Supplementary Information

An entry to 2-(cyclobut-1-en-1-yl)-1*H*-indoles through a cyclobutenylation/deprotection cascade

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1. General Information

Solvents, Reagents & Reactions

Chemical symbols have their usual meaning. SI units and their respective standard symbols are used. Evaporation of solvent was achieved using a Büchi B-481 rotary evaporator under reduced pressure (0 – 1000 mbar) with a bath temperature of 30 °C. Dry dichloromethane (99.9%, extra dry over molecular sieves) and dry diethyl ether (99.9%, extra dry over molecular sieves) were acquired from Acros Organics™ and used without further purification. Reagents were obtained from commercial suppliers and used as received, unless otherwise stated. Reactions were performed in cooled oven-dried glassware (dried at 130 °C for 12 hrs) under a nitrogen atmosphere using standard Schlenk techniques. *n*-Butyllithium was titrated against diphenylacetic acid before use.

Chromatography

Thin layer chromatography (TLC) was conducted on aluminium-backed silica plates precoated with fluorescent indicator (60 F_{254} Merck), and visualized using a Mineralight lamp Multiband UV 254/365 nm and stained with vanillin solution. Flash column chromatography was performed using silica gel (40 – 63 μm, VWR Chemicals) using head pressure achieved by the use of head bellows. All solvents used for chromatography were acquired from commercial suppliers and used as received.

Analysis, Spectroscopy and Spectrometry of compounds

Nuclear magnetic resonance spectra (NMR) were recorded on a Bruker AV-400 (400 MHz for ^{1}H-NMR, 101 MHz for ^{13}C{^{1}H}-NMR and 377 MHz for ^{19}F-NMR) or a Bruker AV-500 (500 MHz for ^{1}H-NMR and 125 MHz for ^{13}C{^{1}H}-NMR) at ambient temperature and referenced to the non-deuterated residual solvent peak. Chemical shifts are reported in parts per million (ppm) and reported to two decimal places for proton shifts, and one decimal place for carbon shifts. Multiplicity of spectral peaks is assigned as follows: singlet (s), doublet (d), triplet (t), quartet (q), pentet (p) or multiplet (m), and combinations thereof. Coupling constants (*J*) are reported to the nearest 0.1 Hz.

Infrared spectra were recorded using an Agilent Cary 630 Fourier Transform Infrared Spectrometer. Samples were loaded neat and absorption frequencies are recorded in cm^{-1}.

Mass spectra were recorded by Imperial College Mass Spectrometry Service using Micromass AutoSpec Premier or Waters LCT Premier instruments and ionized by means of electrospray ionisation (ES), electron ionisation (EI) or atmospheric pressure chemical ionisation (APCI).

Melting points were recorded on an SRS MPA100 Optimelt system and are uncorrected.

2. Reaction Condition Optimisation

Entry	Stoichiometry (ArLi:cyclobutanone)	Base	Temperature (°C)	Deprotonation time (min)	Solvent	Concentration (M)	Protecting group	Yield[a] (%)
Stoichiometry Optimisation								
1	1:1	*n*-BuLi	–78 °C to rt	60	Et_2O	0.25	Boc	20
2	1.5:1	*n*-BuLi	–78 °C to rt	60	Et_2O	0.25	Boc	14
3	2:1	*n*-BuLi	–78 °C to rt	60	Et_2O	0.25	Boc	53
4	3:1	*n*-BuLi	–78 °C to rt	60	Et_2O	0.25	Boc	31
5	1:2	*n*-BuLi	–78 °C to rt	60	Et_2O	0.25	Boc	--
Substrate Concentration Optimisation								
6	2:1	*n*-BuLi	–78 °C to rt	60	Et_2O	0.5	Boc	25
7	2:1	*n*-BuLi	–78 °C to rt	60	Et_2O	1.0	Boc	35
Base Optimisation								
8	2:1	*sec*-BuLi	–78 °C to rt	60	Et_2O	0.25	Boc	23
9	2:1	*tert*-BuLi	–78 °C to rt	60	Et_2O	0.25	Boc	15
10	1:1	LDA	–78 °C to rt	60	THF	0.25	Boc	--
11	2:1	TMPMg.LiCl	–78 °C to rt	60	Et_2O	0.25	Boc	--
12	2:1	*n*-BuLi	–78 °C to rt	10	Et_2O	0.25	Boc	22
Deprotonation Temperature Optimisation								
13	2:1	*n*-BuLi	–40 °C to rt	60	Et_2O	0.25	Boc	16
14	2:1	*n*-BuLi	–78 °C to rt (deprotonation at rt)	60	Et_2O	0.25	Boc	--
Solvent Optimisation								
15	2:1	*n*-BuLi	–78 °C to rt	60	Pentane	0.25	Boc	--
16	2:1	*n*-BuLi	–78 °C to rt	60	*t*BuOMe	0.25	Boc	22
17	2:1	*n*-BuLi	–78 °C to rt	60	Toluene	0.25	Boc	--
Protecting Group Optimisation								
18	2:1	*n*-BuLi	–78 °C to rt	60	Et_2O	0.25	Cbz	--
19	2:1	*n*-BuLi	–78 °C to rt	60	Et_2O	0.25	CO_2Et	--
20	2:1	*n*-BuLi	–78 °C to rt	60	Et_2O	0.25	Tosyl	--
21	2:1	*n*-BuLi	–78 °C to rt	60	Et_2O	0.25	Me	--

Table 1: Summary of reaction optimisation experiments

[a] Yield determined by ^1H NMR spectroscopic analysis of the reaction mixture post-workup using 1,4-dinitrobenzene as an internal standard

3. Deuterium Studies

Experimental

To a solution of *N*-boc protected indole (217 mg, 1.00 mmol) in diethyl ether (4 mL, 0.25 M) cooled to –78 °C was added *n*-butyllithium solution (2.3 M in hexanes, 0.48 mL, 1.1 mmol) as drops and the resulting reaction mixture was allowed to stir at –78 °C. Aliquots (0.2 mL) were removed at different timepoints (30 mins, 1 hour, 1.5 hours, 2 hours) and quenched with deuterium oxide (0.7 mL), before the aqueous phase was extracted with diethyl ether. The organic extract was concentrated under reduced pressure to afford the crude mixture, which was investigated spectroscopically.

Peak integrations of H2 (7.60 ppm) and an indole proton (7.67 ppm)[1] were referenced against H4 (7.57 ppm). Relative integration of the peaks associated to H2, and the proton of deprotected indole gave an indication of the extent of C2-deprotonation and Boc-group deprotection, respectively.

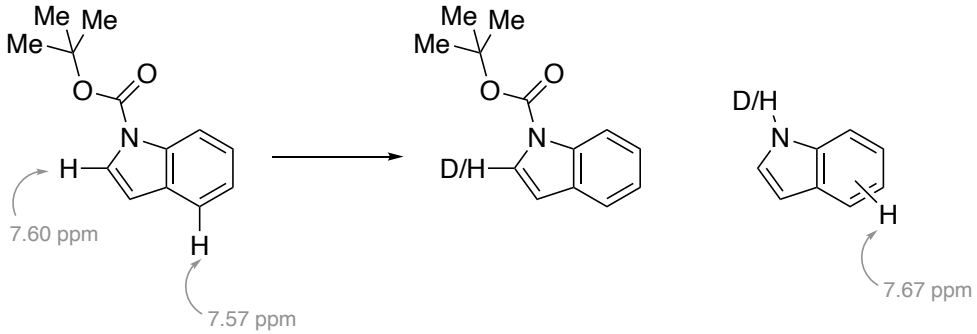
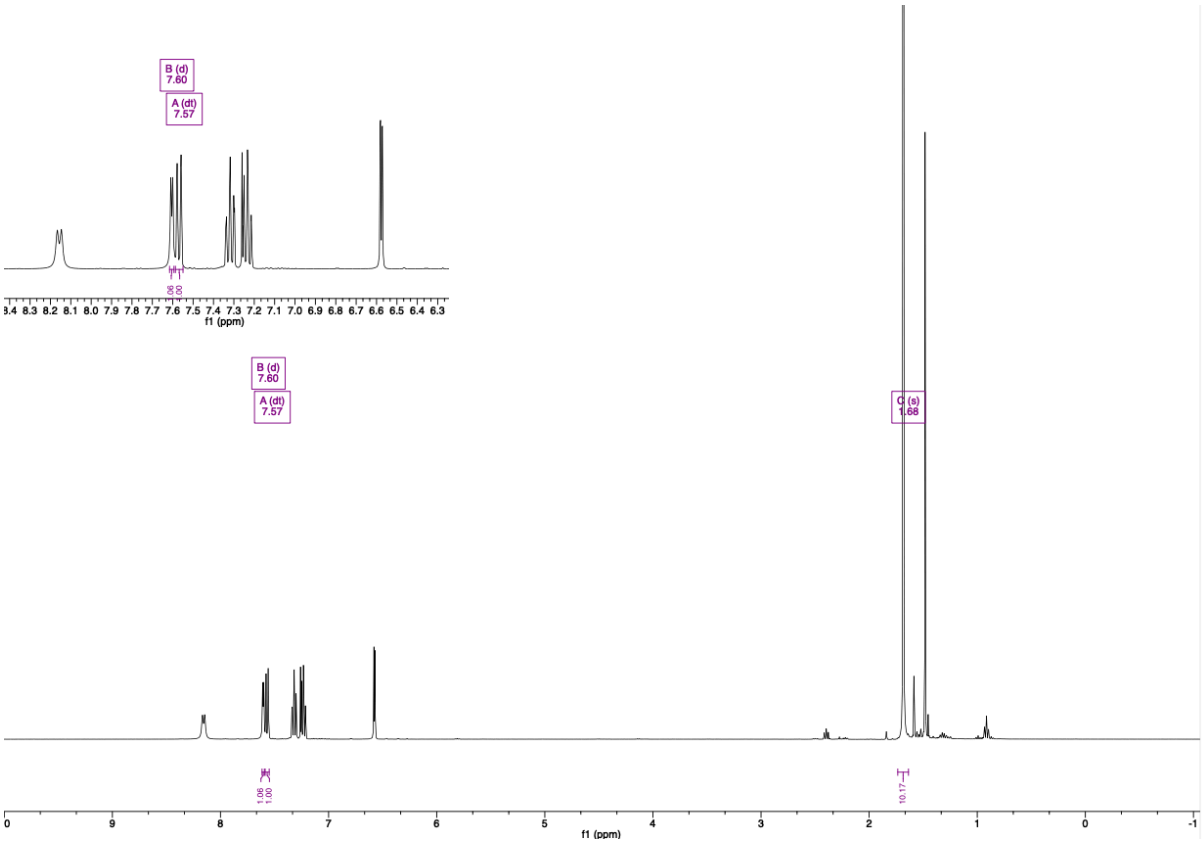


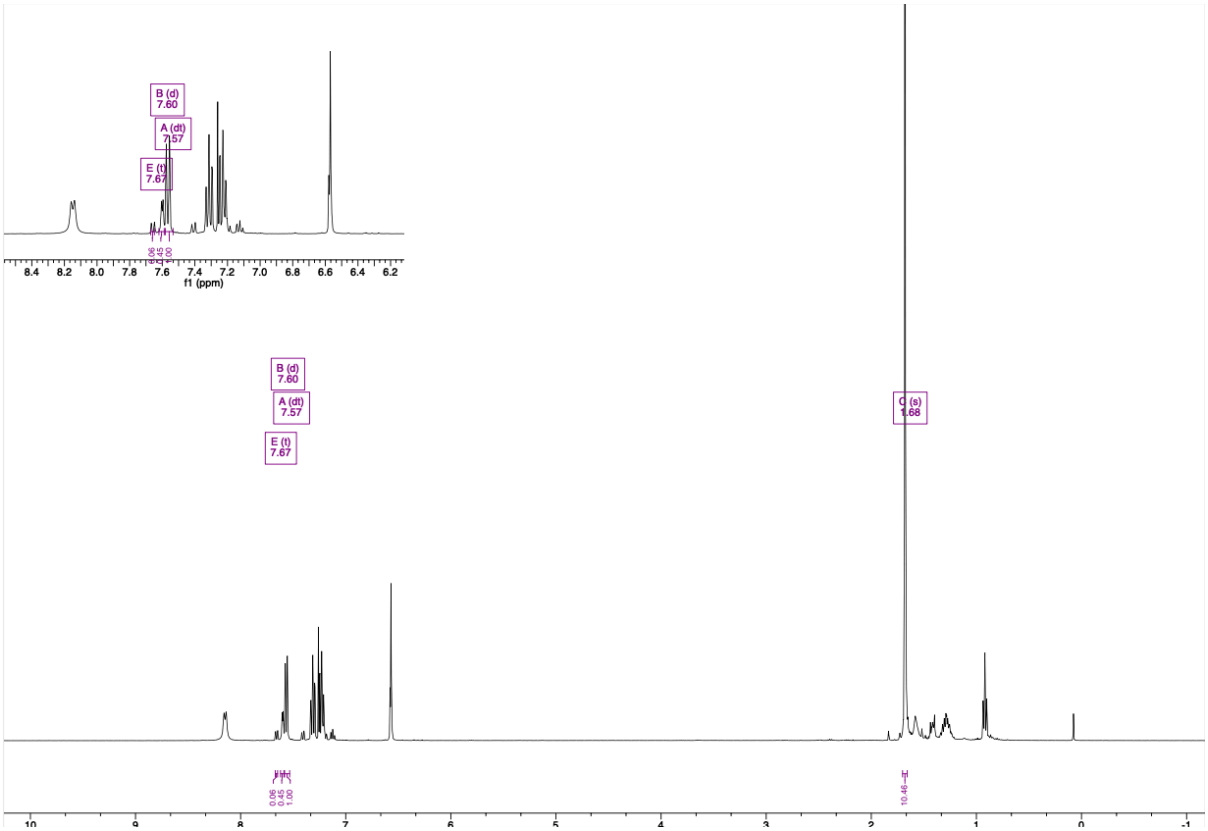
Table 2: Relative integrations of H2 (7.60 ppm) and indole proton (7.67 ppm) *vs* H4 (7.57 ppm).

Time Point [hrs]	Reference integration of H4 of Boc-indole (7.57 ppm)	Relative integration of H2 of Boc-indole (7.60 ppm)	Relative integration of indole proton (7.67 ppm)
0	1.00	1.06	0.00
0.5	1.00	0.45	0.06
1	1.00	0.42	0.10
1.5	1.00	0.43	0.12
2	1.00	0.50	0.09

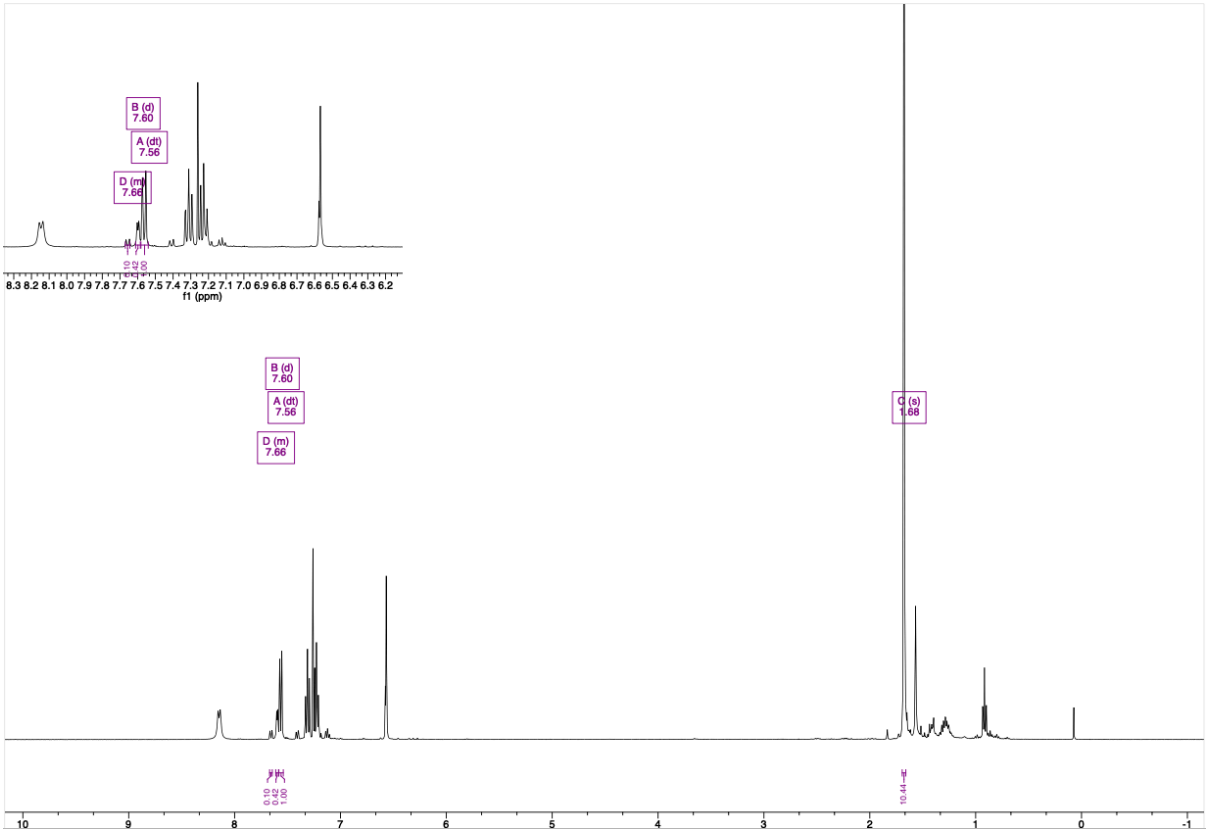
Time point: 0 hours



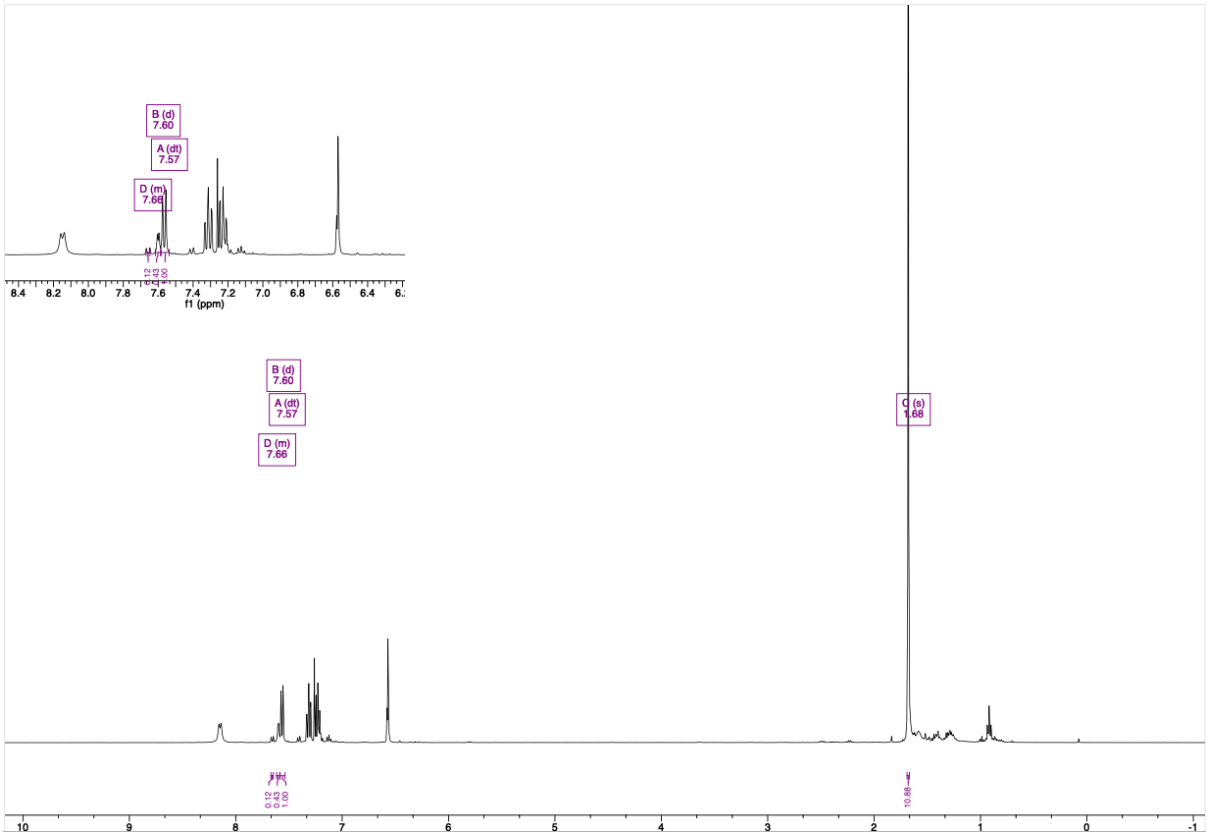
Time point: 0.5 hours after addition of *n*-BuLi



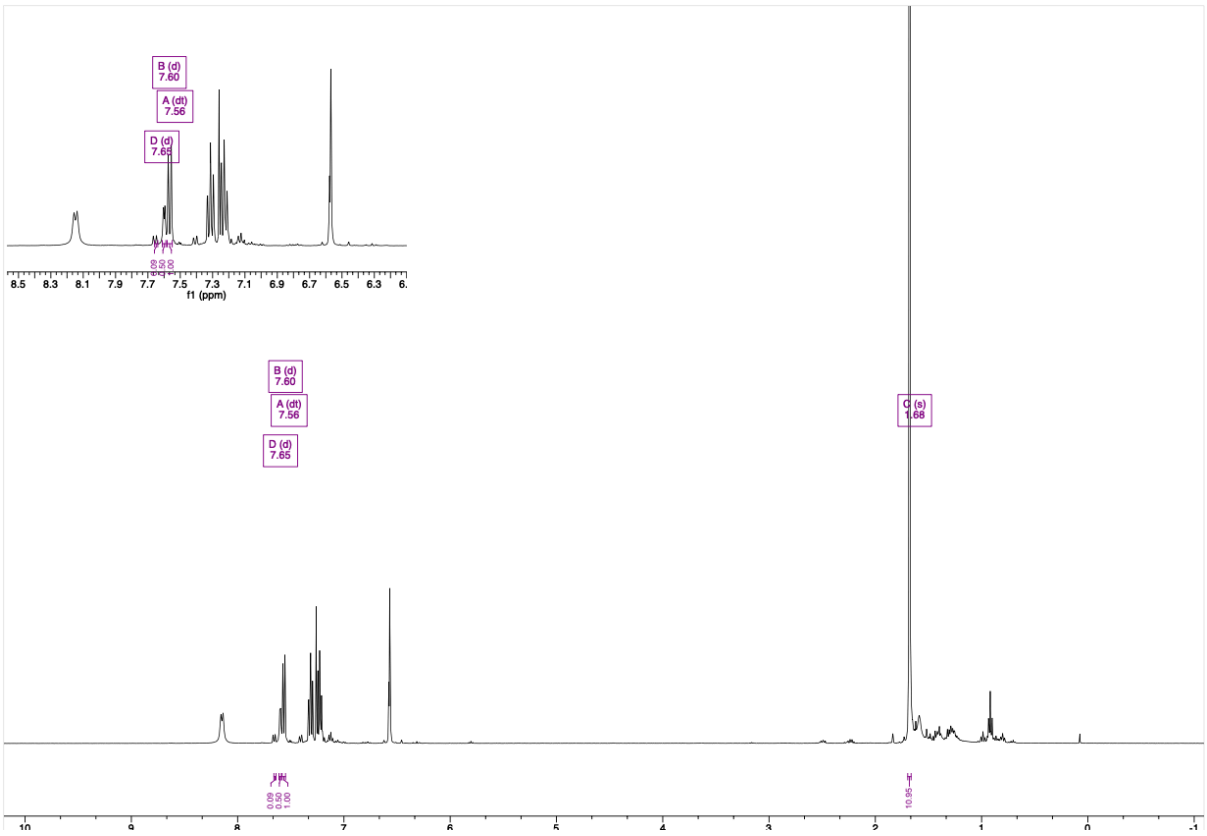
Time point: 1 hour after addition of *n*-BuLi



Time point: 1.5 hours after addition of *n*-BuLi

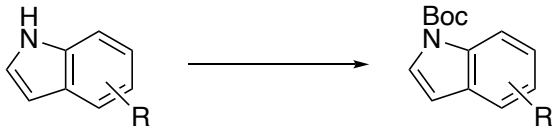


Time point: 2 hours after addition of *n*-BuLi



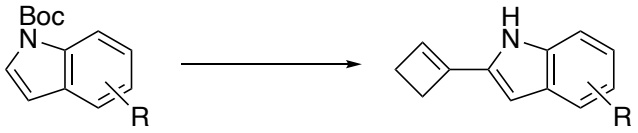
4. General Experimental Procedures

4.1. General procedure A for the synthesis of *N*-boc protected indoles



To a solution of functionalised indole (1 equiv.) in dichloromethane (0.4 M) at room temperature were added 4-dimethylaminopyridine (0.1 equiv.) and di-*tert*-butyl dicarbonate (1.1 equiv.) in sequence. The resulting reaction mixture was allowed to stir at room temperature for 14 hours. Upon completion, the reaction mixture was diluted with dichloromethane and subsequently washed with saturated aqueous sodium chloride solution, saturated aqueous citric acid solution and again with saturated aqueous sodium chloride solution. The organic layer was then dried over magnesium sulfate, filtered, and concentrated under reduced pressure to yield the desired *N*-boc protected indoles, which were purified by flash column chromatography, if required.

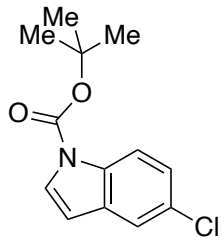
4.2. General procedure B for the synthesis of 2-(cyclobut-1-enyl)-1*H*-indoles



To a solution of *N*-boc protected indole (1.0 mmol, 2 equiv.) in diethyl ether (4 mL, 0.25 M) cooled to –78 °C was added *n*-butyllithium solution (1.1 mmol, 2.1 equiv.) as drops. The resulting reaction mixture was allowed to stir at –78 °C for 1 hr, before cyclobutanone (0.04 mL, 0.5 mmol, 1 equiv.) was added neat in one portion. After complete addition, the reaction mixture was allowed to slowly warm to room temperature (cooling bath was not removed) and stirred until completion of the reaction (4 – 15 hrs). The reaction mixture was then diluted with diethyl ether and quenched by the addition of saturated aqueous ammonium chloride solution (10 mL) at 0 °C. The aqueous phase was extracted with ethyl acetate (2 x 20 mL) and the combined organic phases were washed with saturated aqueous sodium chloride solution (15 mL). The organic phase was then dried over magnesium sulfate, filtered, and concentrated under reduced pressure to yield the crude material, which was purified by flash column chromatography.

5. Characterisation of Compounds

***tert*-Butyl 5-chloro-1*H*-indole-1-carboxylate, 1b**



The title compound was obtained as a white solid (5.0 g, 23 mmol, 90%) from 5-chloroindole (3.87 g, 25.5 mmol) according to **General Procedure A** and was used without further purification.

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 8.07 (1H, d, J = 8.9 Hz), 7.61 (1H, d, J = 3.7 Hz), 7.53 (1H, dd, J = 2.1, 0.6 Hz), 7.26 (1H, m), 6.51 (1H, dd, J = 3.7, 0.8 Hz), 1.67 (9H, s)

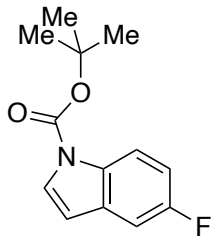
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ_C 149.6, 133.7, 131.8, 128.4, 127.3, 124.5, 120.6, 116.3, 106.7, 84.2, 28.3

IR (neat, ν cm^{-1}): 2977, 1730, 1447, 1314

HRMS (EI$^+$): *m/z* calculated for $C_{13}H_{14}ClNO_2$ $[M]^+$ 250.0631, found 250.0635

The spectroscopic data (^{1}H-NMR, ^{13}C{^{1}H}-NMR and IR) is consistent with literature.[2]

***tert*-Butyl 5-fluoro-1*H*-indole-1-carboxylate, 1c**



The title compound was obtained as a yellow oil (842 mg, 3.58 mmol, 80%) from 5-fluoroindole (604 mg, 4.47 mmol) according to **General Procedure A** and after purification by flash column chromatography (15% Et_2O/pentane).

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 8.14 – 8.02 (1H, br. s), 7.63 (1H, d, J = 3.7 Hz), 7.21 (1H, dd, J = 8.9, 2.6 Hz), 7.03 (1H, td, J = 9.1, 2.6 Hz), 6.52 (1H, dd, J = 3.7, 0.8 Hz), 1.67 (9H, s)

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ_C 159.3 (d, J = 238.7 Hz), 149.7, 131.7, 131.5 (d, J = 9.9 Hz), 127.6, 116.2 (d, J = 9.1 Hz), 112.1 (d, J = 25.0 Hz), 107.1 (d, J = 4.0 Hz), 106.5 (d, J = 23.9 Hz), 84.0, 28.3

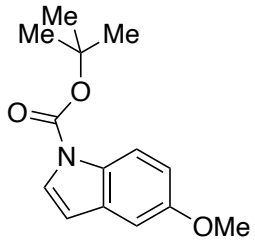
^{19}F-NMR (377 MHz, $CDCl_3$): δ_F –121.23

IR (neat, ν cm^{-1}): 2978, 2932, 1730, 1467, 1443, 1369, 1276, 1253, 1154

HRMS (EI$^+$): *m/z* calculated for $C_{13}H_{14}FNO_2$ $[M]^+$ 235.1003, found 235.0993

The spectroscopic data (^{1}H-NMR, ^{13}C{^{1}H}-NMR, ^{19}F-NMR and IR) is consistent with literature.[3,4]

***tert*-Butyl 5-methoxy-1*H*-indole-1-carboxylate, 1d**



The title compound was obtained as a white solid (962 mg, 3.89 mmol, 87%) from 5-methoxyindole (657 mg, 4.47 mmol) according to **General Procedure A** and used without further purification.

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 8.02 (1H, d, J = 8.3 Hz), 7.57 (1H, d, J = 3.7 Hz), 7.03 (1H, dd, J = 2.6, 0.5 Hz), 6.93 (1H, ddd, J = 9.0, 2.5, 0.5 Hz), 6.50 (1H, m), 3.85 (3H, s), 1.67 (9H, s)

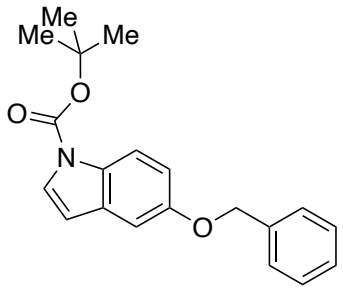
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ_C 155.6, 149.6, 131.2, 129.7, 126.3, 115.7, 112.8, 106.9, 103.3, 83.3, 55.5, 28.0

IR (neat, ν cm^{-1}): 3001, 2988, 2956, 2936, 1724, 1472, 1375, 1356, 1254

HRMS (ES^+): *m/z* calculated for $C_{14}H_{18}NO_3$ $[M + H]^+$ 248.1287, found 248.1293

The spectroscopic data (^{1}H-NMR, ^{13}C{^{1}H}-NMR and IR) is consistent with literature.[2,5]

***tert*-Butyl 5-(benzyloxy)-1*H*-indole-1-carboxylate, 1e**



The title compound was obtained as a yellow solid (1.28 g, 3.96 mmol, 89%) from 5-(benzyloxy)indole (1.00 g, 4.47 mmol) according to **General Procedure A** and used without further purification.

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 8.09 – 7.98 (1H, d, J = 8.2 Hz), 7.57 (1H, d, J = 3.6 Hz), 7.47 (2H, m), 7.40 (2H, ddd, J = 8.0, 7.0, 1.0 Hz), 7.34 (1H, m), 7.11 (1H, d, J = 2.5 Hz), 7.01 (1H, dd, J = 9.0, 2.5 Hz), 6.49 (1H, dd, J = 3.7, 0.8 Hz), 5.12 (2H, s), 1.67 (9H, s)

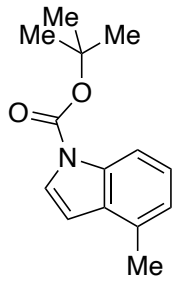
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ_C 154.8, 149.6, 137.2, 131.2, 129.9, 128.4, 127.7, 127.3, 126.4, 115.7, 113.6, 107.0, 104.8, 83.3, 70.4, 28.0

IR (neat, ν cm^{-1}): 3032, 2982, 2857, 1718, 1580, 1471, 1452, 1370

HRMS (ES$^+$): *m/z* calculated for $C_{20}H_{22}NO_3$ $[M + H]^+$ 324.1600, found 324.1603

The spectroscopic data (^{1}H-NMR and IR) is consistent with literature.[6,7]

***tert*-Butyl 4-methyl-1*H*-indole-1-carboxylate, 1f**



The title compound was obtained as a yellow oil (863 mg, 3.73 mmol, 83%) from 4-methylindole (584 mg, 4.47 mmol) according to **General Procedure A** and used without further purification.

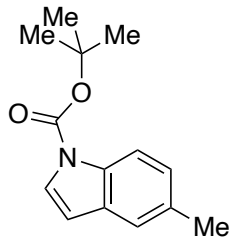
^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.98 (1H, d, J = 8.3 Hz), 7.60 (1H, d, J = 3.8 Hz), 7.22 (1H, dd, J = 8.3, 7.3 Hz), 7.04 (1H, dt, J = 7.3, 0.9 Hz), 6.61 (1H, dd, J = 3.8, 0.8 Hz), 2.53 (3H, d, J = 0.8 Hz), 1.68 (9H, s)

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ_C 149.7, 134.8, 130.1, 130.0, 125.1, 124.0, 122.8, 112.5, 105.5, 83.4, 28.0, 18.3

IR (neat, v cm^{-1}): 2975, 2932, 1726, 1420, 1368, 1344

HRMS (APCI): *m/z* calculated for $C_{14}H_{18}NO_2$ $[M + H]^+$ 232.1332, found 232.1331

***tert*-Butyl 5-methyl-1*H*-indole-1-carboxylate, 1g**



The title compound was obtained as a colourless oil (816 mg, 3.53 mmol, 79%) from 5-methylindole (586 mg, 4.47 mmol) according to **General Procedure A** and after purification by flash column chromatography (10% Et_2O/pentane).

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 8.07 – 7.93 (1H, d, J = 8.5 Hz), 7.55 (1H, d, J = 3.7 Hz), 7.35 (1H, dt, J = 1.7, 0.8 Hz), 7.13 (1H, dd, J = 8.5, 1.8 Hz), 6.49 (1H, dd, J = 3.7, 0.7 Hz), 2.44 (3H, s), 1.67 (9H, s)

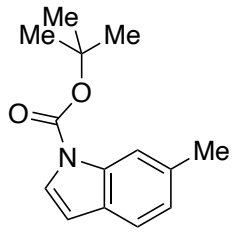
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ_C 149.7, 133.2, 131.9, 130.6, 125.7, 125.4, 120.6, 114.6, 106.8, 85.3, 28.0, 21.1

IR (neat, ν cm^{-1}): 2976, 2932, 1727, 1465, 1364, 1159

HRMS (APCI): *m/z* calculated for $C_{14}H_{18}NO_2$ $[M + H]^+$ 232.1332, found 232.1334

The spectroscopic data (^{1}H-NMR and IR) is consistent with literature.[4,8]

***tert*-Butyl 6-methyl-1*H*-indole-1-carboxylate, 1h**



The title compound was obtained as a colourless oil (1.02 g, 4.41 mmol, 99%) from 6-methylindole (586 mg, 4.47 mmol) according to **General Procedure A** and after purification by flash column chromatography (15% Et_2O/pentane).

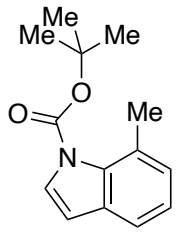
^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 8.06 – 7.97 (1H, br. s), 7.51 (1H, d, J = 3.8 Hz), 7.44 (1H, dd, J = 7.9 Hz), 7.07 (1H, ddd, J = 7.9, 1.5, 0.7 Hz), 6.52 (1H, dd, J = 3.7, 0.8 Hz), 2.49 (3H, s), 1.68 (9H, s)

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ_C 149.7, 135.4, 134.0, 128.0, 125.0, 123.9, 120.3, 115.2, 107.0, 83.2, 28.0, 21.8

IR (neat, ν cm^{-1}): 2976, 2932, 1729, 1368, 1332, 1250

HRMS (APCI): *m/z* calculated for $C_{14}H_{18}NO_2$ $[M + H]^+$ 232.1332, found 232.1335

***tert*-Butyl 7-methyl-1*H*-indole-1-carboxylate, 1i**



The title compound was obtained as a colourless oil (1.01 g, 4.37 mmol, 98%) from 7-methylindole (586 mg, 4.47 mmol) according to **General Procedure A** and after purification by flash column chromatography (10% Et_2O/pentane).

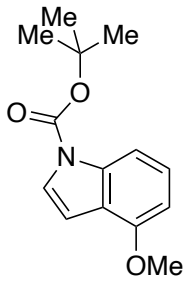
^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.53 (1H, d, J = 3.8 Hz), 7.40 (1H, dd, J = 7.8, 1.4 Hz), 7.15 (1H, t, J = 7.4 Hz), 7.11 (1H, d, J = 7.2 Hz), 6.54 (1H, d, J = 3.8 Hz), 2.65 (3H, s), 1.64 (9H, s)

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ_C 149.4, 134.5, 131.7, 127.9, 127.4, 125.2, 123.0, 118.4, 107.1, 83.1, 27.9, 22.0

IR (neat, ν cm^{-1}): 2976, 2932, 1740, 1320, 1290, 1220

HRMS (ES$^+$): *m/z* calculated for $C_{14}H_{18}NO_2$ $[M + H]^+$ 232.1338, found 232.1340

***tert*-Butyl 4-methoxy-1*H*-indole-1-carboxylate, 1j**



The title compound was obtained as a colourless oil (967 mg, 3.91 mmol, 87%) from 4-methoxyindole (658 mg, 4.47 mmol) according to **General Procedure A** and after purification by flash column chromatography (10% Et_2O/pentane).

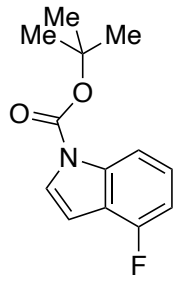
^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.76 (1H, d, J = 8.4 Hz), 7.51 (1H, d, J = 3.8 Hz), 7.25 (1H, m), 6.70 (1H, dd, J = 3.7, 0.8 Hz), 6.67 (1H, dd, J = 8.0, 0.7 Hz), 3.95 (3H, s), 1.67 (9H, s)

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ_C 152.7, 149.7, 136.3, 124.9, 124.2, 120.6, 108.1, 104.0, 102.8, 83.5, 55.2, 28.0

IR (neat, ν cm^{-1}): 2975, 2935, 2838, 1729, 1589, 1491, 1432

HRMS (ES$^+$): *m/z* calculated for $C_{14}H_{18}NO_3$ $[M + H]^+$ 248.1287, found 248.1281

***tert*-Butyl 4-fluoro-1*H*-indole-1-carboxylate, 1k**



The title compound was obtained as a colourless oil, which solidified upon standing (397 mg, 1.69 mmol, 76%) from 4-fluoroindole (300 mg, 2.22 mmol) according to **General Procedure A** and after purification by flash column chromatography (10% Et_2O/pentane).

