Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Aluminium-Catalysed Synthesis of Aryl Enol Ethers from Phenols and Dimethyl Ketals

Kwihwan Kobayashi,*[a] Shingo Komatsuzaki,[a] Shun-ya Onozawa,[a] Koichiro Masuda,*[a] and Shū Kobayashi*[a,b]

[a] *Interdisciplinary Research Center for Catalytic Chemistry, National Institute of Advanced Industrial Science and Technology Central 5, Higashi 1-1-1, Tsukuba, Ibaraki 305-8565, Japan. E-mail: kobayashi-kwihwan@aist.go.jp, koichiro-masuda@aist.go.jp, shu_kobayashi@chem.s.u-tokyo.ac.jp*

[b] *Department of Chemistry, School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 111-0033, Japan.*

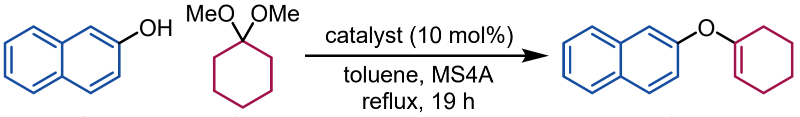
Contents

1. General

^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance NEO 400 MHz NMR spectrometer in $CDCl_3$ unless otherwise noted. Tetramethylsilane (TMS) served as an internal standard ($\delta = 0$) for ^{1}H NMR, and $CDCl_3$ served as an internal standard ($\delta = 77.16$) for ^{13}C NMR. Gas chromatography was measured on Shimadzu GC-2014 spectrometer with N_2 gas as a career, using Agilent Technologies DB-1 column (Length: 30 m, I.D.: 0.250 mm, Film: 0.25 μm). Other chemicals and solvents were purchased from Tokyo Chemical Industry Co., Ltd, FUJIFILM Wako pure chemicals, Kishida chemical Co., Ltd., and Sigma-Aldrich. IR spectra were recorded by Shimadzu IRSpirit. ESI high-resolution mass spectra (HRMS) were measured by JEOL JMS-700T MStation. Melting points were measured by BUCHI M-560. JAI LaboAce LC-5060 Plus II was used for a recycling preparative GPC.

2. Optimizations for the synthesis of aryl enol ethers catalyzed by acids

The reaction was conducted following general procedure GP-1.



1a
10 mmol

2a
1 eq.

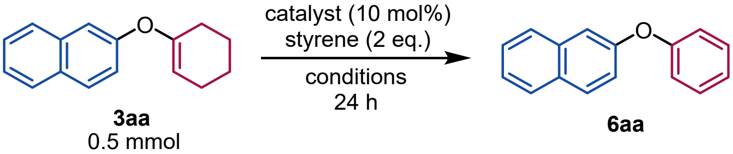
3aa

entry	catalyst	conversion (%)	yield (%)
1	$Al(OEt)_3$	83	72
2	$Ca(OMe)_2$	0	0
3	$Y(OiPr)_3$	35	2
4	$Ti(OiPr)_4$	27	2
5	$Ga(OiPr)_3$	88	58
6	$Zr(OEt)_4$	62	35
7	$Nb(OEt)_5$	64	12
8	$In(OiPr)_3$	43	16
9	$Fe(OEt)_3$	15	0
10	$Ce(OiPr)_4$	17	0
11	$Sn(OEt)_2$	25	1
12	$Sc(OTf)_3$	43	1
13	$B(OEt)_3$	15	1
14	$Al(OiPr)_3$	66	51
15	$AlCl_3$	69	51
16	$Al_2O(OAc)_4 \cdot nH_2O$	33	29
17	$Al(NO_3)_3 \cdot 9H_2O$	23	3
18	$Al(acac)_3$	6	0
19	$AlMe_3$	74	61
20[a]	$AlMe_3$	83	71
21[a,b]	$AlMe_3$	92	74
22[a,b,c]	$AlMe_3$	92	86
23 [a,b,c,d]	$AlMe_3$	93	91

[a] 2 equivalents of **2a** were used. [b] 1 mol% of $AlMe_3$ was used. [c] **2a** was added all at once without syringe pump. [d] 50 mmol of **1a**, 200 mL of toluene, and 100 g of MS 4Å were used.

3. Optimization for the synthesis of diaryl ethers catalyzed by palladium

The reaction was conducted following general procedure GP-3.

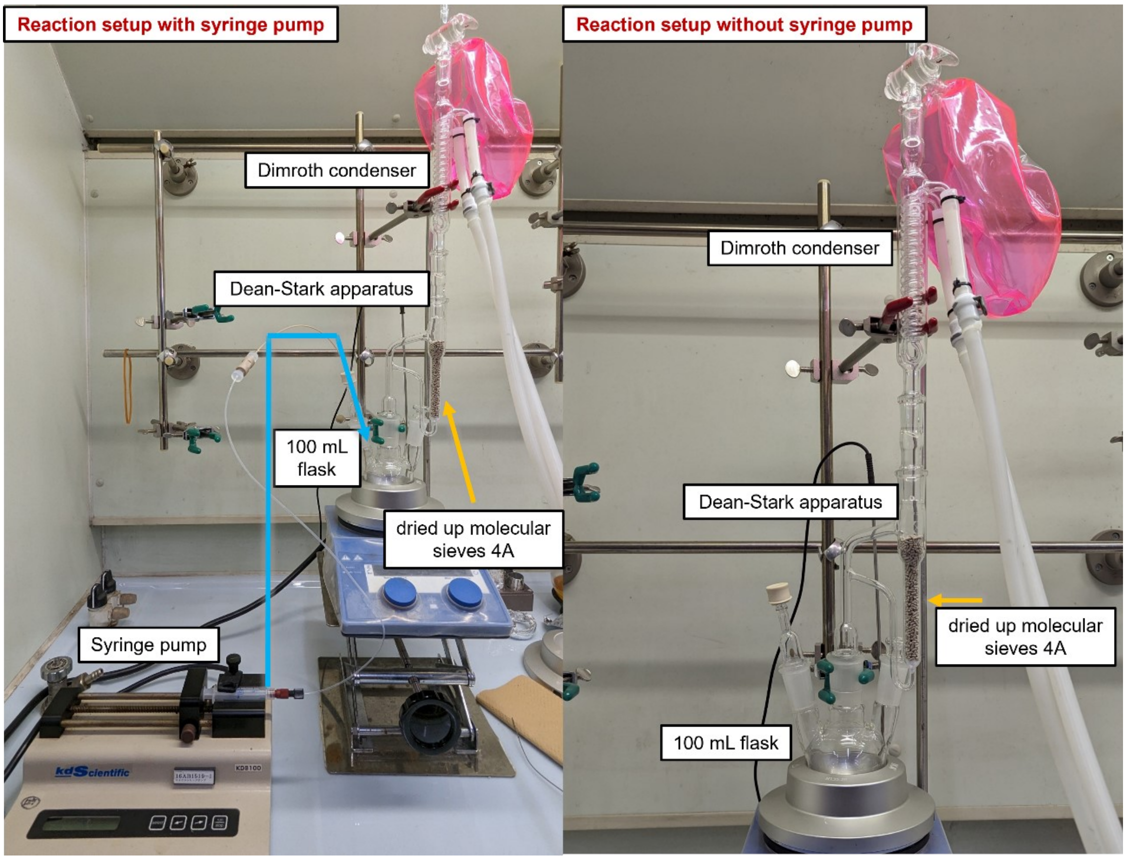


entry	catalyst	condition	GC area ratio of **1a/3aa/6aa**
1	wet $Pd(OH)_2/C$ [wako]	toluene reflux	45/37/18
2	wet Pd/C type NX [NE Chemcat]	toluene reflux	26/40/33
3	wet Pd/C type UR [NE Chemcat]	toluene reflux	20/17/63
4	wet Pd/C type PE [NE Chemcat]	toluene reflux	97/0/3

5	wet Pd/C type E [NE Chemcat]	toluene reflux	46/31/23
6	wet Pd/C type K [NE Chemcat]	toluene reflux	22/55/23
7	wet Pd/C type STD [NE Chemcat]	toluene reflux	75/13/12
8	dry Pd/alumina [wako]	toluene reflux	0/100/0
9	dry Pd/C type PE [NE Chemcat]	toluene reflux	4/78/18
10	dry Pd/C type UR [NE Chemcat]	toluene reflux	6/66/28
11	dry Pd/C type UR [NE Chemcat]	K_2CO_3 (1.0 eq.), toluene reflux	1/95/4
12	dry Pd/C type UR [NE Chemcat]	toluene reflux, under air	8/59/33
13	dry Pd/C type UR [NE Chemcat]	neat, 140 °C	17/0/83(52)[a]
14	dry Pd/C type UR [NE Chemcat]	K_2CO_3 (1.0 eq.), neat, 140 °C	2/71/28
15	dry Pd/C type UR [NE Chemcat]	xylene reflux	16/4/80(64)[a]

In entries 1-7, reactions were conducted without drying up process of catalysts. [a] Isolated yield.

4. Reaction apparatus and setup



5. General procedure for the synthesis of 3aa (GP-1, Table 1)

The reaction was conducted with a reaction setup shown in fig. S4 left, “Reaction setup with syringe pump”. A 100 mL 3-neck round bottom flask was equipped with Dean-Stark apparatus, Dimroth condenser, and syringe pump connected by Teflon tubing. A Dean-Stark apparatus was filled with molecular sieve 4A (7.0 g) which were dried up (200 °C, 6 h, in vacuo) beforehand. 2-Naphthol (1.4 g, 10 mmol), dodecane (10 mol%, as an internal standard), and anhydrous toluene (40 mL) were charged into the flask, and whole apparatus was purged with N_2 using a balloon. The mixture was refluxed for 30 min for the removal of residual water in the system. The reaction mixture was cooled to room temperature, and $AlMe_3$ (1 mol%, 1.8 mol/L in toluene, 60 μL) was added by a syringe. The reaction mixture was stirred at room temperature for 30 min for complete consumption of $AlMe_3$, and the mixture was allowed to reflux. Cyclohexanone dimethyl ketal (2.3 g, 20 mmol) was slowly added by a syringe pump (0.5 mL/h, 3 hours), and the mixture was stirred for additional 16 hours under reflux conditions. After cooling to room temperature, the reaction mixture was quenched with $NaHCO_3$ aq., filtered through a celite, and extracted with ethyl acetate. Obtained solution was analyzed by GC-FID (N_2: 34.0 cm/s, column temperature: 50 °C for 2 min, 20 °C/min heating then 250 °C for 10 min) to determine conversion of **1a** and yield of **3aa**.

6. General procedure for the aryl enol ether synthesis (GP-2, Table 2)

The reaction was conducted with a reaction setup shown in fig. S4 right, "Reaction setup without syringe pump". A 100 mL 3-neck round bottom flask was equipped with Dean-Stark apparatus and Dimroth condenser. A Dean-Stark apparatus was filled with molecular sieve 4A (7.0 g) which were dried up (200 °C, 6 h, in vacuo) beforehand. Phenol derivative (10 mmol) and anhydrous toluene (40 mL) were charged into the flask, and whole apparatus was purged with N_2 using a balloon. The mixture was refluxed for 30 min for the removal of residual water in the system. The reaction mixture was cooled to room temperature, and $AlMe_3$ (1 mol%, 1.8 mol/L in toluene, 60 μL) was added by a syringe. The reaction mixture was stirred at room temperature for 30 min for complete consumption of $AlMe_3$, and the mixture was allowed to reflux. Dimethyl ketal (20 mmol) was added all at once by a syringe and the mixture was stirred for additional 16 hours under reflux conditions. After cooling to room temperature, the reaction mixture was quenched with $NaHCO_3$ aq., filtered through a celite, and extracted with ethyl acetate. Obtained solution was concentrated in vacuo and purified by silica-gel column chromatography (ethyl acetate/hexane) to obtain the corresponding aryl enol ether. If silica-gel column chromatography was not able to completely purify, the product was purified by recycling preparative GPC (chloroform) using part of reaction mixture.

7. General procedure for the diaryl ether synthesis using Pd/C (GP-3, Table 3)

Wet 20% Pd/C [type UR, NE Chemcat] (10 mol%, 106.4 mg) was charged into a screw-capped tube and dried up *in vacuo*. Aryl enol ether (1.0 mmol), anhydrous xylene (5 mL), and styrene (2 eq., 230 μL) were added, and the mixture was stirred at 160 °C for 19 hours. The reaction mixture was cooled to room temperature and was filtered through celite with ethyl acetate as an eluent. The filtrate was concentrated *in vacuo* and purified by silica-gel column chromatography (ethyl acetate/hexane) to obtain the corresponding diaryl ether.

8. General procedure for the diaryl ether synthesis using DDQ (GP-4, Table 3)

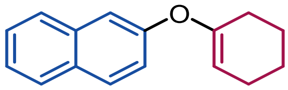
Aryl enol ether (0.2 mmol) was dissolved in anhydrous toluene (2 mL), and DDQ (2 eq., 90.8 mg) was added to the mixture in a screw-capped tube, and the mixture was stirred at 140 °C for 17 hours. The reaction mixture was cooled to room temperature and filtered through celite with ethyl acetate as an eluent. The filtrate was concentrated *in vacuo* and purified by silica-gel preparative thin-layer chromatography (PTLC) (ethyl acetate/hexane) to obtain the corresponding diaryl ether.

9. A procedure for one-pot synthesis of 6aa (Scheme 3)

A Dean-Stark apparatus was filled with molecular sieve 4A (7.0 g) which were dried up (200 °C, 6 h, in vacuo) beforehand. Naphthol (1.4 g, 10.0 mmol) and anhydrous xylene (40 mL) were charged into the flask, and whole apparatus was purged with N_2 using a balloon. The mixture was refluxed for 30 min for the removal of residual water in the system. The reaction mixture was cooled to room temperature, and $AlMe_3$ (1 mol%, 1.8 mol/L in toluene, 60 μL) was added by a syringe. The reaction mixture was stirred at room temperature for 30 min for complete consumption of $AlMe_3$, and the mixture was allowed to reflux. Cyclohexanone dimethyl ketal (2.3 g, 20 mmol) was added all at once by a syringe and the mixture was stirred for additional 16 hours under reflux conditions. The reaction mixture was cooled to room temperature. 4-*tert*-Butyl styrene (20 mmol, 4.1 mL) and wet 20% Pd/C [type UR, NE Chemcat] (5 mol%, 531.8 mg) were added, and the reaction mixture was refluxed again for 19 hours. The reaction mixture was cooled to room temperature, was quenched with $NaHCO_3$ aq., was filtered through a celite, and was extracted with ethyl acetate. Obtained solution was concentrated *in vacuo* and was purified by silica-gel column chromatography (ethyl acetate/hexane) to obtain 2-naphthyl phenyl ether (**6aa**, 1.7 g, 5.1 mmol) in 51% yield.

10. Spectroscopic data of products

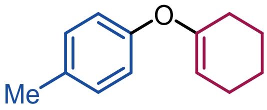
2-(1-Cyclohexenyl)oxynaphthalene (3aa)



According to GP-2, 2-naphthol (**1a**, 1.4 g, 10.0 mmol) and cyclohexanone dimethyl ketal (**2a**, 2.3 g, 20.0 mol) was used. 2-(1-Cyclohexenyl)oxynaphthalene (**3aa**) was obtained by silica-gel column chromatography (ethyl acetate/hexane: 1/50) in 86% yield (1.9 g, 8.6 mmol) as a colorless solid.

MP: 44.2–45.2 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.79–7.76 (m, 2H), 7.73 (d, J = 8.2 Hz, 1H), 7.44 (ddd, J = 7.5, 7.5,1.3 Hz, 1H), 7.36 (ddd, J = 7.5, 7.5, 1.3 Hz, 1H), 7.32 (d, J = 2.4 Hz, 1H), 7.21 (dd, J = 8.9, 2.4 Hz, 1H),5.11 (t, J = 3.9 Hz, 1H),2.26–2.22(m, 2H), 2.14–2.08 (m, 2H), 1.82–1.76 (m, 2H), 1.67–1.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.1, 153.2, 134.4, 129.9, 12.94, 127.7, 127.0, 126.3, 124.3, 120.3, 113.6, 107.5, 26.6, 23.7, 22.9, 22.3; IR (ATR) cm^{-1}: 3053, 3021, 2944, 2928, 2855, 2843, 1682, 1626, 1596, 1559, 1461, 1440, 1385, 1361, 1346, 1336, 1250, 1213, 1167, 1128, 1109, 1081, 1054, 1042, 1016; ESI-HRMS m/z: 225.1280 ($[M+H]^+$); Calcd. for $C_{16}H_{17}O_3$: 225.1279.

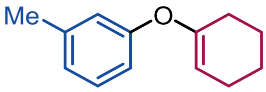
1-(1-Cyclohexenyl)oxy-4-methylbenzene (3ba)



According to GP-2, *p*-cresol (**1b**, 1.1 g, 10.0 mmol) and cyclohexanone dimethyl ketal (**2a**, 2.3 g, 20.0 mol) was used. 1-(1-Cyclohexenyl)oxy-4-methylbenzene (**3ba**) was obtained by silica-gel column chromatography (only hexane) in 75% yield (1.4 g, 7.5 mmol) as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.09 (d, *J* = 8.3 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 2H), 4.95 (t, *J* = 3.9 Hz, 1H), 2.30 (s, 3H), 2.20–2.15(m, 2H), 2.08–2.03 (m, 2H), 1.77–1.71 (m, 2H), 1.61–1.56 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 153.9, 153.6, 132.1, 129.9, 119.0, 105.6, 26.7, 23.6, 22.9, 22.3, 20.6; IR (ATR) cm^{-1}: 3029, 2927, 2859, 2842, 1672, 1610, 1587, 1504, 1458, 1442, 1372, 1364, 1338, 1298, 1265, 1220, 1164, 1131, 1102, 1085, 1078, 1042, 1016; ESI-HRMS m/z: 189.1275 ([M+H]$^+$); Calcd. for $C_{13}H_{17}O_3$: 189.1279.

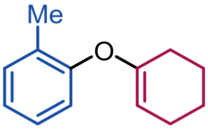
1-(1-Cyclohexenyl)oxy-3-methylbenzene (3ca)



According to GP-2, *m*-cresol (**1c**, 1.1 g, 10.0 mmol) and cyclohexanone dimethyl ketal (**2a**, 2.3 g, 20.0 mol) was used. 1-(1-Cyclohexenyl)oxy-3-methylbenzene (**3ca**) was obtained by silica-gel column chromatography (only hexane) in 64% yield (1.2 g, 6.4 mmol) as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.16 (dd, *J* = 7.5, 7.5 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 6.79–6.77 (m, 2H), 5.03 (t, *J* = 3.9 Hz, 1H), 2.32 (s, 3H), 2.19–2.14 (m, 2H), 2.10–2.05 (m, 2H), 1.78–1.72 (m, 2H), 1.63–1.57 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 156.3, 153.1, 139.5, 129.1, 123.3, 119.4, 115.6, 106.8, 26.6, 23.6, 22.9, 22.2, 21.4; IR (ATR) cm^{-1}: 3030, 2928, 2859, 2842, 1730, 1675, 1609, 1586, 1486, 1444, 1372, 1364, 1338, 1299, 1252, 1155, 1125, 1082, 1041, 1000; ESI-HRMS m/z: 189.1279 ([M+H]$^+$); Calcd. for $C_{13}H_{17}O_3$: 189.1279.

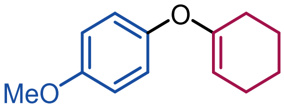
1-(1-Cyclohexenyl)oxy-2-methylbenzene (3da)



According to GP-2, *o*-cresol (**1d**, 1.1 g, 10.0 mmol) and cyclohexanone dimethyl ketal (**2a**, 2.3 g, 20.0 mol) was used. 1-(1-Cyclohexenyl)oxy-2-methylbenzene (**3da**) was obtained by silica-gel column chromatography (only hexane) in 44% yield (822.6 mg, 4.4 mmol) as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.18–7.11 (m, 2H), 6.98 (ddd, *J* = 7.7, 7.7, 1.1 Hz, 1H), 6.93 (d, *J* = 7.7 Hz, 1H), 4.71 (t, *J* = 3.9 Hz, 1H), 2.23–2.20 (m, 5H), 2.05–1.99 (m, 2H), 1.78–1.72 (m, 2H), 1.61–1.55 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 153.8, 153.5, 131.0, 129.7, 126.7, 123.2, 119.5, 103.1, 26.8, 23.5, 22.9, 22.4, 16.0; IR (ATR) cm^{-1}: 3059, 3026, 2928, 2859, 2842, 1674, 1605, 1586, 1488, 1458, 1444, 1372, 1338, 1299, 1265, 1229, 1187, 1143, 1134, 1111, 1085, 1075, 1040; ESI-HRMS m/z: 189.1277 ([M+H]$^+$); Calcd. for $C_{13}H_{17}O_3$: 189.1279.

