Supporting Information

Synthesis of Spirooxindoles via Formal Acetylene Insertion into a Common Palladacycle Intermediate

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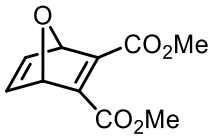
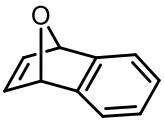
Contents

General Considerations

Reactions were performed under argon in a dry environment unless otherwise stated. Reaction progress was monitored by thin layer chromatography (TLC) and visualized under UV light. Toluene was distilled over calcium hydride. Tetrakis(triphenylphosphine)palladium(0) was purchased from Alfa Aesar and stored in the freezer. Cesium carbonate was purchased from Sigma Aldrich, flame-dried with a Bunsen burner under vacuum and cooled to room temperature before usage, and purged under argon and stored in a desiccator following reaction set-up. 1,3,5-Trimethoxybenzene was purchased from Combi-Blocks and used as received. All other starting materials and reagents were purchased from Sigma, Alfa Aesar, Fisher, Oakwood Chemical or Combi-Blocks and were used as received. Catalytic reactions were performed in 2 dram vials equipped with a teflon septum (ThermoScientific National B7995-15) and a stir bar (Fisher cat no. 14-513-57, 12 x 4.5 mm). An oil bath was used as the heating source for reactions requiring heat. Flash column chromatography was performed with Silicycle 46-60 μm silica gel. Dimethyl 7-oxa-bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate **2** and 1,4-dihydronaphthalene-1,4-epoxide **2'** were synthesized following previous methods.[1,2]



2
1.2 equiv



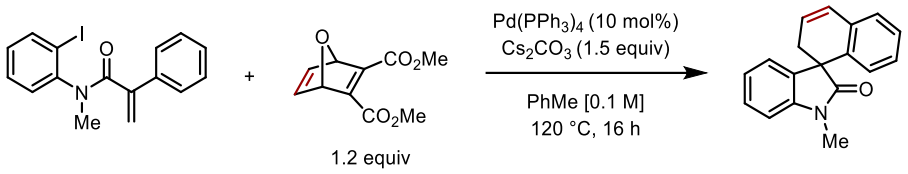
2'
1.2 equiv

^{1}H, ^{13}C and ^{19}F NMR were obtained at 296 K on Agilent DD2 500 equipped with a 5 mm Xses Cold Probe, or a Varian Mercury 300 or 400 or a Bruker Avance III 400. Measurements were referenced to the solvent. NMR data are referenced as chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad), coupling constant (Hz), integration. NMR yields were obtained by ^{1}H NMR analysis using a 10 second relaxation delay and 1,3,5-trimethoxybenzene as an internal standard. HRMS were obtained on a JEOL AccuTOF-DART performed at the Advanced Instrumentation for Molecular Structure (AIMS) at the University of Toronto. IR spectra were aquired on a Perkin-Elmer Spectrum 100 instrument with a single-bounce diamond/ZeSe ATR accessory. Data is presented in wavenumbers (cm^{-1}).

Humidity impacts yields most likely due to the hygroscopic nature of cesium carbonate. As such, catalytic reactions should not be run outside of a glovebox in a humid environment.

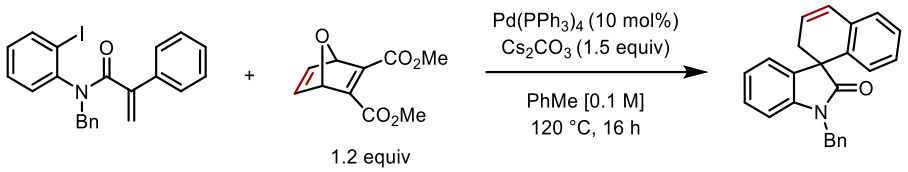
Optimization Tables

Spirooxindole from an Aryl Iodide



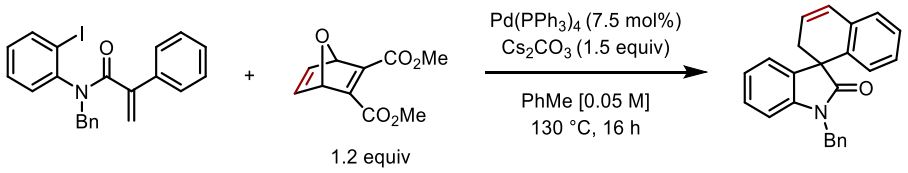
Entry	Variation	Product (%)[a]
1	**None**	**54 (45)[b]**
2	$Pd(OAc)_2$ (10 mol%), PPh_3 (20 mol%)	0
3	$Pd(OAc)_2$ (10 mol%), $PCy_3 \cdot HBF_4$ (20 mol%)	<5
4	$Pd(dba)_2$ (10 mol%), PPh_3 (20 mol%)	28
5	$Pd(dba)_2$ (10 mol%), $PCy_3 \cdot HBF_4$ (20 mol%)	9
6	$Pd(PPh_3)_2Cl_2$ (10 mol%)	0
7	Oxabicycle (2.0 equiv)	56
8	+ PivOH (30 mol%)	46
9	K_2CO_3 instead of Cs_2CO_3	0
10	Ar–Br instead of Ar–I	8

[a]Yields were determined by ^{1}H NMR spectroscopy analysis of crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yield.



Entry	Variations	Product (%)[a]
1	None	59 (55)[b]
2	$Pd(PPh_3)_4$ (5 mol%)	52
3	+ PPh_3 (20 mol%)	51
4	PhMe [0.2 M]	47
5	PhMe [0.05 M]	69
6	130 °C	75
7	PhMe [0.05 M], 130 °C	85
8	**$Pd(PPh_3)_4$ (7.5 mol%), PhMe [0.05 M], 130 °C**	**92 (88)[b]**

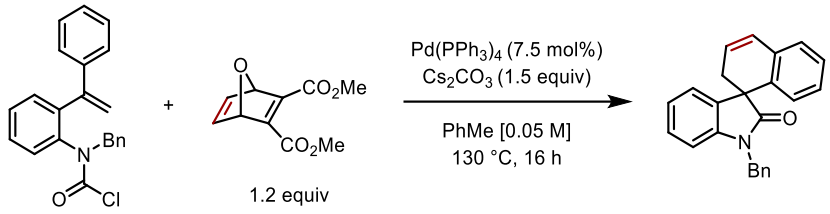
[a]Yields were determined by ^{1}H NMR spectroscopy analysis of crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yield.



Entry	Variations	Product (%)[a]
1	**None**	**92 (88)[b]**
2	$Pd(PPh_3)_4$ (5 mol%)	82
3	1,4-Dioxane	72
4	DMF	40
5	Xylenes	75
6	PhMe [0.1 M]	79
7	140 °C	86
8	0.1 mmol scale	80
9	0.1 mmol, PhMe [0.025 M]	81

[a]Yields were determined by ^{1}H NMR spectroscopy analysis of crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yield.

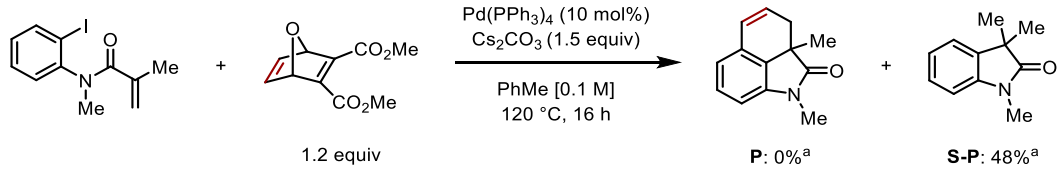
Spirooxindole from a Carbamoyl Chloride



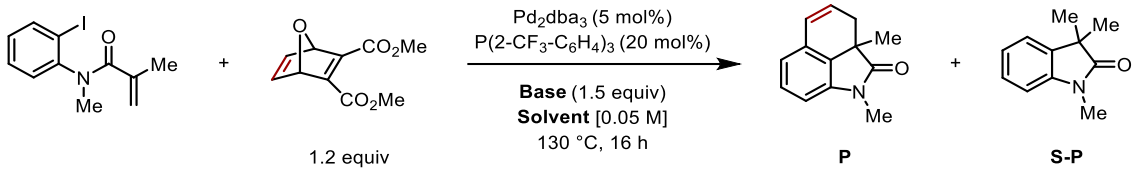
Entry	Variations	Product (%)[a]
1	**None**	**76 (78)[b]**
2	$Pd(PPh_3)_4$ (10 mol%)	63
3	$Pd(PPh_3)_4$ (5 mol%)	73

[a]Yields were determined by ^1H NMR spectroscopy analysis of crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yield.

Dihydrobenzoindolone

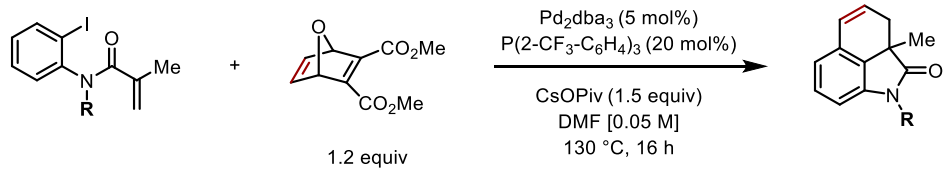


[a]Yields were determined by ^{1}H NMR spectroscopy analysis of crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.



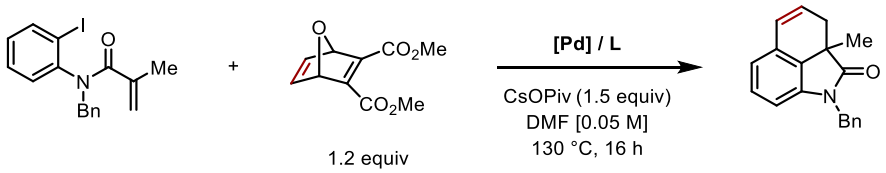
Entry	Base	Solvent	Product (%)[a]	Side-Product (%)[a]
1	Cs_2CO_3	PhMe	0	21
2	Cs_2CO_3	DMF	0	39
3	CsOPiv	PhMe	0	0
4	**CsOPiv**	**DMF**	**12**	**0**

[a]Yields were determined by ^{1}H NMR spectroscopy analysis of crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.



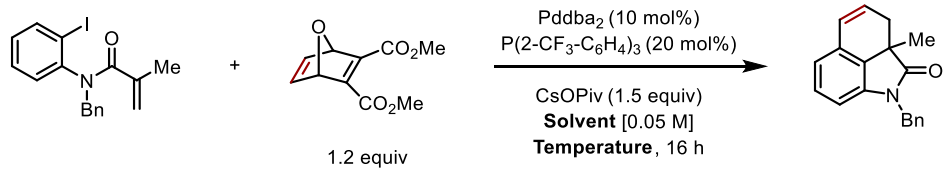
Entry	R	Product (%)[a]
1	Me	12
2	**Bn**	**21**
3	CH_2CO_2t-Bu	17
4	CH_2Mes	18
5	2,4,6-Triisopropylbenzyl	16

[a]Yields were determined by ^{1}H NMR spectroscopy analysis of crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.



Entry	[Pd]	Ligand	Product (%)[a]
1	Pd_2dba_3 (5 mol%)	P(2-CF_3-C_6H_4)$_3$	21
2	Pd_2dba_3 (5 mol%)	P(2-tol)$_3$	17
3	Pd_2dba_3·$CHCl_3$ (5 mol%)	P(2-CF_3-C_6H_4)$_3$	26
4	**Pd(dba)$_2$ (10 mol%)**	**P(2-CF_3-C_6H_4)$_3$**	**27 (29)[b]**
5	[Pd(allyl)Cl]$_2$ (5 mol%)	P(2-CF_3-C_6H_4)$_3$	24

[a]Yields were determined by ^{1}H NMR spectroscopy analysis of crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yield.

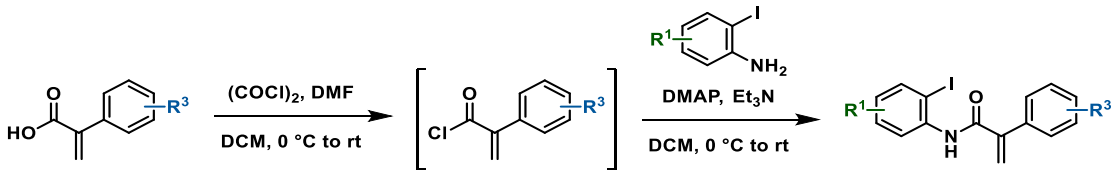


Entry	Temperature / °C	Solvent	Product (%)[a]
1	**130**	**DMF**	**27 (29)[b]**
2	140	DMF	28
3	115	DMF	12
4	115	MeCN	3

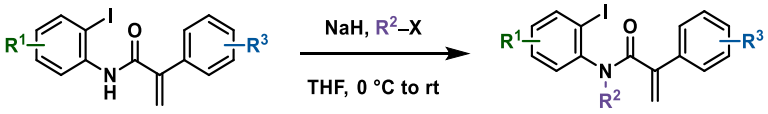
[a]Yields were determined by ^{1}H NMR spectroscopy analysis of crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yield.

Procedures for the Synthesis of Substrates

General Procedure 1 (GP1)

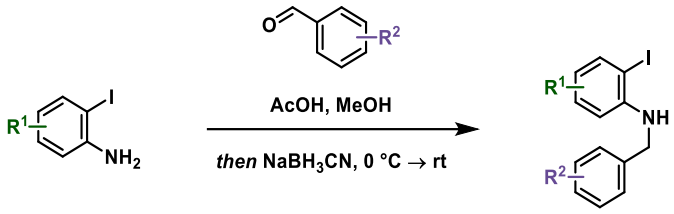


The substituted atropic acid (typically 4.0 mmol) and 3 drops of DMF were stirred in DCM [0.4 M] at 0 °C. Oxalyl chloride (2.0 equiv) was added dropwise to this mixture. The reaction was allowed to warm to room temperature and stirred for 1 h. The resulting solution was concentrated under reduced pressure to provide the acyl chloride as a yellow slurry that was subsequently taken up with the same amount of DCM. A solution of the substituted 2-iodoaniline (1.0 equiv), DMAP (0.05 equiv) and Et_3N (2.0 equiv) was prepared in DCM [0.5 M] and cooled to 0 °C. The acyl chloride solution was added dropwise into the vessel containing the substituted 2-iodoaniline. The reaction was allowed to warm to room temperature and was stirred overnight. The reaction mixture was filtered through a pad of silica, which was washed with EtOAc. The filtrate was concentrated under reduced pressure and the crude mixture was purified by flash chromatography.

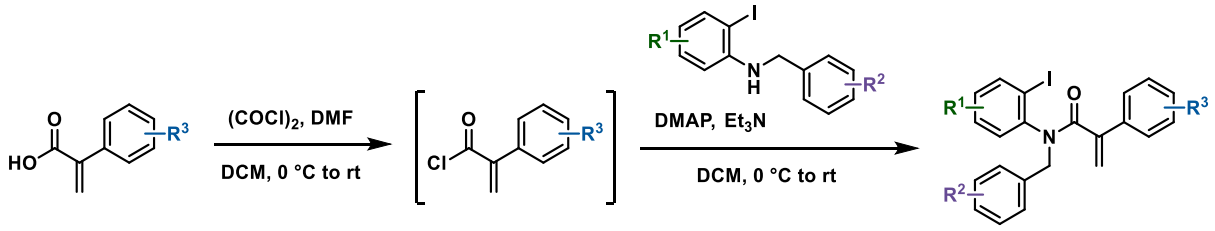


The substituted acrylamide was dissolved in THF [0.2 M] at 0 °C. Sodium hydride (60% w/w, 2.0 equiv) was added to the solution and the mixture was stirred for 5 min followed by addition of the alkyl halide (2.0 equiv). The reaction was allowed to warm to room temperature and was stirred overnight. The reaction was quenched with brine and extracted three times with EtOAc. The combined organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude mixture was purified by flash chromatography.

General Procedure 2 (GP2)

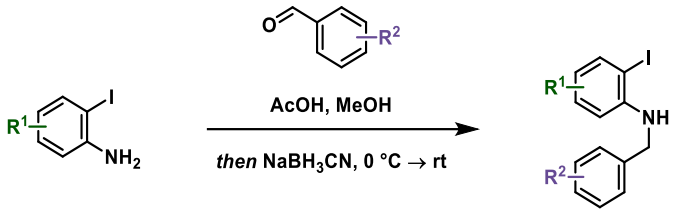


The substituted 2-iodoaniline (typically 4.0 mmol) was dissolved in MeOH [0.4 M]. AcOH (1.5 equiv) and the substituted aldehyde (1.5 equiv) were added to the solution, and the mixture was stirred at room temperature for 30 mins. The mixture was cooled to 0 ºC and $NaBH_3CN$ (1.5 equiv) was added portionwise. The reaction was allowed to warm to room temperature and was stirred for 3 h. The reaction was quenched with sat. $NaHCO_3$ (aq) and brine and extracted three times with EtOAc. The combined organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude mixture was purified by flash chromatography.

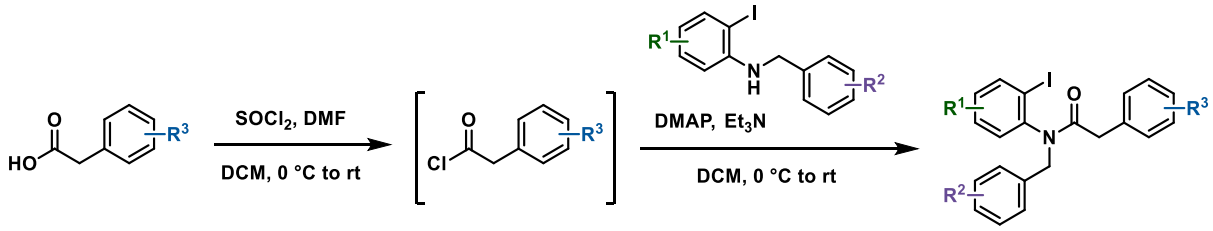


Atropic acid (1.0 equiv) was stirred in DCM [0.4 M] at 0 °C. Oxalyl chloride (2.0 equiv) was added dropwise to this mixture, followed by 3 drops of DMF. The reaction was allowed to warm to room temperature and stirred for 1 h. The resulting solution was concentrated under reduced pressure to provide the acyl chloride as a yellow slurry that was subsequently taken up with the same amount of DCM. A solution of the *N*-alkylated 2-iodoaniline synthesized from the previous step (1.0 equiv), DMAP (0.05 equiv) and Et_3N (2.0 equiv) was prepared in DCM [0.5 M] and cooled to 0 °C. The acyl chloride solution was added dropwise into the vessel containing the *N*-alkylated 2-iodoaniline. The reaction was allowed to warm to room temperature and was stirred overnight. The reaction mixture was filtered through a pad of silica, which was washed with EtOAc. The filtrate was concentrated under reduced pressure and the crude mixture was purified by flash chromatography.

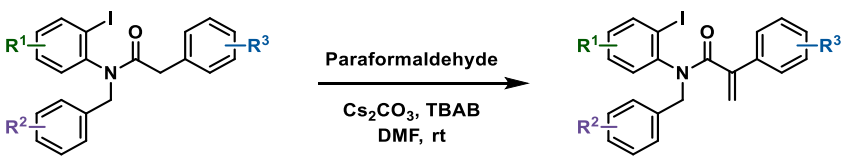
General Procedure 3 (GP3)



The substituted 2-iodoaniline (typically 3.0 to 5.0 mmol) was dissolved in MeOH [0.4 M]. AcOH (1.5 equiv) and the substituted aldehyde (1.5 equiv) were added to the solution, and the mixture was stirred at room temperature for 30 mins. The mixture was cooled to 0 ºC and $NaBH_3CN$ (1.5 equiv) was added portionwise. The reaction was allowed to warm to room temperature and was stirred for 3 h. The reaction was quenched with sat. $NaHCO_3$ (aq) and brine and extracted three times with EtOAc. The combined organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude mixture was purified by flash chromatography.



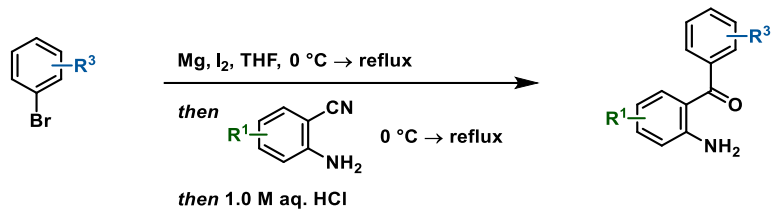
The substituted arylacetic acid (1.0 equiv) was dissolved in DCM [1.3 M] at 0 °C. Thionyl chloride (1.4 equiv) was added dropwise to this mixture, followed by DMF (0.1 equiv). The reaction was allowed to warm to room temperature and stirred for 1 h. The resulting solution was concentrated under reduced pressure to provide the acyl chloride as a yellow slurry that was subsequently taken up with DCM [0.3 M]. A solution of *N*-alkylated 2-iodoaniline synthesized from the previous step and Et_3N (1.2 equiv) was prepared in DCM [1.0 M] and added dropwise into the vessel containing the acyl chloride. The reaction was allowed to warm to room temperature and was stirred overnight. The reaction mixture was filtered through a pad of silica, which was washed with EtOAc. The filtrate was concentrated under reduced pressure and the crude mixture was purified by flash chromatography.



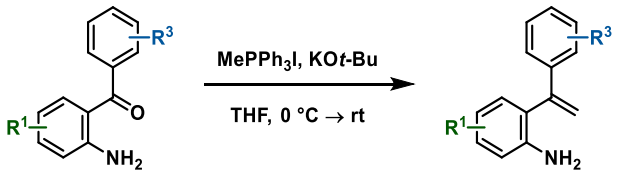
The substituted arylacetamide was dissolved in DMF [0.3 M]. Cesium carbonate (3.0 equiv), tetrabutylammonium bromide (0.3 equiv) and paraformaldehyde (2.5 equiv) were added in that

order to the reaction vessel and the reaction was stirred overnight. The reaction was quenched with brine and extracted three times with EtOAc. The combined organic layers were washed five times with brine, dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude mixture was purified by flash chromatography.

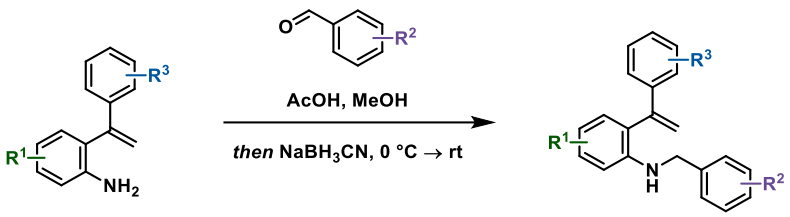
General Procedure 4 (GP4)



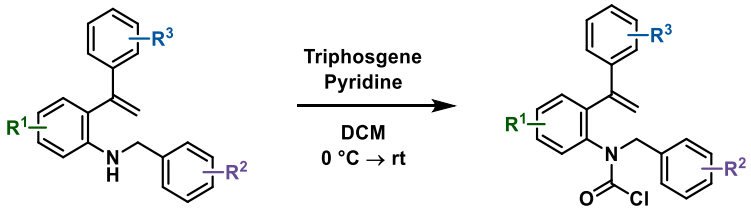
To a stirred mixture of magnesium turnings (3.1 equiv) and an iodine crystal was added a THF solution of bromobenzene or a derivative (0.3 M, 3.0 equiv) at 0 °C dropwise. The reaction mixture was heated to reflux and stirred for 1 to 3 h after which it was cooled to 0 °C. To this in situ generated Grignard reagent solution was added a THF solution of 2-aminobenzonitrile or a derivative (1.0 M, 1.0 equiv, typically 4 to 6 mmol) at 0 °C dropwise. The reaction mixture was heated to reflux and stirred overnight. A 1.0 M aq. HCl solution (typically 20 mL) was slowly added to quench the reaction mixture, which was stirred at room temperature for 15 min. The reaction was diluted with brine and extracted three times with EtOAc. The organic layer was washed with brine, dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude mixture was purified by flash chromatography.



To a stirred suspension of methyltriphenylphosphonium iodide (1.5 equiv) in THF [0.3 M] at 0 °C was added potassium *tert*-butoxide portionwise. The resulting mixture was warmed to room temperature and stirred for 30 min before being cooled to 0 °C. A 1.0 M THF solution of 2′-aminobenzophenone or a derivative was added dropwise to the suspension, which was subsequently warmed to room temperature and stirred overnight. Pentanes (typically 30 to 60 mL) followed by EtOAc (typically 30 to 60 mL) were added to the reaction mixture, which was pushed through a pad of silica under reduced pressure. The filtrate was concentrated under reduced pressure and the crude mixture was purified by flash chromatography.



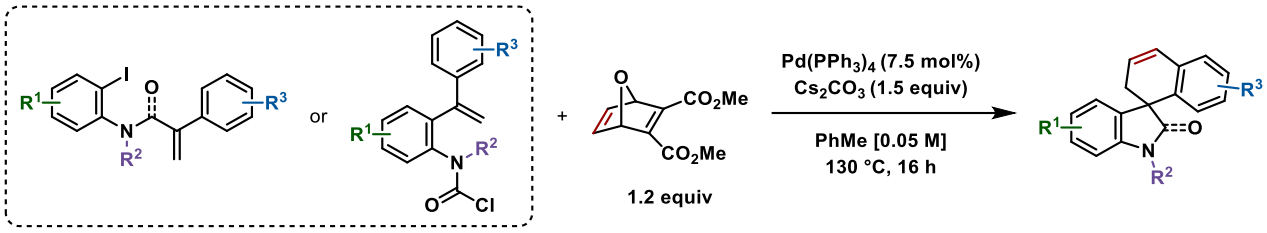
2-(1-phenylvinyl)aniline or a derivative was dissolved in methanol [0.4 M]. Benzaldehyde or a derivative (1.5 equiv) was added followed by acetic acid (1.5 equiv). The reaction was stirred for 30 min before being cooled to 0 °C. Sodium cyanoborohydride (1.5 equiv) was added portionwise to the suspension, which was subsequently warmed to room temperature and stirred for 3 h. The reduction was quenched with sat. $NaHCO_3$ (aq), diluted with distilled water and extracted three times with EtOAc. The organic layer was washed with brine, dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude mixture was purified by flash chromatography.



The secondary amine was dissolved in DCM [0.3 M] and cooled to 0 °C. To this solution was added pyridine (2.0 equiv), followed by triphosgene (0.4 equiv). The reaction was warmed to room temperature and stirred for 3 h. A 1.0 M aq. HCl solution (typically 20 mL) was slowly added to quench the reaction mixture and extracted three times with DCM. The organic layer was washed with brine, dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude mixture was purified by flash chromatography.

Procedure for the Catalytic Reactions

General Procedure 5 (GP5)

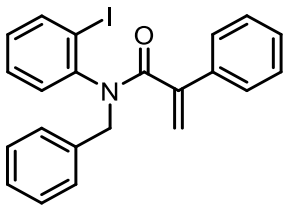


Vials and stir bars were dried in 110 °C oven overnight prior to use. Two 2 dr vials, one equipped with stir bar and one without were cooled to room temperature under argon flow. Cesium carbonate (98 mg, 0.30 mmol, 1.5 equiv), aryl iodide or carbamoyl chloride (0.20 mmol, 1.0 equiv) and tetrakis(triphenylphosphine)palladium(0) (17 mg, 0.015 mmol, 7.5 mol%) were added in that order to the vial with a stir bar. Oxabicycle (56 mg, 1.1·0.24 mmol = 0.26 mmol, 1.1·1.2 equiv = 1.32 equiv) was weighed in the empty vial. Freshly distilled toluene (1.1·4.0 mL = 4.4 mL) was added via syringe to the oxabicycle-containing vial and the vial was sonicated for 15 s to fully dissolve the oxabicycle. 4.0 mL of the resulting solution was transferred via syringe to the first vial (when multiple reactions are set up at the same time, a stock solution of identical concentration is prepared with the amount of oxabicycle and toluene corresponding to the number of reactions; 4.0 mL is transferred to each reaction vessel). The vial was equipped with a Teflon-sealed cap and immediately stirred at 130 °C for 16 h. The reaction was passed through a pad of silica washing with ethyl acetate. The filtrate was concentrated under reduced pressure and the resulting residue purified by flash chromatography.

Characterization of Substrates

Aryl Iodides

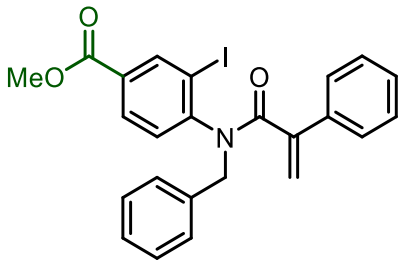
N-Benzyl-*N*-(2-iodophenyl)-2-phenylacrylamide (1a)



Synthesized following **GP1** from atropic acid, 2-iodoaniline and benzyl bromide. Characterization was consistent with literature.[3]

Liang, R.-X.; Chen, R.-Y.; Zhong, C.; Zhu, J.-W.; Cao, Z.-Y.; Jia, Y.-X. 3,3'-Disubstituted Oxindoles Formation via Copper-Catalyzed Arylboration and Arylsilylation of Alkenes. *Org. Lett.* **2020,** *22*, 3215–3218.[3]

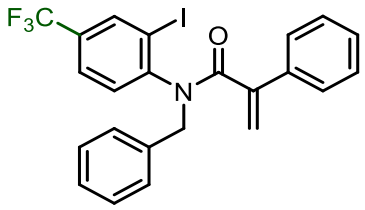
Methyl 4-(*N*-benzyl-2-phenylacrylamido)-3-iodobenzoate (1b)



Synthesized following **GP1** from atropic acid, methyl 4-amino-3-iodobenzoate and benzyl bromide. Characterization was consistent with literature.[4]

Yoon, H.; Lossouarn, A.; Landau, F.; Lautens, M. Pd-Catalyzed Spirocyclization via C–H Activation and Benzyne Insertion. *Org. Lett.* **2016,** *18*, 6324–6327.[4]

***N*-Benzyl-*N*-(2-iodo-4-(trifluoromethyl)phenyl)-2-phenylacrylamide (1c)**



Synthesized following **GP1** from atropic acid, 2-iodo-4-(trifluoromethyl)aniline and benzyl bromide on a 6.0 mmol scale. Obtained 835 mg of a light-yellow solid (27% yield over 2 steps).

Two rotamers were observed in a 12:1 ratio. The major rotamer is reported below.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, J = 1.4 Hz, 1H), 7.31 – 7.25 (m, 3H), 7.24 – 7.13 (m, 5H), 7.07 – 6.99 (m, 3H), 6.19 (d, J = 8.3 Hz, 1H), 5.82 (d, J = 14.3 Hz, 1H), 5.69 (s, 1H), 5.36 (s, 1H), 4.08 (d, J = 14.3 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.6, 146.4, 145.6, 136.9 (d, J = 3.6 Hz), 136.8, 136.3, 132.1, 131.12 (q, J = 33.2 Hz), 129.6, 128.7, 128.6, 128.3, 128.1, 126.1, 125.0 (q, J = 3.7 Hz), 122.5 (q, J = 273.1 Hz), 118.2, 100.4, 51.4.

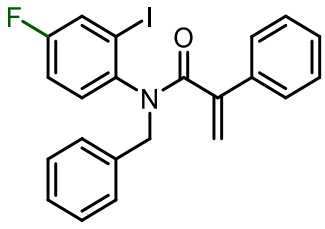
^{19}F NMR (375 MHz, $CDCl_3$) δ -62.8.

IR (ATR) 2986, 1642, 1598, 1499, 1392, 1318, 1167, 1134, 1080, 700

HRMS (DART) m/z: [M + H]+ Calcd for $C_{23}H_{18}NOF_3I$ 508.0380; Found 508.0383

MP 92-95 °C

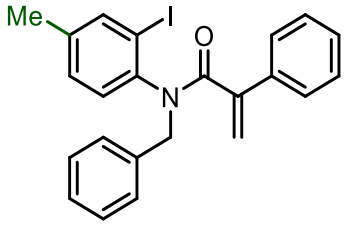
***N*-Benzyl-*N*-(4-fluoro-2-iodophenyl)-2-phenylacrylamide (1d)**



Synthesized following **GP1** from atropic acid, 4-fluoro-2-iodoaniline and benzyl bromide. Characterization was consistent with literature.[4]

Yoon, H.; Lossouarn, A.; Landau, F.; Lautens, M. Pd-Catalyzed Spirocyclization via C–H Activation and Benzyne Insertion. *Org. Lett.* **2016,** *18,* 6324–6327.[4]

***N*-Benzyl-*N*-(2-iodo-4-methylphenyl)-2-phenylacrylamide (1e)**



Synthesized following **GP1** from atropic acid, 2-iodo-4-methylaniline and benzyl bromide on a 4.0 mmol scale. Obtained 170 mg of an off-white solid (9% yield over 2 steps).

Two rotamers were observed in a 15:1 ratio. The major rotamer is reported below.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (dd, J = 2.0, 0.9 Hz, 1H), 7.29 – 7.22 (m, 4H), 7.21 – 7.16 (m, 2H), 7.14 – 7.09 (m, 3H), 6.57 (ddd, J = 8.0, 2.0, 0.8 Hz, 1H), 6.00 (d, J = 8.0 Hz, 1H), 5.81 (d, J = 14.2 Hz, 1H), 5.61 (s, 1H), 5.32 (s, 1H), 4.04 (d, J = 14.2 Hz, 1H), 2.19 (s, 3H).

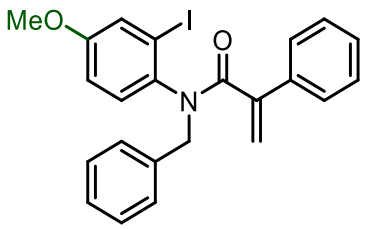
^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 145.6, 140.5, 140.2, 139.6, 137.1, 137.0, 131.3, 129.6, 128.9, 128.5, 128.4, 128.0, 127.7, 126.1, 116.6, 100.0, 51.6, 20.5.

IR (ATR) 2986, 2924, 1642, 1481, 1435, 1392, 1242, 1202, 907, 696

HRMS (DART) m/z: [M + H]+ Calcd for $C_{23}H_{21}NOI$ 454.0662; Found 454.0665

MP 118-120 °C

***N*-Benzyl-*N*-(2-iodo-4-methoxyphenyl)-2-phenylacrylamide (1f)**



Synthesized following **GP1** from atropic acid, 2-iodo-4-methoxyaniline and benzyl bromide on a 2.0 mmol scale. Obtained 639 mg of a beige solid (68% yield over 2 steps).

Two rotamers were observed in a 16:1 ratio. The major rotamer is reported below.

^{1}H NMR (500 MHz, $CDCl_3$) 7.29 – 7.22 (m, 6H), 7.21 – 7.16 (m, 3H), 7.13 – 7.08 (m, 2H), 6.28 (dd, J = 8.8, 2.9 Hz, 1H), 5.97 (d, J = 8.8 Hz, 1H), 5.80 (d, J = 14.1 Hz, 1H), 5.62 (d, J = 0.6 Hz, 1H), 5.33 (d, J = 0.6 Hz, 1H), 4.01 (d, J = 14.1 Hz, 1H), 3.68 (s, 3H).

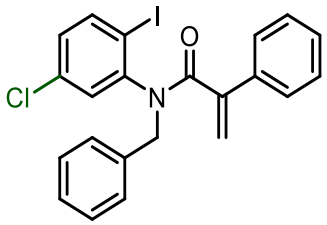
^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4, 158.9, 145.9, 137.2, 137.0, 135.9, 132.0, 129.6, 128.5, 128.4, 128.1, 127.7, 126.1, 124.5, 116.6, 113.7, 100.6, 55.7, 51.7.

IR (ATR) 3028, 2934, 2835, 1637, 1482, 1435, 1286, 1199, 1027, 693.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{23}H_{21}INO_2$ 470.0612; Found 470.0606

MP 60-64 °C

***N*-Benzyl-*N*-(5-chloro-2-iodophenyl)-2-phenylacrylamide (1g)**



Synthesized following **GP1** from atropic acid, 5-chloro-2-iodoaniline and benzyl bromide on a 3.0 mmol scale. Obtained 691 mg of a white solid (49% yield over 2 steps).

Two rotamers were observed in a 12:1 ratio. The major rotamer is reported below.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, J = 8.5 Hz, 1H), 7.31 – 7.26 (m, 3H), 7.24 – 7.18 (m, 5H), 7.08 – 7.00 (m, 2H), 6.82 (dd, J = 8.5, 2.5 Hz, 1H), 6.02 (d, J = 2.5 Hz, 1H), 5.73 (d, J = 14.3 Hz, 1H), 5.68 (s, 1H), 5.34 (s, 1H), 4.08 (d, J = 14.3 Hz, 1H).

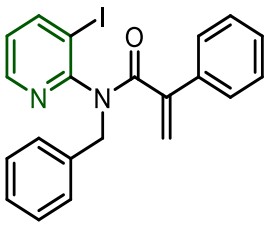
^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8, 145.9, 144.1, 140.3, 137.0, 136.3, 133.9, 132.3, 129.6, 129.5, 128.7, 128.6, 128.3, 128.0, 126.1, 118.0, 97.8, 51.5.

IR (ATR) 3030, 2970, 2932, 1738, 1635, 1451, 1380, 1236, 1202, 699.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{22}H_{18}NOClI$ 474.0116; Found 474.0115

MP 106-110 °C

***N*-Benzyl-*N*-(3-iodopyridin-2-yl)-2-phenylacrylamide (1h)**



Synthesized following **GP2** from 3-iodopyridin-2-amine, benzaldehyde and atropic acid on a 10.0 mmol scale. Obtained 267 mg of a white solid (6% yield over 2 steps).

Two rotamers were observed in a 4:1 ratio. The major rotamer is reported below.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (dd, J = 4.6, 1.7 Hz, 1H), 7.96 (dd, J = 7.9, 1.7 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.25 – 7.17 (m, 8H), 6.73 (dd, J = 7.9, 4.6 Hz, 1H), 5.67 (s, 1H), 5.43 (s, 1H), 5.36 (d, J = 14.7 Hz, 1H), 4.89 (d, J = 14.7 Hz, 1H).

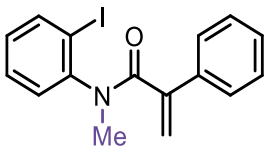
^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 155.9, 148.9, 148.2, 145.7, 136.9, 136.5, 129.2, 128.3, 128.2, 128.0, 127.5, 126.9, 123.6, 119.9, 95.1, 51.6.

IR (ATR) 3028, 2970, 2930, 1736, 1640, 1557, 1427, 1379, 1204, 694.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{21}H_{18}IN_2O$ 441.0458; Found 441.0454

MP 117-120 °C

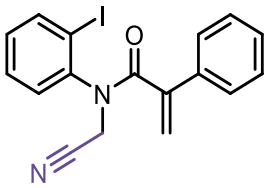
***N*-(2-Iodophenyl)-*N*-methyl-2-phenylacrylamide (1i)**



Synthesized following **GP1** from atropic acid, 2-iodoaniline and methyl iodide. Characterization was consistent with literature.[3]

Liang, R.-X.; Chen, R.-Y.; Zhong, C.; Zhu, J.-W.; Cao, Z.-Y.; Jia, Y.-X. 3,3'-Disubstituted Oxindoles Formation via Copper-Catalyzed Arylboration and Arylsilylation of Alkenes. *Org. Lett.* **2020,** *22,* 3215–3218.[3]

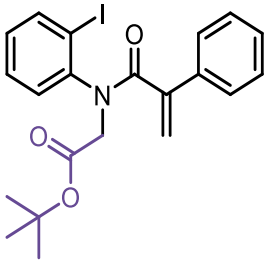
_N_-(Cyanomethyl)-_N_-(2-iodophenyl)-2-phenylacrylamide (1j)



Synthesized following **GP1** from atropic acid, 2-iodoaniline and bromoacetonitrile. Characterization was consistent with literature.[4]

Yoon, H.; Lossouarn, A.; Landau, F.; Lautens, M. Pd-Catalyzed Spirocyclization via C–H Activation and Benzyne Insertion. *Org. Lett.* **2016,** *18,* 6324–6327.[4]

***tert*-Butyl _N_-(2-iodophenyl)-_N_-(2-phenylacryloyl)glycinate (1k)**



Synthesized following **GP1** from atropic acid, 2-iodoaniline and *tert*-butyl bromoacetate on a 2.0 mmol scale. Obtained 484 mg of a white solid (52% yield over 2 steps).

Two rotamers were observed in a 16:1 ratio. The major rotamer is reported below.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (dd, J = 7.9, 1.4 Hz, 1H), 7.30 – 7.21 (m, 6H), 7.06 (ddd, J = 7.9, 7.4, 1.6 Hz, 1H), 6.88 (ddd, J = 7.9, 7.4, 1.6 Hz, 1H), 5.55 (s, 1H), 5.42 (d, J = 0.4 Hz, 1H), 5.00 (d, J = 17.0 Hz, 1H), 3.64 (d, J = 17.0 Hz, 1H), 1.49 (s, 9H).

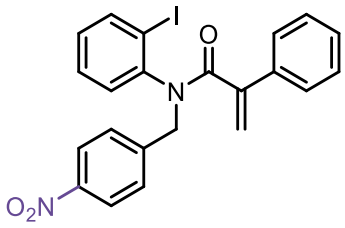
^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 167.8, 144.8, 144.4, 139.7, 136.5, 131.7, 129.5, 128.8, 128.5, 128.2, 126.4, 117.0, 99.8, 82.1, 51.3, 28.3.

IR (ATR) 2974, 2946, 1739, 1646, 1467, 1228, 1150, 1011, 764, 701.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{21}H_{23}INO_3$ 464.0717; Found 464.0708

MP 149-152 °C

***N*-(2-Iodophenyl)-*N*-(4-nitrobenzyl)-2-phenylacrylamide (1l)**



Synthesized following **GP2** from 2-iodoaniline, 4-nitrobenzaldehyde and atropic acid on a 4.0 mmol scale. Obtained 878 mg of a yellow solid (45% yield over 2 steps).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 8.7 Hz, 2H), 7.83 – 7.75 (m, 1H), 7.44 (d, J = 8.7 Hz, 2H), 7.25 – 7.14 (m, 3H), 7.09 – 7.02 (m, 2H), 6.91 – 6.81 (m, 2H), 6.23 – 6.15 (m, 1H), 5.78 (d, J = 14.5 Hz, 1H), 5.65 (s, 1H), 5.35 (s, 1H), 4.24 (d, J = 14.5 Hz, 1H).

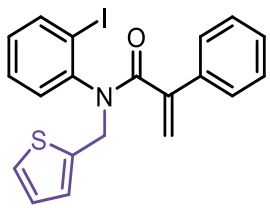
^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3, 147.6, 145.3, 144.2, 142.9, 140.3, 136.9, 131.5, 130.3, 129.7, 128.6, 128.5, 128.3, 126.1, 123.8, 117.8, 100.0, 51.2.

IR (ATR) 2970, 2929, 2851, 1738, 1637, 1516, 1342, 1205, 762, 699.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{22}H_{18}N_2O_3I$ 485.0357; Found 485.0355

MP 99-101 °C

***N*-(2-Iodophenyl)-2-phenyl-*N*-(thiophen-2-ylmethyl)acrylamide (1m)**



Synthesized following **GP2** from 2-iodoaniline, 2-thiophenecarboxaldehyde and atropic acid on a 4.0 mmol scale. Obtained 977 mg of an off-white solid (55% yield over 2 steps).

Two rotamers were observed in a 17:1 ratio. The major rotamer is reported below.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.74 (m, 1H), 7.23 (dd, J = 5.2, 0.8 Hz, 1H), 7.22 – 7.16 (m, 3H), 7.14 – 7.11 (m, 2H), 6.89 – 6.83 (m, 3H), 6.78 (d, J = 3.2 Hz, 1H), 6.34 – 6.27 (m, 1H), 5.84 (dd, J = 14.9, 0.9 Hz, 1H), 5.62 (s, 1H), 5.35 (s, 1H), 4.31 (d, J = 14.9 Hz, 1H).

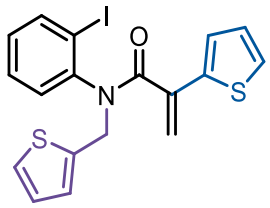
^{13}C NMR (126 MHz, $CDCl_3$) δ 169.9, 145.3, 142.9, 139.8, 138.7, 136.9, 131.7, 129.5, 128.4, 128.3, 128.1, 128.1, 126.5, 126.2, 126.2, 117.0, 100.2, 46.3.

IR (ATR) 2917, 2849, 1649, 1466, 1386, 1233, 1204, 1148, 915, 704.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{20}H_{17}INOS$ 446.0070; Found 446.0075

MP 105-107 °C

***N*-(2-Iodophenyl)-2-(thiophen-2-yl)-*N*-(thiophen-2-ylmethyl)acrylamide (1n)**



Synthesized following **GP3** from 2-iodoaniline, 2-thiophenecarboxaldehyde, 2-thiopheneacetic acid and paraformaldehyde on a 3.0 mmol scale. Obtained 330 mg of a yellow solid (24% yield over 3 steps).

Two rotamers were observed in an 18:1 ratio. The major rotamer is reported below.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, J = 7.8, 1.6 Hz, 1H), 7.24 (dd, J = 5.1, 0.7 Hz, 1H), 7.13 (dd, J = 5.1, 1.2 Hz, 1H), 7.08 (dd, J = 3.6, 1.2 Hz, 1H), 6.99 (ddd, J = 7.8, 7.6, 1.6 Hz, 1H), 6.95 – 6.90 (m, 2H), 6.87 (dd, J = 5.1, 3.4 Hz, 1H), 6.78 (d, J = 3.4 Hz, 1H), 6.49 (dd, J = 7.8, 1.7 Hz, 1H), 5.84 (dd, J = 14.9, 0.9 Hz, 1H), 5.35 (s, 1H), 5.31 (s, 1H), 4.35 (d, J = 14.9 Hz, 1H).

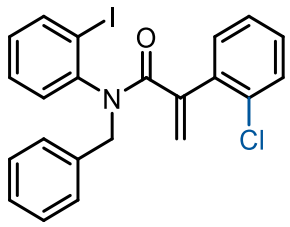
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.8, 143.2, 140.4, 140.0, 138.4, 138.3, 131.1, 129.7, 128.7, 128.2, 127.5, 126.5, 126.3, 126.1, 125.6, 114.5, 99.8, 46.4.

IR (ATR) 3105, 3054, 2938, 1738, 1643, 1465, 1424, 1239, 896, 700.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{18}H_{15}INOS_2$ 451.9634; Found 451.9635

MP 101-103 °C

***N*-Benzyl-2-(2-chlorophenyl)-*N*-(2-iodophenyl)acrylamide (1o)**



Synthesized following **GP1** from 2-(2-chlorophenyl)acrylic acid, 2-iodoaniline and benzyl bromide on a 4.0 mmol scale. Obtained 613 mg of a white solid (32% yield over 2 steps).

^{1}H NMR δ 7.68 (dd, J = 7.8, 1.6 Hz, 1H), 7.25 – 7.22 (m, 5H), 7.14 (dd, J = 8.1, 1.3 Hz, 1H), 7.01 (ddd, J = 8.1, 7.5, 1.7 Hz, 1H), 6.83 (ddd, J = 7.6, 7.5, 1.3 Hz, 1H), 6.74 (ddd, J = 7.8, 7.6, 1.7 Hz, 1H), 6.68 (ddd, J = 7.6, 7.5, 1.6 Hz, 1H), 6.56 (dd, J = 7.6, 1.7 Hz, 1H), 6.23 – 6.15 (m, 2H), 5.69 (d, J = 14.1 Hz, 1H), 5.48 (d, J = 1.3 Hz, 1H), 4.07 (d, J = 14.1 Hz, 1H).

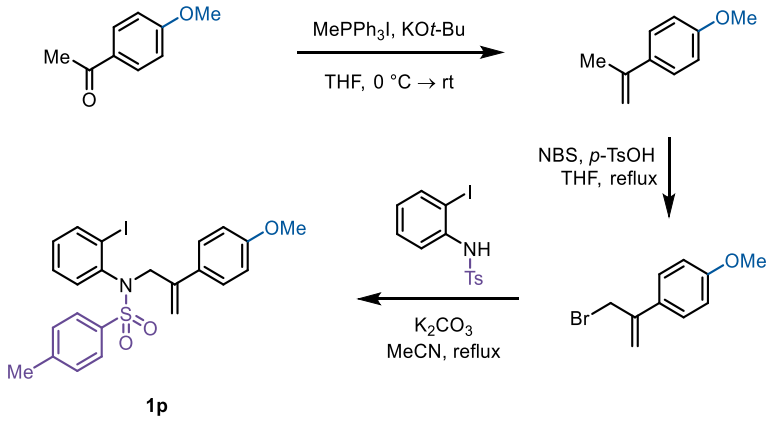
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 144.8, 142.8, 139.8, 137.2, 136.7, 132.4, 131.5, 130.0, 129.9, 129.4, 129.2, 128.7, 128.4, 128.2, 127.7, 127.3, 126.8, 100.1, 52.5.

IR (ATR) 3058, 2932, 1639, 1468, 1383, 1265, 940, 759, 721, 697.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{22}H_{18}NOClI$ 474.0116; Found 474.0118

MP 112-115 °C

_N_-(2-Iodophenyl)-_N_-(2-(4-methoxyphenyl)allyl)-4-methylbenzenesulfonamide (1p)



Two rotamers were observed in a 9:1 ratio. The major rotamer is reported below.

To a stirred suspension of methyltriphenylphosphonium iodide (1.5 equiv) in THF [0.3 M] at 0 °C was added potassium *tert*-butoxide portionwise. The resulting mixture was warmed to room temperature and stirred for 30 min before being cooled to 0 °C. A 1.0 M THF solution of 4′-methoxyacetophenone (10.0 mmol) was added dropwise to the suspension, which was subsequently warmed to room temperature and stirred overnight. Pentanes (60 mL) followed by EtOAc (60 mL) were added to the reaction mixture, which was pushed through a pad of silica under reduced pressure. The filtrate was concentrated under reduced pressure and the crude mixture was purified by flash chromatography 0→5% EtOAc/pentanes.

The following steps are based on literature procedures.[5,6] The resulting 1-methoxy-4-(prop-1-en-2-yl)benzene, *N*-bromosuccinimide (1.1 eq.), and *p*-toluenesulfonic acid monohydrate (0.1 equiv) were dissolved THF [0.3 M]. The solution was heated at reflux and stirred for 4 h before being filtered through a pad of silica and washed with EtOAc. The filtrate was concentrated under reduced pressure and the crude mixture was purified by flash chromatography 0→5% EtOAc/pentanes.

The resulting 1-(3-bromoprop-1-en-2-yl)-4-methoxybenzene was dissolved in MeCN [0.3 M] and added to a mixture of *N*-(2-iodophenyl)-4-methylbenzenesulfonamide (0.9 equiv) and potassium carbonate (1.3 equiv) in MeCN [0.1 M]. The reaction mixture was heated to reflux and stirred overnight. The reaction was quenched with brine and extracted three times with EtOAc. The combined organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude mixture was purified by flash chromatography 0→5% EtOAc/pentanes. Obtained 657 mg of an amber-yellow solid (12% yield over 3 steps).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, J = 7.9, 1.5 Hz, 1H), 7.59 (d, J = 8.3 Hz, 2H), 7.29 – 7.25 (m, 4H), 7.13 (ddd, J = 8.0, 7.4, 1.5 Hz, 1H), 6.93 (ddd, J = 7.9, 7.4, 1.6 Hz, 1H), 6.81 (d, J = 8.9 Hz, 2H), 6.65 (dd, J = 8.0, 1.6 Hz, 1H), 5.18 (d, J = 1.1 Hz, 1H), 4.93 (d, J = 1.1 Hz, 1H), 4.82 (d, J = 14.2 Hz, 1H), 4.55 (d, J = 14.2 Hz, 1H), 3.81 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 143.8, 141.6, 140.8, 140.6, 136.4, 131.8, 131.0, 129.7, 129.6, 128.4, 128.2, 128.1, 116.7, 113.8, 101.8, 55.4, 54.5, 21.7.

IR (ATR) 3078, 2932, 2838, 1606, 1513, 1345, 1158, 879, 656, 550.

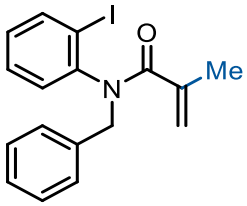
HRMS (DART) m/z: [M + H]+ Calcd for $C_{23}H_{23}NO_3SI$ 520.0438; Found 520.0433

MP 92-94 °C

Li, X.-Tao; Gu, Q.-S.; Dong, X.-Y.; Meng, X.; Liu, X.-Y. A Copper Catalyst with a Cinchona-Alkaloid-Based Sulfonamide Ligand for Asymmetric Radical Oxytrifluoromethylation of Alkenyl Oximes. *Angew. Chem. Int. Ed.* **2018,** *57,* 7668–7672.[5]

Pérez-Gómez, M.; García-López, J.-A. Trapping σ-Alkyl–Palladium(II) Intermediates with Arynes Encompassing Intramolecular C–H Activation: Spirobiaryls through Pd-Catalyzed Cascade Reactions. *Angew. Chem. Int. Ed.* **2016,** *55,* 14389–14393.[6]

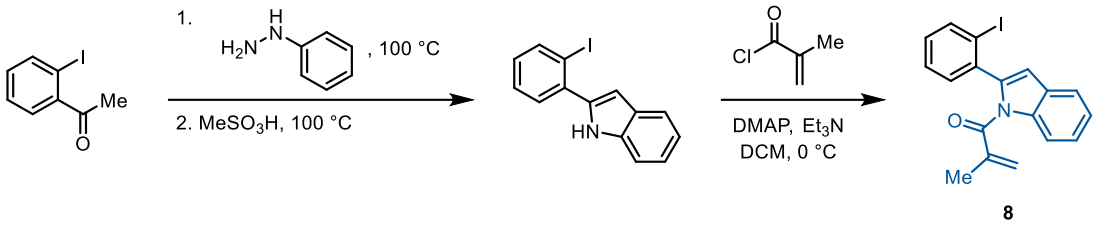
***N*-Benzyl-*N*-(2-iodophenyl)methacrylamide (6)**



Synthesized based on a known literature procedure. Characterization was consistent with literature.[7]

Liu, X.; Ma, X.; Huang, Y.; Gu, Z. Pd-Catalyzed Heck-type Cascade Reaction with *N*-Tosylhydrazones: An Efficient Way to Alkenes Via *in-situ* Generated Alkylpalladium. *Org. Lett.* **2013,** *15,* 4814–4817.[7]

1-(2-(2-Iodophenyl)-1*H*-indol-1-yl)-2-methylprop-2-en-1-one (8)



The following steps are based on literature procedures.[8,9] 2′-iodoacetophenone (3 mmol) and phenylhydrazine (1.05 equiv) were mixed together and heated to 100 °C for 1 h. After cooling the reaction to room temperature, methanesulfonic acid (12.5 equiv) was added and the mixture was heated to 100 °C for 1 h. The reaction was cooled to room temperature, quenched with ice water, followed by brine, and was extracted three times with EtOAc. The combined organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude mixture was purified by flash chromatography 0→5% EtOAc/pentanes.

A solution of the resulting 2-(2-iodophenyl)-1*H*-indole, DMAP (0.2 equiv) and Et_3N (2.0 equiv) was prepared in DCM [0.5 M] and cooled to 0 °C. Methacryloyl chloride (1.2 equiv) was added dropwise into the vessel. The reaction was allowed to warm to room temperature and was stirred overnight. The reaction mixture was filtered through a pad of silica, which was washed with EtOAc. The filtrate was concentrated under reduced pressure and the crude mixture was purified by flash chromatography 0→2.5% EtOAc/pentanes. Obtained 791 mg of a beige solid (68% yield over 2 steps).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (ddd, J = 8.3, 0.9, 0.9 Hz, 1H), 7.92 (dd, J = 8.0, 1.2 Hz, 1H), 7.64 (ddd, J = 7.6, 1.4, 0.7 Hz, 1H), 7.41 – 7.34 (m, 2H), 7.33 – 7.28 (m, 1H), 7.24 (dd, J = 7.6, 1.7 Hz, 1H), 7.04 (ddd, J = 8.0, 7.4, 1.7 Hz, 1H), 6.73 (d, J = 0.8 Hz, 1H), 5.40 – 5.34 (m, 2H), 1.86 (dd, J = 1.6, 1.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 141.0, 140.9, 139.8, 139.3, 137.0, 131.6, 129.6, 128.8, 127.9, 125.2, 124.8, 123.5, 121.0, 114.9, 111.3, 99.7, 18.7.

IR (ATR) 3047, 2919, 1679, 1441, 1316, 1164, 943, 769, 737, 607.

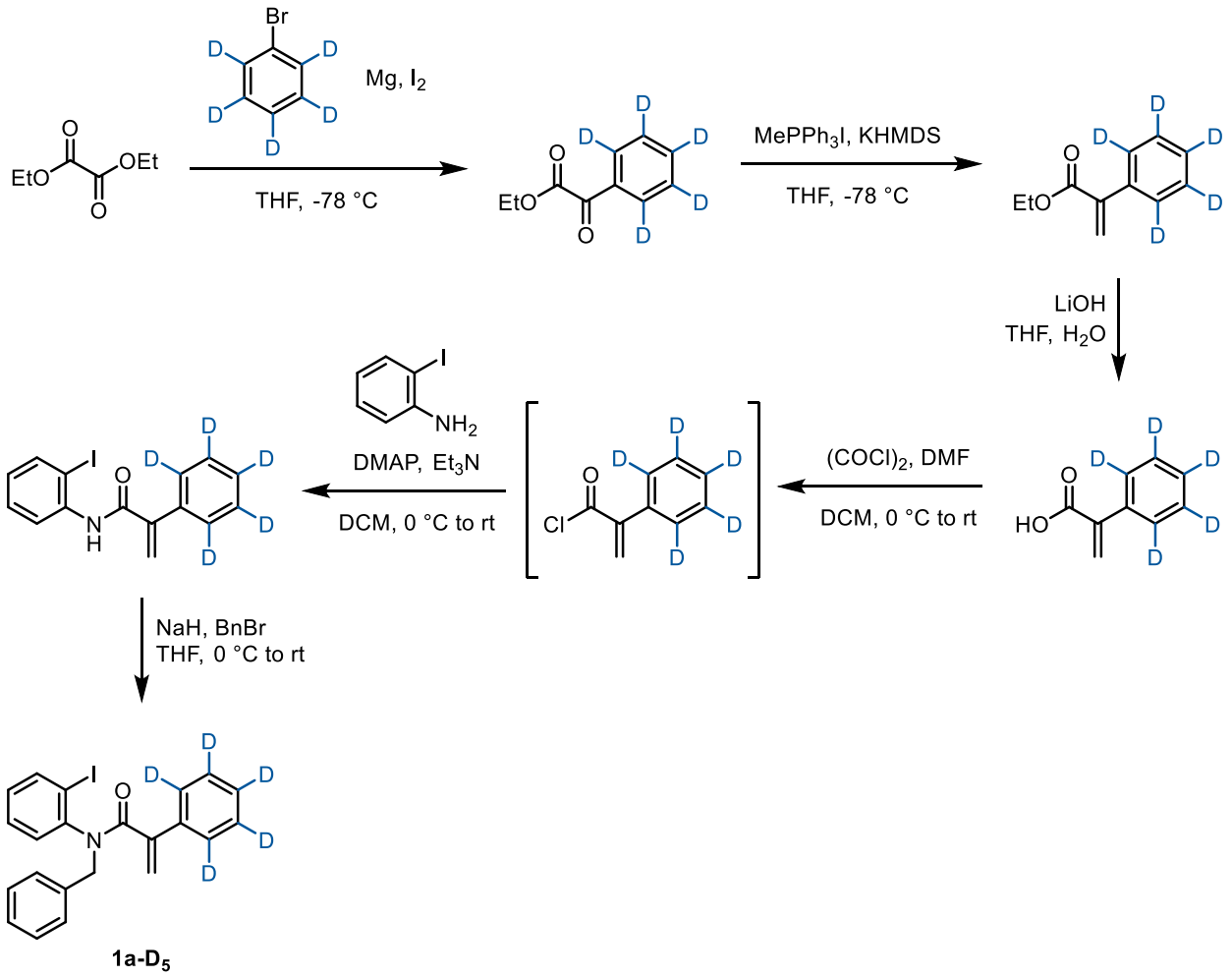
HRMS (DART) m/z: [M + H]+ Calcd for $C_{18}H_{15}NOI$ 388.0193; Found 388.0178

MP 93-96 °C

Daniels, M.; de Jong, F.; Vandermeeren, T. Meervelt, L. V.; Van der Auweraer, M.; Dehaen Bay, W. Substituted Thiaza[5]helicenes: Synthesis and Implications on Structural and Spectroscopic Properties. *J. Org. Chem.* **2019,** *84,* 13528−13539.[8]

Yang, X.; Lu, H.; Zhu, X.; Zhou, L.; Deng, G.; Yang, Y.; Liang, Y. Palladium-Catalyzed Cascade Cyclization of Alkene-Tethered Aryl Halides with o-Bromobenzoic Acids: Access to Diverse Fused Indolo[2,1-*a*]isoquinolines. *Org. Lett.* **2019,** *21,* 7284−7288.[9]

_N_-Benzyl-_N_-(2-iodophenyl)-2-(phenyl-d_5)acrylamide (1a-D_5)



Synthesized based on a known literature procedure[10] and **GP1** from diethyl oxalate, bromobenzene-d_5, 2-iodoaniline and benzyl bromide on a 2.7 mmol scale. Obtained 68 mg of a beige solid (6% yield over 5 steps).

Two rotamers were observed in a 15:1 ratio. The major rotamer is reported below.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (dd, J = 7.7, 1.7 Hz, 1H), 7.29 – 7.22 (m, 5H), 6.82 (ddd, J = 7.7, 7.6, 1.8 Hz, 1H), 6.78 (ddd, J = 7.6, 7.6, 1.7 Hz, 1H), 6.13 (dd, J = 7.6, 1.8 Hz, 1H), 5.83 (d, J = 14.3 Hz, 1H), 5.63 (s, 1H), 5.32 (s, 1H), 4.07 (d, J = 14.3 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0, 145.7, 143.1, 139.9, 136.8, 132.0, 129.6, 129.3, 128.5, 128.1, 127.8, 116.8, 100.3, 51.5.

IR (ATR) 3063, 3032, 2273, 1726, 1486, 1450, 1373, 1221, 1193, 699.

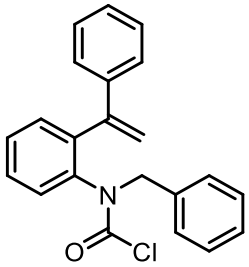
HRMS (DART) m/z: [M + H]+ Calcd for $C_{22}H_{14}NOID_5$ 445.0820; Found 445.0811

MP 95-97 °C

Feng, C.; Loh, T.-P. Directing-Group-Assisted Copper-Catalyzed Olefinic Trifluoromethylation of Electron-Deficient Alkenes. *Angew. Chem. Int. Ed.* **2013,** *52*, 12414 –12417.[10]

Carbamoyl Chlorides

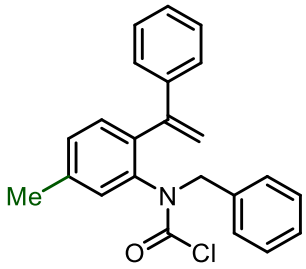
Benzyl(2-(1-phenylvinyl)phenyl)carbamic chloride (1a')



Synthesized following steps 2 to 4 of **GP4** from 2-aminobenzophenone. Characterization was consistent with literature.[10]

Whyte, A.; Burton, K. I.; Zhang, J.; Lautens, M. Enantioselective Intramolecular Copper-Catalyzed Borylacylation. *Angew. Chem. Int. Ed.* **2018,** *57*, 13927–13930.[10]

Benzyl(5-methyl-2-(1-phenylvinyl)phenyl)carbamic chloride (1q')



Synthesized following **GP4** from 2-amino-4-methylbenzonitrile on a 6.0 mmol scale. Obtained 689 mg of a yellow oil (32% yield over 4 steps).

Two rotamers were observed in a 6:1 ratio. The major rotamer is reported below.

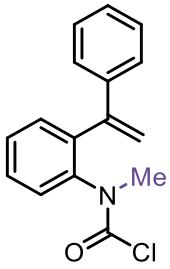
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 6H), 7.29 – 7.26 (m, 3H), 7.21 (ddd, J = 7.7, 1.8, 0.8 Hz, 1H), 7.14 – 7.10 (m, 2H), 6.58 (d, J = 0.8 Hz, 1H), 5.76 (d, J = 1.2 Hz, 1H), 5.43 (d, J = 1.2 Hz, 1H), 4.91 (d, J = 14.6 Hz, 1H), 3.70 (d, J = 14.6 Hz, 1H), 2.25 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.9, 147.0, 140.6, 139.1, 138.6, 137.0, 135.9, 131.5, 131.4, 129.7, 129.1, 128.6, 128.6, 128.3, 128.1, 127.1, 117.7, 54.9, 21.0.

IR (ATR) 3030, 2923, 2859, 1729, 1494, 1370, 1196, 909, 780, 697.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{23}H_{21}NOCl$ 362.1306; Found 362.1309

Methyl(2-(1-phenylvinyl)phenyl)carbamic chloride (1i')

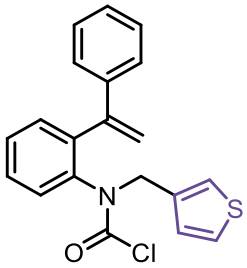


Synthesized following at first step 2 of **GP4** from 2-aminobenzophenone. The following step is based on a literature procedure.[11] To a stirred solution of 2-(1-phenylvinyl)aniline in THF [0.3 M] at -78 °C was added methyllithium (1.6 M in Et_2O, 1.2 equiv) dropwise. The reaction mixture was stirred for 1 h at the same temperature before iodomethane (1.2 equiv) was added dropwise. The reaction was warmed to room temperature and stirred overnight. The reaction was quenched with

distilled water and extracted three times with EtOAc. The organic layer was washed with brine, dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude mixture was purified by flash chromatography to give *N*-methyl-2-(1-phenylvinyl)aniline. This compound was subjected to step 4 of **GP4** to yield the desired product. Characterization was consistent with literature.[10]

Whyte, A.; Burton, K. I.; Zhang, J.; Lautens, M. Enantioselective Intramolecular Copper-Catalyzed Borylacylation. *Angew. Chem. Int. Ed.* **2018,** *57,* 13927–13930.[10]

(2-(1-Phenylvinyl)phenyl)(thiophen-3-ylmethyl)carbamic chloride (1r')



Synthesized following steps 2 to 4 of **GP4** from 2-aminobenzophenone and 3-thiophenecarboxaldehyde on a 4.0 mmol scale. Obtained 1245 mg of a white solid (88% yield over 3 steps).

Two rotamers were observed in a 7:1 ratio. The major rotamer is reported below.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.38 – 7.27 (m, 6H), 7.22 (dd, J = 5.1, 1.2 Hz, 1H), 6.93 – 6.86 (m, 2H), 6.82 – 6.77 (m, 1H), 5.78 (d, J = 1.1 Hz, 1H), 5.44 (d, J = 1.1 Hz, 1H), 4.94 (dd, J = 15.2, 0.8 Hz, 1H), 3.89 (d, J = 15.2 Hz, 1H).

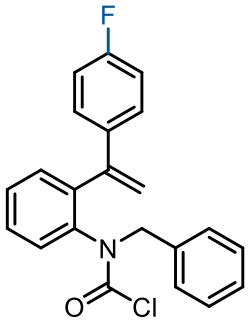
^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 147.1, 140.3, 140.2, 138.9, 137.4, 131.6, 130.8, 129.2, 128.7, 128.7, 128.5, 128.4, 127.0, 126.7, 126.4, 118.1, 49.1.

IR (ATR) 3078, 3025, 2948, 1729, 1376, 1207, 1151, 910, 767, 705.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{20}H_{17}NOSCl$ 354.0714; Found 354.0722

MP 47-50 °C

Benzyl(2-(1-(4-fluorophenyl)vinyl)phenyl)carbamic chloride (1s')



Synthesized following **GP4** from 2-aminobenzonitrile and 1-bromo-4-fluorobenzene on a 6.0 mmol scale. Obtained 657 mg of a white solid (30% yield over 4 steps).

Two rotamers were observed in a 6:1 ratio. The major rotamer is reported below.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 2H), 7.35 – 7.21 (m, 6H), 7.13 – 7.09 (m, 2H), 7.08 – 7.02 (m, 1H), 6.77 (dd, J = 8.1, 1.2 Hz, 1H), 5.74 (d, J = 1.0 Hz, 1H), 5.44 (d, J = 1.0 Hz, 1H), 4.99 (d, J = 14.5 Hz, 1H), 3.73 (d, J = 14.5 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.9 (d, J = 247.9 Hz), 149.8, 146.2, 139.8, 139.1, δ 136.4 (d, J = 3.3 Hz), 135.6, 131.6, 131.1, 129.2, 129.1, 128.7 (d, J = 8.1 Hz), 128.7, 128.7, 128.2, 118.0 (d, J = 1.6 Hz), 115.6 (d, J = 21.6 Hz), 54.9.

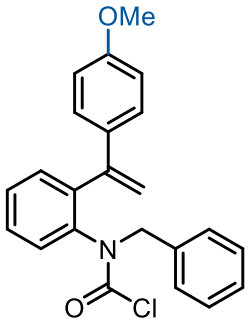
^{19}F NMR (377 MHz, $CDCl_3$) δ -113.4.

IR (ATR) 3065, 3032, 2951, 1715, 1506, 1372, 1217, 1158, 839, 701.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{22}H_{18}NOFCl$ 366.1056; Found 366.1062

MP 76-78 °C

Benzyl(2-(1-(4-methoxyphenyl)vinyl)phenyl)carbamic chloride (1t')



Synthesized following **GP4** from 2-aminobenzonitrile and 4-bromoanisole on a 6.0 mmol scale. Obtained 574 mg of a light-yellow oil (25% yield over 4 steps).

Two rotamers were observed in a 7:1 ratio. The major rotamer is reported below.

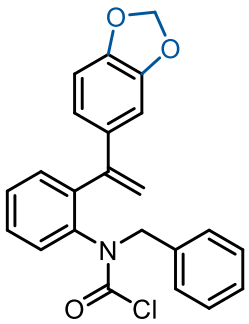
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.29 – 7.25 (m, 4H), 7.22 (ddd, J = 7.9, 7.0, 2.1 Hz, 1H), 7.13 – 7.10 (m, 1H), 6.89 (d, J = 8.9 Hz, 1H), 6.76 (dd, J = 7.9, 0.7 Hz, 1H), 5.73 (d, J = 1.2 Hz, 1H), 5.35 (d, J = 1.2 Hz, 1H), 5.00 (d, J = 14.6 Hz, 1H), 3.82 (s, 3H), 3.73 (d, J = 14.6 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 150.0, 146.3, 140.2, 139.2, 135.8, 132.9, 131.7, 131.0, 129.2, 128.9, 128.6, 128.4, 128.2, 128.1, 116.3, 114.0, 55.4, 54.8.

IR (ATR) 3031, 2934, 2836, 1726, 1605, 1509, 1246, 1029, 835, 698.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{23}H_{21}NO_2Cl$ 378.1255; Found 378.1264

(2-(1-(Benzo[*d*][1,3]dioxol-5-yl)vinyl)phenyl)(benzyl)carbamic chloride (1u')



Synthesized following **GP4** from 2-aminobenzonitrile and 1-bromo-3,4-(methylenedioxy)benzene on a 6.0 mmol scale. Obtained 969 mg of a white solid (41% yield over 4 steps).

Two rotamers were observed in a 7:1 ratio. The major rotamer is reported below.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.29 – 7.25 (m, 3H), 7.22 (ddd, J = 7.9, 6.7, 2.4 Hz, 1H), 7.15 – 7.09 (m, 2H), 6.86 (dd, J = 1.1, 1.1 Hz, 1H), 6.79 – 6.75 (m, 3H), 6.00 – 5.96 (m, 2H), 5.71 (d, J = 1.1 Hz, 1H), 5.35 (d, J = 1.1 Hz, 1H), 5.06 (d, J = 14.5 Hz, 1H), 3.80 (d, J = 14.5 Hz, 1H).

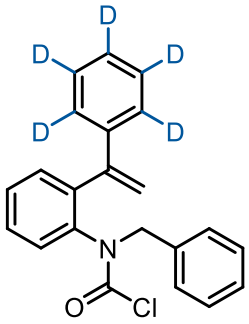
^{13}C NMR (126 MHz, $CDCl_3$) δ 149.9, 148.0, 147.9, 146.5, 140.0, 139.1, 135.8, 134.5, 131.7, 131.1, 129.2, 129.0, 128.6, 128.5, 128.2, 121.0, 116.7, 108.3, 107.3, 101.4, 54.8.

IR (ATR) 3062, 2873, 1721, 1486, 1373, 1196, 1035, 899, 770, 703.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{23}H_{19}NO_3Cl$ 392.1048; Found 392.1049

MP 133-136 °C

Benzyl(2-(1-(phenyl-*d*$_5$)vinyl)phenyl)carbamic chloride (1a'-D$_5$)



Synthesized following **GP4** from 2-aminobenzonitrile and bromobenzene-*d*$_5$ on a 3.0 mmol scale. Obtained 226 mg of a white solid (21% yield over 4 steps).

Two rotamers were observed in a 7:1 ratio. The major rotamer is reported below.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dd, J = 7.6, 1.8 Hz, 1H), 7.41 (ddd, J = 7.6, 7.4, 1.3 Hz, 1H), 7.29 – 7.25 (m, 3H), 7.23 (ddd, J = 7.9, 7.4, 1.8 Hz, 1H), 7.13 – 7.09 (m, 2H), 6.77 (dd, J = 7.9, 1.3 Hz, 1H), 5.81 (d, J = 1.2 Hz, 1H), 5.47 (d, J = 1.2 Hz, 1H), 4.95 (d, J = 14.5 Hz, 1H), 3.70 (d, J = 14.5 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.9, 147.0, 140.1, 139.2, 135.8, 131.7, 131.0, 129.2, 129.0, 128.6, 128.5, 128.1, 118.0, 54.8.

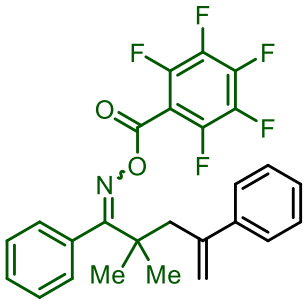
IR (ATR) 3083, 3055, 3028, 2923, 2850, 1641, 1618, 1466, 1197, 906.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{22}H_{14}NOClD_5$ 353.1464; Found 353.1466

MP 92-94 °C

Oxime Ester

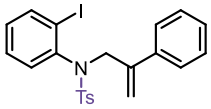
2,2-Dimethyl-1,4-diphenylpent-4-en-1-one *O*-perfluorobenzoyl oxime (4)



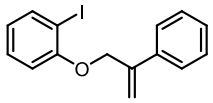
Synthesized based on a known literature procedure.[12] Characterization was consistent with literature.[11]

Wei, W.-X.; Li, Y.; Wen, Y.-T.; Li, M.; Li, X.-S.; Wang, C.-T.; Liu, H.-C.; Xia, Y.; Zhang, B.-S.; Jiao, R.-Q.; Liang, Y.-M. Experimental and Computational Studies of Palladium-Catalyzed Spirocyclization via a Narasaka−Heck/C(sp^3 or sp^2)−H Activation Cascade Reaction. *J. Am. Chem. Soc.*, **2021,** *143,* 7868–7875.[11]

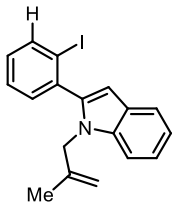
Unsuccessful Substrates



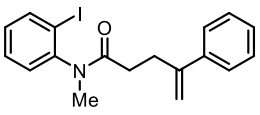
57% NMR
unisolable



<10% NMR
unisolable



44% NMR
unisolable



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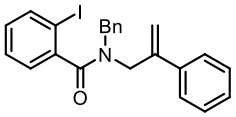

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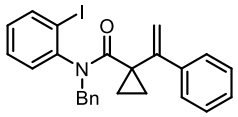

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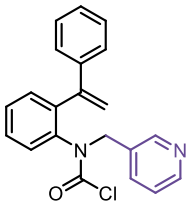
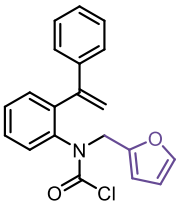
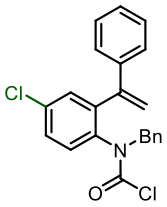


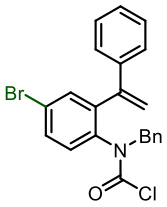
<10% NMR
unisolable



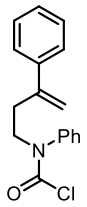
<10% NMR
unisolable



44% NMR
unisolable

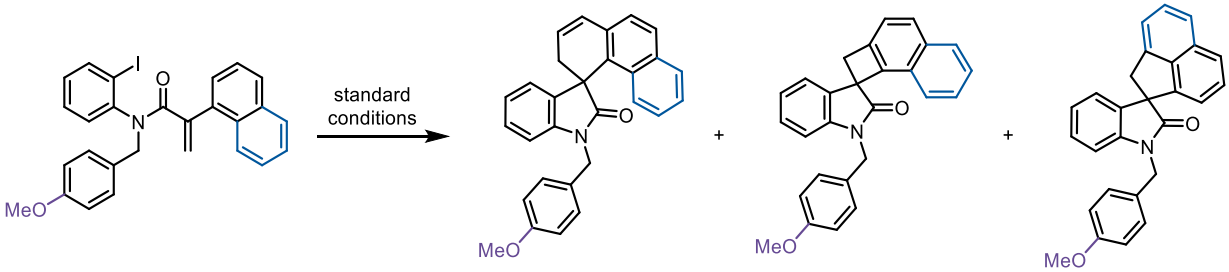


<10% NMR
unisolable



0%

The yields under each structure refer to the corresponding product.



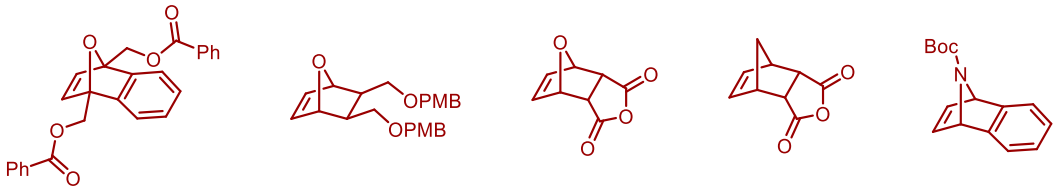
A
23% NMR

B
33%

C
26% NMR

A coelutes with **C**

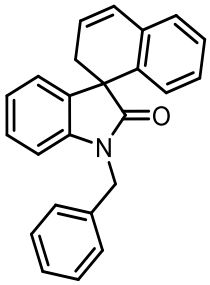
All the following bicycles gave no corresponding spirooxindole-cycloadduct under the standard reaction conditions using **1a** as the coupling partner.



Characterization of Products

Spirooxindoles and Spiroindoline Synthesized from Aryl Iodides

1-Benzyl-2'*H*-spiro[indoline-3,1'-naphthalen]-2-one (3a)



Prepared on 0.2 mmol scale by **GP5**. Purified by flash column chromatography 5⟶10% EtOAc/pentanes. Obtained 59 mg of a white solid (88% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 5H), 7.32 – 7.27 (m, 1H), 7.24 – 7.18 (m, 2H), 7.14 (td, J = 7.7, 1.3 Hz, 1H), 7.10 – 7.06 (m, 1H), 6.90 (ddd, J = 7.7, 7.5, 1.0 Hz, 1H), 6.81 – 6.76 (m, 2H), 6.71 (dd, J = 9.7, 2.9 Hz, 1H), 6.07 (ddd, J = 9.7, 5.5, 3.1 Hz, 1H), 5.04, 5.02 (ABq, J = 15.6, 2H), 3.14 (ddd, J = 17.3, 3.1, 2.9 Hz, 1H), 2.56 (ddd, J = 17.3, 5.5, 1.2 Hz, 1H).

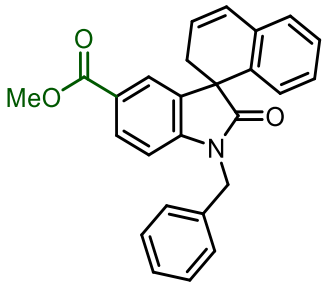
^{13}C NMR (126 MHz, $CDCl_3$) δ 180.0, 140.9, 136.1, 134.7, 134.5, 133.5, 129.0, 128.6, 128.4, 128.2, 128.1, 127.8, 127.4, 127.4, 125.9, 124.8, 123.8, 122.8, 109.5, 51.9, 44.1, 34.2.

IR (ATR) 3032, 2931, 1706, 1608, 1485, 1465, 1345, 1200, 1157, 747, 695

HRMS (DART) m/z: [M + H]+ Calcd for $C_{24}H_{20}NO$ 338.1539; Found 338.1544

MP 47-50 °C

Methyl 1-benzyl-2-oxo-2'*H*-spiro[indoline-3,1'-naphthalene]-5-carboxylate (3b)



Prepared on 0.2 mmol scale by **GP5**. Purified by flash column chromatography 5→20% EtOAc/pentanes. Obtained 54 mg of an off-white solid (68% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dd, J = 1.7, 0.5 Hz, 1H), 7.90 (dd, J = 8.3, 1.7 Hz, 1H), 7.37 – 7.33 (m, 4H), 7.32 – 7.28 (m, 1H), 7.24 – 7.21 (m, 2H), 7.07 (ddd, J = 7.7, 6.2, 2.7 Hz, 1H), 6.83 (dd, J = 8.3, 0.5 Hz, 1H), 6.77 – 6.70 (m, 2H), 6.07 (ddd, J = 9.7, 5.5, 3.2 Hz, 1H), 5.06, 5.03 (ABq, J = 15.7, 2H), 3.81 (s, 3H), 3.12 (ddd, J = 17.3, 3.2, 3.0 Hz, 1H), 2.56 (ddd, J = 17.3, 5.5, 1.2 Hz, 1H).

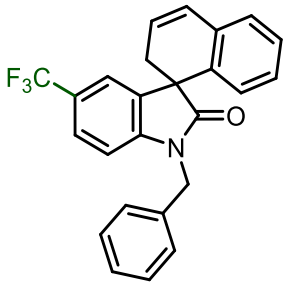
^{13}C NMR (126 MHz, $CDCl_3$) δ 180.3, 166.8, 145.1, 135.6, 134.5, 133.7, 133.5, 130.9, 129.1, 128.8, 128.4, 128.4, 128.0, 127.7, 127.4, 125.7, 125.1, 124.9, 124.4, 109.1, 52.1, 51.7, 44.2, 34.1.

IR (ATR) 2928, 2855, 1706, 1606, 1487, 1431, 1244, 1193, 1117, 764

HRMS (DART) m/z: [M + H]+ Calcd for $C_{26}H_{22}NO_3$ 396.1594; Found 396.1590

MP 138-143 °C

1-Benzyl-5-(trifluoromethyl)-2'*H*-spiro[indoline-3,1'-naphthalen]-2-one (3c)



Prepared on 0.2 mmol scale by **GP5**. Purified by flash column chromatography 5→10% EtOAc/pentanes. Obtained 63 mg of a white solid (78% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 1.8 Hz, 1H), 7.42 (ddd, J = 8.3, 1.8, 0.9 Hz, 1H), 7.40 – 7.29 (m, 5H), 7.28 – 7.21 (m, 2H), 7.11 (ddd, J = 7.6, 7.6, 1.9 Hz, 1H), 6.85 (d, J = 8.3 Hz, 1H), 6.79 – 6.70 (m, 2H), 6.07 (ddd, J = 9.7, 5.6, 3.0 Hz, 1H), 5.07, 5.05 (ABq, J = 15.6, 2H), 3.16 (ddd, J = 17.3, 3.0, 2.9 Hz, 1H), 2.54 (ddd, J = 17.3, 5.6, 1.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 180.0, δ 143.9 (q, J = 1.3 Hz), 135.4, 135.0, 133.5, 133.4, 129.2, 128.9, 128.6, 128.5, 128.1, 127.8, 127.4, 126.0 (q, J = 4.0 Hz), 125.8, 125.1 (q, J = 32.5 Hz), 124.9 (q, J = 271.8 Hz), 124.4, 120.8 (q, J = 3.7 Hz), 109.3, 51.8, 44.3, 34.1.

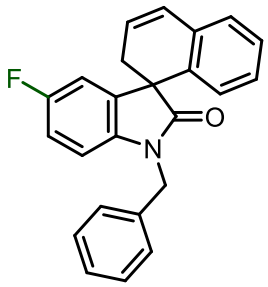
^{19}F NMR (375 MHz, $CDCl_3$) δ -61.5.

IR (ATR) 3028, 2970, 2924, 1723, 1618, 1326, 1154, 1113, 768, 696.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{25}H_{19}NOF_3$ 406.1413; Found 406.1421

MP 70-74 °C

1-Benzyl-5-fluoro-2'*H*-spiro[indoline-3,1'-naphthalen]-2-one (3d)



Prepared on 0.2 mmol scale by **GP5**. Purified by flash column chromatography 5→10% EtOAc/pentanes. Obtained 55 mg of a white solid (78% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 7.25 – 7.19 (m, 2H), 7.13 – 7.05 (m, 2H), 6.82 (ddd, J = 9.0, 8.9, 2.6 Hz, 1H), 6.78 (d, J = 7.6 Hz, 1H), 6.71 (dd, J = 9.7, 2.9 Hz, 1H), 6.67 (dd, J = 8.6, 4.2 Hz, 1H), 6.06 (ddd, J = 9.7, 5.7, 3.0 Hz, 1H), 5.03, 5.01 (ABq, J = 15.6, 2H), 3.16 (ddd, J = 17.2, 3.0, 2.9 Hz, 1H), 2.51 (dd, J = 17.3, 5.7 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 179.8, 159.2 (d, J = 240.9 Hz), δ 136.7 (d, J = 2.0 Hz), 136.1, (d, J = 8.1 Hz), 135.8, 134.0, 133.3, 129.1, 128.9 (d, J = 14.7 Hz), 128.7, 128.4 (d, J = 19.9 Hz), 127.8 (d, J = 40.2 Hz), 127.4, 127.0 (d, J = 82.0 Hz), 125.8, 124.6, 114.5 (d, J = 23.6 Hz), 112.0 (d, J = 25.0 Hz), 110.0 (d, J = 8.1 Hz), 52.3 (d, J = 1.8 Hz), 44.3, 34.1.

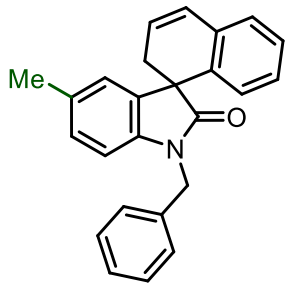
^{19}F NMR (377 MHz, $CDCl_3$) δ -120.0.

IR (ATR) 2982, 2928, 1710, 1618, 1486, 1448, 1340, 1171, 811, 695

HRMS (DART) m/z: [M + H]+ Calcd for $C_{24}H_{19}NOF$ 356.1445; Found 356.1453

MP 110-112 °C

1-Benzyl-5-methyl-2'*H*-spiro[indoline-3,1'-naphthalen]-2-one (3e)



Prepared on 0.2 mmol scale by **GP5**. Purified by flash column chromatography 5→10% EtOAc/pentanes. Obtained 50 mg of a white solid (71% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 4H), 7.31 – 7.27 (m, 1H), 7.25 – 7.19 (m, 2H), 7.14 (d, J = 1.8 Hz, 1H), 7.09 (ddd, J = 7.7, 6.7, 2.1 Hz, 1H), 6.94 (ddd, J = 8.0, 1.8, 0.8 Hz, 1H), 6.78 (d, J = 7.7 Hz, 1H), 6.71 (dd, J = 9.7, 2.9 Hz, 1H), 6.67 (d, J = 8.0 Hz, 1H), 6.07 (ddd, J = 9.7, 5.5, 3.1 Hz, 1H), 5.03, 5.01 (ABq, J = 15.6, 2H), 3.14 (ddd, J = 17.3, 3.1, 2.9 Hz, 1H), 2.55 (ddd, J = 17.3, 5.5, 1.1 Hz, 1H), 2.21 (s, 3H).

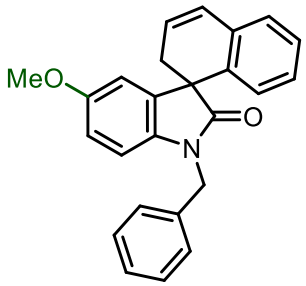
^{13}C NMR (126 MHz, $CDCl_3$) δ 180.0, 138.4, 136.2, 134.8, 134.7, 133.5, 132.4, 128.9, 128.6, 128.5, 128.4, 128.0, 127.7, 127.4, 127.4, 125.9, 124.9, 124.5, 109.3, 52.0, 44.0, 34.2, 21.2.

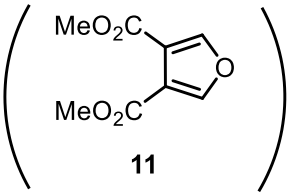
IR (ATR) 3031, 2982, 2920, 1705, 1600, 1492, 1340, 1187, 765, 696

HRMS (DART) m/z: [M + H]+ Calcd for $C_{25}H_{22}NO$ 352.1696; Found 352.1690

MP 60-63 °C

1-Benzyl-5-methoxy-2'*H*-spiro[indoline-3,1'-naphthalen]-2-one (3f)





11

Prepared on 0.2 mmol scale by **GP5**. Due to co-elution with the retro-Diels-Alder furan by-product **11** following flash column chromatography 5→15% EtOAc/pentanes, the mixture was taken up in a 5% KOH solution in EtOH/H_2O (1:1) and stirred for 1 h at 85 °C. The reaction mixture was diluted with EtOAc, dried over magnesium sulfate, pushed through a pad of silica under reduced pressure. The filtrate was concentrated under reduced pressure and the crude mixture was purified by flash column chromatography 15% EtOAc/pentanes. Obtained 57 mg of a white solid (78% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 4H), 7.32 – 7.27 (m, 1H), 7.24 – 7.17 (m, 2H), 7.09 (ddd, J = 7.2, 7.0, 1.8 Hz, 1H), 6.96 (dd, J = 2.1, 1.0 Hz, 1H), 6.79 (d, J = 7.7 Hz, 1H), 6.72 – 6.63 (m, 3H), 6.06 (ddd, J = 9.7, 5.5, 3.1 Hz, 1H), 5.14, 5.12 (ABq, J = 15.6 Hz, 2H), 3.67 (s, 3H), 3.15 (ddd, J = 17.3, 3.1, 3.0 Hz, 1H), 2.55 (ddd, J = 17.3, 5.5, 1.1 Hz, 1H).

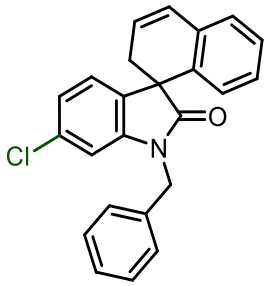
^{13}C NMR (126 MHz, $CDCl_3$) δ 179.7, 156.0, 136.2, 136.0, 134.5, 134.3, 133.4, 128.9, 128.6, 128.4, 128.1, 127.8, 127.5, 127.4, 125.9, 124.8, 112.3, 111.4, 109.8, 55.7, 52.3, 44.2, 34.2.

IR (ATR) 3051, 2924, 1705, 1607, 1484, 1464, 1344, 1186, 744, 695

HRMS (DART) m/z: [M + H]+ Calcd for $C_{25}H_{22}NO_2$ 368.1645; Found 368.1647

MP 53-58 °C

1-Benzyl-6-chloro-2'*H*-spiro[indoline-3,1'-naphthalen]-2-one (3g)



Prepared on 0.2 mmol scale by **GP5**. Purified by flash column chromatography 5→10% EtOAc/pentanes. Obtained 54 mg of a white solid (73% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 5H), 7.25 – 7.17 (m, 3H), 7.09 (ddd, J = 7.4, 7.3, 1.7 Hz, 1H), 6.87 (dd, J = 8.0, 1.9 Hz, 1H), 6.78 (d, J = 1.9 Hz, 1H), 6.75 (d, J = 7.3 Hz, 1H), 6.70 (dd, J = 9.6, 2.8 Hz, 1H), 6.05 (ddd, J = 9.6, 5.5, 3.1 Hz, 1H), 5.00 (s, 2H), 3.12 (ddd, J = 17.3, 3.1, 2.8 Hz, 1H), 2.51 (ddd, J = 17.3, 5.5, 1.2 Hz, 1H).

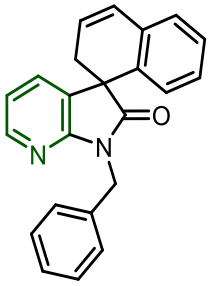
^{13}C NMR (126 MHz, $CDCl_3$) δ 180.0, 142.2, 135.6, 134.0, 134.0, 133.3, 133.0, 129.1, 128.7, 128.5, 128.3, 128.0, 127.6, 127.4, 125.7, 124.8, 124.5, 122.7, 110.0, 51.6, 44.2, 34.2.

IR (ATR) 3051, 2924, 1705, 1607, 1488, 1464, 1430, 1344, 745, 695

HRMS (DART) m/z: [M + H]+ Calcd for $C_{24}H_{19}NOCl$ 372.1150; Found 372.1153

MP 56-60 °C

1'-Benzyl-2*H*-spiro[naphthalene-1,3'-pyrrolo[2,3-*b*]pyridin]-2'(1'*H*)-one (3h)



Prepared on 0.2 mmol scale by **GP5**. Due to co-elution with the retro-Diels-Alder furan by-product **13** following flash column chromatography 5→15% EtOAc/pentanes, the mixture was taken up in a 5% KOH solution in EtOH/H_2O (1:1) and stirred for 1 h at 85 °C. The reaction mixture was

diluted with EtOAc, dried over magnesium sulfate, pushed through a pad of silica under reduced pressure. The filtrate was concentrated under reduced pressure and the crude mixture was purified by flash column chromatography 15% EtOAc/pentanes. Obtained 16 mg of a white solid (24% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (dd, J = 5.3, 1.6 Hz, 1H), 7.55 – 7.48 (m, 3H), 7.37 – 7.31 (m, 2H), 7.31 – 7.27 (m, 1H), 7.24 – 7.16 (m, 3H), 7.04 (ddd, J = 7.5, 7.4, 1.7 Hz, 2H), 6.80 (dd, J = 7.3, 5.3 Hz, 1H), 6.71 – 6.65 (m, 2H), 6.03 (ddd, J = 9.3, 5.9, 2.9 Hz, 1H), 5.14, 5.12 (ABq, J = 14.5, 2H), 3.14 (ddd, J = 17.4, 2.9, 2.9 Hz, 1H), 2.43 (dd, J = 17.4, 5.9 Hz, 1H).

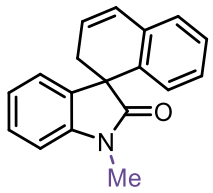
^{13}C NMR (126 MHz, $CDCl_3$) δ 179.4, 154.8, 147.3, 136.9, 133.7, 133.2, 131.0, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 127.7, 127.5, 125.6, 124.6, 118.5, 51.6, 43.0, 33.5.

IR (ATR) 3051, 2924, 1705, 1607, 1484, 1465, 1430, 1344, 745, 697

HRMS (DART) m/z: [M + H]+ Calcd for $C_{23}H_{19}N_2O$ 339.1492; Found 339.1495

MP 125-128 °C

1-Methyl-2'*H*-spiro[indoline-3,1'-naphthalen]-2-one (3i)



Prepared on 0.2 mmol scale by **GP5**. Due to co-elution with the retro-Diels-Alder furan by-product **11** following flash column chromatography 5→15% EtOAc/pentanes, the mixture was taken up in a 5% KOH solution in EtOH/H_2O (1:1) and stirred for 1 h at 85 °C. The reaction mixture was diluted with EtOAc, dried over magnesium sulfate, pushed through a pad of silica under reduced pressure. The filtrate was concentrated under reduced pressure and the crude mixture was purified by flash column chromatography 15% EtOAc/pentanes. Obtained 29 mg of an off-white solid (55% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 7.5 Hz, 1H), 7.26 (ddd, J = 7.8, 7.8, 1.3 Hz, 1H), 7.23 – 7.15 (m, 2H), 7.08 – 7.02 (m, 1H), 6.93 (ddd, J = 7.5, 7.5, 1.0 Hz, 1H), 6.89 (d, J = 7.8 Hz, 1H), 6.73 (d, J = 7.7 Hz, 1H), 6.68 (dd, J = 9.7, 3.0 Hz, 1H), 6.04 (ddd, J = 9.7, 5.6, 3.0 Hz, 1H), 3.34 (s, 3H), 3.08 (ddd, J = 17.4, 3.0, 3.0 Hz, 1H), 2.48 (ddd, J = 17.4, 5.6, 1.1 Hz, 1H).

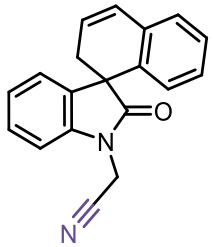
^{13}C NMR (126 MHz, $CDCl_3$) δ 180.0, 141.7, 134.8, 134.5, 133.4, 128.5, 128.3, 128.3, 128.0, 127.3, 125.8, 124.9, 123.7, 122.8, 108.4, 51.9, 33.9, 26.6.

IR (ATR) 3042, 2930, 1711, 1607, 1486, 1465, 1368, 1342, 1131, 755

HRMS (DART) m/z: [M + H]+ Calcd for $C_{18}H_{16}NO$ 262.1226; Found 262.1231

MP 118-120 °C

2-(2-Oxo-2'*H*-spiro[indoline-3,1'-naphthalen]-1-yl)acetonitrile (3j)



Prepared on 0.2 mmol scale by **GP5**. Purified by flash column chromatography 5→20% EtOAc/pentanes. Obtained 19 mg of a white solid (32% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (dd, J = 7.9, 1.2 Hz, 1H), 7.33 (td, J = 7.9, 1.2 Hz, 1H), 7.26 – 7.17 (m, 2H), 7.11 – 7.01 (m, 3H), 6.73 – 6.65 (m, 2H), 6.03 (ddd, J = 9.7, 5.3, 3.4 Hz, 1H), 4.74, 4.72 (ABq, J = 17.6, 2H), 3.03 (ddd, J = 17.3, 3.4, 2.6 Hz, 1H), 2.57 (ddd, J = 17.3, 5.3, 1.3 Hz, 1H).

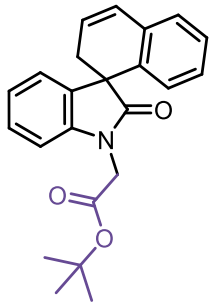
^{13}C NMR (126 MHz, $CDCl_3$) δ 178.9, 138.5, 134.2, 133.5, 133.3, 128.7, 128.6, 128.6, 128.5, 127.6, 125.8, 124.4, 124.3, 124.3, 124.2, 113.9, 108.7, 51.8, 33.9, 27.9.

IR (ATR) 2990, 2924, 1727, 1607, 1487, 1464, 1354, 1199, 1160, 744

HRMS (DART) m/z: [M + H]+ Calcd for $C_{19}H_{15}N_2O$ 287.1179; Found 287.1185

MP 132-136 °C

tert-Butyl 2-(2-oxo-2'*H*-spiro[indoline-3,1'-naphthalen]-1-yl)acetate (3k)



Prepared on 0.2 mmol scale by **GP5**. Purified by flash column chromatography 5→10% EtOAc/pentanes. Obtained 60 mg of a white solid (82% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (ddd, J = 7.5, 1.3, 0.6 Hz, 1H), 7.24 – 7.15 (m, 3H), 7.07 (ddd, J = 7.4, 7.0, 1.8 Hz, 1H), 6.96 – 6.88 (m, 2H), 6.75 (d, J = 7.8 Hz, 1H), 6.68 (dd, J = 9.7, 2.9 Hz, 1H), 6.04 (ddd, J = 9.7, 5.7, 3.0 Hz, 1H), 4.59 (d, J = 17.3 Hz, 1H), 4.37 (d, J = 17.3 Hz, 1H), 3.11 (ddd, J = 17.4, 3.0, 2.9 Hz, 1H), 2.52 (ddd, J = 17.4, 5.7, 1.1 Hz, 1H), 1.47 (s, 9H).

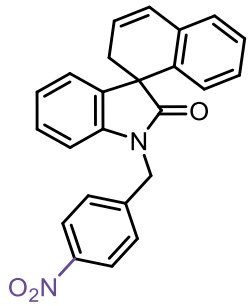
^{13}C NMR (126 MHz, $CDCl_3$) δ 180.0, 166.7, 140.4, 134.6, 134.5, 133.2, 128.5, 128.4, 128.2, 128.0, 127.3, 126.2, 124.7, 123.8, 123.1, 108.4, 82.9, 51.9, 42.5, 33.9, 28.1.

IR (ATR) 2988, 2934, 1714, 1610, 1489, 1466, 1356, 1230, 1151, 748

HRMS (DART) m/z: [M + H]+ Calcd for $C_{23}H_{24}NO_3$ 362.1751; Found 362.1750

MP 100-104 °C

1-(4-Nitrobenzyl)-2'*H*-spiro[indoline-3,1'-naphthalen]-2-one (3l)



Prepared on 0.2 mmol scale by **GP5**. Due to co-elution with the retro-Diels-Alder furan by-product **11** following flash column chromatography 10→30% EtOAc/pentanes, the mixture was taken up

in a 5% KOH solution in EtOH/H_2O (1:1) and stirred for 1 h at 85 °C. The reaction mixture was diluted with EtOAc, dried over magnesium sulfate, pushed through a pad of silica under reduced pressure. The filtrate was concentrated under reduced pressure and the crude mixture was purified by flash column chromatography 30% EtOAc/pentanes. Obtained 65 mg of an off-white solid (85% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, J = 8.9 Hz, 1H), 7.51 (d, J = 8.9 Hz, 1H), 7.36 (ddd, J = 7.5, 1.3, 0.5 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.17 (ddd, J = 7.8, 7.8, 1.3 Hz, 1H), 7.12 – 7.05 (m, 1H), 6.95 (ddd, J = 7.6, 7.6, 1.0 Hz, 1H), 6.75 – 6.66 (m, 3H), 6.06 (ddd, J = 9.8, 5.3, 3.4 Hz, 1H), 5.11 (s, 2H), 3.10 (ddd, J = 17.3, 3.4, 2.6 Hz, 1H), 2.59 (ddd, J = 17.3, 5.3, 1.2 Hz, 1H).

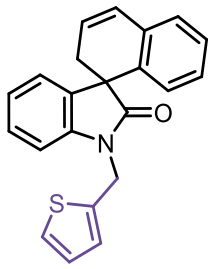
^{13}C NMR (126 MHz, $CDCl_3$) δ 180.0, 147.7, 143.6, 140.3, 134.6, 134.1, 133.5, 128.7, 128.4, 128.3, 128.2, 127.6, 125.7, 124.6, 124.3, 124.3, 123.4, 109.0, 51.9, 43.4, 34.3.

IR (ATR) 2927, 2853, 1711, 1607, 1522, 1486, 1464, 1344, 1196, 747

HRMS (DART) m/z: [M + H]+ Calcd for $C_{24}H_{19}N_2O_3$ 383.1390; Found 383.1382

MP 185-188 °C

1-(Thiophen-2-ylmethyl)-2'*H*-spiro[indoline-3,1'-naphthalen]-2-one (3m)



Prepared on 0.2 mmol scale by **GP5**. Purified by flash column chromatography 2.5→10% EtOAc/pentanes. Obtained 56 mg of an off-white solid (81% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (ddd, J = 7.5, 1.3, 0.6 Hz, 1H), 7.23 (dd, J = 5.1, 1.1 Hz, 1H), 7.22 – 7.17 (m, 3H), 7.11 (dddd, J = 3.4, 1.1, 1.0, 1.0 Hz, 1H), 7.06 (ddd, J = 7.7, 6.8, 2.0 Hz, 1H), 6.97 (dd, J = 5.1, 3.4 Hz, 1H), 6.95 – 6.89 (m, 2H), 6.76 (dd, J = 7.7, 0.6 Hz, 1H), 6.69 (dd, J = 9.7, 2.9 Hz, 1H), 6.04 (ddd, J = 9.7, 5.5, 3.1 Hz, 1H), 5.24 (dd, J = 15.7, 1.0 Hz, 1H), 5.13 (dd, J = 15.7, 1.0 Hz, 1H), 3.11 (ddd, J = 17.3, 3.1, 2.9 Hz, 1H), 2.51 (ddd, J = 17.3, 5.5, 1.1 Hz, 1H).

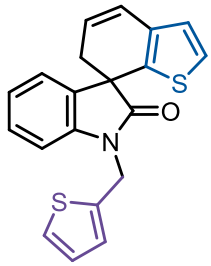
^{13}C NMR (126 MHz, $CDCl_3$) δ 179.6, 140.3, 138.6, 134.7, 134.4, 133.4, 128.6, 128.4, 128.2, 128.1, 127.4, 127.0, 126.6, 125.9, 125.5, 124.7, 123.9, 123.0, 109.2, 51.8, 39.0, 34.0.

IR (ATR) 3043, 2924, 1704, 1606, 1484, 1464, 1345, 1198, 746, 696

HRMS (DART) m/z: [M + H]+ Calcd for $C_{22}H_{18}NOS$ 344.1104; Found 344.1102

MP 62-66 °C

1'-(Thiophen-2-ylmethyl)-6*H*-spiro[benzo[*b*]thiophene-7,3'-indolin]-2'-one (3n)



Prepared on 0.2 mmol scale by **GP5**. Purified by flash column chromatography 2.5→10% EtOAc/pentanes. Obtained 42 mg of a yellow solid (60% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (ddd, J = 7.4, 1.3, 0.6 Hz, 1H), 7.24 – 7.19 (m, 2H), 7.10 (d, J = 5.1 Hz, 1H), 7.08 (ddd, J = 3.3, 1.1, 1.0 Hz, 1H), 6.99 – 6.93 (m, 3H), 6.90 (d, J = 7.8 Hz, 1H), 6.68 (ddd, J = 9.6, 2.5, 1.5 Hz, 1H), 5.92 (ddd, J = 9.6, 4.9, 3.6 Hz, 1H), 5.18 (dd, J = 15.8, 1.1 Hz, 1H), 5.09 (dd, J = 15.8, 1.0 Hz, 1H), 3.09 (ddd, J = 17.3, 3.6, 2.5 Hz, 1H), 2.65 (ddd, J = 17.3, 4.9, 1.5 Hz, 1H).

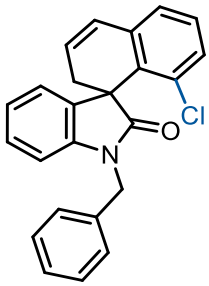
^{13}C NMR (126 MHz, $CDCl_3$) δ 178.5, 140.2, 138.4, 136.5, 134.0, 133.9, 128.7, 127.0, 126.5, 125.8, 125.4, 124.2, 124.0, 123.2, 123.1, 122.3, 109.3, 49.9, 39.0, 35.3.

IR (ATR) 3048, 2924, 1705, 1607, 1484, 1464, 1344, 1185, 744, 695

HRMS (DART) m/z: [M + H]+ Calcd for $C_{20}H_{16}NOS_2$ 350.0668; Found 350.0673

MP 59-63 °C

1-Benzyl-8'-chloro-2'*H*-spiro[indoline-3,1'-naphthalen]-2-one (3o)



Prepared on 0.2 mmol scale by **GP5**. Purified by flash column chromatography 5→10% EtOAc/pentanes. Obtained 59 mg of an off-white solid (78% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.37 – 7.32 (m, 2H), 7.31 – 7.27 (m, 1H), 7.20 – 7.15 (m, 2H), 7.15 – 7.11 (m, 2H), 7.04 (ddd, J = 7.4, 1.3, 0.6 Hz, 1H), 6.90 – 6.81 (m, 2H), 6.66 (dd, J = 9.5, 3.1 Hz, 1H), 6.04 (ddd, J = 9.5, 6.4, 2.7 Hz, 1H), 5.29 (d, J = 15.5 Hz, 1H), 4.79 (d, J = 15.5 Hz, 1H), 3.28 (ddd, J = 17.0, 3.1, 2.7 Hz, 1H), 2.35 (dd, J = 17.0, 6.4 Hz, 1H).

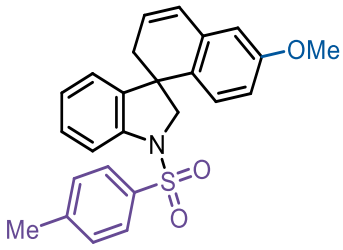
^{13}C NMR (126 MHz, $CDCl_3$) δ 180.5, 141.4, 136.5, 136.0, 133.2, 131.9, 131.8, 129.9, 128.9, 128.8, 128.4, 128.3, 127.9, 127.8, 126.3, 125.3, 123.5, 122.4, 109.4, 51.8, 44.6, 37.0.

