Supporting Information

Alkenylation of the Unactivated Alkanes: Synthesis of *Z*-alkenes via Dual Co-TBADT Catalysis

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1. General considerations

Reagents: Commercially available chemicals were used without any further purification. $CoCl_2 \cdot 6H_2O$ (product code: 31277), Sodium tungstate dihydrate (product code: 223336) were purchased from Sigma-Aldrich (Merck). 4,4′-dimethoxy-2,2′-bipyridine (product code: BD18852) was purchased from BLD pharma. Tetrabutylammonium decatungstate (TBADT) was prepared according to the literature procedure.[1]

Solvents: Acetonitrile (CH_3CN), purchased from Spectrochem, was stirred in CaH_2 for 2 h, refluxed and distilled under air and moisture free condition and degassed with nitrogen flow for 1 h. All the dry solvents were degassed for a minimum of 1 h using a nitrogen balloon and were stored over 4 Å molecular sieves.

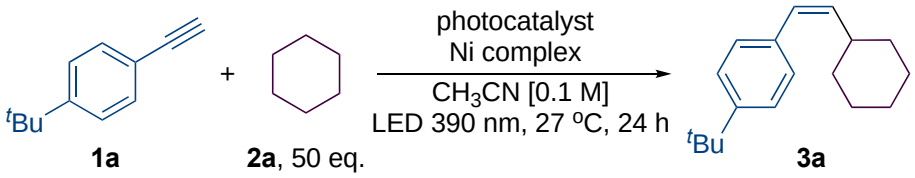
Analytical methods: NMR spectra were recorded using 500 MHz Bruker avance spectrometer at 23 °C, with TMS as an internal standard and ^1H and ^{13}C spectra were reported in δ (ppm) with respect to reference $CDCl_3$, 7.26 ppm for ^1H and 77.06 ppm for ^{13}C. $CDCl_3$ from Sigma Aldrich (cat. No: 151823, 99.8 atom % D) was used as a solvent for most of the NMR analysis. All NMR spectra were recorded on Bruker 500 MHz. Reactions were monitored by GC-Agilent 7890B series (mass detector G7077B series, EI-70 eV, quadrupole ion detector) with silica capillary column (cat. No. 19091S-433UI, HP-5MSUI, with dimensions 30 m x 0.25 mm), GC-Agilent7890B series (with silica capillary column (19091J0-413, HP-5, with dimensions 30 m x 0.32 mm) and thin layer chromatography (Merck, Cat. No. 1.05554.0007, aluminium sheets with TLC Silica gel 60 F_{254} coating). TLC was analysed using shortwave UV-254 nm. GC yields were taken by first calibrating the authentic sample (isolated one) with an internal standard and then analysing the yield using the calibrated values to find the relative yield of the product to that of the internal standard. IR Spectra were recorded on FT-IR Alpha E (Bruker) spectrometer. Solid and liquid compounds were measured by neat condition. The wave numbers are given in [cm^{-1}]. Thermo Scientific Q-Exactive benchtop HRMS (Quadrupole-Orbitrap) was used for the high-resolution mass analysis. The column chromatography was performed using silica gel 230-400 mesh (purchased from FINAR, P. Code: 11457S5K25). Each reaction tube was kept 3 cm away from 3 x 30 W LED [Chanzon High Power LED 385-390 nm, without filter] and temperature was maintained at 27 °C effectively using cooling fans. Unless otherwise mentioned, all the elevated temperature reactions were conducted using heating blocks.

2. Optimization of reaction condition

General procedure A:

Oven dried 10 mL screw-capped culture tubes containing a stirring bar were introduced in an argon-filled glovebox where metal complex (11.2 µmol) and ligand (if any, 11.2 µmol) were carefully weighed and added. The tubes were taken out of the glovebox, TBADT (18 µmol, 59 mg) was added under nitrogen flow. Tubes were capped with rubber septum, evacuated (< 1 mbar) and backfilled with nitrogen three times. Solvent was added to the mixture followed by 1-(tert-butyl)-4-ethynylbenzene (0.15 mmol, 23.7 mg, 27 µL) and cyclohexane (0.8 mL). Rubber septum was replaced with screw cap and irradiated with 390 nm LED (30 Watt). Then, internal standard (0.15 mmol) was added into the tube and analysed using GC. (Note: metal complex and ligand were stirred for 10 minutes with 0.5 mL of CH_3CN before adding other reagents)

Table S1. Preliminary screening with nickel complex:

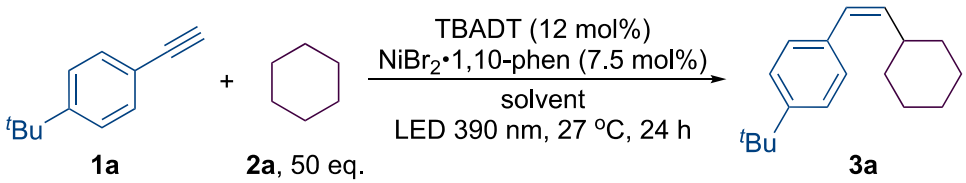


1a **2a**, 50 eq. **3a**

entry	condition	**1a** %	**3a**[a]	***Z*/*E*[b]**
1	5 mol% of TBADT, 10 mol% of $NiCl_2$·bpy	n.d.	44.7	77:23
2	25 eq. of **2a**, 5 mol% of TBADT, 10 mol% of $NiCl_2$·bpy	n.d.	43.5	73:27
3	12 mol% of TBADT, 7.5 mol% of $NiCl_2$·bpy	n.d.	64.7, *31%*[b]	*70:30*
4	12 mol% of TBADT, 7.5 mol% of $NiCl_2$·phen	n.d.	88.1	80:20
5	12 mol% of TBADT, 7.5 mol% of $NiBr_2$·bpy	n.d.	21.9	79:21
6	12 mol% of TBADT, 7.5 mol% of $NiCl_2$·dtbpy	n.d.	83.3, *37%*[b]	*79:21*
7	12 mol% of TBADT, 7.5 mol% of $NiCl_2(PPh_3)_2$	n.d.	n.d.	-
8	12 mol% of TBADT, 7.5 mol% of $NiCl_2$·$(PCy_3)_2$	n.d.	n.d.	-
9	12 mol% of TBADT, 7.5 mol% of $NiCl_2$·dppp	n.d.	n.d.	-
10	12 mol% of TBADT, 7.5 mol% of $NiBr_2$·phen	n.d.	93.3, *40%*[b]	80:20
11	0 mol% of TBADT, 7.5 mol% of $NiBr_2$·phen	99[c]	n.d.	-
12	30 mol% of benzophenone, 7.5 mol% of $NiBr_2$·phen	n.d.	11.2	only *Z*
13	3 mol% of Ir-PC, 7.5 mol% of $NiBr_2$·phen	n.d.	n.d.	-
14	3 mol% of 4czIPN, 7.5 mol% of $NiBr_2$·phen	29[c]	n.d.	-
15[d]	(3+3+3+3) mol% of TBADT, 7.5 mol% of $NiBr_2$·phen	52[c]	83.5	80:20
16	Same as entry 10, with 0.1 M CH_3CN : PhH (4:1)	16[c]	108, *45%*[b]	82:18

[a]GC area w.r.t. internal standard; [b]Yield and *E/Z* ratio for **3a** were calculated based on crude ^1H NMR using 1,3,5-trimethoxybenzene as internal standard; [c]Leftover starting material was calculated using GC calibration; [d]portion wise addition of PC in 6 h intervals; Ir-PC – $Ir[dF(CF_3)ppy]_2(dtbpy)PF_6$; n.d. – not detected.

Table S2. Solvent screening with nickel complex:

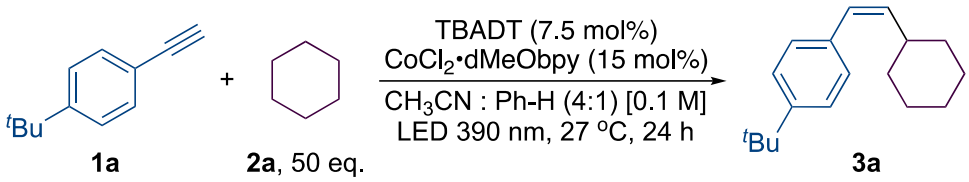


1a **2a**, 50 eq. **3a**

entry	condition	**1a** %[a]	**3a** %[b]	***Z*/*E***
1	0.1 M CH_3CN : PhH (4:1)	16	45	80:20
2	0.1 M CH_3CN : $PhCH_3$ (4:1)	11	25	70:30
3	0.1 M CH_3CN : ethyl acetate (4:1)	19	39, *37*[c]	77:23
4	0.1 M DMSO	71	n.d.	-
5	0.1 M acetone	88	6	66:34
6	0.1 M CH_3CN : acetone (4:1)	7	40	70:30
7	0.1 M CH_3CN : ethyl acetate (3:1)	19	41	75:25
8	0.1 M CH_3CN : DMA (4:1)	45	<5	only *Z*
9	0.1 M CH_3CN : DCM (4:1)	17	36	34:66
10	0.1 M CH_3CN : DCM (1:1)	30	41	26:74
11	0.1 M CH_3CN : DCM (1:4)	70	19	1:99
12	0.1 M CH_3CN : PhH (1:4)	76	<5	55:45

[a]Leftover starting material was calculated using GC; [b]Yields for **3a** were calculated based on crude ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard; [c]Isolated yields; n.d. – not detected;

Table S3. Reaction concentration and control experiments:

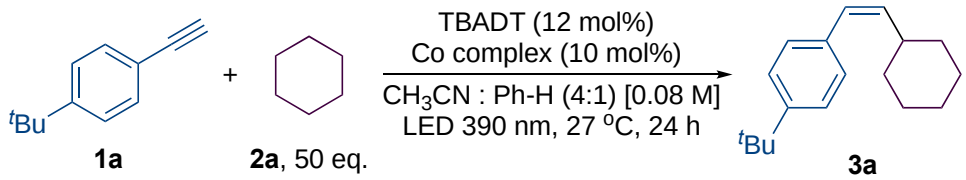


1a **2a**, 50 eq. **3a**

entry	deviation from above	**1a** %[a]	**3a** %[b]	***Z*/*E***
1	0.05 M CH_3CN : PhH (4:1)	23	79	87:13
2	0.08 M CH_3CN : PhH (4:1)	6	93	86:14
3	0.1 M CH_3CN : PhH (4:1)	14	80	85:15
4[c]	Acetone (0.08 M)	88	5	75:25
5[c]	DMSO (0.08 M)	91	traces	-
6	5 eq. of CyH	44	13	-
7	10 eq. of CyH	39	22	80:20
8	25 eq. of CyH	42	37	90:10
9	without TBADT	99	n.d.	-
10	without $CoCl_2$·dMeObpy	92	n.d.	-
11	365 nm light source	<5	78	85:15
12	410 nm light source	34	51	90:10
13[c]	30 mol% of Anthracene added as sensitizer	32	55	91:9
14[c]	20 mol% of Benzophenone added as sensitizer	38	43	85:15
15[d]	Reaction setup **under air**	15	51	89:11
16[d]	10 eq. of **H_2O** added to the reaction mixture	23	55	93:7
17[d]	20 eq. of **H_2O** added to the reaction mixture	15	47	85:15

[a]Leftover starting material was calculated using GC; [b]Yields for **3a** were calculated based on crude ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard; [c]5 mol% of PC, 10 mol% of Co complex and 0.08 M solvent; [d](4+2) mol% of PC, (16+4) mol% of $CoCl_2$·dMeObpy and 0.08 M solvent (48 h); n.d. – not detected;

Table S4. Screening with various cobalt complex:

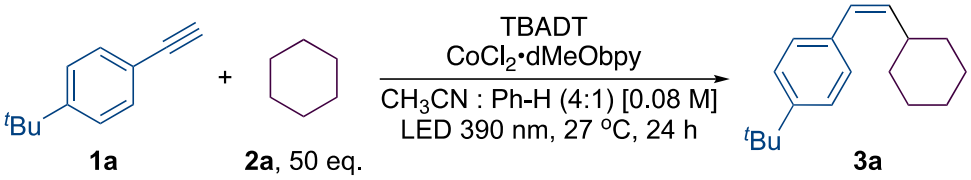


1a **2a**, 50 eq. **3a**

entry	condition	**1a** %[a]	**3a** %[b]	***Z*/*E***
1	$CoBr_2$ and phen	30	63	72:28
2	$CoCl_2$ and phen	25	60	80:20
3	CoI_2 and phen	43	40	75:25
4	$CoBr_2$·phen	20	69	74:26
5	$CoCl_2$·phen	29	67	78:22
6[c]	$CoCl_2$·phen	24	57	82:18
7	$CoCl_2$ and tMephen	29	48	81:19
8	$CoCl_2$ and phen	25	60	80:20
9	$CoCl_2$ and dMebpy	23	61	79:20
10	$CoCl_2$ and dMeObpy	15	74	84:16
11	$CoCl_2$ and dtbpy	18	68	87:13
12	$CoCl_2$ and 20 mol% of dmap	19	32	82:18

[a]Leftover starting material was calculated using GC; [b]Yields for **3a** were calculated based on crude ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard; [b]Isolated yields; [c]7.5 mol% of cobalt complex; bpy – 2,2′-bipyridine; dMeObpy – 4,4′-dimethoxy-2,2′-bipyridine; dMebpy – 4,4′-dimethyl-2,2′-bipyridine; dtbpy – 4,4 -Di-tert-butyl-2,2 -dipyridyl; tMephen – 3,4,7,8-Tetramethyl-1,10-phenanthroline

Table S5. Optimization for catalyst loading:



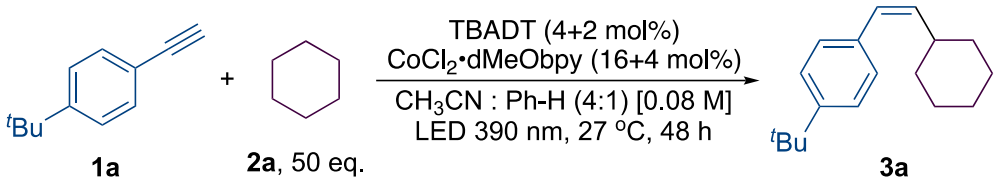
1a **2a**, 50 eq. **3a**

entry	condition	PC/Co	**1a** %[a]	**3a** %[b]	***Z*/*E***
1	3 mol% of PC and 10 mol% of $CoCl_2$·dMeObpy	1:3.3	26	67	93:7
2	5 mol% of PC and 5 mol% of $CoCl_2$·dMeObpy	1:1	22	58	80:20
3	5 mol% of PC and 10 mol% of $CoCl_2$·dMeObpy	1:2	27	71	90:10
4	5 mol% of PC and 15 mol% of $CoCl_2$·dMeObpy	1:3	28	66	94:6
5[c]	5 mol% of PC and 15 mol% of $CoCl_2$·dMeObpy	1:3	20	77, *71*[d]	94:6
6[e]	5 mol% of PC and 15 mol% of $CoCl_2$·dMeObpy	1:3	9	80	91:9
7	5 mol% of PC and 20 mol% of $CoCl_2$·dMeObpy	1:4	25	73	95:5
8	7.5 mol% of PC and 15 mol% of $CoCl_2$·dMeObpy	1:2	6	93	86:14
9	7.5 mol% of PC and 22.5 mol% of $CoCl_2$·dMeObpy	1:3	6	87	92:8
10[c]	7.5 mol% of PC and 22.5 mol% of $CoCl_2$·dMeObpy	1:3	traces	83	91:9
11[f]	(4+2) mol% of PC and (16+4) mol% of $CoCl_2$·dMeObpy	1:3.3	<5	87, *83*[d]	93:7
12	10 mol% of PC and 10 mol% of $CoCl_2$·dMeObpy	1:1	traces	89	80:20

[a]Leftover starting material was calculated using GC; [b]Yields for **3a** were calculated based on crude ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard; [c]reaction time 48 h; [d]Isolated yields; [e]reaction time 60 h; [f]portion wise addition of catalysts in 24 h interval – reaction time 48 h; n.d. – not detected;

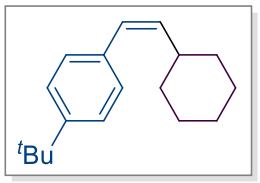
3. Substrate scope:

General procedure B:



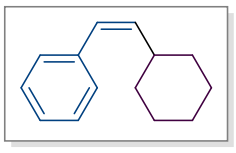
Oven dried 10 mL screw-capped culture tube containing a stirring bar were introduced in an argon-filled glovebox where metal complex was carefully weighed and added. The tube was taken out of the glovebox, TBADT was added under nitrogen flow. Tube was capped with rubber septum, evacuated (< 1 mbar) and backfilled with nitrogen three times. Solvent was added to the mixture followed by 1-(tert-butyl)-4-ethynylbenzene and cyclohexane. Rubber septum was replaced with screw cap and irradiated with 390 nm LED. After 24 h, remaining portion of photocatalyst and cobalt complex were added under nitrogen flow and irradiated again. Then, the volatiles were removed under reduced pressure, diluted with ethyl acetate and filtered through a pad of silica. After removal of solvent, crude material was purified using column chromatography.

(Z)-1-(tert-butyl)-4-(2-cyclohexylvinyl)benzene 3a:



The title product was prepared using 1-(tert-butyl)-4-ethynylbenzene (0.5 mmol, 90 µL) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of *E* and *Z* isomers using silica column chromatography with 83% (100 mg) yield. (Solvent gradient: 1% ethyl acetate in petroleum ether; colourless oil). **^{1}H NMR (500 MHz, $CDCl_3$) (Z/E mixture 93:7)** δ 7.37 (d, *J* = 7.9 Hz, 1.75H, ***Z***), 7.35 – 7.27 (m, 0.5H, ***E***), 7.23 (d, *J* = 8.0 Hz, 1.75H, ***Z***+***E***), 6.37 – 6.25 (m, 1H, ***Z***+***E***), 6.15 (dd, *J* = 16.0, 7.0 Hz, 0.07H, ***E***), 5.46 (dd, *J* = 11.7, 10.0 Hz, 0.93H, ***Z***), 2.69 – 2.59 (m, 0.93H, ***Z***), 2.11 – 2.14 (m, 0.07H, ***E***), 1.80 – 1.66 (m, 5H, ***Z***+***E***), 1.35 (s, 9H, ***Z***+***E***), 1.31 – 1.13 (m, 5H, ***Z***+***E***). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 149.4, 138.5, 135.1, 128.4, 126.6, 125.7, 125.4, 125.2, 37.0, 34.5, 33.4, 33.1, 31.4, 26.1, 25.8. **FT-IR (neat, cm^{-1}):** 2937, 2863, 1455, 1274, 845, 575. **EI-MS (m/z):** [$C_{18}H_{26}$] $[M]^+$ 242.2. Literature[2]

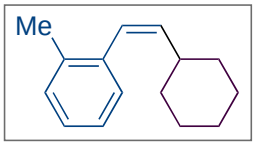
(Z)-(2-cyclohexylvinyl)benzene 3b:



The title product was prepared using phenylacetylene (0.5 mmol, 55 µL) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of *E* and *Z* isomers using silica column chromatography with 81% (75 mg) yield. (Solvent gradient: 1% ethyl acetate in petroleum ether; colourless oil). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 92:8)** δ 7.36 – 7.21 (m, 5H, ***Z***+***E***), 6.32 (d, *J* = 11.8 Hz, 1H, ***Z***+***E***), 6.18 (dd, *J* = 16.0, 6.9 Hz, 0.08H, ***E***), 5.49 (dd, *J* = 11.7, 10.2 Hz, 0.92H, ***Z***), 2.59 (m, 0.92H, ***Z***), 2.16 – 2.11 (m, 0.08H, ***E***), 1.81

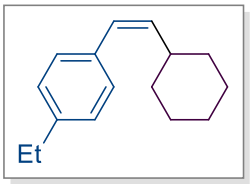
– 1.64 (m, 5H, ***Z***+***E***), 1.32 – 1.15 (m, 5H, ***Z***+***E***). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 139.0, 138.0, 128.6, 128.2, 126.9, 126.4, 36.9, 33.3, 26.1, 25.7. **FT-IR (neat, cm^{-1}):** 2938, 1449, 1281. **EI-MS (m/z):** $[C_{14}H_{18}]$ $[M]^+$ 186.1. Literature[3]

(Z)-1-(2-cyclohexylvinyl)-2-methylbenzene 3c:



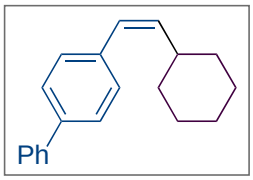
The title product was prepared using 2-ethynyltoluene (0.5 mmol, 64 µL) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of *E* and *Z* isomers (90:10) using silica column chromatography with 70% (70 mg) yield. (Solvent gradient: 1% ethyl acetate in petroleum ether; colourless oil). **^{1}H NMR (500 MHz, $CDCl_3$) (data for *Z*)** δ 7.16 (s, 4H), 6.30 (d, *J* = 11.6 Hz, 1H), 5.56 – 5.49 (m, 1H), 2.35 – 2.29 (m, 1H), 2.25 (s, 3H), 1.70 – 1.60 (m, 6H), 1.24 – 1.12 (m, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 138.8, 137.4, 136.2, 129.7, 128.9, 126.7, 126.0, 125.4, 36.8, 33.3, 26.1, 25.7, 20.0. **FT-IR (neat, cm^{-1}):** 2936, 2863, 1519, 1454, 825. **EI-MS (m/z):** $[C_{15}H_{20}]$ $[M]^+$ 200.1. Literature[4]

(Z)-1-(2-cyclohexylvinyl)-4-ethylbenzene 3d:



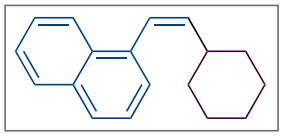
The title product was prepared using 1-ethyl-4-ethynylbenzene (0.5 mmol, 70 µL) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of *E* and *Z* isomers using silica column chromatography with 76% (81 mg) yield. (Solvent gradient: pure petroleum ether; colourless oil). **^{1}H NMR (500 MHz, $CDCl_3$) (data for *Z*/*E* mixture 93:7)** δ 7.21 (q, *J* = 8.2 Hz, 4H), 6.31 (m, 1H, ***Z***+***E***), 6.15 (dd, *J* = 16.1, 10.0 Hz, 0.07H, ***E***), 5.47 (dd, *J* = 11.7, 10.0 Hz, 0.93H, ***Z***), 2.74 – 2.57 (m, 3H), 1.81 – 1.66 (m, 5H), 1.34 – 1.17 (m, 8H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 142.5, 138.4, 135.4, 128.6, 127.7, 126.8, 37.0, 33.4, 28.6, 26.1, 25.8, 15.6. **FT-IR (neat, cm^{-1}):** 2940, 2864, 1456, 850. **HRMS (APCI-QUADRUPOLE-ORBITRAP) m/z:** $[M]^+$ Calcd for $[C_{16}H_{22}]$ 214.1716; Found 214.1716.

(Z)-4-(2-cyclohexylvinyl)-1,1'-biphenyl 3e:



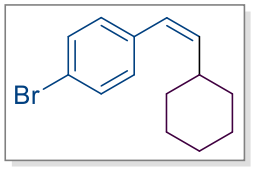
The title product was prepared using 4-ethynyl-1,1'-biphenyl (0.5 mmol, 89 mg) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of E and Z isomers using silica column chromatography with 80% (104.8 mg) yield. (Solvent gradient: 1% ethyl acetate in petroleum ether; colourless viscous oil). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 99:1)** δ 7.70 – 7.55 (m, 4H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 3H), 6.37 (d, *J* = 11.7 Hz, 1H), 5.55 (t, *J* = 11.8 Hz, 1H), 2.72 – 2.60 (m, 1H), 1.83 – 1.66 (m, 5H), 1.39 – 1.18 (m, 5H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 140.9, 139.3, 139.2, 137.0, 129.1, 128.8, 127.2, 127.0, 126.9, 126.4, 37.1, 33.3, 26.1, 25.7. **FT-IR (neat, cm^{-1}):** 2936, 1493, 1455, 854, 701. **EI-MS (m/z):** $[C_{20}H_{22}]$ $[M]^+$ 262.1. Literature.[5]

(Z)-1-(2-cyclohexylvinyl)naphthalene 3f:



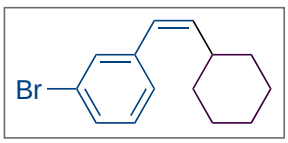
The title product was prepared using 1-ethynylnaphthalene (0.5 mmol, 76 mg) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of E and Z isomers using silica column chromatography with 62% (73 mg) yield. (Solvent gradient: 1% ethyl acetate in petroleum ether; colourless oil). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 71:29)** δ 8.14 (d, *J* = 8.1 Hz, 0.29H, ***E***), 8.07 – 8.00 (m, 0.71H, ***Z***), 7.91 – 7.83 (m, 1H, ***Z***+***E***), 7.81 – 7.71 (m, 1H, ***Z***+***E***), 7.59 – 7.41 (m, 3H, ***Z***+***E***), 7.34 (d, *J* = 7.0 Hz, 0.71H, ***Z***), 7.10 (d, *J* = 15.7 Hz, 0.29H, ***E***), 6.77 (d, *J* = 11.5 Hz, 0.71H, ***Z***), 6.21 (dd, *J* = 15.7, 6.9 Hz, 0.29H, ***E***), 5.77 (t, *J* = 10.8 Hz, 0.71H, ***Z***), 2.38 – 2.24 (m, 1H, ***Z***+***E***), 1.95 – 1.80 (m, 1H, ***Z***+***E***), 1.76 – 1.57 (m, 4H, ***Z***+***E***), 1.42 – 1.12 (m, 5H, ***Z***+***E***). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 140.4, 140.3, 135.9, 135.4, 133.7, 133.5, 132.1, 131.3, 128.5, 128.3, 127.2, 127.1, 126.1, 125.8, 125.7, 125.6, 125.4, 125.2, 125.1, 124.4, 124.0, 123.5, 41.6, 37.2, 33.3, 33.1, 26.3, 26.1, 26.0, 25.6. **FT-IR (neat, cm^{-1}):** 2939, 2865, 973, 782. **HRMS (APCI-QUADRUPOLE-ORBITRAP) m/z:** $[M]^+$ Calcd for $[C_{18}H_{20}]$ 236.1560; Found 236.1560.

(Z)-1-bromo-4-(2-cyclohexylvinyl)benzene 3g:



The title product was prepared using 1-bromo-4-ethynylbenzene (0.5 mmol, 90 mg) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of E and Z isomers using silica column chromatography with 70% (92 mg) yield. (Solvent gradient: 1% ethyl acetate in petroleum ether; pale yellow oil). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 93:7)** δ 7.45 (d, *J* = 8.3 Hz, 1.80H, ***Z***), 7.40 (d, *J* = 8.5 Hz, 0.14H, ***E***), 7.21 (d, *J* = 8.4 Hz, 0.14H, ***E***), 7.12 (d, *J* = 8.3 Hz, 1.80H, ***Z***), 6.32 – 6.14 (m, 1.07H, ***Z***+***E***), 5.52 (dd, *J* = 11.7, 10.2 Hz, 1H, ***Z***), 2.56 – 2.44 (m, 0.93H, ***Z***), 2.15 – 2.08 (m, 0.07H, ***E***), 1.80 – 1.63 (m, 5H, ***Z***+***E***), 1.32 – 1.13 (m, 5H, ***Z***+***E***). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 139.8, 136.9, 131.3, 130.2, 125.8, 120.3, 37.0, 33.2, 26.0, 25.7. **FT-IR (neat, cm^{-1}):** 3309, 2943, 1248, 824, 789, 662. **EI-MS (m/z):** $[C_{14}H_{17}Br]$ $[M]^+$ 264.1. Literature.[6]

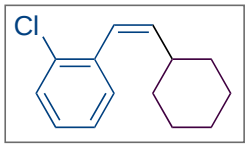
(Z)-1-bromo-3-(2-cyclohexylvinyl)benzene 3h:



The title product was prepared using 1-bromo-3-ethynylbenzene (0.5 mmol, 90 mg) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of E and Z isomers using silica column chromatography with 68% (89 mg) yield. (Solvent gradient: 1% ethyl acetate in petroleum ether; pale yellow oil). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 97:3)** δ 7.50 – 7.30 (m, 2H, ***Z***+***E***), 7.27 – 7.17 (m, 2H, ***Z***+***E***), 6.27 (d, *J* = 11.7 Hz, 1.06H, ***Z***+***E***), 5.57 (dd, *J* = 11.7, 10.2 Hz, 0.97H, ***Z***), 2.59 – 2.50 (m, 0.97H, ***Z***), 2.18 – 2.13 (m, 0.03H, ***E***), 1.79 – 1.67 (m, 5H, ***Z***+***E***), 1.37 – 1.18 (m, 5H, ***Z***+***E***). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 140.3, 140.1, 131.6, 129.7, 129.4, 127.1, 125.5, 122.3, 37.0, 33.2, 26.0, 25.6.

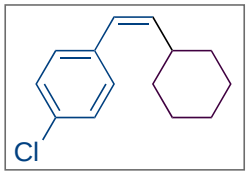
FT-IR (neat, cm^{-1}): 3311, 2945, 1254, 698. **HRMS (ESI-QUADRUPOLE-ORBITRAP) m/z:** $[M+H]^+$ Calcd for $[C_{14}H_{17}Br]$ 265.0586; Found 265.0590.

(Z)-1-chloro-2-(2-cyclohexylvinyl)benzene 3i:



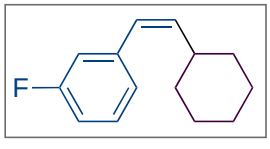
The title product was prepared using 1-chloro-2-ethynylbenzene (0.5 mmol, 68 mg) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of E and Z isomers using silica column chromatography with 75% (82 mg) yield. (Solvent gradient: 1% ethyl acetate in petroleum ether; colourless oil). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 90:10)** δ 7.43 (d, *J* = 9.4 Hz, 0.1H, ***E***), 7.30 (d, *J* = 9.3 Hz, 0.9H, ***Z***), 7.26 – 7.02 (m, 3H, ***Z***+***E***), 6.65 (d, *J* = 15.9 Hz, 0.1H, ***E***), 6.31 (d, *J* = 11.6 Hz, 0.9H, ***Z***), 6.08 (dd, *J* = 15.9, 7.0 Hz, 0.1H, ***E***), 5.53 (t, *J* = 15.9, 0.9H, ***Z***), 2.33 – 2.21 (m, 0.9H, ***Z***), 2.15 – 2.08 (m, 0.1H, ***E***), 1.78 – 1.54 (m, 5H, ***Z***+***E***), 1.27 – 1.05 (m, 5H, ***Z***+***E***). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 140.1, 136.3, 133.6, 130.4, 129.4, 127.9, 126.3, 124.2, 37.0, 33.2, 26.0, 25.6. **FT-IR (neat, cm^{-1}):** 2939, 1451, 1054, 740. **EI-MS (m/z):** $[C_{14}H_{17}Cl]$ $[M]^+$ 220.1. Literature.[6]

(Z)-1-chloro-4-(2-cyclohexylvinyl)benzene 3j:



The title product was prepared using 1-chloro-4-ethynylbenzene (0.5 mmol, 68 mg) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of E and Z isomers using silica column chromatography with 79% (87 mg) yield. (Solvent gradient: 1% ethyl acetate in petroleum ether; colourless oil). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 94:6)** δ 7.30 (d, *J* = 8.3 Hz, 2H, ***Z***+***E***), 7.18 (d, *J* = 8.1 Hz, 2H, ***Z***+***E***), 6.25 (d, *J* = 11.7 Hz, 1H, ***Z***+***E***), 6.15 (dd, *J* = 16.0, 6.9 Hz, 0.06H, ***E***), 5.51 (t, *J* = 10.9 Hz, 0.94H, ***Z***), 2.51 (qt, *J* = 10.6, 3.5 Hz, 0.94H, ***Z***), 2.16 – 2.08 (m, 0.06H, ***E***), 1.78 – 1.64 (m, 5H, ***Z***+***E***), 1.31 – 1.13 (m, 5H, ***Z***+***E***). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 139.7, 136.4, 132.2, 129.9, 128.4, 125.7, 37.0, 33.2, 26.0, 25.7. **FT-IR (neat, cm^{-1}):** 2938, 1496, 1098, 843. **EI-MS (m/z):** $[C_{14}H_{17}Cl]$ $[M]^+$ 220.1. Literature.[2]

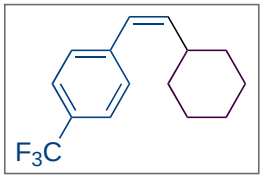
(Z)-1-(2-cyclohexylvinyl)-3-fluorobenzene 3k:



The title product was prepared using 1-ethynyl-3-fluorobenzene (0.5 mmol, 60 mg) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of E and Z isomers using silica column chromatography with 73% (74.4 mg) yield. (Solvent gradient: 1% ethyl acetate in petroleum ether; yellow oil). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 94:6)** δ 7.33 – 7.22 (m, 1H, ***Z***+***E***), 7.04 (d, J = 7.8 Hz, 1H, ***Z***+***E***), 7.02 – 6.86 (m, 2H, ***Z***+***E***), 6.35 – 6.25 (m, 1H, ***Z***+***E***), 6.20 (dd, *J* = 15.9, 6.9 Hz, 0.6H, ***E***), 5.54 (t, J = 10.9 Hz, 0.94H, ***Z***), 2.61 – 2.52 (m, 0.94H, ***Z***), 2.16 – 2.12 (m, 0.06H, ***E***), 1.81 – 1.65 (m, 5H, ***Z***+***E***), 1.36 – 1.14 (m, 5H, ***Z***+***E***). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 163.8 ($^1J_{C-F}$ = 244.9 Hz),

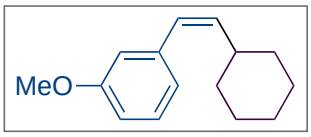
161.8 ($^{1}J_{C-F}$ = 244.9 Hz), 140.2 ($^{3}J_{C-F}$ = 7.7 Hz), 140.2 ($^{3}J_{C-F}$ = 7.7 Hz), 140.1, 129.6 ($^{3}J_{C-F}$ = 8.4 Hz), 129.6 ($^{3}J_{C-F}$ = 8.4 Hz), 125.9 ($^{4}J_{C-F}$ = 2.2 Hz), 125.8 ($^{4}J_{C-F}$ = 2.2 Hz), 124.4 ($^{4}J_{C-F}$ = 2.8 Hz), 124.4 ($^{4}J_{C-F}$ = 2.8 Hz), 115.4 ($^{2}J_{C-F}$ = 21.3 Hz), 115.2 ($^{2}J_{C-F}$ = 21.3 Hz), 113.4 ($^{2}J_{C-F}$ = 21.2 Hz), 113.2 ($^{2}J_{C-F}$ = 21.2 Hz), 37.0, 33.2, 26.0, 25.6. **^{19}F NMR (471 MHz, CDCl$_3$)** δ -113.7 (***Z***), -113.9 (***E***). **FT-IR (neat, cm^{-1}):** 2945, 2867, 989. **EI-MS (m/z):** [$C_{14}H_{17}F$] $[M]^+$ 204.1. Literature.[6]

(Z)-1-(2-cyclohexylvinyl)-4-(trifluoromethyl)benzene 3l:



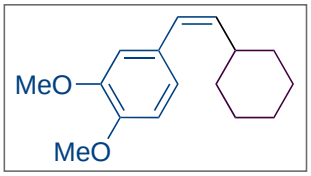
The title product was prepared using 1-ethynyl-4-(trifluoromethyl)benzene (0.5 mmol, 85 mg) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of E and Z isomers using silica column chromatography with 70% (89 mg) yield. (Solvent gradient: 1% ethyl acetate in petroleum ether; yellow oil). **^{1}H NMR (500 MHz, CDCl$_3$) (*Z*/*E* mixture 97:3)** δ 7.58 (d, *J* = 8.0 Hz, 1.92H, ***Z***), 7.53 (d, *J* = 8.1 Hz, 0.08H, ***E***), 7.43 (d, *J* = 8.2 Hz, 0.08H, ***E***), 7.34 (d, *J* = 8.0 Hz, 1.92H, ***Z***), 6.32 (d, *J* = 11.7 Hz, 1H, ***Z***+***E***), 5.60 (dd, *J* = 11.8, 10.2 Hz, 0.97H, ***Z***), 2.52 (qt, *J* = 10.6, 3.4 Hz, 0.97H, ***Z***), 2.17 – 2.14 (m, 0.03H, ***E***), 1.78 – 1.65 (m, 5H, ***Z***+***E***), 1.32 – 1.15 (m, 5H, ***Z***+***E***). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 141.6, 141.0, 128.9 ($^{2}J_{C-F}$ = 32.4 Hz), 128.8, 128.6 ($^{2}J_{C-F}$ = 32.4 Hz), 128.3 ($^{2}J_{C-F}$ = 32.4 Hz), 128.1 ($^{2}J_{C-F}$ = 32.4 Hz), 127.3 ($^{1}J_{C-F}$ = 272.0 Hz), 125.7, 125.4 ($^{1}J_{C-F}$ = 272.0 Hz), 125.2 ($^{3}J_{C-F}$ = 3.8 Hz), 125.2 ($^{3}J_{C-F}$ = 3.8 Hz), 125.1 ($^{3}J_{C-F}$ = 3.8 Hz), 125.1 ($^{3}J_{C-F}$ = 3.8 Hz), 123.3 ($^{1}J_{C-F}$ = 272.0 Hz), 121.3 ($^{1}J_{C-F}$ = 272.0 Hz), 37.1, 33.1, 26.0, 25.6. **^{19}F NMR (471 MHz, CDCl$_3$)** δ -62.4 (***Z***). **FT-IR (neat, cm^{-1}):** 2941, 1330, 1170, 1129, 859. **EI-MS (m/z):** [$C_{15}H_{17}F_3$] $[M]^+$ 254.1. Literature.[6]

(Z)-1-(2-cyclohexylvinyl)-3-methoxybenzene 3m:



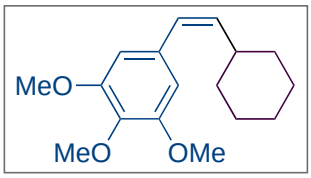
The title product was prepared using 1-ethynyl-3-methoxybenzene (0.5 mmol, 66 mg) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of E and Z isomers using silica column chromatography with 72% (78 mg) yield. (Solvent gradient: 1.5% ethyl acetate in petroleum ether; colourless oil). **^{1}H NMR (500 MHz, CDCl$_3$) (data for *Z*)** δ 7.29 – 7.20 (m, 1H), 6.93 – 6.74 (m, 3H), 6.29 (d, *J* = 11.7 Hz, 1H), 5.49 (dd, *J* = 11.7, 10.1 Hz, 1H), 3.81 (s, 3H), 2.65 – 2.54 (m, 1H), 1.77 – 1.63 (m, 5H), 1.32 – 1.15 (m, 5H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 159.5, 139.4, 139.3, 129.2, 126.8, 121.2, 114.1, 112.1, 55.2, 37.1, 33.3, 26.1, 25.7. **FT-IR (neat, cm^{-1}):** 2939, 1589, 1457, 1054, 793. **EI-MS (m/z):** [$C_{15}H_{20}O$] $[M]^+$ 216.1. Literature.[7]

(Z)-4-(2-cyclohexylvinyl)-1,2-dimethoxybenzene 3n:



The title product was prepared using 4-ethynyl-1,2-dimethoxybenzene (0.5 mmol, 81 mg) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of E and Z isomers using silica column chromatography with 79% (97 mg) yield. (Solvent gradient: 1.5% ethyl acetate in petroleum ether; colourless oil). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 88:12)** δ 6.91 – 6.78 (m, 3H, ***Z***+***E***), 6.25 (d, *J* = 11.8 Hz, 1H, ***Z***+***E***), 6.04 (dd, *J* = 15.9, 6.9 Hz, 0.12H, ***E***), 5.42 (dd, *J* = 11.7, 10.0 Hz, 0.88H, ***Z***), 3.92 – 3.84 (m, 6H, ***Z***+***E***), 2.65 – 2.56 (m, 1H, ***Z***), 2.13 – 2.08 (m, 0.12H, ***E***), 1.79 – 1.64 (m, 5H, ***Z***+***E***), 1.33 – 1.15 (m, 5H, ***Z***+***E***). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 148.5, 147.7, 137.8, 130.9, 126.6, 121.1, 111.9, 111.0, 55.9, 55.7, 37.2, 33.4, 26.1, 25.9. **FT-IR (neat, cm^{-1}):** 2937, 1523, 1272, 1037. **EI-MS (m/z):** $[C_{16}H_{22}O_2]$ $[M]^+$ 246.1. Literature.[5]

(Z)-5-(2-cyclohexylvinyl)-1,2,3-trimethoxybenzene 3o:

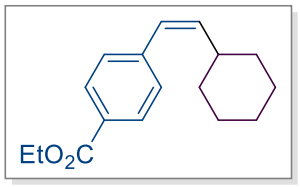


The title product was prepared using 5-ethynyl-1,2,3-trimethoxybenzene (0.5 mmol, 96 mg) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of E and Z isomers using silica column chromatography with 65% (90 mg) yield. (Solvent gradient: 2% ethyl acetate in petroleum ether; pale yellow oil). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z* pure)** δ 6.50 (s, 2H), 6.25 (d, *J* = 11.6 Hz, 1H), 5.46 (dd, *J* = 11.6, 10.1 Hz, 1H), 3.86 (s, 9H), 2.67 – 2.56 (m, 1H), 1.79 – 1.64 (m, 5H), 1.31 – 1.17 (m, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 152.9, 138.6, 136.8, 133.5, 126.9, 105.7, 60.9, 56.0, 37.4, 33.4, 26.0, 25.9. **FT-IR (neat, cm^{-1}):** 2937, 2861, 1242, 1129, 1012, 846. **HRMS (ESI-QUADRUPOLE-ORBITRAP) m/z:** $[M+H]^+$ Calcd for $[C_{17}H_{24}O_3]$ 277.1798; Found 277.1794.

(Z)-1-(2-cyclohexylvinyl)-3-phenoxybenzene 3p:

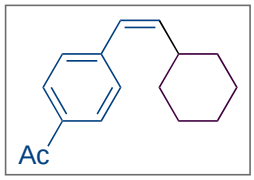
The title product was prepared using 1-ethynyl-3-phenoxybenzene (0.5 mmol, 97 mg) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of E and Z isomers using silica column chromatography with 77% (107 mg) yield. (Solvent gradient: 1.5% ethyl acetate in petroleum ether; pale yellow oil). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z* pure)** δ 7.40 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.93 – 6.87 (m, 2H), 6.26 (d, *J* = 11.7 Hz, 1H), 5.48 (dd, *J* = 11.7, 10.1 Hz, 1H), 2.56 – 2.46 (m, 1H), 1.72 – 1.61 (m, 5H), 1.24 – 1.08 (m, 5H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 157.4, 157.1, 139.7, 139.6, 129.8, 129.5, 126.3, 123.6, 123.4, 119.2, 118.6, 116.9, 37.0, 33.2, 26.0, 25.7. **FT-IR (neat, cm^{-1}):** 2938, 1495, 1248, 698. **HRMS (ESI-QUADRUPOLE-ORBITRAP) m/z:** $[M+H]^+$ Calcd for $[C_{20}H_{22}O]$ 279.1743; Found 279.1745.

ethyl (Z)-4-(2-cyclohexylvinyl)benzoate 3q:



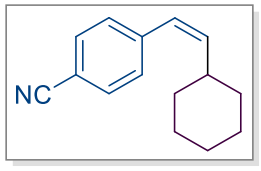
The title product was prepared using ethyl 4-ethynylbenzoate (0.5 mmol, 87 mg) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of *E* and *Z* isomers using silica column chromatography with 72% (93 mg) yield. (Solvent gradient: 10% ethyl acetate in petroleum ether; colourless oil). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 73:27)** δ 7.98 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 6.40 – 6.27 (m, 1.25H), 5.58 (dd, *J* = 11.7, 10.2 Hz, 0.73H), 4.42 – 4.33 (m, 2H), 2.58 – 2.49 (m, 0.73H, ***Z***), 2.18 – 2.12 (m, 0.27H, ***E***), 1.83 – 1.65 (m, 5H), 1.39 (t, *J* = 7.1, 2.7 Hz, 3H), 1.34 – 1.14 (m, 5H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 141.0, 129.9, 129.5, 128.5, 126.2, 125.8, 60.9, 37.1, 33.1, 26.0, 25.6, 14.4. **FT-IR (neat, cm^{-1}):** 2973, 2864, 1724, 1278, 1107. **EI-MS (m/z):** [$C_{17}H_{22}O_2$] $[M]^+$ 258.1. Literature[8]

(Z)-1-(4-(2-cyclohexylvinyl)phenyl)ethan-1-one 3r:



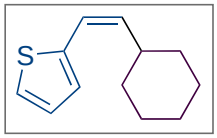
The title product was prepared using 1-(4-ethynylphenyl)ethan-1-one (0.5 mmol, 72 mg) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of *E* and *Z* isomers using silica column chromatography with 72% (82 mg) yield. (Solvent gradient: 2.5% ethyl acetate in petroleum ether; colourless oil). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 71:29)** δ 7.92 (d, *J* = 8.1 Hz, 1.39H, ***Z***), 7.88 (d, *J* = 8.1 Hz, 0.6H, ***E***), 7.41 (d, *J* = 8.1 Hz, 0.59H, ***E***), 7.33 (d, *J* = 8.1 Hz, 1.4H, ***Z***), 6.41 – 6.28 (m, 1.29H, ***Z***+***E***), 5.60 (t, *J* = 11.0 Hz, 0.71H, ***Z***), 2.59 (s, 3H, ***Z***+***E***), 2.57 – 2.50 (m, 0.71H, ***Z***), 2.19 – 2.11 (m, 0.29H, ***E***), 1.83 – 1.66 (m, 5H, ***Z***+***E***), 1.34 – 1.15 (m, 6H, ***Z***+***E***). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 197.7, 143.0, 141.2, 140.1, 135.1, 128.7, 128.7, 128.4, 126.5, 126.0, 126.0, 41.3, 37.2, 33.1, 32.7, 26.6, 26.1, 26.0, 26.0, 25.6. **FT-IR (neat, cm^{-1}):** 3055, 2985, 1682, 1265, 1181. **EI-MS (m/z):** [$C_{16}H_{20}O$] $[M]^+$ 228.1. Literature.[2]

(Z)-4-(2-cyclohexylvinyl)benzonitrile 3s:



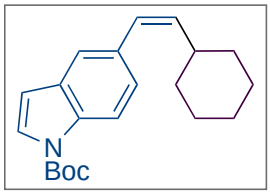
The title product was prepared using 4-ethynylbenzonitrile (0.5 mmol, 63 mg) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of *E* and *Z* isomers using silica column chromatography with 73% (77 mg) yield. (Solvent gradient: 3% ethyl acetate in petroleum ether; pale brown oil). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 91:9)** δ 7.65 – 7.54 (m, 2H, ***Z***+***E***), 7.41 (d, *J* = 8.3 Hz, 0.17H, ***E***), 7.33 (d, *J* = 8.1 Hz, 1.83H, ***Z***), 6.34 – 6.32 (m, 0.17 H, ***E***), 6.30 (d, *J* = 11.7 Hz, 0.89H, ***Z***), 5.64 (dd, *J* = 11.8, 10.3 Hz, 0.91H, ***Z***), 2.53 – 2.44 (m, 0.91H, ***Z***), 2.19 – 2.13 (m, 0.09H, ***E***), 1.77 – 1.66 (m, 5H, ***Z***+***E***), 1.32 – 1.15 (m, 6H, ***Z***+***E***). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 142.7, 142.0, 132.1, 129.2, 125.5, 119.1, 109.9, 37.2, 33.0, 25.9, 25.6. **FT-IR (neat, cm^{-1}):** 2939, 2864, 2237, 1456, 860. **EI-MS (m/z):** [$C_{15}H_{17}N$] $[M]^+$ 211.1. Literature.[6]

(Z)-2-(2-cyclohexylvinyl)thiophene 3t:



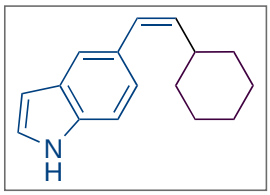
The title product was prepared using 2-ethynylthiophene (0.5 mmol, 54 mg) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of E and Z isomers using silica column chromatography with 65% (62 mg) yield. (Solvent gradient: 2% ethyl acetate in petroleum ether; pale brown oil). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 96:4)** δ 7.30 – 7.26 (m, 1H, ***Z***+***E***), 7.16 – 7.03 (m, 2H, ***Z***+***E***), 6.26 (d, *J* = 11.6 Hz, 1H, ***Z***+***E***), 6.03 (dd, *J* = 16.0, 6.9 Hz, 0.04H, ***E***), 5.44 (dd, *J* = 11.5, 9.7 Hz, 0.96H, ***Z***), 2.64 – 2.57 (m, 0.97H, ***Z***), 2.12 – 2.04 (m, 0.04H, ***E***), 1.79 – 1.66 (m, 5H, ***Z***+***E***), 1.36 – 1.15 (m, 5H, ***Z***+***E***). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 138.9, 138.1, 128.6, 125.0, 122.4, 121.0, 37.6, 33.1, 26.1, 25.8. **FT-IR (neat, cm^{-1}):** 2943, 1524, 1268, 1038. **HRMS (ESI-QUADRUPOLE-ORBITRAP) m/z:** $[M+Na]^+$ Calcd for $[C_{12}H_{16}S+Na]$ 215.0865; Found 215.0867.

tert-butyl (Z)-5-(2-cyclohexylvinyl)-1H-indole-1-carboxylate 3u:



The title product was prepared using tert-butyl 5-ethynyl-1H-indole-1-carboxylate (0.5 mmol, 120 mg) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of E and Z isomers using silica column chromatography with 73% (118.6 mg) yield. (Solvent gradient: 4% ethyl acetate in petroleum ether; yellow oil). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 96:4)** δ 8.07 (d, *J* = 8.8 Hz, 1H, ***Z***), 7.59 (d, *J* = 3.7 Hz, 1H, ***Z***), 7.44 (s, 1H, ***Z***), 7.25 – 7.20 (m, 1H, ***Z***), 6.56 (d, *J* = 3.7 Hz, 1H, ***Z***), 6.42 (d, *J* = 11.6 Hz, 1H, ***Z***), 6.18 (dd, *J* = 15.9, 6.9 Hz, 0.04H, ***E***), 5.48 (t, *J* = 10.8 Hz, 0.96H, ***Z***), 2.67 – 2.58 (m, 0.96H, ***Z***), 2.18 – 2.14 (m, 0.04H, ***E***), 1.80 – 1.70 (m, 5H, ***Z***+***E***), 1.68 (s, 16H, ***Z***), 1.32 – 1.15 (m, 5H, ***Z***+***E***). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 138.3, 132.7, 127.1, 126.2, 125.3, 120.7, 114.7, 107.5, 83.7, 36.9, 33.4, 28.3, 26.1, 25.8. **FT-IR (neat, cm^{-1}):** 2941, 2865, 1745, 1379, 1171, 802. **HRMS (APCI-QUADRUPOLE-ORBITRAP) m/z:** $[M]^+$ Calcd for $[C_{21}H_{27}NO_2]$ 325.2036; Found 325.2037.

(Z)-5-(2-cyclohexylvinyl)-1H-indole 3v:



The title product was prepared using 5-ethynyl-1H-indole (0.5 mmol, 70 mg) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of E and Z isomers using silica column chromatography with 60% (67 mg) yield. (Solvent gradient: 6% ethyl acetate in petroleum ether; yellow oil). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 90:10)** δ 8.09 (s, 1H, ***Z***+***E***), 7.58 (s, 1H, ***Z***+***E***), 7.38 – 7.30 (m, 1H, ***Z***+***E***), 7.24 – 7.11 (m, 2H, ***Z***+***E***), 6.61 – 6.52 (m, 1H, ***Z***+***E***), 6.51 – 6.45 (m, 1H, ***Z***+***E***), 6.17 (dd, *J* = 15.9, 7.0 Hz, 0.1H, ***E***), 5.47 (dd, *J* = 11.6, 10.1 Hz, 1H, ***Z***), 2.76 – 2.67 (m, 1H, ***Z***), 2.21 – 2.18 (m, 1H, ***E***), 1.86 – 1.66 (m, 5H, ***Z***+***E***), 1.37 – 1.19 (m, 5H, ***Z***+***E***). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 137.1, 134.6, 129.9, 127.9, 127.8, 124.5, 123.4, 120.5, 110.6, 102.8, 36.9, 33.5, 26.1, 25.8. **FT-IR (neat, cm^{-1}):** 3420, 3079, 1624, 1479, 1285, 994, 767. **HRMS (ESI-**

QUADRUPOLE-ORBITRAP) m/z: $[M+H]^+$ Calcd for $[C_{16}H_{19}N]$ 226.1590; Found 226.1593.

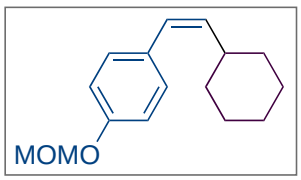
(Z)-4-(2-cyclohexylvinyl)aniline 3w:

The title product was prepared using 4-ethynylaniline (0.5 mmol, 59 mg) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of E and Z isomers using silica column chromatography with 49% (49 mg) yield. (Solvent gradient: 8% ethyl acetate in petroleum ether; yellow oil). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 87:13)** δ 7.17 (d, *J* = 8.4 Hz, 0.27H, ***E***), 7.10 (d, *J* = 8.4 Hz, 1.72H, ***Z***), 6.64 (dd, *J* = 17.2, 8.4 Hz, 2H, ***Z***+***E***), 6.29 – 6.17 (m, 1H, ***Z***+***E***), 5.99 (dd, *J* = 16.0, 7.0 Hz, 0.13H, ***E***), 5.34 (dd, *J* = 11.7, 9.9 Hz, 0.87H, ***Z***), 3.67 (bs, 2H), 2.63 – 2.55 (m, 0.87H, ***Z***), 2.11 – 2.05 (m, 0.13H, ***E***), 1.81 – 1.65 (m, 5H, ***Z***+***E***), 1.33 – 1.14 (m, 5H, ***Z***+***E***). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 144.9, 136.6, 129.7, 128.6, 126.6, 114.9, 37.0, 33.4, 26.1, 25.8. **FT-IR (neat, cm^{-1}):** 3447, 3370, 3005, 1617, 1530, 1279, 825. **HRMS (ESI-QUADRUPOLE-ORBITRAP) m/z:** $[M+H]^+$ Calcd for $[C_{14}H_{19}N]$ 202.1590; Found 202.1595.

(Z)-2-(3-(2-cyclohexylvinyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 3x:

The title product was prepared using 2-(3-ethynylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mmol, 114 mg) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of E and Z isomers using silica column chromatography with 67% (104 mg) yield. (Solvent gradient: 2.5% ethyl acetate in petroleum ether; yellow oil). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 87:13)** δ 7.80 – 7.71 (m, 2H, ***Z***+***E***), 7.36 – 7.24 (m, 2H, ***Z***+***E***), 6.32 (d, *J* = 11.5 Hz, 1H, ***Z***+***E***), 6.25 (dd, *J* = 16.0, 6.8 Hz, 0.13H, ***E***), 5.52 (t, *J* = 10.9 Hz, 0.87H, ***Z***), 2.60 – 2.53 (m, 0.87H, ***Z***), 2.15 – 2.11 (m, 0.13H, ***E***), 1.76 – 1.61 (m, 5H, ***Z***+***E***), 1.35 (s, 12H, ***Z***+***E***), 1.24 – 1.12 (m, 5H, ***Z***+***E***). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 140.9, 139.8, 134.7, 128.0, 126.9, 125.3, 83.8, 37.0, 33.2, 26.0, 25.7, 24.9, 24.8. **FT-IR (neat, cm^{-1}):** 2954, 2861. **HRMS (ESI-QUADRUPOLE-ORBITRAP) m/z:** $[M+H]^+$ Calcd for $[C_{20}H_{29}BO_2]$ 313.2333; Found 313.2337.