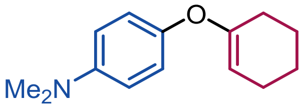
1-(1-Cyclohexenyl)oxy-4-methoxybenzene (3ea)



According to GP-2, 4-methoxyphenol (**1e**, 1.1 g, 10.0 mmol) and cyclohexanone dimethyl ketal (**2a**, 2.3 g, 20.0 mol) was used. The yield of 1-(1-Cyclohexenyl)oxy-4-methoxybenzene (**3ea**, 68% yield) was determined by ^{1}H NMR using ethylene carbonate as an internal standard. Purified **3ea** was obtained by recycling preparative GPC (column: JAIGEL-2HR Plus,ethyl acetate) using part of reaction mixture as a pale yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 6.92 (d, *J* = 9.1 Hz, 2H), 6.83 (d, *J* = 9.1 Hz, 2H), 4.82 (t, *J* = 4.0 Hz, 1H), 3.78 (s, 3H), 2.21–2.16 (m, 2H), 2.05–2.00 (m, 2H), 1.76–1.70 (m, 2H), 1.60–1.54 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 155.4, 154.5, 149.4, 120.8, 114.5, 103.7, 55.6, 26.9, 23.5, 22.9, 22.3; IR (ATR) cm^{-1}: 3000, 2929, 2858, 2838, 1672, 1609, 1592, 1501, 1464, 1441, 1376, 1338, 1296, 1265, 1246, 1209, 1180, 1160, 1130, 1099, 1085, 1075, 1036, 1008; ESI-HRMS m/z: 204.1148 ([M+H]$^+$); Calcd. for $C_{13}H_{16}O_2$: 204.1150.

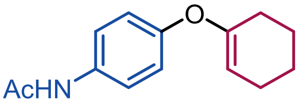
4-(1-Cyclohexenyl)oxy-*N,N*-dimethylaniline (3fa)



According to GP-2, 4-(dimethylamino)phenol (**1f**, 1.4 g, 10.0 mmol) and cyclohexanone dimethyl ketal (**2a**, 2.3 g, 20.0 mol) was used. The yield of 4-(1-Cyclohexenyl)oxy-*N,N*-dimethylaniline (**3fa**, 43% yield) was determined by ^{1}H NMR using ethylene carbonate as an internal standard. Purified **3fa** was obtained by recycling preparative GPC (column: JAIGEL-2HR Plus, ethyl acetate) using part of reaction mixture as a pale yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 6.90 (d, *J* = 9.0 Hz, 2H), 6.70 (d, *J* = 9.0 Hz, 2H), 4.77 (t, *J* = 3.9 Hz, 1H), 2.90 (s, 6H), 2.21–2.17 (m, 2H), 2.04–1.99 (m, 2H), 1.76–1.70 (m, 2H), 1.60–1.54 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 154.9, 147.2, 146.9, 120.8, 113.9, 102.5, 41.3, 27.0, 23.5, 22.9, 22.4; IR (ATR) cm^{-1}: 3043, 2927, 2884, 2856, 2840, 2796, 1670, 1610, 1575, 1510, 1442, 1372, 1362, 1338, 1298, 1265, 1223, 1177, 1163, 1128, 1085, 1074, 1058, 1006; ESI-HRMS m/z: 217.1461 ([M+H]$^+$); Calcd. for $C_{14}H_{19}NO$: 217.1467.

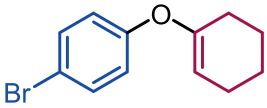
4‘-(1-Cyclohexenyl)oxyacetanilide (3ga)



According to GP-2, 4-acetoamidephenol (**1g**, 1.4 g, 10.0 mmol) and cyclohexanone dimethyl ketal (**2a**, 2.3 g, 20.0 mol) was used. 4‘-(1-Cyclohexenyl)oxyacetanilide (**3ga**) was obtained by silica-gel column chromatography (ethyl acetate/hexane: 1/2) in 26% yield (605.0 mg, 2.6 mmol) as a colorless solid.

MP: 116.5–118.1 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.59 (brs, 1H), 7.40 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 4.97 (t, *J* = 3.9 Hz, 1H), 2.17–2.14 (m, 5H), 2.08–2.02 (m, 2H), 1.76–1.70 (m, 2H), 1.61–1.55 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 168.4, 153.4, 152.6, 132.8, 121.5, 119.4, 106.2, 26.6, 24.3, 23.5, 22.8, 22.2; IR (ATR) cm^{-1}: 3277, 3244, 3191, 3129, 3057, 2941, 2917, 2909, 2892, 2881, 2863, 2838, 1671, 1658, 1606, 1557, 1504, 1457, 1447, 1438, 1404, 1369, 1336, 1319, 1296, 1266, 1233, 1211, 1161, 1143, 1127, 1104, 1082, 1074, 1052, 1040, 1016; ESI-HRMS m/z: 231.1262 ([M+H]$^+$); Calcd. for $C_{14}H_{17}NO_2$: 231.1259.

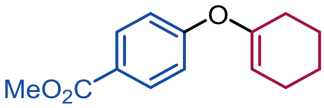
1-Bromo-4-(1-Cyclohexenyl)oxybenzene (3ha)



According to GP-2, 4-bromophenol (**1h**, 1.7 g, 10.0 mmol) and cyclohexanone dimethyl ketal (**2a**, 2.3 g, 20.0 mol) was used. The yield of 1-bromo-4-(1-Cyclohexenyl)oxybenzene (**3ha**, 48% yield) was determined by ^{1}H NMR using ethylene carbonate as an internal standard. Further purification was conducted using a part of reaction mixture by recycling preparative GPC (column: JAIGEL-2HR Plus, ethyl acetate) to obtain an analytical sample of **3ha** as a pale yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.38 (d, *J* = 8.9 HZ, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 5.06 (t, *J* = 3.9 Hz, 1H), 2.16–2.13 (m, 2H), 2.10–2.05 (m, 2H), 1.77–1.71 (m, 2H), 1.62–1.57 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 155.6, 152.8, 132.3, 120.4, 114.9, 107.8, 26.5, 23.6, 22.8, 21.1; IR (ATR) cm^{-1}: 2929, 2886, 2859, 2842, 1674, 1585, 1481, 1458, 1441, 1398, 1372, 1362, 1338, 1229, 1266, 1221, 1163, 1127, 1095, 1166, 1008; ESI-HRMS m/z: 255.0204 ([M+H]$^+$); Calcd. for $C_{12}H_{14}BrO$: 255.0208.

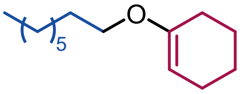
Methyl 4-(1-Cyclohexenyl)oxybenzoate (3ia)



According to GP-2, methyl 4-hydroxybenzoate (**1i**, 1.5 g, 10.0 mmol) and cyclohexanone dimethyl ketal (**2a**, 2.3 g, 20.0 mol) was used. The yield of methyl 4-(1-Cyclohexenyl)oxybenzoate (**3ia**, 49% yield) was determined by ^{1}H NMR using ethylene carbonate as an internal standard. Further purification was conducted using a part of reaction mixture by recycling preparative GPC (column: JAIGEL-2HR Plus, ethyl acetate) to obtain an analytical sample of **3ia** as a pale colorless solid.

MP: 36.5–38.0 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.98 (d, *J* = 8.9 Hz, 2H), 6.98 (*J* = 8.9 Hz, 2H), 5.27 (t, *J* = 3.9 Hz, 1H), 3.89 (s, 3H), 2.16–2.11 (m, 4H), 1.80–1.74 (m, 2H), 1.66–1.60 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 166.7, 160.9, 151.6, 131.5, 123.8, 117.0, 110.9, 61.9, 26.3, 23.7, 22.8, 22.0; IR (ATR) cm^{-1}: 2932, 2859, 2842, 1717, 1684, 1602, 1504, 1434, 1418, 1362, 1338, 1309, 1273, 1229, 1191, 1158, 1141, 1127, 1108, 1097, 1075, 1042, 1012; ESI-HRMS m/z: 232.1095 ([M+H]$^+$); Calcd. for $C_{14}H_{16}O_3$: 232.1099.

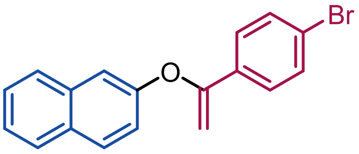
1-(Octyloxy)cyclohex-1-ene (3ja)



According to GP-2, methyl 1-octanol (**1j**, 1.3 g, 10.0 mmol) and cyclohexanone dimethyl ketal (**2a**, 2.3 g, 20.0 mol) was used. The yield of 1-(octyloxy)cyclohex-1-ene (**3ja**, 46% yield) was determined by ^{1}H NMR using ethylene carbonate as an internal standard. Further purification was conducted using a part of reaction mixture by recycling preparative GPC (column: JAIGEL-2HR Plus, ethyl acetate) to obtain an analytical sample of **3ja** as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 4.59 (t, J = 3.0 Hz, 1H), 3.61 (t, J = 6.7 Hz, 2H), 2.07–2.02 (m, 4H), 1.57–1.51 (m, 2H), 1.38–1.28 (m, 10H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 154.7, 93.6, 66.3, 31.8, 29.4, 29.3, 27.9, 26.2, 23.6, 23.0, 22.8, 22.6, 14.1; IR (ATR) cm^{-1}: 2934, 2856, 1665, 1460, 1445, 1433, 1372, 1339, 1305, 1267, 1240, 1187, 1171, 1138, 108, 1075, 1056, 1035; ESI-HRMS m/z: 211.2064 ([M+H]$^+$); Calcd. for $C_{14}H_{27}O$: 211.2062.

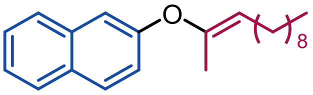
2-((1-(4-Bromophenyl)vinyl)oxy)naphthalene (3ab)



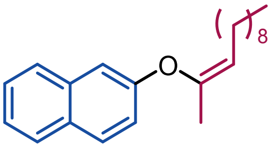
According to GP-2, 2-napthol (**1a**, 1.4 g, 10.0 mmol) and 1-bromo-4-(1,1-dimethoxy)benzene (**2b**, 4.9 g, 20.0 mol) was used. The yield of 2-((1-(4-bromophenyl)vinyl)oxy)naphthalene (**3ab**, 25% yield) was determined by ^{1}H NMR using ethylene carbonate as an internal standard. Further purification was conducted using a part of reaction mixture by recycling preparative GPC (column: JAIGEL-2HR Plus, ethyl acetate) to obtain an analytical sample of **3ab** as a colorless solid.

MP: 81.0–83.2 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.84–7.80 (m, 2H), 7.72 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 7.46–7.39 (m, 3H), 7.29 (dd, J = 8.9, 2.2 Hz, 1H), 5.11 (d, J = 2.5 Hz, 1H), 4.53 (d, J = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 158.6, 153.7, 134.3, 134.1, 131.5, 130.4, 129.8, 127.7, 127.2, 127.2, 126.5, 124.9, 122.9, 120.4, 115.5, 93.3; IR (ATR) cm^{-1}: 3056, 3030, 1915, 1624, 1598, 1586, 1559, 1504, 1486, 1467, 1438, 1392, 1362, 1351, 1305, 1295, 1287, 1279, 1266, 1244, 1213, 1158, 1148, 1121, 1114, 1089, 1072, 1006; ESI-HRMS m/z: 324.0141 ([M+H]$^+$); Calcd. for $C_{18}H_{13}BrO$: 324.0150.

(*E*)-2-(Dodec-2-en-2-yloxy)naphthalene ((*E*)-3ac)



(*Z*)-2-(Dodec-2-en-2-yloxy)naphthalene ((*Z*)-3ac)



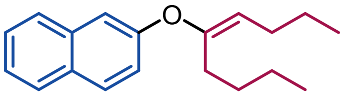
According to GP-2, 2-napthol (**1a**, 721.1 mg, 5.0 mmol) and cyclohexanone dimethyl ketal (**2a**, 2.3 g, 10.0 mol) was used. By silica-gel column chromatography (*E*)-2-(Dodec-2-en-2-yloxy)naphthalene ((*E*)-**3ac**) was obtained in 21% yield (328.7 mg, 1.1 mmol) as a colorless oil, and (*Z*)-2-(Dodec-2-en-2-yloxy)naphthalene ((*Z*)-**3ac**) was obtained in 50% yield (771.6 mg, 2.5 mmol) as a colorless oil (71% in total).

(*E*)-**3ac**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.79–7.76 (m, 2H), 7.71 (dd, J = 8.2, 0.4 Hz, 1H), 7.43 (ddd, J = 7.5, 7.5, 1.3 Hz, 1H), 7.36 (ddd, J = 7.5, 7.5, 1.3 Hz, 1H), 7.26 (d, J = 2.4 Hz, 1H), 7.19 (dd, J = 8.9, 2.4 Hz, 1H), 5.02 (dt, J

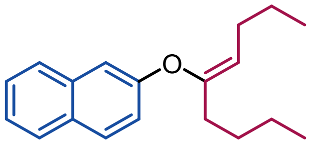
= 7.4, 0.8 Hz, 1H), 2.06 (q, *J* = 7.4 Hz, 2H), 1.92 (d, *J* = 0.8 Hz, 3H), 1.40–1.28 (m, 14H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5, 149.4, 134.4, 129.7, 129.4, 127.7, 126.9, 126.3, 124.1, 119.9, 113.2, 112.6, 31.9, 29.9, 29.6, 29.5, 29.3, 29.2, 26.8, 22.7, 14.6, 14.1; IR (ATR) cm^{-1}: 3059, 3026, 2954, 2922, 2853, 1681, 1653, 1631, 1599, 1510, 1464, 1440, 1382, 1365, 1355, 1265, 1249, 1214, 1165, 1150, 1124, 1019; ESI-HRMS m/z: 310.2291 ([M+H]$^{+}$); Calcd. for $C_{22}H_{30}O$: 310.2297.

(*Z*)-**3ac**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78–7.76 (m, 2H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.43 (ddd, *J* = 7.5, 7.5, 1.2 Hz, 1H), 7.34 (ddd, *J* = 7.5, 7.5, 1.2 Hz, 1H), 7.21–7.18 (m, 2H), 5.07 (dt, *J* = 7.2, 1.0 Hz, 1H), 2.04 (q, *J* = 7.2 Hz, 2H), 1.87 (d, *J* = 1.0 Hz, 3H), 1.38–1.21 (m, 14H), 0.86 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 146.8, 134.5, 129.5, 129.4, 127.7, 126.8, 126.3, 123.8, 118.6, 117.1, 109.9, 31.9, 29.6, 29.4, 29.3, 29.3, 25.2, 22.6, 18.4, 14.1; IR (ATR) cm^{-1}: 3057, 3026, 2952, 2922, 2853, 1689, 1629, 1600, 1511, 1464, 1442, 1387, 1378, 1365, 1355, 1343, 1323, 1305, 1265, 1249, 1213, 1165, 1120, 1076, 1042, 1019; ESI-HRMS m/z: 310.2290 ([M+H]$^{+}$); Calcd. for $C_{22}H_{30}O$: 310.2297.

(*E*)-2-(Non-4-en-5-yloxy)naphthalene ((*E*)-3ad)



(*Z*)-2-(Non-4-en-5-yloxy)naphthalene ((*Z*)-3ad)



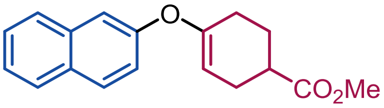
According to GP-2, 2-napthol (**1a**, 1.4 g, 5.0 mmol) and 5,5-dimethoxynonane (**2d**, 3.8 g, 20.0 mol) was used. The yield of (*E*)-2-(non-4-en-5-yloxy)naphthalene (**(*E*)-3ad**, 24% yield) and (*Z*)-2-(non-4-en-5-yloxy)naphthalene **((*E*)-3ad**, 70% yield) was determined by ^{1}H NMR using ethylene carbonate as an internal standard. Further purification was conducted using a part of reaction mixture by recycling preparative GPC (column: JAIGEL-2HR Plus, ethyl acetate) to obtain analytical sample of **(*E*)-3ad** and **(*Z*)-3ad** as a colorless oil.

(*E*)-**3ad**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79–7.76 (m, 2H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.43 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H), 7.36 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H), 7.29 (d, *J* = 2.4 Hz, 1H), 7.20 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.90 (t, *J* = 7.6 Hz, 1H), 2.31 (t, *J* = 7.5 Hz, 2H), 2.04 (q, *J* = 7.6 Hz, 2H), 1.60–1.50 (m, 2H), 1.44–1.34 (m, 4H),. 0.95–0.90 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 154.1, 134.4, 129.8, 129.4, 127.7, 126.9, 126.2, 124.2, 120.2, 113.3, 111.8, 29.6, 28.7, 28.3, 23.3, 22.4, 14.0, 13.8; IR (ATR) cm^{-1}: 3058, 2957, 2928, 2871, 2861, 1672, 1631, 1599, 1510, 1464, 1441, 1378, 1365, 1355, 1287, 1265, 1249, 1213, 1164, 1121, 1068, 1043, 1019, 1006; ESI-HRMS m/z: 268.1832 ([M+H]$^{+}$); Calcd. for $C_{19}H_{24}O$: 268.1827.

(*Z*)-**3ad**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78–7.75 (m, 2H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.42 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.33 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.22–7.18 (m, 2H), 5.09 (t, *J* = 7.3 Hz, 1H), 2.19 (t, *J* = 7.5 Hz, 2H), 2.02 (q, *J* = 7.3 Hz, 2H), 1.51–1.43 (m, 2H), 1.41–1.28 (m, 4H), 0.90–0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 150.8, 134.5, 129.5, 129.3, 127.8, 126.7, 126.3, 123.7, 118.6, 116.2, 109.8, 32.0, 29.1, 27.3, 22.7, 22.2, 13.9, 13.8;

IR (ATR) cm^{-1}: 3057, 3027, 2957, 2929, 2871, 2862, 1684, 1629, 1599, 1511, 1464, 1441, 1387, 1355, 1328, 1312, 1247, 1211, 1164, 1120, 1045, 1018; ESI-HRMS m/z: 268.1820 ([M+H]$^+$); Calcd. for $C_{19}H_{24}O$: 268.1827.

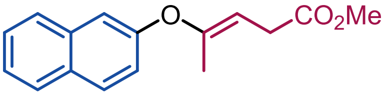
Methyl 4-(naphthalen-2-yloxy)cyclohex-3-ene-1-carboxylate (3ae)



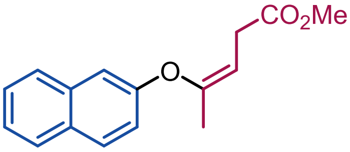
According to GP-2, 2-napthol (**1a**, 1.4 g, 10.0 mmol) and methyl 4,4-dimethoxycyclohexane-1-carboxylate (**2e**, 4.0 g, 20.0 mol) was used. The yield of methyl 4-(naphthalen-2-yloxy)cyclohex-3-ene-1-carboxylate (**3ae**, 80% yield) was determined by ^{1}H NMR using ethylene carbonate as an internal standard. Further purification was conducted using a part of reaction mixture by recycling preparative GPC (column: JAIGEL-2HR Plus, ethyl acetate) to obtain an analytical sample of **3ae** as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.80–7.77 (m, 2H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.45 (ddd, *J* = 7.5, 7.5, 1.3 Hz, 1H), 7.38 (ddd, *J* = 7.5, 7.5, 1.3 Hz, 1H), 7.32 (d, *J* = 2.4 Hz, 1H), 7.19 (dd, *J* = 8.9, 2.4 Hz, 1H), 5.04 (t, *J* = 3.8 Hz, 1H), 3.72 (s, 3H), 2.67–2.60 (m, 1H), 2.39–2.33 (m, 4H), 2.17–2.11 (m, 1H), 1.98–1.88 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 175.7, 153.7, 152.9, 134.3, 130.1, 129.5, 127.7, 127.0, 126.4, 124.5, 120.3, 114.2, 104.8, 51.7, 39.0, 26.1, 25.8, 25.3; IR (ATR) cm^{-1}: 3057, 3026, 2948, 2934, 2845, 1730, 1676, 1653, 1629, 1599, 1509, 1464, 1434, 1364, 1309, 1247, 1213, 1191, 1164, 1131, 1111, 1069, 1042, 1018; ESI-HRMS m/z: 282.1253 ([M+H]$^+$); Calcd. for $C_{18}H_{18}O_3$: 282.1256.

Methyl (*E*)-4-(naphthalen-2-yloxy)pent-3-enoate ((*E*)-3af)



Methyl (*Z*)-4-(naphthalen-2-yloxy)pent-3-enoate ((*Z*)-3af)



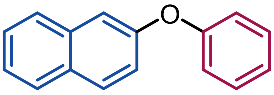
According to GP-2, 2-napthol (**1a**, 721.1 g, 5.0 mmol) and methyl 4,4-dimethoxypentanoate (**2f**, 3.5 g, 20.0 mol) was used. The yield of methyl (*E*)-4-(naphthalen-2-yloxy)pent-3-enoate (**(*E*)-3af**, 19% yield) and methyl (*Z*)-4-(naphthalen-2-yloxy)pent-3-enoate **((*Z*)-3af**, 49% yield) was determined by ^{1}H NMR using ethylene carbonate as an internal standard. Further purification was conducted using a part of reaction mixture by recycling preparative GPC (column: JAIGEL-2HR Plus, ethyl acetate) to obtain analytical sample of **(*E*)-3af** and **(*Z*)-3af** as a colorless oil.