IR (ATR) 3022, 2931, 1708, 1607, 1479, 1339, 1157, 1077, 889, 806.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{24}H_{19}NOCl$ 372.1150; Found 372.1154

MP 140-142 °C

6'-Methoxy-1-tosyl-2'*H*-spiro[indoline-3,1'-naphthalene] (3p)



Prepared on 0.2 mmol scale by **GP5**. Purified by flash column chromatography 2.5→5% EtOAc/pentanes. Obtained 47 mg of an amber-yellow solid (56% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (ddd, J = 8.2, 1.1, 0.6 Hz, 1H), 7.66 (d, J = 8.5 Hz, 2H), 7.29 (ddd, J = 8.2, 7.5, 1.4 Hz, 1H), 7.20 (dd, J = 8.5, 0.7 Hz, 2H), 7.13 (ddd, J = 7.6, 1.4, 0.6 Hz, 1H), 7.05 (ddd, J = 7.6, 7.5, 1.1 Hz, 1H), 6.64 (d, J = 2.7 Hz, 1H), 6.51 (dd, J = 9.9, 2.9 Hz, 1H), 6.46 (dd, J = 8.5, 2.7 Hz, 1H), 6.40 (d, J = 8.5 Hz, 1H), 5.91 (ddd, J = 9.9, 6.0, 2.7 Hz, 1H), 4.16 (d, J = 10.5 Hz, 1H), 3.77 (s, 3H), 3.55 (dd, J = 10.5, 0.7 Hz, 1H), 2.50 (ddd, J = 17.3, 2.9, 2.7 Hz, 1H), 2.38 (s, 3H), 2.18 (dd, J = 17.3, 6.0 Hz, 1H).

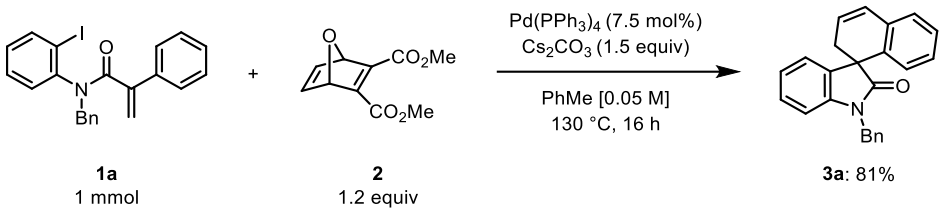
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 144.1, 142.3, 137.8, 134.6, 134.3, 131.3, 129.8, 129.0, 128.7, 127.4, 127.2, 126.6, 124.9, 124.1, 114.7, 112.9, 112.2, 62.6, 55.4, 47.6, 37.0, 21.7.

IR (ATR) 3030, 2923, 2834, 1737, 1598, 1458, 1353, 1160, 1038, 657.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{25}H_{24}NO_3S$ 418.1471; Found 418.1470

MP 52-56 °C

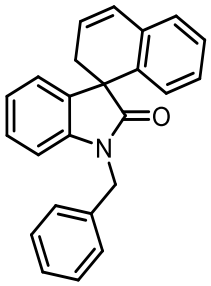
Spirooxindole 3a Synthesized from Aryl Iodide 1a (1 mmol Scale)



Vial and stir bar were dried in 110 °C oven overnight prior to use. A 50 mL round-bottom pressure flask equipped with a stir bar and an empty 9.5 dr vial were cooled to room temperature under argon flow. Cesium carbonate (489 mg, 1.50 mmol, 1.5 equiv), *N*-benzyl-*N*-(2-iodophenyl)-2-phenylacrylamide **1a** (439 mg, 1.00 mmol, 1.0 equiv) and tetrakis(triphenylphosphine)palladium(0) (87 mg, 0.08 mmol, 7.5 mol%) were added in that order to the pressure flask. Oxabicycle **2** (278 mg, 1.1·1.2 mmol = 1.32 mmol, 1.1·1.2 equiv = 1.32 equiv) was weighed in the 9.5 dr vial. Freshly distilled toluene (1.1·20.0 mL = 22.0 mL) was added via syringe to the oxabicycle-containing vial and the vial was sonicated for 15 s to fully dissolve the oxabicycle. 20.0 mL of the resulting solution was transferred via syringe to the pressure flask. The vial was equipped with a Teflon-sealed cap and immediately stirred at 130 °C for 16 h. The reaction was passed through a pad of silica washing with ethyl acetate. The filtrate was concentrated under reduced pressure and the resulting residue purified by flash chromatography 5→10% EtOAc/pentanes. Obtained 272 mg of **3a** (81% yield).

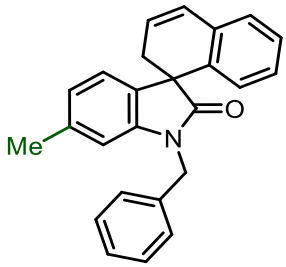
Spirooxindoles Synthesized from Carbamoyl Chlorides

1-Benzyl-2'*H*-spiro[indoline-3,1'-naphthalen]-2-one (3a)



Prepared on 0.2 mmol scale by **GP5**. Purified by flash column chromatography 5→10% EtOAc/pentanes. Obtained 53 mg of a white solid (78% yield).

1-Benzyl-6-methyl-2'*H*-spiro[indoline-3,1'-naphthalen]-2-one (3q)



Prepared on 0.2 mmol scale by **GP5**. Purified by flash column chromatography 2.5→5% EtOAc/pentanes. Obtained 52 mg of a white solid (74% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 4H), 7.32 – 7.27 (m, 1H), 7.23 – 7.15 (m, 3H), 7.07 (ddd, J = 7.1, 6.8, 2.0 Hz, 1H), 6.76 (d, J = 7.5 Hz, 1H), 6.74 – 6.66 (m, 2H), 6.62 (s, 1H), 6.05 (ddd, J = 10.0, 5.4, 3.1 Hz, 1H), 5.02, 5.00 (ABq, J = 15.5 Hz, 2H), 3.12 (ddd, J = 17.3, 3.1, 2.9 Hz, 1H), 2.54 (dd, J = 17.3, 5.4 Hz, 1H), 2.27 (s, 3H).

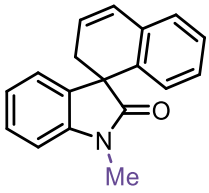
^{13}C NMR (126 MHz, $CDCl_3$) δ 180.3, 141.1, 138.4, 136.3, 134.8, 133.5, 131.9, 129.0, 128.6, 128.4, 128.0, 127.7, 127.4, 127.4, 125.8, 124.8, 123.6, 123.4, 110.2, 51.7, 44.0, 34.3, 21.9.

IR (ATR) 3051, 2925, 1705, 1607, 1484, 1465, 1345, 1186, 745, 695

HRMS (DART) m/z: [M + H]+ Calcd for $C_{25}H_{22}NO$ 352.1696; Found 352.1697

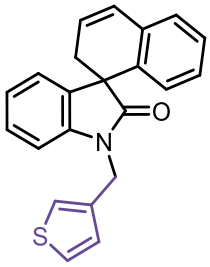
MP 124-127 °C

1-Methyl-2'*H*-spiro[indoline-3,1'-naphthalen]-2-one (3i)



Prepared on 0.2 mmol scale by **GP5**. Due to co-elution with the retro-Diels-Alder furan by-product **11** following flash column chromatography 5→15% EtOAc/pentanes, the mixture was taken up in a 5% KOH solution in EtOH/H_2O (1:1) and stirred for 1 h at 85 °C. The reaction mixture was diluted with EtOAc, dried over magnesium sulfate, pushed through a pad of silica under reduced pressure. The filtrate was concentrated under reduced pressure and the crude mixture was purified by flash column chromatography 15% EtOAc/pentanes. Obtained 27 mg of an off-white solid (51% yield).

1-(Thiophen-3-ylmethyl)-2'*H*-spiro[indoline-3,1'-naphthalen]-2-one (3r)



Prepared on 0.2 mmol scale by **GP5**. Purified by flash column chromatography 2.5→10% EtOAc/pentanes. Obtained 46 mg of a white solid (67% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (ddd, J = 7.5, 1.3, 0.6 Hz, 1H), 7.23 (dd, J = 5.1, 1.1 Hz, 1H), 7.22 – 7.17 (m, 2H), 7.11 (ddd, J = 3.5, 1.1, 1.0 Hz, 1H), 7.06 (ddd, J = 7.7, 6.8, 2.0 Hz, 1H), 6.97 (dd, J = 5.1, 3.5 Hz, 1H), 6.95 – 6.89 (m, 2H), 6.76 (dd, J = 7.7, 0.6 Hz, 1H), 6.69 (dd, J = 9.7, 2.9 Hz, 1H), 6.04 (ddd, J = 9.7, 5.6, 3.1 Hz, 1H), 5.24 (dd, J = 15.7, 1.0 Hz, 1H), 5.13 (dd, J = 15.7, 1.0 Hz, 1H), 3.11 (ddd, J = 17.3, 3.1, 2.9 Hz, 1H), 2.51 (ddd, J = 17.3, 5.6, 1.1 Hz, 1H).

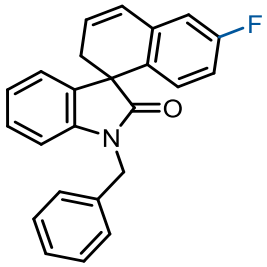
^{13}C NMR (126 MHz, $CDCl_3$) δ 179.6, 140.3, 138.6, 134.7, 134.4, 133.4, 128.6, 128.4, 128.2, 128.1, 127.4, 127.0, 126.6, 125.9, 125.5, 124.7, 123.9, 123.0, 109.2, 51.8, 39.0, 34.0.

IR (ATR) 3042, 2923, 1706, 1606, 1484, 1464, 1344, 1197, 746, 696

HRMS (DART) m/z: [M + H]+ Calcd for $C_{22}H_{18}NOS$ 344.1104; Found 344.1103

MP 51-54 °C

1-Benzyl-6'-fluoro-2'*H*-spiro[indoline-3,1'-naphthalen]-2-one (3s)



Prepared on 0.2 mmol scale by **GP5**. Purified by flash column chromatography 2.5→10% EtOAc/pentanes. Obtained 43 mg of a white solid (60% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 4H), 7.32 – 7.27 (m, 2H), 7.16 (ddd, J = 7.8, 7.8, 1.3 Hz, 1H), 6.94 – 6.89 (m, 2H), 6.80 (d, J = 7.8 Hz, 1H), 6.76 (ddd, J = 8.5, 8.4, 2.7 Hz, 1H), 6.71 (dd, J = 8.5, 5.6 Hz, 1H), 6.65 (d, J = 9.5 Hz, 1H), 6.17 – 6.09 (m, 1H), 5.02 (s, 2H), 3.10 (ddd, J = 17.4, 3.0, 3.0 Hz, 1H), 2.58 (ddd, J = 17.4, 5.4, 1.3 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 179.7, 162.5 (d, J = 245.7 Hz), 140.9, 136.0, 135.6 (d, J = 8.1 Hz), 134.5 (d, J = 0.9 Hz), 130.1 (d, J = 3.2 Hz), 129.0, 128.4, 127.9, 127.9, 127.5 (d, J = 8.4 Hz), 127.5, 126.4, 123.7, 123.0, 114.7 (d, J = 21.6 Hz), 114.1 (d, J = 22.0 Hz), 109.6, 51.3, 44.1, 34.3.

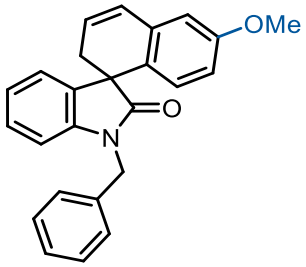
^{19}F NMR (377 MHz, $CDCl_3$) δ -114.7.

IR (ATR) 3051, 2924, 1705, 1607, 1484, 1465, 1344, 1185, 745, 695.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{24}H_{19}NOF$ 356.1445; Found 356.1445

MP 41-44 °C

1-Benzyl-6'-methoxy-2'*H*-spiro[indoline-3,1'-naphthalen]-2-one (3t)



Prepared on 0.2 mmol scale by **GP5**. Due to co-elution with the retro-Diels-Alder furan by-product **11** following flash column chromatography 5→15% EtOAc/pentanes, the mixture was taken up in a 5% KOH solution in EtOH/H_2O (1:1) and stirred for 1 h at 85 °C. The reaction mixture was diluted with EtOAc, dried over magnesium sulfate, pushed through a pad of silica under reduced pressure. The filtrate was concentrated under reduced pressure and the crude mixture was purified by flash column chromatography 15% EtOAc/pentanes. Obtained 46 mg of a white solid (62% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 6H), 7.14 (ddd, J = 7.8, 7.7, 1.3 Hz, 1H), 6.91 (ddd, J = 7.8, 7.7, 1.0 Hz, 1H), 6.78 (ddd, J = 7.8, 1.0, 0.6 Hz, 1H), 6.76 (d, J = 2.7 Hz, 1H), 6.69 – 6.64 (m, 2H), 6.62 (dd, J = 8.5, 2.7 Hz, 1H), 6.08 (ddd, J = 9.7, 5.4, 3.3 Hz, 1H), 5.02, 5.00 (ABq, 15.6 Hz, 2H), 3.78 (s, 3H), 3.08 (ddd, J = 17.3, 3.3, 3.2 Hz, 1H), 2.56 (ddd, J = 17.3, 5.4, 1.3 Hz, 1H).

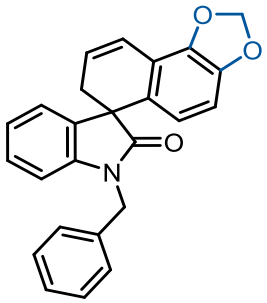
^{13}C NMR (126 MHz, $CDCl_3$) δ 180.1, 159.4, 140.9, 136.2, 135.0, 134.8, 128.9, 128.6, 128.1, 127.8, 127.4, 126.9, 126.7, 125.5, 123.8, 122.8, 113.3, 113.1, 109.4, 55.4, 51.3, 44.0, 34.5.

IR (ATR) 2935, 2848, 1707, 1606, 1484, 1347, 1261, 1047, 745, 696.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{25}H_{22}NO_2$ 368.1645; Found 368.1649

MP 127-130 °C

1-Benzyl-7'*H*-spiro[indoline-3,6'-naphtho[1,2-*d*][1,3]dioxol]-2-one (3u)



Prepared on 0.2 mmol scale by **GP5**. Due to co-elution with the retro-Diels-Alder furan by-product **11** following flash column chromatography 5→15% EtOAc/pentanes, the mixture was taken up in a 5% KOH solution in EtOH/H_2O (1:1) and stirred for 1 h at 85 °C. The reaction mixture was diluted with EtOAc, dried over magnesium sulfate, pushed through a pad of silica under reduced pressure. The filtrate was concentrated under reduced pressure and the crude mixture was purified by flash column chromatography 15% EtOAc/pentanes. Obtained 53 mg of a white solid (69% combined yield, >20:1 rr).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.33 (m, 4H), 7.32 – 7.27 (m, 2H), 7.14 (ddd, J = 7.8, 7.7, 1.2 Hz, 1H), 6.93 (ddd, J = 7.7, 7.6, 1.0 Hz, 1H), 6.83 (ddd, J = 9.8, 1.2, 0.7 Hz, 1H), 6.78 (d, J = 7.8 Hz, 1H), 6.52 (d, J = 8.0 Hz, 1H), 6.23 (dd, J = 8.0, 0.7 Hz, 1H), 6.11 (ddd, J = 9.8, 5.3, 3.5 Hz, 1H), 6.01 – 5.96 (m, 2H), 5.01, 4.99 (ABq, J = 15.5 Hz, 2H), 3.04 (ddd, J = 17.4, 3.5, 2.6 Hz, 1H), 2.57 (ddd, J = 17.4, 5.3, 1.3 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 179.7, 147.2, 144.0, 141.0, 136.1, 134.8, 128.9, 128.2, 128.1, 127.8, 127.4, 125.3, 123.8, 122.9, 121.2, 118.9, 116.4, 109.5, 107.4, 101.5, 51.2, 44.0, 34.3.

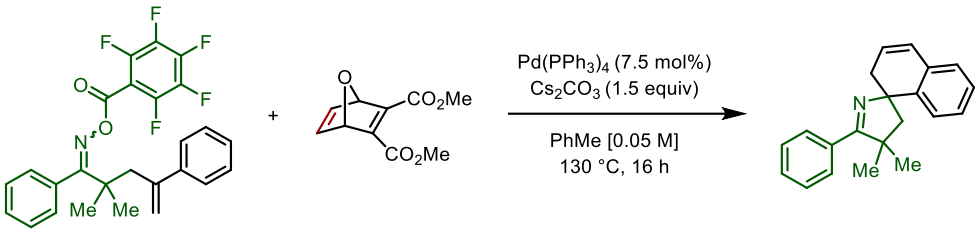
IR (ATR) 3038, 2919, 1709, 1603, 1455, 1356, 1249, 1039, 923, 692.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{25}H_{20}NO_3$ 382.1438; Found 382.1444

MP 149-151 °C

Spirocyclic Pyrroline Synthesized from an Oxime Ester

4',4'-dimethyl-5'-phenyl-3',4'-dihydro-2*H*-spiro[naphthalene-1,2'-pyrrole] (5)



4 | **2** 1.2 equiv | **5**: 14%

Vial and stir bar were dried in 110 °C oven overnight prior to use. Two 2 dr vials, one equipped with stir bar and one without were cooled to room temperature under argon flow. Cesium carbonate (98 mg, 0.30 mmol, 1.5 equiv), 2,2-dimethyl-1,4-diphenylpent-4-en-1-one *O*-perfluorobenzoyl oxime **4** (95 mg, 0.20 mmol, 1.0 equiv) and tetrakis(triphenylphosphine)palladium(0) (17 mg, 0.015 mmol, 7.5 mol%) were added in that order to the vial with a stir bar. Oxabicycle **2** (56 mg, 1.1·0.24 mmol = 0.26 mmol, 1.1·1.2 equiv = 1.32 equiv) was weighed in the empty vial. Freshly distilled toluene (1.1·4.0 mL = 4.4 mL) was added via syringe to the oxabicycle-containing vial and the vial was sonicated for 15 s to fully dissolve the oxabicycle. 4.0 mL of the resulting solution was transferred via syringe to the first vial. The vial was equipped with a Teflon-sealed cap and immediately stirred at 130 °C for 16 h. The reaction was passed through a pad of silica washing with ethyl acetate. The filtrate was concentrated under reduced pressure and the resulting residue purified by flash chromatography 0→2.5% EtOAc/pentanes. Obtained an amber oil, 8 mg (14% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.86 (m, 2H), 7.47 – 7.41 (m, 3H), 7.21 – 7.16 (m, 2H), 7.15 – 7.05 (m, 2H), 6.55 (dd, J = 9.4, 3.0 Hz, 1H), 6.04 (ddd, J = 9.4, 6.3, 2.6 Hz, 1H), 3.02 (ddd, J = 16.7, 3.0, 2.6 Hz, 1H), 2.43 (d, J = 13.3 Hz, 1H), 2.31 (dd, J = 16.7, 6.3 Hz, 1H), 1.91 (d, J = 13.3 Hz, 1H), 1.48 (s, 3H), 1.30 (s, 3H).

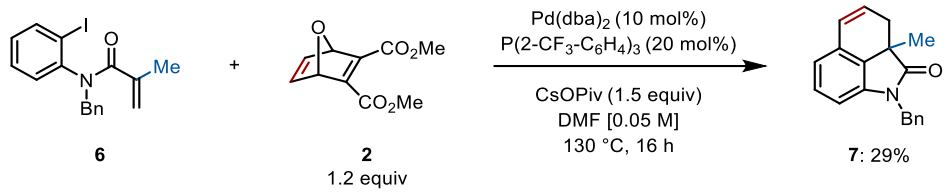
^{13}C NMR (126 MHz, $CDCl_3$) δ 179.9, 142.5, 134.9, 132.6, 129.7, 128.8, 128.4, 128.4, 127.9, 126.9, 126.5, 126.3, 124.0, 74.1, 53.6, 51.4, 38.3, 29.5, 28.7.

IR (ATR) 3710, 3031, 2924, 2868, 1735, 1606, 1447, 1033, 753, 695.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{21}H_{23}N$ 288.1747; Found 288.1733

Dihydrobenzoindolone Synthesized from an Aryl Iodide

1-Benzyl-2a-methyl-2a,3-dihydrobenzo[*cd*]indol-2(1*H*)-one (7)



Vials and stir bars were dried in 110 °C oven overnight prior to use. Two 2 dr vials, one equipped with stir bar and one without were cooled to room temperature under argon flow. In a nitrogen glovebox, cesium pivalate (70 mg, 0.30 mmol, 1.5 equiv), tris(2-(trifluoromethyl)phenyl)phosphane (19 mg, 0.04 mmol, 20 mol%) and bis(dibenzylideneacetone)palladium(0) (12 mg, 0.02 mmol, 10 mol%) were added in that order to the vial with a stir bar. *N*-Benzyl-*N*-(2-iodophenyl)methacrylamide **6** (83 mg, 1.1·0.20 mmol = 0.22 mmol, 1.1·1.0 equiv = 1.10 equiv) and oxabicycle **2** (56 mg, 1.1·0.24 mmol = 0.26 mmol, 1.1·1.2 equiv = 1.32 equiv) were weighed in the empty vial. Anhydrous dimethylformamide (1.1·4.0 mL = 4.4 mL) was added via syringe to the aryl iodide and oxabicycle-containing vial and the vial was sonicated for 15 s to fully dissolve both reagents. 4.0 mL of the resulting solution was transferred via syringe to the first vial. The vial was equipped with a Teflon-sealed cap and immediately stirred at 130 °C for 16 h. The reaction was passed through a pad of silica washing with ethyl acetate. The filtrate was washed with brine four times, dried over magnesium sulfate, passed through another silica pad and concentrated under reduced pressure. The resulting residue was purified by flash chromatography 2.5→5% EtOAc/pentanes. Obtained a white solid, 16 mg (29% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.24 (m, 5H), 7.08 (dd, J = 7.7, 7.7 Hz, 1H), 6.75 (d, J = 7.7 Hz, 1H), 6.59 – 6.52 (m, 2H), 5.98 (ddd, J = 9.6, 6.0, 2.5 Hz, 1H), 5.11 (d, J = 15.5 Hz, 1H), 4.65 (d, J = 15.5 Hz, 1H), 2.56 (ddd, J = 17.1, 6.0, 0.9 Hz, 1H), 2.40 (ddd, J = 17.1, 2.9, 2.5 Hz, 1H), 1.47 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 182.4, 140.7, 136.5, 130.5, 129.8, 128.9, 128.4, 128.2, 127.7, 127.4, 125.7, 118.0, 108.1, 43.8, 41.5, 29.8, 21.9.

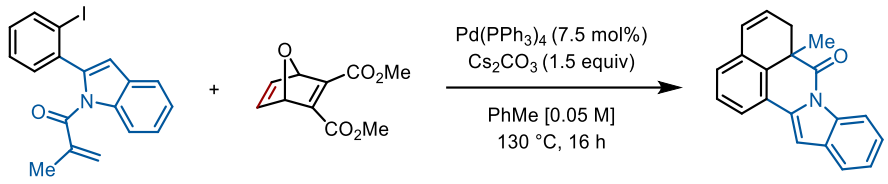
IR (ATR) 2957, 2922, 2851, 1707, 1611, 1467, 1335, 803, 730, 693.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{19}H_{18}NO$ 276.1383; Found 276.1381

MP 97-99 °C

Indolo[2,1-*a*]isoquinolinone Synthesized from an Aryl Iodide

6a-Methyl-6,6a-dihydro-7*H*-benzo[*de*]indolo[2,1-*a*]isoquinolin-7-one (9)



8 **2** 1.2 equiv **9:** 89%

Vial and stir bar were dried in 110 °C oven overnight prior to use. Two 2 dr vials, one equipped with stir bar and one without were cooled to room temperature under argon flow. Cesium carbonate (98 mg, 0.30 mmol, 1.5 equiv), 1-(2-(2-iodophenyl)-1*H*-indol-1-yl)-2-methylprop-2-en-1-one **8** (77 mg, 0.20 mmol, 1.0 equiv) and tetrakis(triphenylphosphine)palladium(0) (17 mg, 0.015 mmol, 7.5 mol%) were added in that order to the vial with a stir bar. Oxabicycle **2** (56 mg, 1.1·0.24 mmol = 0.26 mmol, 1.1·1.2 equiv = 1.32 equiv) was weighed in the empty vial. Freshly distilled toluene (1.1·4.0 mL = 4.4 mL) was added via syringe to the oxabicycle-containing vial and the vial was sonicated for 15 s to fully dissolve the oxabicycle. 4.0 mL of the resulting solution was transferred via syringe to the first vial. The vial was equipped with a Teflon-sealed cap and immediately stirred at 130 °C for 16 h. The reaction was passed through a pad of silica washing with ethyl acetate. The filtrate was concentrated under reduced pressure and the resulting residue purified by flash chromatography 0→2.5% EtOAc/pentanes. Obtained a beige solid, 51 mg (89% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (ddd, J = 8.3, 0.9, 0.8 Hz, 1H), 7.68 (dd, J = 7.8, 1.2 Hz, 1H), 7.60 (ddd, J = 7.7, 1.3, 0.8 Hz, 1H), 7.38 (ddd, J = 8.3, 7.3, 1.3 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.08 (dd, J = 7.5, 1.2 Hz, 1H), 7.01 (d, J = 0.7 Hz, 1H), 6.55 (dd, J = 9.6, 2.9 Hz, 1H), 6.12 (ddd, J = 9.6, 6.4, 2.6 Hz, 1H), 2.92 (ddd, J = 17.9, 6.4, 0.6 Hz, 1H), 2.78 (ddd, J = 17.9, 2.9, 2.6 Hz, 1H), 1.51 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.9, 135.5, 135.4, 132.8, 132.8, 130.7, 127.8, 127.0, 126.7, 126.6, 125.4, 124.5, 123.8, 123.0, 120.6, 116.4, 103.3, 42.7, 31.7, 27.4.

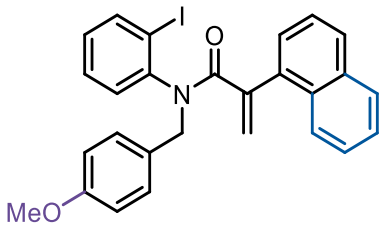
IR (ATR) 2968, 2923, 2863, 1690, 1449, 1367, 1330, 1146, 815, 748.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{20}H_{16}NO$ 286.1226; Found 286.1233

MP 120-122 °C

Naphthalene Derived Spirooxindoles and Aryl Iodide Precursor

N-(2-iodophenyl)-*N*-(4-methoxybenzyl)-2-(naphthalen-1-yl)acrylamide



Synthesized following **GP3** from 2-iodoaniline, *p*-anisaldehyde, 1-naphthaleneacetic acid and paraformaldehyde on a 5.0 mmol scale. Obtained 191 mg of an off-white sticky paste (7% yield over 3 steps).

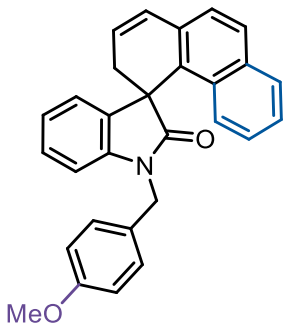
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 8.5 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.62 – 7.55 (m, 2H), 7.39 (ddd, J = 8.2, 6.8, 1.4 Hz, 1H), 7.33 (ddd, J = 8.2, 6.8, 1.4 Hz, 1H), 7.06 (dt, J = 8.2, 3.3 Hz, 3H), 6.76 – 6.66 (m, 3H), 6.61 (dd, J = 7.5, 1.6 Hz, 1H), 6.47 (td, J = 7.5, 1.6 Hz, 1H), 6.27 (d, J = 1.6 Hz, 1H), 5.67 – 5.59 (m, 2H), 5.52 (d, J = 1.6 Hz, 1H), 3.91 (d, J = 14.2 Hz, 1H), 3.75 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4, 159.1, 146.0, 142.8, 139.6, 135.7, 133.4, 131.6, 131.0, 130.9, 128.9, 128.9, 128.1, 128.0, 127.9, 126.2, 125.8, 125.8, 125.6, 125.5, 125.4, 113.7, 100.0, 55.3, 51.7.

IR (ATR) 3054, 2926, 2834, 1737, 1643, 1509, 1467, 1386, 1239, 776.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{27}H_{23}INO_2$ 520.0768; Found 520.0770

1-(4-Methoxybenzyl)-3'*H*-spiro[indoline-3,4'-phenanthren]-2-one (A)



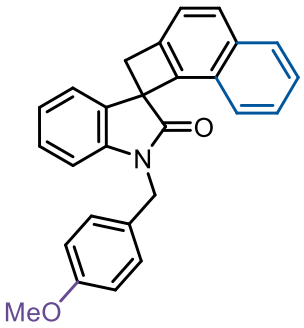
Prepared on 0.2 mmol scale by **GP5**. Due to co-elution with the retro-Diels-Alder furan by-product **13** following flash column chromatography 5→15% EtOAc/pentanes, the mixture was taken up in a 5% KOH solution in EtOH/H_2O (1:1) and stirred for 1 h at 85 °C. The reaction mixture was diluted with EtOAc, dried over magnesium sulfate, pushed through a pad of silica under reduced pressure. The filtrate was concentrated under reduced pressure and the crude mixture was purified by flash column chromatography 15% EtOAc/pentanes, co-eluted with **C**.

^{1}H NMR (500 MHz, $CDCl_3$) See mixture of **A** and **C** in the NMR Spectra section; key peaks identified.

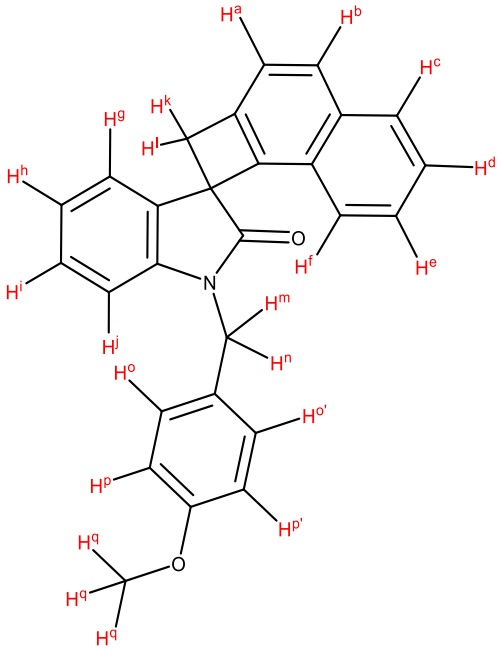
^{13}C NMR (126 MHz, $CDCl_3$) See mixture of **A** and **C** in the NMR Spectra section.

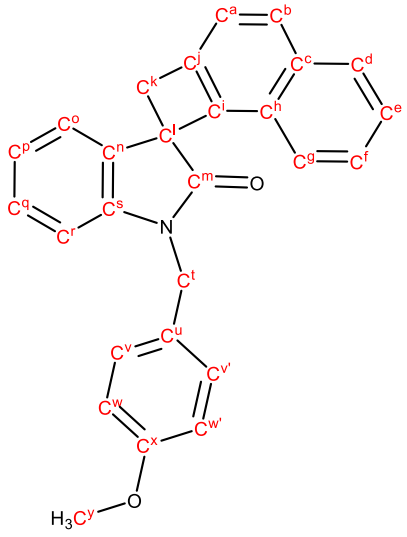
HRMS (DART) m/z: [M + H]+ Calcd for $C_{29}H_{24}NO_2$ 418.1802; Found 418.1802

1'-(4-Methoxybenzyl)-2*H*-spiro[cyclobuta[*a*]naphthalene-1,3'-indolin]-2'-one (B)



Prepared on 0.2 mmol scale by **GP5**. Purified by flash column chromatography 2.5→5% EtOAc/pentanes. Obtained 26 mg of an off-white solid (33% yield).





^{1}H NMR (700 MHz, $CDCl_3$) δ 8.73 (d, J = 8.5 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.88 (dd, J = 8.0, 1.7 Hz, 1H), 7.66 (d, J = 8.1 Hz, 1H), 7.56 (ddd, J = 8.5, 6.7, 1.7 Hz, 1H), 7.53 (ddd, J = 8.0, 6.7, 1.4 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.27 (ddd, J = 8.0, 7.2, 1.1 Hz, 1H), 7.21 (d, J = 8.9 Hz, 1H), 7.19 (ddd, J = 8.1, 7.2, 1.1 Hz, 1H), 6.85 (d, J = 8.9 Hz, 2H), 5.42 (s, 2H), 5.30 (s, 2H), 3.76 (s, 3H).

^{1}H	**σ / ppm**
a	7.34–7.30 (7.33)
b	7.66
c	7.88
d	7.53
e	7.56
f	8.73
g	7.98
h	7.27
i	7.19
j	7.34–7.30 (7.32)
k	5.42
l	5.42
m	5.30
n	5.30
o	7.21
p	6.85
q	3.76

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 153.4, 134.8, 132.7, 129.7, 129.1, 128.5, 128.3, 128.2, 127.3, 125.9, 125.1, 124.9, 124.4, 124.2, 122.9, 121.3, 120.8, 120.2, 114.3, 109.8, 94.1, 74.1, 55.4, 45.1.

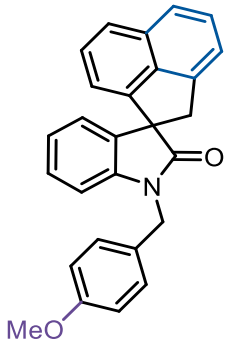
^{13}C	σ / ppm
a	122.9
b	124.2
c	134.8
d	128.5
e	125.9
f	125.1
g	127.3
h	128.2
i	129.7
j	124.9
k	74.1
l	94.1
m	153.4
n	124.4
o	121.3
p	120.8
q	120.2
r	109.8
s	132.7
t	45.1
u	129.1
v	128.3
w	114.3
x	159.2
y	55.4

IR (ATR) 3051, 2932, 2841, 1615, 1492, 1338, 1243, 1003, 801, 736

HRMS (DART) m/z: [M + H]+ Calcd for $C_{27}H_{22}NO_2$ 392.1645; Found 392.1647

MP 130-134 °C

1'-(4-Methoxybenzyl)-2*H*-spiro[acenaphthylene-1,3'-indolin]-2'-one (C)



Prepared on 0.2 mmol scale by **GP5**. Due to co-elution with the retro-Diels-Alder furan by-product **13** following flash column chromatography 5→15% EtOAc/pentanes, the mixture was taken up in a 5% KOH solution in EtOH/H_2O (1:1) and stirred for 1 h at 85 °C. The reaction mixture was diluted with EtOAc, dried over magnesium sulfate, pushed through a pad of silica under reduced pressure. The filtrate was concentrated under reduced pressure and the crude mixture was purified by flash column chromatography 15% EtOAc/pentanes, co-eluted with **A**.

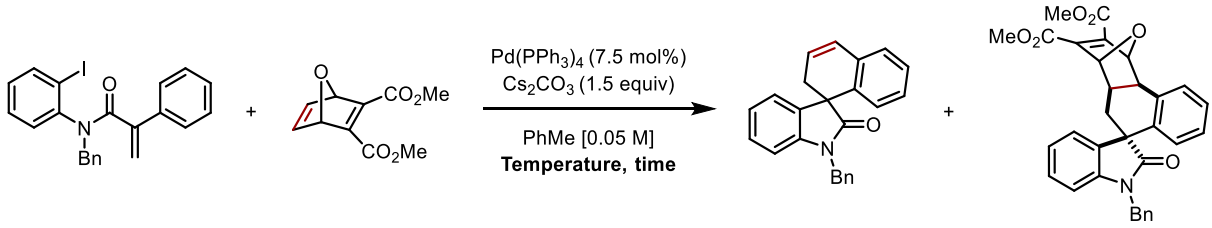
^{1}H NMR (500 MHz, $CDCl_3$) See mixture of **A** and **C** in the NMR Spectra section; postulated key peaks identified.

^{13}C NMR (126 MHz, $CDCl_3$) See mixture of **A** and **C** in the NMR Spectra section.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{27}H_{22}NO_2$ 392.1645; Found 392.1644

Mechanistic Studies

Temperature and Time Studies



1a | **2** 1.2 equiv | **3a** | **3a***

Temperature / °C	Time / h	Conversion of 1	3a	3a*
130	16	100%	88%	0%
130	2	100%	50%	48%
100	16	71%[a]	8%[a]	47%

Reactions were run on 0.2 mmol scale; isolated yields are shown. [a]Yield or conversion was determined by ^{1}H NMR spectroscopy analysis of crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

Vials and stir bars were dried in 110 °C oven overnight prior to use. Three 2 dr vials equipped with stir bars and an empty 9.5 dr vial were cooled to room temperature under argon flow. Cesium carbonate (98 mg, 0.30 mmol, 1.5 equiv), *N*-benzyl-*N*-(2-iodophenyl)-2-phenylacrylamide **1a** (88 mg, 0.20 mmol, 1.0 equiv) and tetrakis(triphenylphosphine)palladium(0) (17 mg, 0.015 mmol, 7.5 mol%) were added in that order to each 2 dr vial. Oxabicycle **2** (167 mg, 3.3·0.24 mmol = 0.79 mmol, 3.3·1.2 equiv = 3.96 equiv) was weighed in the 9.5 dr vial. Freshly distilled toluene (3.3·4.0 mL = 13.2 mL) was added via syringe to the oxabicycle-containing vial and the vial was sonicated for 15 s to fully dissolve the oxabicycle. 4.0 mL of the resulting solution was transferred via syringe to each 2 dr vial. The three vials were equipped with a Teflon-sealed cap and immediately stirred respectively at:

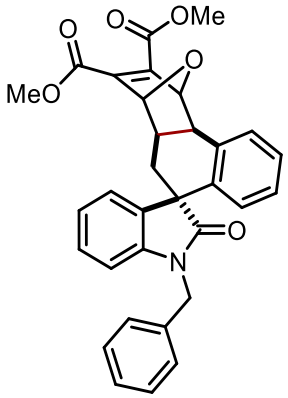
- 130 °C, 16 h
- 130 °C, 2 h
- 100 °C, 16h

The reactions were each passed through a pad of silica washing with ethyl acetate in a scintillation vial containing 8 mg of 1,3,5-trimethoxybenzene. The filtrates were concentrated under reduced pressure and dissolved in 2.0 mL of $CDCl_3$ before being analyzed by ^{1}H NMR spectroscopy. The NMR samples were concentrated under reduced pressure, followed by purification by flash chromatography.

- Reaction carried out at 130 °C, 16 h: **3a** was purified by flash column chromatography 5→10% EtOAc/pentanes and was obtained as 59 mg of a white solid (88% yield).

- Reaction carried out at 130 °C, 2 h: **3a** was purified by flash column chromatography 5→10% EtOAc/pentanes and was obtained as 34 mg of a white solid (50% yield); **3a'** was purified by flash chromatography 5%→30% EtOAc/pentanes and was obtained as 50 mg of a light-yellow solid (48% yield).
- Reaction carried out at 100 °C, 16 h: **3a** (8% NMR yield) co-eluted with **1a** (71% NMR conversion) following flash column chromatography 5→10% EtOAc/pentanes; **3a'** was purified by flash chromatography 5%→30% EtOAc/pentanes and was obtained as 49 mg of a light-yellow solid (48% yield).

Dimethyl (1'*R*,3*R*,4'*S*,4a'*R*,10a'*S*)-1-benzyl-2-oxo-4',4a',10',10a'-tetrahydro-1'*H*-spiro[indoline-3,9'-[1,4]epoxyphenanthrene]-2',3'-dicarboxylate [and enantiomer] (3a*)



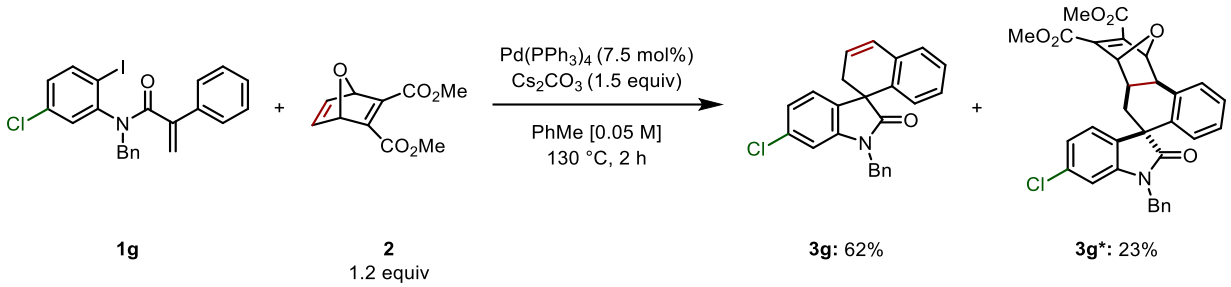
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, J = 7.7 Hz, 1H), 7.34 (ddd, J = 7.7, 7.5, 1.4 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.27 – 7.21 (m, 4H), 7.15 (dd, J = 7.4, 0.8 Hz, 1H), 7.09 (ddd, J = 7.5, 7.4, 1.0 Hz, 1H), 7.07 – 7.03 (m, 1H), 6.80 (d, J = 7.5 Hz, 1H), 6.62 (dd, J = 7.9, 1.3 Hz, 1H), 5.51 (d, J = 1.3 Hz, 1H), 4.96 (d, J = 1.3 Hz, 1H), 4.93 (d, J = 15.7 Hz, 1H), 4.80 (d, J = 15.7 Hz, 1H), 3.92 (s, 3H), 3.84 (s, 3H), 3.47 (d, J = 8.2 Hz, 1H), 3.00 (ddd, J = 12.8, 8.2, 6.8 Hz, 1H), 2.37 (dd, J = 13.1, 6.8 Hz, 1H), 2.15 (dd, J = 13.1, 12.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 177.9, 162.9, 162.7, 144.8, 143.1, 142.5, 137.8, 137.6, 136.0, 133.4, 129.5, 128.9, 128.5, 128.2, 127.7, 127.2, 126.4, 126.4, 124.3, 123.2, 109.4, 88.2, 85.2, 52.6, 52.5, 52.5, 43.8, 41.8, 37.1, 33.9.

IR (ATR) 2949, 1705, 1612, 1487, 1435, 1343, 1266, 1210, 743, 700

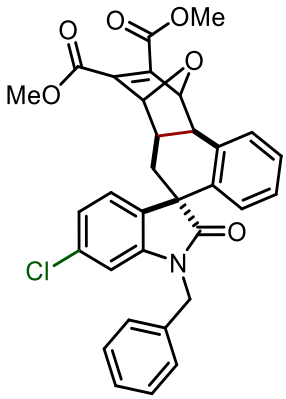
HRMS (DART) m/z: [M + H]+ Calcd for $C_{32}H_{28}NO_6$ 522.1911; Found 522.1908

MP 108-112 °C



Vials and stir bars were dried in 110 °C oven overnight prior to use. Two 2 dr vials, one equipped with stir bar and one without were cooled to room temperature under argon flow. Cesium carbonate (98 mg, 0.30 mmol, 1.5 equiv), *N*-benzyl-*N*-(5-chloro-2-iodophenyl)-2-phenylacrylamide **1g** (0.20 mmol, 1.0 equiv) and tetrakis(triphenylphosphine)palladium(0) (17 mg, 0.015 mmol, 7.5 mol%) were added in that order to the vial with a stir bar. Oxabicycle **2** (56 mg, 1.1·0.24 mmol = 0.26 mmol, 1.1·1.2 equiv = 1.32 equiv) was weighed in the empty vial. Freshly distilled toluene (1.1·4.0 mL = 4.4 mL) was added via syringe to the oxabicycle-containing vial and the vial was sonicated for 15 s to fully dissolve the oxabicycle. 4.0 mL of the resulting solution was transferred via syringe to the first vial. The vial was equipped with a Teflon-sealed cap and immediately stirred at 130 °C for 16 h. The reaction was passed through a pad of silica washing with ethyl acetate. The filtrate was concentrated under reduced pressure and the resulting residue purified by flash chromatography. Obtained 46 mg of **3g** (62%) and 26 mg of **3g*** (23%) as a pale-yellow solid.

Dimethyl (1'*R*,3*R*,4'*S*,4a'*R*,10a'*S*)-1-benzyl-6-chloro-2-oxo-4',4a',10',10a'-tetrahydro-1'*H*-spiro[indoline-3,9'-[1,4]epoxyphenanthrene]-2',3'-dicarboxylate [and enantiomer] (3g*)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, J = 7.8 Hz, 1H), 7.37 – 7.27 (m, 3H), 7.23 – 7.19 (m, 1H), 7.10 – 7.02 (m, 2H), 6.79 (dd, J = 1.7, 0.6 Hz, 1H), 6.60 (dd, J = 7.8, 1.3 Hz, 1H), 5.50 (d, J = 1.3 Hz, 1H), 4.96 (d, J = 1.3 Hz, 1H), 4.90 (d, J = 15.9 Hz, 1H), 4.76 (d, J = 15.9 Hz, 1H), 3.91 (s, 3H), 3.84 (s, 3H), 3.45 (d, J = 8.2 Hz, 1H), 2.97 (ddd, J = 12.8, 8.2, 6.7 Hz, 1H), 2.34 (dd, J = 13.1, 6.7 Hz, 1H), 2.11 (dd, J = 13.1, 12.8 Hz, 1H).

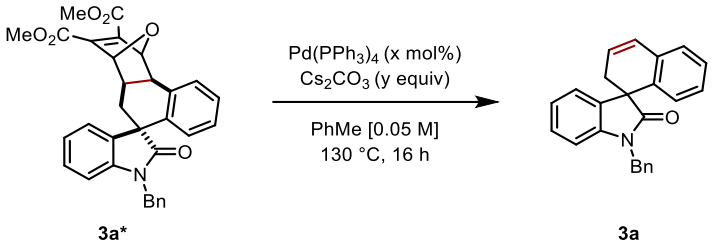
^{13}C NMR (126 MHz, $CDCl_3$) δ 177.8, 162.8, 162.7, 144.8, 144.3, 142.4, 137.7, 137.0, 135.4, 134.3, 131.8, 129.7, 129.1, 128.4, 128.0, 127.2, 126.6, 126.2, 125.2, 123.2, 110.0, 88.2, 85.2, 52.6, 52.5, 52.2, 43.9, 41.8, 37.0, 33.8.

IR (ATR) 3051, 2925, 1705, 1607, 1484, 1464, 1344, 1186, 745, 695

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{32}H_{27}ClNO_6$ 556.1521; Found 556.1522

MP 190-193 °C

Confirmation of 3a* as a Precursor to 3a



3a* **3a**

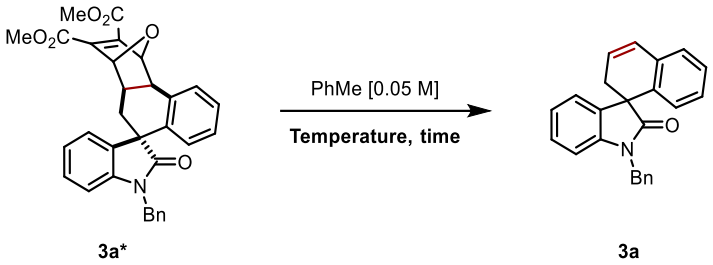
$Pd(PPh_3)_4$ / mol%	**Cs_2CO_3 / equiv**	**Conversion of 3a***	**3a**
7.5	1.5	100%	91%
7.5	0	100%	96%
0	1.5	100%	94%
0	0	100%	95% (97%)[a]

Reactions were run on 0.10 mmol scale; yields or conversions were determined by ^{1}H NMR spectroscopy analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [a]Isolated yield is shown.

Vials and stir bars were dried in 110 °C oven overnight prior to use. Four 2 dr vials equipped with a stir bar were cooled to room temperature under argon flow. Cesium carbonate (98 mg, 0.30 mmol, 1.5 equiv or 0 mg, 0 mmol, 0 equiv), **3a*** (52 mg, 0.10 mmol) and tetrakis(triphenylphosphine)palladium(0) (17 mg, 0.015 mmol, 7.5 mol% or 0 mg, 0 mmol, 0 mol%) were added in that order to each 2 dr vial. Freshly distilled toluene (2.0 mL) was added via syringe to each vial, which were equipped with a Teflon-sealed cap and immediately stirred at 130 °C for 16 h. The reactions were each passed through a pad of silica washing with ethyl acetate in a scintillation vial containing 8 mg of 1,3,5-trimethoxybenzene. The filtrates were concentrated under reduced pressure and dissolved in 2.0 mL of $CDCl_3$ before being analyzed by ^{1}H NMR spectroscopy.

The residue pertaining to the reaction run with $Pd(PPh_3)_4$ (0 mol%) and Cs_2CO_3 (0 equiv) was purified by flash chromatography 5→10% EtOAc/pentanes. Obtained 32 mg of **3a** (97% yield).

Conversion of 3a* to 3a at a Reduced Temperature, and at a Reduced Reaction Time



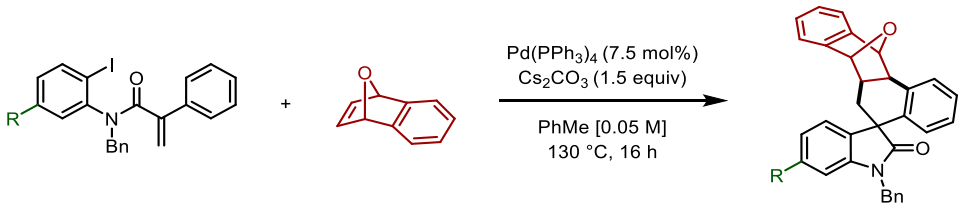
3a* **3a**

Temperature / °C	Time / h	Conversion of 3a	3a*
130	2	48%	48% (quant. yield brsm)
100	16	35%	35% (quant. yield brsm)

Reactions were run on 0.10 mmol scale; isolated yields are shown.

Vials and stir bars were dried in 110 °C oven overnight prior to use. Two 2 dr vials equipped with a stir bar were cooled to room temperature under argon flow. **3a*** (52 mg, 0.10 mmol) was added to each 2 dr vial. Freshly distilled toluene (2.0 mL) was added via syringe to each vial, which were equipped with a Teflon-sealed cap. One vial was stirred at 130 °C for 2 h, and the other, at 100 °C for 16 h. The reactions were each passed through a pad of silica washing with ethyl acetate and the filtrates were concentrated under reduced pressure. The crude mixtures were purified by flash chromatography 5→10% EtOAc/pentanes. Obtained 16 mg of **3a** (48% yield, quantitative yield based on recovered starting material **3a***: 27 mg) for the reaction run at 130 °C for 2 h and 12 mg of **3a** (32% yield, quantitative yield based on recovered starting material **3a***: 34 mg) for the reaction run at 100 °C for 16 h.

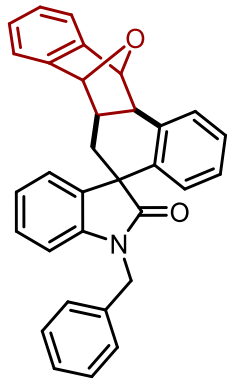
Insertion of an Oxabicycle that Cannot Undergo a Retro-Diels-Alder Step



R: H (**1a**), Cl (**1g**) **2'** 1.2 equiv R: H (**10a**), Cl (**10g**)

Vial and stir bar were dried in 110 °C oven overnight prior to use. A 2 dr vial equipped with a stir bar was cooled to room temperature under argon flow. Cesium carbonate (98 mg, 0.30 mmol, 1.5 equiv), oxabicycle **2'** (35 mg, 0.24 mmol, 1.2 equiv), aryl iodide **1a** or **1g** (0.20 mmol, 1.0 equiv) and tetrakis(triphenylphosphine)palladium(0) (17 mg, 0.015 mmol, 7.5 mol%) were added in that order to the vial. Freshly distilled toluene (4.0 mL) was added via syringe to the vial, which was equipped with a Teflon-sealed cap and immediately stirred at 130 °C for 16 h. The reaction was passed through a pad of silica washing with ethyl acetate. The filtrate was concentrated under reduced pressure and the resulting residue purified by flash chromatography, followed by trituration.

(3*R*,6a'*S*,7'*R*,12'*S*,12a'*R*)-1-Benzyl-6a',7',12',12a'-tetrahydro-6'*H*-spiro[indoline-3,5'-[7,12]epoxytetraphen]-2-one [and enantiomer] (10a)



Prepared on 0.2 mmol scale. Purified at first by flash column chromatography 2.5→7.5% EtOAc/pentanes. The resulting impure off-white solid was triturated three times by dissolving the compound in DCM (0.5 mL), adding pentanes (6 mL), waiting for the product to crash out of solution, and decantation. Obtained 20 mg of a white solid (22% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 7.7 Hz, 1H), 7.45 (d, J = 6.4 Hz, 1H), 7.37 (ddd, J = 7.7, 7.5, 1.4 Hz, 1H), 7.35 – 7.18 (m, 10H), 7.12 (ddd, J = 7.5, 7.5, 1.0 Hz, 1H), 7.08 – 7.03 (m, 1H), 6.81 (d, J = 7.8 Hz, 1H), 6.65 (dd, J = 7.8, 1.4 Hz, 1H), 5.72 (s, 1H), 5.09 (s, 1H), 4.85, 4.83 (ABq, J = 15.8 Hz, 2H), 3.37 (d, J = 8.2 Hz, 1H), 2.94 (ddd, J = 12.4, 8.2, 7.1 Hz, 1H), 2.42 – 2.28 (m, 2H).

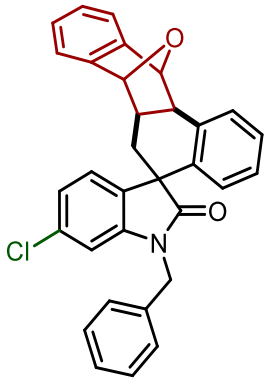
^{13}C NMR (126 MHz, $CDCl_3$) δ 178.0, 146.2, 144.3, 143.1, 138.7, 137.6, 136.1, 133.9, 129.5, 128.9, 128.4, 128.1, 127.7, 127.2, 127.0, 126.9, 126.5, 126.1, 124.3, 123.2, 119.7, 118.9, 109.3, 86.5, 84.0, 52.5, 44.1, 43.7, 37.6, 36.3.

IR (ATR) 2968, 1710, 1611, 1486, 1350, 1152, 996, 852, 752, 697.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{32}H_{26}NO_2$ 456.1958; Found 456.1963

MP 269-271 °C

(3*R*,6a'*S*,7'*R*,12'*S*,12a'*R*)-1-Benzyl-6-chloro-6a',7',12',12a'-tetrahydro-6'*H*-spiro[indoline-3,5'-[7,12]epoxytetraphen]-2-one [and enantiomer] (10g)



Prepared on 0.2 mmol scale. Purified at first by flash column chromatography 2.5→7.5% EtOAc/pentanes. The resulting impure off-white solid was triturated three times by dissolving the compound in DCM (0.5 mL), adding pentanes (6 mL), waiting for the product to crash out of solution, and decantation. Obtained 10 mg of a white solid (11% yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 7.7 Hz, 1H), 7.45 (d, J = 6.4 Hz, 1H), 7.37 (ddd, J = 7.7, 7.5, 1.4 Hz, 1H), 7.35 – 7.17 (m, 3H), 7.12 – 7.08 (m, 1H), 7.08 – 7.04 (m, 1H), 6.80 (dd, J = 1.6, 0.7 Hz, 1H), 6.63 (dd, J = 7.8, 1.4 Hz, 1H), 5.71 (s, 1H), 5.08 (s, 1H), 4.82, 4.79 (ABq, J = 15.8 Hz, 2H), 3.35 (d, J = 8.2 Hz, 1H), 2.90 (ddd, J = 12.5, 8.2, 6.9 Hz, 1H), 2.38 – 2.25 (m, 2H).

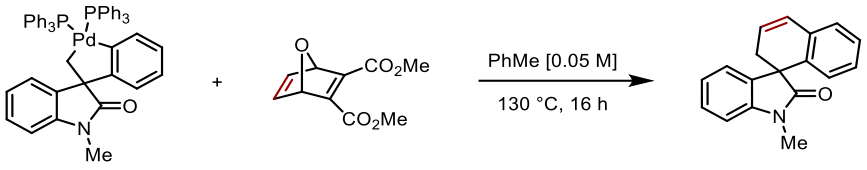
^{13}C NMR (126 MHz, $CDCl_3$) δ 177.9, 146.1, 144.3, 144.2, 138.7, 137.0, 135.5, 134.1, 132.2, 129.7, 129.1, 128.3, 127.9, 127.2, 127.1, 127.0, 126.4, 126.2, 125.3, 123.2, 119.7, 118.9, 109.9, 86.5, 83.9, 52.2, 44.1, 43.8, 37.6, 36.2.

IR (ATR) 3027, 2998, 2969, 2922, 1715, 1609, 1493, 1371, 1216, 760.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{32}H_{25}NO_2Cl$ 490.1568; Found 490.1573

MP 270-272 °C

Palladacycle as a Competent Intermediate in the Catalytic Cycle



3i-Pd **2** 1.2 equiv **3i:** 55%[b]

Palladacycle **3i-Pd** was synthesized based on a known literature procedure.[4] Characterization was consistent with literature.[4]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 7H), 7.31 – 7.26 (m, 6H), 7.26 – 7.17 (m, 7H), 7.14 – 7.09 (m, 6H), 7.08 – 7.03 (m, 6H), 6.99 (ddd, J = 7.6, 7.5, 1.0 Hz, 1H), 6.85 – 6.81 (m, 1H), 6.79 (d, J = 7.6 Hz, 1H), 6.63 (ddd, J = 7.3, 7.3, 1.2 Hz, 1H), 6.41 (ddd, J = 7.5, 2.6, 1.4 Hz, 1H), 6.37 – 6.32 (m, 1H), 3.25 (s, 3H), 2.17 – 2.05 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 181.7 (d, J = 4.8 Hz), 170.6 (dd, J = 112.7, 11.7 Hz), 158.9 (dd, J = 3.5, 3.5 Hz), 143.2, 140.8 (dd, J = 10.9, 4.3 Hz), 138.9 (d, J = 4.5 Hz), 134.9 (d, J = 13.3 Hz), 134.6 (d, J = 2.1 Hz), 134.4 (d, J = 12.7 Hz), 133.5 (dd, J = 32.7, 2.1 Hz), 129.3 (dd, J = 7.8, 1.9 Hz), 127.9 (dd, J = 9.4, 6.4 Hz), 126.6, 124.6, 124.1 (dd, J = 8.1, 2.9 Hz), 123.0, 122.5 (d, J = 3.1 Hz), 121.9, 107.2, 69.0 (dd, J = 7.4, 5.0 Hz), 47.6 (dd, J = 90.4, 8.0 Hz), 26.4.

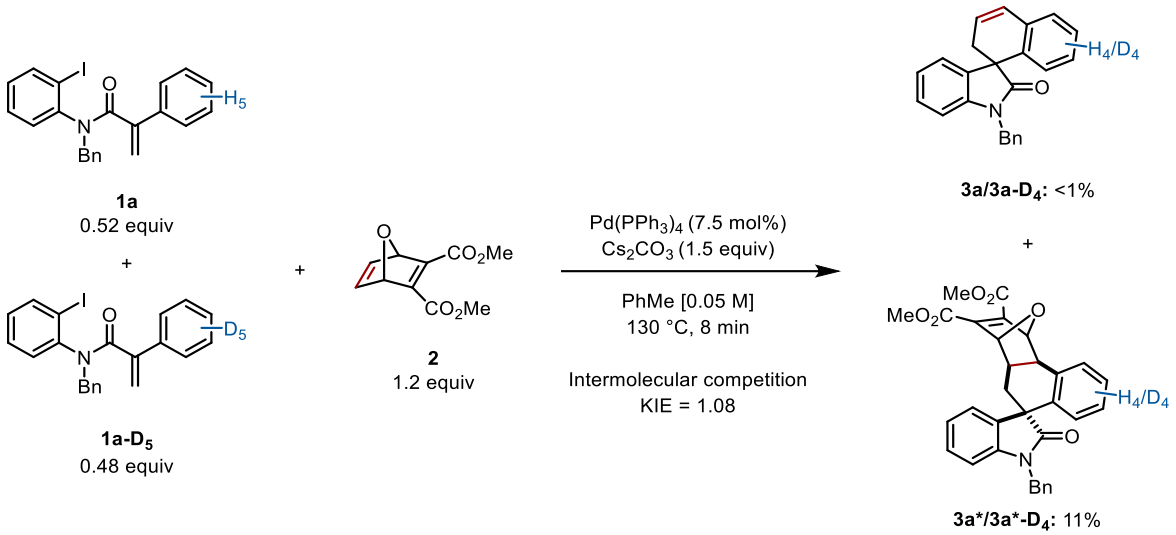
^{31}P NMR (121 MHz, $CDCl_3$) δ 25.12 (dd, J = 108.8, 22.6 Hz).

Yoon, H.; Lossouarn, A.; Landau, F.;Lautens, M. *Org. Lett.* **2016,** *18*, 6324–6327.[4]

Vials and stir bar were dried in 110 °C oven overnight prior to use. Two 2 dr vials, one equipped with stir bar and one without were cooled to room temperature under argon flow. Palladacycle **3i-Pd** (85 mg, 0.10 mmol) was added to the vial with a stir bar. Oxabicycle **2** (27 mg, 1.1·0.12 mmol = 0.13 mmol, 1.1·1.2 equiv = 1.32 equiv) was weighed in the empty vial. Freshly distilled toluene (1.1·2.0 mL = 2.2 mL) was added via syringe to the oxabicycle-containing vial and the vial was sonicated for 15 s to fully dissolve the oxabicycle. 2.0 mL of the resulting solution was transferred via syringe to the first vial. The vial was equipped with a Teflon-sealed cap and immediately stirred at 130 °C for 16 h. The reaction was passed through a pad of silica washing with ethyl acetate. The filtrate was concentrated under reduced pressure. Due to co-elution with the retro-Diels-Alder furan by-product **11** following flash column chromatography 5→15% EtOAc/pentanes, the mixture was taken up in a 5% KOH solution in EtOH/H_2O (1:1) and stirred for 1 h at 85 °C. The reaction mixture was diluted with EtOAc, dried over magnesium sulfate, pushed through a pad of silica under reduced pressure. The filtrate was concentrated under reduced pressure and the crude

mixture was purified by flash column chromatography 15% EtOAc/pentanes. Obtained 14 mg of **3i** (55% yield).

KIE Experiment – Aryl Iodide



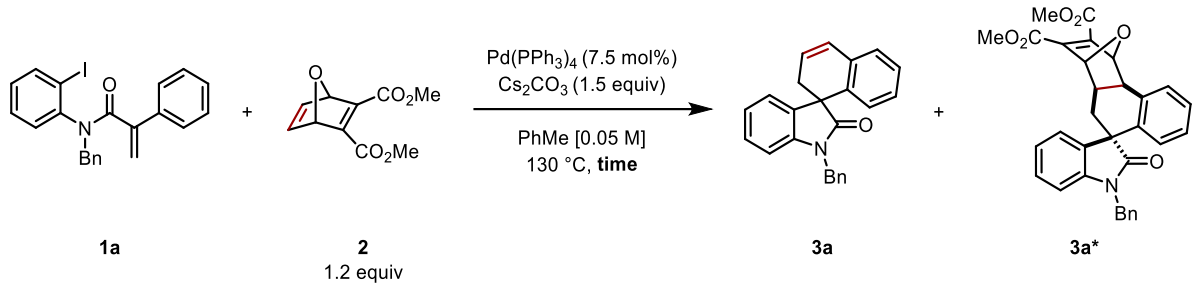
Reactions were run on 0.1 mmol scale; yields were determined by ^{1}H NMR spectroscopy analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

Vials and stir bars were dried in 110 °C oven overnight prior to use. Three 2 dr vials, one equipped with stir bar and two without were cooled to room temperature under argon flow. *N*-Benzyl-*N*-(2-iodophenyl)-2-phenylacrylamide **1a** and *N*-Benzyl-*N*-(2-iodophenyl)-2-(phenyl-d_5)acrylamide **1a-D$_5$** were weighed with the objective of adding exactly 0.50 mmol, 22 mg, 0.50 equiv for the former and 0.50 mmol, 22 mg, 0.50 equiv for the latter to the vial without a stir bar. The mixture was dissolved in $CDCl_3$ (1.4 mL) and subjected to ^{1}H NMR analysis, which revealed 0.52 mmol, 23 mg, 0.52 equiv of **1a** and 0.48 mmol, 21 mg, 0.48 equiv of **1a-D$_5$** were present instead. The solution was concentrated under reduced pressure. The aryl iodides were washed with pentanes and concentrated under reduced pressure three times before being placed under vacuum and lyophilized three times to remove any trace of solvent. Cesium carbonate (49 mg, 0.15 mmol, 1.5 equiv), and tetrakis(triphenylphosphine)palladium(0) (9 mg, 0.0075 mmol, 7.5 mol%) were added in that order to the vial with a stir bar. Oxabicycle **2** (28 mg, 1.1·0.12 mmol = 0.132 mmol, 1.1·1.2 equiv = 1.32 equiv) was weighed in the empty vial. Freshly distilled toluene (1.1·0.50 mL = 0.55 mL) was added via syringe to the oxabicycle-containing vial and the vial was sonicated for 15 s to fully dissolve the oxabicycle. 0.5 mL of the resulting solution was transferred via syringe to the vial containing the aryl iodides to fully dissolve them. The resulting solution was transferred via syringe to the vial with a stir bar. Toluene (0.5 mL) was added via syringe to the previous vial to recover remaining quantities of substrates and the resulting solution was transferred via syringe to

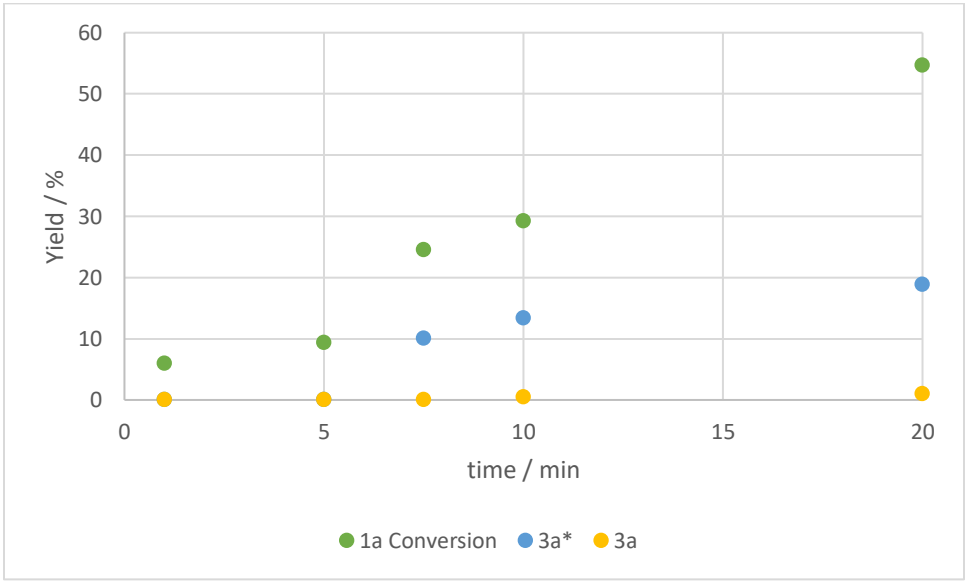
the vial with a stir bar (this process was repeated twice to end up with 2 mL of toluene in the reaction vessel). The vial was equipped with a Teflon-sealed cap and immediately stirred at 130 °C for 8 min. The reaction was passed through a pad of silica washing with ethyl acetate in a scintillation vial containing 8 mg of 1,3,5-trimethoxybenzene. The filtrate was concentrated under reduced pressure and dissolved in 2.0 mL of $CDCl_3$ before being analyzed by ^1H NMR spectroscopy, showing 31% conversion of combined **1a** and **1a-D$_5$**, <1% yield of combined **3a** and **3a-D$_4$** and 11% yield of combined **3a*** and **3a*-D$_4$**. The NMR samples were concentrated under reduced pressure, followed by purification by flash chromatography 5→30% EtOAc/pentanes to obtain a mixture of **3a*** and **3a*-D$_4$**.

$$Intermolecular\ KIE = \frac{k_{H\ product}}{k_{D\ product}} \div \frac{n_{ArI\ H5}}{n_{ArI\ D5}} = \frac{0.54}{0.46} \div \frac{0.52}{0.48} = 1.08$$

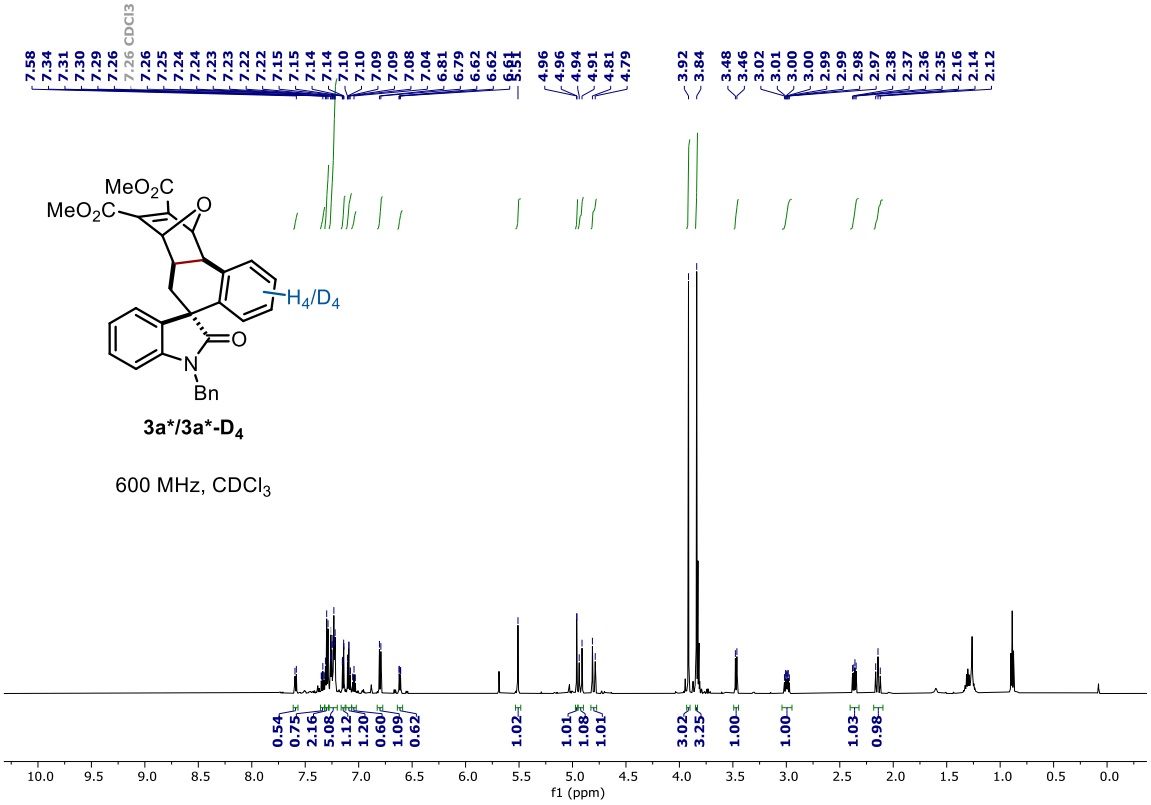
Time Study

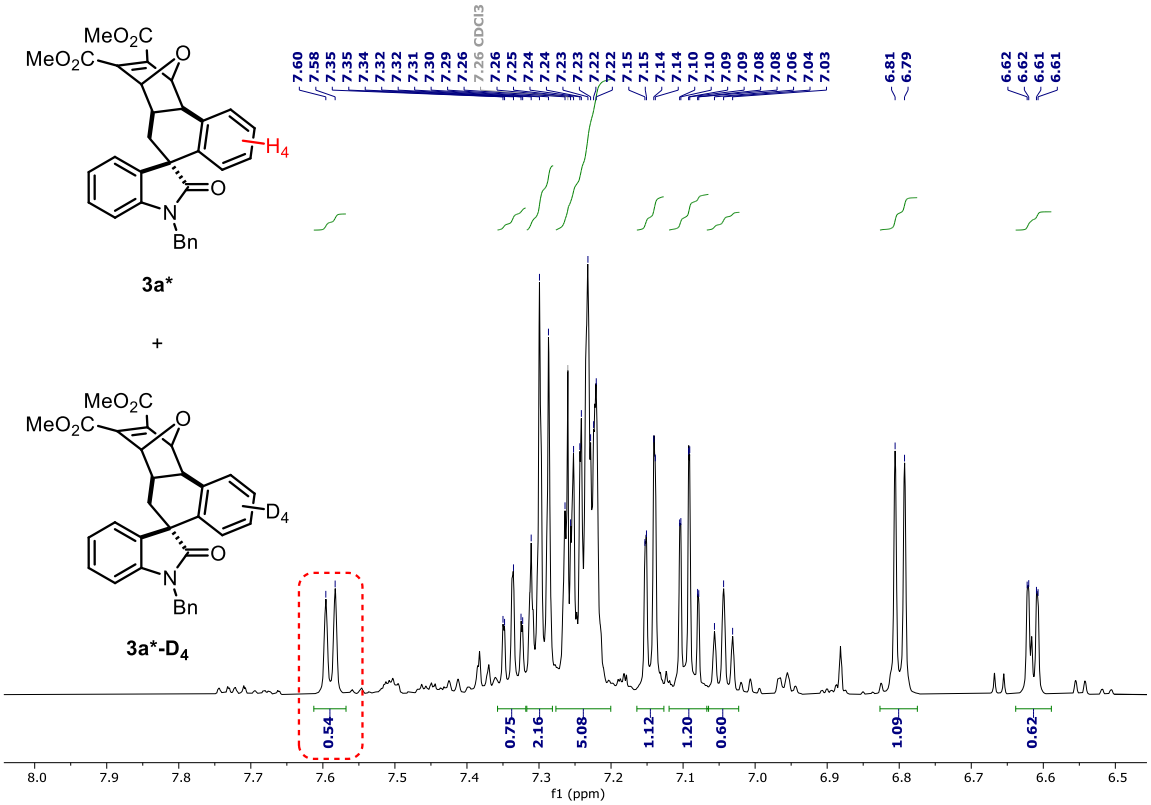


1a | **2** 1.2 equiv | **3a** | **3a***

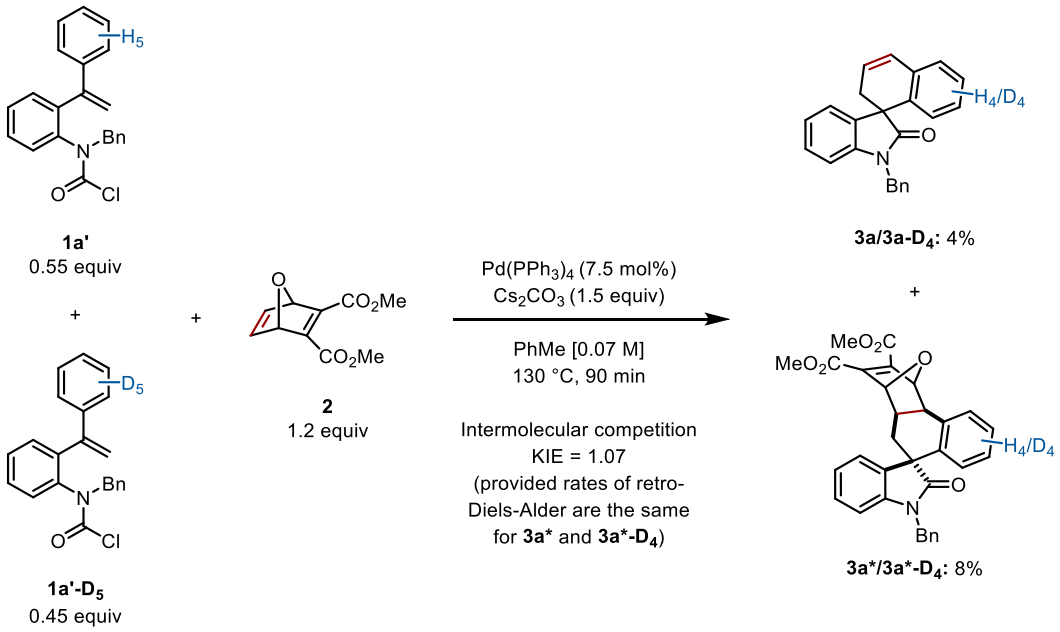


Reactions were run on 0.1 mmol scale; yields were determined by ^1H NMR spectroscopy analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.


MeO2C
MeO2C
O
H4/D4
O
N
Bn
3a*/3a*-D4
600 MHz, CDCl3
f1 (ppm)


MeO2C
MeO2C
O
H4
O
N
Bn
3a*
+
MeO2C
MeO2C
O
D4
O
N
Bn
3a*-D4
f1 (ppm)

KIE Experiment – Carbamoyl Chloride



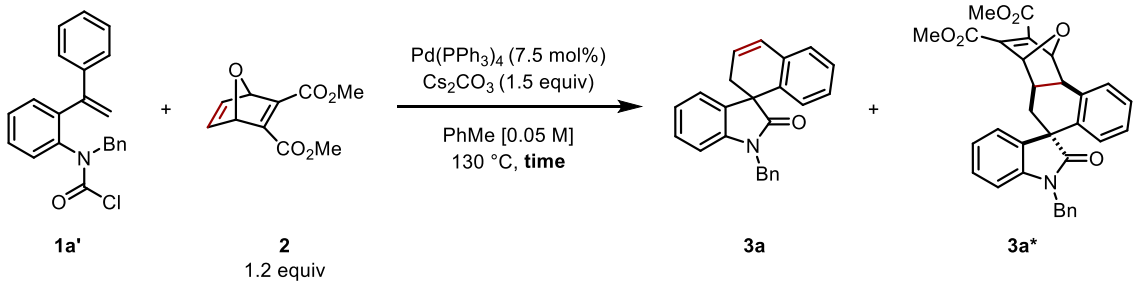
Reactions were run on 0.1 mmol scale; yields were determined by ^{1}H NMR spectroscopy analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

Vials and stir bars were dried in 110 °C oven overnight prior to use. Three 2 dr vials, one equipped with stir bar and two without were cooled to room temperature under argon flow. Benzyl(2-(1-phenylvinyl)phenyl)carbamic chloride **1a'** *N*-Benzyl-*N*-(2-iodophenyl)-2-(phenyl-d_5)acrylamide **1a-D5** and benzyl(2-(1-(phenyl-d_5)vinyl)phenyl)carbamic chloride **1a'-D5** were weighed with the objective of adding exactly 0.50 mmol, 17 mg, 0.50 equiv for the former and 0.50 mmol, 18 mg, 0.50 equiv for the latter to the vial without a stir bar. The mixture was dissolved in $CDCl_3$ (1.0 mL) and subjected to ^{1}H NMR spectroscopy, which revealed 0.55 mmol, 19 mg, 0.55 equiv of **1a** and 0.45 mmol, 16 mg, 0.45 equiv of **1a-D5** were present instead. The solution was concentrated under reduced pressure. The carbamoyl chlorides were washed with pentanes and concentrated under reduced pressure three times before being placed under vacuum and lyophilized three times to remove any trace of solvent. Cesium carbonate (49 mg, 0.15 mmol, 1.5 equiv), and tetrakis(triphenylphosphine)palladium(0) (9 mg, 0.0075 mmol, 7.5 mol%) were added in that order to the vial with a stir bar. Oxabicycle **2** (28 mg, 1.1·0.12 mmol = 0.132 mmol, 1.1·1.2 equiv = 1.32 equiv) was weighed in the empty vial. Freshly distilled toluene (1.1·0.50 mL = 0.55 mL) was added via syringe to the oxabicycle-containing vial and the vial was sonicated for 15 s to fully dissolve the oxabicycle. 0.5 mL of the resulting solution was transferred via syringe to the vial containing the carbamoyl chlorides to fully dissolve them. The resulting solution was transferred via syringe to the vial with a stir bar. Toluene (0.5 mL) was added via syringe to the previous vial to recover remaining quantities of substrates and the resulting solution was transferred via syringe to the vial with a stir bar (this process was repeated twice to end up with 2 mL of toluene in the

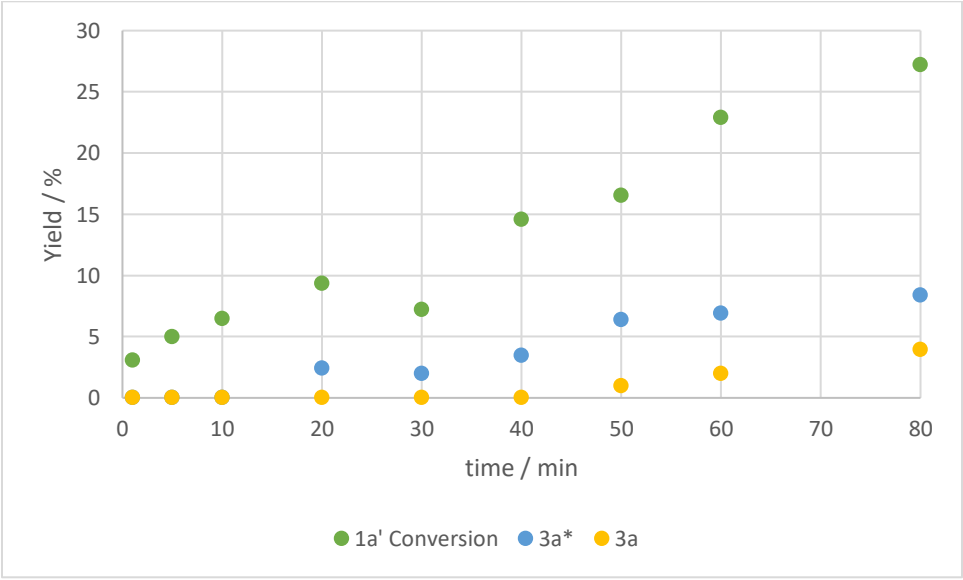
reaction vessel). The vial was equipped with a Teflon-sealed cap and immediately stirred at 130 °C for 90 min. The reaction was passed through a pad of silica washing with ethyl acetate in a scintillation vial containing 8 mg of 1,3,5-trimethoxybenzene. The filtrate was concentrated under reduced pressure and dissolved in 2.0 mL of $CDCl_3$ before being analyzed by ^1H NMR spectroscopy, showing 26% conversion of combined **1a** and **1a-D$_5$**, 4% yield of combined **3a** and **3a-D$_4$** and 8% yield of combined **3a*** and **3a*-D$_4$**. The NMR samples were concentrated under reduced pressure, followed by purification by flash chromatography 5→10% EtOAc/pentanes to obtain a mixture of **3a** and **3a-D$_4$** and 10→30% EtOAc/pentanes to obtain a mixture of **3a***and **3a*-D$_4$**.

$$Intermolecular\ KIE = \frac{k_{H\ product}}{k_{D\ product}} \div \frac{n_{CC\ H5}}{n_{CC\ D5}} = \frac{0.57}{0.43} \div \frac{0.55}{0.45} = 1.07$$

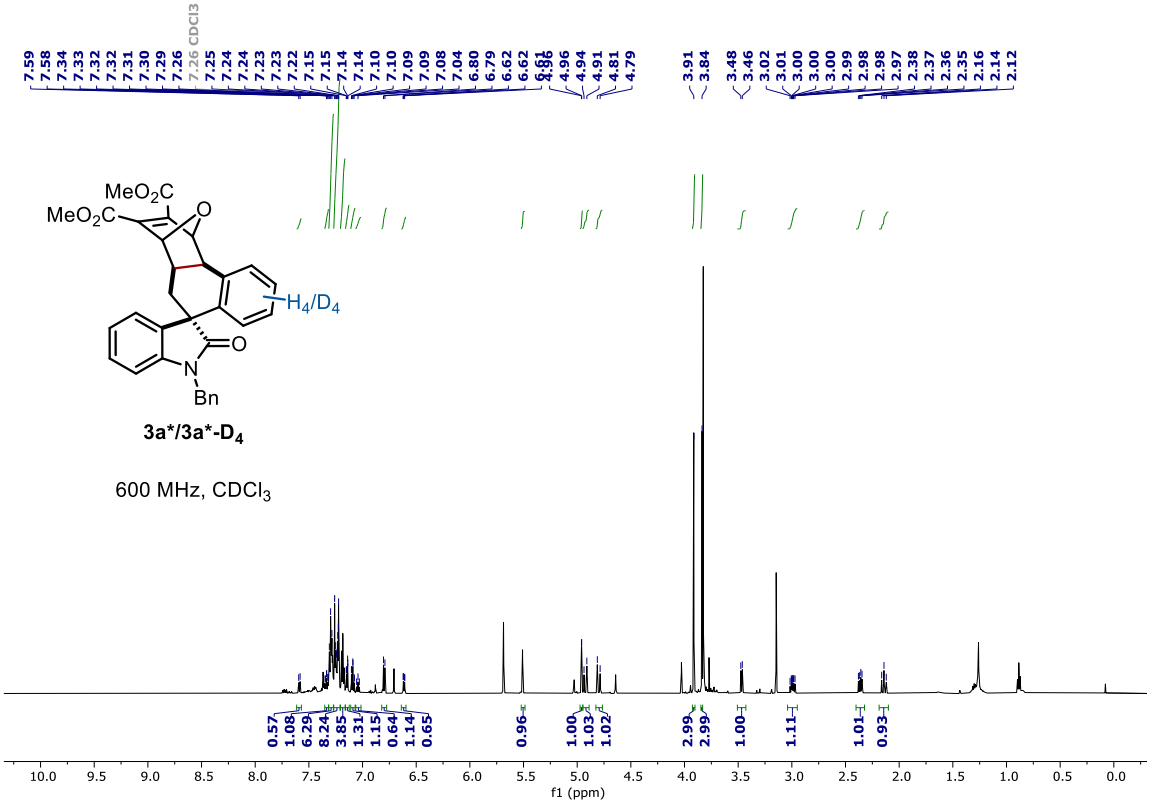
Time Study

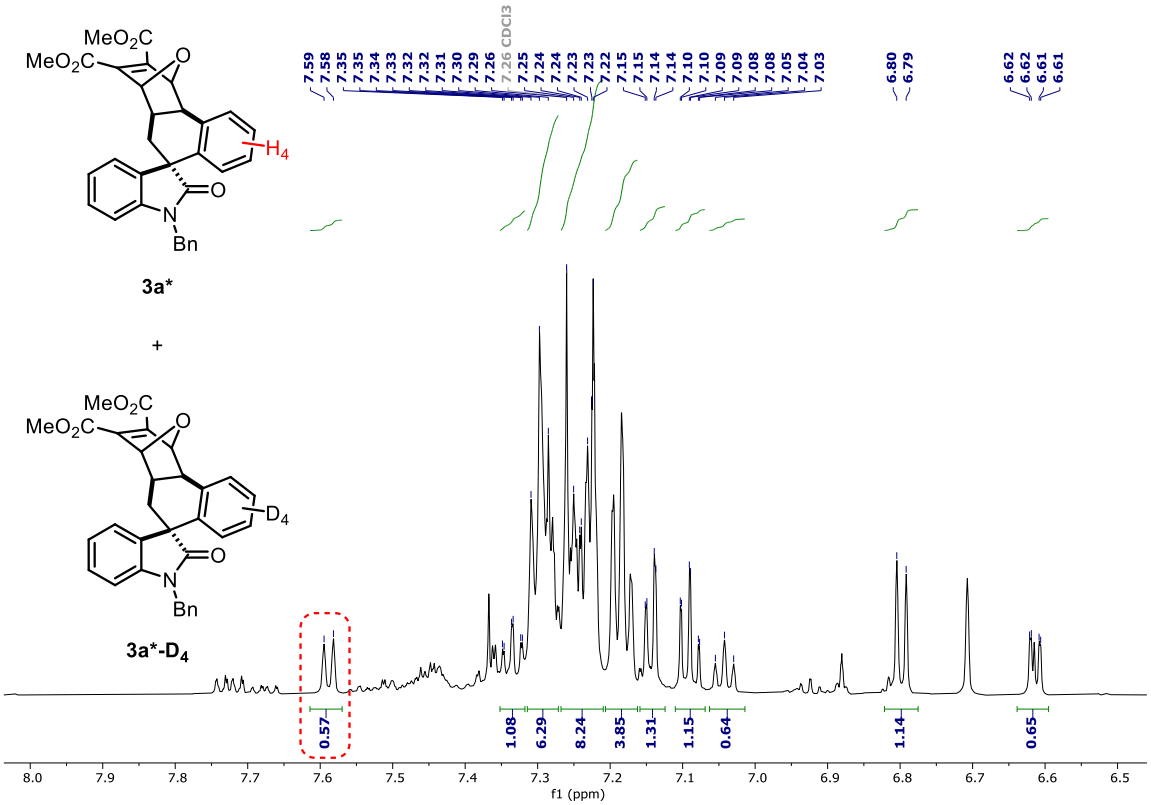


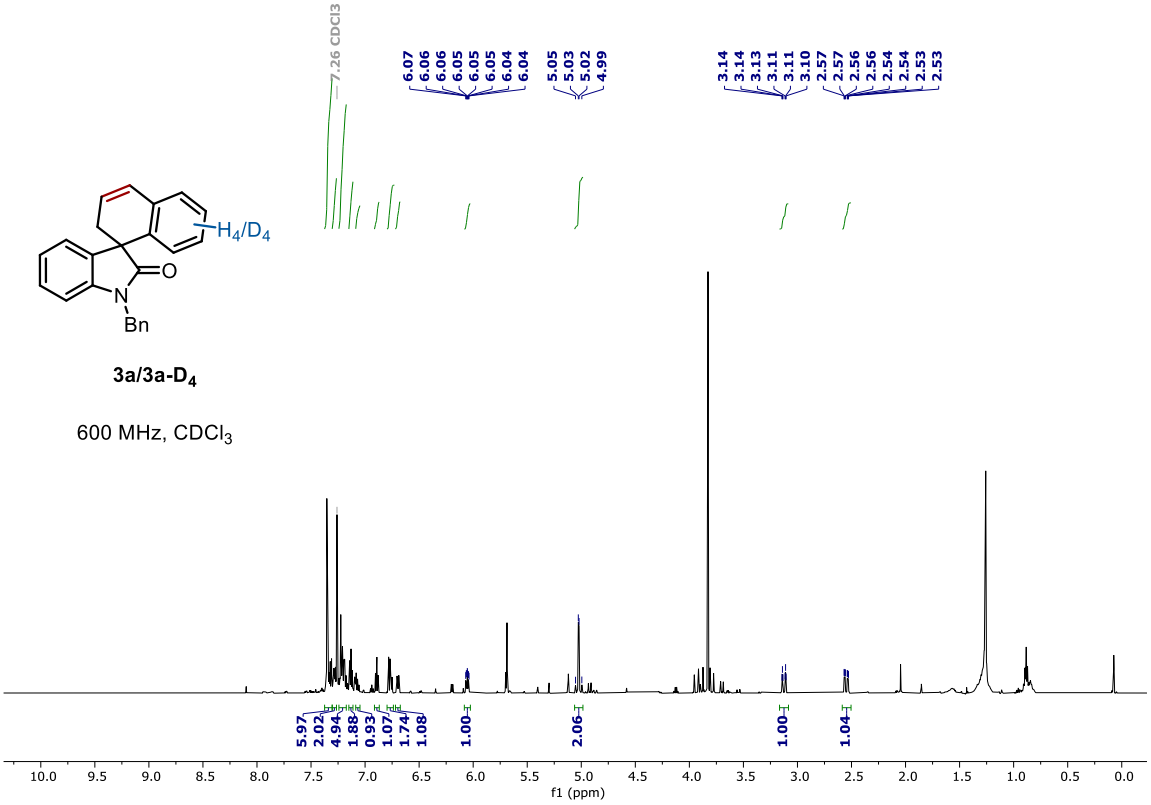
1a' **2** 1.2 equiv **3a** **3a***

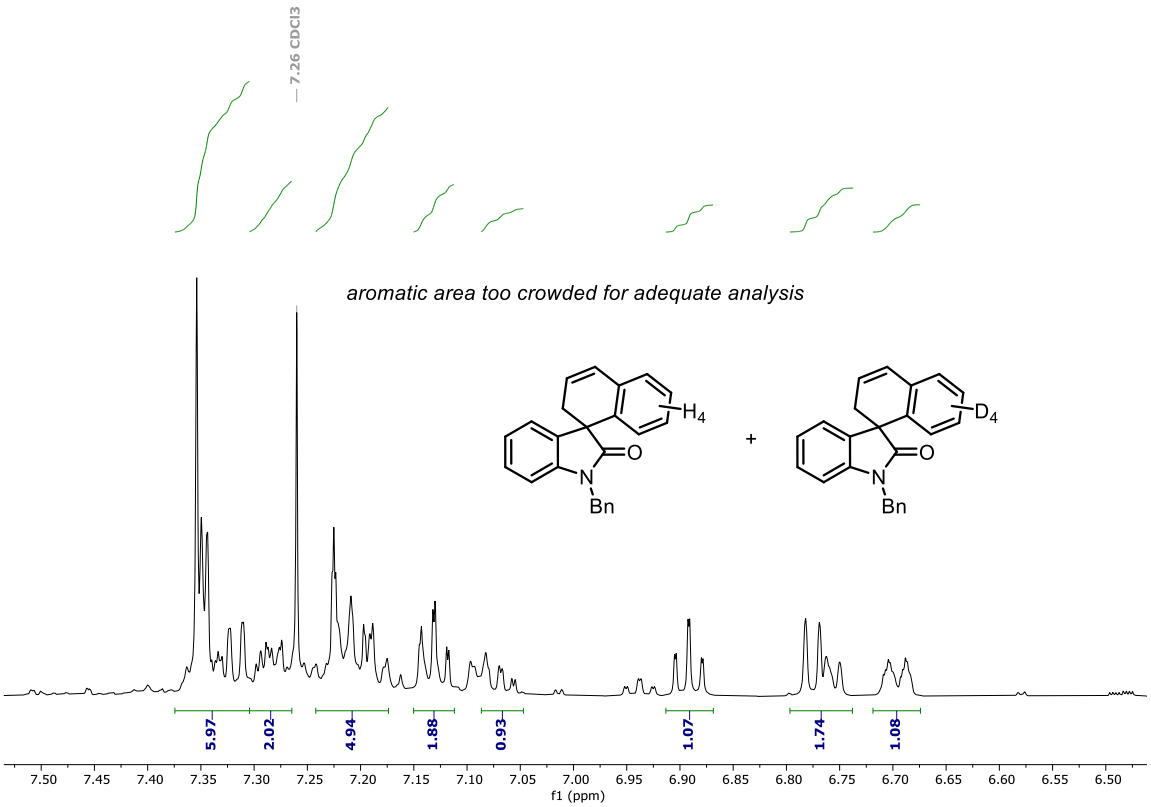


Reactions were run on 0.1 mmol scale; yields were determined by ^1H NMR spectroscopy analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.


MeO2C
MeO2C
O
H4/D4
O
N
Bn
3a*/3a*-D4
600 MHz, CDCl3
f1 (ppm)

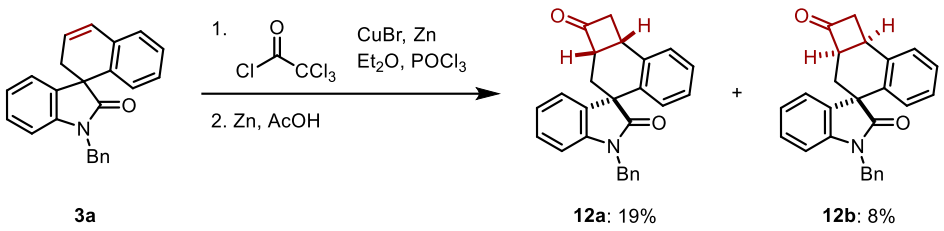

MeO2C
MeO2C
O
H4
O
N
Bn
3a*
+
MeO2C
MeO2C
O
D4
O
N
Bn
3a*-D4
f1 (ppm)


7.26 CDCl3
6.07 6.06 6.06 6.05 6.05 6.05 6.04 6.04
5.05 5.03 5.02 4.99
3.14 3.14 3.13 3.11 3.11 3.10
2.57 2.57 2.56 2.56 2.54 2.54 2.53 2.53
H4/D4
O
N
Bn
3a/3a-D4
600 MHz, CDCl3
5.97 2.02 4.94 1.88 0.93 1.07 1.74 1.08 1.00 2.06 1.00 1.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


7.26 CDCl3
aromatic area too crowded for adequate analysis
H4
D4
+
O
N
Bn
5.97 2.02 4.94 1.88 0.93 1.07 1.74 1.08
7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75 6.70 6.65 6.60 6.55 6.50
f1 (ppm)

Product Derivatizations

Ketene [2+2] Cycloaddition then Dehalogenation

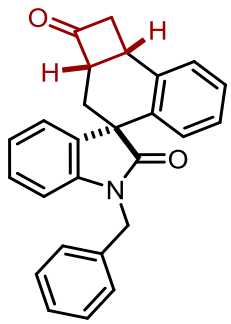


3a **12a**: 19% **12b**: 8%

Synthesized based on a known literature procedure.[13] Vial and stir bar were dried in 110 °C oven overnight prior to use. A 2 dr vial with stir bar was cooled to room temperature under argon flow. Copper(I) bromide (129 mg, 0.90 mmol, 6.0 equiv) and zinc (59 mg, 0.90 mmol, 6.0 equiv) were added to the vial. Diethyl ether (1.5 mL) was added to the vial via syringe and the resulting mixture was refluxed for 2 h. The heterogeneous mixture was then cooled to room temperature and **3a** (51 mg, 0.15 mmol, 1.0 equiv), freshly distilled trichloroacetyl chloride (67 µL, 0.60 mmol, 4.0 equiv), and $POCl_3$ (31 µL, 0.33 mmol, 2.2 equiv) were added to the vial. The reaction was then flushed with argon and stirred vigorously under reflux for 18 h. The reaction mixture was then cooled to room temperature and filtered over celite washing with ethyl acetate. The filtrate was concentrated under reduced pressure and the resulting crude mixture was dissolved in acetic acid (1.5 mL). Zinc (98 mg, 1.50 mmol, 10.0 equiv) was added to the solution and the mixture was stirred vigorously for 24 h. The solution was then filtered over a cotton plug washing with ethyl acetate. The resulting solution was then washed three times with sat. $NaHCO_3$ (aq), water and then brine. The organic layer was dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude mixture was purified by flash chromatography 5→30% EtOAc/pentanes. Obtained 11 mg of a white solid (**12a**, 19%) and 4 mg of a white solid (**12b**, 8%), i.e., 27% combined yield.

We thank Dr Andrei Kutateladze (University of Denver) for proposing the regioisomers **12a** and **12b**, using a machine learning-augmented DFT method, DU8ML, developed in his laboratory, which we confirmed using H2BC NMR spectroscopy.

(2a*S*,4*S*,8b*S*)-1'-Benzyl-1,2a,3,8b-tetrahydro-2*H*-spiro[cyclobuta[*a*]naphthalene-4,3'-indoline]-2,2'-dione [and enantiomer] (12a)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, J = 7.7 Hz, 1H), 7.35 – 7.19 (m, 7H), 7.14 (ddd, J = 7.4, 1.6, 0.6 Hz, 1H), 7.10 (ddd, J = 7.4, 7.4, 1.0 Hz, 1H), 7.08 – 7.04 (m, 1H), 6.81 (d, J = 7.9 Hz, 1H), 6.65 (dd, J = 7.9, 1.3 Hz, 1H), 4.89, 4.85 (ABq, J = 15.7 Hz, 2H), 4.27 – 4.18 (m, 1H), 4.14 (ddd, J = 9.9, 9.8, 6.3 Hz, 1H), 3.77 (ddd, J = 17.8, 9.9, 4.2 Hz, 1H), 3.29 (ddd, J = 17.8, 6.3, 2.9 Hz, 1H), 2.32 (dd, J = 13.9, 11.2 Hz, 1H), 2.21 (dd, J = 13.9, 9.5 Hz, 1H).

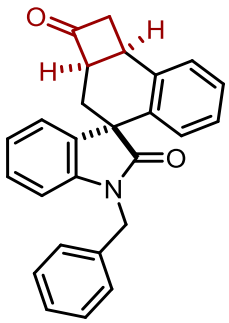
^{13}C NMR (126 MHz, $CDCl_3$) δ 210.4, 177.6, 143.1, 139.2, 136.6, 135.9, 132.8, 129.4, 129.0, 128.7, 128.6, 127.8, 127.1, 126.6, 126.5, 124.4, 123.3, 109.5, 54.4, 53.2, 51.4, 43.7, 30.9, 26.4.

IR (ATR) 3028, 2923, 2854, 1774, 1703, 1610, 1348, 1167, 747, 696.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{26}H_{22}NO_2$ 380.1645; Found 380.1643.

MP 83-86 °C

(2a*R*,4*S*,8b*R*)-1'-Benzyl-1,2a,3,8b-tetrahydro-2*H*-spiro[cyclobuta[*a*]naphthalene-4,3'-indoline]-2,2'-dione [and enantiomer] (12b)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 7H), 7.18 (ddd, J = 7.8, 7.6, 1.5 Hz, 1H), 7.13 – 7.09 (m, 1H), 7.02 (ddd, J = 7.5, 1.5, 0.6 Hz, 1H), 6.98 (ddd, J = 7.6, 7.5, 1.0 Hz, 1H), 6.81 (d, J = 7.8 Hz, 1H), 6.76 (dd, J = 7.9, 1.3 Hz, 1H), 4.99, 4.97 (ABq, J = 15.6 Hz, 2H), 3.96 (ddd, J = 9.5, 9.4, 6.6 Hz, 1H), 3.89 – 3.80 (m, 1H), 3.72 (ddd, J = 17.8, 9.5, 4.2 Hz, 1H), 3.55 (ddd, J = 17.8, 6.6, 2.9 Hz, 1H), 2.48 (dd, J = 14.0, 8.1 Hz, 1H), 2.15 (dd, J = 14.0, 8.4 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 208.4, 178.9, 142.3, 138.1, 135.9, 135.7, 133.7, 129.6, 129.0, 128.5, 128.4, 127.9, 127.4, 127.2, 127.2, 124.2, 123.0, 109.7, 55.0, 54.5, 51.9, 44.0, 31.0, 26.4.

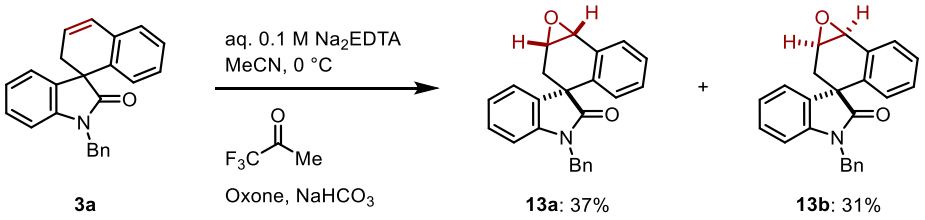
IR (ATR) 3710, 2921, 2850, 1777, 1705, 1608, 1346, 1032, 1014, 750.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{26}H_{22}NO_2$ 380.1645; Found 380.1647.

MP 62-65 °C

Surendra, K.; Rajendar, G.; Corey, E. J. Useful Catalytic Enantioselective Cationic Double Annulation Reactions Initiated at an Internal π-Bond: Method and Applications. *J. Am. Chem. Soc.* **2014,** *136*, 642−645.[12]

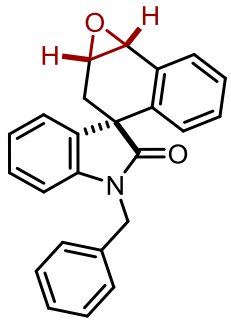
Epoxidation



Synthesized based on a known literature procedure.[14] **3a** (51 mg, 1.5 mmol, 1.0 equiv) was added to a 2 dr vial with stir bar, followed by acetonitrile (1.13 mL) and aqueous 0.1 M Na_2EDTA

(750µL, 0.075 mmol, 0.5 equiv) via syringe. The solution was stirred and cooled to 0°C. Trifluoroacetone (0.15mL, 1.68 mmol, 11.2 equiv) was added dropwise to the vial via syringe. A mixture of solid Oxone® (114.2mg, 0.75 mmol, 5.0 equiv) and sodium bicarbonate (97.5 mg, 1.16 mmol, 7.7 equiv) was added portionwise to the vial over an hour (10 roughly even portions) at 0°C. The solution was stirred at 0°C for 8 h before being brought to room temperature and quenched with EtOAc. The phases were separated and the aqueous phase was extracted with EtOAc twice. The combined organic phases were washed with saturated sodium thiosulfate followed by brine, dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude mixture was purified by flash chromatography 5→20% EtOAc/pentanes. Obtained 20 mg of a white solid (**13a**, 37%) and 16 mg of a white solid (**13b**, 31%), i.e., 68% combined yield (97% combined yield based on recovered starting material **3a**: 15 mg).

(1a'*S*,3*S*,7b'*R*)-1-Benzyl-1a',7b'-dihydro-2'*H*-spiro[indoline-3,3'-naphtho[1,2-*b*]oxiren]-2-one [and enantiomer] (13a)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, J = 7.6, 1.3 Hz, 1H), 7.54 (dd, J = 7.5, 1.5 Hz, 1H), 7.42 – 7.35 (m, 4H), 7.33 – 7.29 (m, 1H), 7.25 (ddd, J = 7.5, 7.5, 1.3 Hz, 1H), 7.20 (ddd, J = 7.6, 7.5, 1.5 Hz, 1H), 7.13 (ddd, J = 7.7, 7.7, 1.3 Hz, 1H), 6.97 (ddd, J = 7.7, 7.6, 1.1 Hz, 1H), 6.83 (d, J = 7.7 Hz, 1H), 6.75 (ddd, J = 7.6, 1.2, 0.5 Hz, 1H), 5.06 (s, 2H), 4.08 (d, J = 4.2 Hz, 1H), 3.89 (ddd, J = 4.2, 2.5, 1.7 Hz, 1H), 2.73 (dd, J = 15.1, 1.7 Hz, 1H), 2.45 (dd, J = 15.1, 2.5 Hz, 1H).

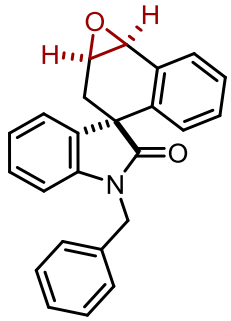
^{13}C NMR (126 MHz, $CDCl_3$) δ 180.0, 141.9, 136.2, 136.0, 135.3, 132.9, 130.8, 129.8, 129.0, 127.9, 127.8, 127.6, 127.6, 127.6, 127.3, 123.3, 109.3, 53.6, 52.7, 51.7, 44.3, 32.5.

IR (ATR) 3025, 2923, 2851, 1705, 1606, 1465, 1346, 1167, 750, 694.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{24}H_{20}NO_2$ 354.1489; Found 354.1488

MP 61-65 °C

(1a'*R*,3*S*,7b'*S*)-1-Benzyl-1a',7b'-dihydro-2'*H*-spiro[indoline-3,3'-naphtho[1,2-*b*]oxiren]-2-one [and enantiomer] (13b)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (dd, J = 7.4, 1.5 Hz, 1H), 7.35 – 7.31 (m, 4H), 7.30 – 7.26 (m, 2H), 7.21 – 7.15 (m, 2H), 7.08 (ddd, J = 7.5, 1.3, 0.6 Hz, 1H), 6.99 (ddd, J = 7.6, 7.5, 1.0 Hz, 1H), 6.80 (d, J = 7.7 Hz, 1H), 6.68 (ddd, J = 7.9, 1.3, 0.6 Hz, 1H), 5.03 (d, J = 15.5 Hz, 1H), 4.92 (d, J = 15.5 Hz, 1H), 4.09 (d, J = 4.1 Hz, 1H), 3.82 (ddd, J = 4.1, 4.1, 2.3 Hz, 1H), 2.73 (dd, J = 15.3, 2.3 Hz, 1H), 2.39 (dd, J = 15.3, 4.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.1, 142.0, 136.1, 136.0, 135.1, 133.1, 131.5, 129.7, 128.9, 128.5, 127.9, 127.8, 127.6, 127.3, 123.9, 123.2, 109.4, 51.7, 51.2, 51.1, 44.1, 34.1.

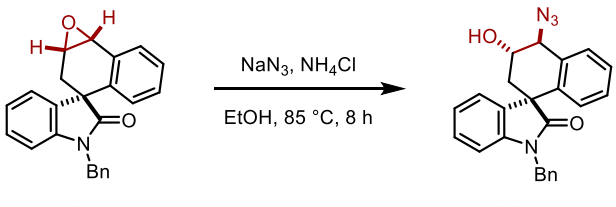
IR (ATR) 3030, 2921, 2851, 1707, 1608, 1485, 1464, 1343, 1166, 750.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{24}H_{20}NO_2$ 354.1489; Found 354.1485

MP 50-54 °C

Yang, D.; Wong, M.-K.; Yip, Y.-C. Epoxidation of Olefins Using Methyl(trifluoromethyl)dioxirane Generated in Situ. *J. Org. Chem.* **1995,** *60,* 3887–3889.[13]

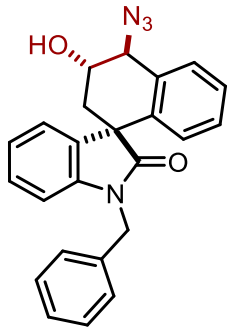
Epoxide Ring Opening with Sodium Azide



13a **14**: 70%

13a (10 mg, 0.029 mmol, 1.0 equiv) was added to a 2 dr vial with stir bar, followed by ethanol (0.30 mL) via syringe. Sodium azide (4 mg, 0.058 mmol) and ammonium chloride (4 mg, 0.072 mmol) were added to the vial and the reaction mixture was stirred at 85°C for 6 h. The resulting solution was diluted with EtOAc and washed with water twice. The organic layer was then dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude mixture was purified via filtration through a pad of silica washing with ethyl acetate, followed by concentration of the filtrate under reduced pressure. Obtained 8 mg of a white solid (70% yield).

