# Catalytic Enantioselective Synthesis of 2-Aryl Chromenes

**Bi-Shun Zeng, Xinyi Yu, Paul W. Siu, and Karl A. Scheidt***

Department of Chemistry, Center for Molecular Innovation and Drug Discovery, Northwestern University
2145 Sheridan Road, Evanston IL 60208

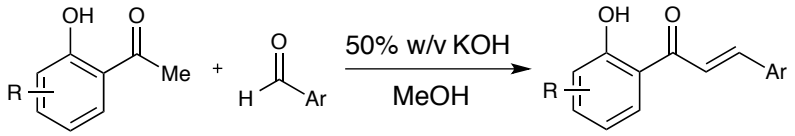
**Table of Contents**

## General Information

All reactions were carried out under a nitrogen atmosphere in flame-dried glassware with magnetic stirring. THF, toluene, and dichloromethane were purified by passage through a bed of activated alumina.[1] Reagents were purified prior to use unless otherwise stated following the guidelines of Perrin and Armarego.[2] Purification of reaction products was carried out by flash chromatography using EM Reagent or Silicycle silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and ceric ammonium nitrate stain or potassium permanganate stain followed by heating. Infrared spectra were recorded on a Bruker Tensor 37 FT-IR spectrometer. $^{1}$H-NMR spectra were recorded on a Bruker Avance 500 MHz w/ direct cryoprobe (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm). Data are reported as (ap = apparent, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad; coupling constant(s) in Hz; integration). Proton-decoupled $^{13}$C-NMR spectra were recorded on a Bruker Avance 500 MHz w/ direct cryoprobe (125 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.2 ppm). Mass spectra data were obtained on a Waters Acquity Single Quadrupole ESI Spectrometer, Micromass Quadro II Spectrometer and Agilent 7890 GC-TOF.

Benzaldehyde and 2'-hydroxyacetophenone derivatives were obtained from commercial sources (Sigma Aldrich, Oakwood). Chalcones[3] and phosphoramidites[4] were prepared according to published procedures.

## General Procedure for the Synthesis of 2'-Hydroxychalcone Derivatives




2'-Hydroxychalcones were prepared using a modified literature procedure.[3] Into a round bottom flask equipped with magnetic stirring bar was dissolved acetophenone derivative (15 mmol, 1 equiv) in methanol (100 mL) and 50% w/v KOH (17 mL). The reaction was stirred at 0 °C for 30 min. The aldehyde (18 mmol, 1.2 equiv) was added in one portion, and the mixture was stirred at 23 °C for 12-24 h. The solution was neutralized with 12 M HCl. The precipitate was removed by vacuum filtration, washed with water, dried, and recrystallized from methanol or dichloromethane/hexanes. When no precipitate was formed upon neutralization, the solution was extracted with EtOAc, and the combined organics were dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by flash chromatography using

---

[1] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, and F. J. Timmers, *Organometallics*, 1996, **15**, 1518-1520.

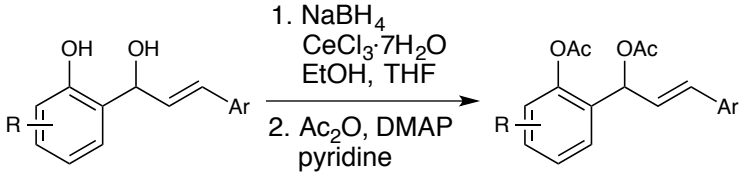
[2] D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*; 3rd Ed., Pergamon Press, Oxford. 1988.

[3] L. D. Chiaradia, A. Mascarello, M. Purificacao, J. Vernal, M. N. S. Cordeiro, M. E. Zenteno, A. Villarino, R. J. Nunes, R. A. Yunes, and H. Terenzi, *Bioorg. Med. Chem. Lett.*, 2008, **18**, 6227-6230.

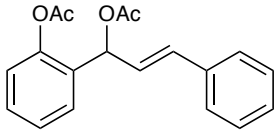
[4] A. Alexakis, J. Burton, J. Vastra, C. Benhaim, X. Fournioux, A. van den Heuvel, J. M. Leveque, F. Maze, and S. Rosset, *Eur. J. Org. Chem.*, 2000, 4011-4027.

10% EtOAc/hexanes or recrystallization with hot methanol to afford the chalcones as a yellow solid.

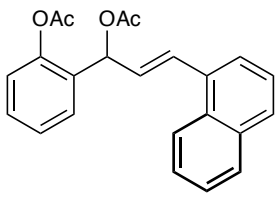
**General Procedure for the Synthesis of Bis-acetates**




Into a round bottom flask equipped with magnetic stir bar was loaded 2'-hydroxychalcone derivative (2.5 mmol, 1 equiv), $CeCl_3 \cdot 7H_2O$ (5.5 mmol, 2.2 equiv), ethanol (200 proof, 8.8 equiv), and THF (0.1 M 25 mL). The mixture was cooled to 0 °C before $NaBH_4$ (5.5 mmol, 2.2 equiv) was added in one portion and allowed to slowly warmed to 23 °C. Upon consumption of the 2'-hydroxychalcone, 4-dimethylaminopyridine (3.75 mmol, 1.5 equiv), pyridine (37.5 mmol, 15 equiv), and acetic anhydride (37.5 mmol, 15 equiv) were successively added. The reaction was stirred for 12-18 h and concentrated. The unpurified residue was taken up in EtOAc and quenched with a saturated solution of sodium bicarbonate. The layers were separated and the aqueous layer was back extracted with EtOAc. The combined organics were washed with DI $H_2O$, saturated copper(II) sulfate, and brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography using EtOAc/hexanes to afford the corresponding bis-acetates.

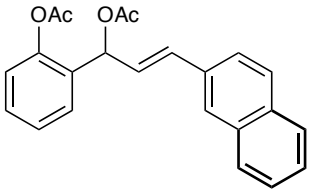



**(*E*)-1-(2-Acetoxy-3-methylphenyl)-3-phenylallyl acetate (1a).** Prepared according to the general procedure using (*E*)-2-(1-hydroxy-3-phenylallyl)-phenol. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford **1a** as a clear crystal (450 mg, 74%). Analytical data for **1a**: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.52 (dt, $J$ = 7.7, 1.5 Hz, 1H), 7.39 – 7.34 (m, 3H), 7.35 – 7.23 (m, 4H), 7.11 (dt, $J$ = 8.1, 1.3 Hz, 1H), 6.62 (d, $J$ = 16.0, 1H), 6.61 (d, $J$ = 6.5 Hz, 1H), 6.35 (dd, $J$ = 15.8, 6.6 Hz, 1H), 2.32 (s, 3H), 2.11 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 170.0, 169.5, 148.4, 136.2, 132.9, 131.1, 129.5, 128.7, 128.6, 128.3, 126.8, 126.5, 126.2, 123.3, 71.3, 21.3, 21.2; IR (film): 3061, 3027, 2938, 1765, 1738, 1650, 1586, 1491, 1452, 1369, 1233, 1197, 1173, 1098, 1063, 1015, 964, 911, 877 cm$^{-1}$; LRMS (ESI): Mass calculated for $[M+H]^+$ $C_{19}H_{19}O_4$: 311.1; found: 311.1.

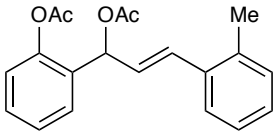



**(*E*)-2-(1-Acetoxy-3-(naphthalen-1-yl)allyl)phenyl acetate (1b).** Prepared according to the general procedure using (*E*)-1-(2-hydroxyphenyl)-3-(naphthalen-1-yl)prop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford **1b** as a

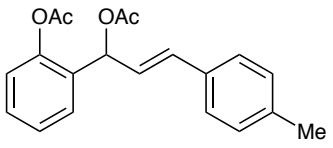
colorless oil (290 mg, 40%). Analytical data for **1b**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.6, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.59 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.49 – 7.39 (m, 3H), 7.34 (td, *J* = 7.6, 1.3 Hz, 1H), 7.17 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.76 (dd, *J* = 6.5, 1.3 Hz, 1H), 6.41 (dd, *J* = 15.6, 6.5 Hz, 1H), 2.36 (s, 3H), 2.18 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 170.0, 169.6, 148.5, 134.0, 133.7, 131.3, 131.1, 130.4, 129.6, 129.4, 128.8, 128.7, 128.6, 126.5, 126.4, 126.0, 125.7, 124.3, 123.8, 123.4, 71.5, 21.4, 21.2; IR (film): 3060, 3046, 3014, 2936, 1765, 1737, 1369, 1233, 1198 $cm^{-1}$; LRMS (ESI): Mass calculated for $[M+H]^+$ $C_{23}H_{21}O_4$: 361.1; found: 361.0.



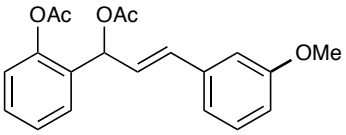

***(E)*-2-(1-Acetoxy-3-(naphthalen-2-yl)allyl)phenyl acetate (1c).** Prepared according to the general procedure using (*E*)-1-(2-hydroxyphenyl)-3-(naphthalen-2-yl)prop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford **1c** as a colorless oil (250 mg, 57%). Analytical data for **1c**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.73 (m, 4H), 7.57 (ddd, *J* = 9.4, 8.2, 1.7 Hz, 2H), 7.49 – 7.42 (m, 2H), 7.38 (td, *J* = 7.6, 1.7 Hz, 1H), 7.30 (td, *J* = 7.6, 1.3 Hz, 1H), 7.12 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.78 (d, *J* = 15.9 Hz, 1H), 6.67 (dd, *J* = 6.5, 1.3 Hz, 1H), 6.47 (dd, *J* = 15.9, 6.4 Hz, 1H), 2.33 (s, 3H), 2.14 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 170.0, 169.6, 148.4, 133.63, 133.59, 133.3, 133.0, 131.1, 129.5, 128.8, 128.4, 128.2, 127.8, 127.2, 126.54, 126.51, 126.49, 126.3, 123.6, 123.3, 71.3, 21.3, 21.2; IR (film): 3057, 2936, 2854, 1766, 1737, 1651, 1607, 1507, 1369, 1233, 1198, 1174 $cm^{-1}$; LRMS (ESI): Mass calculated for $[M+H]^+$ $C_{23}H_{21}O_4$: 361.1; found: 361.3.



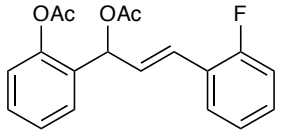

**(*E*)-2-(1-Acetoxy-3-(*o*-tolyl)allyl)phenyl acetate (1d).** Prepared according to the general procedure using (*E*)-1-(2-hydroxyphenyl)-3-(o-tolyl)prop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford **1d** as a colorless oil (290 mg, 40%). Analytical data for **1d**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.46 – 7.40 (m, 1H), 7.37 (td, *J* = 7.8, 1.7 Hz, 1H), 7.28 (td, *J* = 7.6, 1.2 Hz, 1H), 7.19 – 7.09 (m, 4H), 6.85 (dd, *J* = 15.9, 1.3 Hz, 1H), 6.62 (dd, *J* = 6.6, 1.3 Hz, 1H), 6.24 (dd, *J* = 15.7, 6.6 Hz, 1H), 2.34 (s, 3H), 2.33 (s, 3H), 2.11 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 169.9, 169.4, 148.3, 135.8, 135.2, 131.1, 130.9, 130.4, 129.4, 128.6, 128.0, 127.4, 126.4, 126.2, 125.8, 123.2, 71.5, 21.2, 21.1, 19.8; IR (film): 3098,3063, 3017, 2912, 2860, 1924, 1724, 1719, 1572, 1463, 1426 $cm^{-1}$; LRMS (ESI): Mass calculated for $[M+H]^+$ $C_{20}H_{21}O_4$: 325.1; found: 325.5.



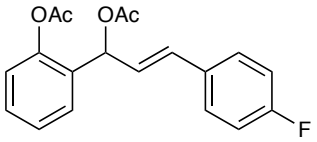
**(*E*)-2-(1-Acetoxy-3-(*p*-tolyl)allyl)phenyl acetate (1e).** Prepared according to the general procedure using (*E*)-1-(2-hydroxyphenyl)-3-(p-tolyl)prop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford **1e** as a colorless oil (170 mg, 62%). Analytical data for **1e**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.36 (td, *J* = 7.7, 1.7 Hz, 1H), 7.29 – 7.26 (m, 3H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.10 (dd, *J* = 8.3, 1.3 Hz, 1H), 6.60 (d, *J* = 7.5 Hz, 1H), 6.59 (d, J = 15.4 Hz, 1 H), 6.34 – 6.25 (m, 1H), 2.33 (s, 3H), 2.31 (s, 3H), 2.11 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 170.0, 169.5, 148.4, 138.2, 133.4, 132.9, 131.2, 129.4, 128.7, 126.7, 126.4, 125.1, 123.3, 71.4, 21.4, 21.3, 21.2; IR (film): 3087, 3023, 2973, 2921, 2858, 1777, 1769, 1588, 1371, 1282, 1245 cm$^{-1}$; LRMS (ESI): Mass calculated for $[M+H]^+$ $C_{20}H_{21}O_4$: 325.1.



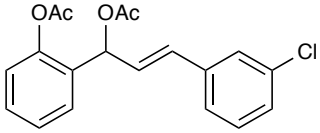

**(*E*)-2-(1-Acetoxy-3-(3-methoxyphenyl)allyl)phenyl acetate (1f).** Prepared according to the general procedure using (*E*)-1-(2-hydroxyphenyl)-3-(3-methoxyphenyl)prop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford **1f** as a colorless oil (330 mg, 42%). Analytical data for **1f**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.37 (ddd, *J* = 8.1, 7.4, 1.7 Hz, 1H), 7.28 (td, *J* = 7.8, 1.5 Hz, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 7.11 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.97 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.90 (dd, *J* = 2.6, 1.5 Hz, 1H), 6.81 (ddd, *J* = 8.3, 2.6, 0.9 Hz, 1H), 6.61 (d, *J* = 6.5 Hz, 1H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.34 (dd, *J* = 15.6, 6.7 Hz, 1H), 3.80 (s, 3H), 2.32 (s, 3H), 2.11 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 169.7, 169.3, 159.6, 148.1, 137.3, 132.5, 130.8, 129.5, 129.2, 128.5, 126.25, 126.20, 123.0, 119.2, 113.7, 111.7, 70.9, 55.1, 21.0, 20.9; IR (film): 3063, 3038, 3005, 2959, 2940,1766, 1599, 1489,1466, 1370, 1234, 1042 cm$^{-1}$; LRMS (ESI): Mass calculated for $[M+H]^+$ $C_{20}H_{21}O_5$: 341.1; found 341.1.



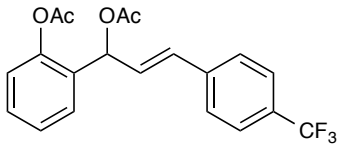

**(*E*)-2-(1-Acetoxy-3-(2-fluorophenyl)allyl)phenyl acetate (1g).** Prepared according to the general procedure using (*E*)-3-(2-fluorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford **1g** as a colorless oil (229 mg, 47%). Analytical data for **1g**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.42 (td, *J* = 7.7, 1.7 Hz, 1H), 7.37 (td, *J* = 7.7, 1.7 Hz, 1H), 7.28 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.22 (dddd, *J* = 8.1, 7.1, 5.2, 1.8 Hz, 1H), 7.11 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.08 (td, *J* = 7.6, 1.2 Hz, 1H), 7.03 (ddd, *J* = 10.8, 8.3, 1.2 Hz, 1H), 6.80 (dd, *J* = 16.3, 1.2 Hz, 1H), 6.61 (dd, *J* = 6.6, 1.3 Hz, 1H), 6.43 (dd, *J* = 16.1, 6.5 Hz, 1H), 2.33 (s, 3H), 2.12 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 169.9, 169.5, 160.5 (d, *J* = 249.8 Hz), 148.4, 130.9, 129.56 (d, *J* = 8.6 Hz), 129.56, 128.74 (d, *J* = 5.5 Hz), 128.69, 127.8 (d, *J* = 3.5 Hz), 126.5, 125.1 (d, *J* = 3.6 Hz), 124.3 (d, *J* = 3.6 Hz), 124.0 (d, *J* = 12.0 Hz), 123.3, 115.9 (d, *J* = 22.0 Hz), 71.3, 21.3, 21.2; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -117.57; IR (film): 3064, 3040, 2935, 2853, 1766, 1741, 1609, 1579, 1488, 1455, 1370, 1231, 1199, 1174, 1096, 1066, 1016, 968 cm$^{-1}$; LRMS (ESI): Mass calculated for $[M+H]^+$ $C_{19}H_{18}FO_4$: 329.1; found: 329.2.




**(*E*)-2-(1-Acetoxy-3-(4-fluorophenyl)allyl)phenyl acetate (1h).** Prepared according to the general procedure using (*E*)-3-(4-fluorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford **1h** as a white solid (285 mg, 39%). Analytical data for **1h**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.40 – 7.30 (m, 3H), 7.29 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.10 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.99 (t, *J* = 8.7 Hz, 2H), 6.59 – 6.55 (m, 2H) 6.26 (dd, *J* = 15.6, 6.9 Hz, 1H), 2.31 (s, 3H), 2.11 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 170.0, 169.5, 162.7 (d, *J* = 247.8 Hz), 148.3, 132.3 (d, *J* = 3.2 Hz), 131.8, 131.0, 129.5, 128.7, 128.4 (d, *J* = 8.0 Hz), 126.5, 126.0 (d, *J* = 2.3 Hz), 123.3, 115.7 (d, *J* = 21.7 Hz), 71.2, 21.3, 21.2; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -113.62; IR (film): 3041, 2937, 1769, 1765, 1736, 1729, 1655, 1601, 1509, 1489, 1453, 1431, 1371, 1297, 1158, 1096, 1040, 1012, 970 cm$^{-1}$; LRMS (ESI): Mass calculated for $[M-H]^-$ $C_{19}H_{16}FO_4$: 327.1; found: 327.0.

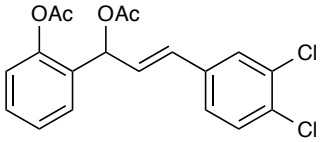



**(*E*)-2-(1-Acetoxy-3-(3-chlorophenyl)allyl)phenyl acetate (1i).** Prepared according to the general procedure using (*E*)-3-(3-chlorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford **1i** as a colorless oil (683 mg, 64%). Analytical data for **1i**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.41 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.39 (t, *J* = 1.6 Hz, 1H), 7.31 (td, *J* = 7.6, 1.2 Hz, 1H), 7.26 (m, 3H), 7.14 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.63 (dd, *J* = 6.2, 1.3 Hz, 1H), 6.58 (dd, *J* = 15.9, 1.4 Hz, 1H), 6.39 (dd, *J* = 15.9, 6.3 Hz, 1H), 2.35 (s, 3H), 2.14 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 169.9, 169.5, 148.4, 138.0, 134.7, 131.3, 130.8, 130.0, 129.6, 128.7, 128.2, 127.8, 126.7, 126.5, 125.1, 123.3, 70.9, 21.25, 21.18; IR (film): 3064, 3038, 2936, 2850, 1765, 1739, 1593, 1566, 1489, 1453, 1428, 1369, 1232, 1198, 1174, 1096, 1077, 1066, 1015, 962, 911, 777, 757 cm$^{-1}$; LRMS (ESI): Mass calculated for $[M+H]^+$ $C_{19}H_{18}ClO_4$: 345.1; found: 345.1.

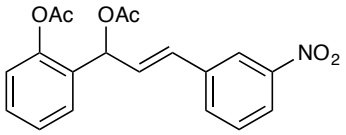



**(*E*)-2-(1-Acetoxy-3-(4-(trifluoromethyl)phenyl)allyl)phenyl acetate (1j).** Prepared according to the general procedure using (*E*)-1-(2-hydroxyphenyl)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford **1j** as a colorless oil (230 mg, 49%). Analytical data for **1j**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.1 Hz, 2H), 7.50 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.38 (td, *J* = 7.8, 1.7 Hz, 1H), 7.29 (td, *J* = 7.5, 1.3 Hz, 1H), 7.11 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.63 (d, *J* = 15.9 Hz, 1H), 6.62 (d, *J* = 6.5 Hz, 1H) 6.43 (dd, *J* = 15.9, 6.2 Hz, 1H), 2.32 (s, 3H), 2.13 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 169.9, 169.5, 148.4, 139.7, 131.2, 130.7, 130.0 (d, *J* = 32.4 Hz), 129.7, 129.0, 128.8, 127.0, 126.6, 125.7 (q, *J* = 3.8 Hz), 124.2 (d, *J* = 272.0 Hz), 123.4, 70.8, 21.3, 21.2; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -62.62; IR (film): 3085, 3044,2937,1926, 1782, 1726, 1657, 1615,

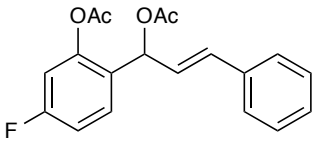
1587, 1494, 1455, 1415, 1365, 1316, 1282, 1252, 1137, 1097 $cm^{-1}$; LRMS (ESI): Mass calculated for $[M+H]^+$ $C_{20}H_{18}F_3O_4$: 379.1; found: 379.2.




**(*E*)-2-(1-Acetoxy-3-(3,4-dichlorophenyl)allyl)phenyl acetate (1k).** Prepared according to the general procedure using its (*E*)-3-(3,4-dichlorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford **1k** as a colorless oil (230 mg, 28%). Analytical data for **1k**: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.35 (s, 1H), 7.31 – 7.26 (m, 2H), 7.22 – 7.14 (m, 1H), 7.08 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.01 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.49 (dd, *J* = 6.1, 1.4 Hz, 1H), 6.40 (dd, *J* = 15.9, 1.4 Hz, 1H), 6.24 (dd, *J* = 15.9, 6.2 Hz, 1H), 2.22 (s, 3H), 2.02 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 169.9, 169.5, 148.3, 136.3, 132.9, 131.9, 130.64, 130.60, 130.2, 129.7, 128.7, 128.5, 128.4, 126.6, 126.0, 123.3, 70.7, 21.24, 21.18; IR (film): 3063, 3038, 2926, 2852, 1767, 1739, 1608, 1587, 1554, 1473, 1454, 1431, 1370, 1233, 1198, 1174, 1133, 1026 $cm^{-1}$; LRMS (ESI): Mass calculated for $[M+H]^+$ $C_{19}H_{17}Cl_2O_4$: 379.1; found: 379.1.

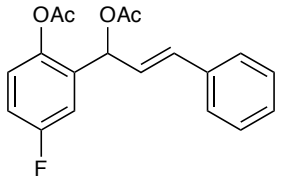



**(*E*)-2-(1-Acetoxy-3-(3-nitrophenyl)allyl)phenyl acetate (1l).** Prepared according to the general procedure using (*E*)-1-(2-hydroxyphenyl)-3-(3-nitrophenyl)prop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford **1l** as a colorless oil (352 mg, 54%). Analytical data for **1l**: $^1$H NMR (500 MHz, $CDCl_3$) δ 8.23 (t, *J* = 1.9 Hz, 1H), 8.10 (ddd, *J* = 8.4, 2.3, 1.1 Hz, 1H), 7.66 (dt, *J* = 8.0, 1.3 Hz, 1H), 7.57 – 7.45 (m, 2H), 7.40 (td, *J* = 7.8, 1.7 Hz, 1H), 7.30 (td, *J* = 7.6, 1.3 Hz, 1H), 7.12 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.65 (d, *J* = 16.0 Hz, 1H), 6.63 (d, *J* = 6.0 Hz, 1H), 6.49 (dd, *J* = 16.0, 5.9 Hz, 1H), 2.34 (s, 3H), 2.20 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 169.9, 169.5, 148.7, 148.4, 138.0, 132.6, 130.4, 130.2, 129.8, 129.7 (2C), 128.8, 126.6, 123.4, 122.8, 121.4, 70.6, 21.24, 21.20; IR (film): 3087, 3068, 3039, 2937, 2869, 2310, 2281, 1825, 1780, 1721, 1656, 1608, 1587, 1490, 1431, 1378, 1341, 1262, 1158, 1043, 1023, 975 $cm^{-1}$; LRMS (ESI): Mass calculated for $[M+H]^+$ $C_{19}H_{18}NO_6$: 356.1; found: 356.2.

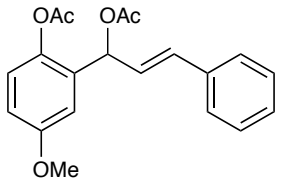



**(*E*)-2-(1-Acetoxy-3-phenylallyl)-5-fluorophenyl acetate (1m).** Prepared according to the general procedure using (*E*)-1-(4-fluoro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford **1m** as a colorless oil (485 mg, 70%). Analytical data for **1m**: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 8.7, 6.2 Hz, 1H), 7.39 – 7.27 (m, 5H), 6.99 (ddd, *J* = 8.6, 7.9, 2.6 Hz, 1H), 6.89 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.57 (dd, *J* = 6.4, 1.4 Hz, 1H), 6.32 (dd, *J* = 15.9, 6.4 Hz, 1H), 2.32 (s, 3H), 2.10 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 169.9, 169.0, 162.5 (d, *J* = 249.3

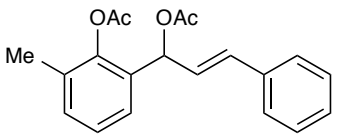
Hz), 149.1 (d, $J$ = 10.9 Hz), 136.0, 132.9, 129.9 (d, $J$ = 9.6 Hz), 128.8, 128.4, 127.2 (d, $J$ = 3.6 Hz), 126.8, 126.0, 113.6 (d, $J$ = 21.3 Hz), 111.2 (d, $J$ = 24.4 Hz), 70.7, 21.3, 21.1; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -112.10; IR (film): 3082, 3028, 2938, 1951, 1890, 1732, 1651, 1603, 1578, 1504, 1425, 1371, 1235, 1143, 1091 and 1015 cm-$^{1}$; LRMS (ESI): Mass calculated for $[M+H]^+$ $C_{19}H_{18}FO_4$: 329.1; found: 329.2.




**(*E*)-2-(1-Acetoxy-3-phenylallyl)-4-fluorophenyl acetate (1n).** Prepared according to the general procedure using (*E*)-1-(5-fluoro-2-hydroxyphenyl)-3-phenylprop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford **1n** as a yellow oil (382.1 mg, 63%). Analytical data for **1n**: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 4H), 7.28 – 7.24 (m, 1H), 7.22 (dd, $J$ = 8.9, 2.8 Hz, 1H), 7.10 – 7.02 (m, 2H), 6.63 (dd, $J$ = 15.9, 1.3 Hz, 1H), 6.56 (dd, $J$ = 6.8, 1.3 Hz, 1H), 6.28 (dd, $J$ = 15.9, 6.6 Hz, 1H), 2.30 (s, 3H), 2.13 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 169.8, 169.5, 160.4 (d, $J$ = 245.3 Hz), 144.0 (d, $J$ = 2.9 Hz), 135.9, 133.5, 133.1 (d, $J$ = 7.4 Hz), 128.8, 128.4, 126.8, 125.5, 124.7 (d, $J$ = 8.5 Hz), 116.1 (d, $J$ = 23.4 Hz), 115.1 (d, $J$ = 24.4 Hz), 70.7, 21.3, 21.1; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -115.63; IR (film): 3082, 3060, 3028., 2935, 2851, 1766, 1651, 1619, 1579, 1494, 1370, 1269, 1205, 1171, 1065, 1017, 968, 941, 901, 879 cm$^{-1}$; LRMS (ESI): Mass calculated for $[M+H]^+$ $C_{19}H_{18}FO_4$: 329.1; found: 329.1.

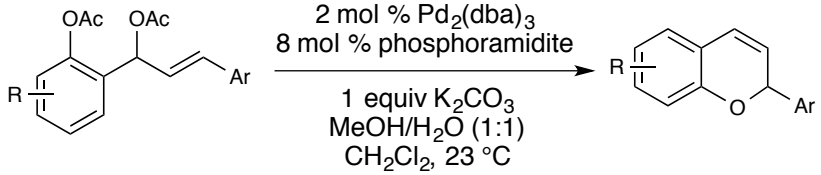



**(*E*)-2-(1-Acetoxy-3-phenylallyl)-4-methoxyphenyl acetate (1o).** Prepared according to the general procedure using (*E*)-1-(2-hydroxy-5-methoxyphenyl)-3-phenylprop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford **1o** as a colorless oil (380 mg, 61%). Analytical data for **1o**: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, $J$ = 7.0 Hz, 2H), 7.31 (t, $J$ = 7.4 Hz, 2H), 7.24 (d, $J$ = 7.3 Hz, 1H), 7.03 (d, $J$ = 1.8 Hz, 1H), 7.02 (d, $J$ = 4.1 Hz, 1H), 6.88 (dd, $J$ = 8.9, 3.1 Hz, 1H), 6.62 (dd, $J$ = 15.9, 1.3 Hz, 1H), 6.55 (dd, $J$ = 6.5, 1.4 Hz, 1H), 6.32 (dd, $J$ = 15.9, 6.5 Hz, 1H), 3.81 (s, 3H), 2.29 (s, 3H), 2.12 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 169.93, 169.91, 157.6, 141.7, 136.1, 133.0, 132.0, 128.7, 128.3, 126.8, 126.0, 124.0, 114.2, 113.9, 71.2, 55.8, 21.3, 21.1; IR (film): 3086, 3061, 3032, 2999, 2917, 2849, 2832, 1608, 1578, 1488, 1433, 1372, 1307, 1269, 1165, 1029 cm$^{-1}$; LRMS (ESI): Mass calculated for $[M+H]^+$ $C_{20}H_{21}O_5$: 341.1; found 341.1.

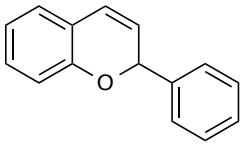


**(*E*)-1-(2-Acetoxy-3-methylphenyl)-3-phenylallyl acetate (1p).** Prepared according to the general procedure using (*E*)-1-(2-hydroxy-3-methylphenyl)-3-phenylprop-2-en-1-one. The residue was purified by flash chromatography using 15% EtOAc/hexanes to afford **1p** as a yellow oil (280 mg, 47%). Analytical data for **1p**: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.15 (m, 8H), 6.62 (dd, *J* = 15.9, 1.4 Hz, 1H), 6.55 (m, 1 H), 6.36 (dd, *J* = 15.9, 6.5 Hz, 1H), 2.33 (s, 3H), 2.17 (s, 3H), 2.10 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 170.0, 169.0, 147.4, 136.2, 131.5, 131.4, 131.3, 128.7, 128.2, 127.3, 126.8, 126.5, 126.4, 126.3, 76.2, 21.3, 20.9, 16.5; IR (film): 3060, 3027, 2957, 2925, 2855, 1762, 1740, 1598, 1577, 1496, 1468, 1437, 1369, 1232, 1209, 1165, 1089, 1016, 966 and 907 cm$^{-1}$; LRMS (ESI): Mass calculated for $[M+H]^+$ $C_{20}H_{21}O_4$: 325.1; found: 325.1.

**General Procedure for Enantioselective Synthesis of Chromenes**

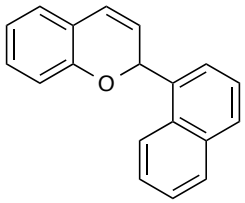



Into an oven-dried, screw-capped reaction tube-vial equipped with magnetic stirbar was loaded bis-acetate (0.36 mmol, 1 equiv). The vial was taken into a nitrogen-filled drybox at which time $Pd_2(dba)_3$ (7.2 μmol, 0.02 equiv) and phosphoramidite (29 μmol, 0.08 equiv) were added. The vial was capped with a septum cap, removed from the drybox and put under positive $N_2$ pressure. The mixture was diluted with $CH_2Cl_2$ (3.6 mL) and stirred for 10 min under static nitrogen pressure. A solution of $K_2CO_3$ (0.36 mmol, 1 equiv) in methanol:water (1.8 mL:1.8 mL) was added. The resulting biphasic mixture was stirred at 23 °C for 19-48 h. Reaction was extracted with $CH_2Cl_2$. The combined organic layers were filtered through a Biotage ISOLUTE® phase separator, and the organic filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography using EtOAc/hexanes to afford the corresponding chromene.

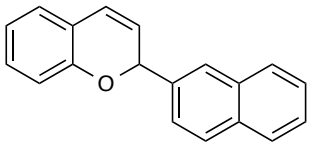



**2-Phenyl-2*H*-chromene** (**2a**). Prepared according to the general procedure using **1a**. The residue was purified by flash chromatography using 1% EtOAc/hexanes to afford **2a** as a light yellow oil (53 mg, 71%). Analytical data for **2a**: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.43 (m, 2H), 7.43 – 7.36 (m, 2H), 7.36 – 7.31 (m, 1H), 7.12 (td, *J* = 7.8, 1.7 Hz, 1H), 7.02 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.87 (td, *J* = 7.4, 1.1 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.54 (dd, *J* = 9.8, 1.9 Hz, 1H), 5.93 (dd, *J* = 3.4, 1.9 Hz, 1H), 5.81 (dd, *J* = 9.8, 3.4 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 153.5, 141.2, 129.9, 129.1, 128.8, 127.4, 127.0, 125.2, 124.4, 121.7, 121.6, 116.4, 77.5; IR (film): 3043, 2919, 2851,1573, 1510, 1485, 1456, 1227, 1201, 1112, 1060, 857 cm$^{-1}$; HRMS (EI): Mass calculated for $[M]^+$ $C_{15}H_{12}O$: 208.0888; found 208.0869; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OJ-H; 100% hexanes; 0.7 mL/min, 280 nm), $Rt_1$ (minor) = 61.4, $Rt_2$ (major) = 74.8 min; er = 95:5. The absolute configuration of the chromenes was determined by comparison of optical rotation to literature value of the known enantiomer.[5]

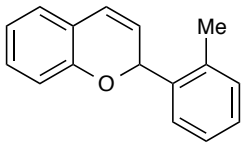
[5] H. He, K. Y. Ye, Q. F. Wu, L. X. Dai, and S. L. You, *Adv. Synth. Catal.*, 2012, **354**, 1084-1094.



**2-(Naphthalen-1-yl)-2*H*-chromene (2b).** Prepared according to the general procedure using **1b**. The residue was purified by flash chromatography using 1% EtOAc/hexanes to afford **2b** as a light yellow oil (66 mg, 71%). Analytical data for **2b**: $^1$H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, $J$ = 8.4 Hz, 1H), 7.90 (dd, $J$ = 7.9, 1.7 Hz, 1H), 7.84 (d, $J$ = 8.2 Hz, 1H), 7.65 (dd, $J$ = 7.0, 1.1 Hz, 1H), 7.54 (dddd, $J$ = 20.2, 8.0, 6.7, 1.4 Hz, 2H), 7.45 (dd, $J$ = 8.2, 7.1 Hz, 1H), 7.11 (td, $J$ = 7.7, 1.7 Hz, 1H), 7.08 (dd, $J$ = 7.4, 1.6 Hz, 1H), 6.90 (td, $J$ = 7.4, 1.1 Hz, 1H), 6.79 (d, $J$ = 8.0 Hz, 1H), 6.65 (dd, $J$ = 9.7, 2.1 Hz, 1H), 6.62 (t, $J$ = 2.7 Hz, 1H), 5.92 (dd, $J$ = 9.8, 3.3 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 153.9, 135.8, 134.5, 131.3, 129.9, 129.6, 129.2, 127.1, 126.8, 126.24, 126.16, 125.7, 125.3, 125.2, 124.4, 122.0, 121.7, 116.6, 75.2; IR (film): 3072, 3042, 1640, 1605, 1510, 1485, 1456, 1307, 1228, 1200, 1112, 1060, 1036, 1010, 959, 944 cm$^{-1}$; HRMS (EI): Mass calculated for $[M]^+$ $C_{19}H_{14}O$: 258.1045; found 258.1036; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OJ-H; 100% hexanes; 0.7 mL/min, 280 nm), $Rt_1$ (minor) =61.2, $Rt_2$ (major) = 83.9 min; er = 94:6.

