Supporting Information

Suzuki-Miyaura/Mizoroki-Heck Coupling Cascade to Access 2,2′-Bifunctionalized Biaryls

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1. General Information

Materials

Unless otherwise noted, all the reactions were performed using an oven-dried Schlenk tube. The palladium catalysts and all the ligands were purchased from Sigma-Aldrich Co. All the alkenes and phenylboronic acid derivatives were purchased from GLR Innovation and directly used in the reaction. The solvents THF and TFE were purchased from Finar and used directly as received. The other solvents were purchased from Spectrochem, Loba Chemie, and used directly. All the other reagents were purchased from Alfa Aesar, Avra Synthesis Pvt. Ltd., GLR Innovation, Sigma-Aldrich, and TCI and used as received. The reactions were monitored by Merck silica gel 60 F_{254} precoated plates (0.25 mm) visualizing under UV light (254 nm) or I_2 staining. The temperature mentioned for any reaction is corresponding to the oil bath temperature. Column chromatography was performed using silica gel 60-120 Å or 100-200 Å mesh of Merck Company.

Analytical Methods

^{1}H, $^{13}C\{^{1}H\}$, ^{19}F and ^{31}P nuclear magnetic resonance were recorded on Bruker Avance III 500 MHz / 400 MHz spectrometer at 25 ℃. NMRs of the products were measured in $CDCl_3$ or DMSO-d_6. The chemical shifts in ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra are reported in parts per million (ppm) relative to the residual solvent signal as the internal standard; ^{1}H NMR spectra ($CDCl_3$ δ 7.26 ppm/TMS δ 0.00 ppm),^{13}C NMR ($CDCl_3$ δ 77.16). The coupling constant (J) was reported in Hertz (Hz). Splitting patterns are denoted as “s” for singlet; “d” for doublet; “t” for triplet; “q” for quartet; “sext” for sextet; “sept” for septet; “m” for multiplet; “br” for broad; “dd” for doublet of doublet; “dt” for doublet of triplet; “td” for triplet of doublet. ESI-HRMS were recorded on AGILENT 6520 QTOF spectrometer. UV-vis spectra were acquired with JASCO V-770 spectrometer. Photoluminescence spectra and quantum yield measurements were conducted with FluoroMax+, Horiba Scientific spectrofluorometer equipped with PMT detectors.

Table S1: Cyclic diaryliodonium salts employed in the reaction

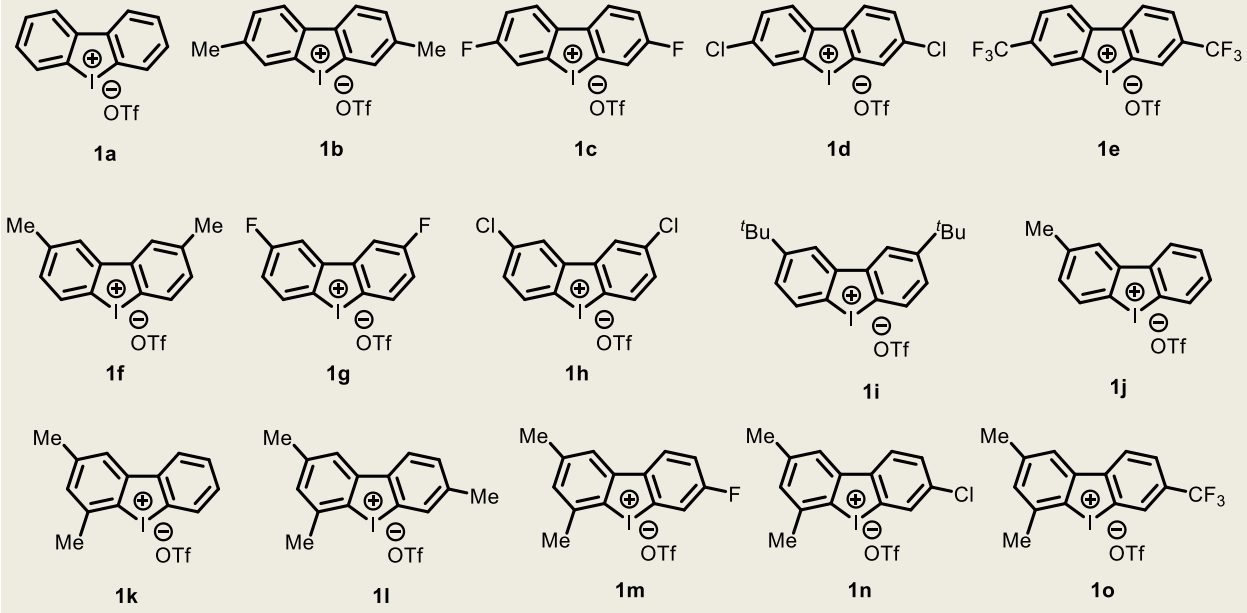


Table S2: Alkenes employed in the reaction

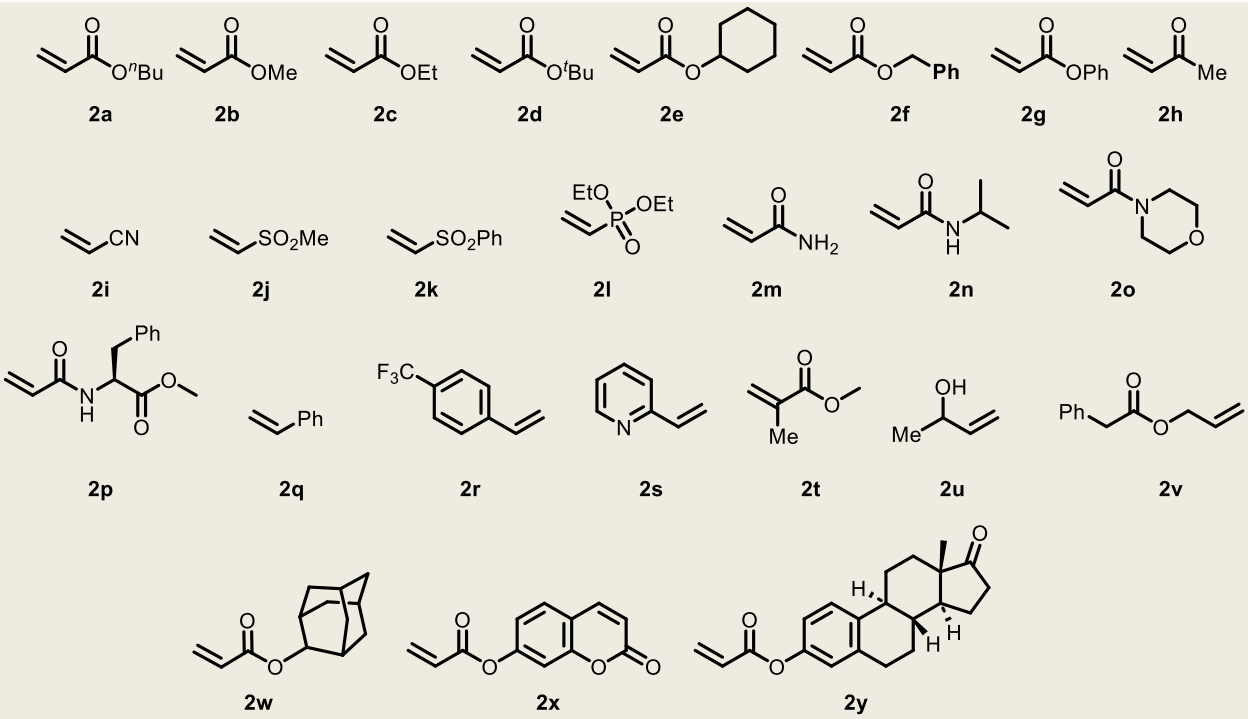


Table S3: Boronic acids employed in the reaction

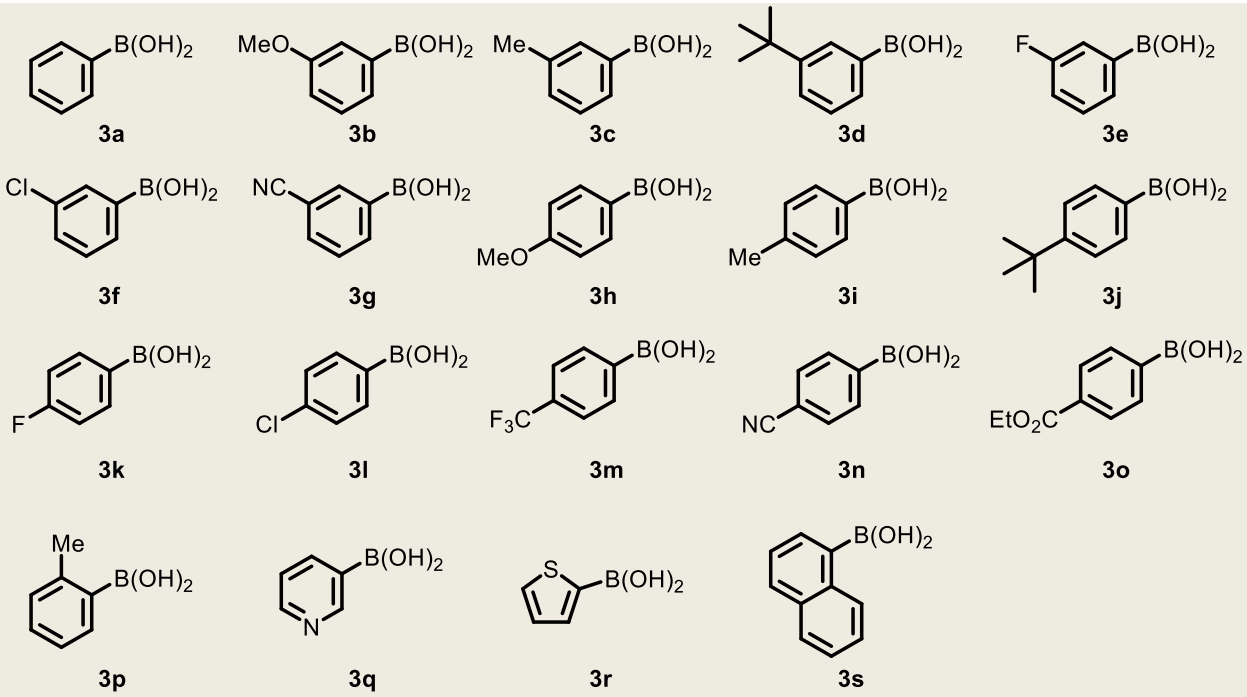
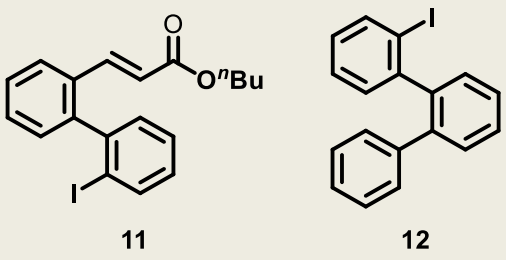
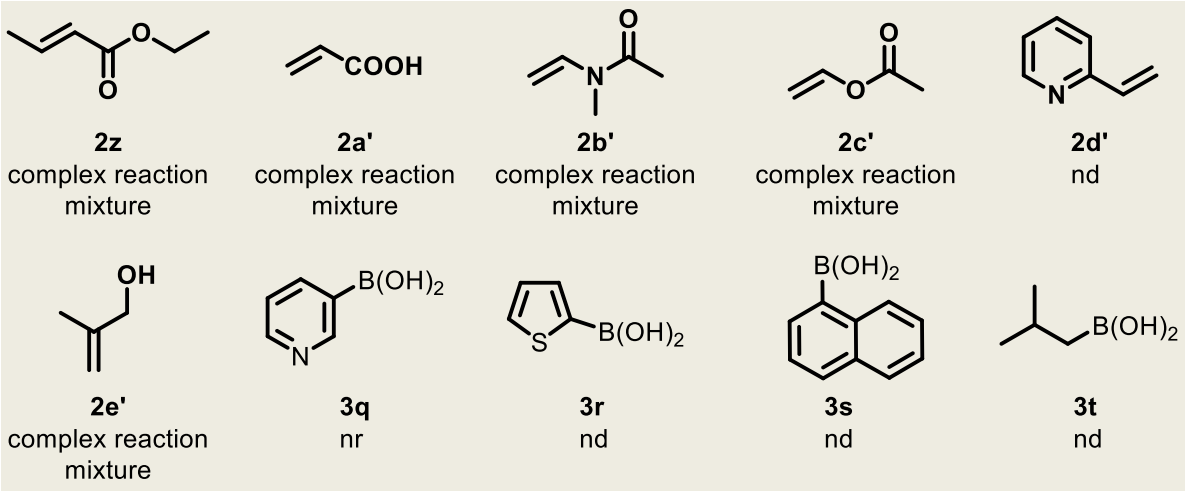


Table S4: Intermediates employed in the reaction



11 12

Table S5: Unsuccessful substrates

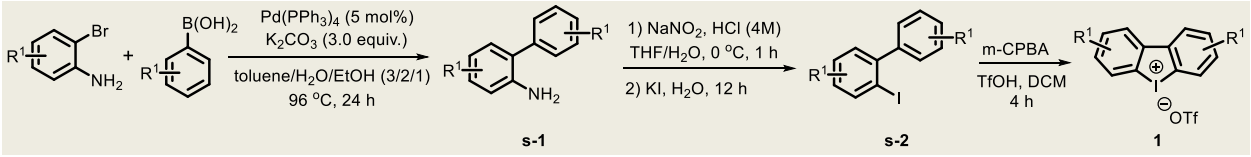


2z complex reaction mixture	**2a'** complex reaction mixture	**2b'** complex reaction mixture	**2c'** complex reaction mixture	**2d'** nd
2e' complex reaction mixture	**3q** nr	**3r** nd	**3s** nd	**3t** nd

2. Experimental procedures:

The substrate **2p**[1] was prepared from L-phenylalanine according to the literature procedure. The intermediates **11**[2] and **12**[3] were prepared according to the literature procedures.

2.1 General procedure for the preparation of cyclic diaryliodonium salts:[4]



s-1 s-2 1

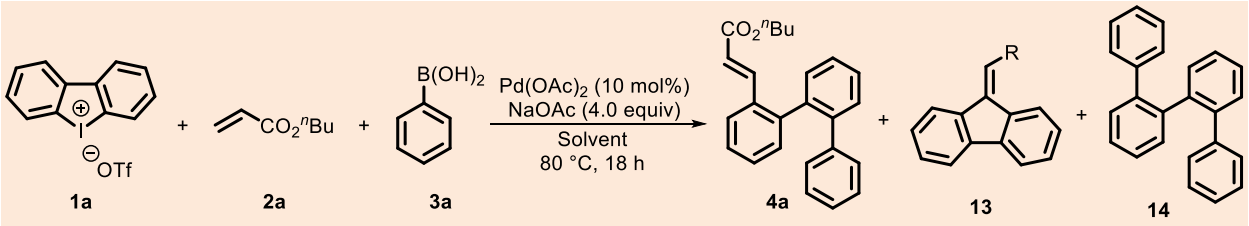
To a stirred solution of substituted 2-bromoaniline (4.0 mmol, 1.0 equiv) in toluene/H_2O/EtOH (15/10/5 mL) was added phenylboronic acid (6.0 mmol, 1.5 equiv), K_2CO_3 (9 mmol, 3.0 equiv), $Pd(PPh_3)_4$ (0.2 mmol, 5 mol%). The reaction mixture was stirred at 96 °C for 24 h under a nitrogen atmosphere. After cooling to room temperature, the organic phase was separated and the aqueous phase was extracted with EtOAc (3 times). The combined organic phases were washed with brine and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and purified by column chromatography to afford the corresponding [1,1'-biphenyl]-2-amine (**s-1**).

To a stirred solution of the corresponding **s-1** (3.0 mmol, 1.0 equiv) in THF/H_2O (4/8 mL) was added 4 M aqueous HCl (3.6 mL), and the solution was cooled in an ice water bath. A solution of $NaNO_2$ (4.5 mmol, 1.5 equiv) in H_2O (1.0 mL) was added dropwise and stirred for 1 h at the same temperature. A solution of KI (6.0 mmol, 2.0 equiv) in H_2O (1 mL) was added dropwise. The reaction mixture was stirred for 5 min in the ice water bath, then slowly warmed up to r.t. and stirred overnight. After completion, 1M aqueous $Na_2S_2O_3$ was added until the colour of the mixture didn't change. The phases were separated, and the aqueous phase was extracted with EtOAc (3 times). The combined organic layers were washed with H_2O and brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography to yield corresponding 2-iodo-1,1'-biphenyl **(s-2)**.

In a 50 mL round bottom flask, m-chloroperbenzoic acid (4.2 mmol, 1.4 equiv) was taken. To this, a solution of 2-iodobiaryl derivative (3.0 mmol, 1.4 equiv) in anhydrous DCM (10 mL) was added, followed by dropwise addition of TfOH (9.0 mmol, 3 equiv) with constant stirring at ice-bath. The solution was stirred for 3h at r.t. and then the solvent was evaporated under reduced pressure. Et_2O (10 mL) was added to the remaining solid, and the mixture was stirred for 20 min, and filtered. The collected solid was washed with Et_2O (3 times) and dried in a high vacuum pump to provide the required cyclic diaryliodonium salts **1**.

3. Optimization of the reaction conditions for bifunctionalization

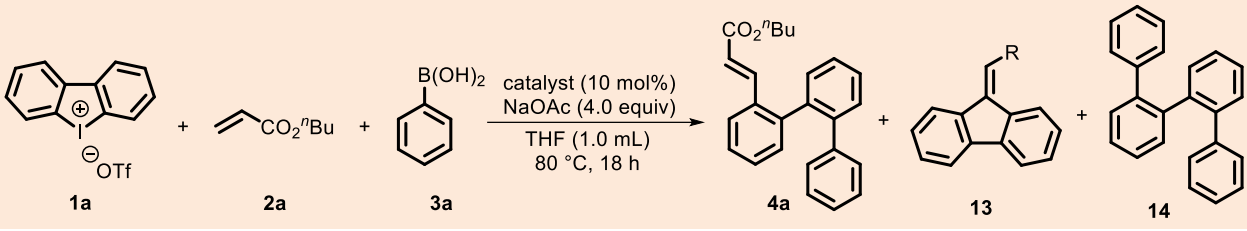
Table S6: Screening of Solvents[a,b]



Entry	Solvent	Yield (%) of 4a	Yield (%) of 13	Yield (%) of 14
1	THF	54(47)	<5	5
2	TFE	25	-	-
3	ACN	16	-	8
4	HFIP	Trace	-	-
5	EtOH	8	<5	-
6	1,4-Dioxane/110 °C	37	-	-
7	Toluene/110 °C	21	<5	-
8	ODCB/130 °C	24	-	-
9	DMF/130 °C	nd	-	-
10	DMSO/130 °C	nd	-	-
11	DCE	27	-	-

[a]Conditions: **1a** (1.0 equiv), **2a** (1.5 equiv), **3a** (1.5 equiv), $Pd(OAc)_2$ (10 mol%), NaOAc (4.0 equiv), Solvent (1.0 mL), 80 °C, 18 h. [b]The yields were determined by ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. Isolated yield in parentheses. THF = Tetrahydrofuran, TFE = 2,2,2-Trifluoroethanol, ACN = Acetonitrile, HFIP = 1,1,1,3,3,3-Hexafluoro-2-propanol, ODCB = 1,2-Dichlorobenzene, DMF = N,N-Dimethylformamide, DMSO = Dimethyl sulfoxide, DCE = 1,2-Dichloroethane. nd = not detected.

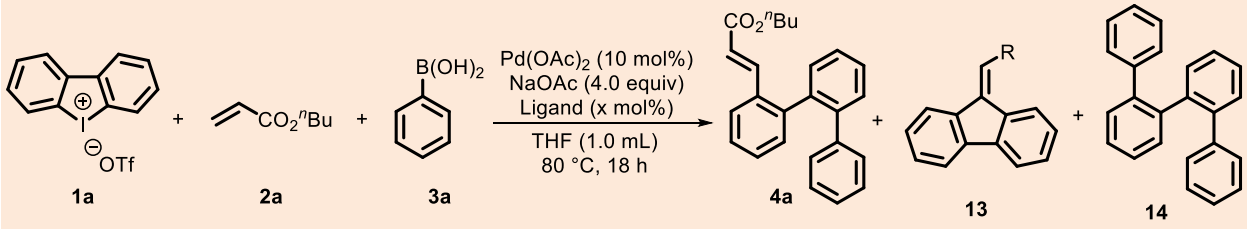
Table S7: Screening of catalysts[a,b]



Entry	Catalyst	Yield (%) of 4a	Yield (%) of 13	Yield (%) of 14
1	$PdCl_2$	32	-	12
2	$Pd(TFA)_2$	35	-	<5
3	$Pd(PPh_3)Cl_2$	Trace	-	-
4	$(Allyl\text{-}PdCl_2)_2$	15	-	-
5	$Pd(PPh_3)_4$	Trace	-	-
6	$Pd_2(dba)_3$	29	-	-
7	$Ni(OAc)_2.4H_2O$	nd	-	-
8	CuI	nd	-	-
9	$Cu(OAc)_2.H_2O$	nd	-	-

[a]Conditions: **1a** (1.0 equiv), **2a** (1.5 equiv), **3a** (1.5 equiv), Metal (10 mol%), NaOAc (4.0 equiv), THF (1.0 mL), 80 °C, 18 h. [b]The yields were determined by ^{1}H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. Isolated yield in parentheses. nd = not detected.

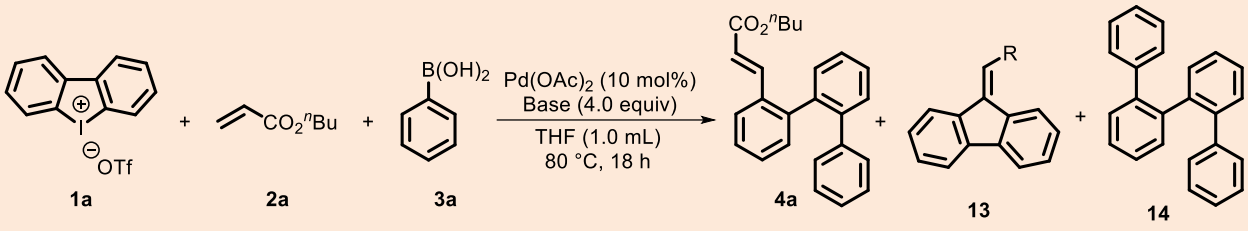
Table S8: Screening of ligands[a,b]



Entry	Ligand (x mol%)	Yield (%) of 4a	Yield (%) of 13	Yield (%) of 14
1	R-BINOL (10 mol%)	39	<5	<5
2	Xantphos (10 mol%)	23	6	-
3	DPPP (10 mol%)	Trace	-	-
4	DPPE (10 mol%)	7	8	-
5	PCy_3(20 mol%)	12	-	-
6	CyJohnPhos (20 mol%)	14	-	-
7	$P(o\text{-}tol)_3$ (10 mol%)	9	-	-
8	1,10-Phen (10 mol%)	nd	-	-
9	2,2'-bipyridyl (10 mol%)	nd	-	-
10	Pyridine (20 mol%)	15	-	-

[a]Conditions: **1a** (1.0 equiv), **2a** (1.5 equiv), **3a** (1.5 equiv), $Pd(OAc)_2$ (10 mol%), Ligand (x mol%), NaOAc (4.0 equiv), THF (1.0 mL), 80 °C, 18 h. [b]The yields were determined by ^{1}H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. Isolated yield in parentheses. nd = not detected.

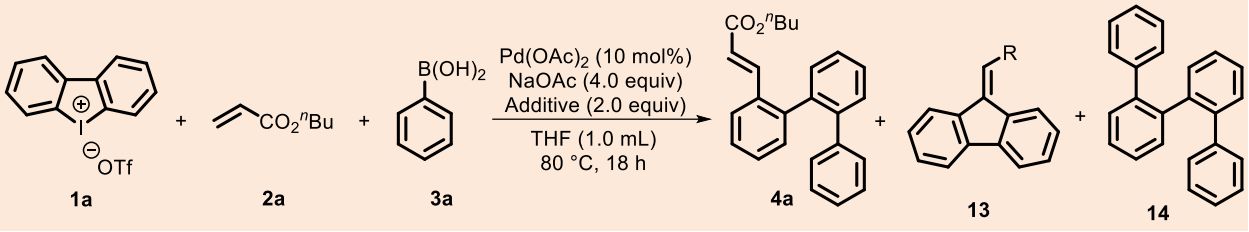
Table S9: Screening of base[a,b]



Entry	Base	Yield (%) of 4a	Yield (%) of 13	Yield (%) of 14
1	KOAc	44	6	<5
2	CsOAc	56	<5	7
3	LiOAc	31	-	<5
4	NH_4OAc	9	-	-
5	NaOAc (2.0 equiv)	26	-	-
6	$NaHCO_3$	28	<5	<5
7	Na_2CO_3	36	-	<5
8	Cs_2CO_3	8	-	-
9	NaO^tBu	nd	-	-
10	K_3PO_4	16	trace	<5
11	KH_2PO_4	nd	-	-

[a]Conditions: **1a** (1.0 equiv), **2a** (1.5 equiv), **3a** (1.5 equiv), $Pd(OAc)_2$ (10 mol%), Base (4.0 equiv), THF (1.0 mL), 80 °C, 18 h. [b]The yields were determined by ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. Isolated yield in parentheses. nd = not detected.

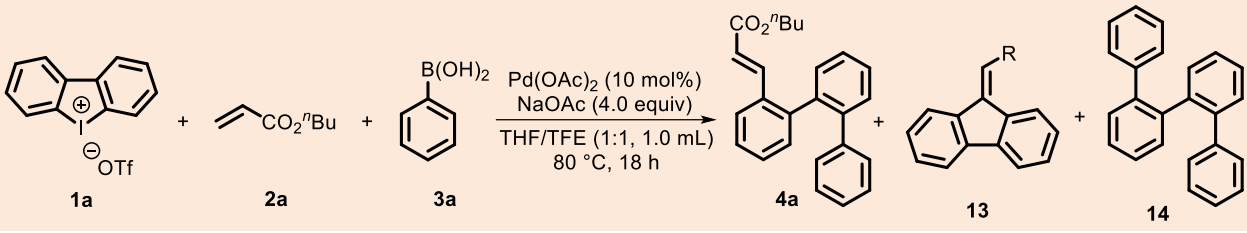
Table S10: Screening of additive[a,b]



Entry	Additive	Yield (%) of 4a	Yield (%) of 13	Yield (%) of 14
1	H_2O	38	<5	-
2	AcOH	45	<5	-
3	PivOH	56	<5	-
4	$PhCO_2H$	28	-	-
5	$Zn(OAc)_2.2H_2O$	32	-	-
6	TBABr	nd	-	-
7	AgOAc	51	-	<5
8	AgOAc (1.0 equiv)	58	-	-
9	AgOAc (0.5 equiv)	53(48)	-	-

[a]Conditions: **1a** (1.0 equiv), **2a** (1.5 equiv), **3a** (1.5 equiv), $Pd(OAc)_2$ (10 mol%), NaOAc (4.0 equiv), Additive (2.0 equiv), THF (1.0 mL), 80 °C, 18 h. [b]The yields were determined by ^1H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. Isolated yield in parentheses. nd = not detected.

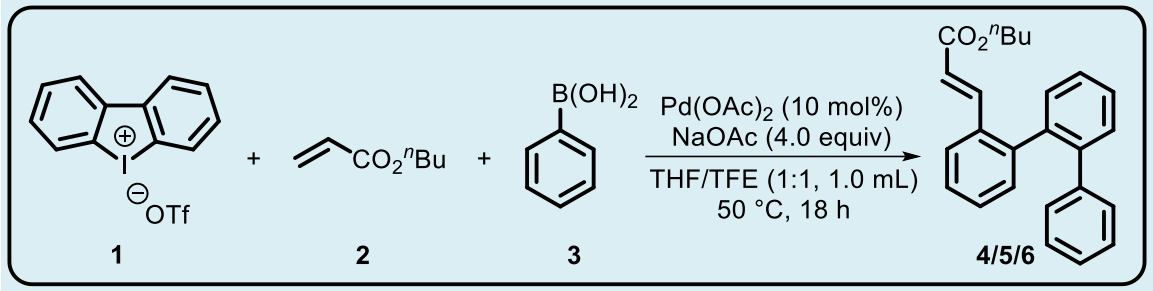
Table S11: Additional screening[a,b]



Entry	Condition	Yield (%) of 4a	Yield (%) of 13	Yield (%) of 14
1	THF/TFE (0.5 mL/0.5 mL)	53	<5	<5
2	THF/HFIP	32	trace	trace
3	THF/EtOH	18	<5	<5
4	THF/^{i}PrOH	8	trace	trace
5	DCE/THF	32	-	-
6	Toluene/THF	38	trace	-
7	THF/TFE/H_2O	43	<5	trace
8	AgOAc (0.5 equiv), THF/TFE (0.5 mL/0.5 mL)	59	<5	trace
9	**1a** (1.0 equiv), **2a** (4.0 equiv), **3a** (4.0 equiv)	46	-	-
10	**1a** (4.0 equiv), **2a** (1.0 equiv), **3a** (4.0 equiv)	97(91)	-	27
11	**1a** (4.0 equiv), **2a** (4.0 equiv), **3a** (1.0 equiv)	70	7	-
12	**1a** (2.0 equiv), **2a** (1.0 equiv), **3a** (2.0 equiv)	75	-	7
13	**1a** (3.0 equiv), **2a** (1.0 equiv), **3a** (3.0 equiv)	84	-	29
14	**1a** (2.0 equiv), **2a** (1.0 equiv), **3a** (4.0 equiv)	76	-	11
15	**1a** (4.0 equiv), **2a** (1.0 equiv), **3a** (2.0 equiv)	80	-	25
16	**1a** (2.0 equiv), **2a** (1.0 equiv), **3a** (2.0 equiv), THF (1.0 mL)	47	-	8
17	**1a** (2.0 equiv), **2a** (1.0 equiv), **3a** (2.0 equiv), TFE (1.0 mL)	23		<5
18[c]	**1a** (2.0 equiv), **2a** (1.0 equiv), **3a** (2.0 equiv)	73	-	9
19[d]	**1a** (2.0 equiv), **2a** (1.0 equiv), **3a** (2.0 equiv)	60	-	<5
20[e]	**1a** (2.0 equiv), **2a** (1.0 equiv), **3a** (2.0 equiv)	69	-	6
21[f]	**1a** (2.0 equiv), **2a** (1.0 equiv), **3a** (2.0 equiv)	93(89)	-	<5
22[f,g]	**1a** (2.0 equiv), **2a** (1.0 equiv), **3a** (2.0 equiv)	73(66)	-	<5
23[h]	**1a** (2.0 equiv), **2a** (1.0 equiv), **3a** (2.0 equiv)	80	-	5
24[f,i]	**1a** (2.0 equiv), **2a** (1.0 equiv), **3a** (2.0 equiv)	95(88)	-	<5
25[f,j]	**1a** (2.0 equiv), **2a** (1.0 equiv), **3a** (2.0 equiv)	83(77)	-	<5
26[f]	**1a** (2.0 equiv), **2a** (1.0 equiv), **3a** (2.0 equiv)/without base	nd	-	-
27[f]	**1a** (2.0 equiv), **2a** (1.0 equiv), **3a** (2.0 equiv)/without $Pd(OAc)_2$	nd	-	-

[a]Conditions: **1a** (1.0 equiv), **2a** (1.5 equiv), **3a** (1.5 equiv), $Pd(OAc)_2$ (10 mol%), NaOAc (4.0 equiv), THF/TFE (1:1, 1.0 mL), 80 °C, 18 h. [b]The yields were determined by ^{1}H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard. Isolated yield in parentheses. [c]$Pd(OAc)_2$ (5 mol%). [d]NaOAc (2.0 equiv). [e]NaOAc (3.0 equiv). [f]50 °C. [g]10 h. [h]rt for 48 h. [i]$Pd_2(dba)_3$ (5 mol%). [j]$Pd(OAc)_2$ (10 mol%), PPh_3 (20 mol%). nd = not detected.

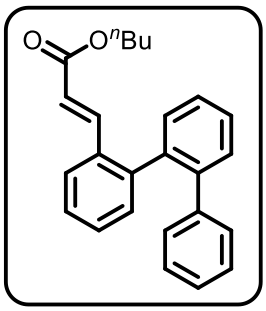
4. General procedure for the synthesis of bifunctionalized biaryls (4/5/6)



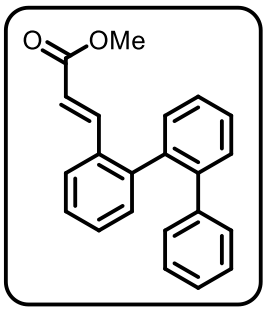
To an oven-dried Schlenk tube equipped with a magnetic stir bar was charged with cyclic diaryliodonium salt **1** (0.4 mmol, 2.0 equiv), alkene **2** (0.2 mmol, 1.0 equiv), boronic acid **3** (0.4 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.02 mmol, 0.1 equiv) and NaOAc (0.8 mmol, 4.0 equiv) in THF/TFE (1:1 v/v, 4.0 mL). The Schlenk tube was sealed with a stopper and stirred at 50 °C in a preheated oil bath for 18 h. After cooling to room temperature, the reaction mixture was diluted with DCM, filtered through a pad of Celite, and washed with DCM. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel 100-200 mesh (EtOAc in hexane) to yield the corresponding product **4/5/6**.

5. Characterization data of isolated products

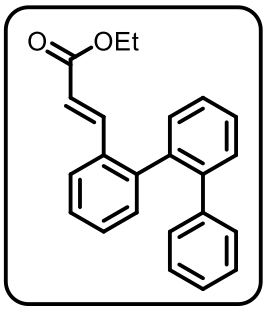
Butyl (E)-3-([1,1':2',1''-terphenyl]-2-yl)acrylate (4a): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2a** (25.6 mg, 0.2 mmol), **3a** (48.7 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 3% EtOAc in hexane) furnished **4a** (63.4 mg, 89% yield) as a white solid. R_f = 0.33 (5% EtOAc in hexane). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.53 – 7.42 (m, 5H), 7.33 – 7.27 (m, 3H), 7.24 – 7.22 (m, 1H), 7.15 – 7.11 (m, 3H), 7.07 – 7.03 (m, 2H), 6.07 (d, *J* = 15.9 Hz, 1H), 4.14 (t, *J* = 6.6 Hz, 2H), 1.68 – 1.62 (m, 2H), 1.45 – 1.37 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 167.0, 143.2, 142.6, 141.8, 141.0, 138.4, 133.2, 131.6, 131.3, 130.3, 129.8, 129.5, 128.3, 127.8, 127.5, 127.3, 126.6, 126.1, 118.7, 64.2, 30.9, 19.3, 13.8. **Melting point:** 62-64 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{25}H_{25}O_2$ 357.1855; Found: 357.1854.



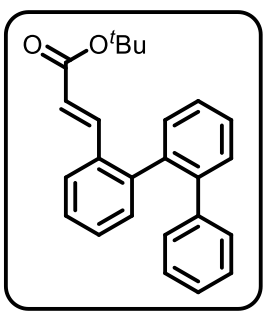
Methyl (E)-3-([1,1':2',1''-terphenyl]-2-yl)acrylate (4b): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2b** (17.2 mg, 0.2 mmol), **3a** (48.7 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 3% EtOAc in hexane) furnished **4b** (52.8 mg, 84% yield) as a white solid. R_f = 0.23 (5% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48 – 7.38 (m, 5H), 7.30 – 7.21 (m, 3H), 7.19 – 7.16 (m, 1H), 7.12 – 7.06 (m, 3H), 7.05 – 7.00 (m, 2H), 6.04 (d, *J* = 15.9 Hz, 1H), 3.70 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 167.3, 143.5, 142.6, 141.7, 141.0, 138.4, 133.0, 131.7, 131.3, 130.3, 129.8, 129.5, 128.4, 127.8, 127.5, 127.4, 126.6, 126.2, 118.3, 51.6. **Melting point:** 128-130 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{19}O_2$ 315.1385; Found: 315.1386.



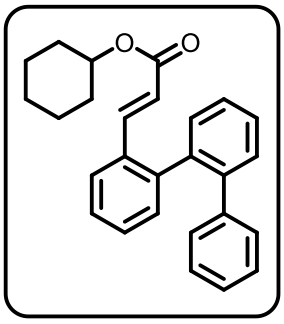
Ethyl (E)-3-([1,1':2',1''-terphenyl]-2-yl)acrylate (4c): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3a** (48.7 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 3% EtOAc in hexane) furnished **4c** (57.1 mg, 87% yield) as a white solid. R_f = 0.25 (5% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.49 – 7.38 (m, 5H), 7.30 – 7.22 (m, 3H), 7.20 – 7.18 (m, 1H), 7.13 – 7.07 (m, 3H), 7.05 – 7.01 (m, 2H), 6.03 (d, *J* = 15.9 Hz, 1H), 4.20 – 4.14 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 166.9, 143.3, 142.6, 141.8, 141.0, 138.4, 133.1, 131.6, 131.3, 130.3, 129.8, 129.5, 128.3, 127.8, 127.5, 127.4, 126.6, 126.1, 118.7, 60.3, 14.4. **Melting point:** 70-72 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{21}O_2$ 329.1542; Found: 329.1539.



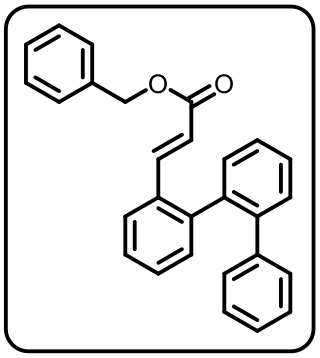
tert-Butyl (E)-3-([1,1':2',1''-terphenyl]-2-yl)acrylate (4d): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2d** (25.6 mg, 0.2 mmol), **3a** (48.7 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 3% EtOAc in hexane) furnished **4d** (60.6 mg, 85% yield) as oil. R_f = 0.25 (5% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48 – 7.43 (m, 3H), 7.42 – 7.38 (m, 1H), 7.33 (d, *J* = 15.9 Hz, 1H), 7.31 – 7.28 (m, 1H), 7.27 – 7.22 (m, 2H), 7.21 – 7.18 (m, 1H), 7.12 – 7.08 (m, 3H), 7.05 – 7.02 (m, 2H), 5.97 (d, *J* = 15.9 Hz, 1H), 1.46 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.2, 142.5, 142.2, 141.8, 141.1, 138.5, 133.3, 131.5, 131.3, 130.3, 129.9, 129.3, 128.3, 127.7, 127.5, 127.3, 126.6, 125.9, 120.4, 80.2, 28.3. **HRMS** (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{25}H_{24}NaO_2$ 379.1674; Found: 379.1682.



Cyclohexyl (E)-3-([1,1':2',1''-terphenyl]-2-yl)acrylate (4e): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2e** (30.8 mg, 0.2 mmol), **3a** (48.7 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 2% EtOAc in hexane) furnished **4e** (62.7 mg, 82% yield) as a white solid. R_f = 0.33 (5% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.49 – 7.44 (m, 3H), 7.42 – 7.38 (m, 2H), 7.31 – 7.23 (m, 3H), 7.22 – 7.20 (m, 1H), 7.11 – 7.06 (m, 3H), 7.05 – 7.01 (m, 2H), 6.01 (d, *J* = 15.9 Hz, 1H), 4.83 – 4.77 (m, 1H), 1.88 – 1.80 (m, 2H), 1.74 – 1.64 (m, 2H), 1.56 – 1.50 (m, 1H), 1.49 – 1.35 (m, 4H), 1.33 – 1.25 (m, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 166.3, 142.9, 142.5, 141.7, 141.0, 138.4, 133.1, 131.5, 131.2, 130.2, 129.8, 129.4, 128.3, 127.7, 127.4, 127.3, 126.5, 126.0, 119.1, 72.3, 31.7, 25.5, 23.7. **Melting point:** 104-106 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{27}H_{26}NaO_2$ 405.1830; Found: 405.1830.

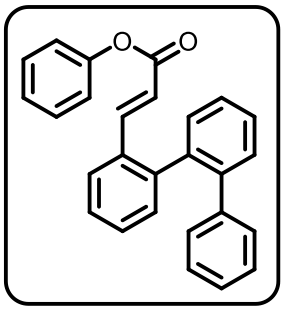


Benzyl (E)-3-([1,1':2',1''-terphenyl]-2-yl)acrylate (4f): The representative general procedure



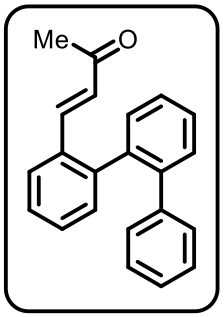
was followed using **1a** (171.2 mg, 0.4 mmol), **2f** (32.4 mg, 0.2 mmol), **3a** (48.7 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 3% EtOAc in hexane) furnished **4f** (67.9 mg, 87% yield) as viscous oil. R_f = 0.25 (5% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.50 – 7.45 (m, 3H), 7.44 – 7.41 (m, 2H), 7.40 – 7.32 (m, 5H), 7.31 – 7.24 (m, 3H), 7.23 – 7.20 (m, 1H), 7.10 – 7.05 (m, 1H), 7.05 – 7.01 (m, 2H), 6.99 – 6.95 (m, 2H), 6.07 (d, *J* = 15.9 Hz, 1H), 5.16 (s, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 166.6, 143.8, 142.7, 141.8, 140.9, 138.3, 136.4, 132.9, 131.6, 131.3, 130.3, 129.8, 129.6, 128.6, 128.3, 128.2, 128.1, 127.7, 127.5, 127.4, 126.6, 126.1, 118.2, 66.0. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{28}H_{23}O_2$ 391.1698; Found: 391.1697.

Phenyl (E)-3-([1,1':2',1''-terphenyl]-2-yl)acrylate (4g): The representative general procedure



was followed using **1a** (171.2 mg, 0.4 mmol), **2g** (29.6 mg, 0.2 mmol), **3a** (48.7 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 3% EtOAc in hexane) furnished **4g** (66.2 mg, 88% yield) as a white solid. R_f = 0.26 (5% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.60 (d, *J* = 15.9 Hz, 1H), 7.57 – 7.54 (m, 1H), 7.50 – 7.47 (m, 2H), 7.46 – 7.43 (m, 1H), 7.42 – 7.38 (m, 2H), 7.37 – 7.34 (m, 2H), 7.33 – 7.28 (m, 2H), 7.26 – 7.22 (m, 1H), 7.17 – 7.13 (m, 4H), 7.12 – 7.11 (m, 1H), 7.10 – 7.06 (m, 2H), 6.21 (d, *J* = 15.9 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 165.2, 150.9, 145.2, 142.8, 141.7, 140.9, 138.2, 132.8, 131.7, 131.3, 130.3, 130.0, 129.9, 129.4, 128.5, 127.8, 127.6, 127.4, 126.7, 126.2, 125.7, 121.7, 117.5. **Melting point:** 72-74 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{27}H_{21}O_2$ 377.1542; Found: 377.1532.

(E)-4-([1,1':2',1''-terphenyl]-2-yl)but-3-en-2-one (4h): The representative general procedure



was followed using **1a** (171.2 mg, 0.4 mmol), **2h** (14.2 mg, 0.2 mmol), **3a** (48.7 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 3% EtOAc in hexane) furnished **4h** (33.4 mg, 56% yield) as a white solid. R_f = 0.35 (10% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.55 – 7.51 (m, 3H), 7.50 – 7.46 (m, 1H), 7.39 – 7.37 (m, 1H), 7.36 – 7.32 (m, 2H), 7.31 – 7.28 (m, 2H), 7.18 – 7.14 (m, 3H), 7.09 – 7.05 (m, 2H), 6.34 (d, *J* = 16.2 Hz, 1H), 2.18 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 198.4, 142.8, 142.2, 141.6, 140.8, 138.3, 133.0, 131.6, 131.3, 130.2, 129.8, 129.6, 128.5, 127.8, 127.7, 127.6, 127.4, 126.7, 126.1, 27.1.

Melting point: 120-122 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{19}O$ 299.1436; Found: 299.1424.

(E)-3-([1,1':2',1''-terphenyl]-2-yl)acrylonitrile (4i): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2i** (10.6 mg, 0.2 mmol), **3a** (48.7 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 3% EtOAc in hexane) furnished **4i** (28.1 mg, 50% yield) as a white solid. R_f = 0.30 (5% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.53 – 7.47 (m, 2H), 7.46 – 7.42 (m, 1H), 7.38 – 7.34 (m, 2H), 7.30 – 7.26 (m, 3H), 7.18 – 7.13 (m, 3H), 7.10 (d, *J* = 16.6 Hz, 1H), 7.03 – 7.01 (m, 2H), 5.41 (d, *J* = 16.6 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 149.4, 142.3, 141.8, 140.6, 137.7, 132.2, 131.8, 131.1, 130.5, 130.4, 129.7, 128.7, 128.0, 127.8, 127.6, 126.8, 125.3, 118.4, 96.5. **Melting point:** 98-100 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{21}H_{16}N$ 282.1283; Found: 280.1286.

(E)-2-(2-(methylsulfonyl)vinyl)-1,1':2',1''-terphenyl (4j): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2j** (21.2 mg, 0.2 mmol), **3a** (48.7 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 20% EtOAc in hexane) furnished **4j** (58.8 mg, 88% yield) as a white solid. R_f = 0.30 (30% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.50 – 7.38 (m, 5H), 7.35 – 7.28 (m, 4H), 7.16 – 7.11 (m, 3H), 7.07 – 7.03 (m, 2H), 6.44 (d, *J* = 15.4 Hz, 1H), 2.83 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 143.4, 142.3, 141.6, 140.7, 137.7, 131.9, 131.1, 130.8, 130.6, 130.5, 129.9, 128.8, 127.9, 127.8, 127.7, 126.7, 126.2, 43.1. **Melting point:** 128-130 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{21}H_{19}O_2S$ 335.1106; Found: 335.1081.

(E)-2-(2-(phenylsulfonyl)vinyl)-1,1':2',1''-terphenyl (4k): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2k** (33.6 mg, 0.2 mmol), **3a** (48.7 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 20% EtOAc in hexane) furnished **4k** (68.2 mg, 86% yield) as a white solid. R_f = 0.30 (30% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.80 – 7.77 (m, 2H), 7.63 – 7.58 (m, 1H), 7.54 – 7.47 (m, 3H), 7.45 – 7.39 (m, 2H), 7.38 – 7.31 (m, 3H), 7.27 – 7.21 (m, 3H), 7.11 – 7.03 (m, 3H), 6.98 – 6.95 (m, 2H), 6.42 (d, *J* = 15.4 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 143.1, 141.6, 141.1, 140.8, 140.6, 137.8, 133.3, 131.8, 131.0, 130.9, 130.5, 130.4, 129.7, 129.2, 128.7, 127.9, 127.6, 127.6, 127.6, 127.5, 126.9, 126.6. **Melting point:** 156-158 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{26}H_{20}NaO_2S$ 419.1082; Found: 419.1082.

diethyl (E)-(2-([1,1':2',1''-terphenyl]-2-yl)vinyl)phosphonate (4l): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2l** (32.8 mg, 0.2 mmol), **3a** (48.7 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 25% EtOAc in hexane) furnished **4l** (60.4 mg, 77% yield) as a white solid. R_f = 0.17 (40% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.52 – 7.48 (m, 1H), 7.47 – 7.44 (m, 2H), 7.42 – 7.37 (m, 1H), 7.28 – 7.25 (m, 2H), 7.26 – 7.22 (m, 2H), 7.18 – 7.13 (m, 2H), 7.12 – 7.10 (m, 2H), 7.08 – 7.03 (m, 2H), 5.96 (dd, *J* = 18.8, 17.5 Hz, 1H), 4.04 – 3.93 (m, 4H), 1.25 (td, *J* = 7.0, 4.3 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 146.7 (d, *J* = 7.1 Hz), 142.3, 141.6, 140.9, 138.3, 133.5 (d, *J* = 22.7 Hz), 131.6, 131.2, 130.4, 129.8, 129.4, 128.3, 127.8, 127.5, 127.3, 126.5, 125.9, 114.6 (d, *J* = 191.3 Hz), 61.8 (m, 2C), 16.4 (d, *J* = 6.5 Hz). **^{31}P NMR (161 MHz, $CDCl_3$)**: δ 19.1. **Melting point:** 76-78 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{24}H_{25}NaO_3P$ 415.1439; Found: 415.1442.

(E)-3-([1,1':2',1''-terphenyl]-2-yl)acrylamide (4m): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2m** (14.2 mg, 0.2 mmol), **3a** (48.7 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 35% EtOAc in hexane) furnished **4m** (46.7 mg, 78% yield) as a white solid. R_f = 0.32 (60% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.46 – 7.42 (m, 3H), 7.41 – 7.38 (m, 1H), 7.34 – 7.28 (m, 2H), 7.27 – 7.21 (m, 2H), 7.19 – 7.17 (m, 1H), 7.12 – 7.09 (m, 3H), 7.06 – 7.01 (m, 2H), 5.99 (d, *J* = 15.7 Hz, 1H), 5.55 – 5.43 (br, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 167.8, 142.4, 141.7, 141.1, 140.9, 138.5, 133.3, 131.7, 131.3, 130.4, 129.8, 129.2, 128.4, 127.8, 127.5, 127.4, 126.5, 126.2, 120.6. **Melting point:** 170-172 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{21}H_{18}NO$ 300.1388; Found: 300.1380.

(E)-3-([1,1':2',1''-terphenyl]-2-yl)-N-isopropylacrylamide (4n): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2n** (22.6 mg, 0.2 mmol), **3a** (48.7 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 20% EtOAc in hexane) furnished **4n** (56.0 mg, 82% yield) as a white solid. R_f = 0.33 (30% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.45 – 7.37 (m, 4H), 7.33 (d, *J* = 15.6 Hz, 1H), 7.30 – 7.28 (m, 1H), 7.25 – 7.20 (m, 2H), 7.18 – 7.16 (m, 1H), 7.11 – 7.09 (m, 3H), 7.07 – 7.04 (m, 2H), 5.92 (d, *J* = 15.6 Hz, 1H), 5.22 (d, *J* = 7.0 Hz, 1H), 4.19 – 4.07 (m, 1H), 1.17 (d, *J* = 7.0 Hz, 6H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 165.0, 142.2, 141.6, 141.2, 139.2, 138.6, 133.7, 131.6, 131.3, 130.3, 129.8, 128.8, 128.2, 127.7, 127.4, 127.3, 126.4, 125.9, 121.9,

41.5, 22.9, 22.8. **Melting point:** 180-182 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{24}H_{24}NO$ 342.1858; Found: 342.1858.

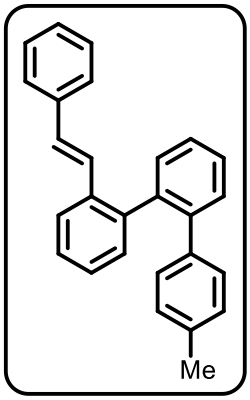
(E)-3-([1,1':2',1''-terphenyl]-2-yl)-1-morpholinoprop-2-en-1-one (4o): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2o** (28.2 mg, 0.2 mmol), **3a** (48.7 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 25% EtOAc in hexane) furnished **4o** (53.2 mg, 72% yield) as a white solid. R_f = 0.23 (40% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.45 – 7.37 (m, 5H), 7.31 – 7.29 (m, 1H), 7.26 – 7.23 (m, 2H), 7.19 – 7.15 (m, 1H), 7.12 – 7.08 (m, 3H), 7.07 – 7.02 (m, 2H), 6.33 (d, *J* = 15.4 Hz, 1H), 3.65 (br, 6H), 3.39 (br, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 165.6, 142.1, 141.9, 141.5, 141.1, 138.8, 134.0, 131.6, 131.1, 130.4, 129.8, 128.9, 128.2, 127.7, 127.4, 126.7, 126.4, 117.8, 66.9. **Melting point:** 124-126 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{25}H_{24}NO_2$ 370.1807; Found: 370.1801.

methyl (E)-(3-([1,1':2',1''-terphenyl]-2-yl)acryloyl)phenylalaninate (4p): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2p** (46.6 mg, 0.2 mmol), **3a** (48.7 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 15% EtOAc in hexane) furnished **4p** (83.1 mg, 90% yield) as a white solid. R_f = 0.23 (20% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.47 – 7.41 (m, 3H), 7.35 – 7.18 (m, 9H), 7.10 – 6.98 (m, 7H), 5.99 – 5.93 (m, 1H), 5.84 (t, *J* = 7.1 Hz, 1H), 4.97 – 4.92 (m, 1H), 3.73 (d, *J* = 8.3 Hz, 3H), 3.21 – 3.10 (m, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 172.1, 165.3, 142.4, 141.7, 141.6, 141.1, 140.3, 140.1, 138.5, 135.9, 133.4, 133.3, 131.6, 131.2, 131.1, 130.3, 129.8, 129.8, 129.3, 129.1, 128.7, 128.3, 127.7, 127.4, 127.2, 126.5, 126.4, 126.1, 126.0, 120.8, 120.6, 53.3, 52.4, 38.0, 38.0. **Melting point:** 60-62 °C **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{31}H_{28}NO_3$ 462.2069; Found: 462.2072.

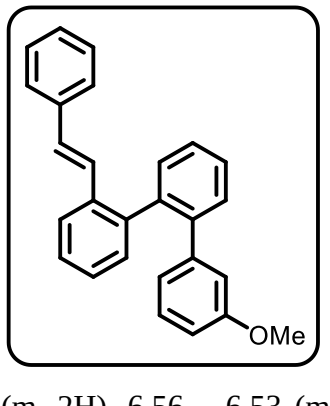
(E)-2-styryl-1,1':2',1''-terphenyl (4q): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2q** (20.8 mg, 0.2 mmol), **3a** (48.7 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 1% EtOAc in hexane) furnished **4q** (49.8 mg, 75% yield) as viscous oil. R_f = 0.23 (in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.56 (d, *J* = 7.8 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.43 – 7.38 (m, 1H), 7.36 – 7.33 (m, 1H), 7.29 – 7.16 (m, 6H), 7.15 – 7.09 (m, 2H), 7.09 – 7.03 (m, 5H), 6.85 (d, *J* = 16.2 Hz, 1H), 6.74 (d, *J* = 16.2 Hz, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 141.7, 141.3,

140.8, 139.4, 137.8, 135.9, 131.5, 131.4, 130.2, 129.6, 129.3, 128.6, 127.9, 127.7, 127.5, 127.4, 127.4, 127.2, 127.1, 126.6, 126.5, 125.2. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{26}H_{21}$ 333.1643; Found: 333.1638.

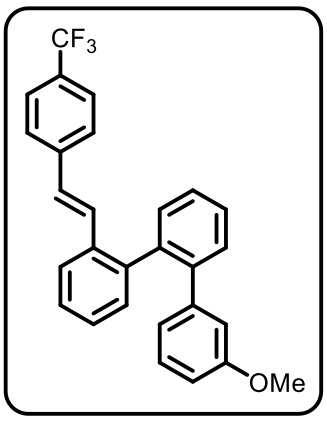
(E)-2-(4-methylstyryl)-1,1':2',1''-terphenyl (4r): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2q** (20.8 mg, 0.2 mmol), **3i** (54.4 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 1% EtOAc in hexane) furnished **4r** (54.0 mg, 78% yield) as white solid. R_f = 0.21 (in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.58 (d, J = 7.8 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.40 – 7.36 (m, 1H), 7.34 – 7.31 (m, 1H), 7.29 – 7.23 (m, 5H), 7.21 – 7.13 (m, 2H), 7.12 – 7.09 (m, 1H), 6.97 – 6.93 (m, 2H), 6.89 – 6.84 (m, 3H), 6.76 (d, J = 16.2 Hz, 1H), 2.22 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 141.6, 141.0, 139.3, 138.4, 137.8, 136.0, 135.9, 131.5, 131.4, 130.2, 129.4, 129.2, 128.6, 128.5, 127.9, 127.5, 127.4, 127.3, 127.1, 126.9, 126.6, 125.2, 21.2. **Melting point:** 108-110 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{27}H_{23}$ 347.1800; Found: 347.1788.



(E)-2-styryl-1,1':2',1''-terphenyl (4s): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2q** (20.8 mg, 0.2 mmol), **3b** (60.8 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 1% EtOAc in hexane) furnished **4s** (56.5 mg, 78% yield) as oil. Rf = 0.60 (5% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.56 (d, J = 7.7 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.43 – 7.39 (m, 1H), 7.37 – 7.34 (m, 1H), 7.27 – 7.22 (m, 5H), 7.20 – 7.13 (m, 3H), 6.98 (t, J = 7.9 Hz, 1H), 6.84 (d, J = 16.2 Hz, 1H), 6.72 (d, J = 16.2 Hz, 1H), 6.68 – 6.62 (m, 2H), 6.56 – 6.53 (m, 1H), 3.42 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 159.0, 142.6, 141.5, 140.9, 139.4, 137.8, 136.0, 131.4, 131.2, 130.0, 129.3, 128.7, 128.6, 127.9, 127.4, 127.3, 127.2, 126.6, 125.2, 122.1, 114.4, 113.3, 54.9. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{27}H_{23}O$ 363.1749; Found: 363.1765.

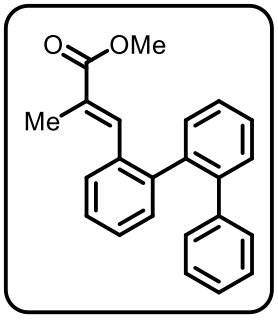


(E)-2-(4-(trifluoromethyl)styryl)-1,1':2',1''-terphenyl (4t): The representative general procedure was followed using **3a** (171.2 mg, 0.4 mmol), **2r** (34.4 mg, 0.2 mmol), **3b** (60.8 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 1% EtOAc in hexane) furnished **4t** (71.4 mg, 83% yield) as a white solid. R_f = 0.42 (5% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.56 – 7.53 (m, 1H), 7.52 (s, 1H), 7.50 (s, 1H), 7.49 – 7.45 (m, 2H), 7.45 – 7.40 (m, 1H), 7.38 – 7.35 (m,



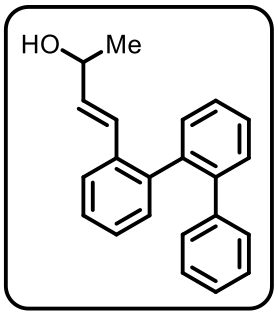
1H), 7.32 – 7.26 (m, 3H), 7.25 – 7.21 (m, 2H), 6.96 (t, *J* = 7.9 Hz, 1H), 6.88 (d, *J* = 16.2 Hz, 1H), 6.68 (d, *J* = 16.2 Hz, 1H), 6.63 (dd, *J* = 7.9, 2.1 Hz, 2H), 6.53 – 6.50 (m, 1H), 3.41 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 159.0, 142.5, 141.5, 141.2, 139.2, 135.3, 131.4, 131.4, 130.1, 130.0, 129.0 (q, *J* = 32.3 Hz), 128.8, 128.2, 127.8, 127.7, 127.6, 127.4, 126.6, 125.5 (q, *J* = 3.7 Hz), 125.3, 124.4 (q, *J* = 271.7 Hz), 122.1, 114.4, 113.2, 54.9. **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -62.4. **Melting point:** 106-108 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{28}H_{22}F_3O$ 431.1623; Found: 431.1619.

methyl (E)-3-([1,1':2',1''-terphenyl]-2-yl)-2-methylacrylate (4v): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2t** (20.0 mg, 0.2 mmol), **3a** (48.7 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 3% EtOAc in hexane) furnished **4v** (39.4 mg, 60% yield) as a white solid. R_f = 0.28 (5% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.46 – 7.37 (m, 3H), 7.34 – 7.24 (m, 4H), 7.16 – 7.09 (m, 5H), 7.01 – 6.96 (m, 2H), 3.70 (s, 3H), 1.52 (d, *J* = 1.3 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 168.9, 142.0, 141.7, 141.5, 139.0, 138.7, 134.9, 131.1, 131.0, 130.3, 129.6, 129.1, 128.7, 128.2, 128.0, 127.6, 127.2, 126.7, 126.5, 51.9, 13.6. **Melting point:** 116-118 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{23}H_{20}NaO_2$ 351.1361; Found: 351.1350.



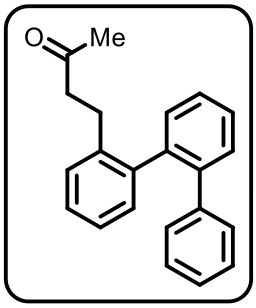
(E)-4-([1,1':2',1''-terphenyl]-2-yl)but-3-en-2-one (4w) and 4-([1,1':2',1''-terphenyl]-2-yl)butan-2-ol (4w′): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2u** (14.4 mg, 0.2 mmol), **3a** (48.7 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh furnished **4w** (21.0 mg, 35% yield) as oil and **4w′** (16.8 mg, 28% yield) as oil.

(E)-4-([1,1':2',1''-terphenyl]-2-yl)but-3-en-2-one (4w):



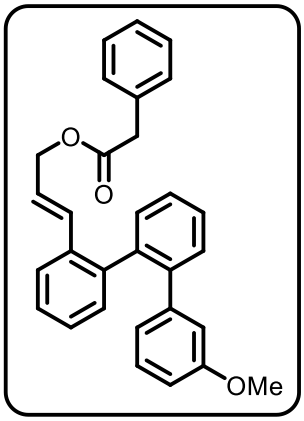
R_f = 0.13 (10% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48 – 7.38 (m, 4H), 7.33 – 7.30 (m, 1H), 7.24 – 7.13 (m, 6H), 7.11 – 7.05 (m, 2H), 6.30 – 6.21 (m, 1H), 5.94 – 5.80 (m, 1H), 4.25 – 4.14 (m, 1H), 1.20 (dd, *J* = 6.3, 2.9 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 141.5, 141.4, 141.3, 140.6, 140.5, 139.4, 139.3, 135.1, 135.0, 133.9, 133.8, 131.5, 131.4, 131.3, 131.3, 130.1, 129.7, 129.6, 128.7, 128.3, 128.0, 127.9, 127.8, 127.7, 127.4, 127.3, 127.3, 127.3, 127.2, 126.7, 126.6, 126.5, 125.3, 69.3, 69.1, 23.1, 22.9. **HRMS** (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{22}H_{20}NaO$ 323.1412; Found: 323.1412.

4-([1,1':2',1''-terphenyl]-2-yl)butan-2-ol (4w′):



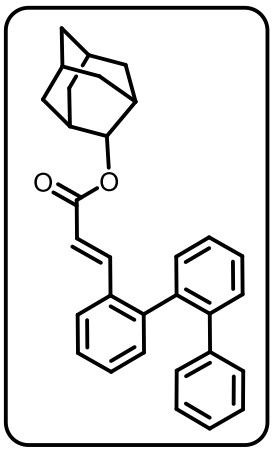
R_f = 0.30 (10% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.46 – 7.43 (m, 2H), 7.42 – 7.37 (m, 1H), 7.30 – 7.27 (m, 1H), 7.24 – 7.20 (m, 2H), 7.19 – 7.15 (m, 4H), 7.14 – 7.10 (m, 2H), 7.04 – 7.01 (m, 1H), 2.53 – 2.31 (m, 3H), 2.03 – 1.95 (m, 1H), 1.93 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 208.2, 141.3, 141.1, 140.8, 139.9, 138.5, 131.3, 131.1, 130.1, 129.7, 128.5, 127.9, 127.5, 127.3, 126.6, 125.9, 44.1, 29.8, 26.9. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{21}O$ 301.1592; Found: 301.1585.

(E)-3-([1,1':2',1''-terphenyl]-2-yl)allyl 2-phenylacetate (4x): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2v** (35.2 mg, 0.2 mmol), **3b** (60.8 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 1% EtOAc in hexane) furnished **4x** (19.9 mg, 23% yield) as oil.



R_f = 0.28 (5% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.50 – 7.45 (m, 2H), 7.44 – 7.39 (m, 2H), 7.33 – 7.29 (m, 3H), 7.28 – 7.20 (m, 4H), 7.19 – 7.16 (m, 1H), 7.13 – 7.10 (m, 1H), 7.05 (t, J = 7.9 Hz, 1H), 6.70 – 6.66 (m, 2H), 6.53 – 6.52 (m, 1H), 6.38 (d, J = 15.9 Hz, 1H), 5.92 (dt, J = 15.8, 6.2 Hz, 1H), 4.54 – 4.51 (m, 2H), 3.59 (s, 2H), 3.52 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 171.3, 158.9, 142.5, 141.4, 140.8, 139.1, 134.9, 134.1, 132.3, 131.3, 131.2, 130.0, 129.4, 128.8, 128.7, 128.0, 127.6, 127.4, 127.3, 127.2, 125.5, 123.6, 122.1, 114.7, 113.0, 65.6, 55.1, 41.4. **HRMS** (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{30}H_{26}NaO_3$ 457.1780; Found: 457.1801.

(1r,3r)-adamantan-2-yl (E)-3-([1,1':2',1''-terphenyl]-2-yl)acrylate (4y): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2w** (41.2 mg, 0.2 mmol), **3a** (48.7 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 3% EtOAc in hexane) furnished **4y** (73.0 mg, 84% yield) as oil.



R_f = 0.33 (5% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.53 – 7.50 (m, 1H), 7.47 – 7.38 (m, 4H), 7.32 – 7.28 (m, 2H), 7.27 – 7.21 (m, 2H), 7.13 – 7.08 (m, 3H), 7.06 – 7.02 (m, 2H), 6.08 (d, J = 15.9 Hz, 1H), 4.96 (t, J = 3.2 Hz, 1H), 1.99 (bs, 2H), 1.94 – 1.84 (m, 5H), 1.81 – 1.72 (m, 5H), 1.55 – 1.51 (m, 2H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 166.2, 142.9, 142.7, 141.7, 141.0, 138.5, 133.2, 131.4, 131.2, 130.2, 129.8, 129.4, 128.2, 127.8, 127.5, 127.3, 126.6, 125.9, 119.2, 76.7, 37.5, 36.5, 36.4, 32.1, 32.0, 31.9, 31.9, 27.4, 27.1. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{31}H_{31}O_2$ 435.2324; Found: 435.2311.

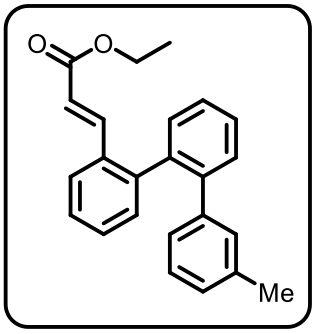
2-oxo-2H-chromen-7-yl (E)-3-([1,1':2',1''-terphenyl]-2-yl)acrylate (4z): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2y** (43.2 mg, 0.2 mmol), **3a** (48.7 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 6% EtOAc in hexane) furnished **4y** (54.4 mg, 61% yield) as white solid. R_f = 0.20 (20% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.69 (d, J = 9.5 Hz, 1H), 7.60 (d, J = 15.9 Hz, 1H), 7.56 – 7.53 (m, 1H), 7.50 – 7.48 (m, 1H), 7.48 – 7.45 (m, 2H), 7.44 – 7.40 (m, 1H), 7.39 – 7.29 (m, 4H), 7.16 – 7.11 (m, 4H), 7.09 – 7.02 (m, 3H), 6.39 (d, J = 9.5 Hz, 1H), 6.17 (d, J = 15.9, 1H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 164.5, 160.5, 154.8, 153.5, 146.4, 143.1, 143.0, 141.7, 140.8, 138.1, 132.5, 131.8, 131.3, 130.4, 130.3, 129.9, 128.6, 128.6, 127.9, 127.7, 127.5, 126.8, 126.3, 118.5, 116.6, 116.6, 116.0, 110.5. **Melting point:** 156-158 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{30}H_{21}O_4$ 445.1440; Found: 445.1450.

(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl (E)-3-([1,1':2',1''-terphenyl]-2-yl)acrylate (4aa): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2z** (64.8 mg, 0.2 mmol), **3a** (48.7 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 8% EtOAc in hexane) furnished **4aa** (87.4 mg, 79% yield) as white solid. R_f = 0.34 (20% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.60 – 7.53 (m, 2H), 7.47 – 7.40 (m, 3H), 7.38 – 7.27 (m, 5H), 7.16 – 7.11 (m, 3H), 7.09 – 7.04 (m, 2H), 6.91 – 6.83 (m, 2H), 6.18 (d, J = 15.9 Hz, 1H), 2.96 – 2.89 (m, 2H), 2.55 – 2.48 (m, 1H), 2.46 – 2.39 (m, 1H), 2.35 – 2.26 (m, 1H), 2.20 – 1.95 (m, 4H), 1.67 – 1.43 (m, 6H + water), 0.92 (s, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 220.8, 165.5, 148.8, 145.1, 142.8, 141.7, 140.9, 138.2, 138.0, 137.3, 132.7, 131.7, 131.3, 130.3, 130.0, 129.9, 128.5, 127.8, 127.6, 127.4, 126.7, 126.4, 126.2, 121.7, 118.8, 117.6, 50.5, 48.0, 44.2, 38.1, 35.9, 31.6, 29.5, 26.4, 25.9, 21.7, 13.9. **Melting point:** 202-204 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{39}H_{37}O_3$ 553.2743; Found: 553.2731.

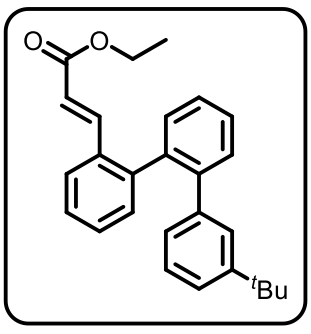
Ethyl (E)-3-(3''-methoxy-[1,1':2',1''-terphenyl]-2-yl)acrylate (5a): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3b** (60.8 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 4% EtOAc in hexane) furnished **5a** (68.1 mg, 95% yield) as a white solid. R_f = 0.32 (10% EtOAc in hexane). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.54 – 7.51 (m, 1H), 7.51 – 7.41 (m, 4H), 7.35 – 7.31 (m, 2H), 7.30 – 7.27 (m, 1H), 7.26 –

7.23 (m, 1H), 7.05 (t, *J* = 7.9 Hz, 1H), 6.71 – 6.66 (m, 2H), 6.59 – 6.57 (m, 1H), 6.08 (d, *J* = 15.9 Hz, 1H), 4.20 (qd, *J* = 7.1, 1.9 Hz, 2H), 3.58 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 166.9, 159.0, 143.2, 142.7, 142.3, 141.6, 138.4, 133.2, 131.6, 131.3, 130.2, 129.5, 128.8, 128.4, 127.5, 127.4, 126.1, 122.4, 118.7, 114.9, 113.1, 60.3, 55.1, 14.4. **Melting point:** 84-86 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{24}H_{23}O_3$ 359.1647; Found: 459.1641.

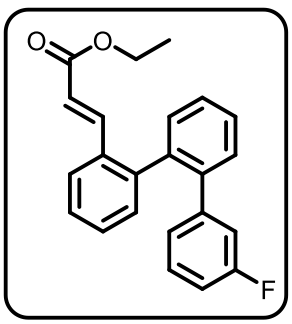
Ethyl (E)-3-(3''-methyl-[1,1':2',1''-terphenyl]-2-yl)acrylate (5b): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3c** (54.4 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 3% EtOAc in hexane) furnished **5b** (63.0 mg, 92% yield) as a white solid. R_f = 0.24 (5% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48 – 7.45 (m, 2H), 7.44 – 7.35 (m, 3H), 7.31 – 7.23 (m, 3H), 7.21 – 7.19 (m, 1H), 6.97 – 6.90 (m, 3H), 6.74 (d, *J* = 7.2 Hz, 1H), 6.02 (d, *J* = 15.9 Hz, 1H), 4.17 (qd, *J* = 7.1, 2.6 Hz, 2H), 2.16 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.9, 143.4, 142.7, 141.9, 140.9, 138.4, 137.3, 133.1, 131.6, 131.2, 130.7, 130.2, 129.5, 128.3, 127.5, 127.4, 127.3, 127.2, 126.9, 126.0, 118.5, 60.3, 21.3, 14.4. **Melting point:** 82-84 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{24}H_{23}O_3$ 343.1698; Found: 343.1699.



Ethyl (E)-3-(3''-(tert-butyl)-[1,1':2',1''-terphenyl]-2-yl)acrylate (5c): The representative general procedure was followed using **1a** (20.0 mg, 0.2 mmol), **2c** (71.2 mg, 0.4 mmol), **3d** (171.2 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 2% EtOAc in hexane) furnished **5c** (67.0 mg, 87% yield) as oil. R_f = 0.38 (5% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.50 – 7.44 (m, 3H), 7.43 – 7.38 (m, 2H), 7.33 – 7.27 (m, 2H), 7.25 – 7.20 (m, 2H), 7.14 – 7.07 (m, 2H), 7.01 – 6.98 (m, 1H), 6.89 (s, 1H), 5.99 (d, *J* = 15.9 Hz, 1H), 4.15 (qd, *J* = 7.1, 2.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.04(s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.9, 150.2, 143.3, 142.9, 142.3, 140.3, 138.5, 133.1, 131.6, 131.2, 130.1, 129.6, 128.4, 127.7, 127.6, 127.4, 127.3, 126.8, 126.1, 123.4, 118.5, 60.3, 34.4, 31.2, 14.4. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{27}H_{29}O_2$ 385.2168; Found: 385.2171.

