

Supporting Information

Simple improvements to Gilch synthesis and molecular weight modulation of MEH-PPV

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Experimental:

1.1. General experimental

Commercial reagents were purchased from Univar, Sigma-Aldrich, AK scientific, Matrix Scientific, Ajax Finechem, and Labchem, and were used as received. Anhydrous toluene, diethyl ether, dichloromethane, and tetrahydrofuran were obtained from alumina drying columns. For reactions carried out under inert conditions, standard Schlenk techniques were used. Solvents were sparged with nitrogen gas for several hours prior to use, and the reaction vessels were sealed with a rubber septum under a nitrogen atmosphere. Thin layer chromatography (TLC) was done using Merck-Millipore Silica gel glass plates (60G F₂₅₄), with a 254 nm and 365 nm light mercury lamp used for identifying spots. ¹H-NMR (600 MHz) and ¹³C-NMR (150 MHz) were obtained in CDCl₃, on a 600 MHz Varian spectrometer. NMR peaks were referenced to the CHCl₃ solvent peak. UV-Vis Spectroscopy was performed on Agilent Technologies Cary 50 UV-Vis. Photoluminescent spectroscopy was performed on Varian Cary Eclipse fluorimeter.

1.2. Monomer synthesis

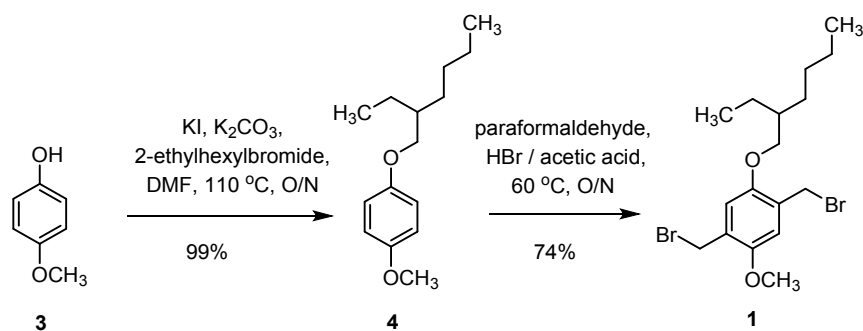


Figure S1. Synthesis of 1,4-bis(bromomethyl)-2-((2-ethylhexyl)oxy)-5-methoxybenzene.

Synthesis of 1-((2-ethylhexyl)oxy)-4-methoxybenzene:

4-methoxyphenol (10g, 80 mmol), potassium carbonate (22.2g, 160 mmol), potassium iodide (1g, 6 mmol), 2-ethylhexyl bromide (28 mL, 160 mmol) were stirred in 60 mL of DMF and heated to 110 °C overnight under a nitrogen atmosphere. The mixture was then cooled and extracted into hexanes and washed with water and then further washed with dilute sodium hydroxide. The organic layer was then collected and dried over magnesium sulfate, then filtered. The solvent was then evaporated and the excess 2-ethylhexyl bromide was removed via vacuum distillation to afford the product as a pale yellow oil.

mass = 18.85 g (99%)

¹H NMR (600 MHz, CDCl₃) δ: 6.84 (m, 4H), 3.80 (dd, *J* = 2.4, 5.8 Hz, 2H), 3.77 (s, 3H), 1.70 (sept, *J* = 6.1 Hz, 1H), 1.55-1.37 (m, 4H), 1.33 (m, 4H), 0.92 (m, 6H).

¹³C NMR (150 MHz, CDCl₃) δ: 153.77, 153.75, 115.57, 114.74, 71.36, 55.89, 39.61, 30.68, 29.24, 24.00, 23.21, 14.23, 11.24.

Spectra matched with literature values.¹²

Synthesis of 1,4-bis(bromomethyl)-2-((2-ethylhexyl)oxy)-5-methoxybenzene:

1-((2-ethylhexyl)oxy)-4-methoxybenzene (18.85g, 79 mmol) and paraformaldehyde (12g, 400 mmol) was stirred in a mixture of 40 mL of HBr (33% solution in acetic acid) and 40 mL of glacial acetic acid. The mixture was then heated to 60 °C overnight. The mixture was then cooled and poured into water and the crude product was removed via vacuum filtration. The solid was then dissolved in ethyl acetate and washed with saturated sodium bicarbonate solution, the organic layer was then collected and dried over magnesium sulfate, then filtered. The solvent was then evaporated and the product was then stirred in 50mL of cold hexanes for 30 minutes before filtering. The solid was then dried in a vacuum oven at 60 °C overnight.

mass = 27.35 g (74%)

^1H NMR (600 MHz, CDCl_3) δ : 6.86 (d, J = 4.2 Hz, 2H), 4.53 (s, 4H), 3.88 (d, J = 5.2 Hz, 2H), 3.86 (s, 3H), 1.76 (sept, J = 6.1 Hz, 1H), 1.60-1.41 (m, 4H), 1.34 (m, 4H), 0.95 (t, J = 7.4 Hz, 3H), 0.92 (t, J = 6.4 Hz, 3H).

^{13}C NMR (150 MHz, CDCl_3) δ : 151.15, 151.11, 127.61, 127.47, 114.43, 113.91, 71.08, 56.39, 39.74, 30.77, 29.25, 28.82, 28.76, 24.16, 23.19, 14.23, 11.38.