(3*S*,3'*S*,4'*S*)-4'-Azido-1-benzyl-3'-hydroxy-3',4'-dihydro-2'*H*-spiro[indoline-3,1'-naphthalen]-2-one [and enantiomer] (14)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 7.9 Hz, 1H), 7.35 – 7.27 (m, 6H), 7.23 (ddd, J = 7.9, 6.1, 2.9 Hz, 1H), 7.12 – 7.07 (m, 1H), 7.06 – 7.01 (m, 2H), 6.84 (d, J = 7.9 Hz, 1H), 6.45 (dd, J = 7.9, 1.3 Hz, 1H), 5.09 – 5.01 (m, 1H), 5.00 (d, J = 15.5 Hz, 2H), 4.85 (d, J = 15.5 Hz, 1H), 4.56 (d, J = 8.8 Hz, 1H), 2.90 (br s, 1H), 2.36 – 2.31 (m, 2H).

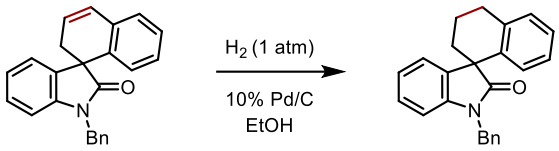
^{13}C NMR (126 MHz, $CDCl_3$) δ 178.9, 142.8, 135.9, 135.2, 135.1, 135.1, 129.0, 128.7, 128.6, 128.5, 128.4, 127.9, 127.7, 127.5, 124.1, 123.6, 109.4, 67.4, 67.1, 52.9, 44.0, 39.5.

IR (ATR) 3411, 2922, 2852, 2098, 1699, 1610, 1465, 1345, 1028, 743.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{24}H_{21}N_4O_2$ 397.1659; Found 397.1662

MP 60-64 °C

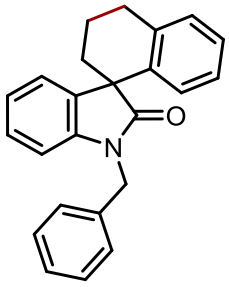
Hydrogenation



3a **15**: 79%

Vial and stir bar were dried in 110 °C oven overnight prior to use. A 2 dr vial with stir bar was cooled to room temperature under argon flow. **3a** (51 mg, 1.5 mmol, 1.0 equiv) was added to the vial. Ethanol (1.5 mL) was added via syringe to the vial and the resulting solution was sparged with H_2 gas (1 atm) using a balloon for 10 min. 10% Pd/C (10 mg) was subsequently added and the resulting reaction mixture was stirred at room temperature for 16 h. The reaction was passed through a pad of celite washing with ethanol. The filtrate was concentrated under reduced pressure and the resulting residue purified by flash chromatography 5→10% EtOAc/pentanes. Obtained 40 mg of a white solid (79% yield).

1-Benzyl-3',4'-dihydro-2'*H*-spiro[indoline-3,1'-naphthalen]-2-one (15)



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 4H), 7.31 – 7.27 (m, 1H), 7.24 – 7.12 (m, 3H), 7.07 (dd, J = 7.5, 0.9 Hz, 1H), 7.03 – 6.94 (m, 2H), 6.82 (d, J = 7.8 Hz, 1H), 6.52 (dd, J = 7.8, 1.3 Hz, 1H), 5.01, 4.97 (ABq, J = 15.6 Hz, 2H), 3.11 – 2.95 (m, 2H), 2.51 – 2.39 (m, 1H), 2.34 – 2.24 (m, 1H), 2.11 – 2.00 (m, 2H).

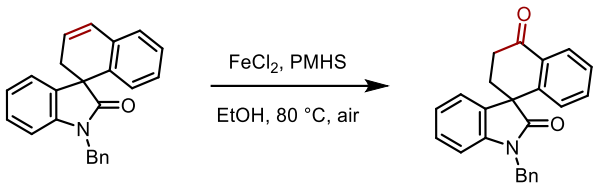
^{13}C NMR (126 MHz, $CDCl_3$) δ 180.6, 142.3, 138.0, 137.4, 136.3, 135.3, 129.8, 128.9, 128.1, 127.9, 127.7, 127.5, 127.2, 126.5, 124.2, 122.9, 109.2, 52.2, 43.9, 34.4, 29.4, 18.9.

IR (ATR) 3021, 2919, 2859, 1709, 1603, 1462, 1342, 1175, 954, 737.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{24}H_{22}NO$ 340.1696; Found 340.1701

MP 41-45 °C

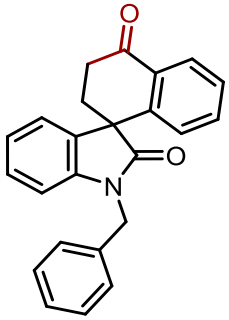
Iron-Catalyzed Wacker Oxidation



3a **16:** 58%

Synthesized based on a known literature procedure.[15] **3a** (51 mg, 1.5 mmol, 1.0 equiv) was added to a 2 dr vial with stir bar, followed by anhydrous ethanol (666 µL) via syringe. Iron(II) chloride (2 mg, 0.015 mmol, 0.1 equiv) and polymethylhydrosiloxane (102 µL, 0.45 mmol, 3.0 equiv) were added to the vial. The reaction was stirred at 80 °C for 14 h open to air. The reaction was passed through a pad of silica washing with ethyl acetate. The filtrate was concentrated under reduced pressure and the resulting residue purified by flash chromatography 5→25% EtOAc/pentanes. The resulting foam was then triturated with pentanes. Obtained 31 mg of a white solid (58% yield).

1-Benzyl-2',3'-dihydro-4'*H*-spiro[indoline-3,1'-naphthalene]-2,4'-dione (16)



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 – 8.17 (m, 1H), 7.43 – 7.37 (m, 2H), 7.36 – 7.28 (m, 5H), 7.27 – 7.23 (m, 1H), 7.09 (ddd, J = 7.4, 1.6, 0.6 Hz, 1H), 7.05 (ddd, J = 7.4, 7.4, 1.0 Hz, 1H), 6.86 (d, J = 7.8 Hz, 1H), 6.72 – 6.66 (m, 1H), 4.98, 4.95 (ABq, J = 15.6 Hz, 2H), 3.50 (ddd, J = 17.6, 10.8, 5.9 Hz, 1H), 2.84 (ddd, J = 17.6, 5.9, 5.0 Hz, 1H), 2.59 – 2.45 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 177.7, 142.7, 142.4, 135.9, 134.1, 133.7, 133.2, 129.0, 128.8, 128.3, 128.1, 127.9, 127.4, 127.4, 124.2, 123.3, 109.7, 51.7, 44.0, 33.6, 32.9.

IR (ATR) 3058, 3028, 2918, 2859, 1705, 1682, 1596, 1465, 1341, 749.

HRMS (DART) m/z: [M + H]+ Calcd for $C_{24}H_{20}NO_2$ 354.1489; Found 354.1493

MP 48-52 °C

Liu, B.; Jin, F.; Wang, T.; Yuan, X.; Han, W. Wacker-Type Oxidation Using an Iron Catalyst and Ambient Air: Application to Late-Stage Oxidation of Complex Molecules. *Angew. Chem. Int. Ed.* **2017,** *56,* 12712–12717.[14]

Single Crystal X-Rays

Spirooxindole (After the Retro-Diels-Alder Step)

The sample was prepared by dissolving **3i** in a minimum amount of DCM, then recrystallizing from pentanes. Data were collected on a Bruker Kappa APEX-DUO diffractometer using CuKα radiation from an Incoatec IμS source with multi-layer optics and a PHOTON II CMOS detector and were measured using a combination of ϕ scans and ω scans. The data were processed using APEX3 and SAINT (Bruker, 2019). Absorption corrections were carried out using SADABS (Bruker, 2019). The structures were solved with SHELXT (Sheldrick, 2015a) and refined using SHELXL-2018 (Sheldrick, 2015b) for full-matrix least-squares refinement that was based on F^2. H atoms were included in calculated positions and allowed to refine in riding-motion approximation with U~iso~ tied to the carrier atom.

Bruker (2007). APEX2, SAINT & SADABS Bruker AXS Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (2015a). Acta Cryst. A71, 3-8.

Sheldrick, G. M. (2015b). Acta Cryst. C71, 3-8.

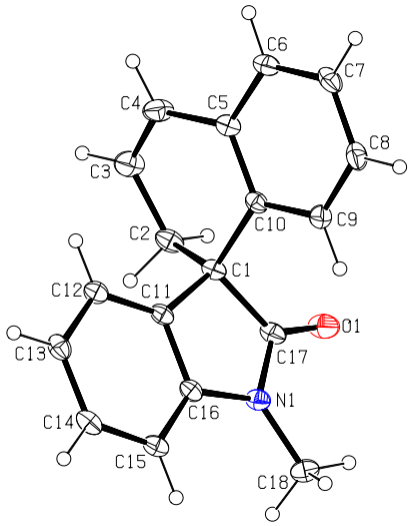


*Figure S1. The molecular structure of compound **3i**. The displacement ellipsoids are drawn the 30% probability level.*

Table 1. Crystal data and structure refinement for d2224_a.

Identification code	d2224_a
Empirical formula	C18 H15 N O
Formula weight	261.31

Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 13.3846(8) Å	□= 90°.
	b = 6.8793(4) Å	□= 103.033(3)°.
	c = 14.7878(8) Å	□ = 90°.
Volume	1326.54(13) $Å^3$	
Z	4	
Density (calculated)	1.308 Mg/m^3	
Absorption coefficient	0.635 mm^{-1}	
F(000)	552	
Crystal size	0.210 x 0.200 x 0.140 mm^3	
Theta range for data collection	4.027 to 66.431°.	
Index ranges	-15<=h<=15, -8<=k<=8, -17<=l<=17	
Reflections collected	27011	
Independent reflections	2284 [R(int) = 0.0418]	
Completeness to theta = 66.431°	97.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.6950	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2284 / 0 / 182	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0346, wR2 = 0.0881	
R indices (all data)	R1 = 0.0384, wR2 = 0.0900	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.170 and -0.158 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for d2224_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	4761(1)	6526(2)	8960(1)	40(1)
N(1)	5814(1)	4606(2)	8308(1)	26(1)
C(1)	4855(1)	6986(2)	7331(1)	24(1)
C(2)	5071(1)	9191(2)	7432(1)	31(1)
C(3)	4563(1)	10334(2)	6594(1)	38(1)
C(4)	3677(1)	9762(2)	6062(1)	38(1)
C(5)	3182(1)	7948(2)	6236(1)	26(1)
C(6)	2169(1)	7529(2)	5787(1)	30(1)
C(7)	1722(1)	5771(2)	5916(1)	32(1)
C(8)	2280(1)	4397(2)	6504(1)	33(1)
C(9)	3278(1)	4811(2)	6976(1)	28(1)
C(10)	3735(1)	6571(2)	6851(1)	23(1)
C(11)	5586(1)	5924(2)	6852(1)	23(1)
C(12)	5775(1)	6128(2)	5980(1)	27(1)
C(13)	6509(1)	4934(2)	5724(1)	29(1)
C(14)	7036(1)	3564(2)	6338(1)	29(1)
C(15)	6859(1)	3341(2)	7225(1)	27(1)
C(16)	6126(1)	4538(2)	7462(1)	24(1)
C(17)	5111(1)	6056(2)	8304(1)	28(1)
C(18)	6193(1)	3322(2)	9090(1)	32(1)

Table 3. Bond lengths [Å] and angles [°] for d2224_a.

O(1)-C(17)	1.2125(15)
N(1)-C(17)	1.3710(16)
N(1)-C(16)	1.4054(16)
N(1)-C(18)	1.4520(16)
C(1)-C(11)	1.5180(16)
C(1)-C(10)	1.5336(16)
C(1)-C(17)	1.5406(17)
C(1)-C(2)	1.5451(18)
C(2)-C(3)	1.4948(19)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(4)	1.3260(19)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.4632(19)
C(4)-H(4A)	0.9500
C(5)-C(6)	1.3984(17)
C(5)-C(10)	1.4034(17)
C(6)-C(7)	1.3809(19)
C(6)-H(6A)	0.9500
C(7)-C(8)	1.3830(19)
C(7)-H(7A)	0.9500
C(8)-C(9)	1.3909(18)
C(8)-H(8A)	0.9500
C(9)-C(10)	1.3881(18)
C(9)-H(9A)	0.9500
C(11)-C(12)	1.3765(18)
C(11)-C(16)	1.3971(17)
C(12)-C(13)	1.3970(18)
C(12)-H(12A)	0.9500
C(13)-C(14)	1.3862(19)
C(13)-H(13A)	0.9500
C(14)-C(15)	1.3925(18)
C(14)-H(14A)	0.9500
C(15)-C(16)	1.3853(17)
C(15)-H(15A)	0.9500
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800

C(17)-N(1)-C(16)	111.20(10)
C(17)-N(1)-C(18)	124.21(11)
C(16)-N(1)-C(18)	124.59(10)
C(11)-C(1)-C(10)	111.07(9)
C(11)-C(1)-C(17)	101.81(9)
C(10)-C(1)-C(17)	110.07(10)
C(11)-C(1)-C(2)	113.04(10)
C(10)-C(1)-C(2)	111.66(10)

C(17)-C(1)-C(2)	108.70(10)
C(3)-C(2)-C(1)	113.36(10)
C(3)-C(2)-H(2A)	108.9
C(1)-C(2)-H(2A)	108.9
C(3)-C(2)-H(2B)	108.9
C(1)-C(2)-H(2B)	108.9
H(2A)-C(2)-H(2B)	107.7
C(4)-C(3)-C(2)	120.93(13)
C(4)-C(3)-H(3A)	119.5
C(2)-C(3)-H(3A)	119.5
C(3)-C(4)-C(5)	121.95(13)
C(3)-C(4)-H(4A)	119.0
C(5)-C(4)-H(4A)	119.0
C(6)-C(5)-C(10)	118.83(12)
C(6)-C(5)-C(4)	121.48(11)
C(10)-C(5)-C(4)	119.68(11)
C(7)-C(6)-C(5)	121.21(12)
C(7)-C(6)-H(6A)	119.4
C(5)-C(6)-H(6A)	119.4
C(6)-C(7)-C(8)	119.76(11)
C(6)-C(7)-H(7A)	120.1
C(8)-C(7)-H(7A)	120.1
C(7)-C(8)-C(9)	119.81(12)
C(7)-C(8)-H(8A)	120.1
C(9)-C(8)-H(8A)	120.1
C(10)-C(9)-C(8)	120.90(12)
C(10)-C(9)-H(9A)	119.5
C(8)-C(9)-H(9A)	119.5
C(9)-C(10)-C(5)	119.43(11)
C(9)-C(10)-C(1)	120.96(11)
C(5)-C(10)-C(1)	119.52(11)
C(12)-C(11)-C(16)	119.83(11)
C(12)-C(11)-C(1)	131.42(11)
C(16)-C(11)-C(1)	108.76(10)
C(11)-C(12)-C(13)	118.85(12)
C(11)-C(12)-H(12A)	120.6
C(13)-C(12)-H(12A)	120.6
C(14)-C(13)-C(12)	120.53(12)
C(14)-C(13)-H(13A)	119.7
C(12)-C(13)-H(13A)	119.7
C(13)-C(14)-C(15)	121.46(11)
C(13)-C(14)-H(14A)	119.3
C(15)-C(14)-H(14A)	119.3
C(16)-C(15)-C(14)	117.00(11)
C(16)-C(15)-H(15A)	121.5
C(14)-C(15)-H(15A)	121.5
C(15)-C(16)-C(11)	122.33(11)
C(15)-C(16)-N(1)	127.94(11)
C(11)-C(16)-N(1)	109.72(10)

O(1)-C(17)-N(1)	125.36(12)
O(1)-C(17)-C(1)	126.32(11)
N(1)-C(17)-C(1)	108.31(10)
N(1)-C(18)-H(18A)	109.5
N(1)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
N(1)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for d2224_a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	39(1)	53(1)	26(1)	-3(1)	6(1)	17(1)
N(1)	24(1)	29(1)	24(1)	-2(1)	2(1)	3(1)
C(1)	20(1)	27(1)	26(1)	-4(1)	2(1)	3(1)
C(2)	23(1)	30(1)	37(1)	-10(1)	2(1)	1(1)
C(3)	34(1)	23(1)	54(1)	-1(1)	2(1)	-2(1)
C(4)	33(1)	28(1)	46(1)	4(1)	-3(1)	2(1)
C(5)	23(1)	26(1)	28(1)	-4(1)	3(1)	2(1)
C(6)	23(1)	36(1)	29(1)	-2(1)	1(1)	5(1)
C(7)	19(1)	47(1)	31(1)	-6(1)	5(1)	-4(1)
C(8)	28(1)	39(1)	35(1)	0(1)	11(1)	-9(1)
C(9)	26(1)	33(1)	26(1)	2(1)	7(1)	0(1)
C(10)	20(1)	28(1)	22(1)	-5(1)	5(1)	1(1)
C(11)	16(1)	24(1)	28(1)	-5(1)	1(1)	-3(1)
C(12)	22(1)	29(1)	28(1)	-3(1)	2(1)	-2(1)
C(13)	23(1)	37(1)	28(1)	-7(1)	6(1)	-4(1)
C(14)	21(1)	32(1)	36(1)	-10(1)	6(1)	0(1)
C(15)	20(1)	26(1)	32(1)	-5(1)	2(1)	1(1)
C(16)	18(1)	25(1)	26(1)	-6(1)	2(1)	-4(1)
C(17)	21(1)	34(1)	26(1)	-6(1)	2(1)	3(1)
C(18)	35(1)	32(1)	26(1)	-1(1)	-1(1)	4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for d2224_a.

	x	y	z	U(eq)
H(2A)	4830	9680	7975	37
H(2B)	5821	9406	7552	37
H(3A)	4879	11486	6440	46
H(4A)	3355	10554	5553	45
H(6A)	1780	8471	5386	36
H(7A)	1035	5506	5602	39
H(8A)	1981	3175	6585	40
H(9A)	3653	3875	7391	34
H(12A)	5412	7066	5559	32
H(13A)	6648	5061	5125	35
H(14A)	7530	2760	6150	35
H(15A)	7225	2410	7648	32
H(18A)	5854	3635	9593	48
H(18B)	6935	3496	9307	48
H(18C)	6046	1970	8896	48

Table 6. Torsion angles [°] for d2224_a.

C(11)-C(1)-C(2)-C(3)	85.38(13)
C(10)-C(1)-C(2)-C(3)	-40.74(15)
C(17)-C(1)-C(2)-C(3)	-162.36(11)
C(1)-C(2)-C(3)-C(4)	31.01(19)
C(2)-C(3)-C(4)-C(5)	-3.3(2)
C(3)-C(4)-C(5)-C(6)	167.95(14)
C(3)-C(4)-C(5)-C(10)	-13.4(2)
C(10)-C(5)-C(6)-C(7)	-2.15(19)
C(4)-C(5)-C(6)-C(7)	176.50(12)
C(5)-C(6)-C(7)-C(8)	0.48(19)
C(6)-C(7)-C(8)-C(9)	1.3(2)
C(7)-C(8)-C(9)-C(10)	-1.5(2)
C(8)-C(9)-C(10)-C(5)	-0.20(19)
C(8)-C(9)-C(10)-C(1)	-176.71(11)
C(6)-C(5)-C(10)-C(9)	1.99(18)
C(4)-C(5)-C(10)-C(9)	-176.69(12)
C(6)-C(5)-C(10)-C(1)	178.54(11)
C(4)-C(5)-C(10)-C(1)	-0.13(18)
C(11)-C(1)-C(10)-C(9)	76.05(14)
C(17)-C(1)-C(10)-C(9)	-35.94(15)
C(2)-C(1)-C(10)-C(9)	-156.76(11)
C(11)-C(1)-C(10)-C(5)	-100.45(13)
C(17)-C(1)-C(10)-C(5)	147.56(11)
C(2)-C(1)-C(10)-C(5)	26.73(15)
C(10)-C(1)-C(11)-C(12)	65.86(16)
C(17)-C(1)-C(11)-C(12)	-176.98(12)
C(2)-C(1)-C(11)-C(12)	-60.56(16)
C(10)-C(1)-C(11)-C(16)	-114.46(11)
C(17)-C(1)-C(11)-C(16)	2.69(12)
C(2)-C(1)-C(11)-C(16)	119.11(11)
C(16)-C(11)-C(12)-C(13)	-0.02(17)
C(1)-C(11)-C(12)-C(13)	179.63(12)
C(11)-C(12)-C(13)-C(14)	0.12(18)
C(12)-C(13)-C(14)-C(15)	-0.38(19)
C(13)-C(14)-C(15)-C(16)	0.52(17)
C(14)-C(15)-C(16)-C(11)	-0.43(17)
C(14)-C(15)-C(16)-N(1)	-179.53(11)
C(12)-C(11)-C(16)-C(15)	0.18(17)
C(1)-C(11)-C(16)-C(15)	-179.53(10)
C(12)-C(11)-C(16)-N(1)	179.43(10)
C(1)-C(11)-C(16)-N(1)	-0.28(13)
C(17)-N(1)-C(16)-C(15)	176.51(11)
C(18)-N(1)-C(16)-C(15)	-2.91(19)
C(17)-N(1)-C(16)-C(11)	-2.68(13)
C(18)-N(1)-C(16)-C(11)	177.89(11)
C(16)-N(1)-C(17)-O(1)	-174.99(12)
C(18)-N(1)-C(17)-O(1)	4.4(2)

C(16)-N(1)-C(17)-C(1)	4.43(13)
C(18)-N(1)-C(17)-C(1)	-176.15(10)
C(11)-C(1)-C(17)-O(1)	175.15(12)
C(10)-C(1)-C(17)-O(1)	-66.97(16)
C(2)-C(1)-C(17)-O(1)	55.62(16)
C(11)-C(1)-C(17)-N(1)	-4.26(12)
C(10)-C(1)-C(17)-N(1)	113.62(11)
C(2)-C(1)-C(17)-N(1)	-123.79(11)

Symmetry transformations used to generate equivalent atoms:

Spirooxindole (Before the Retro-Diels-Alder Step)

The sample was prepared by dissolving **3g*** in a minimum amount of DCM, then recrystallizing from pentanes. Data were collected on a Bruker Kappa APEX-DUO diffractometer using CuKα radiation from an Incoatec IμS source with multi-layer optics and a PHOTON II CMOS detector and were measured using a combination of ϕ scans and ω scans. The data were processed using APEX3 and SAINT (Bruker, 2019). Absorption corrections were carried out using SADABS (Bruker, 2019). The structures were solved with SHELXT (Sheldrick, 2015a) and refined using SHELXL-2018 (Sheldrick, 2015b) for full-matrix least-squares refinement that was based on F^2. H atoms were included in calculated positions and allowed to refine in riding-motion approximation with U~iso~ tied to the carrier atom.

Bruker (2007). APEX2, SAINT & SADABS Bruker AXS Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (2015a). Acta Cryst. A71, 3-8.

Sheldrick, G. M. (2015b). Acta Cryst. C71, 3-8.

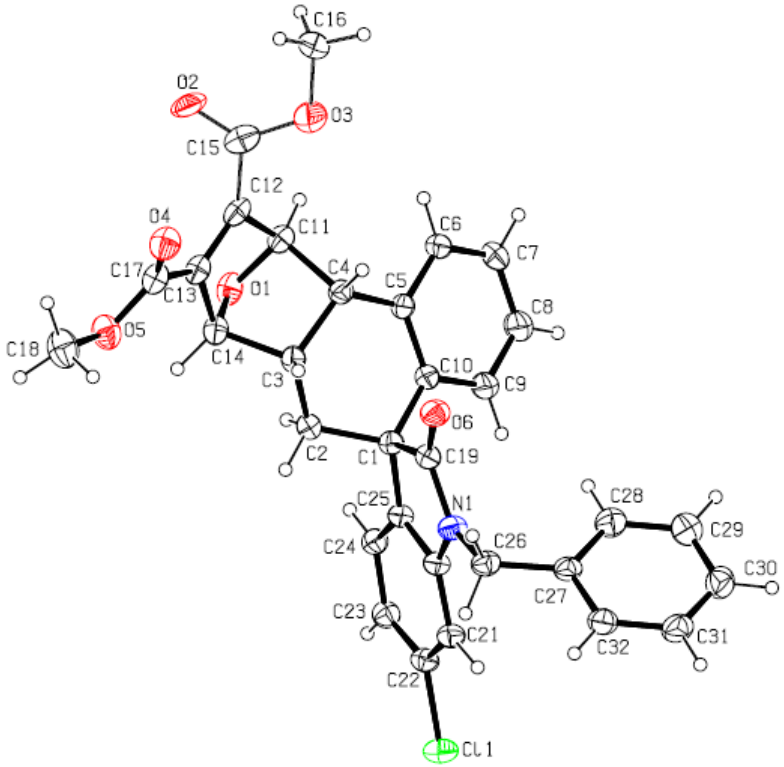


*Figure S2. The molecular structure of compound **3g***. The displacement ellipsoids are drawn the 30% probability level.*

Table 1. Crystal data and structure refinement for d22117_a.

Identification code	d22117_a	
Empirical formula	C32 H26 Cl N O6	
Formula weight	555.99	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 15.0119(6) Å	□= 90°.
	b = 9.3425(3) Å	□= 99.233(3)°.
	c = 19.5240(8) Å	□ = 90°.
Volume	2702.74(18) $Å^3$	
Z	4	
Density (calculated)	1.366 Mg/m^3	
Absorption coefficient	1.647 mm^{-1}	
F(000)	1160	
Crystal size	0.200 x 0.100 x 0.030 mm^3	
Theta range for data collection	3.458 to 66.135°.	
Index ranges	-17<=h<=17, -10<=k<=10, -22<=l<=23	
Reflections collected	48973	
Independent reflections	4657 [R(int) = 0.1342]	
Completeness to theta = 66.135°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.5790	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4657 / 50 / 393	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0523, wR2 = 0.1228	
R indices (all data)	R1 = 0.0875, wR2 = 0.1426	
Extinction coefficient	0.0070(5)	
Largest diff. peak and hole	0.333 and -0.328 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for d22117_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	3295(1)	-613(1)	9461(1)	51(1)
O(1)	7184(1)	4706(2)	7148(1)	49(1)
O(4)	5974(1)	5707(2)	4830(1)	55(1)
O(5)	6284(1)	3421(2)	5153(1)	56(1)
O(6)	3773(1)	5566(2)	7174(1)	46(1)
N(1)	3289(1)	3742(2)	7813(1)	41(1)
C(1)	4865(2)	4124(3)	7974(1)	37(1)
C(2)	5444(2)	3535(3)	7455(1)	39(1)
C(3)	5625(2)	4617(3)	6911(1)	40(1)
C(4)	5915(2)	6111(3)	7222(1)	37(1)
C(5)	5835(2)	6331(2)	7981(1)	36(1)
C(6)	6241(2)	7536(3)	8325(2)	44(1)
C(7)	6183(2)	7795(3)	9011(2)	53(1)
C(8)	5705(2)	6873(3)	9367(2)	64(1)
C(9)	5284(2)	5695(3)	9033(2)	53(1)
C(10)	5340(2)	5405(3)	8343(1)	38(1)
C(11)	6908(2)	6174(3)	7079(1)	44(1)
C(12)	6858(2)	6393(3)	6298(1)	46(1)
C(13)	6568(2)	5146(3)	6010(1)	45(1)
C(14)	6480(2)	4171(3)	6615(1)	45(1)
O(2)	7543(8)	7740(7)	5551(7)	61(2)
O(3)	6615(7)	8877(9)	6157(7)	82(3)
C(16)	6868(4)	10147(4)	5875(3)	75(2)
C(15)	7049(2)	7728(4)	5964(2)	59(1)
O(2A)	6712(13)	8702(19)	6234(13)	54(4)
O(3A)	7640(20)	8074(18)	5544(18)	65(5)
C(16A)	7679(8)	9527(11)	5373(6)	66(4)
C(15A)	7049(2)	7728(4)	5964(2)	59(1)
C(17)	6246(2)	4827(3)	5264(2)	49(1)
C(18)	5953(2)	2957(4)	4449(2)	66(1)
C(19)	3931(2)	4599(3)	7594(1)	39(1)
C(20)	3684(2)	2742(3)	8306(1)	37(1)
C(21)	3251(2)	1684(3)	8623(1)	40(1)
C(22)	3800(2)	751(3)	9050(1)	40(1)
C(23)	4736(2)	863(3)	9158(1)	42(1)
C(24)	5149(2)	1970(3)	8852(1)	40(1)
C(25)	4618(2)	2920(3)	8426(1)	37(1)
C(26)	2325(2)	3795(3)	7538(1)	43(1)
C(27)	1771(2)	4576(3)	7994(1)	41(1)
C(28)	2121(2)	5600(3)	8475(2)	55(1)
C(29)	1566(2)	6314(3)	8871(2)	63(1)
C(30)	659(2)	5999(3)	8790(2)	60(1)
C(31)	305(2)	4990(3)	8304(2)	57(1)
C(32)	848(2)	4291(3)	7912(2)	50(1)

Table 3. Bond lengths [Å] and angles [°] for d22117_a.

Cl(1)-C(22)	1.742(3)
O(1)-C(11)	1.433(3)
O(1)-C(14)	1.447(3)
O(4)-C(17)	1.204(3)
O(5)-C(17)	1.334(3)
O(5)-C(18)	1.451(4)
O(6)-C(19)	1.219(3)
N(1)-C(19)	1.373(3)
N(1)-C(20)	1.402(3)
N(1)-C(26)	1.461(3)
C(1)-C(25)	1.512(3)
C(1)-C(10)	1.515(3)
C(1)-C(2)	1.540(4)
C(1)-C(19)	1.542(4)
C(2)-C(3)	1.521(4)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(14)	1.547(4)
C(3)-C(4)	1.555(3)
C(3)-H(3A)	1.0000
C(4)-C(5)	1.521(4)
C(4)-C(11)	1.560(4)
C(4)-H(4A)	1.0000
C(5)-C(6)	1.399(3)
C(5)-C(10)	1.403(4)
C(6)-C(7)	1.376(4)
C(6)-H(6A)	0.9500
C(7)-C(8)	1.380(4)
C(7)-H(7A)	0.9500
C(8)-C(9)	1.380(4)
C(8)-H(8A)	0.9500
C(9)-C(10)	1.390(4)
C(9)-H(9A)	0.9500
C(11)-C(12)	1.529(4)
C(11)-H(11A)	1.0000
C(12)-C(13)	1.336(4)
C(12)-C(15A)	1.457(4)
C(12)-C(15)	1.457(4)
C(13)-C(17)	1.487(4)
C(13)-C(14)	1.515(4)
C(14)-H(14A)	1.0000
O(2)-C(15)	1.179(8)
O(3)-C(15)	1.341(9)
O(3)-C(16)	1.386(11)
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800

O(2A)-C(15A)	1.203(13)
O(3A)-C(15A)	1.336(13)
O(3A)-C(16A)	1.402(14)
C(16A)-H(16D)	0.9800
C(16A)-H(16E)	0.9800
C(16A)-H(16F)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(20)-C(21)	1.383(3)
C(20)-C(25)	1.394(3)
C(21)-C(22)	1.384(4)
C(21)-H(21A)	0.9500
C(22)-C(23)	1.390(4)
C(23)-C(24)	1.390(4)
C(23)-H(23A)	0.9500
C(24)-C(25)	1.379(3)
C(24)-H(24A)	0.9500
C(26)-C(27)	1.502(4)
C(26)-H(26A)	0.9900
C(26)-H(26B)	0.9900
C(27)-C(28)	1.384(4)
C(27)-C(32)	1.395(4)
C(28)-C(29)	1.393(4)
C(28)-H(28A)	0.9500
C(29)-C(30)	1.378(5)
C(29)-H(29A)	0.9500
C(30)-C(31)	1.382(5)
C(30)-H(30A)	0.9500
C(31)-C(32)	1.369(4)
C(31)-H(31A)	0.9500
C(32)-H(32A)	0.9500

C(11)-O(1)-C(14)	95.60(19)
C(17)-O(5)-C(18)	115.6(2)
C(19)-N(1)-C(20)	111.2(2)
C(19)-N(1)-C(26)	124.7(2)
C(20)-N(1)-C(26)	124.1(2)
C(25)-C(1)-C(10)	116.8(2)
C(25)-C(1)-C(2)	109.6(2)
C(10)-C(1)-C(2)	108.8(2)
C(25)-C(1)-C(19)	101.8(2)
C(10)-C(1)-C(19)	108.90(19)
C(2)-C(1)-C(19)	110.7(2)
C(3)-C(2)-C(1)	113.8(2)
C(3)-C(2)-H(2A)	108.8
C(1)-C(2)-H(2A)	108.8
C(3)-C(2)-H(2B)	108.8
C(1)-C(2)-H(2B)	108.8

H(2A)-C(2)-H(2B)	107.7
C(2)-C(3)-C(14)	109.5(2)
C(2)-C(3)-C(4)	113.3(2)
C(14)-C(3)-C(4)	101.0(2)
C(2)-C(3)-H(3A)	110.9
C(14)-C(3)-H(3A)	110.9
C(4)-C(3)-H(3A)	110.9
C(5)-C(4)-C(3)	116.1(2)
C(5)-C(4)-C(11)	113.3(2)
C(3)-C(4)-C(11)	100.4(2)
C(5)-C(4)-H(4A)	108.9
C(3)-C(4)-H(4A)	108.9
C(11)-C(4)-H(4A)	108.9
C(6)-C(5)-C(10)	118.6(2)
C(6)-C(5)-C(4)	118.8(2)
C(10)-C(5)-C(4)	122.6(2)
C(7)-C(6)-C(5)	121.2(3)
C(7)-C(6)-H(6A)	119.4
C(5)-C(6)-H(6A)	119.4
C(6)-C(7)-C(8)	119.9(3)
C(6)-C(7)-H(7A)	120.0
C(8)-C(7)-H(7A)	120.0
C(9)-C(8)-C(7)	119.7(3)
C(9)-C(8)-H(8A)	120.2
C(7)-C(8)-H(8A)	120.2
C(8)-C(9)-C(10)	121.3(3)
C(8)-C(9)-H(9A)	119.3
C(10)-C(9)-H(9A)	119.3
C(9)-C(10)-C(5)	119.2(2)
C(9)-C(10)-C(1)	121.1(2)
C(5)-C(10)-C(1)	119.7(2)
O(1)-C(11)-C(12)	100.9(2)
O(1)-C(11)-C(4)	102.5(2)
C(12)-C(11)-C(4)	106.7(2)
O(1)-C(11)-H(11A)	115.0
C(12)-C(11)-H(11A)	115.0
C(4)-C(11)-H(11A)	115.0
C(13)-C(12)-C(15A)	129.2(3)
C(13)-C(12)-C(15)	129.2(3)
C(13)-C(12)-C(11)	105.3(2)
C(15A)-C(12)-C(11)	125.4(3)
C(15)-C(12)-C(11)	125.4(3)
C(12)-C(13)-C(17)	128.3(3)
C(12)-C(13)-C(14)	105.0(2)
C(17)-C(13)-C(14)	126.0(3)
O(1)-C(14)-C(13)	102.0(2)
O(1)-C(14)-C(3)	101.0(2)
C(13)-C(14)-C(3)	108.1(2)
O(1)-C(14)-H(14A)	114.7

C(13)-C(14)-H(14A)	114.7
C(3)-C(14)-H(14A)	114.7
C(15)-O(3)-C(16)	113.4(7)
O(3)-C(16)-H(16A)	109.5
O(3)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
O(3)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
O(2)-C(15)-O(3)	124.9(5)
O(2)-C(15)-C(12)	120.3(5)
O(3)-C(15)-C(12)	114.8(6)
C(15A)-O(3A)-C(16A)	116.1(13)
O(3A)-C(16A)-H(16D)	109.5
O(3A)-C(16A)-H(16E)	109.5
H(16D)-C(16A)-H(16E)	109.5
O(3A)-C(16A)-H(16F)	109.5
H(16D)-C(16A)-H(16F)	109.5
H(16E)-C(16A)-H(16F)	109.5
O(2A)-C(15A)-O(3A)	116.8(9)
O(2A)-C(15A)-C(12)	108.9(12)
O(3A)-C(15A)-C(12)	132.7(8)
O(4)-C(17)-O(5)	125.2(3)
O(4)-C(17)-C(13)	124.9(3)
O(5)-C(17)-C(13)	109.9(2)
O(5)-C(18)-H(18A)	109.5
O(5)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
O(5)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
O(6)-C(19)-N(1)	124.9(2)
O(6)-C(19)-C(1)	126.9(2)
N(1)-C(19)-C(1)	108.2(2)
C(21)-C(20)-C(25)	122.9(2)
C(21)-C(20)-N(1)	127.2(2)
C(25)-C(20)-N(1)	109.8(2)
C(20)-C(21)-C(22)	116.3(2)
C(20)-C(21)-H(21A)	121.9
C(22)-C(21)-H(21A)	121.9
C(21)-C(22)-C(23)	122.2(2)
C(21)-C(22)-Cl(1)	118.5(2)
C(23)-C(22)-Cl(1)	119.25(19)
C(24)-C(23)-C(22)	120.0(2)
C(24)-C(23)-H(23A)	120.0
C(22)-C(23)-H(23A)	120.0
C(25)-C(24)-C(23)	118.9(2)
C(25)-C(24)-H(24A)	120.5
C(23)-C(24)-H(24A)	120.5

C(24)-C(25)-C(20)	119.5(2)
C(24)-C(25)-C(1)	131.2(2)
C(20)-C(25)-C(1)	109.0(2)
N(1)-C(26)-C(27)	114.1(2)
N(1)-C(26)-H(26A)	108.7
C(27)-C(26)-H(26A)	108.7
N(1)-C(26)-H(26B)	108.7
C(27)-C(26)-H(26B)	108.7
H(26A)-C(26)-H(26B)	107.6
C(28)-C(27)-C(32)	118.1(3)
C(28)-C(27)-C(26)	123.5(2)
C(32)-C(27)-C(26)	118.3(2)
C(27)-C(28)-C(29)	120.8(3)
C(27)-C(28)-H(28A)	119.6
C(29)-C(28)-H(28A)	119.6
C(30)-C(29)-C(28)	120.1(3)
C(30)-C(29)-H(29A)	120.0
C(28)-C(29)-H(29A)	120.0
C(29)-C(30)-C(31)	119.3(3)
C(29)-C(30)-H(30A)	120.4
C(31)-C(30)-H(30A)	120.4
C(32)-C(31)-C(30)	120.7(3)
C(32)-C(31)-H(31A)	119.6
C(30)-C(31)-H(31A)	119.6
C(31)-C(32)-C(27)	121.0(3)
C(31)-C(32)-H(32A)	119.5
C(27)-C(32)-H(32A)	119.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for d22117_a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	56(1)	47(1)	50(1)	10(1)	6(1)	-15(1)
O(1)	41(1)	60(1)	47(1)	1(1)	10(1)	12(1)
O(4)	59(1)	61(1)	46(1)	11(1)	10(1)	9(1)
O(5)	66(1)	55(1)	47(1)	-2(1)	7(1)	10(1)
O(6)	44(1)	40(1)	54(1)	11(1)	9(1)	4(1)
N(1)	34(1)	38(1)	50(1)	8(1)	5(1)	-1(1)
C(1)	37(1)	33(1)	43(1)	2(1)	11(1)	0(1)
C(2)	43(2)	34(1)	42(1)	-3(1)	10(1)	1(1)
C(3)	40(2)	39(1)	42(1)	-1(1)	11(1)	4(1)
C(4)	33(1)	36(1)	42(1)	2(1)	8(1)	0(1)
C(5)	31(1)	34(1)	45(2)	0(1)	9(1)	3(1)
C(6)	39(2)	36(1)	58(2)	-4(1)	13(1)	-3(1)
C(7)	59(2)	39(2)	63(2)	-15(1)	15(2)	-5(1)
C(8)	86(2)	55(2)	57(2)	-19(2)	30(2)	-15(2)
C(9)	69(2)	44(2)	52(2)	-9(1)	26(2)	-11(1)
C(10)	36(1)	33(1)	46(2)	-2(1)	11(1)	0(1)
C(11)	37(2)	49(2)	47(2)	0(1)	10(1)	0(1)
C(12)	33(2)	59(2)	50(2)	5(1)	17(1)	1(1)
C(13)	39(2)	53(2)	46(2)	0(1)	14(1)	4(1)
C(14)	44(2)	48(2)	44(2)	-2(1)	12(1)	6(1)
O(2)	55(3)	62(3)	73(3)	18(3)	29(2)	-16(3)
O(3)	101(5)	55(3)	104(6)	11(3)	57(5)	0(3)
C(16)	94(4)	37(2)	103(4)	-2(2)	49(3)	-7(2)
C(15)	50(2)	70(2)	58(2)	7(2)	9(2)	-15(2)
O(2A)	52(6)	52(6)	60(7)	8(5)	14(5)	-29(5)
O(3A)	60(8)	63(7)	77(7)	29(6)	22(6)	-21(6)
C(16A)	63(8)	65(6)	71(8)	22(5)	10(6)	-25(5)
C(15A)	50(2)	70(2)	58(2)	7(2)	9(2)	-15(2)
C(17)	43(2)	58(2)	48(2)	-1(1)	16(1)	3(1)
C(18)	83(2)	69(2)	45(2)	-6(2)	4(2)	12(2)
C(19)	40(2)	33(1)	44(2)	-1(1)	8(1)	-1(1)
C(20)	37(1)	33(1)	41(1)	1(1)	5(1)	-4(1)
C(21)	37(2)	39(1)	44(2)	-2(1)	5(1)	-7(1)
C(22)	45(2)	35(1)	38(1)	-1(1)	5(1)	-8(1)
C(23)	47(2)	39(1)	39(1)	4(1)	6(1)	2(1)
C(24)	38(2)	40(1)	43(2)	1(1)	8(1)	0(1)
C(25)	38(1)	32(1)	42(1)	-2(1)	9(1)	-5(1)
C(26)	36(2)	43(2)	49(2)	5(1)	4(1)	-2(1)
C(27)	39(2)	36(1)	48(2)	9(1)	7(1)	0(1)
C(28)	47(2)	58(2)	61(2)	-4(2)	10(2)	-7(1)
C(29)	67(2)	59(2)	63(2)	-8(2)	14(2)	-3(2)
C(30)	65(2)	52(2)	66(2)	11(2)	25(2)	13(2)
C(31)	43(2)	50(2)	79(2)	14(2)	17(2)	4(1)
C(32)	43(2)	39(2)	67(2)	4(1)	10(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for d22117_a.

	x	y	z	U(eq)
H(2A)	6029	3204	7715	47
H(2B)	5135	2694	7216	47
H(3A)	5093	4702	6533	47
H(4A)	5554	6865	6938	44
H(6A)	6562	8187	8081	52
H(7A)	6473	8609	9238	64
H(8A)	5665	7048	9841	77
H(9A)	4949	5069	9279	64
H(11A)	7309	6861	7377	53
H(14A)	6521	3125	6514	54
H(16A)	6475	10923	5984	112
H(16B)	6814	10047	5370	112
H(16C)	7495	10369	6072	112
H(16D)	8143	9668	5079	100
H(16E)	7830	10092	5798	100
H(16F)	7092	9837	5122	100
H(18A)	6165	1982	4383	100
H(18B)	6178	3604	4121	100
H(18C)	5292	2971	4368	100
H(21A)	2612	1602	8551	48
H(23A)	5093	183	9441	50
H(24A)	5787	2071	8934	48
H(26A)	2096	2803	7468	51
H(26B)	2243	4267	7078	51
H(28A)	2747	5818	8536	66
H(29A)	1814	7020	9197	75
H(30A)	281	6471	9065	71
H(31A)	-322	4779	8241	68
H(32A)	592	3603	7580	60

Table 6. Torsion angles [°] for d22117_a.

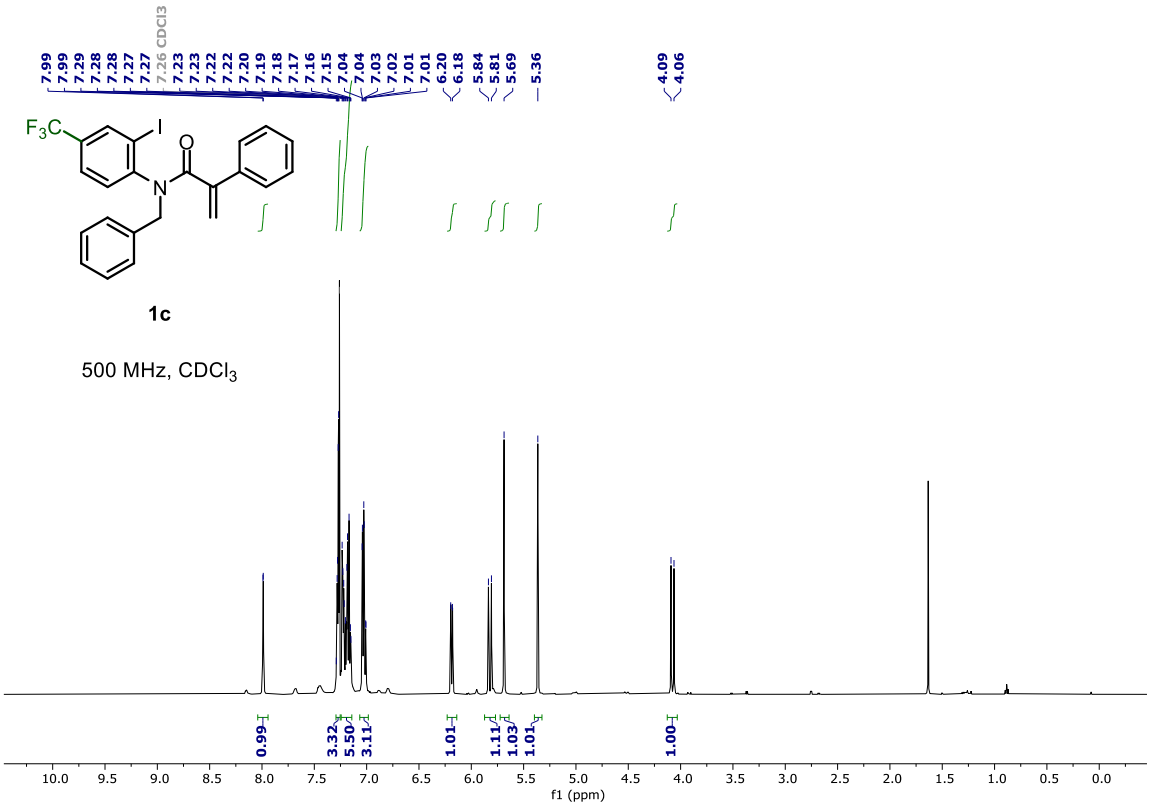
C(25)-C(1)-C(2)-C(3)	172.3(2)
C(10)-C(1)-C(2)-C(3)	-58.9(3)
C(19)-C(1)-C(2)-C(3)	60.7(3)
C(1)-C(2)-C(3)-C(14)	157.7(2)
C(1)-C(2)-C(3)-C(4)	45.9(3)
C(2)-C(3)-C(4)-C(5)	-9.0(3)
C(14)-C(3)-C(4)-C(5)	-125.9(2)
C(2)-C(3)-C(4)-C(11)	113.5(2)
C(14)-C(3)-C(4)-C(11)	-3.4(2)
C(3)-C(4)-C(5)-C(6)	168.0(2)
C(11)-C(4)-C(5)-C(6)	52.6(3)
C(3)-C(4)-C(5)-C(10)	-14.6(3)
C(11)-C(4)-C(5)-C(10)	-130.1(2)
C(10)-C(5)-C(6)-C(7)	2.0(4)
C(4)-C(5)-C(6)-C(7)	179.4(2)
C(5)-C(6)-C(7)-C(8)	-1.2(4)
C(6)-C(7)-C(8)-C(9)	-0.1(5)
C(7)-C(8)-C(9)-C(10)	0.8(5)
C(8)-C(9)-C(10)-C(5)	0.0(4)
C(8)-C(9)-C(10)-C(1)	-179.0(3)
C(6)-C(5)-C(10)-C(9)	-1.4(4)
C(4)-C(5)-C(10)-C(9)	-178.7(2)
C(6)-C(5)-C(10)-C(1)	177.7(2)
C(4)-C(5)-C(10)-C(1)	0.3(4)
C(25)-C(1)-C(10)-C(9)	-21.0(3)
C(2)-C(1)-C(10)-C(9)	-145.7(2)
C(19)-C(1)-C(10)-C(9)	93.6(3)
C(25)-C(1)-C(10)-C(5)	160.0(2)
C(2)-C(1)-C(10)-C(5)	35.2(3)
C(19)-C(1)-C(10)-C(5)	-85.5(3)
C(14)-O(1)-C(11)-C(12)	-52.0(2)
C(14)-O(1)-C(11)-C(4)	58.1(2)
C(5)-C(4)-C(11)-O(1)	91.3(2)
C(3)-C(4)-C(11)-O(1)	-33.2(2)
C(5)-C(4)-C(11)-C(12)	-163.2(2)
C(3)-C(4)-C(11)-C(12)	72.3(2)
O(1)-C(11)-C(12)-C(13)	35.1(3)
C(4)-C(11)-C(12)-C(13)	-71.7(3)
O(1)-C(11)-C(12)-C(15A)	-147.8(3)
C(4)-C(11)-C(12)-C(15A)	105.4(3)
O(1)-C(11)-C(12)-C(15)	-147.8(3)
C(4)-C(11)-C(12)-C(15)	105.4(3)
C(15A)-C(12)-C(13)-C(17)	-8.7(5)
C(15)-C(12)-C(13)-C(17)	-8.7(5)
C(11)-C(12)-C(13)-C(17)	168.3(3)
C(15A)-C(12)-C(13)-C(14)	-179.2(3)
C(15)-C(12)-C(13)-C(14)	-179.2(3)

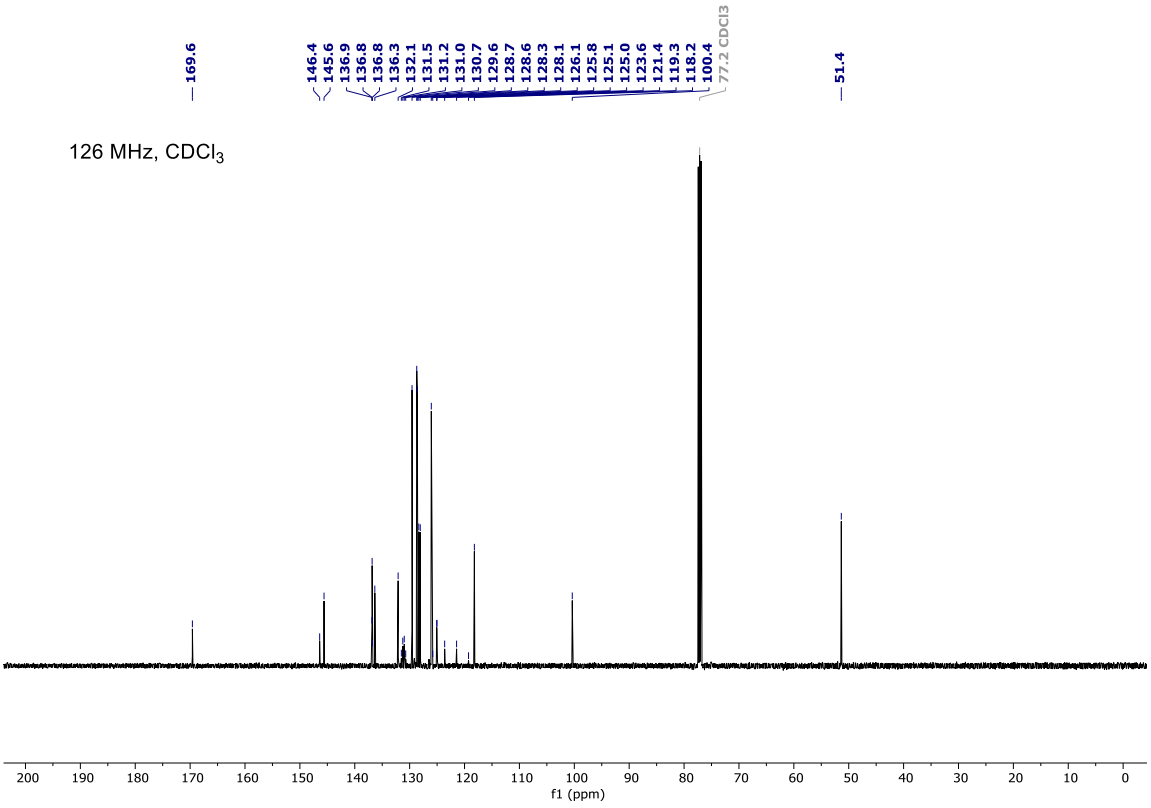
C(11)-C(12)-C(13)-C(14)	-2.2(3)
C(11)-O(1)-C(14)-C(13)	51.3(2)
C(11)-O(1)-C(14)-C(3)	-60.1(2)
C(12)-C(13)-C(14)-O(1)	-31.1(3)
C(17)-C(13)-C(14)-O(1)	158.2(2)
C(12)-C(13)-C(14)-C(3)	74.9(3)
C(17)-C(13)-C(14)-C(3)	-95.9(3)
C(2)-C(3)-C(14)-O(1)	-81.1(2)
C(4)-C(3)-C(14)-O(1)	38.6(2)
C(2)-C(3)-C(14)-C(13)	172.3(2)
C(4)-C(3)-C(14)-C(13)	-68.0(2)
C(16)-O(3)-C(15)-O(2)	-6.3(16)
C(16)-O(3)-C(15)-C(12)	174.9(7)
C(13)-C(12)-C(15)-O(2)	-53.2(10)
C(11)-C(12)-C(15)-O(2)	130.4(9)
C(13)-C(12)-C(15)-O(3)	125.7(7)
C(11)-C(12)-C(15)-O(3)	-50.7(7)
C(16A)-O(3A)-C(15A)-O(2A)	-10(4)
C(16A)-O(3A)-C(15A)-C(12)	-174.4(13)
C(13)-C(12)-C(15A)-O(2A)	133.7(12)
C(11)-C(12)-C(15A)-O(2A)	-42.7(13)
C(13)-C(12)-C(15A)-O(3A)	-61(2)
C(11)-C(12)-C(15A)-O(3A)	122(2)
C(18)-O(5)-C(17)-O(4)	-1.1(4)
C(18)-O(5)-C(17)-C(13)	177.6(2)
C(12)-C(13)-C(17)-O(4)	-20.7(5)
C(14)-C(13)-C(17)-O(4)	147.9(3)
C(12)-C(13)-C(17)-O(5)	160.6(3)
C(14)-C(13)-C(17)-O(5)	-30.8(4)
C(20)-N(1)-C(19)-O(6)	-179.2(2)
C(26)-N(1)-C(19)-O(6)	4.6(4)
C(20)-N(1)-C(19)-C(1)	0.5(3)
C(26)-N(1)-C(19)-C(1)	-175.7(2)
C(25)-C(1)-C(19)-O(6)	179.0(2)
C(10)-C(1)-C(19)-O(6)	55.0(3)
C(2)-C(1)-C(19)-O(6)	-64.6(3)
C(25)-C(1)-C(19)-N(1)	-0.7(3)
C(10)-C(1)-C(19)-N(1)	-124.7(2)
C(2)-C(1)-C(19)-N(1)	115.7(2)
C(19)-N(1)-C(20)-C(21)	-177.9(2)
C(26)-N(1)-C(20)-C(21)	-1.7(4)
C(19)-N(1)-C(20)-C(25)	0.0(3)
C(26)-N(1)-C(20)-C(25)	176.2(2)
C(25)-C(20)-C(21)-C(22)	-2.8(4)
N(1)-C(20)-C(21)-C(22)	174.8(2)
C(20)-C(21)-C(22)-C(23)	0.0(4)
C(20)-C(21)-C(22)-Cl(1)	-179.62(19)
C(21)-C(22)-C(23)-C(24)	2.4(4)
Cl(1)-C(22)-C(23)-C(24)	-178.0(2)

C(22)-C(23)-C(24)-C(25)	-2.0(4)
C(23)-C(24)-C(25)-C(20)	-0.7(4)
C(23)-C(24)-C(25)-C(1)	-173.5(2)
C(21)-C(20)-C(25)-C(24)	3.2(4)
N(1)-C(20)-C(25)-C(24)	-174.8(2)
C(21)-C(20)-C(25)-C(1)	177.5(2)
N(1)-C(20)-C(25)-C(1)	-0.5(3)
C(10)-C(1)-C(25)-C(24)	-67.4(4)
C(2)-C(1)-C(25)-C(24)	56.9(3)
C(19)-C(1)-C(25)-C(24)	174.1(3)
C(10)-C(1)-C(25)-C(20)	119.2(2)
C(2)-C(1)-C(25)-C(20)	-116.5(2)
C(19)-C(1)-C(25)-C(20)	0.7(3)
C(19)-N(1)-C(26)-C(27)	-101.7(3)
C(20)-N(1)-C(26)-C(27)	82.6(3)
N(1)-C(26)-C(27)-C(28)	23.6(4)
N(1)-C(26)-C(27)-C(32)	-158.7(2)
C(32)-C(27)-C(28)-C(29)	0.6(4)
C(26)-C(27)-C(28)-C(29)	178.3(3)
C(27)-C(28)-C(29)-C(30)	0.5(5)
C(28)-C(29)-C(30)-C(31)	-1.2(5)
C(29)-C(30)-C(31)-C(32)	0.9(4)
C(30)-C(31)-C(32)-C(27)	0.2(4)
C(28)-C(27)-C(32)-C(31)	-0.9(4)
C(26)-C(27)-C(32)-C(31)	-178.7(3)

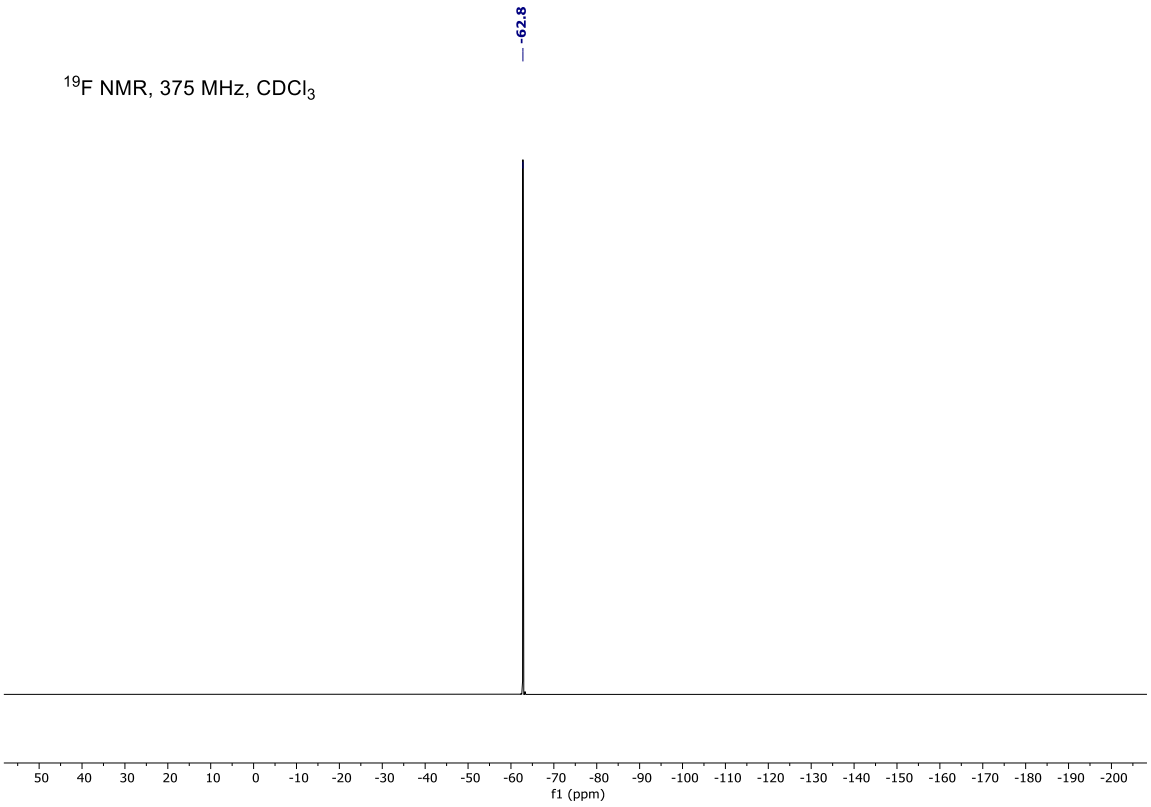
Symmetry transformations used to generate equivalent atoms:

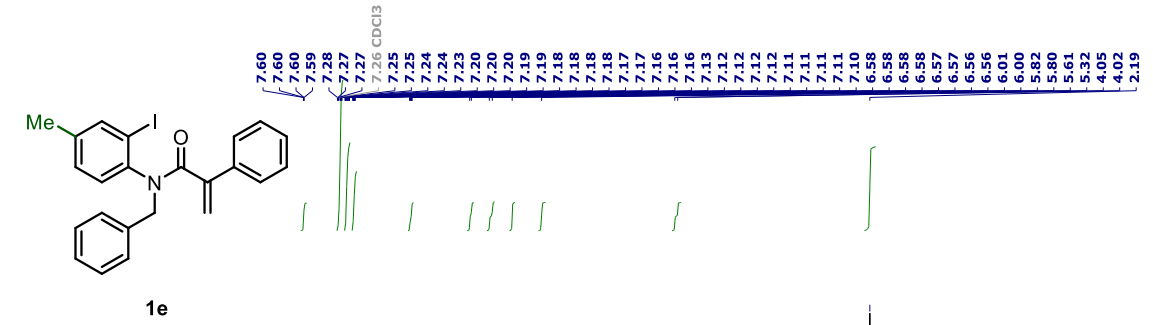
NMR Spectra


7.99
7.99
7.29
7.28
7.28
7.27
7.27
7.26 CDCl3
7.23
7.23
7.22
7.22
7.20
7.19
7.18
7.17
7.16
7.15
7.04
7.03
7.02
7.01
7.01
6.20
6.18
5.84
5.81
5.69
5.36
4.09
4.06
F3C
I
O
N
1c
500 MHz, CDCl3
0.99
3.32
5.50
3.11
1.01
1.11
1.03
1.01
1.00
f1 (ppm)


169.6
146.4
145.6
136.9
136.8
136.8
136.3
132.1
131.5
131.2
131.0
130.7
129.6
128.7
128.6
128.3
128.1
126.1
125.8
125.1
125.0
123.6
121.4
119.3
118.2
100.4
77.2 CDCl3
51.4
126 MHz, CDCl3
f1 (ppm)

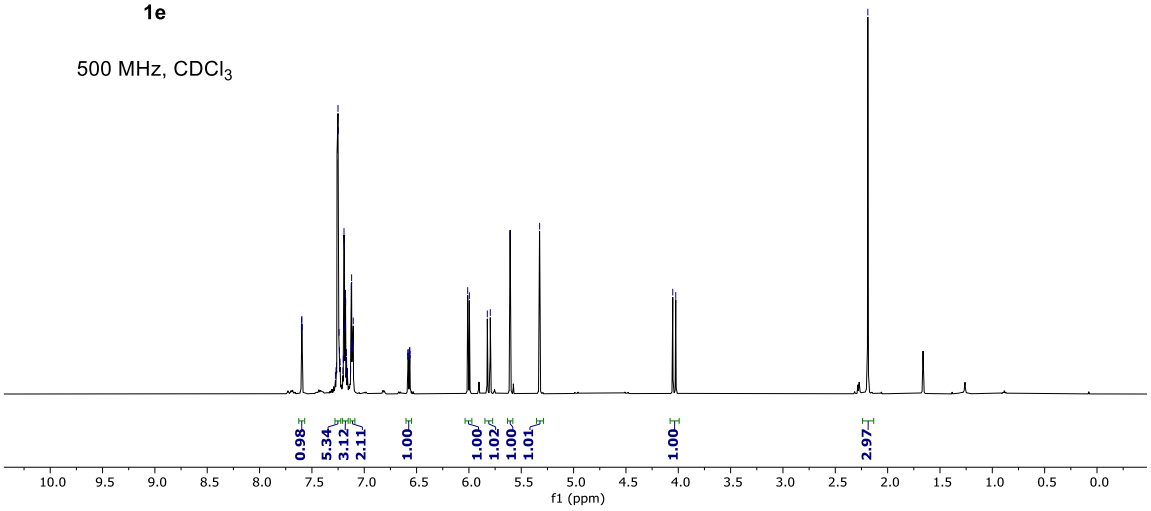
^{19}F NMR, 375 MHz, $CDCl_3$



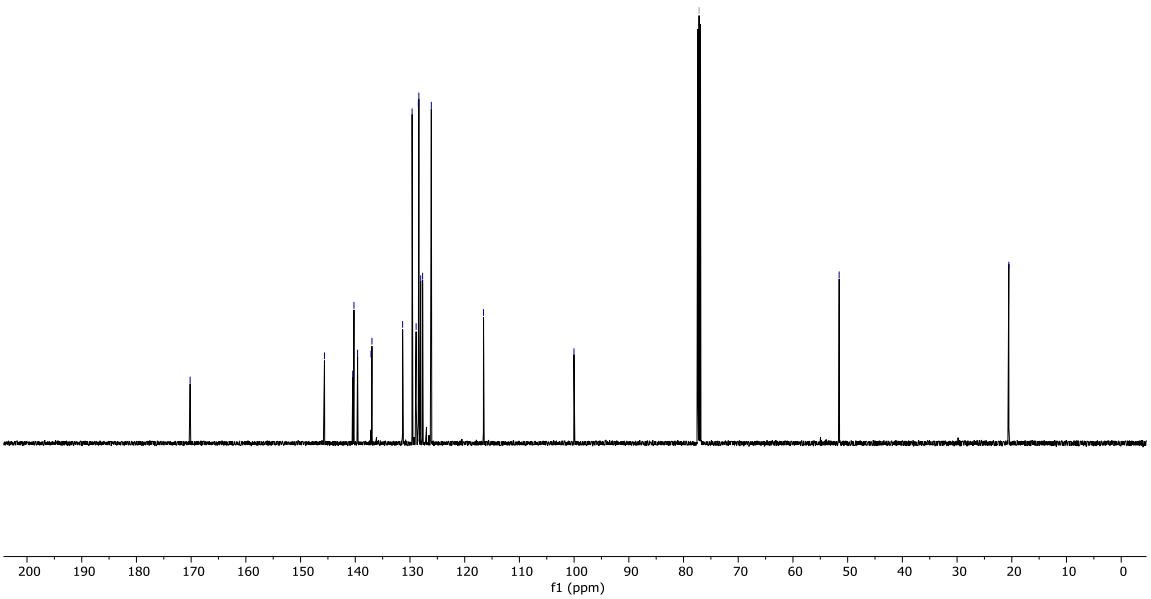


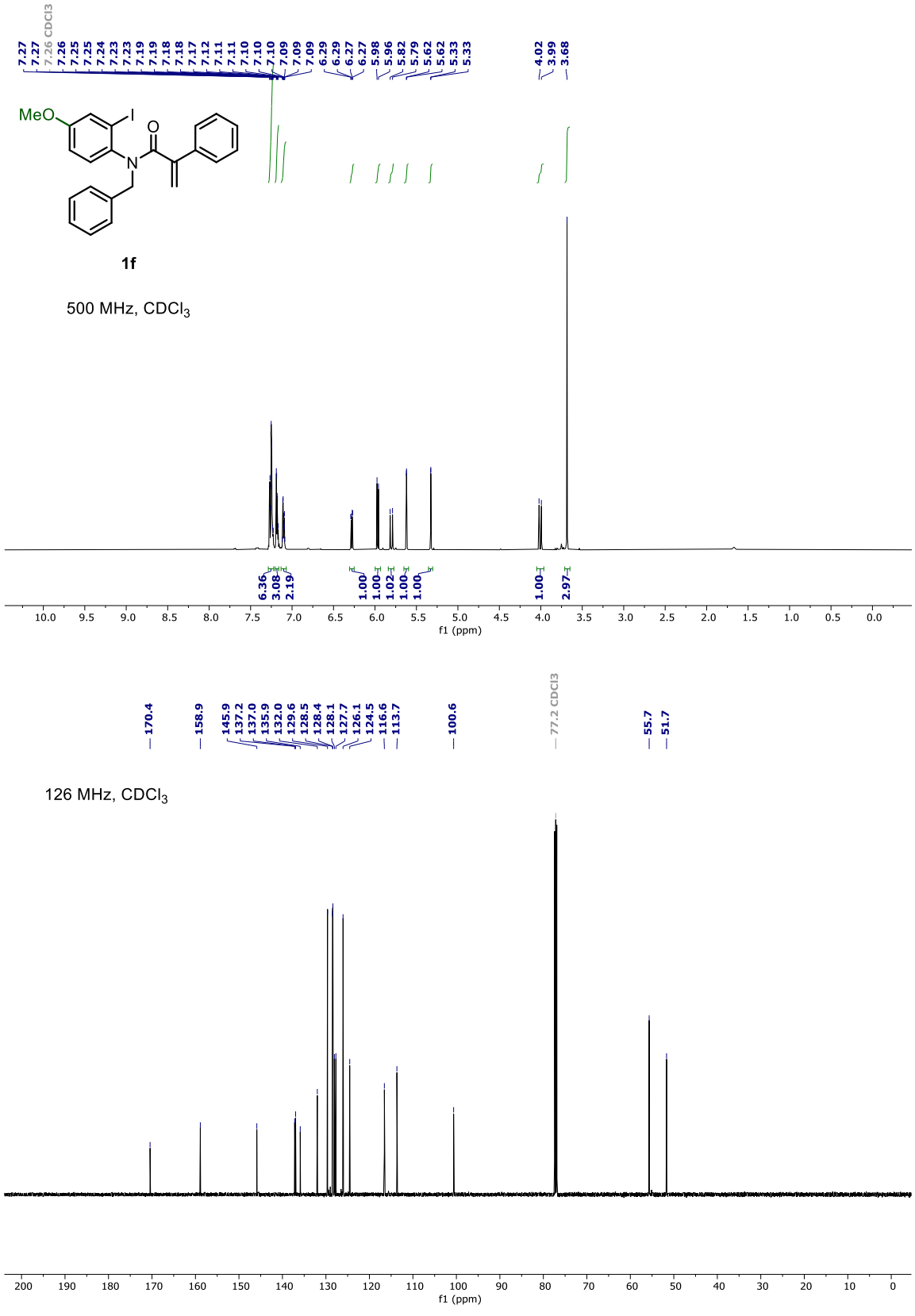
1e

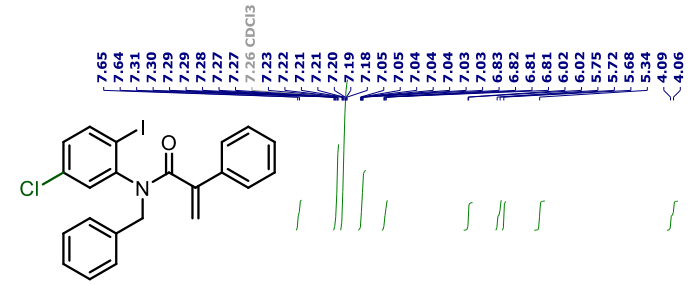
500 MHz, $CDCl_3$



126 MHz, $CDCl_3$

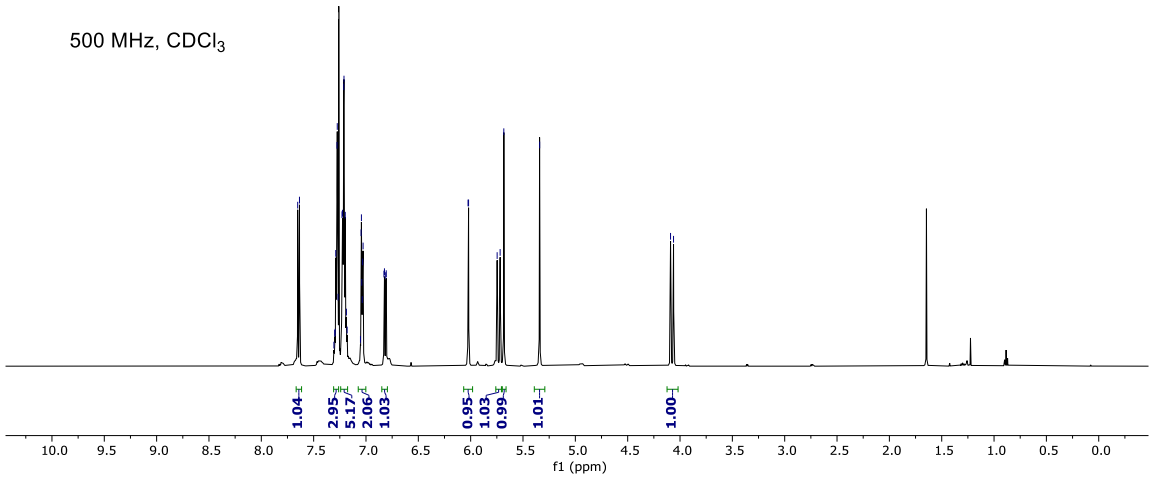


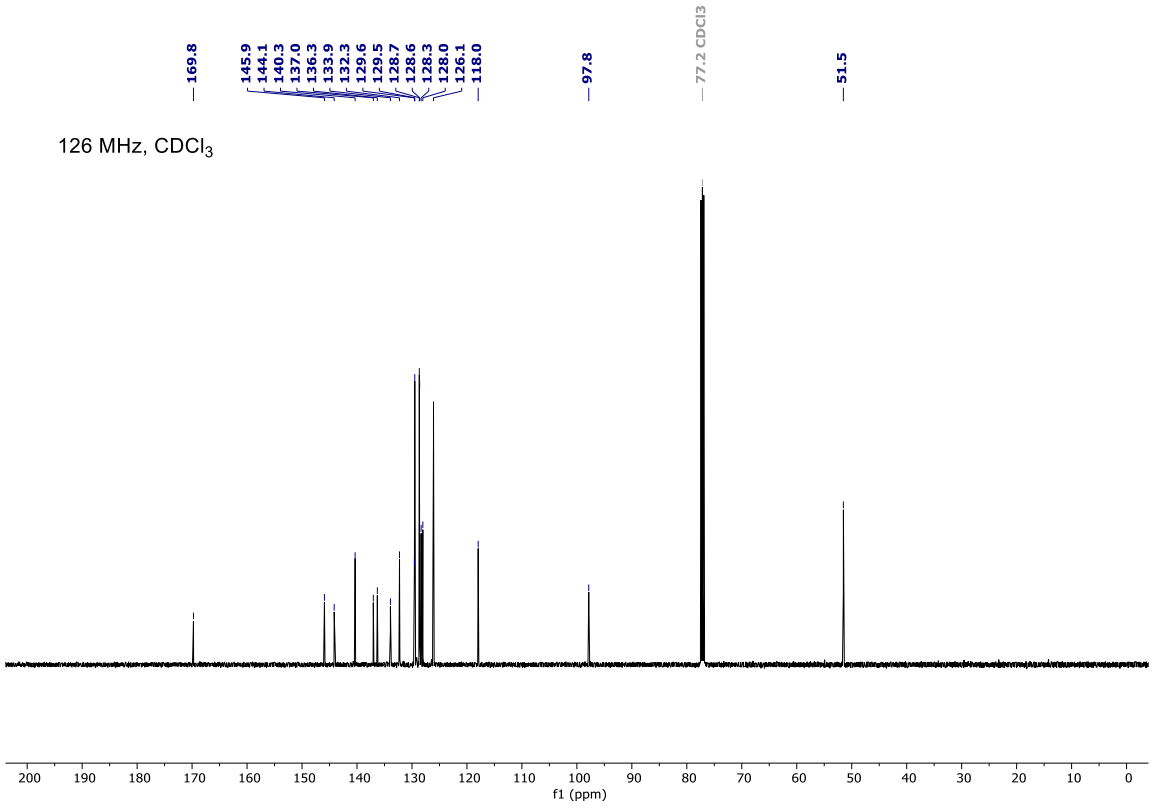

7.27
7.27
7.26 CDCl3
7.26
7.25
7.25
7.24
7.23
7.23
7.19
7.19
7.18
7.18
7.17
7.12
7.11
7.11
7.10
7.10
7.10
7.09
7.09
7.09
6.29
6.29
6.27
6.27
5.98
5.96
5.82
5.79
5.62
5.62
5.33
5.33
4.02
3.99
3.68
MeO
I
O
N
1f
500 MHz, CDCl3
6.36
3.08
2.19
1.00
1.00
1.02
1.00
1.00
1.00
2.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
170.4
158.9
145.9
137.2
137.0
135.9
132.0
129.6
128.5
128.4
128.1
127.7
126.1
124.5
116.6
113.7
100.6
77.2 CDCl3
55.7
51.7
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



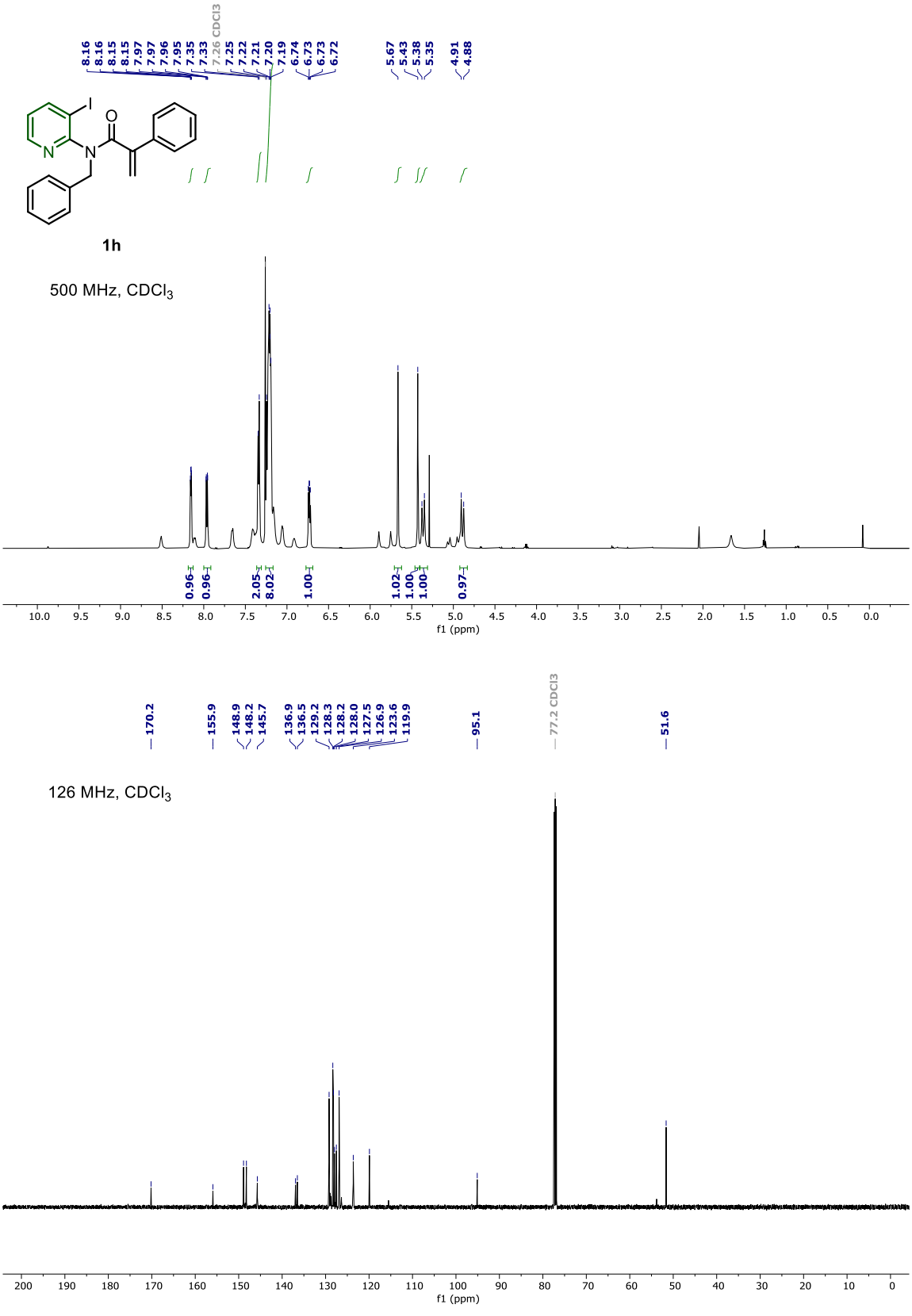
1g

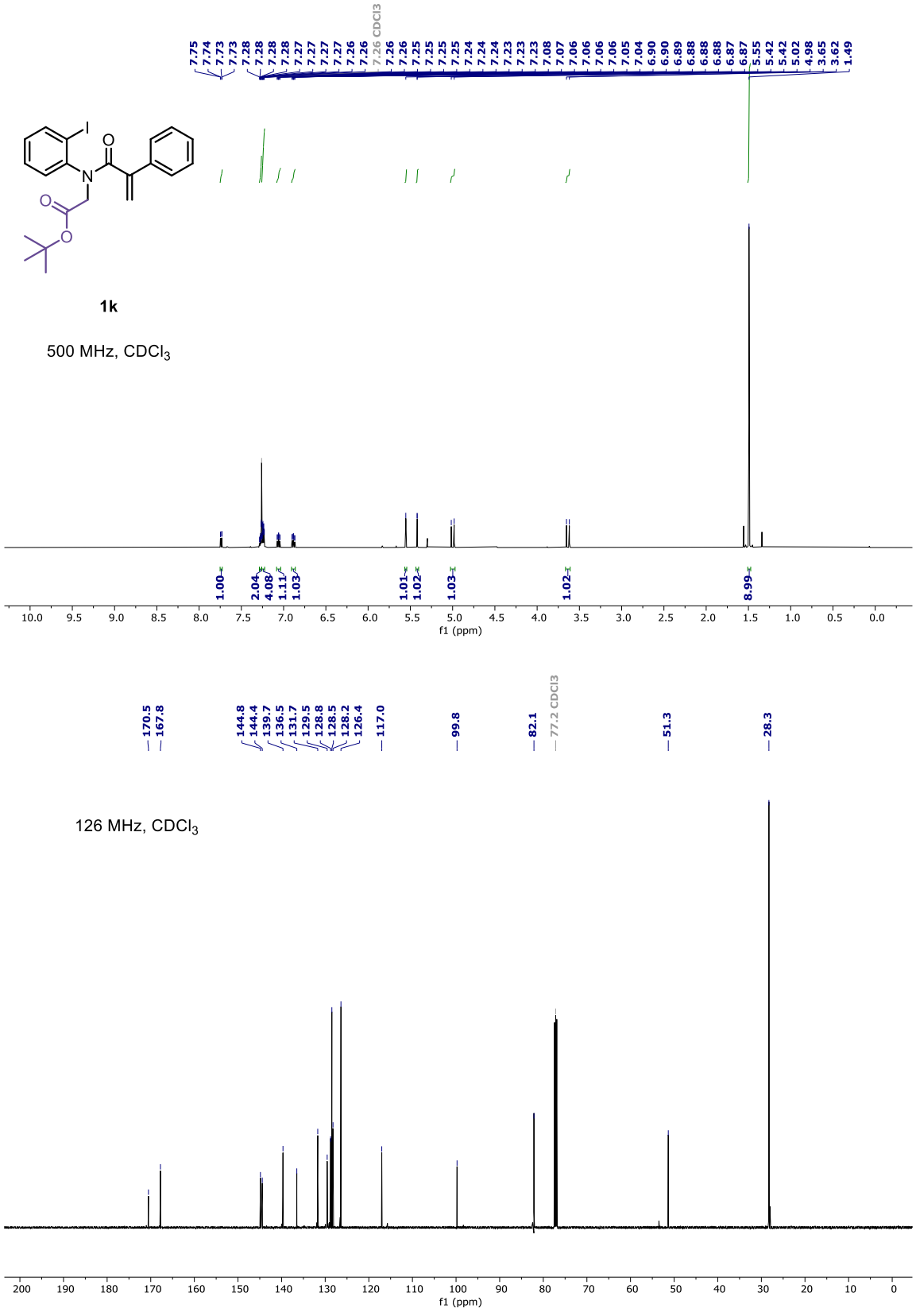
500 MHz, $CDCl_3$

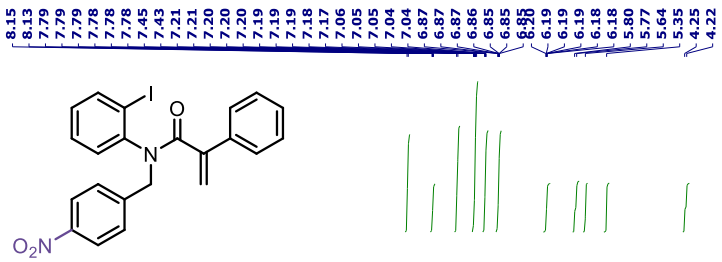




126 MHz, $CDCl_3$

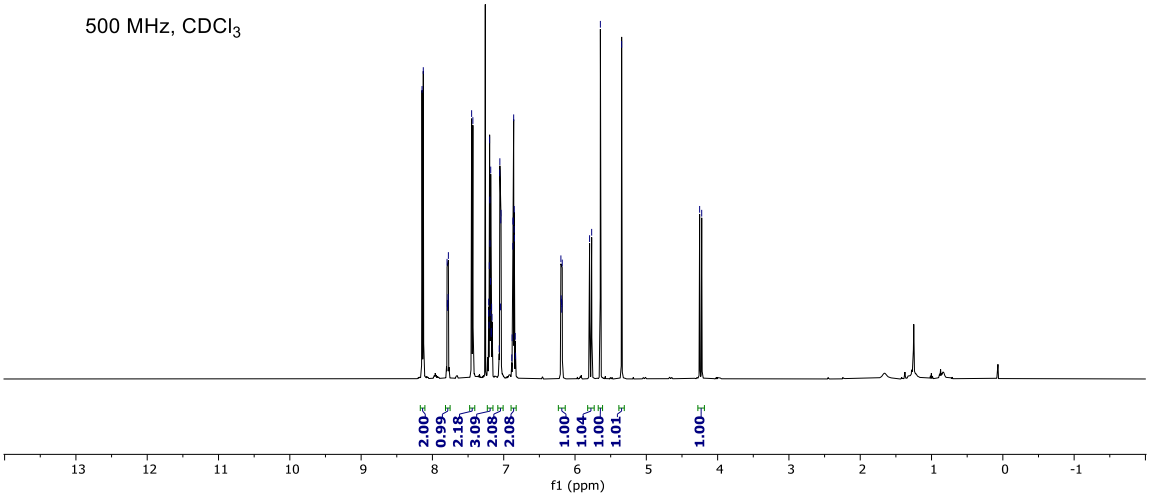

8.16
8.16
8.15
8.15
7.97
7.97
7.96
7.95
7.35
7.33
7.26 CDCl3
7.25
7.22
7.21
7.20
7.19
6.74
6.73
6.73
6.72
5.67
5.43
5.38
5.35
4.91
4.88
I
O
N
N
1h
500 MHz, CDCl3
0.96
0.96
2.05
8.02
1.00
1.02
1.00
1.00
0.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
170.2
155.9
148.9
148.2
145.7
136.9
136.5
129.2
128.3
128.2
128.0
127.5
126.9
123.6
119.9
95.1
77.2 CDCl3
51.6
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

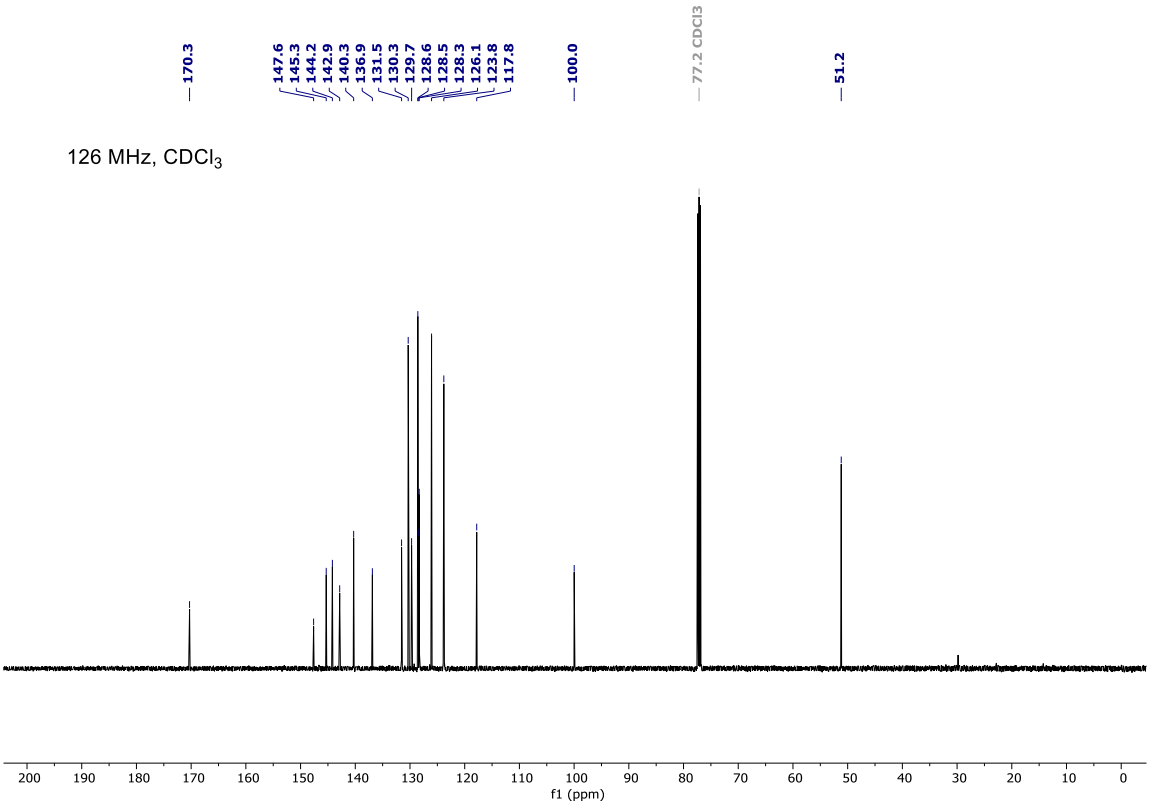

7.75 7.74 7.73 7.73 7.28 7.28 7.28 7.28 7.27 7.27 7.27 7.27 7.26 7.26 7.26 7.26 CDCl3 7.25 7.25 7.25 7.24 7.24 7.24 7.23 7.23 7.23 7.08 7.07 7.06 7.06 7.06 7.06 7.05 7.04 6.90 6.90 6.89 6.88 6.88 6.88 6.87 6.87 5.55 5.42 5.42 5.02 4.98 3.65 3.62 1.49
1k
500 MHz, CDCl3
1.00 2.04 4.08 1.11 1.03 1.01 1.02 1.03 1.02 8.99
f1 (ppm)
170.5 167.8 144.8 144.4 139.7 136.5 131.7 129.5 128.8 128.5 128.2 126.4 117.0 99.8 82.1 77.2 CDCl3 51.3 28.3
126 MHz, CDCl3
f1 (ppm)



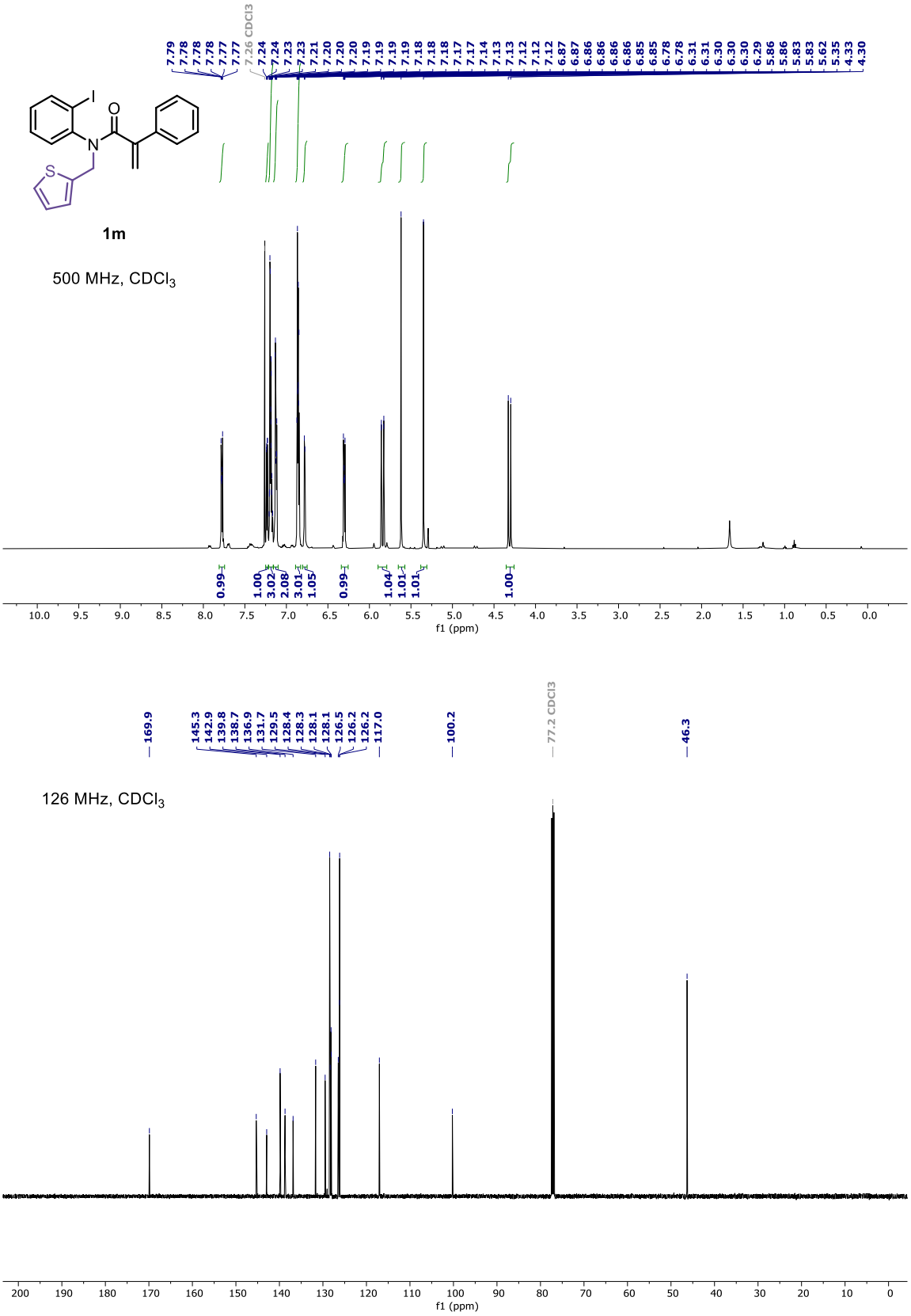
1l

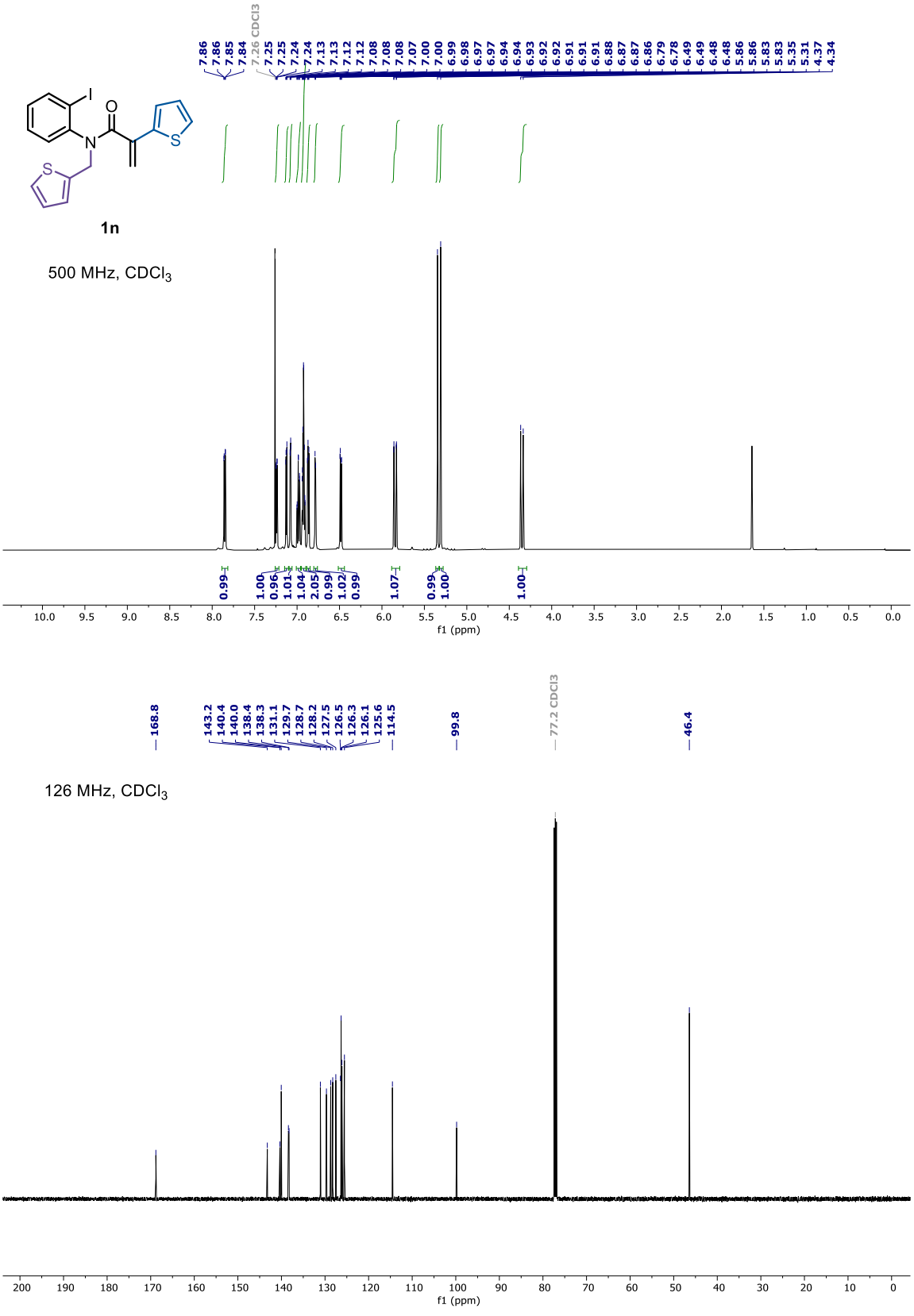
500 MHz, $CDCl_3$

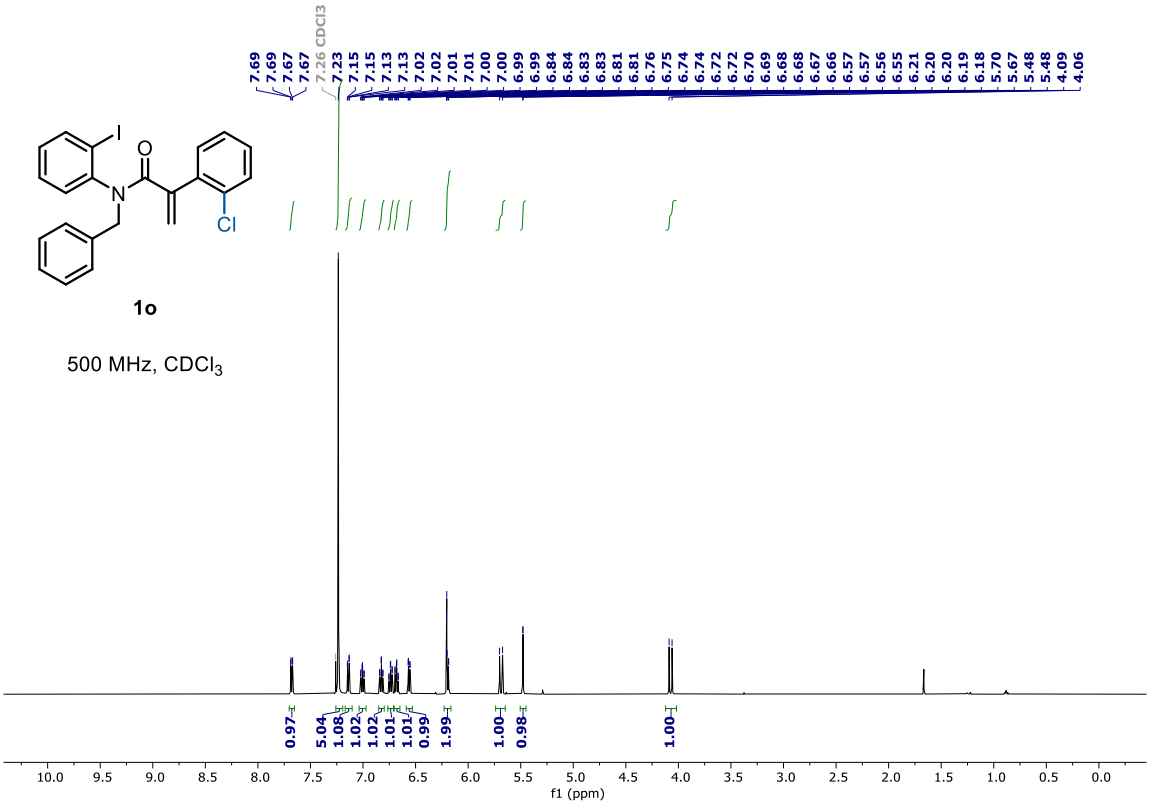


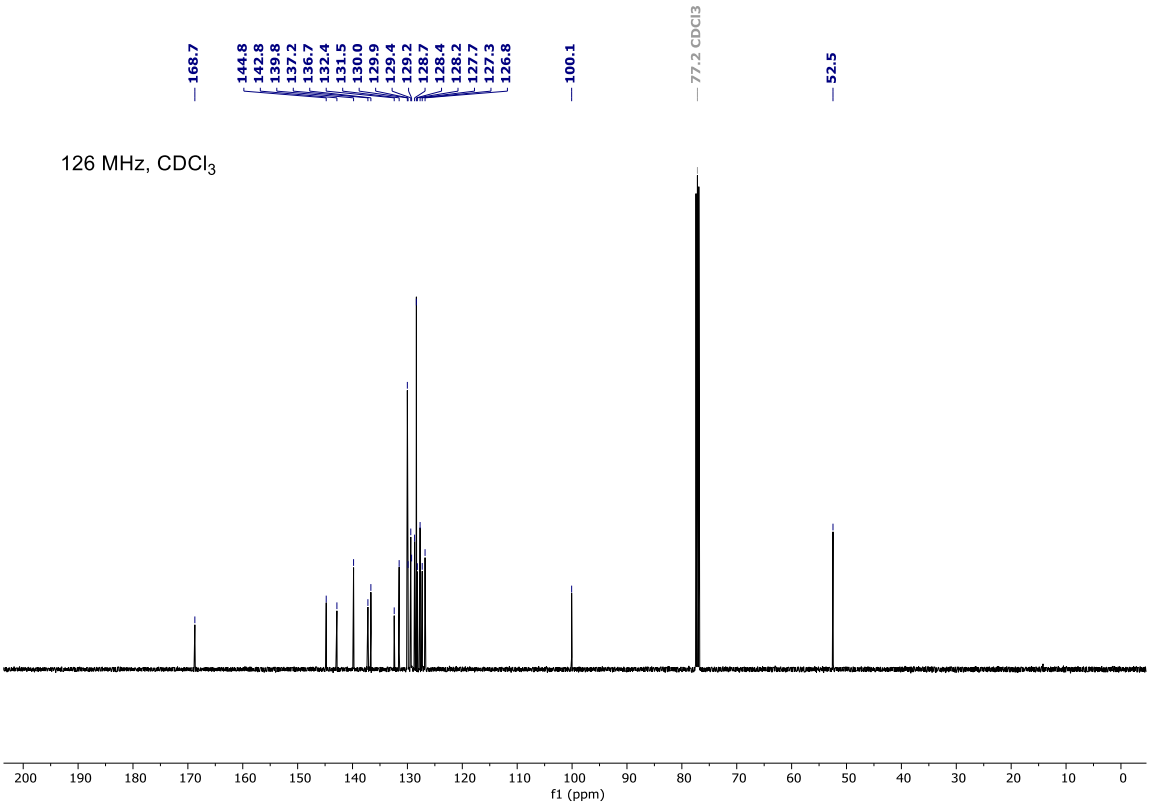


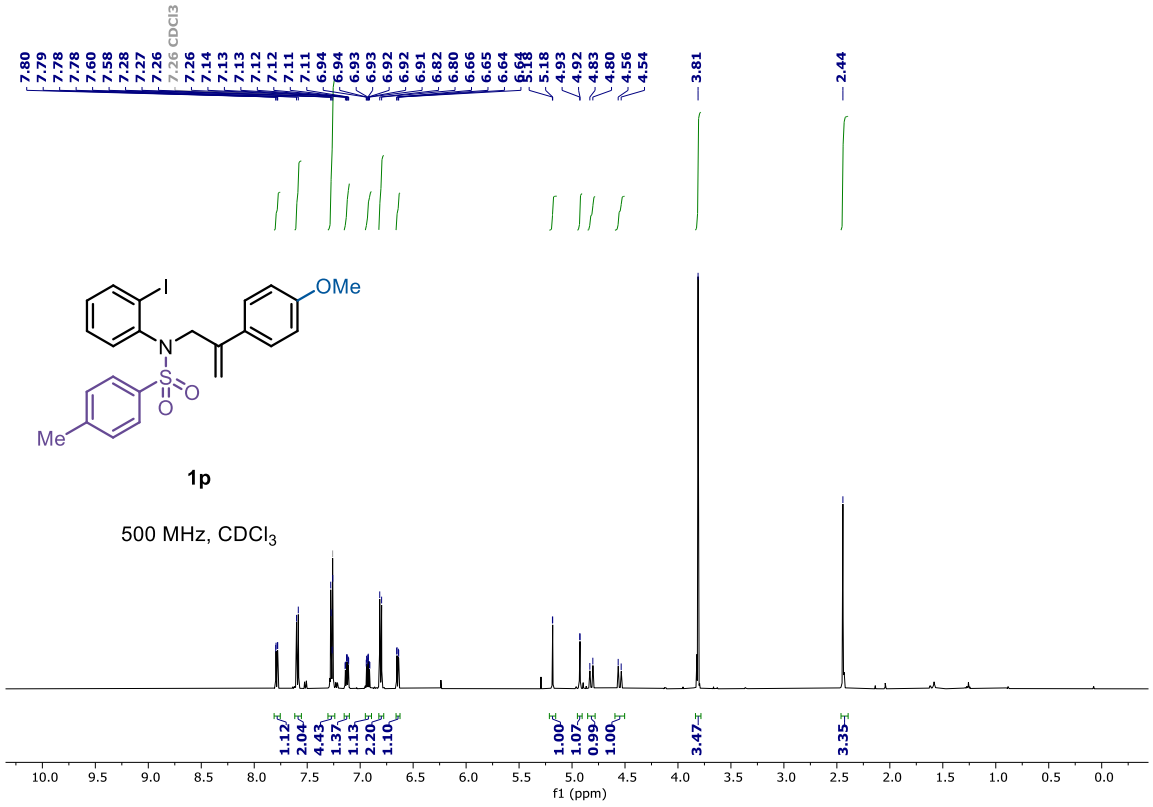
126 MHz, $CDCl_3$

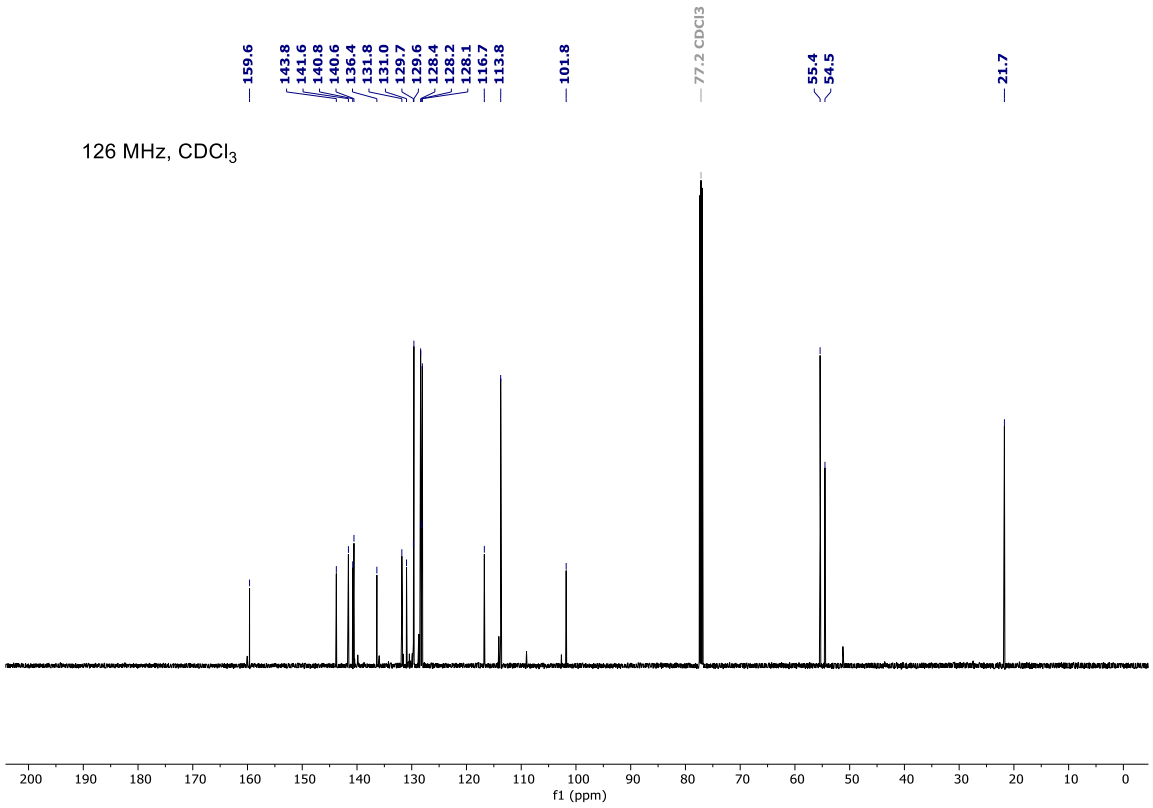

7.79 7.78 7.78 7.78 7.77 7.77 7.26 CDCl3 7.24 7.24 7.23 7.23 7.21 7.20 7.20 7.20 7.19 7.19 7.19 7.19 7.18 7.18 7.18 7.17 7.17 7.14 7.13 7.13 7.12 7.12 7.12 6.87 6.87 6.86 6.86 6.86 6.86 6.85 6.85 6.78 6.78 6.31 6.31 6.30 6.30 6.30 6.29 5.86 5.86 5.83 5.83 5.62 5.35 4.33 4.30
I
O
N
S
1m
500 MHz, CDCl3
0.99 1.00 3.02 2.08 3.01 1.05 0.99 1.04 1.01 1.01 1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
169.9 145.3 142.9 139.8 138.7 136.9 131.7 129.5 128.4 128.3 128.1 128.1 126.5 126.2 126.2 117.0 100.2 77.2 CDCl3 46.3
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