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.93 (1H, br. d, J = 8.3 Hz), 7.57 (1H, d, J = 3.8 Hz), 7.23 (1H, m), 6.91 (1H, ddd, J = 9.7, 8.0, 0.7 Hz), 6.67 (1H, dd, J = 3.7, 0.8 Hz), 1.68 (9H, s)

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ_C 155.6 (d, J = 247.3 Hz), 149.3, 137.2 (d, J = 10.3 Hz), 125.7, 124.7 (d, J = 7.5 Hz), 119.2 (d, J = 22.5 Hz), 111.1 (d, J = 3.9 Hz), 107.7 (d, J = 18.6 Hz), 102.6, 84.0, 28.0

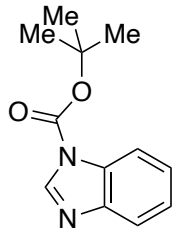
^{19}F-NMR (377 MHz, $CDCl_3$): δ_F –122.25

IR (neat, ν cm^{-1}): 3008, 2979, 2933, 1718, 1431, 1318, 1301

HRMS (EI$^+$): *m/z* calculated for $C_{13}H_{14}FNO_2$ $[M]^+$ 235.1003, found 235.1011

The spectroscopic data (^{19}F-NMR and IR) is consistent with literature.[4,9]

***tert*-Butyl 1*H*-benzo[*d*]imidazole-1-carboxylate, 1l**



The title compound was obtained as a white solid (823 mg, 3.77 mmol, 84%) from benzimidazole (530 mg, 4.49 mmol) according to **General Procedure A** and after purification by flash column chromatography (10% Et_2O/pentane).

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 8.44 (1H, s), 7.99 (1H, m), 7.79 (1H, m), 7.43 – 7.30 (2H, m), 1.70 (9H, s)

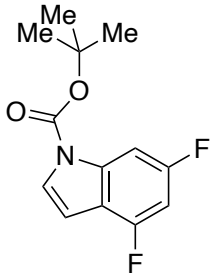
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ_C 147.9, 143.9, 141.9, 131.2, 125.0, 124.1, 120.4, 114.2, 85.4, 27.9

IR (neat, ν cm^{-1}): 3111, 2979, 1734, 1446, 1366, 1250, 1146

HRMS (ES$^+$): *m/z* calculated for $C_{12}H_{15}N_2O_2$ $[M + H]^+$ 219.1134, found 219.1140

The spectroscopic data (^{1}H-NMR, ^{13}C{^{1}H}-NMR and IR) is consistent with literature.[10]

***tert*-Butyl 4,6-difluoro-1*H*-indole-1-carboxylate, 1m**



The title compound was obtained as a white solid (662 mg, 2.61 mmol, 58%) from 4,6-difluoroindole (690 mg, 4.50 mmol) according to **General Procedure A** and after purification by flash column chromatography (10% Et_2O/pentane).

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.70 (1H, br. d, J = 9.9 Hz), 7.53 (1H, d, J = 3.8 Hz), 6.73 (1H, td, J = 9.7, 2.1 Hz), 6.62 (1H, dd, J = 3.8, 0.8 Hz), 1.67 (9H, s)

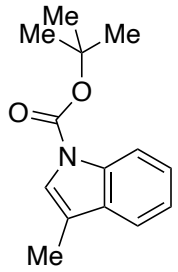
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ_C 160.33 (dd, J = 241.2, 11.6 Hz), 154.9 (dd, J = 249.6, 14.8 Hz), 149.1, 136.4, 125.7 (d, J = 3.7 Hz), 115.5 (d, J = 22.2 Hz), 102.4, 98.6 (dd, J = 28.6, 4.4 Hz, 97.9 (dd, J = 28.4, 23.0 Hz), 84.4, 27.9

^{19}F-NMR (377 MHz, $CDCl_3$): δ_F –114.96, –119.03

IR (neat, ν cm^{-1}): 3126, 2980, 2935, 1725, 1643, 1588, 1489, 1428

HRMS (EI$^+$): *m/z* calculated for $C_{13}H_{13}F_2NO_2$ $[M]^+$ 253.0909, found 253.0916

***tert*-Butyl 3-methyl-1*H*-indole-1-carboxylate, 1n**



The title compound was obtained as a colourless oil (671 mg, 2.90 mmol, 64%) from 3-methylindole (590 mg, 4.50 mmol) according to **General Procedure A** and after purification by flash column chromatography (10% Et_2O/pentane).

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 8.12 (1H, br. s), 7.50 (1H, ddd, J = 7.6, 1.5, 0.8 Hz), 7.36 (1H, br. s), 7.32 (1H, ddd, J = 8.4, 7.2, 1.4 Hz), 7.28 – 7.23 (1H, m), 2.28 (3H, d, J = 1.3 Hz), 1.67 (9H, s)

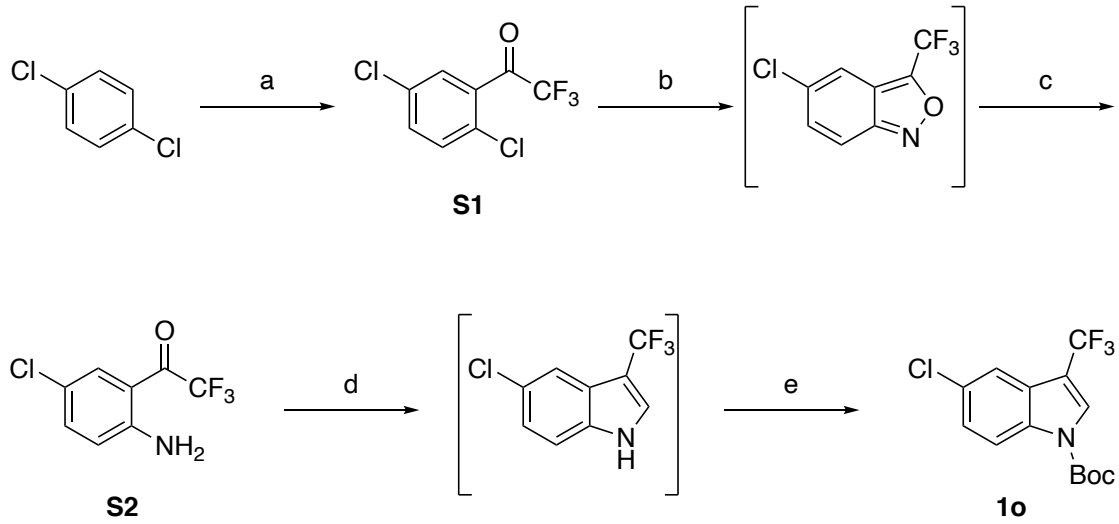
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ_C 150.0, 135.6, 131.6, 124.3, 122.9, 122.4, 119.0, 116.5, 115.3, 83.3, 28.4, 9.7

IR (neat, ν cm^{-1}): 2974, 2932, 1724, 1450, 1387, 1367, 1344, 1223

HRMS (APCI): *m/z* calculated for $C_{14}H_{18}NO_2$ $[M + H]^+$ 232.1332, found 232.1332

The spectroscopic data (^{1}H-NMR, ^{13}C{^{1}H}-NMR and IR) is consistent with literature.[11]

Synthesis of *tert*-Butyl 5-chloro-3-(trifluoromethyl)-1*H*-indole-1-carboxylate, 1o



1-(2,5-Dichlorophenyl)-2,2,2-trifluoroethanone, **S1**: Following a procedure by Golubev and co-workers.[12] To a solution of 1,4-dichlorobenzene (10 g, 68 mmol) in THF cooled to –78 °C was added *n*-butyllithium solution (2.1 M in hexanes, 36 mL, 76 mmol) as drops at a rate that maintained the internal temperature below –70 °C. The reaction mixture was stirred at the same temperature for one hour, before a solution of ethyl trifluoroacetate (9.1 mL, 76 mmol) in THF (15 mL) was added as drops at –80 °C. The resulting reaction mixture was stirred at the same temperature for 30 minutes, before it was allowed to warm to –50 °C and carefully treated with 10% aqueous hydrochloric acid solution (20 mL). After complete addition, the reaction mixture was allowed to warm to 0 °C and again treated with 10% aqueous hydrochloric acid solution (20 mL). The aqueous phase was separated and extracted with diethyl ether (3 x 50 mL) and the combined organic extracts were washed with saturated aqueous sodium chloride solution (2 x 30 mL), dried over magnesium sulfate, filtered and concentrated under reduced pressure to afford the crude product, which was used without further purification (10.4 g, 42.2 mmol, 62%). An analytically pure sample was purified by vacuum distillation (b.p. 75 – 85 °C, 3.4 Torr) to afford the title compound, **S1** as a colourless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.65 (1H, ddq, J = 2.2, 1.6, 1.0 Hz), 7.59 – 7.42 (2H, m)

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ_C 181.0 (q, J = 37.2 Hz), 134.2, 133.3, 132.8, 132.2, 132.0, 129.8 (d, J = 5.0 Hz), 115.7 (q, J = 291.7 Hz)

^{19}F-NMR (377 MHz, $CDCl_3$): δ_F –73.36

IR (neat, ν cm^{-1}): 3200, 1735, 1464, 1138

The spectroscopic data (^{1}H-NMR, ^{13}C{^{1}H}-NMR and ^{19}F-NMR) is consistent with literature.[13]

1-(2-Amino-5-chlorophenyl)-2,2,2-trifluoroethan-1-one, **S2**: Following a procedure by Golubev and co-workers.[12] To a suspension of sodium azide (1.75 g, 26.9 mmol) in DMF (60 mL) was added 1-(2,5-dichlorophenyl)-2,2,2-trifluoroethanone, **S1** (6.14 g, 25.2 mmol) as drops, before the reaction mixture was heated to 105 °C. During this process, the formation of a dark precipitate was observed. The reaction progress was monitored by ^{19}F NMR and upon completion, the reaction mixture was cooled to room temperature and poured into ice-cold deionised water (900 mL). The aqueous phase was separated and extracted with diethyl ether/pentane (1:1, 3 x 100 mL), and the combined organic extracts were washed with 5% aqueous citric acid solution (3 x 100 mL), saturated aqueous sodium chloride solution (2 x 50 mL), dried over magnesium sulfate, filtered and concentrated under reduced pressure to yield the crude product as a brown oil. Purification by vacuum distillation (b.p. 40 – 45 °C, 3.37 Torr) afforded 5-chloro-3-(trifluoromethyl)-2,1-benzisoxazole (2.06 g) as a yellow oil, which was subjected to the next synthetic step without further purification.

To a solution of 5-chloro-3-(trifluoromethyl)-2,1-benzisoxazole (2.06 g) in ethyl acetate (80 mL) was added 10% Pd/C (175 mg). The suspension was subjected to hydrogenation using a Parr hydrogenation apparatus (3 bar) and reaction progress was monitored by ^{19}F NMR (≈ 30 hours). Upon completion, the reaction mixture was filtered through Celite®, and the filtrate was concentrated under reduced pressure to yield the crude product as a brown oil. Purification by flash column chromatography (8% EtOAc/pentane) afforded the title compound, **S2** (1.54 g, 6.88 mmol, 27% over two steps) as orange crystals.

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.70 (1H, p, J = 2.2 Hz), 7.32 (1H, dd, J = 9.0, 2.4 Hz), 6.69 (1H, d, J = 9.0 Hz), 6.47 (2H, br. s)

^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ_C 180.4 (q, J = 34.3 Hz), 151.7, 137.0, 130.2 (q, J = 4.4 Hz), 121.1, 119.2, 117.3 (q, J = 291.6 Hz), 111.6

^{19}F-NMR (377 MHz, $CDCl_3$): δ_F −69.81

IR (neat, ν cm^{-1}): 3495, 2924, 1619, 1586, 1129

Melting point: 90.9 – 94.3 ºC (literature melting point: 91 – 92 °C, pentane)[12]

The spectroscopic data (^{1}H-NMR, $^{13}C\{^{1}H\}$-NMR and ^{19}F-NMR) is consistent with literature.[12,14]

tert-Butyl 5-chloro-3-(trifluoromethyl)-1H-indole-1-carboxylate, **1o**: To a suspension of 1-(2-amino-5-chlorophenyl)-2,2,2-trifluoroethan-1-one, **S2** (1.16 g, 5.18 mmol) and caesium carbonate (3.25 g, 9.97 mmol) in methanol (40 mL) heated to 60 °C was added (trimethylsilyl)diazomethane solution (2.0 M in hexanes, 8.0 mL, 16 mmol) as drops over ten minutes. The resulting solution was heated to 60 °C for 1.5 hours, before it was cooled to 0 °C and carefully treated with saturated aqueous ammonium chloride solution (100 mL). The aqueous phase was separated and extracted with ethyl acetate (3 x 50 mL). The combined organic extracts were washed with saturated aqueous sodium chloride solution (3 x 50 mL), dried over magnesium sulfate, filtered and concentrated under reduced pressure to afford 5-chloro-3-trifluoromethyl-1*H*-indole (760 mg) as a yellow oil, which was used without further purification.

The title compound was then obtained as a colourless oil (44 mg, 0.14 mmol, 22% over two steps) from crude 5-chloro-3-trifluoromethyl-1*H*-indole (109 mg) according to **General Procedure A** and after purification by flash column chromatography (10% Et_2O/pentane).

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 8.22 (1H, d, J = 9.0 Hz), 7.59 (1H, d, J = 2.1 Hz), 7.39 (1H, dd, J = 9.1, 2.2 Hz), 7.09 (1H, s), 1.69 (9H, s)

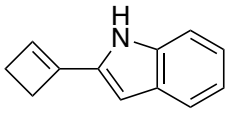
$^{13}C\{^{1}H\}$-NMR (101 MHz, $CDCl_3$): δ_C 148.4, 136.2, 129.3, 128.1 (q, J = 39.2 Hz), 127.7, 127.4, 121.5, 120.4 (q, J = 267.1 Hz), 117.4, 112.6 (q, J = 5.1 Hz), 86.1, 28.0

^{19}F-NMR (377 MHz, $CDCl_3$): δ_F –58.36

IR (neat, ν cm^{-1}): 2984, 1744, 1382, 1314, 1236, 1134

HRMS (ES^+) m/z calculated for $C_{14}H_{13}ClF_3NO_2$ $[M - Boc]^+$ 217.9986, found 217.9986

2-(Cyclobut-1-en-1-yl)-1*H*-indole, 2a



The title compound was obtained as an off-white solid (40 mg, 0.24 mmol, 41%) from *tert*-butyl-1*H*-indole-1-carboxylate (1.2 mmol) and cyclobutanone (0.6 mmol) according to **General Procedure B** and after purification by flash column chromatography (5% Et_2O/pentane).

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 8.04 (1H, s), 7.58 (1H, dd, J = 7.9, 1.1 Hz), 7.35 – 7.30 (1H, m), 7.22 – 7.14 (1H, m), 7.09 (1H, ddd, J = 8.0, 7.0, 1.1 Hz), 6.46 (1H, d, J = 2.0 Hz), 6.14 (1H, t, J = 1.4 Hz), 2.94 – 2.85 (2H, m), 2.65 (2H, dt, J = 4.0, 1.8 Hz)

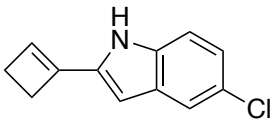
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ_C 138.7, 136.6, 133.8, 128.8, 126.4, 122.7, 120.9, 120.2, 110.8, 100.4, 29.3, 27.9

IR (neat, ν cm^{-1}): 3389, 3050, 2953, 2917, 2832, 1449, 1410, 1338, 1295

HRMS (EI$^+$): *m/z* calculated for $C_{12}H_{11}N$ $[M]^+$ 169.0891, found 169.0892

Melting point: 104.5 – 108.6 °C

2-(Cyclobut-1-en-1-yl)-5-chloro-1*H*-indole, 2b



The title compound was obtained as a yellow solid (36 mg, 0.18 mmol, 35%) from *tert*-butyl 5-chloro-1*H*-indole-1-carboxylate, **1b** according to **General Procedure B** and after purification by flash column chromatography (10% Et_2O/pentane).

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 8.05 (1H, br. s), 7.52 (1H, d, J = 2.0 Hz), 7.22 (1H, dt, J = 8.6, 0.8 Hz), 7.14 – 7.07 (1H, dd, J = 8.6, 2.0 Hz), 6.38 (1H, d, J = 2.1 Hz), 6.17 (1H, m), 2.87 (2H, m), 2.64 (2H, ddd, J = 4.2, 2.9, 1.4 Hz)

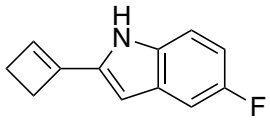
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ_C 138.1, 135.0, 134.7, 129.8, 127.4, 125.6, 122.8, 120.1, 111.6, 99.8, 29.2, 27.9

IR (neat, ν cm^{-1}): 3399, 2954, 2918, 1657, 1442, 1364

HRMS (EI$^+$): *m/z* calculated for $C_{12}H_{10}ClN$ $[M]^+$ 204.0580, found 204.0589

Melting point: 129.2 – 132.5 °C

2-(Cyclobut-1-en-1-yl)-5-fluoro-1*H*-indole, 2c



The title compound was obtained as a white solid (21 mg, 0.11 mmol, 22%) from *tert*-butyl 5-fluoro-1*H*-indole-1-carboxylate, **1c** according to **General Procedure B** and after purification by flash column chromatography (10% Et_2O/pentane).

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 8.02 (1H, br. s), 7.24 – 7.18 (2H, m), 6.91 (1H, td, J = 9.1, 2.5 Hz), 6.41 (1H, d, J = 2.1 Hz), 6.16 (1H, d, J = 1.4 Hz), 2.87 (2H, m), 2.64 (2H, m)

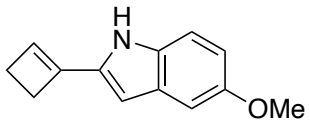
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ_C 158.1 (d, J = 234.1 Hz), 138.3, 135.4, 132.9, 129.1, 127.1, 111.2 (d, J = 9.7 Hz), 110.8 (d, J = 26.4 Hz), 105.5 (d, J = 23.4 Hz), 100.3 (d, J = 4.7 Hz), 29.2, 27.8

^{19}F-NMR (377 MHz, $CDCl_3$): δ_F –124.50

IR (neat, ν cm^{-1}): 3461, 3423, 2954, 2930, 2861, 1584, 1485, 1466, 1448, 1410, 1320

HRMS (ES^+): *m/z* calculated for $C_{12}H_{11}NF$ $[M + H]^+$ 188.0876, found 188.0877

2-(Cyclobut-1-en-1-yl)-5-methoxy-1*H*-indole, 2d



The title compound was obtained as a white solid (27 mg, 0.14 mmol, 28%) from *tert*-butyl 5-methoxy-1*H*-indole-1-carboxylate, **1d** according to **General Procedure B** and after purification by flash column chromatography (20% Et_2O/pentane). A crystal suitable for x-ray crystallography was recrystallised from chloroform.

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.95 (1H, br. s), 7.20 (1H, dt, J = 8.8, 0.7 Hz), 7.03 (1H, d, J = 2.4 Hz), 6.83 (1H, dd, J = 8.8, 2.5 Hz), 6.39 (1H, s), 6.12 (1H, m), 3.84 (3H, s), 2.86 (2H, m), 2.63 (2H, m)

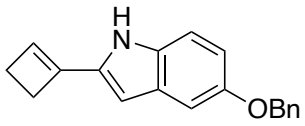
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ_C 154.3, 138.6, 134.4, 131.5, 129.1, 126.1, 112.8, 111.3, 102.3, 100.1, 55.8, 29.2, 27.7

IR (neat, ν cm^{-1}): 3416, 2950, 2916, 2831, 1620, 1582, 1477, 1452, 1215

HRMS (ES$^+$): *m/z* calculated for $C_{13}H_{14}ON$ $[M + H]^+$ 200.1070, found 200.1075

Melting point: decomposition above 35.1 °C

5-(Benzyloxy)-2-(cyclobut-1-en-1-yl)-1*H*-indole, 2e



The title compound was obtained as a white solid (40 mg, 0.15 mmol, 29%) from *tert*-butyl 5-benzyloxy-1*H*-indole-1-carboxylate, **1e** according to **General Procedure B** and after purification by flash column chromatography (10% Et_2O/pentane).

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.94 (1H, br. s), 7.47 (2H, m), 7.39 (2H, m), 7.33 (1H, m), 7.21 (1H, d, J = 8.8 Hz), 7.11 (1H, d, J = 2.4 Hz), 6.92 (1H, dd, J = 8.8, 2.4 Hz), 6.38 (1H, d, J = 2.0 Hz), 6.12 (1H, t, J = 1.3 Hz), 5.10 (2H, s), 2.86 (2H, m), 2.63 (2H, m)

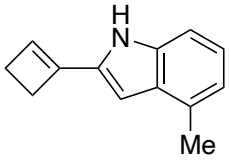
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ_C 153.5, 138.6, 137.7, 134.5, 131.7, 129.1, 128.5, 127.8, 127.6, 126.1, 113.6, 111.3, 104.0, 100.2, 70.9, 29.2, 27.8

IR (neat, ν cm^{-1}): 3426, 3049, 3034, 2950, 2909, 2835, 1446, 1407, 1211

HRMS (ES$^+$): *m/z* calculated for $C_{19}H_{18}NO$ $[M + H]^+$ 276.1388, mass found 276.1392

Melting point: 111.4 – 120.3 °C

2-(Cyclobut-1-en-1-yl)-4-methyl-1*H*-indole, 2f



The title compound was obtained as a white solid (23 mg, 0.13 mmol, 25%) from *tert*-butyl 4-methyl-1*H*-indole-1-carboxylate, **1f** according to **General Procedure B** and after purification by flash column chromatography (5% Et_2O/pentane).

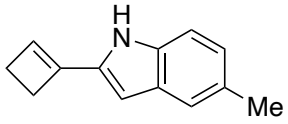
^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 8.05 (1H, br. s), 7.16 (1H, d, J = 8.1 Hz), 7.09 (1H, dd, J = 8.2, 7.1 Hz), 6.89 (1H, dt, J = 7.1, 1.0 Hz), 6.48 (1H, s), 6.13 (1H, t, J = 1.4 Hz), 2.90 (2H, m), 2.65 (2H, m), 2.54 (3H, s)

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ_C 138.6, 136.1, 133.1, 130.4, 128.5, 125.9, 122.7, 120.1, 108.2, 98.9, 29.2, 27.8, 18.8

IR (neat, ν cm^{-1}): 3384, 3048, 2950, 2913, 2833, 1409, 1336, 1257

HRMS (ES$^+$): *m/z* calculated for $C_{13}H_{14}N$ $[M + H]^+$ 184.1126, found 184.1117

2-(Cyclobut-1-en-1-yl)-5-methyl-1*H*-indole, 2g



The title compound was obtained as a white solid (47 mg, 0.26 mmol, 51%) from *tert*-butyl 5-methyl-1*H*-indole-1-carboxylate, **1g** according to **General Procedure B** and after purification by flash column chromatography (5% Et_2O/pentane).

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.96 (1H, s), 7.36 (1H, s), 7.20 (1H, d, J = 8.2 Hz), 7.00 (1H, dd, J = 8.3, 1.6 Hz), 6.38 (1H, s), 6.11 (1H, d, J = 1.4 Hz), 2.87 (2H, m), 2.64 (2H, m), 2.43 (3H, s)

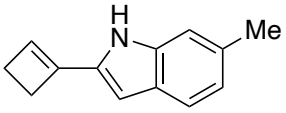
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ_C 138.7, 134.7, 133.8, 129.2, 128.9, 125.9, 124.2, 120.4, 110.3, 99.9, 29.2, 27.7, 21.5

IR (neat, ν cm^{-1}): 3390, 3329, 2951, 2909, 2831, 1409, 1318

HRMS (ES$^+$): *m/z* calculated for $C_{13}H_{14}N$ $[M + H]^+$ 184.1126, found 184.1130

Melting point: decomposition above 64.3 °C

2-(Cyclobut-1-en-1-yl)-6-methyl-1*H*-indole, 2h



The title compound was obtained as a white solid (18 mg, 0.10 mmol, 20%) from *tert*-butyl 6-methyl-1*H*-indole-1-carboxylate, **1h** according to **General Procedure B** and after purification by flash column chromatography (5% Et_2O/pentane).

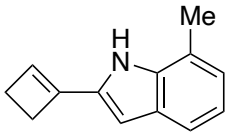
^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.91 (1H, br. s), 7.46 (1H, d, J = 8.0 Hz), 7.10 (1H, dq, J = 1.8, 0.9 Hz), 6.93 (1H, dd, J = 8.0, 1.4 Hz), 6.41 (1H, d, J = 2.0 Hz), 6.10 (1H, t, J = 1.4 Hz), 2.87 (2H, m), 2.64 (2H, ddt, J = 4.5, 2.1, 0.9 Hz), 2.46 (3H, s)

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ_C 138.7, 136.9, 133.2, 132.5, 126.4, 125.5, 121.8, 120.4, 110.6, 100.2, 29.2, 27.7, 21.8

IR (neat, v cm^{-1}): 3418, 2952, 2915, 2865, 1448, 1391, 1344, 1329, 1148

HRMS (ES$^+$): *m/z* calculated for $C_{13}H_{14}N$ $[M + H]^+$ 184.1126, found 184.1124

2-(Cyclobut-1-en-1-yl)-7-methyl-1*H*-indole, 2i



The title compound was obtained as a white solid (28 mg, 0.15 mmol, 31%) from *tert*-butyl 7-methyl-1*H*-indole-1-carboxylate, **1i** according to **General Procedure B** and after purification by flash column chromatography (5% Et_2O/pentane).

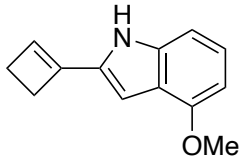
^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.97 (1H, br. s), 7.45 (1H, m), 7.07 – 6.96 (2H, m), 6.48 (1H, d, J = 2.1 Hz), 6.18 (1H, t, J = 1.4 Hz), 2.91 (2H, m), 2.67 (2H, m), 2.51 (3H, d, J = 0.8 Hz)

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ_C 138.7, 136.0, 133.5, 128.2, 126.0, 123.2, 120.2, 119.8, 118.5, 100.9, 29.3, 27.8, 16.8

IR (neat, ν cm^{-1}): 3446, 3049, 2951, 2915, 2835, 1330, 1301

HRMS (ES$^+$): *m/z* calculated for $C_{13}H_{14}N$ $[M + H]^+$ 184.1126, found 184.1122

2-(Cyclobut-1-en-1-yl)-4-methoxy-1*H*-indole, 2j



The title compound was obtained as a white solid (12 mg, 0.060 mmol, 12%) from *tert*-butyl 4-methoxy-1*H*-indole-1-carboxylate, **1j** according to **General Procedure B** and after purification by flash column chromatography (5% Et_2O/pentane).

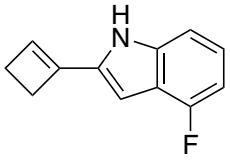
^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 8.06 (1H, br. s), 7.10 (1H, t, J = 7.9 Hz), 6.95 (1H, d, J = 8.1 Hz), 6.56 (1H, d, J = 2.1 Hz), 6.50 (1H, d, J = 7.7 Hz), 6.09 (1H, d, J = 1.4 Hz), 3.95 (3H, s), 2.87 (2H, m), 2.63 (2H, dd, J = 4.9, 2.2 Hz)

^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ_C 153.4, 138.5, 137.7, 132.4, 125.5, 123.4, 119.3, 104.0, 99.8, 97.7, 55.3, 29.1, 27.7

IR (neat, ν cm^{-1}): 3396, 2952, 2836, 2835, 1583, 1509, 1353, 1261, 1247

HRMS (ES$^+$): *m/z* calculated for $C_{13}H_{14}NO$ $[M + H]^+$ 200.1075, found 200.1078

2-(Cyclobut-1-en-1-yl)-4-fluoro-1*H*-indole, 2k



The title compound was obtained as a colourless oil (32 mg, 0.17 mmol, 34%) from *tert*-butyl 4-fluoro-1*H*-indole-1-carboxylate, **1k** according to **General Procedure B** and after purification by flash column chromatography (5% Et_2O/pentane).

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 8.13 (1H, s), 7.13 – 7.02 (2H, m), 6.75 (1H, ddd, J = 10.3, 6.6, 2.0 Hz), 6.52 (1H, d, J = 2.1 Hz), 6.17 (1H, m), 2.88 (2H, m), 2.65 (2H, m)

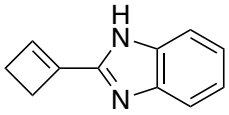
^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ_C 156.3 (d, J = 247.2 Hz), 138.6 (d, J = 11.3 Hz), 137.9, 133.4, 126.9, 122.8 (d, J = 7.7 Hz), 117.7 (d, J = 22.6 Hz), 106.5 (d, J = 3.5 Hz), 104.6 (d, J = 19.1 Hz), 96.0, 30.0, 27.6

^{19}F-NMR (377 MHz, $CDCl_3$): δ_F –122.05

IR (neat, ν cm^{-1}): 3452, 3423, 3043, 2952, 2914, 2833, 1624, 1577, 1501, 1409, 1340, 1223

HRMS (ES^+): *m/z* calculated for $C_{12}H_{11}NF$ $[M + H]^+$ 188.0876, found 188.0879

2-(Cyclobut-1-en-1-yl)-1*H*-benzo[*d*]imidazole, 2l



The title compound was obtained as a white solid (23 mg, 0.14 mmol, 27%) from *tert*-butyl 1*H*-benzo[*d*]imidazole-1-carboxylate, **1l** according to **General Procedure B** and after purification by flash column chromatography (70% Et_2O/pentane).

NB: Deprotonation time was reduced to 40 minutes for this substrate.

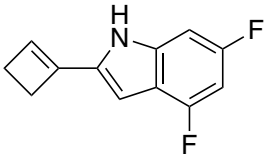
^{1}H-NMR (400 MHz, DMSO-d_6): δ_H 12.56 (1H, br. s), 7.51 (2H, q, J = 8.1, 6.3 Hz), 7.17 (2H, m), 6.61 (1H, t, J = 1.3 Hz), 2.90 (2H, m), 2.61 (2H, ddd, J = 4.5, 2.1, 1.2 Hz)

^{13}C{^{1}H}-NMR (101 MHz, DMSO-d_6): δ_C 147.5, 138.0, 134.9, 122.5 (broad), 29.5, 28.0
***Note**: Due to the presence of rapid tautomerism in DMSO-d_6, some $^{13}C\{^1H\}$-NMR signals could not be detected for this compound. Only distinct signals are reported.*

IR (neat, ν cm^{-1}): 3055, 2958, 2928, 1662, 1443, 1412, 1275

HRMS (ES$^+$): *m/z* calculated for $C_{11}H_{11}N_2$ $[M + H]^+$ 171.0922, found 171.0921

2-(Cyclobut-1-en-1-yl)-4,6-difluoro-1*H*-indole, 2m



The title compound was obtained as a colourless oil (8 mg, 0.04 mmol, 8%) from *tert*-butyl 4,6-difluoro-1*H*-indole-1-carboxylate, **1m** according to **General Procedure B** and after purification by flash column chromatography (5% Et_2O/pentane).

NB: Deprotonation time was reduced to 30 minutes for this substrate.

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 8.12 (1H, s), 6.81 (1H, dq, J = 8.9, 0.9 Hz), 6.58 (1H, td, J = 10.1, 2.0 Hz), 6.46 (1H, d, J = 2.1 Hz), 6.14 (1H, d, J = 1.4 Hz), 2.86 (2H, m), 2.64 (2H, t, J = 3.2 Hz)

^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): δ_C 159.9 (dd, J = 239.0, 10.3 Hz), 155.7 (dd, J = 248.8, 14.2 Hz), 137.7, 137.6 (m), 133.8, 126.9, 114.3 (d, J = 22.3 Hz), 96.0, 95.4 (dd, J = 28.9, 23.4 Hz), 93.2 (dd, J = 26.4, 4.5 Hz), 29.0, 27.7

^{19}F-NMR (377 MHz, $CDCl_3$): δ_F –117.59, –118.70

IR (neat, ν cm^{-1}): 3465, 2955, 2919, 2836, 1646, 1629, 1590, 1510, 1449, 1355, 1274

HRMS (APCI): *m/z* calculated for $C_{12}H_{10}F_2N$ $[M + H]^+$ 206.0787, found 206.0780

6. Computational Methods

Computational Energy Estimates with Density Functional Theory

The ground state and transition state geometry optimisations were accomplished with B3LYP density functional theory and 6-31G(d,p) basis set[15–17] in diethyl ether with the IEF-PCM solvation model.[18] The initial geometries for conformational search were generated with RDKit's ETKDG functionality.[19] Frequency calculation was used to confirm that the optimised structures are at local minima with no imaginary frequencies or at a transition state with exactly one imaginary frequency. DFT calculations used UltraFine, a pruned (99,590) grid. Internal reaction coordinate (IRC) calculations in both the forward and reverse direction were utilised to confirm the appropriate transition state was found. Single-point energy calculation was done with a larger basis set, 6-311++G(d,p), in diethyl ether. The GoodVibes package[20] was used to obtain the quasi-harmonic thermodynamic correction at 195.15 K and 1 atm. In combination with the single-point energy gives the corrected Gibbs free energy. All energy differences were calculated from the structure with the lowest corrected Gibbs free energy from each conformational search. Gaussian 16 program[21] was used for all the density functional calculations.

Computational Estimates of p*K*a in Et_2O

A direct scheme[22] was used to estimate the p*K*a value from the solution phase Gibbs free energy of reaction (eq. 1, 2). Ground state solution phase energies of **C** and **D**, and their deprotonated counterparts were calculated as per previous section. The solvation free energy of a proton was obtained by subtracting two free diethyl ethers from a $[Et_2O\text{-}H\text{-}OEt_2]^+$ complex.[23]

$$A \overset{\Delta G}{\rightarrow} A^- + H^+ \quad (1)$$

$$pKa = \frac{\Delta G}{RTln(10)} \quad (2)$$

Single-point Energy with Quasi-harmonic Thermodynamic Correction

	Zero-Point Energy (Hartree)	Correction (Hartree)	Gibbs Free Energy (Hartree)
A	-709.286916	0.218574	-709.068342
B	-940.625002	0.311656	-940.313346
C	-940.642421	0.310512	-940.331909
D	-518.717731	0.174630	-518.543101
TS1	-940.582571	0.307972	-940.274599
TS2	-940.615063	0.310212	-940.304851
TS3	-940.623813	0.308324	-940.315489
Cyclobutanone	-231.297815	0.073326	-231.224489
OBoc	-421.911934	0.118052	-421.793882
C^-	-940.137085	0.270135	-939.866950
D^-	-518.238655	0.146492	-518.092163

Magnitude of the imaginary frequency for the transition states

	TS1	TS2	TS3
Magnitude (km/mol)	55.4468	213.4471	406.0548

Cartesian Coordinates of Optimised Structures

A

Center Number	Atomic Number	Atomic Type	Coordinates (Å) X	Y	Z
1	6	0	1.691999	-0.099531	0.000008
2	6	0	2.622085	0.977610	0.000002
3	6	0	3.996055	0.685708	-0.000016
4	6	0	4.420069	-0.644767	-0.000031
5	6	0	3.487739	-1.692721	-0.000047
6	6	0	2.110718	-1.430577	-0.000026
7	7	0	0.410253	0.506606	0.000020
8	6	0	0.474869	1.965855	-0.000012
9	6	0	1.842972	2.191297	0.000001
10	6	0	-0.753930	-0.233961	0.000118
11	8	0	-0.787284	-1.463000	0.000130
12	8	0	-1.857045	0.549227	-0.000025
13	6	0	-3.196300	-0.043418	-0.000063
14	6	0	-3.424471	-0.867379	-1.273463
15	6	0	-4.100974	1.192703	-0.000029
16	6	0	-3.424423	-0.867298	1.273443
17	1	0	4.725698	1.493408	-0.000005
18	1	0	5.484099	-0.872466	-0.000046
19	1	0	3.832982	-2.723847	-0.000071
20	1	0	1.386687	-2.234361	-0.000049
21	1	0	2.288620	3.184113	0.000002
22	1	0	-4.470761	-1.187668	-1.322289
23	1	0	-3.214023	-0.258336	-2.158325
24	1	0	-2.783031	-1.747932	-1.290972
25	1	0	-3.911568	1.806349	0.885141
26	1	0	-3.913652	1.805223	-0.886438
27	1	0	-5.153307	0.892112	0.001267
28	1	0	-2.782060	-1.747179	1.291337
29	1	0	-3.214891	-0.257898	2.158282
30	1	0	-4.470374	-1.188696	1.321873

B

Center Number	Atomic Number	Atomic Type	Coordinates (Å) X	Y	Z
1	6	0	-1.815826	-0.595160	-0.202874
2	6	0	-2.738286	0.382460	0.301991
3	6	0	-4.054219	-0.027852	0.588135
4	6	0	-4.413599	-1.356670	0.382949
5	6	0	-3.486534	-2.298457	-0.114097
6	6	0	-2.179017	-1.929390	-0.415907
7	7	0	-0.626688	0.052301	-0.409024
8	6	0	-0.742846	1.358091	-0.051885
9	6	0	-2.023220	1.628851	0.389610
10	6	0	0.774525	-0.366481	-0.822225
11	8	0	0.896883	-1.066185	-1.852657
12	8	0	1.296232	-0.872615	0.447253
13	6	0	2.484235	-1.685089	0.444485
14	6	0	2.896229	-1.726015	1.923352
15	6	0	3.613772	-1.066778	-0.396437
16	6	0	2.158211	-3.109867	-0.040544
17	6	0	1.214157	2.658409	1.028743
18	6	0	0.727758	4.041784	0.524782
19	6	0	0.575359	3.433465	-0.894573
20	6	0	0.596797	2.010960	-0.260607
21	8	0	1.351587	1.046201	-0.954675
22	1	0	-4.782303	0.684463	0.970010
23	1	0	-5.427923	-1.677891	0.606650
24	1	0	-3.800842	-3.327829	-0.265752
25	1	0	-1.454148	-2.634597	-0.808958
26	1	0	-2.414027	2.581362	0.720826
27	1	0	3.784982	-2.351096	2.065887
28	1	0	2.084353	-2.135960	2.532739
29	1	0	3.116861	-0.718205	2.287572
30	1	0	3.320500	-1.030421	-1.446123
31	1	0	3.821317	-0.045456	-0.064770
32	1	0	4.529775	-1.661432	-0.296659
33	1	0	3.034729	-3.764145	0.045867
34	1	0	1.824984	-3.075642	-1.077425
35	1	0	1.353594	-3.533664	0.570946
36	1	0	0.853767	2.300067	1.996955
37	1	0	2.303599	2.565623	0.989388
38	1	0	1.412764	4.887305	0.635844
39	1	0	-0.237680	4.321098	0.957984
40	1	0	1.479686	3.570870	-1.494908
41	1	0	-0.299755	3.706668	-1.491655