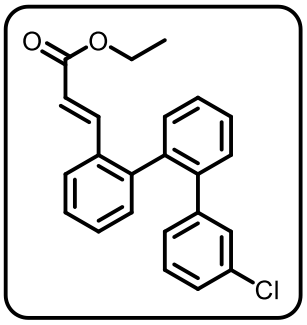


Ethyl (E)-3-(3''-fluoro-[1,1':2',1''-terphenyl]-2-yl)acrylate (5d): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3e** (56.0 mg, 0.4 mmol), (171.2 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 3% EtOAc in hexane) furnished

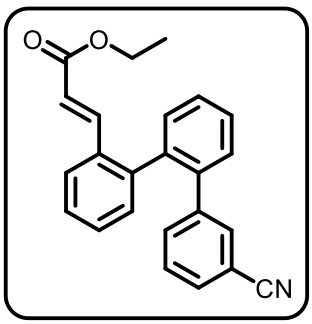


5d (63.0 mg, 91% yield) as a white solid. R_f = 0.22 (5% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.51 – 7.41 (m, 4H), 7.40 (d, *J* = 15.9 Hz, 1H), 7.33 – 7.24 (m, 3H), 7.22 – 7.18 (m, 1H), 7.04 (td, *J* = 8.1, 6.1 Hz, 1H), 6.84 – 6.73 (m, 3H), 6.05 (d, *J* = 15.9 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.8, 162.3 (d, *J* = 245.2 Hz), 143.3 (d, *J* = 7.7 Hz), 143.0, 142.1, 140.5 (d, *J* = 1.7 Hz), 138.4, 133.1, 131.5, 131.4, 130.1, 129.7, 129.1 (d, *J* = 8.3 Hz), 128.4, 127.8, 127.7, 126.2, 125.6 (d, *J* = 2.7 Hz), 118.8, 116.7 (d, *J* = 21.9 Hz), 113.5 (d, *J* = 21.1 Hz), 60.4, 14.4. **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -114.0. **Melting point:** 72-74 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{20}FO_2$ 347.1447; Found: 347.1441.

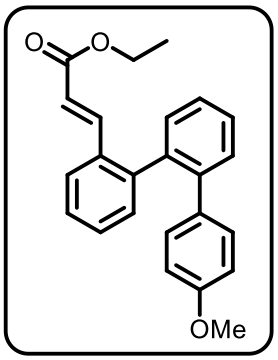
Ethyl (E)-3-(3''-chloro-[1,1':2',1''-terphenyl]-2-yl)acrylate (5e): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3f** (62.5 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 3% EtOAc in hexane) furnished **5e** (67.5 mg, 93% yield) as a white solid. R_f = 0.30 (5% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.50 – 7.40 (m, 4H), 7.37 (d, *J* = 15.9 Hz, 1H), 7.33 – 7.26 (m, 3H), 7.25 – 7.20 (m, 1H), 7.12 – 7.05 (m, 2H), 6.98 (t, *J* = 7.8 Hz, 1H), 6.82 – 6.77 (m, 1H), 6.03 (d, *J* = 15.9 Hz, 1H), 4.21 – 4.15 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.8, 143.0, 142.8, 141.9, 140.4, 138.5, 133.7, 133.1, 131.5, 131.3, 130.1, 129.9, 129.7, 128.8, 128.5, 128.0, 127.9, 127.8, 126.7, 126.2, 118.8, 60.4, 14.4. **Melting point:** 118-120 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{20}ClO_2$ 363.1152; Found: 363.1144.



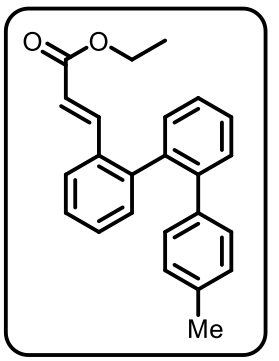
Ethyl (E)-3-(3''-cyano-[1,1':2',1''-terphenyl]-2-yl)acrylate (5f): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3g** (58.8 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 5% EtOAc in hexane) furnished **5f** (56.5 mg, 80% yield) as a white solid. R_f = 0.24 (10% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.52 – 7.45 (m, 3H), 7.42 – 7.39 (m, 2H), 7.37 – 7.33 (m, 3H), 7.33 – 7.31 (m, 1H), 7.30 – 7.29 (m, 1H), 7.25 – 7.22 (m, 1H), 7.20 – 7.15 (m, 2H), 5.99 (d, *J* = 15.9 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H) 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.7, 142.7, 142.3, 141.4, 139.5, 138.4, 134.1, 133.3, 132.9, 131.5, 131.4, 130.3, 129.9, 129.8, 128.7, 128.5, 128.1, 126.2, 119.0, 118.6, 112.0, 60.5, 14.3. **Melting point:** 146-148 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{24}H_{19}NO_2$ 354.1494; Found: 354.1411.



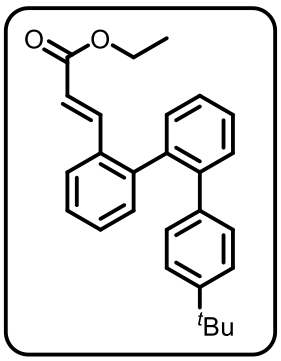
Ethyl (E)-3-(4''-methoxy-[1,1':2',1''-terphenyl]-2-yl)acrylate (5g): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3h** (60.8 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 5% EtOAc in hexane) furnished **5g** (61.6 mg, 86% yield) as oil. R_f = 0.38 (10% EtOAc in hexane). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.53 (d, J = 7.6 Hz, 1H), 7.49 – 7.44 (m, 3H), 7.43 – 7.39 (m, 1H), 7.34 – 7.28 (m, 3H), 7.27 – 7.23 (m, 1H), 6.98 (d, J = 8.6 Hz, 2H), 6.68 (d, J = 8.7 Hz, 2H), 6.09 (d, J = 15.9 Hz, 1H), 4.21 (qd, J = 7.1, 1.3 Hz, 2H), 3.75 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 166.9, 158.4, 143.3, 142.8, 141.3, 138.3, 133.5, 133.1, 131.6, 131.3, 130.9, 130.2, 129.6, 128.3, 127.4, 127.0, 126.2, 118.6, 113.3, 60.3, 55.2, 14.4. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{24}H_{23}O_3$ 359.1647; Found: 359.1651.



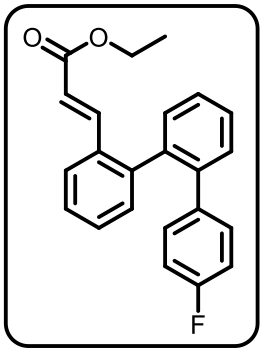
Ethyl (E)-3-(4''-methyl-[1,1':2',1''-terphenyl]-2-yl)acrylate (5h): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3i** (54.4 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 5% EtOAc in hexane) furnished **5h** (65.7 mg, 96% yield) as oil. R_f = 0.38 (10% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.50 – 7.47 (m, 1H), 7.46 – 7.41 (m, 3H), 7.40 – 7.36 (m, 1H), 7.29 – 7.22 (m, 3H), 7.20 – 7.17 (m, 1H), 6.91 (s, 4H), 6.04 (d, J = 15.9 Hz, 1H), 4.17 (q, J = 7.1, Hz, 2H), 2.24 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.9, 143.3, 142.8, 141.7, 138.3, 138.1, 136.2, 133.1, 131.6, 131.3, 130.3, 129.7, 129.5, 128.5, 128.3, 127.4, 127.1, 126.1, 118.7, 60.3, 21.2, 14.4. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{24}H_{23}O_3$ 343.1698; Found: 343.1697.



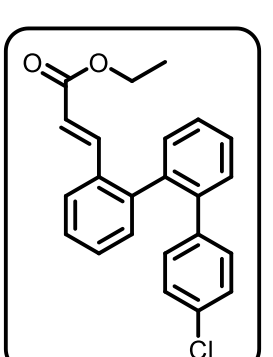
Ethyl (E)-3-(4''-(tert-butyl)-[1,1':2',1''-terphenyl]-2-yl)acrylate (5i): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3j** (71.2 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 3% EtOAc in hexane) furnished **5i** (63.8 mg, 83% yield) as oil. R_f = 0.30 (5% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48 – 7.42 (m, 3H), 7.41 – 7.35 (m, 2H), 7.32 – 7.25 (m, 3H), 7.24 – 7.20 (m, 1H), 7.13 – 7.08 (m, 2H), 6.96 – 6.91 (m, 2H), 5.92 (d, J = 15.9 Hz, 1H), 4.16 (qd, J = 7.1, 1.7 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H), 1.24 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.8, 149.6, 143.5, 142.6, 141.6, 138.4, 137.9, 133.4, 131.7, 131.4, 130.3, 129.5, 128.4, 127.5, 127.1, 126.1, 124.7, 118.5, 60.2, 34.5, 31.4, 14.4. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{27}H_{29}O_2$ 385.2168; Found: 385.2165.



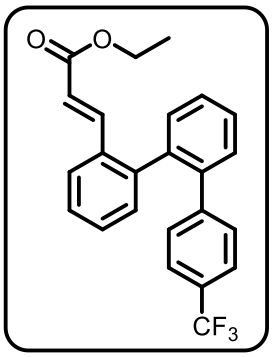
Ethyl (E)-3-(4''-fluoro-[1,1':2',1''-terphenyl]-2-yl)acrylate (5j): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3k** (56.0 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 3% EtOAc in hexane) furnished **5j** (59.6 mg, 86% yield) as a white solid. R_f = 0.32 (5% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.50 – 7.47 (m, 1H), 7.46 – 7.43 (m, 1H), 7.43 – 7.36 (m, 3H), 7.32 – 7.23 (m, 3H), 7.21 – 7.17 (m, 1H), 7.01 – 6.95 (m, 2H), 6.82 – 6.75 (m, 2H), 6.05 (d, *J* = 15.9 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.8, 161.8 (d, *J* = 245.9 Hz), 143.1, 142.3, 140.7, 138.4, 137.0 (d, *J* = 3.3 Hz), 133.0, 131.5, 131.4, 131.3, 130.2, 129.6, 128.4, 127.6, 127.5, 126.2, 118.7, 114.7 (d, *J* = 21.3 Hz), 60.3, 14.4. **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -116.0. **Melting point:** 102-104 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{20}FO_2$ 347.1447; Found: 347.1448.



Ethyl (E)-3-(4''-chloro-[1,1':2',1''-terphenyl]-2-yl)acrylate (5k): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3l** (62.5 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 3% EtOAc in hexane) furnished **5k** (63.8 mg, 88% yield) as a white solid. R_f = 0.28 (5% EtOAc in hexane). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.55 – 7.52 (m, 1H), 7.51 – 7.48 (m, 1H), 7.47 – 7.40 (m, 3H), 7.35 – 7.28 (m, 3H), 7.24 – 7.21 (m, 1H), 7.12 – 7.09 (m, 2H), 7.00 – 6.97 (m, 2H), 6.10 (d, *J* = 15.9 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 166.8, 143.0, 142.2, 140.5, 139.6, 138.4, 133.1, 132.8, 131.5, 131.4, 131.1, 130.1, 129.7, 128.5, 128.0, 127.8, 127.7, 126.3, 118.9, 60.3, 14.4. **Melting point:** 98-100 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{20}ClO_2$ 363.1152; Found: 363.1152.



Ethyl (E)-3-(4''-(trifluoromethyl)-[1,1':2',1''-terphenyl]-2-yl)acrylate (5l): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3m** (76.0 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 3% EtOAc in hexane) furnished **5l** (65.8 mg, 83% yield) as oil. R_f = 0.26 (5% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.52 – 7.42 (m, 4H), 7.40 – 7.36 (m, 2H), 7.35 – 7.32 (m, 2H), 7.31 – 7.26 (m, 2H), 7.22 – 7.18 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.02 (d, *J* = 15.9 Hz, 1H), 4.17 (qd, *J* = 7.1, 1.0 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.8, 144.8, 142.9, 141.8, 140.3, 138.5, 133.1, 131.6, 131.5, 130.2, 130.1, 129.7, 128.7 (q, *J* = 32.1 Hz), 128.6, 128.2, 127.9, 126.3, 124.7 (q, *J* = 3.6 Hz),



124.3 (q, J = 271.9 Hz), 119.1, 60.4, 14.4. **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -62.4. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{24}H_{20}F_3O_2$ 397.1415; Found: 397.1412.

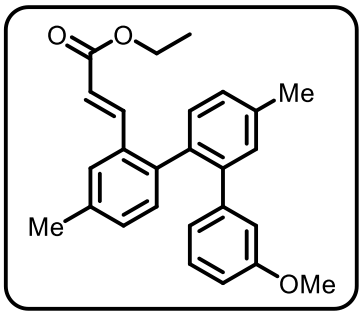
Ethyl (E)-3-(4''-cyano-[1,1':2',1''-terphenyl]-2-yl)acrylate (5m): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3n** (58.7 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 3% EtOAc in hexane) furnished **5m** (54.4 mg, 77% yield) as oil. R_f = 0.26 (10% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.52 – 7.46 (m, 3H), 7.43 – 7.39 (m, 2H), 7.38 – 7.35 (m, 2H), 7.34 – 7.29 (m, 3H), 7.21 – 7.18 (m, 1H), 7.15 – 7.11 (m, 2H), 6.04 (d, J = 15.9 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.7, 145.9, 142.7, 141.5, 139.8, 138.4, 132.9, 131.5, 131.5, 131.4, 130.4, 129.9, 129.8, 128.6, 128.5, 128.0, 126.3, 119.1, 118.9, 110.4, 60.4, 14.4. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{24}H_{20}NO_2$ 354.1494; Found: 354.1503.

Ethyl (E)-2''-(3-ethoxy-3-oxoprop-1-en-1-yl)-[1,1':2',1''-terphenyl]-4-carboxylate (5n): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3o** (77.6 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 6% EtOAc in hexane) furnished **5n** (66.5 mg, 83% yield) as oil. R_f = 0.28 (10% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.81 – 7.77 (m, 2H), 7.51 – 7.43 (m, 4H), 7.41 (d, J = 15.9 Hz, 1H), 7.33 – 7.23 (m, 3H), 7.20 – 7.17 (m, 1H), 7.12 – 7.08 (m, 2H), 6.04 (d, J = 15.9 Hz, 1H), 4.32 (q, J = 7.1 Hz, 2H), 4.17 (q, J = 7.1 2H), 1.35 (t, J = 7.1 Hz, 3H), 1.28 (t, J = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.8, 166.6, 145.8, 142.9, 142.1, 140.7, 138.4, 133.1, 131.5, 131.4, 130.2, 129.7, 129.6, 129.1, 128.6, 128.5, 128.0, 127.8, 126.3, 119.0, 60.9, 60.4, 14.4. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{26}H_{25}O_4$ 401.1753; Found: 401.1750.

Ethyl (E)-3-(2''-methyl-[1,1':2',1''-terphenyl]-2-yl)acrylate (5o): The representative general procedure was followed using **1a** (171.2 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3p** (54.4 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 4% EtOAc in hexane) furnished **5o** (41.1 mg, 60% yield) as a white solid. R_f = 0.33 (5% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.56 (d, J = 15.9 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.47 – 7.40 (m, 2H), 7.37 – 7.27 (m, 2H), 7.22 – 7.15 (m, 2H), 7.13 – 6.90 (m, 5H), 6.20 (d, J = 15.9 Hz, 1H), 4.22 – 4.11 (m, 2H), 2.04 – 2.01 (m, 3H), 1.31 – 1.26 (m, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 167.0, 166.8, 143.6, 143.2, 142.7, 142.2, 141.3,

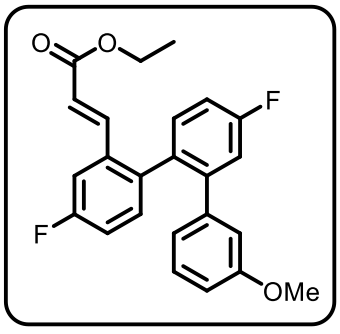
141.1, 140.7, 140.1, 139.0, 136.1, 135.5, 132.9, 132.1, 131.4, 131.1, 130.9, 130.7, 130.1, 129.5, 129.2, 128.9, 127.7, 127.4, 127.1, 127.0, 126.1, 125.9, 125.0, 124.8, 118.7, 118.4, 60.3, 20.4, 20.3, 14.4. **Melting point:** 94-96 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{24}H_{23}O_2$ 343.1698; Found: 343.1698.

Ethyl (E)-3-(3''-methoxy-4,4'-dimethyl-[1,1':2',1''-terphenyl]-2-yl)acrylate (6a): The



representative general procedure was followed using **1b** (182.5 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3b** (60.8 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 5% EtOAc in hexane) furnished **6a** (71.8 mg, 93% yield) as oil. R_f = 0.37 (10% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.47 (d, *J* = 15.9 Hz, 1H), 7.32 (s, 1H), 7.29 (s, 1H), 7.24 – 7.17 (m, 2H), 7.10 (s, 2H), 7.03 (t, *J* = 7.9 Hz, 1H), 6.70 – 6.64 (m, 2H), 6.58 (s, 1H), 6.07 (d, *J* = 15.9 Hz, 1H), 4.18 (q, *J* = 7.0 Hz, 2H), 3.57 (s, 3H), 2.46 (s, 3H), 2.34 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 167.0, 158.9, 143.6, 142.6, 141.5, 139.9, 137.8, 136.8, 135.4, 133.0, 131.5, 131.4, 130.9, 130.5, 128.7, 128.1, 126.5, 122.3, 118.1, 114.8, 112.9, 60.2, 55.0, 21.3, 21.2, 14.4. **HRMS** (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{26}H_{26}NaO_3$ 409.1780; Found: 409.1790.

Ethyl (E)-3-(4,4'-difluoro-3''-methoxy-[1,1':2',1''-terphenyl]-2-yl)acrylate (6b): The



representative general procedure was followed using **1c** (185.6 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3b** (60.8 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 4% EtOAc in hexane) furnished **6b** (52.0 mg, 66% yield) as a white solid. R_f = 0.56 (10% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.32 (dd, *J* = 15.9, 1.6 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.20 – 7.16 (m, 2H), 7.15 – 7.09 (m, 2H), 7.06 – 7.02 (m, 1H), 7.02 – 6.97 (m, 1H), 6.72 – 6.68 (m, 1H), 6.59 – 6.55 (m, 1H), 6.53 – 6.52 (m, 1H), 6.03 (d, *J* = 15.9 Hz, 1H), 4.18 (qd, *J* = 7.1, 1.0 Hz, 2H), 3.60 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.4, 162.6 (d, *J* = 247.9 Hz), 162.1 (d, *J* = 246.7 Hz), 159.2, 143.8 (d, *J* = 7.9 Hz), 141.8 (d, *J* = 2.4 Hz), 141.1 (d, *J* = 1.3 Hz), 137.6 (d, *J* = 3.0 Hz), 135.2 (d, *J* = 7.6 Hz), 133.4 (d, *J* = 3.2 Hz), 133.2 (d, *J* = 8.0 Hz), 132.9 (d, *J* = 8.3 Hz), 129.0, 122.1, 120.0, 117.0 (d, *J* = 21.9 Hz), 116.7 (d, *J* = 21.4 Hz), 114.8, 114.4 (d, *J* = 21.1 Hz), 113.4, 112.5 (d, *J* = 22.1 Hz), 60.6, 55.1, 14.4. **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -114.0, -114.4. **Melting point:** 108-110 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{24}H_{21}F_2O_3$ 395.1459; Found: 395.1478.

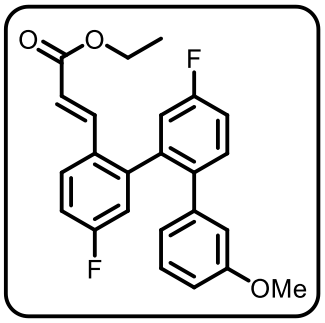
Ethyl (E)-3-(4,4'-dichloro-3''-methoxy-[1,1':2',1''-terphenyl]-2-yl)acrylate (6c): The representative general procedure was followed using **1d** (198.8 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3b** (60.8 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 5% EtOAc in hexane) furnished **6c** (47.0 mg, 55% yield) as oil. R_f = 0.43 (10% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.47 (d, *J* = 2.1 Hz, 2H), 7.39 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.30 (d, *J* = 15.9 Hz, 1H), 7.26 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.19 (d, *J* = 8.5 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 7.04 (t, *J* = 7.9 Hz, 1H), 6.73 – 6.69 (m, 1H), 6.58 – 6.53 (m, 2H), 6.05 (d, *J* = 15.9 Hz, 1H), 4.19 (qd, *J* = 7.1, 0.6 Hz, 2H), 3.61 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.3, 159.2, 143.3, 141.4, 140.7, 139.7, 135.7, 134.8, 134.5, 133.8, 132.7, 132.4, 130.3, 129.6, 129.1, 127.6, 126.1, 122.1, 120.2, 114.8, 113.5, 60.6, 55.1, 14.4. **HRMS** (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{24}H_{20}Cl_2NaO_3$ 449.0687; Found: 449.0689.

Ethyl (E)-3-(3''-methoxy-4,4'-bis(trifluoromethyl)-[1,1':2',1''-terphenyl]-2-yl)acrylate (6d): The representative general procedure was followed using **1e** (225.6 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3b** (60.8 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 4% EtOAc in hexane) furnished **6d** (70.2 mg, 71% yield) as oil. R_f = 0.48 (10% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.76 (s, 2H), 7.70 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.58 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 15.9 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.06 (t, *J* = 7.9 Hz, 1H), 6.76 – 6.72 (m, 1H), 6.60 – 6.57 (m, 1H), 6.56 – 6.53 (m, 1H), 6.14 (d, *J* = 15.9 Hz, 1H), 4.22 – 4.17 (m, 2H), 3.59 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.2, 159.4, 144.4, 142.4, 140.9, 140.7, 140.3, 133.9, 131.9, 131.6, 131.3 (q, *J* = 32.6 Hz), 130.6 (q, *J* = 32.7 Hz), 129.3, 127.3 (q, *J* = 3.6 Hz), 126.0 (q, *J* = 3.4 Hz), 124.4 (q, *J* = 3.6 Hz), 124.0 (q, *J* = 272.4 Hz), 123.8 (q, *J* = 272.5 Hz), 123.2 (q, *J* = 3.7 Hz), 122.1, 121.1, 114.9, 113.8, 60.7, 55.1, 14.3. **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -62.6, -62.8. **HRMS** (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{26}H_{20}F_6NaO_3$ 517.1214; Found: 517.1238.

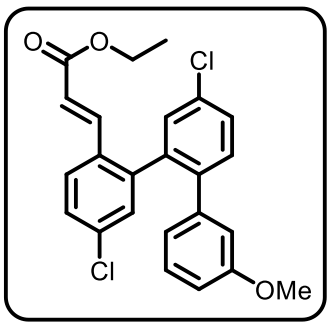
Ethyl (E)-3-(3''-methoxy-5,5'-dimethyl-[1,1':2',1''-terphenyl]-2-yl)acrylate (6e): The representative general procedure was followed using **1f** (182.5 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3b** (60.8 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 5% EtOAc in hexane) furnished **6e** (61.8 mg, 80% yield) as oil. R_f = 0.36 (10% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.39 – 7.34 (m, 3H), 7.28 – 7.26 (m, 1H), 7.12 – 7.06 (m, 3H), 7.02 – 6.98 (m, 1H),

6.66 – 6.62 (m, 2H), 6.56 – 6.54 (m, 1H), 5.98 (d, *J* = 15.9 Hz, 1H), 4.15 (qd, *J* = 7.1, 1.6 Hz, 2H), 3.55 (s, 3H), 2.43 (s, 3H), 2.32 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 167.1, 158.9, 143.3, 142.8, 142.3, 139.8, 138.8, 138.4, 137.1, 132.1, 131.8, 130.4, 130.0, 129.0, 128.7, 128.3, 125.9, 122.3, 117.4, 114.8, 112.9, 60.2, 55.0, 21.4, 21.2, 14.4. **HRMS** (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{26}H_{26}NaO_3$ 409.1780; Found: 409.1779.

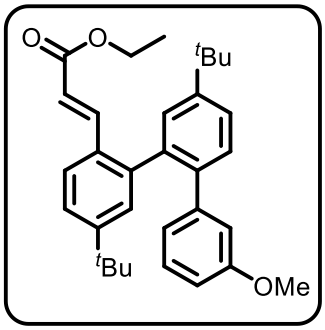
Ethyl (E)-3-(5,5'-difluoro-3''-methoxy-[1,1':2',1''-terphenyl]-2-yl)acrylate (6f): The representative general procedure was followed using **1g** (185.6 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3b** (60.8 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 6% EtOAc in hexane) furnished **6f** (58.4 mg, 74% yield) as a white solid. R_f = 0.33 (10% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.49 – 7.41 (m, 2H), 7.31 (d, *J* = 15.9 Hz, 1H), 7.19 (td, *J* = 8.3, 2.7 Hz, 1H), 7.05 – 6.93 (m, 4H), 6.71 – 6.66 (m, 1H), 6.60 – 6.56 (m, 1H), 6.56 – 6.53 (m, 1H), 5.98 (d, *J* = 15.9 Hz, 1H), 4.17 (qd, *J* = 7.1, 1.7 Hz, 2H), 3.59 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.6, 163.1 (d, *J* = 251.6 Hz), 161.9 (d, *J* = 248.1 Hz), 159.1, 143.6 (d, *J* = 8.0 Hz), 141.5, 140.9, 139.1 (d, *J* = 8.4 Hz), 137.7 (d, *J* = 3.1 Hz), 131.9 (d, *J* = 8.3 Hz), 129.4 (d, *J* = 3.1 Hz), 128.9, 128.2 (d, *J* = 8.7 Hz), 122.2, 118.8, 117.9 (d, *J* = 21.9 Hz), 117.6 (d, *J* = 21.8 Hz), 115.7 (d, *J* = 20.9 Hz), 115.3 (d, *J* = 21.7 Hz), 114.9, 113.2, 60.4, 55.1, 14.3. **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -110.6, -114.9. **Melting point:** 106-108 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{24}H_{21}F_2O_3$ 395.1459; Found: 395.1477.



Ethyl (E)-3-(5,5'-dichloro-3''-methoxy-[1,1':2',1''-terphenyl]-2-yl)acrylate (6g): The representative general procedure was followed using **1h** (198.8 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3b** (60.8 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 6% EtOAc in hexane) furnished **6g** (33.3 mg, 39% yield) as a white solid. R_f = 0.32 (10% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48 – 7.44 (m, 1H), 7.41 – 7.37 (m, 2H), 7.32 – 7.29 (m, 2H), 7.28 – 7.21 (m, 2H), 7.03 (t, *J* = 7.9 Hz, 1H), 6.71 – 6.67 (m, 1H), 6.59 – 6.52 (m, 2H), 5.96 (d, *J* = 15.8 Hz, 1H), 4.17 (qd, *J* = 7.1, 2.0 Hz, 2H), 3.59 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.4, 159.2, 142.7, 141.3, 140.7, 140.2, 138.7, 135.5, 133.5, 131.7, 131.5, 131.0, 130.7, 129.0, 128.9, 128.3, 127.5, 122.2, 119.4, 114.8, 113.5, 60.5, 55.1, 14.4. **Melting point:** 104-106 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{24}H_{21}Cl_2O_3$ 427.0868; Found: 427.0900.

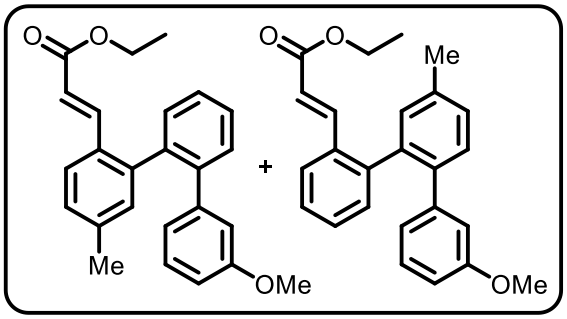


Ethyl (E)-3-(5,5'-di-tert-butyl-3''-methoxy-[1,1':2',1''-terphenyl]-2-yl)acrylate (6h): The



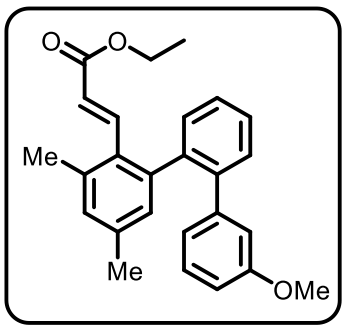
representative general procedure was followed using **1i** (216.1 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3b** (60.8 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 4% EtOAc in hexane) furnished **6h** (54.6 mg, 58% yield) as viscous oil. R_f = 0.45 (10% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.63 (d, *J* = 15.9 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.49 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 1.9 Hz, 1H), 7.28 – 7.26 (m, 1H), 7.08 (d, *J* = 2.0 Hz, 1H), 7.05 (t, *J* = 7.9 Hz, 1H), 6.71 – 6.65 (m, 2H), 6.49 – 6.47 (m, 1H), 6.18 (d, *J* = 15.9 Hz, 1H), 4.18 (qd, *J* = 7.1, 3.2 Hz, 2H), 3.51 (s, 3H), 1.39 (s, 9H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.14 (s, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 167.1, 159.0, 152.7, 150.1, 143.5, 142.5, 142.4, 138.8, 138.1, 130.5, 129.9, 129.5, 129.1, 128.8, 126.1, 125.0, 124.3, 122.3, 118.0, 114.8, 113.0, 60.3, 55.1, 34.7, 34.7, 31.5, 31.0, 14.4. **HRMS** (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{32}H_{38}NaO_3$ 493.2719; Found: 493.2718.

[Ethyl (E)-3-(3''-methoxy-5-methyl-[1,1':2',1''-terphenyl]-2-yl)acrylate] + [ethyl (E)-3-(3''-methoxy-5'-methyl-[1,1':2',1''-terphenyl]-2-yl)acrylate] (6i + 6i′): The representative general



procedure was followed using **1j** (176.8 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3b** (60.8 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 4% EtOAc in hexane) furnished **6i + 6i′** (59.6 mg, 80% yield) as viscous oil. R_f = 0.40 (10% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.52 – 7.36 (m, 4H), 7.33 – 7.23 (m, 3H), 7.13 – 6.99 (m, 2H), 6.69 – 6.62 (m, 2H), 6.59 – 6.53 (m, 1H), 6.06 – 5.99 (m, 1H), 4.20 – 4.13 (m, 2H), 3.57 – 3.54 (m, 3H), 2.44 – 2.31 (m, 3H), 1.30 – 1.25 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 167.0, 166.9, 158.9, 143.3, 143.2, 142.8, 142.6, 142.4, 142.3, 141.6, 139.8, 138.8, 138.5, 138.2, 137.1, 133.1, 132.1, 131.9, 131.5, 131.2, 130.4, 130.1, 130.0, 129.5, 129.1, 128.7, 128.4, 128.2, 127.4, 127.4, 126.0, 122.3, 118.5, 117.5, 114.8, 114.8, 113.1, 112.8, 60.3, 60.2, 55.0, 21.4, 21.2, 14.4. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{25}H_{25}O_3$ 373.1804; Found: 373.1814.

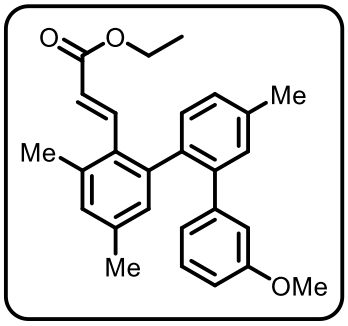
Ethyl (E)-3-(3''-methoxy-3,5-dimethyl-[1,1':2',1''-terphenyl]-2-yl)acrylate (6j): The



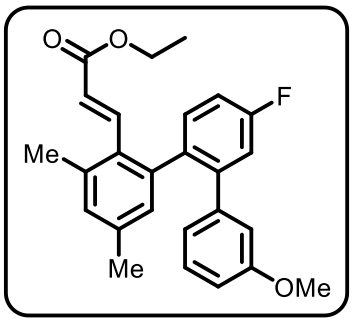
representative general procedure was followed using **1k** (182.5 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3b** (60.8 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 4% EtOAc in hexane) furnished **6j** (61.1 mg, 79% yield) as viscous oil. R_f =

0.42 (10% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.42 – 7.36 (m, 3H), 7.31 – 7.29 (m, 1H), 7.24 (d, *J* = 16.3 Hz, 1H), 7.06 (t, *J* = 7.9 Hz, 1H), 6.95 (d, *J* = 5.3 Hz, 2H), 6.71 – 6.68 (m, 1H), 6.64 – 6.61 (m, 1H), 6.55 – 6.54 (m, 1H), 5.44 (d, *J* = 16.3 Hz, 1H), 4.13 (qd, *J* = 7.1, 0.8 Hz, 2H), 3.58 (s, 3H), 2.29 (s, 3H), 2.24 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.9, 158.9, 142.9, 142.6, 142.1, 140.9, 139.8, 138.1, 136.8, 131.0, 130.6, 130.5, 130.1, 129.9, 128.6, 127.9, 127.4, 122.6, 122.2, 114.6, 113.1, 60.2, 55.0, 21.3, 21.2, 14.4. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{26}H_{27}O_3$ 387.1960; Found: 387.1973.

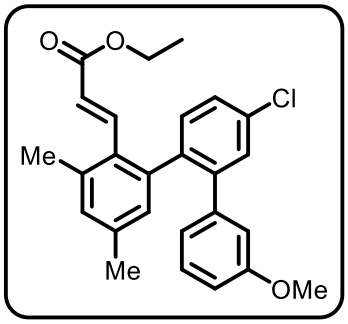
Ethyl (E)-3-(3''-methoxy-3,4',5-trimethyl-[1,1':2',1''-terphenyl]-2-yl)acrylate (6k): The representative general procedure was followed using **1l** (188.1 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3b** (60.8 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 4% EtOAc in hexane) furnished **6k** (44.1 mg, 55% yield) as viscous oil. R_f = 0.40 (10% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.25 (d, *J* = 16.3 Hz, 1H), 7.21 (s, 1H), 7.18 (d, *J* = 0.9 Hz, 2H), 7.04 (t, *J* = 7.9 Hz, 1H), 6.93 (s, 2H), 6.70 – 6.67 (m, 1H), 6.63 – 6.60 (m, 1H), 6.54 – 6.52 (m, 1H), 5.46 (d, *J* = 16.3 Hz, 1H), 4.17 – 4.12 (m, 2H), 3.57 (s, 3H), 2.43 (s, 3H), 2.27 (s, 3H), 2.24 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 167.0, 158.8, 143.1, 142.8, 142.2, 140.8, 138.1, 137.5, 136.9, 136.7, 130.9, 130.8, 130.6, 130.5, 130.1, 128.6, 128.1, 122.5, 122.2, 114.6, 113.0, 60.2, 55.0, 21.4, 21.3, 21.2, 14.4. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{27}H_{29}O_3$ 401.2117; Found: 401.2106.



Ethyl (E)-3-(4'-fluoro-3''-methoxy-3,5-dimethyl-[1,1':2',1''-terphenyl]-2-yl)acrylate (6l): The representative general procedure was followed using **1m** (189.7 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3b** (60.8 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 4% EtOAc in hexane) furnished **6l** (35.6 mg, 44% yield) as white solid. R_f = 0.38 (10% EtOAc in hexane). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.27 – 7.24 (m, 1H), 7.20 (d, *J* = 16.3 Hz, 1H), 7.13 – 7.10 (m, 1H), 7.09 – 7.04 (m, 2H), 6.94 (s, 1H), 6.91 (s, 1H), 6.72 – 6.70 (m, 1H), 6.59 (d, *J* = 7.6 Hz, 1H), 6.51 (s, 1H), 5.43 (d, *J* = 16.3 Hz, 1H), 4.14 (qd, *J* = 7.1, 1.7 Hz, 2H), 3.57 (s, 3H), 2.28 (s, 3H), 2.23 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 166.8, 162.3 (d, *J* = 246.3 Hz), 159.0, 142.9 (d, *J* = 7.7 Hz), 142.8, 141.5, 141.0, 138.2, 136.9, 135.8, 132.5 (d, *J* = 7.9 Hz), 130.8, 130.0, 128.8, 122.8, 122.0, 116.7 (d, *J* = 21.8 Hz), 114.5, 114.2 (d, *J* = 20.9 Hz), 113.6, 60.3, 55.1, 21.3, 21.2, 14.4. **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -115.1. **Melting point:** 70-72 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{26}H_{26}FO_3$ 405.1866; Found: 405.1864.

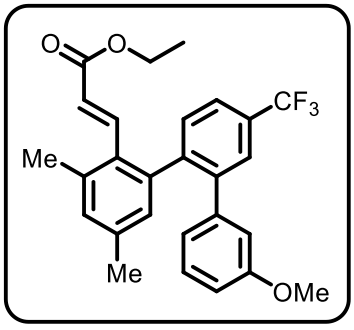


Ethyl (E)-3-(4'-chloro-3''-methoxy-3,5-dimethyl-[1,1':2',1''-terphenyl]-2-yl)acrylate (6m):



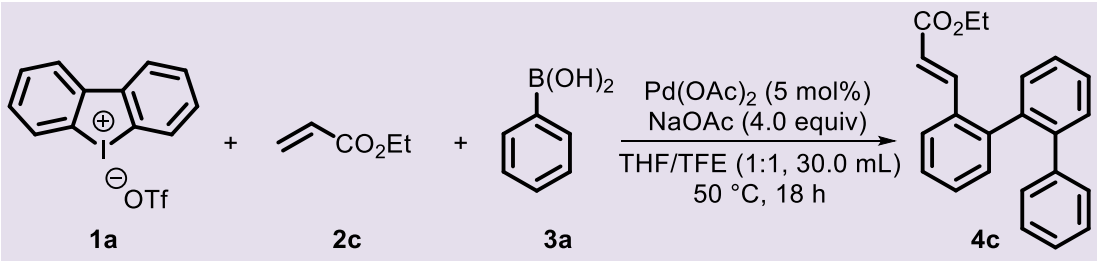
The representative general procedure was followed using **1n** (196.2 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3b** (60.8 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 4% EtOAc in hexane) furnished **6m** (52.2 mg, 62% yield) as viscous oil. R_f = 0.40 (10% EtOAc in hexane). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.43 (d, *J* = 2.1 Hz, 1H), 7.39 – 7.37 (m, 1H), 7.28 (d, *J* = 6.8 Hz, 1H), 7.23 (d, *J* = 16.3 Hz, 1H), 7.09 (t, *J* = 7.9 Hz, 1H), 6.98 (s, 1H), 6.93 (s, 1H), 6.76 – 6.73 (m, 1H), 6.63 – 6.61 (m, 1H), 6.54 – 6.53 (m, 1H), 5.48 (d, *J* = 16.3 Hz, 1H), 4.18 (qd, *J* = 7.1, 1.4 Hz, 2H), 3.61 (s, 3H), 2.31 (s, 3H), 2.26 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (125 MHz, $CDCl_3$)**: δ 166.7, 159.0, 142.7, 142.6, 141.3, 140.8, 138.4, 138.3, 136.9, 133.6, 132.3, 130.9, 130.6, 129.9, 129.8, 128.8, 127.4, 123.0, 122.0, 114.5, 113.7, 60.3, 55.1, 21.2, 21.1, 14.4. **HRMS** (ESI/Q-TOF) m/z: $[M + Na]^+$ Calcd. for $C_{26}H_{25}ClNaO_3$ 443.1390; Found: 443.1391.

Ethyl (E)-3-(3''-methoxy-3,5-dimethyl-4'-(trifluoromethyl)-[1,1':2',1''-terphenyl]-2-yl)acrylate (6n):



The representative general procedure was followed using **1o** (209.7 mg, 0.4 mmol), **2c** (20.0 mg, 0.2 mmol), **3b** (60.8 mg, 0.4 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and NaOAc (65.6 mg, 0.8 mmol) in THF/TFE (1:1, 4.0 mL) at 50 °C for 18 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 4% EtOAc in hexane) furnished **6n** (61.8 mg, 68% yield) as viscous oil. R_f = 0.40 (10% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.64 – 7.62 (m, 2H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 16.3, Hz, 1H), 7.08 (t, *J* = 7.9 Hz, 1H), 6.97 (s, 1H), 6.93 (s, 1H), 6.75 – 6.72 (m, 1H), 6.60 (d, *J* = 7.6 Hz, 1H), 6.52 – 6.51 (m, 1H), 5.42 (d, *J* = 16.3 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.59 (s, 3H), 2.30 (s, 3H), 2.23 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.6, 159.1, 143.6, 142.4, 141.7, 141.2, 140.6, 138.4, 137.0, 131.6, 131.2, 130.6, 130.1 (q, *J* = 32.6 Hz), 129.6, 129.0, 126.9 (q, *J* = 3.6 Hz), 124.3 (q, *J* = 272.2 Hz), 124.1 (q, *J* = 3.7 Hz), 123.3, 122.1, 114.6, 113.7, 60.3, 55.1, 21.2, 21.1, 14.3. **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -62.4. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{27}H_{26}F_3O_3$ 455.1834; Found: 455.1830.

6. Scale up reaction on 5.0 mmol scale

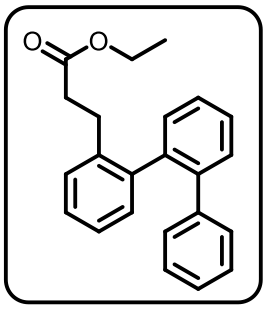


A round bottom flask equipped with a magnetic stir bar was charged with cyclic diaryliodonium

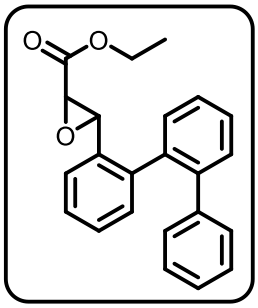
salt **1a** (10.0 mmol, 2.0 equiv), ethyl acrylate **2c** (5.0 mmol, 1.0 equiv), phenylboronic acid **3a** (10 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.25 mmol, 0.05 equiv) and NaOAc (20.0 mmol, 4.0 equiv) in THF/TFE (1:1, 30.0 mL). The flask was sealed with a stopper and stirred at 50 ^oC in a preheated oil bath for 18 h. After cooling to room temperature, the reaction mixture was diluted with DCM, filtered through a pad of celite, and the celite was washed with DCM. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel 100-200 mesh (2% EtOAc in hexane) to yield **4c** (1.38 g, 84%).

7. Synthetic modifications

Ethyl 3-([1,1':2',1''-terphenyl]-2-yl)propanoate (7): Ethyl (E)-3-([1,1':2',1''-terphenyl]-2-yl)acrylate **(4c)** (65.6 mg, 0.2 mmol) and 10% Pd/C (21.3 mg, 0.02 mmol) in MeOH (2.0 mL) was stirred under H_2 balloon at room temperature for 4 h. Purification by column chromatography on silica gel 100-200 mesh (eluted with 3% EtOAc in hexane) furnished **7** (47.0 mg, 71% yield) as oil. R_f = 0.34 (5% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.46 – 7.43 (m, 2H), 7.42 – 7.38 (m, 1H), 7.31 – 7.29 (m, 1H), 7.22 – 7.18 (m, 3H), 7.17 – 7.14 (m, 3H), 7.13 – 7.10 (m, 2H), 7.09 – 7.06 (m, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 2.64 – 2.56 (m, 1H), 2.52 – 2.45 (m, 1H), 2.32 – 2.24 (m, 1H), 2.05 – 1.97 (m, 1H), 1.19 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 173.0, 141.3, 141.2, 140.9, 139.8, 138.1, 131.2, 131.0, 130.1, 129.6, 128.4, 127.8, 127.4, 127.2, 126.6, 125.9, 60.3, 34.7, 28.0, 14.3. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{23}O_2$ 331.1698; Found: 331.1695.



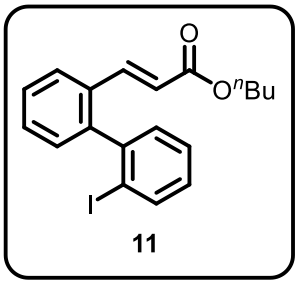
Ethyl 3-([1,1':2',1''-terphenyl]-2-yl)oxirane-2-carboxylate (8)[5]: Ethyl (E)-3-([1,1':2',1''-terphenyl]-2-yl)acrylate **(4c)** (65.6 mg, 0.2 mmol) was dissolved in DCM (1.5 mL) and saturated aqueous solution of sodium bicarbonate (1.5 mL) was added with stirring. To this was added mCPBA (69.0 mg, 0.4 mmol) and refluxed for 24 hours. After completion of the reaction, the organic phase was separated and the water phase was extracted with DCM. The combined organic layer was washed with saturated sodium bicarbonate and then 10% sodium bisulfite solution, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel 100-200 mesh (eluted with 4% EtOAc in hexane) furnishing **8** (35.1 mg, 51% yield) as oil. R_f = 0.25 (5% EtOAc in hexane). Calculated dr = 1:1.2. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48 – 7.39 (m, 3H), 7.38 – 7.28 (m, 2H), 7.28 – 7.24 (m, 1H), 7.23 – 7.08 (m, 5H), 7.01 – 6.93 (m, 2H), 4.31 – 4.12 (m, 2H), 3.79 (d, *J* = 1.6 Hz, 0.41H), 3.76 (d, *J* = 1.5 Hz, 0.48H), 3.30 (d, *J* = 1.7 Hz, 0.41H), 2.82 (d, *J* = 1.7 Hz, 0.48H). 1.33 – 1.25 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 168.1, 168.0, 142.1, 141.5, 141.1, 141.0, 140.8, 140.6, 138.0, 137.8, 133.3, 132.6, 130.9, 130.9, 130.6, 129.9, 129.6, 129.4, 128.5, 128.3, 128.0, 127.9, 127.6, 127.6, 127.5, 127.1, 126.8, 126.7, 124.3, 123.7, 61.6, 61.5, 56.9, 56.7, 56.7, 55.5, 14.3, 14.2. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{21}O_3$ 345.1491; Found: 345.1487.



(E)-3-([1,1':2',1''-terphenyl]-2-yl)acrylic acid (9): To a stirred solution of Ethyl (E)-3-([1,1':2',1"-terphenyl]-2-yl)acrylate **(4c)** (98.5 mg, 0.3 mmol) in THF:H_2O (2:1, 3.0 mL) was added LiOH (28.7 mg, 1.2 mmol). The reaction mixture was stirred at 50 °C for 12 h. After completion of the reaction, the reaction mixture was diluted with HCl (1M, 10 mL) and the aqueous phase was extracted with EtOAc (3X). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel 100-200 mesh (eluted with 25% EtOAc in hexane) furnishing **9** (88.3 mg, 98% yield) as a white crystal. R_f = 0.38 (40% EtOAc in hexane). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.54 – 7.47 (m, 4H), 7.46 – 7.41 (m, 1H), 7.35 – 7.28 (m, 3H), 7.27 – 7.23 (m, 1H), 7.15 – 7.11 (m, 3H), 7.06 – 7.03 (m, 2H), 6.03 (d, *J* = 15.9 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 172.4, 145.7, 142.9, 141.8, 140.9, 138.2, 132.7, 131.7, 131.3, 130.4, 130.0, 129.8, 128.5, 127.8, 127.6, 127.4, 126.7, 126.4, 117.7. **Melting point:** 166-168 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{21}H_{17}O_2$ 301.1229; Found: 301.1224.

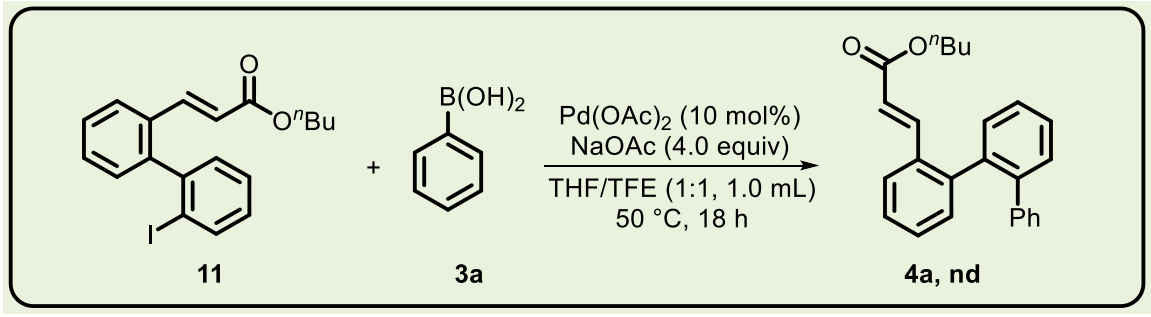
(E)-3-([1,1':2',1''-terphenyl]-2-yl)-N-(pyridin-3-yl)acrylamide (10): To a stirred solution of (E)-3-([1,1':2',1"-terphenyl]-2-yl)acrylic acid (**9**) (90.0 mg, 0.3 mmol) in dry DCM (2.0 mL) was added catalytic amount of DMF (1 drop) under N_2-atm. The reaction mixture was cooled to 0 °C on an ice bath and then oxalyl chloride (57.0 mg, 0.45 mmol) was added dropwise. The reaction mixture was warm to room temperature and was stirred for 3 h. After completion of the reaction, the solvent was removed under reduced pressure. The residue was redissolved in dry DCM and was added dropwise to the stirred solution of 3-amino pyridine (33.8 mg, 0.36 mmol) and NEt_3 (91.0 mg, 0.9 mmol) in dry DCM at 0 °C under N_2-atm. The reaction mixture was warmed to room temperature and stirred overnight. After completion of the reaction, a saturated solution of $NaHCO_3$ was added and the aqueous phase was extracted with DCM (3X). The combined organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel 100-200 mesh (eluted with 40% EtOAc in hexane) furnishing **10** (91.5 mg, 81% yield) as a white solid. R_f = 0.22 (60% EtOAc in hexane). **^{1}H NMR (400 MHz, DMSO-d6):** δ 10.27 (s, 1H), 8.77 (d, *J* = 2.3 Hz, 1H), 8.27 (dd, *J* = 4.6, 1.4 Hz, 1H), 8.09 – 8.06 (m, 1H), 7.61 – 7.53 (m, 2H), 7.52 – 7.46 (m, 2H), 7.38 – 7.28 (m, 5H), 7.21 – 7.18 (m, 1H), 7.14 – 7.11 (m, 3H), 7.04 – 7.00 (m, 2H), 6.53 (d, *J* = 15.5 Hz, 1H). **^{13}C NMR (100 MHz, DMSO-d6)**: δ 164.2, 144.7, 142.4, 141.5, 141.2, 141.0, 139.3, 138.5, 136.3, 133.1, 131.7, 131.5, 130.5, 129.7, 129.7, 128.8, 128.2, 128.1, 127.8, 127.0, 126.5, 125.9, 124.1, 122.3. **Melting point:** 122-124 °C. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{26}H_{21}N_2O$ 377.1654; Found: 377.1678.

Butyl (E)-3-(2'-iodo-[1,1'-biphenyl]-2-yl)acrylate (11): To a reaction tube, was added cyclic diaryliodonium salt **1a** (86.27 mg, 0.2 mmol), alkene **2a** (34.58 mg, 0.4 mmol), $Pd(PPh_3)_4$ (23.21mg, 0.02 mmol), NEt_3 (60.98 mg, 0.6 mmol), and DCE (3.00 mL). Then, the tube was degassed and recharged with argon and stirred at 100 °C for 1 h. After completion, the reaction mixture was diluted with dichloromethane and washed with H_2O, and brine. The organic phase was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on a silica gel 100-200 mesh (eluted with 2% EtOAc in hexane) furnishing **11** (18.7 mg, 23% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.97 – 7.94 (m, 1H), 7.76 – 7.70 (m, 1H), 7.46 – 7.34 (m, 4H), 7.24 – 7.18 (m, 2H), 7.08 (td, *J* = 7.6, 1.6 Hz, 1H), 6.35 (d, *J* = 15.9 Hz, 1H), 4.11 (t, *J* = 6.5 Hz, 2H), 1.63 – 1.58 (m, 2H), 1.39 – 1.32 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.9, 145.2, 144.8, 142.5, 139.3, 132.8, 130.6, 130.5, 129.7, 129.4, 128.5, 128.2, 126.2, 119.5, 100.0, 64.4, 30.4, 19.3, 13.8. **HRMS** (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd. for $C_{19}H_{20}IO_2$ 407.0508; Found: 407.0502.



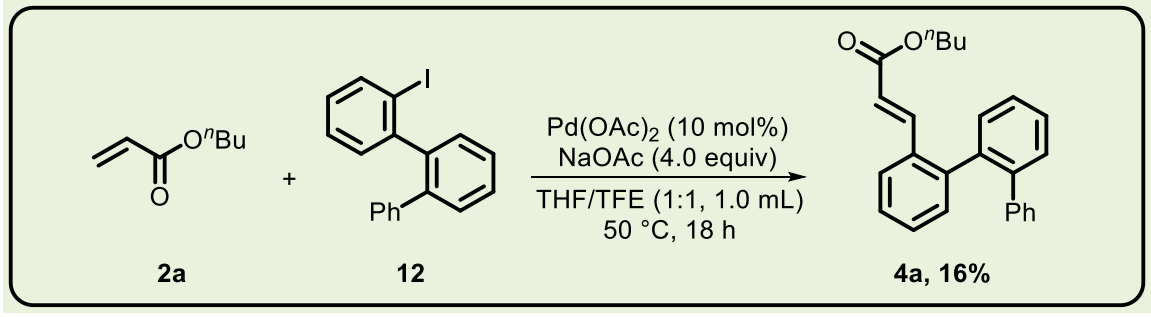
8. Control experiments

(a) Reaction with intermediate 11



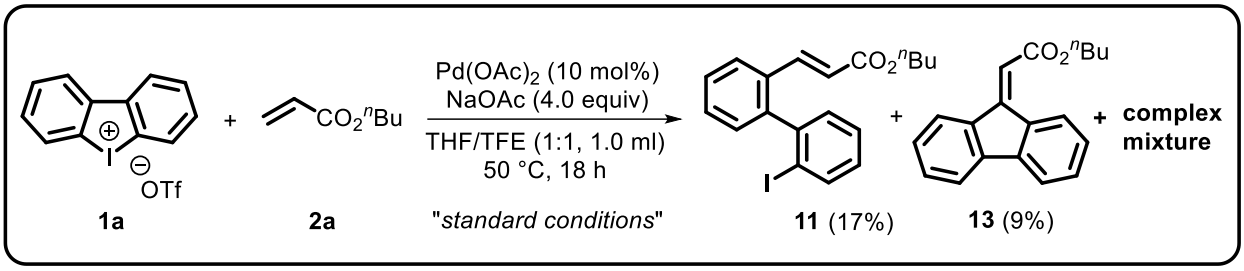
An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with **11** (0.1 mmol, 1.0 equiv), phenylboronic acid **3a** (0.2 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.01 mmol, 0.1 equiv) and NaOAc (0.4 mmol, 4.0 equiv) in THF/TFE (1:1, 1.0 mL). The Schlenk tube was sealed with a stopper and stirred at 50 ^{o}C in a preheated oil bath for 18 h. After cooling to room temperature, the reaction mixture was diluted with DCM, filtered through a pad of celite and the celite was washed with DCM. The solvent was evaporated under reduced pressure. The product was not observed in TLC, ES-MS and crude NMR analysis.

(b) Reaction with intermediate 12



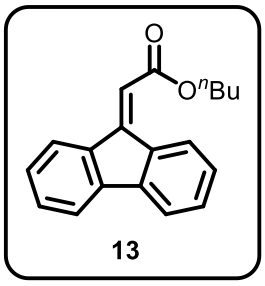
An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with **2a** (0.1 mmol, 1.0 equiv), **12** (0.2 mmol, 1.5 equiv), $Pd(OAc)_2$ (0.01 mmol, 0.1 equiv) and NaOAc (0.4 mmol, 4.0 equiv) in THF/TFE (1:1, 1.0 mL). The Schlenk tube was sealed with a stopper and stirred at 50 °C in a preheated oil bath for 18 h. After cooling to room temperature, the reaction mixture was diluted with DCM, filtered through a pad of celite and the celite was washed with DCM and then 1,3,5-trimethoxybenzene was added as an internal standard. The solvent was removed under reduced pressure and the yield of **4a** was analyzed by ^{1}H NMR spectroscopy (16% NMR yield).

(c) Competition experiment 1



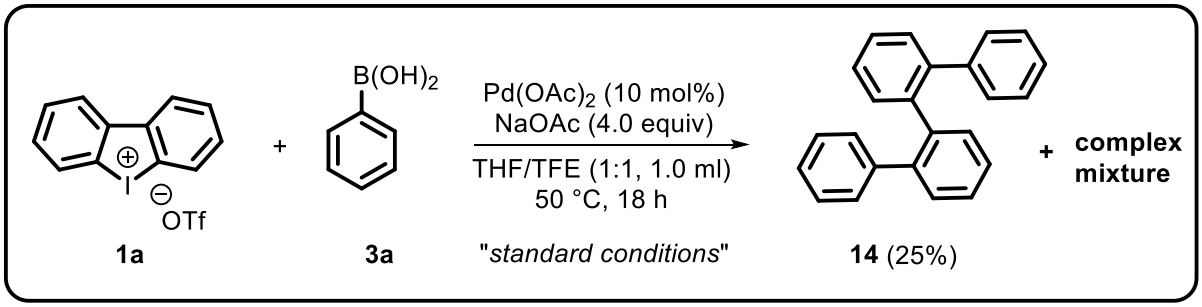
An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with **1a** (0.2 mmol, 2.0 equiv), **2a** (0.1 mmol, 1.0 equiv), $Pd(OAc)_2$ (0.01 mmol, 0.1 equiv) and NaOAc (0.4 mmol, 4.0 equiv) in THF/TFE (1:1, 1.0 mL). The Schlenk tube was sealed with a stopper and stirred at 50 °C in a preheated oil bath for 18 h. After cooling to room temperature, the reaction mixture was diluted with DCM, filtered through a pad of celite and the celite was washed with DCM and then 1,3,5-trimethoxybenzene was added as an internal standard. The solvent was removed under reduced pressure and the yield of **11** and **13** was analyzed by ^{1}H NMR spectroscopy.

Butyl 2-(9H-fluoren-9-ylidene)acetate (13):



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89 (d, J = 7.8 Hz, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.64 – 7.60 (m, 2H), 7.42 – 7.36 (m, 2H), 7.33 – 7.29 (m, 1H), 7.28 – 7.24 (m, 1H), 6.75 (s, 1H), 4.28 (t, J = 6.7 Hz, 2H), 1.78 – 1.71 (m, 2H), 1.50 – 1.43 (m, 2H), 0.98 (t, J = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.5, 148.3, 142.6, 140.8, 138.9, 135.3, 130.9, 130.6, 129.3, 128.1, 127.5, 121.3, 119.8, 119.6, 114.0, 64.7, 30.9, 19.3, 13.8.

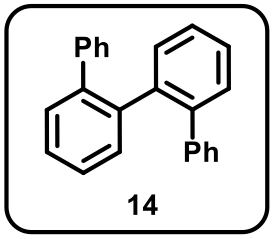
(d) Competition experiment 2



An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with **1a** (0.2 mmol, 1.0 equiv), **3a** (0.2 mmol, 1.0 equiv), $Pd(OAc)_2$ (0.02 mmol, 0.1 equiv) and NaOAc (0.4 mmol, 4.0 equiv) in THF/TFE (1:1, 1.0 mL). The Schlenk tube was sealed with a stopper and stirred at

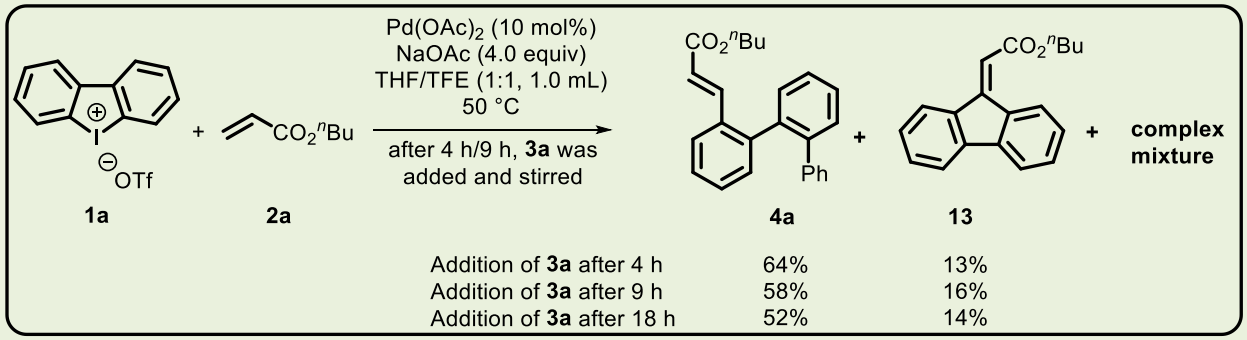
50 °C in a preheated oil bath for 18 h. After cooling to room temperature, the reaction mixture was diluted with DCM, filtered through a pad of celite and the celite was washed with DCM and then 1,3,5-trimethoxybenzene was added as an internal standard. The solvent was removed under reduced pressure and the yield of **14** was analyzed by ^{1}H NMR spectroscopy.

1,1':2',1'':2'',1'''-quaterphenyl (14):



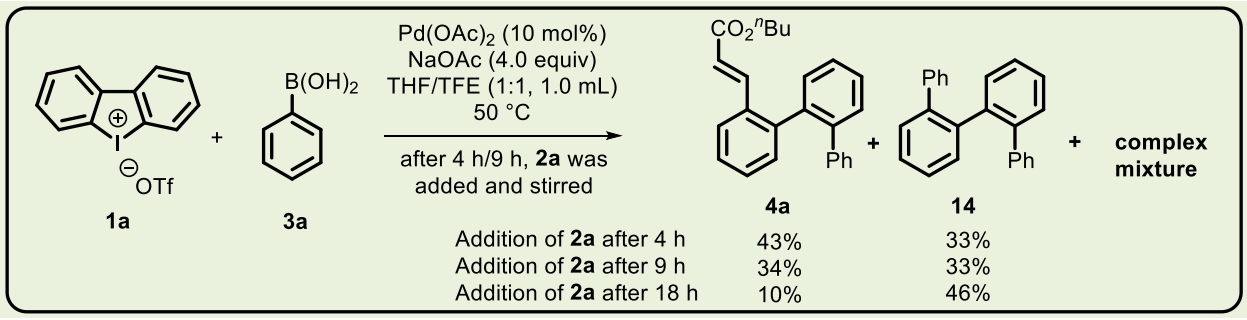
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.39 (m, 2H), 7.37 – 7.30 (m, 4H), 7.19 – 7.15 (m, 2H), 7.10 – 7.05 (m, 2H), 7.02 – 6.97 (m, 4H), 6.63 – 6.60 (m, 4H). **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 141.1, 141.0, 140.1, 131.8, 130.0, 129.4, 127.6, 127.5, 127.2, 126.0.

(e) Competition experiment 3



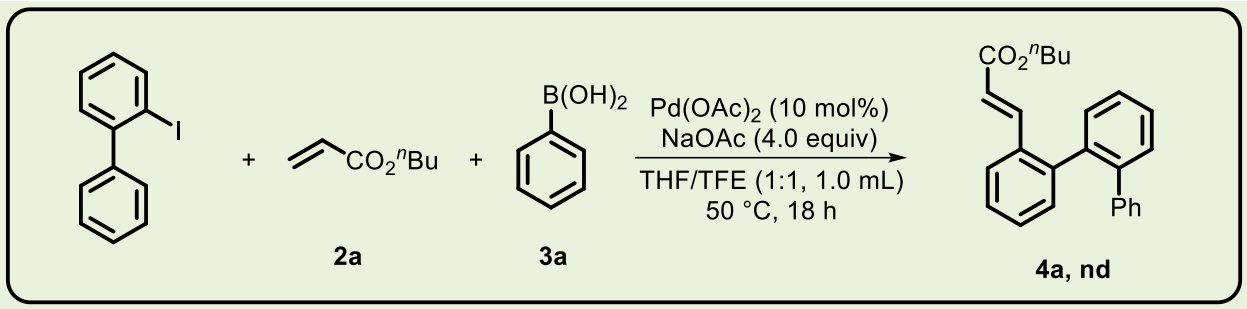
Two sets of oven-dried Schlenk tubes equipped with a magnetic stir bar were charged with **2a** (0.3 mmol, 1.0 equiv), **1a** (0.6 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.03 mmol, 0.1 equiv) and NaOAc (1.2 mmol, 4.0 equiv) in THF/TFE (1:1, 6.0 mL). Both the Schlenk tubes were sealed with a stopper and stirred at 50 °C in a preheated oil bath. After 4 h and 9 h, **3a** (0.6 mmol, 2.0 equiv) was added and stirred for another 14 h and 9 h. After cooling to room temperature, the reaction mixture was diluted with DCM, filtered through a pad of celite and the celite was washed with DCM and then 1,3,5-trimethoxybenzene was added as an internal standard. The solvent was removed under reduced pressure and the yield of product was analyzed by ^{1}H NMR spectroscopy.

(f) Competition experiment 4



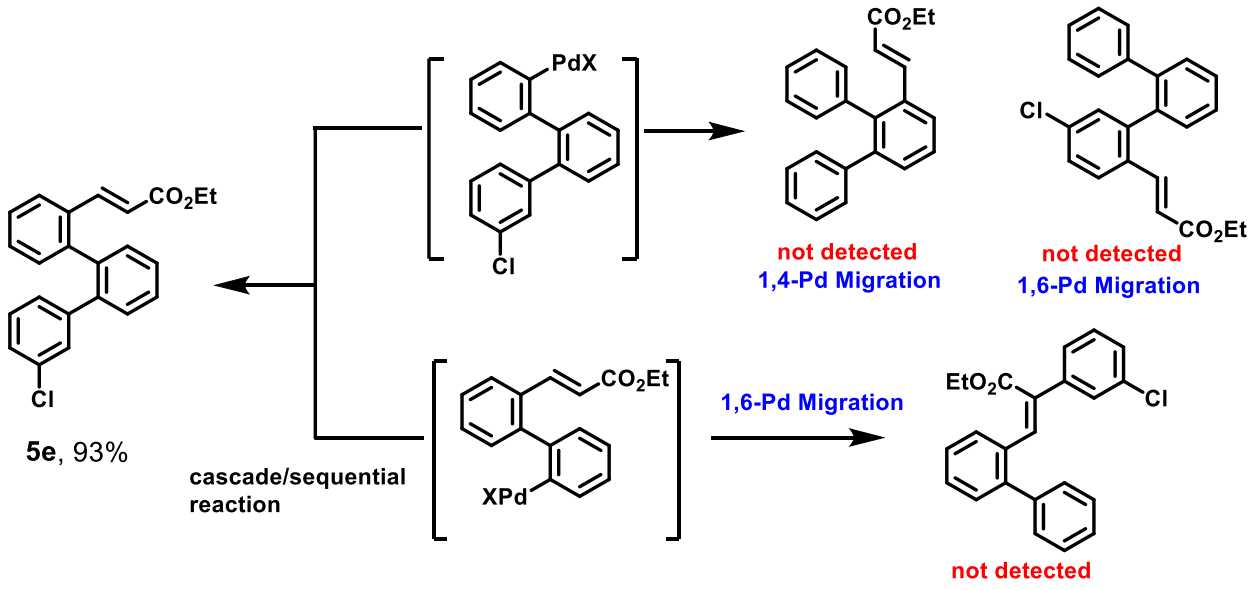
Two sets of oven-dried Schlenk tubes equipped with a magnetic stir bar were charged with **1a** (0.1 mmol, 1.0 equiv), **3a** (0.15 mmol, 1.5 equiv), $Pd(OAc)_2$ (0.01 mmol, 0.1 equiv) and NaOAc (0.4 mmol, 4.0 equiv) in THF/TFE (1:1, 1.0 mL). Both the Schlenk tubes were sealed with a stopper and stirred at 50 °C in a preheated oil bath. After 4 h and 9 h, **2a** was added and stirred for another 14 h and 9 h. After cooling to room temperature, the reaction mixture was diluted with DCM, filtered through a pad of celite and the celite was washed with DCM and then 1,3,5-trimethoxybenzene was added as an internal standard. The solvent was removed under reduced pressure and the yield of product was analyzed by ^{1}H NMR spectroscopy.

(g) Competition experiment 5

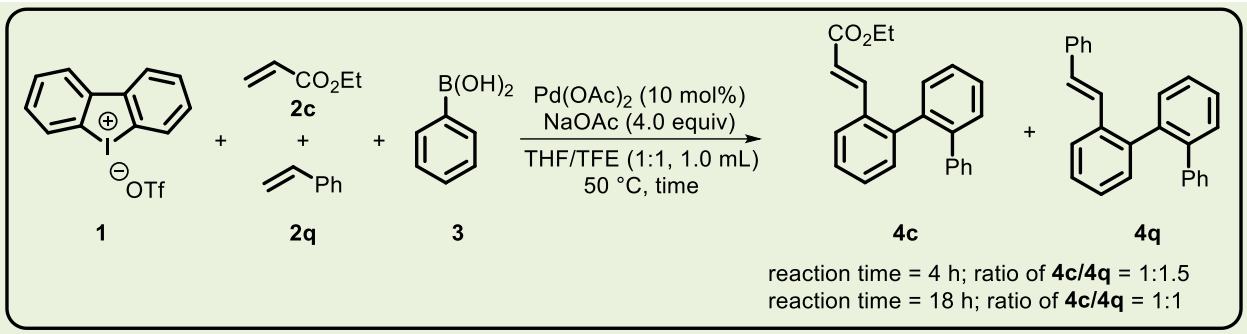


An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with 2-iodobiphenyl (0.2 mmol, 2.0 equiv), **2a** (0.1 mmol, 1.0 equiv), **3a** (0.2 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.01 mmol, 0.1 equiv) and NaOAc (0.4 mmol, 4.0 equiv) in THF/TFE (1:1, 1.0 mL). The Schlenk tube was sealed with a stopper and stirred at 50 °C in a preheated oil bath for 18 h. After cooling to room temperature, the reaction mixture was diluted with DCM, filtered through a pad of celite and the celite was washed with DCM and the solvent was removed under reduced pressure. The product was not observed in TLC, ES-MS and crude NMR analysis.

In addition, the expected products as shown below from 1,4- or 1,6-[Pd] migration resulting from intermediates were not detected in our conditions, ruling out the possibility in the reaction mechanism.



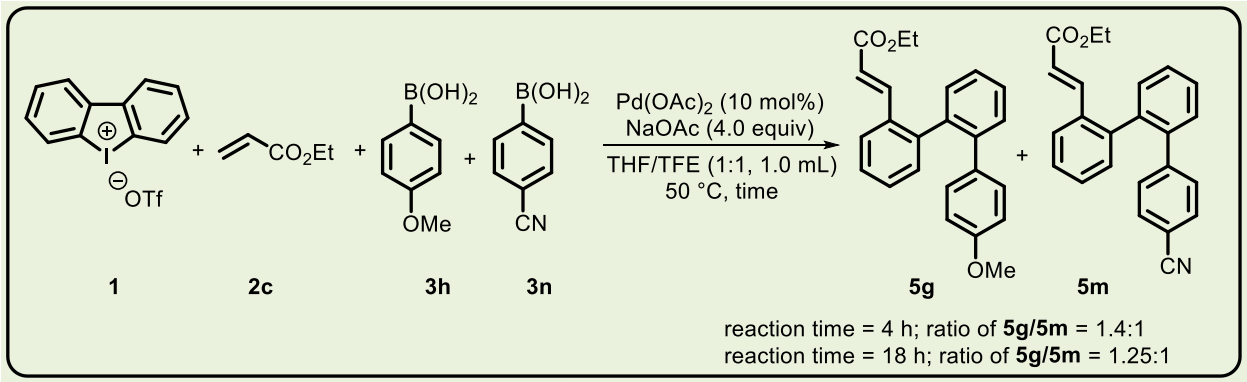
(h) Competition experiment between alkenes



Two sets of oven-dried Schlenk tubes equipped with a magnetic stir bar were charged with **1a** (0.2 mmol, 2.0 equiv), **2c** (0.05 mmol, 0.5 equiv), **2q** (0.05 mmol, 0.5 equiv), **3a** (0.2 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.01 mmol, 0.1 equiv) and NaOAc (0.4 mmol, 4.0 equiv) in THF/TFE (1:1, 1.0 mL). Both the Schlenk tube were sealed with a stopper and stirred at 50 ^oC in a preheated oil bath for 4 h and 18 h. After cooling to room temperature, the reaction mixture was diluted with DCM, filtered through a pad of celite and the celite was washed with DCM and the solvent was removed under reduced pressure. The residue was taken for ^1H-NMR analysis and the formation of corresponding products **4c** and **4q** was summarised in the below table:

Time	4c/4q ratio
4 h	1:1.5
18 h	1:1

(i) Competition experiment between boronic acids



Two sets of oven-dried Schlenk tube equipped with a magnetic stir bar was charged with **1a** (0.2 mmol, 2.0 equiv), **2c** (0.1 mmol, 1.0 equiv), **3h** (0.1 mmol, 1.0 equiv), **3n** (0.1 mmol, 1.0 equiv), $Pd(OAc)_2$ (0.01 mmol, 0.1 equiv) and NaOAc (0.4 mmol, 4.0 equiv) in THF/TFE (1:1, 1.0 mL). Both the Schlenk tube was sealed with a stopper and stirred at 50 ^oC in a preheated oil bath for 4 h and 18 h. After cooling to room temperature, the reaction mixture was diluted with DCM, filtered through a pad of celite and the celite was washed with DCM and the solvent was removed under reduced pressure. The residue was taken for ^1H-NMR analysis and the formation of corresponding products **5g** and **5m** was summarised in the below table:

Time	**5g**/**5m** ratio
4 h	1.4:1

18 h	1.25:1

9. Photophysical properties:

Given the extended π-conjugation offered in the products, we have measured the absorbance and photoluminescence of selected compounds to evaluate their photophysical properties (Figure S-01). The absorption, emission maxima, and quantum yield data are summarized in Supporting Information (Table S12). While exhibiting a similar pattern, all the compounds displayed maximum absorption bands in the 280-318 nm range. All the compounds displayed a broad emission band ranging from 320-570 nm in the fluorescence spectra.

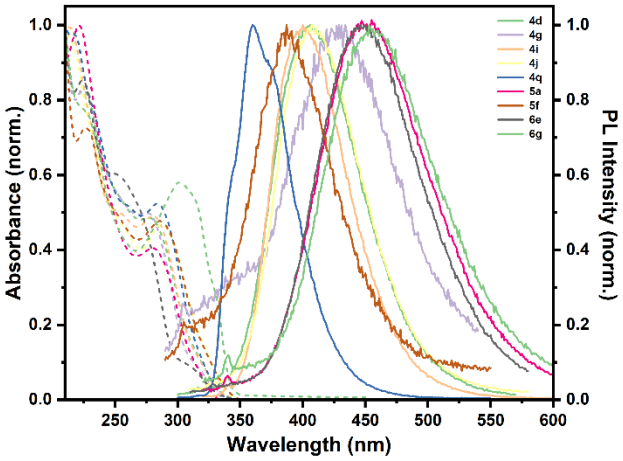


Figure S-01. Normalized absorbance (dashed line) and PL spectra (solid line) of **4d, 4g, 4i, 4j, 4q, 5a, 5f, 6e,** and **6g** in ethanol (19.6 mM solution).