(*E*)-**3af**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.80–7.78 (m, 2H), 7.74 (dd, *J* = 8.2, 0.6 Hz, 1H), 7.45 (ddd, *J* = 8.2, 6.9, 1.4 Hz, 1H), 7.38 (ddd, *J* = 8.2, 6.9, 1.4 Hz, 1H), 7.34 (d, *J* = 2.3 Hz, 1H), 7.21 (dd, *J* = 8.8, 2.3 Hz, 1H), 5.02 (ddd, *J* = 7.7, 7.7, 0.8 Hz, 1H), 3.69 (s, 3H), 3.08 (dd, *J* = 7.7, 0.8 Hz, 2H), 1.97 (d, *J* = 0.9 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 172.2, 153.6, 153.5, 134.3, 130.1, 129.6, 127.7, 127.1, 126.3, 124.6, 120.3, 114.4, 102.4, 51.9, 32.4, 15.2;

IR (ATR) cm^{-1}: 3057, 3024, 2998, 2951, 2925, 2845, 1737, 1682, 1653, 1631, 1599, 1510, 1464, 1435, 1385, 1355, 1308, 1247, 1213, 1197, 1163, 1145, 1120; ESI-HRMS m/z: 256.1095 ([M+H]$^+$); Calcd. for $C_{16}H_{16}O_3$: 256.1099.

(*Z*)-**3af**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79–7.77 (m, 2H), 7.71 (dd, *J* = 8.2, 0.4 Hz,1H), 7.44 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.36 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.25 (d, *J* = 2.5 Hz, 1H), 7.19 (dd, *J* = 8.8, 2.5 Hz, 1H), 5.29 (ddd, *J* = 7.0, 7.0, 1.2 Hz, 1H), 3.64 (s, 3H), 3.17 (dd, *J* = 7.0, 1.2 Hz, 2H), 1.91 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 153.6, 150.0, 134.3, 129.7, 127.7, 126.9, 126.5, 124.2, 118.8, 110.9, 107.8, 51.7, 30.7, 18.3; IR (ATR) cm^{-1}: 3057, 3024, 2988, 2951, 2921, 2845, 1737, 1694, 1654, 1628, 1599, 1560, 1540, 1510, 1465, 1435, 1409, 1381, 1351, 1295, 1247, 1211, 1197, 1164, 1148, 1118, 1042, 1010; ESI-HRMS m/z: 256.1101 ([M+H]$^+$); Calcd. for $C_{16}H_{16}O_3$: 256.1099.

2-Phenoxynaphthalene (6aa) [1]

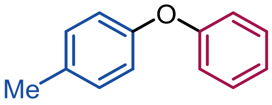


According to GP-3, 2-(1-Cyclohexenyl)oxynaphthalene (**3aa**, 224.2 mg, 1.0 mmol) was used. 2-Phenoxynaphthalene (**6aa**) was obtained by silica-gel column chromatography (ethyl acetate/hexane: 1/50) in 64% yield (143.8mg, 0.6 mmol) as a colorless solid.

According to GP-4, 2-(1-Cyclohexenyl)oxynaphthalene (**3aa**, 44.8 mg, 0.20 mmol) was used. 2-Phenoxynaphthalene (**6aa**) was obtained by PTLC (only hexane) in 89% yield (39.2 mg, 0.18 mmol) as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–7.80 (m, 2H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.46–7.36 (m, 4H), 7.31 (d, *J* = 2.4 Hz, 1H), 7.26 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.13 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.07 (dd, *J* = 8.6, 1.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2, 155.1, 134.3, 130.2, 129.8, 129.8, 127.7, 127.1, 126.5, 124.7, 123.4, 120.0, 119.1, 114.1.

1-Methyl-4-phenoxybenzene (6ba) [2]

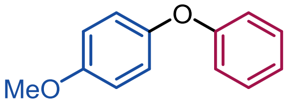


According to GP-3, 1-(1-Cyclohexenyl)oxy-4-methylbenzene (**3ba**, 188.0 mg, 1.0 mmol) was used. 1-Methyl-4-phenoxybenzene (**6ba**) was obtained by silica-gel column chromatography (only hexane) in 35% yield (63.8 mg, 0.4 mmol) as a colorless oil.

According to GP-4, 1-(1-Cyclohexenyl)oxy-4-methylbenzene (**3ba**, 37.5 mg, 0.20 mmol) was used. 1-Methyl-4-phenoxybenzene (**6ba**) was obtained by PTLC (only hexane) in 68% yield (25.1 mg, 0.14 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.24 (m, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.06 (dd, *J* = 7.4, 7.4 Hz, 2H), 6.97 (dd, *J* = 8.6, 1.0 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 154.8, 132.9, 130.2, 129.6, 122.8, 119.1, 118.4, 20.7.

1-Methoxy-4-phenoxybenzene (6ea) [2]

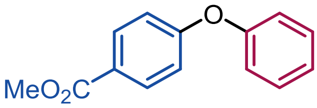


According to GP-3, 1-(1-Cyclohexenyl)oxy-4-methoxybenzene (**3ea**, 204.1 mg, 1.0 mmol) was used. 1-Methoxy-4-phenoxybenzene (**6ea**) was obtained by silica-gel column chromatography (ethyl acetate/hexane: 1/50) in 54% yield (109.0 mg, 0.5 mmol) as a colorless oil.

According to GP-4, 1-(1-Cyclohexenyl)oxy-4-methoxybenzene (**3ea**, 40.9 mg, 0.20 mmol) was used. 1-Methoxy-4-phenoxybenzene (**6ea**) was obtained by PTLC (ethyl acetate/hexane: 1/50) in 85% yield (34.2 mg, 0.17 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.04 (ddd, *J* = 7.6, 7.6, 0.9 Hz, 1H), 6.98 (d, *J* = 9.0 Hz, 2H), 6.94 (dd, *J* = 7.6, 0.9 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 155.9, 150.1, 129.6, 122.4, 120.8, 117.6, 114.9, 55.6.

Methyl 4-phenoxybenzoate (6ha) [2]

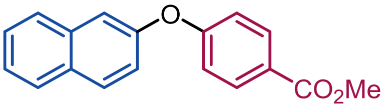


According to GP-3, methyl 4-(1-Cyclohexenyl)oxybenzoate (**3ha**, 232.8 mg, 1.0 mmol) was used. Methyl 4-phenoxybenzoate (**6ha**) was obtained by silica-gel column chromatography (ethyl acetate/hexane: 1/20) in 20% yield (45.4 mg, 0.2 mmol) as a colorless solid.

According to GP-4, methyl 4-(1-Cyclohexenyl)oxybenzoate (**3ha**, 46.4 mg, 0.20 mmol) was used. Methyl 4-phenoxybenzoate (**6ha**) was obtained by PTLC (ethyl acetate/hexane: 1/20) in 90% yield (40.8 mg, 0.18 mmol) as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.9 Hz, 2H), 7.41–7.37 (m, 2H), 7.19 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.06 (dd, *J* = 8.6, 1.0 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 161.8, 155.6, 131.7, 130.0, 124.5(2C), 120.1, 117.3, 52.0.

Methyl 4-(naphthalen-2-yloxy)benzoate (6ab) [3]



According to GP-4, methyl 4-(naphthalen-2-yloxy)cyclohex-3-ene-1-carboxylate (**3ab**, 56.6 mg, 0.20 mmol) was used. Methyl 4-(naphthalen-2-yloxy)benzoate (**6ab**) was obtained by PTLC (ethyl acetate/hexane: 1/20) in 80% yield (44.4 mg, 0.16 mmol) as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.9 Hz, 2H), 7.89–7.84 (m, 2H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.51–7.43 (m, 3H), 7.25 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.04 (d, *J* = 8.9 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 161.8, 153.4, 134.3, 131.7, 130.7, 130.2, 127.8, 127.3, 126.7, 125.3, 124.7, 120.3, 117.5, 116.1, 52.0.

11. References

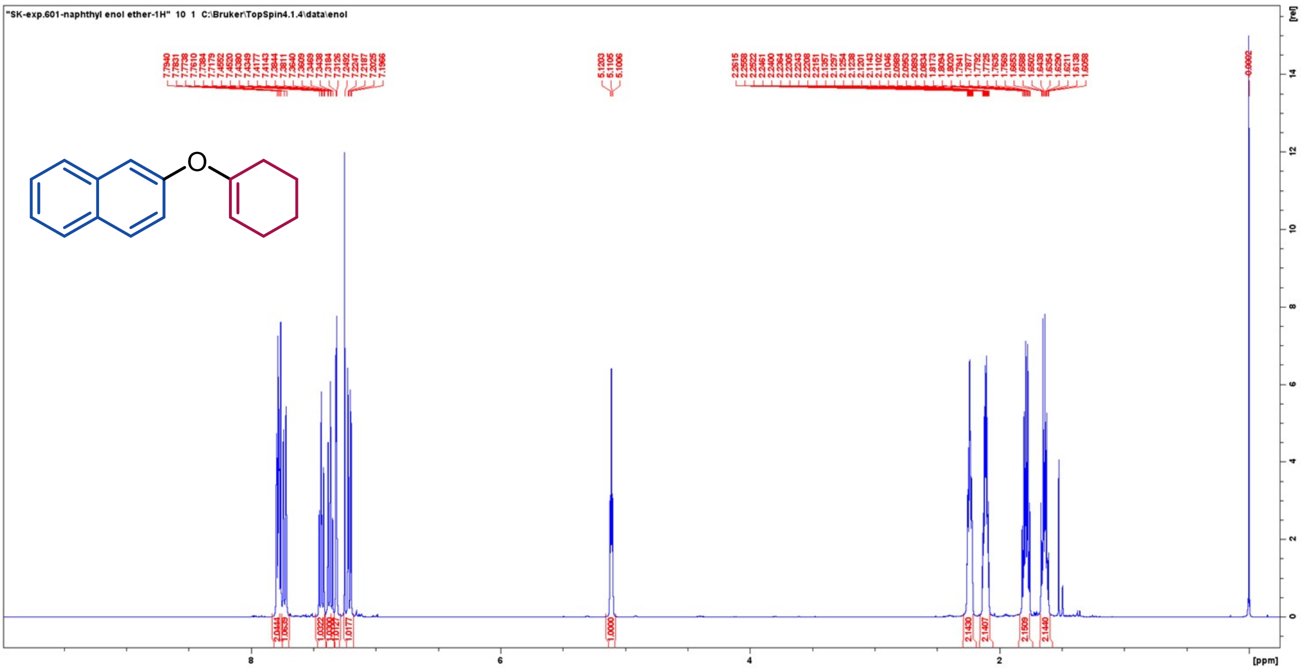
[1] Masahito Murai, Kazuki Origuchi, and Kazuhiko Takai *Org. Lett.* **2014**, *16*, 3828–3831.

[2] Kotaro Kikushima, Naoki Miyamoto, Kazuma Watanabe, Daichi Koseki, Yasuyuki Kita, and Toshifumi Dohi *Org. Lett.* **2022**, *24*, 1924–1928.

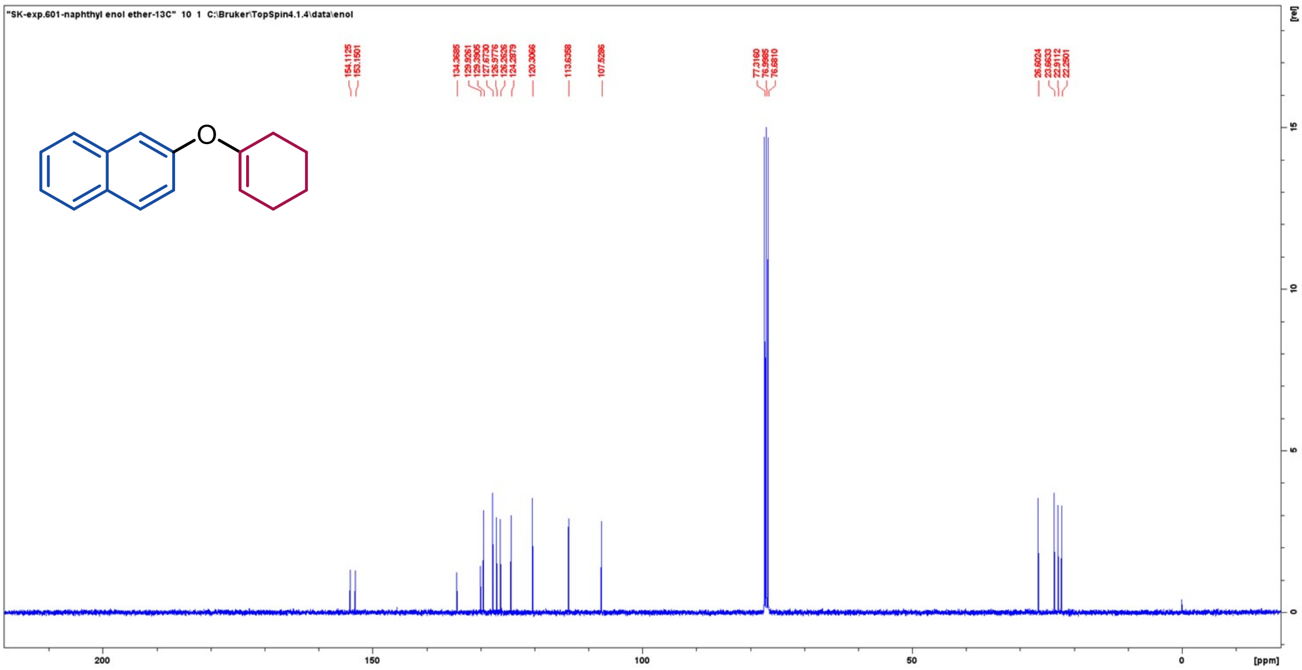
[3] Rory T. Gallagher, Souradeep Basu, David R. Stuart *Adv. Synth. Catal.* **2020**, *362*, 320–325.

12. ^{1}H and ^{13}C spectra of products

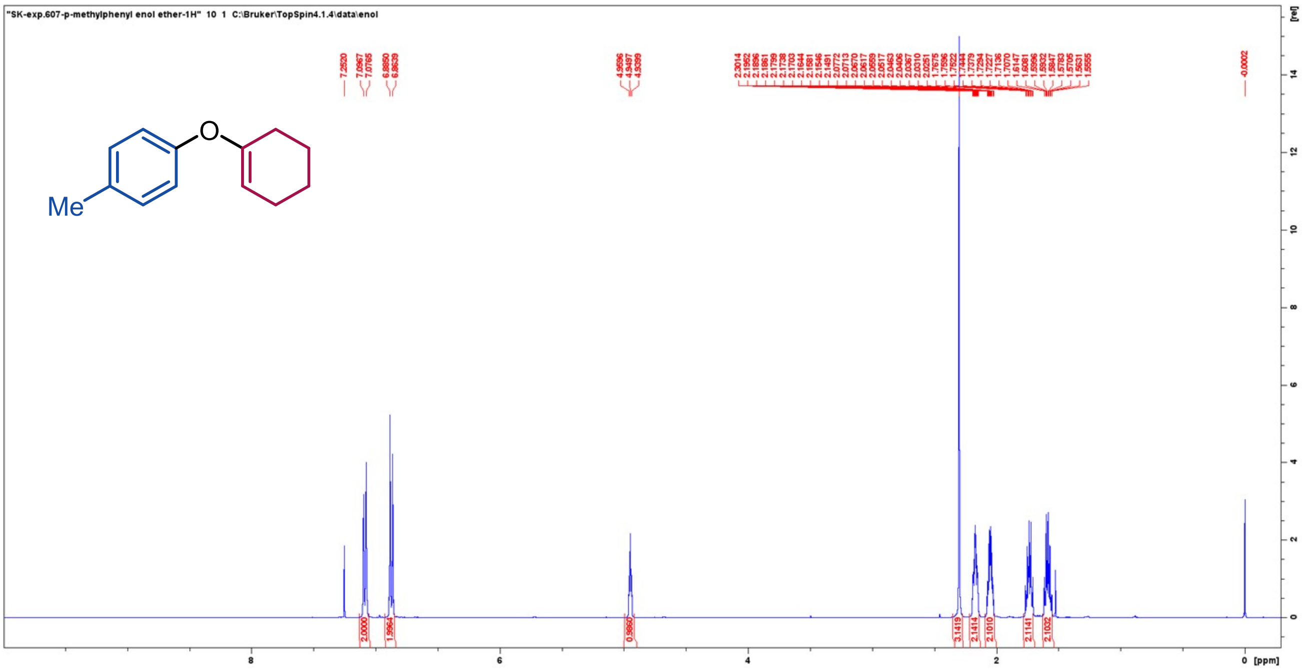
^{1}H NMR of **3aa** ($CDCl_3$, 400 Hz)



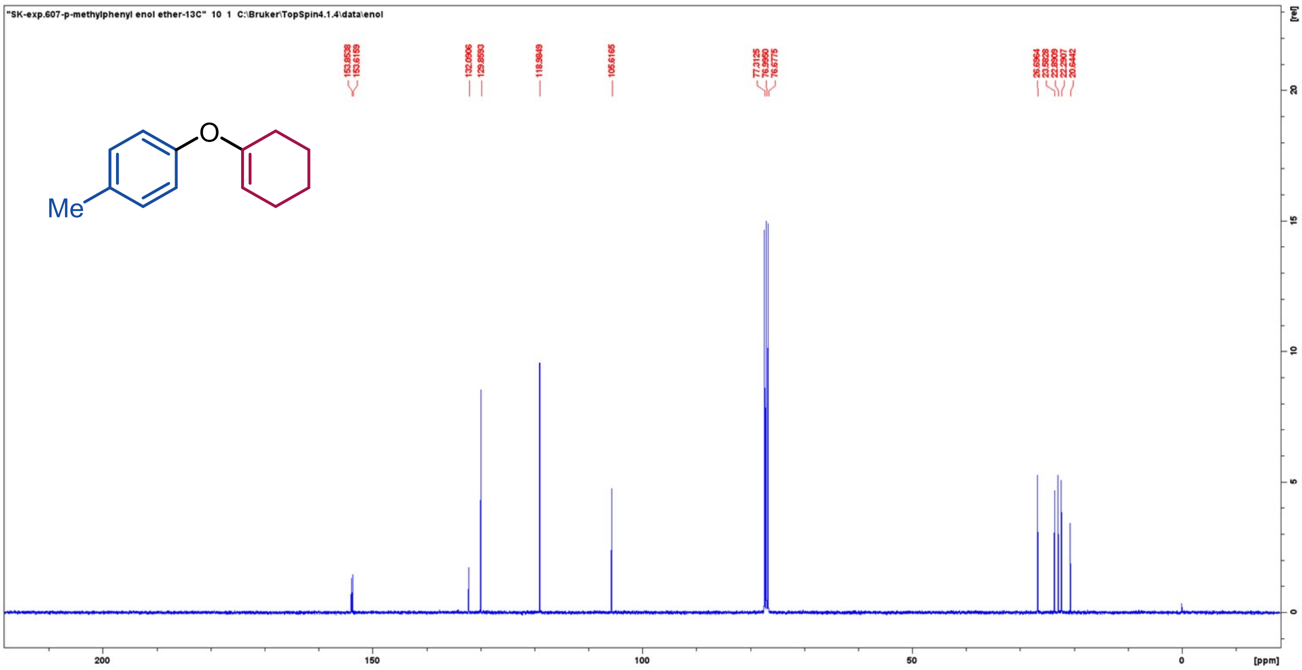
^{13}C NMR of **3aa** ($CDCl_3$, 100 Hz)



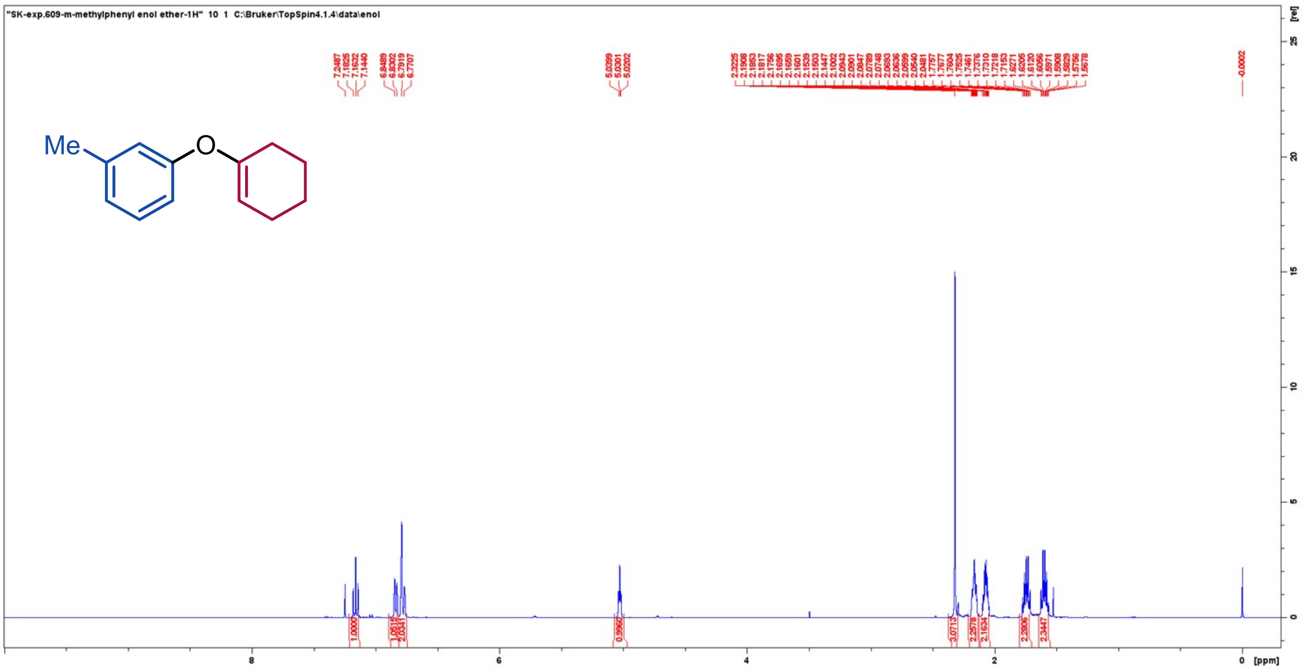
^{1}H NMR of **3ba** ($CDCl_3$, 400 Hz)