C

Center Number	Atomic Number	Atomic Type	Coordinates (Å) X	Y	Z
1	6	0	2.807018	-0.456959	-0.697191
2	6	0	2.800631	-0.525965	0.750769
3	6	0	3.756537	-1.323455	1.414981
4	6	0	4.690010	-2.035153	0.669967
5	6	0	4.695240	-1.966892	-0.745296
6	6	0	3.767167	-1.188239	-1.426956
7	7	0	1.822517	0.361829	-1.170537
8	6	0	1.183389	0.808112	-0.046765
9	6	0	1.726922	0.314021	1.148003
10	6	0	0.018408	1.744449	-0.198287
11	6	0	0.310112	2.973154	-1.092383
12	6	0	0.533734	3.799457	0.203027
13	6	0	-0.256322	2.712344	0.979570
14	8	0	-1.165119	1.037577	-0.737557
15	6	0	-1.854916	0.235013	0.072258
16	8	0	-1.692602	0.090402	1.269663
17	8	0	-2.792646	-0.369068	-0.687138
18	6	0	-3.755254	-1.310424	-0.093681
19	6	0	-3.017072	-2.524218	0.479284
20	6	0	-4.614986	-0.598252	0.955963
21	6	0	-4.605595	-1.714686	-1.300873
22	1	0	3.764739	-1.387718	2.502849
23	1	0	5.427977	-2.654006	1.176761
24	1	0	5.437564	-2.534669	-1.302981
25	1	0	3.771470	-1.137745	-2.514534
26	1	0	1.384455	0.509462	2.156090
27	1	0	1.133400	2.863331	-1.799097
28	1	0	-0.596372	3.289847	-1.617655
29	1	0	1.586970	3.821294	0.495164
30	1	0	0.138217	4.818885	0.223378
31	1	0	-1.320845	2.957437	1.032878
32	1	0	0.093107	2.417002	1.969280
33	1	0	-2.378029	-2.973488	-0.286805
34	1	0	-2.397594	-2.242058	1.330737
35	1	0	-3.743265	-3.276888	0.803210
36	1	0	-5.089368	0.286943	0.520178
37	1	0	-5.405811	-1.272554	1.299989
38	1	0	-4.015549	-0.292545	1.813431
39	1	0	-3.982108	-2.173351	-2.073355
40	1	0	-5.103409	-0.841442	-1.732491
41	1	0	-5.370364	-2.435667	-0.997360

D

Center Number	Atomic Number	Atomic Type	Coordinates (Å) X	Y	Z
1	6	0	-1.229210	-0.683403	-0.017919
2	6	0	-1.331026	0.787955	-0.011242
3	6	0	-2.618032	1.415946	0.026122
4	6	0	-3.730167	0.623203	0.055572
5	6	0	-3.631712	-0.818379	0.049355
6	6	0	-2.429315	-1.467209	0.013862
7	7	0	0.021402	-1.120107	-0.052041
8	6	0	0.795527	0.051627	-0.072705
9	6	0	-0.034368	1.245124	-0.042492
10	6	0	2.153688	0.012728	-0.127580
11	6	0	3.237541	1.063884	-0.078252
12	6	0	4.243096	-0.071912	0.293160
13	6	0	3.147732	-1.118678	-0.083160
14	1	0	-2.700760	2.499164	0.030604
15	1	0	-4.718444	1.072404	0.084336
16	1	0	-4.552777	-1.394168	0.073799
17	1	0	-2.363718	-2.550696	0.008945
18	1	0	0.318251	2.268152	-0.048317
19	1	0	3.437153	1.494878	-1.067199
20	1	0	3.099121	1.887229	0.628915
21	1	0	4.480171	-0.083230	1.359087
22	1	0	5.170657	-0.106276	-0.281053
23	1	0	3.307273	-1.564397	-1.072728
24	1	0	2.930736	-1.927633	0.619570

TS1

Center Number	Atomic Number	Atomic Type	Coordinates (Å) X	Y	Z
1	6	0	-0.571459	1.672077	0.003261
2	6	0	0.514675	2.592711	-0.029064
3	6	0	0.249237	3.970133	0.034916
4	6	0	-1.068990	4.415372	0.128566
5	6	0	-2.128561	3.497134	0.157482
6	6	0	-1.892212	2.118342	0.094819
7	7	0	0.021911	0.382284	-0.081877
8	6	0	1.469096	0.464388	-0.161145
9	6	0	1.722490	1.816013	-0.127318
10	6	0	-0.623901	-0.841305	-0.143582
11	8	0	-0.070218	-1.913081	-0.334178
12	8	0	-1.963748	-0.708027	0.040932
13	6	0	-2.856846	-1.873498	-0.013267
14	6	0	-4.235291	-1.253248	0.236280
15	6	0	-2.805317	-2.519022	-1.402449
16	6	0	-2.509434	-2.863901	1.103948
17	6	0	3.687350	-1.050778	1.250804
18	6	0	3.010841	-2.369621	0.777495
19	6	0	3.284394	-2.001908	-0.709472
20	6	0	3.745467	-0.606998	-0.230393
21	8	0	4.393551	0.271753	-0.780484
22	1	0	1.070951	4.682664	0.010906
23	1	0	-1.278718	5.481434	0.179750
24	1	0	-3.152439	3.855061	0.231593
25	1	0	-2.718185	1.422271	0.119708
26	1	0	2.724303	2.231238	-0.173124
27	1	0	-5.003337	-2.032509	0.230568
28	1	0	-4.478576	-0.523576	-0.541659
29	1	0	-4.261990	-0.748353	1.206450
30	1	0	-3.560956	-3.308724	-1.468559
31	1	0	-3.023578	-1.773656	-2.173672
32	1	0	-1.824026	-2.950676	-1.597330
33	1	0	-3.258199	-3.662438	1.131688
34	1	0	-2.516619	-2.357004	2.074103
35	1	0	-1.526118	-3.304414	0.943268
36	1	0	4.708891	-1.201167	1.630558
37	1	0	3.139892	-0.414106	1.945921
38	1	0	1.942157	-2.392001	0.985613
39	1	0	3.478532	-3.292649	1.133803
40	1	0	2.428360	-2.038690	-1.381280
41	1	0	4.130357	-2.549220	-1.150612

TS2

Center Number	Atomic Number	Atomic Type	Coordinates (Å) X	Y	Z
1	6	0	1.738788	-0.835809	-0.052942
2	6	0	2.921245	-0.006697	-0.090229
3	6	0	4.187395	-0.622696	-0.046550
4	6	0	4.271560	-2.008388	0.043172
5	6	0	3.107173	-2.807214	0.084104
6	6	0	1.840546	-2.233312	0.031253
7	7	0	0.636320	-0.025652	-0.138683
8	6	0	1.074107	1.257175	-0.184543
9	6	0	2.458967	1.345913	-0.171295
10	6	0	-1.145068	0.122638	0.283012
11	8	0	-1.302524	0.042794	1.507466
12	8	0	-1.754327	-0.760680	-0.616424
13	6	0	-2.761885	-1.695700	-0.151113
14	6	0	-3.934767	-0.957742	0.513459
15	6	0	-2.158012	-2.750386	0.788401
16	6	0	-3.235243	-2.362484	-1.449408
17	6	0	-0.232971	3.196843	1.056324
18	6	0	-0.713835	4.294509	0.069868
19	6	0	-0.133357	3.448252	-1.094859
20	6	0	-0.076251	2.214568	-0.152996
21	8	0	-1.233914	1.405500	-0.367596
22	1	0	5.093663	-0.020304	-0.077774
23	1	0	5.247433	-2.487063	0.082471
24	1	0	3.203493	-3.887951	0.156123
25	1	0	0.946315	-2.848797	0.058963
26	1	0	3.061751	2.244389	-0.207981
27	1	0	-3.610628	-0.480192	1.437984
28	1	0	-4.747822	-1.658639	0.734516
29	1	0	-4.320934	-0.186343	-0.161210
30	1	0	-1.367572	-3.307242	0.273952
31	1	0	-2.927056	-3.467134	1.099441
32	1	0	-1.734433	-2.268842	1.669208
33	1	0	-3.657011	-1.619262	-2.133095
34	1	0	-2.398388	-2.854919	-1.954105
35	1	0	-4.002645	-3.114350	-1.236972
36	1	0	0.738417	3.433899	1.501449
37	1	0	-0.918046	2.859248	1.835910
38	1	0	-0.310352	5.302500	0.205154
39	1	0	-1.804722	4.358184	0.023821
40	1	0	0.872260	3.768537	-1.385189
41	1	0	-0.742200	3.316113	-1.993408

TS3

Center Number	Atomic Number	Atomic Type	Coordinates (Å) X	Y	Z
1	6	0	3.028014	-0.199852	-0.597230
2	6	0	2.654301	-0.690632	0.727859
3	6	0	3.341164	-1.802338	1.290699
4	6	0	4.355538	-2.393423	0.572600
5	6	0	4.727167	-1.908843	-0.722978
6	6	0	4.088082	-0.837365	-1.304000
7	7	0	2.285894	0.845855	-0.990594
8	6	0	1.423488	1.069867	0.076594
9	6	0	1.619342	0.144260	1.147132
10	6	0	0.506407	2.118761	0.059495
11	6	0	-0.217688	2.856013	1.165348
12	6	0	-0.631616	3.936016	0.119661
13	6	0	0.347338	3.276090	-0.898199
14	8	0	-1.359799	1.205415	-0.753564
15	6	0	-1.950704	0.355643	-0.019495
16	8	0	-1.893410	0.210077	1.214386
17	8	0	-2.763397	-0.479122	-0.796966
18	6	0	-3.547190	-1.550262	-0.209209
19	6	0	-4.247175	-2.172616	-1.424574
20	6	0	-4.590793	-0.994423	0.770485
21	6	0	-2.635595	-2.588395	0.459932
22	1	0	3.066951	-2.178291	2.274087
23	1	0	4.890814	-3.243764	0.987568
24	1	0	5.534758	-2.407547	-1.253708
25	1	0	4.372743	-0.474806	-2.288366
26	1	0	1.035329	0.095499	2.056152
27	1	0	0.501661	3.234177	1.903892
28	1	0	-0.996066	2.288332	1.675616
29	1	0	-1.673486	3.837807	-0.187284
30	1	0	-0.425123	4.975669	0.388131
31	1	0	1.292881	3.819861	-1.013222
32	1	0	-0.035854	3.025326	-1.888323
33	1	0	-4.887437	-3.005999	-1.116580
34	1	0	-3.510023	-2.547982	-2.141143
35	1	0	-4.867465	-1.427682	-1.932638
36	1	0	-4.098608	-0.530800	1.625165
37	1	0	-5.246924	-1.798193	1.123461
38	1	0	-5.211952	-0.243233	0.270748
39	1	0	-3.224314	-3.446414	0.804085
40	1	0	-2.115156	-2.145019	1.308421
41	1	0	-1.891620	-2.949903	-0.257460

Cyclobutanone

Center Number	Atomic Number	Atomic Type	Coordinates (Å) X	Y	Z
1	6	0	0.384586	-1.110166	0.017013
2	6	0	1.479553	-0.000002	-0.026858
3	6	0	0.384589	1.110167	0.017021
4	6	0	-0.675359	-0.000001	0.006677
5	8	0	-1.882675	0.000001	-0.016535
6	1	0	0.362178	-1.718282	0.927741
7	1	0	0.334353	-1.783852	-0.844635
8	1	0	2.070060	0.000009	-0.944947
9	1	0	2.158062	-0.000011	0.827977
10	1	0	0.362186	1.718355	0.927698
11	1	0	0.334349	1.783787	-0.844681

OBoc

Center Number	Atomic Number	Atomic Type	Coordinates (Å) X	Y	Z
1	8	0	-2.515015	-0.891168	0.000009
2	6	0	-1.573044	-0.079191	-0.000048
3	8	0	-1.575328	1.171918	-0.000087
4	8	0	-0.300139	-0.758115	0.000430
5	6	0	0.949505	-0.043632	0.000039
6	6	0	1.100690	0.812402	-1.268535
7	6	0	1.101127	0.812393	1.268564
8	6	0	2.004969	-1.160245	-0.000286
9	1	0	0.327253	1.579944	-1.287015
10	1	0	2.089099	1.286491	-1.304073
11	1	0	0.993917	0.182781	-2.159144
12	1	0	0.326260	1.578511	1.287948
13	1	0	0.996543	0.182548	2.159291
14	1	0	2.088670	1.288332	1.302862
15	1	0	3.018247	-0.742524	-0.000114
16	1	0	1.892298	-1.793522	-0.886401
17	1	0	1.892088	-1.794012	0.885419

C^-

Center Number	Atomic Number	Atomic Type	Coordinates (Å) X	Y	Z
1	6	0	-5.618812	0.134074	0.619633
2	6	0	-5.624367	-0.769458	-0.518756
3	6	0	-6.763779	-1.566075	-0.769195
4	6	0	-7.861724	-1.476144	0.078293
5	6	0	-7.854006	-0.597237	1.190473
6	6	0	-6.748809	0.201195	1.462472
7	7	0	-4.449642	0.827805	0.713106
8	6	0	-3.699981	0.382631	-0.348949
9	6	0	-4.362413	-0.586853	-1.130989
10	6	0	-2.365241	0.906958	-0.566844
11	6	0	-1.375712	0.734191	-1.477718
12	6	0	-0.420411	1.713820	-0.825860
13	6	0	-1.555286	1.915141	0.240758
14	8	0	3.713564	0.420733	-0.114924
15	6	0	4.936962	0.569161	0.046351
16	8	0	5.620498	1.602623	0.220807
17	8	0	5.623572	-0.701250	0.013551
18	6	0	7.046026	-0.805962	0.199543
19	6	0	7.465386	-0.282731	1.583162
20	6	0	7.806486	-0.079964	-0.922689
21	6	0	7.311548	-2.316999	0.115669
22	1	0	-6.786108	-2.246595	-1.620286
23	1	0	-8.741444	-2.088778	-0.110611
24	1	0	-8.727577	-0.550823	1.838188
25	1	0	-6.744796	0.874938	2.318076
26	1	0	-3.973566	-1.086699	-2.011078
27	1	0	-1.283316	0.113610	-2.366028
28	1	0	0.522369	1.304445	-0.440128
29	1	0	-0.177474	2.613888	-1.408335
30	1	0	-1.974663	2.927322	0.293909
31	1	0	-1.294503	1.597891	1.257136
32	1	0	6.911820	-0.814825	2.365255
33	1	0	7.236568	0.780550	1.654182
34	1	0	8.537077	-0.442723	1.753617
35	1	0	8.889398	-0.220079	-0.817141
36	1	0	7.505534	-0.479825	-1.897306
37	1	0	7.571747	0.983871	-0.892025
38	1	0	6.980969	-2.710274	-0.851268
39	1	0	6.760288	-2.845059	0.900634
40	1	0	8.378897	-2.536795	0.233872

D$^-$

Center Number	Atomic Number	Atomic Type	Coordinates (Å) X	Y	Z
1	6	0	1.247094	-0.684198	-0.001809
2	6	0	1.309110	0.767285	-0.000797
3	6	0	2.565180	1.412255	0.001507
4	6	0	3.726171	0.648719	0.002267
5	6	0	3.665253	-0.767586	0.000777
6	6	0	2.444995	-1.431577	-0.001354
7	7	0	-0.035104	-1.142946	-0.002301
8	6	0	-0.802910	-0.003972	-0.001611
9	6	0	-0.044028	1.184198	-0.000812
10	6	0	-2.247358	-0.077659	-0.000229
11	6	0	-3.170323	-1.069214	0.003855
12	6	0	-4.365856	-0.137214	0.001997
13	6	0	-3.306396	1.021568	-0.002407
14	1	0	2.628064	2.500232	0.002583
15	1	0	4.696944	1.140713	0.004061
16	1	0	4.590966	-1.340004	0.001423
17	1	0	2.400789	-2.519230	-0.002136
18	1	0	-0.426889	2.198560	-0.000542
19	1	0	-3.090156	-2.151862	0.006052
20	1	0	-5.014365	-0.169008	-0.885090
21	1	0	-5.013094	-0.163427	0.890114
22	1	0	-3.325272	1.667263	0.884484
23	1	0	-3.326861	1.661748	-0.893151

7. X-Ray Crystallography

Manuscript: An entry to 2-(cyclobut-1-en-1-yl)-1*H*-indoles through a cyclobutenylation/deprotection cascade

Authors: Philipp Natho, Zeyu Yang, Lewis A.T. Allen, Juliette Rey, Andrew J.P. White and Philip J. Parsons

The X-ray crystal structure of 2d

Crystal data for **2d**: $C_{13}H_{13}NO$, $M = 199.24$, orthorhombic, *Pbca* (no. 61), $a = 12.5334(11)$, $b = 9.3516(8)$, $c = 17.8360(15)$ Å, $V = 2090.5(3)$ Å^3, $Z = 8$, $D_c = 1.266$ g cm^{-3}, μ(Mo-Kα) = 0.080 mm^{-1}, $T = 173$ K, colourless blocky needles, Agilent Xcalibur 3 E diffractometer; 2325 independent measured reflections ($R_{int} = 0.0328$), F^2 refinement,[X1,X2] R_1(obs) = 0.0415, wR_2(all) = 0.0951, 1294 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$], completeness to $\theta_{full}(25.2°) = 99.9\%$], 142 parameters. CCDC 2057801.

The crystal of **2d** that was studied was found to be a two component twin in a *ca*. 54:46 ratio, with the two lattices related by the approximate twin law [1.00 0.00 –0.01 0.00 –1.00 0.00 –0.04 0.00 –1.00]. The N1–H hydrogen atom was located from a Δ*F* map and refined freely subject to an N–H distance constraint of 0.90 Å.

References

[X1] SHELXTL v5.1, Bruker AXS, Madison, WI, 1998.

[X2] SHELX-2013, G.M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.

Figures

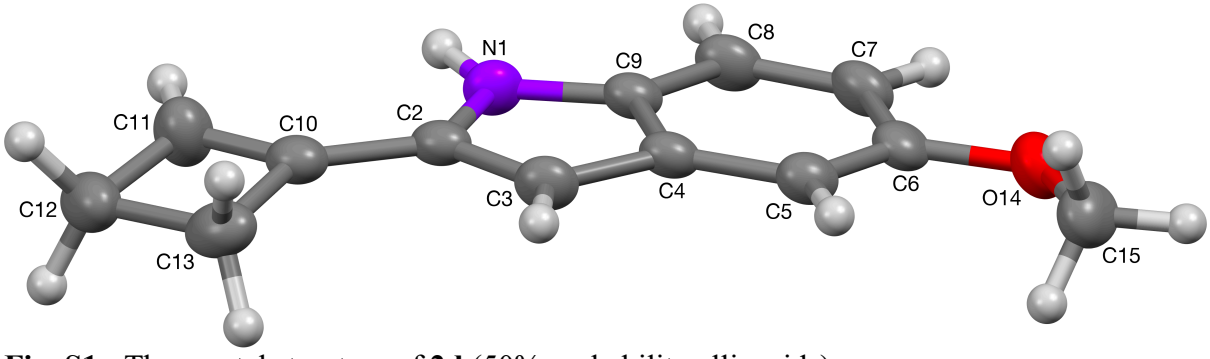
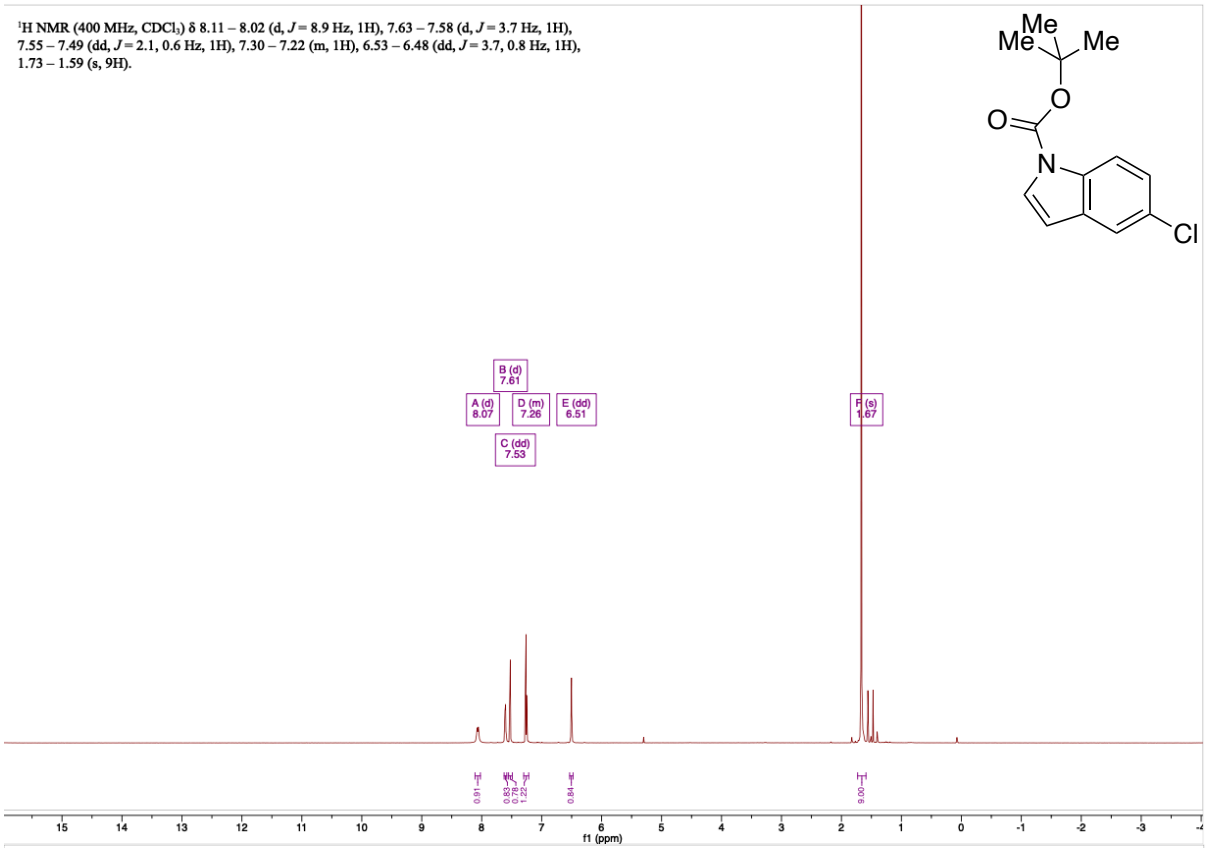
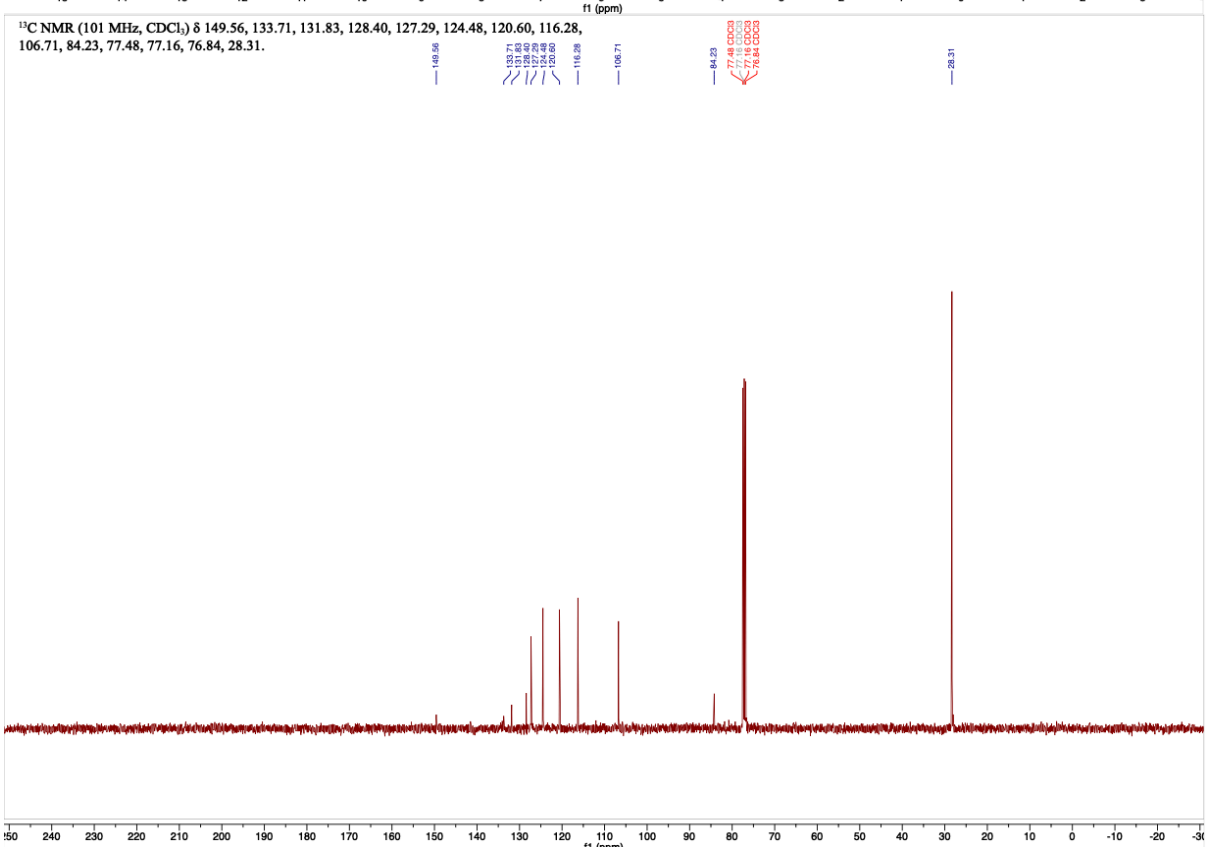


Fig. S1 The crystal structure of **2d** (50% probability ellipsoids).

8. NMR Spectra

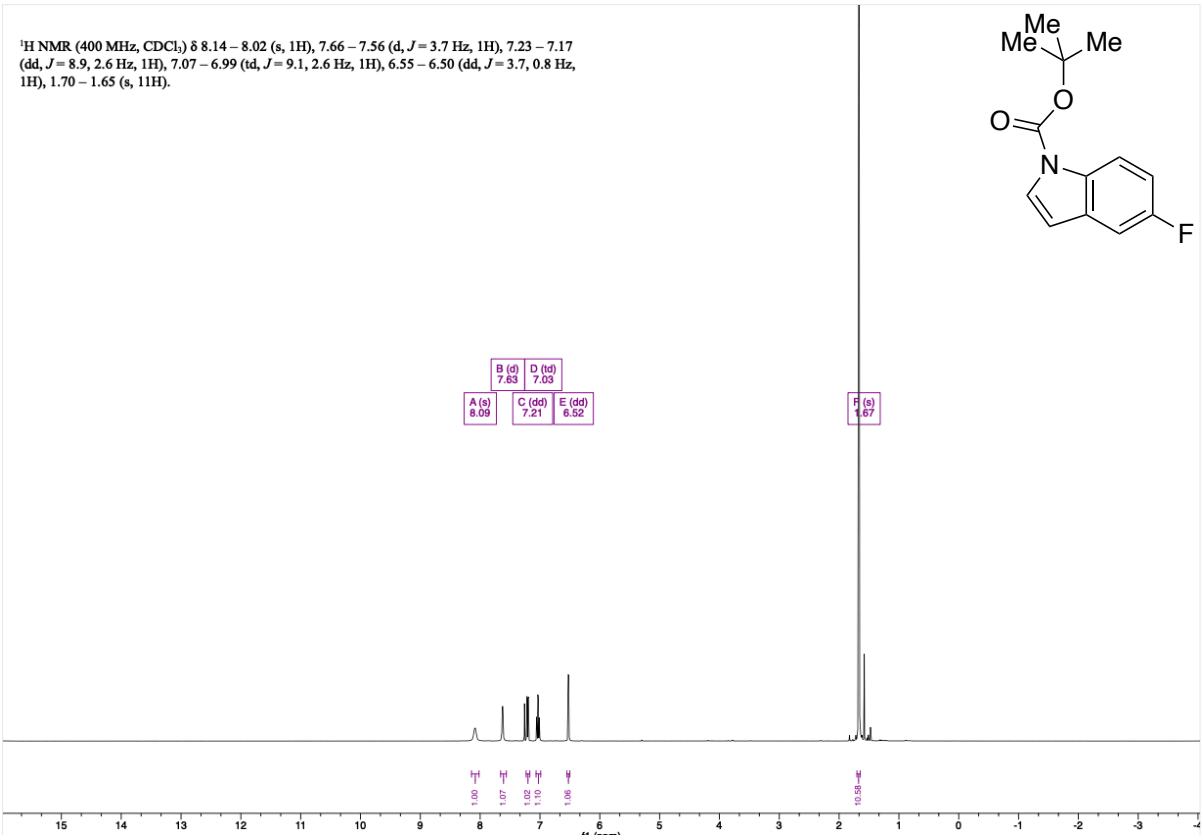
tert-Butyl 5-chloro-1*H*-indole-1-carboxylate, 1b



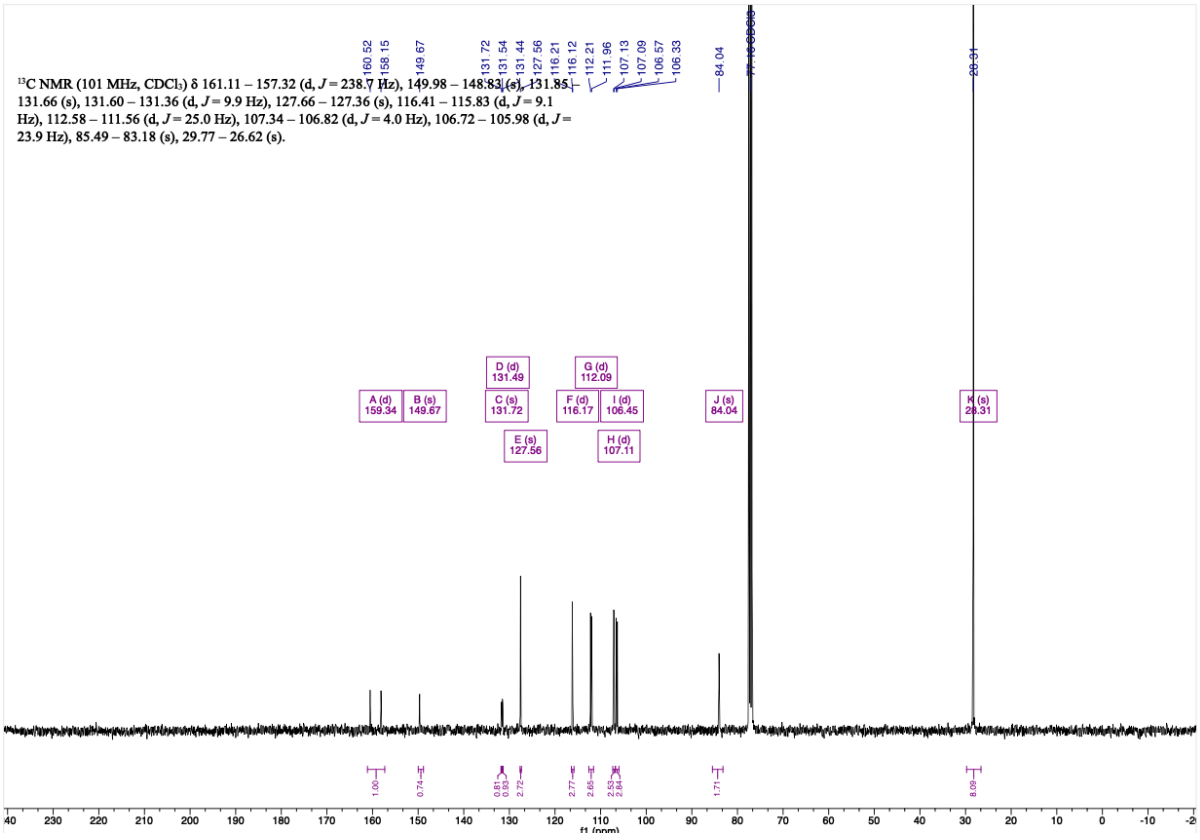


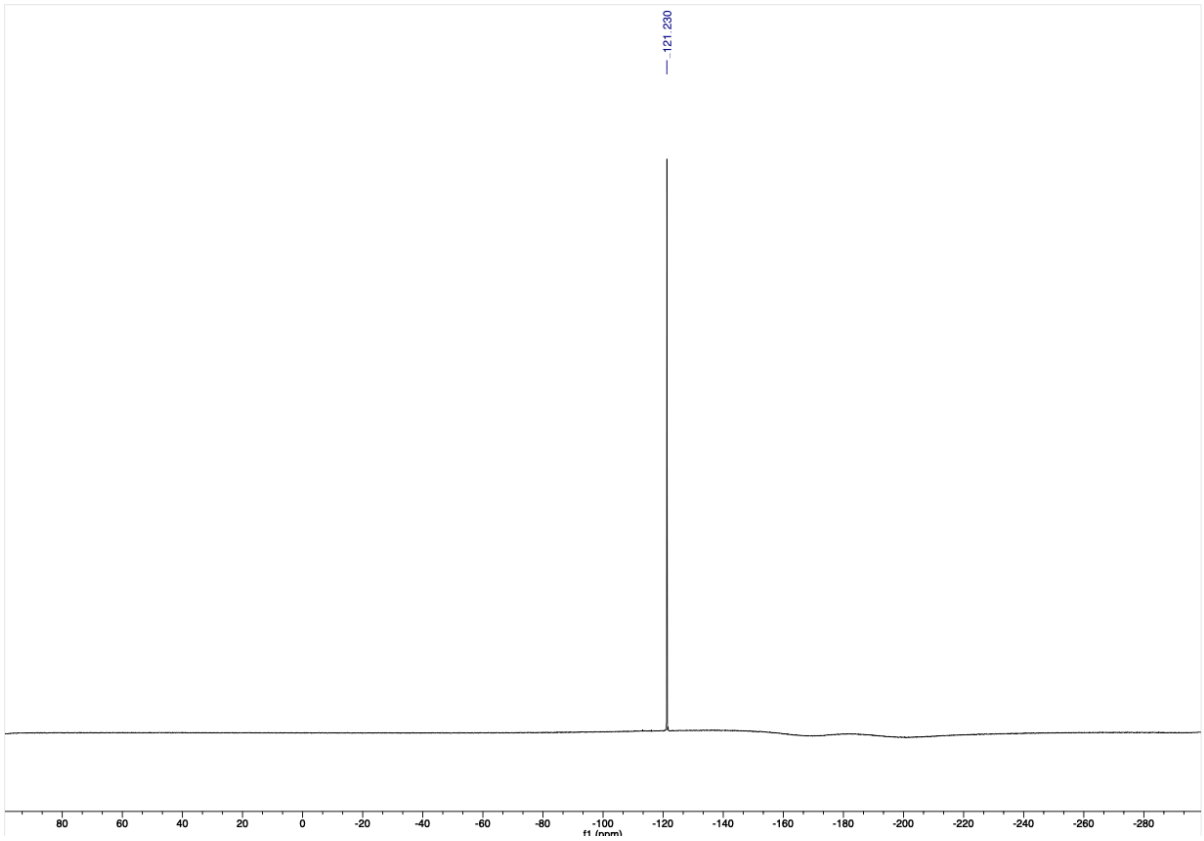
tert-Butyl 5-fluoro-1*H*-indole-1-carboxylate, 1c

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.02 (s, 1H), 7.66 – 7.56 (d, *J* = 3.7 Hz, 1H), 7.23 – 7.17 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.07 – 6.99 (td, *J* = 9.1, 2.6 Hz, 1H), 6.55 – 6.50 (dd, *J* = 3.7, 0.8 Hz, 1H), 1.70 – 1.65 (s, 11H).



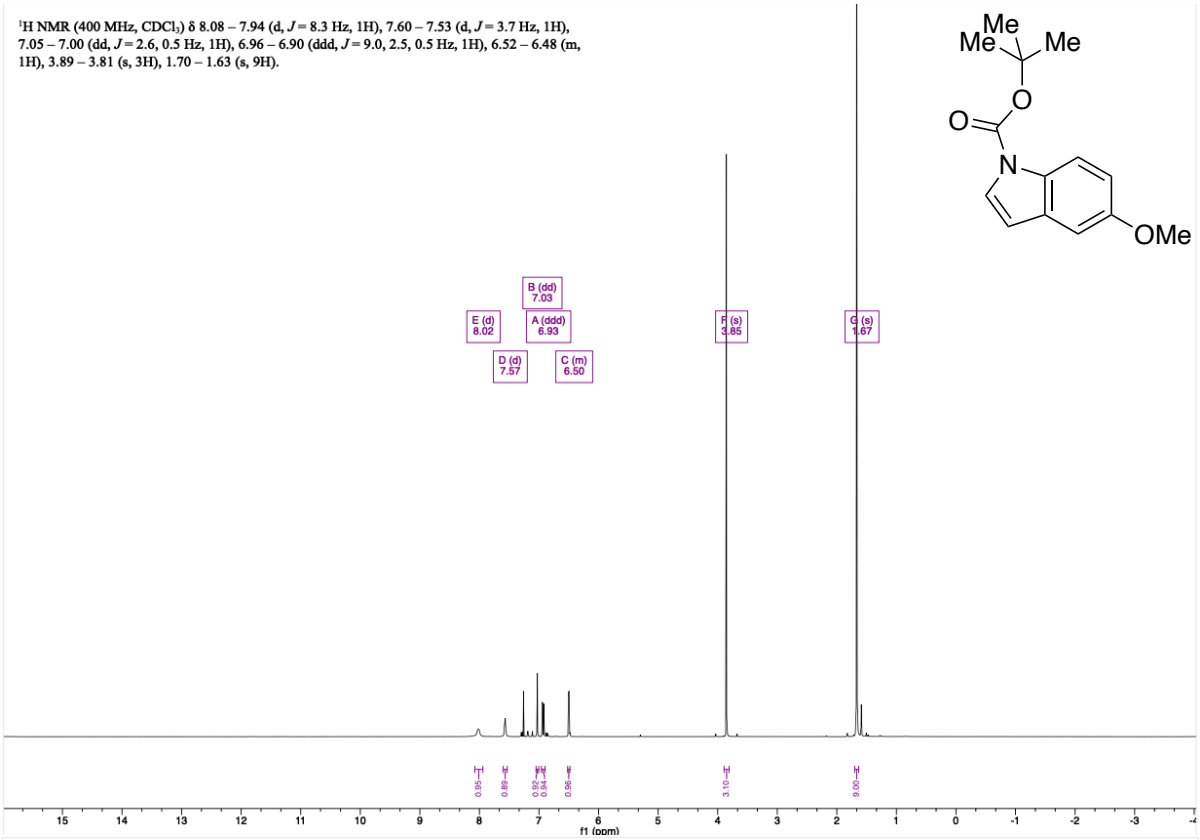
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.11 – 157.32 (d, *J* = 238.7 Hz), 149.98 – 148.83 (s), 131.85 – 131.66 (s), 131.60 – 131.36 (d, *J* = 9.9 Hz), 127.66 – 127.36 (s), 116.41 – 115.83 (d, *J* = 9.1 Hz), 112.58 – 111.56 (d, *J* = 25.0 Hz), 107.34 – 106.82 (d, *J* = 4.0 Hz), 106.72 – 105.98 (d, *J* = 23.9 Hz), 85.49 – 83.18 (s), 29.77 – 26.62 (s).