Table S12: Photophysical data

S.No	Compound	λ_{abs}(nm)	ε (M^{-1} cm^{-1})	$\lambda_{PL}{}^{a}$ (nm)	ϕ (%)
1	**4d**	280	23.04	406	3.57
2	**4g**	286	17.31	429	0.76
3	**4i**	318	3.42	400	10.83
4	**4j**	312	3.07	407	11.22
5	**4q**	300	25.25	360	8.09
6	**5a**	280	17.28	451	1.89
7	**5f**	280	17.52	387	1.12
8	**6e**	287	17.57	447	3.69
9	**6g**	284	19.01	455	0.89
10	**4k**	290	-	412	-
11	**4l**	300	-	385	-
12	**4n**	270	-	387	-
13	**4o**	270	-	br 327,392	-
14	**4r**	280	-	362	-
15	**4s**	290	-	363	-
16	**5g**	270	-	484	-
17	**5n**	280	-	395	-
18	**6a**	280	-	438	-

19	**6c**	121	-	453	-
20	**9**	260	-	417	-

[a] Excited wavelength corresponding to λ_{abs}.

Photoluminescence Quantum Yield (PLQY %) Calculation:

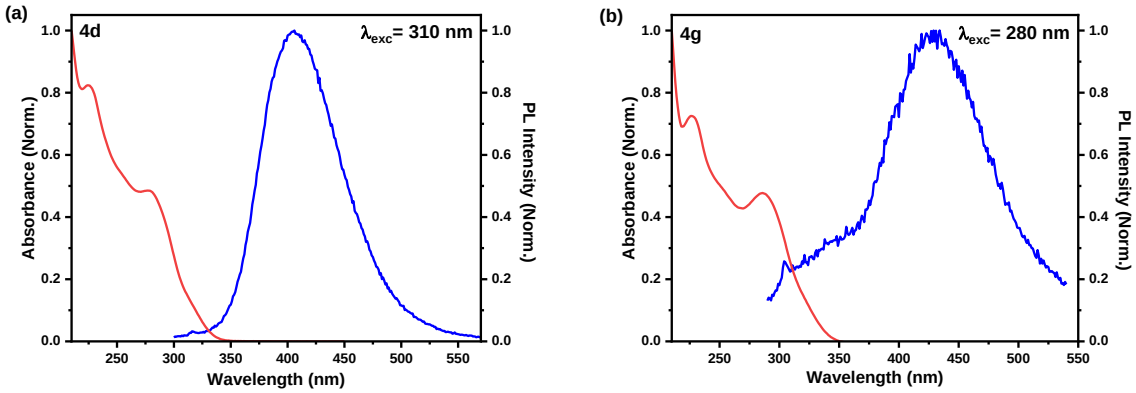
The relative quantum yield (QY) method was used to figure out PLQY,[6] (Equation (1)).

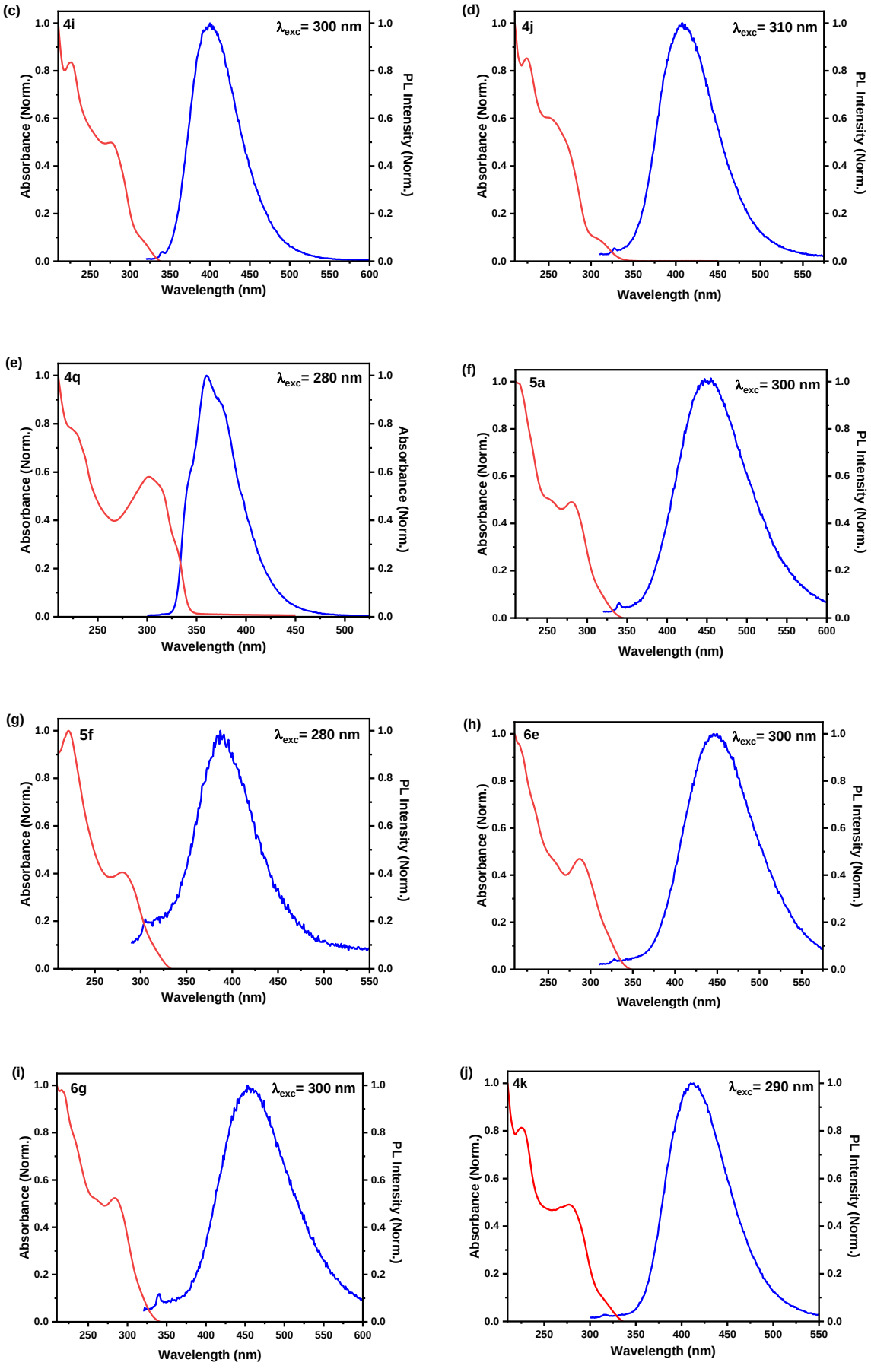
$$\phi_S = \phi_R \times \frac{I_S A_R \eta_S^2}{I_R A_S \eta_R^2} \quad (1)$$

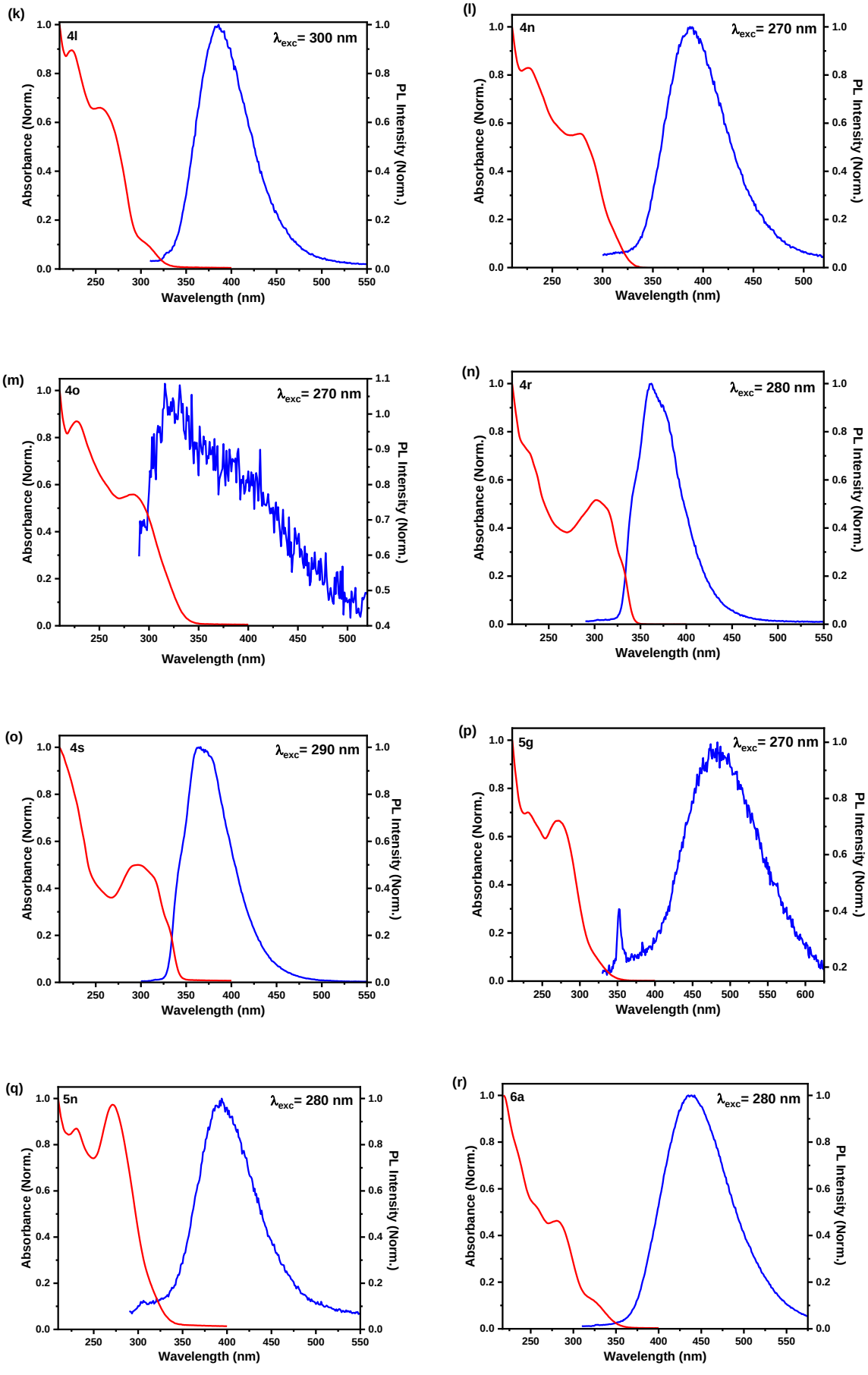
The unidentified sample exhibits a quantum yield (QY) denoted as ϕ_S, while the reference, 2,6-diaminopurine (DAP) in phosphate buffer (pH 7.4), has a QY represented as ϕ_R. The respective integrated photoluminescence (PL) intensities for the sample and reference are denoted as I_S and I_R. The absorbance of the sample and reference at the excitation wavelength (standardized at ~290 nm for this study) is expressed as A_S and A_R, respectively. The refractive indices of the solvents used for dissolving the sample and reference are indicated as η_S and η_R. Specifically, η_S for ethanol is 1.3614, while η_R for phosphate buffer is 1.335. The known quantum yield value (ϕ_R) for DAP dissolved in phosphate buffer is 3.7%.

Photophysical Spectra:

A 1 M stock solution of all compounds was prepared in ethanol. Absorbance and PL spectra were measured by adding 20 µl from 1 M stock solution to 1 ml ethanol.




(c)
4i
λexc= 300 nm
(d)
4j
λexc= 310 nm
(e)
4q
λexc= 280 nm
(f)
5a
λexc= 300 nm
(g)
5f
λexc= 280 nm
(h)
6e
λexc= 300 nm
(i)
6g
λexc= 300 nm
(j)
4k
λexc= 290 nm
Absorbance (Norm.)
PL Intensity (Norm.)
Absorbance (Norm.)
Wavelength (nm)


(k)
4l
λexc= 300 nm
(l)
4n
λexc= 270 nm
(m)
4o
λexc= 270 nm
(n)
4r
λexc= 280 nm
(o)
4s
λexc= 290 nm
(p)
5g
λexc= 270 nm
(q)
5n
λexc= 280 nm
(r)
6a
λexc= 280 nm
Absorbance (Norm.)
PL Intensity (Norm.)
Wavelength (nm)

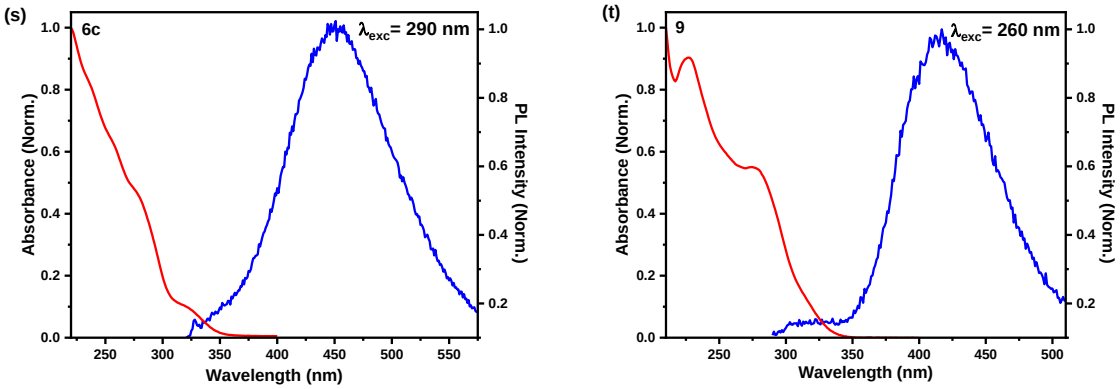
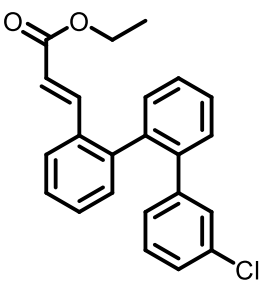


Figure S-02: Optical characteristics of compounds are shown in (a-t). Normalized absorbance (red) and PL (blue) spectra of compounds are recorded in ethanol (19.6mM).

10. Crystal structure



5e
CCDC No. 2327958

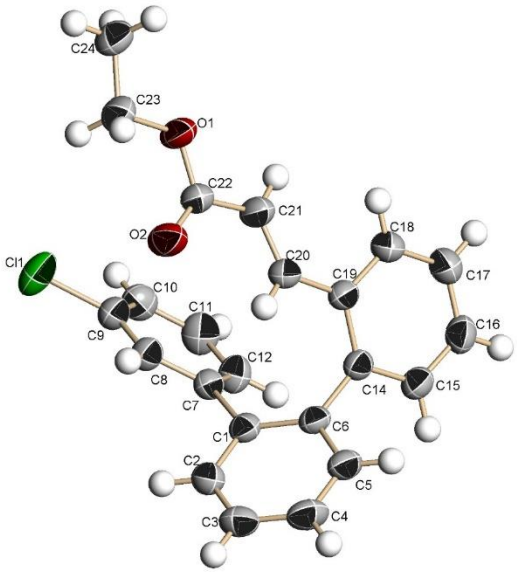


Figure S-03: ORTEP diagram drawn with 50% ellipsoid probability for non-H atoms of the crystal structure of compound **5e** determined at 293(2)K.

Crystallization: Crystals of compound **5e** were grown from the solvent DCM/hexane by slow evaporation method.

X-Ray Data Collection and Structure Refinement Details:

A good quality single crystal of size 0.22 x 0.18 x 0.15 mm, was selected under a polarizing microscope and was mounted on a glass fiber for data collection. Single crystal X-ray data for compound **5e** were collected on the Rigaku XtaLAB Synergy-S single crystal X-ray diffractometer equipped with a HyPix-6000HE Hybrid Photon Counting (HPC) detector and dual Mo and Cu microfocus sealed X-ray source with kappa goiniometer at 293(2) K. Data collection

cell determination, and data reduction was performed using the CrysAlisPro[7] software. Structure solution and refinement were performed by using SHELX-97[8]. Refinement of coordinates and anisotropic thermal parameters of non-hydrogen atoms were carried out by the full-matrix least-squares method. The hydrogen atoms attached to carbon atoms were generated with idealized geometries and isotropically refined using a riding model.

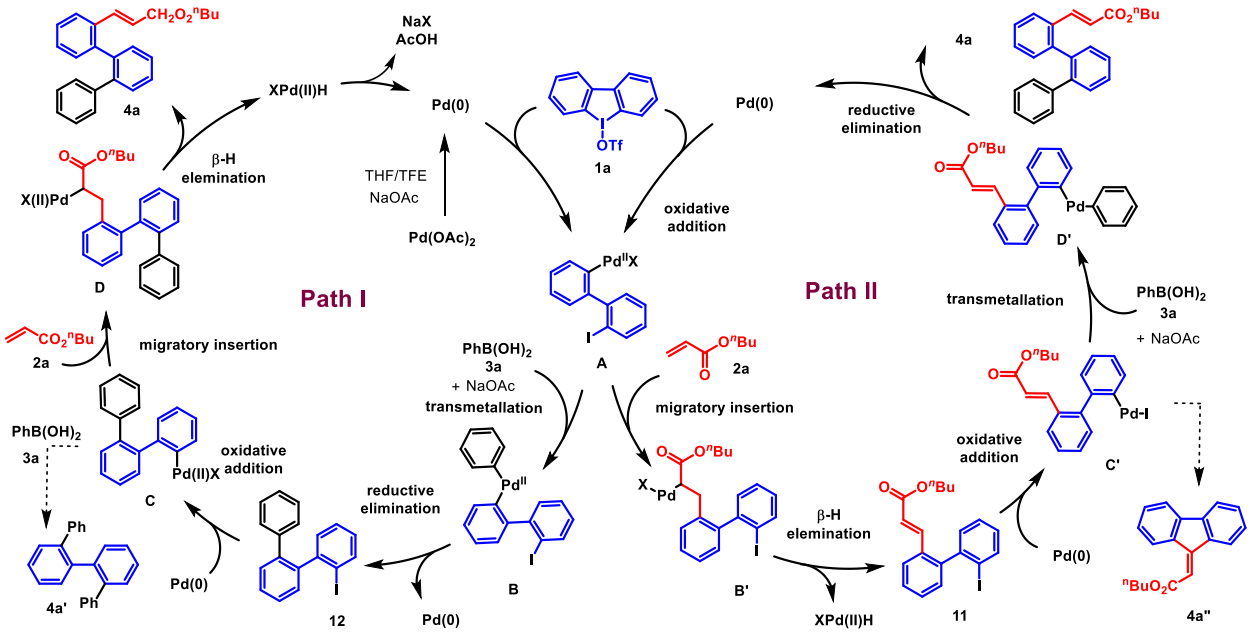
Table S13: Crystal data and structure refinement details for **5e**

Compound	**5e**
Empirical formula	$C_{23}\ H_{19}\ Cl\ O_2$
Formula weight	362.83
Crystal System	Triclinic
Space group	P-1
a (Å)	7.87220(10)
b (Å)	11.3433(2)
c (Å)	11.65270(10)
α (°)	102.5890(10)
β (°)	97.7710(10)
γ (°)	108.9250(10)
V (Å^3)	936.44(2)
Z	2
D_c (g/cm^3)	1.287
F_{000}	380
μ (mm^{-1})	1.907
θ_{max} (°)	77.75
Total reflections	11487
Unique reflections	3763
Reflections [$I > 2\sigma(I)$]	3369
Parameters	237
R_{int}	0.0282
Goodness-of-fit	1.070
R [$F^2 > 2\sigma(F^2)$]	0.0402
wR (F^2, all data)	0.1105
CCDC No.	2327958

11. Plausible mechanism

We have proposed a plausible mechanism based on the previous reports and our experimental details for the cascade difunctionalization (Scheme S1). Initially, the cyclic diaryliodonium salt **1a** undergoes oxidative addition, generating **A** with the in situ generated Pd(0). Intermediate **A** can react with alkene (**2**) or boronic acid (**3**). Path **I** starts by reacting **A** with phenylboronic acid to generate intermediate **B** via transmetallation. Further reductive elimination provides intermediate **12**. Subsequently, oxidative addition followed by migratory insertion with alkene **2a** gives intermediate **C**, which, upon β-H elimination, produces the desired product **4a.** The generated Pd(II)H gets reduced to Pd(0) for the next catalytic cycle. The competition reaction with another boronic acid produces a side product **4a'** from **C**. On the other hand, Path **II** starts

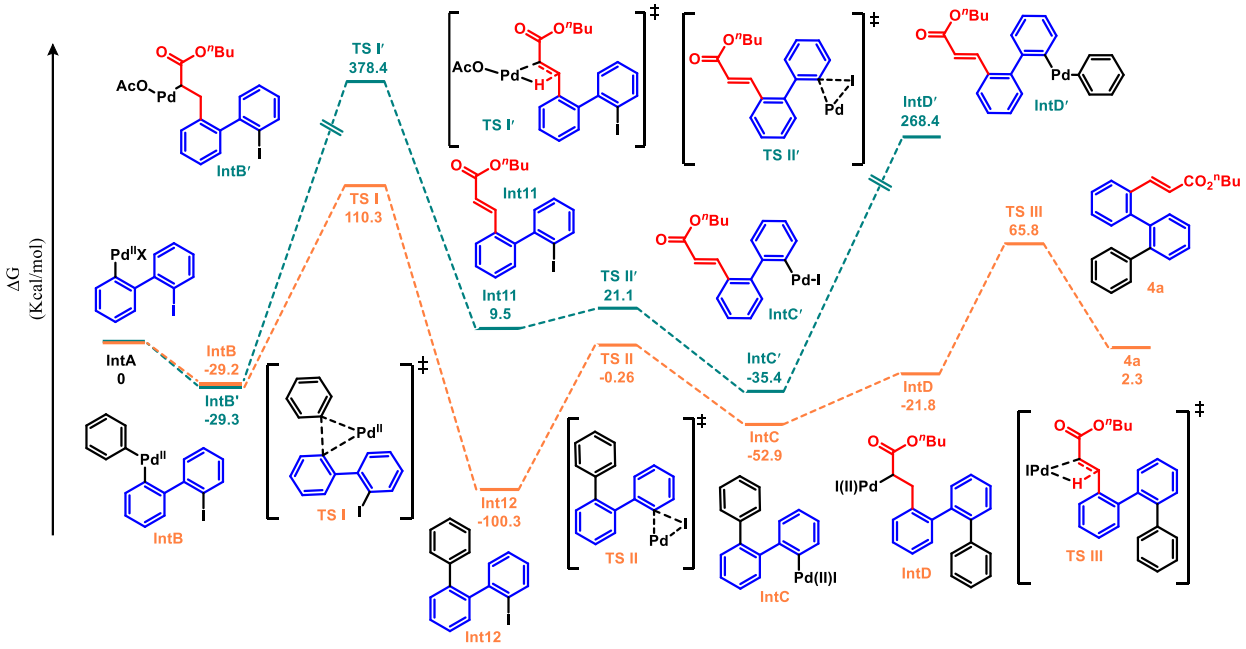
with the Mizoroki-Heck reaction whereby generation of **B'** via migratory insertion of **A** on alkene **2a** followed by β-H elimination provides intermediate **11**. Further oxidative addition followed by transmetallation gives **11→C'→D'**. Finally, the reductive elimination of **D'** furnishes the desired product and the regeneration of Pd(0) for the next catalytic cycle. The reaction proceeds to provide previously reported product **4a"** by the interception of **C'**. Based on our experimental results, Path **I** is more likely to proceed for the desired product formation in this cascade reaction.



Scheme S1: Plausible reaction mechanism

12. Density Functional Theory (DFT) Calculations

In order to get insights in to the energy changes driving the reaction, DFT calculations were performed on Gaussian-16 program package. Geometry optimization of all the compounds in this study were performed with the help of hybrid density functional B3PW91-D3[9a] using the basis set BS-I which include basis set 6-311G(d) employed for H, C, O and B atoms and basis set LANL2DZ employed for Pd and I atoms with effective core potentials (ECPs) for its core electrons[9b]. To check if the optimized geometry is an equilibrium structure or a transition state, vibrational frequencies were calculated. The solvent effect of THF:TFE (1:1)[9c] was evaluated by the conductor-like polarizable continuum model (CPCM). Relative Gibbs free energy was used in this discussion. Thermal corrections and entropy contributions to the Gibbs energy change were evaluated at the same B3PW91-D3/BS-I level at 298.15 K.



Scheme S2: Relative free energy profile (ΔG in kcal/mol) evaluated at B3PW91-D3/BS-I level at 298.15 K. Solvent effect for THF:TFE evaluated by CPCM model.

Table S14: Absolute Calculation Energies, Zero-point energies, and Free Energies

Geometry	E_{solv}[1]	ZPE[2]	E_{corr}[3]	G_{corr}[4]	IF[5]
2a	-424.352424	0.18054	0.191228	0.143046	-
3a	-408.201535	0.124768	0.132727	0.091468	-
Pd(0)	-126.749788	0	0.001416	-0.016592	-
PdHI	-138.797576	0.005757	0.011077	-0.022252	-
PdOAcH	-355.834077	0.057818	0.064368	0.025402	-
PdI	-138.235411	0.00032	0.003341	-0.026835	-
NaOAc	-390.815751	0.049796	0.056149	0.017778	-
A	-828.681662	0.210514	0.227322	0.163031	-
B	-831.838307	0.249404	0.267238	0.200224	-
B′	-1253.120031	0.396744	0.425186	0.332936	-
12	-705.06526	0.251466	0.266834	0.206358	-
11	-897.226487	0.332437	0.354058	0.276513	-
C	-831.914622	0.251954	0.269496	0.202893	-
C′	-1024.084944	0.333615	0.356784	0.276252	-
D	-1256.341029	0.438027	0.466364	0.374039	-
D′	-1244.171701	0.421243	0.448217	0.359428	-
4a	-1117.387455	0.423336	0.448004	0.365111	-

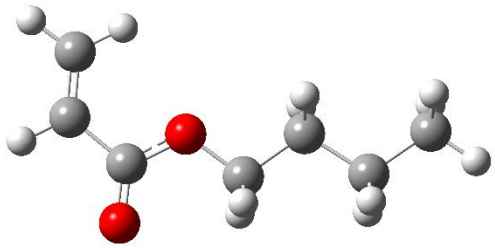
TS I	-831.641043	0.245174	0.265482	0.184729	-195.55
TS I′	-1252.437406	0.37024	0.394835	0.310259	-86.99
TS II	-831.818921	0.248603	0.26597	0.198365	-111.89
TS II′	-1023.946323	0.32981	0.353402	0.268336	-93.52
TS III	-1256.222032	0.434153	0.462684	0.367531	-81.44
$AcOB(OH)_2$	-405.093986	0.086706	0.094186	0.054629	-
$IB(OH)_2$	-188.023873	0.033789	0.38545	0.004318	-

[1]The electronic energy calculated by B3PW91-D3/BS-I level in THF:TFE (1:1) solvent system. [2]Zero point energy [3]The thermal correction to energy calculated by B3PW91-D3/BS-I level. [4] The thermal correction to Gibbs free energy calculated by B3PW91-D3/BS-I level. [5]Imaginary frequencies for the transition states.

Table S15: Geometries for All Optimized Structures

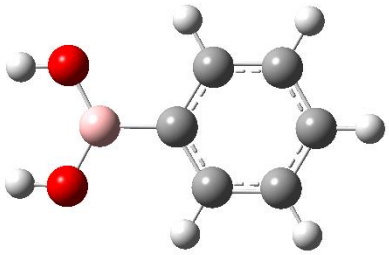
2a [EE: -424.352424 a.u.]

Centre number	Atomic number	Coordinates (Angstroms)		
1	6	-3.071317	1.649067	0.000047
2	1	-2.143569	2.210830	0.000029
3	1	-3.996052	2.217015	0.000085
4	6	-3.082805	0.317517	0.000023
5	1	-4.013308	-0.241590	0.000041
6	6	-1.875049	-0.537036	-0.000035
7	8	-1.924805	-1.748873	-0.000035
8	8	-0.731400	0.157917	-0.000012
9	6	0.487843	-0.612126	-0.000028
10	1	0.495325	-1.256153	-0.883921
11	1	0.495316	-1.256205	0.883828
12	6	1.649017	0.357115	0.000007
13	1	1.572815	1.006629	0.879907
14	1	1.572823	1.006682	-0.879854
15	6	2.997028	-0.361097	-0.000008
16	1	3.061205	-1.017638	-0.876552
17	1	3.061195	-1.017694	0.876494
18	6	4.177075	0.604208	0.000029
19	1	5.130132	0.067675	0.000016
20	1	4.161511	1.251135	-0.883034
21	1	4.161502	1.251077	0.883133



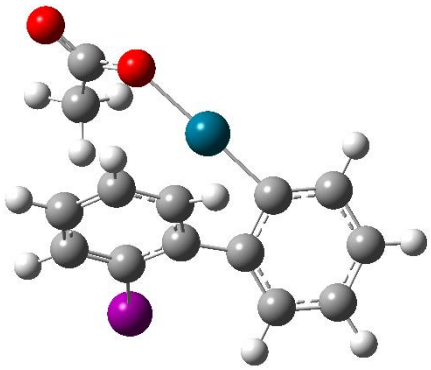
3a [EE: -408.201535 a.u.]

Centre number	Atomic number	Coordinates (Angstroms)		
1	6	-1.942488	1.205723	-0.000377
2	6	-2.640923	0.000000	0.000000
3	6	-1.942488	-1.205723	0.000377
4	6	-0.551022	-1.201527	0.000312
5	6	0.172114	0.000000	-0.000000
6	6	-0.551022	1.201527	-0.000312
7	1	-2.484180	2.147283	-0.000709
8	1	-3.727187	0.000000	0.000000
9	1	-2.484180	-2.147283	0.000709
10	1	-0.012760	-2.144958	0.000553
11	1	-0.012760	2.144958	-0.000553
12	5	1.738014	0.000000	-0.000000
13	8	2.380258	1.207866	0.000948
14	1	3.340923	1.165220	0.001311
15	8	2.380258	-1.207866	-0.000948
16	1	3.340923	-1.165220	-0.001311



A [EE: -828.681662 a.u.]

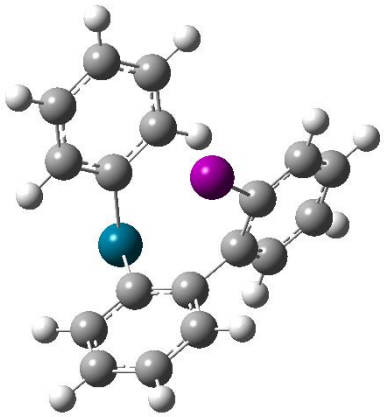
Centre number	Atomic number	Coordinates (Angstroms)		
1	6	0.607780	-1.215896	0.806476
2	6	-0.268301	-2.162722	1.304219
3	6	-1.393015	-1.777869	2.052215
4	6	-1.629194	-0.449027	2.317351
5	6	-0.730013	0.529323	1.843541
6	6	0.417306	0.154917	1.072603
7	1	-0.107908	-3.213755	1.093333
8	1	-2.070427	-2.542662	2.415378
9	1	-2.488549	-0.139790	2.900162
10	1	-0.756193	1.526473	2.277043
11	6	1.245310	1.286580	0.583365
12	6	0.410424	2.175633	-0.082558
13	6	2.610773	1.522064	0.694717
14	6	0.906465	3.328091	-0.675225
15	6	3.116324	2.690529	0.126636
16	1	3.262919	0.820116	1.203878
17	6	2.276910	3.579357	-0.548717
18	1	0.264961	4.019471	-1.213590
19	1	4.175873	2.911519	0.206822
20	1	2.693666	4.484207	-0.982016



21	46	-1.347004	1.291494	-0.196552
22	53	2.171664	-1.860423	-0.481681
23	8	-3.220800	0.317537	-0.311451
24	6	-3.481659	-0.806066	-0.895185
25	8	-4.587448	-1.344747	-0.858107
26	6	-2.339835	-1.457244	-1.666517
27	1	-1.975765	-0.783415	-2.448222
28	1	-1.498057	-1.665295	-0.999779
29	1	-2.666214	-2.391518	-2.123569

B [EE: -831.838307 a.u.]

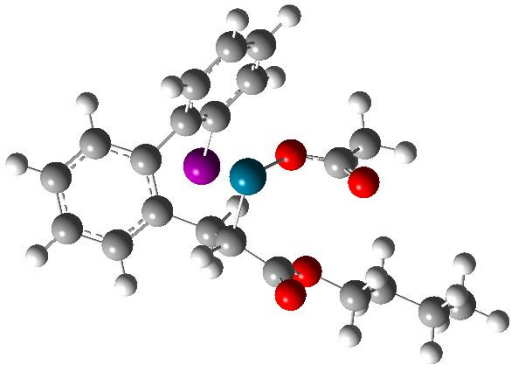
Centre number	Atomic number	Coordinates (Angstroms)		
1	6	-2.382829	1.726304	-1.251277
2	6	-1.965129	2.997499	-1.641115
3	6	-0.855456	3.581579	-1.035980
4	6	-0.162815	2.879633	-0.057038
5	6	-0.570735	1.600461	0.338312
6	6	-1.712078	1.021204	-0.242761
7	6	0.213491	0.876702	1.370787
8	6	1.500664	0.379687	1.149133
9	6	2.199366	-0.319785	2.130161
10	6	1.606996	-0.541646	3.367847
11	6	0.324354	-0.062066	3.618024
12	6	-0.354051	0.638720	2.629819
13	46	-2.500216	-0.674858	0.384571
14	6	-1.017376	-1.580482	-0.534246
15	6	-0.076971	-2.257231	0.251329
16	6	0.901725	-3.049626	-0.345680
17	6	0.963377	-3.166135	-1.731788
18	6	0.044079	-2.478554	-2.519712
19	6	-0.936446	-1.683273	-1.926717
20	53	2.427794	0.550124	-0.768528
21	1	-3.243450	1.281058	-1.743001
22	1	-2.506788	3.528420	-2.419372
23	1	-0.524970	4.572851	-1.331235
24	1	0.715152	3.319440	0.408124
25	1	3.190270	-0.707880	1.924888
26	1	2.149105	-1.093169	4.129517
27	1	-0.146626	-0.232519	4.580895
28	1	-1.352445	1.019404	2.820681
29	1	-0.086174	-2.150477	1.332147



30	1	1.628426	-3.563582	0.278135
31	1	1.733132	-3.776234	-2.195681
32	1	0.093470	-2.551909	-3.603189
33	1	-1.633245	-1.136471	-2.554805

B′ [EE: -1253.120031 a.u.]

Centre number	Atomic number	Coordinates (Angstroms)		
1	6	-2.241414	-1.338121	-2.684197
2	6	-3.583511	-1.661741	-2.842640
3	6	-4.473662	-1.435329	-1.796778
4	6	-4.005818	-0.885897	-0.609630
5	6	-2.656853	-0.551071	-0.446653
6	6	-1.753403	-0.784014	-1.497128
7	6	-2.230671	0.001684	0.865388
8	6	-1.817898	1.319975	1.073369
9	6	-1.421173	1.778409	2.324725
10	6	-1.444627	0.910591	3.410241
11	6	-1.877469	-0.399250	3.242177
12	6	-2.265154	-0.839899	1.984691
13	6	-0.276754	-0.498461	-1.391031
14	6	0.548301	-1.748435	-1.152391
15	6	2.025416	-1.632930	-1.339912
16	46	0.364714	-2.448424	0.717332
17	8	2.754372	-2.577873	-1.570621
18	8	2.459300	-0.374989	-1.223656
19	6	3.887113	-0.185964	-1.241093
20	6	4.152758	1.286071	-1.029394
21	6	5.645370	1.603207	-1.012550
22	6	5.921672	3.084645	-0.781004
23	8	0.821922	-0.600835	1.422789
24	6	2.040822	-0.334366	1.771502
25	6	2.177555	1.090464	2.274483
26	8	2.992366	-1.108378	1.731383
27	53	-1.841710	2.743132	-0.529904
28	1	-1.547086	-1.517666	-3.501348
29	1	-3.932860	-2.086787	-3.778709
30	1	-5.525595	-1.680733	-1.905016
31	1	-4.693299	-0.699893	0.210252
32	1	-1.098098	2.804414	2.456230
33	1	-1.129851	1.268138	4.385572
34	1	-1.905209	-1.080933	4.086157
35	1	-2.595454	-1.864829	1.844195



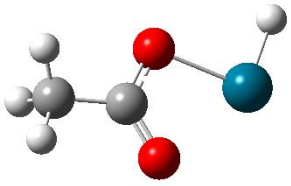
36	1	0.061755	-0.032813	-2.326293
37	1	-0.051945	0.217396	-0.601749
38	1	0.186102	-2.624621	-1.704882
39	1	4.316758	-0.791887	-0.440207
40	1	4.282527	-0.540291	-2.197710
41	1	3.654892	1.860777	-1.819409
42	1	3.698502	1.592185	-0.081453
43	1	6.133926	1.010826	-0.228833
44	1	6.098548	1.286907	-1.960381
45	1	6.994811	3.295984	-0.770093
46	1	5.469874	3.698448	-1.567179
47	1	5.507204	3.418075	0.176047
48	1	1.564514	1.221584	3.169163
49	1	3.218221	1.317209	2.504971
50	1	1.798250	1.789239	1.526115

Pd [EE: -126.749788 a.u.]

Centre number	Atomic number	Coordinates (Angstroms)		
1	46	0.000000	0.000000	0.000000

OAcPdH [EE: -355.834077 a.u.]

Centre number	Atomic number	Coordinates (Angstroms)		
1	46	1.070703	0.021432	0.003756
2	1	1.850563	-1.279318	0.004973
3	8	-1.055144	1.226690	-0.011997
4	6	-1.505199	0.067827	-0.017332
5	8	-0.717256	-0.957263	-0.022343
6	6	-2.977646	-0.226674	0.014086
7	1	-3.541288	0.640490	-0.329092
8	1	-3.212742	-1.098507	-0.597808
9	1	-3.272620	-0.450865	1.043362

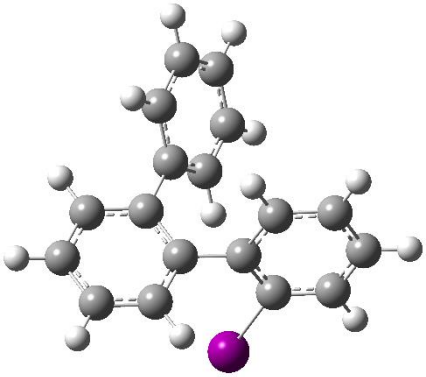


IPdH [EE: -138.797576 a.u.]

Centre number	Atomic number	Coordinates (Angstroms)		
1	46	0.000000	0.000000	-1.494848
2	1	0.000000	0.000000	-3.013520
3	53	0.000000	0.000000	1.354274

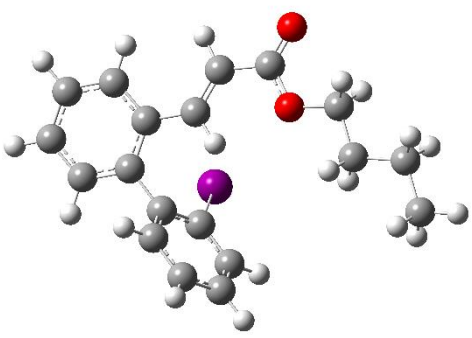
12 [EE: -705.06526 a.u.]

Centre number	Atomic number	Coordinates (Angstroms)		
1	6	-1.304029	-0.957849	0.556921
2	6	-1.656668	-2.266192	0.875941
3	6	-0.904374	-2.968266	1.811389
4	6	0.193787	-2.363718	2.415785
5	6	0.530474	-1.058489	2.085714
6	6	-0.210744	-0.323136	1.152075
7	1	-2.504861	-2.739122	0.394837
8	1	-1.178545	-3.988718	2.059065
9	1	0.787693	-2.908326	3.142526
10	1	1.388676	-0.581965	2.548971
11	6	0.197944	1.074277	0.852691
12	6	1.393767	1.353484	0.166866
13	6	-0.587862	2.127186	1.327544
14	6	1.767292	2.690537	-0.015331
15	6	-0.207040	3.448920	1.133443
16	1	-1.504172	1.897607	1.862588
17	6	0.978250	3.730749	0.459396
18	1	2.682780	2.910428	-0.556384
19	1	-0.830073	4.253921	1.510184
20	1	1.285962	4.759418	0.299180
21	53	-2.440434	0.030374	-0.964782
22	6	2.258357	0.274676	-0.370224
23	6	3.623602	0.248255	-0.066768
24	6	1.735555	-0.725256	-1.198461
25	6	4.443925	-0.758123	-0.568074
26	1	4.039733	1.012518	0.583185
27	6	2.554712	-1.728685	-1.702333
28	1	0.681790	-0.708700	-1.456257
29	6	3.911638	-1.751153	-1.386083
30	1	5.499646	-0.768691	-0.314324
31	1	2.132549	-2.493794	-2.346843
32	1	4.550289	-2.537706	-1.776231



11 [EE: -897.226487 a.u.]

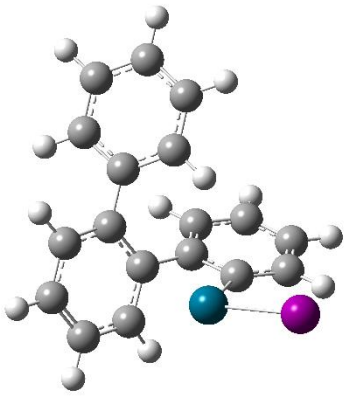
Centre number	Atomic number	Coordinates (Angstroms)		
1	6	4.492575	1.175333	-1.227600
2	6	3.651942	0.070183	-1.290635
3	6	2.282444	0.200294	-1.061072
4	6	1.736304	1.470574	-0.773223
5	6	2.600420	2.574275	-0.721549



6	6	3.961833	2.431664	-0.941199
7	1	5.556906	1.057472	-1.403974
8	1	4.058201	-0.912225	-1.509414
9	1	2.198759	3.562255	-0.522673
10	1	4.609618	3.301264	-0.897582
11	6	1.424269	-1.010826	-1.146575
12	6	1.149218	-1.556278	-2.406556
13	6	0.865162	-1.645801	-0.032302
14	6	0.340571	-2.676308	-2.552118
15	1	1.574396	-1.073043	-3.280599
16	6	0.052564	-2.768033	-0.161587
17	6	-0.212239	-3.280106	-1.427682
18	1	0.139970	-3.073236	-3.541788
19	1	-0.369162	-3.243645	0.716138
20	1	-0.848551	-4.153544	-1.526953
21	6	0.300183	1.594640	-0.544320
22	1	-0.293642	0.720316	-0.792511
23	6	-0.354661	2.653755	-0.044138
24	1	0.142882	3.569038	0.258054
25	6	-1.808627	2.671882	0.174988
26	8	-2.404068	3.628841	0.627728
27	8	-2.411000	1.521940	-0.165239
28	6	-3.832984	1.447017	0.042137
29	1	-4.049760	1.649789	1.095349
30	1	-4.321158	2.223242	-0.555195
31	6	-4.275740	0.060112	-0.365969
32	1	-3.998774	-0.108242	-1.413265
33	1	-3.723790	-0.677644	0.228086
34	6	-5.777696	-0.142221	-0.184773
35	1	-6.321081	0.607731	-0.772954
36	1	-6.047033	0.039193	0.863193
37	6	-6.228878	-1.539756	-0.594608
38	1	-7.306487	-1.668610	-0.458861
39	1	-6.000527	-1.735749	-1.647353
40	1	-5.724479	-2.307976	0.000583
41	53	1.264987	-0.931416	1.943670

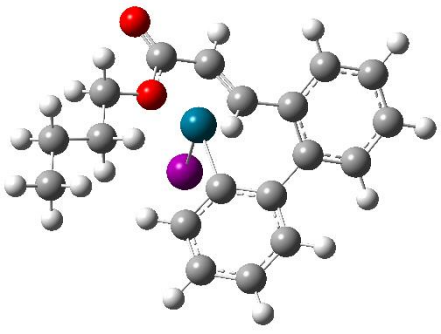
C [EE: -831.914622 a.u.]

Centre number	Atomic number	Coordinates (Angstroms)		
1	6	-1.708410	-1.336738	2.099212
2	6	-1.192768	-2.573431	2.481606
3	6	0.137447	-2.899093	2.215310
4	6	0.985554	-2.010502	1.546484
5	6	0.454167	-0.783092	1.178905
6	6	-0.862528	-0.439237	1.458903
7	1	-1.829865	-3.289133	2.991315
8	1	0.526548	-3.865160	2.523856
9	1	2.009167	-2.282429	1.323191
10	6	-1.166283	0.937232	0.972106
11	6	-2.131137	1.220268	-0.030739
12	6	-0.437695	1.998716	1.561809
13	6	-2.327983	2.544933	-0.401602
14	6	-0.645728	3.323008	1.144797
15	1	0.173576	1.797357	2.436582
16	6	-1.587011	3.587358	0.167633
17	1	-3.055372	2.769626	-1.175525
18	1	-0.084734	4.126441	1.609376
19	1	-1.761001	4.606791	-0.160969
20	6	-2.904533	0.137994	-0.679953
21	6	-2.258747	-0.961822	-1.257406
22	6	-4.299995	0.209506	-0.737881
23	6	-2.994018	-1.967627	-1.872581
24	1	-1.175369	-1.019808	-1.231681
25	6	-5.035773	-0.801164	-1.349207
26	1	-4.810978	1.052722	-0.282493
27	6	-4.385003	-1.893192	-1.916681
28	1	-2.479078	-2.811404	-2.321462
29	1	-6.119187	-0.736868	-1.376881
30	1	-4.958404	-2.682555	-2.392803
31	46	1.087173	0.746580	0.141196
32	53	3.216261	-0.390448	-0.947373
33	1	-2.744402	-1.073212	2.288941



C′ [EE: -1024.084944 a.u.]

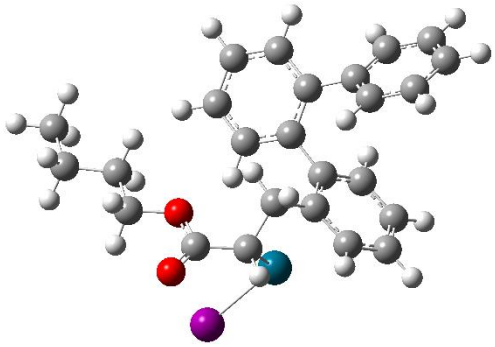
Centre number	Atomic number	Coordinates (Angstroms)		
1	6	1.654497	3.290866	-1.128741
2	6	1.069470	2.349854	-0.283636
3	6	1.714961	1.968441	0.913167
4	6	2.935942	2.555484	1.237064



5	6	3.512506	3.500566	0.391749
6	6	2.875509	3.866571	-0.790856
7	1	1.141901	3.586897	-2.038427
8	1	4.468202	3.943313	0.653421
9	1	3.326810	4.601457	-1.449418
10	6	1.074691	0.933203	1.749167
11	6	1.024242	1.062575	3.144318
12	6	0.408425	-0.159002	1.172014
13	6	0.325955	0.151939	3.927120
14	1	1.510076	1.915627	3.609120
15	6	-0.307789	-1.065582	1.939677
16	6	-0.352456	-0.903202	3.325079
17	1	0.296036	0.277476	5.004620
18	1	-0.812115	-1.905354	1.475686
19	1	-0.908857	-1.614966	3.927270
20	6	-0.230470	1.724716	-0.568944
21	1	-0.946137	1.710492	0.248610
22	6	-0.675990	1.281432	-1.785624
23	1	-0.073949	1.384926	-2.685196
24	6	-2.063502	0.816699	-2.026820
25	8	-2.480776	0.547469	-3.131063
26	8	-2.778396	0.720162	-0.904359
27	6	-4.129917	0.231957	-1.035872
28	1	-4.676236	0.887664	-1.719759
29	1	-4.097364	-0.767426	-1.479727
30	6	-4.741933	0.218253	0.345534
31	1	-4.130658	-0.413625	1.000199
32	1	-4.705306	1.232287	0.760217
33	6	-6.182679	-0.286127	0.326974
34	1	-6.209765	-1.299564	-0.092180
35	1	-6.779838	0.338999	-0.348427
36	6	-6.814740	-0.288277	1.714361
37	1	-7.845248	-0.653246	1.683432
38	1	-6.255100	-0.929681	2.402875
39	1	-6.831595	0.719420	2.142132
40	46	0.498135	-0.447926	-0.801160
41	53	2.125529	-2.496258	-0.405504
42	1	3.454945	2.248365	2.139610

D [EE: -1256.341029 a.u.]

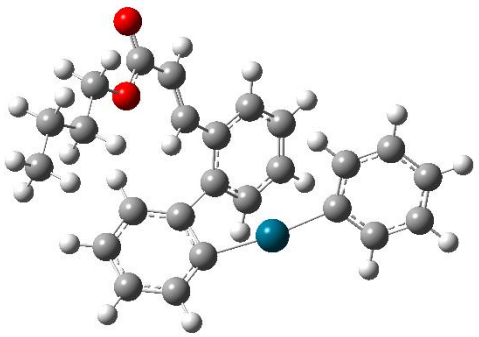
Centre number	Atomic number	Coordinates (Angstroms)		
1	6	2.485955	-1.305964	-1.332402
2	6	2.492773	-2.701284	-1.255296
3	6	1.845302	-3.346607	-0.215470
4	6	1.167506	-2.588744	0.746501
5	6	1.135218	-1.171849	0.673161
6	6	1.821978	-0.525141	-0.393144
7	1	3.020165	-3.275798	-2.009837
8	1	1.866898	-4.427487	-0.131358
9	1	0.758349	-3.083068	1.622342
10	6	1.891405	0.955021	-0.520054
11	6	3.128544	1.617963	-0.390858
12	6	0.751384	1.689529	-0.858877
13	6	3.186529	2.995215	-0.628603
14	6	0.827593	3.057816	-1.091890
15	1	-0.201392	1.179082	-0.953189
16	6	2.050028	3.712620	-0.980818
17	1	4.137689	3.507291	-0.518131
18	1	-0.064448	3.608846	-1.368585
19	1	2.117633	4.780930	-1.161229
20	6	4.364110	0.892841	-0.006019
21	6	4.403860	0.093555	1.142301
22	6	5.518468	1.000751	-0.787876
23	6	5.562807	-0.588601	1.492898
24	1	3.521420	0.014391	1.769508
25	6	6.678756	0.315247	-0.440031
26	1	5.497375	1.608994	-1.687413
27	6	6.703793	-0.483879	0.699733
28	1	5.576173	-1.201759	2.388831
29	1	7.562563	0.401091	-1.064919
30	1	7.607565	-1.021209	0.970068
31	1	3.019988	-0.810535	-2.136454
32	6	0.458202	-0.417736	1.813336
33	1	0.926385	-0.655707	2.773795
34	1	0.528216	0.656597	1.652394
35	6	-0.989844	-0.889255	1.754304
36	1	-1.207192	-1.759384	2.374081
37	6	-2.065186	0.129842	1.943943
38	46	-0.912381	-1.628237	-0.126614
39	53	-3.479043	-1.511158	-0.846084
40	8	-1.853352	1.234691	1.225454
41	8	-3.006689	-0.024830	2.688756



42	6	-2.893669	2.230328	1.265004
43	1	-3.004557	2.588953	2.292517
44	1	-3.834406	1.756958	0.967628
45	6	-2.493306	3.335849	0.318149
46	1	-2.361727	2.909544	-0.683078
47	1	-1.517814	3.728373	0.625151
48	6	-3.518660	4.464205	0.272365
49	1	-4.494833	4.061090	-0.024325
50	1	-3.652763	4.878030	1.279491
51	6	-3.108035	5.574874	-0.688235
52	1	-2.998574	5.193286	-1.708668
53	1	-3.848394	6.379518	-0.711800
54	1	-2.148247	6.013780	-0.396544

D′ [EE: -1244.171701 a.u.]

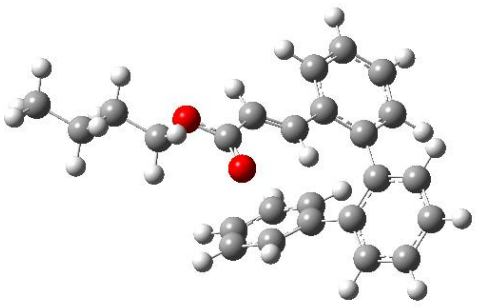
Centre number	Atomic number	Coordinates (Angstroms)		
1	6	3.091511	1.578396	1.243704
2	6	3.977783	2.458740	1.863688
3	6	5.267051	2.036560	2.187273
4	6	5.661505	0.734396	1.888721
5	6	4.766643	-0.143497	1.271356
6	6	3.464310	0.261658	0.961353
7	1	2.098159	1.931623	0.968874
8	1	3.666572	3.476378	2.087122
9	1	5.963892	2.723292	2.659527
10	1	6.669202	0.402950	2.127515
11	1	5.099195	-1.153634	1.034111
12	46	2.088336	-1.127720	0.366548
13	6	0.512099	-2.366682	-0.256812
14	6	-0.131658	-3.548987	0.116713
15	6	-0.129236	-1.550692	-1.200660
16	6	-1.354826	-3.900073	-0.463517
17	1	0.309737	-4.212148	0.858728
18	6	-1.360259	-1.868999	-1.772673
19	6	-1.967673	-3.067029	-1.401673
20	1	-1.838303	-4.832951	-0.182786
21	1	-1.835062	-1.205949	-2.491448
22	1	-2.918827	-3.352150	-1.841486
23	6	0.676532	-0.328645	-1.452493
24	6	0.168121	0.998395	-1.390625
25	6	2.052841	-0.530898	-1.781718
26	6	1.029672	2.056907	-1.677626



27	6	2.887524	0.576888	-2.057010
28	1	2.372182	-1.521565	-2.097974
29	6	2.372196	1.854885	-2.009726
30	1	0.659139	3.074456	-1.603923
31	1	3.924810	0.404017	-2.320004
32	1	3.008795	2.709886	-2.208616
33	6	-1.213717	1.212376	-0.976533
34	1	-1.658471	0.413211	-0.390888
35	6	-1.975497	2.281259	-1.256211
36	1	-1.625949	3.103205	-1.872491
37	6	-3.361174	2.435059	-0.787951
38	8	-3.789090	1.400598	-0.048284
39	8	-4.051352	3.399057	-1.051164
40	6	-5.145051	1.463757	0.431044
41	1	-5.262499	2.359717	1.048154
42	1	-5.820130	1.556960	-0.425150
43	6	-5.405783	0.199477	1.218182
44	1	-5.227336	-0.666170	0.569588
45	1	-4.679935	0.134380	2.037180
46	6	-6.826040	0.150445	1.775397
47	1	-6.999738	1.027609	2.411097
48	1	-7.545079	0.225355	0.950157
49	6	-7.093339	-1.120866	2.573548
50	1	-8.114463	-1.140654	2.964930
51	1	-6.957590	-2.012786	1.953185
52	1	-6.409408	-1.204149	3.424487

4a [EE: -1117.387455 a.u.]

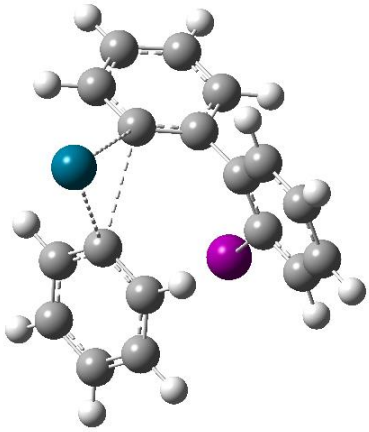
Centre number	Atomic number	Coordinates (Angstroms)		
1	6	-0.265242	-2.357862	2.456730
2	6	-0.852678	-1.708514	3.538947
3	6	-1.980527	-0.917162	3.334772
4	6	-2.513892	-0.771968	2.058528
5	6	-1.931865	-1.418046	0.961084
6	6	-0.801819	-2.215723	1.180989
7	6	-2.521119	-1.317783	-0.399769
8	6	-2.787805	-2.503619	-1.097239
9	6	-3.373331	-2.493699	-2.356747
10	6	-3.711333	-1.281221	-2.948356
11	6	-3.448489	-0.094757	-2.274504
12	6	-2.847345	-0.087909	-1.010146
13	6	-2.580637	1.235860	-0.377903
14	6	-1.271044	1.716784	-0.146406



15	6	-1.112598	2.983834	0.438260
16	6	-2.204494	3.762968	0.785005
17	6	-3.493119	3.292921	0.540070
18	6	-3.671154	2.043296	-0.040085
19	6	-0.115875	0.924581	-0.558377
20	6	1.167270	1.119694	-0.215976
21	6	2.216846	0.233492	-0.743702
22	8	3.424349	0.600040	-0.282224
23	8	2.046553	-0.707785	-1.491680
24	6	4.546452	-0.189169	-0.722075
25	6	5.795058	0.387311	-0.091812
26	6	7.051492	-0.381092	-0.496180
27	6	8.317872	0.190488	0.131498
28	1	0.616489	-2.974475	2.603593
29	1	-0.435734	-1.819280	4.535351
30	1	-2.451956	-0.414291	4.173951
31	1	-3.402068	-0.165599	1.915115
32	1	-0.328279	-2.714037	0.340266
33	1	-2.552252	-3.452113	-0.623990
34	1	-3.573343	-3.430314	-2.867975
35	1	-4.172700	-1.256291	-3.930668
36	1	-3.691835	0.854758	-2.742071
37	1	-0.113848	3.376078	0.599272
38	1	-2.052402	4.740241	1.232029
39	1	-4.356419	3.898029	0.798807
40	1	-4.675011	1.671834	-0.222565
41	1	-0.317103	0.086089	-1.220240
42	1	1.490647	1.906177	0.457084
43	1	4.383260	-1.228858	-0.423934
44	1	4.591324	-0.157959	-1.814541
45	1	5.890610	1.439216	-0.385724
46	1	5.684136	0.373181	0.998839
47	1	6.943694	-1.434397	-0.208940
48	1	7.148729	-0.372940	-1.588906
49	1	9.203193	-0.375360	-0.172262
50	1	8.473171	1.232686	-0.165666
51	1	8.266733	0.163356	1.224771

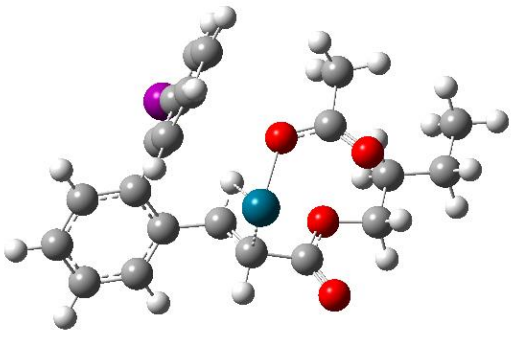
TS I [EE: -831.641043 a.u.]

Centre number	Atomic number	Coordinates (Angstroms)		
1	6	-0.550994	2.741285	-1.624382
2	6	0.365260	3.789896	-1.632785
3	6	1.340516	3.880914	-0.640512
4	6	1.409849	2.901489	0.354570
5	6	0.488506	1.831247	0.360828
6	6	-0.499505	1.774276	-0.617050
7	6	0.608931	0.792119	1.412817
8	6	1.595508	-0.197110	1.412505
9	6	1.660989	-1.189254	2.389313
10	6	0.721293	-1.211054	3.405519
11	6	-0.284266	-0.240759	3.441184
12	6	-0.329725	0.745229	2.452183
13	46	-4.316077	-0.089543	0.084335
14	6	-0.854507	-0.936351	-1.123036
15	6	-0.480208	-1.965009	-0.248367
16	6	0.243646	-3.060266	-0.718322
17	6	0.623206	-3.144080	-2.048514
18	6	0.282592	-2.103042	-2.928242
19	6	-0.440795	-1.004065	-2.462914
20	53	2.979962	-0.309361	-0.210022
21	1	-1.287053	2.680375	-2.418336
22	1	0.309872	4.544016	-2.408534
23	1	2.059229	4.694153	-0.635320
24	1	2.178398	2.940434	1.116243
25	1	2.434394	-1.951363	2.334905
26	1	0.766216	-1.983930	4.159679
27	1	-1.033527	-0.250351	4.229723
28	1	-1.108022	1.504918	2.489528
29	1	-0.741497	-1.906571	0.811507
30	1	0.517074	-3.857223	-0.013038
31	1	1.195494	-3.992232	-2.410104
32	1	0.593873	-2.144021	-3.964755
33	1	-0.684685	-0.195936	-3.148507



TS I′ [EE: -1252.437406 a.u.]

Centre number	Atomic number	Coordinates (Angstroms)		
1	6	2.402734	2.409576	-2.129471
2	6	3.780730	2.591358	-2.217739
3	6	4.618884	1.880187	-1.363577
4	6	4.073984	0.987654	-0.446133

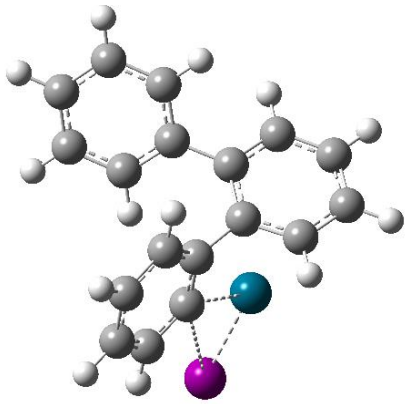


5	6	2.687515	0.804847	-0.357443
6	6	1.836934	1.525040	-1.202570
7	6	2.191063	-0.148077	0.670853
8	6	1.617151	-1.387021	0.395429
9	6	1.184516	-2.244122	1.405963
10	6	1.333515	-1.863565	2.733853
11	6	1.915067	-0.642085	3.051578
12	6	2.326604	0.203435	2.018270
13	6	0.331981	1.427180	-1.129941
14	6	-0.214545	2.447225	-0.460294
15	6	-1.701856	2.610185	-0.526105
16	46	-0.100583	0.830198	2.129907
17	8	-2.283326	3.655902	-0.296310
18	8	-2.315958	1.477071	-0.869568
19	6	-3.757614	1.497942	-0.832527
20	6	-4.235198	0.124800	-1.273546
21	6	-5.759755	0.025792	-1.265159
22	6	-6.249289	-1.351945	-1.700887
23	8	-0.709426	-0.930697	1.320784
24	6	-1.981296	-1.142168	1.194490
25	6	-2.260794	-2.476720	0.529150
26	8	-2.881152	-0.394054	1.564254
27	53	1.444055	-2.090691	-1.626122
28	1	1.746839	2.975689	-2.781909
29	1	4.195577	3.284021	-2.942349
30	1	5.697586	2.001093	-1.426420
31	1	4.721850	0.424924	0.217015
32	1	0.733444	-3.199587	1.156988
33	1	0.991848	-2.526575	3.520749
34	1	2.035922	-0.329862	4.082529
35	1	2.784853	1.170627	2.258912
36	1	0.005714	0.426831	-0.836580
37	1	0.064276	3.501019	-0.658192
38	1	-4.071080	1.720257	0.192402
39	1	-4.121390	2.284511	-1.500895
40	1	-3.849643	-0.082764	-2.288650
41	1	-3.805826	-0.632327	-0.606367
42	1	-6.133456	0.240593	-0.249528
43	1	-6.186888	0.791287	-1.918119
44	1	-7.343179	-1.410848	-1.682417
45	1	-5.915309	-1.590502	-2.716613
46	1	-5.853409	-2.141921	-1.035249
47	1	-1.823391	-3.283154	1.136607
48	1	-3.332344	-2.633598	0.413564

49	1	-1.773171	-2.515067	-0.445188

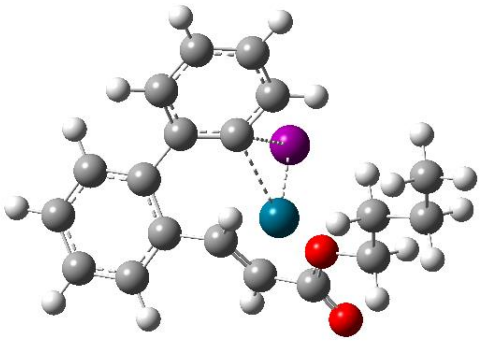
TS II [EE: -831.818921 a.u.]

Centre number	Atomic number	Coordinates (Angstroms)		
1	6	-2.308349	-1.486382	2.048746
2	6	-1.923673	-2.787435	2.376560
3	6	-0.610638	-3.211824	2.151252
4	6	0.331688	-2.365287	1.563604
5	6	-0.023888	-1.051081	1.225964
6	6	-1.351640	-0.628670	1.499504
7	1	-2.660278	-3.471583	2.811636
8	1	-0.316817	-4.235693	2.400225
9	1	1.339820	-2.725293	1.362138
10	6	-1.532676	0.818216	1.179608
11	6	-2.216885	1.234555	-0.010357
12	6	-1.025987	1.775340	2.082649
13	6	-2.236012	2.603513	-0.292577
14	6	-1.070866	3.150561	1.781793
15	1	-0.639766	1.450471	3.043242
16	6	-1.636799	3.532968	0.572775
17	1	-2.724122	2.934032	-1.195817
18	1	-0.637377	3.881166	2.465241
19	1	-1.657470	4.594901	0.302364
20	6	-2.941535	0.263116	-0.860828
21	6	-2.353029	-0.892910	-1.379503
22	6	-4.296349	0.497590	-1.145597
23	6	-3.084567	-1.800013	-2.137968
24	1	-1.294208	-1.076203	-1.194149
25	6	-5.050033	-0.405775	-1.901659
26	1	-4.784694	1.390898	-0.738398
27	6	-4.436921	-1.560502	-2.388697
28	1	-2.604049	-2.683560	-2.529047
29	1	-6.087653	-0.215160	-2.089261
30	1	-5.010407	-2.263821	-2.978325
31	46	1.461394	0.933679	-0.107958
32	53	3.580896	-0.481593	-0.700120
33	1	-3.325598	-1.120875	2.220979



TS II′ [EE: -1023.946323 a.u.]

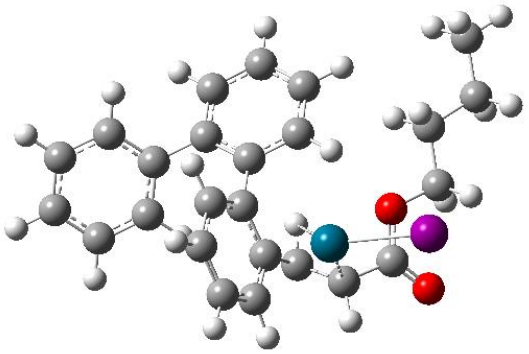
Centre number	Atomic number	Coordinates (Angstroms)		
1	6	1.582753	2.581564	-2.304747
2	6	0.943996	2.161086	-1.139780
3	6	1.463397	2.515037	0.124899
4	6	2.614145	3.297583	0.185930
5	6	3.244359	3.720617	-0.981990
6	6	2.732397	3.361678	-2.225910
7	1	1.165909	2.315658	-3.270900
8	1	4.144837	4.323084	-0.918543
9	1	3.225537	3.690260	-3.134910
10	6	0.774718	2.004409	1.327205
11	6	0.559667	2.829644	2.440070
12	6	0.224298	0.713658	1.357668
13	6	-0.185628	2.392151	3.527625
14	1	0.953673	3.841732	2.425549
15	6	-0.537225	0.270109	2.428883
16	6	-0.746776	1.118963	3.516650
17	1	-0.343790	3.052164	4.374401
18	1	-0.950224	-0.732006	2.435737
19	1	-1.338736	0.771026	4.357690
20	6	-0.287977	1.358540	-1.154148
21	1	-1.091312	1.700490	-0.507233
22	6	-0.572749	0.311169	-1.989144
23	1	0.123523	-0.007863	-2.761036
24	6	-1.903279	-0.340349	-2.056632
25	8	-2.180030	-1.178849	-2.885053
26	8	-2.737361	0.088924	-1.107767
27	6	-4.043756	-0.522574	-1.067123
28	1	-4.534684	-0.368957	-2.032270
29	1	-3.919608	-1.599334	-0.918768
30	6	-4.808758	0.120574	0.066088
31	1	-4.250990	-0.021682	0.998917
32	1	-4.861502	1.201306	-0.109420
33	6	-6.215978	-0.454864	0.204277
34	1	-6.153277	-1.536492	0.376404
35	1	-6.757084	-0.327719	-0.741549
36	6	-7.002036	0.199308	1.334994
37	1	-8.006371	-0.224970	1.421048
38	1	-6.499002	0.061517	2.297604
39	1	-7.109103	1.276333	1.169834
40	46	0.685040	-1.056986	-0.781774
41	53	2.339198	-2.442539	0.749442



42	1	3.038621	3.550973	1.152309

TS III [EE: -1256.222032 a.u.]