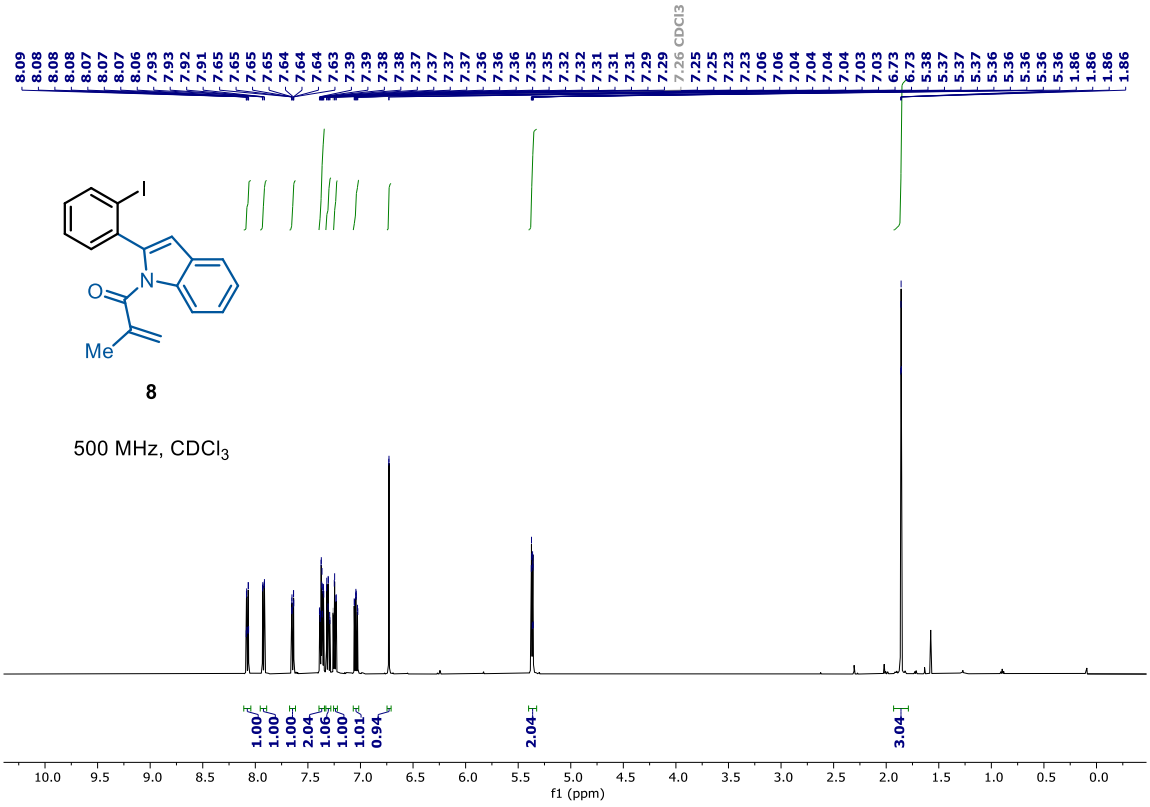

7.86 7.86 7.85 7.84 7.26 CDCl3 7.25 7.25 7.24 7.24 7.13 7.13 7.12 7.12 7.08 7.08 7.08 7.07 7.00 7.00 6.99 6.98 6.97 6.97 6.94 6.94 6.93 6.92 6.92 6.91 6.91 6.91 6.88 6.87 6.87 6.86 6.79 6.78 6.49 6.49 6.48 6.48 5.86 5.86 5.83 5.83 5.35 5.31 4.37 4.34
I
O
N
S
S
1n
500 MHz, CDCl3
0.99 1.00 0.96 1.01 1.04 2.05 0.99 1.02 0.99 1.07 0.99 1.00 1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
168.8 143.2 140.4 140.0 138.4 138.3 131.1 129.7 128.7 128.2 127.5 126.5 126.3 126.1 125.6 114.5 99.8 77.2 CDCl3 46.4
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

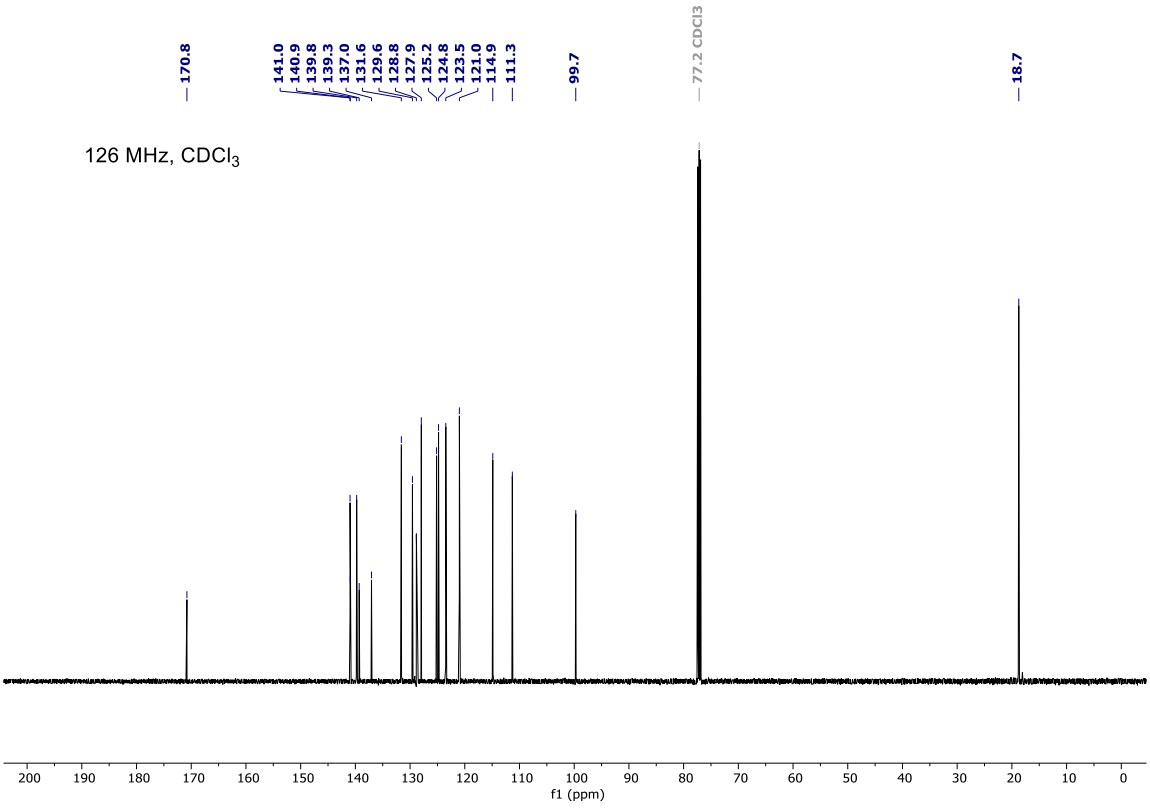

7.69
7.69
7.67
7.67
7.26 CDCl3
7.23
7.15
7.15
7.13
7.13
7.02
7.02
7.01
7.01
7.00
7.00
6.99
6.99
6.84
6.84
6.83
6.83
6.81
6.81
6.76
6.75
6.74
6.74
6.72
6.72
6.70
6.69
6.68
6.68
6.67
6.66
6.57
6.57
6.56
6.55
6.21
6.20
6.20
6.19
6.18
5.70
5.67
5.48
5.48
4.09
4.06
I
O
N
Cl
1o
500 MHz, CDCl3
0.97
5.04
1.08
1.02
1.02
1.01
1.01
0.99
1.99
1.00
0.98
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

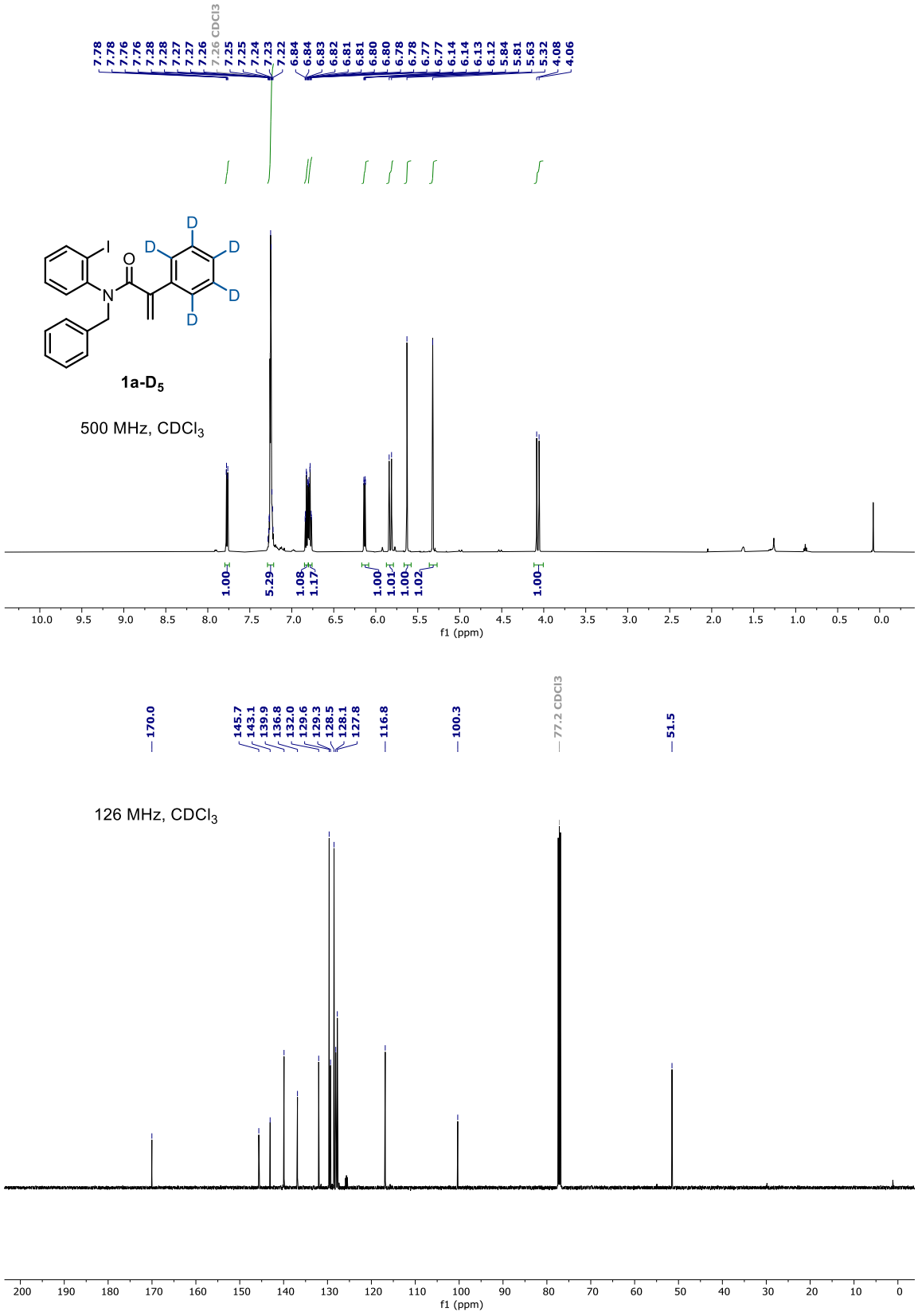

168.7
144.8
142.8
139.8
137.2
136.7
132.4
131.5
130.0
129.9
129.4
129.2
128.7
128.4
128.2
127.7
127.3
126.8
100.1
77.2 CDCl3
52.5
126 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

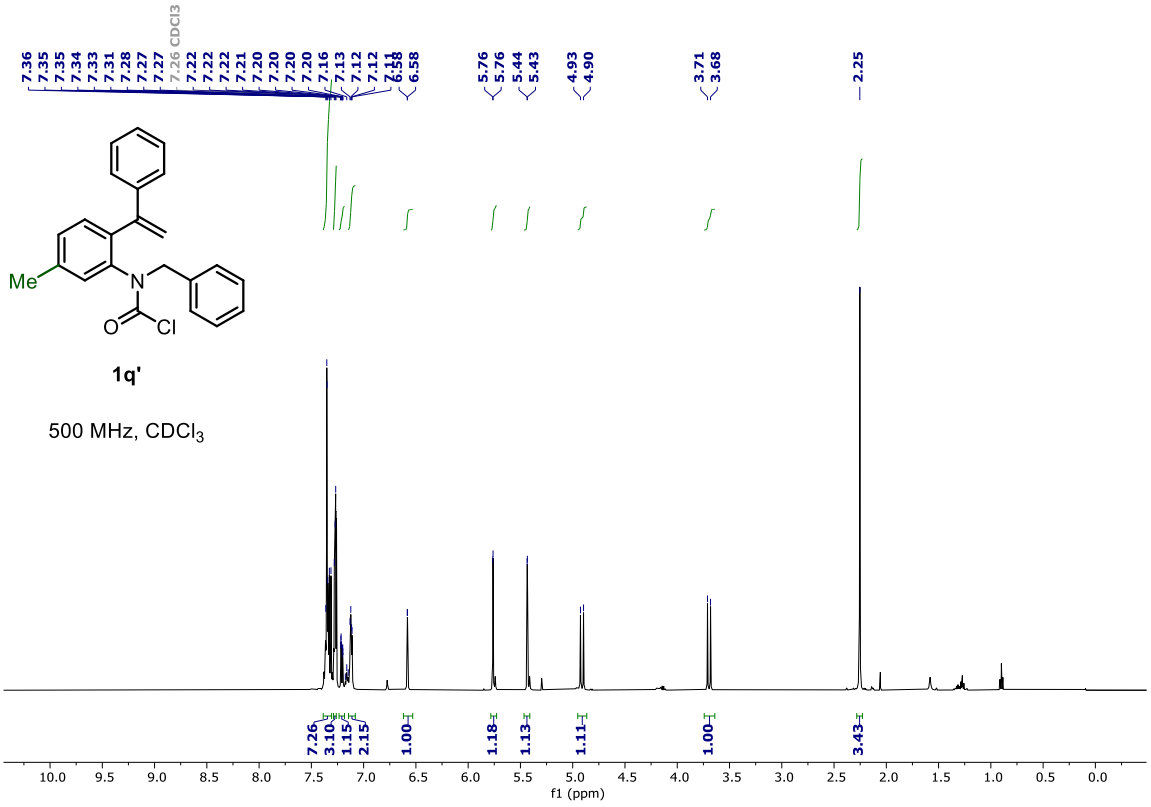

7.80
7.79
7.78
7.78
7.60
7.58
7.28
7.27
7.26 CDCl3
7.26
7.14
7.13
7.12
7.12
7.11
7.11
6.94
6.94
6.93
6.93
6.92
6.92
6.91
6.82
6.80
6.66
6.65
6.64
5.18
4.93
4.92
4.83
4.80
4.56
4.54
3.81
2.44
I
OMe
N
S
O
O
Me
1p
500 MHz, CDCl3
1.12
2.04
4.43
1.37
1.13
2.20
1.10
1.00
1.07
0.99
1.00
3.47
3.35
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

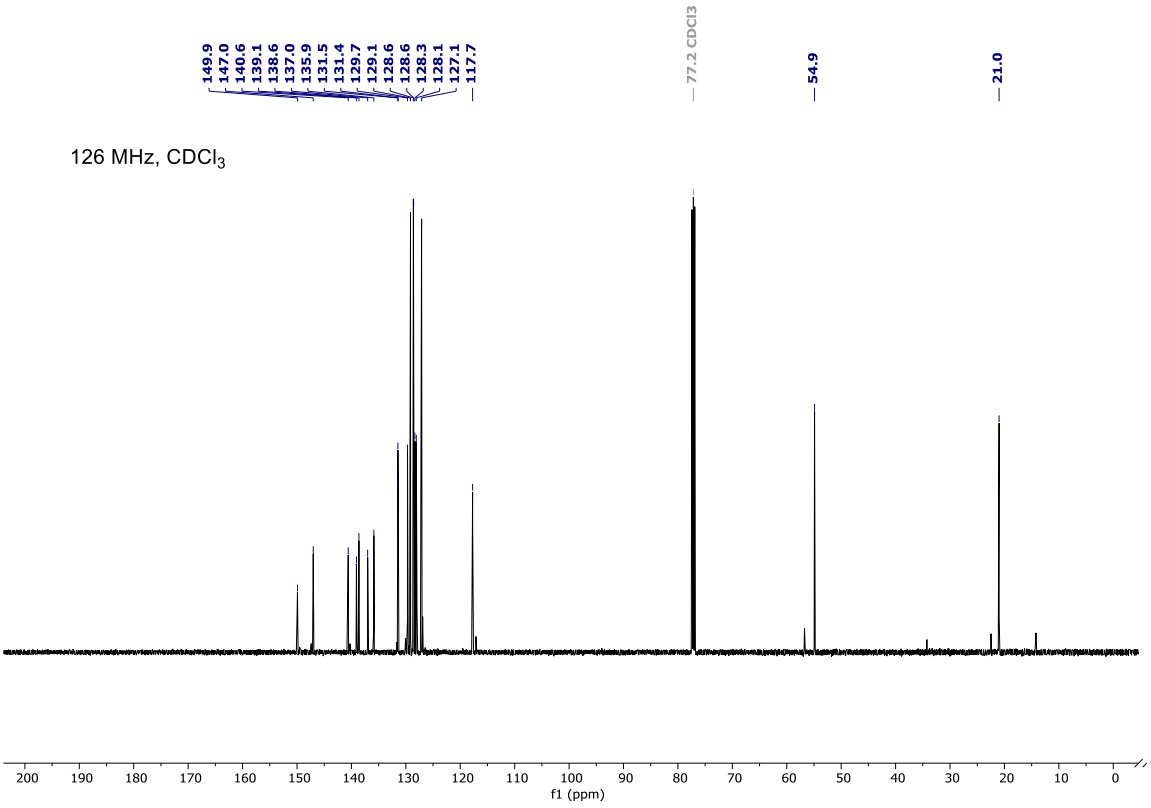

159.6
143.8
141.6
140.8
140.6
136.4
131.8
131.0
129.7
129.6
128.4
128.2
128.1
116.7
113.8
101.8
77.2 CDCl3
55.4
54.5
21.7
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

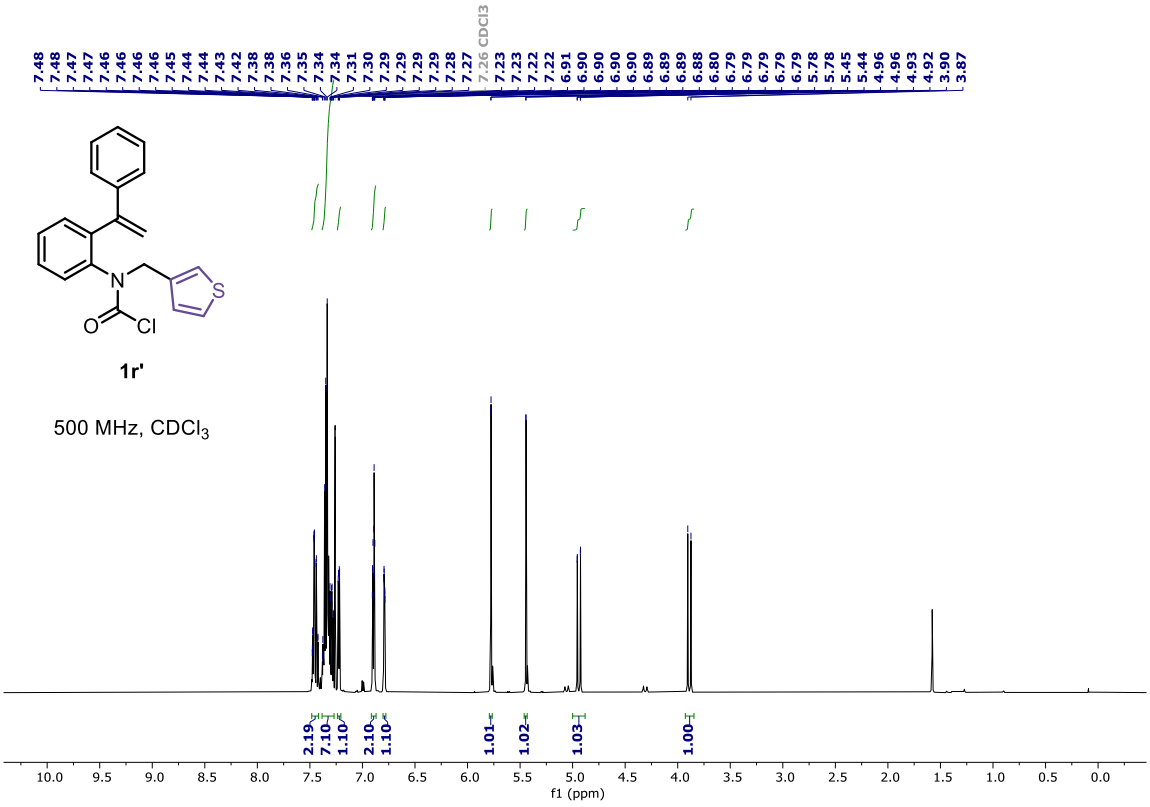

8.09 8.08 8.08 8.08 8.07 8.07 8.07 8.06 7.93 7.93 7.92 7.91 7.65 7.65 7.65 7.64 7.64 7.64 7.63 7.39 7.39 7.38 7.38 7.37 7.37 7.37 7.37 7.36 7.36 7.36 7.35 7.32 7.31 7.31 7.31 7.29 7.29 7.26 CDCl3 7.25 7.25 7.23 7.23 7.06 7.06 7.04 7.04 7.04 7.04 7.03 7.03 6.73 5.38 5.37 5.37 5.37 5.36 5.36 5.36 5.36 1.86 1.86 1.86 1.86
I
N
O
Me
8
500 MHz, CDCl3
1.00 1.00 1.00 2.04 1.06 1.00 1.01 0.94 2.04 3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

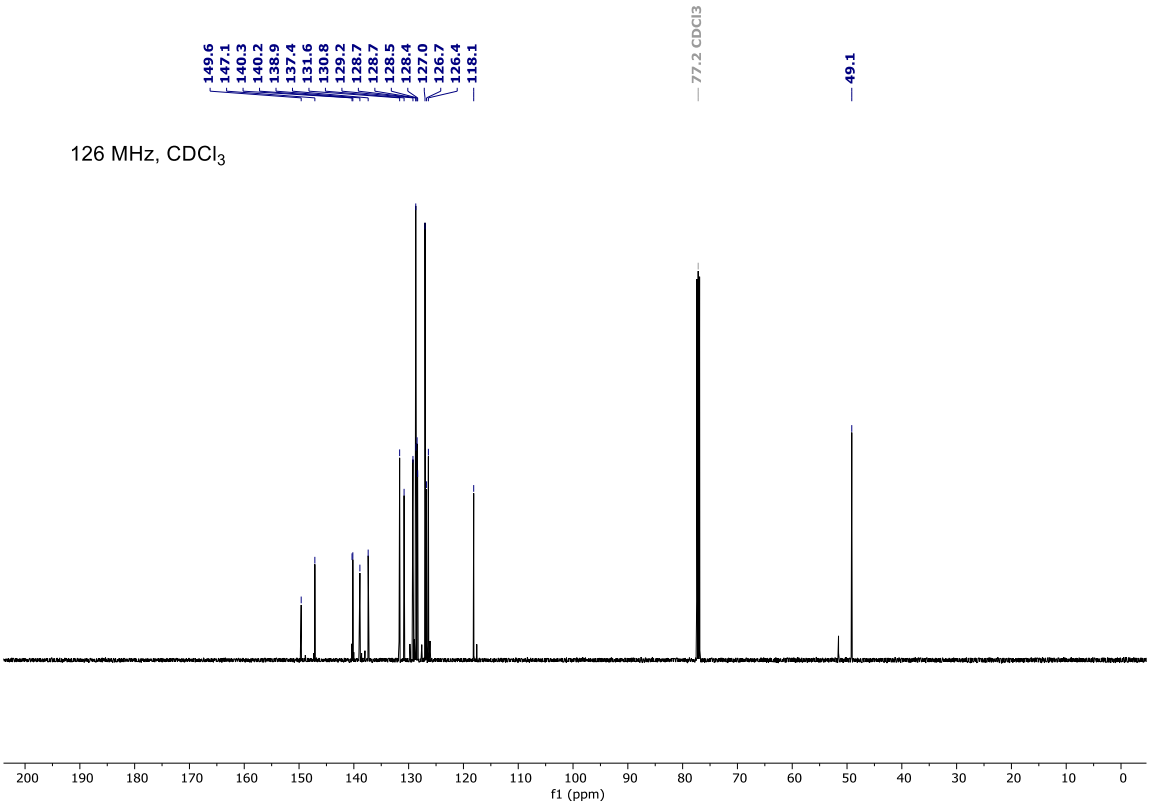

170.8 141.0 140.9 139.8 139.3 137.0 131.6 129.6 128.8 127.9 125.2 124.8 123.5 121.0 114.9 111.3 99.7 77.2 CDCl3 18.7
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

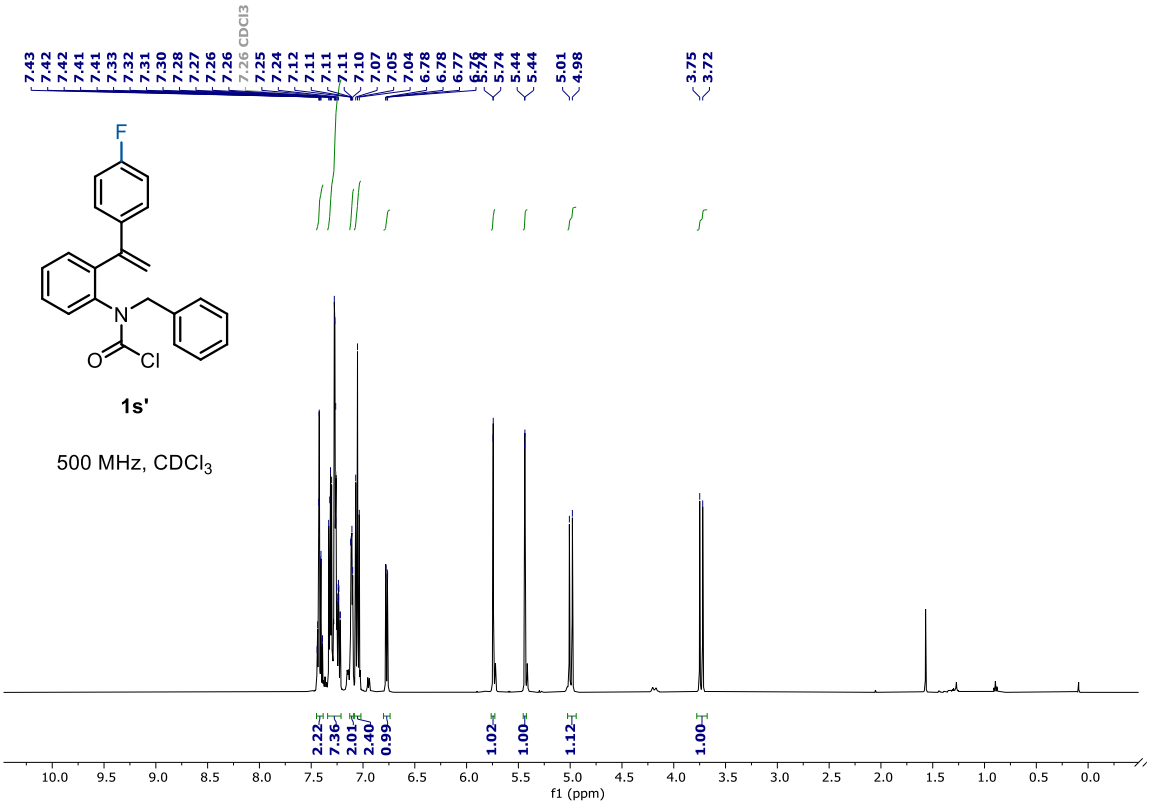

7.78
7.78
7.76
7.76
7.28
7.28
7.27
7.27
7.26
7.26 CDCl3
7.25
7.25
7.24
7.23
7.22
6.84
6.84
6.83
6.82
6.81
6.81
6.80
6.80
6.78
6.78
6.77
6.77
6.14
6.14
6.13
6.12
5.84
5.81
5.63
5.32
4.08
4.06
D
D
D
D
D
I
O
N
1a-D5
500 MHz, CDCl3
1.00
5.29
1.08
1.17
1.00
1.01
1.00
1.02
1.00
f1 (ppm)
170.0
145.7
143.1
139.9
136.8
132.0
129.6
129.3
128.5
128.1
127.8
116.8
100.3
77.2 CDCl3
51.5
126 MHz, CDCl3
f1 (ppm)

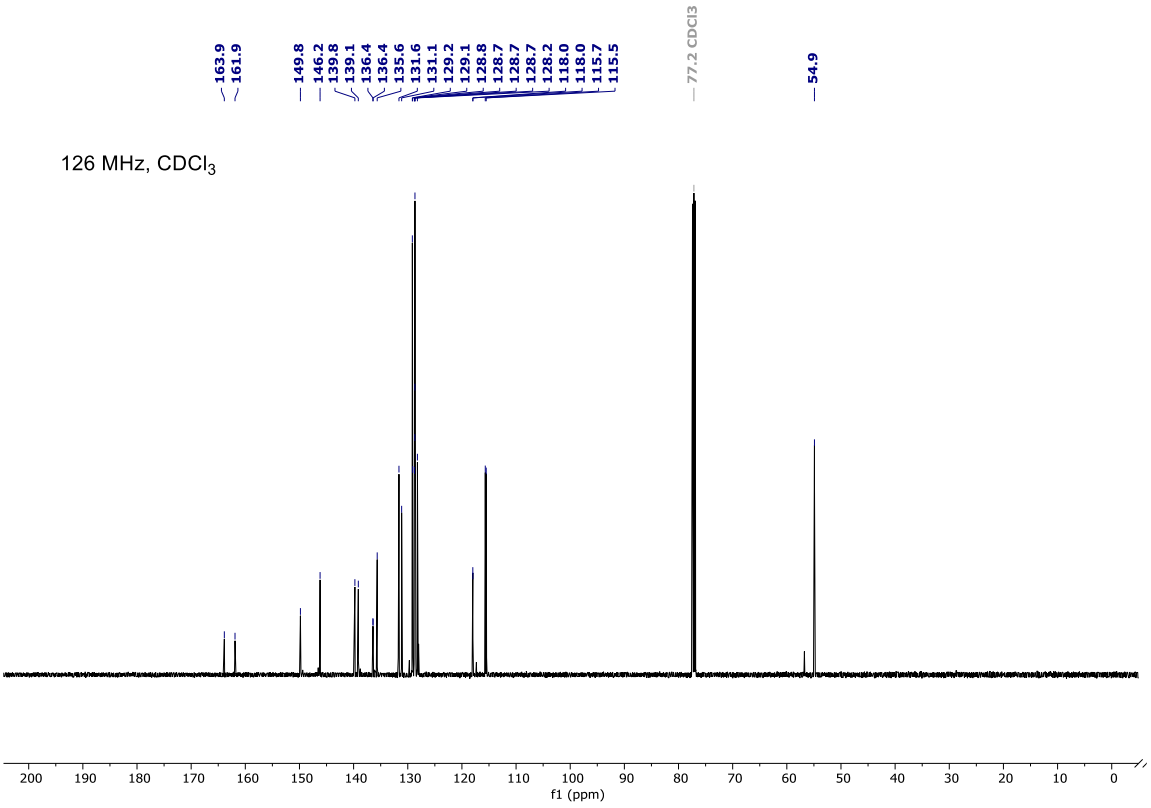

7.36
7.35
7.35
7.34
7.33
7.31
7.28
7.27
7.27
7.26 CDCl3
7.22
7.22
7.22
7.21
7.20
7.20
7.20
7.20
7.16
7.13
7.12
7.12
7.11
6.58
6.58
5.76
5.76
5.44
5.43
4.93
4.90
3.71
3.68
2.25
Me
N
O
Cl
1q'
500 MHz, CDCl3
7.26
3.10
1.15
2.15
1.00
1.18
1.13
1.11
1.00
3.43
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


149.9
147.0
140.6
139.1
138.6
137.0
135.9
131.5
131.4
129.7
129.1
128.6
128.6
128.3
128.1
127.1
117.7
77.2 CDCl3
54.9
21.0
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

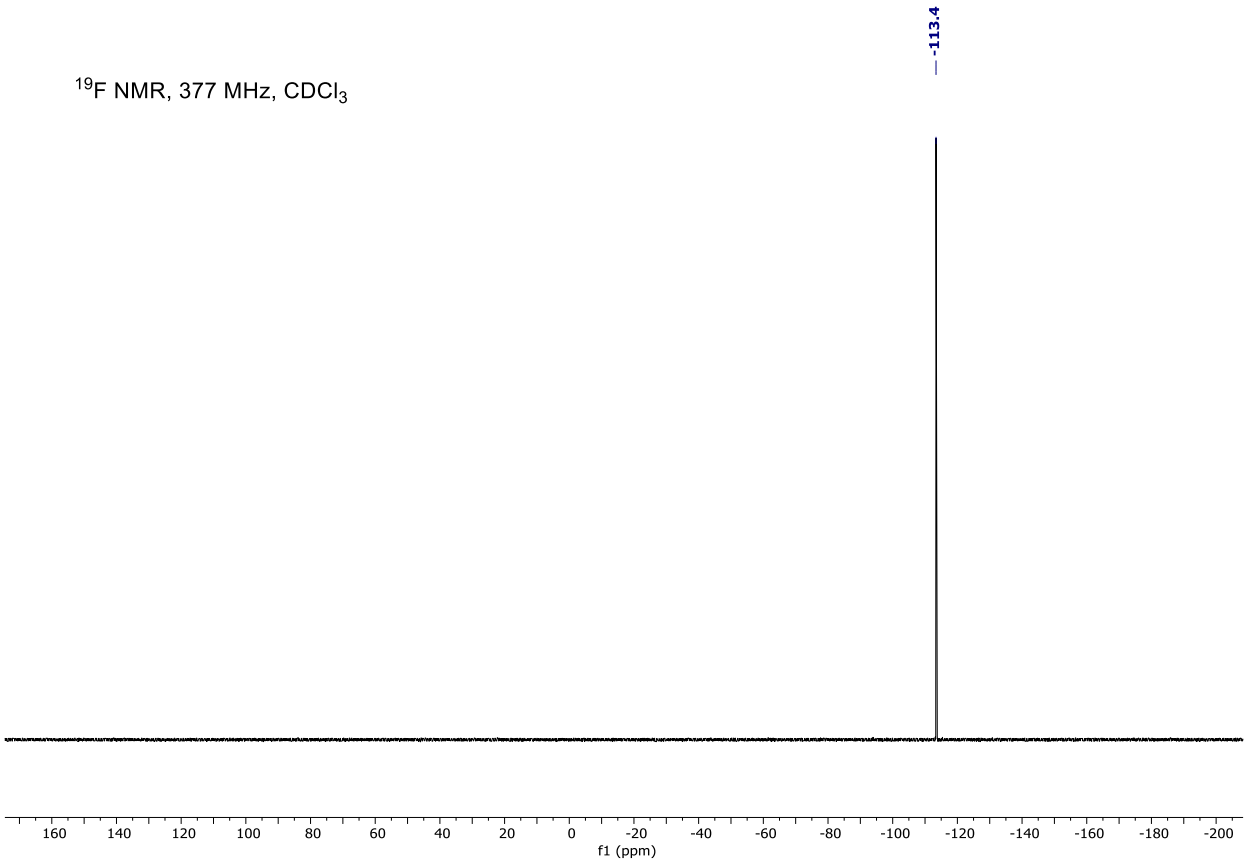

7.48 7.48 7.47 7.47 7.46 7.46 7.46 7.45 7.44 7.44 7.43 7.42 7.38 7.38 7.36 7.35 7.34 7.34 7.31 7.30 7.29 7.29 7.29 7.29 7.28 7.27 7.26 CDCl3 7.23 7.23 7.22 7.22 6.91 6.90 6.90 6.90 6.90 6.89 6.89 6.89 6.88 6.80 6.79 6.79 6.79 6.79 5.78 5.78 5.45 5.44 4.96 4.96 4.93 4.92 3.90 3.87
N
O
Cl
S
1r'
500 MHz, CDCl3
2.19 7.10 1.10 2.10 1.10 1.01 1.02 1.03 1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

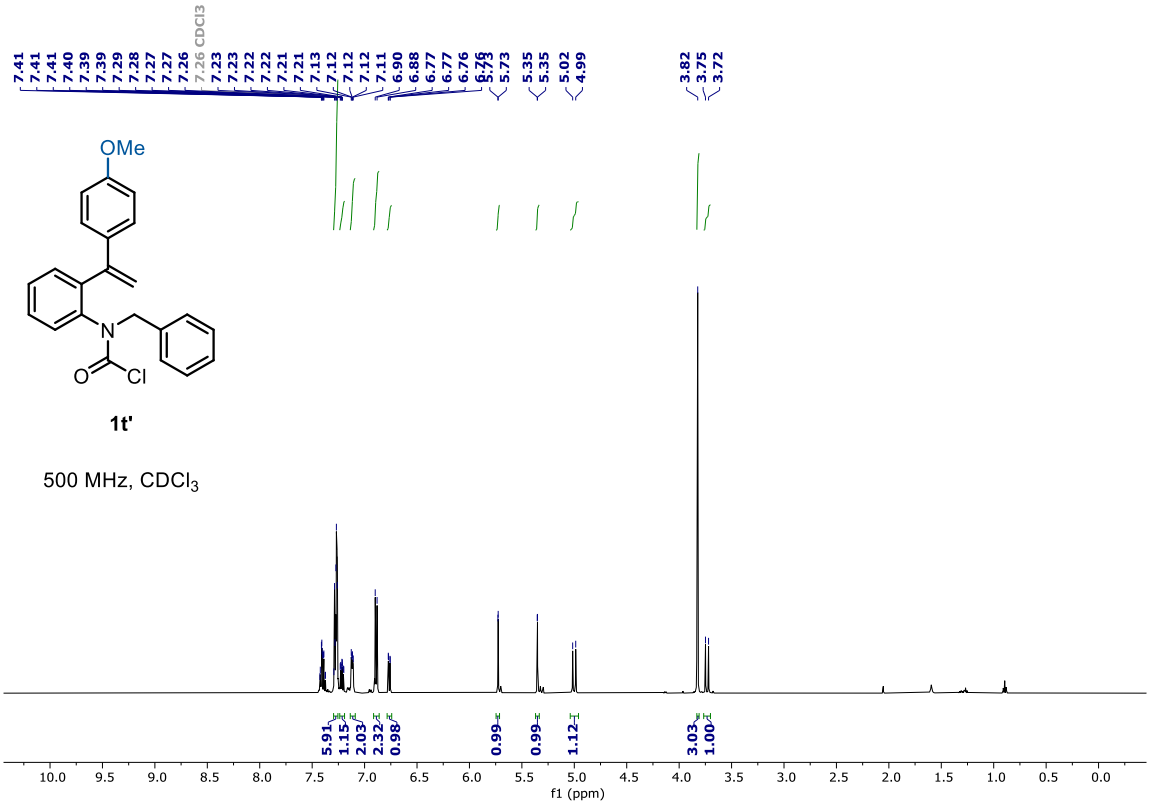

149.6 147.1 140.3 140.2 138.9 137.4 131.6 130.8 129.2 128.7 128.7 128.5 128.4 127.0 126.7 126.4 118.1
77.2 CDCl3
49.1
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.43
7.42
7.42
7.41
7.41
7.33
7.32
7.31
7.30
7.28
7.27
7.26
7.26 CDCl3
7.25
7.24
7.12
7.11
7.11
7.11
7.10
7.07
7.05
7.04
6.78
6.78
6.77
5.74
5.74
5.44
5.44
5.01
4.98
3.75
3.72
F
N
O
Cl
1s'
500 MHz, CDCl3
2.22
7.36
2.01
2.40
0.99
1.02
1.00
1.12
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


163.9
161.9
149.8
146.2
139.8
139.1
136.4
136.4
135.6
131.6
131.1
129.2
129.1
128.8
128.7
128.7
128.7
128.2
118.0
118.0
115.7
115.5
77.2 CDCl3
54.9
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

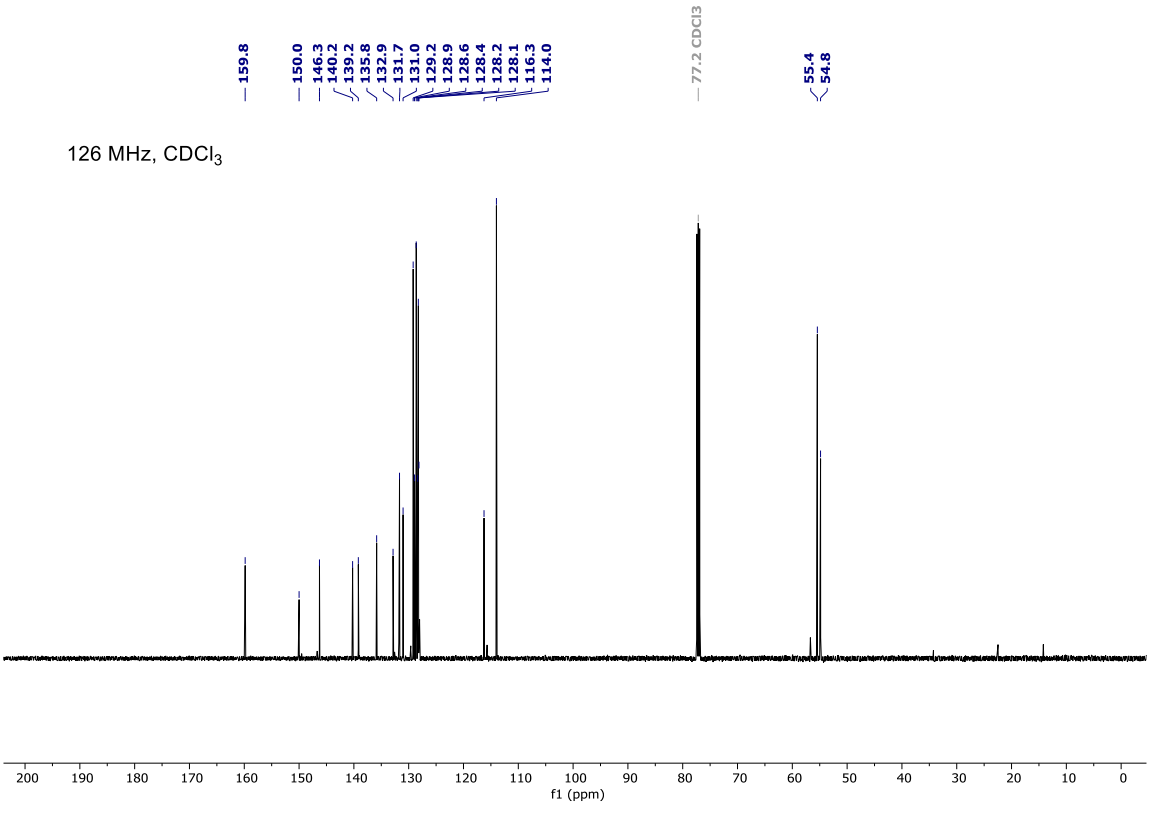
^{19}F NMR, 377 MHz, $CDCl_3$



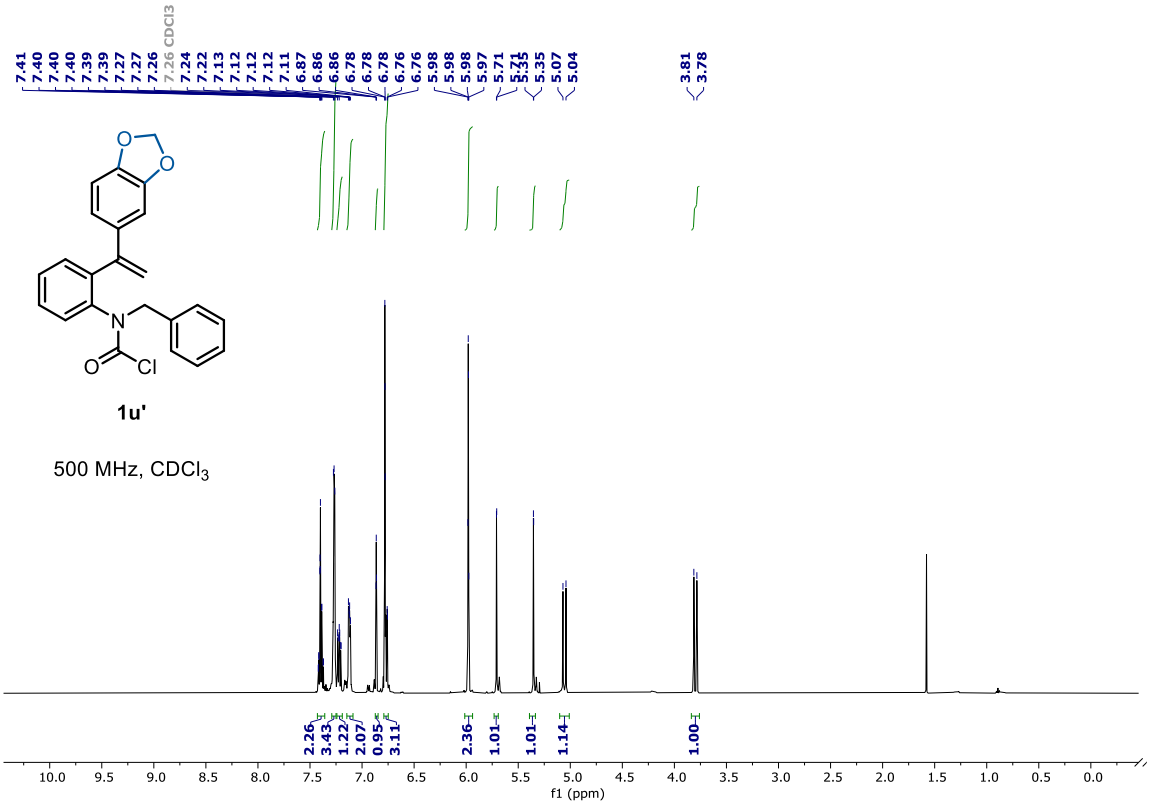


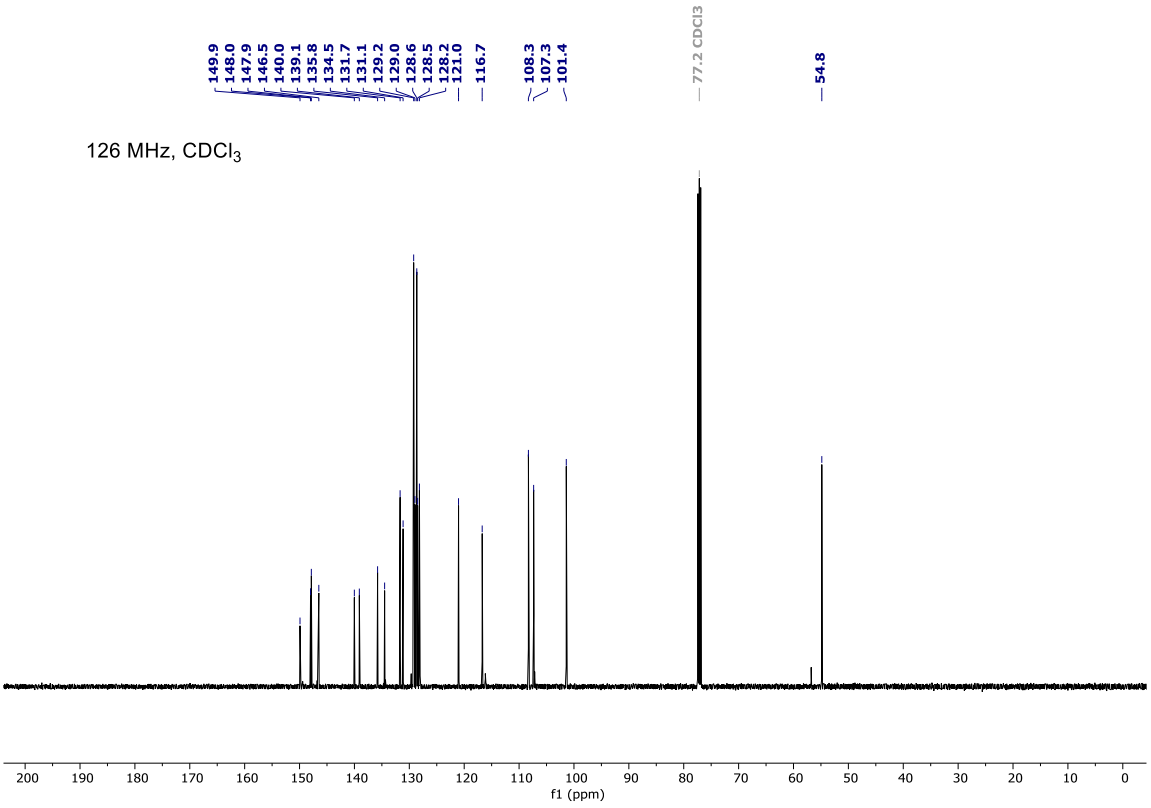
1t'

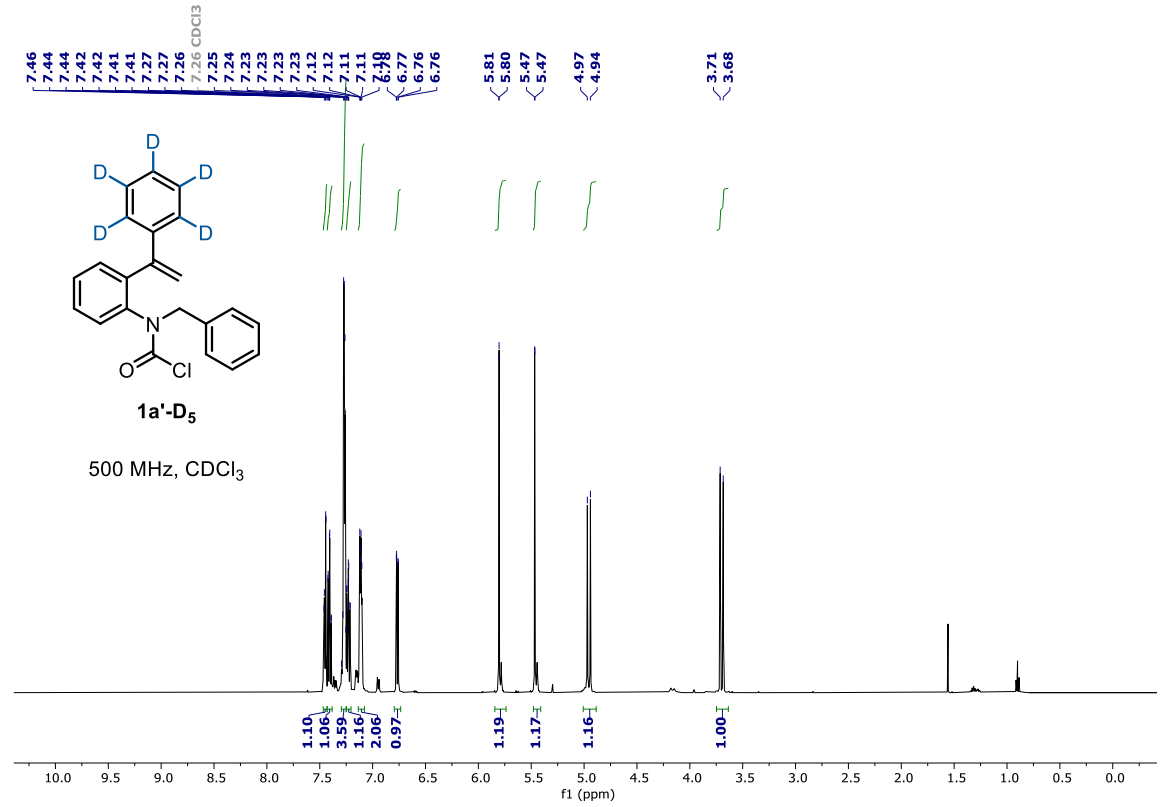
500 MHz, $CDCl_3$

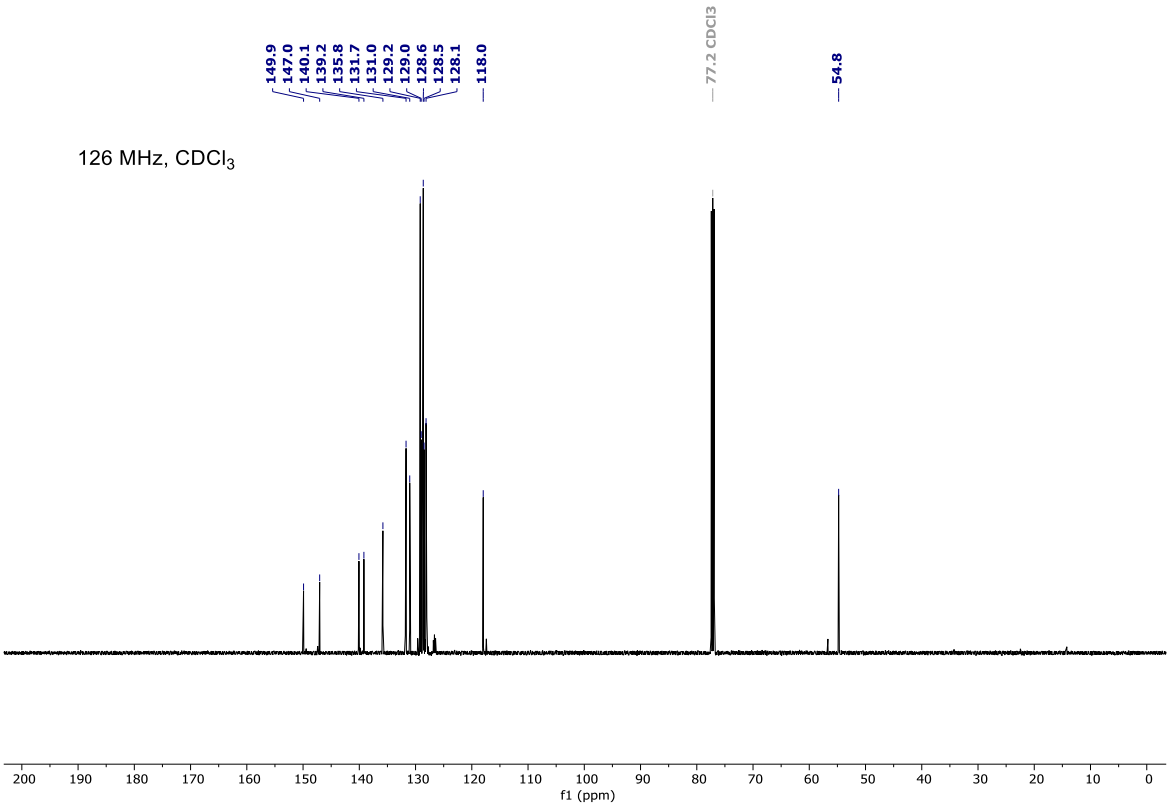


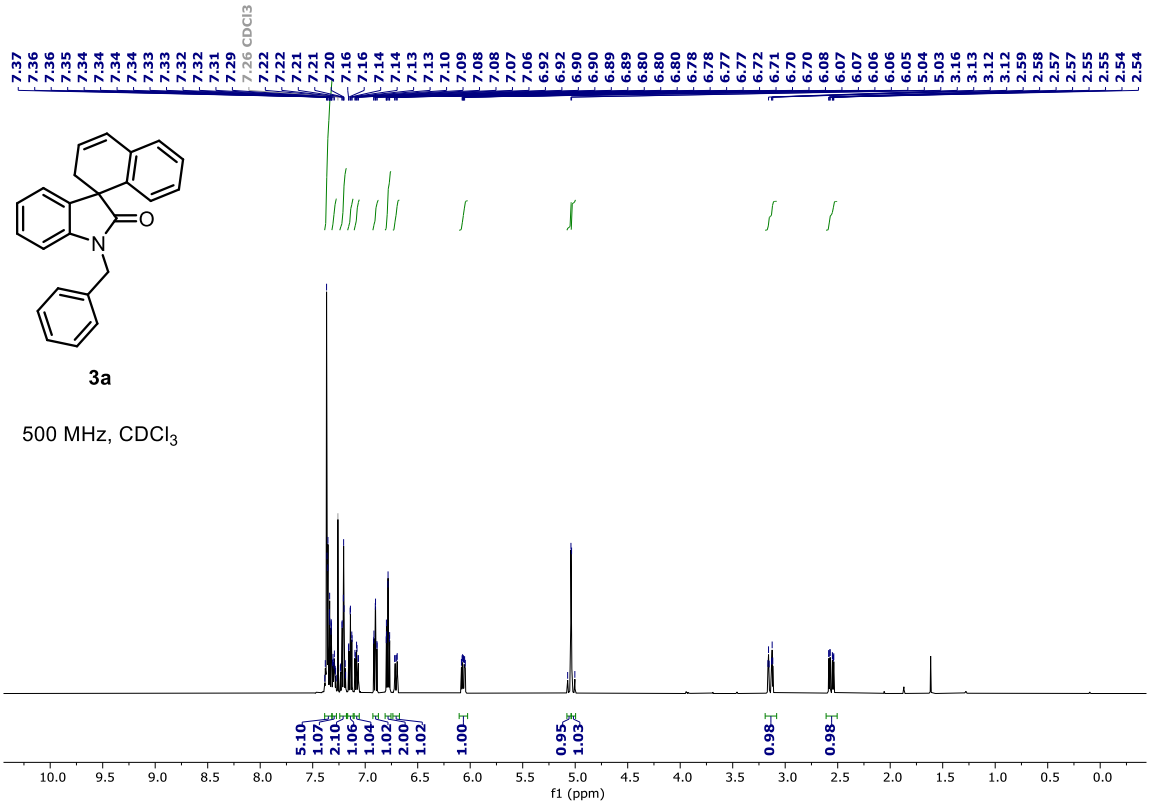
126 MHz, $CDCl_3$

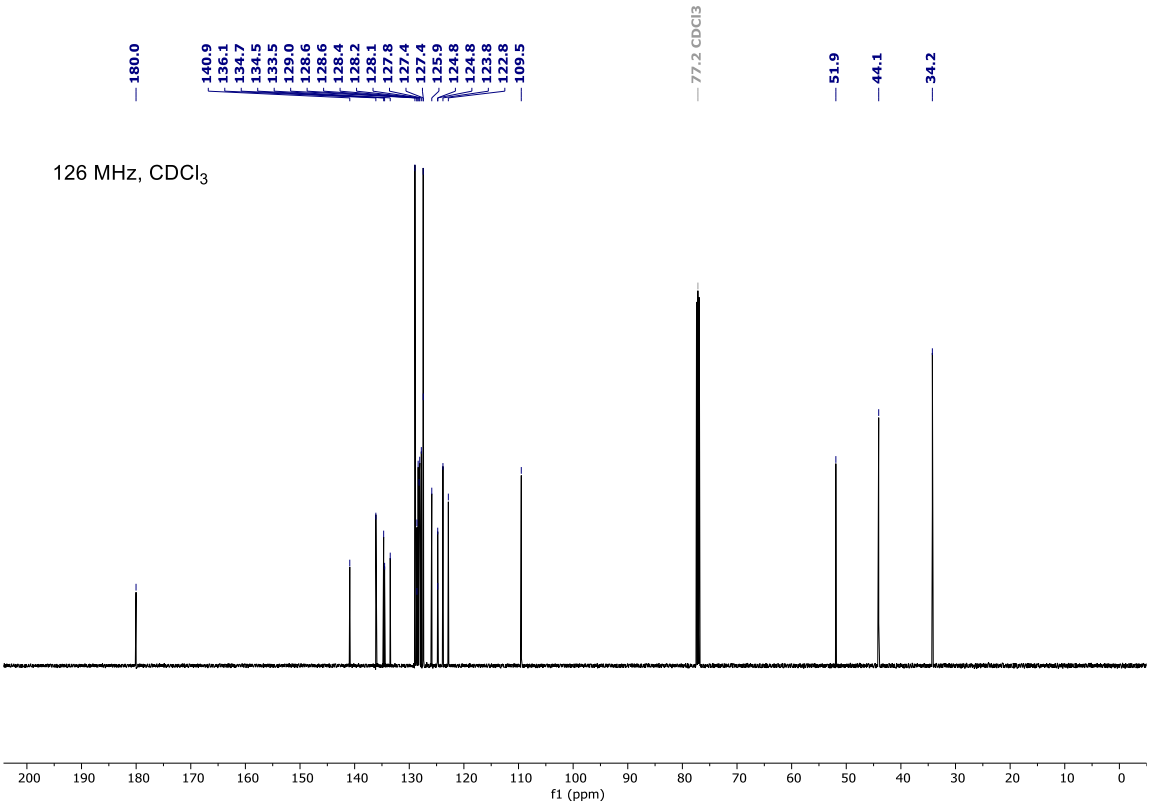

7.41 7.40 7.40 7.40 7.39 7.39 7.27 7.27 7.26 7.26 CDCl3 7.24 7.22 7.13 7.12 7.12 7.12 7.11 6.87 6.86 6.86 6.78 6.78 6.78 6.76 6.76 5.98 5.98 5.97 5.71 5.35 5.07 5.04 3.81 3.78
O
O
N
O
Cl
1u'
500 MHz, CDCl3
2.26 3.43 1.22 2.07 0.95 3.11 2.36 1.01 1.01 1.14 1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

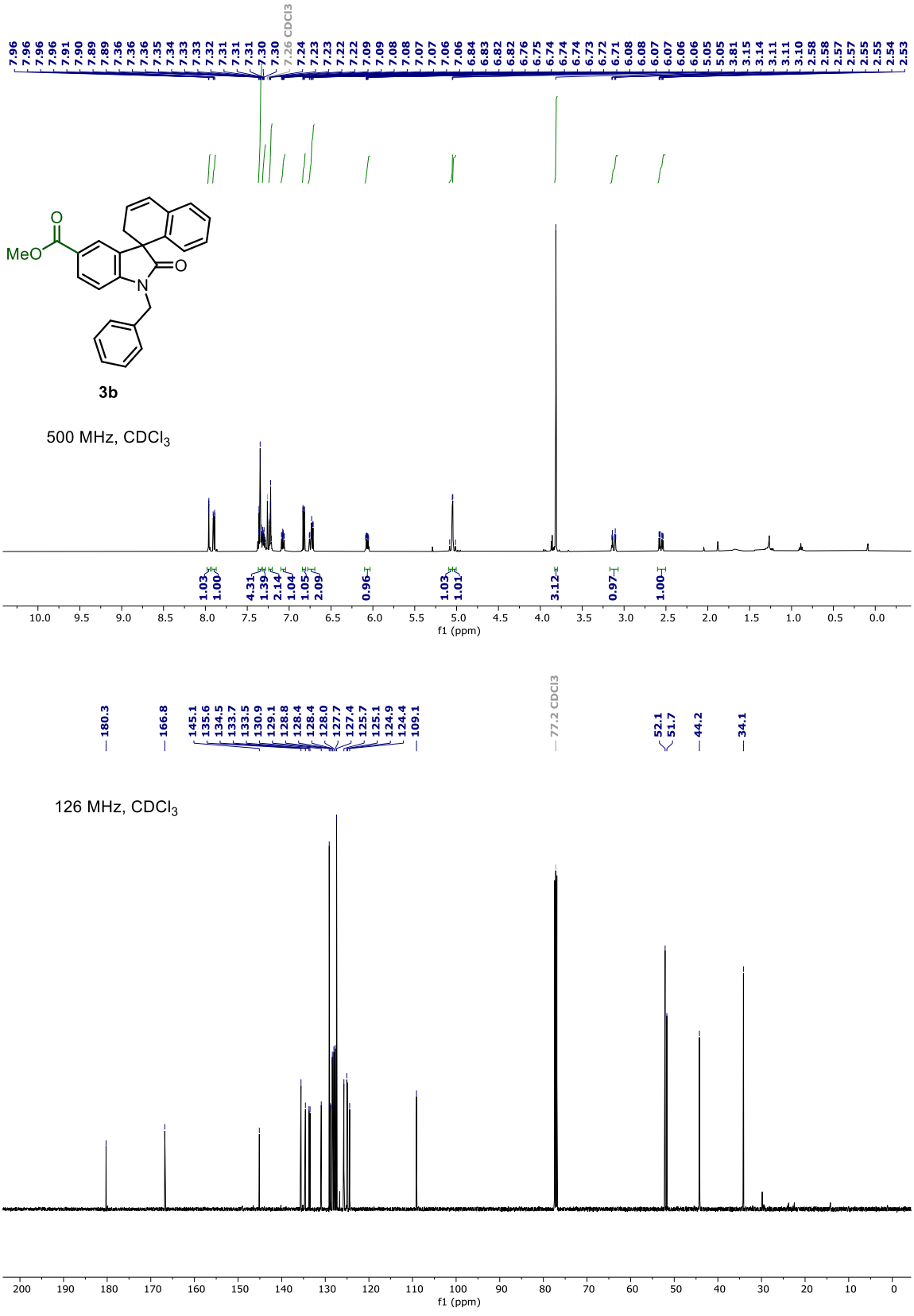

149.9 148.0 147.9 146.5 140.0 139.1 135.8 134.5 131.7 131.1 129.2 129.0 128.6 128.5 128.2 121.0 116.7 108.3 107.3 101.4 77.2 CDCl3 54.8
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

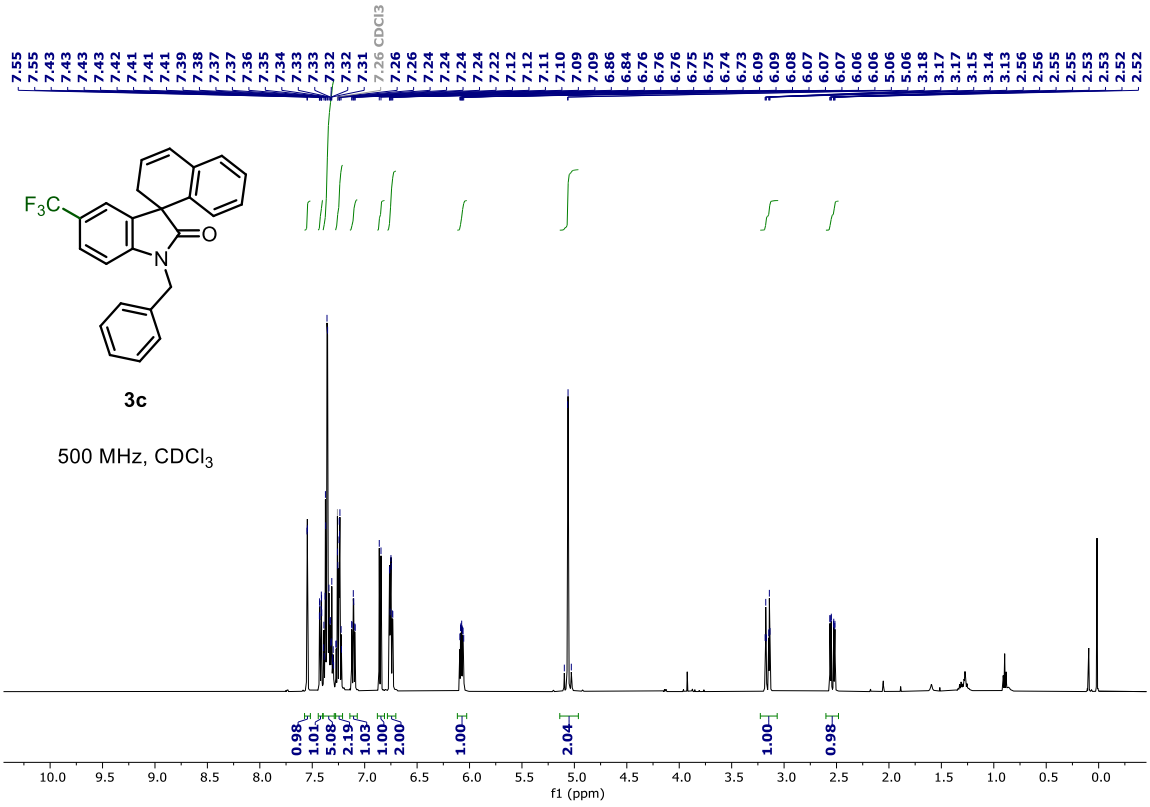

7.46
7.44
7.44
7.42
7.42
7.41
7.41
7.27
7.27
7.26
7.26 CDCl3
7.25
7.24
7.23
7.23
7.23
7.12
7.12
7.11
7.11
6.78
6.77
6.76
6.76
5.81
5.80
5.47
5.47
4.97
4.94
3.71
3.68
D
D
D
D
D
N
O
Cl
1a'-D5
500 MHz, CDCl3
1.10
1.06
3.59
1.16
2.06
0.97
1.19
1.17
1.16
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


149.9
147.0
140.1
139.2
135.8
131.7
131.0
129.2
129.0
128.6
128.5
128.1
118.0
77.2 CDCl3
54.8
126 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.37 7.36 7.36 7.35 7.34 7.34 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.29 7.26 CDCl3 7.22 7.22 7.21 7.21 7.20 7.16 7.16 7.14 7.14 7.13 7.13 7.10 7.09 7.08 7.08 7.07 7.06 6.92 6.92 6.90 6.90 6.89 6.89 6.80 6.80 6.80 6.78 6.78 6.77 6.77 6.72 6.71 6.70 6.70 6.08 6.07 6.07 6.06 6.06 6.05 5.04 5.03 3.16 3.13 3.12 3.12 2.59 2.58 2.57 2.57 2.55 2.54 2.54
O
N
3a
500 MHz, CDCl3
5.10 1.07 2.10 1.06 1.04 1.02 2.00 1.02 1.00 0.95 1.03 0.98 0.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

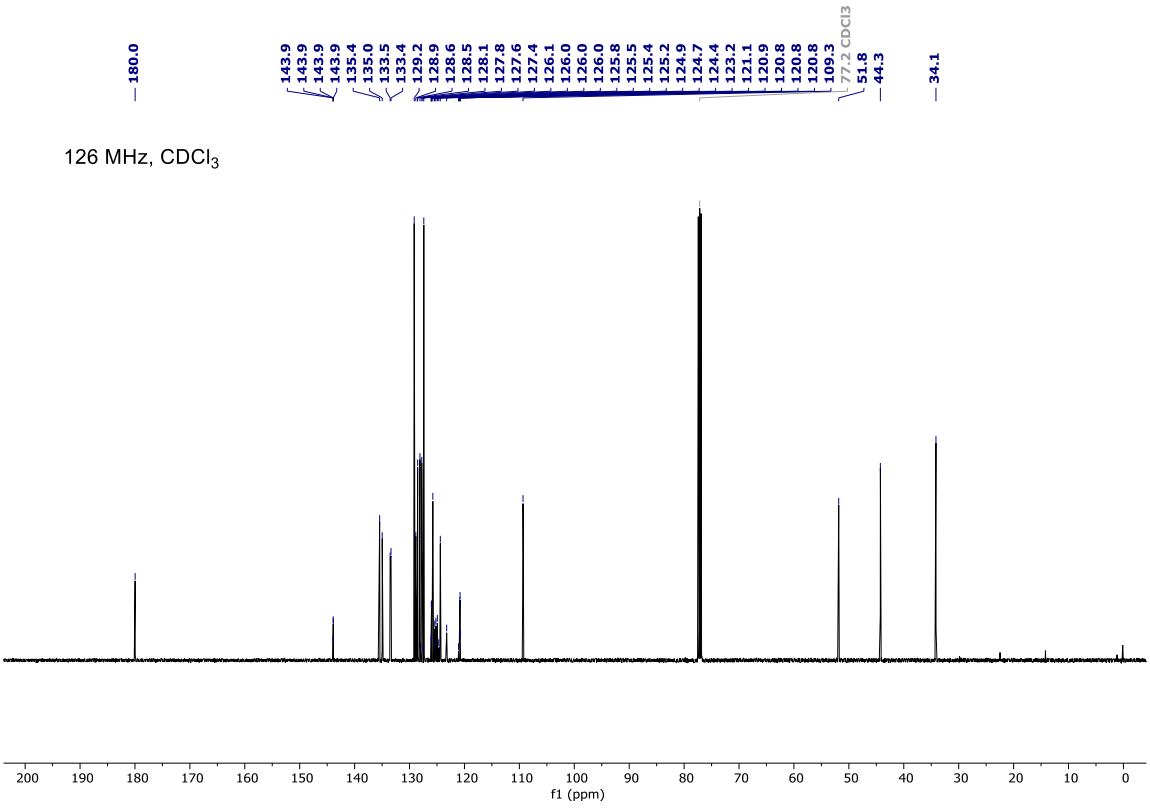

180.0
140.9 136.1 134.7 134.5 133.5 129.0 128.6 128.6 128.4 128.2 128.1 127.8 127.4 127.4 125.9 124.8 124.8 123.8 122.8 109.5
77.2 CDCl3
51.9
44.1
34.2
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.96 7.96 7.96 7.96 7.91 7.90 7.89 7.89 7.36 7.36 7.35 7.34 7.33 7.33 7.32 7.31 7.31 7.31 7.30 7.30 CDCl3 7.26 7.24 7.23 7.23 7.22 7.22 7.09 7.09 7.08 7.08 7.07 7.07 7.06 7.06 6.84 6.83 6.82 6.82 6.76 6.75 6.74 6.74 6.74 6.73 6.72 6.71 6.08 6.08 6.07 6.07 6.06 6.06 5.05 5.05 3.81 3.15 3.14 3.11 3.11 3.10 2.58 2.58 2.57 2.57 2.55 2.54 2.53
MeO
O
O
N
3b
500 MHz, CDCl3
1.03 1.00 4.31 1.39 2.14 1.04 1.05 2.09 0.96 1.03 1.01 3.12 0.97 1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
180.3 166.8 145.1 135.6 134.5 133.7 133.5 130.9 129.1 128.8 128.4 128.4 128.0 127.7 127.4 125.7 125.1 124.9 124.4 109.1 77.2 CDCl3 52.1 51.7 44.2 34.1
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



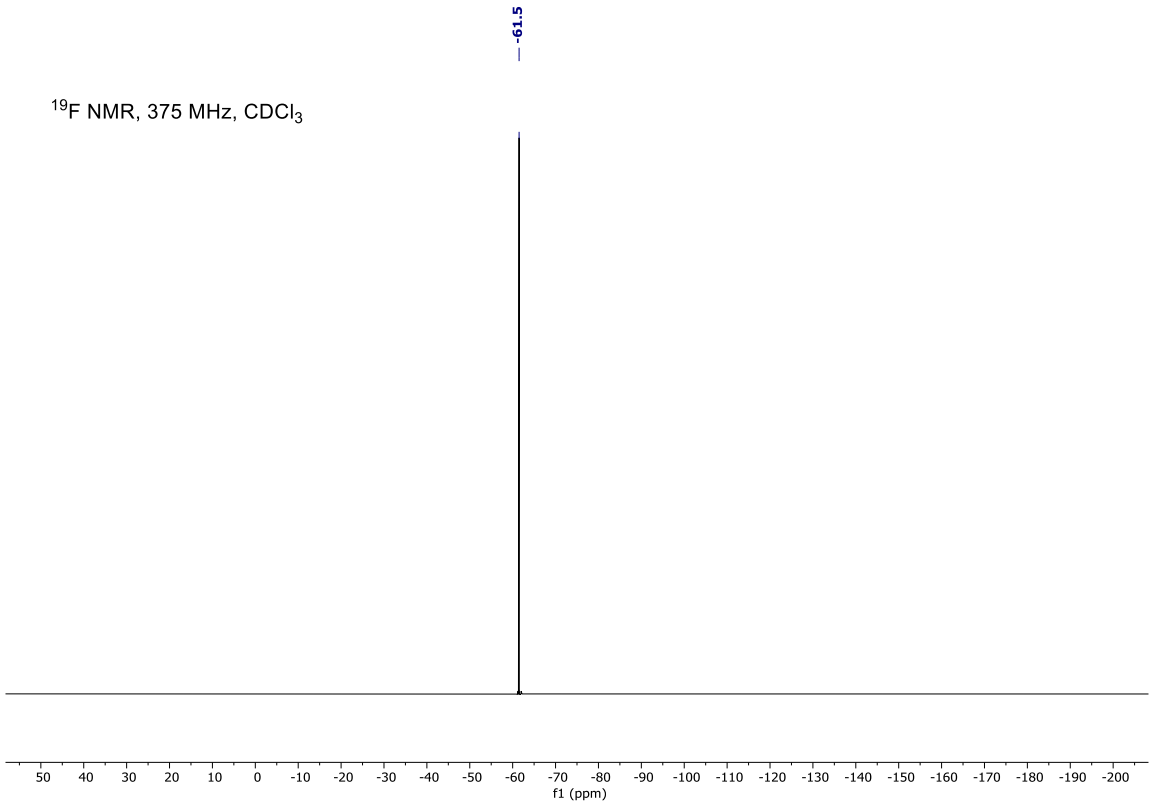
3c

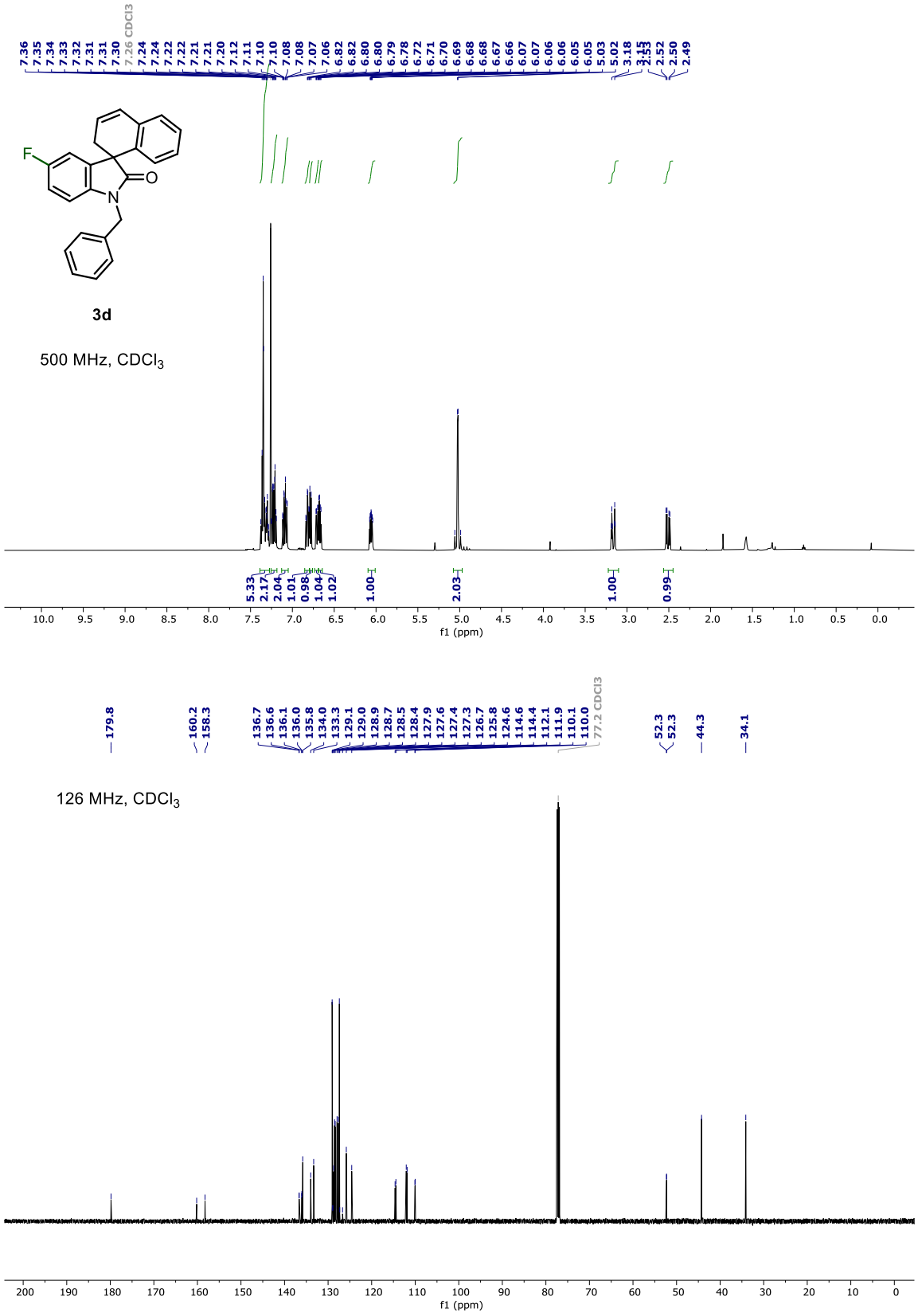
500 MHz, $CDCl_3$



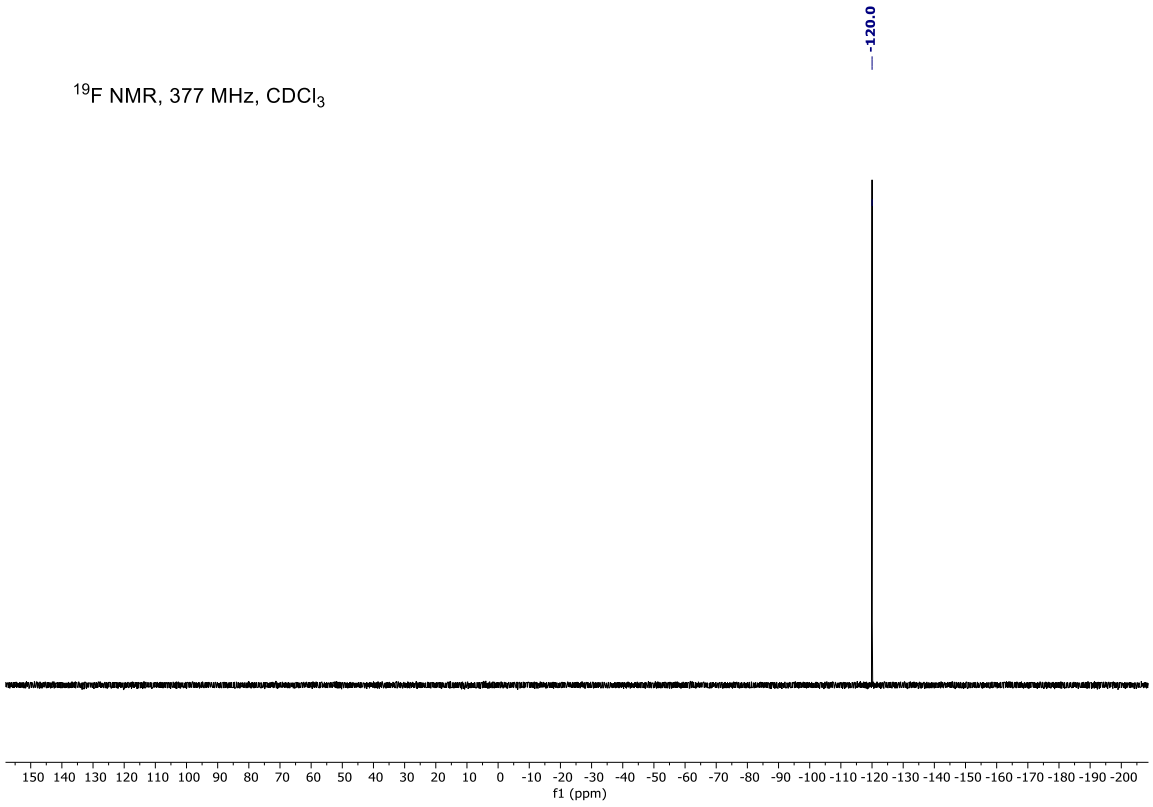
126 MHz, $CDCl_3$

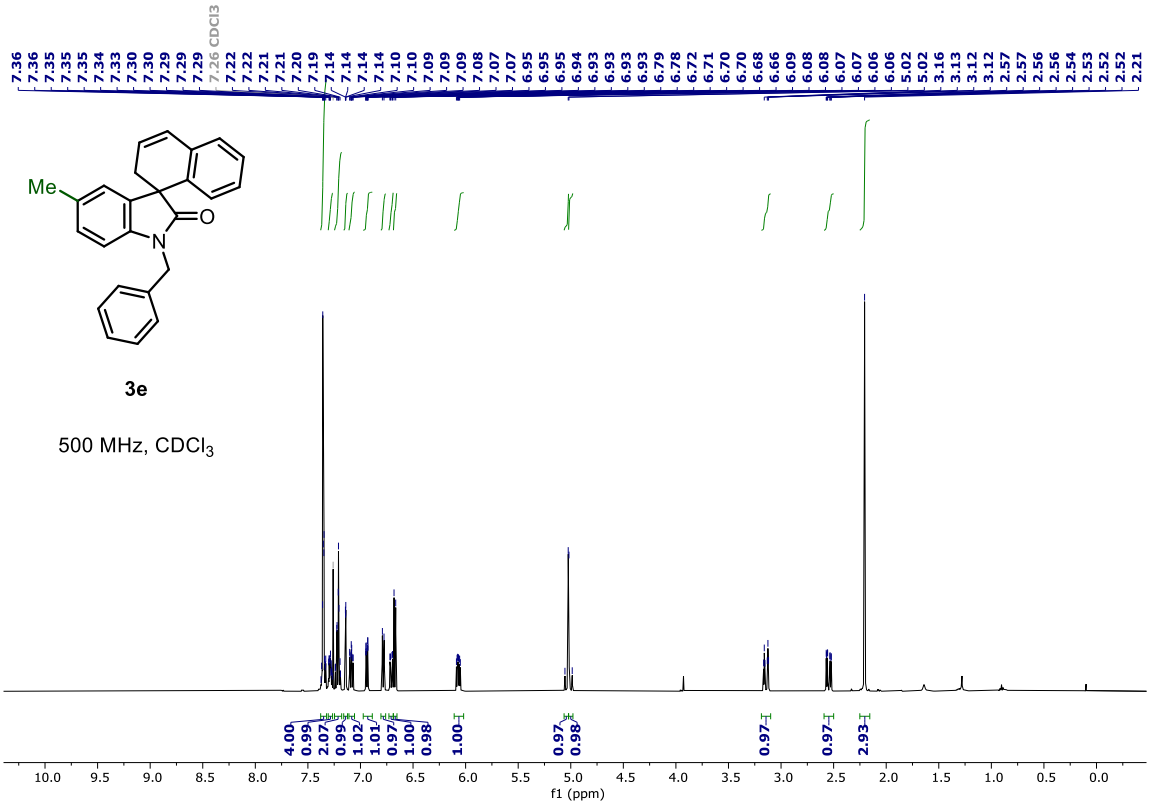
^{19}F NMR, 375 MHz, $CDCl_3$

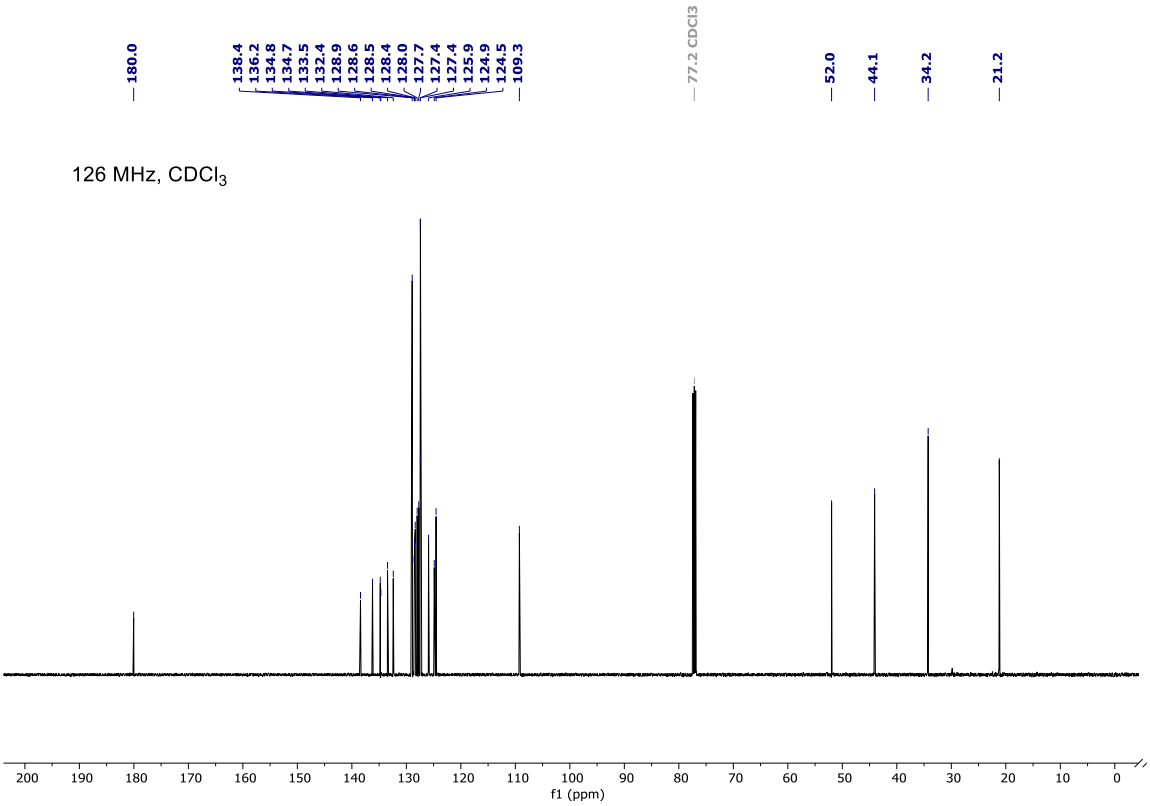


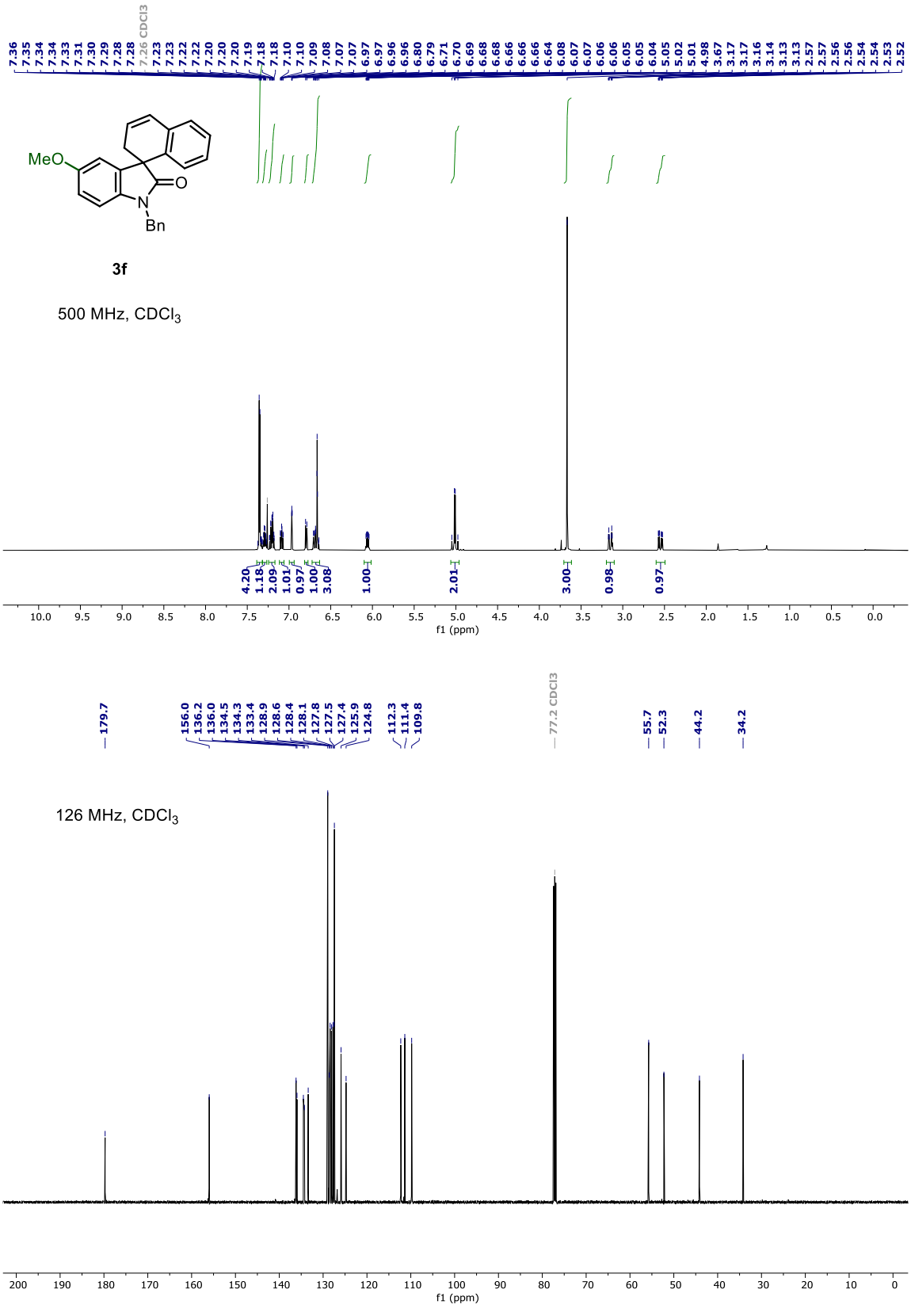

7.36 7.35 7.34 7.33 7.32 7.31 7.31 7.30 7.26 CDCl3 7.24 7.24 7.22 7.22 7.21 7.21 7.20 7.12 7.11 7.10 7.10 7.08 7.08 7.07 7.06 6.82 6.82 6.80 6.80 6.79 6.78 6.72 6.71 6.70 6.69 6.68 6.68 6.67 6.66 6.07 6.07 6.06 6.06 6.05 6.05 5.03 5.02 3.18 3.15 2.53 2.52 2.50 2.49
F
O
N
3d
500 MHz, CDCl3
5.33 2.17 2.04 1.01 0.98 1.04 1.02 1.00 2.03 1.00 0.99
f1 (ppm)
179.8 160.2 158.3 136.7 136.6 136.1 136.0 135.8 134.0 133.3 129.1 129.0 128.9 128.7 128.5 128.4 127.9 127.6 127.4 127.3 126.7 125.8 124.6 114.6 114.4 112.1 111.9 110.1 110.0 77.2 CDCl3 52.3 52.3 44.3 34.1
126 MHz, CDCl3
f1 (ppm)

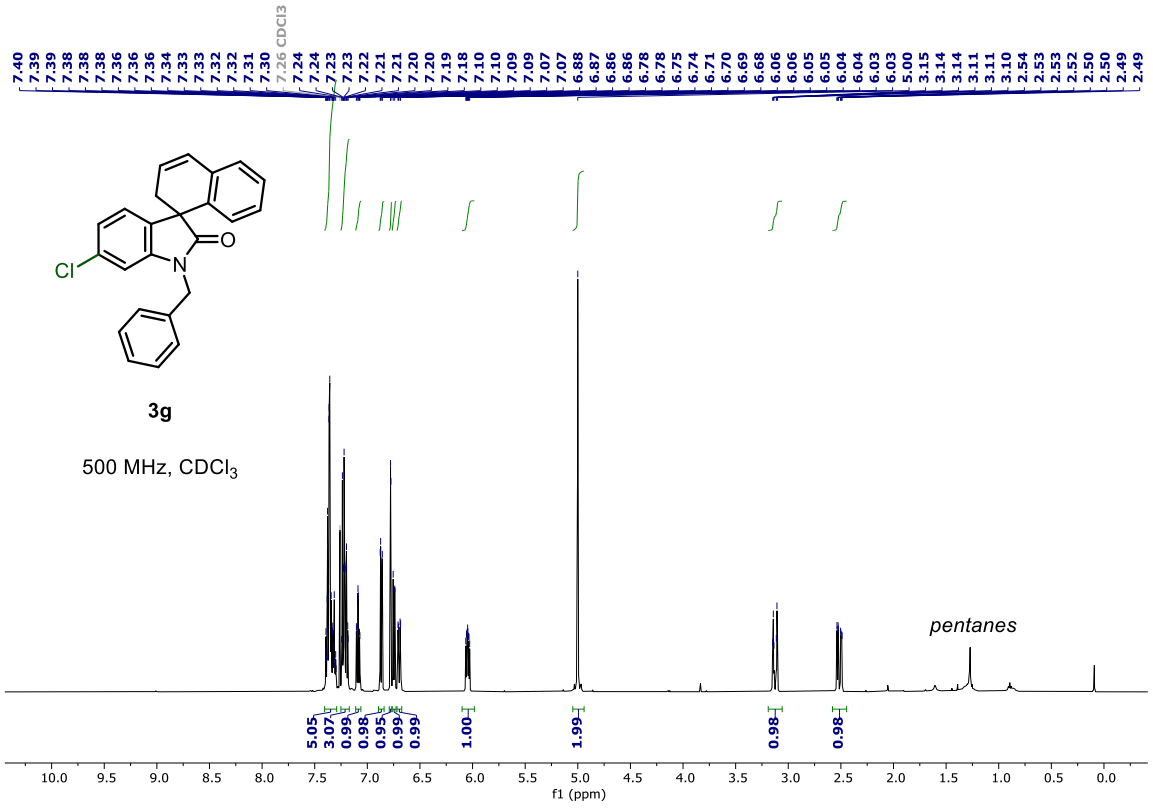
^{19}F NMR, 377 MHz, $CDCl_3$

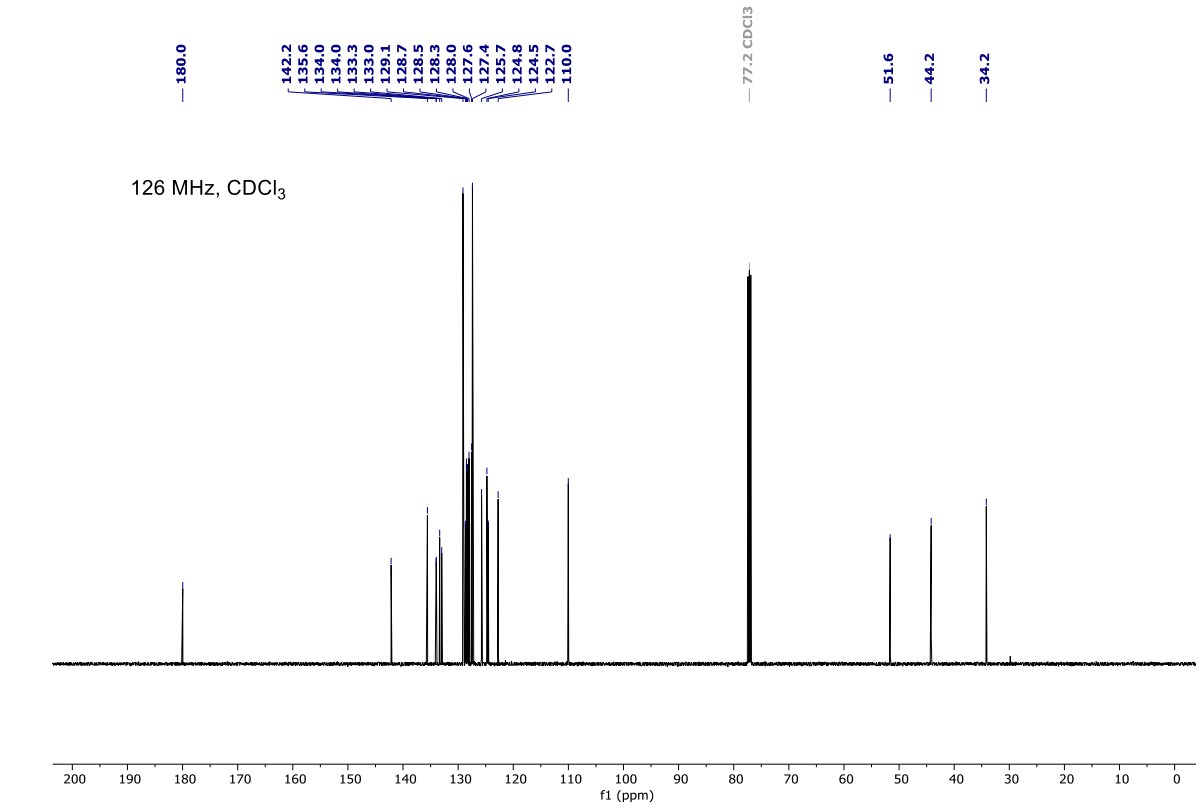


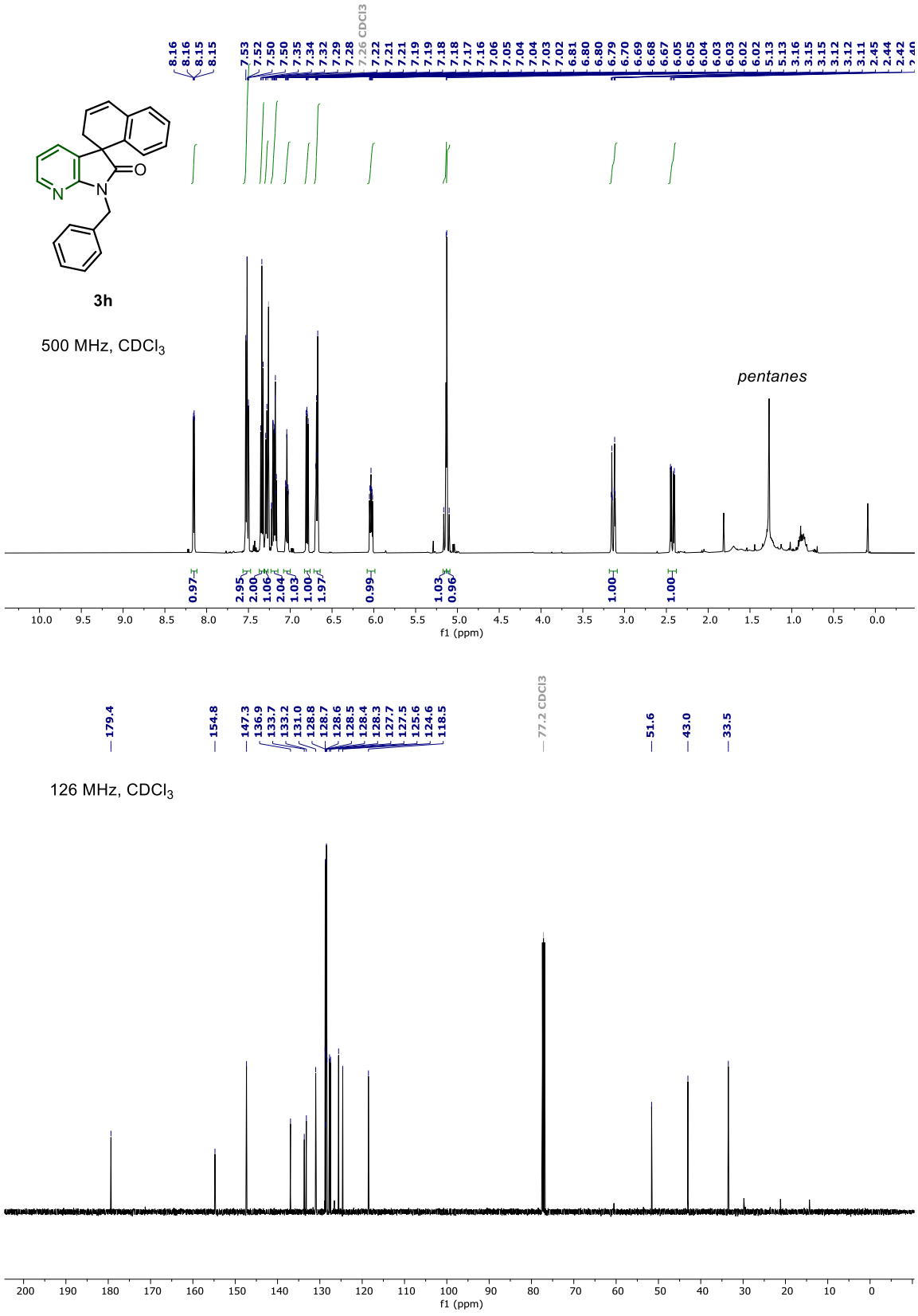

7.26 CDCl3
Me
O
N
3e
500 MHz, CDCl3
f1 (ppm)

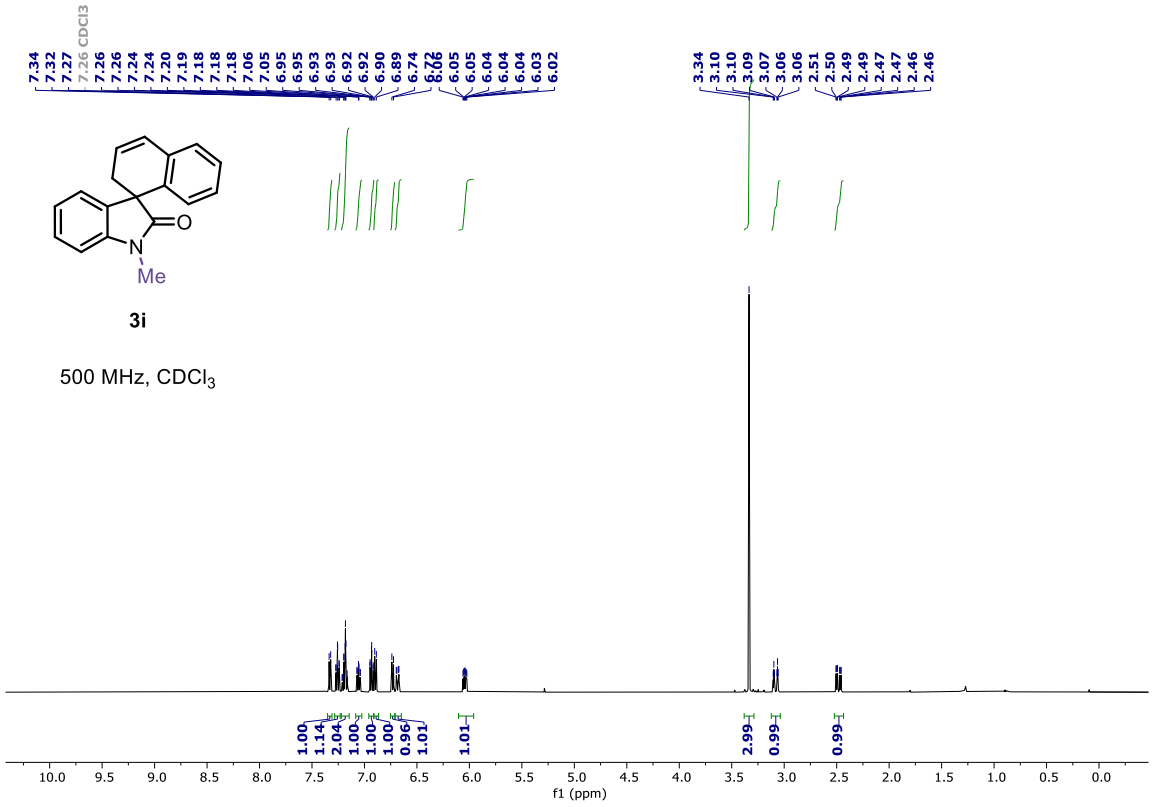

77.2 CDCl3
126 MHz, CDCl3
f1 (ppm)


MeO
O
N
Bn
3f
500 MHz, CDCl3
126 MHz, CDCl3
f1 (ppm)
f1 (ppm)


