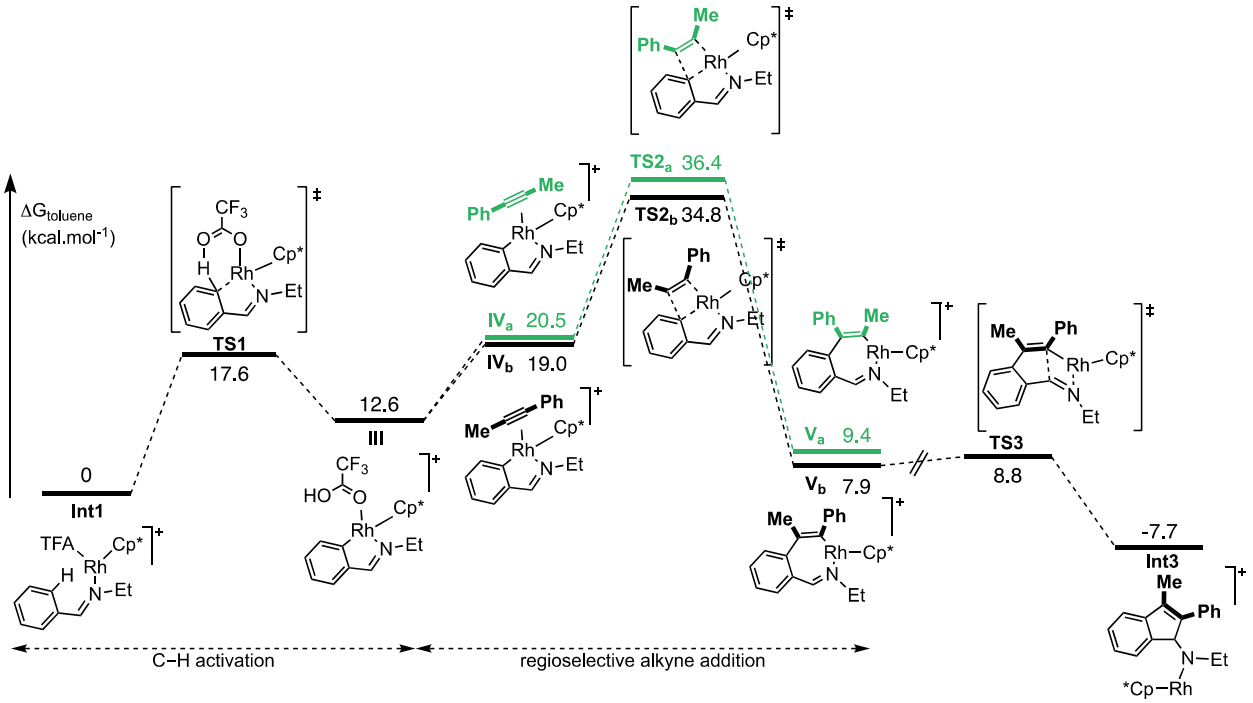
4) Computational studies

a) Computational details

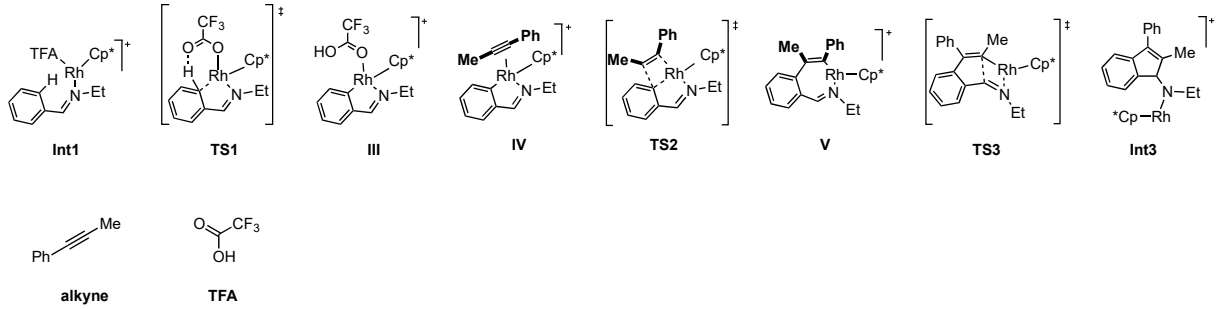
The theoretical calculations[2] were carried out by using Gaussian 09 program. Geometry optimizations were performed using the B3LYP functional with a standard 6-31G(d) basis set (lanl2DZ basis set for Rh) using CPCM solvation model (solvent = toluene). Throughout the paper, the energies presented are the calculated Gibbs free energies in toluene as solvent with B3LYP-calculated thermodynamic corrections.

b) Summary of calculation results.

i) Scheme S1. DFT computed mechanism pathway.



ii) Scheme S2. List of intermediates and transition states



c) Various energy values for all the relevant intermediates and transition states

Int1

Zero-point correction= 0.435668 (Hartree/Particle)
Thermal correction to Energy= 0.467175
Thermal correction to Enthalpy= 0.468119
Thermal correction to Gibbs Free Energy= 0.370065
Sum of electronic and zero-point Energies= -1429.250365
Sum of electronic and thermal Energies= -1429.218858
Sum of electronic and thermal Enthalpies= -1429.217914

Sum of electronic and thermal Free Energies= -1429.315967

TS1

Zero-point correction= 0.430904 (Hartree/Particle)
Thermal correction to Energy= 0.461238
Thermal correction to Enthalpy= 0.462182
Thermal correction to Gibbs Free Energy= 0.369462
Sum of electronic and zero-point Energies= -1429.226534
Sum of electronic and thermal Energies= -1429.196200
Sum of electronic and thermal Enthalpies= -1429.195256
Sum of electronic and thermal Free Energies= -1429.287976

TFA

Zero-point correction= 0.037675 (Hartree/Particle)
Thermal correction to Energy= 0.044018
Thermal correction to Enthalpy= 0.044963
Thermal correction to Gibbs Free Energy= 0.006301
Sum of electronic and zero-point Energies= -526.597762
Sum of electronic and thermal Energies= -526.591419
Sum of electronic and thermal Enthalpies= -526.590475
Sum of electronic and thermal Free Energies= -526.629136

III

Zero-point correction= 0.435116 (Hartree/Particle)
Thermal correction to Energy= 0.465566
Thermal correction to Enthalpy= 0.466510
Thermal correction to Gibbs Free Energy= 0.372004
Sum of electronic and zero-point Energies= -1429.232856
Sum of electronic and thermal Energies= -1429.202406
Sum of electronic and thermal Enthalpies= -1429.201462
Sum of electronic and thermal Free Energies= -1429.295967

Alkyne

Zero-point correction= 0.139600 (Hartree/Particle)
Thermal correction to Energy= 0.147816
Thermal correction to Enthalpy= 0.148760
Thermal correction to Gibbs Free Energy= 0.105145
Sum of electronic and zero-point Energies= -347.506531
Sum of electronic and thermal Energies= -347.498316
Sum of electronic and thermal Enthalpies= -347.497371
Sum of electronic and thermal Free Energies= -347.540986

IV

Zero-point correction= 0.538434 (Hartree/Particle)
Thermal correction to Energy= 0.570848
Thermal correction to Enthalpy= 0.571792

Thermal correction to Gibbs Free Energy= 0.476249
Sum of electronic and zero-point Energies= -1250.132982
Sum of electronic and thermal Energies= -1250.100568
Sum of electronic and thermal Enthalpies= -1250.099624
Sum of electronic and thermal Free Energies= -1250.195167

TS2

Zero-point correction= 0.537599 (Hartree/Particle)
Thermal correction to Energy= 0.569138
Thermal correction to Enthalpy= 0.570082
Thermal correction to Gibbs Free Energy= 0.476347
Sum of electronic and zero-point Energies= -1250.108614
Sum of electronic and thermal Energies= -1250.077076
Sum of electronic and thermal Enthalpies= -1250.076132
Sum of electronic and thermal Free Energies= -1250.169866

V

Zero-point correction= 0.539640 (Hartree/Particle)
Thermal correction to Energy= 0.571385
Thermal correction to Enthalpy= 0.572329
Thermal correction to Gibbs Free Energy= 0.476691
Sum of electronic and zero-point Energies= -1250.149867
Sum of electronic and thermal Energies= -1250.118122
Sum of electronic and thermal Enthalpies= -1250.117177
Sum of electronic and thermal Free Energies= -1250.212816

TS3

Zero-point correction= 0.537375 (Hartree/Particle)
Thermal correction to Energy= 0.568696
Thermal correction to Enthalpy= 0.569641
Thermal correction to Gibbs Free Energy= 0.475319
Sum of electronic and zero-point Energies= -1250.131803
Sum of electronic and thermal Energies= -1250.100482
Sum of electronic and thermal Enthalpies= -1250.099537
Sum of electronic and thermal Free Energies= -1250.193859

Int3

Zero-point correction= 0.541150 (Hartree/Particle)
Thermal correction to Energy= 0.571260
Thermal correction to Enthalpy= 0.572204
Thermal correction to Gibbs Free Energy= 0.481260
Sum of electronic and zero-point Energies= -1250.160252
Sum of electronic and thermal Energies= -1250.130142
Sum of electronic and thermal Enthalpies= -1250.129198
Sum of electronic and thermal Free Energies= -1250.220142

d) Cartesian coordinates for all the relevant intermediates and transition states

Int1

Symbolic Z-matrix:
Charge = 1 Multiplicity = 1

C	-4.32514	2.82062	-0.44076
C	-3.43721	3.11292	0.60345
C	-2.33626	2.27897	0.84117
C	-2.12363	1.15253	0.03499
C	-3.01159	0.86017	-1.00904
C	-4.11226	1.69428	-1.24702
H	-5.16561	3.45743	-0.62243
H	-3.59984	3.97281	1.21914
H	-2.84917	0.00008	-1.62449
H	-4.79009	1.47114	-2.04432
C	-1.35981	2.60009	1.9881
H	-1.52163	3.46005	2.60383
N	-0.34383	1.82972	2.20663
Rh	0.72634	-0.58011	0.55091
C	2.00666	-3.19184	0.31246
C	1.01184	-3.26149	1.64589
C	-0.42956	-3.40205	1.15045
C	1.09246	-3.05945	-0.95379
C	-0.49041	-3.05987	-0.4502
H	-1.28322	0.51566	0.21659
C	2.90527	1.79812	-0.06954
O	2.8035	1.21371	-1.17932
C	3.98523	2.87656	0.1366
F	5.11704	2.29864	0.59219
F	3.54952	3.78369	1.03646
F	4.23596	3.49263	-1.03816
O	2.09803	1.49106	0.90386
C	3.38693	-3.87312	0.26539
H	3.9226	-3.65622	1.16588
H	3.25939	-4.9314	0.17235
H	3.93785	-3.50504	-0.5748
C	1.51724	-3.59512	-2.33369
H	0.86438	-3.20255	-3.08509
H	2.52219	-3.29133	-2.54024
H	1.46028	-4.66358	-2.33452
C	-1.69053	-3.50198	-1.308
H	-1.62858	-3.04188	-2.27205
H	-1.67682	-4.5661	-1.41911
H	-2.60006	-3.20509	-0.82888
C	-1.6267	-3.16654	2.0901

H	-1.95411	-2.15159	2.00305
H	-2.42672	-3.8238	1.82019
H	-1.331	-3.36055	3.09998
C	1.39375	-3.91628	2.98641
H	2.36853	-3.58646	3.27953
H	0.68247	-3.63678	3.7353
H	1.39562	-4.98056	2.87579
C	0.58967	2.13558	3.30009
H	0.06568	2.63761	4.08638
C	1.19416	0.82624	3.84038
H	0.41067	0.1959	4.20602
H	1.71821	0.3242	3.05411
H	1.87361	1.04889	4.63642
H	1.37313	2.76584	2.93436

TS1

Symbolic Z-matrix:

Charge = 1 Multiplicity = 1

C	-2.41903	4.03271	-0.30654
C	-1.965	3.48808	0.90443
C	-1.15148	2.35035	0.8799
C	-0.73458	1.74301	-0.36418
C	-1.22424	2.32361	-1.55115
C	-2.05824	3.44965	-1.52816
H	-3.0429	4.91871	-0.28879
H	-2.24845	3.94119	1.84879
H	-0.90156	1.90824	-2.49908
H	-2.40997	3.88603	-2.45685
C	-0.66768	1.70776	2.09342
H	-0.69752	2.22707	3.0556
N	-0.16964	0.51104	1.99374
C	0.45469	-0.14675	3.16427
H	0.10248	-1.1794	3.21006
Rh	-0.4159	-0.39635	0.06764
C	-2.46796	-1.19345	-0.04917
C	-1.99499	-1.15773	-1.42887
C	-0.83217	-1.98614	-1.51993
C	-1.67887	-2.20833	0.65451
C	-0.64987	-2.66097	-0.22867
H	0.6409	1.74638	-0.48178
C	2.39406	0.58078	-0.4674
O	1.9026	1.74947	-0.58965
C	3.91008	0.43822	-0.61514
F	4.46159	1.46239	-1.35617
F	4.23392	-0.75908	-1.22046
F	4.4987	0.46119	0.64645

O	1.74927	-0.48009	-0.16444
C	-2.69039	-0.47987	-2.5662
H	-3.20611	0.4374	-2.27384
H	-2.02098	-0.25846	-3.40008
H	-3.44998	-1.17549	-2.95143
C	-3.74017	-0.57302	0.43636
H	-3.91848	0.40154	-0.02867
H	-4.60373	-1.21304	0.19145
H	-3.73151	-0.43895	1.51909
C	-1.96423	-2.70287	2.03591
H	-2.33265	-1.90919	2.69246
H	-2.75643	-3.46621	1.98582
H	-1.09247	-3.17114	2.50305
C	0.42493	-3.65941	0.05417
H	0.35133	-4.06261	1.06479
H	0.37399	-4.49751	-0.65536
H	1.42076	-3.20723	-0.07339
C	-0.00315	-2.25547	-2.73467
H	1.05156	-2.38499	-2.47252
H	-0.34306	-3.1794	-3.22709
H	-0.07402	-1.4447	-3.46438
C	1.9884	-0.1293	3.04551
H	2.4278	-0.50667	3.97667
H	2.33188	-0.76764	2.22406
H	2.36658	0.88816	2.87772
H	0.12184	0.36561	4.07784

TFA

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

H	1.17953	1.6448	-0.8628
C	2.27594	0.06499	-0.43411
O	2.02334	1.28174	-1.14166
C	3.72378	-0.36214	-0.12929
F	3.79628	-1.70956	-0.08826
F	4.10102	0.14534	1.06346
F	4.54325	0.10338	-1.09586
O	1.31513	-0.65672	-0.06054

III

Symbolic Z-matrix:

Charge = 1 Multiplicity = 1

C	0.30694	4.66498	-0.12233
C	0.06624	3.98107	1.07408
C	-0.19978	2.60209	1.04533
C	-0.25098	1.87591	-0.18116

C	0.02271	2.58014	-1.36631
C	0.29418	3.96507	-1.33381
H	0.5121	5.72923	-0.10963
H	0.09384	4.50969	2.02239
H	0.00559	2.07564	-2.32692
H	0.49178	4.48927	-2.2634
C	-0.39851	1.8067	2.23706
H	-0.34648	2.25372	3.23049
N	-0.61741	0.5334	2.09035
C	-0.77976	-0.34158	3.27043
H	-1.76369	-0.81587	3.19965
Rh	-0.67706	-0.11913	0.05304
C	-2.79846	-0.56772	-0.30138
C	-2.22144	-0.22165	-1.59448
C	-1.20221	-1.18685	-1.8724
C	-2.29269	-1.90679	0.07388
C	-1.29852	-2.25904	-0.85312
H	1.89791	1.60653	-0.70287
C	2.56403	-0.17073	-0.2119
O	2.73814	1.06964	-0.64866
C	3.87807	-0.95022	-0.17277
F	3.635	-2.28184	0.07298
F	4.69148	-0.45687	0.83068
F	4.54968	-0.83887	-1.37261
O	1.49933	-0.69677	0.15233
C	-3.96851	0.11222	0.33939
H	-3.97538	1.18503	0.13076
H	-4.90843	-0.30721	-0.04604
H	-3.96969	-0.02184	1.42459
C	-2.68774	0.88553	-2.48594
H	-3.57926	0.55409	-3.03548
H	-2.96017	1.78222	-1.92405
H	-1.93469	1.16373	-3.22655
C	-0.36471	-1.28374	-3.11124
H	-0.86346	-1.91291	-3.86135
H	-0.19247	-0.30535	-3.56768
H	0.60885	-1.73734	-2.9034
C	-0.44647	-3.48911	-0.85444
H	-0.59638	-4.0635	-1.77714
H	0.61915	-3.23551	-0.79981
H	-0.67682	-4.13972	-0.008
C	-2.81049	-2.74363	1.20851
H	-2.73579	-3.80786	0.96622
H	-2.26556	-2.58944	2.14544
H	-3.86412	-2.52202	1.40271
H	-0.78101	0.27946	4.17578

C	0.32109	-1.40448	3.35713
H	0.33525	-2.04013	2.46655
H	1.30563	-0.93713	3.4599
H	0.14986	-2.03934	4.23252

Alkyne

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	-0.91877	-0.07236	2.6331
C	-0.10189	-0.94958	2.55504
C	0.94535	-2.07424	2.45495
H	0.98721	-2.43404	1.44813
H	1.90475	-1.69447	2.73817
H	0.67171	-2.87563	3.10901
C	-1.96604	1.05227	2.73317
C	-3.32603	0.74098	2.73308
C	-1.55502	2.38207	2.824
C	-4.27472	1.75936	2.82313
H	-3.64977	-0.30745	2.66068
C	-2.50385	3.40081	2.91507
H	-0.48317	2.62758	2.82426
C	-3.86354	3.0897	2.91452
H	-5.3467	1.51412	2.82244
H	-2.17947	4.44917	2.98709
H	-4.61172	3.89248	2.98557