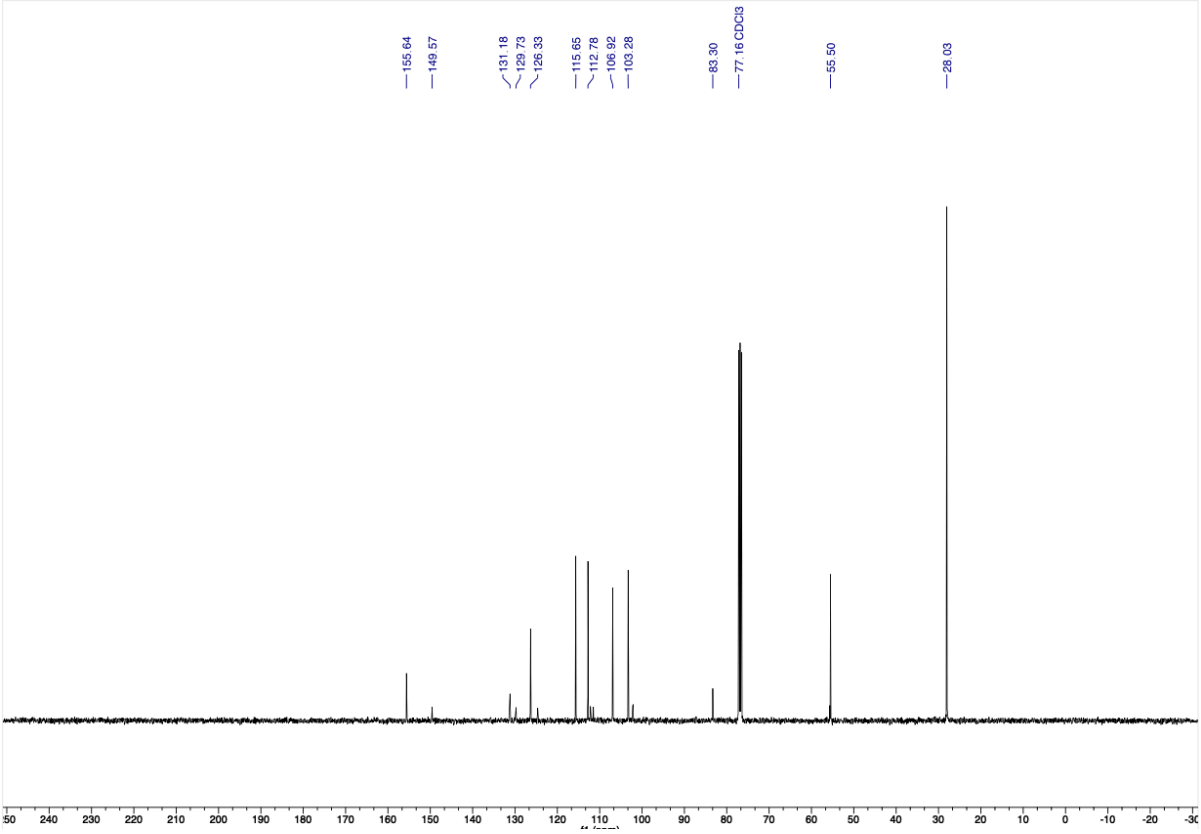



-121.230
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
f1 (ppm)

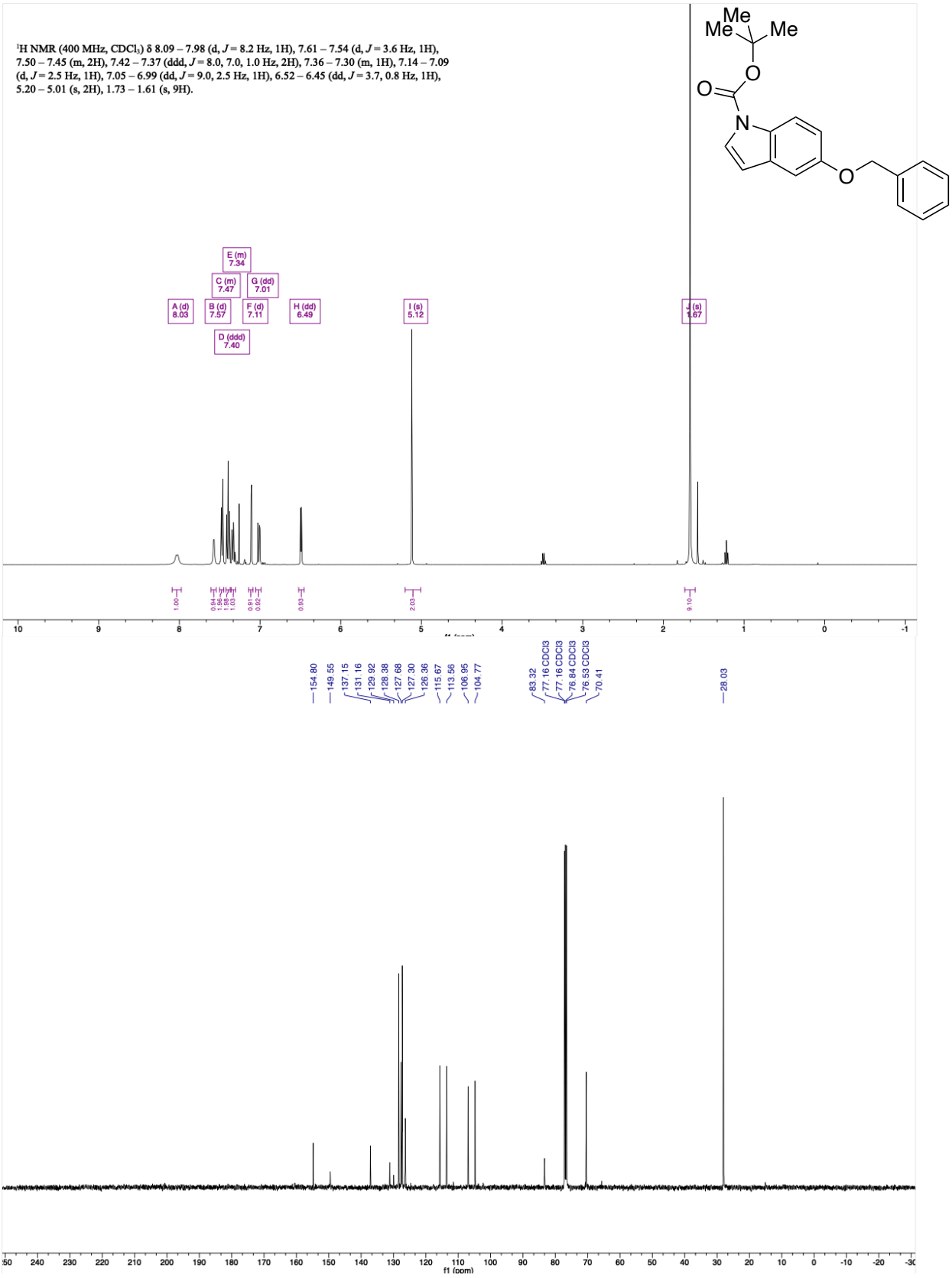
tert-Butyl 5-methoxy-1*H*-indole-1-carboxylate, 1d

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.94 (d, *J* = 8.3 Hz, 1H), 7.60 – 7.53 (d, *J* = 3.7 Hz, 1H), 7.05 – 7.00 (dd, *J* = 2.6, 0.5 Hz, 1H), 6.96 – 6.90 (ddd, *J* = 9.0, 2.5, 0.5 Hz, 1H), 6.52 – 6.48 (m, 1H), 3.89 – 3.81 (s, 3H), 1.70 – 1.63 (s, 9H).



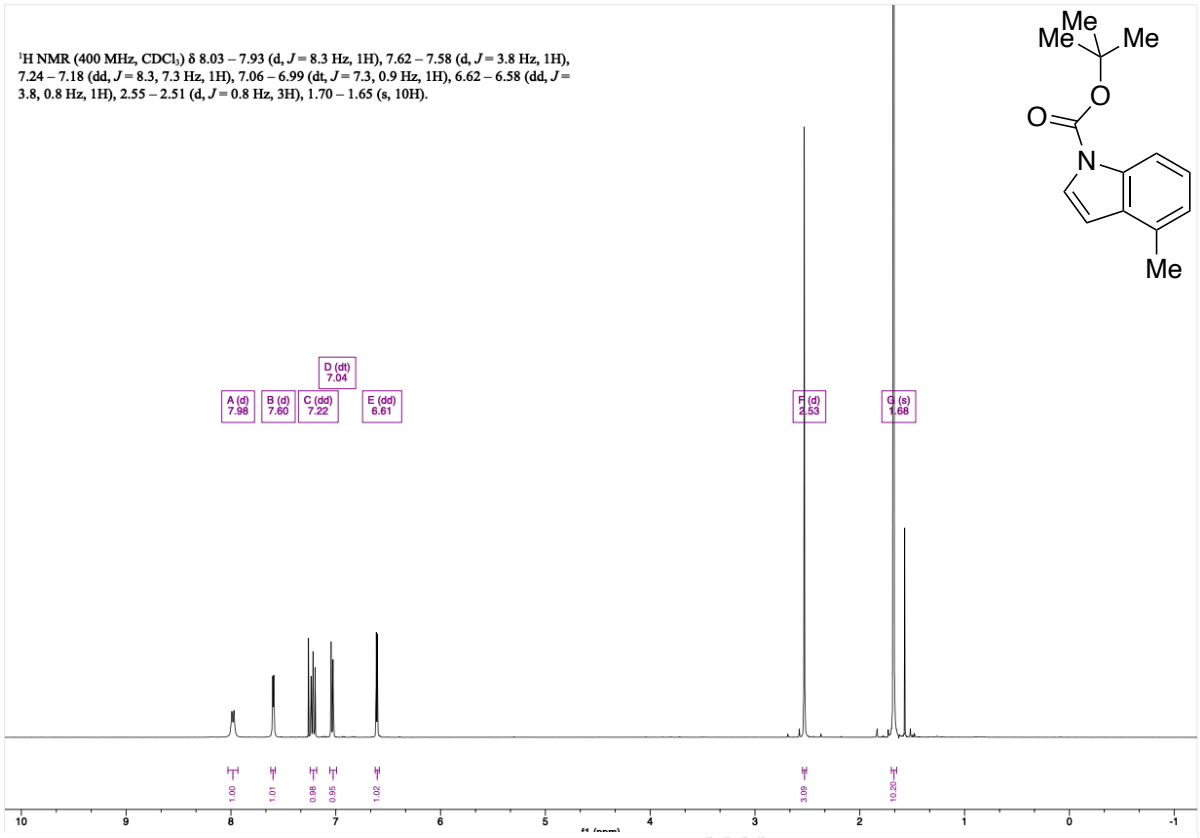


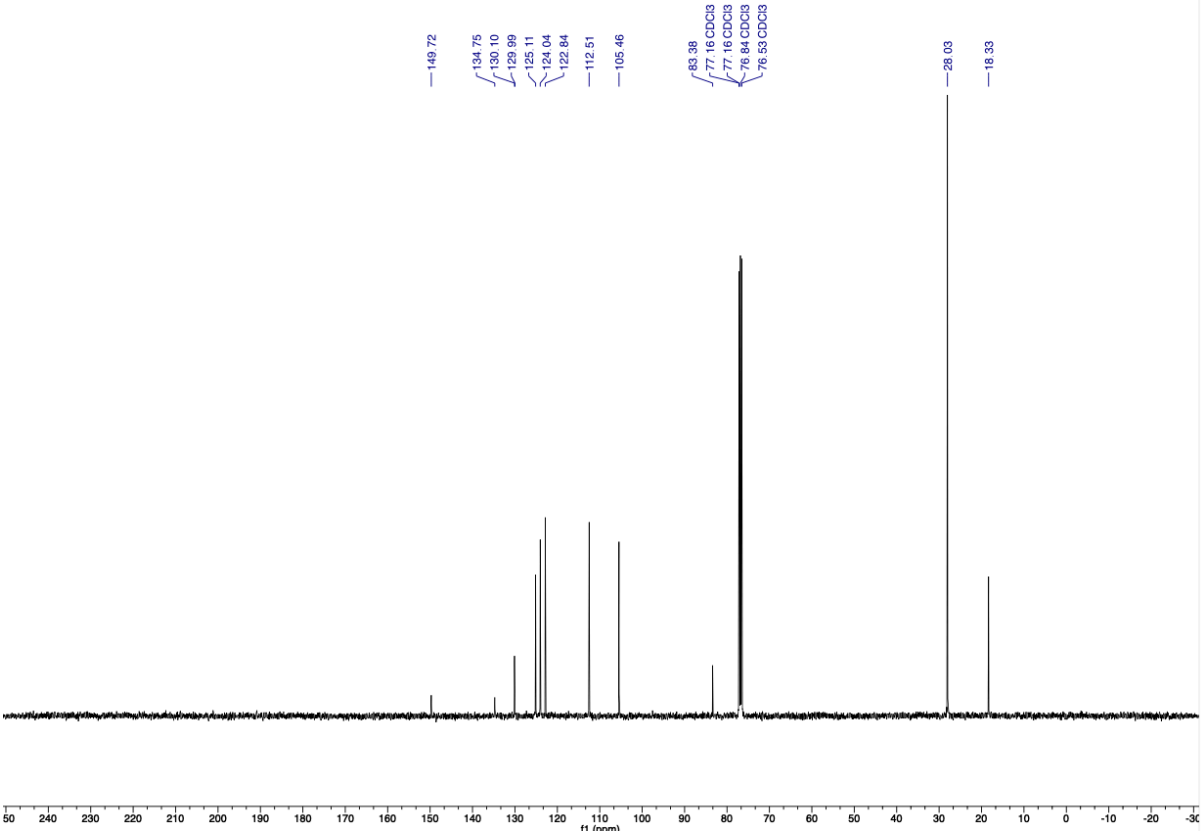
tert-Butyl 5-(benzyloxy)-1*H*-indole-1-carboxylate, 1e



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 7.98 (d, *J* = 8.2 Hz, 1H), 7.61 – 7.54 (d, *J* = 3.6 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.42 – 7.37 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 2H), 7.36 – 7.30 (m, 1H), 7.14 – 7.09 (d, *J* = 2.5 Hz, 1H), 7.05 – 6.99 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.52 – 6.45 (dd, *J* = 3.7, 0.8 Hz, 1H), 5.20 – 5.01 (s, 2H), 1.73 – 1.61 (s, 9H).

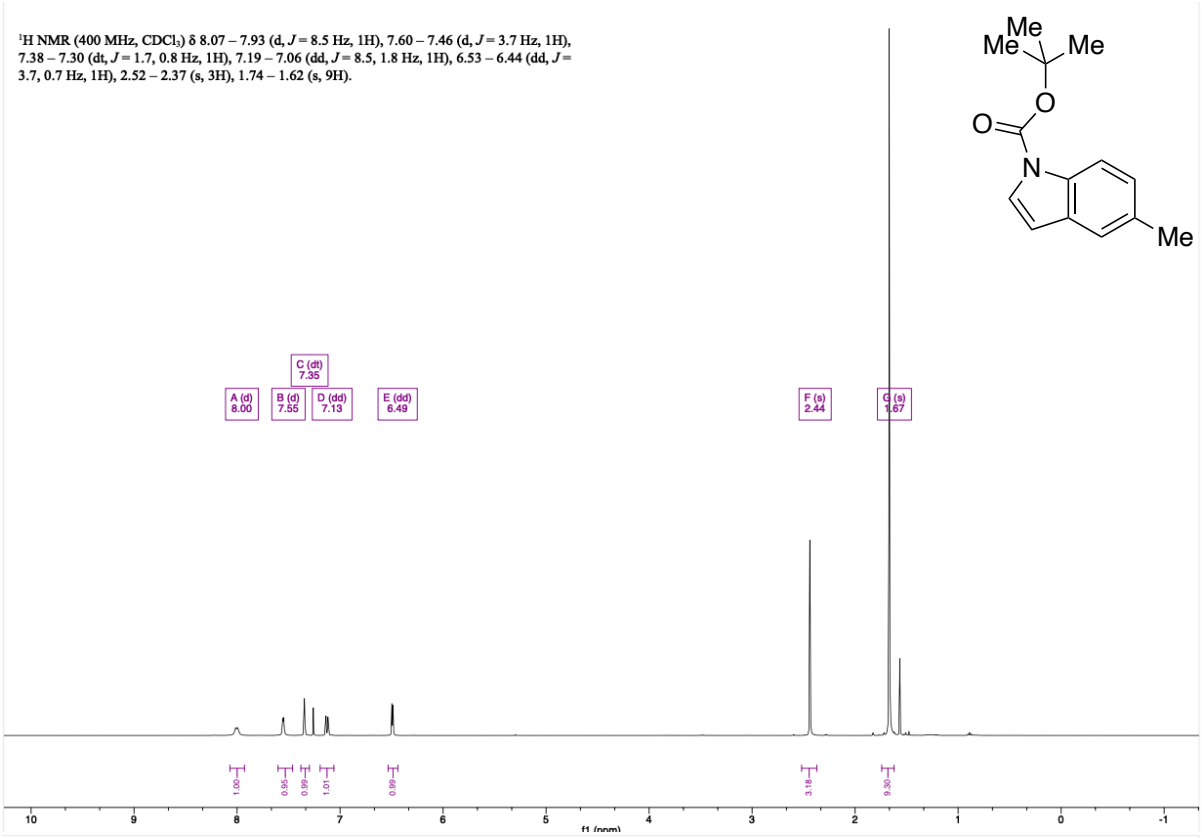
tert-Butyl 4-methyl-1*H*-indole-1-carboxylate, 1f

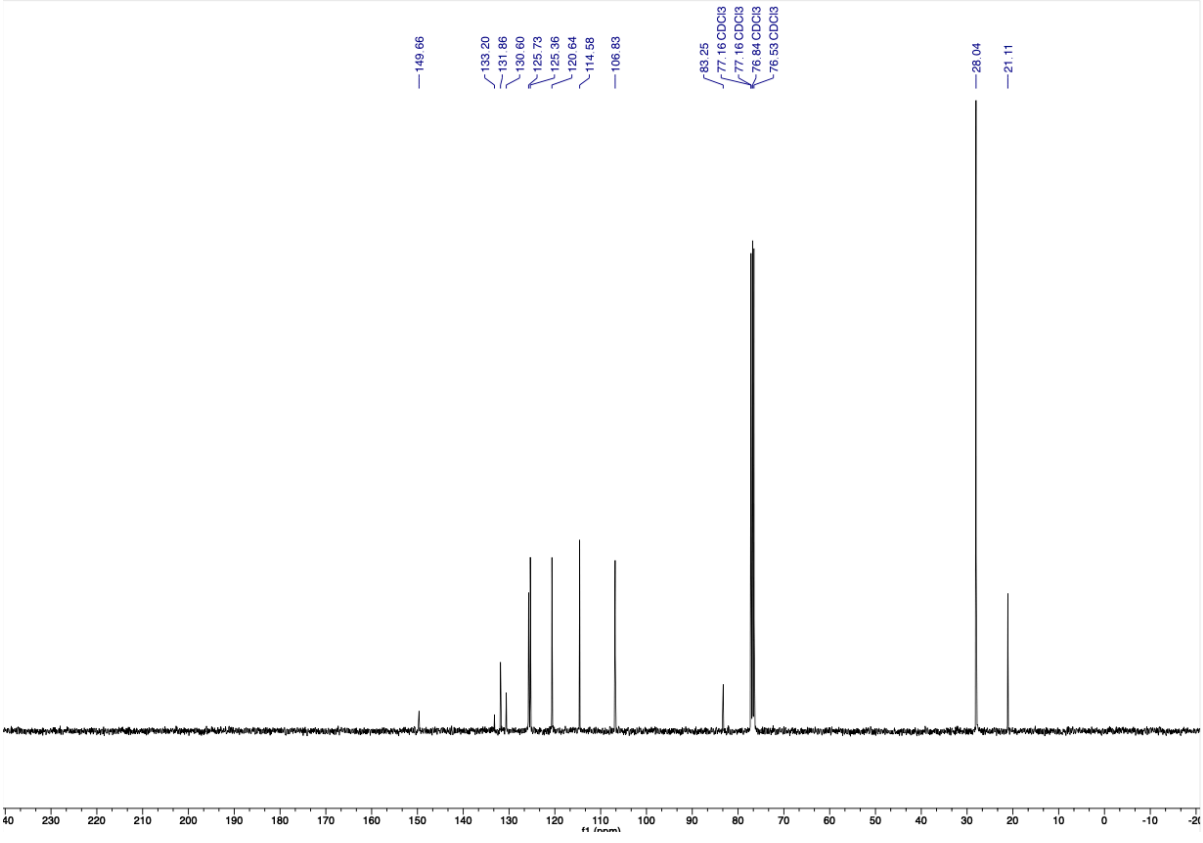




tert-Butyl 5-methyl-1*H*-indole-1-carboxylate, 1g

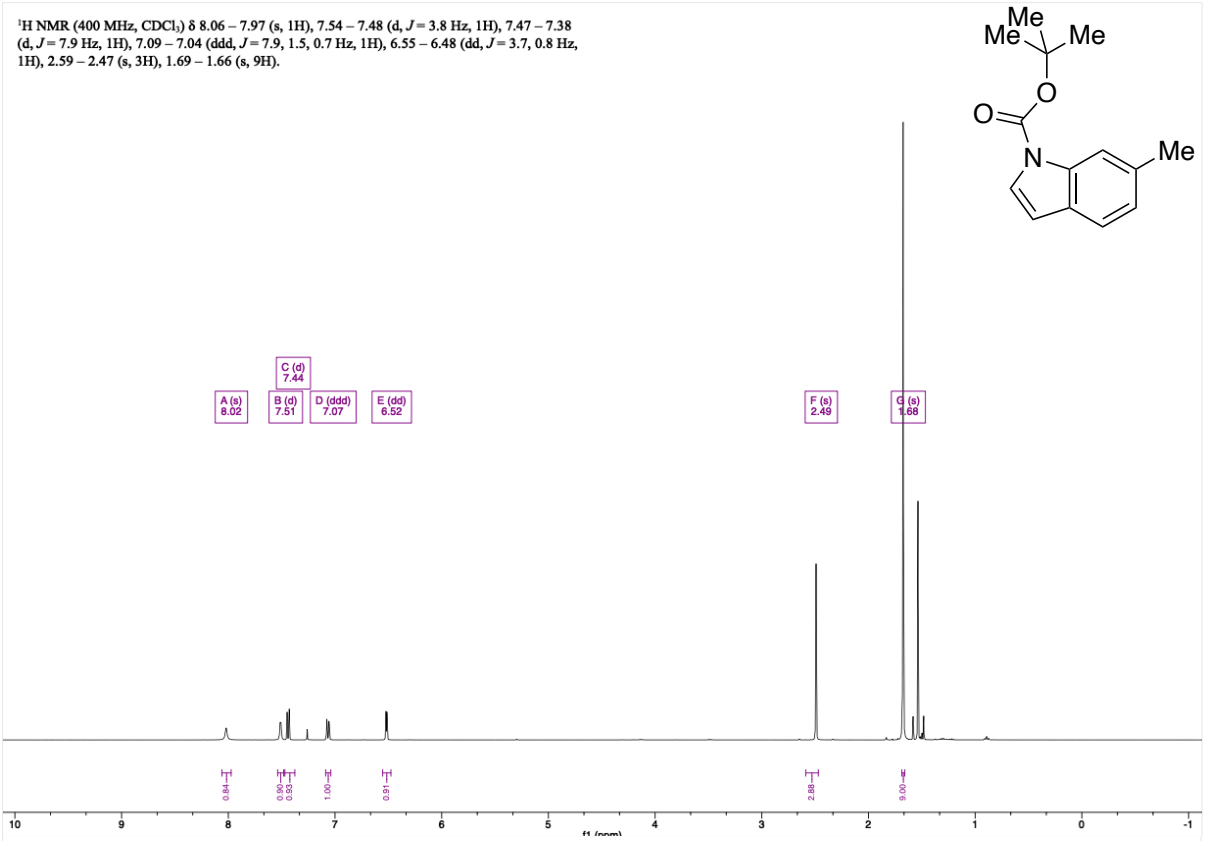
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.93 (d, *J* = 8.5 Hz, 1H), 7.60 – 7.46 (d, *J* = 3.7 Hz, 1H), 7.38 – 7.30 (dt, *J* = 1.7, 0.8 Hz, 1H), 7.19 – 7.06 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.53 – 6.44 (dd, *J* = 3.7, 0.7 Hz, 1H), 2.52 – 2.37 (s, 3H), 1.74 – 1.62 (s, 9H).

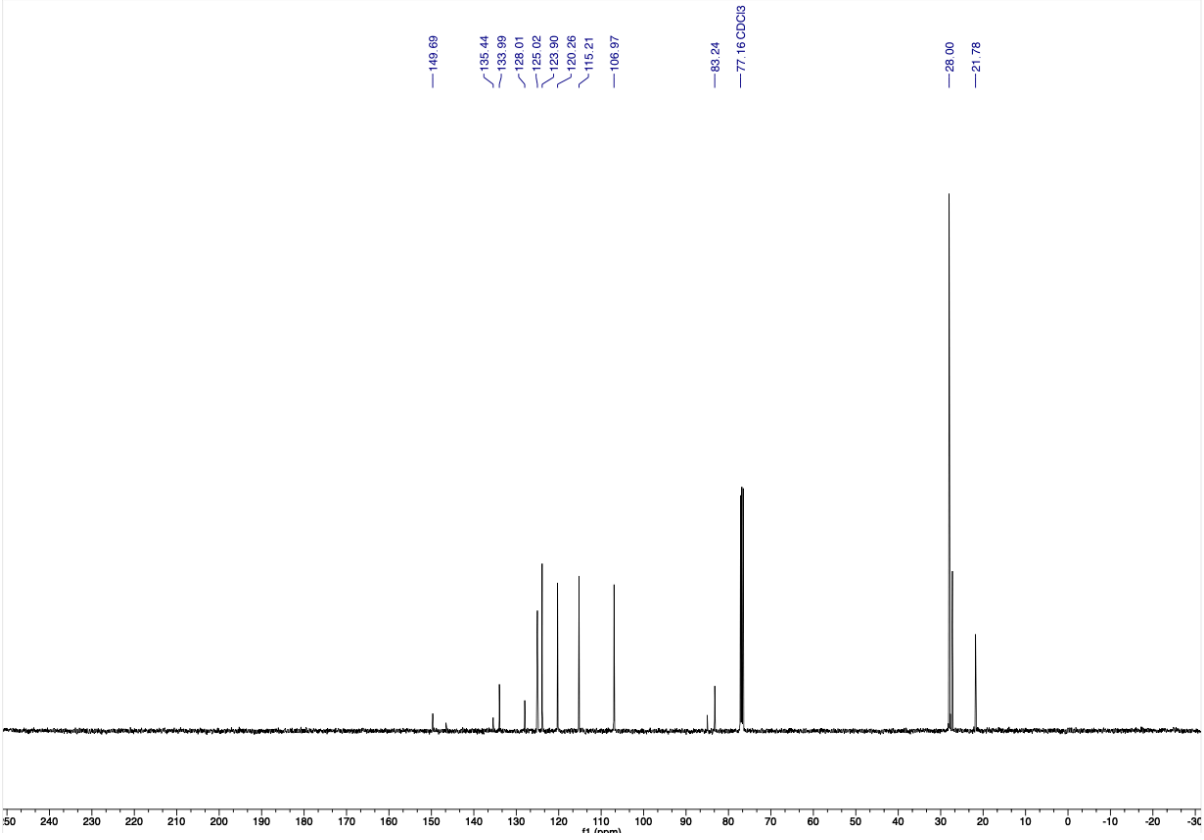




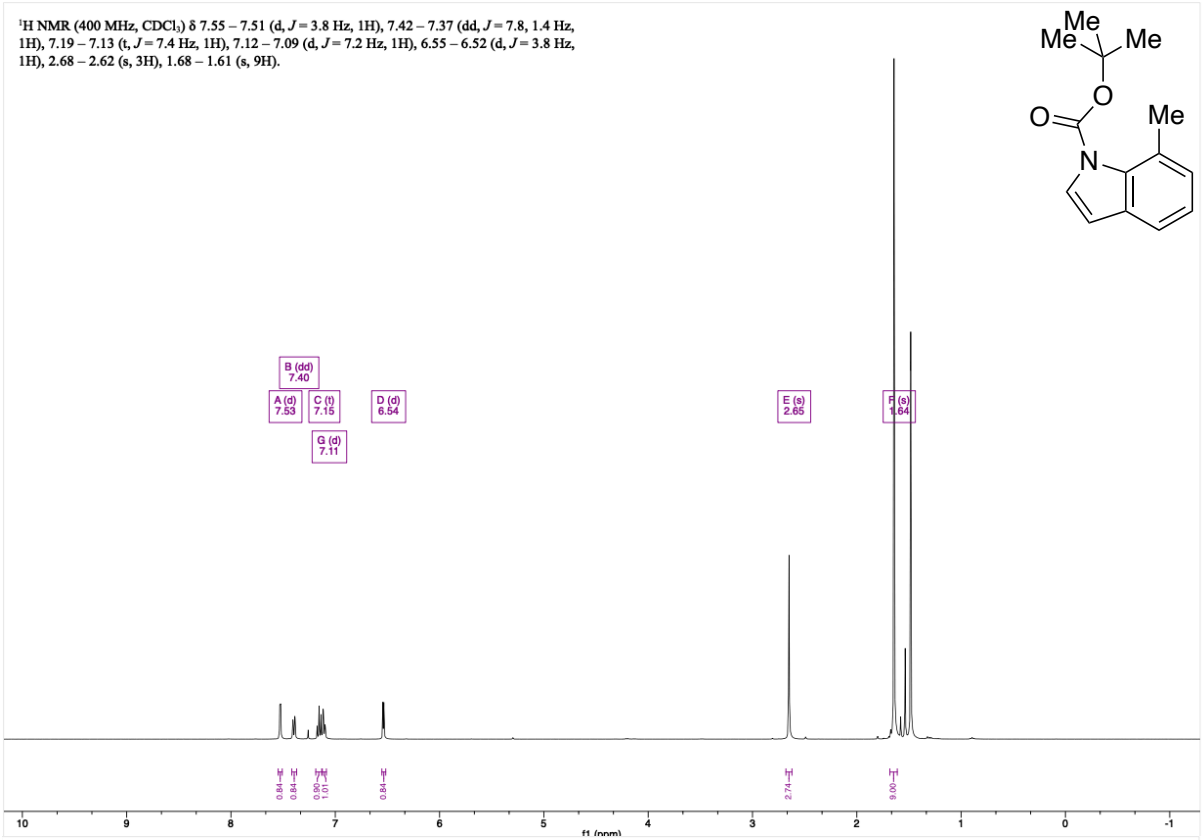
tert-Butyl 6-methyl-1*H*-indole-1-carboxylate, 1h

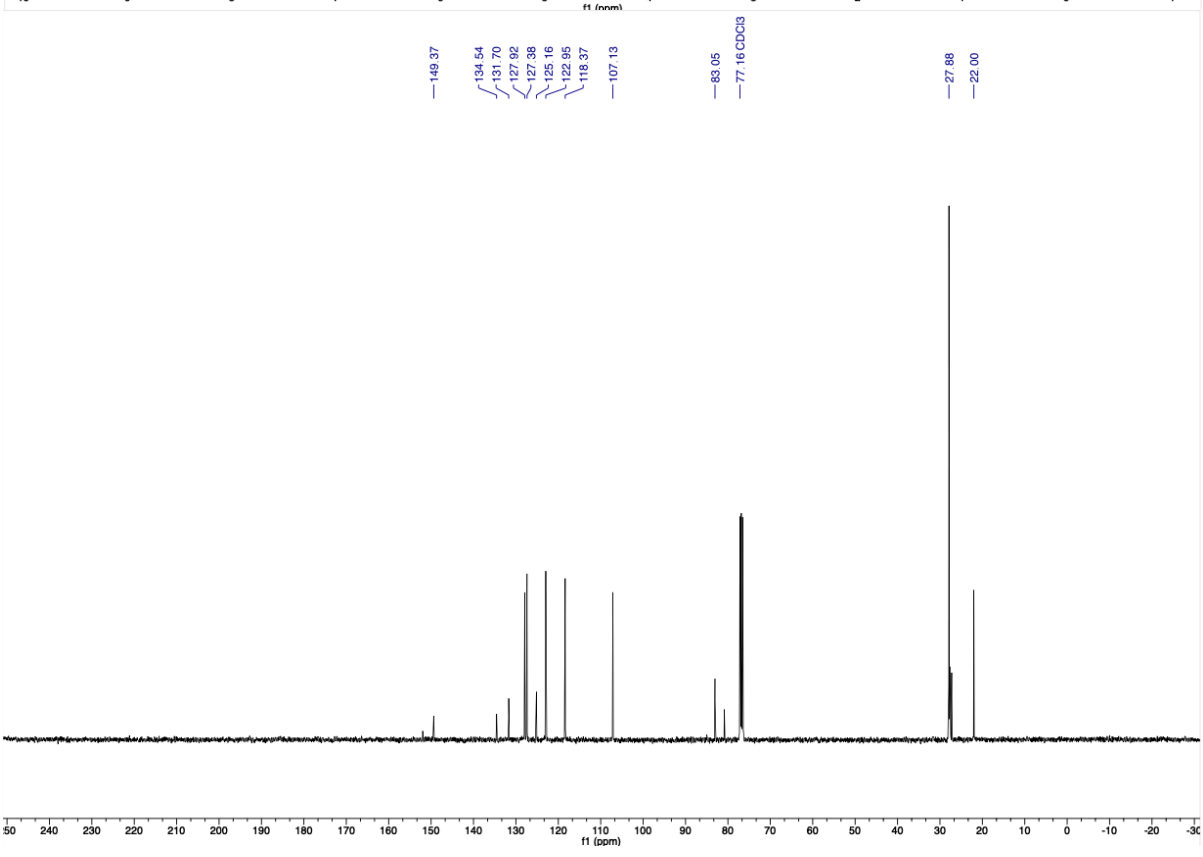
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.97 (s, 1H), 7.54 – 7.48 (d, *J* = 3.8 Hz, 1H), 7.47 – 7.38 (d, *J* = 7.9 Hz, 1H), 7.09 – 7.04 (ddd, *J* = 7.9, 1.5, 0.7 Hz, 1H), 6.55 – 6.48 (dd, *J* = 3.7, 0.8 Hz, 1H), 2.59 – 2.47 (s, 3H), 1.69 – 1.66 (s, 9H).





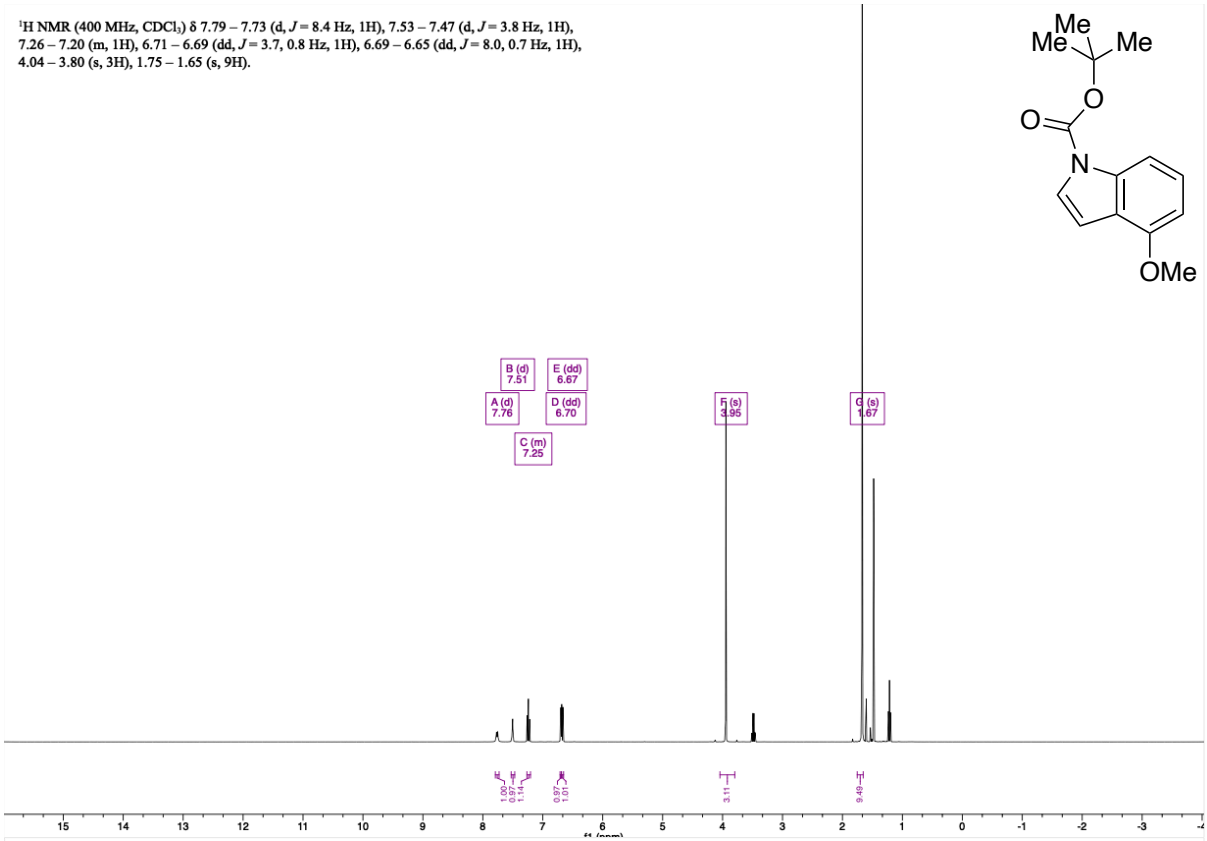
tert-Butyl 7-methyl-1*H*-indole-1-carboxylate, 1i

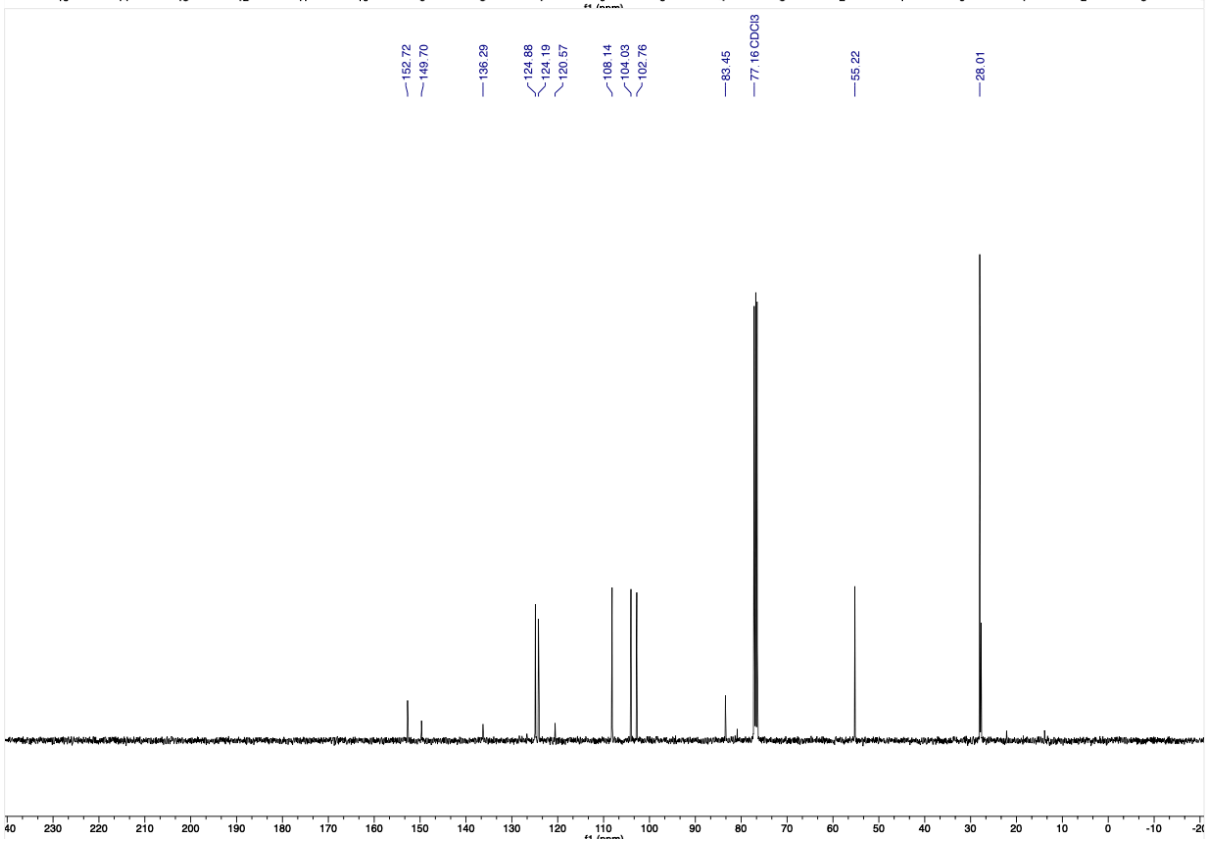




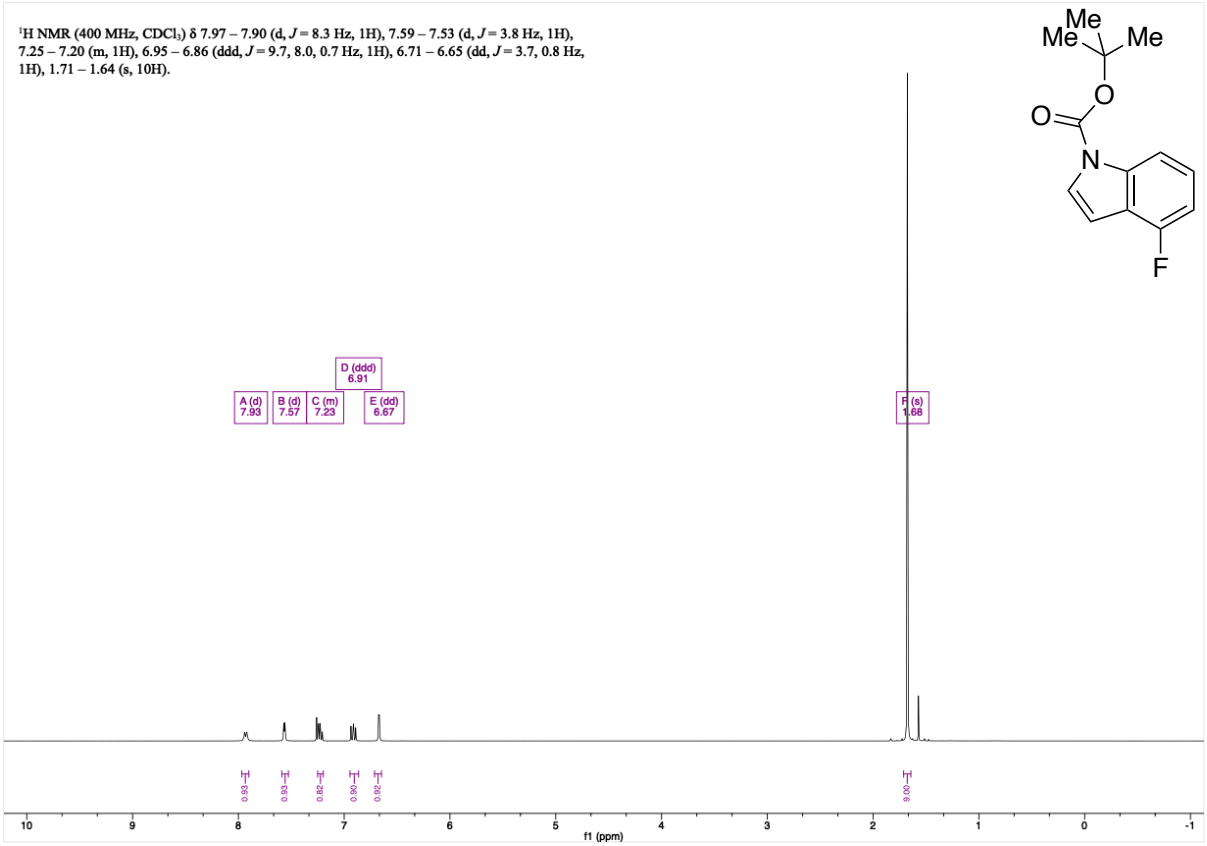
tert-Butyl 4-methoxy-1*H*-indole-1-carboxylate, 1j

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.73 (d, *J* = 8.4 Hz, 1H), 7.53 – 7.47 (d, *J* = 3.8 Hz, 1H), 7.26 – 7.20 (m, 1H), 6.71 – 6.69 (dd, *J* = 3.7, 0.8 Hz, 1H), 6.69 – 6.65 (dd, *J* = 8.0, 0.7 Hz, 1H), 4.04 – 3.80 (s, 3H), 1.75 – 1.65 (s, 9H).