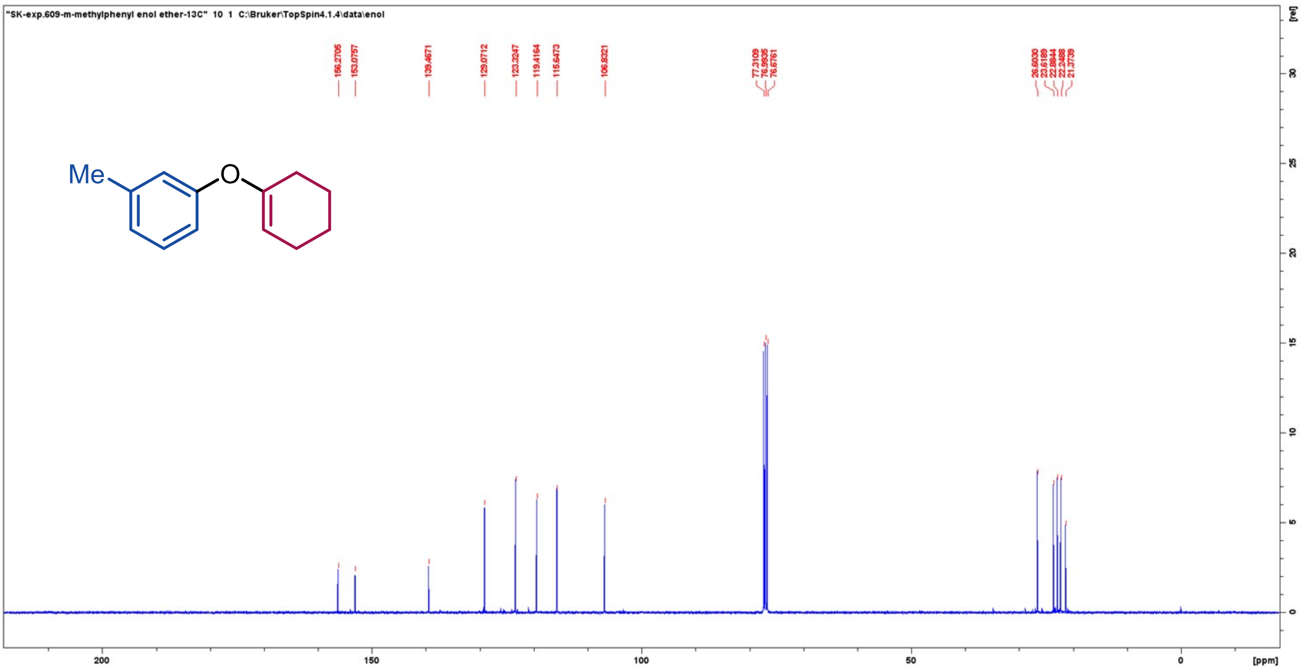
^{13}C NMR of **3ba** ($CDCl_3$, 100 Hz)



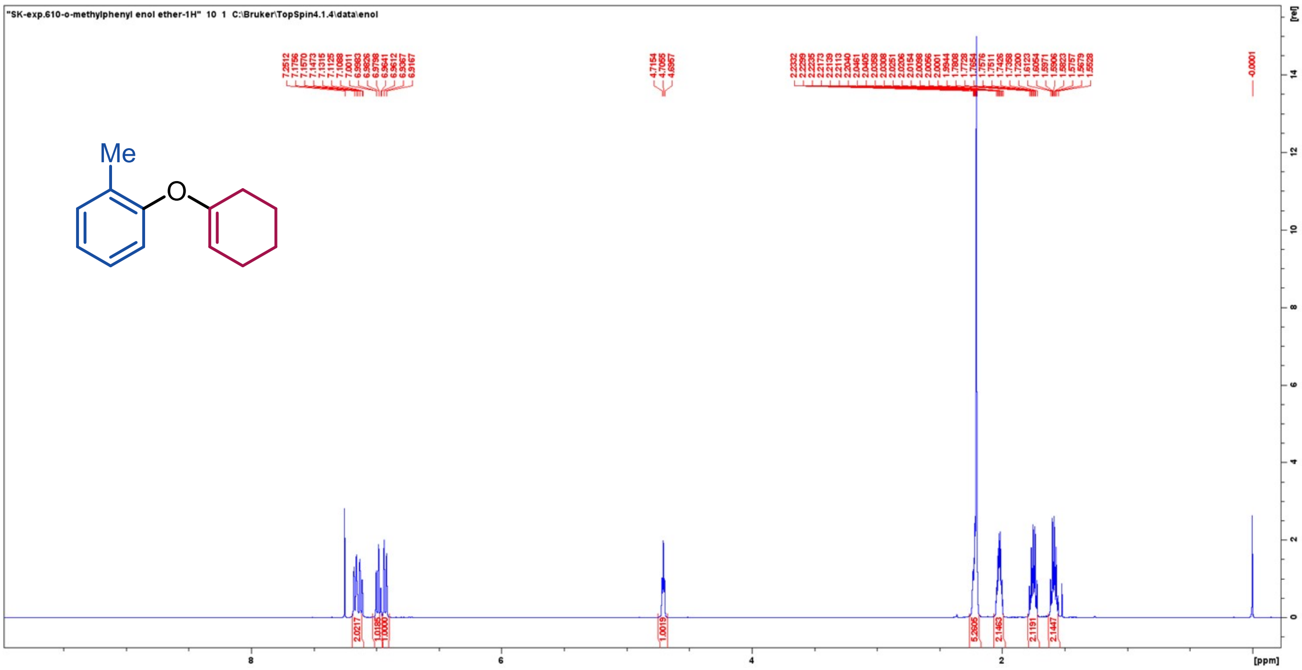
^{1}H NMR of **3ca** ($CDCl_3$, 400 Hz)



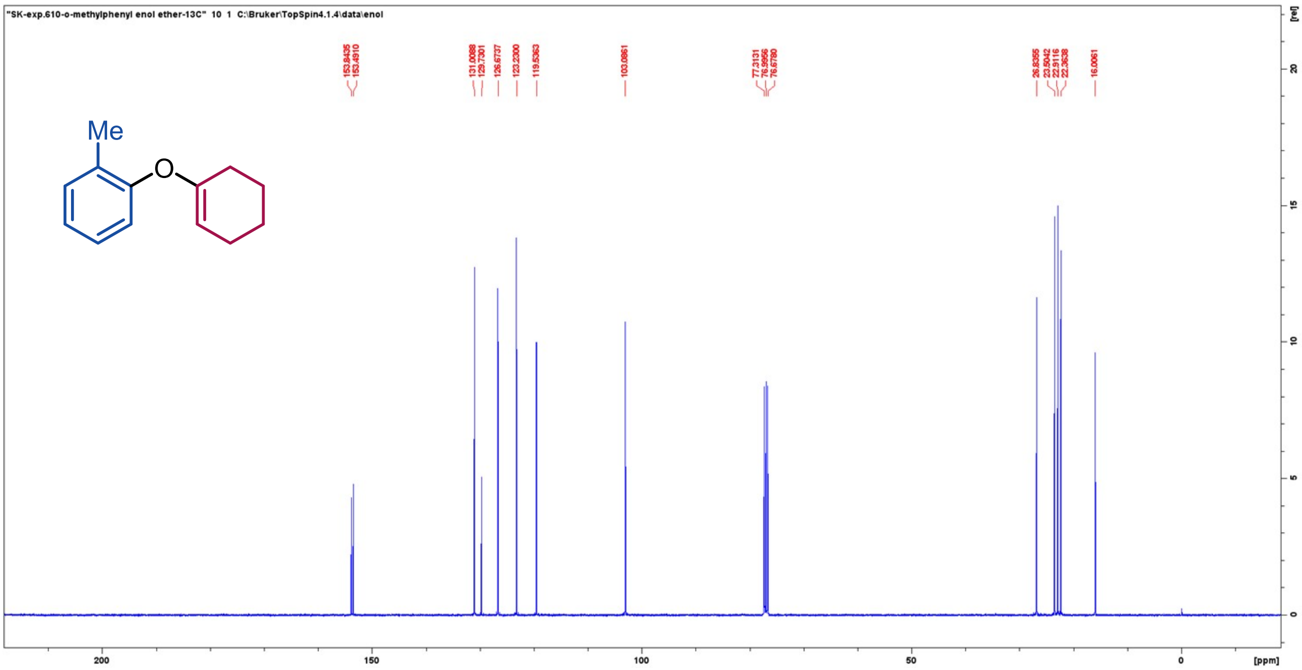
^{13}C NMR of **3ca** ($CDCl_3$, 100 Hz)



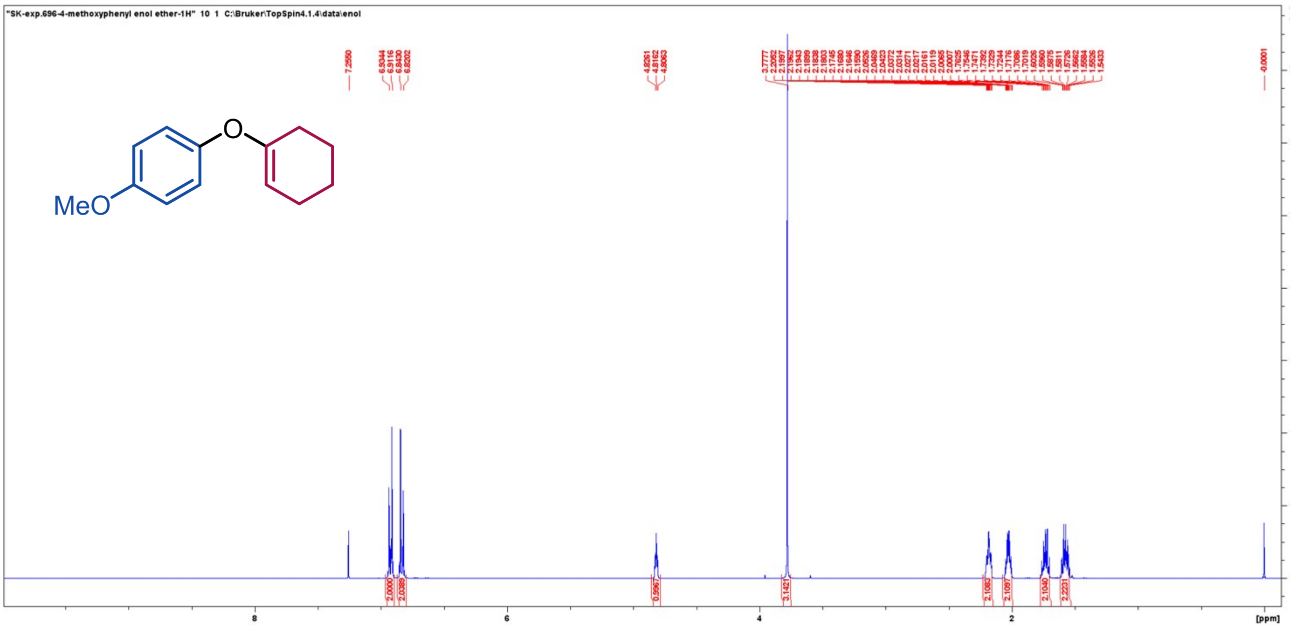
^{1}H NMR of **3da** (CDCl$_3$, 400 Hz)



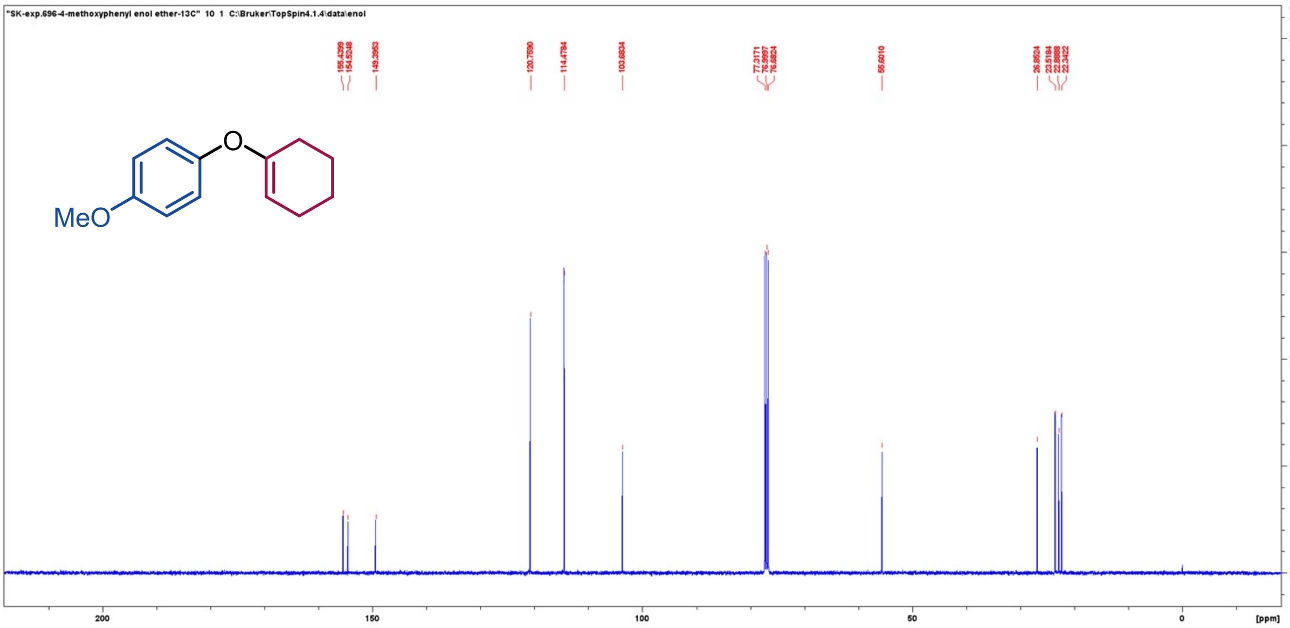
^{13}C NMR of **3da** (CDCl$_3$, 100 Hz)



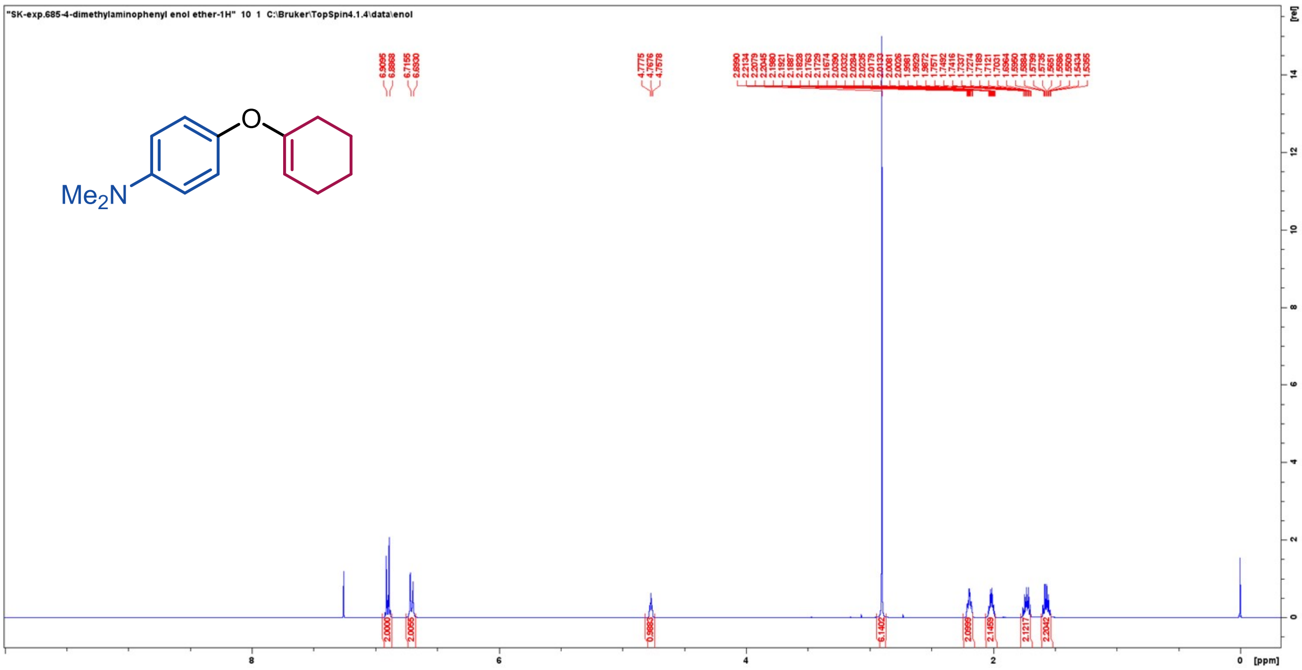
^{1}H NMR of **3ea** ($CDCl_3$, 400 Hz)



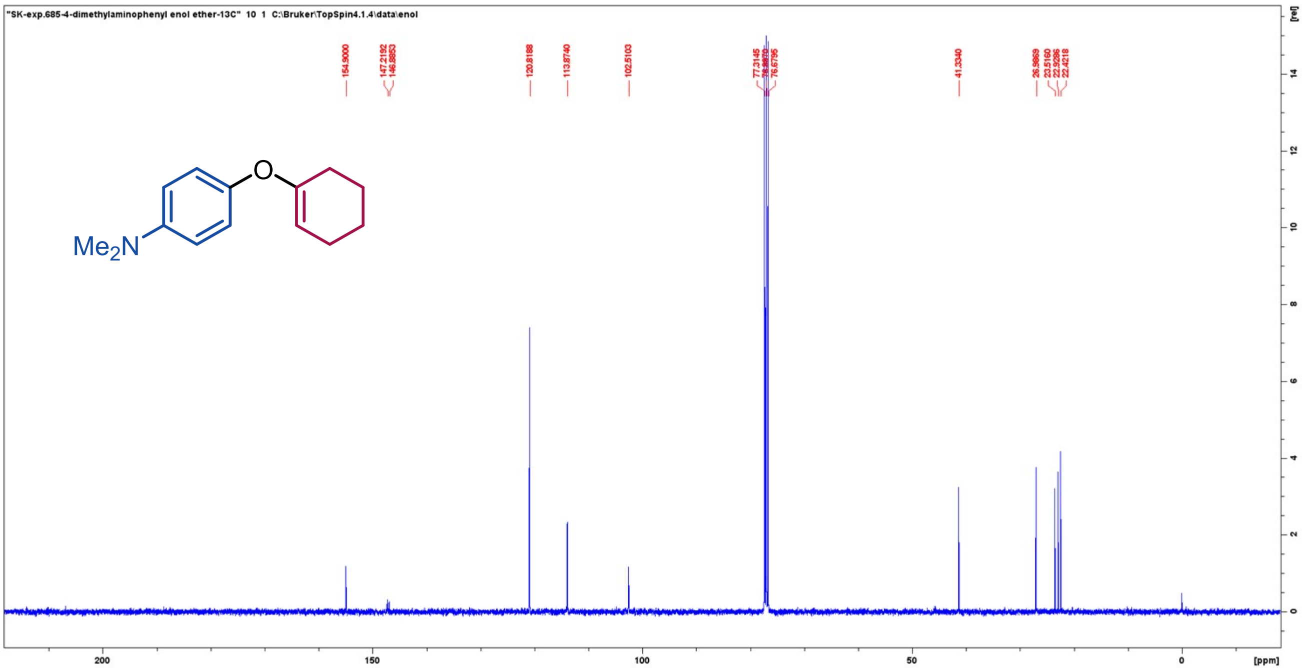
^{13}C NMR of **3ea** ($CDCl_3$, 100 Hz)



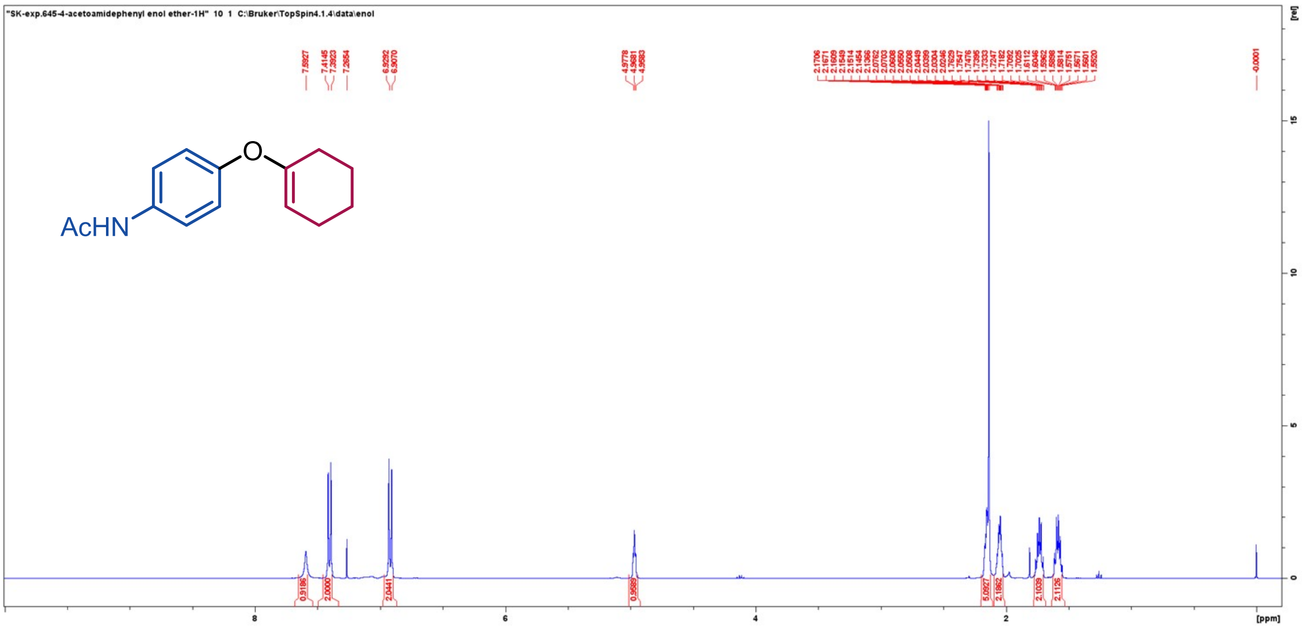
^{1}H NMR of **3fa** (CDCl$_3$, 400 Hz)