IV

Symbolic Z-matrix:

Charge = 1 Multiplicity = 1

C	3.08512	-2.11612	-1.89687
C	3.08052	-0.71819	-1.95789
C	1.98532	0.01332	-1.47718
C	0.84764	-0.69564	-0.90867
C	0.88583	-2.09774	-0.86476
C	1.99364	-2.8018	-1.35371
H	3.92709	-2.66285	-2.26739
H	3.92024	-0.20293	-2.37537
H	0.0581	-2.63588	-0.45232
H	2.00499	-3.87083	-1.31136
C	2.04757	1.56702	-1.58144
Rh	-0.84057	0.21013	-0.15435
C	-3.65155	1.00273	-0.24303
C	-3.18498	0.62096	-1.81918
C	-2.9146	-0.91614	-1.86723
C	-3.77177	-0.32137	0.48025

C	-3.32129	-1.512	-0.52383
C	0.7575	1.06453	2.28481
C	1.55657	0.03137	1.70494
C	0.72559	2.04972	3.46823
H	1.20228	2.96447	3.18355
H	-0.29013	2.24679	3.74122
H	1.24251	1.62254	4.30203
C	2.87766	-0.73369	1.90816
C	3.70159	-0.42959	3.00029
C	3.25618	-1.73351	1.00197
C	4.90379	-1.12528	3.18646
H	3.4127	0.33385	3.69213
C	4.45859	-2.42919	1.18816
H	2.62729	-1.96579	0.16804
C	5.28236	-2.12506	2.2804
H	5.53267	-0.89305	4.02044
H	4.7477	-3.1926	0.49636
H	6.20038	-2.65622	2.42259
C	-3.86273	-0.45899	2.01139
H	-4.88154	-0.62167	2.2951
H	-3.26678	-1.28825	2.33088
H	-3.50296	0.43728	2.47204
C	-2.93613	-2.92681	-0.05358
H	-2.66769	-2.89768	0.98183
H	-3.768	-3.5862	-0.18796
H	-2.10504	-3.27954	-0.62779
C	-3.02869	-1.76198	-3.14923
H	-2.58157	-2.72019	-2.9853
H	-4.06059	-1.88848	-3.40231
H	-2.52324	-1.26502	-3.95075
C	-4.54159	2.18915	0.17124
H	-5.55259	1.99595	-0.12107
H	-4.49525	2.31605	1.23264
H	-4.19521	3.07987	-0.30996
C	-3.67159	1.40874	-3.04967
H	-4.69729	1.17241	-3.24176
H	-3.57634	2.45782	-2.86192
H	-3.07914	1.14341	-3.90027
N	1.03652	2.1599	-1.13047
C	0.84329	3.6169	-1.10398
H	1.79355	4.10126	-1.01856
H	2.88334	2.08594	-2.00215
H	0.23212	3.8805	-0.2662
C	0.1526	4.06669	-2.40478
H	-0.79791	3.58261	-2.48964
H	0.01228	5.12724	-2.38576

H	0.7634	3.80267	-3.24269

TS2

Symbolic Z-matrix:

Charge = 1 Multiplicity = 1

C	2.71784	3.82704	0.21872
C	2.12958	3.29271	1.34843
C	1.4481	2.06962	1.27372
C	1.42446	1.22925	0.12615
C	1.99109	1.8706	-1.0075
C	2.61422	3.12791	-0.97041
H	3.23808	4.7626	0.26176
H	2.18537	3.81927	2.27879
H	1.95015	1.35886	-1.94529
H	3.01954	3.54694	-1.86746
C	0.65004	1.5917	2.52174
H	0.89672	1.97124	3.49008
N	-0.34464	0.74485	2.39103
C	-0.99415	0.17738	3.5798
H	-1.78498	0.82587	3.89483
Rh	-1.28883	0.05794	-0.2977
C	-4.09995	-0.54059	-0.75924
C	-3.85533	1.08278	-1.17783
C	-2.95734	1.11671	-2.43356
C	-3.47134	-1.39512	-1.8649
C	-2.76059	-0.46278	-2.87023
C	1.18784	-1.6055	0.50089
C	2.33868	-0.79143	0.52448
C	1.16908	-3.10711	0.83968
H	1.94173	-3.32175	1.54685
H	0.21971	-3.36556	1.25924
H	1.33285	-3.67776	-0.05208
C	3.81088	-1.17778	0.75966
C	4.15685	-2.51522	1.00343
C	4.80698	-0.19384	0.71703
C	5.50207	-2.87089	1.17612
H	3.39485	-3.26456	1.05656
C	6.15176	-0.55015	0.8883
H	4.54102	0.82924	0.55082
C	6.50086	-1.88957	1.11028
H	5.76669	-3.89111	1.35762
H	6.91245	0.20122	0.84994
H	7.52947	-2.16239	1.23041
C	-1.67869	-0.93054	-3.86618

H	-2.12337	-1.09223	-4.82537
H	-0.92124	-0.17914	-3.94594
H	-1.23989	-1.84458	-3.51983
C	-2.94734	2.25224	-3.4725
H	-2.10488	2.13413	-4.11887
H	-3.8478	2.21582	-4.04965
H	-2.88398	3.19517	-2.97001
C	-4.89323	2.17736	-0.87424
H	-4.44467	3.14026	-0.99903
H	-5.72094	2.07942	-1.54514
H	-5.23666	2.07244	0.13379
C	-5.3206	-1.07347	0.01942
H	-5.5045	-0.44459	0.8661
H	-6.18172	-1.07319	-0.61672
H	-5.12326	-2.07091	0.3514
C	-3.07712	-2.86793	-1.64294
H	-2.42335	-2.93878	-0.79947
H	-3.95735	-3.44809	-1.46182
H	-2.5772	-3.23991	-2.51381
C	-1.57766	-1.20869	3.24577
H	-2.29745	-1.11343	2.46011
H	-0.79113	-1.86209	2.93124
H	-2.05091	-1.61315	4.11608
H	-0.27384	0.08253	4.36447

V

Symbolic Z-matrix:

Charge = 1 Multiplicity = 1

C	-1.99582	4.44318	0.27381
C	-1.27592	3.96552	-0.82571
C	-1.26859	2.59715	-1.13781
C	-1.98541	1.69126	-0.31371
C	-2.74548	2.19679	0.75389
C	-2.74012	3.5594	1.05699
H	-1.97733	5.48586	0.51432
H	-0.72685	4.65155	-1.43538
H	-3.33281	1.52653	1.34631
H	-3.3057	3.92515	1.88627
C	-0.52565	2.16948	-2.4222
H	-0.46145	2.87062	-3.22688
N	0.03212	1.02775	-2.57283
C	0.29433	0.4967	-3.92126
H	0.2881	-0.57326	-3.89239
Rh	0.87904	-0.41886	-0.19984
C	3.45295	-1.75051	0.48911

C	3.68183	-0.15706	0.76893
C	2.81648	0.23582	1.95858
C	2.36898	-2.27494	1.58908
C	1.9928	-1.09207	2.47339
C	-1.03536	-0.69822	-0.8143
C	-2.05787	0.15889	-0.52262
C	-1.36525	-1.98653	-1.59239
H	-2.37197	-2.28155	-1.37928
H	-1.25947	-1.80763	-2.64088
H	-0.69493	-2.7661	-1.29324
C	-3.4638	-0.45363	-0.3581
C	-3.65383	-1.84218	-0.40643
C	-4.56092	0.3951	-0.15976
C	-4.94285	-2.37703	-0.25548
H	-2.81836	-2.49307	-0.5572
C	-5.84783	-0.13887	-0.02049
H	-4.41555	1.45414	-0.11813
C	-6.03943	-1.5242	-0.06608
H	-5.09002	-3.4364	-0.28447
H	-6.68613	0.51328	0.12017
H	-7.02331	-1.93254	0.04491
C	2.36023	-3.71997	2.11894
H	3.1904	-3.86311	2.77865
H	1.44813	-3.90084	2.64957
H	2.43542	-4.39986	1.297
C	1.58402	-1.3023	3.9445
H	0.87501	-2.10122	4.00728
H	2.44957	-1.54721	4.52413
H	1.14296	-0.40434	4.32566
C	3.2358	1.36879	2.91191
H	2.40722	1.63873	3.53087
H	4.04796	1.03853	3.5243
H	3.54468	2.21849	2.33827
C	4.54342	-2.66987	-0.09066
H	5.29221	-2.8461	0.65269
H	4.10453	-3.59972	-0.38436
H	4.99032	-2.20085	-0.94269
C	5.01168	0.55429	0.45719
H	5.74828	0.26051	1.1748
H	5.34184	0.27988	-0.52412
H	4.86871	1.61235	0.50216
C	1.67145	0.99663	-4.39829
H	2.42689	0.659	-3.72055
H	1.8705	0.61339	-5.37599
H	1.67053	2.06706	-4.42746
H	-0.46379	0.83666	-4.59679

TS3

Symbolic Z-matrix:

Charge = 1 Multiplicity = 1

C	3.03305	1.99811	1.60759
C	1.66955	1.83438	1.33314
C	1.20319	0.56911	0.96207
C	2.10333	-0.50915	0.78923
C	3.46535	-0.34092	1.08691
C	3.92148	0.91477	1.49584
H	3.40303	2.96493	1.9309
H	0.98028	2.66383	1.44728
H	4.16265	-1.16432	0.97606
H	4.97243	1.05786	1.72183
C	-0.23336	0.22611	0.76367
H	-0.73131	-0.23724	1.62698
Rh	-0.26632	-0.03889	-1.83206
C	-1.13833	0.64049	-4.33574
C	0.02352	1.32966	-3.9768
C	1.11615	0.34939	-3.92837
C	-0.78652	-0.76533	-4.59592
C	0.60617	-0.91304	-4.44235
C	0.24794	-1.47305	-0.36784
C	1.43925	-1.70669	0.27032
C	-0.85765	-2.46084	-0.66494
H	-1.25529	-2.9203	0.24938
H	-1.72176	-1.98379	-1.16576
H	-0.5186	-3.2558	-1.33912
C	-2.45475	1.05483	0.13487
H	-2.65097	0.91359	1.1772
N	-1.00196	0.88438	-0.13604
C	2.00068	-3.11104	0.5605
C	1.79983	-3.69881	1.80976
C	2.71035	-3.79538	-0.42621
C	2.30914	-4.97036	2.07239
H	1.23888	-3.16069	2.58758
C	3.21903	-5.06774	-0.16399
H	2.86859	-3.33235	-1.41094
C	3.01868	-5.65523	1.08511
H	2.15126	-5.4321	3.05787
H	3.77818	-5.60724	-0.9423
H	3.42011	-6.65782	1.29239
C	-2.82402	2.49129	-0.27963
H	-3.88856	2.59916	-0.28258
H	-2.39727	3.18392	0.41539

H	-2.44279	2.68887	-1.2597
H	-3.01878	0.35185	-0.44184
C	0.1417	2.81753	-3.59748
H	0.13466	2.91561	-2.53201
H	1.05684	3.21306	-3.98603
H	-0.68429	3.35768	-4.01085
C	2.59116	0.67042	-3.6236
H	2.9703	1.3428	-4.36458
H	2.66499	1.12537	-2.65795
H	3.16302	-0.23385	-3.6365
C	-2.55839	1.22797	-4.43516
H	-2.83979	1.6427	-3.48979
H	-2.57552	1.99537	-5.18061
H	-3.24653	0.45401	-4.70414
C	-1.77517	-1.85289	-5.0557
H	-2.54341	-1.97048	-4.32025
H	-2.2147	-1.5644	-5.98762
H	-1.25431	-2.77944	-5.17866
C	1.42866	-2.19821	-4.65078
H	2.41663	-1.94132	-4.97144
H	1.48226	-2.74063	-3.73002
H	0.95855	-2.80564	-5.39572

Int3

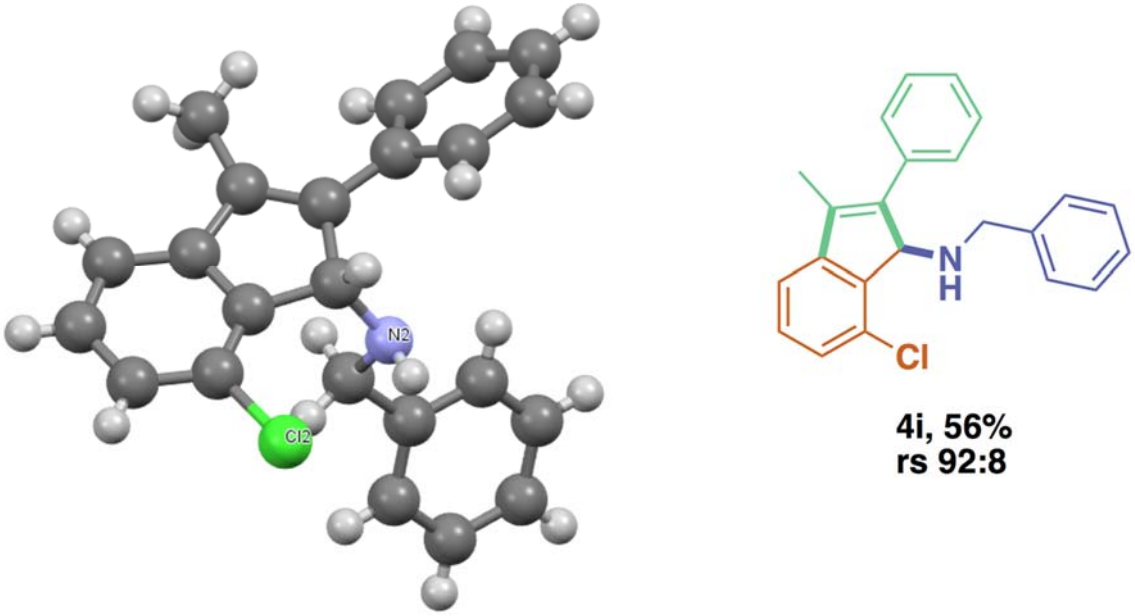
Symbolic Z-matrix:

Charge = 1 Multiplicity = 1

C	0.48112	1.50244	3.70341
C	1.54939	1.35597	2.79287
C	1.546	0.23652	1.96664
C	0.49079	-0.64625	1.95132
C	-0.55388	-0.56123	2.86562
C	-0.55477	0.53177	3.75755
H	0.45317	2.34749	4.35912
H	2.33879	2.07675	2.74515
H	-1.33328	-1.29402	2.88636
H	-1.34174	0.63242	4.47549
C	2.62263	-0.23028	0.96959
H	3.04129	0.57173	0.39824
Rh	2.80428	-3.12291	3.32654
C	4.15079	-3.62857	5.997
C	2.68746	-4.24117	5.95746
C	2.71976	-5.46676	4.9205
C	5.02685	-4.29216	4.68431
C	4.22014	-5.59924	4.32193
C	1.85284	-1.2559	0.10687

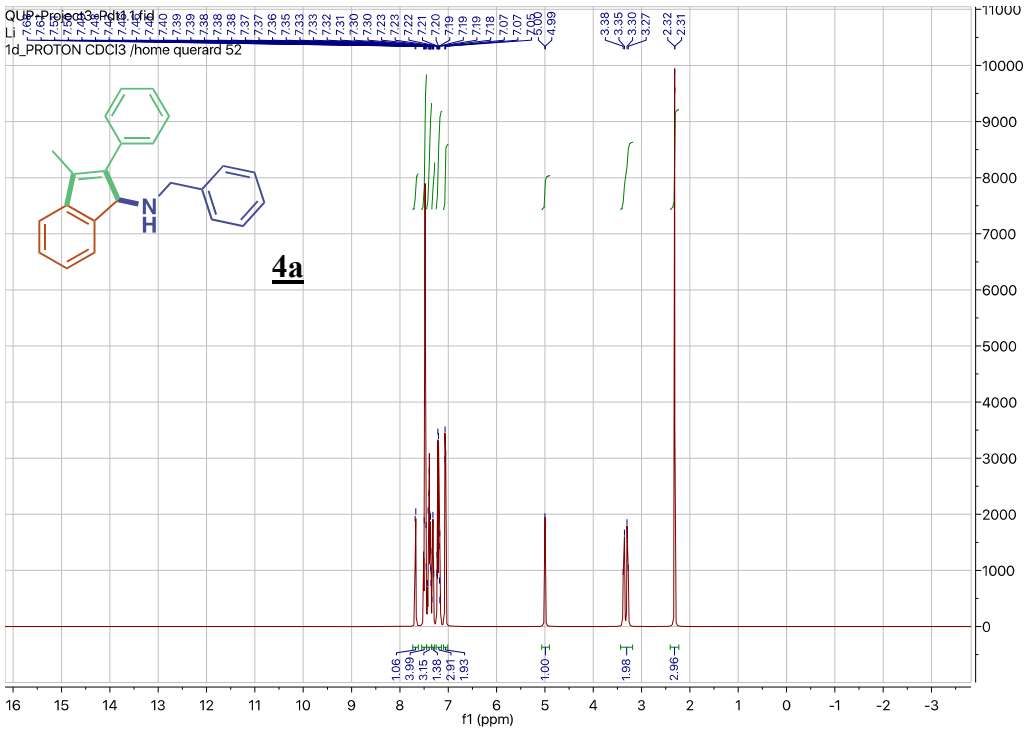
C	0.68152	-1.63115	0.78783
C	2.29144	-1.77421	-1.27539
H	1.89032	-1.13976	-2.03786
H	3.35988	-1.77166	-1.3348
H	1.92891	-2.77131	-1.41392
C	4.38033	0.05625	2.57915
N	3.7131	-0.90447	1.68884
H	5.17485	-0.43409	3.10178
C	1.78991	-4.17751	7.20724
H	0.79267	-4.46342	6.94513
H	2.16826	-4.8456	7.95247
H	1.78515	-3.17928	7.59245
C	4.45975	-2.23367	6.57204
H	3.83435	-1.506	6.09836
H	4.27298	-2.23281	7.62559
H	5.48661	-1.99302	6.39167
C	6.55831	-4.19585	4.55445
H	6.86512	-3.18063	4.6962
H	7.01872	-4.8145	5.29616
H	6.85514	-4.52552	3.58073
C	4.51646	-6.43445	3.06236
H	4.48535	-5.80224	2.1997
H	5.48795	-6.87492	3.14693
H	3.78202	-7.20653	2.96542
C	1.84378	-6.72407	5.07367
H	1.86352	-7.28562	4.1631
H	2.22179	-7.32693	5.87275
H	0.8374	-6.43322	5.29162
H	3.67287	0.4398	3.28436
C	4.95397	1.21643	1.74461
H	5.43997	1.91555	2.39255
H	5.66113	0.83278	1.03918
H	4.15936	1.70704	1.22226
C	-0.25514	-2.79569	0.41666
C	-0.1268	-4.03196	1.06394
C	-1.23605	-2.61897	-0.56844
C	-0.97996	-5.09132	0.72664
H	0.62251	-4.16701	1.81576
C	-2.08901	-3.67836	-0.90593
H	-1.3337	-1.67511	-1.06287
C	-1.96105	-4.91453	-0.25831
H	-0.88226	-6.03515	1.22112
H	-2.83802	-3.54338	-1.658
H	-2.61242	-5.7234	-0.5159