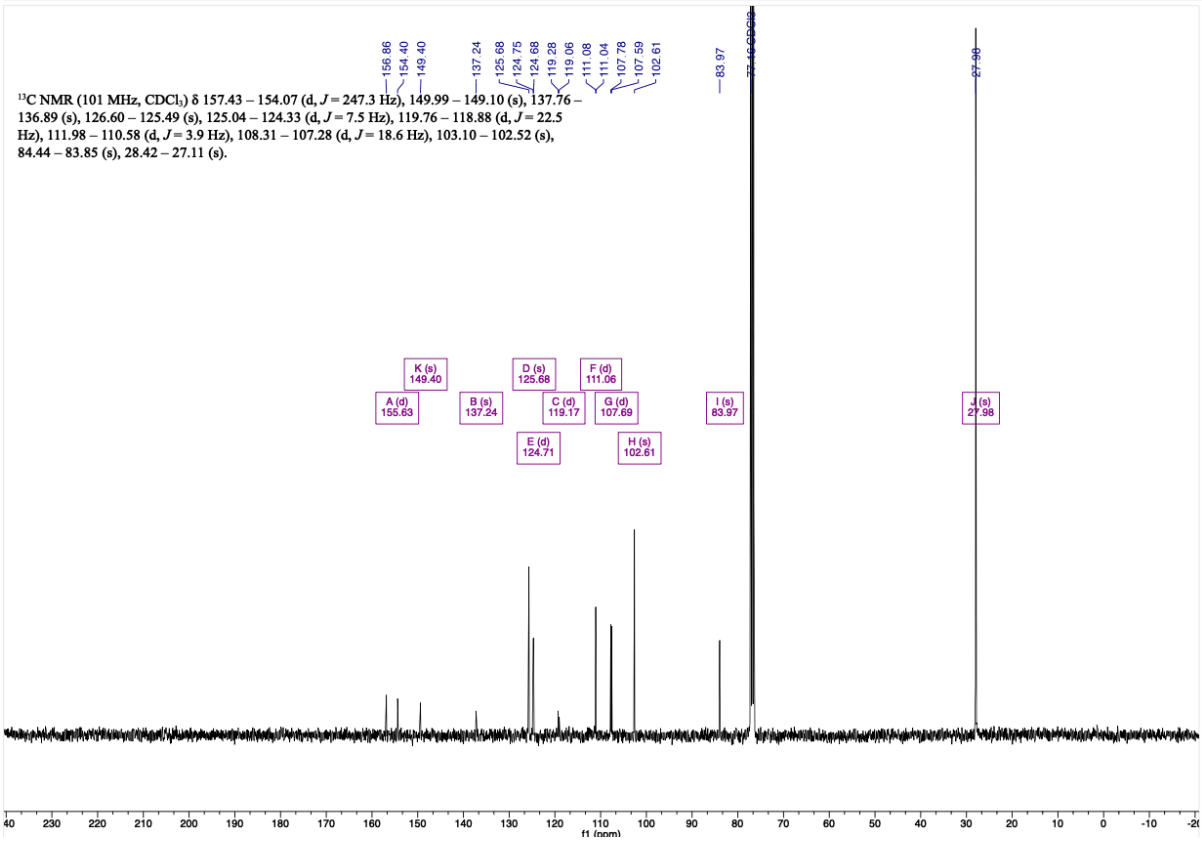




tert-Butyl 4-fluoro-1*H*-indole-1-carboxylate, 1k

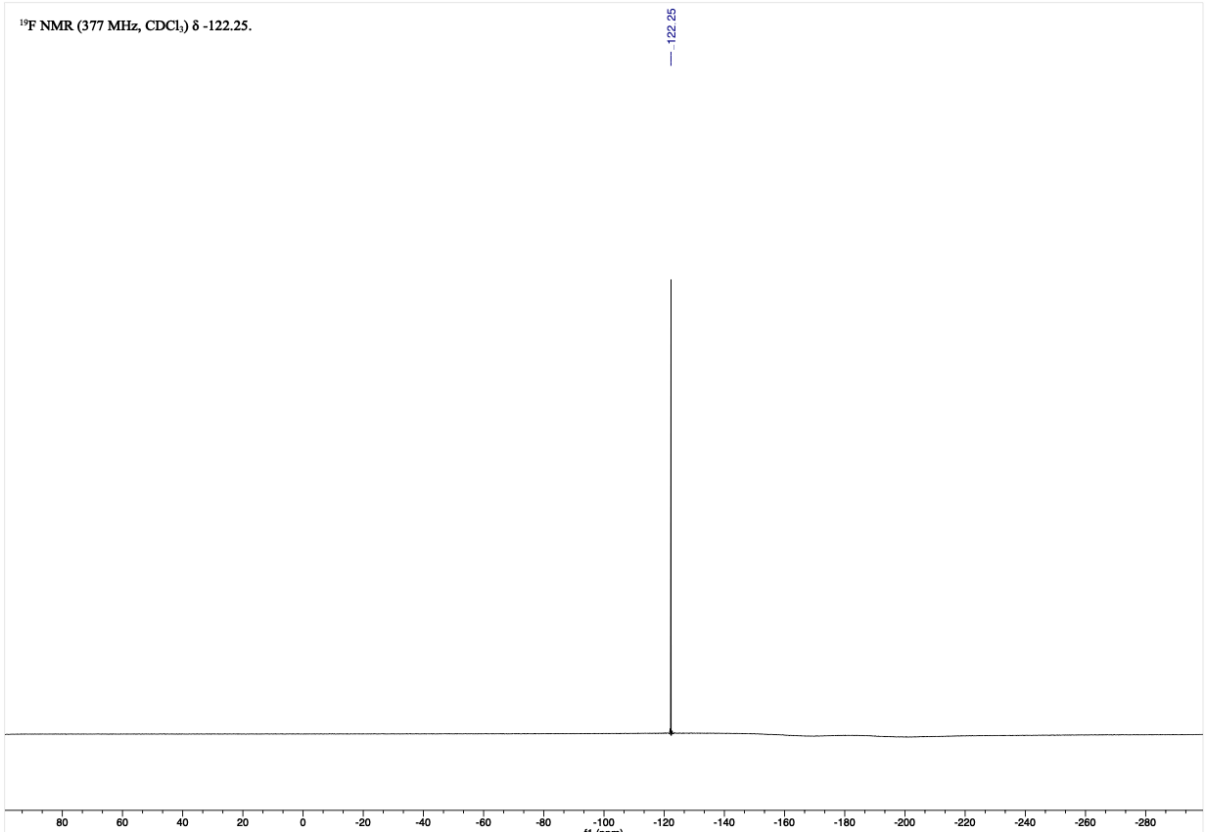


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.90 (d, J = 8.3 Hz, 1H), 7.59 – 7.53 (d, J = 3.8 Hz, 1H), 7.25 – 7.20 (m, 1H), 6.95 – 6.86 (ddd, J = 9.7, 8.0, 0.7 Hz, 1H), 6.71 – 6.65 (dd, J = 3.7, 0.8 Hz, 1H), 1.71 – 1.64 (s, 10H).



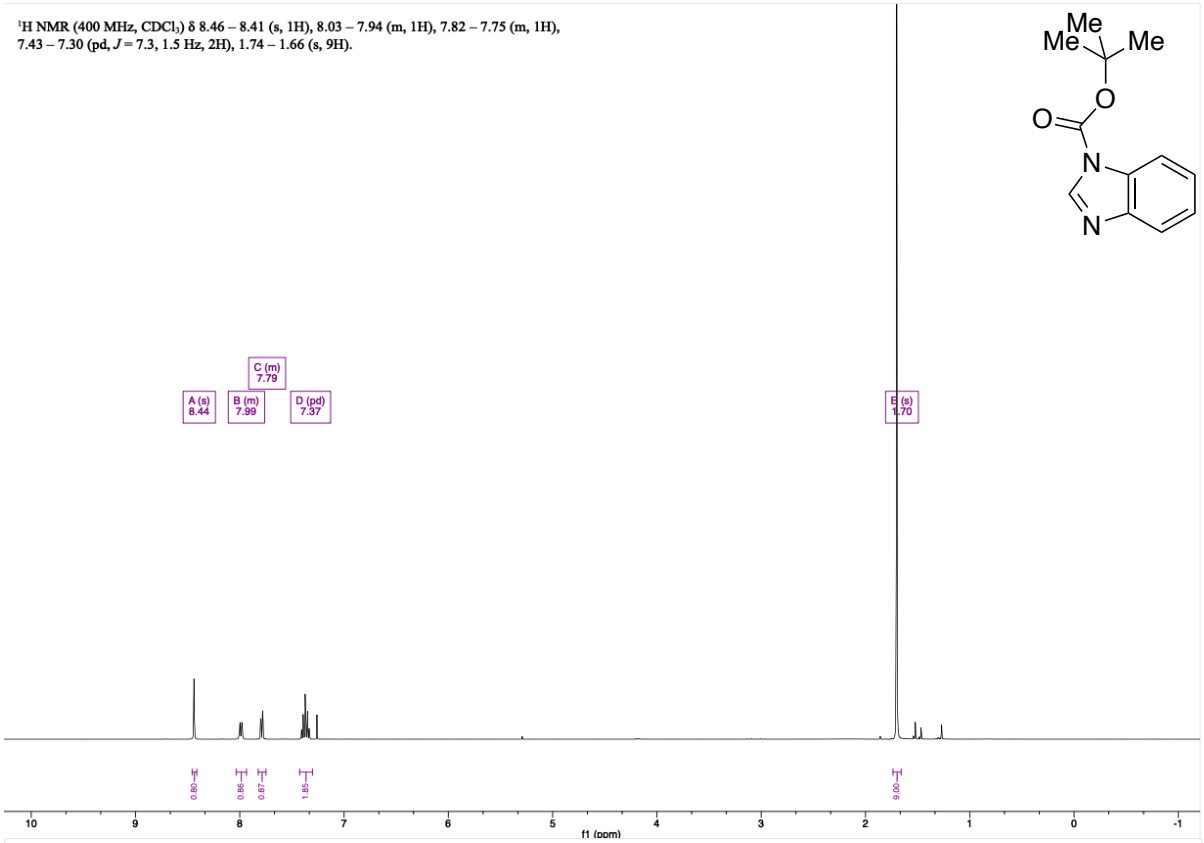
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.43 – 154.07 (d, J = 247.3 Hz), 149.99 – 149.10 (s), 137.76 – 136.89 (s), 126.60 – 125.49 (s), 125.04 – 124.33 (d, J = 7.5 Hz), 119.76 – 118.88 (d, J = 22.5 Hz), 111.98 – 110.58 (d, J = 3.9 Hz), 108.31 – 107.28 (d, J = 18.6 Hz), 103.10 – 102.52 (s), 84.44 – 83.85 (s), 28.42 – 27.11 (s).

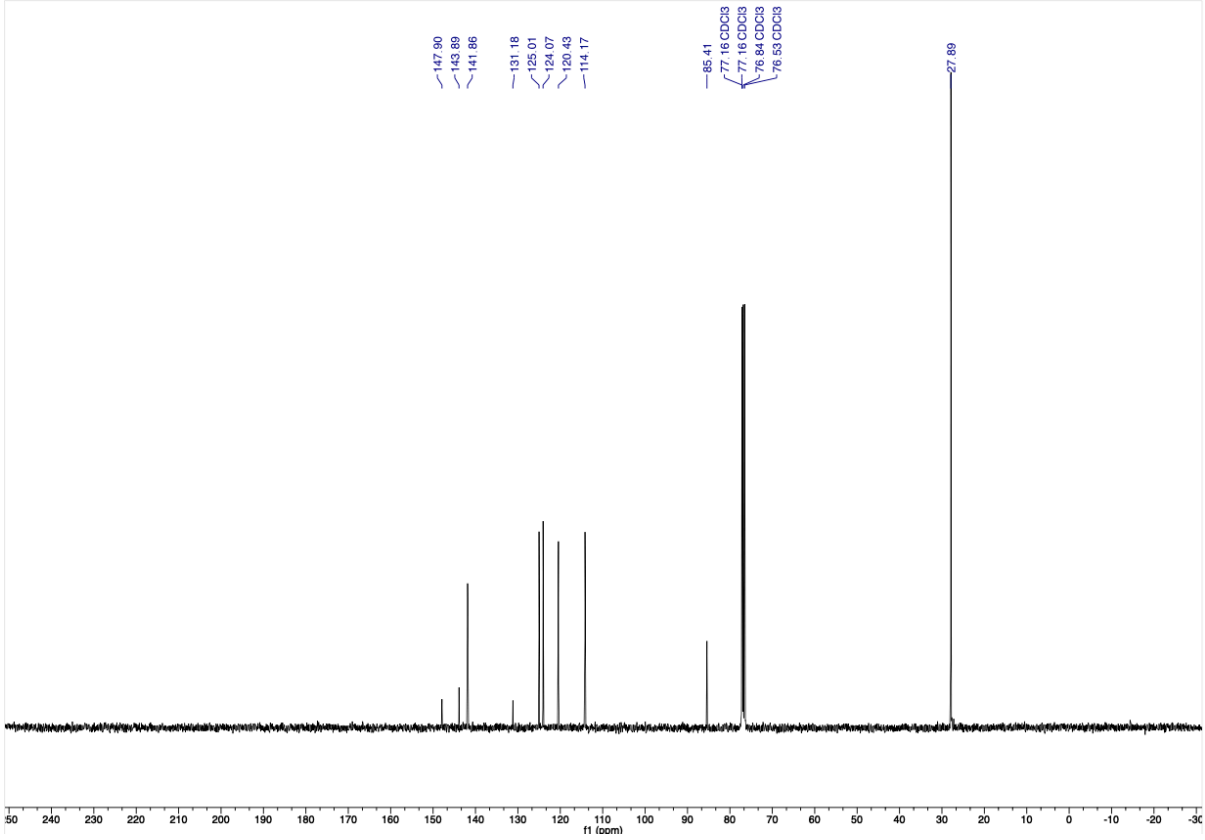
^{19}F NMR (377 MHz, $CDCl_3$) δ -122.25.



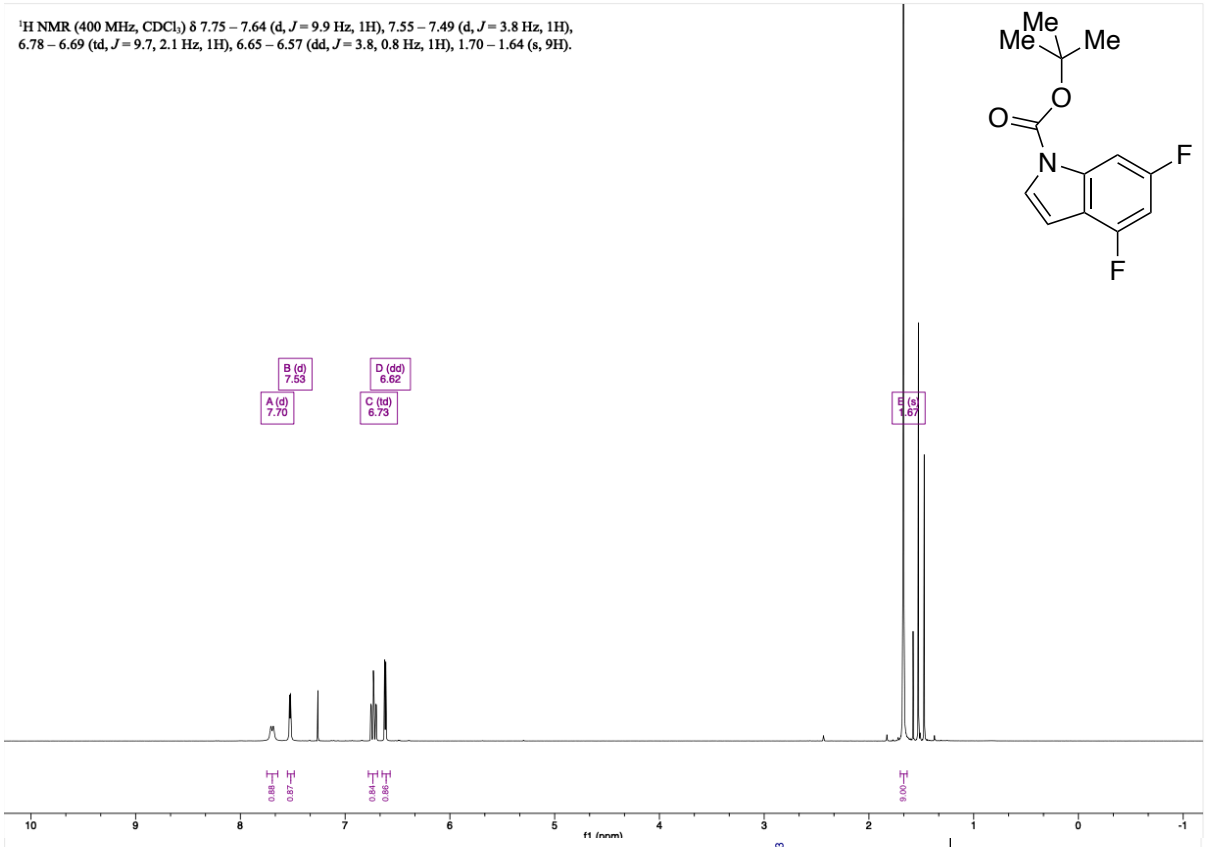
tert-Butyl 1*H*-benzo[*d*]imidazole-1-carboxylate, 1l

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 – 8.41 (s, 1H), 8.03 – 7.94 (m, 1H), 7.82 – 7.75 (m, 1H), 7.43 – 7.30 (pd, *J* = 7.3, 1.5 Hz, 2H), 1.74 – 1.66 (s, 9H).

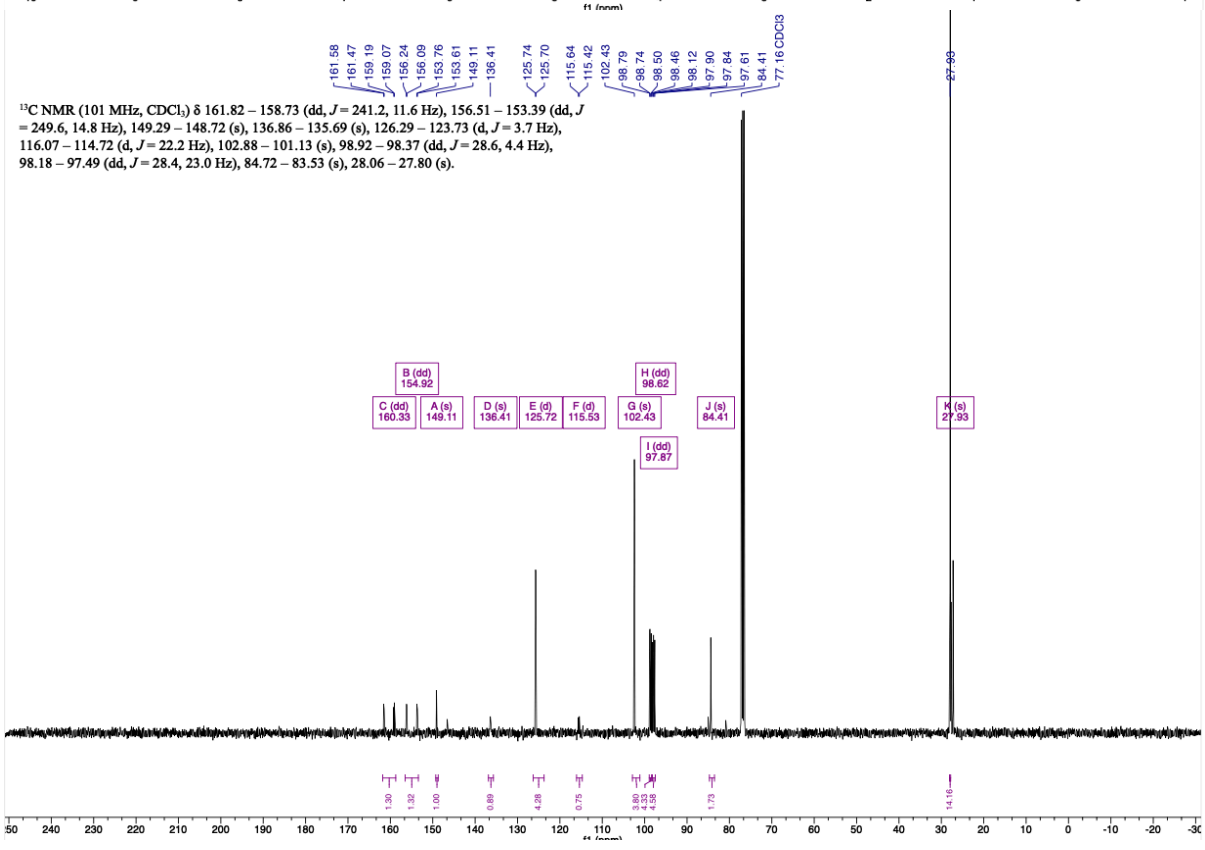




tert-Butyl 4,6-difluoro-1*H*-indole-1-carboxylate, 1m

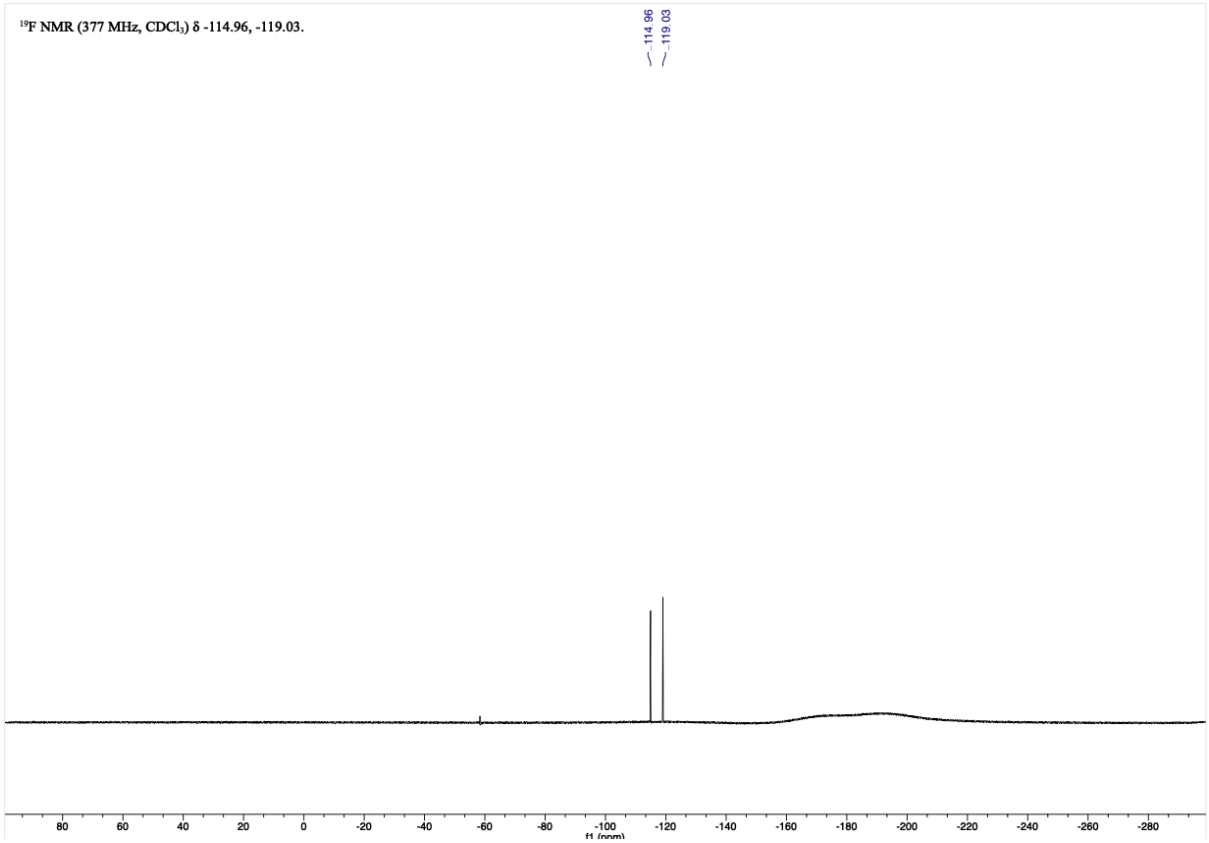


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.64 (d, J = 9.9 Hz, 1H), 7.55 – 7.49 (d, J = 3.8 Hz, 1H), 6.78 – 6.69 (td, J = 9.7, 2.1 Hz, 1H), 6.65 – 6.57 (dd, J = 3.8, 0.8 Hz, 1H), 1.70 – 1.64 (s, 9H).



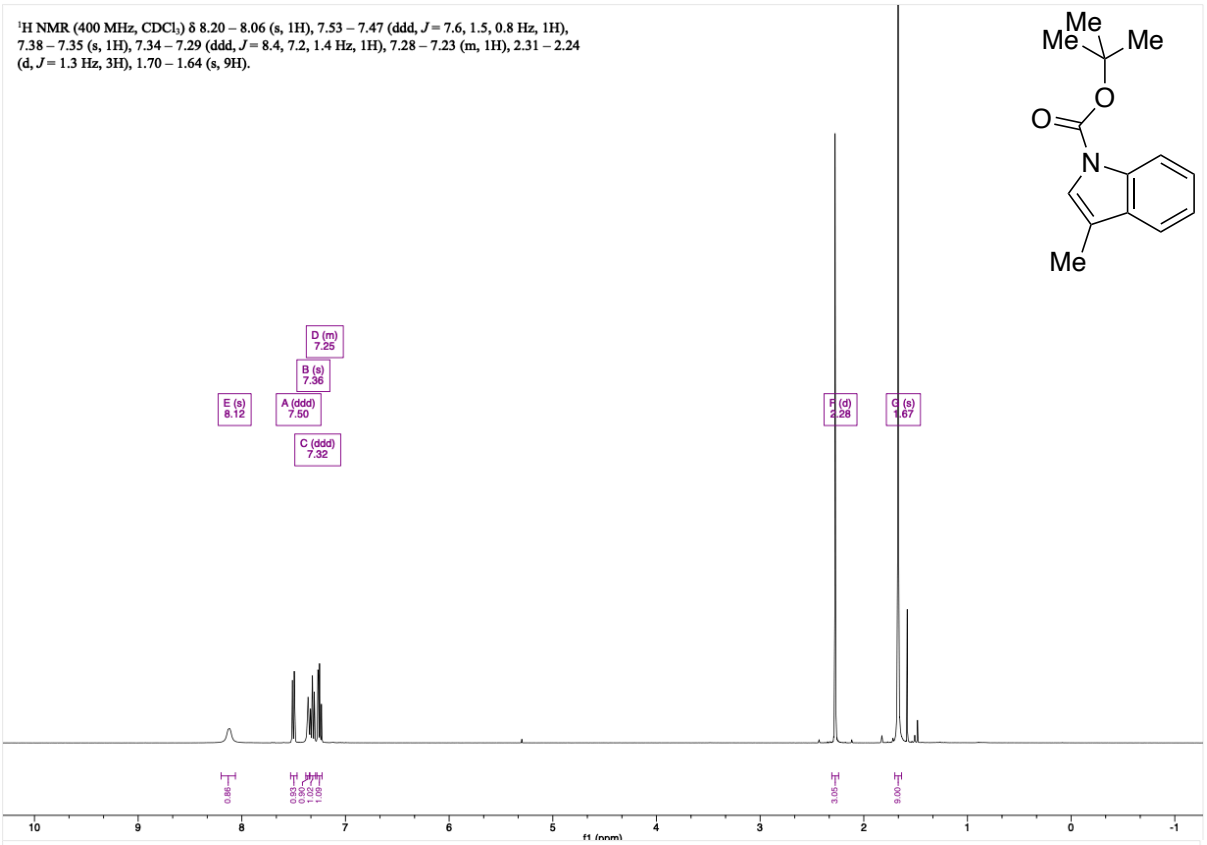
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.82 – 158.73 (dd, J = 241.2, 11.6 Hz), 156.51 – 153.39 (dd, J = 249.6, 14.8 Hz), 149.29 – 148.72 (s), 136.86 – 135.69 (s), 126.29 – 123.73 (d, J = 3.7 Hz), 116.07 – 114.72 (d, J = 22.2 Hz), 102.88 – 101.13 (s), 98.92 – 98.37 (dd, J = 28.6, 4.4 Hz), 98.18 – 97.49 (dd, J = 28.4, 23.0 Hz), 84.72 – 83.53 (s), 28.06 – 27.80 (s).

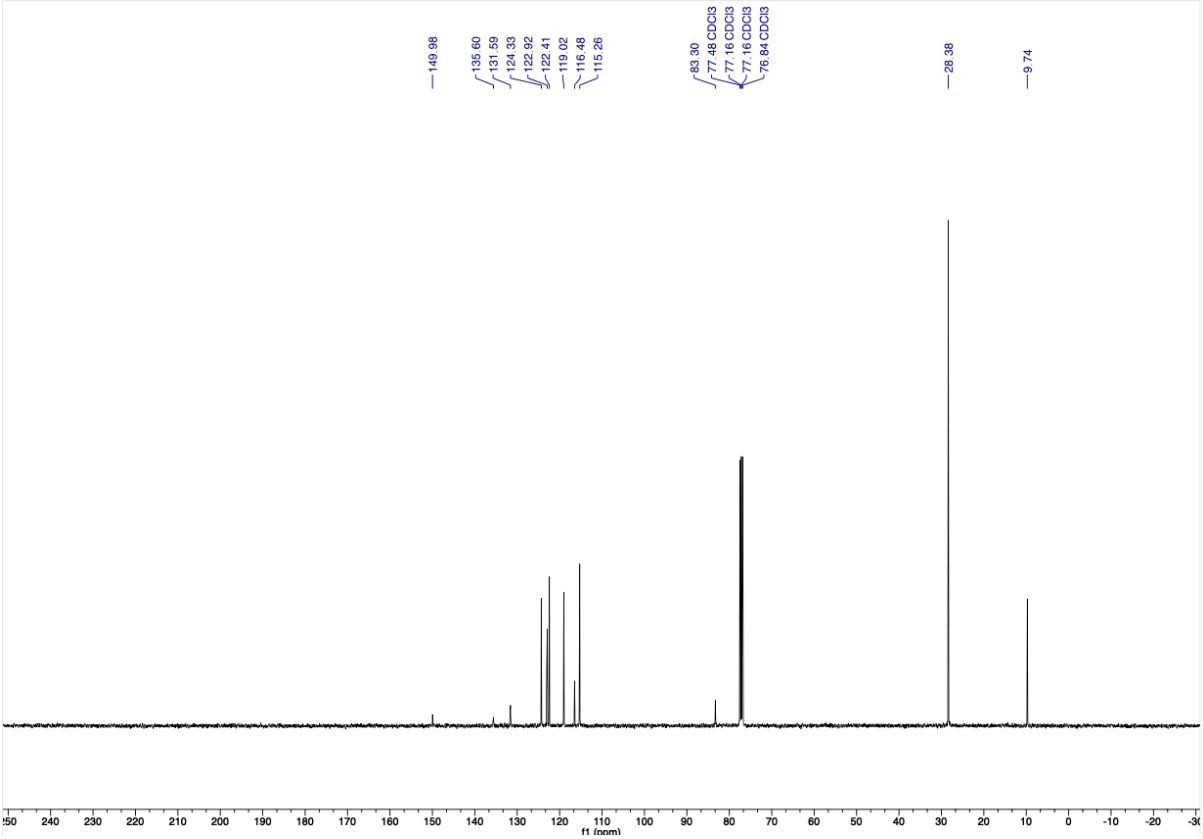
^{19}F NMR (377 MHz, $CDCl_3$) δ -114.96, -119.03.



tert-Butyl 3-methyl-1*H*-indole-1-carboxylate, 1n

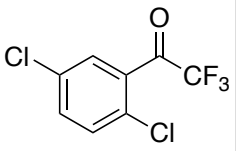
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.06 (s, 1H), 7.53 – 7.47 (ddd, *J* = 7.6, 1.5, 0.8 Hz, 1H), 7.38 – 7.35 (s, 1H), 7.34 – 7.29 (ddd, *J* = 8.4, 7.2, 1.4 Hz, 1H), 7.28 – 7.23 (m, 1H), 2.31 – 2.24 (d, *J* = 1.3 Hz, 3H), 1.70 – 1.64 (s, 9H).

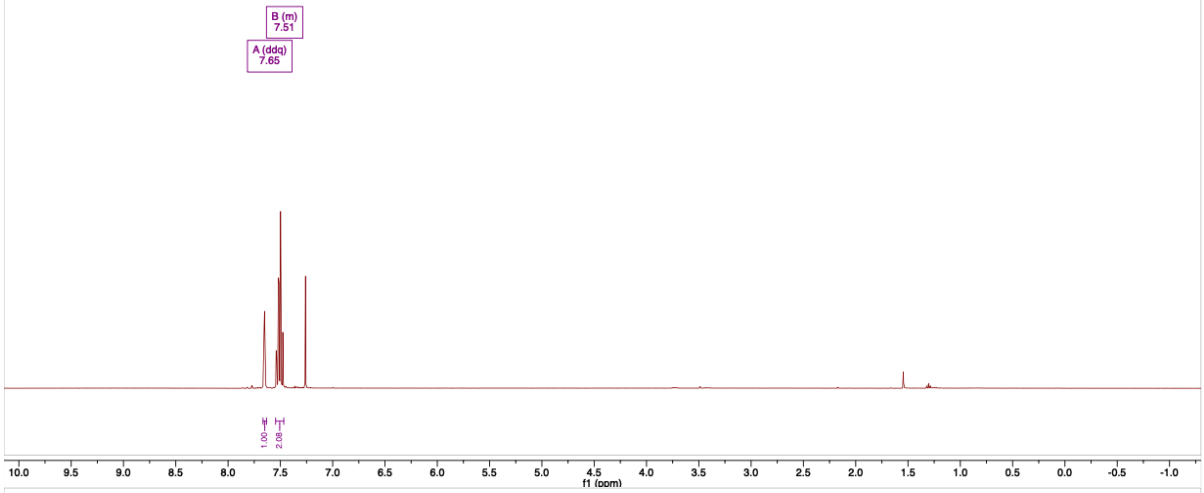




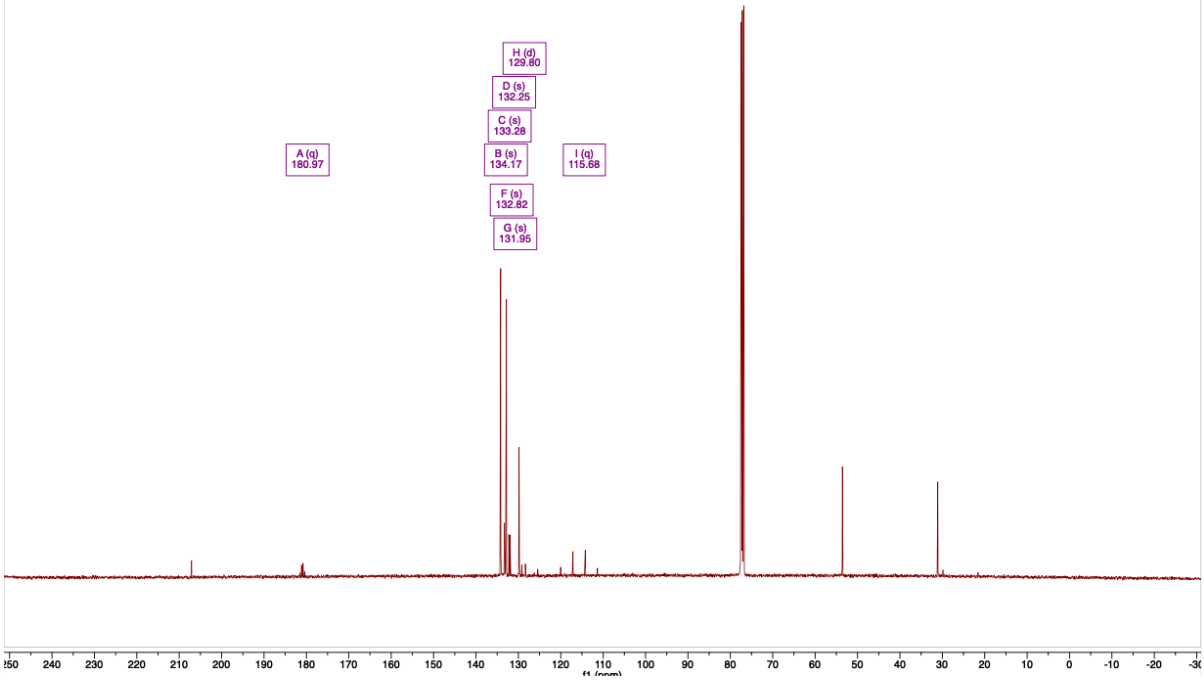
1-(2, 5-Dichlorophenyl)-2,2,2-trifluoroethanone, S1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.63 (ddq, J = 2.2, 1.6, 1.0 Hz, 1H), 7.55 – 7.47 (m, 2H).