Centre number	Atomic number	Coordinates (Angstroms)		
1	6	2.210730	-1.517822	-0.990552
2	6	2.150334	-2.880812	-0.688029
3	6	1.566097	-3.309271	0.491797
4	6	1.019229	-2.365533	1.368978
5	6	1.055782	-0.978988	1.068699
6	6	1.676772	-0.555971	-0.140559
7	1	2.576112	-3.601131	-1.378967
8	1	1.537739	-4.362355	0.748805
9	1	0.665200	-2.687043	2.343739
10	6	1.813002	0.877647	-0.512023
11	6	3.090226	1.468311	-0.592718
12	6	0.687676	1.624216	-0.872894
13	6	3.199593	2.783830	-1.055488
14	6	0.815117	2.930428	-1.331020
15	1	-0.295497	1.170250	-0.805664
16	6	2.075648	3.511201	-1.427026
17	1	4.182705	3.242057	-1.106962
18	1	-0.067731	3.489421	-1.620913
19	1	2.183346	4.530742	-1.783876
20	6	4.315227	0.731847	-0.195832
21	6	4.416048	0.122787	1.060336
22	6	5.398311	0.637569	-1.075336
23	6	5.564041	-0.571615	1.422732
24	1	3.590937	0.202789	1.761155
25	6	6.547212	-0.060655	-0.715209
26	1	5.328374	1.096390	-2.057254
27	6	6.632636	-0.669921	0.533706
28	1	5.625708	-1.035329	2.402530
29	1	7.374247	-0.133802	-1.414946
30	1	7.527304	-1.217205	0.814168
31	1	2.695493	-1.192267	-1.904970
32	6	0.525593	-0.010897	2.121664
33	1	0.741906	0.899868	1.569080
34	6	-0.769527	-0.342840	2.241027
35	1	-1.113521	-1.215193	2.790847
36	6	-1.767656	0.763109	2.348252
37	46	-0.965619	-1.870511	-0.333418
38	53	-3.576930	-1.696725	-0.852987



39	8	-1.563203	1.724143	1.444702
40	8	-2.644890	0.791220	3.181780
41	6	-2.541309	2.780967	1.405334
42	1	-2.539684	3.303738	2.366270
43	1	-3.528887	2.330704	1.265872
44	6	-2.169964	3.694028	0.261908
45	1	-2.152233	3.107337	-0.663826
46	1	-1.151248	4.063831	0.421200
47	6	-3.133848	4.867150	0.115804
48	1	-4.152872	4.488585	-0.031568
49	1	-3.154219	5.442646	1.049575
50	6	-2.753266	5.782429	-1.042804
51	1	-2.756891	5.238247	-1.992923
52	1	-3.448919	6.621043	-1.137320
53	1	-1.749087	6.196566	-0.904855