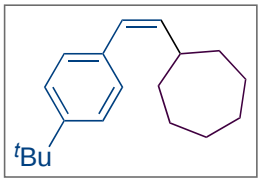
(Z)-1-(2-cyclohexylvinyl)-4-(methoxymethoxy)benzene 3y:



The title product was prepared using 1-ethynyl-4-(methoxymethoxy)benzene (0.5 mmol, 81 mg) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of E and Z isomers using silica column chromatography with 69% (85 mg) yield. (Solvent gradient: 2% ethyl acetate in petroleum ether; colourless oil). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 94:6)** δ 7.30 – 7.19 (m, 2H, ***Z***+***E***), 7.04 – 6.96 (m, 2H, ***Z***+***E***), 6.26 (d, *J* = 11.7 Hz, 1H, ***Z***+***E***), 6.06 (dd, *J* =

16.0, 7.0 Hz, 0.06H, ***E***), 5.42 (t, *J* = 10.8 Hz, 0.94H, ***Z***), 5.19 (s, 2H, ***Z***+***E***), 3.50 (s, 3H, ***Z***+***E***), 2.62 – 2.54 (m, 0.94H, ***Z***), 2.12 – 2.10 (m, 0.06H, ***E***), 1.78 – 1.65 (m, 5H, ***Z***+***E***), 1.33 – 1.14 (m, 5H, ***Z***+***E***). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 155.8, 137.9, 131.8, 129.8, 126.2, 116.0, 94.5, 56.0, 36.9, 33.3, 26.1, 25.7. **FT-IR (neat, cm^{-1}):** 2937, 2863, 1515, 1156, 1003, 844. **HRMS (ESI-QUADRUPOLE-ORBITRAP) m/z:** $[M+H]^+$ Calcd for $[C_{16}H_{22}O_2]$ 247.1693; Found 247.1692.

(Z)-(4-(tert-butyl)styryl)cycloheptane 3aa:

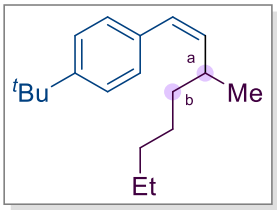


The title product was prepared using 1-(tert-butyl)-4-ethynylbenzene (0.5 mmol, 90 µL) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of *E* and *Z* isomers using silica column chromatography with 39% (50 mg) yield. (Solvent gradient: 1% ethyl acetate in petroleum ether; colourless oil). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 87:13)** δ 7.37 (d, *J* = 8.2 Hz, 1.67H, ***Z***), 7.34 – 7.27 (m, 0.68H, ***E***), 7.23 (d, *J* = 8.1 Hz, 1.67H, ***Z***), 6.31 (d, *J* = 15.9 Hz, 0.13H, ***E***), 6.27 – 6.16 (m, 1H, ***Z***+***E***), 5.56 (t, *J* = 11.0 Hz, 0.87H, ***Z***), 2.85 – 2.74 (m, 0.87H, ***Z***), 2.36 – 2.29 (m, 0.13H, ***E***), 1.86 – 1.40 (m, 12H, ***Z***+***E***), 1.33 (s, 9H, ***Z***+***E***). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 149.3, 139.3, 135.1, 128.5, 125.1, 125.0, 38.3, 35.3, 31.4, 28.5, 26.4. **FT-IR (neat, cm^{-1}):** 2930, 1477, 1370, 849. **EI-MS (m/z):** $[C_{19}H_{28}]$ $[M]^+$ 256.2. Literature.[2]

(Z)-(4-(tert-butyl)styryl)cyclooctane 3ab:

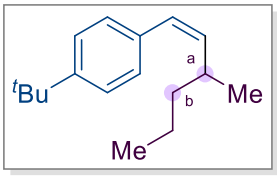
The title product was prepared using 1-(tert-butyl)-4-ethynylbenzene (0.5 mmol, 90 µL) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of *E* and *Z* isomers using silica column chromatography with 44% (59 mg) yield. (Solvent gradient: 1% ethyl acetate in petroleum ether; colourless oil). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 88:12)** δ 7.39 – 7.27 (m, 2.37H, ***Z***+***E***), 7.23 (d, *J* = 8.1 Hz, 1.77H, ***Z***), 6.31 (d, *J* = 15.9 Hz, 0.12H, ***E***), 6.21 (d, *J* = 11.6 Hz, 1H, ***Z***+***E***), 5.56 (t, *J* = 11.0 Hz, 0.88H, ***Z***), 2.92 – 2.82 (m, 0.88H, ***Z***), 2.43 – 2.32 (m, 0.12H, ***E***), 1.76 – 1.67 (m, 4H, ***Z***+***E***), 1.62 – 1.48 (m, 10H, ***Z***+***E***), 1.33 (s, 9H, ***Z***+***E***). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 149.3, 139.4, 135.1, 128.4, 125.6, 125.4, 125.1, 125.0, 36.3, 34.5, 32.7, 31.4, 27.3, 26.2, 25.1. **FT-IR (neat, cm^{-1}):** 2935, 2872, 1477, 1276, 851. **EI-MS (m/z):** $[C_{20}H_{30}]$ (M+) 270.2. Literature.[2]

[(Z)-1-(tert-butyl)-4-(3-methyloct-1-en-1-yl)benzene + (Z)-1-(tert-butyl)-4-(3-ethylhept-1-en-1-yl)benzene] 3ac:



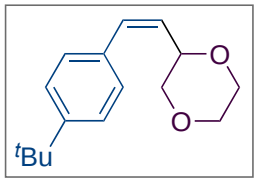
The title product was prepared using 1-(tert-butyl)-4-ethynylbenzene (0.5 mmol, 90 µL) and n-heptane (25 mmol, 3.66 mL) by following general procedure. Product was isolated as a mixture of *E*, *Z* and regioisomers using silica column chromatography with 45% (58 mg) yield. (Solvent gradient: pure petroleum ether; colourless oil). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 94:6 + [a + b] regiomers 1.2:1)** δ 7.37 – 7.33 (m, 2H, ***Z***+***E***), 7.26 – 7.21 (m, 2H, ***Z***+***E***), 6.33 (d, *J* = 11.7 Hz, 0.43H, ***Z***), 5.40 (t, *J* = 11.0 Hz, 0.51H, ***Z***), 5.35 (t, *J* = 11.1 Hz, 0.43H, ***Z***), 2.83 – 2.76 (m, 0.5H, ***Z***), 2.58 – 2.66 (m, 0.4H, ***Z***), 1.34 (s, 9H), 1.31 – 1.17 (m, 7H), 1.05 (d, *J* = 6.5 Hz, 2H), 0.87 (dt, *J* = 14.7, 7.2 Hz, 5H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 149.3, 149.2, 139.2, 138.1, 137.9, 135.3, 135.2, 128.6, 128.4, 127.1, 125.7, 125.4, 125.1, 125.0, 39.0, 38.2, 37.7, 37.2, 35.2, 34.5, 32.3, 32.1, 31.4, 29.5, 28.5, 27.1, 23.1, 22.7, 21.1, 20.5, 14.5, 14.1, 11.7. **FT-IR (neat, cm^{-1}):** 2881, 1477, 1276, 851. **HRMS (APCI-QUADRUPOLE-ORBITRAP) m/z:** $[M]^+$ Calcd for $[C_{19}H_{30}]$ 258.2342; Found 258.2342.

[(Z)-1-(tert-butyl)-4-(3-methylhex-1-en-1-yl)benzene + (Z)-1-(tert-butyl)-4-(3-ethylpent-1-en-1-yl)benzene] 3ad:



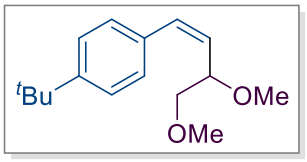
The title product was prepared using 1-(tert-butyl)-4-ethynylbenzene (0.5 mmol, 90 µL) and n-pentane (25 mmol, 2.88 mL) by following general procedure. Product was isolated as a mixture of *E*, *Z* and regioisomers using silica column chromatography with 43% (49.5 mg) yield. (Solvent gradient: pure petroleum ether; colourless oil). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 95:5 + [a + b] regiomers 3:1)** δ 7.31 – 7.23 (m, 2H), 7.19 – 7.12 (m, 2H), 6.36 (d, *J* = 11.8 Hz, 0.22H, ***Z***), 6.24 (d, *J* = 11.9 Hz, 0.67H, ***Z***), 6.16 – 6.10 (m, 0.05H), 5.97 (dd, *J* = 15.9, 8.0 Hz, 0.05H), 5.60 – 5.53 (m, 0.06H), 5.37 (d, *J* = 10.6 Hz, 0.04H), 5.31 (t, *J* = 11.0 Hz, 0.67H, ***Z***), 5.25 (t, *J* = 11.2 Hz, 0.22H, ***Z***), 2.77 – 2.65 (m, 0.67H), 2.51 – 2.42 (m, 0.22H), 2.23 – 2.18 (m, 0.06H), 2.13 – 2.08 (m, 0.04H), 1.24 (m, 14H), 0.96 (d, *J* = 6.5 Hz, 2H), 0.79 (m, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 149.3, 139.1, 137.5, 135.1, 128.8, 128.4, 128.4, 127.0, 125.1, 125.0, 40.6, 40.0, 34.5, 32.1, 31.4, 28.1, 21.1, 20.6, 14.3, 11.7. **FT-IR (neat, cm^{-1}):** 2893, 1465, 1289. **HRMS (APCI-QUADRUPOLE-ORBITRAP) m/z:** $[M]^+$ Calcd for $[C_{17}H_{26}]$ 230.2029; Found 230.2029.

(Z)-2-(4-(tert-butyl)styryl)-1,4-dioxane 3ae:



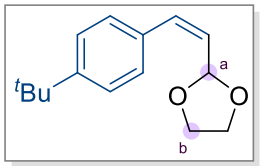
The title product was prepared using 1-(tert-butyl)-4-ethynylbenzene (0.5 mmol, 90 µL) and 1,4-dioxane (15 mmol, 1.28 mL) by following general procedure. Product was isolated as a mixture of *E* and *Z* isomers using silica column chromatography with 47% (58 mg) yield. (Solvent gradient: 6% ethyl acetate in petroleum ether; colourless oil). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 88:12)** δ 7.39 (d, *J* = 8.0 Hz, 1.75H, *Z*), 7.38 – 7.31 (m, 0.5H, *E*), 7.25 (d, *J* = 8.3 Hz, 1.75H, *Z*), 6.66 (d, *J* = 11.7 Hz, 1H, *Z*+*E*), 6.05 (dd, *J* = 16.1, 6.3 Hz, 0.12H, *E*), 5.51 (dd, *J* = 11.8, 8.8 Hz, 0.88H, *Z*), 4.59 – 4.51 (m, 0.88H, *Z*), 4.28 – 4.20 (m, 0.12H, *E*), 3.88 – 3.64 (m, 5H, *Z*+*E*), 3.51 – 3.38 (m, 1H, *Z*+*E*), 1.33 (s, 9H, *Z*+*E*). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 150.7, 134.2, 133.5, 128.5, 126.6, 125.4, 72.3, 70.2, 66.3, 66.1, 34.6, 31.3. **FT-IR (neat, cm^{-1}):** 2975, 1243, 1049, 912, 733. **HRMS (ESI-QUADRUPOLE-ORBITRAP) m/z:** $[M+H]^+$ Calcd for $[C_{16}H_{22}O_2]$ 247.1693; Found 247.1692.

(Z)-1-(tert-butyl)-4-(3,4-dimethoxybut-1-en-1-yl)benzene 3af:



The title product was prepared using 1-(tert-butyl)-4-ethynylbenzene (0.5 mmol, 90 µL) and n-pentane (25 mmol, 2.6 mL) by following general procedure. Product was isolated as pure *Z* isomers using silica column chromatography with 51% (63 mg) yield. (Solvent gradient: 5% ethyl acetate in petroleum ether; colourless oil). **^{1}H NMR (500 MHz, $CDCl_3$) (pure *Z*)** δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 11.9 Hz, 1H), 5.52 (dd, *J* = 11.9, 9.4 Hz, 1H), 4.49 – 4.43 (m, 1H), 3.59 – 3.51 (m, 2H), 3.43 (s, 3H), 3.28 (s, 3H), 1.33 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 150.4, 133.8, 133.6, 129.2, 128.6, 125.3, 76.2, 75.3, 59.4, 56.4, 34.6, 31.3. **FT-IR (neat, cm^{-1}):** 2972, 1469, 1106, 848. **HRMS (ESI-QUADRUPOLE-ORBITRAP) m/z:** $[M+H]^+$ Calcd for $[C_{16}H_{24}O_2]$ 249.1849; Found 249.1847.

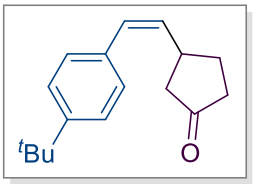
(Z)-2-(4-(tert-butyl)styryl)-1,3-dioxolane 3ag:



The title product was prepared using 1-(tert-butyl)-4-ethynylbenzene (0.5 mmol, 90 µL) and 1,3-dioxalane (25 mmol, 1.75 mL) by following general procedure. Product was isolated as a mixture of E, Z and regioisomers using silica column chromatography with 38% (44 mg) yield. (Solvent gradient: 5% ethyl acetate in petroleum ether; colourless oil). **^{1}H NMR (500 MHz, $CDCl_3$) [*Z*/*E* mixture 57:43; a:b (1:2.3)]** δ 7.40 – 7.30 (m, 3.5H, ***Z***+***E***), 7.21 (d, *J* = 8.0 Hz, 0.6H, ***Z***+***E***), 6.80 (d, *J* = 11.6 Hz, 0.4H, ***Z***), 6.73 (d, *J* = 11.6 Hz, 0.3H, ***Z***), 6.66 (d, *J* = 15.9 Hz, 0.3H, ***E***), 6.13 (dd, *J* = 15.8, 7.5 Hz, 0.3H, ***E***), 5.68 (dd, *J* = 11.6, 8.1 Hz, 0.7H, ***Z***), 5.55 (d, *J* = 7.5 Hz, 0.4H, ***Z***), 5.12 (s, 0.6H, ***E***), 5.00 (s, 0.3H, ***Z***), 4.95 (s, 0.3H, ***Z***), 4.87 (q, *J* = 7.3 Hz, 0.3H, ***E***), 4.60 (q, *J* = 7.0 Hz, 0.3H, ***Z***), 4.13 – 4.05 (m, 1.4H, ***Z***), 3.95 – 3.91 (m, 0.8H, ***Z***), 3.62 – 3.58 (m, 0.6H, ***Z***), 1.32 (d, *J* = 5.3 Hz, 9H, ***E***+***Z***). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 150.7, 134.3, 133.5, 128.5, 126.6, 125.6, 125.4, 72.4, 70.2, 66.3,

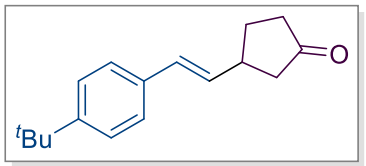
66.1, 34.6, 31.4, 31.3. **FT-IR (neat, cm-1):** 2993, 1475, 940. **HRMS (ESI-QUADRUPOLE-ORBITRAP) m/z:** $[M+H]^+$ Calcd for $[C_{15}H_{20}O_2]$ 233.1536; Found 233.1539.

(Z)-3-(4-(tert-butyl)styryl)cyclopentan-1-one 3ah-*Z*:



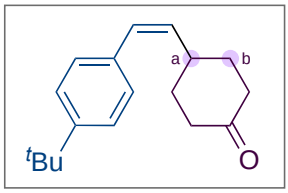
The title product (*Z*+*E*) was prepared using 1-(tert-butyl)-4-ethynylbenzene (0.5 mmol, 90 µL) and cyclopentanone (25 mmol, 2.21 mL) by following general procedure. Product was isolated as pure *E* and pure *Z* isomers using silica column chromatography with 90% (105 mg of *Z* isomer + 4 mg of *E* isomer-data given below) yield. (Solvent gradient: 5% ethyl acetate in petroleum ether; colourless oil). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*-pure)** δ 7.38 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 6.48 (d, *J* = 11.5 Hz, 1H), 5.56 (t, *J* = 10.6 Hz, 1H), 3.45 – 3.34 (m, 1H), 2.51 – 2.43 (m, 1H), 2.40 – 2.33 (m, 1H), 2.27 – 2.15 (m, 2H), 2.09 – 2.02 (m, 1H), 1.82 – 1.74 (m, 1H), 1.34 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 150.1, 134.3, 134.2, 129.7, 128.3, 125.3, 45.8, 38.3, 36.0, 34.6, 31.3, 30.6. **FT-IR (neat, cm^{-1}):** 2875, 1748, 1411, 1163, 973, 818. **HRMS (ESI-QUADRUPOLE-ORBITRAP) m/z:** $[M+H]^+$ Calcd for $[C_{17}H_{22}O]$ 243.1743; Found 243.1744.

(E)-3-(4-(tert-butyl)styryl)cyclopentan-1-one 3ah-*E*,



^{1}H NMR (500 MHz, $CDCl_3$) (*E*-pure) δ 7.36 – 7.29 (m, 4H), 6.44 (d, *J* = 15.9 Hz, 1H), 6.18 (dd, *J* = 15.8, 7.2 Hz, 1H), 3.06 – 2.96 (m, 1H), 2.52 – 2.45 (m, 1H), 2.41 – 2.34 (m, 1H), 2.29 – 2.18 (m, 2H), 2.16 – 2.09 (m, 1H), 1.85 – 1.77 (m, 1H), 1.31 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 150.6, 134.2, 131.3, 129.5, 125.9, 125.6, 44.9, 40.3, 38.3, 34.6, 31.3, 30.0. **FT-IR (neat, cm^{-1}):** 2976, 1752, 1117, 850. **HRMS (ESI-QUADRUPOLE-ORBITRAP) m/z:** $[M+H]^+$ Calcd for $[C_{17}H_{22}O]$ 243.1743; Found 243.1745.

(Z)-4-(4-(tert-butyl)styryl)cyclohexan-1-one 3ai:



The title product was prepared using 1-(tert-butyl)-4-ethynylbenzene (0.5 mmol, 90 µL) and cyclohexanone (25 mmol, 2.58 mL) by following general procedure. Product was isolated as mixture of constitutional isomers (only Z) using silica column chromatography with 59% (76 mg of *a* and *b* isomers) yield. (Solvent gradient: 5% ethyl acetate in petroleum ether; colourless oil). **^{1}H NMR (500 MHz, $CDCl_3$) [99:1; a:b (1.9:1)]** δ 7.42 (d, *J* = 8.0 Hz, 0.7H), 7.38 (d, *J* = 8.1 Hz, 1.3H), 7.32 – 7.23 (m, 0.7H), 7.18 (d, *J* = 8.0 Hz, 1.3H), 6.44 (d, *J* = 11.5 Hz, 0.3H, ***Z***), 6.41 (d, *J* = 11.5 Hz, 0.7H, ***Z***), 5.54 – 5.46 (m, 1H), 3.18 – 3.05 (m, 1H), 2.52 – 2.23 (m, 4H), 2.14 – 2.08 (m, 1H), 1.98 – 1.91 (m, 1H), 1.79 – 1.57 (m, 3H), 1.35 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 210.3, 209.7, 149.0, 148.9, 133.8, 133.5, 133.1, 127.8, 127.6, 127.3, 127.2, 124.3, 124.3, 46.9, 40.2, 39.5, 37.0, 34.3, 33.5, 32.1, 30.8, 30.3, 30.3, 24.1. **FT-IR (neat, cm^{-1}):** 2980, 1739, 1320. **HRMS (ESI-QUADRUPOLE-ORBITRAP) m/z:** $[M+H]^+$ Calcd for $[C_{18}H_{24}O]$ 257.1827; Found 257.1830.

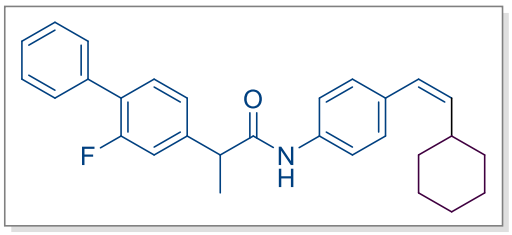
(Z)-2-(1-(4-chlorobenzoyl)-6-methoxy-2-methyl-1H-indol-3-yl)-N-(4-(2-cyclohexylvinyl)phenyl)acetamide 3aj:

The title product was prepared using 2-(1-(4-chlorobenzoyl)-6-methoxy-2-methyl-1H-indol-3-yl)-N-(4-ethynylphenyl)acetamide (0.5 mmol, 228 mg) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of E, Z and regioisomers using silica column chromatography with 59% (159 mg) yield. (Solvent gradient: 15% ethyl acetate in petroleum ether; gummy yellow solid). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 81:19)** δ 7.69 (d, *J* = 8.3 Hz, 2H, ***Z***+***E***), 7.50 (d, *J* = 8.4 Hz, 2H, ***Z***+***E***), 7.37 – 7.27 (m, 3H, ***Z***+***E***), 7.17 (d, *J* = 8.2 Hz, 1H, ***Z***+***E***), 6.95 (d, *J* = 2.6 Hz, 1H, ***Z***+***E***), 6.87 (d, *J* = 9.0 Hz, 1H, ***Z***+***E***), 6.72 (dd, *J* = 9.0, 2.5 Hz, 1H, ***Z***+***E***), 6.24 (dd, *J* = 19.3, 13.8 Hz, 1H, ***Z***+***E***), 6.09 (dd, *J* = 16.0, 6.9 Hz, 0.19H, ***E***), 5.44 (t, *J* = 10.9 Hz, 0.81H, ***Z***), 3.81 (d, *J* = 2.5 Hz, 5H, ***Z***+***E***), 2.54 – 2.49 (m, 0.81H, ***Z***), 2.45 (d, *J* = 4.4 Hz, 3H, ***Z***+***E***), 2.36 – 2.32 (m, 0.19H, ***E***), 1.75 – 1.60 (m, 5H, ***Z***+***E***), 1.25 – 1.09 (m, 6H, ***Z***+***E***). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 168.4, 168.1, 156.5, 138.9, 136.7, 134.5, 133.5, 131.3, 131.0, 129.3, 129.2, 126.4, 126.1, 119.9, 115.3, 112.6, 112.4, 100.7, 55.8, 36.9, 33.4, 33.2, 33.0, 29.7, 26.0, 25.7, 13.4. **FT-IR (neat, cm^{-1}):** 2938, 2864, 1746, 1690, 1668, 1324, 1240, 844. **HRMS (APCI-QUADRUPOLE-ORBITRAP) m/z:** $[M+H]^+$ Calcd for $[C_{33}H_{33}ClN_2O_3]$ 541.2252; Found 541.2253.

(Z)-N-(4-(2-cyclohexylvinyl)phenyl)-2-(2-((2,6-dichlorophenyl)amino)phenyl)acetamide 3ak:

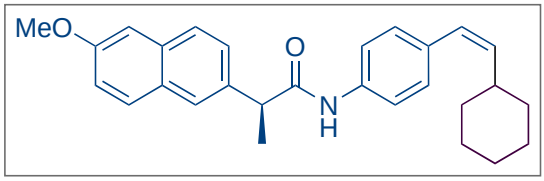
The title product was prepared using 2-(2-((2,6-dichlorophenyl)amino)phenyl)-N-(4-ethynylphenyl)acetamide (0.5 mmol, 164.5 mg) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of E and Z using silica column chromatography with 47% (97 mg) yield. (Solvent gradient: 12% ethyl acetate in petroleum ether; gummy yellow solid). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 87:13)** δ 7.56 (m, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.26 (m, 1H), 7.17 (dd, *J* = 18.2, 8.1 Hz, 3H), 6.99 (dt, *J* = 23.4, 7.7 Hz, 2H), 6.90 (s, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 6.23 (d, *J* = 11.7 Hz, 1H, ***Z***+***E***), 6.09 (dd, *J* = 16.0, 7.0 Hz, 0.13H, ***E***), 5.44 (t, *J* = 10.9 Hz, 0.87H, ***Z***), 3.86 (s, 2H), 2.53 (q, *J* = 10.9 Hz, 0.87H, ***Z***), 2.33 (d, *J* = 7.0 Hz, 0.13H, ***Z***+***E***), 1.73 – 1.62 (m, 6H), 1.27 (d, *J* = 11.6 Hz, 10H), 0.90 (tt, *J* = 18.8, 9.7 Hz, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 169.3, 142.7, 138.8, 137.3, 135.9, 134.4, 131.0, 130.3, 129.2, 128.9, 128.4, 126.4, 126.2, 124.7, 123.8, 121.9, 120.2, 119.9, 117.5, 68.2, 42.0, 36.9, 33.2, 33.0, 29.7, 26.1, 25.7, 11.0. **FT-IR (neat, cm^{-1}):** 3085, 1540, 667. **HRMS (APCI-QUADRUPOLE-ORBITRAP) m/z:** $[M]^+$ Calcd for $[C_{28}H_{28}Cl_2N_2O]$ 479.1651; Found 479.1657.

(Z)-N-(4-(2-cyclohexylvinyl)phenyl)-2-(2-fluoro-[1,1'-biphenyl]-4-yl)propenamide 3al:



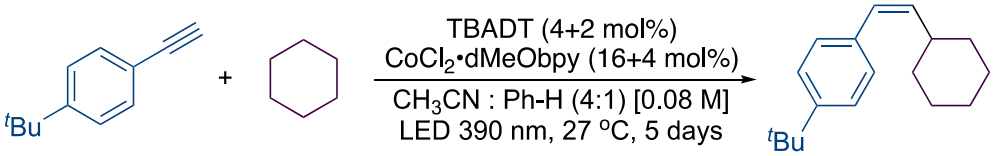
The title product was prepared using N-(4-ethynylphenyl)-2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanamide (0.5 mmol, 171.5 mg) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of E and Z using silica column chromatography with 55% (117 mg) yield. (Solvent gradient: 12% ethyl acetate in petroleum ether; gummy yellow solid). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 86:14)** δ 7.54 (d, *J* = 7.6 Hz, 2H, ***Z***+***E***), 7.48 – 7.36 (m, 6H, ***Z***+***E***), 7.28 (s, 1H, ***Z***+***E***), 7.24 – 7.18 (m, 3H, ***Z***+***E***), 6.24 (d, *J* = 11.7 Hz, 1H, ***Z***+***E***), 6.10 (dd, *J* = 16.0, 6.9 Hz, 0.14H, ***E***), 5.45 (t, *J* = 10.9 Hz, 0.86H, ***Z***), 3.73 (p, *J* = 7.1 Hz, 1H, ***Z***+***E***), 2.57 – 2.48 (m, 0.87H, ***Z***), 2.11 – 2.09 (m, 0.14H, ***Z***+***E***), 1.78 – 1.65 (m, 5H, ***Z***+***E***), 1.63 (d, *J* = 7.0 Hz, 3H, ***Z***+***E***), 1.29 – 1.10 (m, 6H, ***Z***+***E***). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.6, 139.8, 137.0, 136.3, 135.4, 132.3, 130.2, 130.0, 129.9, 129.5, 128.8, 127.5, 127.2, 124.6, 124.6, 120.6, 116.5, 116.3, 48.6, 37.9, 34.2, 27.0, 26.7, 19.7. **^{19}F NMR (471 MHz, $CDCl_3$)** δ -116.7. **FT-IR (neat, cm^{-1}):** 2933, 2854, 1742, 1660, 1517, 941. **HRMS (APCI-QUADRUPOLE-ORBITRAP) m/z:** $[M]^+$ Calcd for $[C_{29}H_{30}FNO]$ 428.2384; Found 428.2387.

(S,Z)-N-(4-(2-cyclohexylvinyl)phenyl)-2-(6-methoxynaphthalen-2-yl)propenamide 3am:



The title product was prepared using (S)-N-(4-ethynylphenyl)-2-(6-methoxynaphthalen-2-yl)propanamide (0.5 mmol, 164.5 mg) and cyclohexane (25 mmol, 2.7 mL) by following general procedure. Product was isolated as a mixture of E and Z using silica column chromatography with 62% (128 mg) yield. (Solvent gradient: 12% ethyl acetate in petroleum ether; gummy yellow solid). **^{1}H NMR (500 MHz, $CDCl_3$) (*Z*/*E* mixture 92:8)** δ 7.80 – 7.70 (m, 3H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 26.6 Hz, 4H), 7.06 (s, 1H), 6.29 – 6.15 (m, 1H, ***Z***+***E***), 6.07 (dd, *J* = 16.0, 7.0 Hz, 0.1H, ***E***), 5.42 (t, *J* = 11.0 Hz, 0.92H, ***Z***), 3.93 (s, 3H), 3.86 (q, *J* = 7.3 Hz, 1H), 2.50 (q, *J* = 11.0 Hz, 0.93H), 2.11 – 2.04 (m, 0.08H), 1.75 – 1.57 (m, 9H), 1.28 – 1.09 (m, 5H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 172.5, 157.9, 138.7, 136.2, 136.0, 134.1, 133.9, 129.3, 129.1, 129.1, 127.9, 126.4, 126.2, 119.4, 119.4, 105.7, 55.4, 48.1, 36.9, 33.2, 33.0, 26.0, 25.7, 18.6. **FT-IR (neat, cm^{-1}):** 2961, 2885, 2375, 1662, 684. **HRMS (ESI-QUADRUPOLE-ORBITRAP) m/z:** $[M+H]^+$ Calcd for $[C_{28}H_{31}NO_2]$ 414.2428; Found 414.2431.

Large scale reaction:

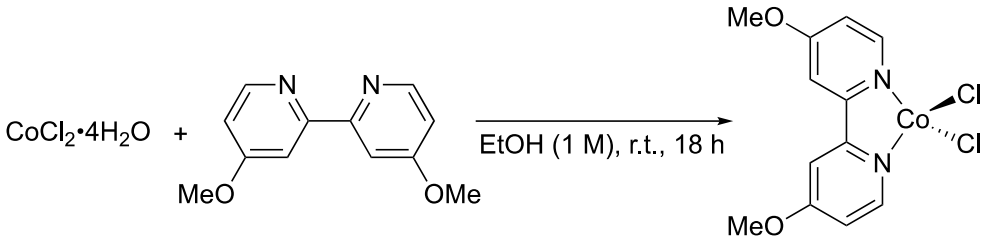


1a (4 mmol) **2a**, 50 eq. **3a**, 0.68 g (70%)

Oven dried 150 mL Schlenk round bottomed flask containing a stirring bar were introduced in an argon-filled glovebox where metal complex was carefully weighed and added. The flask was taken out of the glovebox, TBADT was added under nitrogen flow. Flask was capped with rubber septum. Solvent (degassed) was added to the mixture followed by 1-(tert-butyl)-4-ethynylbenzene (4 mmol, 632 mg) and cyclohexane (21.5 mL). Reaction mixture was irradiated with 390 nm LED (3 x 30 Watts). After 24 h, remaining portion of photocatalyst and cobalt complex were added under nitrogen flow and irradiated again until complete alkyne consumption (~4 days). Then, the volatiles were removed under reduced pressure, diluted with ethyl acetate and filtered through a pad of silica. After removal of solvent, crude material was purified using column chromatography (eluted with 2% ethyl acetate in hexane) to obtain 0.68 g (70%; Z/E mixture 92:8) of alkene product **3a**.

4. Synthesis of catalyst and starting materials

Synthesis of cobalt(II) chloride 4,4'-dimethoxy-2,2'-bipyridine complex:



To an oven dried Schlenk flask with a magnetic stir bar, a solution of $CoCl_2 \cdot 4H_2O$ (2.5 mmol, 0.5 g) in ethanol was made. In another oven dried round bottomed flask, a solution of 4,4'-dimethoxy-2,2'-bipyridine was prepared in ethanol (slightly warmed to get homogeneous solution) and added dropwise into cobalt chloride solution. After stirring overnight, a greenish blue solution with light green precipitate was obtained. Ethanol was removed using syringe and washed with small amount of ethanol. The obtained light green precipitate was dried vigorously under reduced pressure and transfer to a vial (inside Glove box). Yield obtained was 84% (0.86 g). **HRMS (ESI-QUADRUPOLE-ORBITRAP) m/z:** $[M+Na]^+$ Calcd for $[Cl_2CoC_{12}H_{12}N_2O_2Na]$ 367.9500; Found 367.9497.

Synthesis of alkynes:

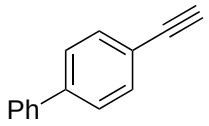
Alkynes **1a**, **1b**, **1c**, **1d**, **1g**, **1k**, **1l**, **1t**, **1w** are commercially available and used without further purification. All the alkanes were commercially available and used after CaH_2 distillation.

General procedure C for Corey-Fuchs alkyne synthesis:

Step 1: To an oven dried round bottomed flask with a magnetic stir bar, a solution of PPh_3 (4 eq.) and CBr_4 (2 eq.) in anhydrous DCM (0.15 M) was added and stirred at 0 °C for 30 minutes. The aldehyde was added over a period of five minutes, and the mixture continued stirring at 0 °C for one hour. Reaction was quenched with water and extracted with DCM (three times). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. To the crude product solution of 5% ethyl acetate in pet-ether was added and vigorously stirred for 15 minutes and filtered through a silica pad. Crude product was directly taken to the next step.

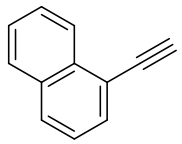
Step 2: An oven dried round bottomed flask with a magnetic stir bar was evacuated and refilled with nitrogen (3 times). A solution of gem-dibromo olefin (prepared in the previous step) in anhydrous THF (0.4 M) was made and the temperature was maintained at −78 °C. *n*-BuLi (2.1 eq., 1.6 M in *n*-hexane) was added over a period of 30 minutes and the mixture was stirred at −40 °C for 15 minutes then allowed to warm to room temperature and stirred for one hour. Reaction was quenched with water and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4, the solvent was removed under reduced pressure and the crude product was subjected to silica column chromatography.

4-ethynyl-1,1'-biphenyl 1e:



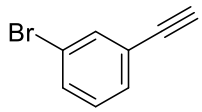
Title compound was synthesized using general procedure C (Corey-Fuchs reaction) starting from (1,1'-biphenyl)-4-carbaldehyde (5 mmol, 0.91 g). Title compound was obtained by doing silica column chromatography using 2% ethyl acetate in pet-ether and the overall yield was 0.7 g (overall 79%; waxy white solid). **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.61 – 7.54 (m, 6H), 7.48 – 7.42 (m, 2H), 7.40 – 7.34 (m, 1H), 3.13 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ: 141.6, 140.3, 132.6, 128.9, 127.8, 127.1, 127.1, 121.0, 83.6, 77.8. **FT-IR (neat, cm^{-1}):** 3286, 2989, 2105. **EI-MS (m/z):** [$C_{14}H_{10}$] $[M]^+$ 178.1. Literature.[9]

1-ethynylnaphthalene 1f:



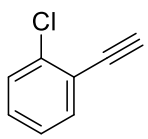
Title compound was synthesized using general procedure C (Corey-Fuchs reaction) starting from 1-naphthaldehyde (10 mmol, 1.56 g). Title compound was obtained by doing silica column chromatography using 1% ethyl acetate in pet-ether and the overall yield was 0.77 g (overall 51%; yellow oil). **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 8.38 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.76 (m, 1H), 7.60 (m, 1H), 7.53 (m, 1H), 7.44 (dd, *J* = 8.3, 7.2 Hz, 1H), 3.49 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ: 133.5, 133.1, 131.3, 129.3, 128.3, 127.0, 126.5, 126.1, 125.1, 119.8, 82.0, 81.8. **FT-IR (neat, cm^{-1}):** 3281, 3157, 1394, 780, 788. **EI-MS (m/z):** [$C_{12}H_8$] $[M]^+$ 152.1. Literature.[10]

1-bromo-3-ethynylbenzene 1h:



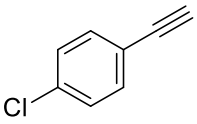
Title compound was synthesized using general procedure C (Corey-Fuchs reaction), starting from 3-bromobenzaldehyde (8 mmol, 1.47 g). Title compound was obtained by doing silica column chromatography and the overall yield was 0.96 g (overall yield 67%; solvent gradient: 1% ethyl acetate in pet-ether; pale yellow gummy solid). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.64 (t, J = 1.8 Hz, 1H), 7.49 (d, J = 8.2 Hz, 1H), 7.42 (d, J = 7.8 Hz, 1H), 7.19 (t, J = 7.9 Hz, 1H), 3.12 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 134.9, 132.1, 130.7, 129.8, 124.1, 122.1, 82.1, 78.6. **FT-IR (neat, cm^{-1}):** 3064, 2959, 1590, 1560, 996, 818. **EI-MS (m/z):** [C_8H_5Br] $[M]^+$ 179.9, 181.9. Literature.[11]

1-chloro-2-ethynylbenzene 1i:



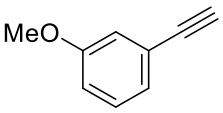
Title compound was synthesized using general procedure C (Corey-Fuchs reaction), starting from 2-chlorobenzaldehyde (10 mmol, 1.4 g). Title compound was obtained by doing silica column chromatography and the overall yield was 0.81 g (overall yield 60%; solvent gradient: 1% ethyl acetate in pet-ether; white gummy solid). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.53 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.25 (m, 1H), 7.25 – 7.19 (m, 1H), 3.37 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 136.3, 134.0, 129.9, 129.4, 126.5, 122.1, 82.4, 80.3. **FT-IR (neat, cm^{-1}):** 3289, 2101, 1600, 1487, 1072, 1023. **EI-MS (m/z):** [C_8H_5Cl] $[M]^+$ 136.1. Literature.[9]

1-chloro-4-ethynylbenzene 1j:



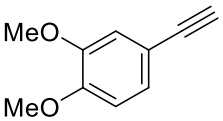
Title compound was synthesized using general procedure C (Corey-Fuchs reaction) starting from 4-chlorobenzaldehyde (15.1 mmol, 2.16 g, 1.8 mL). Title compound was obtained by doing silica column chromatography using only pet-ether and the overall yield was 1.42 g (69%; White solid; Melting point: 43-45 ^{o}C). **^{1}H NMR (500 MHz, CDCl$_3$)** δ: 7.44 – 7.40 (m, 2H), 7.32 – 7.28 (m, 2H), 3.11 (s, 1H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ: 134.9, 133.4, 128.7, 120.6, 82.6, 78.2. **FT-IR (neat, cm^{-1}):** 3310, 2114, 1489, 1081, 831. **EI-MS (m/z):** [C_8H_5Cl] $[M]^+$ 136.1. Literature.[9]

1-ethynyl-3-methoxybenzene 1m:



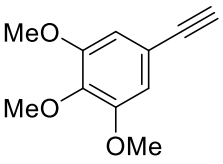
Title compound was synthesized using general procedure C (Corey-Fuchs reaction) starting from 3-methoxybenzaldehyde (12 mmol, 1.63 g). Title compound was obtained by doing silica column chromatography using 2% ethyl acetate in pet-ether and the overall yield was 1.15 g (73%; colourless oil). **^{1}H NMR (500 MHz, CDCl$_3$)** δ: 7.23 (t, *J* = 7.9 Hz, 1H), 7.09 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.02 (dd, *J* = 2.7, 1.4 Hz, 1H), 6.91 (dt, *J* = 8.4, 1.7 Hz, 1H), 3.80 (s, 3H), 3.06 (s, 1H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ: 159.3, 129.4, 124.7, 123.1, 117.0, 115.5, 83.6, 55.3. **FT-IR (neat, cm^{-1}):** 3305, 2110, 1491, 1054. **EI-MS (m/z):** [C_9H_8O] $[M]^+$ 132.1. Literature.[12]

4-ethynyl-1,2-dimethoxybenzene 1n:



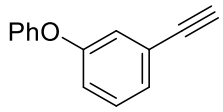
Title compound was synthesized using general procedure C (Corey-Fuchs reaction) starting from 3,4-dimethoxybenzaldehyde (10 mmol, 1.66 g). Title compound was obtained by doing silica column chromatography using 3% ethyl acetate in pet-ether and the overall yield was 1.33 g (overall 82%; White solid). **^{1}H NMR (500 MHz, CDCl$_3$)** δ: 7.09 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.97 (d, *J* = 2.0 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 3.86 (d, *J* = 5.3 Hz, 6H), 3.00 (s, 1H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ: 149.9, 148.6, 125.5, 114.7, 114.2, 110.9, 83.8, 75.7, 55.9. **FT-IR (neat, cm^{-1}):** 3250, 2971, 1597, 1452, 1263, 1035, 860. **EI-MS (m/z):** [$C_{10}H_{10}O_2$] $[M]^+$ 162.1. Literature.[9]

5-ethynyl-1,2,3-trimethoxybenzene 1o:



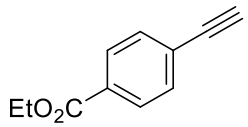
Title compound was synthesized using general procedure C (Corey-Fuchs reaction) starting from 3,4,5-trimethoxybenzaldehyde (10 mmol, 1.96 g). Title compound was obtained by doing silica column chromatography using 4% ethyl acetate in pet-ether and the overall yield was 1.53 g (overall 80%; pale yellow solid). **^{1}H NMR (500 MHz, CDCl$_3$)** δ: 6.71 (s, 2H), 3.84 (s, 3H), 3.83 (s, 6H), 3.02 (s, 1H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ: 153.1, 139.3, 117.1, 109.3, 83.7, 76.3, 60.9, 56.1. **FT-IR (neat, cm^{-1}):** 3244, 2990, 1965, 1570, 1452, 1001, 951. **EI-MS (m/z):** [$C_{11}H_{12}O_3$] $[M]^+$ 192.1. Literature.[13]

1-ethynyl-3-phenoxybenzene 1p:



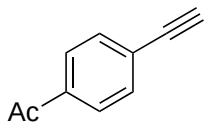
Title compound was synthesized using general procedure C (Corey-Fuchs reaction) starting from 3-phenoxybenzaldehyde (10 mmol, 1.98 g). Title compound was obtained by doing silica column chromatography using 3% ethyl acetate in pet-ether and the overall yield was 1.49 g (overall 77%; pale yellow oil). **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.40 – 7.32 (m, 2H), 7.32 – 7.25 (m, 2H), 7.26 – 7.20 (m, 1H), 7.17 – 7.09 (m, 2H), 7.05 – 6.99 (m, 3H), 3.07 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ: 157.3, 156.6, 129.9, 129.8, 127.0, 123.8, 123.5, 122.0, 119.6, 119.3, 83.0, 77.6. **FT-IR (neat, cm^{-1}):** 3251, 3001, 2940, 1514, 1138. **EI-MS (m/z):** $[C_{14}H_{10}O]$ $[M]^+$ 194.1. Literature.[10]

ethyl 4-ethynylbenzoate 1q:



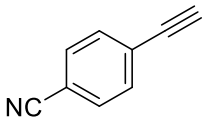
Title compound was synthesized using general procedure C (Corey-Fuchs reaction) with base modification in the second step [Cs_2CO_3 (2.5 eq.) was used instead of *n*-BuLi, room temperature, and DMF as solvent], starting from ethyl 4-formylbenzoate (12 mmol, 2.13 g). Title compound was obtained by doing silica column chromatography and the overall yield was 1.36 g (overall yield 65%; solvent gradient: 6% ethyl acetate in pet-ether; yellow oil). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.22 (s, 1H), 1.39 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 166.0, 132.1, 130.5, 129.4, 126.6, 82.9, 80.0, 61.2, 14.3. **FT-IR (neat, cm^{-1}):** 2983, 1753, 1064. **EI-MS (m/z):** $[C_{11}H_{10}O_2]$ $[M]^+$ 174.1. Literature.[14]

1-(4-ethynylphenyl)ethan-1-one 1r:



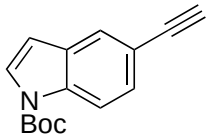
4'-Bromoacetophenone (1 g, 5.2 mmol) was added to a round bottom flask with a magnetic stirring bar under argon. THF (16 mL) was added, followed by bis(triphenylphosphine) palladium dichloride (185 mg, 0.26 mmol) and copper(I) iodide (100 mg, 0.52 mmol) in one portion. This mixture was sparged with argon for 30 min and then trimethylsilylacetylene (1.04 g, 105 mmol) was added and the mixture heated to reflux until starting material consumption. The mixture was cooled to room temperature and KF (0.61 g, 10.5 mmol) was added along with MeOH (11 mL), and the mixture allowed to stir for 30 min. Solvents were removed from the the mixture and the crude crude was purified using column chromatography (using 5% ethyl acetate in pet-ether) and afforded 0.60 g (80%) of 4'-ethynylacetophenone (yellow oil). **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.90 (d, *J* = 8.1 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 3.25 (s, 1H), 2.59 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ: 197.2, 136.4, 132.2, 128.7, 126.8, 82.7, 80.3, 26.6. **FT-IR (neat, cm^{-1}):** 3221, 2106. **EI-MS (m/z):** $[C_{14}H_8O]$ $[M]^+$ 144.1. Literature.[15]

4-ethynylbenzonitrile 1s:



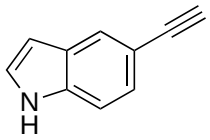
Title compound was synthesized using general procedure C (Corey-Fuchs reaction) with base modification in the second step [DBU (4 eq.) was used instead of *n*-BuLi, room temperature, and acetonitrile as solvent][10], starting from 4-formylbenzonitrile (10 mmol, 1.27 g). Title compound was obtained by doing silica column chromatography and the overall yield was 0.91 g (overall yield 72%; solvent gradient: 5% ethyl acetate in pet-ether; yellow oil). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.62 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 3.30 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 132.7, 132.0, 127.0, 118.2, 112.4, 81.9, 81.5. **FT-IR (neat, cm^{-1}):** 3234, 2225, 1602, 1407, 731. **EI-MS (m/z):** [C_9H_5N] $[M]^+$ 127.1. Literature.[10]

tert-butyl 5-ethynyl-1H-indole-1-carboxylate 1u:



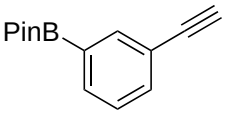
Title compound was prepared according to the reported procedure.[16] **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 8.09 (d, *J* = 8.7 Hz, 1H), 7.72 (d, *J* = 1.6 Hz, 1H), 7.61 (d, *J* = 3.7 Hz, 1H), 7.44 (dd, *J* = 8.5, 1.6 Hz, 1H), 6.54 (d, *J* = 3.7 Hz, 1H), 3.04 (s, 1H), 1.67 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ: 149.5, 135.1, 130.4, 128.2, 126.9, 125.1, 116.2, 115.2, 107.0, 84.4, 84.1, 75.8, 28.2. **FT-IR (neat, cm^{-1}):** 3299, 2977, 1735, 1460, 1250, 1160. **EI-MS (m/z):** [$C_{15}H_{15}NO_2$] $[M]^+$ 241.1. Literature.[17]

5-ethynyl-1H-indole 1v:



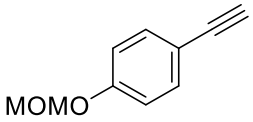
Title compound was prepared according to the reported procedure.[18] **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 8.20 (s, 1H), 7.84 (s, 1H), 7.33 (s, 2H), 7.23 (t, *J* = 2.9 Hz, 1H), 6.55 (s, 1H), 3.01 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ: 135.7, 127.7, 126.0, 125.4, 125.2, 113.2, 111.1, 102.9, 85.3, 74.7. **FT-IR (neat, cm^{-1}):** 3425, 3281, 1616, 1339, 1301. **EI-MS (m/z):** [$C_{10}H_7N$] $[M]^+$ 141.0. Literature.[19]

2-(3-ethynylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 1x:



Title compound was prepared according to the literature procedure.[20] **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.75 (d, *J* = 7.1 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 2H), 3.14 (s, 1H), 1.34 (s, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ: 134.6, 131.3, 124.8, 84.0, 83.8, 82.9, 78.4, 24.9. **EI-MS (m/z):** [$C_{14}H_{17}BO_2$] $[M]^+$ 228.1. Literature.[20]

1-ethynyl-4-(methoxymethoxy)benzene 1y:

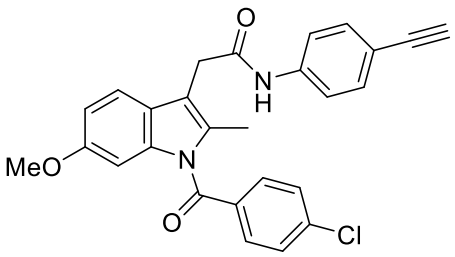


Title compound was synthesized using general procedure C (Corey-Fuchs reaction) starting from 4-(methoxymethoxy)benzaldehyde (10 mmol, 1.66 g). Title compound was obtained by doing silica column chromatography using 4% ethyl acetate in pet-ether and the overall yield was 1.05 g (overall

65%; colourless oil). **^{1}H NMR (500 MHz, $CDCl_3$)** δ: 7.43 (d, *J* = 8.7 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 5.18 (s, 2H), 3.47 (s, 3H), 3.00 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ: 157.6, 133.6, 116.2, 115.4, 94.3, 83.5, 76.1, 56.1. **FT-IR (neat, cm^{-1}):** 3267, 2989, 1254. **EI-MS (m/z):** $[C_{10}H_{10}O_2]$ $[M]^+$ 162.1. Literature.[21]

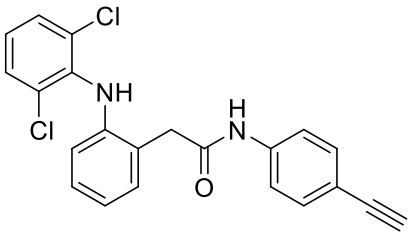
2-(1-(4-chlorobenzoyl)-6-methoxy-2-methyl-1H-indol-3-yl)-N-(4-ethynylphenyl)acetamide 1aj:

A 100 mL round bottomed flash was loaded with 2-(1-(4-chlorobenzoyl)-6-methoxy-2-methyl-1H-indol-3-yl)acetic acid [Indometacin] (0.5 g, 1.4 mmol) and 4-ethynylaniline (164 mg, 1.4 mmol) followed by DCM (10 mL). Then, EDC·HCL was added portion wise to the reaction mixture and stirred until the complete consumption of starting materials. Solvents were removed under reduced pressure and crude material was purified using column chromatography (using 35% ethyl acetate in pet-ether). A pale yellow waxy solid was obtained in 85% yield (540 mg). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.42 – 7.34 (m, 5H), 6.93 (d, *J* = 2.5 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 1H), 6.72 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.80 (s, 5H), 3.03 (s, 1H), 2.44 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 168.4, 168.2, 156.5, 139.8, 137.9, 136.8, 133.5, 132.9, 131.3, 131.0, 130.1, 129.3, 119.6, 118.1, 115.3, 112.5, 112.1, 100.7, 83.3, 55.8, 33.4, 13.4. **FT-IR (neat, cm^{-1}):** 3288, 3261, 1663, 1320, 838. **HRMS (ESI-QUADRUPOLE-ORBITRAP) m/z:** $[M+H]^+$ Calcd for $[C_{27}H_{21}ClN_2O_3]$ 457.1313; Found 457.1315.

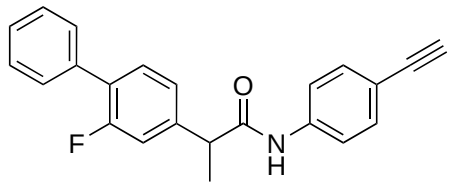


2-(2-((2,6-dichlorophenyl)amino)phenyl)-N-(4-ethynylphenyl)acetamide 1ak:

Title compound was prepared by following same procedure that was used to make compound **1aj**, using 2-(2-((2,6-dichlorophenyl)amino)phenyl)acetic acid [Diclofenac] (0.6 g, 2.0 mmol) and 4-ethynylaniline (234 mg, 2.0 mmol). Crude compound was purified using column chromatography (using 40% ethyl acetate in pet-ether) and 0.55 g was obtained (70%, waxy brown solid). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.62 (s, 1H), 7.49 – 7.38 (m, 4H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.06 – 6.95 (m, 2H), 6.74 (s, 1H), 6.54 (d, *J* = 8.1 Hz, 1H), 3.85 (s, 2H), 3.03 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 169.4, 142.6, 138.1, 137.2, 132.9, 131.1, 130.2, 129.0, 128.6, 124.8, 123.6, 122.0, 119.6, 117.9, 117.6, 83.4, 42.0. **FT-IR (neat, cm^{-1}):** 3077, 1631, 730. **HRMS (ESI-QUADRUPOLE-ORBITRAP) m/z:** $[M+H]^+$ Calcd for $[C_{22}H_{16}Cl_2N_2O]$ 395.0712; Found 395.0715.

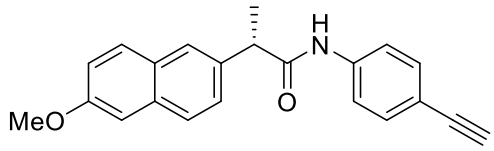


N-(4-ethynylphenyl)-2-(2-fluoro-[1,1'-biphenyl]-4-yl)propenamide 1al:



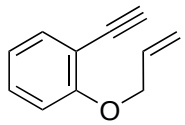
Title compound was prepared by following same procedure that was used to make compound **1aj**, using 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoic acid [Flurbiprofen] (0.49 g, 2.0 mmol) and 4-ethynylaniline (234 mg, 2.0 mmol). Crude compound was purified using column chromatography (using 25% ethyl acetate in pet-ether) and 0.54 g was obtained (80%, waxy white solid). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.54 (d, J = 7.6 Hz, 2H), 7.47 – 7.37 (m, 7H), 7.25 – 7.15 (m, 3H), 3.73 (q, J = 7.1 Hz, 1H), 3.04 (s, 1H), 1.62 (d, J = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 171.6, 159.9 (d, J = 249.6 Hz), 142.0 (d, J = 7.4 Hz), 138.2, 135.2, 132.9, 131.4 (d, J = 4.0 Hz), 128.9 (d, J = 3.0 Hz), 128.5, 128.4 (d, J = 13.7 Hz), 127.9, 83.3, 76.9, 47.7, 18.6. **^{19}F NMR (471 MHz, CDCl$_3$)** δ -116.5. **FT-IR (neat, cm^{-1}):** 2990, 1647, 984. **HRMS (ESI-QUADRUPOLE-ORBITRAP) m/z:** $[M+H]^+$ Calcd for $[C_{23}H_{18}FNO]$ 344.1445; Found 344.1450.

(S)-N-(4-ethynylphenyl)-2-(6-methoxynaphthalen-2-yl)propenamide 1am:



Title compound was prepared by following above procedure using (S)-2-(6-methoxynaphthalen-2-yl)propanoic acid [Naproxen] (0.6 g, 2.6 mmol) and 4-ethynylaniline (304 mg, 2.6 mmol). Crude compound was purified using column chromatography (using 20% ethyl acetate in pet-ether) and 0.7 g was obtained (82%, waxy tan solid). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.78 – 7.70 (m, 3H), 7.43 – 7.35 (m, 4H), 7.23 – 7.11 (m, 3H), 3.93 (s, 3H), 3.84 (q, *J* = 7.1 Hz, 1H), 3.02 (s, 1H), 1.66 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 172.6, 158.0, 138.3, 135.7, 134.0, 132.9, 129.3, 129.0, 128.0, 126.4, 126.1, 119.5, 119.2, 117.6, 105.7, 83.4, 55.4, 48.1, 29.7, 18.5. **FT-IR (neat, cm^{-1}):** 3226, 3171, 2372, 1661, 1527, 754, 683. **HRMS (ESI-QUADRUPOLE-ORBITRAP) m/z:** $[M+H]^+$ Calcd for $[C_{22}H_{19}NO_2]$ 330.1489; Found 330.1493.