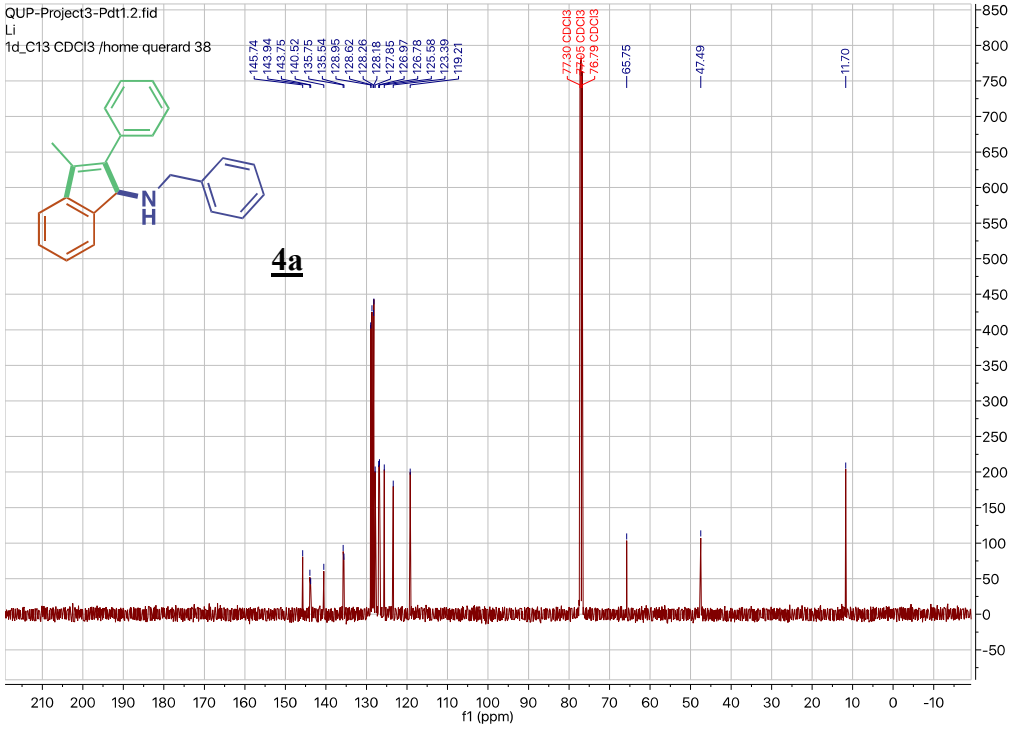
e) X-ray structure of compound 4i.