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14. NMR Spectra

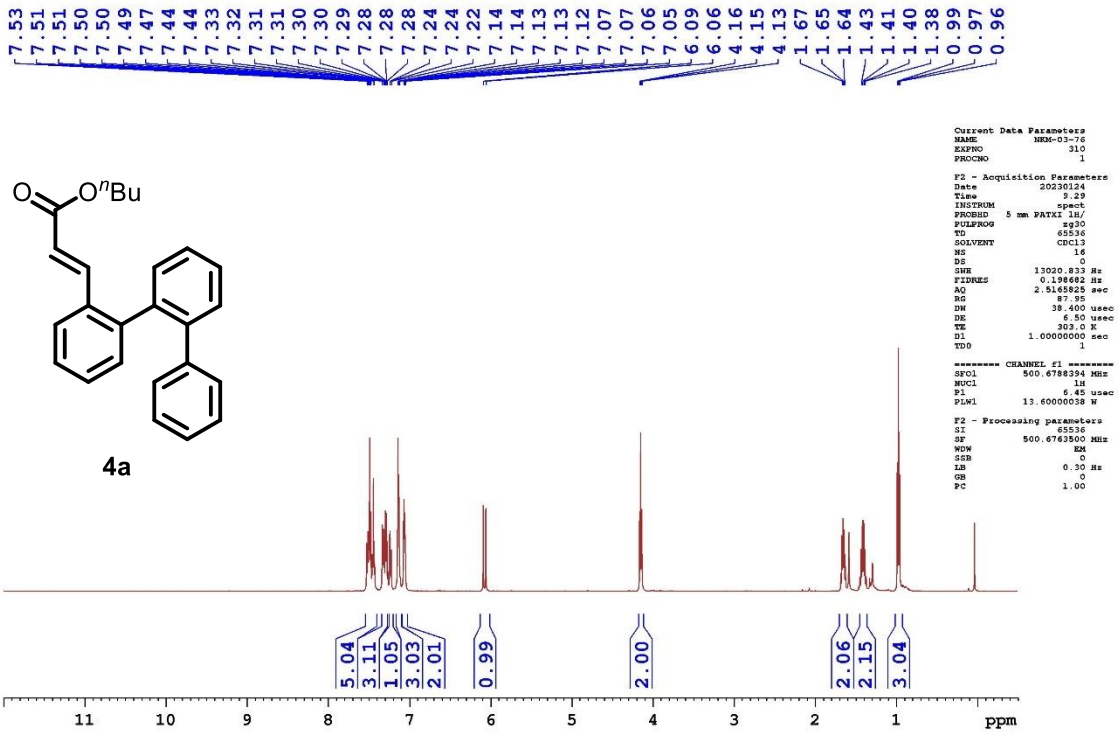

Figure S-04: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4a**

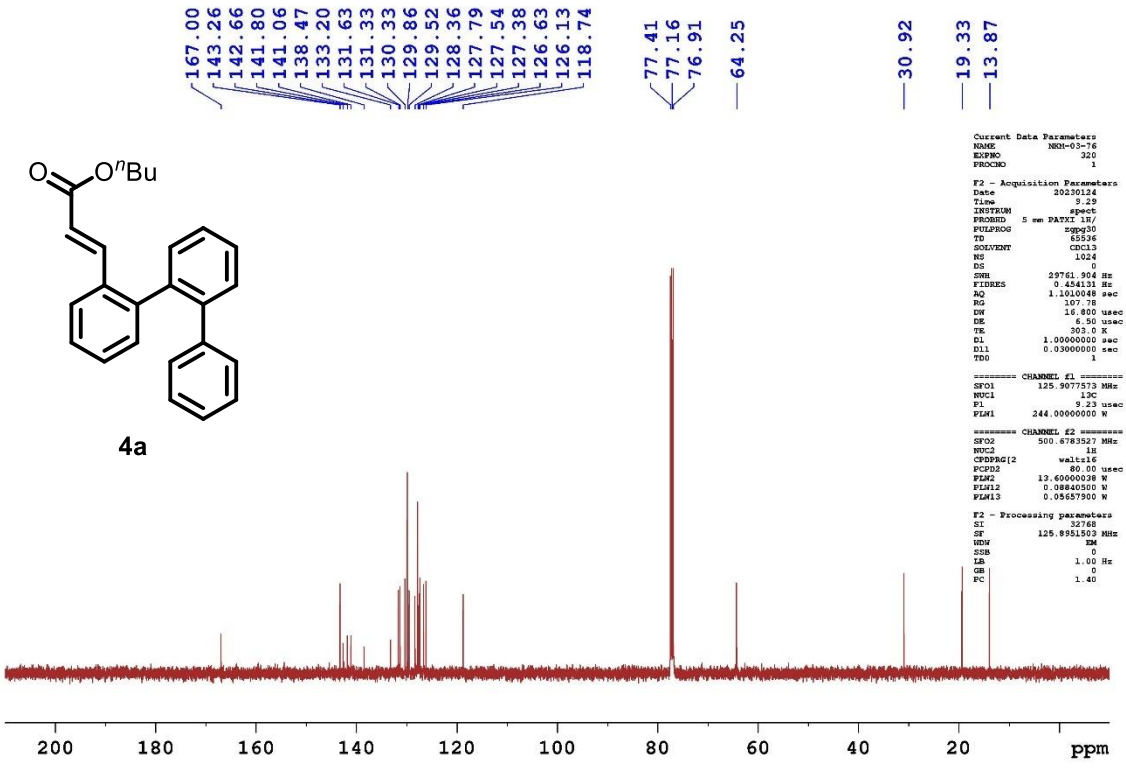

Figure S-05: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4a**

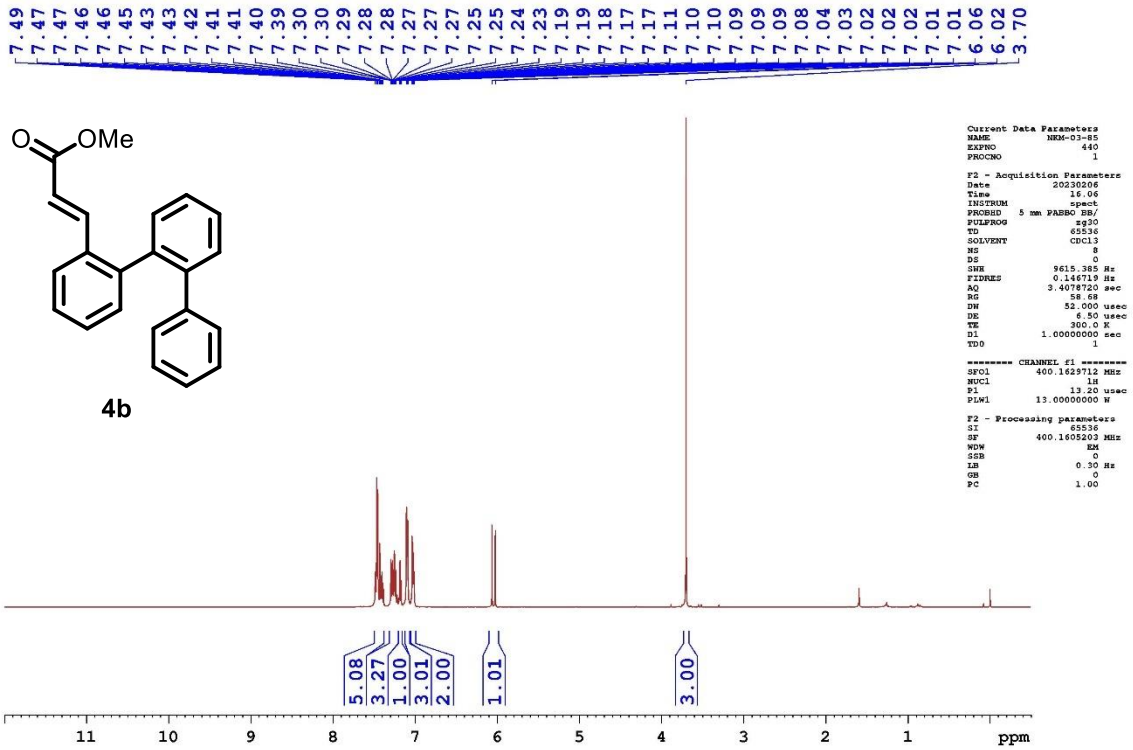

Figure S-06: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4b**

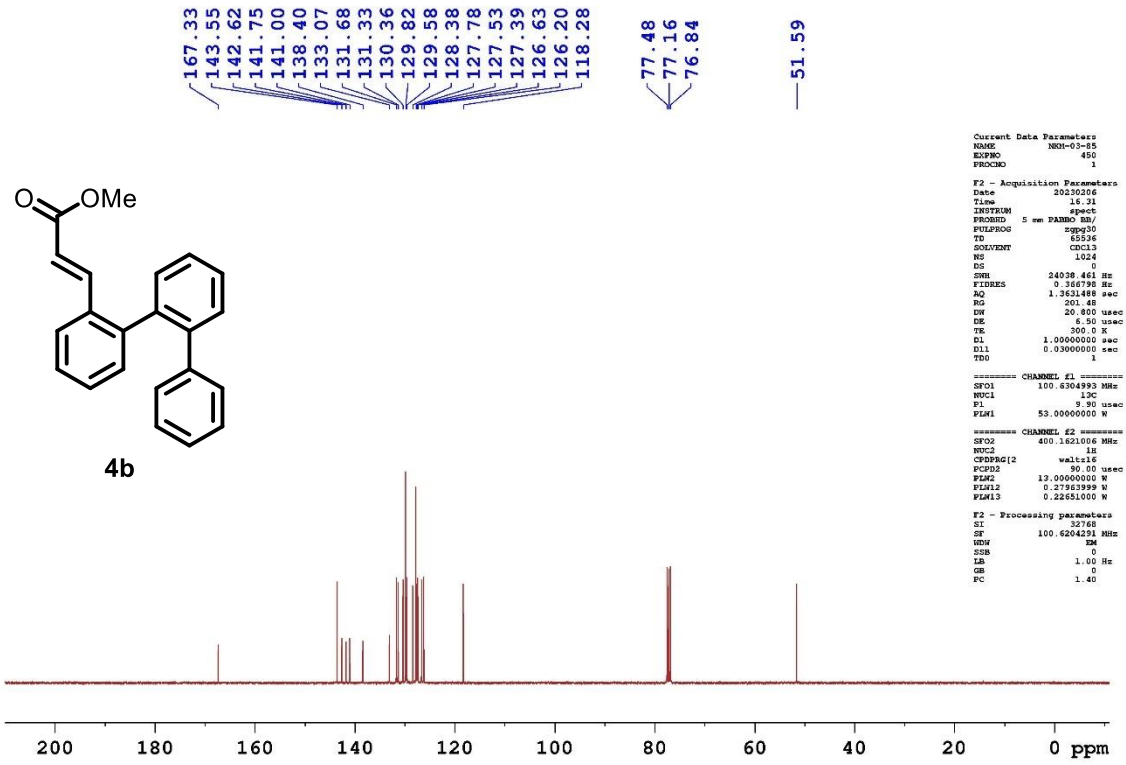

Figure S-07: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4b**

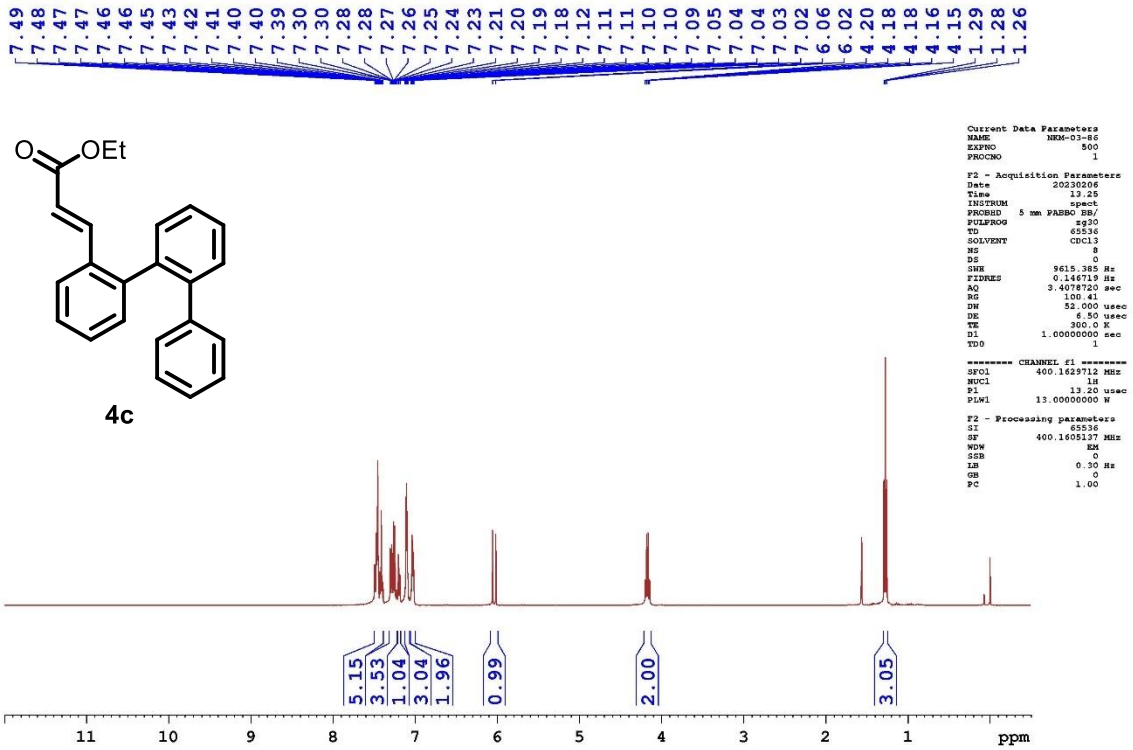

Figure S-08: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4c**

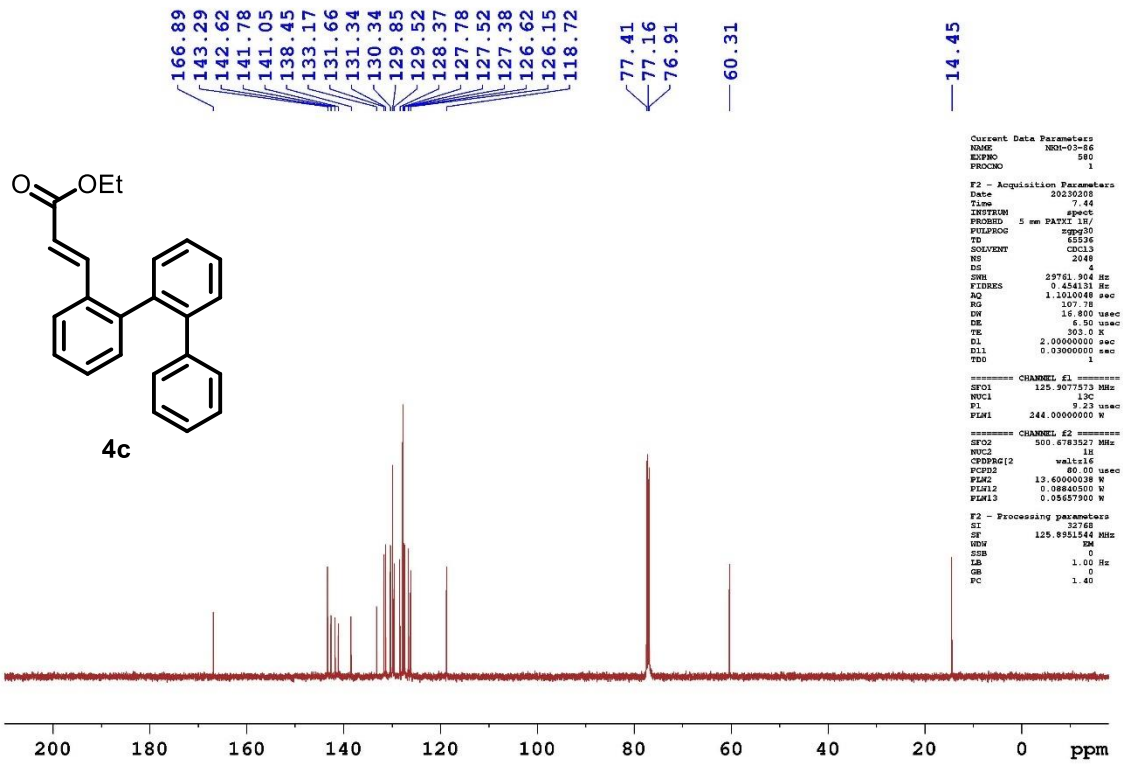

Figure S-09: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4c**

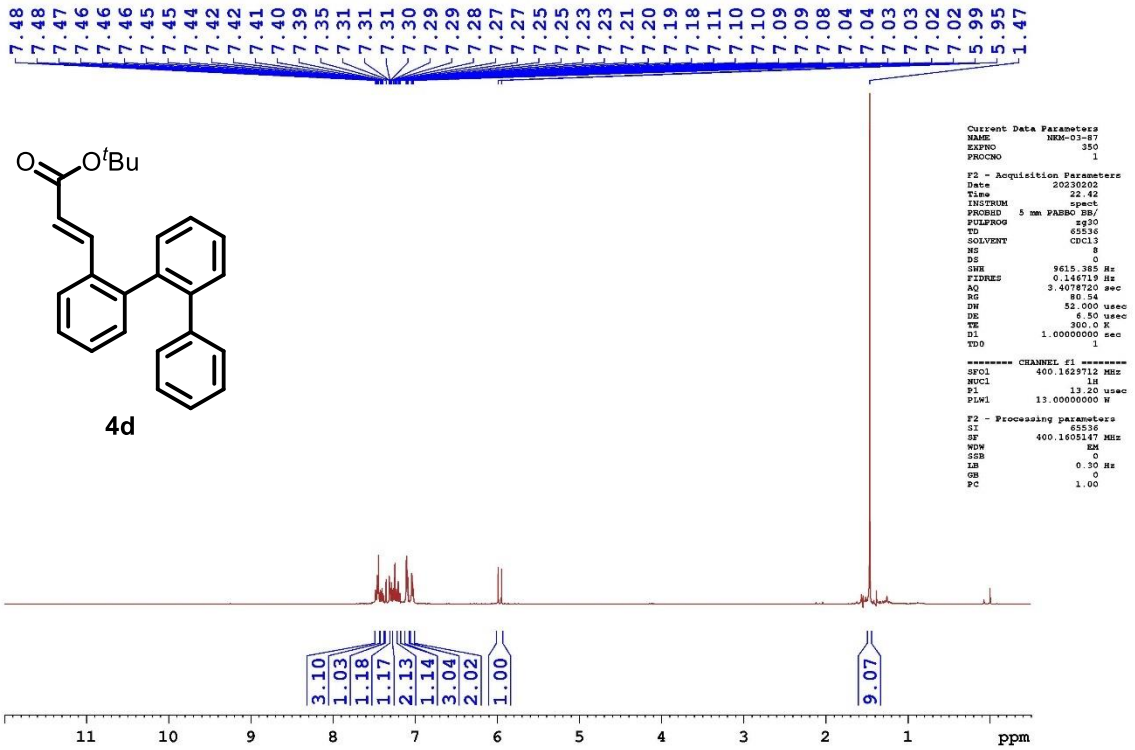

Figure S-10: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4d**

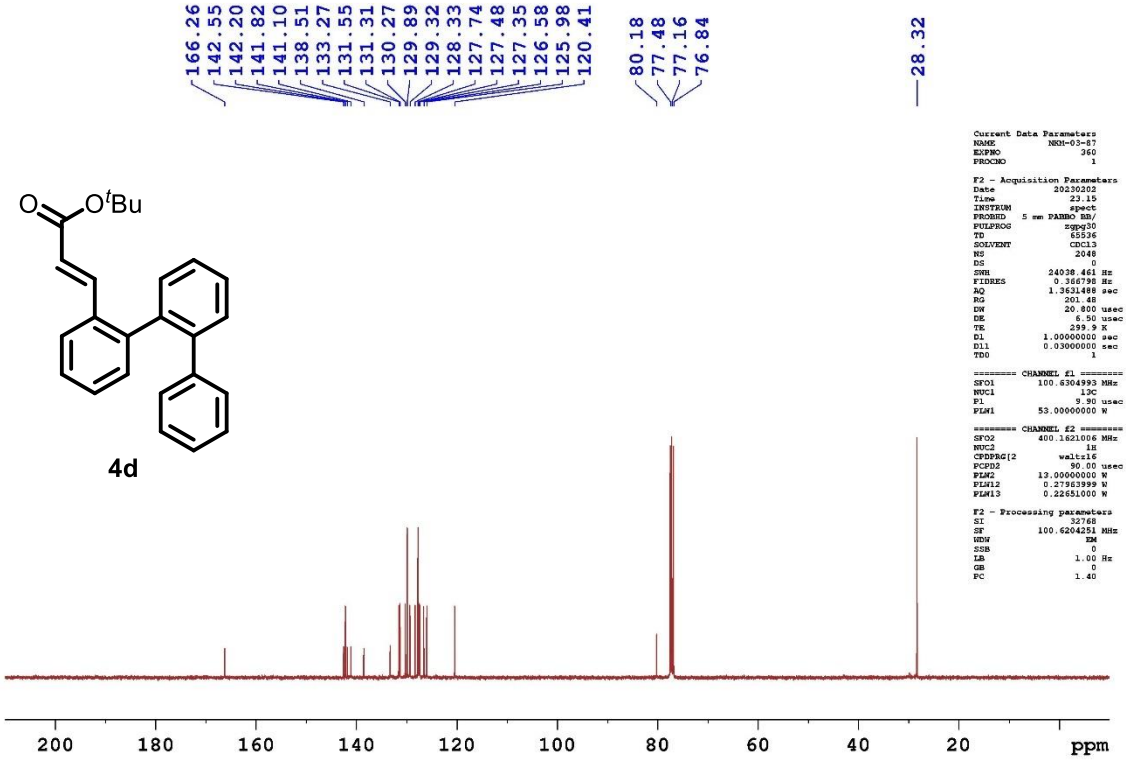

Figure S-11: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4d**

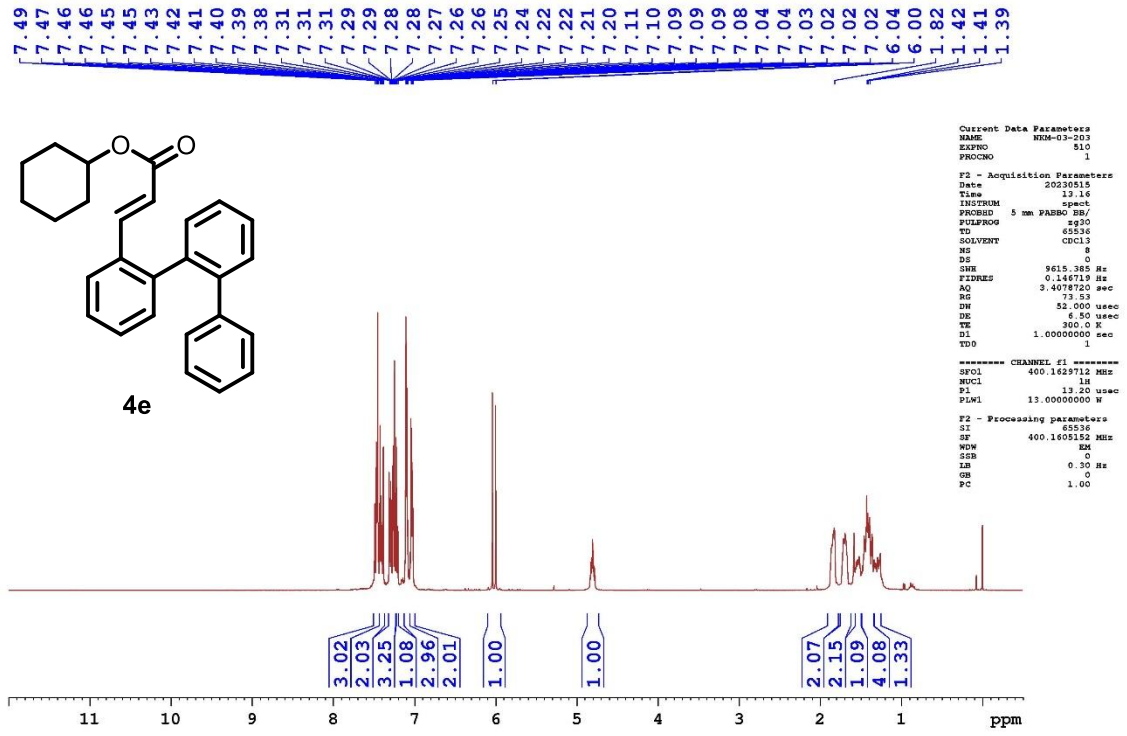

Figure S-12: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4e**

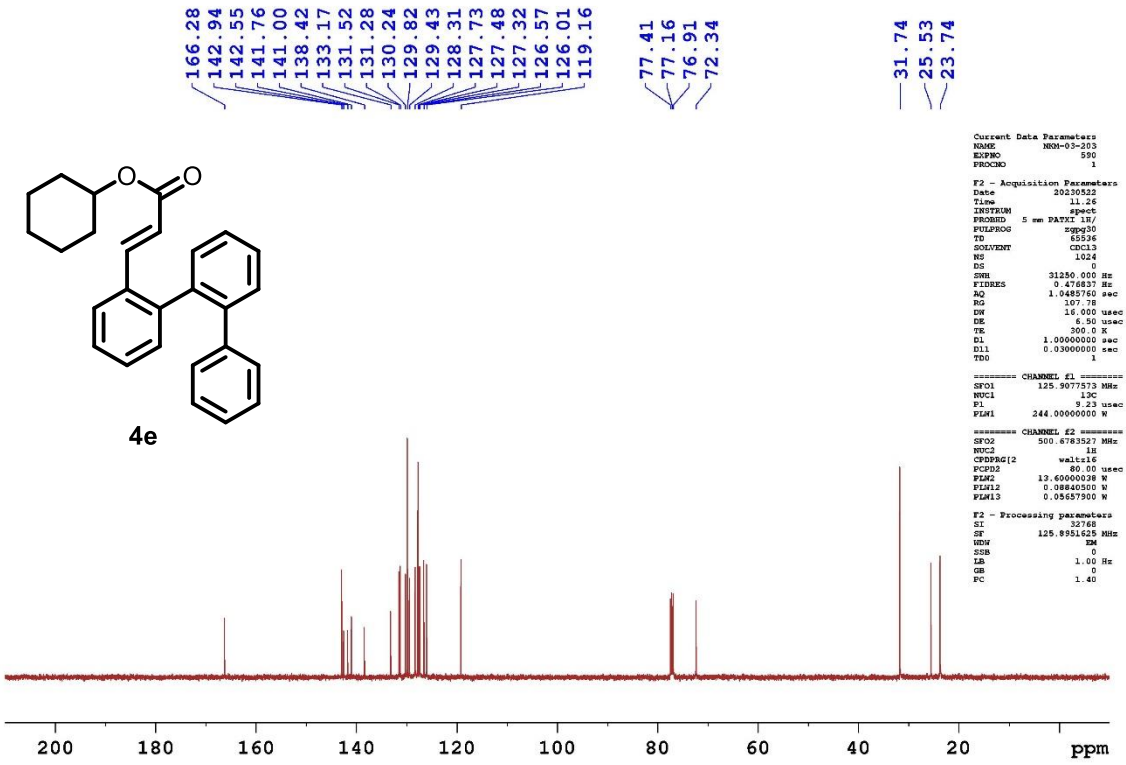

Figure S-13: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4e**

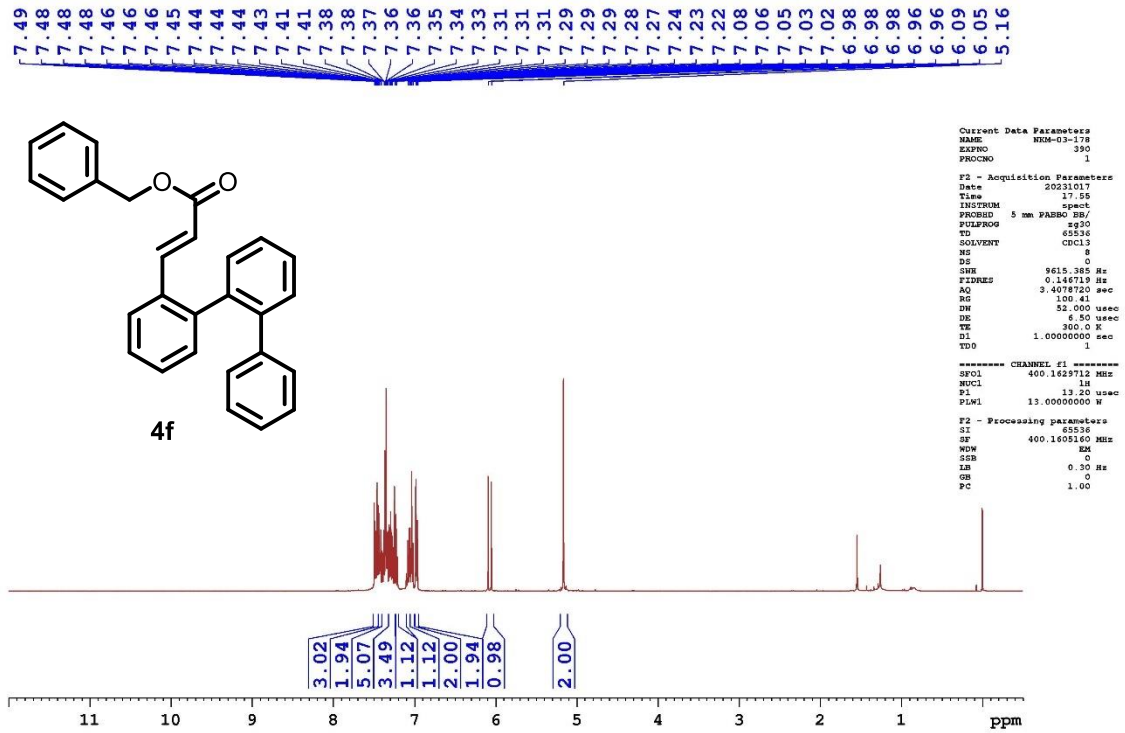

Figure S-14: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4f**

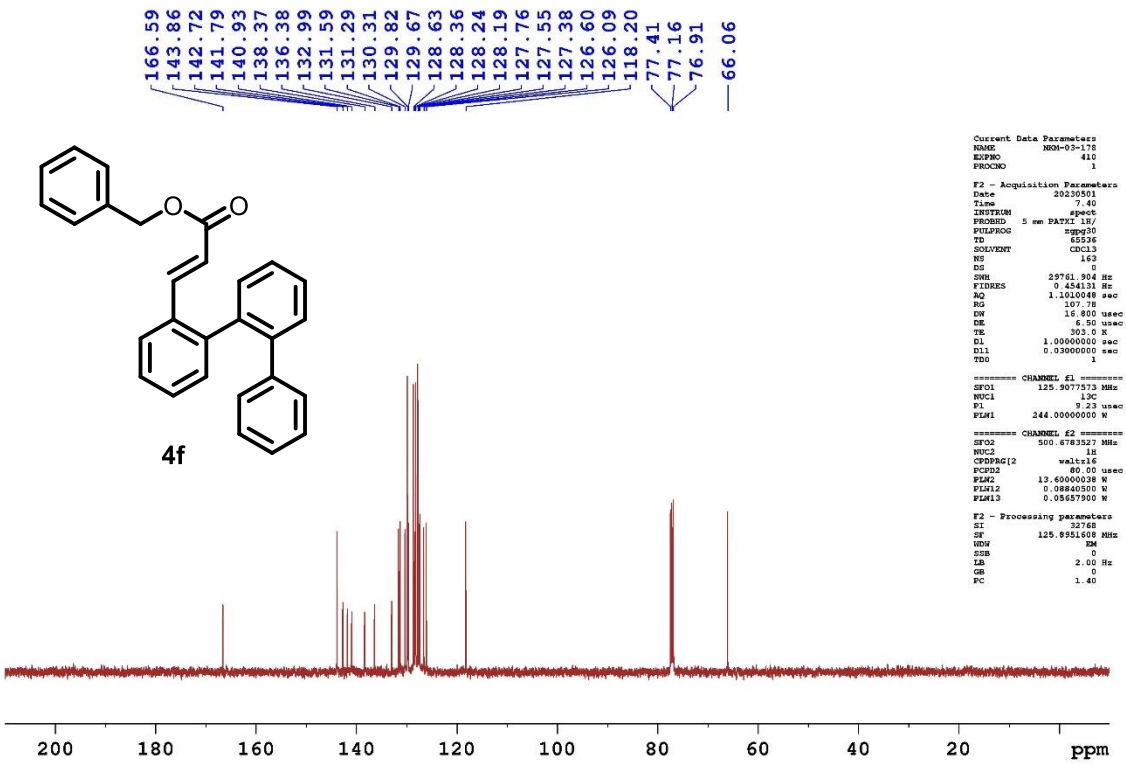

Figure S-15: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4f**

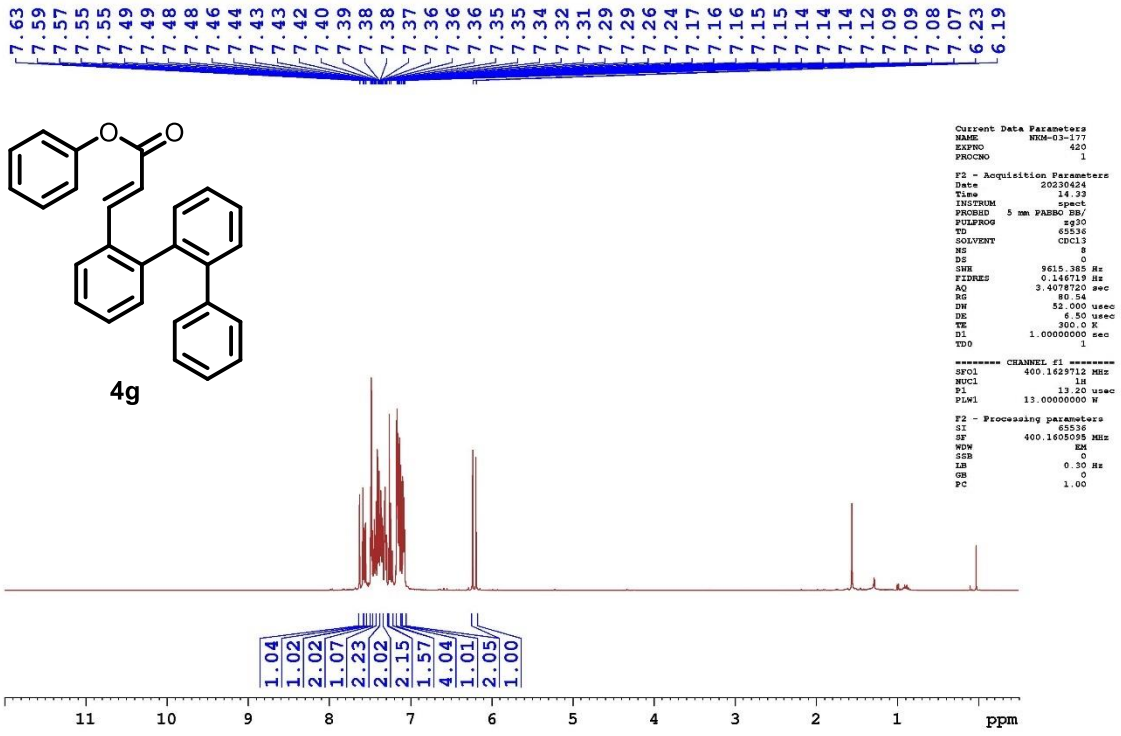

Figure S-16: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4g**

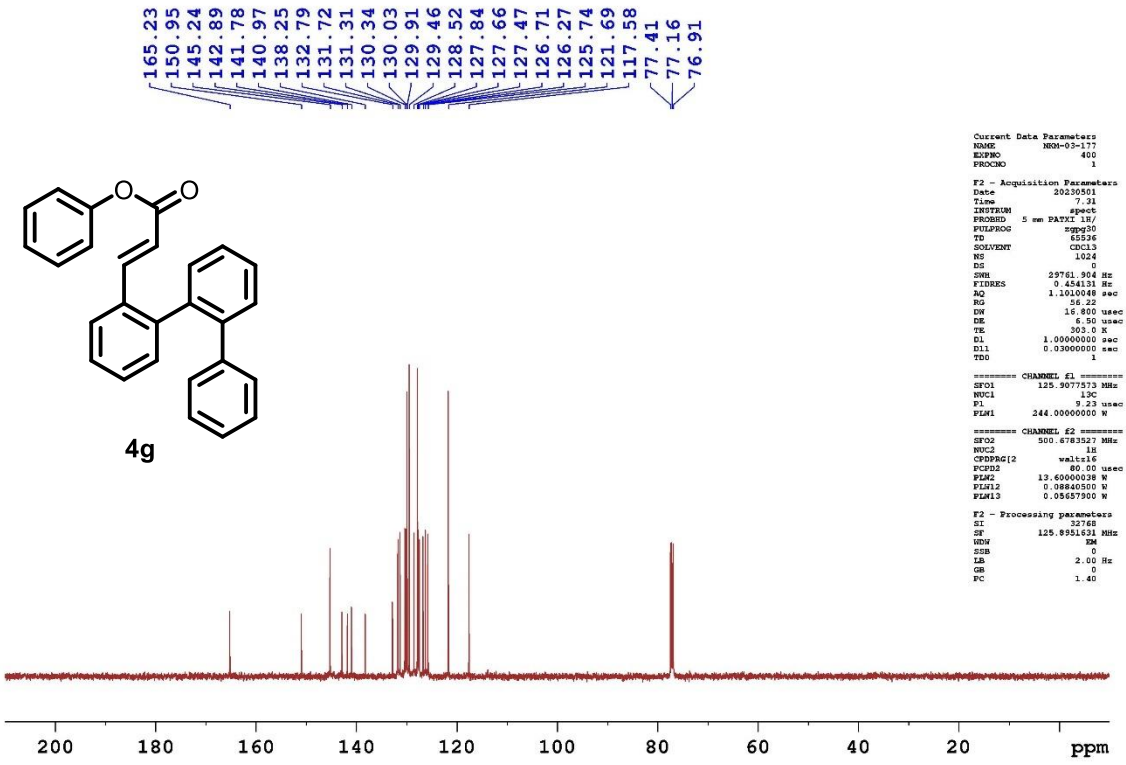

Figure S-17: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4g**

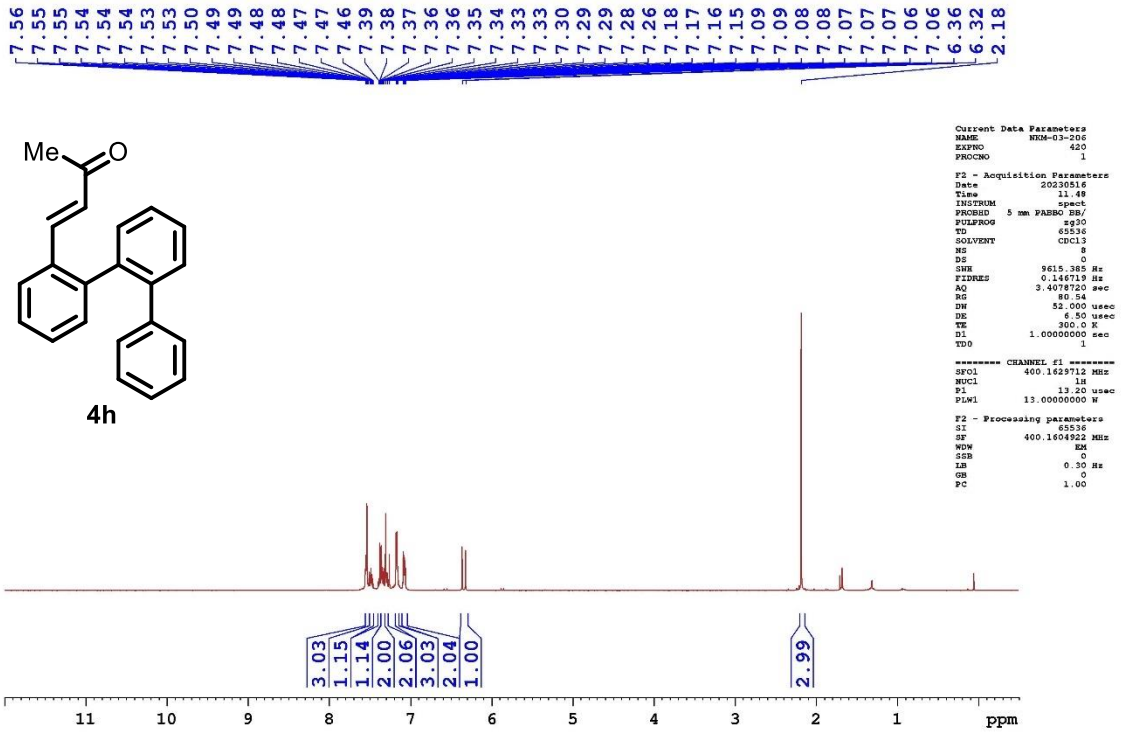

Figure S-18: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4h**

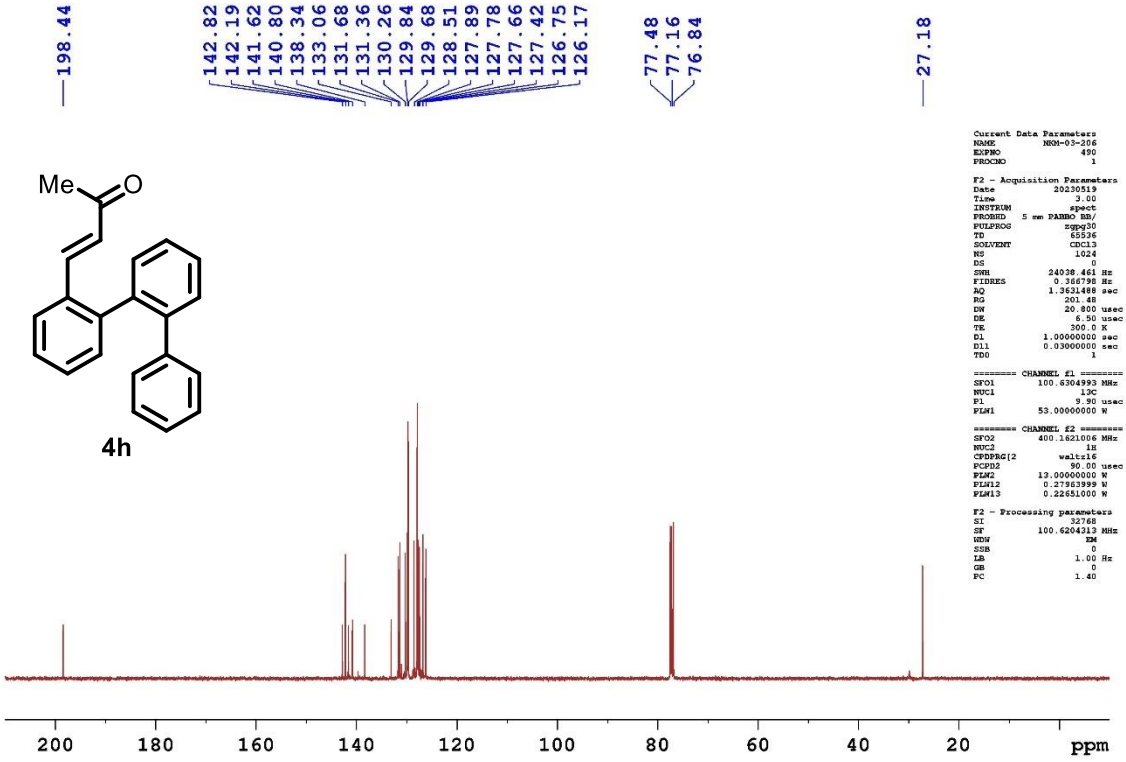

Figure S-19: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4h**

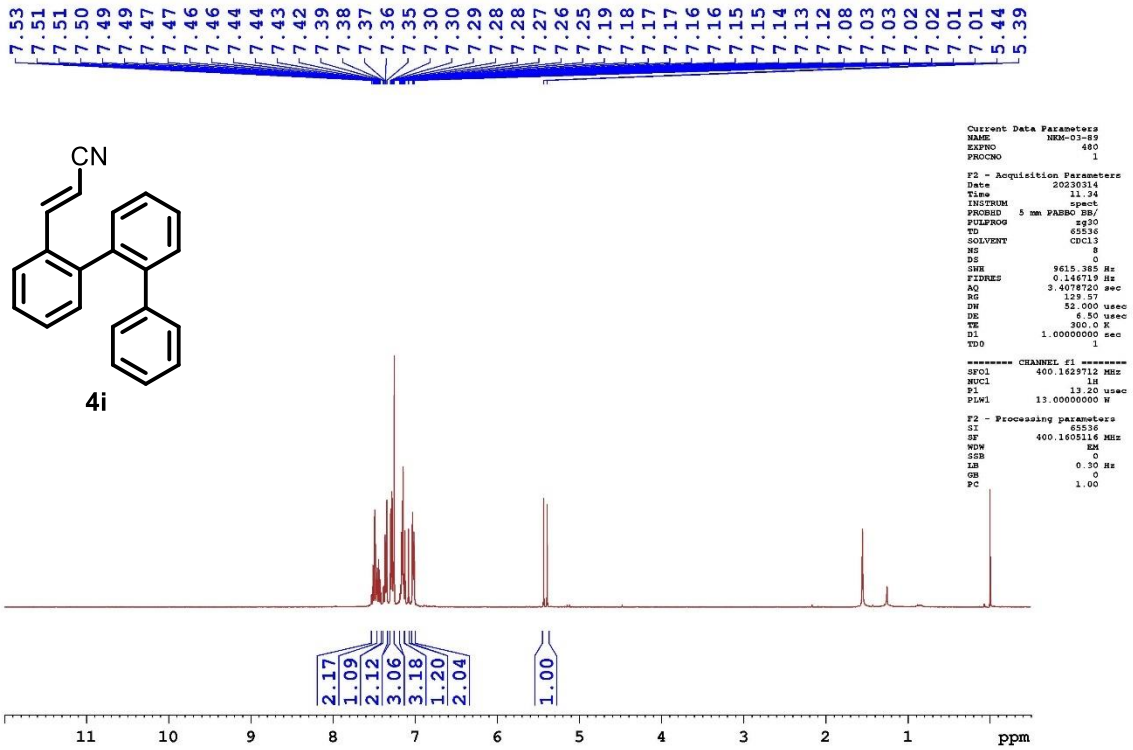

Figure S-20: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4i**

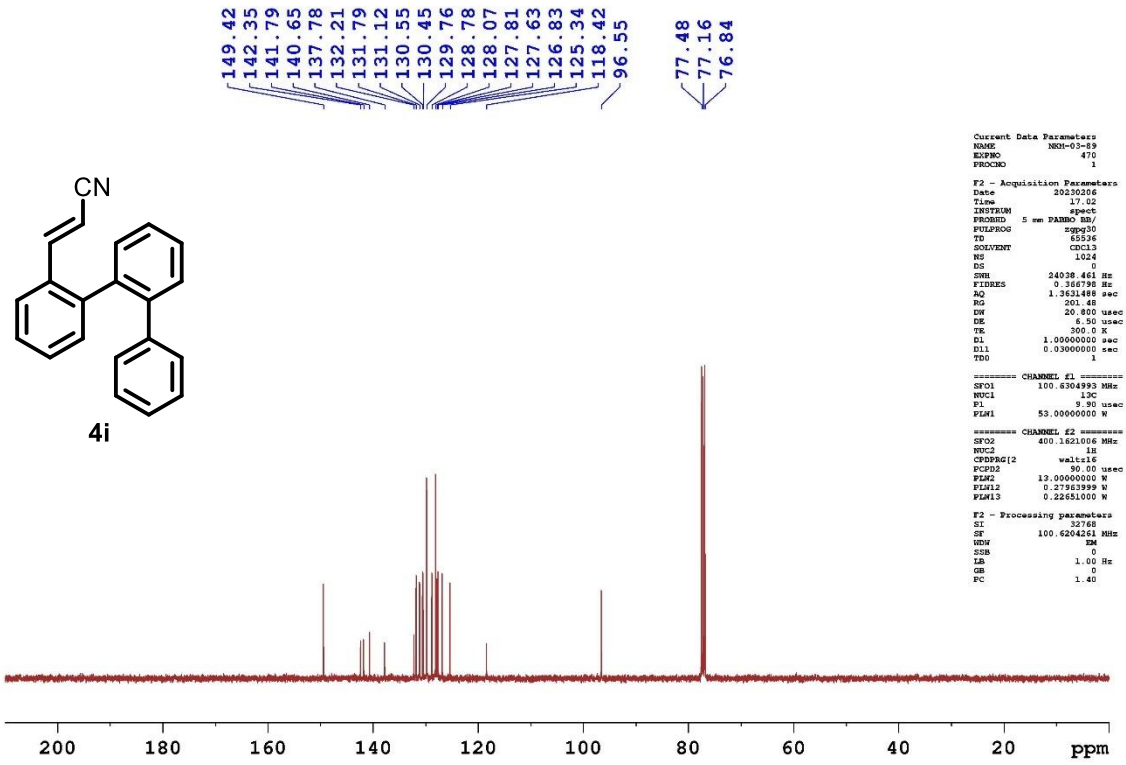

Figure S-21: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4i**

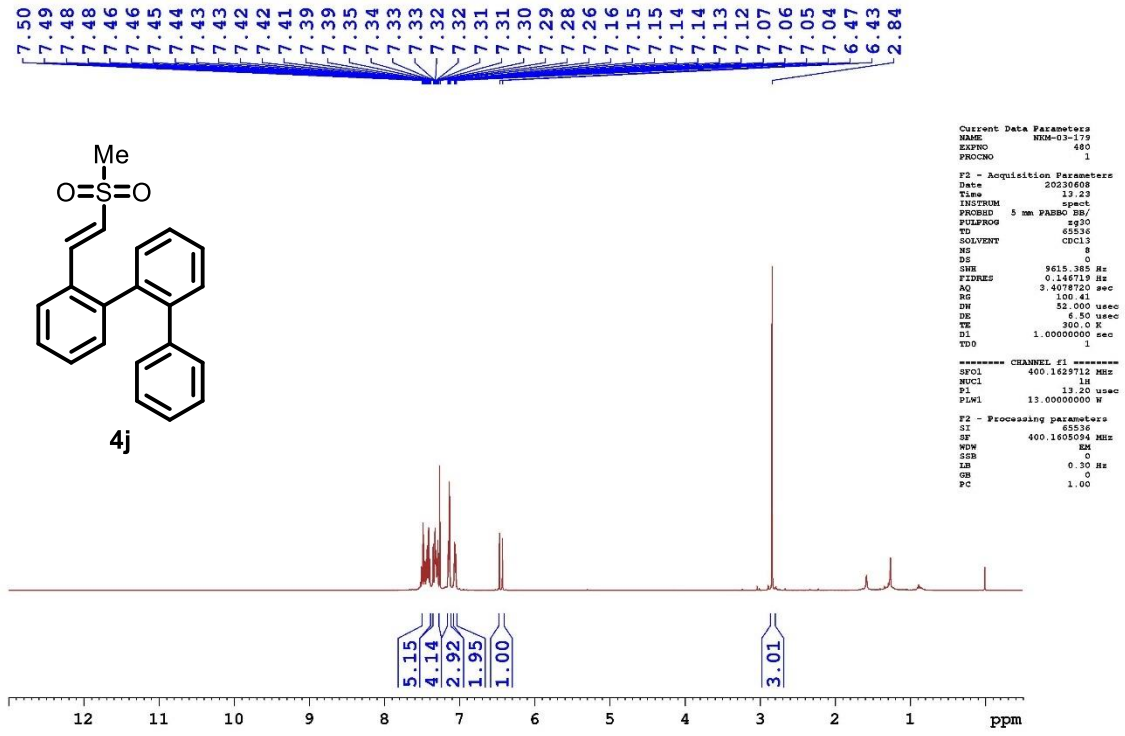

Figure S-22: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4j**

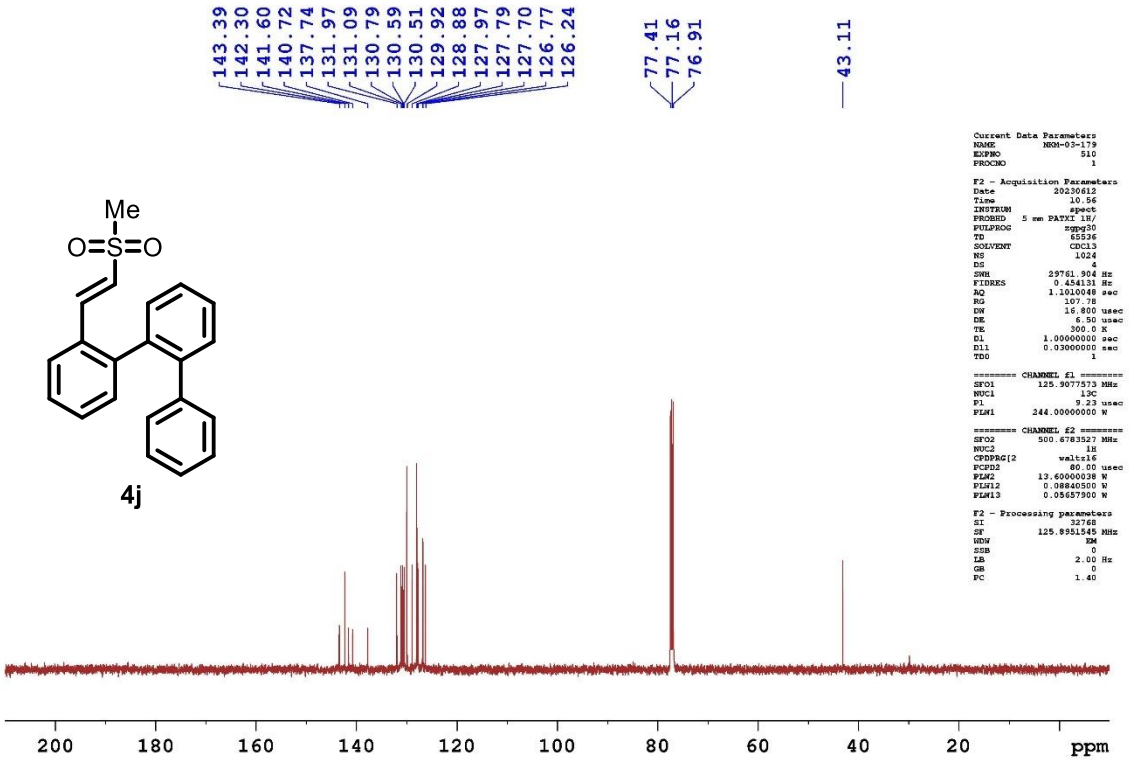

Figure S-23: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4j**

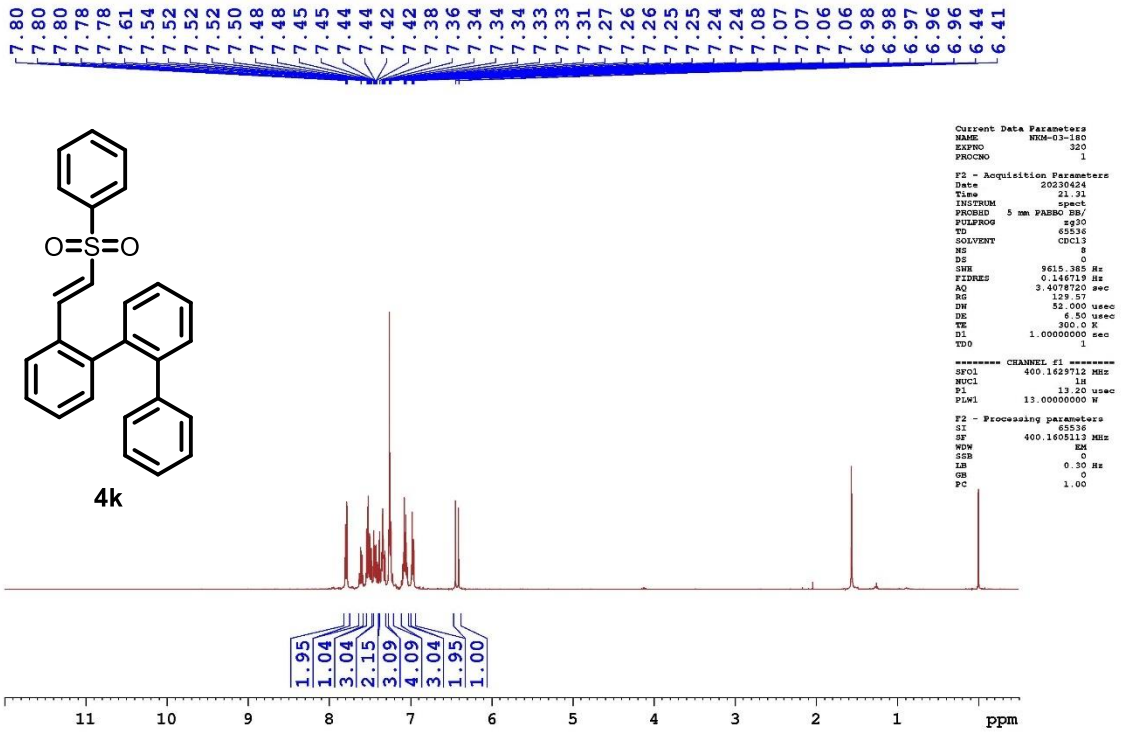

Figure S-24: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4k**

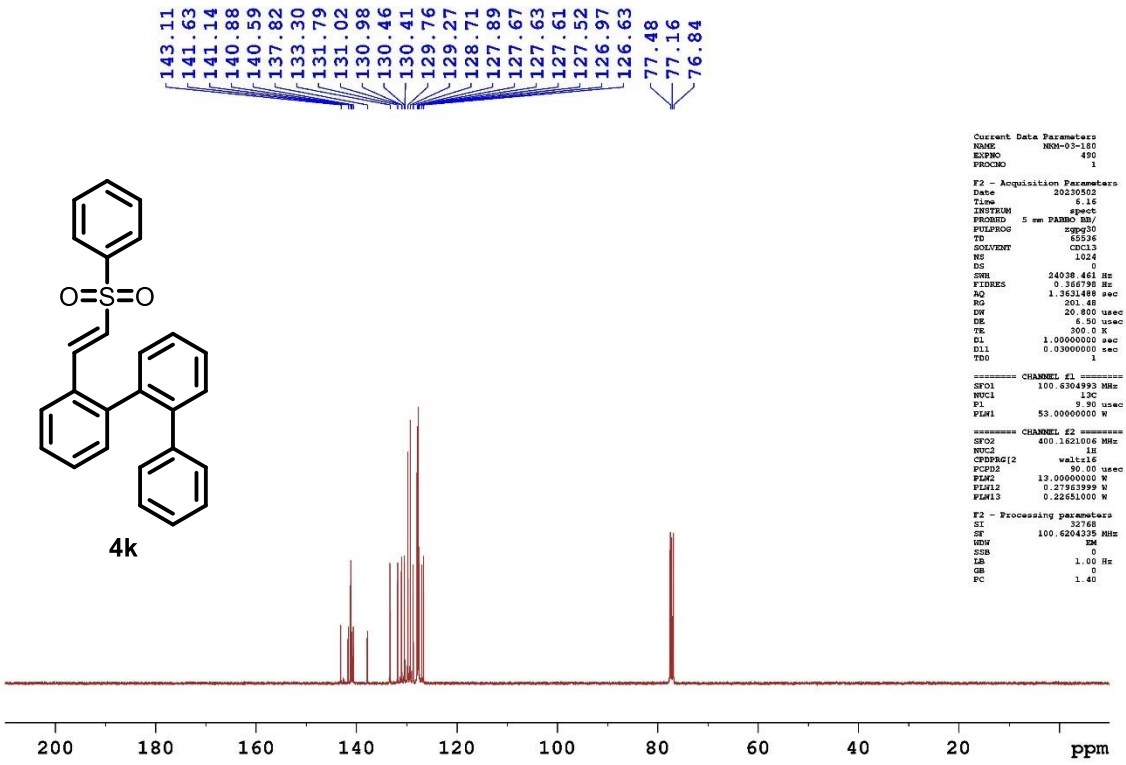

Figure S-25: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4k**

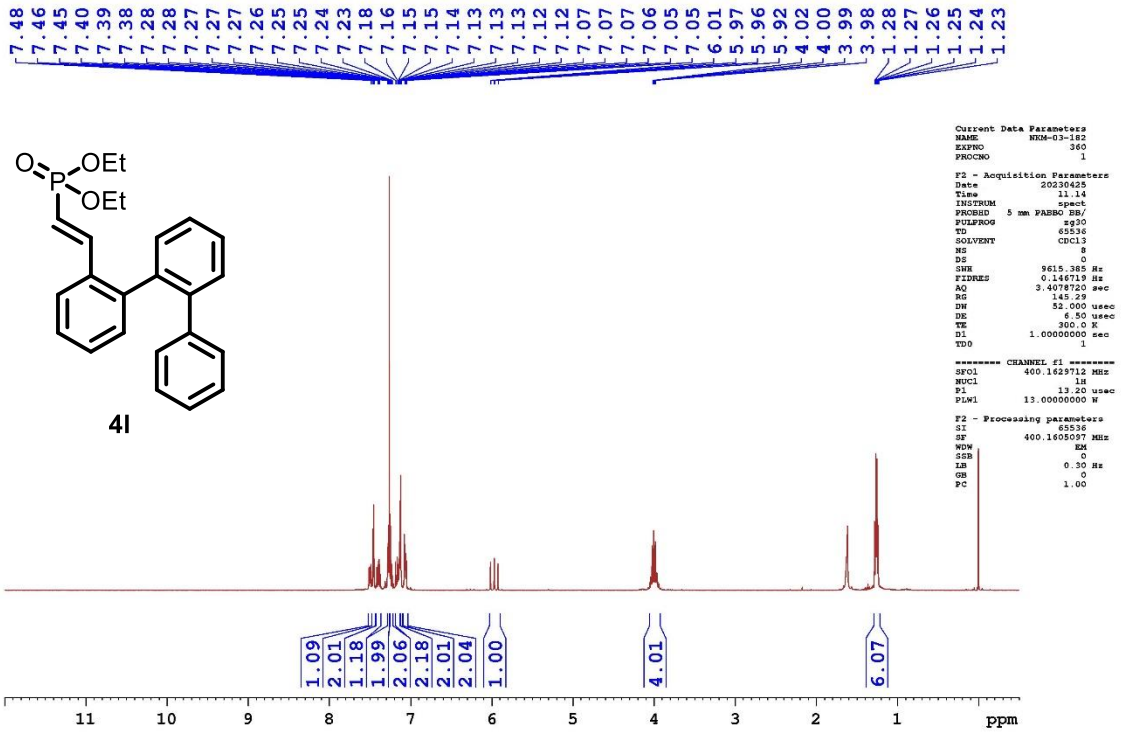

Figure S-26: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4l**

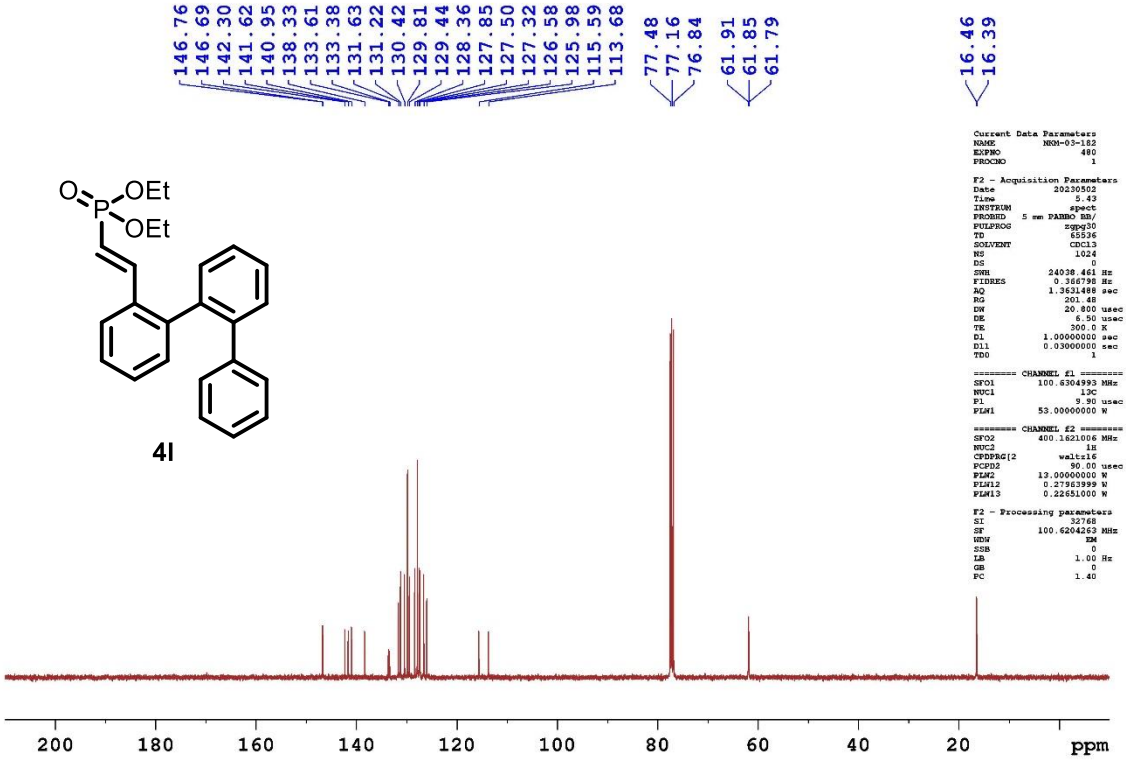

Figure S-27: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4l**

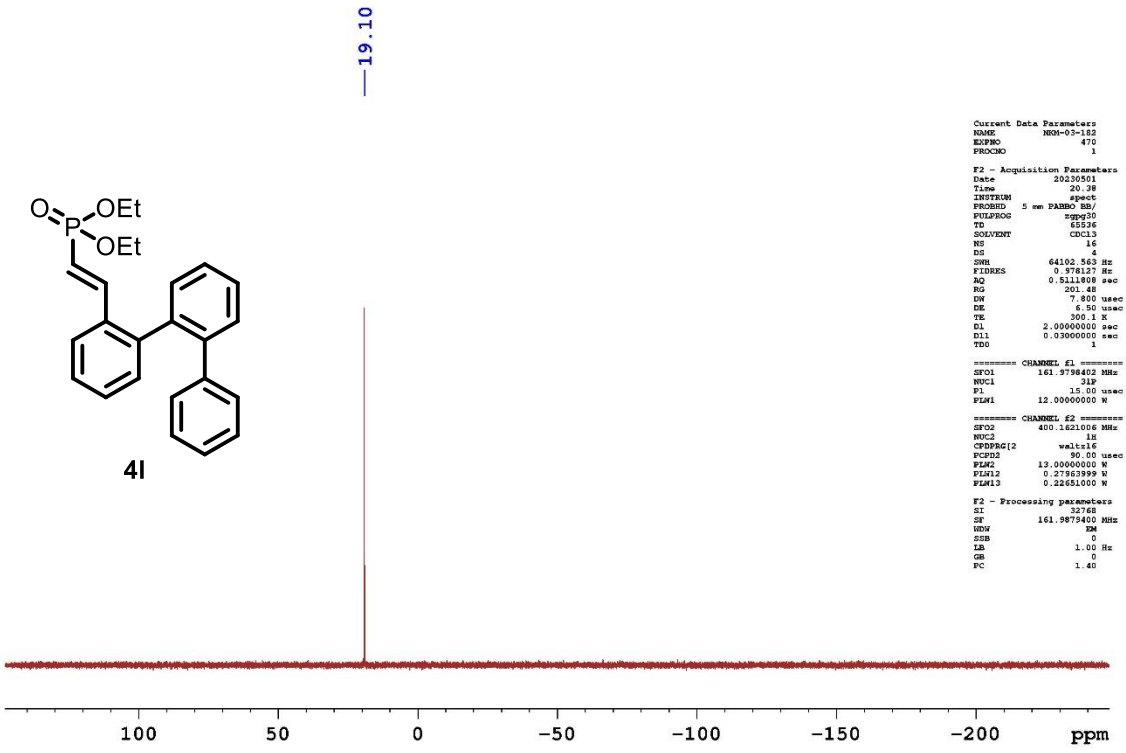

Figure S-28: ^{31}P NMR (161 MHz, $CDCl_3$) spectrum of compound **4l**

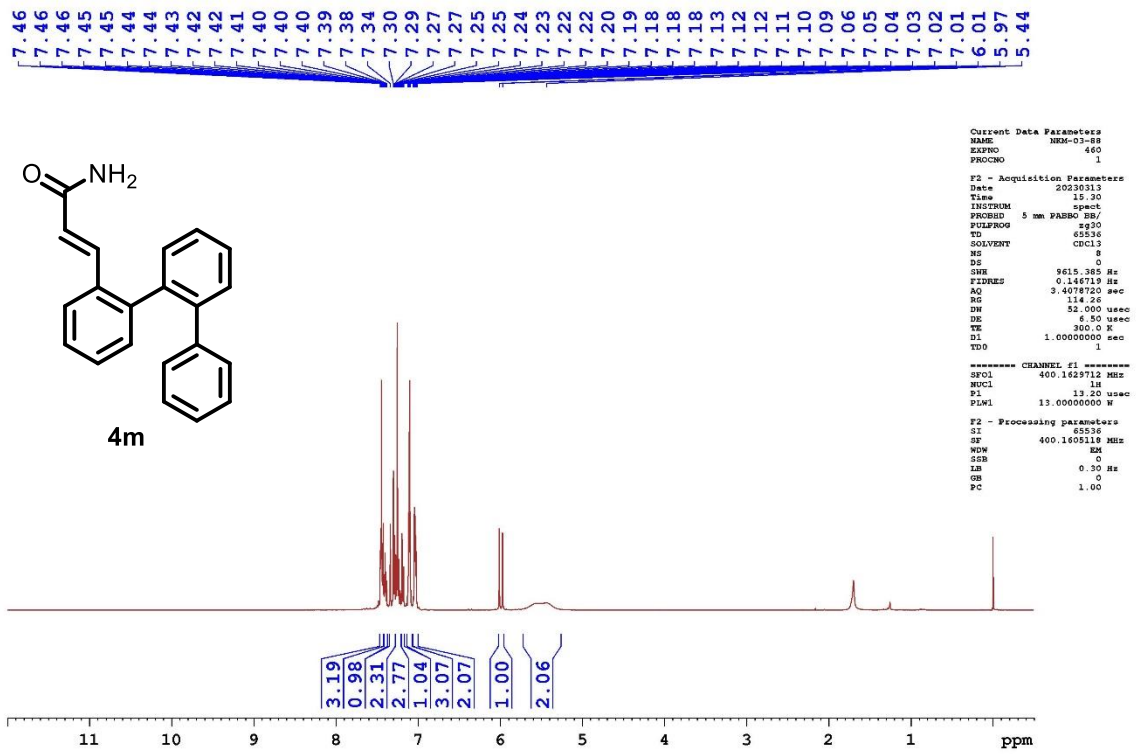

Figure S-29: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4m**

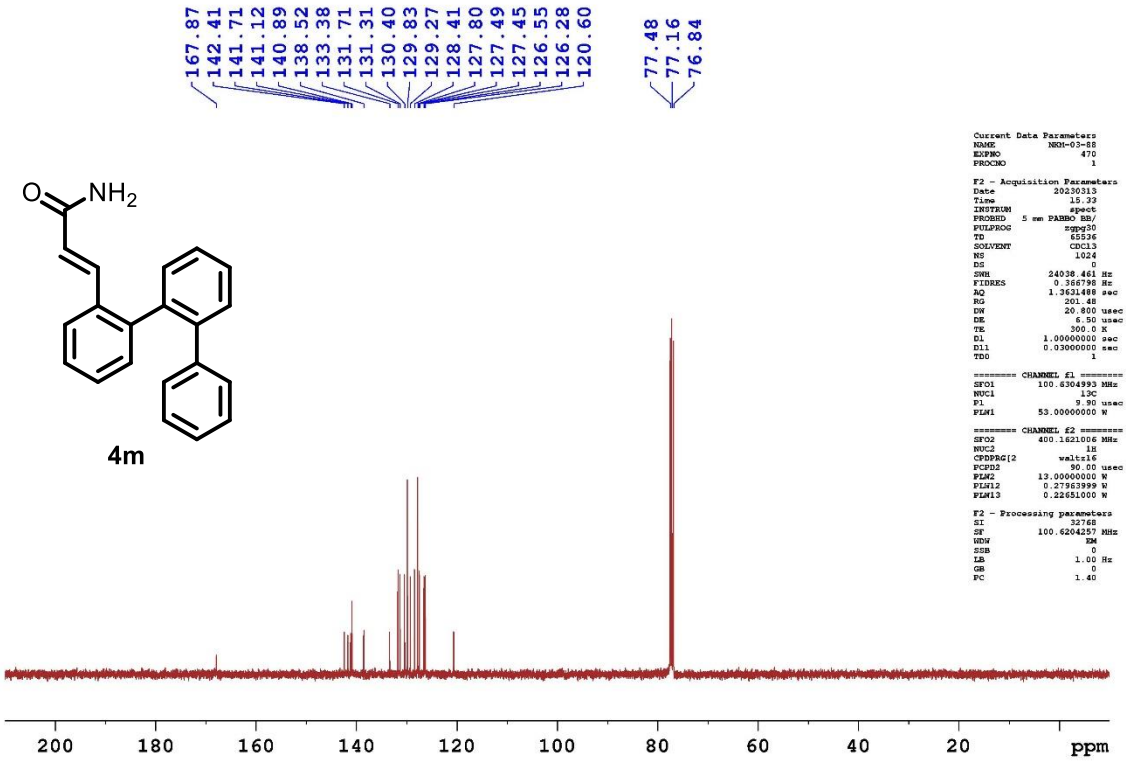

Figure S-30: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4m**

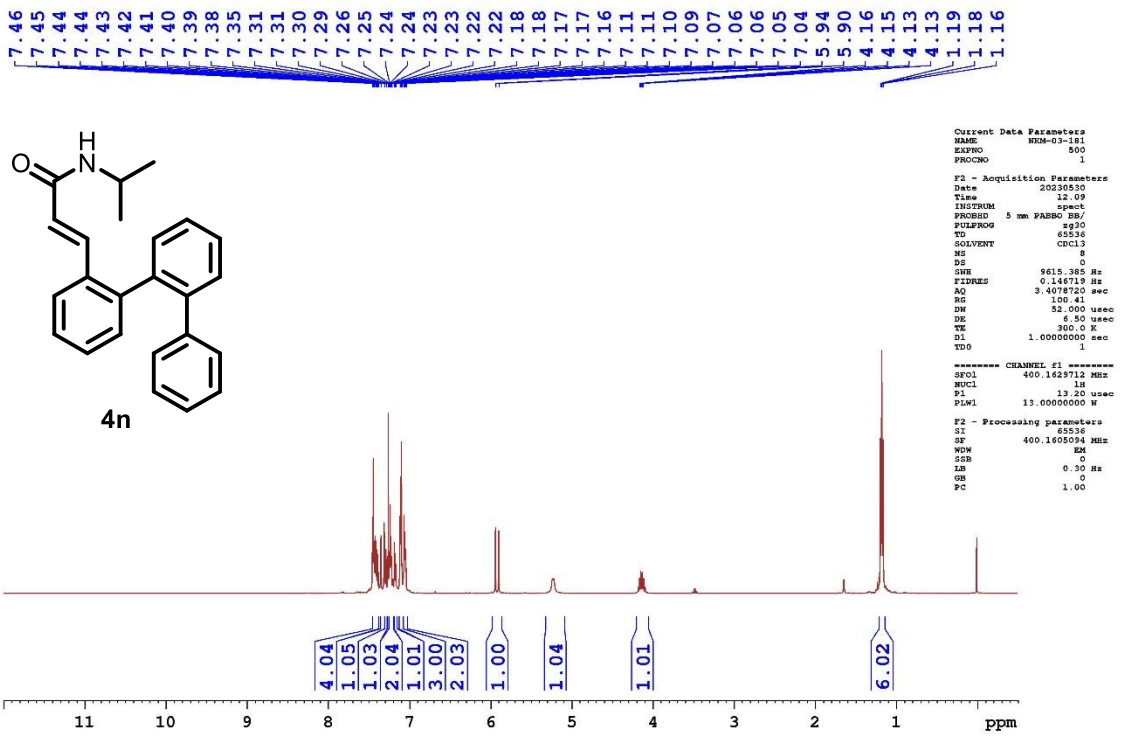

Figure S-31: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4n**

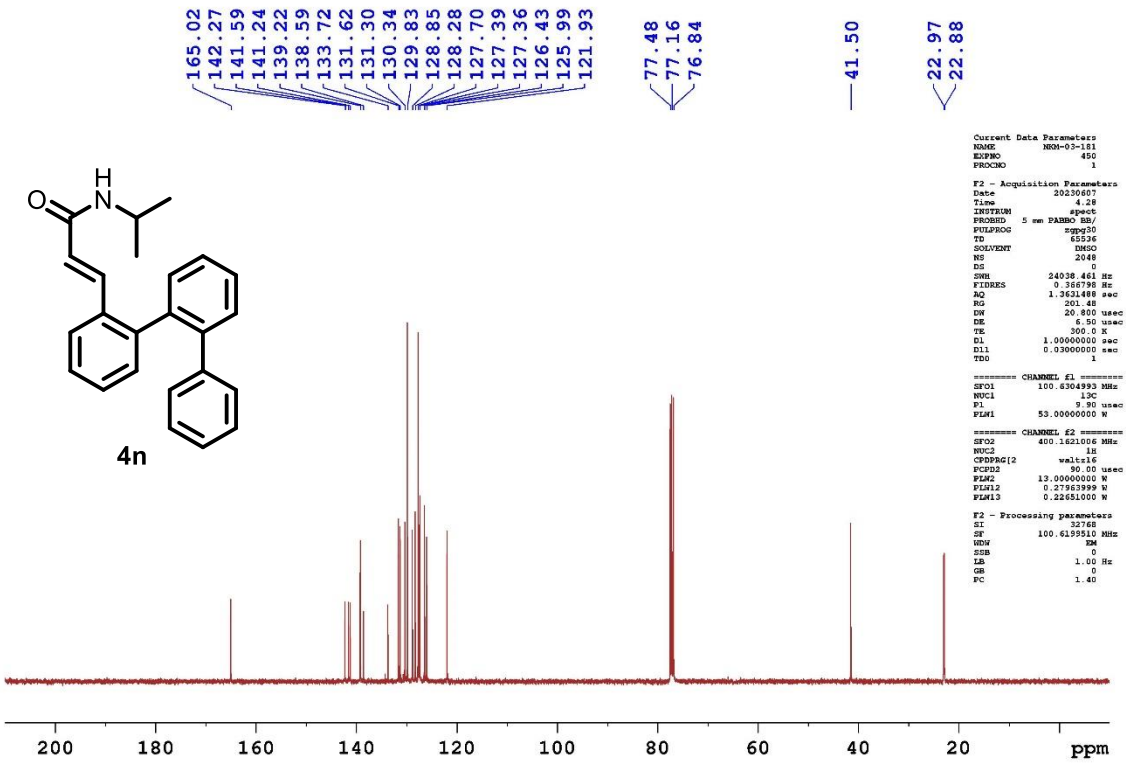

Figure S-32: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4n**

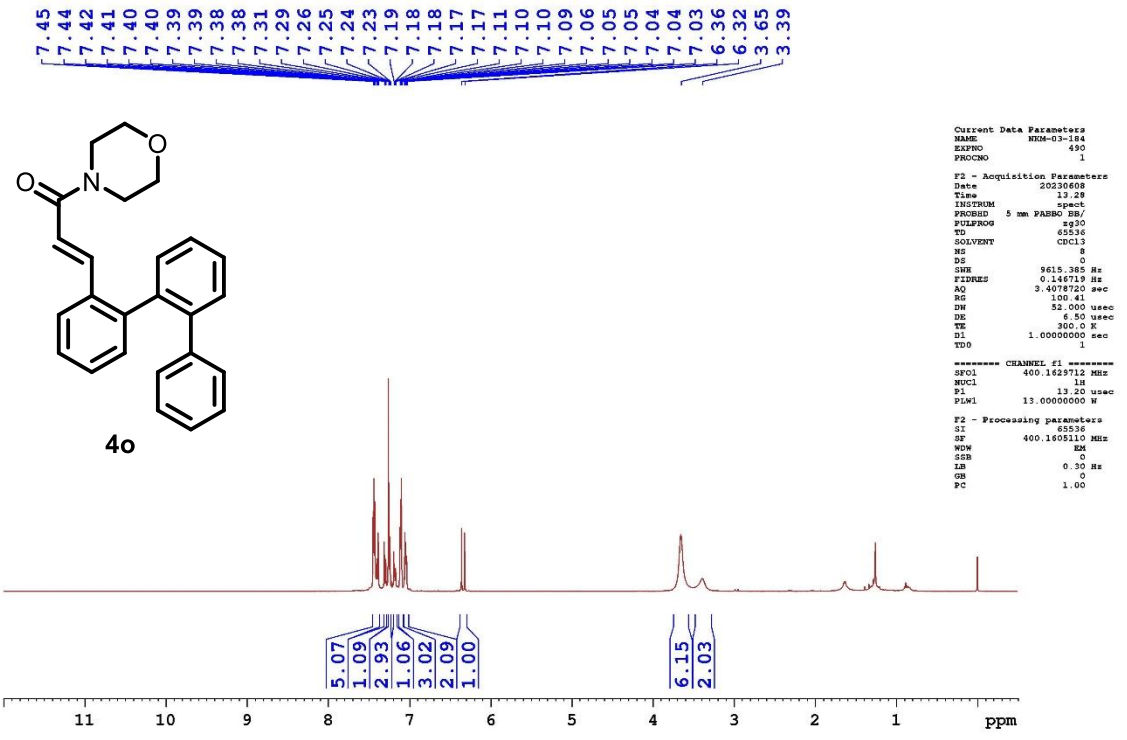

Figure S-33: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4o**

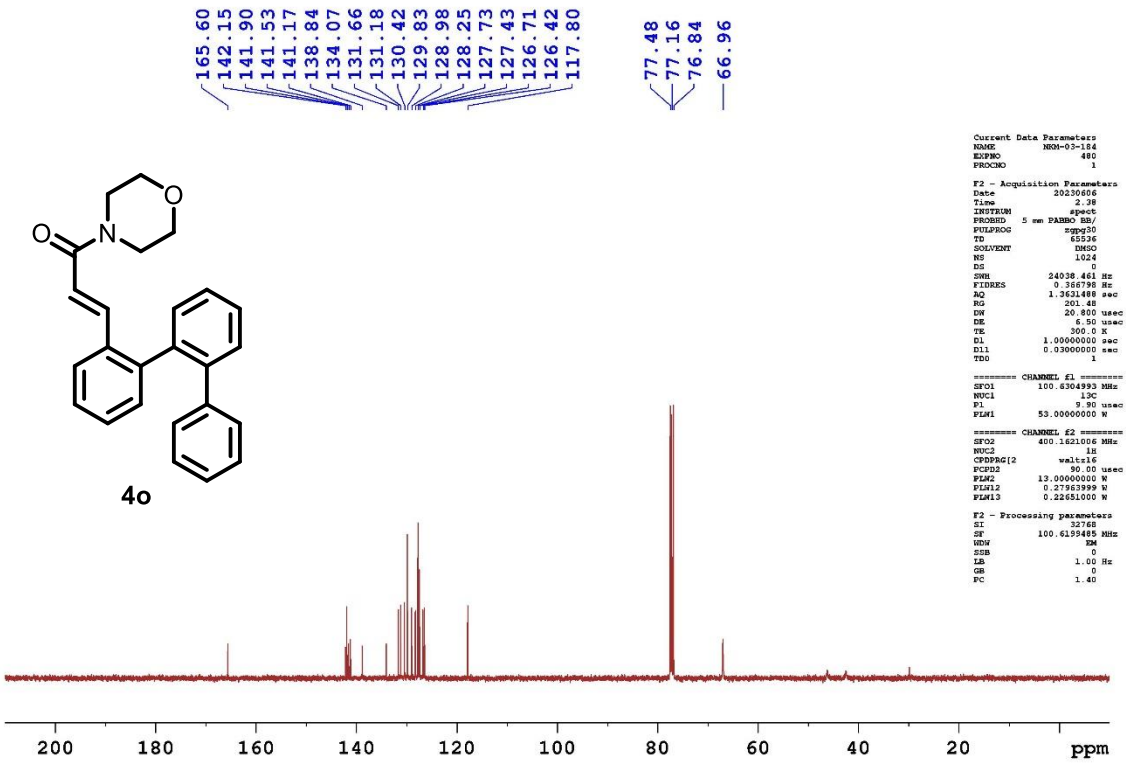

Figure S-34: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4o**

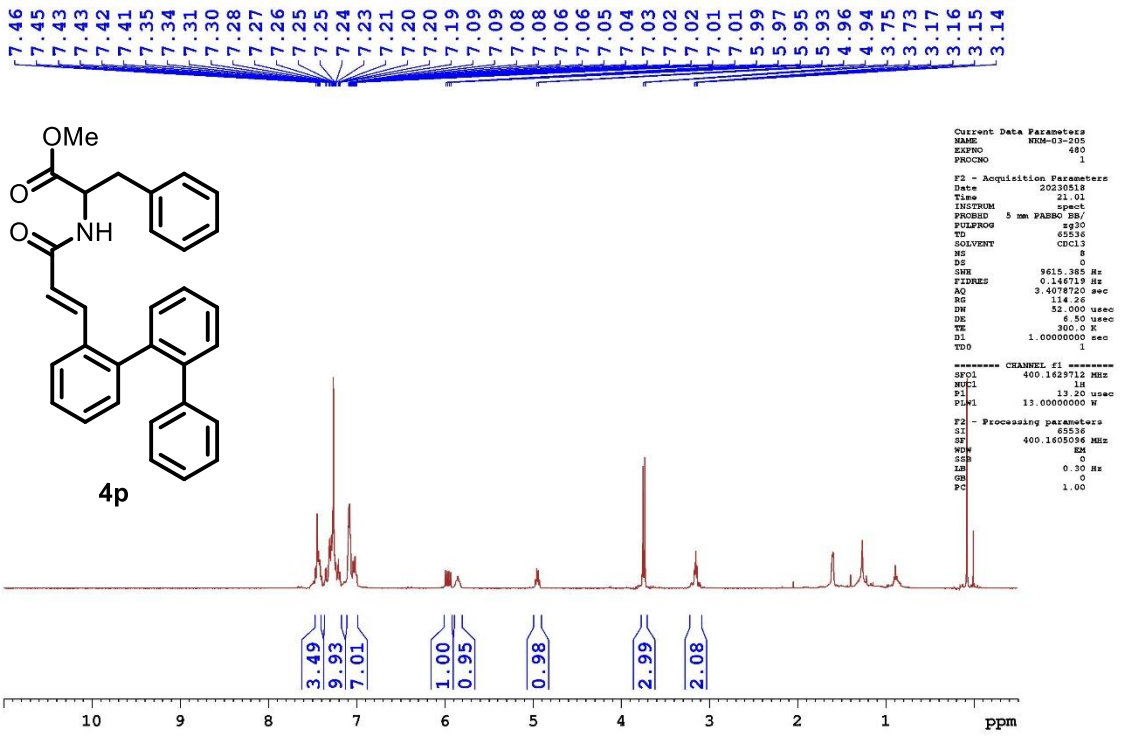

Figure S-35: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4p**

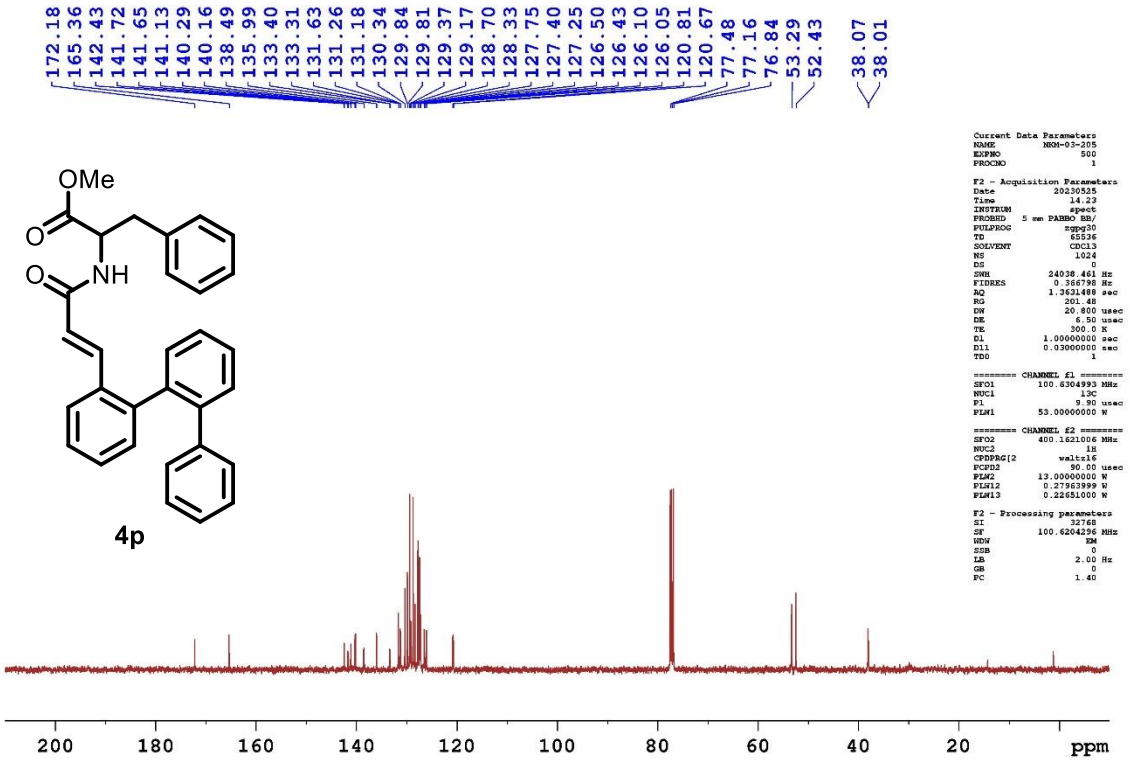

Figure S-36: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4p**

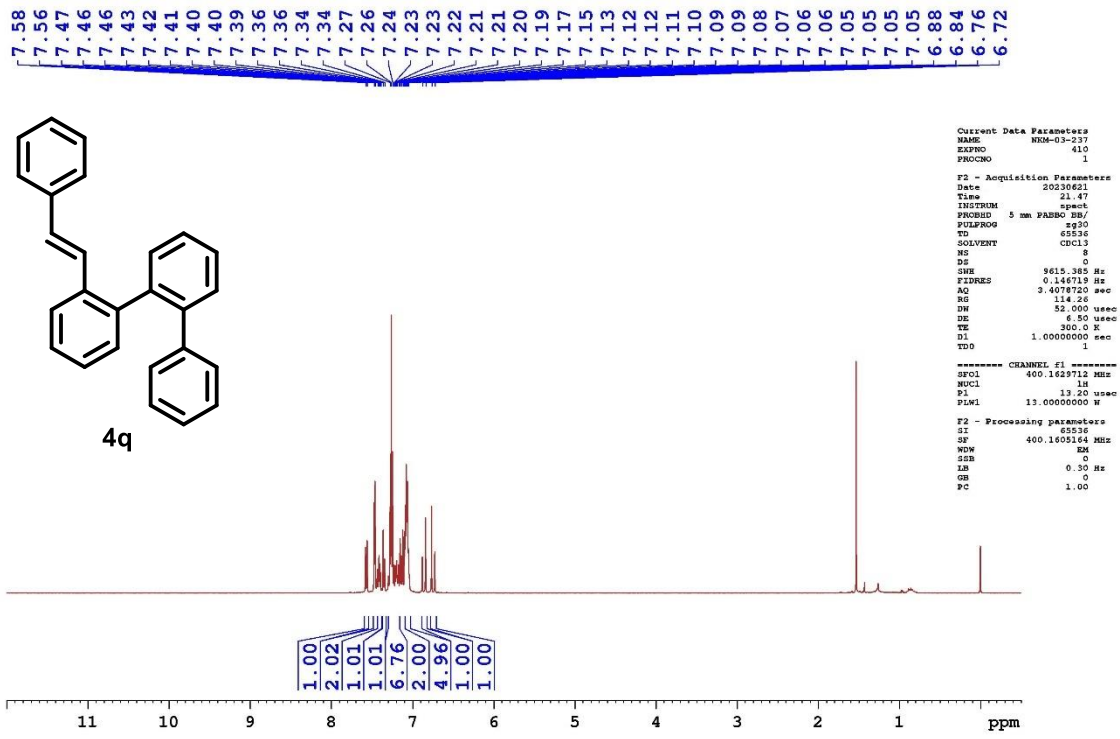

Figure S-37: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4q**

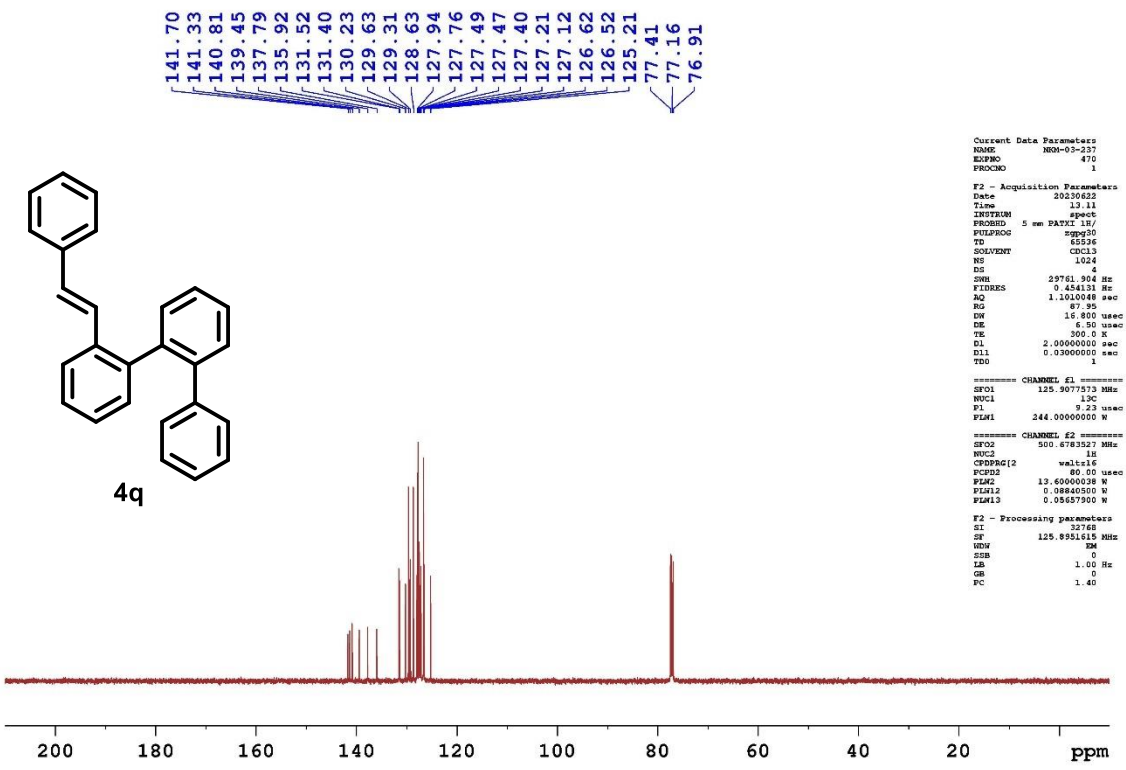

Figure S-38: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4q**

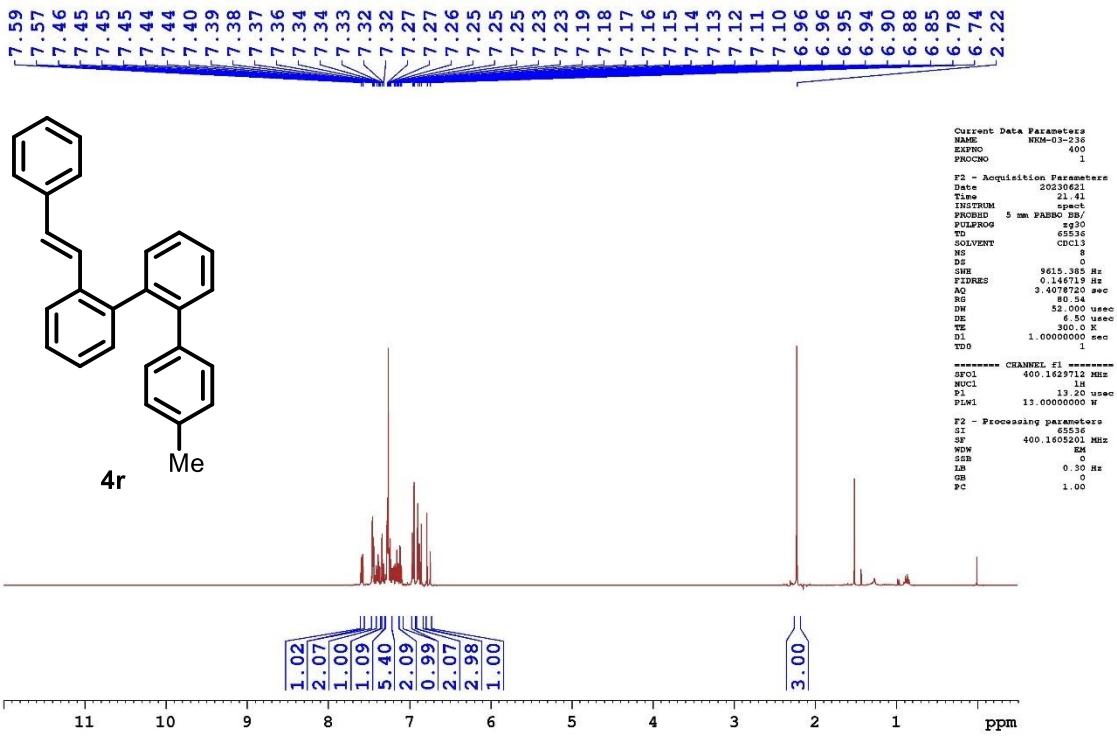

Figure S-39: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4r**

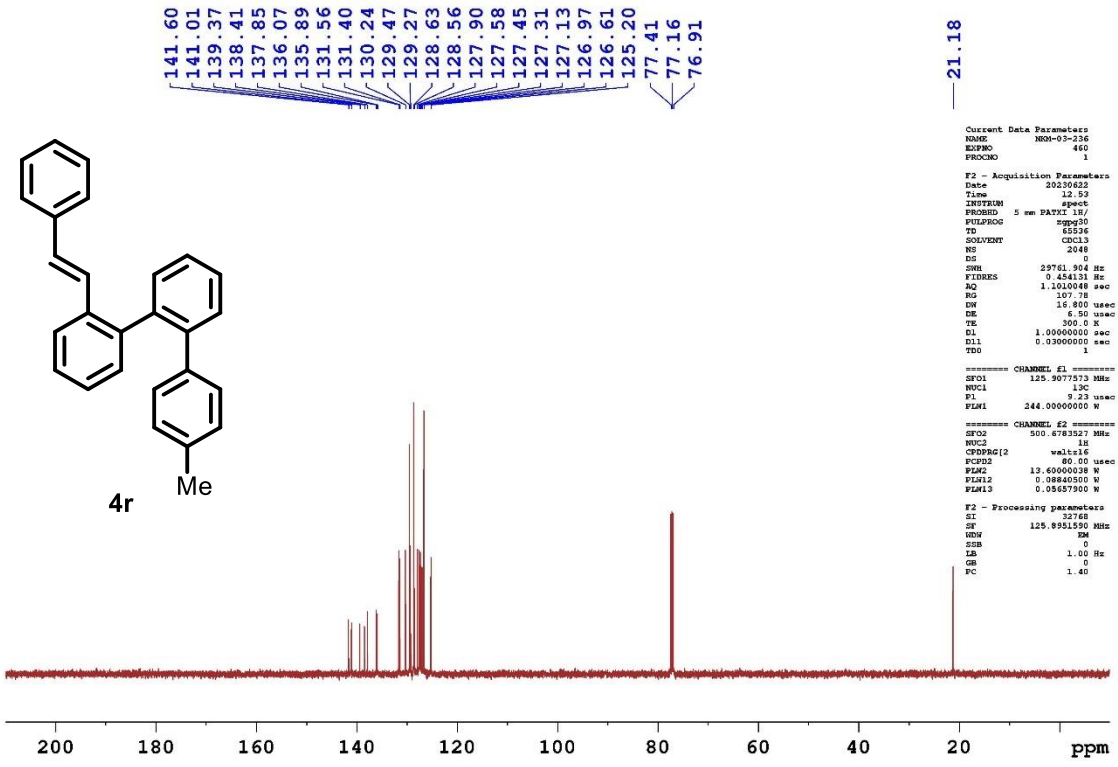

Figure S-40: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4r**

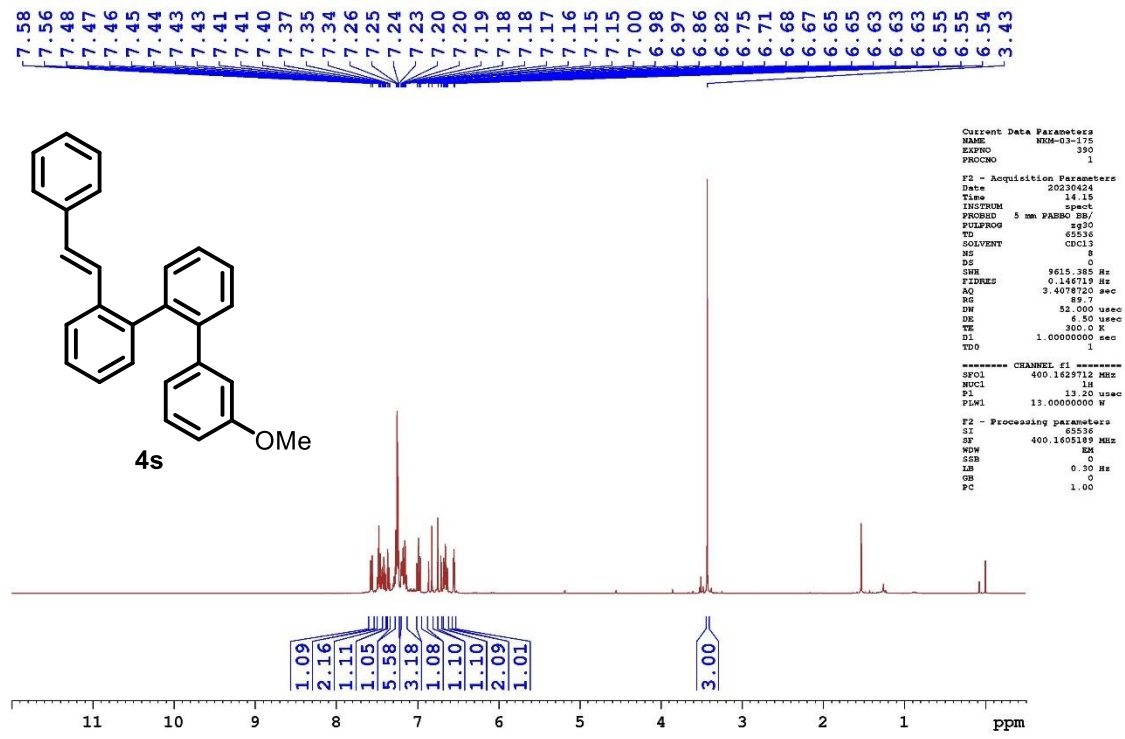

Figure S-41: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4s**

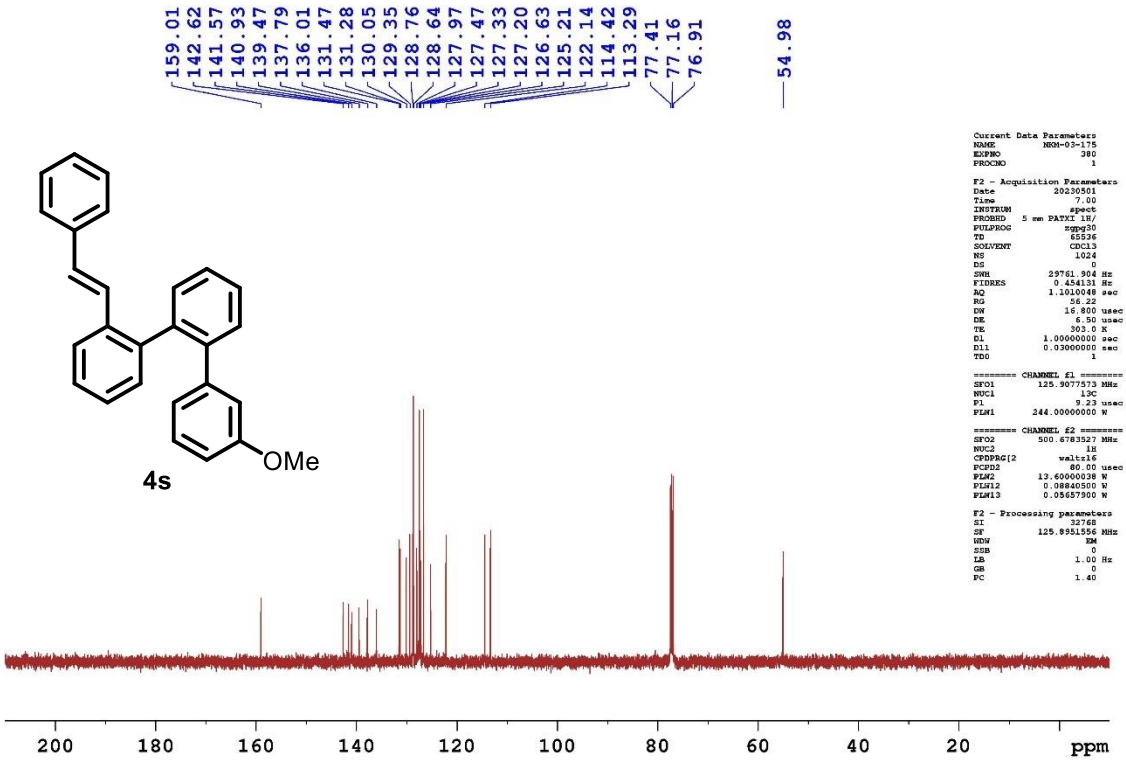

Figure S-42: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4s**

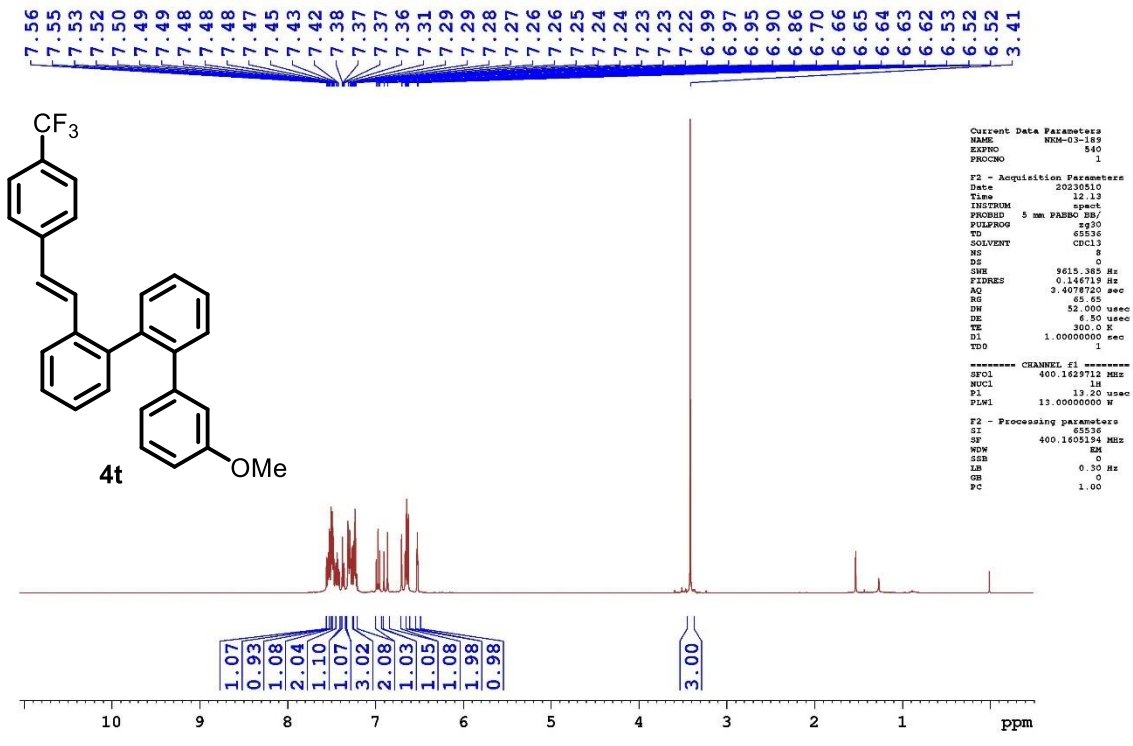

Figure S-43: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4t**

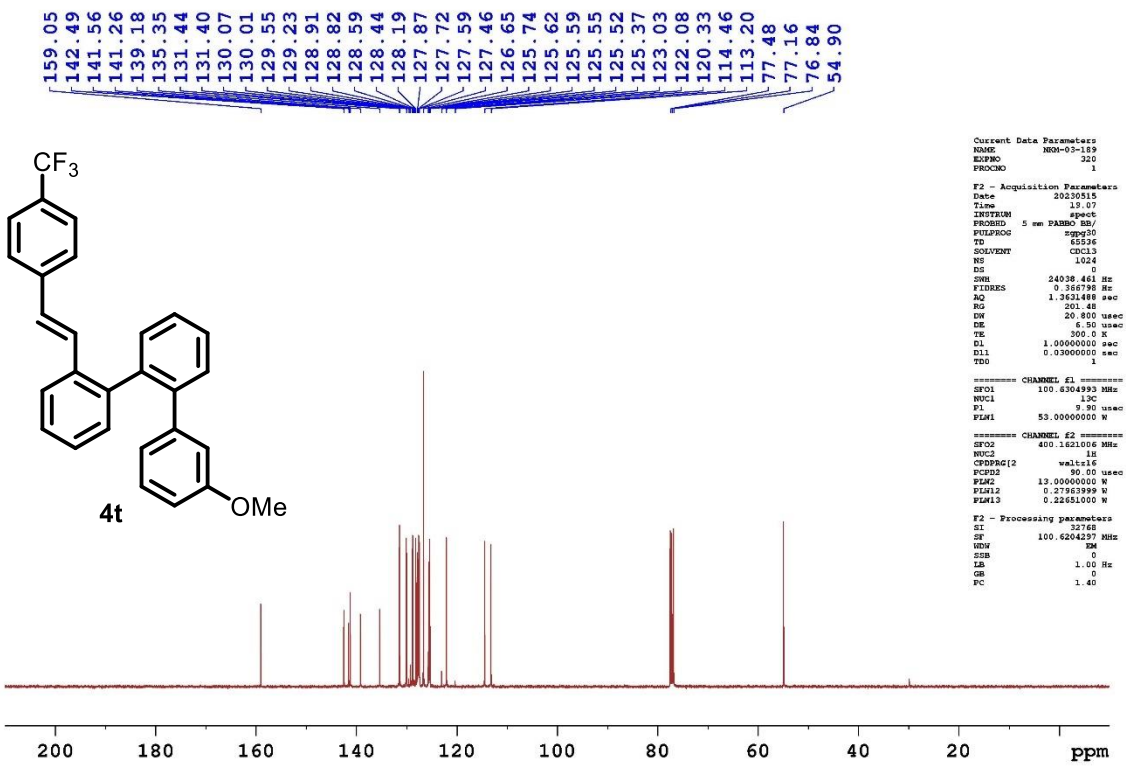

Figure S-44: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4t**

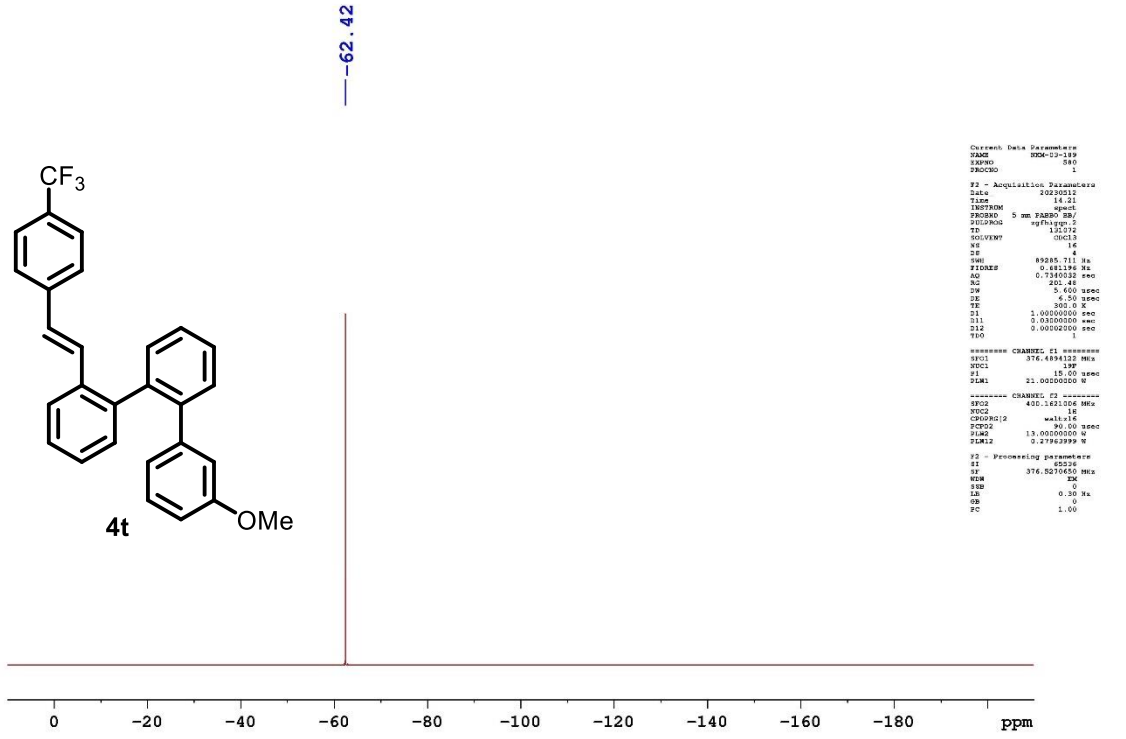

Figure S-45: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **4t**

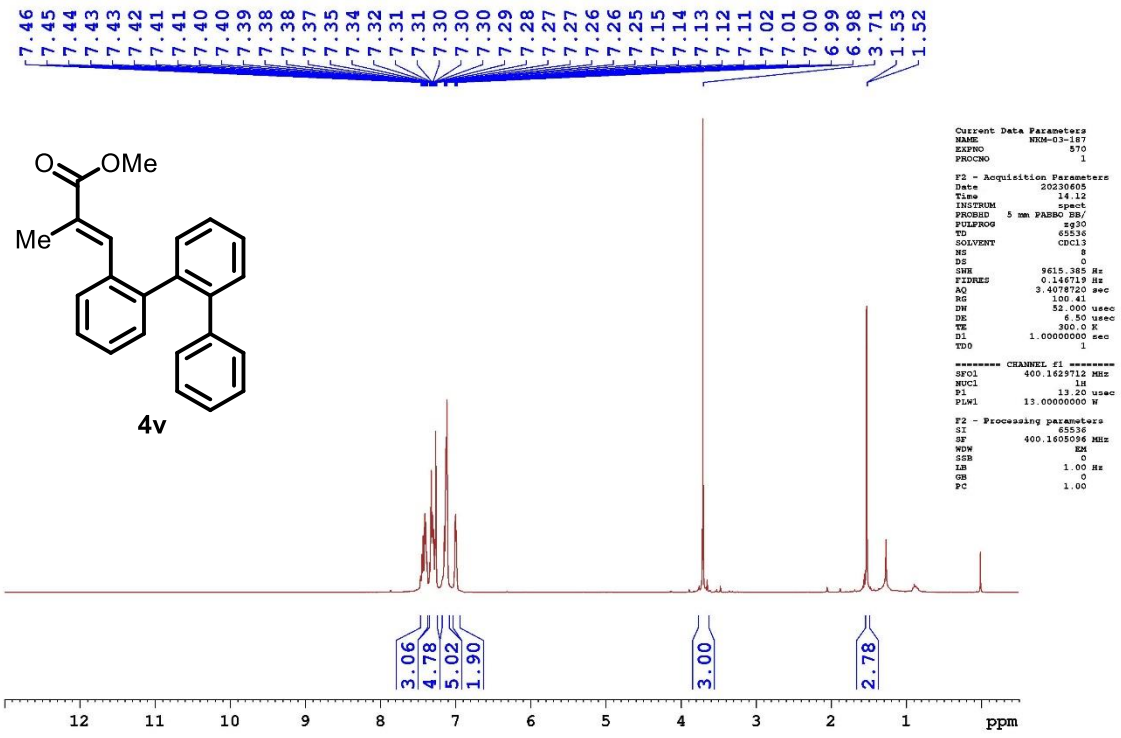

Figure S-46: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4v**

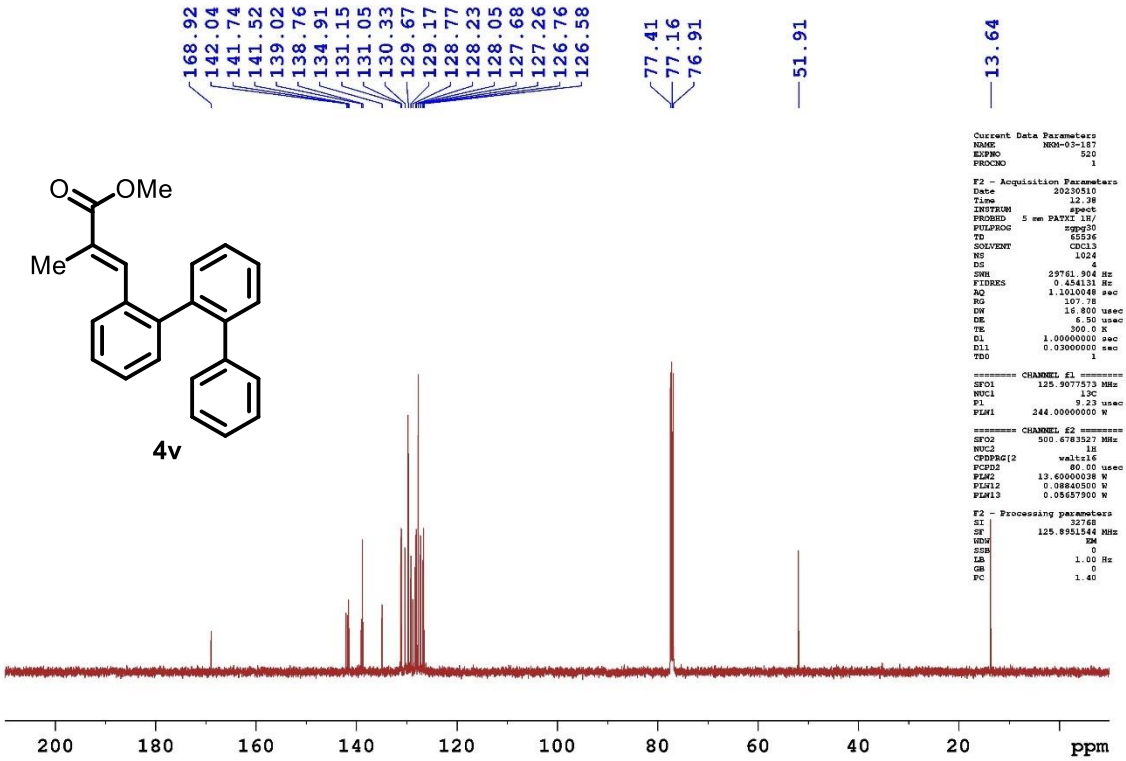

Figure S-47: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4v**

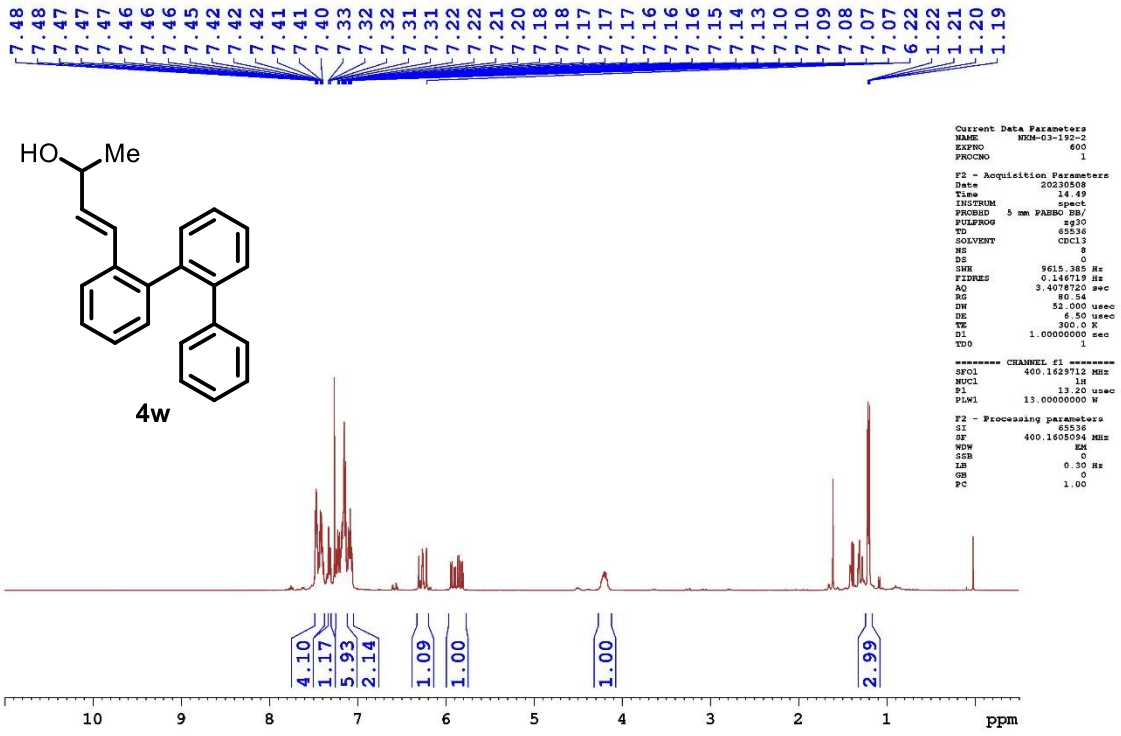

Figure S-48: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4w**

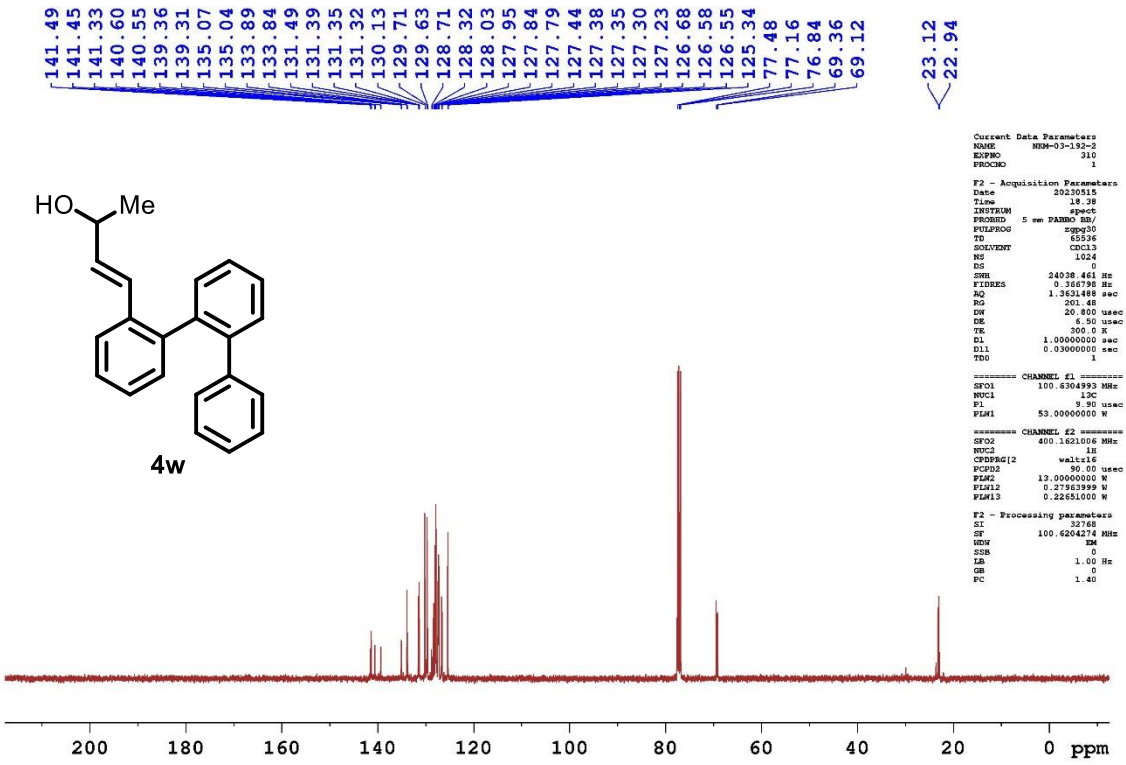

Figure S-49: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4w**

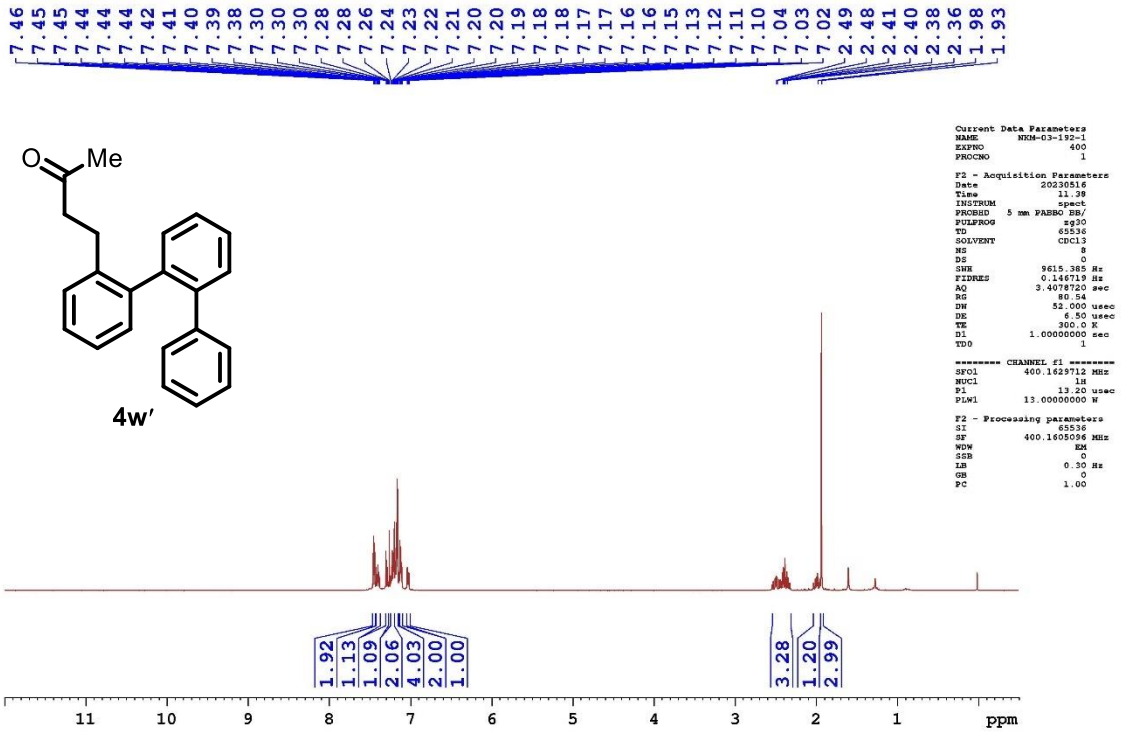

Figure S-50: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4w′**

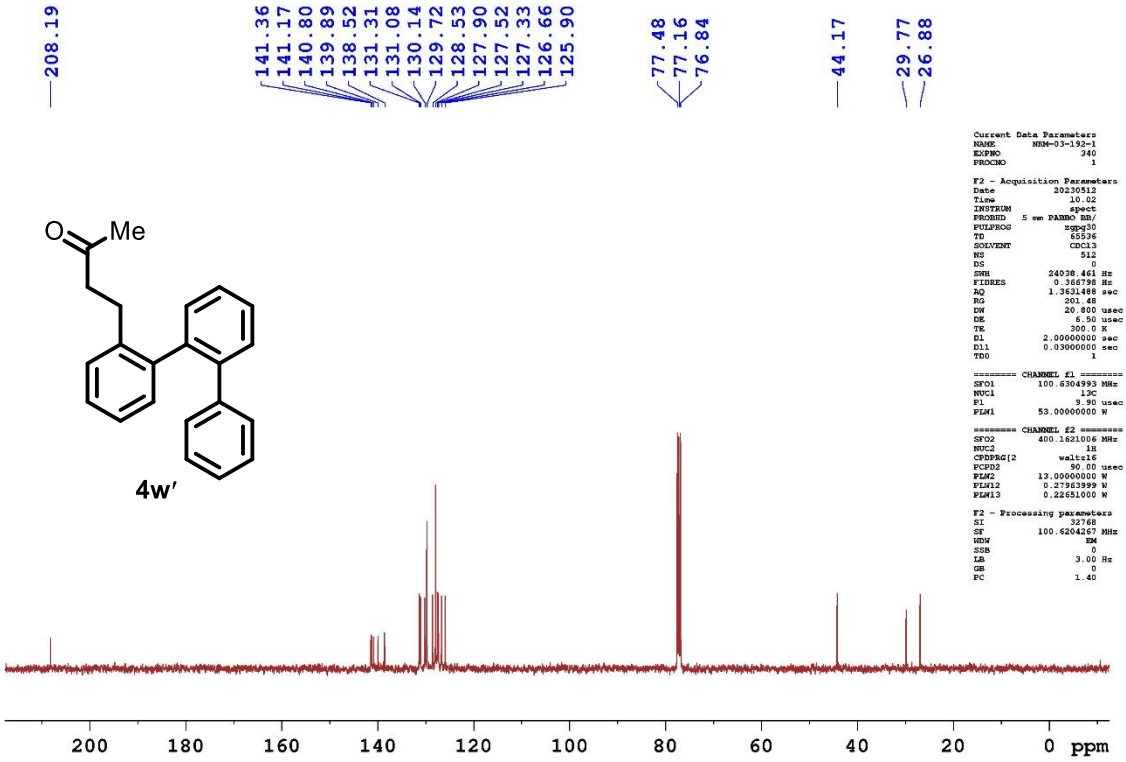

Figure S-51: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4w′**

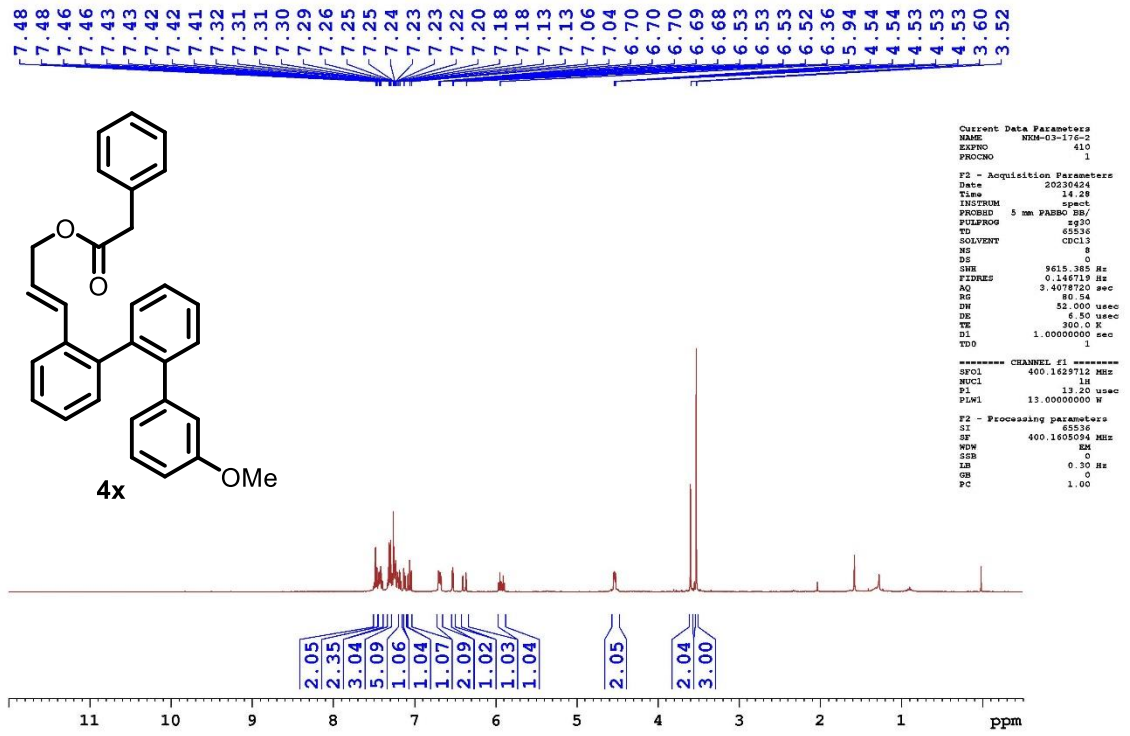

Figure S-52: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4x**

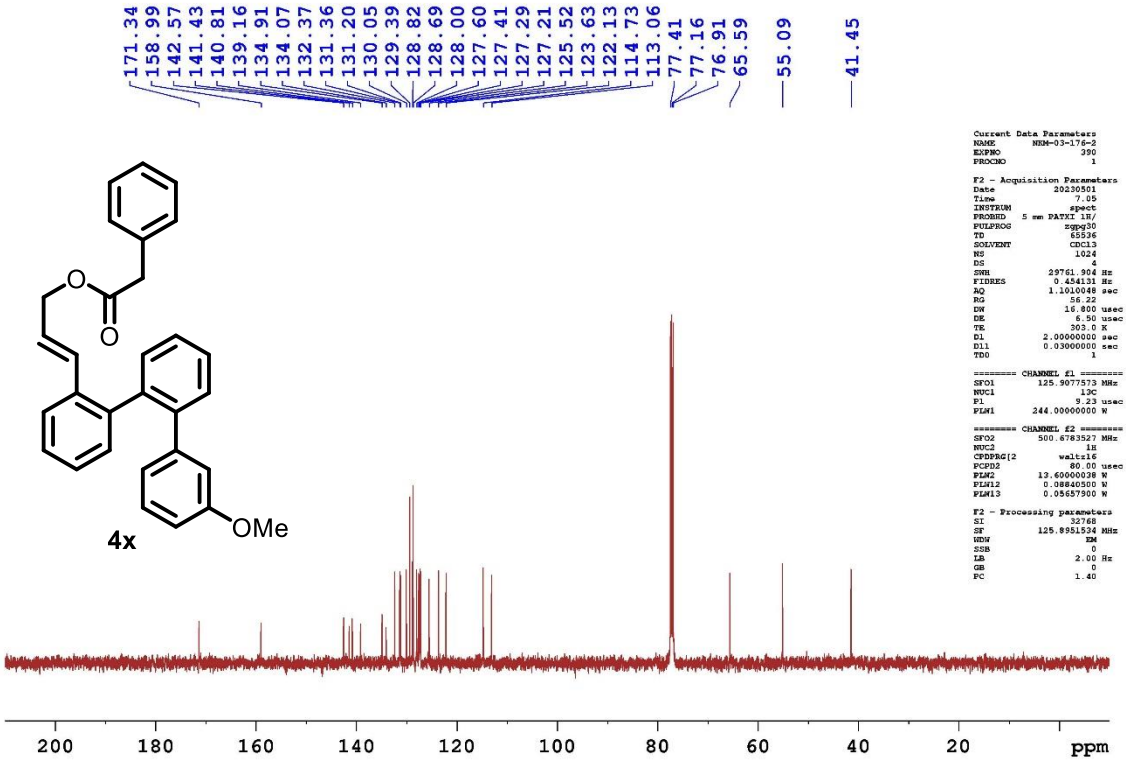

Figure S-53: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4x**

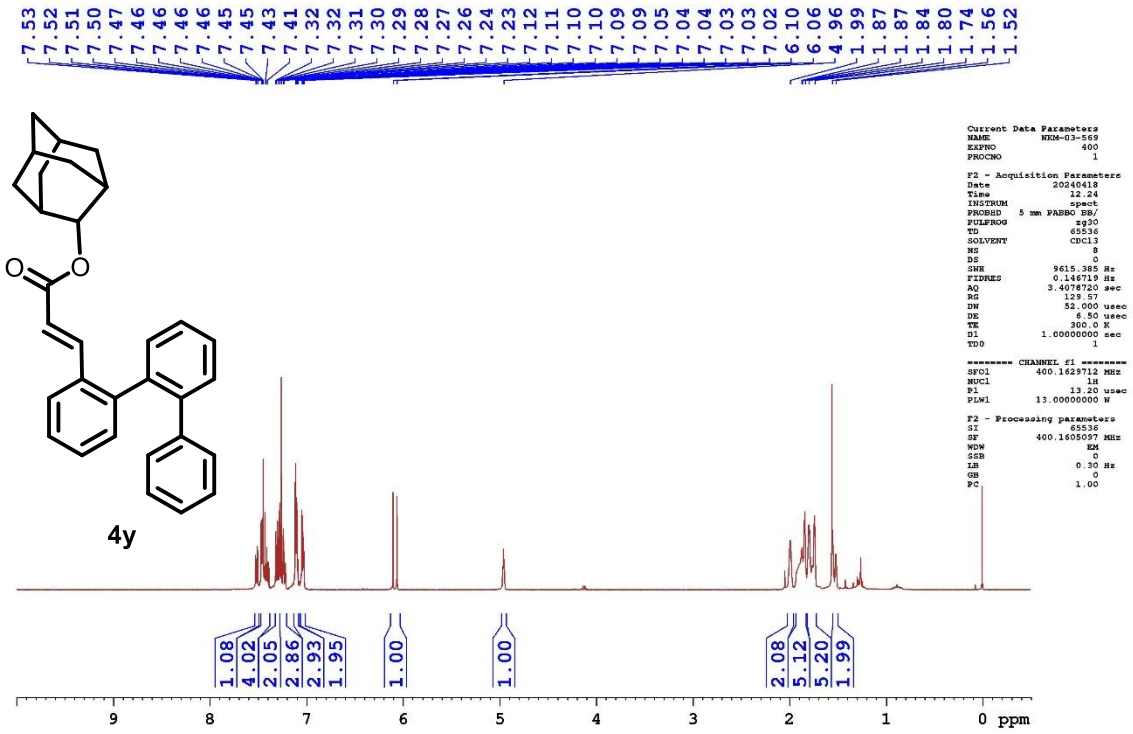

Figure S-54: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4y**

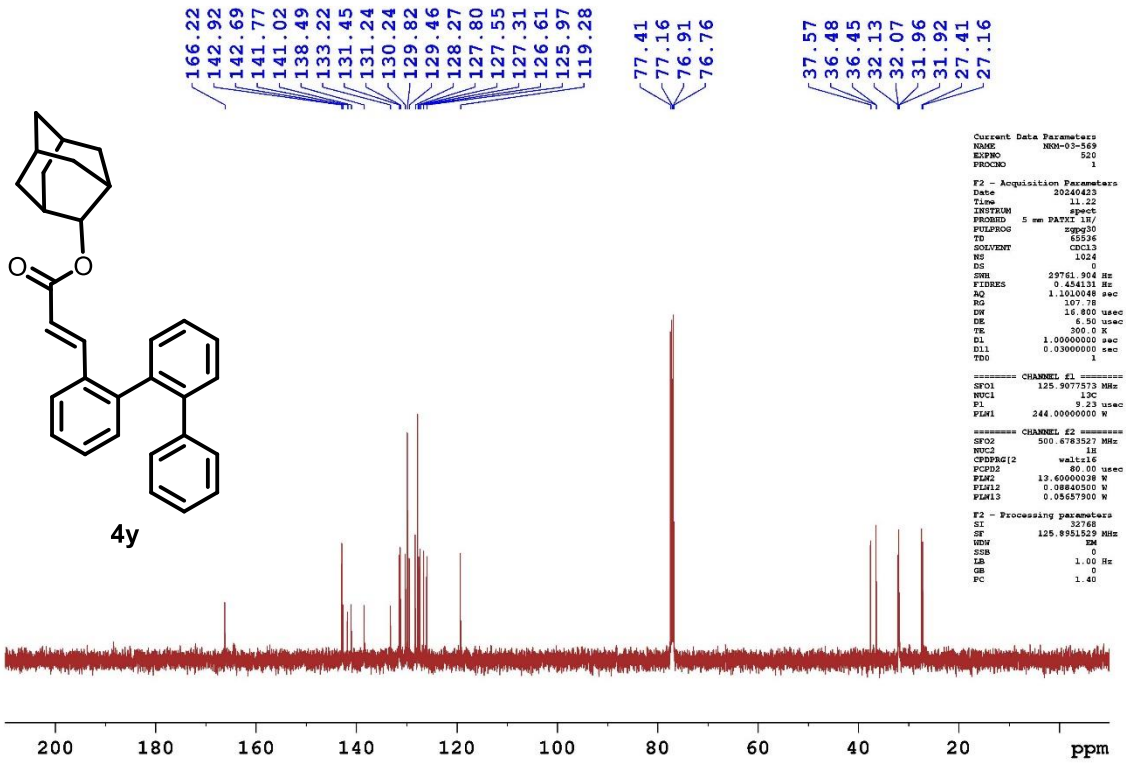

Figure S-55: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4y**

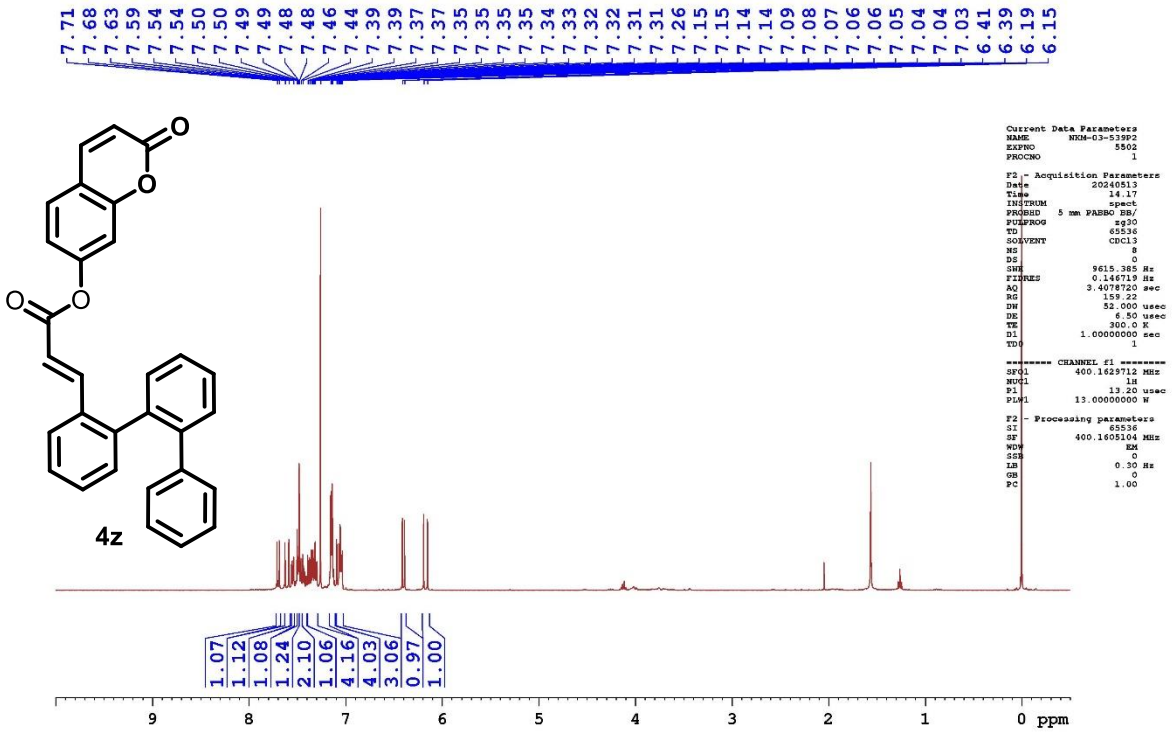

Figure S-56: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4z**

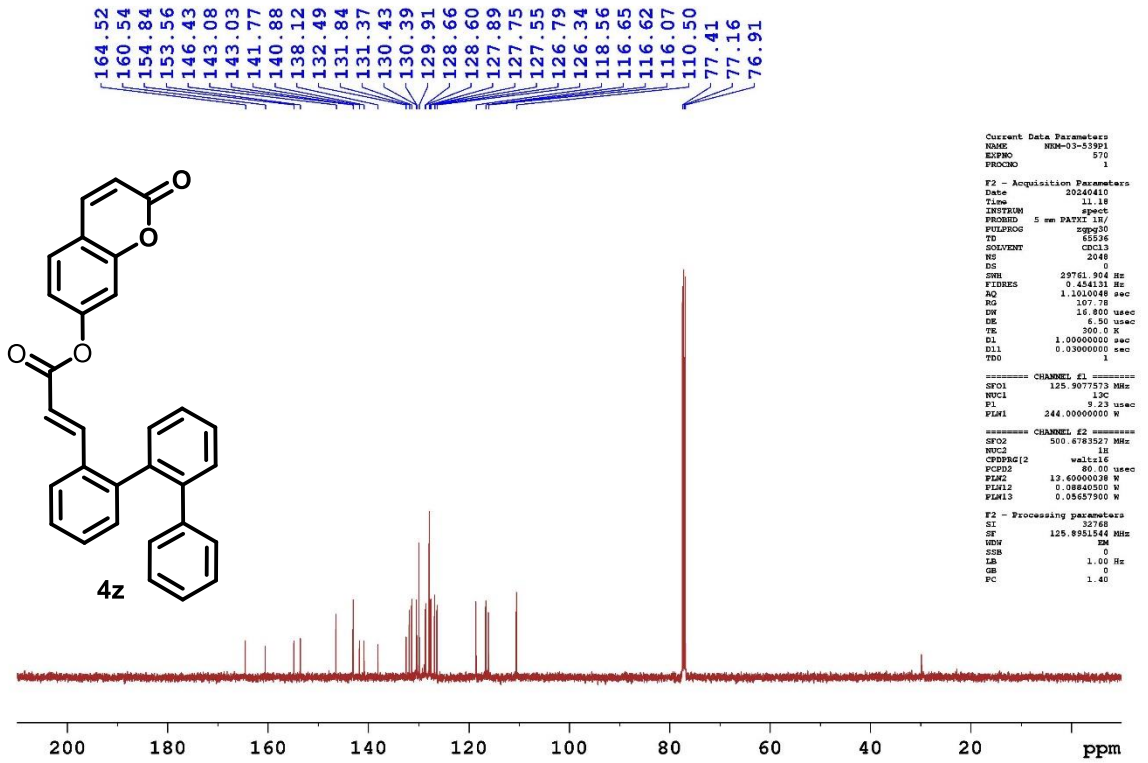

Figure S-57: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4z**

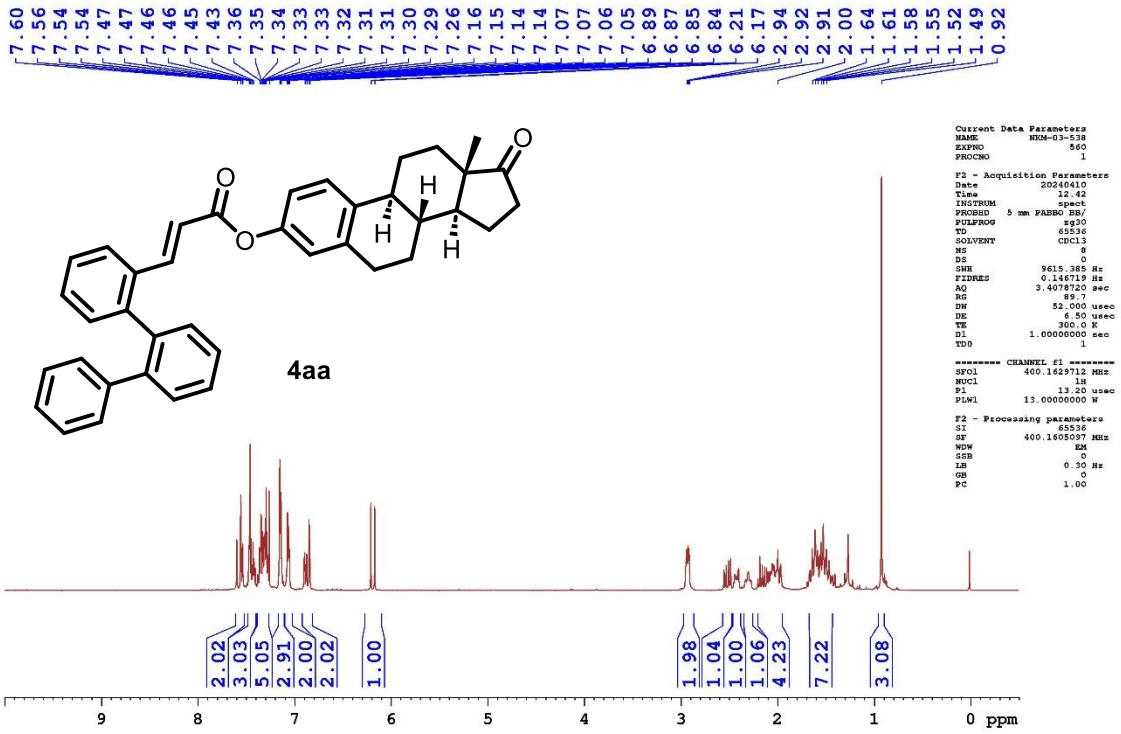

Figure S-58: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4aa**

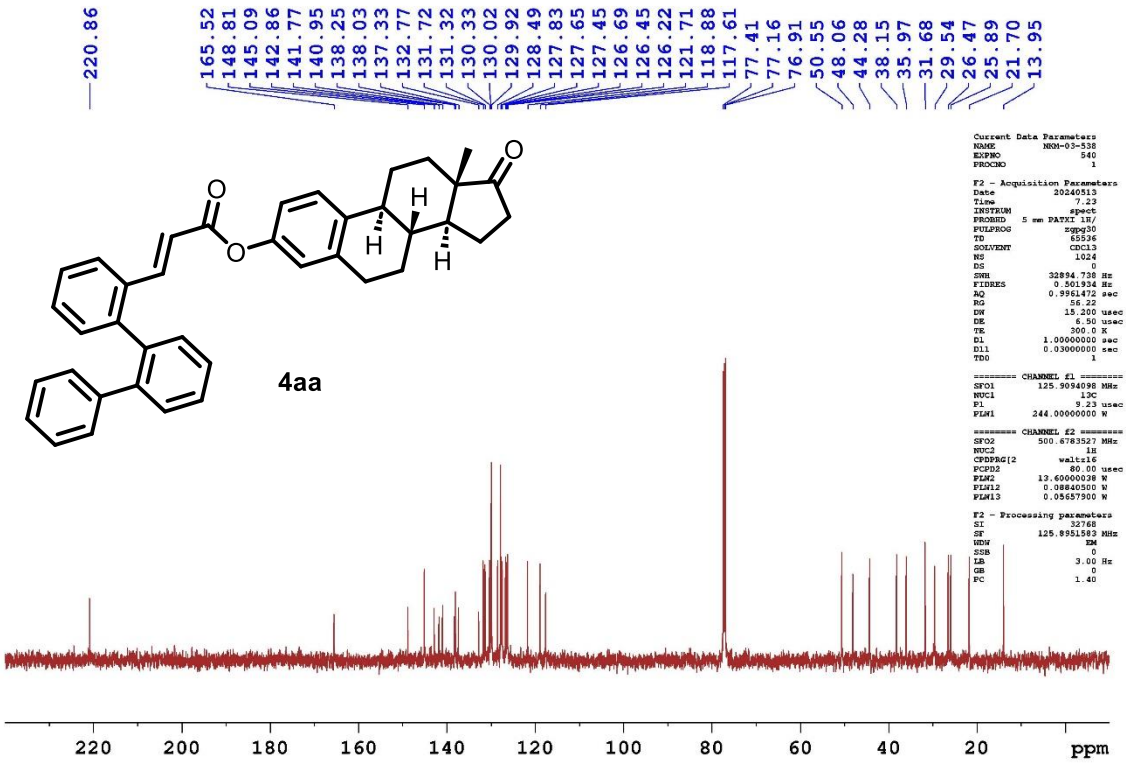

Figure S-59: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4aa**

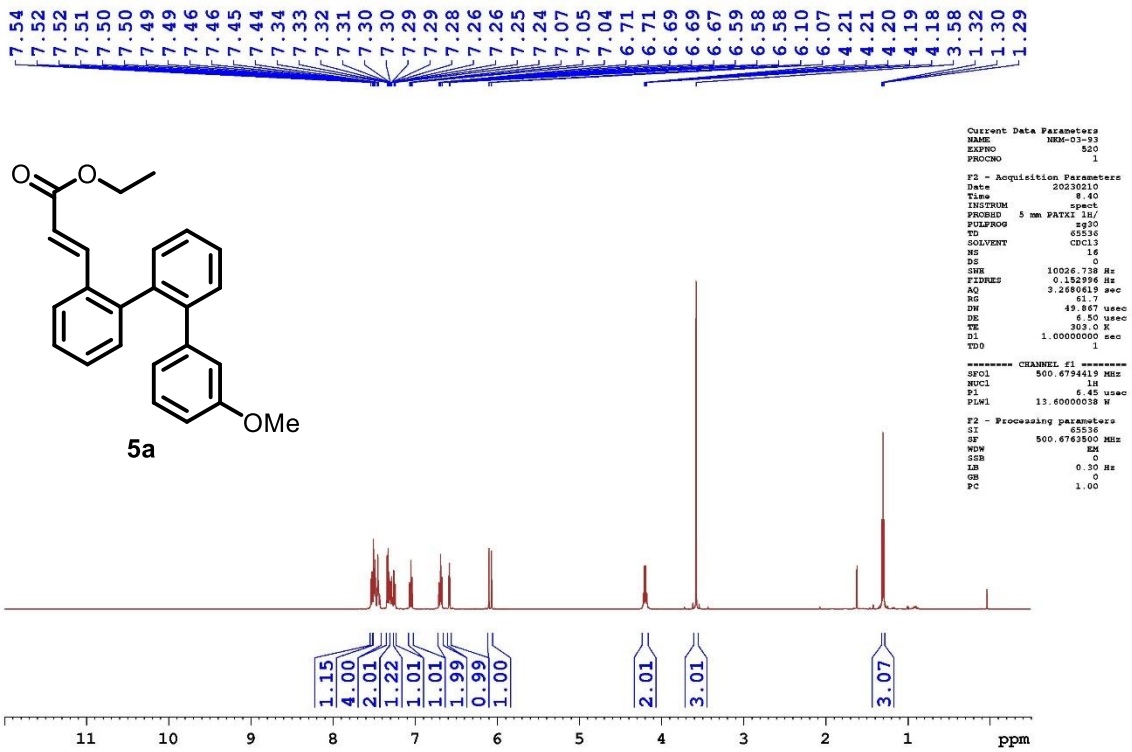

Figure S-60: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **5a**

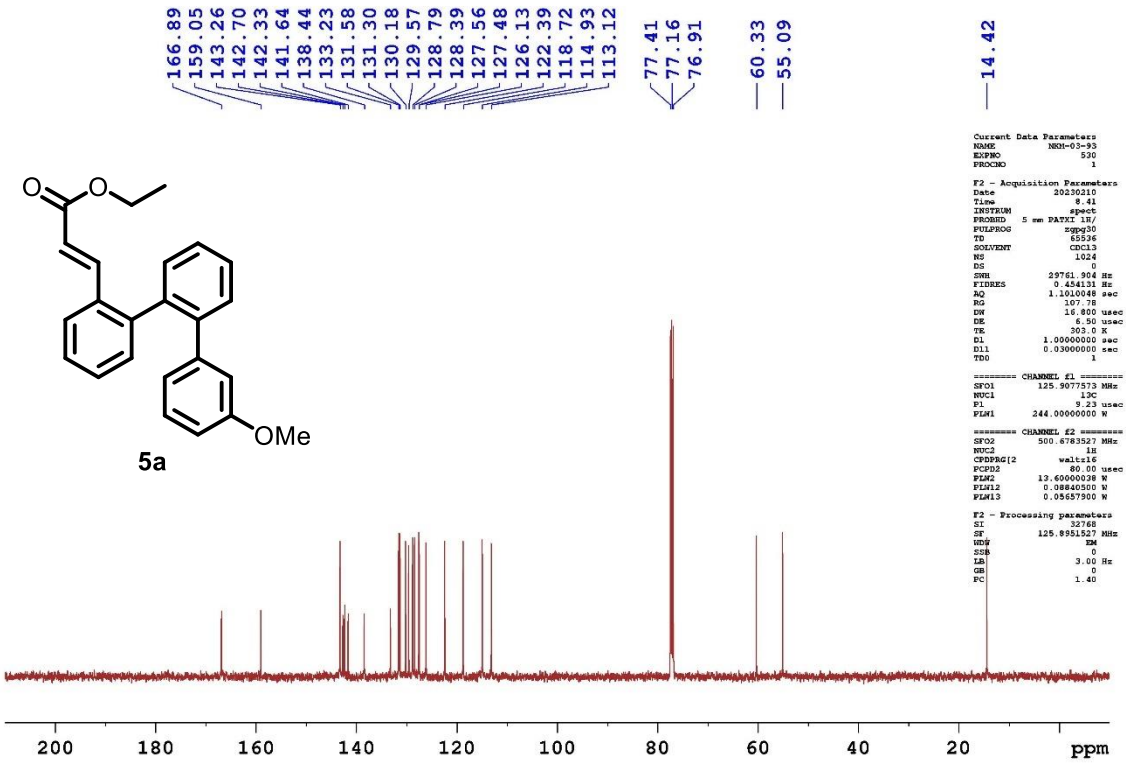

Figure S-61: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **5a**

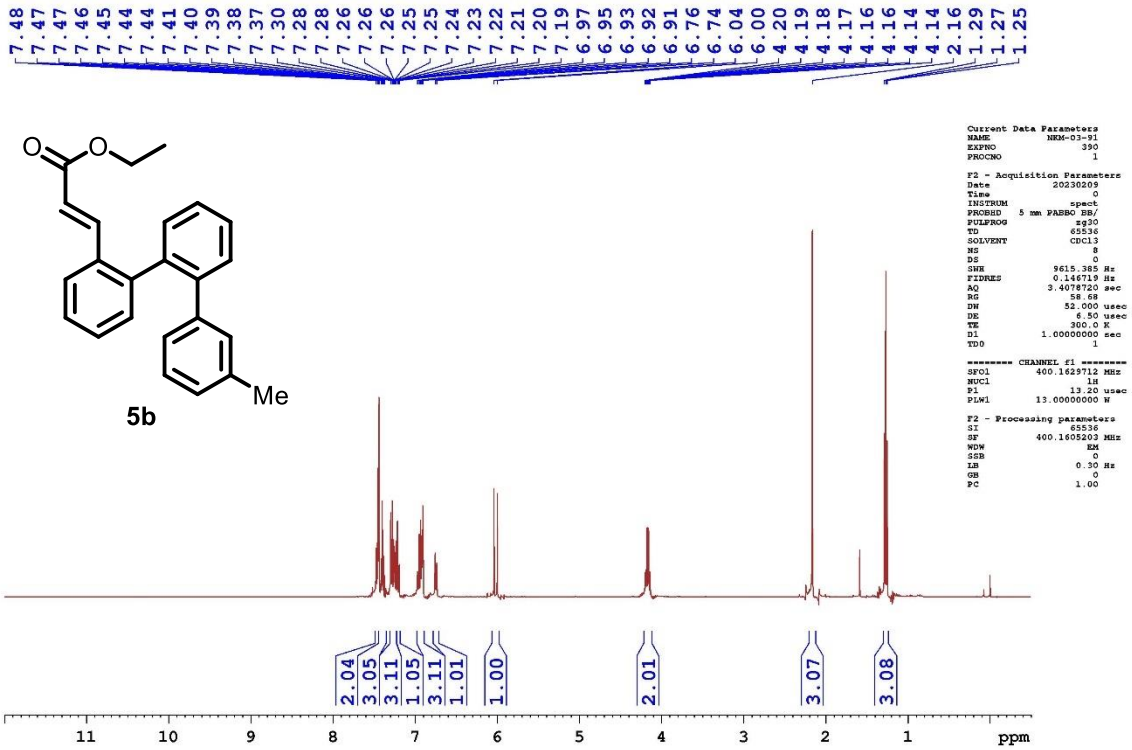

Figure S-62: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5b**

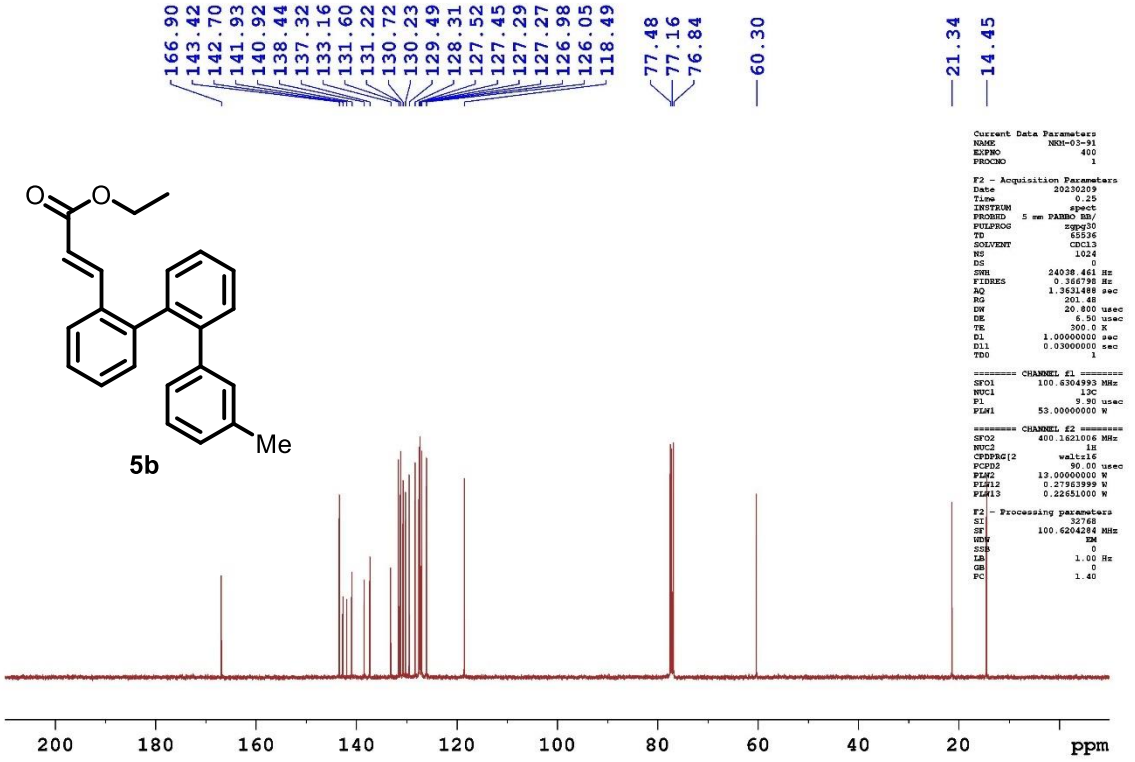

Figure S-63: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5b**

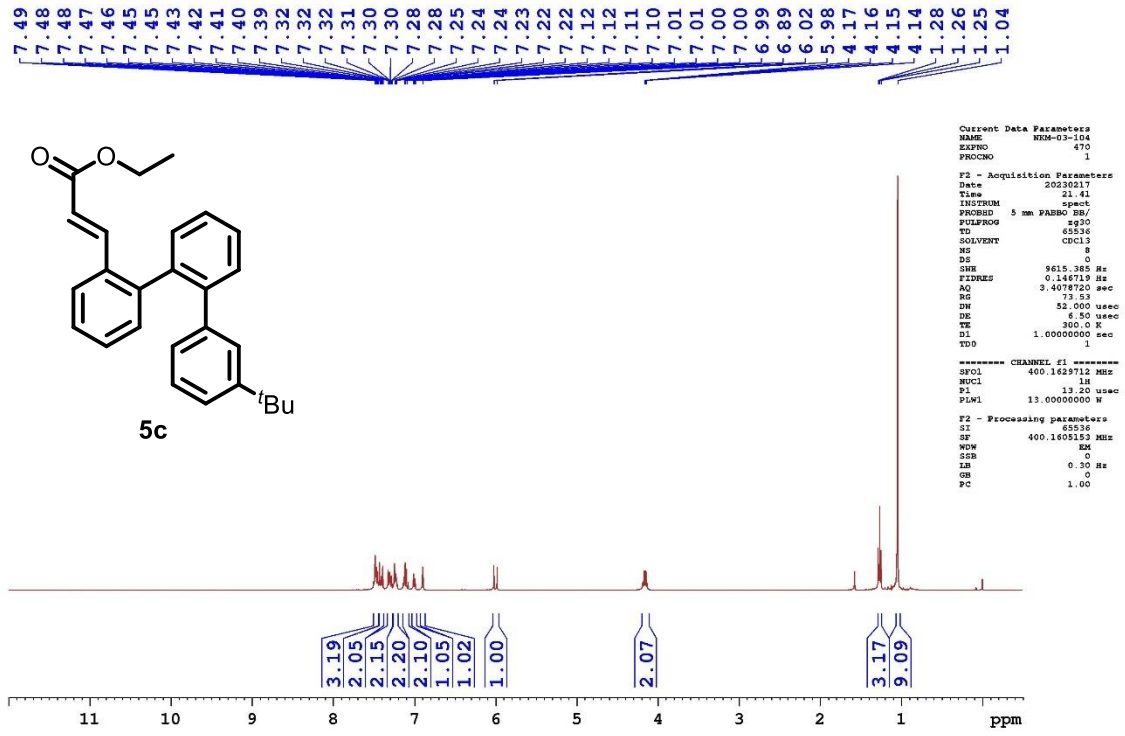

Figure S-64: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5c**

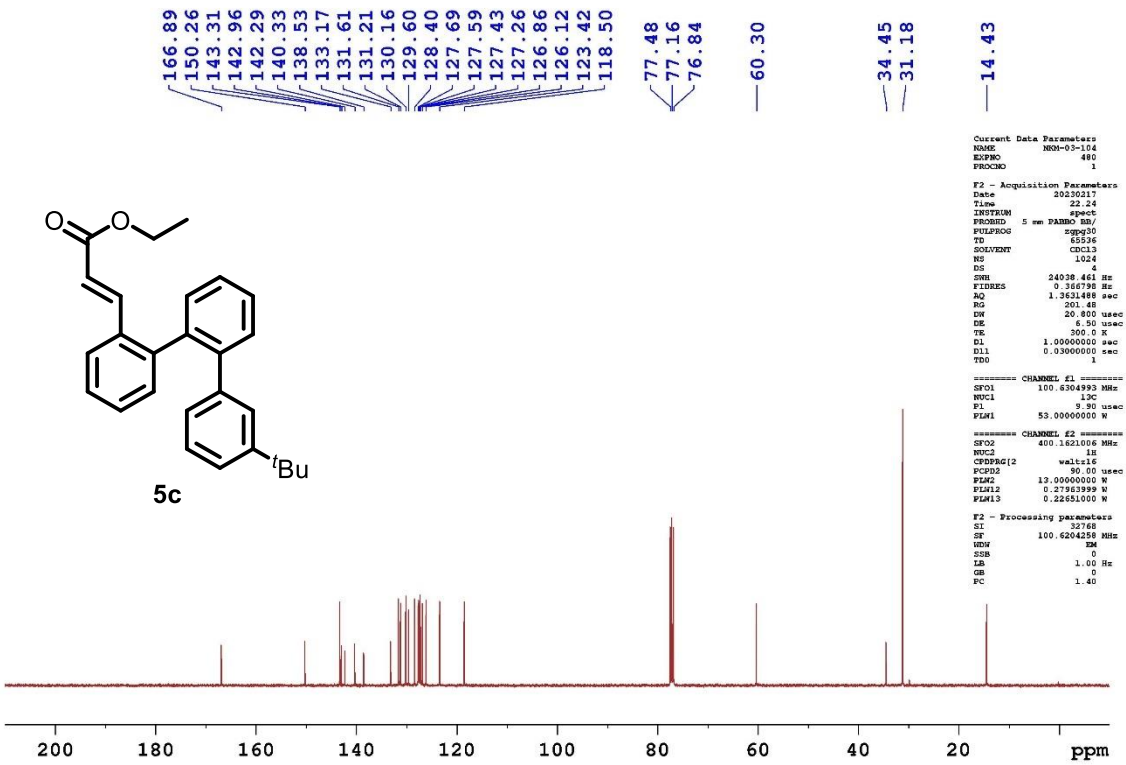

Figure S-65: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5c**

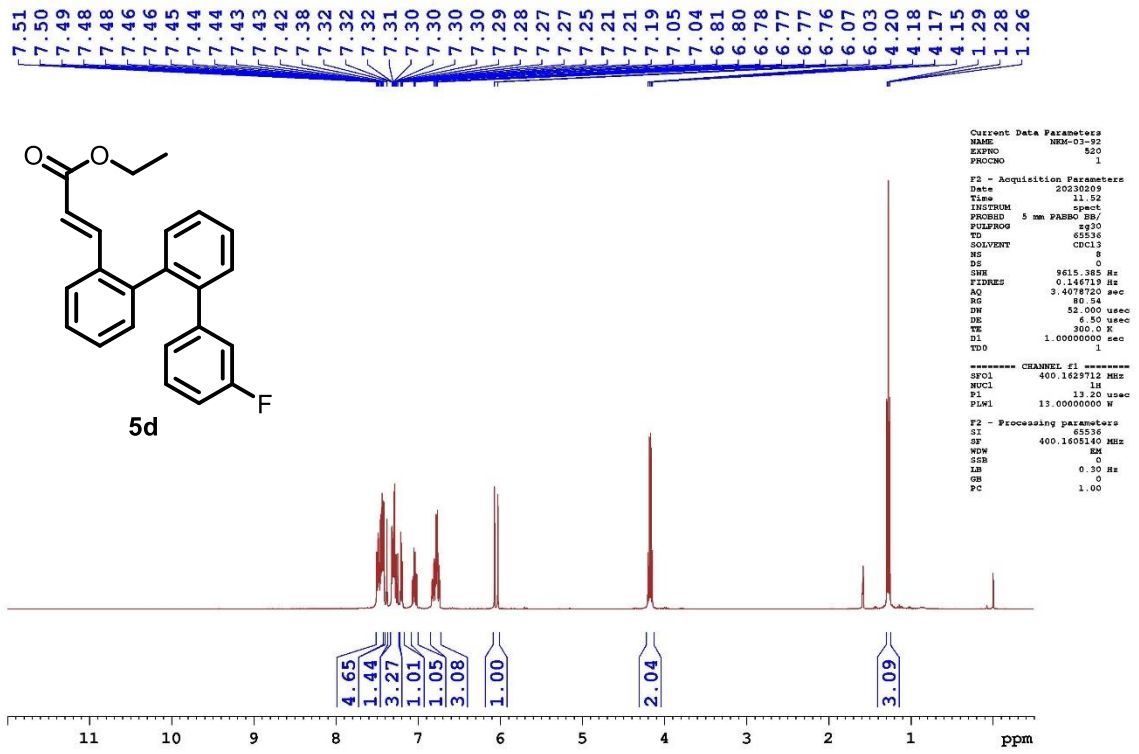

Figure S-66: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5d**

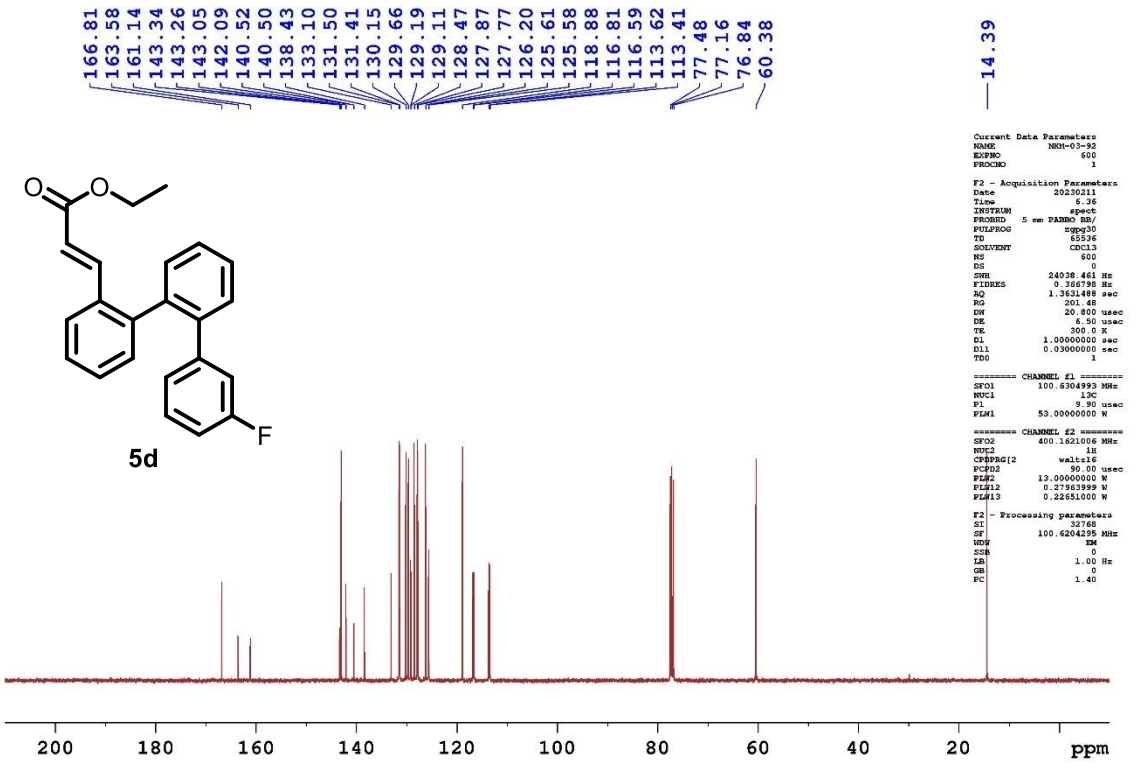

Figure S-67: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5d**

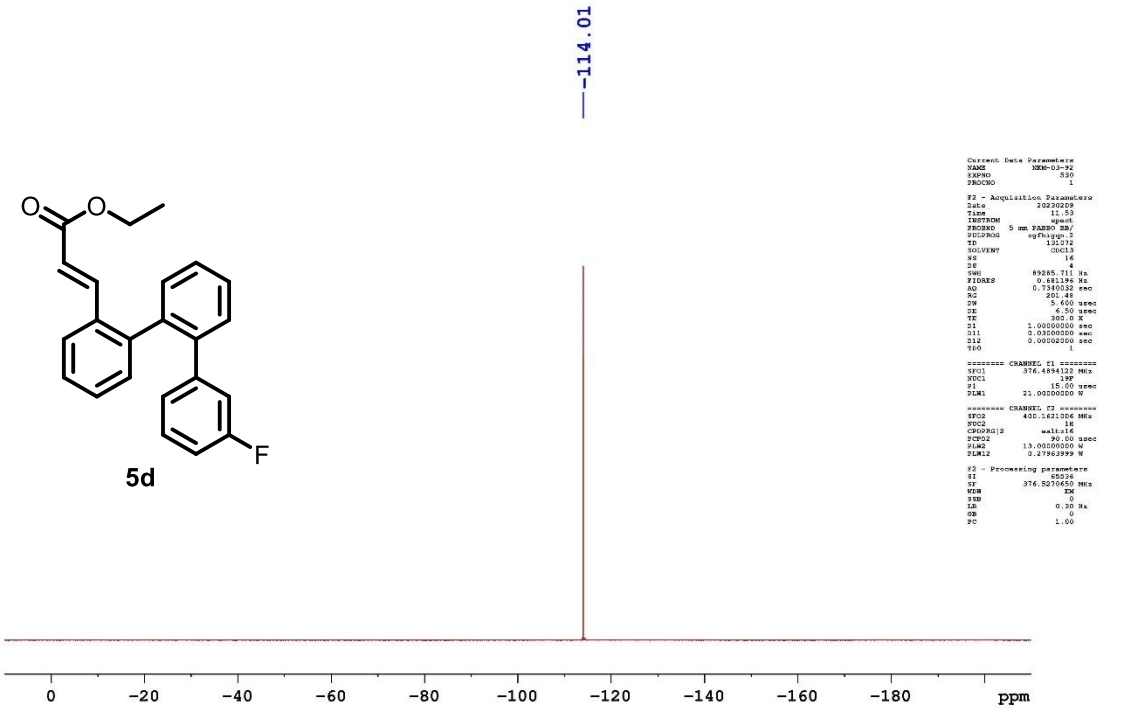

Figure S-68: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5d**

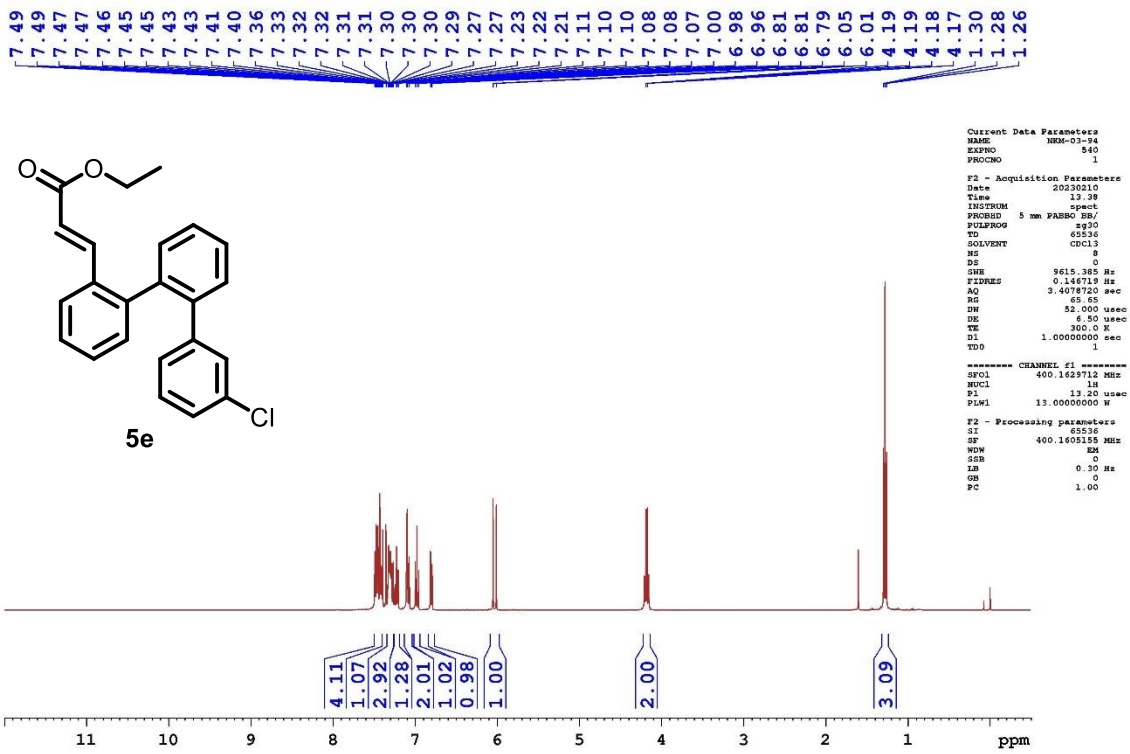

Figure S-69: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5e**

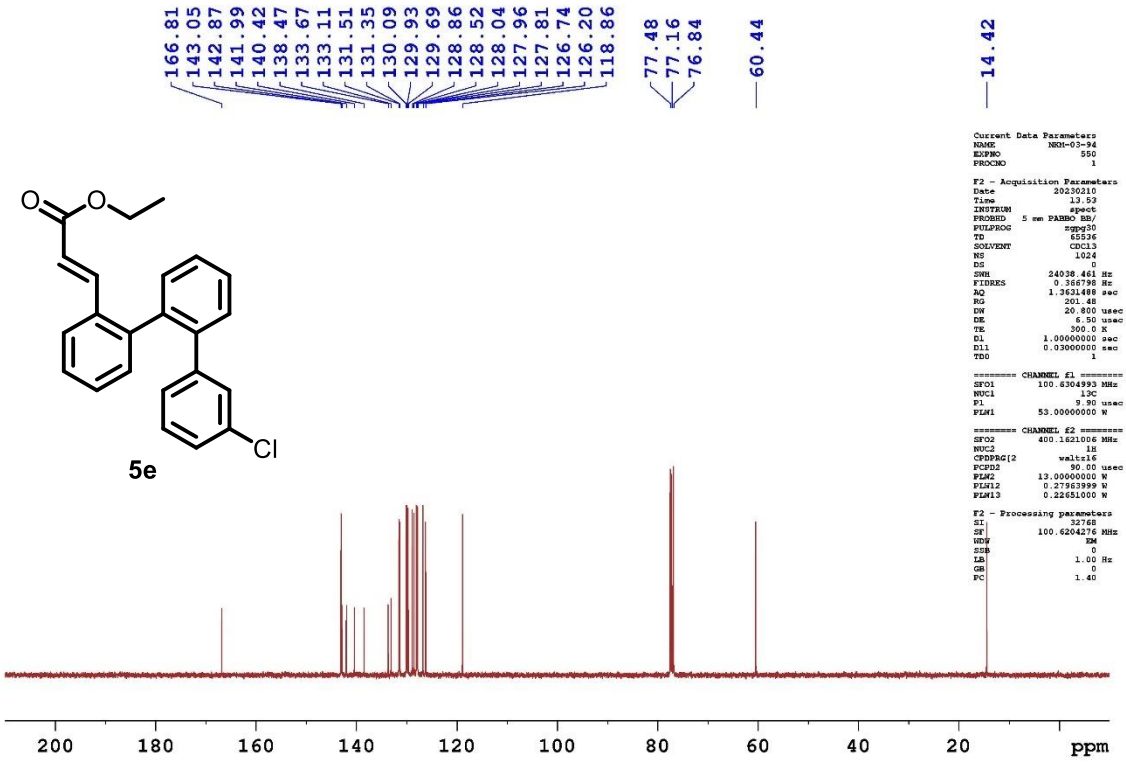

Figure S-70: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5e**

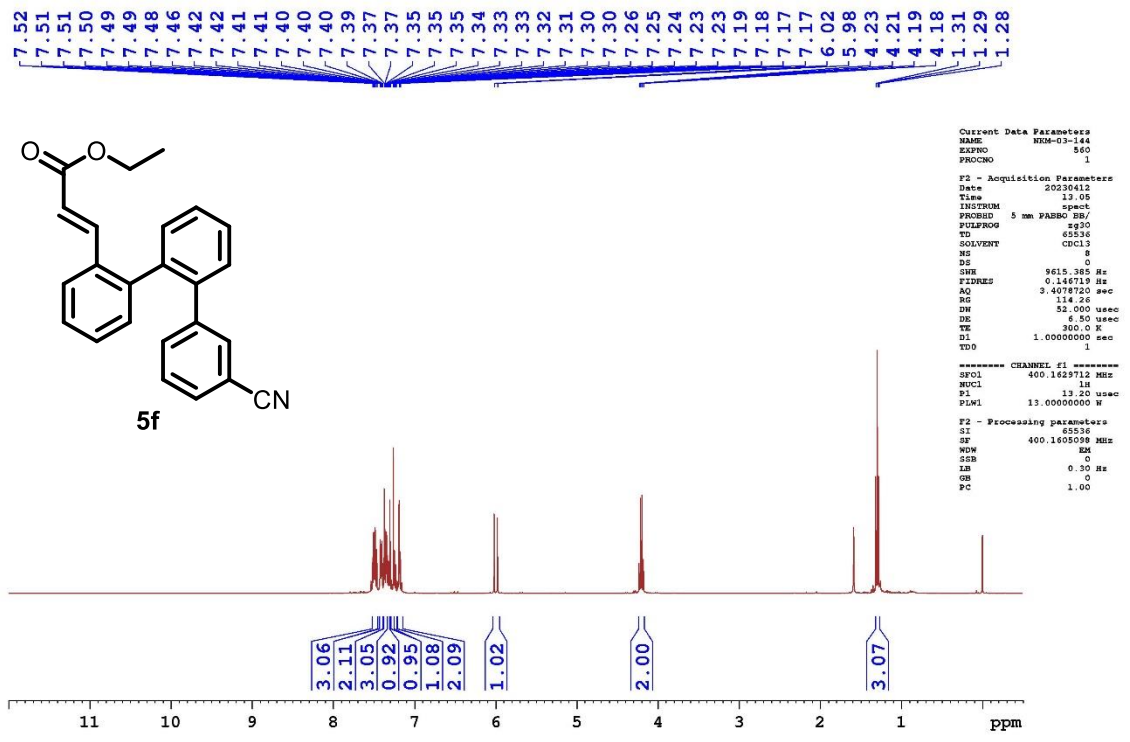

Figure S-71: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5f**

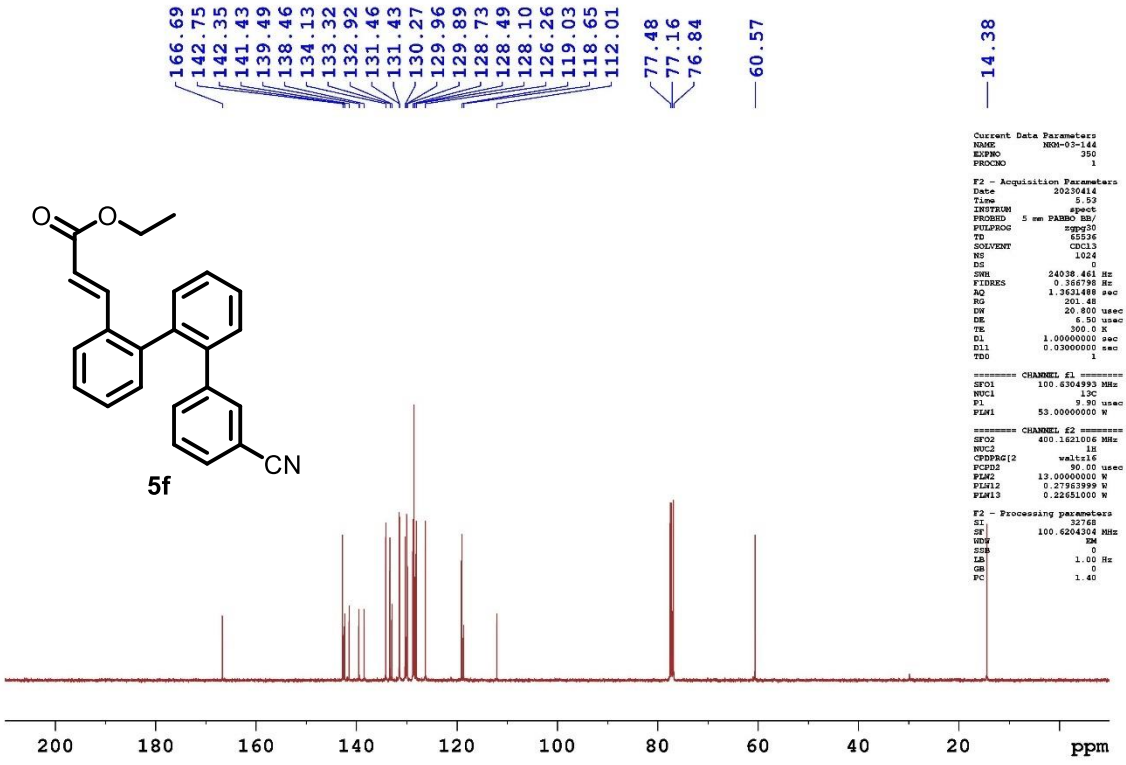

Figure S-72: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5f**

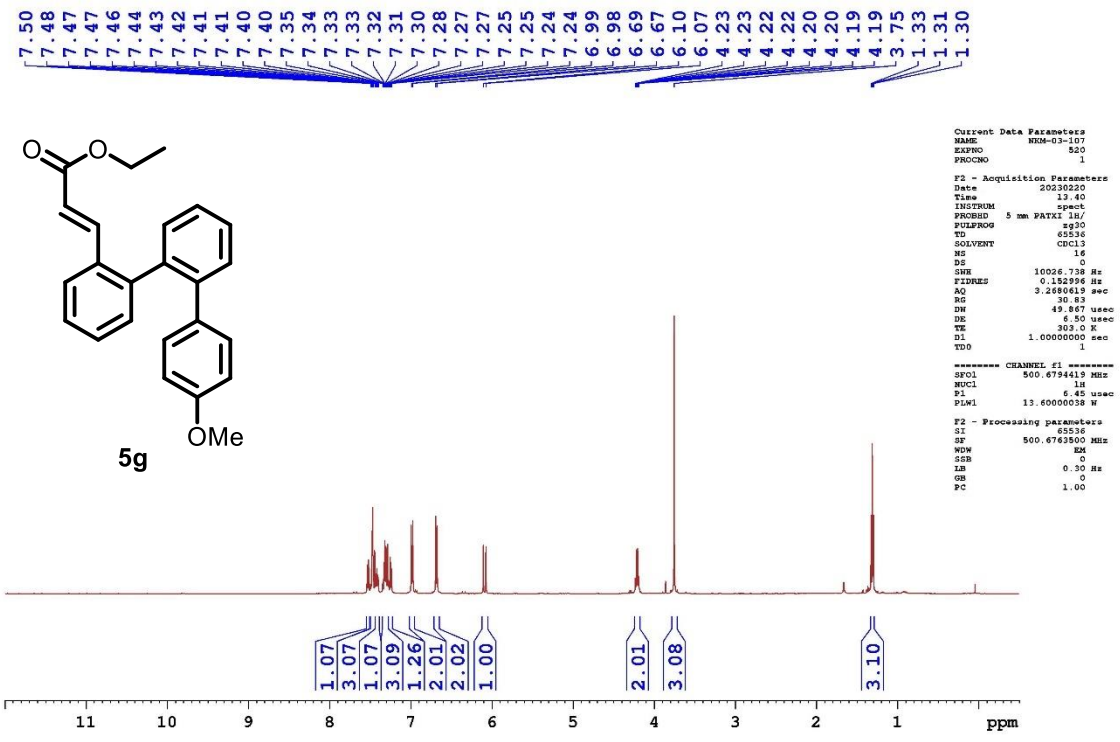

Figure S-73: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **5g**

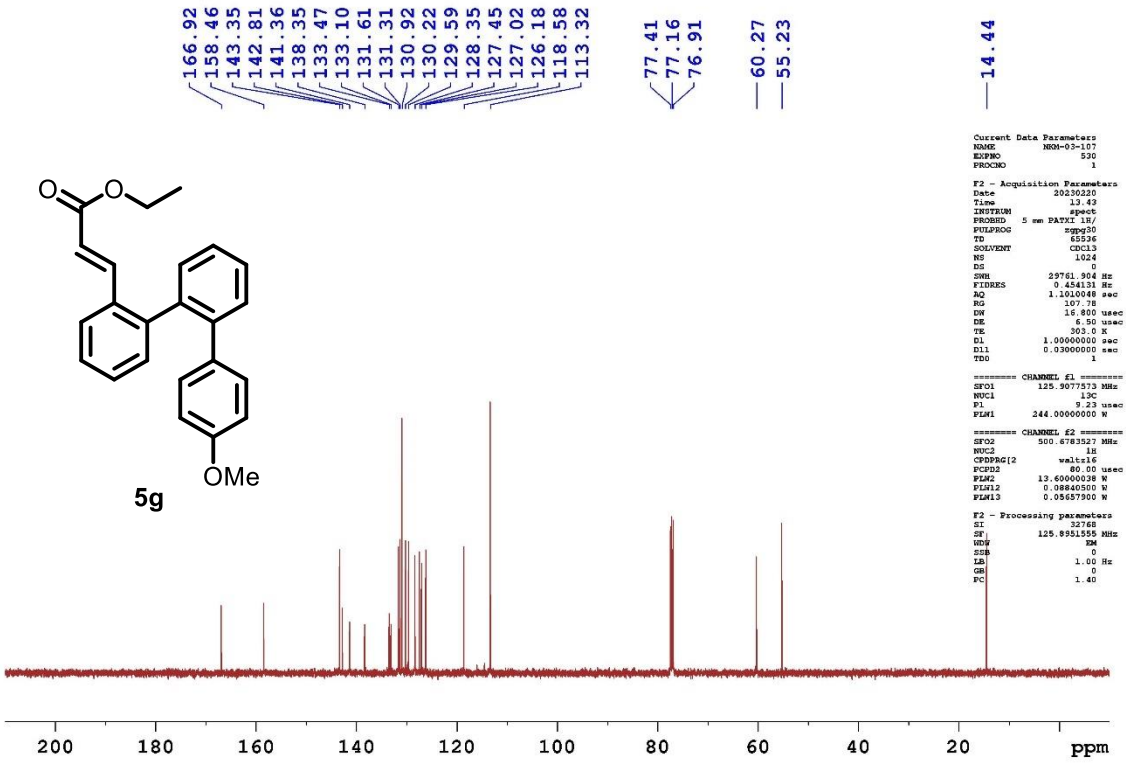

Figure S-74: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **5g**

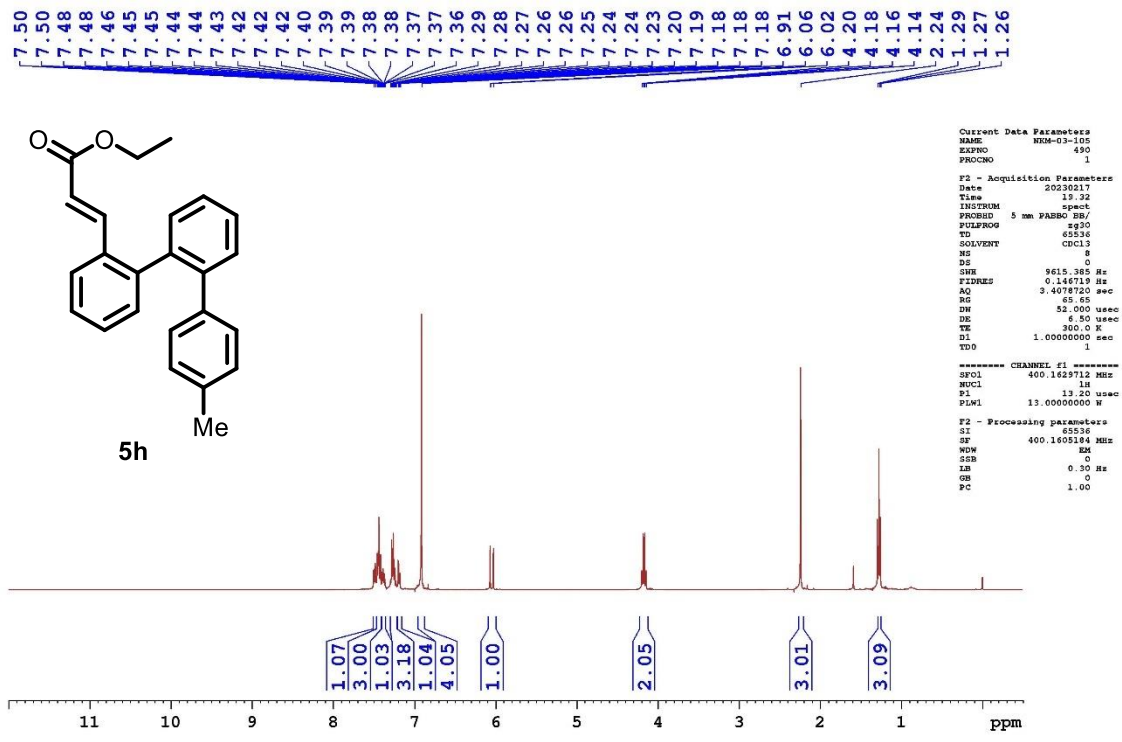

Figure S-75: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5h**

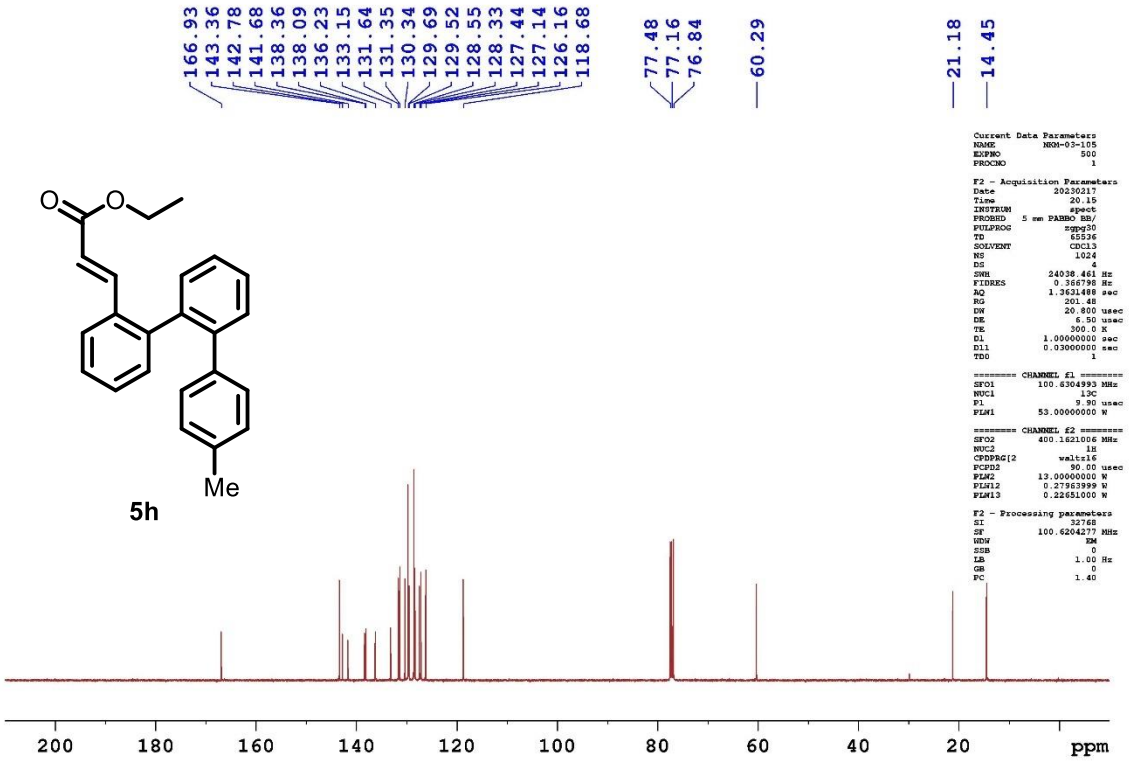

Figure S-76: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5h**

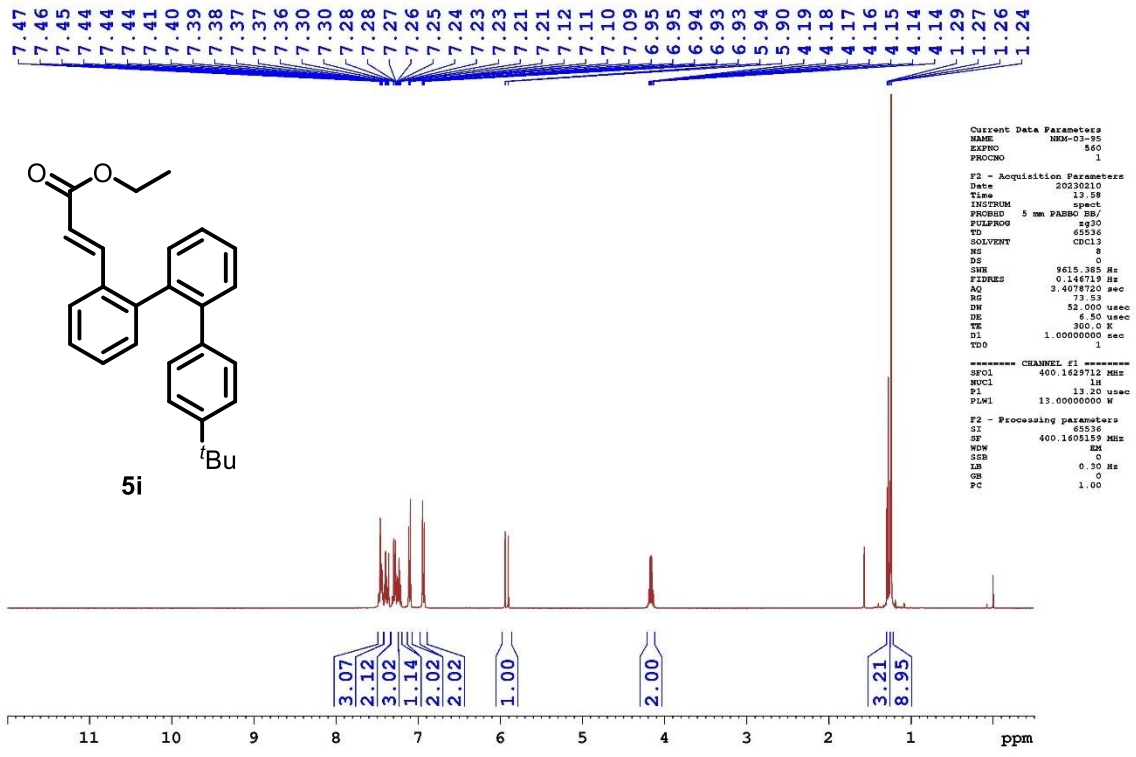

Figure S-77: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5i**

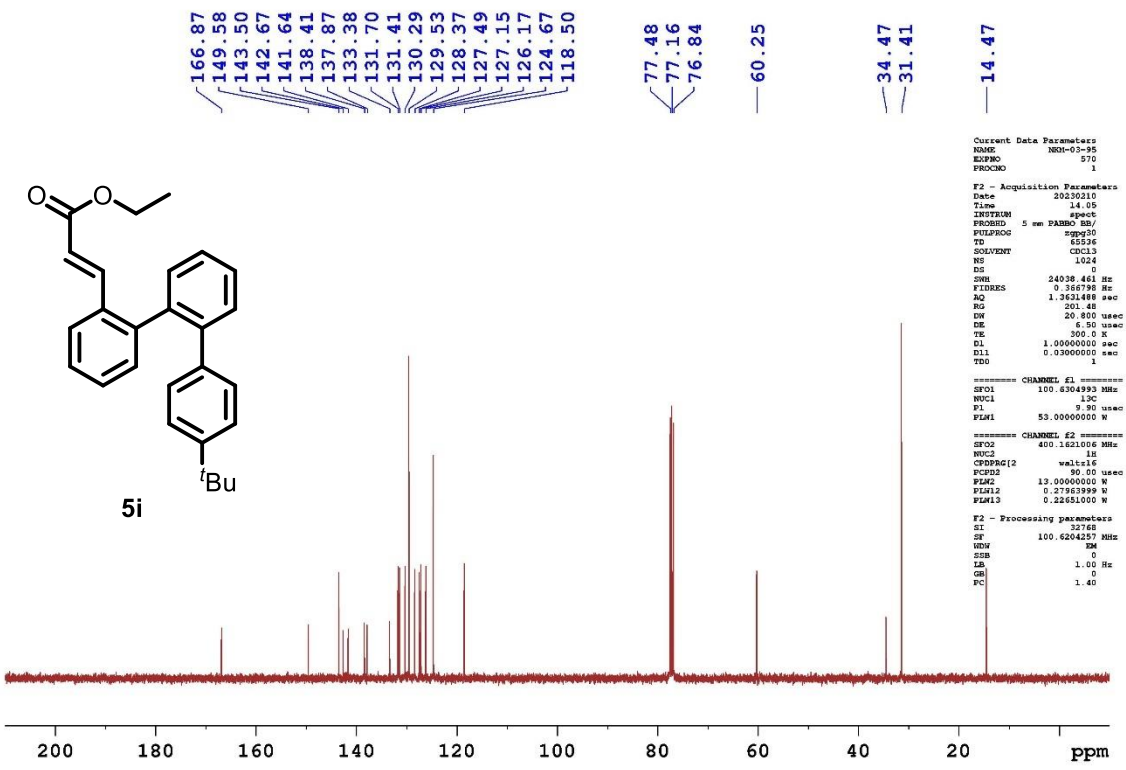

Figure S-78: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5i**

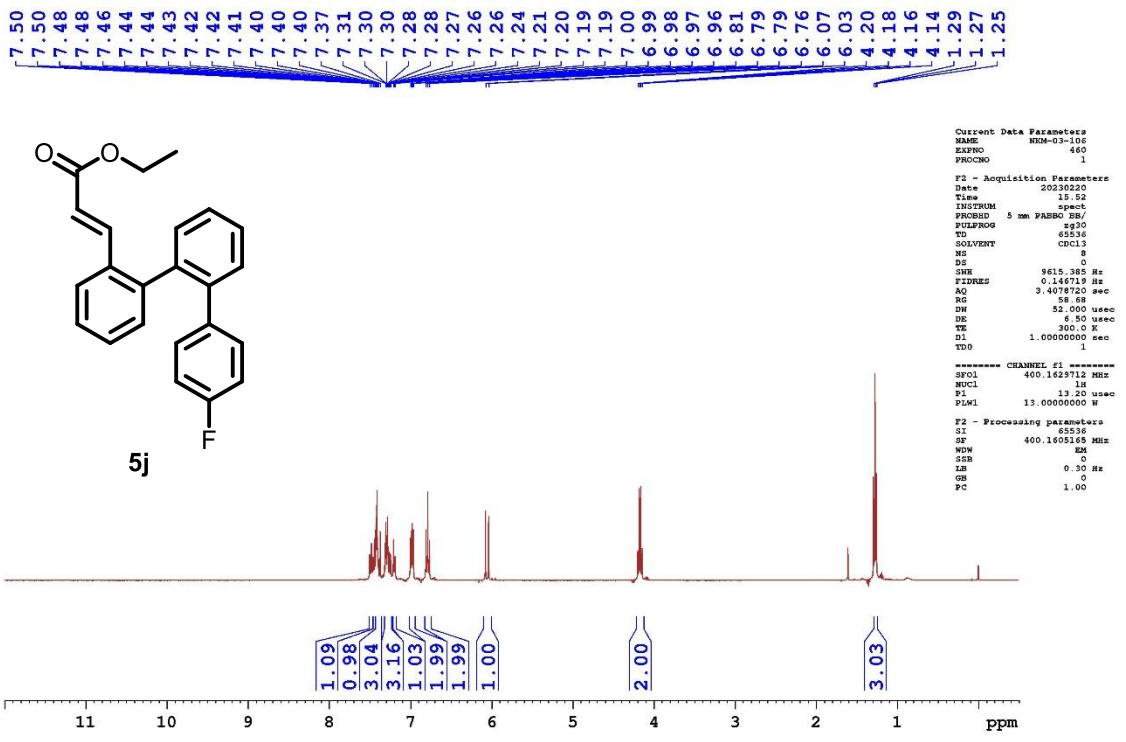

Figure S-79: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5j**

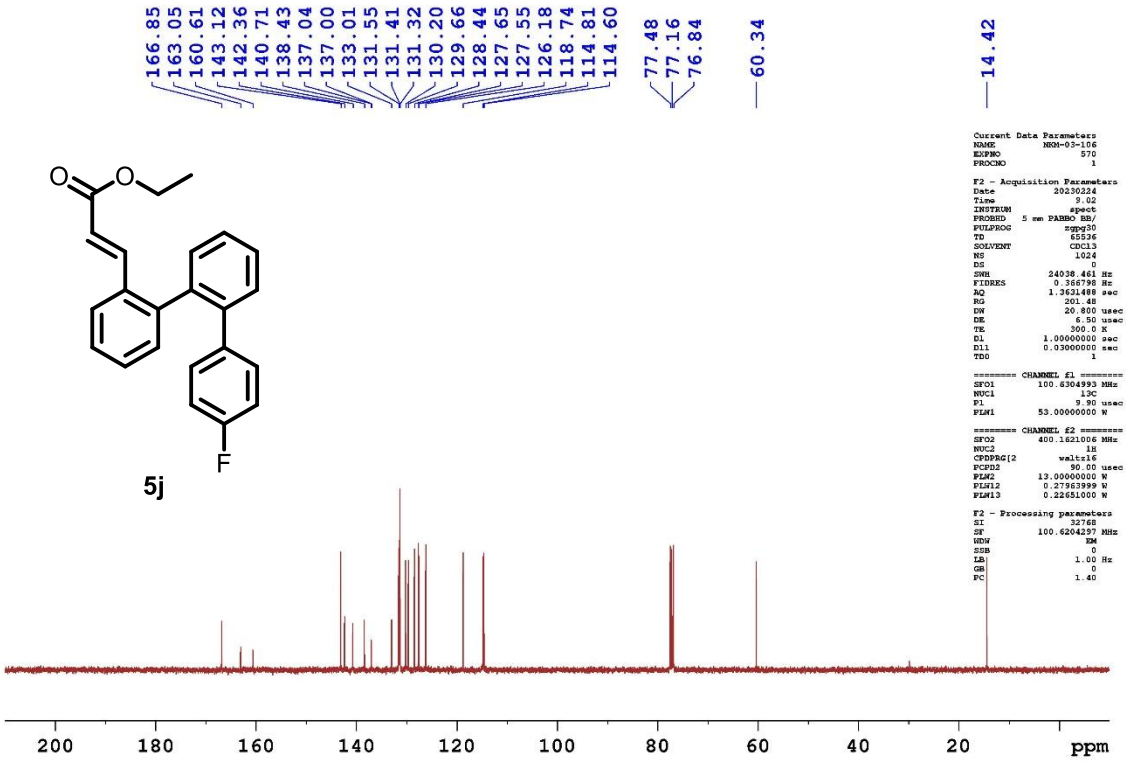

Figure S-80: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5j**

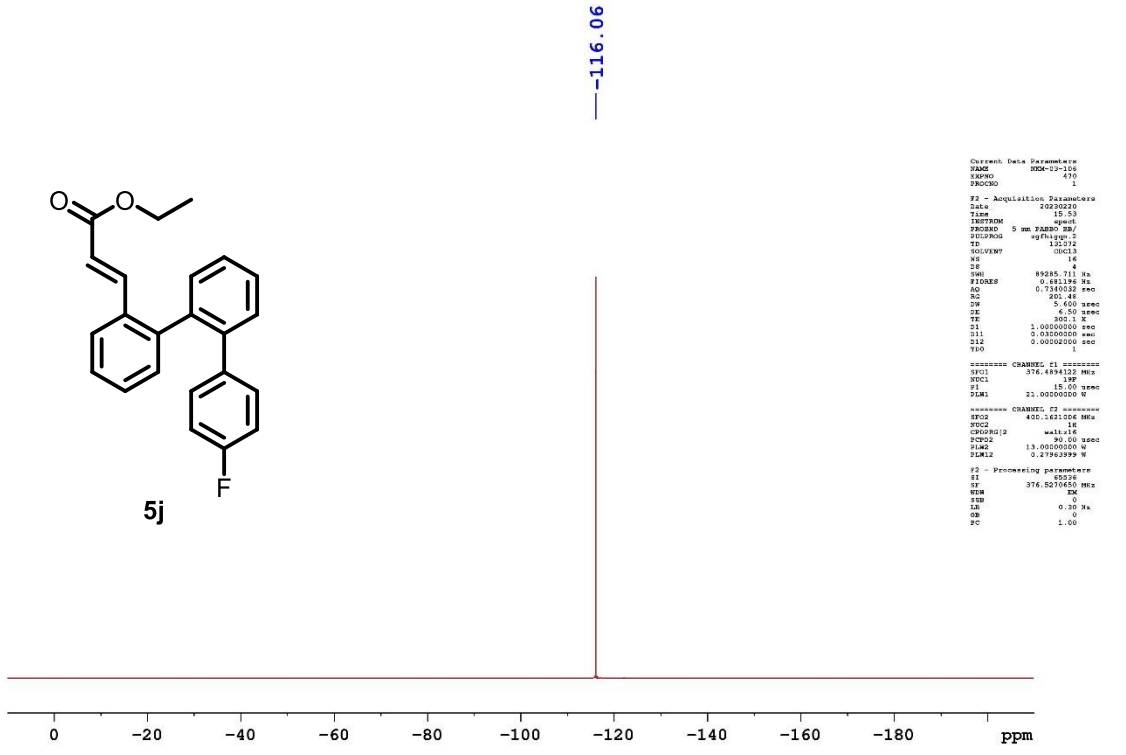

Figure S-81: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5j**

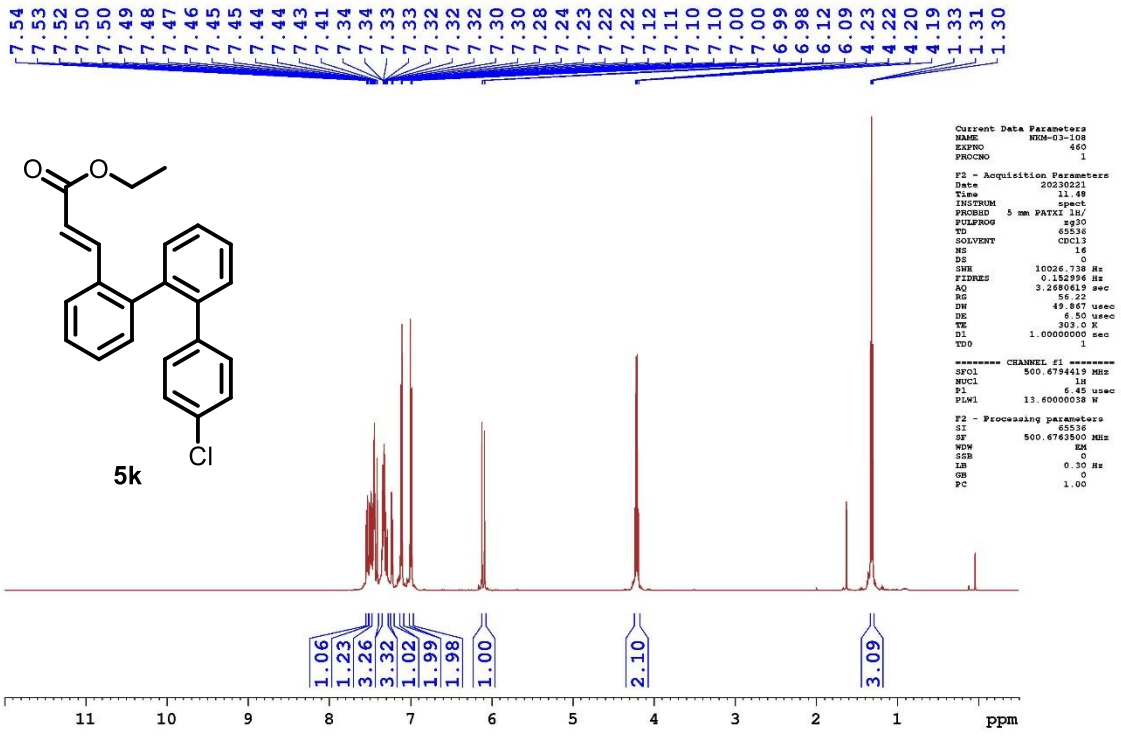

Figure S-82: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **5k**

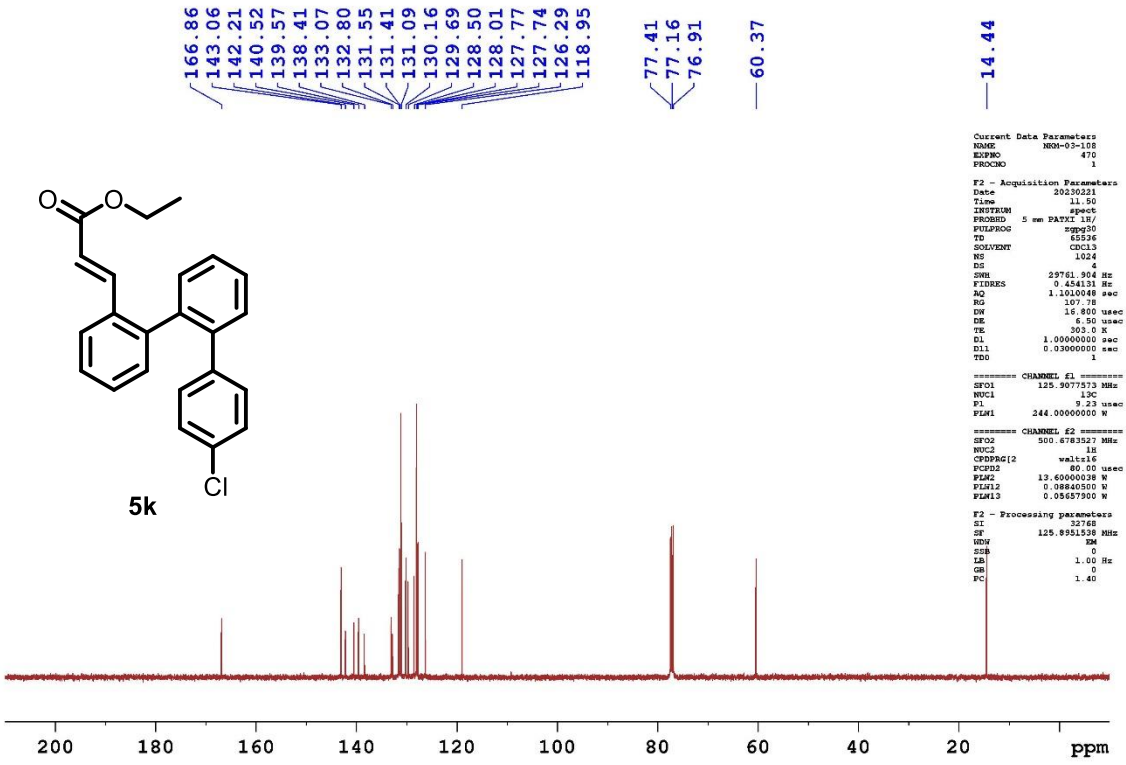

Figure S-83: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **5k**

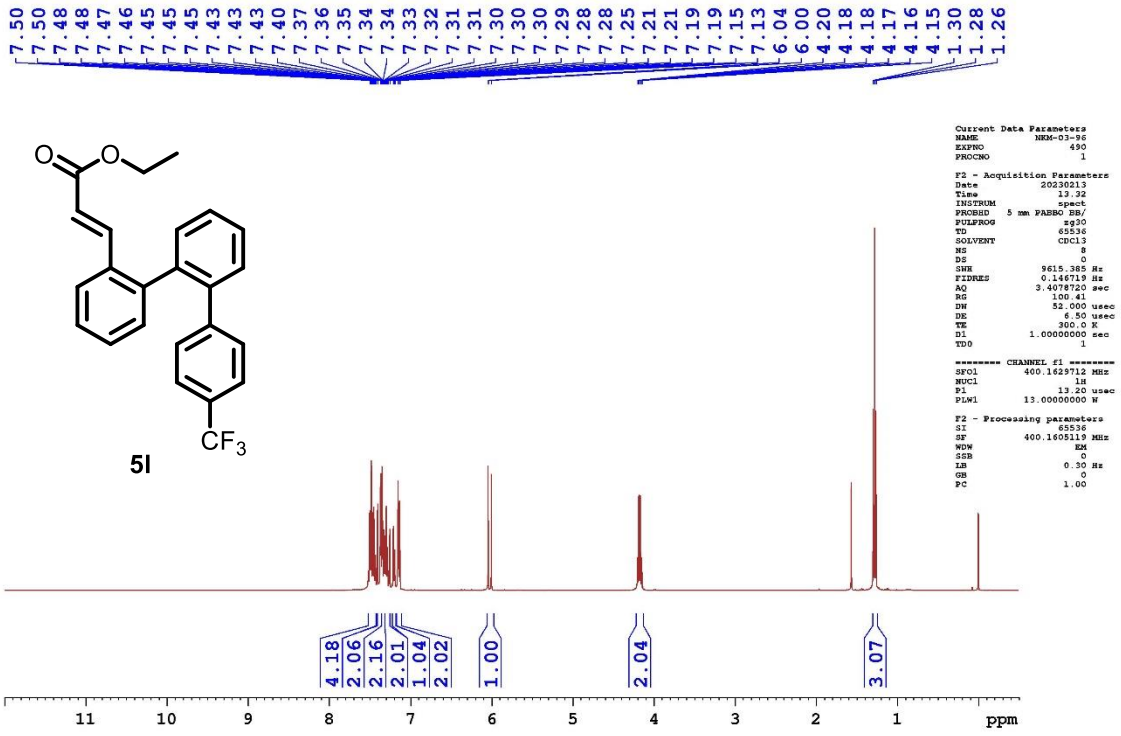

Figure S-84: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5l**

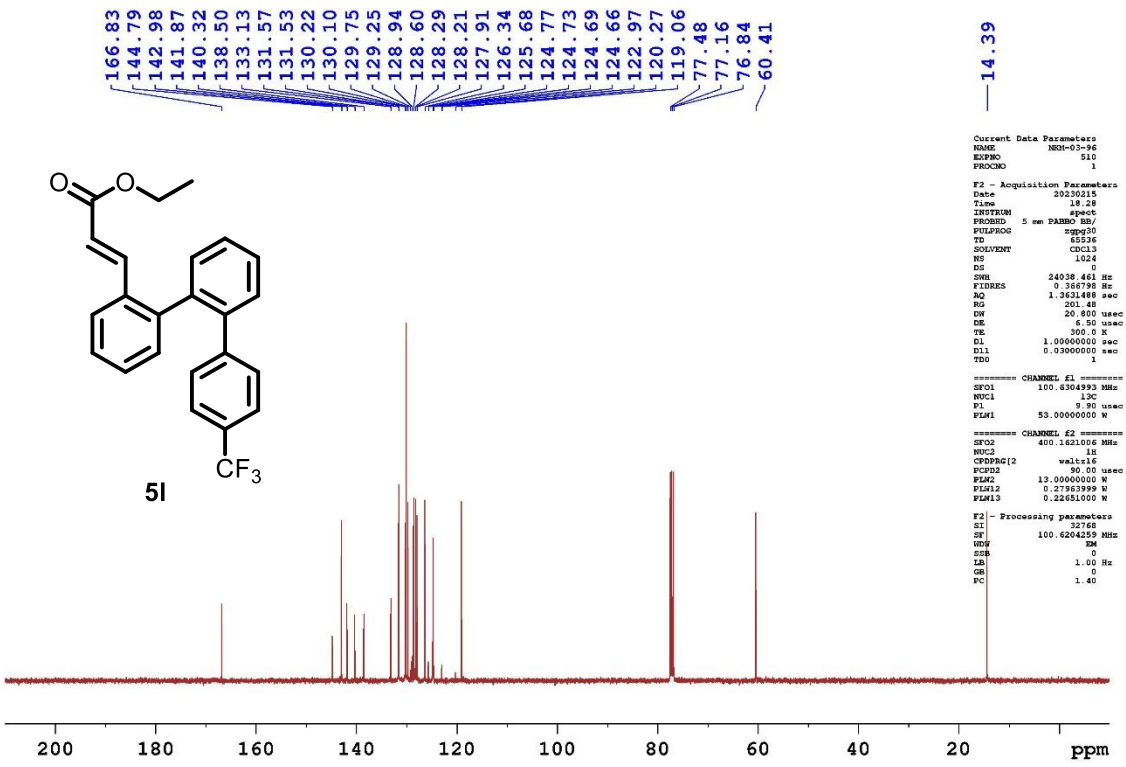

Figure S-85: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5l**

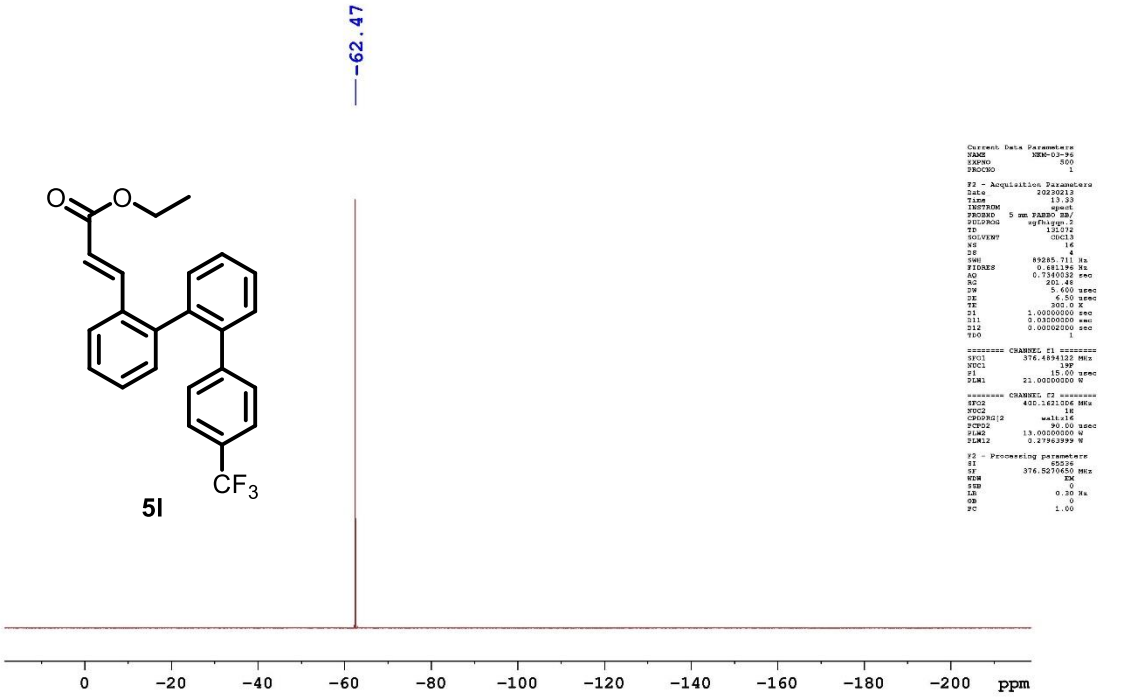

Figure S-86: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **5l**

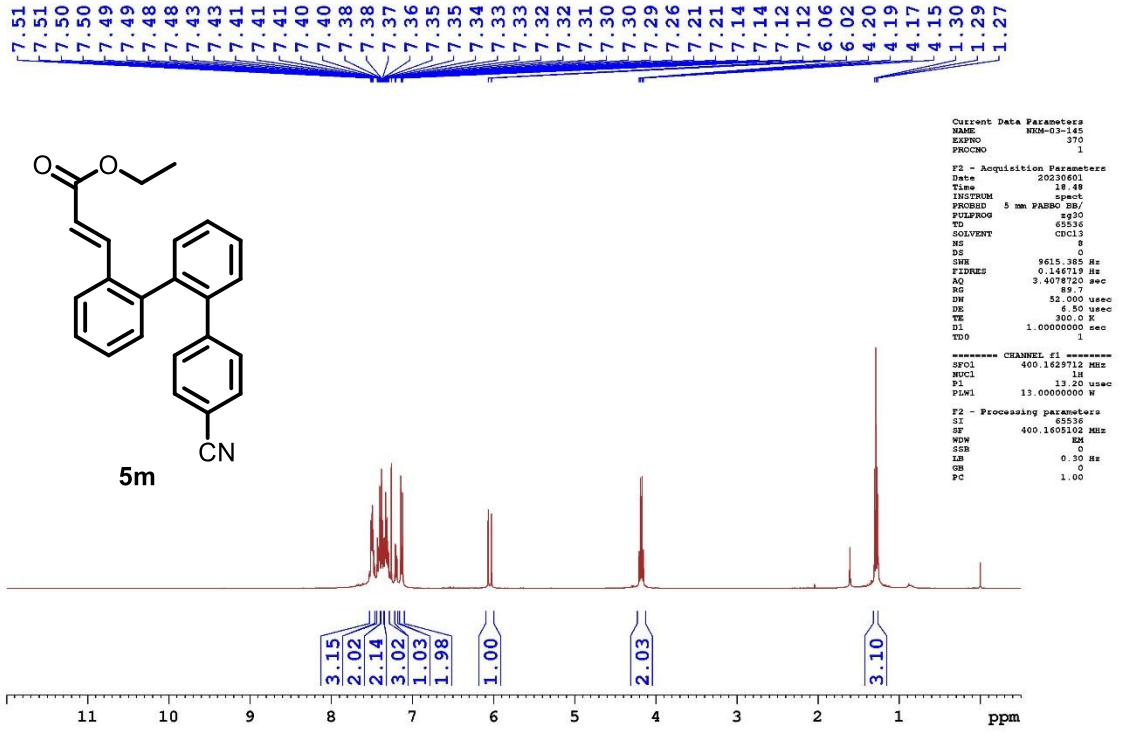

Figure S-87: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5m**

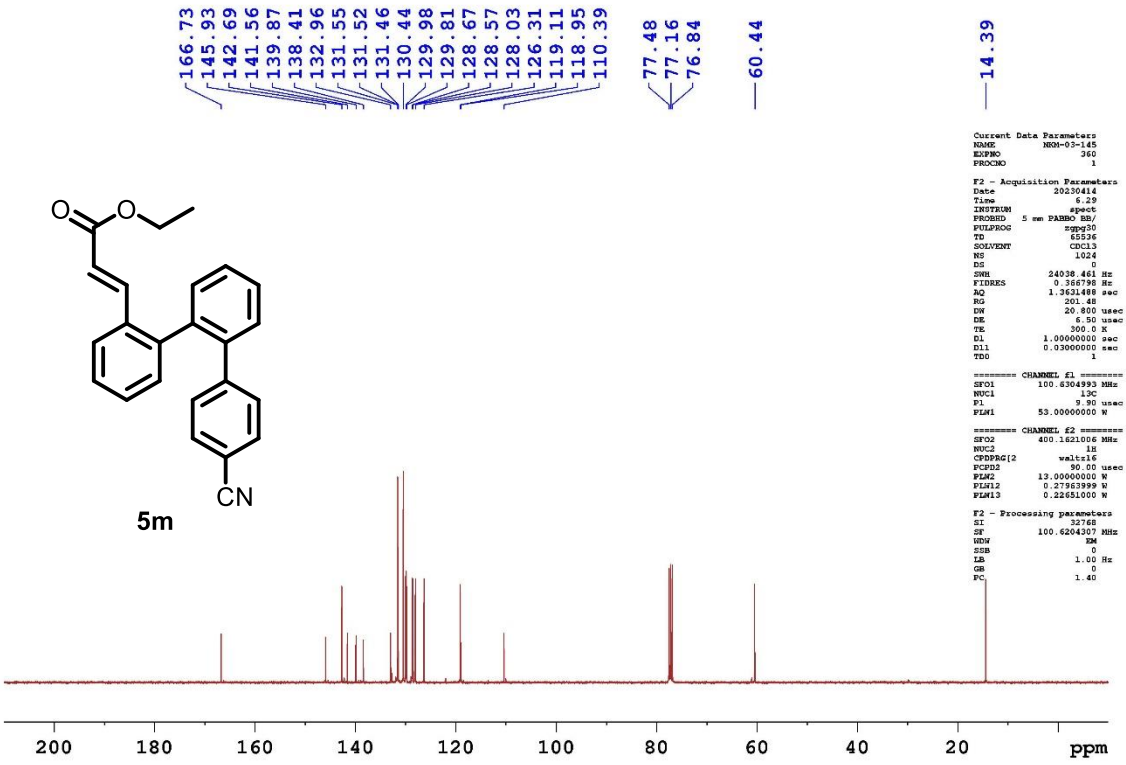

Figure S-88: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5m**

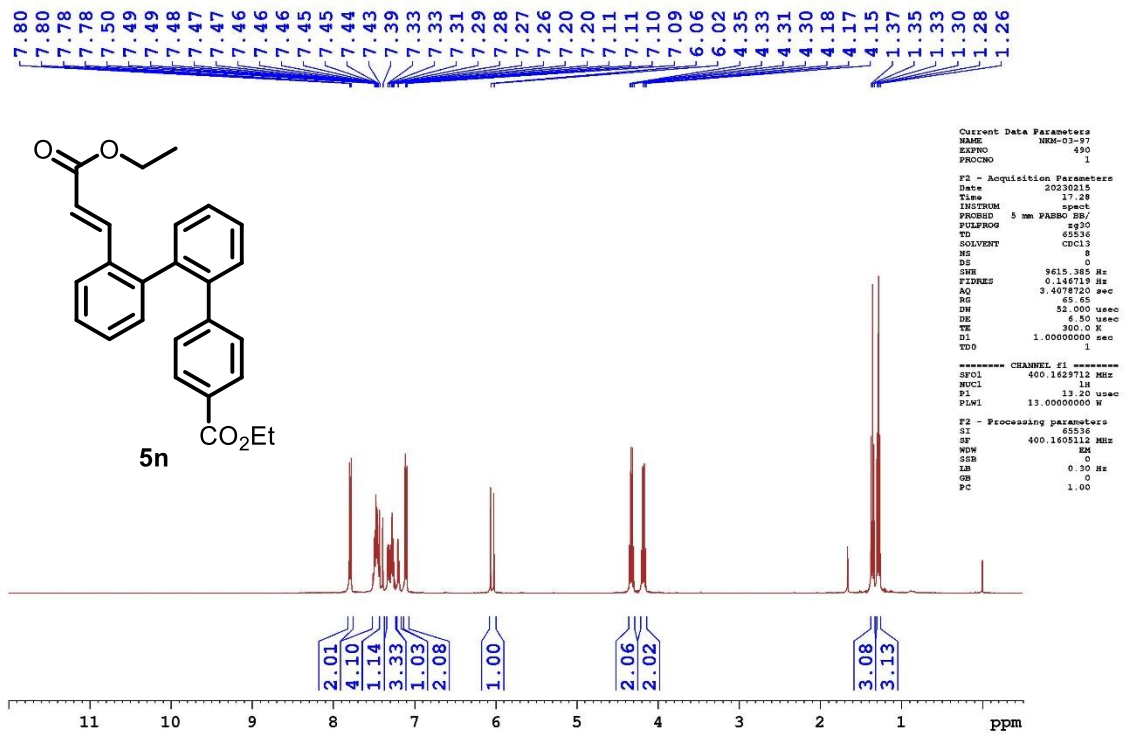

Figure S-89: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5n**

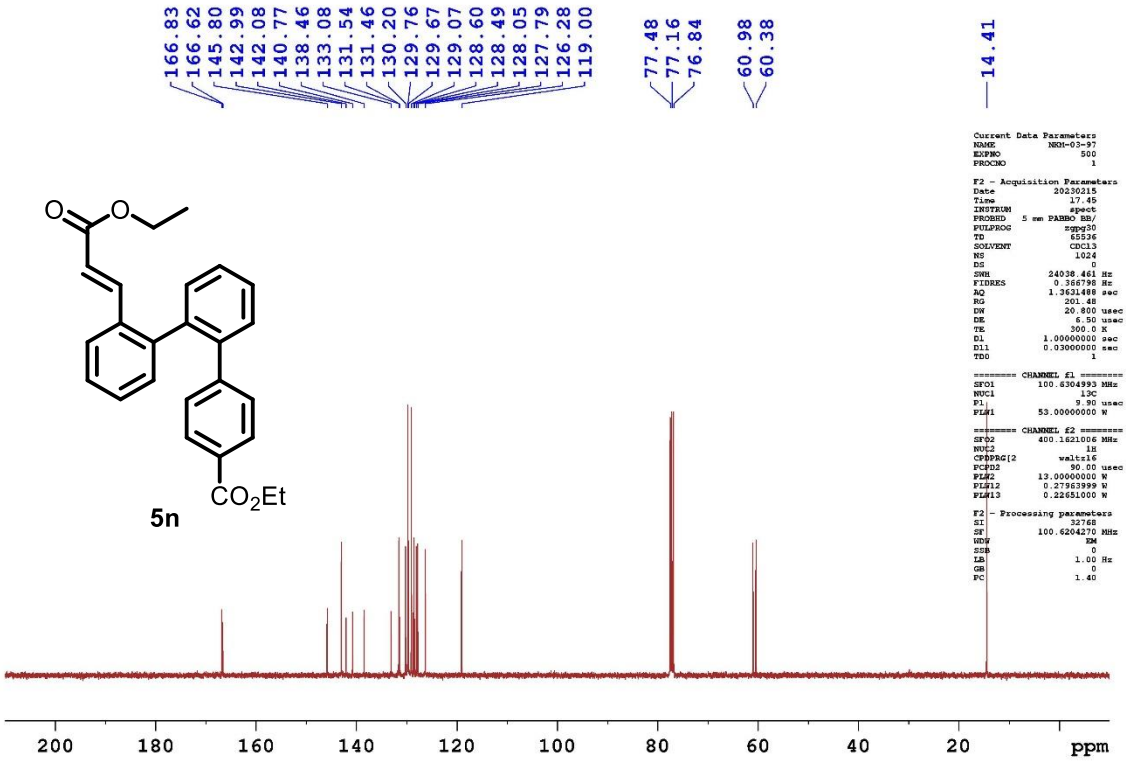

Figure S-90: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5n**

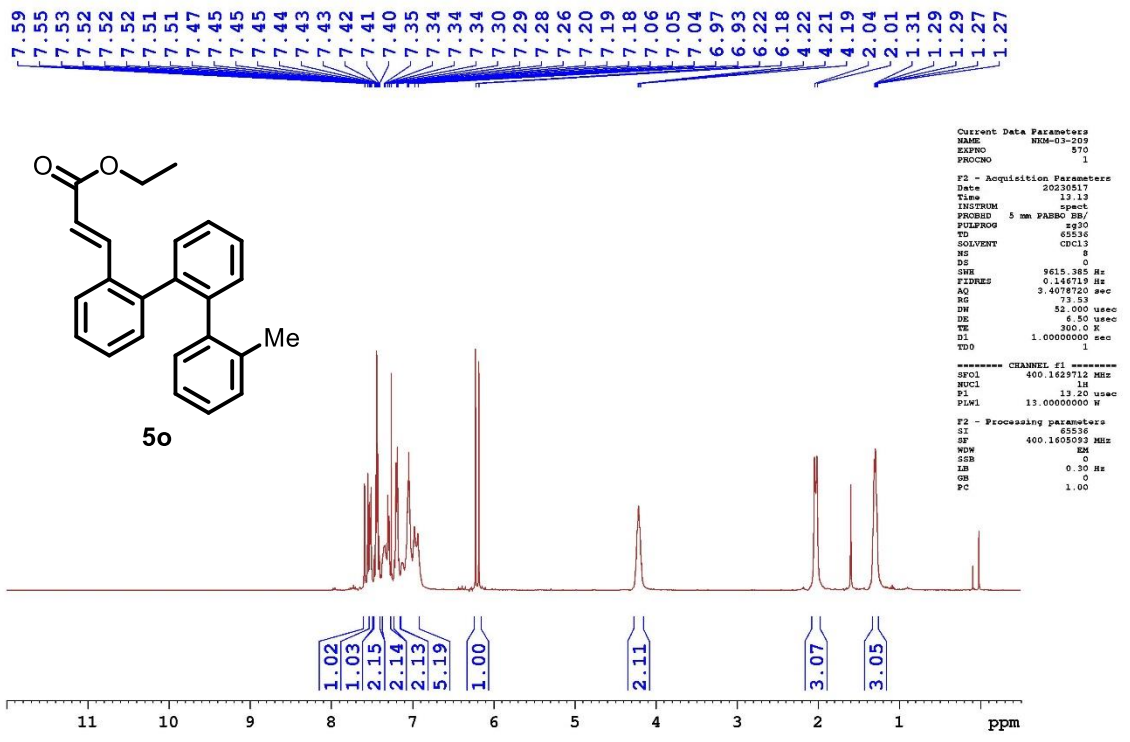

Figure S-91: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5o**

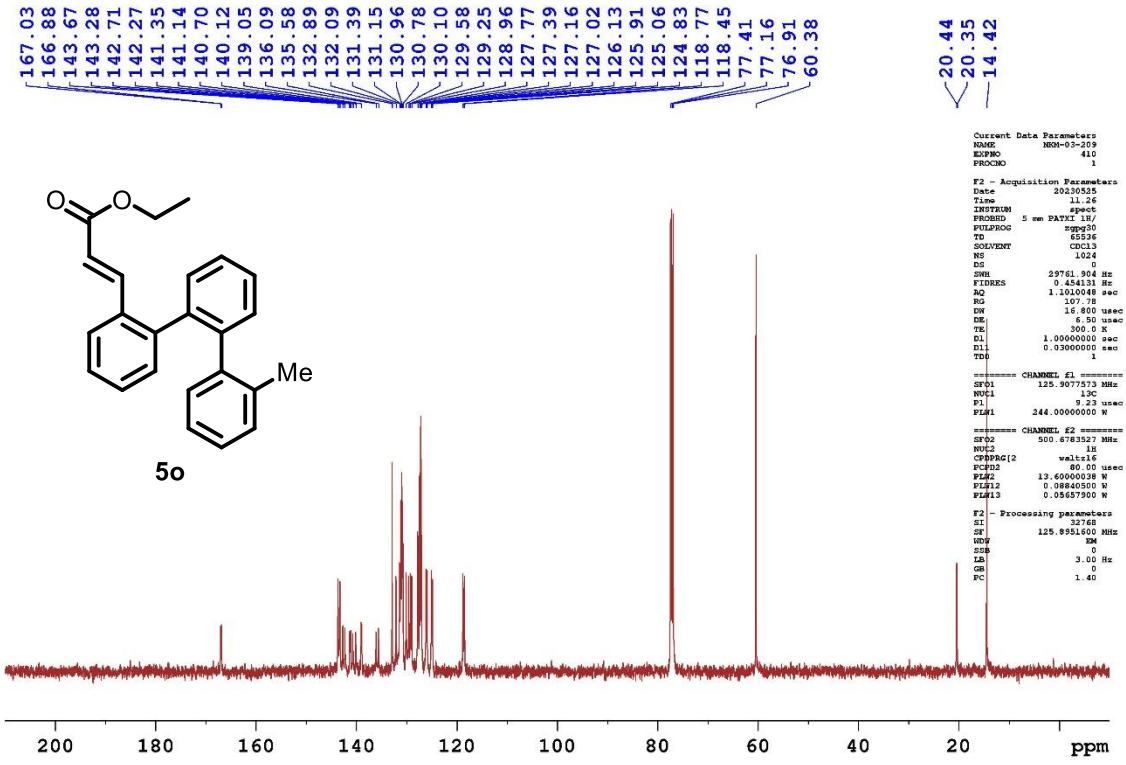

Figure S-92: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **5o**

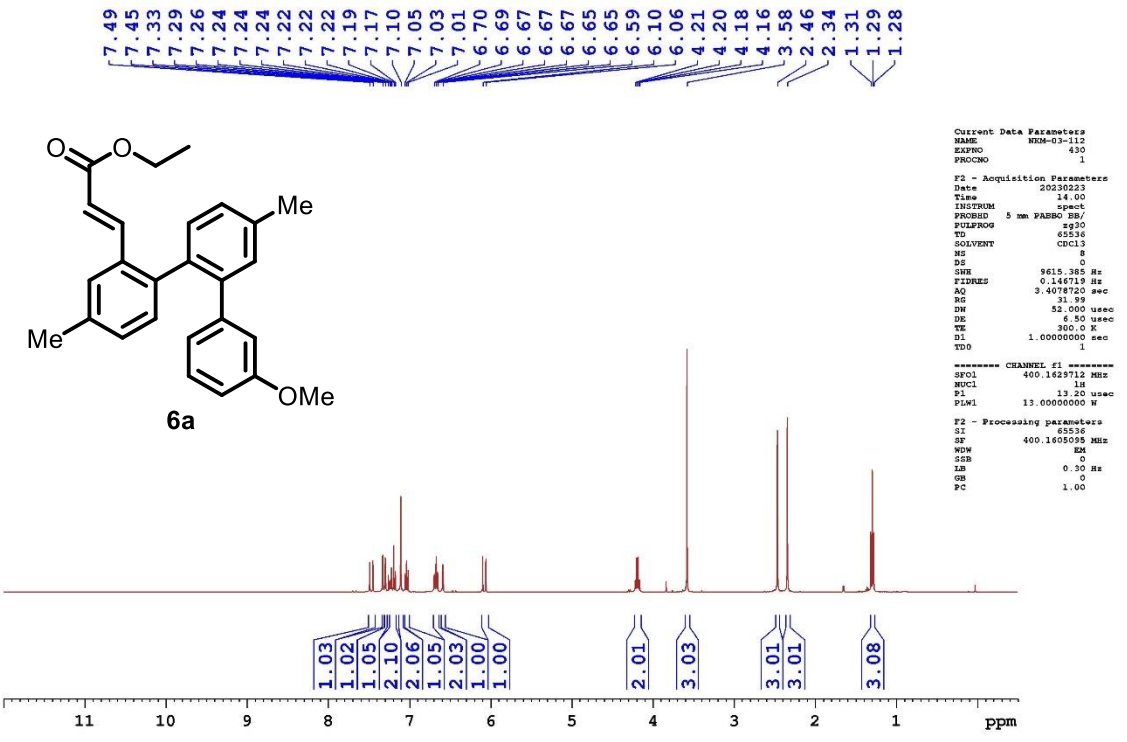

Figure S-93: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6a**

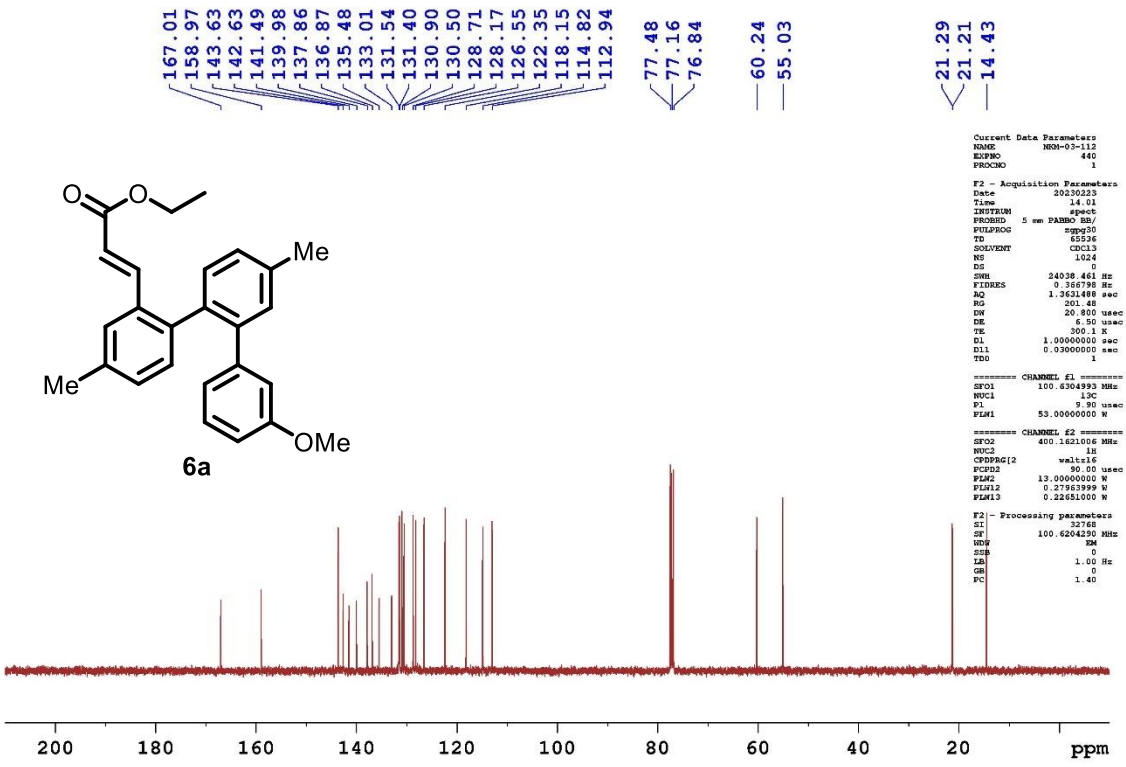

Figure S-94: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6a**

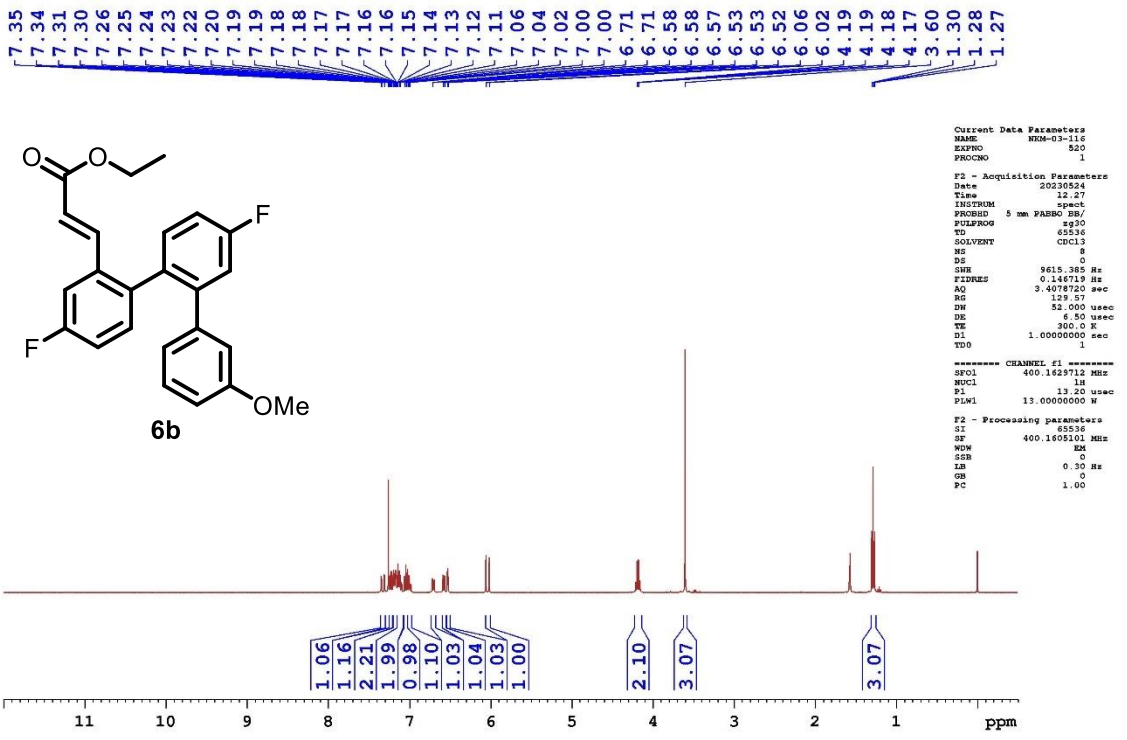

Figure S-95: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6b**

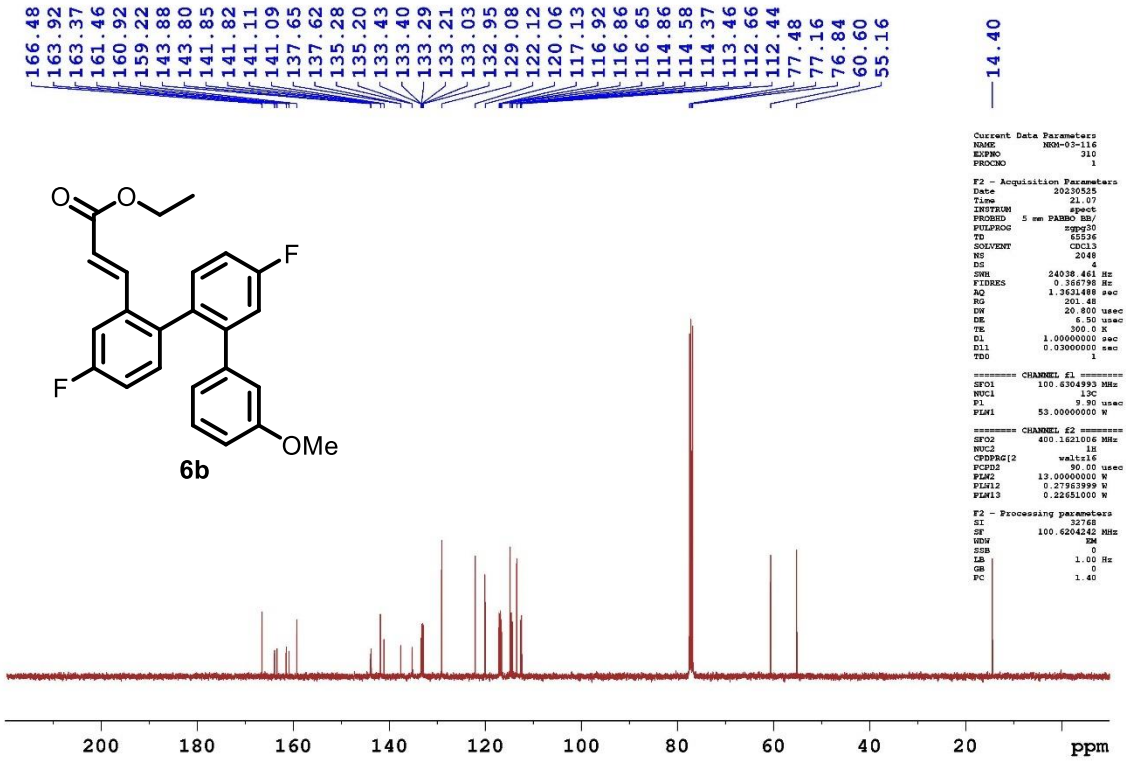

Figure S-96: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6b**

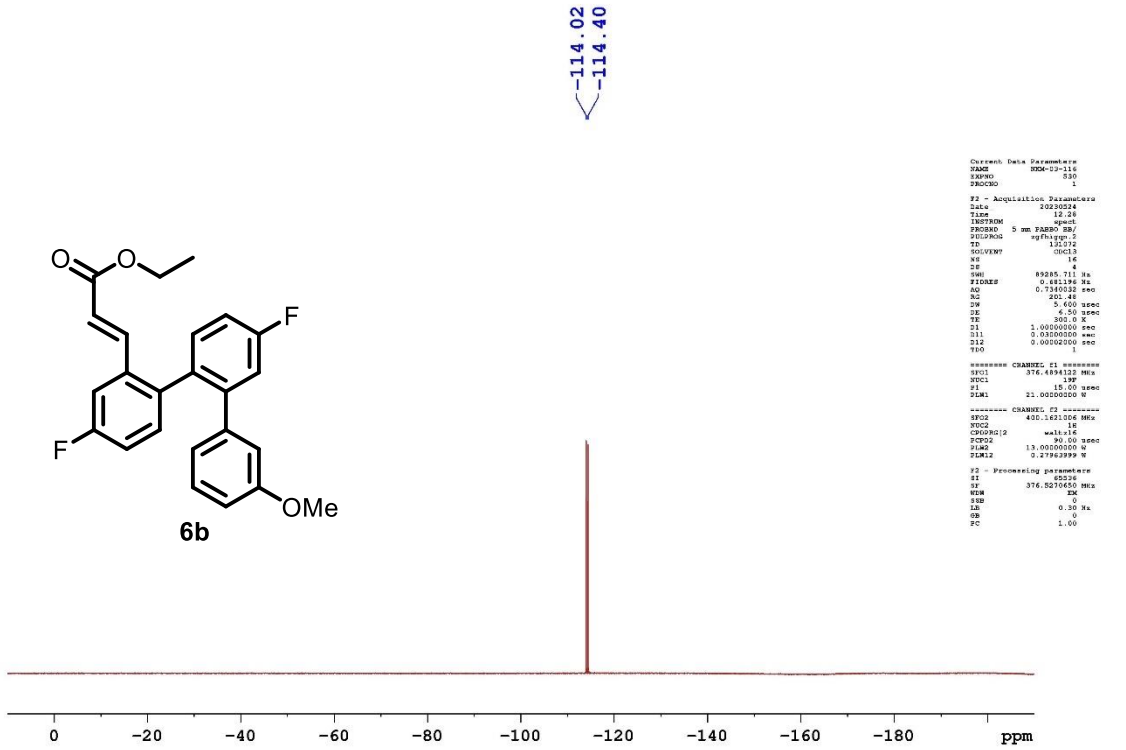

Figure S-97: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **6b**

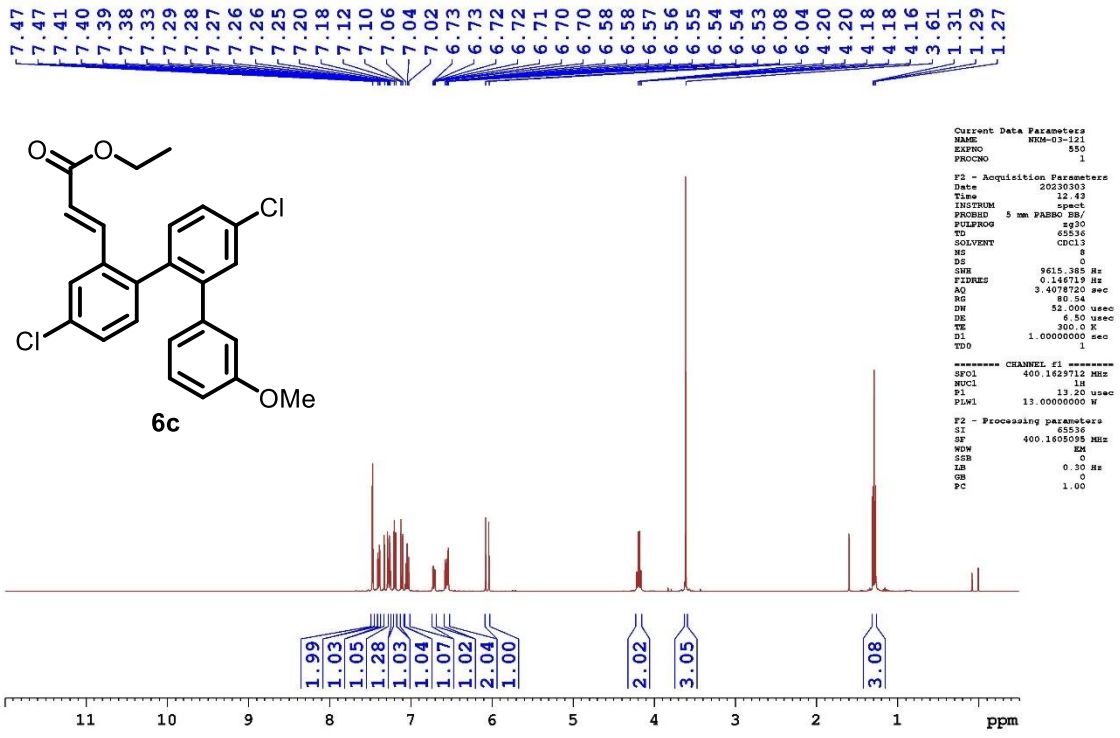

Figure S-98: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6c**

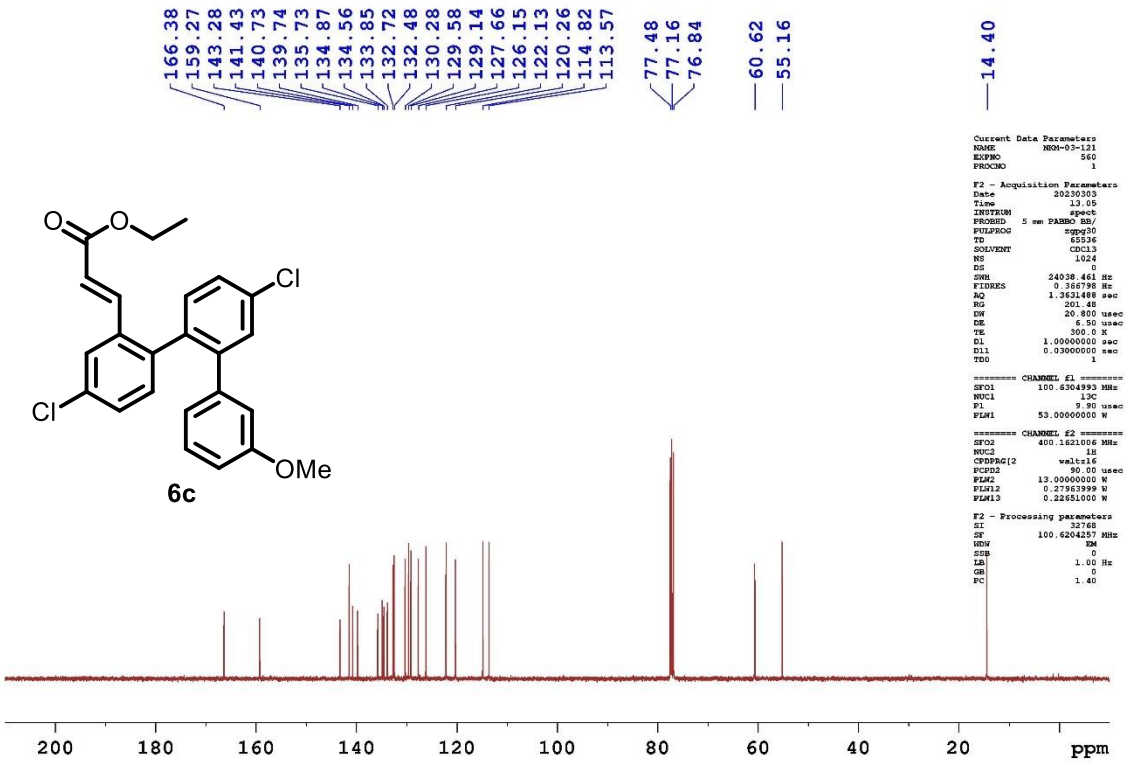

Figure S-99: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6c**

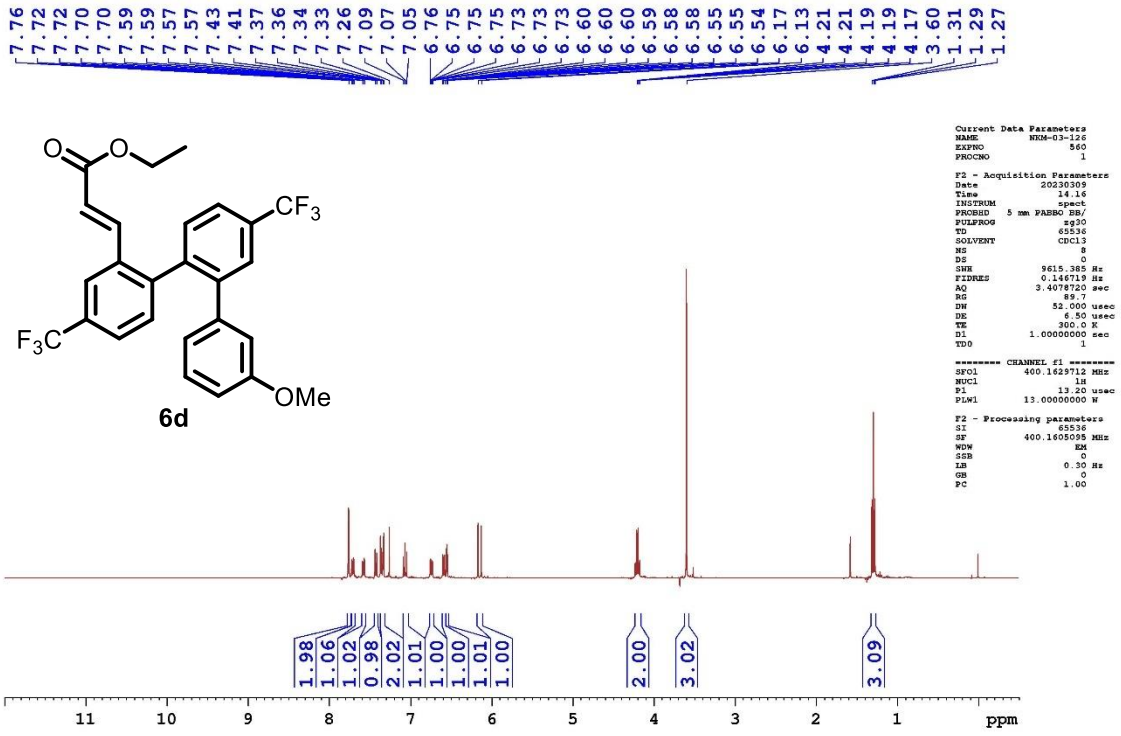

Figure S-100: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6d**

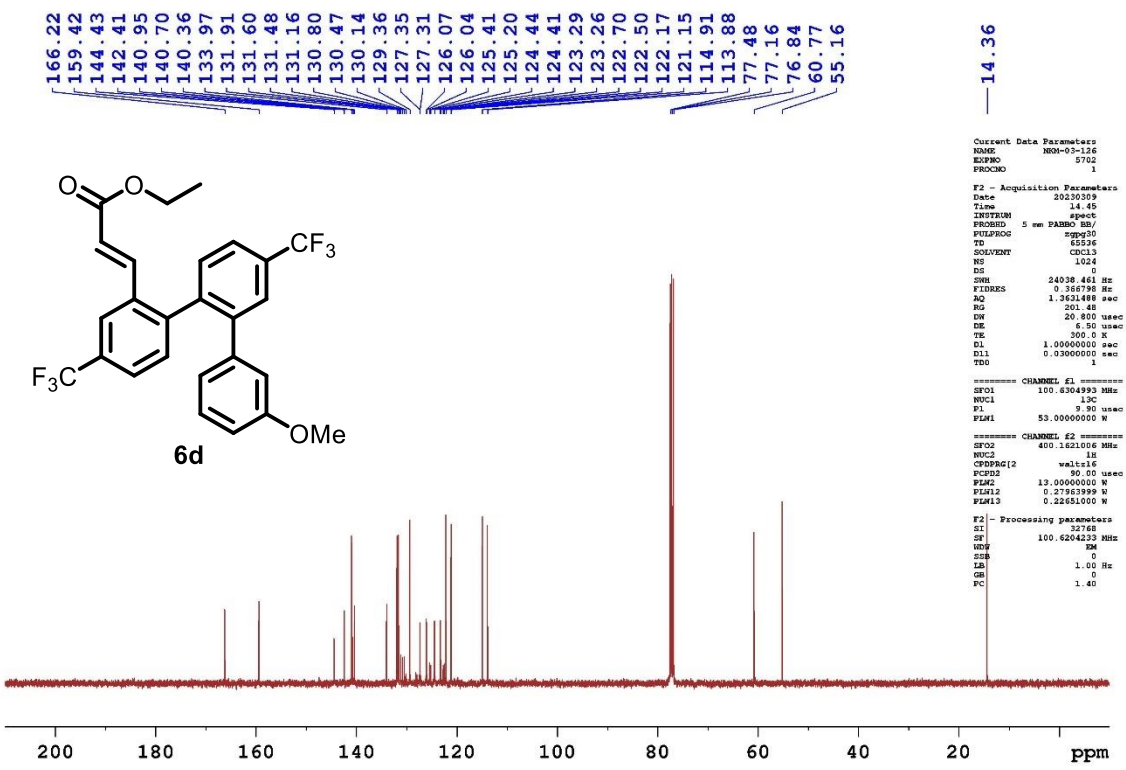

Figure S-101: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6d**

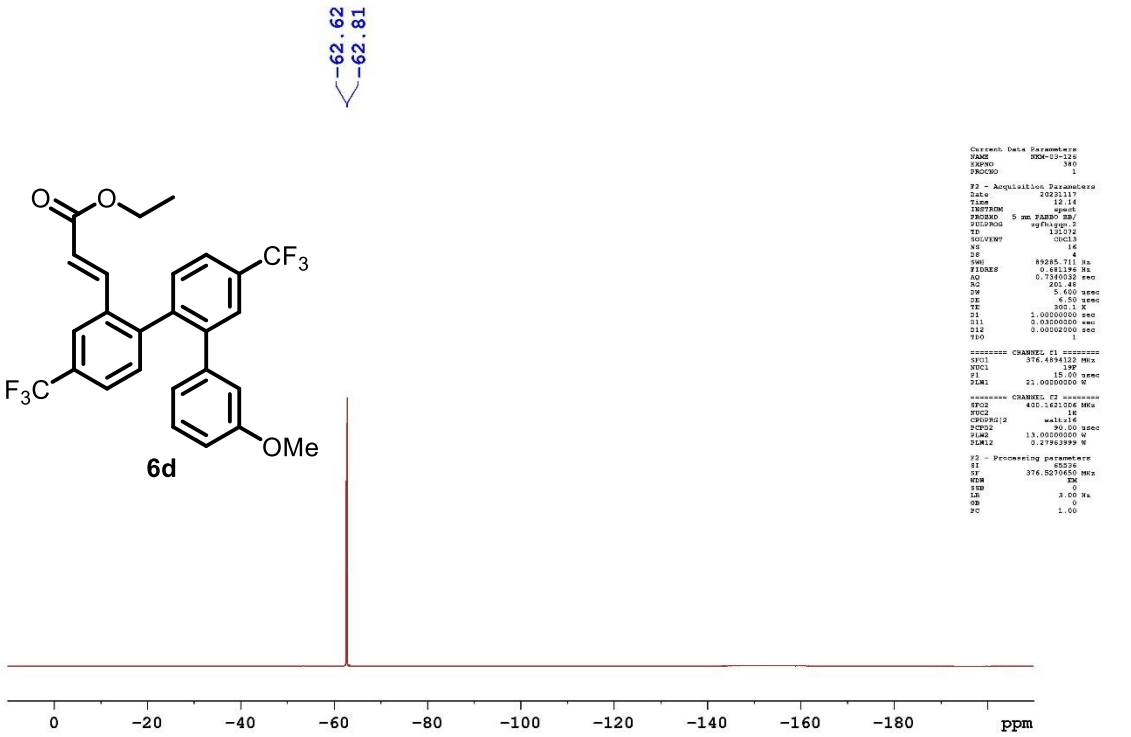

Figure S-102: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **6d**

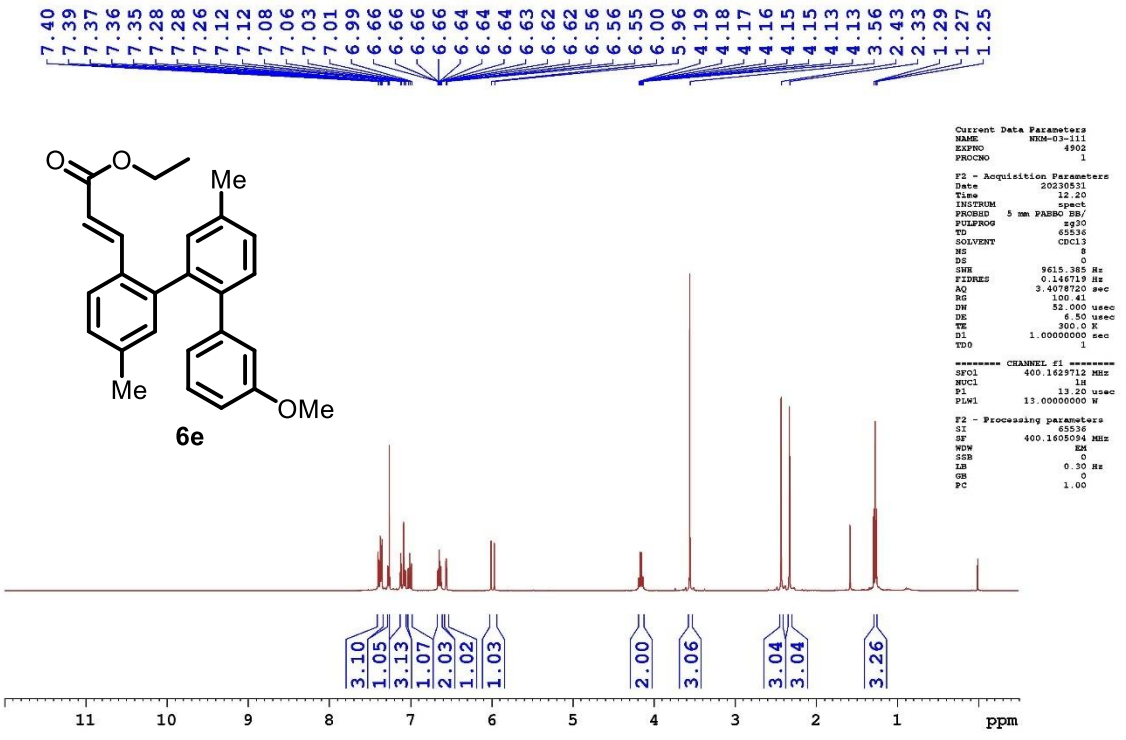

Figure S-103: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6e**

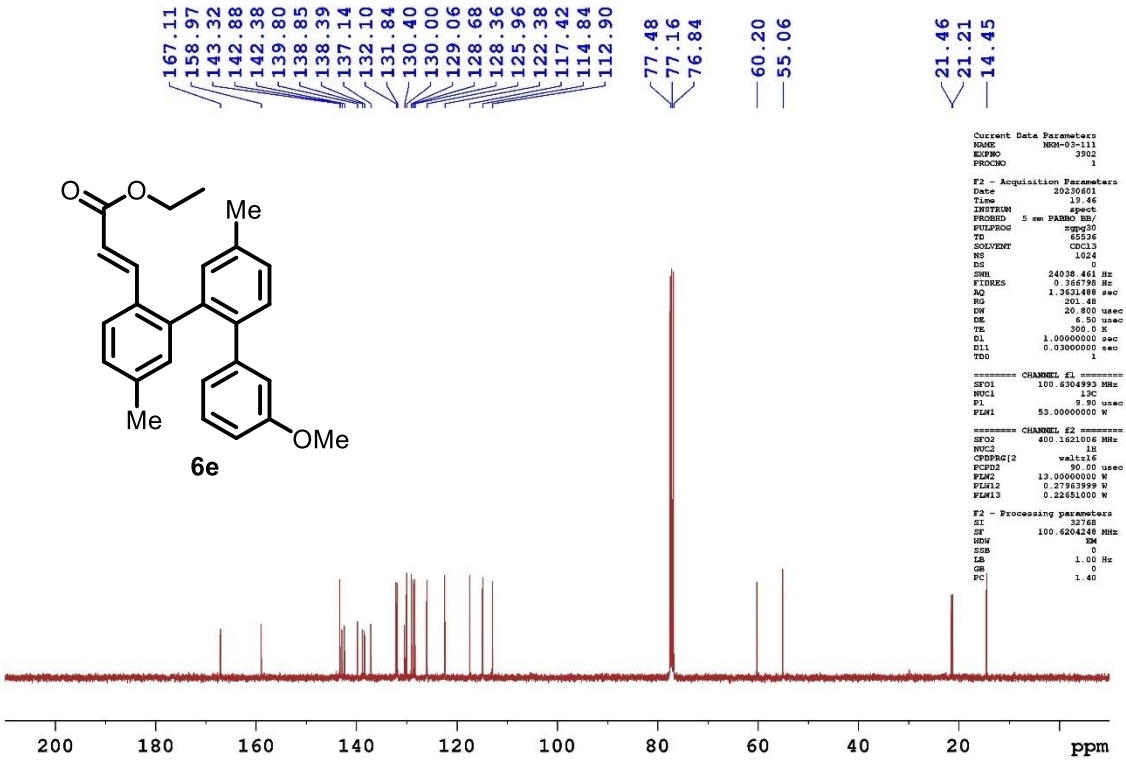

Figure S-104: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6e**

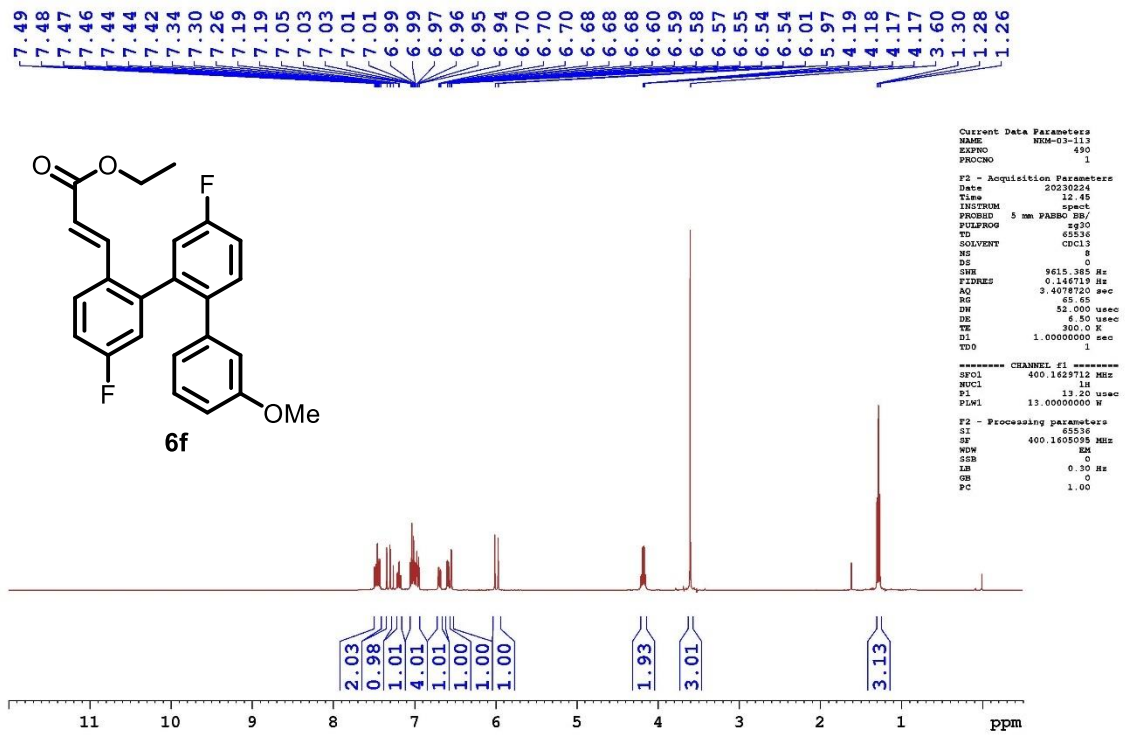

Figure S-105: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6f**

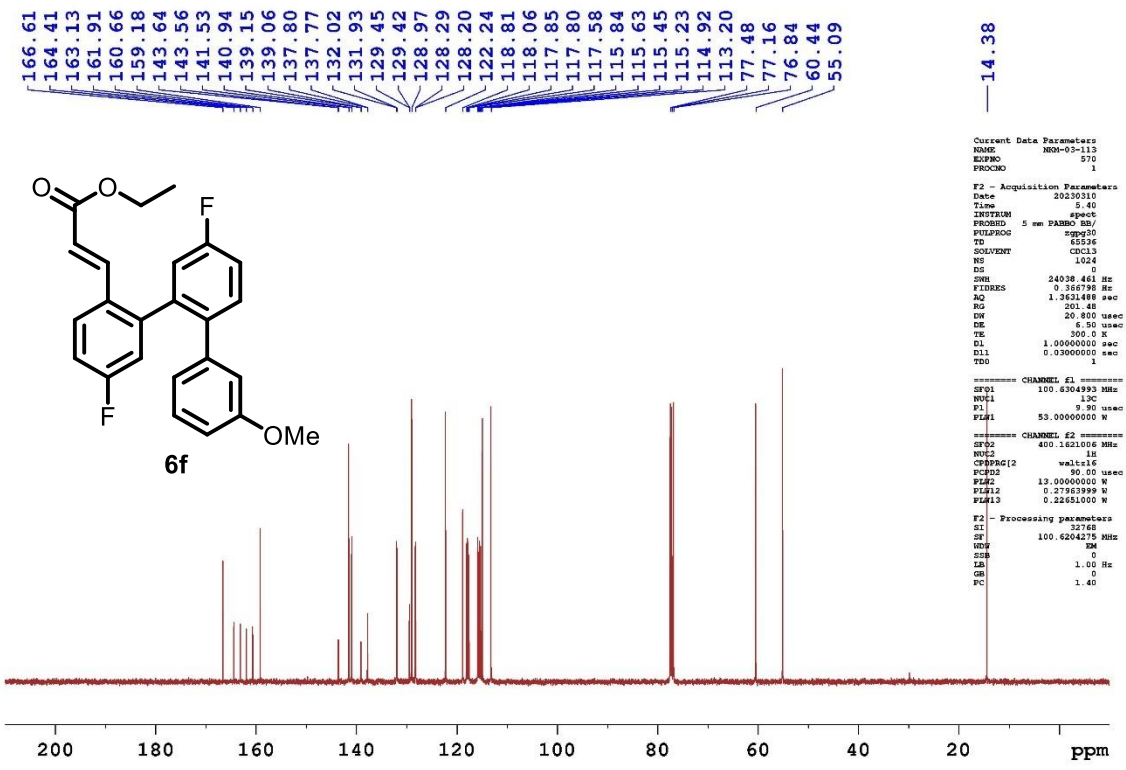