Spectra matched with literature values.¹²

1.3. General polymerization method

In an oven dried RBF under nitrogen atmosphere, KO^tBu (5eq) was dissolved in degassed solvent (to a concentration of 70 mM). The monomer (1eq) was dissolved in a separate flask in dry degassed solvent (to a concentration of 79 mM), the solution of monomer was then added with a syringe pump (at 10 mL / hour) to the solution of KO^tBu whilst stirring at 700 RPM (Final monomer concentration = 12 mM). The mixture was then stirred at room temperature for 24 hrs, the mixture was then slowly poured into methanol with vigorous stirring (10 times the reaction volume). The mixture was then centrifuged in a pre-weighed centrifuge tube, and the precipitate was washed with methanol and recentrifuged three times, then washed with hexanes and recentrifuged three times. The tube was then dried in a vacuum oven at 60 °C for 24 hrs, the dried tube is then weighed after cooling to determine the yield. A solution of 1-2 mg / mL in chloroform was prepared for GPC analysis.

For samples in Table 2 and Table 3, the mixture of KO^tBu in methyl tert-butyl ether was either heated in an oil bath at the desired temperature for 10 mins, or cooled using a cryostat for 30mins with an acetone bath to the desired temperature before the addition of the monomer.

1.4. Example procedure:

Table 1 entry 12 – Diethyl ether: In an oven dried 50mL RBF under nitrogen atmosphere, KO^tBu (0.13g) was dissolved in degassed diethyl ether (17mL). The monomer (0.1g) was dissolved in a separate flask in dry degassed diethyl ether (3mL), the solution of monomer was then added with a syringe pump (at 10 mL / hour) to the solution of KO^tBu whilst stirring at 700 RPM. The mixture was then stirred at room temperature for 24 hrs, the mixture was then slowly poured into methanol with vigorous stirring (200mL). The mixture was then centrifuged in a pre-weighed centrifuge tube, and the precipitate was washed with methanol and recentrifuged three times, then washed with hexanes and recentrifuged three times. The tube was then dried in a vacuum oven at 60 °C for 24 hrs, the dried tube is then weighed after cooling to determine the yield. A solution of 1-2 mg / mL in chloroform was prepared for GPC analysis.

mass = 50.7 mg (82%)

Ranking tables:

Table S1. Normalized ranking for reaction conditions (ranked from highest to lowest) for the production of low molecular weight polymers with high reaction yields.

Entry	Solvent	Temperature (°C)	Normalized Low Rank
1	n-Pentane	55	61
2	MTBE	-15	30
3	Diethyl ether	25	26
4	MTBE	55	24
5	n-Hexane	25	22

6	MTBE	0	22
7	Hexanes	25	20
8	MTBE	-30	16
9	α,α,α -Trifluorotoluene	25	13
10	Chlorobenzene	25	9
11	Perfluorodecalin / n-hexane (3:1)	25	9
12	1,4-Dimethoxyethane	25	9
13	MTBE	40	8
14	MTBE	25	7
15	Cyclohexane	25	7
16	DMF	25	5
17	THF	55	4
18	1,4-Dioxane	25	2
19	Chlorobenzene	55	2
20	DMAc	25	2
21	Toluene	55	1
22	THF	25	1
23	Toluene	25	1

Table S2. Normalized ranking for reaction conditions (ranked from highest to lowest) for the production of high molecular weight polymers with high reaction yields.

Entry	Solvent	Temperature (°C)	Normalized high rank
1	Toluene	55	65

2	THF	25	51
3	Toluene	25	50
4	THF	55	49
5	1,4-Dioxane	25	38
6	Chlorobenzene	25	29
7	1,4-Dimethoxyethane	25	29
8	MTBE	25	21
9	Chlorobenzene	55	20
10	Cyclohexane	25	19
11	α,α,α -Trifluorotoluene	25	18
12	Diethyl ether	25	17
13	MTBE	55	16
14	MTBE	40	12
15	Perfluorodecalin / n-hexane (3:1)	25	12
16	n-Pentane	25	11
17	MTBE	-15	8
18	n-Hexane	25	7
19	MTBE	0	6
20	Hexanes	25	5
21	MTBE	-30	4
22	DMAc	25	1
23	DMF	25	1

Additional MTBE data:

Table S3. GPC data for polymers produced using MTBE as a solvent at 25 °C, where entry 1 is the previously shown value from Table 1.

Entry	Mn (g/mol)	Mw (g/mol)	Mp (g/mol)	Đ	Yield
1	20,000	98,500	75,600	4.94	73%
2	8,000	20,900	13,000	2.62	48%
3	13,300	39,800	35,700	2.98	37%
4	22,000	92,300	85,400	4.21	65%
5	13,800	58,200	41,000	4.23	56%

UV-Vis absorbance spectra:

Table S4. Summary of the UV-Vis absorbance maxima, photoluminescence maxima (in nm), and the relative photoluminescence quantum yield of polymers produced under different polymerization conditions.

Entry	Solvent	Absorbance maxima (nm)	Fluorescence maxima (nm)	PLQY (Rhodamine 6G reference)	M _p (g/mol)
1	DMF	493	556	0.22	19,400
2	n-Pentane	482	558	0.21	19,400
3	Hexanes	485	554	0.25	21,600
4	MTBE (-15 °C)	492	558	0.25	22,900
5	MTBE (0 °C)	495	558	0.24	23,500