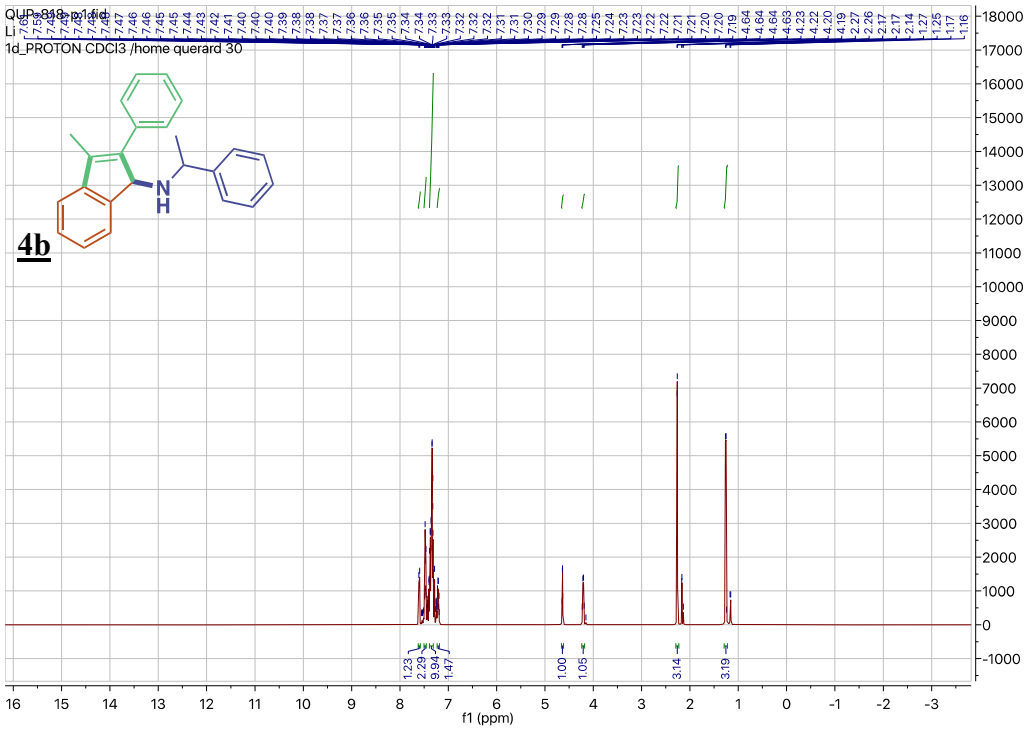


Scheme S3. X-ray structure of **4i**

5) NMR spectra






QUP-818-p.1.fid
Li
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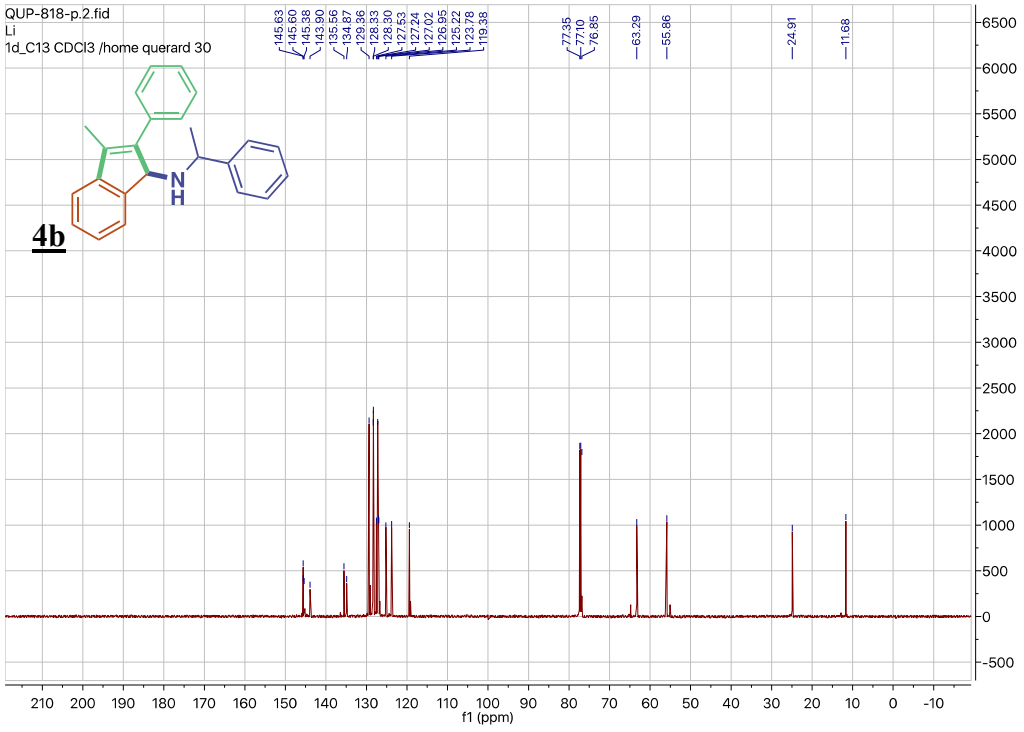
4b
f1 (ppm)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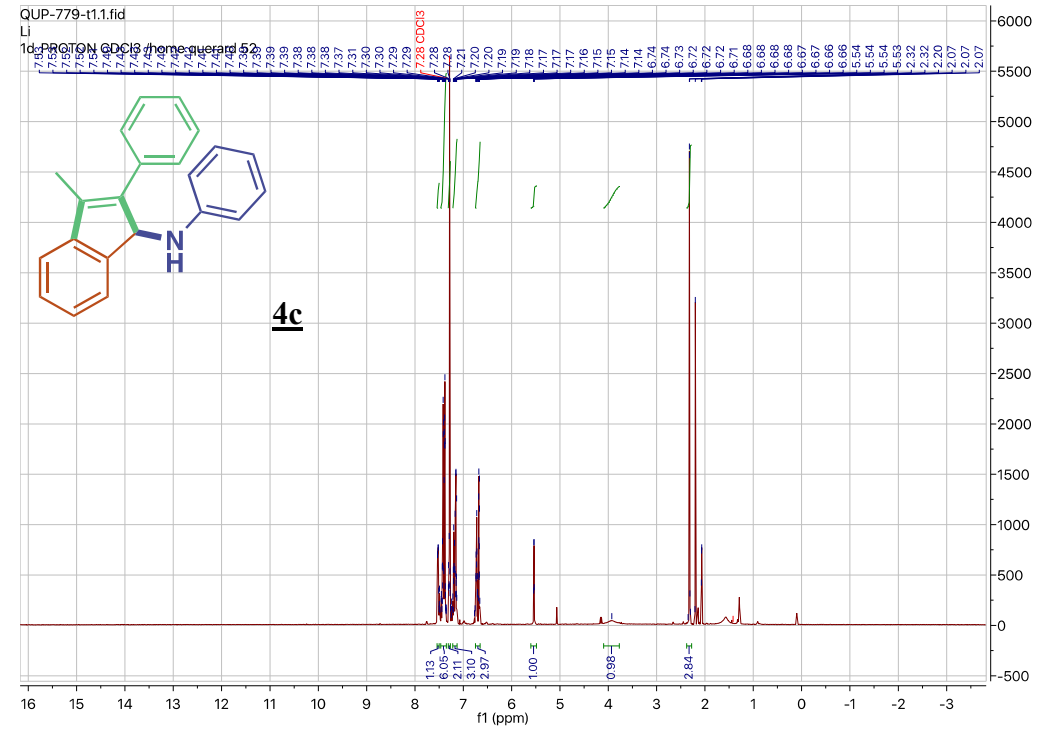
4b
f1 (ppm)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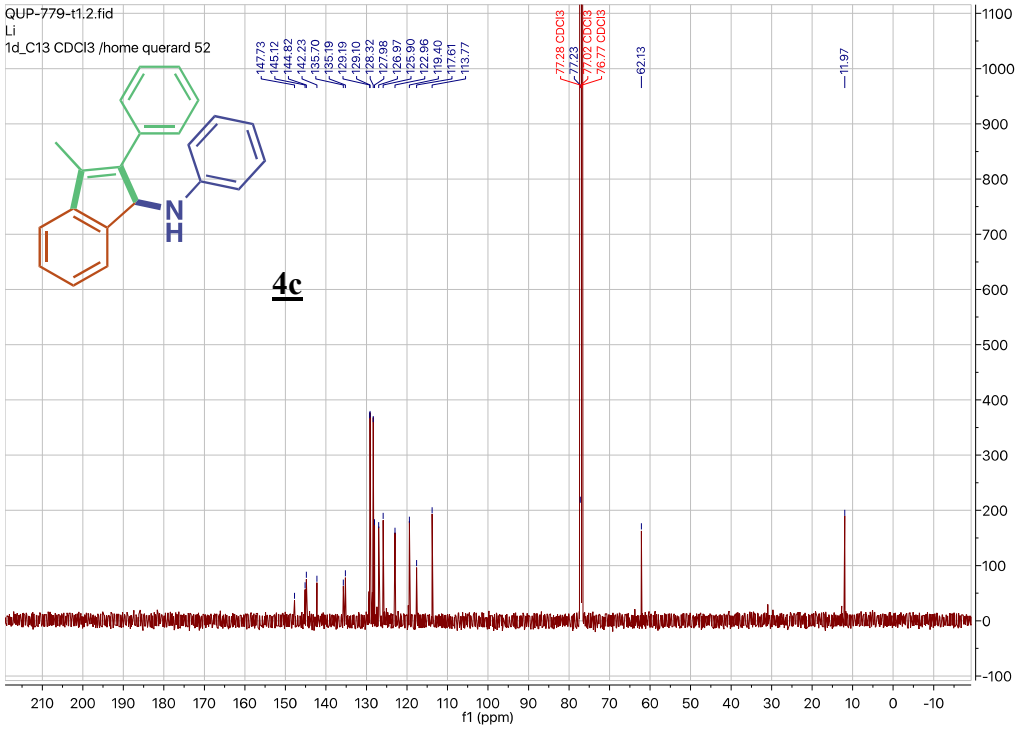
Li
1d_PROTON CDCl3 /home querard 52
4c
f1 (ppm)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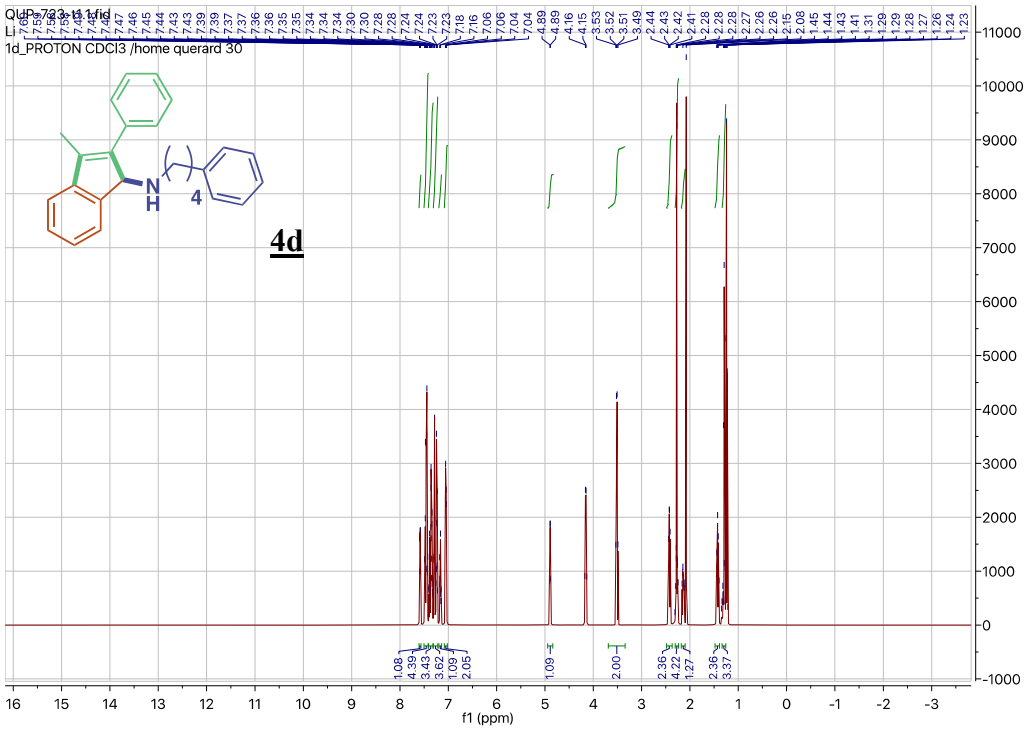
1d_C13 CDCl3 /home querard 52
4c
f1 (ppm)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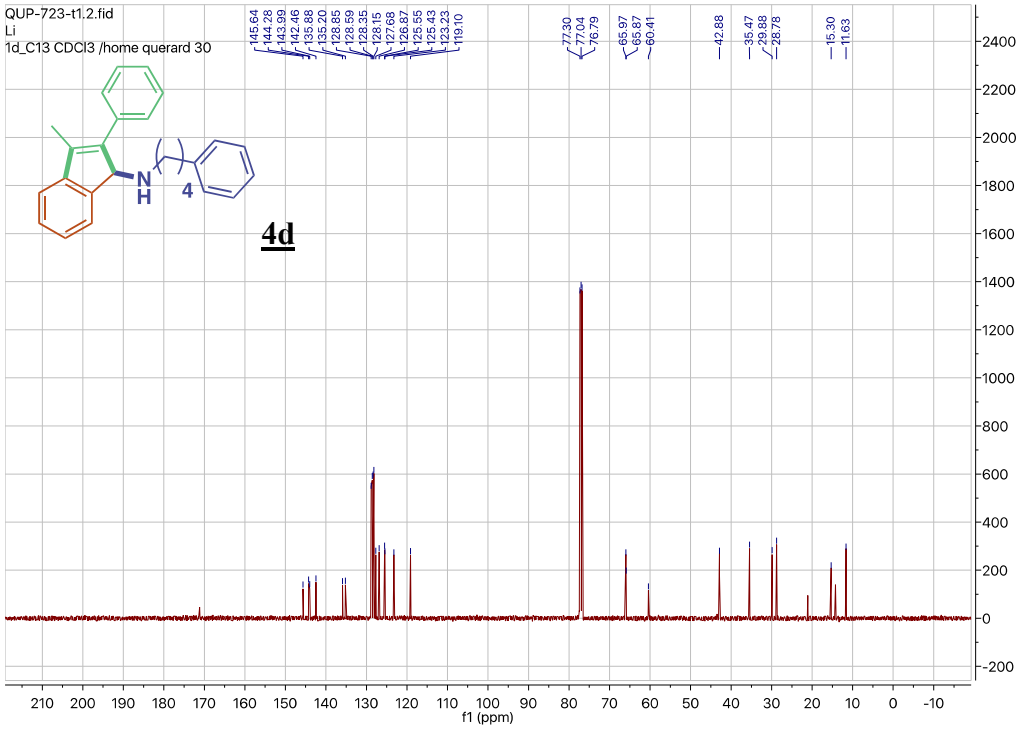
Li
1d_PROTON CDCl3 /home querard 30
4d
f1 (ppm)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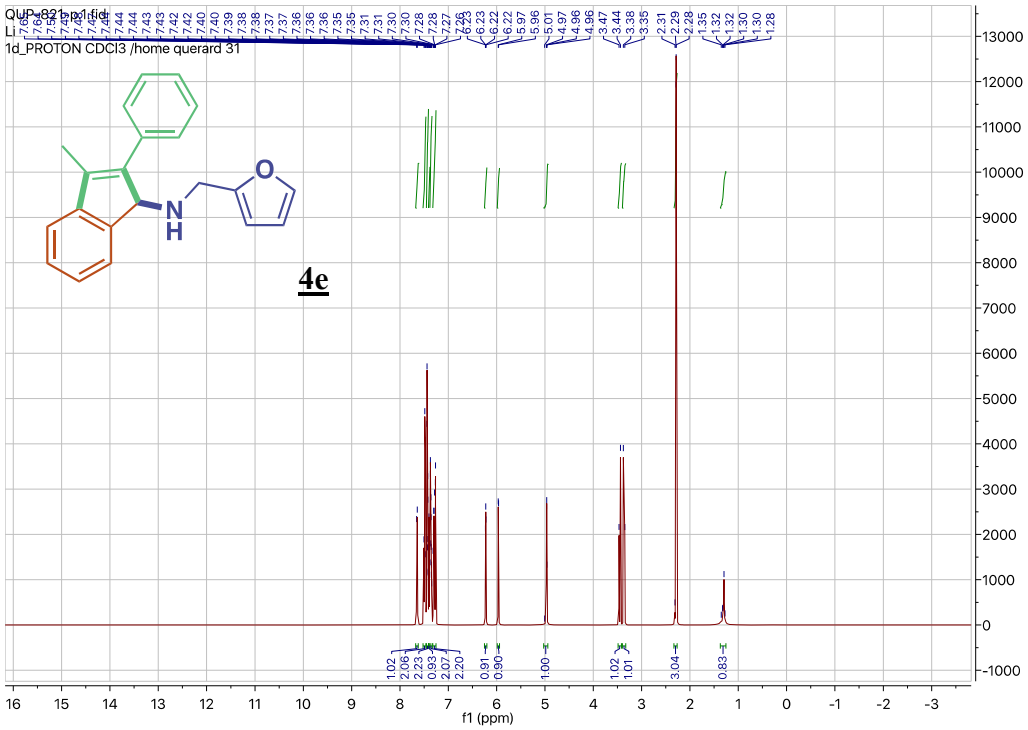
1d_C13 CDCl3 /home querard 30
4d
f1 (ppm)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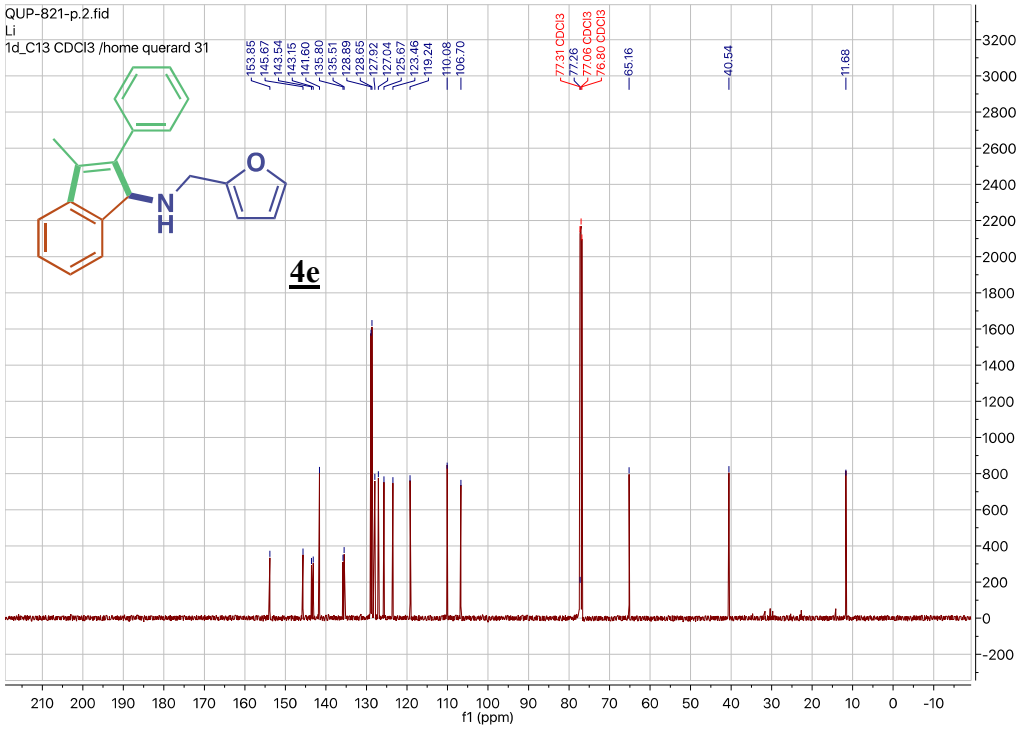
1d_PROTON CDCl3 /home querard 31
4e
f1 (ppm)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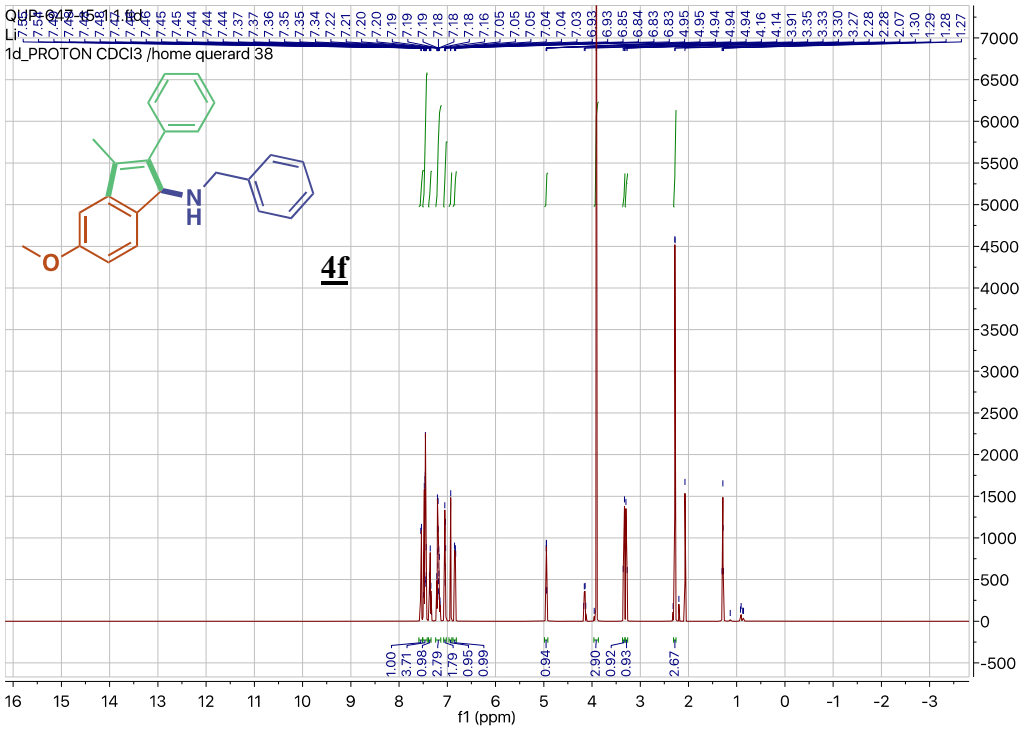
1d_C13 CDCl3 /home querard 31
4e
f1 (ppm)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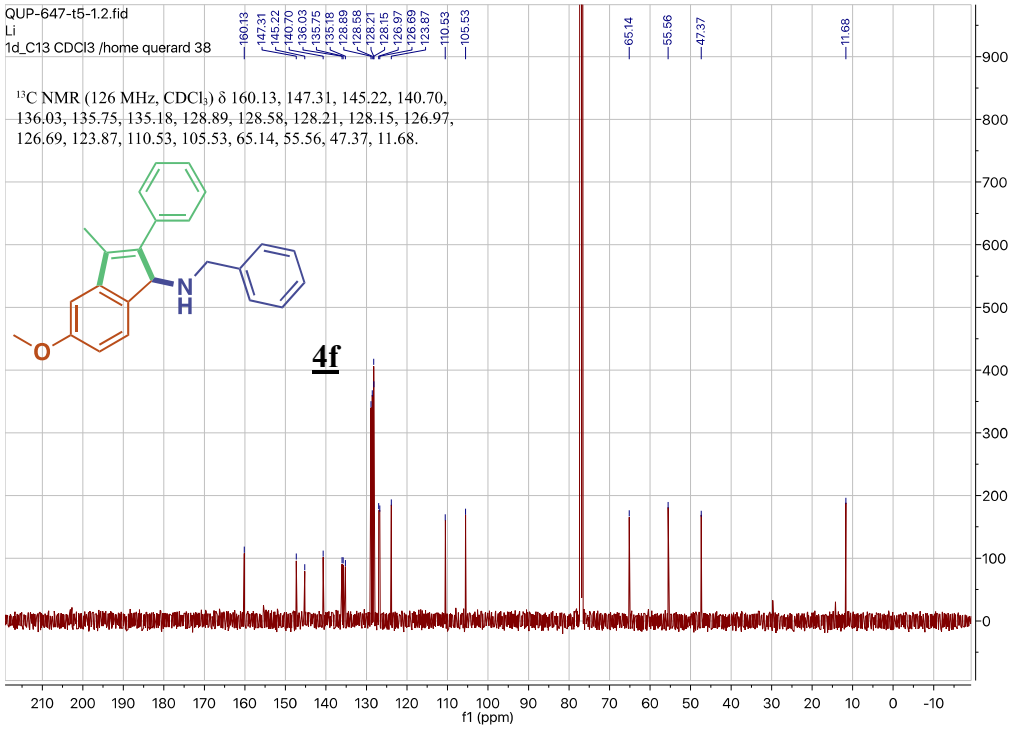
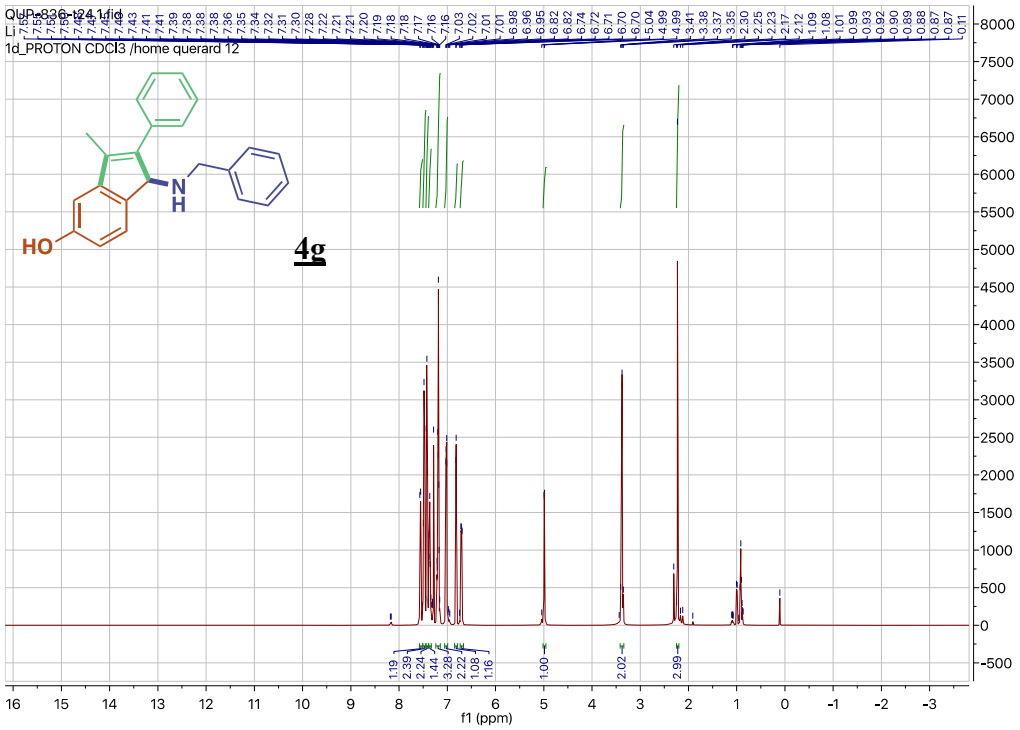
Li
1d_PROTON CDCl3 /home querard 38
4f
f1 (ppm)


QUP-647-t5-1.2.fid
Li
1d_C13 CDCl3 /home querard 38
160.13
147.31
145.22
140.70
136.03
135.75
135.18
128.89
128.58
128.21
128.15
126.97
126.69
123.87
110.53
105.53
65.14
55.56
47.37
11.68
13C NMR (126 MHz, CDCl3) δ 160.13, 147.31, 145.22, 140.70, 136.03, 135.75, 135.18, 128.89, 128.58, 128.21, 128.15, 126.97, 126.69, 123.87, 110.53, 105.53, 65.14, 55.56, 47.37, 11.68.
4f
f1 (ppm)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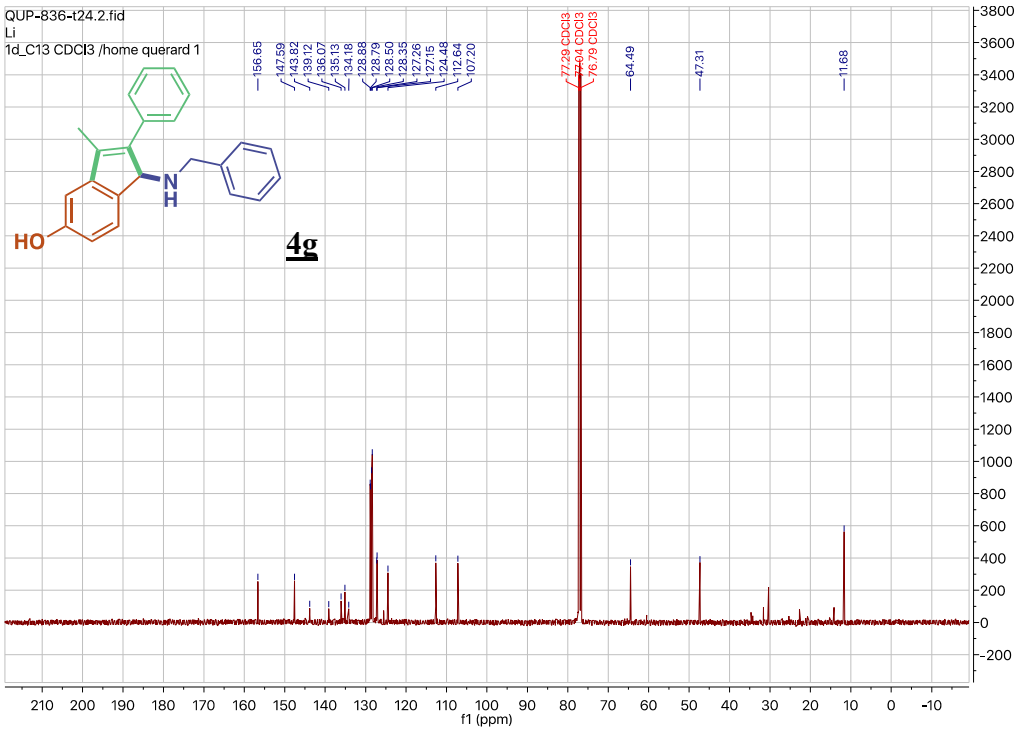
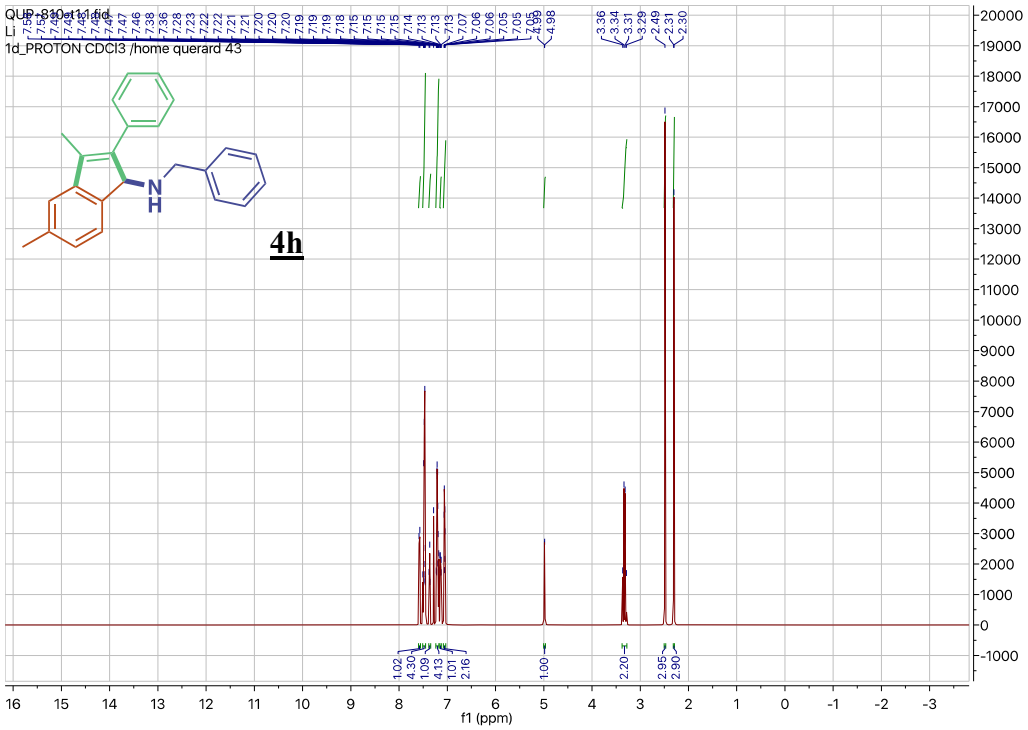
Li
1d_PROTON CDCl3 /home querard 12
HO
N
H
4g
f1 (ppm)