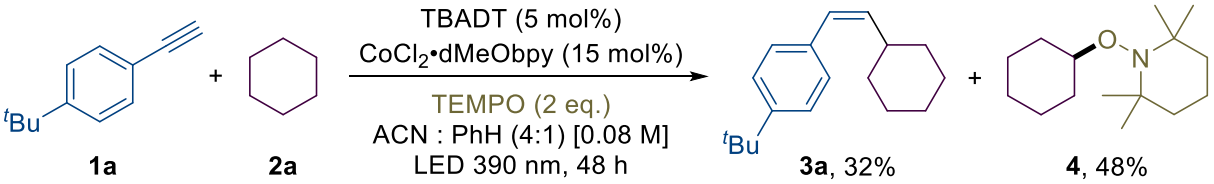
1-(allyloxy)-2-ethynylbenzene 1aq:



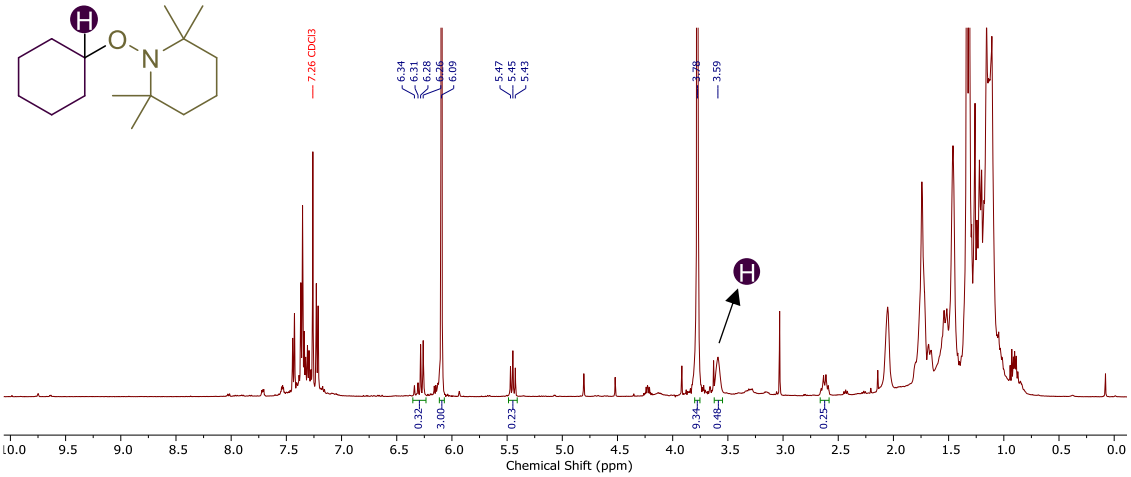
Title compound was prepared according to the literature procedure.[22] **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.47 (d, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 8.0 Hz, 1H), 6.96 – 6.84 (m, 2H), 6.07 (m, 1H), 5.47 (d, *J* = 17.2 Hz, 1H), 5.30 (d, *J* = 10.6 Hz, 1H), 4.64 (d, *J* = 5.0 Hz, 2H), 3.30 (s, 1H). **^{13}C NMR (126 MHz, CDCl$_3$)** δ 159.7, 134.2, 132.9, 130.1, 120.7, 117.6, 112.4, 111.8, 81.2, 80.1, 69.3. **EI-MS (m/z):** $[C_{11}H_{10}O]$ $[M]^+$ 158.1. Literature.[23]

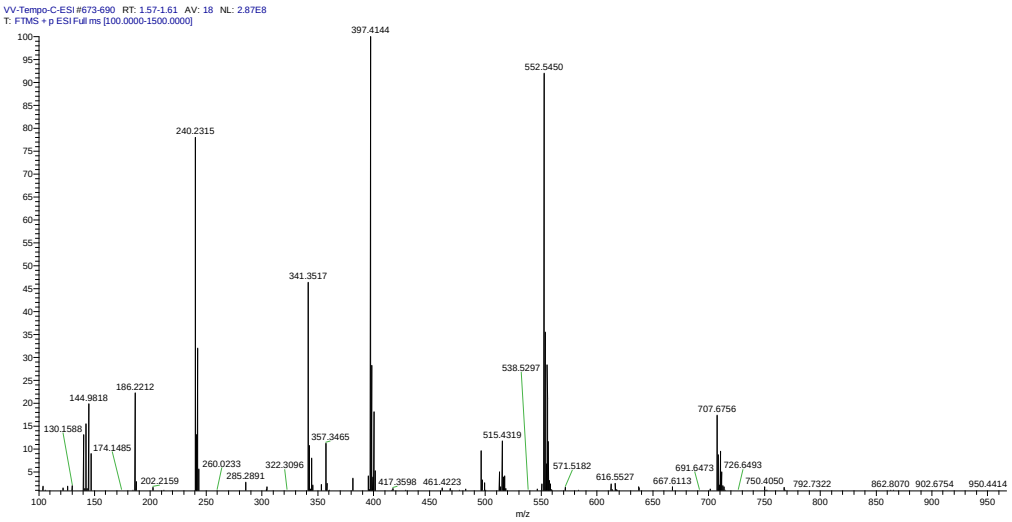
5. Mechanistic studies:

Radical trap experiment:

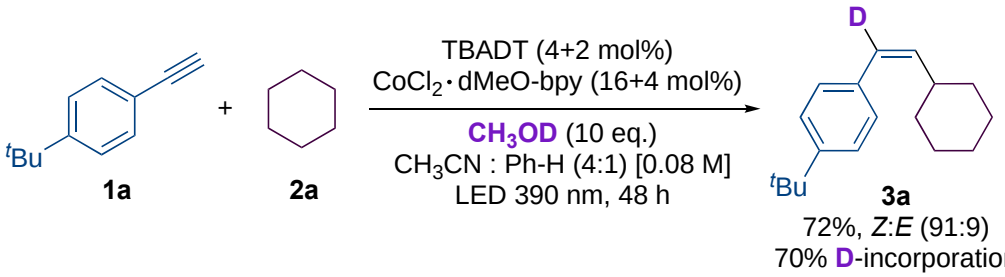


Oven dried 10 mL screw-capped culture tubes containing a stirring bar were introduced in an argon-filled glovebox where cobalt complex (11.2 µmol) was carefully weighed and added. The tubes were taken out of the glovebox, TBADT (18 µmol, 59 mg) and TEMPO (0.3 mmol, 47 mg) were added under nitrogen flow. Tubes were capped with rubber septum, evacuated (< 1 mbar) and backfilled with nitrogen three times. Solvent was added to the mixture followed by 1-(tert-butyl)-4-ethynylbenzene (0.15 mmol, 23.7 mg, 27 µL) and cyclohexane (0.8 mL) were added to the tube. Rubber septum was replaced with screw cap and irradiated with 390 nm LED. Then, internal standard (1,3,5-trimethoxybenzene, 0.15 mmol, 25 mg) was added into the tube and diluted with ethyl acetate. After stirring for 24 h, an aliquot was taken from the reaction tube and analysed using GC. **HRMS (ESI-QUADRUPOLE-ORBITRAP) m/z:** $[M+H]^+$ Calcd for $[C_{15}H_{29}NO]$ 240.2322; Found 240.2315. Literature.[24]

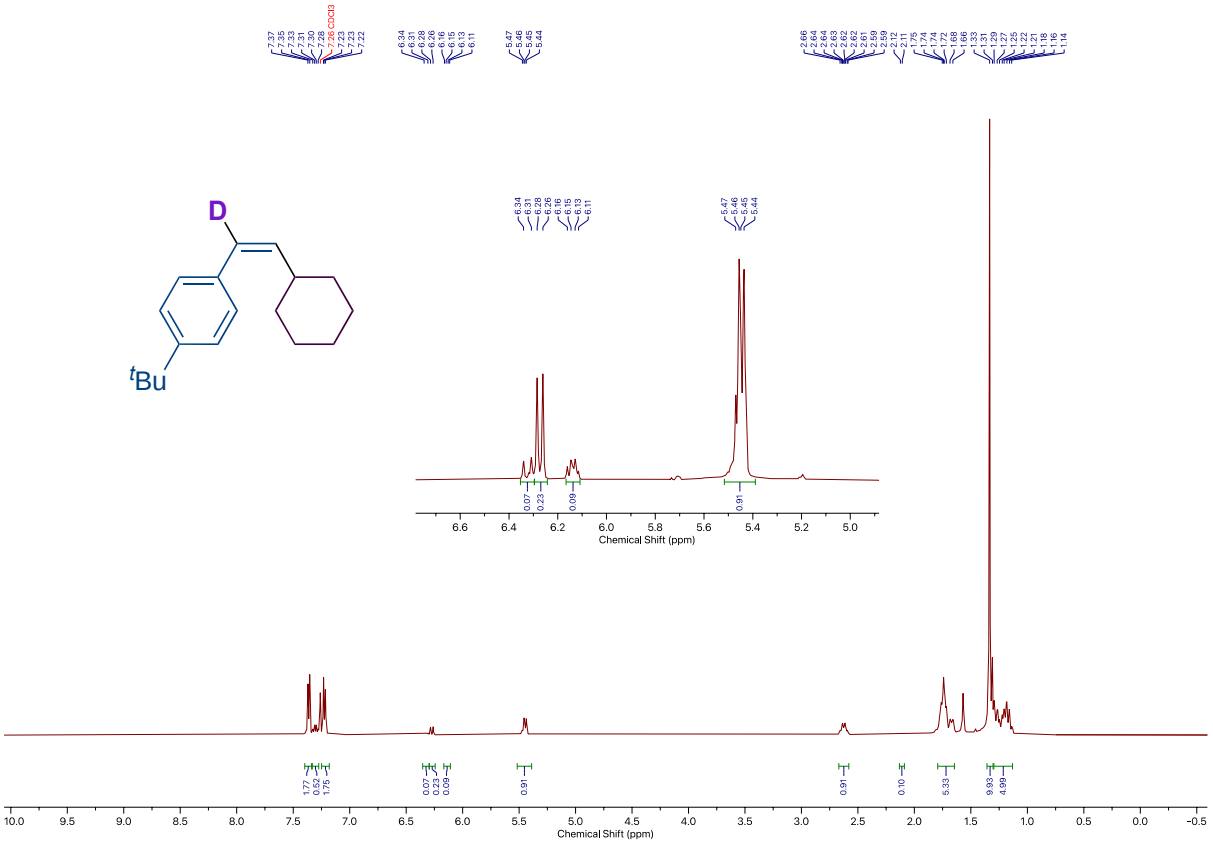


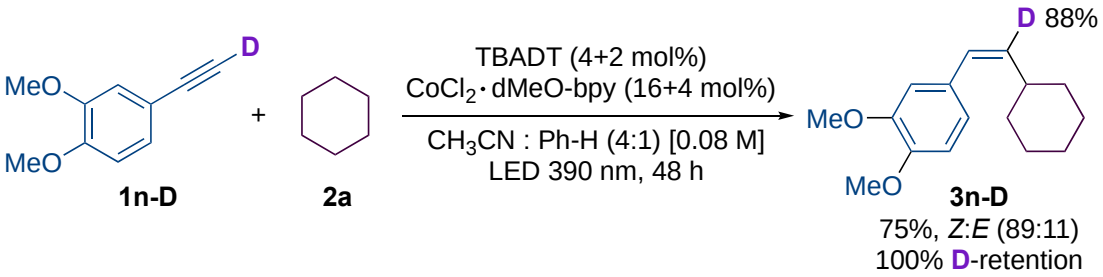


Deuterium labelling experiments:

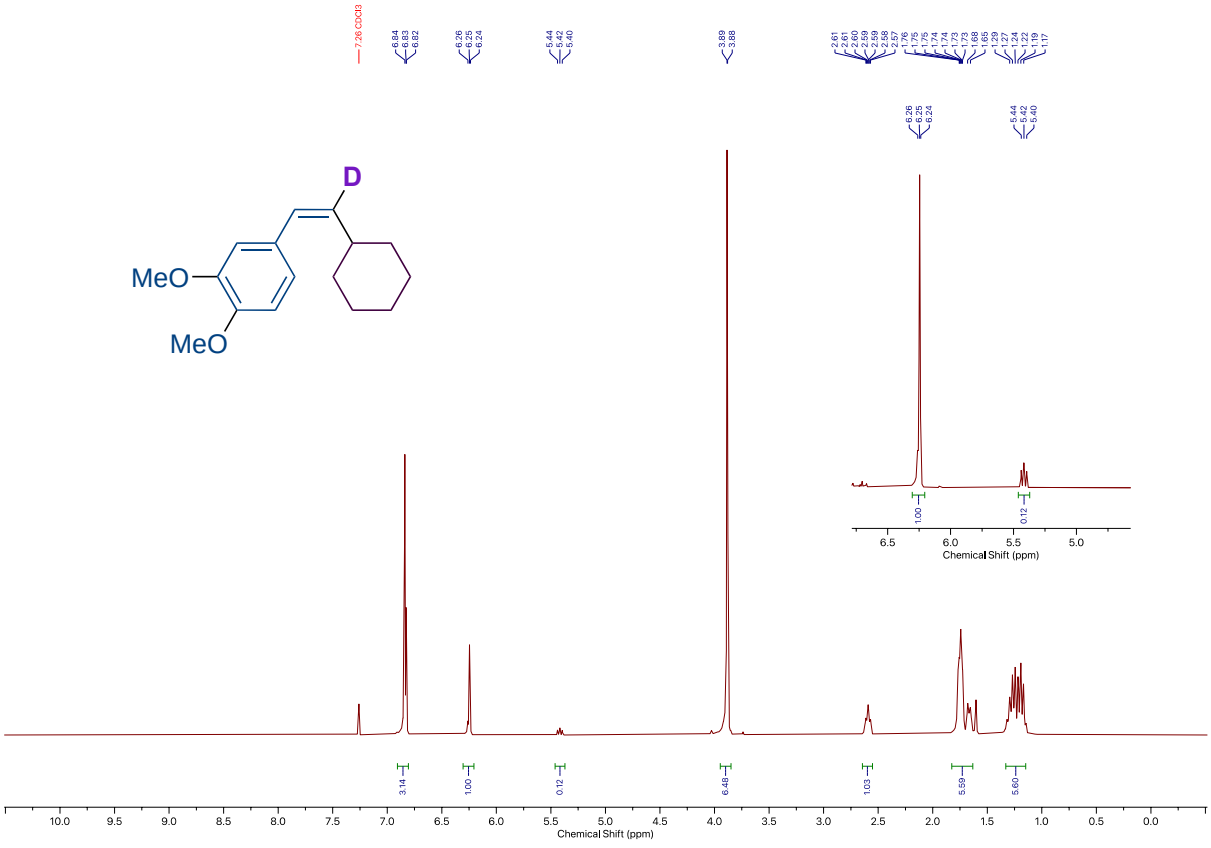


Oven dried 10 mL screw-capped culture tubes containing a stirring bar were introduced in an argon-filled glovebox where cobalt complex (11.2 µmol) was carefully weighed and added. The tubes were taken out of the glovebox, TBADT (18 µmol, 59 mg) was added under nitrogen flow. Tubes were capped with rubber septum, evacuated (< 1 mbar) and backfilled with nitrogen three times. Solvent was added to the mixture followed by 1-(tert-butyl)-4-ethynylbenzene (0.15 mmol, 23.7 mg, 27 µL), cyclohexane (0.8 mL) and methanol-D_4 (10 eq.) were added to the tube. Rubber septum was replaced with screw cap and irradiated with 390 nm LED. After 48 h reaction time, solvents were removed under reduced pressure and crude was purified using column chromatography.

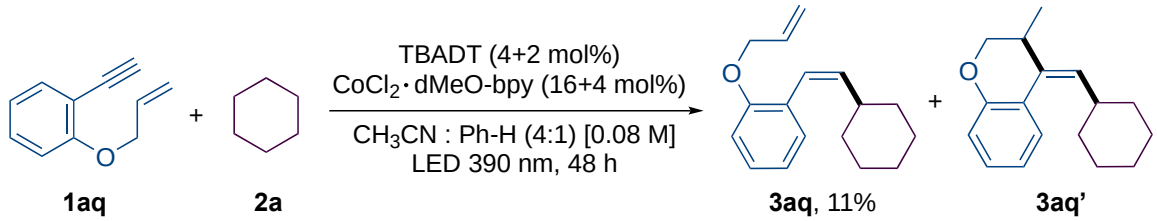




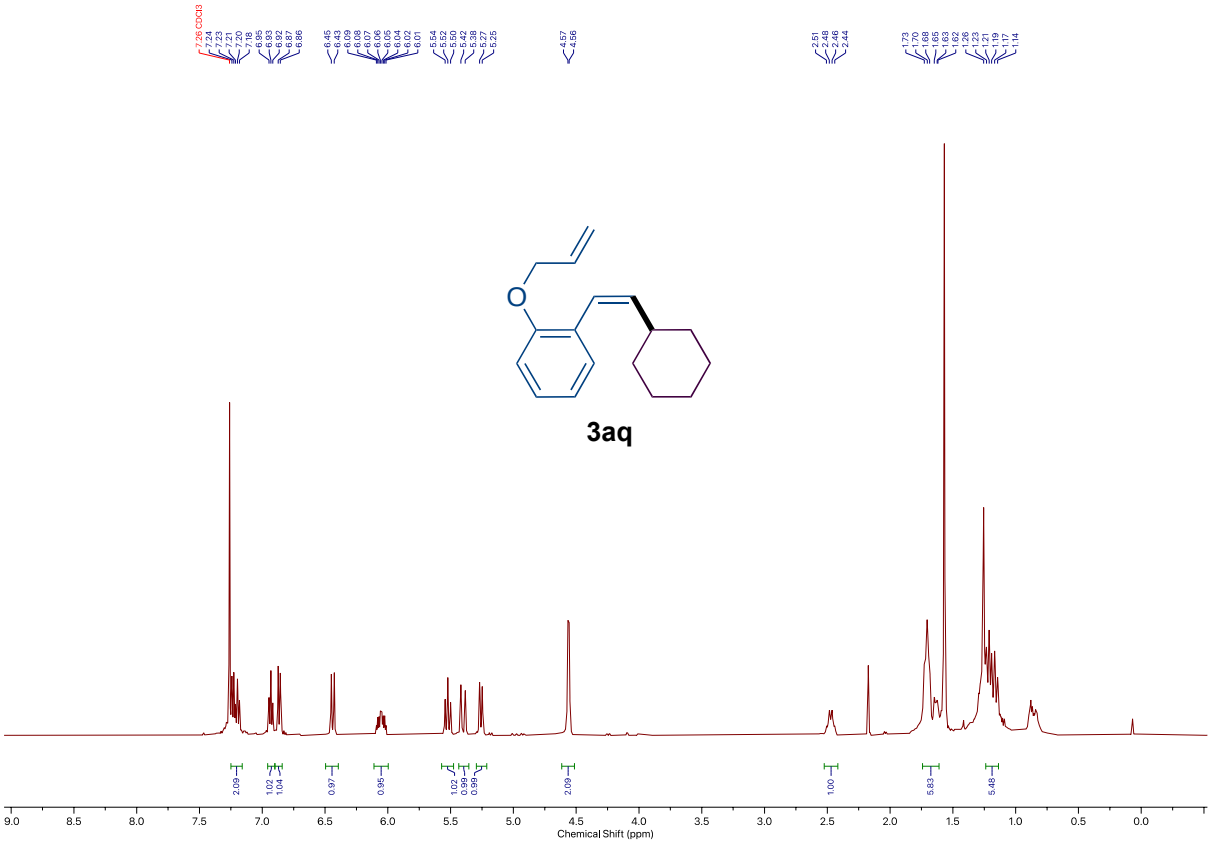
Oven dried 10 mL screw-capped culture tubes containing a stirring bar were introduced in an argon-filled glovebox where cobalt complex (11.2 µmol) was carefully weighed and added. The tubes were taken out of the glovebox, TBADT (18 µmol, 59 mg) was added under nitrogen flow. Tubes were capped with rubber septum, evacuated (< 1 mbar) and backfilled with nitrogen three times. Solvent was added to the mixture followed by 4-(ethynyl-d)-1,2-dimethoxybenzene[25] (0.15 mmol, 23.7 mg, 27 µL), cyclohexane (0.8 mL) and methanol-D_4 (10 eq.) were added to the tube. Rubber septum was replaced with screw cap and irradiated with 390 nm LED. After 48 h reaction time, solvents were removed under reduced pressure and crude was purified using column chromatography.



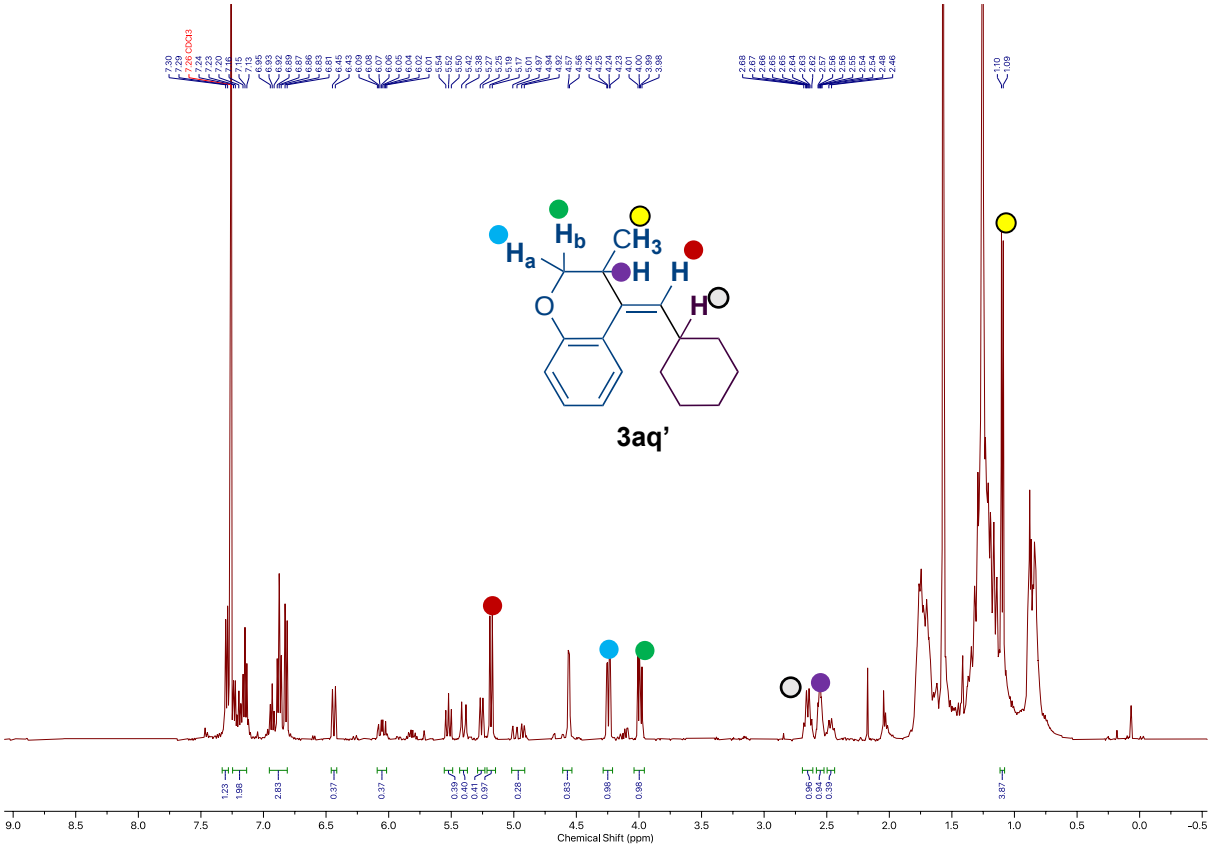
Radical clock experiment:

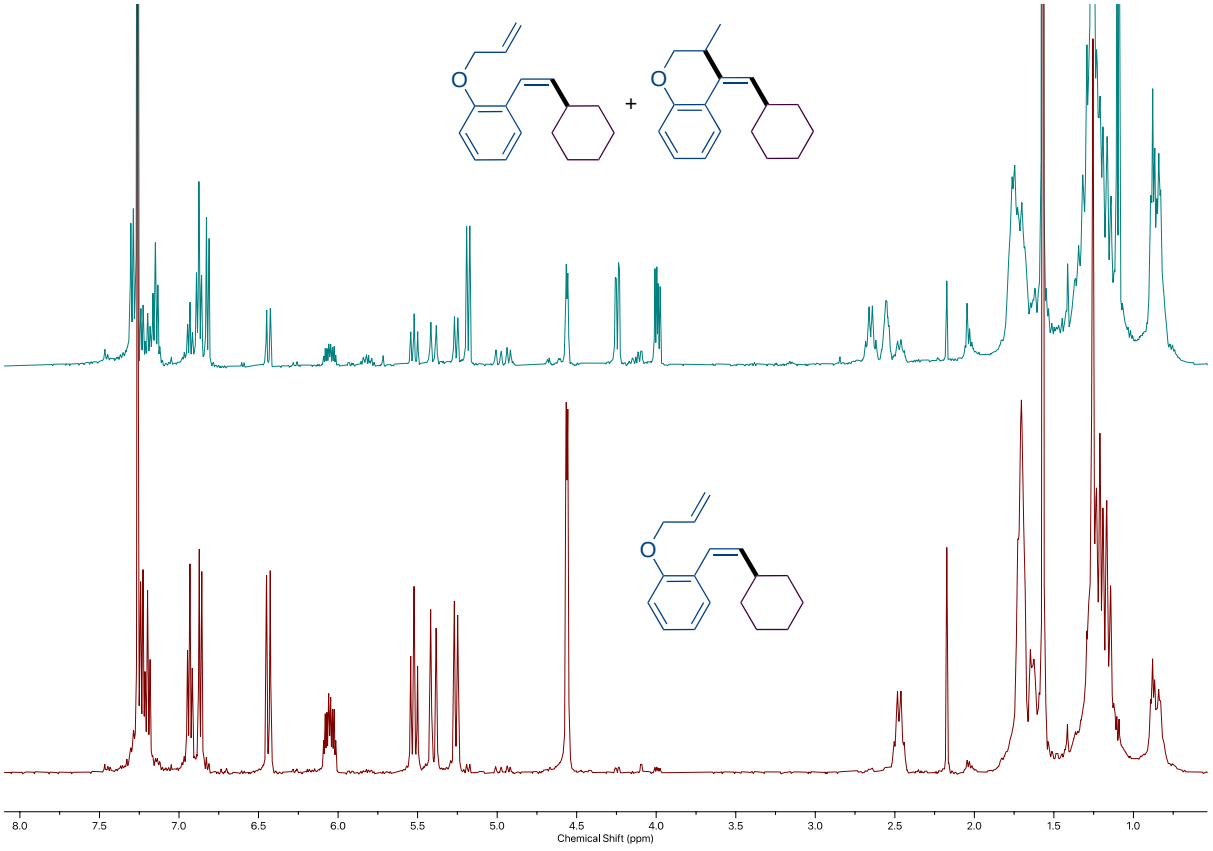


Oven dried 10 mL screw-capped culture tubes containing a stirring bar were introduced in an argon-filled glovebox where cobalt complex (11.2 µmol) was carefully weighed and added. The tubes were taken out of the glovebox, TBADT (18 µmol, 59 mg) was added under nitrogen flow. Tubes were capped with rubber septum, evacuated (< 1 mbar) and backfilled with nitrogen three times. Solvent was added to the mixture followed by 1-(allyloxy)-2-ethynylbenzene (0.15 mmol, 23.7 mg) and cyclohexane (0.8 mL) were added to the tube. Rubber septum was replaced with screw cap and irradiated with 390 nm LED. After 48 h reaction time, solvents were removed under reduced pressure and products were purified using column chromatography. [compounds **3aq** and **3aq'** has same R_f]



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.16 (m, 2H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.44 (d, *J* = 11.7 Hz, 1H), 6.11 – 6.00 (m, 1H), 5.52 (t, *J* = 10.9 Hz, 1H), 5.40 (d, *J* = 17.3 Hz, 1H), 5.26 (d, *J* = 10.5 Hz, 1H), 4.56 (d, *J* = 4.9 Hz, 2H), 2.52 – 2.42 (m, 1H), 1.77 – 1.61 (m, 5H), 1.28 – 1.11 (m, 5H). **HRMS (APCI-QUADRUPOLE-ORBITRAP) m/z:** $[M]^+$ Calcd for $[C_{17}H_{22}O]$ 242.1671; Found 242.1668.

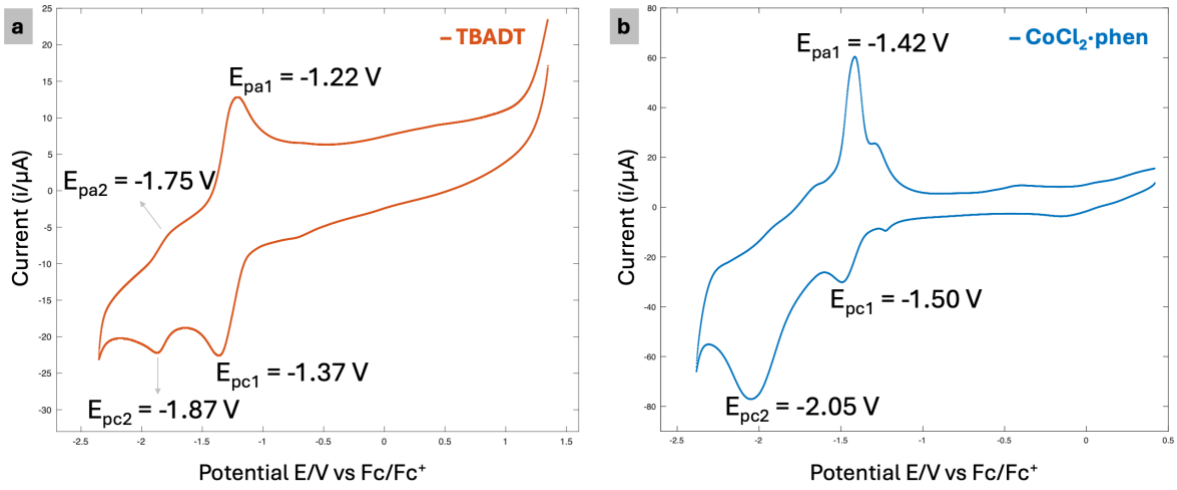

Ha
Hb
CH3
H
H
H
O
3aq'
Chemical Shift (ppm)


O
+
O
O
Chemical Shift (ppm)

Cyclic voltammetry:

To provide insight of intermediate formed in the catalytic cycle, cyclic voltametric studies were conducted for TBADT and $CoCl_2$·phen complex. Cyclic voltammetry experiments were performed in a three-electrode cell connected to nitrogen at room temperature in 0.1 M Bu_4NPF_6 as electrolyte with glassy carbon as working electrode, Pt wire as counter electrode and Pt wire as pseudo reference electrode. Each sample was then calibrated to a Fc/Fc^+ reference potential, 0.5 mM Fc. Scan rate was set to 0.1 V/s.

CVs are plotted in IUPAC convention, with negative currents corresponding to the reduction (E_{pa}, E_{pc} are peak anodic and peak cathodic potentials).



6. Reference:

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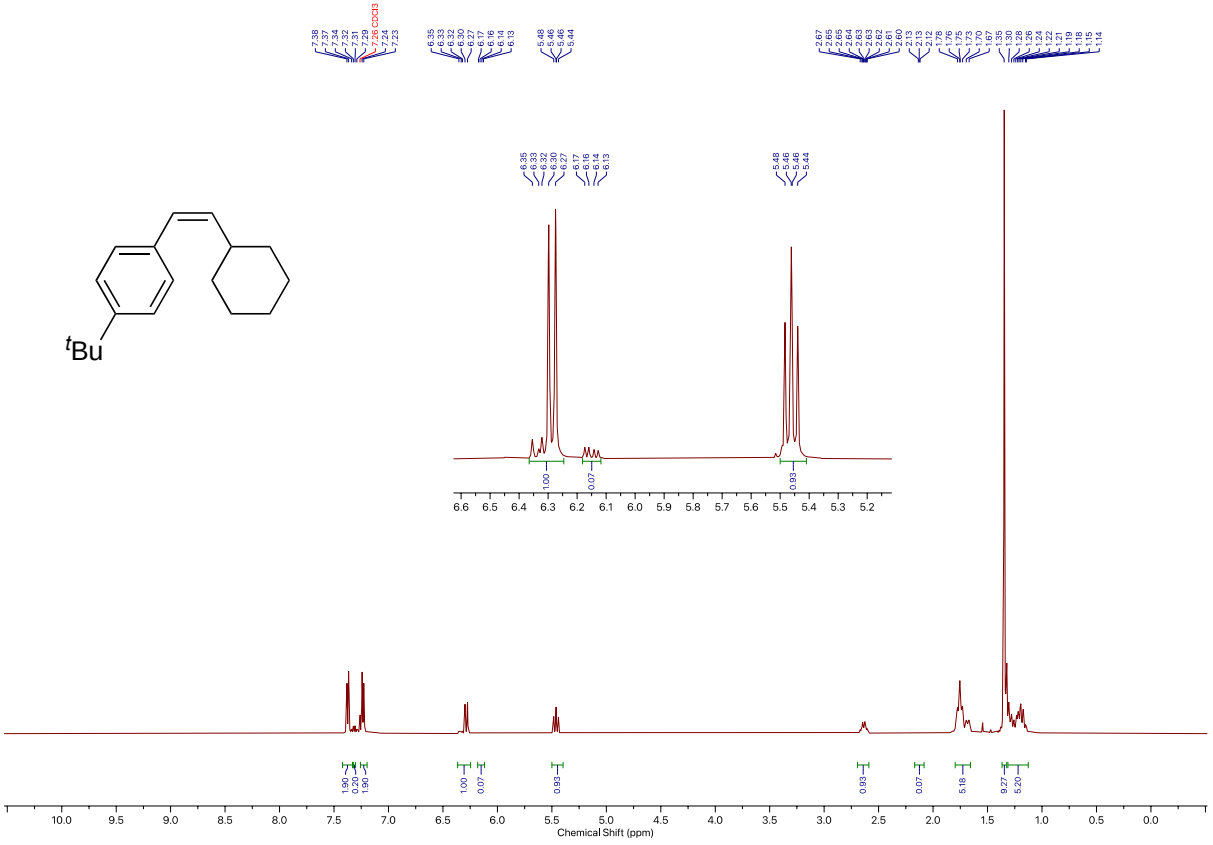
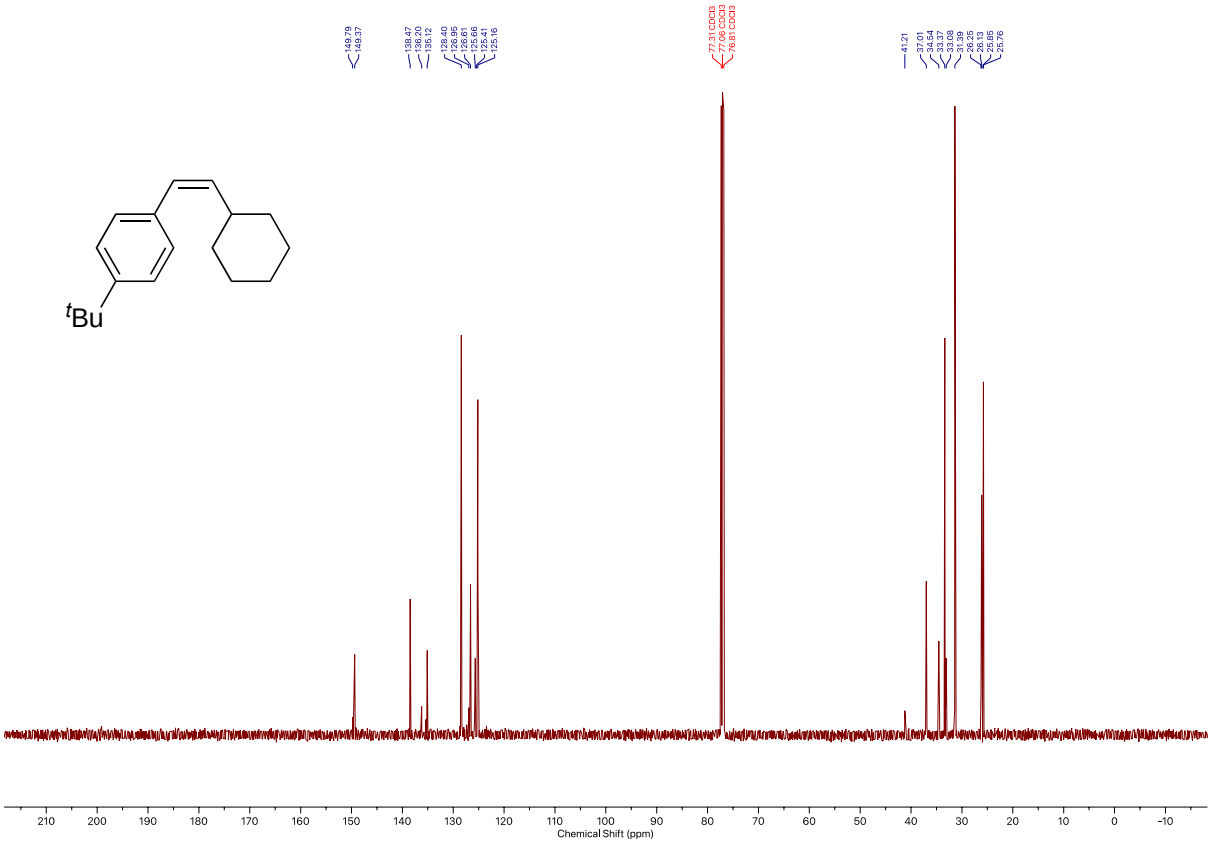
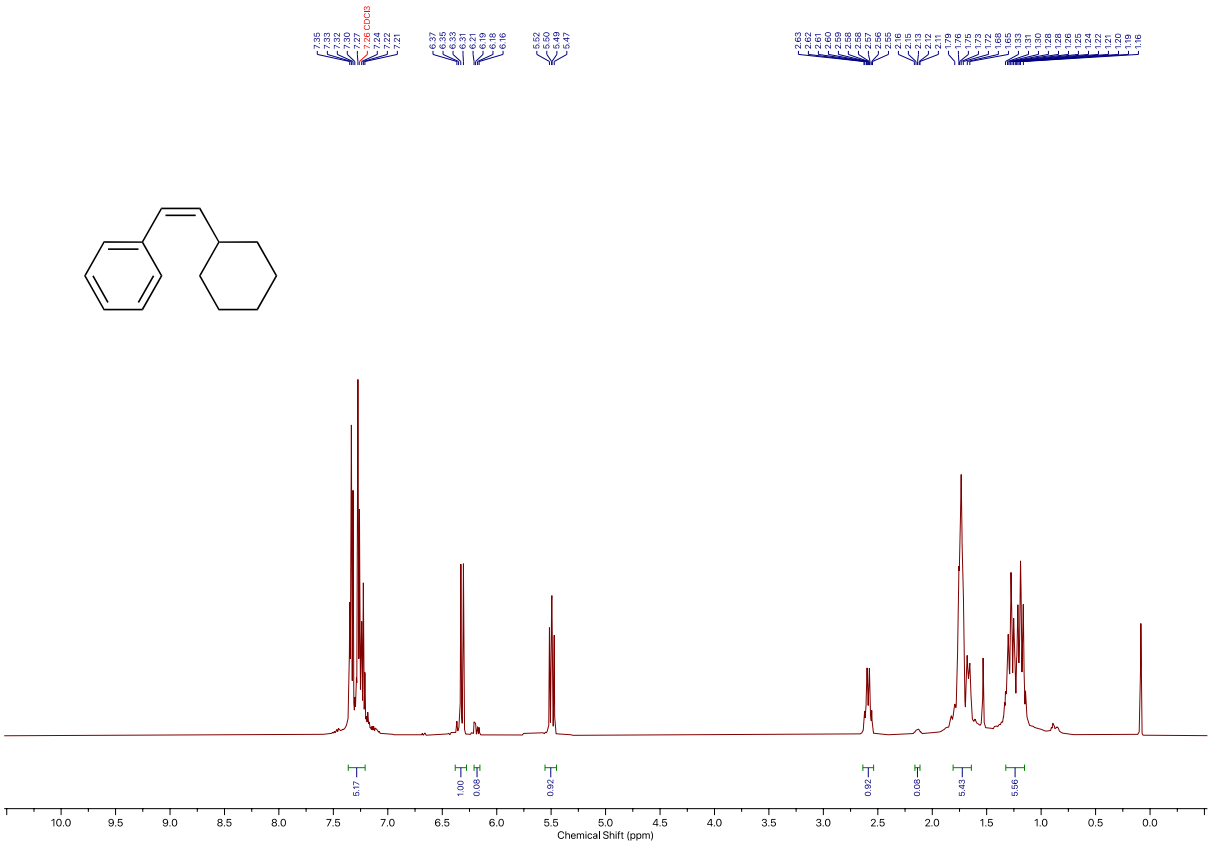
7. NMR Data:

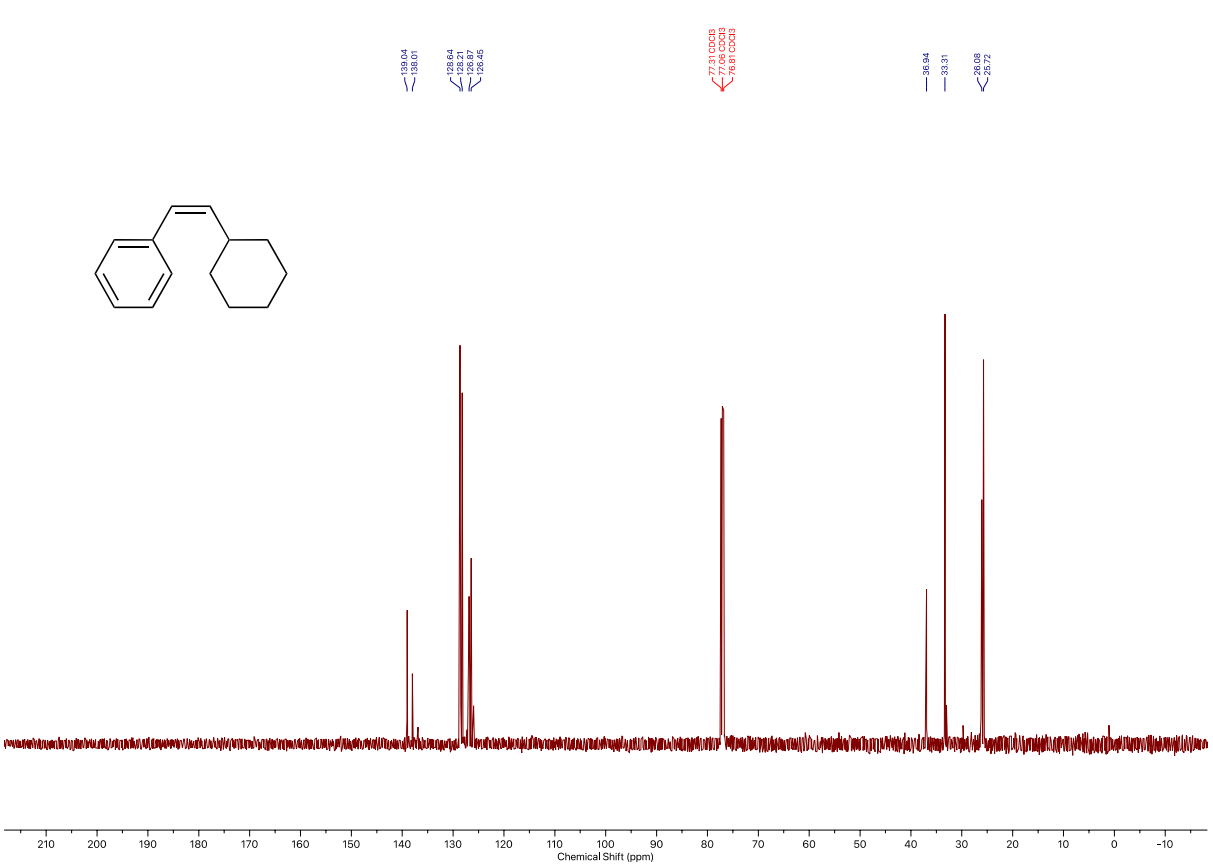
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3a:**



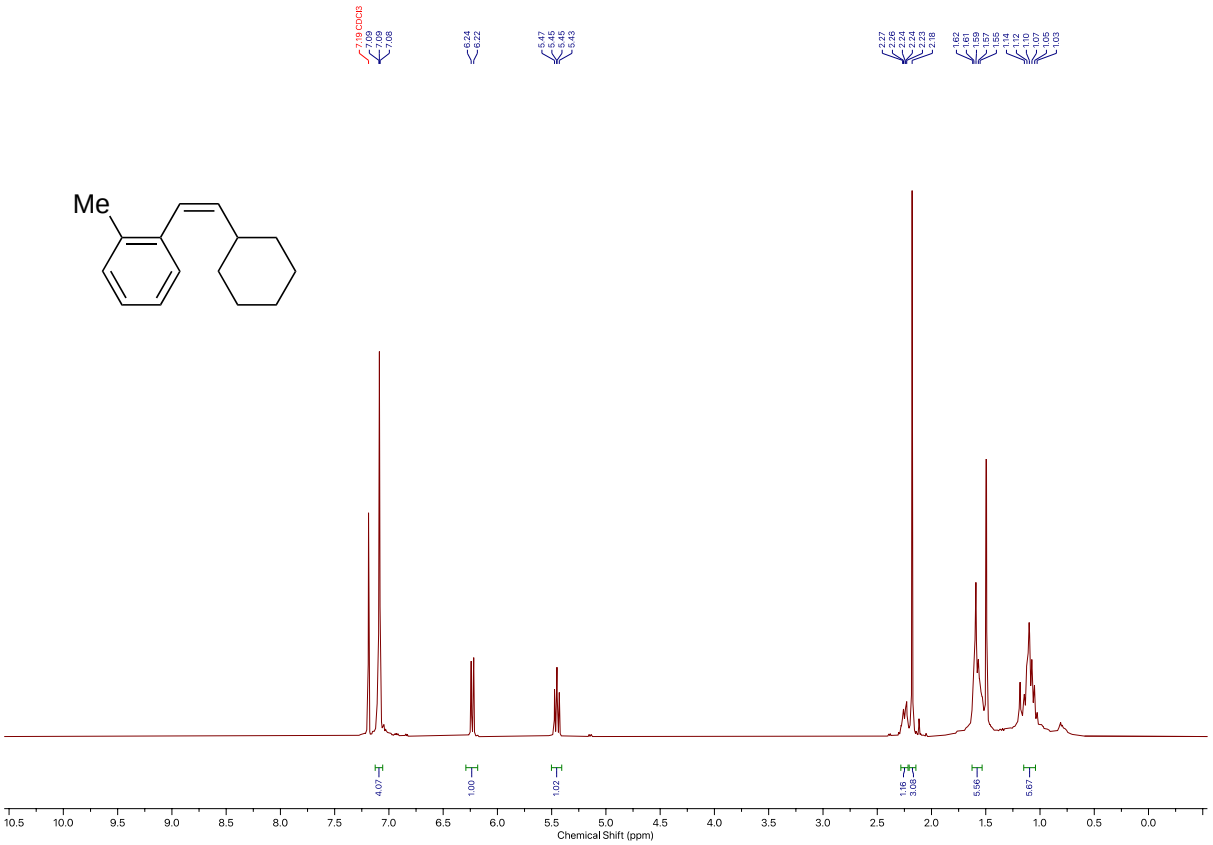


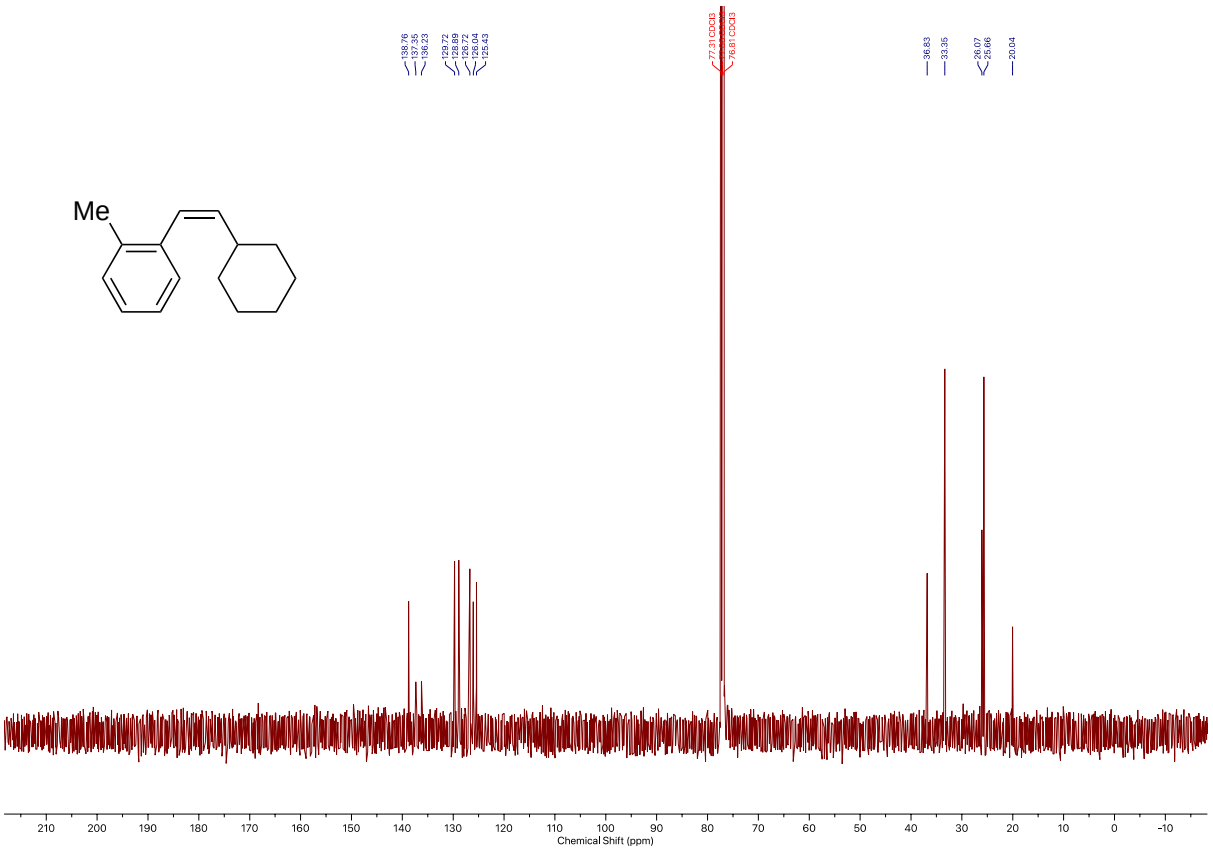
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3b:**



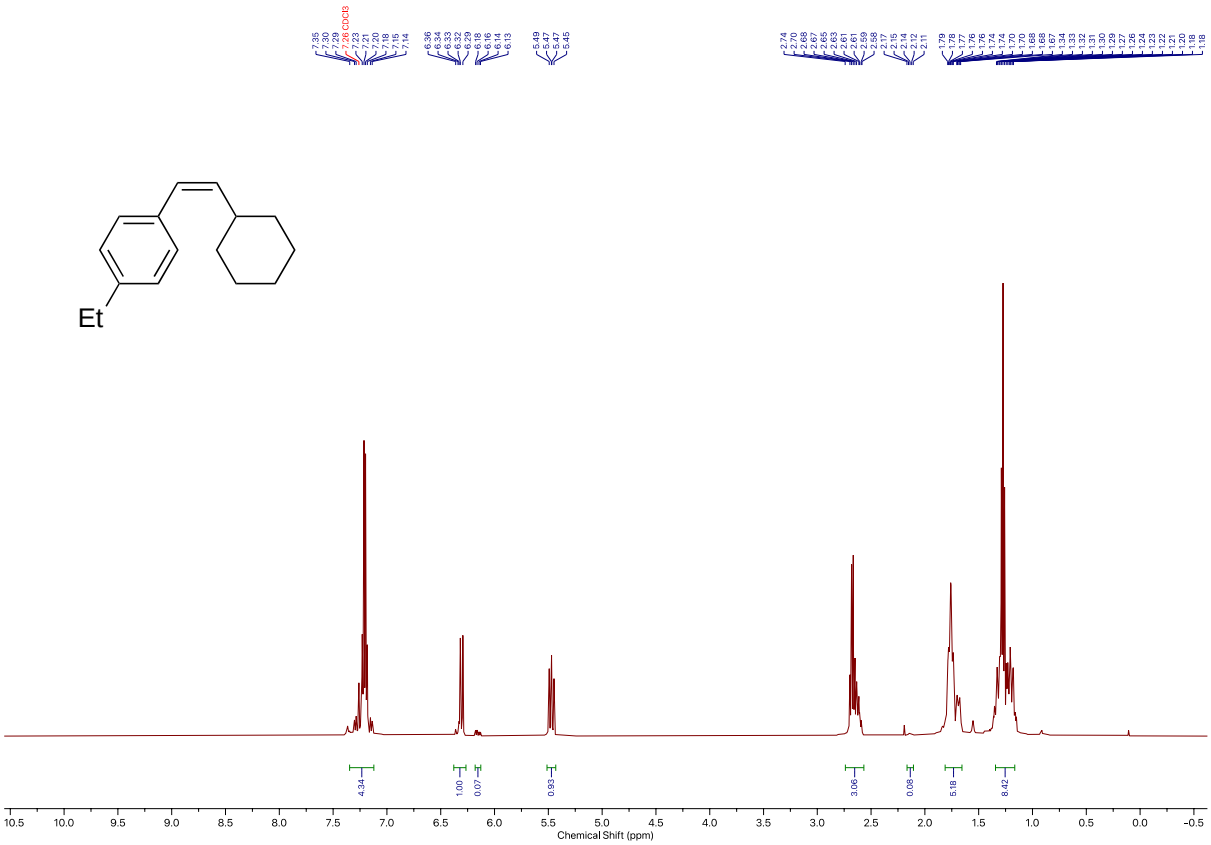


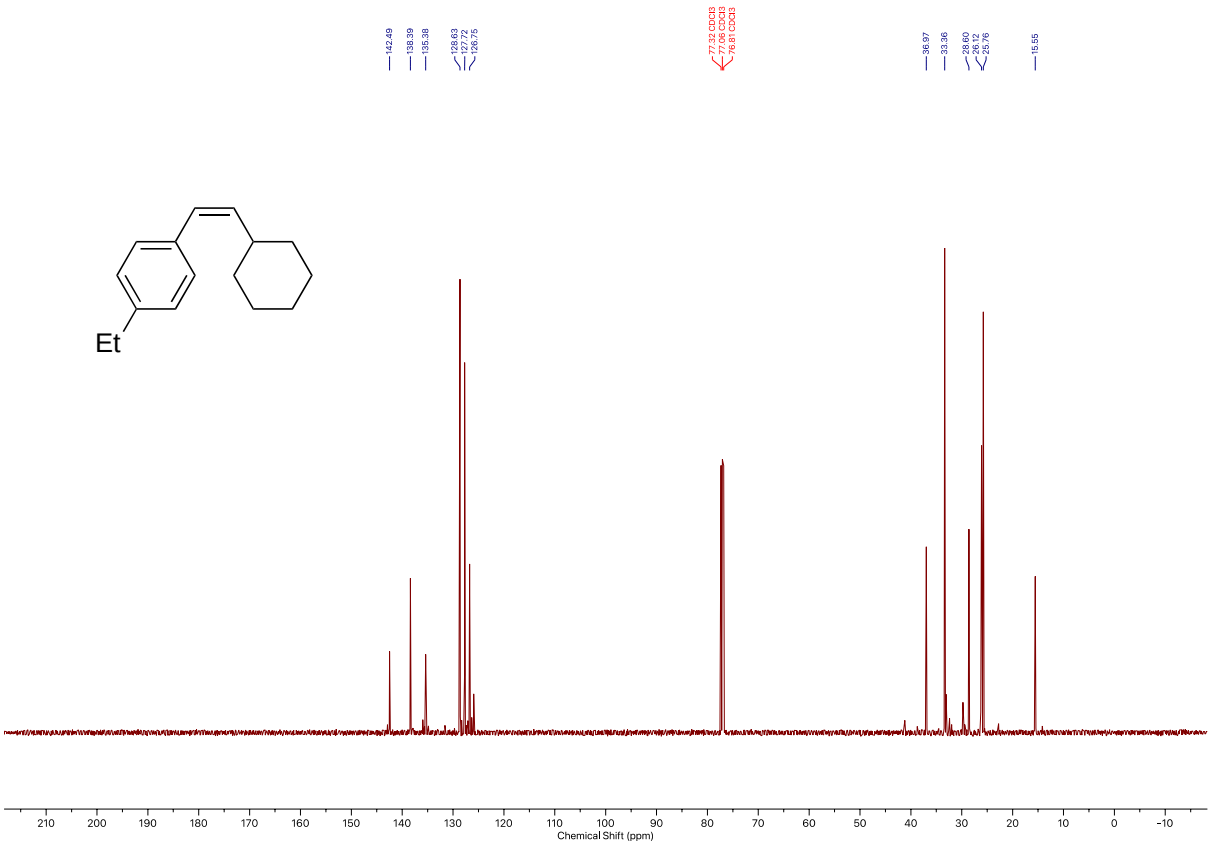
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3c:**