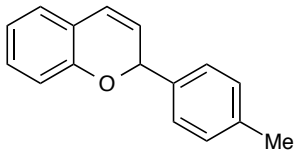


**2-(Naphthalen-2-yl)-2*H*-chromene (2c).** Prepared according to the general procedure using **1c**. The residue was purified by flash chromatography using 1% EtOAc/hexanes to afford **2c** as a light yellow oil (81 mg, 87%). Analytical data for **2c**: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 4H), 7.61 (dd, $J$ = 8.5, 1.8 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.12 (td, $J$ = 7.8, 1.7 Hz, 1H), 7.04 (dd, $J$ = 7.5, 1.6 Hz, 1H), 6.88 (td, $J$ = 7.5, 1.2 Hz, 1H), 6.81 (dt, $J$ = 8.2, 1.0 Hz, 1H), 6.59 (ddd, $J$ = 10.0, 1.9, 0.8 Hz, 1H), 6.09 (dd, $J$ = 3.4, 1.9 Hz, 1H), 5.88 (dd, $J$ = 9.9, 3.4 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 153.3, 138.2, 133.4, 133.3, 129.7, 128.8, 128.3, 127.8, 126.8, 126.4 (2C), 126.2, 125.1, 124.8, 124.4, 121.5, 121.4, 116.2, 77.4; IR (film): 3072, 1640, 1510, 1228 cm$^{-1}$; HRMS (EI): Mass calculated for $[M]^+$ $C_{19}H_{14}O$: 258.1045; found 258.1022; Enantiomeric ratio was measured by chiral phase HPLC (Whelk-O; 100% hexanes; 0.7 mL/min, 280 nm), $Rt_1$ (minor) =35.7, $Rt_2$ (major) = 66.8 min; er = 91:9.

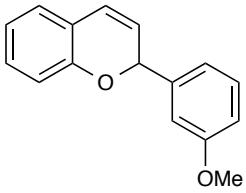



**2-(*o*-Tolyl)-2*H*-chromene (2d).** Prepared according to the general procedure using **1d**. The residue was purified by flash chromatography using 1% EtOAc/hexanes to afford **2d** as a yellow oil (58 mg, 72%). Analytical data for **2d**: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.48 (dt, $J$ = 7.0, 1.2 Hz, 1H), 7.24 – 7.18 (m, 3H), 7.11 (td, $J$ = 7.8, 1.7 Hz, 1H), 7.02 (dd, $J$ = 7.4, 1.7 Hz, 1H), 6.87 (td, $J$ = 7.4, 1.1 Hz, 1H), 6.77 (dt, $J$ = 8.1, 0.9 Hz, 1H), 6.56 (dd, $J$ = 9.8, 2.1 Hz, 1H), 6.15 (dd, $J$ = 3.1,

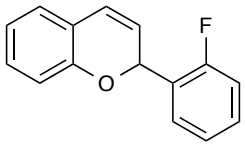
2.1 Hz, 1H), 5.75 (dd, *J* = 9.8, 3.2 Hz, 1H), 2.47 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 153.6, 138.4, 136.1, 131.0, 129.5, 128.5, 127.8, 126.7, 126.3, 124.7, 124.6, 121.5, 121.3, 116.1, 74.8, 19.4; IR (film): 3061, 3022, 2971, 2924, 1646,1633, 1586,1563, 1485 cm$^{-1}$; HRMS (EI): Mass calculated for $[M]^+$ $C_{16}H_{14}O$: 222.1045; found 222.1018; Enantiomeric ratio was measured by chiral phase HPLC (Whelk-O; 100% hexanes; 0.1 mL/min, 280 nm), $Rt_1$ (minor) =100.9, $Rt_2$ (major) = 118.5 min; er = 92:8.




**2-(*p*-Tolyl)-2*H*-chromene (2e).** Prepared according to the general procedure using **1e**. The residue was purified by flash chromatography using 1% EtOAc/hexanes to afford **2e** as a yellow oil (58 mg, 73%). Analytical data for **2e**: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.12 (td, *J* = 7.7, 1.7 Hz, 1H), 7.03 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.88 (td, *J* = 7.5, 1.2 Hz, 1H), 6.80 (dt, *J* = 8.1, 0.9 Hz, 1H), 6.55 (dd, *J* = 9.9, 1.9 Hz, 1H), 5.90 (dd, *J* = 3.4, 1.9 Hz, 1H), 5.81 (dd, *J* = 9.8, 3.4 Hz, 1H), 2.37 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 153.3, 138.4, 138.0, 129.6, 129.5, 127.2, 126.7, 125.1, 124.1, 121.5, 121.3, 116.2, 77.4, 21.6; IR (film): 3044, 2958, 2851,1633,1484 cm$^{-1}$; HRMS (EI): Mass calculated for $[M]^+$ $C_{16}H_{14}O$: 222.1045; found 222.1015; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OJ-H; 100% hexanes; 0.7 mL/min, 280 nm), $Rt_1$ (major) =62.3, $Rt_2$ (minor) =124.4 min; er = 93:7.

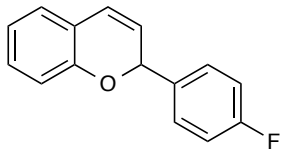



**2-(3-Methoxyphenyl)-2*H*-chromene (2f).** Prepared according to the general procedure using **1f**. The residue was purified by flash chromatography using 1.5% EtOAc/hexanes to afford **2f** as a light yellow oil (67 mg, 78%). Analytical data for **2f**: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.9 Hz, 1H), 7.14 – 7.08 (m, 1H), 7.06 – 6.98 (m, 3H), 6.89 – 6.84 (m, 2H), 6.80 (dt, *J* = 8.0, 0.9 Hz, 1H), 6.55 – 6.50 (m, 1H), 5.91 – 5.87 (m, 1H), 5.79 (dd, *J* = 9.8, 3.4 Hz, 1H), 3.80 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 160.2, 153.5, 142.8, 130.1, 129.9, 127.0, 125.2, 124.4, 121.7, 121.6, 119.7, 116.4, 114.2, 112.9, 55.6, 53.8; IR (film): 3043, 3009, 2959, 2834, 1610,1485,1286,1227, 788 cm$^{-1}$; HRMS (EI): Mass calculated for $[M]^+$ $C_{16}H_{14}O_2$: 238.0994; found 238.0983; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OJ-H; 100% hexanes; 0.7 mL/min, 280 nm), $Rt_1$ (minor) =102.8, $Rt_2$ (major) = 127.3 min; er = 94:6.

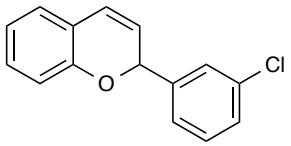



**2-(2-Fluorophenyl)-2*H*-chromene (2g).** Prepared according to the general procedure using **1g**. The residue was purified by flash chromatography using 0.8% EtOAc/hexanes to afford **2g** as a light yellow oil (61 mg, 75%). Analytical data for **2g**: $^1$H NMR (500 MHz, $CDCl_3$) δ7.51 (td, *J* =

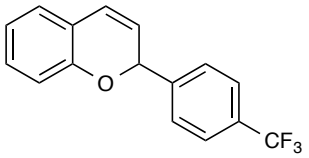
7.6, 1.8 Hz, 1H), 7.30 (dddd, *J* = 8.2, 7.2, 5.3, 1.8 Hz, 1H), 7.15 – 7.11 (m, 2H), 7.08 (ddd, *J* = 10.3, 8.3, 1.2 Hz, 1H), 7.01 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.88 (td, *J* = 7.4, 1.1 Hz, 1H), 6.81 (dt, *J* = 8.1, 1.0 Hz, 1H), 6.54 (ddd, *J* = 9.9, 1.9, 0.8 Hz, 1H), 6.29 (dd, *J* = 3.6, 1.9 Hz, 1H), 5.79 (ddd, *J* = 10.0, 3.6, 1.1 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 159.6 (d, *J* = 247.4 Hz), 153.2, 130.0 (d, *J* = 8.2 Hz), 129.7, 128.7 (d, *J* = 3.9 Hz), 128.1 (d, *J* = 13.4 Hz), 126.8, 124.5 (d, *J* = 3.6 Hz), 124.4, 123.8, 121.5, 121.2, 116.1, 115.7 (d, *J* = 21.4 Hz), 71.2 (d, *J* = 3.8 Hz); IR (film): 3044, 2923, 2851, 1641, 1485 cm$^{-1}$; HRMS (EI): Mass calculated for $[M]^+$ $C_{15}H_{11}FO$: 226.0794; found: 226.0808; Enantiomerljic ratio was measured by chiral phase HPLC (Chiralcel OJ-H; 100% hexanes; 0.7 mL/min, 280 nm), $Rt_1$ (minor) =22.2, $Rt_2$ (major) = 35.3 min; er = 91:9.



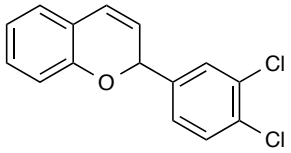

**2-(4-Fluorophenyl)-2*H*-chromene (2h).** Prepared according to the general procedure using **1h**. The residue was purified by flash chromatography using 1% EtOAc/hexanes to afford **2h** as a light yellow oil (69 mg, 84%). Analytical data for **2h**: $^1$H NMR (500 MHz, $CDCl_3$) δ7.43 (td, *J* = 5.9, 5.3, 1.9 Hz, 2H), 7.12 (td, *J* = 7.8, 1.7 Hz, 1H), 7.05 (t, *J* = 8.7 Hz, 2H), 7.02 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.88 (td, *J* = 7.4, 1.1 Hz, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 6.56 (dd, *J* = 9.9, 1.9 Hz, 1H), 5.90 (dd, *J* = 3.5, 1.9 Hz, 1H), 5.78 (dd, *J* = 9.9, 3.4 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 162.8 (d, *J* = 246.8 Hz), 153.0, 136.7 (d, *J* = 3.2 Hz), 129.7, 129.1 (d, *J* = 8.3 Hz), 126.8, 124.6, 124.4, 121.44, 121.35, 116.2, 115.7 (d, *J* = 21.5 Hz), 76.5; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -113.75; IR (film): 2922, 2852, 1719, 1603, 1509, 1484, 1457, 1224, 1204 cm$^{-1}$; HRMS (EI): Mass calculated for $[M]^+$ $C_{15}H_{11}FO$: 226.0794; found: 226.0764 ; Enantiomeric ratio was measured by chiral phase HPLC (Whelk-O; 100% hexanes; 1.0 mL/min, 280 nm), $Rt_1$ (minor) =9.5, $Rt_2$ (major) = 10.5 min; er = 95:5.



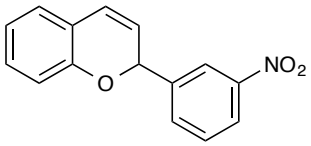

**2-(3-Chlorophenyl)-2*H*-chromene (2i).** Prepared according to the general procedure using **1i**. The residue was purified by flash chromatography using 0.6% EtOAc/hexanes to afford **2i** as a light yellow oil (71 mg, 81%). Analytical data for **2i**: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.46 (q, *J* = 1.4 Hz, 1H), 7.34 (qd, *J* = 4.3, 1.5 Hz, 1H), 7.32 – 7.30 (m, 2H), 7.14 (td, *J* = 7.8, 1.7 Hz, 1H), 7.03 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.89 (td, *J* = 7.4, 1.2 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.56 (dd, *J* = 9.9, 1.9 Hz, 1H), 5.90 (dd, *J* = 3.5, 1.9 Hz, 1H), 5.78 (dd, *J* = 9.9, 3.4 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 152.9, 142.9, 134.6, 130.1, 129.8, 128.6, 127.3, 126.8, 125.2, 124.6, 124.1, 121.6, 121.2, 116.1, 76.4; IR (film): 3048, 2923, 2847,1638, 1602, 1574, 1483, 1457, 1430, 1349 cm$^{-1}$; HRMS (EI): Mass calculated for $[M]^+$ $C_{15}H_{11}ClO$: 242.0498; found: 242.0508; Enantiomeric ratio was measured by chiral phase HPLC (Whelk-O; 100% hexanes; 0.35 mL/min, 280 nm), $Rt_1$ (minor) =27.0, $Rt_2$ (major) = 31.7 min; er = 93:7.




**2-(4-(Trifluoromethyl)phenyl)-2*H*-chromene (2j).** Prepared according to the general procedure using **1j**. The residue was purified by flash chromatography using 1% EtOAc/hexanes to afford **2j** as a light yellow oil (66 mg, 84%). Analytical data for **2j**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.14 (td, *J* = 7.8, 1.6 Hz, 1H), 7.02 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.89 (td, *J* = 7.5, 1.1 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.57 (dd, *J* = 9.8, 1.8 Hz, 1H), 5.97 (s, 1H), 5.79 (dd, *J* = 9.8, 3.5 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 152.9, 144.8, 130.5 (d, *J* = 32.4 Hz), 129.9, 127.3, 126.9, 125.8 (q, *J* = 3.8 Hz), 124.7, 124.1 (d, *J* = 272.0 Hz), 124.0, 121.7, 121.2, 116.1, 76.4; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -62.64; IR (film): 3047, 2925, 2854, 1620, 1574, 1485, 1457, 1418, 1325 cm$^{-1}$; HRMS (EI): Mass calculated for $[M]^+$ $C_{16}H_{11}F_3O$: 276.0762; found: 276.0736; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OJ-H; 100% hexanes; 0.7 mL/min, 280 nm), $Rt_1$ (minor) =30.8, $Rt_2$ (major) =44.4 min; er = 83:17.

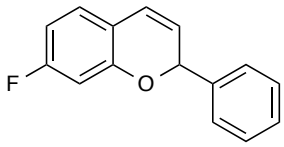



**2-(3,4-Dichlorophenyl)-2*H*-chromene (2k).** Prepared according to the general procedure using **1k**. The residue was purified by flash chromatography using 1% EtOAc/hexanes to afford **2k** as a light yellow oil (74 mg, 74%). Analytical data for **2k**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 2.1 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.29 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.13 (td, *J* = 7.8, 1.7 Hz, 1H), 7.02 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.89 (td, *J* = 7.5, 1.1 Hz, 1H), 6.79 (dt, *J* = 8.0, 0.9 Hz, 1H), 6.57 (dd, *J* = 9.7, 1.4 Hz, 1H), 5.87 (dd, *J* = 3.6, 1.8 Hz, 1H), 5.76 (dd, *J* = 9.8, 3.5 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 153.0, 141.3, 133.1, 132.7, 131.0, 130.2, 129.5, 127.2, 126.7, 125.2, 123.9, 122.0, 121.4, 116.4, 76.0; IR (film): 3076, 2924, 2827, 1641, 1486 cm$^{-1}$; HRMS (EI): Mass calculated for $[M]^+$ $C_{15}H_{10}Cl_2O$: 276.0109; found: 276.0137; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OJ-H; 100% hexanes; 0.5 mL/min, 280 nm), $Rt_1$ (major) =78.0, $Rt_2$ (minor) =133.5 min; er = 90:10.

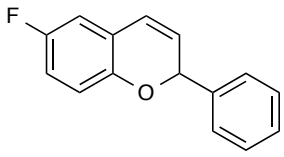



**2-(3-Nitrophenyl)-2*H*-chromene (2l).** Prepared according to the general procedure using **1l**. The residue was purified by flash chromatography using 1% EtOAc/hexanes to afford **2l** as a light yellow oil (65 mg, 71%). Analytical data for **2l**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.32 (q, *J* = 1.9 Hz, 1H), 8.18 (ddt, *J* = 8.4, 2.6, 1.3 Hz, 1H), 7.81 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.55 (td, *J* = 8.0, 1.8 Hz, 1H), 7.15 (tt, *J* = 7.6, 1.7 Hz, 1H), 7.04 (dt, *J* = 7.6, 1.8 Hz, 1H), 6.90 (tt, *J* = 7.5, 1.4 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.62 (dt, *J* = 10.0, 1.9 Hz, 1H), 6.02 (dd, *J* = 3.7, 1.9 Hz, 1H), 5.83 (ddd, *J* = 9.8, 3.6, 1.7 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 152.7, 148.5, 143.0, 133.2, 130.0, 129.8, 127.0, 125.3, 123.4, 123.3, 122.1, 121.9, 121.2, 116.2, 75.7; IR (film): 3065, 3032, 2920, 2845, 1645, 1612, 1587, 1500, 1454, 1432, 1264, 1160, 1138, 1105, 1036, 982 cm$^{-1}$; HRMS

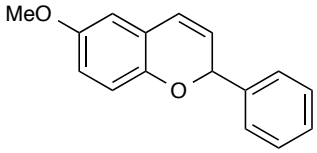
(EI): Mass calculated for $[M]^+$ $C_{15}H_{11}NO_3$: 253.0739; found: 253.0715; Enantiomeric ratio was measured by chiral phase HPLC (Whelk-O; 100% hexanes; 0.2 mL/min, 280 nm), $Rt_1$ (minor) =48.0, $Rt_2$ (major) =51.8 min; er = 92:8.




**7-Fluoro-2-phenyl-2*H*-chromene (2m).** Prepared according to the general procedure using **1m**. The residue was purified by flash chromatography using 0.5% EtOAc/hexanes to afford **2m** as a light yellow oil (56 mg, 69%). Analytical data for **2m**: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.32 (m, 5H), 6.96 (dd, *J* = 8.3, 6.4 Hz, 1H), 6.57 (td, *J* = 8.4, 2.5 Hz, 1H), 6.51 (ddd, *J* = 10.0, 3.7, 2.1 Hz, 2H), 5.91 (q, *J* = 3.1, 1.9 Hz, 1H), 5.76 (dd, *J* = 9.9, 3.4 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 163.4 (d, *J* = 246.7 Hz), 154.5 (d, *J* = 12.4 Hz), 140.5, 128.9, 128.7, 127.55 (d, *J* = 10.0 Hz), 127.2, 123.6 (d, *J* = 2.6 Hz), 123.3, 117.7 (d, *J* = 3.2 Hz), 108.0 (d, *J* = 21.9 Hz), 104.1 (d, *J* = 25.1 Hz), 77.4; IR (film): 3065, 3032, 2920, 2845, 1645,1612, 1587, 1500, 1454, 1432, 1264, 1160, 1137, 1105, 1036, 982, 852 $cm^{-1}$; HRMS (EI): Mass calculated for $[M]^+$ $C_{15}H_{11}FO$: 226.0794; found: 226.0804; Enantiomeric ratio was measured by chiral phase HPLC (Whelk-O; 100% hexanes; 0.2 mL/min, 280 nm), $Rt_1$ (minor) =45.9, $Rt_2$ (major) =52.6 min; er = 90:10.

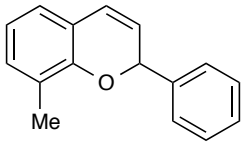



**6-Fluoro-2-phenyl-2*H*-chromene (2n).** Prepared according to the general procedure using **1n**. The residue was purified by flash chromatography using 0.5% EtOAc/hexanes to afford **2n** as white solids (59 mg, 72%). Analytical data for **2n**: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.43 (dt, *J* = 6.9, 2.1, 1.6 Hz, 2H), 7.40 – 7.31 (m, 3H), 6.79 (td, *J* = 8.5, 3.0 Hz, 1H), 6.76 – 6.69 (m, 2H), 6.49 (dt, *J* = 7.7, 3.1, 2.6 Hz, 1H), 5.91 – 5.85 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 157.4 (d, *J* = 238.3 Hz), 149.1 (d, *J* = 1.8 Hz), 140.3, 128.7, 128.6, 127.1, 126.4, 123.6 (d, *J* = 2.1 Hz), 122.3 (d, *J* = 8.4 Hz), 116.9 (d, *J* = 8.1 Hz), 115.5 (d, *J* = 23.2 Hz), 112.8 (d, *J* = 23.8 Hz), 77.2; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -123.28; IR (film): 3063, 3032, 2954, 2921, 2851, 1639, 1582, 1485, 1455, 1441, 1371 $cm^{-1}$; HRMS (EI): Mass calculated for $[M]^+$ $C_{15}H_{11}FO$: 226.0794; found: 226.0798; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OJ-H; 100% hexanes; 0.7 mL/min, 280 nm), $Rt_1$ (minor) =66.2, $Rt_2$ (major) =77.0 min; er = 97:3.




**6-Methoxy-2-phenyl-2*H*-chromene (2o).** Prepared according to the general procedure using **1o**. The residue was purified by flash chromatography using 1% EtOAc/hexanes to afford **2o** as a light yellow oil (68 mg, 80%). Analytical data for **2o**: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2H), 7.40 – 7.29 (m, 3H), 6.73 (d, *J* = 8.8 Hz, 1H), 6.67 (ddd, *J* = 8.9, 3.1, 1.2 Hz, 1H), 6.59 (dd, *J* = 3.2, 1.2 Hz, 1H), 6.54 – 6.46 (m, 1H), 5.88 – 5.82 (m, 2H), 3.76 (d, *J* = 1.4 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 154.1, 147.1, 140.8, 128.8, 128.5, 127.2, 126.0, 124.3, 122.2, 116.7,

114.6, 111.9, 77.1, 55.9; IR (film): 3033, 2998, 2915, 2831, 1609, 1576, 1490, 1429, 1344, 1307, 1265, 1208, 1158, 1117, 1045 $cm^{-1}$; HRMS (EI): Mass calculated for $[M]^+$ $C_{16}H_{14}O_2$: 238.0994; found 238.0970; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OJ-H; 40% IPA/ hexanes; 1.0 mL/min, 280 nm), $Rt_1$ (minor) =23.4, $Rt_2$ (major) =33.6 min; er = 86:14.



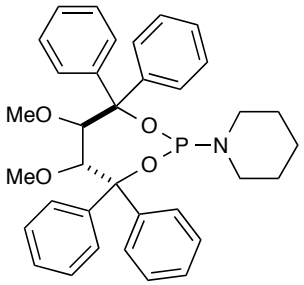

**8-Methyl-2-phenyl-2*H*-chromene (2p).** Prepared according to the general procedure using **1p**. The residue was purified by flash chromatography using 0.1% EtOAc/hexanes to afford **2p** as a light yellow oil (58 mg, 73%). Analytical data for **2p**: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.5 Hz, 2H), 7.39 – 7.29 (m, 3H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.77 (t, *J* = 7.5 Hz, 1H), 6.52 (dd, *J* = 9.9, 1.8 Hz, 1H), 5.94 (dd, *J* = 3.7, 1.8 Hz, 1H), 5.82 (dd, *J* = 9.8, 3.6 Hz, 1H), 2.16 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 151.5, 141.6, 131.3, 128.9 (2C), 128.5, 127.1 (2C), 125.6, 124.9, 124.7 (2C), 121.3, 120.9, 77.0, 16.0; IR (film): 3062, 3044, 3029, 2920, 2851, 1644, 1602, 1494, 1455, 1390, 1344, 1304, 1264, 1208, 1178, 1156, 1082, 1055, 1029, 1001, 968, 939, 917 $cm^{-1}$; HRMS (EI): Mass calculated for $[M]^+$ $C_{16}H_{14}O$: 222.1045; found 222.1031; Enantiomeric ratio was measured by chiral phase HPLC (Chiralcel OJ-H; 5 %IPA/ hexanes; 1.0 mL/min, 280 nm), $Rt_1$ (minor) =8.7, $Rt_2$ (major) =12.5 min; er = 85:15.

**General Procedure for Racemic Synthesis of Chromenes**

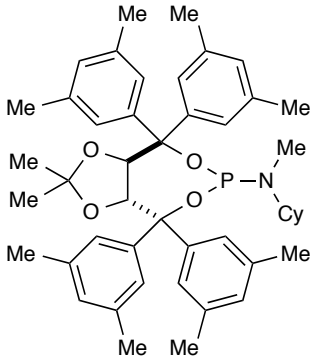
To a round bottom flask equipped with magnetic stir bar was dissolved 2'-hydroxychalcone derivative (0.5 mmol, 1 equiv) in isopropanol (5 mL). Mixture was heated to 70 °C before $NaBH_4$ (1.5 mmol, 3 equiv.) was added in one portion and was slowly cooled to 23 °C. Ice was added and the resulting solution was acidified using 10% glacial acetic acid to pH 5. The solution was extracted with $CH_2Cl_2$, organics washed with brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography with EtOAc/hexanes to afford the corresponding chromenes.

**Synthesis of Ligand**

To a solution of diol (2.94 mmol, 1 equiv) and triethylamine (14.68 mmol, 5 equiv) in dry, oxygen-free THF (18 mL) at 0 °C was added $PCl_3$ (3.52 mmol, 1.2 equiv). After stirring for 2 h at 23 °C under positive $N_2$ pressure, reaction was cooled to 0 °C before a solution of piperidine (5.87 mmol, 2 equiv) in dry, oxygen-free THF (10 mL) was slowly added via cannula. The resulting mixture was slowly warmed to 23 °C and stirred for 20 h under positive $N_2$ pressure. Reaction was diluted with $Et_2O$, filtered through a plug of Celite®, and concentrated under reduced pressure. The residue was purified by flash chromatography using EtOAc/hexanes to afford the corresponding phosphoramidites.

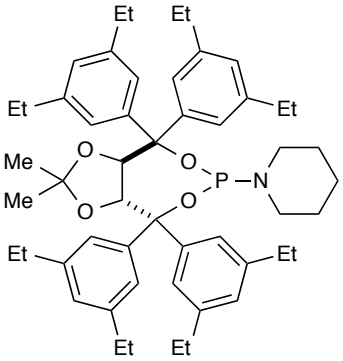



**1-((5*R*,6*R*)-5,6-Dimethoxy-4,4,7,7-tetraphenyl-1,3,2-dioxaphosphepan-2-yl)piperidine (L4).** Prepared according to the general procedure using (2*R*,3*R*)-2,3-dimethoxy-1,1,4,4-tetraphenylbutane-1,4-diol. The residue was purified by flash chromatography using 1% EtOAc/hexanes to afford **L4** as a white foam (44 mg, 65%). Analytical data for **L4**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.0 Hz, 2H), 7.53 (d, *J* = 7.3 Hz, 2H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.36 – 7.18 (m, 14H), 4.50 (dd, *J* = 7.3, 3.6 Hz, 1H), 4.30 (d, *J* = 7.3 Hz, 1H), 3.26 (s, 3H), 3.16 (dtd, *J* = 15.1, 7.0, 3.1 Hz, 2H), 2.83 (m, 2H), 2.58 (s, 3H), 1.54 – 1.37 (m, 6H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 146.6, 146.5, 142.3, 141.92, 141.89, 129.10, 129.08, 128.7, 128.0, 127.6, 127.43, 127.39, 127.3, 127.24, 127.22, 126.88, 126.85, 126.8, 84.74, 84.69, 83.7, 82.4, 82.3, 81.0, 80.9, 59.7, 59.4, 45.1, 44.9, 26.94, 26.91, 25.1; $^{31}$P NMR (162 MHz, $CDCl_3$) δ 133.2; IR (film): 3089, 3057, 3034, 3024, 2932, 2848, 2831, 1599, 1582, 1492,1445, 1372, 1334, 1316, 1265, 1213, 1184.22 1128, 1041, 974, 947, 805 $cm^{-1}$; LRMS (ESI): Mass calculated for $[M+H]^+$ $C_{35}H_{39}NO_4P$: 568.3; found 568.4.




**(3a*R*,8a*R*)-*N*-cyclohexyl-4,4,8,8-tetrakis(3,5-dimethylphenyl)-*N*,2,2-trimethyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-amine (L3j).** Prepared according to the general procedure using ((4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(bis(3,5-dimethylphenyl)methanol). The residue was purified by flash chromatography using 1% EtOAc/hexanes to afford **L3j** as a white foam (195 mg, 77%). Analytical data for **L3j**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.45 (s, 2H), 7.21 (s, 2H), 7.06 (d, *J* = 10.2 Hz, 4H), 6.88 – 6.78 (m, 4H), 5.07 (dd, *J* = 8.5, 3.5 Hz, 1H), 4.65 (d, *J* = 8.5 Hz, 1H), 3.25 (tdd, *J* = 11.8, 8.2, 3.4 Hz, 1H), 2.81 (d, *J* = 7.6 Hz, 3H), 2.29 (s, 6H), 2.27 (s, 6H), 2.26 (s, 12H), 1.88 – 1.70 (m, 4H), 1.60 (d, *J* = 14.4 Hz, 1H), 1.54 – 1.47 (m, 2H), 1.45 (s, 3H), 1.27 (ddt, *J* = 20.8, 12.7, 3.6 Hz, 2H), 1.05 (ddd, *J* = 16.6, 8.4, 3.5 Hz, 1H), 0.22 (s, 3H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 147.5, 147.04, 147.02, 142.3, 142.1, 137.1, 136.8, 136.7, 136.3, 129.0, 128.9, 128.8, 128.7, 127.1, 126.64, 126.61, 125.2, 111.2, 83.61, 83.59, 83.0, 82.8, 81.2, 81.1, 80.72, 80.70, 57.5, 57.2, 32.60, 32.55, 32.5, 32.4, 27.9, 27.6, 27.5, 26.50, 26.48, 25.9, 25.4, 21.84, 21.78, 21.7; $^{31}$P NMR (162 MHz, $CDCl_3$) δ 140.0; IR (film): 3047, 2990, 2930, 2855, 2731, 1787, 1754, 1600, 1450, 1380, 1265, 1214,

1159, 1066, 969, 942, 861, 785, 738, 690, 601, 574, 508, 413 $cm^{-1}$; LRMS (ESI): Mass calculated for $[M+H]^+$ $C_{46}H_{59}NO_4P$: 720.4; found 720.6.




**1-((3a*R*,8a*R*)-4,4,8,8-Tetrakis(3,5-diethylphenyl)-2,2-dimethyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-yl)piperidine (L3k).** Prepared according to the general procedure using ((4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(bis(3,5-diethylphenyl)methanol). The residue was purified by flash chromatography using 1% EtOAc/hexanes to afford **L3k** as a white foam (2.15 g, 91%). Analytical data for **L3k**: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 1.6 Hz, 2H), 7.30 (d, *J* = 1.6 Hz, 2H), 7.13 (s, 2H), 7.05 (d, *J* = 1.6 Hz, 2H), 6.92-6.82 (m, 4H), 5.15 (dd, *J* = 8.5, 3.1 Hz, 1H), 4.78 (d, *J* = 8.5 Hz, 1H), 3.38 – 3.26 (m, 2H), 3.16 (ddd, *J* = 15.0, 8.8, 5.4 Hz, 2H), 2.66 – 2.51 (m, 16H), 1.65 – 1.51 (m, 6H) 1.36 (s, 3H), 1.19 (dtt, *J* = 7.1, 4.3, 2.1 Hz, 24H), 0.18 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 147.2, 146.9, 143.4, 142.9, 142.5, 142.1, 142.0, 126.3, 126.2, 126.2, 126.04, 125.99, 125.96, 124.4, 124.3, 110.9, 83.33, 83.31, 82.8, 82.7, 81.6, 81.5, 81.3, 45.1, 44.9, 29.1, 29.0, 28.93, 28.91, 27.7, 27.2, 27.1, 25.3, 25.1, 15.9, 15.6, 15.4; $^{31}$P NMR (162 MHz, $CDCl_3$) δ 137.2; IR (film): 2964, 2933, 2873, 1600, 1459, 1371, 1333, 1247, 1215, 1160, 1072, 1038, 949, 875, 853, 783, 739, 703, 506, 432, 411 $cm^{-1}$; LRMS (ESI): Mass calculated for $[M+H]^+$ $C_{52}H_{71}NO_4P$: 804.5; found 804.5.

**Synthesis of [Pd($\eta^3$-1,3-diphenylallyl){(*S,S*)-L3g}]$BF_4$**

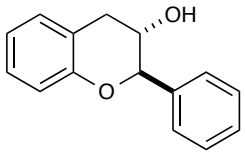
**Bis[($\mu$-chloro)($\eta^3$-1,3-diphenylallyl)palladium(II)].** Prepared according to procedure described by Pregosin and co-workers.[6] $PdCl_2$ (350 mg, 1.95 mmol) and LiCl (350 mg, 8.3 mmol) were stirred in $H_2O$ (2.3 mL) for 45 min. Ethanol (3.9 mL) and (rac)-(*E*)- 3-acetoxy-1,3-diphenyl-1-propene (1 g, 3.97 mmol) in THF (11 mL) were then added, and the brown solution was cooled to 0 °C. After the addition of 1.2 mL of concentrated HCl, carbon monoxide was slowly bubbled through the solution for 15 min. Another 0.8 mL of concentrated HCl was added and CO bubbled for 1.5 h. The stream of CO was then stopped and the solution stirred under CO atmosphere for 7 h at 23 °C. The yellow mixture was filtered, washed with MeOH and $Et_2O$, and dried under vacuum overnight. Spectroscopic data was consistent with those previously reported.[5]

**[Pd($\eta^3$-1,3-diphenylallyl){(*S,S*)-L3g}]$BF_4$.** To a solution of bis[($\mu$-chloro)($\eta^3$-1,3-diphenylallyl)palladium(II)] (12 mg, 0.018 mmol) in anhydrous acetone was added (*S,S*)-**L3g** (25 mg, 0.035 mmol). The mixture was stirred for 2 h at 23 °C. To the yellow solution was added

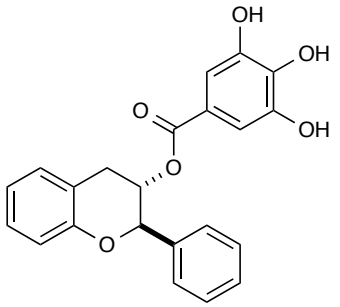
[6] P. Barbaro, A. Currao, J. Herrmann, R. Nesper, P. S. Pregosin, and R. Salzmann, *Organometallics*, 1996, **15**, 1879-1888.

a solution of silver tetrafluoroborate (7.59 mg, 0.039 mmol) in THF. The filtrate was concentrated at reduced pressure, and $CH_2Cl_2$ was added. Pentane was carefully layered on top to induce crystallization and afford **[Pd($\eta^3$-1,3-diphenylallyl){(*S*,*S*)-L3g}]$BF_4$** as yellow needles.

**Synthetic Transformations**



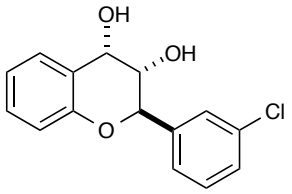

**(2*R*,3*S*)-2-Phenylchroman-3-ol (7).** A solution of 2-phenyl-2*H*-chromene (**2a**) (167 mg, 0.8 mmol) and 1 molar $BH_3$-THF (16 mL) was stirred for 2 h at 23 °C. Solution was cooled to 0 °C before a 20% (w/w) aqueous solution of NaOH (4.8 mL) and 30% (w/w) aqueous solution of $H_2O_2$ (4.9 mL) were added. The reaction was slowly warmed to 23 °C and stirred for 12 h. The solution was then diluted with $Et_2O$ and $H_2O$ followed by acidification with 10% (w/w) aqueous HCl and extraction with $Et_2O$. The organics were combined, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Purification by flash chromatography with 10% EtOAc/hexanes afforded **7** as a white solid (115 mg, 63%). Spectroscopic data was consistent with those previously reported.[2]



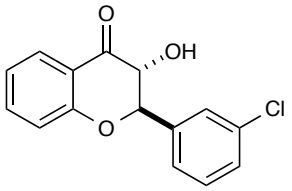

**(2*R*,3*S*)-2-Phenylchroman-3-yl 3,4,5-trihydroxybenzoate (8).** Prepared using a modified literature procedure.[7] To a solution of (2*R*,3*S*)-2-phenylchroman-3-ol (**7**) (91 mg, 0.4 mmol) in $CH_2Cl_2$ (2 mL) was added DMAP (28 mg, 0.23 mmol), $Et_3N$ (0.167 mL, 1.2 mmol) and tri-*O*Bn gallic acid chloride (184 mg, 0.4 mmol). The reaction was stirred for 12 h at 23 °C, washed with $H_2O$ followed by brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The protected gallate ester was taken up in EtOAc (4 mL). To the solution was added 10 wt. % Pd/C (255 mg, 2.4 mmol). The mixture was stirred under an atmosphere of $H_2$ for 14 h, filtered through a plug of Celite®, dried over sodium sulfate, filtered, and concentrated under reduced pressure. Purification by flash chromatography with 30% EtOAc/hexanes afforded **8** as a white solid (89 mg, 59%). Analytical data for **8**: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 7.5, 1.8 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.21 (td, *J* = 7.8, 7.4, 1.7 Hz, 1H), 7.10 (s, 2H), 7.09 – 7.05 (m, 1H), 7.01 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.93 (td, *J* = 7.4, 1.2 Hz, 1H), 5.70 (bs, 1H), 5.55 (td, *J* = 6.0, 4.9 Hz, 1H), 5.46 (bs, 2H), 5.33 (d, *J* = 5.7 Hz, 1H), 3.11 (dd, *J* = 16.7, 4.8 Hz, 1H), 2.96 (dd, *J* = 16.6, 6.1 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 143.1,

[7] J. C. Anderson, R. A. McCarthy, S. Paulin and P. W. Taylor, *Bioorg. Med. Chem. Lett.*, 2011, **21**, 6996-7000.