7.40 7.39 7.39 7.38 7.38 7.38 7.36 7.36 7.36 7.34 7.33 7.33 7.32 7.32 7.31 7.30 7.26 CDCl3 7.24 7.24 7.23 7.23 7.22 7.21 7.21 7.20 7.20 7.19 7.18 7.10 7.10 7.09 7.09 7.07 7.07 6.88 6.87 6.86 6.86 6.78 6.78 6.75 6.74 6.71 6.70 6.69 6.68 6.06 6.06 6.05 6.05 6.04 6.04 6.03 6.03 5.00 3.15 3.14 3.11 3.11 3.10 2.54 2.53 2.53 2.52 2.50 2.50 2.49 2.49
Cl
O
N
3g
500 MHz, CDCl3
pentanes
5.05 3.07 0.99 0.98 0.95 0.99 0.99 1.00 1.99 0.98 0.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

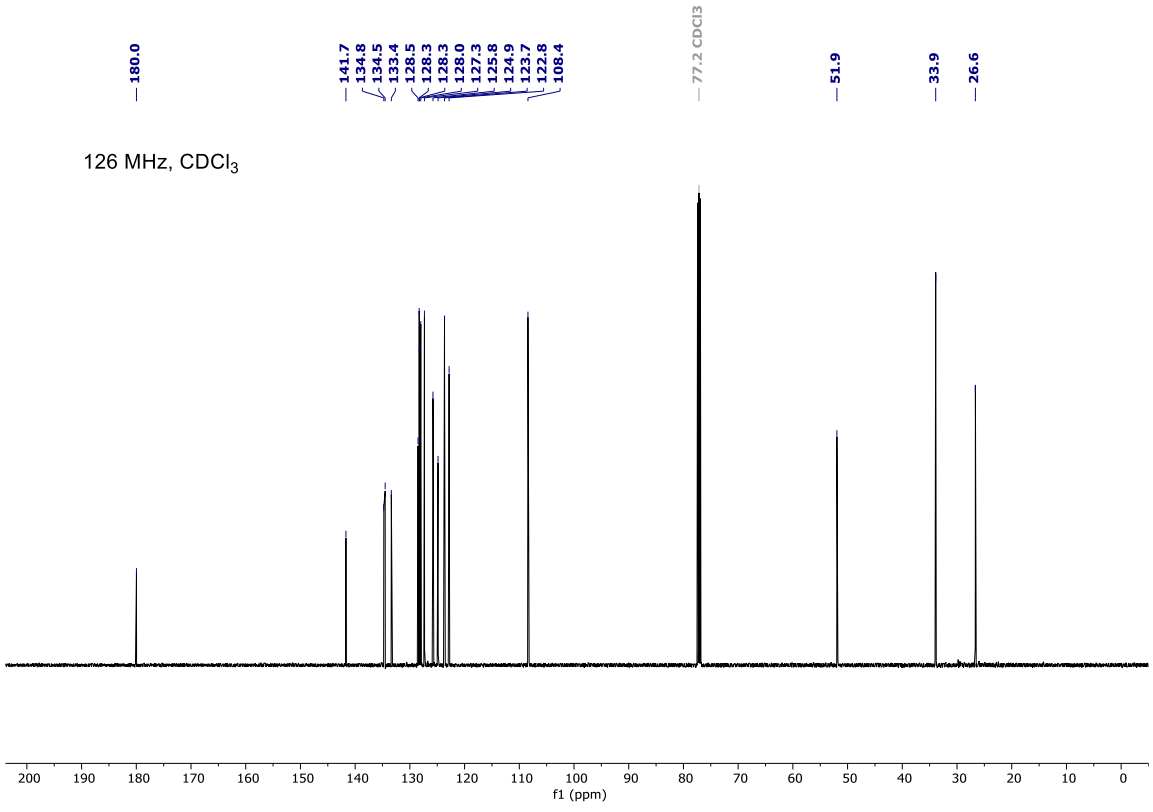

180.0 142.2 135.6 134.0 134.0 133.3 133.0 129.1 128.7 128.5 128.3 128.0 127.6 127.4 125.7 124.8 124.5 122.7 110.0 77.2 CDCl3 51.6 44.2 34.2
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


3h
500 MHz, CDCl3
pentanes
f1 (ppm)
126 MHz, CDCl3
f1 (ppm)

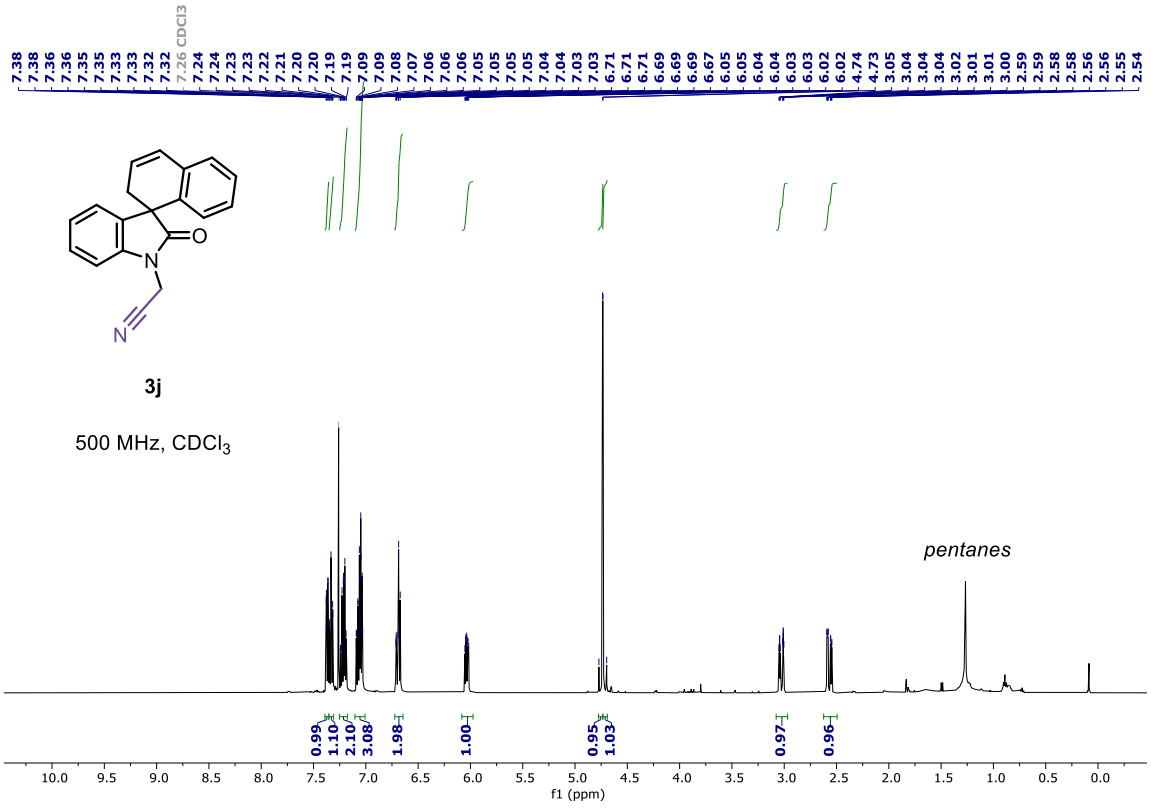


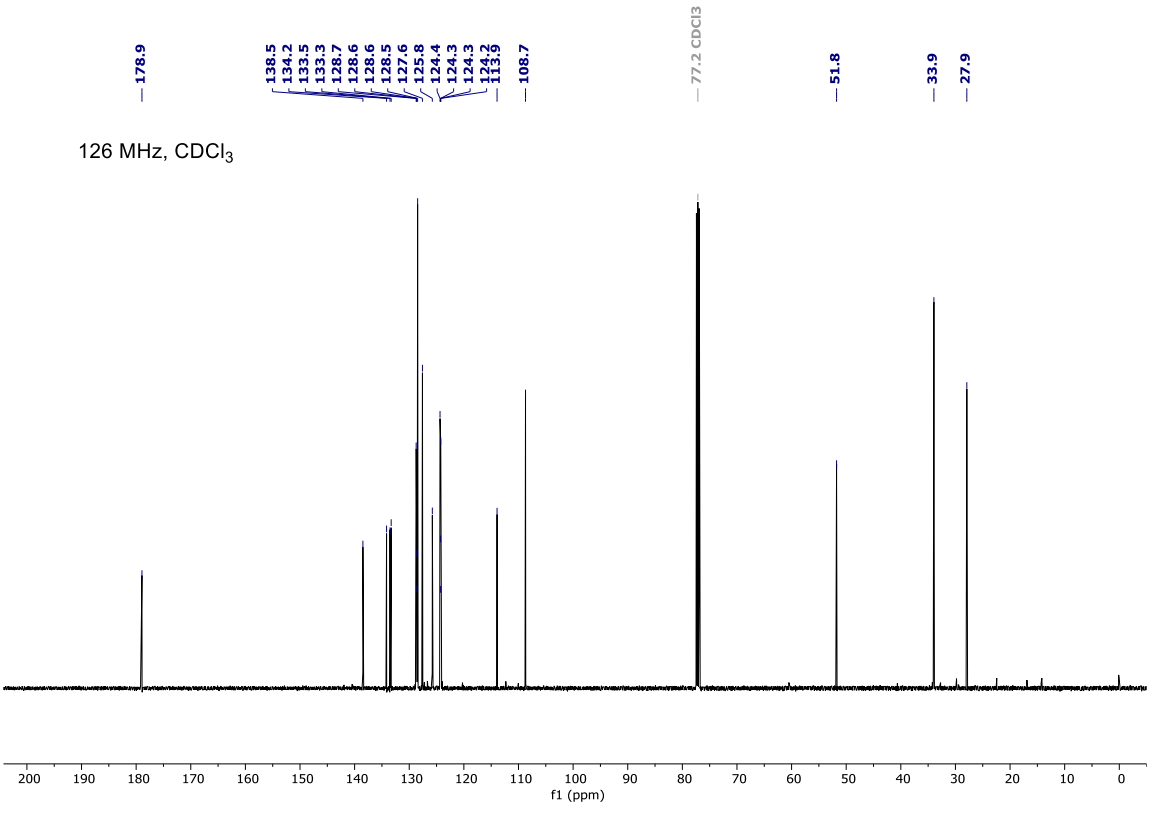
3i

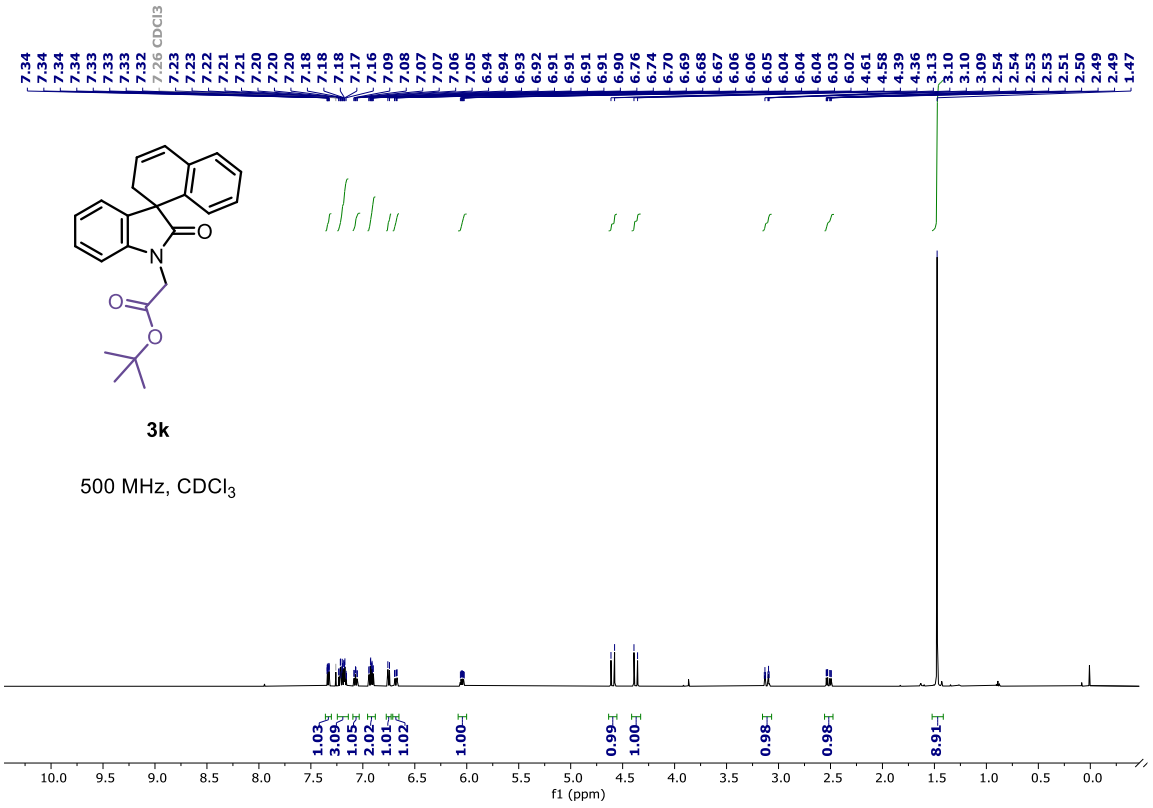
500 MHz, $CDCl_3$

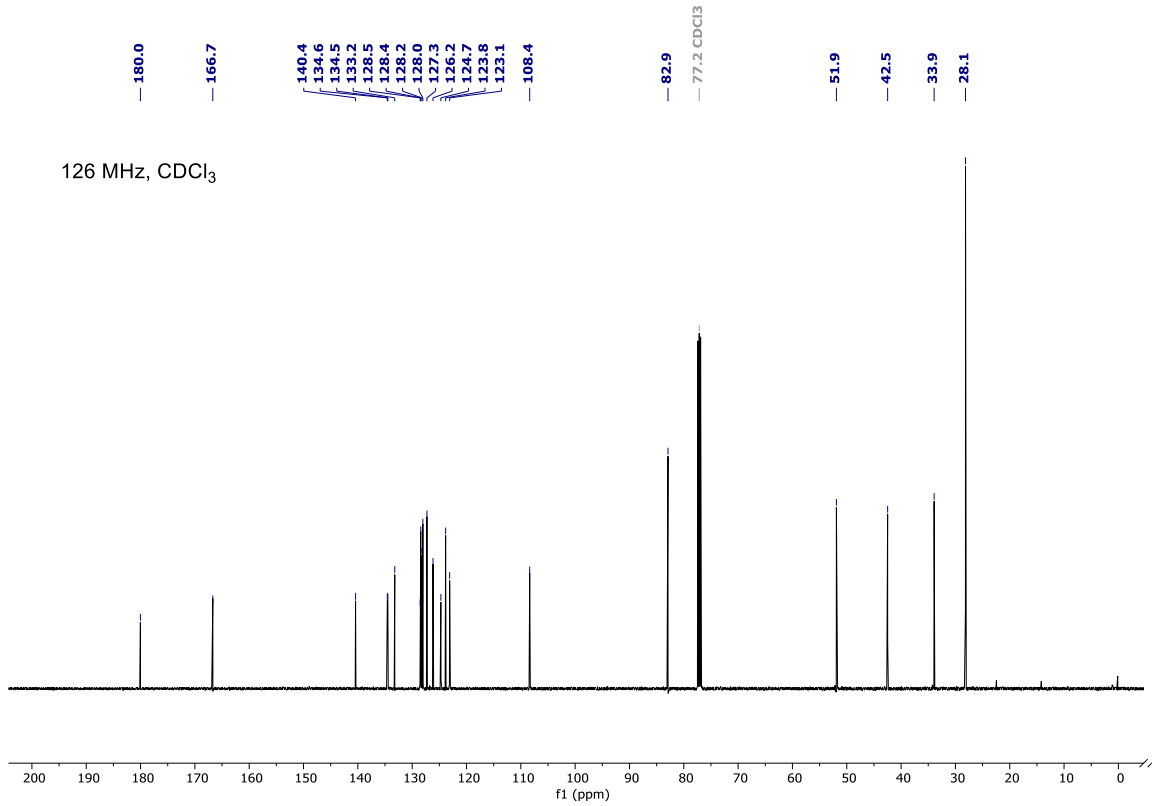


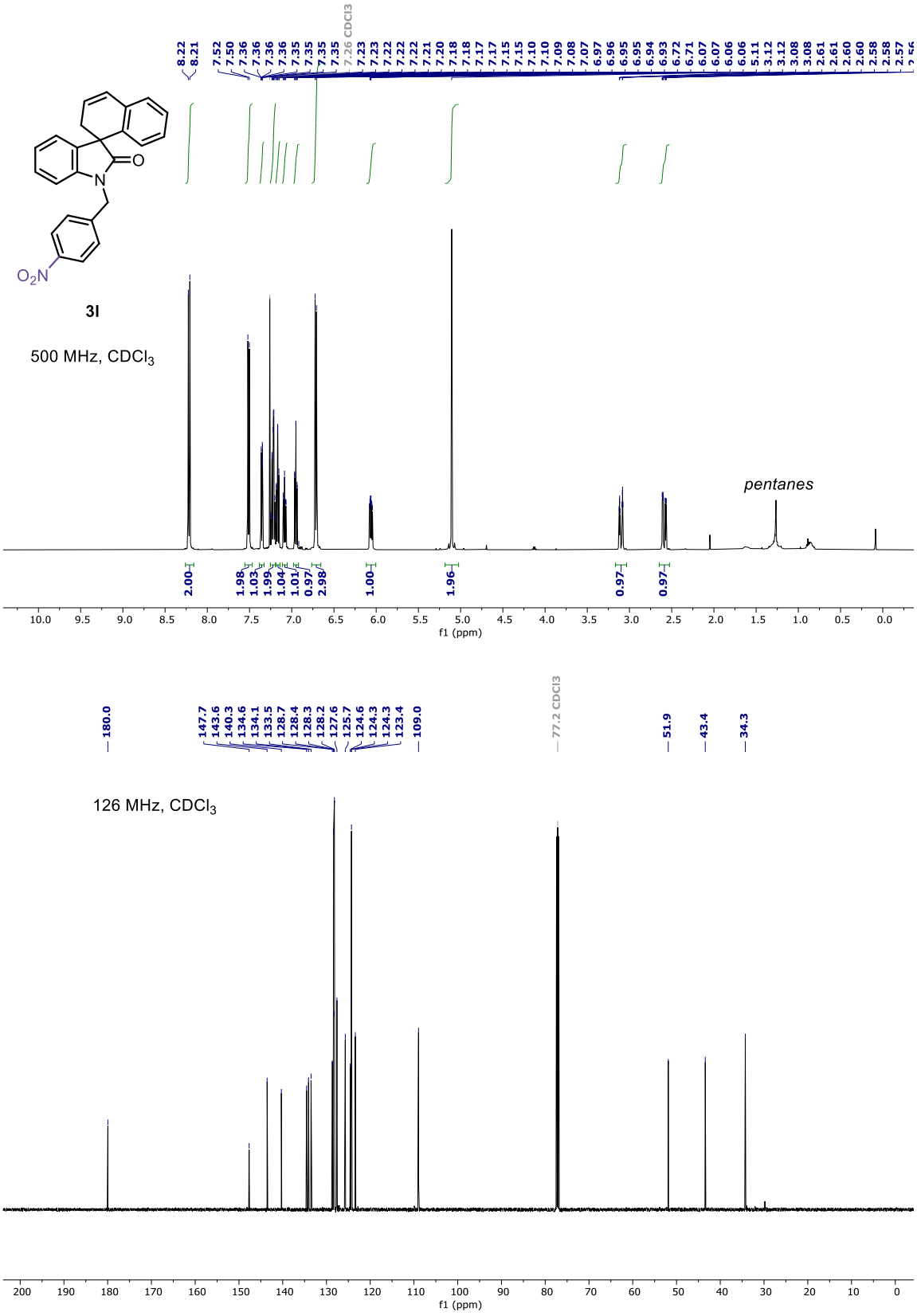
126 MHz, $CDCl_3$

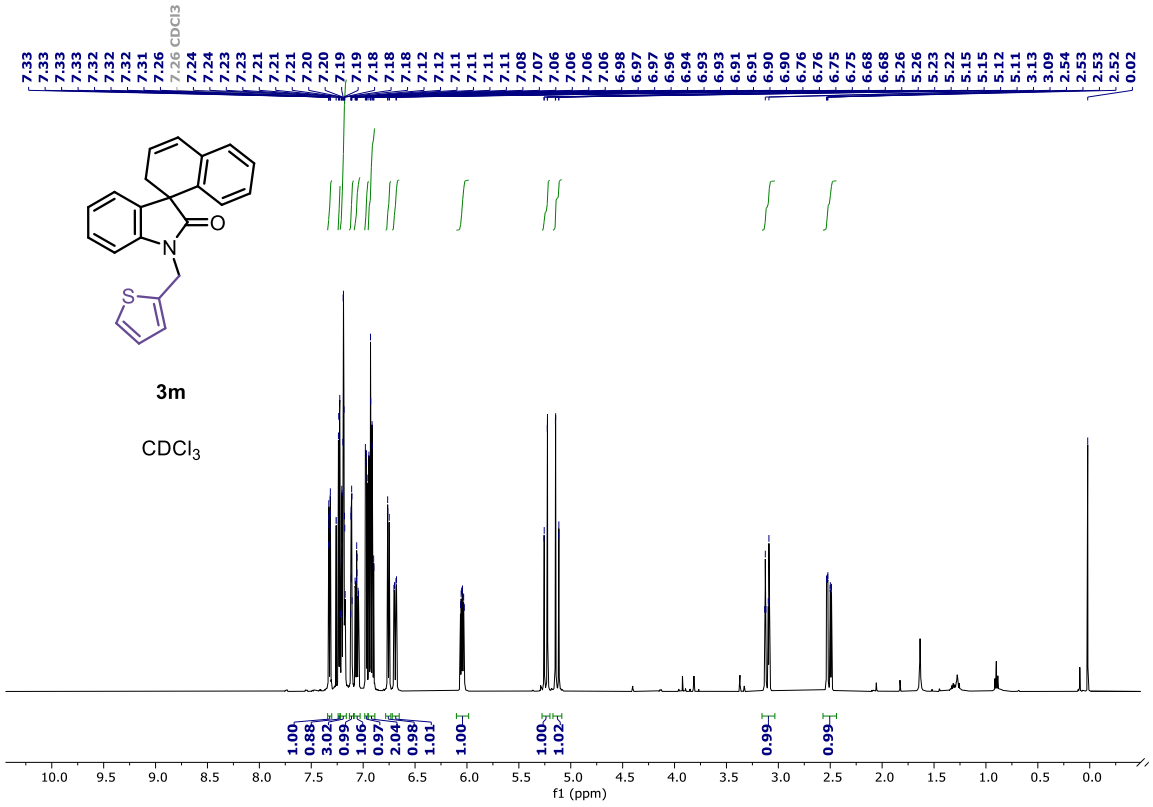

7.38 7.38 7.36 7.36 7.35 7.35 7.33 7.33 7.32 7.32 7.26 CDCl3 7.24 7.24 7.23 7.23 7.22 7.21 7.20 7.20 7.19 7.19 7.09 7.09 7.08 7.07 7.06 7.06 7.06 7.05 7.05 7.05 7.05 7.04 7.04 7.03 7.03 6.71 6.71 6.71 6.69 6.69 6.69 6.67 6.05 6.05 6.04 6.04 6.03 6.03 6.02 6.02 4.74 4.73 3.05 3.04 3.04 3.02 3.01 3.01 3.00 2.59 2.59 2.58 2.58 2.56 2.56 2.55 2.54
O
N
N
3j
500 MHz, CDCl3
pentanes
0.99 1.10 2.10 3.08 1.98 1.00 0.95 1.03 0.97 0.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

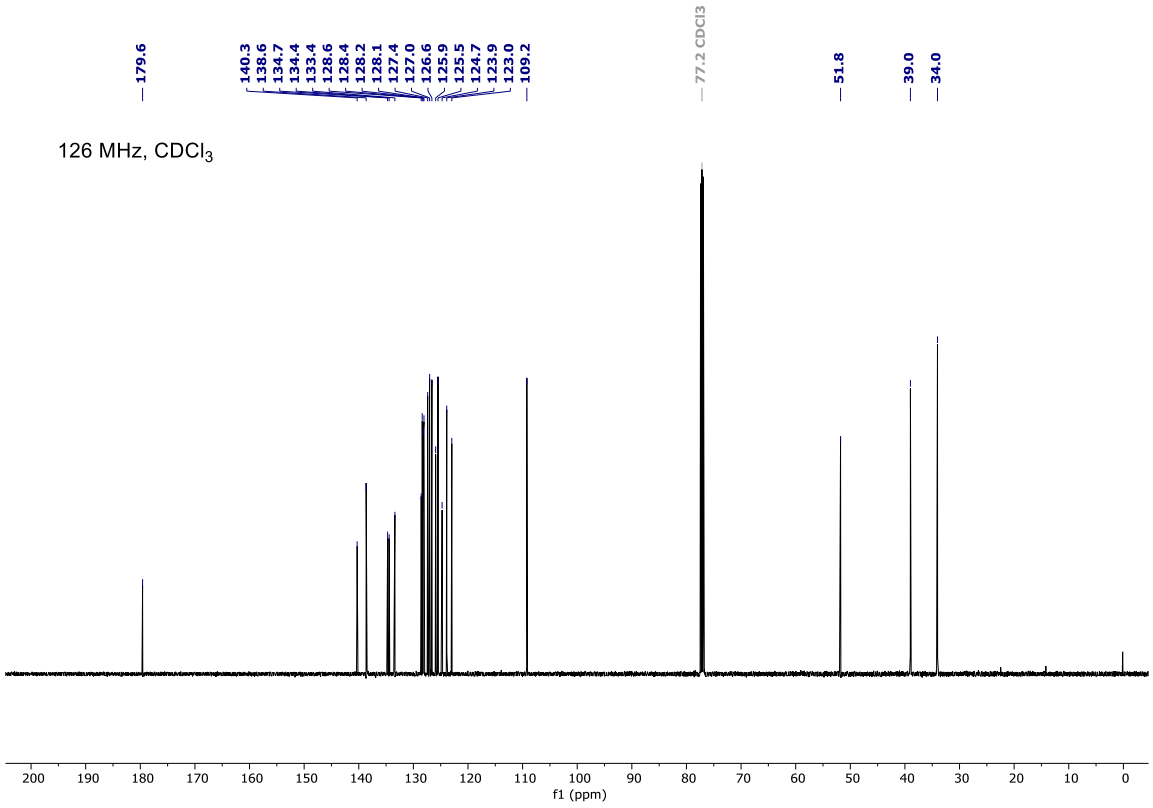

178.9
138.5 134.2 133.5 133.3 128.7 128.6 128.6 128.5 127.6 125.8 124.4 124.3 124.3 124.2 113.9
108.7
77.2 CDCl3
51.8
33.9
27.9
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

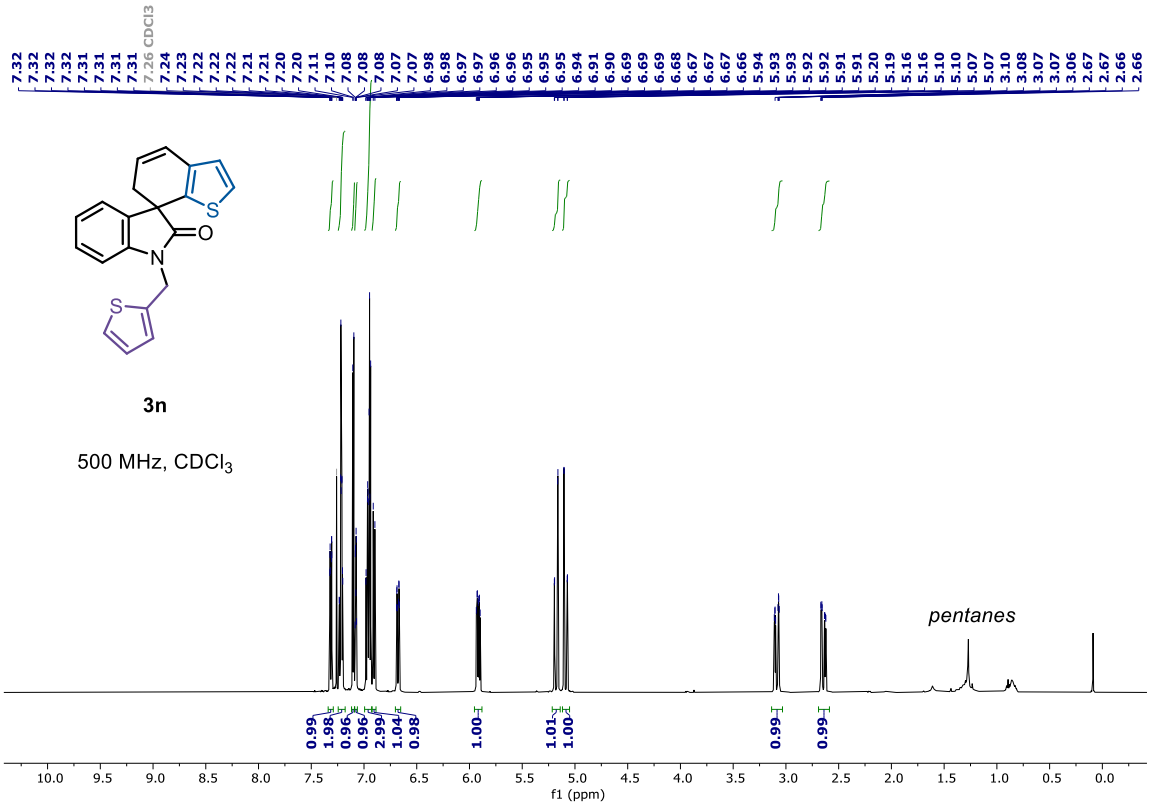

7.26 CDCl3
O
N
O
O
O
3k
500 MHz, CDCl3
1.03
3.09
1.05
2.02
1.01
1.02
1.00
0.99
1.00
0.98
0.98
8.91
f1 (ppm)

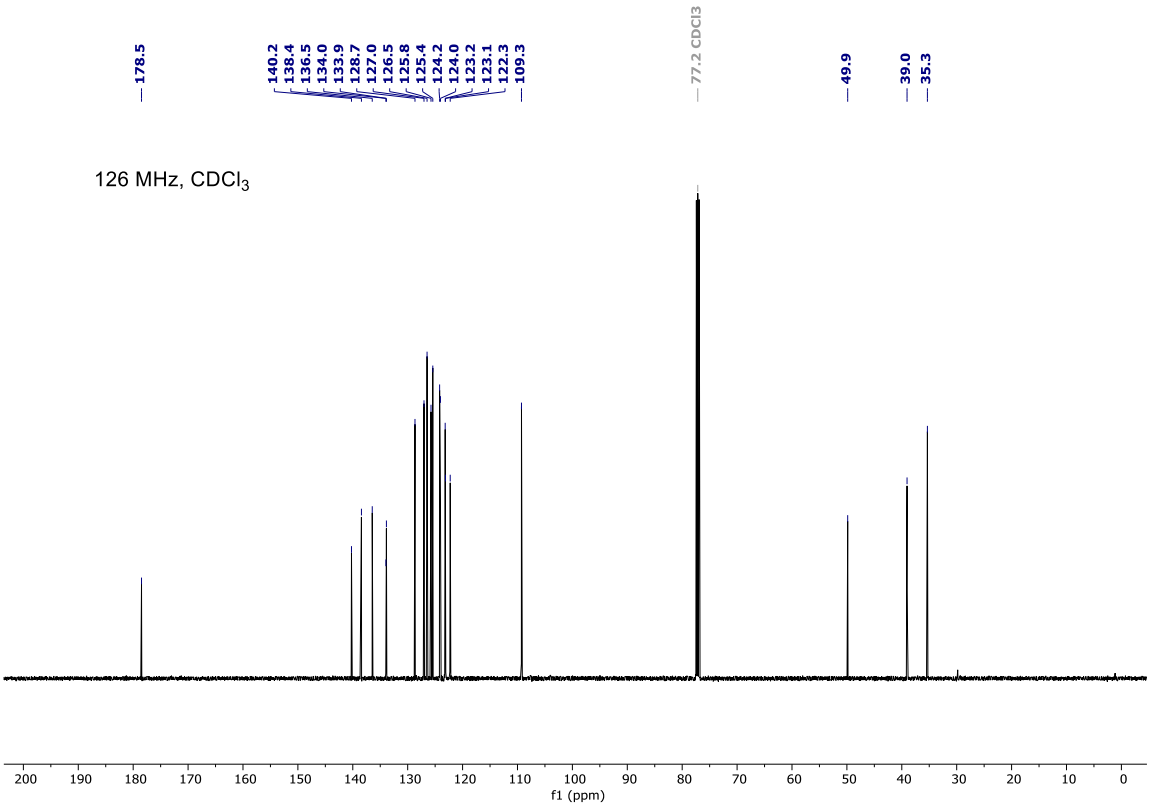

180.0
166.7
140.4
134.6
134.5
133.2
128.5
128.4
128.2
128.0
127.3
126.2
124.7
123.8
123.1
108.4
82.9
77.2 CDCl3
51.9
42.5
33.9
28.1
126 MHz, CDCl3
f1 (ppm)

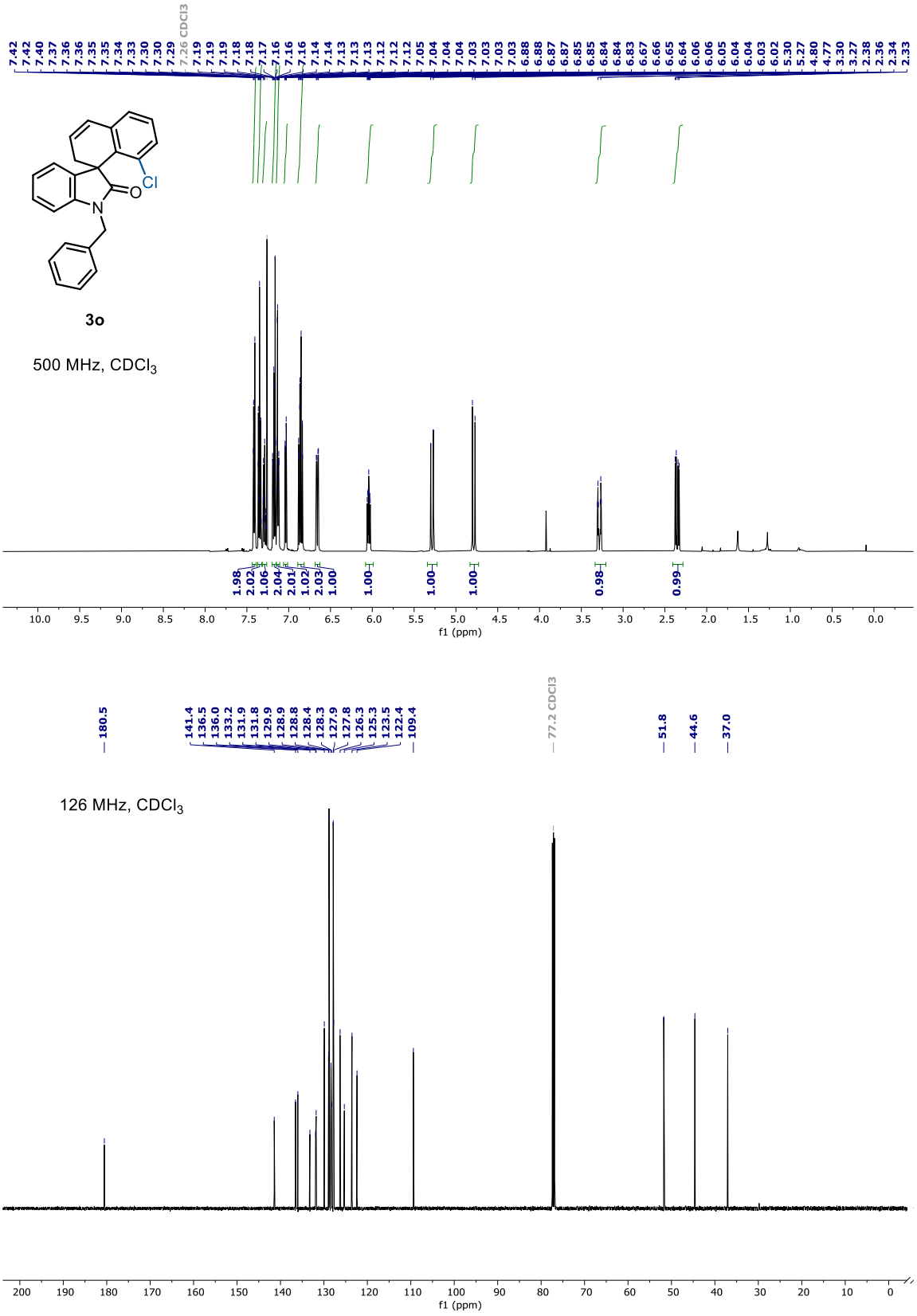

3l
500 MHz, CDCl3
pentanes
f1 (ppm)
126 MHz, CDCl3
f1 (ppm)

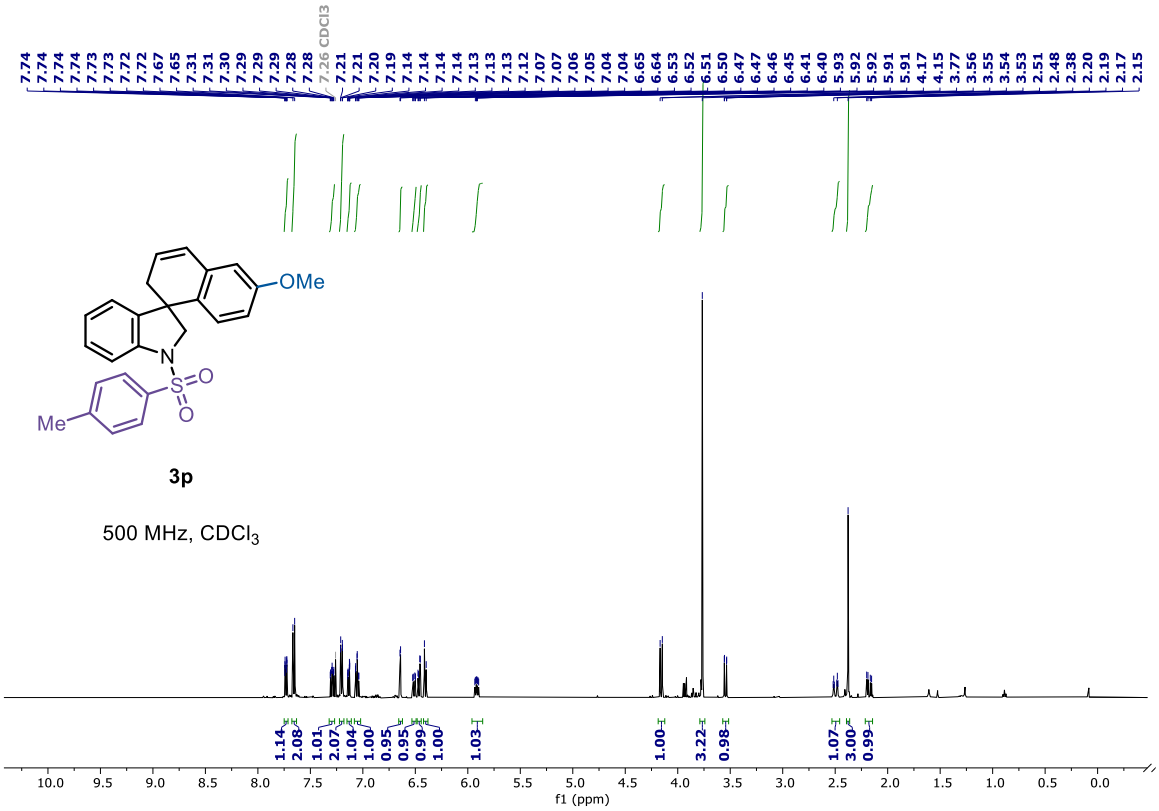

7.33 7.33 7.33 7.33 7.32 7.32 7.32 7.31 7.26 7.26 CDCl3 7.24 7.24 7.23 7.23 7.21 7.21 7.21 7.20 7.20 7.19 7.19 7.18 7.18 7.18 7.12 7.12 7.11 7.11 7.11 7.11 7.08 7.07 7.06 7.06 7.06 7.06 6.98 6.97 6.97 6.96 6.94 6.93 6.93 6.91 6.91 6.90 6.90 6.76 6.76 6.75 6.75 6.68 6.68 5.26 5.26 5.23 5.22 5.15 5.15 5.12 5.11 3.13 3.09 2.54 2.53 2.53 2.52 0.02
O
N
S
3m
CDCl3
1.00 0.88 3.02 0.99 1.06 0.97 2.04 0.98 1.01 1.00 1.00 1.02 0.99 0.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

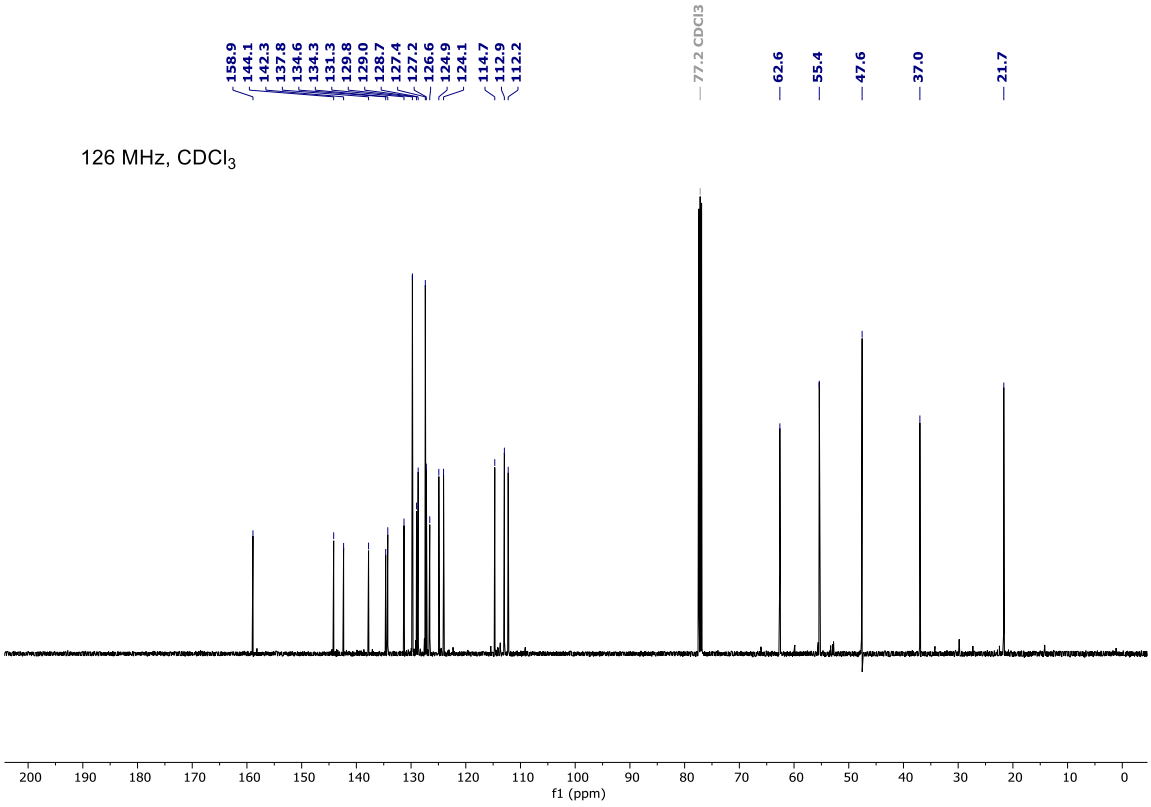

179.6
140.3 138.6 134.7 134.4 133.4 128.6 128.4 128.2 128.1 127.4 127.0 126.6 125.9 125.5 124.7 123.9 123.0
109.2
77.2 CDCl3
51.8
39.0
34.0
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

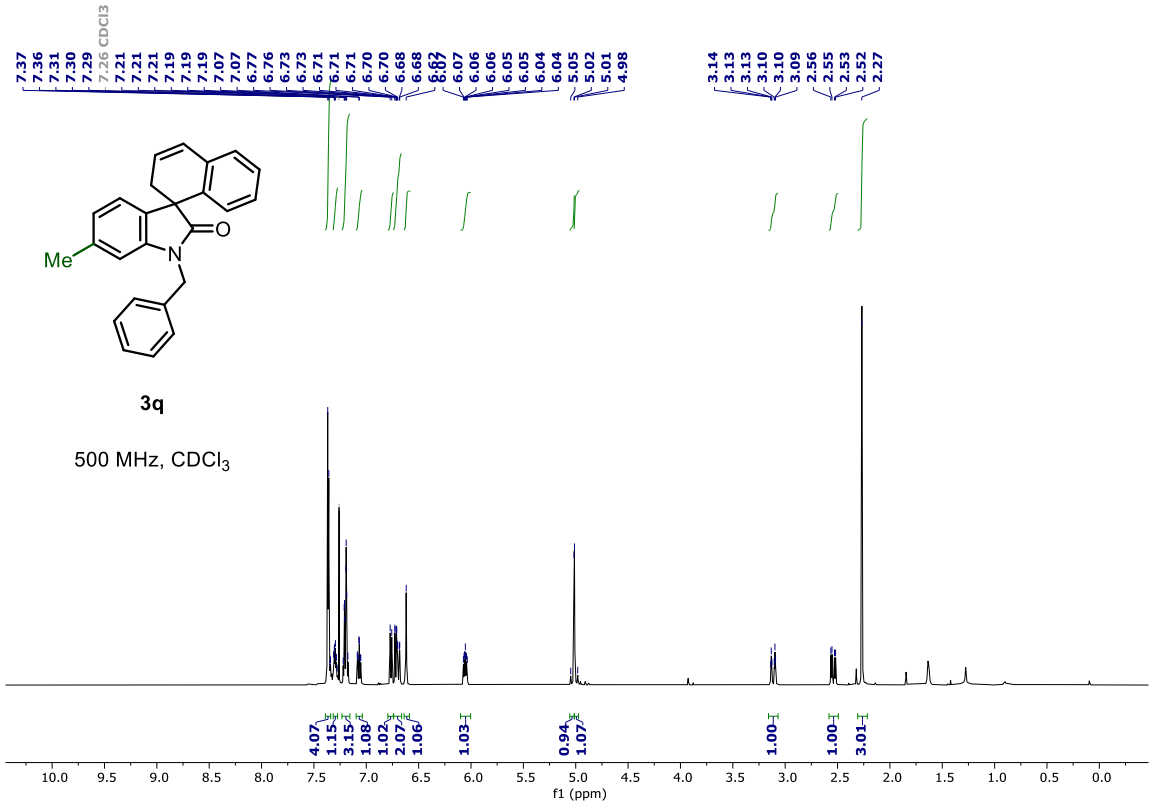

7.26 CDCl3
3n
500 MHz, CDCl3
pentanes
f1 (ppm)

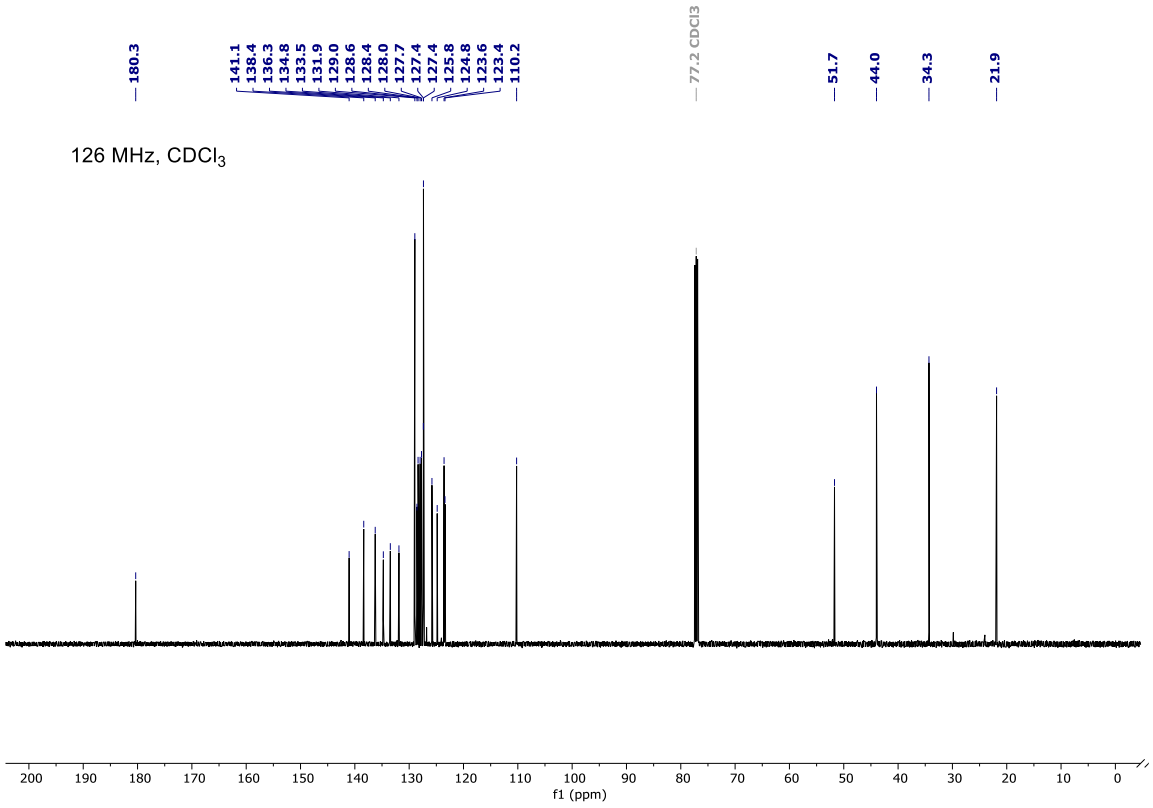

77.2 CDCl3
126 MHz, CDCl3
f1 (ppm)

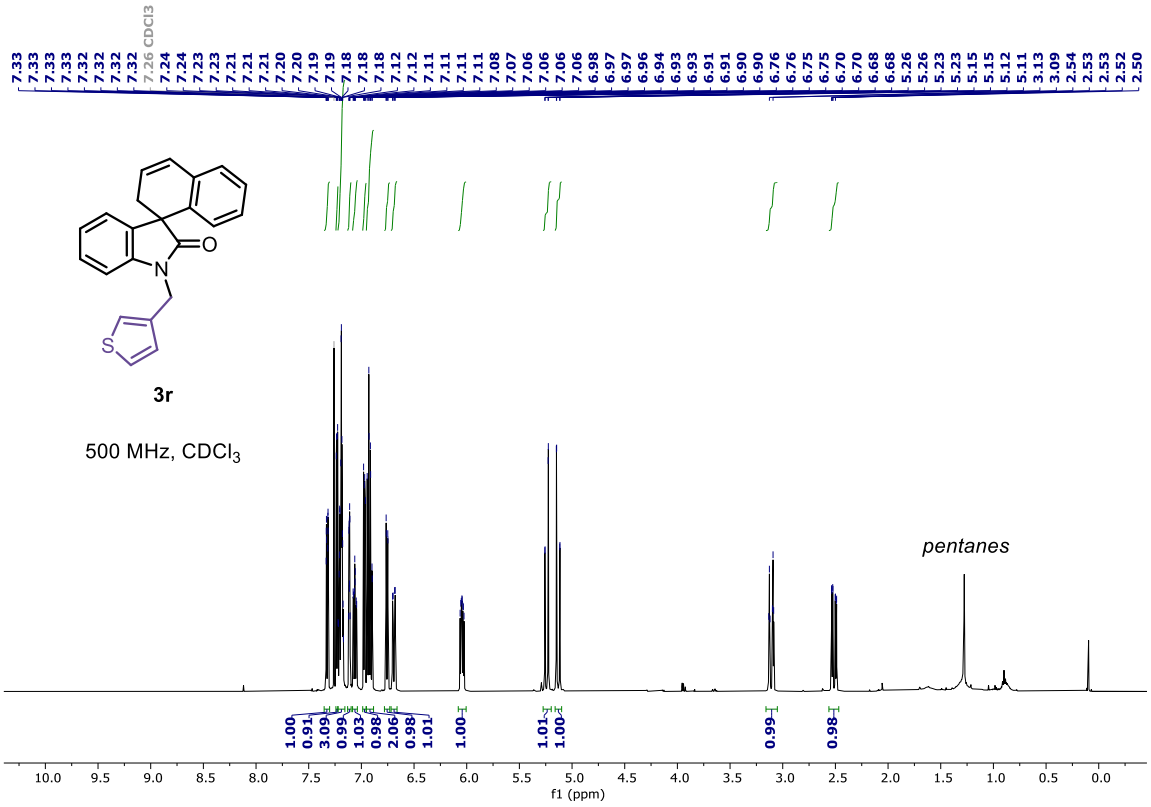

7.26 CDCl3
Cl
O
N
3o
500 MHz, CDCl3
1.98
2.02
1.06
2.04
2.01
1.02
2.03
1.00
1.00
1.00
1.00
0.98
0.99
f1 (ppm)
180.5
141.4
136.5
136.0
133.2
131.9
131.8
129.9
128.9
128.8
128.4
128.3
127.9
127.8
126.3
125.3
123.5
122.4
109.4
77.2 CDCl3
51.8
44.6
37.0
126 MHz, CDCl3
f1 (ppm)

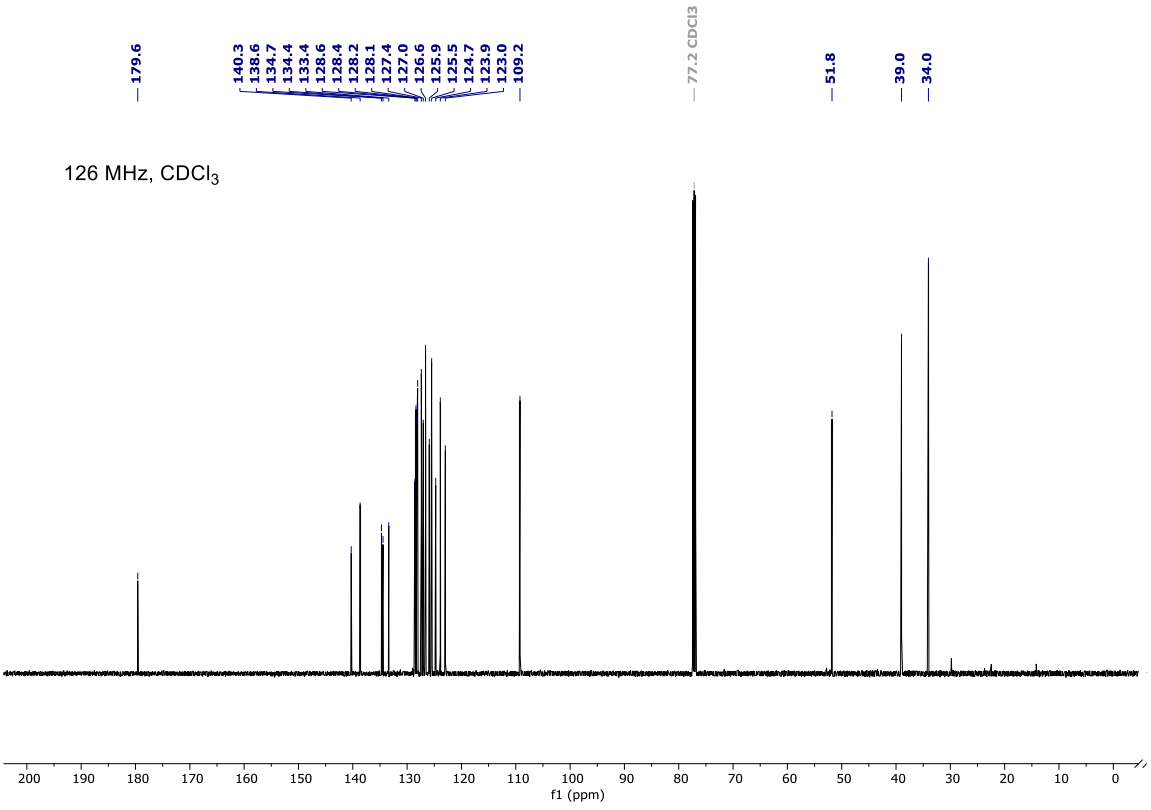

7.74 7.74 7.74 7.74 7.73 7.73 7.72 7.72 7.67 7.65 7.31 7.31 7.30 7.29 7.29 7.29 7.28 7.28 7.26 CDCl3 7.21 7.21 7.20 7.19 7.14 7.14 7.14 7.14 7.13 7.13 7.13 7.12 7.07 7.07 7.06 7.05 7.04 7.04 6.65 6.64 6.53 6.52 6.51 6.50 6.47 6.47 6.46 6.45 6.41 6.40 5.93 5.92 5.92 5.91 5.91 4.17 4.15 3.77 3.56 3.55 3.54 3.53 2.51 2.48 2.38 2.20 2.19 2.17 2.15
OMe
N
S
O
O
Me
3p
500 MHz, CDCl3
1.14 2.08 1.01 2.07 1.04 1.00 0.95 0.99 1.00 1.03 1.00 3.22 0.98 1.07 3.00 0.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

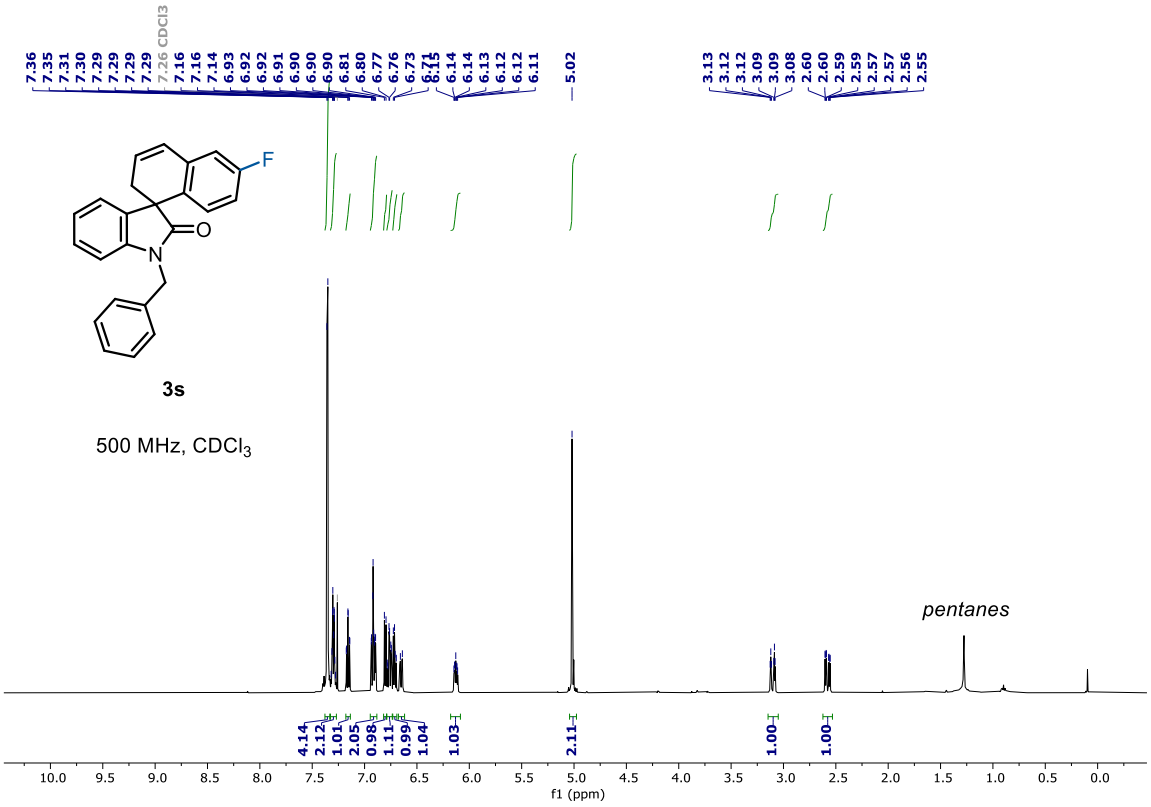

158.9 144.1 142.3 137.8 134.6 134.3 131.3 129.8 129.0 128.7 127.4 127.2 126.6 124.9 124.1 114.7 112.9 112.2
77.2 CDCl3
62.6 55.4 47.6 37.0 21.7
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

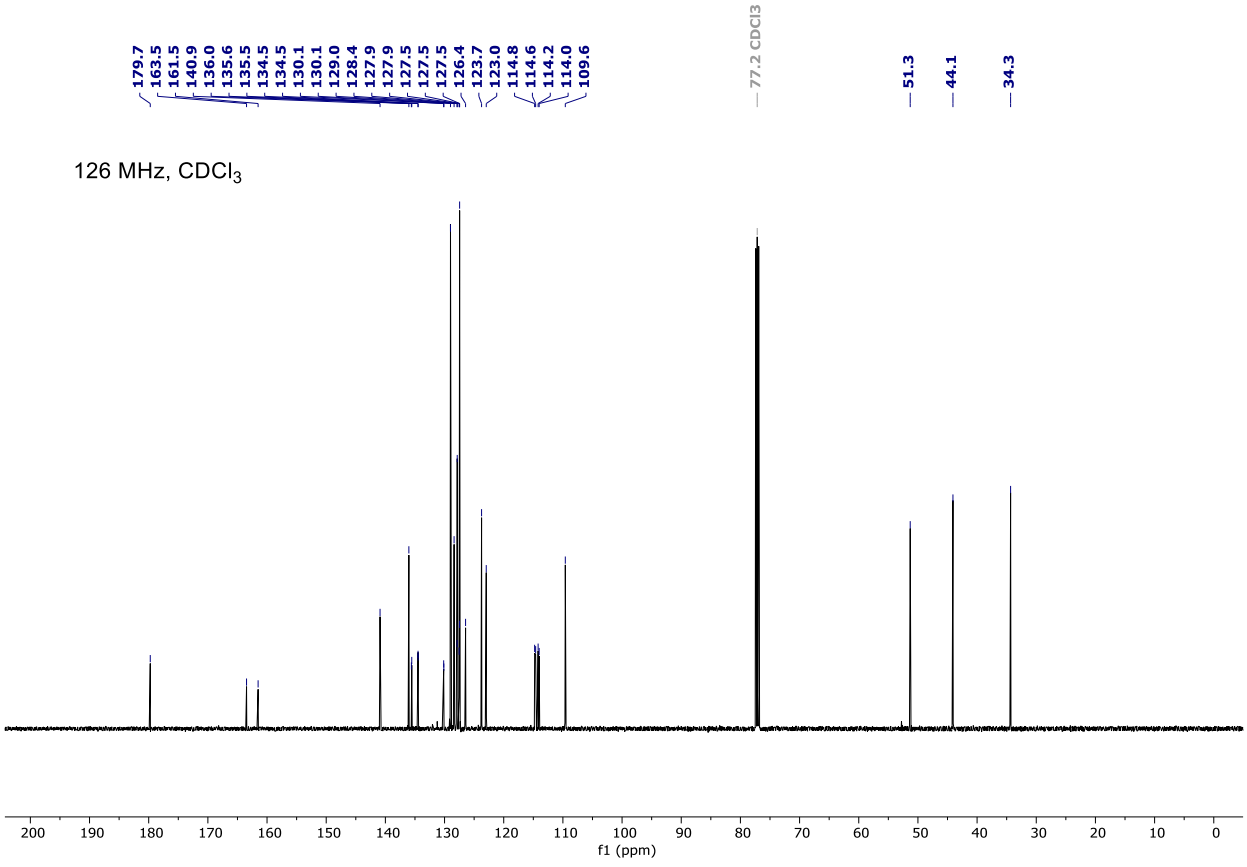

7.37
7.36
7.31
7.30
7.29
7.26 CDCl3
7.21
7.21
7.21
7.19
7.19
7.19
7.07
7.07
6.77
6.76
6.73
6.73
6.71
6.71
6.71
6.70
6.70
6.68
6.68
6.67
6.67
6.07
6.06
6.06
6.05
6.05
6.04
6.04
5.05
5.02
5.01
4.98
3.14
3.13
3.13
3.10
3.10
3.09
2.56
2.55
2.53
2.52
2.27
Me
O
N
3q
500 MHz, CDCl3
4.07
1.15
3.15
1.08
1.02
2.07
1.06
1.03
0.94
1.07
1.00
1.00
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


180.3
141.1
138.4
136.3
134.8
133.5
131.9
129.0
128.6
128.4
128.0
127.7
127.4
127.4
125.8
124.8
123.6
123.4
110.2
77.2 CDCl3
51.7
44.0
34.3
21.9
126 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

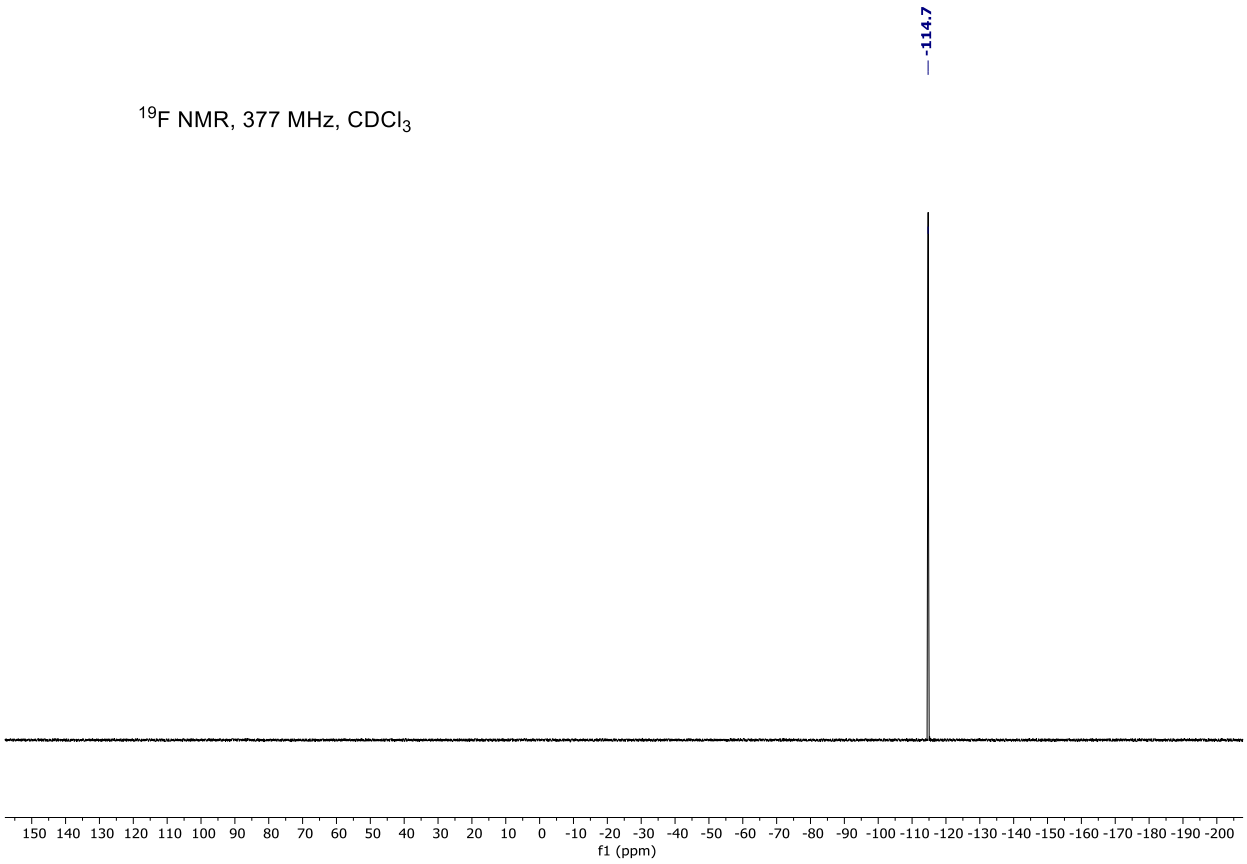

7.26 CDCl3
O
N
S
3r
500 MHz, CDCl3
pentanes
1.00 0.91 3.09 0.99 1.03 0.98 2.06 0.98 1.01 1.00 1.01 1.00 0.99 0.98
f1 (ppm)

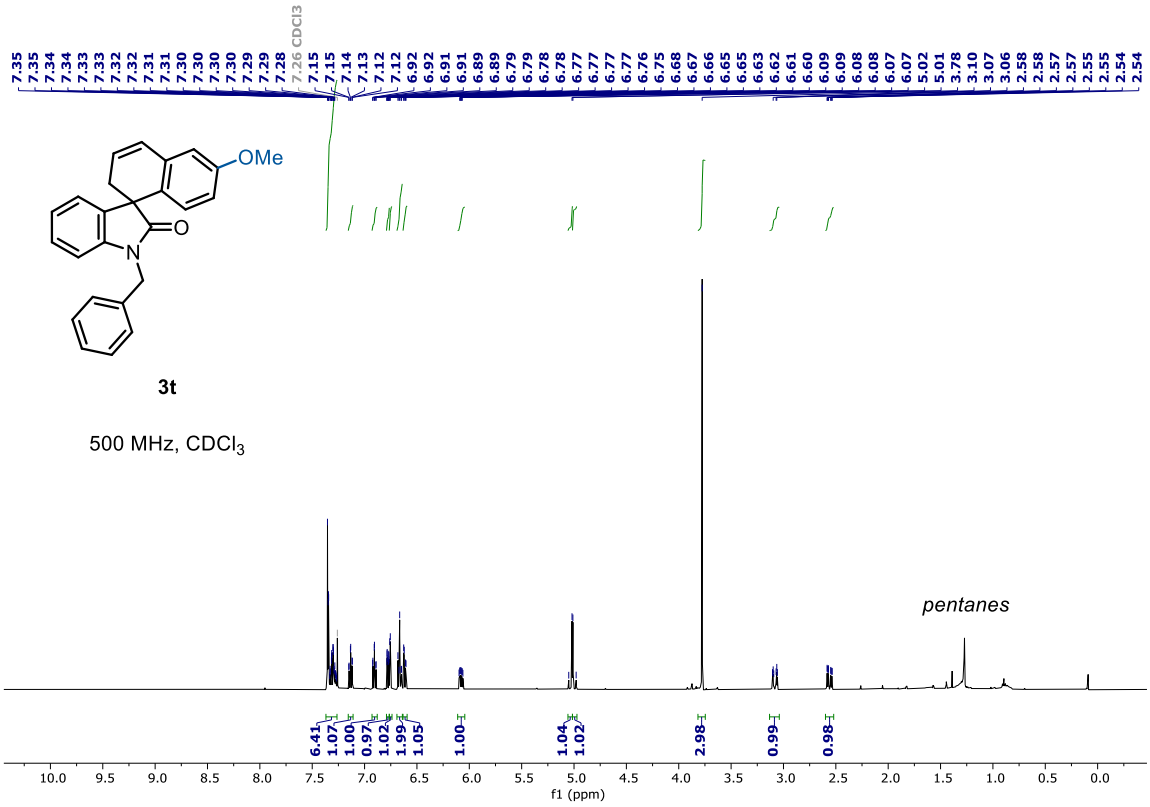

179.6
140.3 138.6 134.7 134.4 133.4 128.6 128.4 128.2 128.1 127.4 127.0 126.6 125.9 125.5 124.7 123.9 123.0 109.2
77.2 CDCl3
51.8
39.0
34.0
126 MHz, CDCl3
f1 (ppm)


7.36
7.35
7.31
7.30
7.29
7.29
7.29
7.29
7.26 CDCl3
7.16
7.16
7.14
6.93
6.92
6.92
6.91
6.90
6.90
6.90
6.81
6.80
6.77
6.76
6.73
6.71
6.15
6.14
6.14
6.13
6.12
6.12
6.11
5.02
3.13
3.12
3.12
3.09
3.09
3.08
2.60
2.60
2.59
2.59
2.57
2.57
2.56
2.55
F
O
N
3s
500 MHz, CDCl3
pentanes
4.14
2.12
1.01
2.05
0.98
1.11
0.99
1.04
1.03
2.11
1.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


179.7
163.5
161.5
140.9
136.0
135.6
135.5
134.5
134.5
130.1
130.1
129.0
128.4
127.9
127.9
127.5
127.5
127.5
126.4
123.7
123.0
114.8
114.6
114.2
114.0
109.6
77.2 CDCl3
51.3
44.1
34.3
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

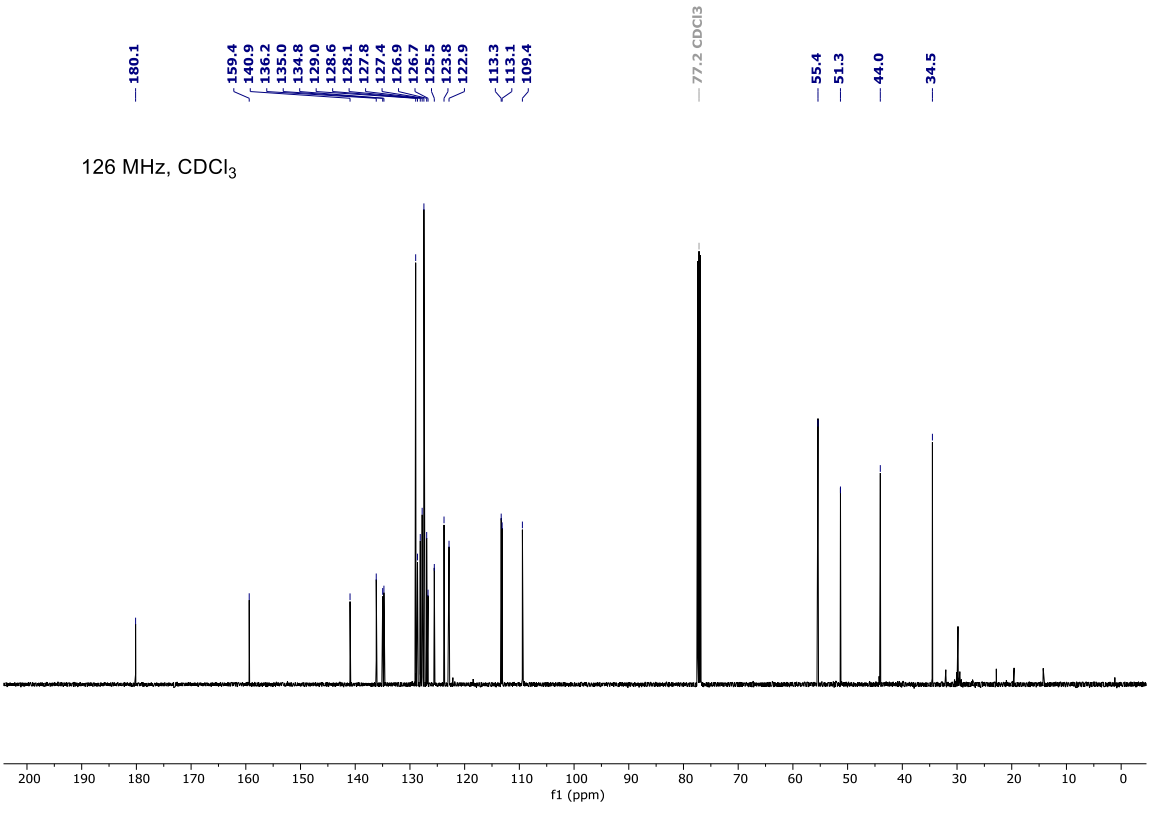
^{19}F NMR, 377 MHz, $CDCl_3$



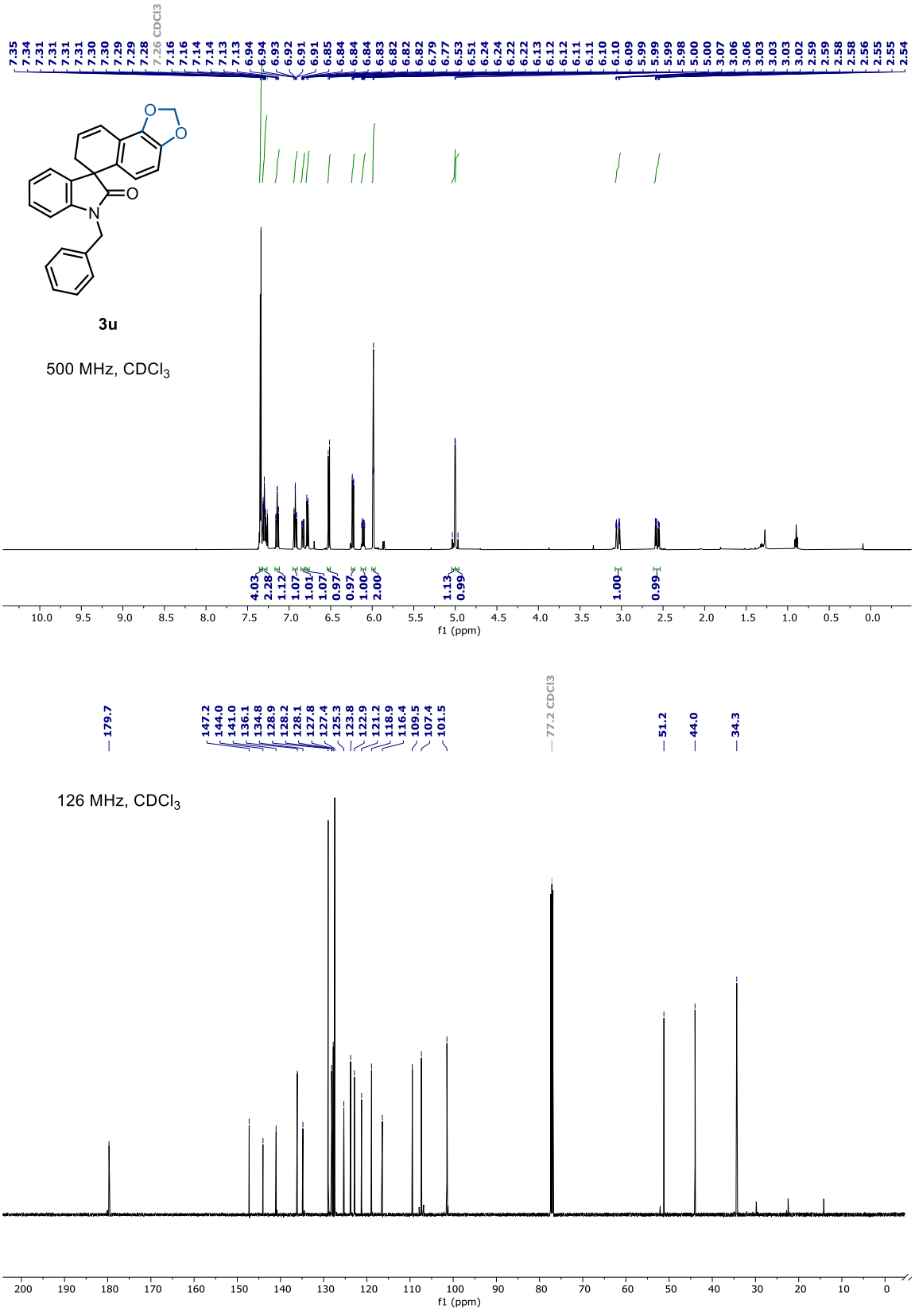


3t

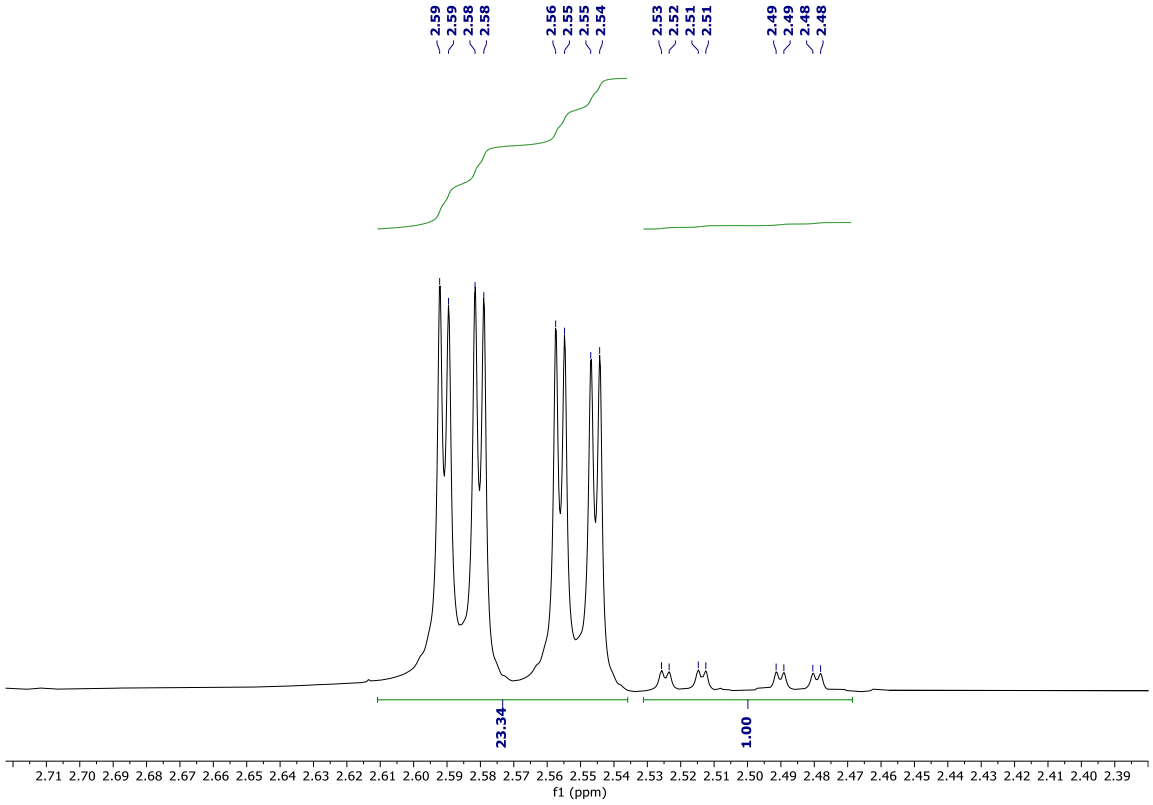
500 MHz, $CDCl_3$

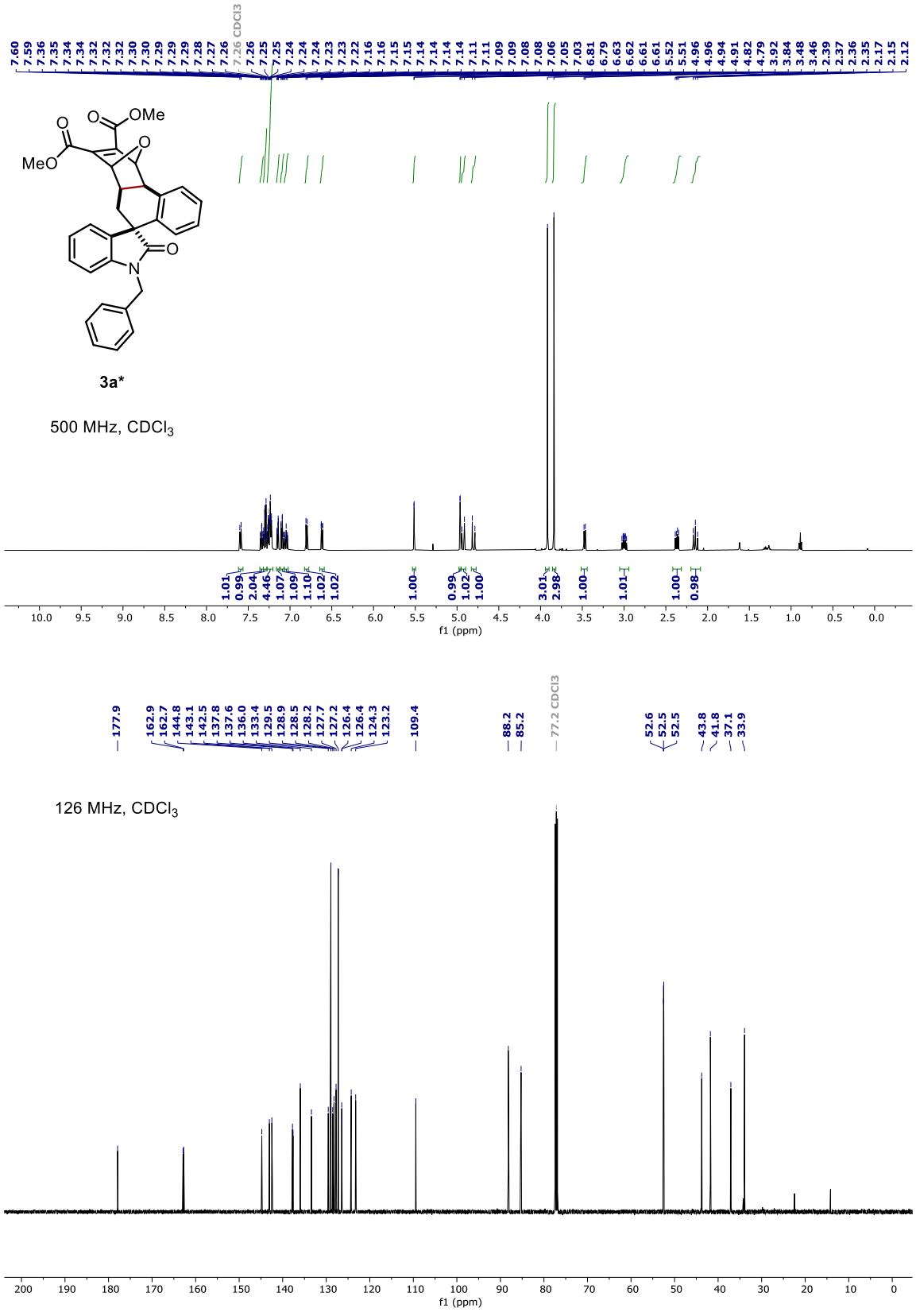


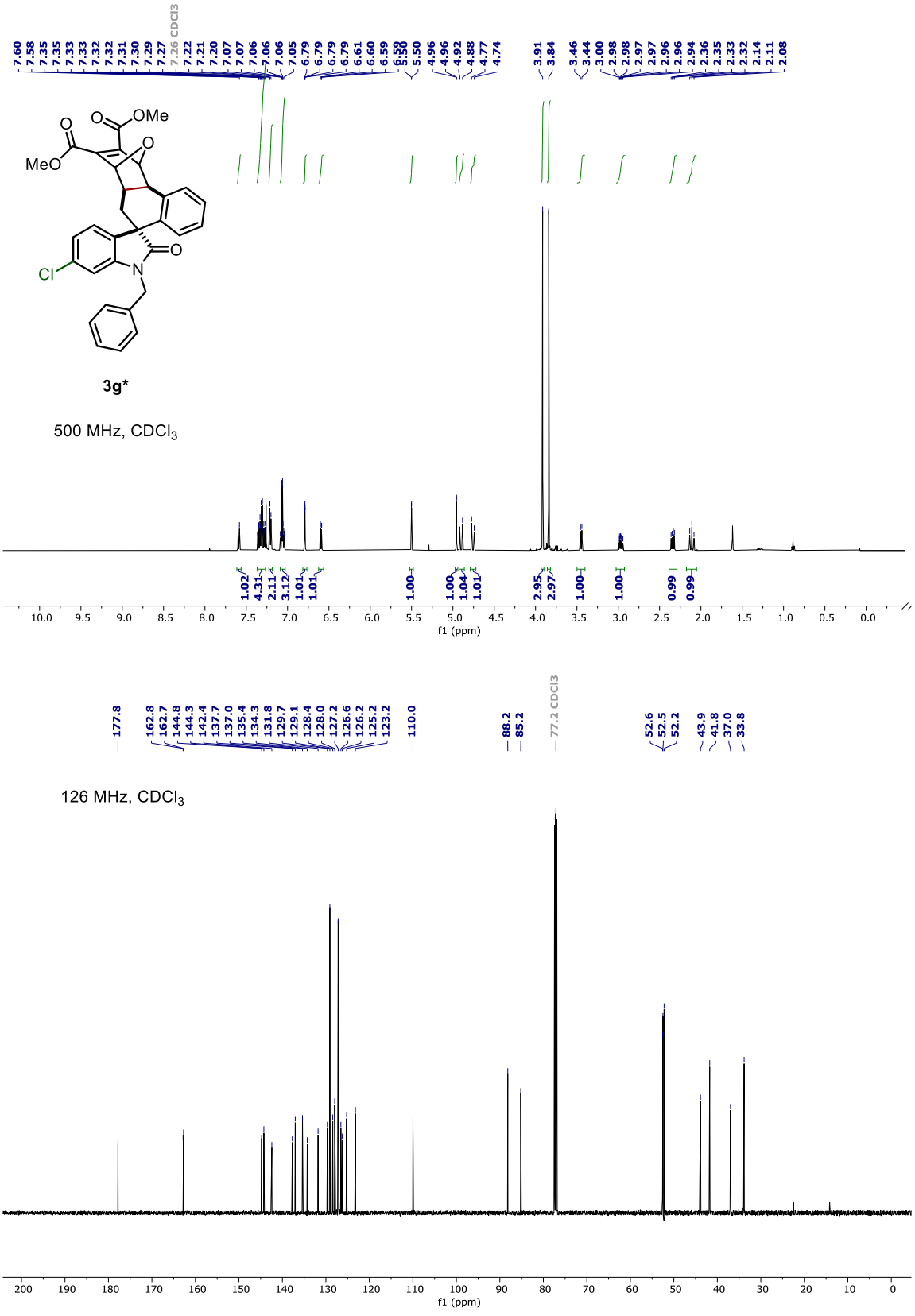
126 MHz, $CDCl_3$

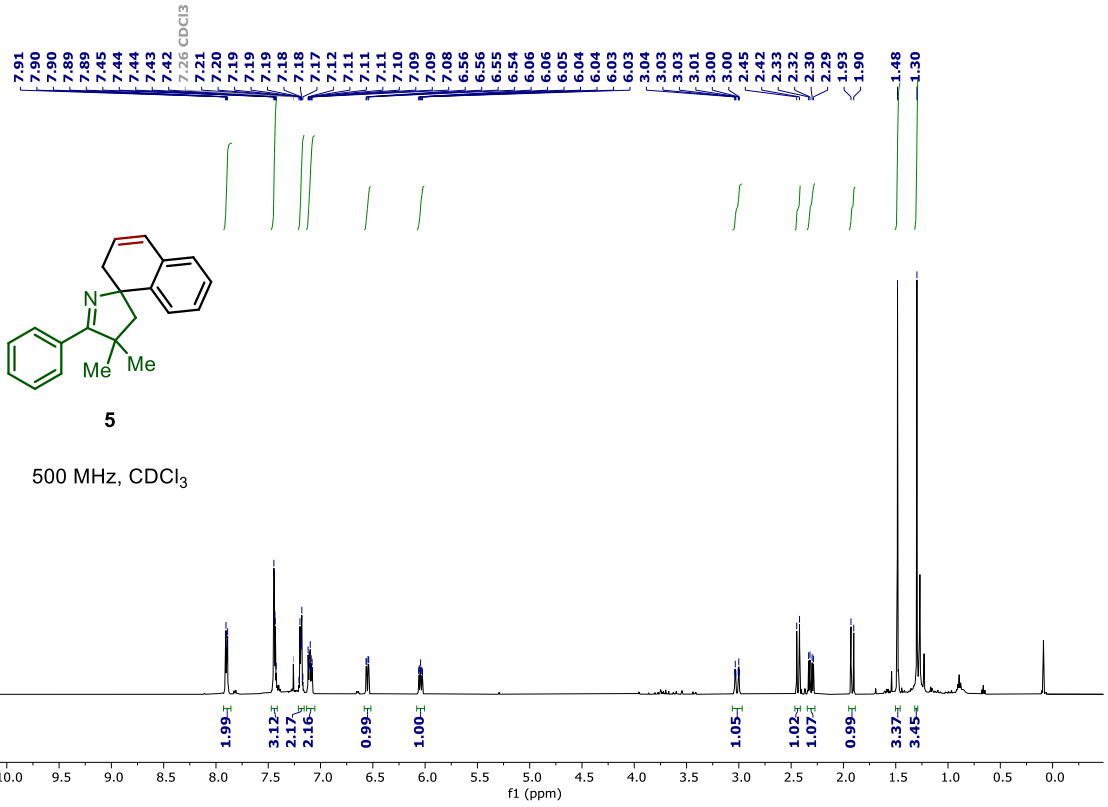

7.26 CDCl3
3u
500 MHz, CDCl3
4.03
2.28
1.12
1.07
1.01
1.07
0.97
1.00
2.00
1.13
0.99
1.00
0.99
f1 (ppm)
179.7
147.2
144.0
141.0
136.1
134.8
128.9
128.2
128.1
127.8
127.4
125.3
123.8
122.9
121.2
118.9
116.4
109.5
107.4
101.5
77.2 CDCl3
51.2
44.0
34.3
126 MHz, CDCl3
f1 (ppm)

^{1}H NMR shows >20:1 rr



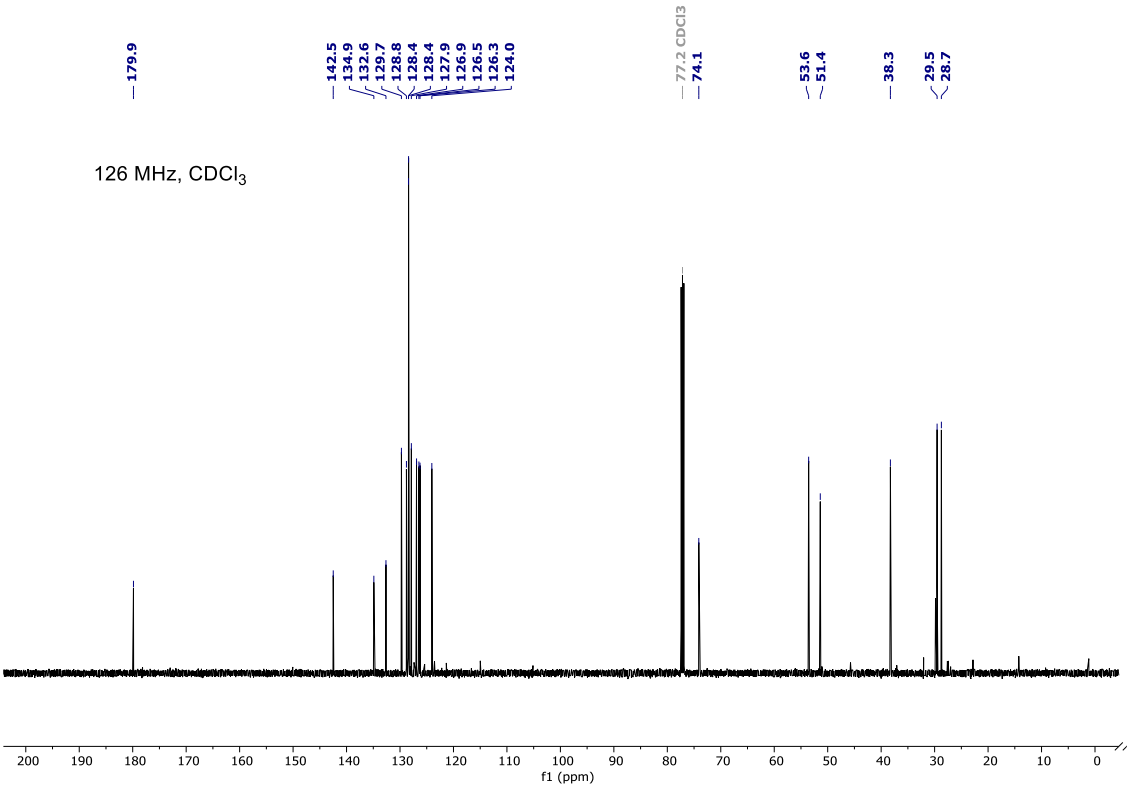

7.26 CDCl3
MeO
OMe
O
N
3a*
500 MHz, CDCl3
f1 (ppm)
77.2 CDCl3
126 MHz, CDCl3
f1 (ppm)


7.60 7.58 7.35 7.35 7.33 7.33 7.32 7.32 7.31 7.30 7.29 7.27 7.26 CDCl3 7.22 7.21 7.20 7.07 7.07 7.06 7.06 7.06 7.05 6.79 6.79 6.79 6.79 6.61 6.60 6.59 6.59 5.50 5.50 4.96 4.96 4.92 4.88 4.77 4.74 3.91 3.84 3.46 3.44 3.00 2.98 2.98 2.97 2.97 2.96 2.96 2.94 2.36 2.35 2.33 2.32 2.14 2.11 2.08
O
OMe
MeO
O
O
Cl
N
O
3g*
500 MHz, CDCl3
1.02 4.31 2.11 3.12 1.01 1.01 1.00 1.00 1.04 1.01 2.95 2.97 1.00 1.00 0.99 0.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
177.8 162.8 162.7 144.8 144.3 142.4 137.7 137.0 135.4 134.3 131.8 129.7 129.1 128.4 128.0 127.2 126.6 126.2 125.2 123.2 110.0 88.2 85.2 77.2 CDCl3 52.6 52.5 52.2 43.9 41.8 37.0 33.8
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

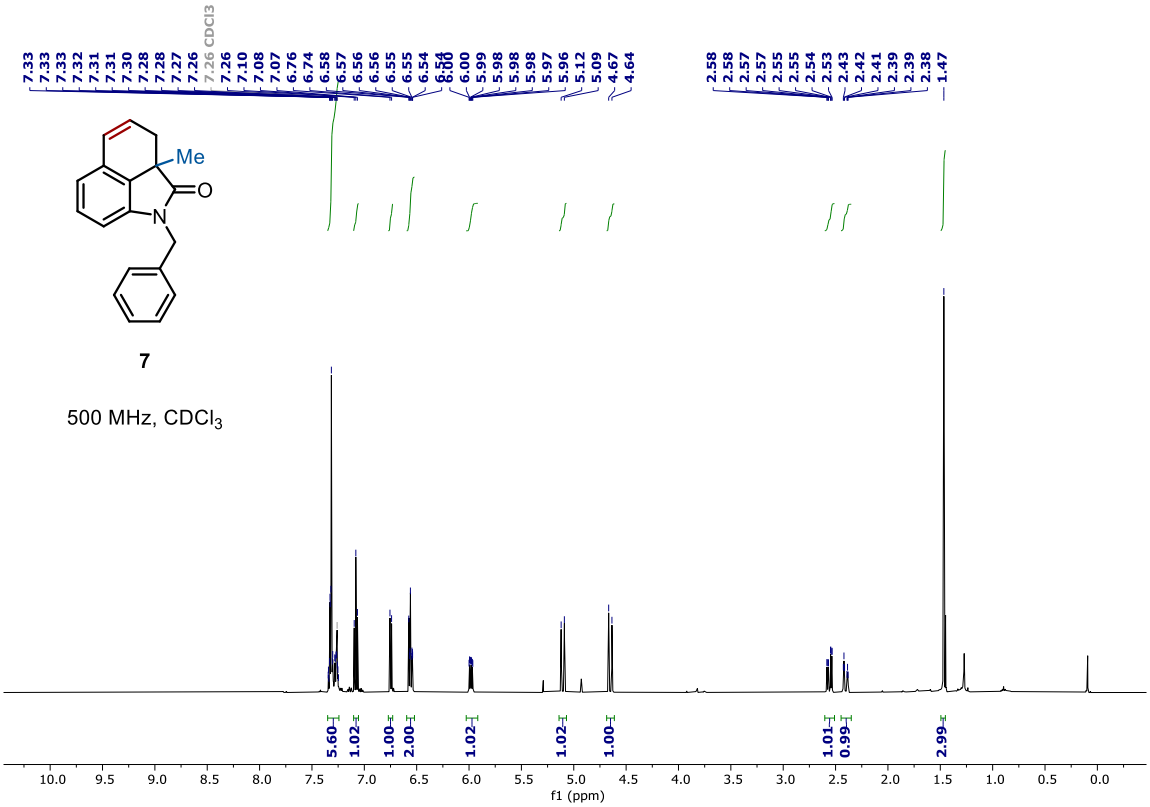


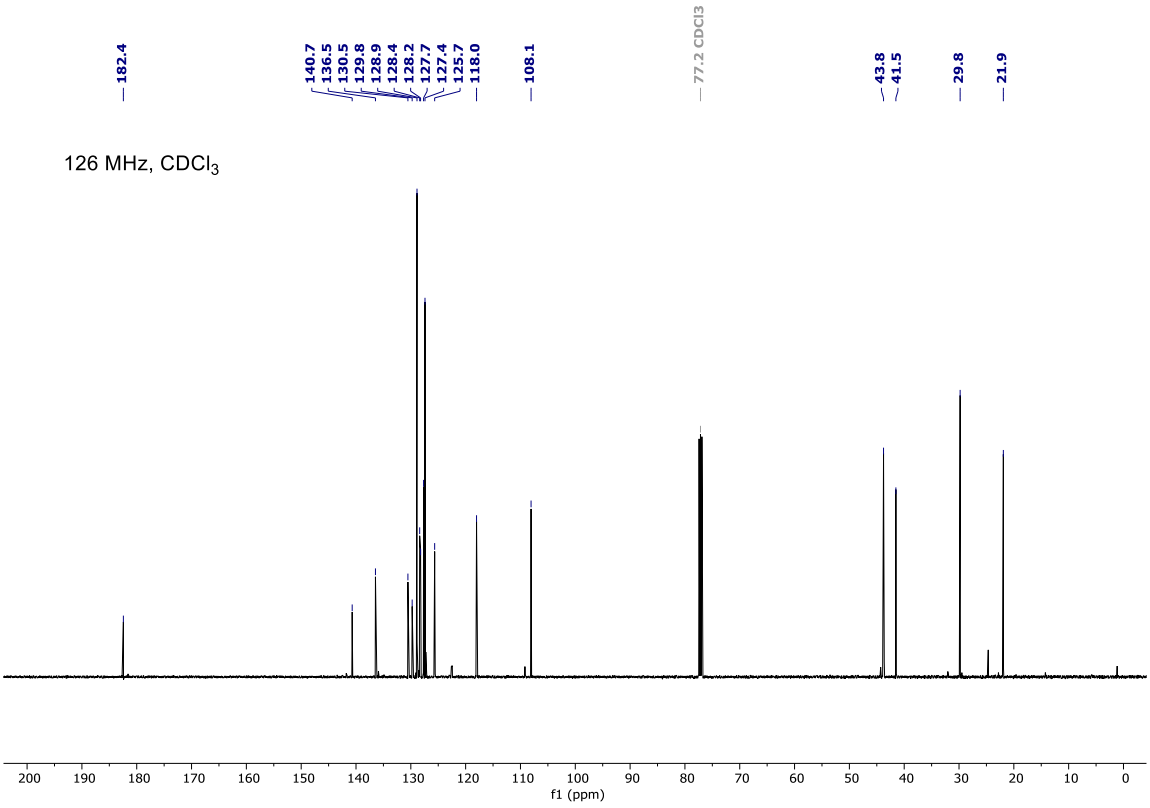
5

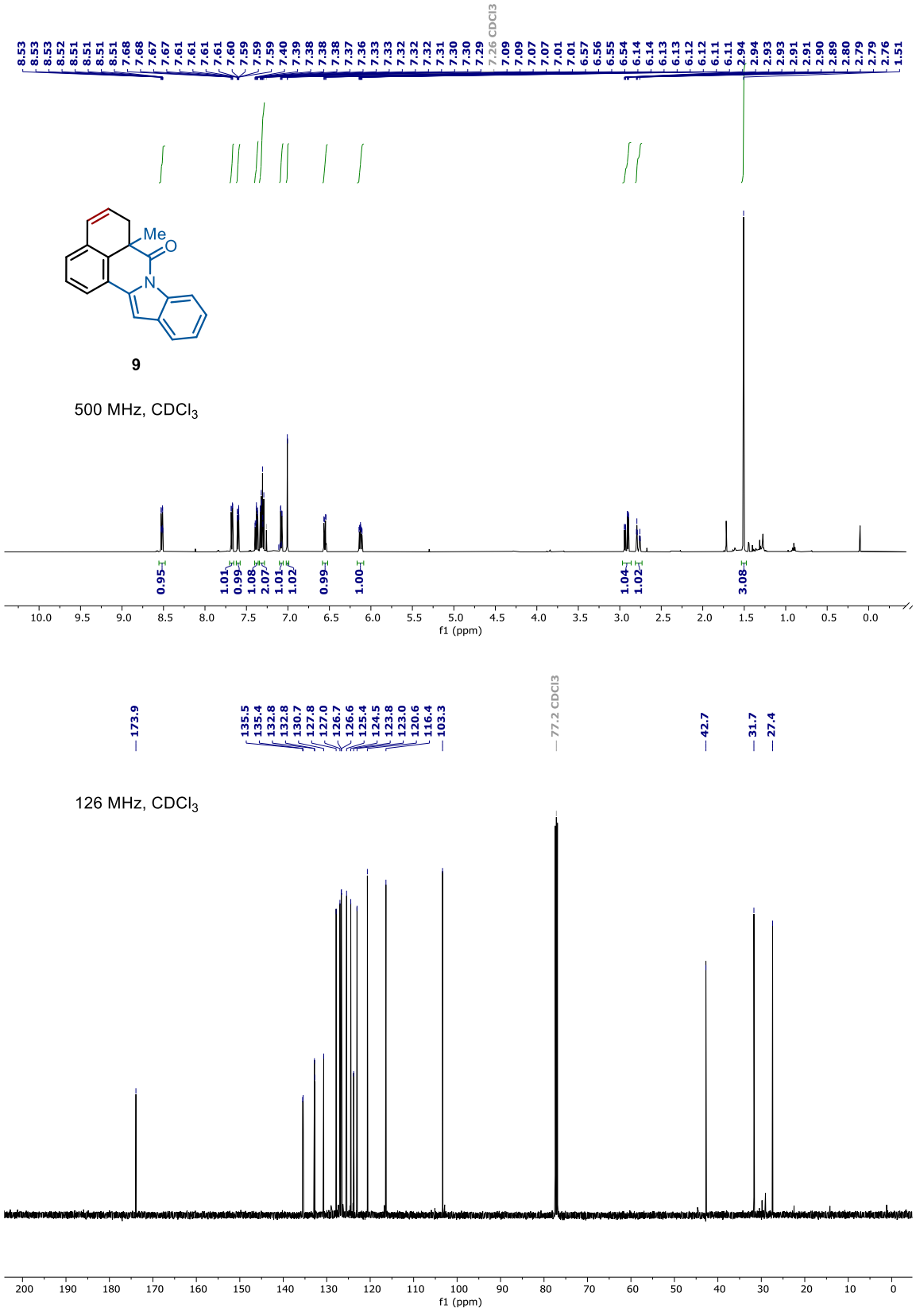
500 MHz, $CDCl_3$

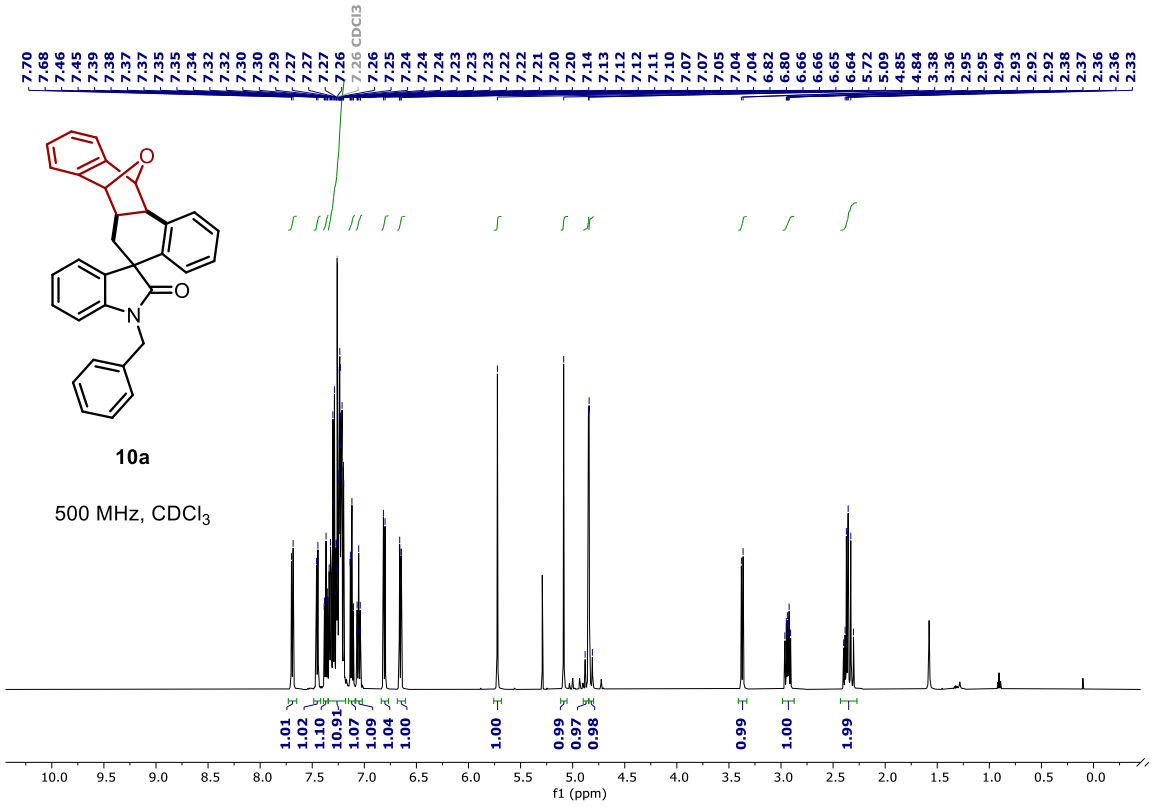


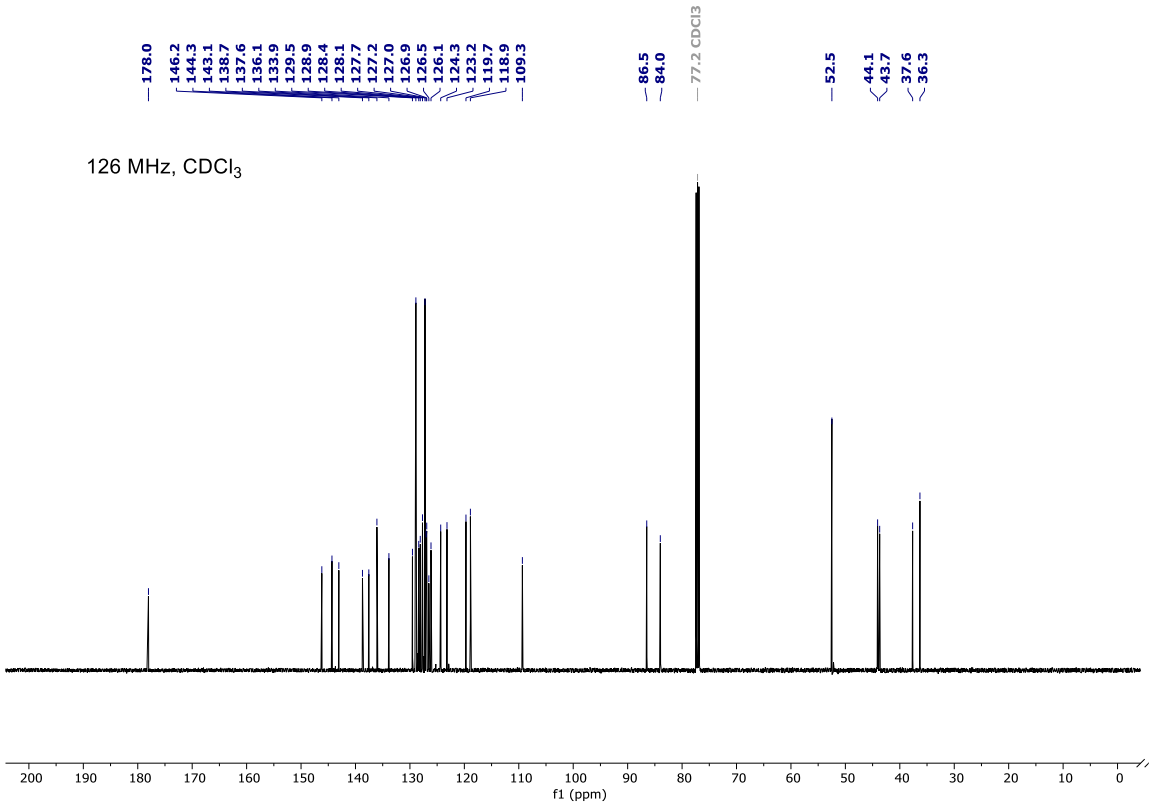
126 MHz, $CDCl_3$

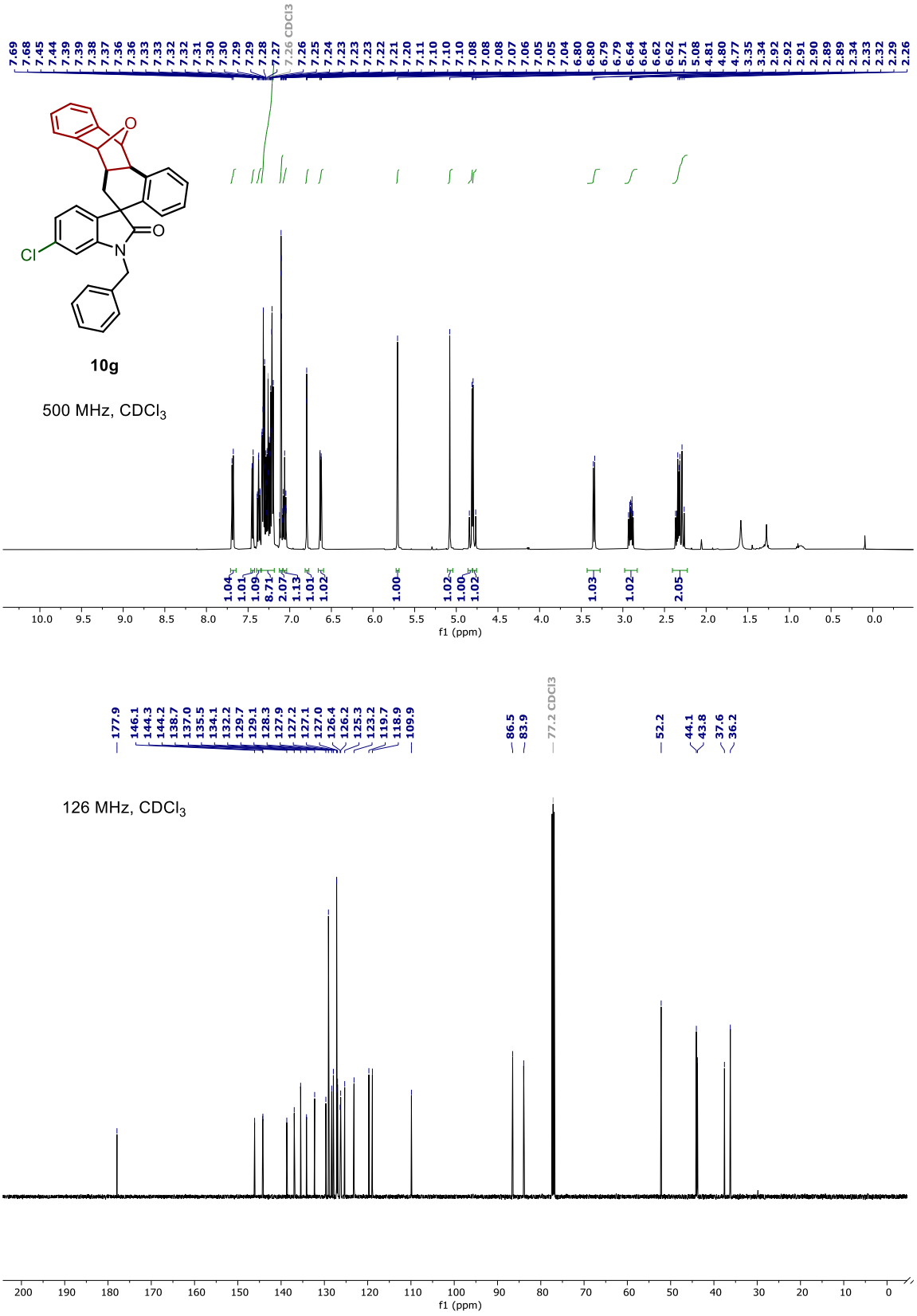

7.33 7.33 7.33 7.32 7.31 7.31 7.30 7.28 7.28 7.27 7.26 7.26 CDCl3 7.26 7.10 7.08 7.07 6.76 6.74 6.58 6.57 6.56 6.56 6.55 6.55 6.54 6.54 6.00 6.00 5.99 5.98 5.98 5.98 5.97 5.96 5.12 5.09 4.67 4.64
2.58 2.58 2.57 2.57 2.55 2.55 2.54 2.53 2.43 2.42 2.41 2.39 2.39 2.38 1.47
Me
O
N
7
500 MHz, CDCl3
5.60 1.02 1.00 2.00 1.02 1.02 1.00 1.01 0.99 2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