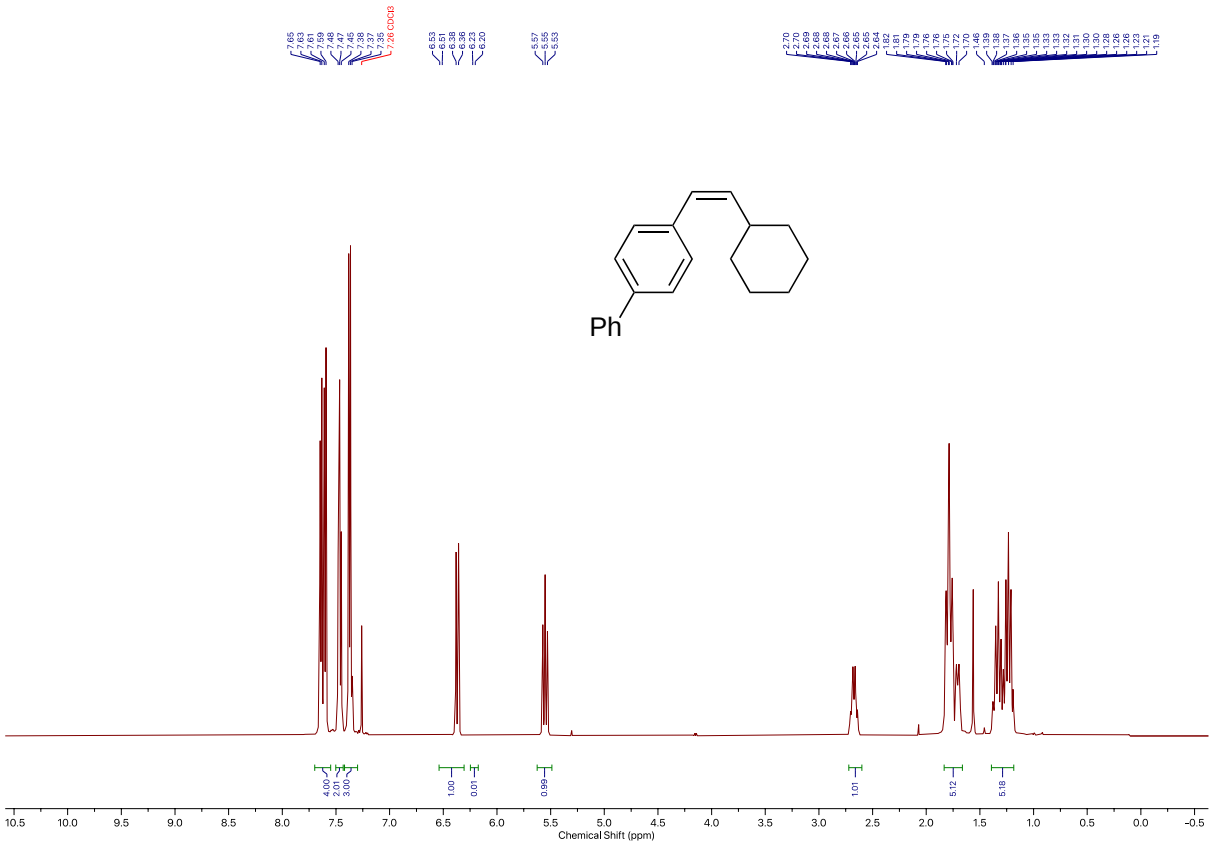


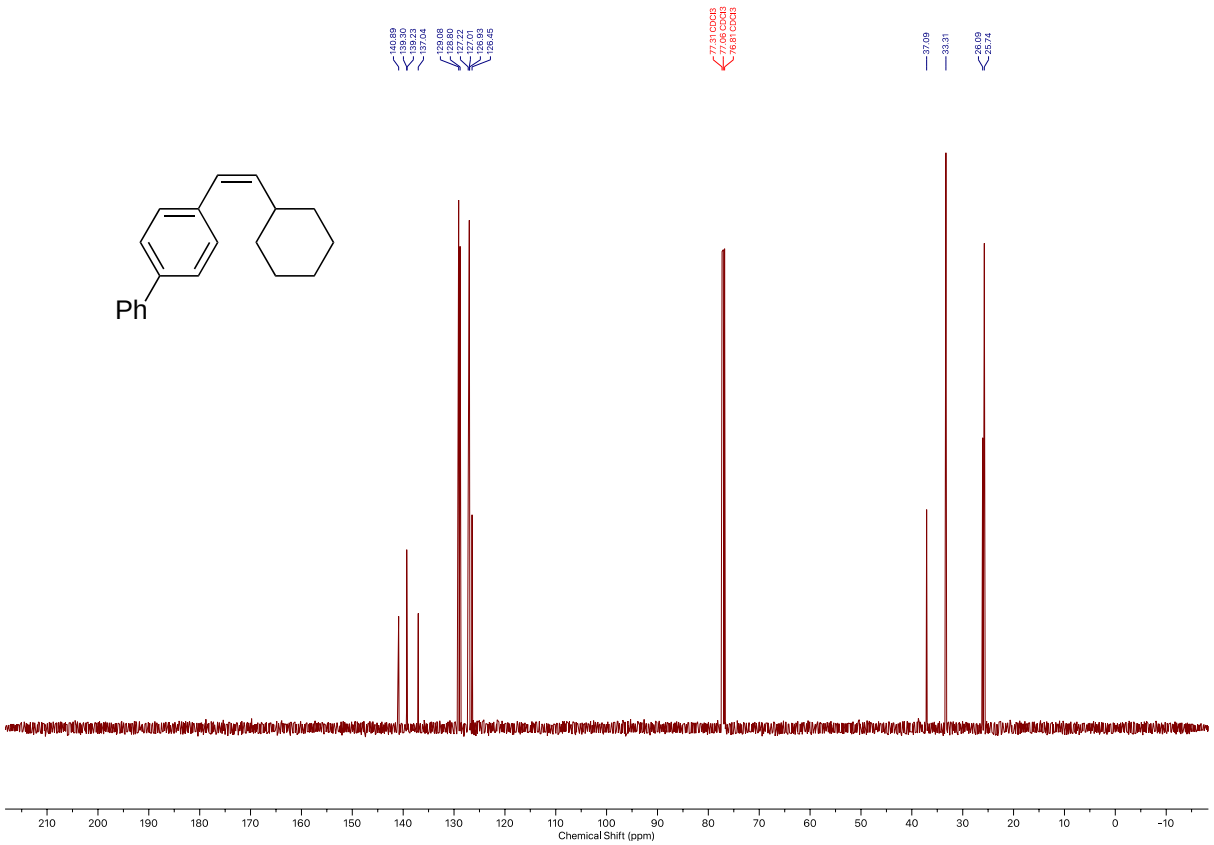
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3d:**



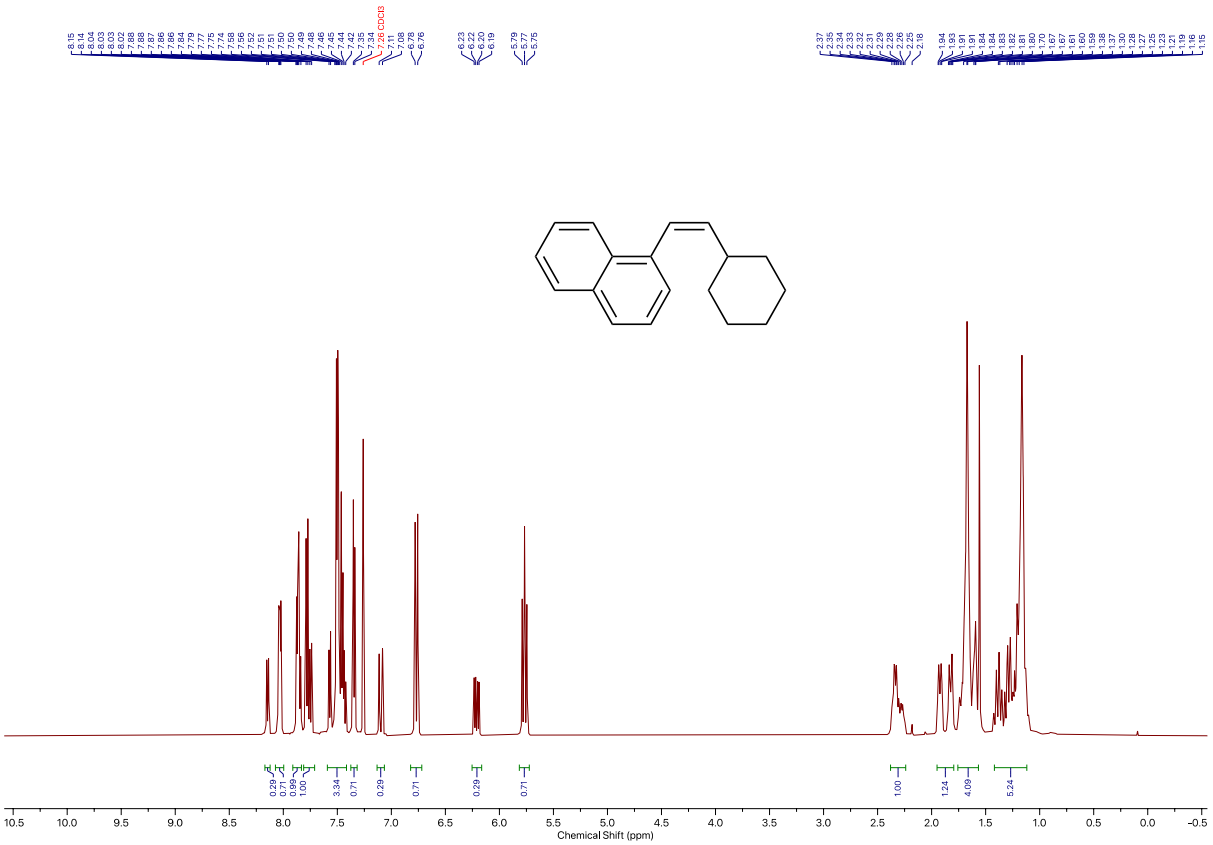


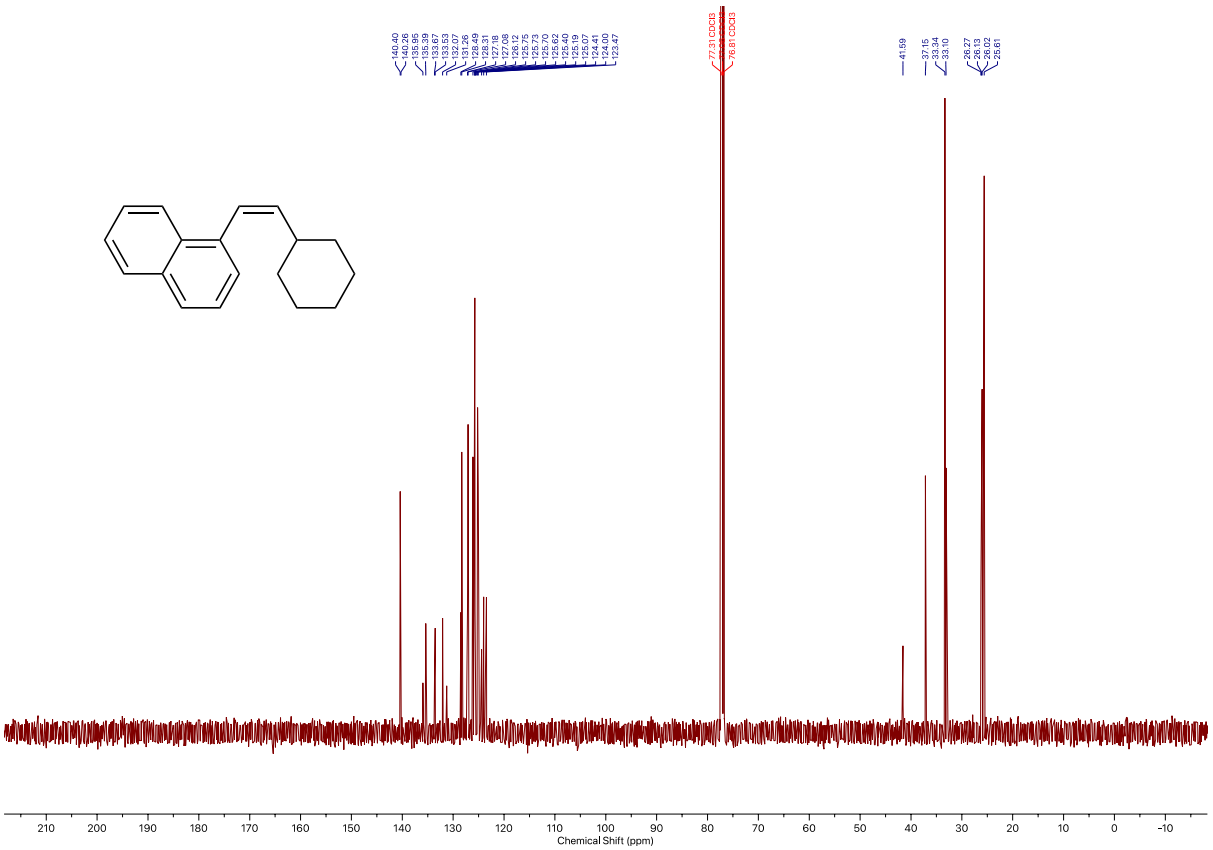
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3e:**



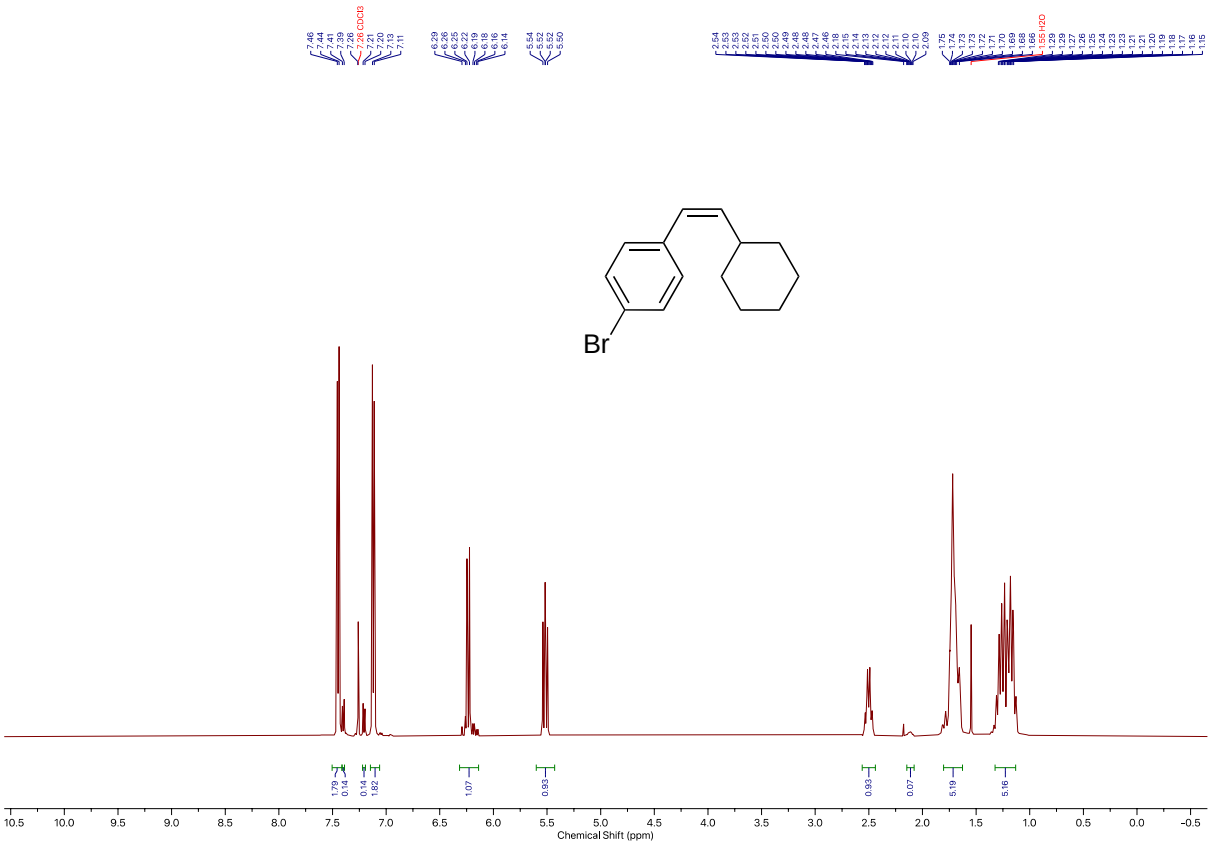


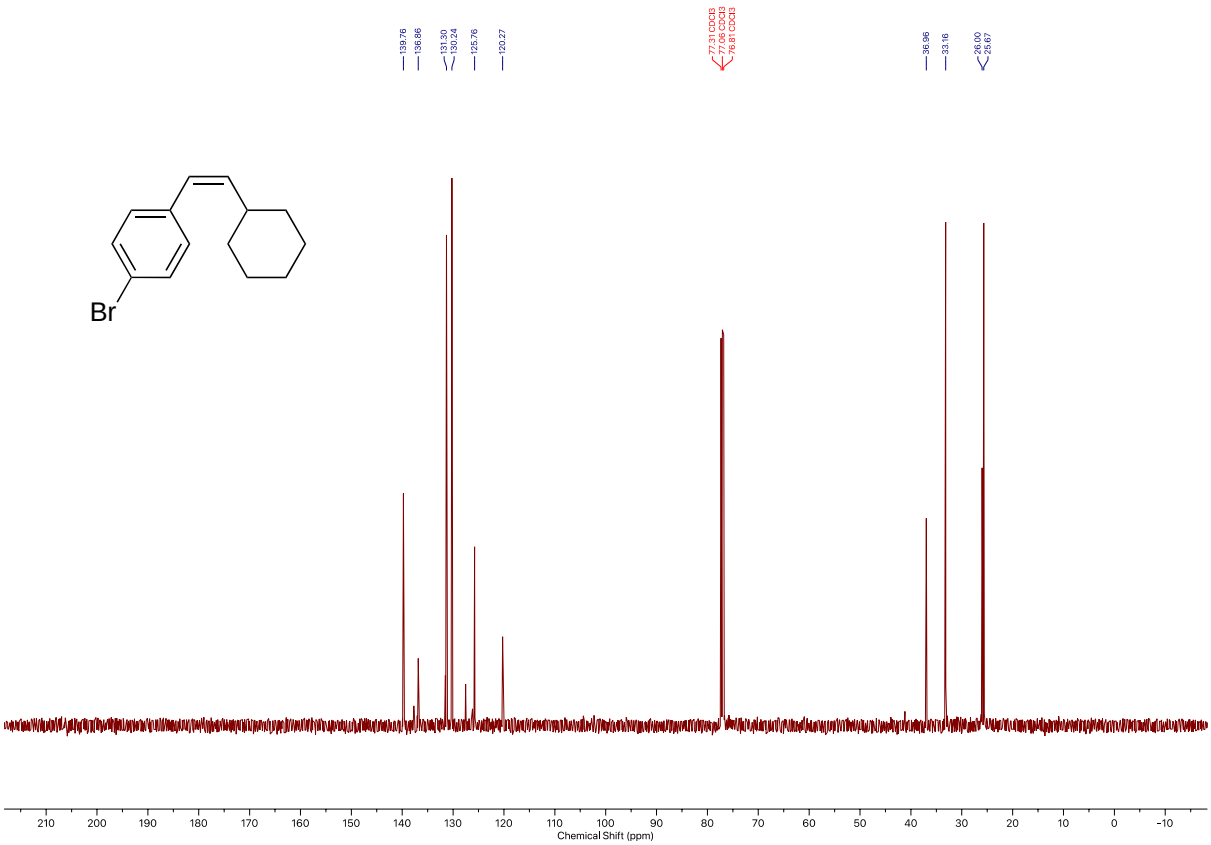
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3f:**



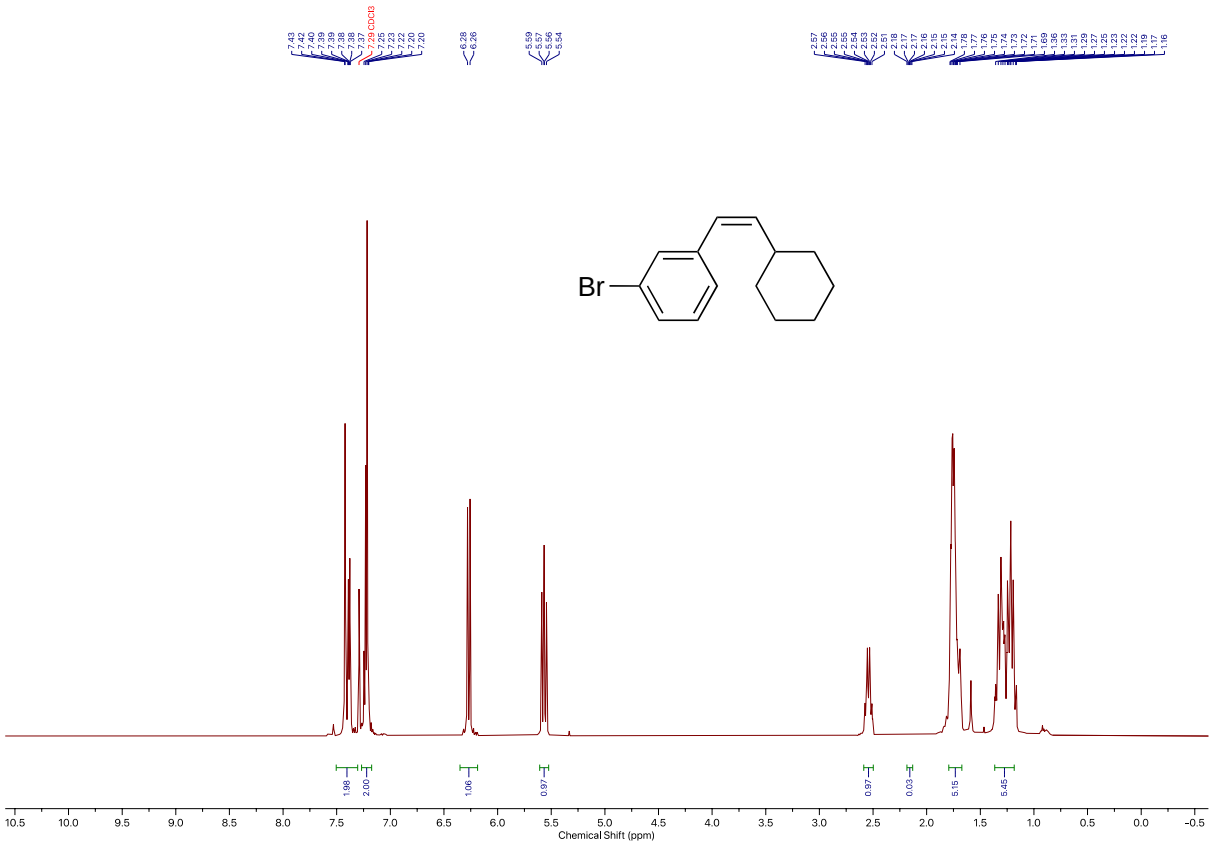


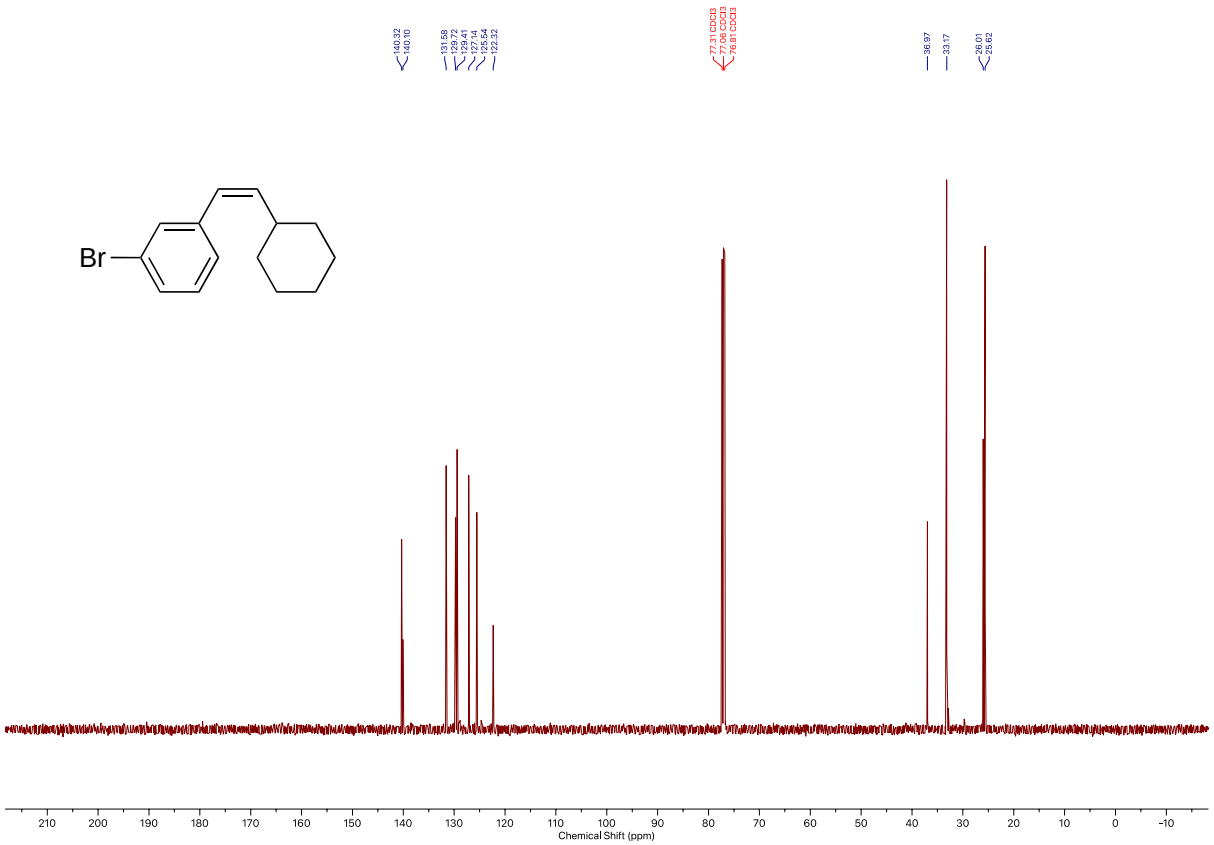
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3g:**



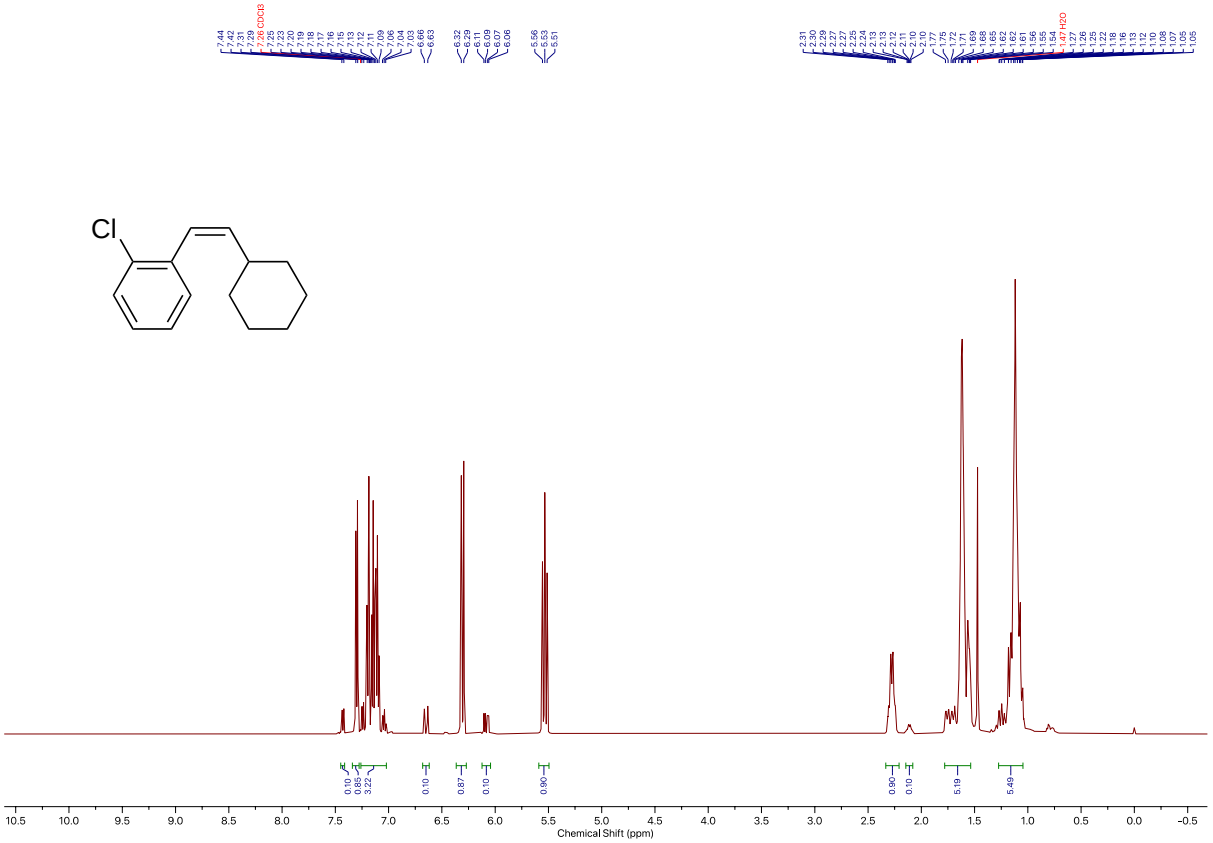


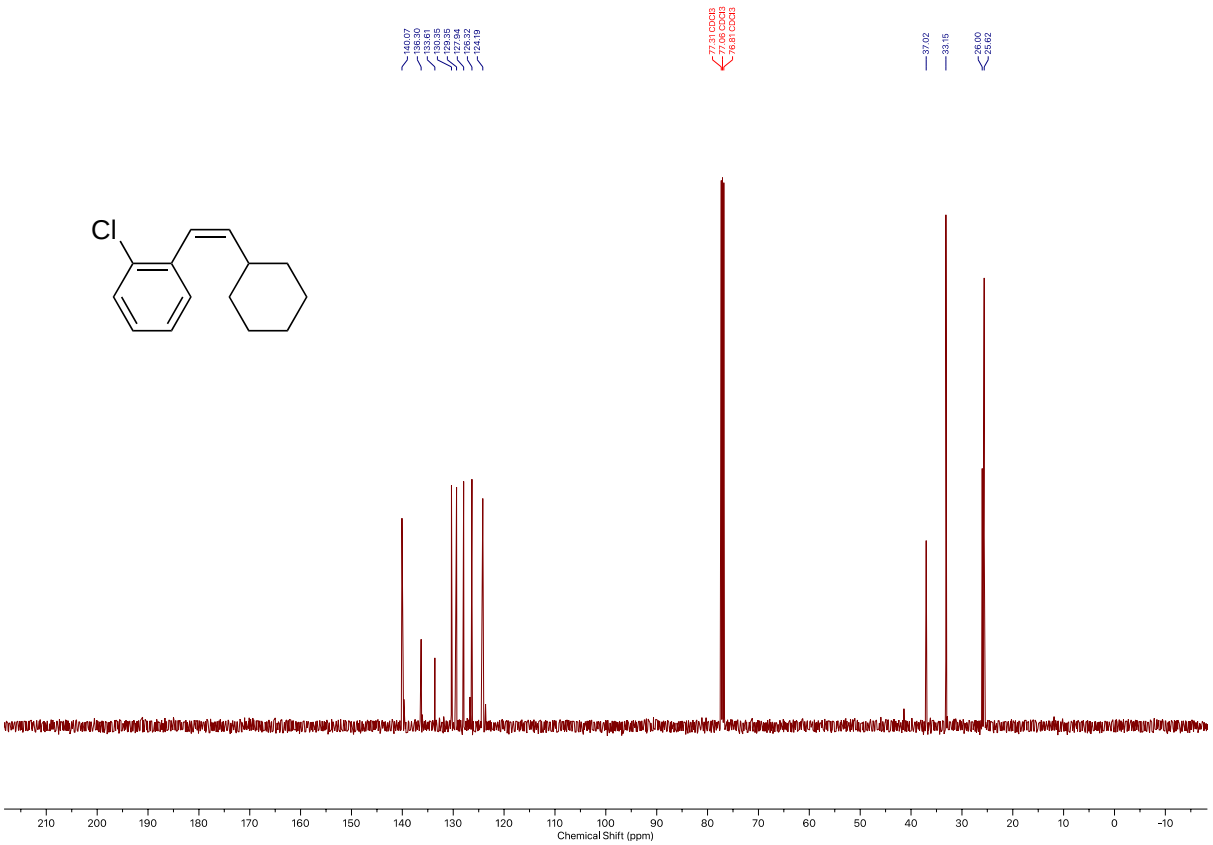
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3h:**



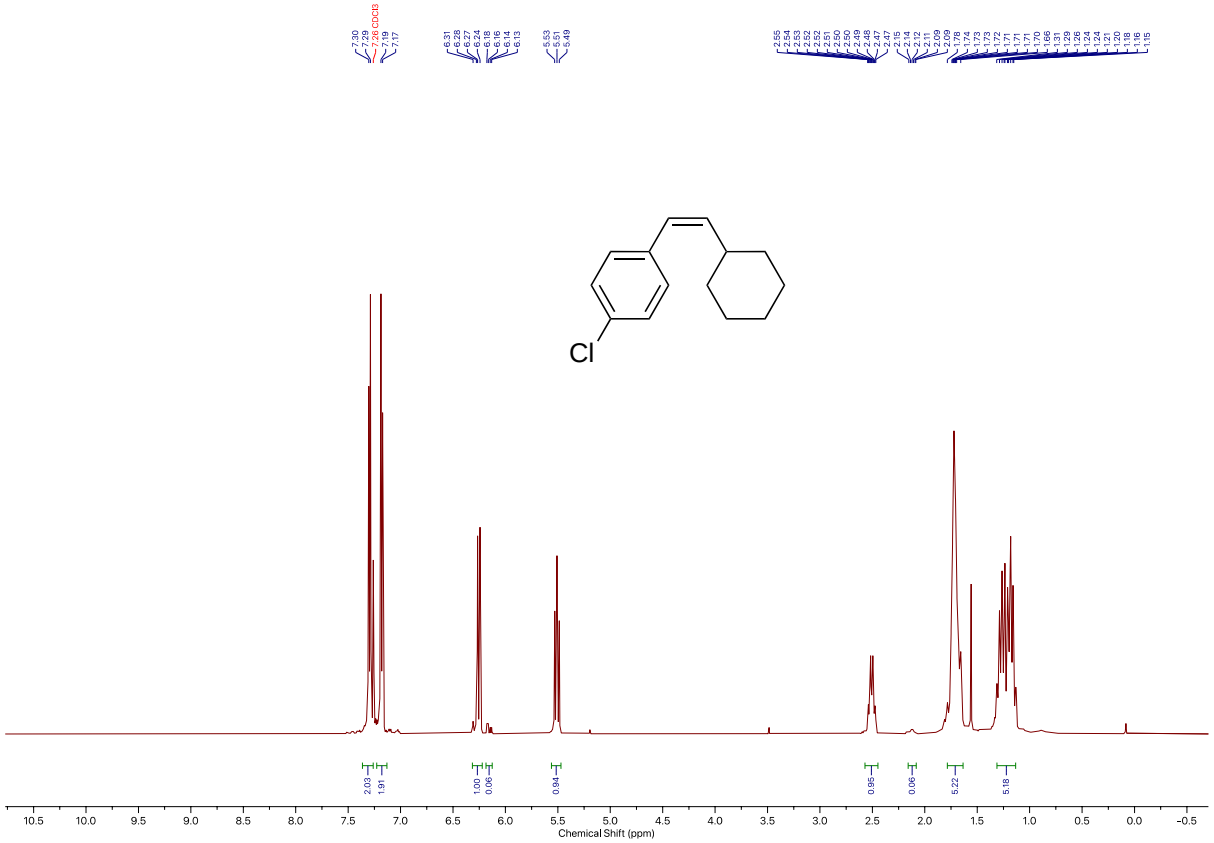


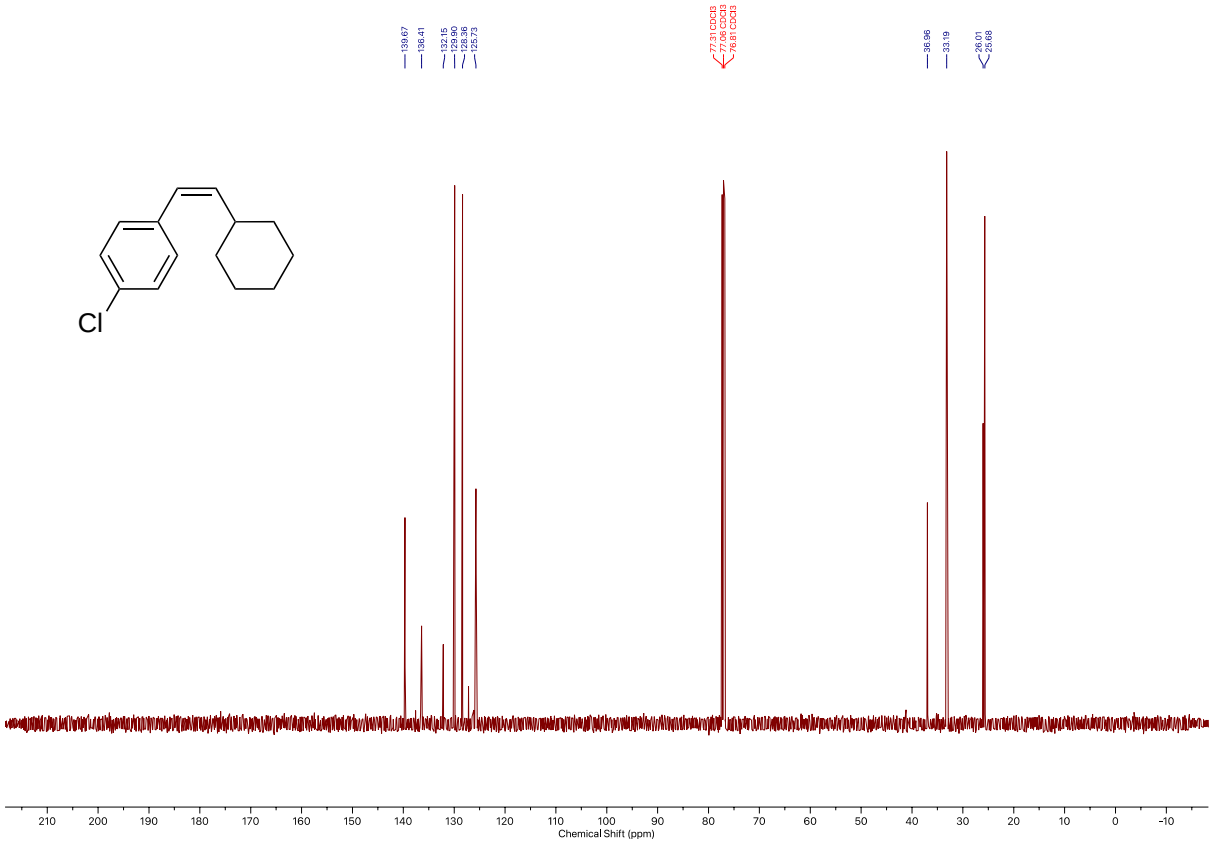
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3i:**



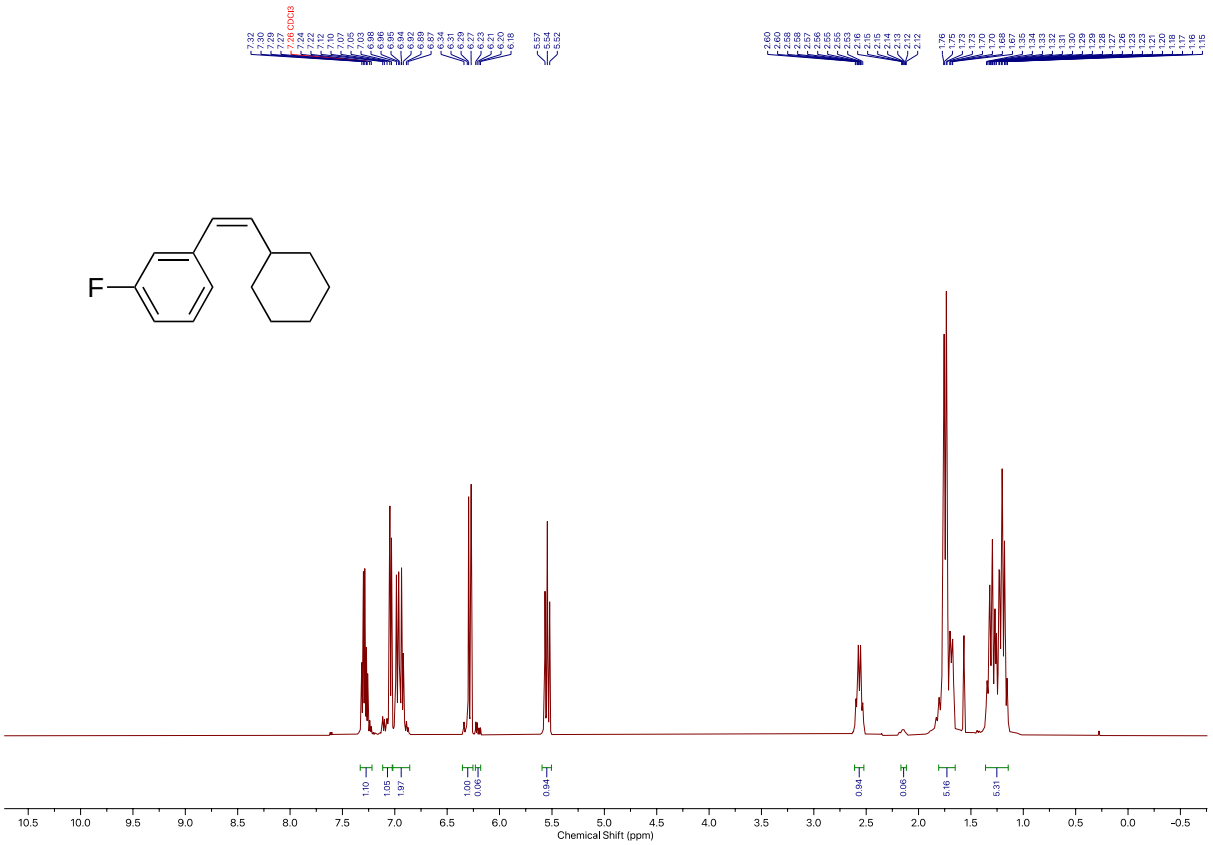


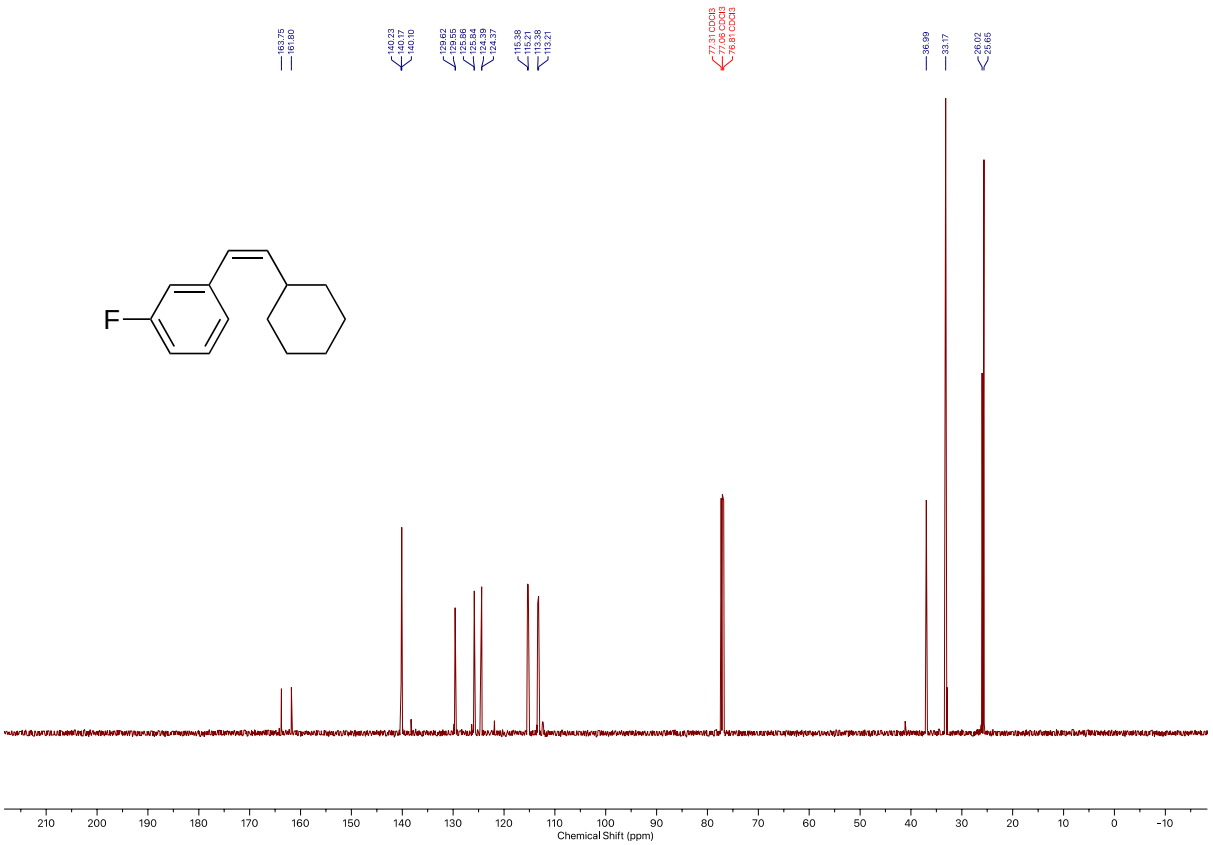
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3j:**



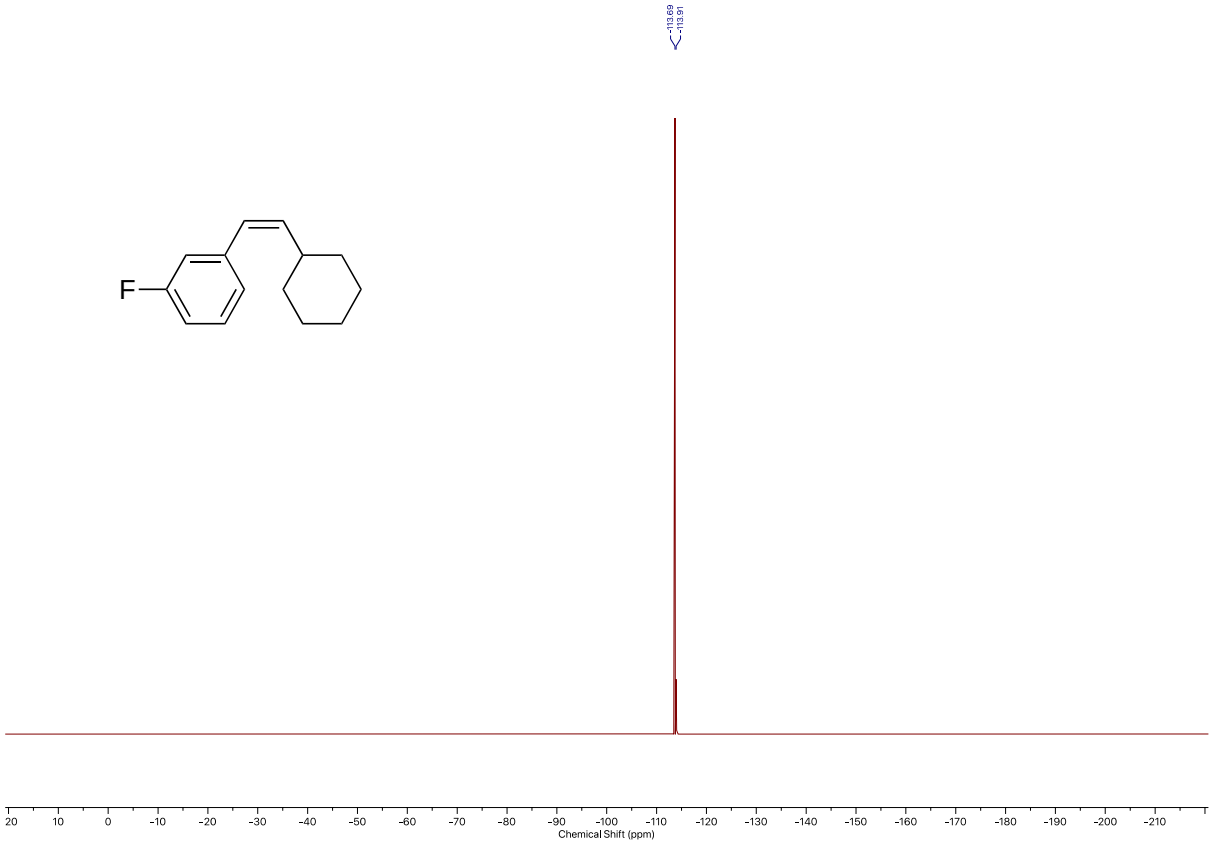


^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3k:**

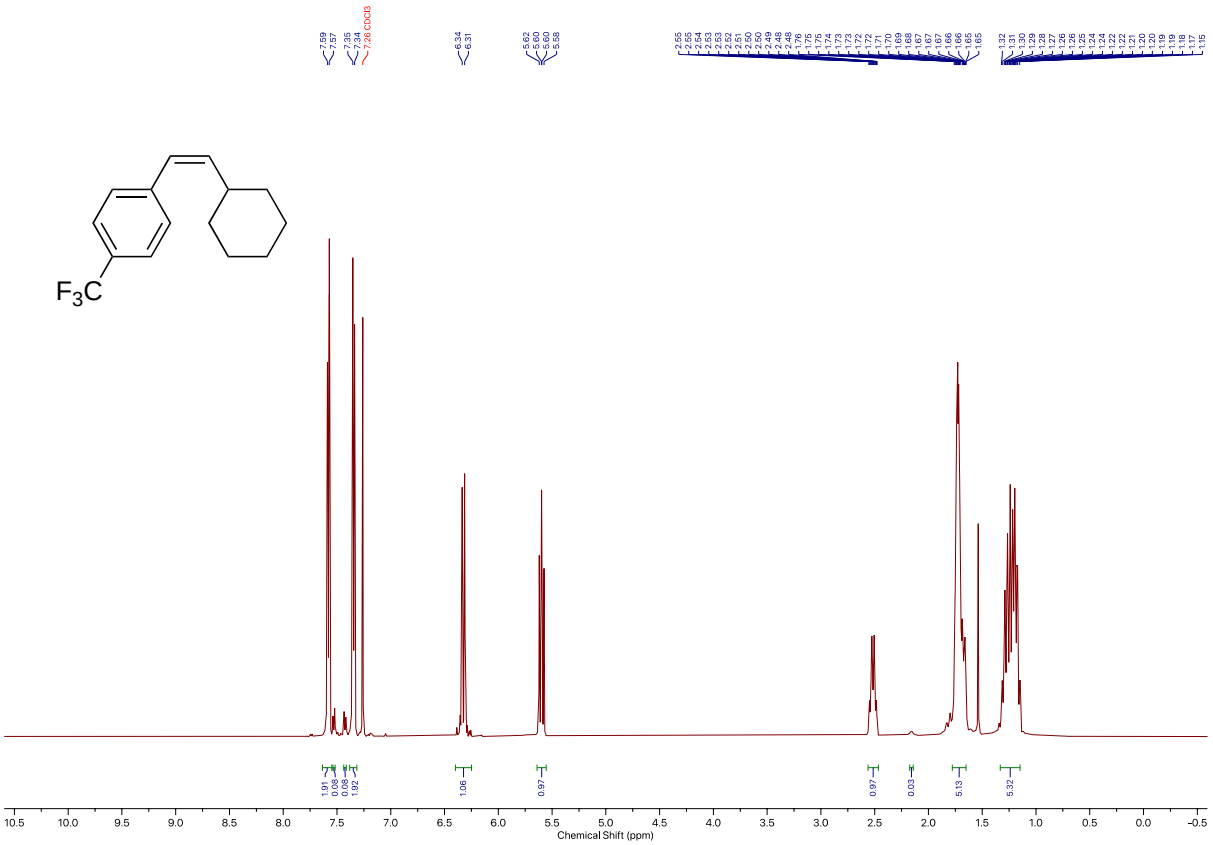


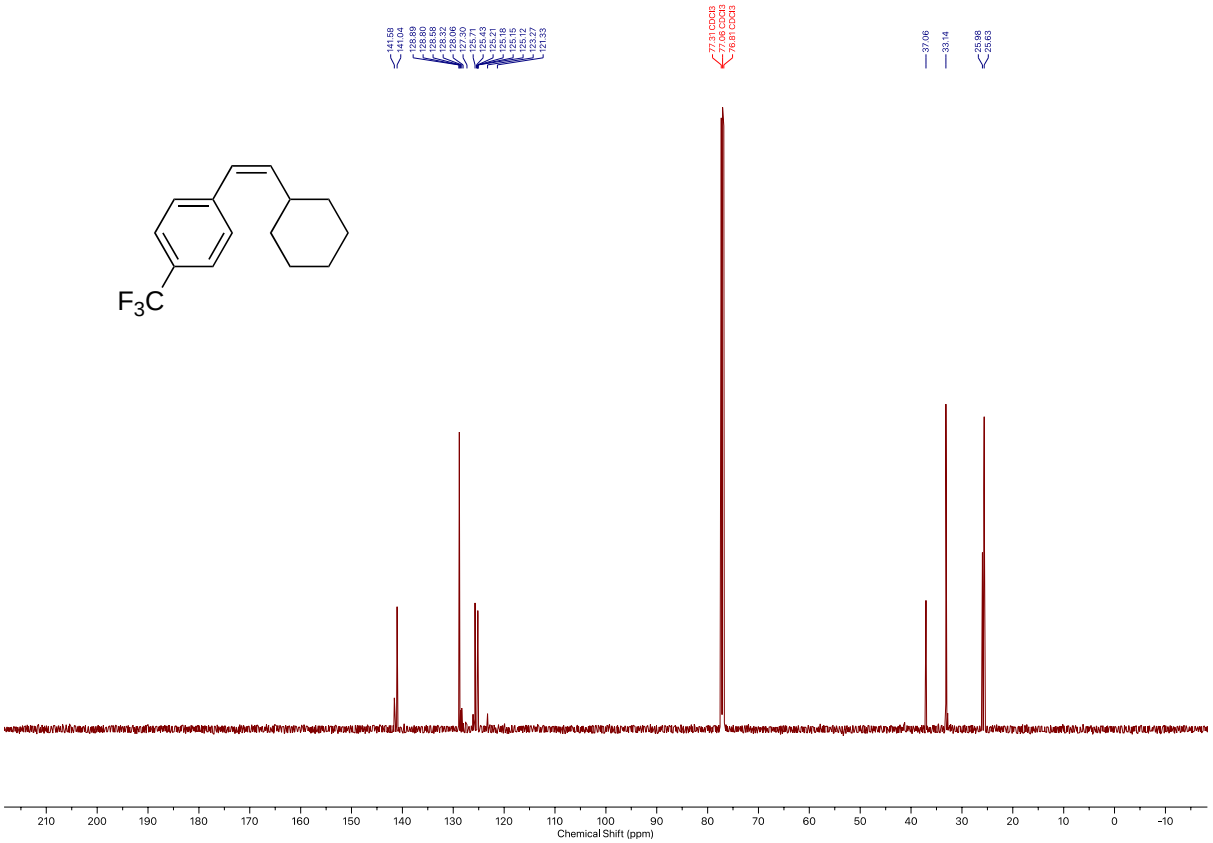


^{19}F NMR (471 MHz, $CDCl_3$) for 3k:



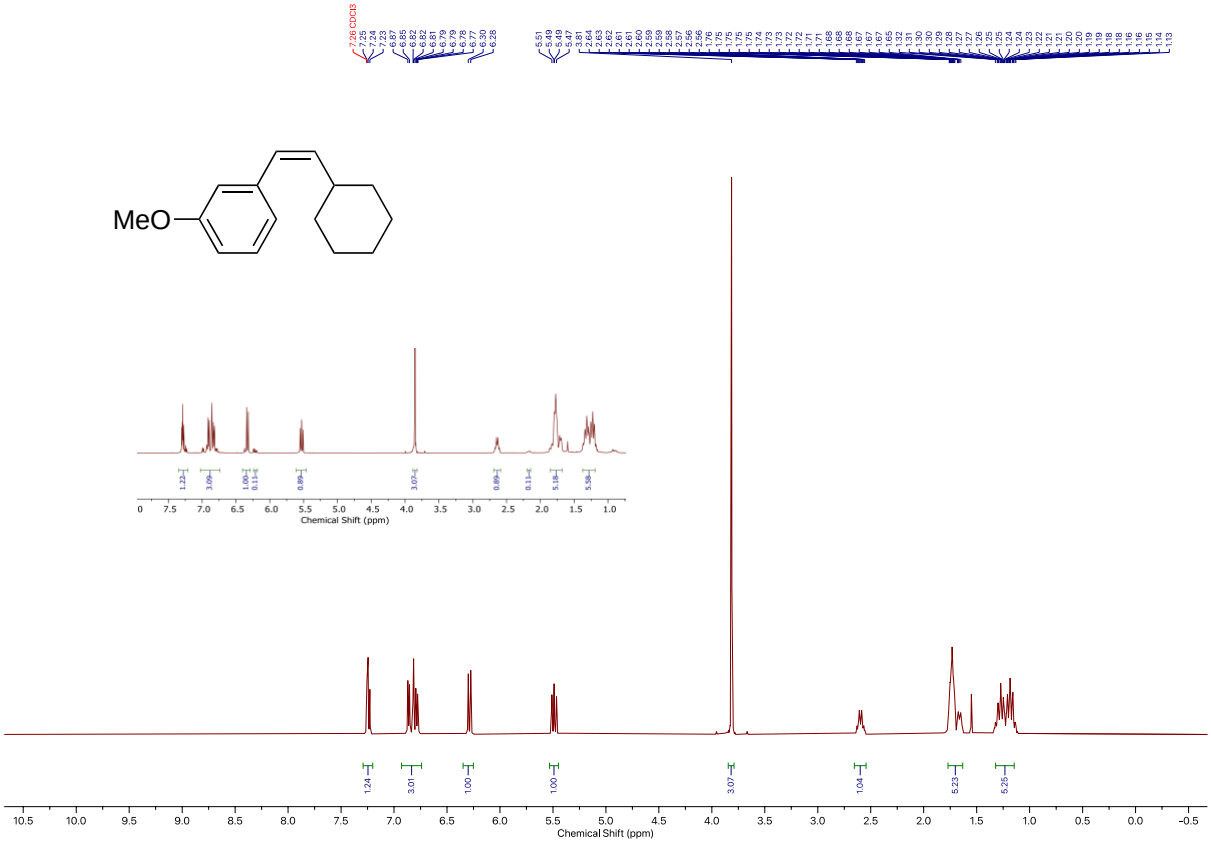
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3l:**

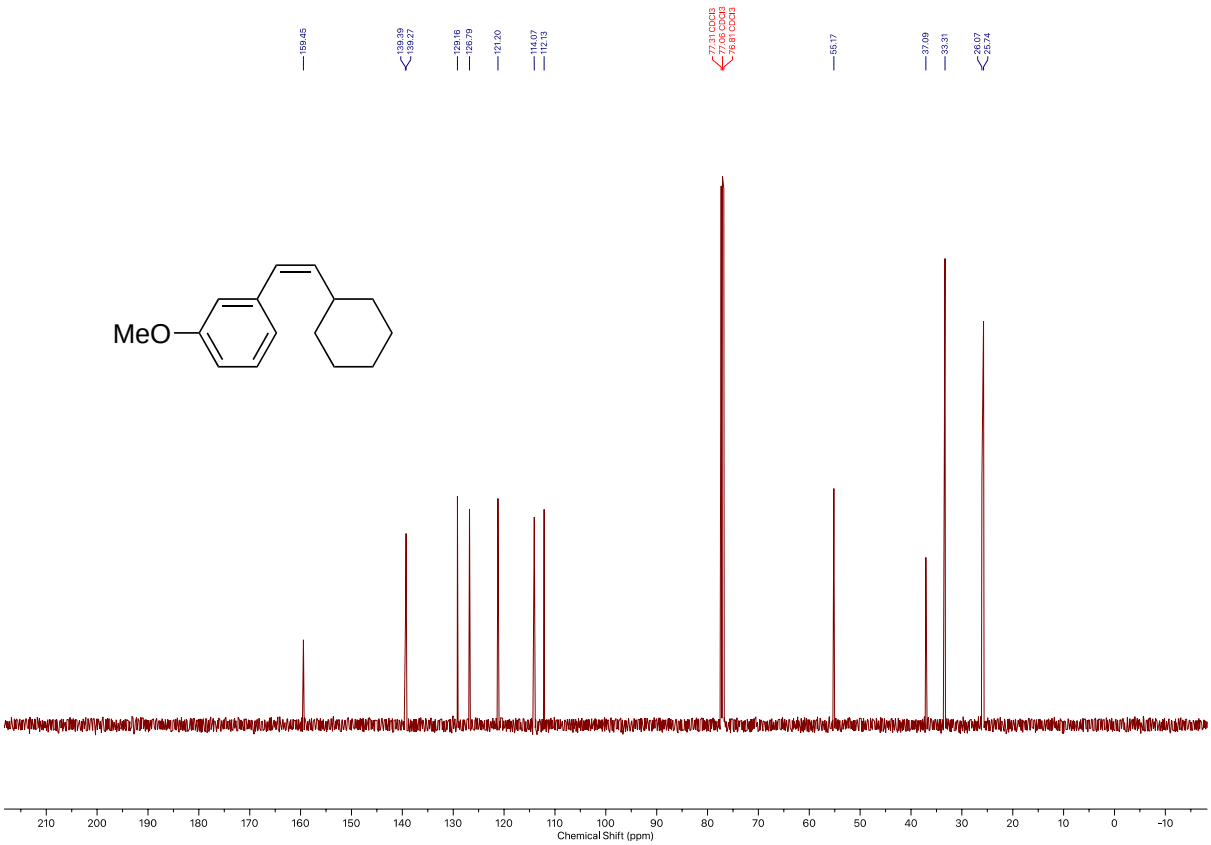




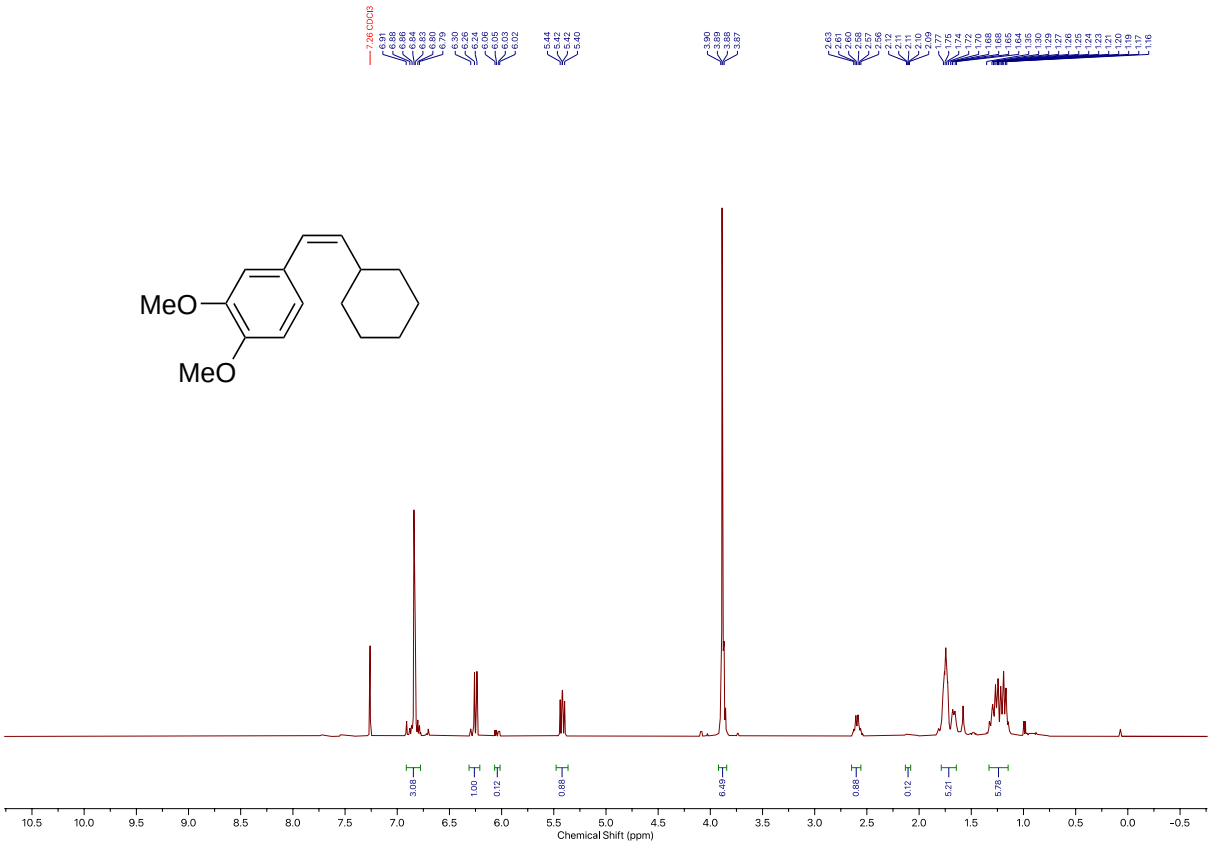
^{19}F NMR (471 MHz, $CDCl_3$) for 3l:

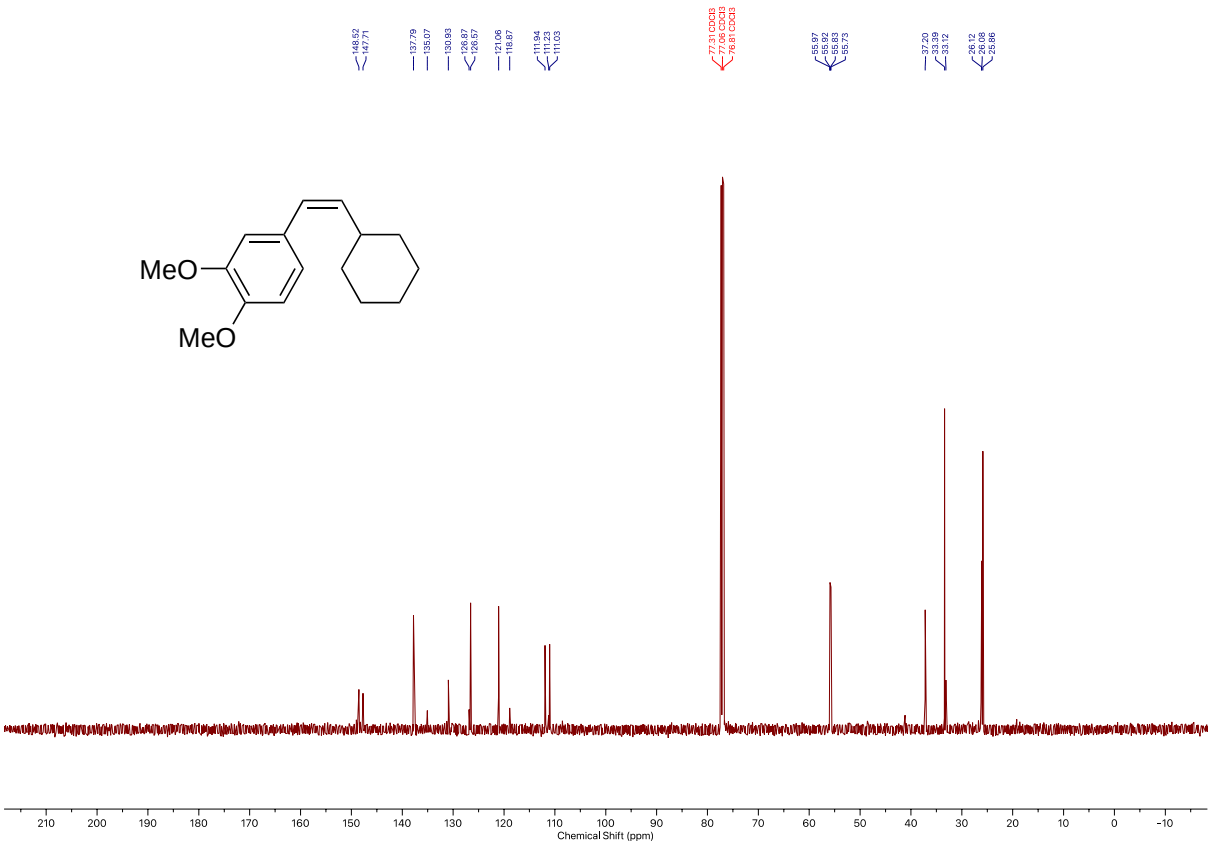
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3m:**



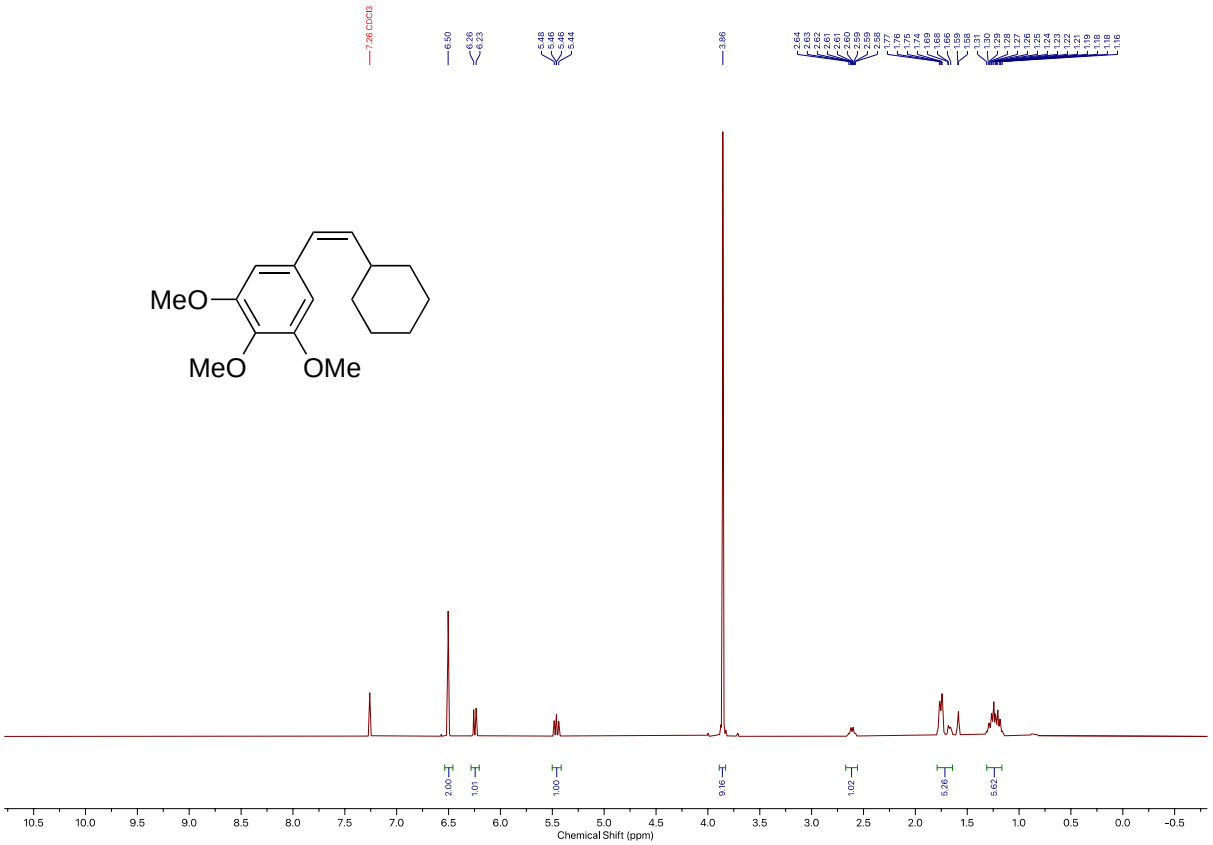


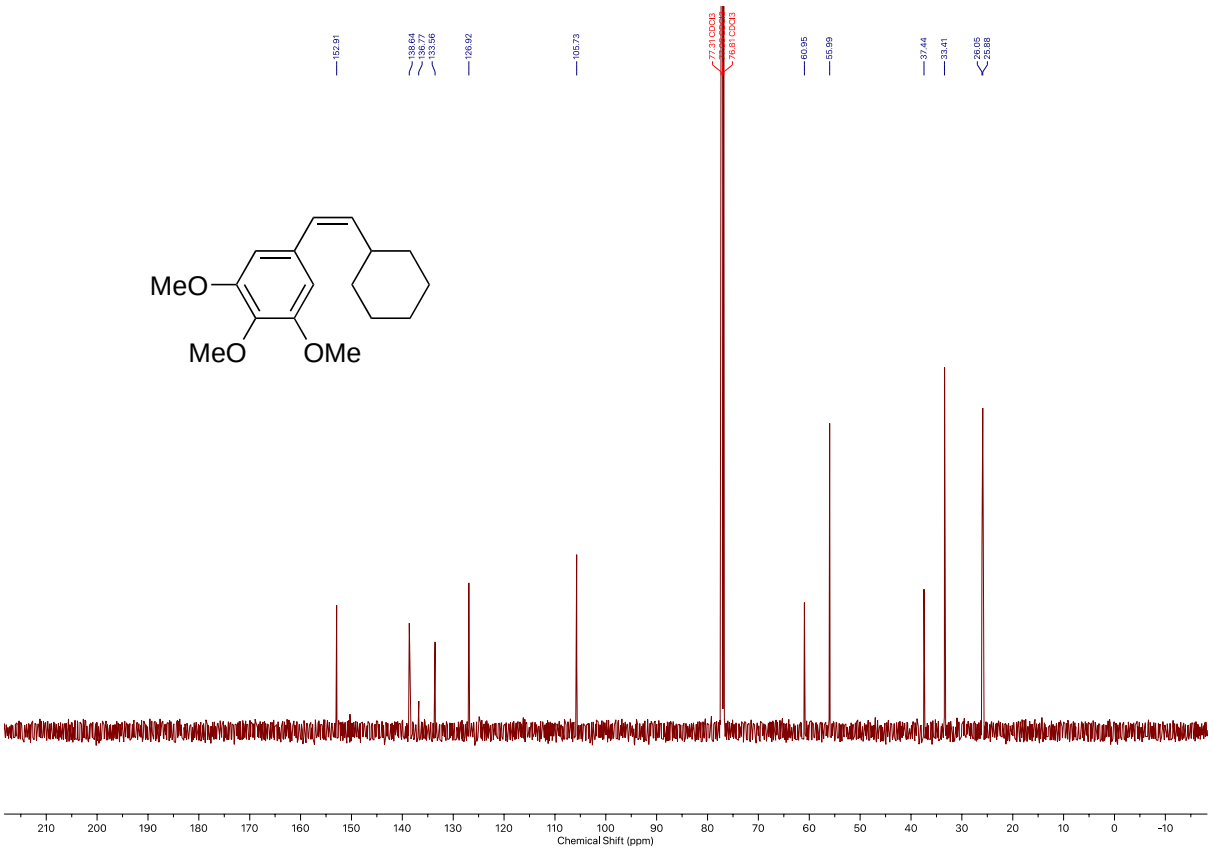
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3n:**



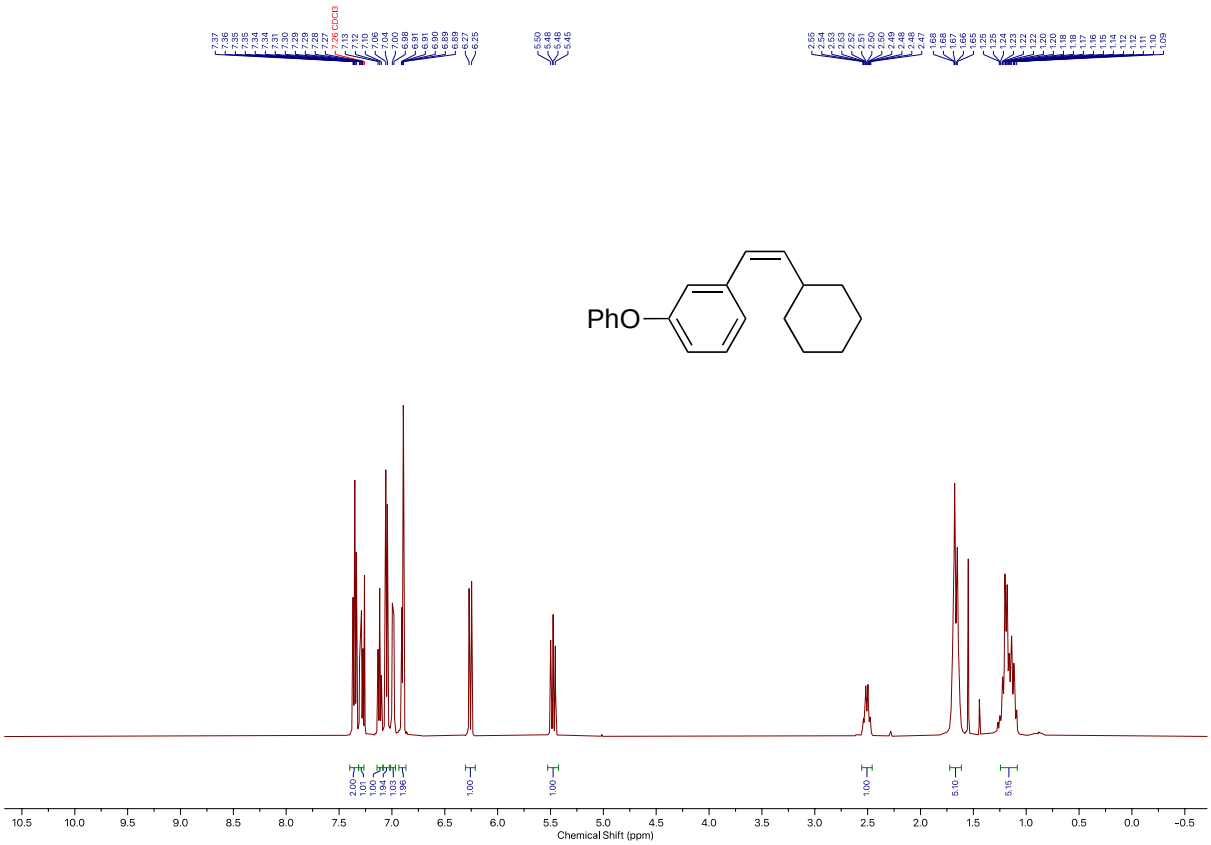


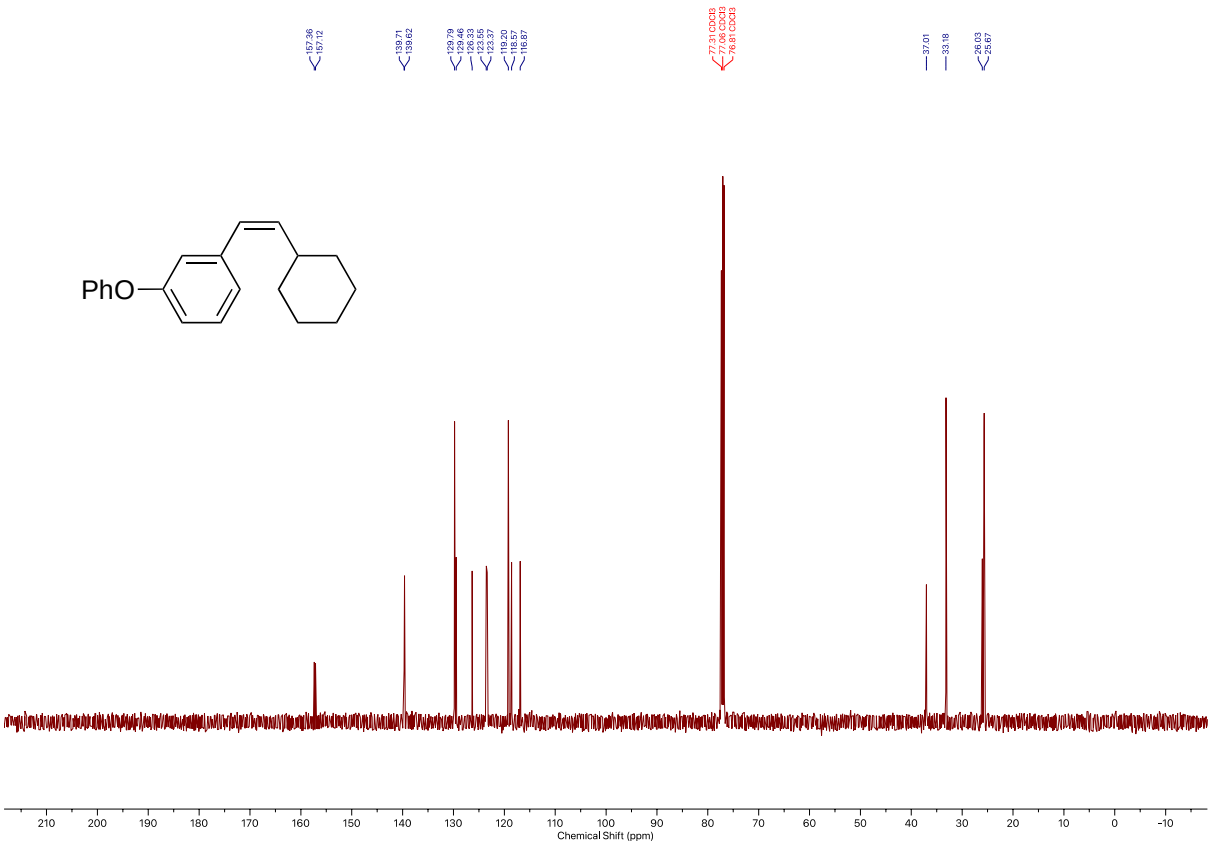
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3o:**



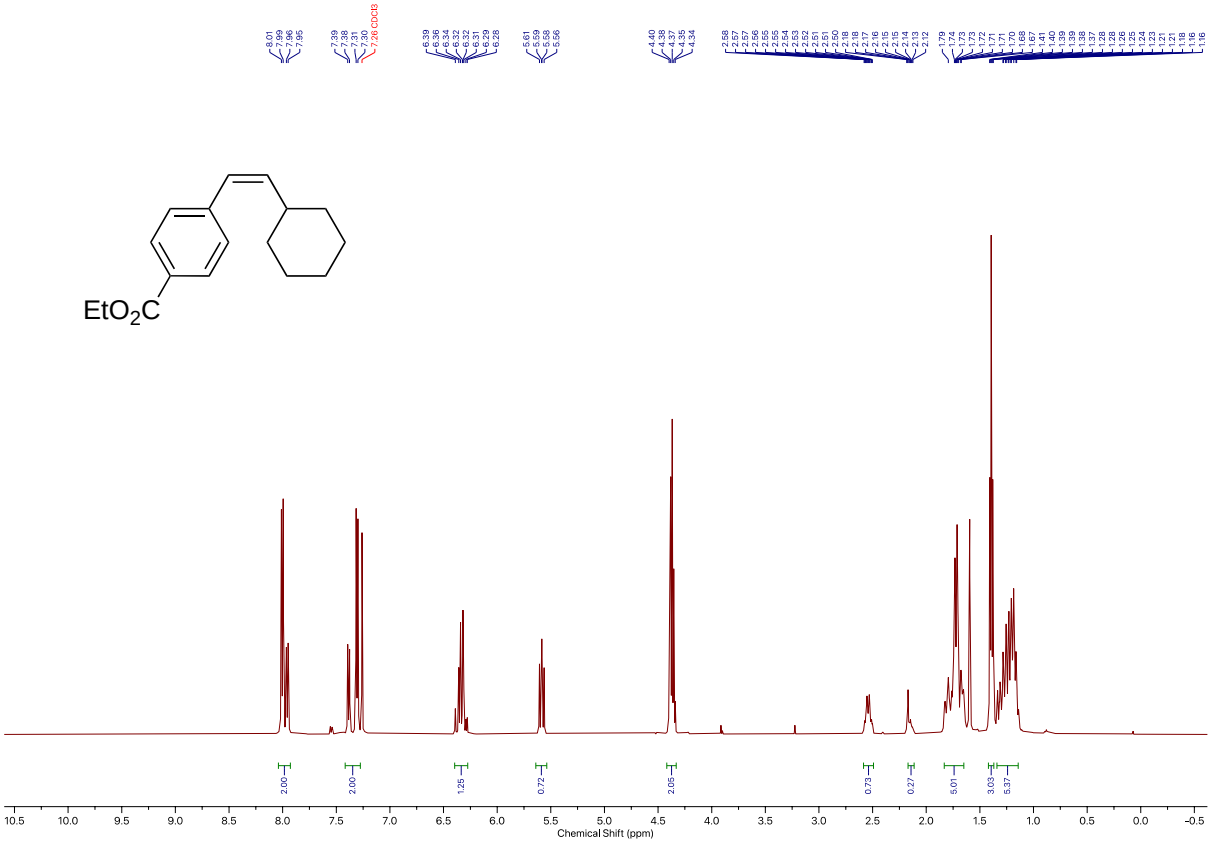


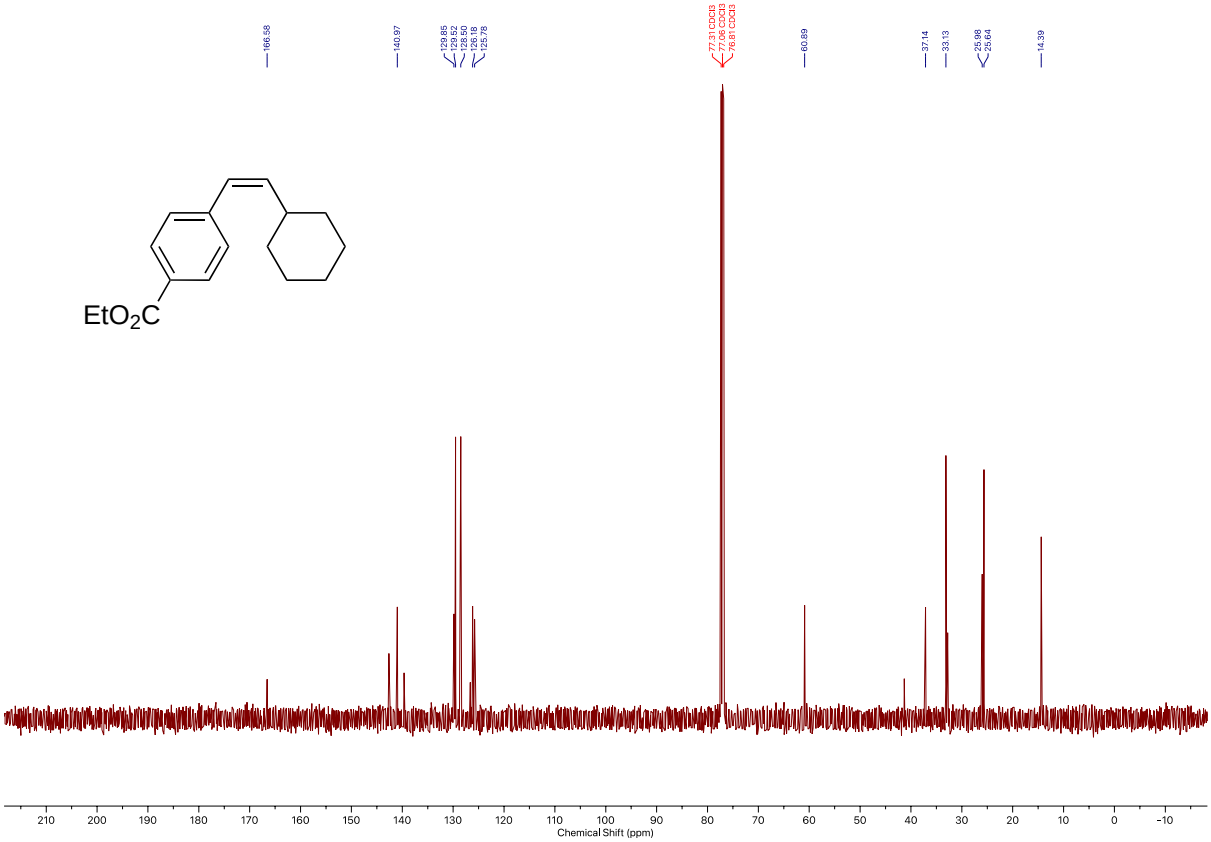
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3p:**



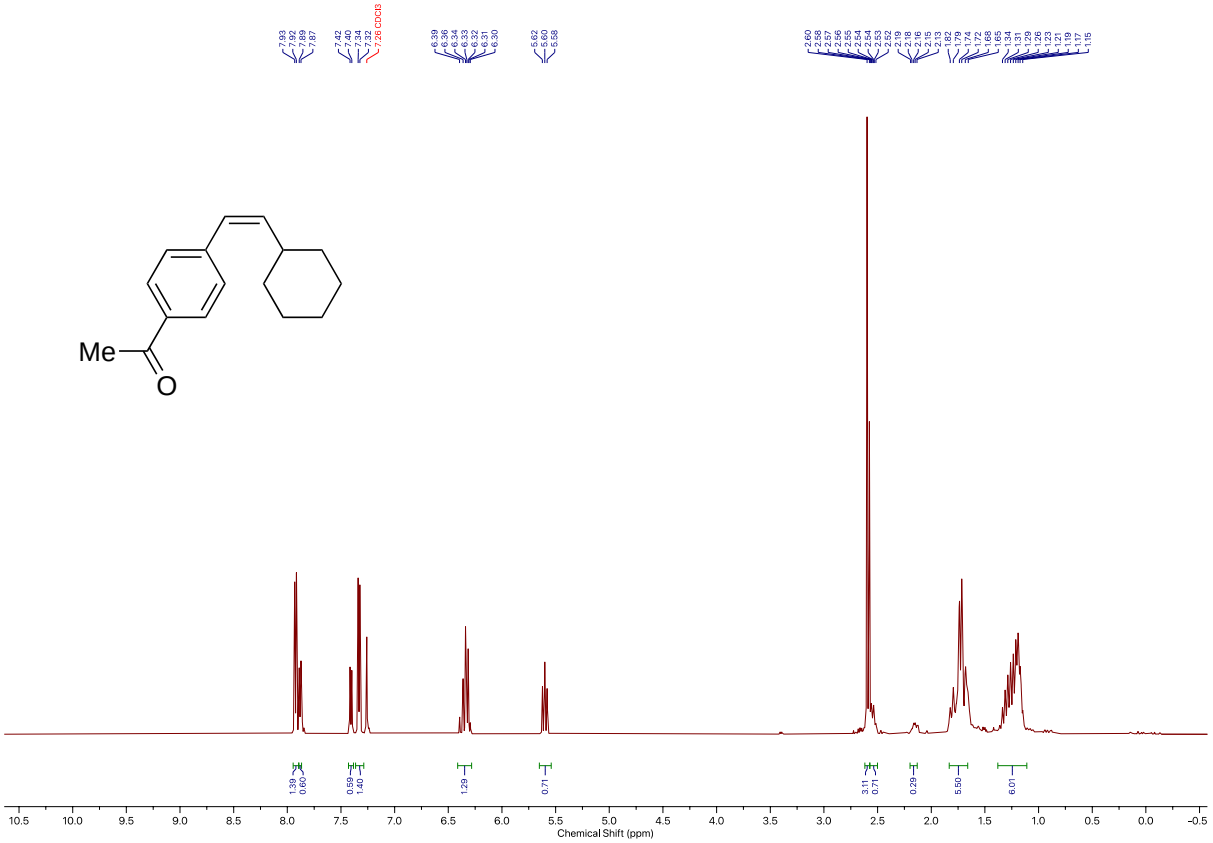


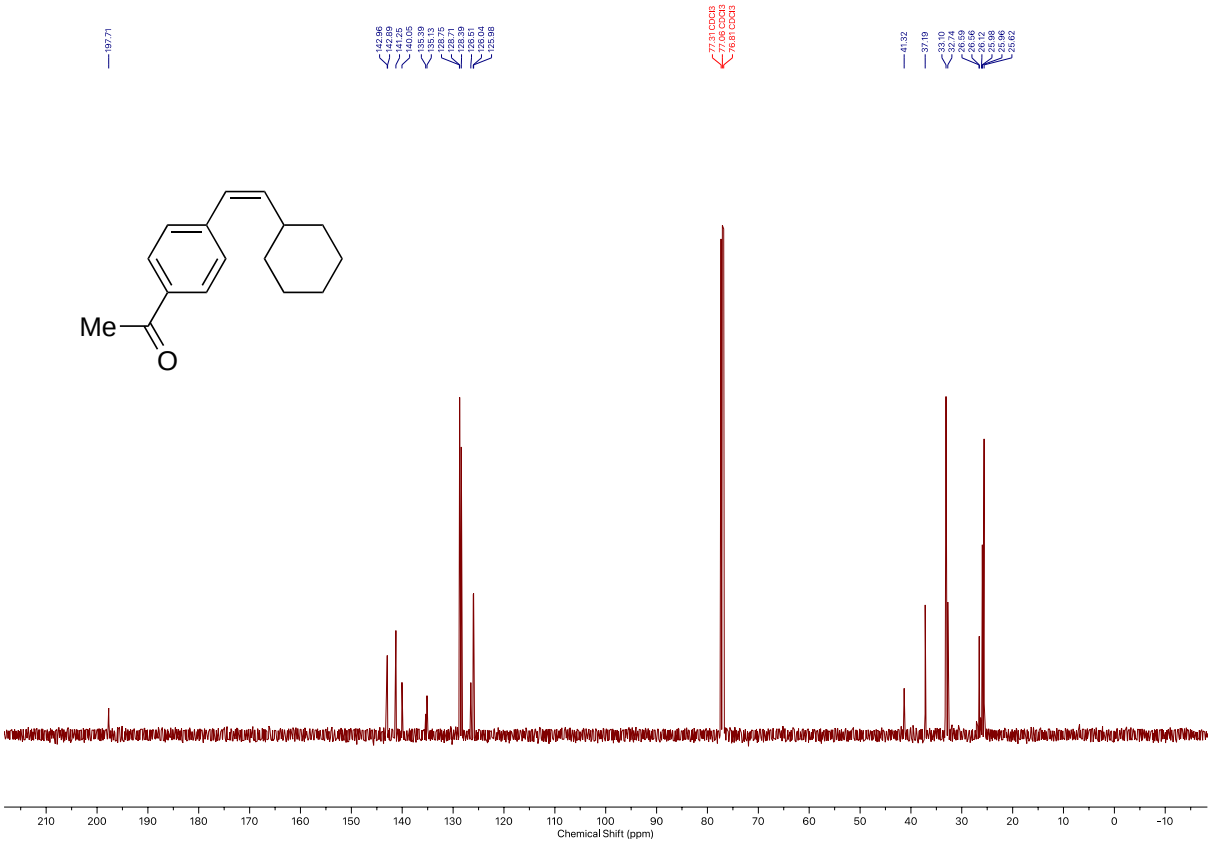
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3q:**



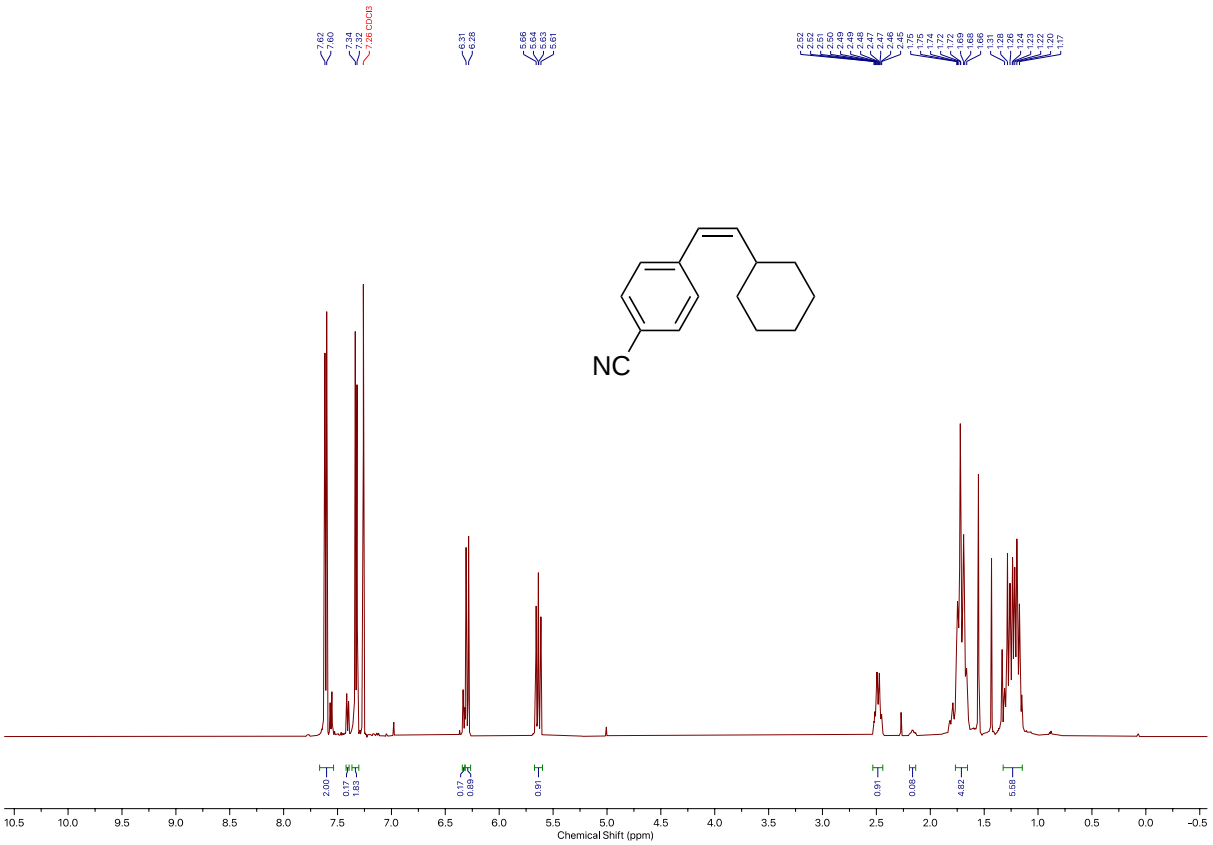


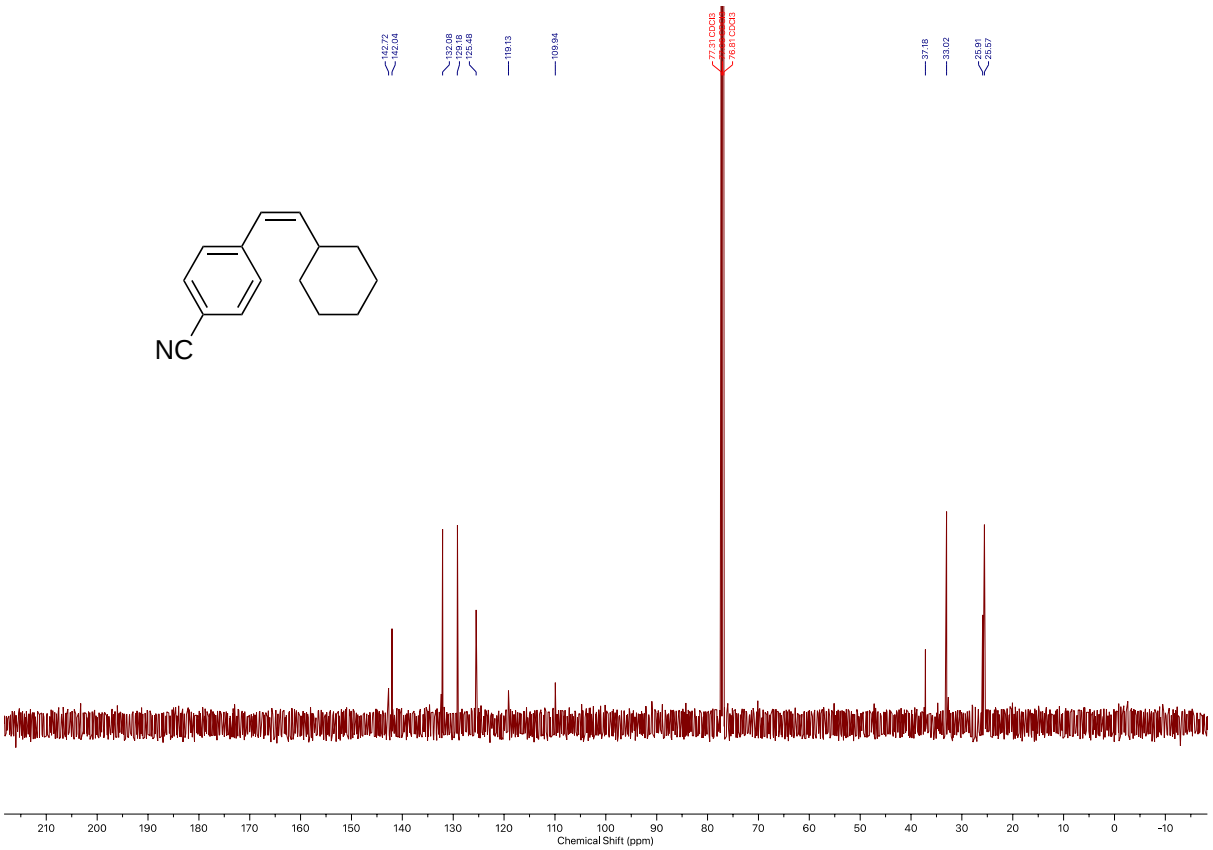
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3r:**



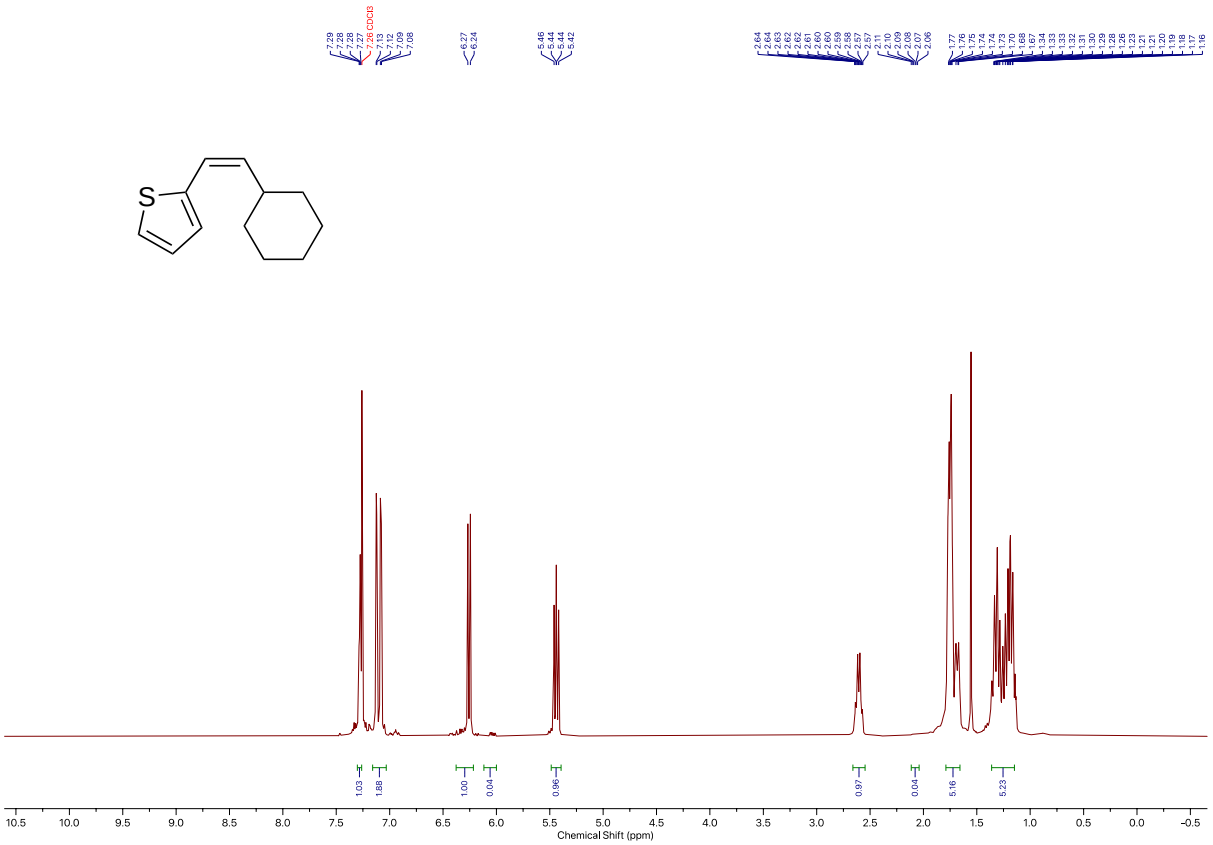


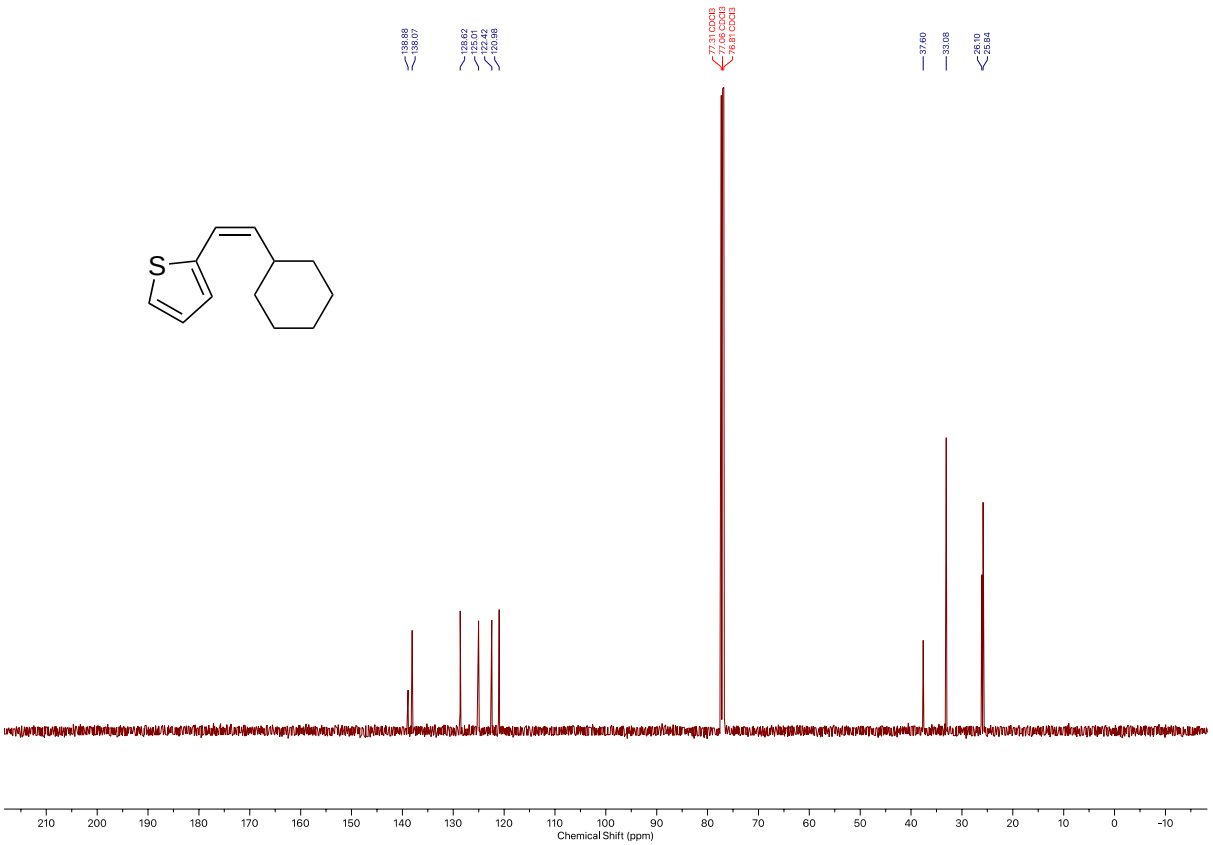
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3s:**



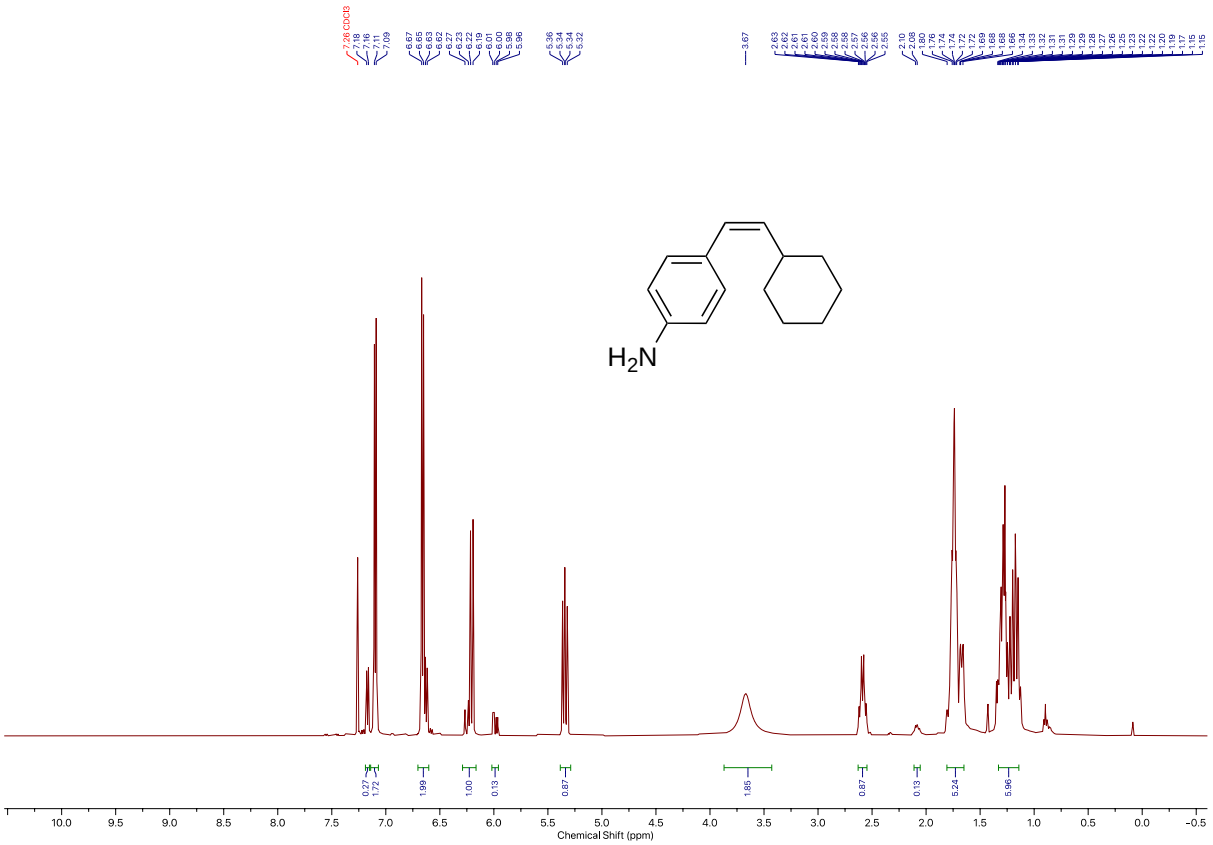


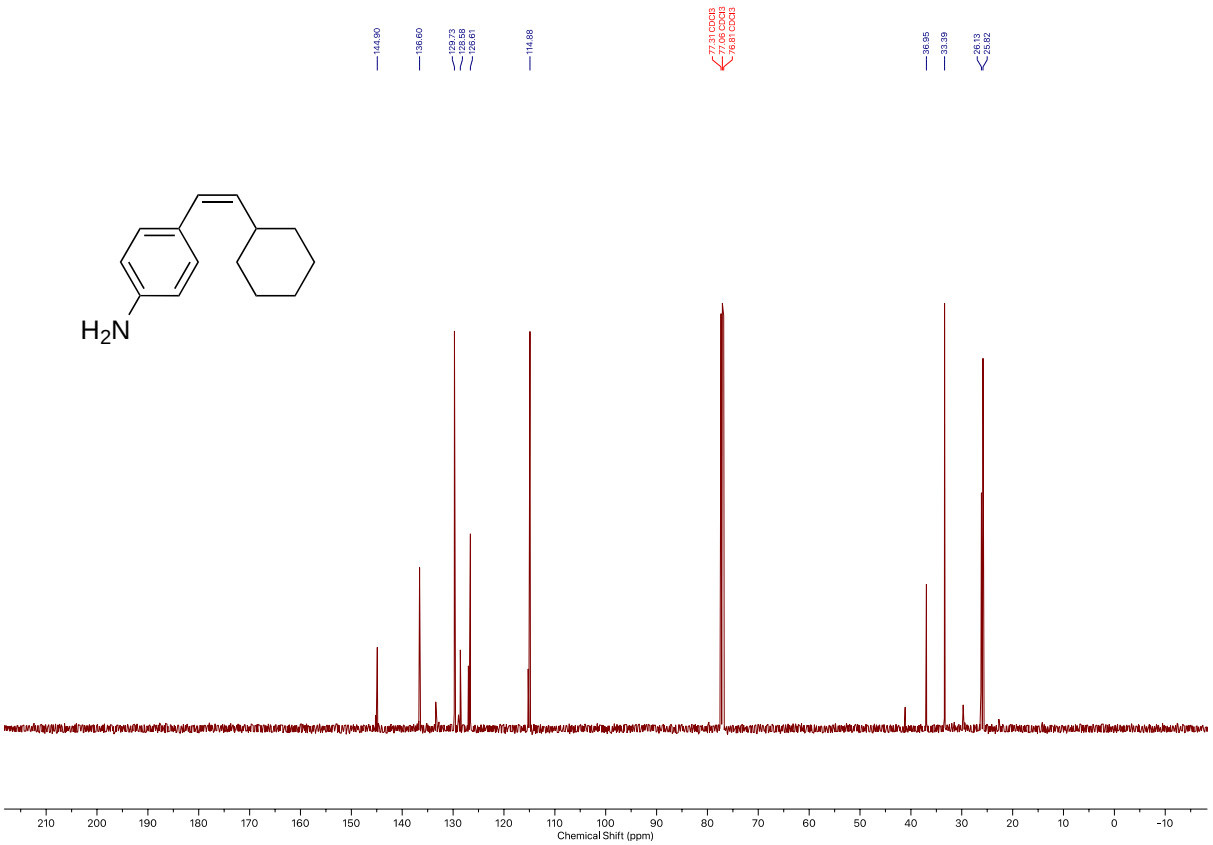
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3t:**