6	MTBE (-30 °C)	485	555	0.26	23,600
7	n-Hexane	485	557	0.22	25,500
8	Toluene	498	556	0.26	31,900
9	Diethyl ether	501	558	0.24	36,200
10	MTBE (55 °C)	501	557	0.22	37,700
11	DMAc	485	557	0.24	42,600
12	Perfluorodecalin / n-hexane (3:1)	481	556	0.28	50,900
13	α,α,α - Trifluorotoluene	493	557	0.27	54,100
14	MTBE (40 °C)	497	557	0.25	54,200
15	MTBE	501	559	0.25	75,600
16	Cyclohexane	493	554	0.25	77,000
17	Chlorobenzene	475	555	0.23	80,100
18	1,4- Dimethoxyethane	499	557	0.26	82,800
19	Chlorobenzene	494	557	0.24	151,000
20	Toluene (55 °C)	502	557	0.27	167,000
21	1,4-Dioxane	501	557	0.25	202,000
22	THF (55 °C)	498	557	0.27	300,000
23	THF	501	558	0.26	311,000

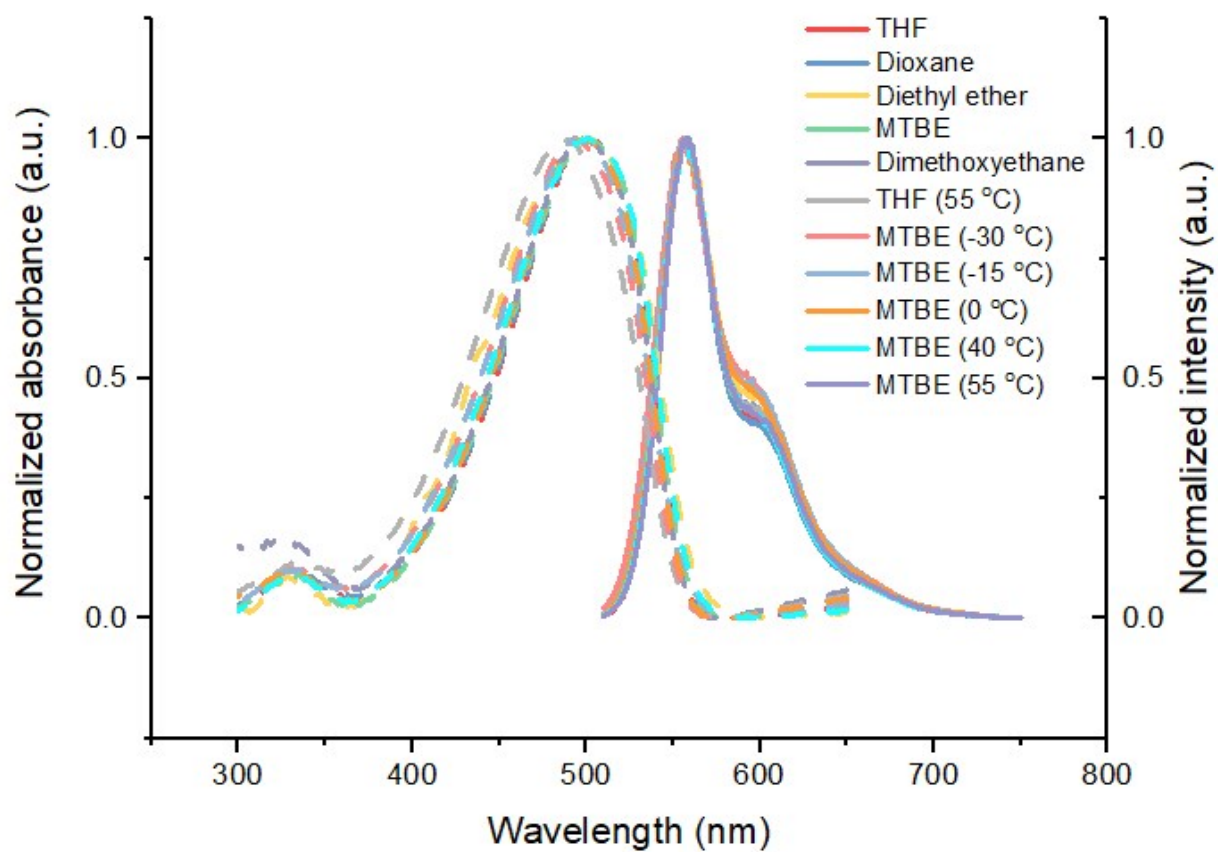


Figure S2. UV-Vis absorbance (dashed line) and fluorescence (solid line) spectra in chloroform for the reaction conditions with ethers as the solvent.