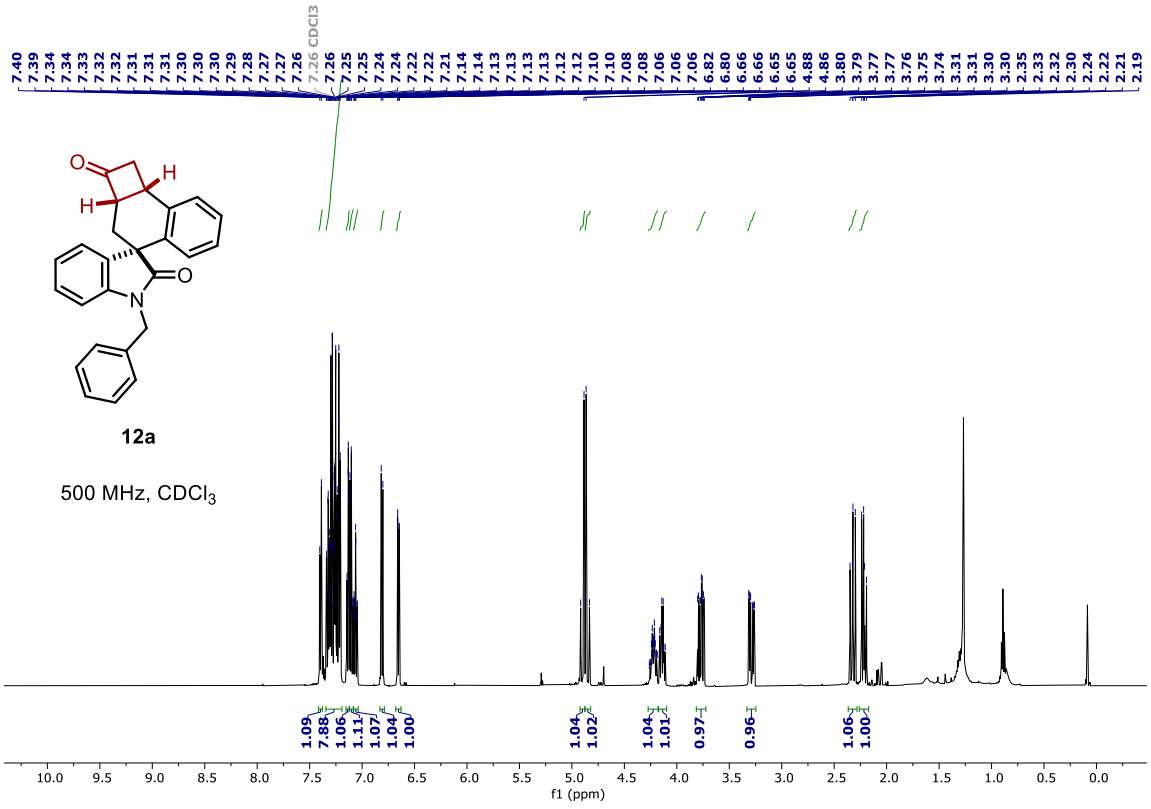

182.4
140.7 136.5 130.5 129.8 128.9 128.4 128.2 127.7 127.4 125.7 118.0
108.1
77.2 CDCl3
43.8 41.5
29.8
21.9
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

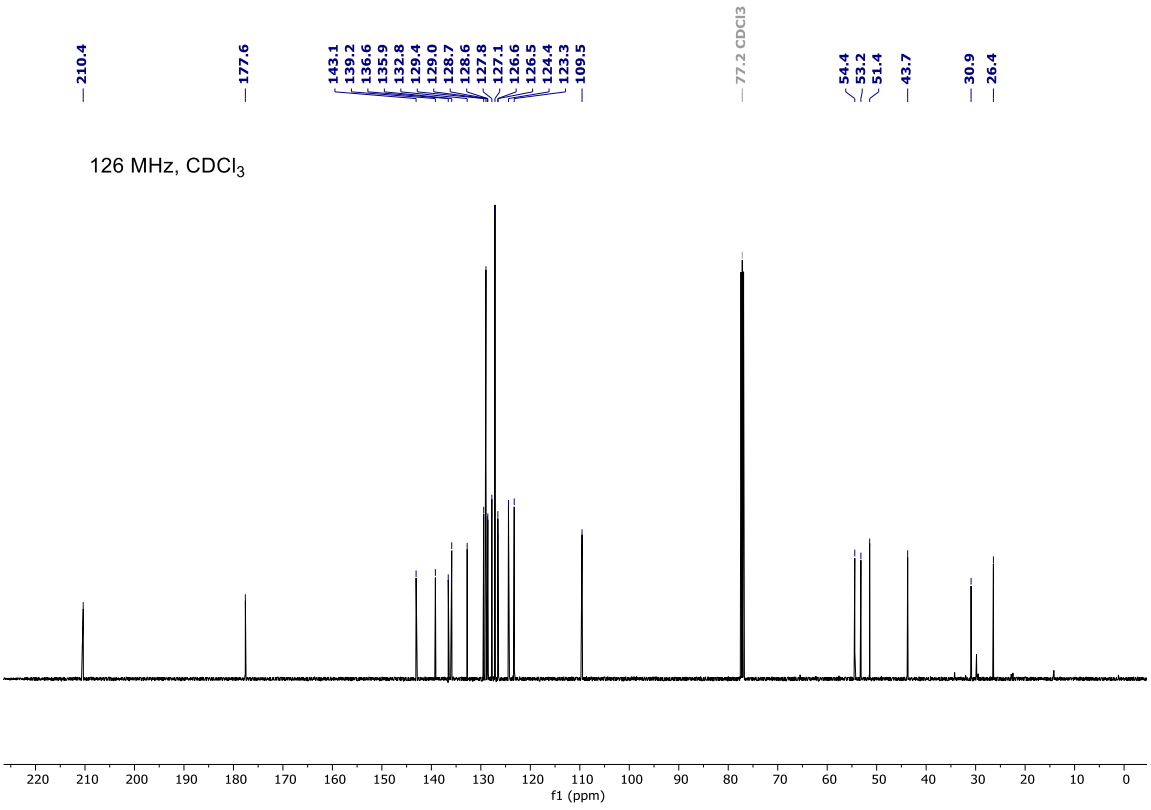

8.53 8.53 8.53 8.52 8.51 8.51 8.51 8.51 7.68 7.68 7.67 7.67 7.61 7.61 7.61 7.61 7.60 7.59 7.59 7.59 7.40 7.39 7.38 7.38 7.37 7.36 7.33 7.33 7.32 7.32 7.31 7.30 7.30 7.29 7.26 CDCl3 7.09 7.09 7.07 7.07 7.01 7.01 6.57 6.56 6.55 6.54 6.14 6.14 6.13 6.13 6.12 6.11 6.11 2.94 2.94 2.93 2.93 2.91 2.91 2.90 2.89 2.80 2.79 2.79 2.76 1.51
Me
O
N
9
500 MHz, CDCl3
0.95 1.01 0.99 1.08 2.07 1.01 1.02 0.99 1.00 1.04 1.02 3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
173.9 135.5 135.4 132.8 132.8 130.7 127.8 127.0 126.7 126.6 125.4 124.5 123.8 123.0 120.6 116.4 103.3 77.2 CDCl3 42.7 31.7 27.4
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.70 7.68 7.46 7.45 7.39 7.38 7.37 7.37 7.35 7.35 7.34 7.32 7.32 7.30 7.30 7.29 7.27 7.27 7.27 7.26 7.26 CDCl3 7.26 7.25 7.24 7.24 7.24 7.23 7.23 7.23 7.22 7.22 7.21 7.20 7.20 7.14 7.13 7.12 7.12 7.11 7.10 7.07 7.07 7.05 7.04 7.04 6.82 6.80 6.66 6.66 6.65 6.64 5.72 5.09 4.85 4.84 3.38 3.36 2.95 2.95 2.94 2.93 2.92 2.92 2.38 2.37 2.36 2.36 2.33
O
O
N
10a
500 MHz, CDCl3
1.01 1.02 1.10 10.91 1.07 1.09 1.04 1.00 1.00 0.99 0.97 0.98 0.99 1.00 1.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

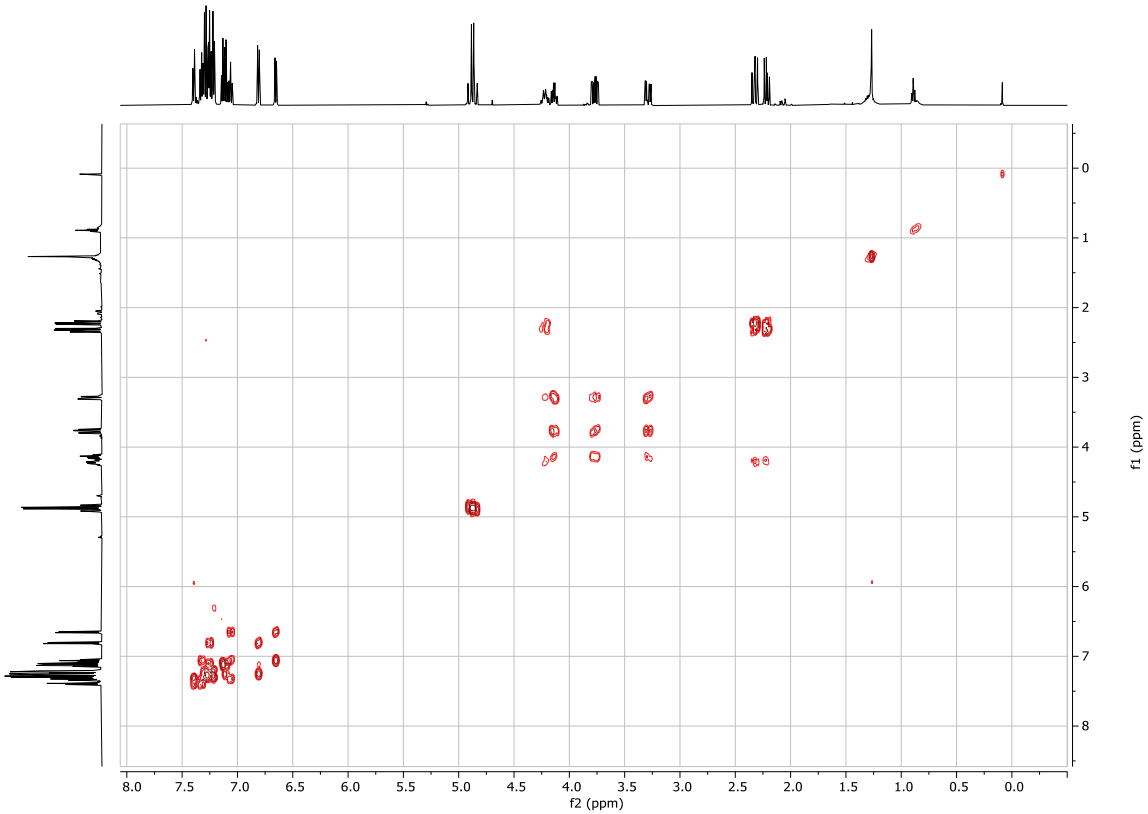

178.0 146.2 144.3 143.1 138.7 137.6 136.1 133.9 129.5 128.9 128.4 128.1 127.7 127.2 127.0 126.9 126.5 126.1 124.3 123.2 119.7 118.9 109.3
86.5 84.0 77.2 CDCl3
52.5 44.1 43.7 37.6 36.3
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

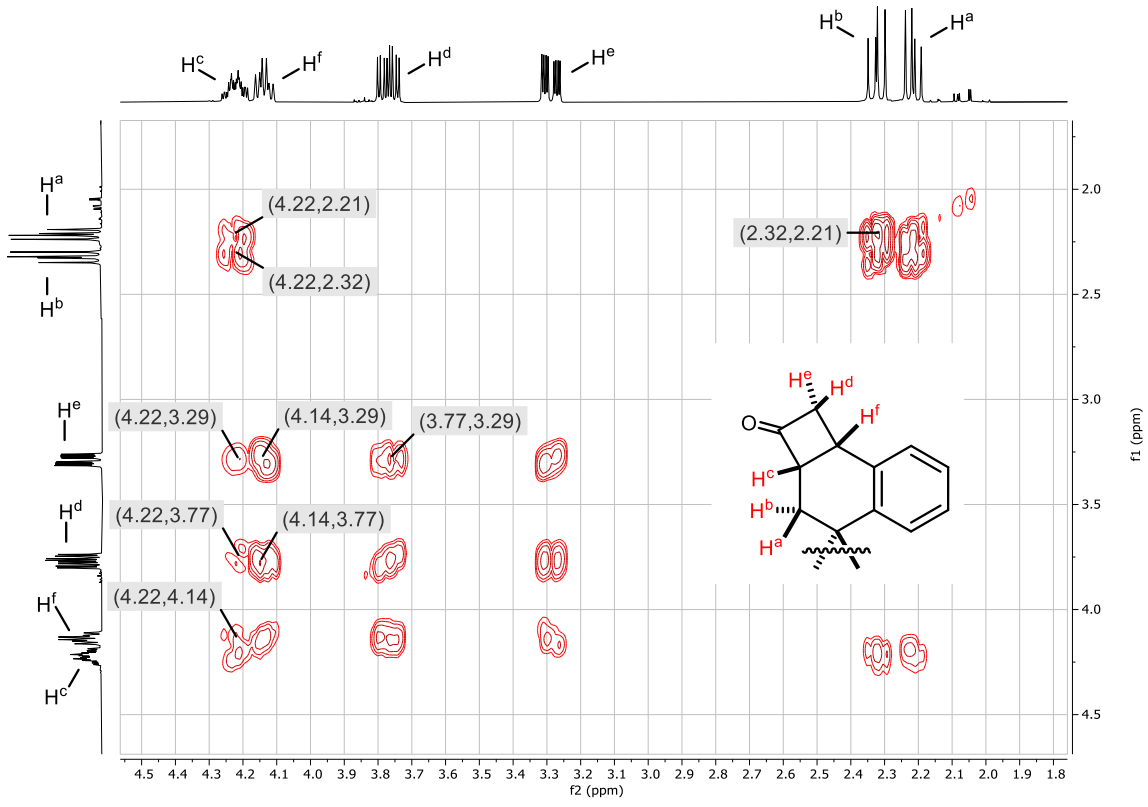

7.69 7.68 7.45 7.44 7.39 7.39 7.38 7.37 7.36 7.36 7.33 7.33 7.32 7.32 7.31 7.30 7.30 7.29 7.29 7.28 7.27 7.26 CDCl3 7.26 7.25 7.24 7.23 7.23 7.22 7.21 7.20 7.11 7.10 7.10 7.08 7.08 7.08 7.07 7.06 7.05 7.05 7.04 6.80 6.80 6.79 6.79 6.64 6.64 6.62 6.62 5.71 5.08 4.81 4.80 4.77 3.35 3.34 2.92 2.92 2.91 2.90 2.89 2.89 2.34 2.33 2.32 2.29 2.26
O
O
N
Cl
10g
500 MHz, CDCl3
1.04 1.01 1.09 8.71 2.07 1.13 1.01 1.02 1.00 1.02 1.00 1.02 1.03 1.02 2.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
177.9 146.1 144.3 144.2 138.7 137.0 135.5 134.1 132.2 129.7 129.1 128.3 127.9 127.2 127.1 127.0 126.4 126.2 125.3 123.2 119.7 118.9 109.9 86.5 83.9 77.2 CDCl3 52.2 44.1 43.8 37.6 36.2
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.40 7.39 7.34 7.34 7.33 7.32 7.32 7.31 7.31 7.31 7.30 7.30 7.30 7.29 7.28 7.27 7.27 7.26 7.26 CDCl3 7.25 7.25 7.24 7.24 7.22 7.22 7.21 7.14 7.13 7.13 7.13 7.12 7.12 7.10 7.10 7.08 7.08 7.06 7.06 7.06 6.82 6.80 6.66 6.66 6.65 6.65 4.88 4.86 3.80 3.79 3.77 3.77 3.76 3.75 3.74 3.31 3.31 3.30 3.30 2.35 2.33 2.32 2.30 2.24 2.22 2.21 2.19
O
H
H
O
N
12a
500 MHz, CDCl3
1.09 7.88 1.06 1.11 1.07 1.04 1.00 1.04 1.02 1.04 1.01 0.97 0.96 1.06 1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

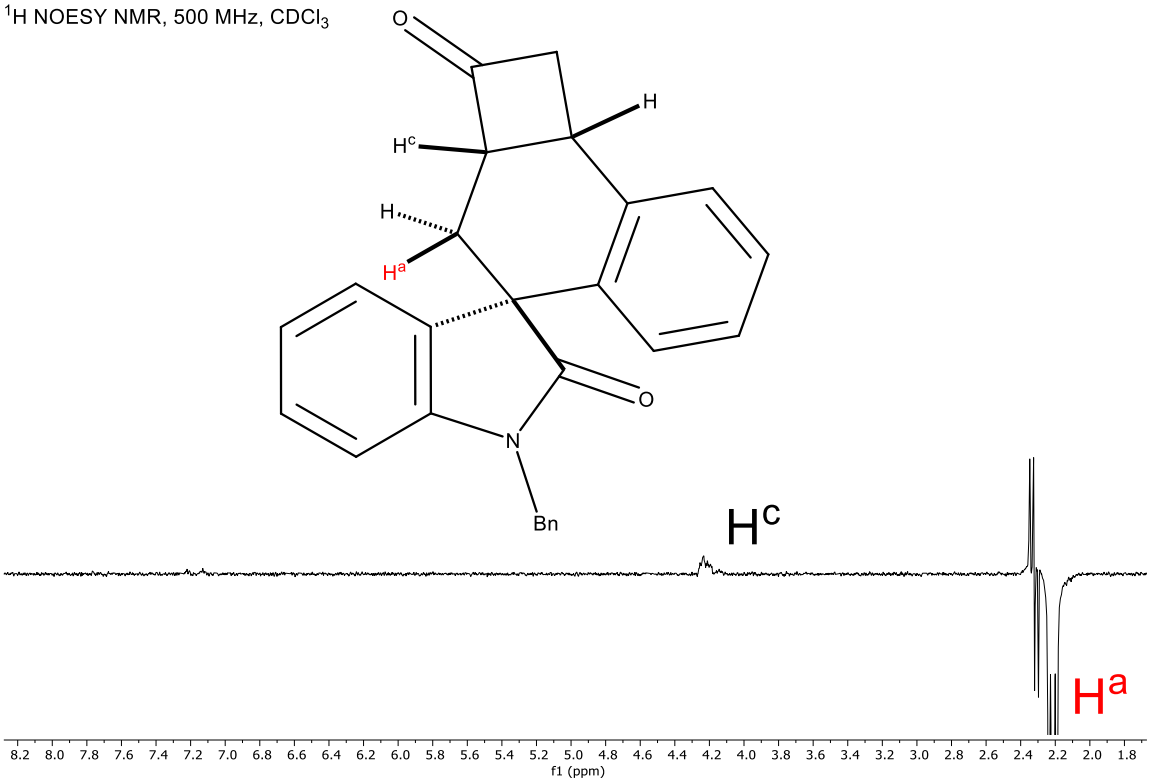

210.4 177.6 143.1 139.2 136.6 135.9 132.8 129.4 129.0 128.7 128.6 127.8 127.1 126.6 126.5 124.4 123.3 109.5 77.2 CDCl3 54.4 53.2 51.4 43.7 30.9 26.4
126 MHz, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

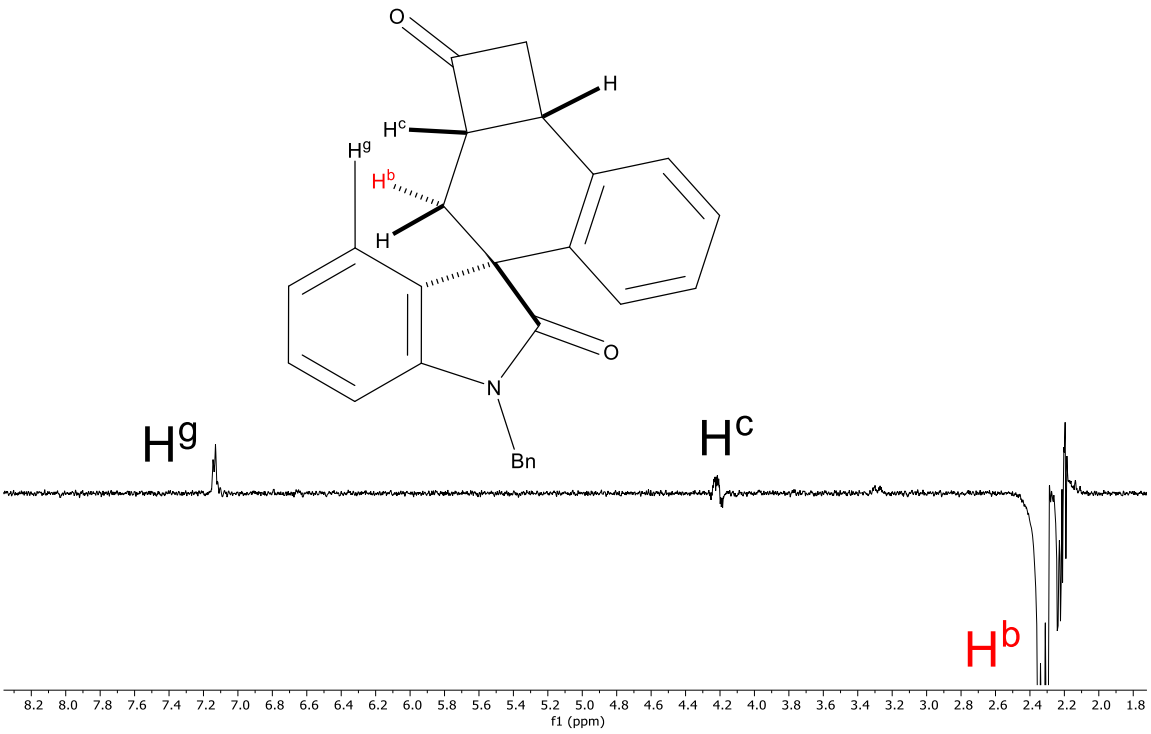
^{1}H-^{1}H COSY NMR, 500 MHz, $CDCl_3$



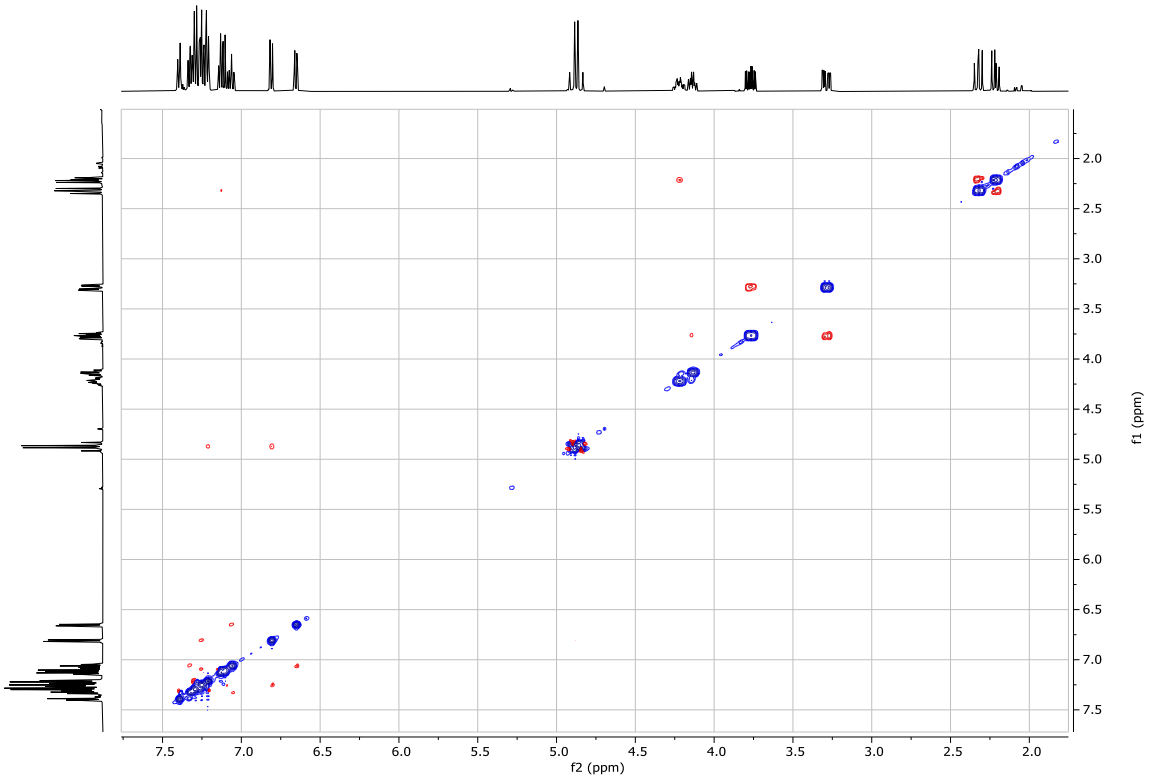


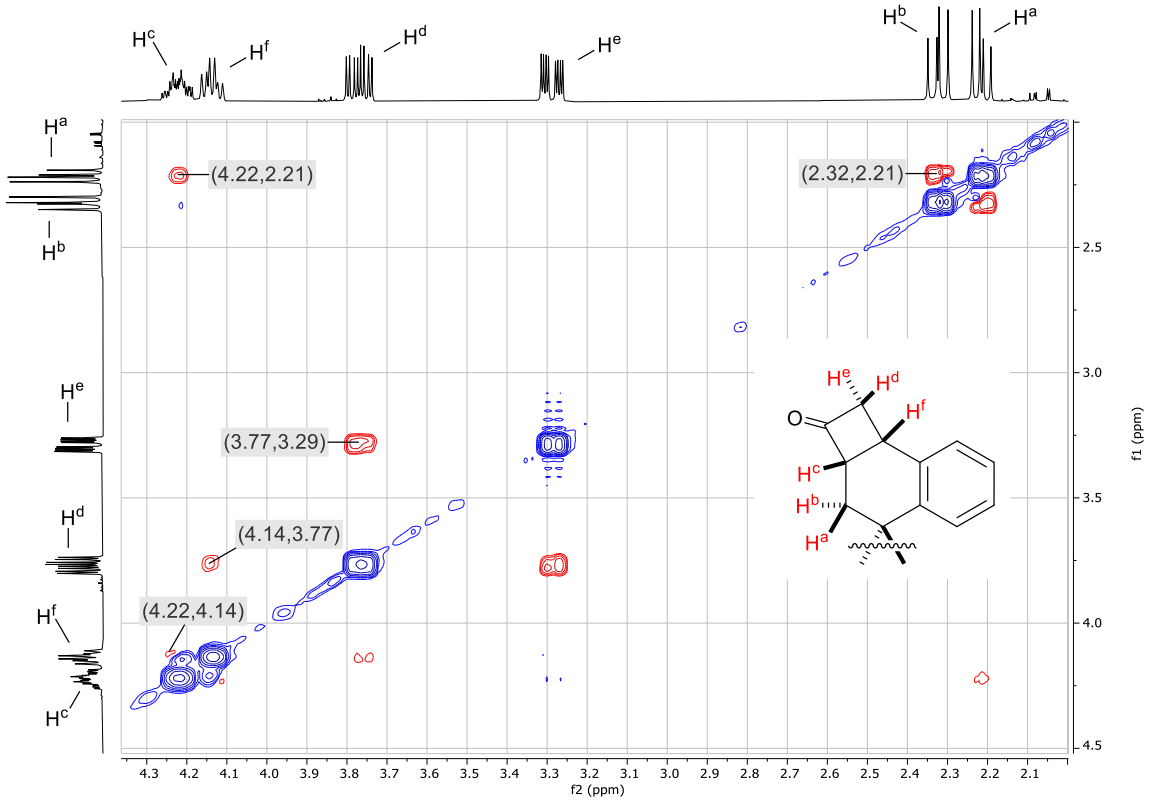
^{1}H NOESY NMR, 500 MHz, $CDCl_3$

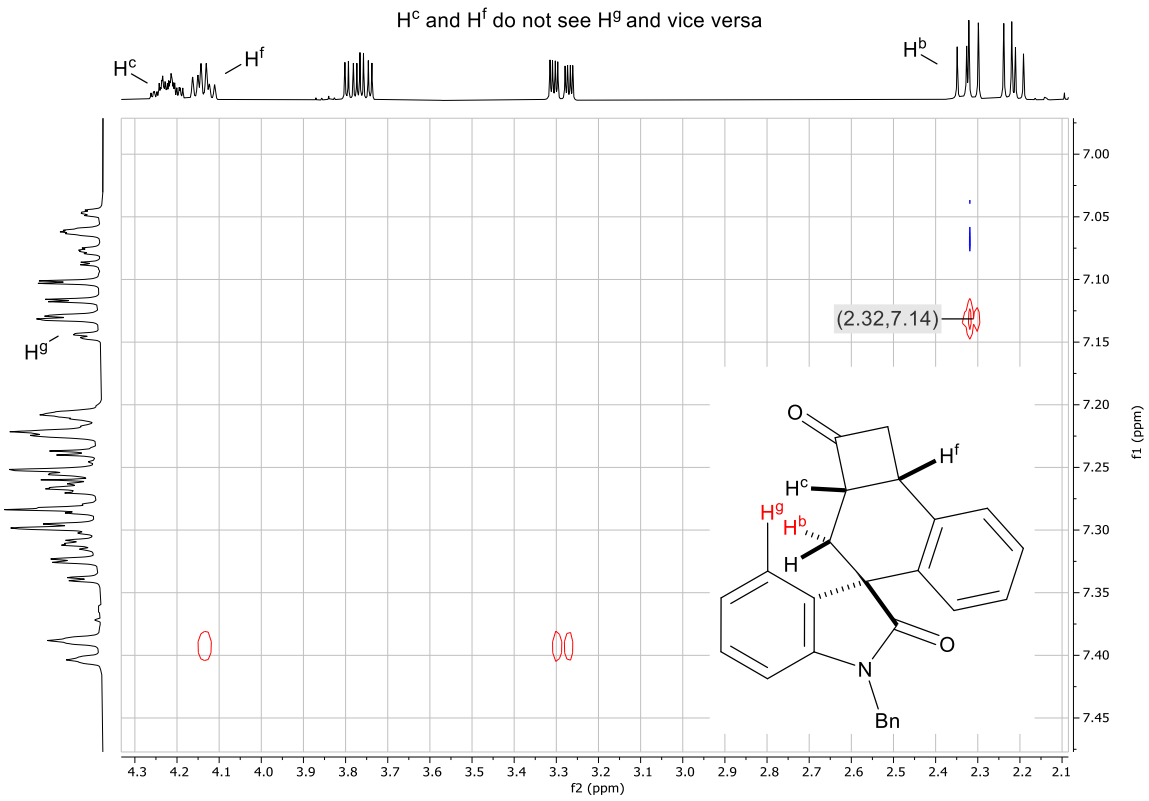




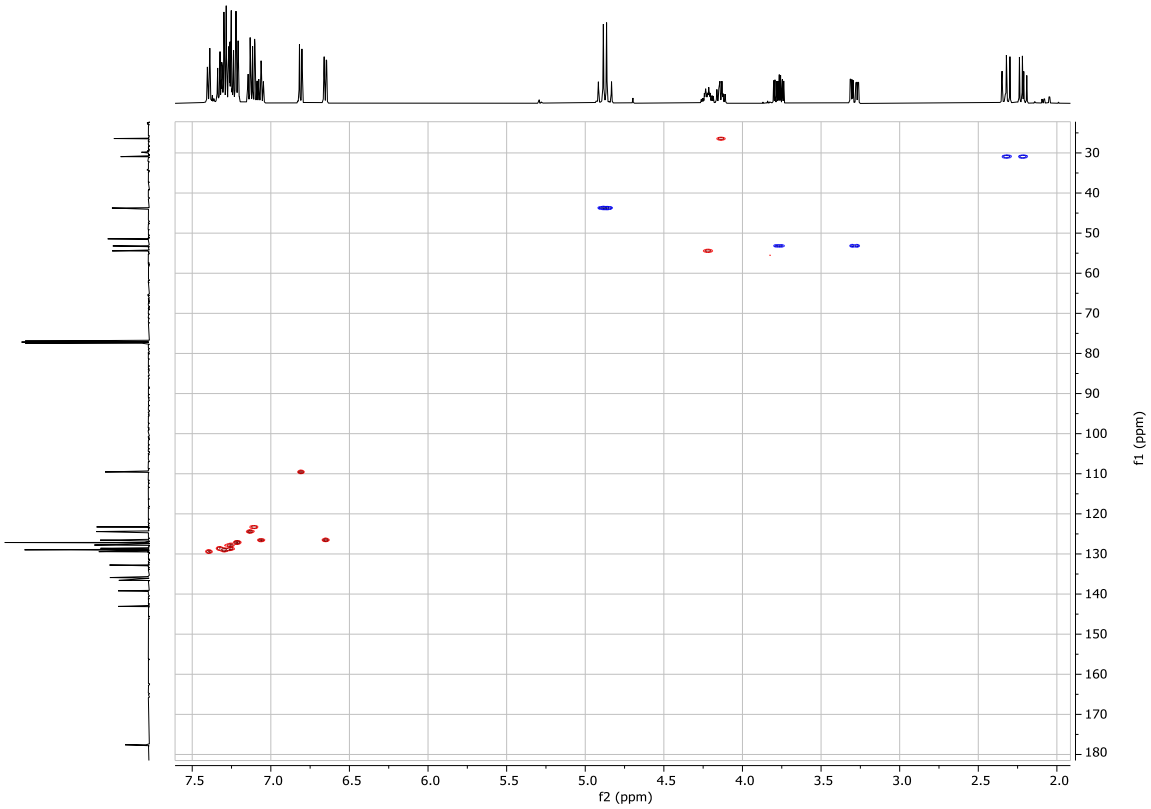
^{1}H-^{1}H NOESY NMR, 600 MHz, $CDCl_3$

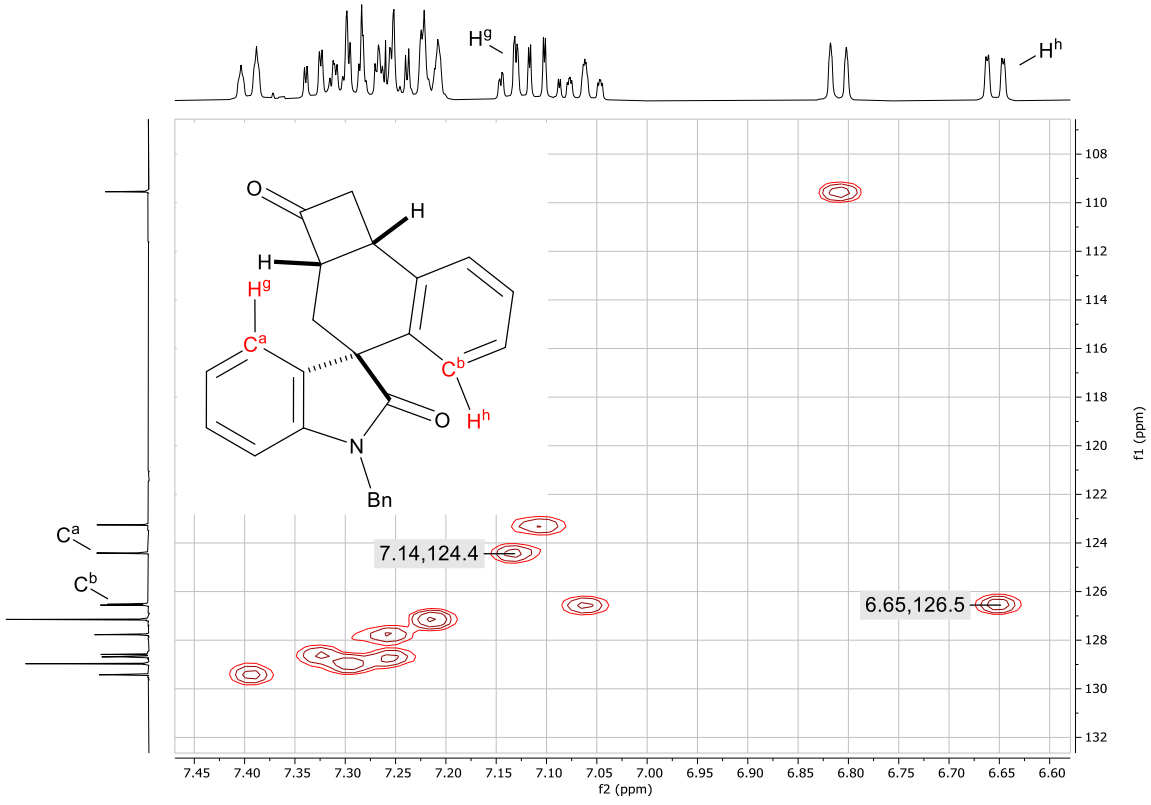


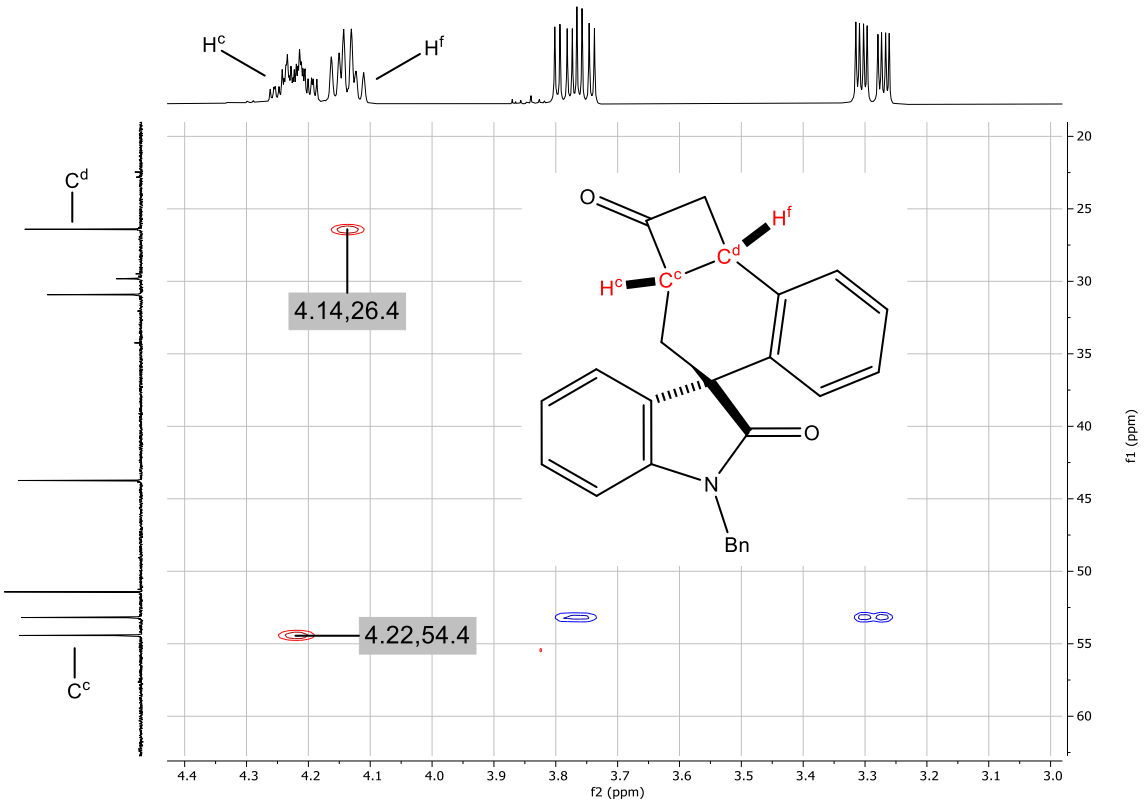



Hc and Hf do not see Hg and vice versa
Hc
Hf
Hb
Hg
(2.32,7.14)
O
Hf
Hc
Hg
Hb
H
O
N
Bn
f2 (ppm)
f1 (ppm)

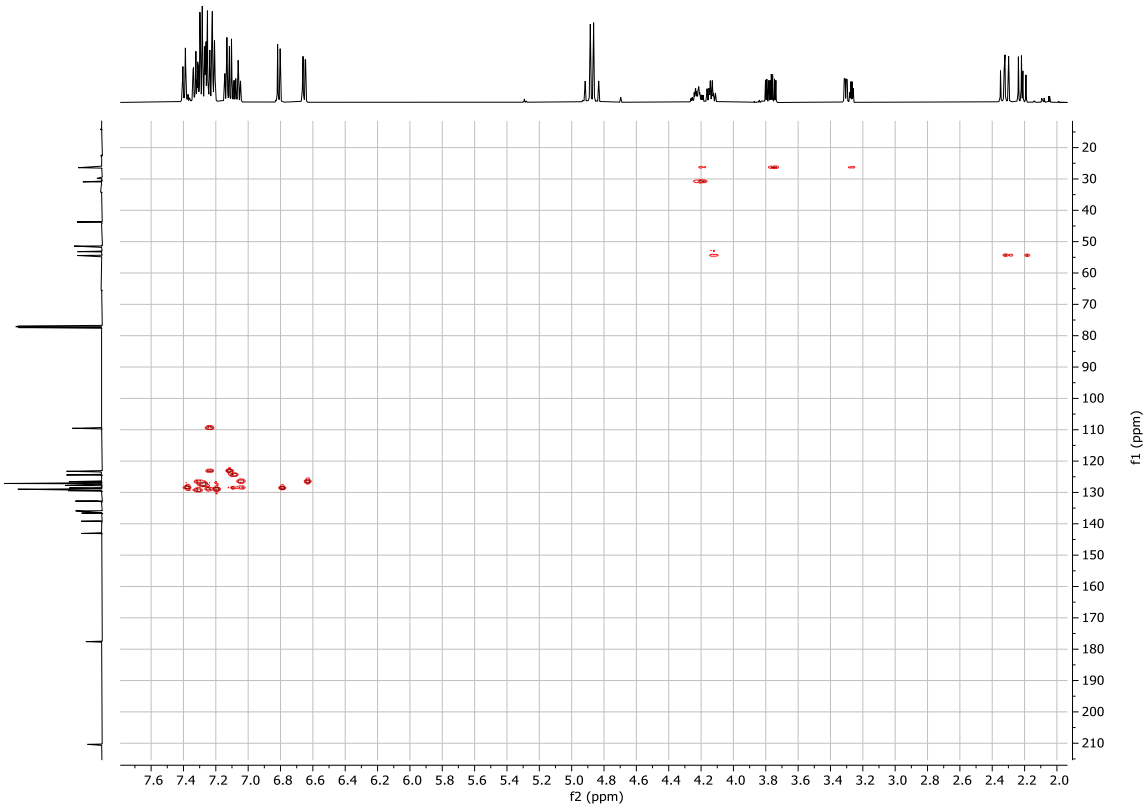
^{1}H-^{13}C HSQC NMR, 700 MHz, $CDCl_3$

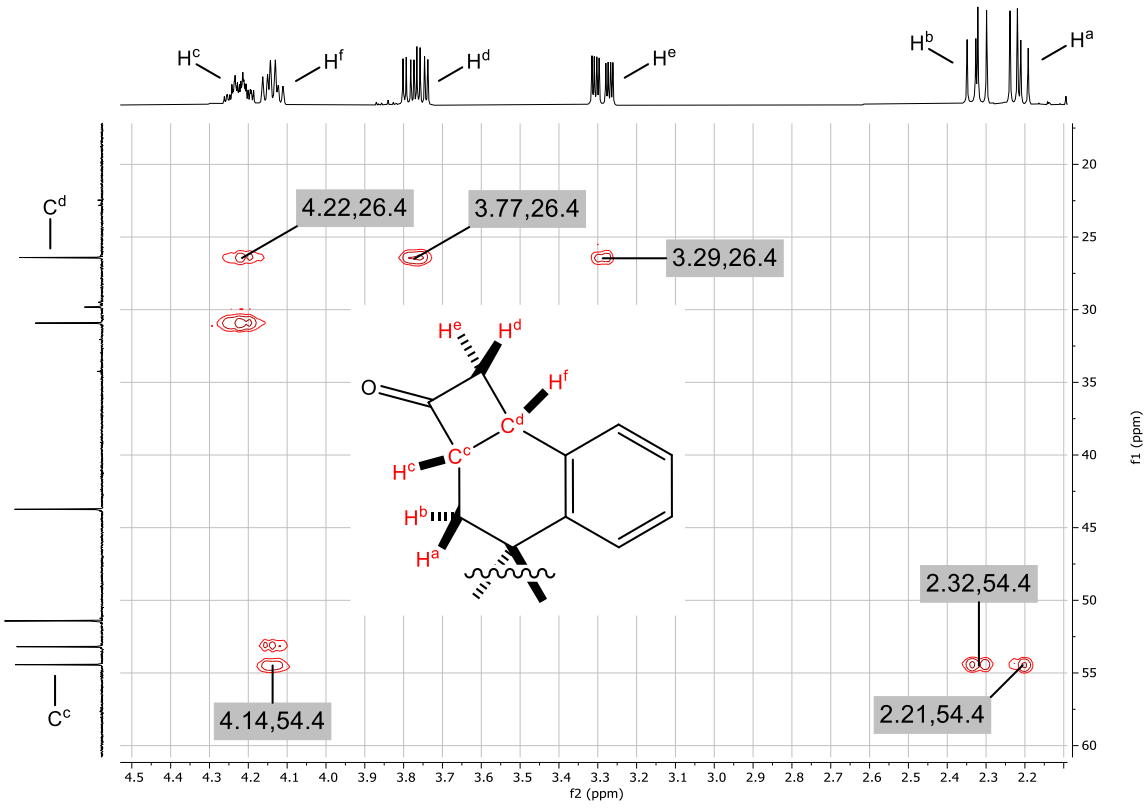




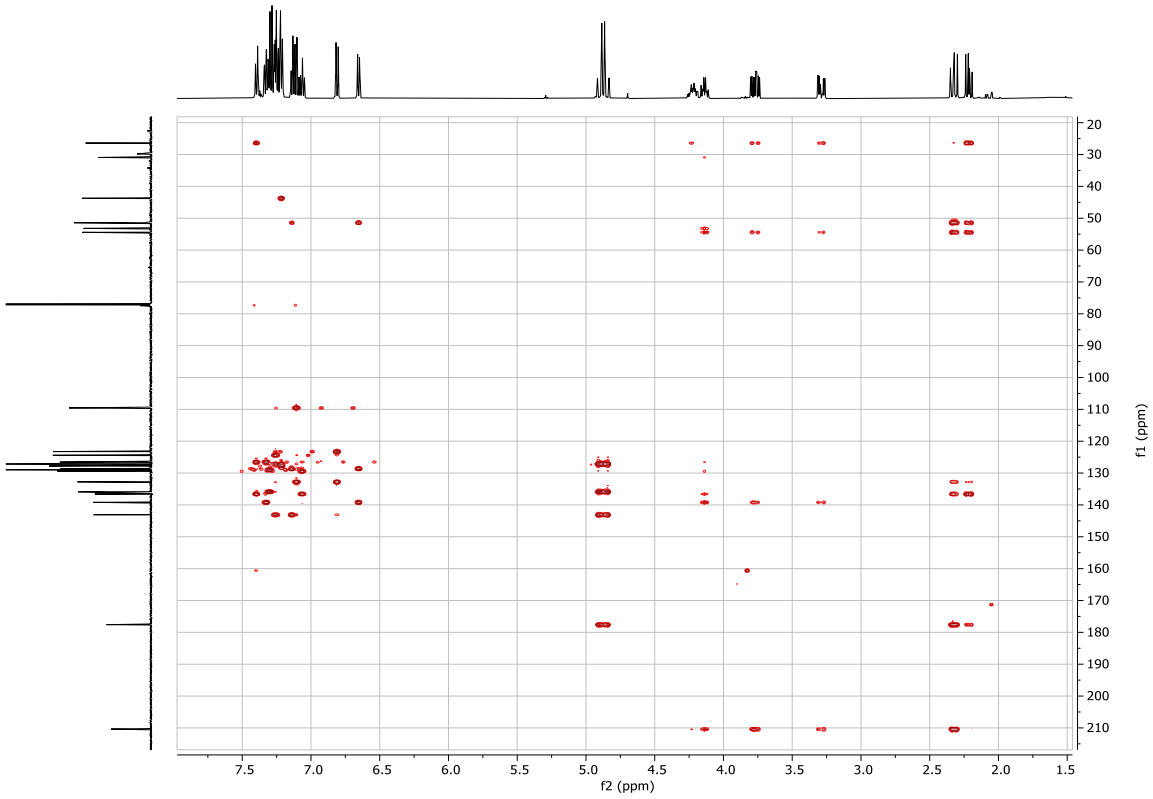

Hc
Hf
Cd
Cc
4.14,26.4
4.22,54.4
O
Hf
Cd
Hc
Cc
O
N
Bn
20
25
30
35
40
45
50
55
60
f1 (ppm)
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
f2 (ppm)

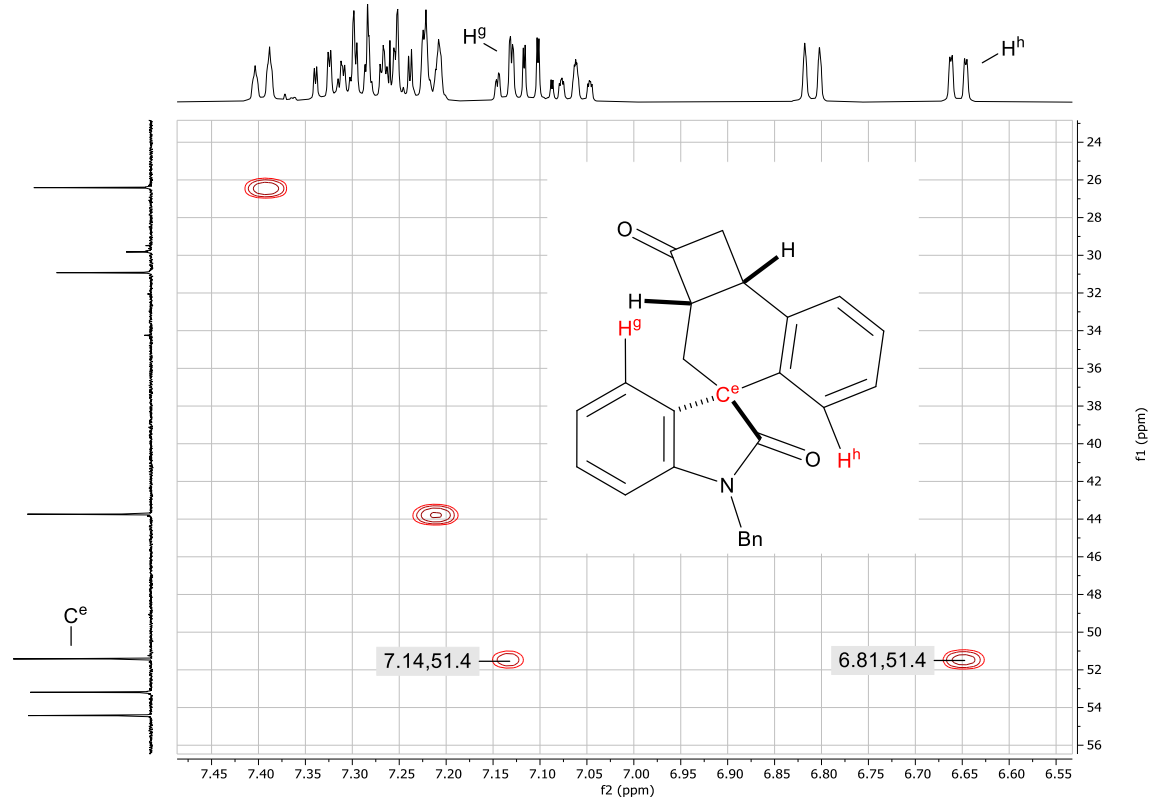
^{1}H-^{13}C H2BC NMR, 700 MHz, $CDCl_3$

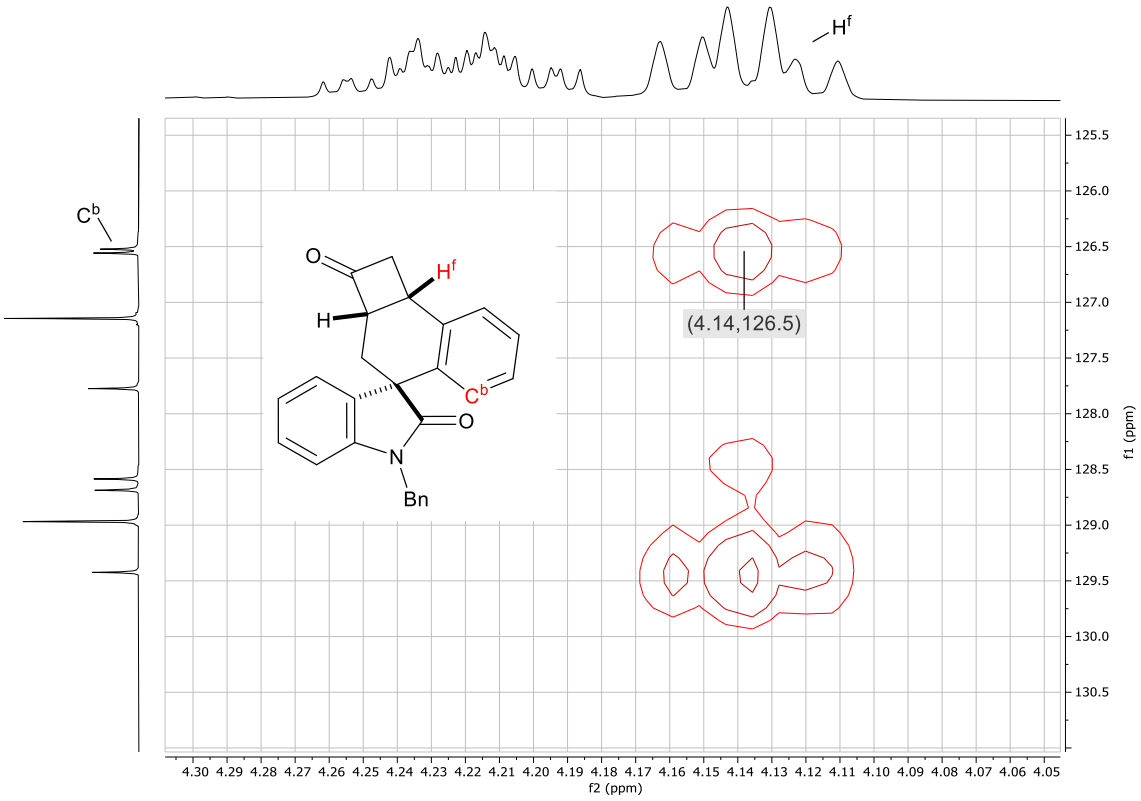


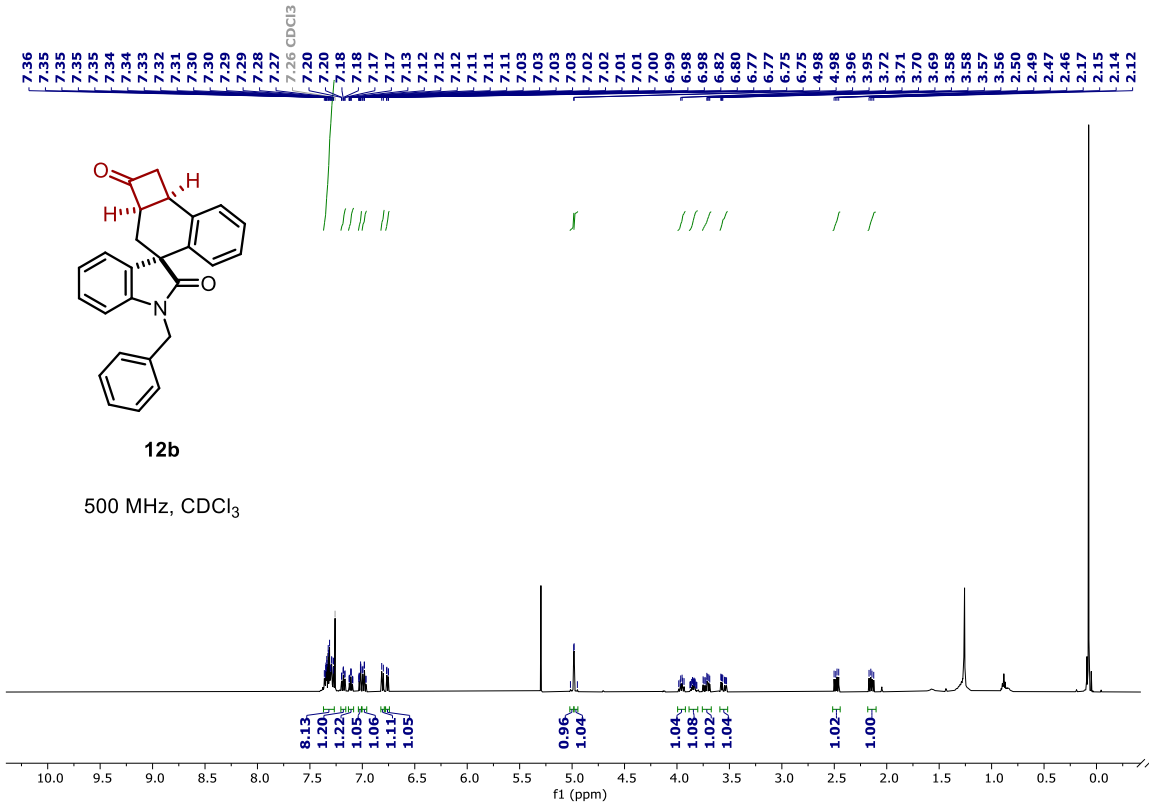


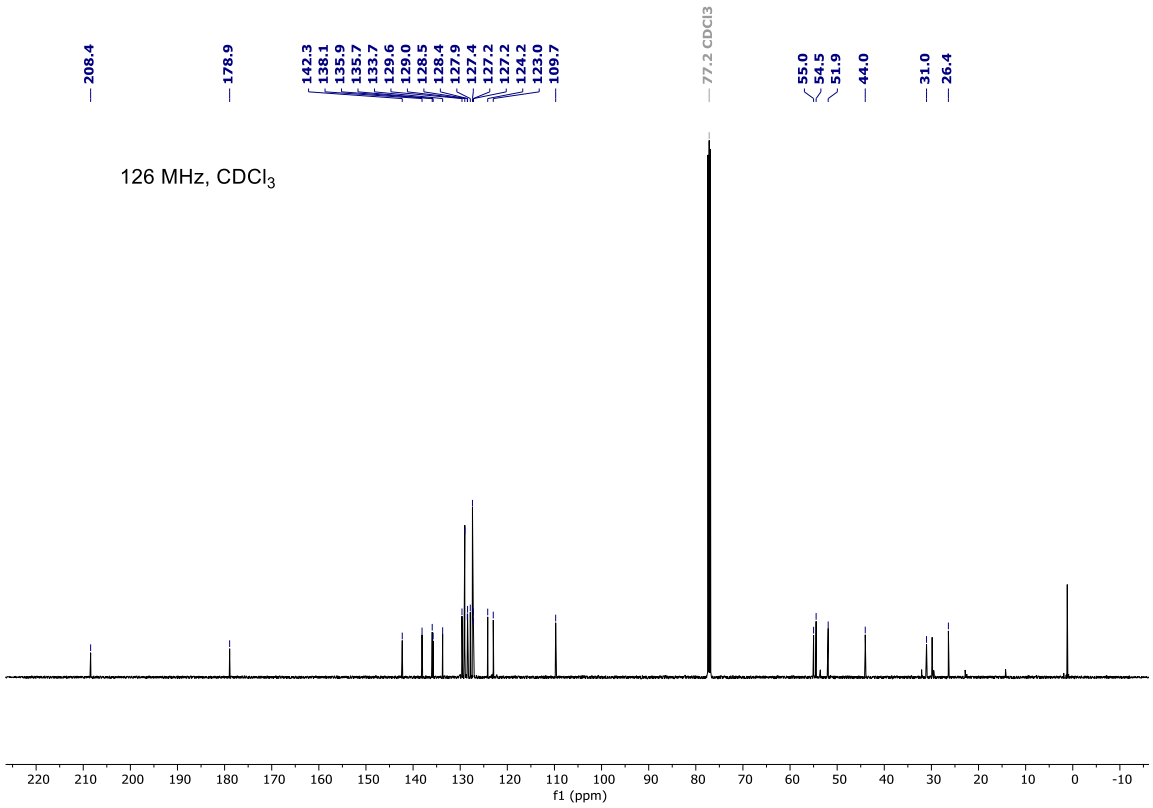
^{1}H-^{13}C HMBC NMR, 700 MHz, $CDCl_3$



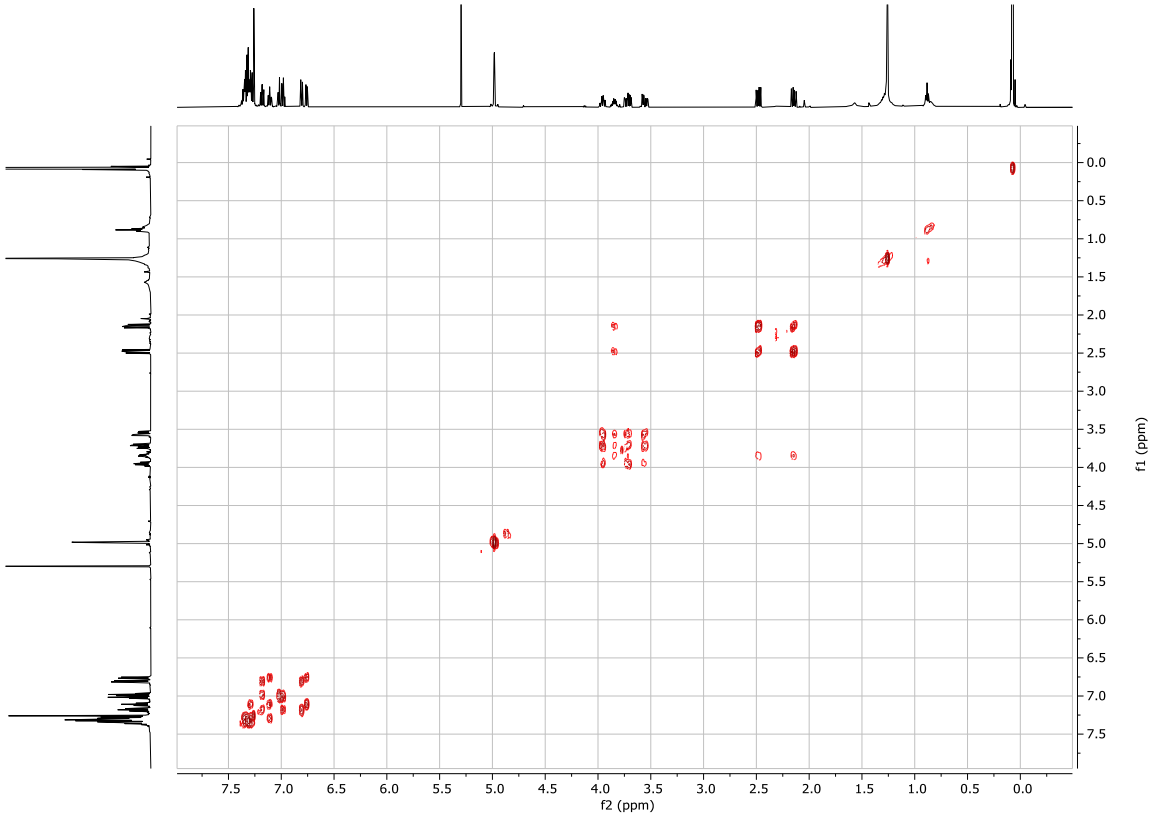


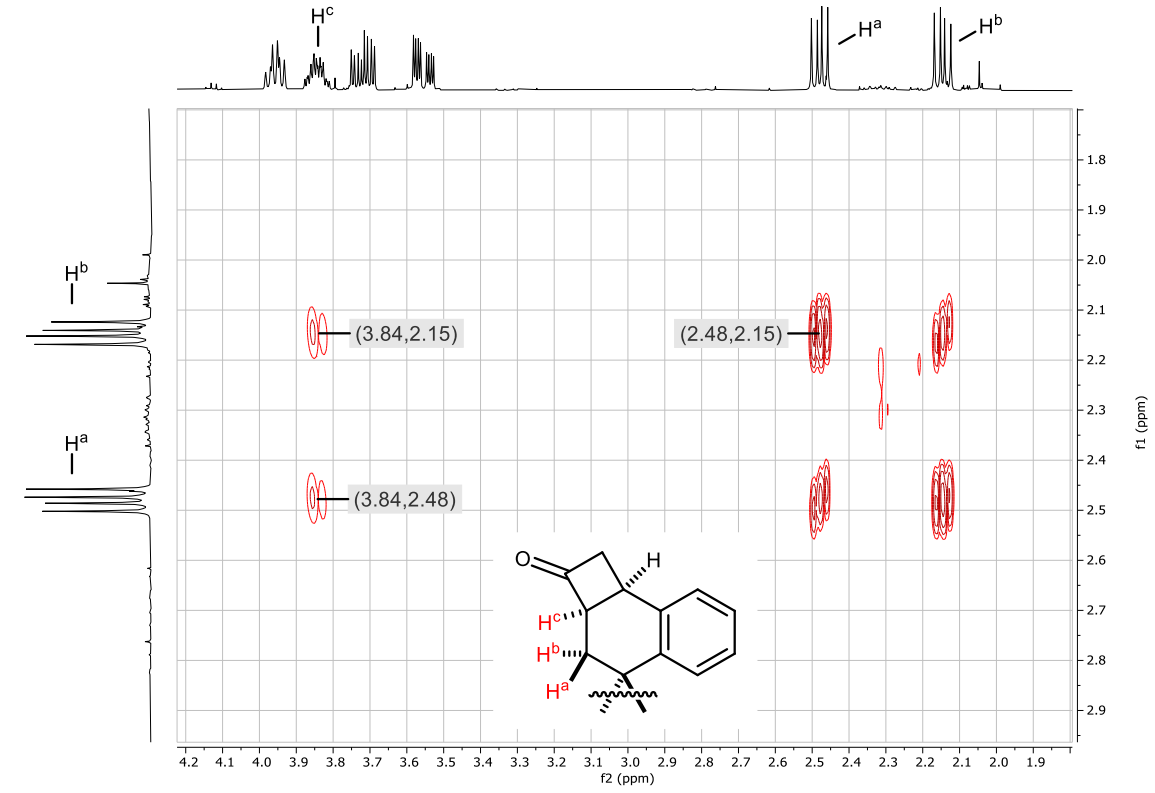

H^f
C^b
O
H^f
H
C^b
O
N
Bn
(4.14,126.5)
125.5
126.0
126.5
127.0
127.5
128.0
128.5
129.0
129.5
130.0
130.5
f1 (ppm)
4.30 4.29 4.28 4.27 4.26 4.25 4.24 4.23 4.22 4.21 4.20 4.19 4.18 4.17 4.16 4.15 4.14 4.13 4.12 4.11 4.10 4.09 4.08 4.07 4.06 4.05
f2 (ppm)

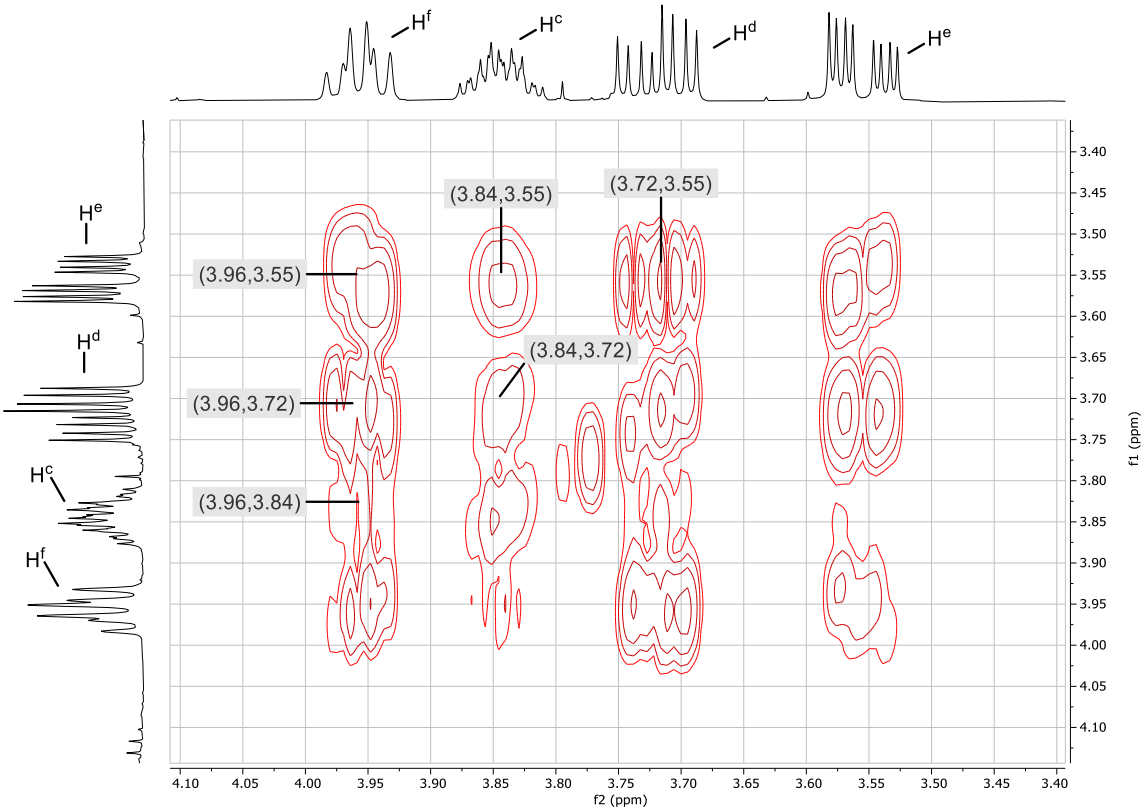

7.26 CDCl3
O
H
H
O
N
12b
500 MHz, CDCl3
8.13
1.20
1.22
1.05
1.06
1.11
1.05
0.96
1.04
1.04
1.08
1.02
1.04
1.02
1.00
f1 (ppm)

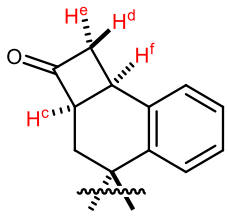

208.4
178.9
142.3
138.1
135.9
135.7
133.7
129.6
129.0
128.5
128.4
127.9
127.4
127.2
127.2
124.2
123.0
109.7
77.2 CDCl3
55.0
54.5
51.9
44.0
31.0
26.4
126 MHz, CDCl3
f1 (ppm)

^{1}H-^{1}H COSY NMR, 700 MHz, $CDCl_3$

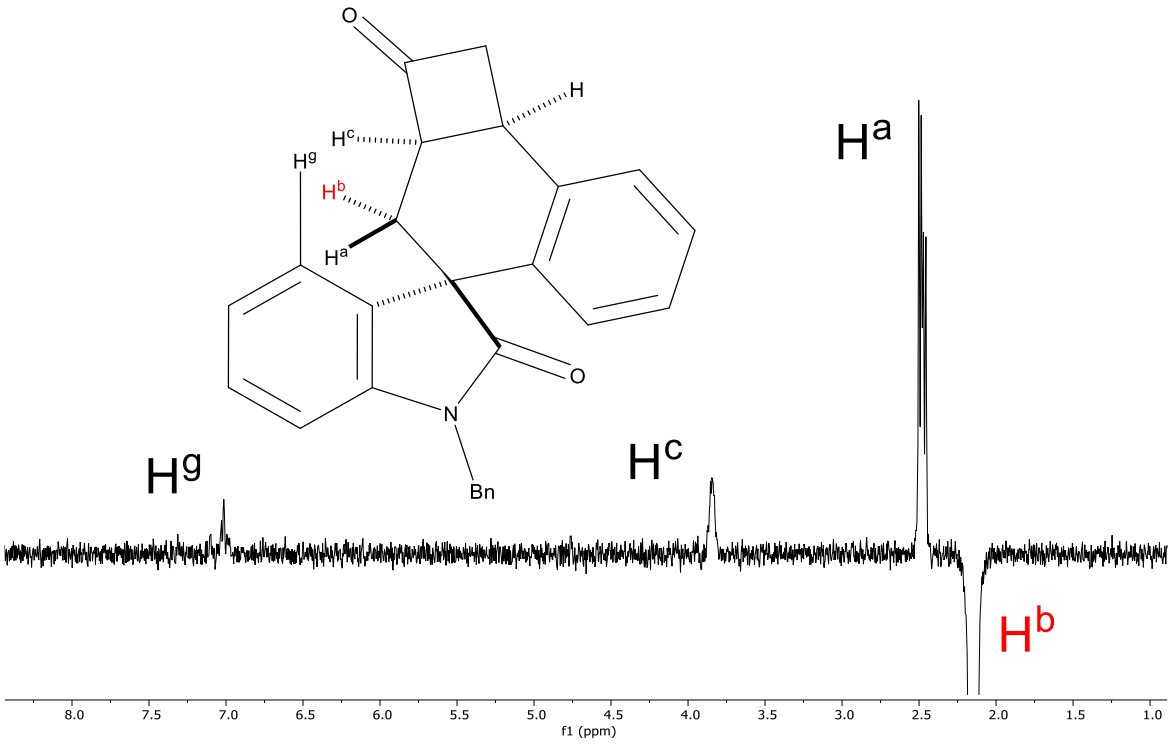


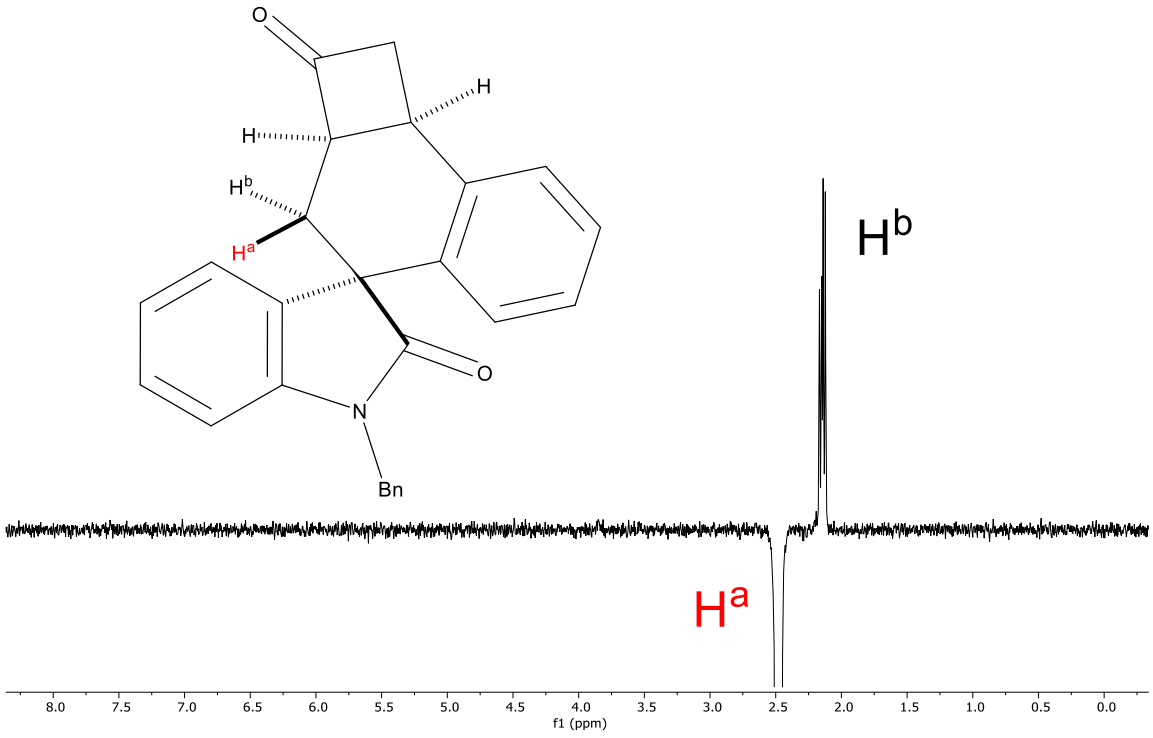


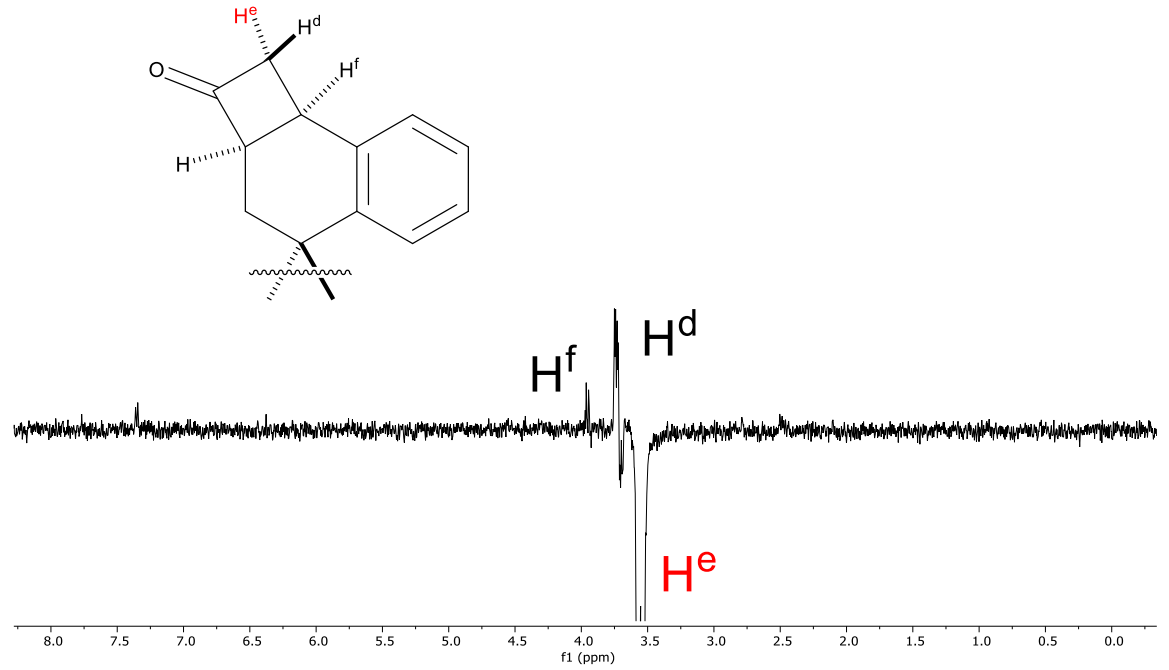

Hf
Hc
Hd
He
(3.84,3.55)
(3.72,3.55)
(3.96,3.55)
(3.84,3.72)
(3.96,3.72)
(3.96,3.84)
f2 (ppm)
f1 (ppm)

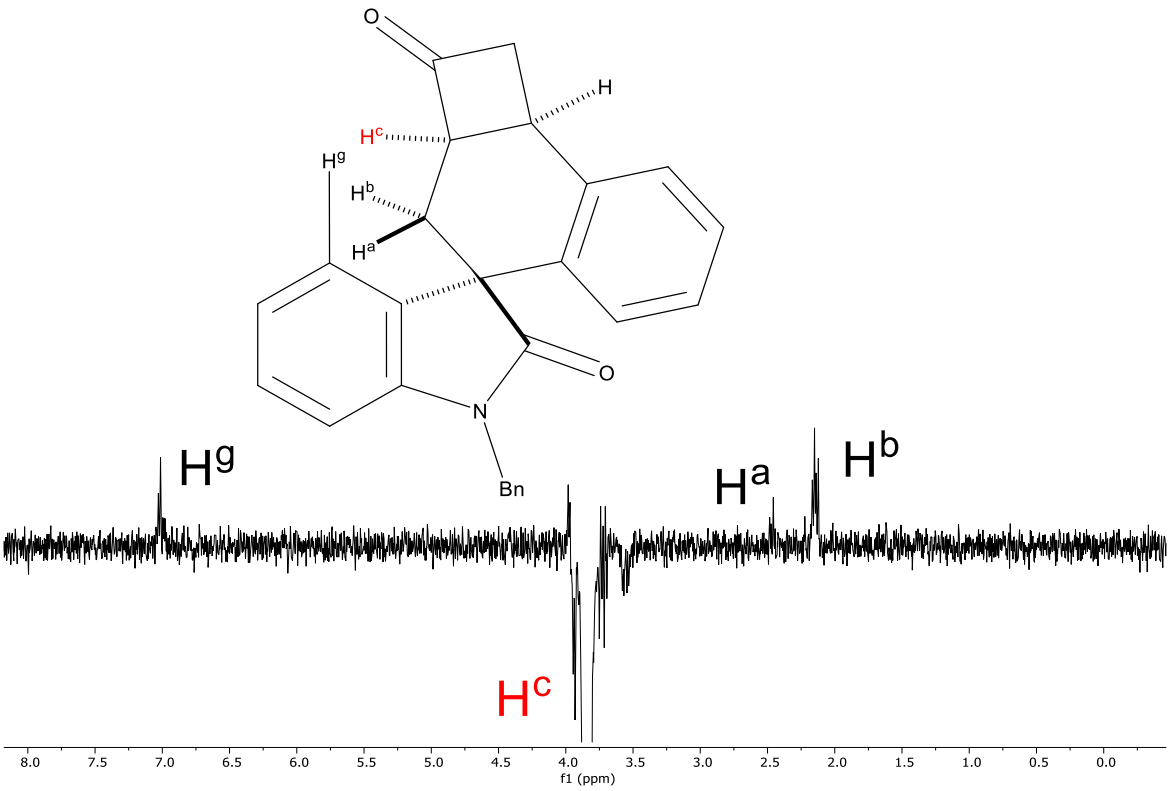

He
Hd
Hf
O
Hc

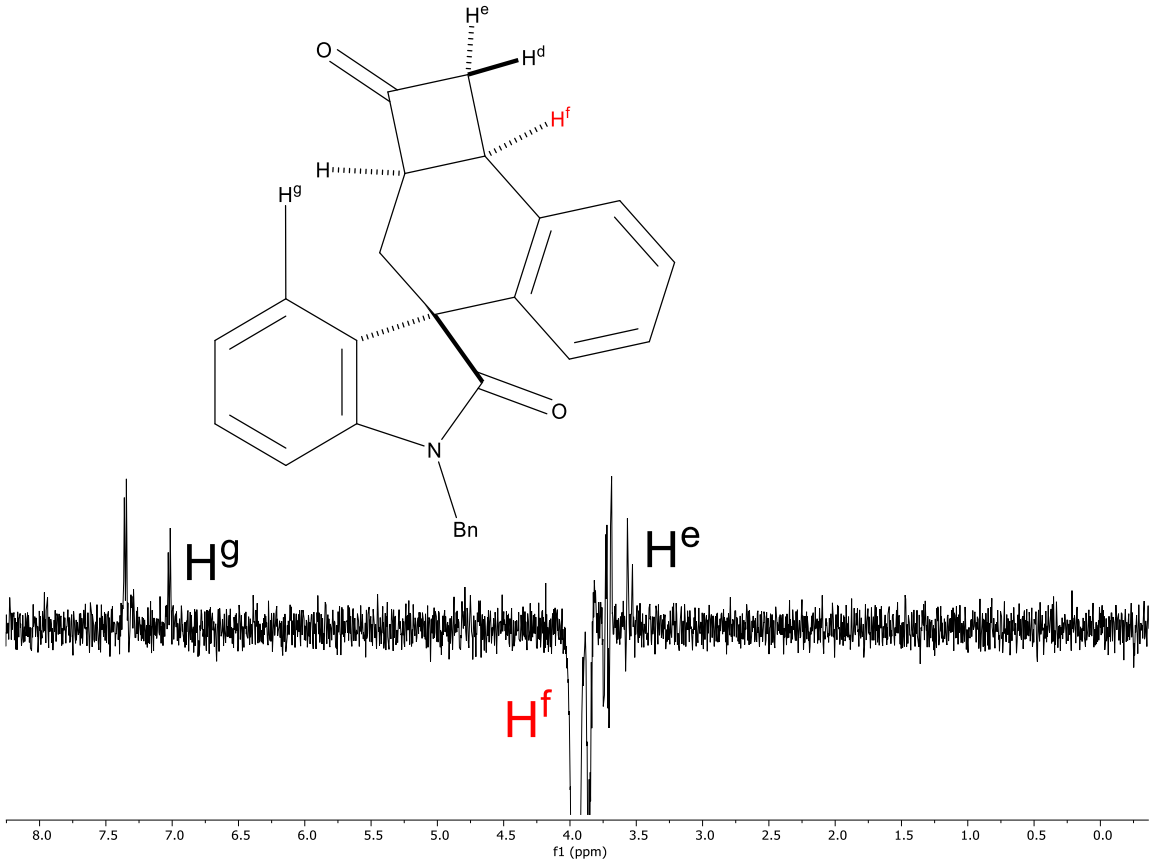
^{1}H NOESY NMR, 500 MHz, $CDCl_3$



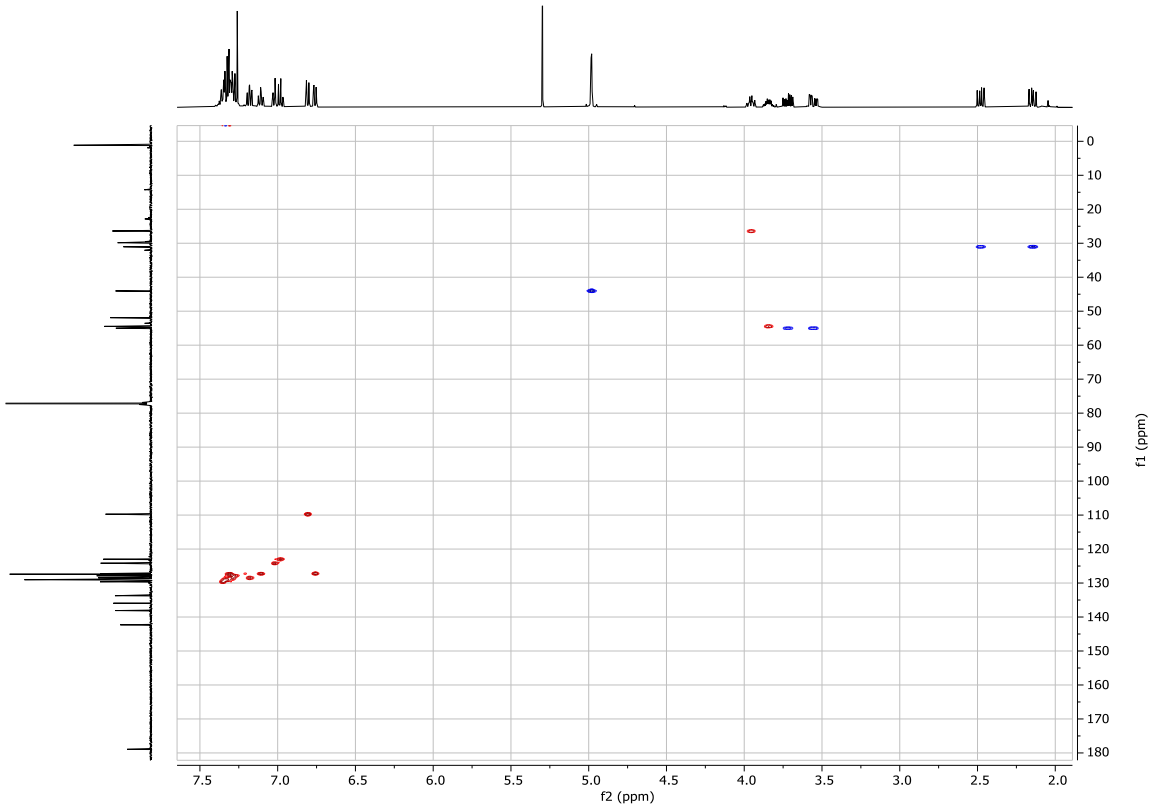


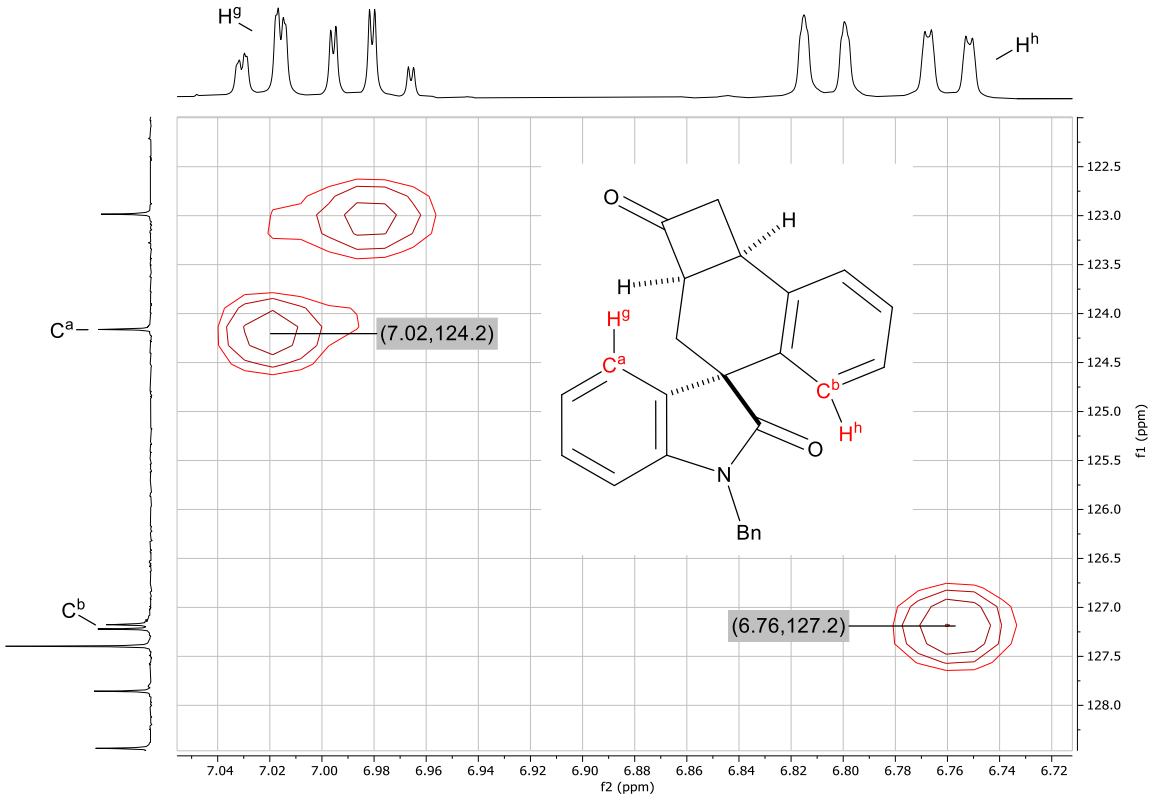

H^e
H^d
H^f
O
H
H^f
H^d
H^e
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

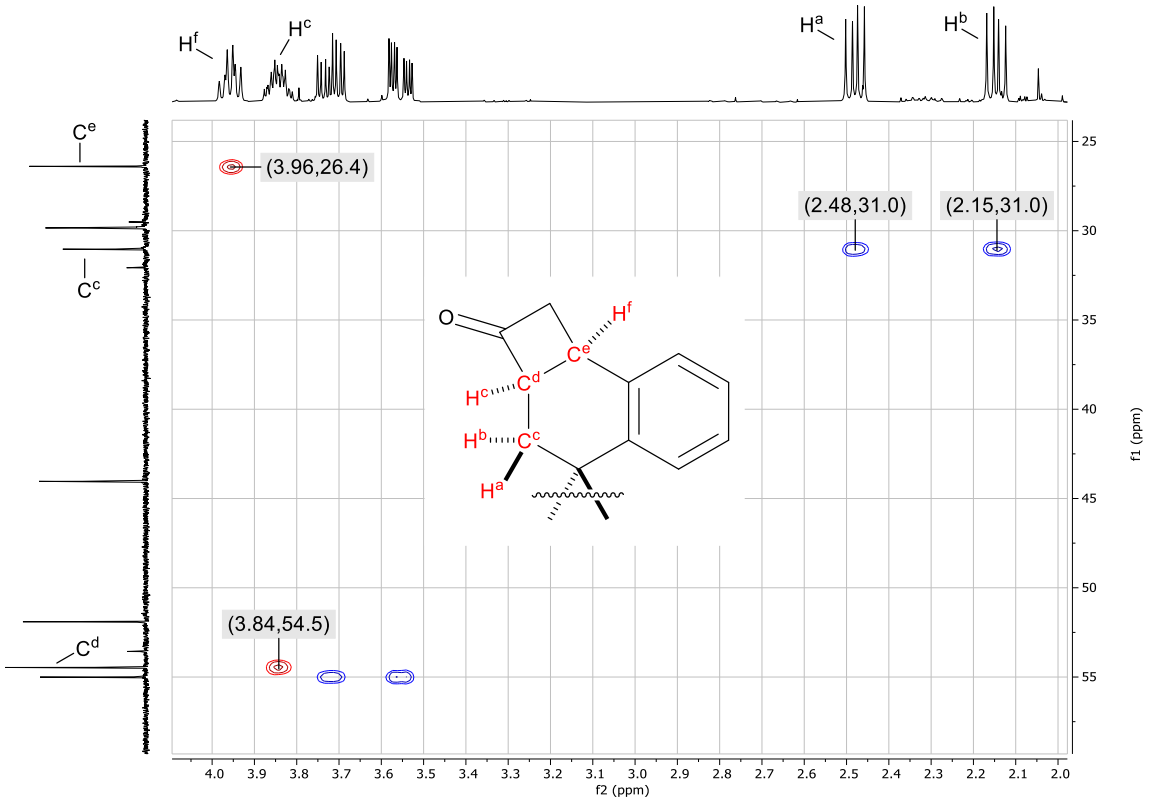

O
H
H^c
H^g
H^b
H^a
O
N
Bn
H^g
H^a
H^b
H^c
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


H^e
O
H^d
H^f
H
H^g
O
N
Bn
H^g
H^e
H^f
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

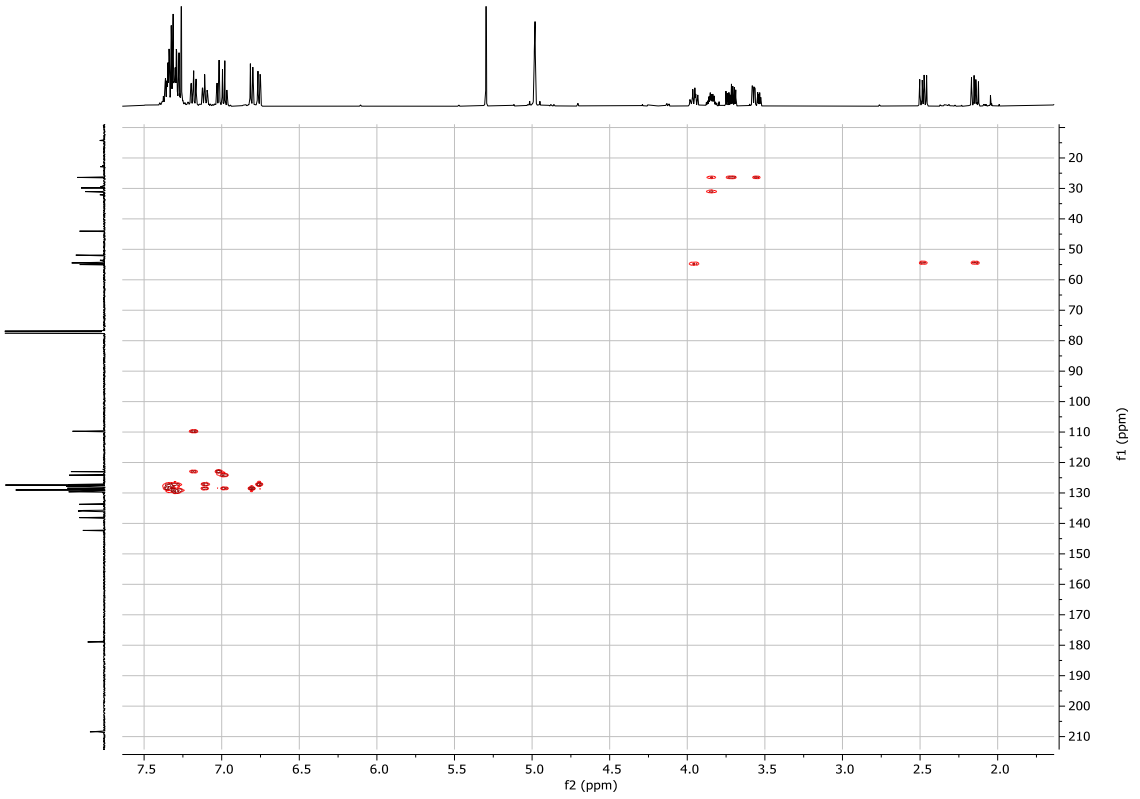
^{1}H-^{13}C HSQC NMR, 700 MHz, $CDCl_3$

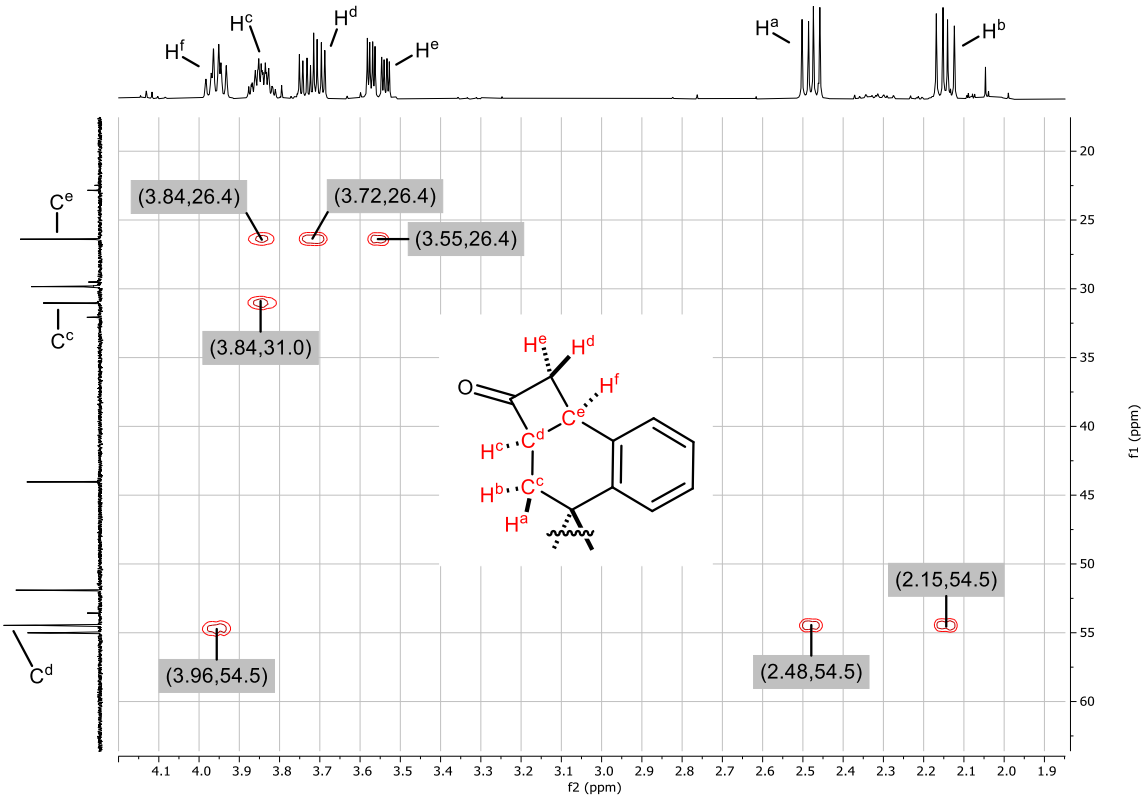




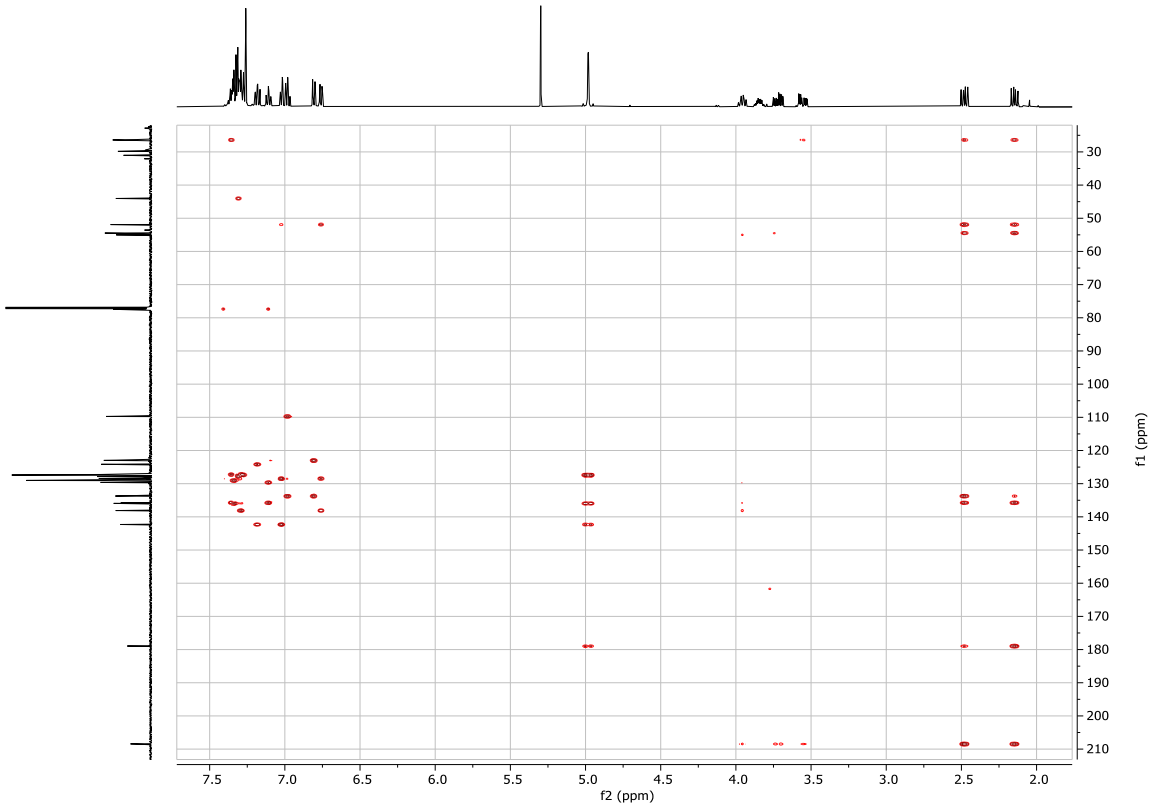

H^f
H^c
H^a
H^b
C^e
C^c
C^d
(3.96,26.4)
(2.48,31.0)
(2.15,31.0)
(3.84,54.5)
O
H^f
C^e
C^d
H^c
H^b
C^c
H^a
f2 (ppm)
f1 (ppm)