138.2, 129.8, 128.6, 128.3, 127.9, 126.2, 121.0, 116.5, 109.9, 78.4, 69.9, 28.6. Other spectroscopic data was consistent with those previously reported.[6]



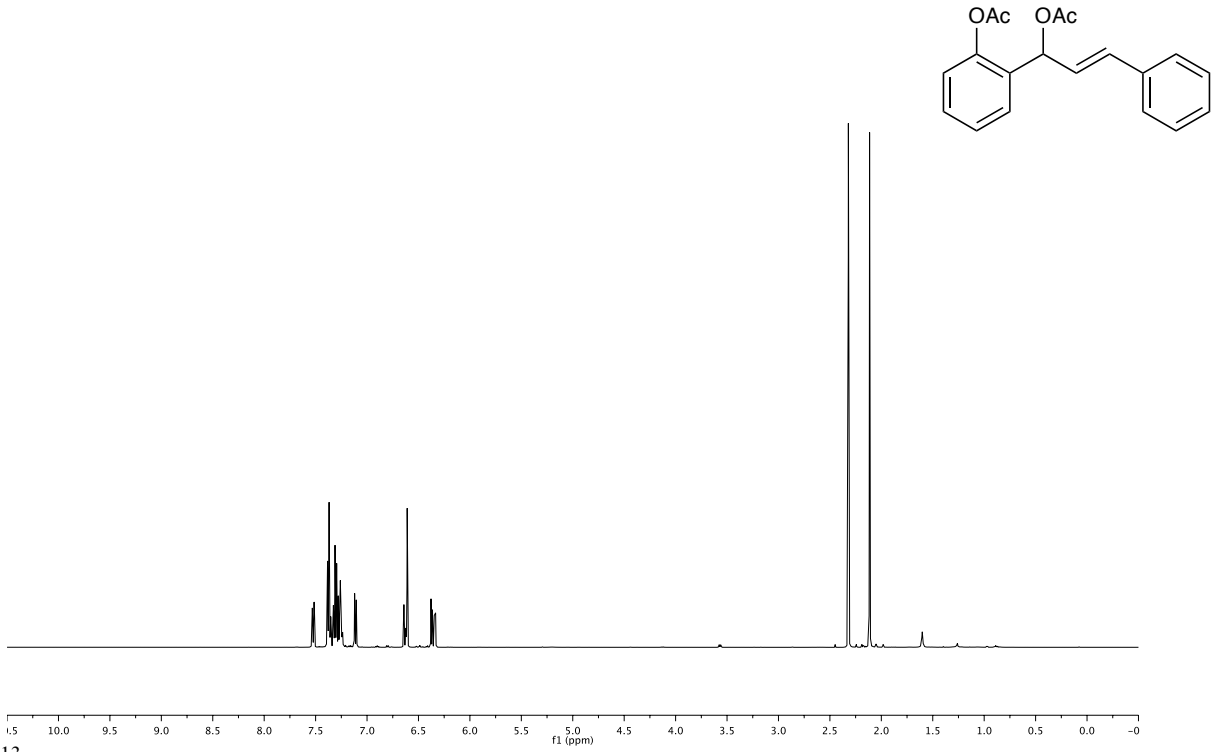

**(2*R*,3*S*,4*S*)-2-(3-Chlorophenyl)chromane-3,4-diol (9).** To a solution of 2-(3-chlorophenyl)-2*H*-chromene (**2i**) (72.8 mg, 0.3 mmol) and 4-methylmorpholine *N*-oxide (52.7 mg, 0.45 mmol) in THF (3 mL) and water (0.116 mL) was added a 2.5 wt % solution of osmium tetraoxide in *t*-BuOH (0.118 mL). The mixture was stirred at 23 °C for 16 h and was then quenched with a saturated solution of sodium thiosulfate. The mixture was extracted with EtOAc. The combined organics was washed with brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude was purified by flash chromatography using 20% EtOAc/hexanes to afford **9** as an off-white solid (76 mg, 91%). Analytical data for **9**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 1H), 7.39 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.37 (d, *J* = 1.4 Hz, 3H), 7.30 (ddd, *J* = 8.6, 7.3, 1.7 Hz, 1H), 7.02 (td, *J* = 7.4, 1.2 Hz, 1H), 6.96 (dd, *J* = 8.2, 1.1 Hz, 1H), 5.05 (d, *J* = 9.5 Hz, 1H), 4.81 (t, *J* = 3.7 Hz, 1H), 4.04 (ddd, *J* = 9.5, 6.6, 3.7 Hz, 1H), 2.57 (d, *J* = 3.7 Hz, 1H), 2.25 (d, *J* = 6.6 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 154.0, 139.9, 134.8, 130.9, 130.7, 130.1, 129.0, 127.8, 125.9, 122.0, 121.7, 117.0, 76.2, 71.1, 66.2; IR (film): 3407, 2919, 2851, 1583, 1485, 1455, 1239, 1036, 1012, 754, 701, 511 cm$^{-1}$; LRMS (ESI): Mass calculated for $[M+H]^+$ $C_{15}H_{14}ClO_3$: 277.1; found 277.1



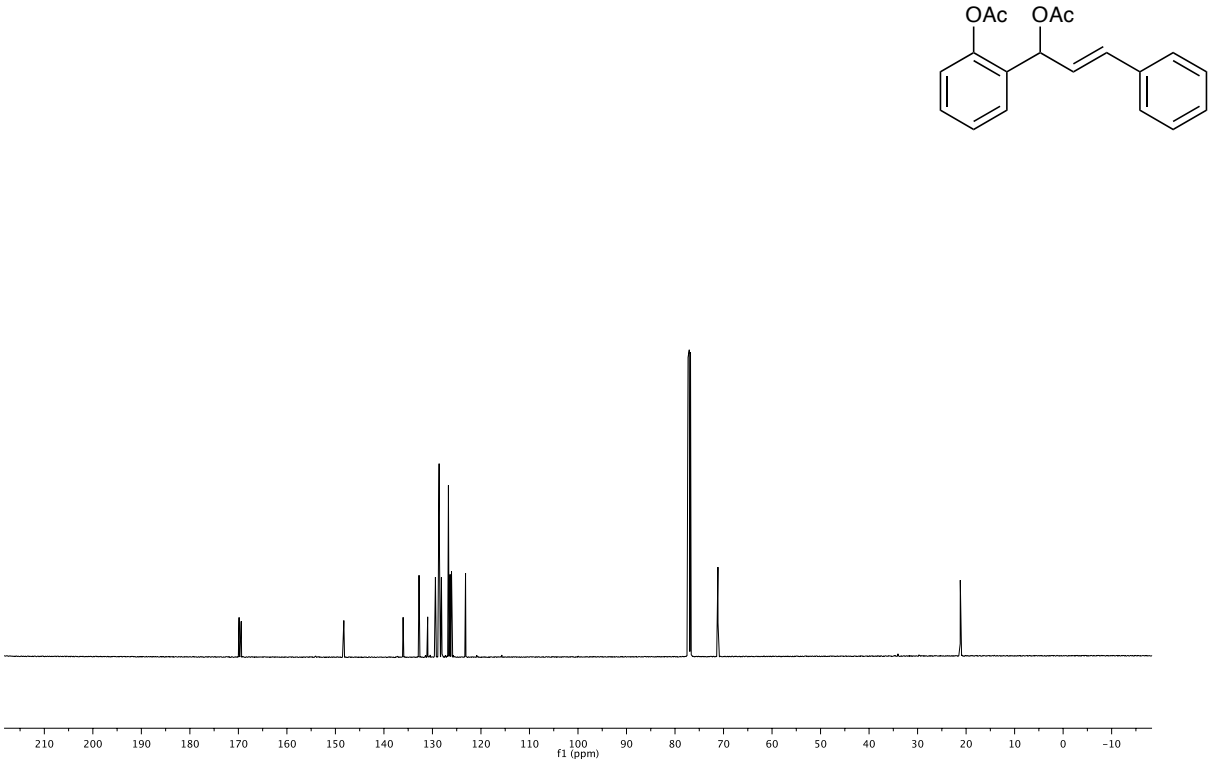

**(2*R*,3*R*)-2-(3-Chlorophenyl)-3-hydroxychroman-4-one (10).** To a solution of (2*R*,3*S*,4*S*)-2-(3-chlorophenyl)chromane-3,4-diol (**9**) (28 mg, 0.1 mmol) in $CH_2Cl_2$ (2 mL) was added manganese dioxide (44 mg, 0.5 mmol). The mixture was stirred at 23 °C for 24 h, filtered through a plug of Celite®, and concentrated under reduced pressure. The crude was purified by flash chromatography using 7% EtOAc/hexanes to afford **10** as a solid (16 mg, 59%). Analytical data for **9**: $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.58 (ddd, *J* = 8.6, 7.2, 1.8 Hz, 1H), 7.48 – 7.45 (m, 1H), 7.42 – 7.38 (m, 2H), 7.14 (ddd, *J* = 8.0, 7.2, 1.0 Hz, 1H), 7.07 (dd, *J* = 8.4, 1.0 Hz, 1H), 5.12 (d, *J* = 12.3 Hz, 1H), 4.57 (dd, *J* = 12.3, 1.9 Hz, 1H), 3.70 (d, *J* = 1.9 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 193.8, 161.5, 138.3, 137.1, 134.6, 129.9, 129.4, 127.6, 127.4, 125.8, 122.4, 118.4, 118.1, 83.0, 73.6; IR (film): 3461, 2921, 2851, 2361, 2341, 1695, 1608, 1579, 1466, 1300, 1229, 1138, 1104, 1009, 861, 764, 693, 419, 405 cm$^{-1}$; LRMS (ESI): Mass calculated for $[M+H]^+$ $C_{15}H_{12}ClO_3$: 275.0; found 275.1.

**Selected NMR Spectra**

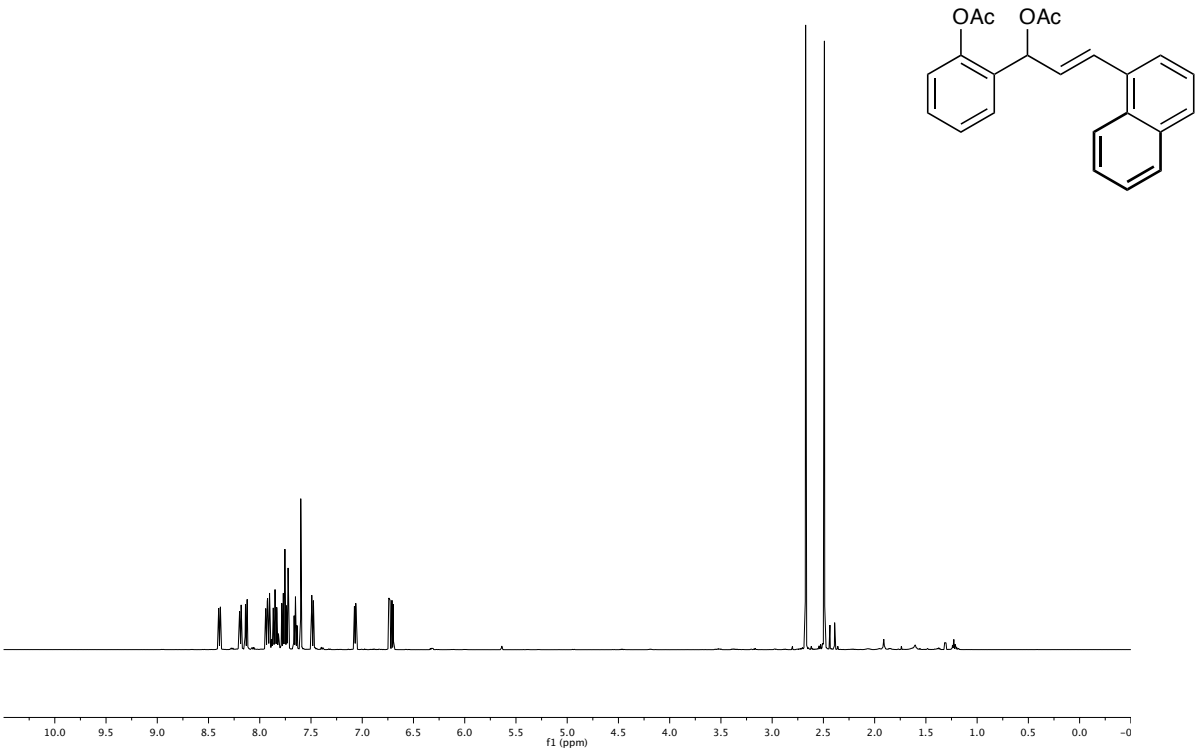
$^{1}$H NMR Spectrum of **1a** (500 MHz, $CDCl_3$):



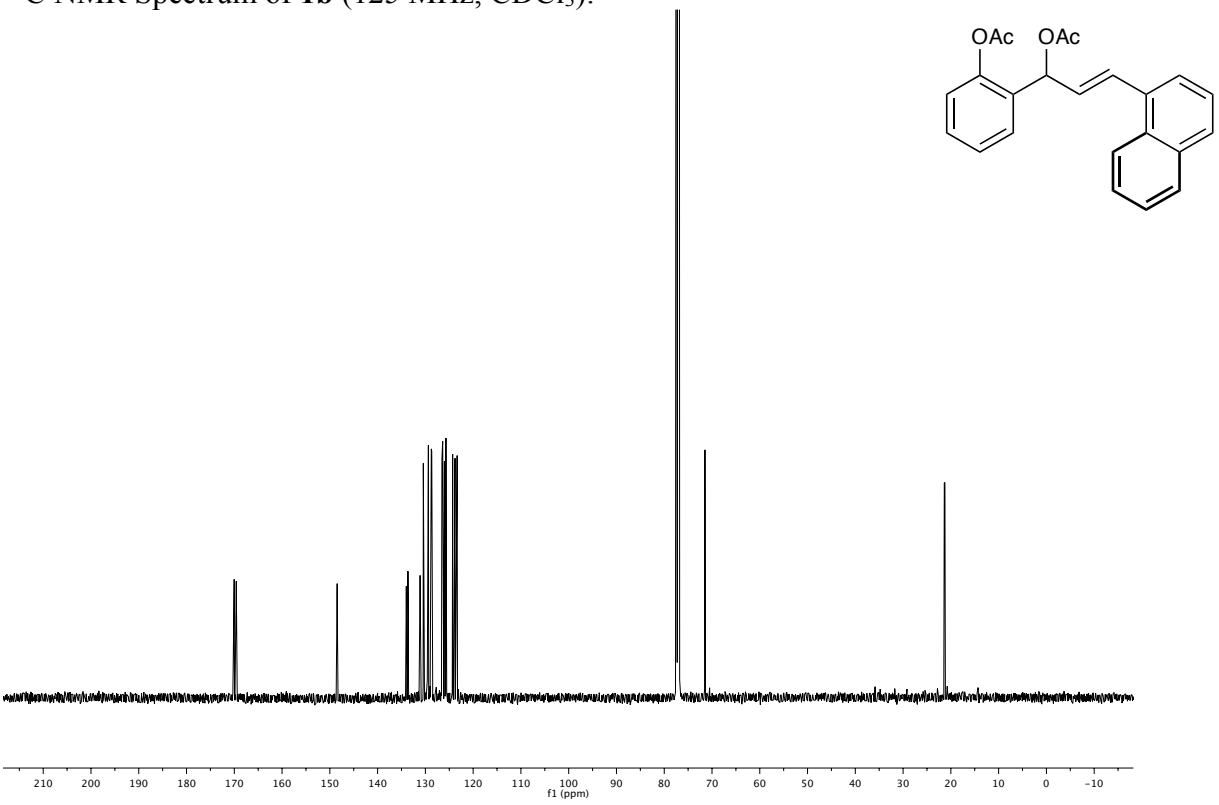

$^{13}$C NMR Spectrum of **1a** (125 MHz, $CDCl_3$):



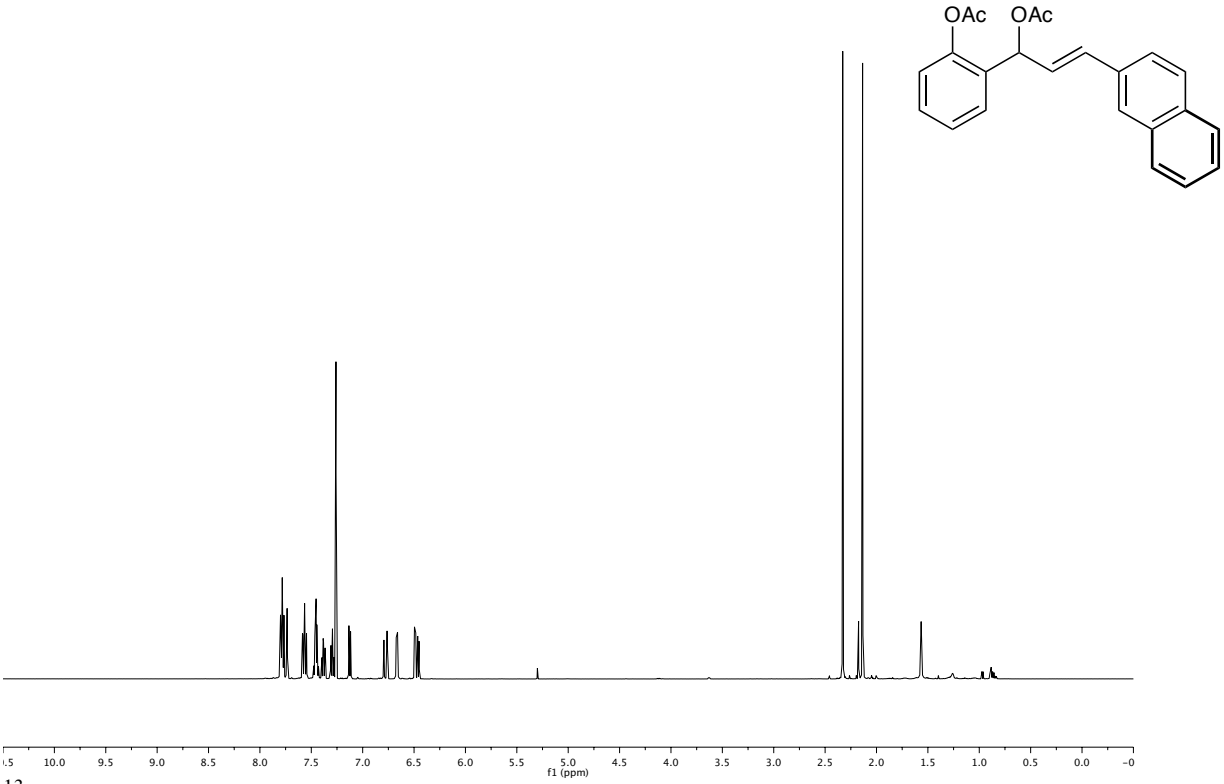
$^{1}$H NMR Spectrum of **1b** (500 MHz, $CDCl_3$):



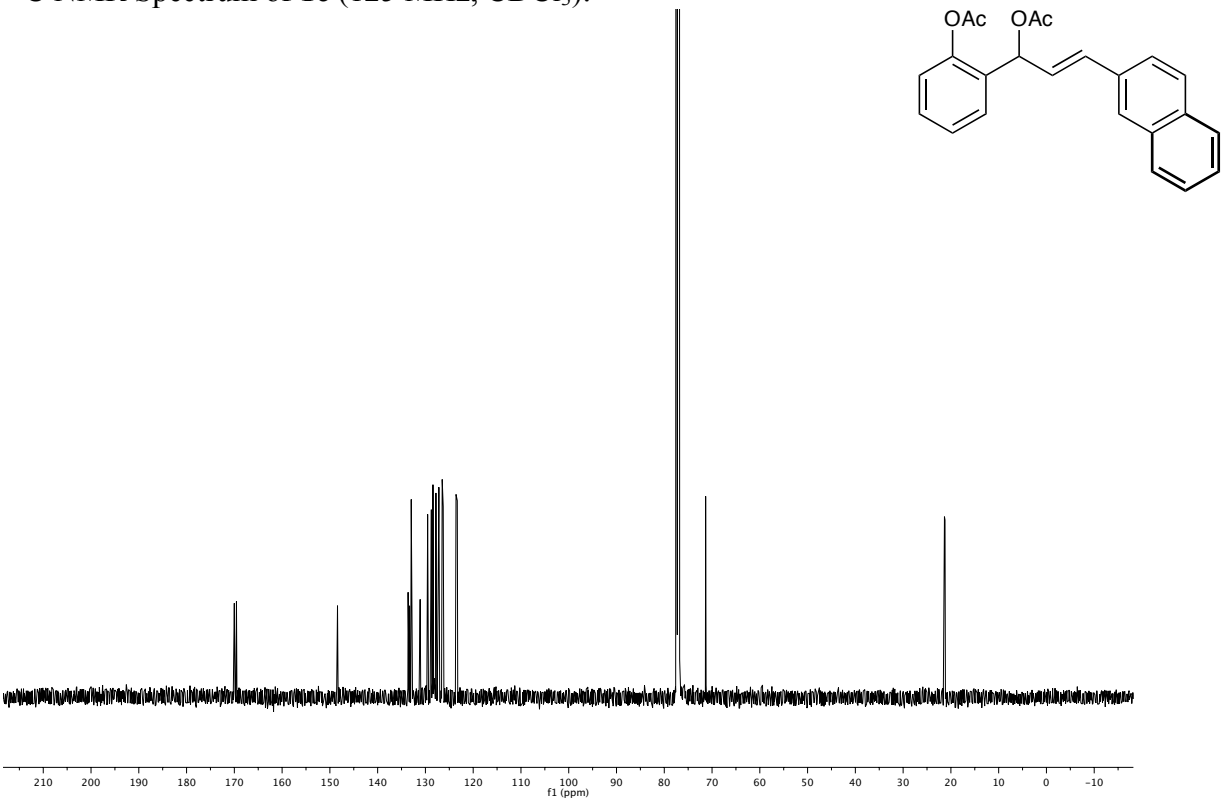

$^{13}$C NMR Spectrum of **1b** (125 MHz, $CDCl_3$):



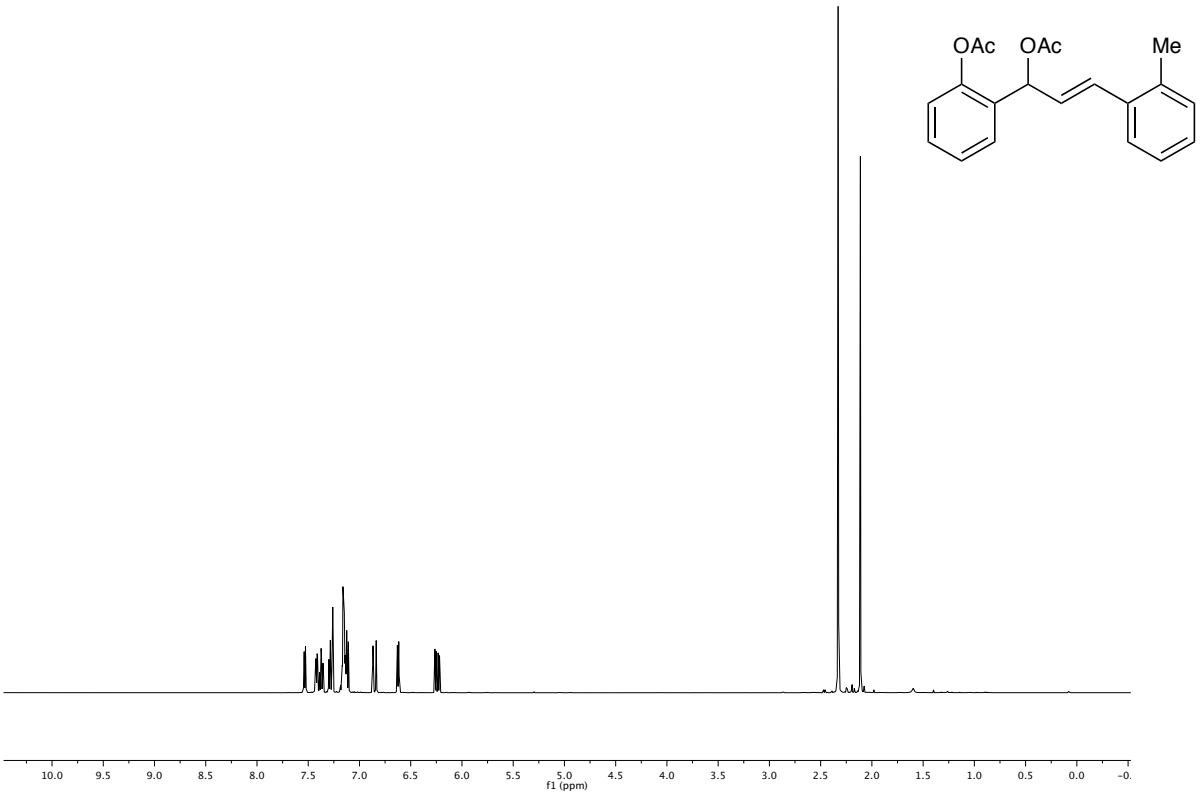
$^{1}$H NMR Spectrum of **1c** (500 MHz, $CDCl_3$):



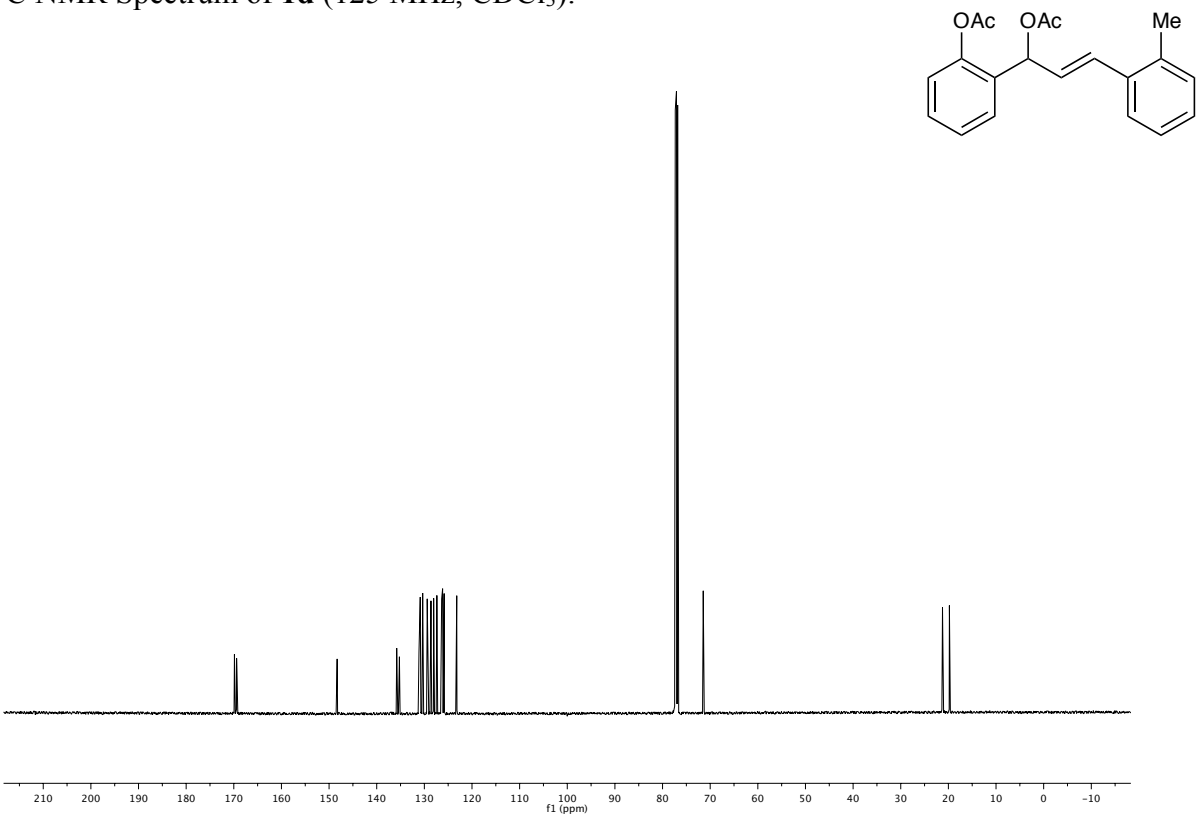

$^{13}$C NMR Spectrum of **1c** (125 MHz, $CDCl_3$):



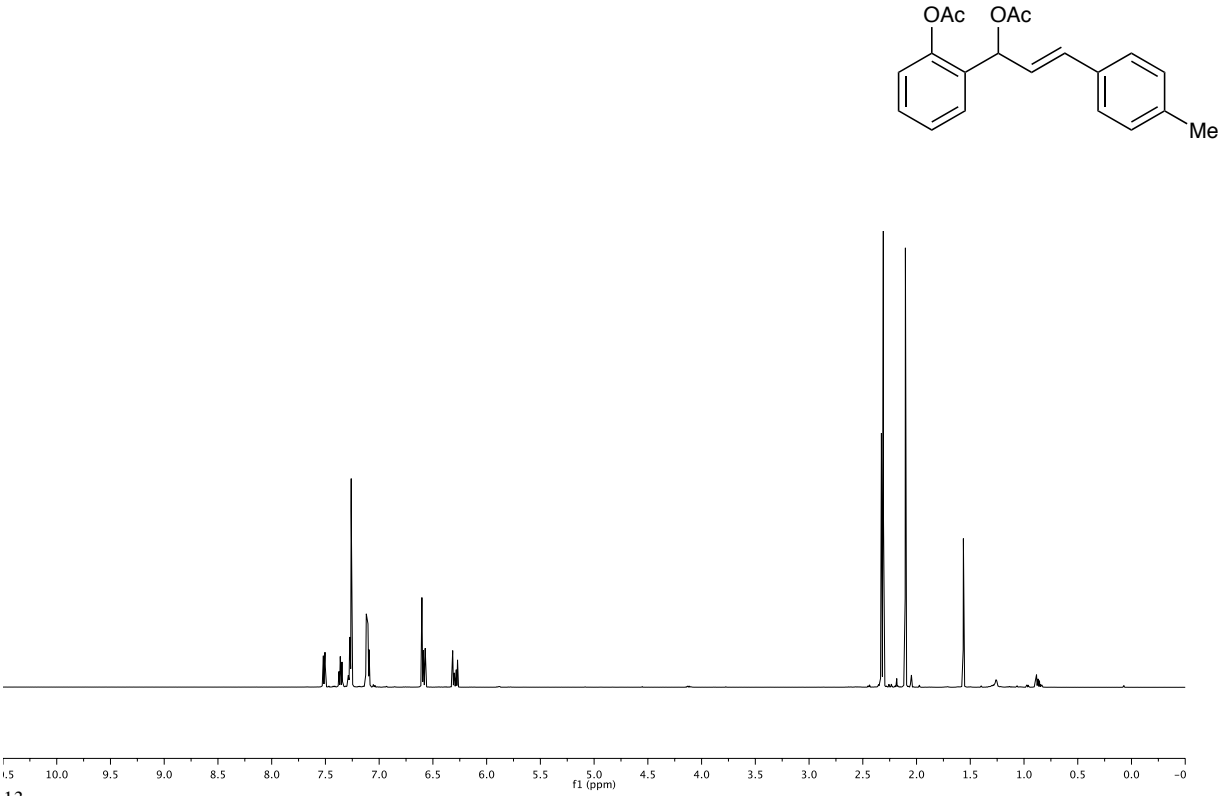
$^{1}$H NMR Spectrum of **1d** (500 MHz, $CDCl_3$):



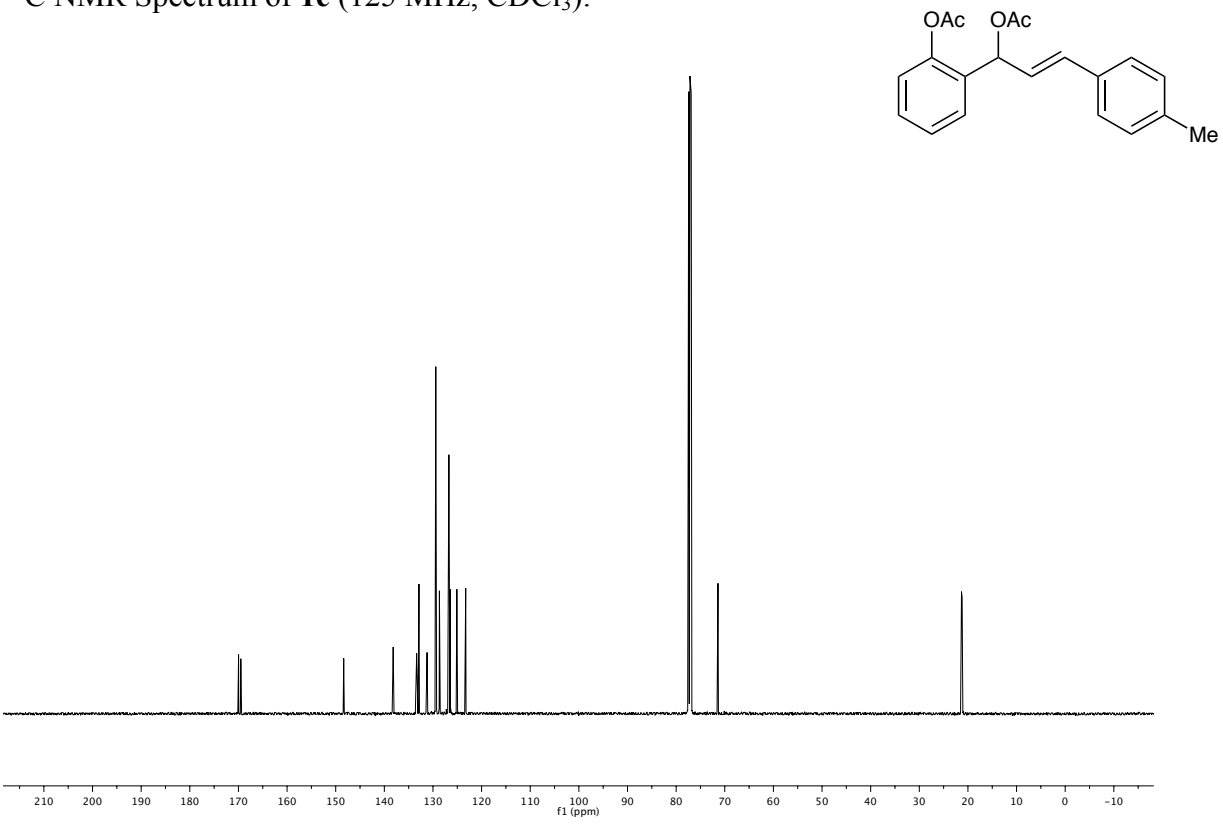

$^{13}$C NMR Spectrum of **1d** (125 MHz, $CDCl_3$):