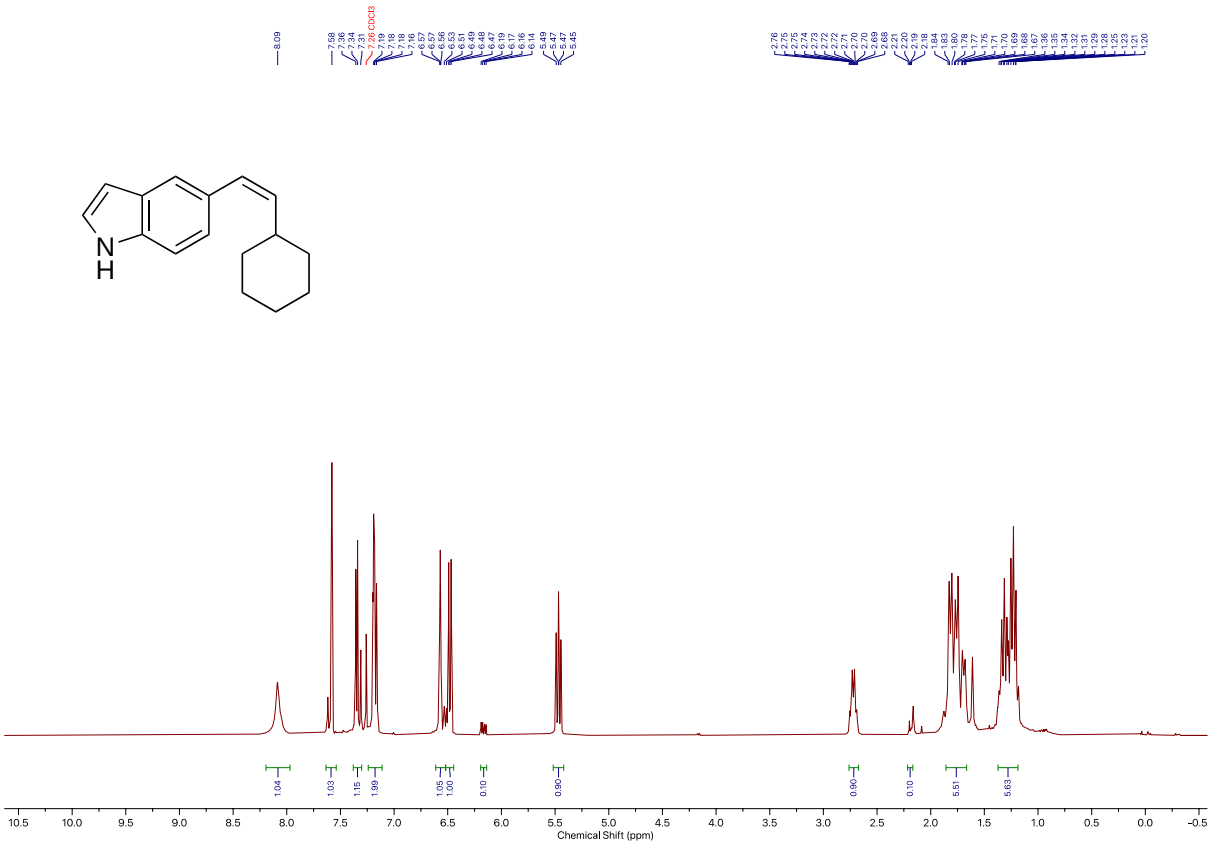


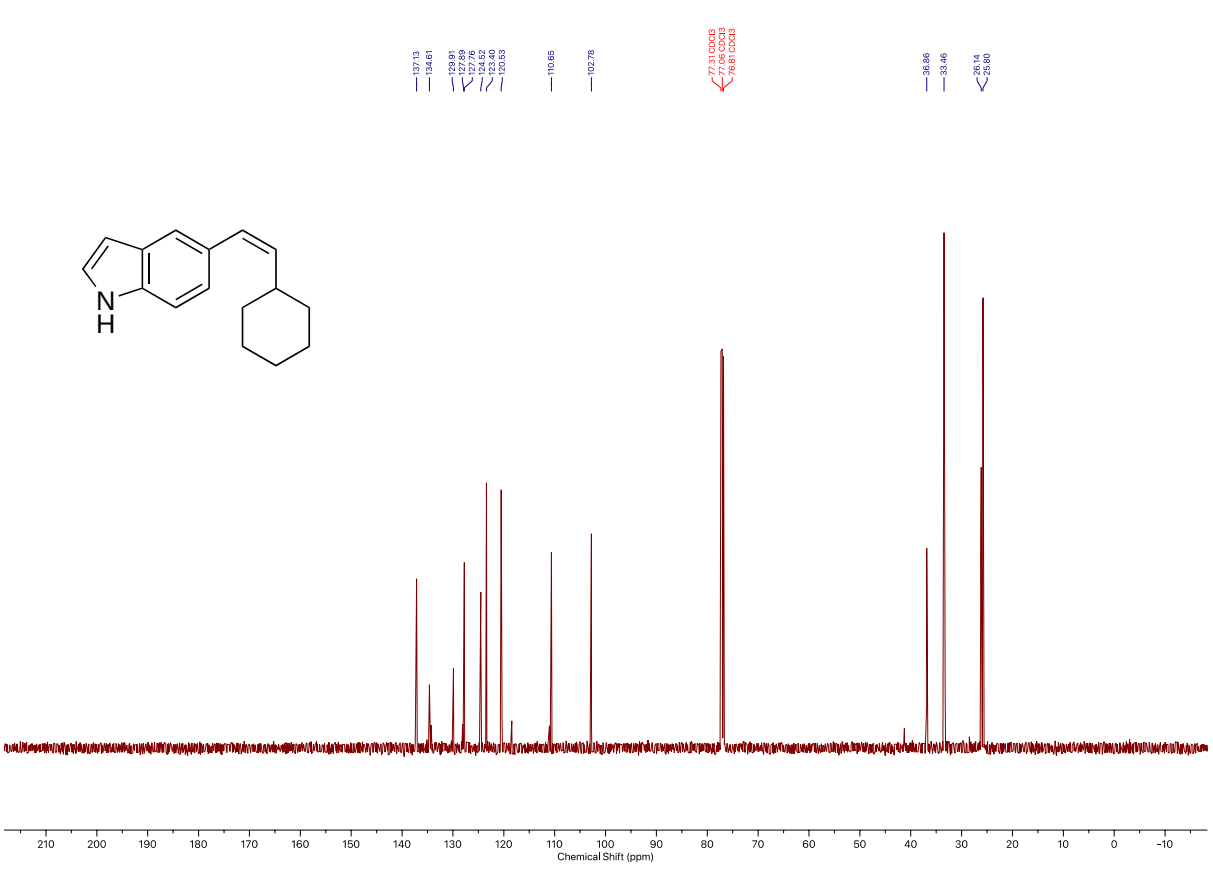
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3w:**



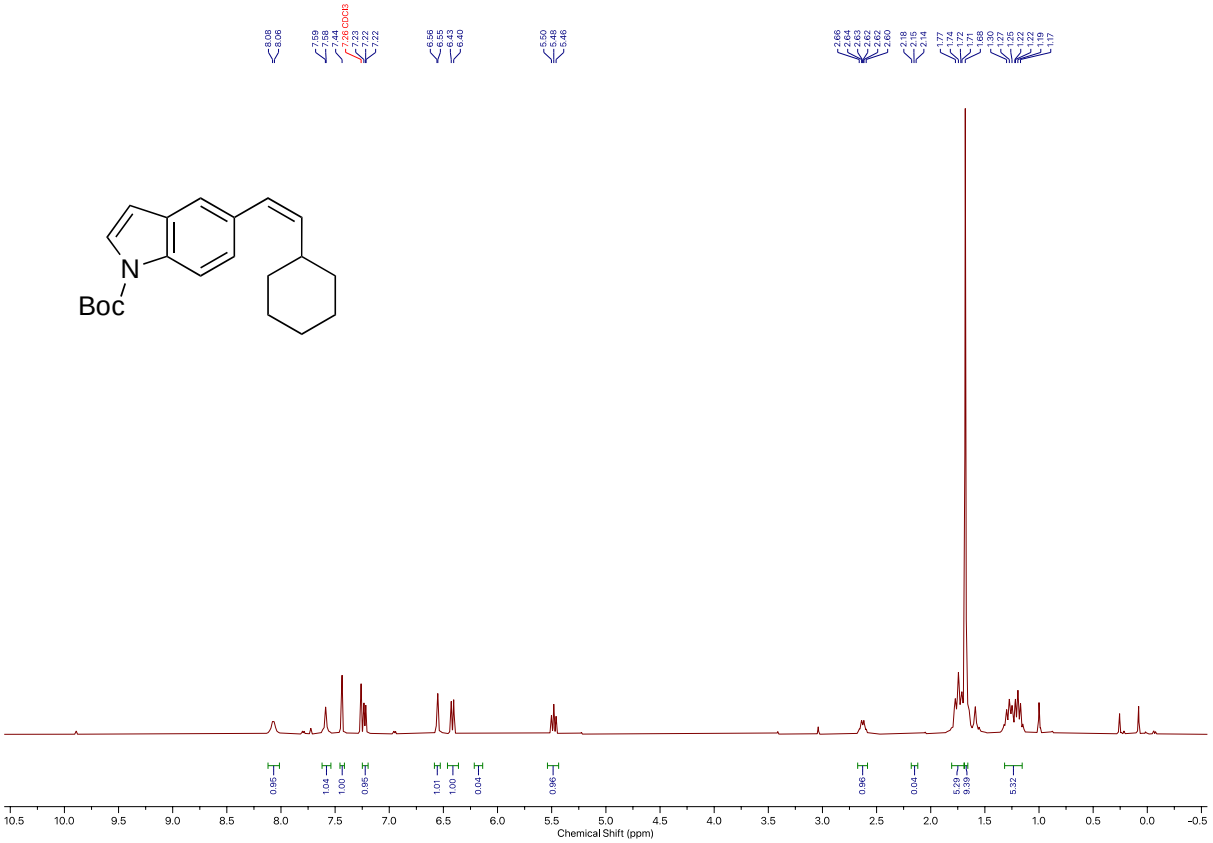


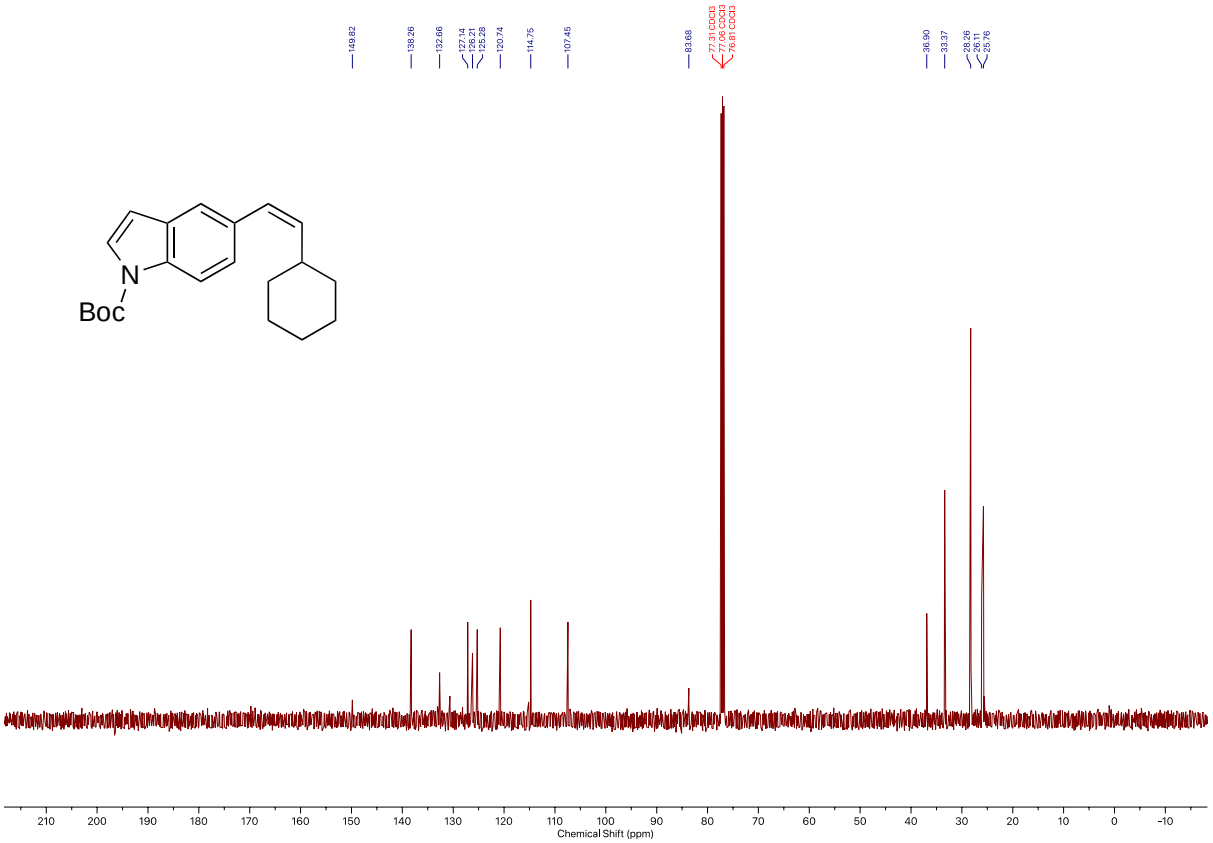
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3v:**



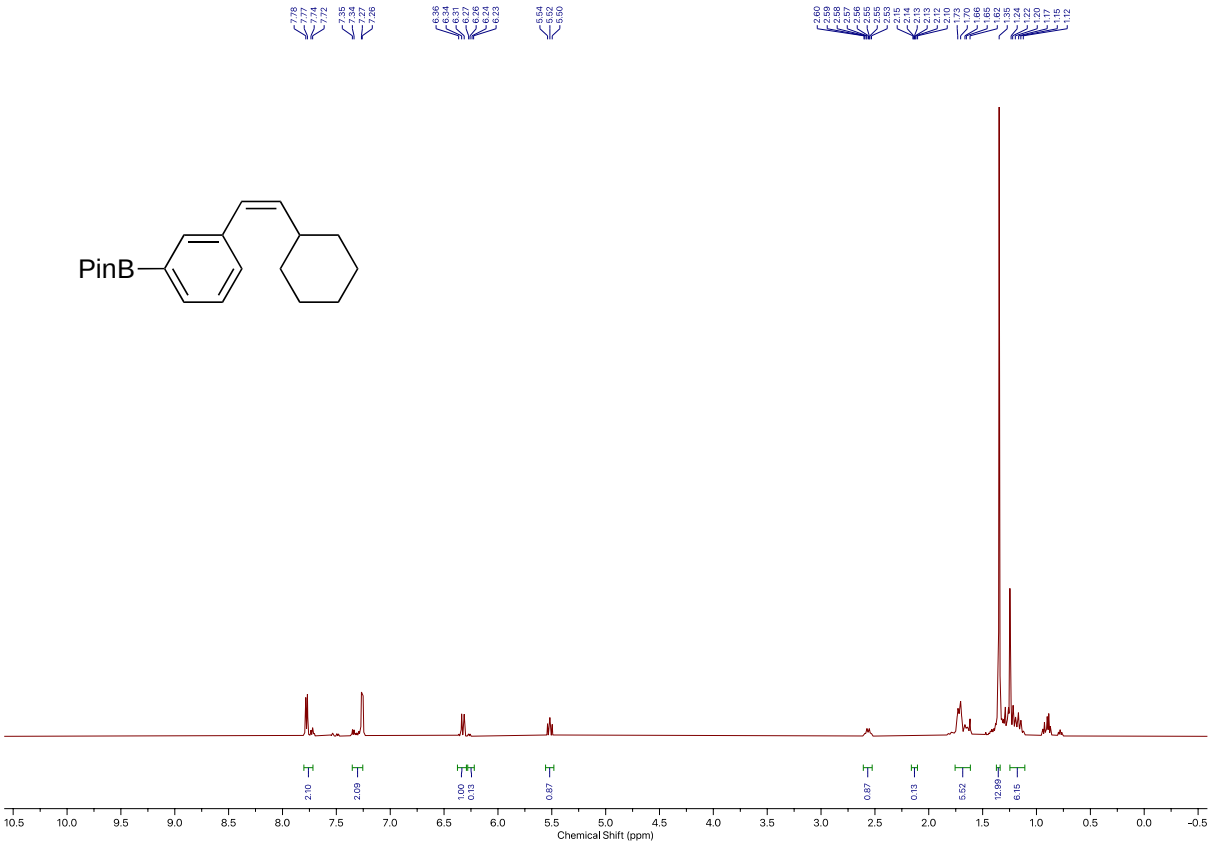


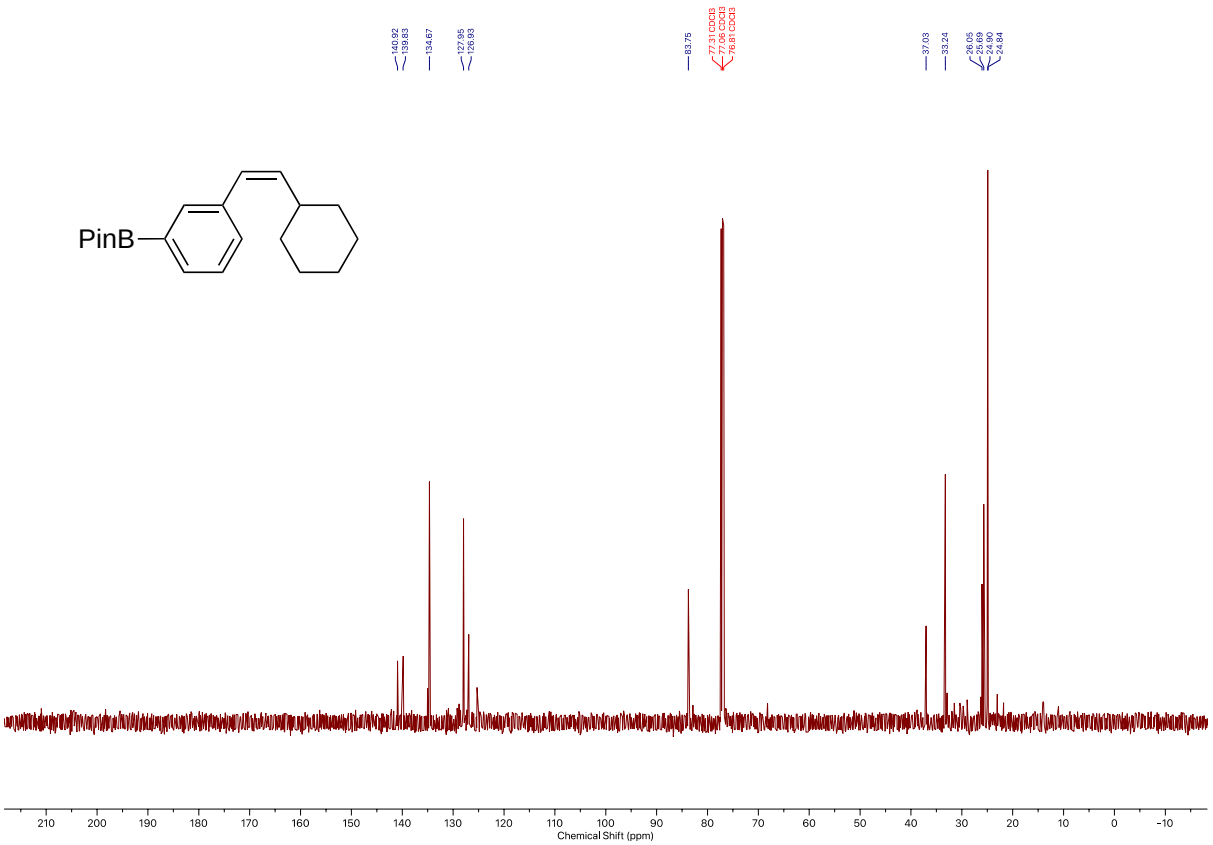
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3u:**



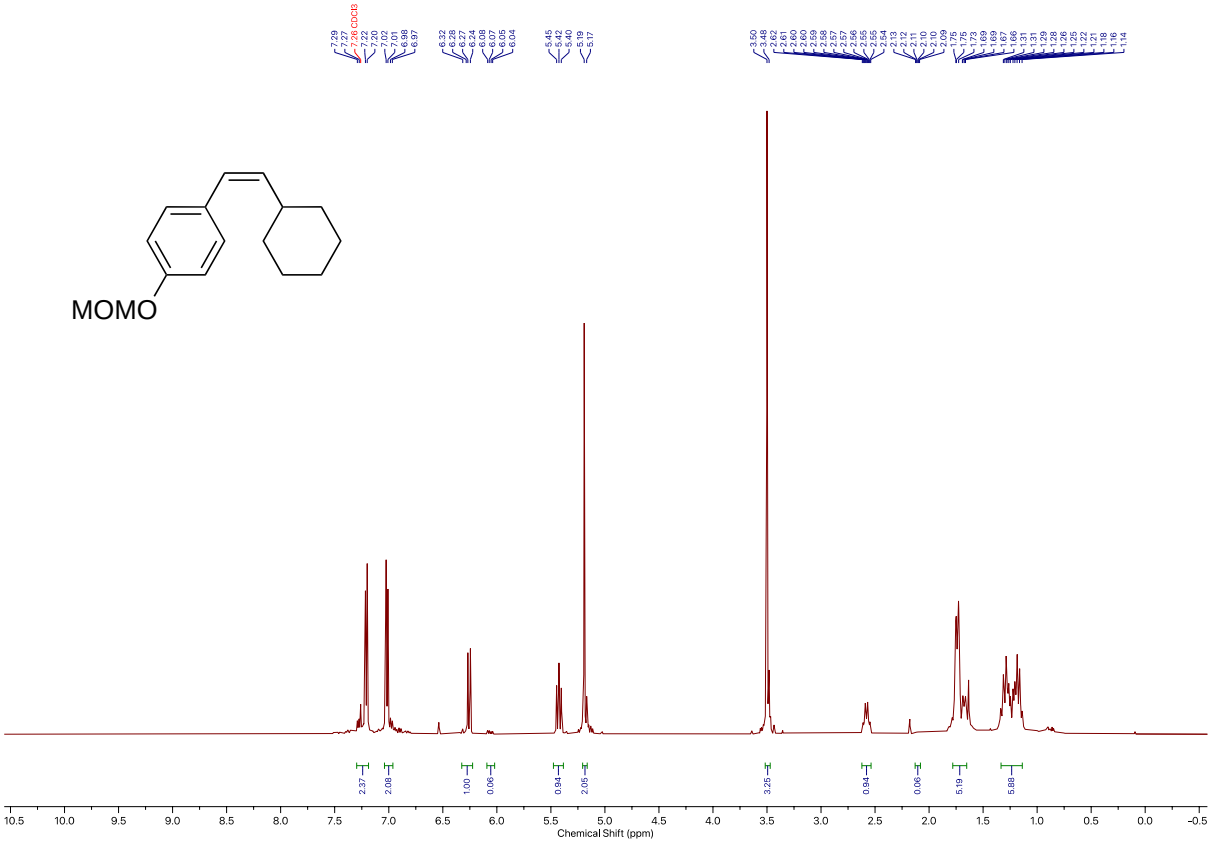


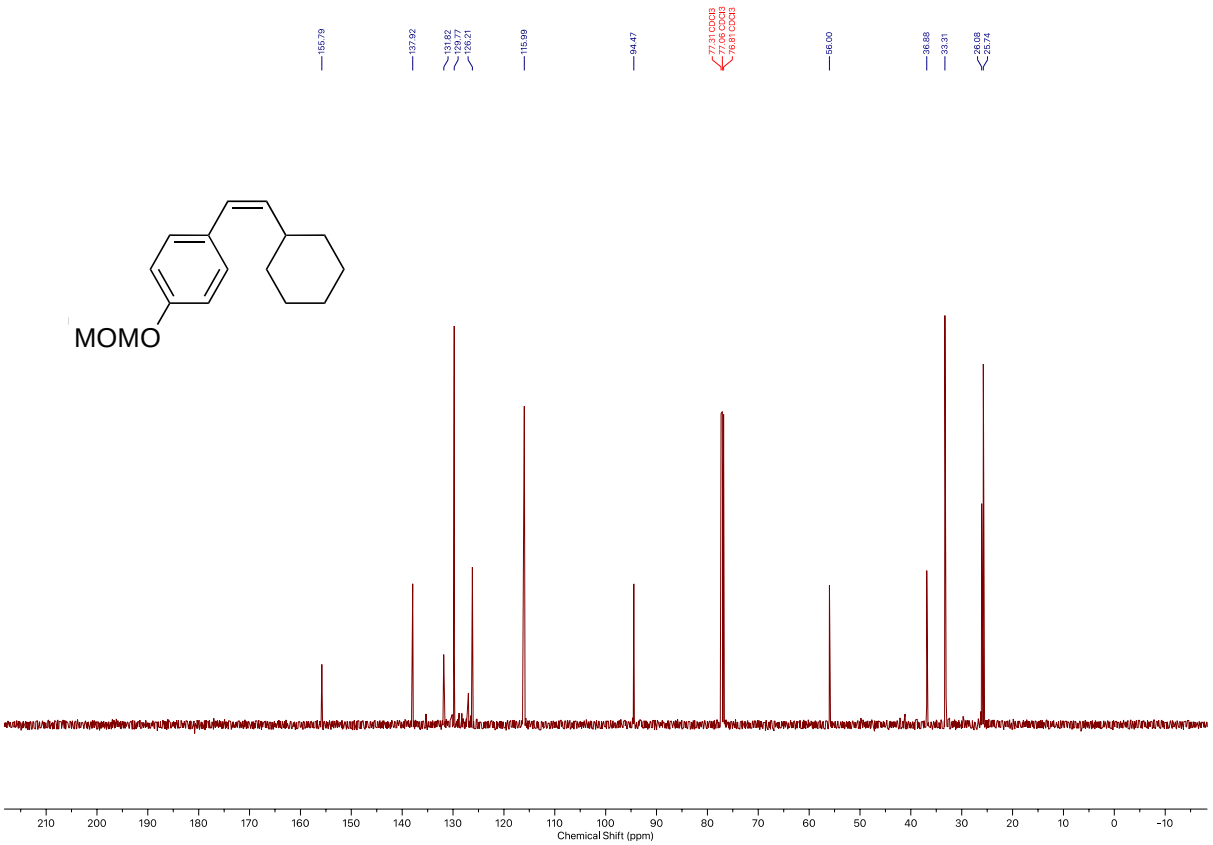
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3x:**



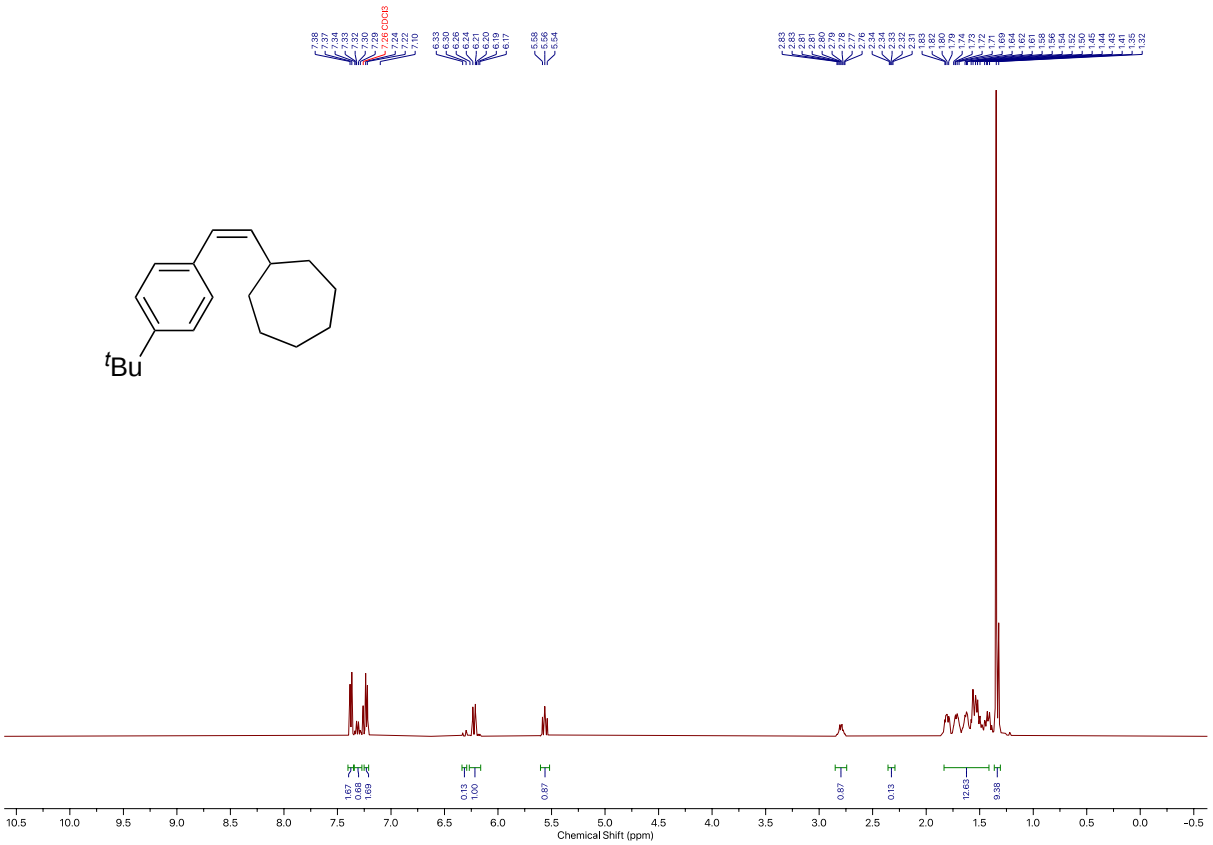


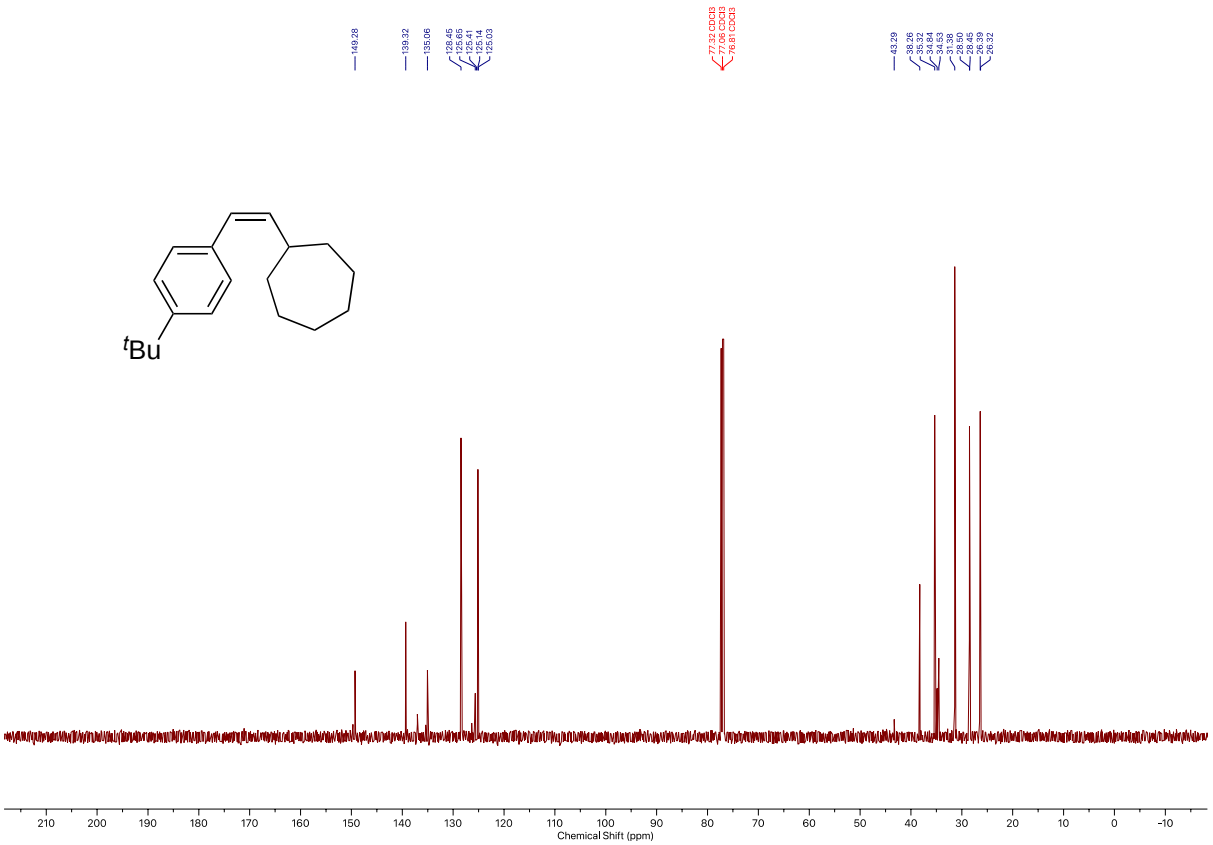
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3y:**



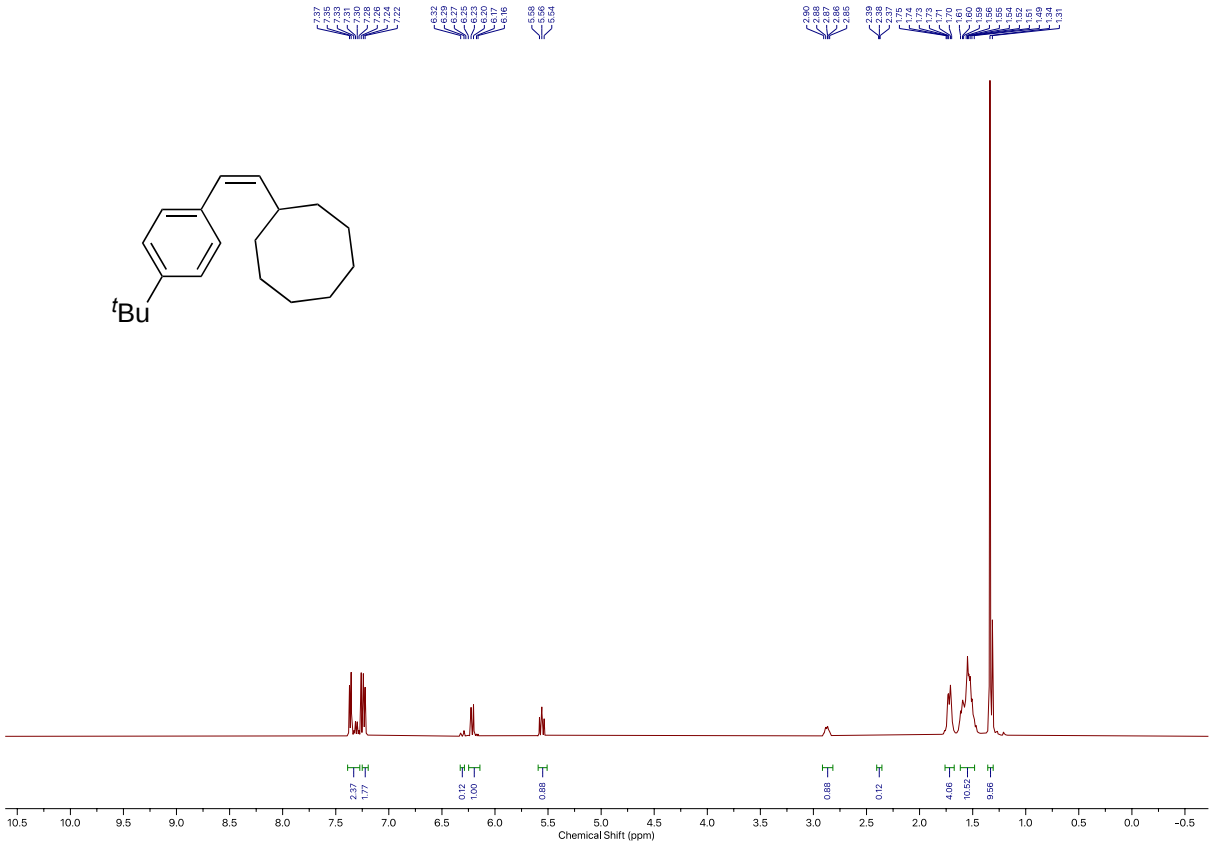


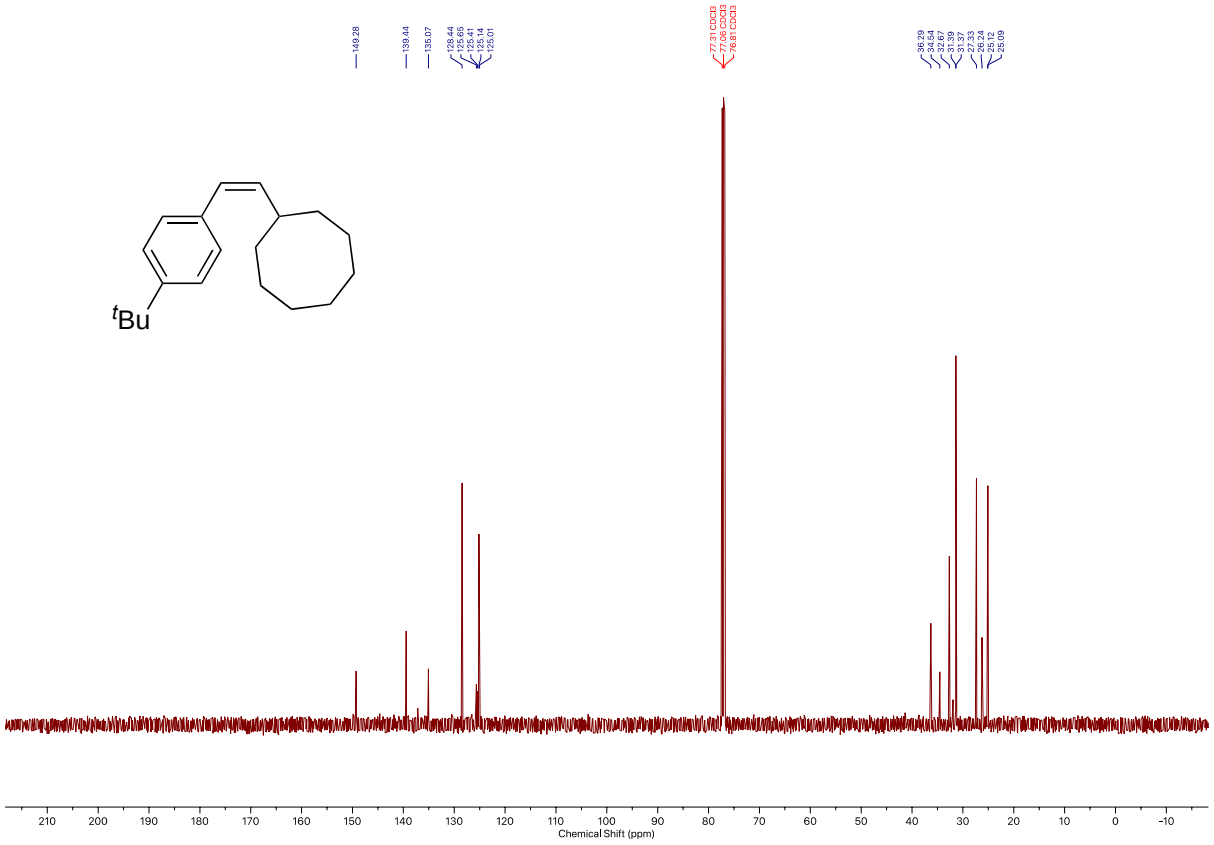
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3aa:**



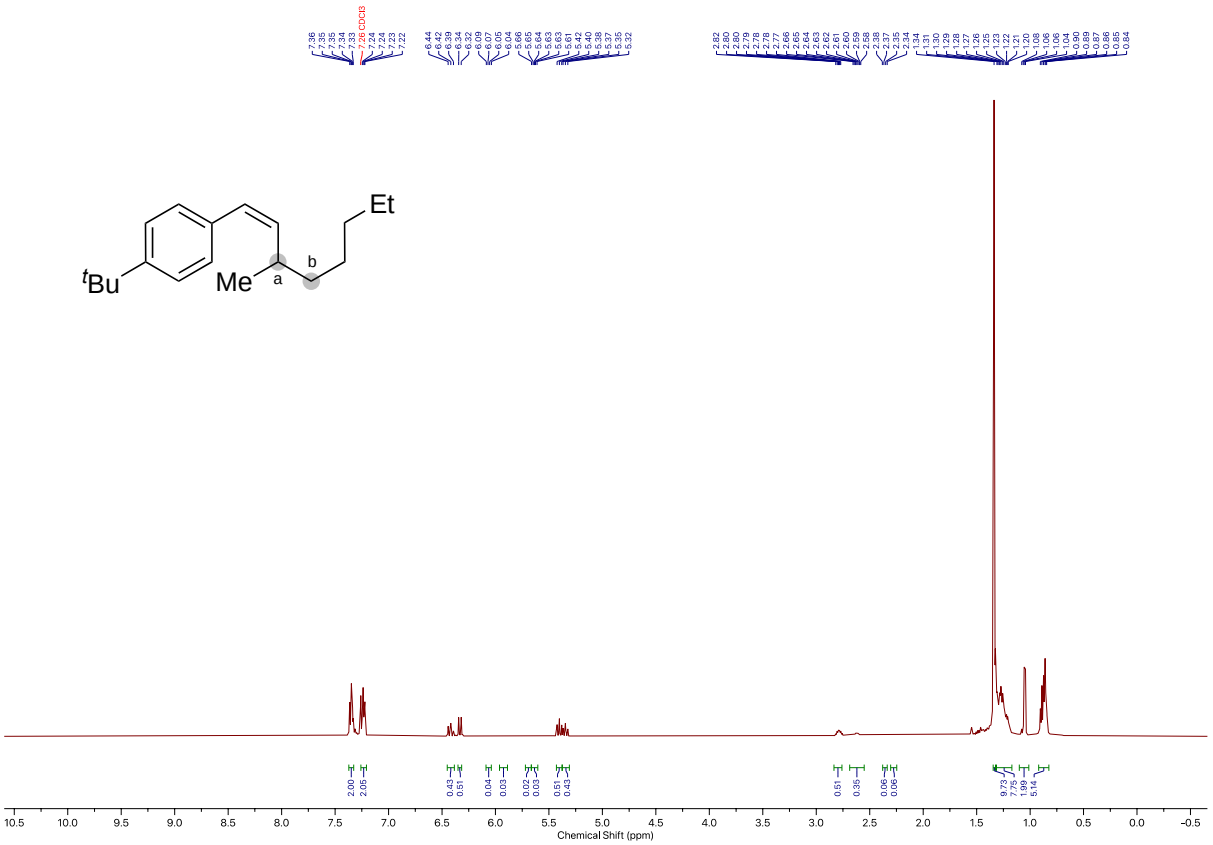


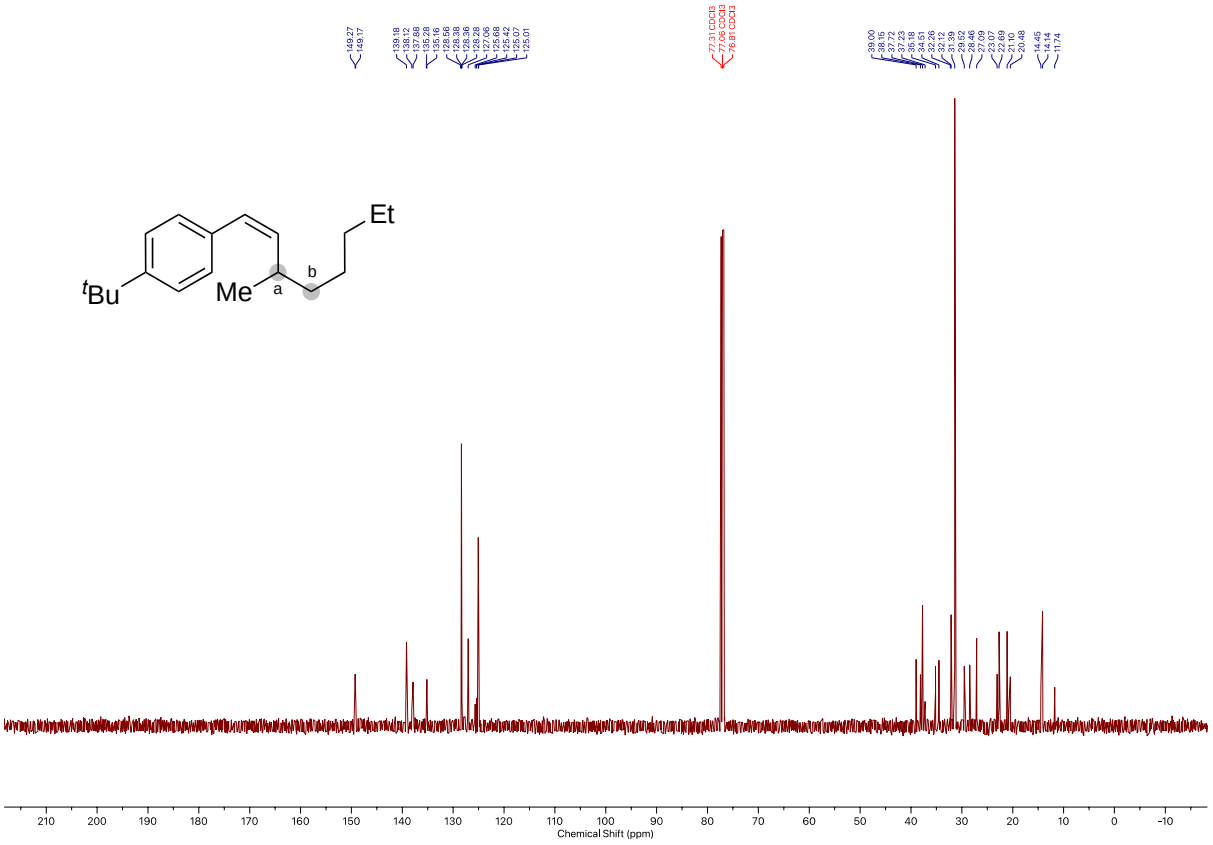
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3ab:**



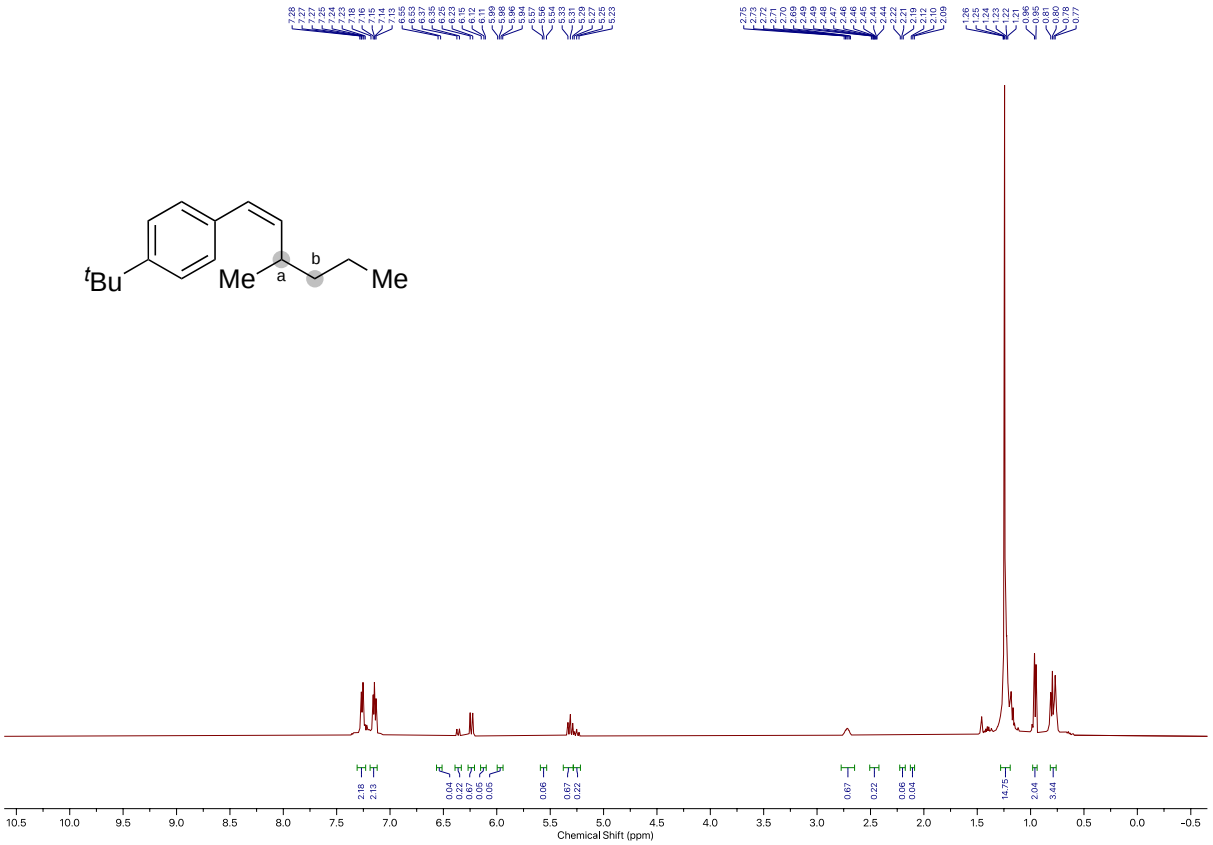


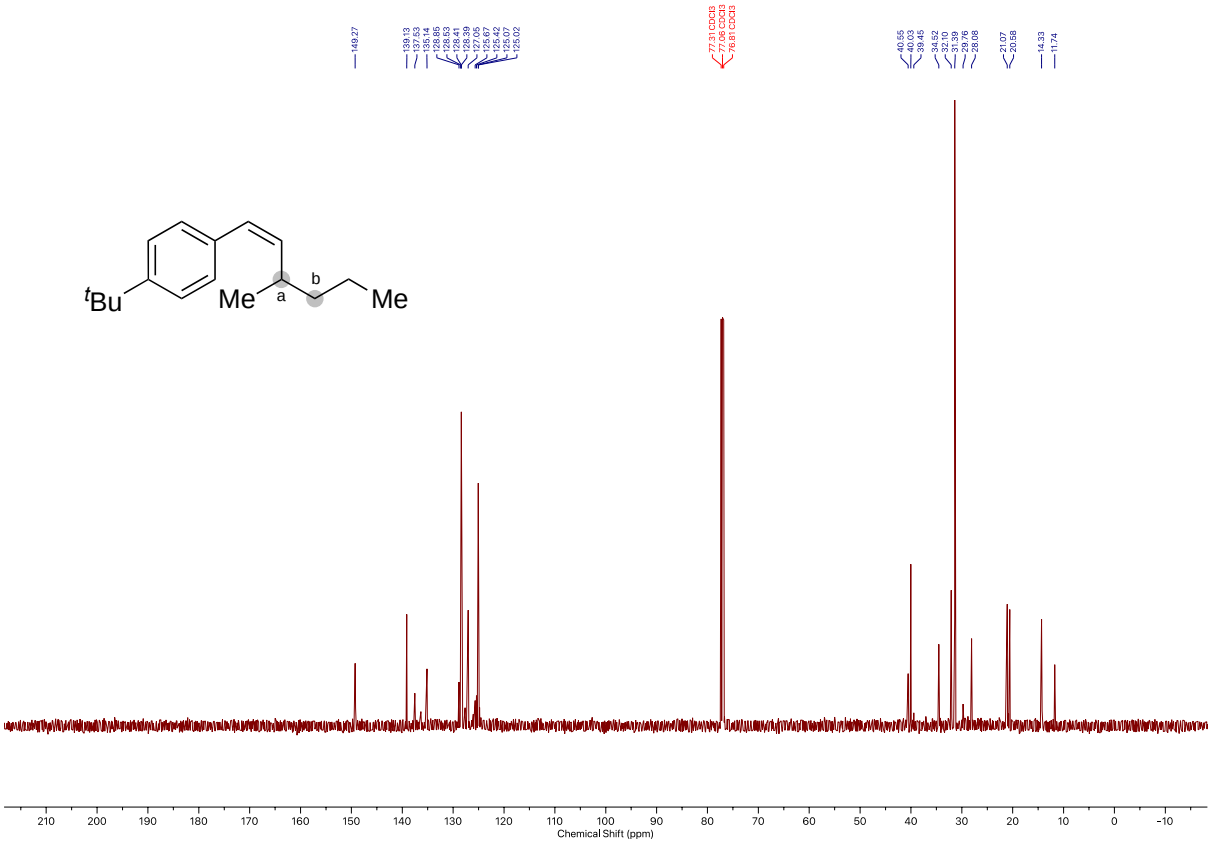
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3ac:**



