Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information

Radical Addition Reaction between Chromenols and Toluene Derivatives Initiated by Brønsted Acid Catalyst under Light Irradiation

Jun Kikuchi, Shota Kodama, Masahiro Terada*

e-mail: mterada@tohoku.ac.jp

Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan.

Contents

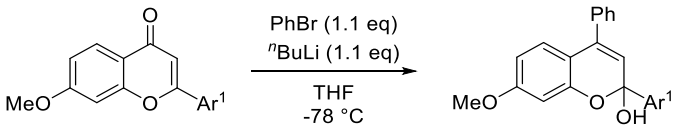
1. General Information
2. Preparation of substrates
3. Preparation of catalyst
4. Radical addition reaction between chromenol and toluene derivatives
5. Enantioselective radical addition reaction using chiral phosphoric acid catalyst
6. Additional screening
7. UV-Vis absorption spectroscopy
8. Stern-Volmer fluorescence quenching experiments
9. Light ON/OFF Experiment
10. Theoretical studies
11. X-ray crystallographic analysis
12. NMR spectra
13. HPLC chart

1. General Information

All reactions were carried out under argon atmosphere in flame-dried glassware. Dichloromethane (CH_2Cl_2), and toluene were supplied from KANTO Chemical Co., Inc. as “Dehydrated solvent system”. Other solvents and reagents were purchased from commercial suppliers and used without further purification. Photo-reactions were carried out using Techno Sigma-PER-AMP. Purification of reaction products was carried out by flash column chromatography using silica gel 60 N (Merck 40-63 μm). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF 254, 0.25 mm). ^{1}H NMR spectra were recorded on a JEOL ECA-600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane or solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm, TMS: 0.00 ppm, C_6D_6: 7.16 ppm). ^{13}C NMR spectra were recorded on a JEOL ECA-600 (151 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm, C_6D_6: 128.06 ppm). ^{31}P NMR spectra were recorded on a JEOL JNM-ECA600 (243 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with 85% H_3PO_4 solution as an external standard (0.0 ppm in $CDCl_3$). ^{19}F NMR spectra were recorded on JEOL ECA-600 (565 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the $C_6H_5CF_3$ (-67.2 ppm) resonance as the external standard. Infrared spectra were recorded on a Jasco FT/IR-4100 spectrometer. Mass spectra analysis using ESI ionization method was performed on a Bruker Daltonics solariX 9.4T spectrometer at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University. X-ray crystallography analysis was carried out using a Rigaku XtaLAB mini diffractometer using graphite monochromated Mo-Ka radiation at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University. UV/Vis absorption spectra were recorded on a JASCO V650DS spectrometer. Fluorescence spectra were recorded on a HITACHI F-4500.

2. Preparation of substrates

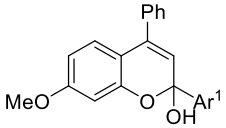
Representative procedure for the synthesis of novel chromenols[1]



S1 (Ar^1: 4-MeC_6H_4) **1b**

To a solution of PhBr (414.5 mg, 2.64 mmol) in THF (10.6 ml) was added ^{n}BuLi (1.6 M in hexane, 1.7 mL, 2.64 mmol) at -78 °C. The resulting mixture was stirred for 30 min at -78 °C. To a solution of **S1** (639.1 mg, 2.4 mmol) in THF (24 mL) was added a resulting PhLi solution at -78 °C. After stirring for 2 h at -78 °C, the reaction mixture was quenched by water, and then extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc/Et_3N = 7/1/0.01) to give **1b** (586.9 mg, 1.7 mmol, 71% yield) as a yellow solid.

2-(4-methylphenyl)-7-methoxy-4-phenyl-2H-chromen-2-ol (**1b**)

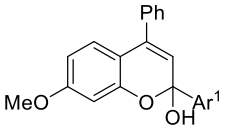


1b

(Ar^1: 4-MeC_6H_4)

Yellow solid (586.9 mg, 1.7 mmol, 71% yield); R_f = 0.51 (hexane/EtOAc = 4/1); ^{1}H NMR (600 MHz, C_6D_6) δ 7.60 (d, *J* = 8.4Hz, 2H), 7.41-7.36 (m, 5H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 9.0 Hz, 1H), 6.70 (d, *J* = 2.4 Hz, 1H), 6.53 (dd, *J* = 9.0 Hz, 2.4 Hz, 1H), 5.75 (s, 1H), 3.80 (s, 3H), 3.35 (brs, 1H), 2.36 (s, 3H); ^{13}C NMR (151 MHz, C_6D_6) δ 161.7, 154.0, 141.4, 138.3, 138.0, 136.6, 129.2, 129.1, 128.7, 128.2, 127.3, 126.5, 122.6, 114.2, 108.5, 102.9, 97.7, 55.0, 21.1; IR (ATR) 3370, 3027, 2955, 2835, 1613, 1505, 1444, 1357, 1275, 1199, 1160, 1113, 1031, 991, 822, 747 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{20}NaO_3$ 367.1310, found: 367.1304.

2-(4-bromophenyl)-7-methoxy-4-phenyl-2H-chromen-2-ol (**1c**)



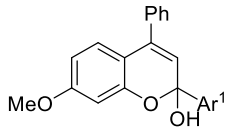
1c

(Ar^1: 4-BrC_6H_4)

Yellow solid (458.4 mg, 1.1 mmol, 56% yield); R_f = 0.51 (hexane/EtOAc = 4/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.42-7.37 (m, 5H), 7.12 (d, *J* = 9.0 Hz, 1H), 6.70 (d, *J* = 2.4 Hz, 1H), 6.55 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 5.71 (s, 1H), 3.82 (s, 3H), 3.35 (brs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.3, 152.5, 142.0, 137.2, 137.1, 131.4, 128.7, 128.4, 128.3, 127.7, 127.1, 122.7, 120.7, 113.3, 108.4, 102.3, 96.9, 55.5; IR (ATR) 3384, 3055, 2955, 2836, 1613, 1504, 1487, 1444, 1395, 1358, 1323, 1288, 1252, 1199, 1161, 1122, 1072, 1009, 830 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{17}BrNaO_3$ 431.0259, found: 431.0253.

[1] M. Terada, T. Yamanaka and Y. Toda, *Chem. Eur. J.* 2013, **19**, 13658–13662.

7-methoxy-4-phenyl-2-(4-(trifluoromethyl)phenyl)-2H-chromen-2-ol (**1d**)

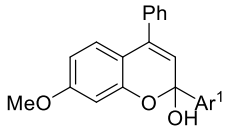


1d

(Ar^1: 4-$CF_3C_6H_4$)

Yellow solid (652.5 mg, 1.6 mmol, 78% yield); R_f = 0.50 (hexane/EtOAc = 4/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.43-7.38 (m, 5H), 7.13 (d, *J* = 9.0 Hz, 1H), 6.71 (d, *J* = 2.4 Hz, 1H), 6.56 (dd, *J* = 9.0 Hz, 2.4 Hz, 1H), 5.71 (s, 1H), 3.82 (s, 3H), 3.42 (br, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.4, 152.5, 146.7, 137.4, 137.2, 130.7 (q, *J* = 33.2 Hz), 128.7, 128.5, 128.3, 127.2, 126.4, 125.3 (q, *J* = 2.9 Hz), 124.1 (q, *J* = 272 Hz), 120.5, 113.3, 108.5, 102.4, 96.8, 55.5; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.5; IR (ATR) 3357, 2955, 1613, 1505, 1325, 1275, 1164, 1125, 1068, 1019, 846, 749 cm^{-1}; HRMS (FD+) m/z: [M] Calcd for $C_{23}H_{17}F_3O_3$ 398.1130, found:398.1128.

2-(3-bromophenyl)-7-methoxy-4-phenyl-2H-chromen-2-ol (**1e**)

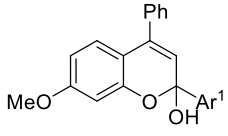


1e

(Ar^1: 3-BrC_6H_4)

Yellow solid (424.4 mg, 1.0 mmol, 61% yield); R_f = 0.55 (hexane/EtOAc = 4/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (t, *J* = 1.8 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.42-7.35 (m, 5H), 7.28 (t, *J* = 8.4 Hz, 1H),7.12 (d, *J* = 9.0 Hz, 1H), 6.71 (d, *J* = 2.4 Hz, 1H), 6.55 (dd, *J* = 9.0 Hz, 2.4 Hz, 1H), 5.71 (s, 1H), 3.82 (s, 3H), 3.33 (brs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.2, 152.5, 145.2, 137.2, 137.1, 131.5, 129.9, 129.6, 129.2, 128.7, 128.4, 128.3, 127.1, 124.6, 122.4, 120.6, 113.3, 108.4, 102.4, 96.6, 55.5; IR (ATR) 3360, 3055, 2955, 2835, 1613, 1504, 1444, 1358, 1323, 1288, 1252, 1199, 1161, 1122, 1072, 1030, 845 cm^{-1}; HRMS (FD+) m/z: [M] Calcd for $C_{22}H_{17}BrNaO_3$ 408.0361, found: 408.0360.

2-(2-methylphenyl)-7-methoxy-4-phenyl-2H-chromen-2-ol (**1f**)

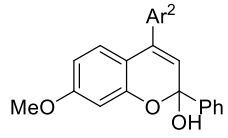


1f

(Ar^1: 2-MeC_6H_4)

Yellow solid (529.0 mg, 1.5 mmol, 64% yield); R_f = 0.53 (hexane/EtOAc = 4/1); ^{1}H NMR (600 MHz, C_6D_6) δ 8.06 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.25-7.22 (m, 2H), 7.19-7.15 (m, 3H), 7.15-7.10 (m, 3H), 7.05 (d, *J* = 6.0 Hz, 1H), 6.73 (d, *J* = 2.4 Hz, 1H), 6.51 (dd, *J* = 9.0 Hz, 2.4 Hz, 1H), 5.54 (s, 1H), 3.25 (s, 3H), 2.75 (brs, 1H), 2.40 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.2, 152.8, 140.1, 137.5, 137.3, 136.9, 131.9, 128.8, 128.7, 128.4, 128.1, 127.1, 125.6, 125.4, 120.3, 113.3, 108.2, 102.2, 96.9, 55.4, 21.2; IR (ATR) 3357, 3063, 3008, 2965, 1613, 1541, 1444, 1357, 1275, 1198, 1162, 1110, 1032, 749 cm^{-1}; HRMS (FD+) m/z: [M] Calcd for $C_{23}H_{20}O_3$ 344.1412, found:344.1411.

7-methoxy-2-phenyl-4-(p-tolyl)-2H-chromen-2-ol (1g)

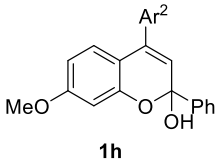


1g

(Ar^2: 4-MeC_6H_4)

Yellow solid (702.6 mg, 2.0 mmol, 68% yield); R_f = 0.35 (hexane/EtOAc = 4/1); ^{1}H NMR (600 MHz, C_6D_6) δ 7.80 (dm, *J* = 7.2 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 2 H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.11 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 2.4 Hz, 1H), 6.54 (d, *J* = 8.4 Hz, 1H), 5.72 (s, 1H), 3.27 (s, 3H), 2.87 (br, 1H), 2.14 (s, 3H); ^{13}C NMR (151 MHz, C_6D_6) δ 161.8, 154.0, 144.2, 137.8, 136.7, 135.3, 129.4, 129.2, 128.42, 128.36, 127.4, 126.5, 122.0, 114.3, 108.5, 102.9, 97.7, 55.0, 21.2; IR (ATR) 3381, 3026, 2934, 1613, 1504, 1448, 1356, 1273, 1199, 1121, 1032, 816, 765, 700 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{20}NaO_3$ 367.1310, found: 367.1304.

4-(4-chlorophenyl)-7-methoxy-2-phenyl-2H-chromen-2-ol (1h)

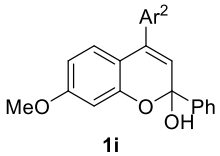


1h
(Ar^2: 4-ClC_6H_4)

Yellow solid (488.9 mg, 1.3 mmol, 67% yield); R_f = 0.37 (hexane/EtOAc = 4/1); ^{1}H NMR (600 MHz, C_6D_6) δ 7.77 (dd, *J* = 8.4 Hz, 1.2 Hz, 2H), 7.19 (t, *J* = 7.8 Hz, 2H), 7.12 (tt, *J* = 7.2 Hz, 1.2 Hz, 1H), 7.08 (dt, *J* = 8.4 Hz, 1.8 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 2H), 6.80 (d, *J* = 2.4 Hz, 1H), 6.54 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 5.54 (s, 1H), 3.27 (s, 3H), 2.75 (br, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.3, 152.8, 143.0, 135.9, 135.7, 134.1, 130.1, 128.6, 128.5, 128.3, 126.7, 125.7, 121.5, 113.2, 108.2, 102.5, 97.1, 55.4; IR (ATR) 3408, 3060, 2959, 2837, 1612, 1566, 1504, 1489, 1448, 1354, 1275, 1199, 1160, 1089, 1014, 820, 741, 700 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{17}ClNaO_3$ 387.0764, found: 387.0758.

7-methoxy-4-(4-methoxyphenyl)-2-phenyl-2H-chromen-2-ol (1i)

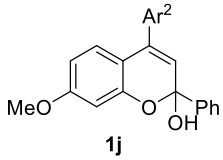
Yellow solid (800.1 mg, 2.2 mmol, 74% yield); R_f = 0.27 (hexane/EtOAc = 4/1); ^{1}H NMR (600 MHz, C_6D_6) δ 7.74-7.72 (m, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.38-7.33 (m, 3H), 7.16 (d, *J* = 9.0 Hz, 1H), 6.94 (d, *J* = 9.0 Hz, 2H), 6.71 (d, *J* = 2.4 Hz, 1H), 6.55 (dd, *J* = 9.0 Hz, 2.4 Hz, 1H), 5.74 (s, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 3.35 (brs, 1H); ^{13}C NMR (151 MHz, C_6D_6) δ 161.8, 160.1, 154.0, 144.3, 136.4, 130.4, 128.42, 128.36, 127.4, 126.5, 121.8, 114.5, 114.2, 108.6, 102.9, 97.7, 55.0, 54.9, one carbon was not found due to overlapping; IR (ATR) 3401, 3066, 3006, 2960, 2835, 1613, 1564, 1504, 1448, 1355, 1318, 1275, 1198, 1161, 1124, 1027, 1006, 809 cm^{-1}; HRMS (FD) m/z: [M] Calcd for $C_{23}H_{20}O_4$ 360.1362, found 360.1361.



1i
(Ar^2: 4-$MeOC_6H_4$)

7-methoxy-2-phenyl-4-(3-(trifluoromethyl)phenyl)-2H-chromen-2-ol (1j)

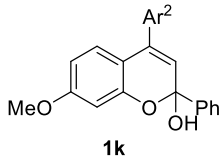
Yellow solid (541.8 mg, 1.4 mmol, 68% yield); R_f = 0.49 (hexane/EtOAc = 4/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.2 Hz, 2H), 7.67 (s, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.8Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.72 (d, *J* = 3.0 Hz, 1H), 6.55 (dd, *J* = 9.0 Hz, 2.4 Hz, 1H), 5.77 (s, 1H), 3.81 (s, 3H), 3.45 (brs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.4, 152.8, 142.9, 138.4, 135.6, 132.1, 130.9 (q, *J* = 31.9 Hz), 128.9, 128.6, 128.4, 126.5, 125.7, 125.6 (q, *J* = 2.9 Hz), 124.9 (q, *J* = 2.9 Hz), 122.3 (q, *J* = 273 Hz), 122.1, 113.0, 108.4, 102.6, 97.1, 55.5; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.5; IR (ATR) 3407, 3066, 2938, 2838, 1613, 1567, 1505, 1444, 1325, 1252, 1160, 1122, 1073, 1008, 804, 739 cm^{-1}; HRMS (FD+) m/z: [M] Calcd for $C_{23}H_{17}F_3O_3$421.1027, found: 421.1022.



1j
(Ar^2: 3-$CF_3C_6H_4$)

4-(3-bromophenyl)-7-methoxy-2-phenyl-2H-chromen-2-ol (1k)

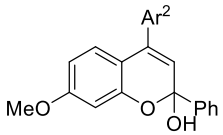
Yellow solid (442.0 mg, 1.1 mmol, 54% yield); R_f = 0.48 (hexane/EtOAc = 4/1); ^{1}H NMR (600 MHz, C_6D_6) δ 7.75 (d, *J* = 7.2 Hz, 2H), 7.46 (s, 1H), 7.26 (d, *J* = 7.8 Hz, 1H), 7.19 (t, *J* = 8.4 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 1H), 6.98-6.95 (m, 2H), 6.78 (d, *J* = 2.4 Hz, 1H), 6.72 (t, *J* = 7.8 Hz, 1H), 6.45 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 5.48 (s, 1H), 3.26 (s, 3H), 2.73 (brs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.3, 152.8, 142.9, 139.6, 135.5, 131.7, 131.2, 129.9, 128.6, 128.4, 127.4, 126.7, 125.7, 122.5, 121.8, 113.1, 108.3, 102.5, 97.1, 55.5; IR (ATR) 3388, 3063, 3006, 2963, 2835, 1613, 1563, 1504, 1472, 1449, 1416, 1355, 1319, 1275, 1260, 1199, 1161, 1125, 1032, 1005, 810, 764, 750 cm^{-1}; HRMS (FD+) m/z: $[M]^+$ Calcd for $C_{22}H_{17}BrO_3$ 408.0361, found: 408.0358.



1k
(Ar^2: 3-BrC_6H_4)

7-methoxy-2-phenyl-4-(o-tolyl)-2H-chromen-2-ol (**1l**)

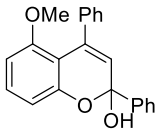
Yellow solid (743.9 mg, 2.2 mmol, 72% yield); R_f = 0.40 (hexane/EtOAc = 4/1); ^{1}H NMR (600 MHz, $CDCl_3$, mixture of two rotamers) δ 7.73-7.70 (m, 2H), 7.43-7.39 (m, 2H), 7.37-7.33 (m, 1H), 7.30-7.06 (m, 4H), 6.71-6.67 (m, 2H), 6.48-6.45 (m, 1H), 5.67-5.65 (m, 1H), 3.81-3.79 (m, 3H), 3.47-3.33 (m, 1H), 2.32-2.05 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$, mixture of two rotamers) δ 161.1, 152.4, 152.1, 143.21, 143.17, 136.9, 136.8, 136.4, 136.24, 136.21, 135.9, 133.1, 130.0, 129.5, 129.3, 128.5, 128.4, 128.32, 128.29, 128.1, 127.9, 126.8, 126.6, 125.8, 125.72, 125.69, 125.64, 121.4, 113.7, 113.6, 108.3, 108.1, 102.2, 102.0, 97.5, 97.3, 55.4, 19.7, some carbons were not found due to overlapping; IR (ATR) 3420, 3060, 3015, 2951, 2836, 1613, 1504, 1448, 1356, 1273, 1199, 1121, 1032, 814, 765, 700 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{20}NaO_3$ 367.1310, found: 367.1305.



1l
(Ar^2: 2-MeC_6H_4)

5-methoxy-2,4-diphenyl-2H-chromen-2-ol (**1n**)

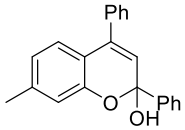
Yellow solid (463 mg, 1.4 mmol, 70% yield); R_f = 0.39 (hexane/EtOAc = 4/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.4 Hz, 1.8 Hz, 2H), 7.55 (tt, *J* = 7.2 Hz, 1.2 Hz, 1H), 7.49 (s, 1H), 7.46-7.41 (m, 4H), 7.37-7.32 (m, 3H), 7.20 (t, *J* = 8.4 Hz, 1H), 6.68 (dd, *J* = 8.4 Hz, 1.2 Hz, 1H), 6.43 (dd, *J* = 8.4 Hz, 0.6 Hz, 1H), 6.11 (brs, 1H), 3.49 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.3, 157.5, 154.6, 146.6, 140.2, 137.5, 133.1, 130.0, 129.2, 128.8, 128.5, 128.4, 127.0, 126.2, 116.0, 110.2, 103.7, 55.6; IR (ATR) 3336, 3057, 3020, 2937, 2836, 2372, 2350, 1595, 1489, 1466, 1448, 1437, 1362, 1264, 1218, 1177, 1087, 1041, 1020 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{18}NaO_3$ 353.1154, found: 353.1149.



1n

7-methyl-2,4-diphenyl-2H-chromen-2-ol (**1o**)

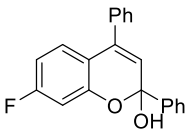
Yellow solid (434 mg, 1.4 mmol, 69% yield); R_f = 0.50 (hexane/EtOAc = 4/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.21-7.18 (m, 2H), 7.13-7.02 (m, 7H), 6.92 (s, 1H), 6.56 (d, *J* = 7.8 Hz, 1H), 5.68 (s, 1H), 3.54 (s, 1H), 2.02 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.4, 144.2, 140.4, 138.1, 136.7, 129.3, 128.7, 128.4, 126.5, 126.2, 124.0, 122.5, 118.4, 97.3, 21.4, some carbons were not found due to overlapping; IR (ATR) 3527, 3393, 3058, 2920, 2279, 1563, 1490, 1447, 1417, 1355, 1329, 1309, 1219, 1169, 1154, 1123, 1076, 1010, 920 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{18}NaO_2$ 337.1204, found: 337.1200.



1o

7-fluoro-2,4-diphenyl-2H-chromen-2-ol (**1p**)

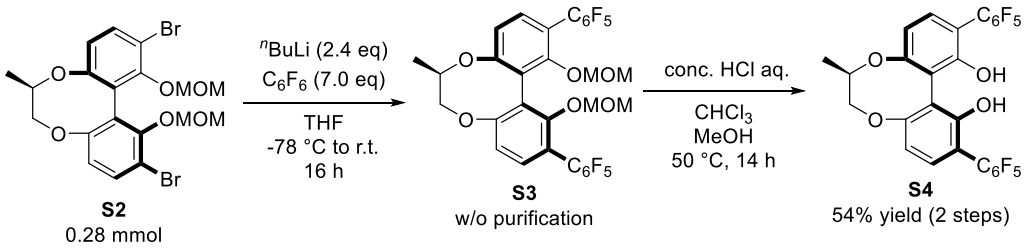
Yellow solid (471 mg, 1.5 mmol, 74% yield); R_f = 0.49 (hexane/EtOAc = 4/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60-7.57 (m, 2H), 7.11-7.02 (m, 10H), 6.94 (dd, *J* = 9.0 Hz, 6.6 Hz, 1H), 6.82 (dd, *J* = 10.8 Hz, 3.0 Hz, 1H), 6.40 (dt, *J* = 7.8 Hz, 2.4 Hz, 1H), 5.58 (s, 1H), 2.67 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.0 (d, *J* = 248.7 Hz), 153.8 (d, *J* = 13.0 Hz), 147.7, 136.2, 129.1, 128.5, 128.4, 127.7, 127.6, 126.3, 123.8, 117.5, 108.6 (d, *J* = 21.7 Hz), 105.3 (d, *J* = 26.0 Hz), 97.6, some carbons were not found due to overlapping; ^{19}F NMR (565 MHz, $CDCl_3$) δ -110.3 to -110.4 (m); IR (ATR) 3544, 3370, 3059, 2354, 1810, 1581, 1498,



1p

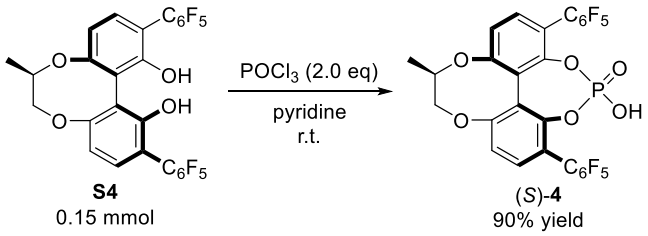
1491, 1447, 1355, 1313, 1273, 1218, 1175, 1144, 1107, 1078, 995 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{15}FNaO_2$ 341.0954, found: 341.0949.

3. Preparation of Catalyst



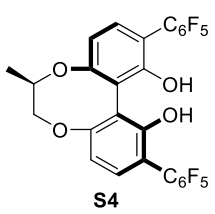
To a solution of **S2** (141.2 mg, 0.28 mmol) in THF (1.4 mL), ^{n}BuLi (1.6 M in hexane, 0.42 mL, 0.67 mmol) was added slowly at -78 °C, and the reaction mixture was stirred at -78 °C for 1 h. To the resulting solution was added C_6F_6 (4.2 M in THF, 0.48 mL, 2.0 mmol) at -78 °C. The reaction mixture allowed warming at room temperature and stirred for 12 h. The reaction was quenched with saturated NH_4Cl aq. and the aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The residual crude product was used for next stp without purification.

To the solution of crude **S3** in MeOH (4.7 mL) and CH_2Cl_2 (4.7 mL) was added conc HCl aq. (0.2 mL) at room temperature. The reaction mixture was stirred for 14 h at 50 °C. After cooling to 0 °C, saturated $NaHCO_3$ solution (5.0 mL) was added. The resulting mixuture was extracted with CH_2Cl_2, and the combined extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The residual crude product was chromatographed on silica gel (hexane/EtOAc = 4:1 to hexane/CH_2Cl_2 = 1:2) to give the product **S4** as white solid (89.3 mg, 54% yield).



To the solution of **S4** (88.6 mg, 0.15 mmol) in pyridine (1.5 mL) was slowly added $POCl_3$ (46.0 mg, 0.3 mmol). The reaction mixture was stirred at room temperature for 12 h. To the resulting solution was added H_2O (1.0 mL) at room temperature, and then the reaction mixture was stirred for additional 30 min. After cooling to 0 °C, 6 M HCl aq. (2.0 mL) was added and aqueous layer was extracted with CH_2Cl_2. The combined extracts were washed with 6 M HCl aq., dried over Na_2SO_4 and concentrated under reduced pressure. The residual crude product was chromatographed on silica gel (CH_2Cl_2/MeOH = 5:1). The obtained product was dissolved in Et_2O, washed with 6 M HCl aq. (x3), dried over Na_2SO_4 and concentrated under reduced pressure to give the product 1c as white solid (88.1 mg, 90% yield).

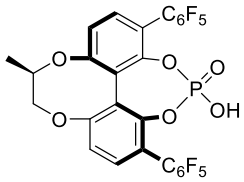
(*R*)-6-methyl-2,11-bis(6,6,6,6,6-pentafluoro-6l8-hexa-1,3,5-triyn-1-yl)-6,7-dihydrodibenzo[e,g][1,4]dioxocine-1,12-diol (S4)



S4

White solid (89.3 mg, 0.15 mmol, 54% yield); $[\alpha]^{25.3}_D$ = +64.5 (*c* = 0.5, $CHCl_3$, >99% ee); R_f = 0.38 (hexane/EtOAc = 4/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (t, *J* = 9.0 Hz, 2H), 6.95 (dd, *J* = 8.4 Hz, 4.2 Hz, 2H), 5.60 (s, 1H), 5.57 (s, 1H), 4.45 (dd, *J* = 12.0 Hz, 3.6 Hz, 1H), 4.39-4.32 (m, 1H), 3.81 (dd, *J* = 12.0 Hz, 10.2 Hz, 1H), 1.37 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.3, 160.8, 150.9, 150.8, 144.4 (dm, *J* = 251.6 Hz), 140.7 (dm, *J* = 258.8 Hz), 137.6 (dm, *J* = 250.1 Hz), 133.2, 116.1, 116.0, 115.54, 115.49, 112.2-111.8 (m), 81.8, 79.0, 16.8, some carbon were not found due to overlapping; ^{19}F NMR (565 MHz, $CDCl_3$) δ -139.3 to -139.5 (m, 2F), -139.8 to -140.0 (m, 2F), -154.8 to -154.9 (m, 2F), -162.1 to -162.4 (m, 4F); IR (ATR) 3299, 2983, 2937, 1654, 1603, 1582, 1522, 1496, 1450, 1408, 1323, 1283, 1255, 1218, 1167, 1133, 1060, 1049, 1026, 984, 916, 863, 825 cm^{-1}; HRMS (FD+) m/z: [M] Calcd for $C_{27}H_{12}F_{10}O_4$ 590.0576, found: 590.0574.

(6*R*,12a*S*)-14-hydroxy-6-methyl-2,11-bis(6,6,6,6,6-pentafluoro-6l8-hexa-1,3,5-triyn-1-yl)-6,7-dihydro-1,12-(epoxyphosphanooxy)dibenzo[e,g][1,4]dioxocine 14-oxide ((*S*)-4)

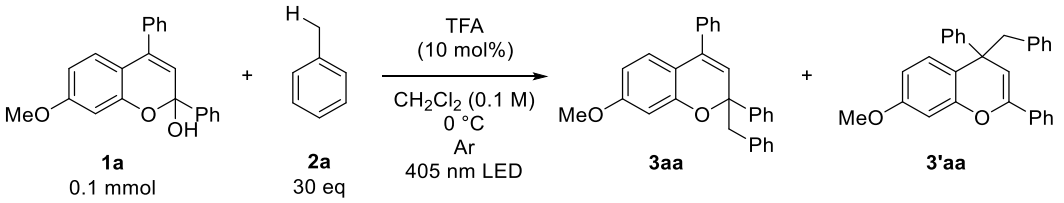


(*S*)-**4**

White solid (88.1 mg, 0.14 mmol, 90% yield); $[\alpha]^{25.0}_D$ = +7.2 (*c* = 1.0, $CHCl_3$, >99% ee); R_f = 0.56 (EtOAc); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (t, *J* = 9.0 Hz, 2H), 7.25 (ddd, *J* = 8.4 Hz, 3.6 Hz, 1.2 Hz, 2H), 4.87 (brs, 1H), 4.54 (dd, *J*= 12.0 Hz, 3.0 Hz, 1H), 4.45-4.38 (m, 1H), 3.88 (dd, *J* = 11.4 Hz, 10.8 Hz, 1H), 1.44 (d, *J* = 6.0 Hz); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.6, 160.3, 145.8 (t, *J* = 7.1 Hz), 144.3 (dm, *J* = 257.3 Hz), 141.4 (dm, *J* = 252.9 Hz), 137.7 (dm, *J* = 250.1 Hz), 137.4 (dm, *J* = 261.7 Hz), 133.1, 133.0, 120.9, 120.8, 120.1, 120.0, 115.8, 115.7, 110.1 (t, *J* = 17.4 Hz), 80.8, 78.2, 17.1, some carbon were not found due to overlapping; ^{31}P NMR (243 MHz, $CDCl_3$) δ 2.49; ^{19}F NMR (565 MHz, $CDCl_3$) δ -138.4 to -138.7 (m, 2F), -140.7 to -140.9 (m, 2F), -154.2 to -154.4 (m, 2F), -162.2 to -162.5 (m, 2F), -162.7 to -162.9 (m, 2F); IR (ATR) 2983, 2931, 1608, 1570, 1524, 1496, 1452, 1414, 1277, 1226, 1122, 1053, 1029, 991, 927, 893, 864, 836 cm^{-1}; HRMS (FD+) m/z: [M] Calcd for $C_{27}H_{11}F_{10}O_6P$ 652.0134, found: 652.0129.

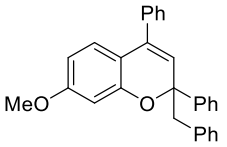
4. Radical addition reaction between chromenol and toluene derivatives

Representative procedure for the radical addition reaction of **1** with **2**



To a mixture of **1a** (33.0 mg, 0.1 mmol) and **2a** (276.4 mg, 3.0 mmol) was added TFA (10 mol%, 1.1 mg, 0.01 mmol) in CH_2Cl_2 (1.0 ml) at -0 ˚C under argon atmosphere. The resulting mixture was stirred at 0 ˚C for 2 h under LED irradiation (405 nm). The reaction was quenched with sat. $NaHCO_3$ aq., and the aqueous phase was extracted with EtOAc. The combined organic phases were dried over Na_2SO_4, and evaporated. The residue was purified by column chromatography (hexane/EtOAc = 10/1) to give a corresponding product as a mixture of regioisomers (32.8 mg, 81% yield, **3aa**/**3'aa** = 95/5).

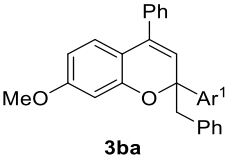
2-benzyl-7-methoxy-2,4-diphenyl-2H-chromene (3aa)



3aa

Colorless oil (32.8 mg, 0.08 mmol, 81% yield, **3aa**/**3'aa** = 95/5); R_f = 0.41 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45-7.42 (m, 2H), 7.40-7.33 (m, 3H), 7.32-7.27 (m, 4H), 7.22 (tt, *J*= 7.8 Hz, 1.8 Hz), 7.16-7.13 (m, 3H), 7.00-7.96 (m, 2H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.59 (d, *J* = 2.4 Hz, 1H), 6.32 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 5.91 (s, 1H), 3.79 (s, 3H), 3.39-3.34 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.7, 154.6, 144.4, 138.5, 135.92, 135.89, 130.9, 128.7, 128.3, 127.9, 127.7, 127.6, 127.2, 126.6, 126.3, 125.8, 123.6, 115.9, 106.5, 102.5, 81.3, 55.4, 48.8; IR (ATR) 3083, 3058, 3027, 3003, 2935, 2834, 1611, 1567, 1503, 1493, 1444, 1355, 1314, 1271, 1196, 1124, 1075, 1031, 1000, 912, 837, 808, 758, 737 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{24}NaO_2$ 427.1674, Found 427.1669.

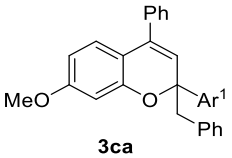
2-benzyl-7-methoxy-4-phenyl-2-(*p*-tolyl)-2H-chromene (3ba)



3ba
(Ar^1: 4-MeC_6H_4)

Colorless oil (30.6 mg, 0.07 mmol, 73% yield, **3ba**/**3'ba** = 93/7); R_f = 0.39 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39-7.30 (m, 7H), 7.16-7.14 (m, 3H), 7.09 (d, *J* = 7.8 Hz, 2H), 7.01-6.99 (m, 2H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 2.4 Hz, 1H), 6.30 (dd, *J* = 8.4 Hz, 3.0 Hz, 1H), 5.89 (s, 1H), 3.79 (s, 3H), 3.37 (d, *J* = 13.8 Hz, 1H), 3.33 (d, *J* = 13.8 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.6, 154.6, 141.4, 138.6, 136.7, 136.0, 135.8, 130.9, 128.7, 128.6, 128.2, 127.65, 127.57, 126.5, 126.3, 125.7, 123.7, 115.9, 106.4, 102.5, 81.2, 55.3, 48.8, 21.1; IR (ATR) 3082, 3058, 3028, 2919, 2836, 2356, 1567, 1504, 1443, 1356, 1318, 1276, 1217, 1198, 1159, 1125, 1075, 994, 837 cm^{-1}; HRMS (FD+) m/z: [M] Calcd for $C_{30}H_{26}O_2$ 418.1933, Found: 418.1932.

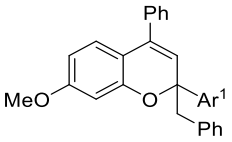
2-benzyl-2-(4-bromophenyl)-7-methoxy-4-phenyl-2H-chromene (3ca)



3ca
(Ar^1: 4-BrC_6H_4)

Colorless oil (29.5 mg, 0.06 mmol, 61% yield, **3ca**/**3'ca** = 95/5); R_f = 0.48 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41-7.35 (m, 5H), 7.32-7.28 (m, 4H), 7.18-7.15 (m, 3H), 6.99-6.95 (m, 2H), 6.83 (d, *J* = 8.4 Hz), 6.58 (d, *J* = 2.4 Hz, 1H), 6.34 (dd, *J* = 8.4 Hz, 3.0 Hz, 1H), 5.88 (s, 1H), 3.80 (s, 3H), 3.35 (d, *J* = 13.8 Hz, 1H), 3.32 (d, *J* = 13.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.8, 154.3, 143.4, 138.3, 136.4, 135.4, 130.94, 130.89, 128.7, 128.3, 127.9, 127.7, 126.7, 126.5, 122.8, 121.2, 115.9, 106.7, 102.6, 80.8, 55.4, 48.6; IR (ATR) 3480, 3409m 2921, 2853, 1612, 1522, 1455, 1412, 1275, 1160, 1198, 1160, 1111, 1073, 1010, 818, 700 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{23}BrNaO_2$ 505.0779, Found: 505.0773.

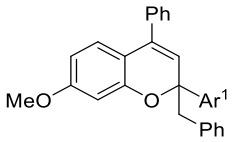
2-benzyl-7-methoxy-4-phenyl-2-(4-(trifluoromethyl)phenyl)-2H-chromene (3da)



3da
(Ar^1: 4-$CF_3C_6H_4$)

Colorless oil (28.4 mg, 0.06 mmol, 60% yield, **3da**/**3'da** = 90/10); R_f = 0.40 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (m, 4H), 7.40-7.34 (m, 3H), 7.31-7.29 (m, 2H), 7.18-7.15 (m, 3H), 6.98-6.95 (m, 2H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.61 (d, *J* = 2.4 Hz, 1H), 6.35 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 5.92 (s, 1H), 3.80 (s, 3H), 3.37 (d, *J* = 13.8 Hz, 1H), 3.35 (d, *J* = 13.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.9, 154.3, 148.5, 138.2, 136.7, 135.3, 130.9, 129.2 (q, *J* = 33.2 Hz), 128.7, 128.3, 127.9, 127.7, 126.8, 126.6, 126.2, 124.9 (q, *J* = 2.9 Hz), 124.1 (q, *J* = 273.3 Hz), 122.7, 115.7, 106.8, 102.6, 80.9, 55.4, 48.7; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.3; IR (ATR) 3063, 3029, 2936, 1613, 1567, 1504, 1444, 1408, 1323, 1275, 1160, 1122, 1068, 1033, 841, 764, 700 cm^{-1}; HRMS (FD+) m/z: [M] Calcd for $C_{30}H_{23}F_3O_2$ 472.1650, Found: 472.1649.

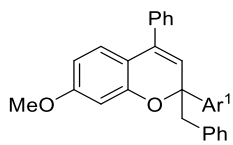
2-benzyl-2-(3-bromophenyl)-7-methoxy-4-phenyl-2H-chromene (3ea)



3ea
(Ar^1: 3-BrC_6H_4)

Colorless oil (30.0 mg, 0.06 mmol, 62% yield, **3ea**/**3'ea** = 97/3); R_f = 0.43 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (t, *J* = 1.8 Hz, 1H), 7.441-7.32 (m, 5H), 7.32-7.29 (m, 2H), 7.18-7.16 (m, 3H), 7.14 (t, *J* = 7.8 Hz, 1H), 7.00-6.96 (m, 2H), 6.84 (d, *J* = 9.0 Hz, 1H), 6.60 (d, *J* = 3.0 Hz, 1H), 6.35 (dd, *J* = 9.0 Hz, 2.4 Hz, 1H), 5.85 (s, 1H), 3.80 (s, 3H), 3.34-3.32 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.9, 154.3, 146.9, 138.3, 136.5, 135.4, 130.9, 130.3, 129.5, 129.0, 128.7, 128.3, 127.9, 127.7, 126.7, 126.6, 124.5, 122.7, 122.2, 115.7, 106.8, 102.6, 80.8, 55.4, 48.7; IR (ATR) 3028, 2992, 2952, 2918, 2835, 1611, 1563, 1502, 1468, 1356, 1316, 1275, 1197, 1161, 1126, 1032, 763, 749, 699 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{23}BrNaO_2$ 505.0779, Found: 505.0774.

2-benzyl-7-methoxy-4-phenyl-2-(*o*-tolyl)-2H-chromene (3fa)

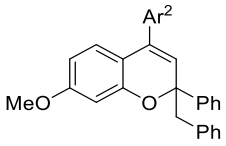


3fa
(Ar^1: 2-MeC_6H_4)

Colorless oil (35.6 mg, 0.09 mmol, 85% yield, **3fa**/**3'fa** = 93/7); R_f = 0.44 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.8 Hz, 1H), 7.39-7.33 (m, 3H), 7.31-7.28 (m, 2H), 7.16-7.12 (m, 5H), 7.07-7.02 (m, 3H), 6.77 (d, *J* = 7.8 Hz, 1H), 6.56 (d, *J* = 2.4 Hz, 1H), 6.29 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 5.87 (s, 1H), 3.77 (s, 3H), 3.52 (d, *J* = 13.8 Hz, 1H), 3.46 (d, *J* = 13.8 Hz, 1H), 2.64 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.6, 154.8, 141.9, 138.7, 136.13, 136.12, 135.4, 132.4, 131.0, 128.7, 128.3, 127.64, 127.58, 127.51, 127.3, 126.6, 126.4, 125.2, 123.5, 116.0, 106.4, 102.2, 82.6, 55.3, 46.9, 22.3; IR (ATR) 3059, 3027, 2958, 2931, 2835, 1613, 1567, 1504, 1455, 1443, 1357, 1314, 1285, 1196, 1160, 1125, 1075,

1032, 988, 910, 836, 804, 762, 734, 700, 671, 648 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{26}NaO_2$ 441.1830, Found: 441.1825.

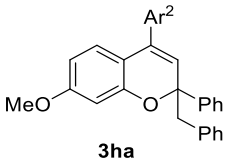
2-benzyl-7-methoxy-2-phenyl-4-(*p*-tolyl)-2H-chromene (3ga)



3ga
(Ar^2: 4-MeC_6H_4)

Colorless oil (37.7 mg, 0.09 mmol, 86% yield, **3ga**/**3'ga** = 96/4); R_f = 0.42 (hexane/EtOAc = 10/1); ^1H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.23-7.17 (m, 5H), 7.15-7.12 (m, 3H), 6.99-6.95 (m, 2H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.58 (d, *J* = 2.4 Hz, 1H), 6.31 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 5.90 (s, 1H), 3.79 (s, 3H), 3.36-3.34 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.6, 154.6, 144.5, 137.5, 135.9, 135.8, 135.6, 130.9, 128.9, 128.6, 127.9, 127.6, 127.1, 126.6, 126.3, 125.8, 123.2, 116.0, 106.5, 102.5, 81.3, 55.4, 48.9, 21.2; IR (ATR) 3057, 3004, 2921, 1611, 1501, 1445, 1275, 1261, 1197, 1160, 1125, 1032, 814 cm^{-1}; HRMS (FD+) m/z: [M] Calcd for $C_{30}H_{26}O_2$ 418.1933, Found: 418.1931.

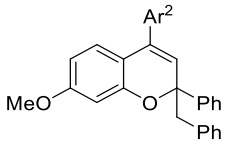
2-benzyl-4-(4-chlorophenyl)-7-methoxy-2-phenyl-2H-chromene (3ha)



3ha
(Ar^2: 4-ClC_6H_4)

Colorless oil (39.9 mg, 0.09 mmol, 91% yield, **3ha**/**3'ha** = 93/7); R_f = 0.39 (hexane/EtOAc = 10/1); ^1H NMR (600 MHz, $CDCl_3$) δ 7.43-7.41 (m, 2H), 7.34 (dt, *J* = 9.0 Hz, 2.4 Hz, 2H), 7.29 (tt, *J* = 7.8 Hz, 1.8 Hz, 2H), 7.25-7.21 (m, 3H), 7.16-7.14 (m, 3H), 6.99-6.95 (m, 2H), 6.76 (d, *J* = 9.0 Hz, 1H), 6.59 (d, *J* = 2.4 Hz, 1H), 6.32 (dd, *J* = 9.0 Hz, 2.4 Hz, 1H), 5.90 (s, 1H), 3.80 (s, 3H), 3.40-3.30 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.9, 154.6, 144.2, 136.9, 135.8, 135.0, 133.6, 130.9, 130.1, 128.5, 127.9, 127.6, 127.2, 126.4, 126.3, 125.7, 123.9, 115.5, 106.6, 102.7, 81.3, 55.4, 48.8; IR (ATR) 3061, 3029, 2931, 2835, 1612, 1504, 1489, 1444, 1353, 1316, 1275, 1197, 1160, 1125, 1089, 1032, 1014,1001, 911, 837, 749, 699 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{23}ClNaO_2$ 461.1284, Found: 461.1279.

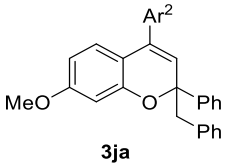
2-benzyl-7-methoxy-4-(4-methoxyphenyl)-2-phenyl-2H-chromene (3ia)



3ia
(Ar^2: 4-$MeOC_6H_4$)

White solid (13.0 mg, 0.03 mmol, 29% yield, **3ia**/**3'ia** = 95/5); R_f = 0.73 (hexane/EtOAc = 4/1); ^1H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.25 (dt, *J* = 8.4 Hz, 2.4 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.16-7.12 (m, 3H), 6.99-6.95 (m, 2H), 6.91 (dt, *J* = 9.0 Hz, 2.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.59 (d, *J* = 2.4 Hz, 1H), 6.32 (dd, *J* = 9.0 Hz, 3.0 Hz, 1H), 5.88 (s, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 3.36-3.34 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.7, 159.2, 154.7, 144.5, 136.0, 135.5, 130.9, 129.9, 127.9, 127.6, 127.1, 126.6, 126.3, 125.8, 123.0, 116.2, 113.7, 106.5, 102.6, 81.3, 55.4, 55.3, 48.9; IR (ATR) 2936, 2878, 2356, 1739, 1510, 1453, 1254, 1162, 1111, 1031, 830 cm^{-1}; HRMS (FD+) m/z: [M] Calcd for $C_{30}H_{26}O_3$ 434.1882, Found: 434.1880.

2-benzyl-7-methoxy-2-phenyl-4-(3-(trifluoromethyl)phenyl)-2H-chromene (3ja)

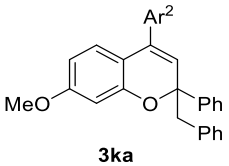


3ja
(Ar^2: 3-$CF_3C_6H_4$)

Colorless oil (42.5 mg, 0.09 mmol, 90% yield, **3ja**/**3'ja** = 94/6); R_f = 0.46 (hexane/EtOAc = 10/1); ^1H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 6.6 Hz, 1H), 7.55 (s, 1H), 7.51-7.46 (m, 2H), 7.45-7.42 (m, 2H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.23 (tt, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.17-7.15 (m, 3H), 7.01-6.98 (m, 2H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.61 (d, *J* = 2.4 Hz, 1H), 6.33 (dd, *J* = 8.4 Hz, 3.0 Hz, 1H), 5.93 (s,

1H), 3.80 (s, 3H), 3.39-3.35 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.1, 154.6, 144.2, 139.4, 135.8, 134.9, 132.1, 130.9, 130.8 (q, J = 33.2 Hz), 128.8, 128.0, 127.6, 127.3, 126.5, 126.2, 125.7, 125.4 (q, J = 4.4 Hz), 124.6, 124.5 (q, J = 2.9 Hz), 124.1 (q, J = 254.6 Hz), 115.2, 106.7, 102.7, 81.4, 55.4, 48.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.4; IR (ATR) 3063, 3030, 2935, 2916, 2837, 1613, 1504, 1443, 1327, 1276, 1259, 1161, 1125, 1032, 910, 806, 750, 700 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{23}F_3NaO_2$ 495.1548, Found: 495.1542.

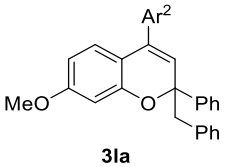
2-benzyl-4-(3-bromophenyl)-7-methoxy-2-phenyl-2H-chromene (3ka)



3ka
(Ar^2: 3-BrC_6H_4)

Colorless oil (32.9 mg, 0.07 mmol, 68% yield, **3ka**/**3'ka** = 96/4); R_f = 0.45 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49-7.45 (m, 2H), 7.44-7.41 (m, 2H), 7.30 (t, J = 7.8 Hz, 2H), 7.25-7.21 (m, 3H), 7.17-7.14 (3H), 6.99-6.96 (m, 2H), 6.77 (d, J = 8.4 Hz, 1H), 6.59 (d, J = 3.0 Hz, 1H), 6.34 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 5.91 (s, 1H), 3.80 (s, 3H), 3.38-3.32 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.9, 154.6, 144.2, 140.6, 135.8, 134.8, 131.6, 130.9, 130.8, 129.8, 128.0, 127.6, 127.4, 127.3, 126.4, 126.3, 125.7, 124.3, 122.3, 115.3, 106.7, 102.7, 81.3, 55.4, 48.8; IR (ATR) 3060, 3028, 2954, 2927, 2835, 1612, 1564, 1504, 1472, 1444, 1352, 1275, 1197, 1160, 1128, 1032, 910, 750, 698 cm^{-1}; HRMS (FD+) m/z: [M] Calcd for $C_{29}H_{23}BrO_2$ 482.0881, Found: 482.0880.

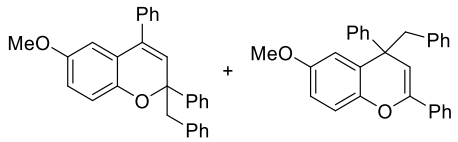
2-benzyl-7-methoxy-2-phenyl-4-(*o*-tolyl)-2H-chromene (3la)



3la
(Ar^2: 2-MeC_6H_4)

Colorless oil (28.0 mg, 0.07 mmol, 67% yield, **3la**/**3'la** = 98/2); R_f = 0.45 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$, mixture of two rotamers) δ 7.53-7.43 (m, 2H), 7.34-7.28 (m, 2H), 7.26-7.22 (m, 2H), 7.21-7.15 (m, 5H), 7.13-7.09 (m, 2H), 7.04-7.01 (m, 1H), 6.60-6.57 (m, 1H), 6.40-6.35 (m, 1H), 6.26-6.21 (m, 1H), 5.79-5.77 (m, 1H), 3.78-3.76 (m, 3H), 3.45-3.23 (m, 2H), 2.05-1.82 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$, mixture of two rotamers) δ 160.8, 160.7, 154.1, 154.0, 145.4, 144.8, 138.01, 137.93, 136.63, 136.61, 136.0, 135.4, 135.2, 130.9, 130.8, 129.9, 129.8, 129.6, 129.4, 128.1, 127.9, 127.8, 127.7, 127.6, 127.2, 127.1, 126.4, 126.2, 125.7, 125.6, 125.5, 123.6, 123.5, 115.8, 115.7, 106.5, 106.4, 102.3, 102.2, 81.6, 81.5, 55.35, 55.30, 49.5, 48.9, 19.6, 19.3; IR (ATR) 3059, 3027, 2958, 2931, 2835, 1613, 1567, 1504, 1455, 1443, 1357, 1314, 1285, 1196, 1160, 1125, 1032, 910, 836, 762, 734, 700 cm^{-1}; HRMS (FD+) m/z: [M] Calcd for $C_{30}H_{26}O_2$ 418.1933, Found: 418.1933.

2-benzyl-6-methoxy-2,4-diphenyl-2H-chromene (3ma) and **4-benzyl-6-methoxy-2,4-diphenyl-4H-chromene (3'ma)**

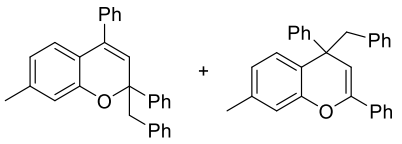


3ma + **3'ma**

Colorless oil (racemic reaction: 28.3 mg, 0.07 mmol, 70% yield, **3ma**/**3'ma** = 64/36, enantioselective reaction: 14.2 mg, 0.035 mmol, 35% yield, **3ma**/**3'ma** = 74/26); $[\alpha]^{25.1}_D$ = +4.5 (c = 0.4, $CHCl_3$, **3ma** = 60% ee, **3'ma** = 26% ee); R_f = 0.42 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) **3ma**: δ 7.58-7.53 (m, 1H), 7.43-7.41 (m, 2H), 7.41-7.30 (m, 4H), 7.27 (m, 1H), 7.21 (tt, J = 7.8 Hz, 1.8 Hz, 1H), 7.16-7.13 (m, 3H), 6.97-6.94 (m, 3H), 6.81-6.78 (m, 1H), 6.71 (dd, J = 9.0 Hz, 3.6 Hz, 1H), 6.47 (d, J = 3.6 Hz, 1H), 6.11 (s, 1H), 3.61 (s, 3H), 3.36-3.34 (m, 2H); **3'ma**: δ7.58-7.53 (m, 1H), 7.40-7.30 (m, 7H), 7.29-7.25 (m, 4H), 7.25-7.22 (m, 1H), 7.09-7.01 (m, 3H), 6.69 (dd, J = 9.0 Hz, 3.0 Hz, 1H), 6.58 (d, J = 2.4 Hz, 1H), 5.27 (s, 1H), 3.71 (s, 3H), 3.64-3.61 (m, 1H), 3.38-3.36 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) (for mixture of regioisomers) δ 155.2, 153.6, 149.4, 147.8, 147.2, 145.8, 144.2, 138.2, 137.6,

136.3, 135.9, 134.4, 130.9, 130.6, 128.8, 128.4, 128.3, 128.2, 127.9, 127.8, 127.6, 127.34, 127.29, 127.1, 126.4, 126.1, 125.9, 124.8, 123.3, 117.5, 116.9, 114.4, 113.6, 113.3, 111.5, 103.3, 80.6, 55.6, 48.7, 47.8, 46.2; IR (ATR) 3059, 3029, 2917, 2832, 1601, 1575, 1487, 1446, 1427, 1264, 1181, 1051, 699 cm^{-1}; HRMS (FD+) m/z: $[M]^+$ Calcd for $C_{29}H_{24}O_2$ 404.1776, Found: 404.1776.

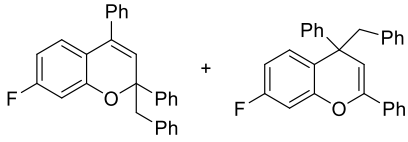
2-benzyl-7-methyl-2,4-diphenyl-2H-chromene (3oa) and **4-benzyl-7-methyl-2,4-diphenyl-4H-chromene (3'oa)**



3oa **3'oa**

Colorless oil (26.4 mg, 0.07 mmol, 68% yield, **3oa**/**3'oa** = 80/20); R_f = 0.43 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) **3oa**: δ 7.55 (t, *J* = 7.2 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.39-7.30 (m, 5H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.16-7.13 (m, 2H), 7.00-6.97 (m, 2H), 6.85 (s, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 1H), 5.99 (s, 1H), 3.37-3.35 (m, 2H), 2.30 (s, 3H); **3'oa**: δ 7.45-7.41 (m, 1H), 7.40-7.30 (m, 5H), 7.23 (d, *J* = 7.2 Hz, 2H), 7.22-7.19 (m, 1H),7.16-7.13 (m, 2H), 7.06 (d, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 7.2 Hz, 2H), 6.95 (d, *J* = 7.8 Hz, 1H), 6.80 (d, *J* = 9.6 Hz, 1H), 6.77-6.57 (m, 1H), 6.69 (s, 1H), 5.31 (s, 1H), 3.58 (d, *J* = 13.2 Hz, 1H), 3.38 (d, *J* = 12.6 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) (for mixture of regioisomers) δ 153.2, 151.0, 149.8, 144.5, 139.7, 138.5, 137.8, 137.4, 136.1, 136.0, 134.4, 130.9, 130.6, 128.8, 128.3, 128.2, 127.93, 127.86, 127.7, 127.6, 127.3, 127.1, 126.3, 126.2, 126.0, 125.8, 125.5, 125.3, 124.7, 124.2, 121.5, 119.9, 117.5, 116.5, 104.2, 80.9, 48.9, 47.8, 21.4, 21.0, some carbon were not found due to overlapping; IR (ATR) 3059, 3029, 2921, 2856, 2350, 1575, 1541, 1495, 1445, 1410, 1375, 1331, 1306, 1267, 1219, 1148, 1075, 1028 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{24}NaO$ 411.1725, Found: 411.1721.

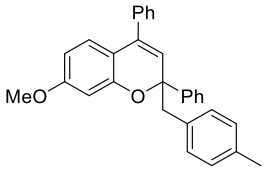
2-benzyl-7-fluoro-2,4-diphenyl-2H-chromene (3pa) and **4-benzyl-7-fluoro-2,4-diphenyl-4H-chromene (3'pa)**



3pa **3'pa**

Colorless oil (20.0 mg, 0.05 mmol, 51% yield, **3pa**/**3'pa** = 70/30); R_f = 0.42 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) **3pa**: δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.40-7.27 (m, 7H), 7.24 (tt, *J* = 7.2 Hz, 1.2 Hz, 1H), 7.17-7.14 (m, 3H), 7.00-6.97 (m, 2H), 6.83 (dd, *J* = 7.8 Hz, 6.6 Hz, 1H), 6.75-6.70 (m, 1H), 6.44 (dt, *J* = 8.4 Hz, 2.4 Hz, 1H), 5.99 (s, 1H), 3.38 (d, *J* = 13.8 Hz, 1H), 3.34 (d, *J* = 13.8 Hz, 1H); **3'pa**: δ 7.55-7.51 (m, 4H), 7.40-7.27 (m, 7H), 7.08 (tt, *J* = 7.2 Hz, 1.8 Hz, 1H), 7.03 (t, *J* = 7.8 Hz, 2H), 7.00-6.97 (m, 1H), 6.75-6.71 (m, 2H), 6.57 (dd, *J* = 9.6 Hz, 2.4 Hz, 1H), 5.33 (s, 1H), 3.54 (d, *J* = 12.6 Hz, 1H), 3.38 (d, *J* = 12.6 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) (for mixture of regioisomers) δ 163.2 (d, *J* = 247.2 Hz), 161.5 (d, *J* = 245.8 Hz), 154.7 (d, *J* = 11.6 Hz), 152.0 (d, *J* = 13.0 Hz), 149.33, 147.5, 144.1, 138.1, 137.3, 135.6, 135.5, 133.8, 130.9, 130.6, 130.3 (d, *J* = 8.8 Hz), 128.7, 128.5, 128.4, 128.3, 128.2, 128.0, 127.95, 127.93, 127.7, 127.4, 126.8 (d, *J* = 10.1 Hz), 126.5, 126.2, 125.7, 125.1, 124.7, 122.0 (d, *J* = 2.9 Hz), 118.8 (d, *J* = 2.9 Hz), 110.6 (d, *J* = 21.7 Hz), 107.6 (d, *J* = 21.6 Hz), 104.5 (d, *J* = 24.4 Hz), 104.4, 103.2 (d, *J* = 24.6 Hz), 81.7, 49.0, 48.0, some carbon were not found due to overlapping; ^{19}F NMR (565 MHz, $CDCl_3$) **3pa**: δ -111.2 to -111.2 (m); **3'pa**: δ -114.3 to -114.5 (m); IR (ATR) 3060, 3030, 2925, 2309, 1541, 1497, 1447, 1423, 1354, 1330, 1311, 1270, 1219, 1146, 1110, 1073, 1025 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{21}FNaO$ 415.1474, Found: 415.1470.

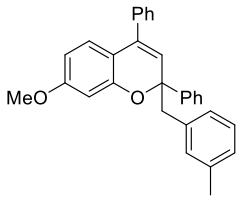
7-methoxy-2-(4-methylbenzyl)-2,4-diphenyl-2H-chromene (3ab)



3ab

Colorless oil (35.2 mg, 0.08 mmol, 84% yield, **3ab**/**3'ab** = 92/8); R_f = 0.50 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.2 Hz), 7.40-7.34 (m, 3H), 7.33-7.30 (m, 2H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 2H), 6.86-6.81 (m, 3H), 6.59 (d, *J* = 2.4 Hz, 1H), 6.32 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 5.92 (s, 1H), 3.79 (s, 3H), 3.36-3.33 (m, 2H), 2.27 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.7, 154.6, 144.5, 138.6, 135.9, 135.8, 132.8, 130.8, 128.8, 128.33, 128.25, 127.9, 127.7, 127.1, 126.6, 125.9, 123.7, 116.0, 106.5, 102.6, 81.3, 55.4, 48.4, 21.0; IR (ATR) 3051, 3026, 3003, 2919, 2835, 1611, 1567, 1504. 1444, 1356, 1314, 1286, 1270, 1197, 1160, 1125, 1033 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ $C_{30}H_{26}NaO_2$ 441.1830, Found 441.1825.

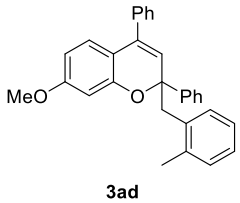
7-methoxy-2-(3-methylbenzyl)-2,4-diphenyl-2H-chromene (3ac)



3ac

Colorless oil (36.0 mg, 0.09 mmol, 86% yield, **3ac**/**3'ac** = 98/2); R_f = 0.50 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46-7.43 (m, 2H), 7.39-7.34 (m, 3H), 7.33-7.27 (m, 4H), 7.22 (tt, *J* = 7.2 Hz, 1.2 Hz, 1H), 7.03 (t, *J* = 7.8 Hz, 1H), 6.96 (d, *J* = 7.2 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 2H), 6.59 (d, *J* = 2.4 Hz, 1H), 6.32 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 5.91 (s, 1H), 3.79 (s, 3H), 3.34 (d, *J* = 13.8 Hz, 1H), 3.31 (d, *J* = 13.8 Hz, 1H), 2.21 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.7, 154.7, 144.5, 138.6, 137.0, 135.9, 135.7, 131.9, 128.8, 128.3, 127.9, 127.8, 127.7, 127.4, 127.13, 127.06, 126.5, 125.9, 123.6, 115.9, 106.5, 102.5, 81.3, 55.4, 48.8, 21.3; IR (ATR) 3057, 3026, 2921, 2835, 1610, 1504, 1491, 1444, 1274, 1197, 1159, 1125, 1072, 1032, 765, 700 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{26}NaO_2$ 441.1830, Found 441.1825.

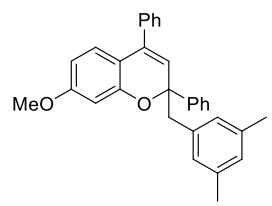
7-methoxy-2-(2-methylbenzyl)-2,4-diphenyl-2H-chromene (3ad)



3ad

Colorless oil (36.8 mg, 0.09 mmol, 88% yield, **3ad**/**3'ad** = 95/5); R_f = 0.52 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.2 Hz, 2H), 7.40-7.35 (m, 3H), 7.34-7.31 (m, 2H), 7.27 (t, *J* = 7.2 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.10-7.00 (m, 4H), 6.79 (d, *J* = 9.0 Hz, 1H), 6.56 (d, *J* = 2.4 Hz, 1H), 6.29 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 5.97 (s, 1H), 3.78 (s, 3H), 3.42 (d, *J* = 13.8 Hz, 1H), 3.36 (d, *J* = 13.8 Hz, 1H), 2.07 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.7, 154.6, 144.9, 138.6, 137.9, 135.9, 134.3, 131.8, 130.0, 128.7, 128.3, 127.9, 127.7, 127.2, 126.5, 125.8, 125.0, 123.6, 115.7, 106.4, 102.4, 81.7, 55.4, 45.7, 20.0; IR (ATR) 3058, 3022, 2956, 2931, 2864, 2835, 1611, 1567, 1504, 1491, 1462, 1444, 1356, 1313, 1274, 1197, 1159, 1124, 1071, 1031, 992, 842, 808, 757, 719, 699 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{26}NaO_2$ 441.1830, Found 441.1825.

2-(3,5-dimethylbenzyl)-7-methoxy-2,4-diphenyl-2H-chromene (3ae)

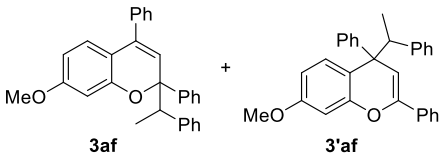


3ae

Colorless oil (30.3 mg, 0.07 mmol, 70% yield, **3ae**/**3'ae** = 97/3); R_f = 0.51 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46-7.43 (m, 2H), 7.40-7.34 (m, 3H), 7.33-7.27 (m, 4H), 7.22 (tt, *J* = 7.2 Hz, 1.8 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.78 (m, 1H), 6.58 (d, *J* = 2.4 Hz, 1H), 6.55 (m, 2H), 6.31 (dd, *J* = 9.0 Hz, 2.4 Hz, 1H), 5.90 (s, 1H), 3.79 (s, 3H), 3.30 (d, *J* = 13.2 Hz, 1H), 3.26 (d, *J* = 13.2 Hz, 1H), 2.17 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.6,

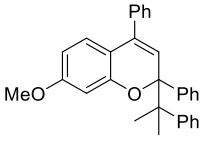
154.7, 144.5, 138.6, 136.8, 135.8, 135.5, 128.9, 128.8, 128.2, 127.9, 127.8, 127.7, 127.1, 126.5, 125.9, 123.6, 116.0, 106.5, 102.5, 81.3, 55.3, 48.7, 21.2; IR (ATR) 3056, 3024, 2916, 2835, 1567, 1504, 1491, 1463, 1443, 1355, 1314, 1284, 1269, 1196, 1125, 1073, 1032, 848, 738, 718, 699 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{31}H_{28}NaO_2$ 455.1987, Found: 455.1981.

7-methoxy-2,4-diphenyl-2-(1-phenylethyl)-2H-chromene (3af) and **7-methoxy-2,4-diphenyl-4-(1-phenylethyl)-4H-chromene (3'af)**



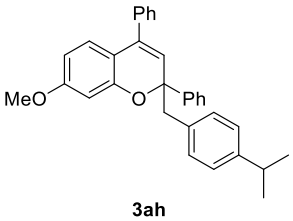
Colorless oil (34.7 mg, 0.08 mmol, 83% yield, **3af**/**3'af** = 86/14, **3af** : 51/49 dr, **3'af**: 51/49 dr); R_f = 0.45 (hexane/EtOAc = 10/1); ^1H NMR (600 MHz, $CDCl_3$) **3af** (for mixture of diastereomers) δ7.40-7.00 (m, 30H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.65-6.63 (m, 1H), 6.62-6.60 (m, 1H), 6.31 (dt, *J* = 9.0 Hz, 2.4 Hz, 1H), 6.26 (dt, *J* = 8.4 Hz, 2.4 Hz, 1H), 5.98 (s, 1H), 5.87 (s, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.39-3.34 (m, 2H), 1.43 (d, *J* = 7.2 Hz, 3H), 1.41 (d, *J* = 7.2 Hz, 3H); **3'af** (for mixture of diastereomers) δ 7.70 (d, *J* = 7.2 Hz, 2H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.45-7.03 (m, 19H), 6.97 (t, *J* = 7.8 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.89 (d, *J* = 7.2 Hz, 2H), 6.67 (d, *J* = 8.4 Hz, 1H), 6.58 (t, *J* = 2.4 Hz, 1H), 6.47 (dt, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.18 (t, *J* = 2.4 Hz, 1H), 5.69 (s, 1H), 5.43 (s, 1H), 3.80 (s, 3H), 3.65 (s, 3H), 2.96-2.91 (m, 1H), 2.82-2.77 (m, 1H), 1.30 (d, *J* = 7.2 Hz, 3H), 1.28 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) (for mixture of regioisomers and their diastereomers) δ 160.74, 160.68, 158.9, 158.4, 154.8, 154.7, 152.7, 150.7, 149.3, 147.8, 147.6, 147.5, 145.8, 144.8, 143.7, 142.7, 142.6, 141.8, 141.5, 138.7, 135.8, 135.4, 134.5, 134.2, 129.8, 129.7, 129.5, 129.3, 128.74, 128.72, 128.4, 128.3, 128.24, 128.18, 128.0, 127.9, 127.80, 127.76, 127.68, 127.65, 127.59, 127.52, 127.33, 127.30, 126.93, 126.89, 126.7, 126.5, 126.4, 126.3, 126.14, 126.05, 125.99, 125.93, 125.89, 125.7, 124.9, 124.7, 123.9, 123.0, 119.4, 117.3, 115.7, 115.6, 110.2, 106.4, 106.1, 103.6, 102.5, 102.3, 100.8, 100.3, 100.1, 83.7, 83.3, 55.4, 55.3, 51.2, 50.6, 48.7, 48.5, 48.4, 48.0, 47.2, 46.4, 17.9, 17.8, 16.3, 15.7, some carbon could not be assigned due to presence of regioisomers and their diastereomers; IR (ATR) 3082, 3058, 3027, 2968, 2934, 2907, 2876, 2830, 2249, 1568, 1541, 1492, 1374, 1322, 1275, 1218, 1197, 1160, 1072, 1032, 1020, 987 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{26}NaO_2$ 441.1830, Found: 441.1825.

7-methoxy-2,4-diphenyl-2-(2-phenylpropan-2-yl)-2H-chromene (3ag)



Colorless oil (31.6 mg, 0.07 mmol, 73% yield, **3ag**/**3'ag** = 91/9); R_f = 0.42 (hexane/EtOAc = 10/1); ^1H NMR (600 MHz, $CDCl_3$) δ 7.39-7.33 (m, 4H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.19-7.15 (m, 3H), 7.13-7.09 (m, 5H), 7.06 (d, *J* = 6.6 Hz, 2H), 6.72 (d, *J* = 9.0 Hz, 1H), 6.56 (t, *J* = 3.0 Hz, 1H), 6.24 (dt, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.12 (s, 1H), 3.77 (s, 3H), 1.56 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.6, 154.7, 144.4, 142.2, 138.9, 135.8, 129.1, 128.8, 128.3, 128.1, 127.6, 126.8, 126.4, 126.1, 122.9, 115.8, 106.1, 102.5, 85.1, 55.3, 46.3, 24.8, 24.4; IR (ATR) 3056, 3027, 2959, 2933, 2835, 2370, 1782, 1569, 1504, 1463, 1443, 1386, 1357, 1307, 1274, 1197, 1160, 1123, 1033, 1014, 970 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{31}H_{28}NaO_2$ 455.1987, Found:455.1982.

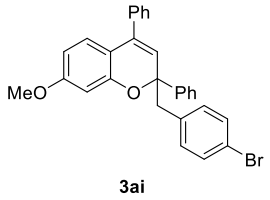
2-(4-isopropylbenzyl)-7-methoxy-2,4-diphenyl-2H-chromene (3ah)



3ah

Colorless oil (39.7 mg, 0.09 mmol, 89% yield, **3ah**/**3'ah** = 92/8); R_f = 0.40 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47-7.44 (m, 2H), 7.39-7.33 (m, 3H), 7.32-7.27 (m, 4H), 7.22 (tt, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.59 (d, *J* = 2.4 Hz, 1H), 6.31 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 5.91 (s, 1H), 3.79 (s, 3H), 3.35 (d, *J* = 13.8 Hz, 1H), 3.31 (d, *J* = 13.8 Hz, 1H), 2.82 (sep, 7.2 Hz, 1H), 1.19 (d, *J* = 7.2 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.7, 154.7, 146.8, 144.6, 138.6, 135.9, 133.2, 130.8, 128.8, 128.2, 127.9, 127.7, 127.1, 126.5, 125.9, 125.7, 123.7, 115.9, 106.4, 102.6, 81.4, 55.4, 48.5, 33.6, 23.98, 23.96; IR (ATR) 3079, 3056, 2959, 2929, 1611, 1567, 1505, 1462, 1444, 1315, 1275, 1197, 1160, 1125, 1033, 910, 749, 700 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{32}H_{30}NaO_2$ 469.2143, Found: 469.2138.

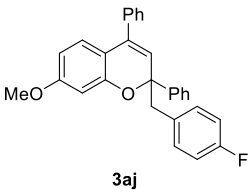
2-(4-bromobenzyl)-7-methoxy-2,4-diphenyl-2H-chromene (3ai)



3ai

Colorless oil (10.2 mg, 0.02 mmol, 21% yield, **3ai**/**3'ai** = 95/5); R_f = 0.40 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.2 Hz, 2H), 7.40-7.33 (m, 3H), 7.32 (d, *J* = 1.2 Hz, 1H), 7.32-7.30 (m, 1H), 7.29 (s, 1H), 7.28-7.27 (m, 1H), 7.27-7.25 (m, 1H), 7.22 (tt, *J* = 7.2 Hz, 1.2 Hz, 1H), 6.85-6.82 (m, 3H), 6.57 (d, *J* = 2.4 Hz, 1H), 6.34 (dd, *J* = 9.0 Hz, 2.4 Hz, 1H), 5.88 (s, 1H), 3.79 (s, 3H), 3.32 (d, *J* = 13.2 Hz, 1H), 3.28 (d, *J* = 13.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.8, 154.4, 144.0, 138.4, 136.2, 134.9, 132.5, 130.7, 128.7, 128.3, 128.0, 127.8, 127.3, 126.7, 125.7, 123.3, 120.5, 115.8, 106.6, 102.6, 81.0, 55.4, 48.1; IR (ATR) 3058, 3027, 2933, 2835, 1611, 1504, 1488, 1444, 1274, 1197, 1160, 1125, 1071, 1032, 1012, 759, 699 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{23}BrNaO_2$ 505.0779, Found: 505.0773.

2-(4-fluorobenzyl)-7-methoxy-2,4-diphenyl-2H-chromene (3aj)

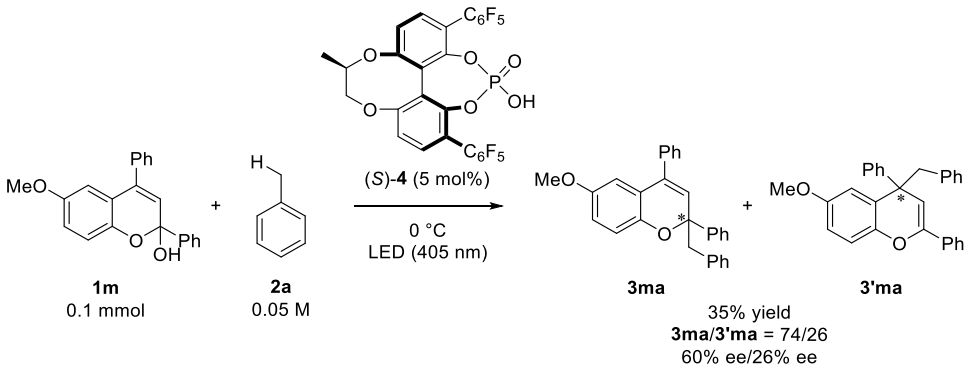


3aj

Colorless oil (34.6 mg, 0.08 mmol, 82% yield, **3aj**/**3'aj** = 96/4); R_f = 0.40 (hexane/EtOAc = 10/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 8.4 Hz, 1.2 Hz, 2H), 7.40-7.33 (m, 3H), 7.32-7.27 (m, 4H), 7.22 (tt, *J* = 7.2 Hz, 1.8 Hz, 1H), 6.95-6.91 (m, 2H), 6.85-6.81 (m, 3H), 6.58 (d, *J* = 3.0 Hz, 1H), 6.32 (dd, *J* = 9.0 Hz, 2.4 Hz, 1H), 5.89 (s, 1H), 3.80 (s, 3H), 3.33 (d, *J* = 13.8 Hz, 1H), 3.31 (d, *J* = 13.8 Hz, 1H), ; ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.7 (d, *J* = 244.3 Hz), 160.8, 154.5, 144.2, 138.4, 136.1, 132.3 (d, *J* = 7.2 Hz), 131.6 (d, *J* =2.9 Hz), 128.7, 128.3, 128.0, 127.8, 127.2, 126.7, 125.7, 123.4, 115.8, 114.4 (21.7 Hz) , 106.5, 102.6, 81.1, 55.4, 48.0; ^{19}F NMR (565 MHz, $CDCl_3$) δ -116.7 to -116.8; IR (ATR) 3057, 3027, 3002, 2929, 2854, 1724, 1610, 1567, 1508, 1444, 1356, 1313, 1286, 1271, 1257, 1221, 1197, 1159, 1032, 835, 700 cm^{-1}; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{23}FNaO_2$ 445.1580, Found: 445.1574.

5. Enantioselective radical addition reaction using chiral phosphoric acid catalyts

Procedure for the enantioselective radical addition reaction between chromenol **1m** and toluene **2a** catalyzed by chiral phosphoric acid (*S*)-**4**.



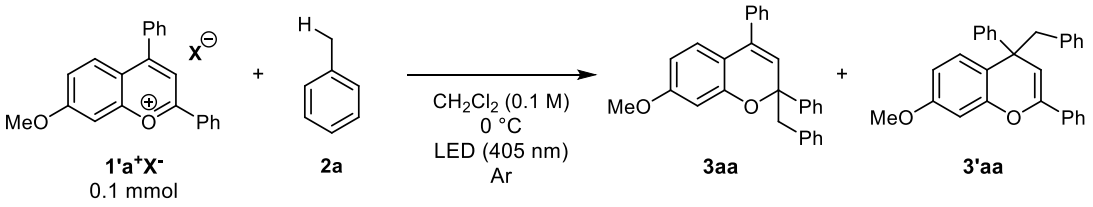
1m 0.1 mmol + **2a** 0.05 M → **3ma** + **3'ma**

35% yield
3ma/**3'ma** = 74/26
60% ee/26% ee

To a mixture of **1m** (0.1 mmol) and (*S*)-**4** (5 mol%) was added toluene (1.0 ml) under argon atmosphere. The reaction mixture was stirred -75 ˚C for 12 h under LED irradiation (405 nm). The reaction mixture was purified by flash column chromatography (Hexane/ EtOAc = 10/1) to give a mixture of **3ma** and **3'ma** (14.2 mg, 35% yield, **3ma**/**3'ma** = 74/26, ee of **3ma** = 60%, ee of **3'ma** = 26%). The enantiomeric excess was determined by chiral stationary phase HPLC analysis (CHIRALPAK AD-3 (hexane:^{i}PrOH = 99/1, 1.0 mL/min, 30 °C, 254 nm) 14.7 min (minor of **3ma**), 17.4 min (major of **3ma**), 18.8 min (minor of **3'ma**), 21.5 min (major of **3'ma**).

6. Additional screening

6-1. The reaction of benzopyrylium cation salts **1'a$^+$X$^-$**

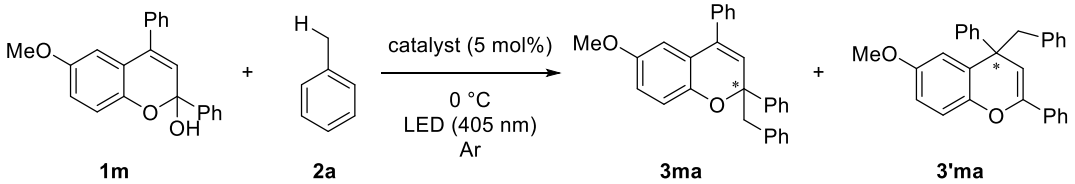


1'a$^+$X$^-$ 0.1 mmol | **2a** | **3aa** | **3'aa**

entry	**1'a$^+$X$^-$**	time (h)	yield (%)[a]	**3aa**/**3'aa**
1	**X** = BF_4	3	<1	-
2	**X** = ClO_4	3	<1	-
3	**X** = OTf	3	3	89/11

[a] NMR yield.

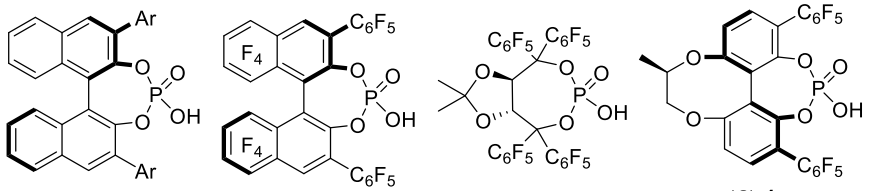
6-2. Screening of chiral phosphoric acids for enantioselective reaction



1m 0.1 mmol | **2a** (0.05 M) | **3ma** | **3'ma**

entry	catalyst	time (h)	yield(%)[a]	**3ma**/**3'ma**	ee (%) of **3ma**/**3'ma**
1	(*R*)-**5a**	6	<1	-	-
2	(*R*)-**5b**	6	44	86/14	-33/-47
3	(*R*)-**6**	2.5	67	43/57	-21/-8
4	(*R*)-**7**	1.5	80	66/34	-15/-10
5	(*S*)-**4**	1	72	67/33	31/25

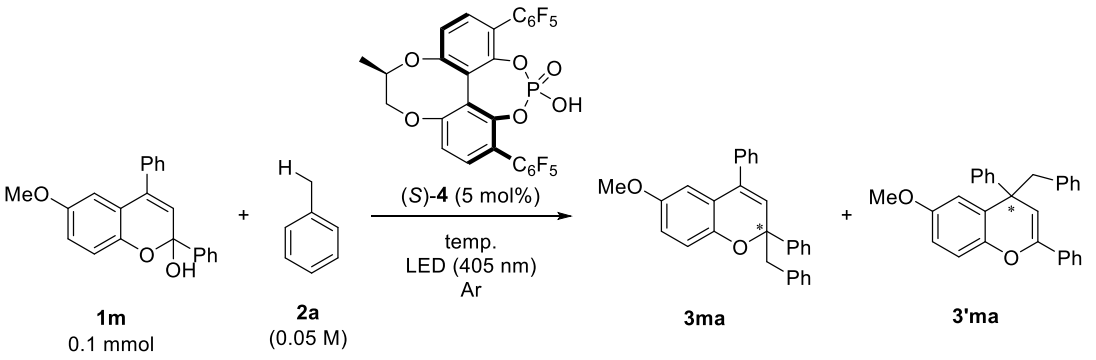
[a] NMR yield



(*R*)-**5a** (Ar = Ph)
(*R*)-**5b** (Ar = C_6F_5)
(*R*)-**6**
(*R*)-**7**
(*S*)-**4**

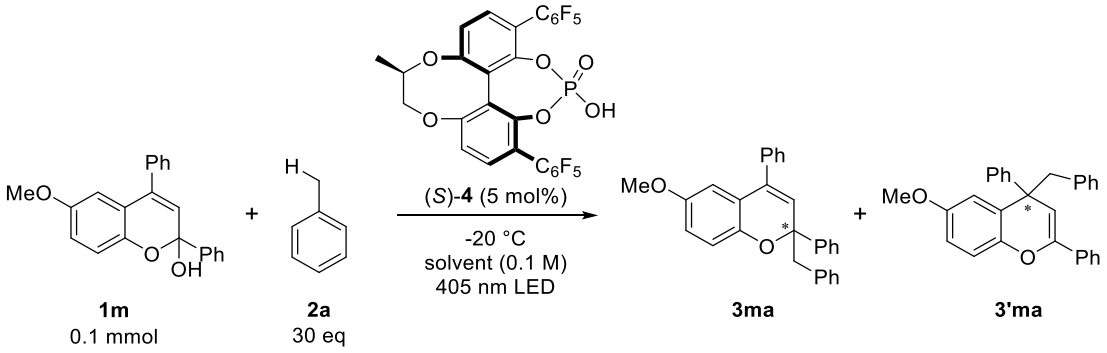
In the case of using (*R*)-**5** (especially in using (*R*)-**5a**), the degradation of the catalysts was observed probably due to the oxidation of catalysts. In contrast, no degradation of the catalysts was observed when (*R*)-**6**, (*R*)-**7**, and (*S*)-**4** were used in this reaction conditions.

6-3. Investigation of reaction conditions



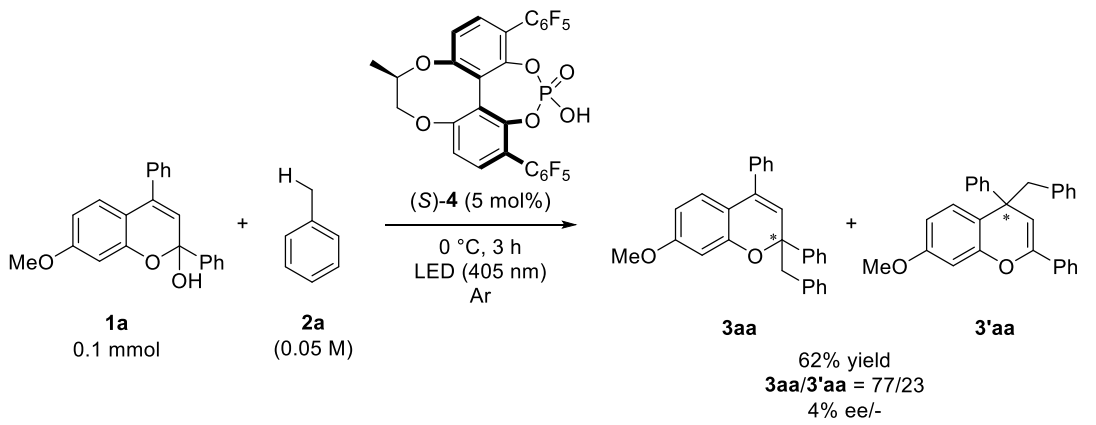
entry	temp. (°C)	time (h)	yield (%)	**3ma**/**3'ma**	ee (%) of **3ma**/**3'ma**
1	0	1	72	67/33	31/25
2[a]	-20	2	68	68/32	-40/-17
3	-40	6	57	74/26	55/25
4	-50	9	56	75/25	54/25
5	-75	12	35	74/26	60/26

[a] (*R*)-**4** was used.



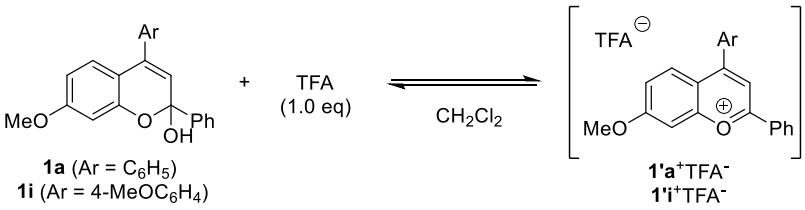
entry	solvent	time (h)	yield(%)	**3ma**/**3'ma**	ee (%) of **3ma**/**3'ma**
1	CH_2Cl_2	2	37	62/38	15/6
2	THF	3	62	68/32	36/22
3	MTBE	9	23	70/30	32/21
4	MeCN	7	10	56/44	17/11

6-4. Enantioselective reaction of **1a**



7. UV-Vis absorption spectroscopy

To a solution of **1a** or **1i** in CH_2Cl_2 (1.0×10^{-5} M) was added 1.0 equiv of TFA, and then a UV/Vis spectra was recorded (Figure S1). The spectra data indicates that the treatment of TFA enables the formation of the benzopyrylium cation intermediates. As shown in Figure S1c, the introduction of the methoxy group leads to a redshift in the absorption spectra of the generated benzopyrylium cation intermediate.



1a (Ar = C_6H_5)
1i (Ar = 4-$MeOC_6H_4$)

1'a$^+$TFA$^-$
1'i$^+$TFA$^-$

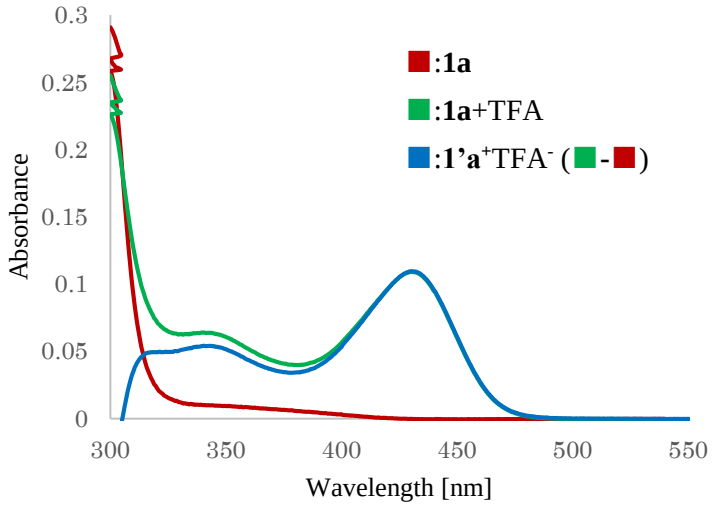


Figure S1a. UV/Vis spectroscopy analysis of **1'a**$^+$TFA$^-$

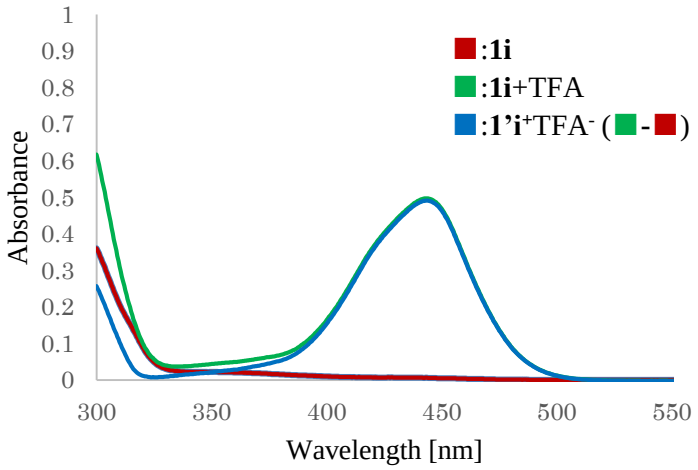


Figure S1b. UV/Vis spectroscopy analysis of **1'i**$^+$TFA$^-$

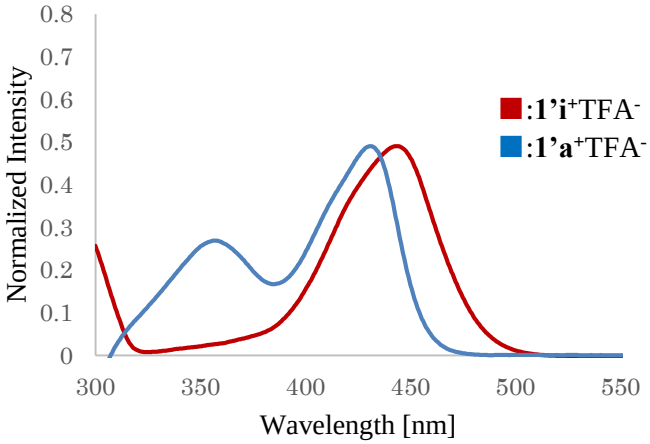
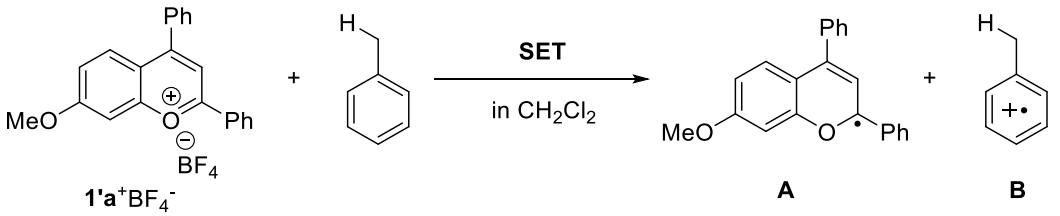


Figure S1c. UV/Vis spectroscopy analysis of **1'a**$^{+}$TFA^{-} and **1'i**$^{+}$TFA^{-}

8. Stern-Volmer luminescence quenching experiments

Emission intensities were recorded on a HITACHI F-4500. The solutions were excited at 360 nm and the luminescence was measured at 479 nm. Stern-Volmer luminescence quenching experiments were run with prepared mixture of **1'a**$^{+}$$BF_4^{-}$ (1.0×10^{-6} M) and toluene (indicated concentration) in CH_2Cl_2 solutions (Figure S2). The data shows that toluene is competent at quenching the excited state of the **1'a**$^{+}$$BF_4^{-}$.



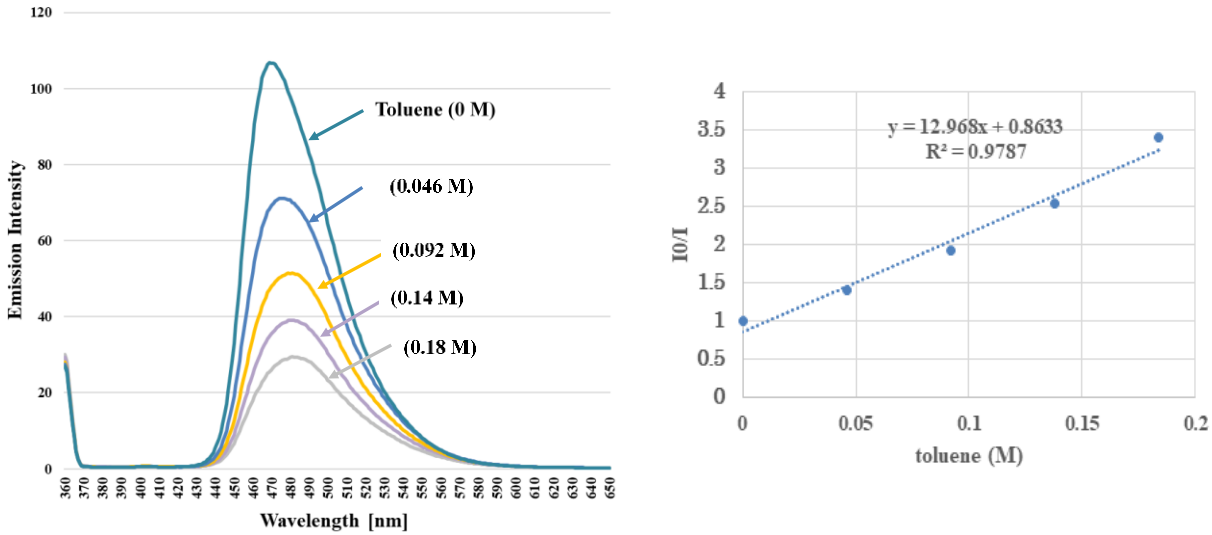
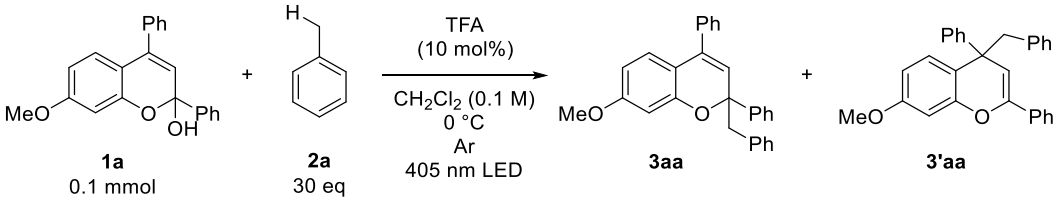
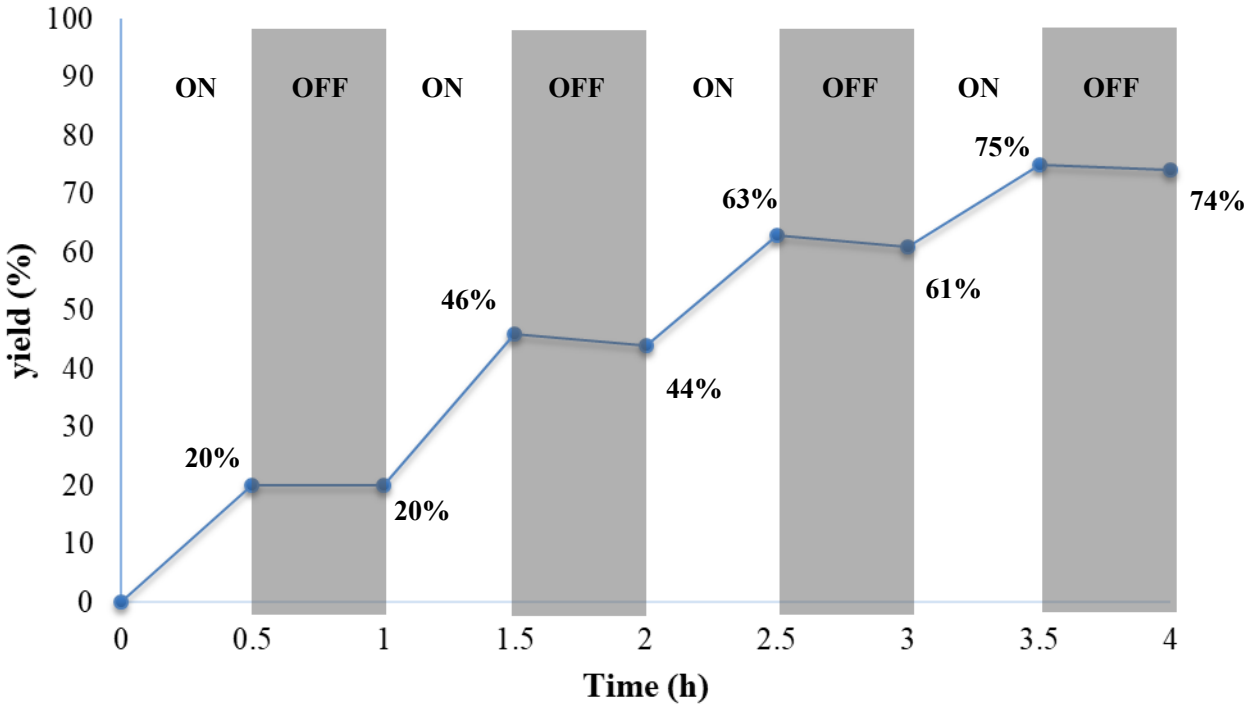


Figure S2. (a) Fluorescence spectra of **1'a**$^{+}$$BF_4^{-}$ in DCM with increasing amount of toluene. (b) The Stern-Volmer plots.

9. Light ON/OFF Experiment

Light On/Off experiment was conducted to confirm if the reaction proceeds in a chain process or not. As a result, the present reaction proceeded only in the presence of light irradiation. This result indicates that the present reaction does not proceed in a chain process.



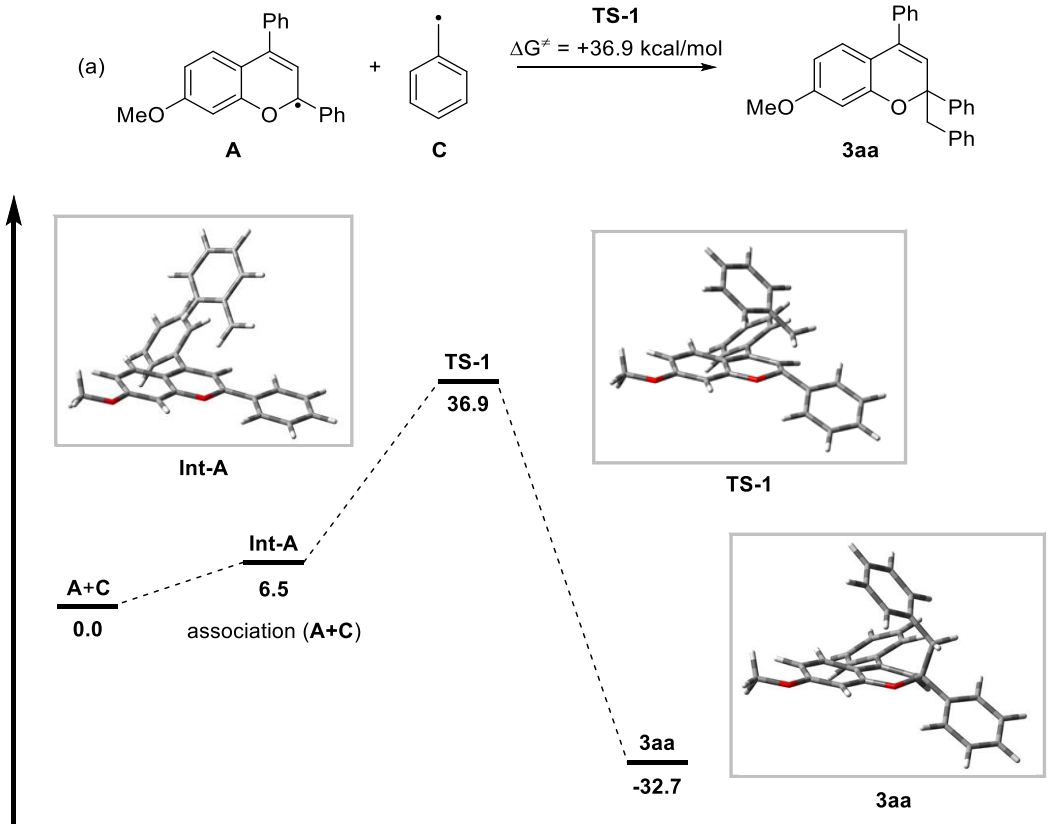


10. Theoretical Studies

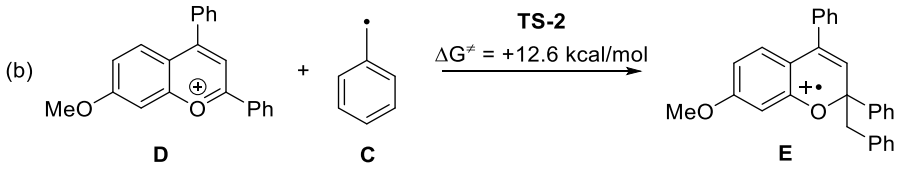
10-1. Energy profile in the carbon-carbon bond forming step

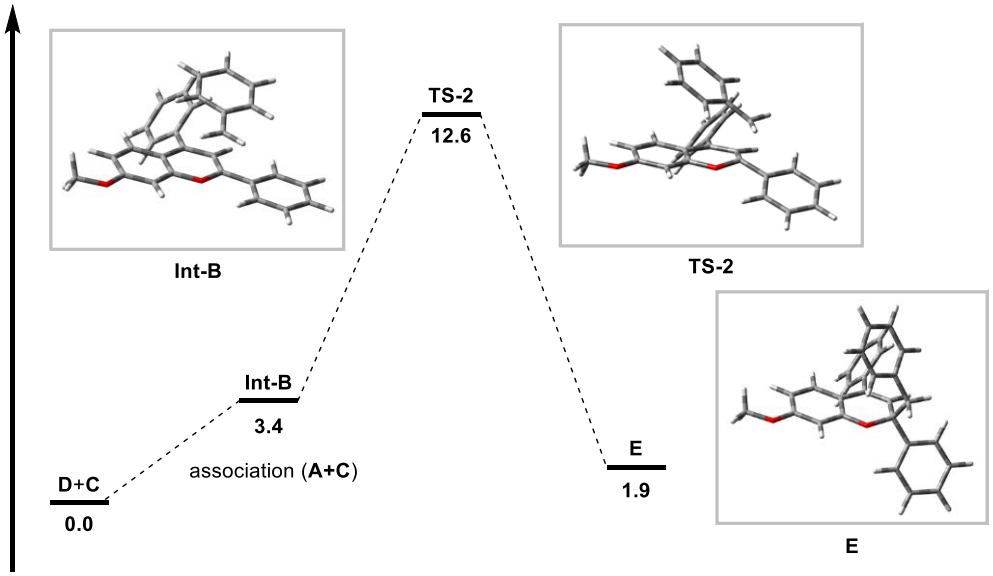
DFT calculation was conducted to determine the actual reaction pathway in the carbon-carbon bond formation step. All calculations were performed with the Gaussian 16 package (Revision B.01). Geometries were optimized and characterized using frequency calculations at the UM06-2X/6-311+G(d,p) level. Gibbs free energies in the solution phase were calculated using single-point energy calculations at the same level according to the SMD solvation model (dichloromethane: $\varepsilon = 8.93$) for the optimized structures.

(a) Radical coupling pathway

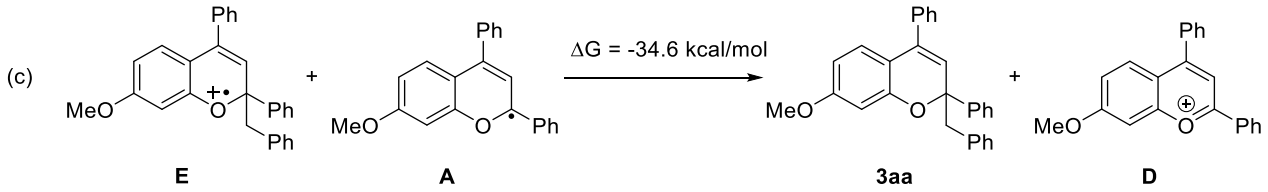


(b) Radical addition pathway





(c) Electron transfer process



Cartesian coordinates

Benzopyrylium radical (A)
UM062X/6-311g(d,p)
E(UM062X) = -998.835704 hartree
Zero-point Energy Correction = 0.329416 hartree
Thermal Correction to Energy = 0.348528 hartree
Thermal correction to Enthalpy = 0.349472 hartree
Thermal correction to Gibbs Free Energy = 0.279545 hartree
Sum of electronic and Zero-point Energies = -998.506288 hartree
Sum of electronic and thermal Energies = -998.487176 hartree
Sum of electronic and thermal Enthalpies = -998.486231 hartree
Sum of electronic and thermal Free Energies= -998.556159 hartree
SMD(CH_2Cl_2)/UM062X/6-311g(d,p)
E(UM062X) = -998.86523 hartree
Gibbs Free Energy in CH_2Cl_2 = -998.58568 hartree
The number of Imaginary frequencies = 0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.654434	4.718728	0.110435
2	6	0	3.015223	3.672177	0.954807
3	6	0	1.603822	4.544852	-0.784936
4	6	0	2.336537	2.461839	0.901562
5	1	0	3.822135	3.803169	1.666375
6	6	0	0.923033	3.334918	-0.838758
7	1	0	1.318894	5.351021	-1.450821
8	6	0	1.277419	2.271514	0.002296
9	1	0	2.603220	1.662519	1.583763
10	1	0	0.120230	3.197203	-1.554828
11	6	0	0.517524	1.011606	-0.031377
12	6	0	1.154550	-0.288651	-0.036621
13	6	0	-0.875748	1.035567	-0.048057
14	6	0	2.530158	-0.518880	-0.159619
15	6	0	0.329822	-1.432601	0.023971
16	6	0	-1.640306	-0.109684	0.003379
17	6	0	3.069151	-1.799521	-0.173391
18	1	0	3.195509	0.328499	-0.263900
19	6	0	0.841242	-2.714336	0.017583
20	6	0	2.220413	-2.903793	-0.072446
21	1	0	0.177953	-3.567545	0.070273
22	1	0	3.186289	5.661565	0.151881
23	1	0	-1.382265	1.990972	-0.044868
24	6	0	-3.092517	-0.191039	0.028228
25	6	0	-3.729240	-1.431403	0.197887
26	6	0	-3.895455	0.954023	-0.117205
27	6	0	-5.114656	-1.517512	0.227913
28	1	0	-3.128477	-2.323727	0.308606
29	6	0	-5.276750	0.858994	-0.084884
30	1	0	-3.442021	1.926072	-0.263867
31	6	0	-5.897929	-0.376942	0.088817
32	1	0	-5.584740	-2.484707	0.361921
33	1	0	-5.874940	1.755197	-0.199624
34	1	0	-6.978484	-0.447097	0.112602
35	8	0	-1.030247	-1.333587	0.081556
36	1	0	4.138656	-1.921560	-0.271231
37	8	0	2.636171	-4.193207	-0.066806
38	6	0	4.024133	-4.438702	-0.167460
39	1	0	4.565348	-3.990870	0.671425
40	1	0	4.140619	-5.519420	-0.138666
41	1	0	4.425514	-4.053873	-1.109794

Benzyl radical (C)
UM062X/6-311g(d,p)
E(UM062X) = -270.852205 hartree
Zero-point Energy Correction = 0.115117 hartree
Thermal Correction to Energy = 0.120795 hartree
Thermal correction to Enthalpy = 0.121739 hartree
Thermal correction to Gibbs Free Energy = 0.085448 hartree
Sum of electronic and Zero-point Energies = -270.737088 hartree
Sum of electronic and thermal Energies = -270.731410 hartree
Sum of electronic and thermal Enthalpies = -270.730466 hartree
Sum of electronic and thermal Free Energies = -270.766757 hartree
SMD(CH_2Cl_2)/UM062X/6-311g(d,p)
E(UM062X) = -270.863067 hartree
Gibbs Free Energy in CH_2Cl_2 = -270.77762 hartree
The number of Imaginary frequencies = 0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.832861	0.000000	-0.000010
2	6	0	-1.130222	-1.207353	-0.000005
3	6	0	0.251932	-1.212821	0.000003
4	6	0	0.987232	0.000000	0.000005
5	6	0	0.251932	1.212821	0.000000
6	6	0	-1.130222	1.207353	-0.000008
7	1	0	-2.915847	0.000000	-0.000016
8	1	0	-1.671470	-2.146260	-0.000006
9	1	0	0.793878	-2.152360	0.000007
10	1	0	0.793877	2.152360	0.000002
11	1	0	-1.671470	2.146260	-0.000012
12	6	0	2.396542	0.000000	0.000013
13	1	0	2.952519	-0.927818	0.000017
14	1	0	2.952519	0.927818	0.000015

Int-A
UM062X/6-311g(d,p)
E(UM062X) = -1269.704040 hartree
Zero-point Energy Correction = 0.445344 hartree
Thermal Correction to Energy = 0.471111 hartree
Thermal correction to Enthalpy = 0.472055 hartree
Thermal correction to Gibbs Free Energy= 0.386886 hartree
Sum of electronic and Zero-point Energies = -1269.258696 hartree
Sum of electronic and thermal Energies = -1269.232929 hartree
Sum of electronic and thermal Enthalpies = -1269.231985 hartree
Sum of electronic and thermal Free Energies = -1269.317154 hartree
SMD(CH_2Cl_2)/UM062X/6-311g(d,p)
E(UM062X) = -1269.739887 hartree
Gibbs Free Energy in CH_2Cl_2 = -1269.353 hartree
The number of Imaginary frequencies = 0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.842827	4.784274	-0.464954
2	6	0	-3.197440	3.783520	-1.365350
3	6	0	-1.735116	4.602252	0.357721
4	6	0	-2.459111	2.609402	-1.437878
5	1	0	-4.047218	3.922977	-2.023455
6	6	0	-0.995654	3.428978	0.285726
7	1	0	-1.450881	5.373985	1.063695
8	6	0	-1.344374	2.408026	-0.610469
9	1	0	-2.723521	1.850925	-2.165739
10	1	0	-0.146044	3.283872	0.944046
11	6	0	-0.524492	1.191198	-0.700726
12	6	0	-1.092293	-0.137403	-0.801372
13	6	0	0.865688	1.281716	-0.667830
14	6	0	-2.449370	-0.454114	-0.669023
15	6	0	-0.210400	-1.225385	-0.973787
16	6	0	-2.918500	-1.759137	-0.749586
17	1	0	-3.155501	0.341313	-0.468584
18	6	0	-0.651791	-2.530108	-1.068933
19	6	0	-2.014347	-2.802877	-0.958422
20	1	0	0.056896	-3.337249	-1.201125
21	1	0	-3.421508	5.698281	-0.408164
22	1	0	1.327527	2.254357	-0.566399
23	8	0	1.140079	-1.049506	-1.040467
24	1	0	-3.976665	-1.947918	-0.634307
25	6	0	1.684771	0.182572	-0.799829
26	6	0	3.136720	0.162310	-0.728787
27	6	0	3.871221	1.306222	-0.370035
28	6	0	3.841192	-1.025677	-0.986587
29	6	0	5.253338	1.261732	-0.281608
30	1	0	3.362259	2.235558	-0.146775
31	6	0	5.225832	-1.061472	-0.894629
32	1	0	3.291171	-1.917398	-1.255429
33	6	0	5.942099	0.078311	-0.542988
34	1	0	5.798198	2.155495	-0.001215
35	1	0	5.749089	-1.988322	-1.098848
36	1	0	7.022271	0.046996	-0.470241
37	6	0	2.005452	-1.612594	2.008239
38	1	0	2.116243	-2.667187	1.792405
39	1	0	2.894667	-0.995848	2.010210
40	6	0	0.734865	-1.059764	2.273292
41	6	0	-0.432713	-1.866748	2.275017
42	6	0	0.576378	0.323307	2.539039
43	6	0	-1.676288	-1.318622	2.521112
44	1	0	-0.335404	-2.927213	2.067951
45	6	0	-0.673994	0.861997	2.786366
46	1	0	1.457758	0.957284	2.537491
47	6	0	-1.808916	0.049635	2.774497
48	1	0	-2.555322	-1.952863	2.505359
49	1	0	-0.776987	1.922074	2.987482
50	1	0	-2.786225	0.478794	2.960013
51	8	0	-2.360475	-4.111215	-1.049907
52	6	0	-3.728285	-4.440052	-0.920840
53	1	0	-4.324417	-3.964776	-1.705644
54	1	0	-3.788877	-5.520889	-1.024071
55	1	0	-4.114212	-4.145470	0.060078

TS-1
UM062X/6-311g(d,p)
E(UM062X) = -1269.656599 hartree
Zero-point Energy Correction = 0.445911 hartree
Thermal Correction to Energy = 0.471321 hartree
Thermal correction to Enthalpy = 0.472265 hartree
Thermal correction to Gibbs Free Energy= 0.388688 hartree
Sum of electronic and Zero-point Energies = -1269.210688 hartree
Sum of electronic and thermal Energies = -1269.185278 hartree
Sum of electronic and thermal Enthalpies = -1269.184334 hartree
Sum of electronic and thermal Free Energies = -1269.267911 hartree
SMD(CH_2Cl_2)/UM062X/6-311g(d,p)
E(UM062X) = -1269.2679 hartree
Gibbs Free Energy in CH_2Cl_2 = -796477.67 hartree
The number of Imaginary frequencies = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.971348	5.059087	-0.931440
2	6	0	-2.474476	4.022463	-1.716532
3	6	0	-0.906998	4.802543	-0.071343

4	6	0	-1.939424	2.746975	-1.629056
5	1	0	-3.279745	4.215803	-2.416016
6	6	0	-0.361557	3.529674	0.012752
7	1	0	-0.499385	5.600523	0.538800
8	6	0	-0.877354	2.459879	-0.746902
9	1	0	-2.308213	1.967986	-2.285072
10	1	0	0.460373	3.346547	0.695421
11	6	0	-0.279219	1.138963	-0.646233
12	6	0	-0.989695	-0.074804	-0.738804
13	6	0	1.160250	1.031121	-0.426795
14	6	0	-2.405676	-0.206537	-0.785493
15	6	0	-0.267606	-1.310925	-0.722150
16	6	0	-3.033398	-1.423258	-0.932781
17	1	0	-3.011563	0.681025	-0.665748
18	6	0	-0.886861	-2.534638	-0.901819
19	6	0	-2.269549	-2.601446	-1.028094
20	1	0	-0.296844	-3.442134	-0.904145
21	1	0	-2.392484	6.054487	-1.001628
22	1	0	1.780937	1.914197	-0.470223
23	8	0	1.070739	-1.357576	-0.505423
24	1	0	-4.114083	-1.458340	-0.954168
25	6	0	1.758584	-0.196892	-0.145158
26	6	0	3.231365	-0.369670	-0.339298
27	6	0	4.114836	0.633797	0.068338
28	6	0	3.745844	-1.533942	-0.909412
29	6	0	5.482943	0.484679	-0.110311
30	1	0	3.732921	1.535817	0.534033
31	6	0	5.118880	-1.680855	-1.084553
32	1	0	3.068779	-2.316310	-1.224852
33	6	0	5.991898	-0.675374	-0.688733
34	1	0	6.154248	1.273401	0.207980
35	1	0	5.504512	-2.587438	-1.535920
36	1	0	7.060004	-0.792881	-0.825766
37	6	0	1.695563	-0.461313	1.834487
38	1	0	2.187092	-1.430309	1.850878
39	1	0	2.332301	0.361242	2.145694
40	6	0	0.316439	-0.420672	2.278834
41	6	0	-0.476519	-1.579836	2.278115
42	6	0	-0.286598	0.799866	2.633250
43	6	0	-1.824963	-1.518956	2.603941
44	1	0	-0.024440	-2.526998	2.003393
45	6	0	-1.632544	0.860525	2.952426
46	1	0	0.314837	1.703279	2.636811
47	6	0	-2.408469	-0.299945	2.936652
48	1	0	-2.423208	-2.422743	2.587663
49	1	0	-2.083734	1.811964	3.208714
50	1	0	-3.462904	-0.250248	3.181279
51	8	0	-2.794102	-3.840505	-1.201051
52	6	0	-4.197745	-3.954346	-1.313858
53	1	0	-4.573127	-3.383015	-2.168115
54	1	0	-4.401939	-5.011455	-1.467077
55	1	0	-4.697037	-3.616720	-0.400335

3aa

UM062X/6-311g(d,p)
E(UM062X) = -1269.774432 hartree
Zero-point Energy Correction = 0.451798 hartree
Thermal Correction to Energy = 0.476746 hartree
Thermal correction to Enthalpy = 0.477690 hartree
Thermal correction to Gibbs Free Energy = 0.395930 hartree
Sum of electronic and Zero-point Energies = -1269.322635 hartree
Sum of electronic and thermal Energies = -1269.297686 hartree
Sum of electronic and thermal Enthalpies = -1269.296742 hartree
Sum of electronic and thermal Free Energies = -1269.378502 hartree
SMD(CH_2Cl_2)/UM062X/6-311g(d,p)
E(UM062X) = -1269.8113 hartree
Gibbs Free Energy in CH_2Cl_2 = -1269.4154 hartree
The number of Imaginary frequencies = 0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.170352	5.284683	-0.880218
2	6	0	-1.425068	4.355786	-1.886032
3	6	0	-0.551743	4.874231	0.295110
4	6	0	-1.066048	3.024817	-1.715715
5	1	0	-1.901500	4.670509	-2.807064
6	6	0	-0.187811	3.541937	0.463364
7	1	0	-0.357019	5.589808	1.085307
8	6	0	-0.434979	2.603809	-0.540723
9	1	0	-1.258645	2.303033	-2.501799
10	1	0	0.281695	3.216067	1.384673
11	6	0	-0.008241	1.192007	-0.369237
12	6	0	-0.945537	0.096700	-0.645803
13	6	0	1.240743	0.889706	0.005795
14	6	0	-2.323098	0.242957	-0.772107
15	6	0	-0.412264	-1.195659	-0.782611
16	6	0	-3.152421	-0.832209	-1.078491
17	1	0	-2.762516	1.222770	-0.625686
18	6	0	-1.205679	-2.270422	-1.136466
19	6	0	-2.581243	-2.089539	-1.281004
20	1	0	-0.773671	-3.256086	-1.251862
21	1	0	-1.454820	6.321748	-1.012524
22	1	0	1.976315	1.670375	0.163916
23	8	0	0.911032	-1.440154	-0.588417
24	1	0	-4.218580	-0.676369	-1.159288
25	6	0	1.681020	-0.537674	0.221723
26	6	0	3.137181	-0.717834	-0.196704
27	6	0	4.132131	0.036564	0.430028
28	6	0	3.506043	-1.628750	-1.183536
29	6	0	5.467248	-0.115374	0.078465
30	1	0	3.868425	0.755161	1.199208
31	6	0	4.845211	-1.781747	-1.534228
32	1	0	2.742580	-2.213137	-1.677957
33	6	0	5.829496	-1.028890	-0.906956
34	1	0	6.224565	0.480450	0.574084
35	1	0	5.116183	-2.493957	-2.304859
36	1	0	6.870213	-1.149377	-1.182887
37	6	0	1.534776	-0.969347	1.714401
38	1	0	1.874030	-2.007422	1.773074
39	1	0	2.224410	-0.361867	2.305553
40	6	0	0.134646	-0.831492	2.251923
41	6	0	-0.774007	-1.885091	2.149836
42	6	0	-0.304853	0.379248	2.789441
43	6	0	-2.101910	-1.719316	2.525829
44	1	0	-0.442204	-2.832353	1.737328
45	6	0	-1.630698	0.551140	3.170840
46	1	0	0.398762	1.198895	2.894526
47	6	0	-2.535833	-0.496068	3.027604
48	1	0	-2.798360	-2.543003	2.419464
49	1	0	-1.958141	1.502135	3.574814
50	1	0	-3.572384	-0.361775	3.313751
51	8	0	-3.285384	-3.205246	-1.600468
52	6	0	-4.686493	-3.083778	-1.729513
53	1	0	-4.950543	-2.382656	-2.527010
54	1	0	-5.052438	-4.075959	-1.983502
55	1	0	-5.142853	-2.756160	-0.790274

Benzopyrylium cation (D)

UM062X/6-311g(d,p)
E(UM062X) = -998.636397 hartree
Zero-point Energy Correction = 0.332247 hartree
Thermal Correction to Energy = 0.351097 hartree
Thermal correction to Enthalpy = 0.352041 hartree
Thermal correction to Gibbs Free Energy= 0.283910 hartree
Sum of electronic and Zero-point Energies = -998.304150 hartree
Sum of electronic and thermal Energies = -998.285301 hartree
Sum of electronic and thermal Enthalpies = -998.284357 hartree
Sum of electronic and thermal Free Energies = -998.352487 hartree
SMD(CH_2Cl_2)/UM062X/6-311g(d,p)
E(UM062X) = -998.716682 hartree
Gibbs Free Energy in CH_2Cl_2 = -998.43277 hartree
The number of Imaginary frequencies = 0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.617019	4.685525	0.160251
2	6	0	2.948726	3.652616	1.032467
3	6	0	1.602290	4.511606	-0.776684
4	6	0	2.281804	2.437699	0.958083
5	1	0	3.724023	3.795602	1.774790
6	6	0	0.912508	3.309007	-0.838102
7	1	0	1.347765	5.313655	-1.458165
8	6	0	1.257690	2.258045	0.019701
9	1	0	2.522709	1.642732	1.654702
10	1	0	0.128805	3.169490	-1.574523
11	6	0	0.505066	0.995056	-0.037172
12	6	0	1.146002	-0.272940	-0.059100
13	6	0	-0.888145	1.034165	-0.050393
14	6	0	2.541124	-0.481637	-0.174770
15	6	0	0.331806	-1.427558	-0.014009
16	6	0	-1.632813	-0.133737	-0.017311
17	6	0	3.071772	-1.745100	-0.190124
18	1	0	3.194334	0.374840	-0.276960
19	6	0	0.839598	-2.709669	-0.016935
20	6	0	2.220889	-2.876207	-0.094085
21	1	0	0.186424	-3.570949	0.023634
22	1	0	3.145973	5.629118	0.214647
23	1	0	-1.397763	1.984544	0.002026
24	6	0	-3.086983	-0.218617	0.023021
25	6	0	-3.708753	-1.418727	0.397575
26	6	0	-3.870703	0.894184	-0.315252
27	6	0	-5.091153	-1.494880	0.445201
28	1	0	-3.108190	-2.279317	0.661162
29	6	0	-5.252314	0.806424	-0.272597
30	1	0	-3.410138	1.819863	-0.636397
31	6	0	-5.863388	-0.385094	0.111028
32	1	0	-5.568955	-2.419261	0.743819
33	1	0	-5.854546	1.664308	-0.543028
34	1	0	-6.944138	-0.449129	0.146763
35	8	0	-1.019904	-1.310133	0.022013
36	1	0	4.140321	-1.872396	-0.291521
37	8	0	2.654727	-4.130096	-0.091649
38	6	0	4.055322	-4.393226	-0.174503
39	1	0	4.580290	-3.949070	0.673614
40	1	0	4.148869	-5.474306	-0.138590
41	1	0	4.461461	-4.019515	-1.116614

Int-B

UM062X/6-311g(d,p)
E(UM062X) = -1269.509834 hartree
Zero-point Energy Correction = 0.448238 hartree
Thermal Correction to Energy = 0.474662 hartree

Thermal correction to Enthalpy = 0.475606 hartree
Thermal correction to Gibbs Free Energy = 0.388824 hartree
Sum of electronic and Zero-point Energies = -1269.061596 hartree
Sum of electronic and thermal Energies = -1269.035172 hartree
Sum of electronic and thermal Enthalpies = -1269.034228 hartree
Sum of electronic and thermal Free Energies = -1269.121011 hartree
SMD(CH_2Cl_2)/UM062X/6-311g(d,p)
E(UM062X) = -1269.5938 hartree
Gibbs Free Energy in CH_2Cl_2 = -1269.205 hartree
The number of Imaginary frequencies = 0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.474315	4.801336	-0.854059
2	6	0	-2.793308	3.786411	-1.750887
3	6	0	-1.479648	4.603112	0.099935
4	6	0	-2.136072	2.565168	-1.683588
5	1	0	-3.549975	3.948126	-2.508487
6	6	0	-0.802843	3.393206	0.156064
7	1	0	-1.230225	5.393336	0.797172
8	6	0	-1.136902	2.357630	-0.724680
9	1	0	-2.365276	1.787031	-2.402522
10	1	0	-0.034283	3.233070	0.903626
11	6	0	-0.391013	1.088990	-0.677346
12	6	0	-1.034600	-0.176171	-0.734964
13	6	0	1.001258	1.122051	-0.618114
14	6	0	-2.433192	-0.385688	-0.696278
15	6	0	-0.221711	-1.329523	-0.802772
16	6	0	1.741903	-0.046384	-0.656556
17	6	0	-2.967753	-1.644886	-0.786607
18	1	0	-3.087873	0.466036	-0.567590
19	6	0	-0.732463	-2.607649	-0.901884
20	6	0	-2.114942	-2.770946	-0.903112
21	1	0	-0.079311	-3.468041	-0.958385
22	1	0	-2.994410	5.750126	-0.903812
23	1	0	1.515287	2.071537	-0.616439
24	6	0	3.199515	-0.135155	-0.648491
25	6	0	3.831199	-1.328353	-1.023209
26	6	0	3.973986	0.966599	-0.259545
27	6	0	5.215222	-1.410907	-1.016071
28	1	0	3.238383	-2.180587	-1.328273
29	6	0	5.356070	0.874142	-0.249285
30	1	0	3.503871	1.888343	0.060127
31	6	0	5.978593	-0.312885	-0.629614
32	1	0	5.700235	-2.331758	-1.314369
33	1	0	5.950126	1.725143	0.058890
34	1	0	7.059615	-0.381219	-0.623282
35	8	0	1.129493	-1.218570	-0.768453
36	1	0	-4.040349	-1.772269	-0.745518
37	8	0	-2.551474	-4.024106	-0.995252
38	6	0	-3.954394	-4.279750	-1.009919
39	1	0	-4.427512	-3.784502	-1.860408
40	1	0	-4.052124	-5.356385	-1.112091
41	1	0	-4.415705	-3.955980	-0.074321
42	6	0	0.591026	-0.427148	2.510178
43	6	0	-0.270905	-1.551060	2.421308
44	6	0	-1.642885	-1.400717	2.495108
45	6	0	-2.209214	-0.131880	2.648219
46	6	0	-1.381691	0.989832	2.738212
47	6	0	-0.007031	0.848209	2.674745
48	1	0	0.165061	-2.538566	2.309668
49	1	0	-2.282378	-2.274792	2.441795
50	1	0	-3.284687	-0.019900	2.715874
51	1	0	-1.818396	1.973030	2.872060
52	1	0	0.638167	1.715835	2.774295
53	6	0	1.991773	-0.571269	2.435270
54	1	0	2.447661	-1.546685	2.323708
55	1	0	2.645959	0.282579	2.555574

TS-2
UM062X/6-311g(d,p)
E(UM062X) = -1269.499080 hartree
Zero-point Energy Correction = 0.449581 hartree
Thermal Correction to Energy = 0.474588 hartree
Thermal correction to Enthalpy = 0.475533 hartree
Thermal correction to Gibbs Free Energy = 0.393891 hartree
Sum of electronic and Zero-point Energies = -1269.049499 hartree
Sum of electronic and thermal Energies = -1269.024492 hartree
Sum of electronic and thermal Enthalpies = -1269.023548 hartree
Sum of electronic and thermal Free Energies = -1269.105189 hartree
SMD(CH_2Cl_2)/UM062X/6-311g(d,p)
E(UM062X) = -1269.583961 hartree
Gibbs Free Energy in CH_2Cl_2 = -1269.1903 hartree
The number of Imaginary frequencies = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.990067	5.070265	-0.841720
2	6	0	-2.304150	4.081053	-1.768988
3	6	0	-1.107351	4.793620	0.197887
4	6	0	-1.751670	2.812847	-1.650254
5	1	0	-2.974544	4.300117	-2.590849
6	6	0	-0.540116	3.531246	0.309945
7	1	0	-0.859775	5.562054	0.919786
8	6	0	-0.864781	2.524714	-0.605877
9	1	0	-1.978180	2.052844	-2.389387
10	1	0	0.145869	3.318600	1.122211
11	6	0	-0.230985	1.194925	-0.503065
12	6	0	-0.983795	-0.019983	-0.658381
13	6	0	1.123190	1.091192	-0.303744
14	6	0	-2.387969	-0.100831	-0.699419
15	6	0	-0.272074	-1.235067	-0.782901
16	6	0	1.766521	-0.173885	-0.235996
17	6	0	-3.033936	-1.297071	-0.917558
18	1	0	-2.969248	0.799050	-0.543409
19	6	0	-0.892564	-2.441367	-1.043652
20	6	0	-2.282296	-2.477562	-1.116895
21	1	0	-0.315864	-3.349884	-1.156419
22	1	0	-2.426720	6.057170	-0.933312
23	1	0	1.731380	1.980692	-0.211132
24	6	0	3.231925	-0.328500	-0.391159
25	6	0	3.759442	-1.488751	-0.964879
26	6	0	4.098716	0.679261	0.047256
27	6	0	5.134141	-1.627851	-1.109506
28	1	0	3.096853	-2.270390	-1.311527
29	6	0	5.469569	0.532726	-0.098890
30	1	0	3.713273	1.579018	0.513326
31	6	0	5.991031	-0.621404	-0.678461
32	1	0	5.535358	-2.524696	-1.564842
33	1	0	6.132599	1.318299	0.241246
34	1	0	7.062084	-0.733784	-0.792531
35	8	0	1.077731	-1.264613	-0.654431
36	1	0	-4.114417	-1.323082	-0.934132
37	8	0	-2.822465	-3.674398	-1.353518
38	6	0	-4.237886	-3.788743	-1.464374
39	1	0	-4.613047	-3.166765	-2.280083
40	1	0	-4.429921	-4.834860	-1.684027
41	1	0	-4.724025	-3.515944	-0.524720
42	6	0	0.331175	-0.575919	2.269904
43	6	0	-0.370570	-1.800221	2.222757
44	6	0	-1.718672	-1.848599	2.529798
45	6	0	-2.393430	-0.679681	2.885765
46	6	0	-1.713380	0.539191	2.954340
47	6	0	-0.366025	0.591547	2.651134
48	1	0	0.161152	-2.703251	1.941286
49	1	0	-2.247995	-2.793226	2.497478
50	1	0	-3.449325	-0.719441	3.126025
51	1	0	-2.240144	1.438604	3.248985
52	1	0	0.173196	1.530595	2.713328
53	6	0	1.702963	-0.507528	1.883798
54	1	0	2.264373	-1.431274	1.788121
55	1	0	2.283213	0.363895	2.166973

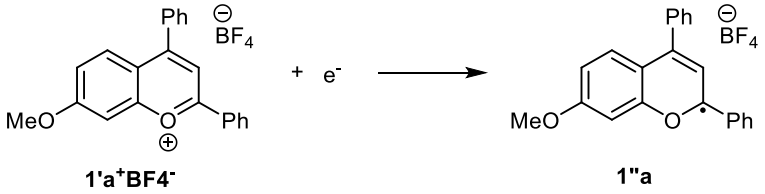
E
UM062X/6-311g(d,p)
E(UM062X) = -1269.514329 hartree
Zero-point Energy Correction = 0.451603 hartree
Thermal Correction to Energy = 0.476738 hartree
Thermal correction to Enthalpy = 0.477682 hartree
Thermal correction to Gibbs Free Energy = 0.394866 hartree
Sum of electronic and Zero-point Energies = -1269.062726 hartree
Sum of electronic and thermal Energies = -1269.037591 hartree
Sum of electronic and thermal Enthalpies = -1269.036647 hartree
Sum of electronic and thermal Free Energies = -1269.119464 hartree
SMD(CH_2Cl_2)/UM062X/6-311g(d,p)
E(UM062X) = -1269.6023 hartree
Gibbs Free Energy in CH_2Cl_2 = -1269.2074 hartree
The number of Imaginary frequencies = 0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.076133	5.302480	-0.842668
2	6	0	-1.374307	4.387840	-1.848536
3	6	0	-0.447581	4.876362	0.323776
4	6	0	-1.055055	3.046334	-1.685981
5	1	0	-1.847466	4.721375	-2.763762
6	6	0	-0.113985	3.538103	0.484391
7	1	0	-0.218169	5.586945	1.108103
8	6	0	-0.421594	2.611235	-0.516293
9	1	0	-1.264216	2.338572	-2.480846
10	1	0	0.364902	3.205139	1.398648
11	6	0	-0.041580	1.192406	-0.353521
12	6	0	-0.950328	0.129478	-0.614002
13	6	0	1.224718	0.853029	0.055933
14	6	0	-2.343044	0.313320	-0.812508
15	6	0	-0.432299	-1.211650	-0.709851
16	6	0	1.667985	-0.549656	0.261600
17	6	0	-3.152897	-0.727115	-1.164301
18	1	0	-2.759828	1.301875	-0.667420
19	6	0	-1.231205	-2.256467	-1.127478
20	6	0	-2.586687	-2.027913	-1.355695
21	1	0	-0.824394	-3.253341	-1.231486
22	1	0	-1.328192	6.348082	-0.970023
23	1	0	1.947033	1.630439	0.280276
24	6	0	3.102527	-0.739868	-0.226821
25	6	0	3.406522	-1.634224	-1.249273
26	6	0	4.126909	-0.002557	0.370462
27	6	0	4.726370	-1.790851	-1.664465
28	1	0	2.622237	-2.211076	-1.719382
29	6	0	5.441129	-0.161468	-0.048435
30	1	0	3.913187	0.699977	1.169660
31	6	0	5.744120	-1.058383	-1.068295
32	1	0	4.954525	-2.490655	-2.459041

33	1	0	6.227777	0.414370	0.423140
34	1	0	6.769014	−1.183425	−1.394792
35	8	0	0.841368	−1.479522	−0.453446
36	1	0	−4.214077	−0.567598	−1.292893
37	8	0	−3.297596	−3.076708	−1.722895
38	6	0	−4.699864	−2.950440	−1.979223
39	1	0	−4.877005	−2.240863	−2.788928
40	1	0	−5.025917	−3.941348	−2.279549
41	1	0	−5.227515	−2.645843	−1.073879
42	6	0	0.163261	−0.846181	2.322835
43	6	0	−0.701752	−1.937282	2.227279
44	6	0	−2.024505	−1.833463	2.648687
45	6	0	−2.495250	−0.635236	3.174000
46	6	0	−1.634780	0.454578	3.294648
47	6	0	−0.315774	0.345280	2.873947
48	1	0	−0.334288	−2.874527	1.821029
49	1	0	−2.680984	−2.692843	2.578923
50	1	0	−3.522200	−0.554019	3.509244
51	1	0	−1.990104	1.382242	3.727030
52	1	0	0.356451	1.191254	2.984646
53	6	0	1.563978	−0.934851	1.786976
54	1	0	1.956016	−1.952602	1.850123
55	1	0	2.239660	−0.279313	2.338773

10-2. The calculation of redox potential

The redox potential of benzopyrylium cation salt (**1'a$^+$BF$_4^-$**) in MeCN was calculated with the UB3LYP/6-31+g(d,p) method.[2] The geometries of benzopyrylium cation salt (**1'a$^+$BF$_4^-$**) and the reduced radical (**1"a**) were fully optimized using the UB3LYP/6-31+g(d,p) methods in solution phase (E) by performing CPCM calculation. The nature of the stationary points and thermal corrections to Gibbs free energy (G) were obtained by frequency calculations at the same level of theory.



1'a$^+$BF4$^-$ **1"a**

G(**1'a$^+$BF$_4^-$**) = –1423.3023 hartree

G(**1"a**) = –1423.4490 hartree

ΔG = G(**1"a**) – G(**1'a$^+$BF$_4^-$**) = –0.146649 hartree = –92.023641 kcal/mol

$$E_{red}(\mathbf{1'a^+BF_4^-/1"}) = \Delta G/nF - E^0(SHE) + E^0(SCE) = 3.990 - 4.281 - 0.141 = -0.432\,V\ (vs\ SCE)$$

n is the number of electrons transferred, *F* is the Faraday constant (23.061 kcal mol^{-1}V^{-1}). E^0(SHE) is the absolute value for the standard hydrogen electrode (4.281 V) and E^0(SCE) is the potential of the saturated calomel electrode (SCE) relative to SHE in acetonitrile (–0.141 V).

From the absorption and fluorescence spectra (Figure S1) of the preformed benzopyrylium cation salt (**1'a$^+$BF$_4^-$**), the redox potential of the excited **1'a^{+*}BF$_4^-$** was estimated employing the following equation.

$$E^*_{red} = E_{red} + E_{0,0}$$

$E_{0,0}$, which is the excited state energy of the benzopyrylium salt, was estimated to $E_{0,0}$ = +2.73 V from the crossing point between the absorption and fluorescence spectra recorded in MeCN (Figure S3).

$$E^*_{red} = +2.30\ V\ (vs\ SCE\ in\ MeCN)$$

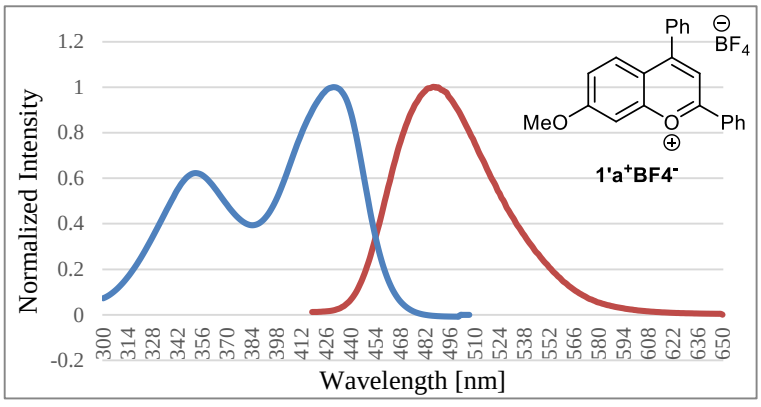


Figure S3. UV-Vis absorption spectrum of **1'a$^+$BF$_4^-$** in MeCN at room temperature (blue). Fluorescence spectrum of **1'a$^+$BF$_4^-$** in MeCN at room temperature upon excitation at 360 nm (orange)

[2] H. G. Roth, N. A. Romero and D. A. Nicewicz, *Synlett* 2016, **27**, 714–723.

Cartesian coordinates

1’a BF_4^-

CPCM(MeCN)/UB3LYP/6-31g(d,p)
E(UB3LYP) = -1423.583168 hartree
Zero-point Energy Correction = 0.343749 hartree
Thermal Correction to Energy = 0.369671 hartree
Thermal correction to Enthalpy = 0.370615 hartree
Thermal correction to Gibbs Free Energy = 0.280846 hartree
Sum of electronic and Zero-point Energies = -1423.239419 hartree
Sum of electronic and thermal Energies = -1423.213497 hartree
Sum of electronic and thermal Enthalpies = -1423.212553 hartree
Sum of electronic and thermal Free Energies= -1423.302322 hartree
The number of Imaginary frequencies = 0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-6.642855	0.049399	-0.320556
2	6	0	-5.856492	-0.748453	-1.157609
3	6	0	-6.033207	0.875570	0.629528
4	6	0	-4.466727	-0.736420	-1.036801
5	1	0	-6.323556	-1.378926	-1.907647
6	6	0	-4.643459	0.909612	0.739196
7	1	0	-6.638595	1.494804	1.283945
8	6	0	-3.844509	0.093434	-0.084420
9	1	0	-3.864258	-1.339551	-1.707860
10	1	0	-4.176726	1.547365	1.483421
11	6	0	-2.372277	0.160083	0.025880
12	6	0	-1.546936	-1.000282	0.099194
13	6	0	-1.752503	1.415513	0.048580
14	6	0	-2.010258	-2.338236	0.199298
15	6	0	-0.136402	-0.815921	0.119533
16	6	0	-0.369051	1.541469	0.081789
17	6	0	-1.133120	-3.398983	0.266642
18	1	0	-3.074772	-2.529981	0.242347
19	6	0	0.768638	-1.862459	0.174803
20	6	0	0.268323	-3.167828	0.239964
21	1	0	1.837778	-1.677737	0.178540
22	1	0	-7.724544	0.031167	-0.411285
23	1	0	-2.358053	2.307249	-0.022156
24	6	0	0.388191	2.790565	0.073345
25	6	0	1.792125	2.768739	-0.070239
26	6	0	-0.270950	4.030643	0.212901
27	6	0	2.510418	3.961675	-0.081313
28	1	0	2.319426	1.828268	-0.177567
29	6	0	0.457049	5.216659	0.203221
30	1	0	-1.345757	4.078607	0.342312
31	6	0	1.848369	5.186868	0.054051
32	1	0	3.589107	3.934655	-0.196639
33	1	0	-0.060384	6.163817	0.315206
34	1	0	2.413044	6.114027	0.045341
35	8	0	0.394373	0.441605	0.095901
36	1	0	-1.523755	-4.404535	0.351048
37	8	0	1.188427	-4.145267	0.291381
38	6	0	0.769489	-5.520736	0.365714
39	1	0	0.176513	-5.792630	-0.511948
40	1	0	1.691627	-6.099206	0.381799
41	1	0	0.201841	-5.703562	1.282408
42	5	0	5.023603	-0.618790	-0.214414
43	9	0	4.074564	-1.596216	0.175263
44	9	0	6.023815	-0.515064	0.777304
45	9	0	5.609575	-0.996970	-1.442692
46	9	0	4.373991	0.628687	-0.364727

1’aa

CPCM(MeCN)/UB3LYP/6-31g(d,p)
E(UB3LYP) = -1423.725140 hartree
Zero-point Energy Correction = 0.340688 hartree
Thermal Correction to Energy = 0.366921 hartree
Thermal correction to Enthalpy = 0.367865 hartree
Thermal correction to Gibbs Free Energy = 0.276169 hartree
Sum of electronic and Zero-point Energies = -1423.384453 hartree
Sum of electronic and thermal Energies = -1423.358219 hartree
Sum of electronic and thermal Enthalpies = -1423.357275 hartree
Sum of electronic and thermal Free Energies= -1423.448971 hartree
The number of Imaginary frequencies = 0

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-6.735460	-0.021960	-0.245801
2	6	0	-5.953584	-0.857921	-1.050717
3	6	0	-6.106532	0.851283	0.648197
4	6	0	-4.560901	-0.826701	-0.959850
5	1	0	-6.428277	-1.531228	-1.758960
6	6	0	-4.713908	0.885123	0.738516
7	1	0	-6.700665	1.502570	1.283100
8	6	0	-3.909727	0.046060	-0.062140
9	1	0	-3.971841	-1.461082	-1.614456
10	1	0	-4.241075	1.555119	1.450755
11	6	0	-2.436854	0.131625	0.014062
12	6	0	-1.568498	-1.033358	0.064109
13	6	0	-1.815597	1.387678	0.043353
14	6	0	-1.992747	-2.372297	0.172235
15	6	0	-0.164527	-0.824118	0.064374
16	6	0	-0.440280	1.554236	0.047925
17	6	0	-1.096064	-3.439652	0.234038
18	1	0	-3.053363	-2.588048	0.220854
19	6	0	0.749896	-1.865782	0.118862
20	6	0	0.283445	-3.186994	0.196438
21	1	0	1.815502	-1.661029	0.112250
22	1	0	-7.818813	-0.049874	-0.315477
23	1	0	-2.434142	2.275853	0.016282
24	6	0	0.296239	2.809293	0.046288
25	6	0	1.710525	2.816893	-0.011335
26	6	0	-0.370369	4.057779	0.104174
27	6	0	2.418025	4.019401	-0.013259
28	1	0	2.253710	1.880614	-0.056595
29	6	0	0.345082	5.251583	0.100951
30	1	0	-1.452845	4.100824	0.155421
31	6	0	1.745800	5.244734	0.042145
32	1	0	3.503201	3.996225	-0.058945
33	1	0	-0.193167	6.194047	0.146700
34	1	0	2.300117	6.178360	0.040583
35	8	0	0.376684	0.439649	0.020392
36	1	0	-1.480820	-4.448355	0.315760
37	8	0	1.247628	-4.150320	0.241296
38	6	0	0.843751	-5.520656	0.328840
39	1	0	0.243460	-5.810945	-0.540216
40	1	0	1.767218	-6.099129	0.344284
41	1	0	0.278837	-5.707363	1.248590
42	5	0	5.206776	-0.567073	-0.166447
43	9	0	4.207264	-1.513596	0.162409
44	9	0	6.215212	-0.584197	0.824492
45	9	0	5.771630	-0.895612	-1.420390
46	9	0	4.630149	0.721925	-0.230914

11. X-ray crystallographic analysis

3ia was recrystallized from DCM/MeOH to give a colorless block crystal. The structure of **3ia** was determined by X-ray crystallographic analysis.[3]

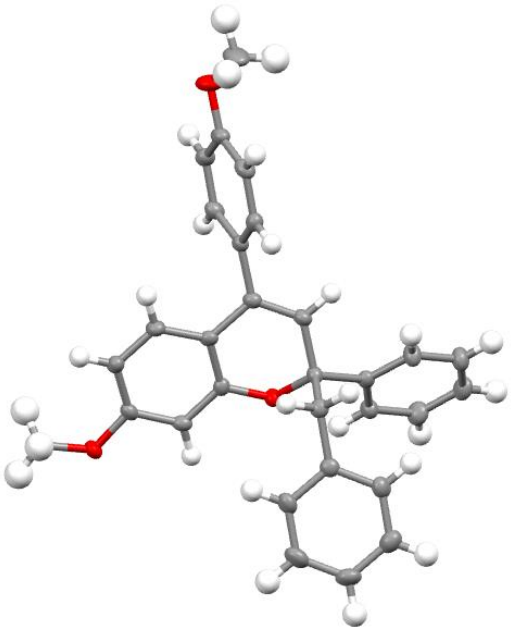


Figure S1: ORTEP Drawing of **3ia**

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{30}H_{26}O_3$
Formula Weight	434.53
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.350 X 0.200 X 0.200 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 10.1631(15) Å
	b = 10.5208(15) Å
	c = 10.9954(16) Å
	β = 102.394(7) º
	V = 1148.3(3) Å^3
Space Group	$P2_1$ (#4)

[3] J. Kikuchi, CCDC 2064775: *CSD Communication*, 2021, DOI: 10.5517/ccdc.csd.cc279kns.

Z value	2
D_{calc}	1.257 g/cm^3
F_{000}	460.00
μ(MoKα)	0.798 cm^{-1}

B. Intensity Measurements

Diffractometer	XtaLAB mini
Radiation	MoKα (λ = 0.71075 Å) graphite monochromated
Voltage, Current	50kV, 12mA
Temperature	-123.0°C
Detector Aperture	75.0 mm (diameter)
Data Images	540 exposures
ω oscillation Range (χ=54.0, ϕ=0.0)	-60.0 - 120.0°
Exposure Rate	48.0 sec./°
Detector Swing Angle	30.00°
ω oscillation Range (χ=54.0, ϕ=120.0)	-60.0 - 120.0°
Exposure Rate	48.0 sec./°
Detector Swing Angle	30.00°
ω oscillation Range (χ=54.0, ϕ=240.0)	-60.0 - 120.0°
Exposure Rate	48.0 sec./°
Detector Swing Angle	30.00°
ω oscillation Range (χ=54.0, ϕ=0.0)	-60.0 - 120.0°
Exposure Rate	48.0 sec./°
Detector Swing Angle	30.00°
ω oscillation Range (χ=54.0, ϕ=120.0)	-60.0 - 120.0°
Exposure Rate	48.0 sec./°
Detector Swing Angle	30.00°
ω oscillation Range (χ=54.0, ϕ=240.0)	-60.0 - 120.0°
Exposure Rate	48.0 sec./°
Detector Swing Angle	30.00°
Detector Position	50.00 mm
Pixel Size	0.073 mm
$2\theta_{max}$	55.0°
No. of Reflections Measured	Total: 12206 Unique: 5252 (R_{int} = 0.1609) Parsons quotients (Flack x parameter): 1432

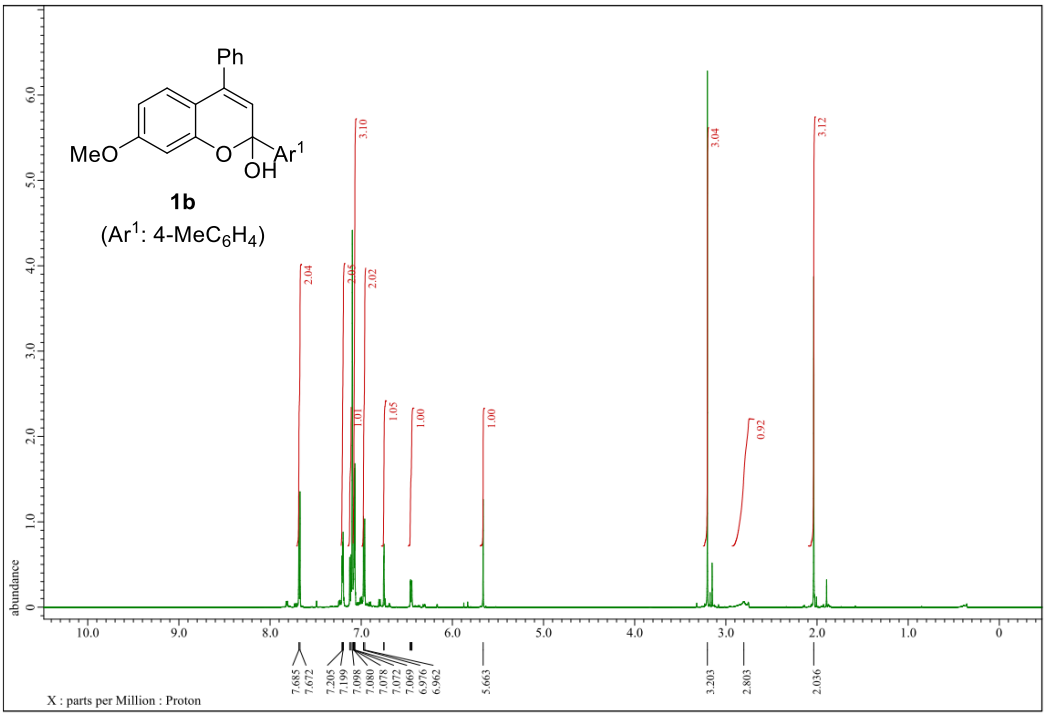
Corrections	Lorentz-polarization Absorption (trans. factors: 0.676 - 0.984)

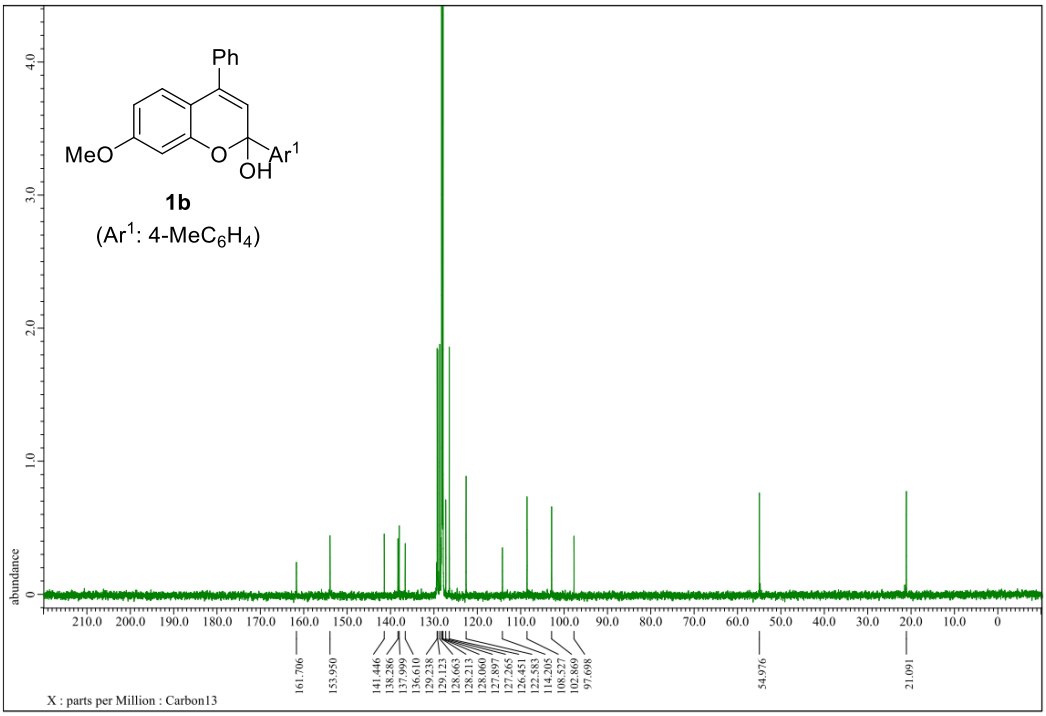
C. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELXT Version 2014/5)
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w $(Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/ [\sigma^2(Fo^2) + (0.0650 \cdot P)^2$ $+ 0.0000 \cdot P]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	54.9^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	5252
No. Variables	298
Reflection/Parameter Ratio	17.62
Residuals: R1 (I>2.00σ(I))	0.0909
Residuals: R (All reflections)	0.0957
Residuals: wR2 (All reflections)	0.2228
Goodness of Fit Indicator	1.029
Flack parameter (Parsons' quotients = 1432)	-1.1(10)
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.39 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.32 $e^-/Å^3$

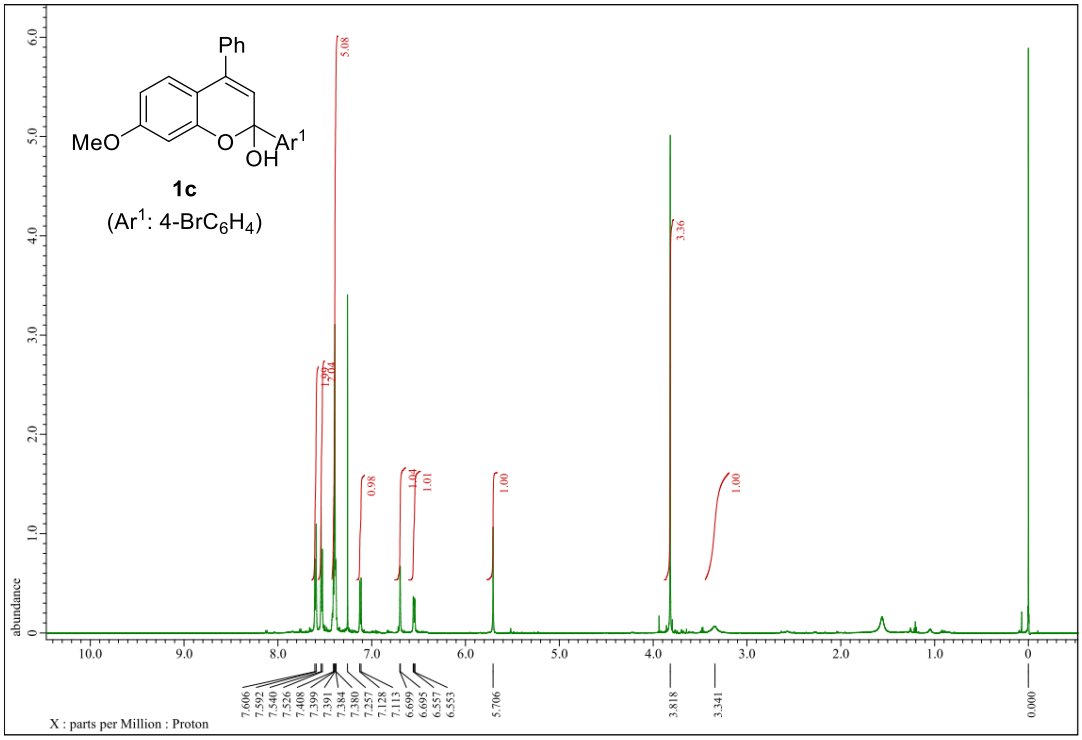
12. NMR Spectra

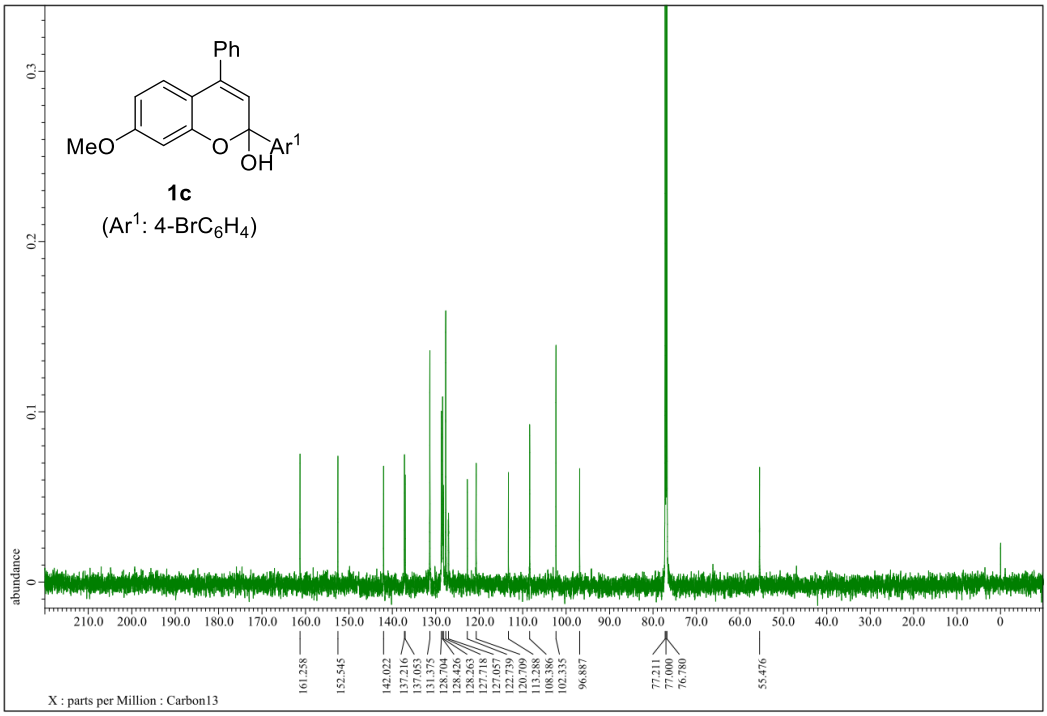
^{1}H NMR (600 MHz, C_6D_6) and ^{13}C NMR (151 MHz, C_6D_6) spectra of **1b**



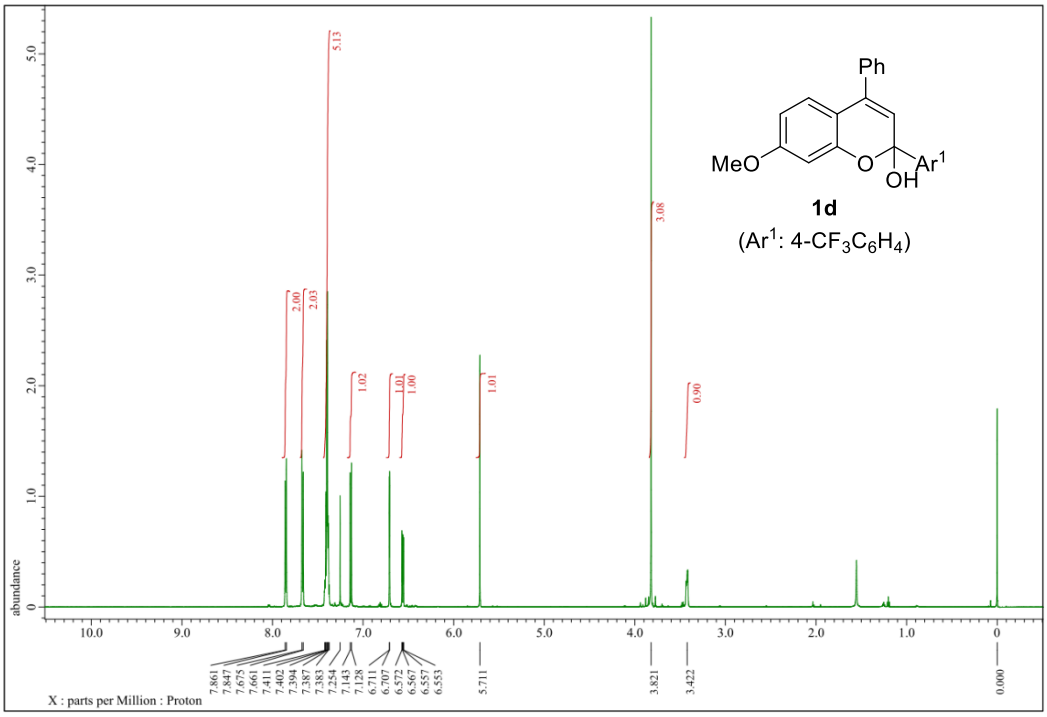


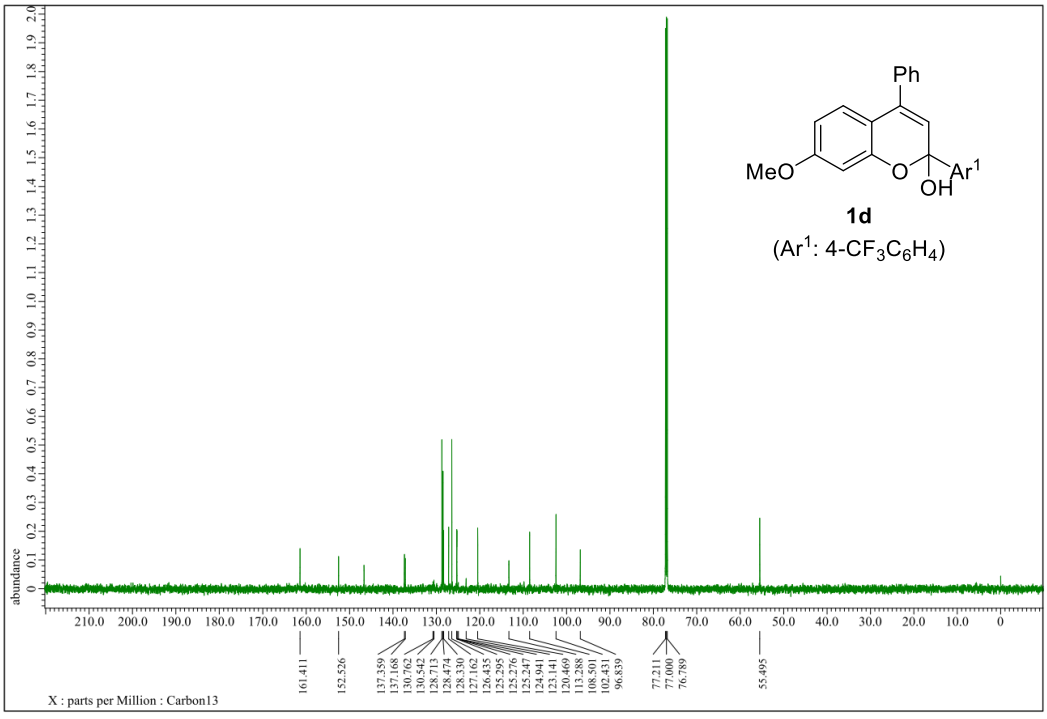
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **1c**



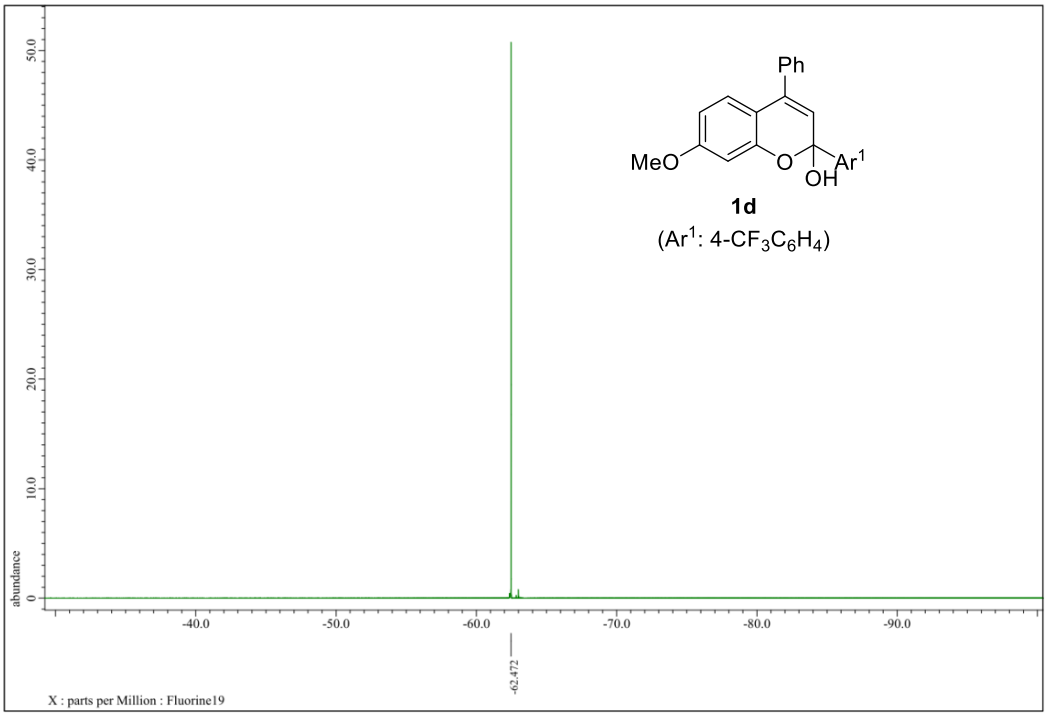


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **1d**

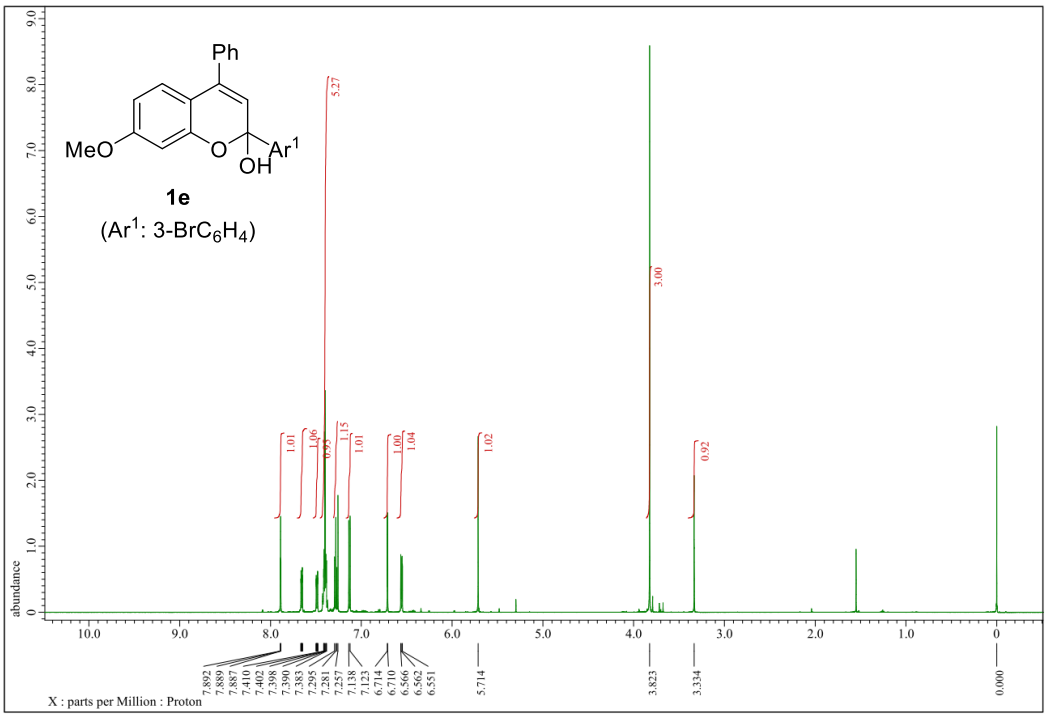


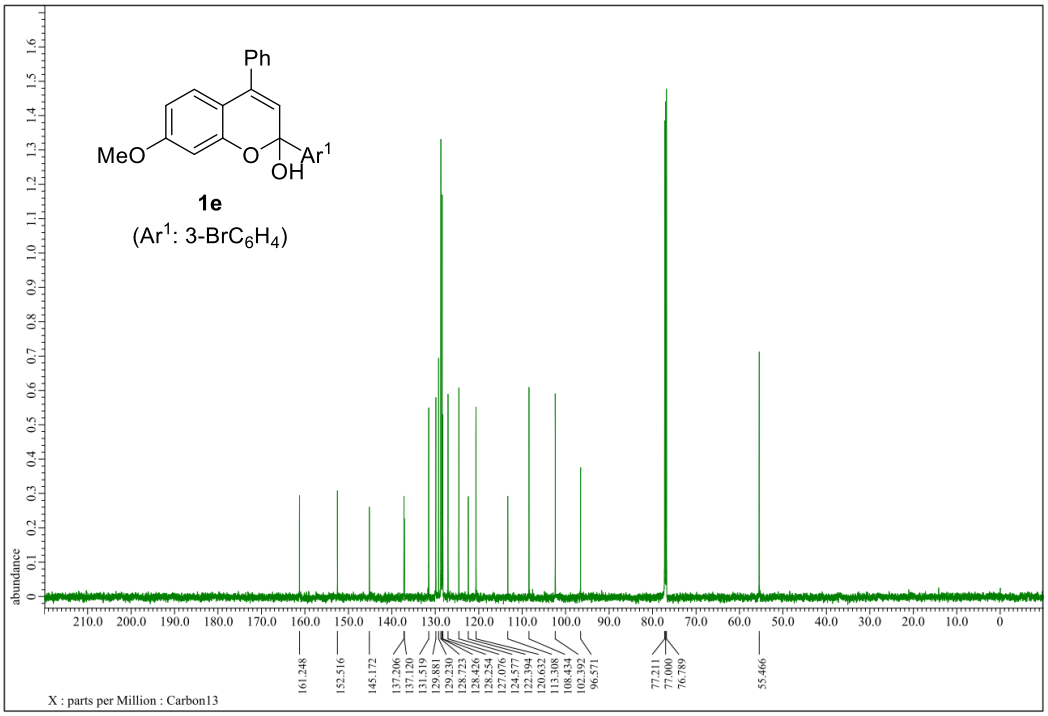


^{19}F NMR (565 MHz, $CDCl_3$) spectra of **1d**

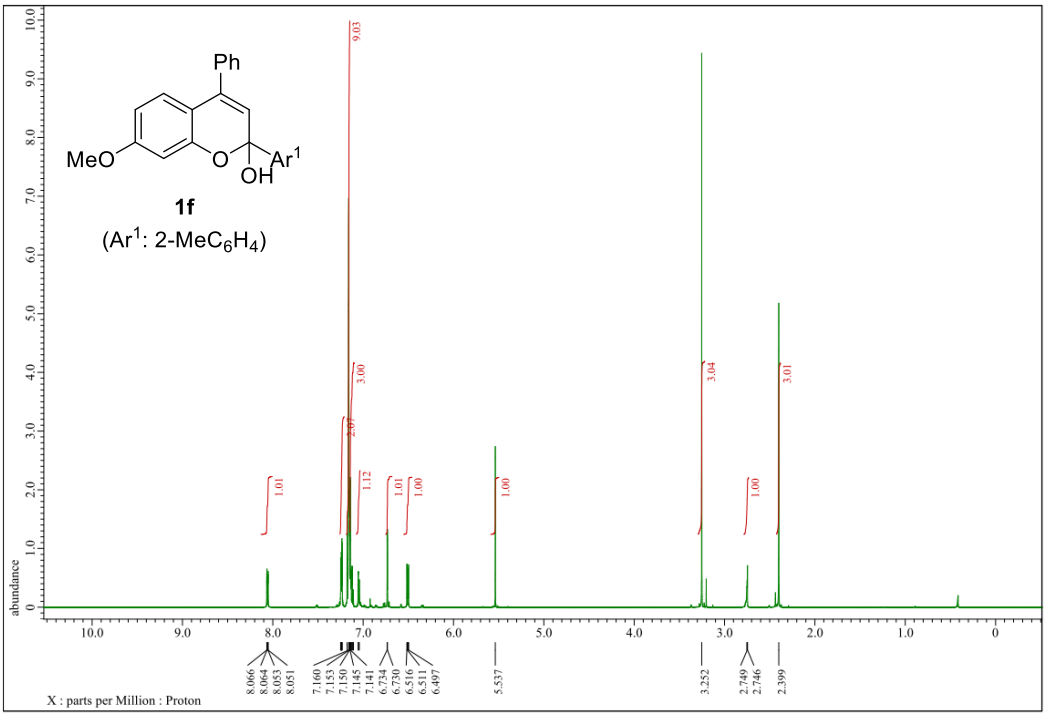


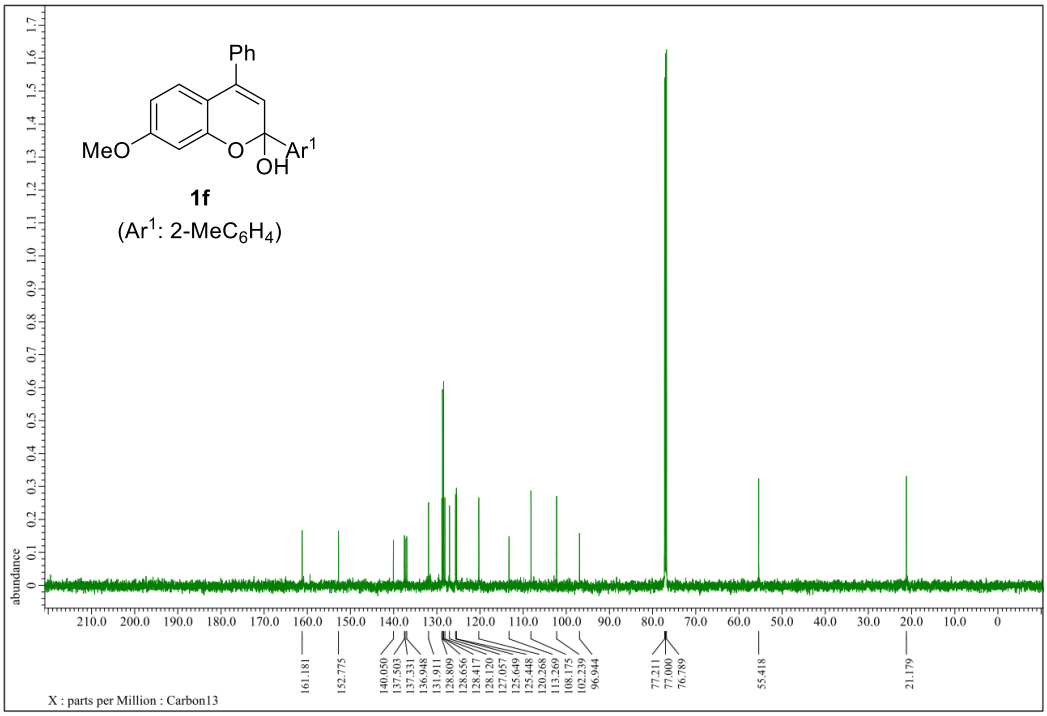
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **1e**



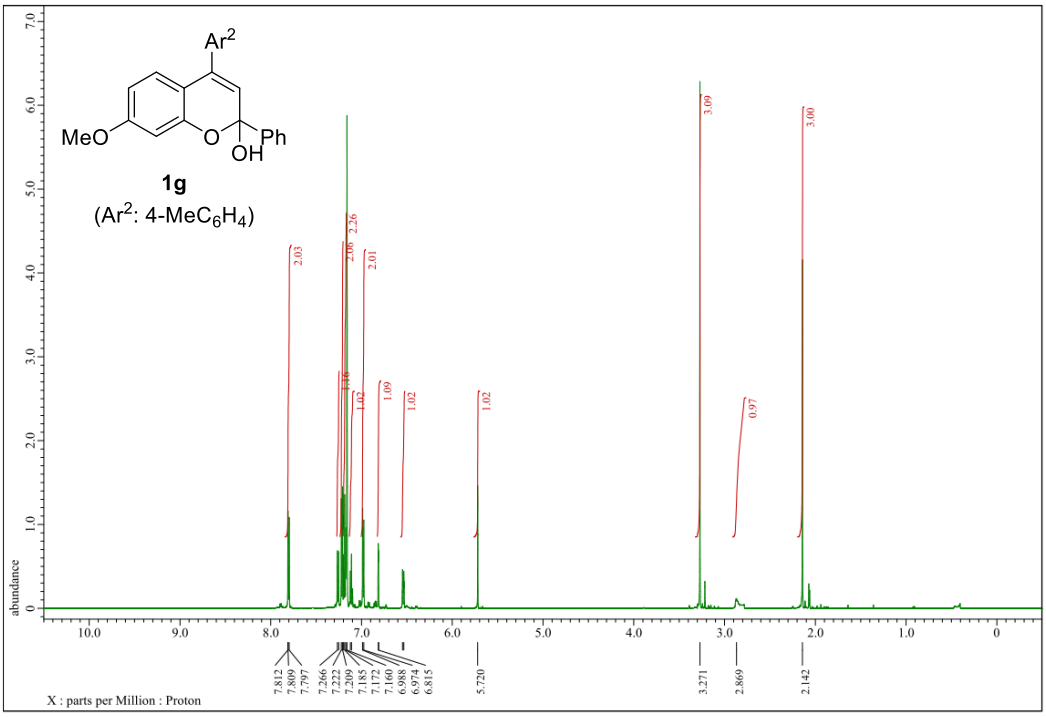


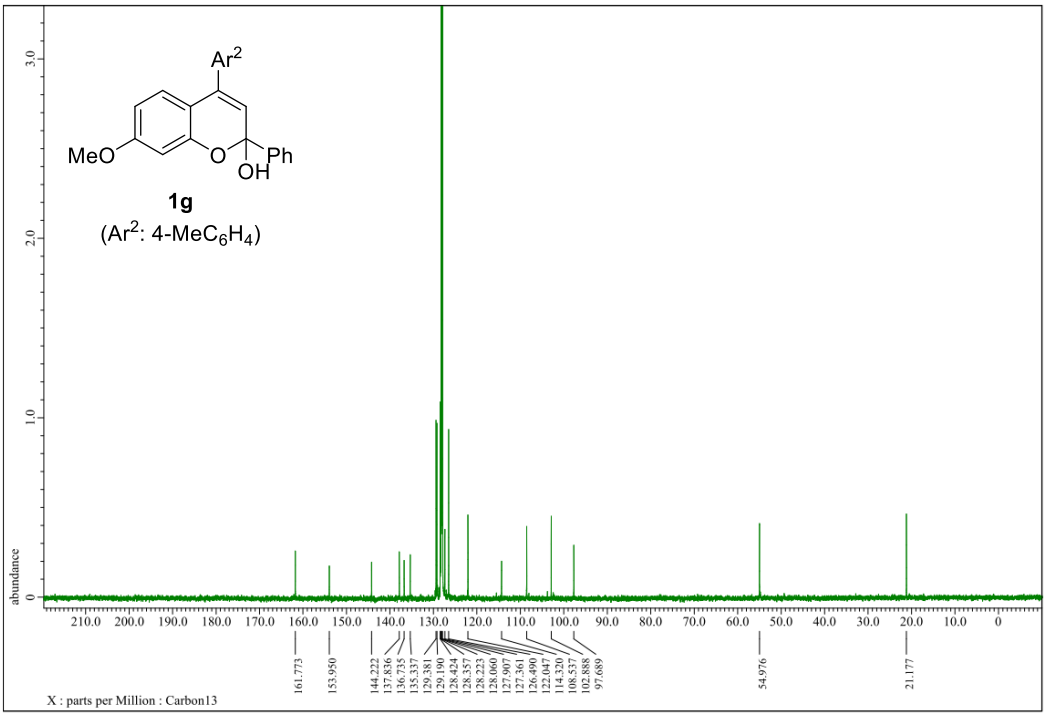
^{1}H NMR (600 MHz, C_6D_6) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **1f**



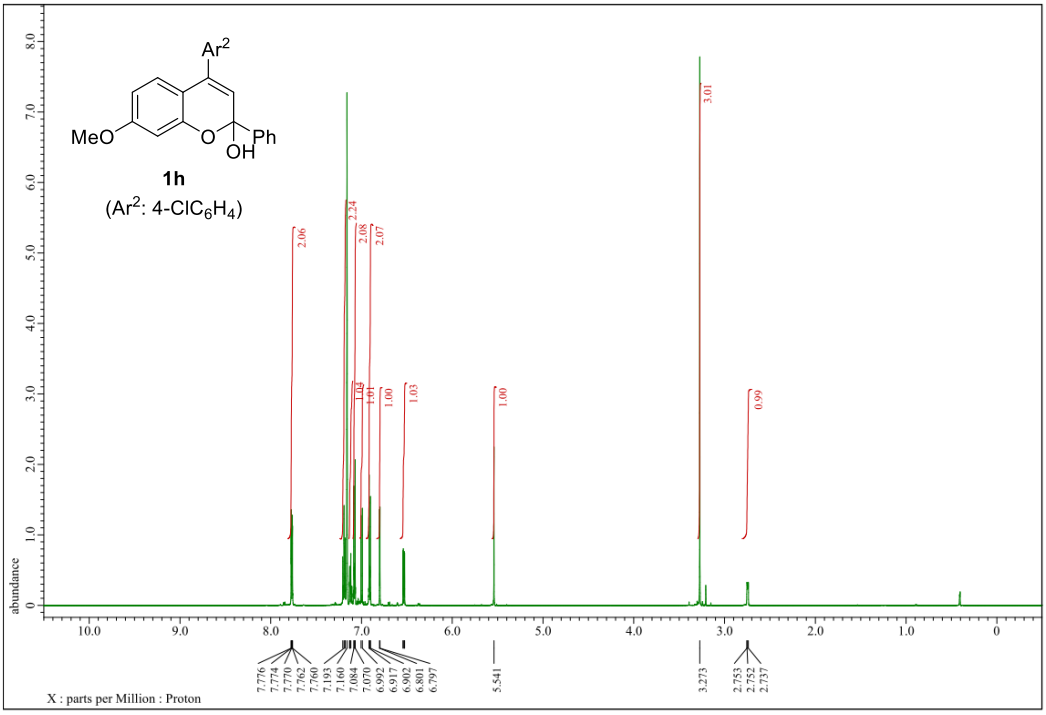


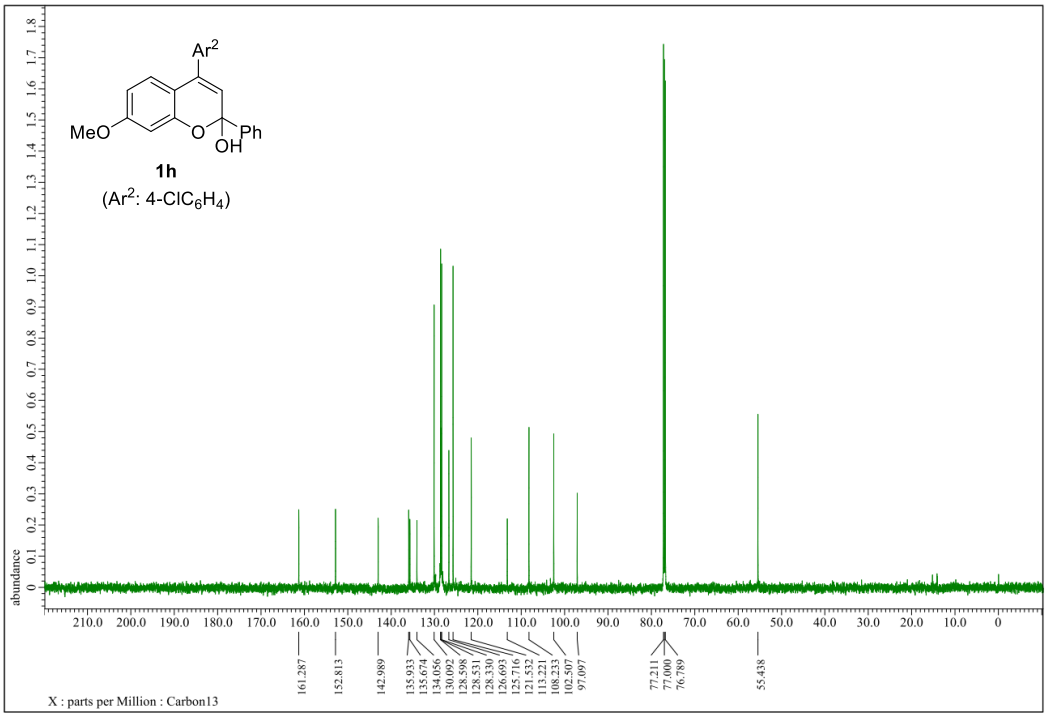
^{1}H NMR (600 MHz, C_6D_6) and ^{13}C NMR (151 MHz, C_6D_6) spectra of **1g**



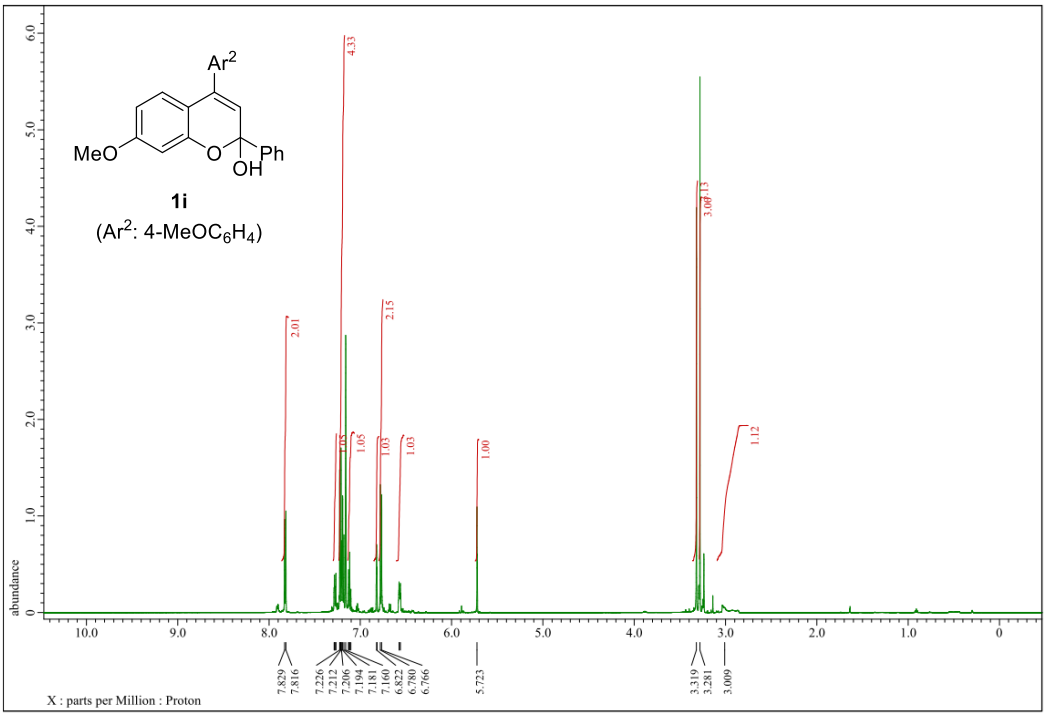


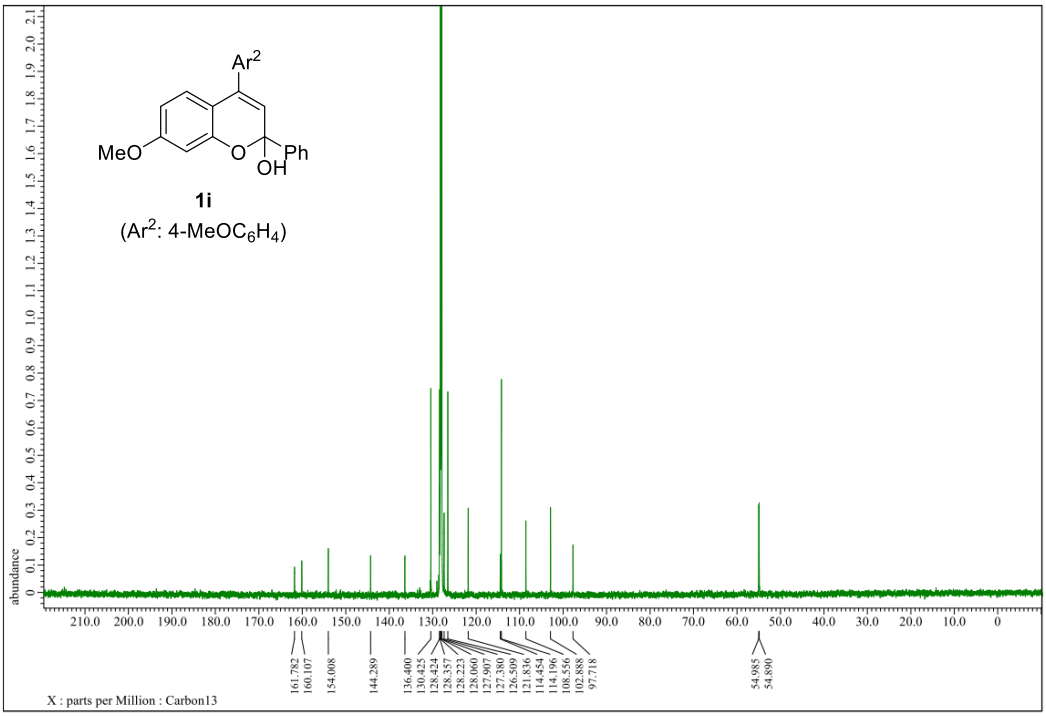
^{1}H NMR (600 MHz, C_6D_6) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **1h**



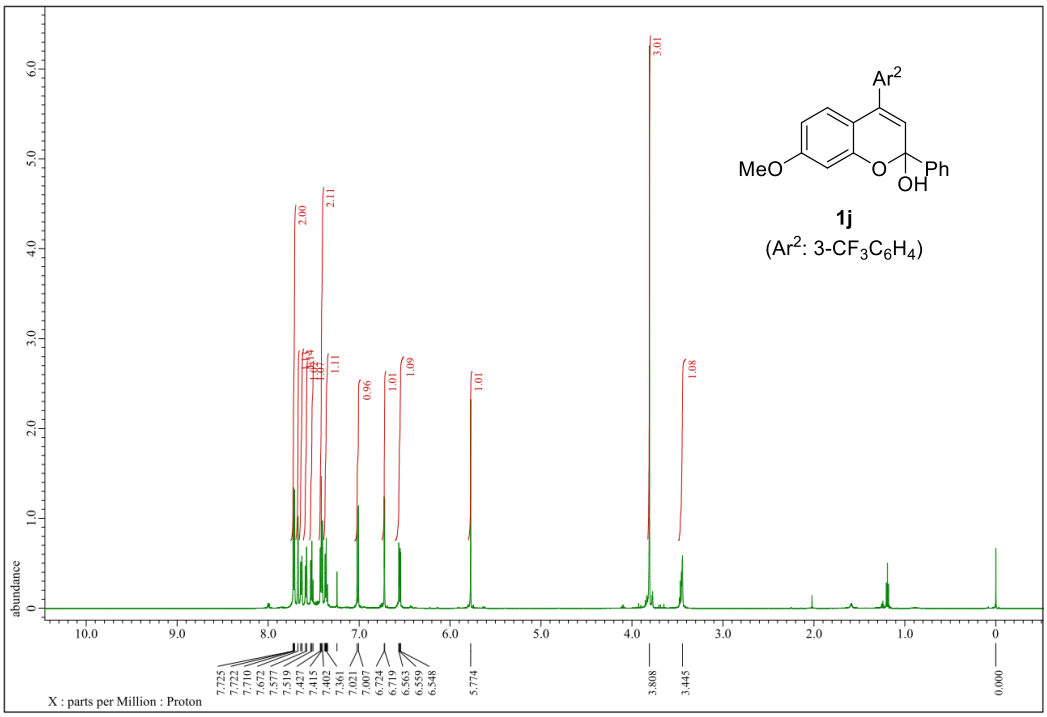


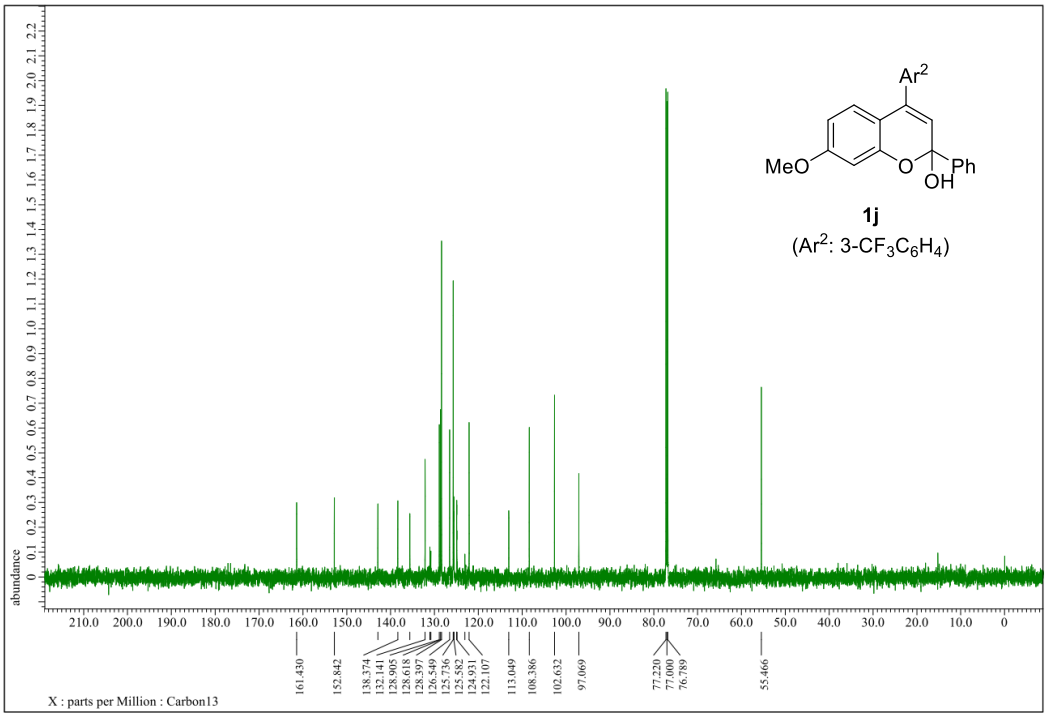
^{1}H NMR (600 MHz, C_6D_6) and ^{13}C NMR (151 MHz, C_6D_6) spectra of **1i**



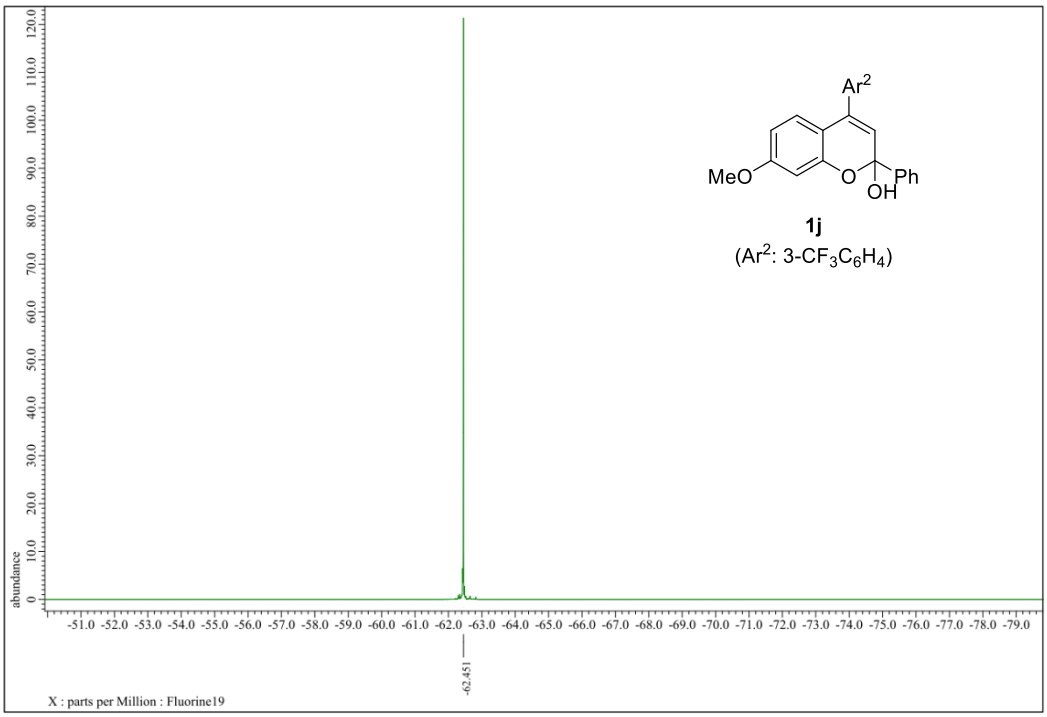


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **1j**

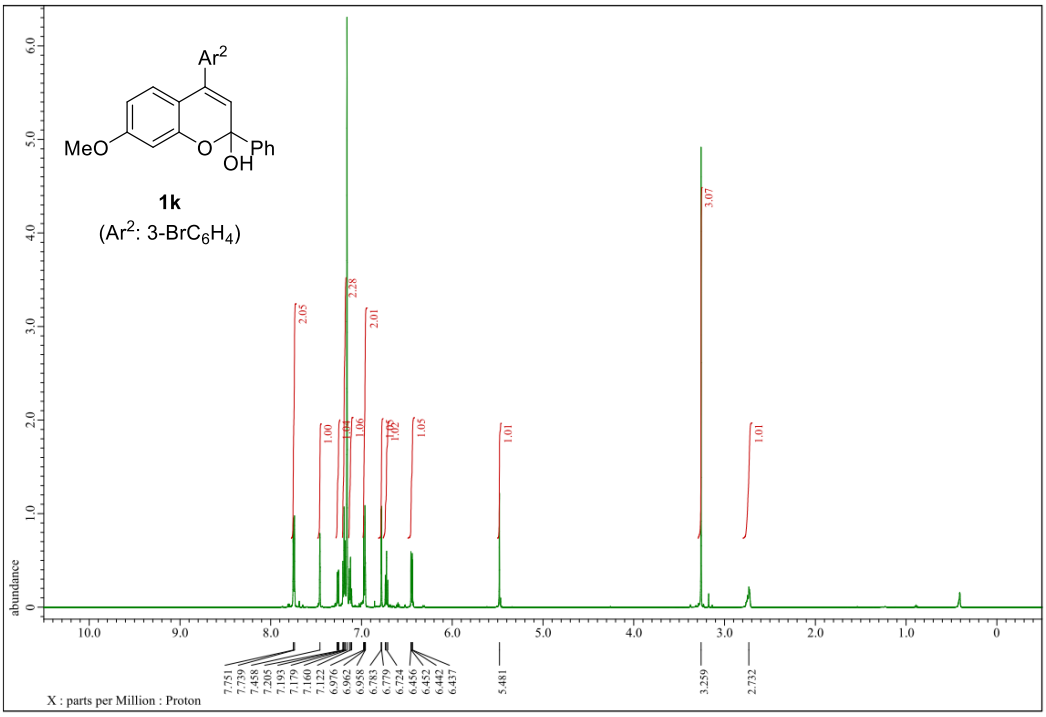


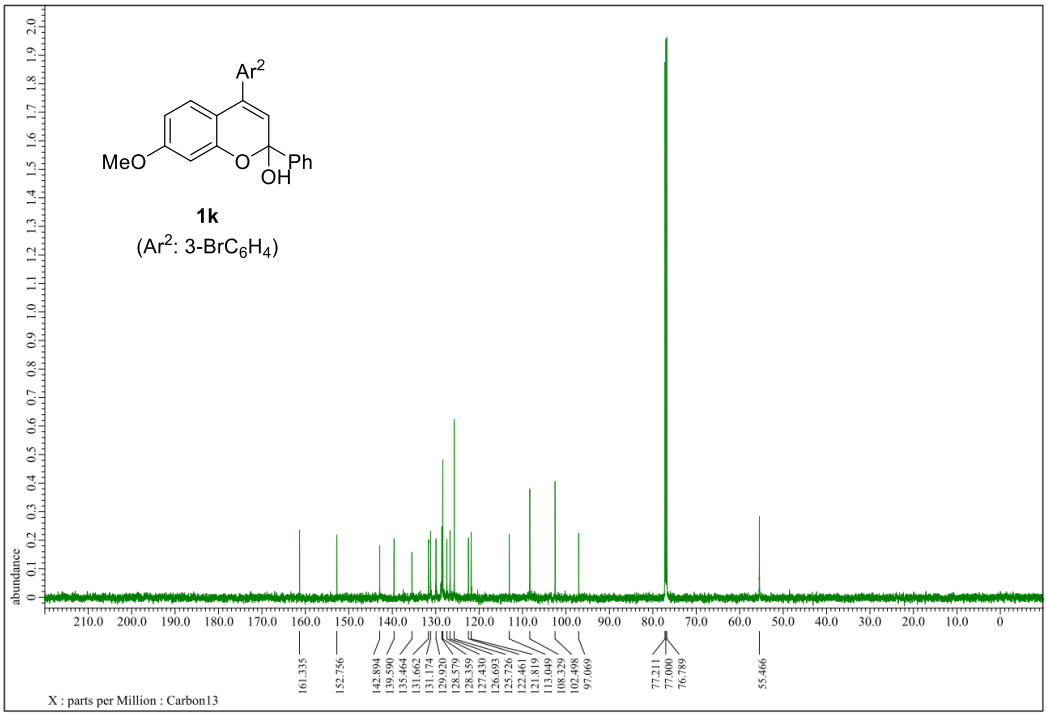


^{19}F NMR (565 MHz, $CDCl_3$) spectra of **1j**

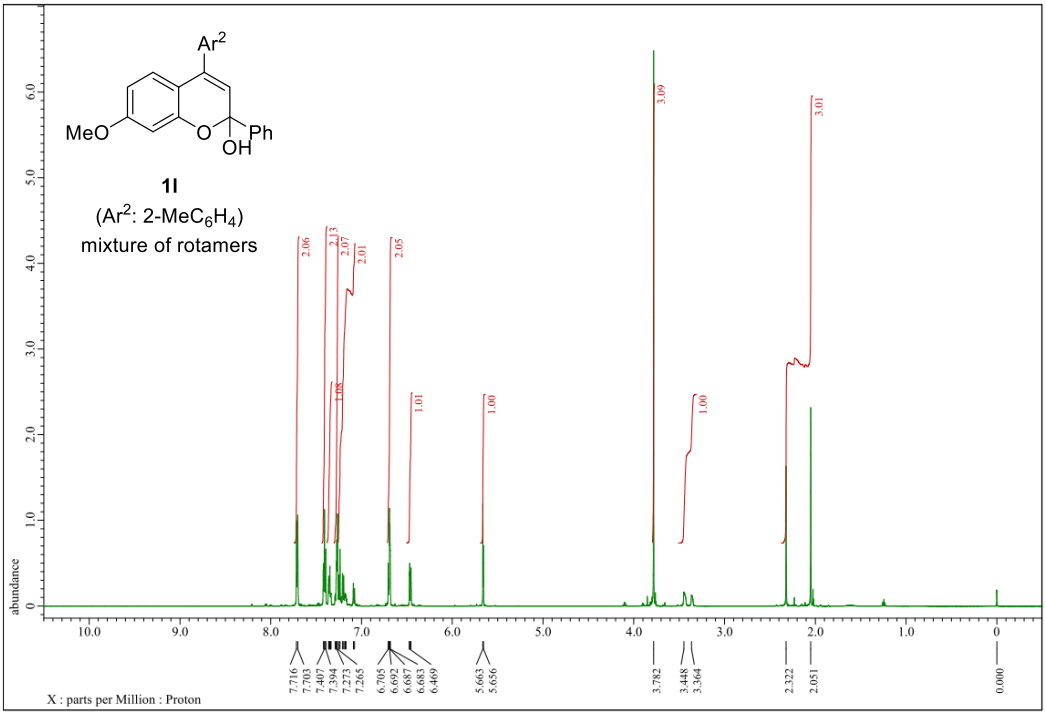


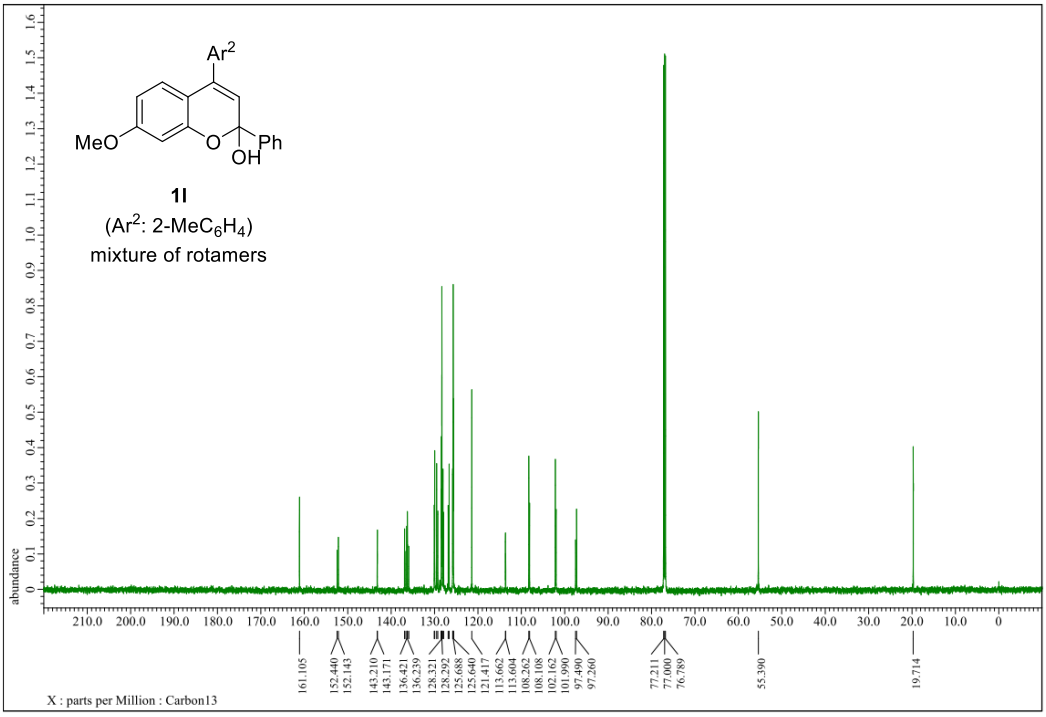
^{1}H NMR (600 MHz, C_6D_6) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **1k**



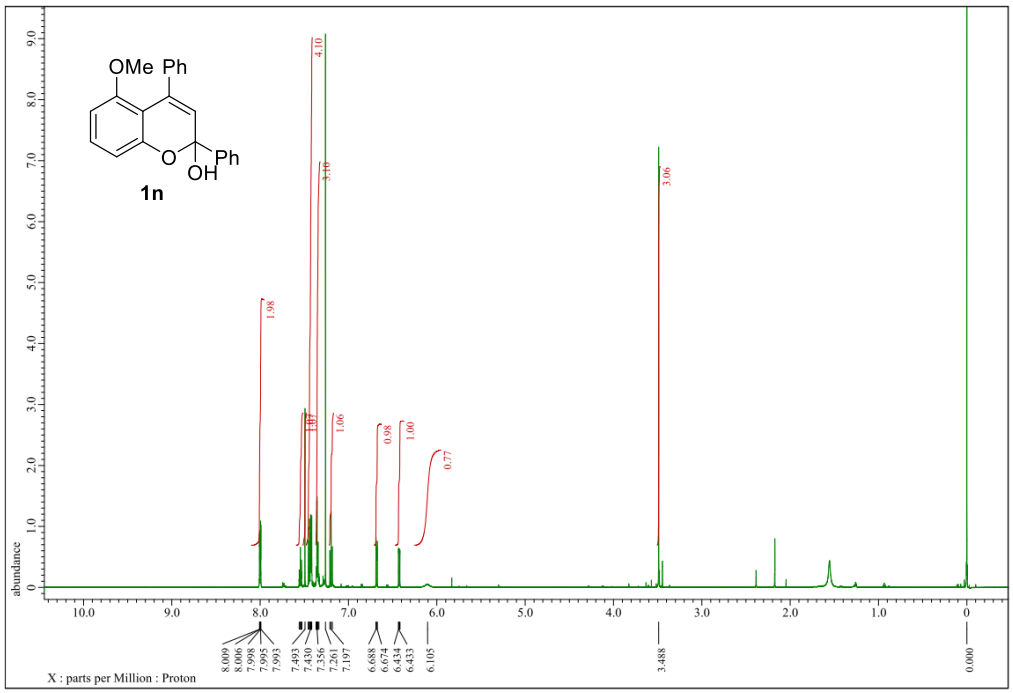


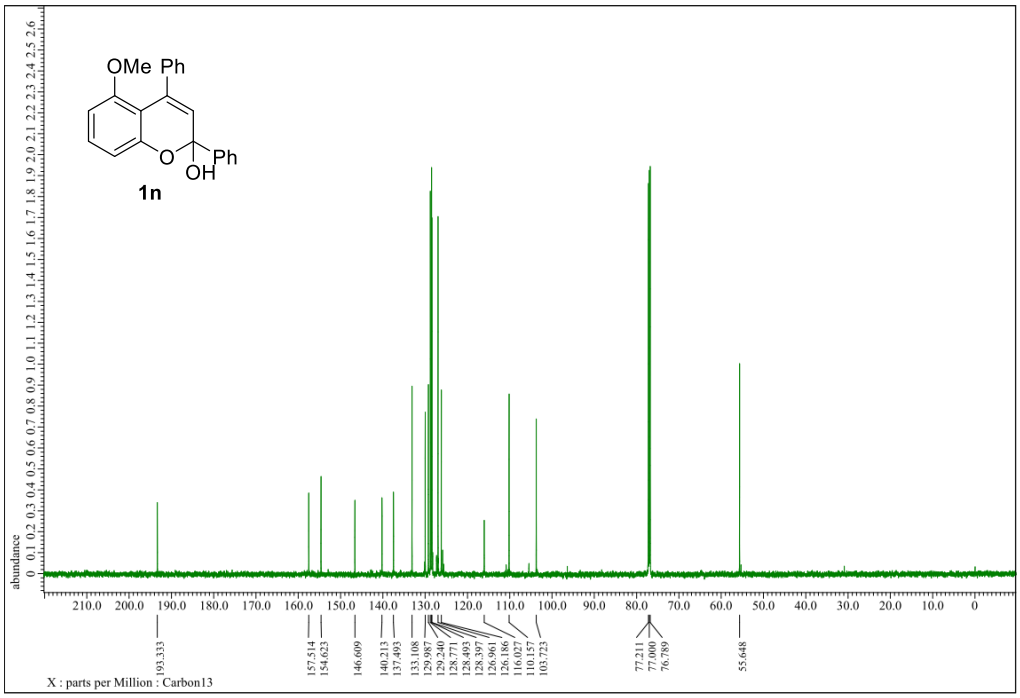
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **1l**



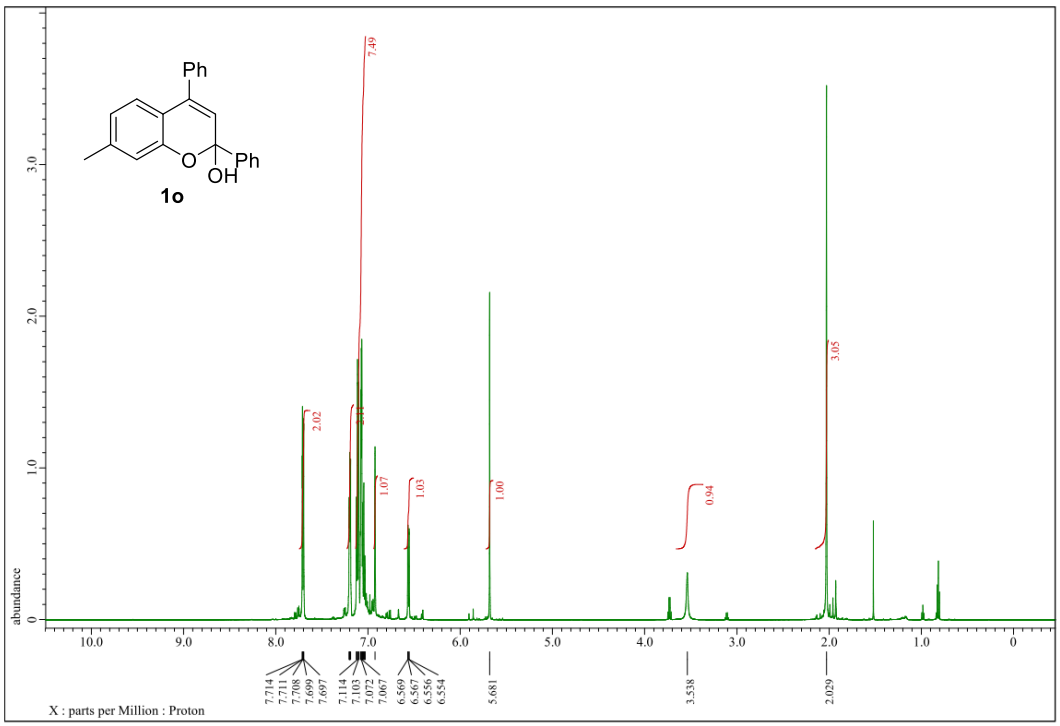


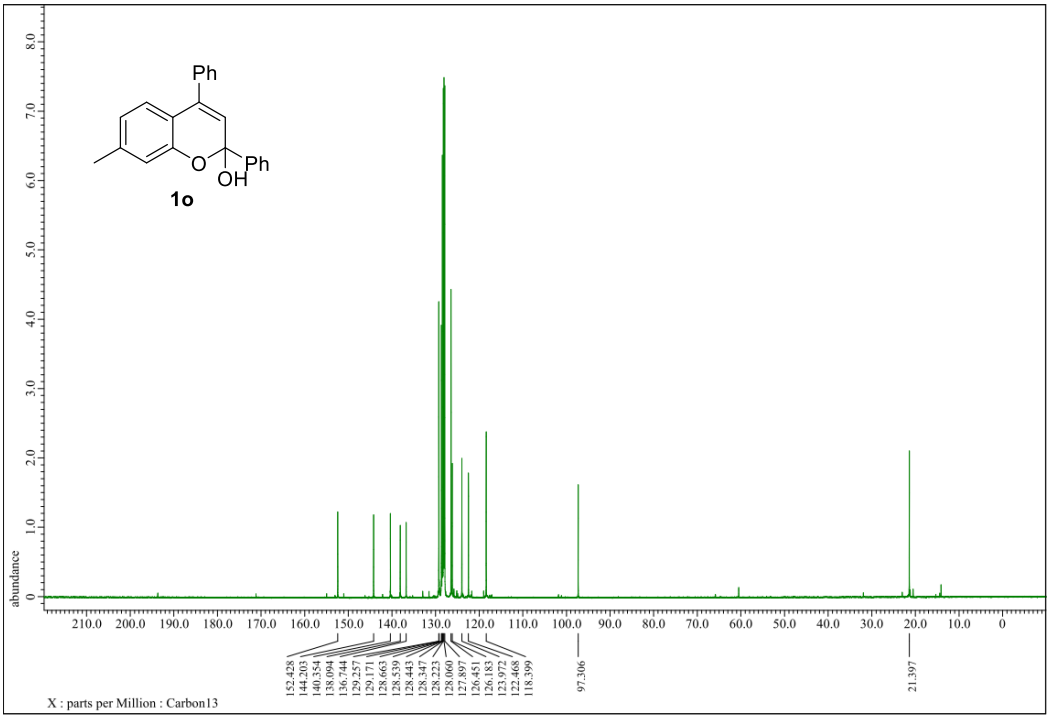
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **1n**



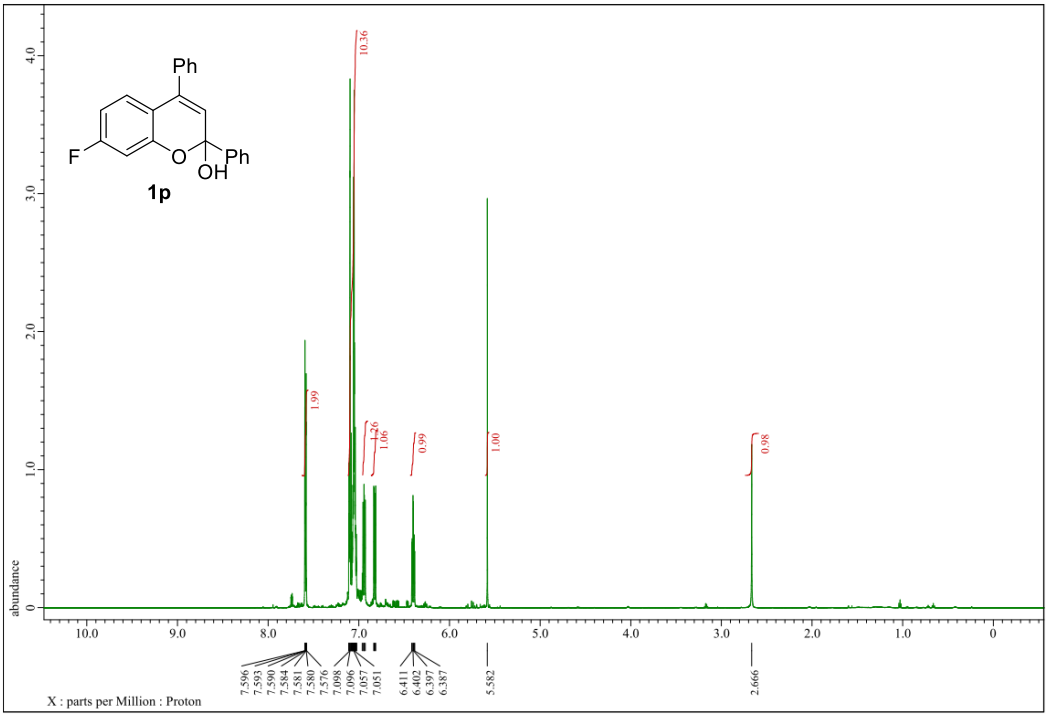


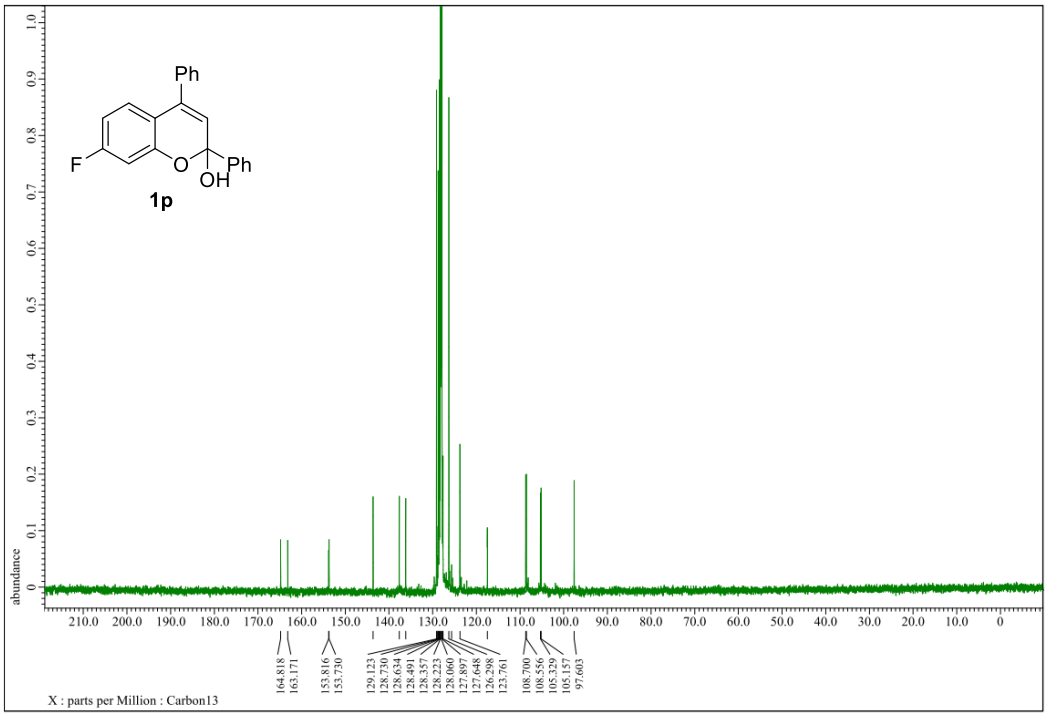
^{1}H NMR (600 MHz, C_6D_6) and ^{13}C NMR (151 MHz, C_6D_6) spectra of **1o**



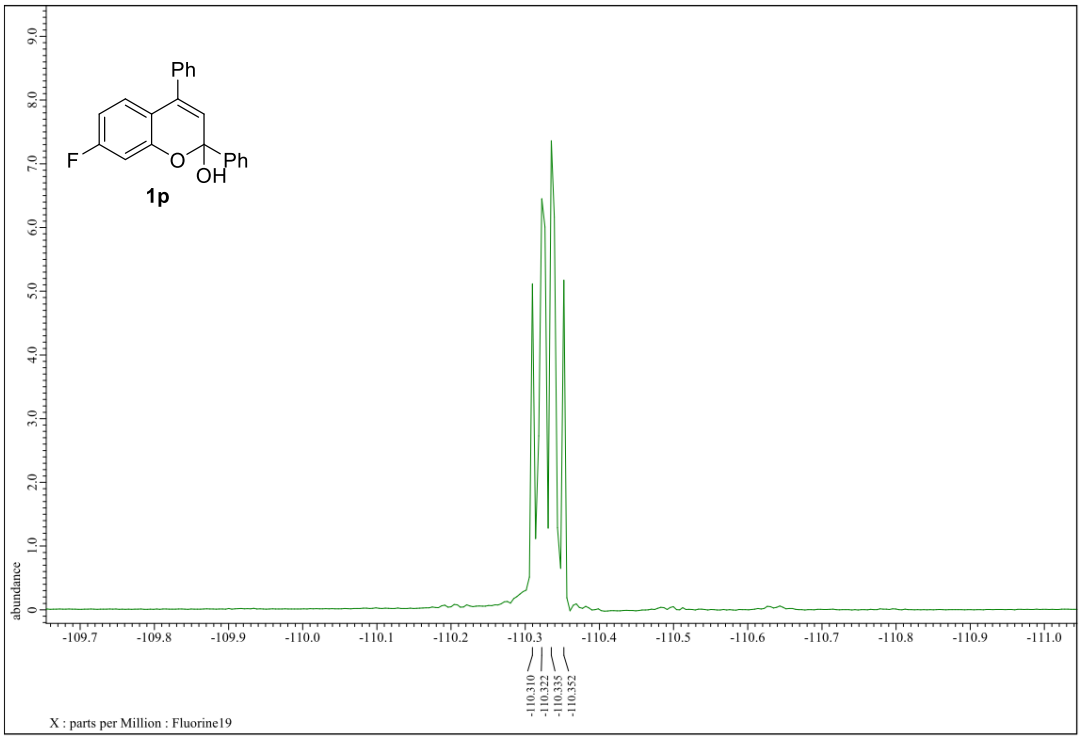


^{1}H NMR (600 MHz, C_6D_6) and ^{13}C NMR (151 MHz, C_6D_6) spectra of **1p**

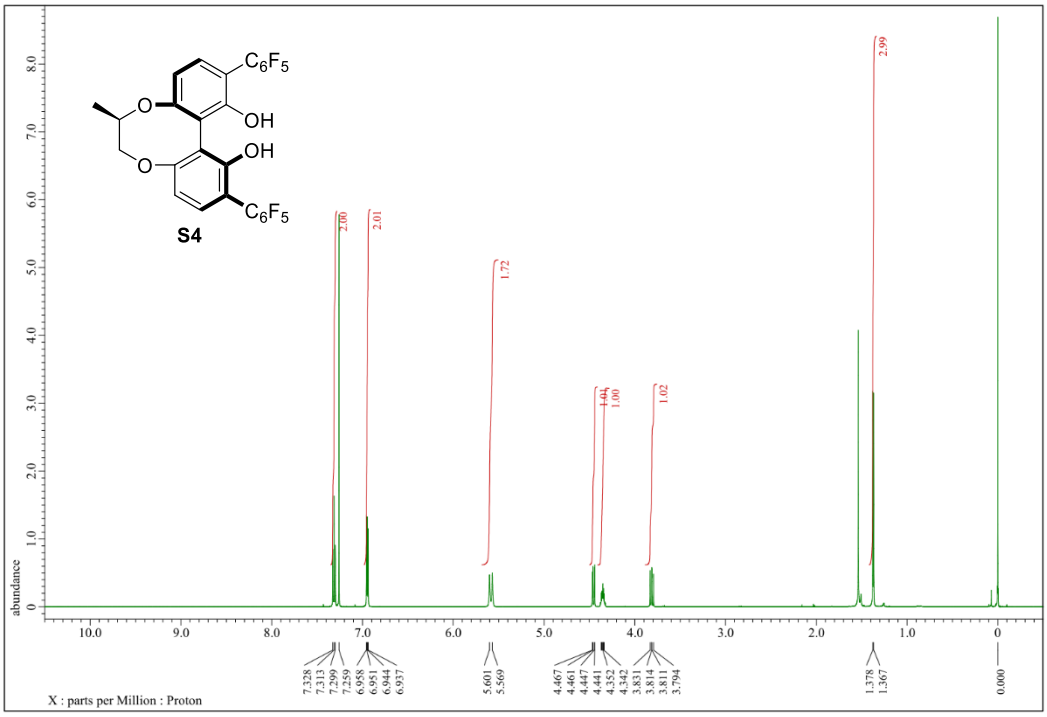


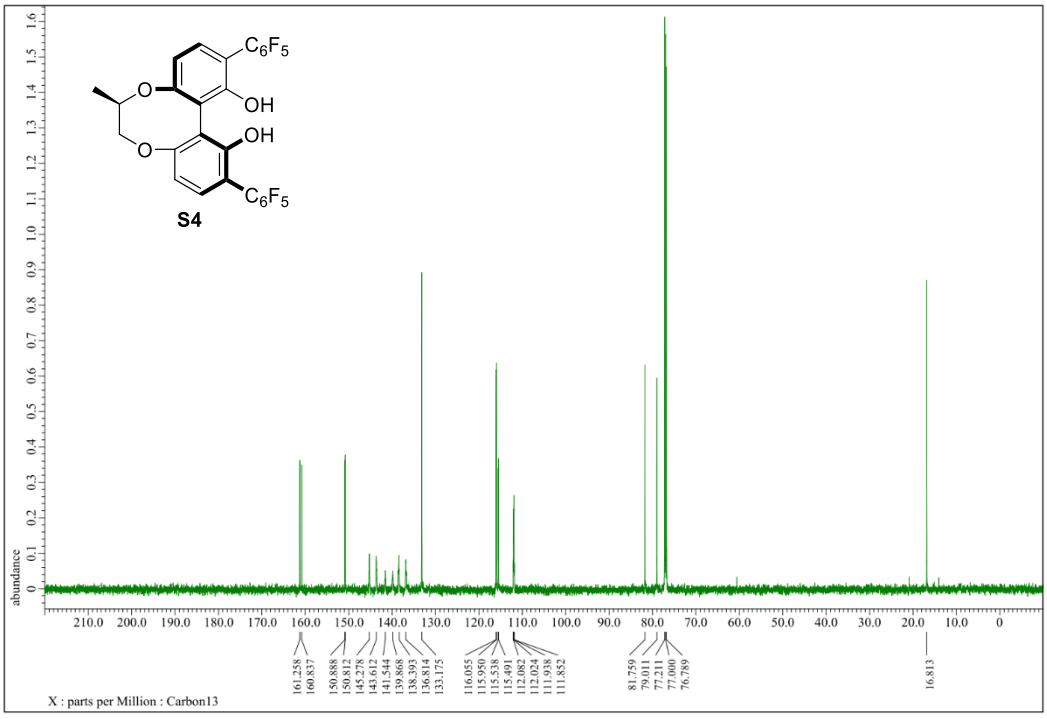


^{19}F NMR (565 MHz, $CDCl_3$) spectra of **1p**

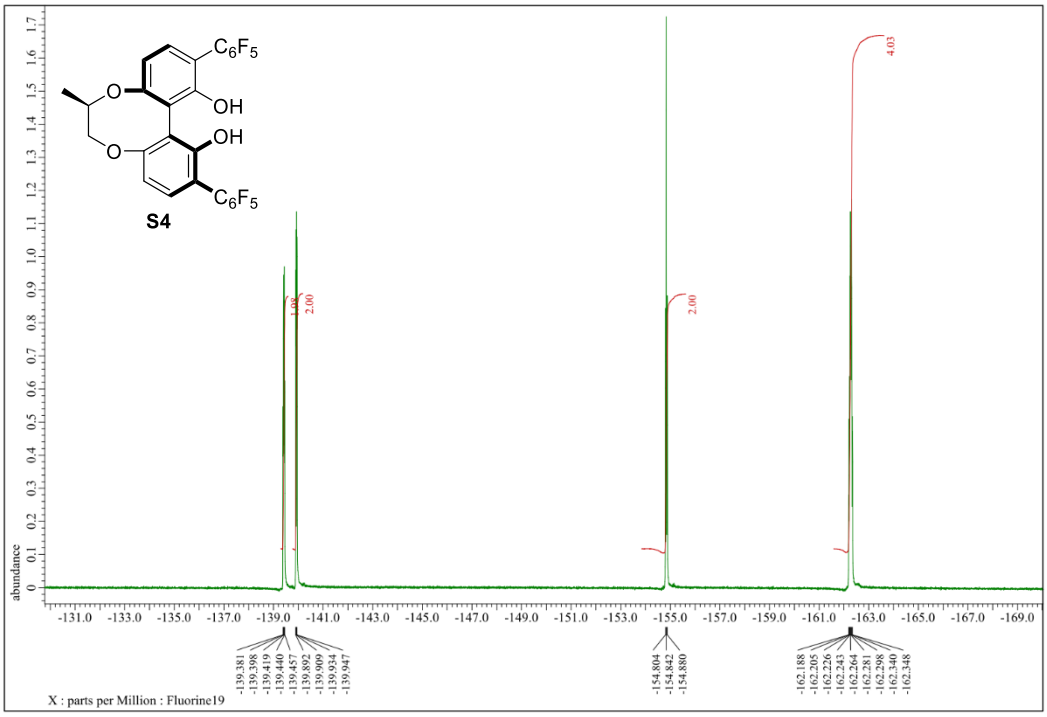


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **S4**

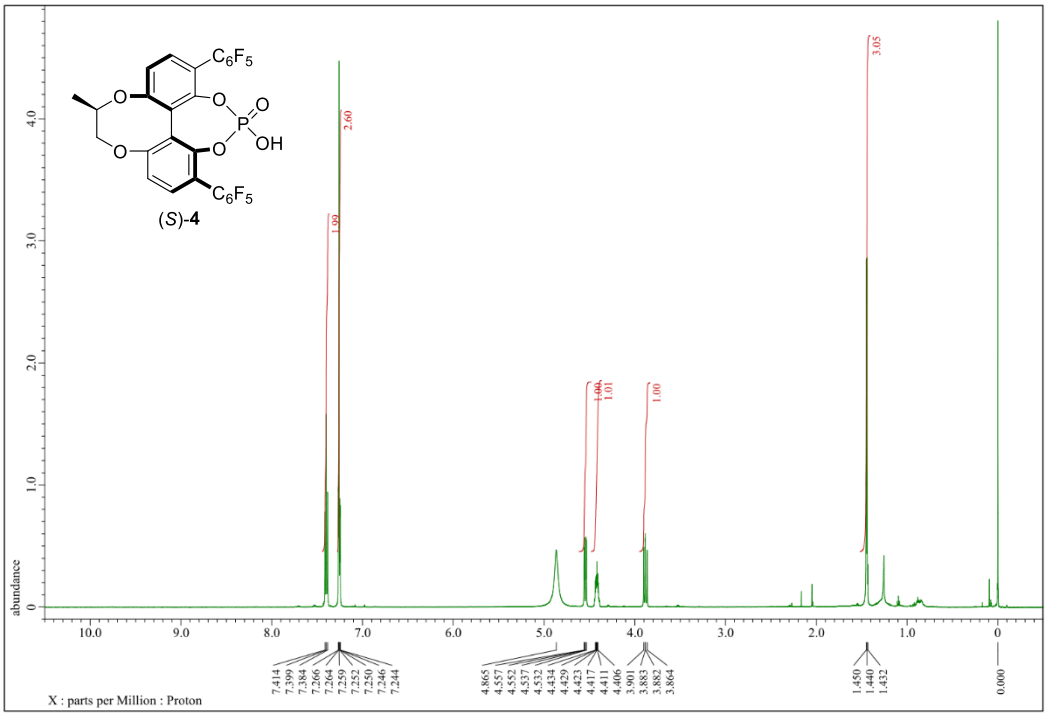


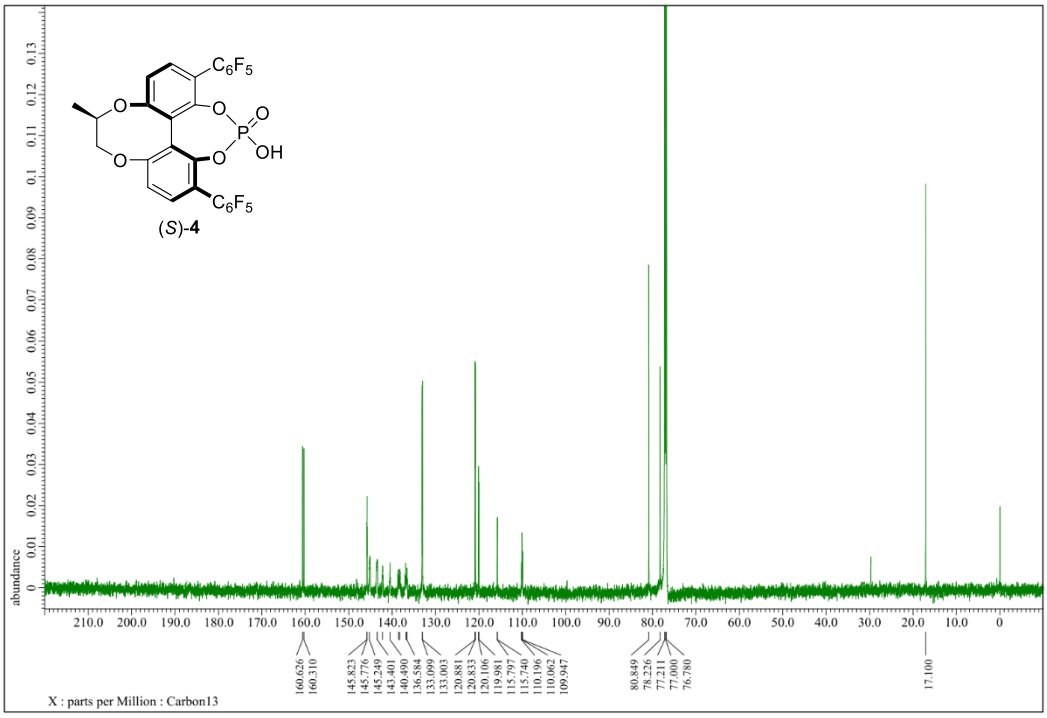


^{19}F NMR (565 MHz, $CDCl_3$) spectra of **S4**

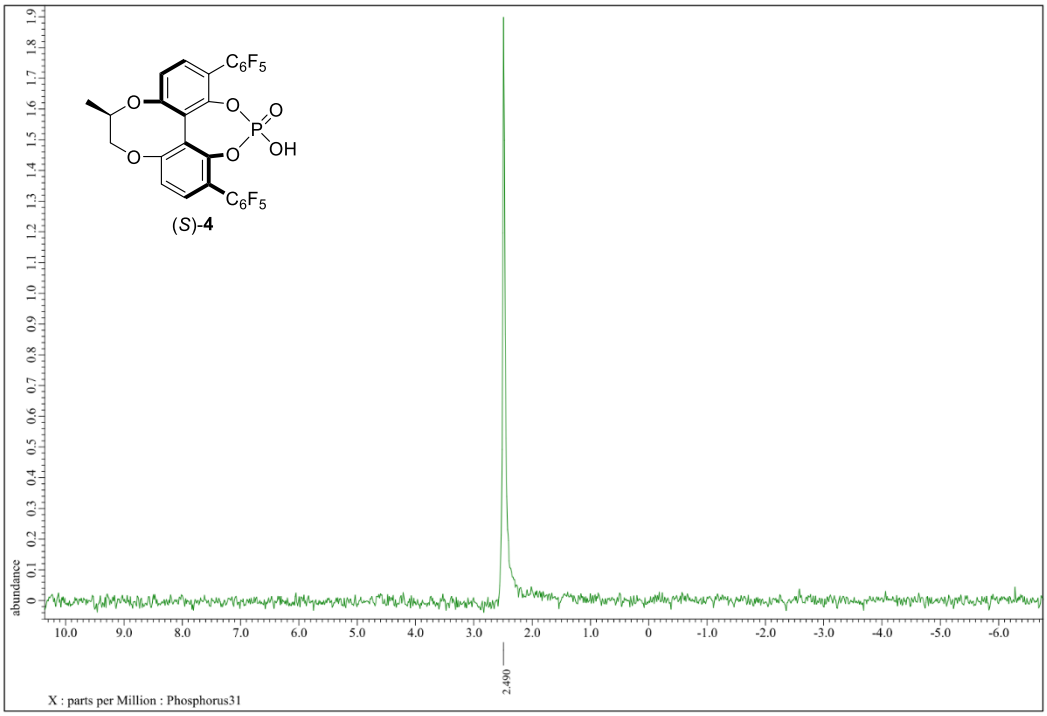


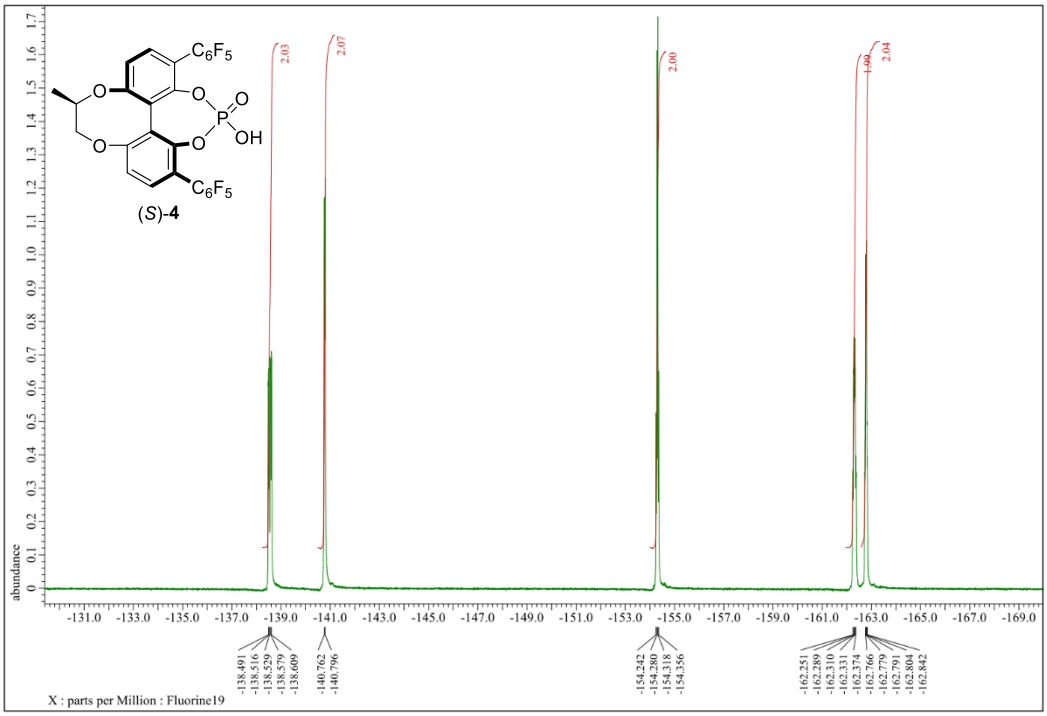
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of (*S*)-**4**



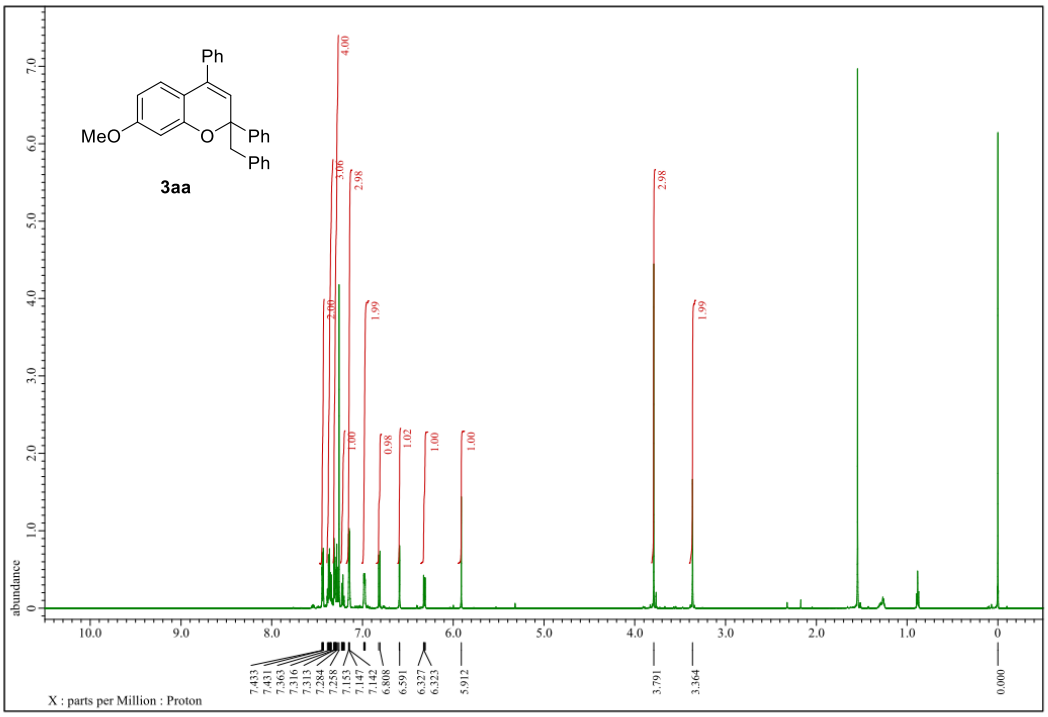


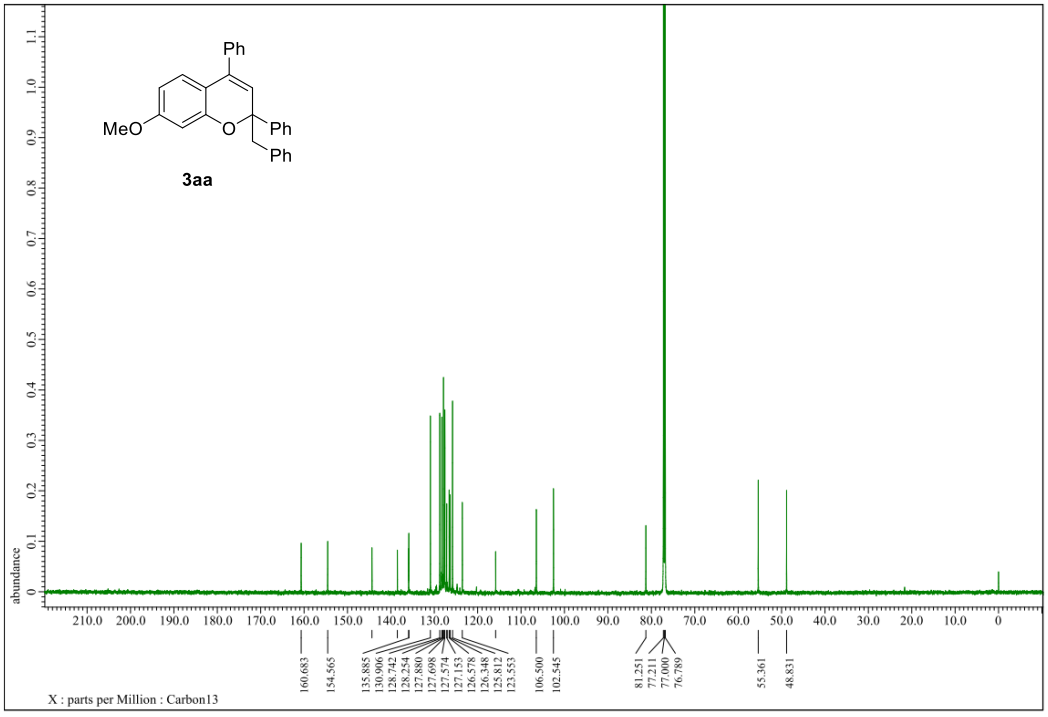
^{31}P NMR (243 MHz, $CDCl_3$) and ^{19}F NMR (565 MHz, $CDCl_3$) spectra of (*S*)-**4**



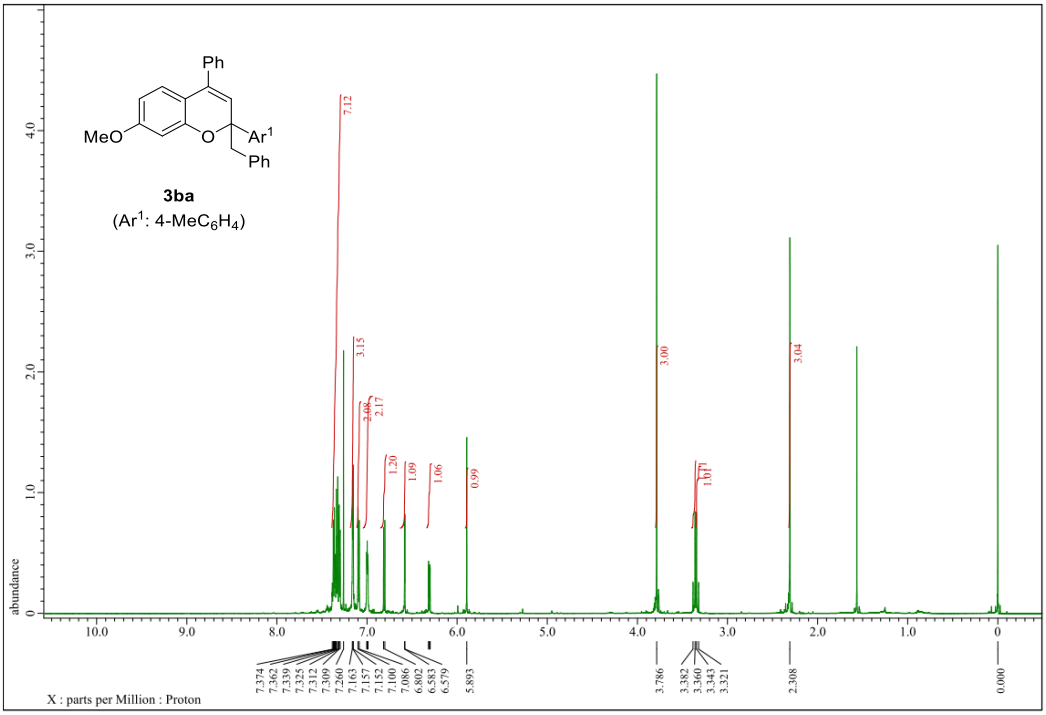


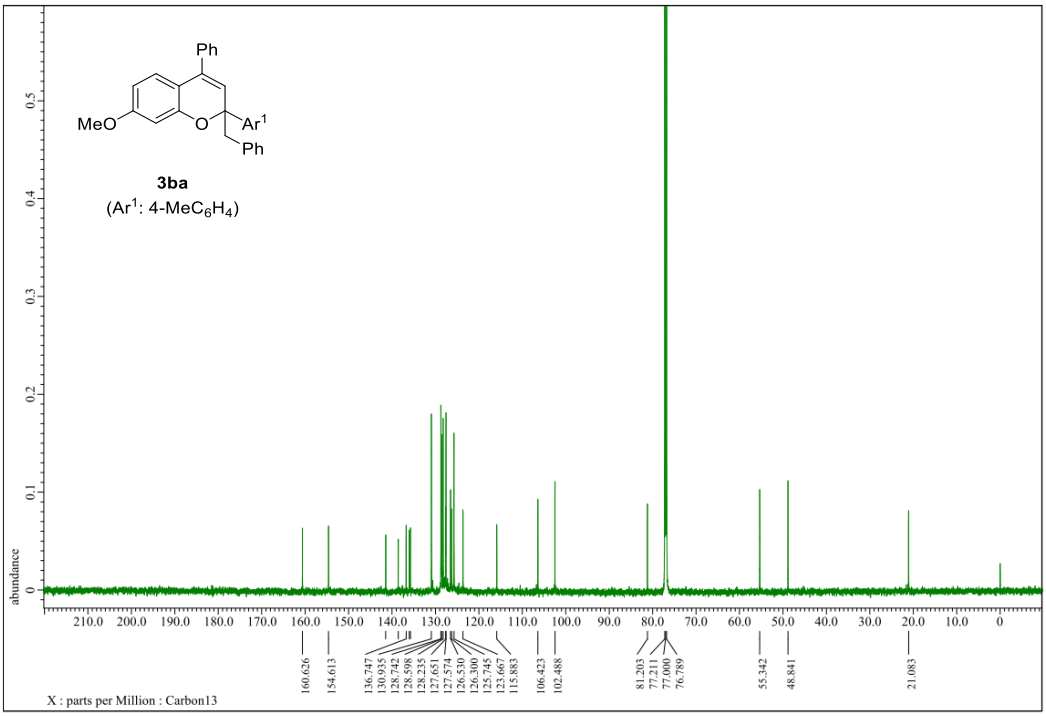
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3aa**



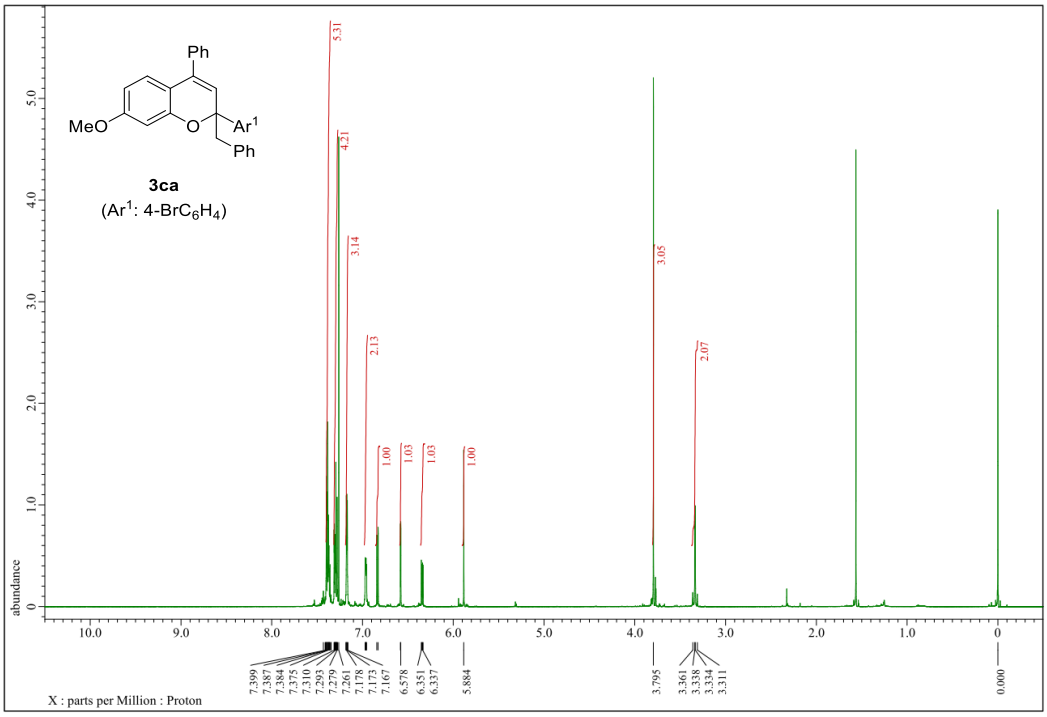


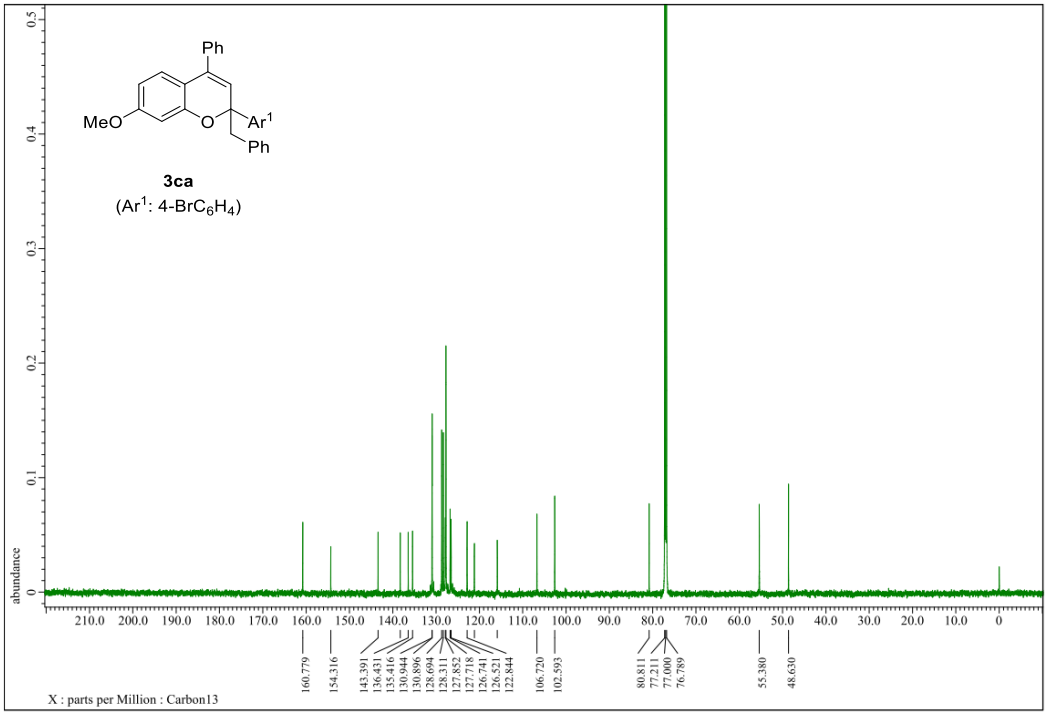
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3ba**



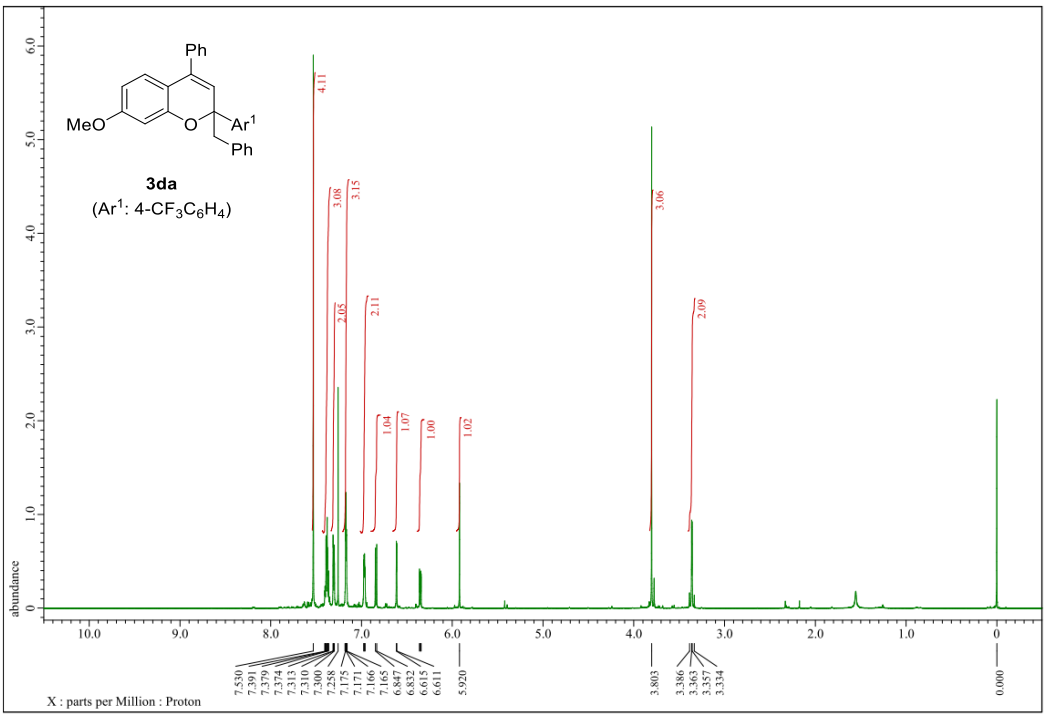


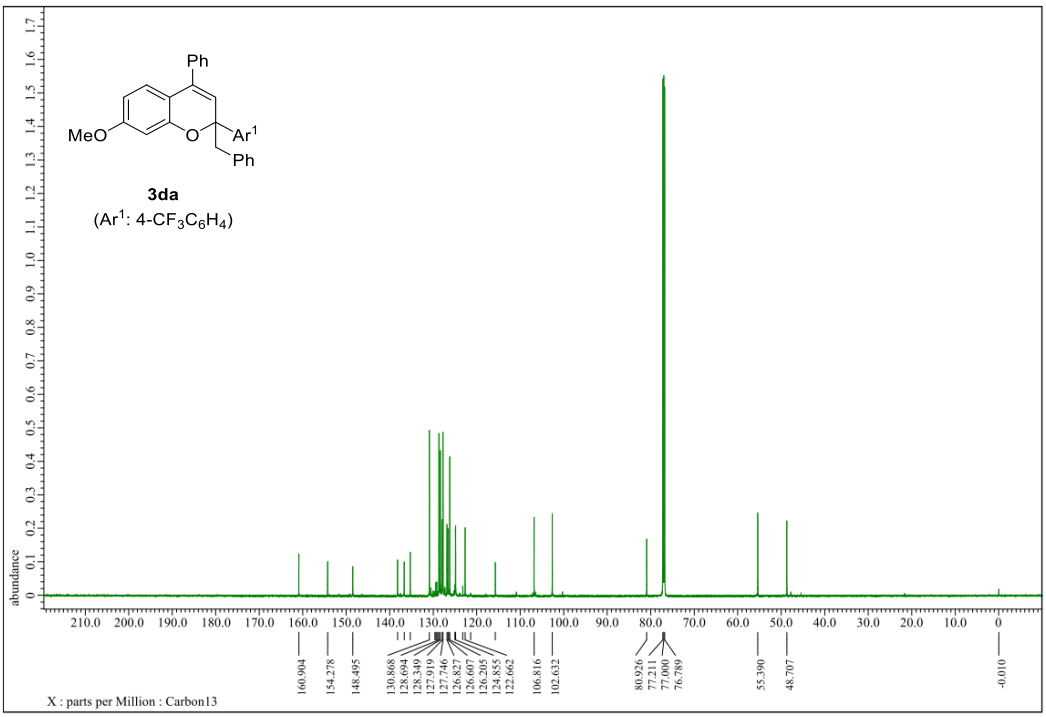
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3ca**



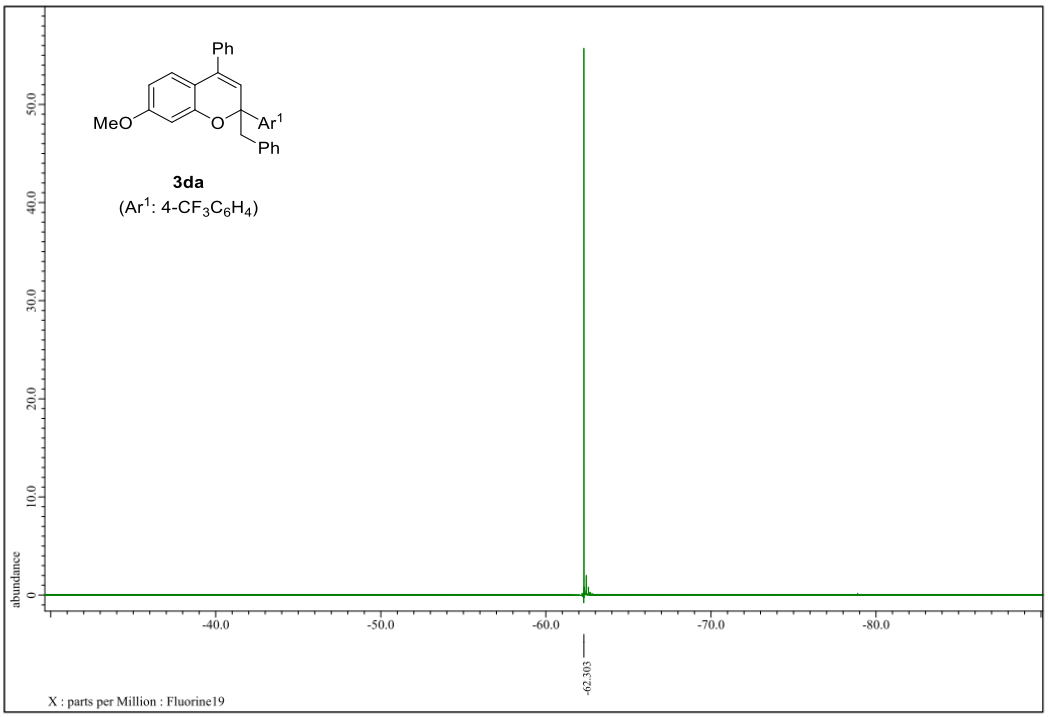


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3da**

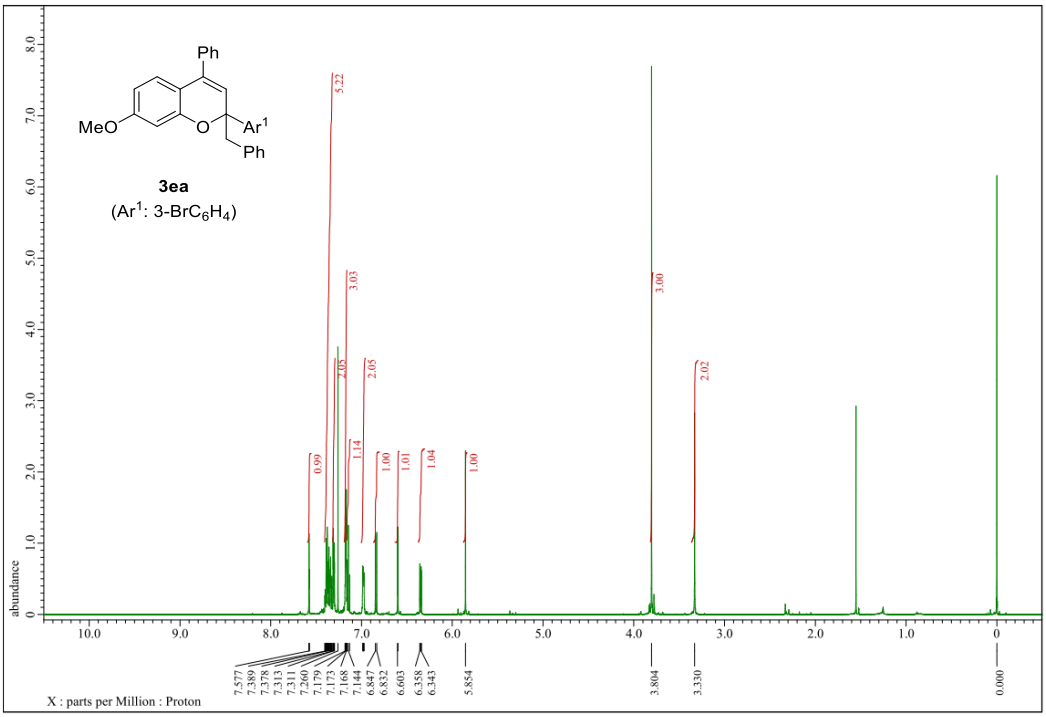


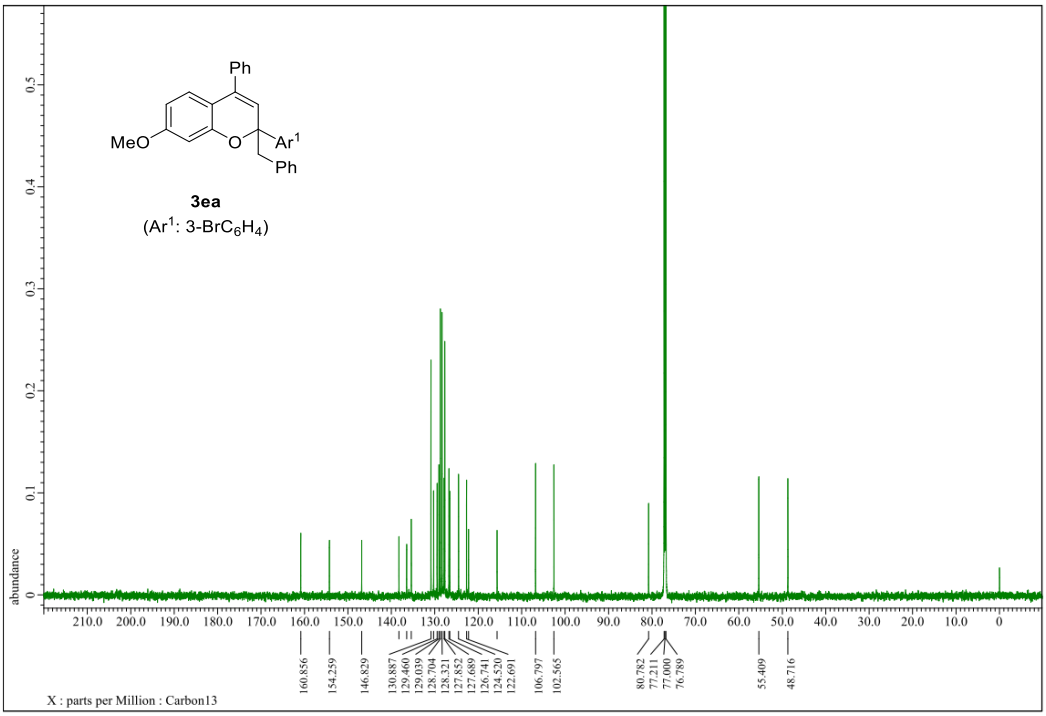


^{19}F NMR (565 MHz, $CDCl_3$) spectra of **3da**

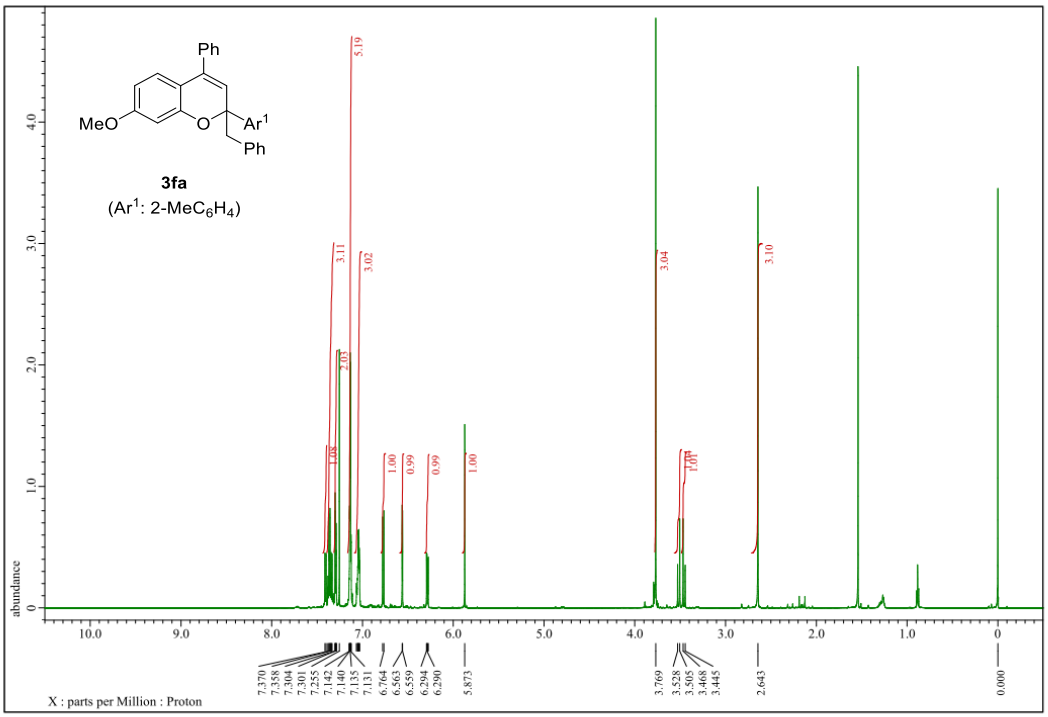


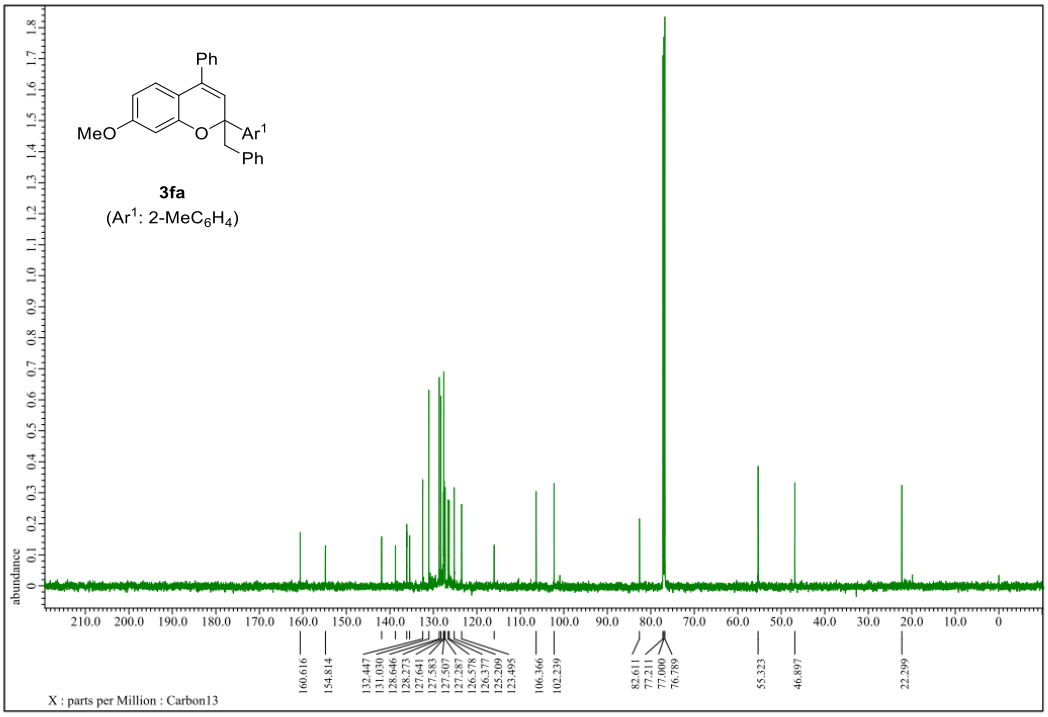
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3ea**



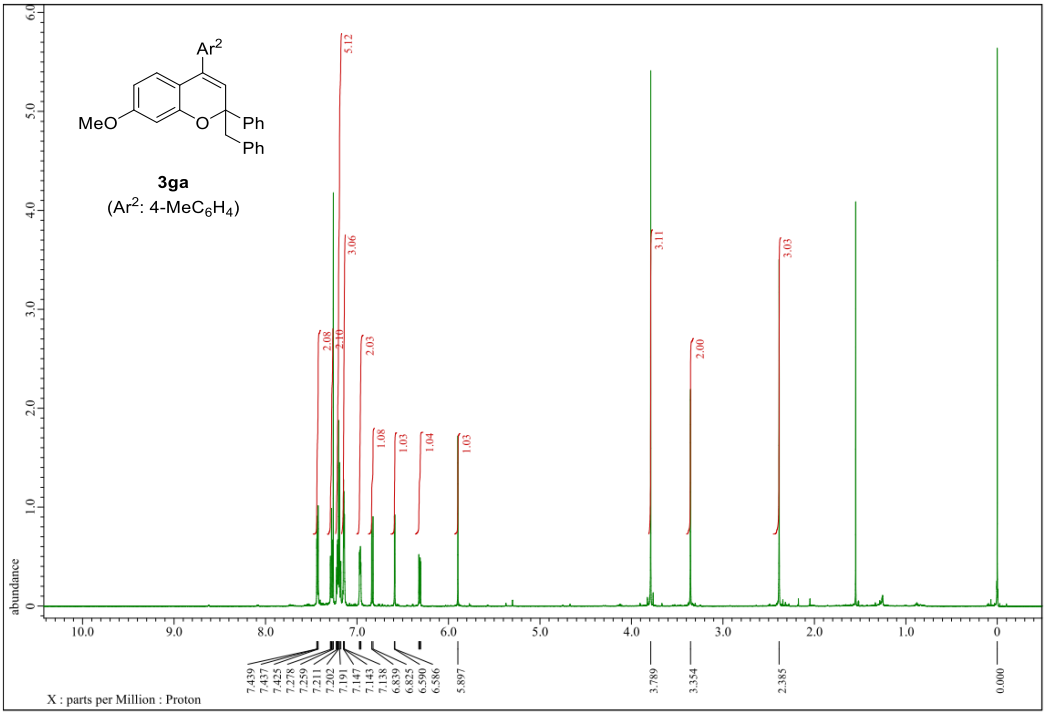


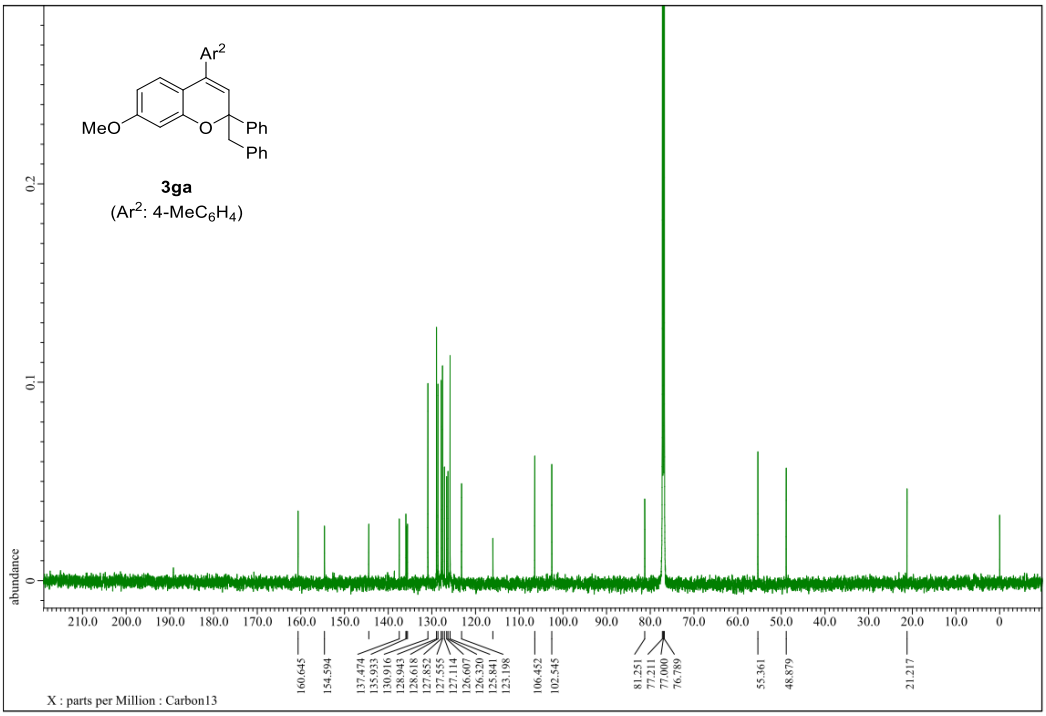
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3fa**



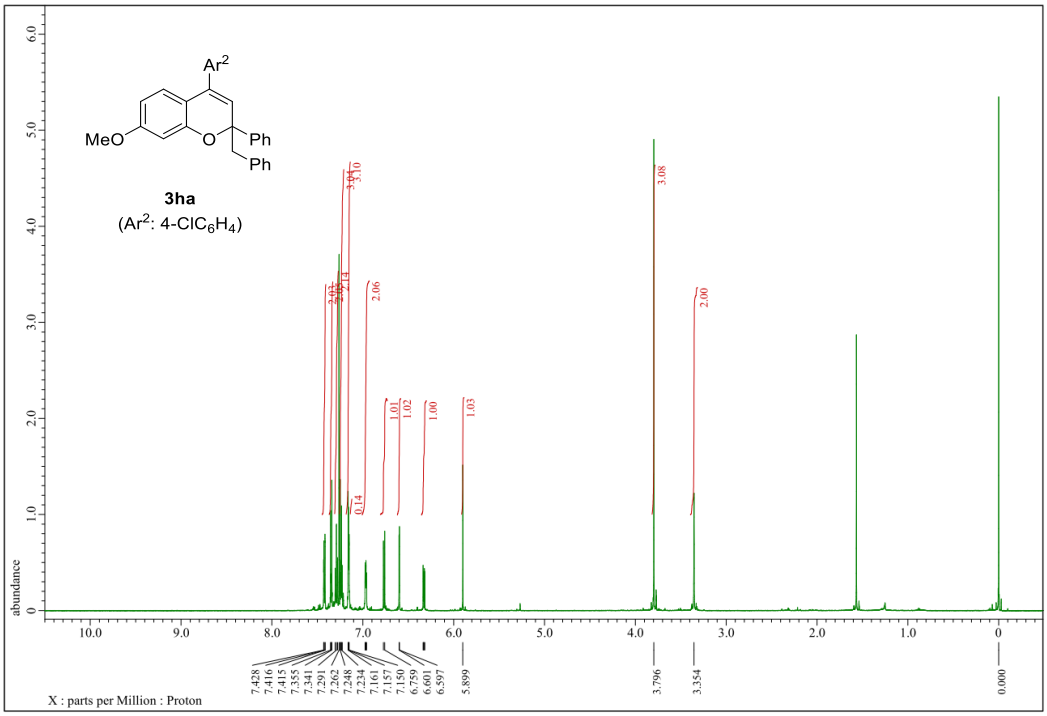


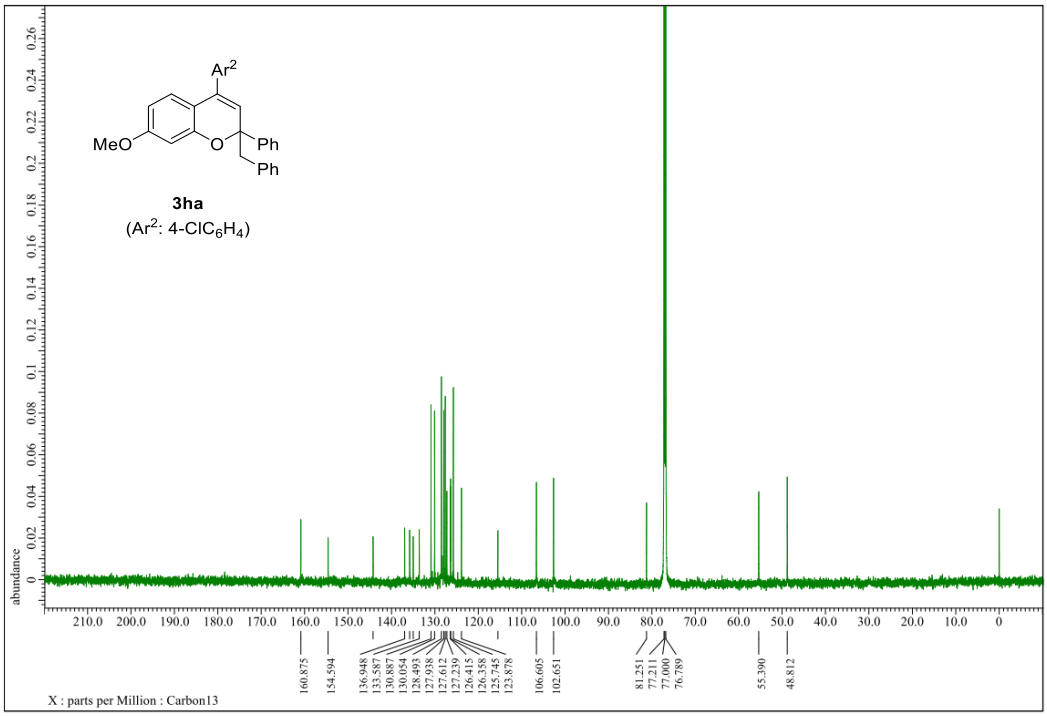
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3ga**



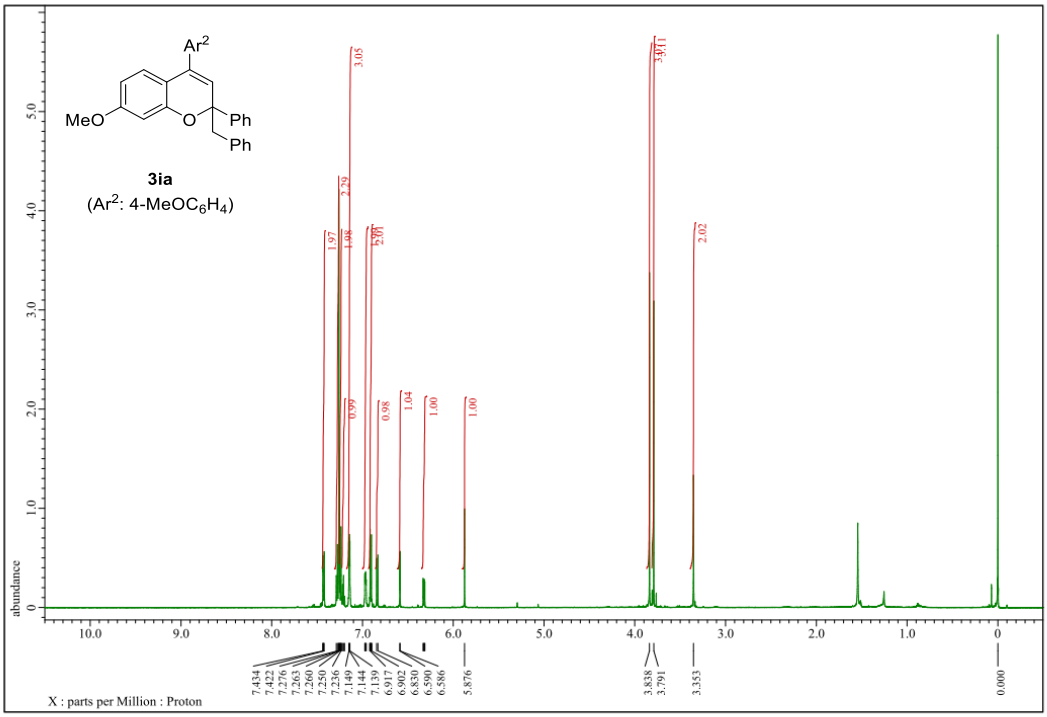


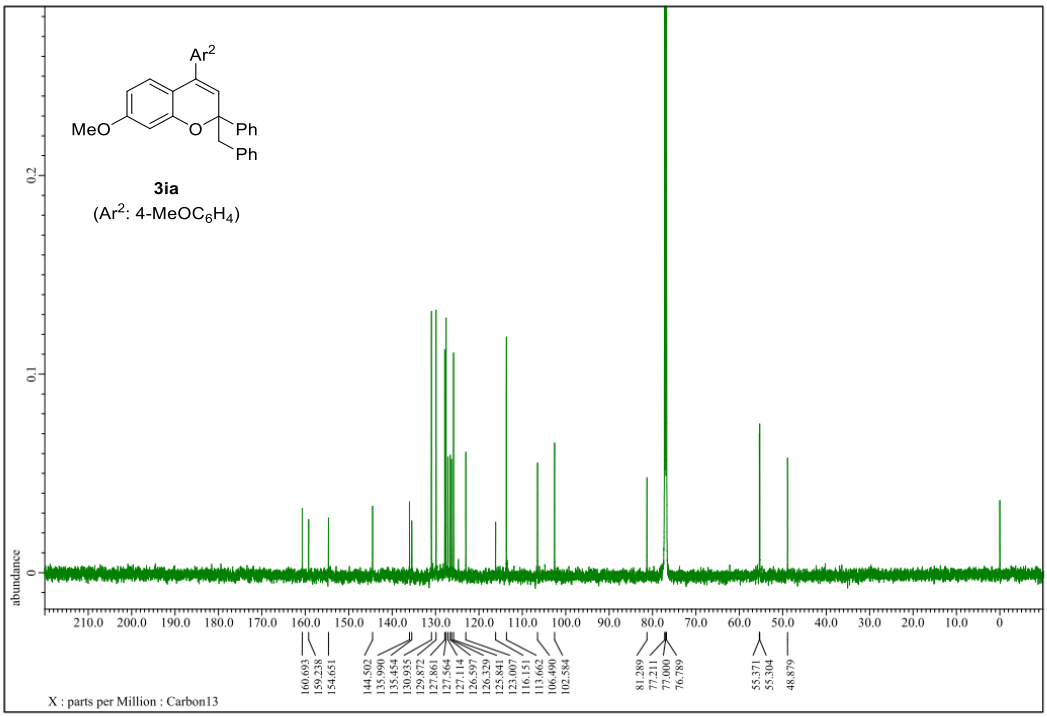
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3ha**



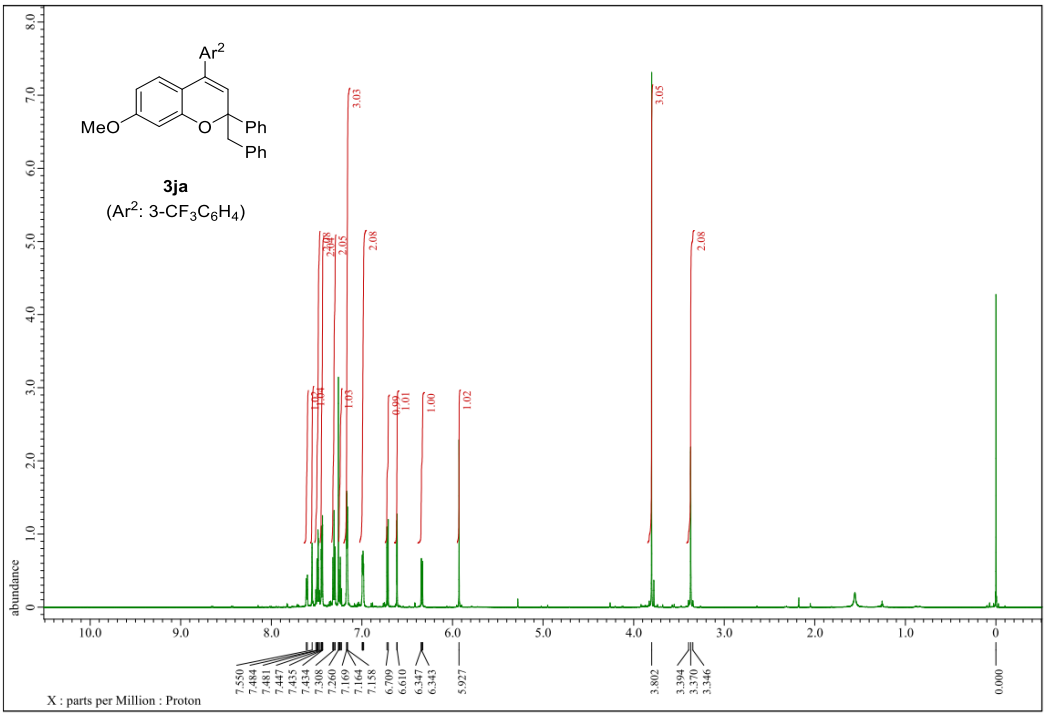


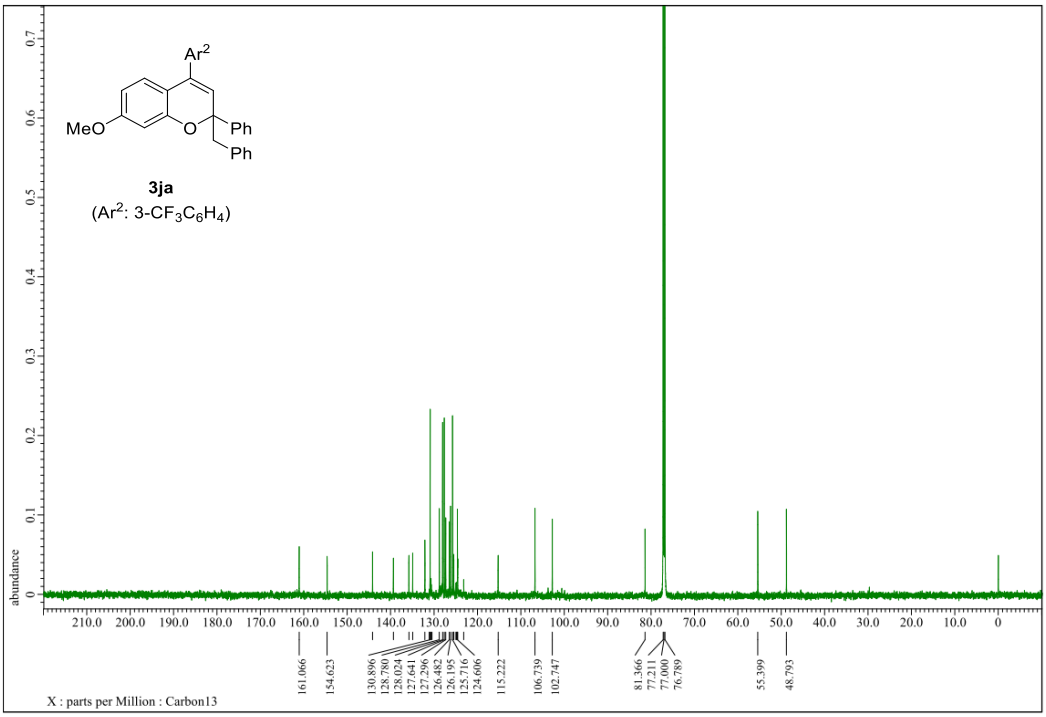
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3ia**



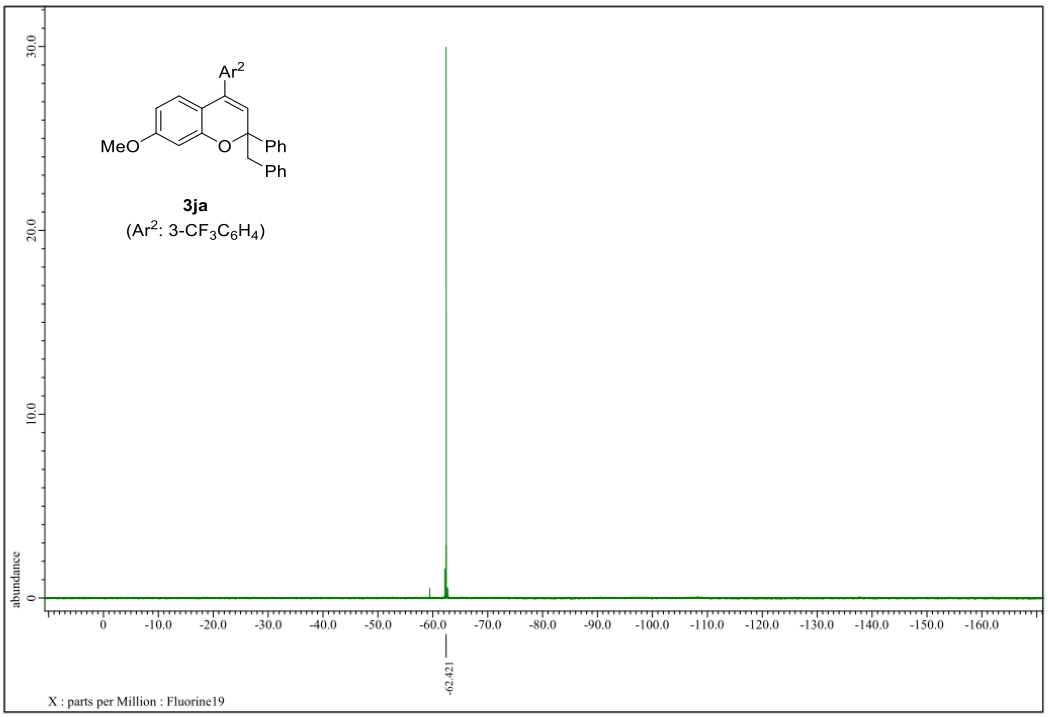


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3ja**

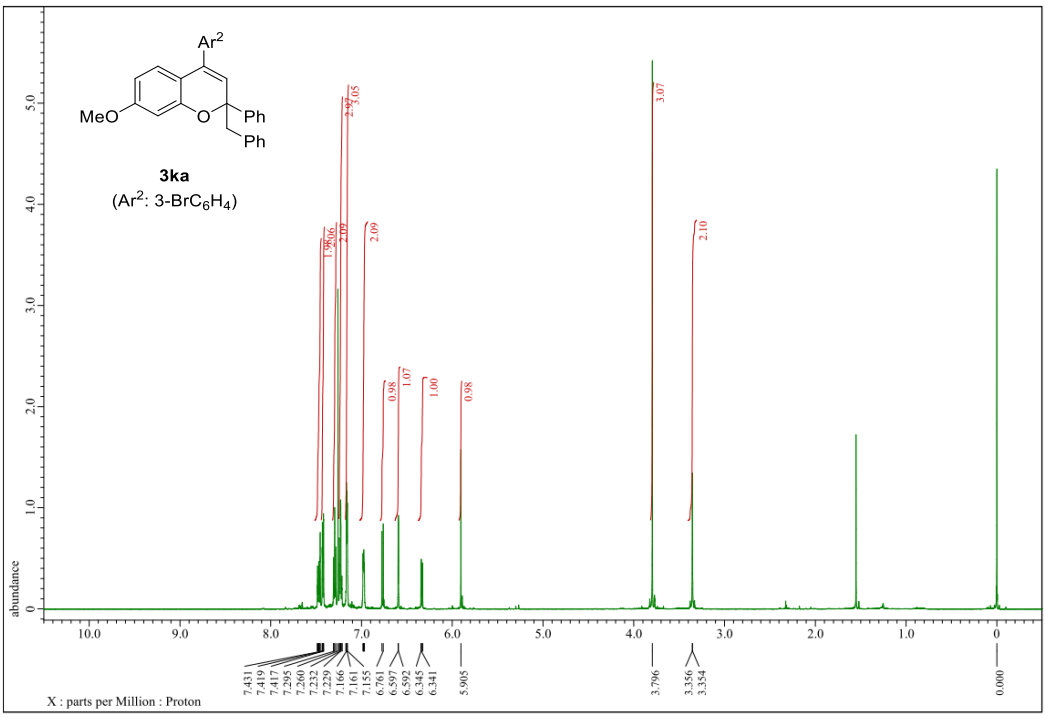


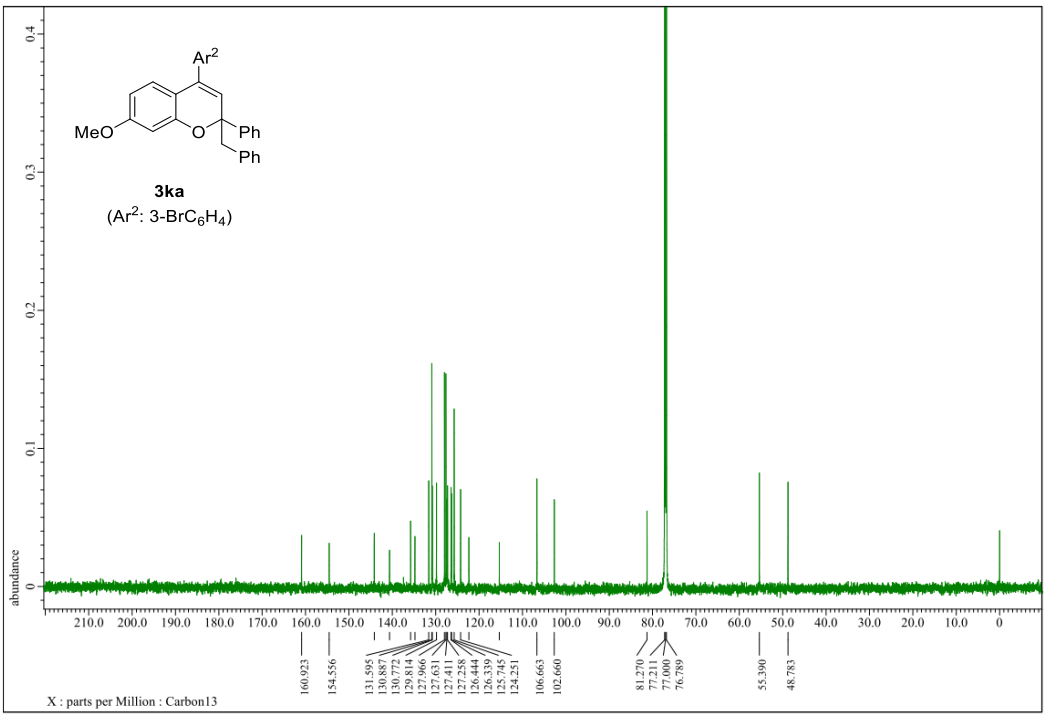


^{19}F NMR (565 MHz, $CDCl_3$) spectra of **3ja**

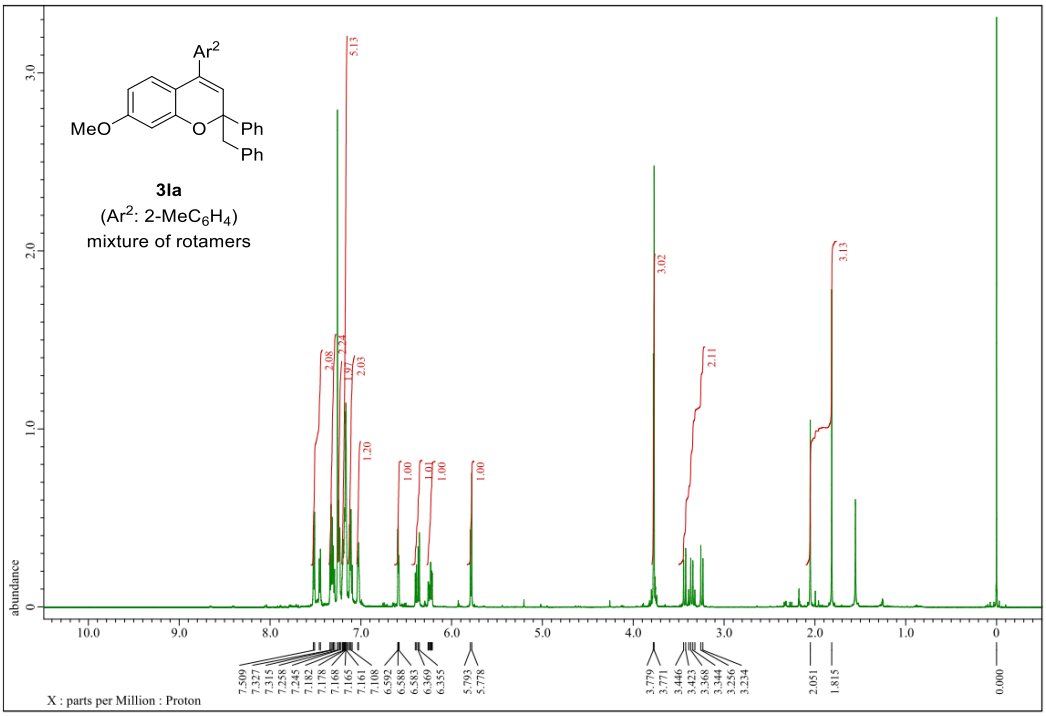


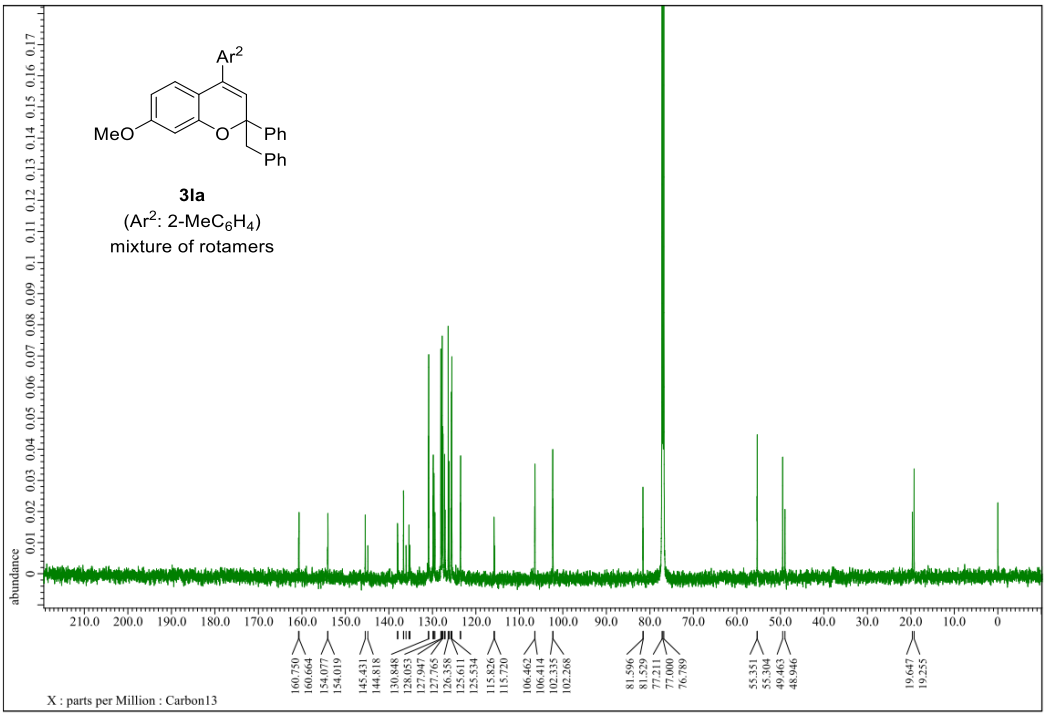
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3ka**



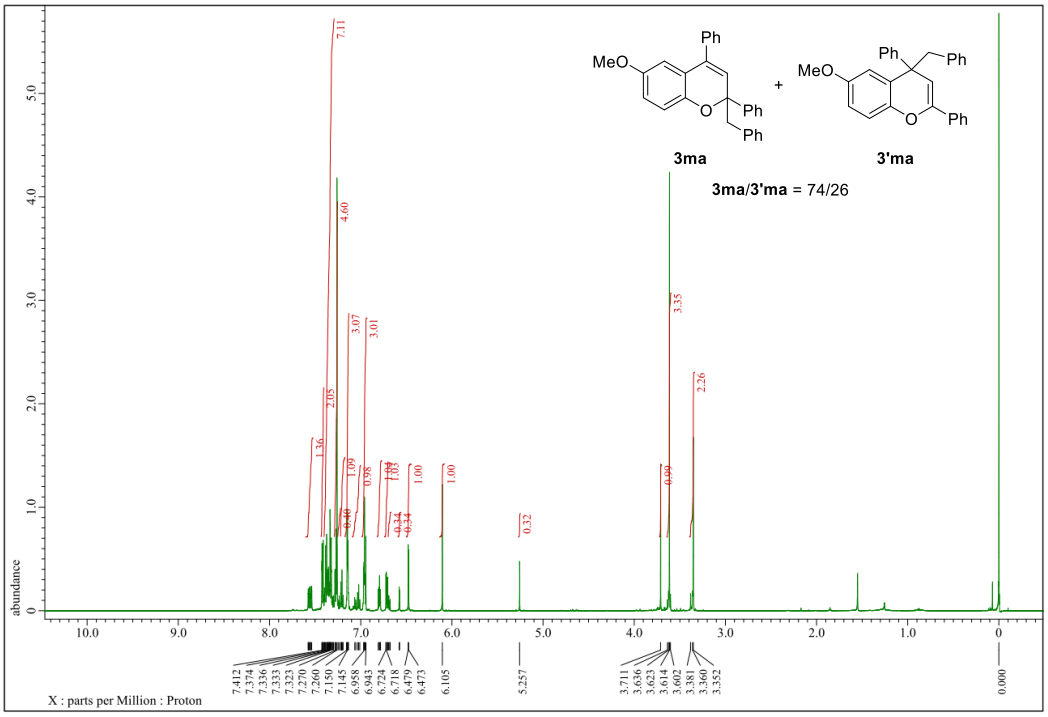


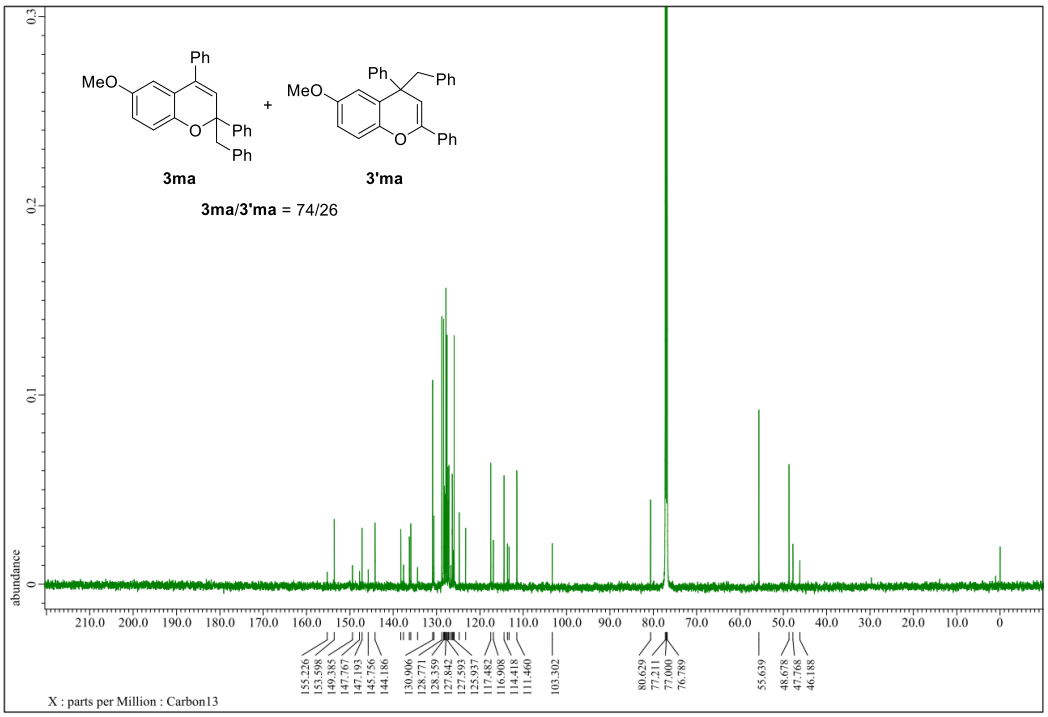
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3la**



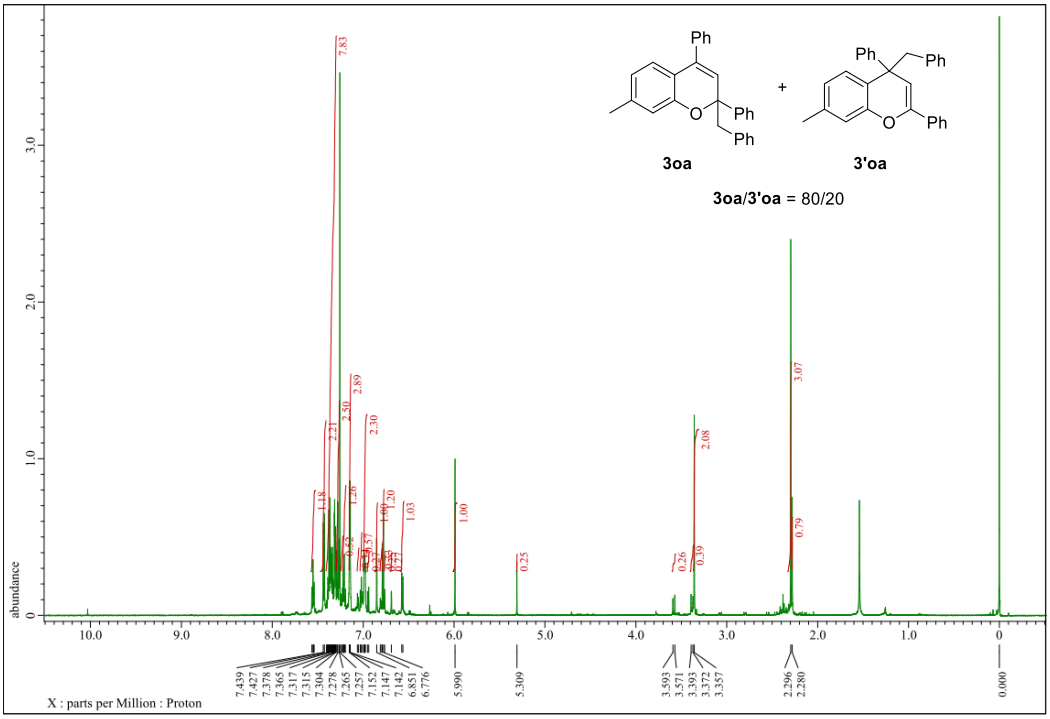


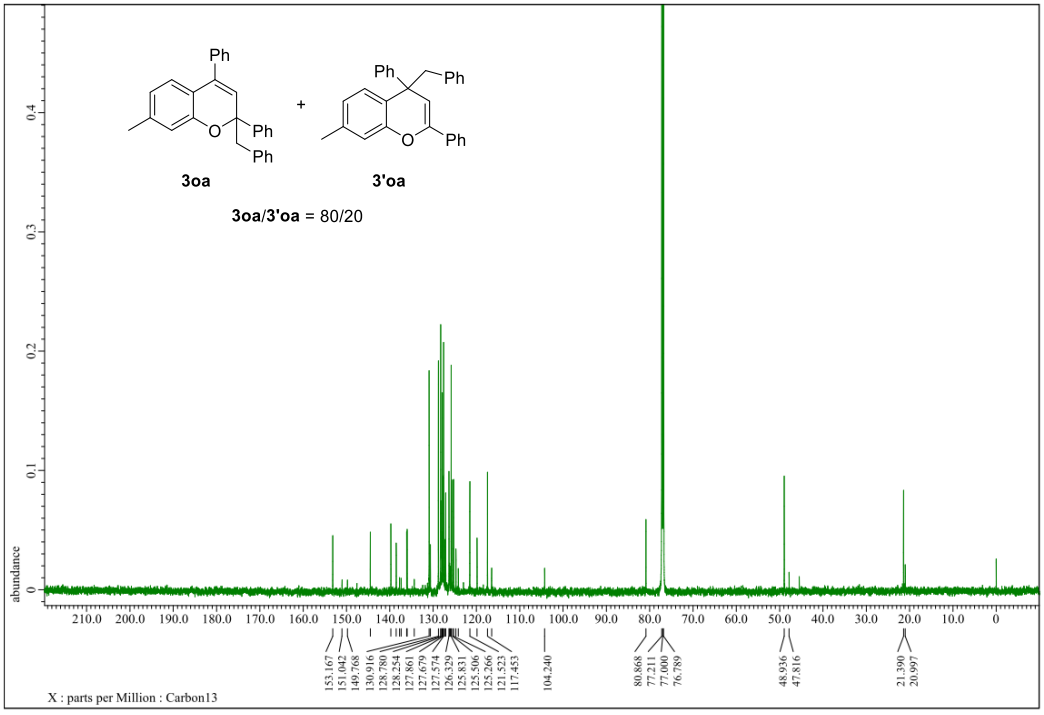
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3ma** and **3'ma**



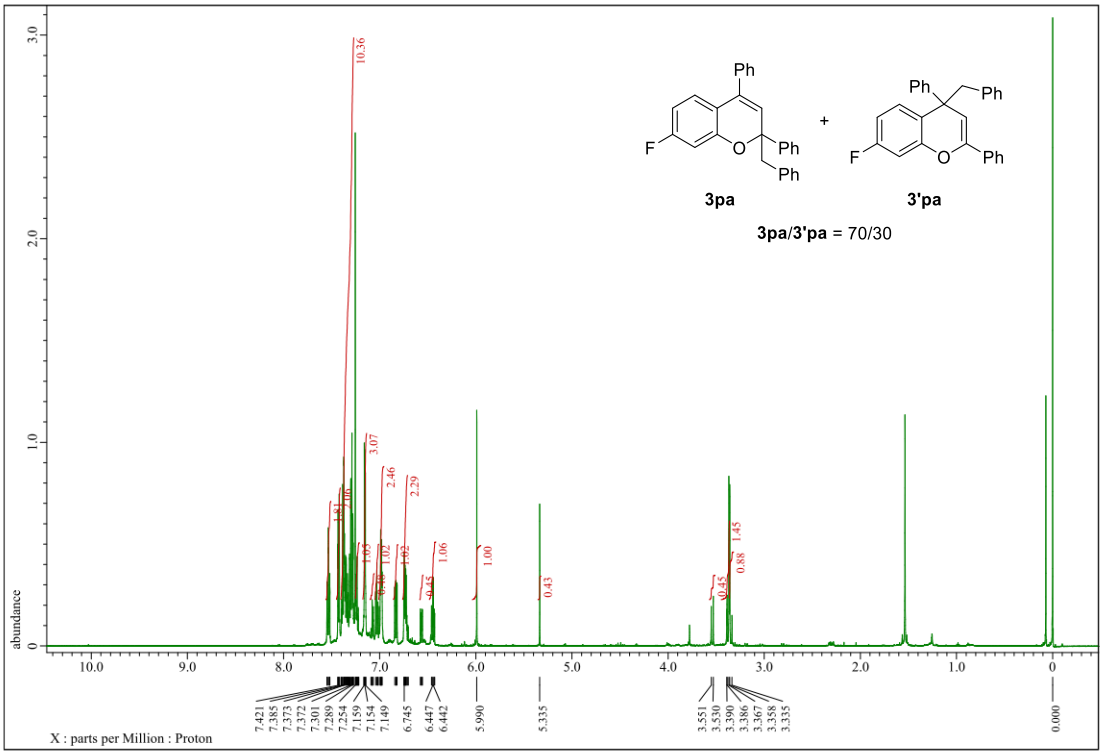


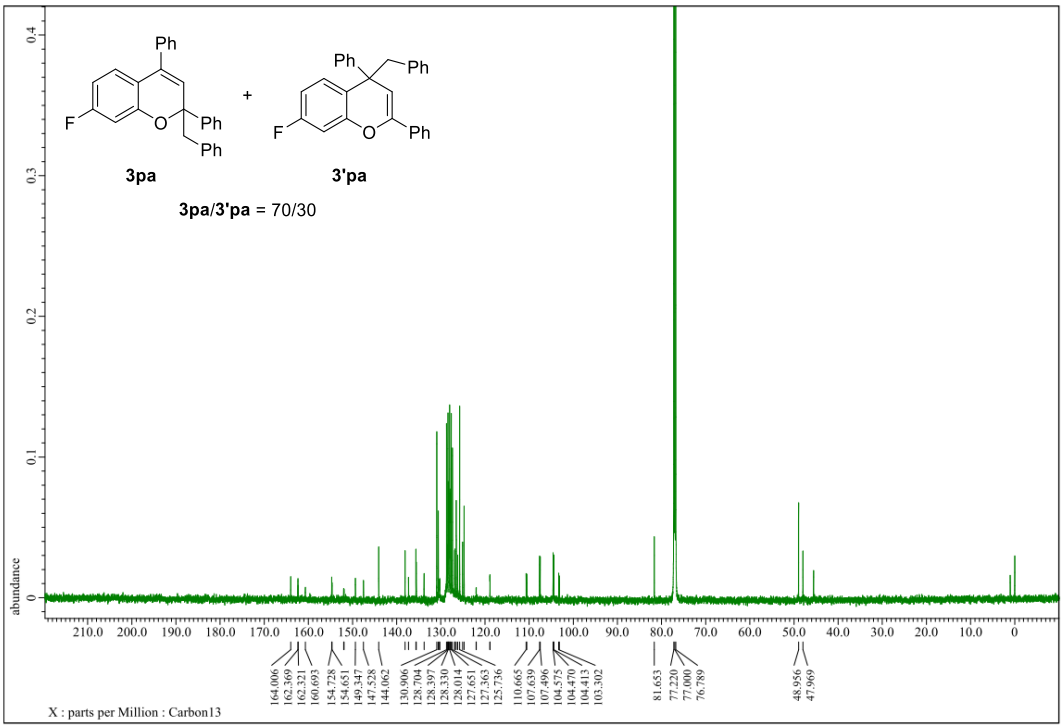
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3oa** and **3'oa**



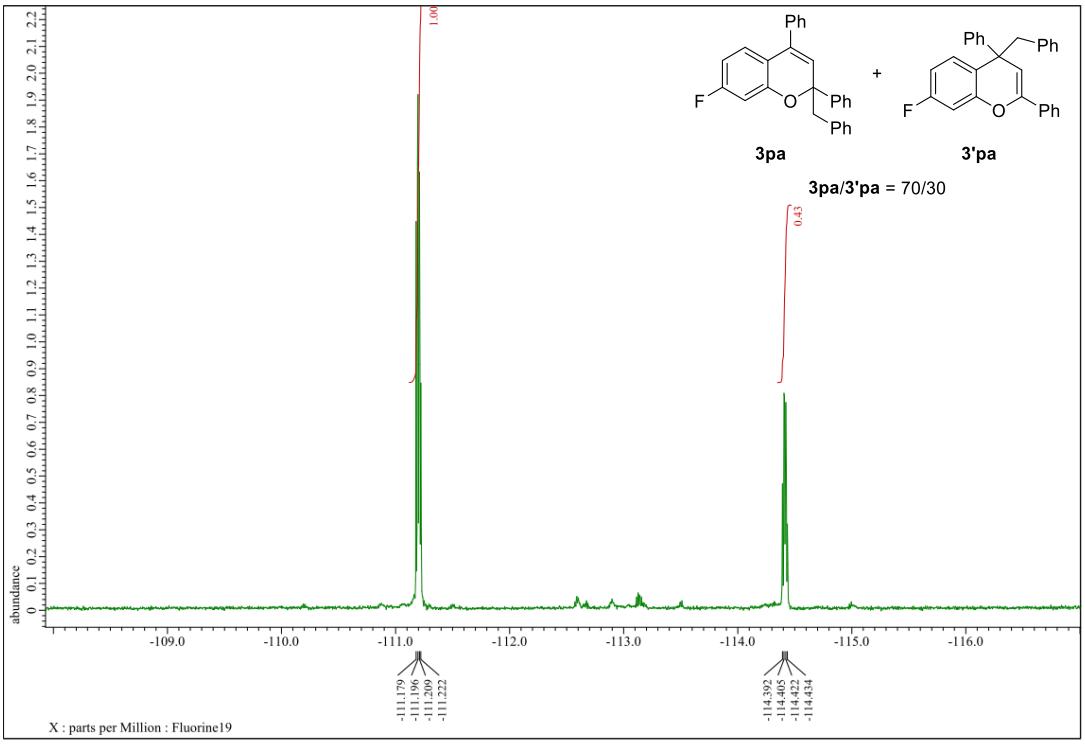


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3pa** and **3'pa**

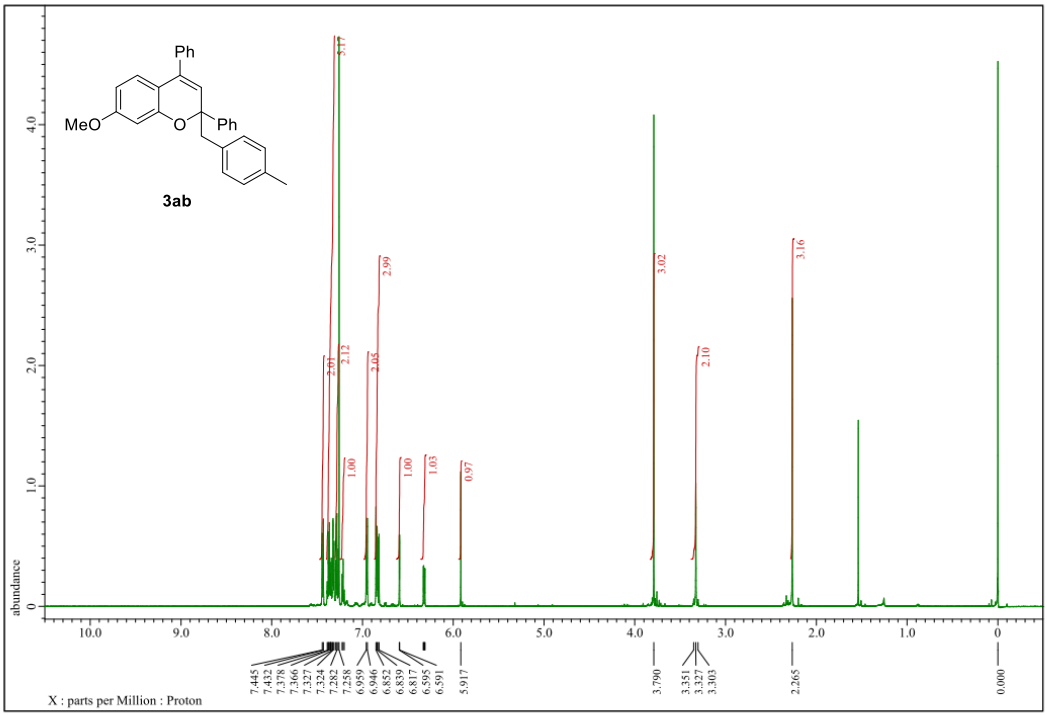


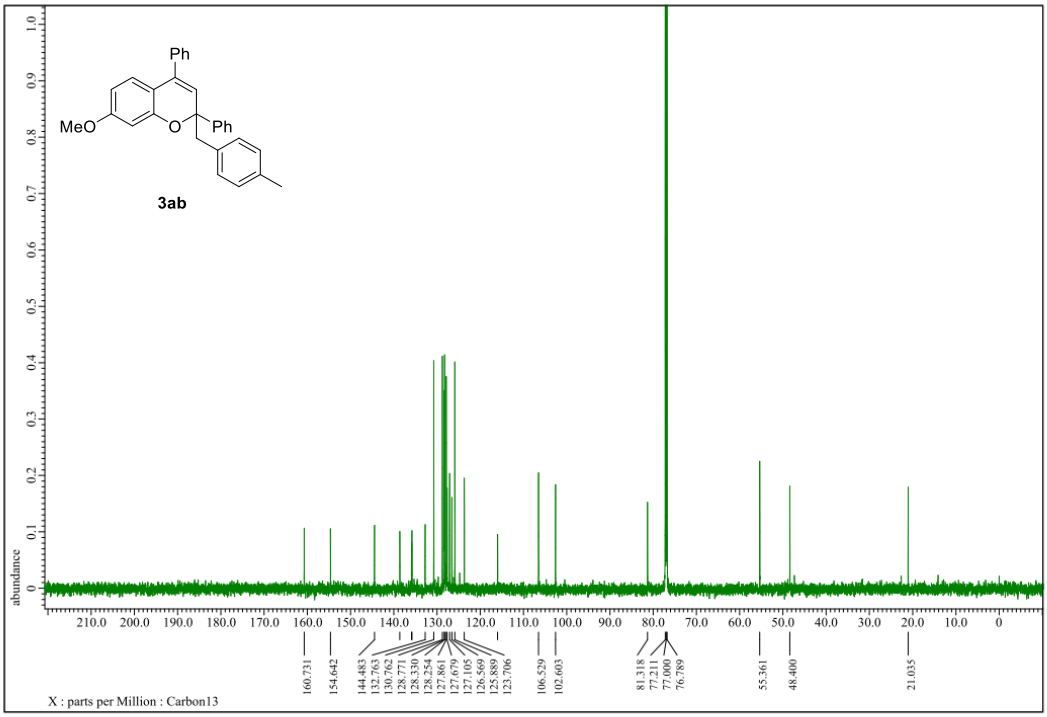


^{19}F NMR (565 MHz, $CDCl_3$) spectra of **3pa** and **3'pa**

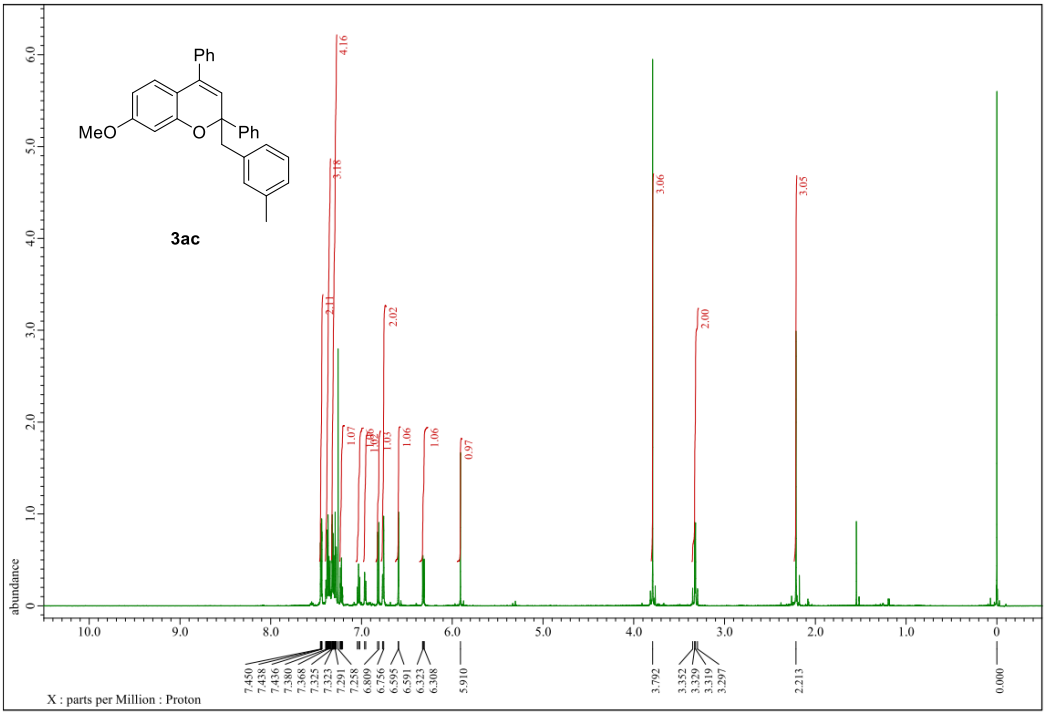


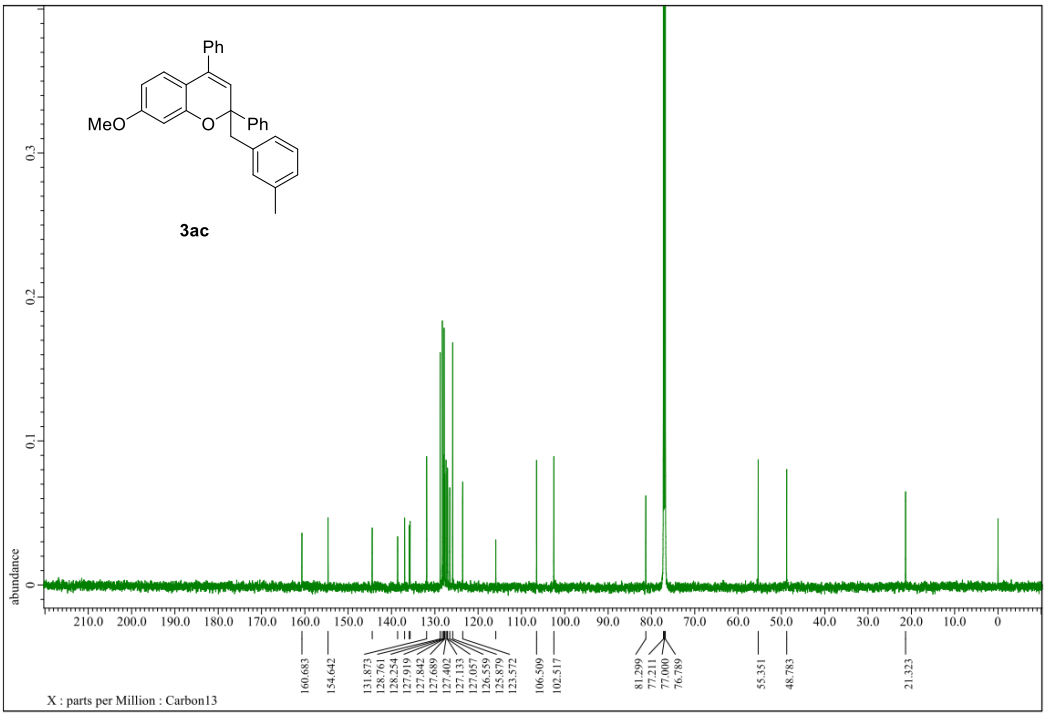
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3ab**



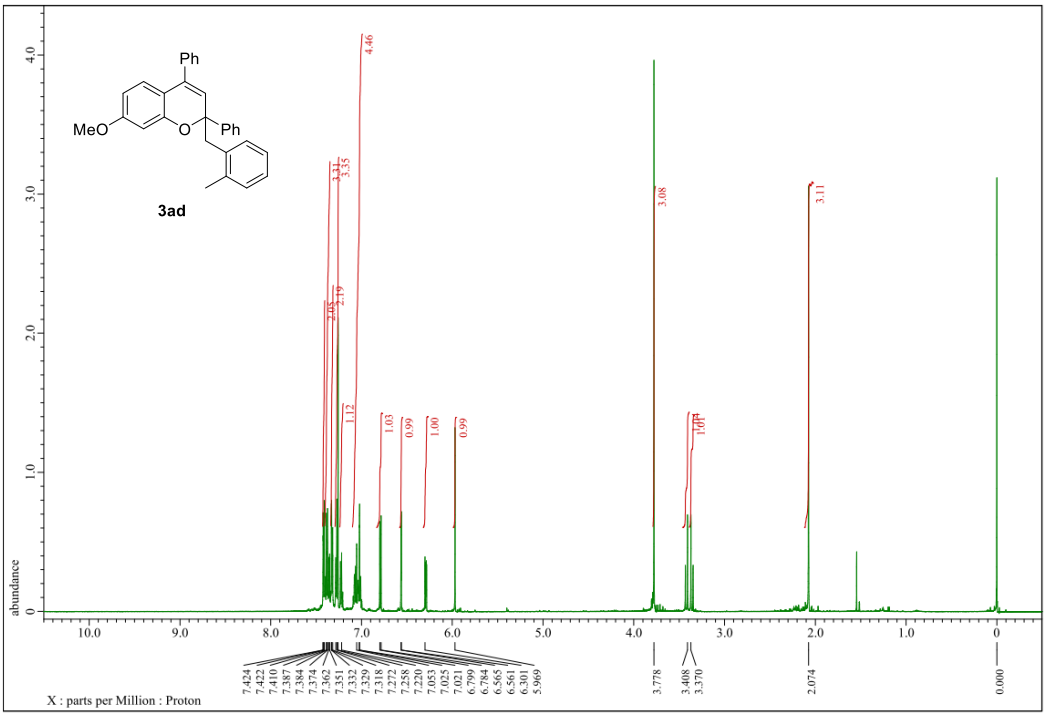


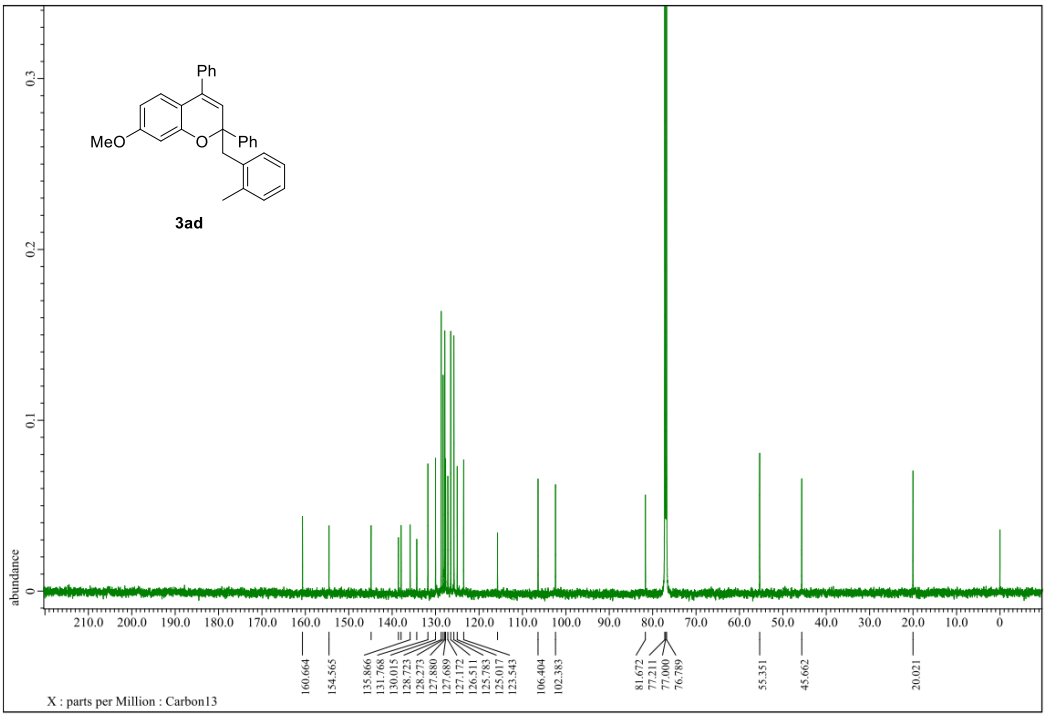
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3ac**



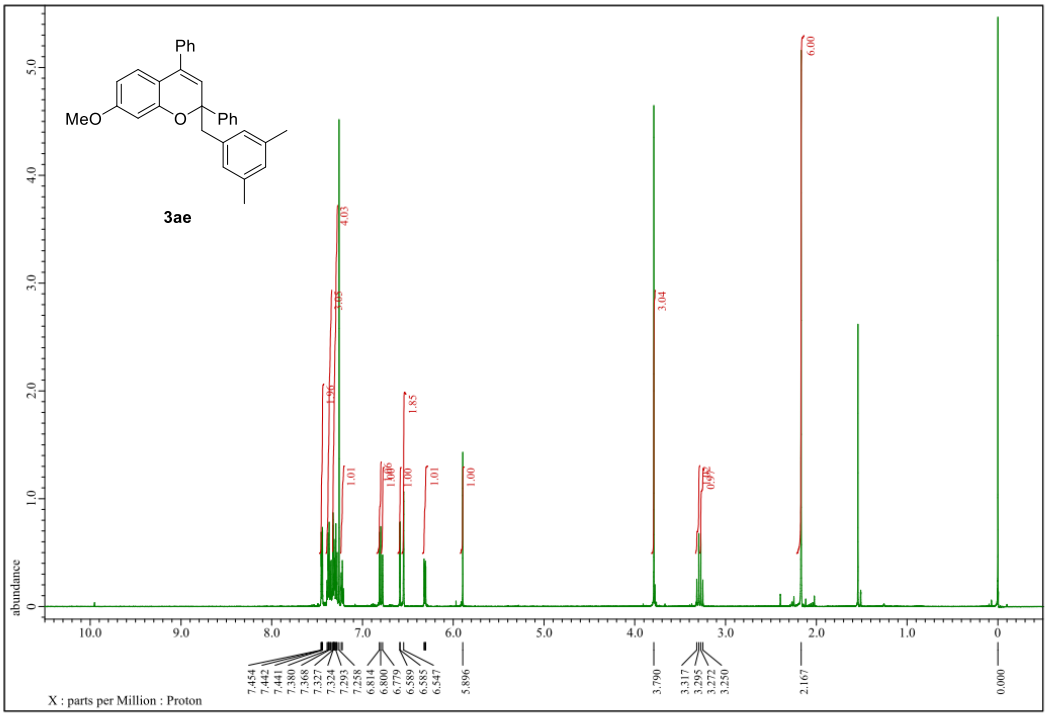


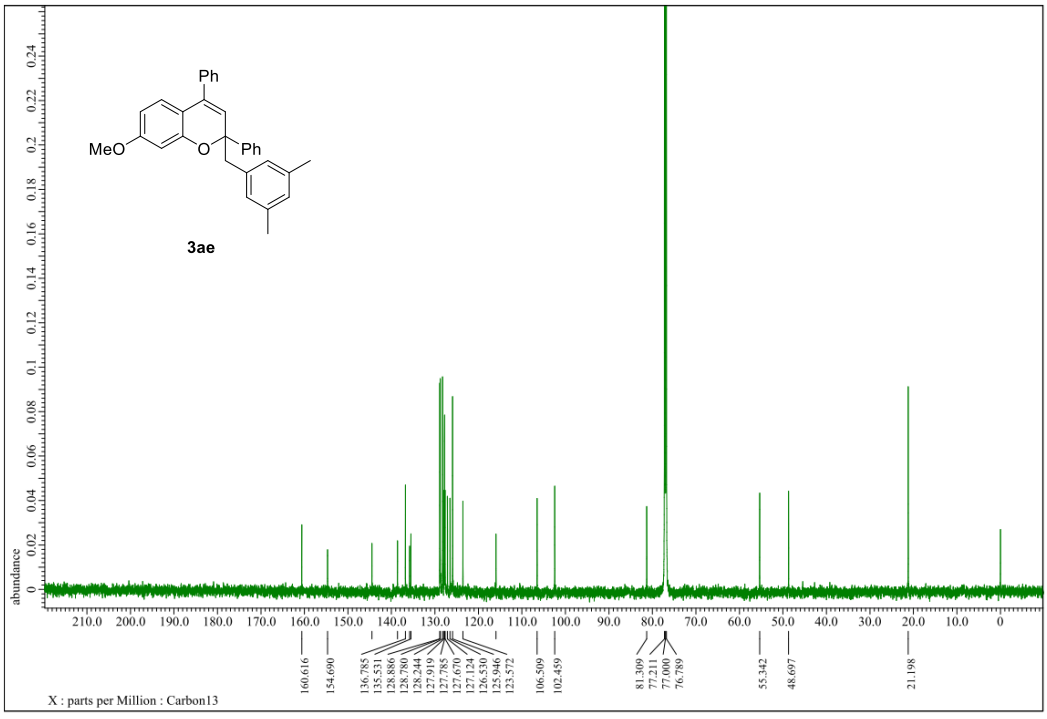
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3ad**



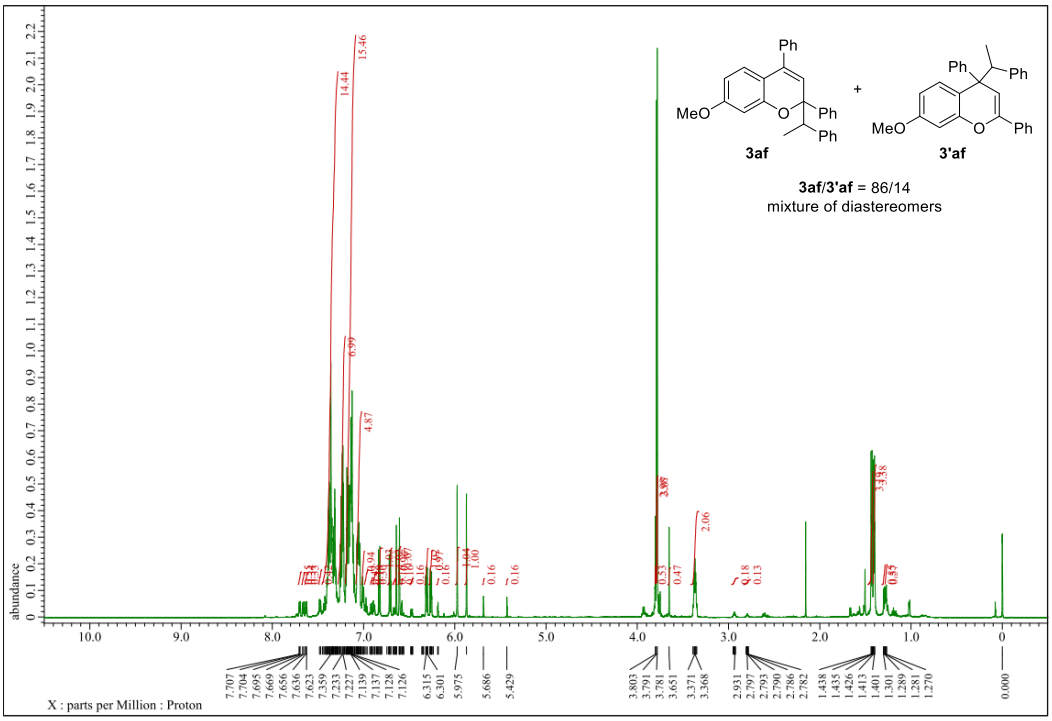


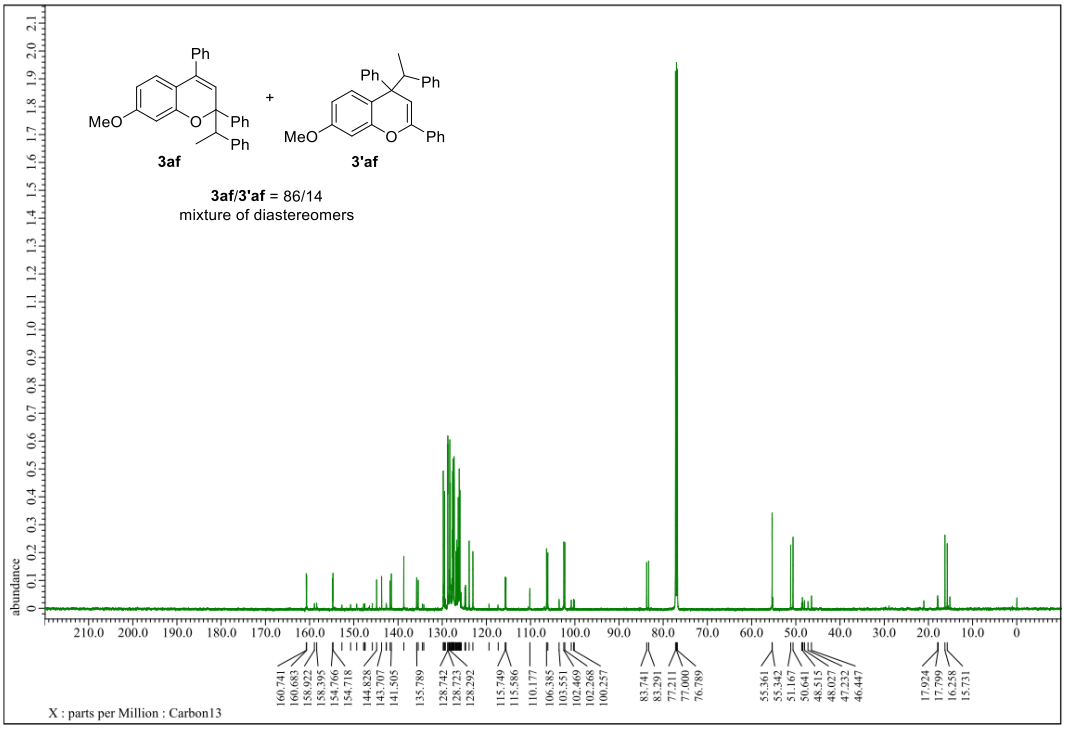
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3ae**



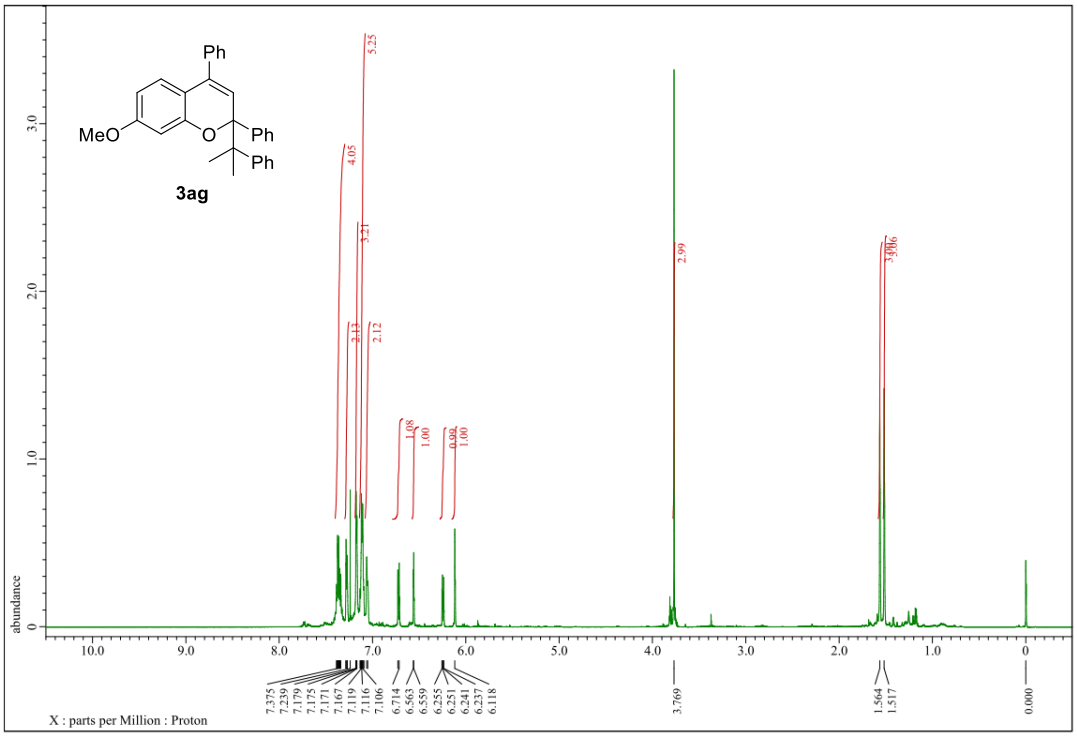


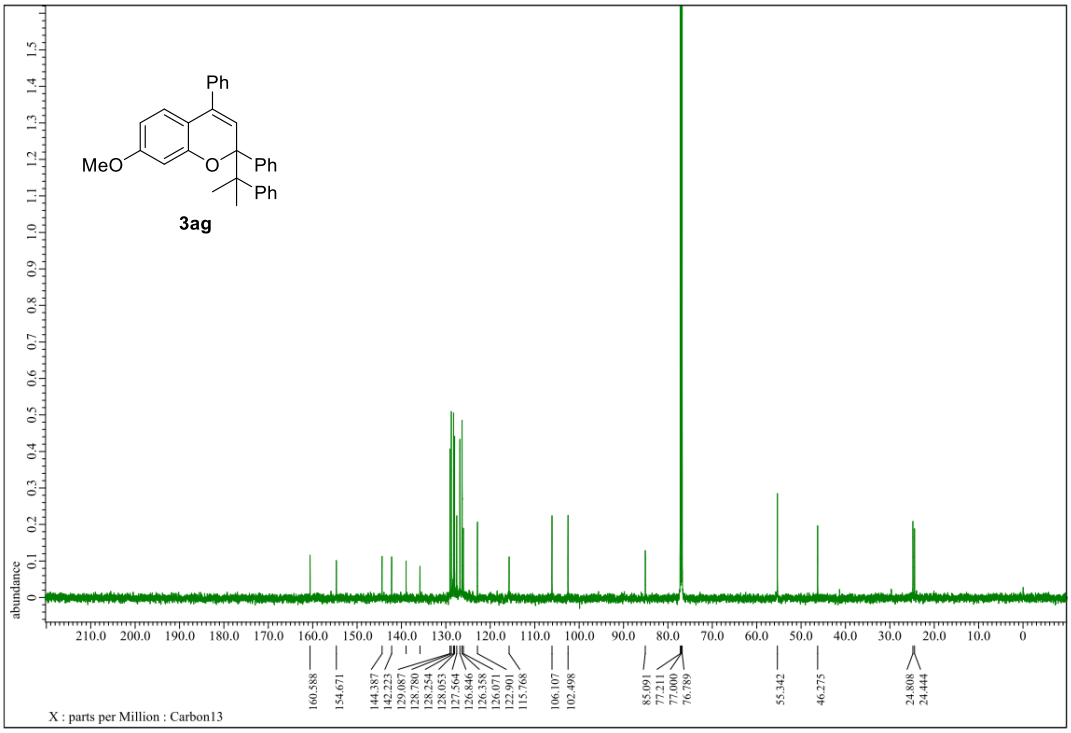
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3af**



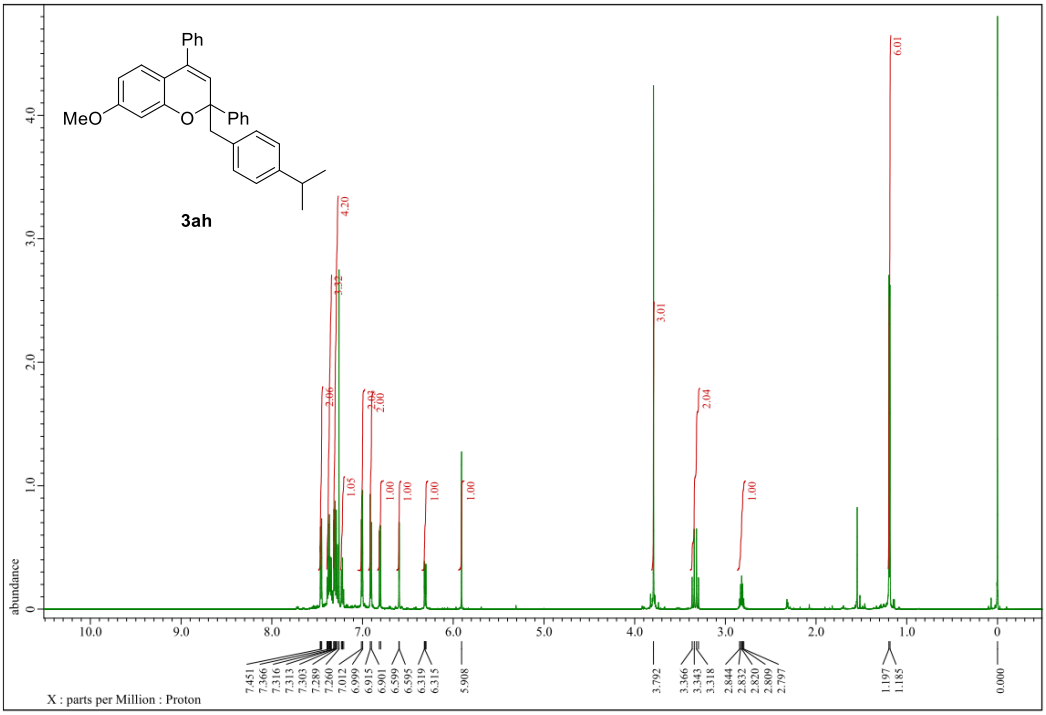


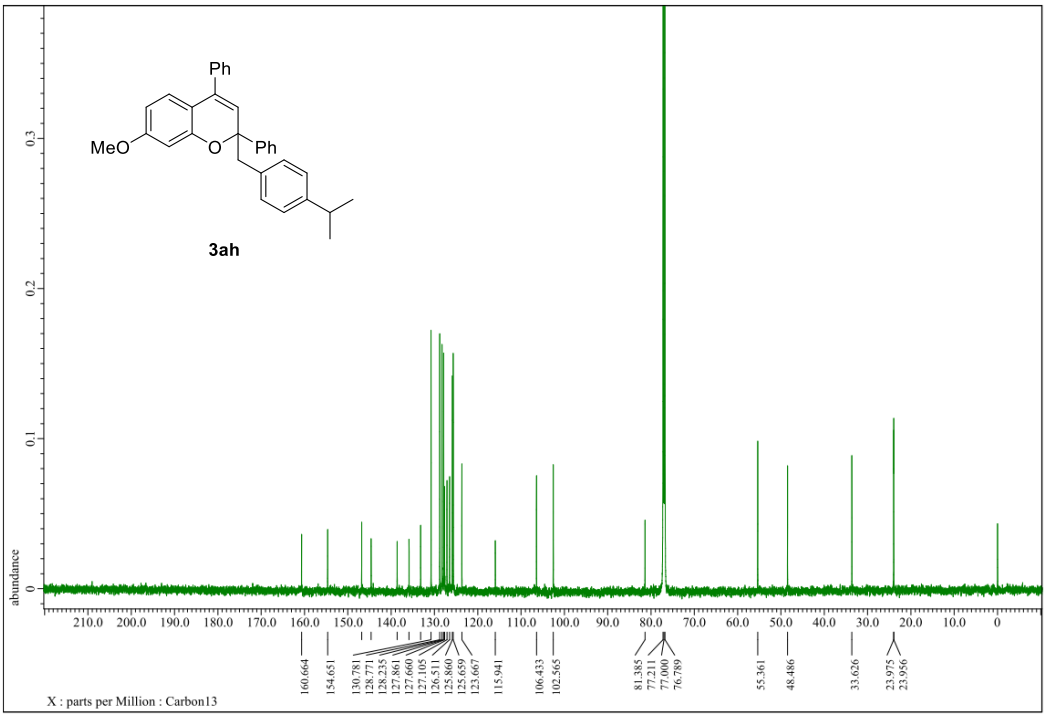
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3ag**



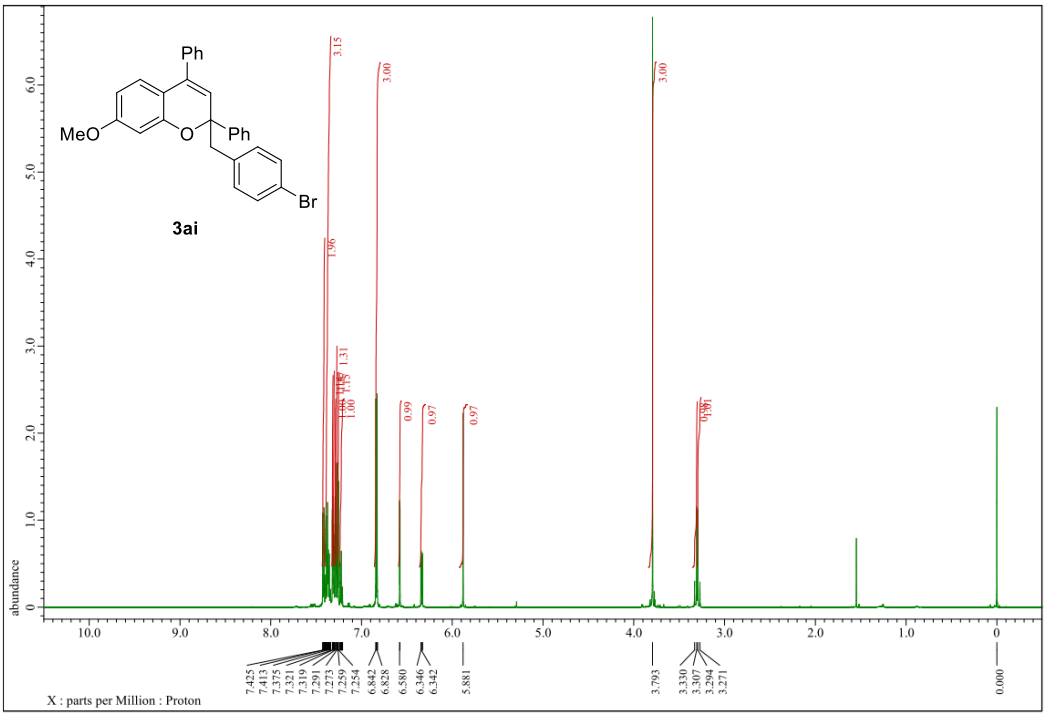


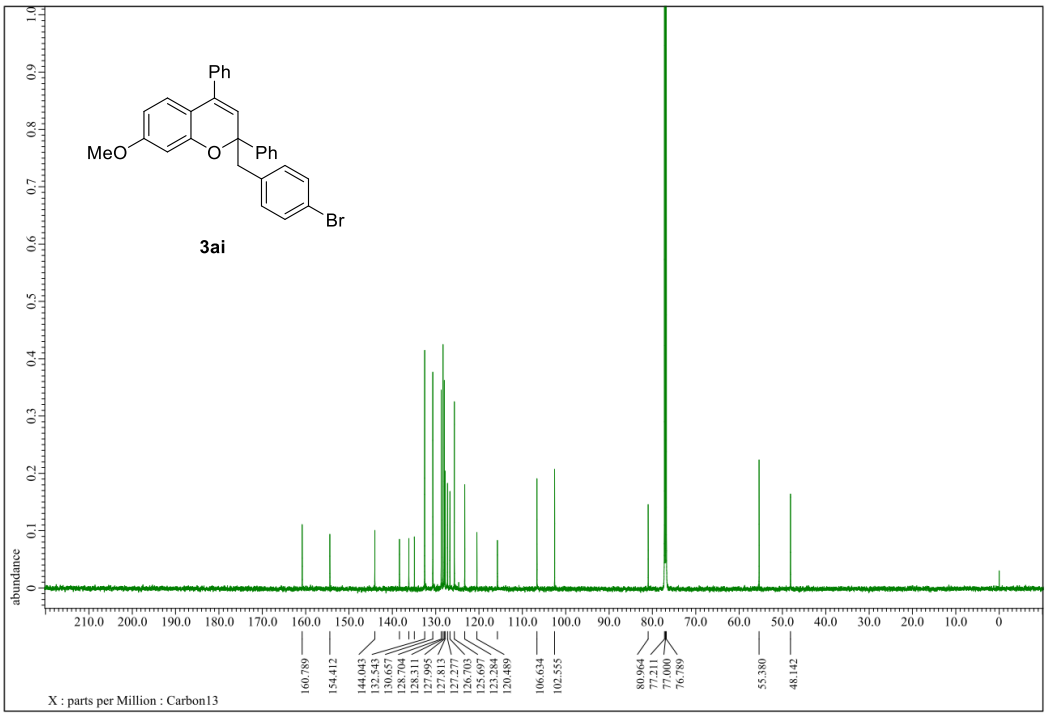
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3ah**



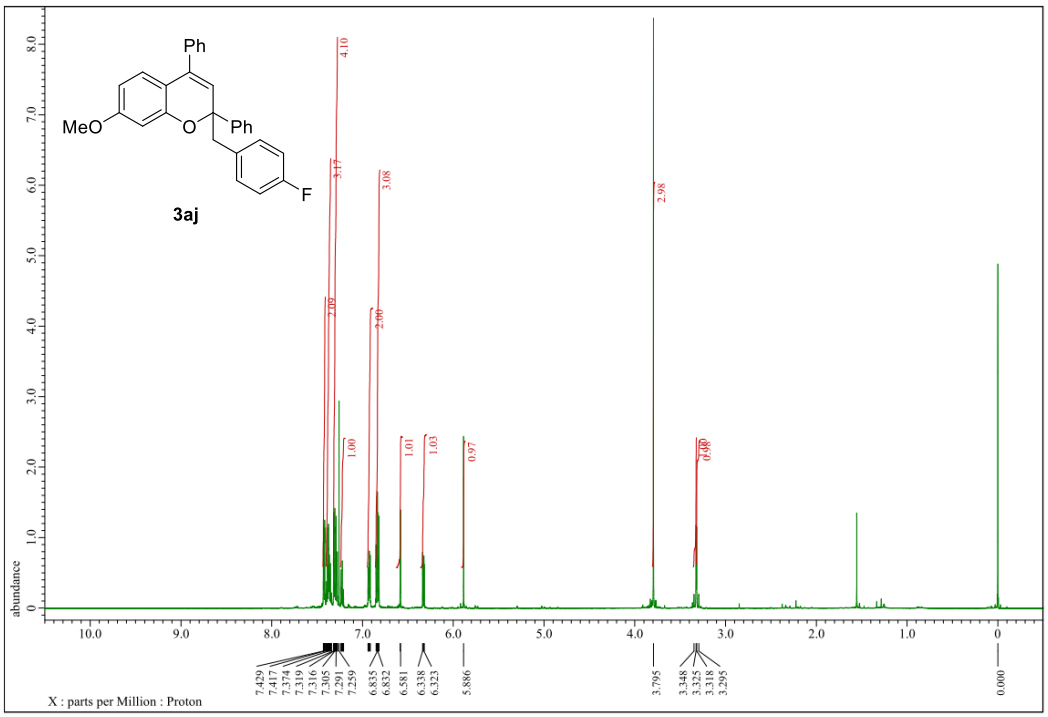


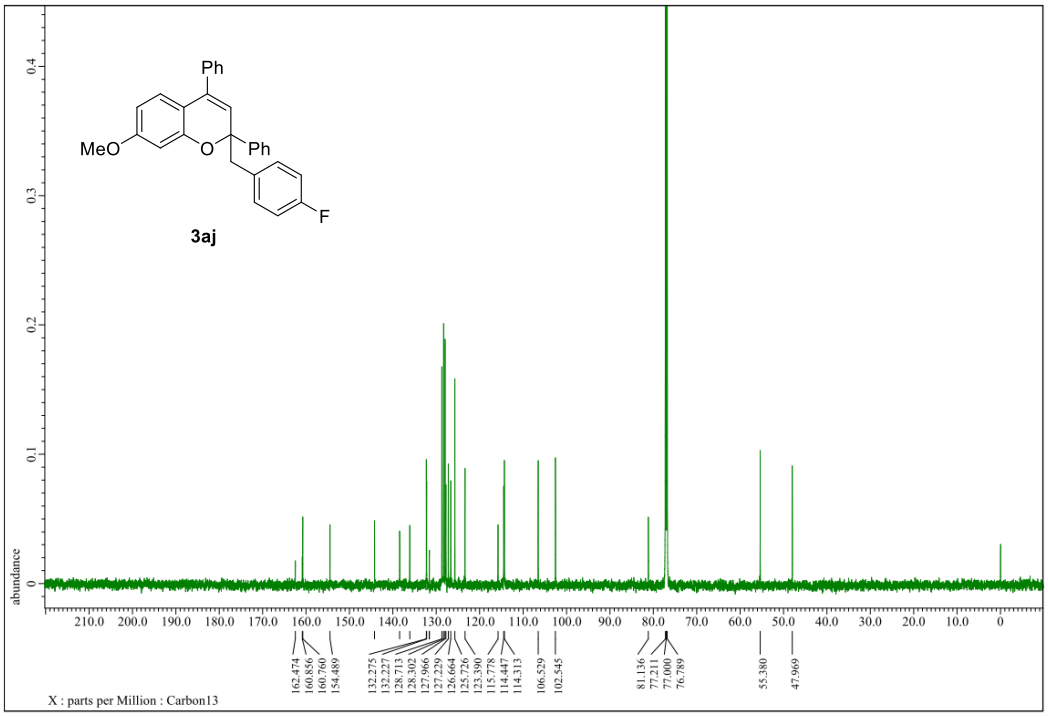
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3ai**



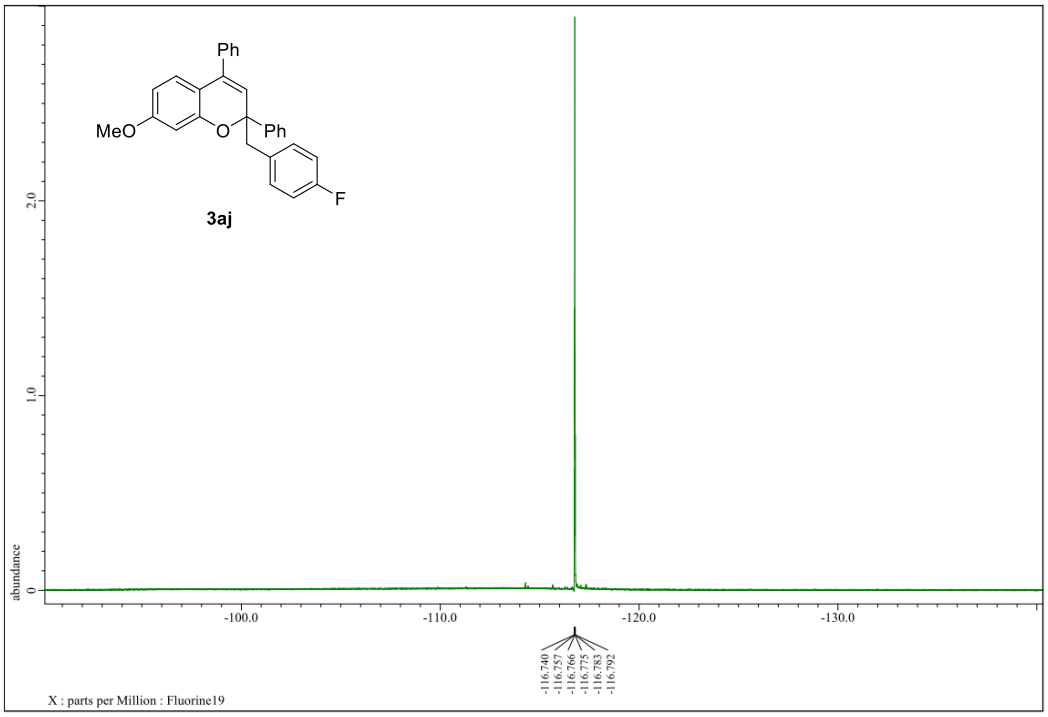


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) spectra of **3aj**

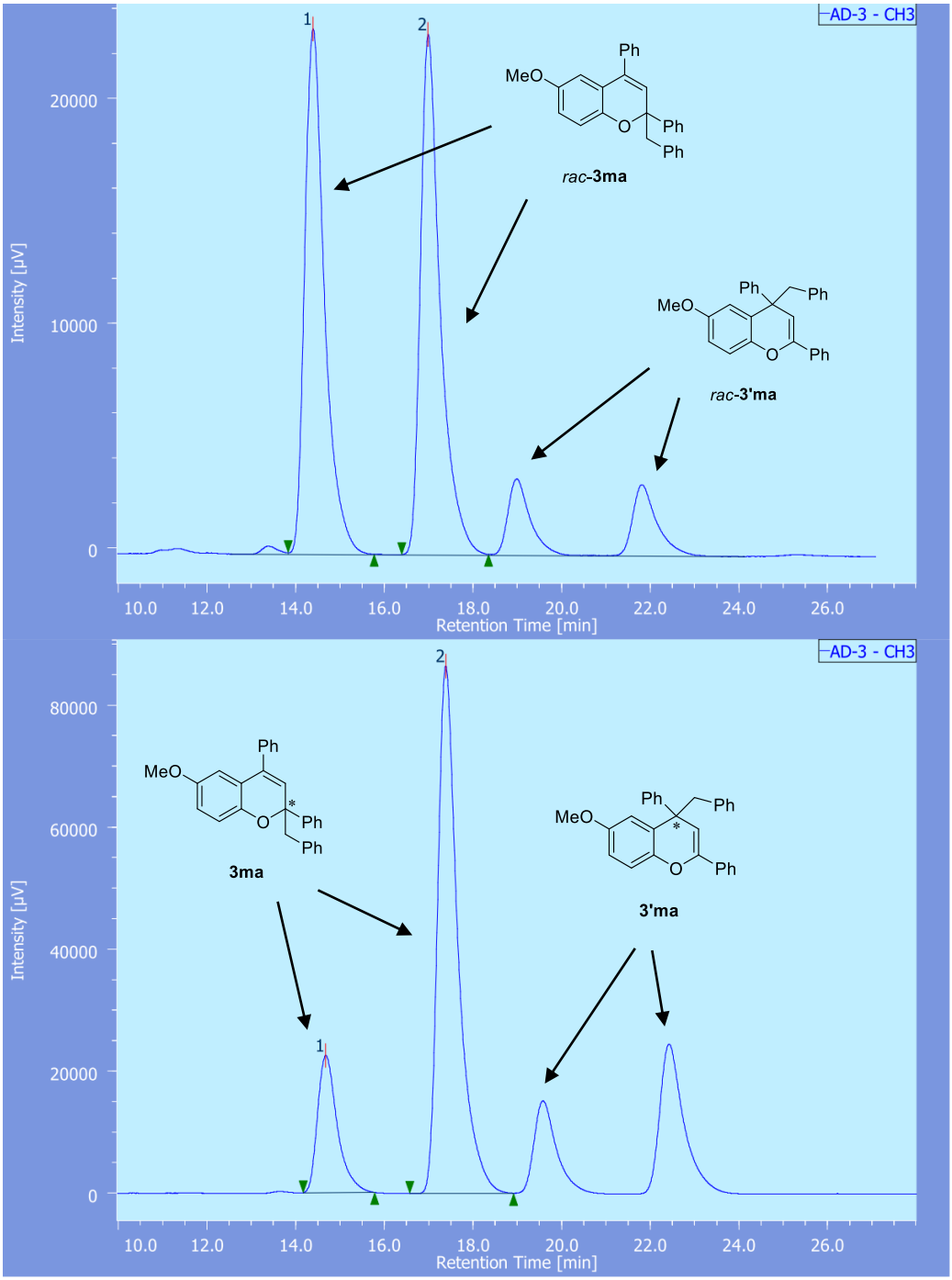




^{19}F NMR (565 MHz, $CDCl_3$) spectra of **3aj**



13. HPLC chart



	Retention Time (1)	Retention Time (2)	%Area (1)	%Area (2)
rac-**3ma**	14.4	17.0	50.0	50.0
3ma	14.7	17.4	20.2	79.8
rac-**3'ma**	19.0	21.8	49.8	50.2
3'ma	18.8	21.5	37.3	62.7