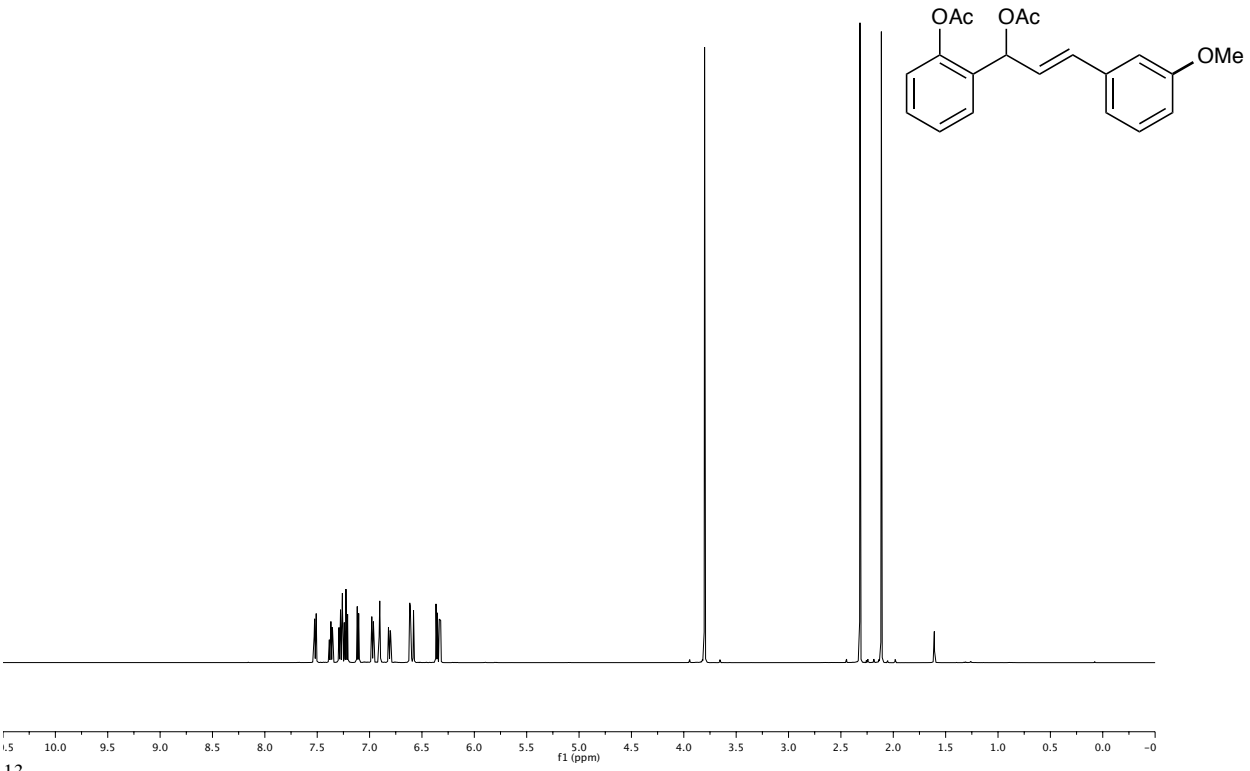
$^{1}$H NMR Spectrum of **1e** (500 MHz, $CDCl_3$):



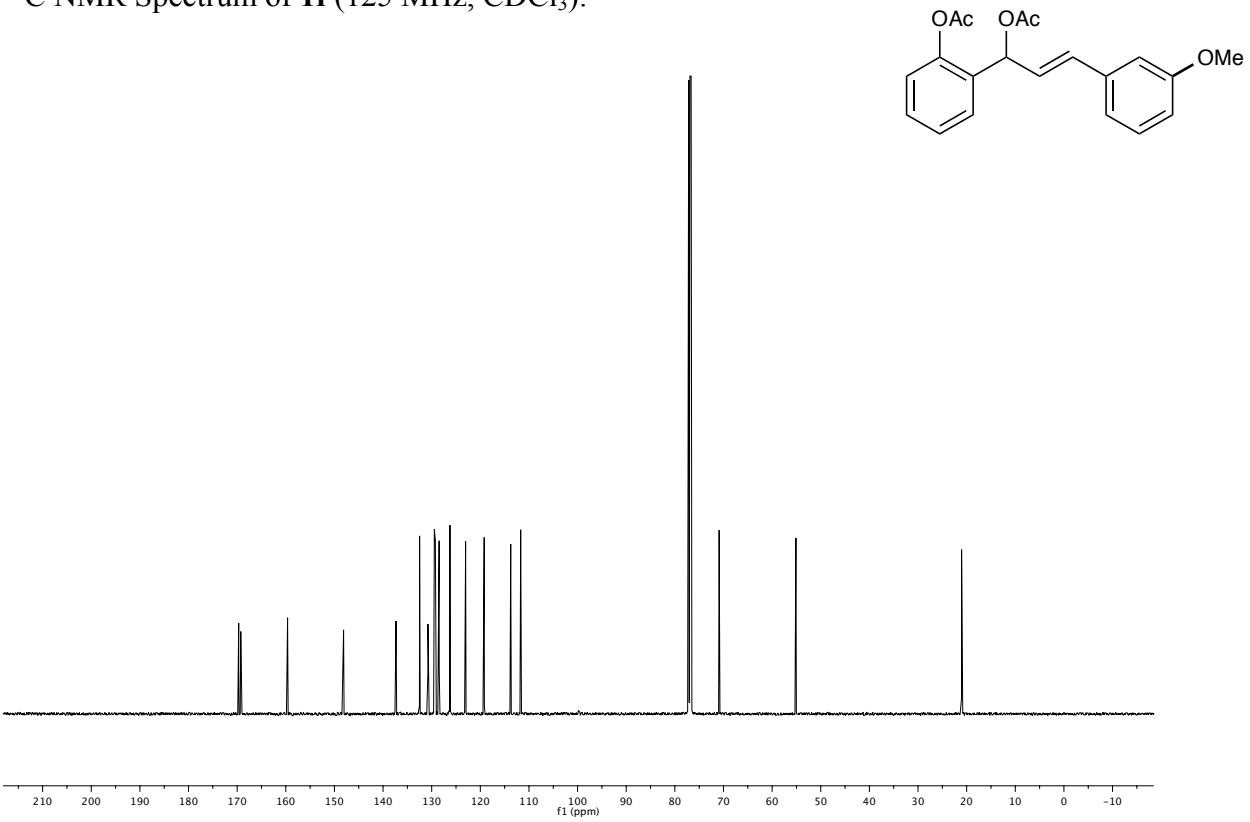

$^{13}$C NMR Spectrum of **1e** (125 MHz, $CDCl_3$):



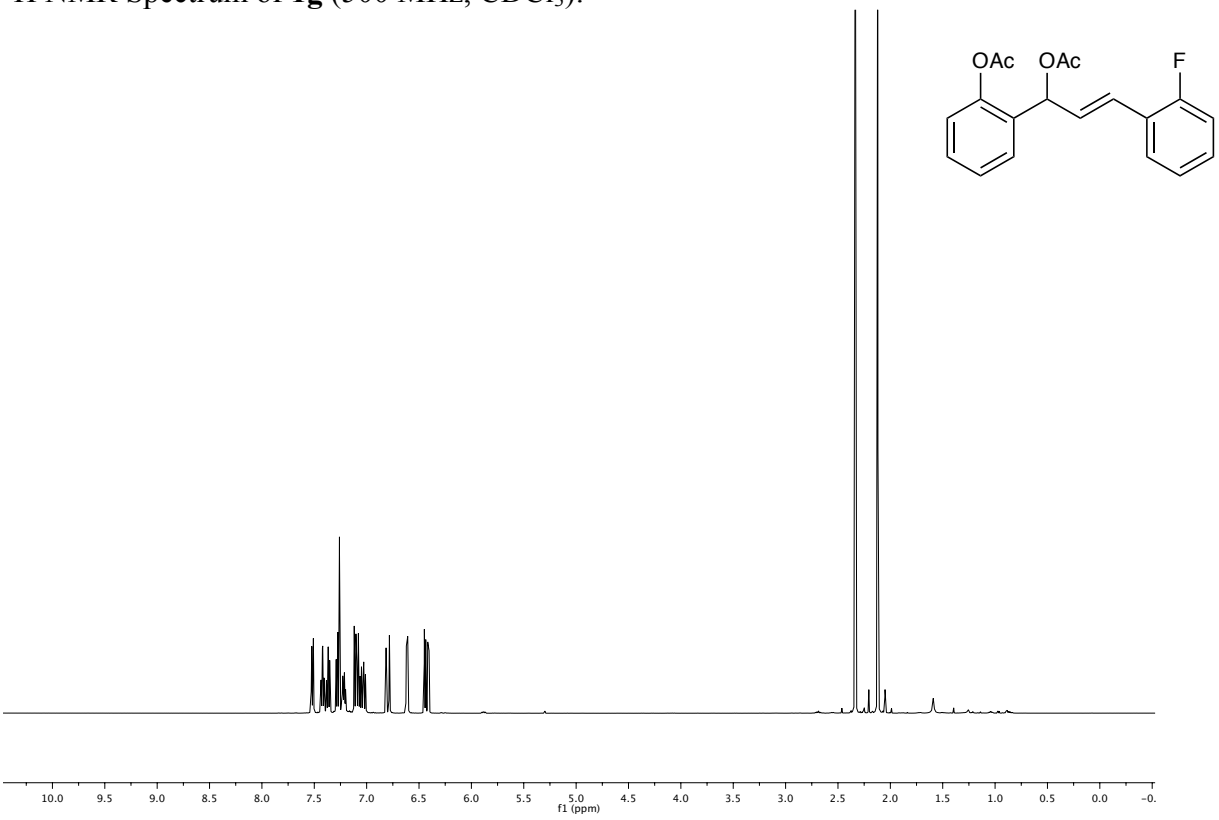
$^{1}$H NMR Spectrum of **1f** (500 MHz, $CDCl_3$):



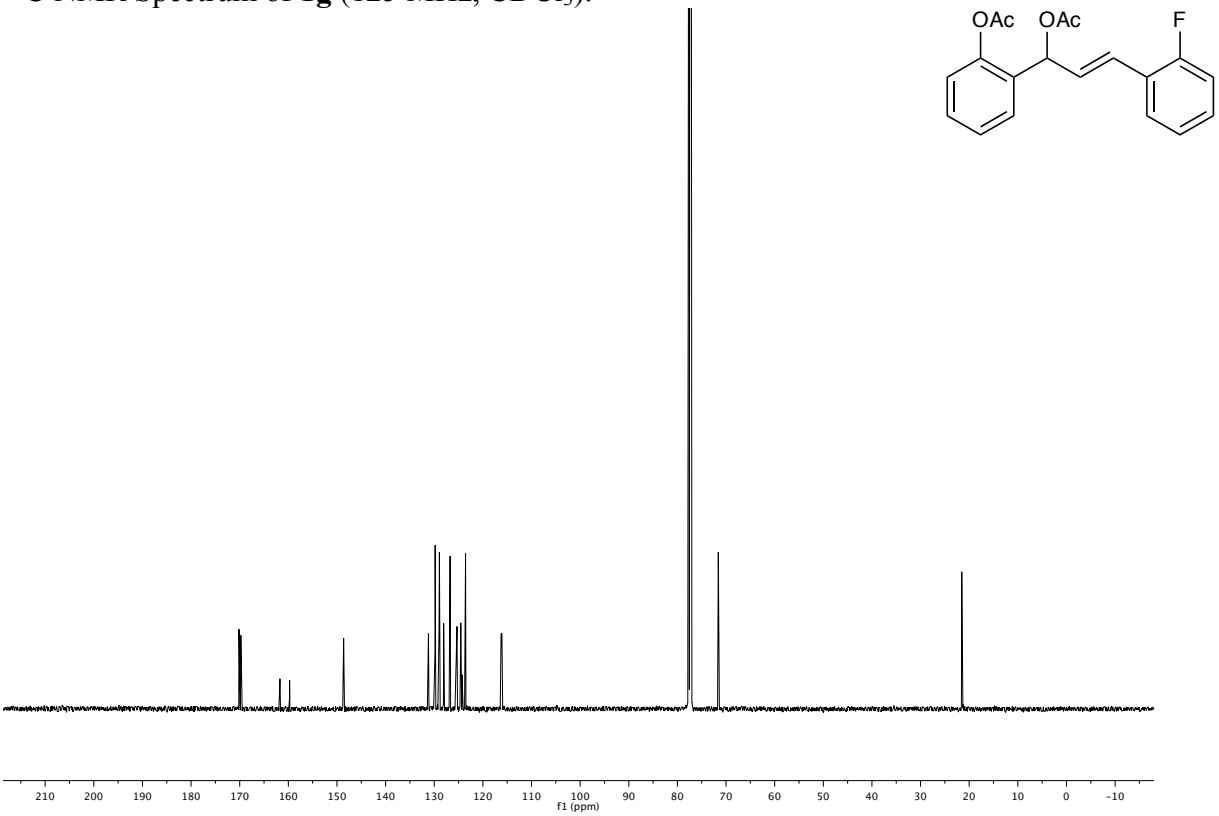

$^{13}$C NMR Spectrum of **1f** (125 MHz, $CDCl_3$):



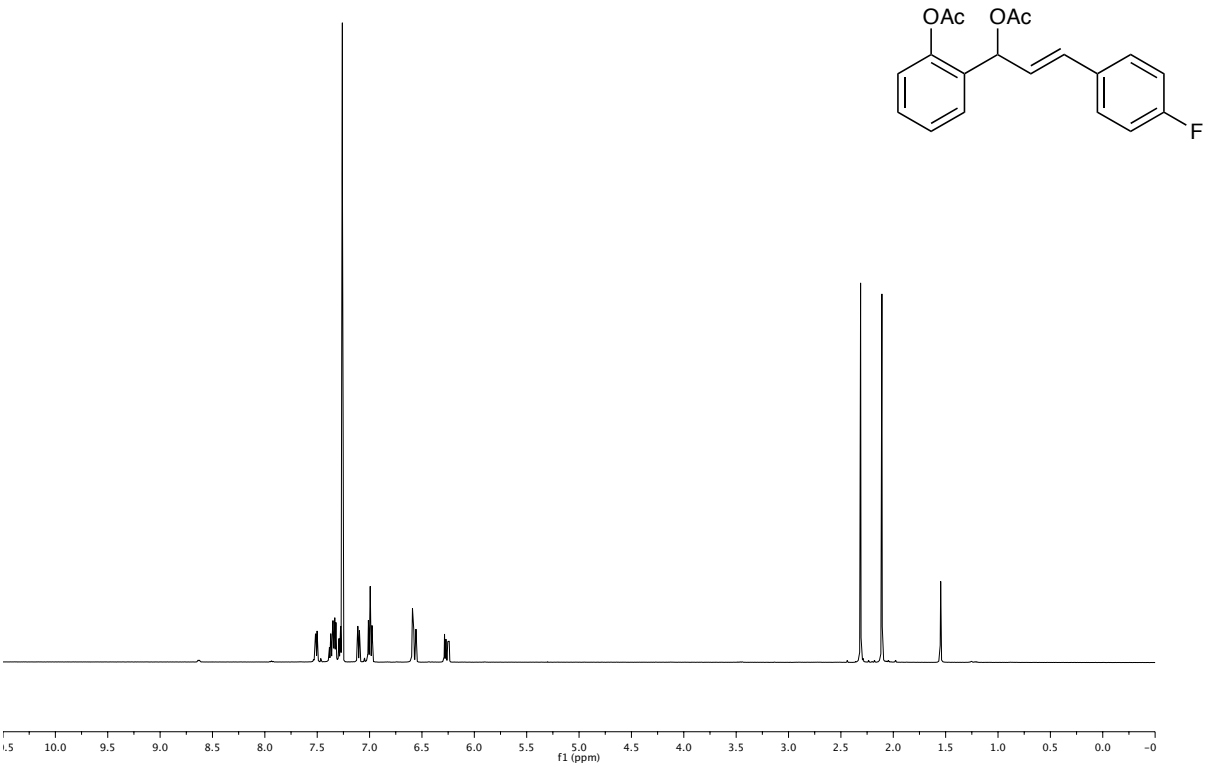
$^{1}$H NMR Spectrum of **1g** (500 MHz, $CDCl_3$):



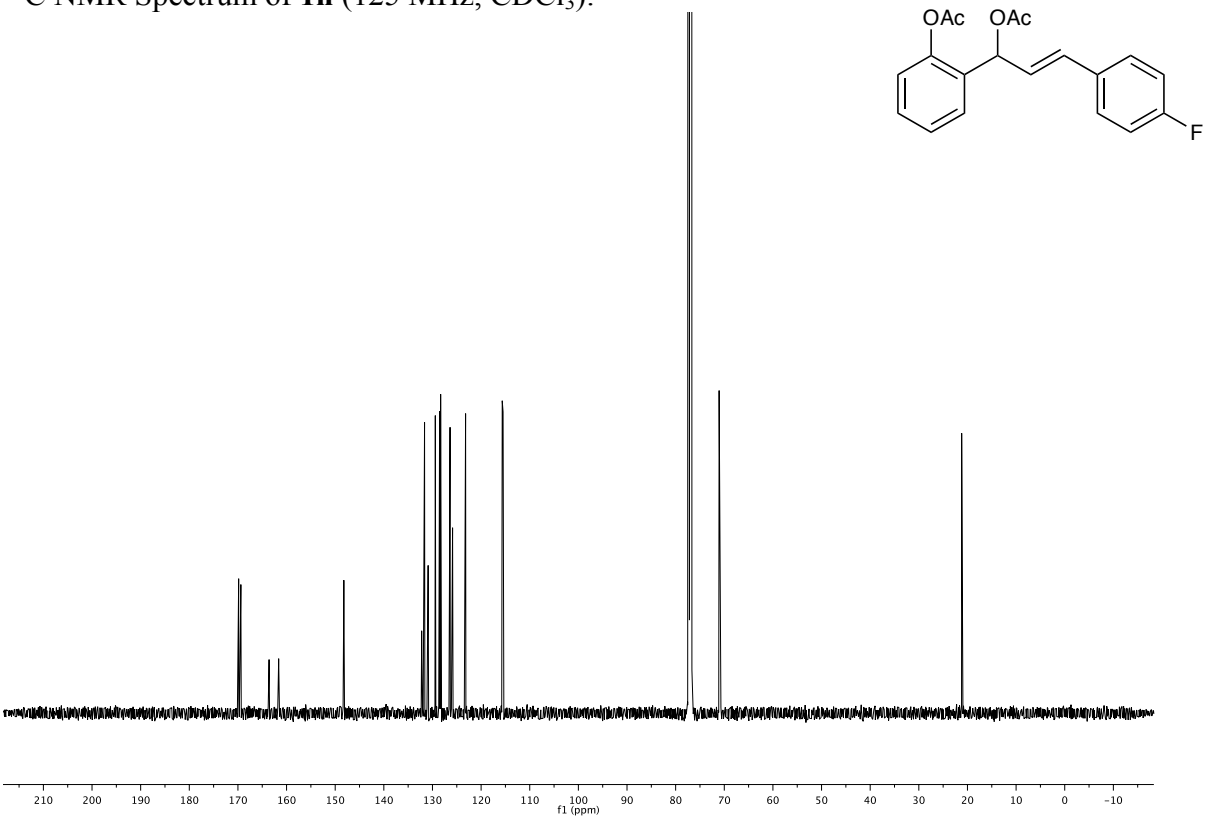

$^{13}$C NMR Spectrum of **1g** (125 MHz, $CDCl_3$):



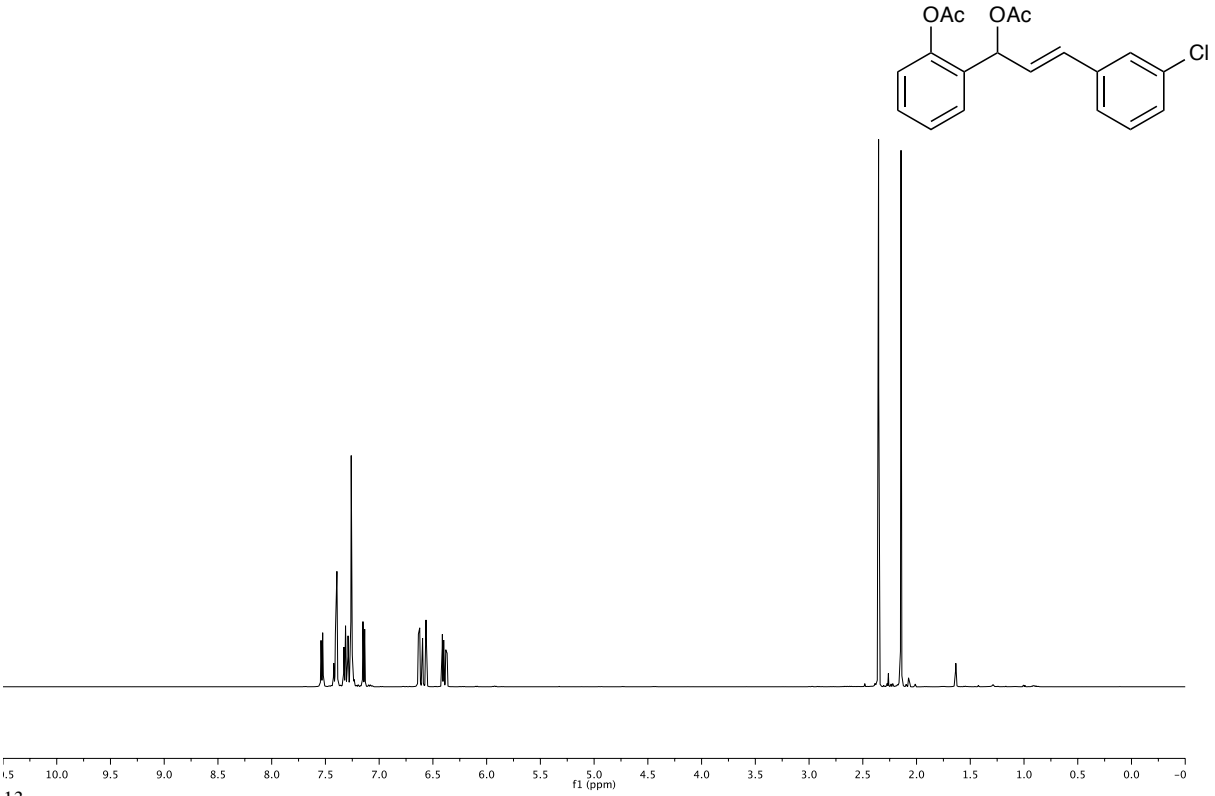
$^{1}$H NMR Spectrum of **1h** (500 MHz, $CDCl_3$):



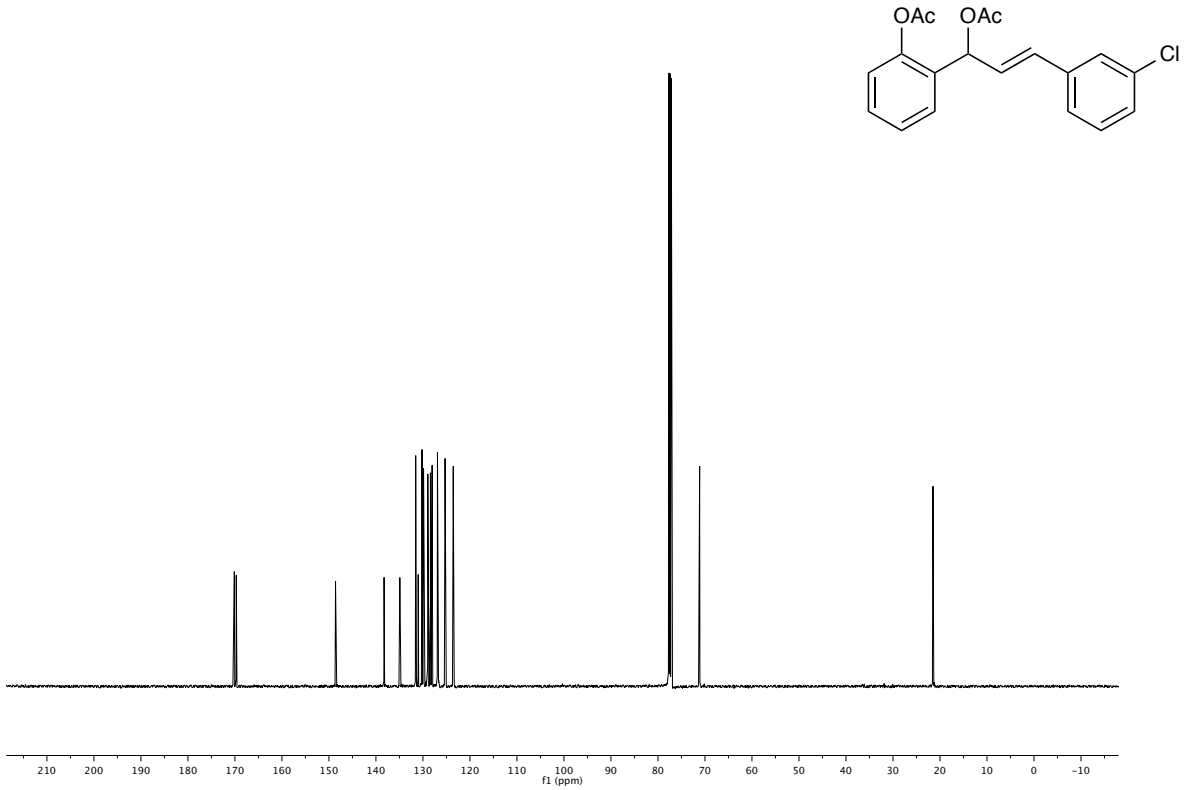

$^{13}$C NMR Spectrum of **1h** (125 MHz, $CDCl_3$):



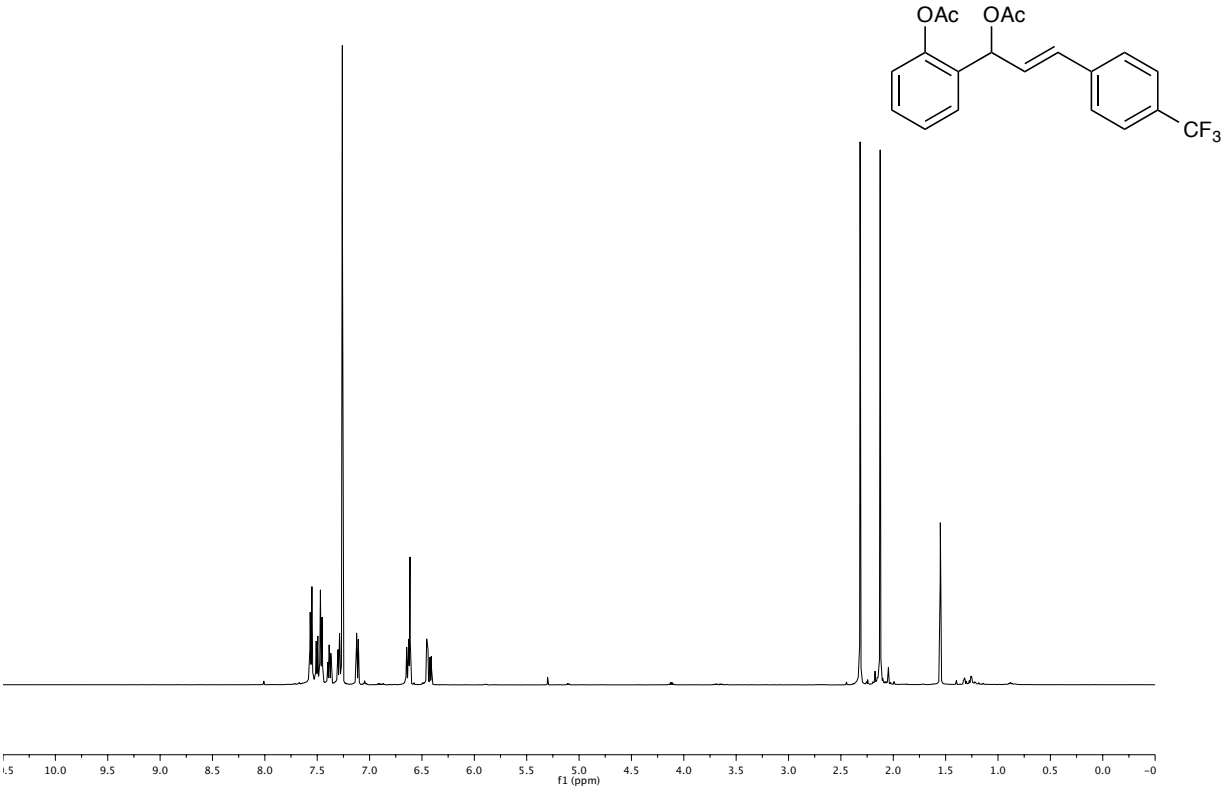
$^{1}$H NMR Spectrum of **1i** (500 MHz, $CDCl_3$):



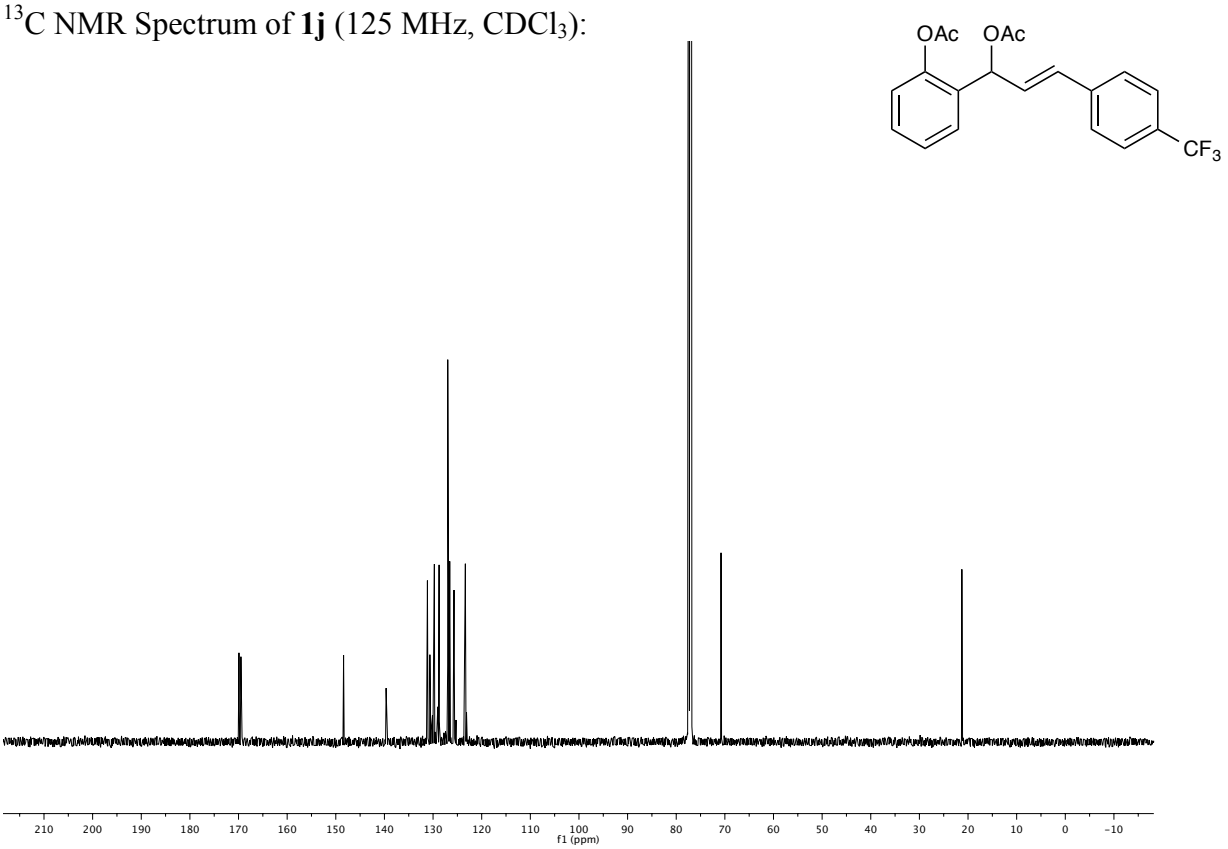

$^{13}$C NMR Spectrum of **1i** (125 MHz, $CDCl_3$):



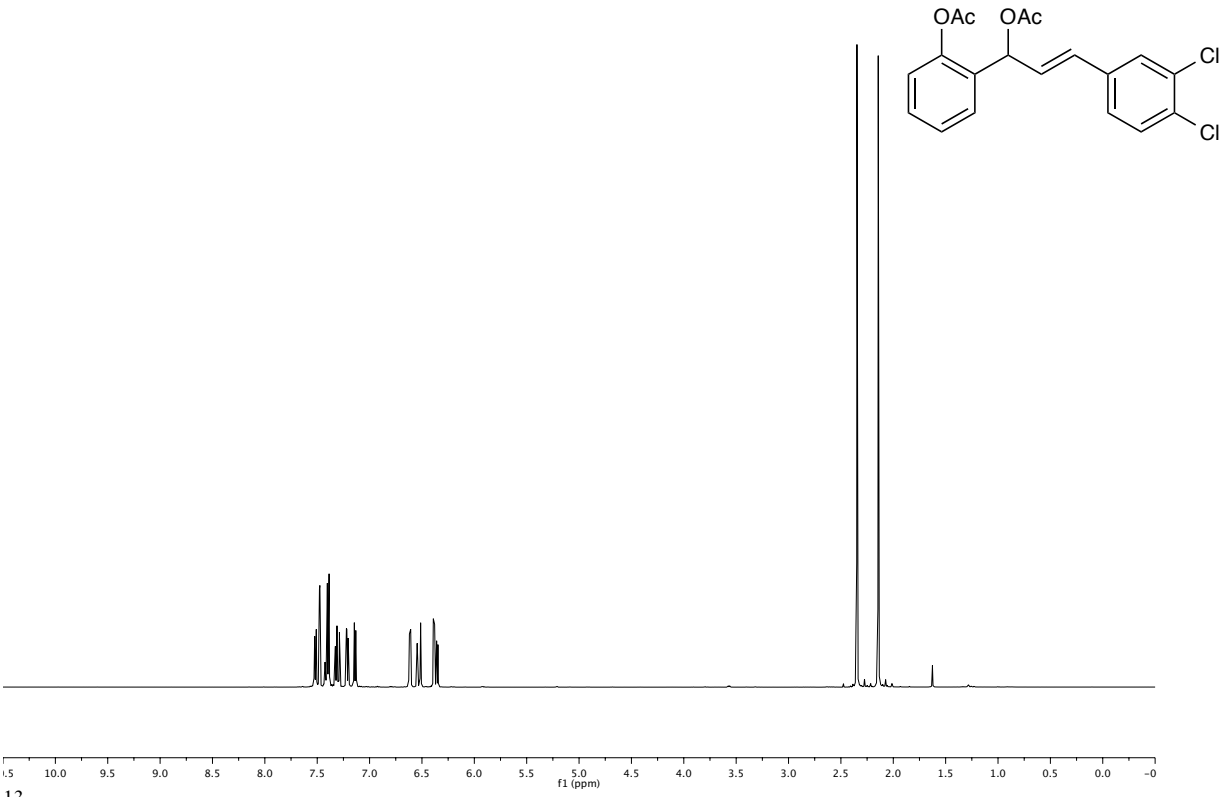
$^{1}$H NMR Spectrum of **1j** (500 MHz, $CDCl_3$):



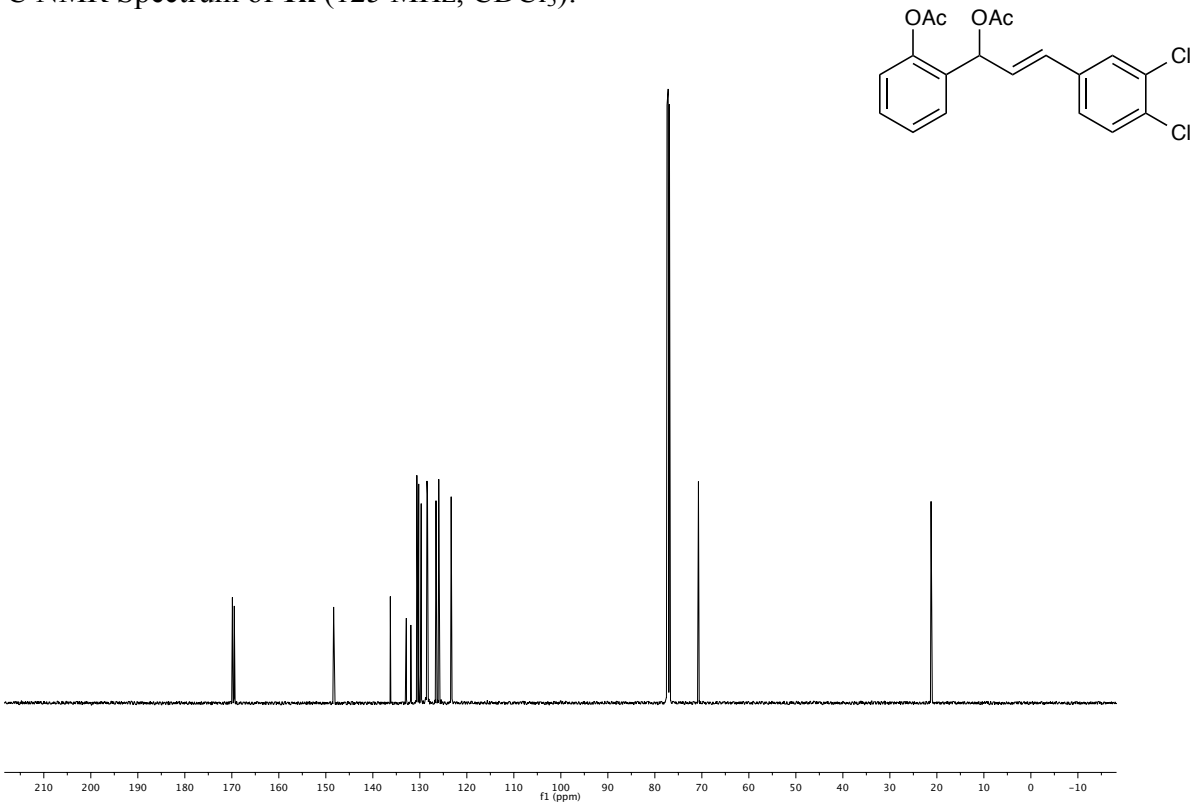

$^{13}$C NMR Spectrum of **1j** (125 MHz, $CDCl_3$):