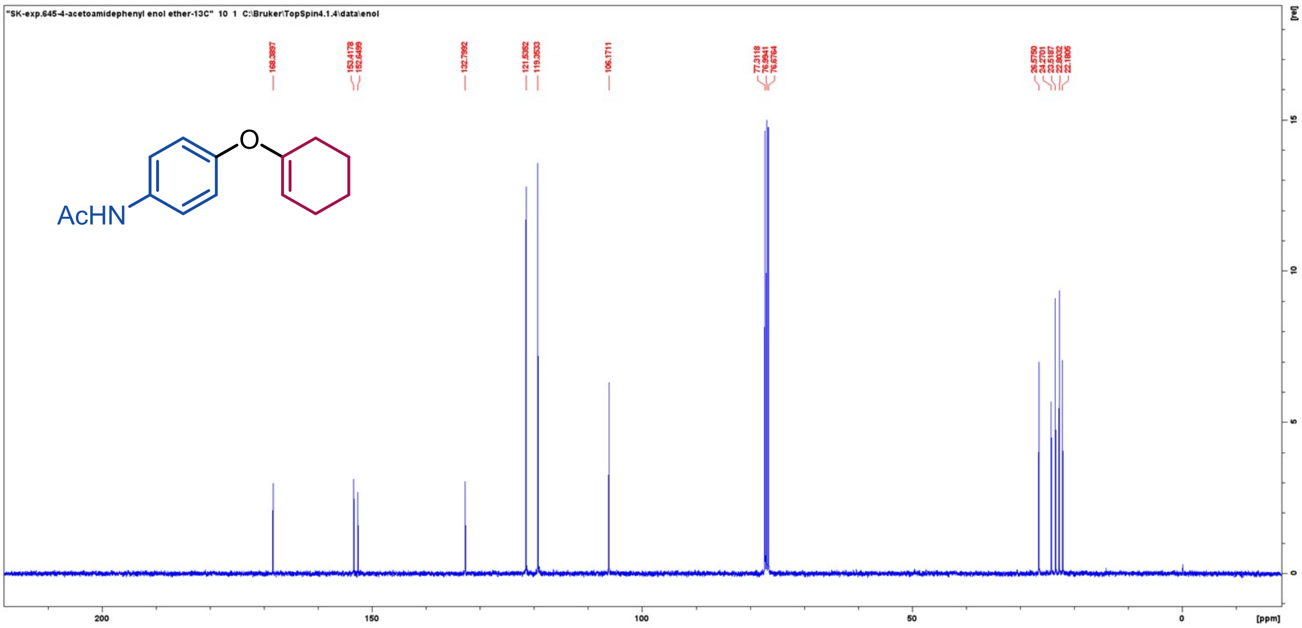
^{13}C NMR of **3fa** (CDCl$_3$, 100 Hz)



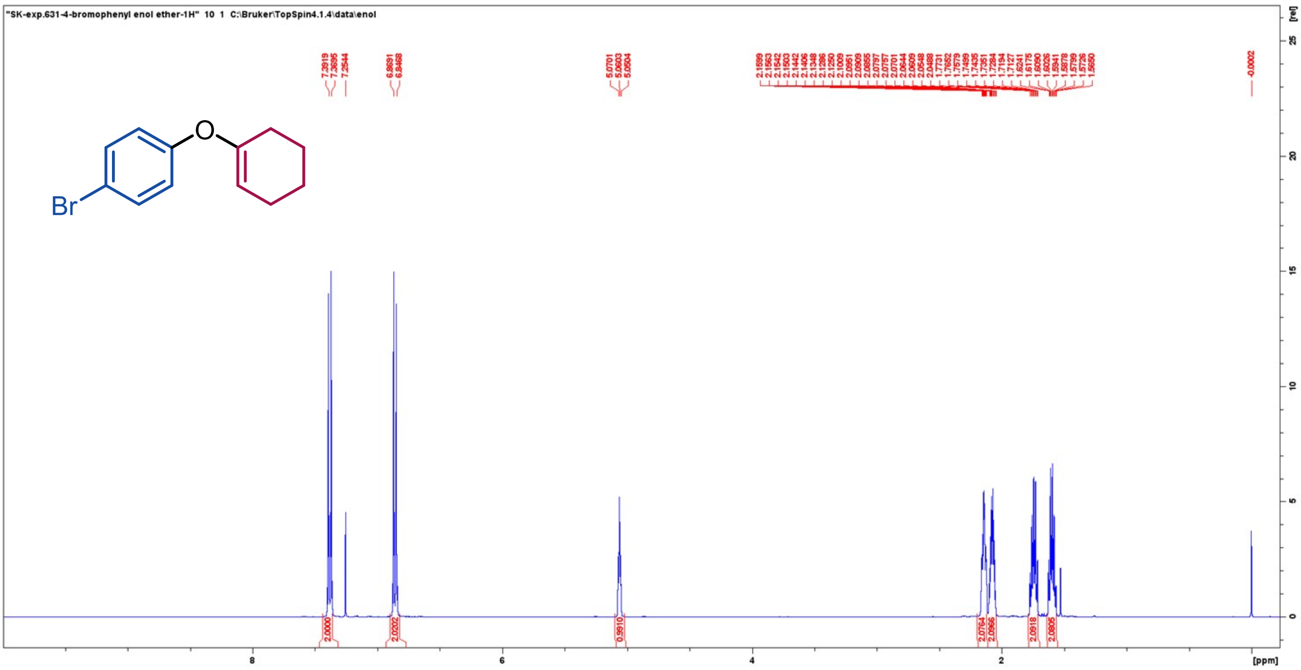
^{1}H NMR of **3ga** ($CDCl_3$, 400 Hz)



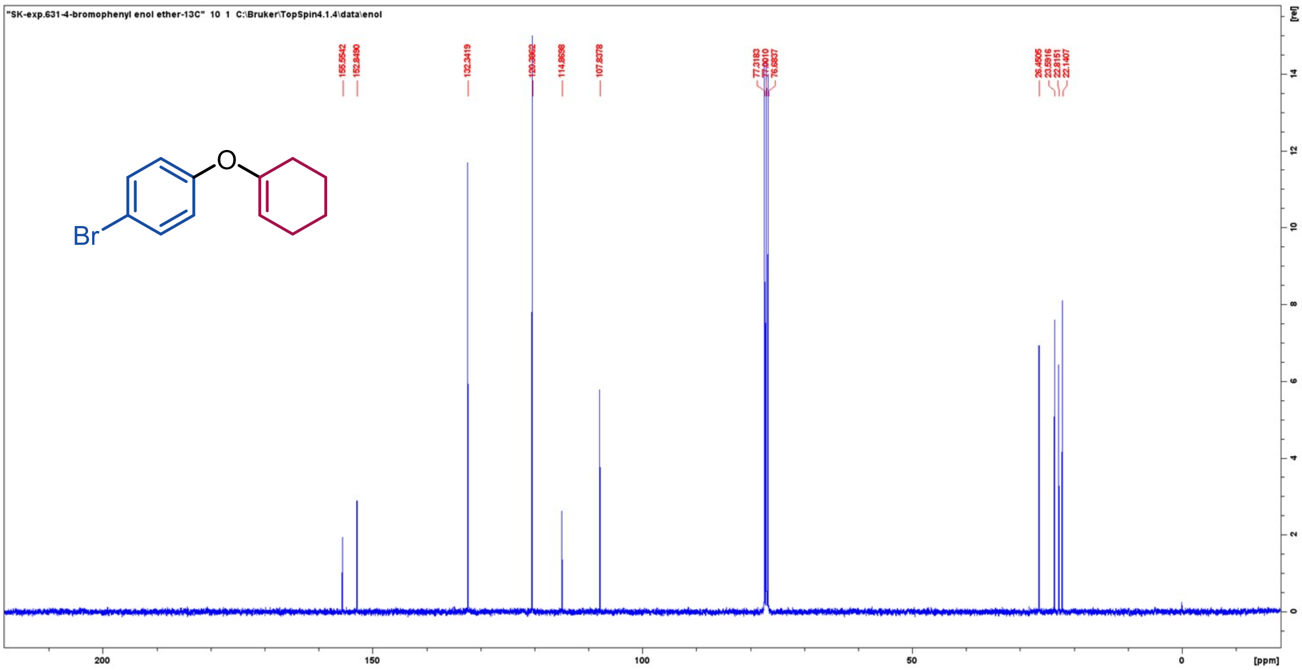
^{13}C NMR of **3ga** ($CDCl_3$, 100 Hz)



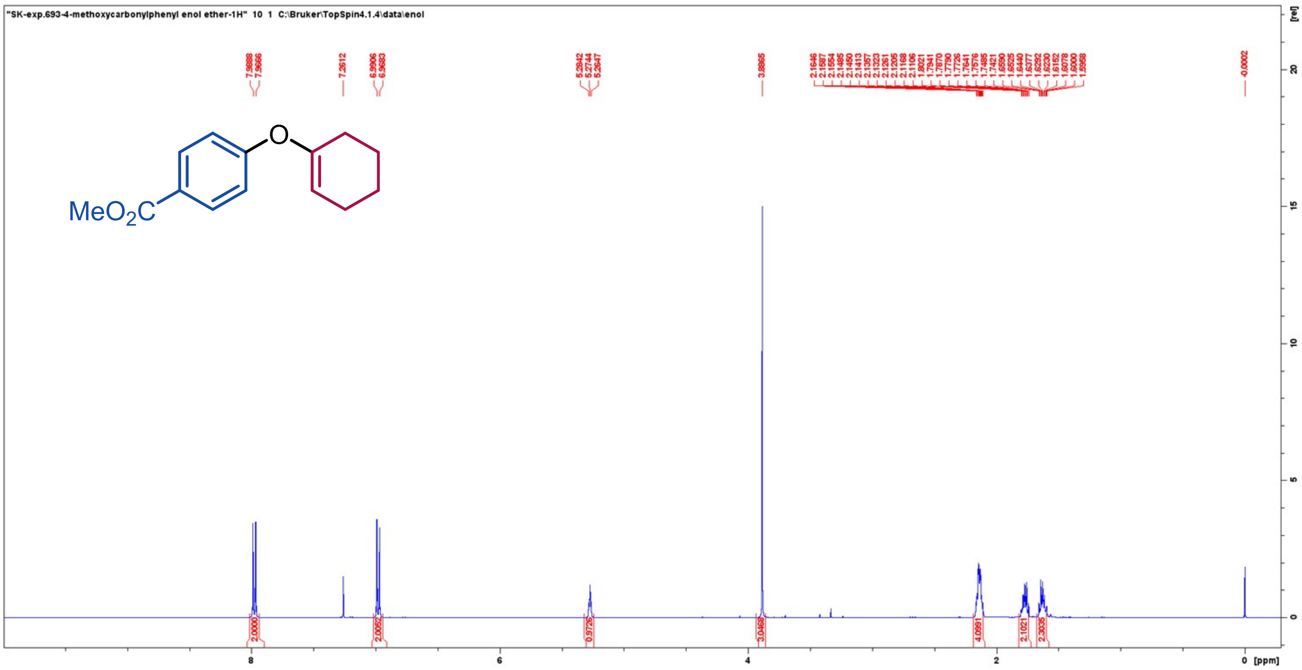
^{1}H NMR of **3ha** (CDCl$_3$, 400 Hz)



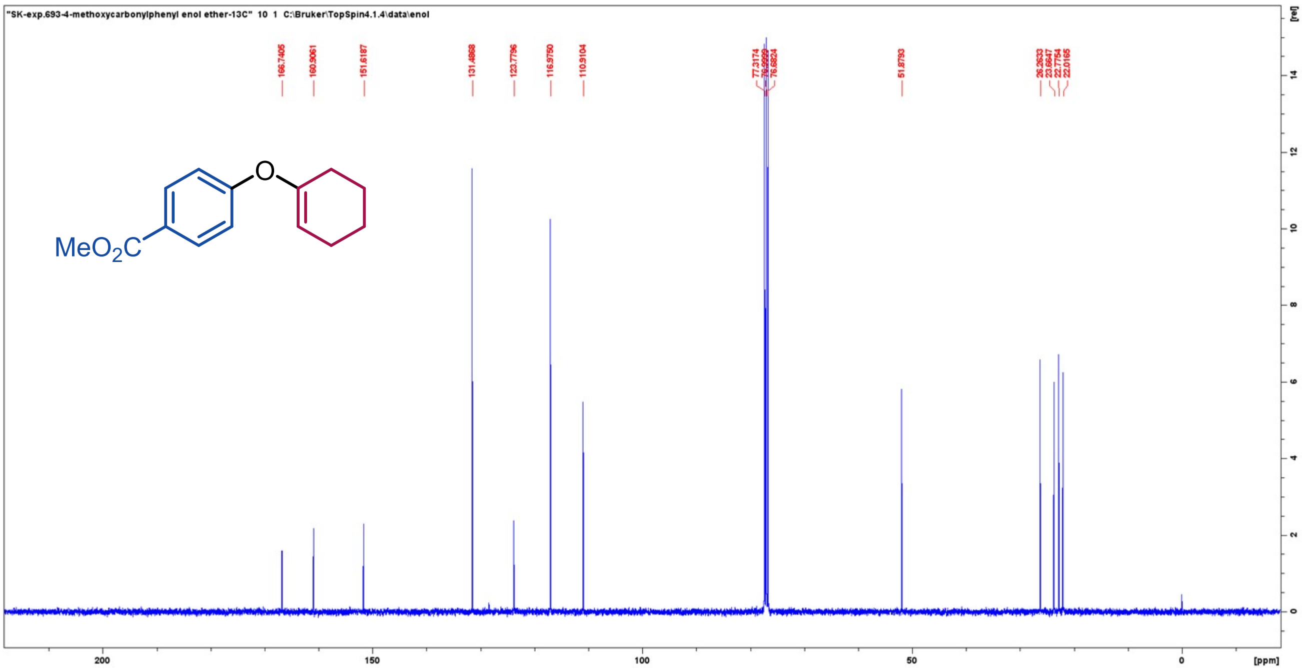
^{13}C NMR of **3ha** (CDCl$_3$, 100 Hz)



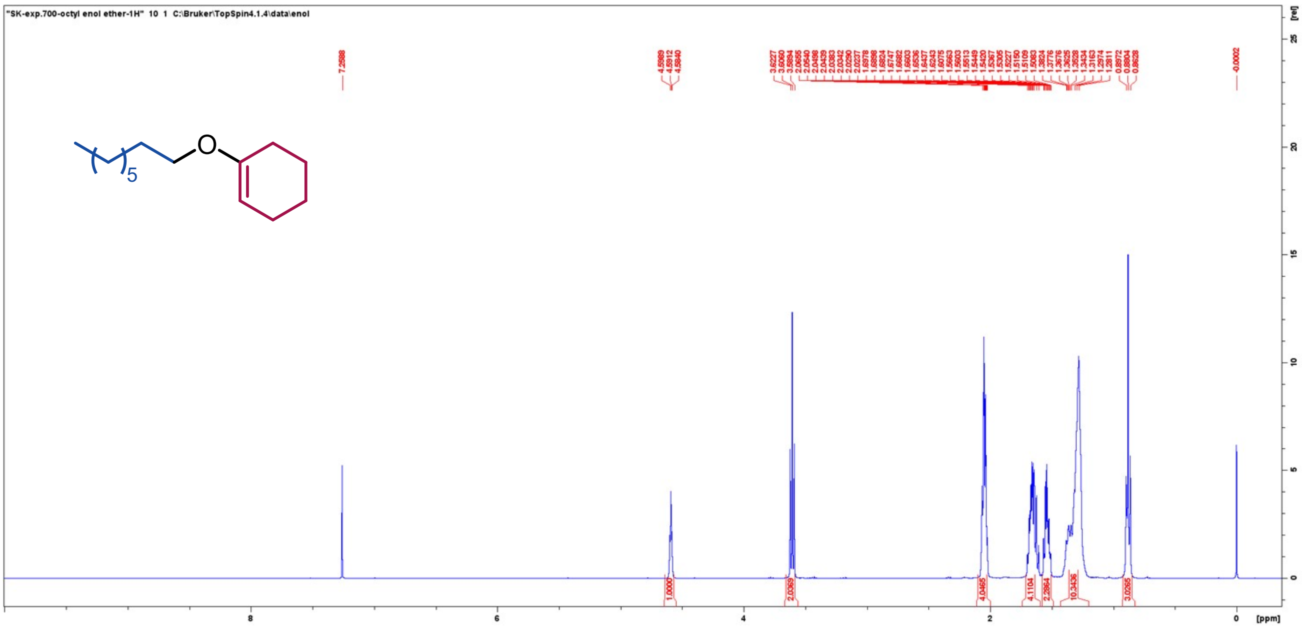
^{1}H NMR of **3ia** ($CDCl_3$, 400 Hz)



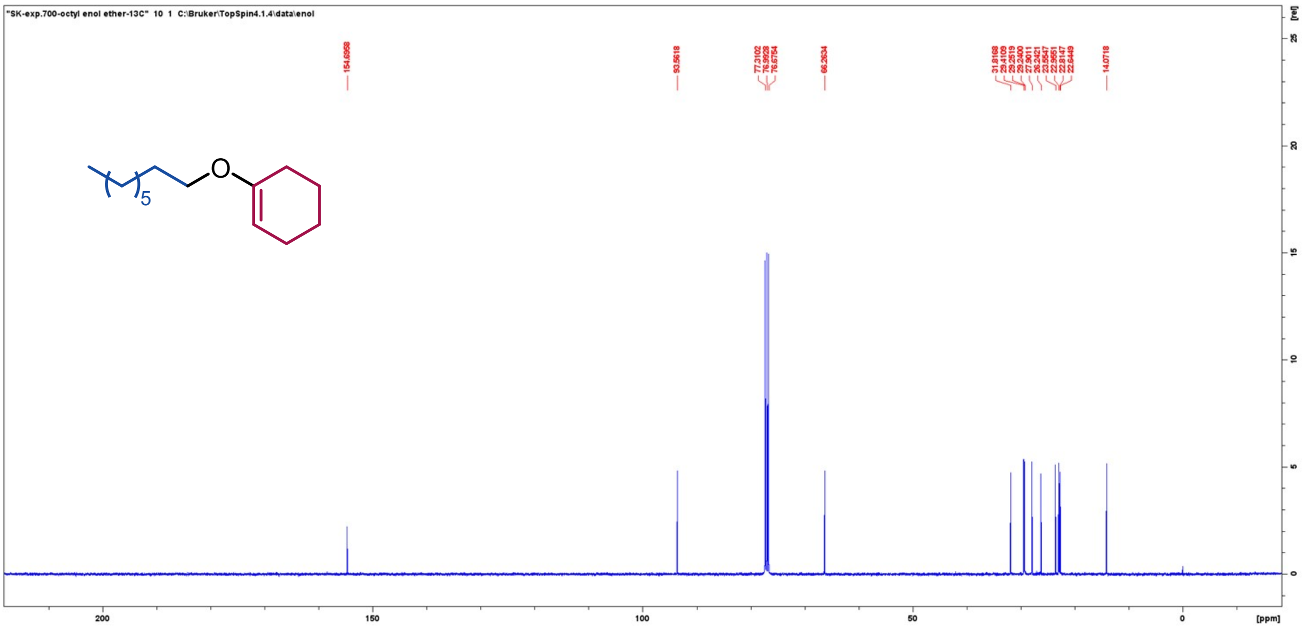
^{13}C NMR of **3ia** ($CDCl_3$, 100 Hz)