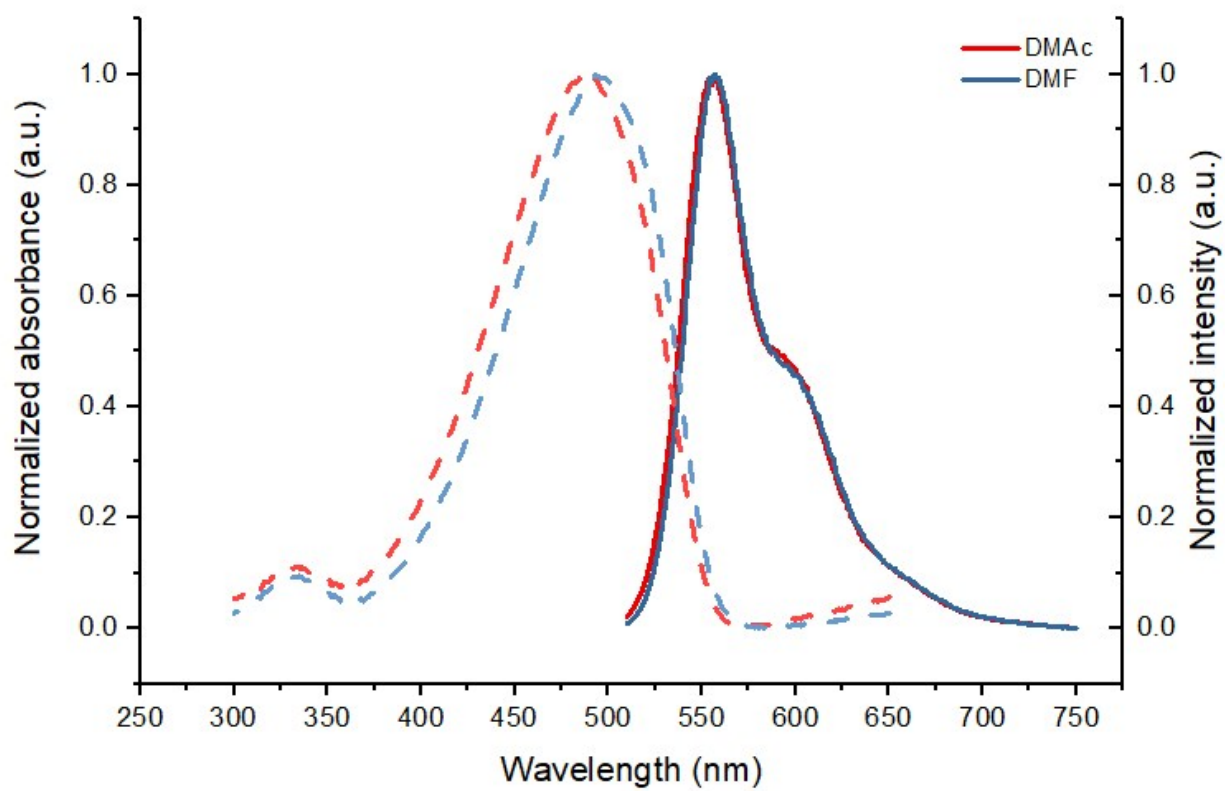


Figure S3. UV-Vis absorbance (dashed line) and fluorescence (solid line) spectra in chloroform for the reaction conditions with amides as the solvent.

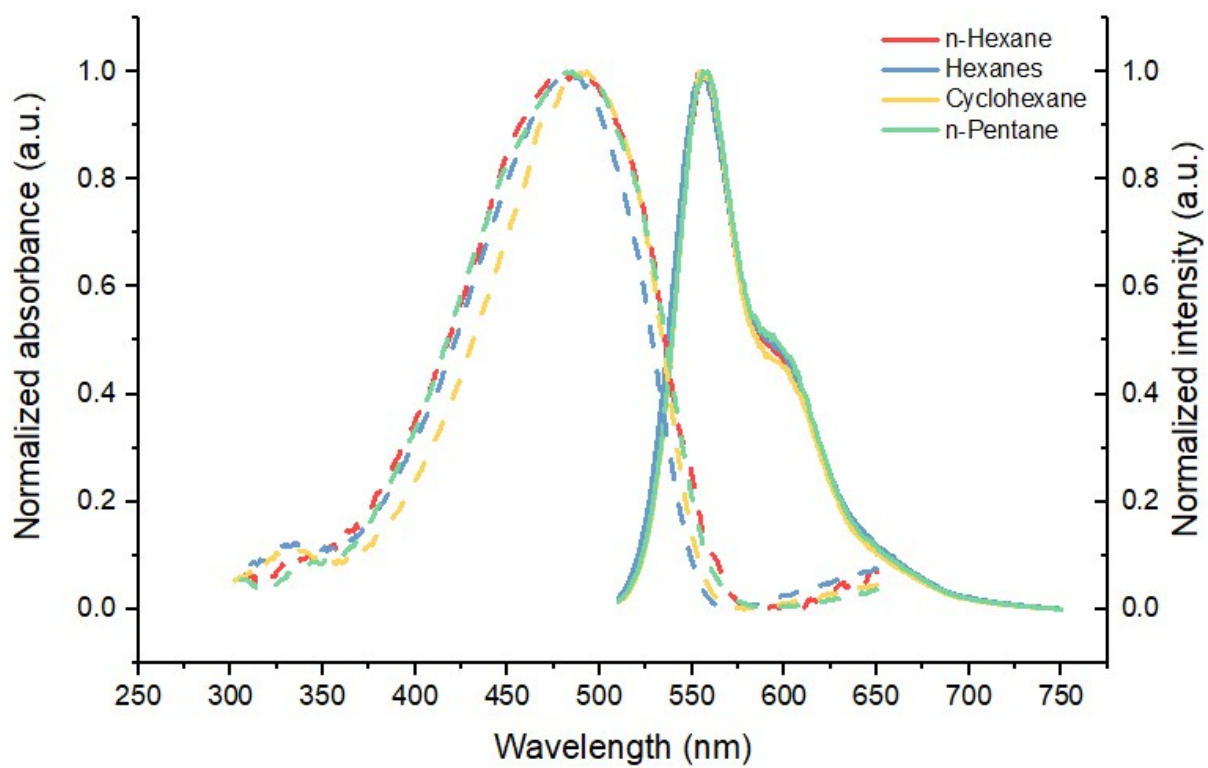


Figure S4. UV-Vis absorbance (dashed line) and fluorescence (solid line) spectra in chloroform for the reaction conditions with alkanes as the solvent.