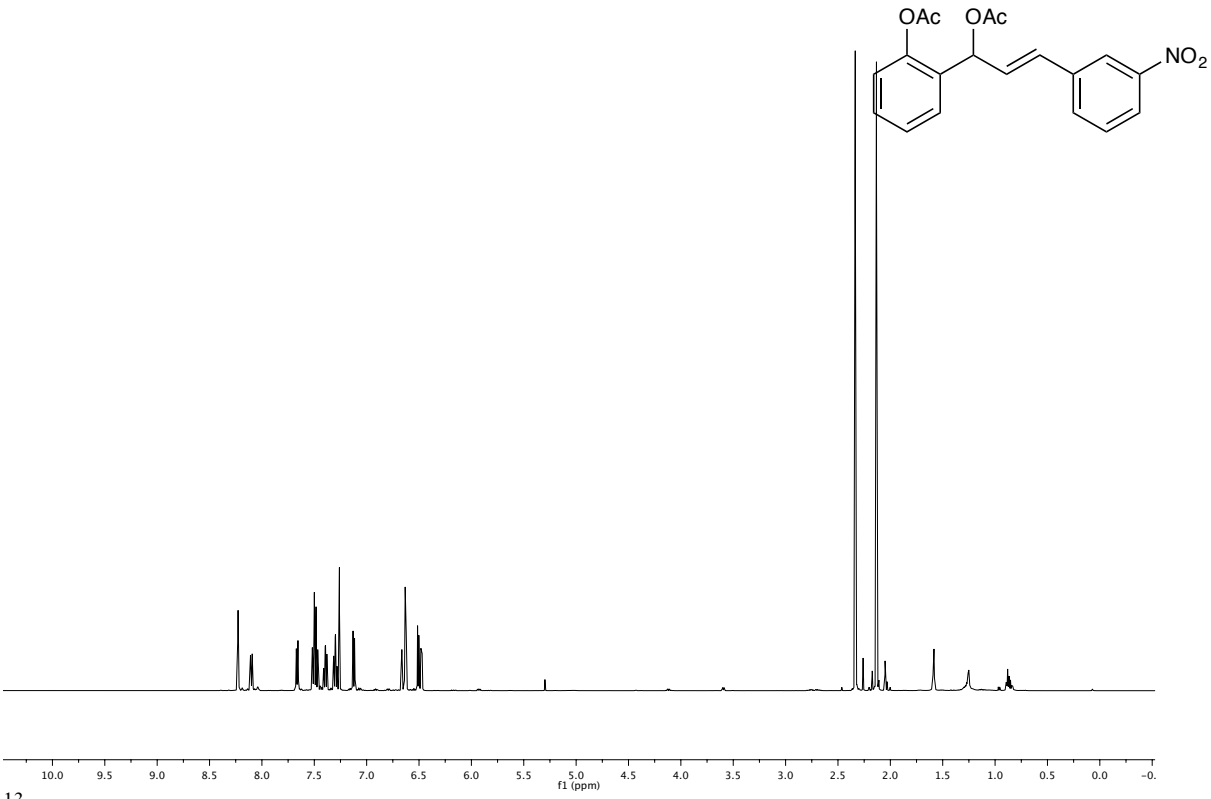
$^{1}$H NMR Spectrum of **1k** (500 MHz, $CDCl_3$):



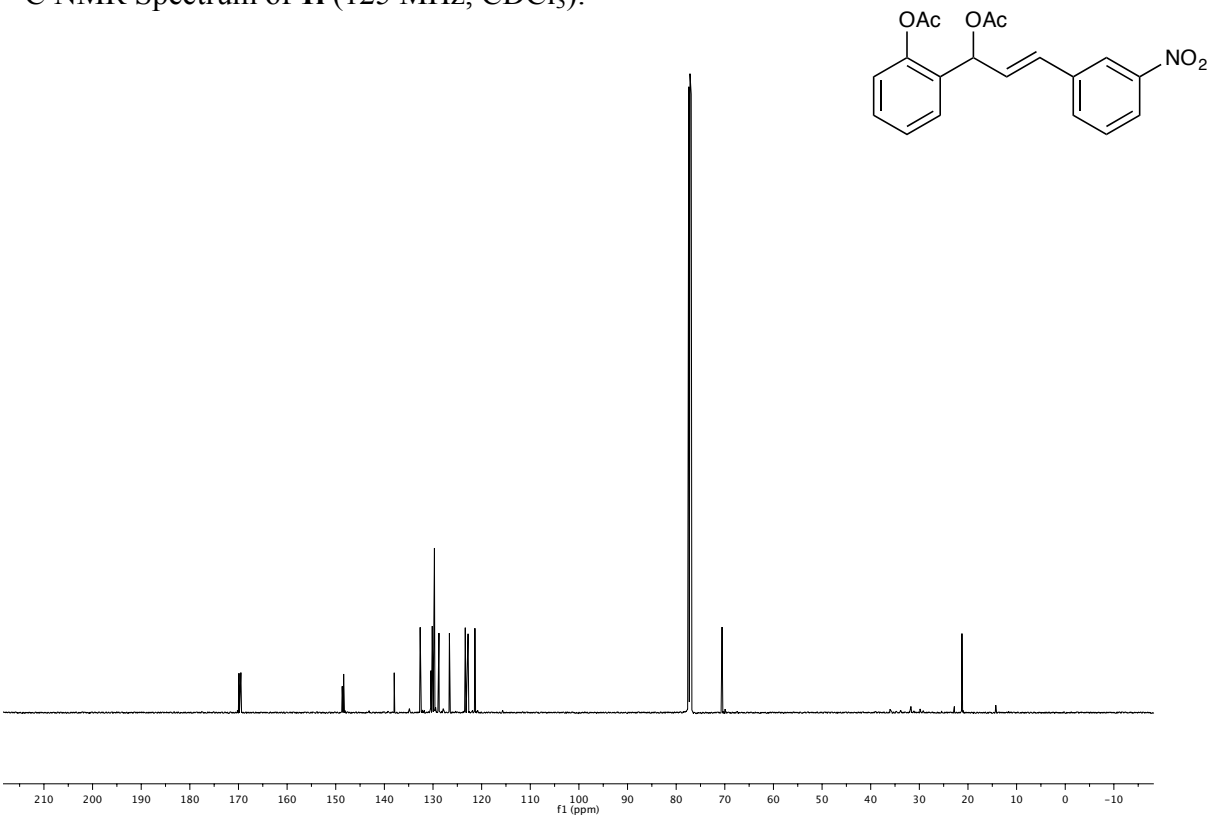

$^{13}$C NMR Spectrum of **1k** (125 MHz, $CDCl_3$):



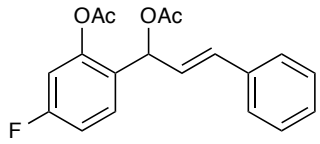
$^{1}$H NMR Spectrum of **1l** (500 MHz, $CDCl_3$):

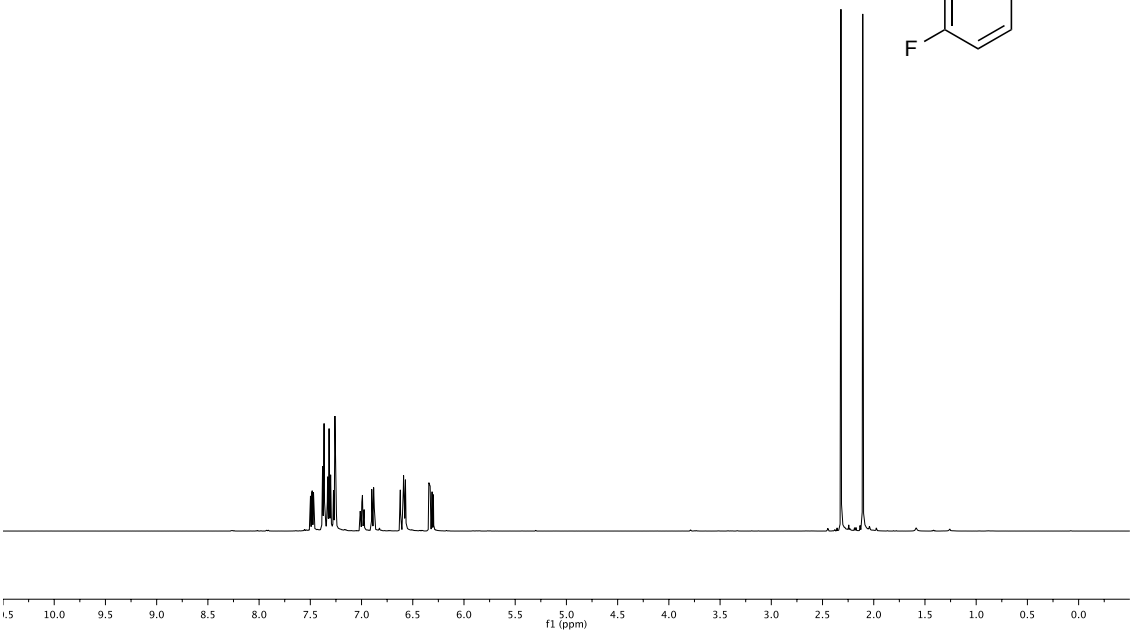



$^{13}$C NMR Spectrum of **1l** (125 MHz, $CDCl_3$):

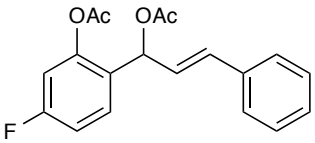


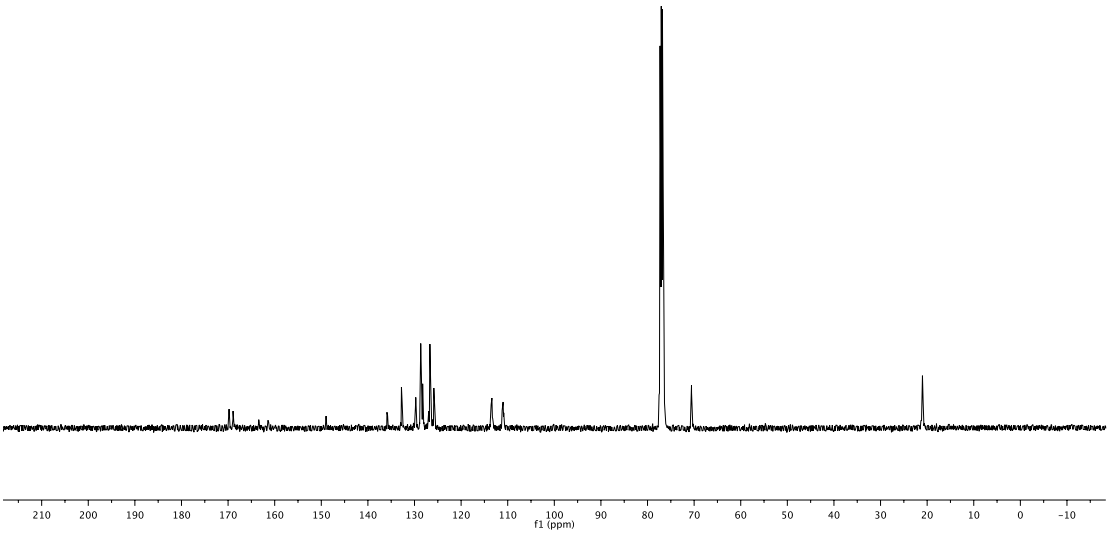
$^{1}$H NMR Spectrum of **1m** (500 MHz, $CDCl_3$):



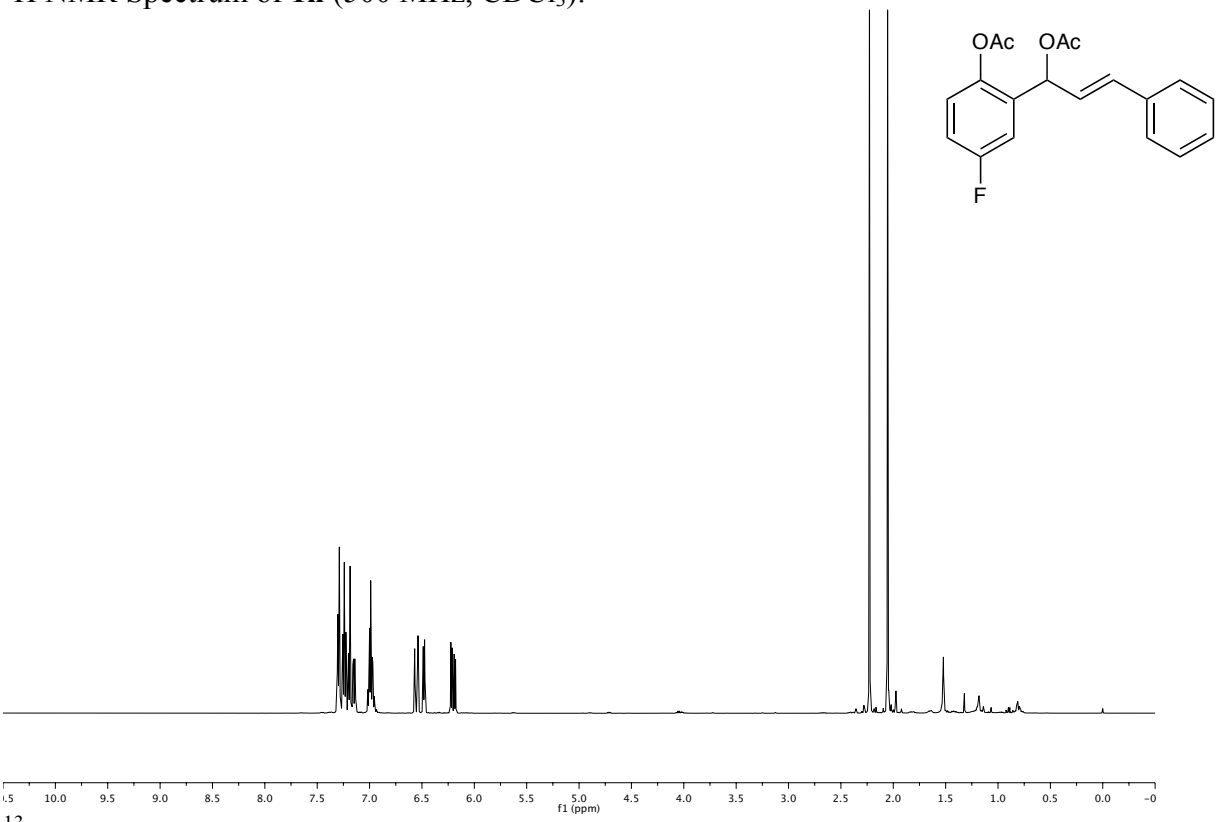




$^{13}$C NMR Spectrum of **1m** (125 MHz, $CDCl_3$):

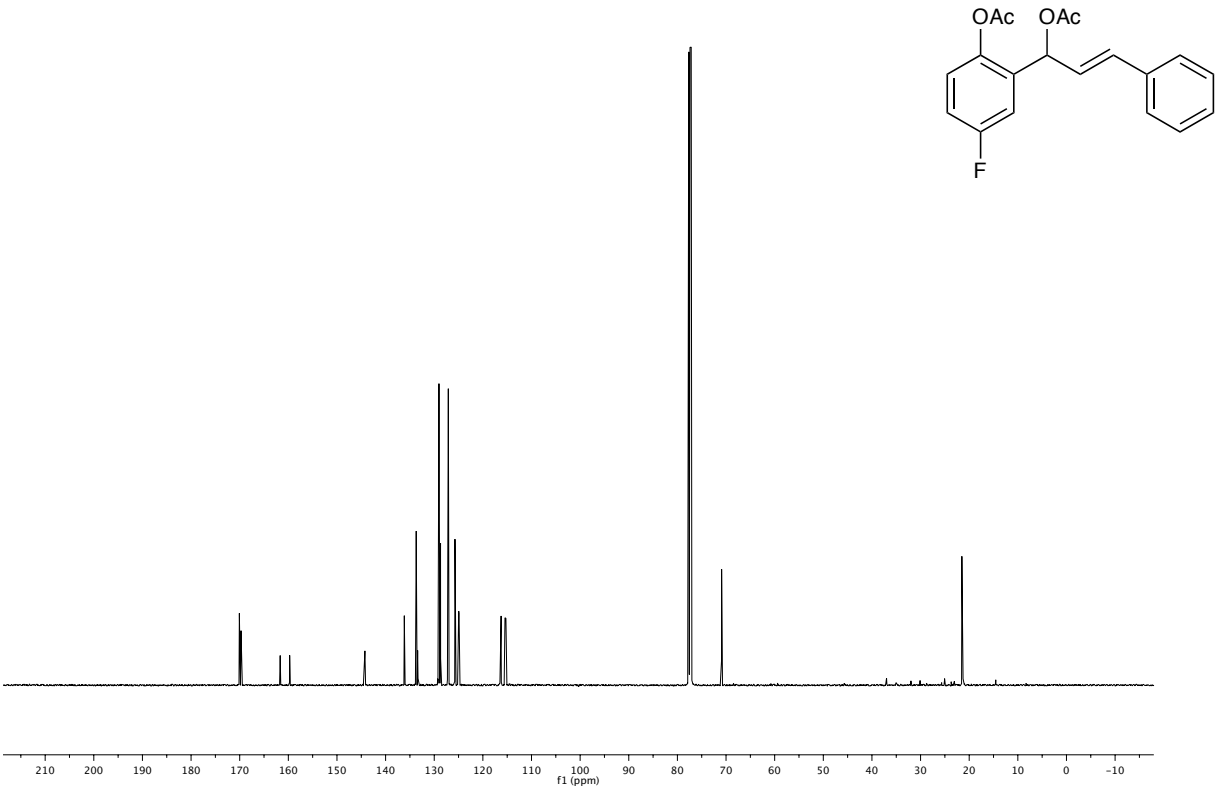


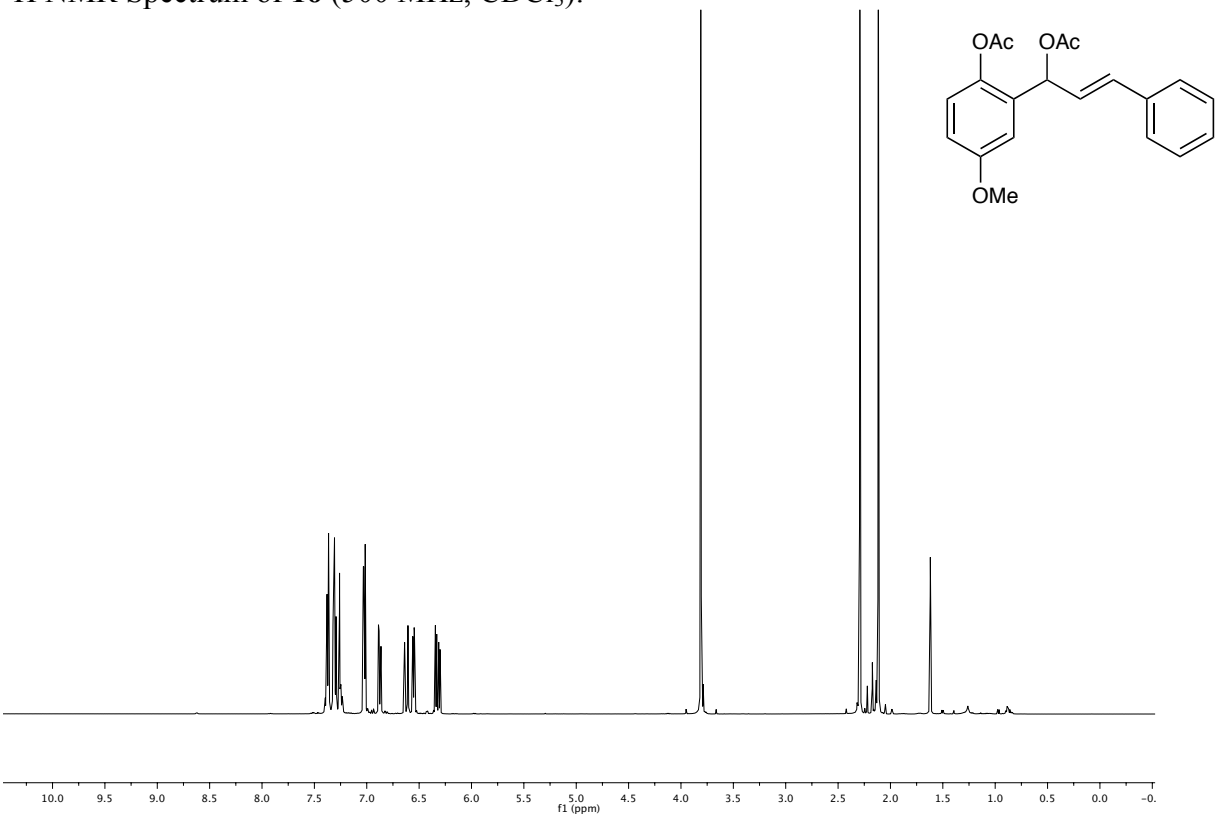
$^{1}$H NMR Spectrum of **1n** (500 MHz, $CDCl_3$):



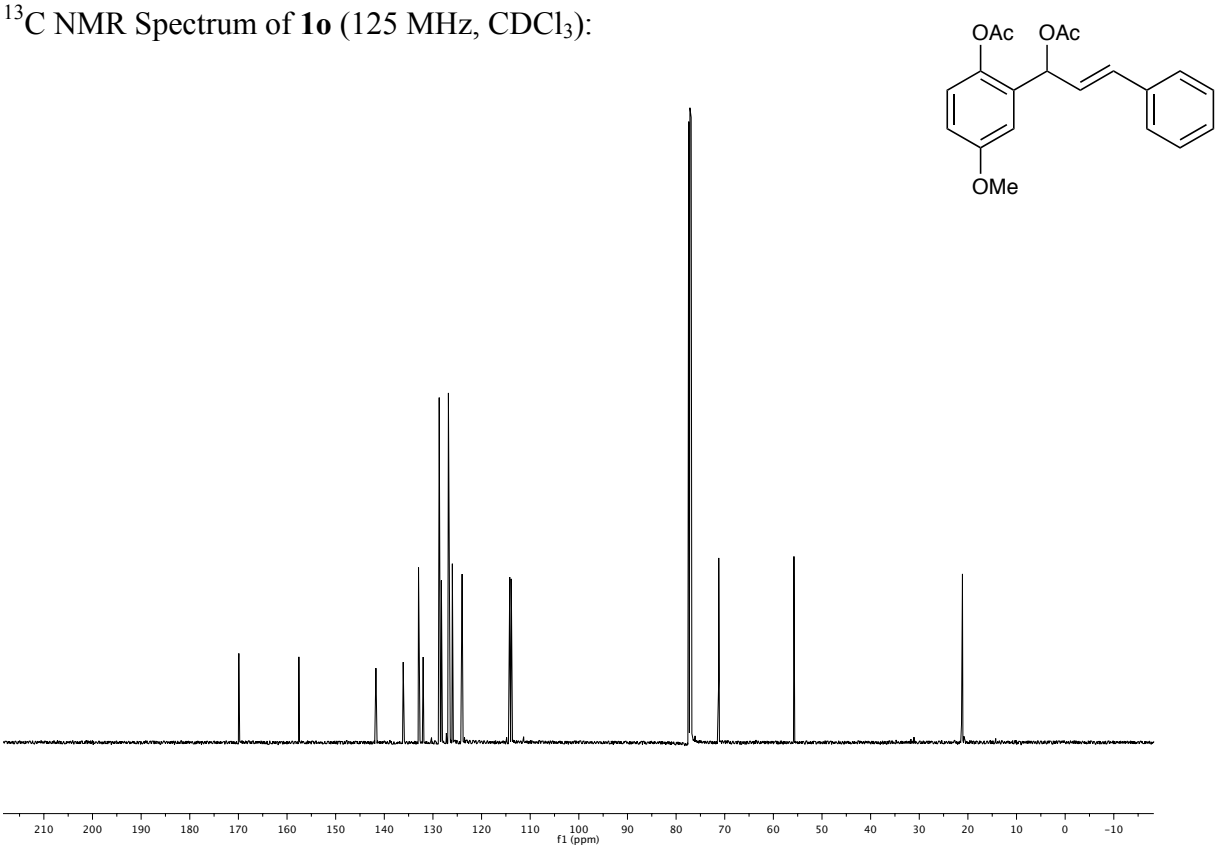

$^{13}$C NMR Spectrum of **1n** (125 MHz, $CDCl_3$):



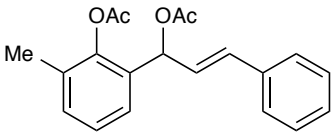
$^{1}$H NMR Spectrum of **1o** (500 MHz, $CDCl_3$):

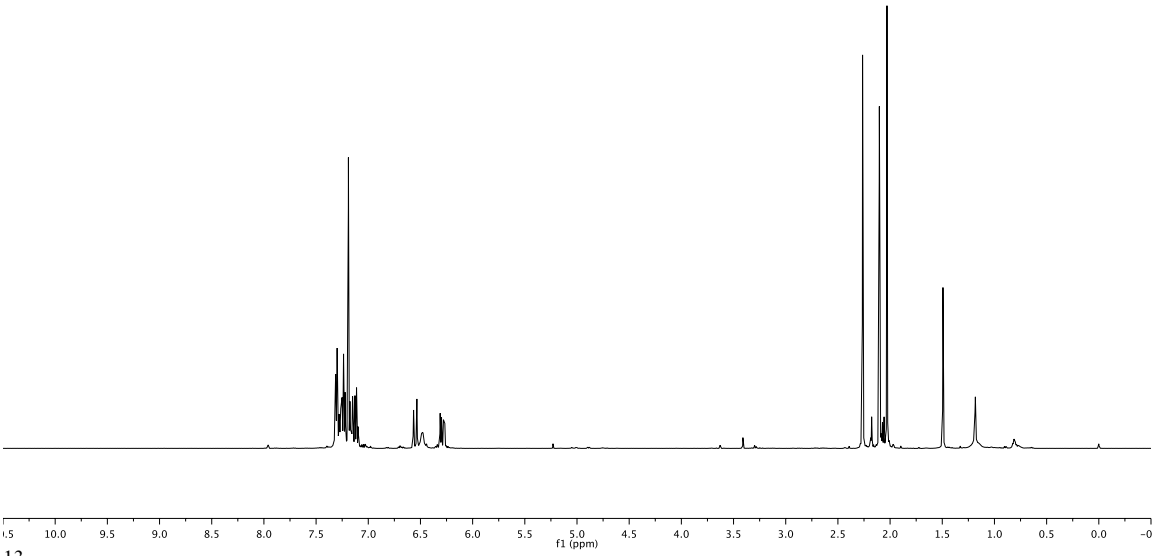



$^{13}$C NMR Spectrum of **1o** (125 MHz, $CDCl_3$):

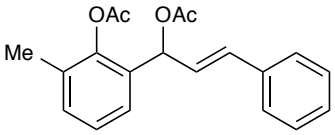


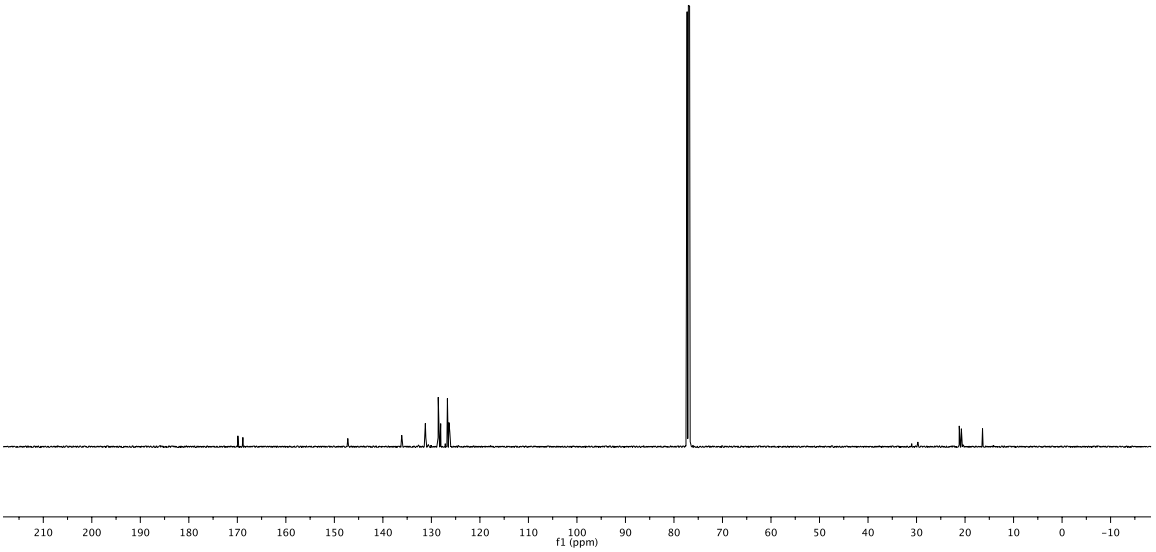
$^{1}$H NMR Spectrum of **1p** (500 MHz, $CDCl_3$):



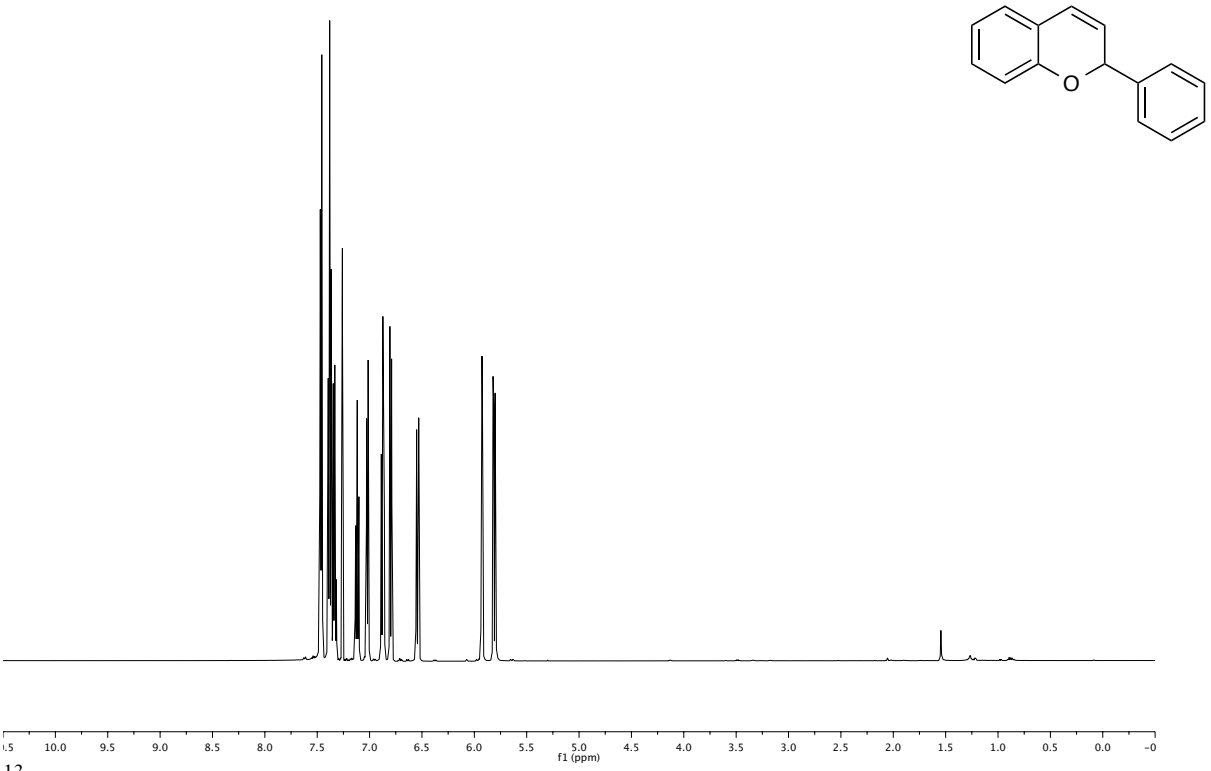




$^{13}$C NMR Spectrum of **1p** (125 MHz, $CDCl_3$):

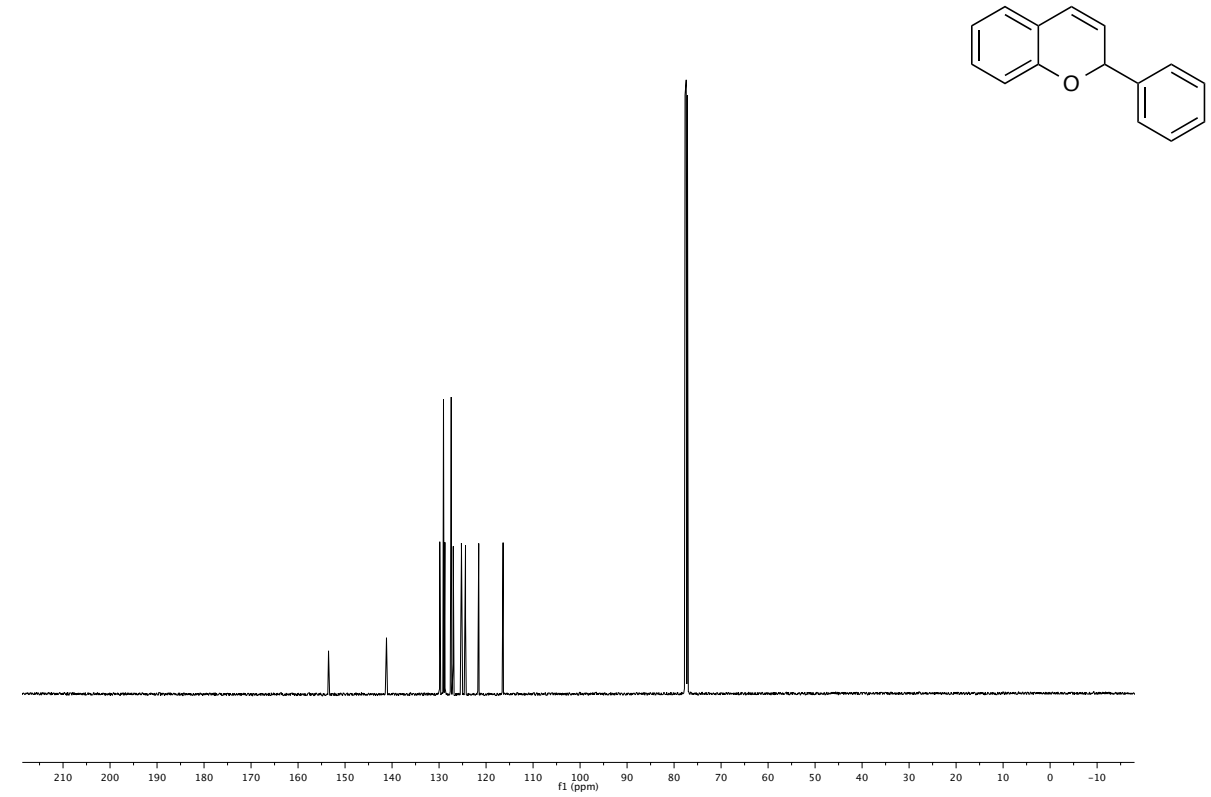


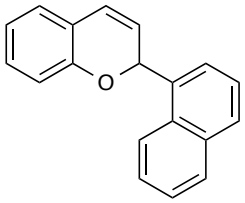
$^{1}$H NMR Spectrum of **2a** (500 MHz, $CDCl_3$):

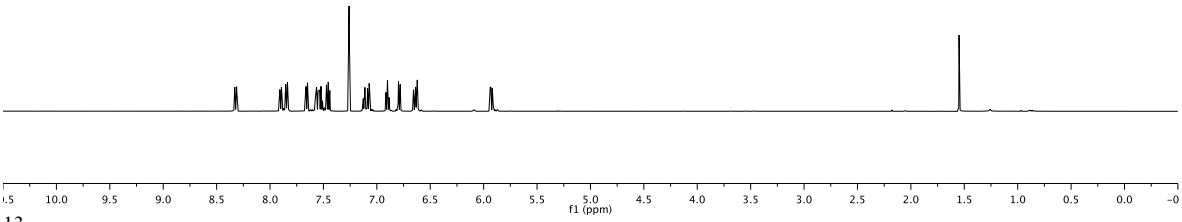



$^{13}$C NMR Spectrum of **2a** (125 MHz, $CDCl_3$):

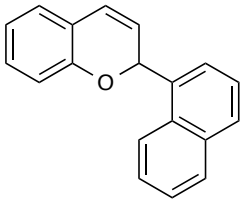


$^{1}$H NMR Spectrum of **2b** (500 MHz, $CDCl_3$):

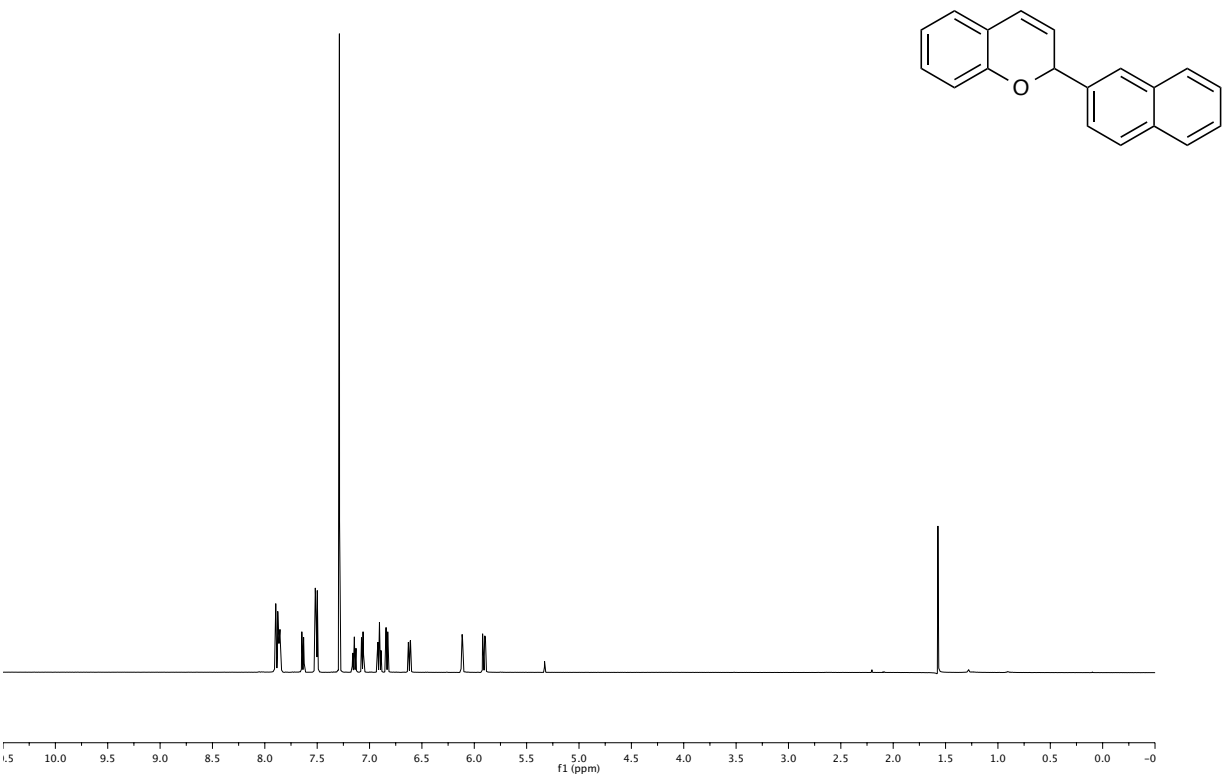


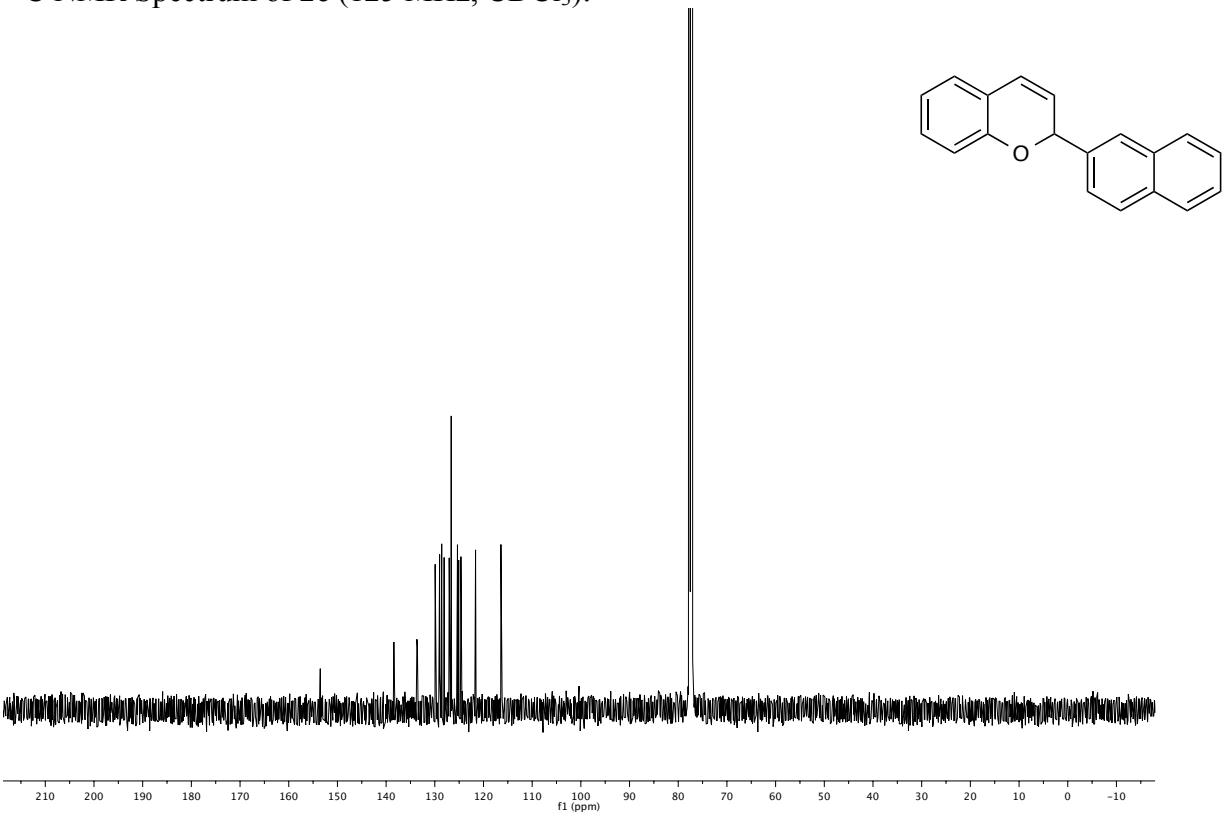

$^{13}$C NMR Spectrum of **2b** (125 MHz, $CDCl_3$):



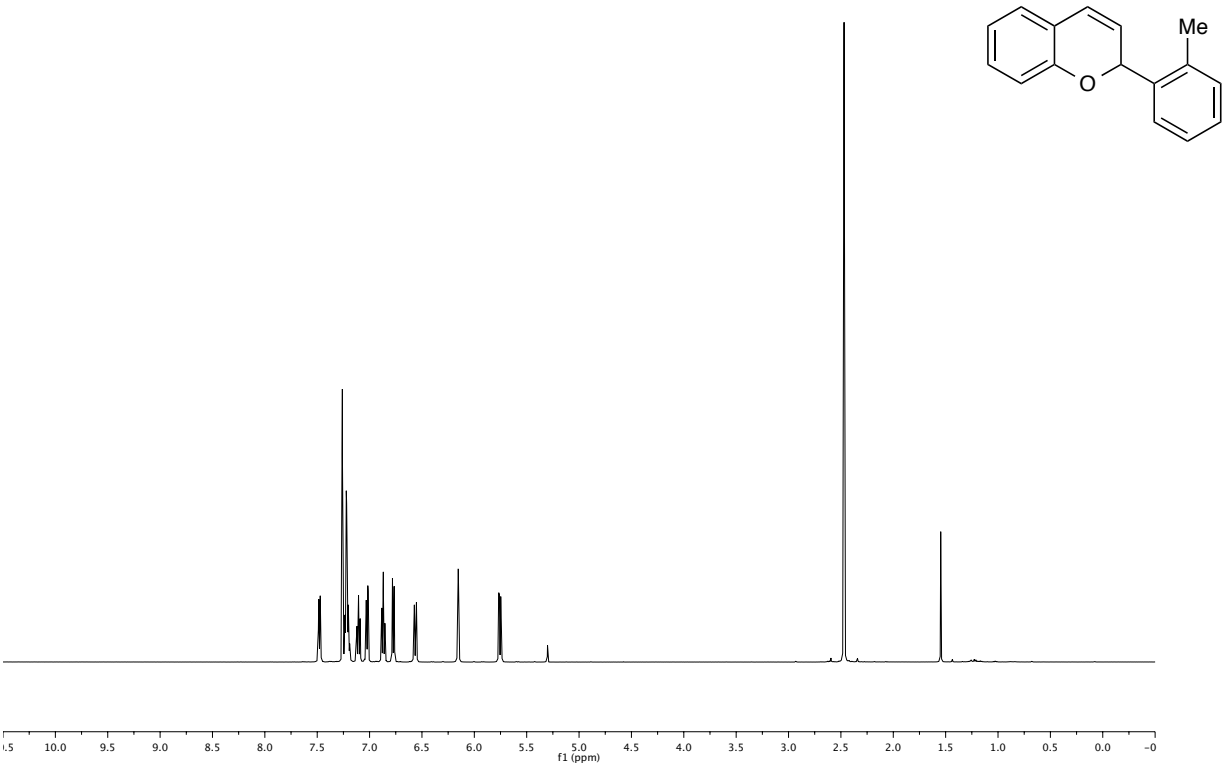
$^{1}$H NMR Spectrum of **2c** (500 MHz, $CDCl_3$):



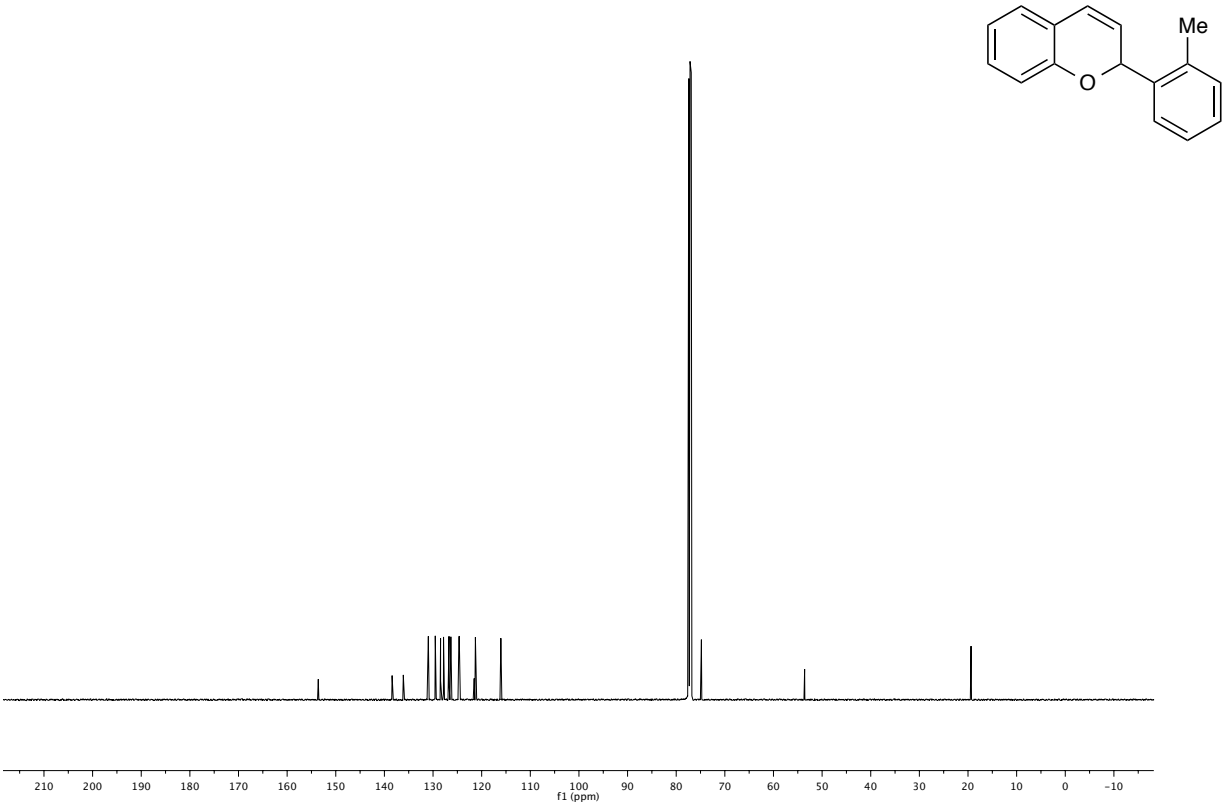

$^{13}$C NMR Spectrum of **2c** (125 MHz, $CDCl_3$):



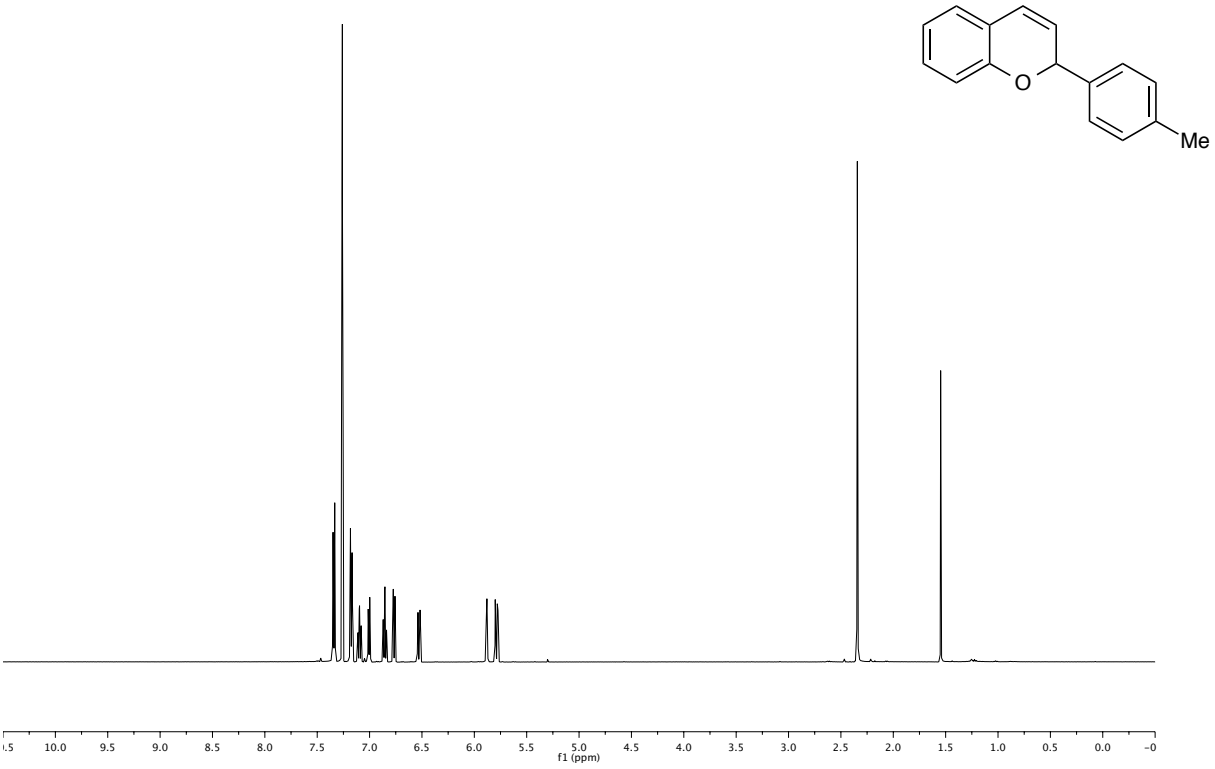
$^{1}$H NMR Spectrum of **2d** (500 MHz, $CDCl_3$):



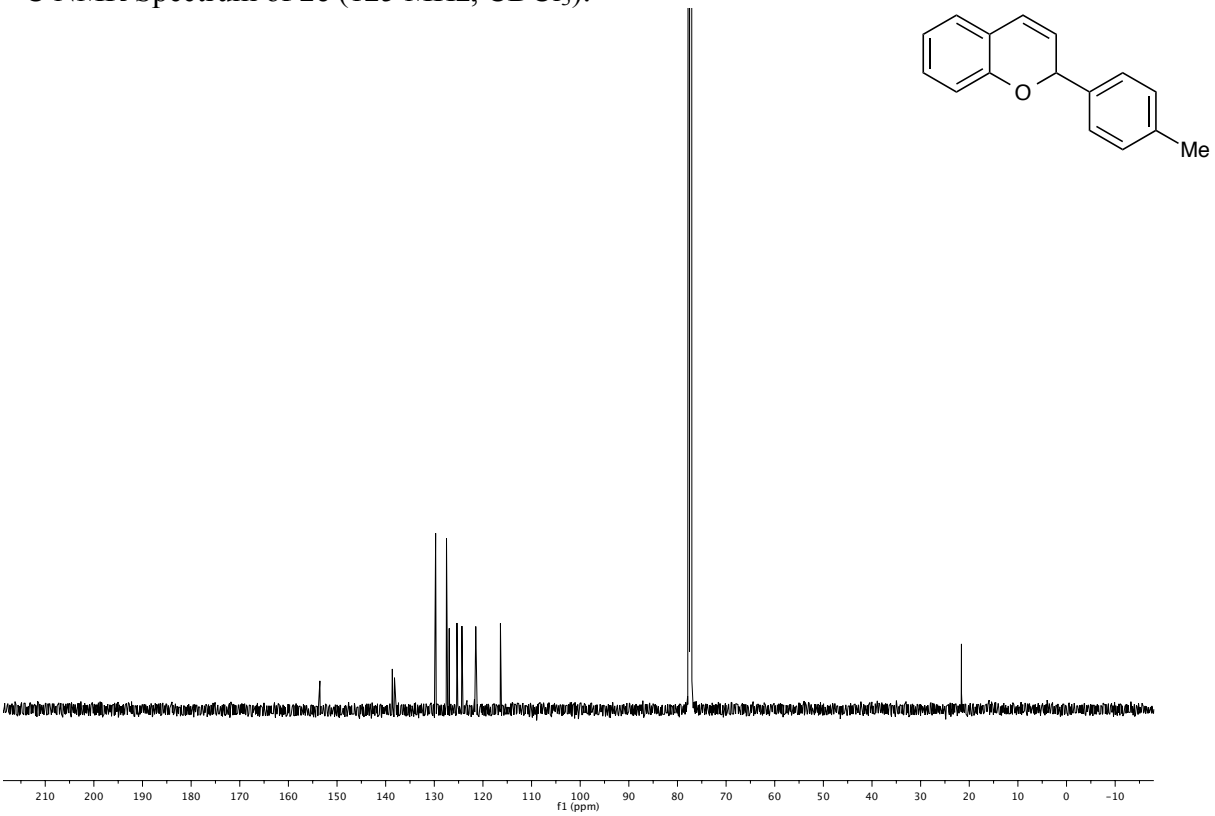

$^{13}$C NMR Spectrum of **2d** (125 MHz, $CDCl_3$):



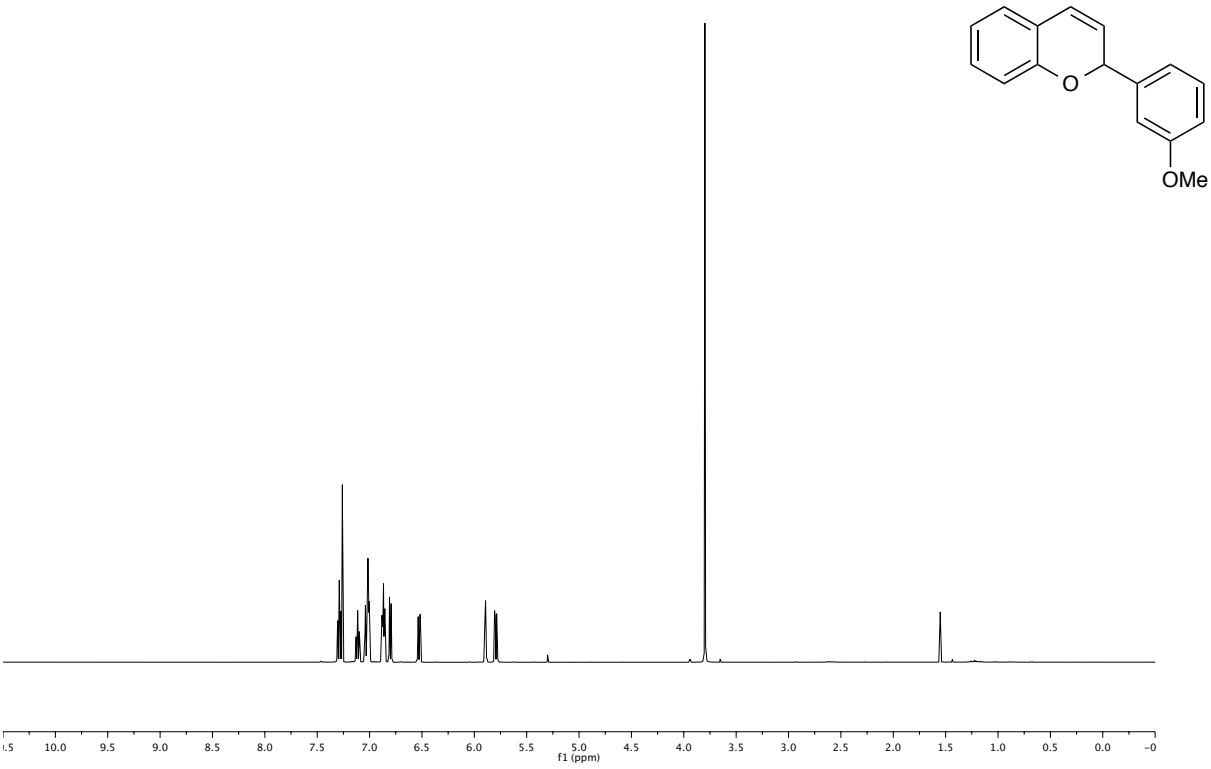
$^{1}$H NMR Spectrum of **2e** (500 MHz, $CDCl_3$):



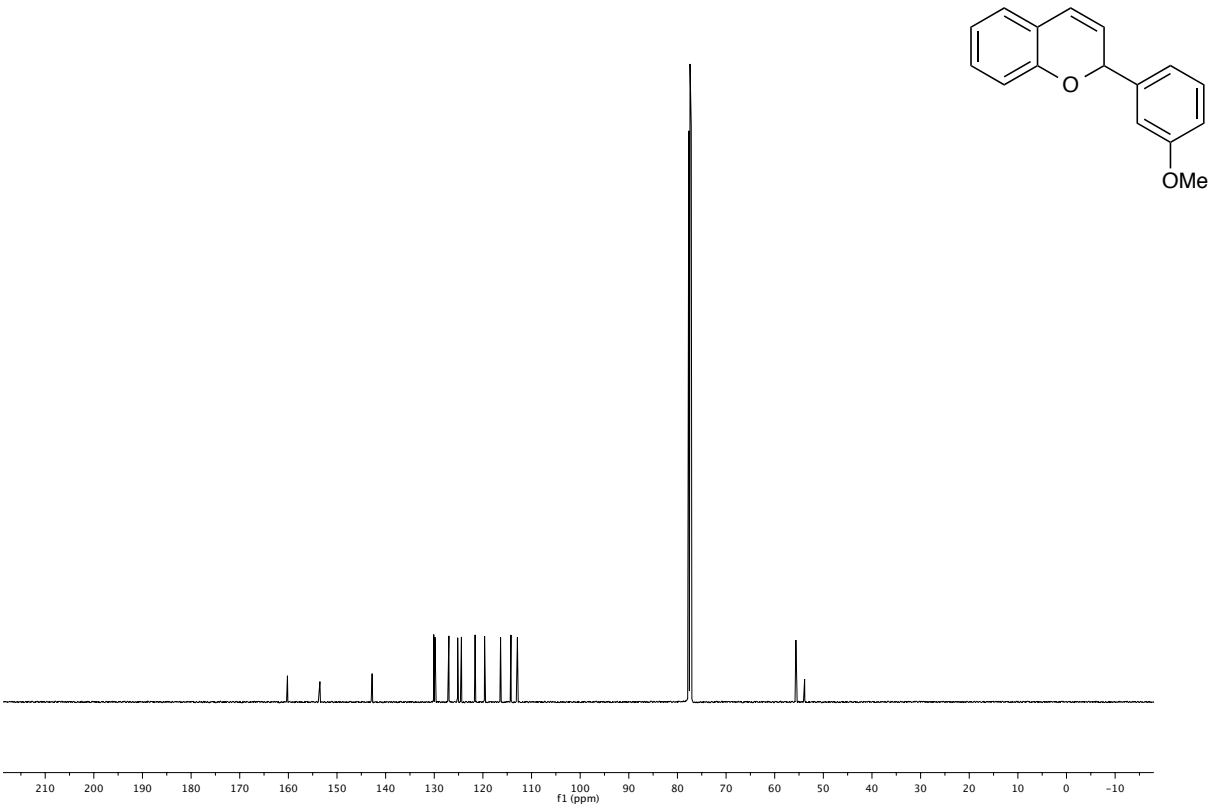

$^{13}$C NMR Spectrum of **2e** (125 MHz, $CDCl_3$):



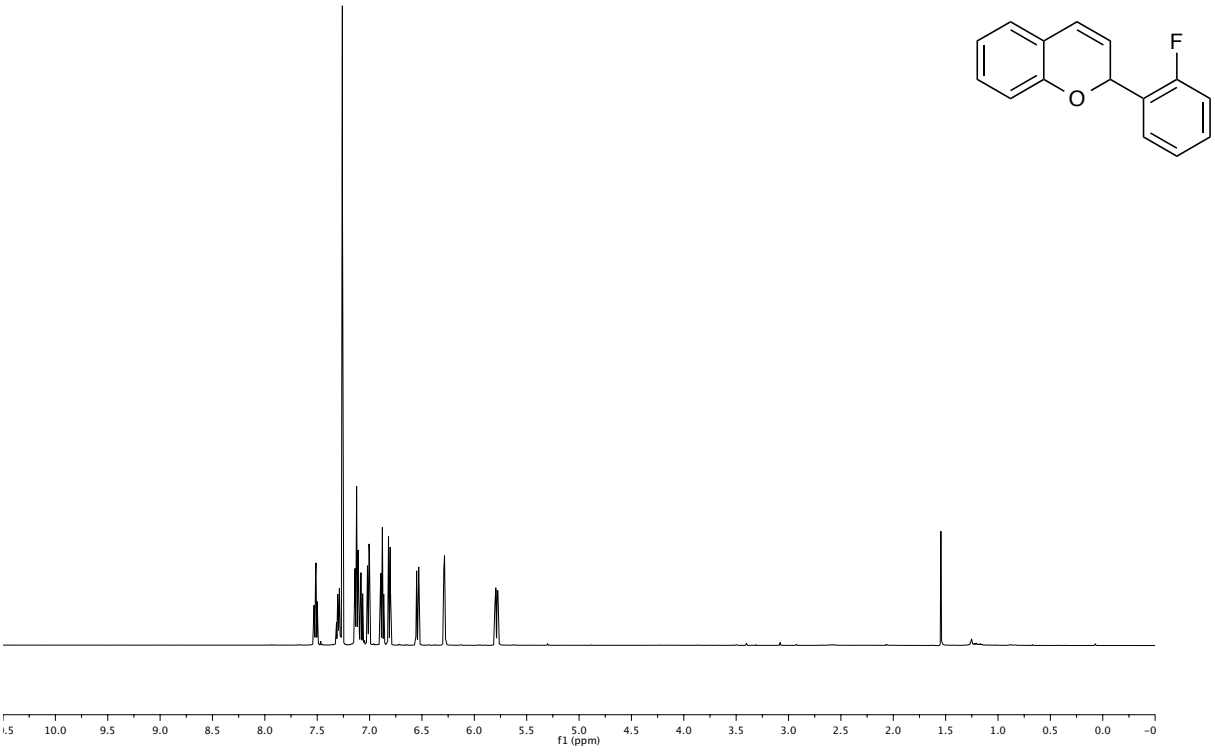
$^{1}$H NMR Spectrum of **2f** (500 MHz, $CDCl_3$):



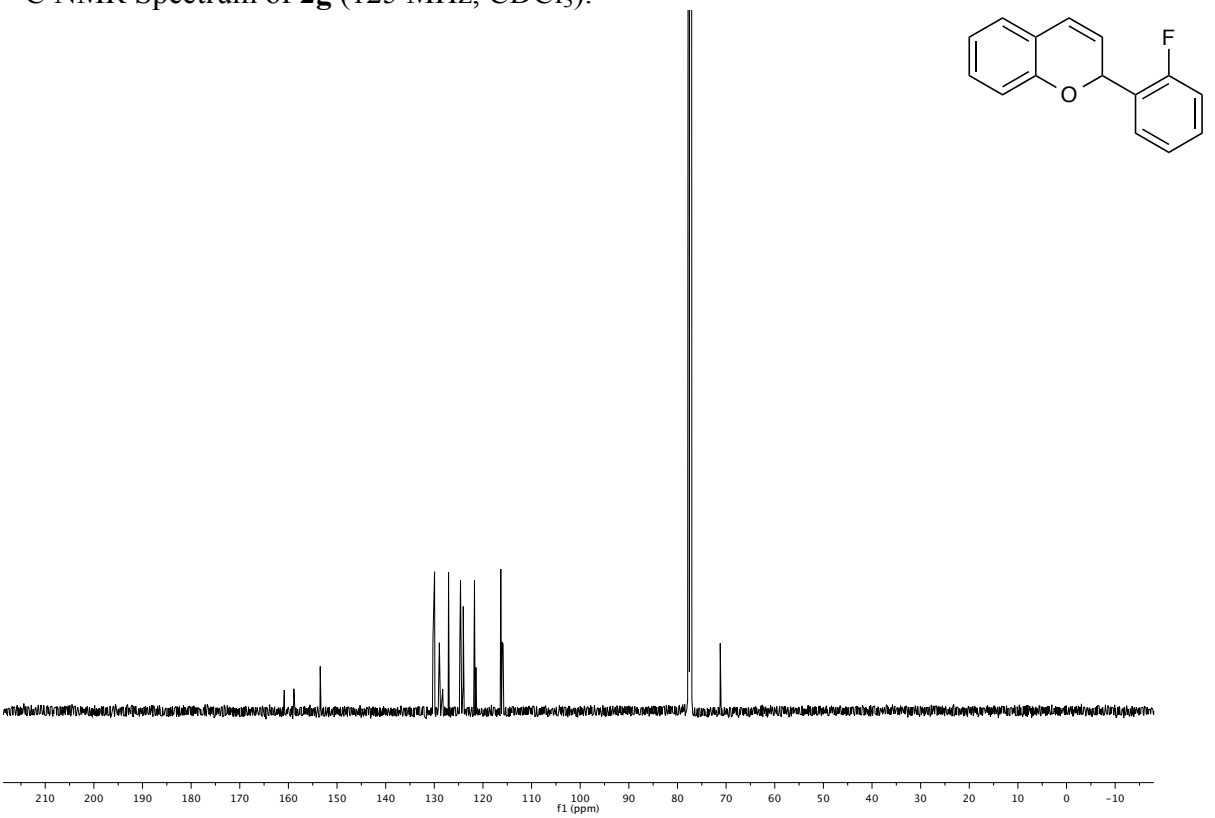

$^{13}$C NMR Spectrum of **2f** (125 MHz, $CDCl_3$):



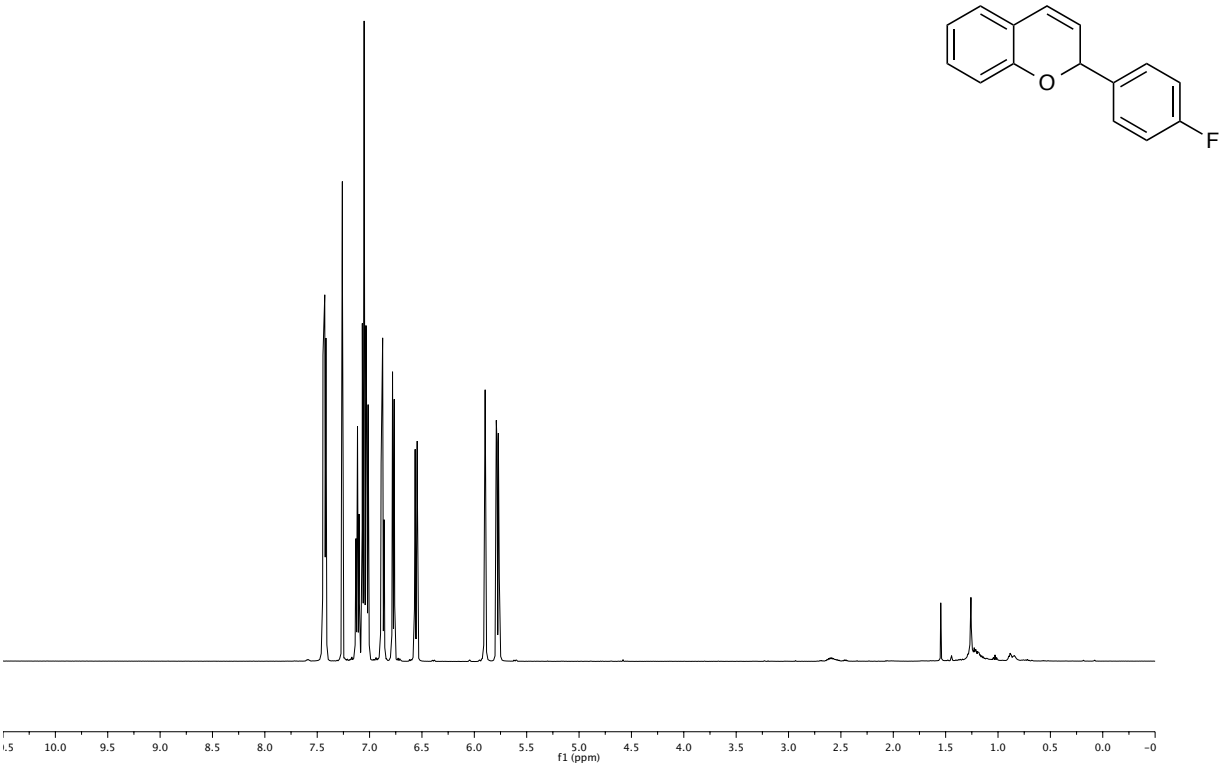
$^{1}$H NMR Spectrum of **2g** (500 MHz, $CDCl_3$):



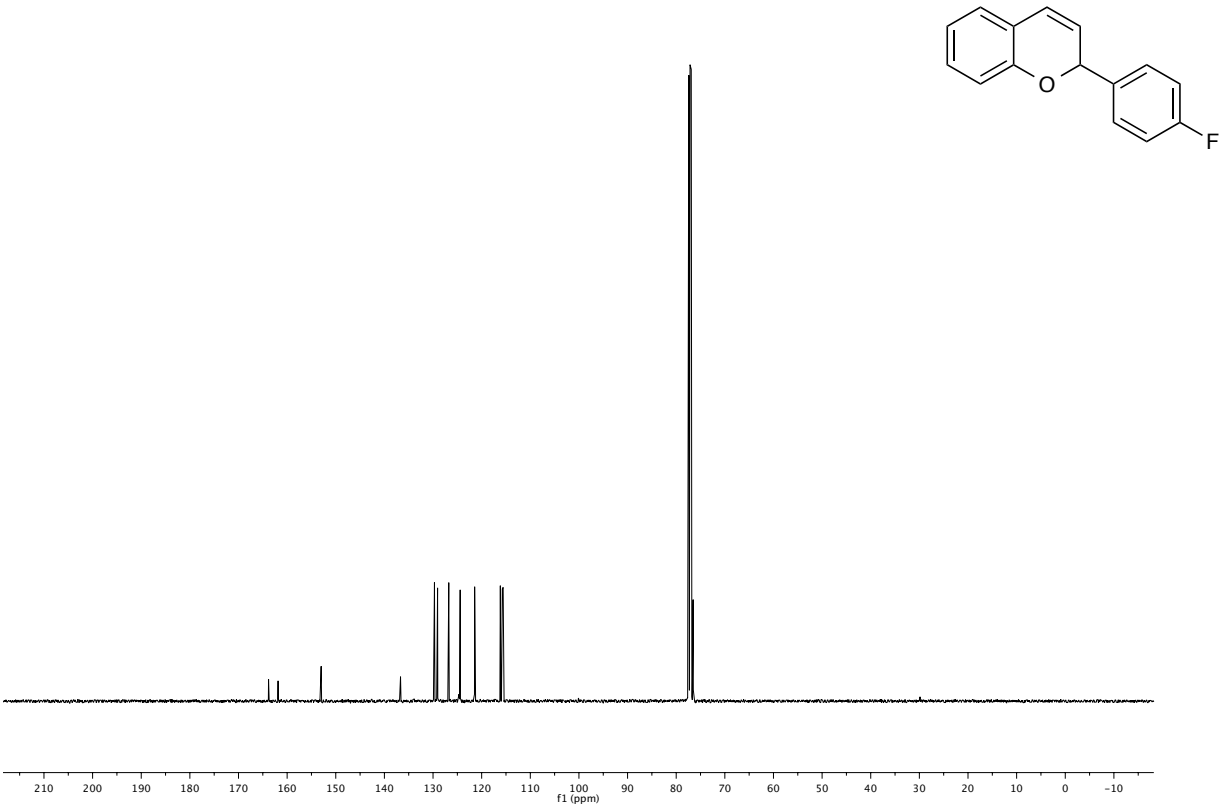

$^{13}$C NMR Spectrum of **2g** (125 MHz, $CDCl_3$):



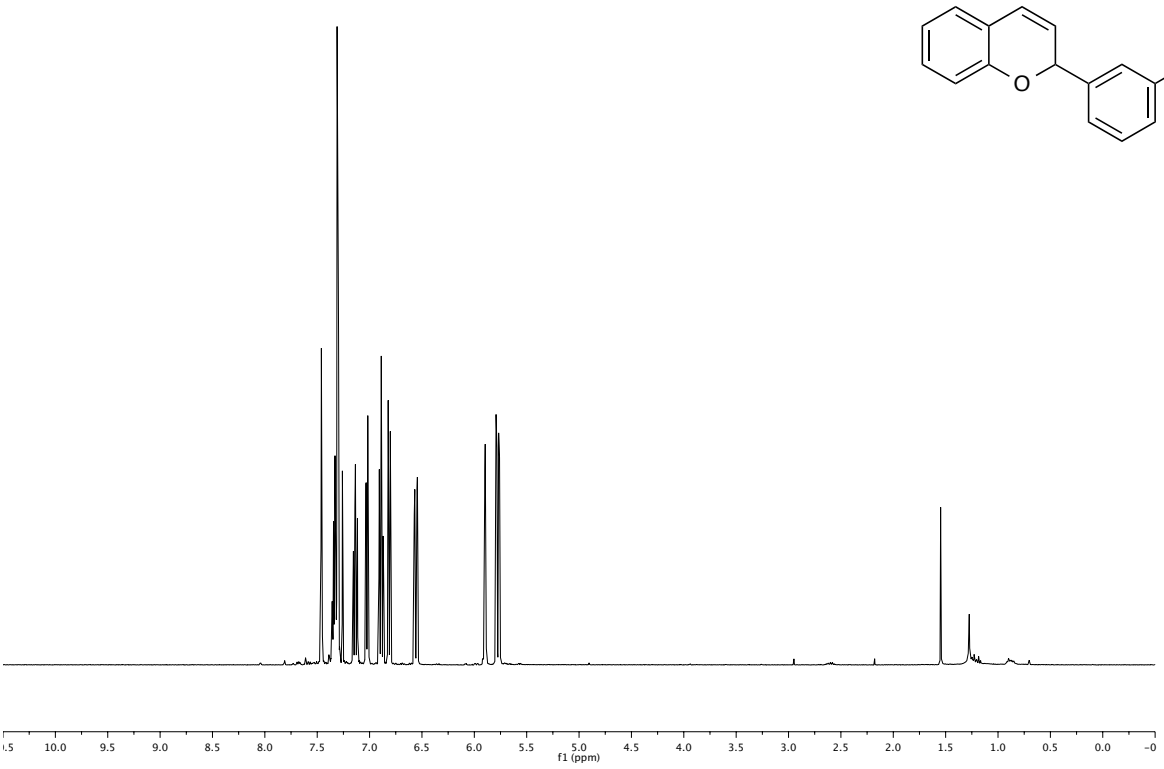
$^{1}$H NMR Spectrum of **2h** (500 MHz, $CDCl_3$):



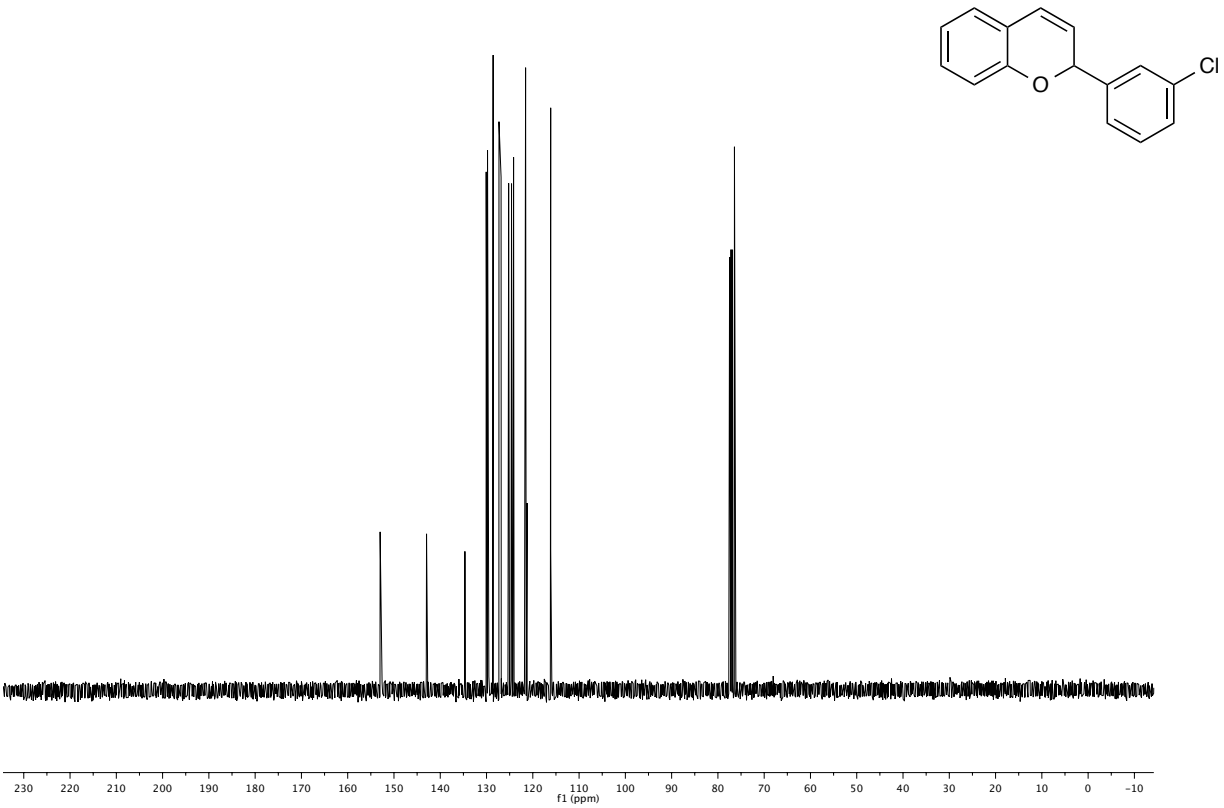

$^{13}$C NMR Spectrum of **2h** (125 MHz, $CDCl_3$):



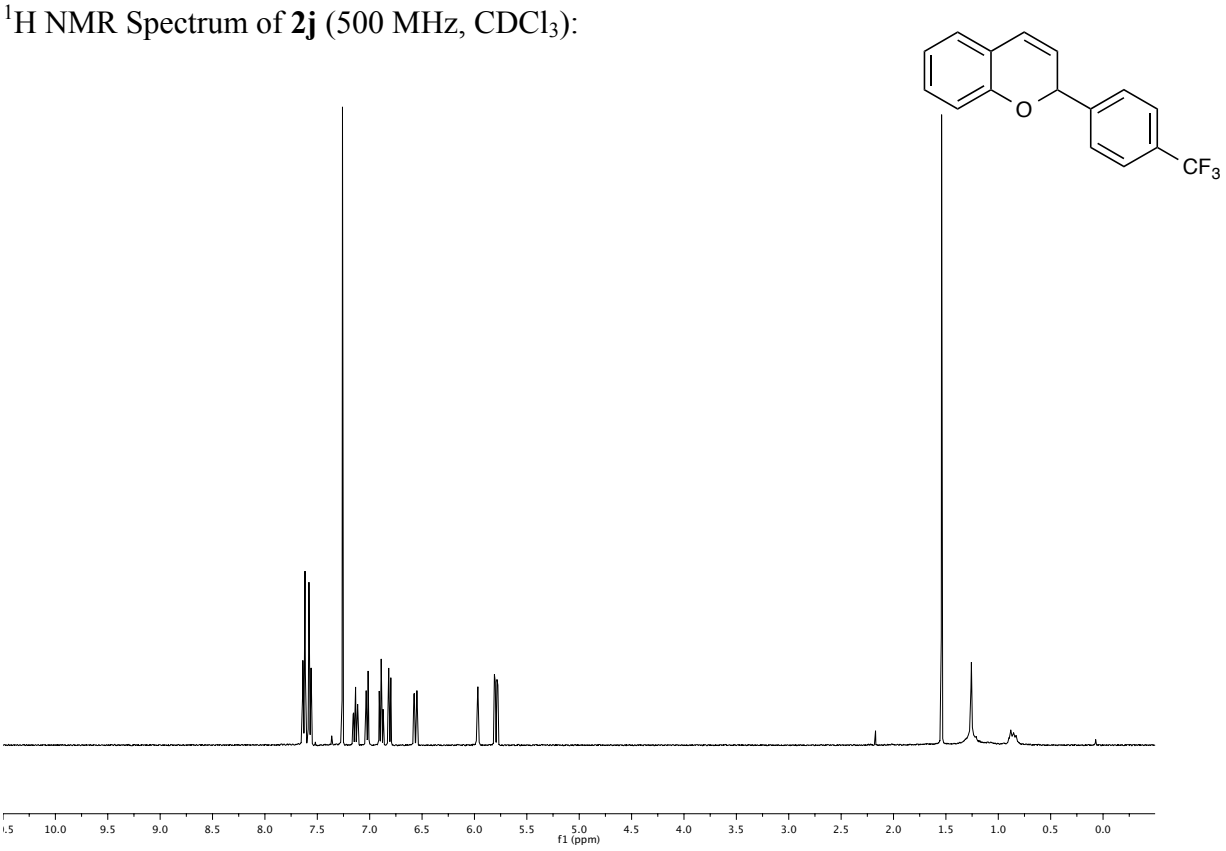
$^{1}$H NMR Spectrum of **2i** (500 MHz, $CDCl_3$):



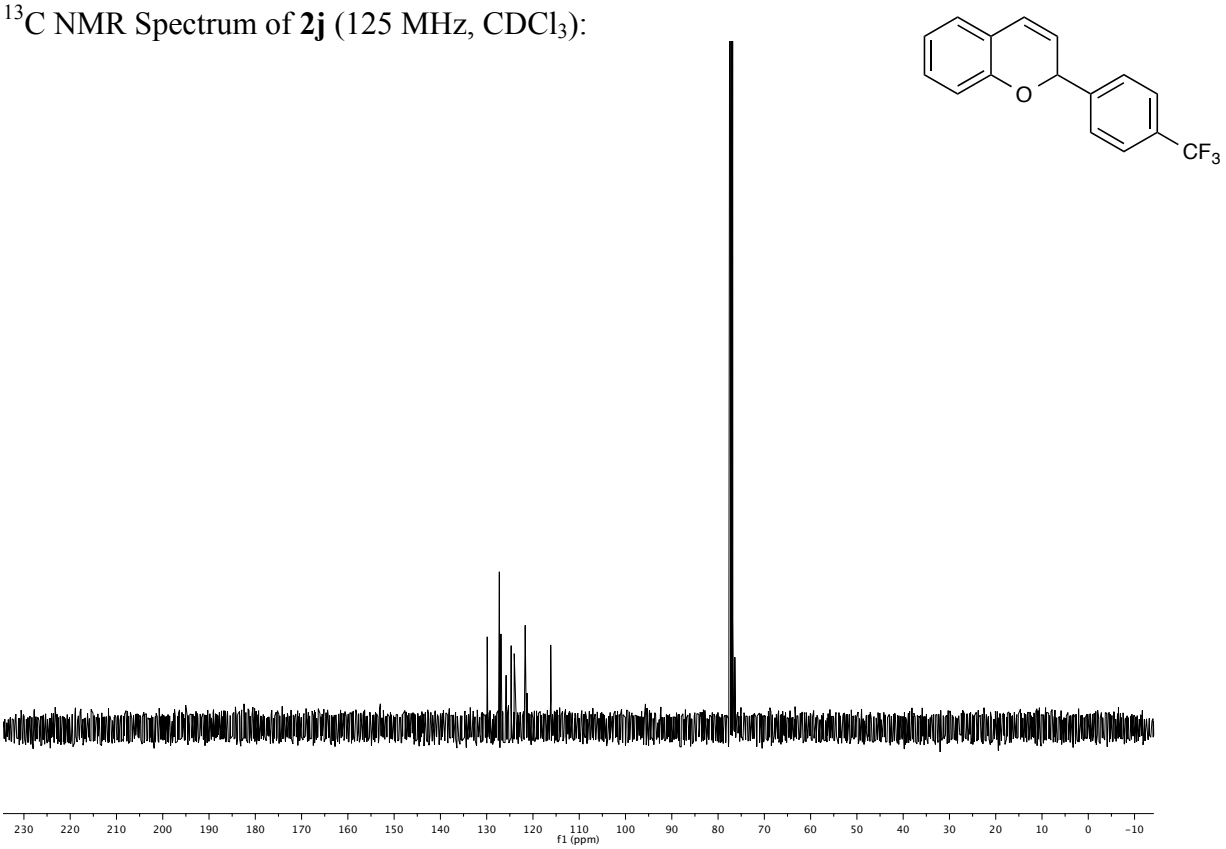

$^{13}$C NMR Spectrum of **2i** (125 MHz, $CDCl_3$):



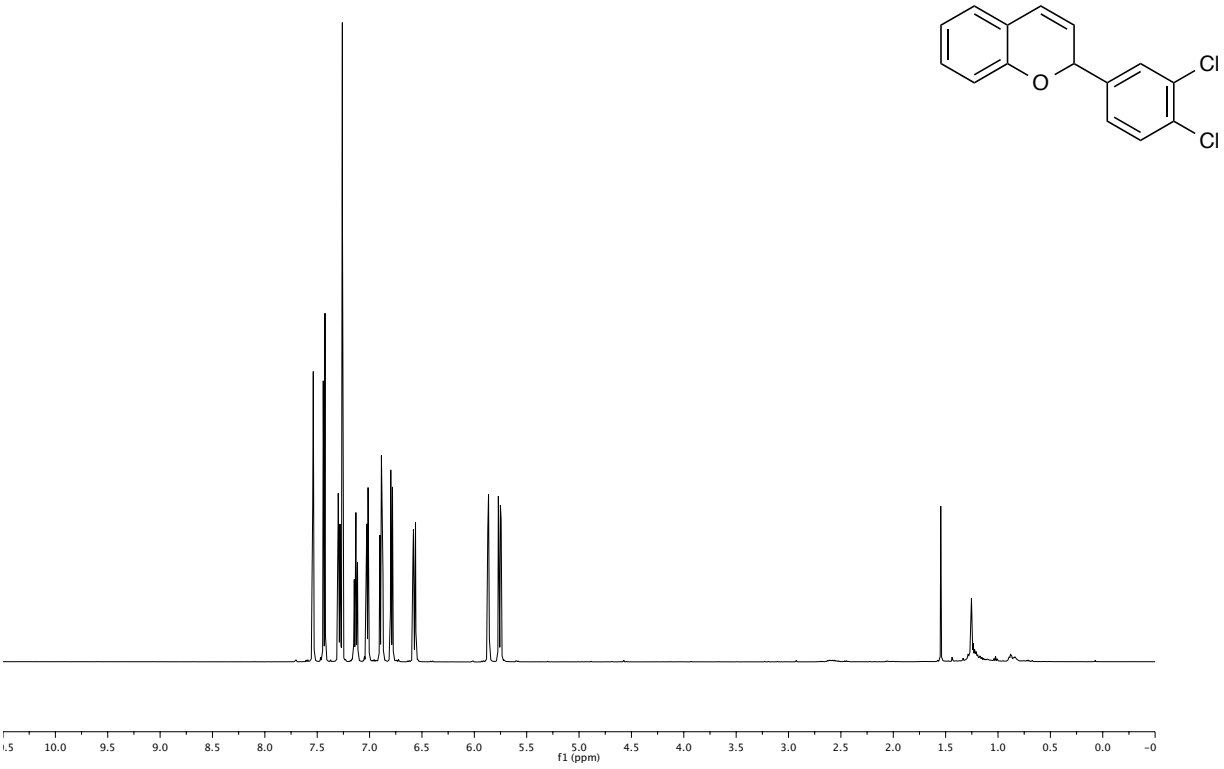
$^{1}$H NMR Spectrum of **2j** (500 MHz, $CDCl_3$):



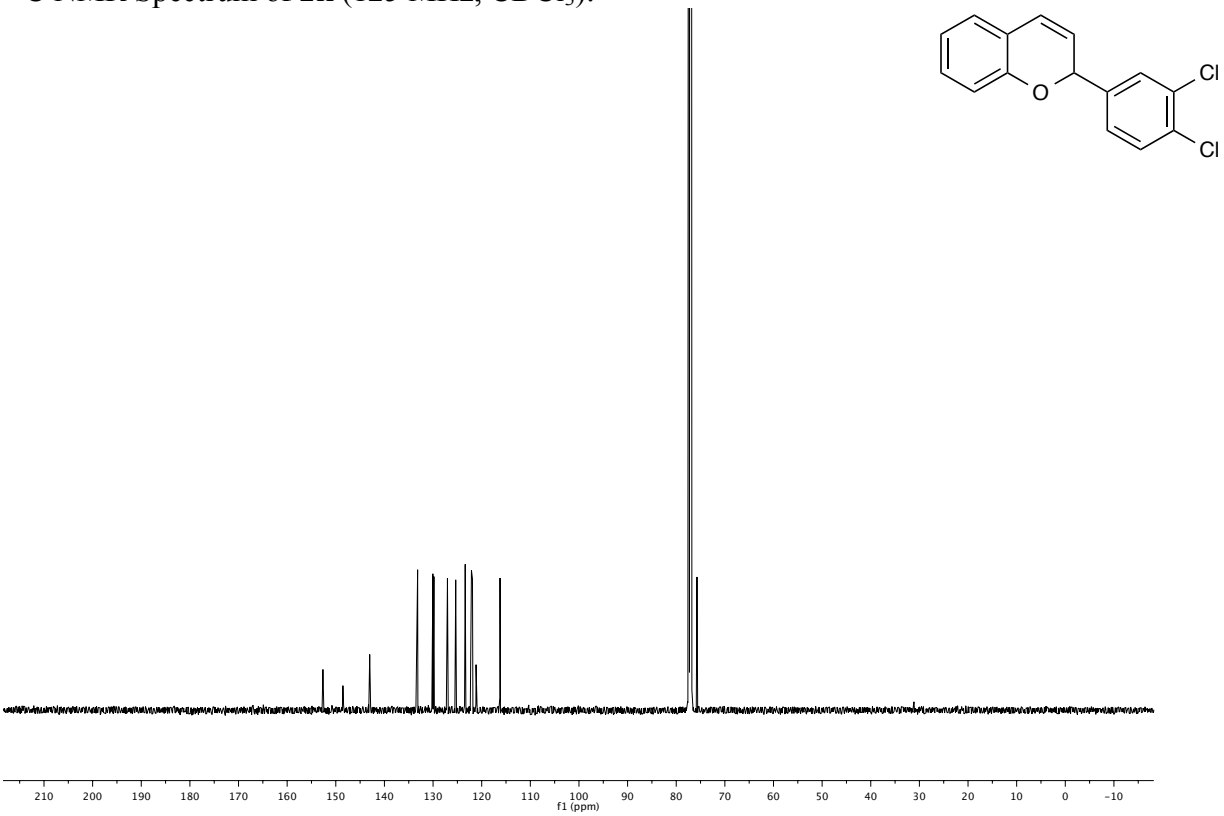

$^{13}$C NMR Spectrum of **2j** (125 MHz, $CDCl_3$):



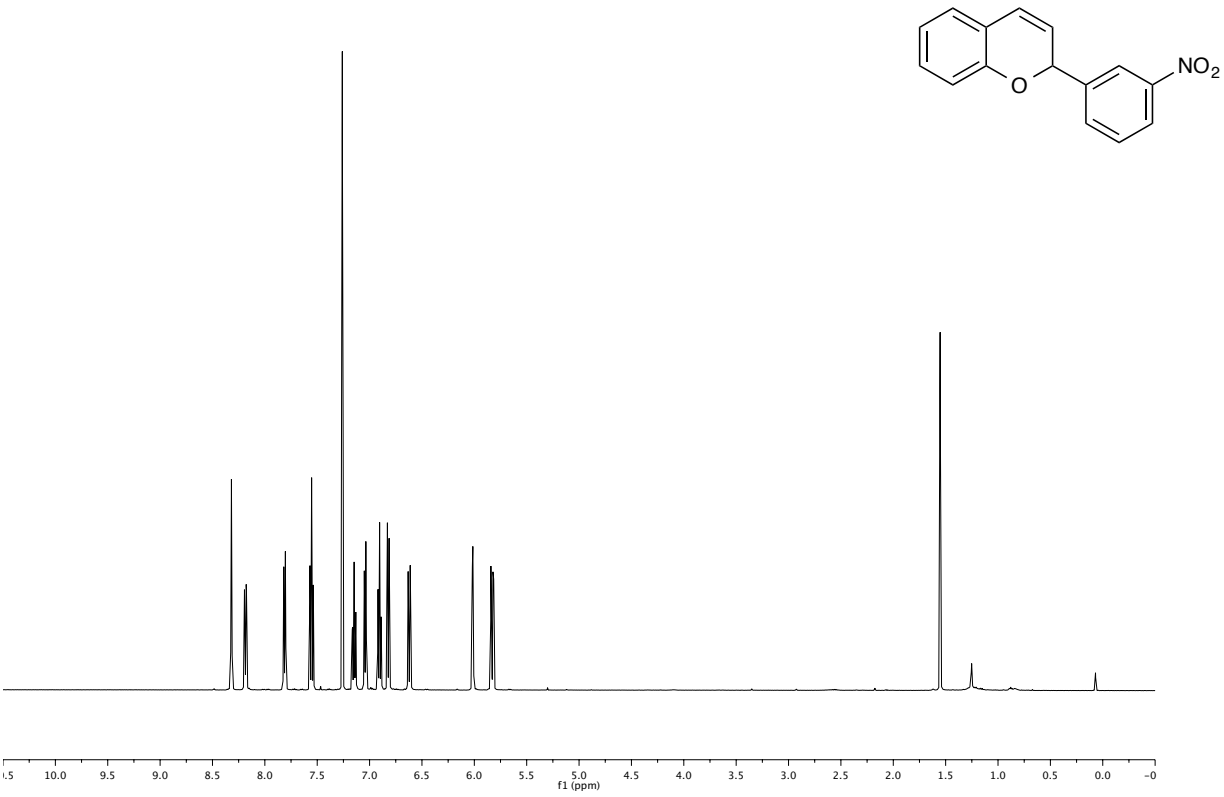
$^{1}$H NMR Spectrum of **2k** (500 MHz, $CDCl_3$):



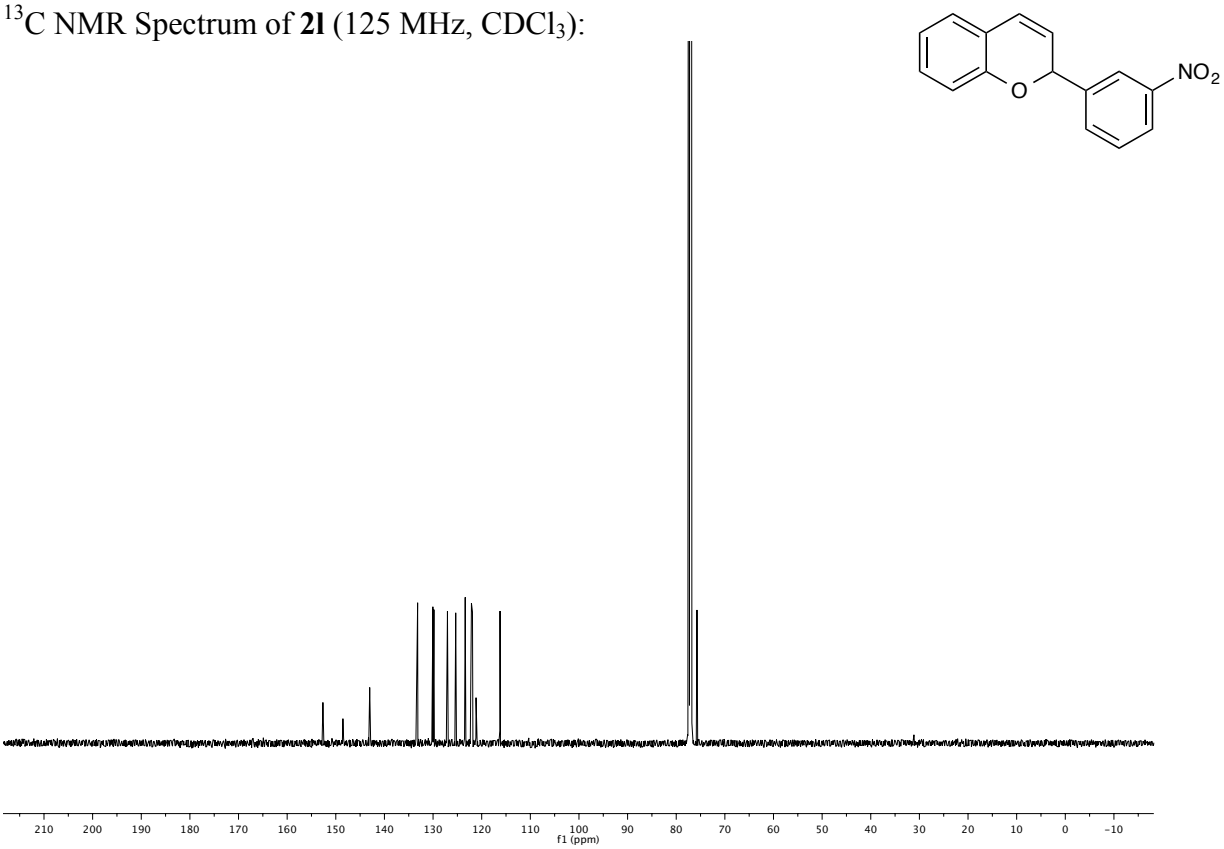

$^{13}$C NMR Spectrum of **2k** (125 MHz, $CDCl_3$):



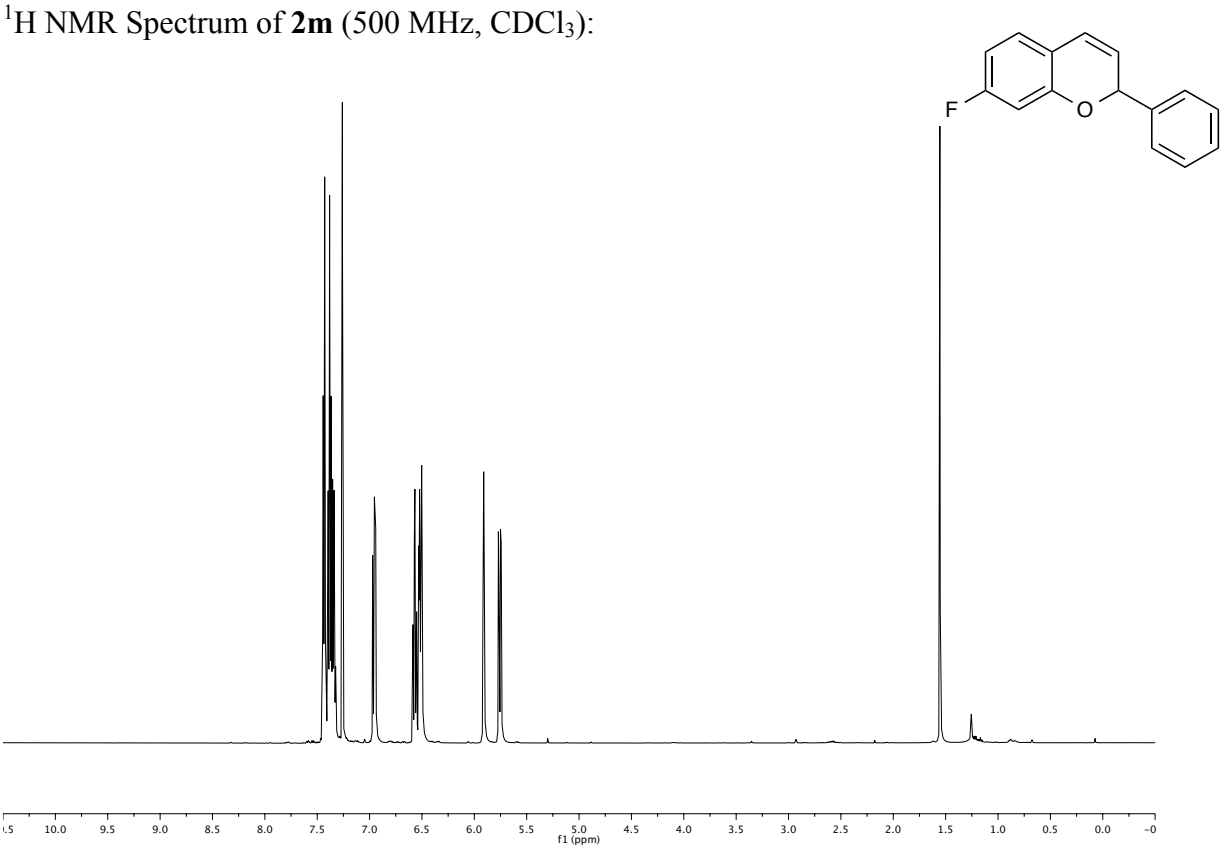
$^{1}$H NMR Spectrum of **2l** (500 MHz, $CDCl_3$):



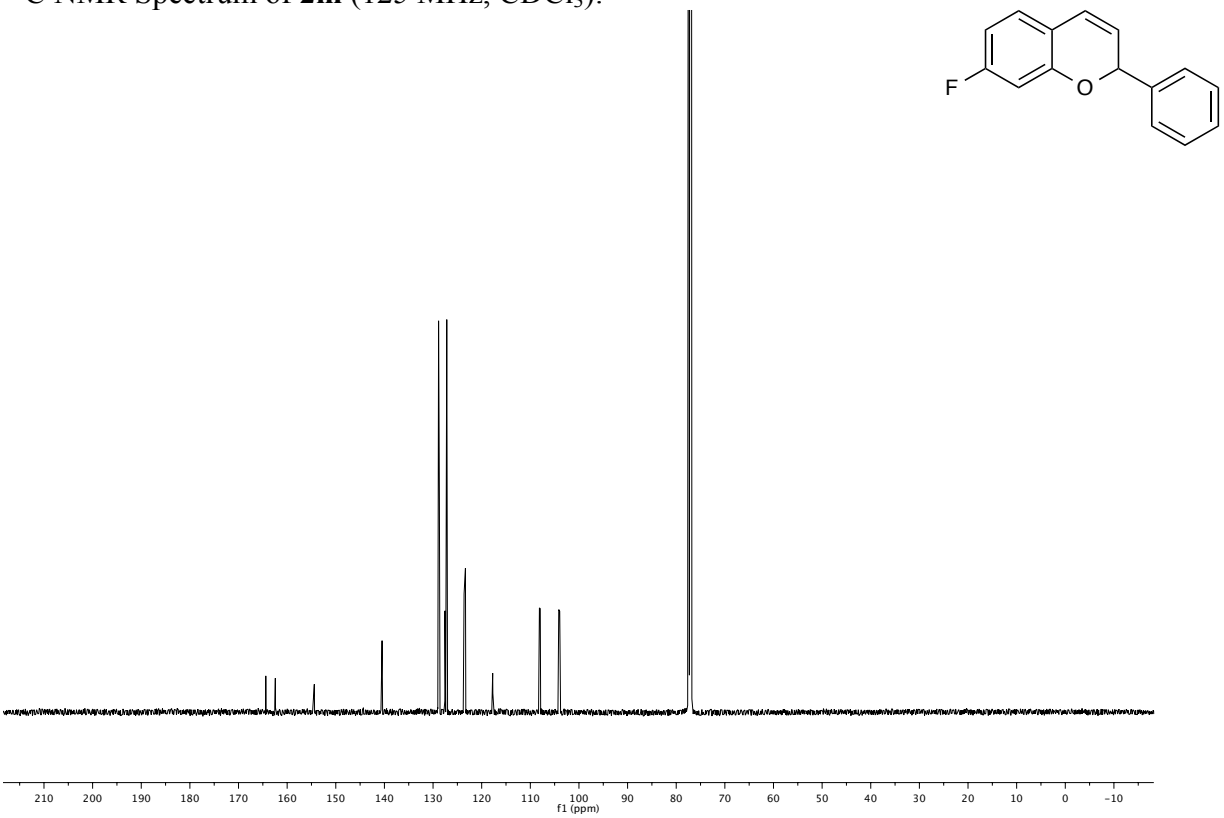

$^{13}$C NMR Spectrum of **2l** (125 MHz, $CDCl_3$):



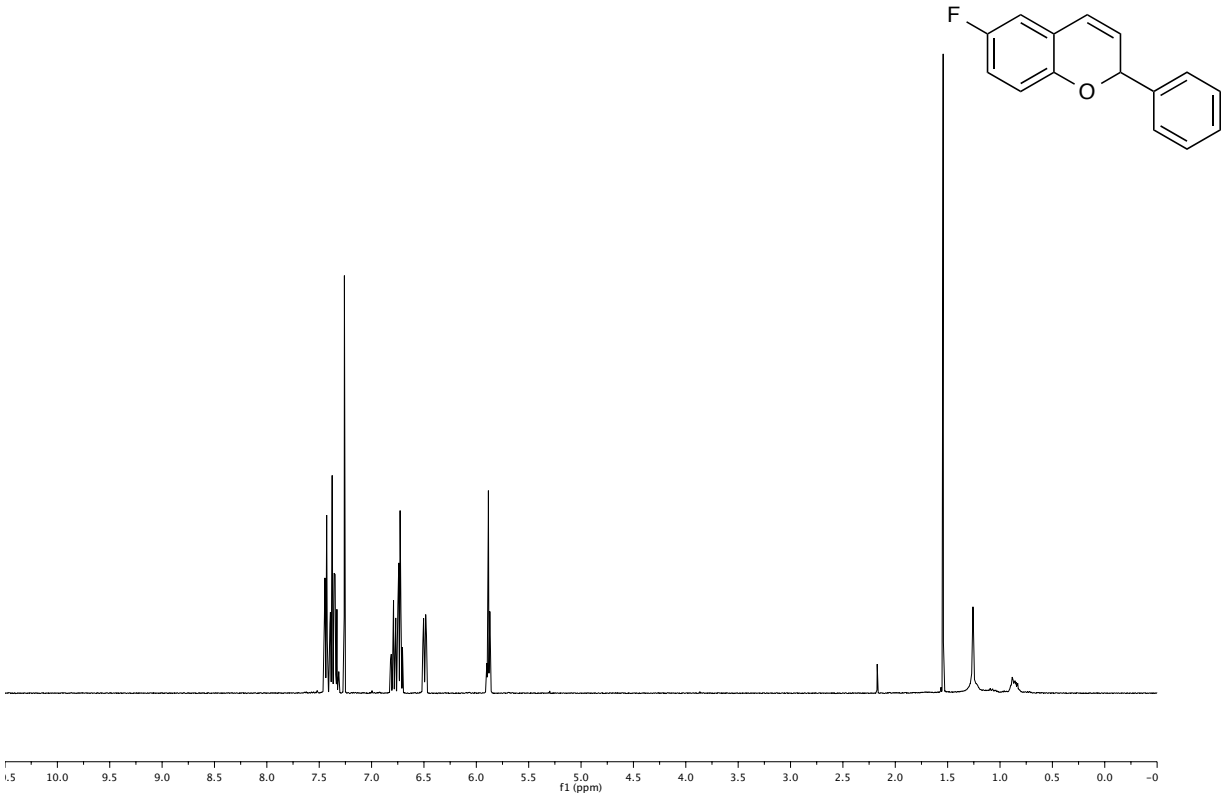
$^{1}$H NMR Spectrum of **2m** (500 MHz, $CDCl_3$):