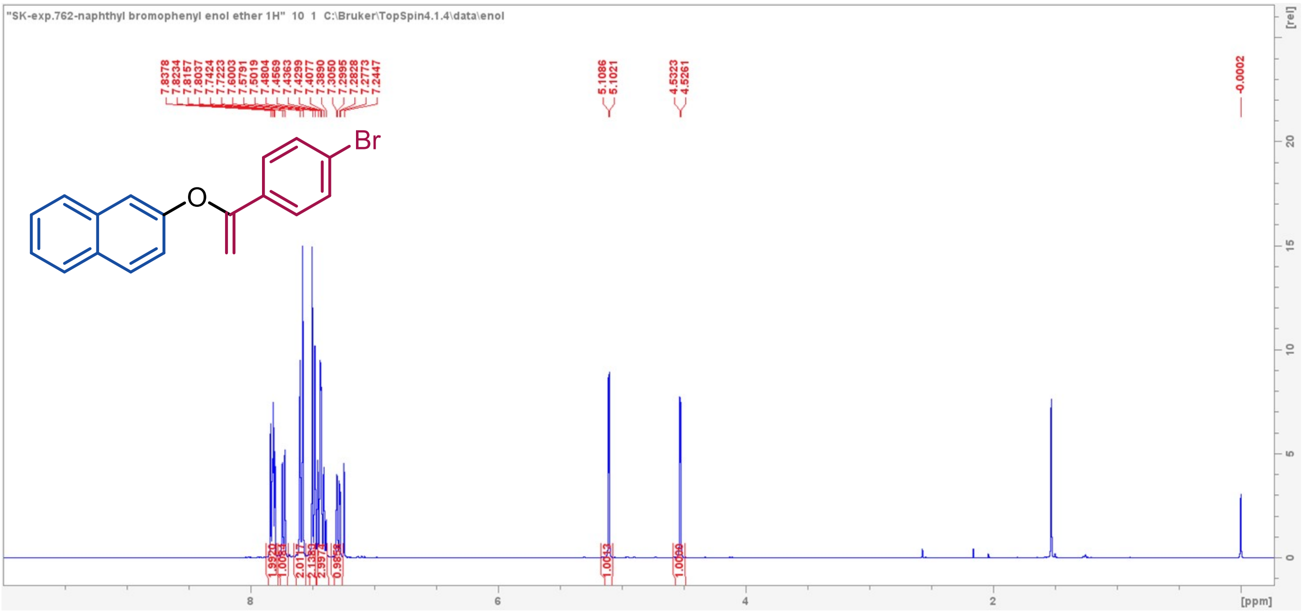
^{1}H NMR of **3ja** ($CDCl_3$, 400 Hz)



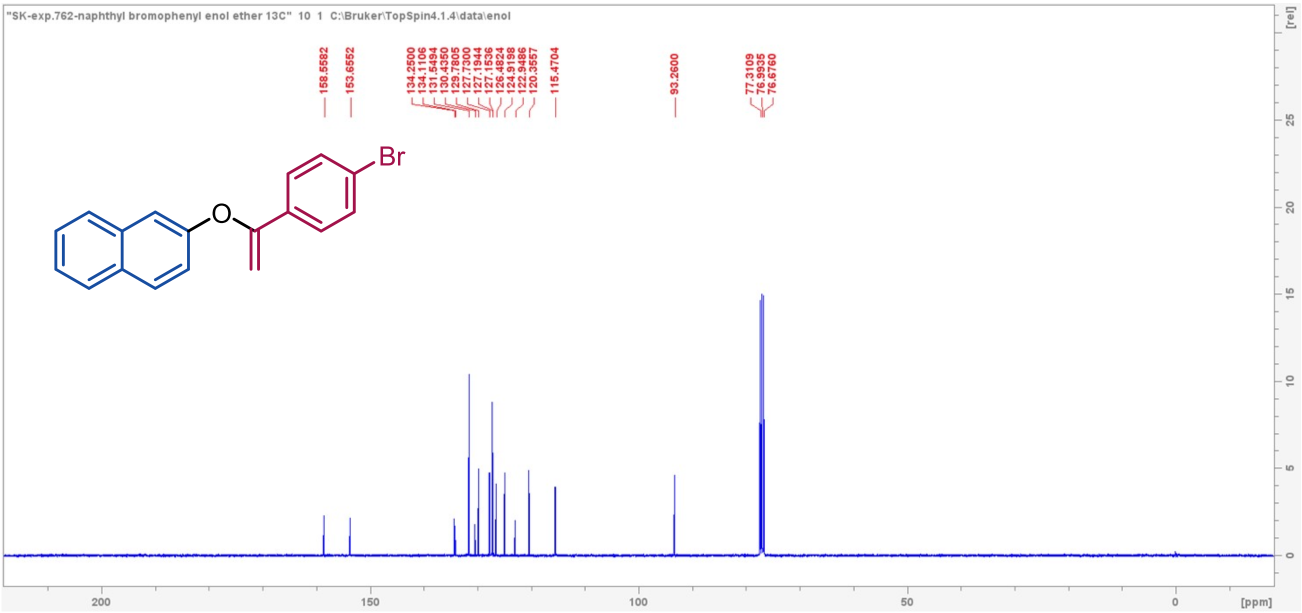
^{13}C NMR of **3ja** ($CDCl_3$, 100 Hz)



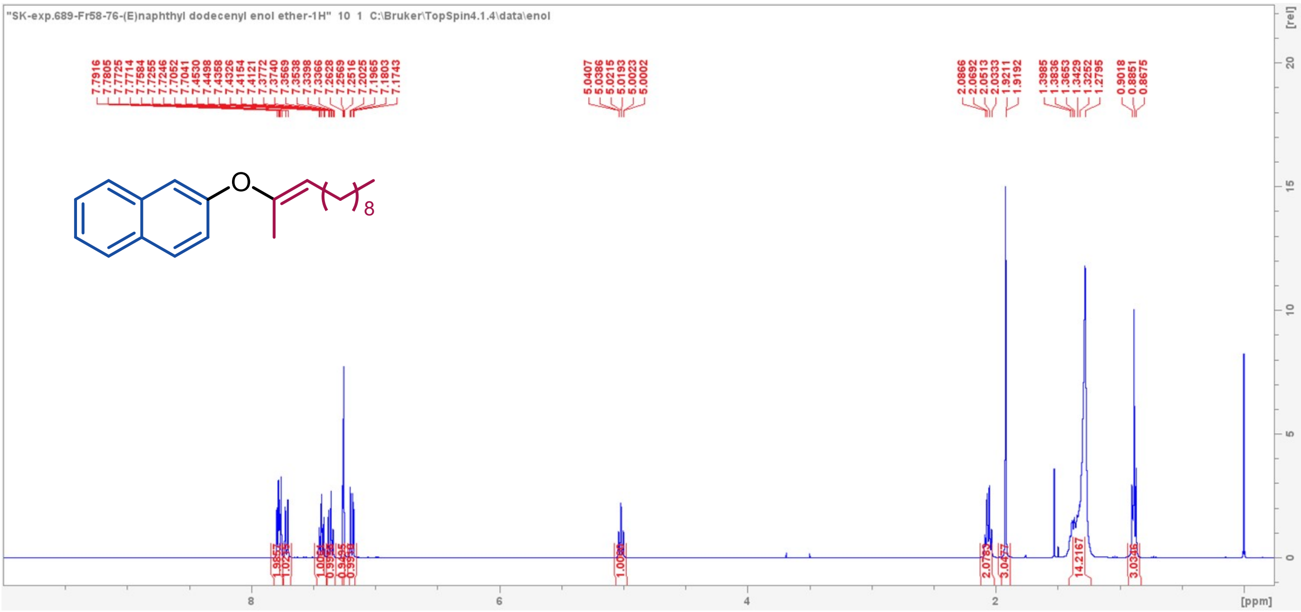
^{1}H NMR of **3ab** ($CDCl_3$, 400 Hz)



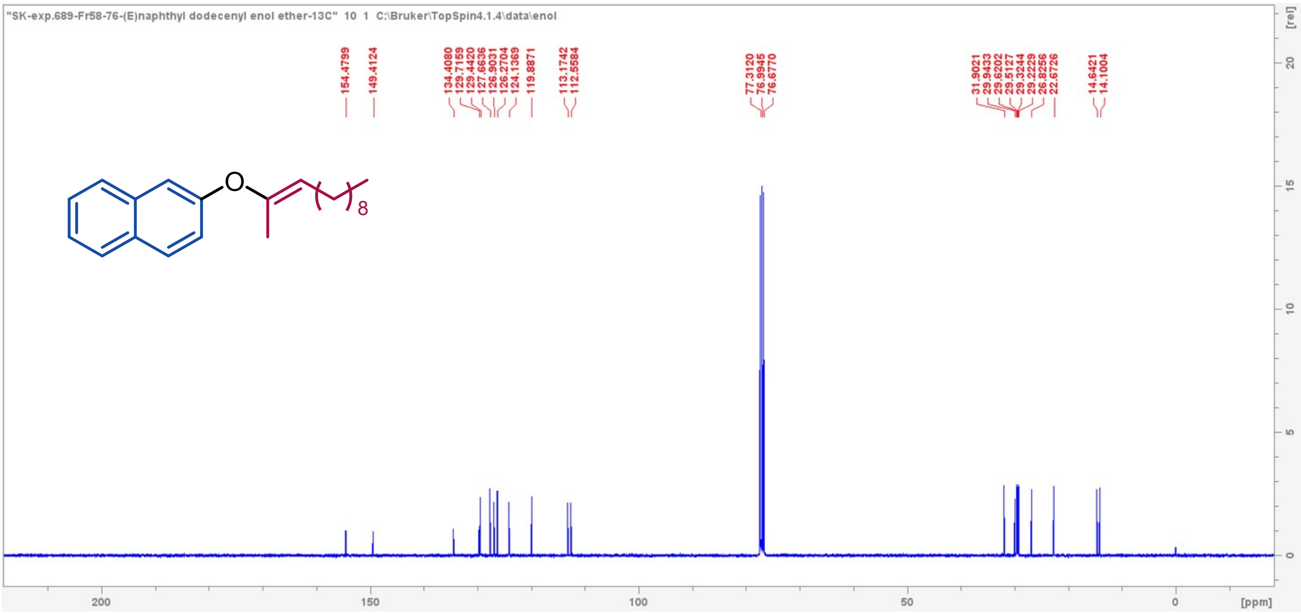
^{13}C NMR of **3ab** ($CDCl_3$, 100 Hz)



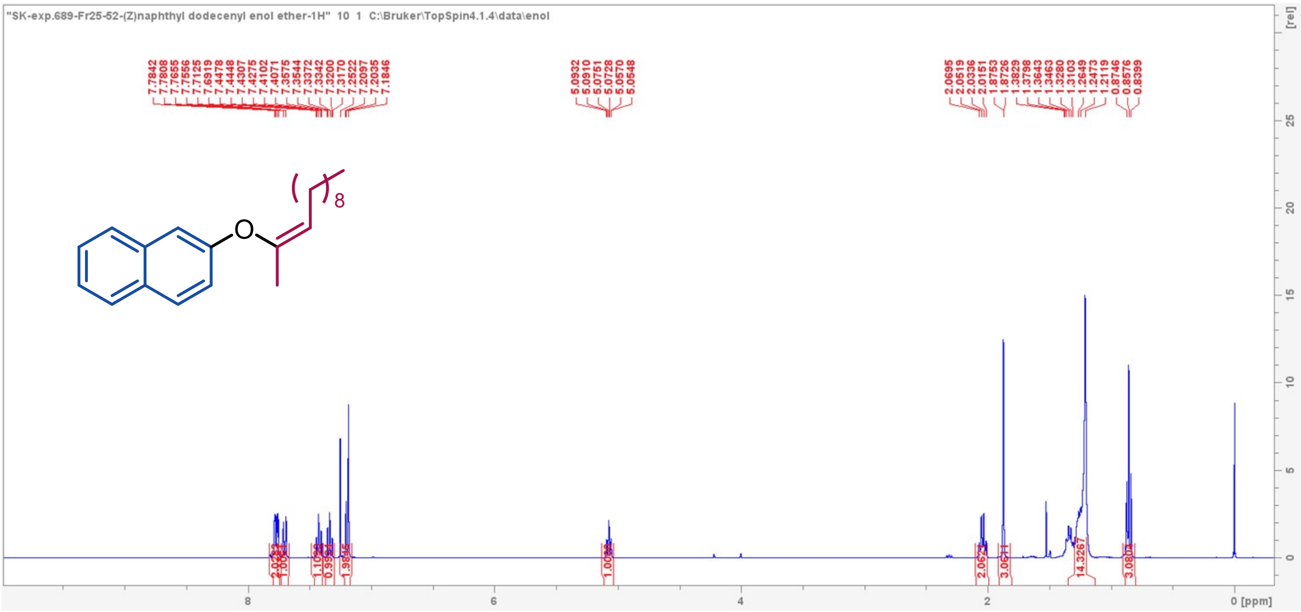
^{1}H NMR of **(*E*)-3ac** ($CDCl_3$, 400 Hz)



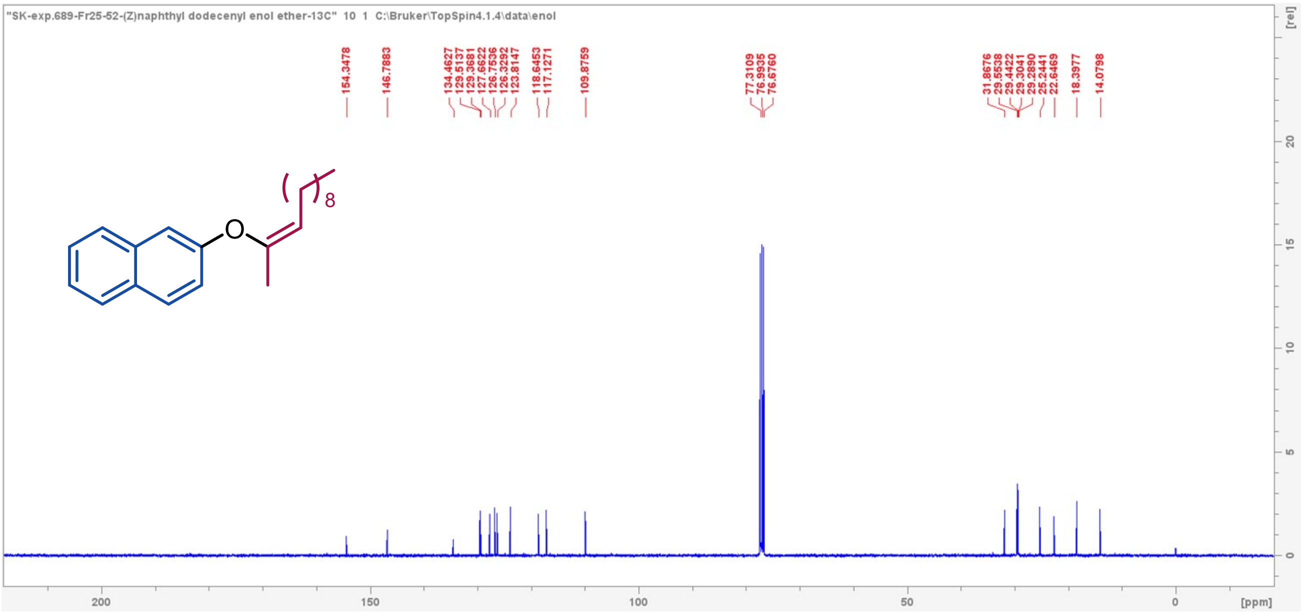
^{13}C NMR of **(*E*)-3ac** ($CDCl_3$, 100 Hz)



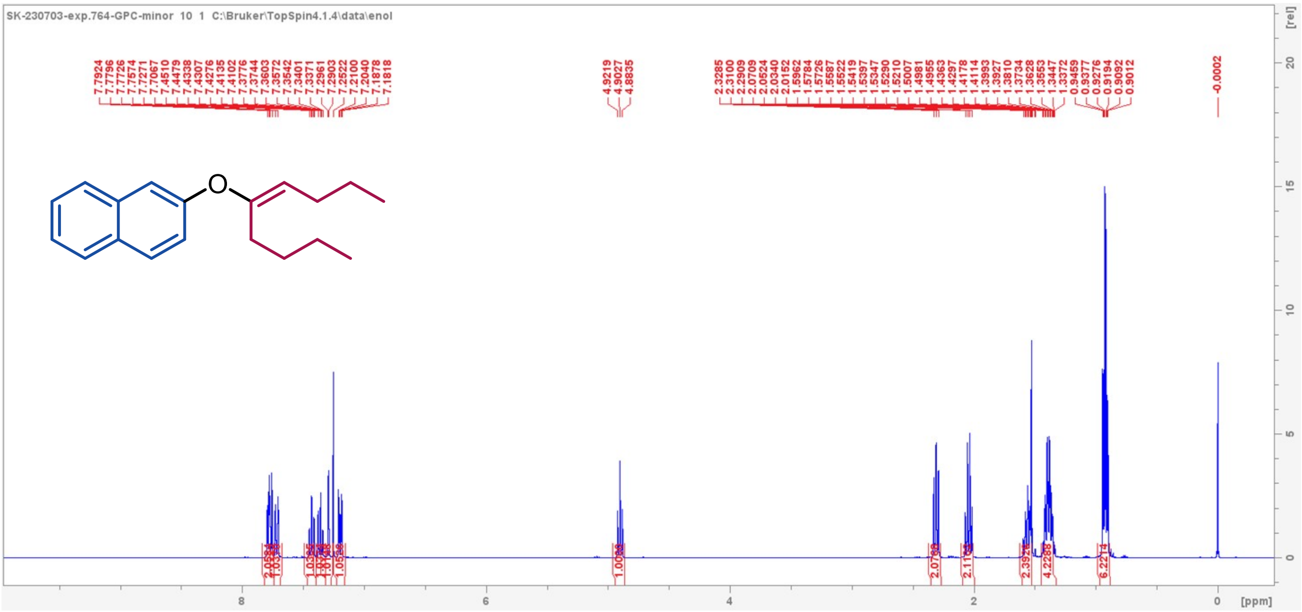
^{1}H NMR of **(*Z*)-3ac** (CDCl$_3$, 400 Hz)



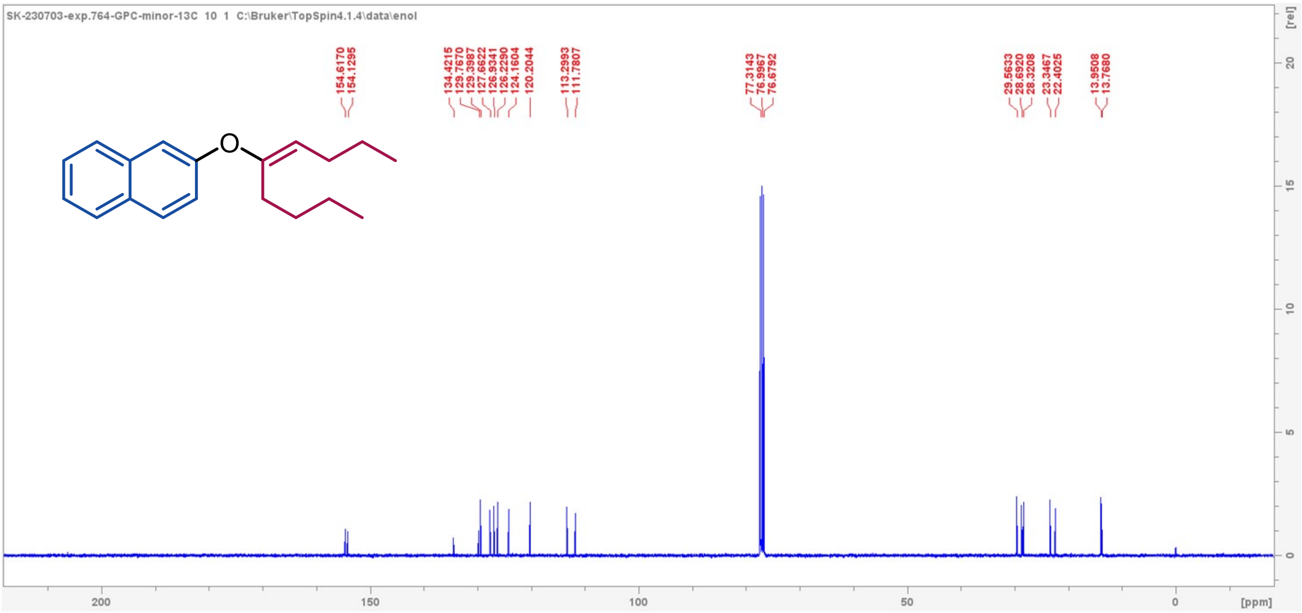
^{13}C NMR of **(*Z*)-3ac** (CDCl$_3$, 100 Hz)



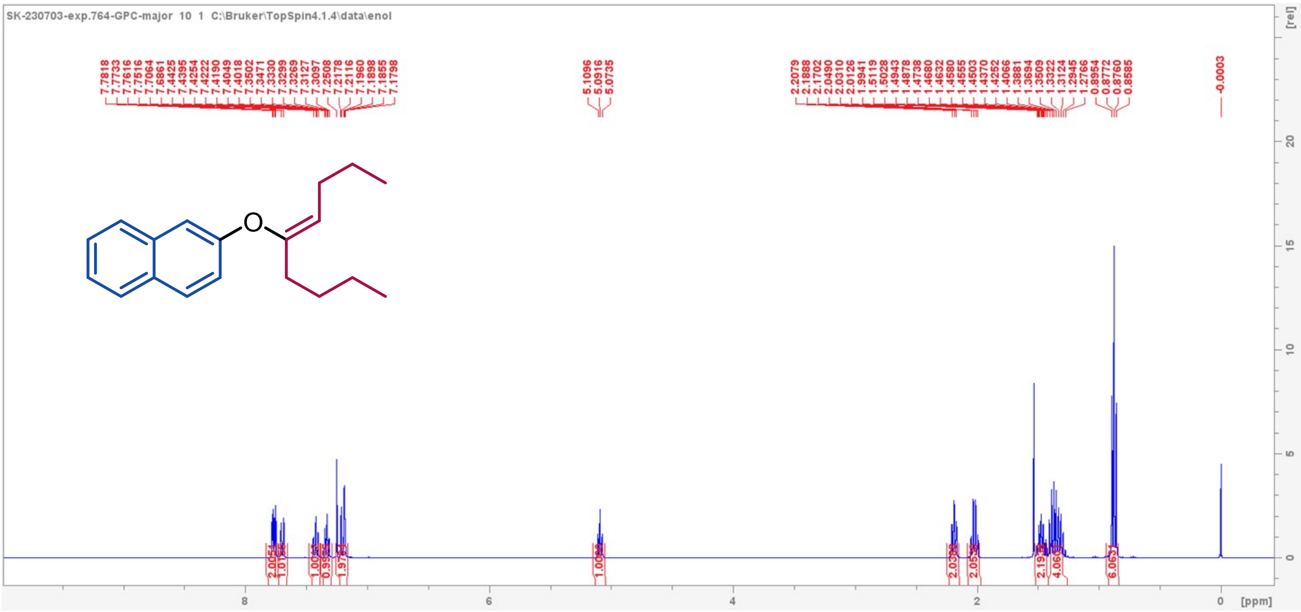
^{1}H NMR of **(*E*)-3ad** (CDCl$_3$, 400 Hz)



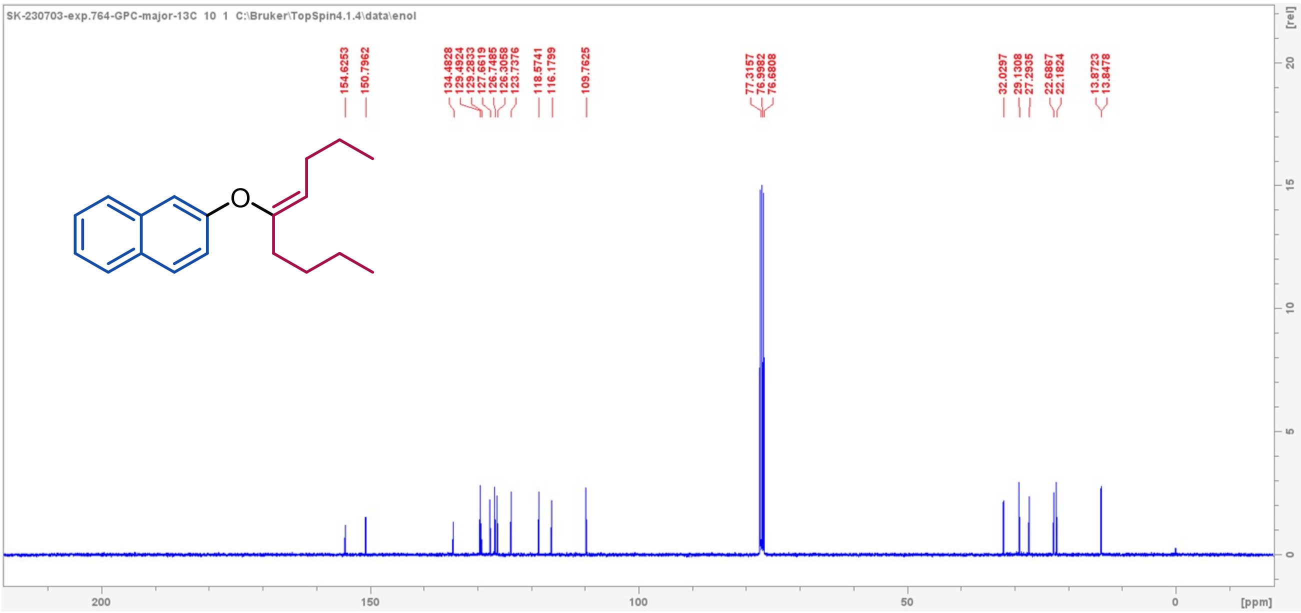
^{13}C NMR of **(*E*)-3ad** (CDCl$_3$, 100 Hz)



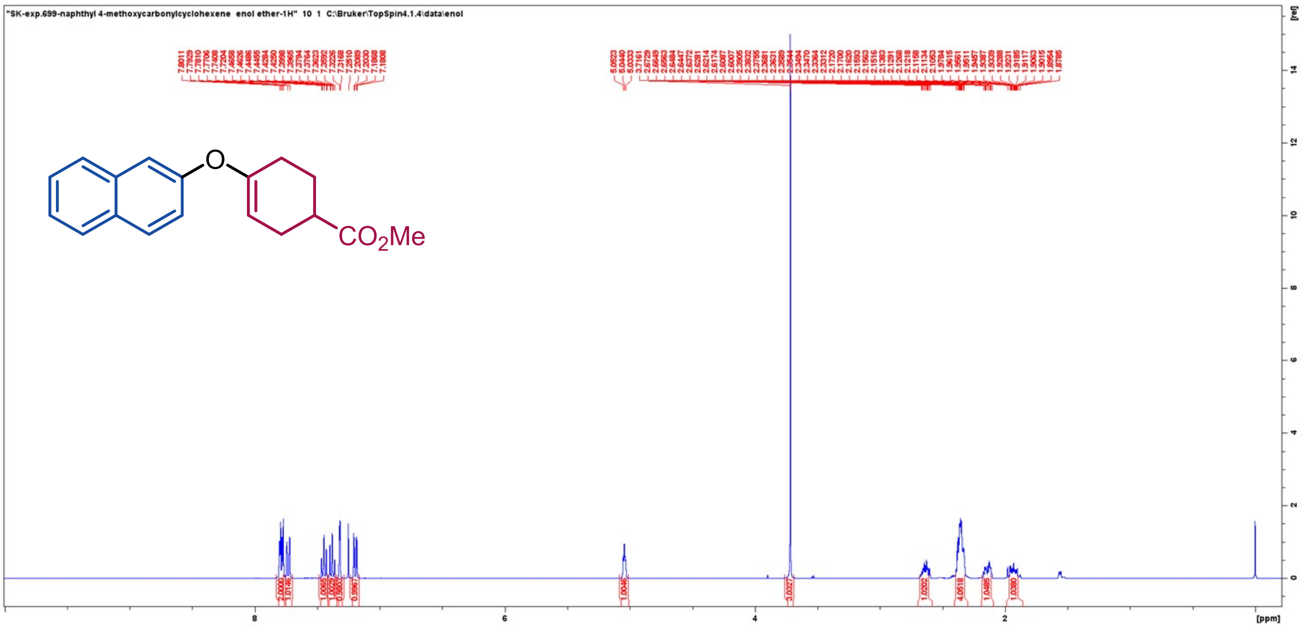
^{1}H NMR of **(*Z*)-3ad** ($CDCl_3$, 400 Hz)



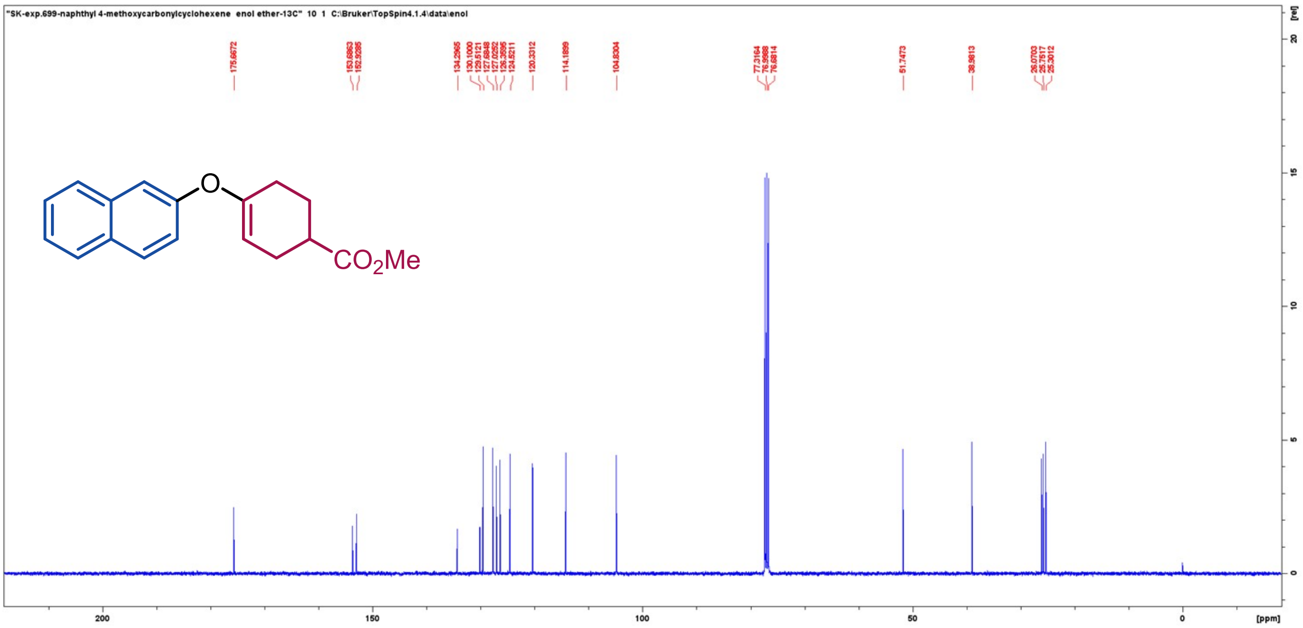
^{13}C NMR of **(*Z*)-3ad** ($CDCl_3$, 100 Hz)



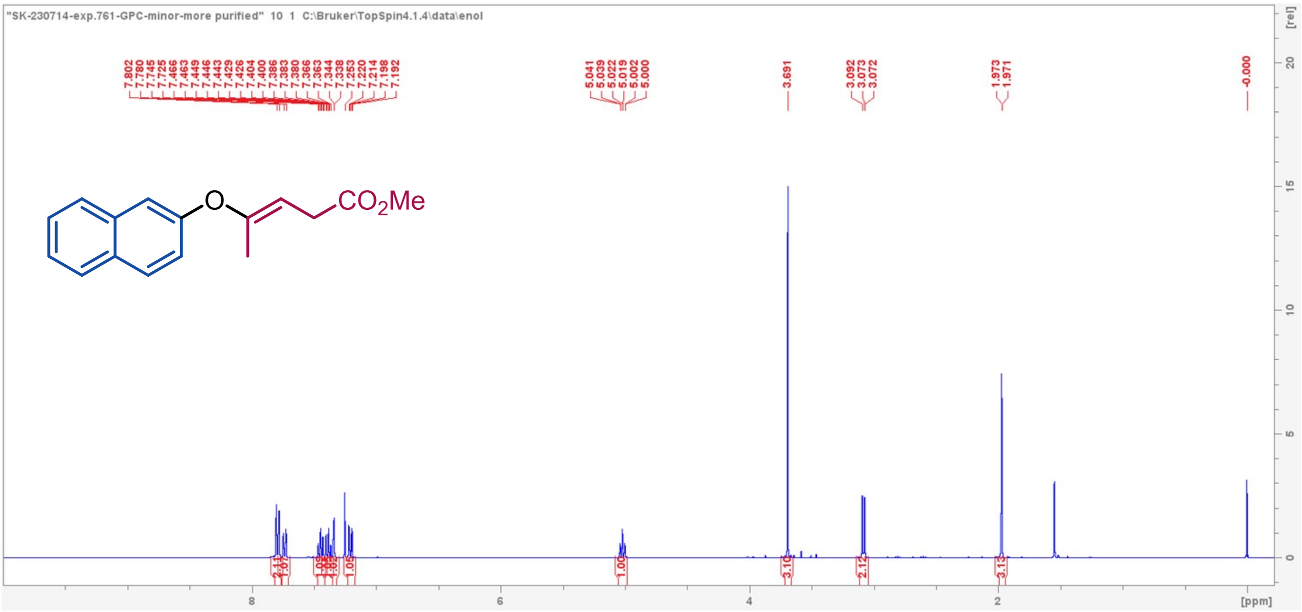
^{1}H NMR of **3ae** ($CDCl_3$, 400 Hz)



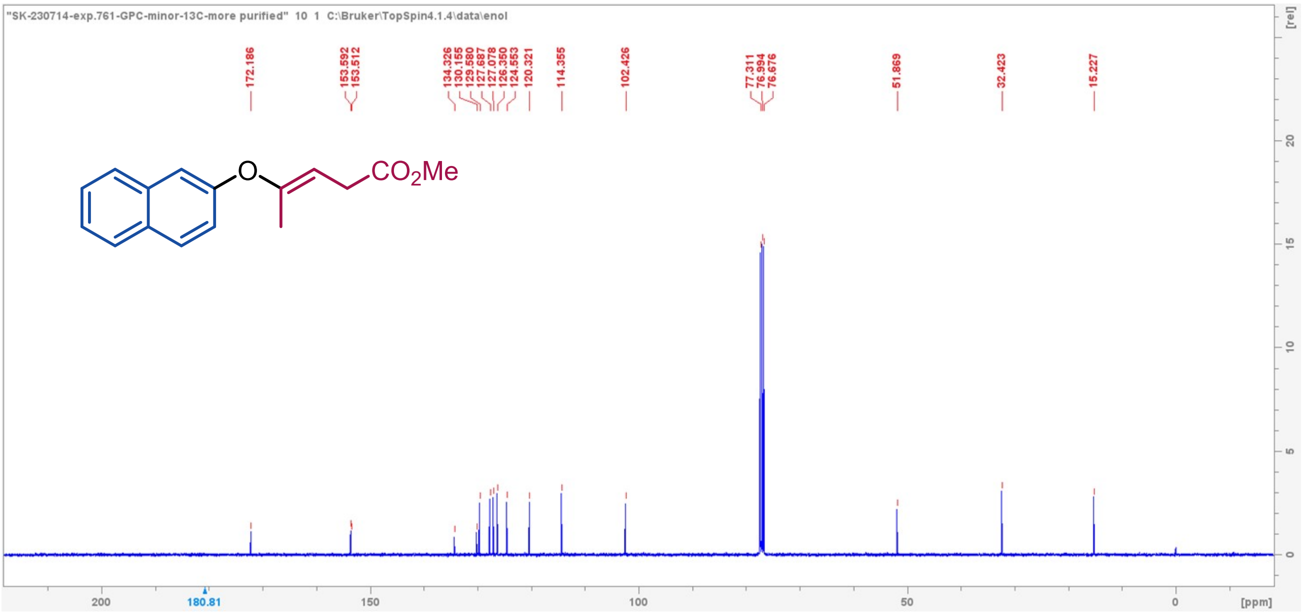
^{13}C NMR of **3ae** ($CDCl_3$, 100 Hz)



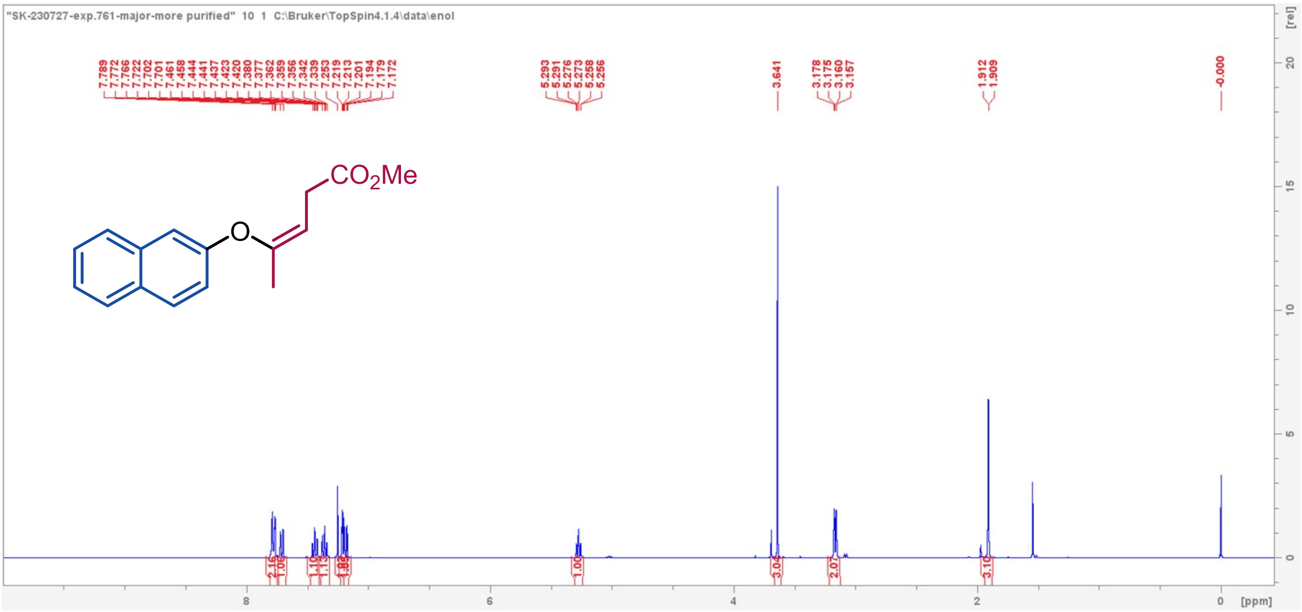
^{1}H NMR of ***(E)*-3af** (CDCl$_3$, 400 Hz)



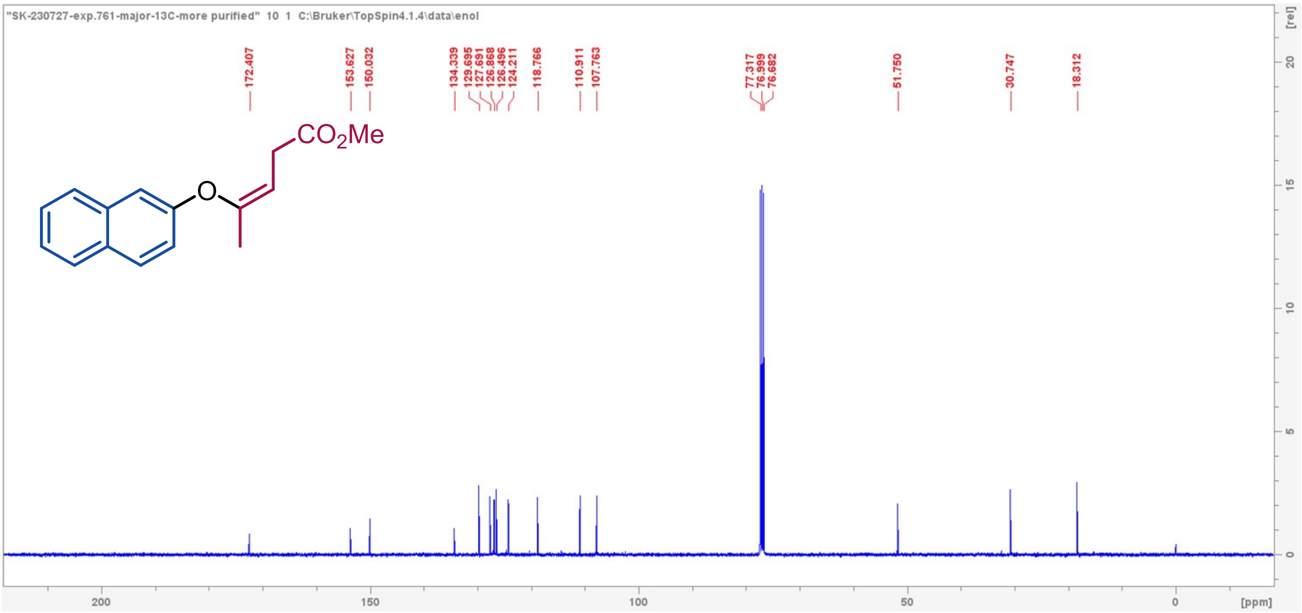
^{13}C NMR of ***(E)*-3af** (CDCl$_3$, 100 Hz)



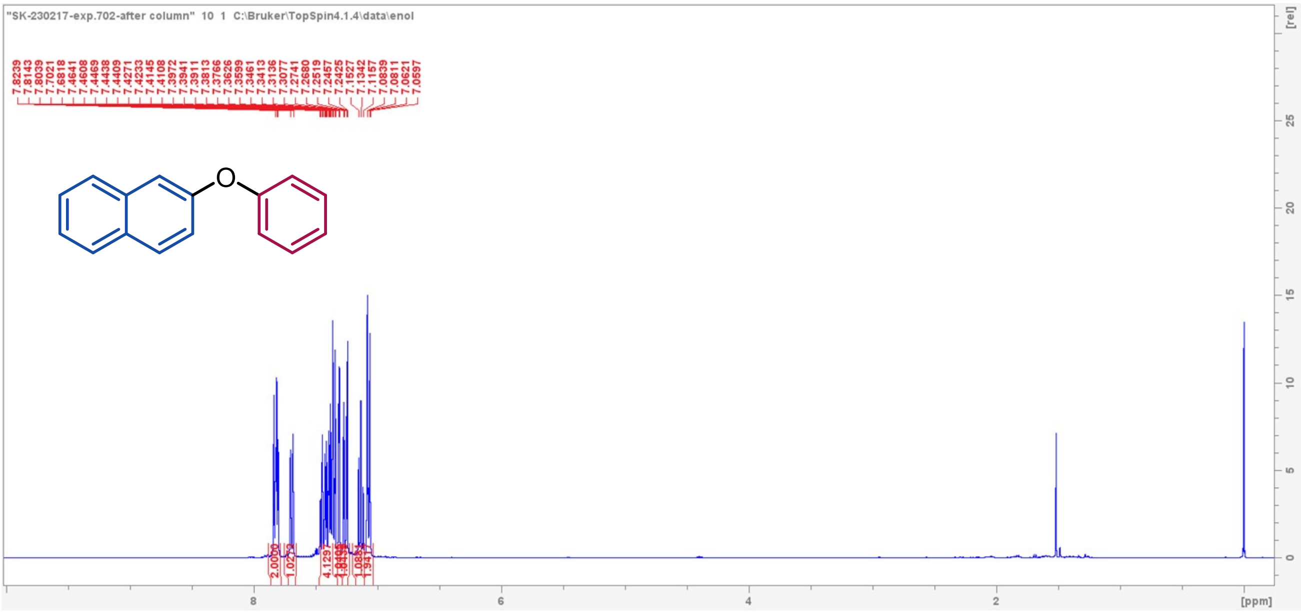
^{1}H NMR of **(*Z*)-3af** (CDCl$_3$, 400 Hz)



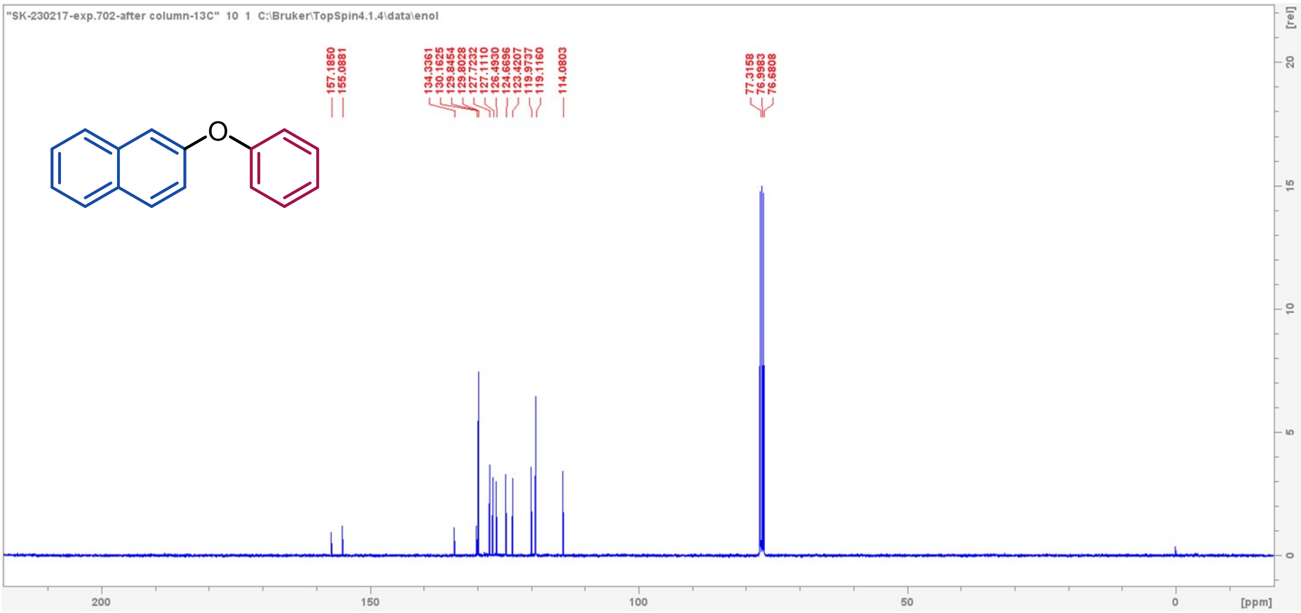
^{13}C NMR of **(*Z*)-3af** (CDCl$_3$, 100 Hz)



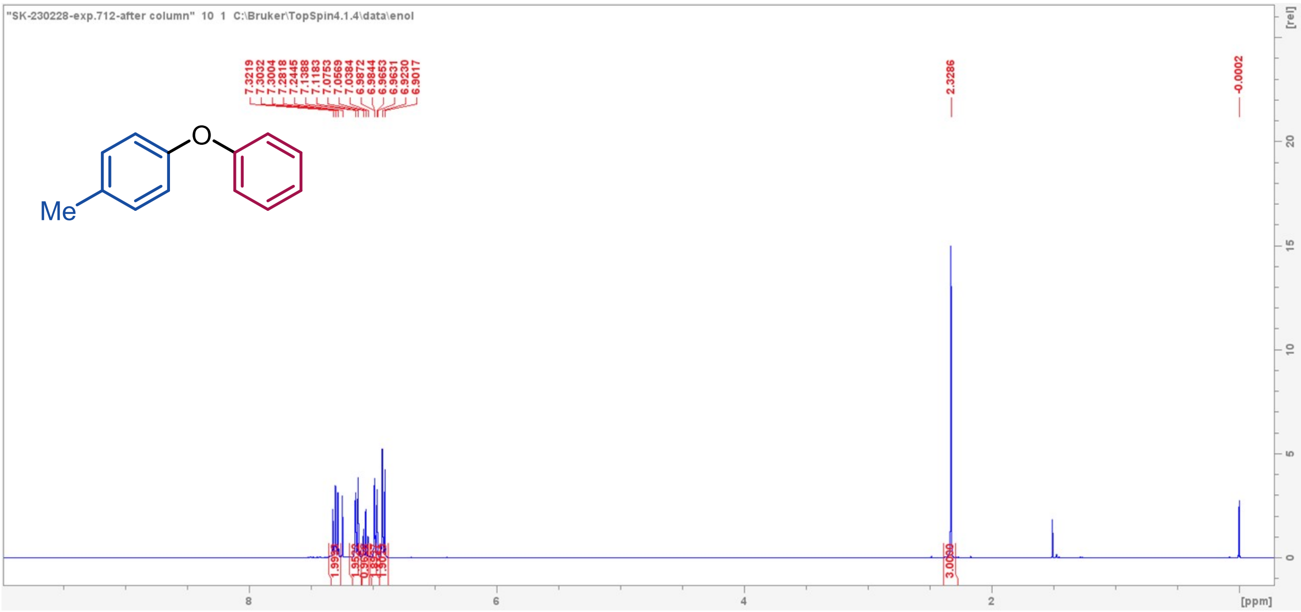
^{1}H NMR of **6aa** (CDCl$_3$, 400 Hz)



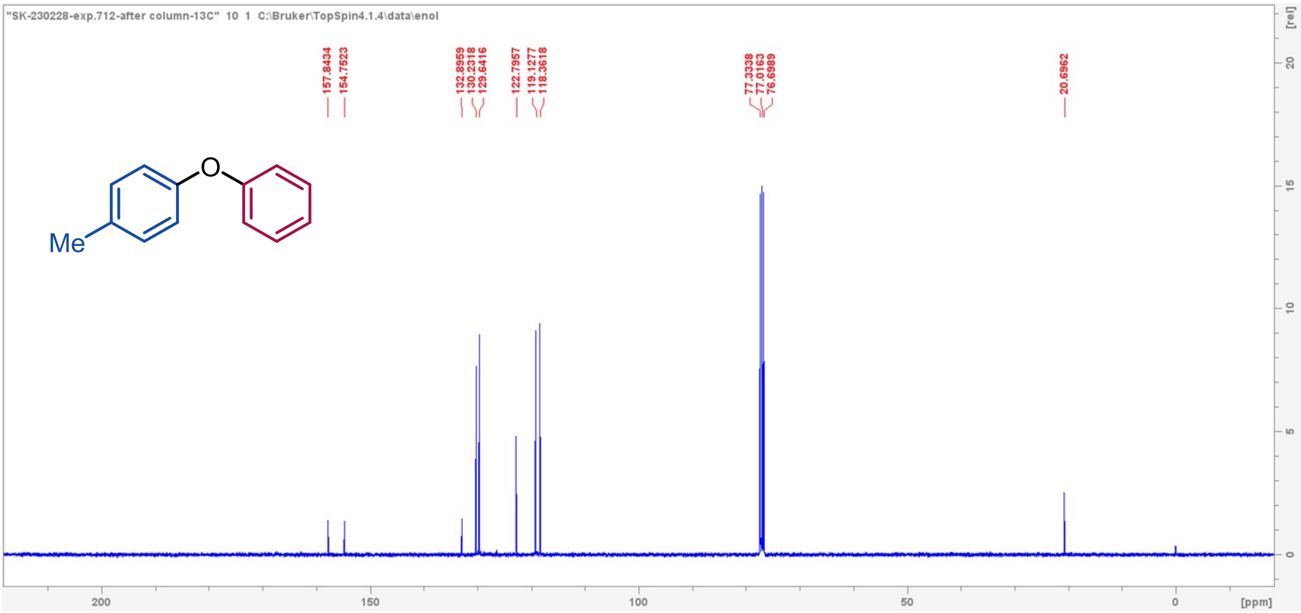
^{13}C NMR of **6aa** (CDCl$_3$, 100 Hz)



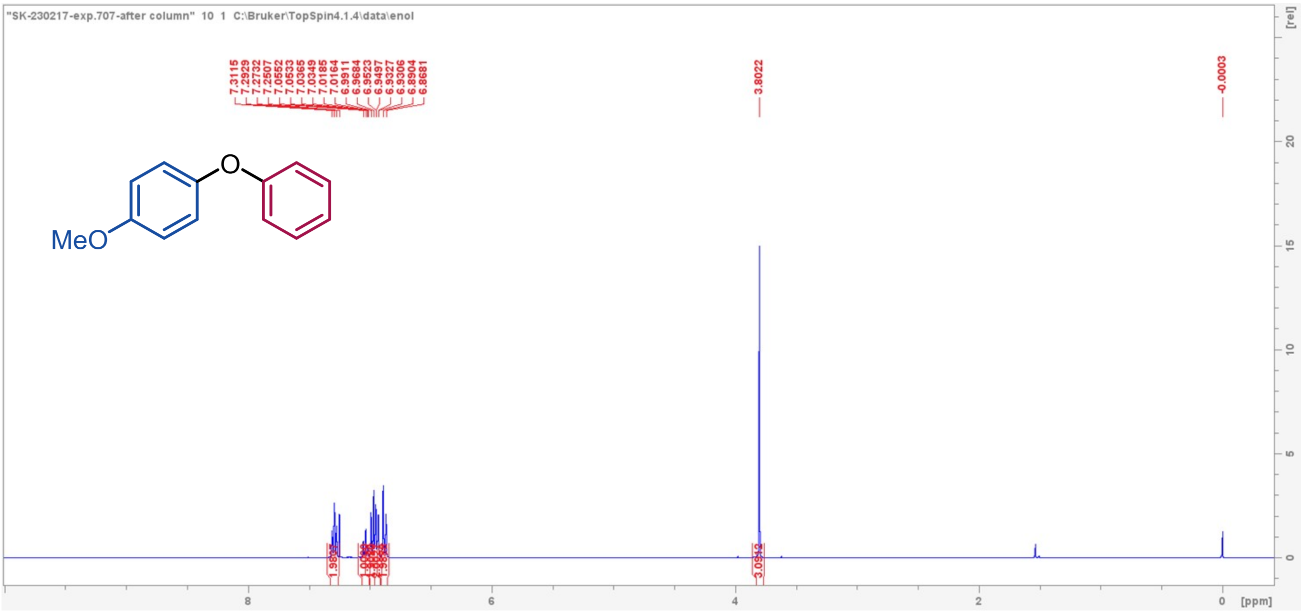
^{1}H NMR of **6ba** ($CDCl_3$, 400 Hz)



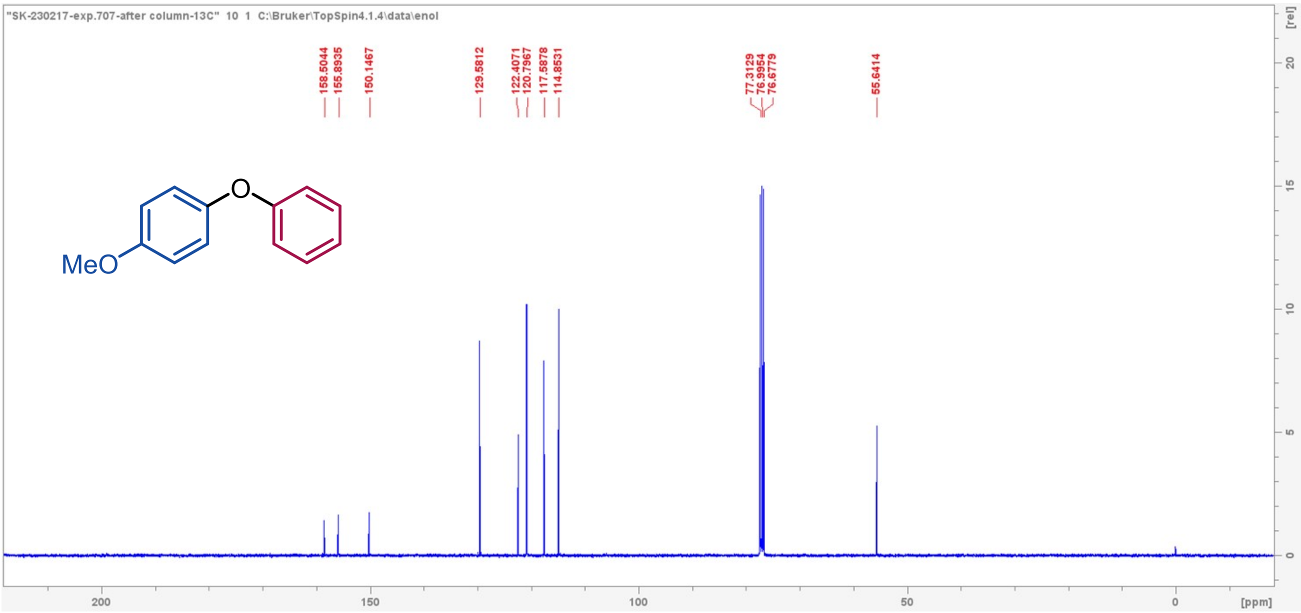
^{13}C NMR of **6ba** ($CDCl_3$, 100 Hz)



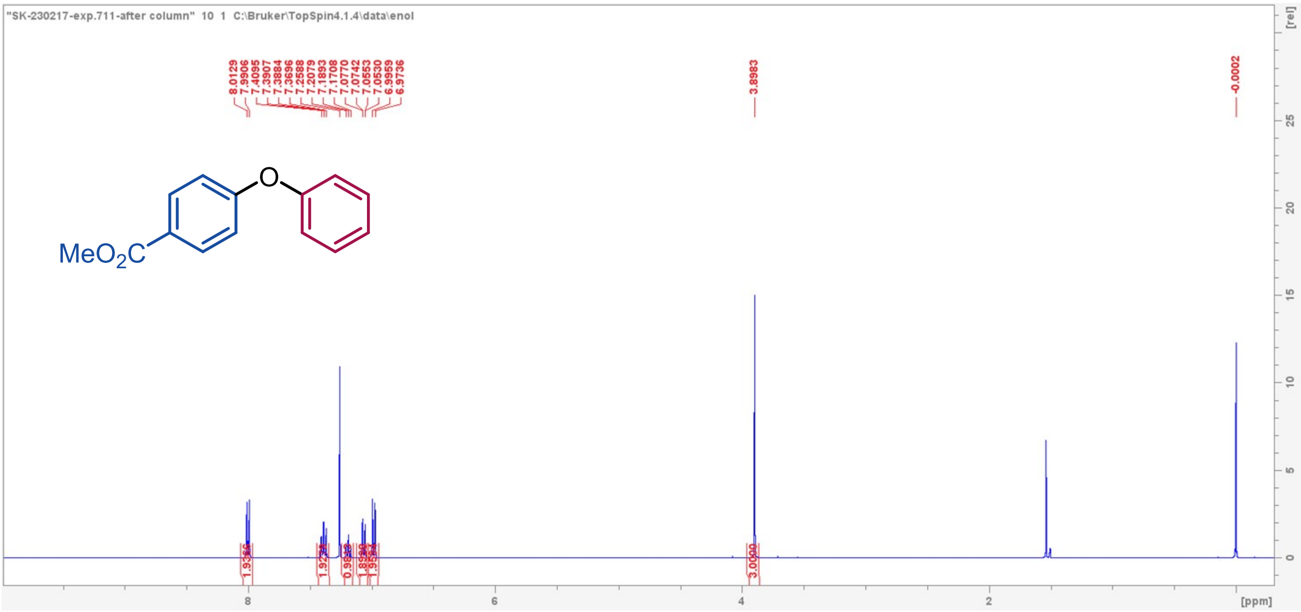
^{1}H NMR of **6ea** (CDCl$_3$, 400 Hz)



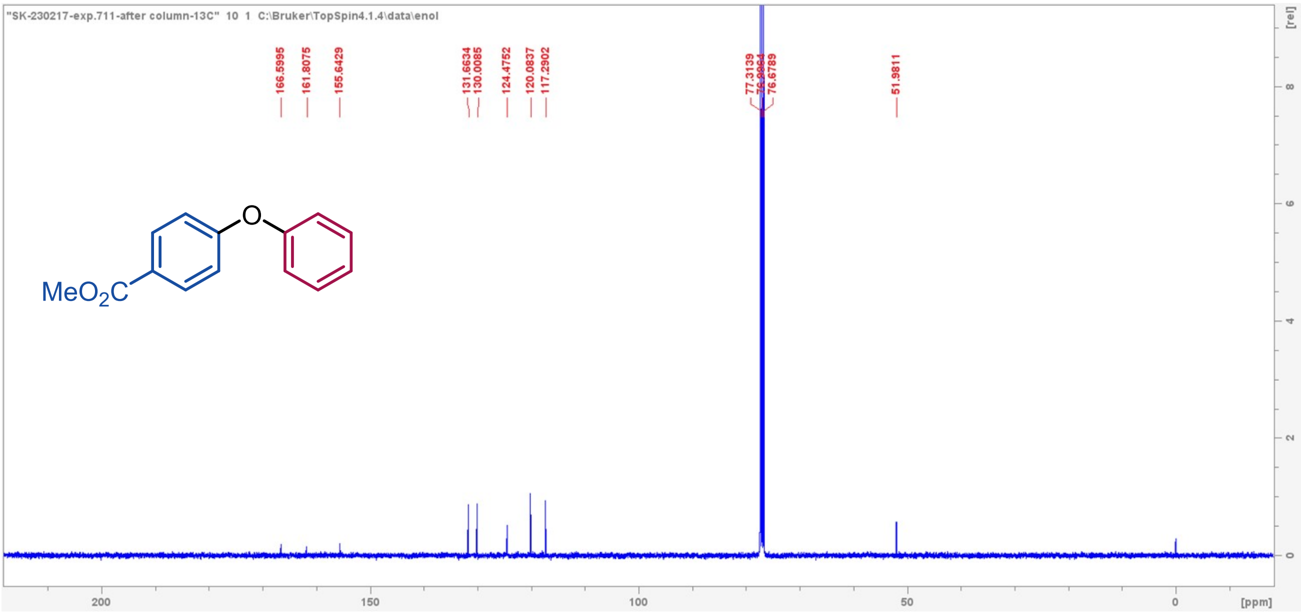
^{13}C NMR of **6ba** (CDCl$_3$, 100 Hz)



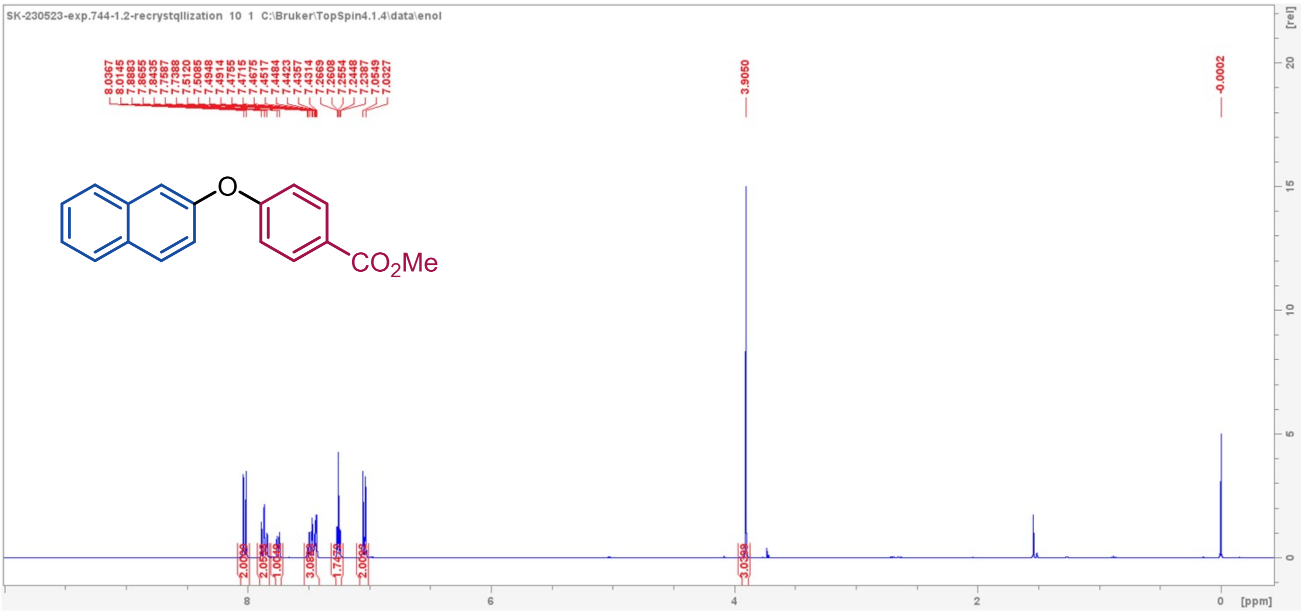
^{1}H NMR of **6ha** ($CDCl_3$, 400 Hz)



^{13}C NMR of **6ha** ($CDCl_3$, 100 Hz)



^{1}H NMR of **6ab** (CDCl$_3$, 400 Hz)



^{13}C NMR of **6ab** (CDCl$_3$, 100 Hz)