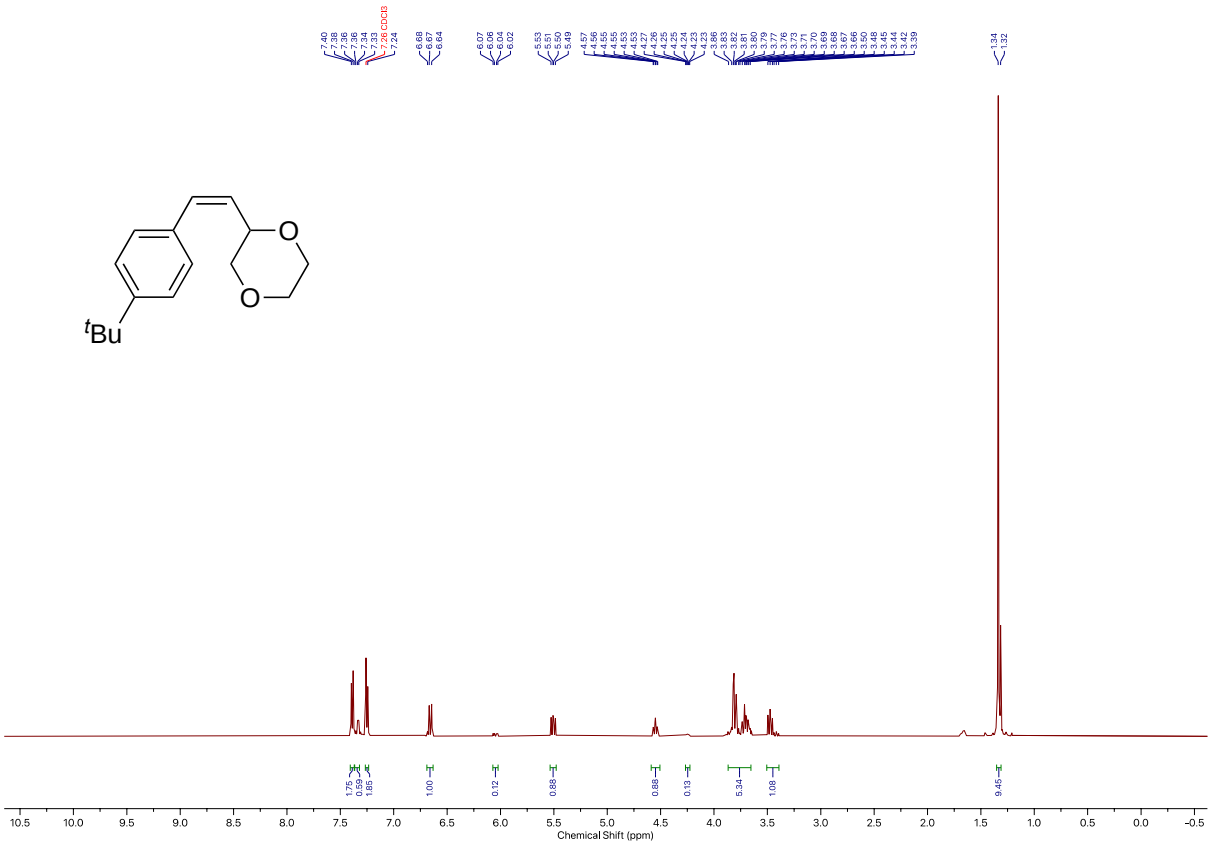


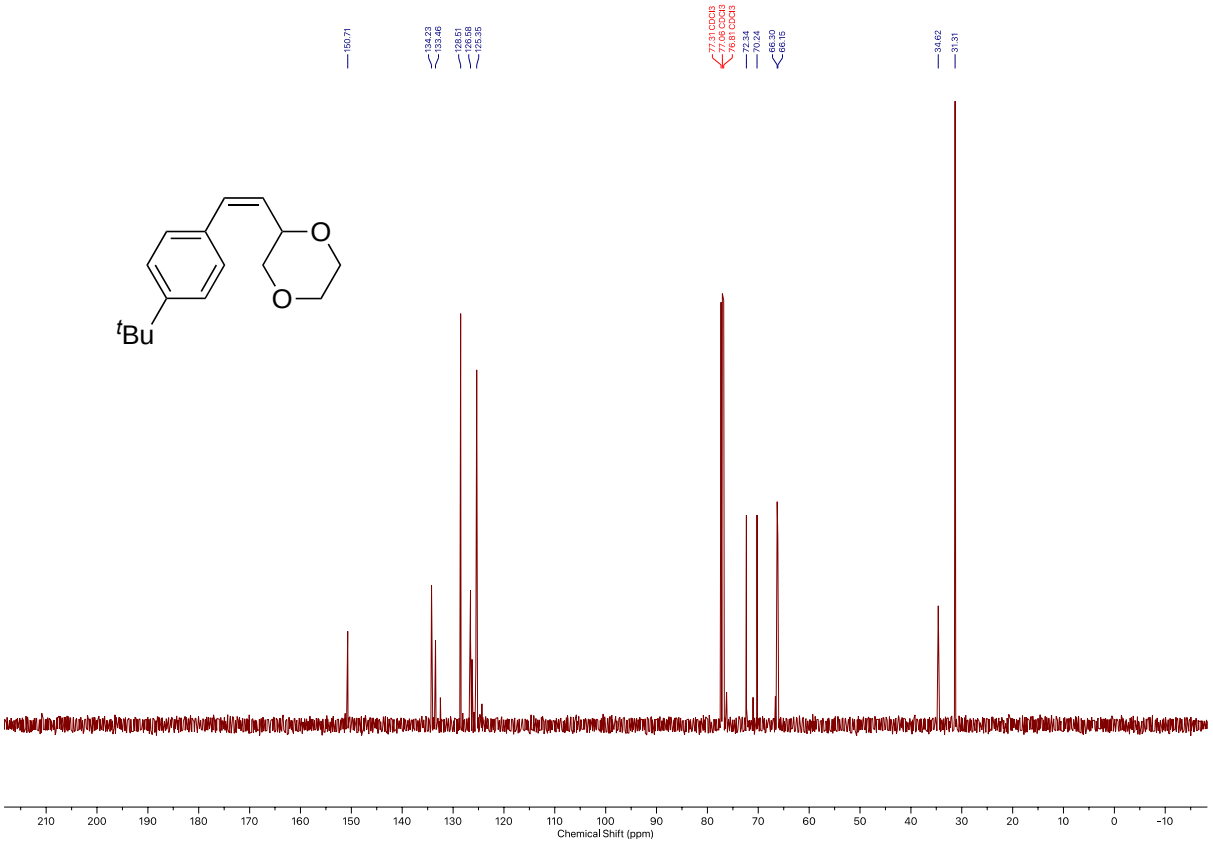
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3ad:**



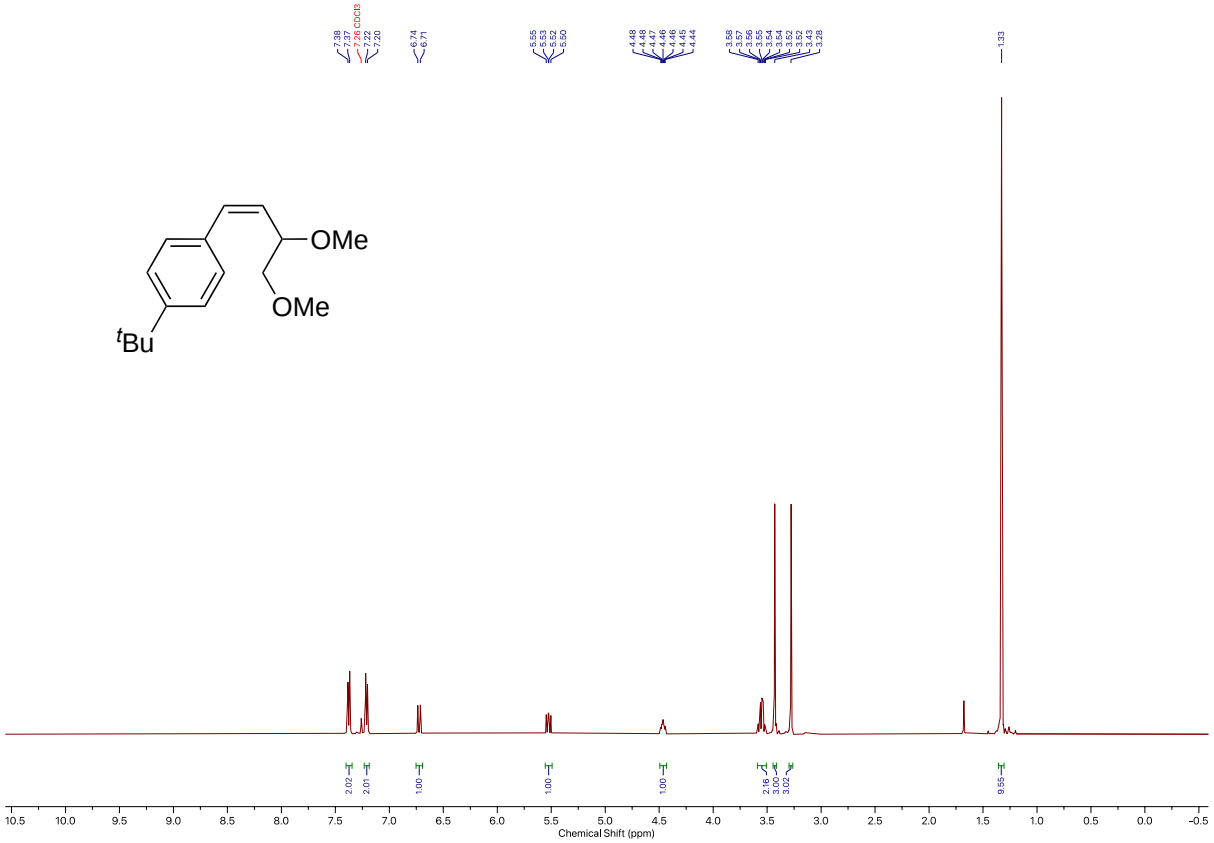


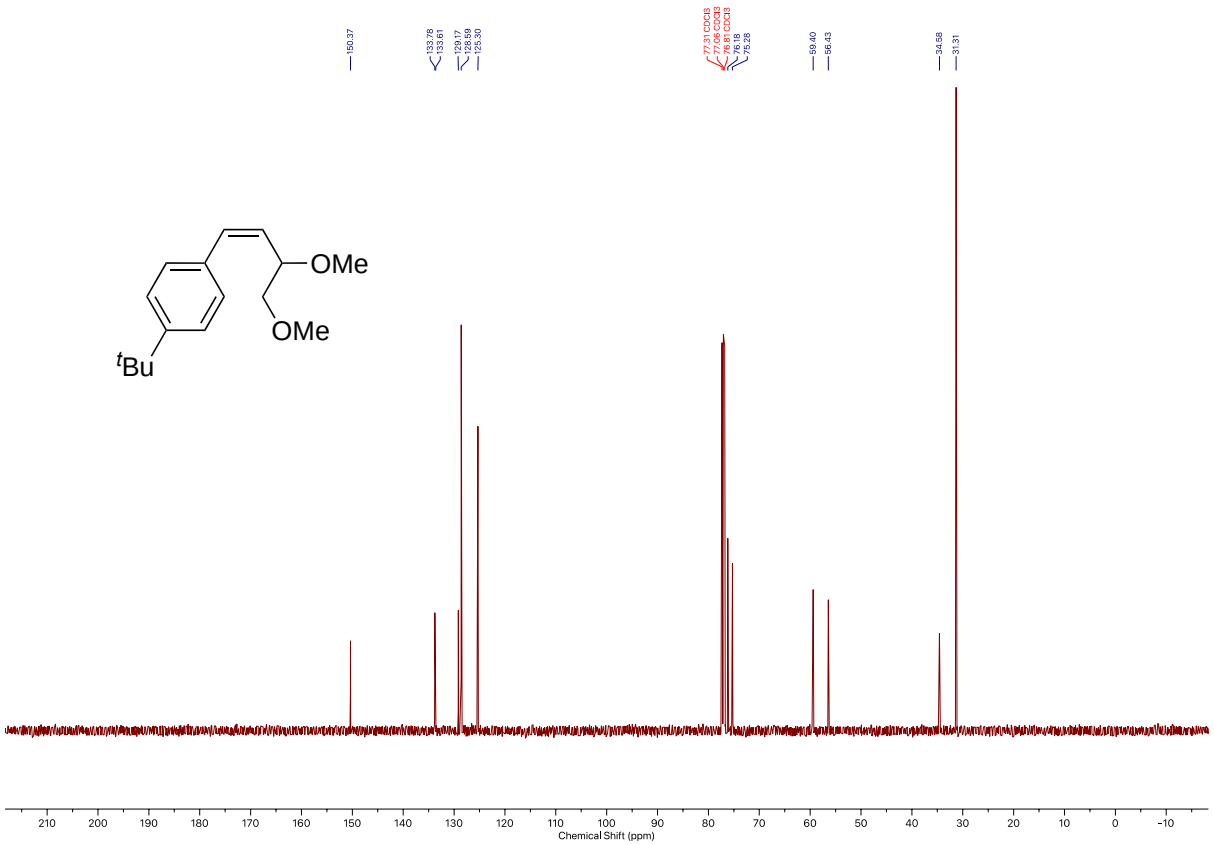
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3ae:**



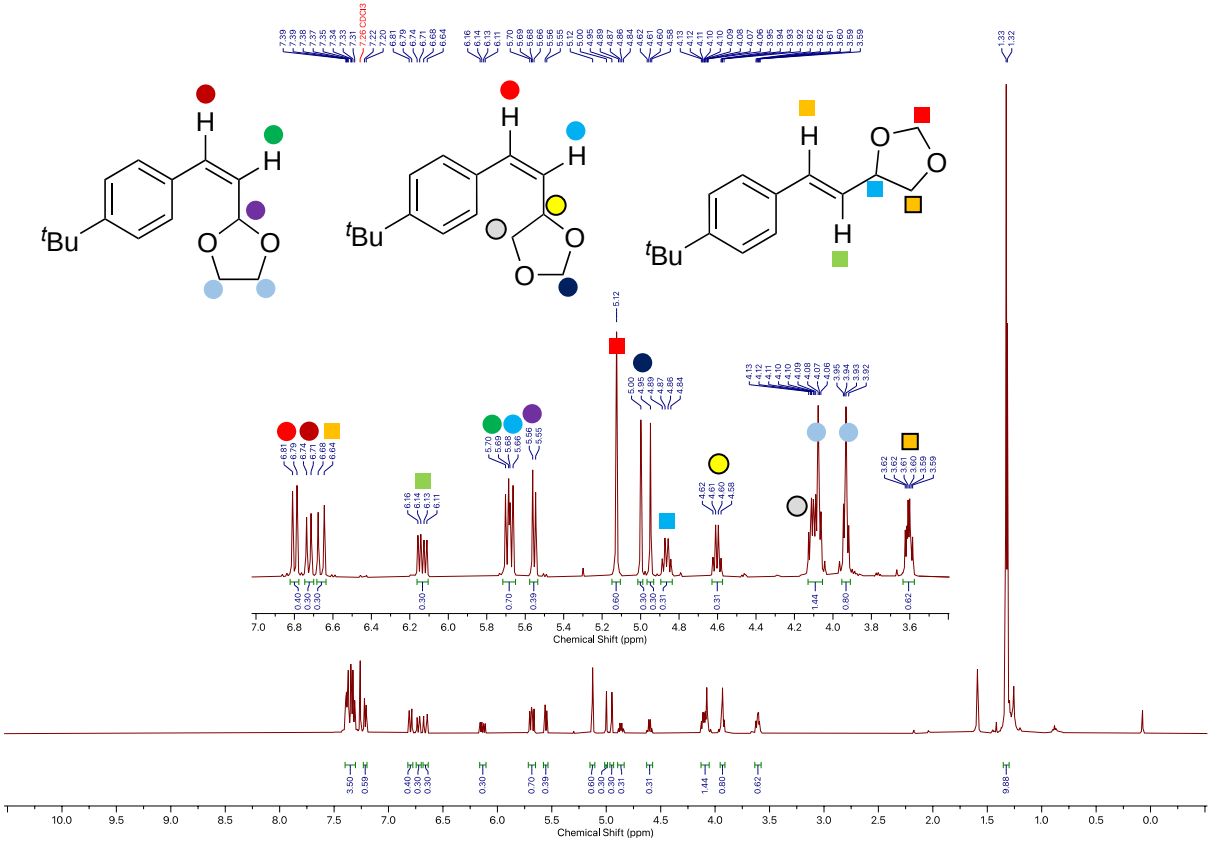


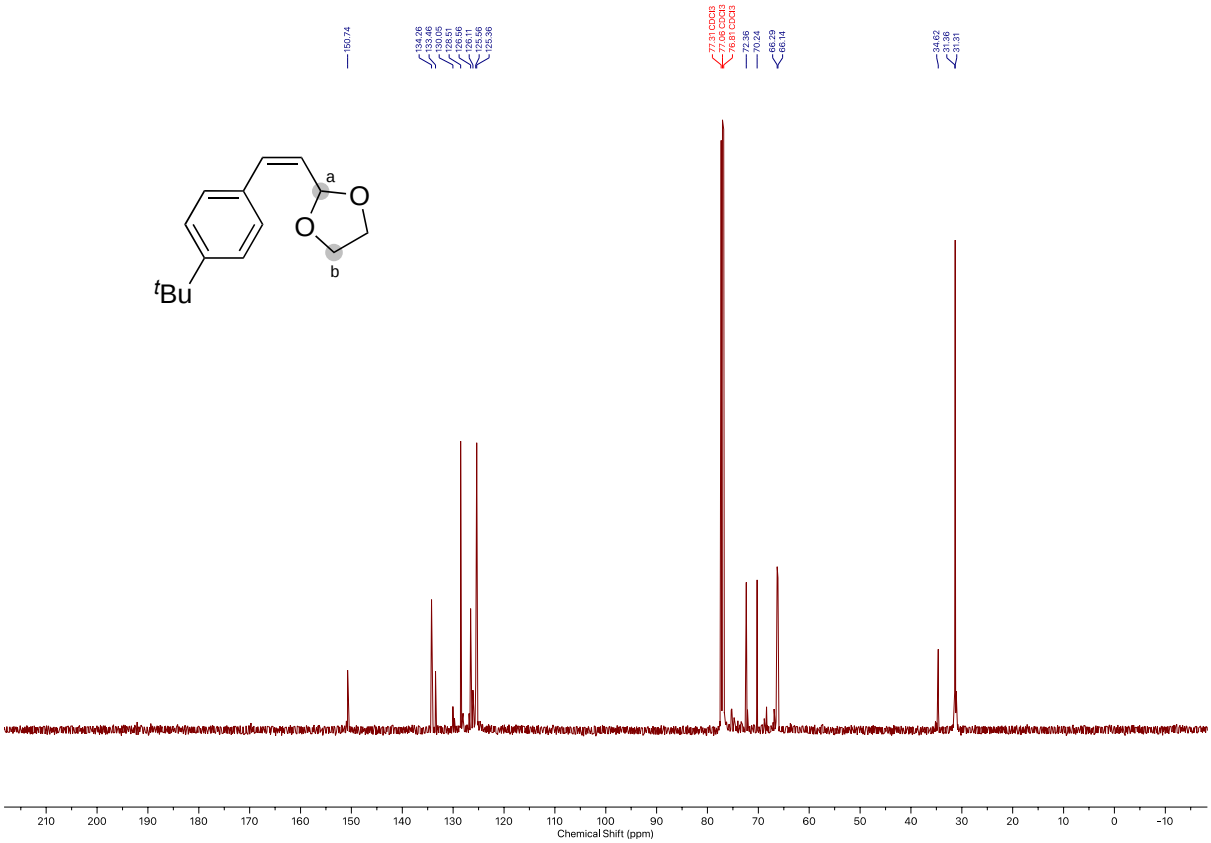
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3af:**



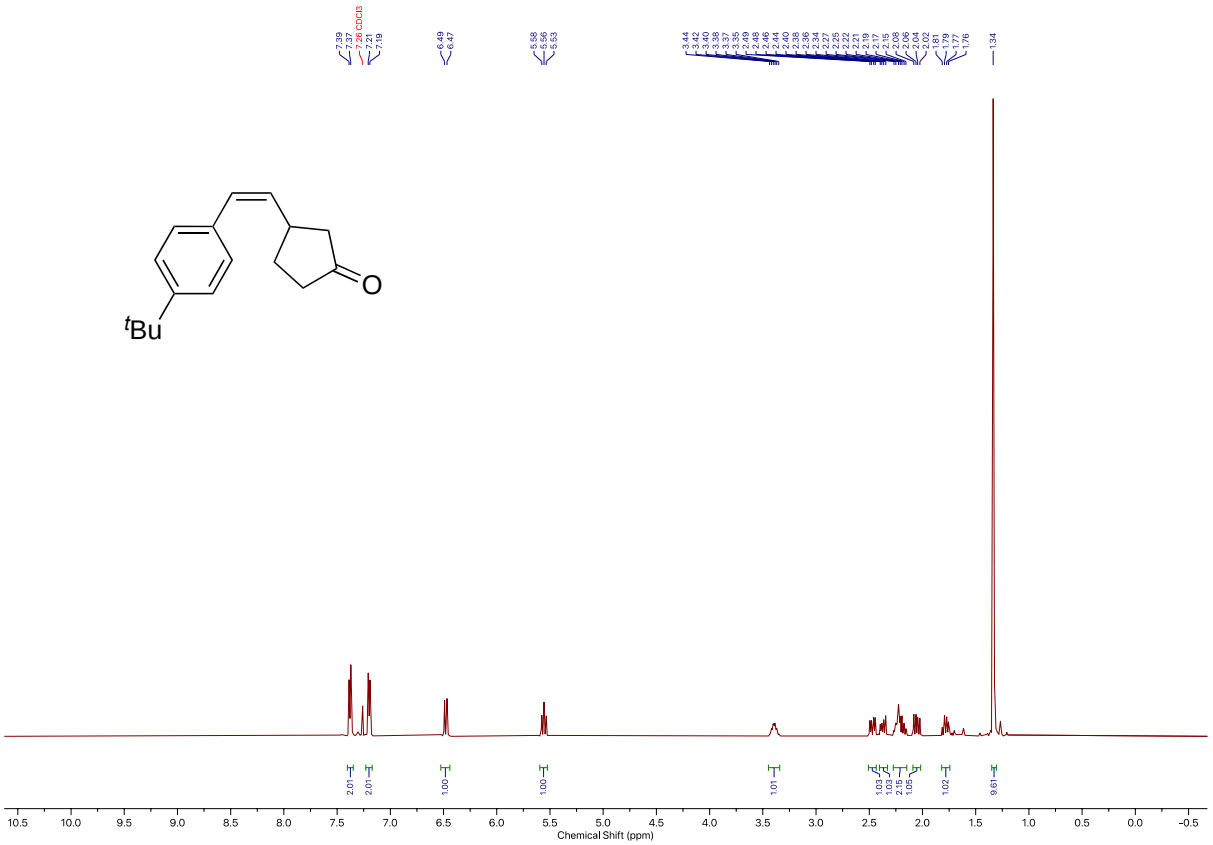


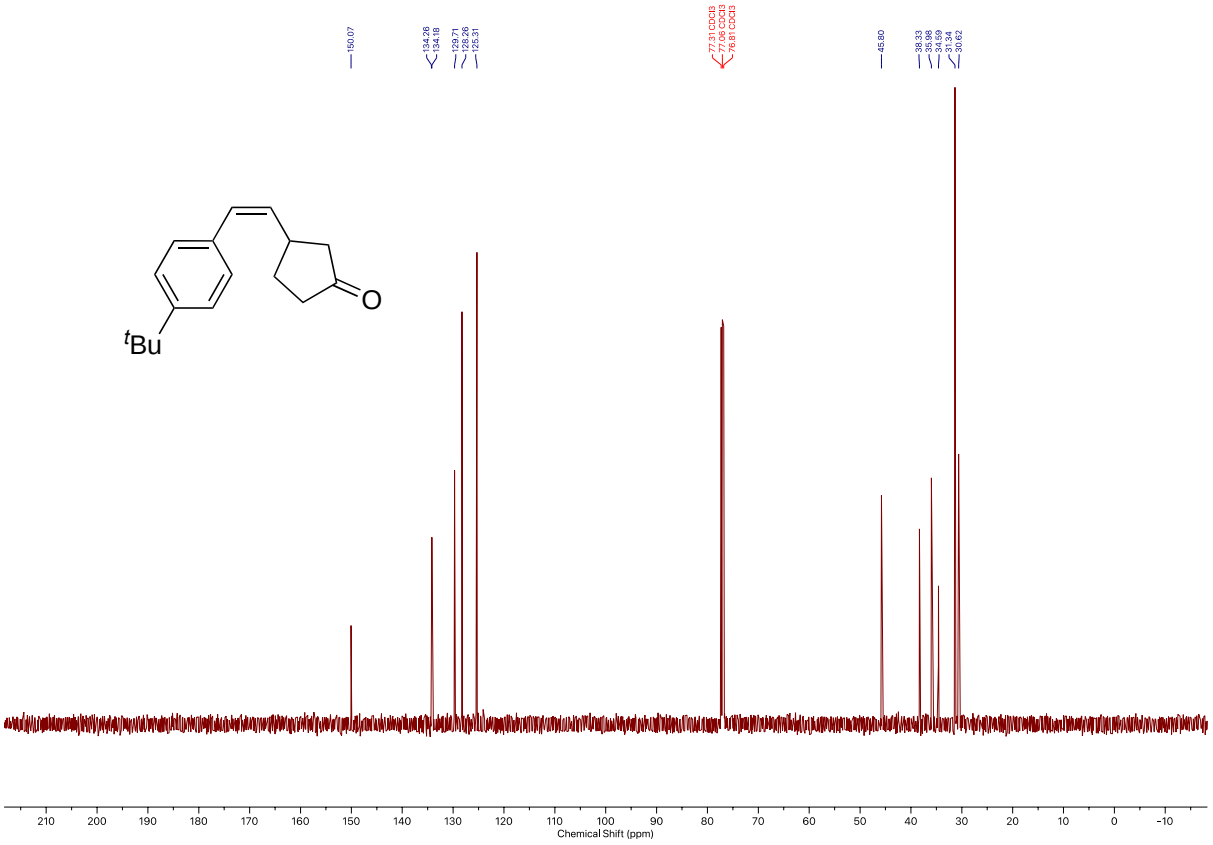
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3ag:**



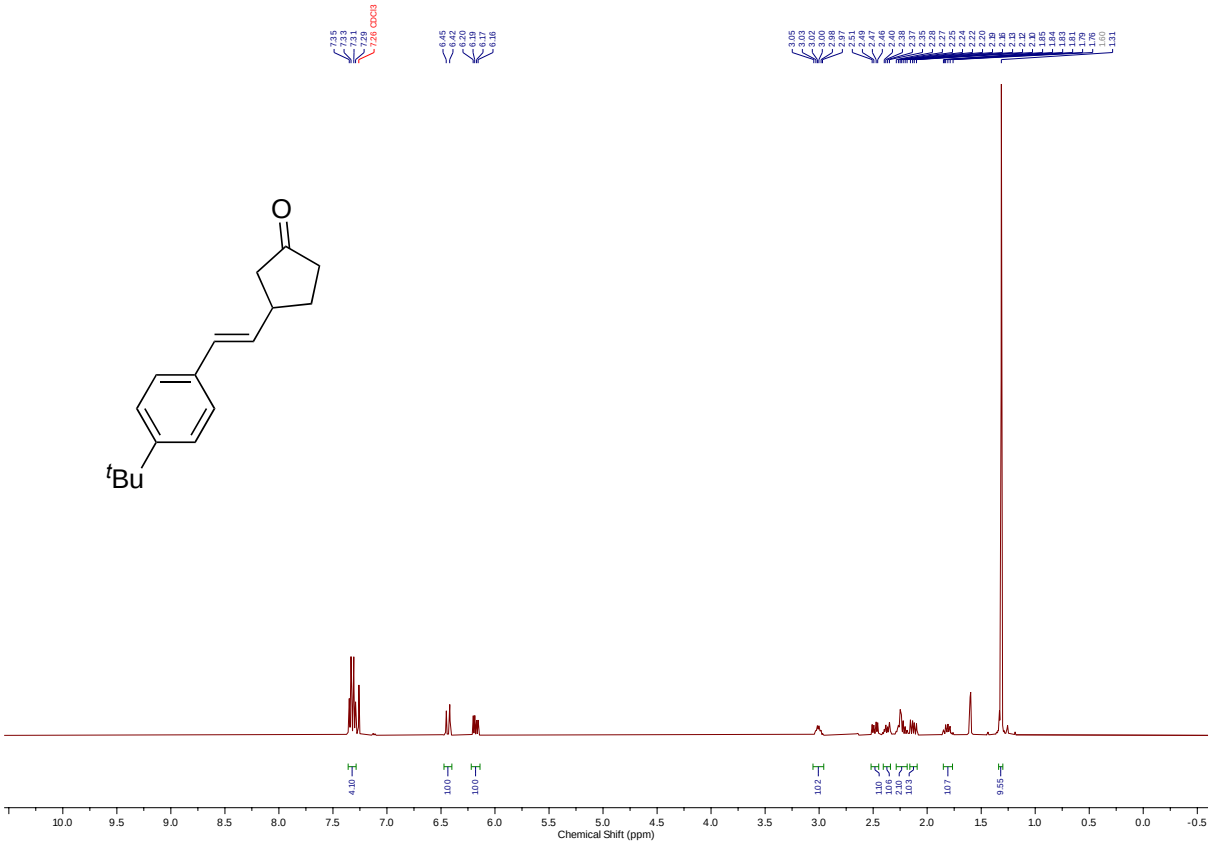


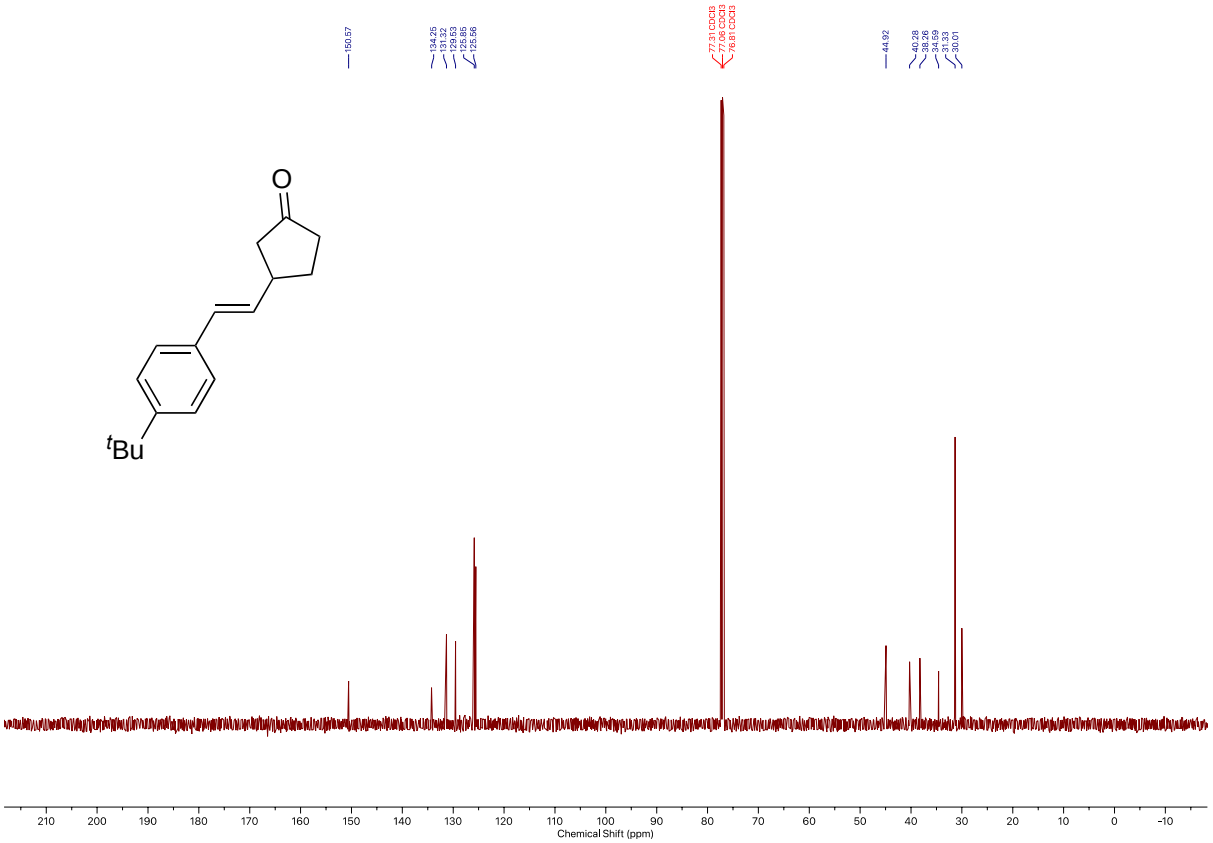
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3ah-*Z*:**



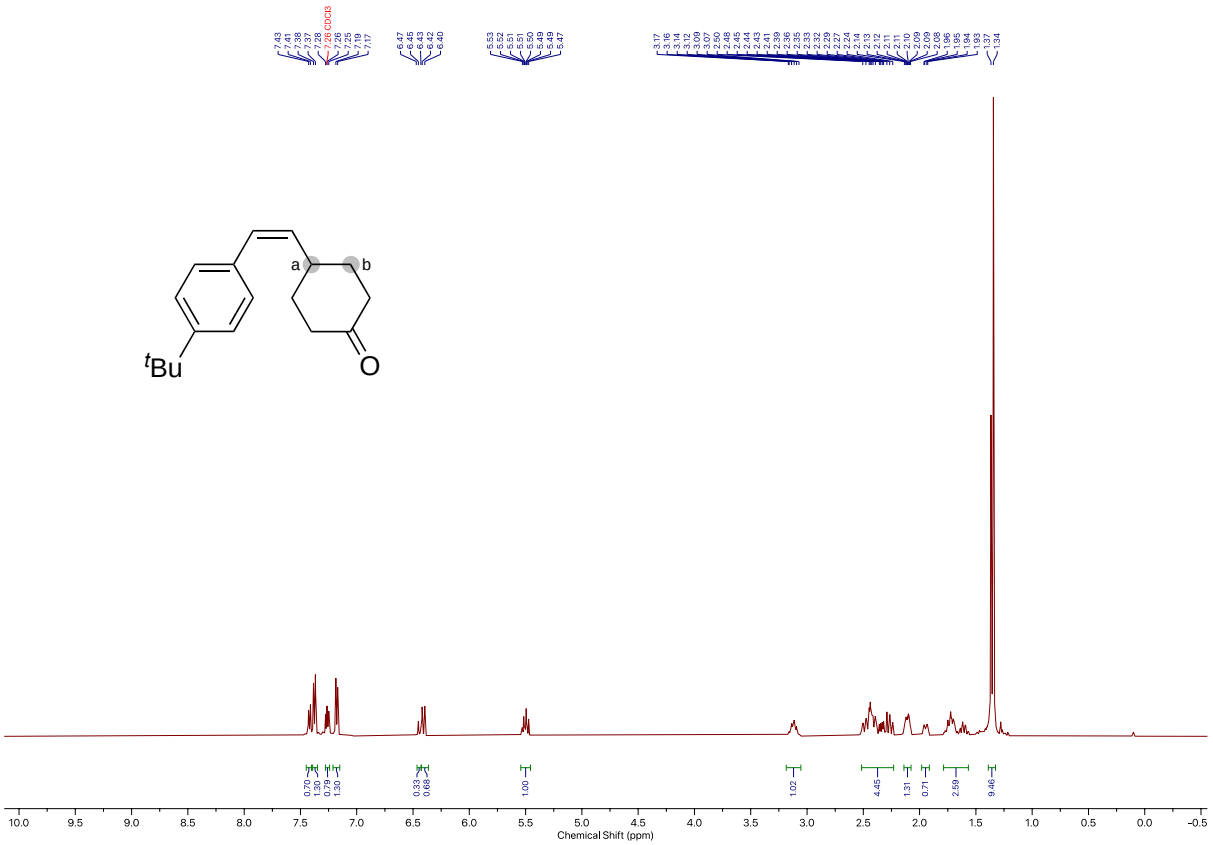


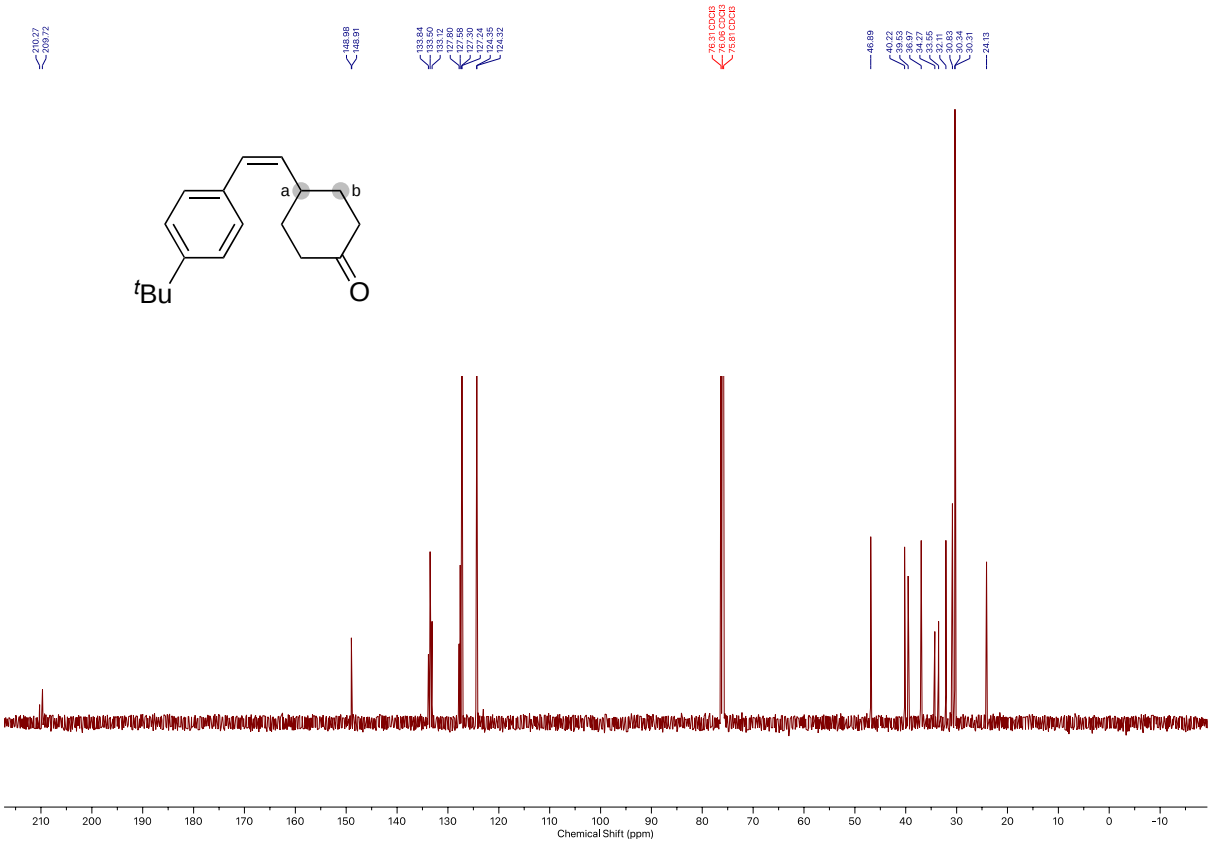
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3ah-*E*:**



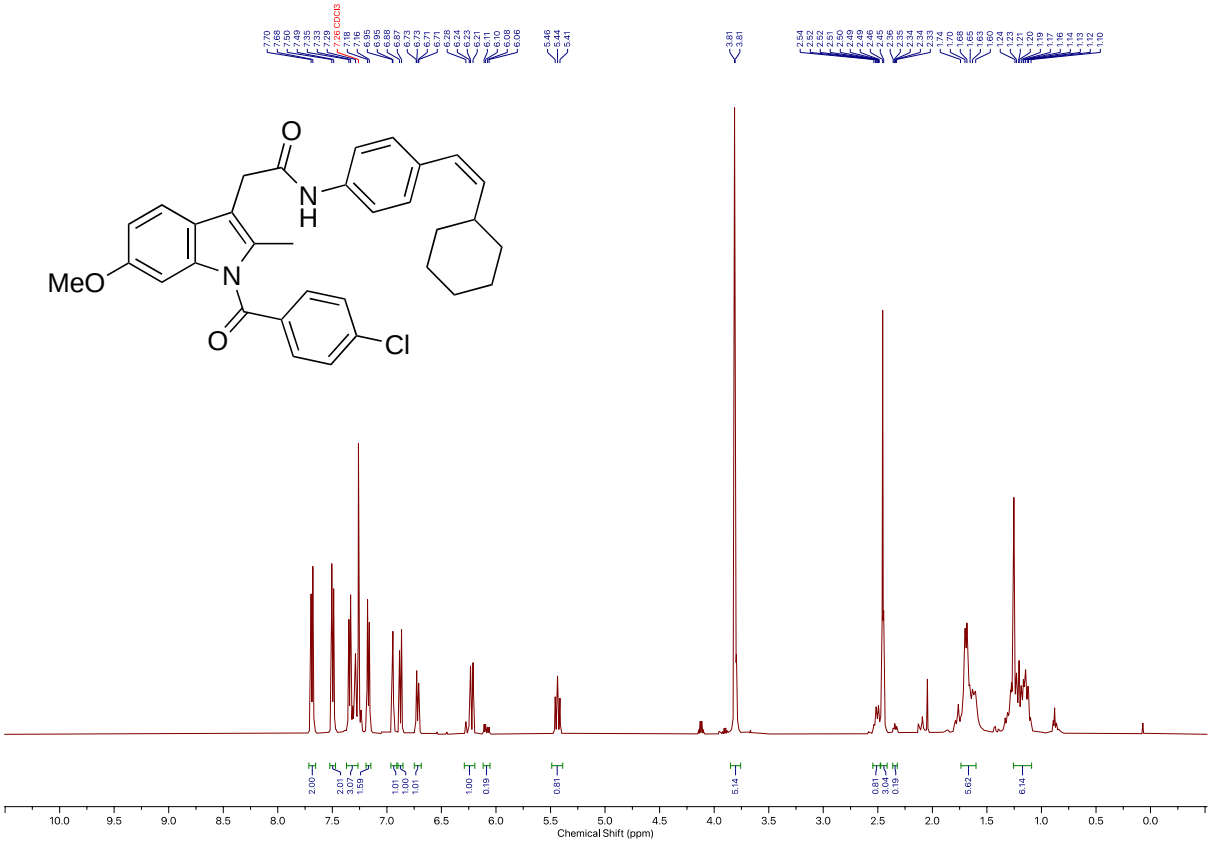


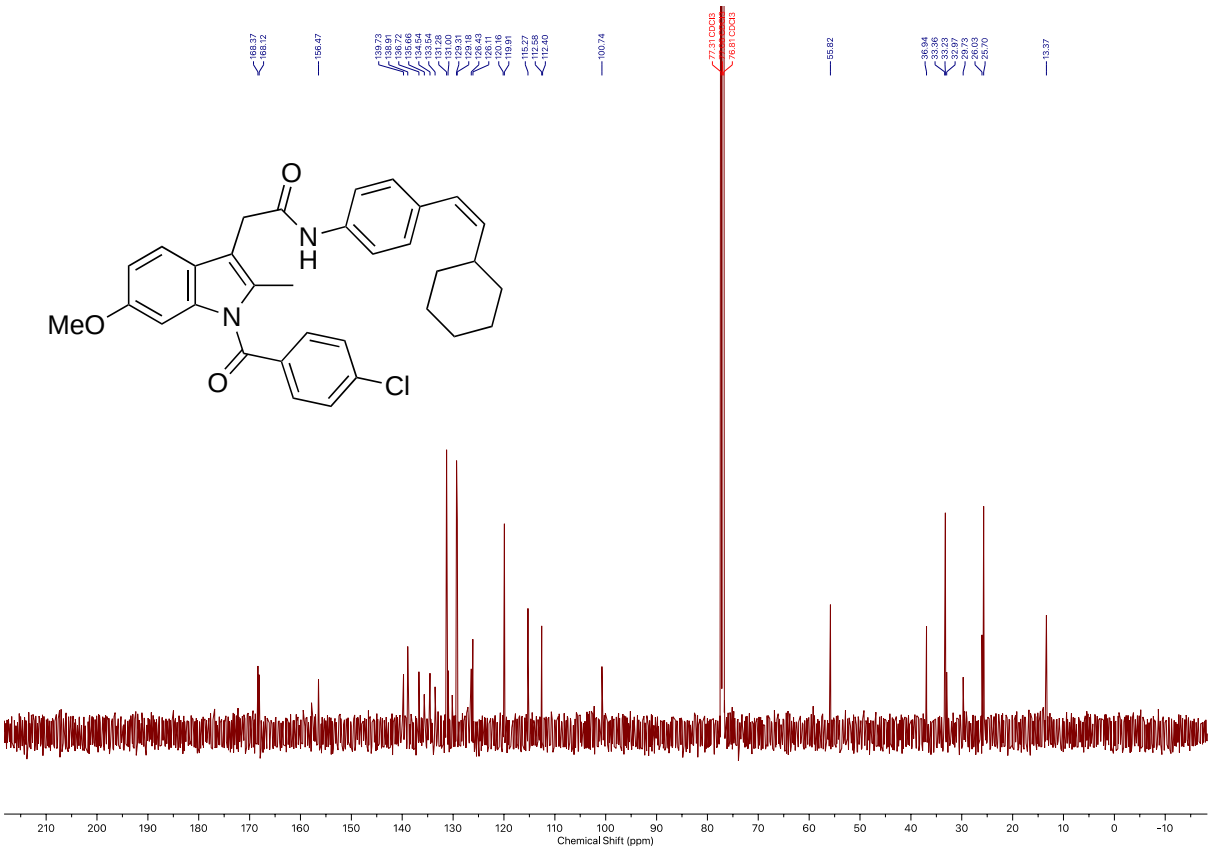
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3ai:**



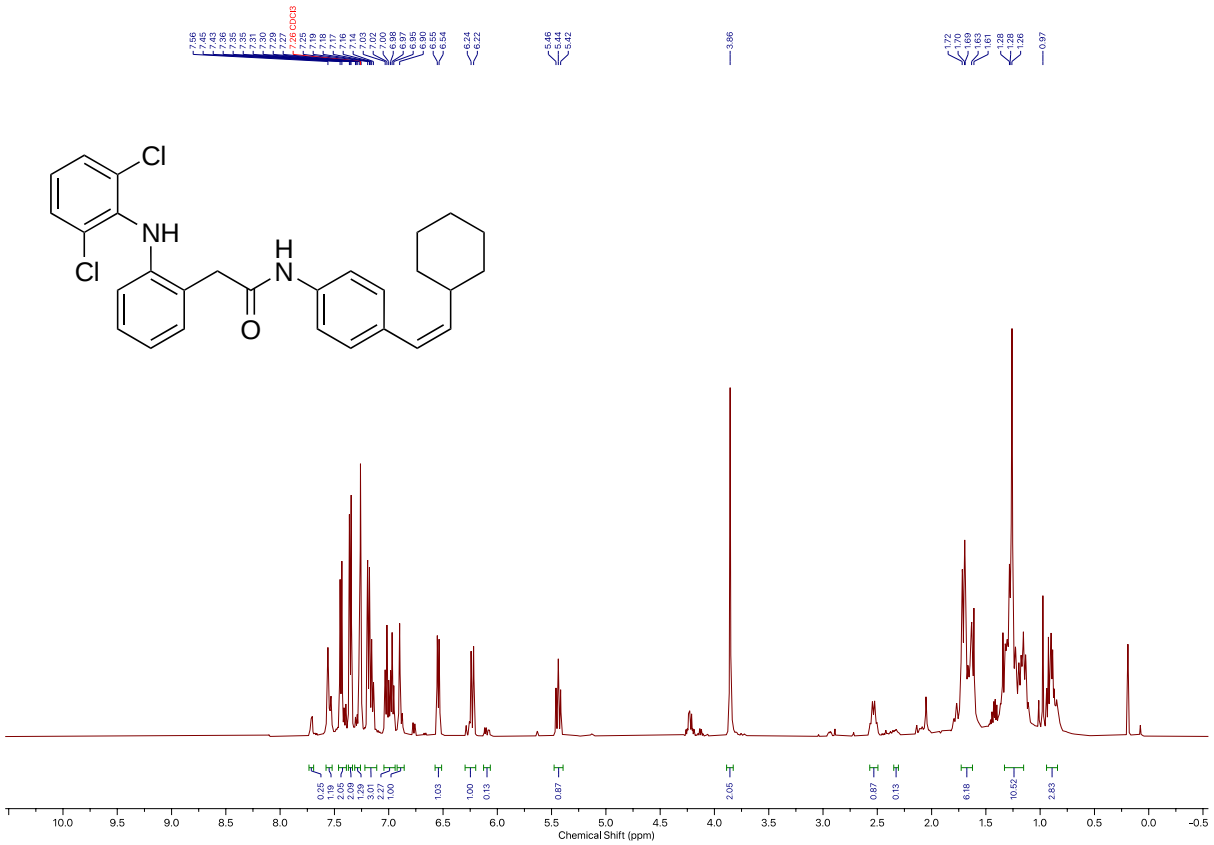


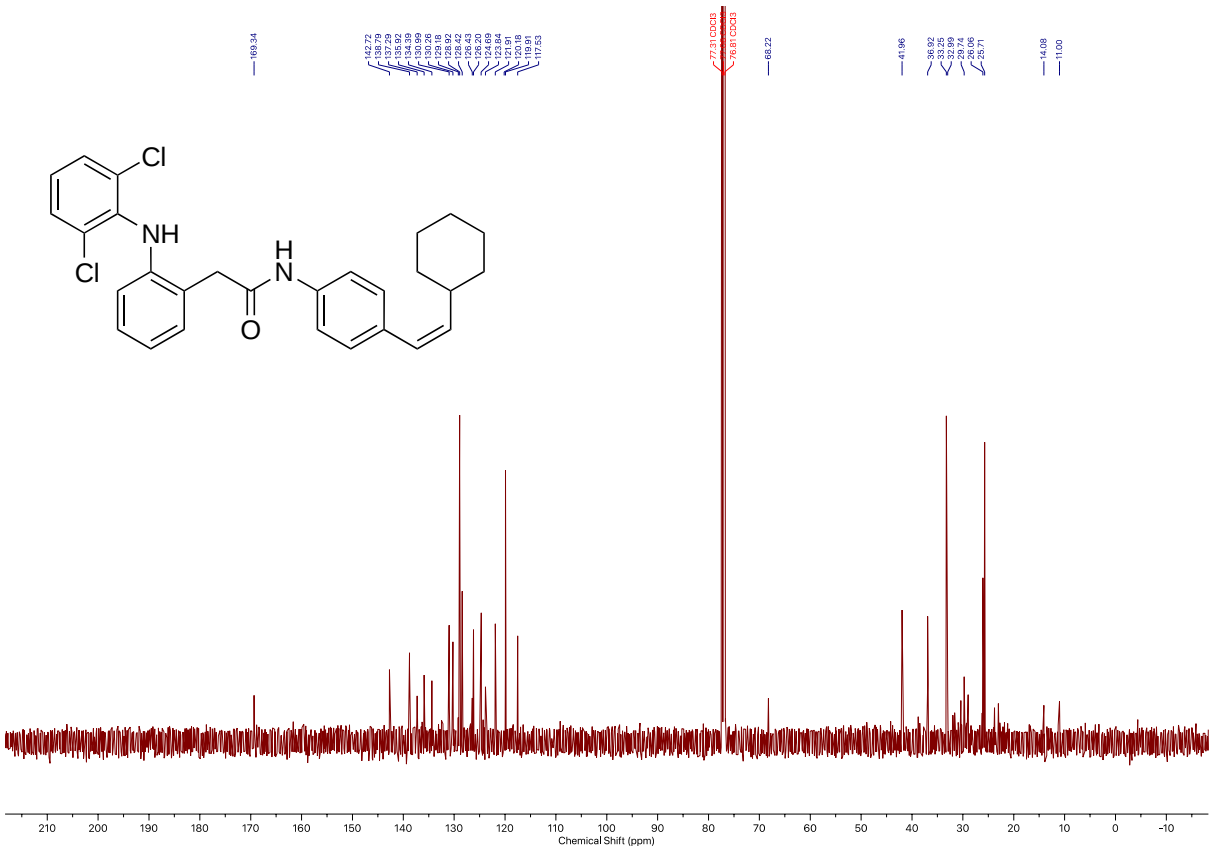
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3aj:**



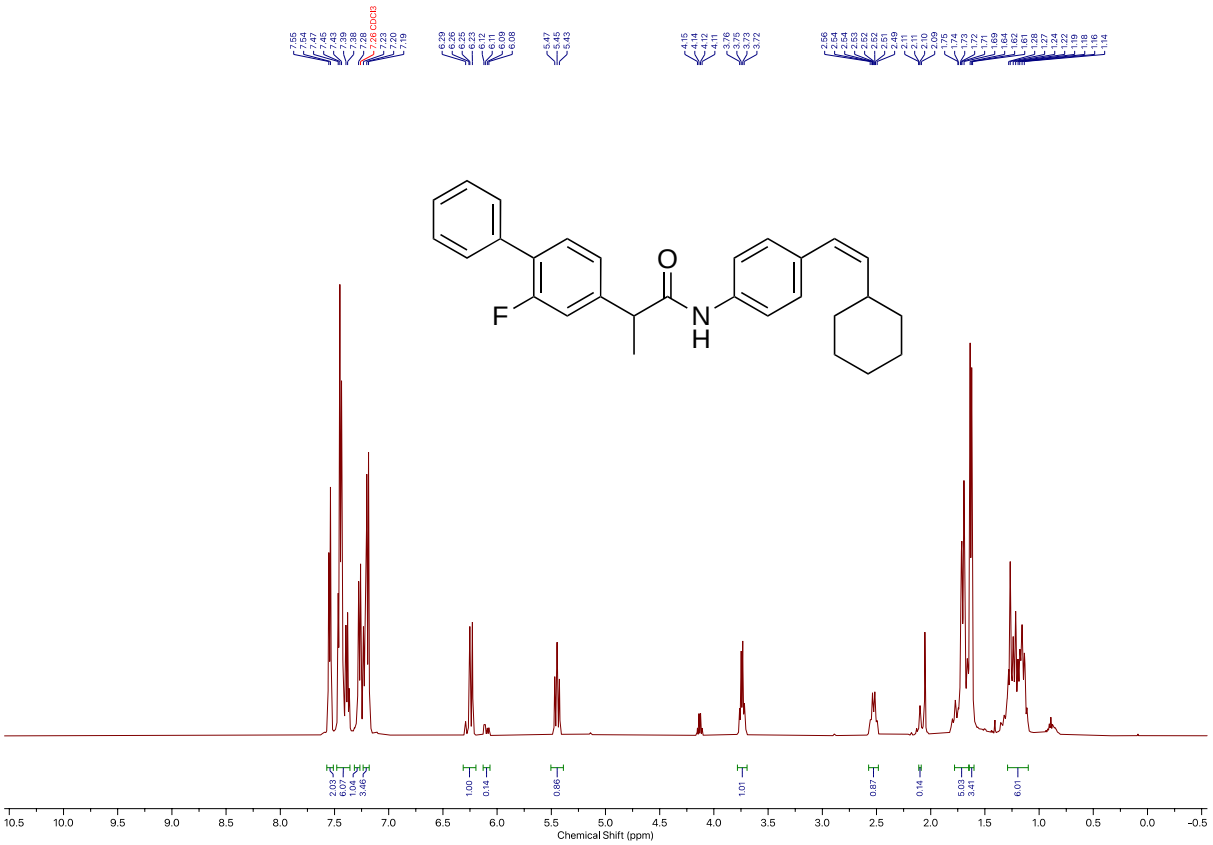


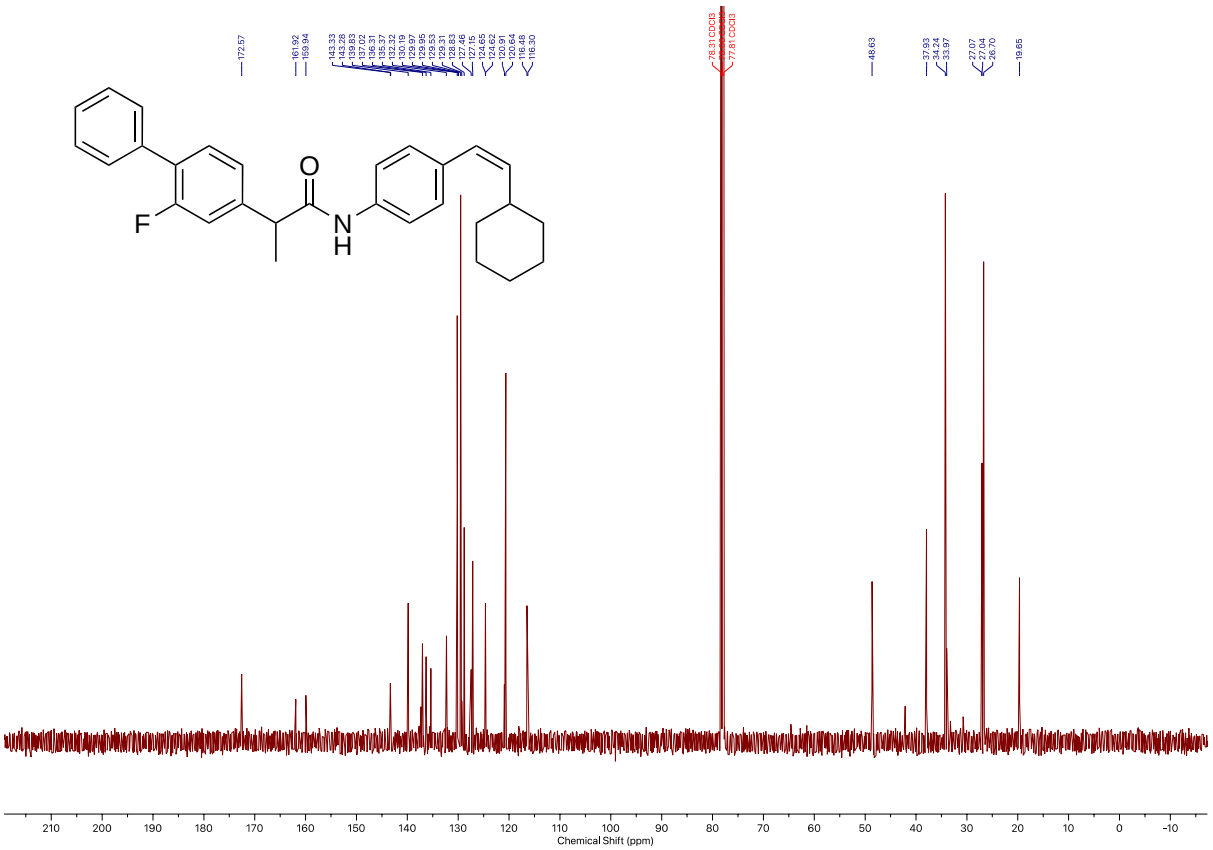
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3ak:**