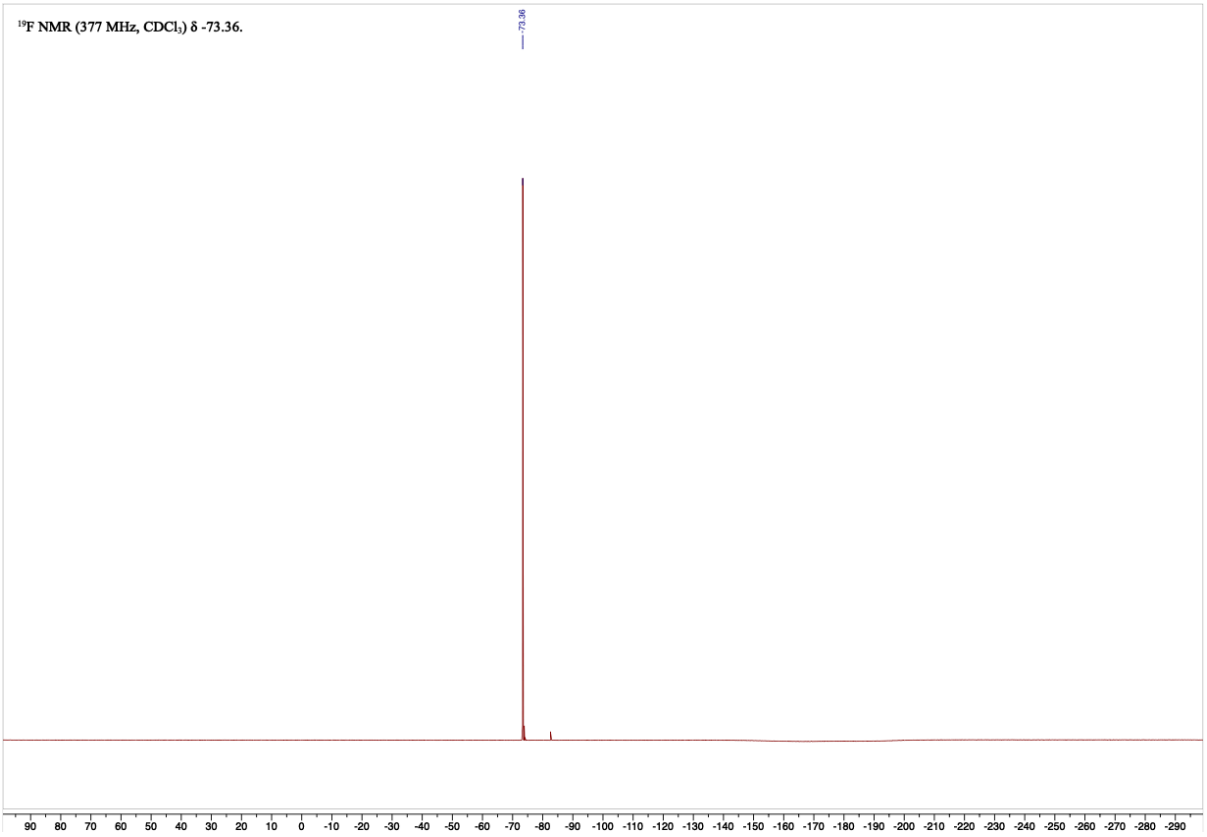




^{13}C NMR (101 MHz, $CDCl_3$) δ 181.69 – 180.12 (q, J = 37.2 Hz), 134.55 – 133.88 (s), 133.53 – 133.18 (s), 133.03 – 132.60 (s), 132.40 – 132.15 (s), 132.08 – 131.80 (s), 130.02 – 129.57 (d, J = 5.0 Hz), 120.30 – 110.82 (q, J = 291.7 Hz).

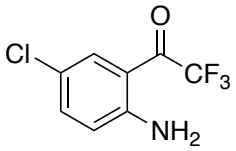


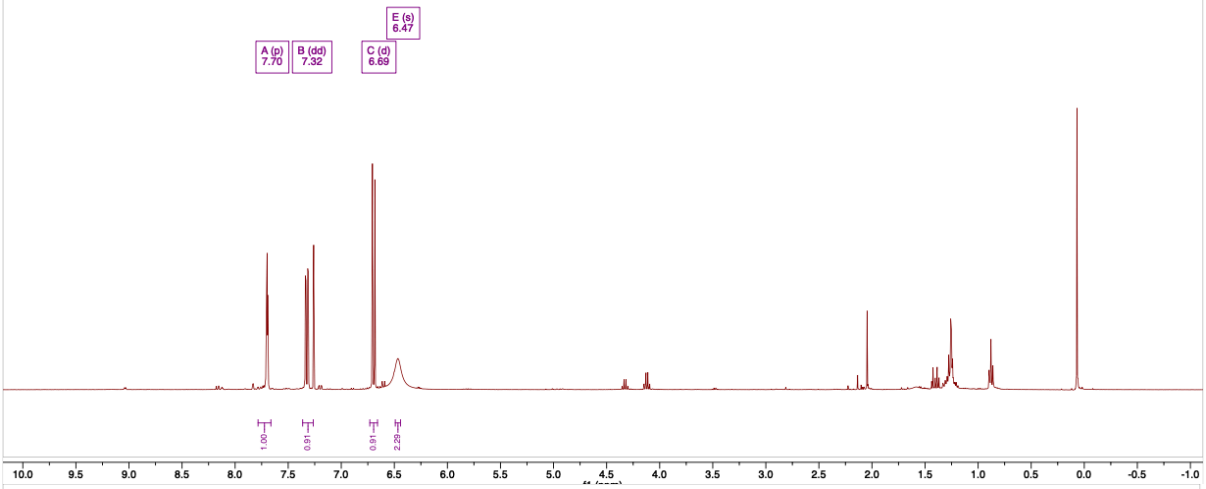
^{19}F NMR (377 MHz, $CDCl_3$) δ -73.36.



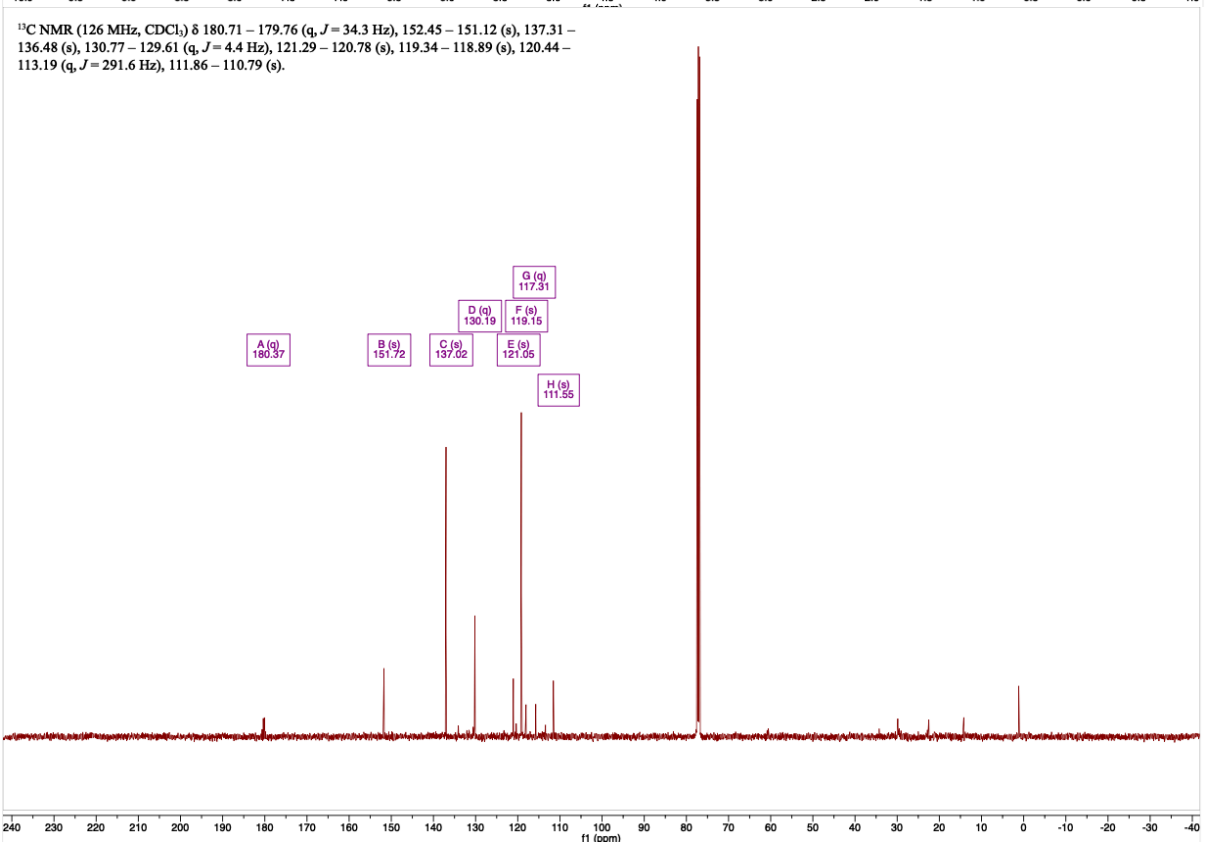
1-(2-Amino-5-chlorophenyl)-2,2,2-trifluoroethan-1-one, S2

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.66 (p, *J* = 2.2 Hz, 1H), 7.36 – 7.26 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.73 – 6.66 (d, *J* = 9.0 Hz, 1H), 6.49 – 6.44 (s, 2H).

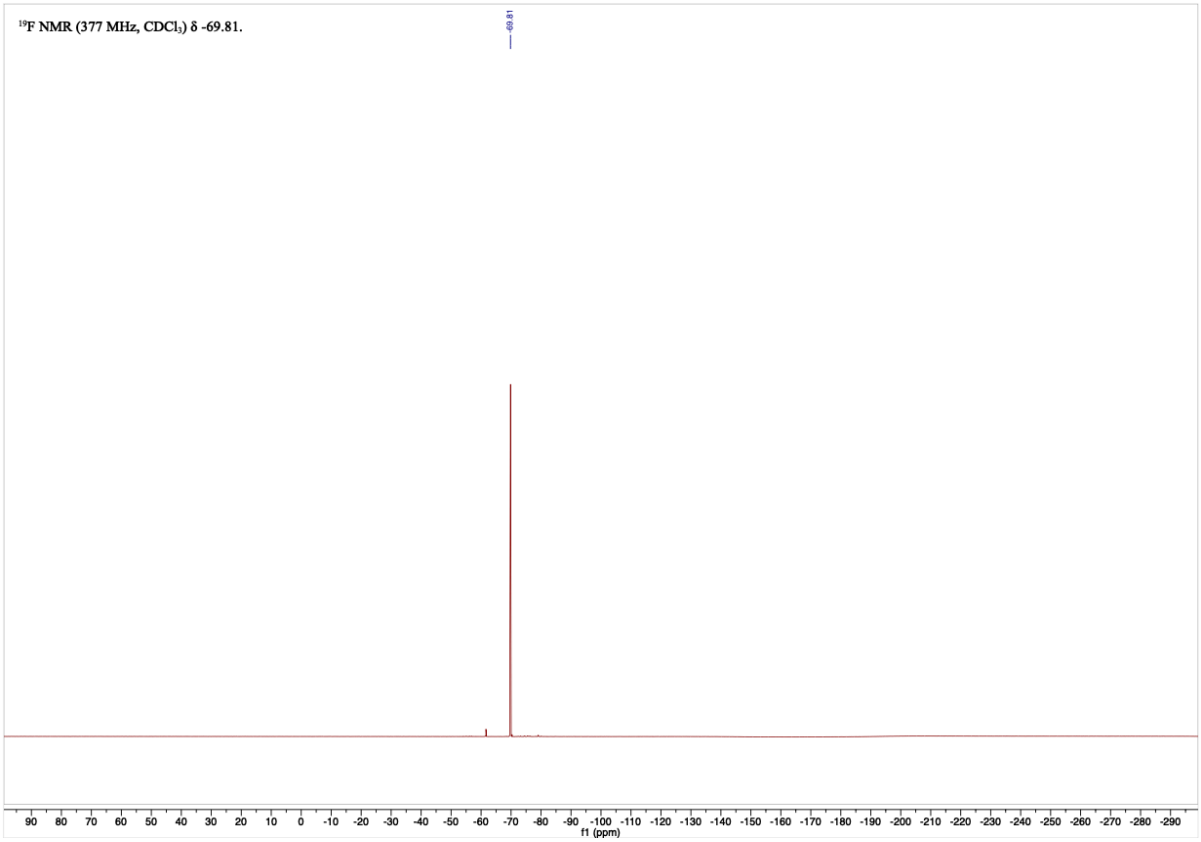




^{13}C NMR (126 MHz, $CDCl_3$) δ 180.71 – 179.76 (q, *J* = 34.3 Hz), 152.45 – 151.12 (s), 137.31 – 136.48 (s), 130.77 – 129.61 (q, *J* = 4.4 Hz), 121.29 – 120.78 (s), 119.34 – 118.89 (s), 120.44 – 113.19 (q, *J* = 291.6 Hz), 111.86 – 110.79 (s).

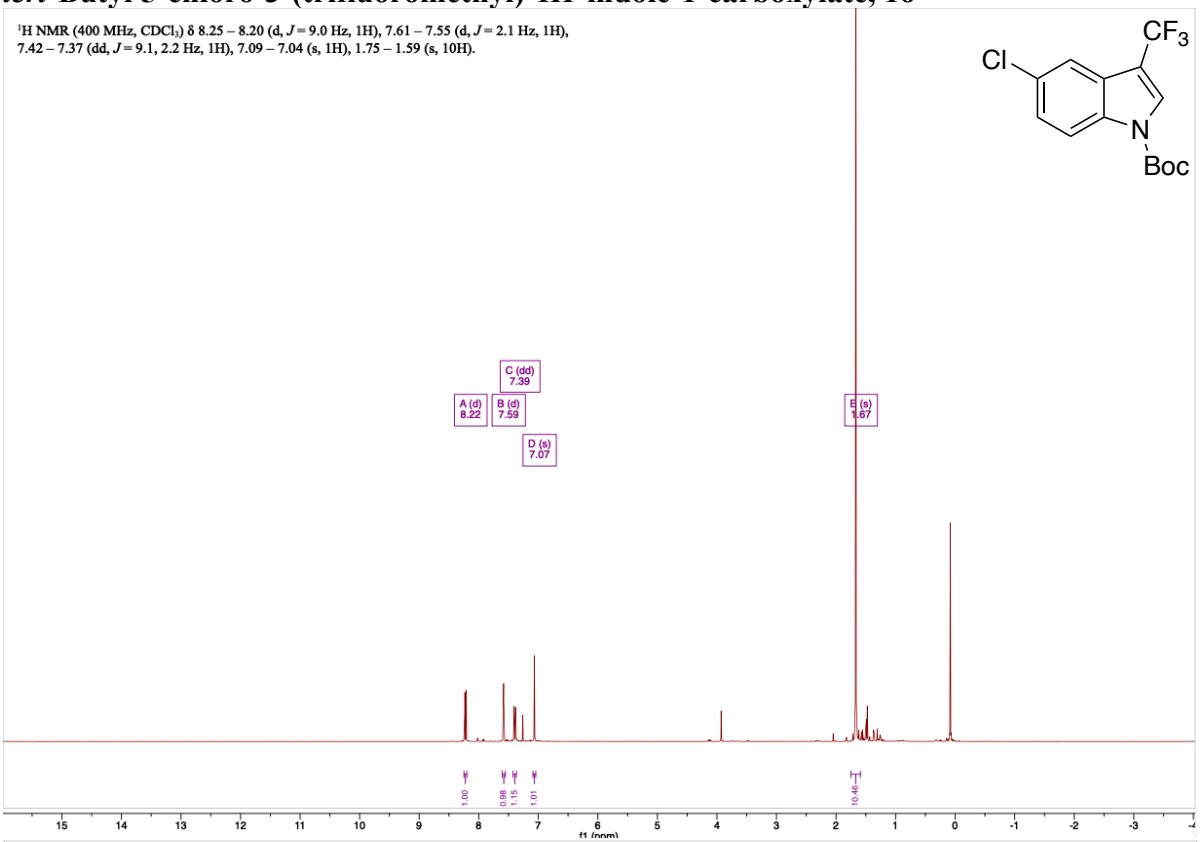


^{19}F NMR (377 MHz, $CDCl_3$) δ -69.81.

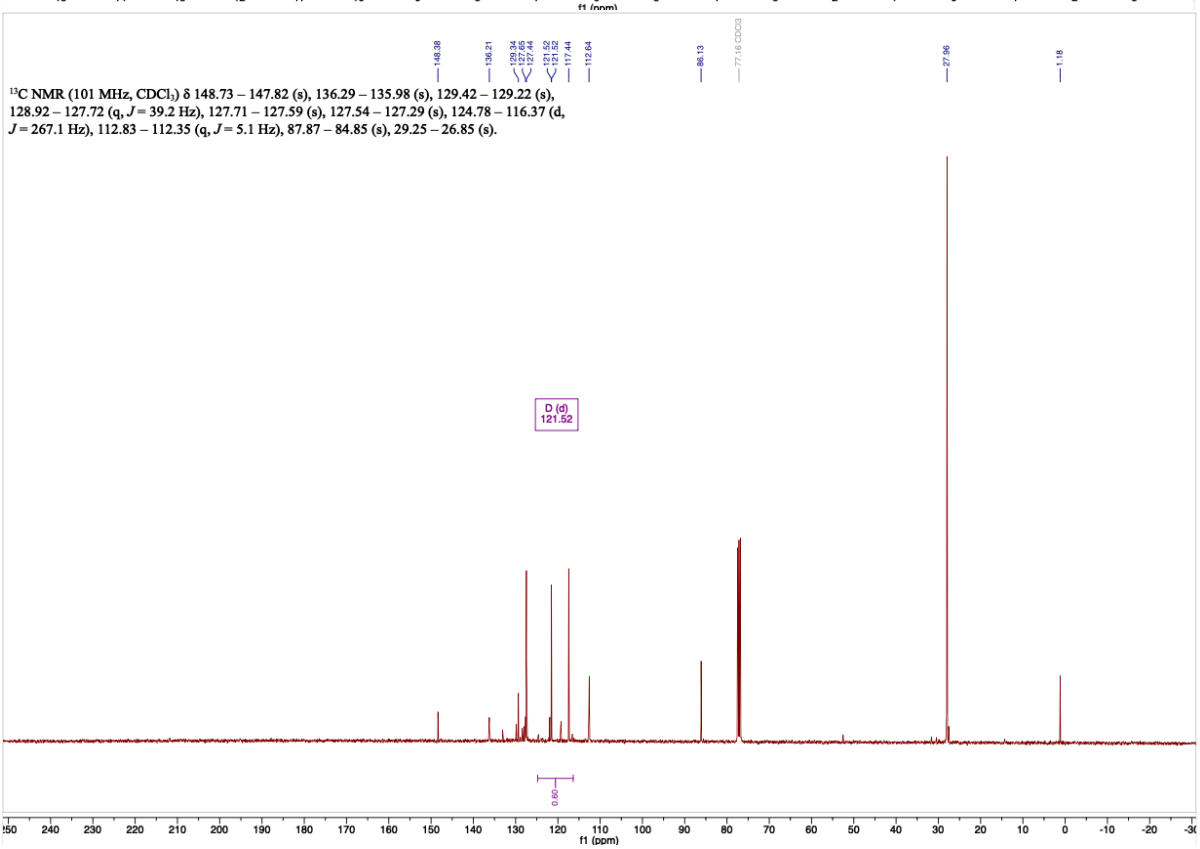


tert-Butyl 5-chloro-3-(trifluoromethyl)-1*H*-indole-1-carboxylate, 1o

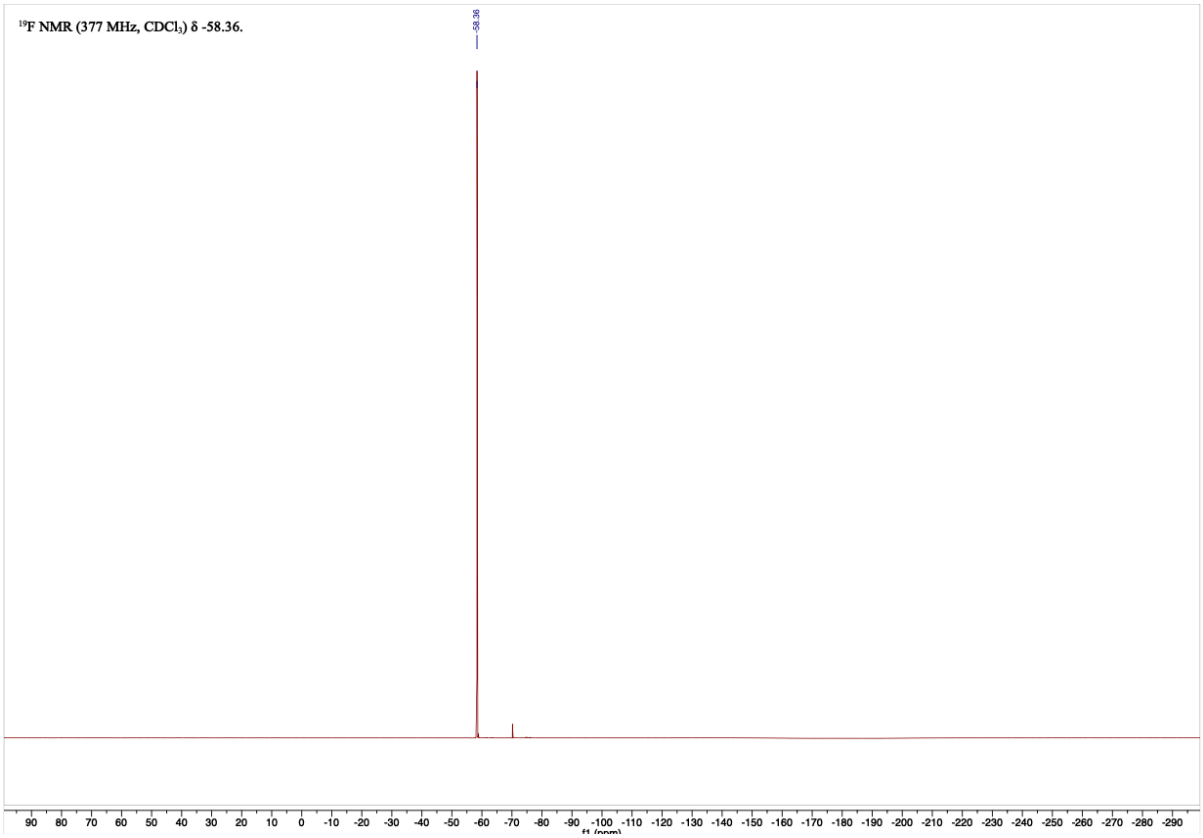
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.20 (d, J = 9.0 Hz, 1H), 7.61 – 7.55 (d, J = 2.1 Hz, 1H), 7.42 – 7.37 (dd, J = 9.1, 2.2 Hz, 1H), 7.09 – 7.04 (s, 1H), 1.75 – 1.59 (s, 10H).



^{13}C NMR (101 MHz, $CDCl_3$) δ 148.73 – 147.82 (s), 136.29 – 135.98 (s), 129.42 – 129.22 (s), 128.92 – 127.72 (q, J = 39.2 Hz), 127.71 – 127.59 (s), 127.54 – 127.29 (s), 124.78 – 116.37 (d, J = 267.1 Hz), 112.83 – 112.35 (q, J = 5.1 Hz), 87.87 – 84.85 (s), 29.25 – 26.85 (s).

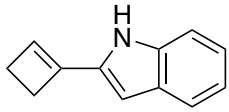


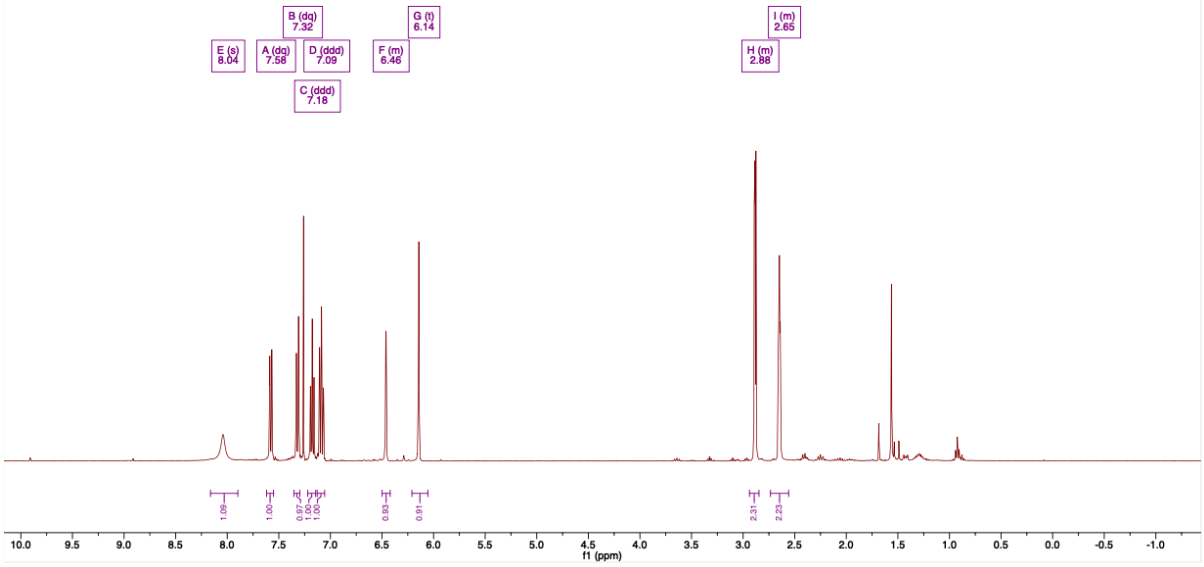
^{19}F NMR (377 MHz, $CDCl_3$) δ -58.36.

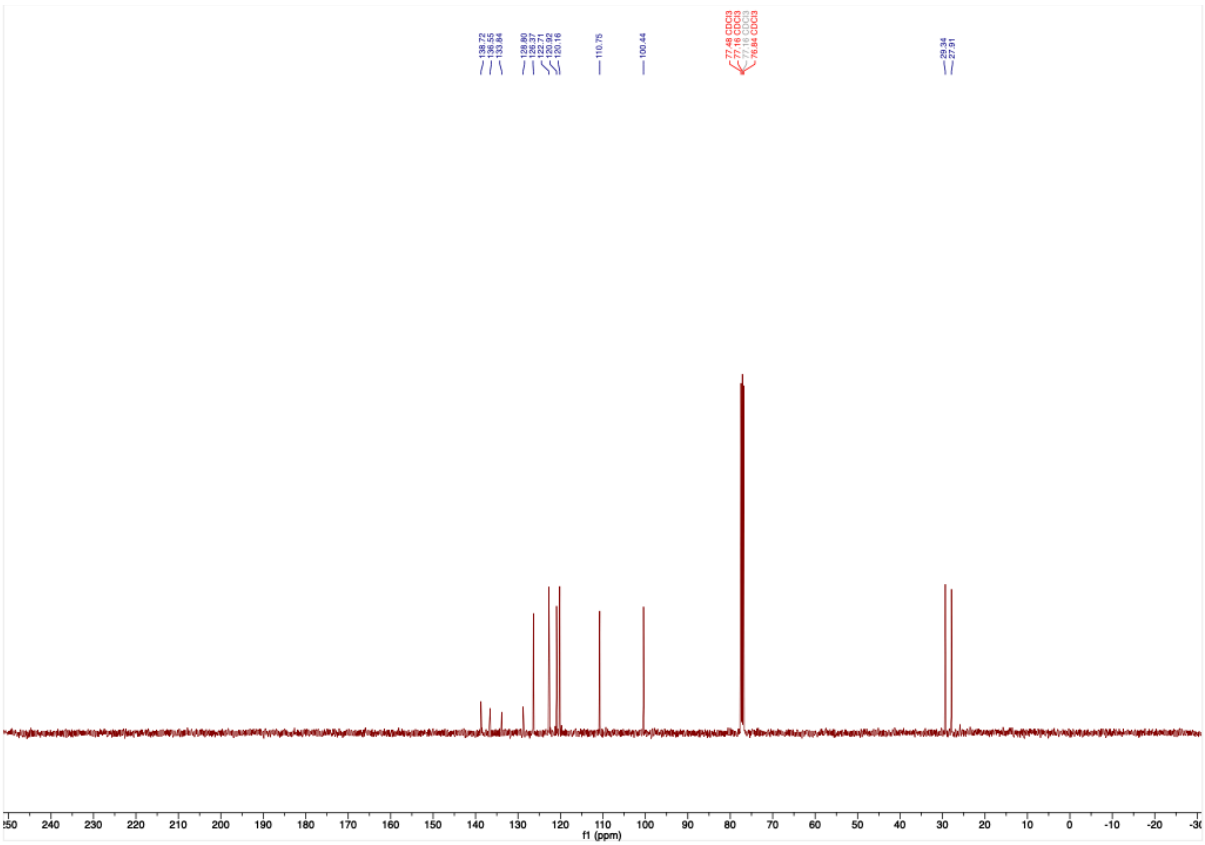


2-(Cyclobut-1-en-1-yl)-1*H*-indole, 2a

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 7.90 (s, 1H), 7.62 – 7.55 (dq, *J* = 7.8, 1.0 Hz, 1H), 7.35 – 7.30 (dq, *J* = 8.1, 0.9 Hz, 1H), 7.22 – 7.14 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.13 – 7.06 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 6.50 – 6.42 (m, 1H), 6.21 – 6.06 (t, *J* = 1.4 Hz, 1H), 2.94 – 2.85 (m, 2H), 2.73 – 2.56 (m, 2H).

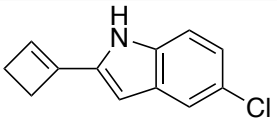


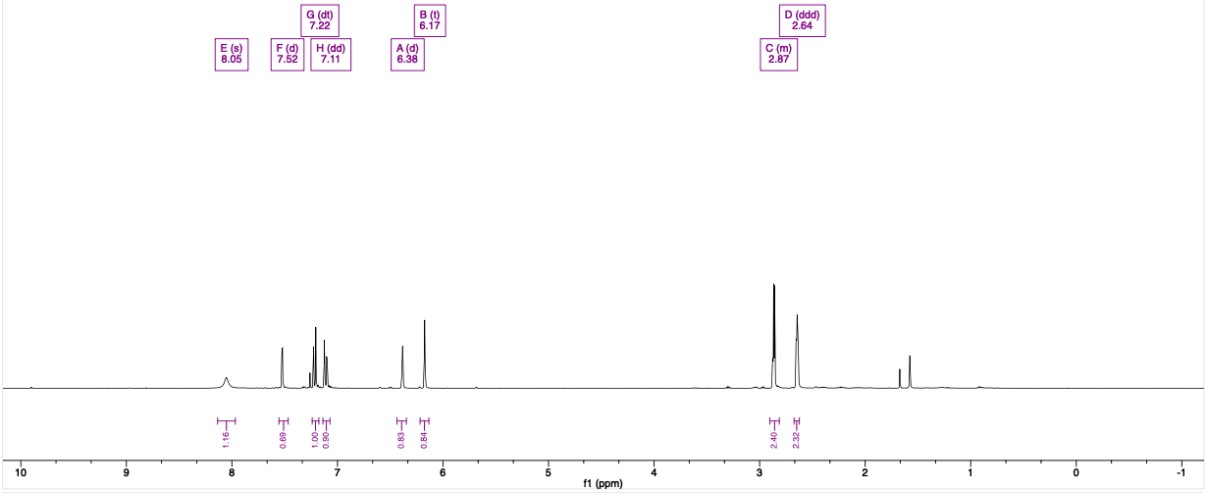


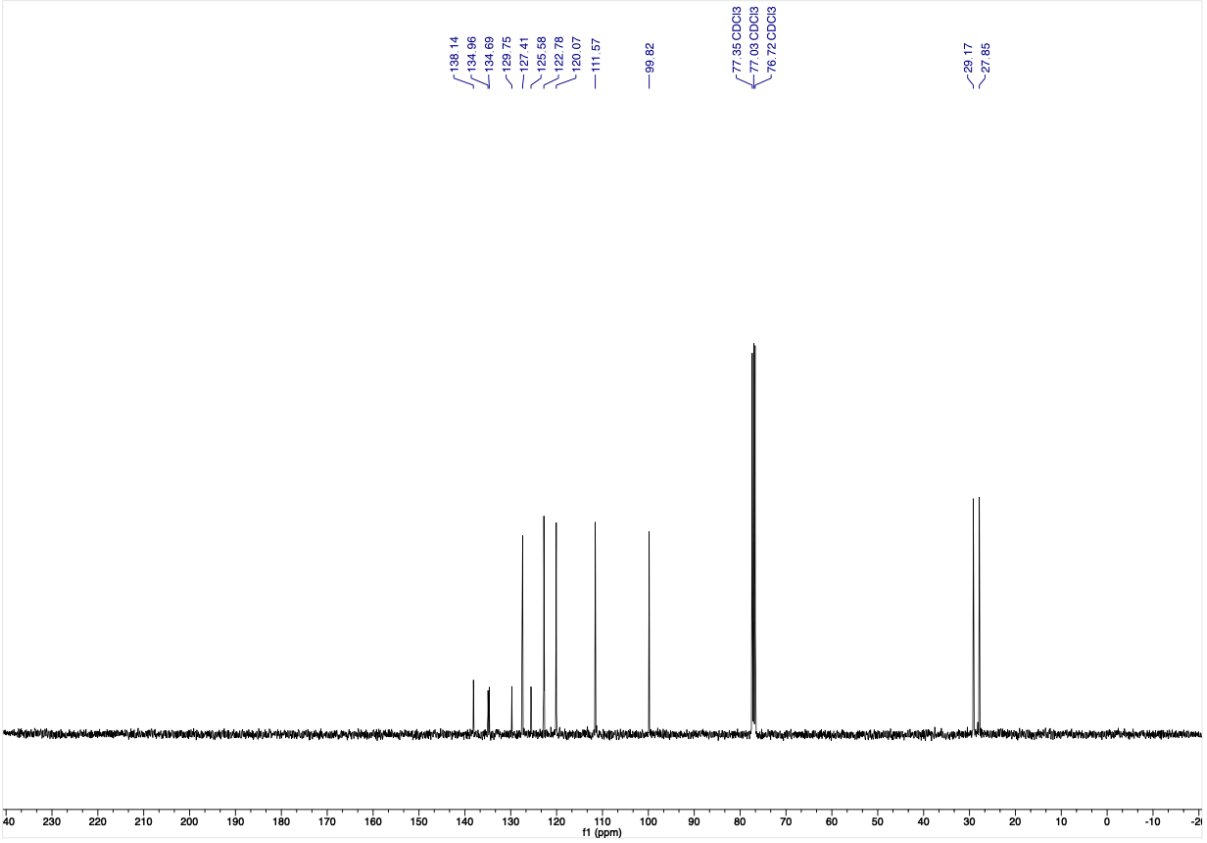


2-(Cyclobut-1-en-1-yl)-5-chloro-1*H*-indole, 2b

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 7.97 (s, 1H), 7.55 – 7.47 (d, *J* = 2.0 Hz, 1H), 7.24 – 7.18 (dt, *J* = 8.6, 0.8 Hz, 1H), 7.14 – 7.07 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.44 – 6.35 (d, *J* = 2.1 Hz, 1H), 6.22 – 6.13 (t, *J* = 1.4 Hz, 1H), 2.90 – 2.81 (m, 2H), 2.67 – 2.62 (ddd, *J* = 4.2, 2.9, 1.4 Hz, 2H).