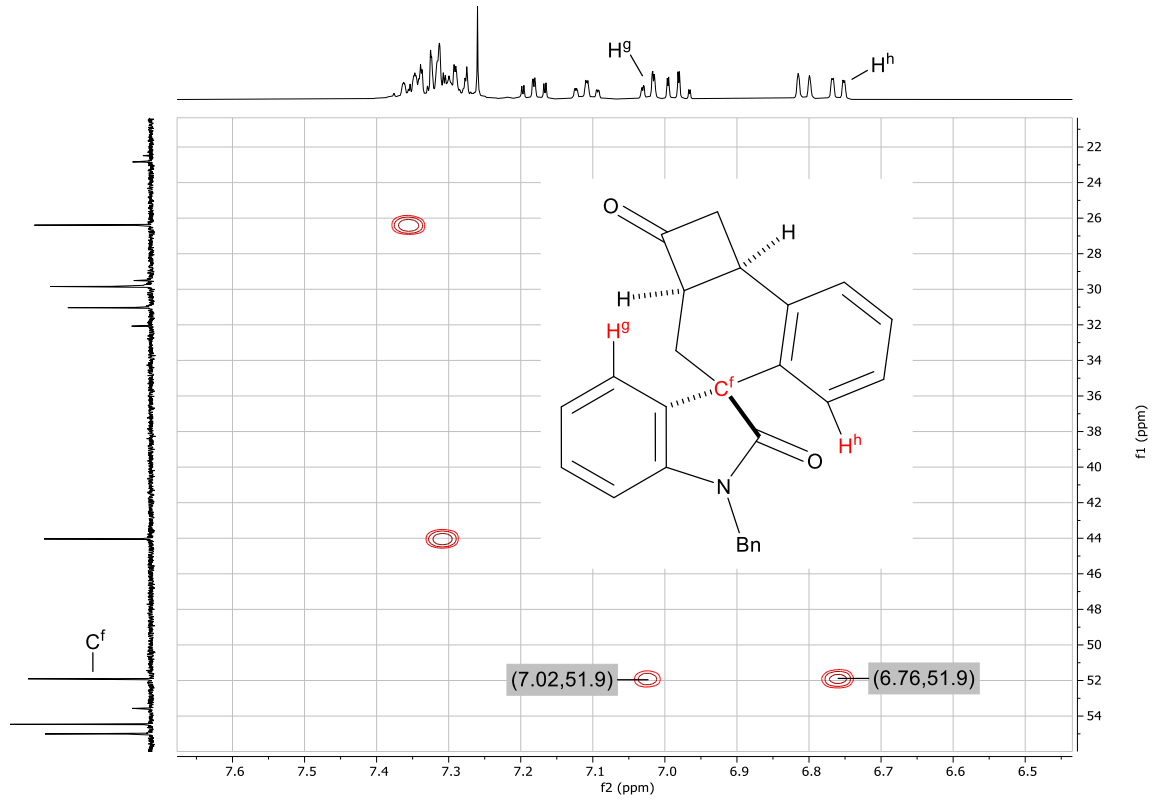
^{1}H-^{13}C H2BC NMR, 700 MHz, $CDCl_3$

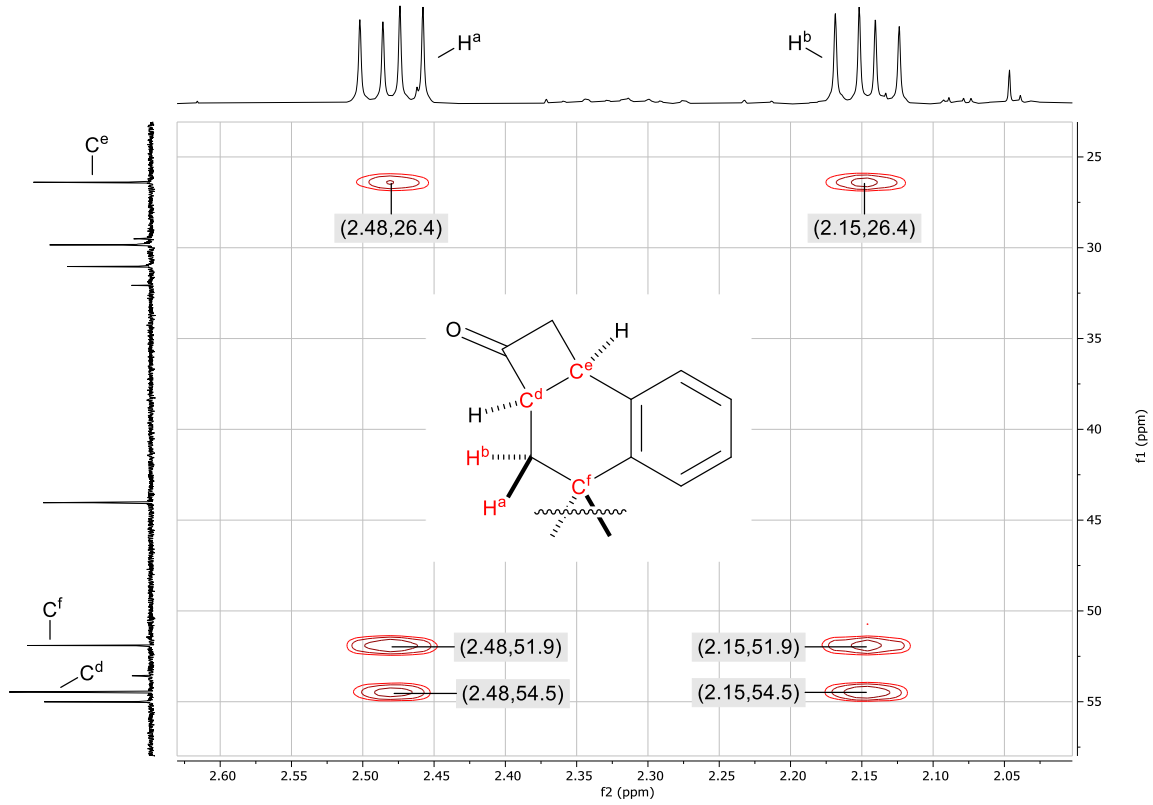


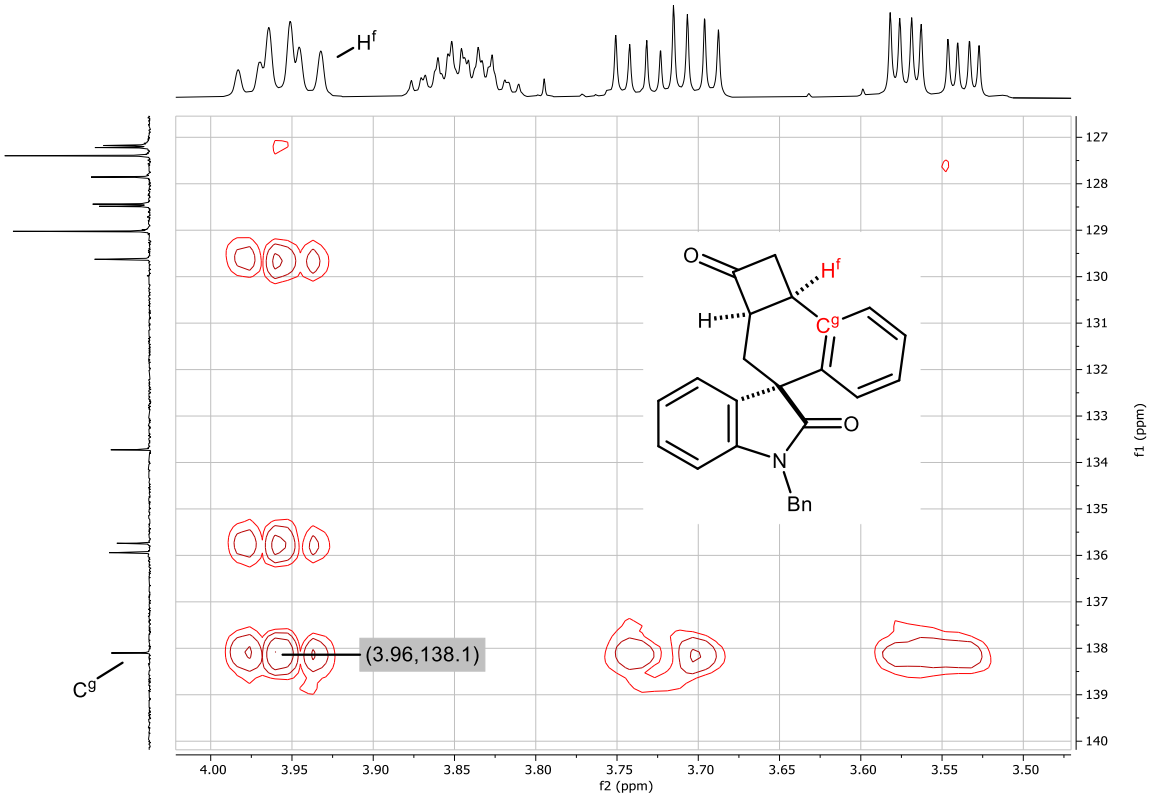


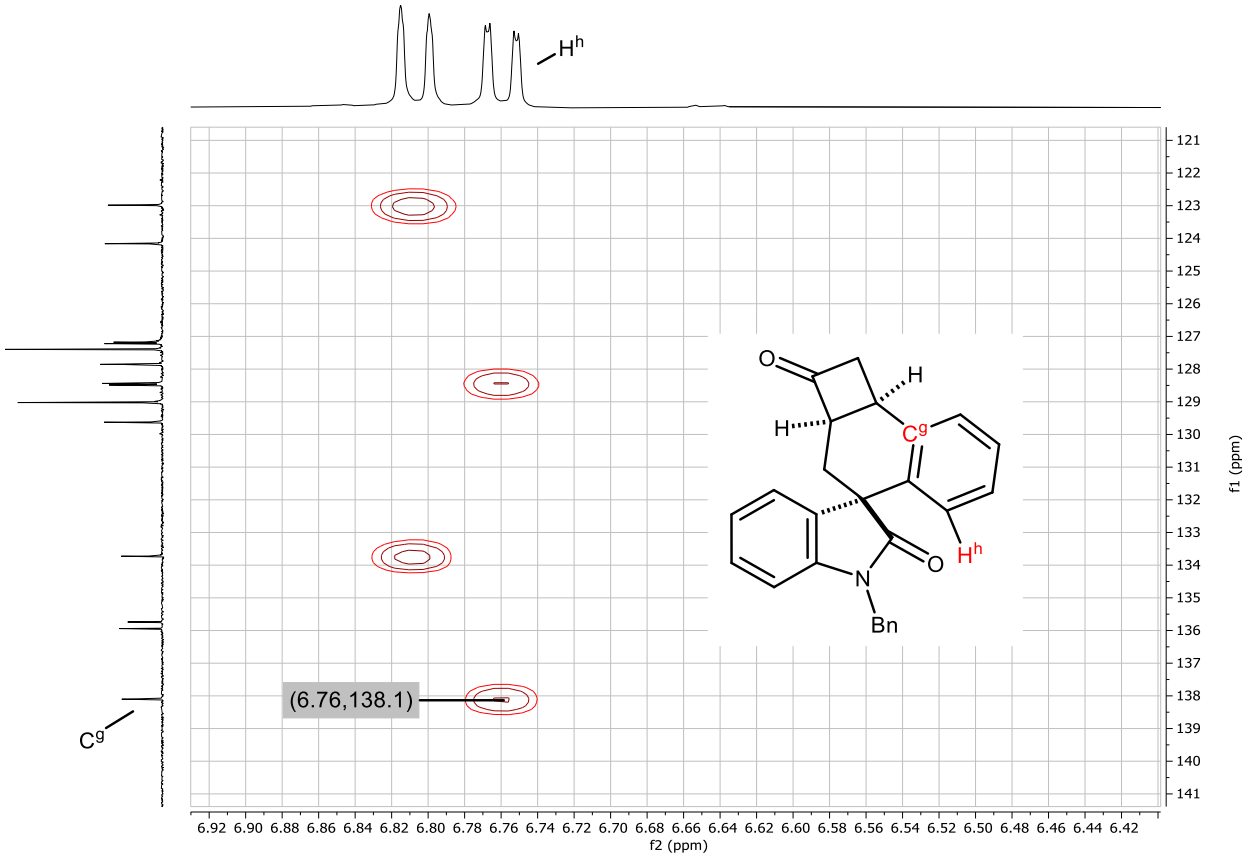
^{1}H-^{13}C HMBC NMR, 700 MHz, $CDCl_3$

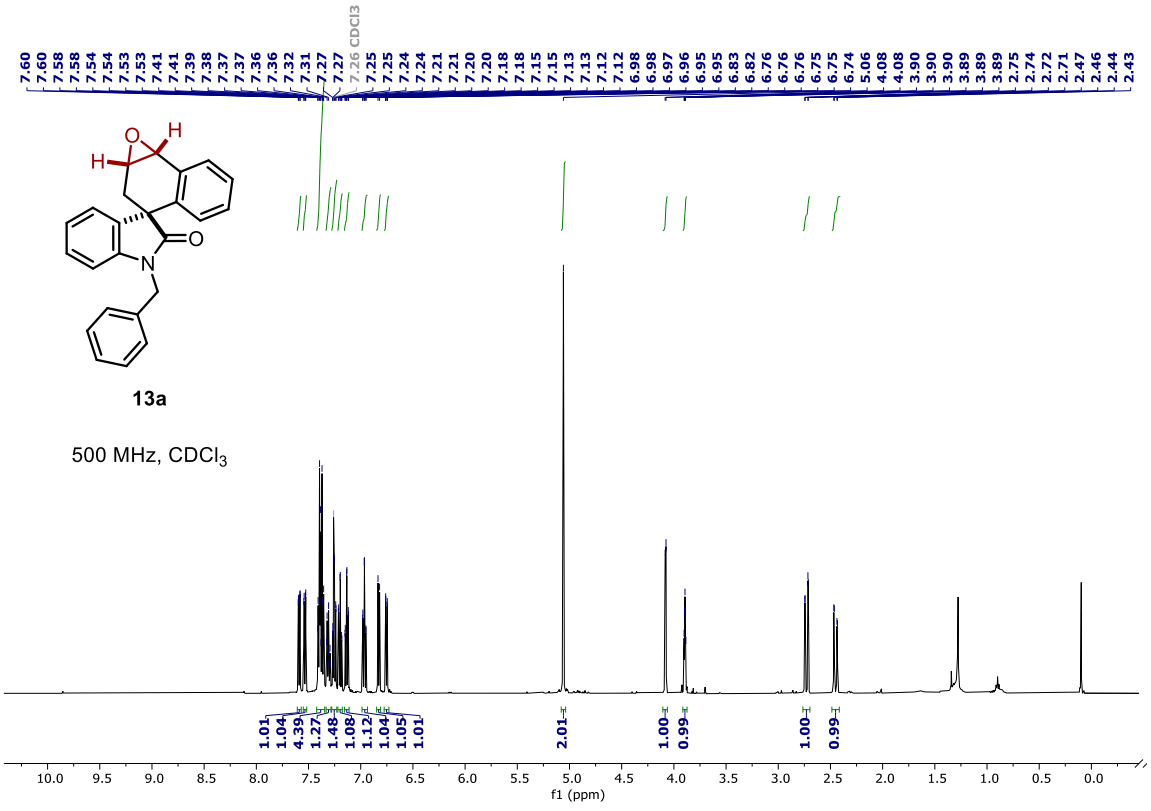


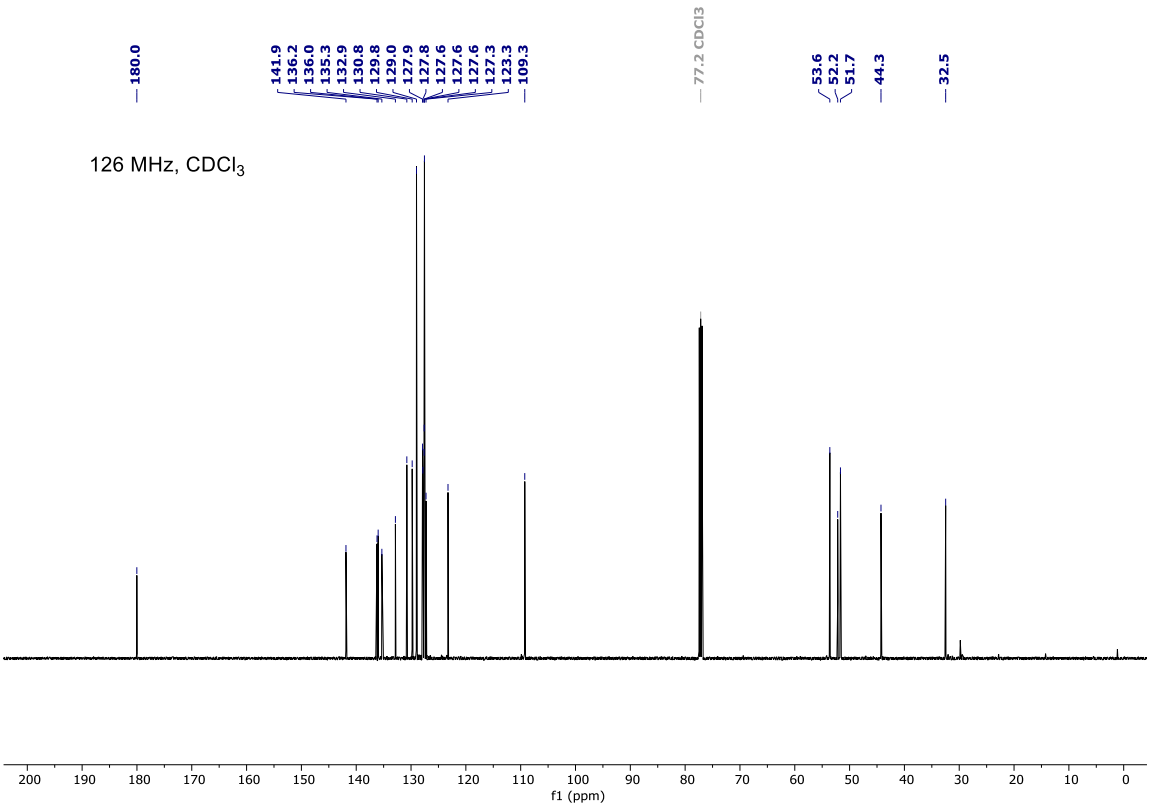



Ha
Hb
Ce
Cf
Cd
(2.48,26.4)
(2.15,26.4)
(2.48,51.9)
(2.48,54.5)
(2.15,51.9)
(2.15,54.5)
f2 (ppm)
f1 (ppm)

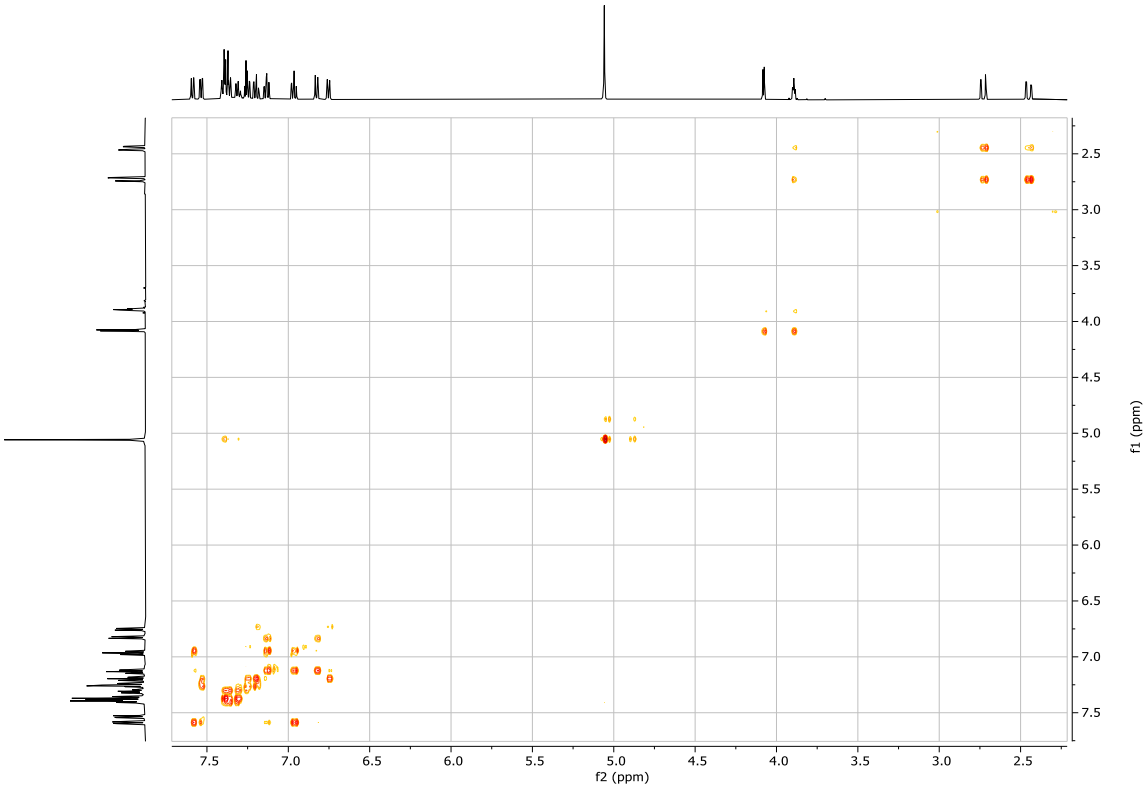

Hf
Cg
(3.96,138.1)
Bn
f2 (ppm)
f1 (ppm)

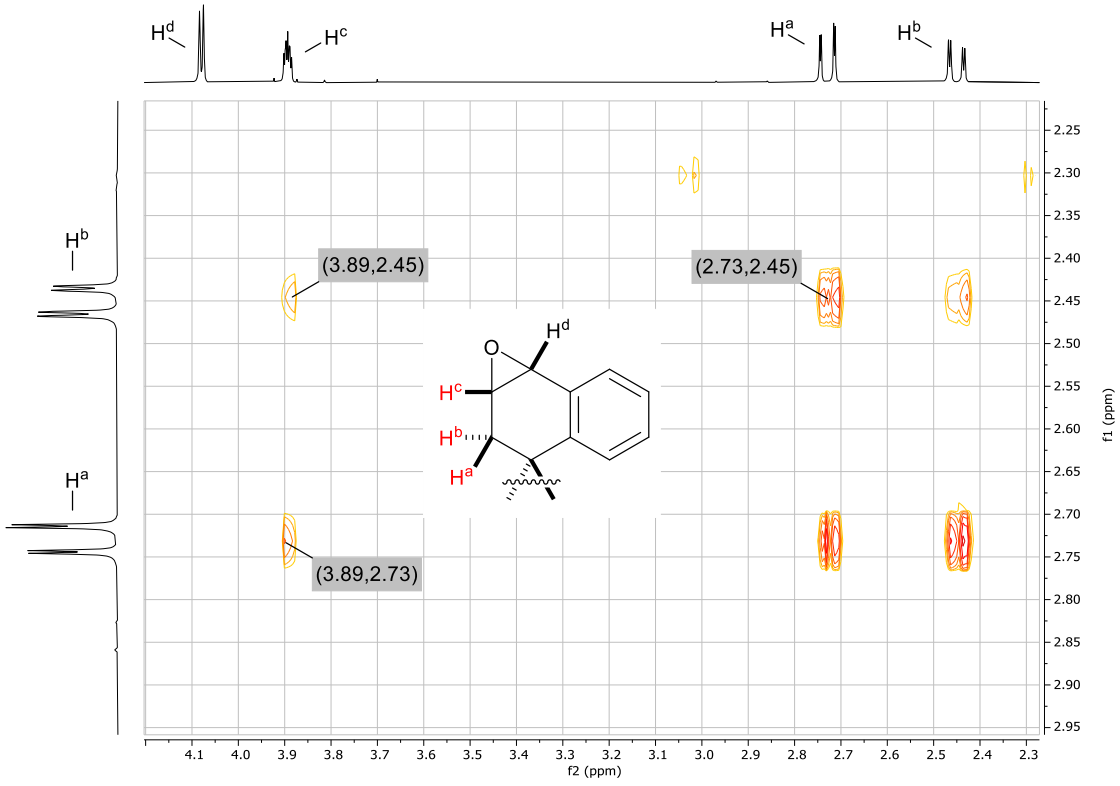

H^h
C^g
(6.76,138.1)
O
H
H
C^g
O
H^h
N
Bn
121 122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141
f1 (ppm)
6.92 6.90 6.88 6.86 6.84 6.82 6.80 6.78 6.76 6.74 6.72 6.70 6.68 6.66 6.64 6.62 6.60 6.58 6.56 6.54 6.52 6.50 6.48 6.46 6.44 6.42
f2 (ppm)

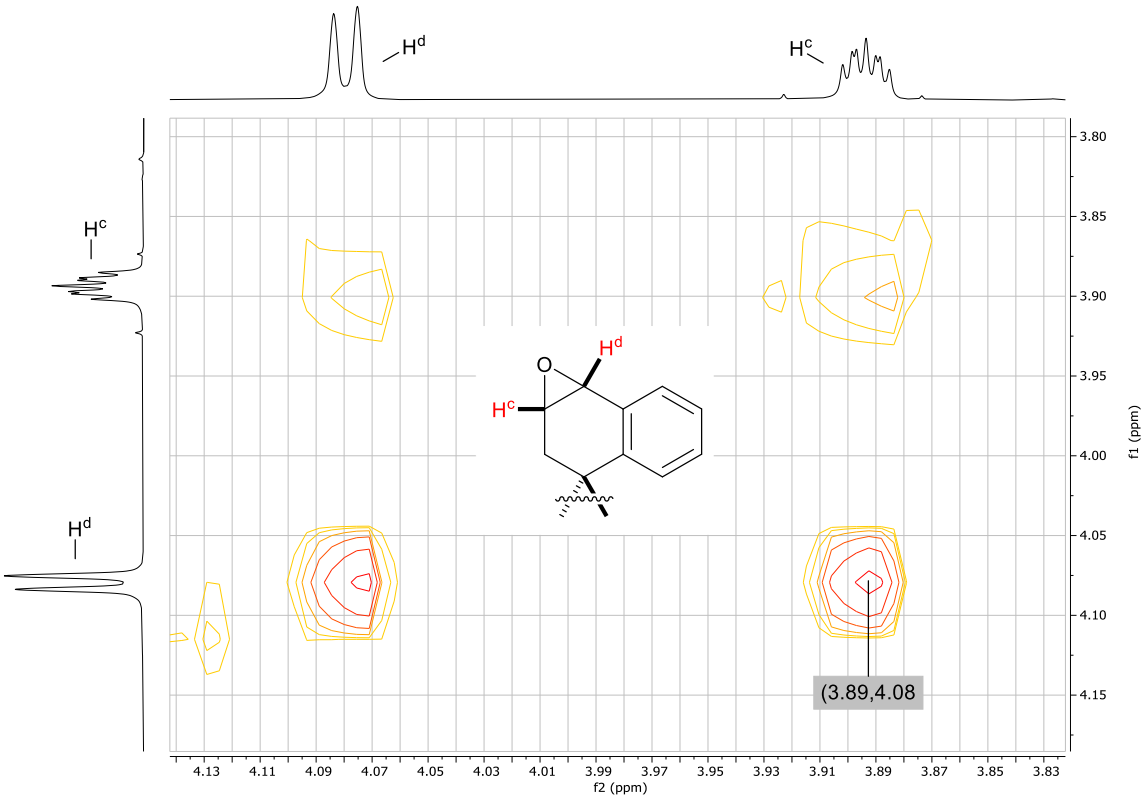

7.60 7.60 7.58 7.58 7.54 7.54 7.53 7.53 7.41 7.41 7.39 7.38 7.37 7.37 7.36 7.36 7.32 7.31 7.27 7.27 7.26 CDCl3 7.25 7.25 7.24 7.24 7.21 7.21 7.20 7.20 7.18 7.18 7.15 7.15 7.13 7.13 7.12 7.12 6.98 6.98 6.97 6.96 6.95 6.95 6.83 6.82 6.76 6.76 6.76 6.75 6.75 6.74 5.06 4.08 4.08 3.90 3.90 3.90 3.89 3.89 3.89 2.75 2.74 2.72 2.71 2.47 2.46 2.44 2.43
O
H
H
O
N
13a
500 MHz, CDCl3
1.01 1.04 4.39 1.27 1.48 1.08 1.12 1.04 1.05 1.01 2.01 1.00 0.99 1.00 0.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


180.0
141.9 136.2 136.0 135.3 132.9 130.8 129.8 129.0 127.9 127.8 127.6 127.6 127.6 127.3 123.3 109.3
77.2 CDCl3
53.6 52.2 51.7 44.3 32.5
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

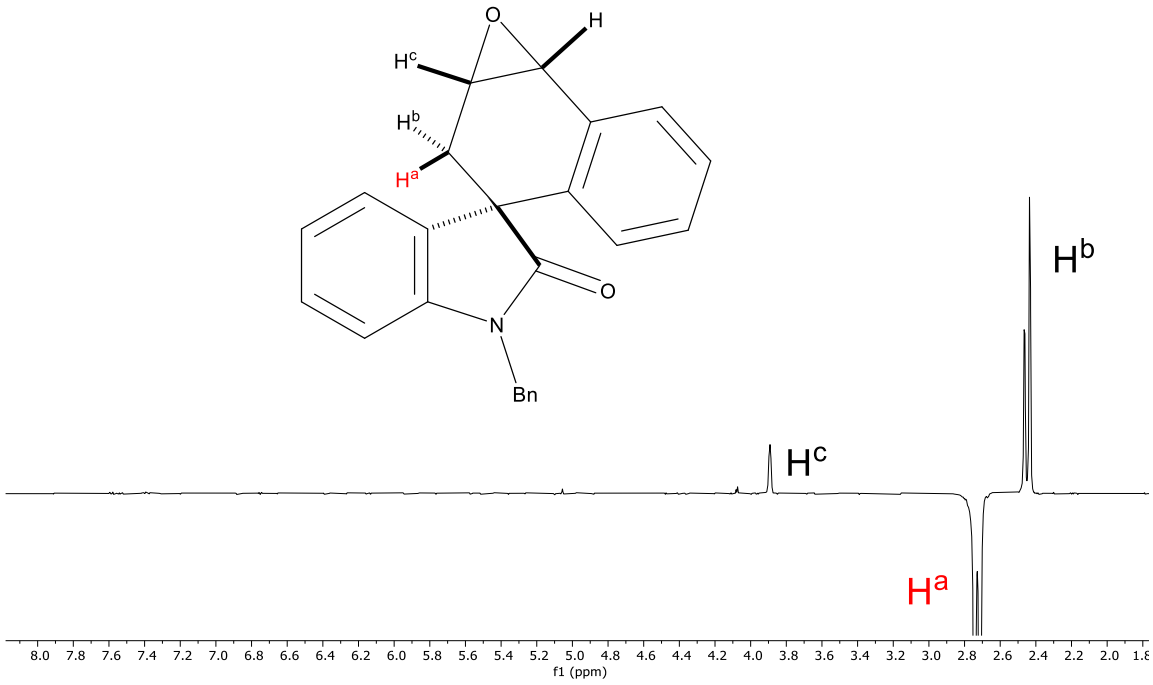
^{1}H-^{1}H COSY NMR, 600 MHz, $CDCl_3$

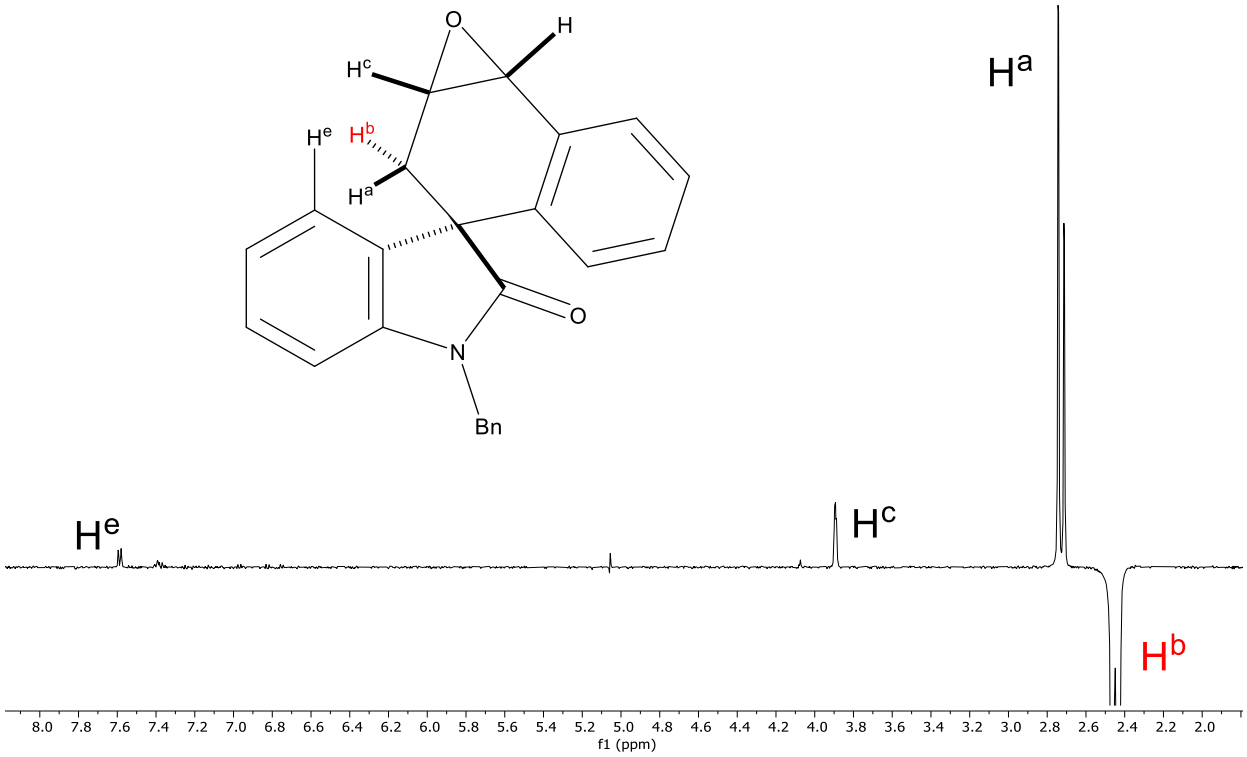


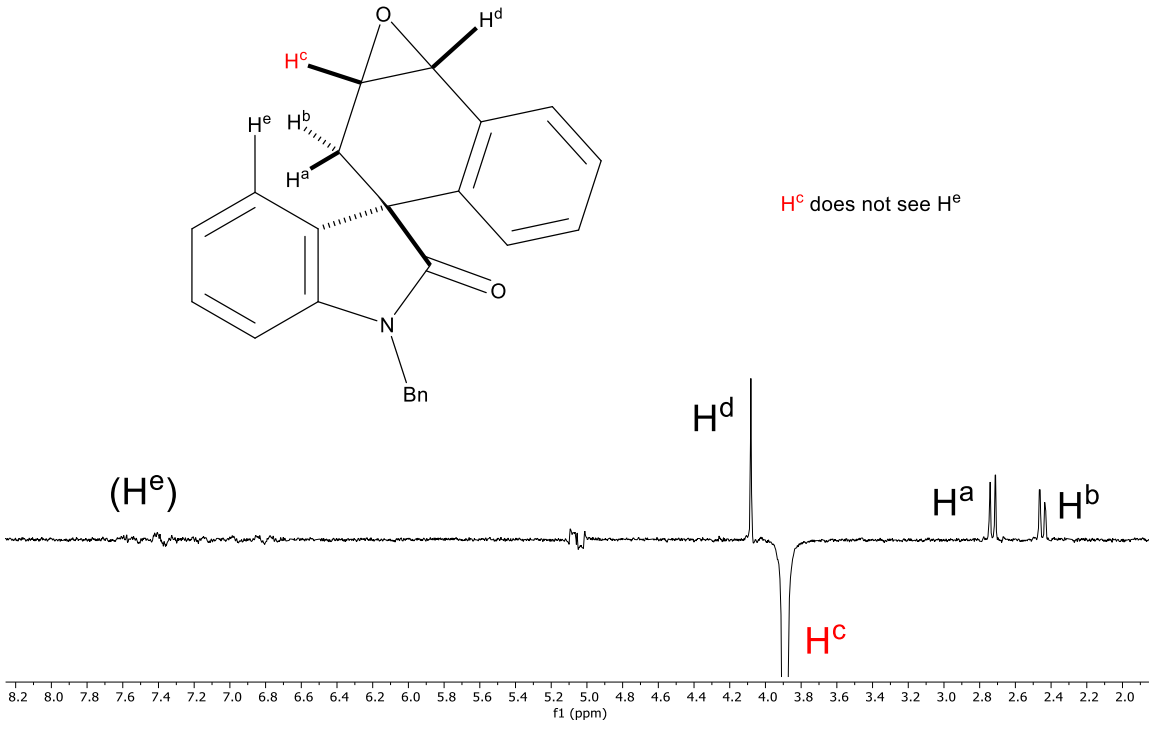


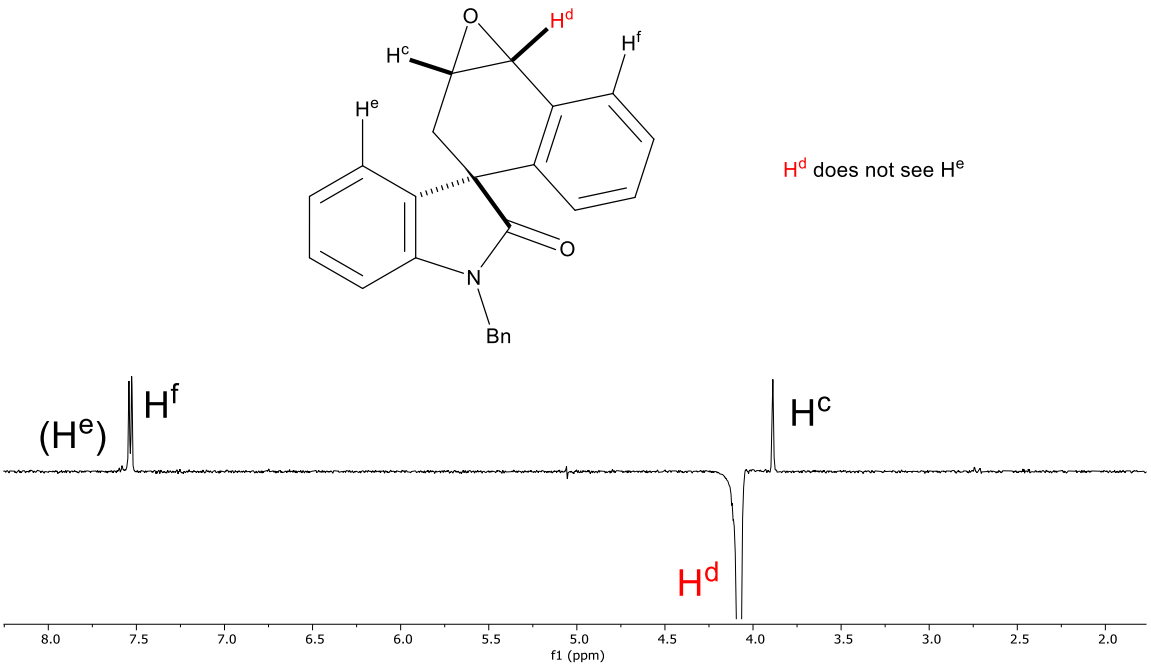


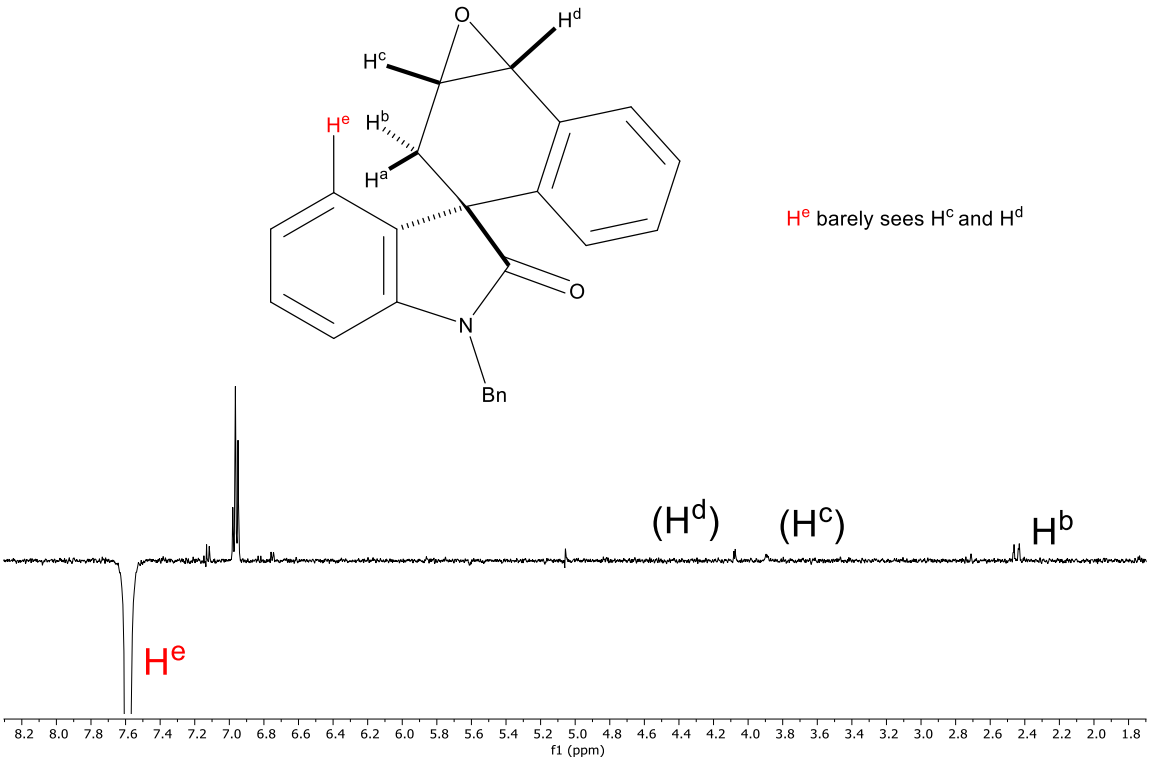
^{1}H NOESY NMR, 500 MHz, $CDCl_3$



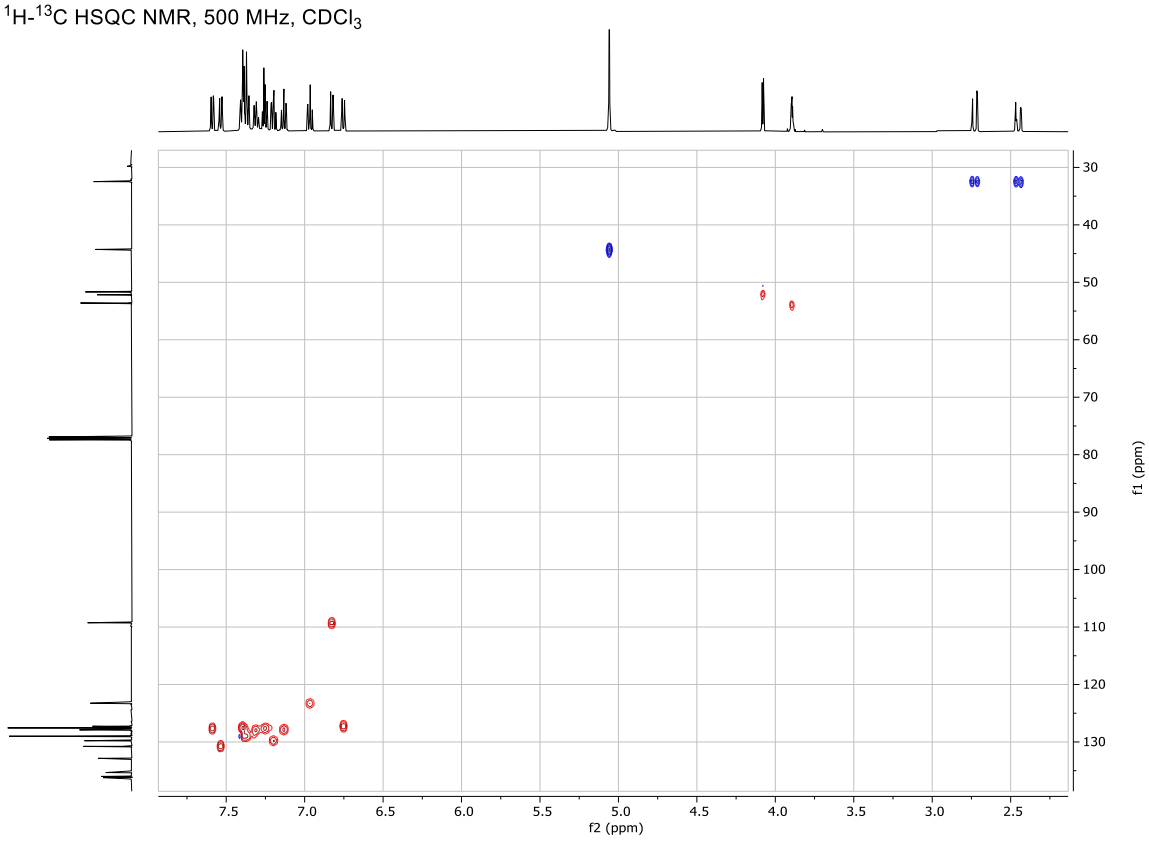

O
H
Hc
He
Hb
Ha
O
N
Bn
Ha
He
Hc
Hb
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0
f1 (ppm)

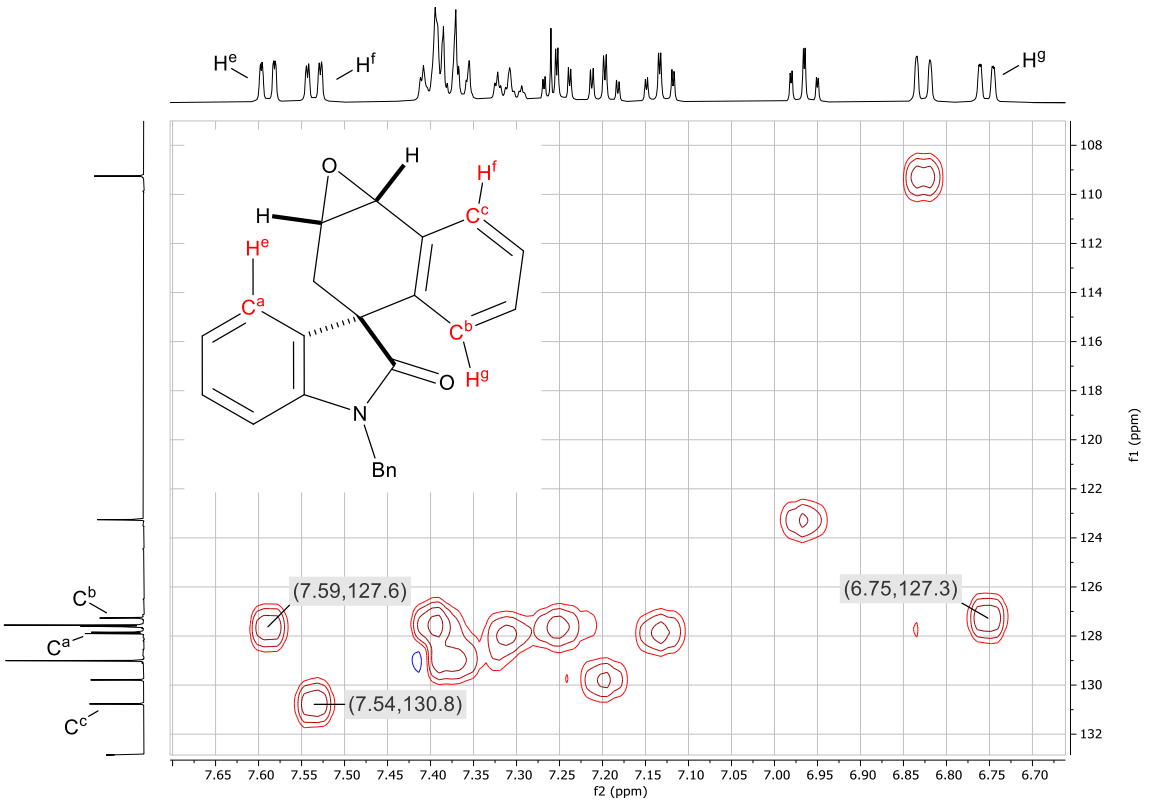

O
Hd
Hc
He
Hb
Ha
O
N
Bn
Hc does not see He
Hd
(He)
Ha
Hb
Hc
8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0
f1 (ppm)

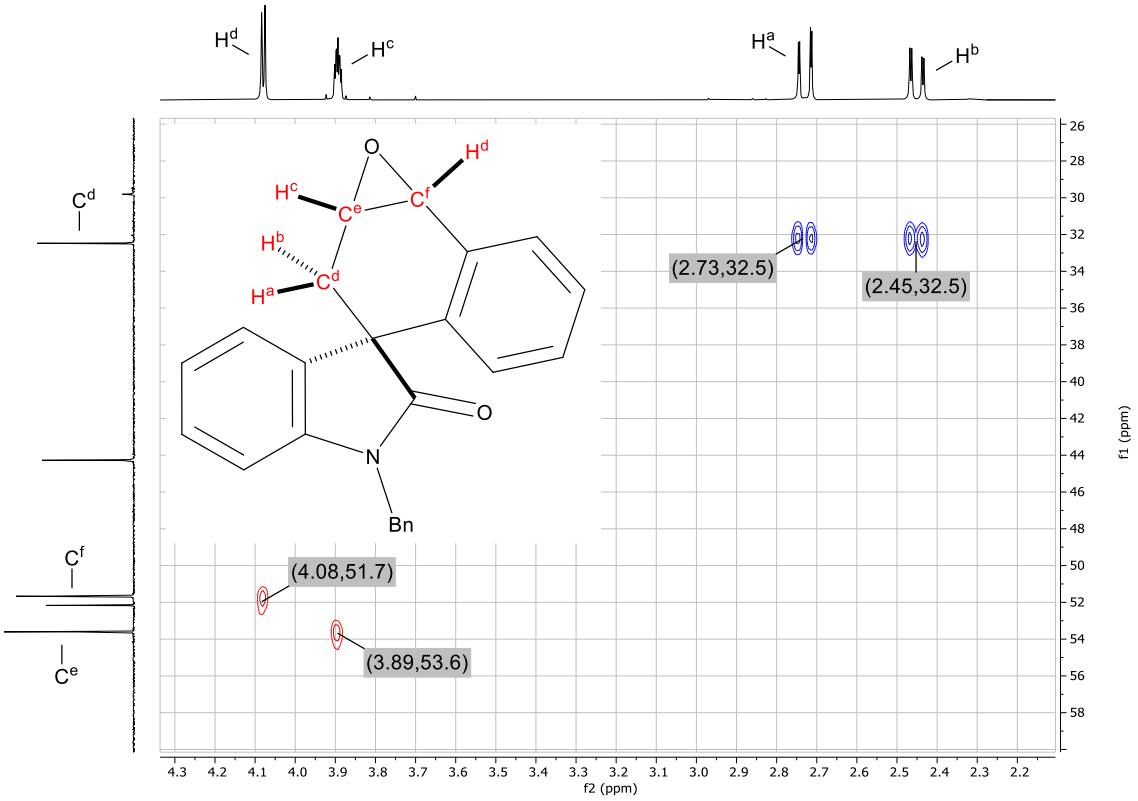

O
Hd
Hc
Hf
He
O
N
Bn
Hd does not see He
(He)
Hf
Hc
Hd
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0
f1 (ppm)


O
Hd
Hc
He
Hb
Ha
O
N
Bn
He barely sees Hc and Hd
(Hd)
(Hc)
Hb
He
8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8
f1 (ppm)

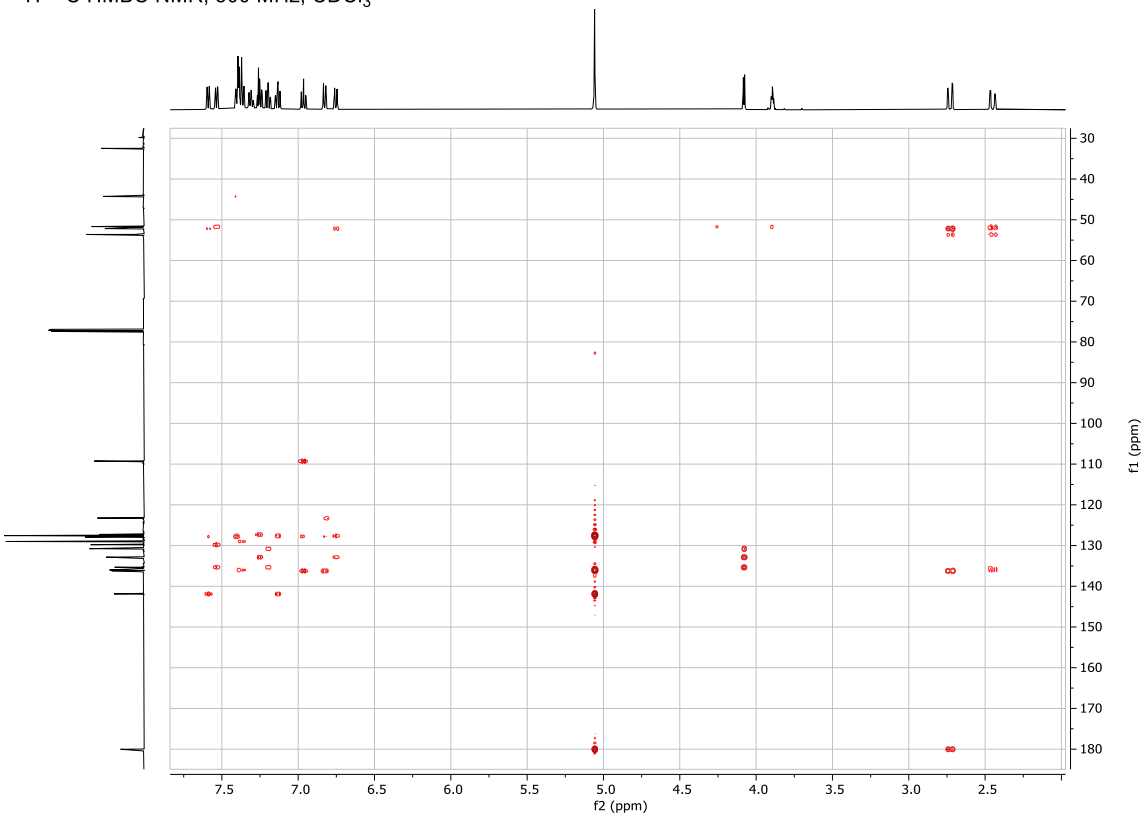
^{1}H-^{13}C HSQC NMR, 500 MHz, $CDCl_3$

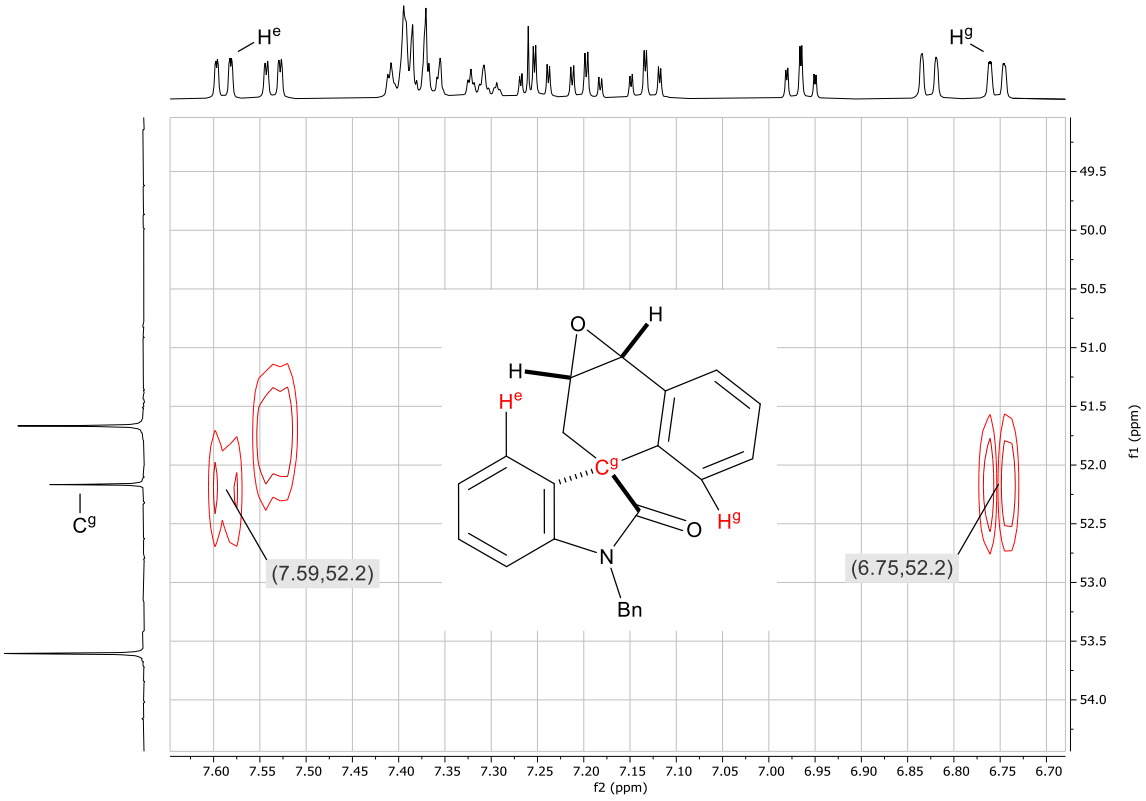


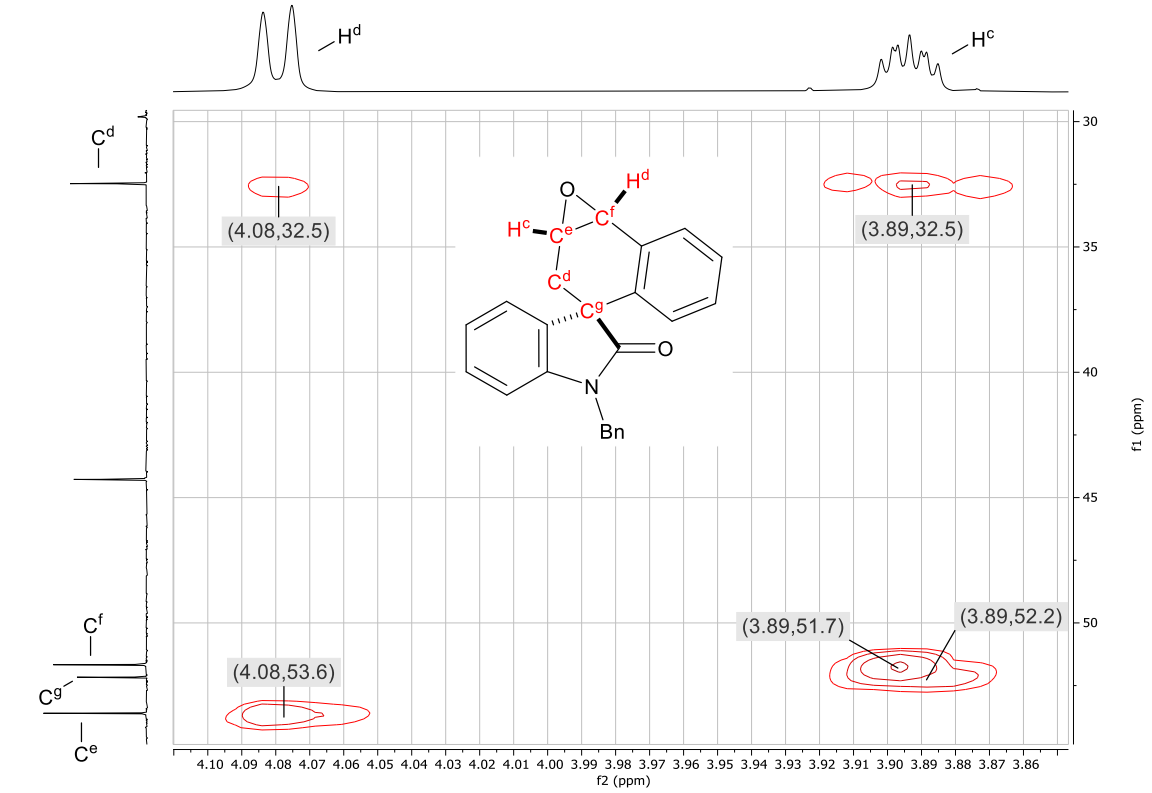


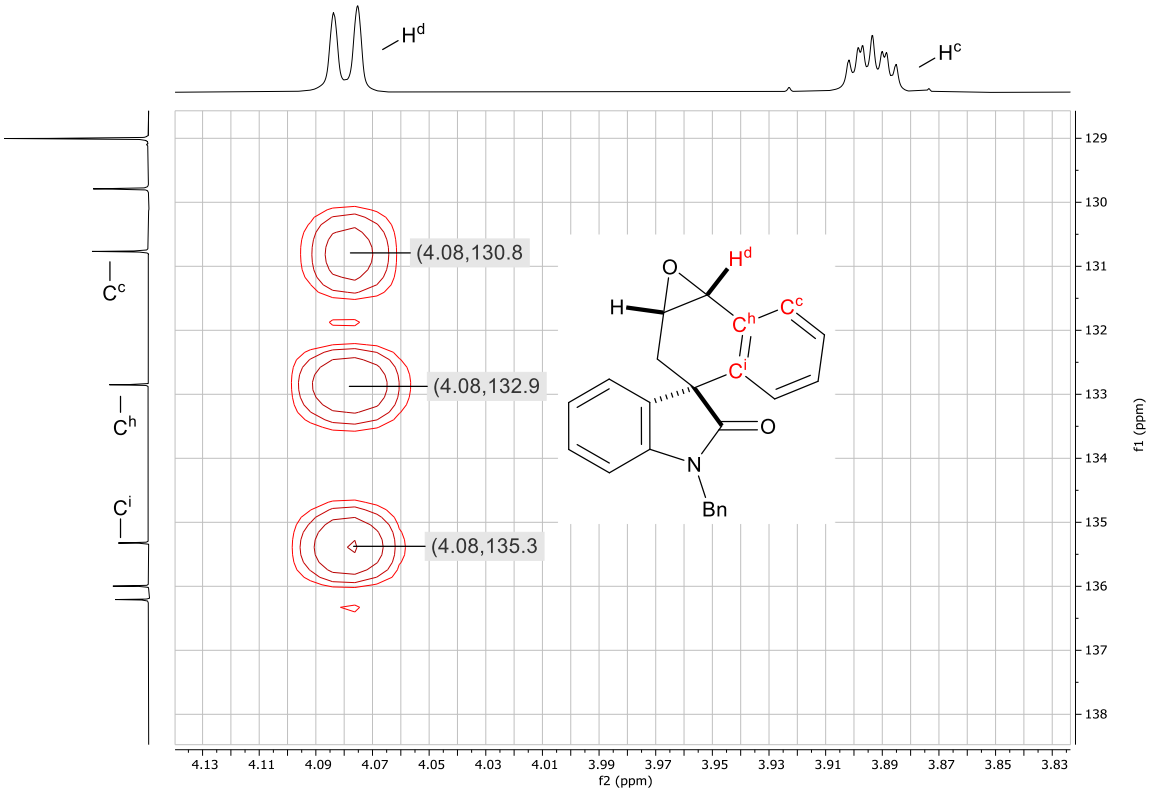

H^d
H^c
H^a
H^b
C^d
C^f
C^e
O
H^d
H^c
C^e
C^f
H^b
C^d
H^a
O
N
Bn
(2.73,32.5)
(2.45,32.5)
(4.08,51.7)
(3.89,53.6)
f2 (ppm)
f1 (ppm)

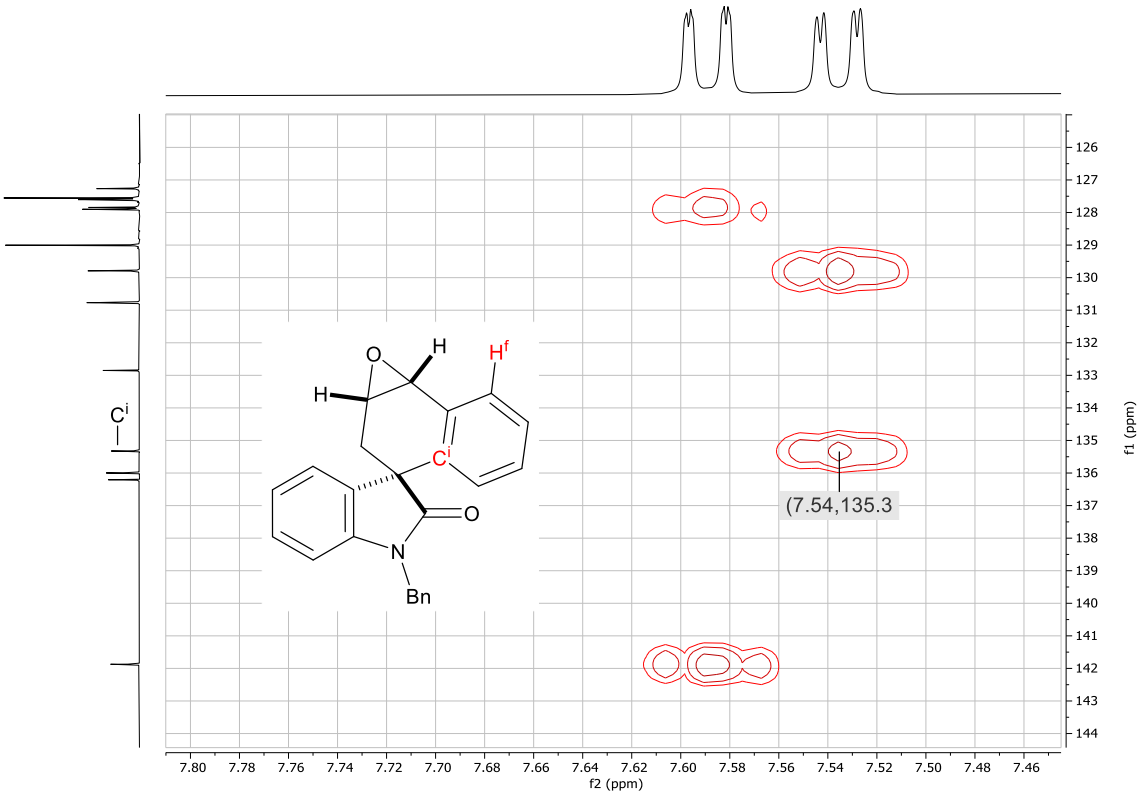
^{1}H-^{13}C HMBC NMR, 500 MHz, $CDCl_3$

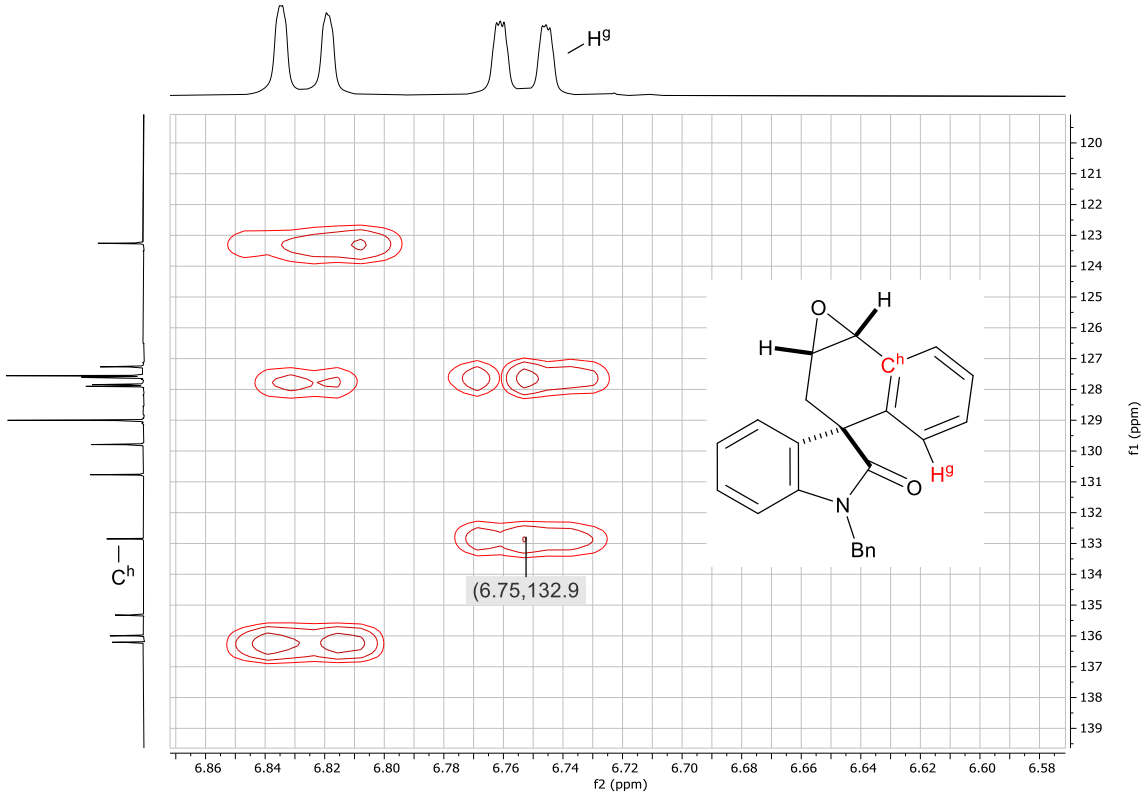


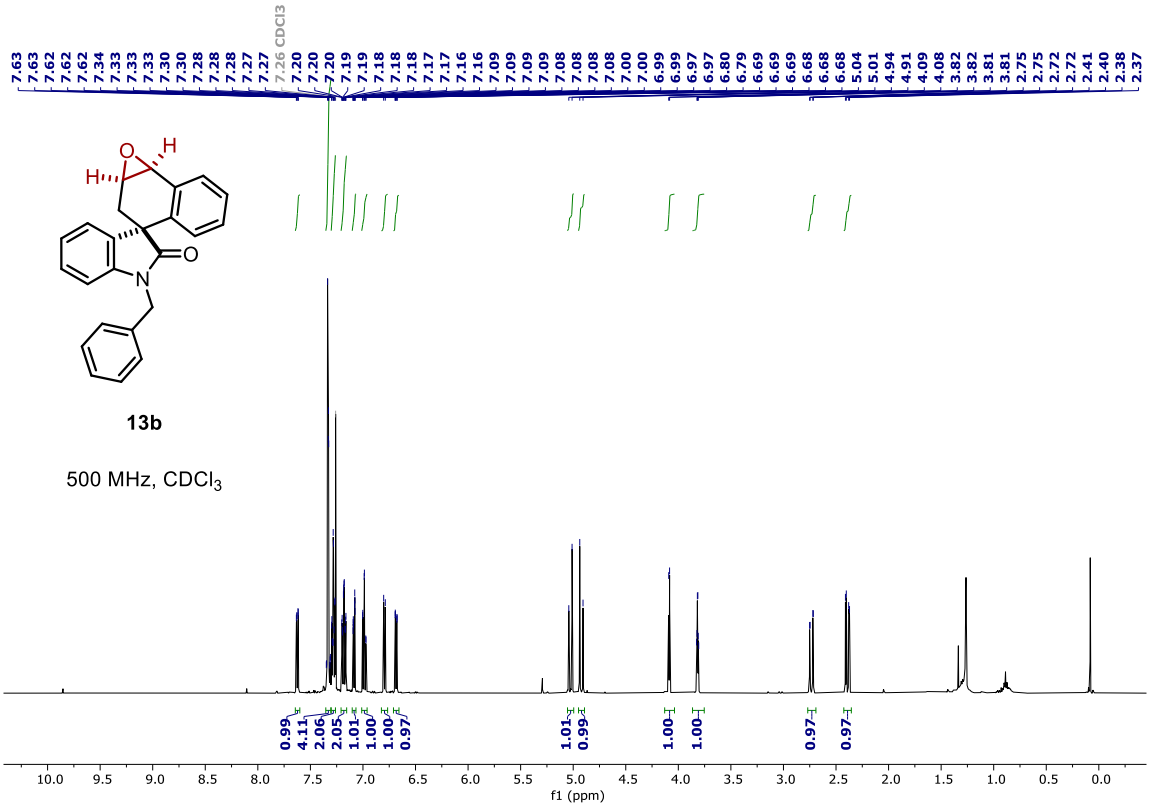


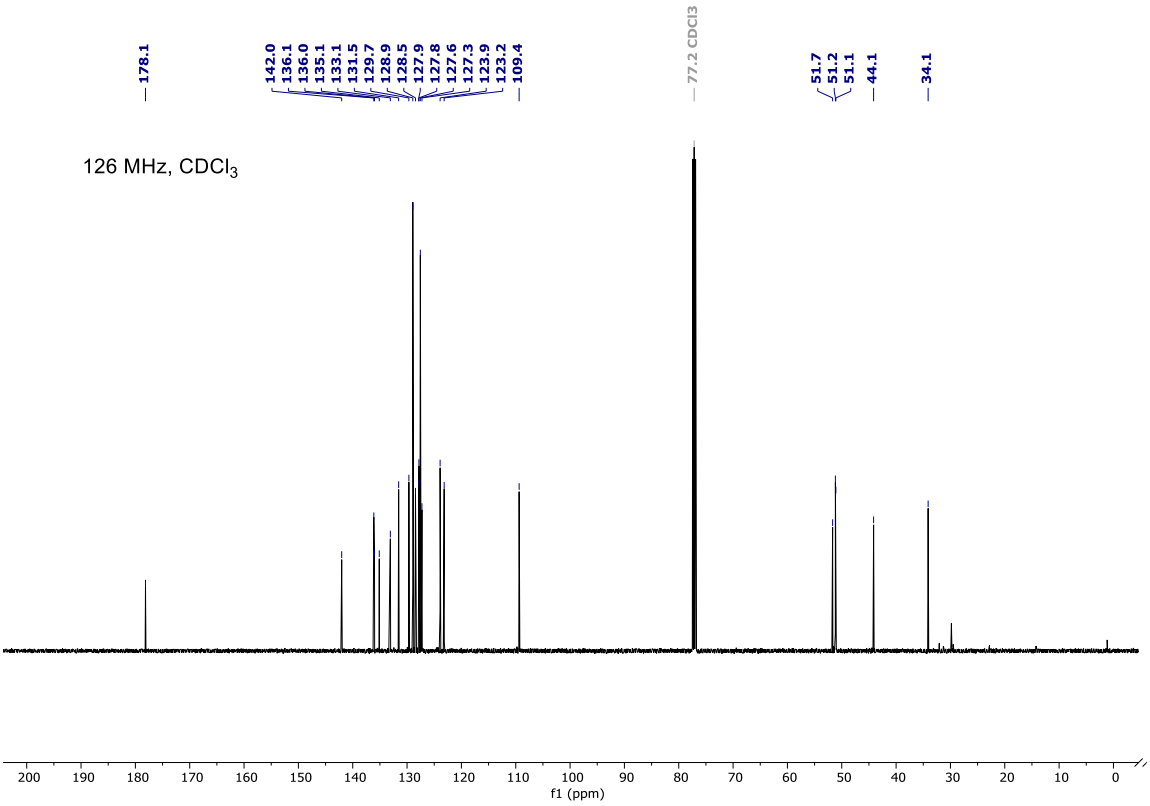

Hd
Hc
Cd
Cf
Cg
Ce
(4.08,32.5)
(3.89,32.5)
(4.08,53.6)
(3.89,51.7)
(3.89,52.2)
Bn
f1 (ppm)
f2 (ppm)


Hd
Hc
Cc
Ch
Ci
(4.08,130.8)
(4.08,132.9)
(4.08,135.3)
Bn
f1 (ppm)
f2 (ppm)

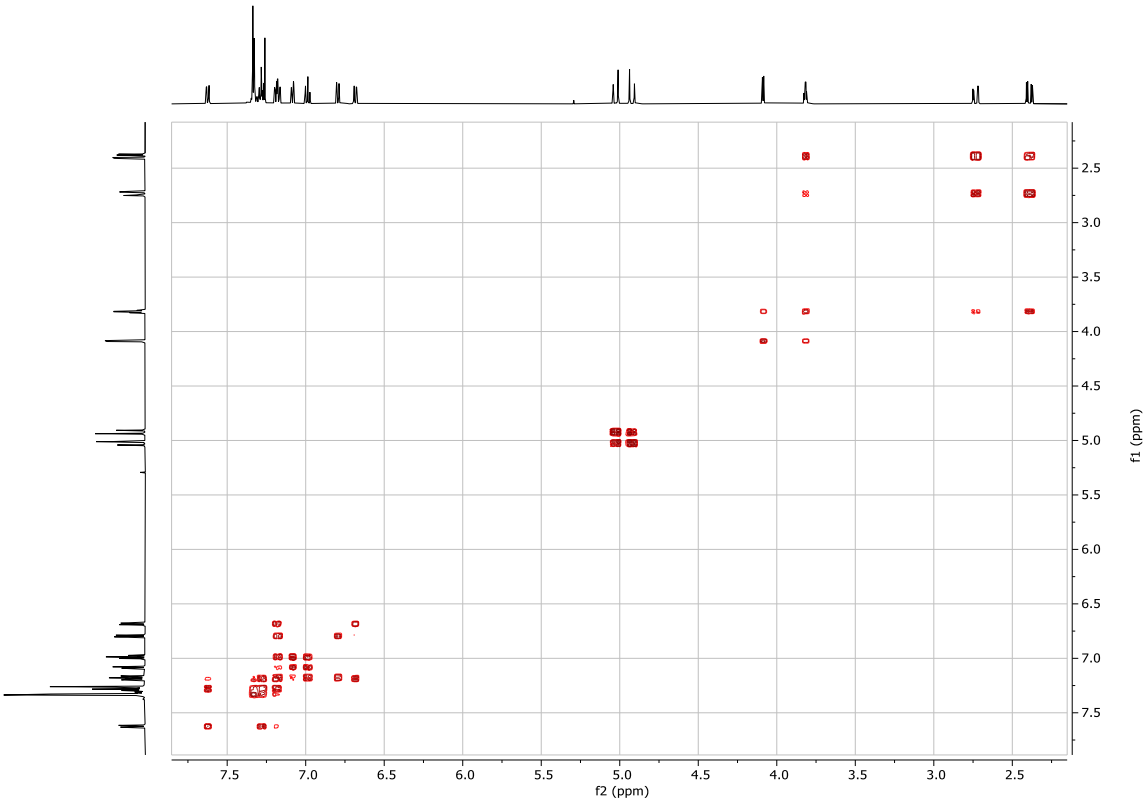

O
H
H
H^f
C^i
O
N
Bn
(7.54,135.3
C^i
f1 (ppm)
f2 (ppm)

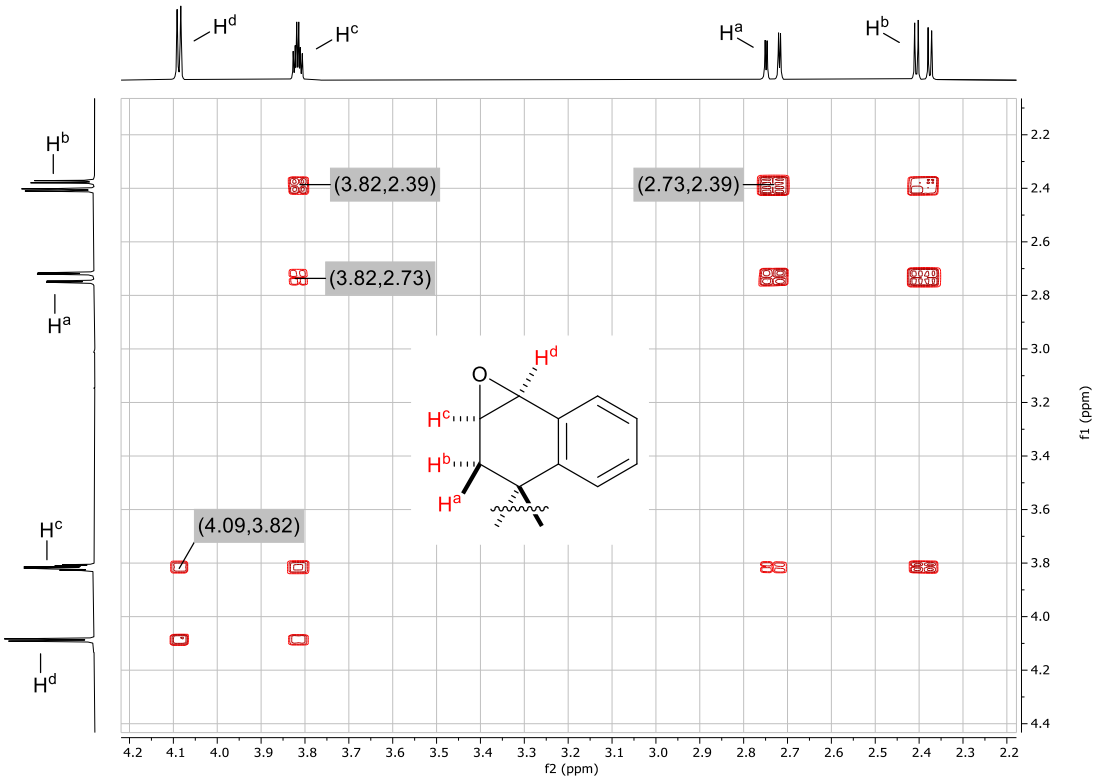

H^g
O
H
H
C^h
H^g
O
N
Bn
(6.75,132.9
C^h
f1 (ppm)
f2 (ppm)


7.26 CDCl3
O
H
H
O
N
13b
500 MHz, CDCl3
0.99
4.11
2.06
2.05
1.01
1.00
1.00
0.97
1.01
0.99
1.00
1.00
0.97
0.97
f1 (ppm)

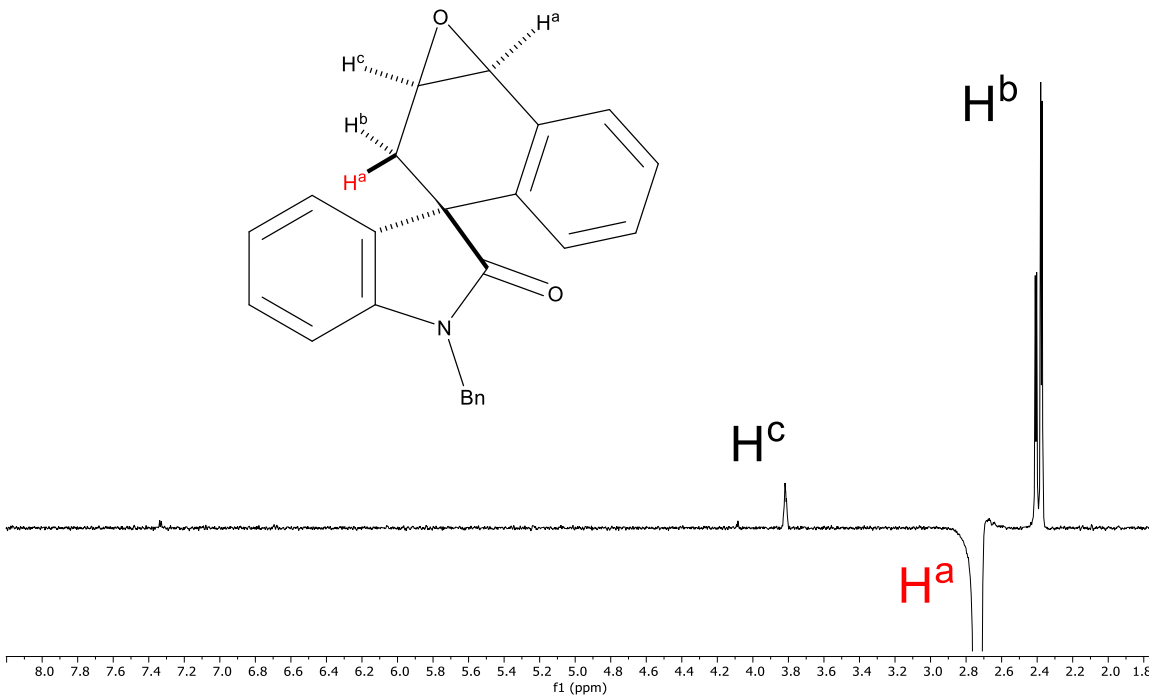

178.1
142.0
136.1
136.0
135.1
133.1
131.5
129.7
128.9
128.5
127.9
127.8
127.6
127.3
123.9
123.2
109.4
77.2 CDCl3
51.7
51.2
51.1
44.1
34.1
126 MHz, CDCl3
f1 (ppm)

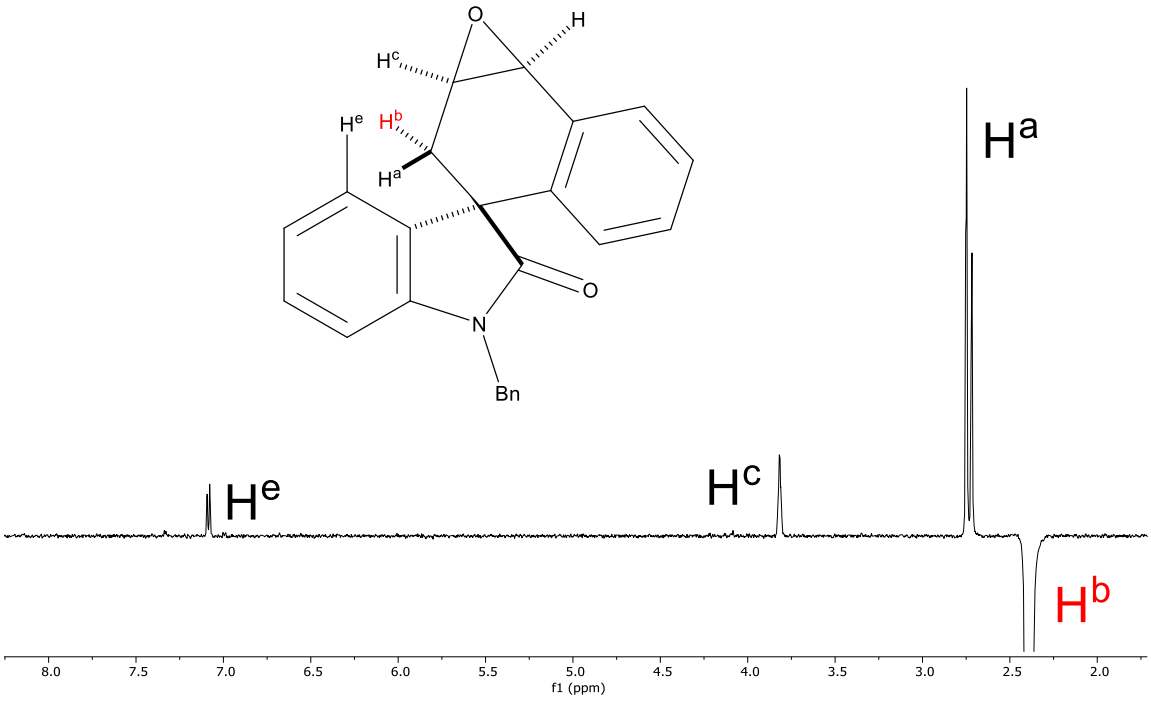
^{1}H-^{1}H COSY NMR, 500 MHz, $CDCl_3$

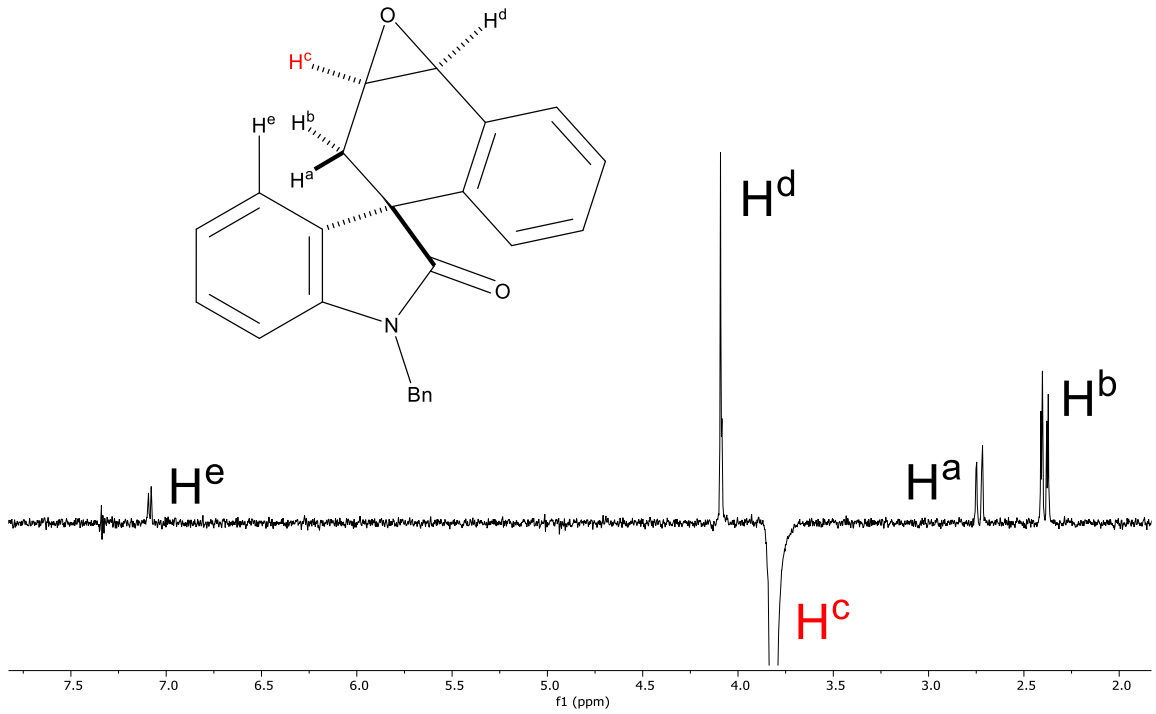


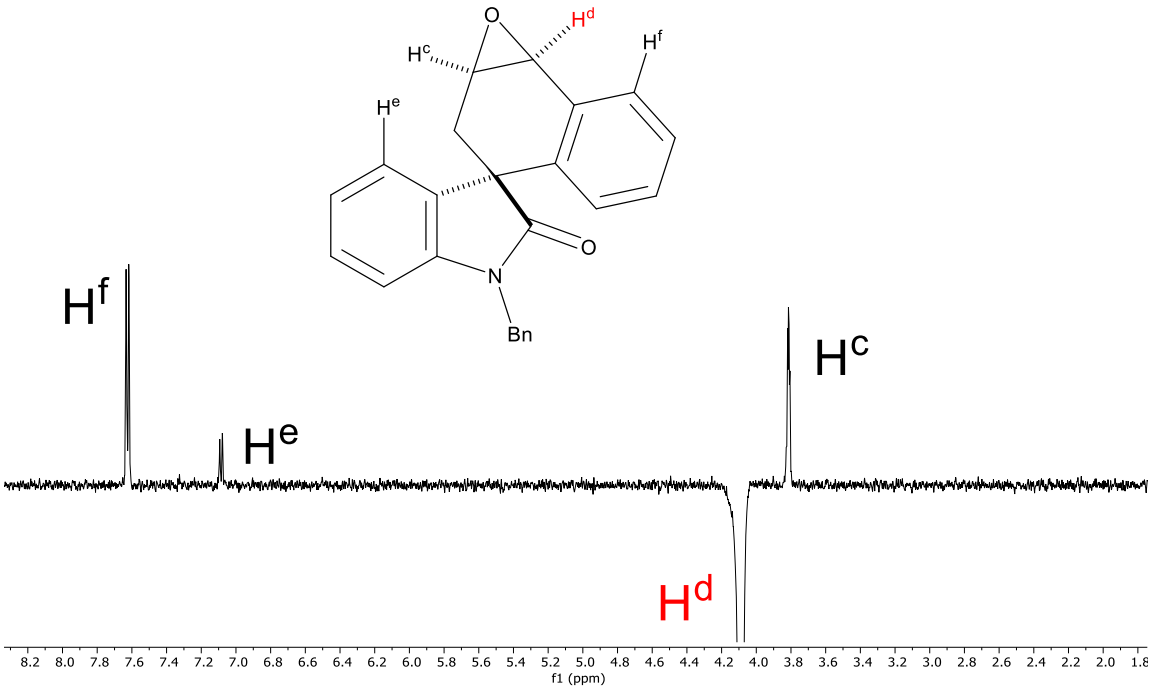


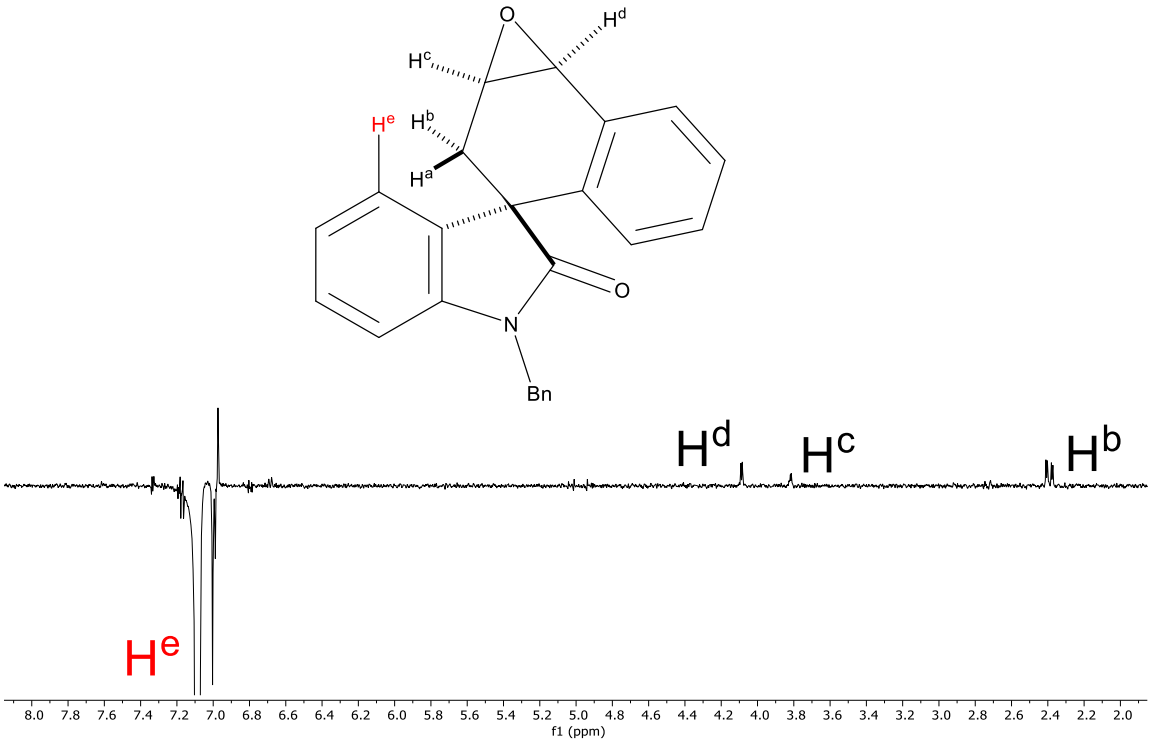
^{1}H NOESY NMR, 500 MHz, $CDCl_3$



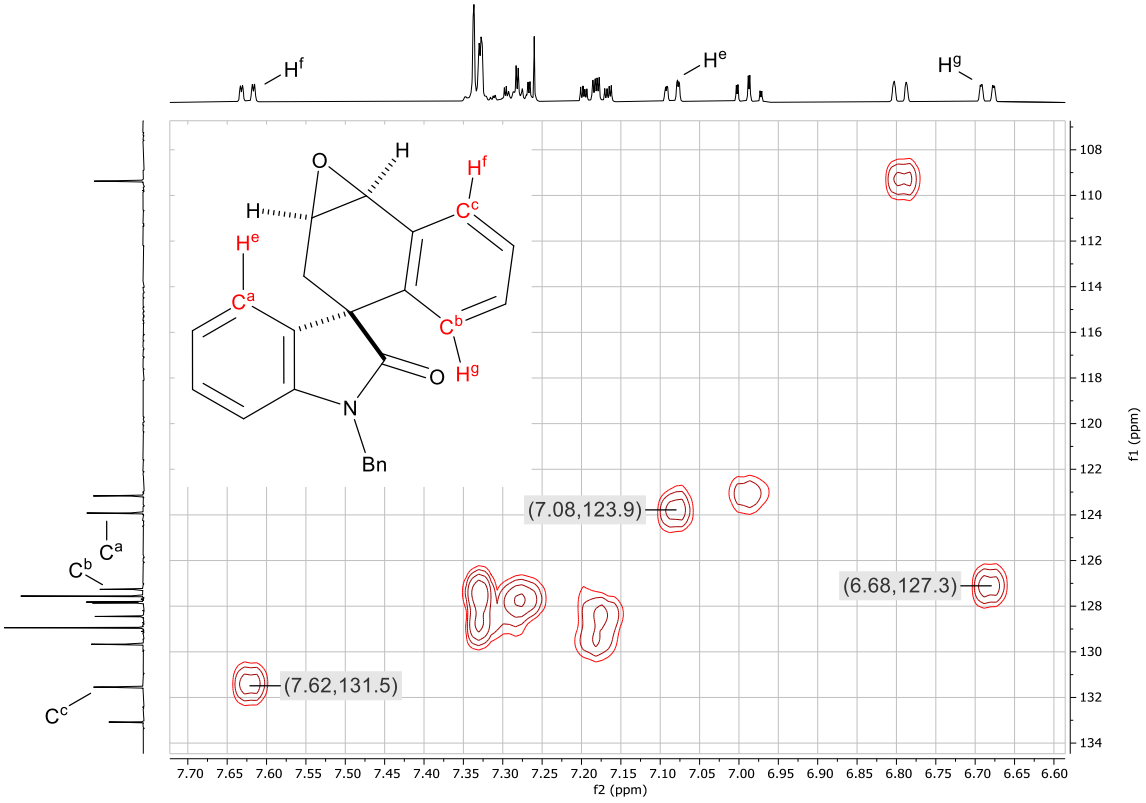


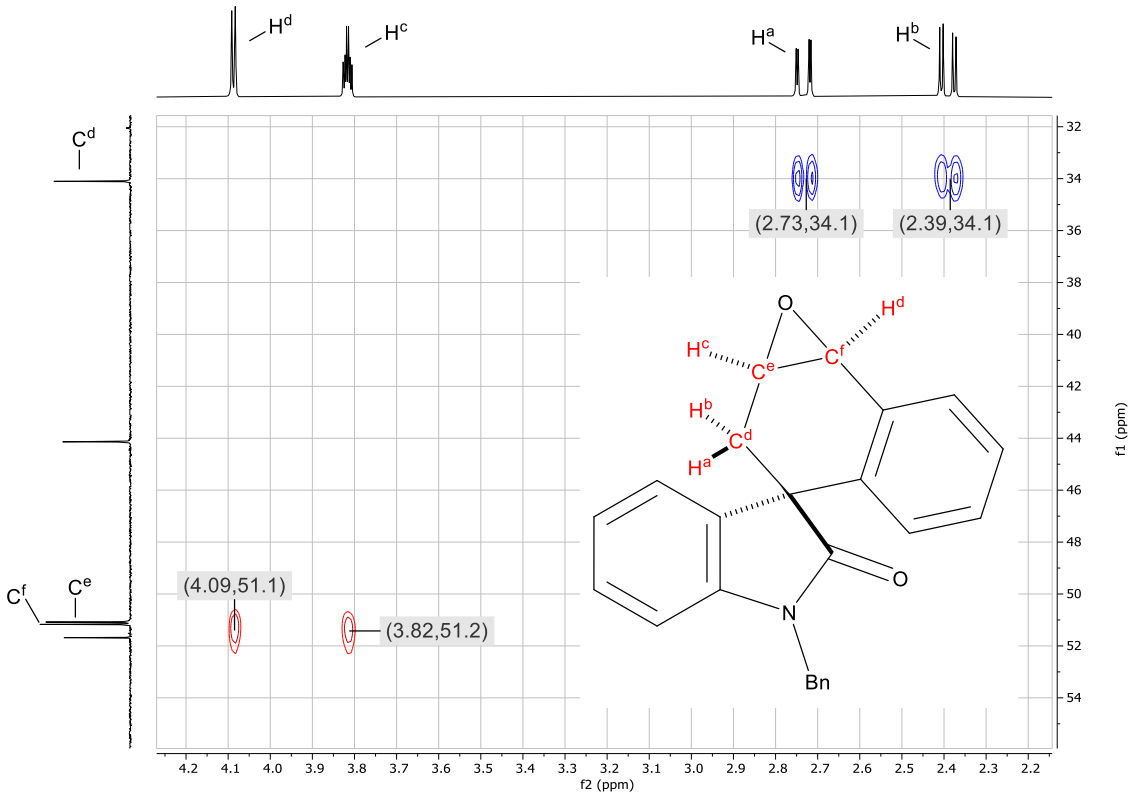

O
Hd
Hc
He
Hb
Ha
O
N
Bn
Hd
Hb
He
Ha
Hc
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)


O
Hd
Hc
Hf
He
O
N
Bn
Hf
He
Hc
Hd
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
f1 (ppm)

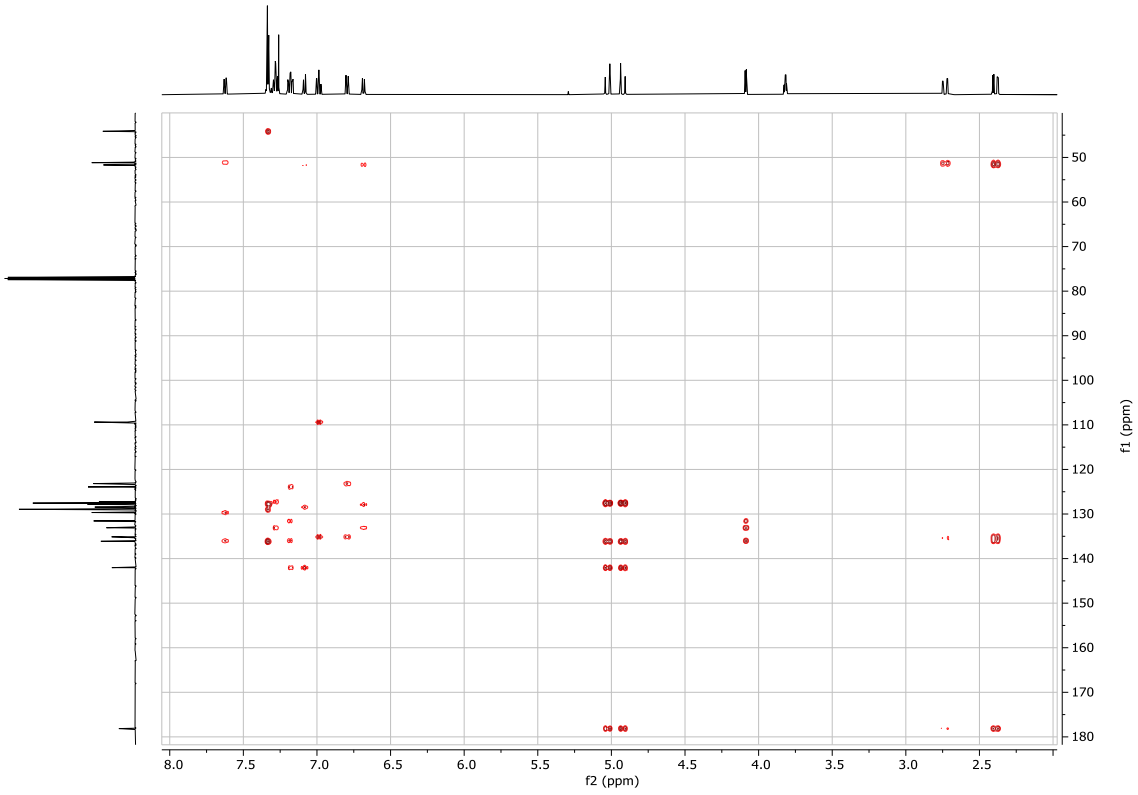

O
Hd
Hc
He
Hb
Ha
O
N
Bn
Hd
Hc
Hb
He
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0
f1 (ppm)

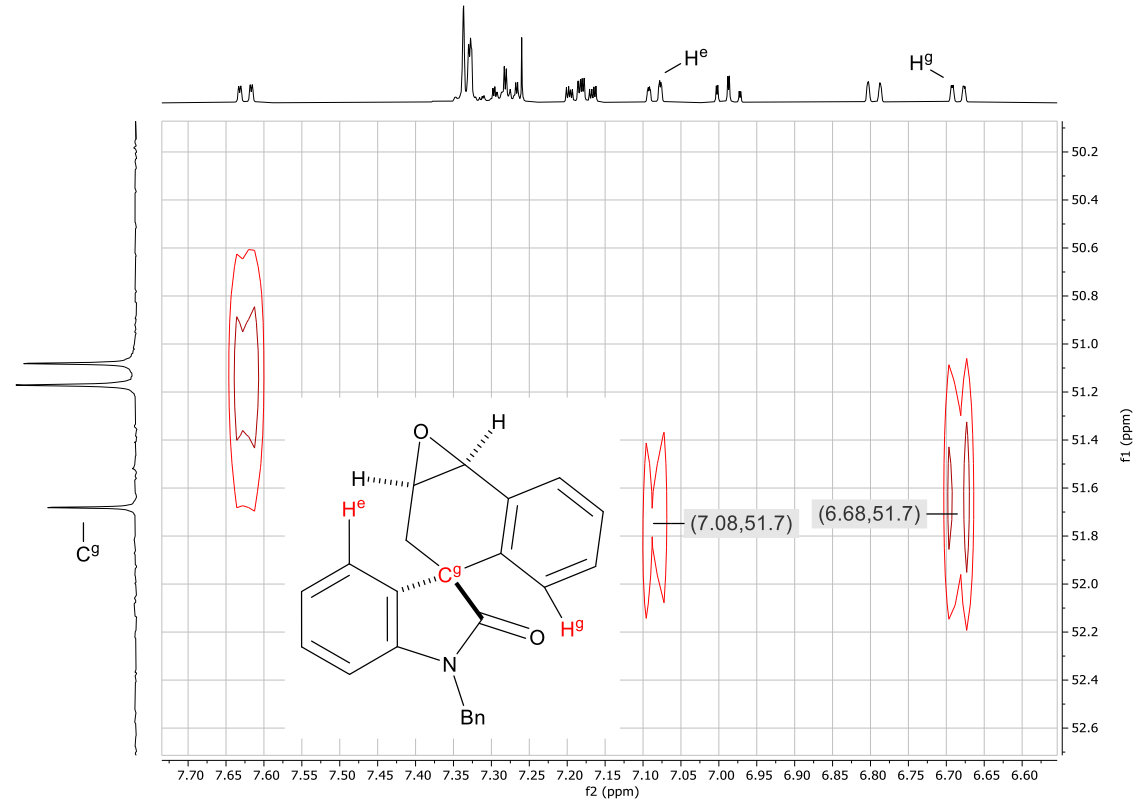
^{1}H-^{13}C HSQC NMR, 500 MHz, $CDCl_3$