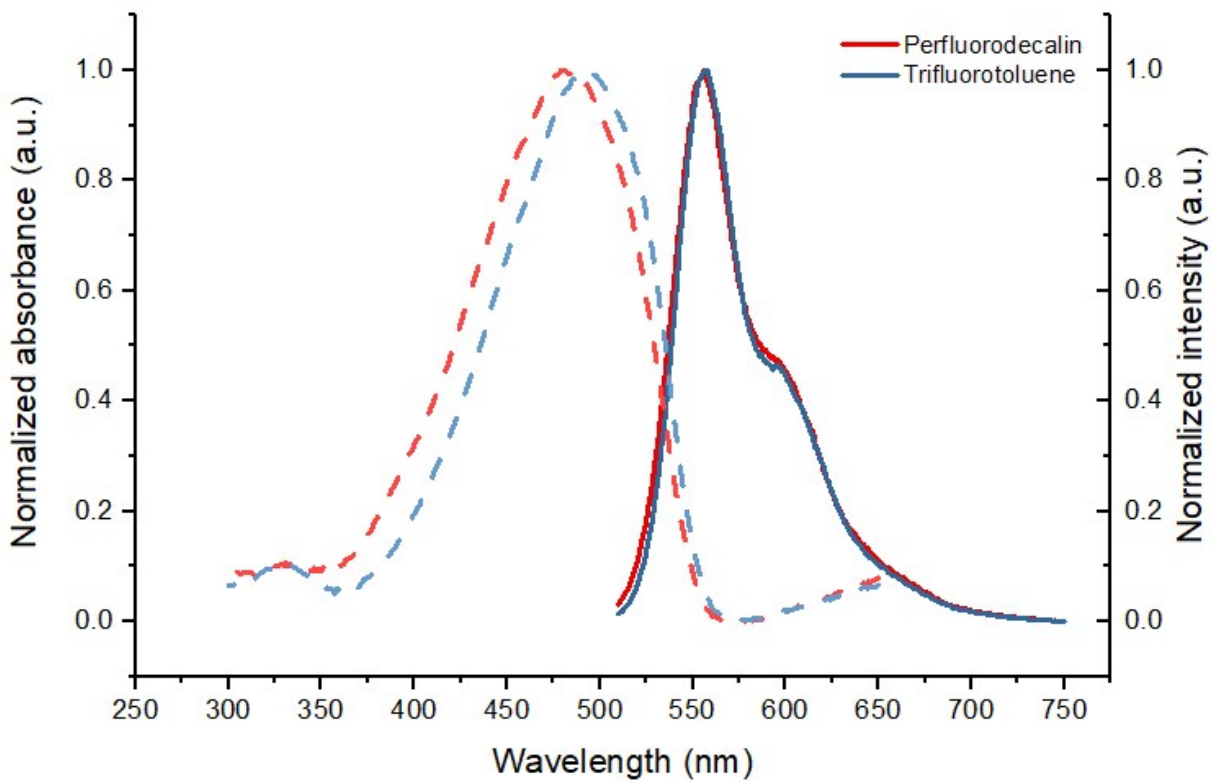


Figure S5. UV-Vis absorbance (dashed line) and fluorescence (solid line) spectra in chloroform for the reaction conditions with fluorinated solvents.

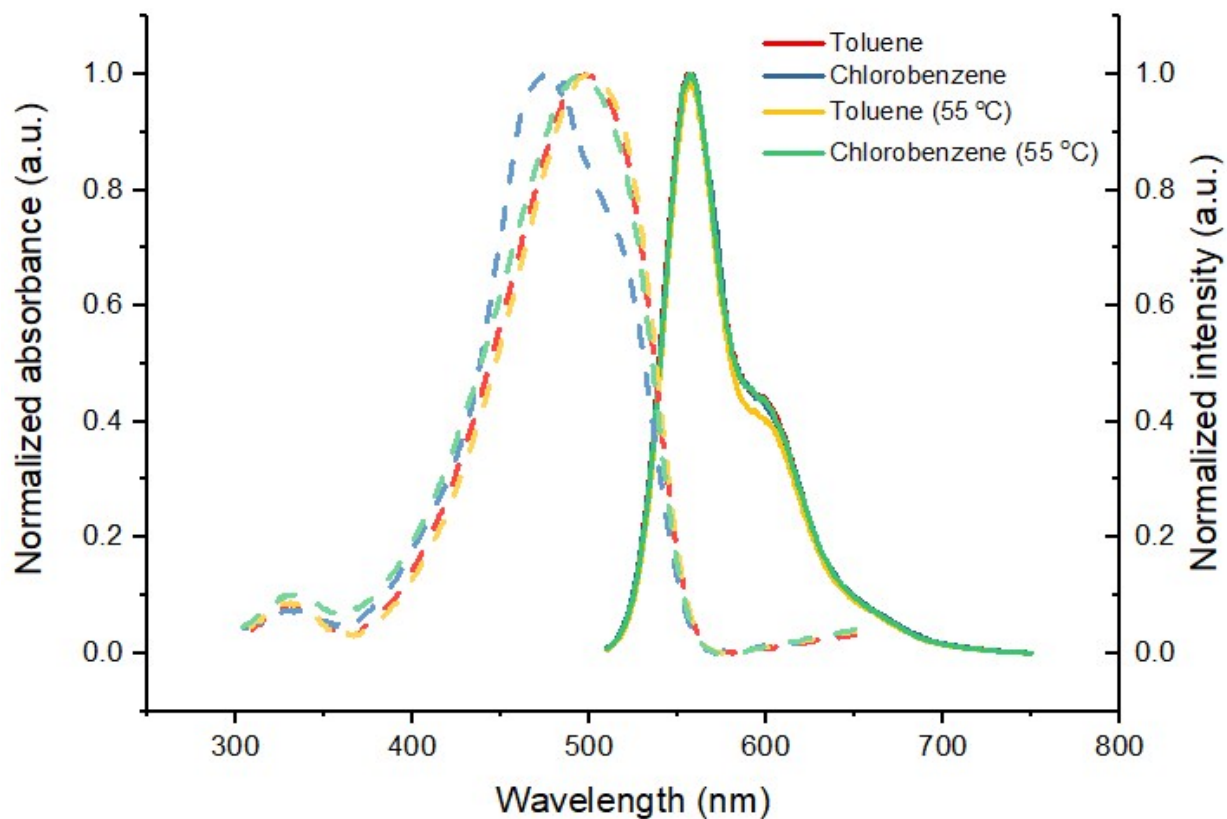


Figure S6. UV-Vis absorbance (dashed line) and fluorescence (solid line) spectra in chloroform for the reaction conditions with aromatic solvents.

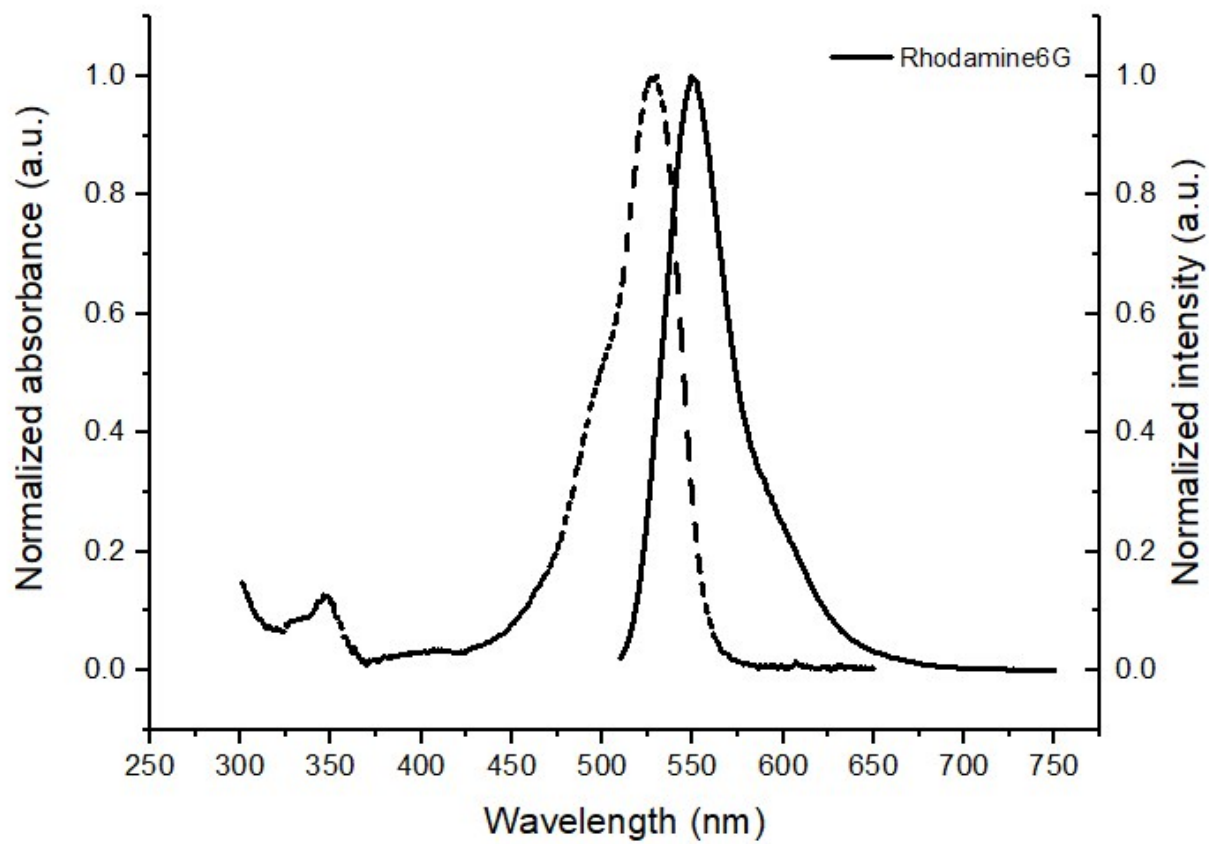


Figure S7. UV-Vis absorbance (dashed line) and fluorescence (solid line) spectra in chloroform for the Rhodamine 6G standard.

NMR spectra:

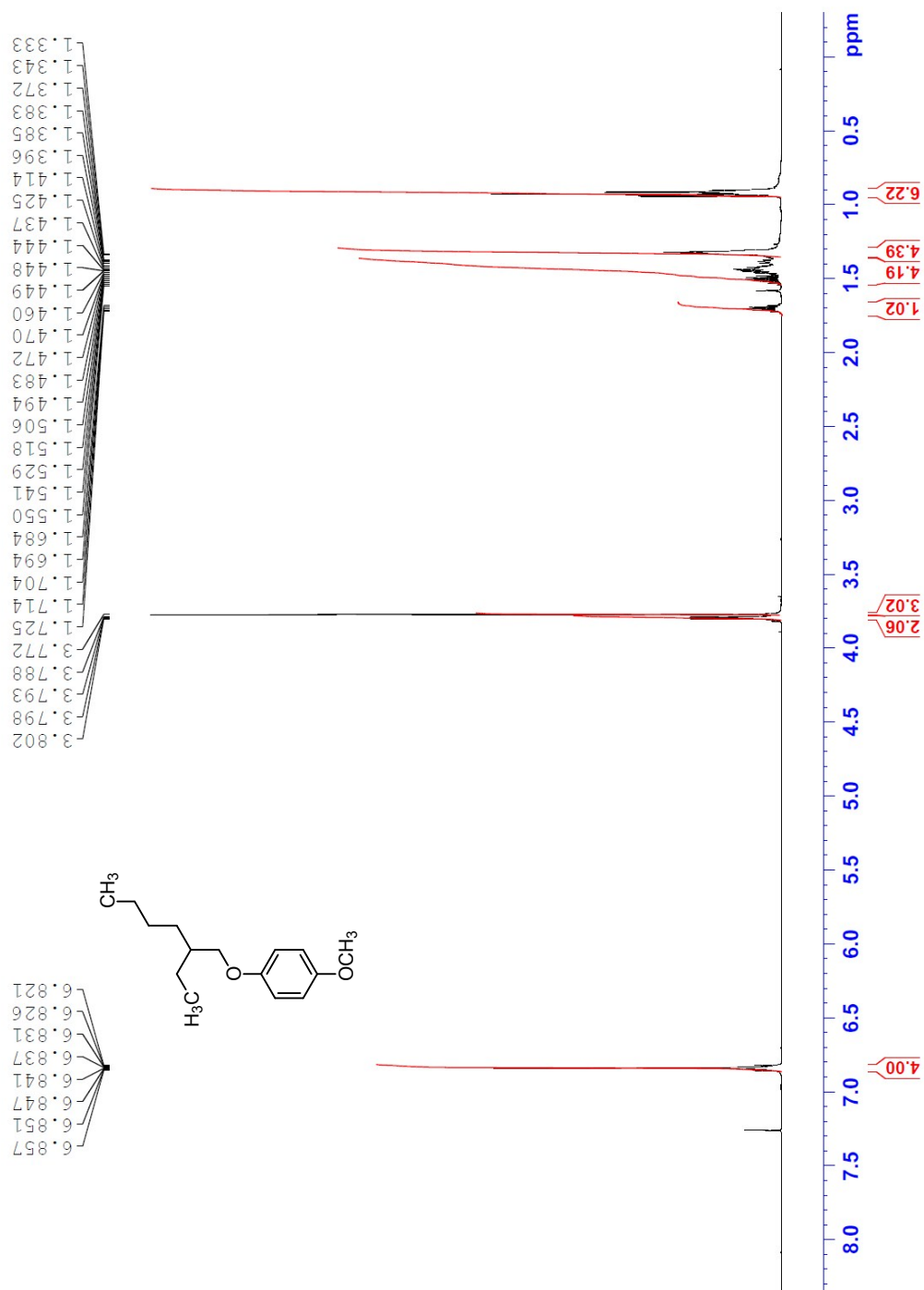


Figure S8. ¹H NMR spectra (600 MHz in CDCl₃) of 1-((2-ethylhexyl)oxy)-4-methoxybenzene.