Figure S-106: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6f**

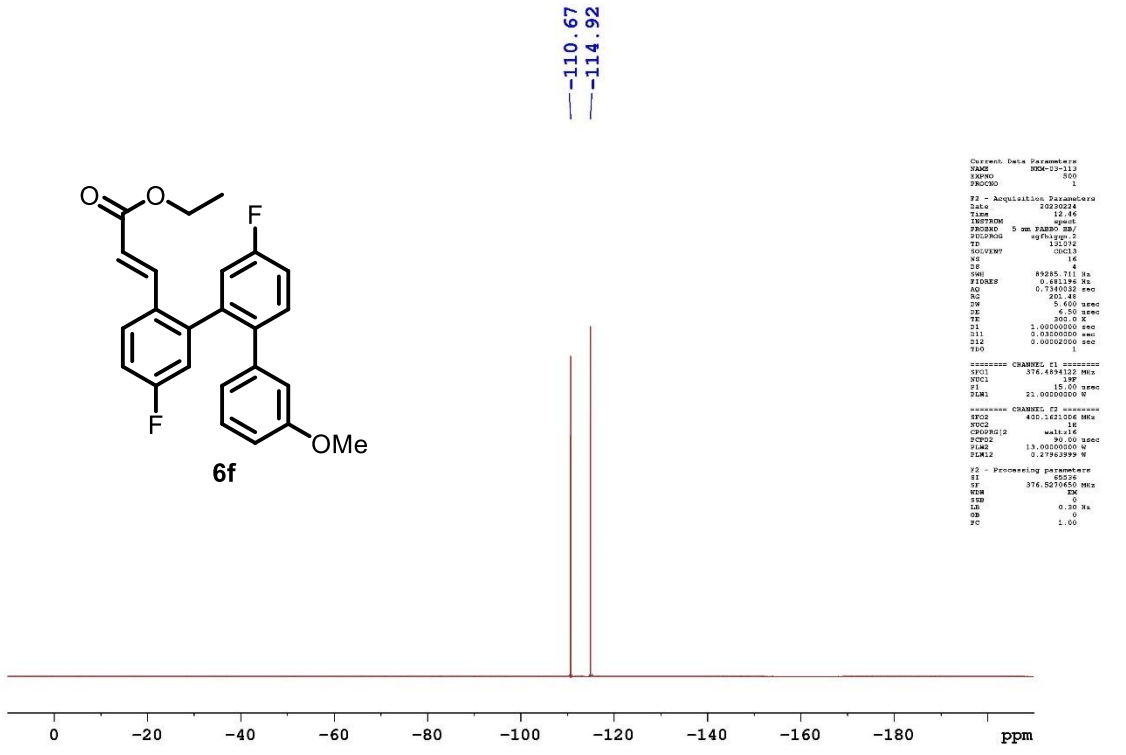

Figure S-107: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **6f**

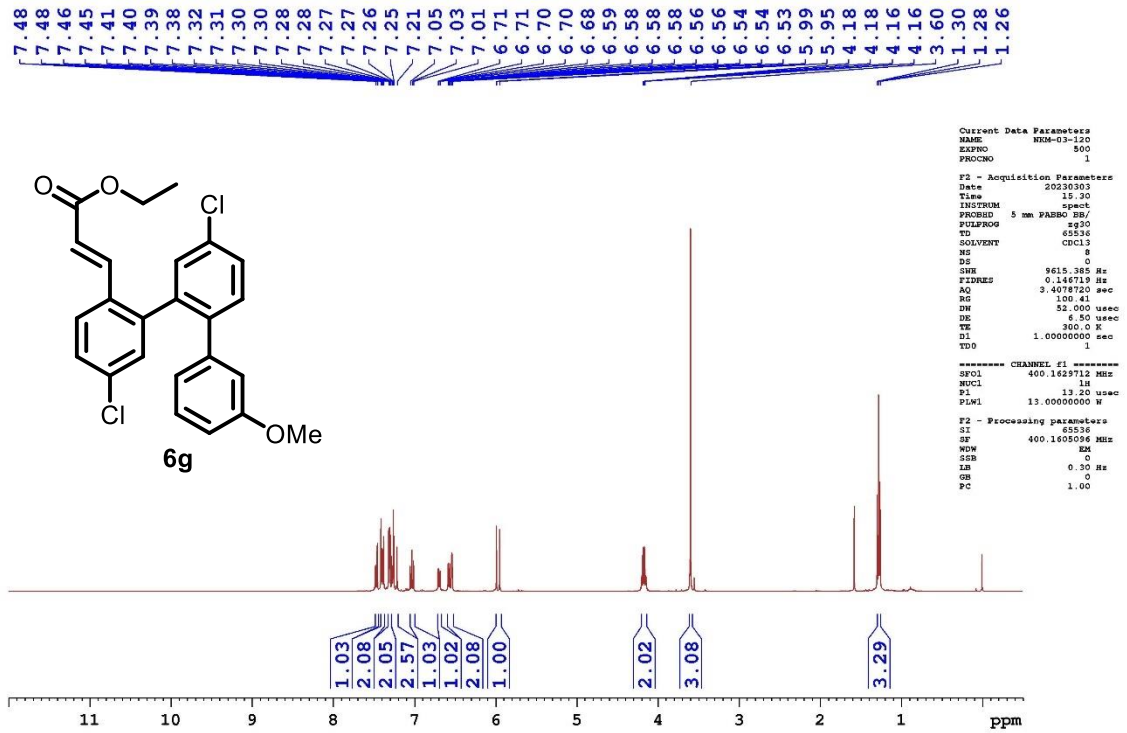

Figure S-108: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6g**

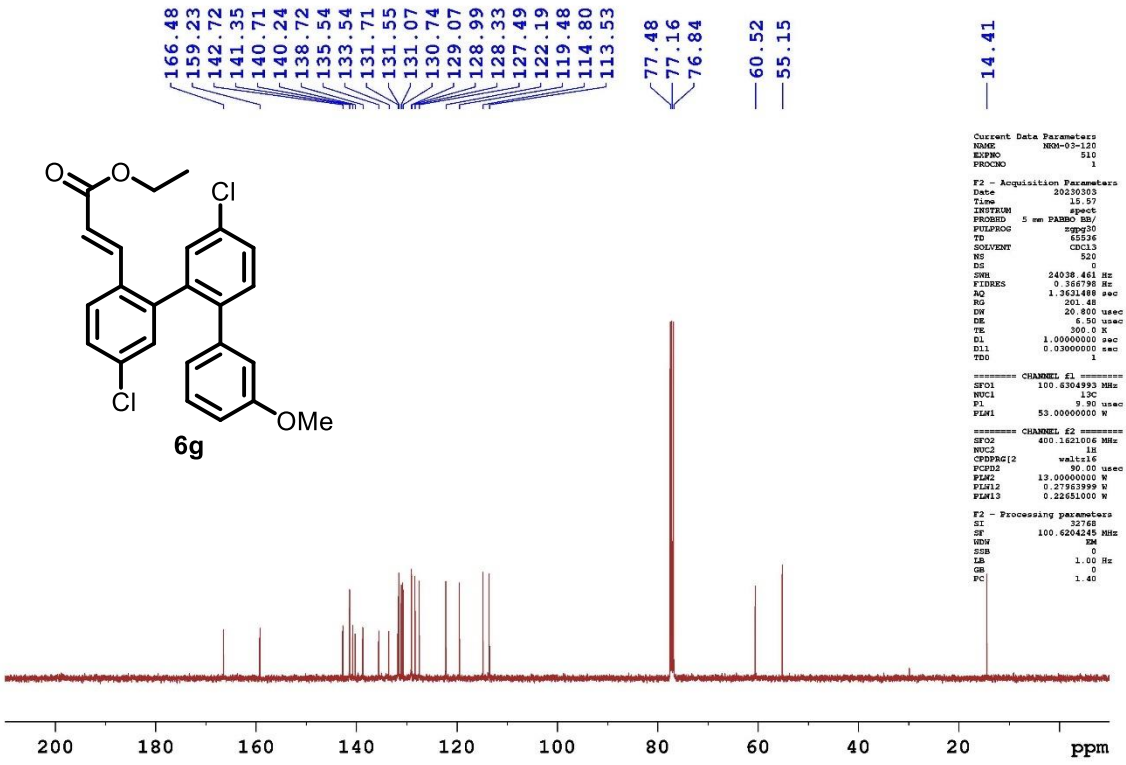

Figure S-109: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6g**

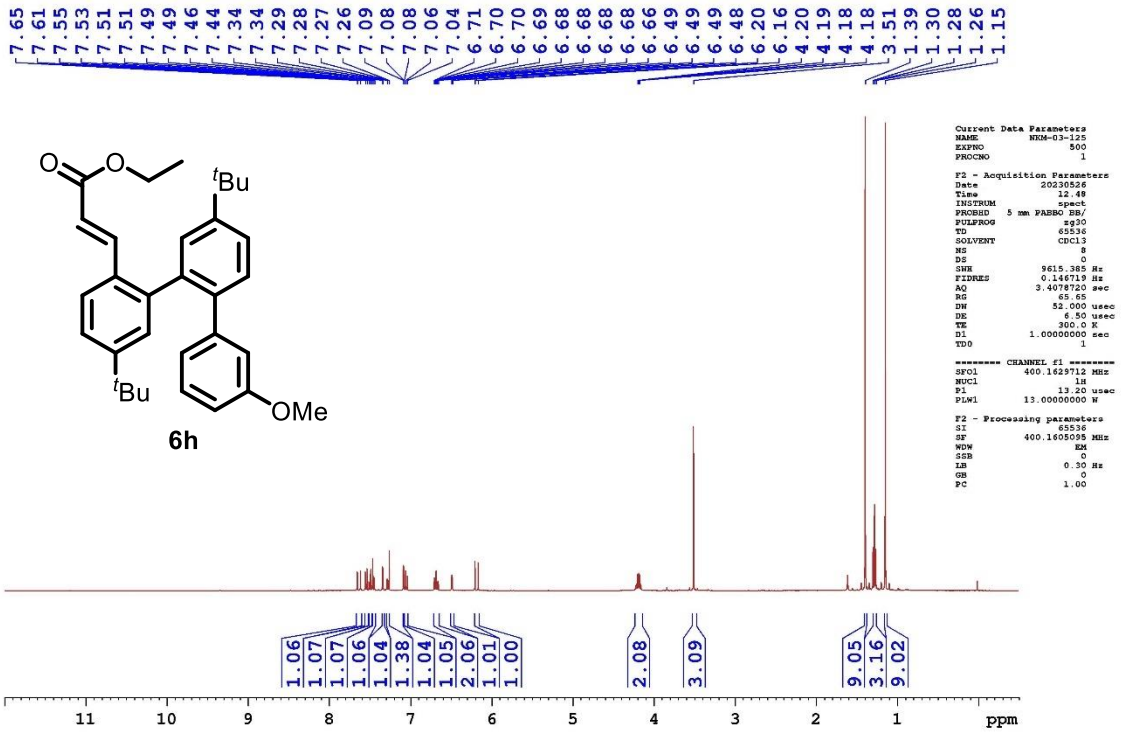

Figure S-110: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6h**

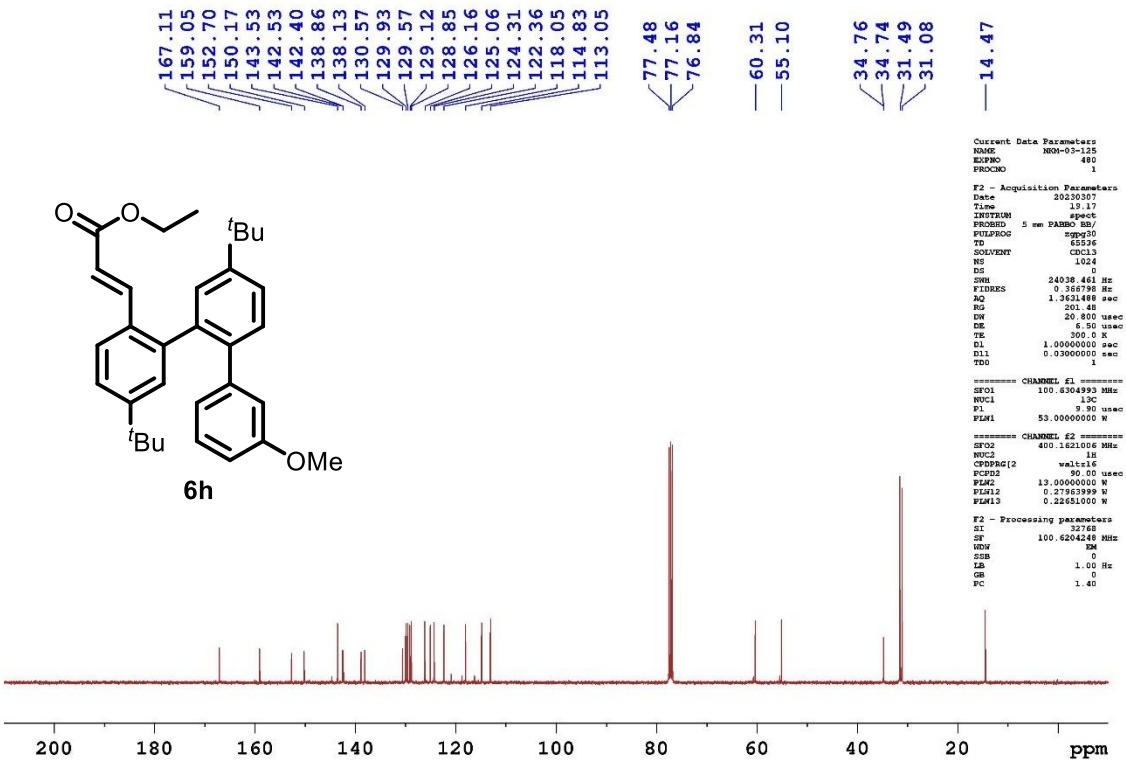

Figure S-111: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6h**

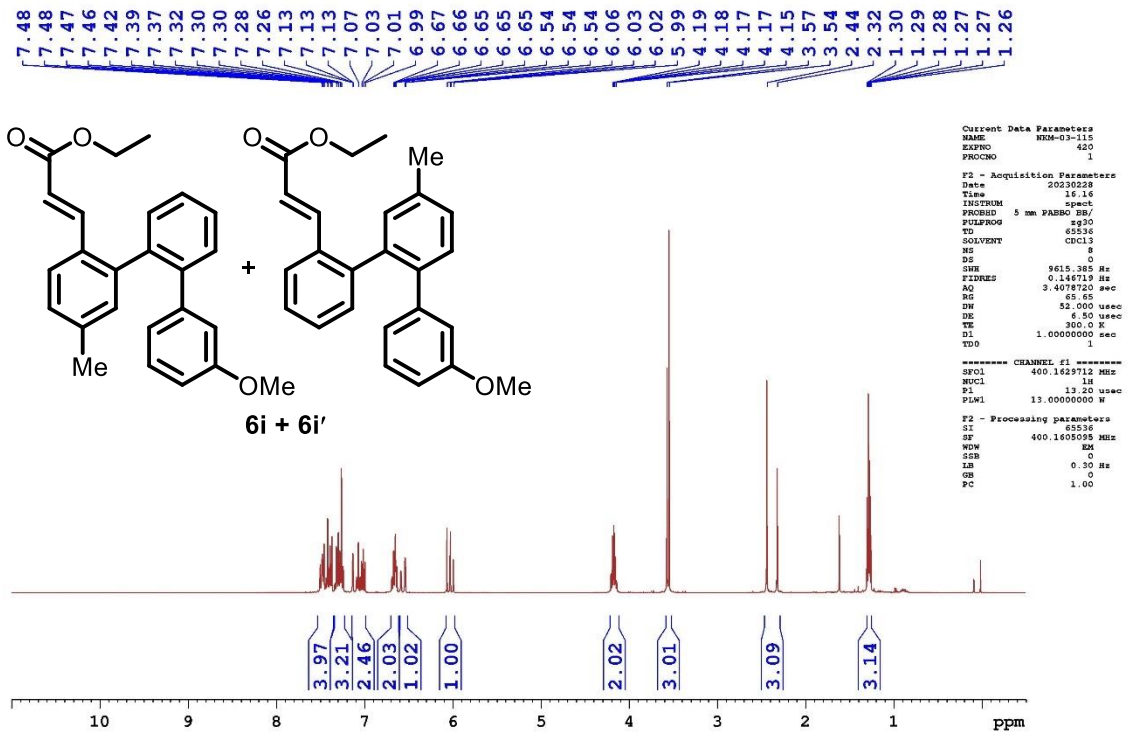

Figure S-112: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6i + 6i′**

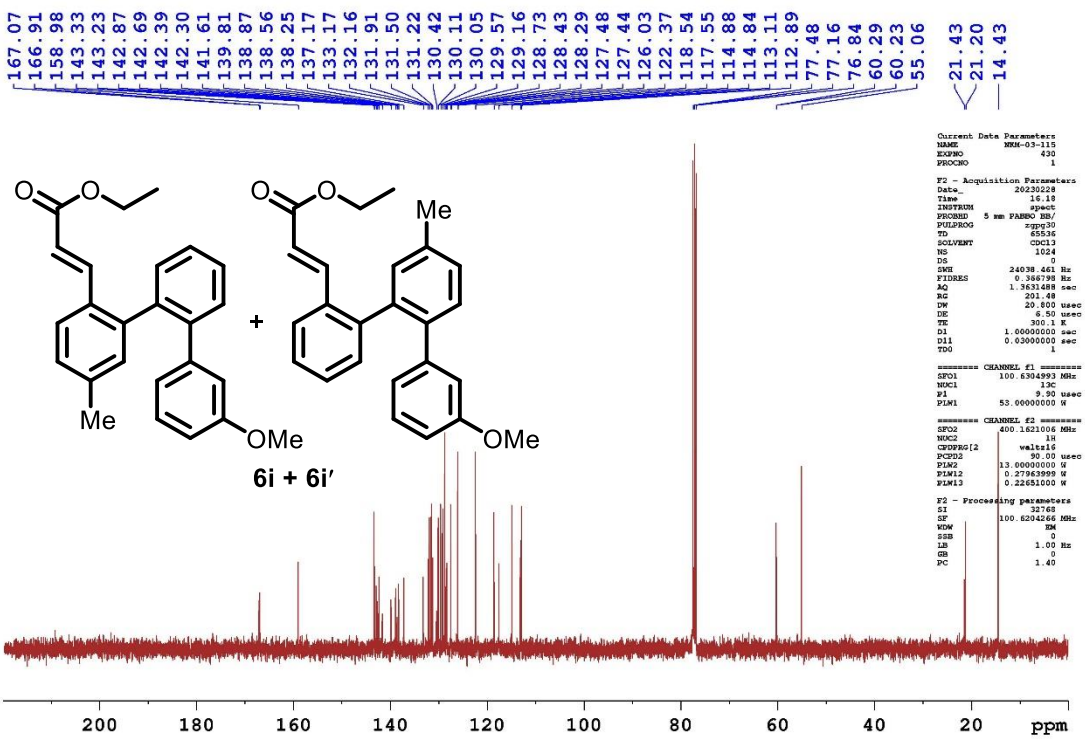

Figure S-113: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6i + 6i′**

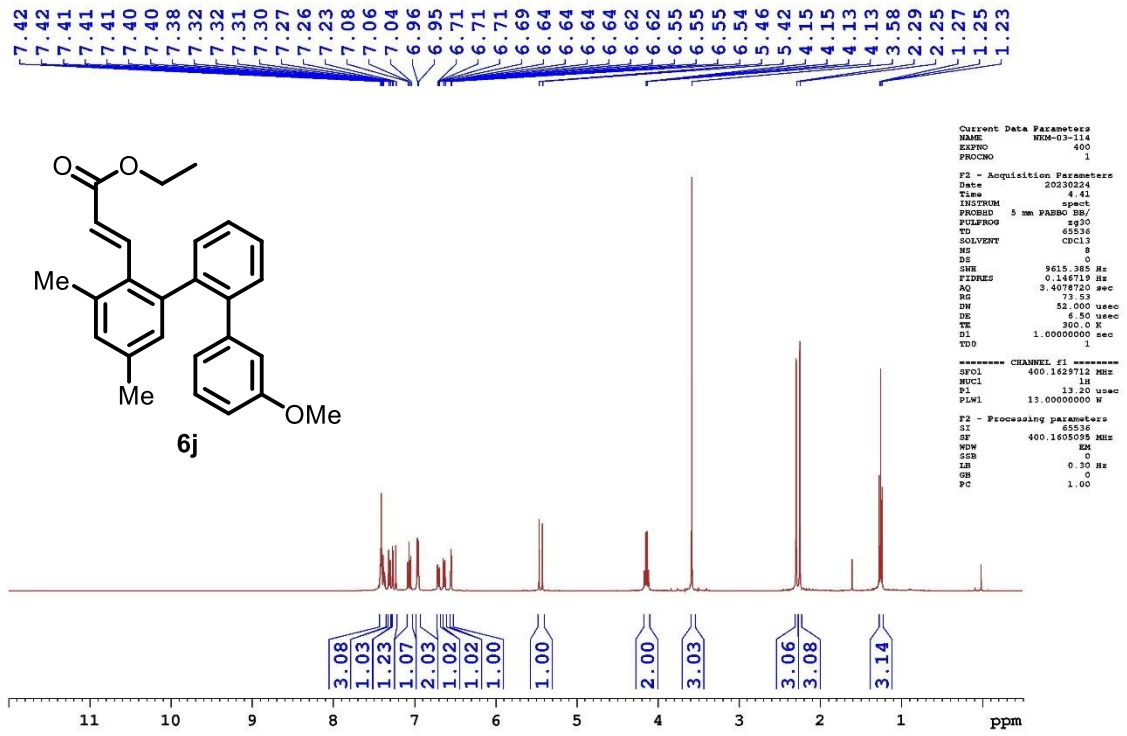

Figure S-114: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6j**

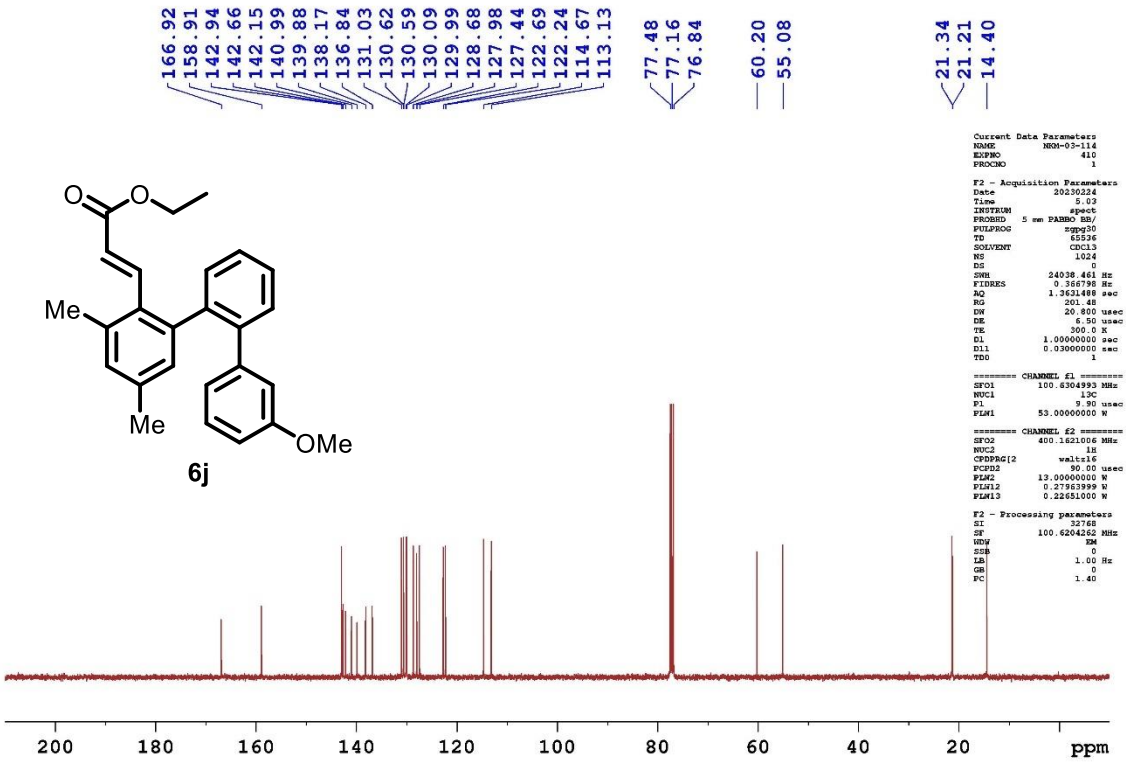

Figure S-115: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6j**

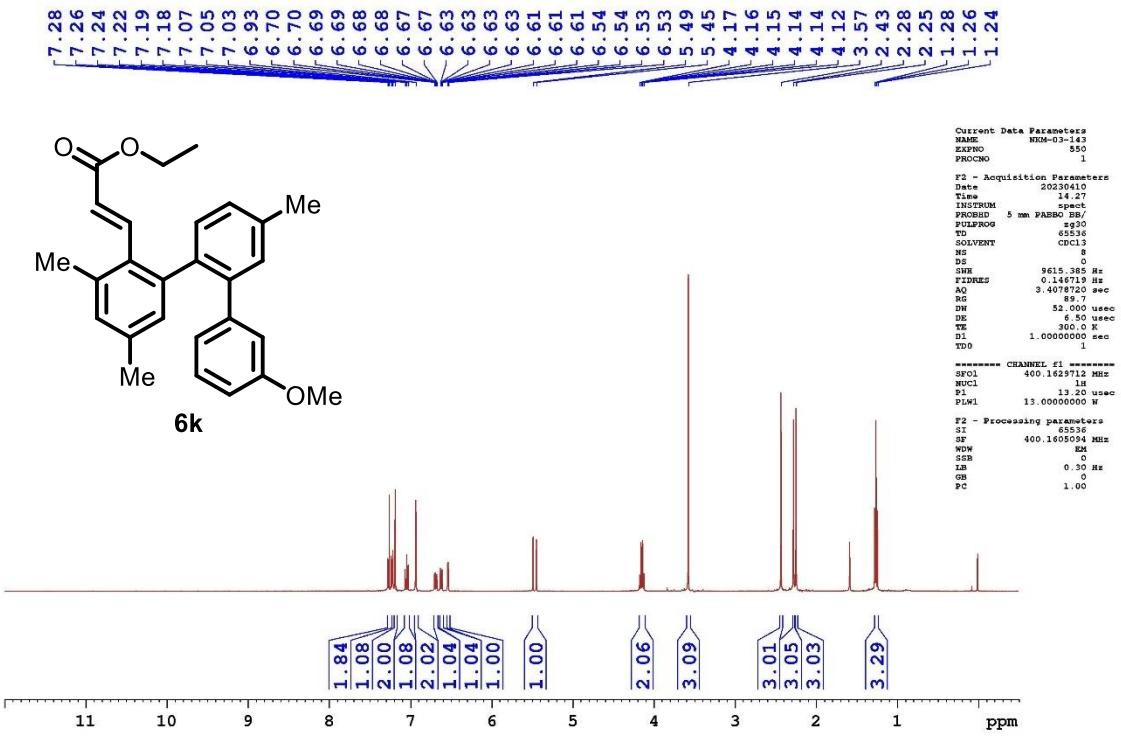

Figure S-116: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6k**

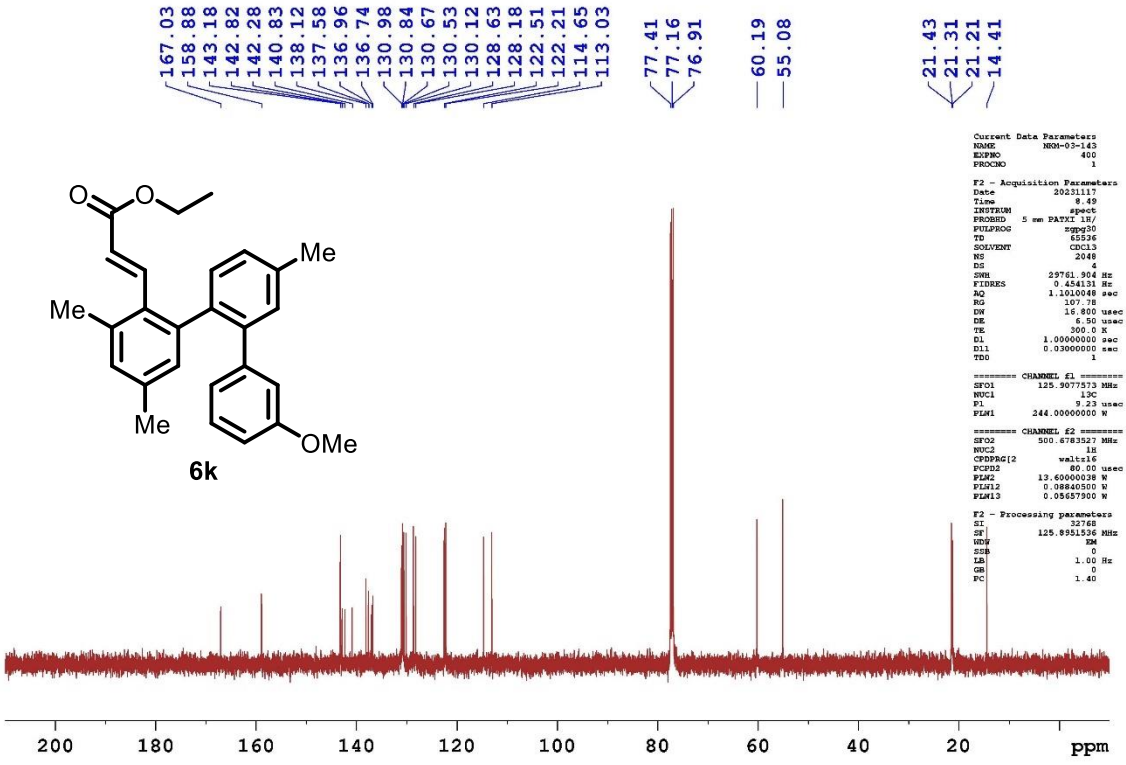

Figure S-117: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **6k**

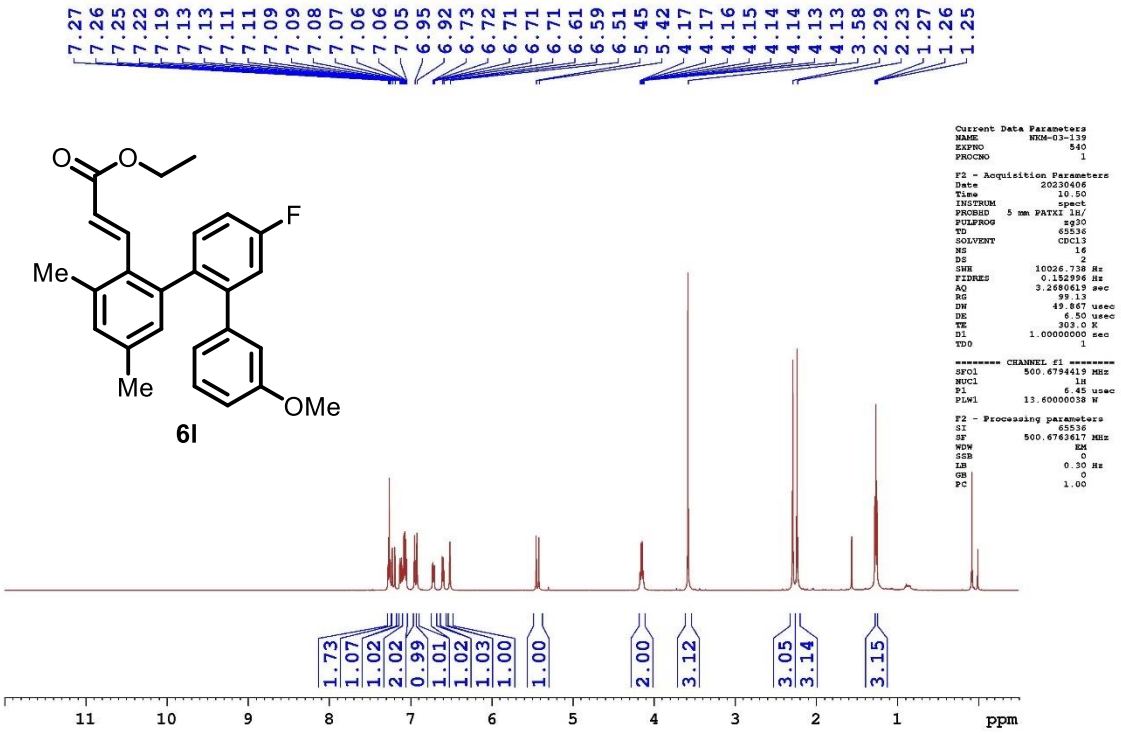

Figure S-118: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **6l**

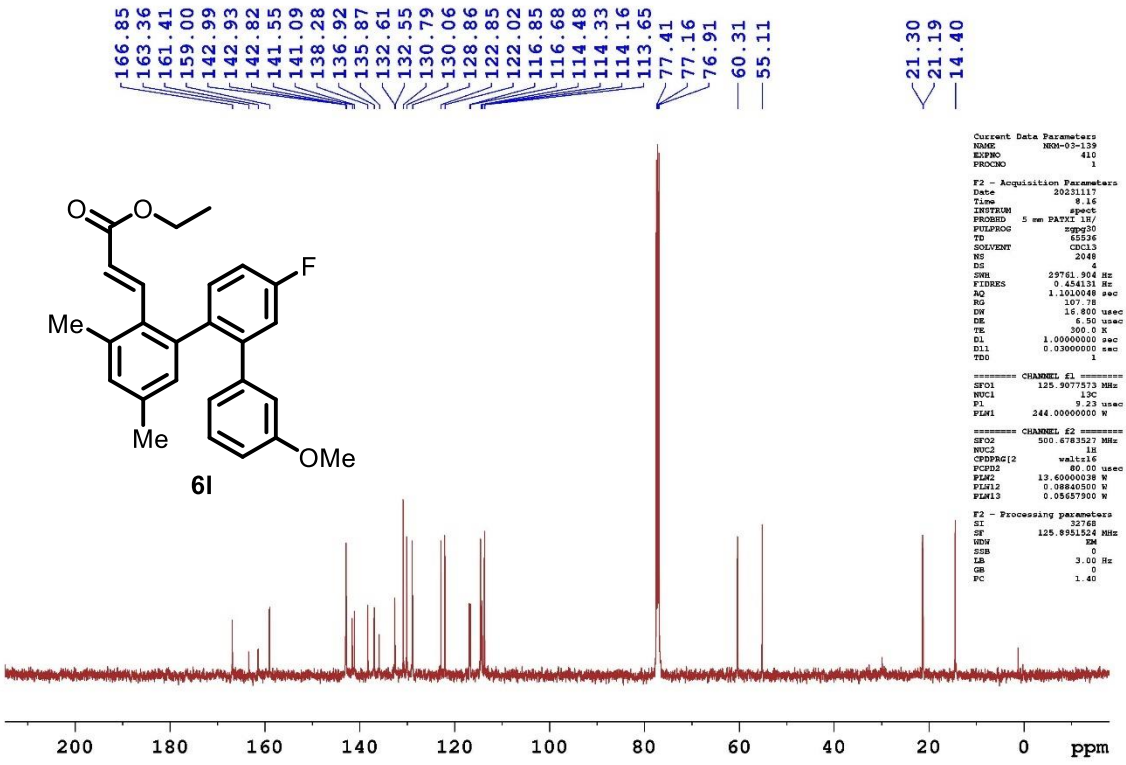

Figure S-119: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **6l**

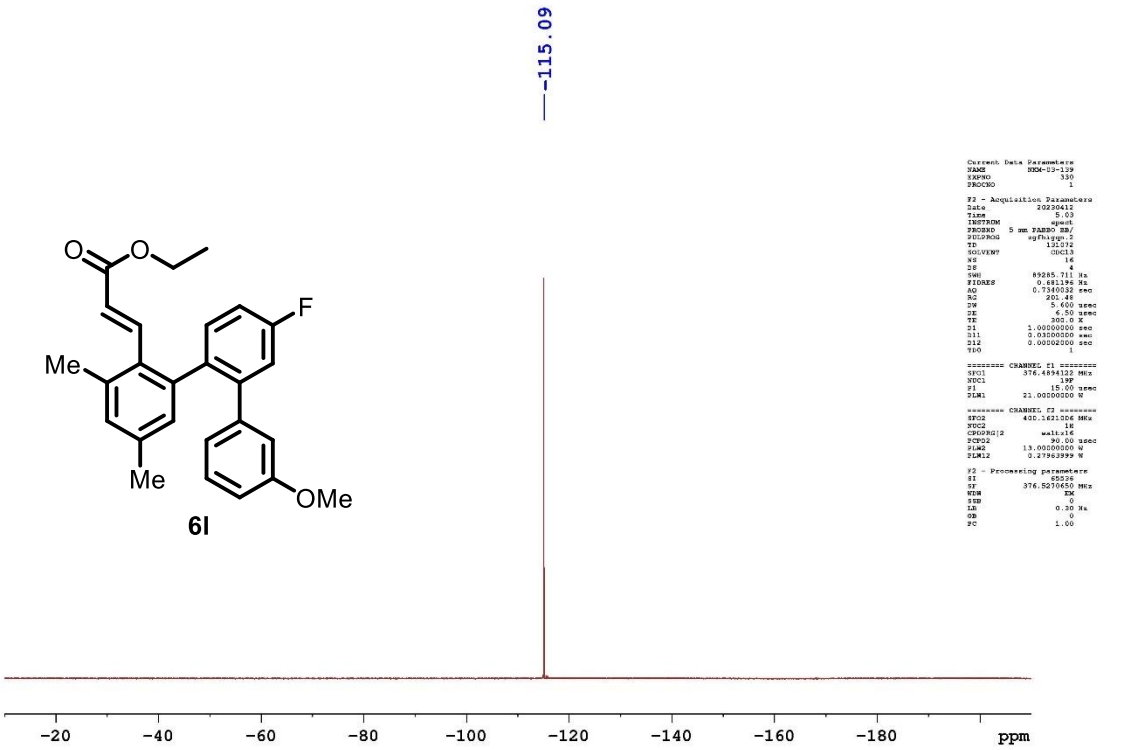

Figure S-120: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **6l**

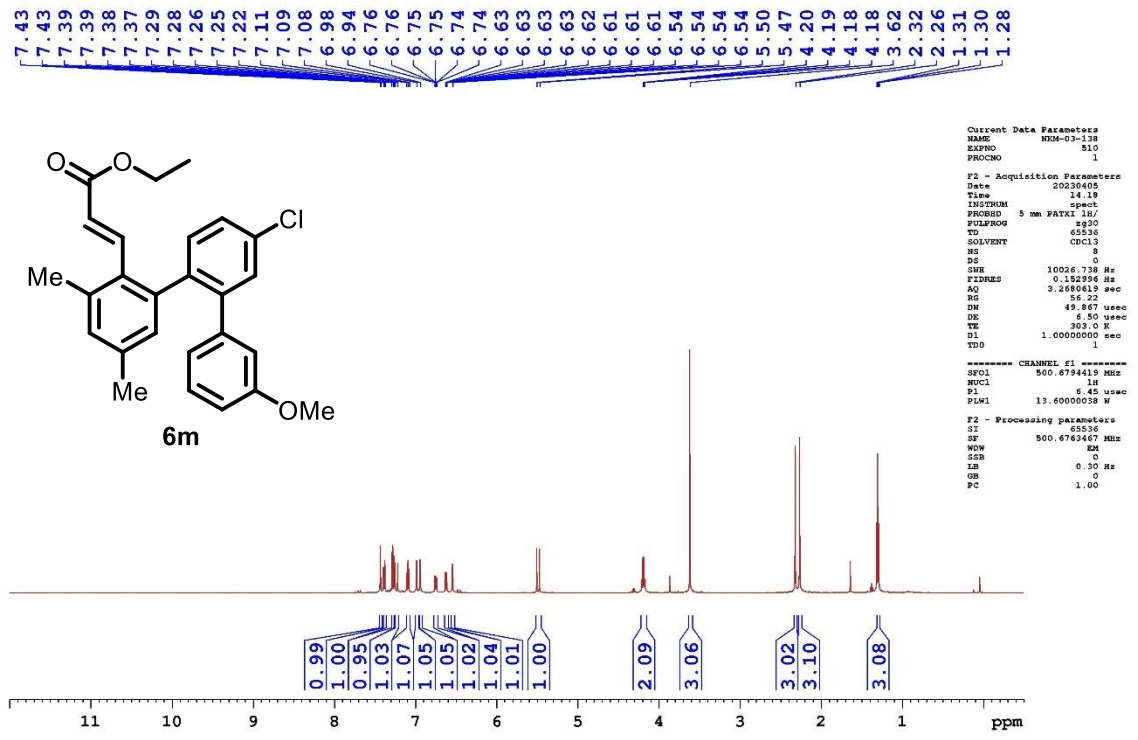

Figure S-121: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **6m**

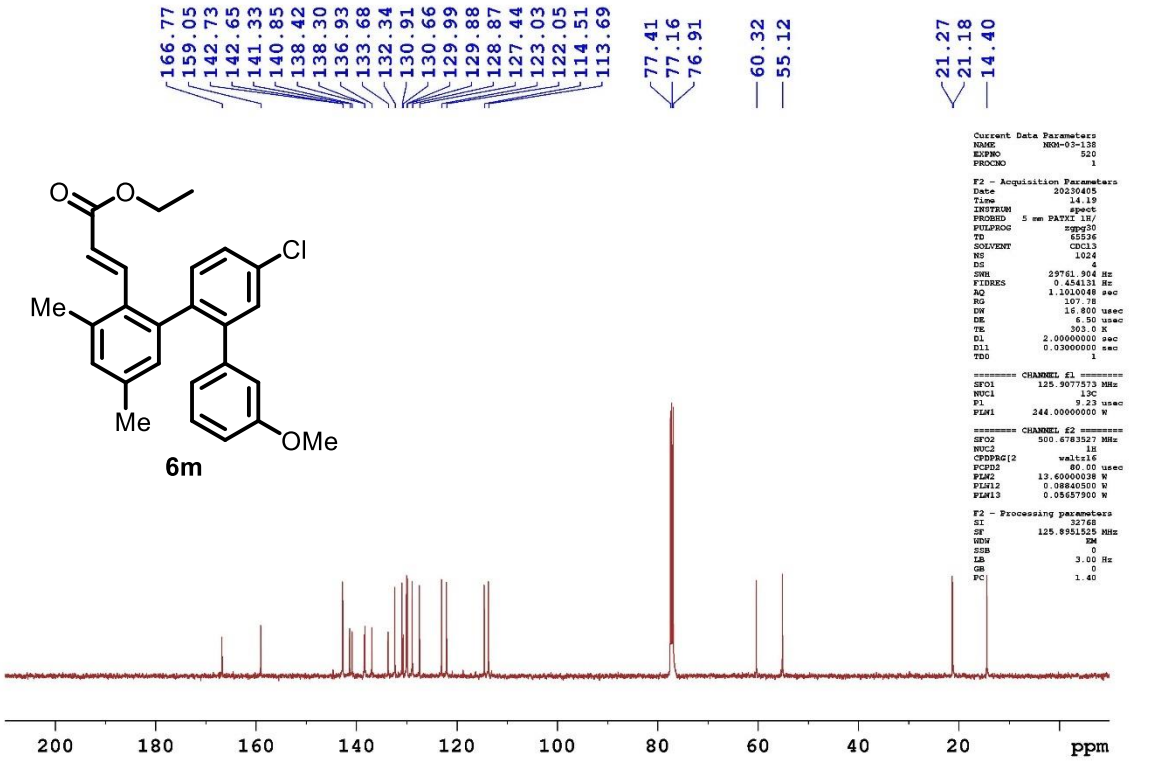

Figure S-122: ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **6m**

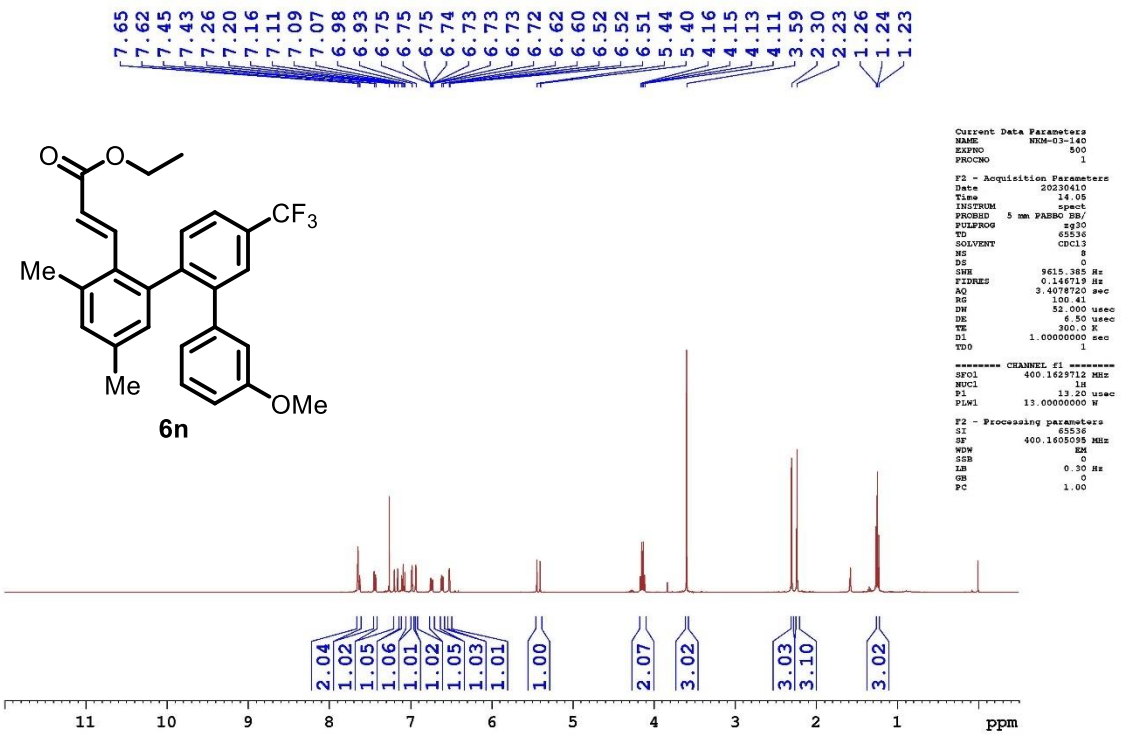

Figure S-123: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6n**

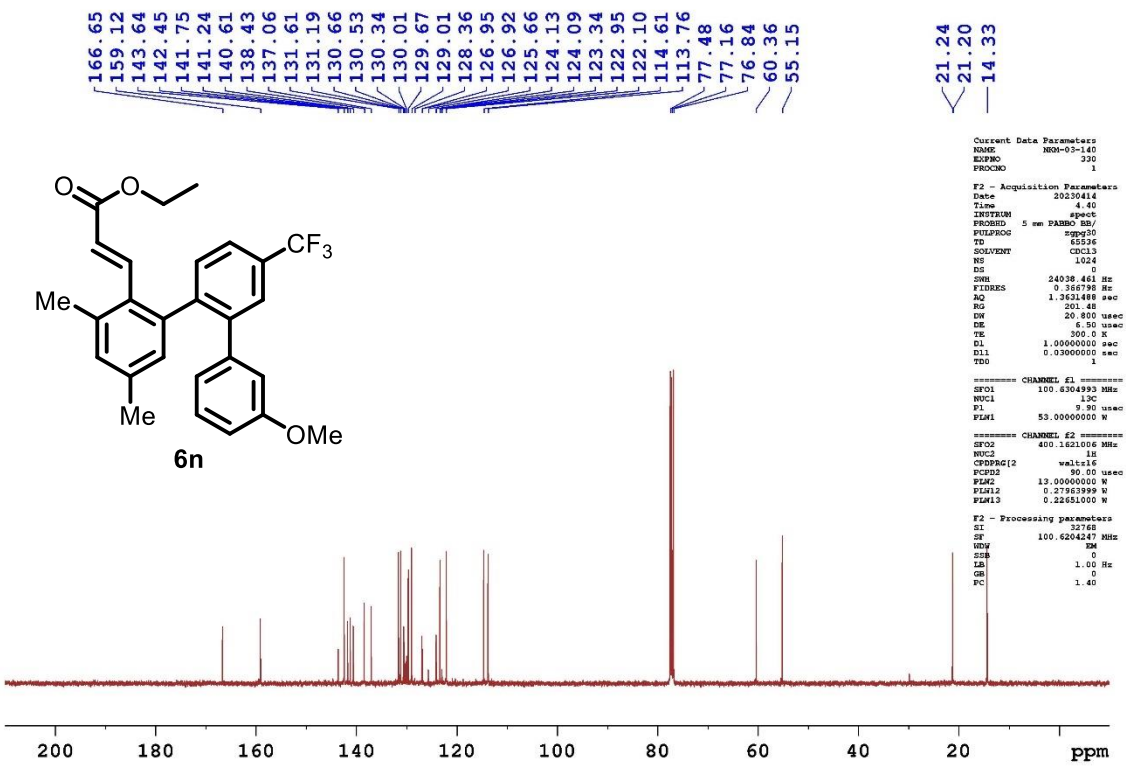

Figure S-124: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6n**

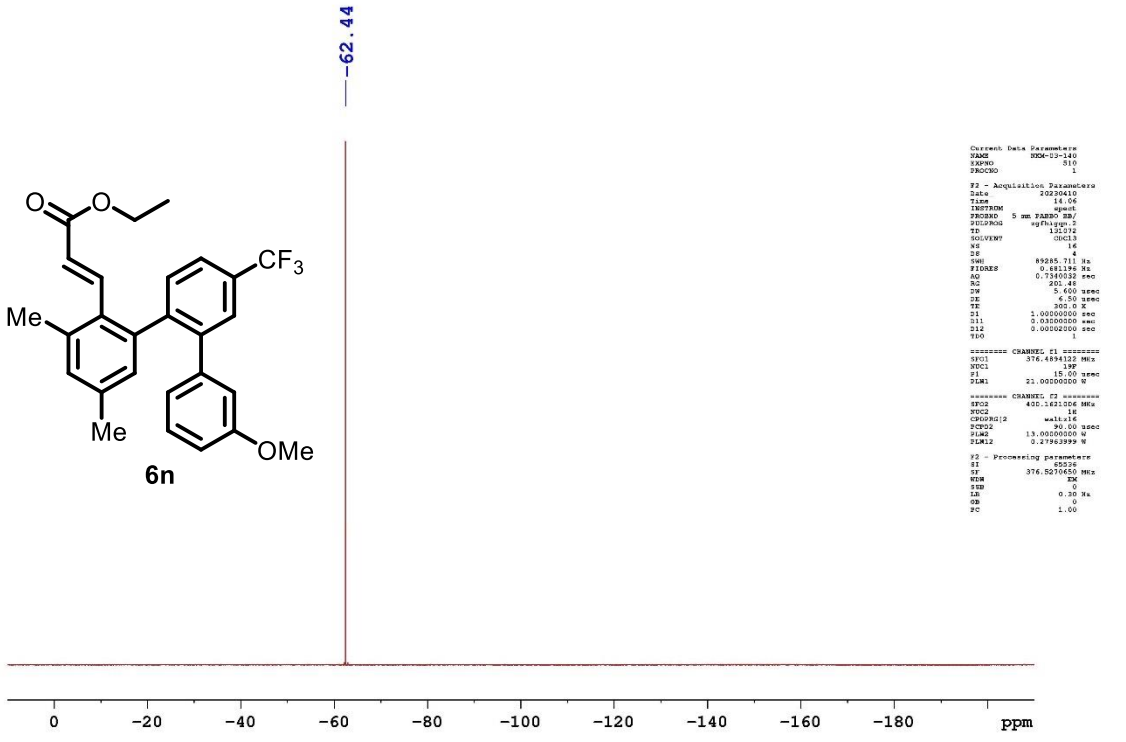

Figure S-125: ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound **6n**

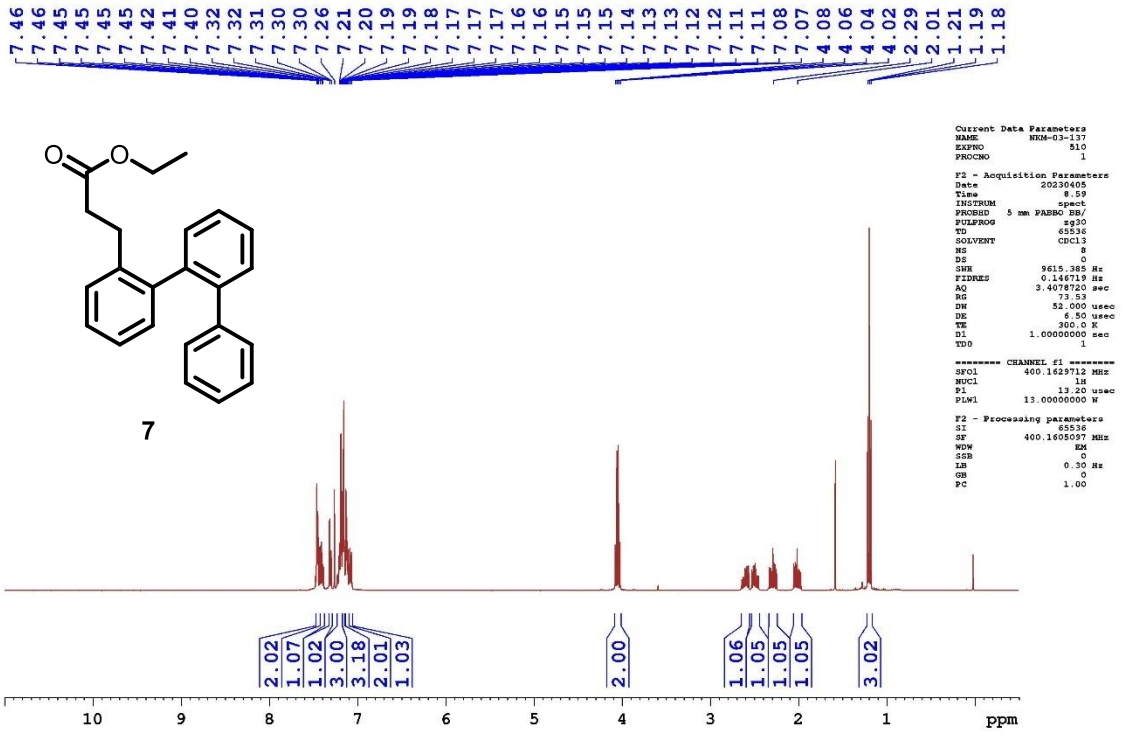

Figure S-126: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **7**

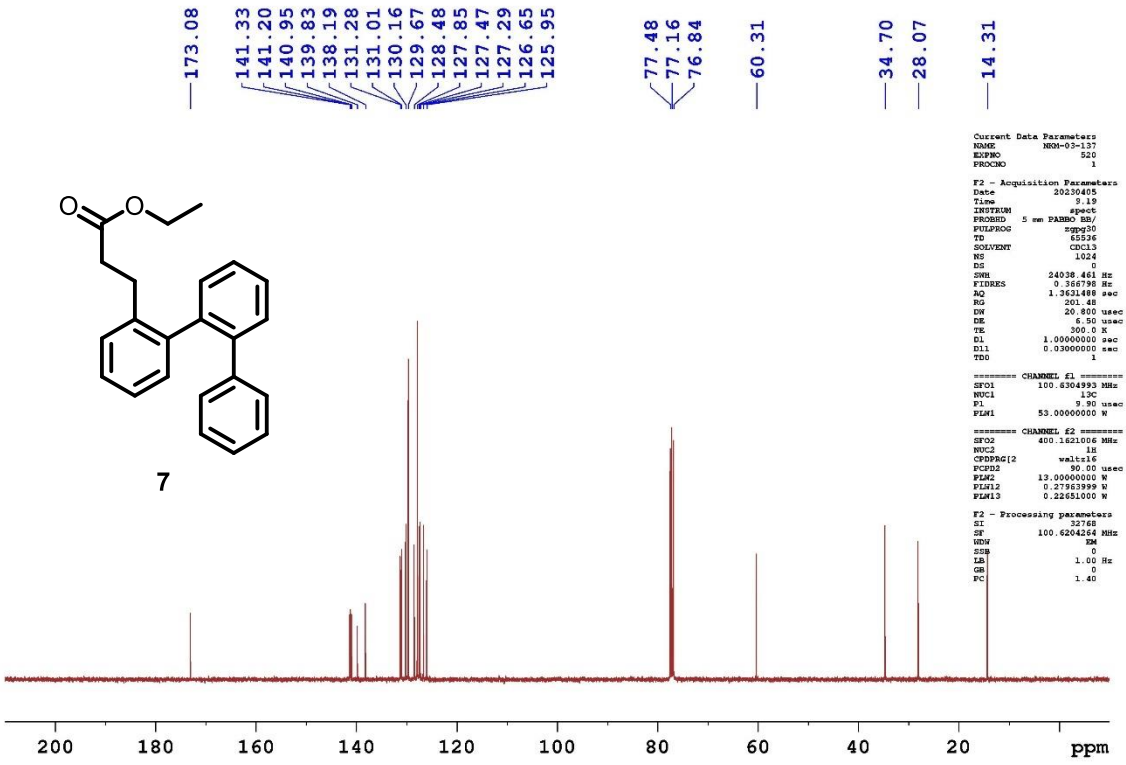

Figure S-127: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **7**

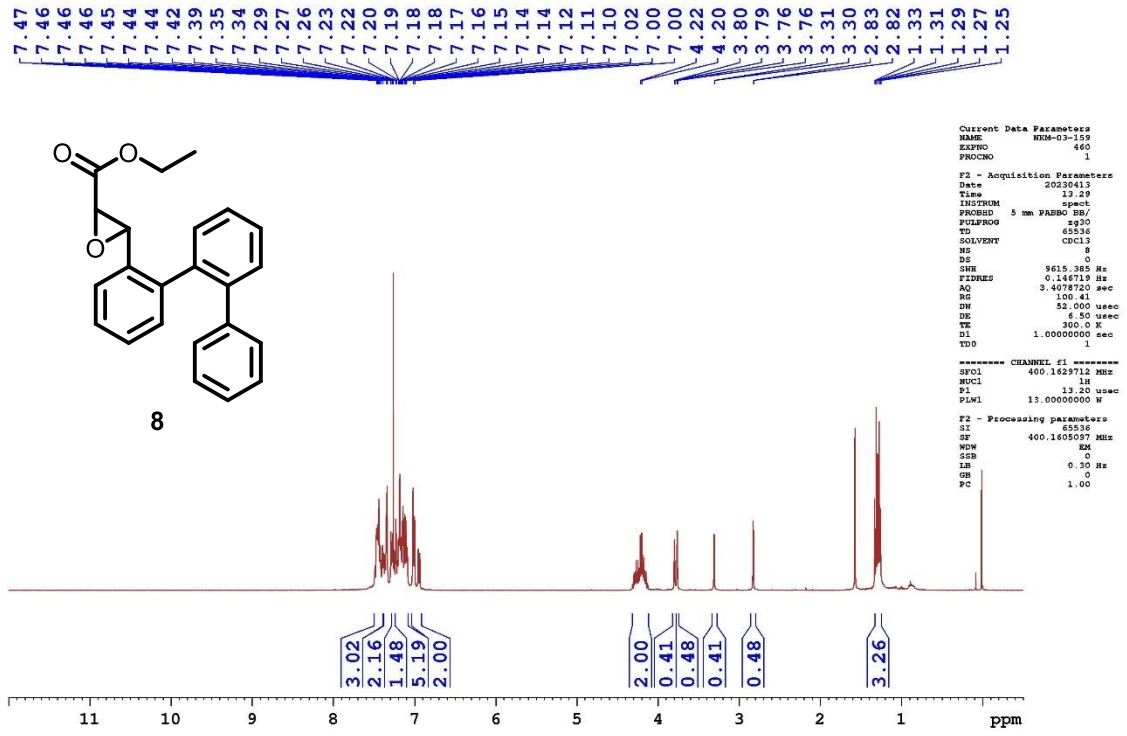

Figure S-128: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **8**

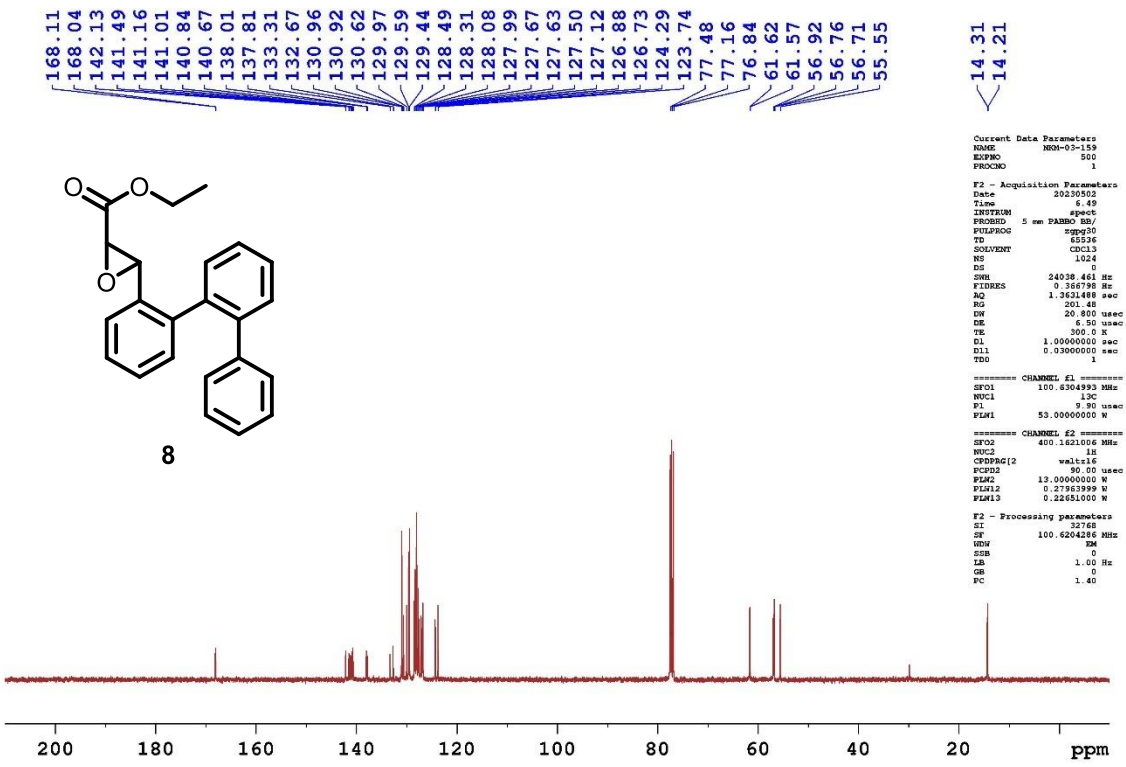

Figure S-129: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **8**

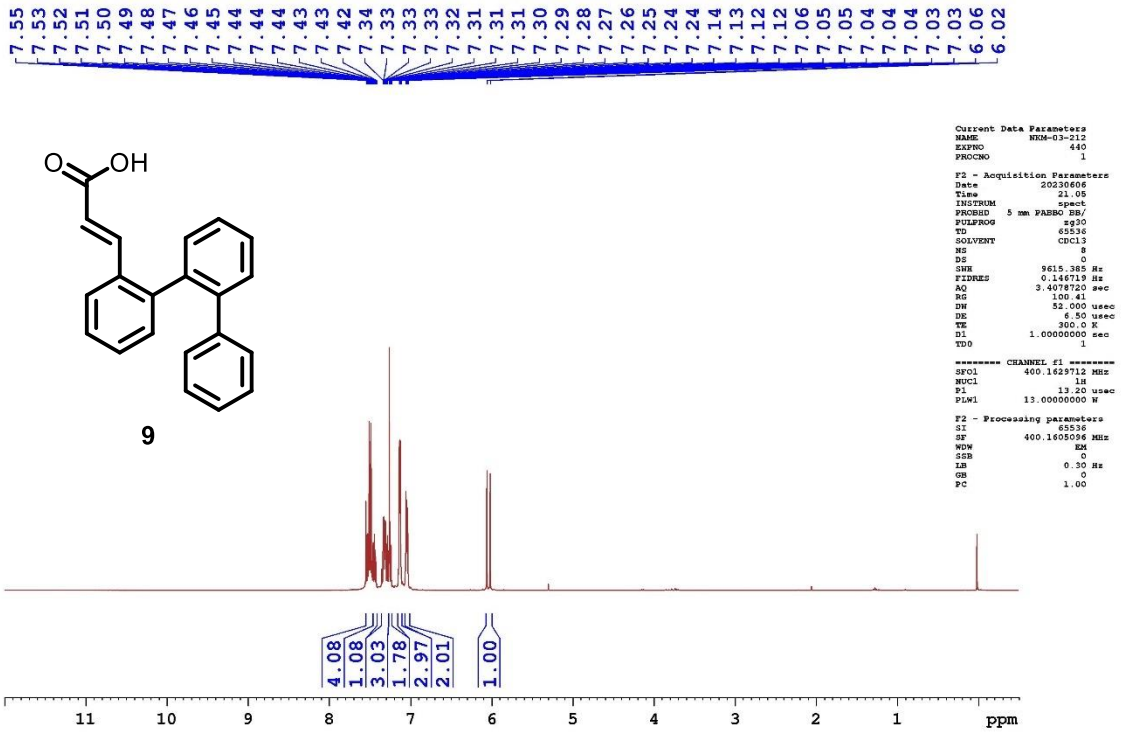

Figure S-130: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **9**

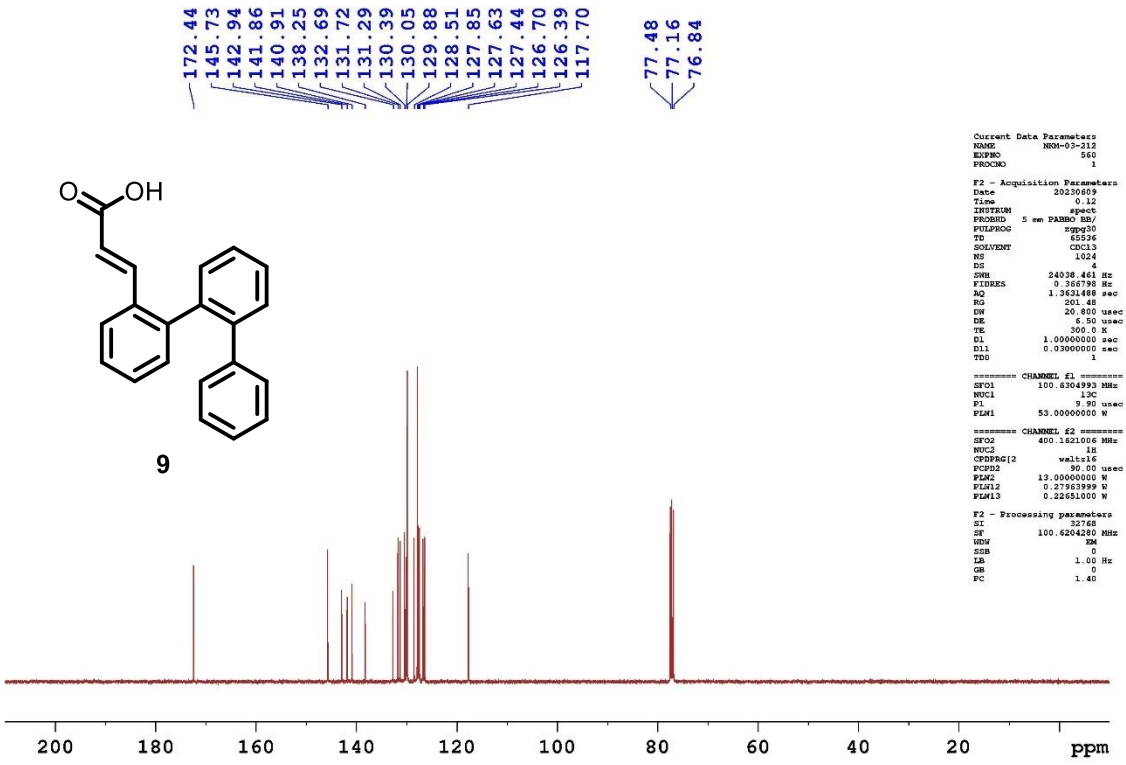

Figure S-131: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **9**

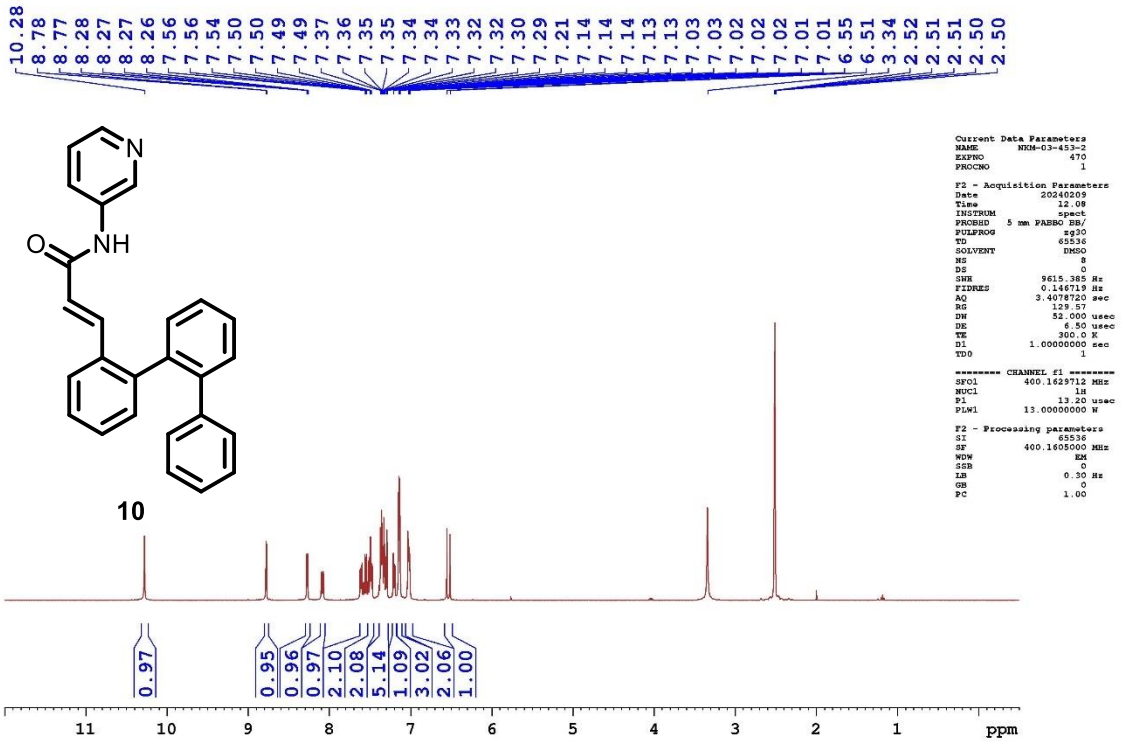

Figure S-132: ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound **10**

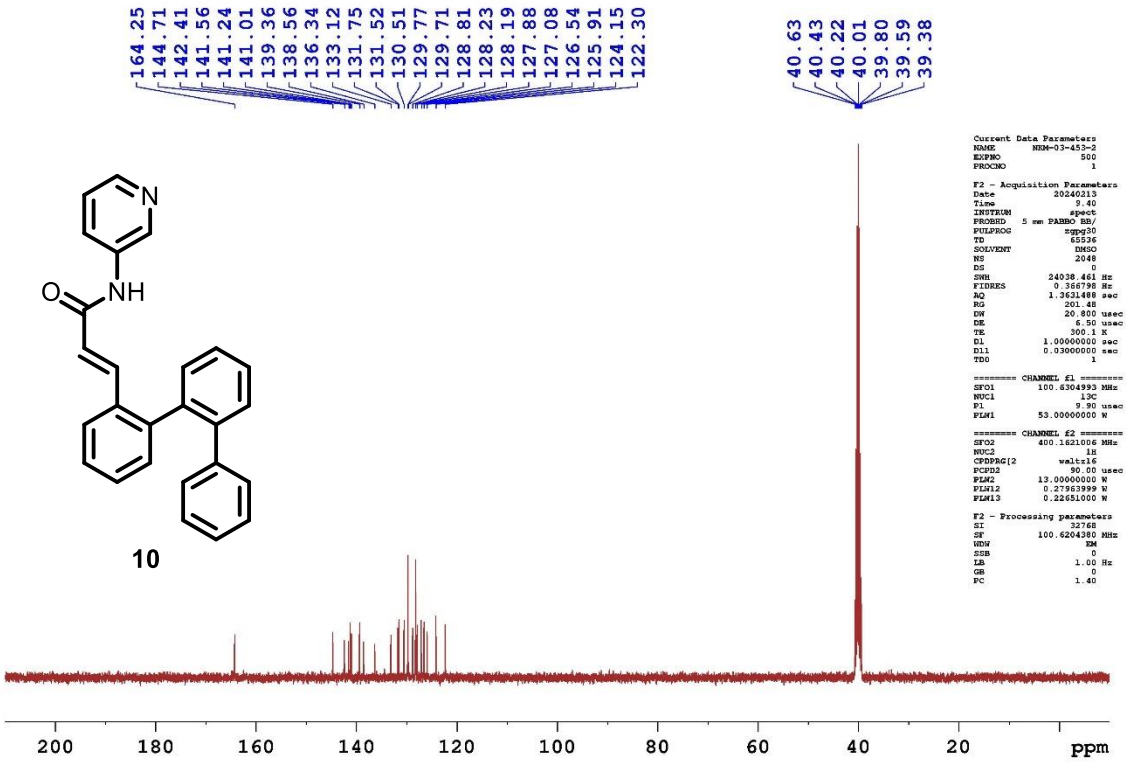

Figure S-133: ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound **10**

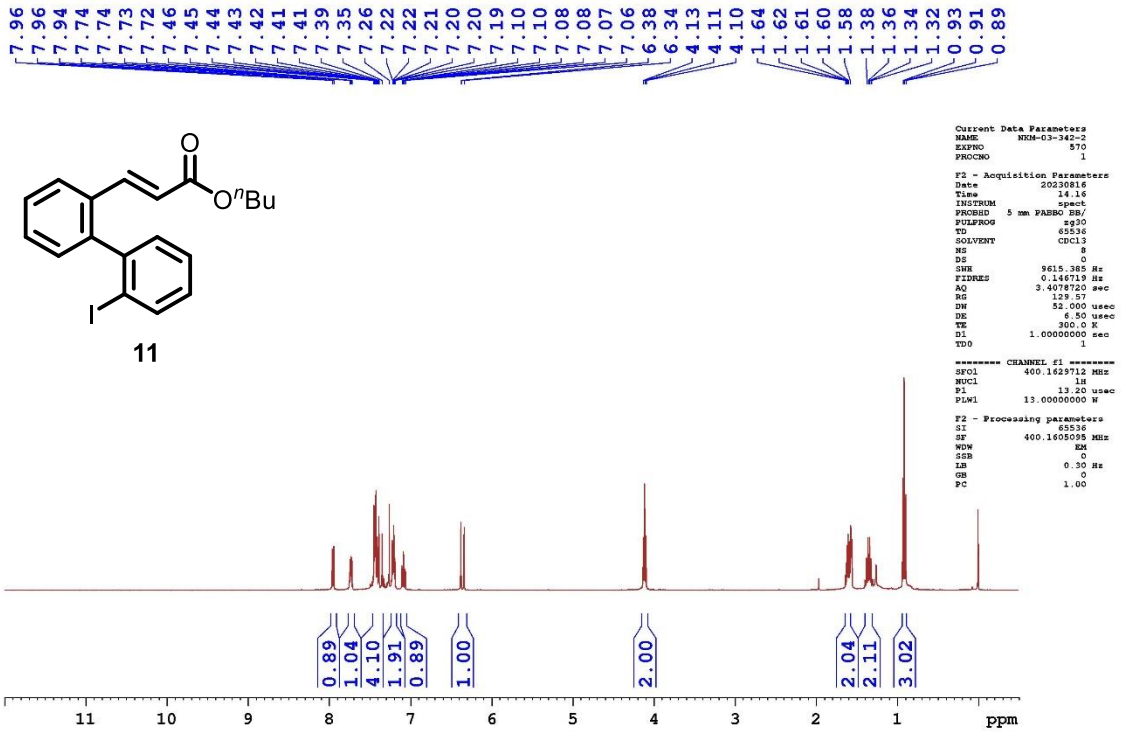

Figure S-134: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **11**

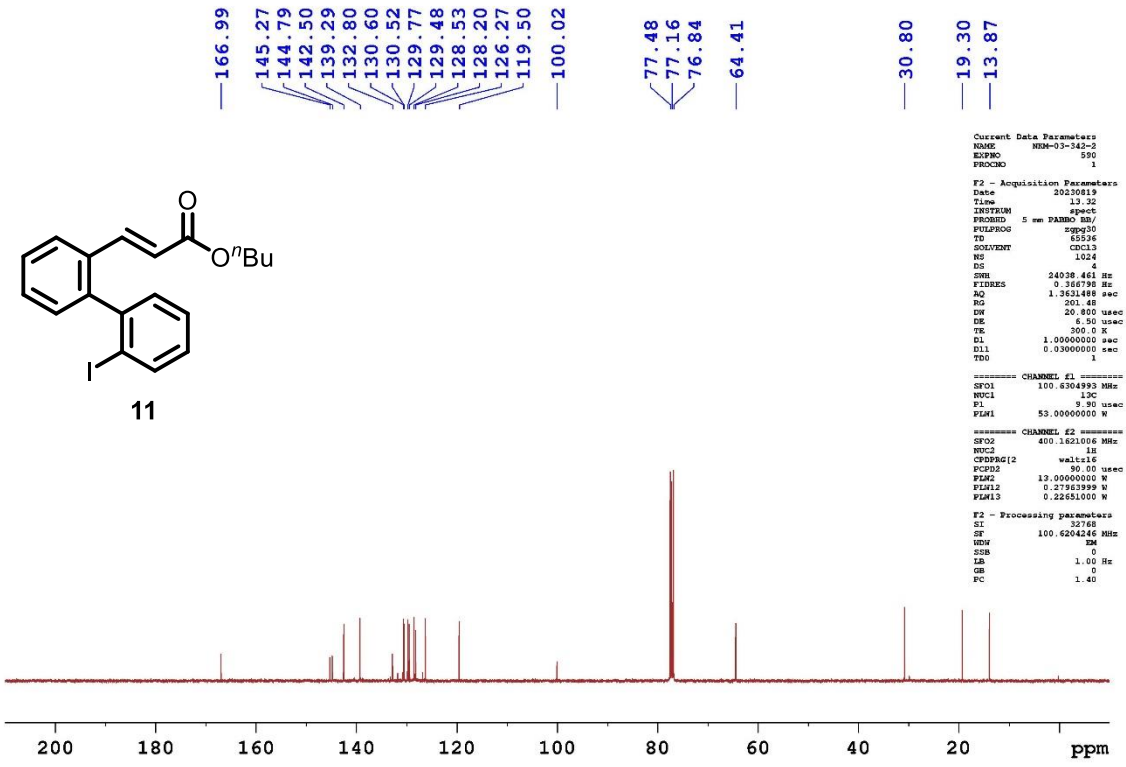

Figure S-135: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **11**

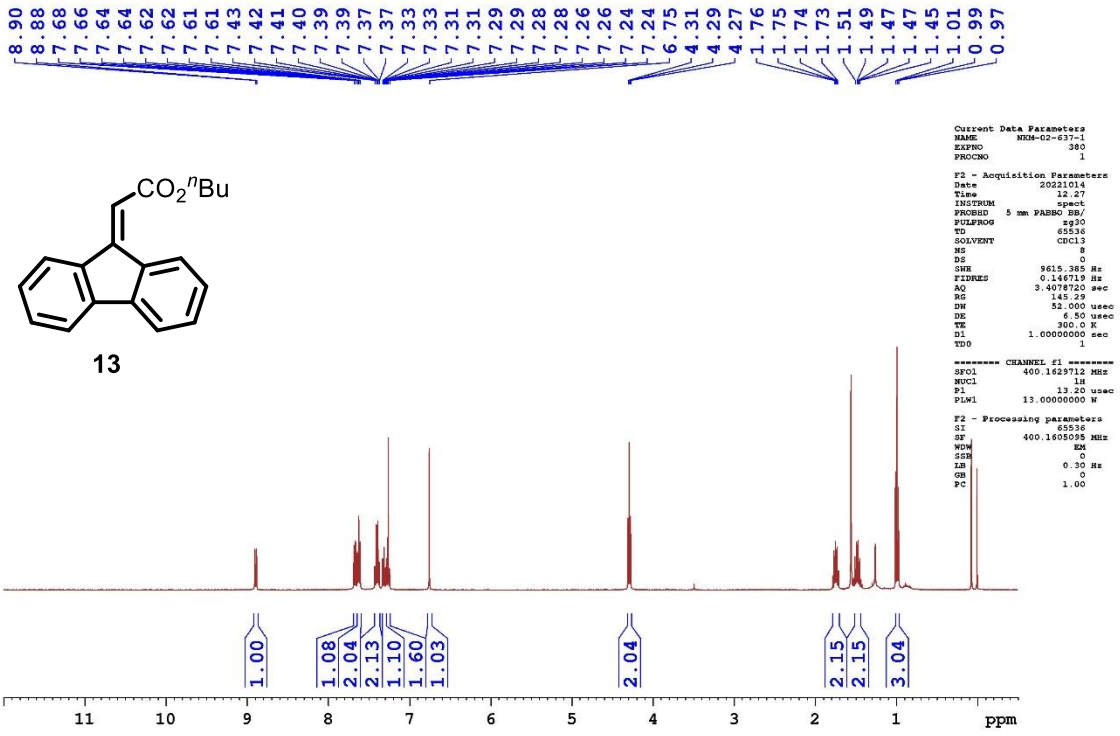

Figure S-136: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **13**

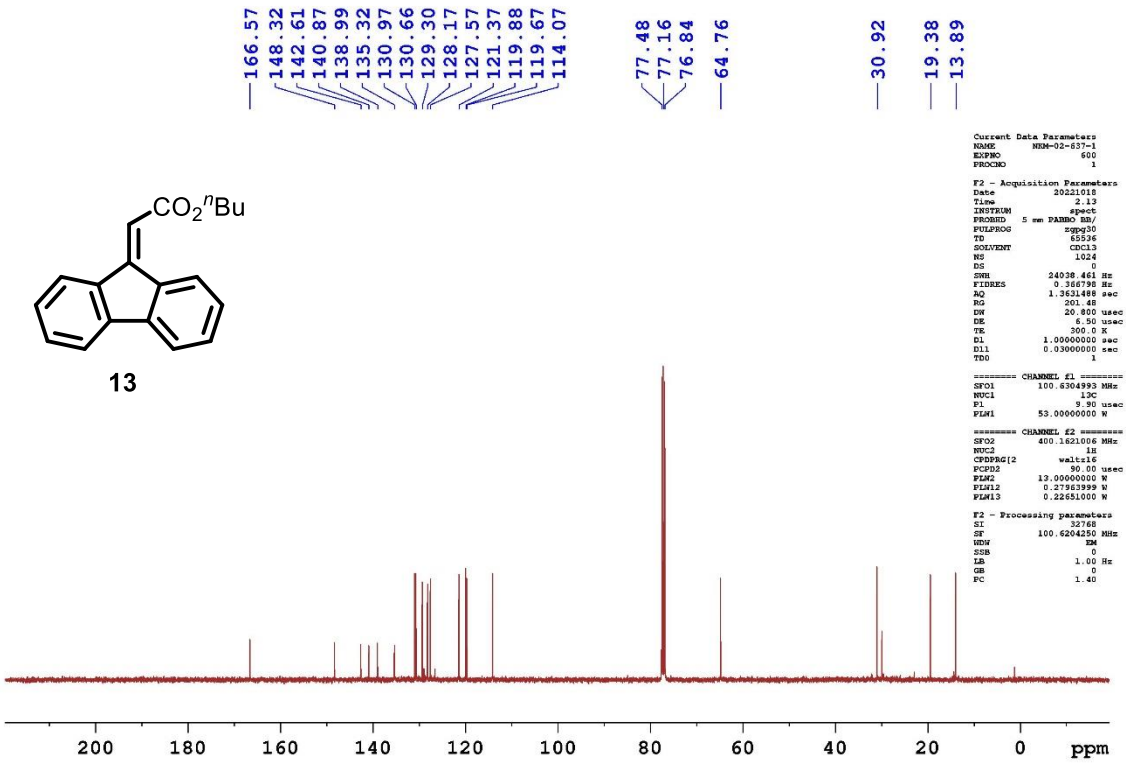

Figure S-137: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **13**

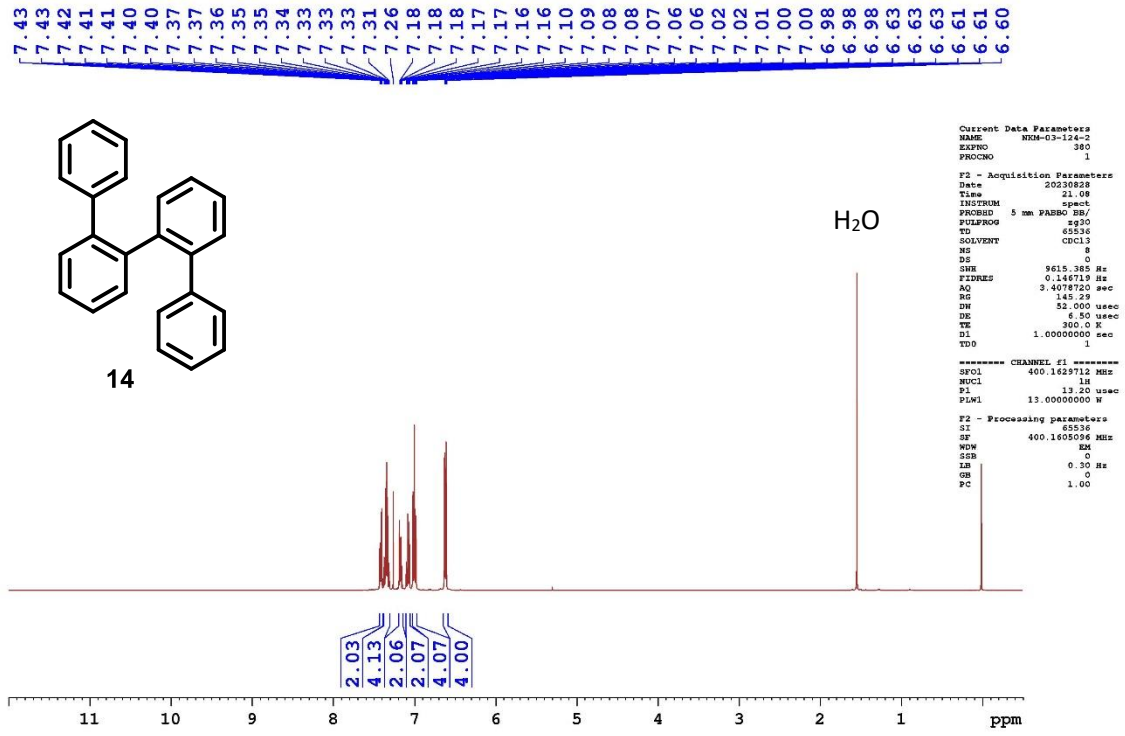

Figure S-138: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **14**

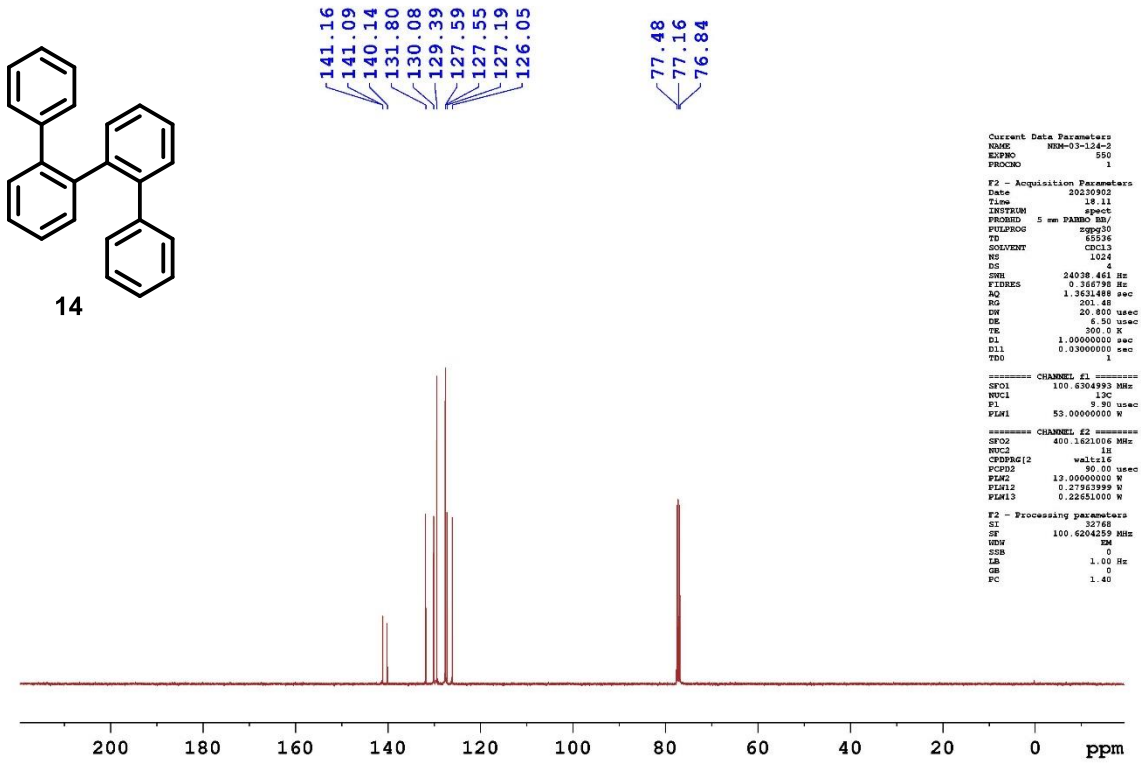

Figure S-139: ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **14**