QUP-836-t24.2.fid
Li
1d_C13 CDCl3 /home querard 1
HO
N
H
4g
f1 (ppm)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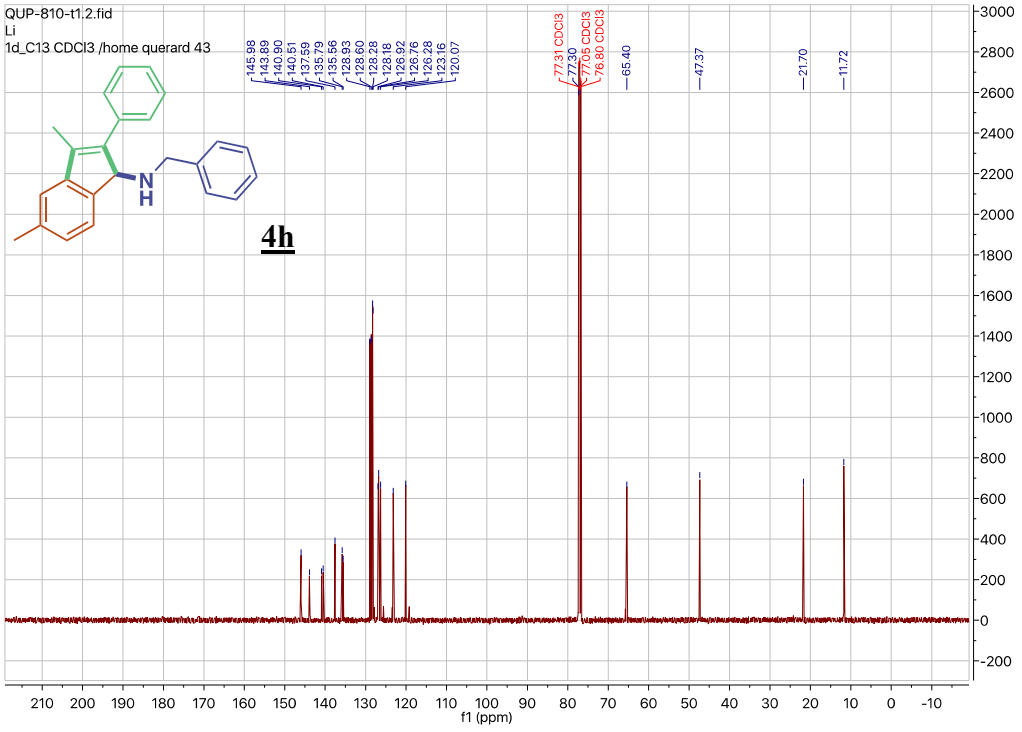
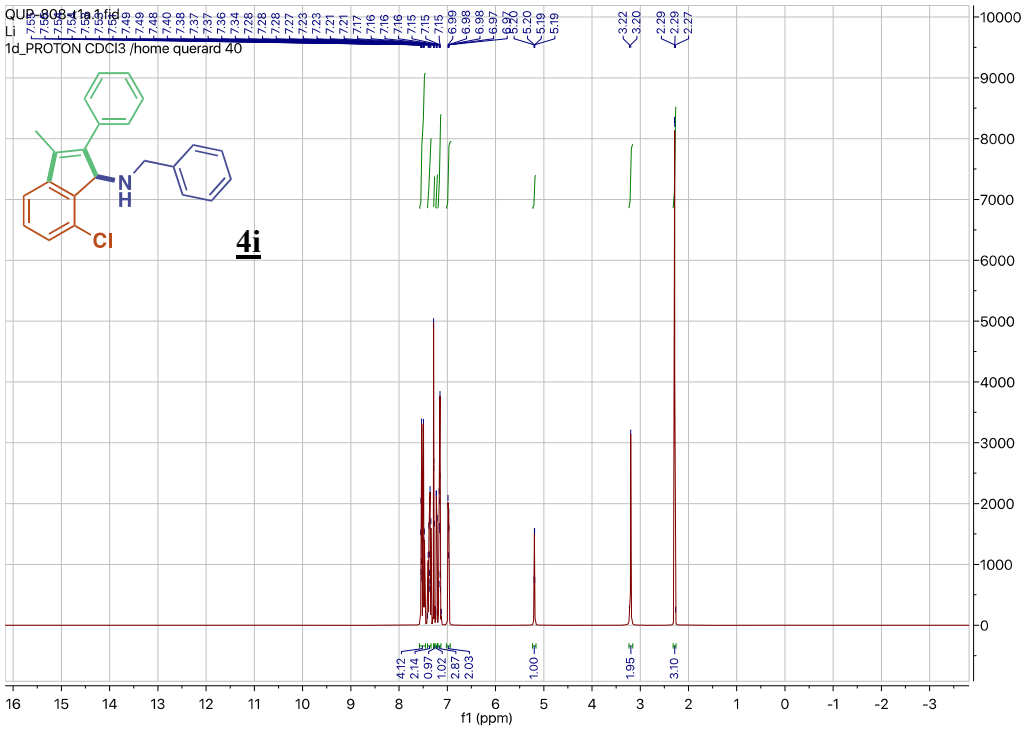
Li
1d_PROTON CDCl3 /home querard 43
4h
f1 (ppm)


QUP-810-t1.2.fid
Li
1d_C13 CDCl3 /home querard 43
4h
77.31 CDCl3
77.00 CDCl3
76.80 CDCl3
f1 (ppm)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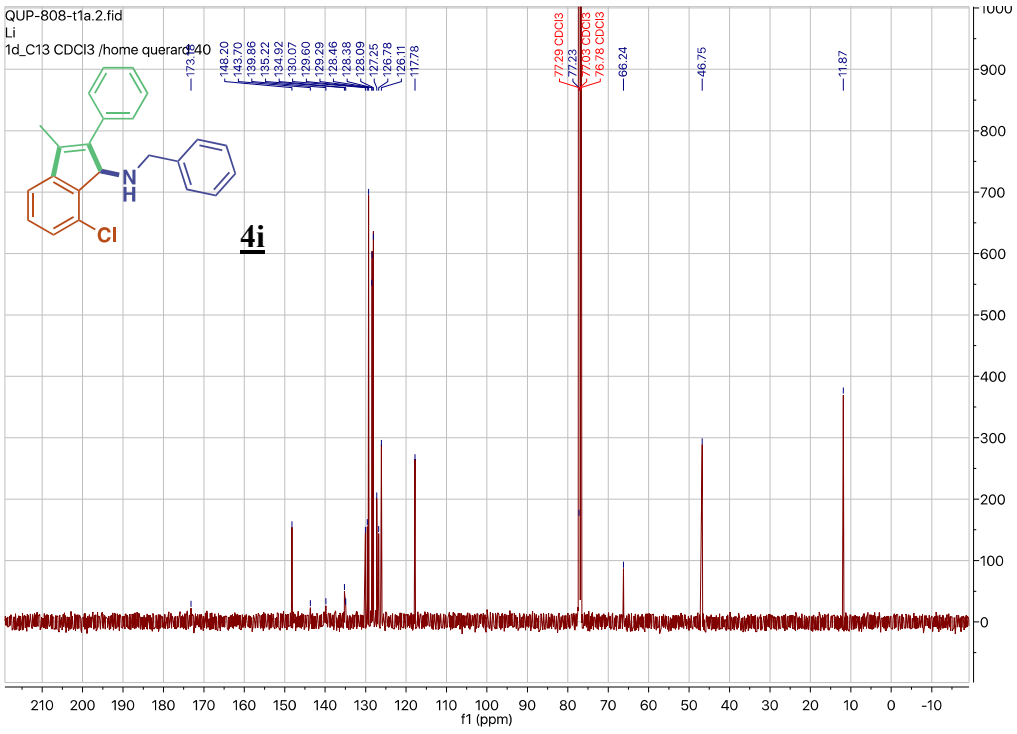
Li
1d_PROTON CDCl3 /home querard 40
Cl
N
H
4i
f1 (ppm)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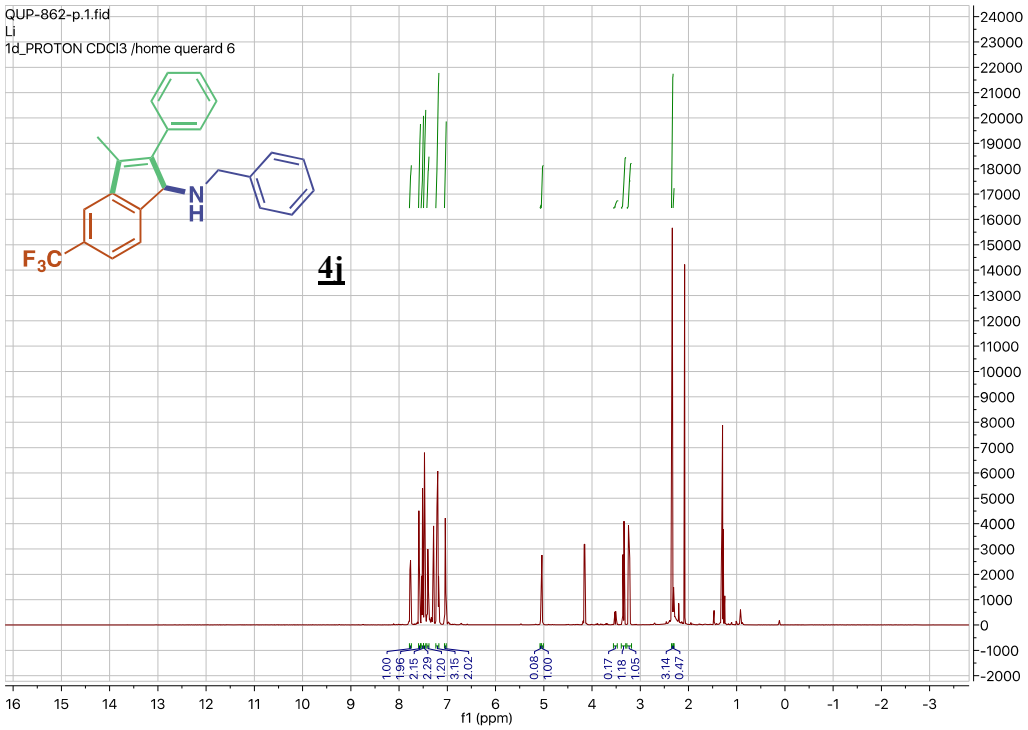
1d_C13 CDCl3 /home querard 40
Cl
N
H
4i
f1 (ppm)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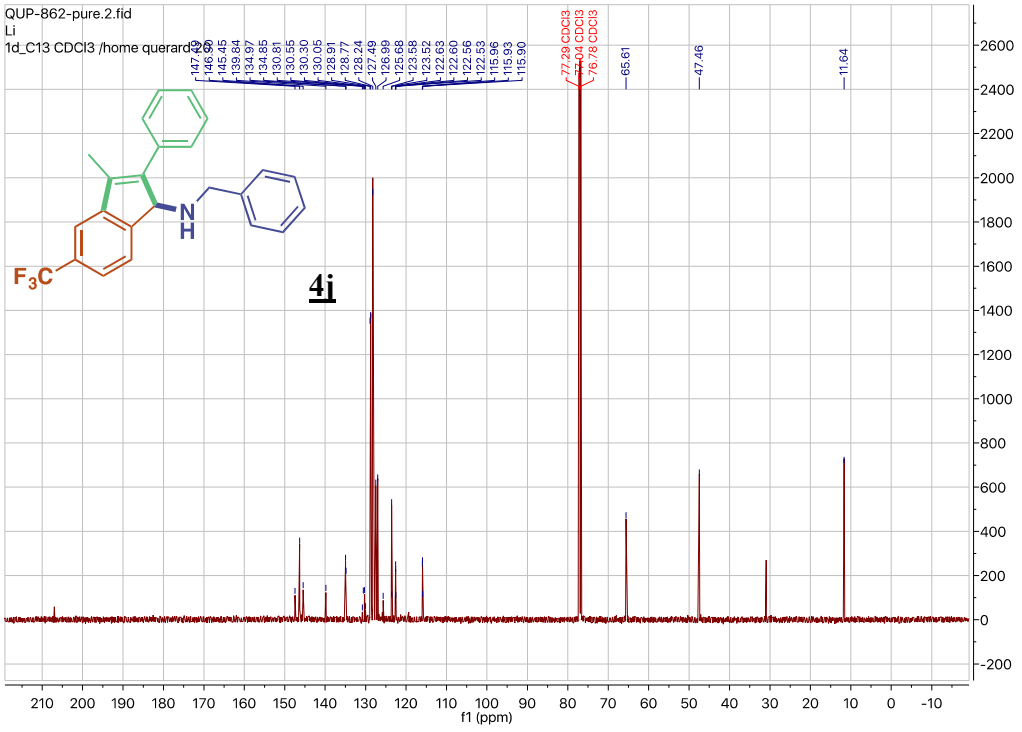
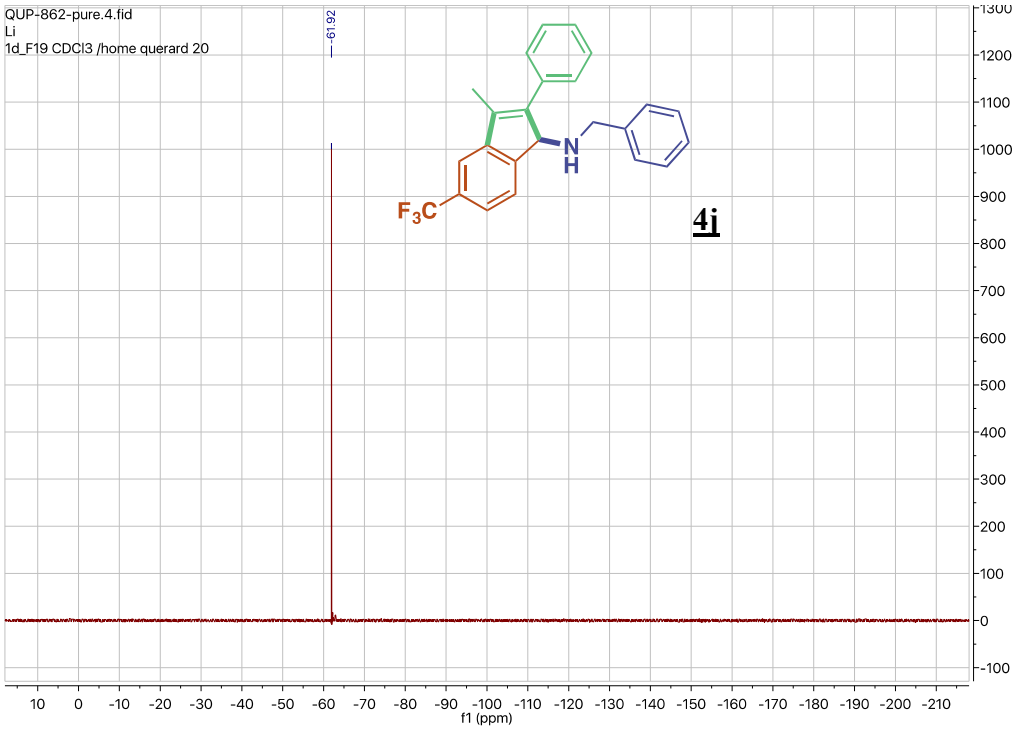
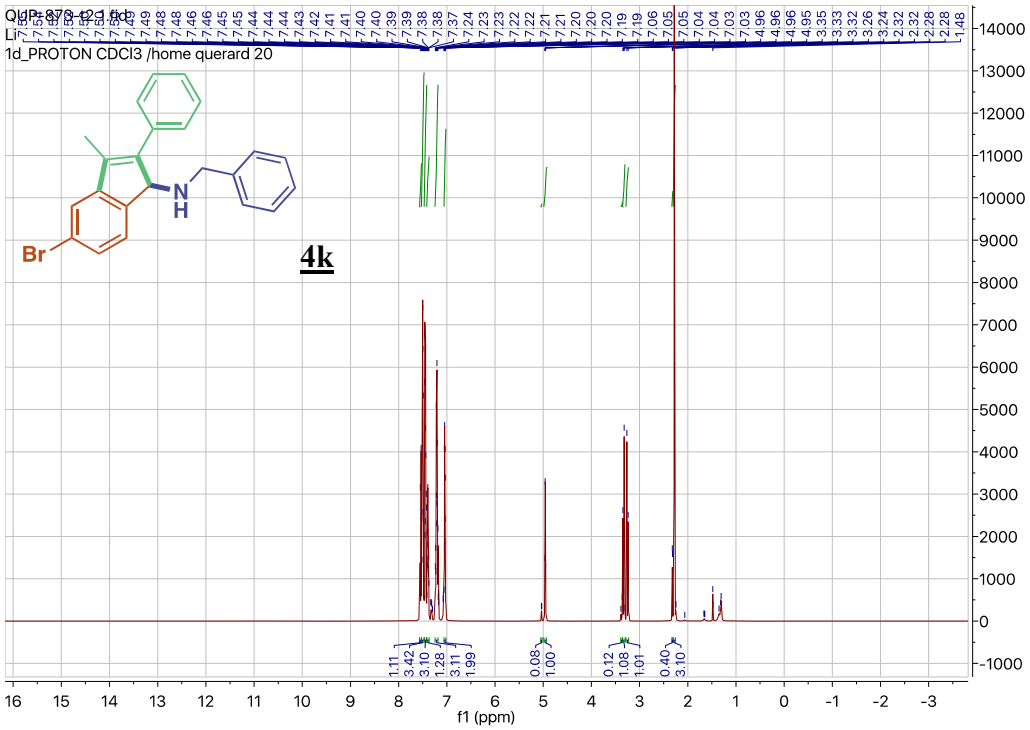
Li
1d_PROTON CDCl3 /home querard 6
4i
f1 (ppm)


QUP-862-pure.2.fid
Li
1d_C13 CDCl3 /home querard 6
4i
77.29 CDCl3
77.04 CDCl3
76.78 CDCl3
65.61
47.46
11.64
f1 (ppm)


QUP-862-pure.4.fid
Li
1d_F19 CDCl3 /home querard 20
-61.92
F3C
N
H
4i
f1 (ppm)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Li
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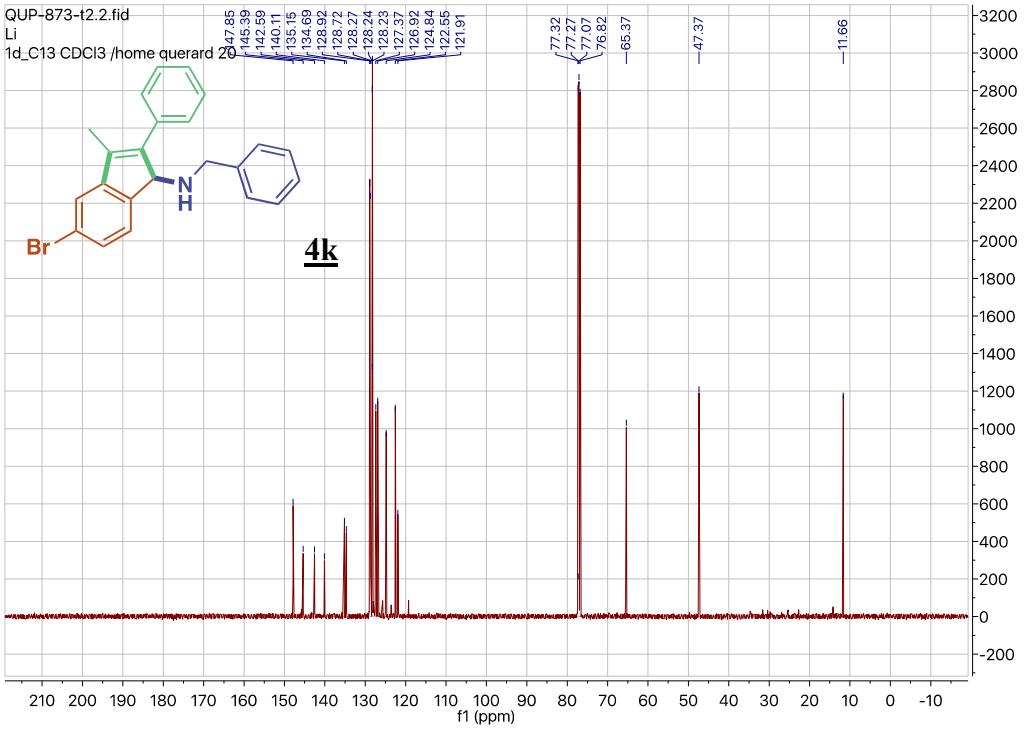
Br
N
H
4k
f1 (ppm)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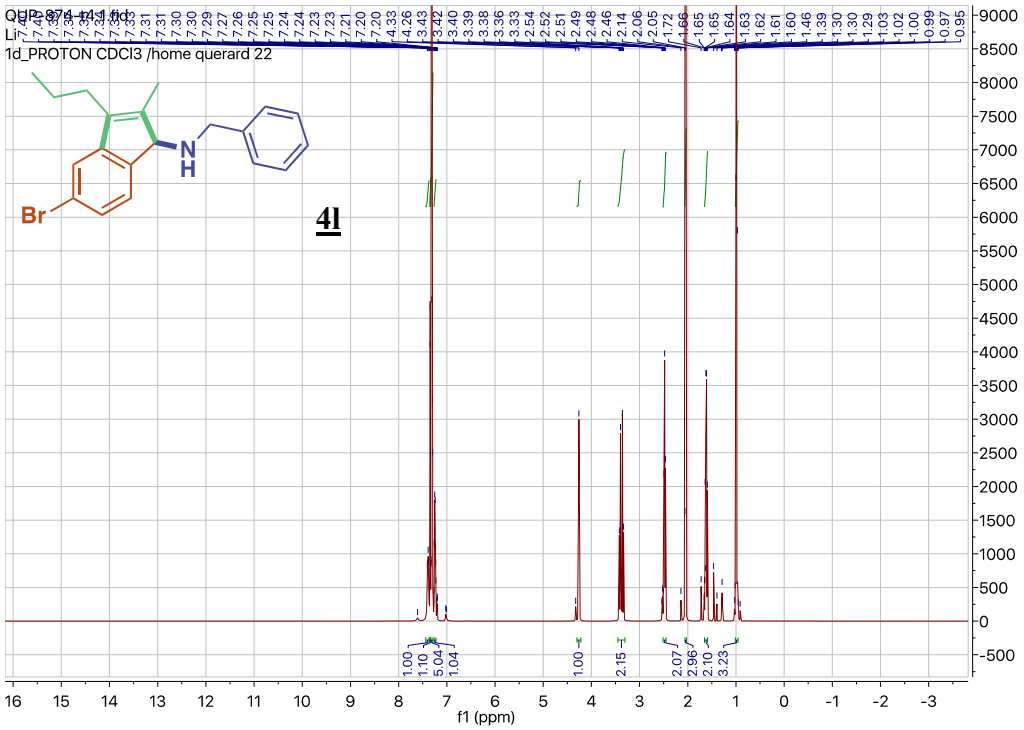
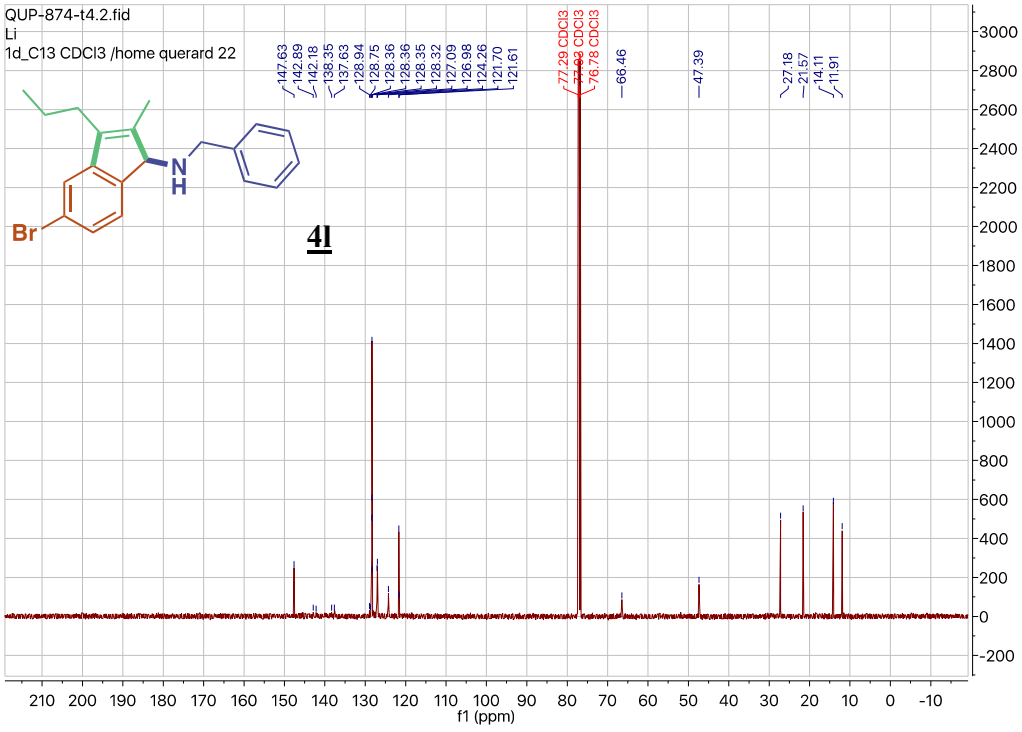
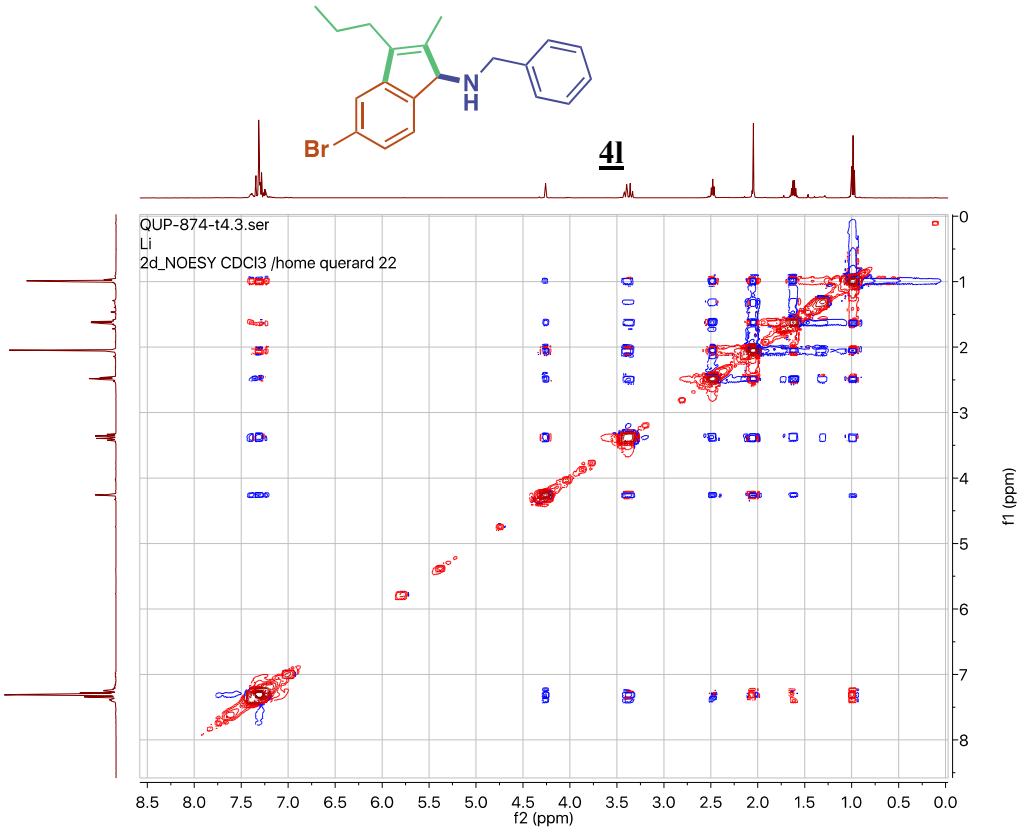
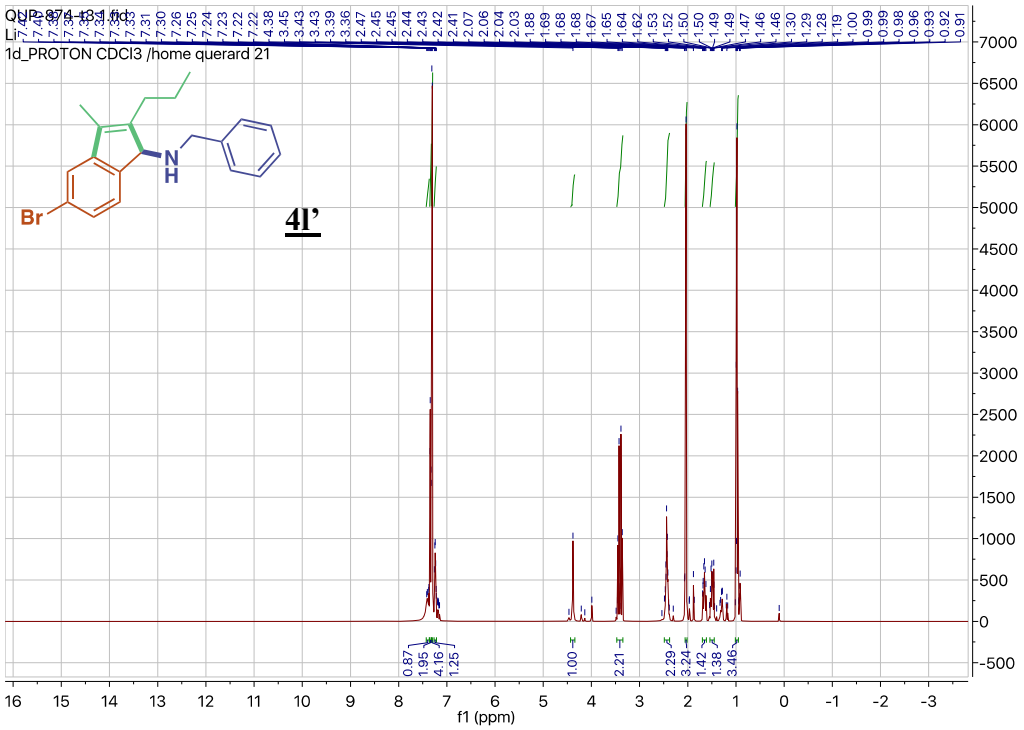
Br
N
H
4k
f1 (ppm)


QUP-874-t4.1.fid
Li
1d_PROTON CDCl3 /home querard 22
Br
N
H
4l
f1 (ppm)


QUP-874-t4.2.fid
Li
1d_C13 CDCl3 /home querard 22
Br
N
H
4l
77.29 CDCl3
76.78 CDCl3
f1 (ppm)


Br
N
H
4l
QUP-874-t4.3.ser
Li
2d_NOESY CDCl3 /home querard 22
f2 (ppm)
f1 (ppm)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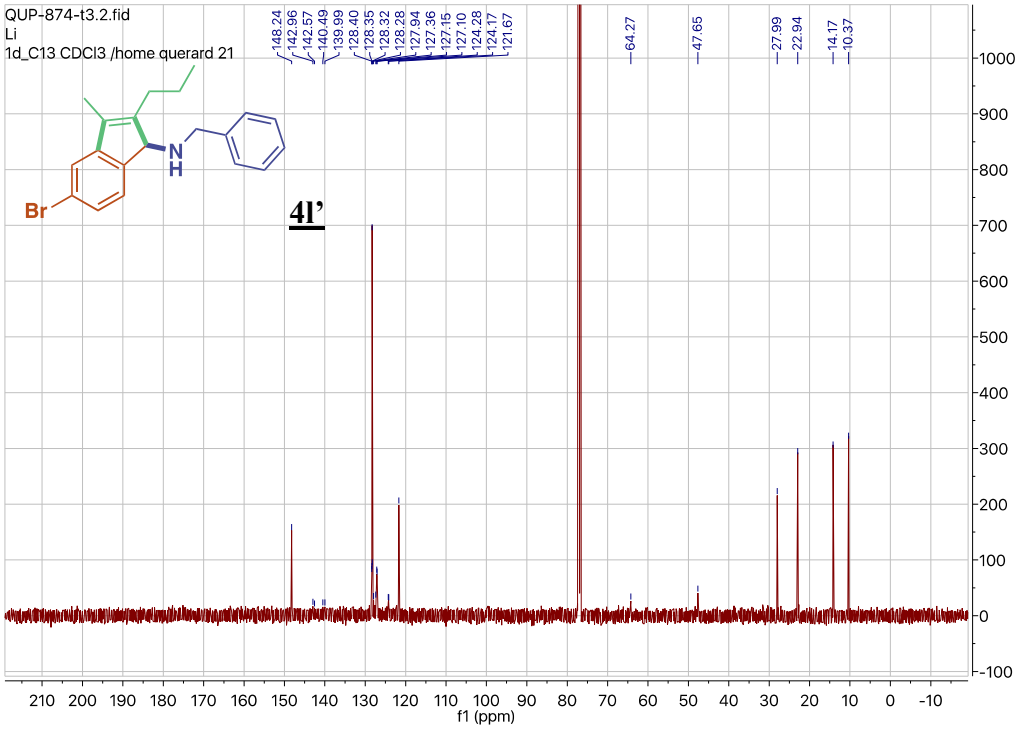
Br
N
H
4l'
f1 (ppm)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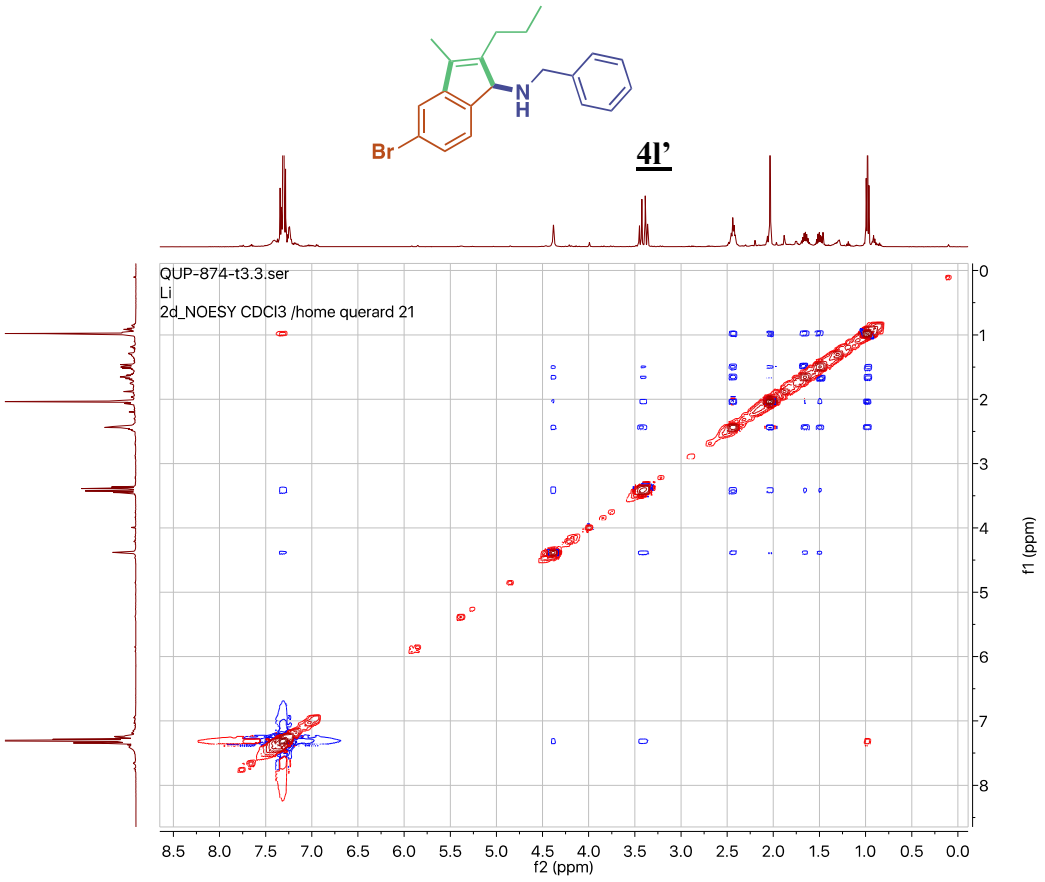
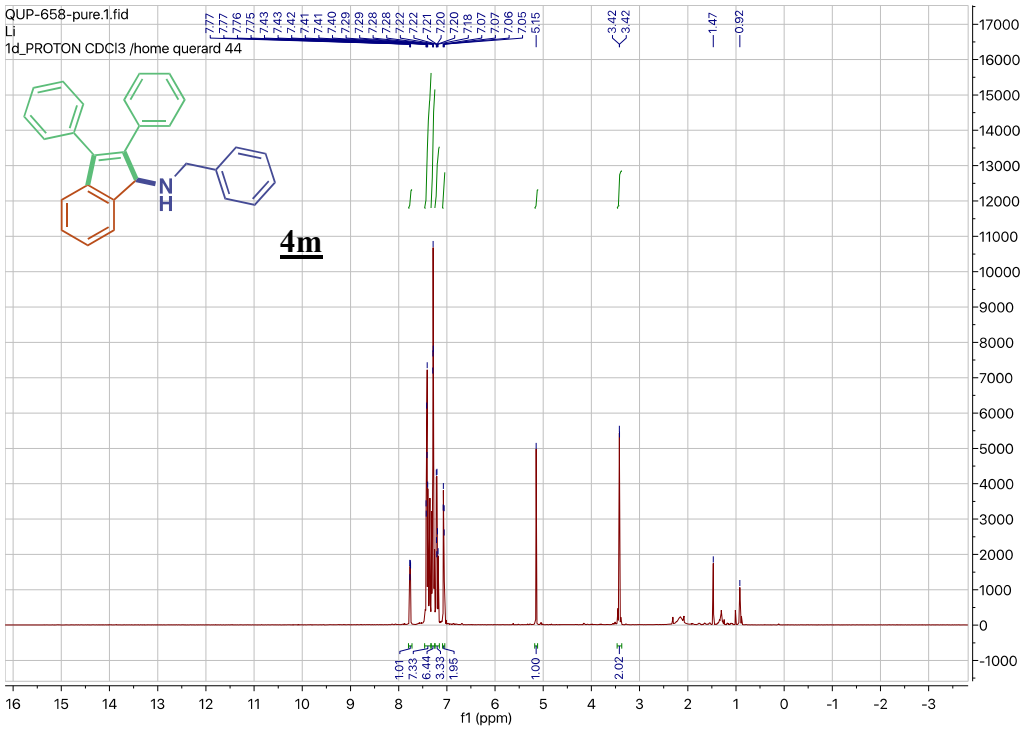
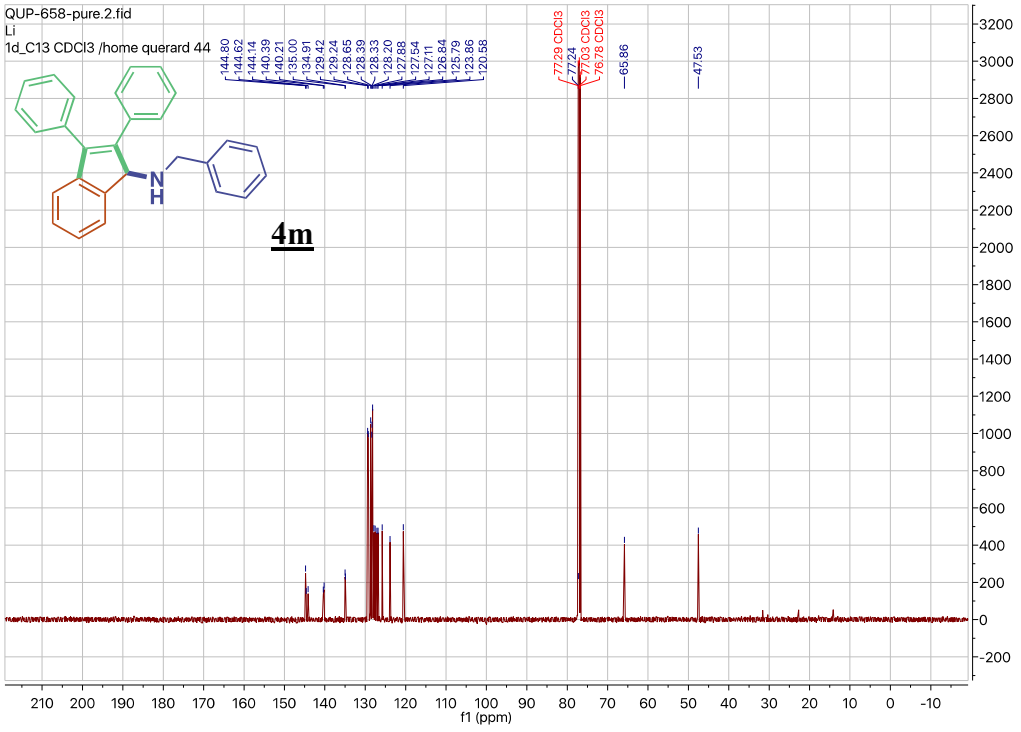
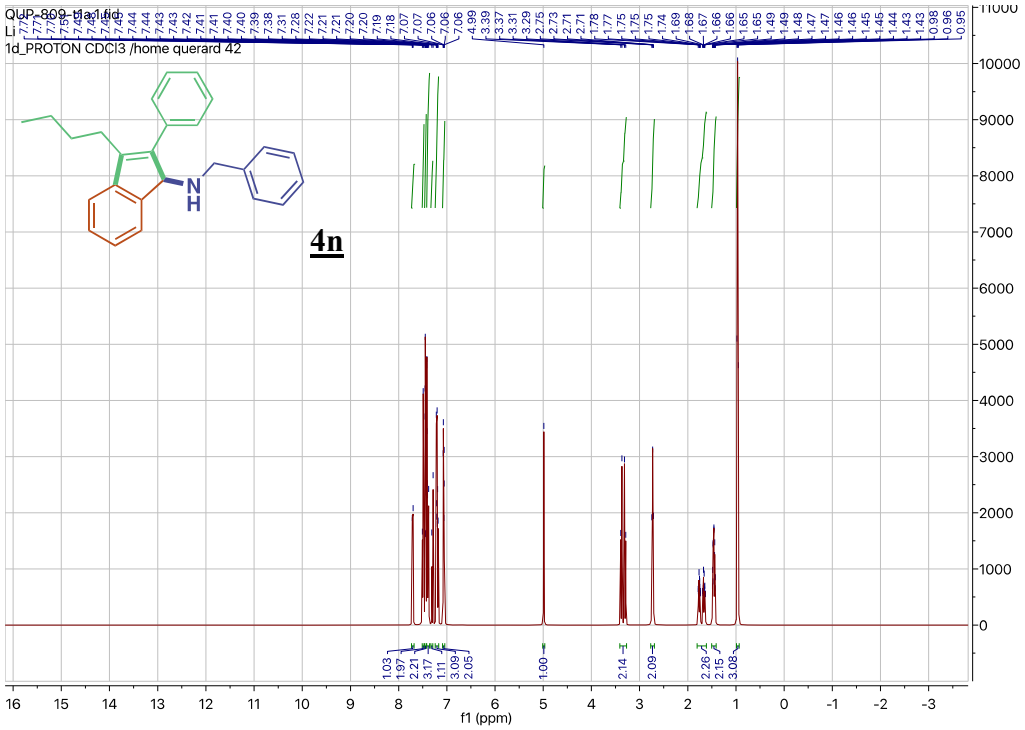
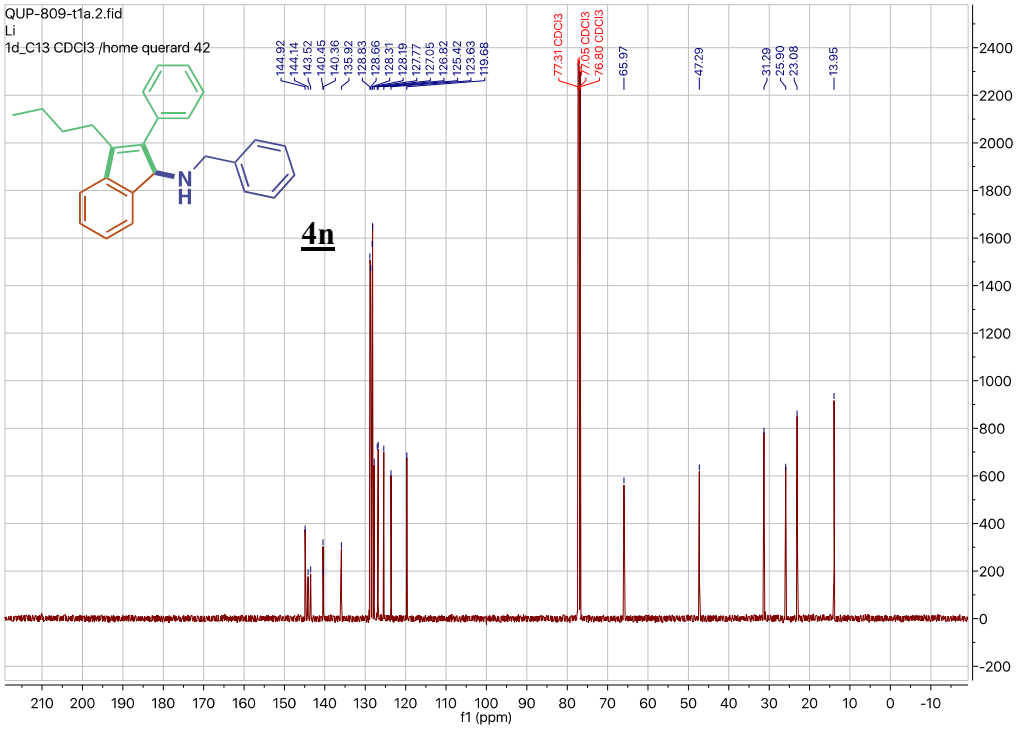
1d_C13 CDCl3 /home querard 21
Br
N
H
4l'
f1 (ppm)


Br
N
H
4l'
QUP-874-t3.3.ser
Li
2d_NOESY CDCl3 /home querard 21
f2 (ppm)
f1 (ppm)


QUP-658-pure.1.fid
Li
1d_PROTON CDCl3 /home querard 44
4m
f1 (ppm)


QUP-658-pure.2.fid
Li
1d_C13 CDCl3 /home querard 44
4m
f1 (ppm)


QUP-809-t1a1.fid
Li
1d_PROTON CDCl3 /home querard 42
4n
f1 (ppm)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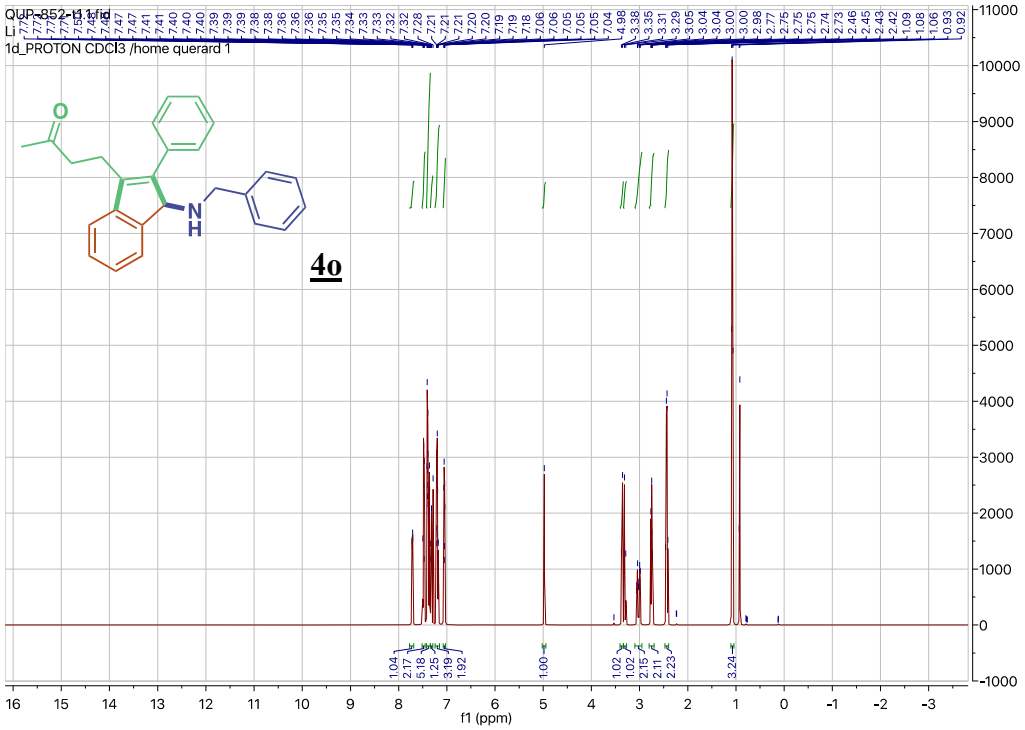
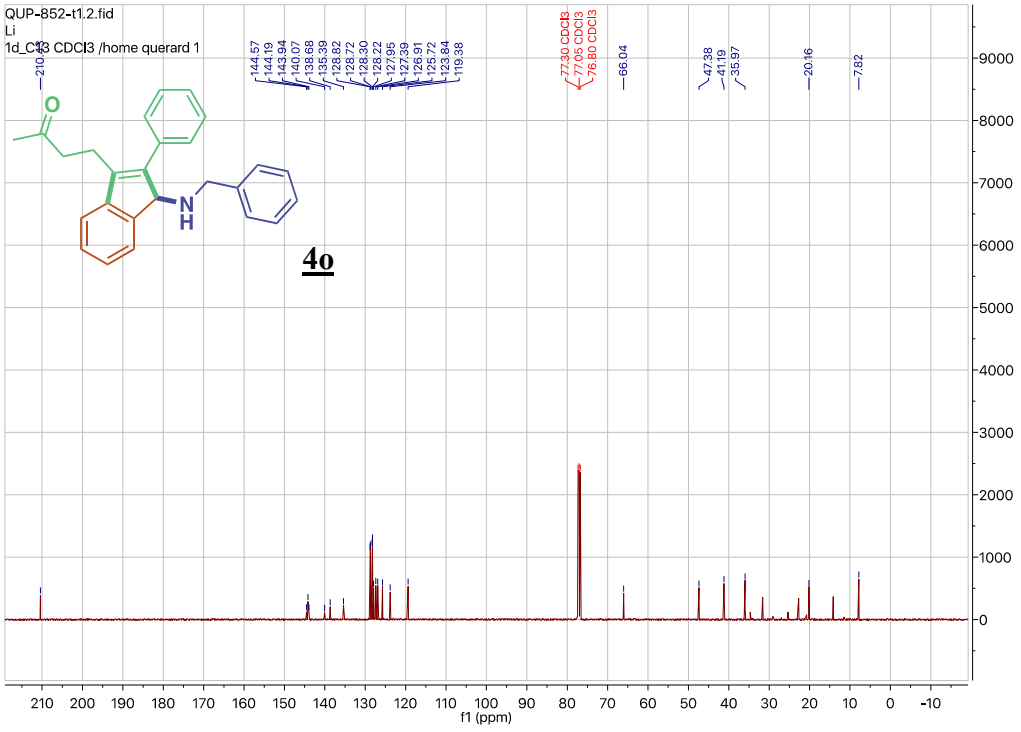
1d_C13 CDCl3 /home querard 42
4n
f1 (ppm)


QUP-852-t1.fid
Li
1d_PROTON CDCl3 /home querard 1
4o
f1 (ppm)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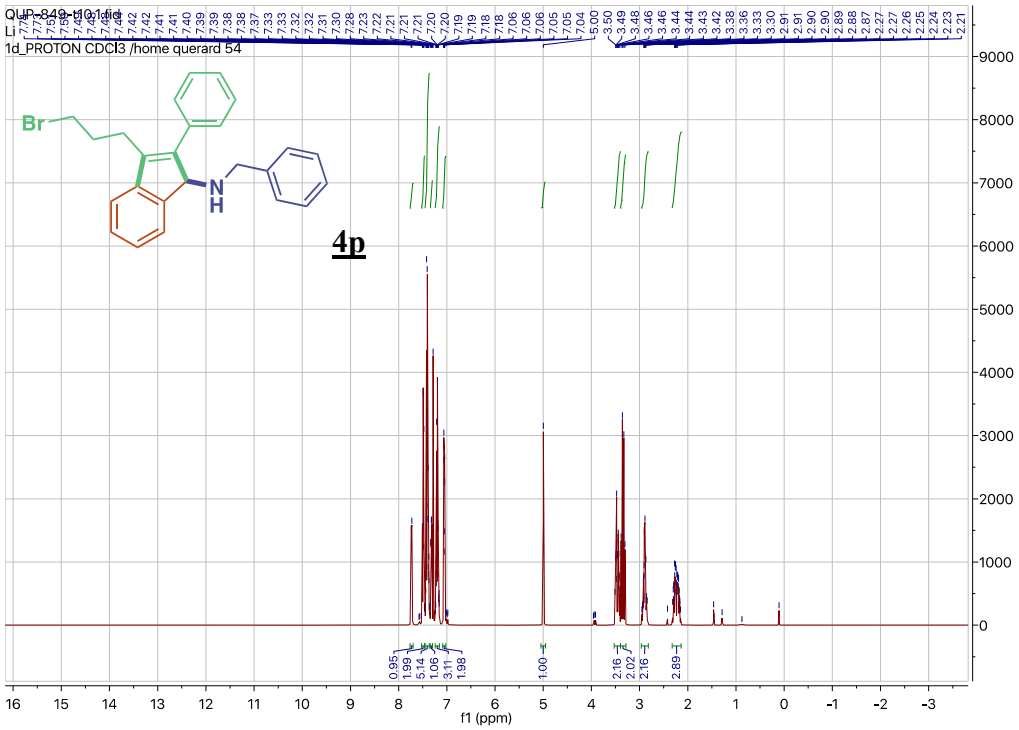
Li
1d_C13 CDCl3 /home querard 1
4o
f1 (ppm)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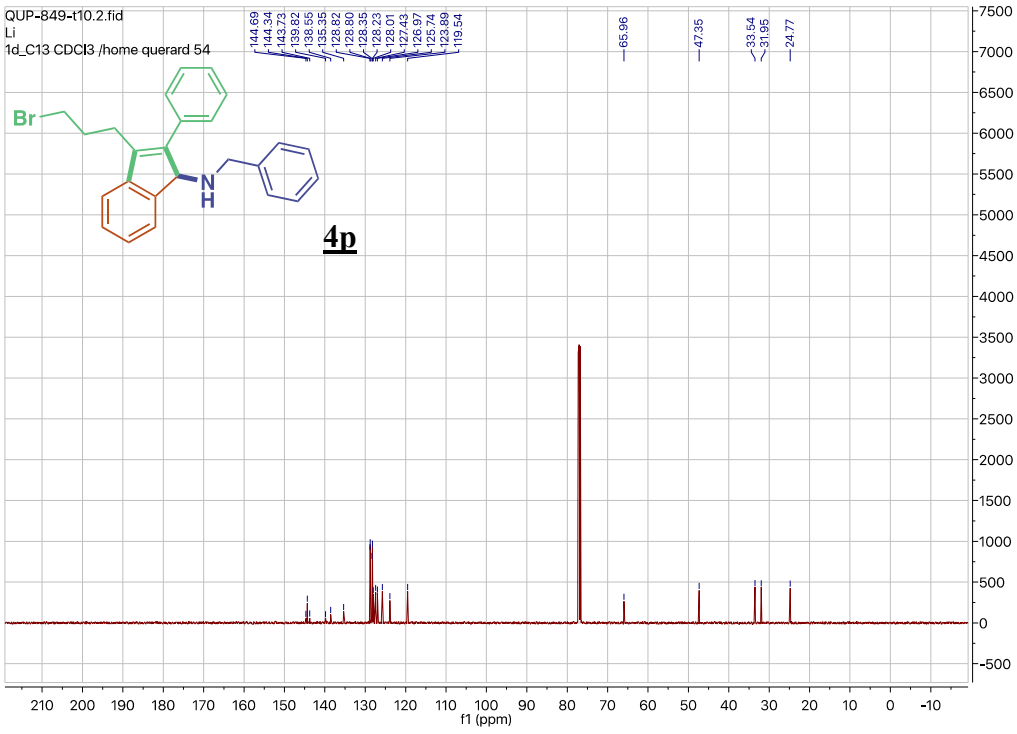
Li
1d_PROTON CDCl3 /home querard 54
Br
N
H
4p
f1 (ppm)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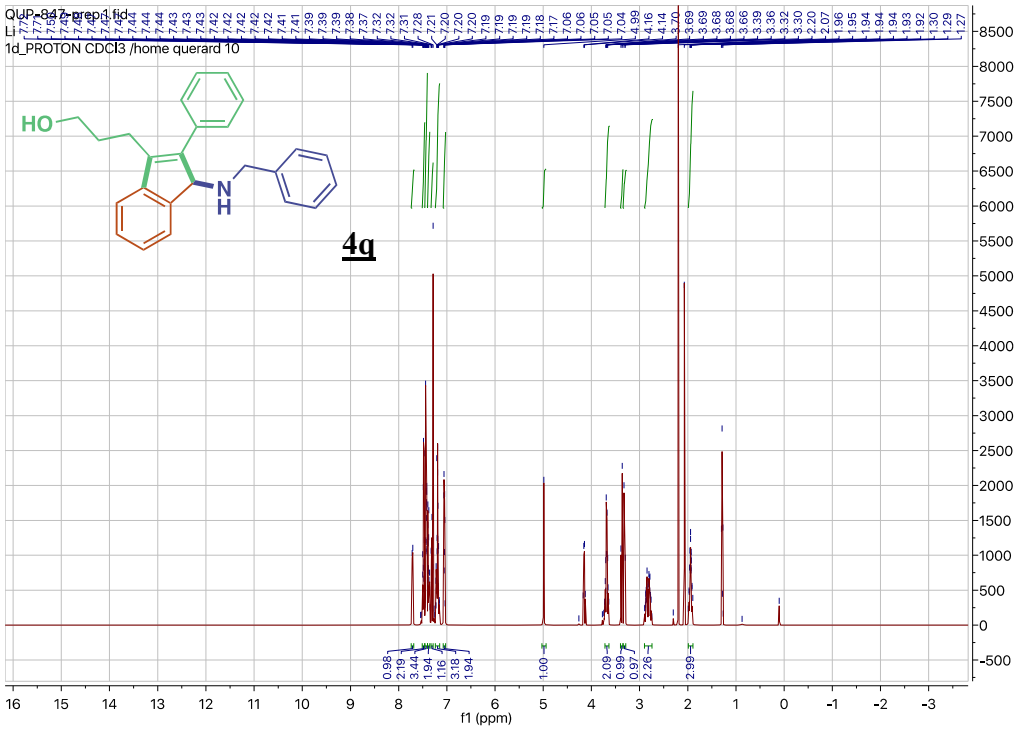
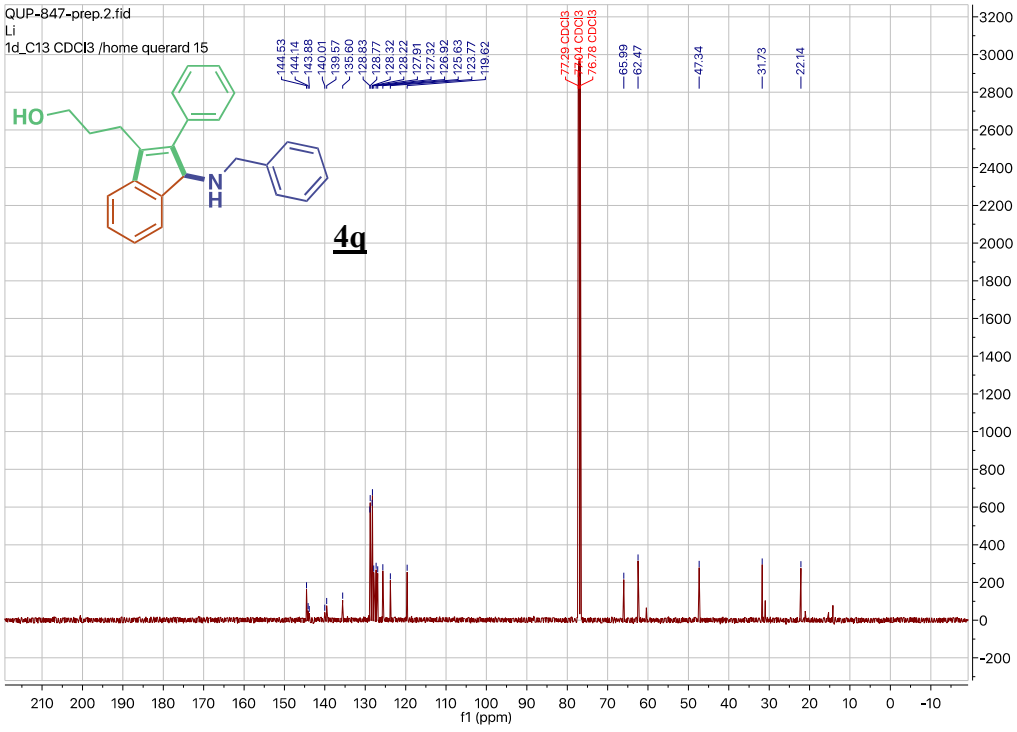
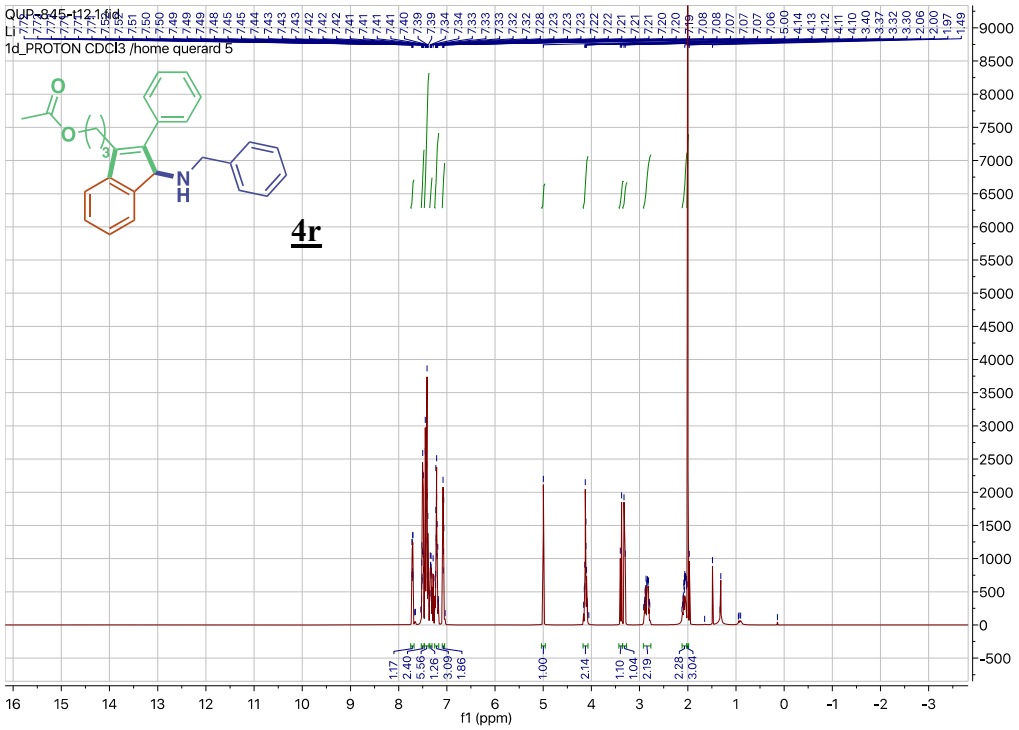
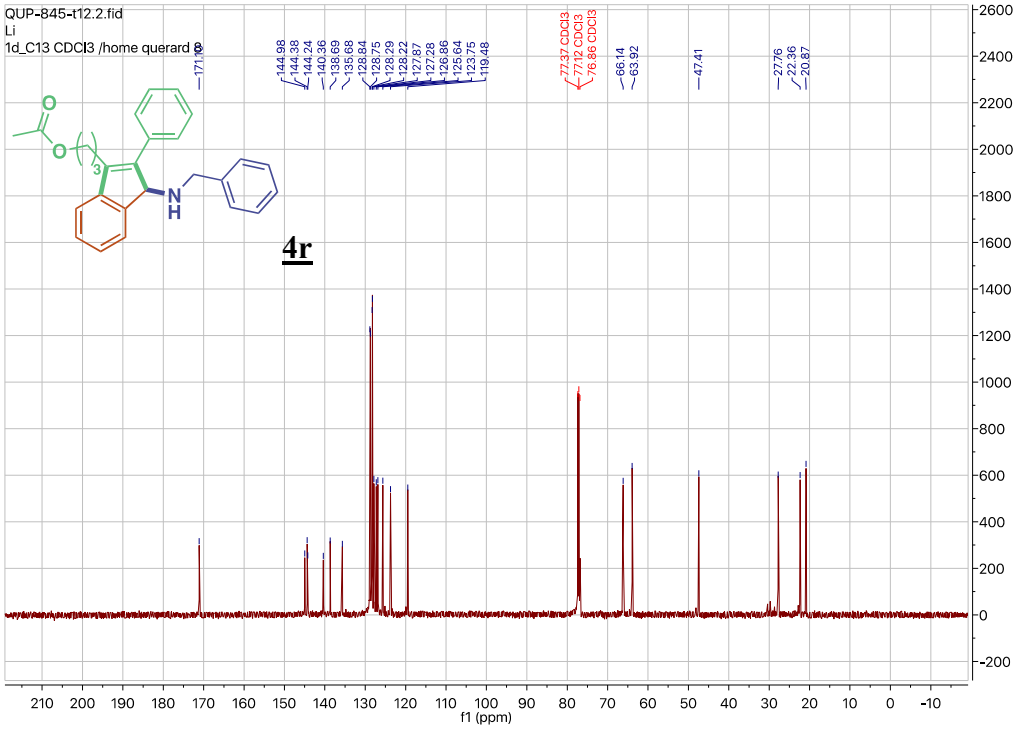
Li
1d_C13 CDCl3 /home querard 54
Br
N
H
4p
f1 (ppm)


QUP-847-prep1.fid
Li
1d_PROTON CDCl3 /home querard 10
HO
N
H
4q
f1 (ppm)


QUP-847-prep.2.fid
Li
1d_C13 CDCl3 /home querard 15
HO
N
H
4q
f1 (ppm)


QUP-845-t12.1.fid
Li
1d_PROTON CDCl3 /home querard 5
4r
f1 (ppm)


QUP-845-t12.2.fid
Li
1d_C13 CDCl3 /home querard 5
4r
77.37 CDCl3
77.12 CDCl3
76.86 CDCl3
f1 (ppm)

6) References

[1] $Cp^*Rh(SbF_6)_2(MeCN)_3$ was synthesized following the literature procedure: Li, Y.; Li, B.-J.; Wang, W.-H.; Huang, W.-P.; Zhang, X.-S.; Chen, K.; Shi, Z.-J., *Angew. Chem. Int. Ed.* 2011**, 50**, 2115.

[2] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.