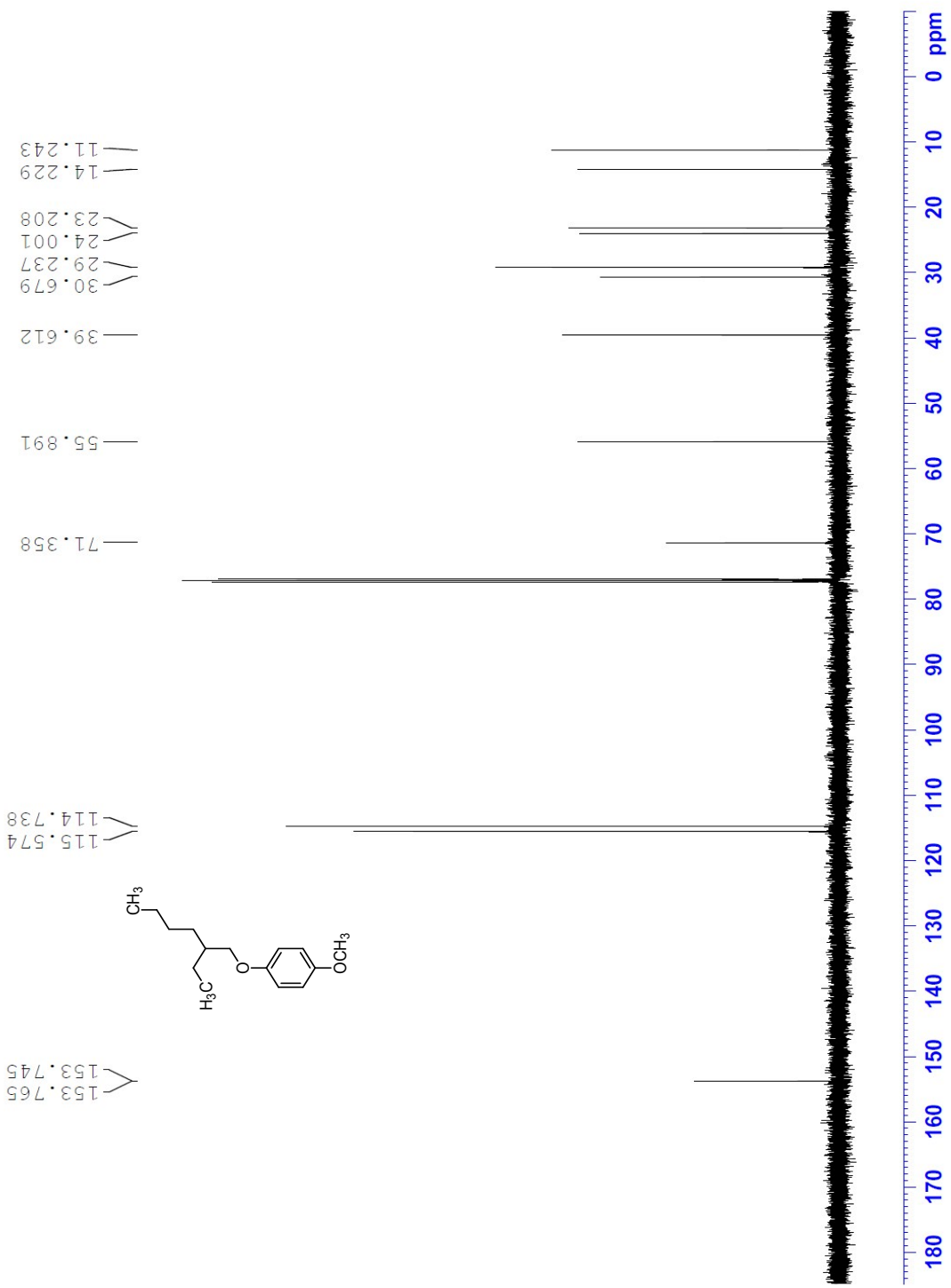


Figure S9. ¹³C NMR spectra (150 MHz in CDCl₃) of 1-((2-ethylhexyl)oxy)-4-methoxybenzene.

Figure S10.
¹H NMR spectra

(600 MHz in C

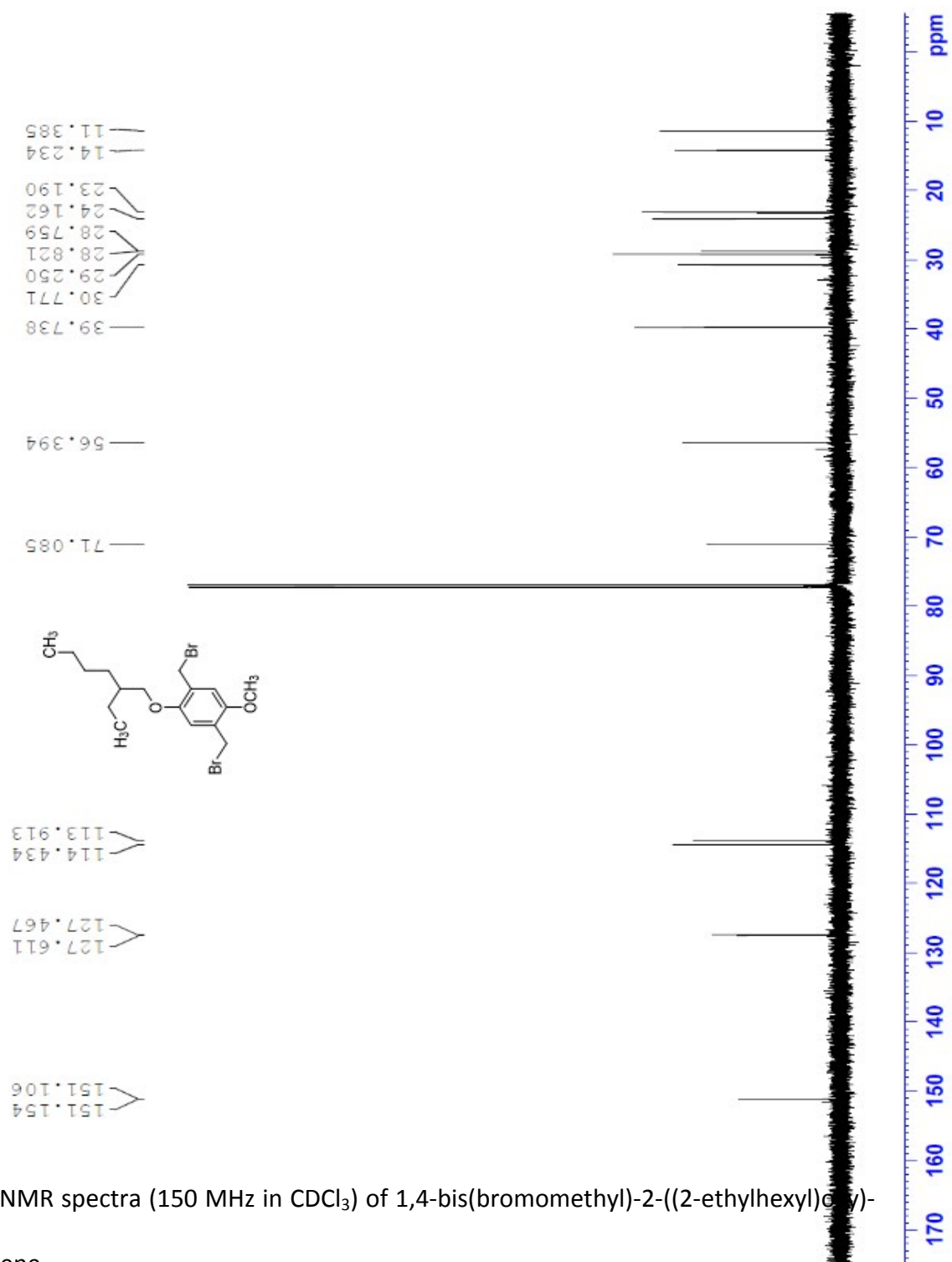


Figure S11. ¹³C NMR spectra (150 MHz in CDCl₃) of 1,4-bis(bromomethyl)-2-((2-ethylhexyl)oxy)-5-methoxybenzene.