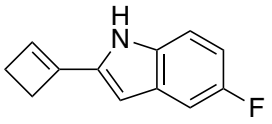


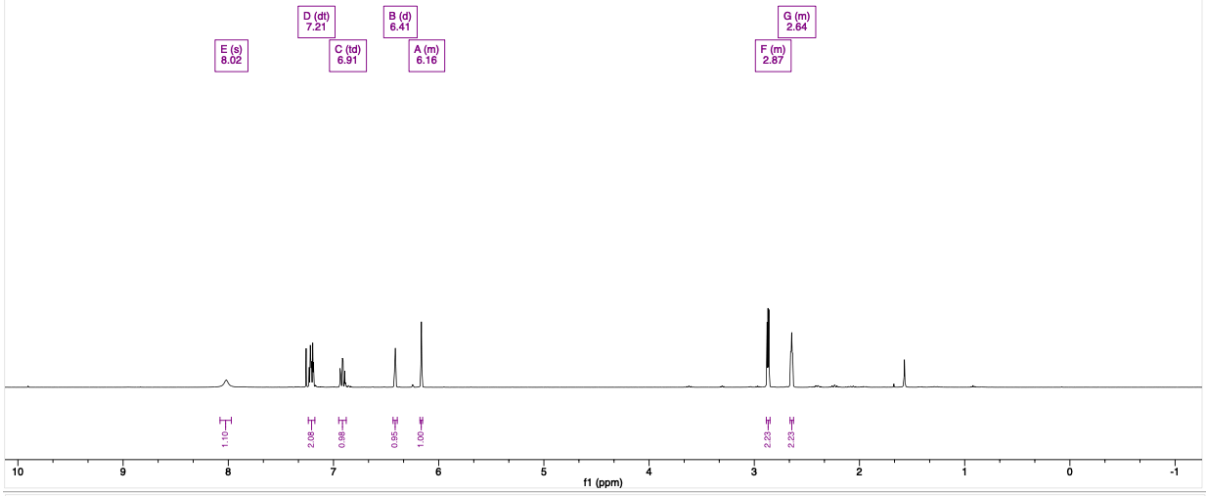




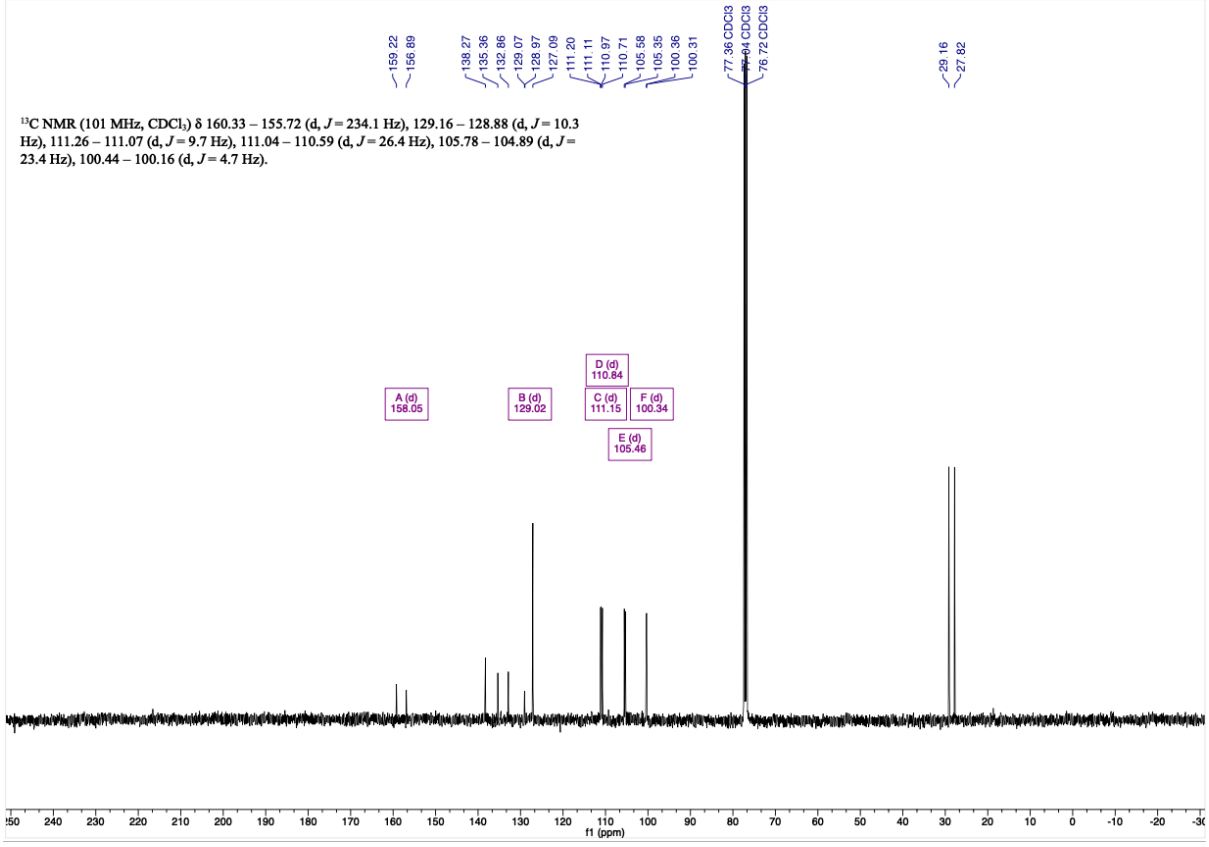
2-(Cyclobut-1-en-1-yl)-5-fluoro-1*H*-indole, 2c

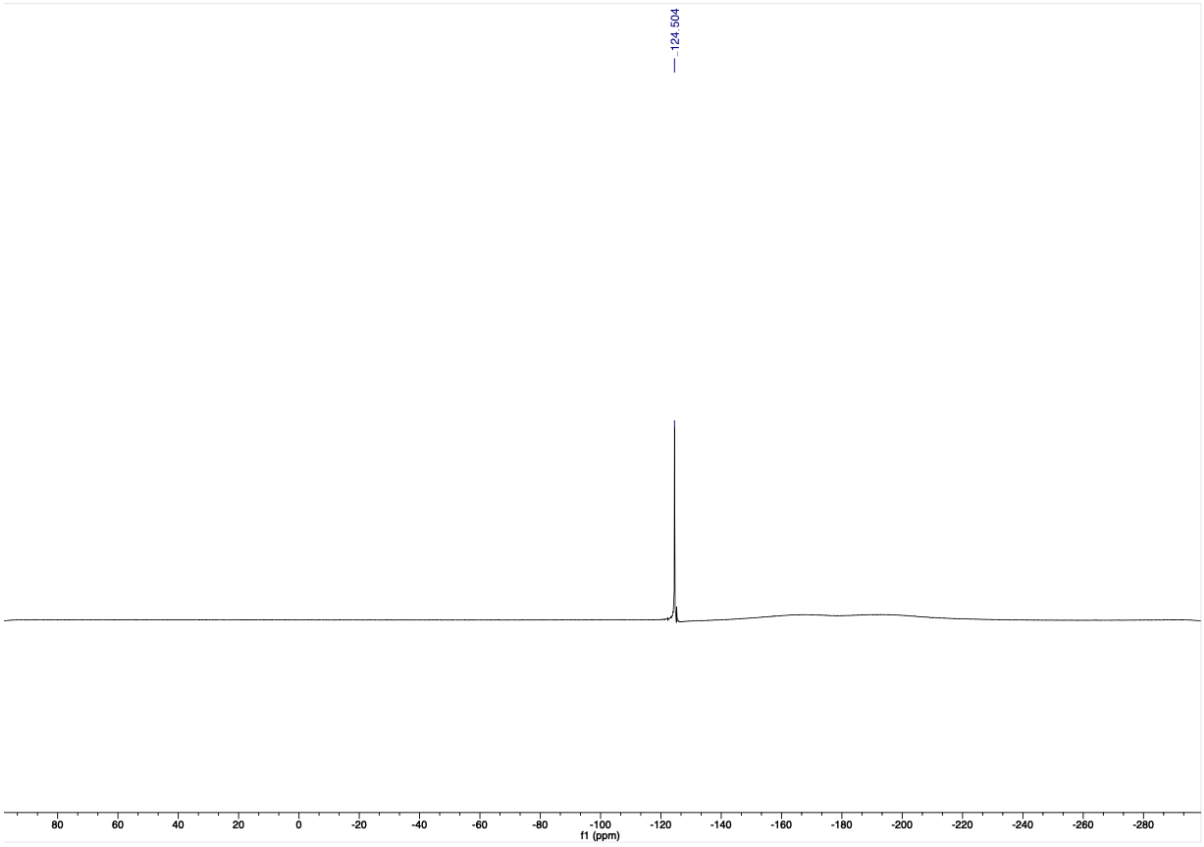
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.97 (s, 1H), 7.24 – 7.18 (dt, *J* = 9.7, 3.5 Hz, 2H), 6.95 – 6.88 (td, *J* = 9.1, 2.5 Hz, 1H), 6.43 – 6.39 (d, *J* = 2.1 Hz, 1H), 6.18 – 6.15 (m, 1H), 2.89 – 2.85 (m, 2H), 2.66 – 2.63 (m, 2H).





^{13}C NMR (101 MHz, $CDCl_3$) δ 160.33 – 155.72 (d, *J* = 234.1 Hz), 129.16 – 128.88 (d, *J* = 10.3 Hz), 111.26 – 111.07 (d, *J* = 9.7 Hz), 111.04 – 110.59 (d, *J* = 26.4 Hz), 105.78 – 104.89 (d, *J* = 23.4 Hz), 100.44 – 100.16 (d, *J* = 4.7 Hz).

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60
40
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-60
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-100
-120
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-160
-180
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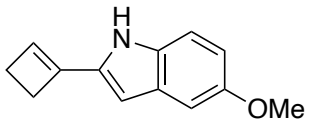
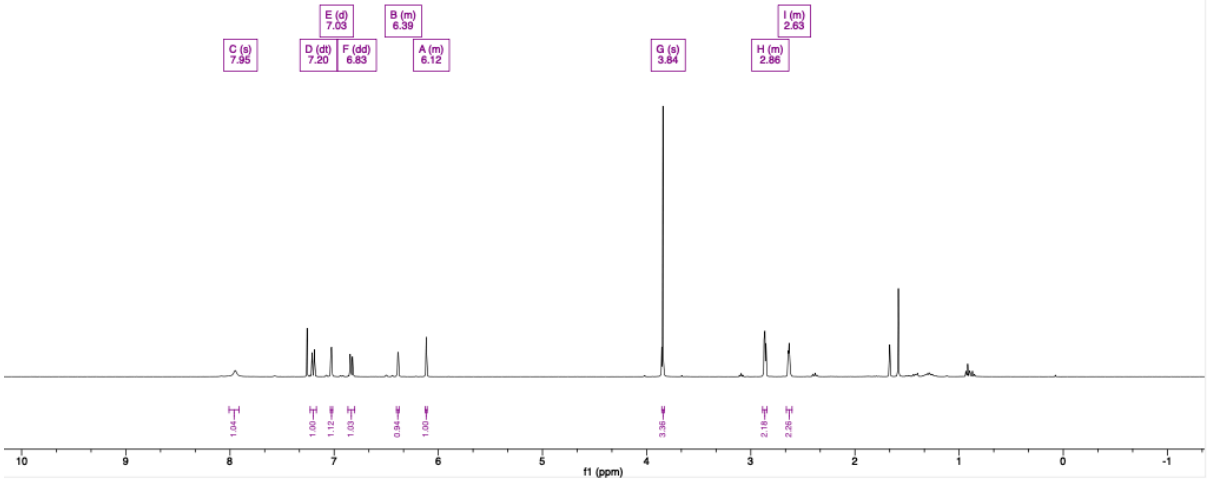
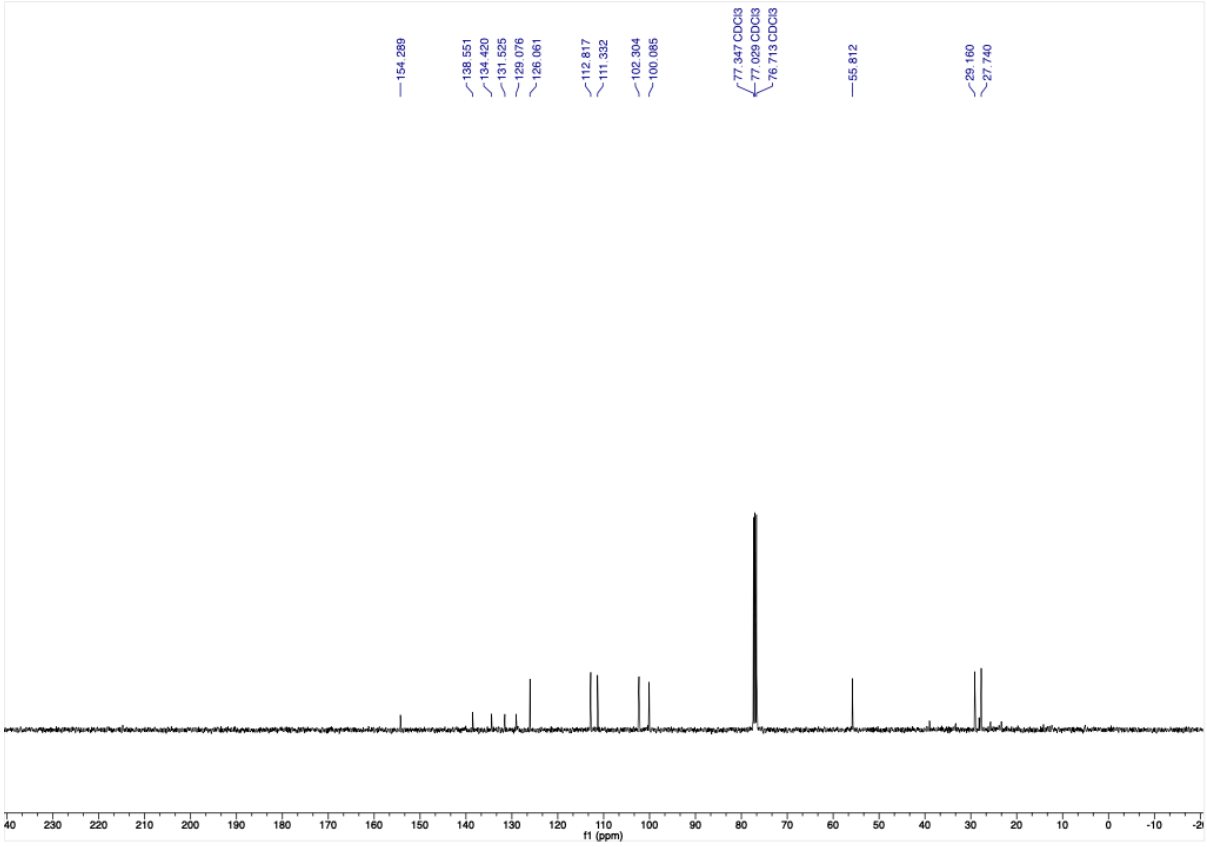
-220
-240
-260
-280
f1 (ppm)

2-(Cyclobut-1-en-1-yl)-5-methoxy-1*H*-indole, 2d

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.91 (s, 1H), 7.23 – 7.17 (dt, *J* = 8.8, 0.7 Hz, 1H), 7.04 – 7.01 (d, *J* = 2.4 Hz, 1H), 6.87 – 6.80 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.40 – 6.38 (m, 1H), 6.13 – 6.11 (m, 1H), 3.85 – 3.83 (s, 3H), 2.89 – 2.84 (m, 2H), 2.66 – 2.60 (m, 2H).

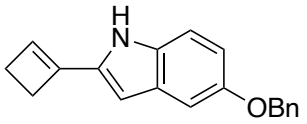


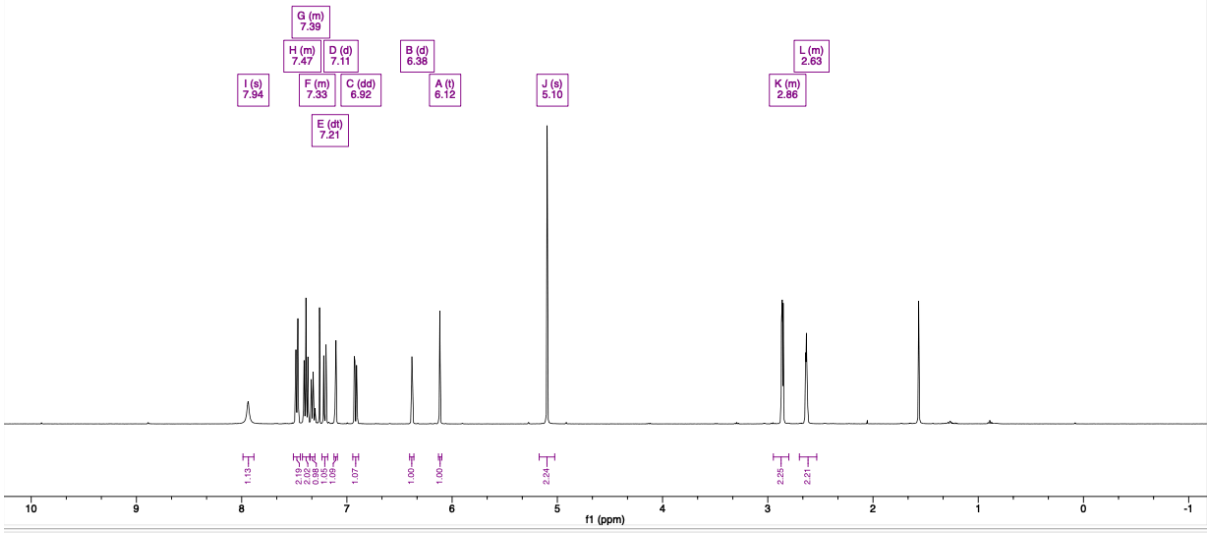


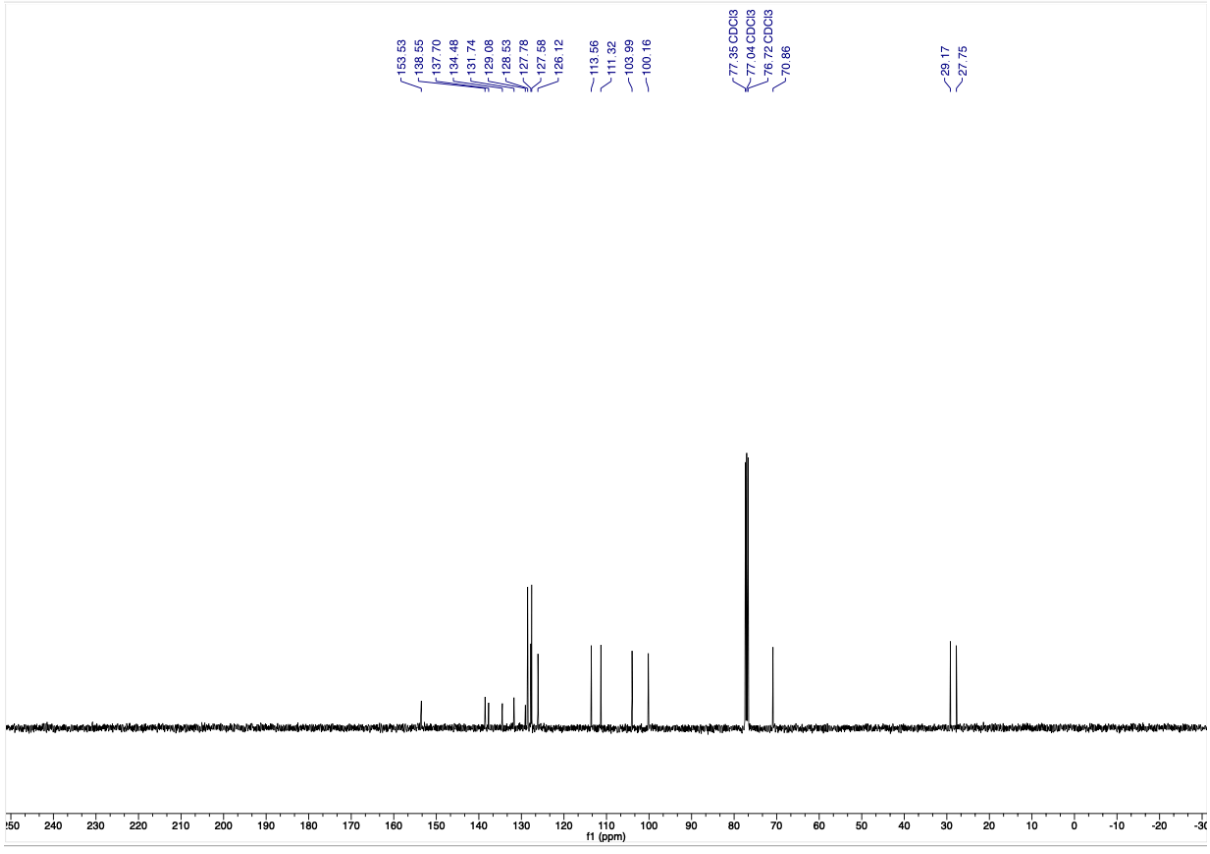


5-(Benzyloxy)-2-(cyclobut-1-en-1-yl)-1*H*-indole, 2e

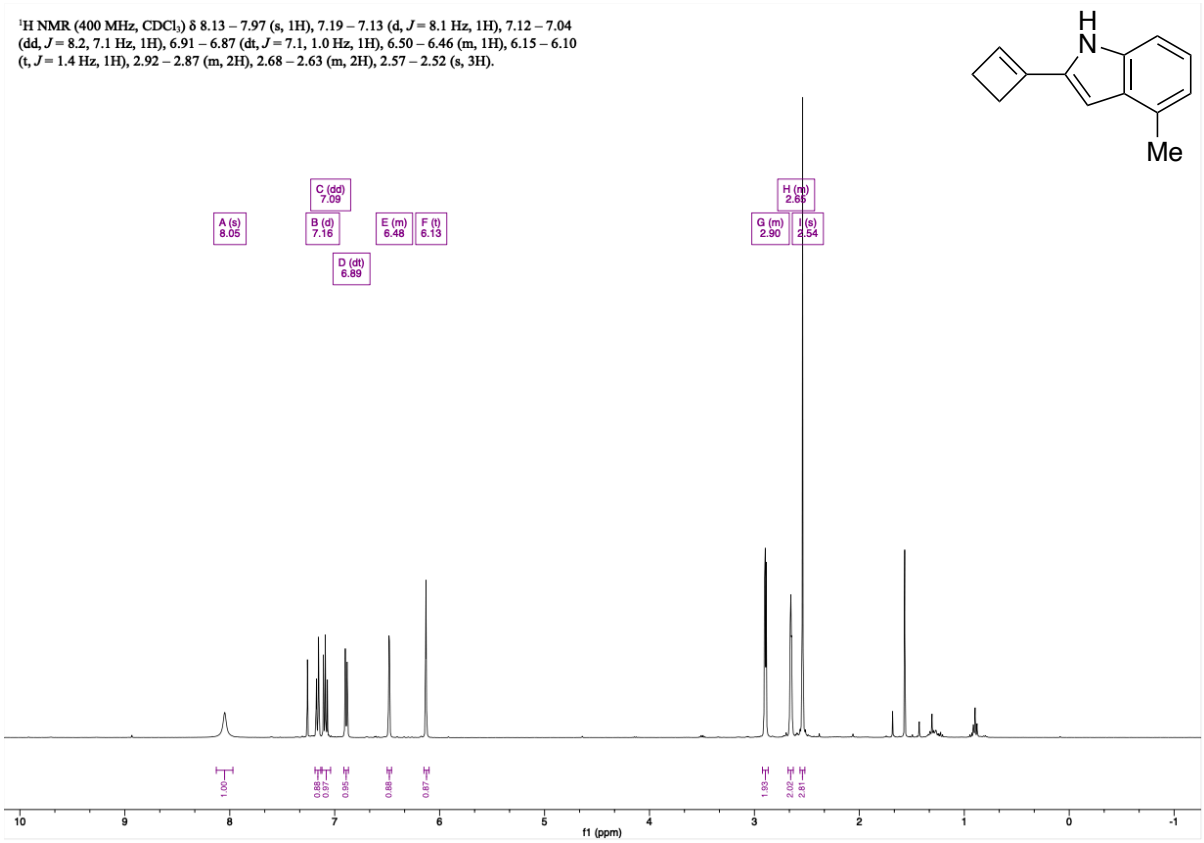
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.88 (s, 1H), 7.51 – 7.44 (m, 2H), 7.42 – 7.35 (m, 2H), 7.35 – 7.30 (m, 1H), 7.24 – 7.18 (dt, *J* = 8.8, 0.7 Hz, 1H), 7.12 – 7.09 (d, *J* = 2.4 Hz, 1H), 6.94 – 6.89 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.40 – 6.36 (d, *J* = 2.0 Hz, 1H), 6.13 – 6.10 (t, *J* = 1.3 Hz, 1H), 5.17 – 5.03 (s, 2H), 2.95 – 2.80 (m, 2H), 2.70 – 2.53 (m, 2H).

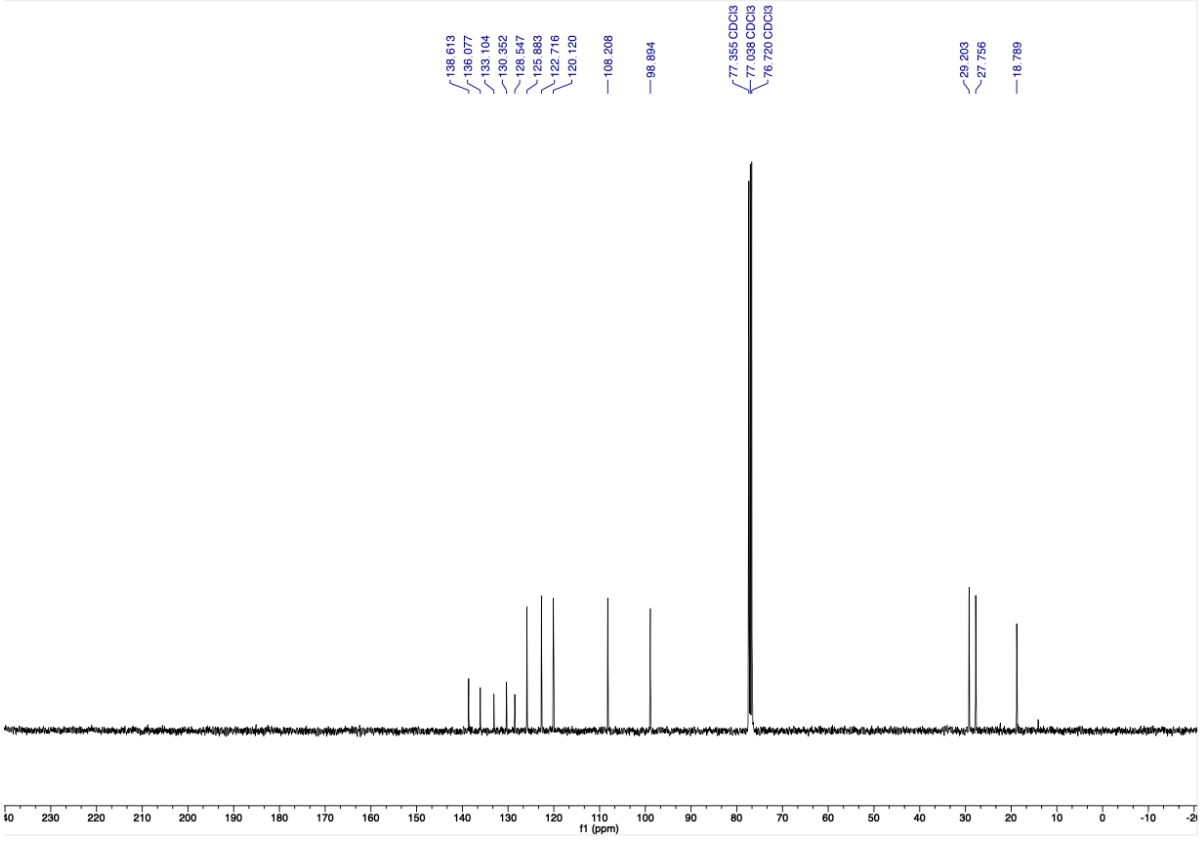






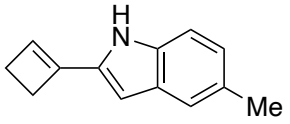
2-(Cyclobut-1-en-1-yl)-4-methyl-1*H*-indole, 2f

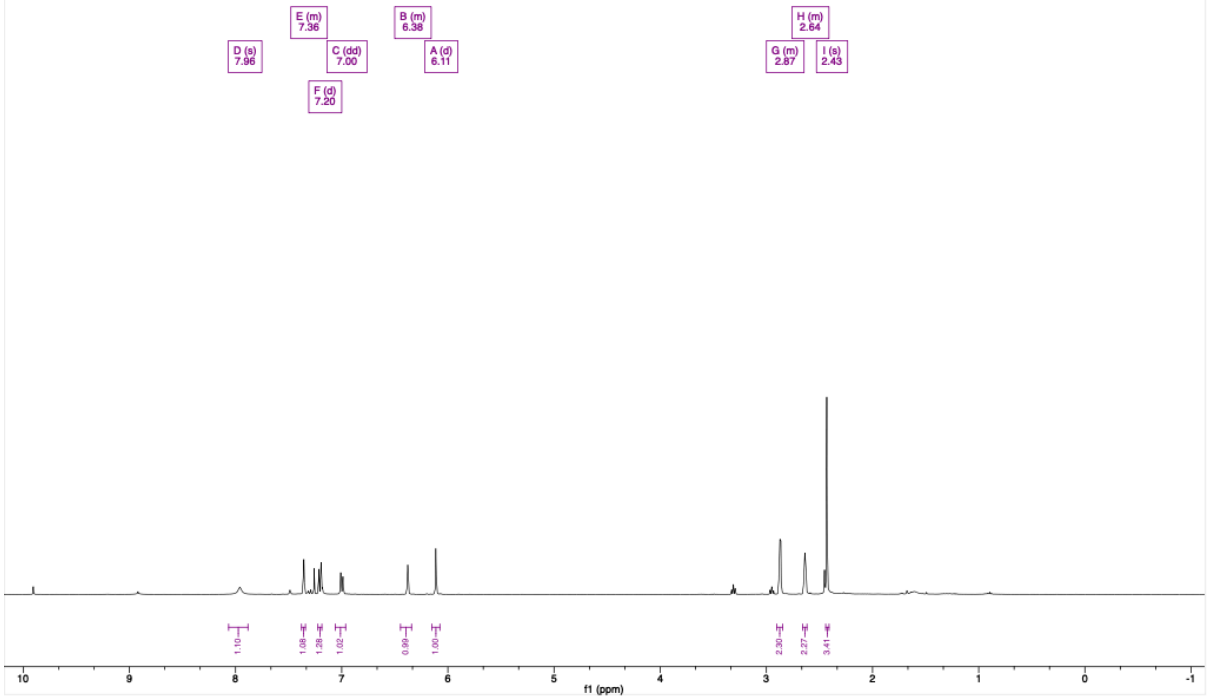


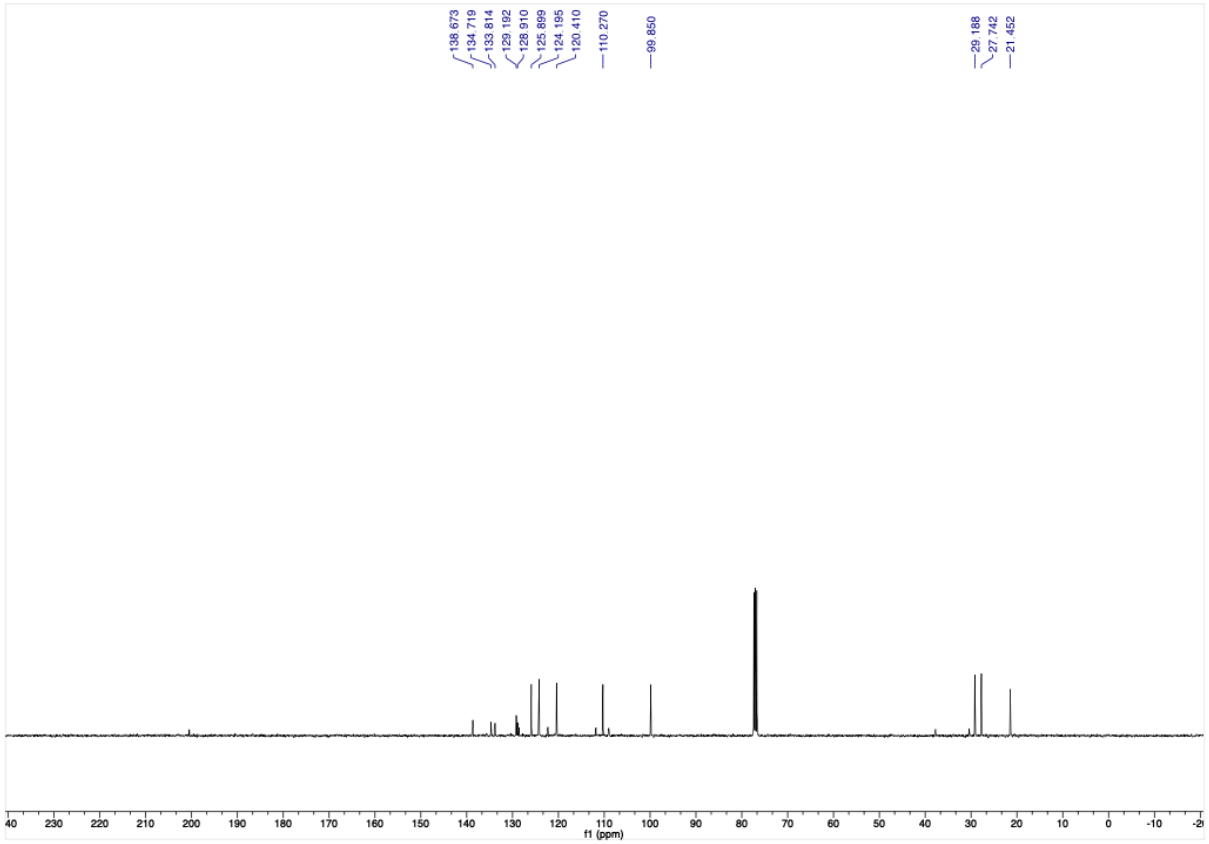


2-(Cyclobut-1-en-1-yl)-5-methyl-1*H*-indole, 2g

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.88 (s, 1H), 7.38 – 7.34 (m, 1H), 7.22 – 7.19 (d, *J* = 8.2 Hz, 1H), 7.06 – 6.96 (dd, *J* = 8.3, 1.6 Hz, 1H), 6.45 – 6.34 (m, 1H), 6.15 – 6.08 (d, *J* = 1.4 Hz, 1H), 2.90 – 2.85 (m, 2H), 2.66 – 2.62 (m, 2H), 2.44 – 2.41 (s, 3H).

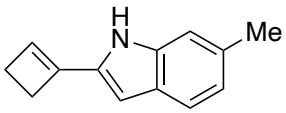


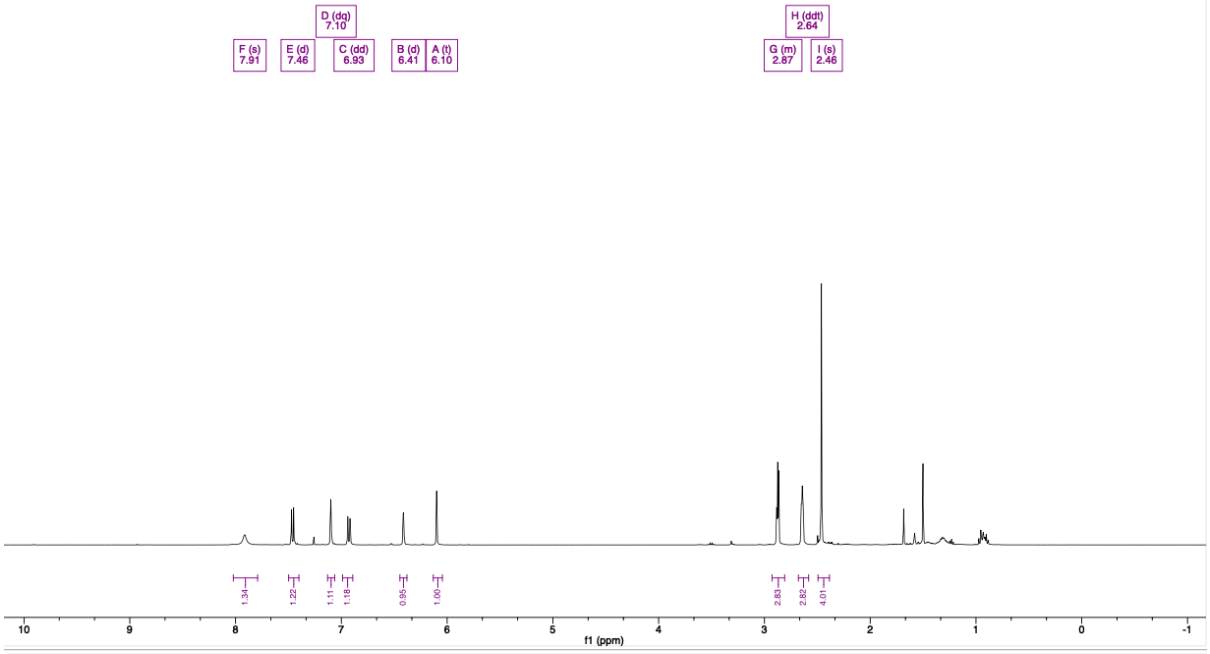


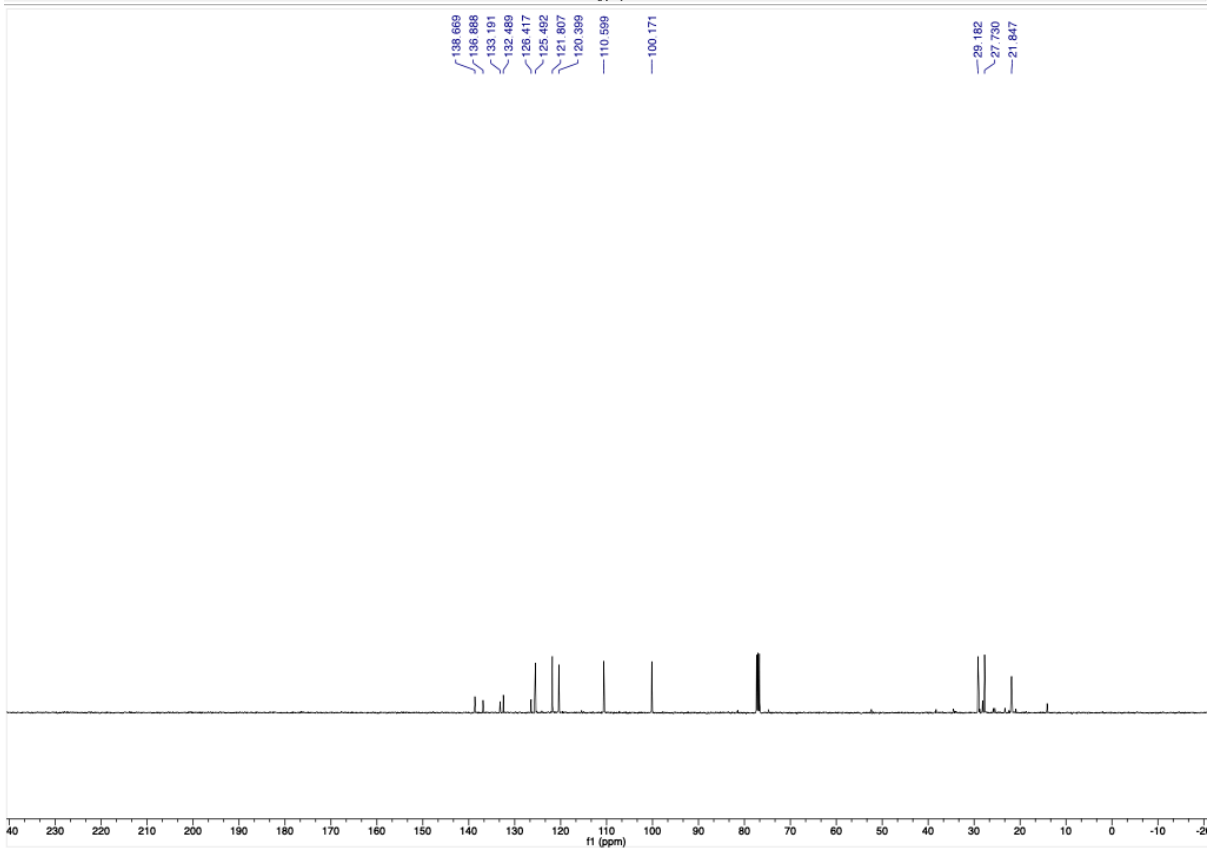


2-(Cyclobut-1-en-1-yl)-6-methyl-1*H*-indole, 2h

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.79 (s, 1H), 7.50 – 7.40 (d, *J* = 8.0 Hz, 1H), 7.13 – 7.06 (dq, *J* = 1.8, 0.9 Hz, 1H), 6.99 – 6.89 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.45 – 6.38 (d, *J* = 2.0 Hz, 1H), 6.13 – 6.04 (t, *J* = 1.4 Hz, 1H), 2.93 – 2.81 (m, 3H), 2.68 – 2.58 (ddt, *J* = 4.5, 2.1, 0.9 Hz, 3H), 2.49 – 2.39 (s, 4H).