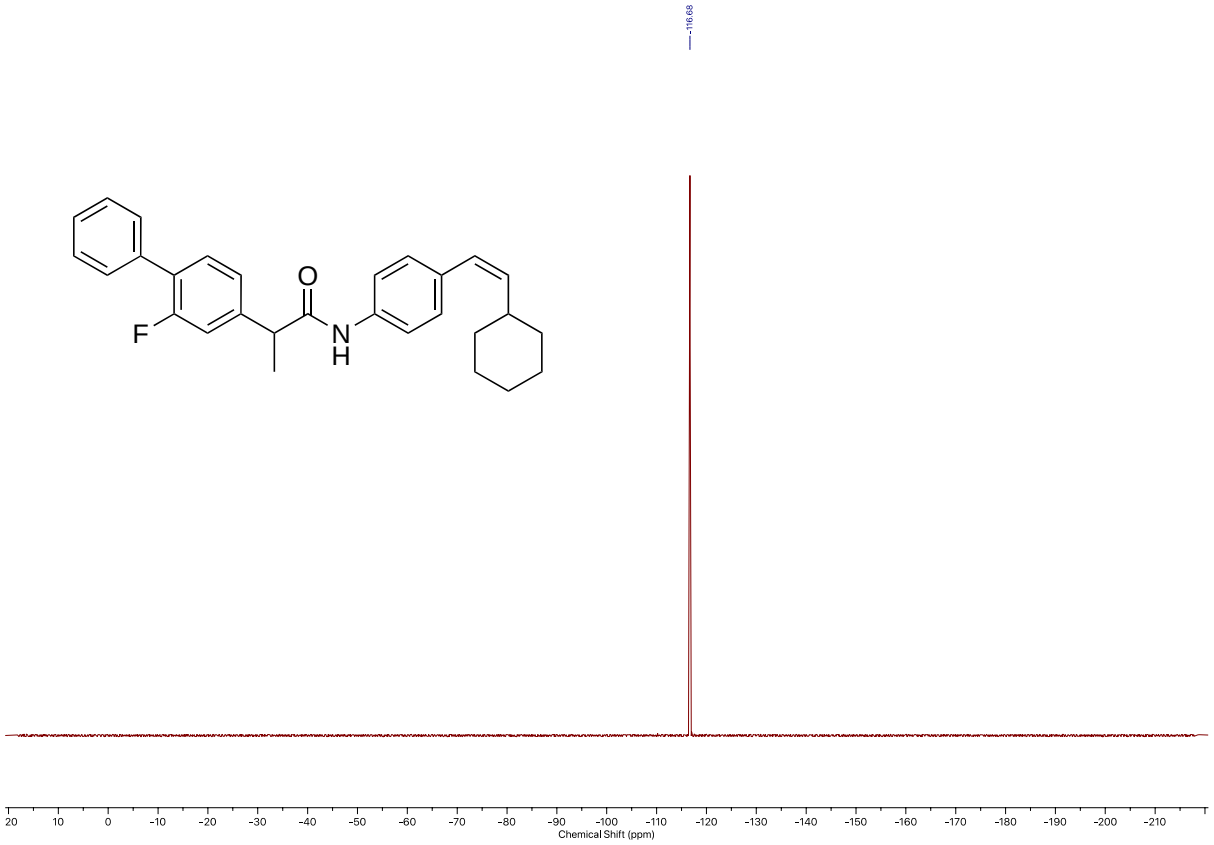


^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3al:**

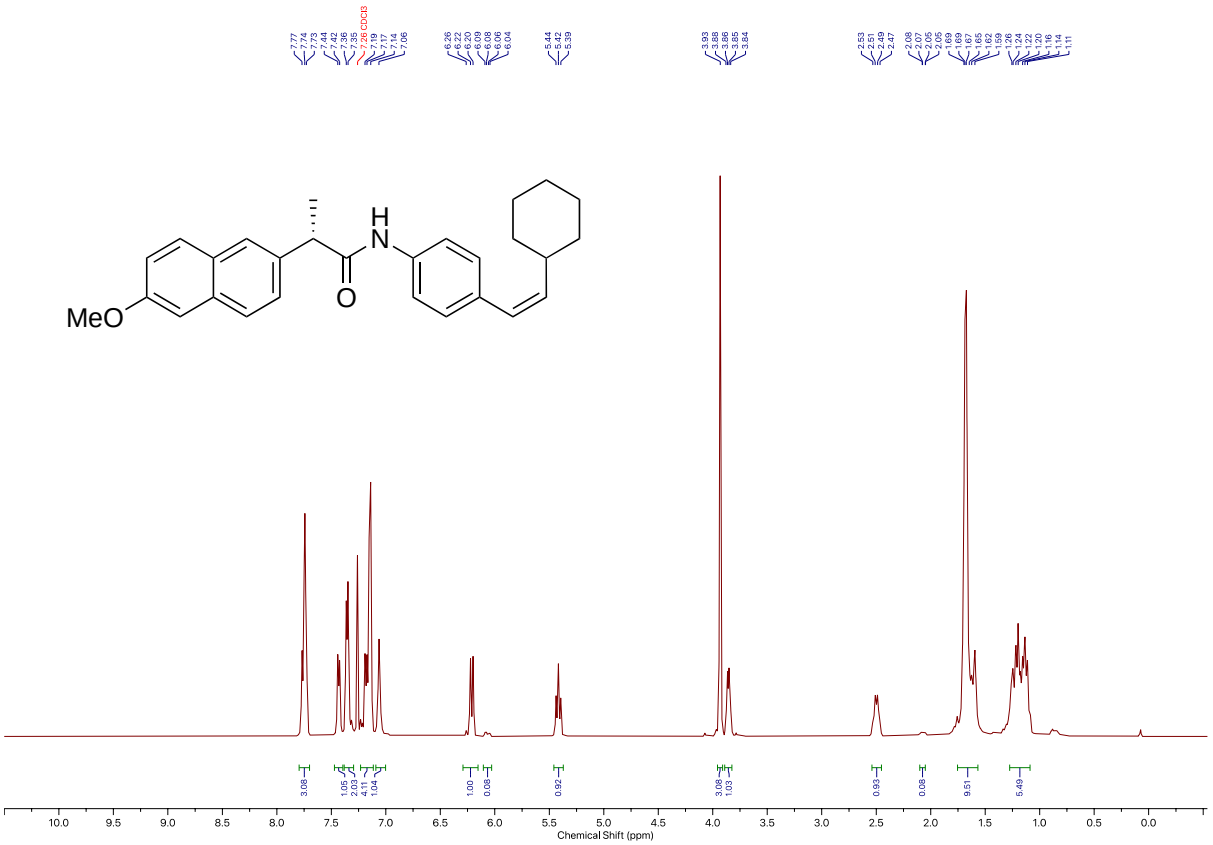


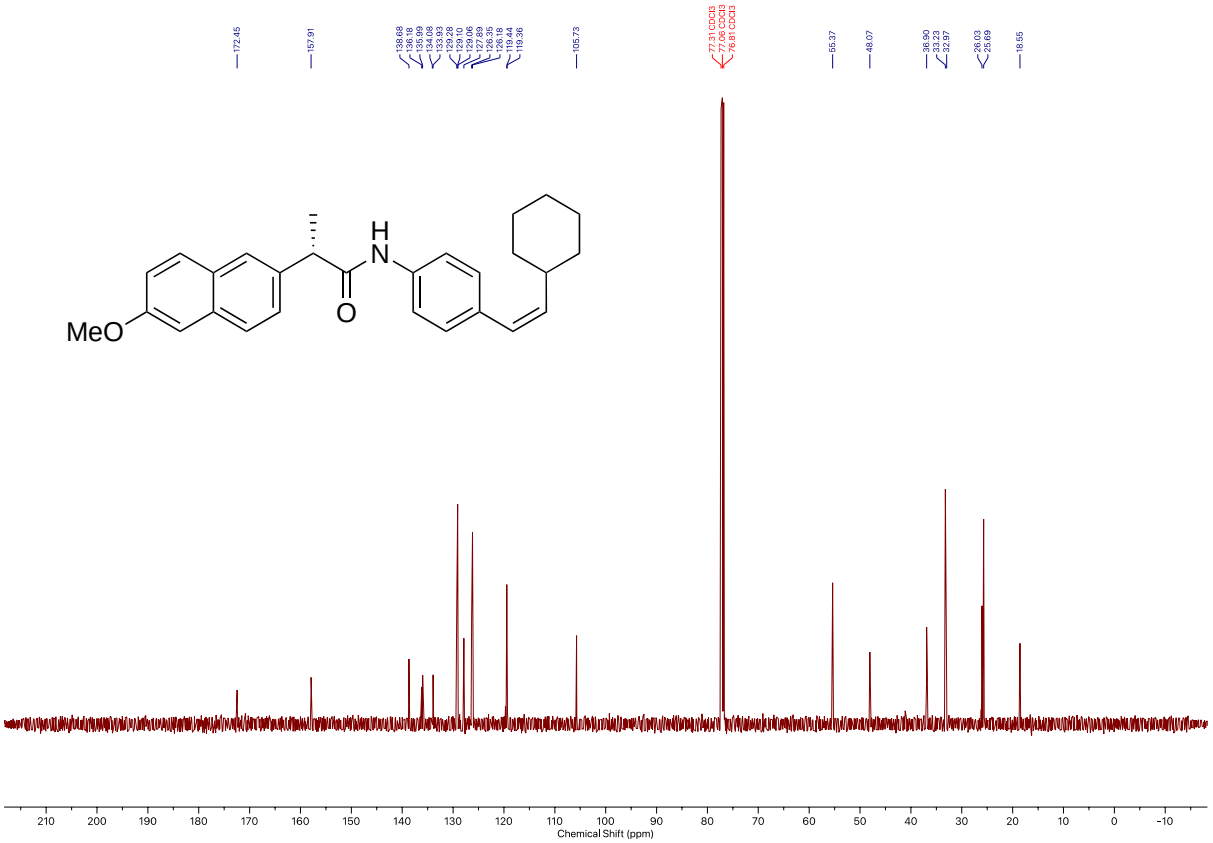


^{19}F NMR (471 MHz, $CDCl_3$) for 3al:

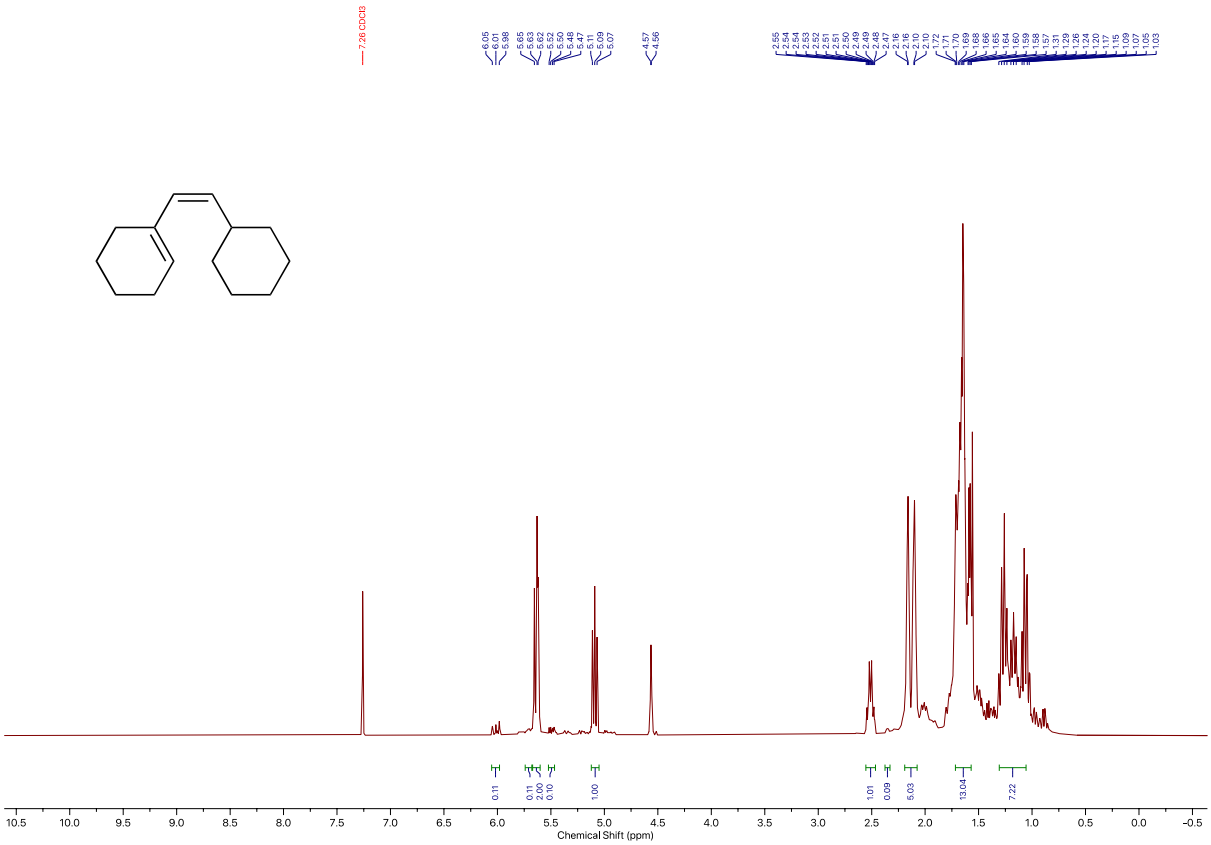


^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3am:**

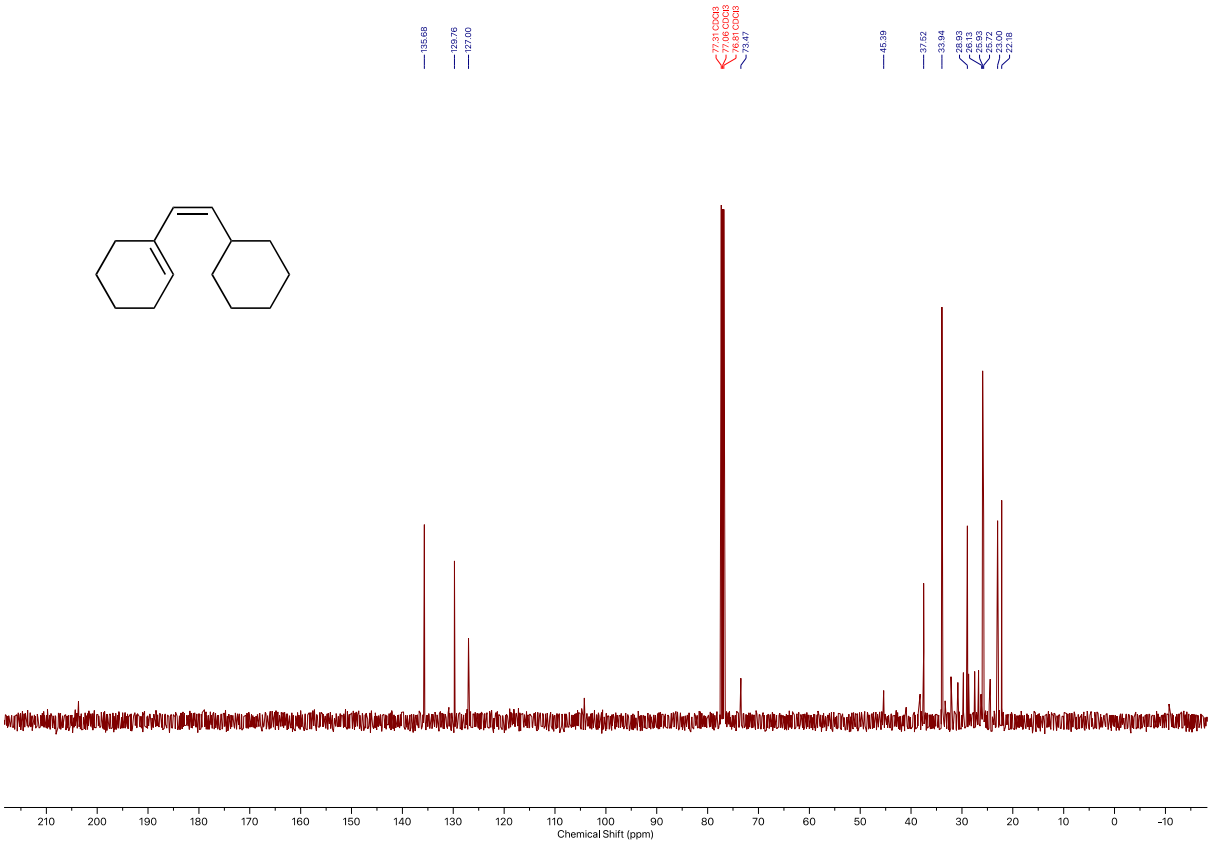




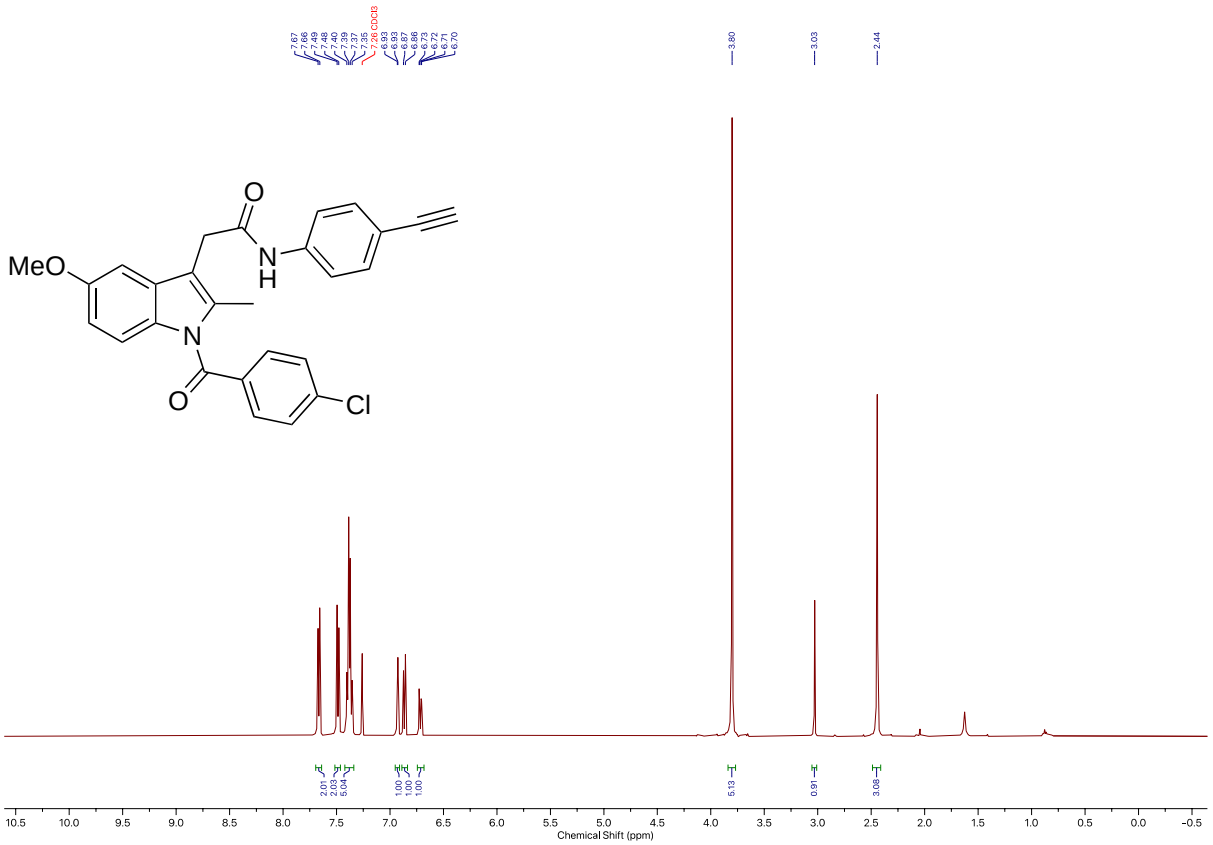
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 3an:**

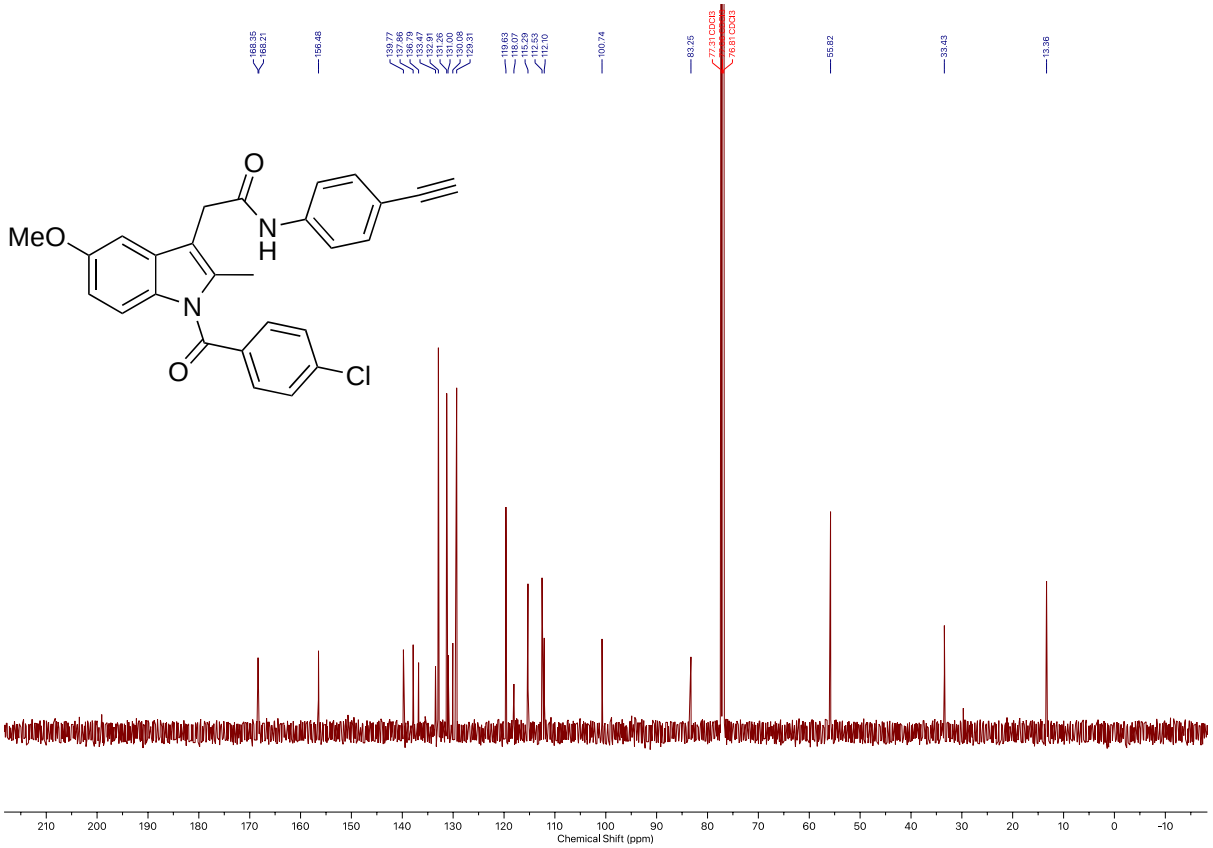


HRMS (ESI-QUADRUPOLE-ORBITRAP) m/z: $[M]^+$ Calcd for $[C_{14}H_{22}]$ 190.1716; Found 190.1715.

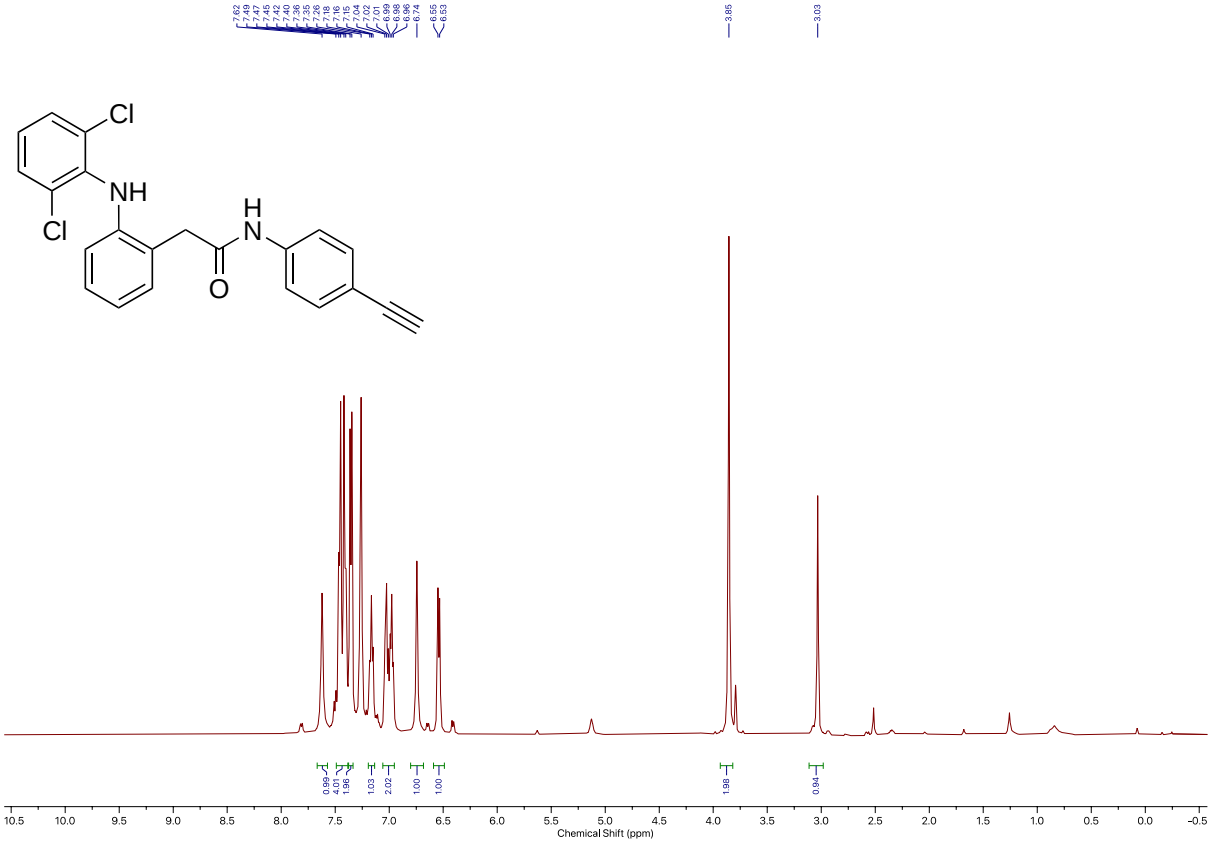


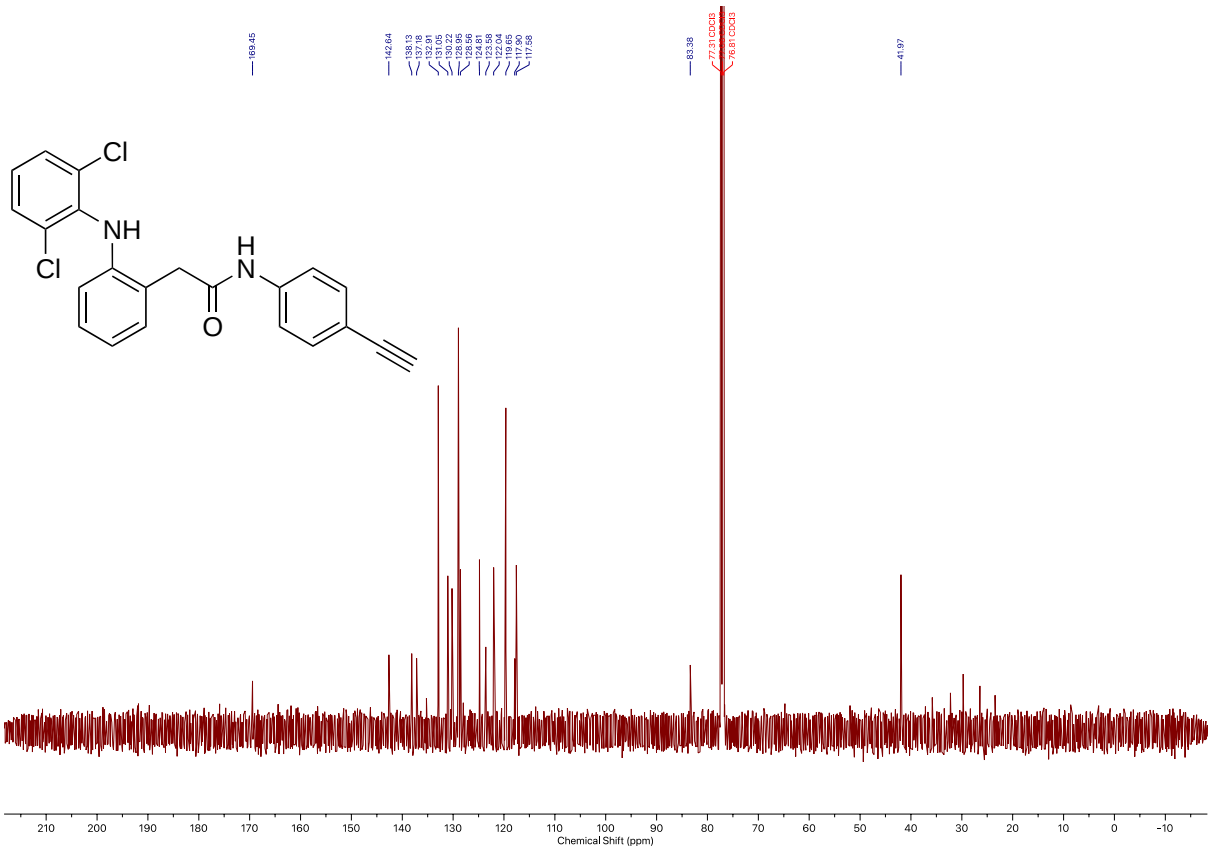
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 1aj:**



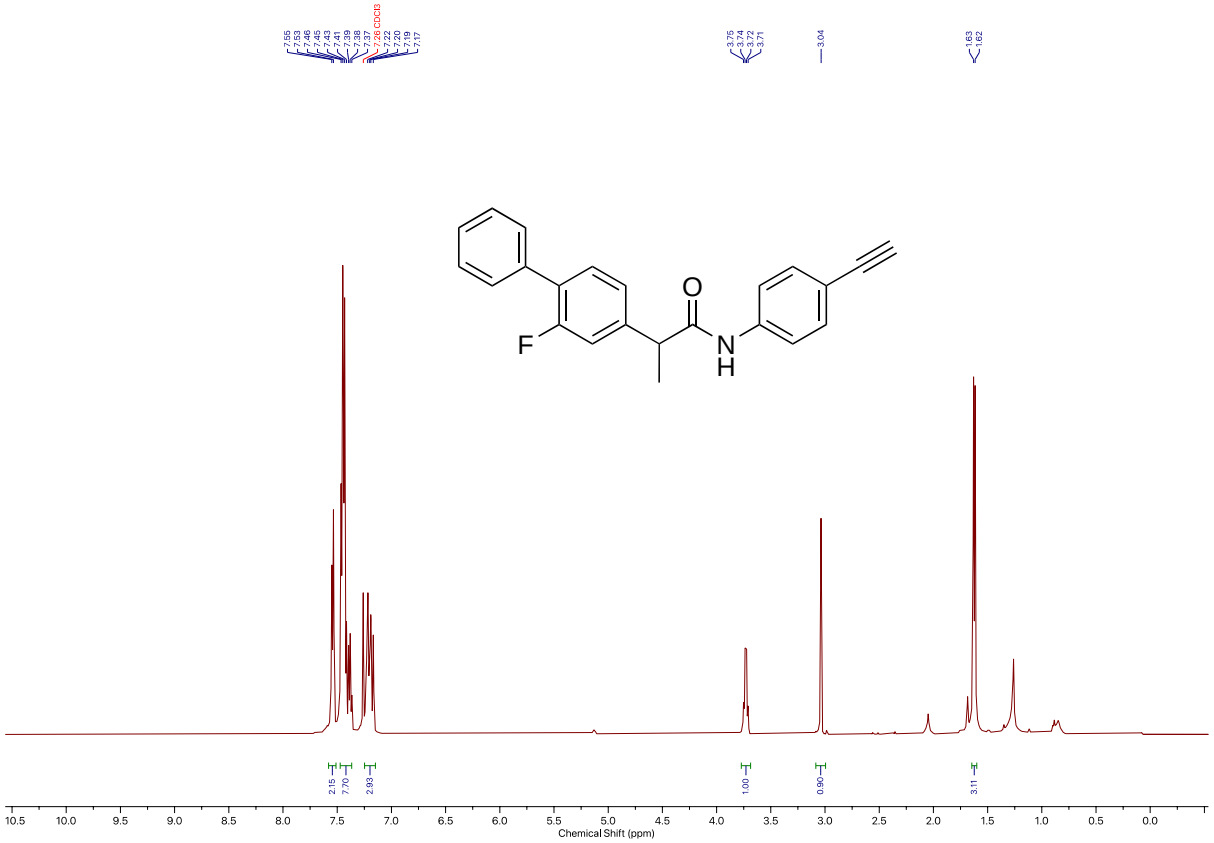


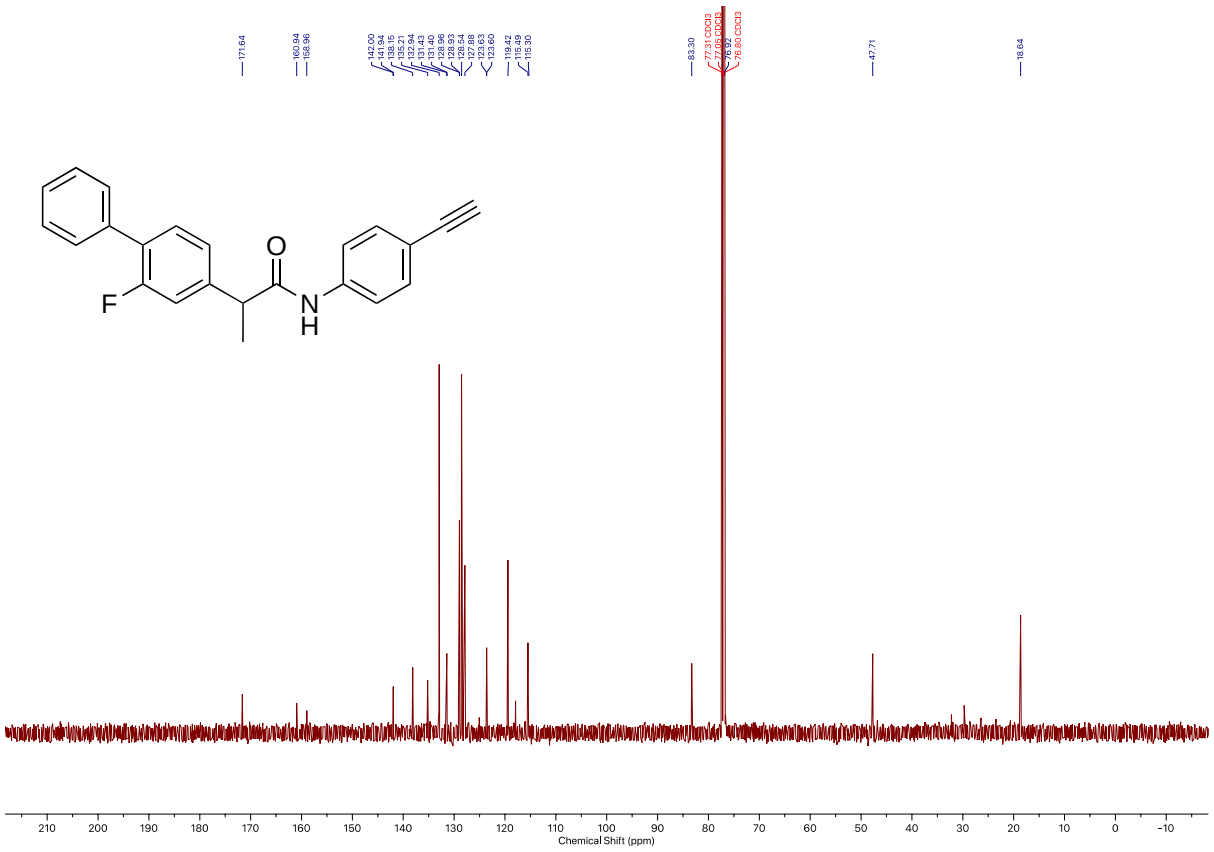
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 1ak:**



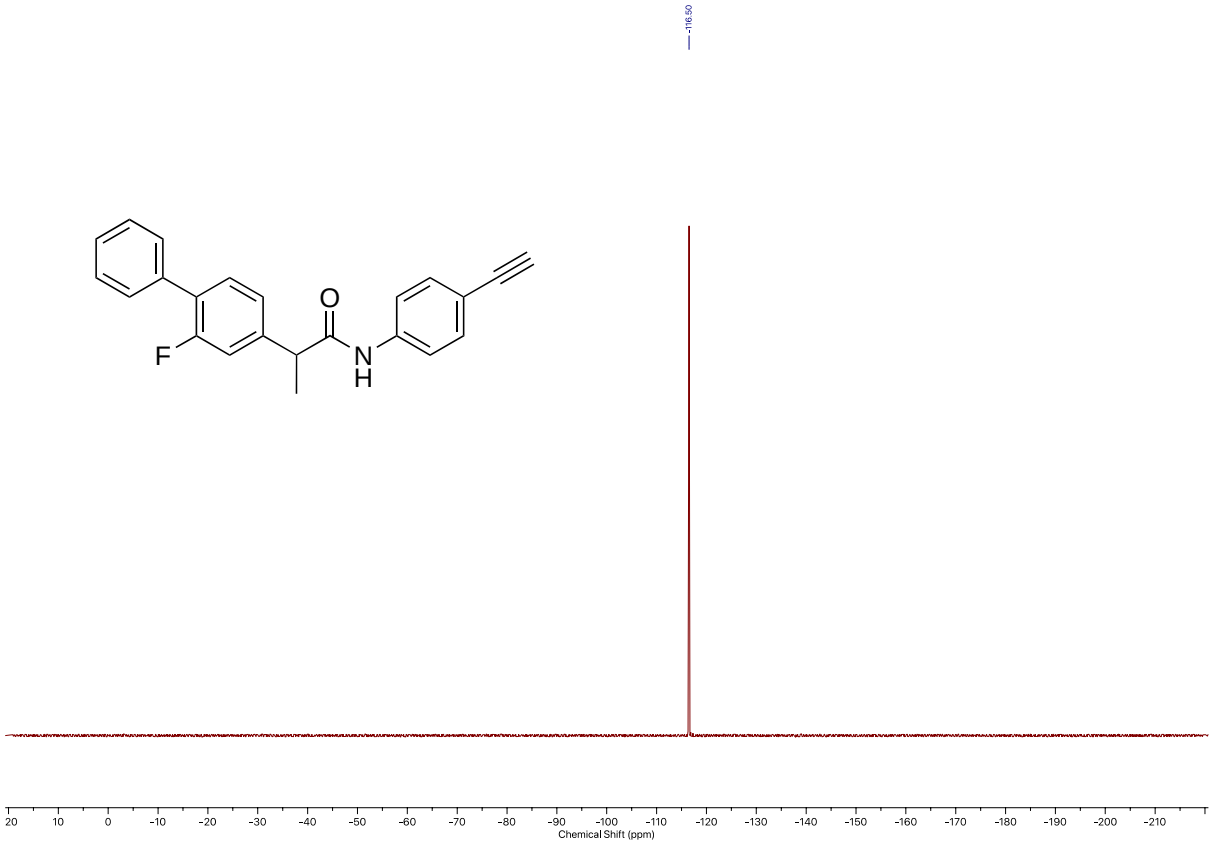


^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 1al:**

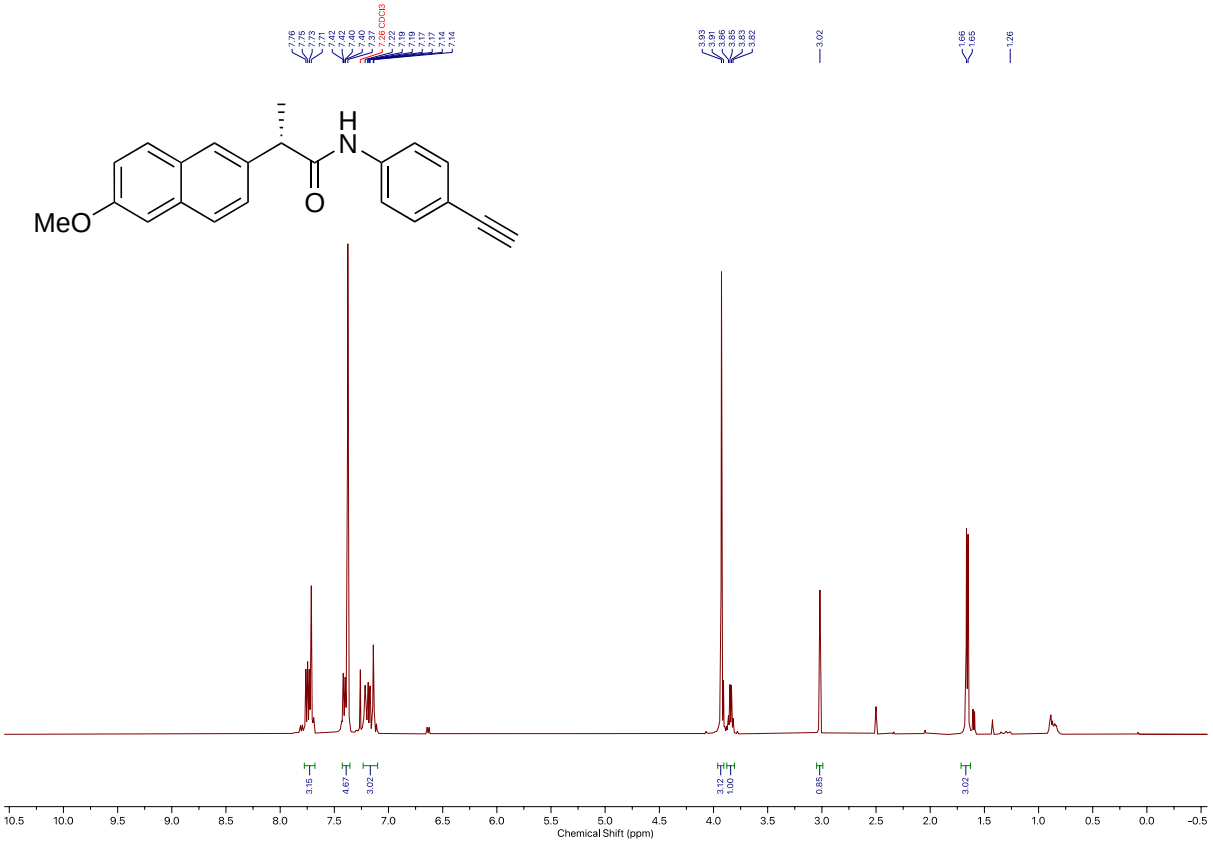


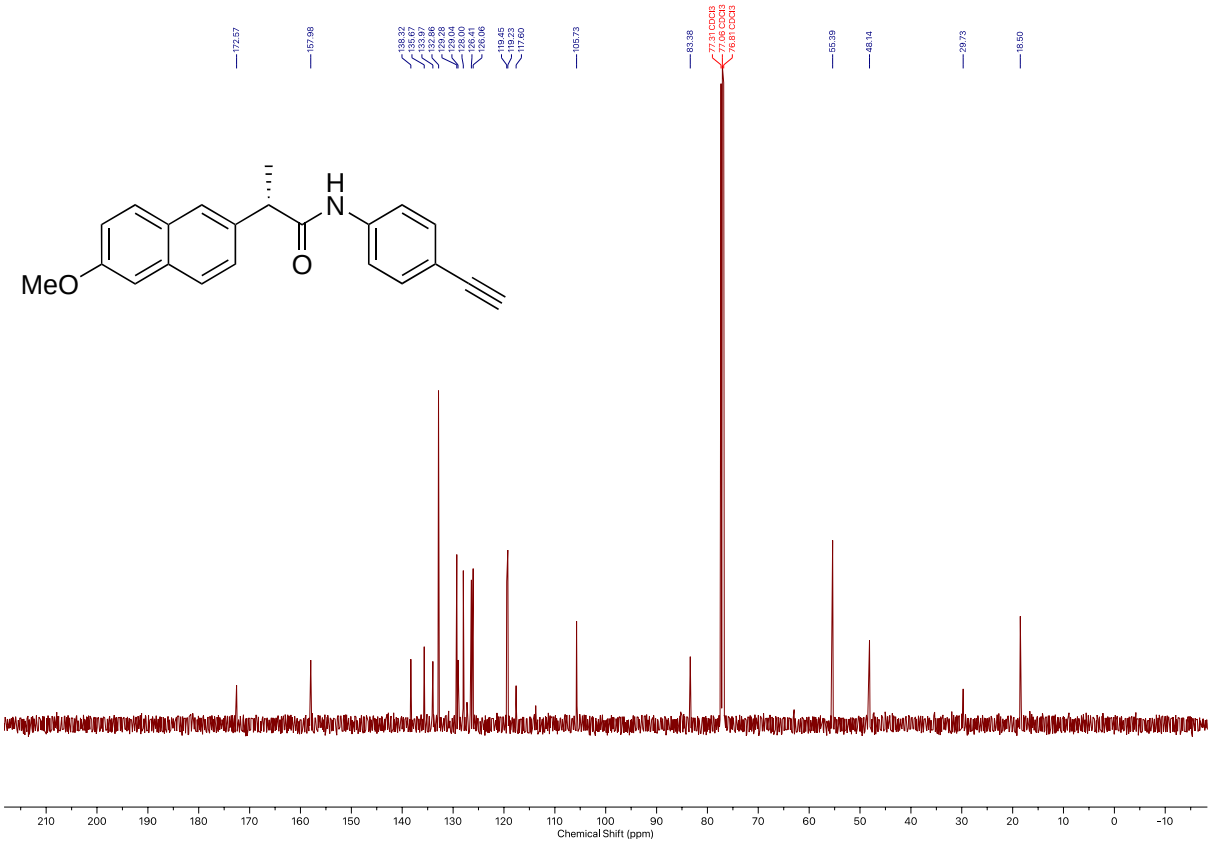


^{19}F NMR (471 MHz, $CDCl_3$) for 1al:

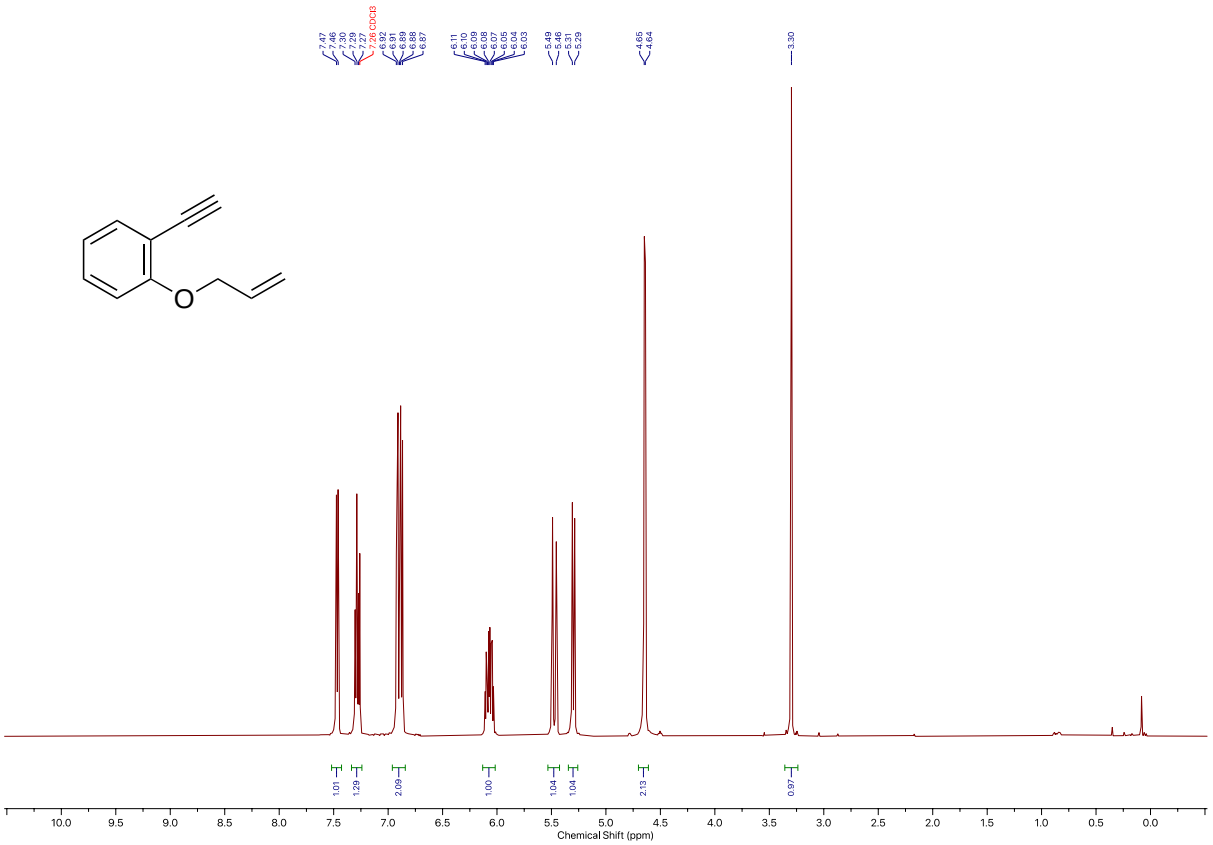


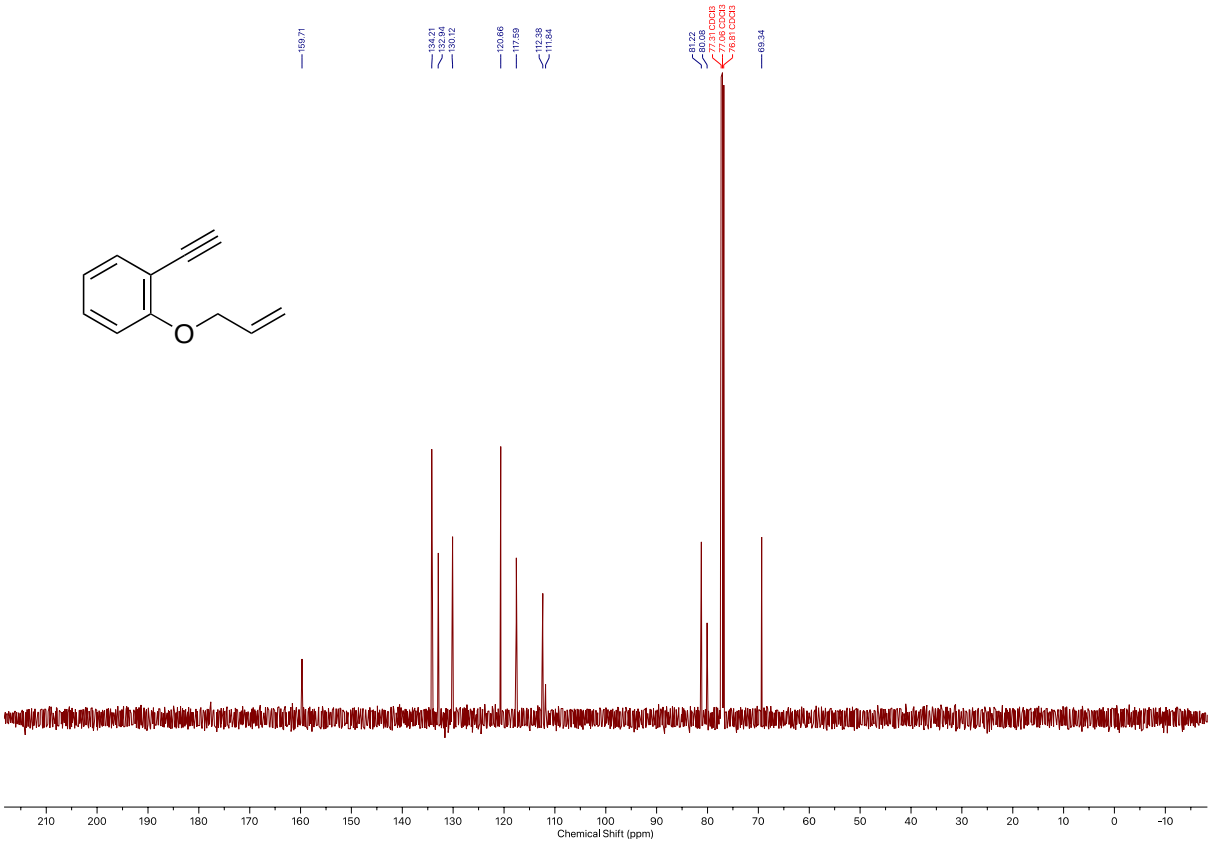
^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 1am:**



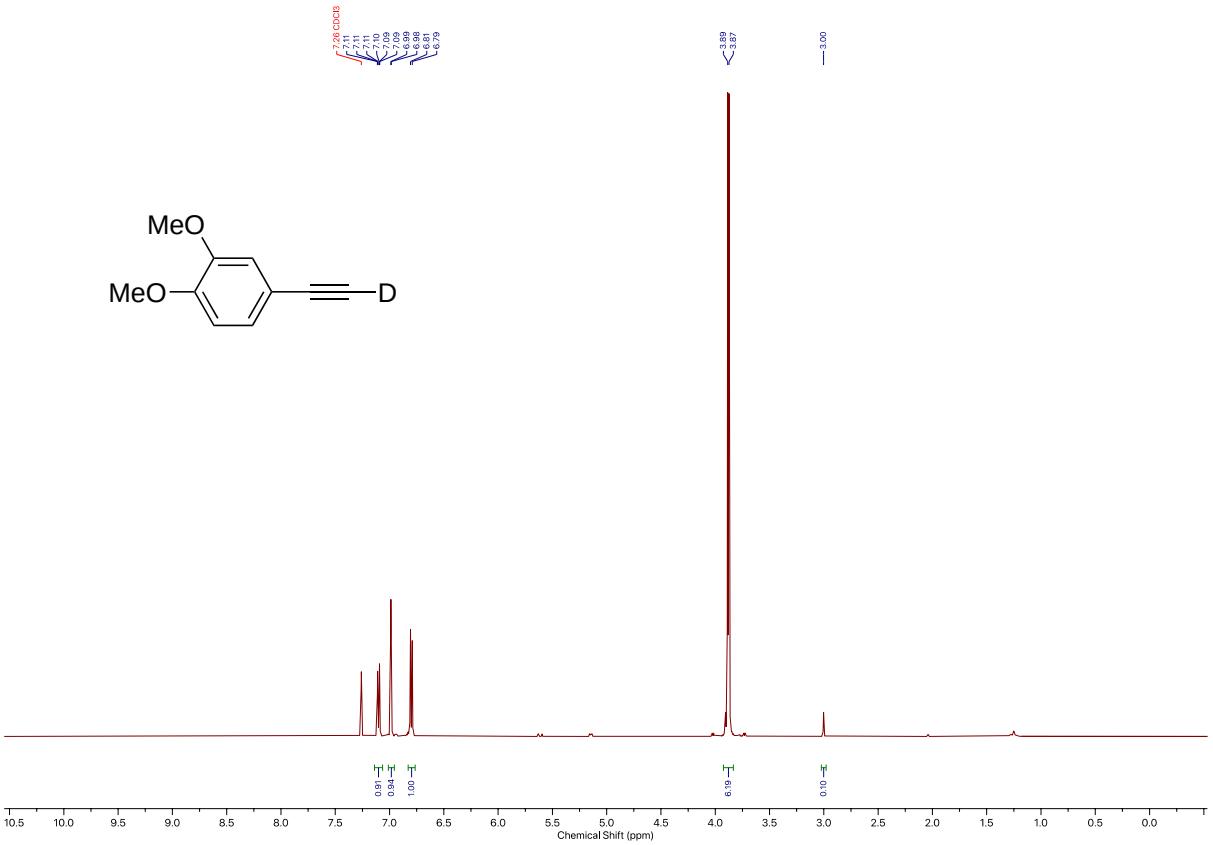


^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 1aq:**





^{1}H NMR (500 MHz, $CDCl_3$) and **^{13}C NMR (126 MHz, $CDCl_3$) for 1n-D:**



8. Unsuccessful substrates: