Supporting Information

Supported Keggin Anion Catalyst: A Study of its Multifunctionality in Retro-Aldol Condensation of 2*H*-chromenes

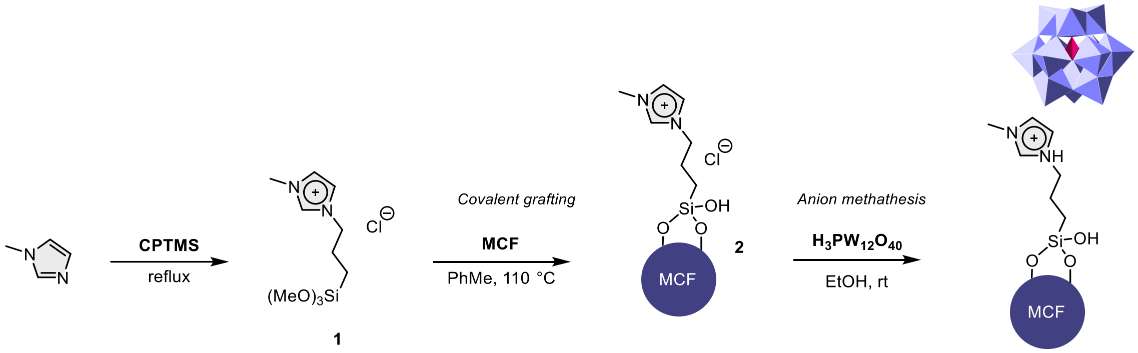
Contents

1 General information

The reaction was monitored by TLC (aluminum sheets, silica gel 60 F/UV254), using a hexane/ethyl acetate mixture as eluent. Visualization was conducted with UV light and iodine. The purification was carried out by column chromatography over silica gel (MN Kieselgel 60, 230-400 mesh). Reactions were sonicated in a Branson 2510 ultrasonic cleaner. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Ultrashield 500 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm, relative to tetramethylsilane (TMS) and $CHCl_3$ as the internal standard. Melting points were determined on a digital Electrothermal 90100 melting point apparatus. Infrared spectra were recorded on potassium bromide plates on a Perkin-Elmer FTIR Spectrum 100 spectrophotometer. High-resolution mass spectra (HRMS) were obtained with electrospray ionization on a Bruker QTOF mass spectrometer. N_2 physisorption samples were dried overnight at 120 °C, degassed at 200 °C under N_2 flow for 3 h, and analysed at 77 K in Micromeritics Tristar II plus 3030. The BET surface area was measured over a relative pressure range of 0.05-0.3. Powder X-ray diffraction was obtained in a PANalytical X Pert Pro MRD diffractometer with Cu Kα radiation. TEM analysed particle morphology on a JEOL JEM-100S and by SEM on a JEOL 5900 LV. XPS spectra were recorded using an Omicron XPS spectrometer equipped with a hemispherical electron multichannel analyser (EA-125) and monochromatized MgKα X-ray source (1253.6 eV). Inductively coupled plasma mass spectrometry (ICP–MS) analysis was conducted using an Agilent 7900 spectrometer.

2 Catalyst preparation

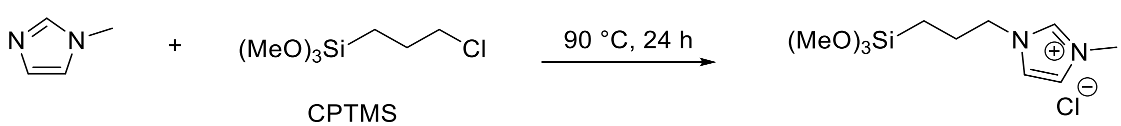
For catalyst synthesis, ordered mesoporous silicas (SBA-15 and MCF) were prepared following reported procedures. Then, the porous supports were functionalized by covalent grafting of the ionic liquid 3-methyl-1-(3-(trimethoxysilyl)propyl)-1*H*-imidazol-3-ium chloride. Finally, the Keggin acid $H_3PW_{12}O_{40}$ (1.0 mmol/g) was immobilized by anion metathesis.



2.1 MCF silica synthesis

Mesocellular silica foam was synthesized as described in the literature.[1] For the typical procedure, Pluronic P123 (16.2 g) and 6.7 mL of 1,3,5-trimethylbenzene (TMB) were dissolved in 375 mL of 1.6 M HCl solution in distilled water, with stirring at 35-40 °C for at least 2 h. Then, 37.0 mL of tetraethyl orthosilicate (TEOS) was added to the previous mixture dropwise. The resulting mixture was stirred at the same temperature for 24 h. Then, the reaction temperature was increased to 110 °C and maintained for 24 h under static conditions. The resulting solid was filtered, thoroughly washed with 650 mL of an EtOH:H_2O (1:1) mixture, and dried overnight at 60 °C. Finally, the surfactant was eliminated by calcination at 550 °C for 6 h.

2.2 Ionic liquid synthesis



In a dry and degassed 25 mL round flask, *N*-methylimidazole (0.03 mol, 5.6 mL) was added and CPTMS (0.03 mol, 2.5 mL). The reaction mixture was stirred under N_2 atmosphere at 100 °C for

[1] P. Schmidt-Winkel, W. W. Lukens, D. Zhao, P. Yang, B. F. Chmelka, G. D. Stucky, *J. Am. Chem. Soc.* **1999**, *121*, 254–255.

24 h. Then, the orange liquid was washed with anhydrous Et_2O (3 x 20 mL). Finally, dried under vacuo and stored under N_2 atmosphere.

3-methyl-1-(3-(trimethoxysilyl) propyl)-1H-imidazol-3-ium chloride

Amber liquid, 95% yield. NMR ^1H (500 MHz, $CDCl_3$) δ 10.53 (s, 1H), 7.59 (t, *J* = 1.6 Hz, 1H), 7.36 (t, *J* = 1.7 Hz, 1H), 4.26 (t, *J* = 7.3 Hz, 2H), 4.06 (s, 3H), 3.50 (s, 9H), 1.99 – 1.89 (m, 3H), 0.60-0.52. (m, 2H). NMR ^{13}C (125 MHz, $CDCl_3$) δ 137.1, 124.4, 120.8, 51.1, 50.5, 36.4, 22.8, 7.5. Spectral data are consistent with the literature.[2]

2.3 MCF silica functionalization[3]

In a dry, degassed 50 mL round-bottom flask, the ionic liquid (1, 1.78 mmol, 0.5 g) was added, followed by the mesoporous silica (16.7 mmol, 1.0 g) and anhydrous PhMe (25 mL). The reaction mixture was stirred under reflux for 24 h. Then cooled to room temperature and filtered under vacuum. The resulting solid was washed successively with 20 mL of anhydrous PhMe and 20 mL of anhydrous DCM. The excess ionic liquid was removed by Soxhlet extraction with DCE for 24 h. Finally, the ionic liquid-functionalized mesoporous silica was dried under vacuum.

2.4 $H_3PW_{12}O_{40}$ immobilization

In a 50 mL round flask, the phosphotungstic acid ($H_3PW_{12}O_{40}$, HPW) was dissolved in 25 mL of absolute EtOH. Then, 1.0 g of MIM-MCF was suspended in the previous solution and stirred at room temperature for 12 h. The resulting solid was filtered under vacuo and washed three times with 25 mL of absolute EtOH. Finally, the catalyst was fully dried under vacuo (50 mbar, 40 °C, 1 h).

[2] J. Xiong, W. Zhu, W. Ding, L. Yang, M. Zhang, W. Jiang, Z. Zhao, H. Li, *RSC Adv.* **2015**, *5*, 16847–16855.

3 Catalyst and supports complementary characterization.

3.1 Nitrogen adsorption-desorption.

Table S1. Textural properties of the mesoporous supports and catalysts.

	Material	S_{BET} (m²/g)	D_p (nm)	V_p (cm³/g)
1	MCF	803	Window: 8.4 Cell: 18.6	1.22
2	MIM-MCF	259	Window: 7.3 Cell: 17.0	0.99
3	HPW@MIM-MCF fresh	72	Window: 6.1 Cell: 15.0	0.29
4	HPW@MIM-MCF reused	44	Window: 8.5 Cell: 14.7	0.15
5	HPW@MIM-SBA-15	107	4.5	0.12
6	HPMo@MIM-MCF	163	4.5	0.23

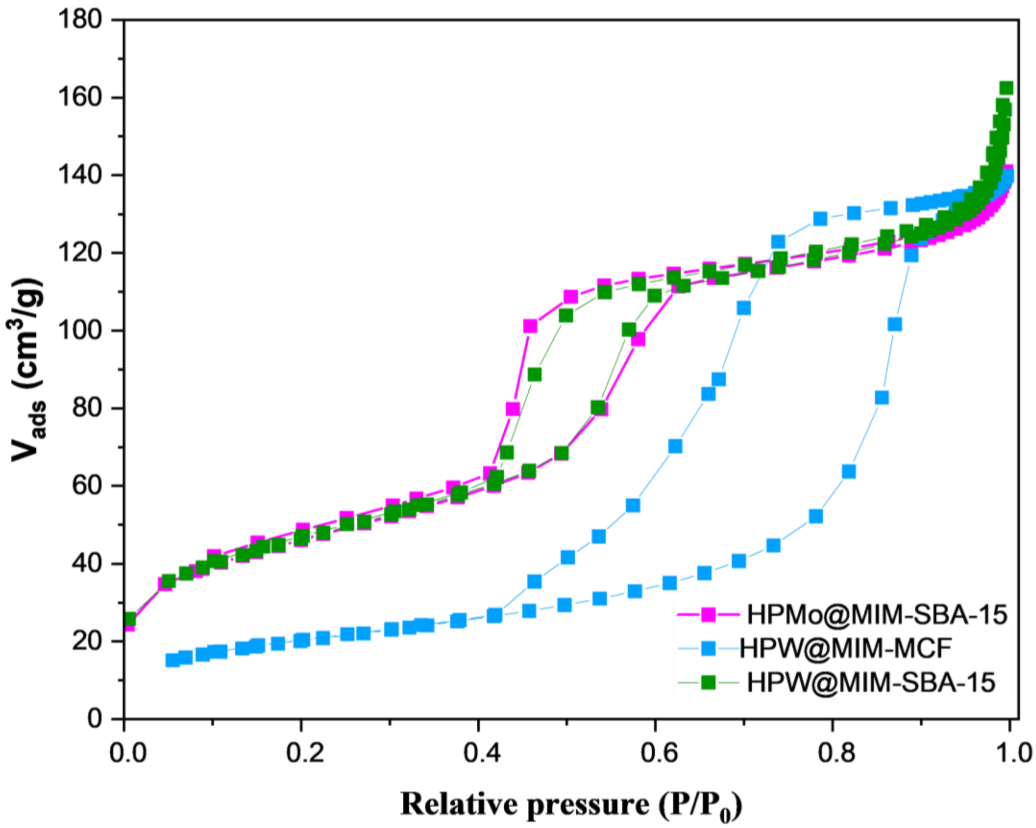


Figure S1. N_2 adsorption-desorption isotherms and pore size distribution of MCF and SBA-15 bases catalysts used during

3.2 X-ray Photoelectron Spectroscopy (XPS)

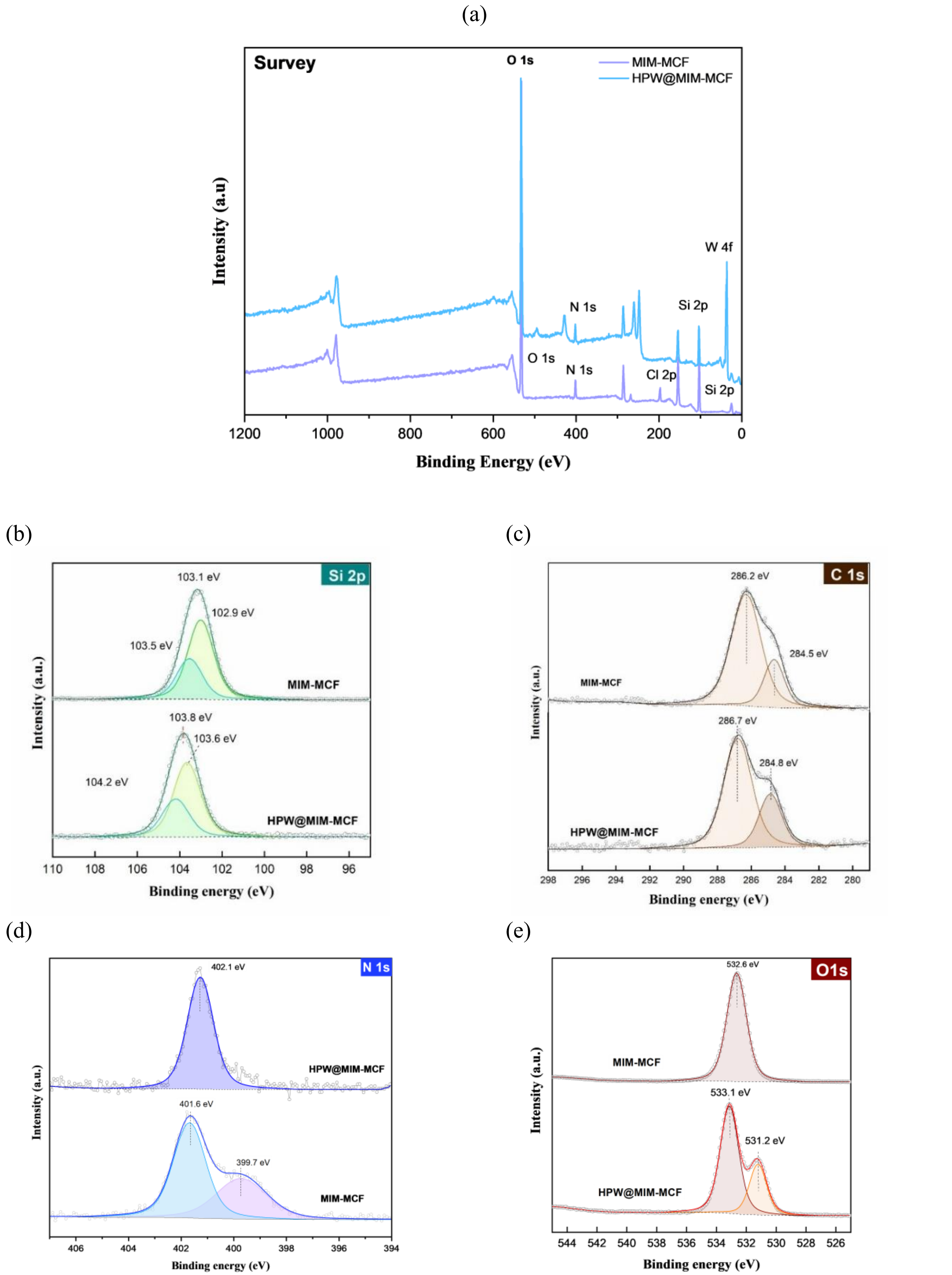


Figure S2. XPS analysis for the catalyst HPW@MIM-MCF and support MIM-MCF, (a) Survey spectra, (b) C1s spectra, (c) Si2p spectra, (d) N1s spectra, and (e) O1s spectra.

3.3 X-ray diffraction (XRD)

The XRD patterns for MCF pure silica, ionic liquid-functionalized silica MIM-MCF, and catalyst HPW@MIM-MCF are compared to those of HPW hexahydrate (**Figure S5**). One broad peak was found at 2θ = 15-30°, corresponding to the amorphous nature of the silica walls. The same behaviour was observed for the covalent grafting and HPW immobilization steps, which indicates good dispersion of ionic liquid groups and the HPW heteropolyanion throughout the mesoporous matrix.

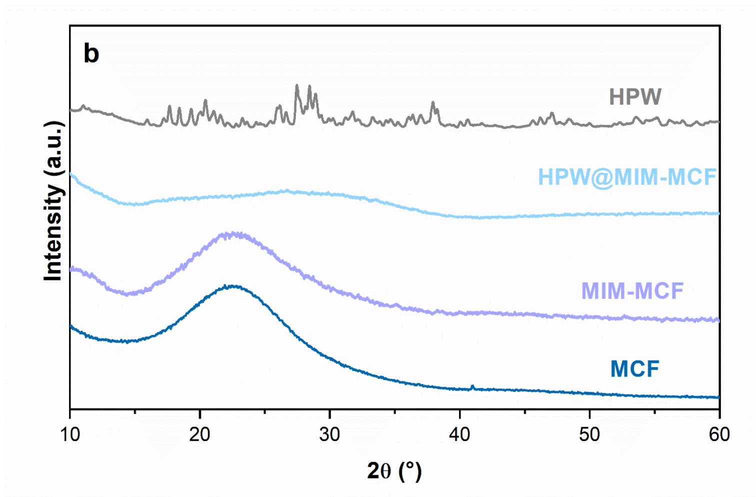


Figure S3. XRD diffractograms for the catalyst HPW@MIM-MCF and support MCF.

3.4 SEM-EDS

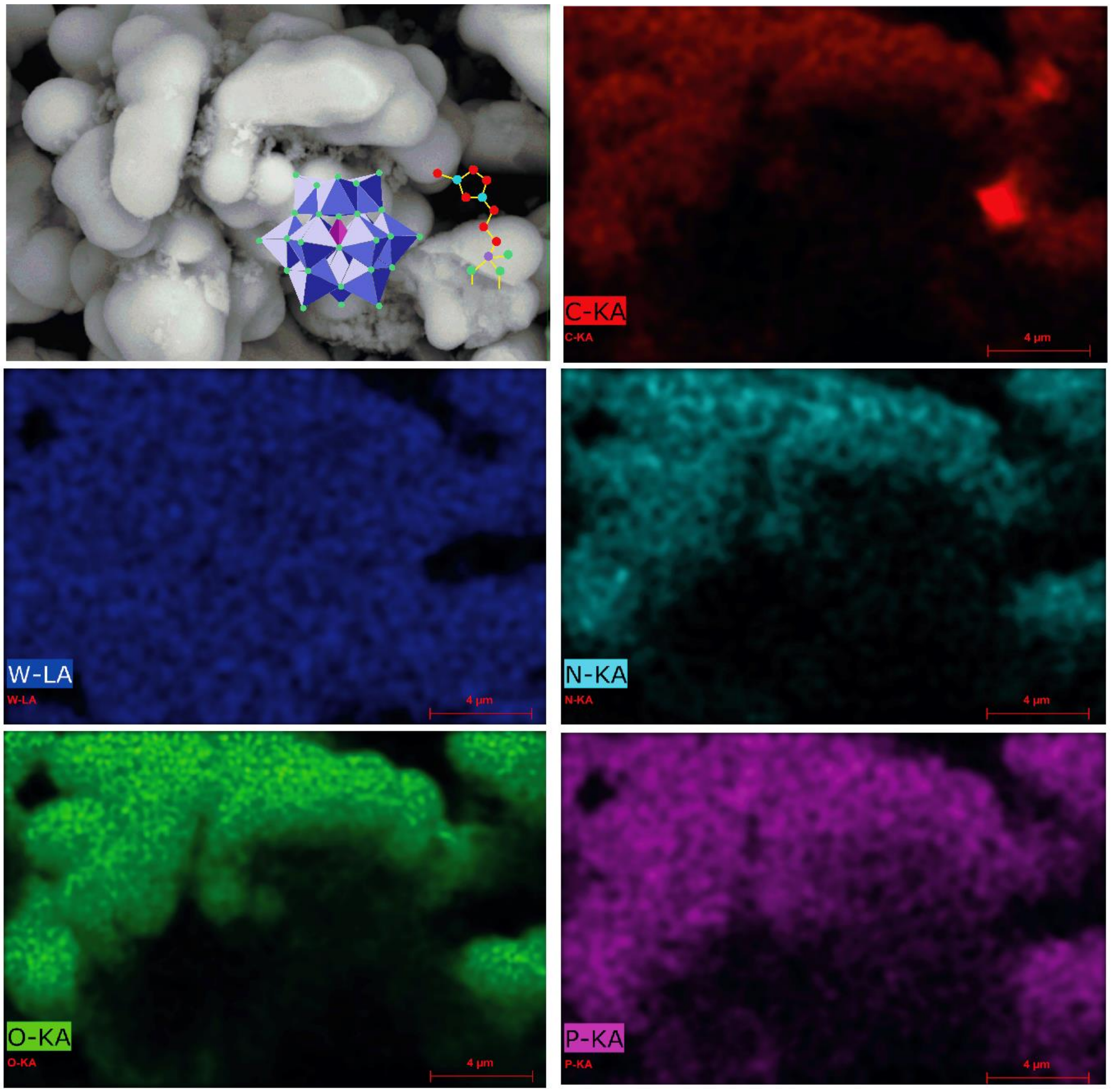


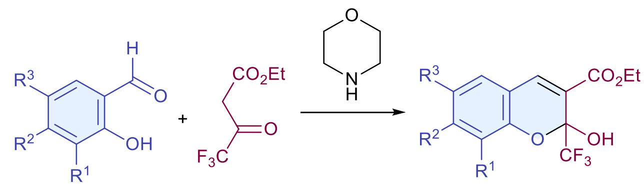
Figure S4. SEM-EDS for HPW@MIM-MCF fresh catalyst.

4 Organic synthesis procedures

4.1 Synthesis optimization for ethyl-2-hydroxy-2-trifluoromethyl-2*H*-chromene-3-carboxylates.

First, the synthesis of compound **1a** was explored using 10-20% mol of catalyst and concentrations of 1.0 to 2.0 M (entries 1-4), being 20% mol and 0.1 M being the best conditions. Next, the scope was extended to seven derivatives (entries 5-11). The salicylaldehyde precursors bearing electron-withdrawing substituents require shorter reaction times (entries 6-8), while electron-donating substituents require longer reaction times (entries 9-11). Additionally, reactions with longer reaction times were replicated using microwave irradiation at 90 °C to increase the yield (entries 12-15).

Table S2. 2H-chromene synthesis.



1a-g

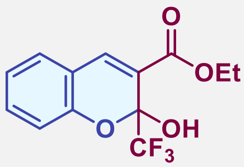
Ent.	R^1	R^2	R^3	Base (%mol)	T (°C)	t (h)	C (M)	Yield (%)
1	H	H	H	20	rt,)))	4.0	1.0	**1a**, 99[a]
2	H	H	H	10	rt,)))	4.0	1.0	**1a**, 47[a]
3	H	H	H	20	rt,)))	4.0	2.0	**1a**, 68[a]
4	H	H	H	10	rt,)))	4.0	2.0	**1a**, 52[a]
5	H	H	H	10	rt,)))	4.0	2.0	**1a**, 92[b]
6	H	H	NO_2	20	rt,)))	1.0	1.0	**1b**, 99[b]
7	Br	H	Br	20	rt,)))	1.0	1.0	**1c**, 99[b]
8	H	H	Br	20	rt,)))	2.5	1.0	**1d**, 99[b]
9	H	NEt_2	H	20	rt,)))	8.0	1.0	**1e**, 15[b]
10	H	H	OMe	20	rt,)))	8.0	1.0	**1f**, 45[b]
11	OEt	H	H	20	rt,)))	5.0	1.0	**1g**, 95[b]
12	H	H	H	20	90[c]	1.0	1.0	**1a**, 90
13	H	NEt_2	H	20	90[c]	1.0	1.0	**1e**, 63
14	H	H	OMe	20	90[c]	1.0	1.0	**1f**, 97
15	OEt	H	H	20	90[c]	1.0	1.0	**1g**, 86

Reaction conditions: aldehyde (0.75 mmol), ETFAA (1.2 equiv.), morpholine (0.1-0.2 equiv.) in absolute EtOH. [a] Yield measured by ^{1}H NMR analysis using 1,4-dioxane as internal standard. [b] Isolated yield. [c] Under microwave irradiation.

4.2 General procedure for the synthesis of ethyl-2-hydroxy-2-trifluoromethyl-2*H*-chromene-3-carboxylates (1a-g).

In a 50 mL round-bottom flask equipped with a magnetic stir bar, the corresponding salicylaldehyde (0.41 mmol, 1.0 equiv.), ETFAA (1.2 equiv.), morpholine (20% mol), and EtOH were added. The reaction mixture was irradiated with microwave (127 W) for 40 min at 100°C or by ultrasound at rt. The progress of the reaction was monitored by TLC (Hex/EtOAc, 9:1) until the starting material was consumed. The reaction crude was recrystallized from EtOH: H_2O (1:1) to afford the pure product.

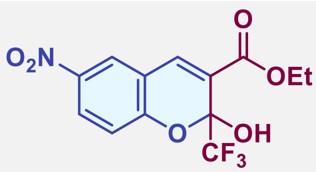
Ethyl 2-hydroxy-2-(trifluoromethyl)-2*H*-chromene-3-carboxylate (**1a**). [1]



1a

White solid (194 mg, 0.75 mmol, yield: 90 %), mp 103.5-104.1 °C.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.49 (s, 1H), 7.38 (t, 1H), 7.25 (d, *J* = 1.8 Hz, 0H), 7.06 – 6.99 (m, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.19, 153.04, 139.76, 134.36, 129.90, 123.09, 123.07 (q, *J* = 292.4 Hz), 117.95, 116.42, 115.17, 95.71 (q, *J* = 35.0 Hz), 62.85, 14.46. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -87.24.

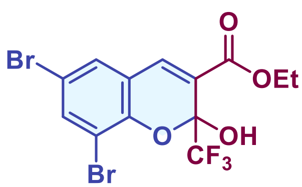
Ethyl 2-hydroxy-6-nitro-2-(trifluoromethyl)-2*H*-chromene-3-carboxylate (**1b**).[2]



1b

Yellow solid (246 mg, 0.75 mmol, yield: 71 %), mp 120.3-121.1 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 8.9, 2.7 Hz, 1H), 8.21 (d, *J* = 2.7 Hz, 1H), 7.80 (s, 1H), 7.13 (d, *J* = 9.0 Hz, 1H), 6.52 (s, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.89, 157.10, 142.93, 137.03z, 128.91, 122.39 (q, *J* = 291.7 Hz), 125.13, 118.15, 117.84, 116.97, 96.67 (q, *J* = 35.5 Hz), 63.09, 14.14. **^{19}F NMR** (375 MHz, $CDCl_3$) δ -86.70.

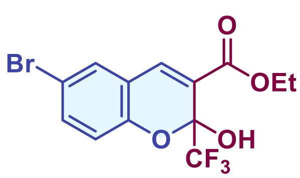
Ethyl 6,8-dibromo-2-hydroxy-2-(trifluoromethyl)-2*H*-chromene-3-carboxylate (**1c**).[3]



1c

White solid (331 mg, 0.75 mmol, yield: 99 %), mp 114.0-115.3 °C.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 2.3 Hz, 1H), 7.65 (s, 1H), 7.34 (d, *J* = 2.3 Hz, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 1.40 (t, 1H). **^{13}C NMR** δ 165.88, 148.87, 138.92, 137.29, 130.85, 122.43 (q, *J* = 292.5 Hz), 120.32, 117.82, 114.75, 111.04, 96.60 (q, *J* = 35.5 Hz), 62.94, 14.17. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -86.73.

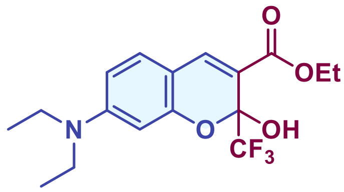
Ethyl 6-bromo-2-hydroxy-2-(trifluoromethyl)-2*H*-chromene-3-carboxylate (**1d**).[1]



1d

White solid (272 mg, 0.75 mmol, yield: 99 %), mp 107.2-108.2 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.46 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.39 (d, *J* = 2.4 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.50, 151.72, 137.98, 136.49, 126.97, 124.07, 122.62 (q, *J* = 292.0 Hz), 121.16, 119.40, 118.75, 118.26, 96.13, 95.78, 95.60 (q, *J* = 35.2 Hz), 95.43, 95.08, 62.85, 14.16.
^{19}F NMR (470 MHz, $CDCl_3$) δ -87.43.

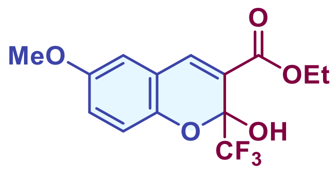
Ethyl 7-(diethylamino)-2-hydroxy-2-(trifluoromethyl)-2*H*-chromene-3-carboxylate (**1e**).[4]



1e

Yellow solid (169 mg, 0.75 mmol, yield: 63%), mp 106.1-107.6 °C.
^{1}H NMR (500 MHz, CDCl3) δ 7.72 (d, J = 23.2 Hz, 2H), 7.04 (d, J = 8.5 Hz, 1H), 6.28 (dd, J = 11.1, 2.3 Hz, 2H), 4.31 (q, J = 7.1 Hz, 2H), 3.37 (ddp, J = 22.1, 14.6, 7.2 Hz, 4H), 1.37 (t, J = 7.1 Hz, 3H), 1.19 (t, J = 7.1 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.81, 155.22, 152.76, 140.17, 131.26, 123.26 (q, *J* = 292.9 Hz), 106.77, 106.46, 95.90 (q, *J* = 34.7 Hz), 106.22, 61.65, 44.90, 14.32, 12.69. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -87.43.

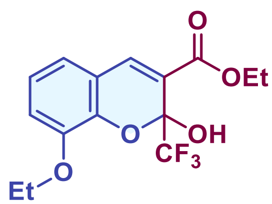
Ethyl 2-hydroxy-6-methoxy-2-(trifluoromethyl)-2*H*-chromene-3-carboxylate (**1f).** [2]



1f

White solid (230 mg, 0.75 mmol, yield: 97 %), mp 98.2-99.4 °C.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 1H), 6.95 (q, *J* = 8.9 Hz, 2H), 6.76 (d, *J* = 2.9 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.89, 154.91, 146.90, 139.57, 122.84 (q, *J* = 292.9 Hz), 120.23, 117.96, 116.96, 115.50, 113.24, 95.46 (q, *J* = 34.9 Hz), 62.59, 55.92, 14.20. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -87.10.

Ethyl 8-ethoxy-2-hydroxy-2-(trifluoromethyl)-2*H*-chromene-3-carboxylate (**1g**). [3]

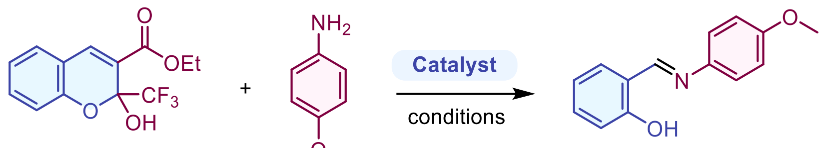


1g

White solid (214 mg, 0.75 mmol, yield: 86%), mp 112.7-113.8 °C.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.46 (s, 1H), 7.01 (dd, *J* = 8.1, 1.2 Hz, 2H), 6.93 (t, *J* = 7.9 Hz, 1H), 6.86 (dd, *J* = 7.5, 1.2 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 4.12 (dddd, *J* = 16.5, 9.5, 7.0, 2.4 Hz, 3H), 1.41 (dt, *J* = 11.1, 7.1 Hz, 8H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.92, 146.94, 142.82, 139.77, 122.85 (q, *J* = 292.6 Hz), 122.50, 121.62, 120.51, 119.56, 118.58, 114.91, 95.58 (q, *J* = 35.1 Hz), 65.68, 62.53, 14.95, 14.19.

4.3 Schiff bases synthesis optimization.

Table S3. 2*H*-chromene transformation into Schiff bases mediated by Keggin heteropolyanion.



Entry	Catalyst	Load (% wt)	2 (equiv)	Solvent	t (h)	C (M)	5c (%)[a]
1	HPW@MIM-MCF	10	1.2	MeCN: H_2O (9:1)	10	0.035	25
2	HPW@MIM-MCF	30	1.2	MeCN: H_2O (9:1)	10	0.035	45
3	HPW@MIM-MCF	50	1.2	MeCN: H_2O (9:1)	10	0.035	40
4	HPW@MIM-MCF	10	1.4	MeCN: H_2O (9:1)	10	0.035	30
5	HPW@MIM-MCF	30	1.4	MeCN: H_2O (9:1)	10	0.035	92
6	HPW@MIM-MCF	50	1.4	MeCN: H_2O (9:1)	10	0.035	66
7	HPW@MIM-MCF	10	2.0	MeCN: H_2O (9:1)	10	0.035	41
8	HPW@MIM-MCF	30	2.0	MeCN: H_2O (9:1)	10	0.035	62
9	HPW@MIM-MCF	50	2.0	MeCN: H_2O (9:1)	10	0.035	70
10	HPW@MIM-MCF	30	1.4	MeCN: H_2O (9:1)	10	0.1	97
11	HPW@MIM-SBA	30	1.4	MeCN: H_2O (9:1)	10	0.035	82
12	HPMo@MIM-SBA	30	1.4	MeCN: H_2O (9:1)	10	0.035	77
13	HPW	30	1.4	MeCN: H_2O (9:1)	10	0.1	94
14	HPMo	30	1.4	MeCN: H_2O (9:1)	10	0.1	84
15	HSiW	30	1.4	MeCN: H_2O (9:1)	10	0.1	47
16	HPW	30	1.4	DCE	120	0.035	n. r.
17	HPW	30	1.4	MeCN	10	0.035	63
18	HPW	30	1.4	EtOH	10	0.035	50
19	HPW	30	1.4	H_2O	10	0.035	65
20	---	0	1.4	MeCN: H_2O (9:1)	120	0.035	n. r.
21	HPW@MIM-MCF	30	--	MeCN: H_2O (9:1)	120	0.035	n. r.

Reaction conditions: **1a** (100 mg, 0.347 mmol), p-anisidine, Keggin catalyst and solvent at 90 °C.

4.4 *2H*-chromene transformation control experiments.

To discard the generation of salicylaldehyde from 2*H*-chromenes during Schiff base synthesis mediated by Keggin heteropolyanion, the compound **1a** was reacted with HPW@MIM-MCF under optimized conditions. Aliquots of the reaction crude were taken each hour, evaporated at reduced pressure (40 mbar, 60 °C, 0.5 h), and analyzed by ^1H NMR in $CDCl_3$. No transformation of **1a** was observed; salicylaldehyde signals were not detected. The comparison of aliquot and commercial salicylaldehyde spectra can be found in Figure S5.

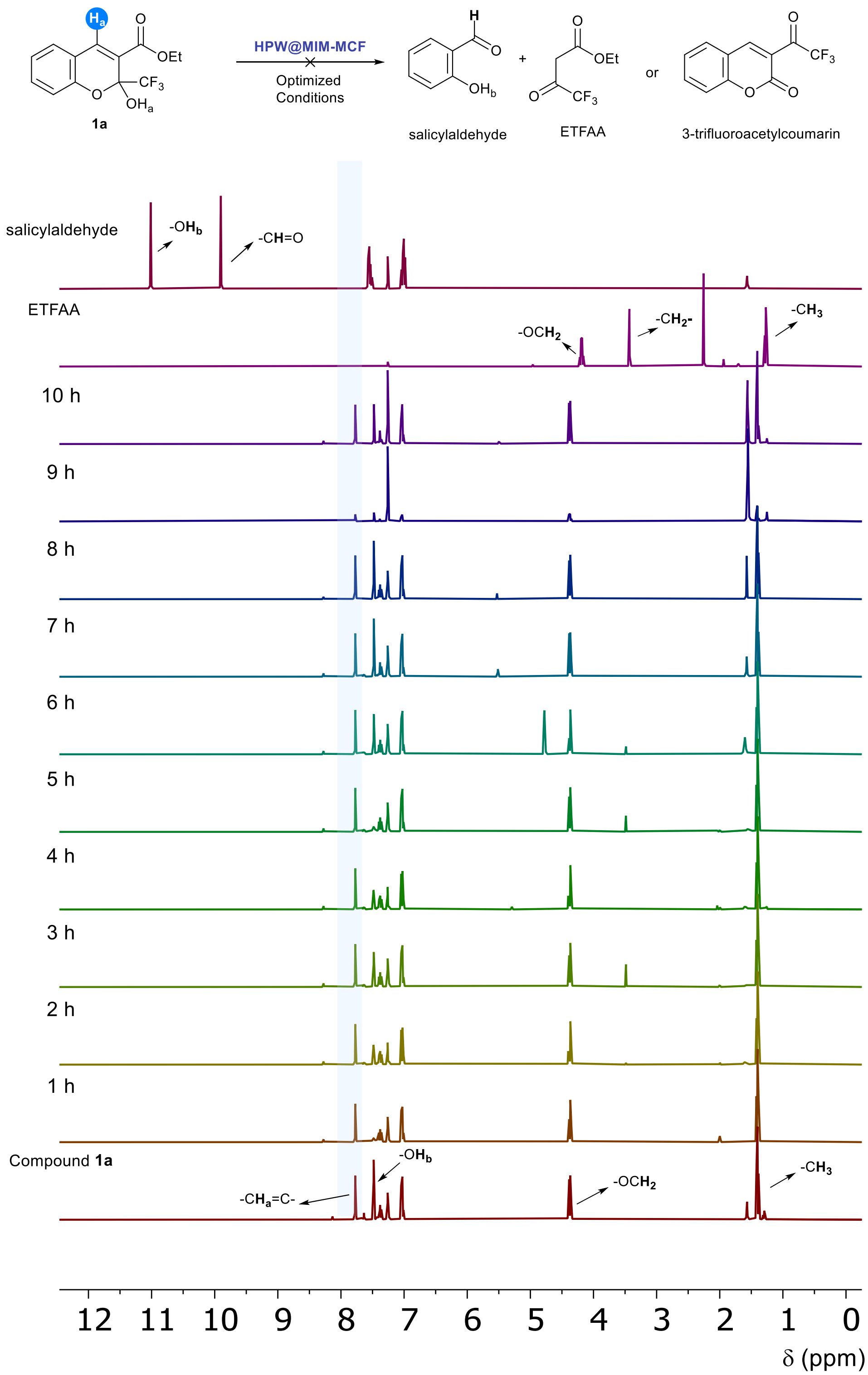


Figure S5. ^{1}H NMR spectra ($CDCl_3$, 400 MHz) comparison along 10 h for the reaction of compound **1a** with HPW@MIM-MCF catalyst in the absence of *p*-anisidine under optimized reaction conditions.

A similar experiment was conducted in the presence of *p*-anisidine. The comparison of ^{1}H NMR spectra for crude aliquots with commercial *p*-anisidine and salicylaldehyde, as well as pure Schiff base **5c**, can be found in Figure S6.

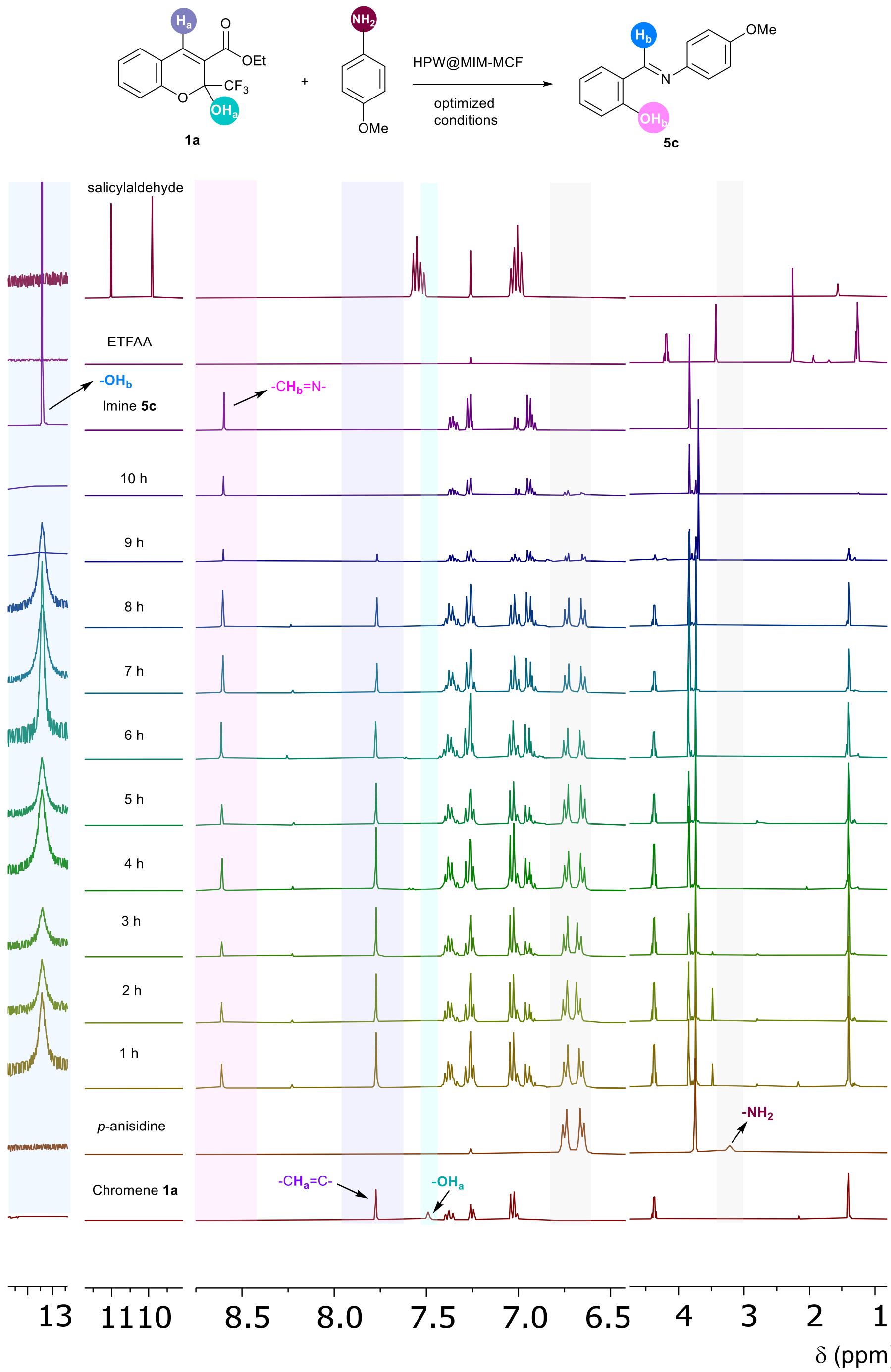
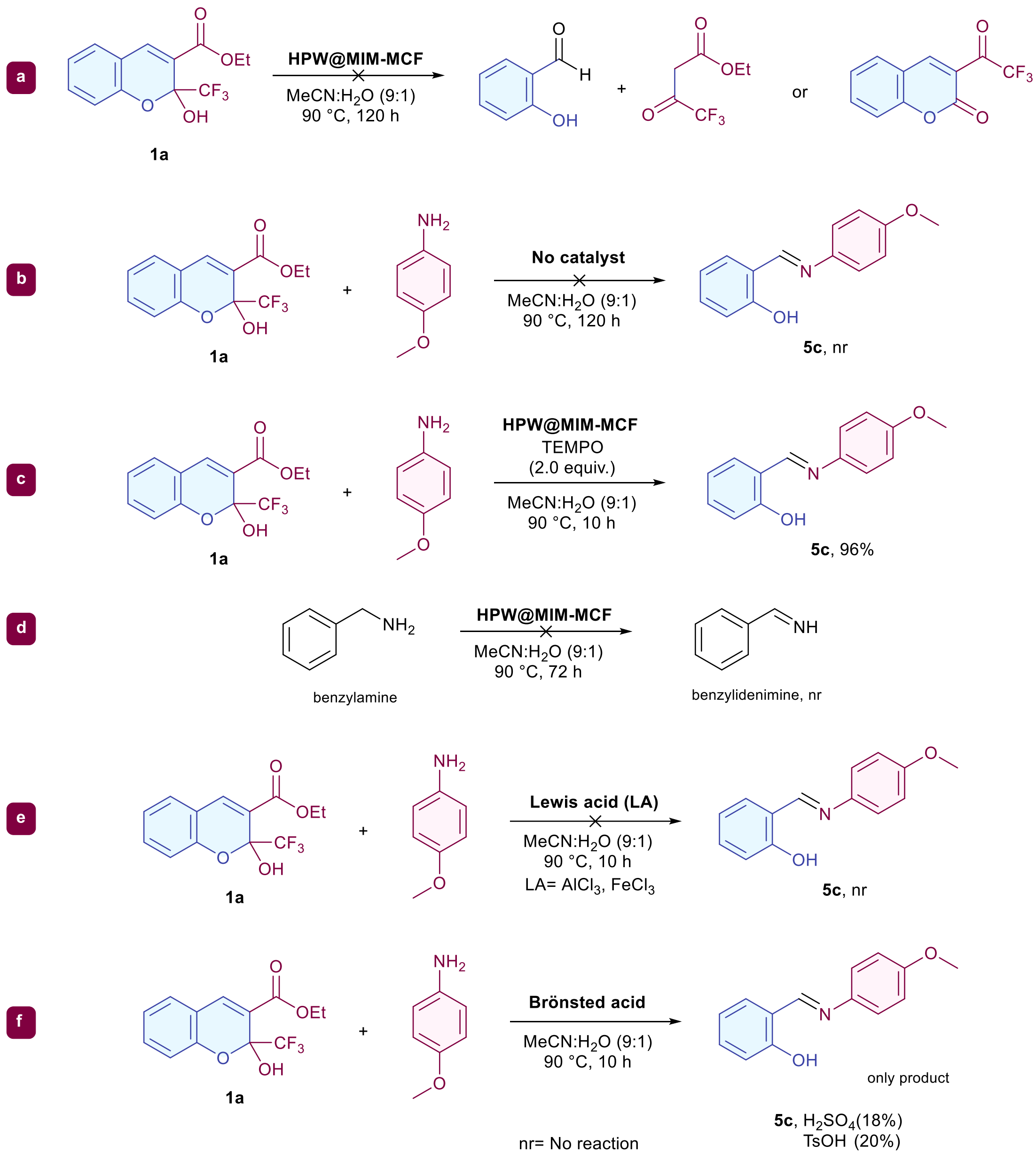
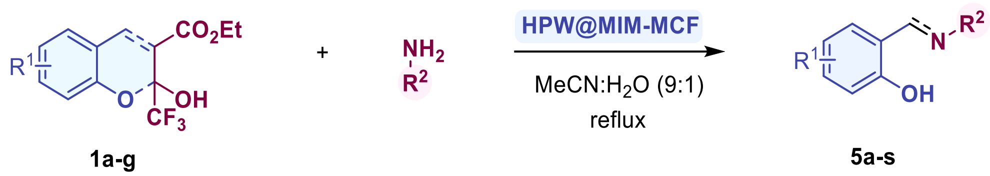


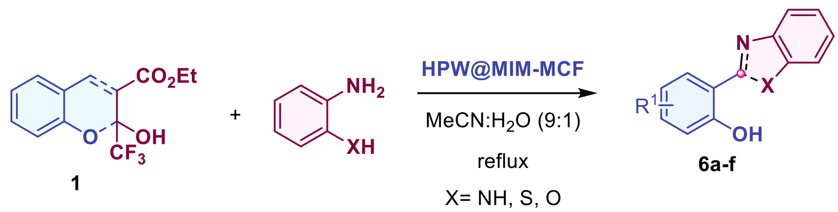
Figure S6. ^{1}H NMR spectra ($CDCl_3$, 400 MHz) comparison along 10 h for the reaction of compound **1a** and *p*-anisidine excess with HPW@MIM-MCF catalyst under optimized reaction conditions.



Scheme S1. Control experiments.

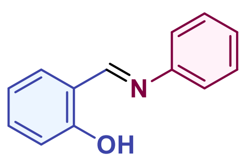
4.5 Schiff bases (5a-p) and benzimidazole derivatives (6a-f) synthesis.





In a 50 mL round-bottom flask with a stir bar, the 2*H*-chromene (100 mg), HPW@MIM-MCF catalyst 30% wt., and 3.5 mL of MeCN/H_2O (9:1) were placed. Then, amine (1.4 equiv.) was added to the reaction mixture and was stirred under reflux until the reaction was complete. The reaction was monitored by TLC (Hex/EtOAc, 9:1). Once the reaction was completed, the solvent system evaporated under vacuo. Then the crude was washed with MeCN. Compounds **5a-p** were recrystallized in MeCN. Product **5e** was purified by column chromatography over silica gel (230-400 mesh) using a Hexane/Ethyl acetate mixture (9:1) as eluent. For benzimidazole derivatives, once the reaction was completed, the solvent system was evaporated under vacuo, and the product was isolated by recrystallization or flash chromatography.

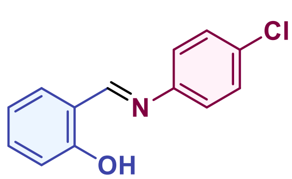
(*E*)-2-((phenylimino)methyl) phenol (**5a**). [5]



5a

Yellow oil (87 mg, 0.5 mmol, yield: 89%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 13.03 (s, 1H), 8.63 (s, 1H), 7.41 (tt, *J* = 9.6, 7.8 Hz, 4H), 7.32 – 7.13 (m, 3H), 7.04 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.95 (td, *J* = 7.5, 1.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.83, 161.31, 148.67, 133.31, 132.43, 129.56, 127.05, 121.32, 119.36, 119.21, 117.42.

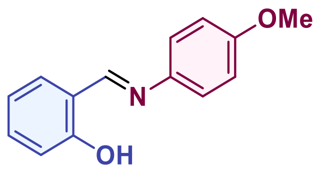
(*E*)-2-(((4-chlorophenyl) imino) methyl) phenol (**5b**). [6]



5b

Yellow solid (107 mg, 0.5 mmol, yield:93 %), mp 103.1-104.5 °C
^{1}H NMR (500 MHz, $CDCl_3$) δ 13.01 (s, 1H), 8.59 (s, 1H), 7.53 – 7.34 (m, 4H), 7.22 (d, *J* = 8.7 Hz, 1H), 7.06 – 7.01 (m, 1H), 6.95 (td, *J* = 7.4, 1.1 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.12, 161.24, 147.18, 133.58, 132.63, 132.54, 129.67, 122.59, 119.34, 119.17, 117.45.

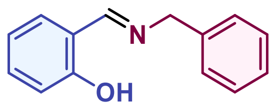
(*E*)-2-(((4-methoxyphenyl) imino) methyl) phenol (**5c**).[5]



5c

Yellow solid (104 mg, 0.5 mmol, yield: 92%), mp 181.9-183.1°C
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.41 (tt, *J* = 9.6, 7.8 Hz, 4H), 7.32 – 7.13 (m, 3H), 7.04 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.95 (td, *J* = 7.5, 1.1 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.12, 160.57, 158.97, 141.51, 132.80, 132.08, 122.42, 119.51, 119.10, 117.28, 114.74, 55.66.

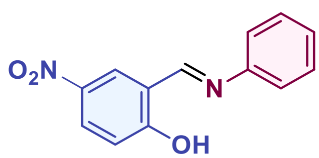
(*E*)-2-((benzylimino)methyl) phenol (**5d**).



5d

Yellow solid (100 mg, 0.5 mmol, yield: 95%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 13.36 (s, 1H), 8.45 (s, 1H), 7.40 – 7.23 (m, 7H), 6.97 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.89 (td, *J* = 7.4, 1.1 Hz, 1H), 4.82 (s, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.74, 161.42, 138.19, 132.57, 131.56, 128.79, 127.87, 127.49, 118.71, 117.22, 63.11.

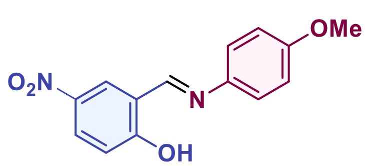
(*E*)-4-nitro-2-((phenylimino)methyl) phenol (**5e**).[7]



5e

Yellow solid (104 mg, 0.5 mmol, yield: 86%), mp 130.5-131.9°C
^{1}H NMR (500 MHz, $CDCl_3$) δ 14.47 (s, 1H), 8.71 (s, 1H), 8.39 (d, *J* = 2.8 Hz, 1H), 8.25 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.39 – 7.30 (m, 3H), 7.09 (d, *J* = 9.2 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.00, 160.73, 146.80, 140.08, 129.81, 128.50, 128.46, 128.21, 121.34, 118.46, 118.25.

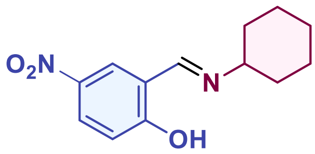
(*E*)-2-(((4-methoxyphenyl) imino) methyl)-4-nitrophenol (**5f**).[8]



5f

Yellow solid (121 mg, 0.5 mmol, yield: 89%), mp 168.4-169.6 °C.
^{1}H NMR (500 MHz, DMSO) δ 14.75 (s, 1H), 9.05 (d, *J* = 5.1 Hz, 1H), 8.54 (d, *J* = 2.9 Hz, 1H), 8.15 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.40 (dd, *J* = 8.8, 2.5 Hz, 2H), 7.00 (dd, *J* = 9.2, 2.2 Hz, 1H), 6.96 (dd, *J* = 9.0, 2.5 Hz, 2H), 3.79 (s, 3H). **^{13}C NMR** (125 MHz, DMSO) δ 166.93, 158.99, 138.85, 138.49, 128.16, 127.39, 122.37, 122.36, 118.10, 117.78, 114.38, 55.07.

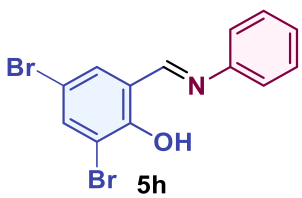
(*E*)-2-((cyclohexylimino)methyl)-4-nitrophenol (**5g**). [9]



5g

Yellow solid (109 mg, 0.5 mmol, yield: 88%), mp 131.2-132.1 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 15.14 (s, 1H), 8.32 (s, 1H), 8.21 (d, *J* = 2.9 Hz, 1H), 8.14 (dd, *J* = 9.3, 2.9 Hz, 1H), 6.86 (d, *J* = 9.4 Hz, 1H), 3.44 (tt, *J* =10.1, 4.0 Hz, 1H), 1.88 (ddt, *J* = 42.8, 13.3, 4.2 Hz, 4H), 1.67 (dp, *J* = 12.8, 4.0 Hz, 1H), 1.56 (dtd, *J* = 12.9, 10.4, 3.5 Hz, 2H), 1.48 – 1.21 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.54, 162.05, 137.75, 129.22, 128.70, 120.45, 115.77, 64.58, 33.72, 25.27, 24.24.

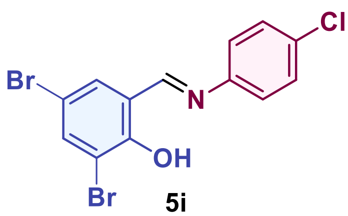
(*E*)-2,4-dibromo-6-((phenylimino)methyl) phenol (**5h**). [10]



5h

Orange solid (157 mg, 0.5 mmol, yield: 89%), mp 84.3-85.1 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 14.48 (s, 1H), 8.53 (s, 1H), 7.74 (d, *J* = 2.4 Hz, 1H), 7.48 (d, *J* = 2.3 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 7.2 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.14, 157.60, 146.79, 138.26, 133.56, 129.78, 128.08, 121.33, 120.79, 112.39, 110.34.

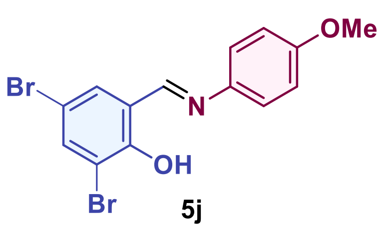
(*E*)-2,4-dibromo-6-(((4-chlorophenyl)imino)methyl)phenol (**5i**). [11]



5i

Orange solid (167 mg, 0.5 mmol, yield: 86%), mp 109.6-110.5 °C **^{1}H NMR** (500 MHz, $CDCl_3$) δ 14.14 (s, 1H), 8.50 (s, 1H), 7.74 (d, *J* = 2.3 Hz, 1H), 7.47 (d, *J* = 2.3 Hz, 1H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 8.7 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.51, 157.29, 142.08, 138.48, 135.03, 133.66, 129.94, 122.63, 120.69, 112.34, 110.59.

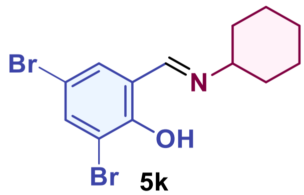
(*E*)-2,4-dibromo-6-(((4-methoxyphenyl)imino)methyl)phenol (**5j**). [11]



5j

Orange solid (173 mg, 0.5 mmol, yield: 90%), mp 117.9-119.1 °C **^{1}H NMR** (400 MHz, $CDCl_3$) δ 14.69 (s, 1H), 8.49 (s, 1H), 7.70 (d, *J* = 2.4 Hz, 1H), 7.44 (d, *J* = 2.3 Hz, 1H), 7.28 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.76, 157.44, 157.42, 139.46, 137.69, 133.19, 122.62, 120.99, 114.96, 112.23, 110.21, 55.70.

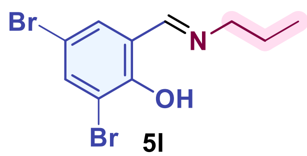
(E)-2,4-dibromo-6-((cyclohexylimino)methyl)phenol (**5k**).



5k

Orange solid (157 mg, 0.5 mmol, yield: 87 %), mp 84.5-85.4 °C.
^{1}H NMR (500 MHz, $CDCl_3$) δ 15.16 (s, 1H), 8.15 (s, 1H), 7.67 (t, J = 2.7 Hz, 1H), 7.26 (d, J = 2.5 Hz, 1H), 3.37 (tt, J = 10.1, 3.8 Hz, 1H), 1.84 (ddq, J = 23.7, 11.7, 3.7 Hz, 4H), 1.69 – 1.59 (m, 2H), 1.52 (tdd, J = 12.0, 10.0, 2.9 Hz, 2H), 1.32 (m, 4H).

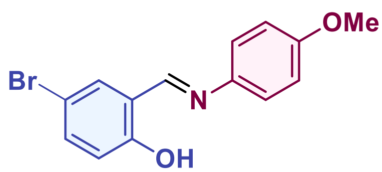
(E)-2,4-dibromo-6-((propylimino)methyl)phenol (**5l**).



5l

Yellow solid (139 mg, 0.5 mmol, yield: 87%), mp 55.3-57.1 °C.
^{1}H NMR (500 MHz, $CDCl_3$) δ 14.93 (s, 1H), 8.16 (s, 1H), 7.69 (d, J = 2.4 Hz, 1H), 7.29 (d, J = 2.4 Hz, 1H), 3.63 – 3.56 (m, 2H), 1.74 (h, J = 7.2 Hz, 2H), 0.99 (t, J = 7.4 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 163.14, 138.04, 132.76, 119.14, 113.71, 108.28, 59.26, 23.83, 11.68.

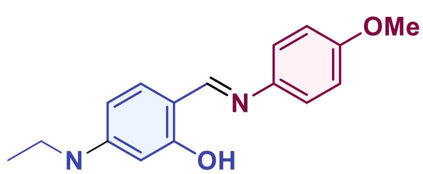
(E)-4-bromo-2-(((4-methoxyphenyl)imino)methyl)phenol (**5m**). [12]



5m

Ligh green solid (131 mg, 0.5 mmol, yield: 86%), mp 156.2-157.4 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 13.45, 8.52, 7.48, 7.48, 7.42, 7.42, 7.40, 7.28, 7.26, 6.94, 6.91, 6.90, 3.84.**^{13}C NMR** (125 MHz, $CDCl_3$) δ 160.14, 159.35, 158.89, 140.89, 135.33, 134.05, 120.94, 119.28, 114.84, 110.55, 55.70.

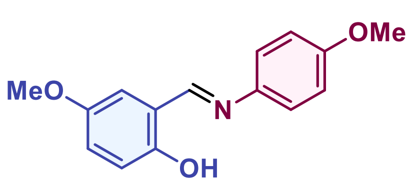
(E)-5-(diethylamino)-2-(((4-methoxyphenyl)imino)methyl)phenol (**5n**). [13]



5n

Yellow solid (82 mg, 0.5 mmol, yield: 55%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 13.96 (s, 1H), 8.46 (s, 1H), 7.35 – 7.18 (m, 3H), 6.98 (d, J = 8.5 Hz, 2H), 6.34 – 6.24 (m, 2H), 3.89 (s, 3H), 3.47 (d, J = 7.1 Hz, 4H), 1.28 (t, J = 7.1 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.06, 159.19, 157.87, 151.65, 142.22, 133.52, 121.83, 114.63, 109.34, 103.73, 98.02, 55.66, 44.69, 12.85.

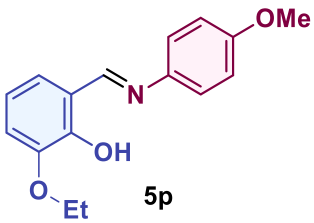
(E)-4-methoxy-2-(((4-methoxyphenyl)imino)methyl)phenol (**5o**). [14]



5o

Light yellow solid (111 mg, 0.5 mmol, yield: 87 %).
^{1}H NMR (500 MHz, $CDCl_3$) δ 12.90 (s, 1H), 8.56 (s, 1H), 7.27 (d, J = 9.0 Hz, 2H), 7.01 – 6.91 (m, 4H), 6.88 (d, J = 2.5 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 160.26, 159.03, 155.37, 152.38, 141.52, 122.44, 120.05, 119.14, 118.07, 115.35, 114.76, 56.09, 55.68.

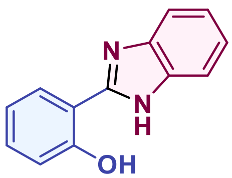
(*E*)-2-ethoxy-6-(((4-methoxyphenyl)imino)methyl)phenol (**5p**). [15]



5p

Light yellow solid (104 mg, 0.5 mmol, yield:77 %).
^{1}H NMR (500 MHz, $CDCl_3$) δ 14.69 (s, 1H), 8.47 (s, 1H), 7.68 (d, *J* = 2.3 Hz, 1H), 7.42 (d, *J* = 2.4 Hz, 1H), 7.30 – 7.23 (m, 2H), 6.97 – 6.91 (m, 2H), 3.83 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.77, 157.43, 139.46, 137.68, 133.18, 122.61, 120.99, 114.96, 112.23, 110.20, 55.70.

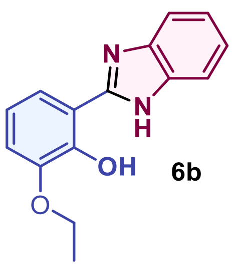
2-(1*H*-benzo[d]imidazol-2-yl)phenol (**6a**). [16]



6a

White solid (97 mg, 0.5 mmol, yield: 93%), mp 236.3-237.8 °C
^{1}H NMR (500 MHz, DMSO-d_6) δ 13.17 (s, 1H), 8.05 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.66 (d, *J* = 45Z.0 Hz, 2H), 7.38 (ddd, *J* = 8.5, 7.2, 1.6 Hz, 1H), 7.29 (s, 1H), 7.03 (m, 4H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 158.06, 151.75, 131.80, 126.25, 119.19, 117.25, 112.65.

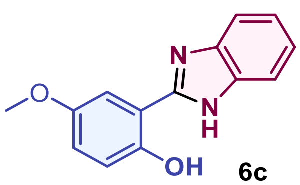
2-(1*H*-benzo[d]imidazol-2-yl)-6-ethoxyphenol (**6b**). [17]



6b

White solid (95 mg, 0.5, yield: 75%), mp 181.9-183.2°C
^{1}H NMR (400 MHz, DMSO-d_6) δ 13.50 – 12.99 (m, 2H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.61 (t, 2H), 7.33 – 7.24 (m, 2H), 7.07 (d, *J* = 7.9 Hz, 1H), 6.93 (t, *J* = 7.9 Hz, 1H), 4.09 (q, *J* = 6.9 Hz, 2H), 1.37 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.99, 148.16, 147.93, 119.77, 118.04, 113.12, 64.64, 49.08, 31.01, 14.95.

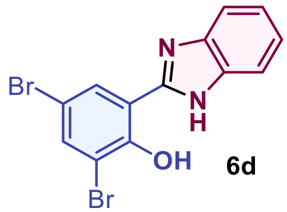
2-(1*H*-benzo[d]imidazol-2-yl)-4-methoxyphenol (**6c**). [18]



6c

White solid (96 mg, 0.5 mmol, yield: 80%), mp 278.9-281.7 °C
^{1}H NMR (400 MHz, DMSO-d_6) δ 13.15 (s, 1H), 12.61 (s, 1H), 7.89 – 7.59 (m, 3H), 7.33 – 7.24 (m, 2H), 7.05 – 6.93 (m, 2H), 3.81 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 152.10, 152.01, 151.65, 123.31, 122.43, 118.79, 118.02, 112.32, 111.52, 109.88, 55.72.

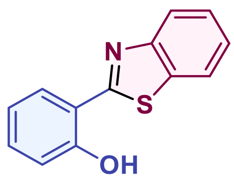
2-(1*H*-benzo[d]imidazol-2-yl)-4,6-dibromophenol (**6d**). [19]



6d

White solid (180 mg, 0.5 mmol, yield: 98%), mp 241.5-242.4°C
^{1}H NMR (400 MHz, DMSO-d_6) δ 13.71 (s, 2H), 8.31 (d, *J* = 2.3 Hz, 1H), 7.89 (d, *J* = 2.3 Hz, 1H), 7.70 (dd, *J* = 5.9, 3.3 Hz, 2H), 7.34 (dd, *J* = 6.1, 3.2 Hz, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 154.39, 149.70, 136.03, 127.71, 123.60, 114.93, 111.89, 110.01.

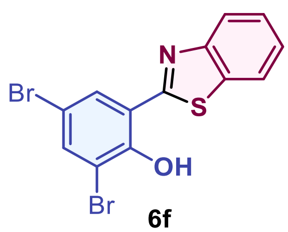
2-(benzo[d]thiazol-2-yl) phenol (**6e**). [20]



6e

White solid (80 mg, 0.5 mmol, yield: 71%), mp 130.4-133.1 °C
^{1}H NMR (400 MHz, $CDCl_3$) δ 12.25 (s, 1H), 7.99 (dd, *J* = 8.1, 0.6 Hz, 1H), 7.90 (dd, *J* = 8.0, 0.6 Hz, 1H), 7.70 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.57 – 7.47 (m, 1H), 7.46 – 7.33 (m, 2H), 7.11 (dd, *J* = 8.3, 1.2 Hz, 1H), 6.96 (ddd, *J* = 7.8, 7.3, 1.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.51, 158.09, 151.90, 132.92, 132.72, 128.55, 126.85, 125.69, 122.30, 121.65, 119.66, 118.02, 116.91.

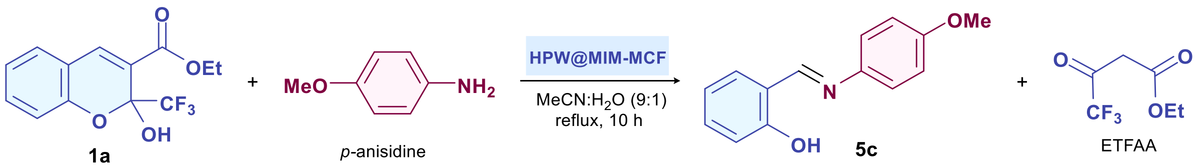
2-(benzo[d]thiazol-2-yl)-4,6-dibromophenol (**6f**). [21]



6f

White solid (150 mg, 0.5 mmol, yield: 78%), mp 147.9-149.6 °C
^{1}H NMR (400 MHz, $CDCl_3$) δ 13.44 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.75 (s, 2H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.47 (t, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 167.16, 154.15, 151.29, 137.90, 132.90, 129.77, 127.36, 126.52, 122.66, 121.86, 118.85, 112.99, 110.99.

4.6 Catalyst recovery and reuse



Catalyst recovery and reuse were studied under optimal reaction conditions at a 1.0 mmol scale; a detailed procedure is described on page S14. After 10 h, the reaction was stopped, 2 mL of acetone was added, the crude was homogenized by sonication for 1 minute and then centrifuged at 1500 rpm for 10 minutes. The supernatant was collected, and this process was repeated three more times to wash the catalyst. The catalyst was recovered by drying under reduced pressure in the same tube, while the collected supernatants were concentrated and analyzed by 1H NMR using 1,4-dioxane as the internal standard. Finally, the test tube containing the dry catalyst was loaded with the starting materials, and a new cycle began.

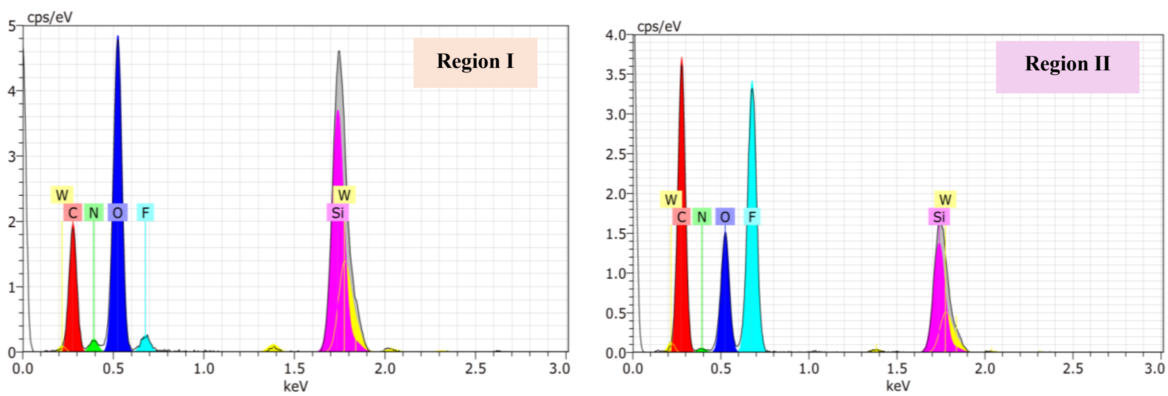


Figure S7. EDS analysis for reused catalyst.

Table S4. EDS weight content.

Element	Fresh Catalyst (% wt.)	Reused catalyst Region I (% wt.)	Reused catalyst Region II (% wt.)
Carbon	9.54	21.32	37.78
Nitrogen	2.16	3.02	1.25
Oxygen	34.41	38.18	15.34
Fluorine	--	2.29	29.43
Silicon	22.92	20.22	9.38
Tungsten	30.95	14.96	6.81

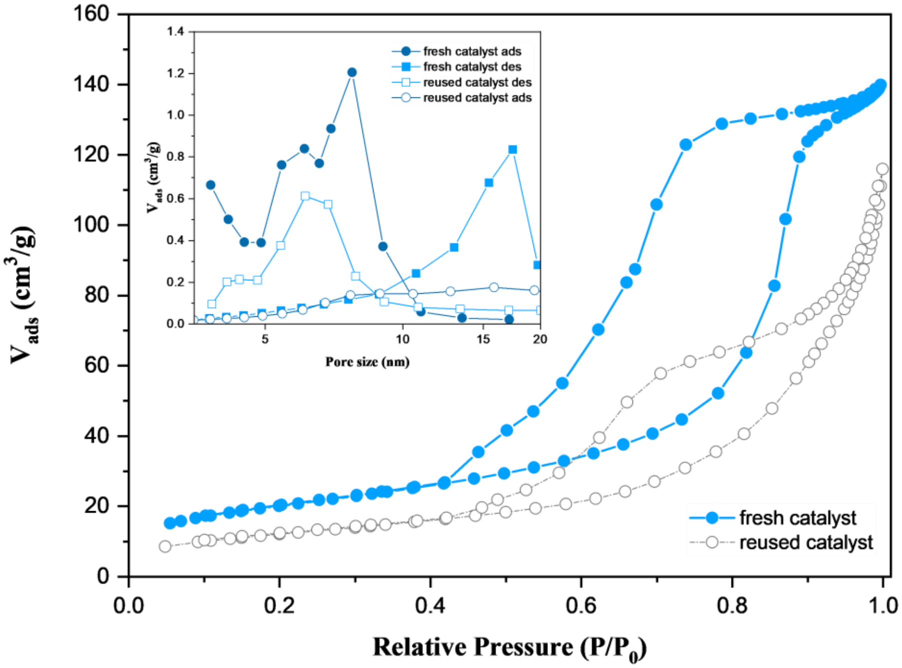


Figure S8. N_2 adsorption-desorption isotherms and pore size distribution for fresh and recycled catalyst. optimization.

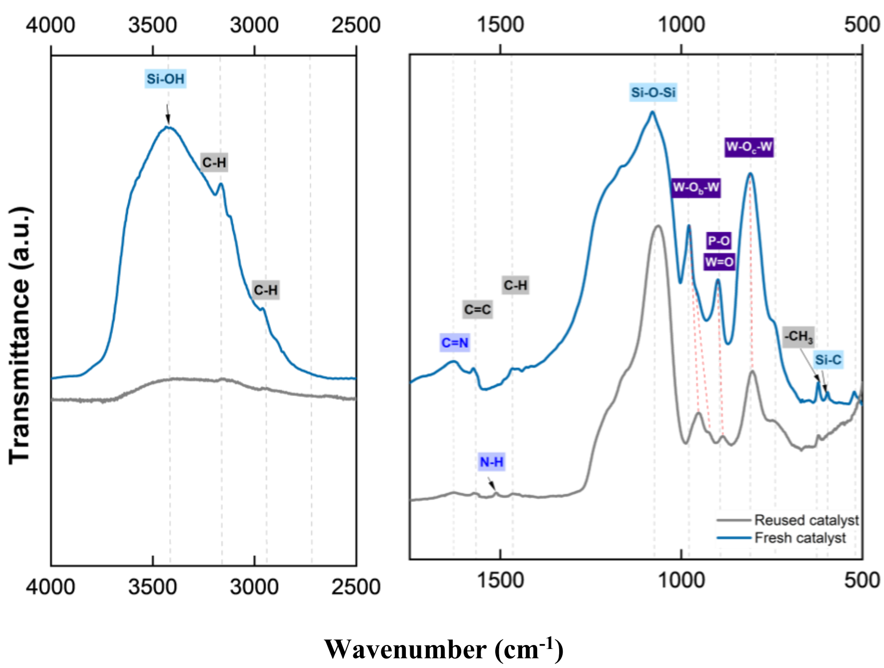


Figure S9. FT-IR spectra for the fresh catalyst and the reused catalyst after ten reaction cycles.

5 Copies of ^{1}H and ^{13}C NMR spectra and HRMS

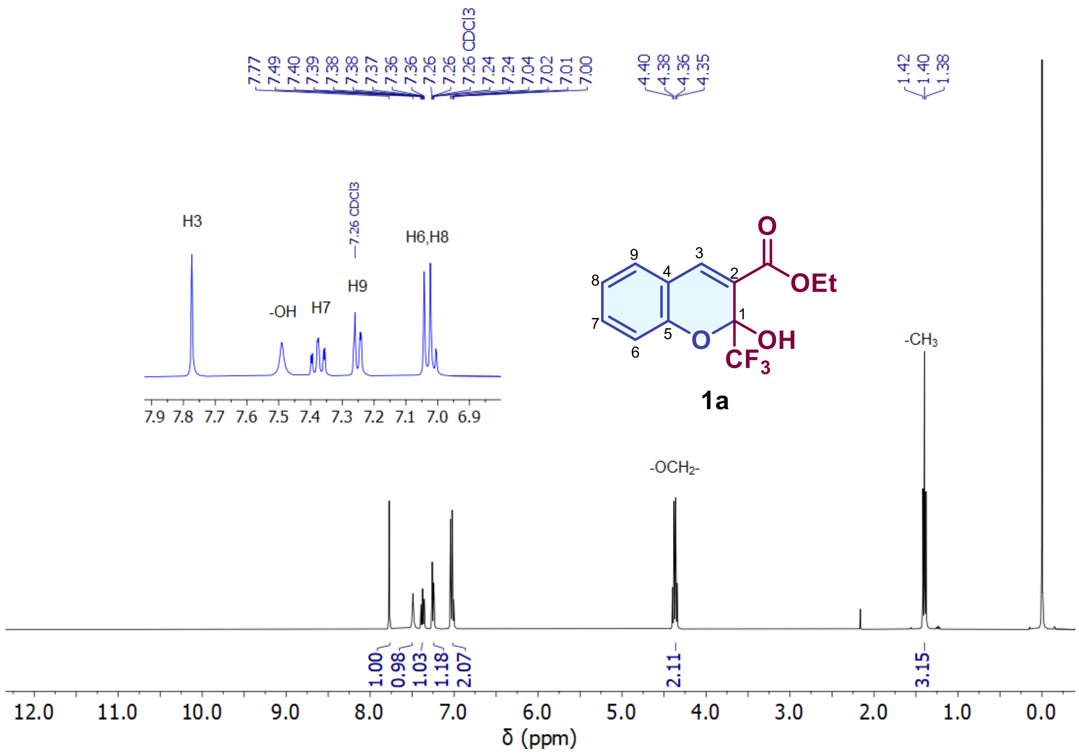


Figure S10. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra for compound **1a**.

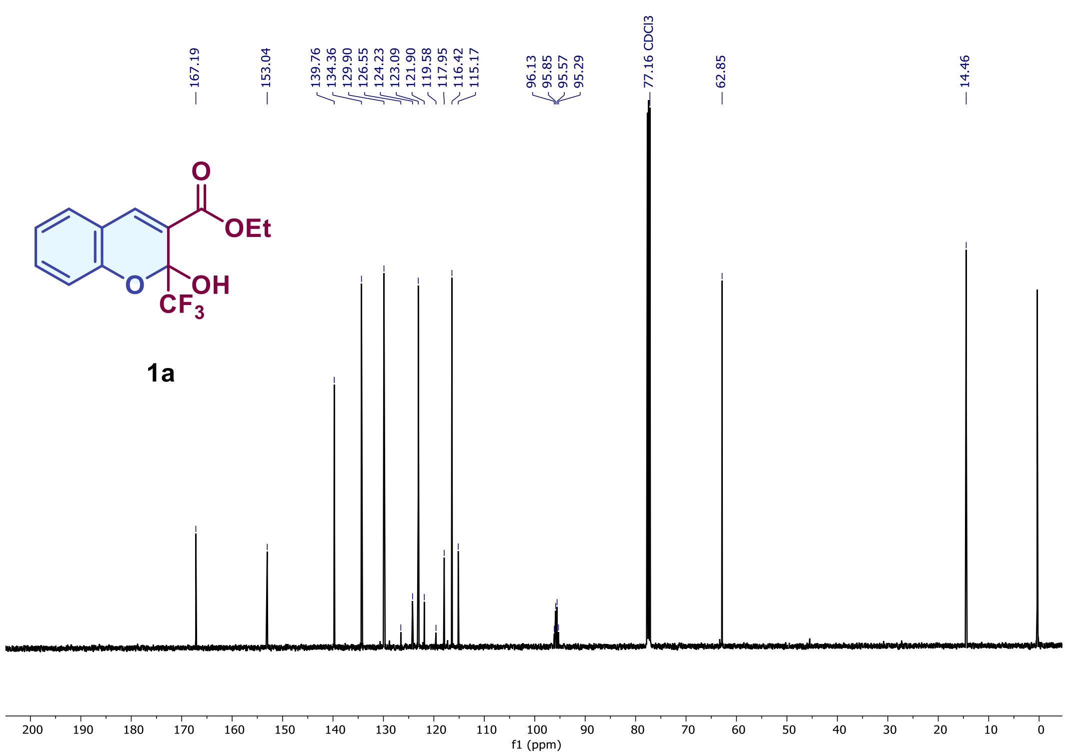


Figure S11. ^{13}C NMR ($CDCl_3$, 100 MHz) spectra for compound **1a**.

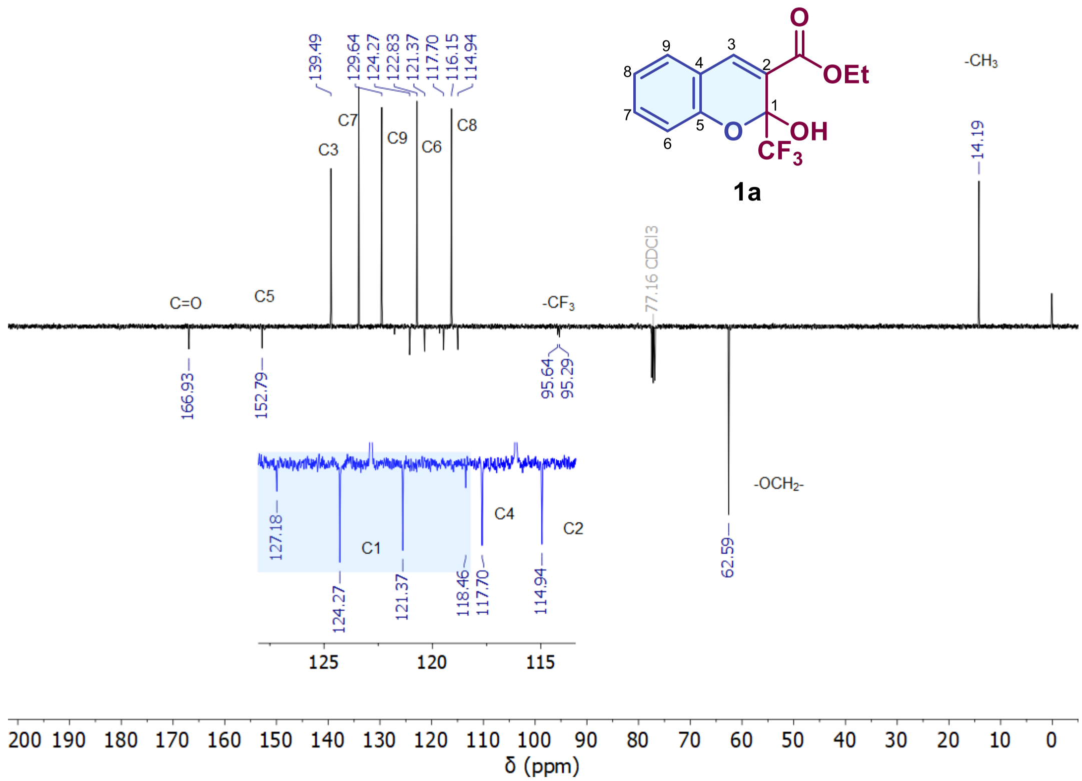


Figure S12. APT ($CDCl_3$, 100 MHz) spectra for compound **1a**.

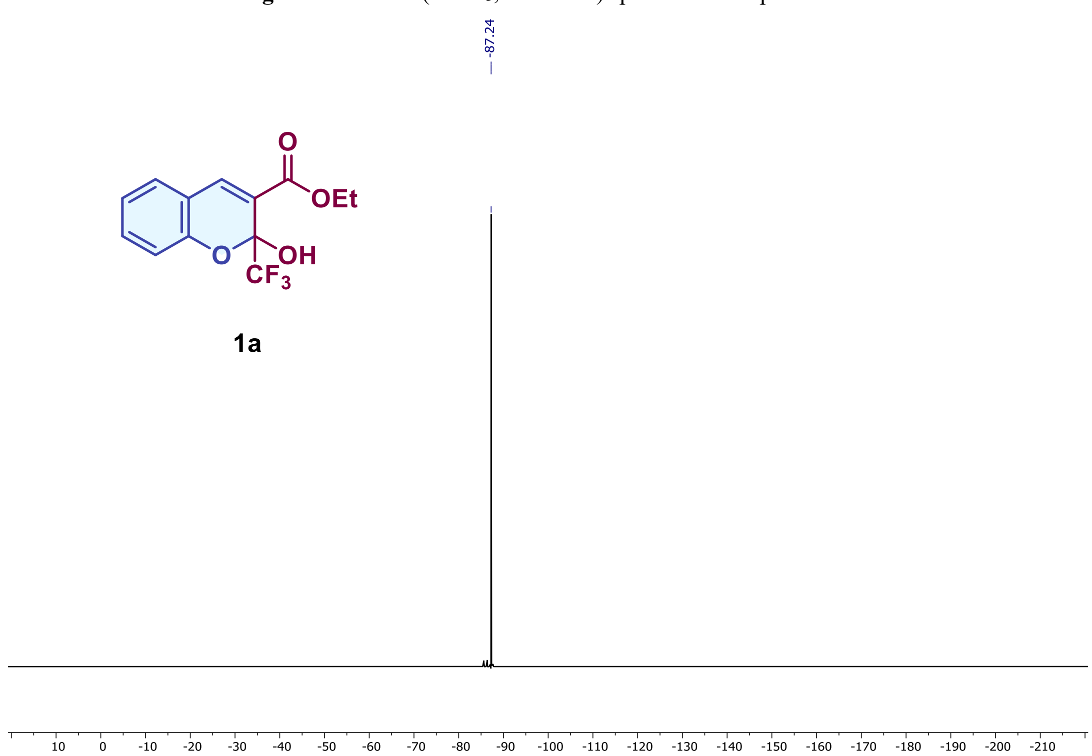


Figure S13. ^{19}F NMR ($CDCl_3$, 470 MHz) spectra for compound **1a**.

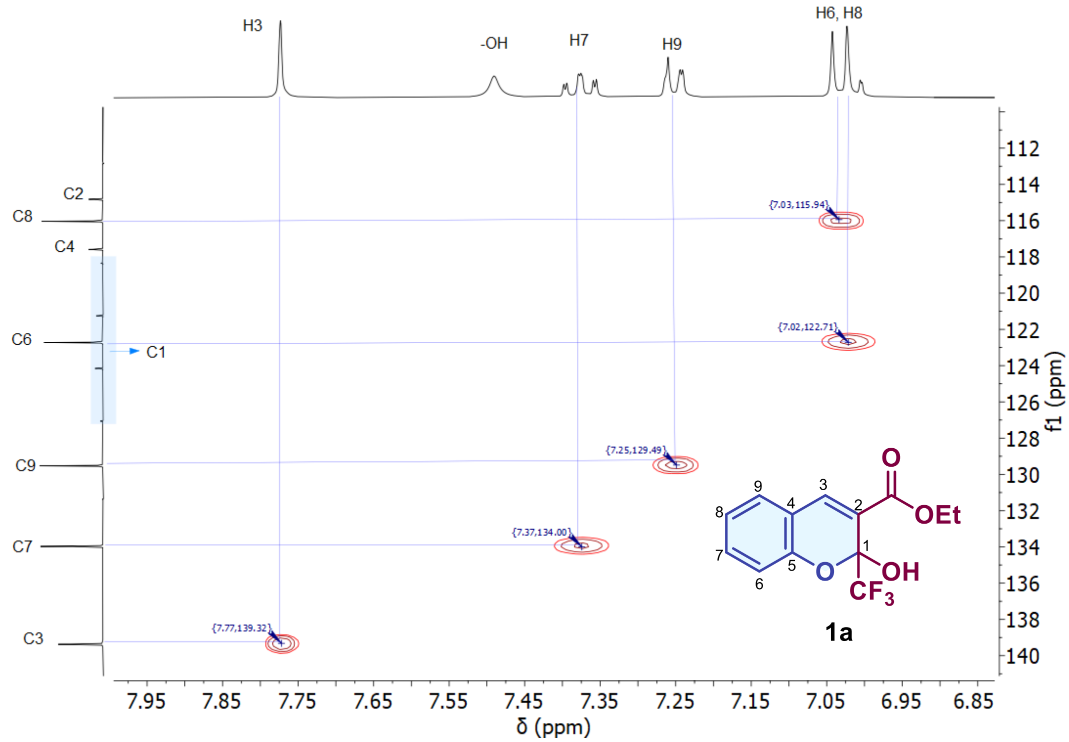


Figure S14. HSQC ($CDCl_3$, 400 MHz) spectra for compound **1a**.

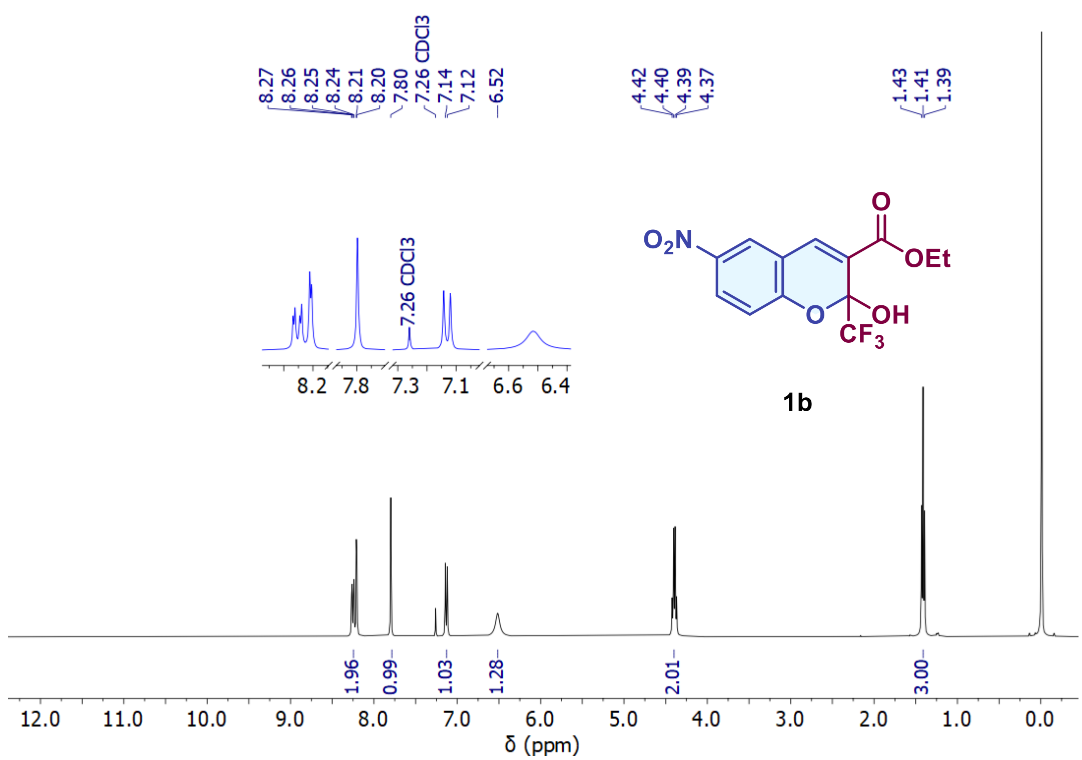


Figure S15. ^1H NMR ($CDCl_3$, 400 MHz) spectra for compound **1b**.

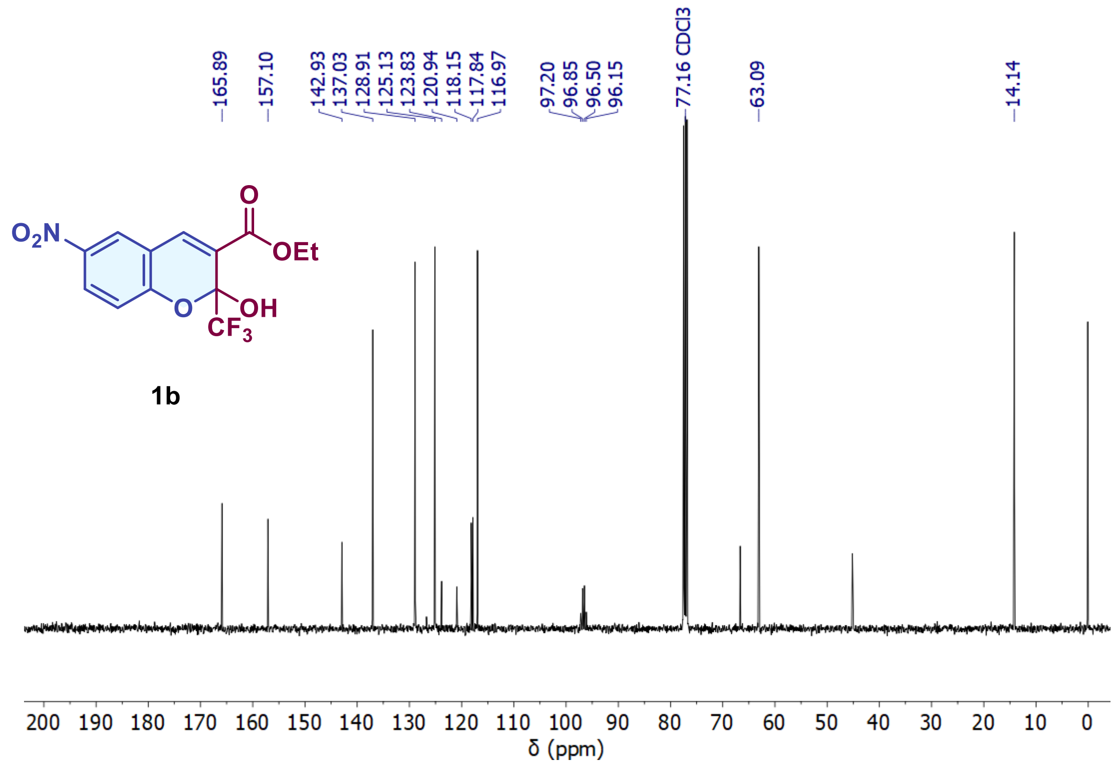


Figure S16. ^{13}C NMR ($CDCl_3$, 100 MHz) spectra for compound **1b**.

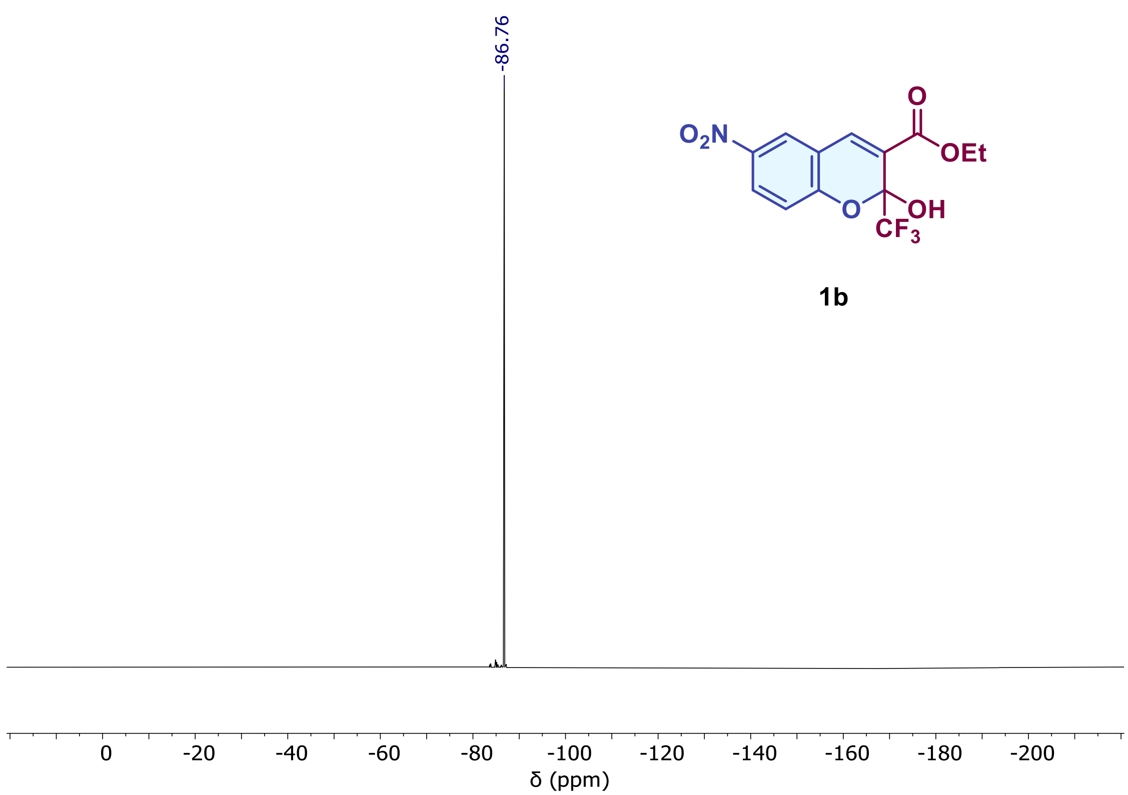


Figure S17. ^{19}F NMR ($CDCl_3$, 375 MHz) spectra for compound **1b**.

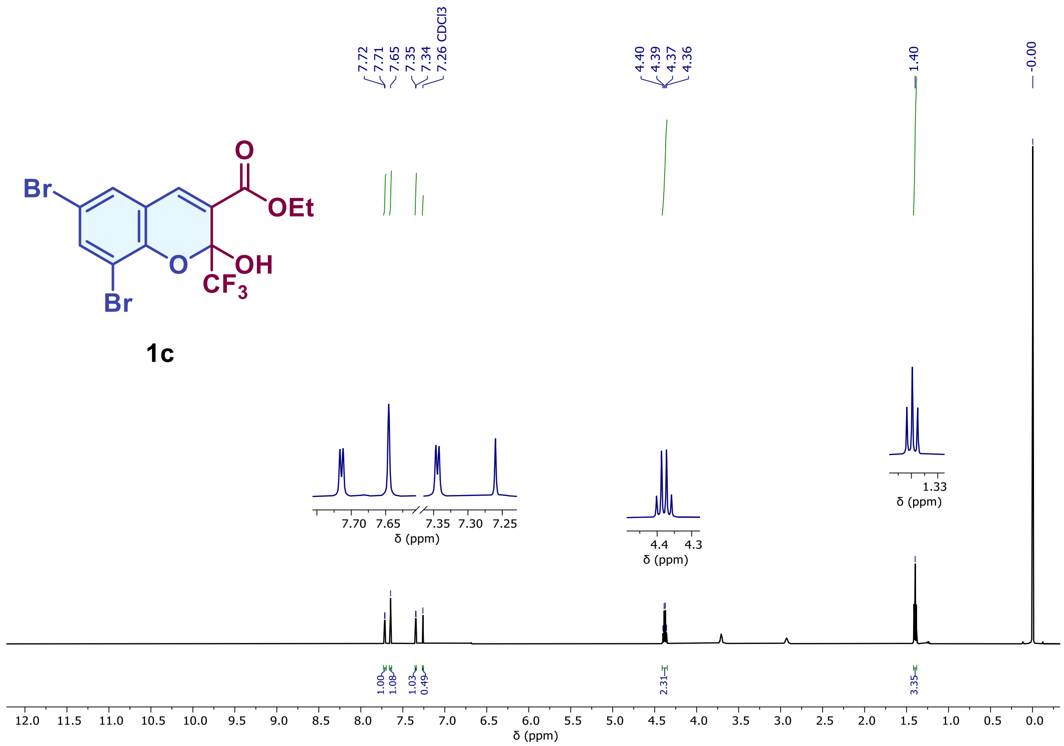


Figure S18. ^{1}H NMR ($CDCl_3$, 500 MHz) spectra for compound **1c**.

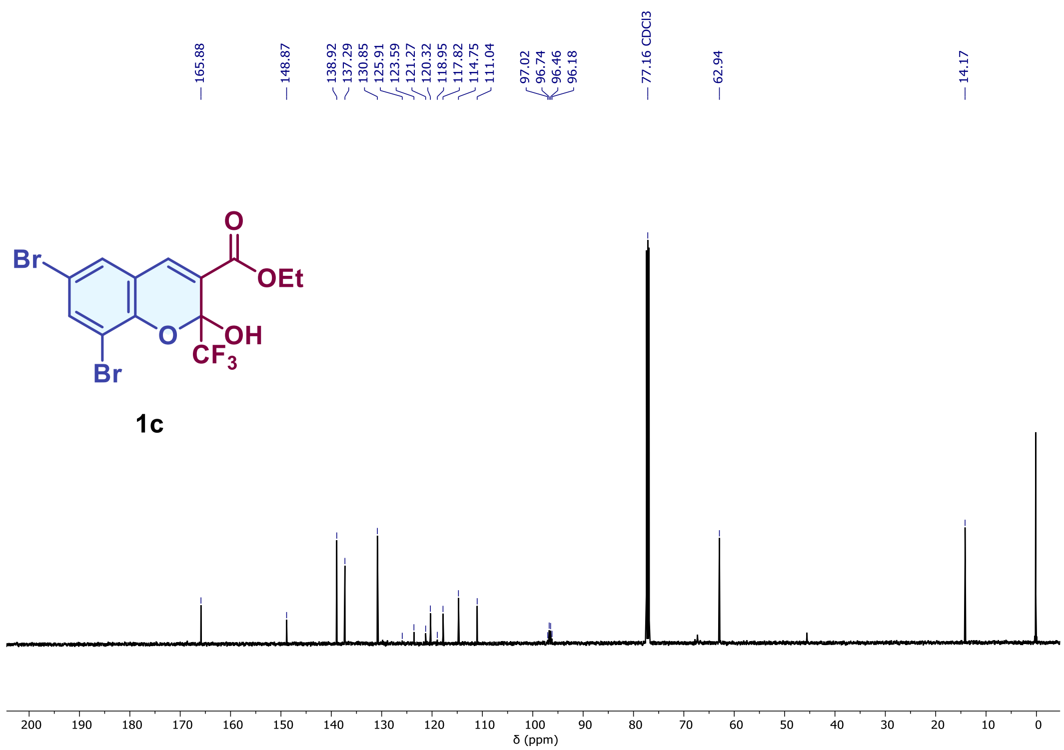


Figure S19. ^{13}C NMR ($CDCl_3$, 125 MHz) spectra for compound **1c**.

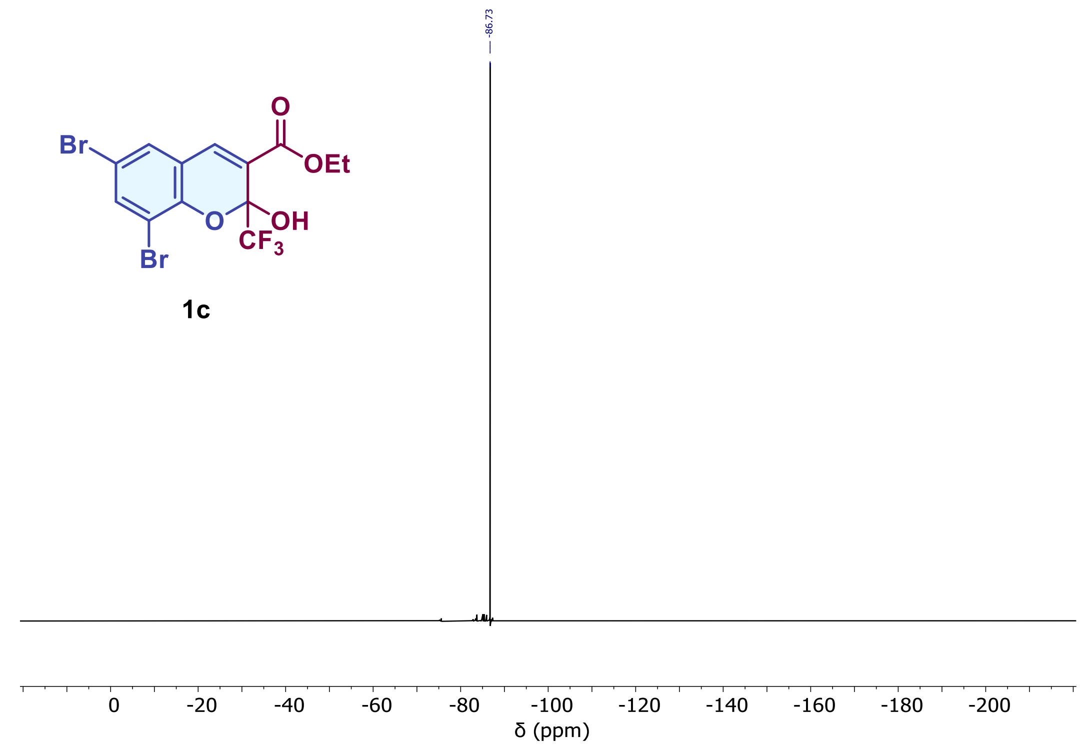


Figure S20. ^{19}F NMR (CDCl3, 470 MHz) spectra for compound **1c**.

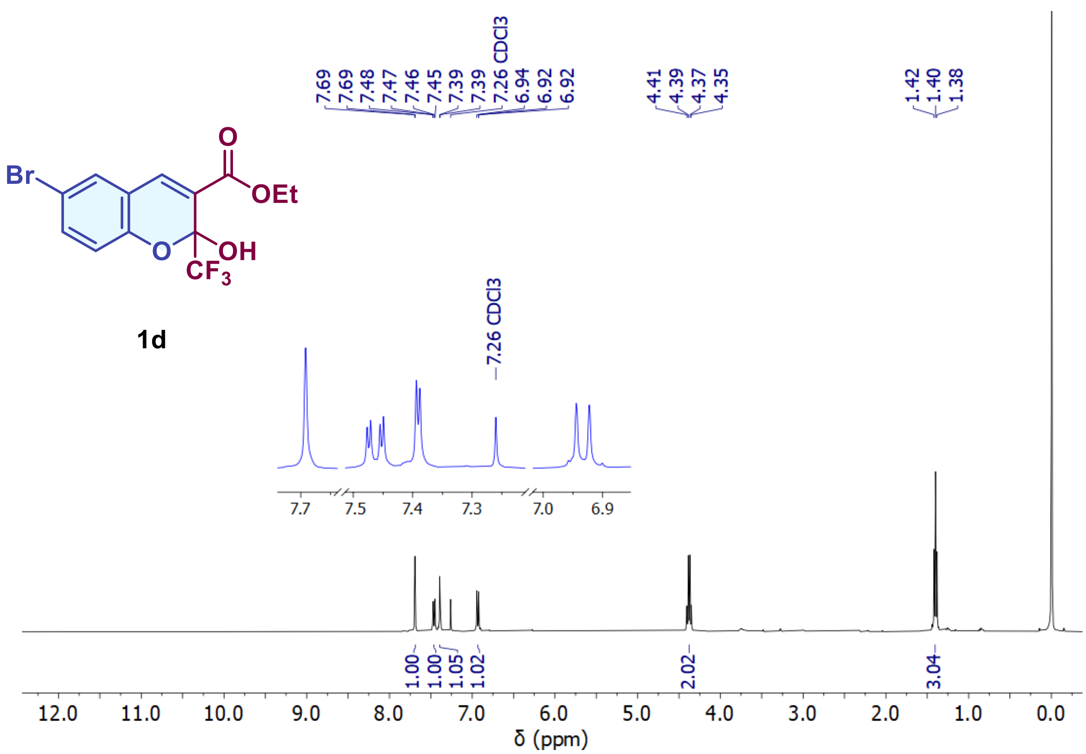


Figure S21. ^{1}H NMR (CDCl3, 500 MHz) spectra for compound **1d**.

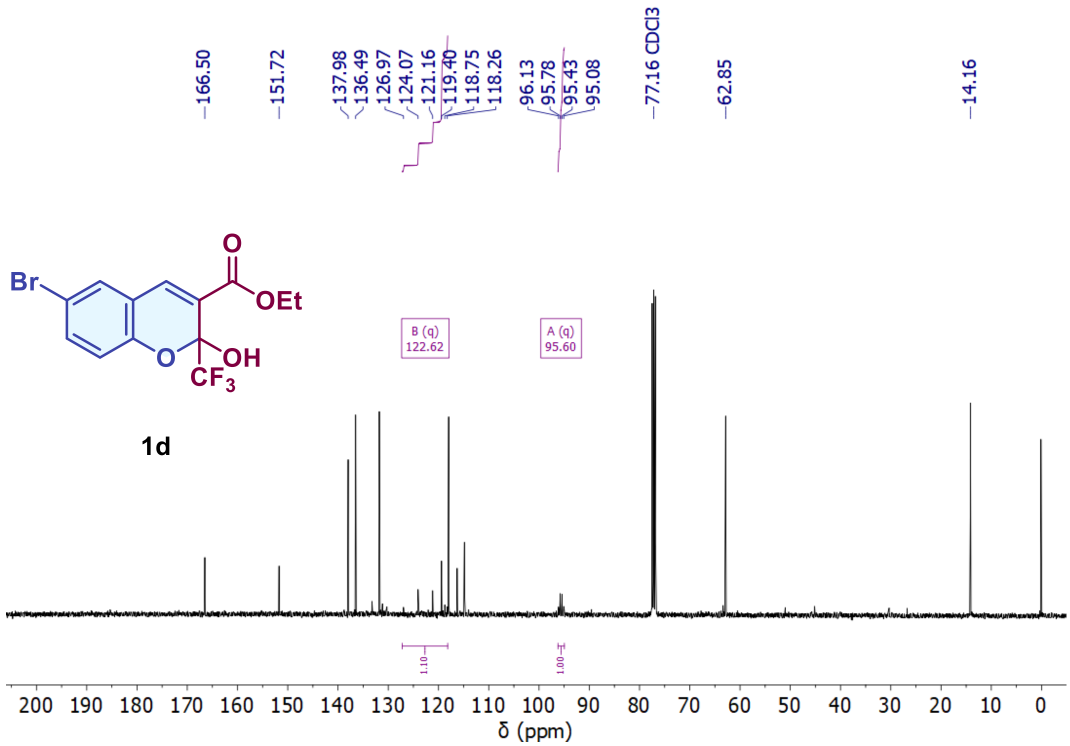


Figure S22. ^{13}C NMR (CDCl3, 125 MHz) spectra for compound **1d**.

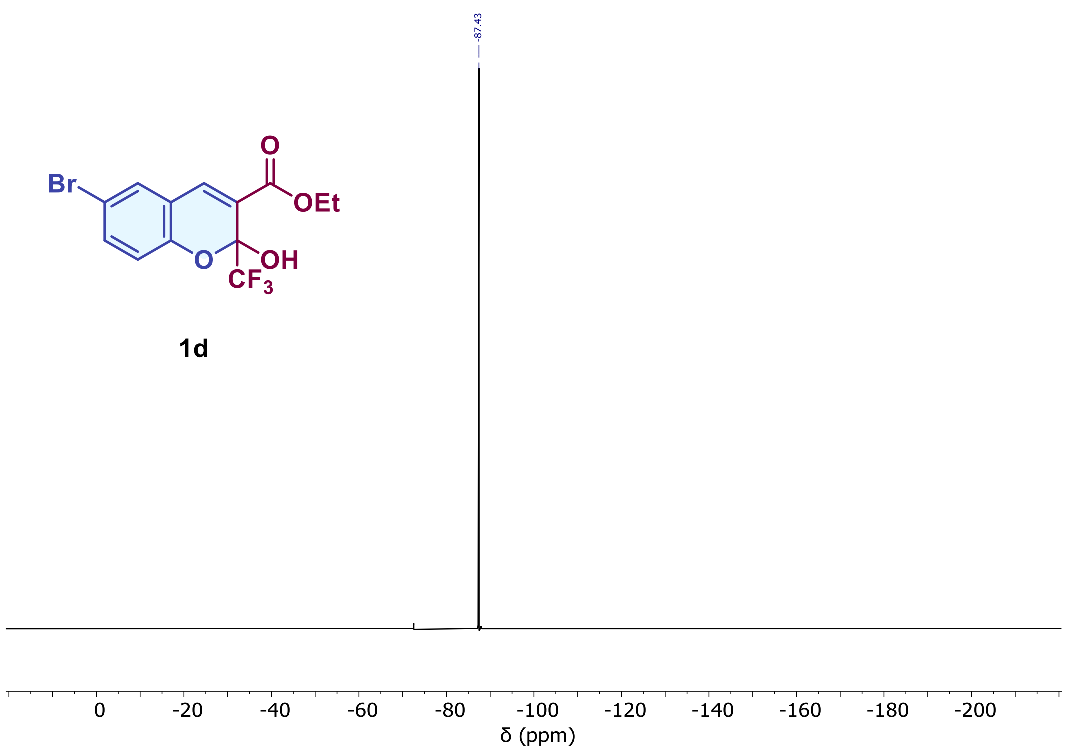


Figure S23. ^{19}F NMR (CDCl3, 470 MHz) spectra for compound **1d**.

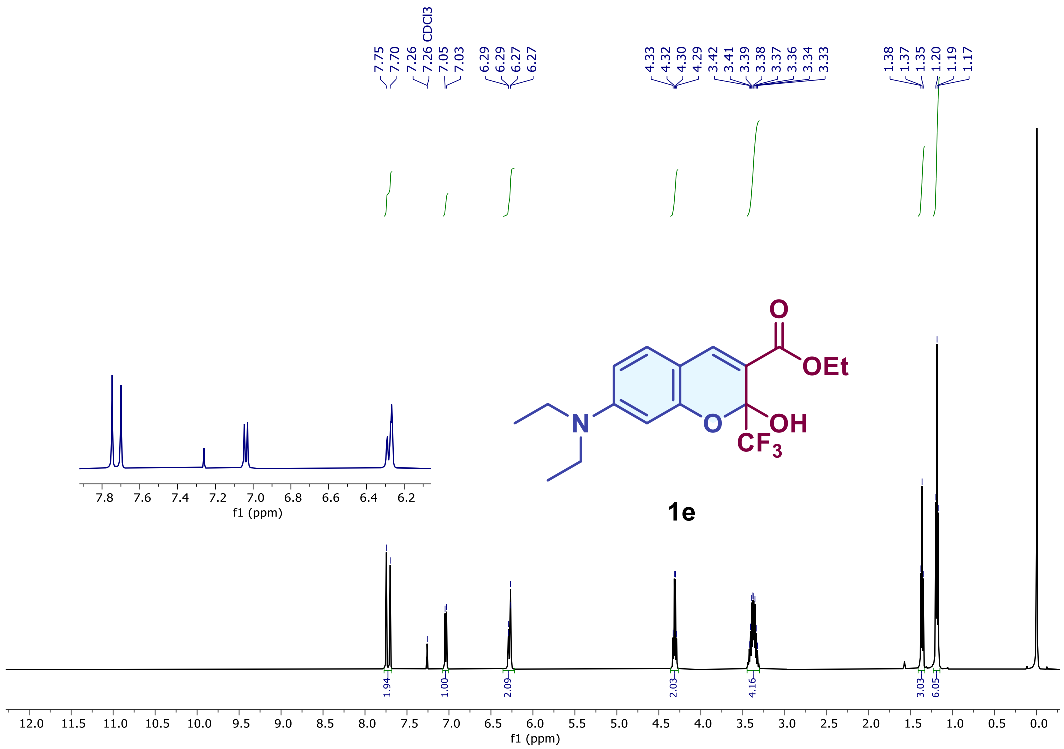


Figure S24. [1]H NMR (CDCl3, 500 MHz) spectra for compound **1e**.

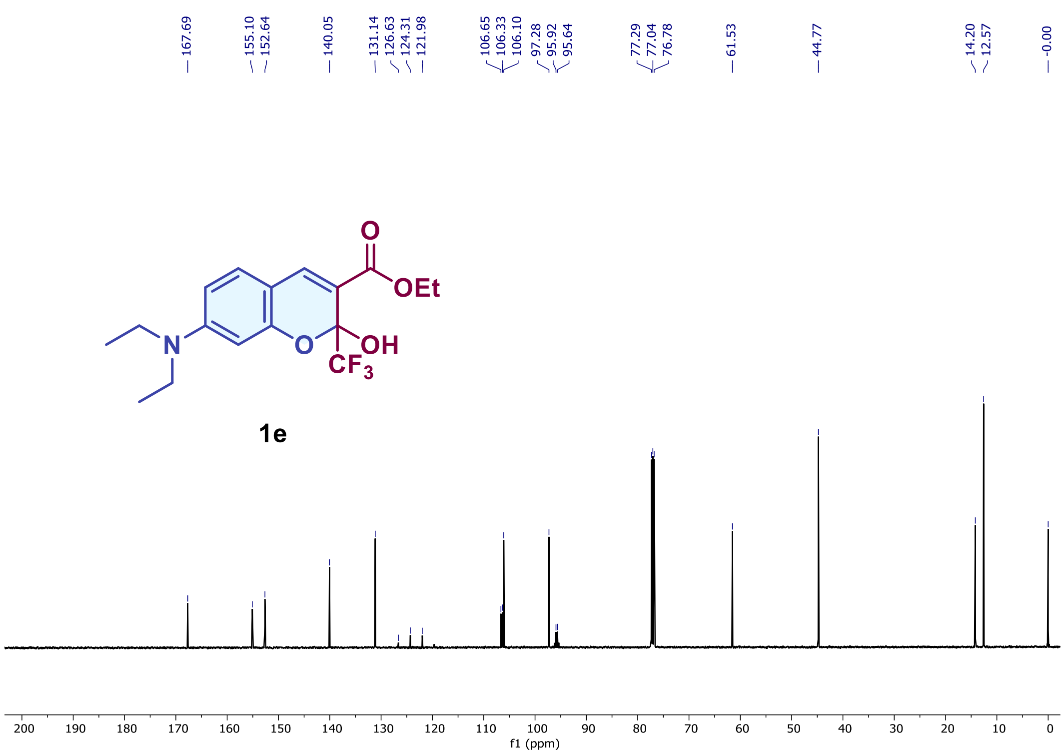


Figure S25.[13]C NMR (CDCl3, 125 MHz) spectra for compound **1e**.

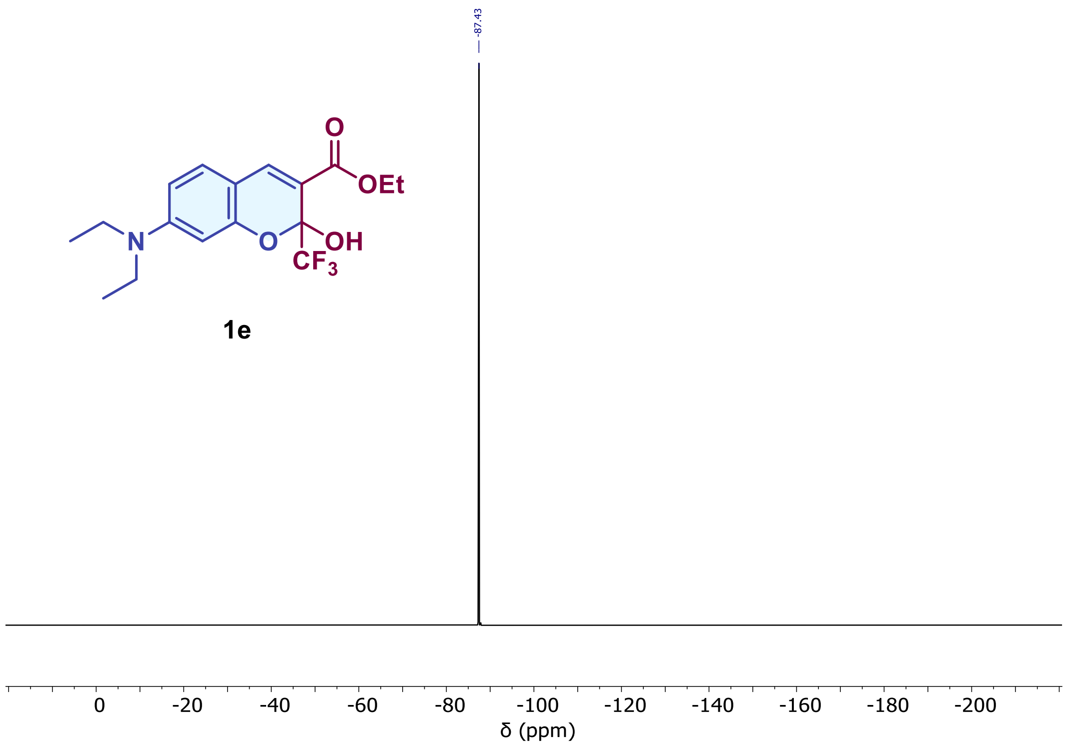


Figure S26. [19]F NMR (CDCl3, 470 MHz) spectra for compound**1e**.

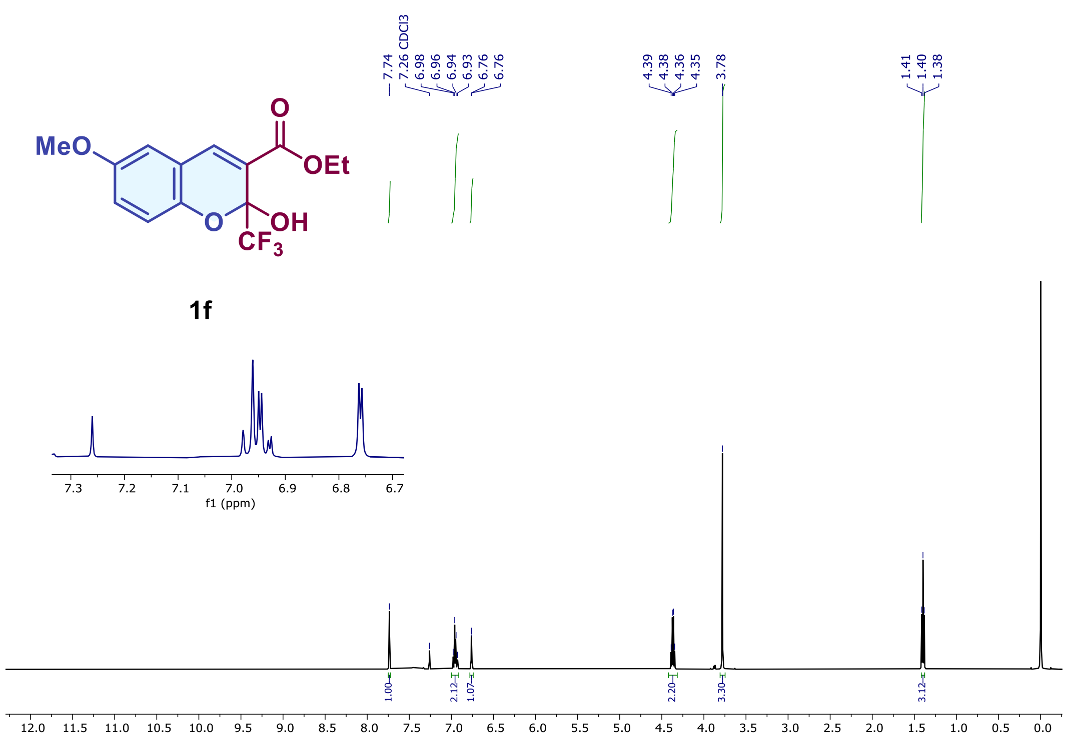


Figure S27. [1]H NMR (CDCl3, 500 MHz) spectra for compound **1f**.

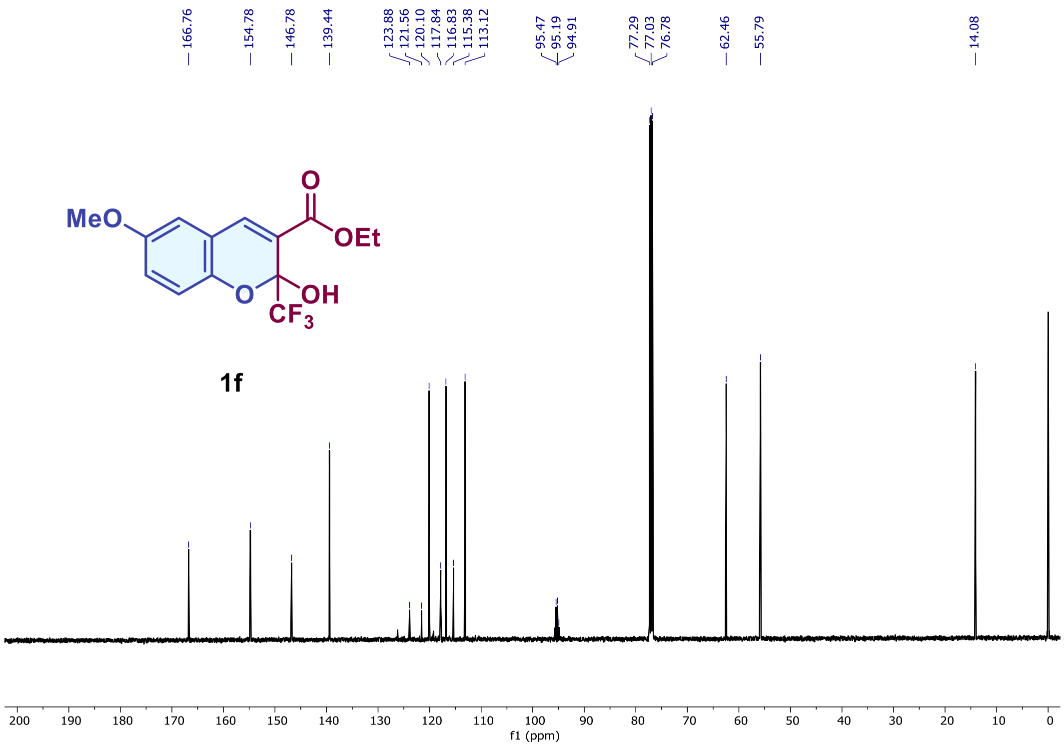


Figure S28.[13]C NMR (CDCl3, 125 MHz) spectra for compound **1f**.

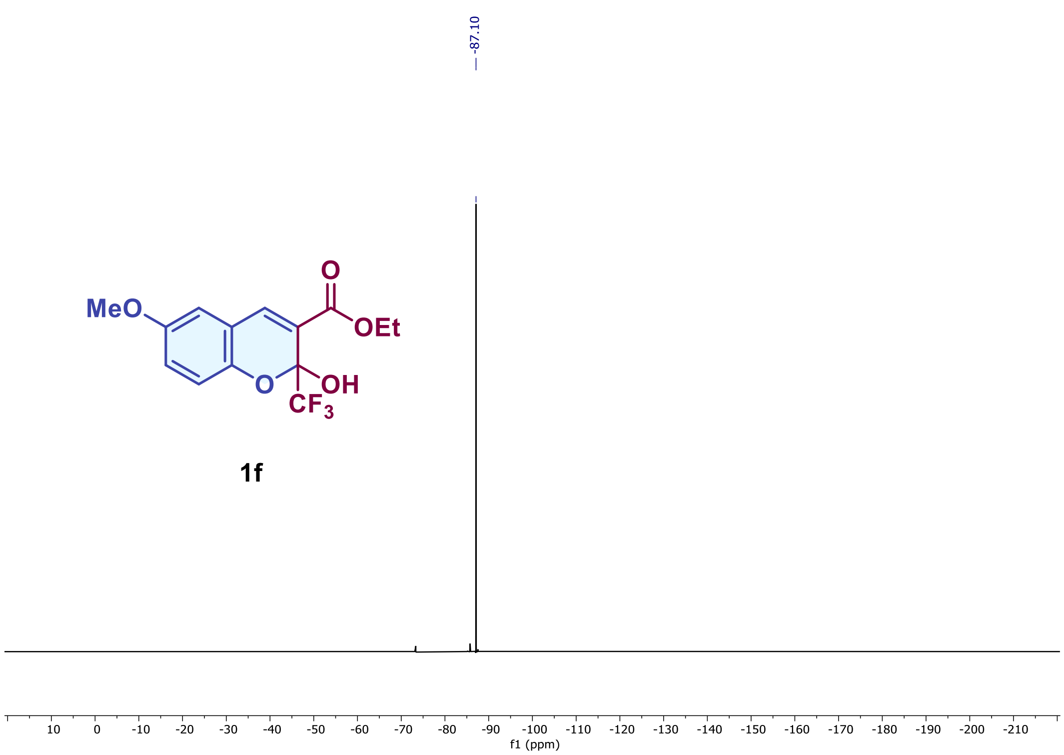


Figure S29. [19]F NMR (CDCl3, 470 MHz) spectra for compound **1f**.

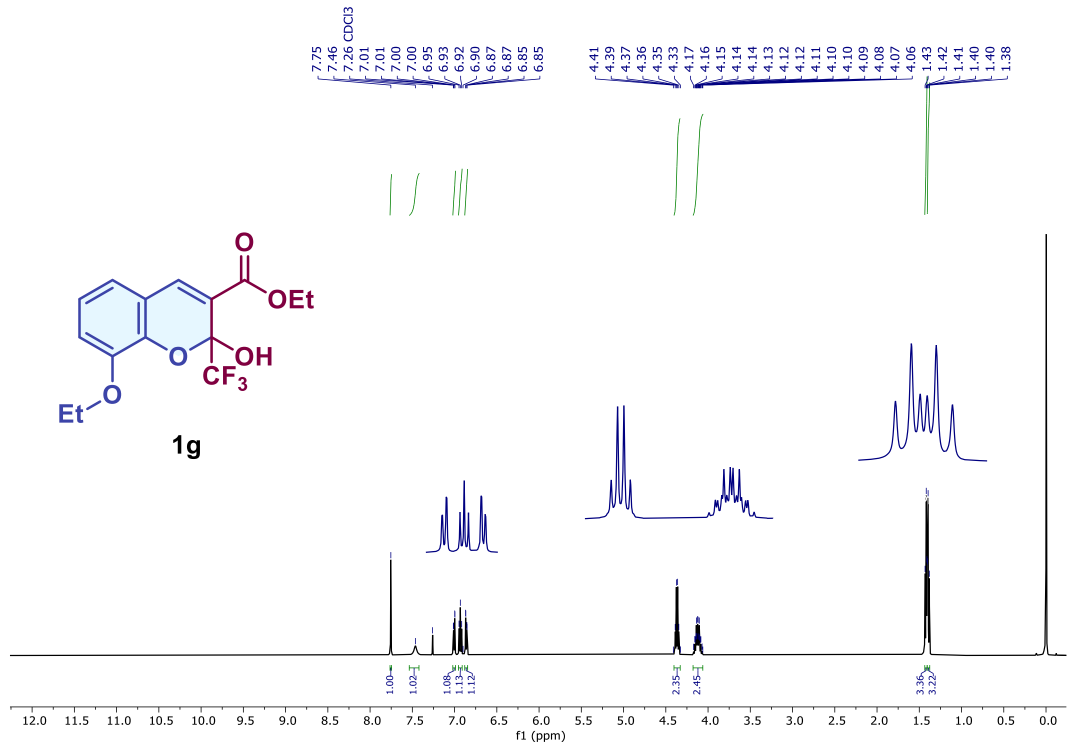


Figure S30. ¹H NMR ($CDCl_3$, 500 MHz) spectra for compound **1g**.

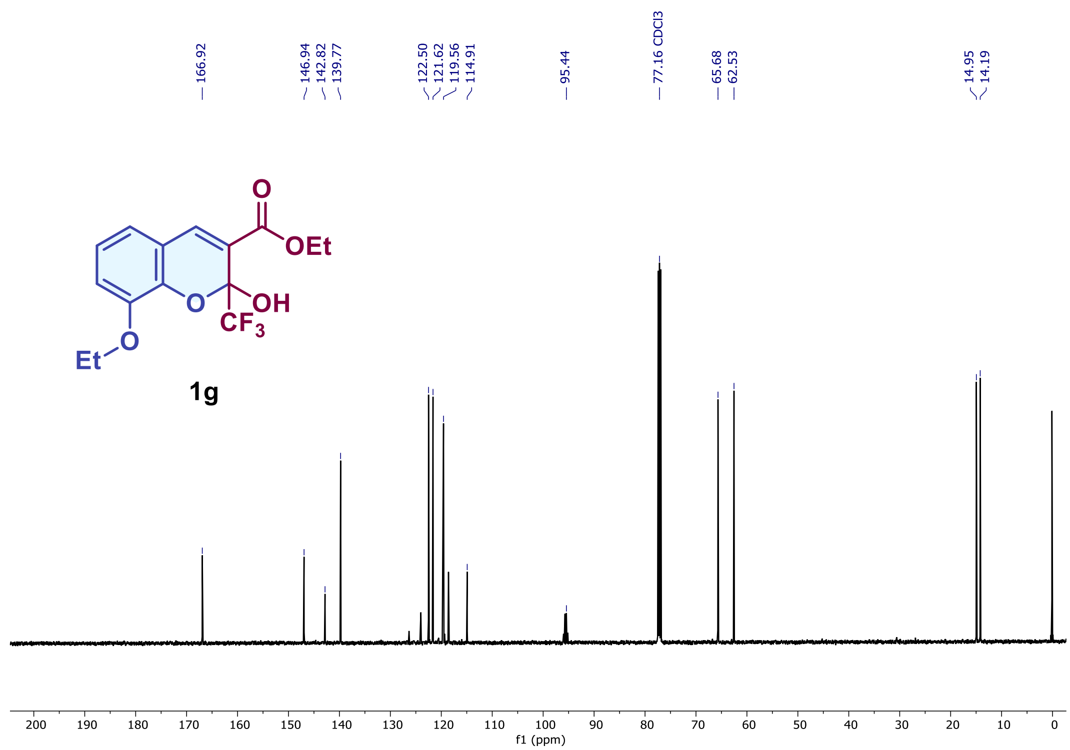


Figure S31. ¹³C NMR ($CDCl_3$, 125 MHz) spectra for 2H-chromene **1g**.

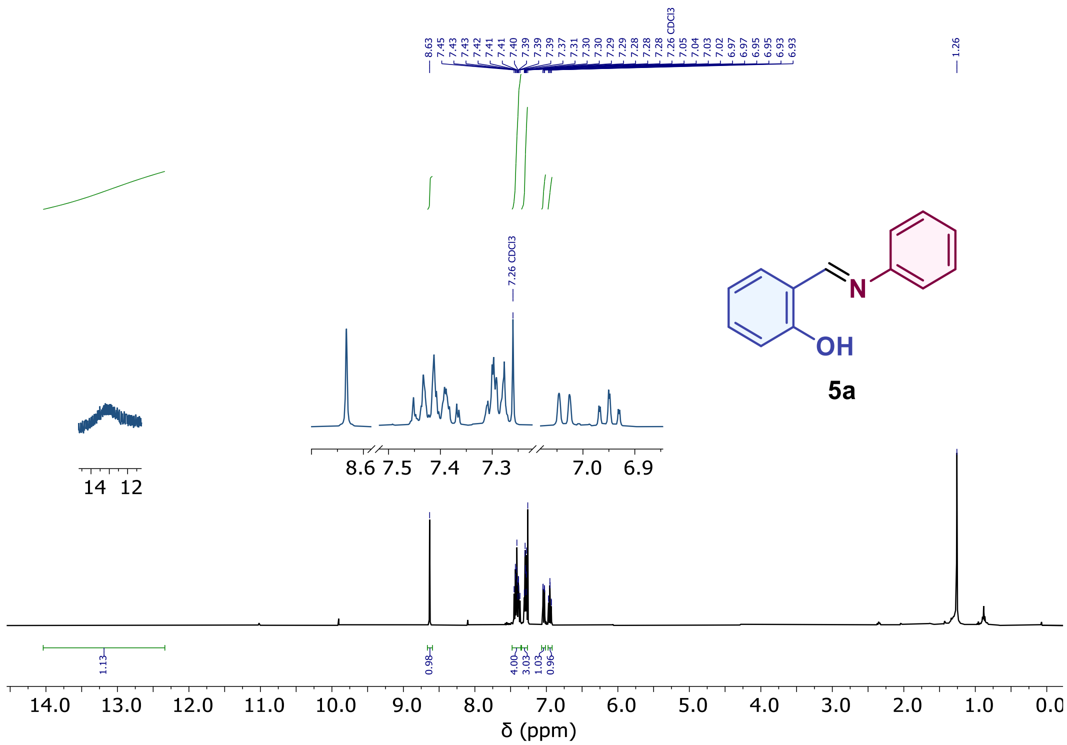


Figure S32. ^{1}H NMR (CDCl3, 500 MHz) spectra for compound **5a**.

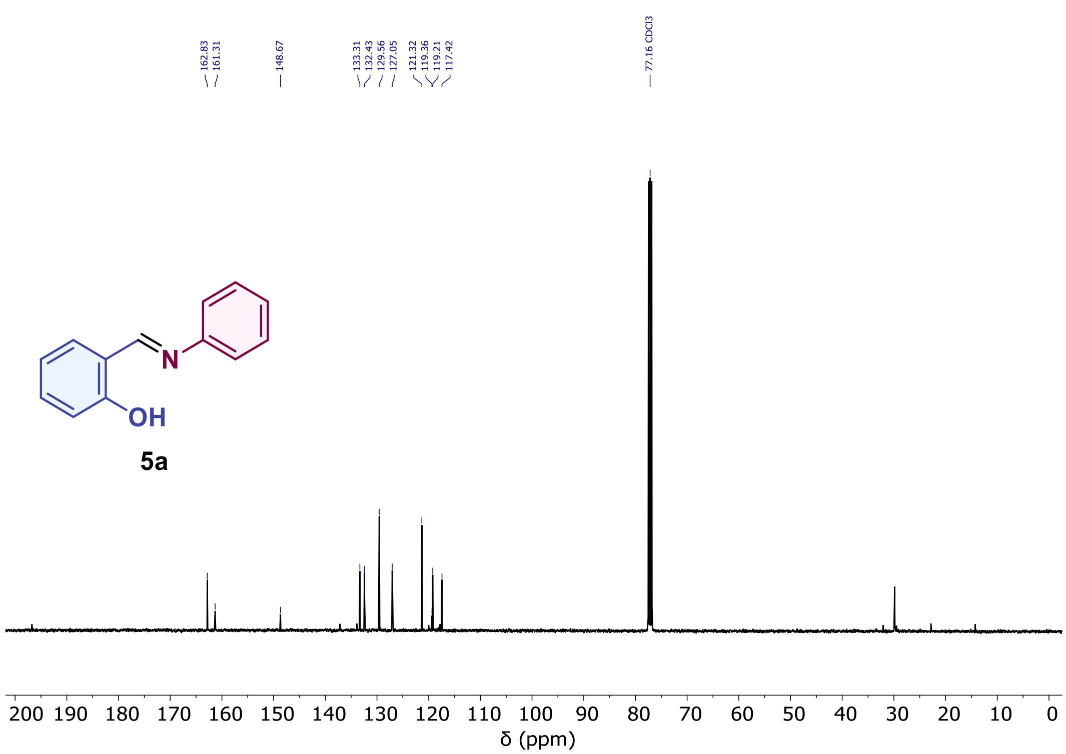


Figure S33.^{13}C NMR ($CDCl_3$, 125 MHz) spectra for compound **5a**.

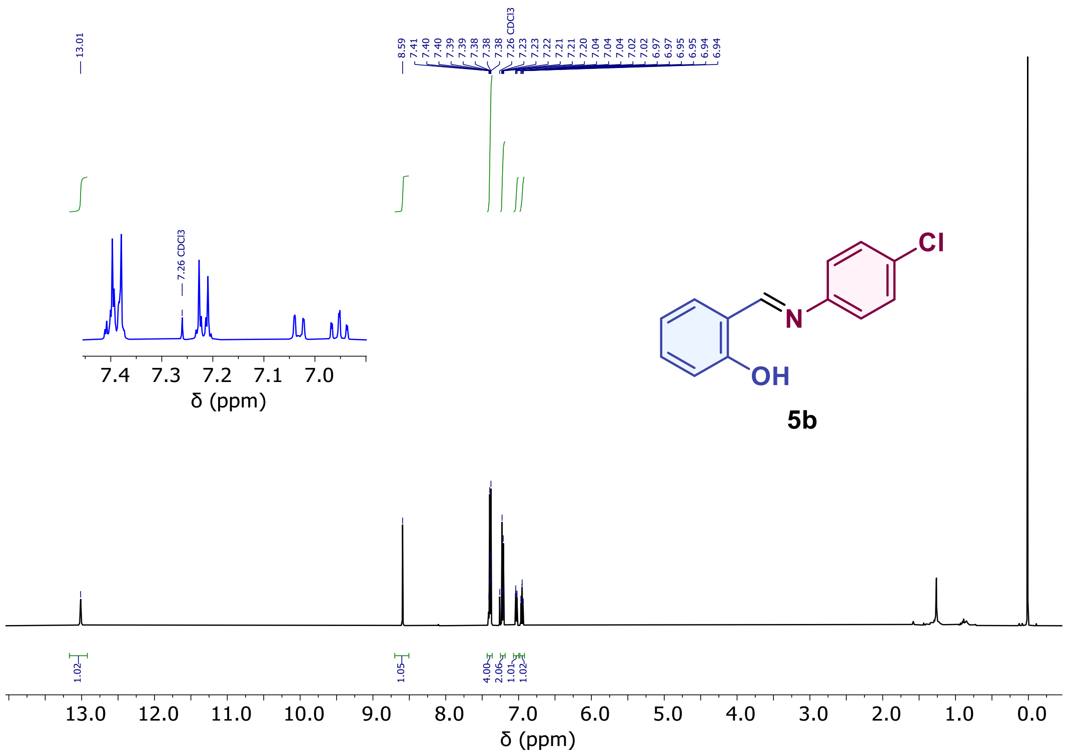


Figure S34. ^{1}H NMR ($CDCl_3$, 500 MHz) spectra for compound **5b**.

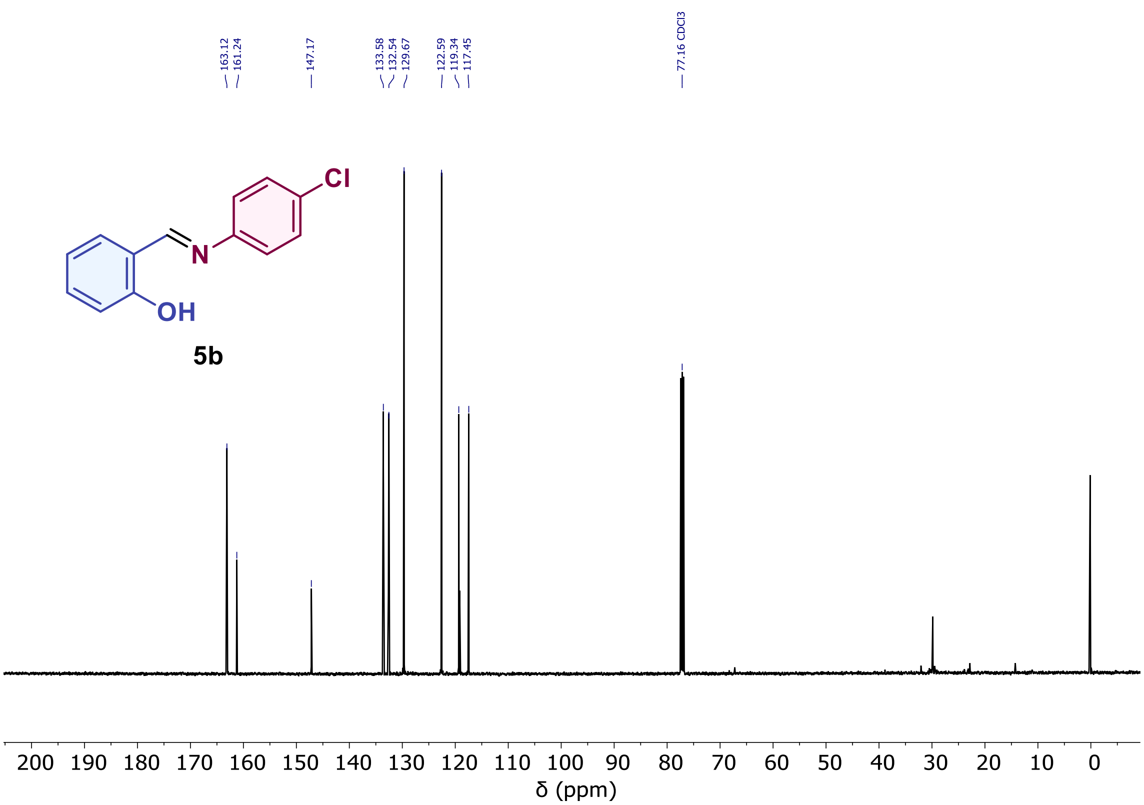


Figure S35. ^{13}C NMR ($CDCl_3$, 125 MHz) spectra for compound **5b**.

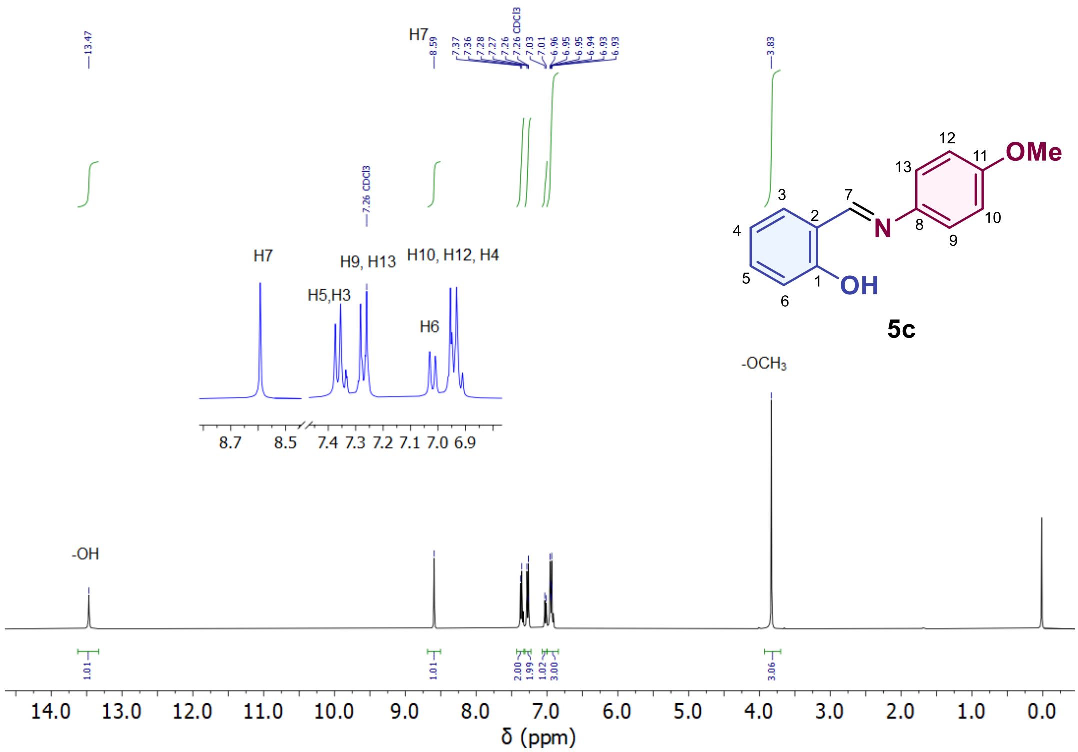


Figure S36. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra for compound **5c**.

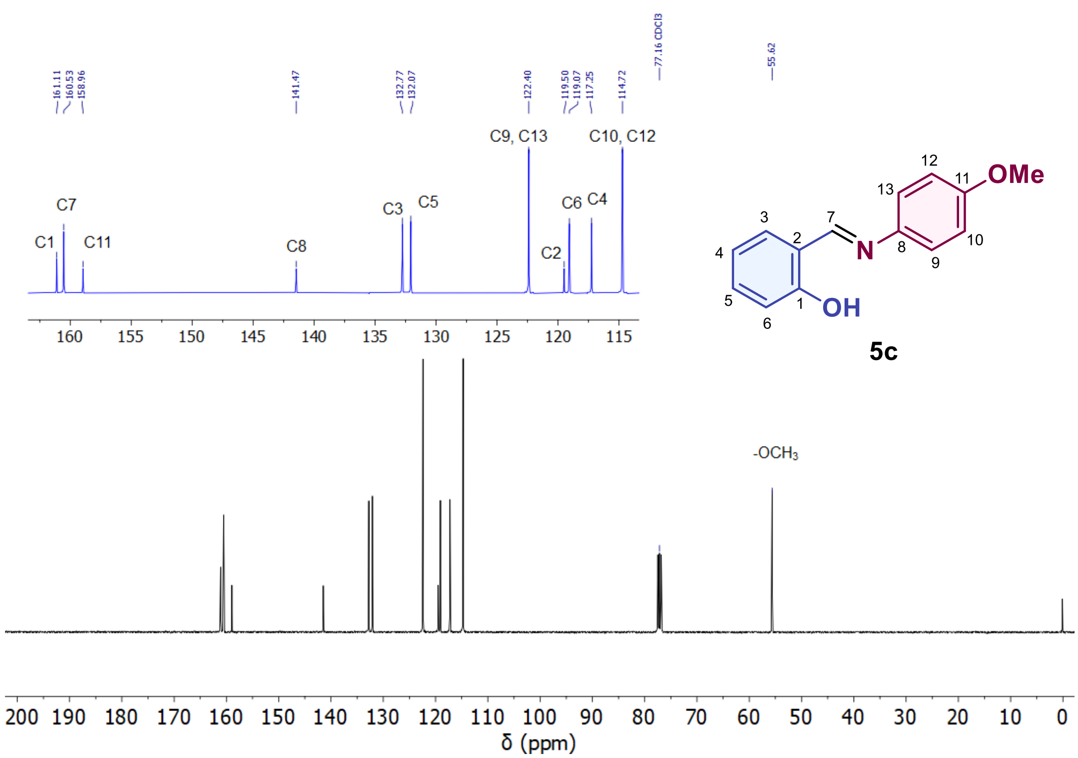


Figure S37. ^{13}C NMR ($CDCl_3$, 100 MHz) spectra for compound **5c**.

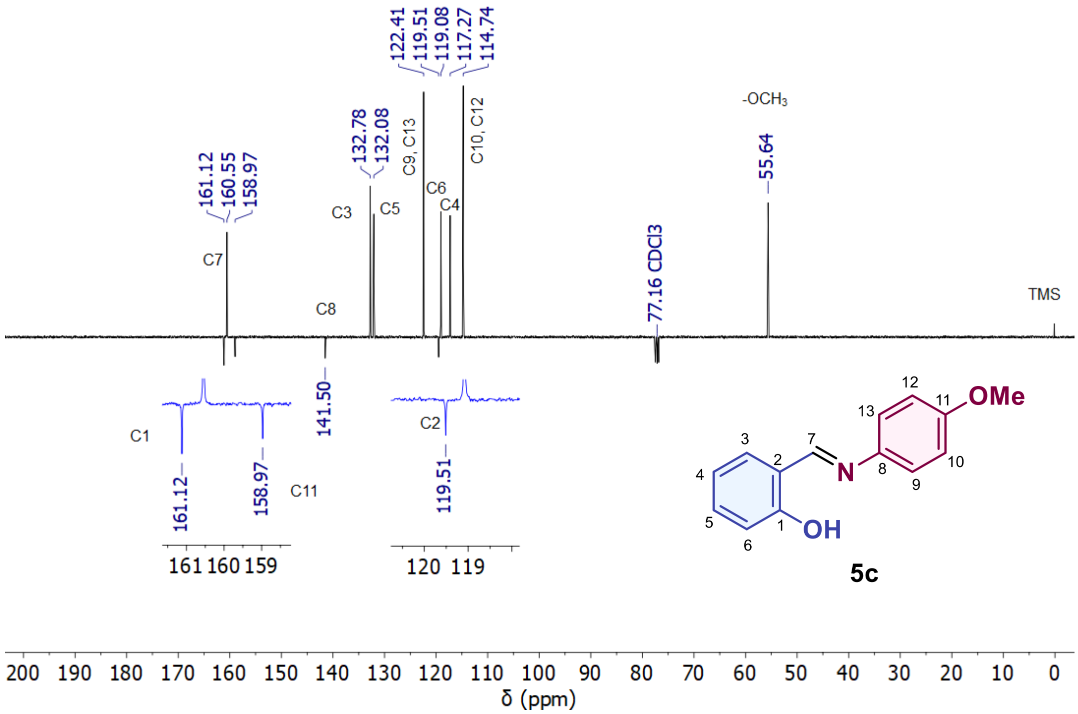


Figure S38. APT ($CDCl_3$, 100 MHz) spectra for compound **5c**.

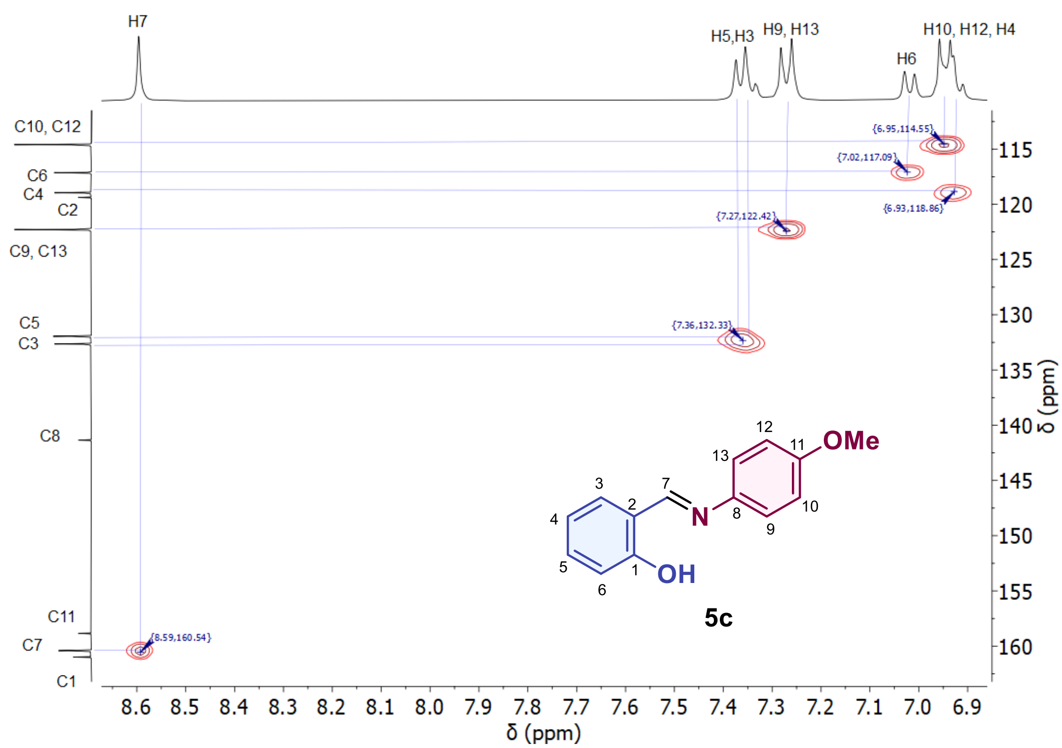


Figure S39. HSQC ($CDCl_3$, 400 MHz) spectra for compound **5c**.

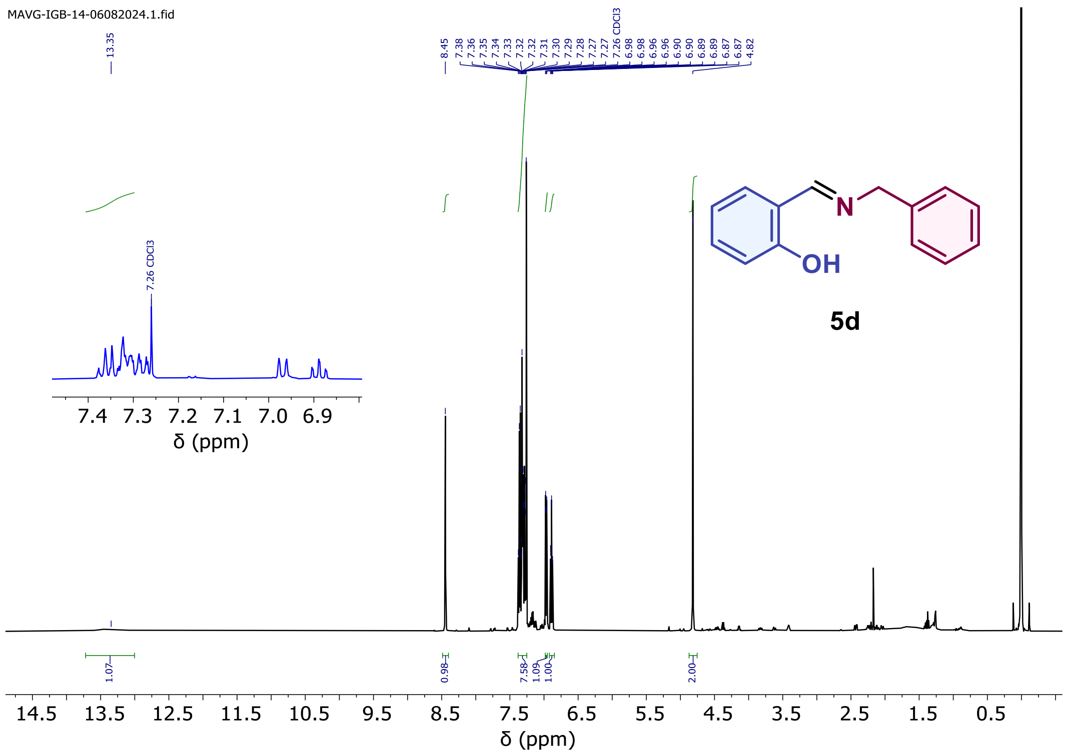


Figure S40. ^{1}H NMR ($CDCl_3$, 500 MHz) spectra for compound **5d**.

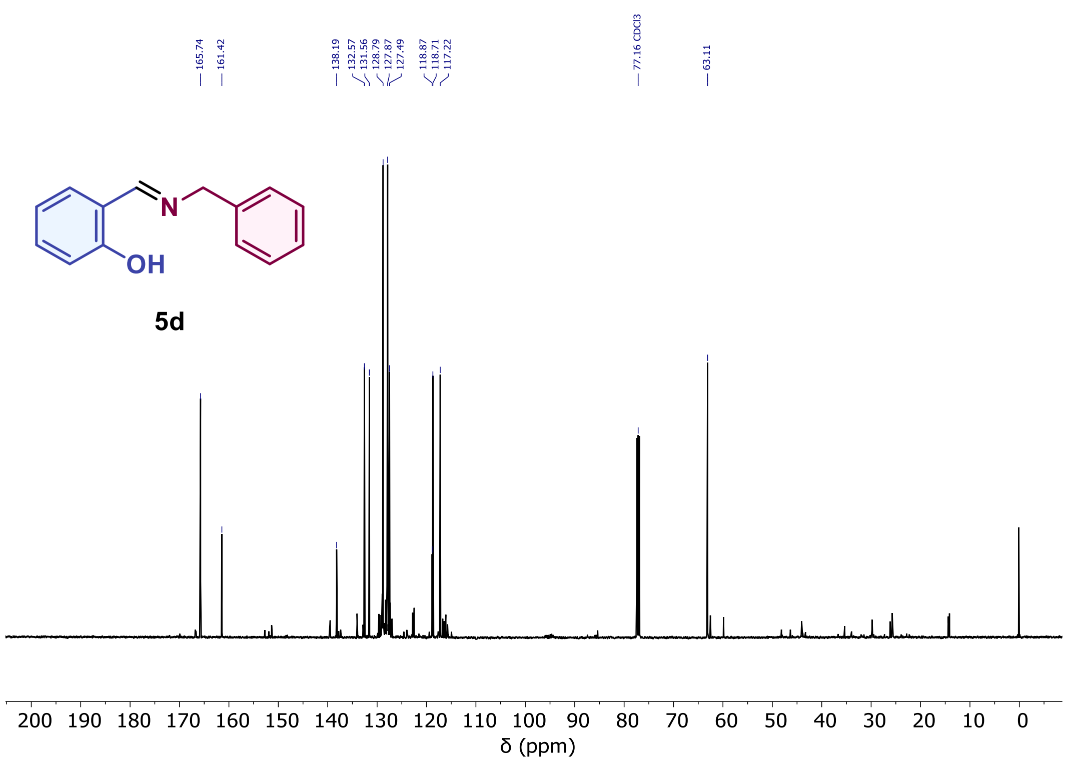


Figure S41. ^{13}C NMR ($CDCl_3$, 125 MHz) spectra for compound **5d**.

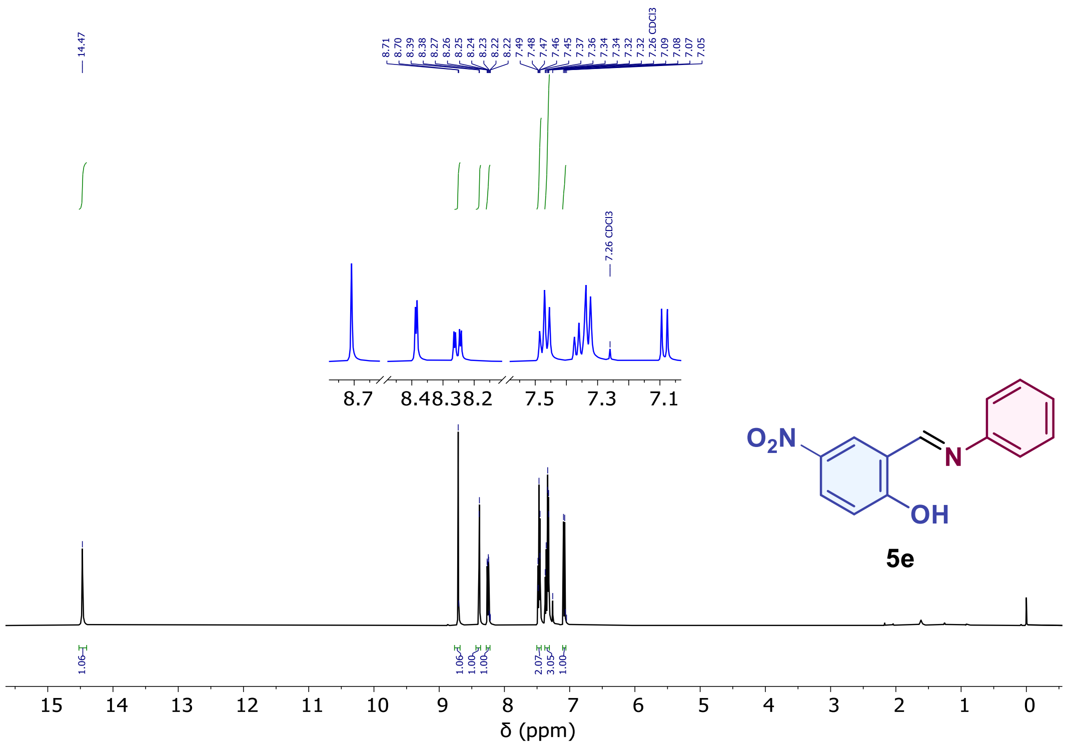


Figure S42. ^{1}H NMR ($CDCl_3$, 500 MHz) spectra for compound **5e**.

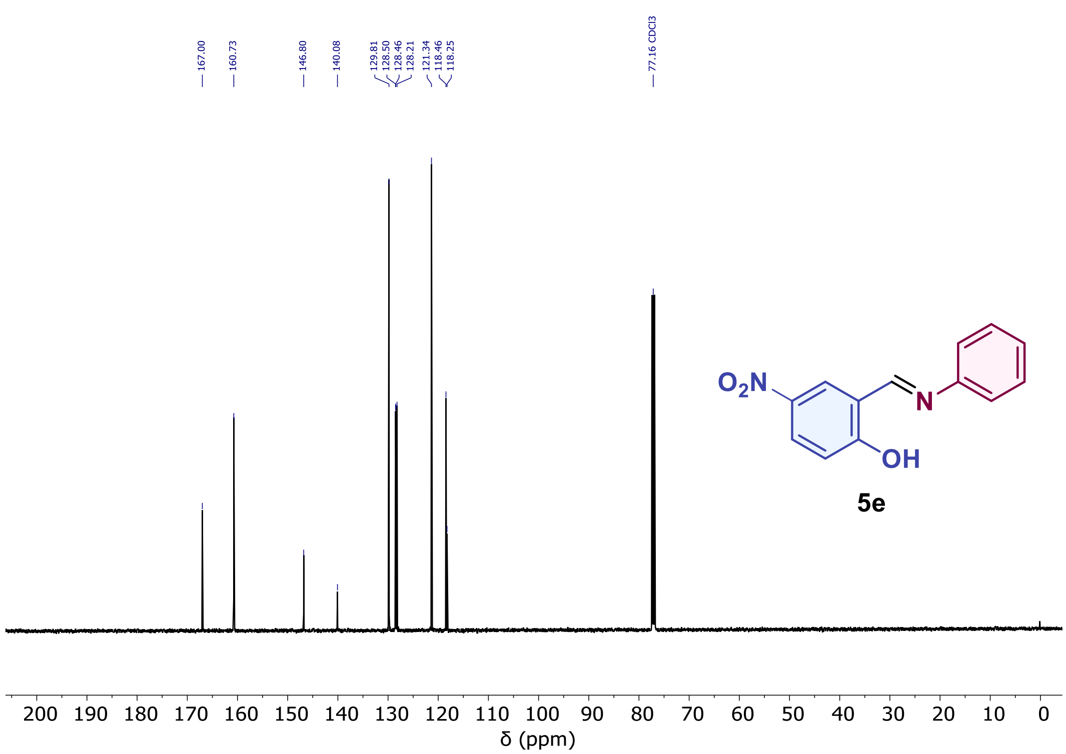


Figure S43. ^{13}C NMR ($CDCl_3$, 125 MHz) spectra for compound **5e**.

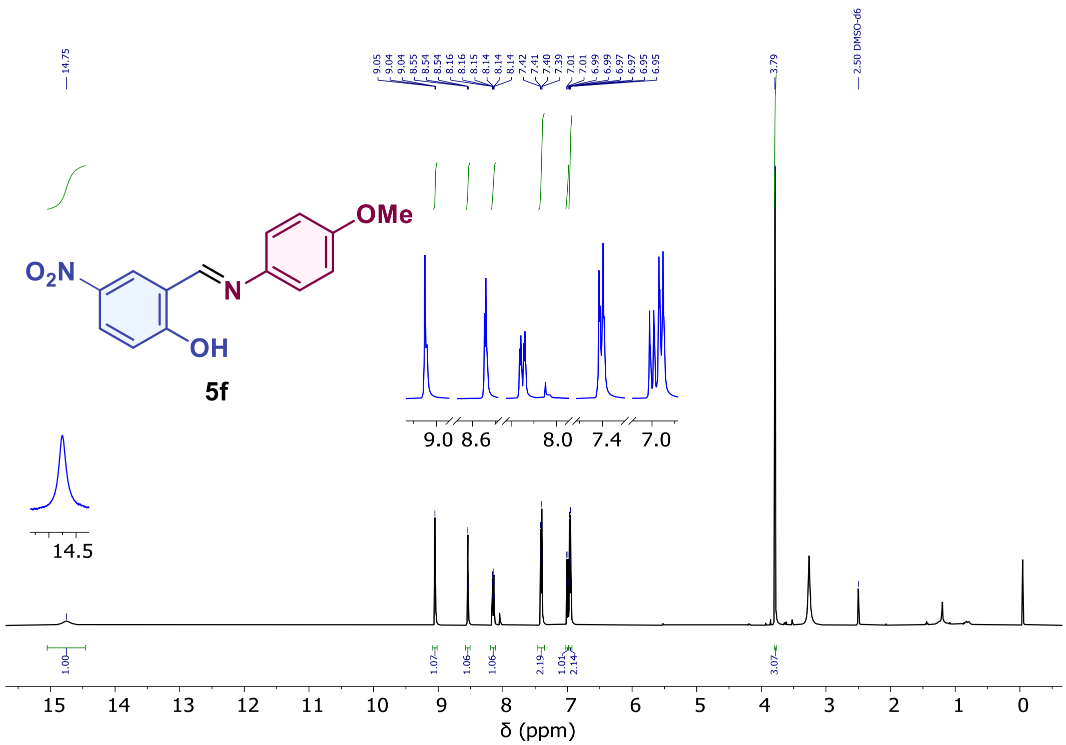


Figure S44. ^{1}H NMR (DMSO-d$_6$, 500 MHz) spectra for compound **5f**.

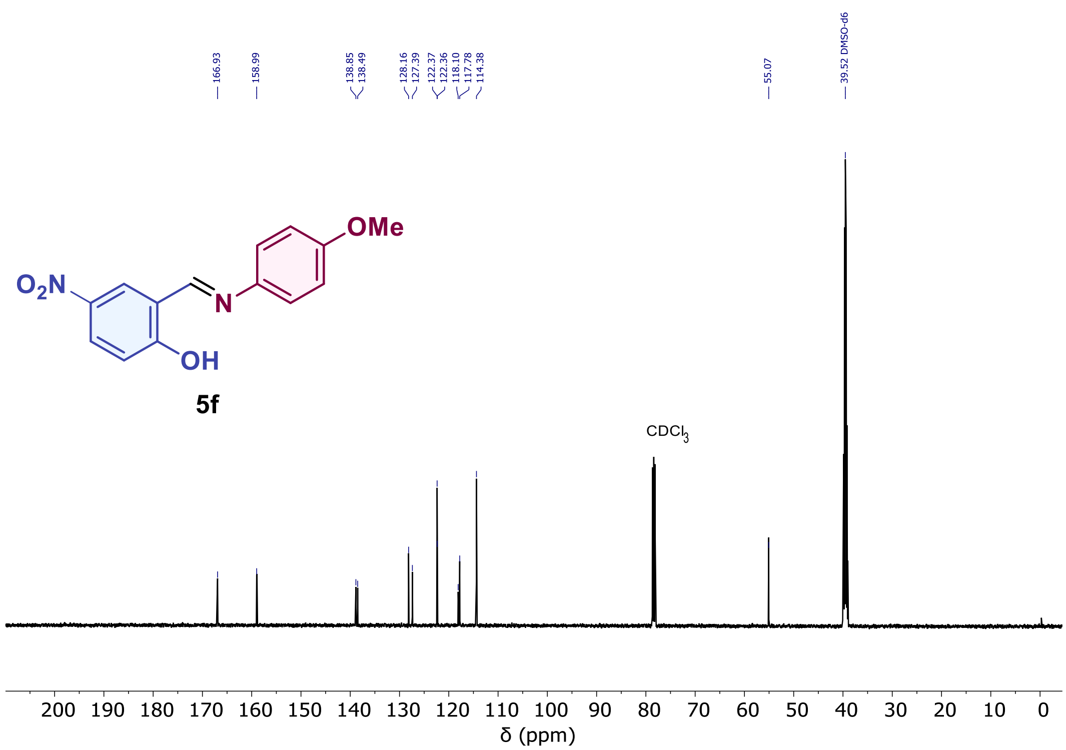


Figure S45. ^{13}C NMR (DMSO-d$_6$, 125 MHz) spectra for compound **5f**.

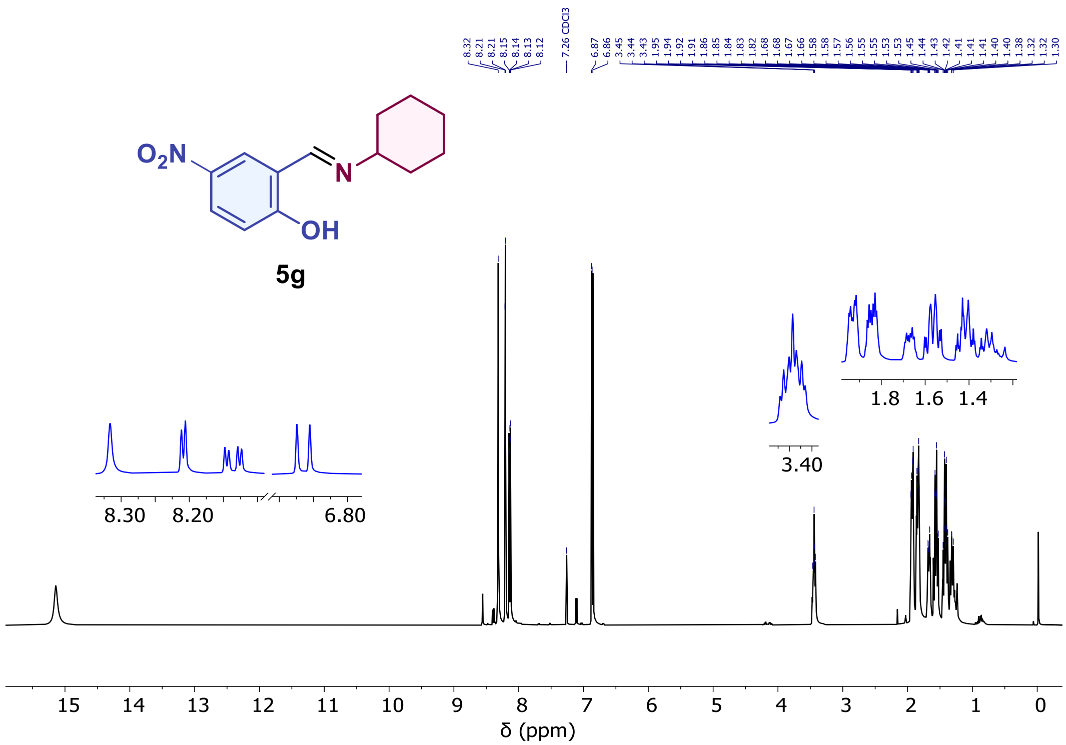


Figure S46. ^{1}H NMR ($CDCl_3$, 500 MHz) spectra for compound **5g**.

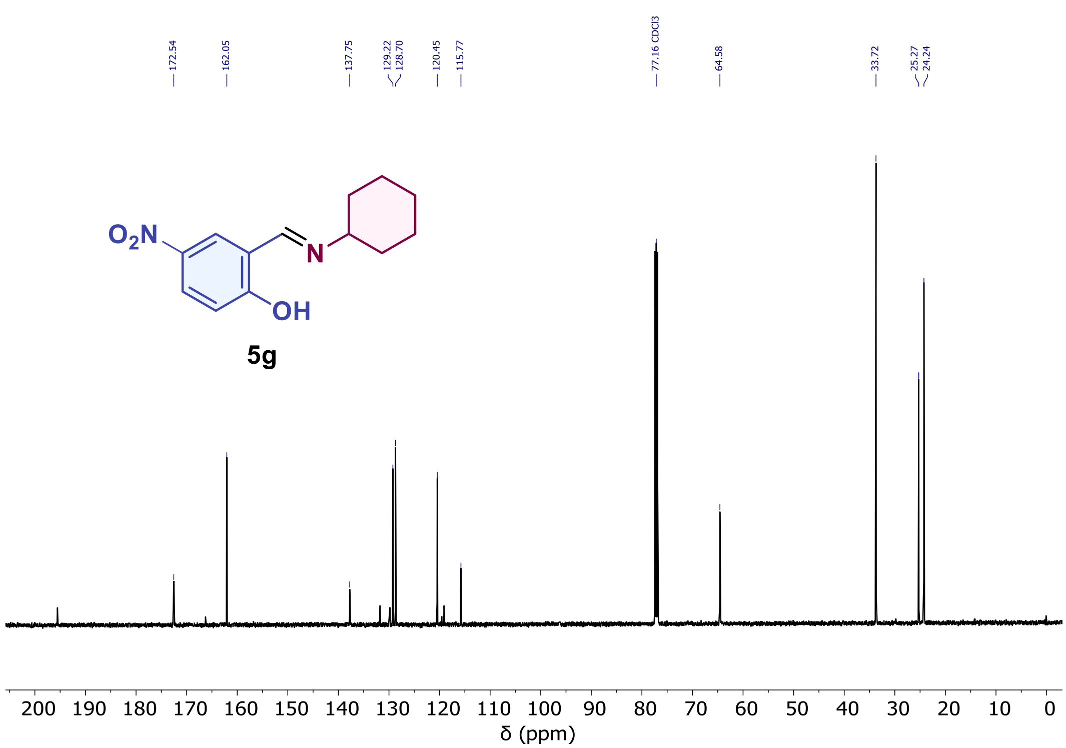


Figure S47. ^{13}C NMR ($CDCl_3$, 125 MHz) spectra for compound **5g**.

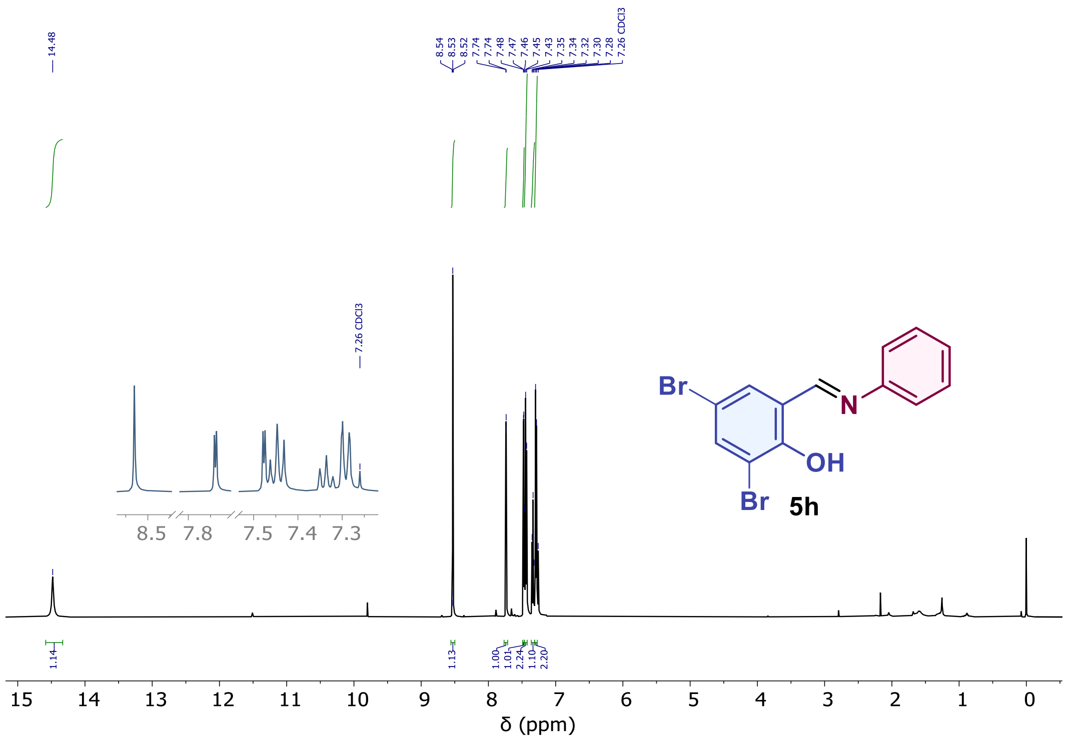


Figure S48. ^{1}H NMR ($CDCl_3$, 500 MHz) spectra for compound **5h**.

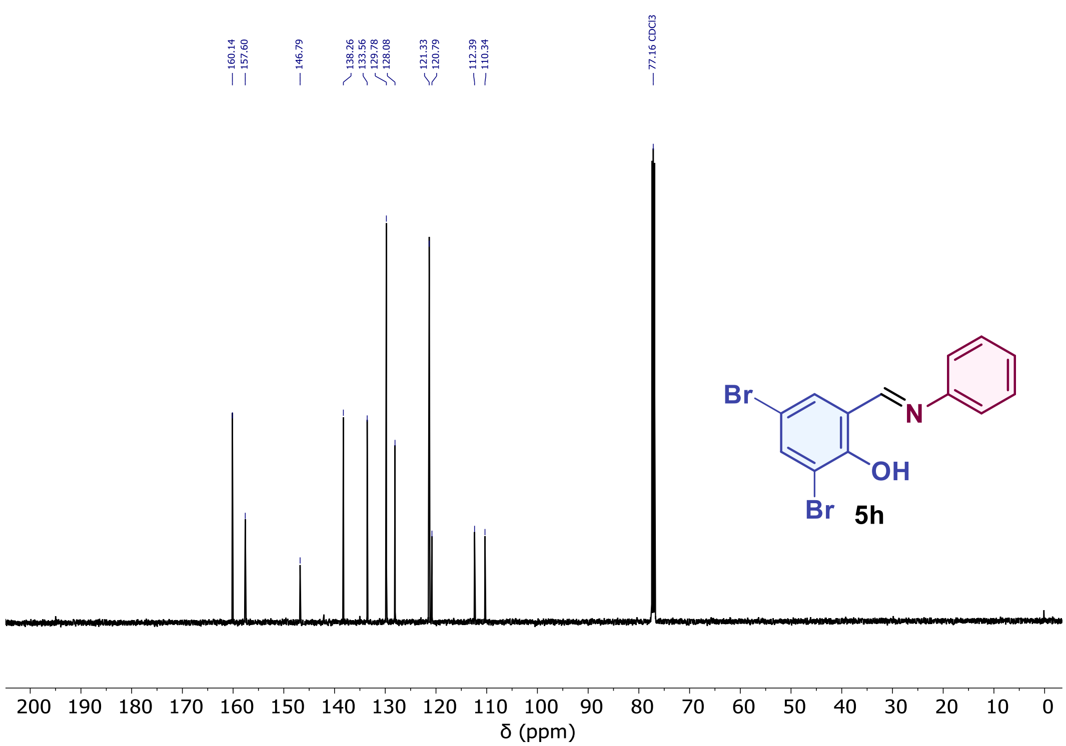


Figure S49. ^{13}C NMR ($CDCl_3$, 125 MHz) spectra for compound **5h**.

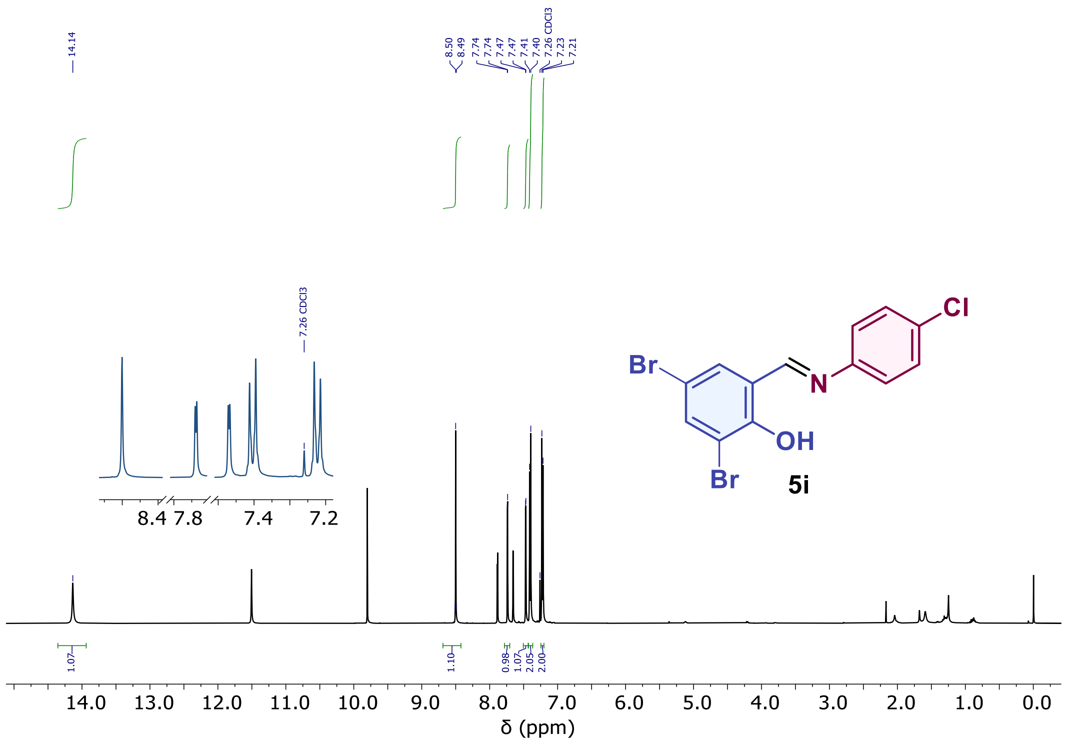


Figure S50. [1]H NMR ($CDCl_3$, 500 MHz) spectra for compound **5i**.

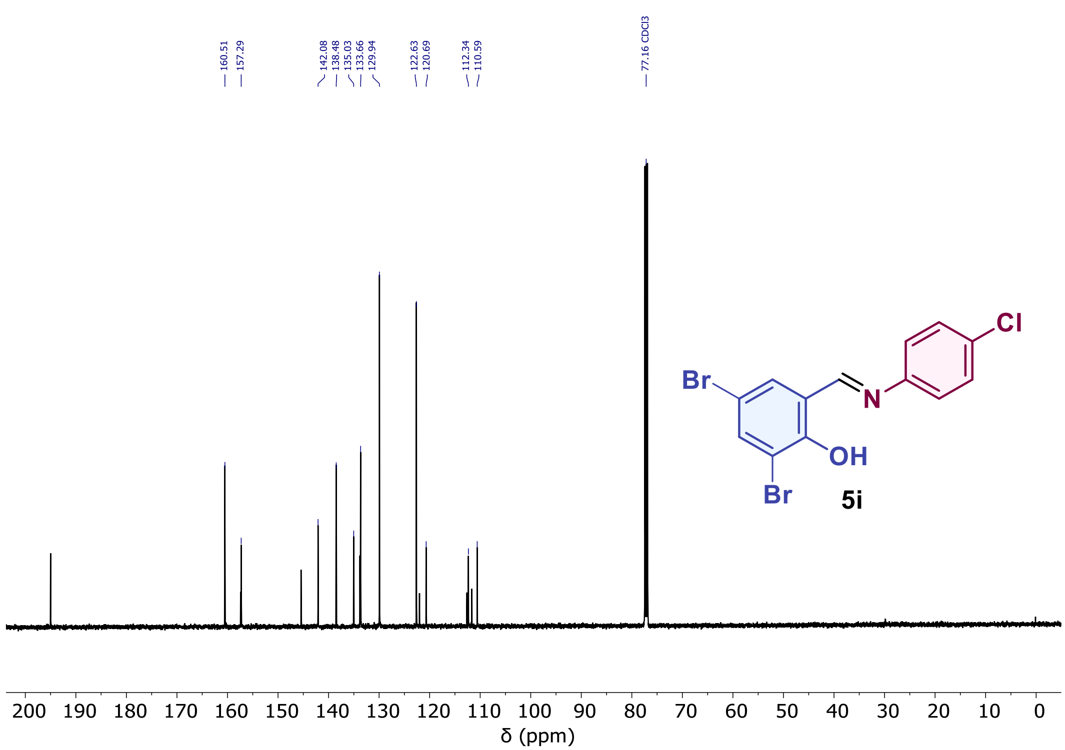


Figure S51. [13]C NMR ($CDCl_3$, 125 MHz) spectra for 2H-chromene **5i**.

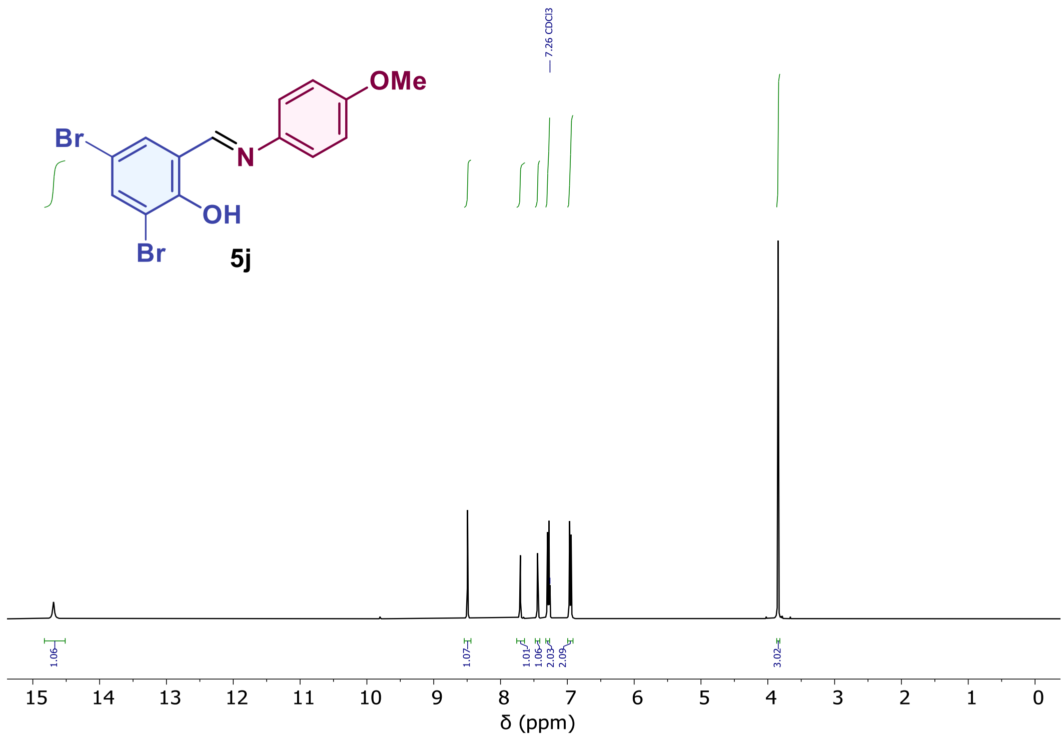


Figure S52. ^{1}H NMR ($CDCl_3$, 500 MHz) spectra for compound **5j**.

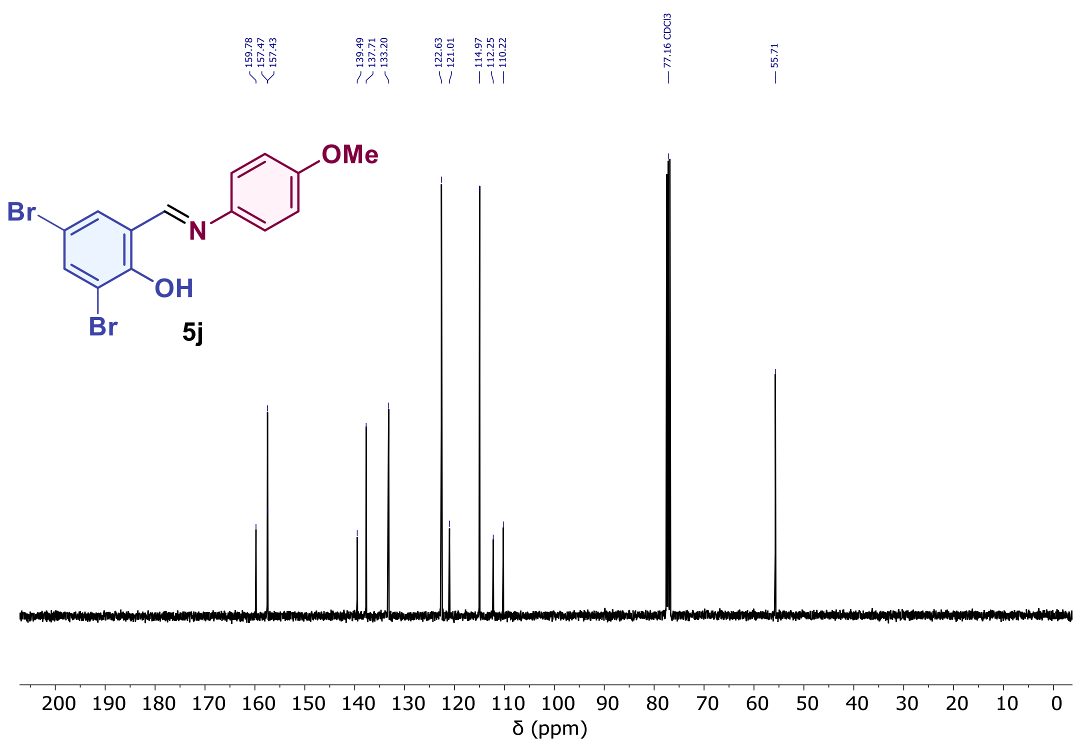


Figure S53. ^{13}C NMR ($CDCl_3$, 125 MHz) spectra for compound **5j**.

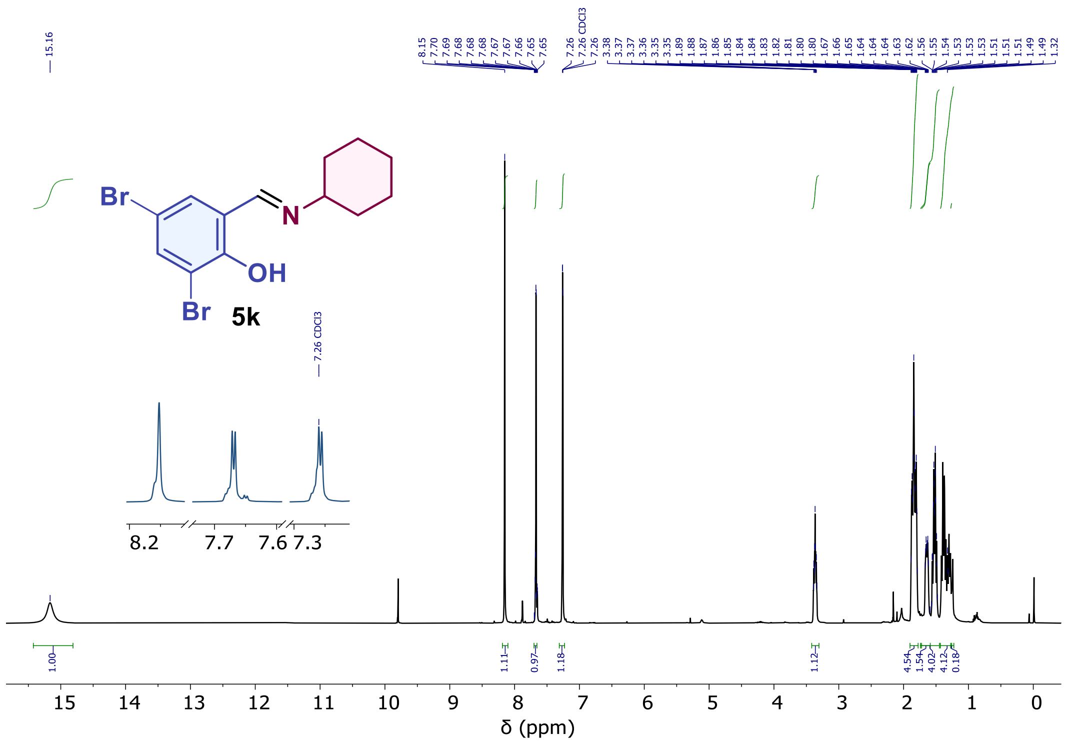


Figure S54. ^{1}H NMR ($CDCl_3$, 500 MHz) spectra for compound **5k**.

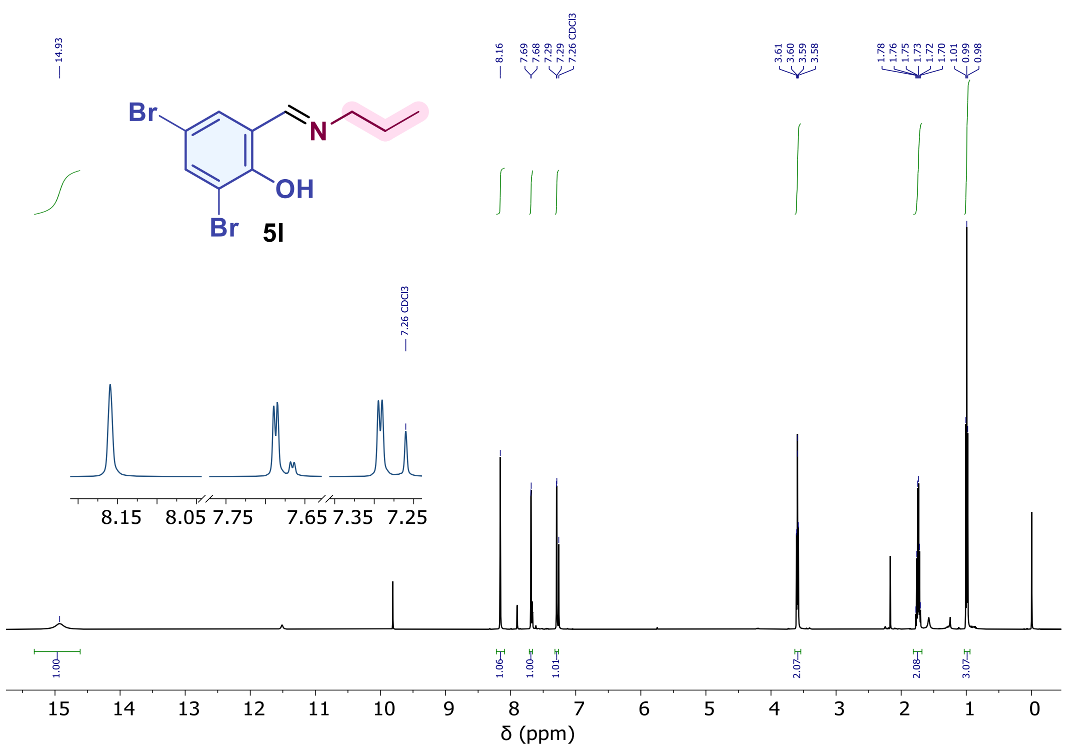


Figure S55. ^{1}H NMR ($CDCl_3$, 500 MHz) spectra for compound **5l**.

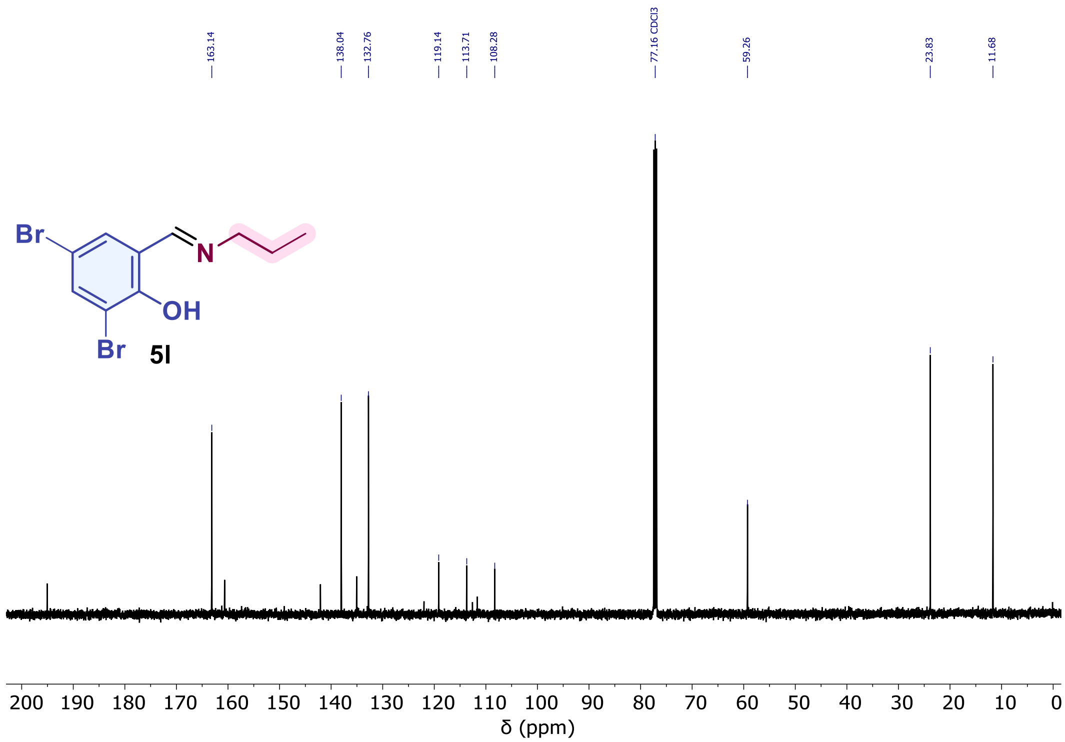


Figure S56. ^{13}C NMR ($CDCl_3$, 125 MHz) spectra for compound **5l**.

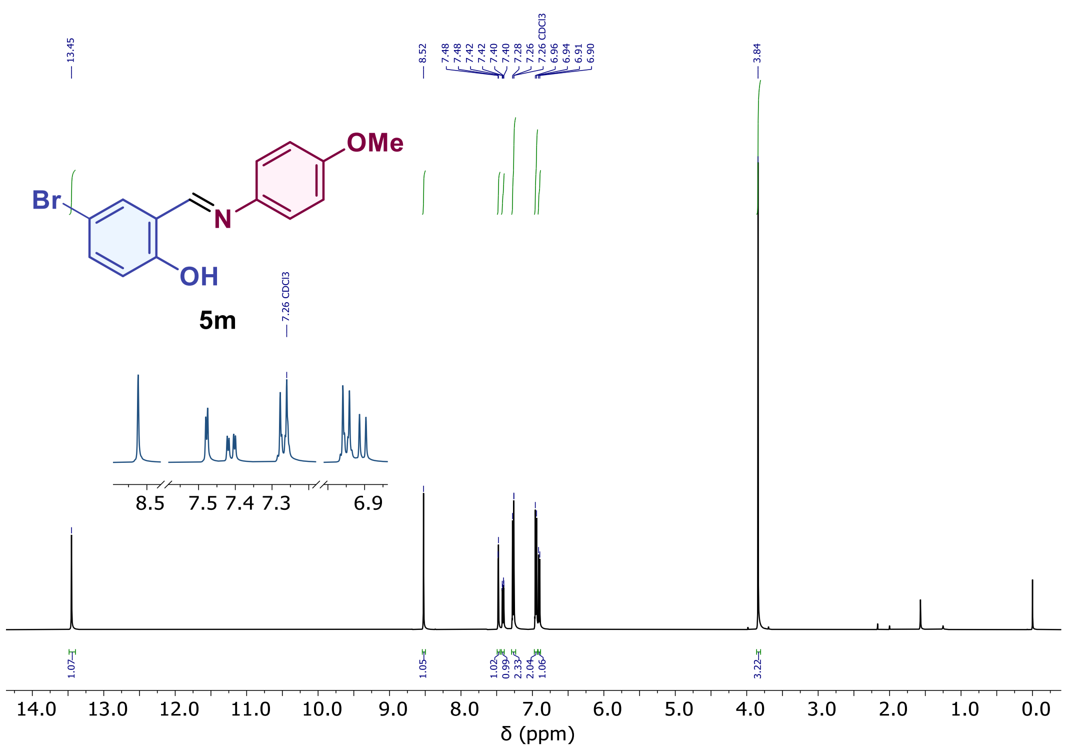


Figure S57. ^{1}H NMR ($CDCl_3$, 500 MHz) spectra for compound **5m**.

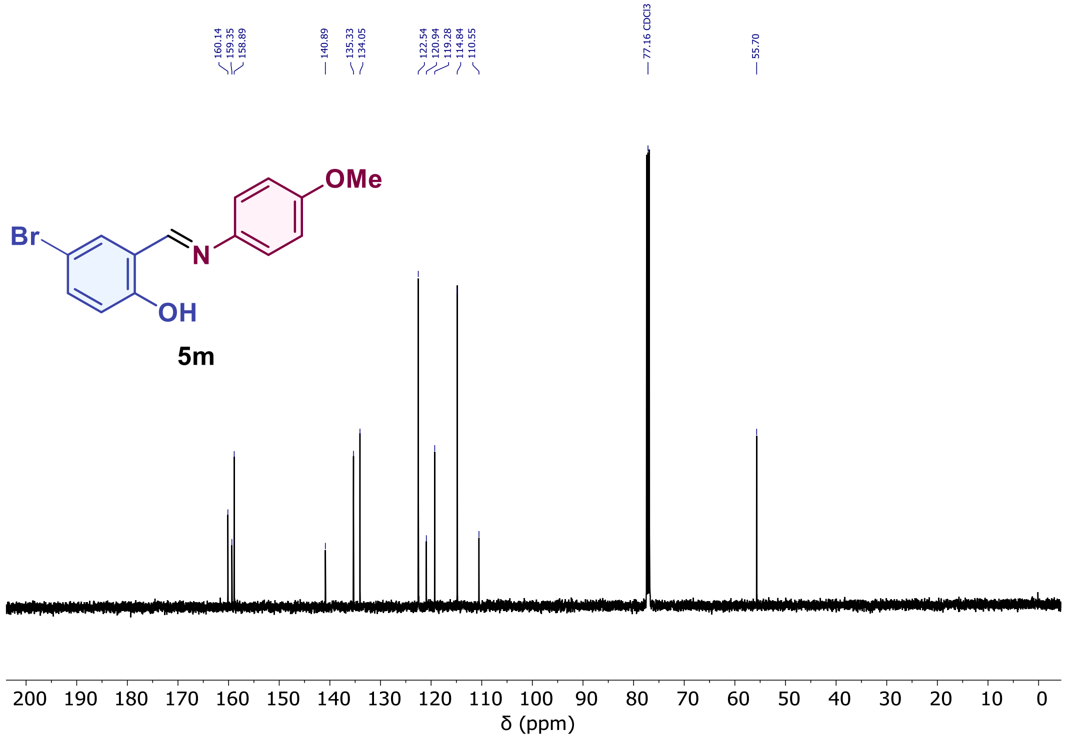


Figure S58. ^{13}C NMR ($CDCl_3$, 125 MHz) spectra for compound **5m**.

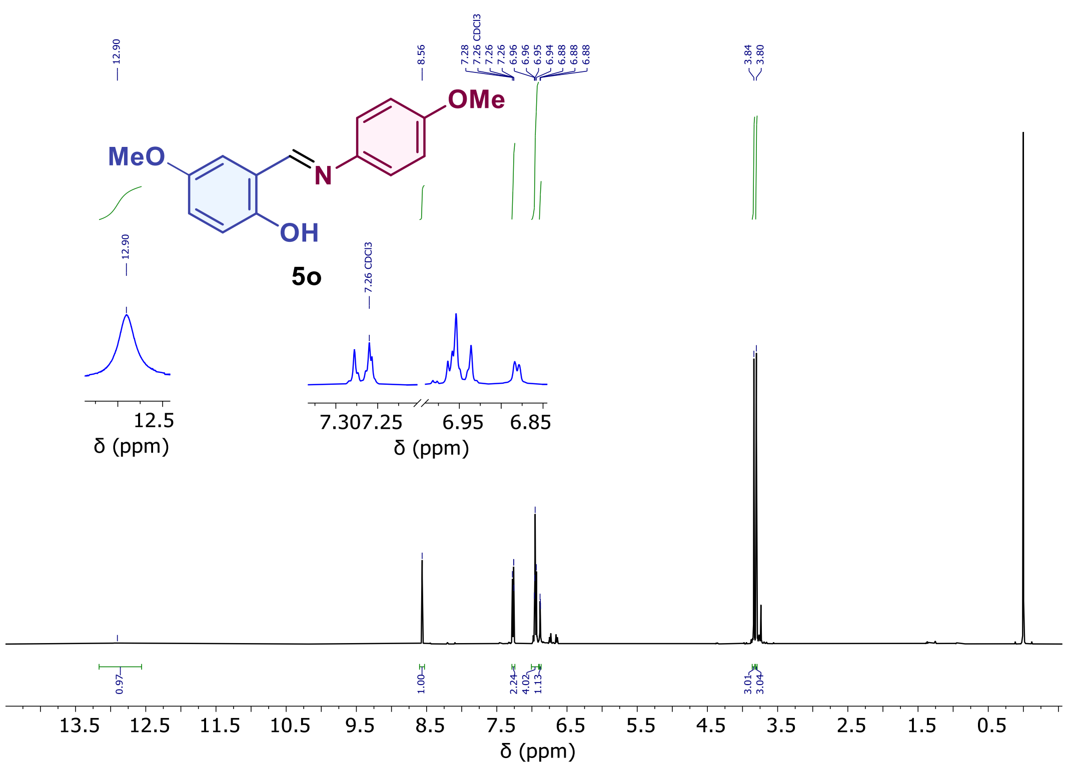


Figure S59. ^{1}H NMR ($CDCl_3$, 500 MHz) spectra for compound **5o**.

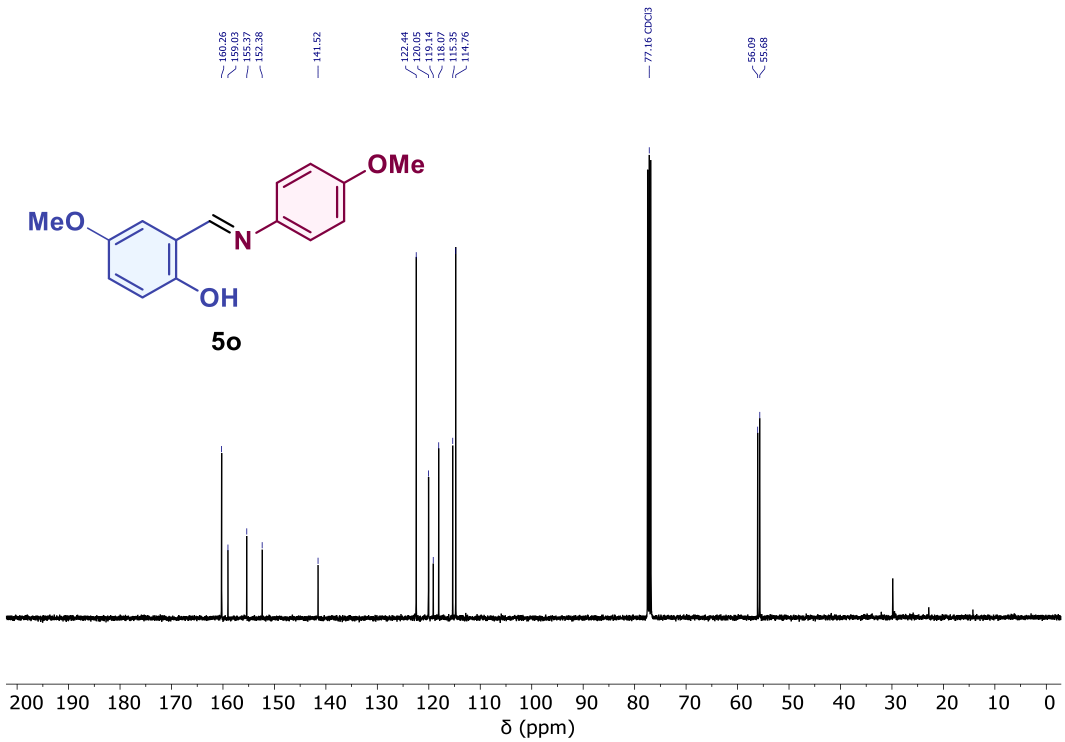


Figure S60. ^{13}C NMR (CDCl$_3$, 125 MHz) spectra for compound **5o**.

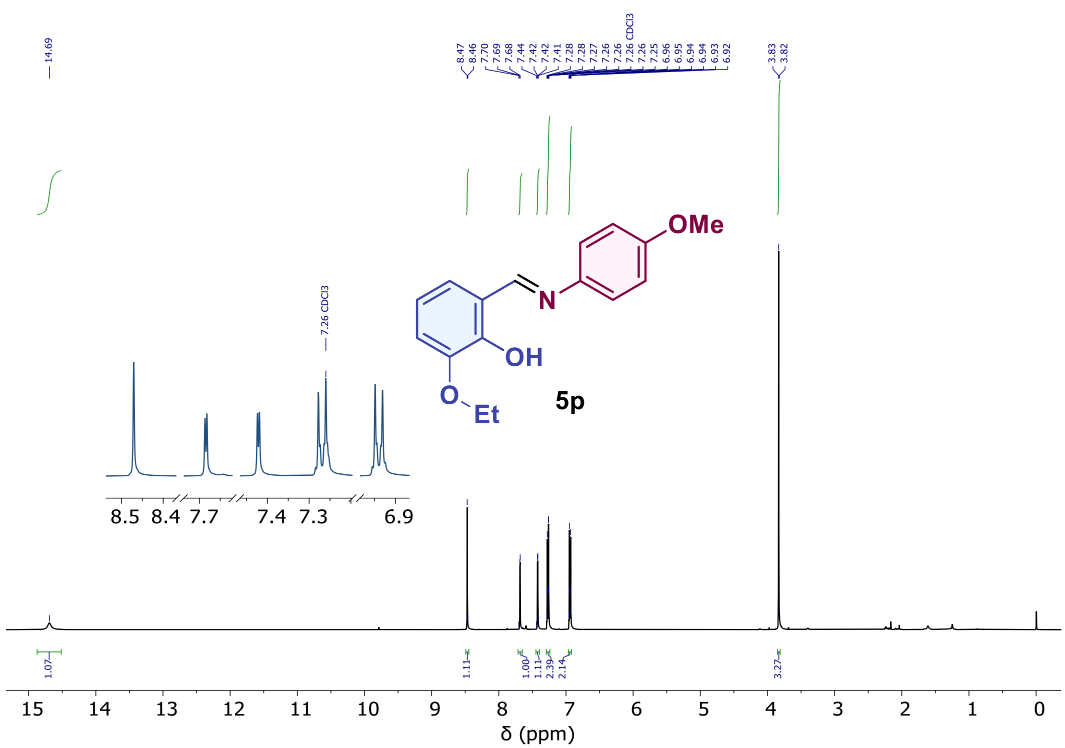


Figure S61. ^{1}H NMR (CDCl$_3$, 500 MHz) spectra for compound **5p.**

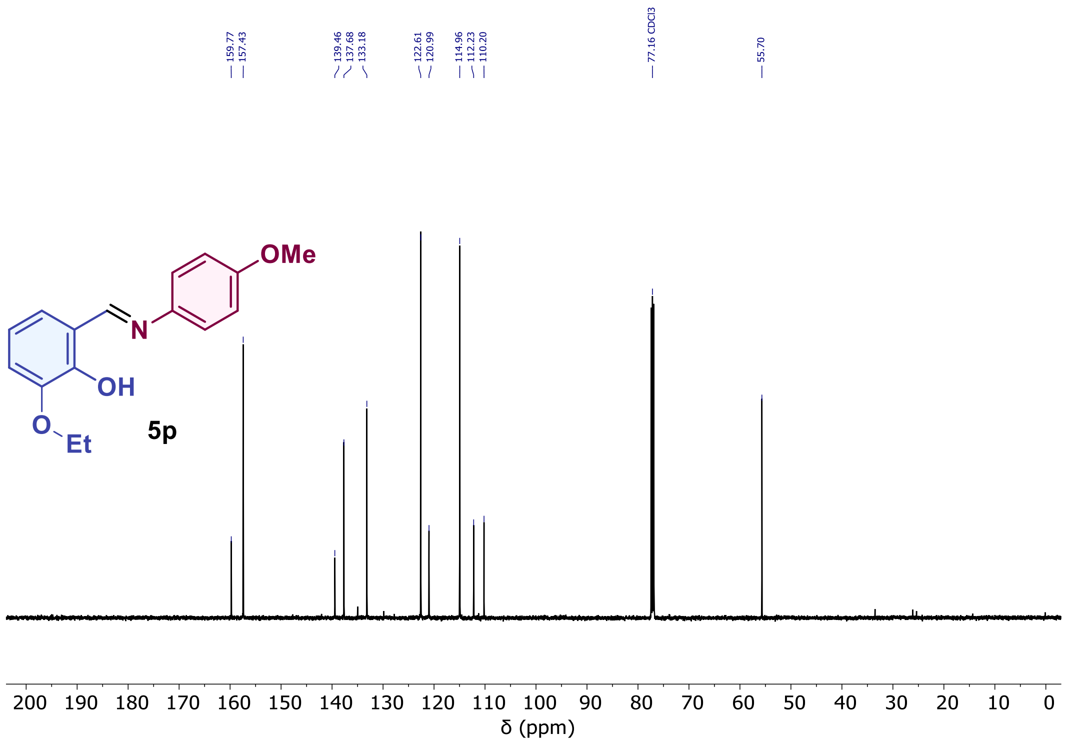


Figure S62. ^{13}C NMR ($CDCl_3$, 125 MHz) spectra for compound **5p**.

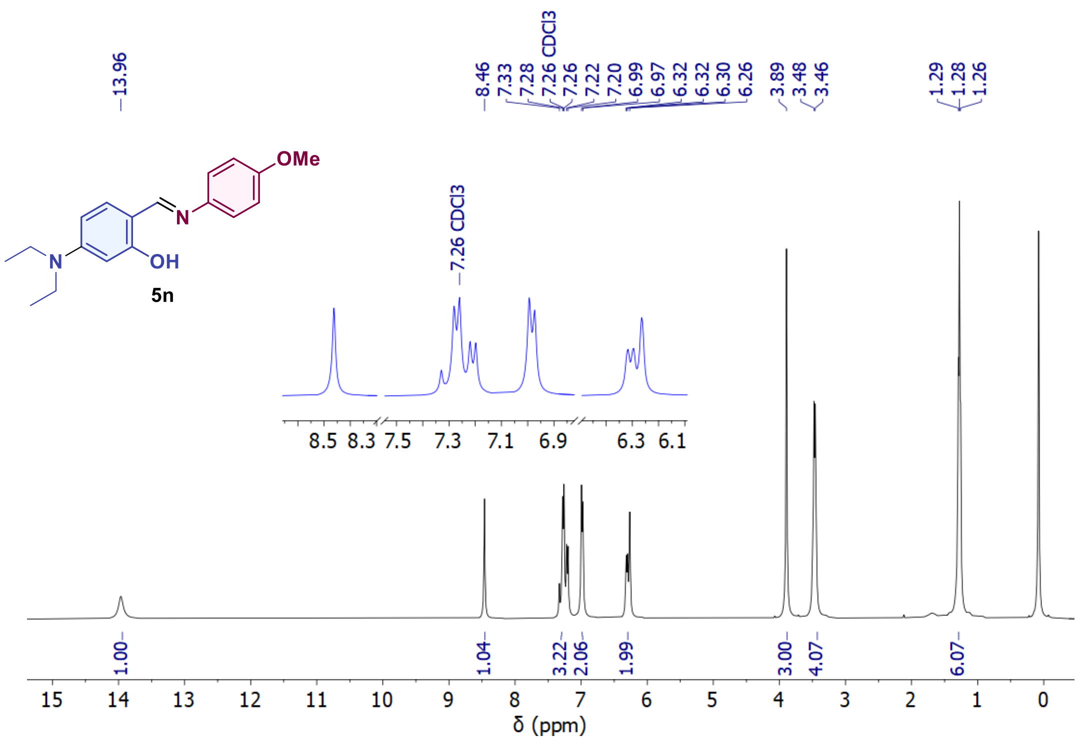


Figure S63. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra for compound **5n.**

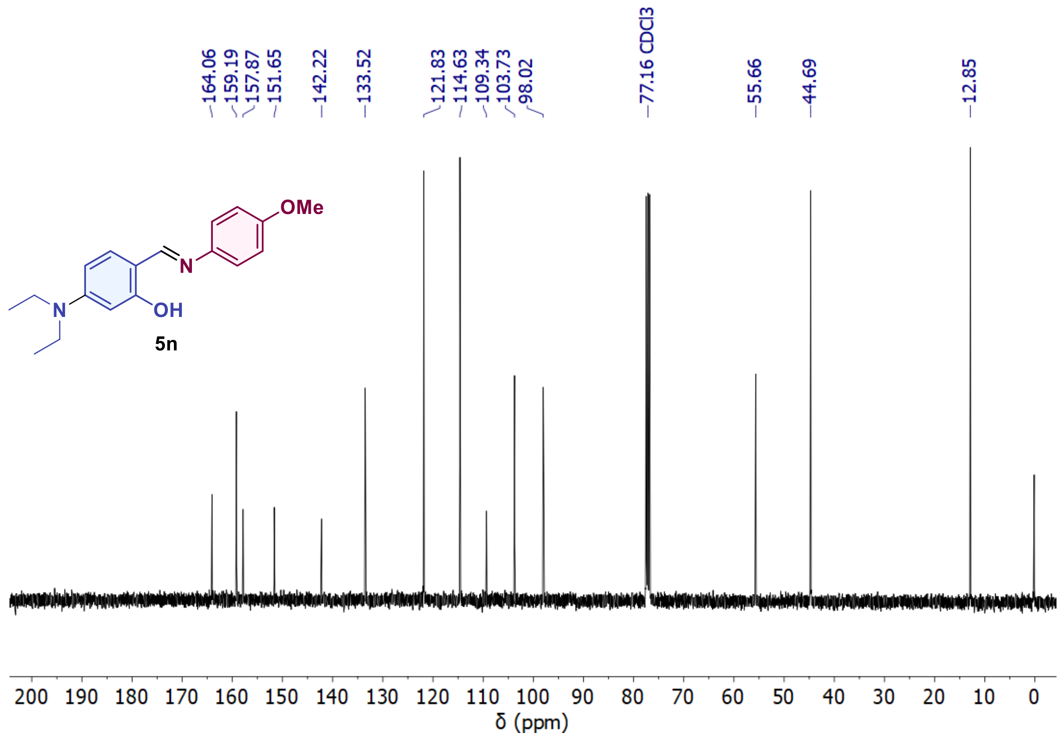


Figure S64. ^{13}C NMR ($CDCl_3$, 100 MHz) spectra for compound **5n**.

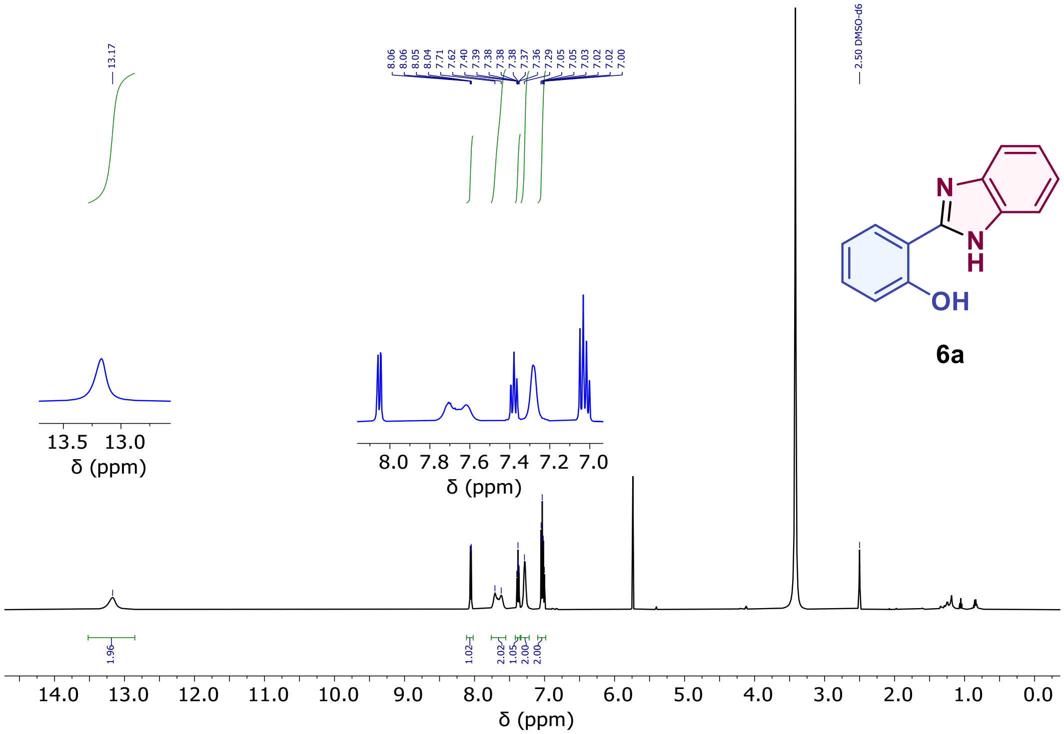


Figure S65. ^{1}H NMR (DMSO-d_6, 500 MHz) spectra for compound **6a**.

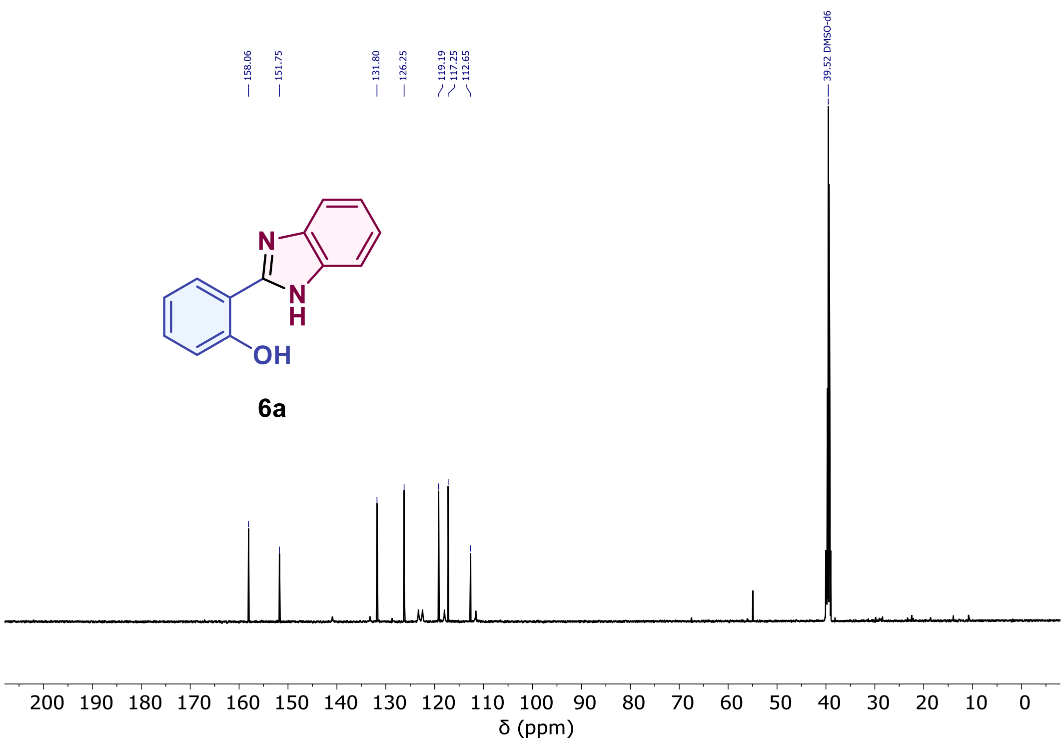


Figure S66. ^{13}C NMR (DMSO-d_6, 125 MHz) spectra for compound **6a**.

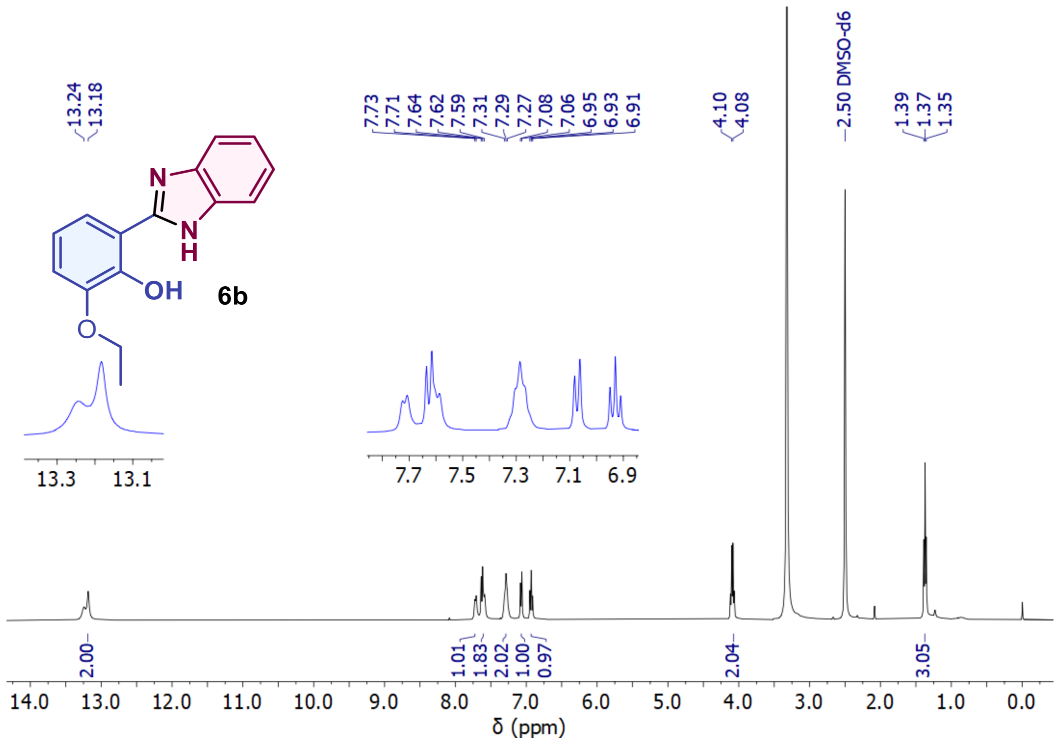


Figure S 67.[1]H NMR (DMSO-d_6, 400 MHz) spectra for compound **6b**.

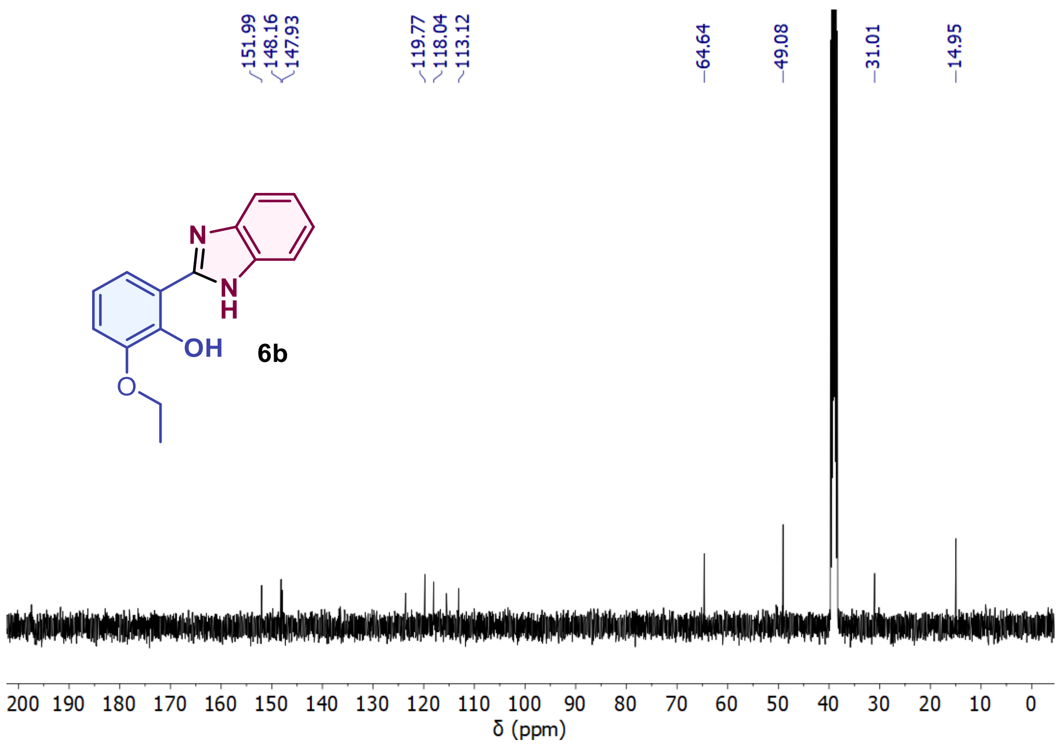


Figure S68.[13]C NMR (DMSO-d_6, 100 MHz) spectra for compound **6b**.

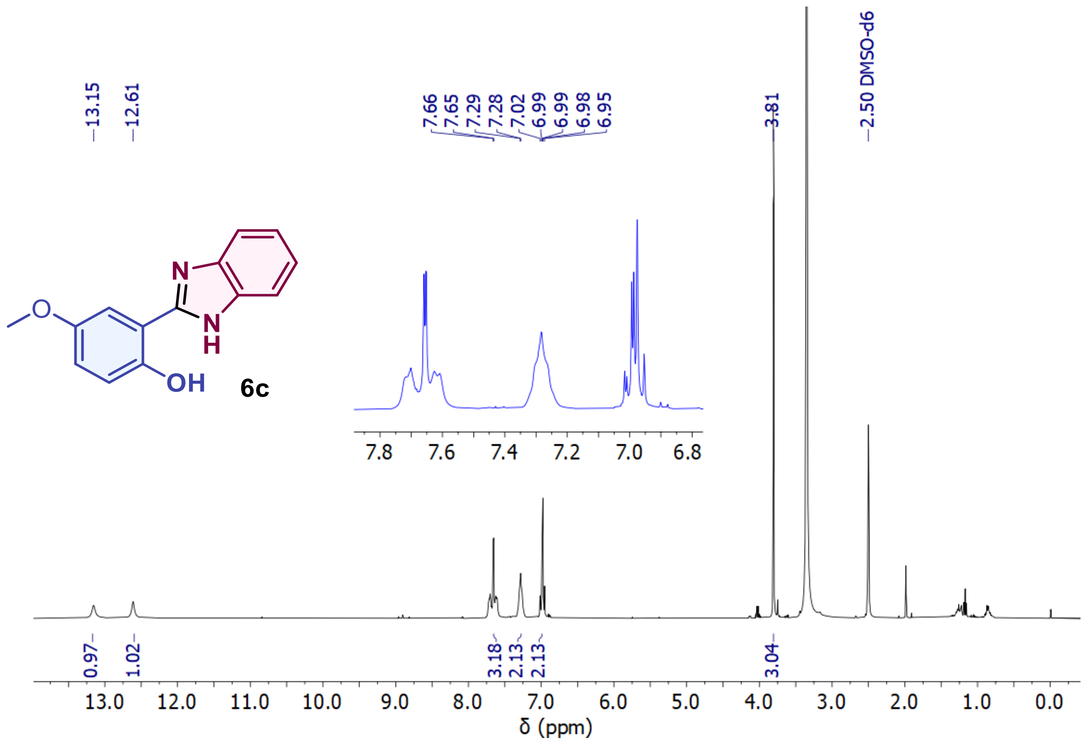


Figure S 69. [1]H NMR (DMSO-d_6, 400 MHz) spectra for compound **6c**.

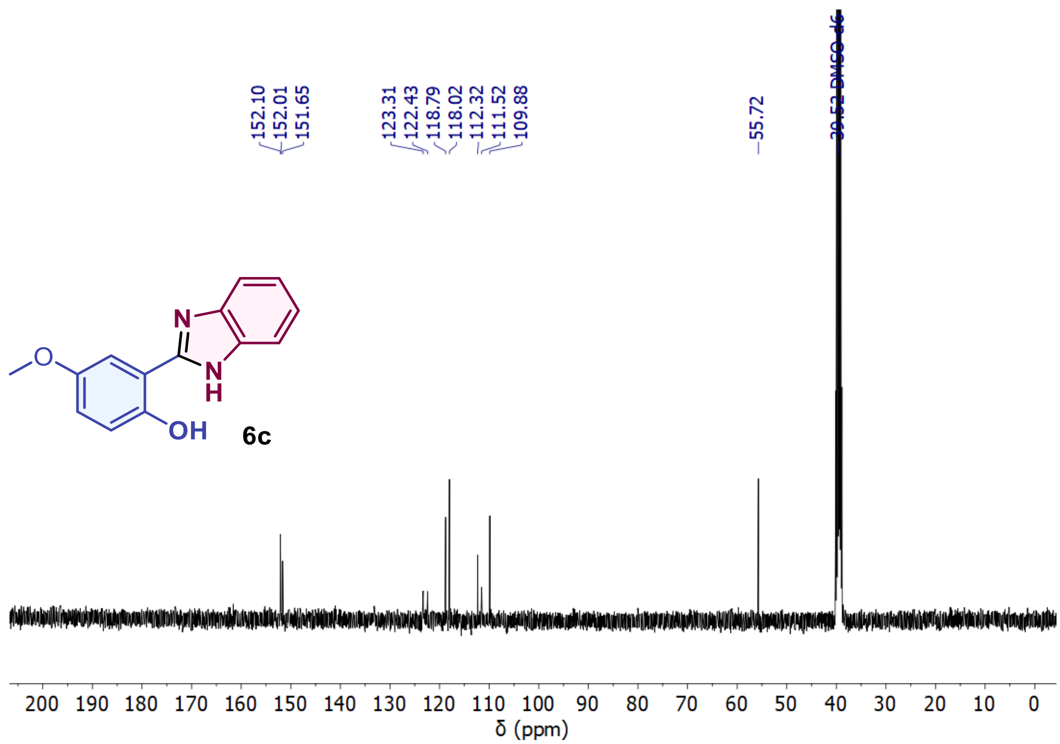


Figure S 70.[13]C NMR (DMSO-d_6, 100 MHz) spectra for compound **6c**.

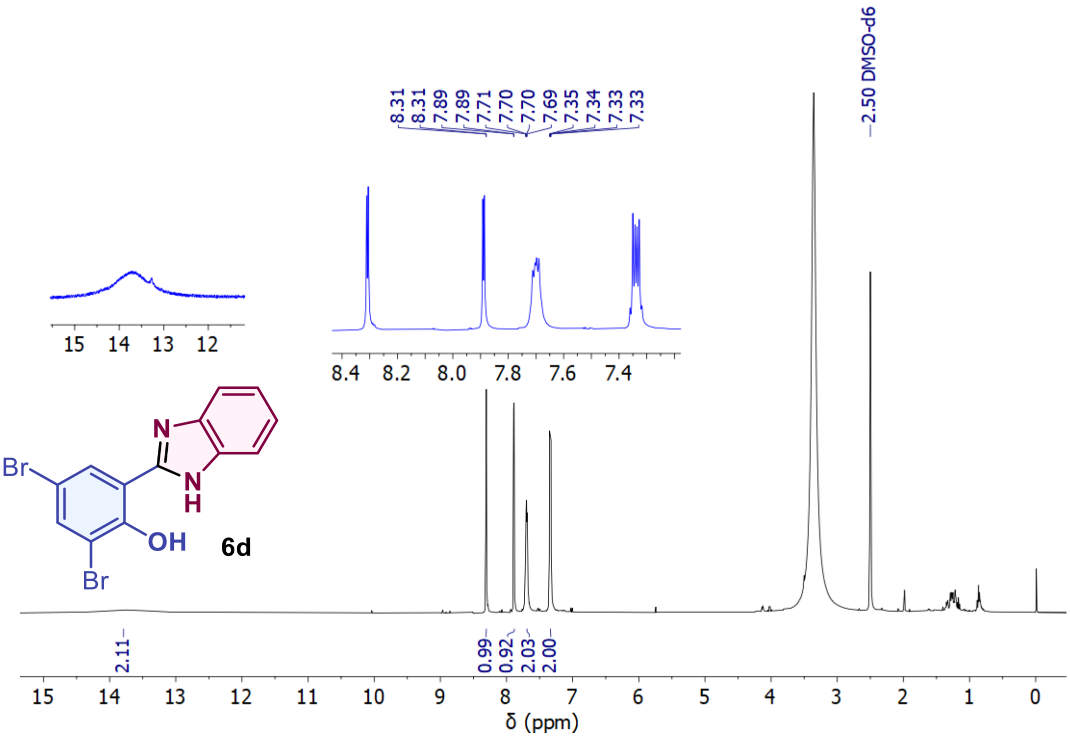


Figure S 71. ^{1}H NMR (DMSO-d_6, 400 MHz) spectra for compound **6d**.

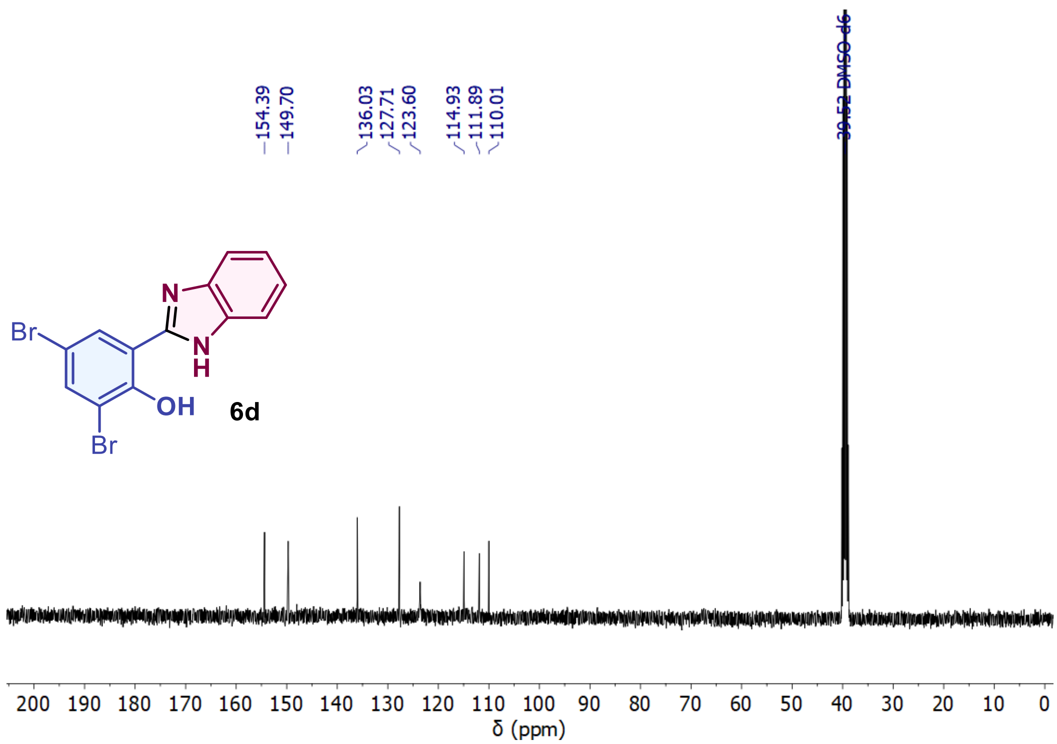


Figure S 72. ^{13}C NMR (DMSO-d_6, 100 MHz) spectra for compound **6d**.

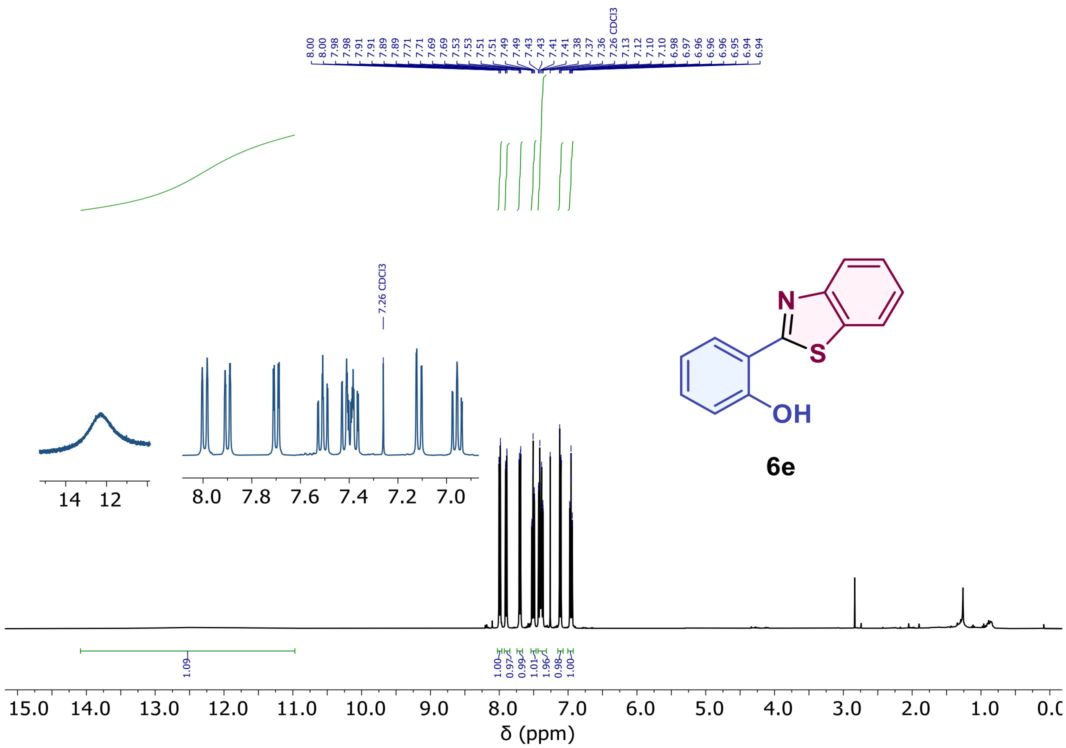


Figure S73.[1]H NMR ($CDCl_3$, 400 MHz) spectra for compound **6e**.

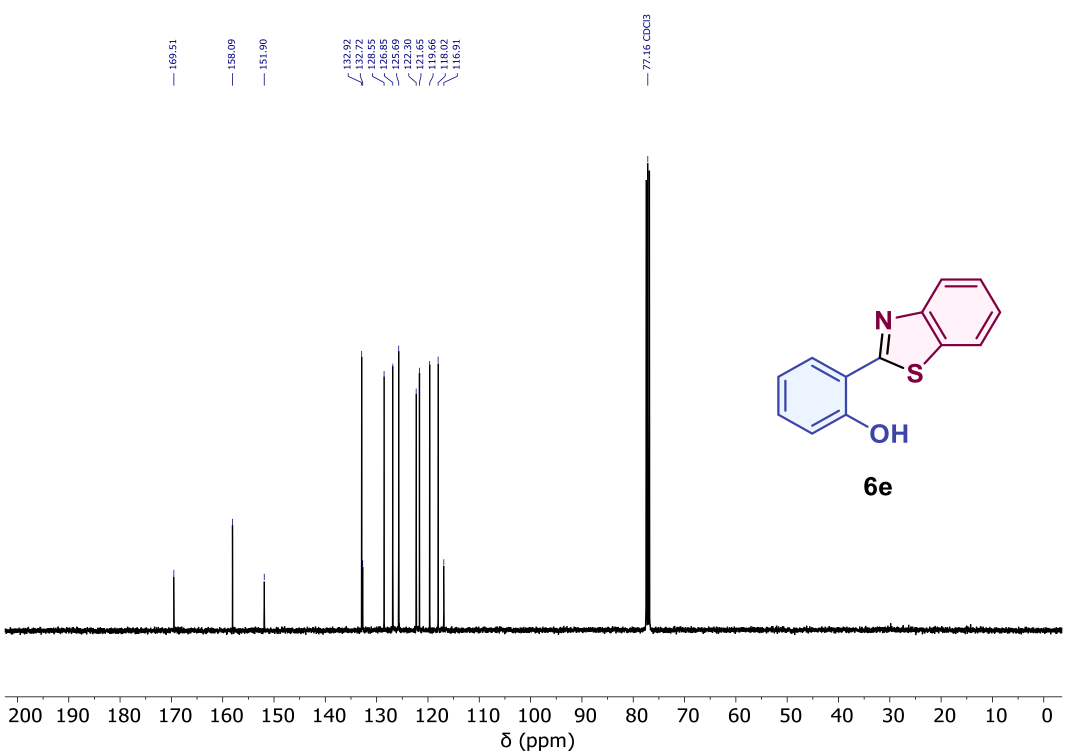


Figure S74.[13]C NMR ($CDCl_3$, 100 MHz) spectra for compound **6e**.

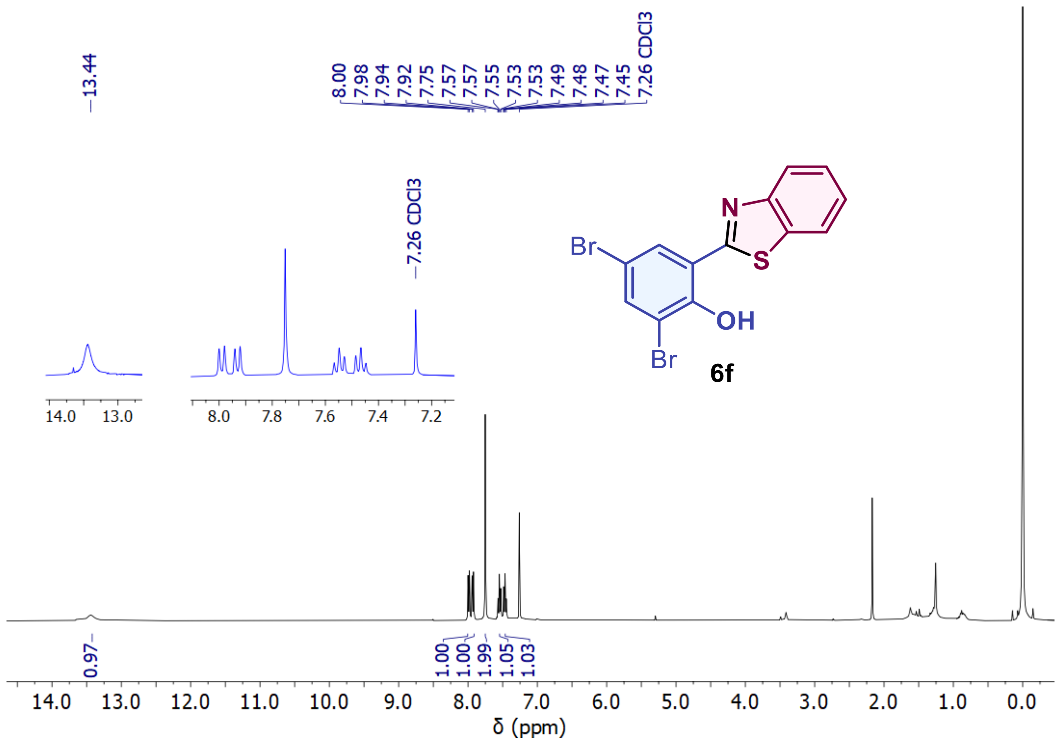


Figure S75. ^{1}H NMR ($CDCl_3$, 400 MHz) spectra for compound **6f**.

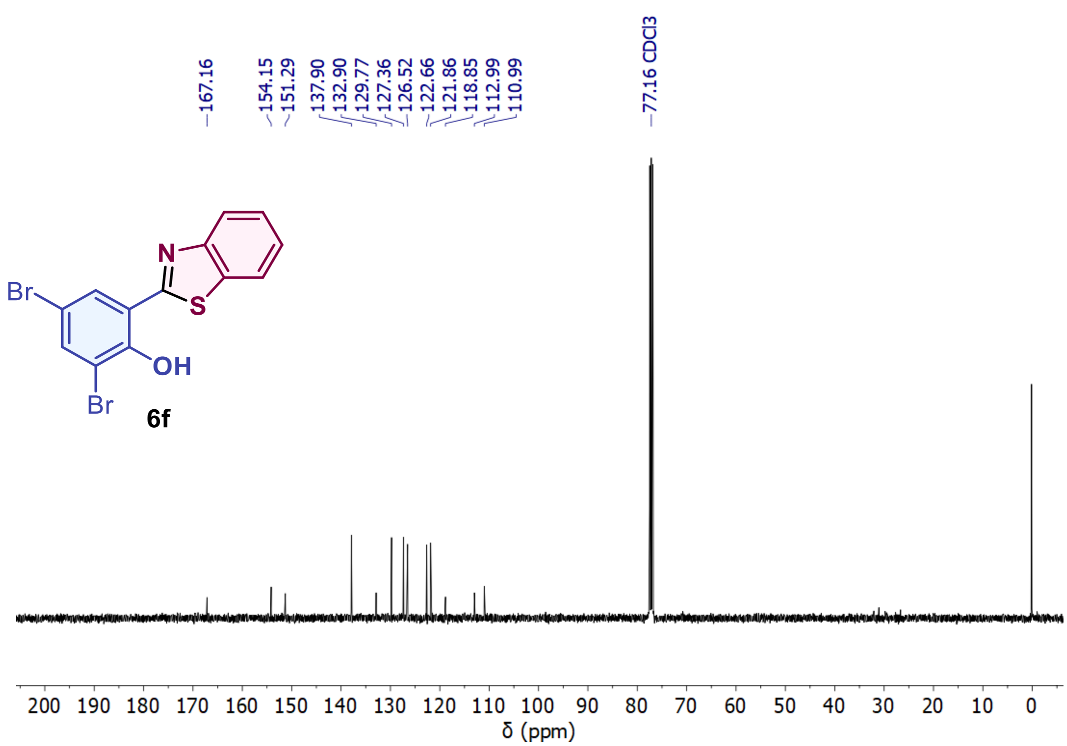


Figure S76. ^{13}C NMR ($CDCl_3$, 100 MHz) spectra for compound **6f**.