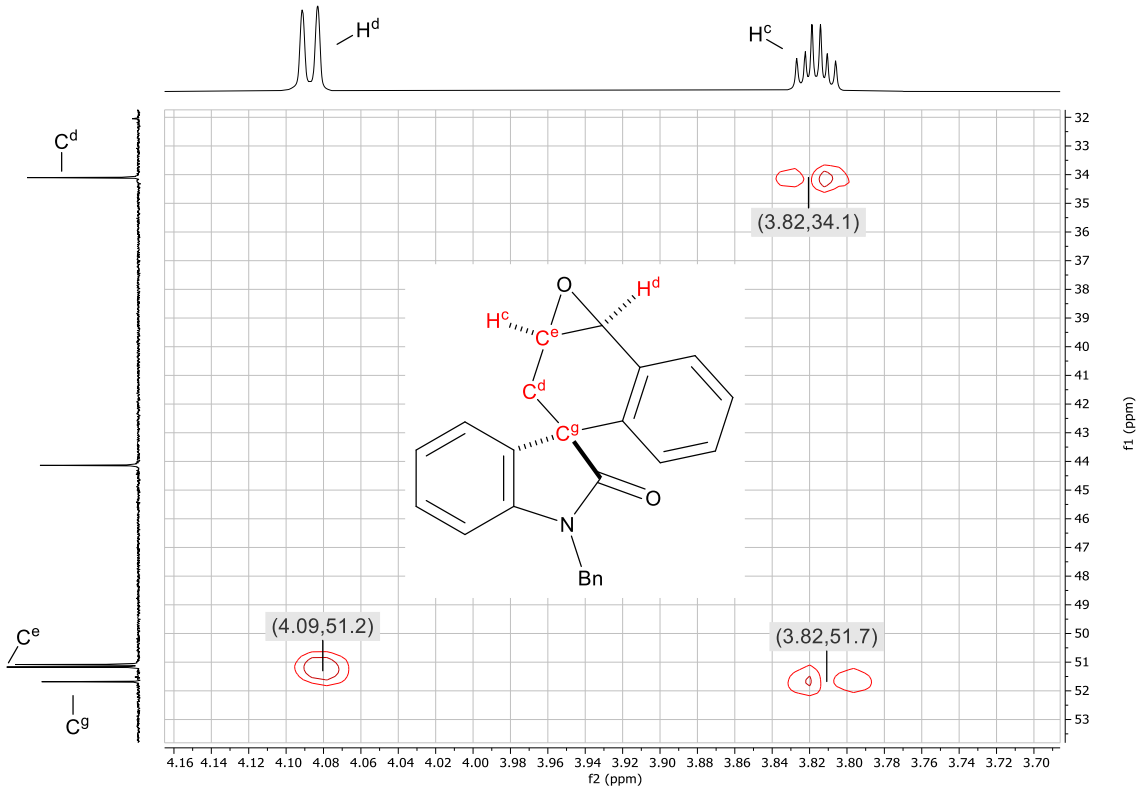


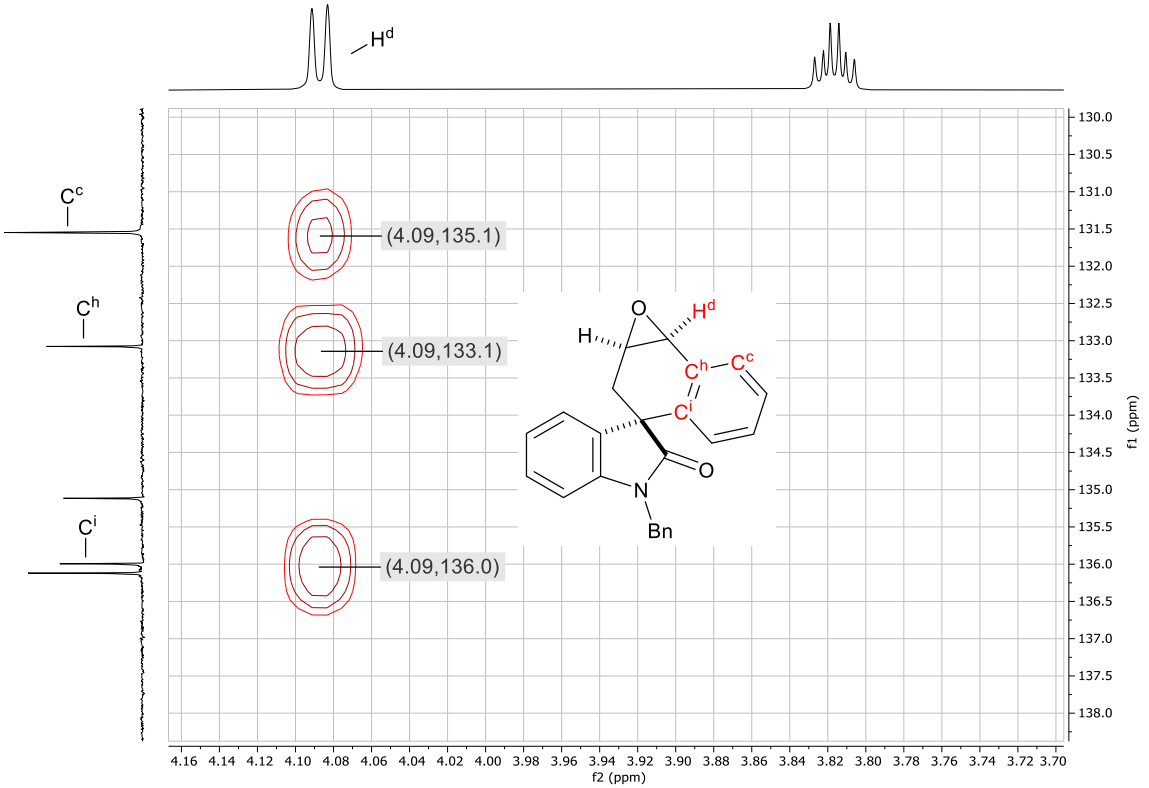

H^d
H^c
H^a
H^b
C^d
C^f
C^e
(2.73,34.1)
(2.39,34.1)
(4.09,51.1)
(3.82,51.2)
O
H^d
H^c
C^e
C^f
H^b
C^d
H^a
O
N
Bn
f2 (ppm)
f1 (ppm)

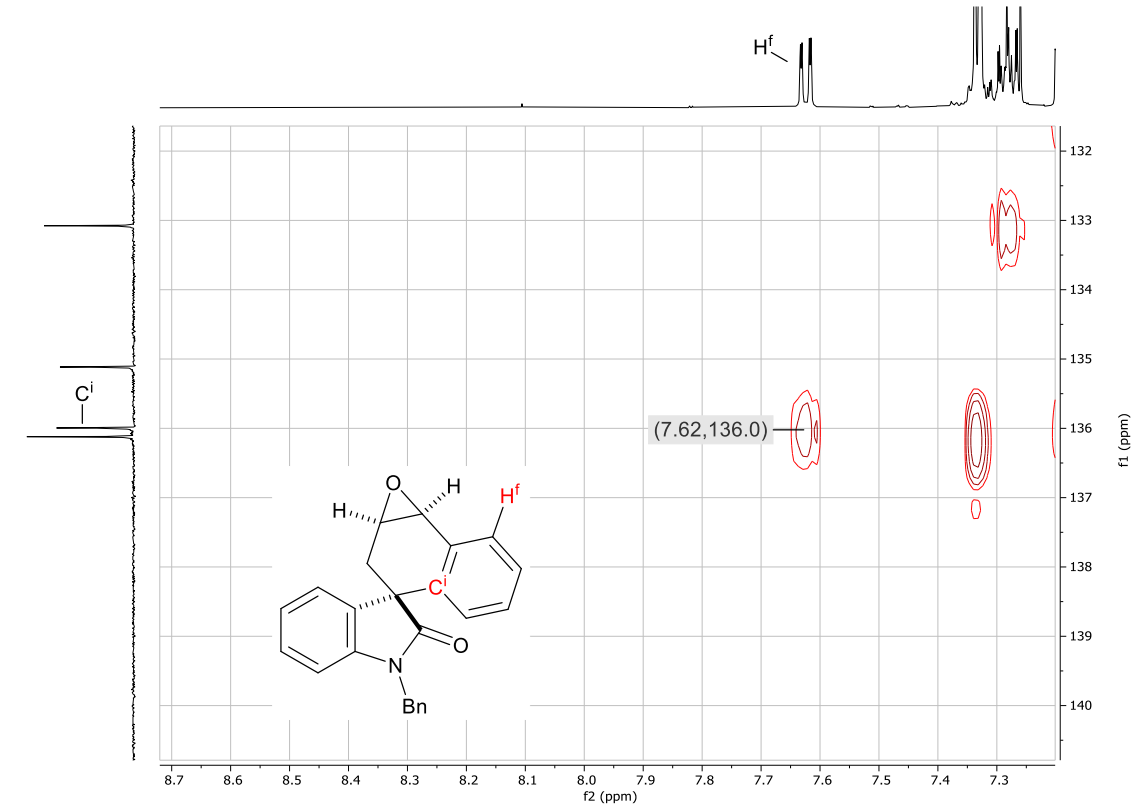
^{1}H-^{13}C HMBC NMR, 500 MHz, $CDCl_3$

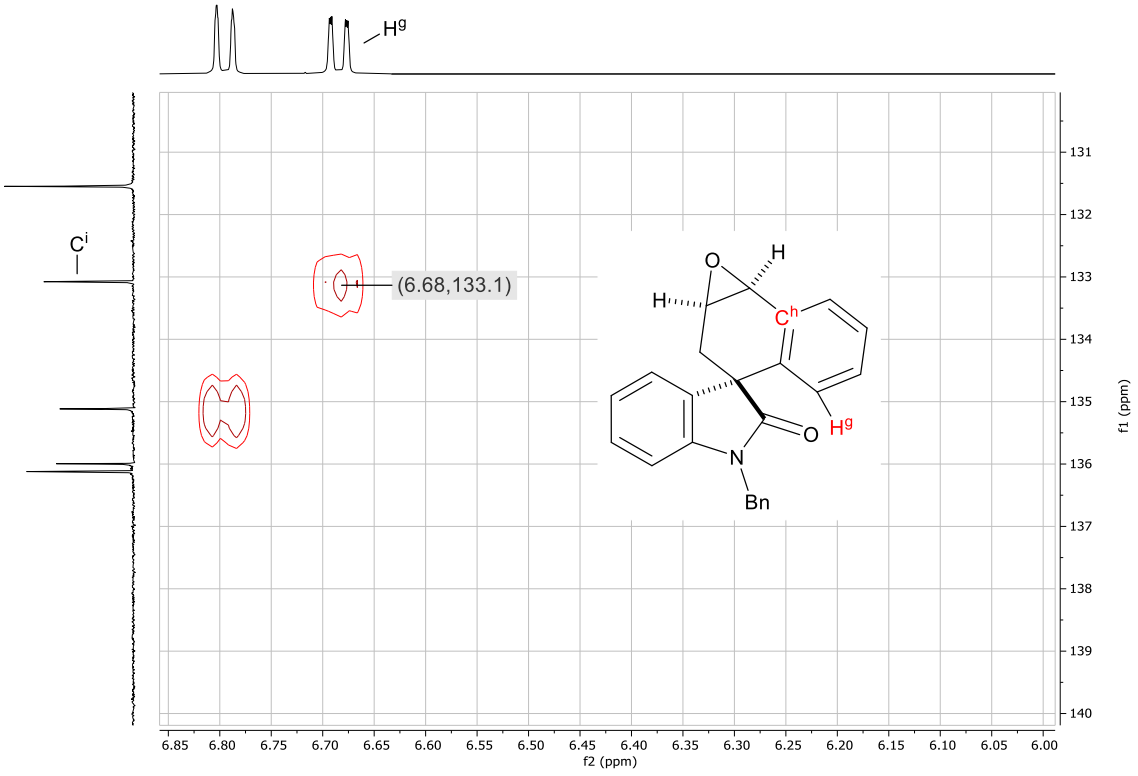


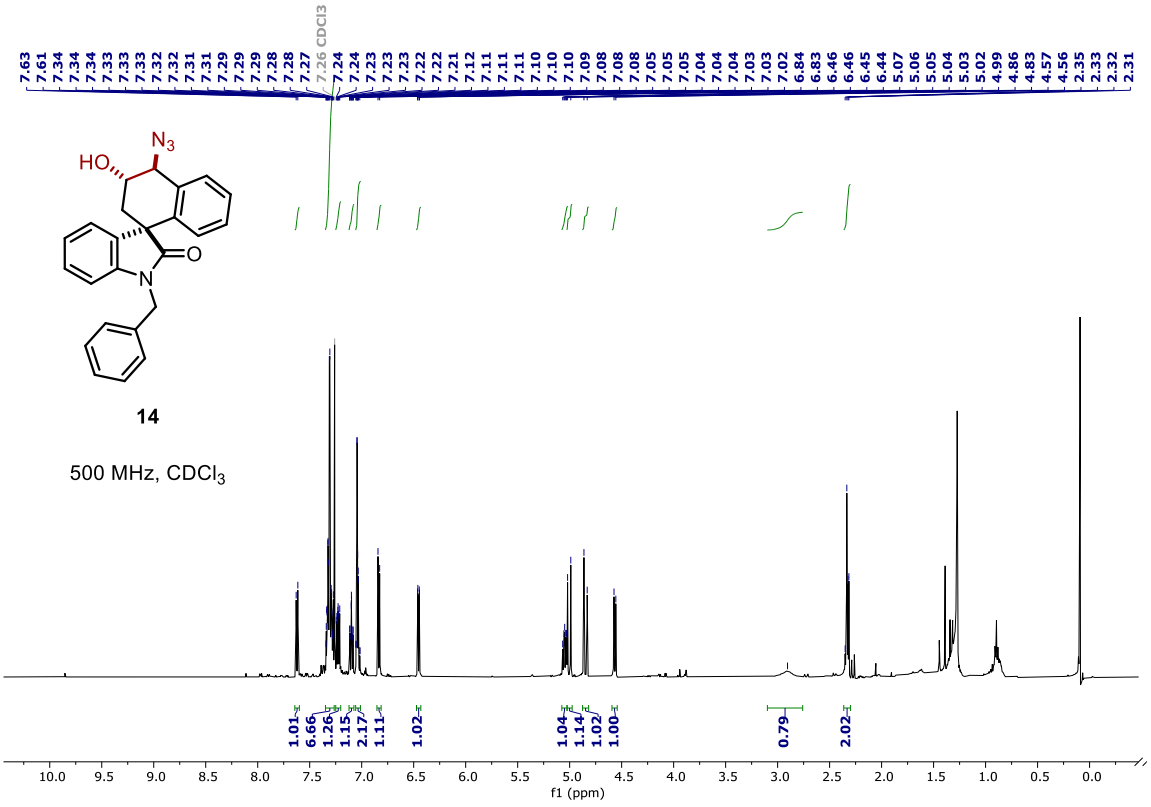


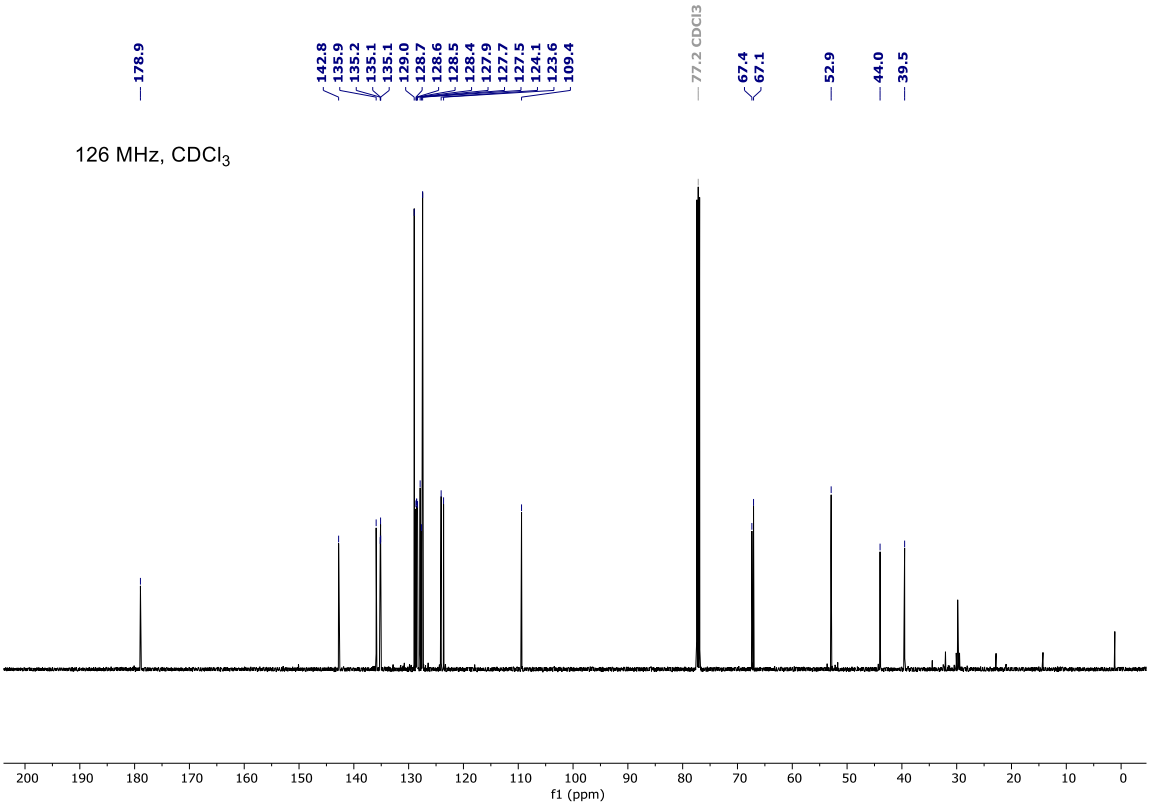

H^d
H^c
C^d
C^e
C^g
(3.82,34.1)
(4.09,51.2)
(3.82,51.7)
Bn
f2 (ppm)
f1 (ppm)

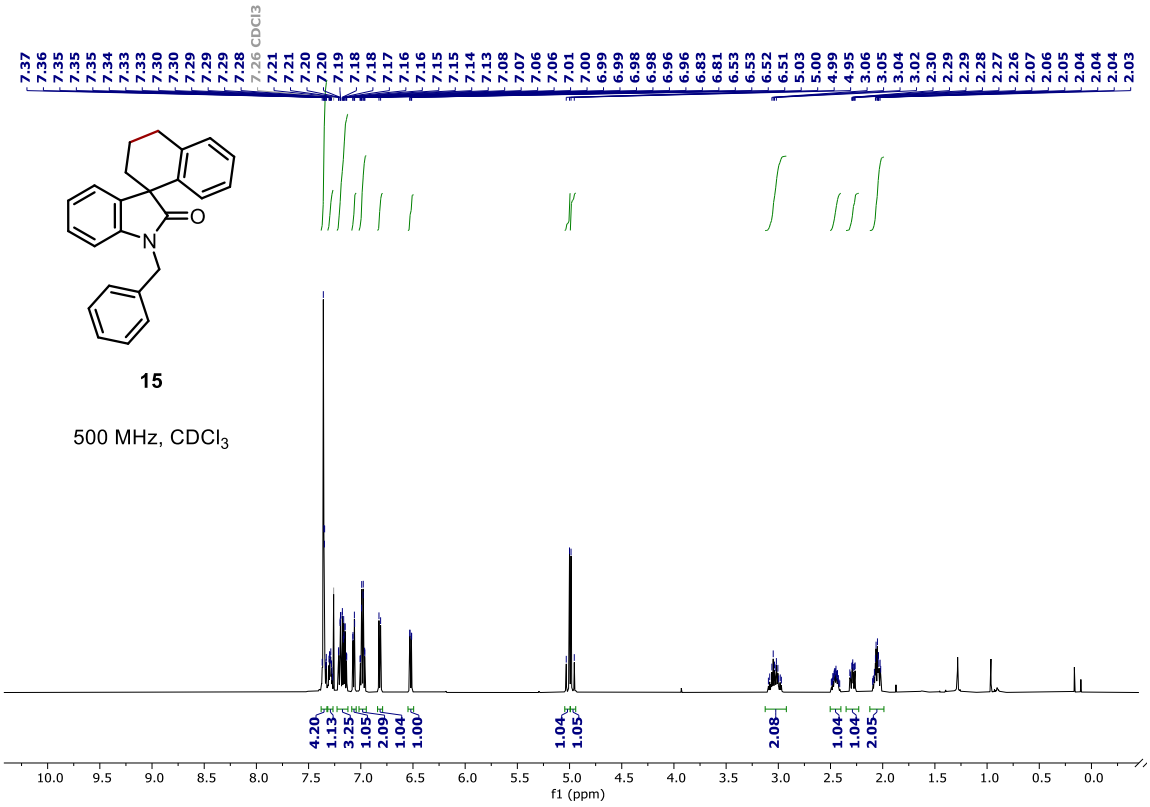

H^d
C^c
C^h
C^i
(4.09,135.1)
(4.09,133.1)
(4.09,136.0)
Bn
f2 (ppm)
f1 (ppm)

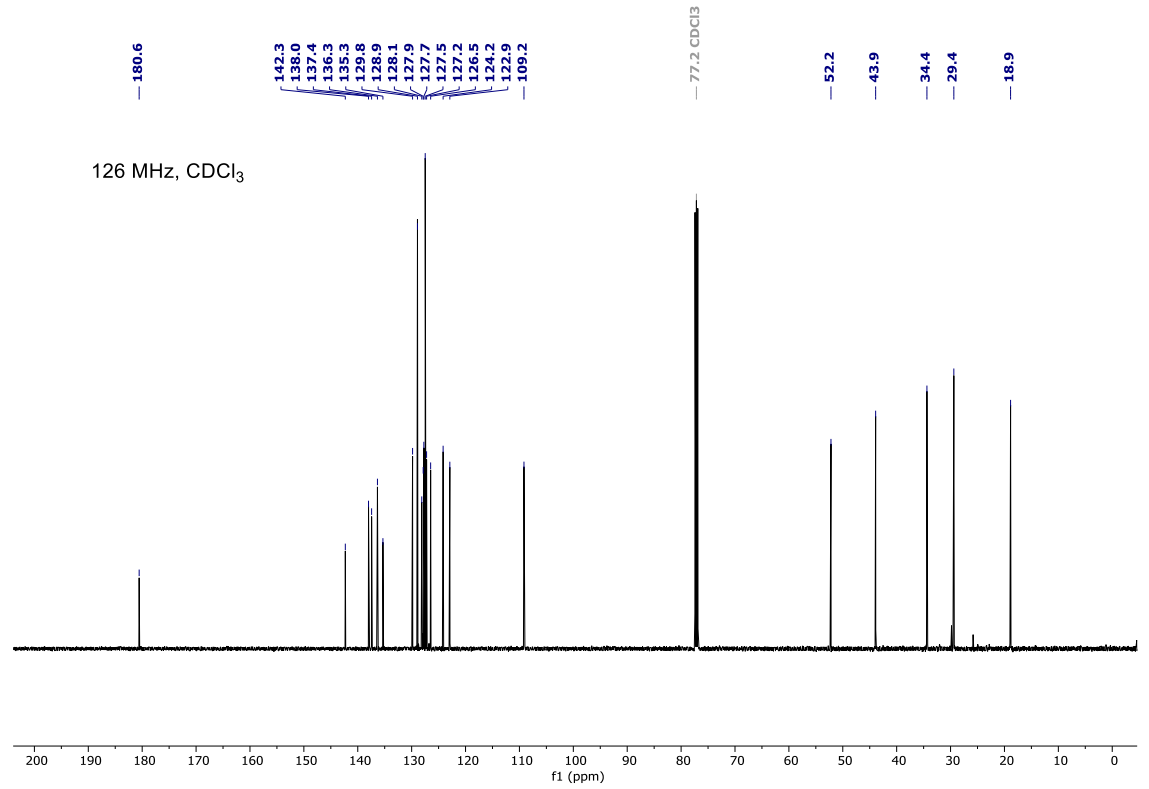

H^f
C^i
(7.62,136.0)
O
H
H
H^f
C^i
O
N
Bn
f1 (ppm)
f2 (ppm)

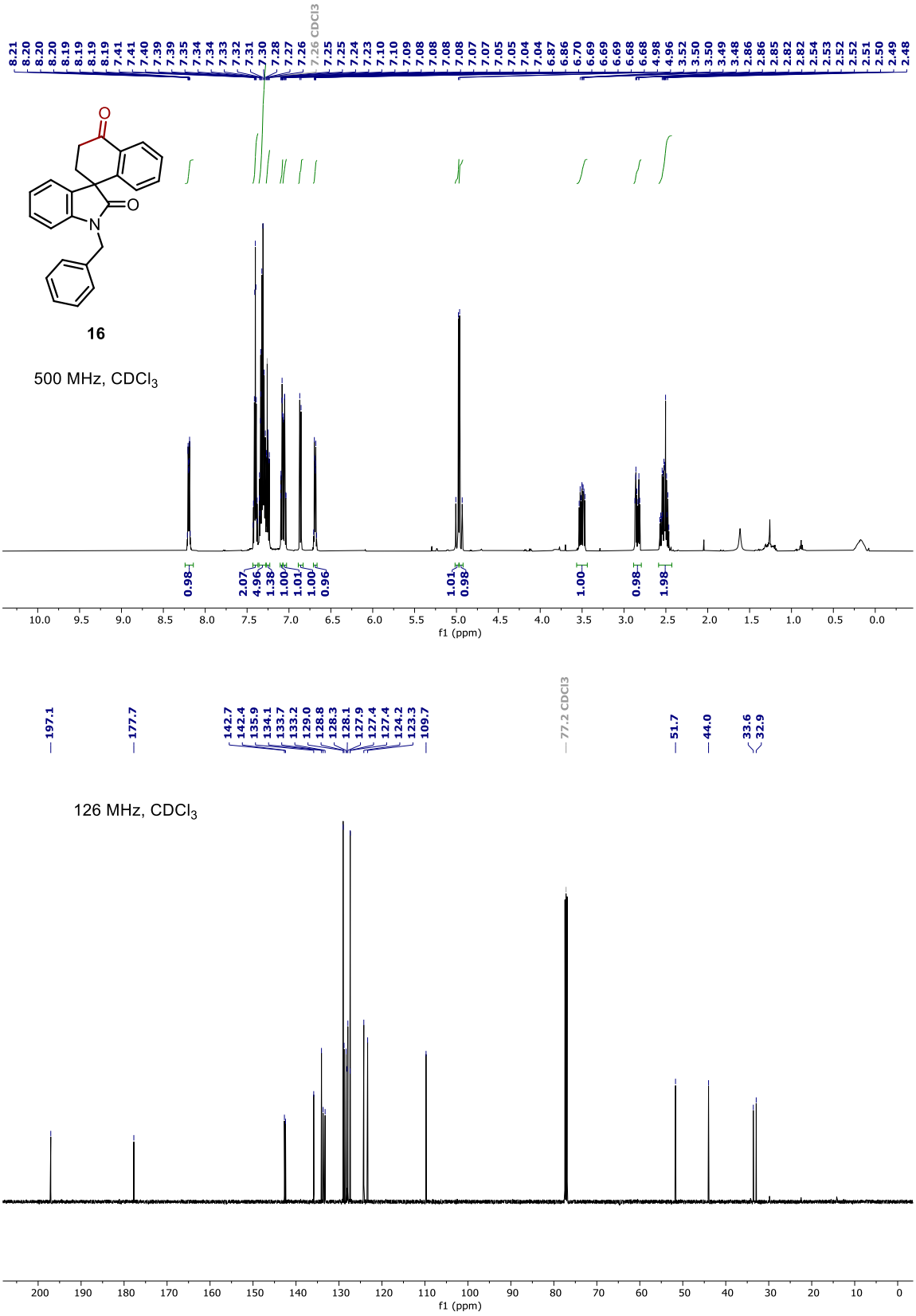

H^g
C^i
(6.68,133.1)
O
H
H
C^h
O
H^g
N
Bn
f1 (ppm)
f2 (ppm)

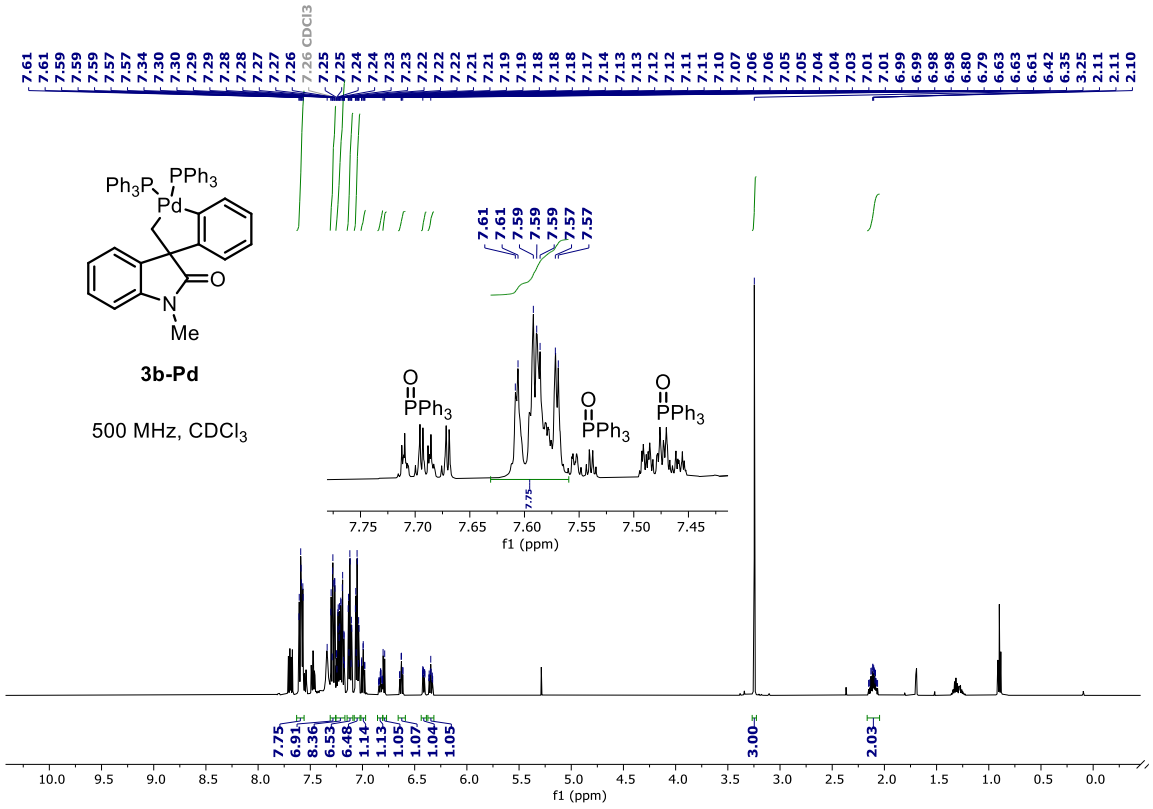

7.63 7.61 7.34 7.34 7.34 7.33 7.33 7.33 7.32 7.32 7.31 7.31 7.29 7.29 7.29 7.28 7.28 7.27 7.26 CDCl3 7.24 7.24 7.23 7.23 7.23 7.22 7.22 7.21 7.12 7.11 7.11 7.11 7.10 7.10 7.10 7.09 7.08 7.08 7.08 7.05 7.05 7.05 7.04 7.04 7.04 7.03 7.03 7.02 6.84 6.83 6.46 6.46 6.45 6.44 5.07 5.06 5.05 5.04 5.03 5.02 4.99 4.86 4.83 4.57 4.56 2.35 2.33 2.32 2.31
HO
N3
O
N
14
500 MHz, CDCl3
1.01 6.66 1.26 1.15 2.17 1.11 1.02 1.04 1.14 1.02 1.00 0.79 2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

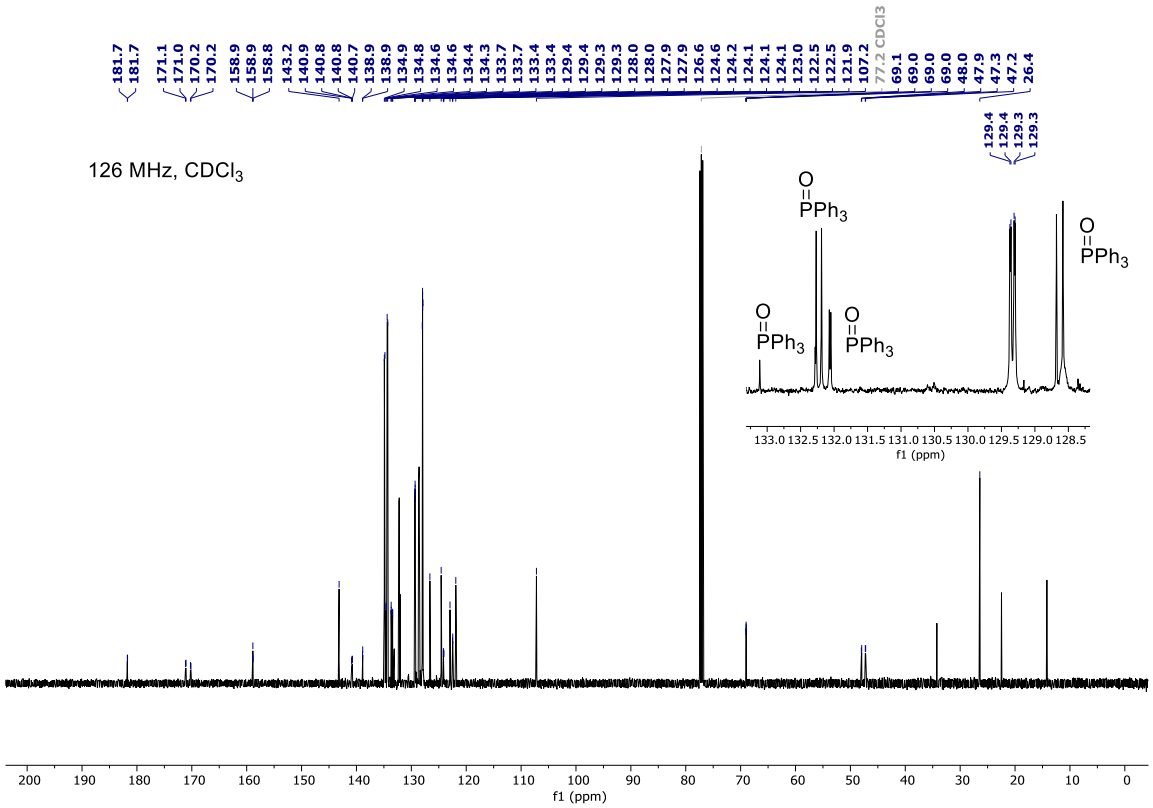

178.9
142.8 135.9 135.2 135.1 135.1 129.0 128.7 128.6 128.5 128.4 127.9 127.7 127.5 124.1 123.6 109.4
77.2 CDCl3
67.4 67.1
52.9
44.0
39.5
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

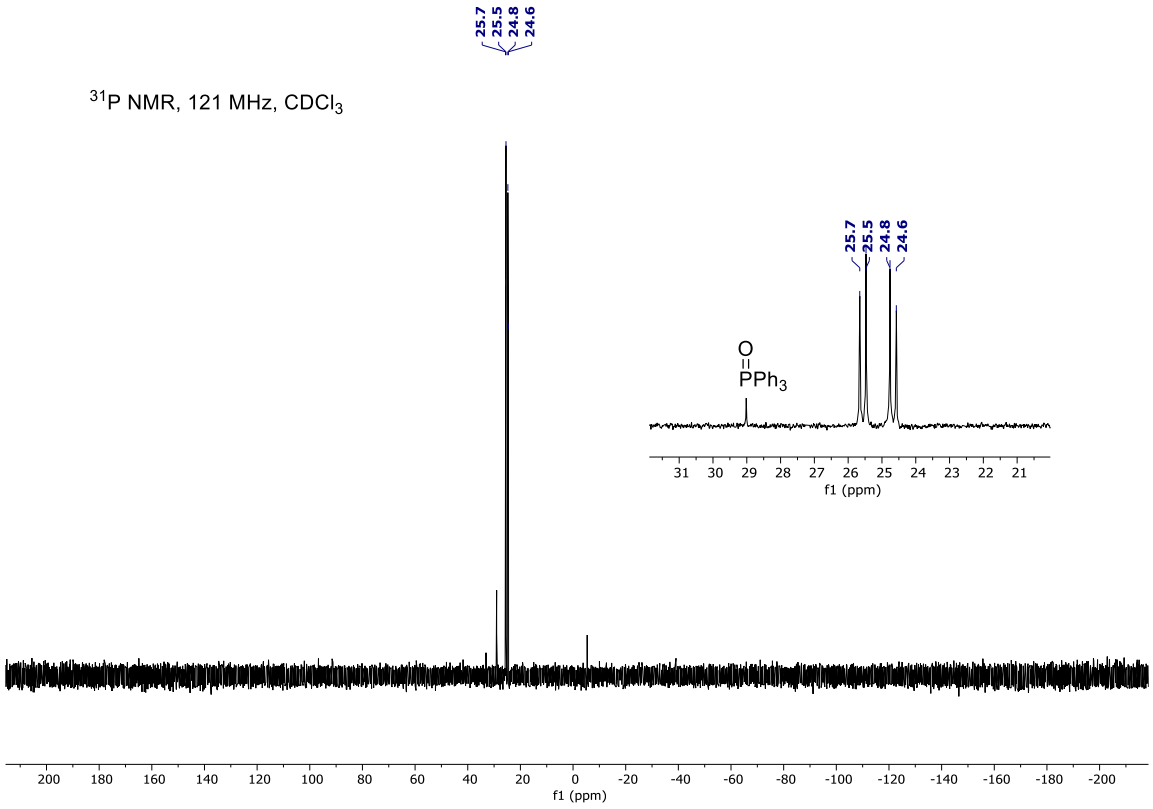

7.26 CDCl3
O
N
15
500 MHz, CDCl3
4.20
1.13
3.25
1.05
2.09
1.04
1.00
1.04
1.05
2.08
1.04
1.04
2.05
f1 (ppm)

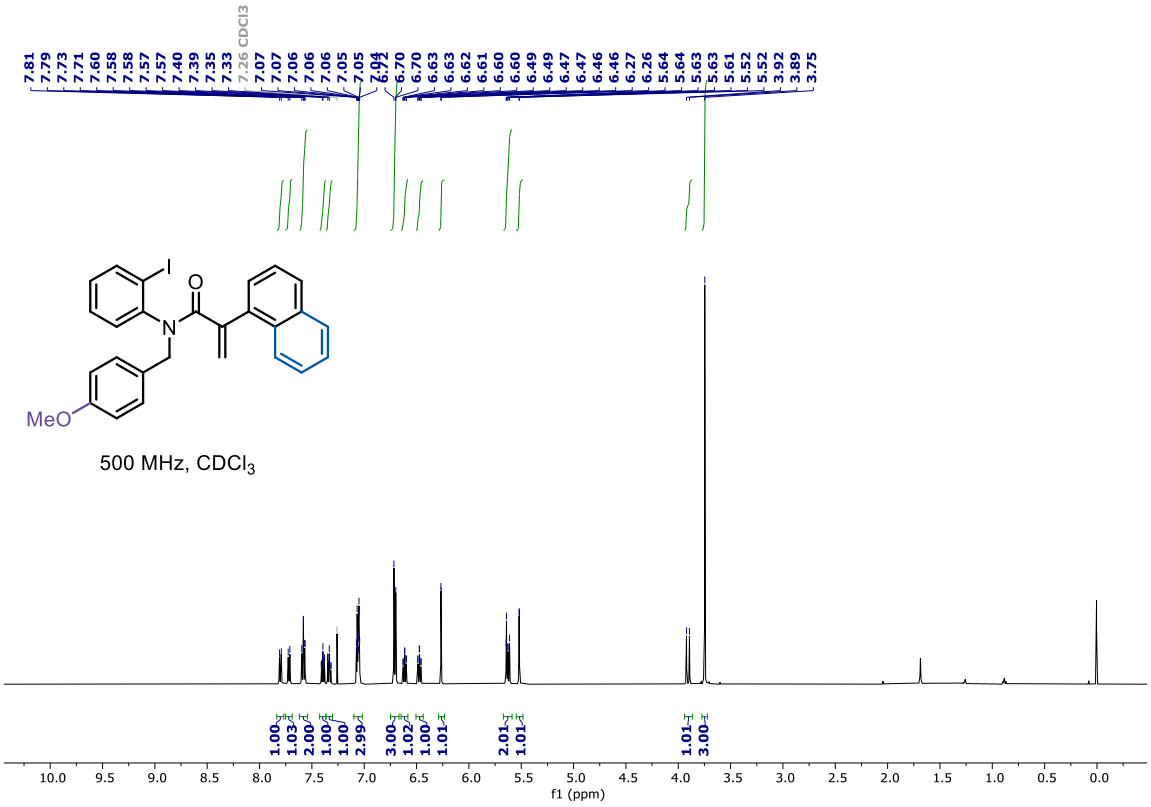

180.6
142.3
138.0
137.4
136.3
135.3
129.8
128.9
128.1
127.9
127.7
127.5
127.2
126.5
124.2
122.9
109.2
77.2 CDCl3
52.2
43.9
34.4
29.4
18.9
126 MHz, CDCl3
f1 (ppm)

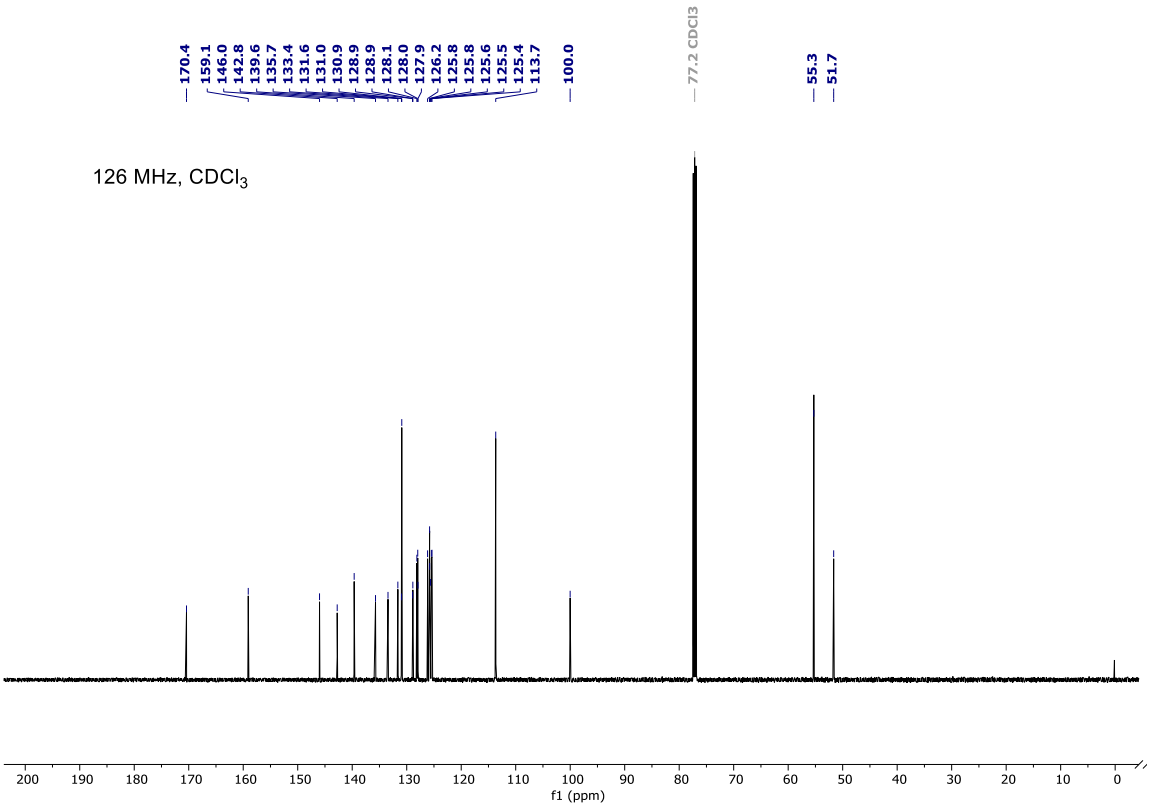

16
500 MHz, CDCl3
126 MHz, CDCl3
f1 (ppm)
f1 (ppm)

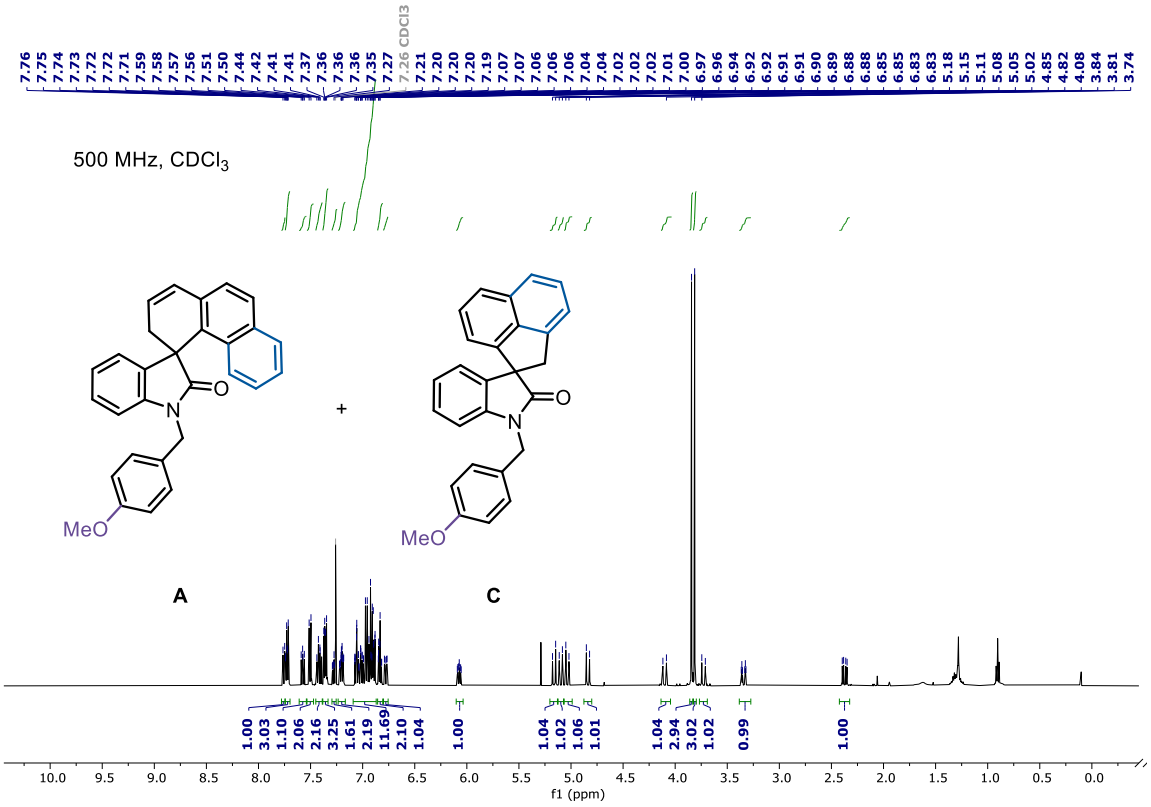

Ph3P
PPh3
Pd
O
N
Me
3b-Pd
500 MHz, CDCl3
O
PPh3
f1 (ppm)

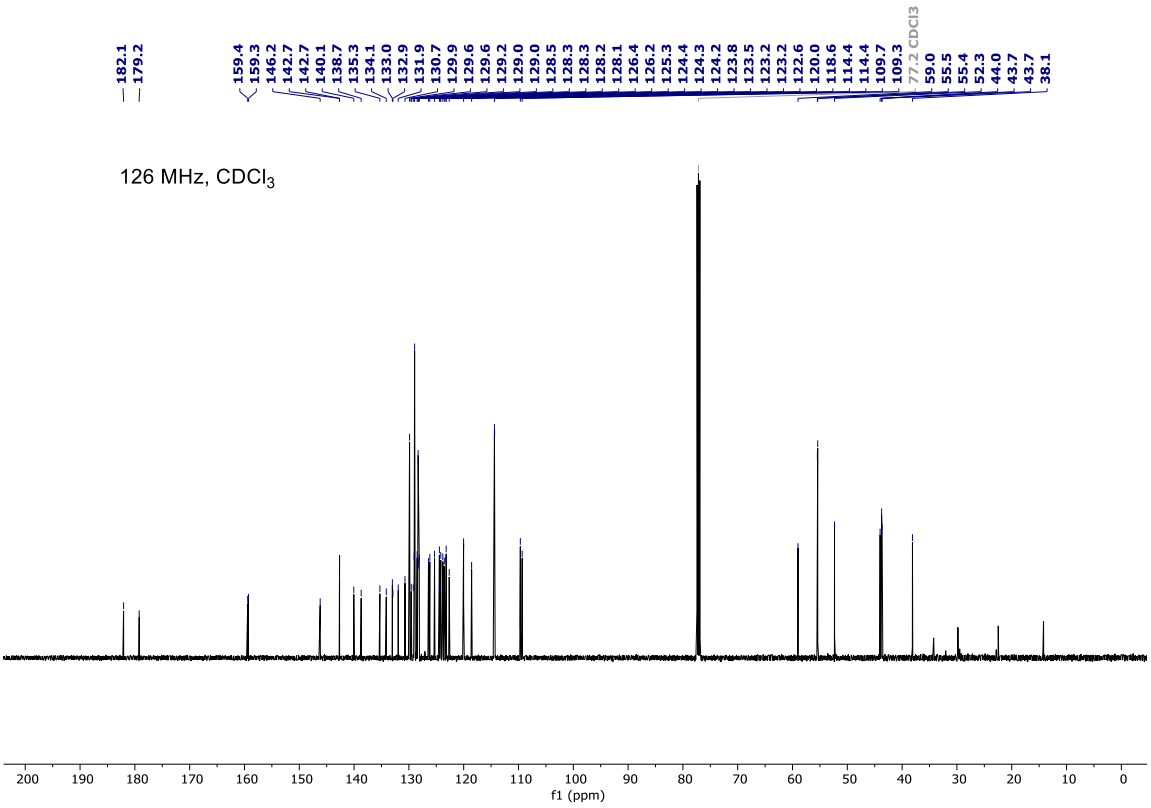

126 MHz, CDCl3
O
PPh3
f1 (ppm)

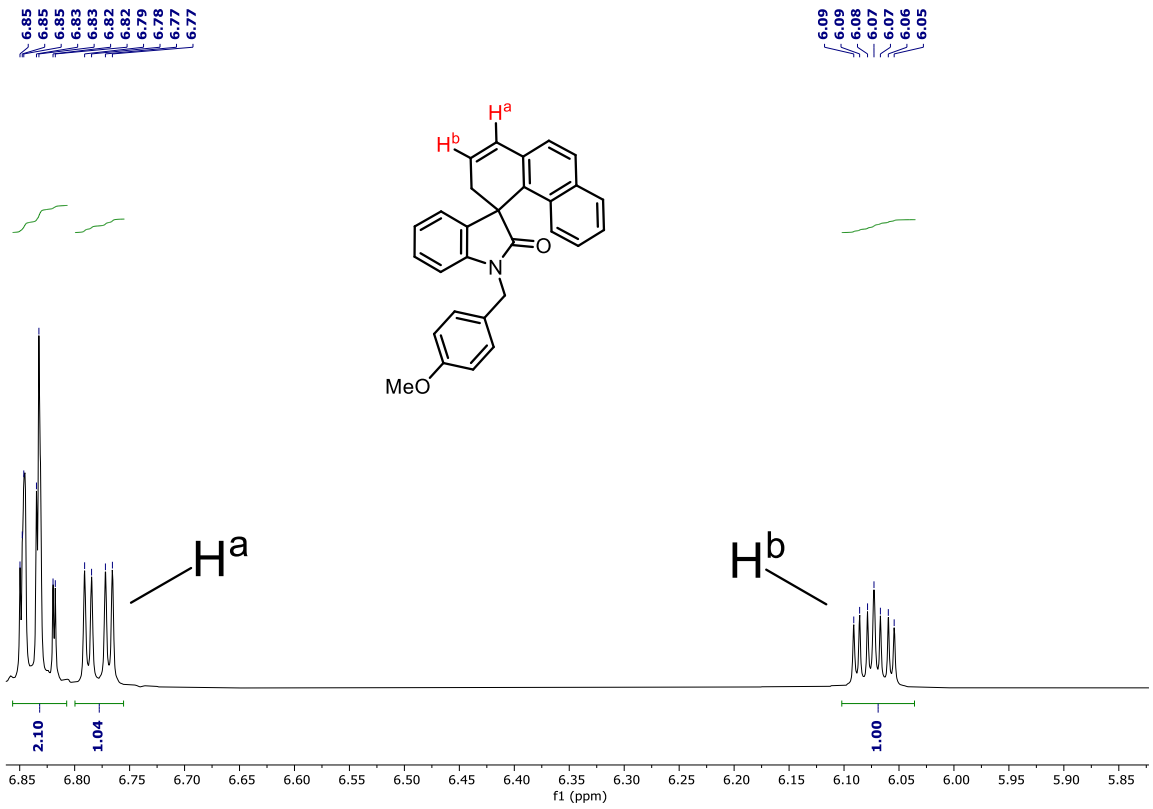

25.7
25.5
24.8
24.6
31P NMR, 121 MHz, CDCl3
O
PPh3
f1 (ppm)
f1 (ppm)

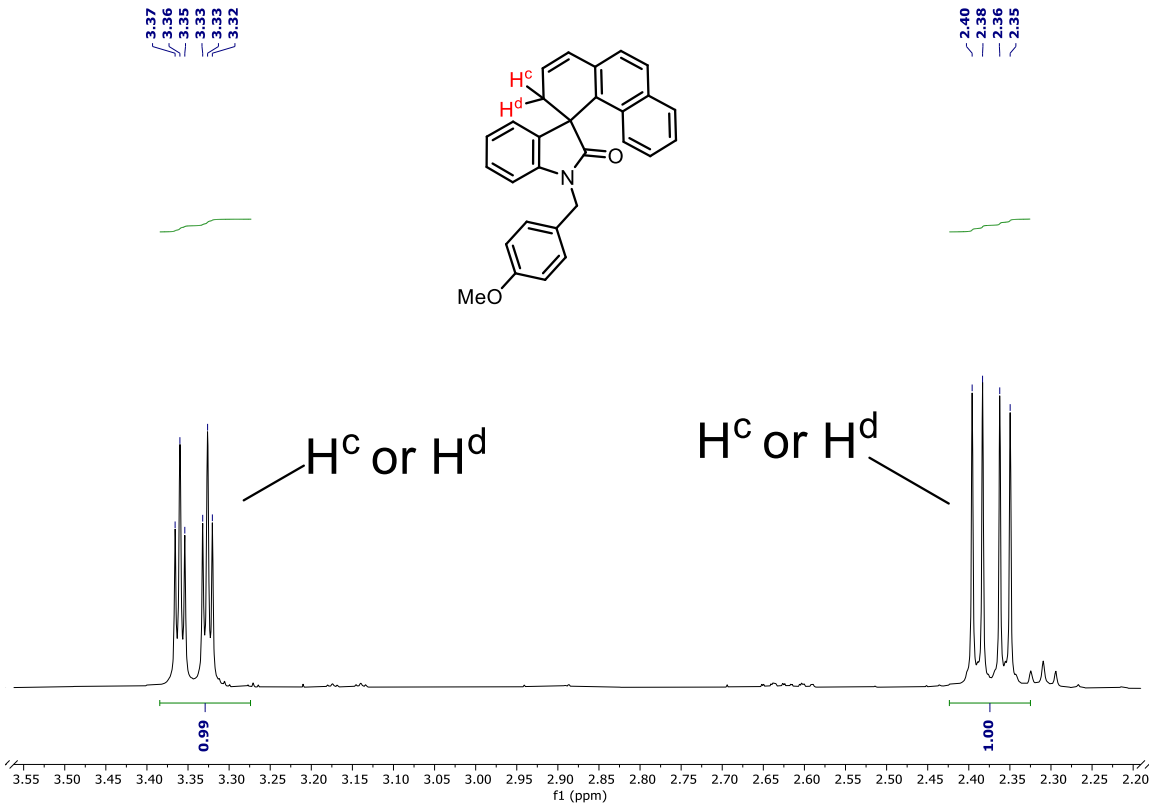

7.81 7.79 7.73 7.71 7.60 7.58 7.57 7.57 7.40 7.39 7.35 7.33 7.26 CDCl3 7.07 7.07 7.06 7.06 7.06 7.05 7.05 7.04 6.70 6.70 6.63 6.63 6.62 6.61 6.60 6.60 6.49 6.49 6.47 6.47 6.46 6.46 6.27 6.26 5.64 5.64 5.63 5.63 5.61 5.52 5.52 3.92 3.89 3.75
I
O
N
MeO
500 MHz, CDCl3
1.00 1.03 2.00 1.00 1.00 2.99 3.00 1.02 1.00 1.01 2.01 1.01 1.01 3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

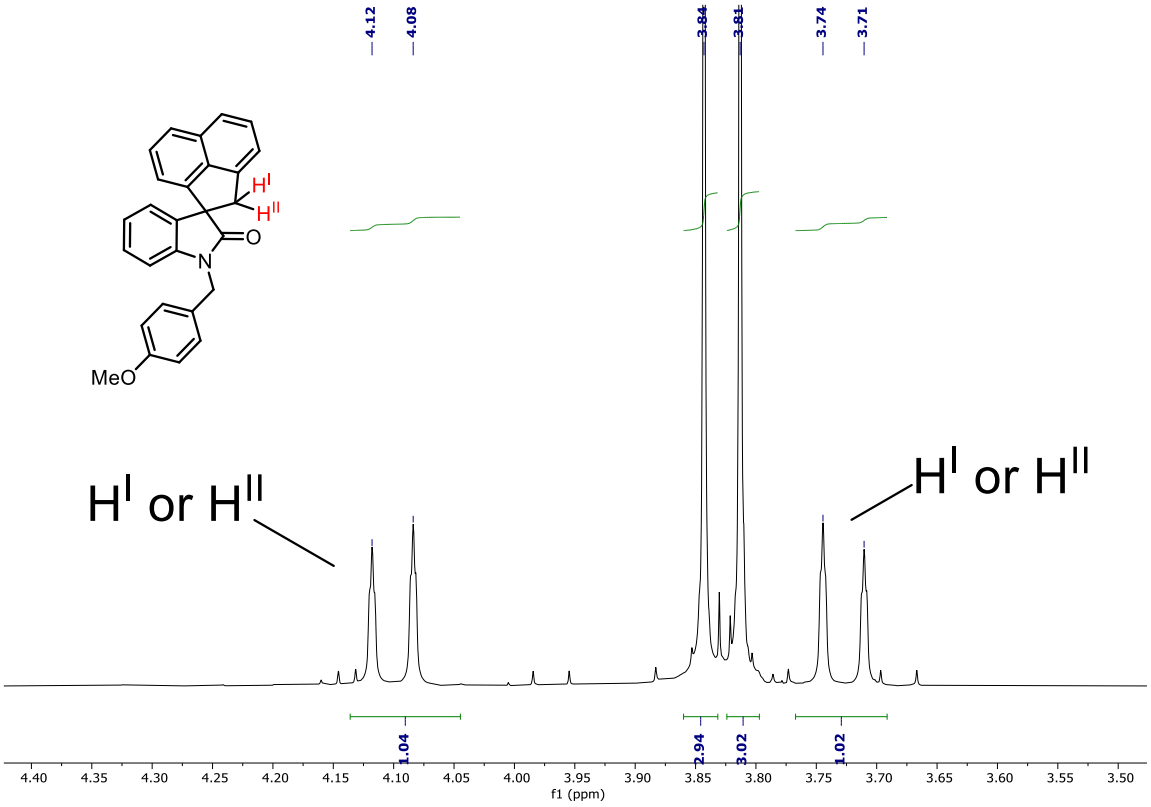

170.4 159.1 146.0 142.8 139.6 135.7 133.4 131.6 131.0 130.9 128.9 128.9 128.1 128.0 127.9 126.2 125.8 125.8 125.6 125.5 125.4 113.7 100.0 77.2 CDCl3 55.3 51.7
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

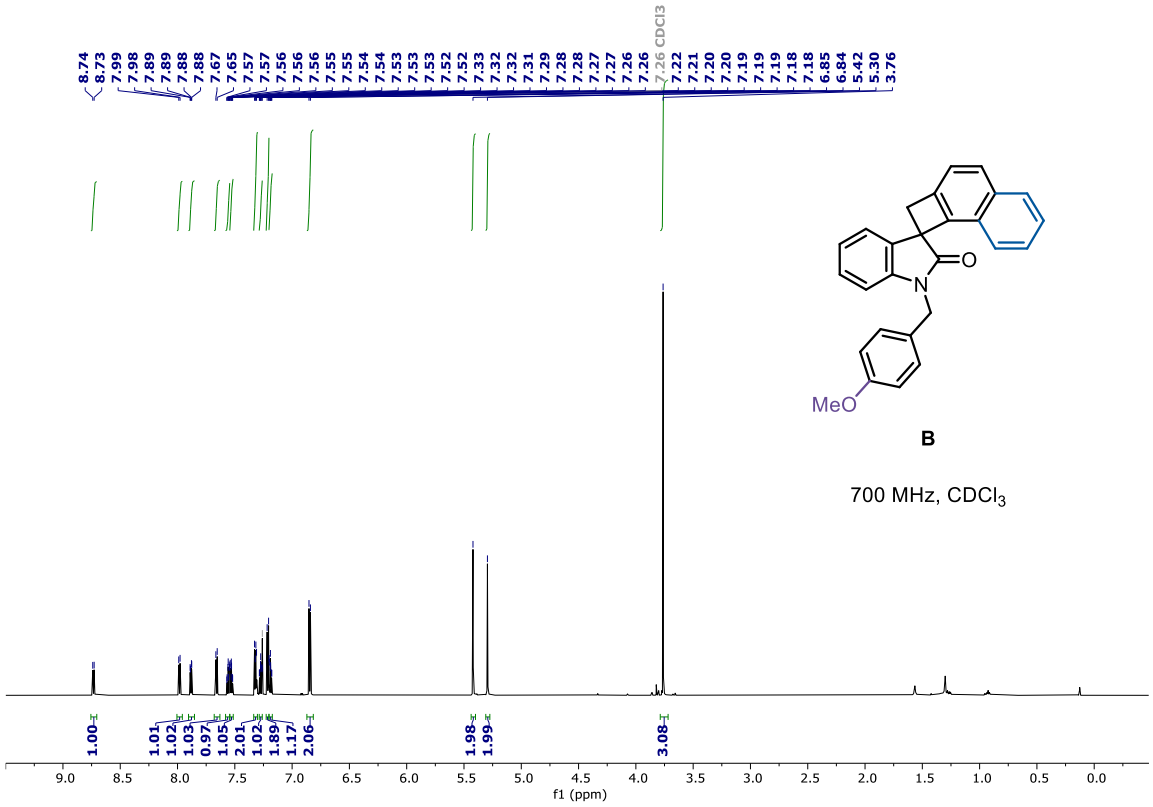

500 MHz, CDCl3
MeO
MeO
A
C
f1 (ppm)

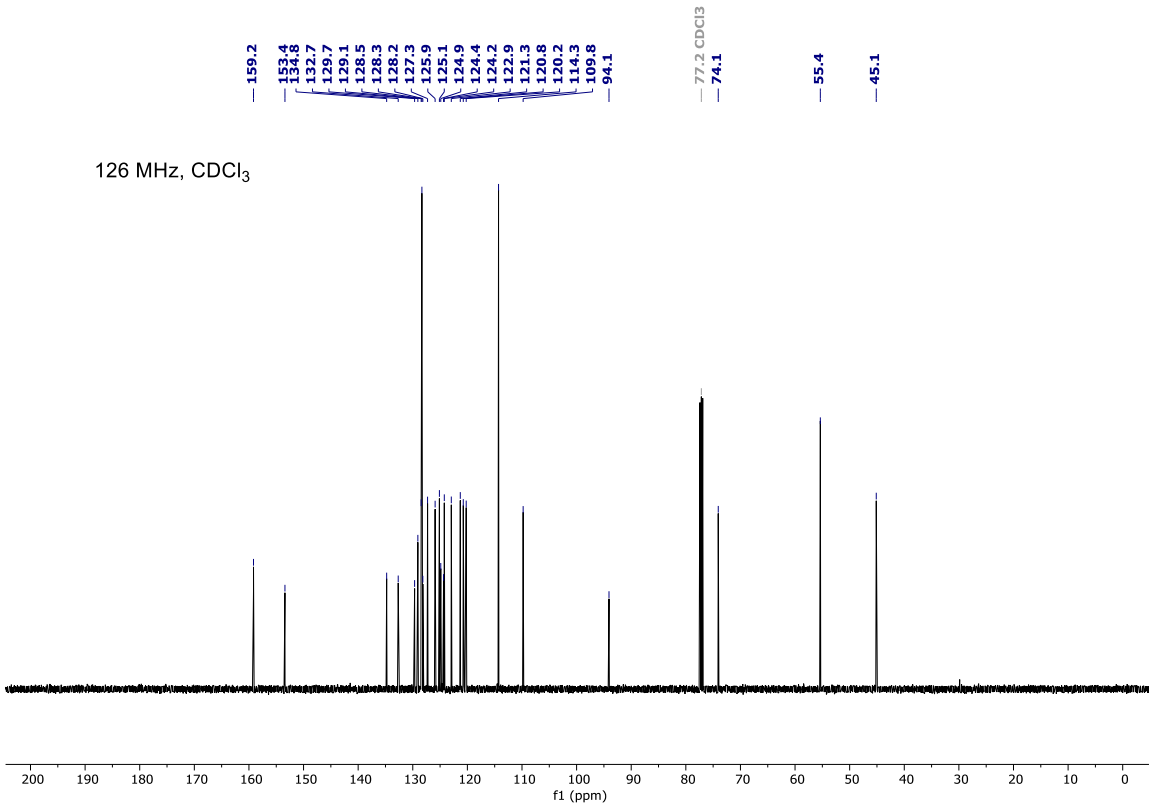

126 MHz, CDCl3
f1 (ppm)

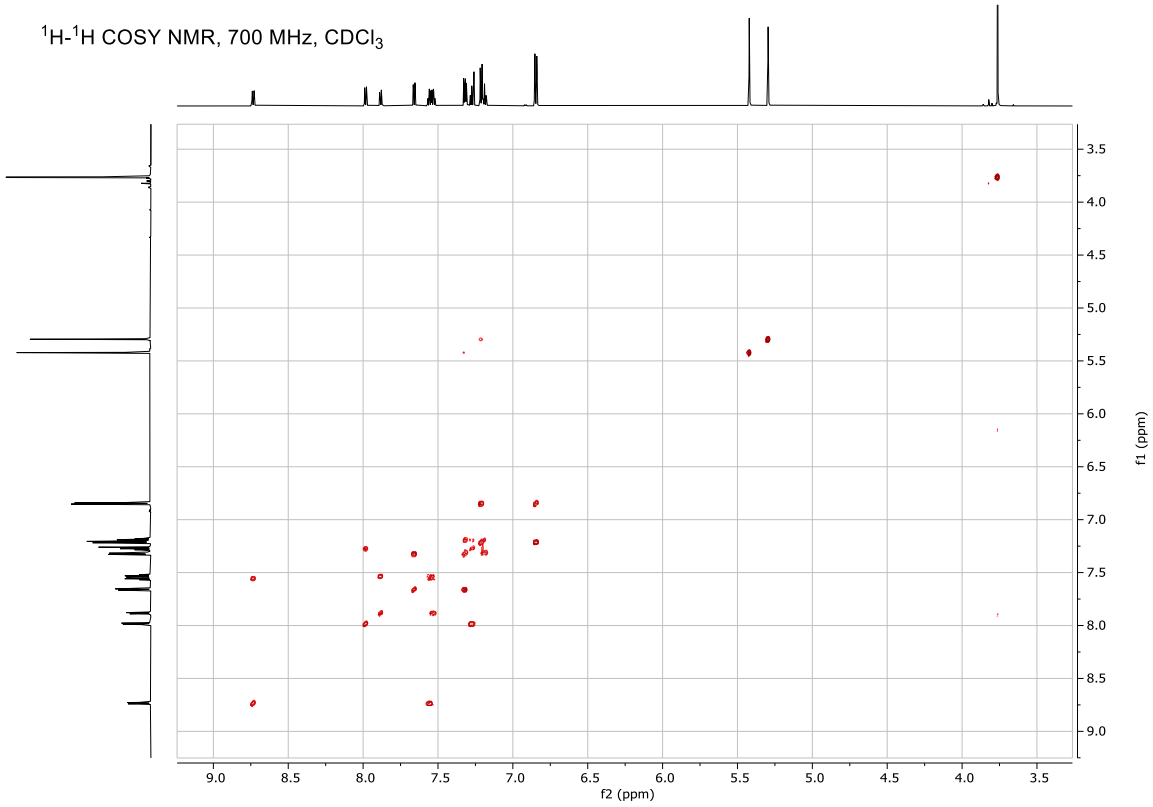

6.85
6.85
6.85
6.83
6.83
6.82
6.82
6.79
6.78
6.77
6.77
6.09
6.09
6.08
6.07
6.07
6.06
6.05
H^a
H^b
O
N
MeO
H^a
H^b
2.10
1.04
1.00
6.85 6.80 6.75 6.70 6.65 6.60 6.55 6.50 6.45 6.40 6.35 6.30 6.25 6.20 6.15 6.10 6.05 6.00 5.95 5.90 5.85
f1 (ppm)

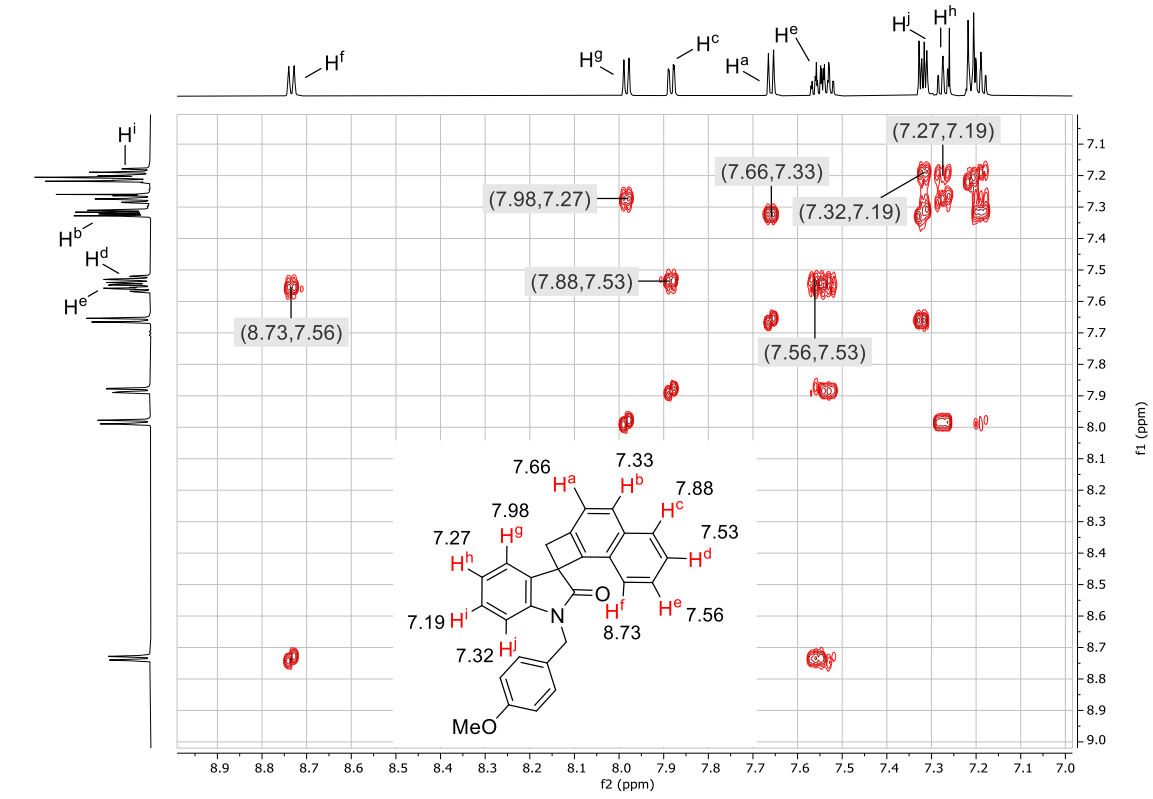

3.37
3.36
3.35
3.33
3.33
3.32
2.40
2.38
2.36
2.35
H^c
H^d
O
N
MeO
H^c or H^d
H^c or H^d
0.99
1.00
3.55 3.50 3.45 3.40 3.35 3.30 3.25 3.20 3.15 3.10 3.05 3.00 2.95 2.90 2.85 2.80 2.75 2.70 2.65 2.60 2.55 2.50 2.45 2.40 2.35 2.30 2.25 2.20
f1 (ppm)

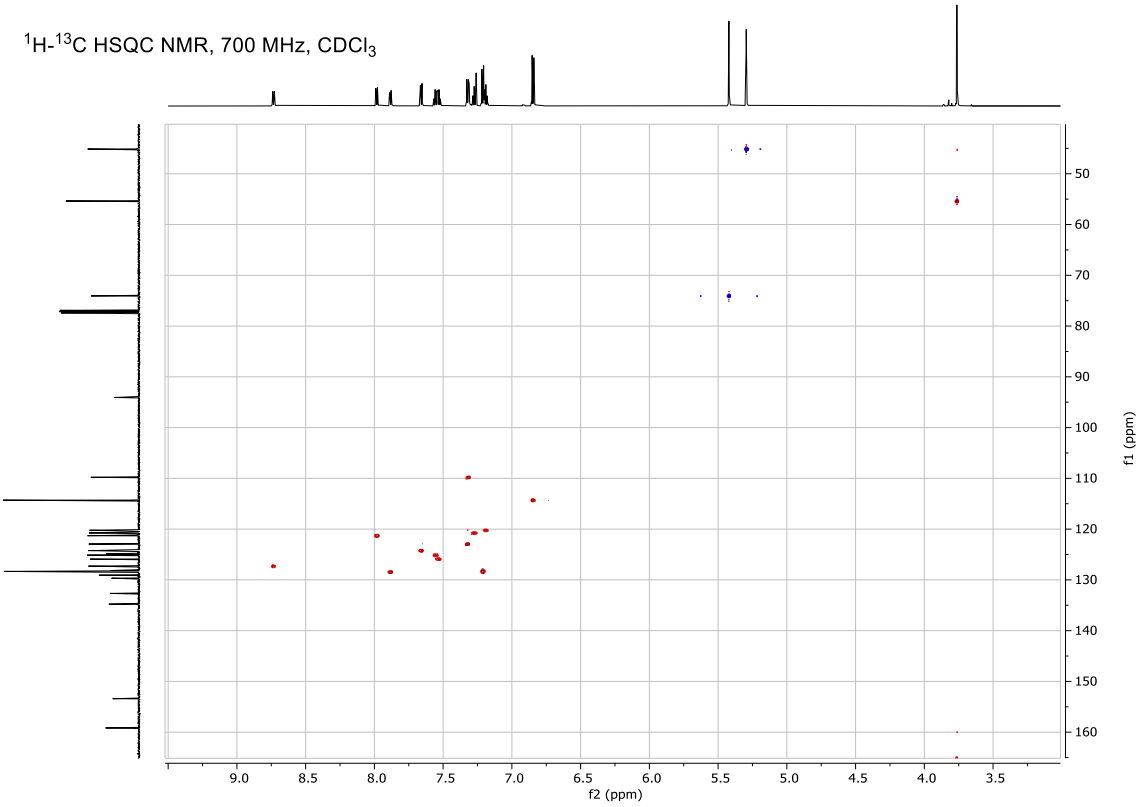

4.12
4.08
3.84
3.81
3.74
3.71
H^I
H^II
O
N
MeO
H^I or H^II
H^I or H^II
1.04
2.94
3.02
1.02
4.40 4.35 4.30 4.25 4.20 4.15 4.10 4.05 4.00 3.95 3.90 3.85 3.80 3.75 3.70 3.65 3.60 3.55 3.50
f1 (ppm)

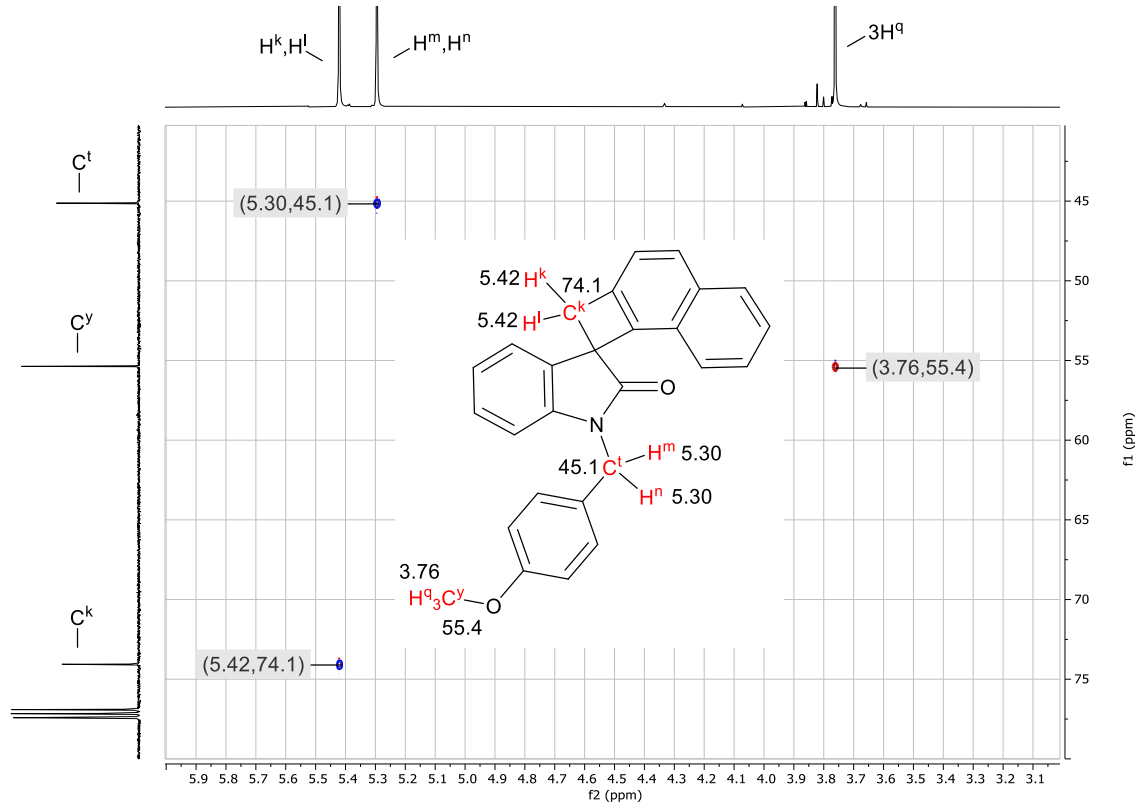

8.74
8.73
7.99
7.98
7.89
7.89
7.88
7.88
7.67
7.65
7.57
7.57
7.56
7.56
7.56
7.55
7.55
7.54
7.54
7.53
7.53
7.53
7.52
7.52
7.33
7.32
7.32
7.31
7.29
7.28
7.28
7.27
7.27
7.26
7.26
7.26 CDCl3
7.22
7.21
7.20
7.20
7.19
7.19
7.19
7.18
7.18
6.85
6.84
5.42
5.30
3.76
O
N
MeO
B
700 MHz, CDCl3
1.00
1.01
1.02
1.03
0.97
1.05
2.01
1.02
1.89
1.17
2.06
1.98
1.99
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

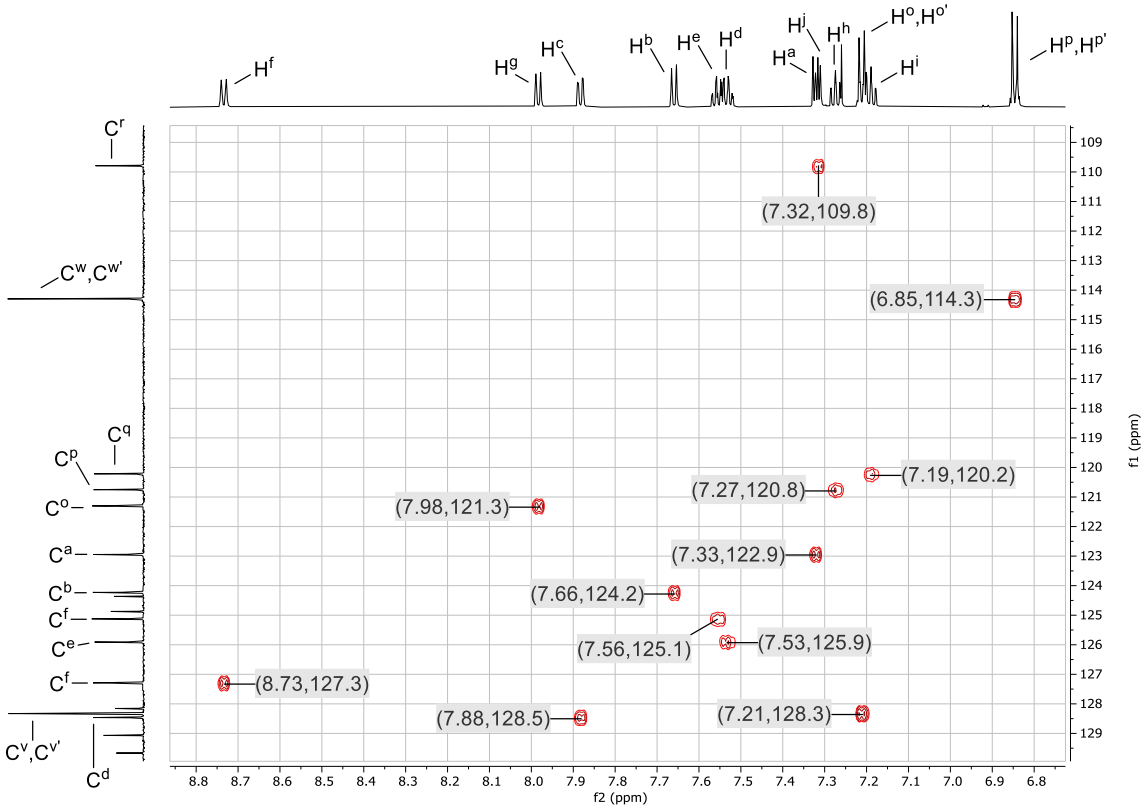

159.2
153.4
134.8
132.7
129.7
129.1
128.5
128.3
128.2
127.3
125.9
125.1
124.9
124.4
124.2
122.9
121.3
120.8
120.2
114.3
109.8
94.1
77.2 CDCl3
74.1
55.4
45.1
126 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

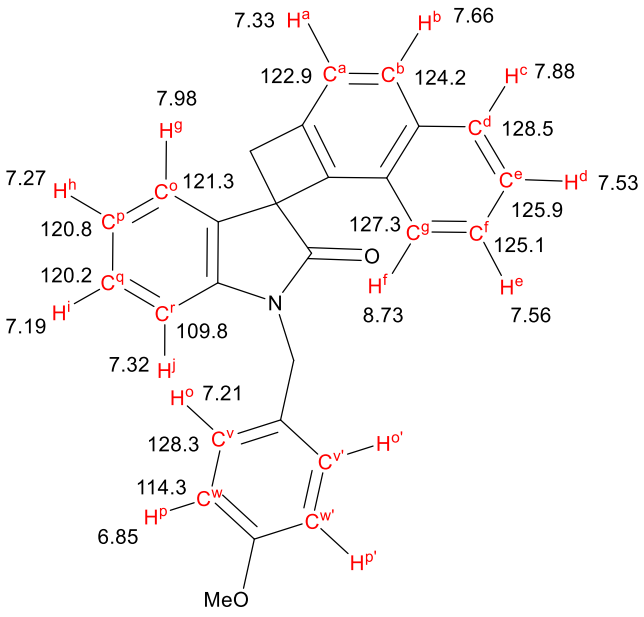

^{1}H-^{1}H COSY NMR, 700 MHz, CDCl$_3$
f2 (ppm)
f1 (ppm)

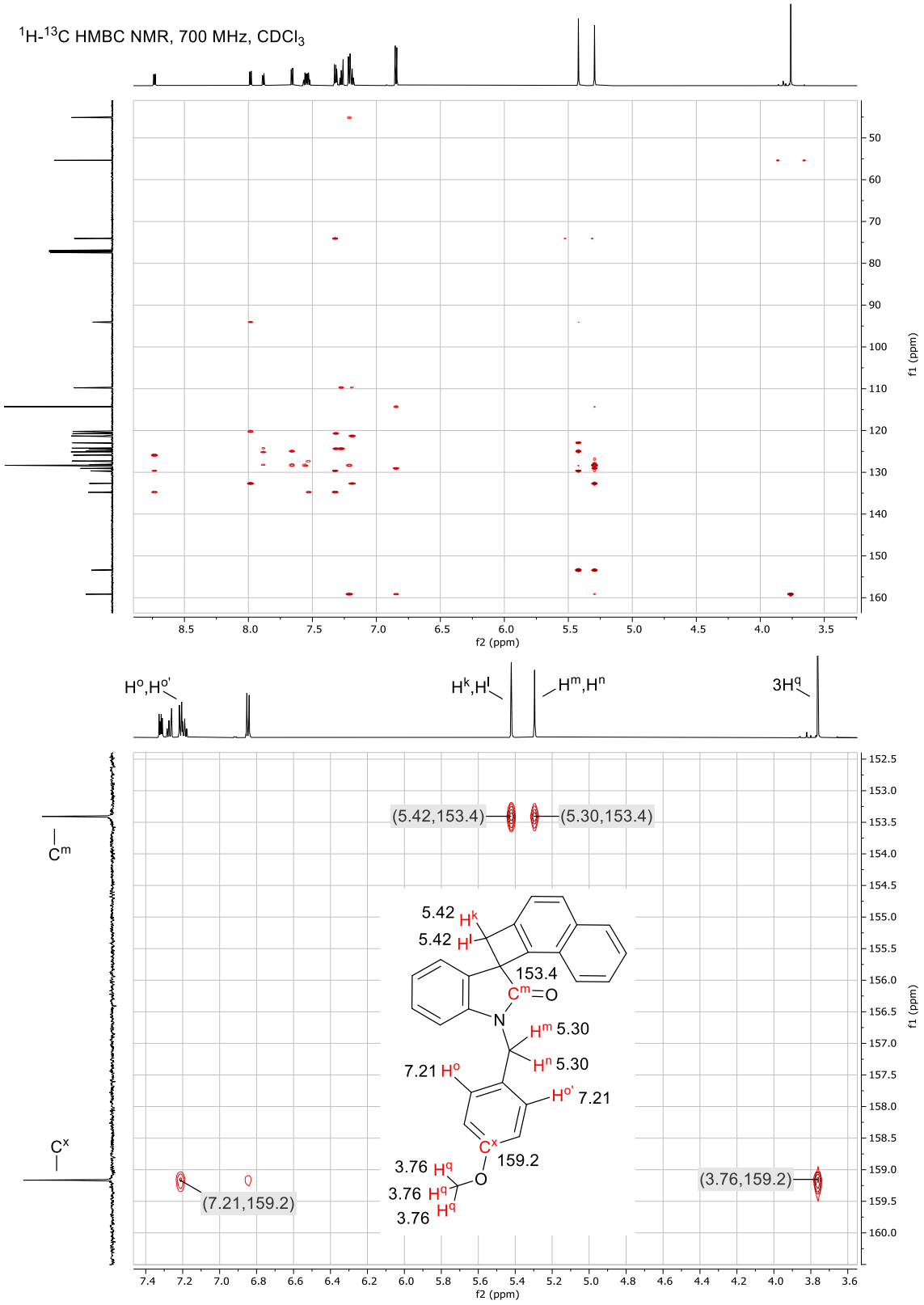

(7.27,7.19)
(7.66,7.33)
(7.98,7.27)
(7.32,7.19)
(7.88,7.53)
(8.73,7.56)
(7.56,7.53)
7.66
7.33
7.88
7.98
7.53
7.27
7.56
7.19
8.73
7.32
MeO
f2 (ppm)
f1 (ppm)

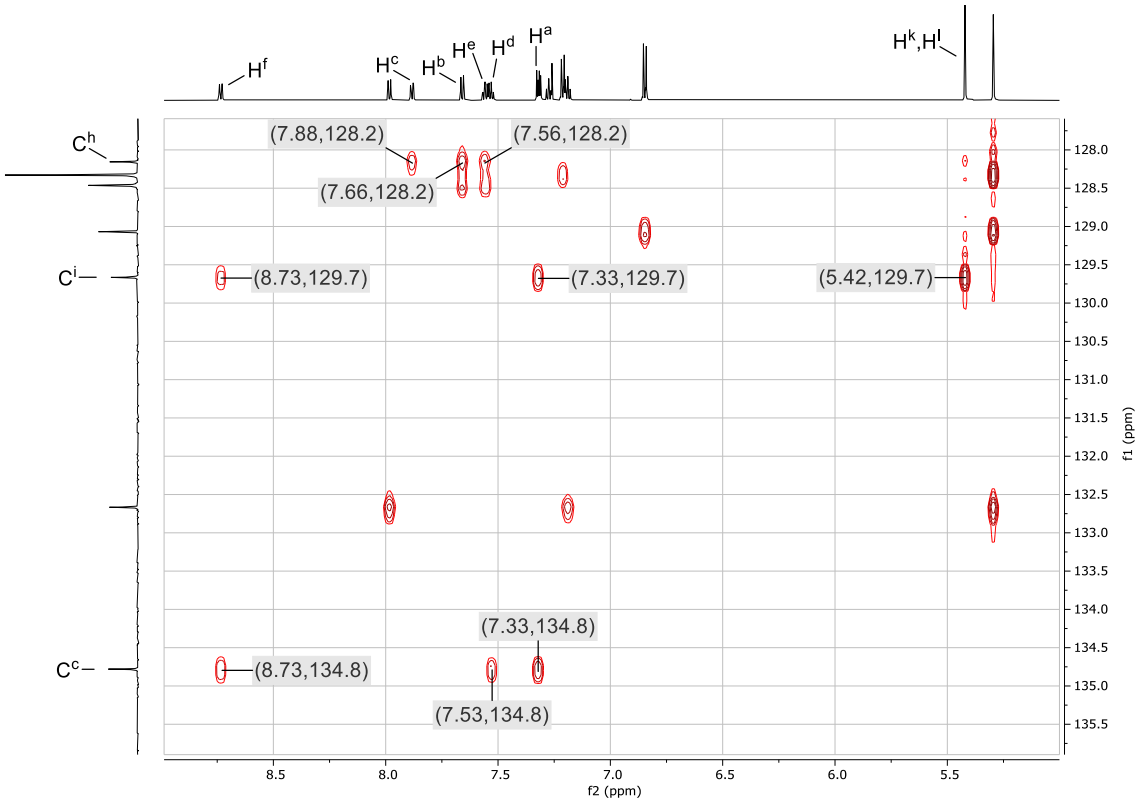

^{1}H-^{13}C HSQC NMR, 700 MHz, CDCl$_3$
f2 (ppm)
f1 (ppm)

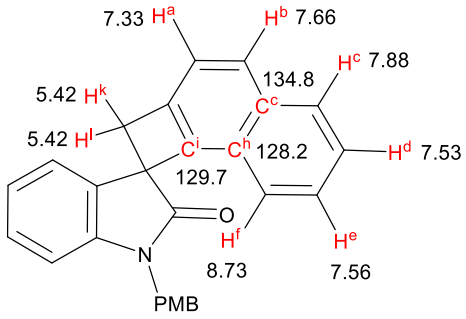

H^k,H^l
H^m,H^n
3H^q
C^t
C^y
C^k
(5.30,45.1)
(5.42,74.1)
(3.76,55.4)
5.42 H^k
74.1
C^k
5.42 H^l
O
N
45.1 C^t
H^m 5.30
H^n 5.30
3.76
H^q$_3$C^y
O
55.4
f2 (ppm)
f1 (ppm)

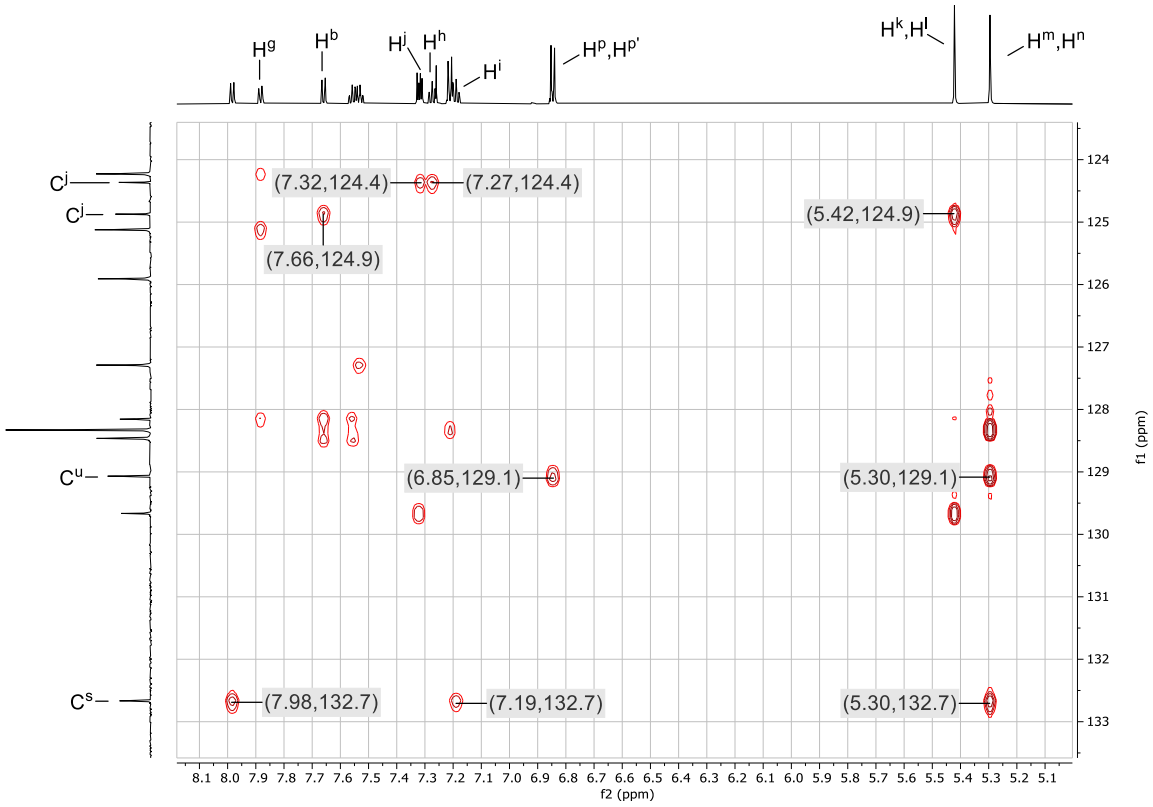

Hf
Hg
Hc
Hb
He
Hd
Ha
Hj
Hh
Ho,Ho'
Hi
Hp,Hp'
Cr
Cw,Cw'
Cp
Cq
Co
Ca
Cb
Cf
Ce
Cf
Cv,Cv'
Cd
(7.32,109.8)
(6.85,114.3)
(7.19,120.2)
(7.27,120.8)
(7.98,121.3)
(7.33,122.9)
(7.66,124.2)
(7.56,125.1)
(7.53,125.9)
(8.73,127.3)
(7.88,128.5)
(7.21,128.3)
f1 (ppm)
f2 (ppm)

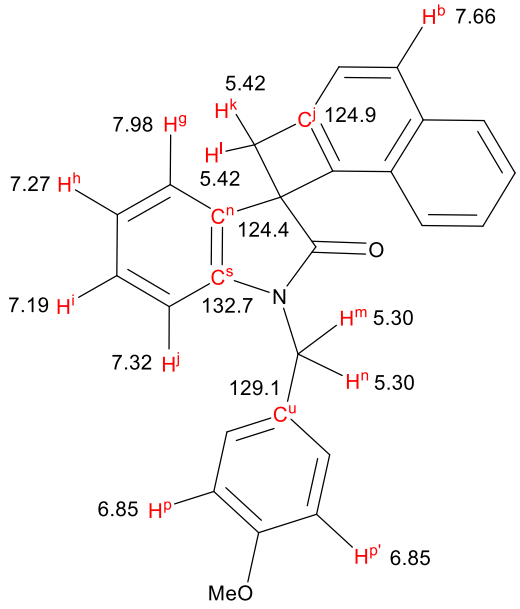

7.33 Ha
Hb 7.66
122.9 Ca
Cb 124.2
Hc 7.88
7.98
Hg
Cd 128.5
7.27 Hh
Co 121.3
Ce
Hd 7.53
120.8 Cp
125.9
127.3 Cg
Cf
125.1
O
120.2 Cq
Hf
He
Cr
N
8.73
7.56
7.19 Hi
109.8
7.32 Hj
Ho 7.21
128.3 Cv
Cv'
Ho'
114.3 Cw
Hp
Cw'
6.85
Hp'
MeO

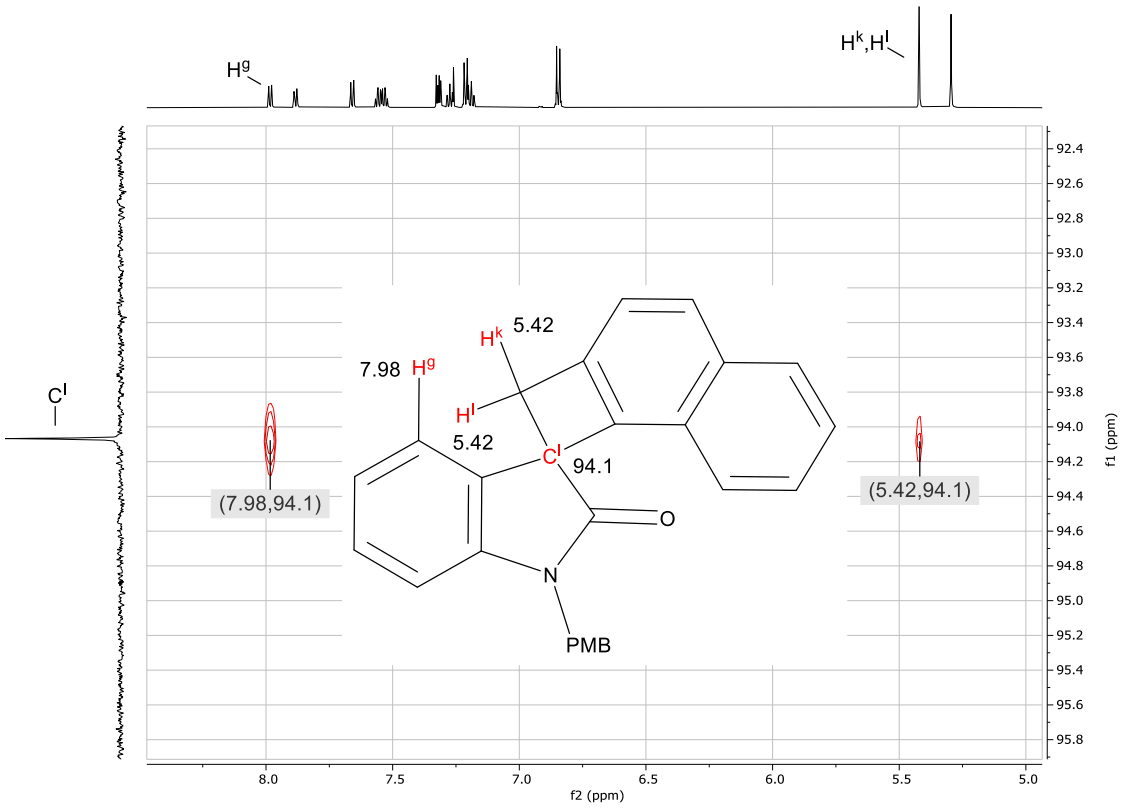

^{1}H-^{13}C HMBC NMR, 700 MHz, CDCl$_3$
f2 (ppm)
f1 (ppm)
H^{o},H$^{o'}$
H^{k},H^{l}
H^{m},H^{n}
3H^{q}
C^{m}
C^{x}
(5.42,153.4)
(5.30,153.4)
(7.21,159.2)
(3.76,159.2)
5.42 H^{k}
5.42 H^{l}
153.4
C^{m}=O
N
H^{m} 5.30
H^{n} 5.30
7.21 H^{o}
H$^{o'}$ 7.21
C^{x}
159.2
3.76 H^{q}
3.76 H^{q}
3.76 H^{q}
O

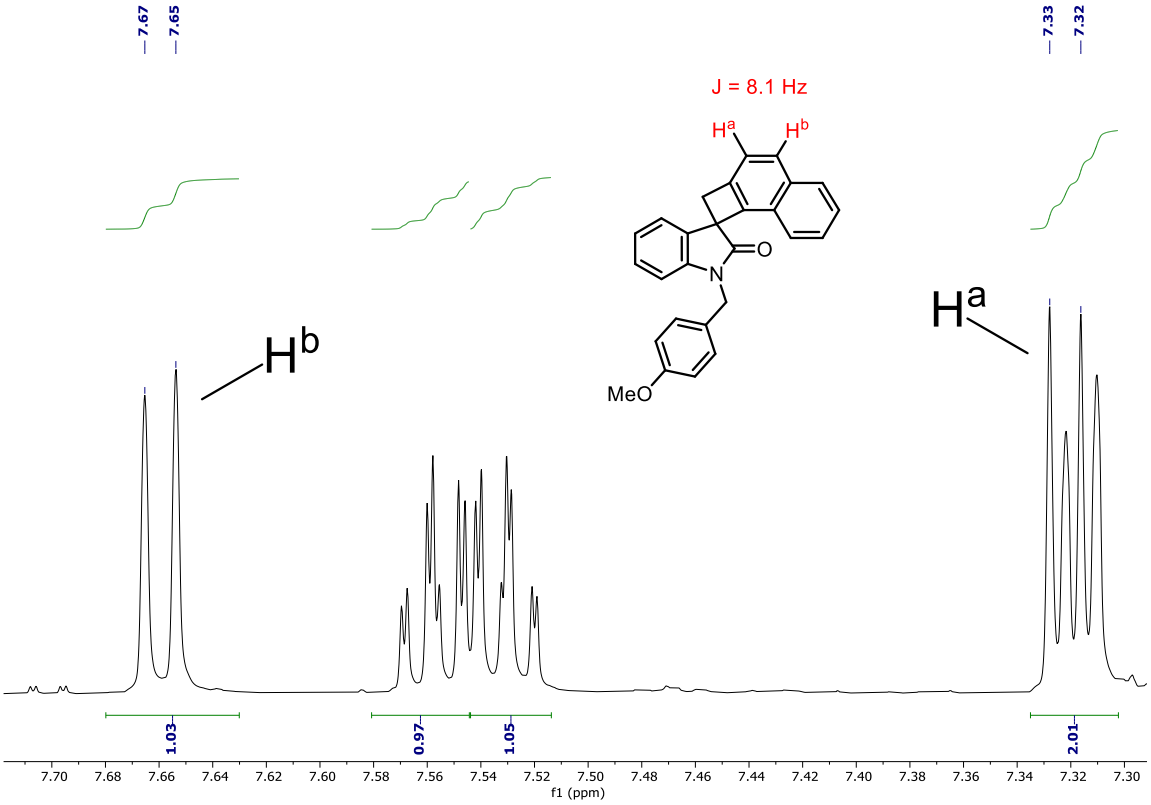

H^f
H^c
H^b
H^e
H^d
H^a
H^k,H^l
C^h
C^i
C^c
(7.88,128.2)
(7.56,128.2)
(7.66,128.2)
(8.73,129.7)
(7.33,129.7)
(5.42,129.7)
(7.33,134.8)
(8.73,134.8)
(7.53,134.8)
f2 (ppm)
f1 (ppm)

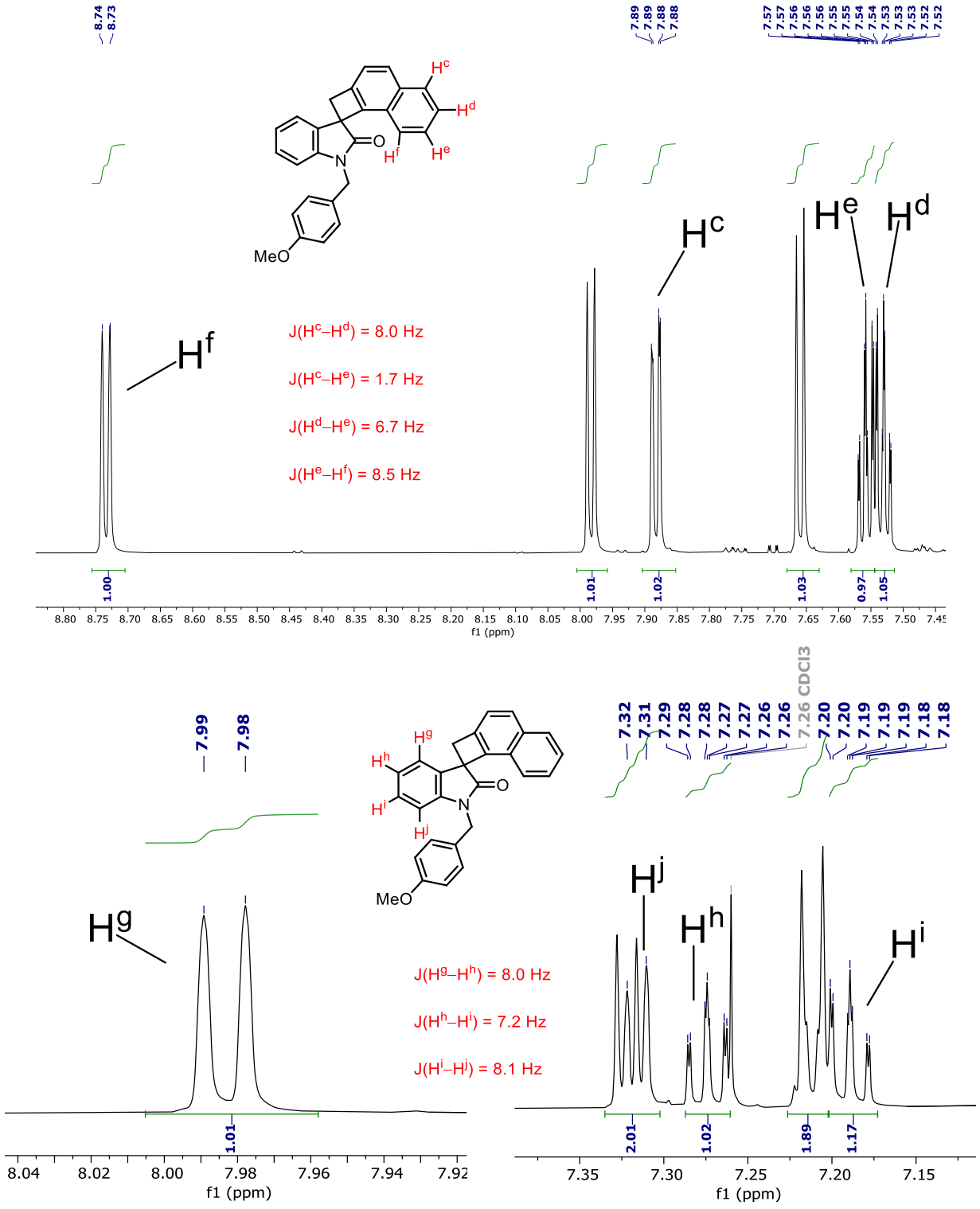

7.33 H^a
H^b 7.66
H^c 7.88
134.8
C^c
5.42 H^k
5.42 H^l
C^i
C^h 128.2
H^d 7.53
129.7
O
H^f
H^e
8.73
7.56
N
PMB


Hg
Hb
Hj
Hh
Hi
Hp,Hp'
Hk,Hl
Hm,Hn
Cj
Cj
Cu
Cs
(7.32,124.4)
(7.27,124.4)
(7.66,124.9)
(5.42,124.9)
(6.85,129.1)
(5.30,129.1)
(7.98,132.7)
(7.19,132.7)
(5.30,132.7)
f1 (ppm)
f2 (ppm)


Hb 7.66
5.42
Hk
Cj 124.9
7.98 Hg
Hl
5.42
7.27 Hh
Cn
124.4
O
Cs
N
7.19 Hi
132.7
Hm 5.30
7.32 Hj
Hn 5.30
129.1
Cu
6.85 Hp
Hp' 6.85
MeO


H^g
H^k,H^l
C^l
(7.98,94.1)
(5.42,94.1)
7.98 H^g
H^k 5.42
H^l
5.42
C^l
94.1
O
N
PMB
f2 (ppm)
f1 (ppm)


7.67
7.65
7.33
7.32
J = 8.1 Hz
H^a
H^b
O
N
MeO
H^b
H^a
1.03
0.97
1.05
2.01
f1 (ppm)


8.74
8.73
7.89
7.89
7.88
7.88
7.57
7.57
7.56
7.56
7.56
7.55
7.55
7.54
7.54
7.53
7.53
7.53
7.52
7.52
Hc
Hd
He
Hf
O
N
MeO
Hf
Hc
He
Hd
J(Hc–Hd) = 8.0 Hz
J(Hc–He) = 1.7 Hz
J(Hd–He) = 6.7 Hz
J(He–Hf) = 8.5 Hz
1.00
1.01
1.02
1.03
0.97
1.05
8.80 8.75 8.70 8.65 8.60 8.55 8.50 8.45 8.40 8.35 8.30 8.25 8.20 8.15 8.10 8.05 8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45
f1 (ppm)
7.99
7.98
7.32
7.31
7.29
7.28
7.28
7.27
7.27
7.26
7.26
7.26 CDCl3
7.20
7.20
7.19
7.19
7.19
7.18
7.18
Hg
Hh
Hi
Hj
O
N
MeO
Hg
Hj
Hh
Hi
J(Hg–Hh) = 8.0 Hz
J(Hh–Hi) = 7.2 Hz
J(Hi–Hj) = 8.1 Hz
1.01
2.01
1.02
1.89
1.17
8.04 8.02 8.00 7.98 7.96 7.94 7.92
f1 (ppm)
7.35 7.30 7.25 7.20 7.15
f1 (ppm)

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