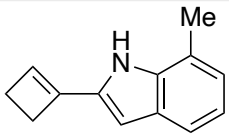


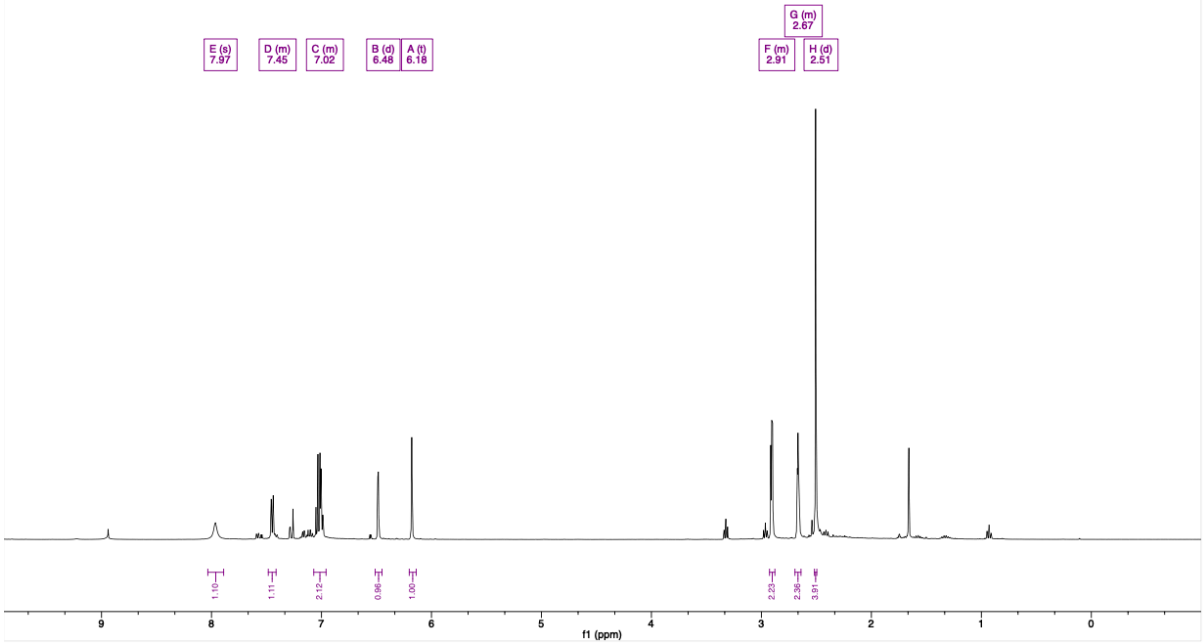


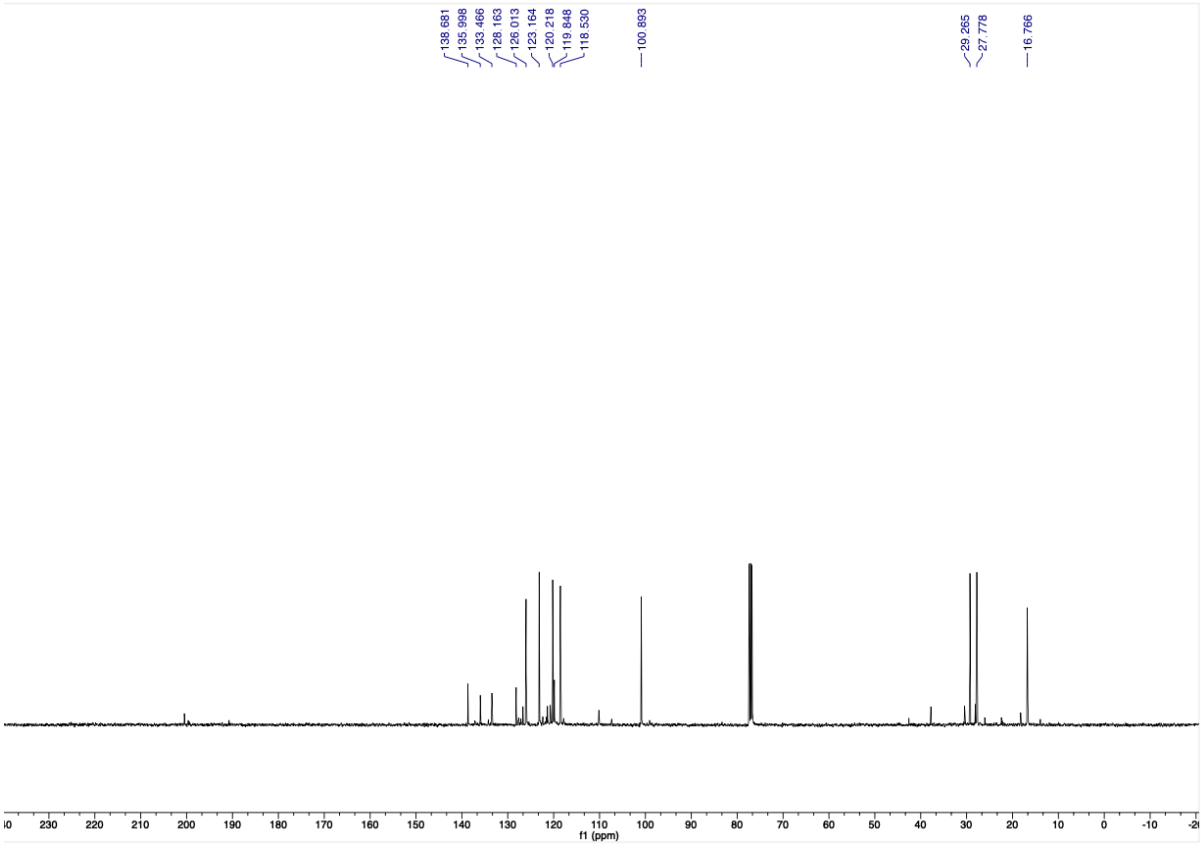


2-(Cyclobut-1-en-1-yl)-7-methyl-1*H*-indole, 2i

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.89 (s, 1H), 7.48 – 7.41 (m, 1H), 7.07 – 6.96 (m, 2H), 6.51 – 6.45 (d, *J* = 2.1 Hz, 1H), 6.20 – 6.14 (t, *J* = 1.4 Hz, 1H), 2.93 – 2.88 (m, 2H), 2.69 – 2.64 (m, 2H), 2.54 – 2.46 (d, *J* = 0.8 Hz, 3H).

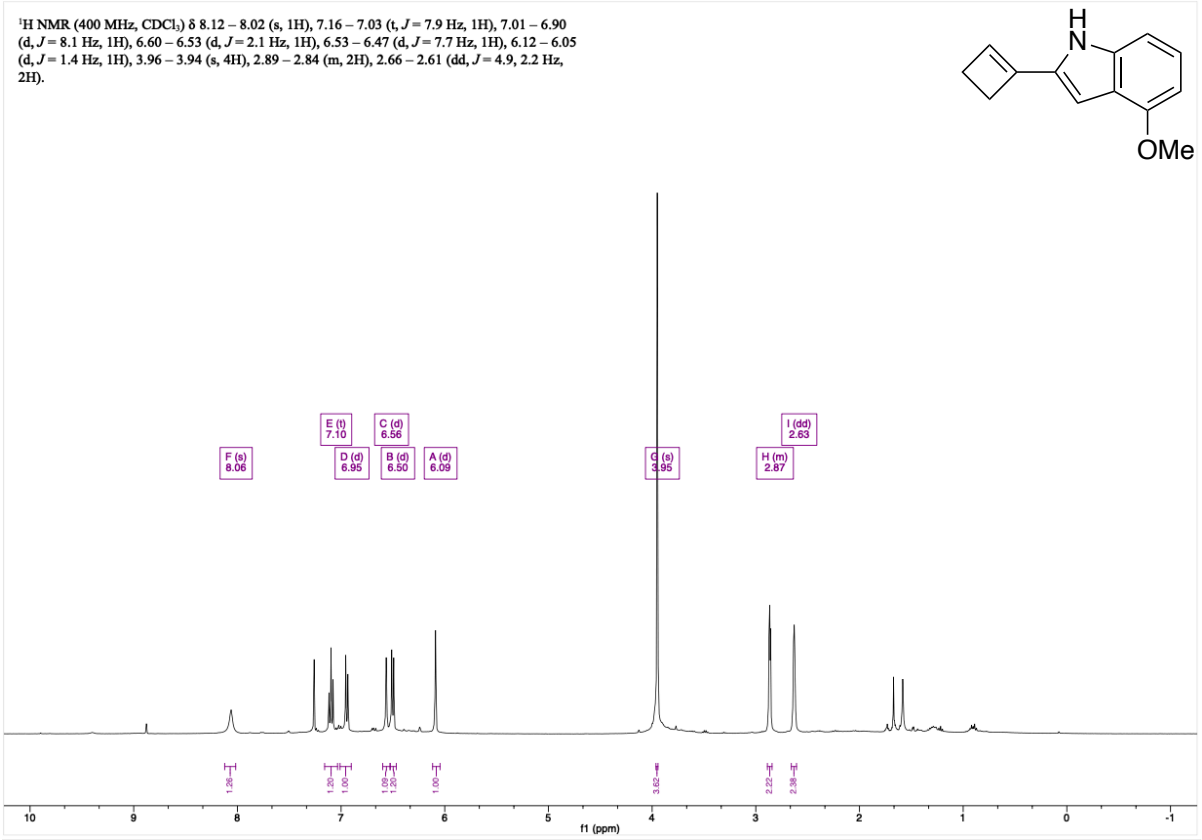


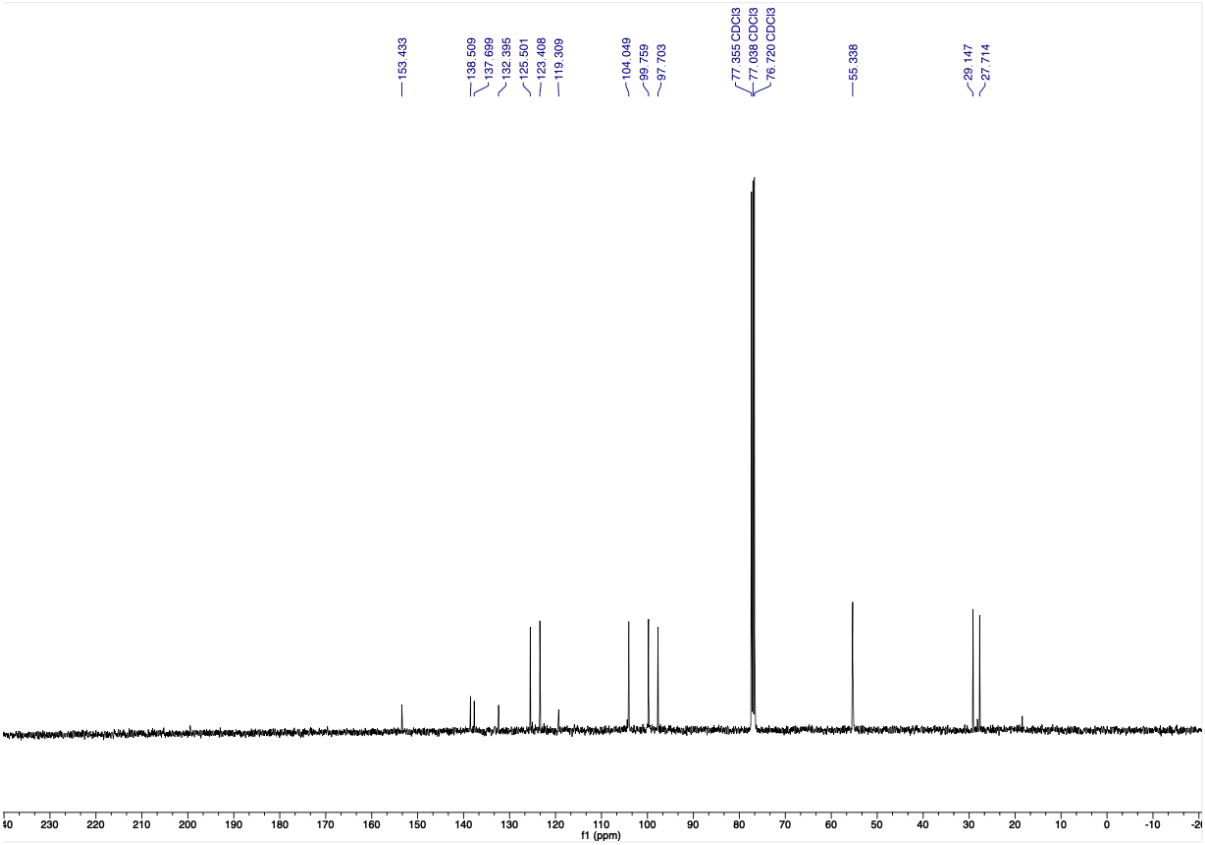




2-(Cyclobut-1-en-1-yl)-4-methoxy-1*H*-indole, 2j

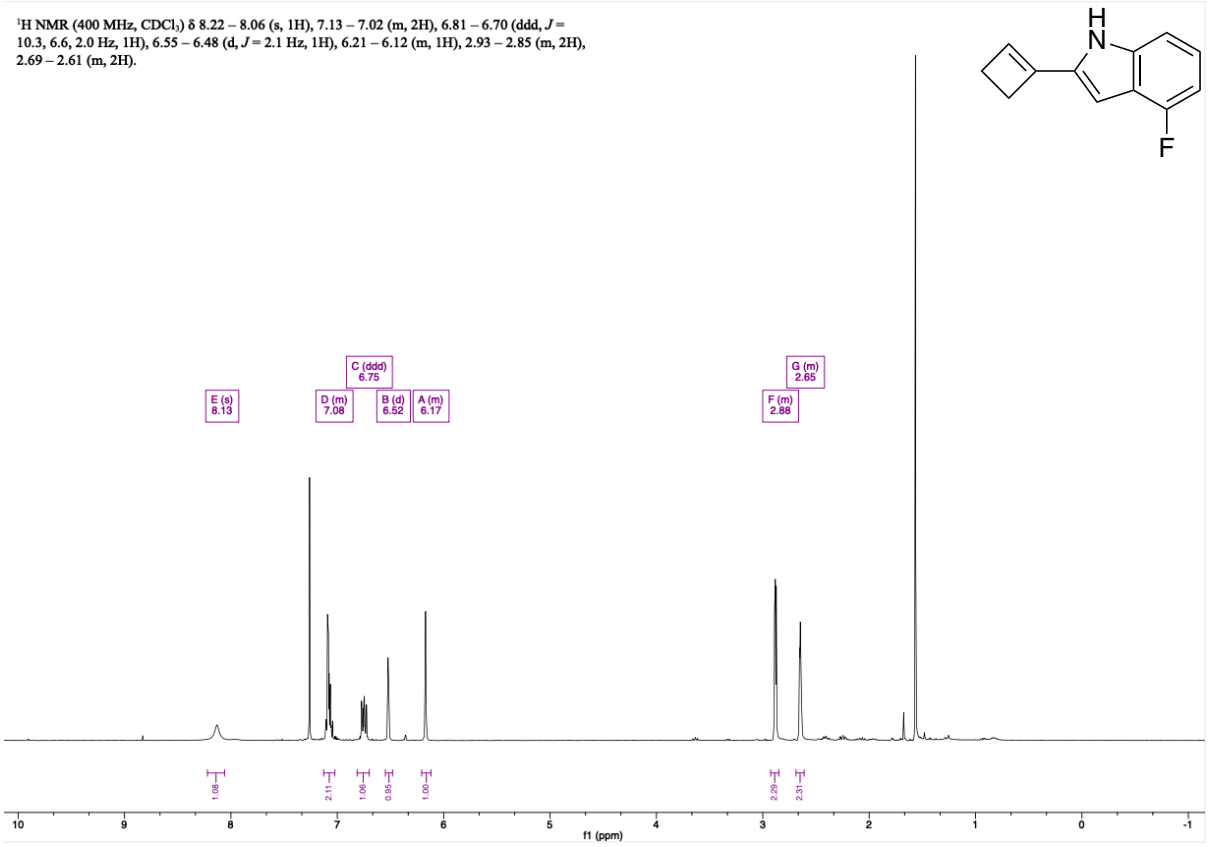
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.02 (s, 1H), 7.16 – 7.03 (t, *J* = 7.9 Hz, 1H), 7.01 – 6.90 (d, *J* = 8.1 Hz, 1H), 6.60 – 6.53 (d, *J* = 2.1 Hz, 1H), 6.53 – 6.47 (d, *J* = 7.7 Hz, 1H), 6.12 – 6.05 (d, *J* = 1.4 Hz, 1H), 3.96 – 3.94 (s, 4H), 2.89 – 2.84 (m, 2H), 2.66 – 2.61 (dd, *J* = 4.9, 2.2 Hz, 2H).



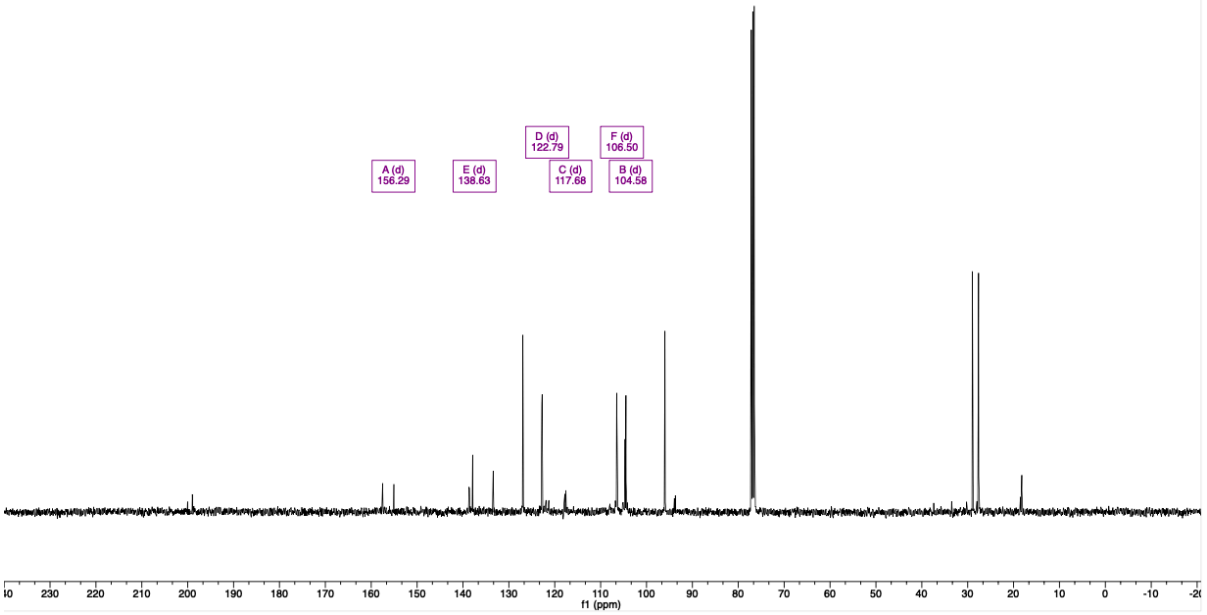


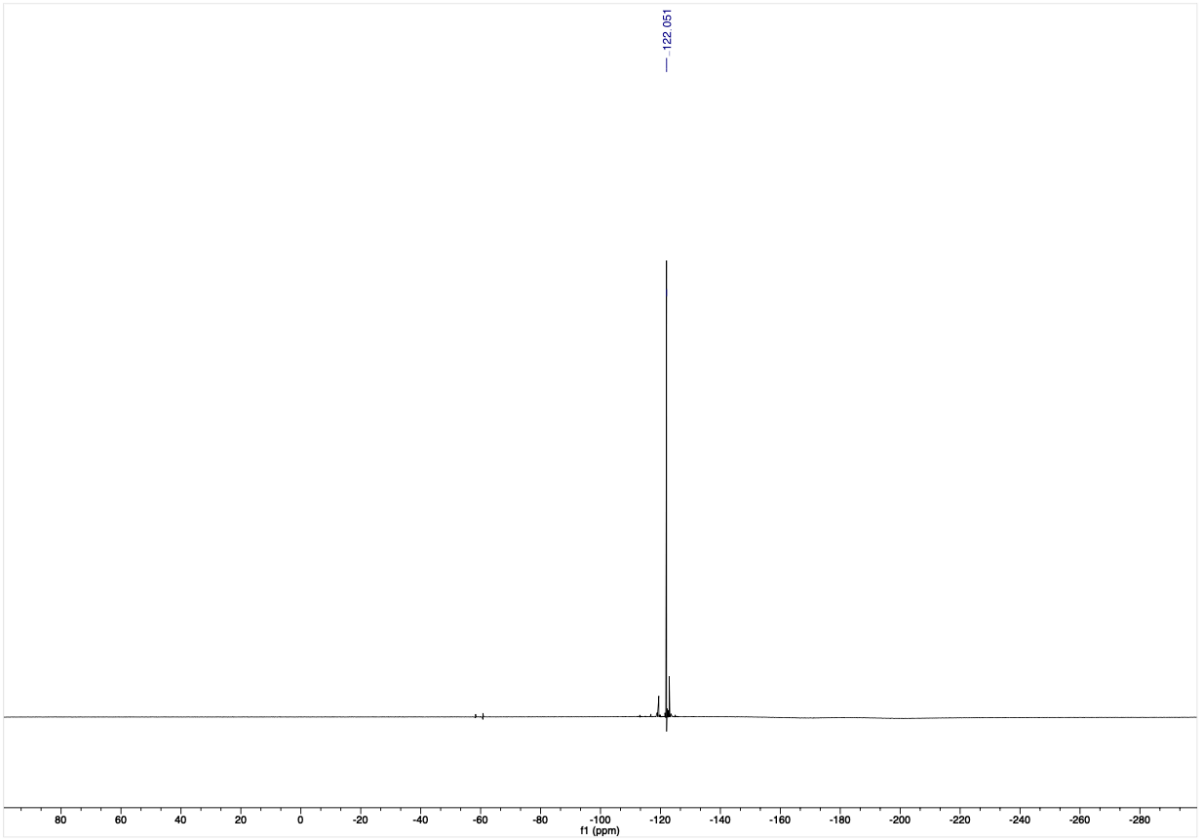
2-(Cyclobut-1-en-1-yl)-4-fluoro-1*H*-indole, 2k

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.06 (s, 1H), 7.13 – 7.02 (m, 2H), 6.81 – 6.70 (ddd, *J* = 10.3, 6.6, 2.0 Hz, 1H), 6.55 – 6.48 (d, *J* = 2.1 Hz, 1H), 6.21 – 6.12 (m, 1H), 2.93 – 2.85 (m, 2H), 2.69 – 2.61 (m, 2H).



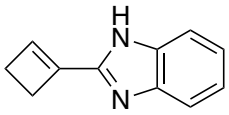
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.25 – 154.62 (d, *J* = 247.2 Hz), 139.05 – 138.52 (d, *J* = 11.3 Hz), 123.25 – 122.65 (d, *J* = 7.7 Hz), 118.16 – 117.56 (d, *J* = 22.6 Hz), 106.85 – 106.47 (d, *J* = 3.5 Hz), 105.23 – 104.38 (d, *J* = 19.1 Hz).

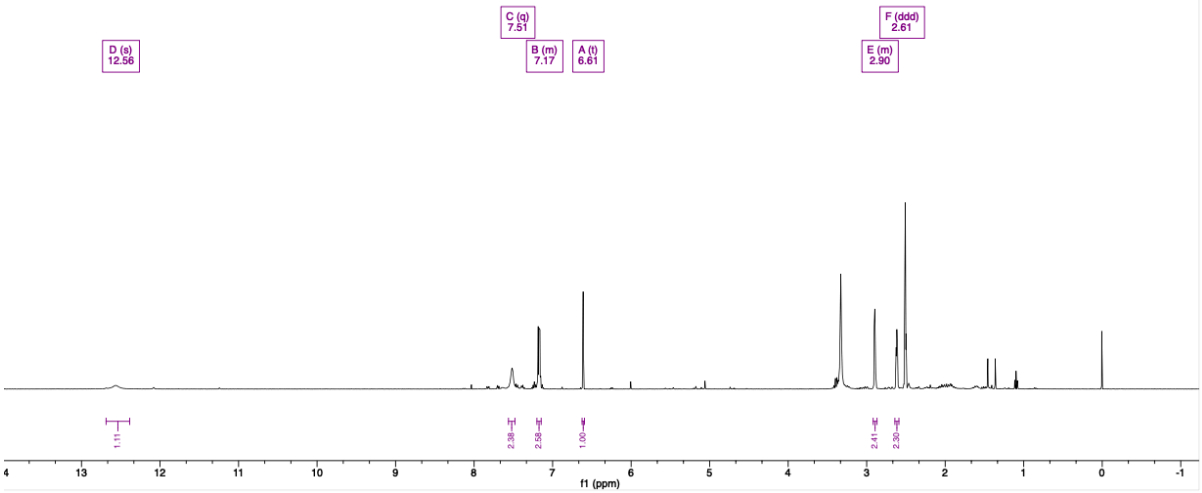


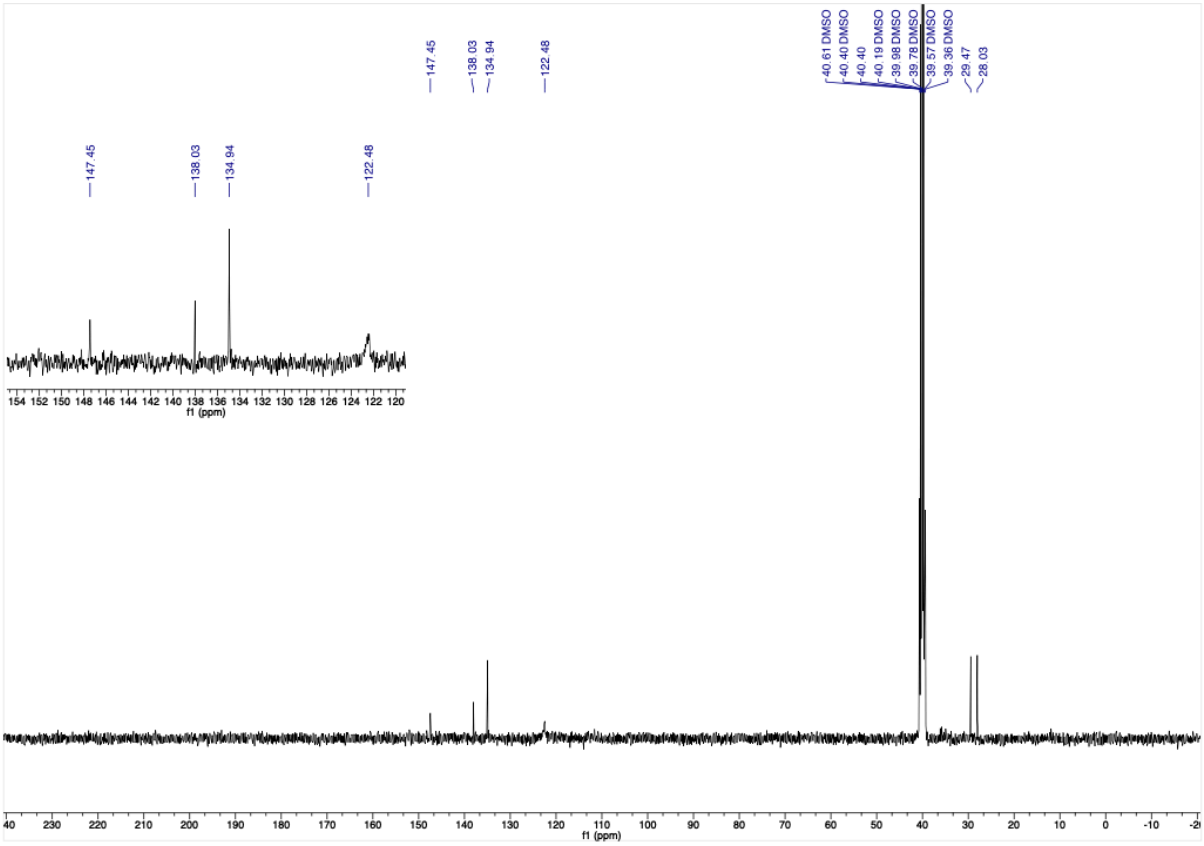

-122.051
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
f1 (ppm)

2-(Cyclobut-1-en-1-yl)-1*H*-benzo[*d*]imidazole, 2l

^{1}H NMR (400 MHz, DMSO) δ 12.69 – 12.39 (s, 1H), 7.56 – 7.48 (q, *J* = 8.1, 6.3 Hz, 2H), 7.20 – 7.15 (m, 3H), 6.62 – 6.60 (t, *J* = 1.3 Hz, 1H), 2.92 – 2.87 (m, 2H), 2.64 – 2.59 (ddd, *J* = 4.5, 2.4, 1.2 Hz, 2H).

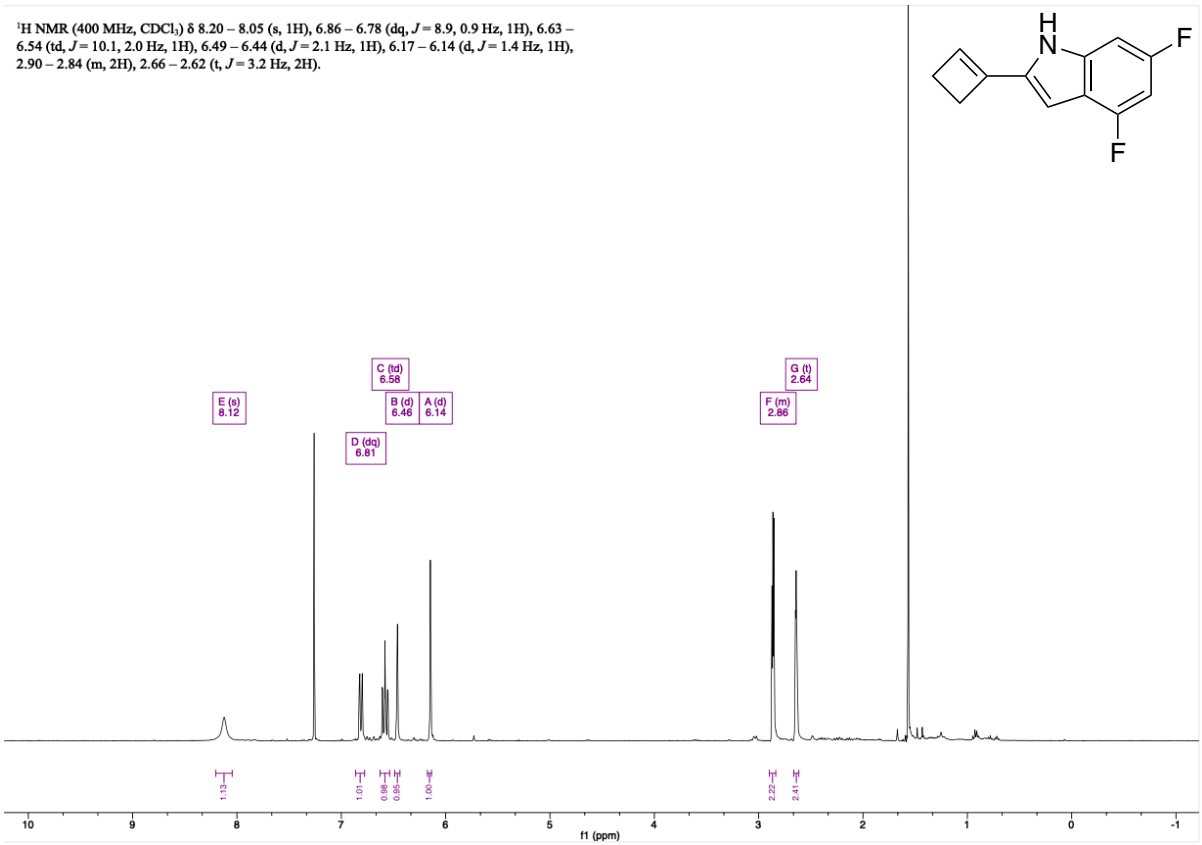




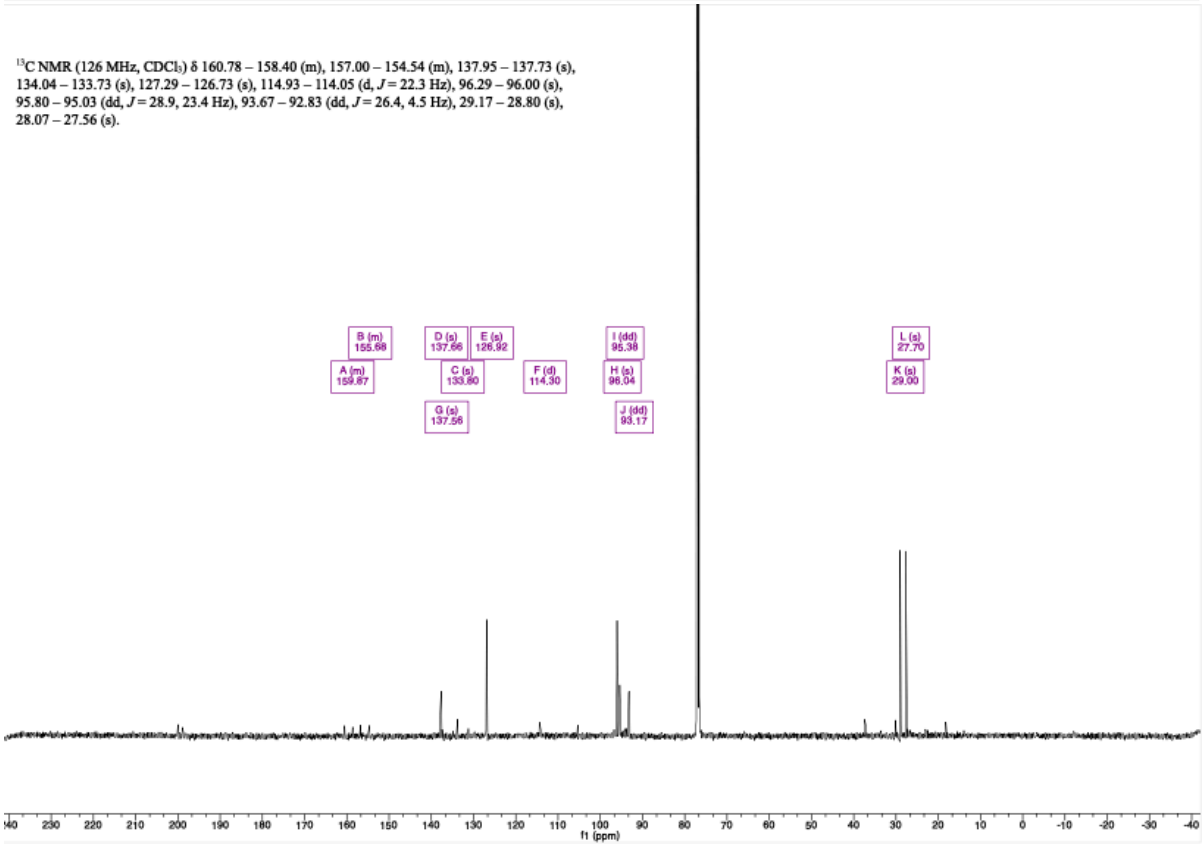


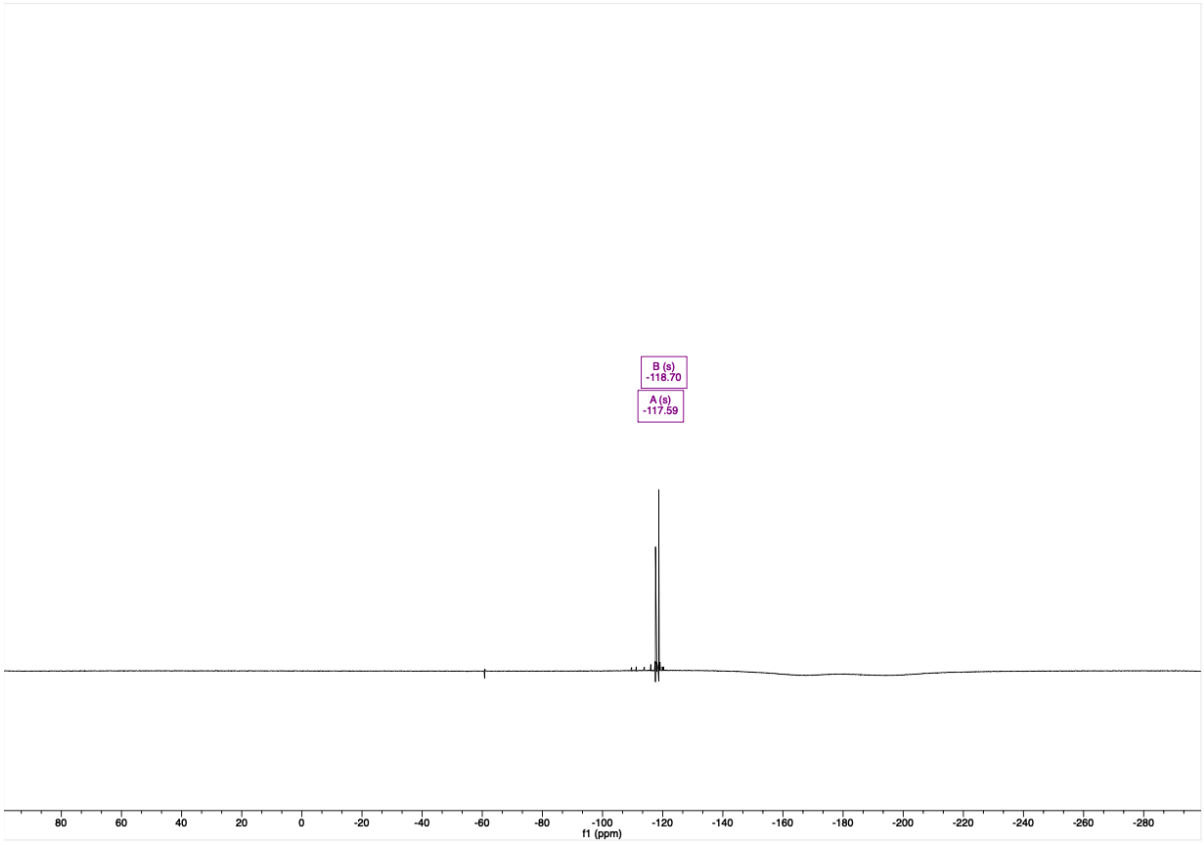
2-(Cyclobut-1-en-1-yl)-4,6-difluoro-1*H*-indole, 2m

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.05 (s, 1H), 6.86 – 6.78 (dq, *J* = 8.9, 0.9 Hz, 1H), 6.63 – 6.54 (td, *J* = 10.1, 2.0 Hz, 1H), 6.49 – 6.44 (d, *J* = 2.1 Hz, 1H), 6.17 – 6.14 (d, *J* = 1.4 Hz, 1H), 2.90 – 2.84 (m, 2H), 2.66 – 2.62 (t, *J* = 3.2 Hz, 2H).



^{13}C NMR (126 MHz, $CDCl_3$) δ 160.78 – 158.40 (m), 157.00 – 154.54 (m), 137.95 – 137.73 (s), 134.04 – 133.73 (s), 127.29 – 126.73 (s), 114.93 – 114.05 (d, *J* = 22.3 Hz), 96.29 – 96.00 (s), 95.80 – 95.03 (dd, *J* = 28.9, 23.4 Hz), 93.67 – 92.83 (dd, *J* = 26.4, 4.5 Hz), 29.17 – 28.80 (s), 28.07 – 27.56 (s).




B (s)
-118.70
A (s)
-117.59
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
f1 (ppm)

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