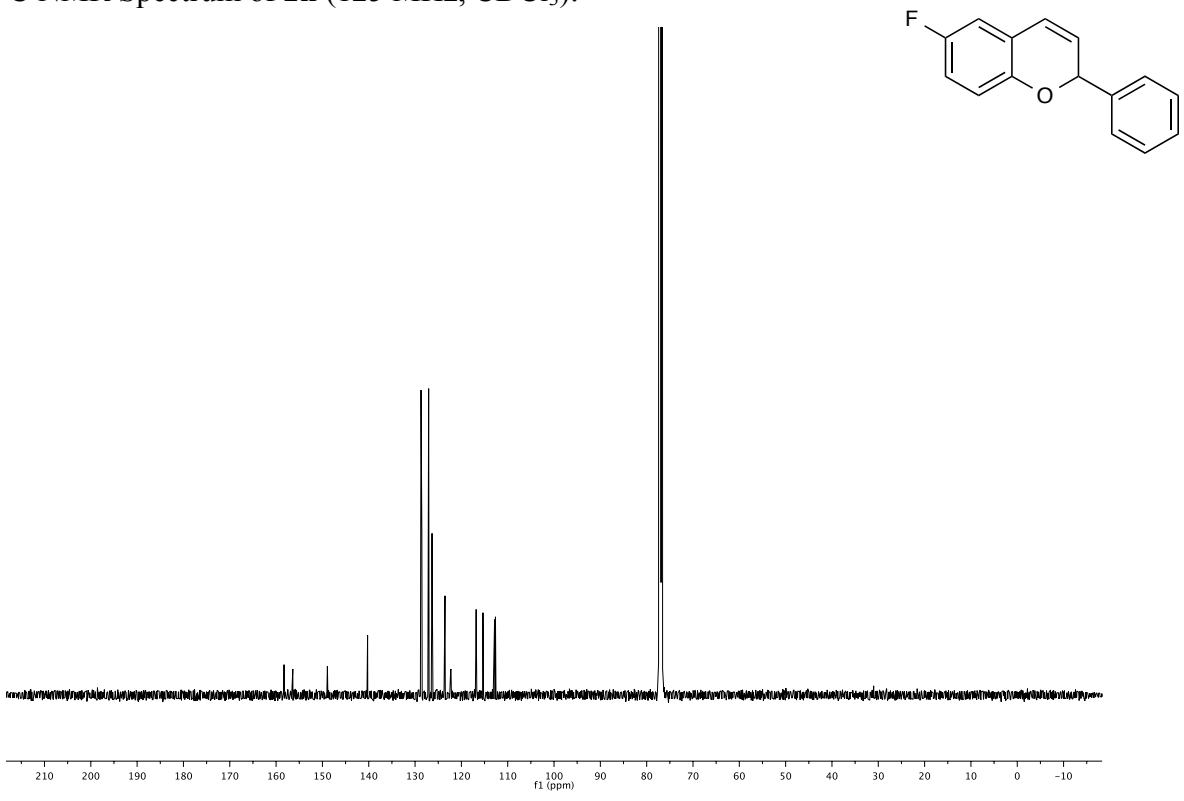

$^{13}$C NMR Spectrum of **2m** (125 MHz, $CDCl_3$):



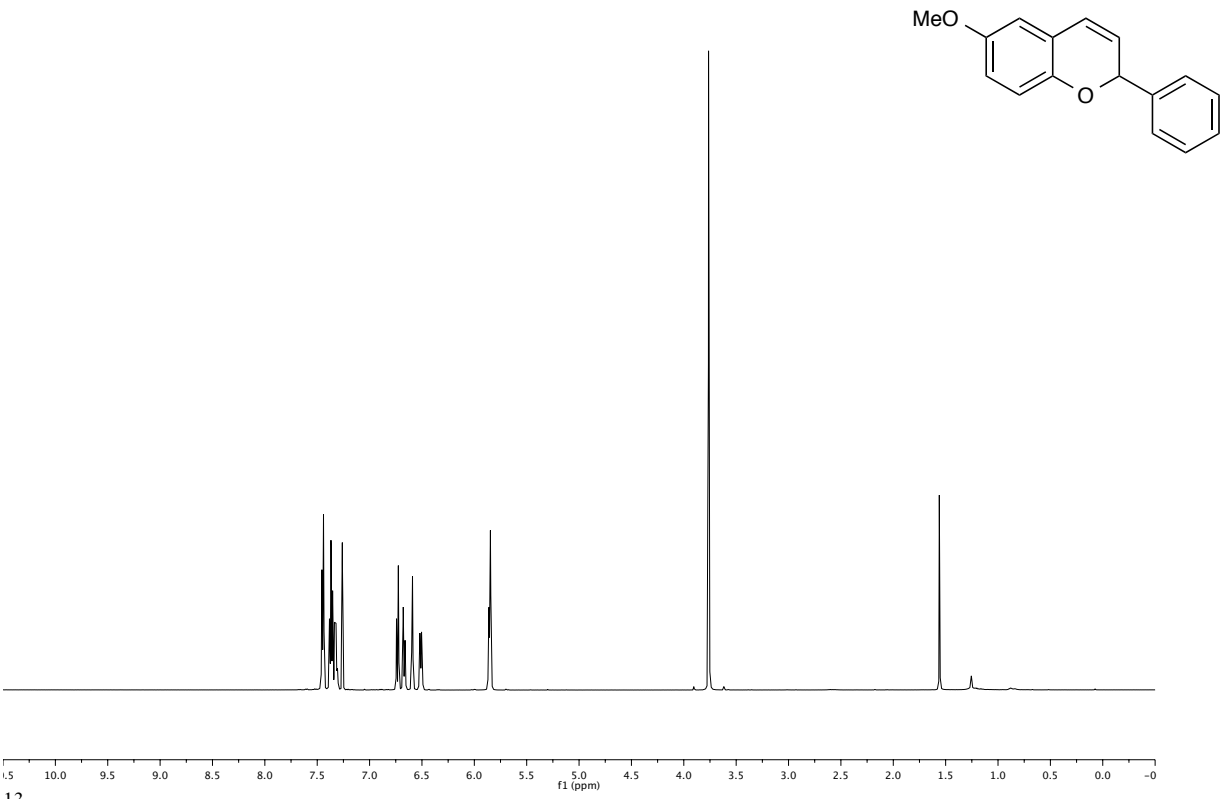
$^{1}$H NMR Spectrum of **2n** (500 MHz, $CDCl_3$):



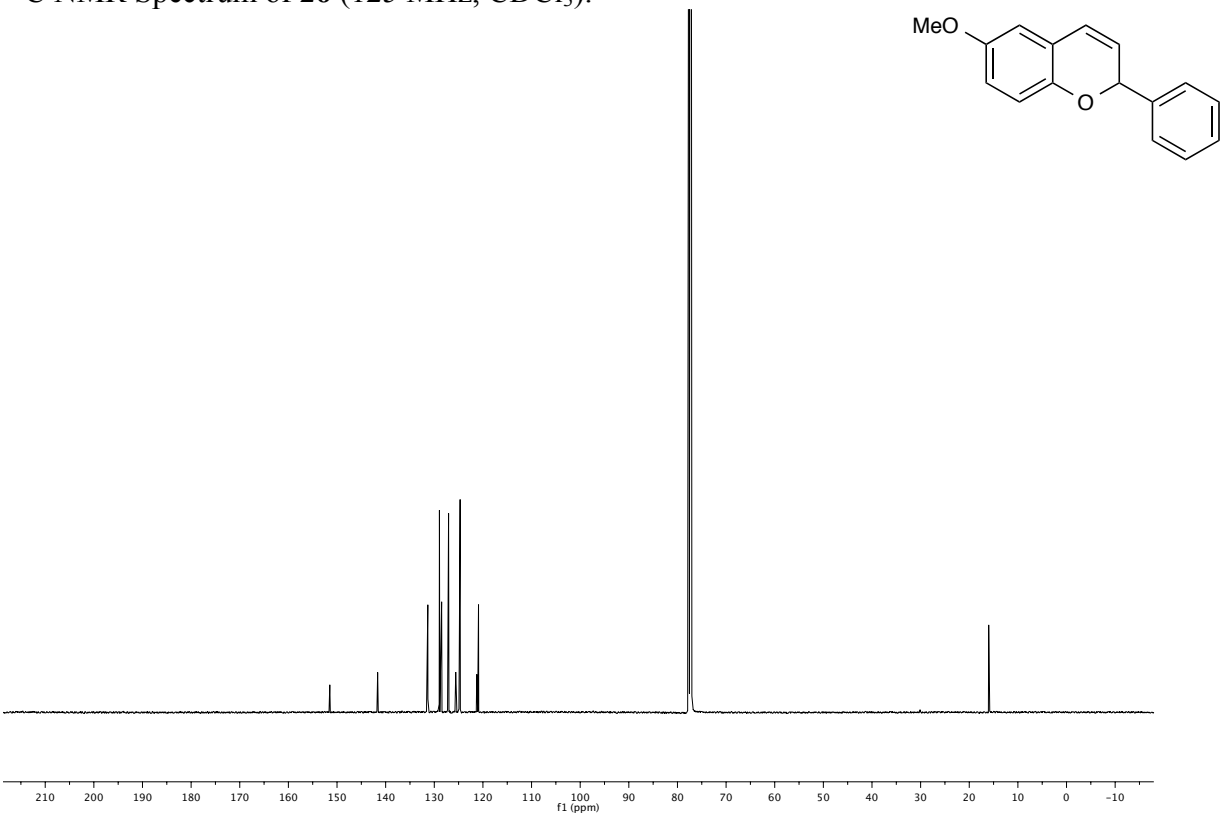

$^{13}$C NMR Spectrum of **2n** (125 MHz, $CDCl_3$):



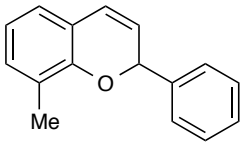
$^{1}$H NMR Spectrum of **2o** (500 MHz, $CDCl_3$):

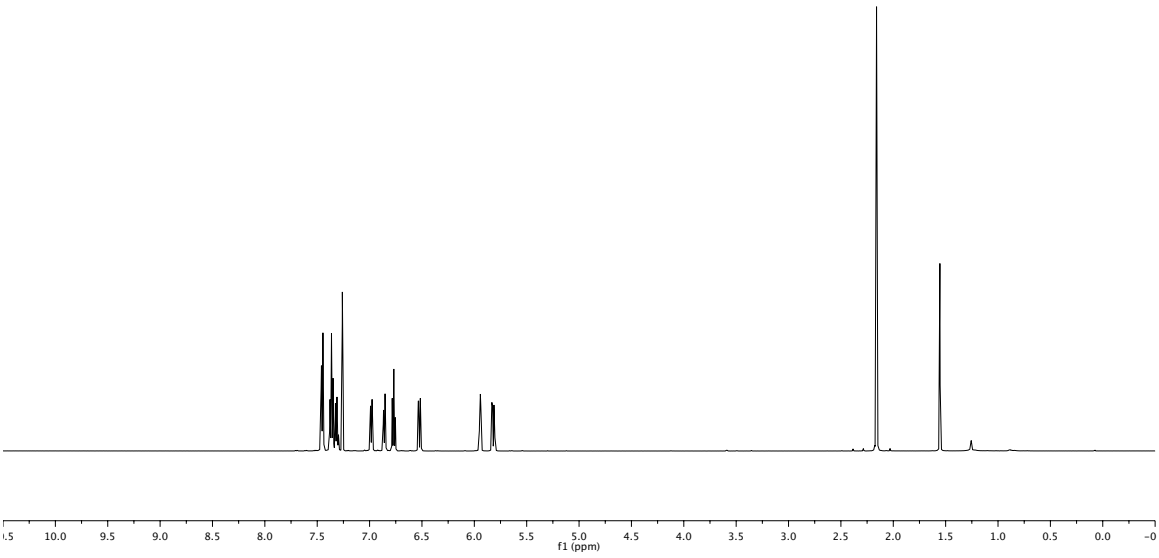



$^{13}$C NMR Spectrum of **2o** (125 MHz, $CDCl_3$):

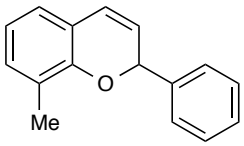


$^{1}$H NMR Spectrum of **2p** (500 MHz, $CDCl_3$):



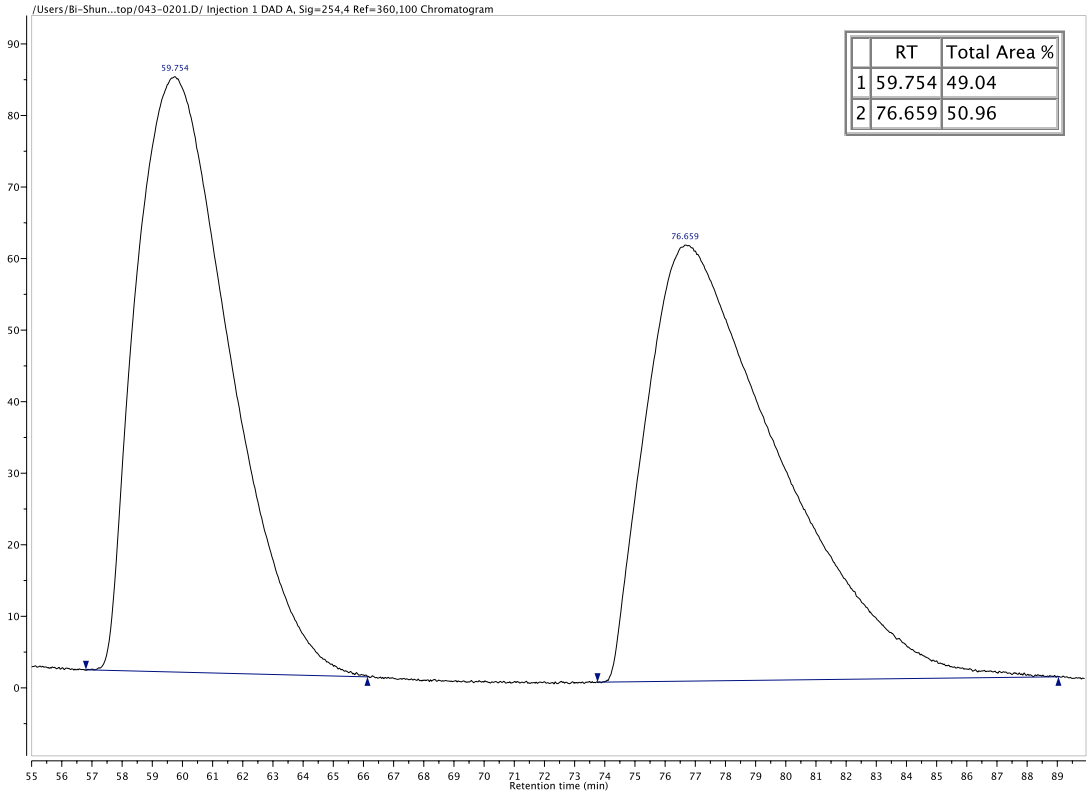




$^{13}$C NMR Spectrum of **2p** (125 MHz, $CDCl_3$):



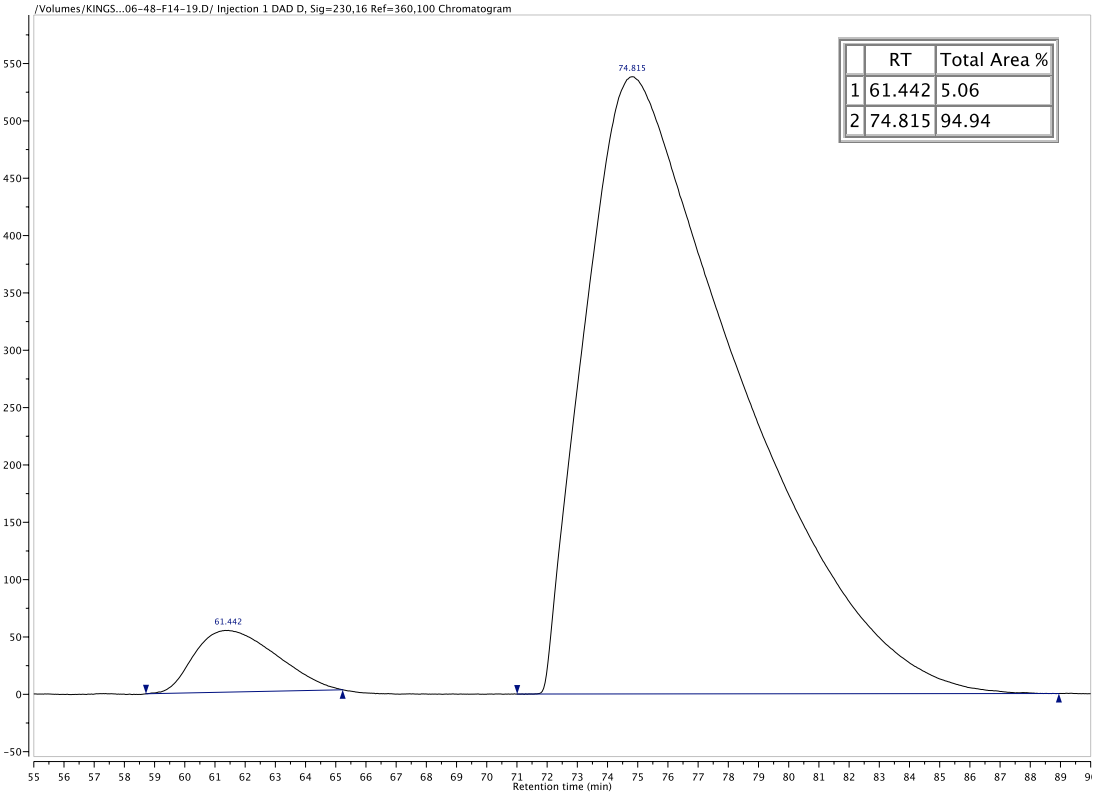
## HPLC Traces of Racemic and Enantioenriched Compounds

Racemic **2a:**



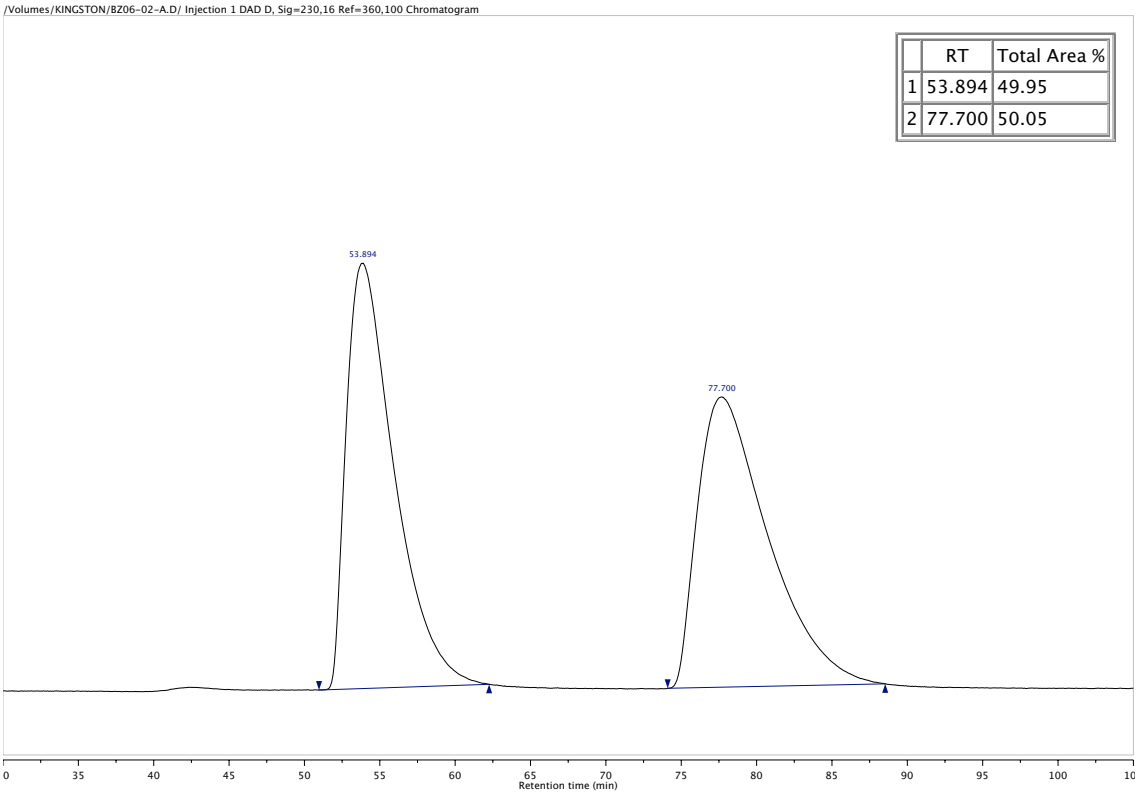

| | RT | Total Area % |
|---|---|---|
| 1 | 59.754 | 49.04 |
| 2 | 76.659 | 50.96 |

Enantioenriched **2a:**

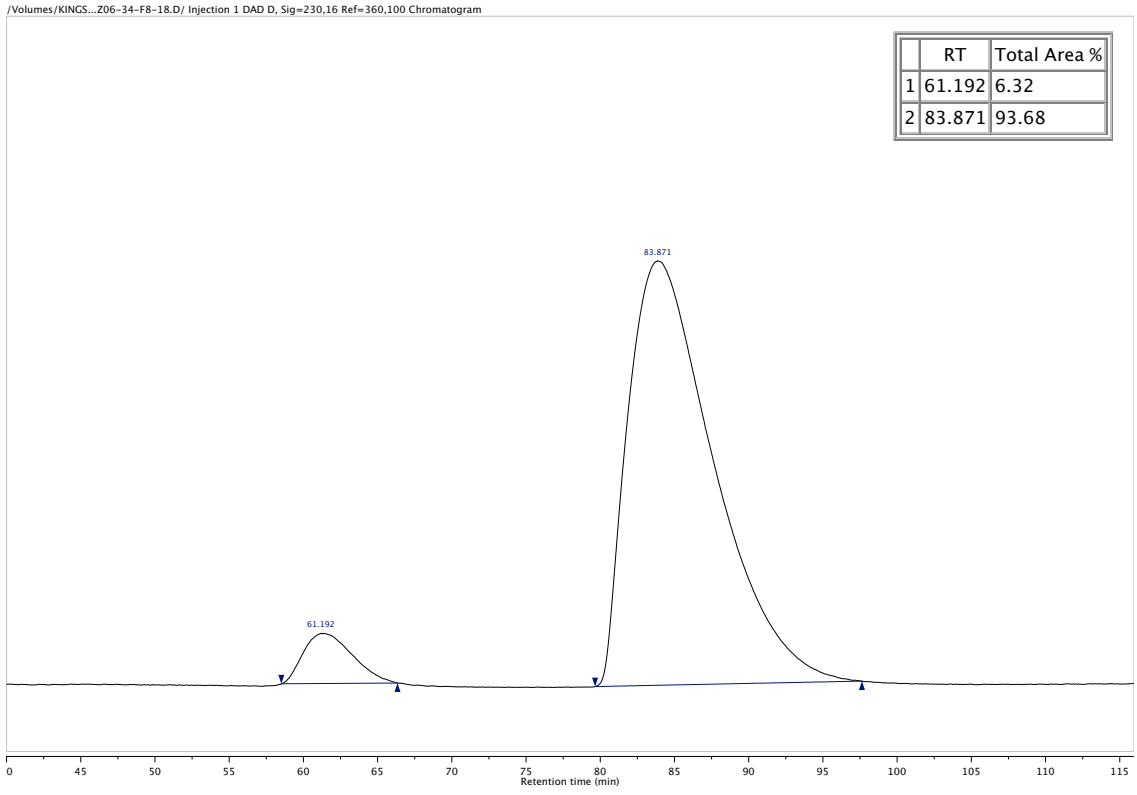



| | RT | Total Area % |
|---|---|---|
| 1 | 61.442 | 5.06 |
| 2 | 74.815 | 94.94 |

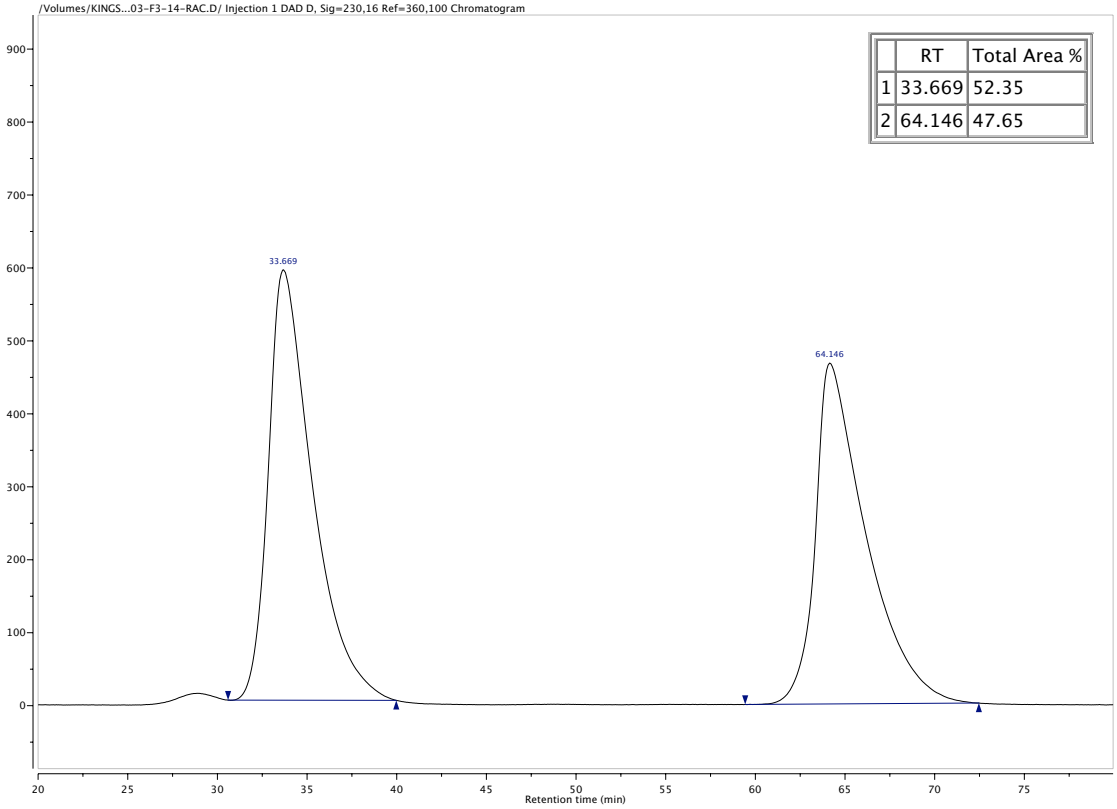
Racemic **2b**:



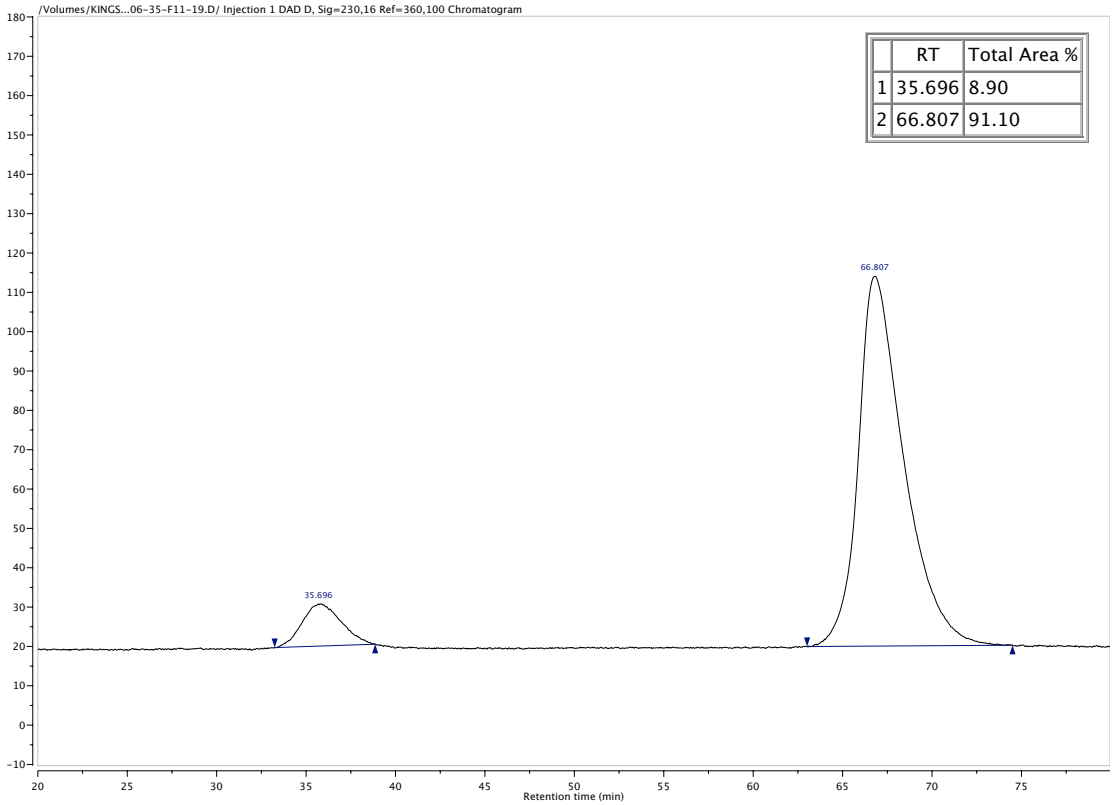

Enantioenriched **2b**:



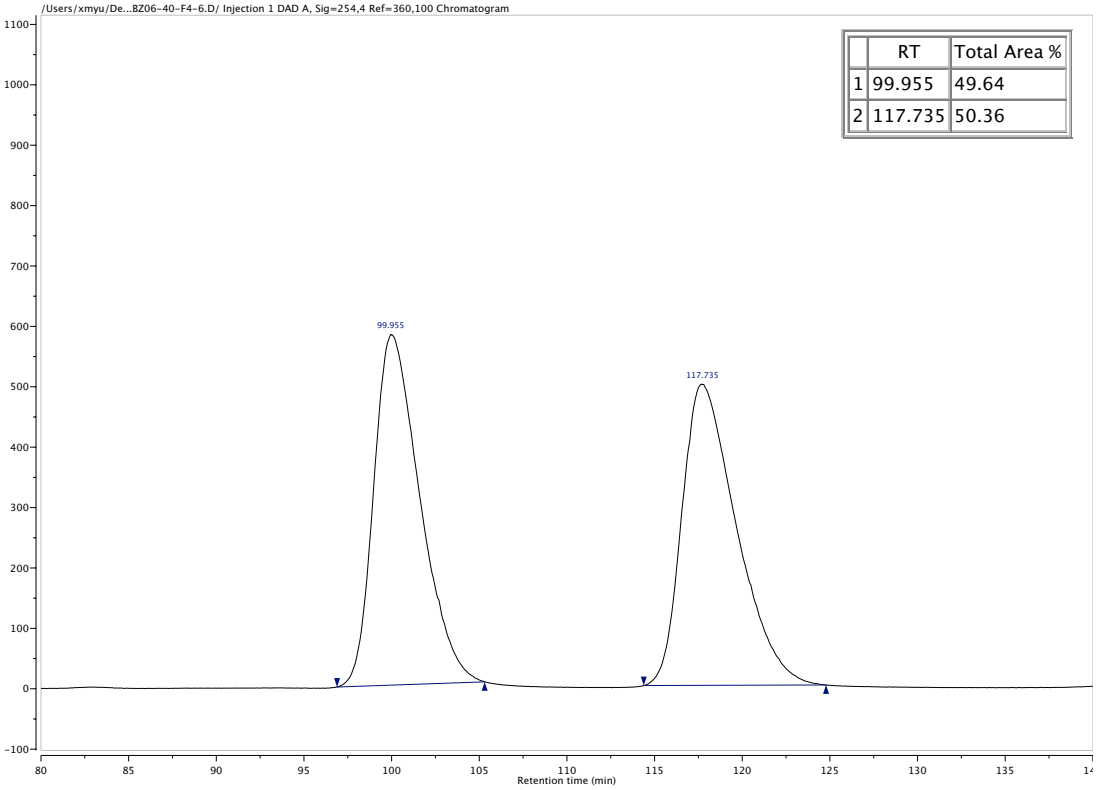
Racemic **2c**:



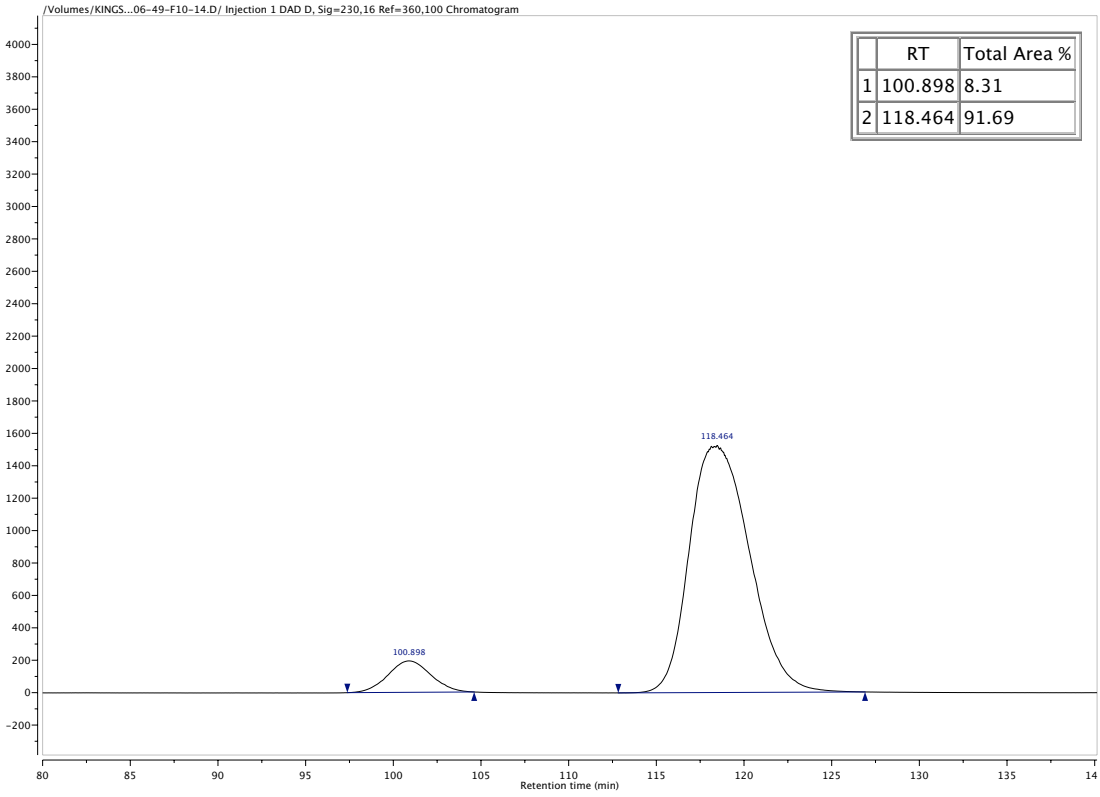

Enantioenriched **2c**:



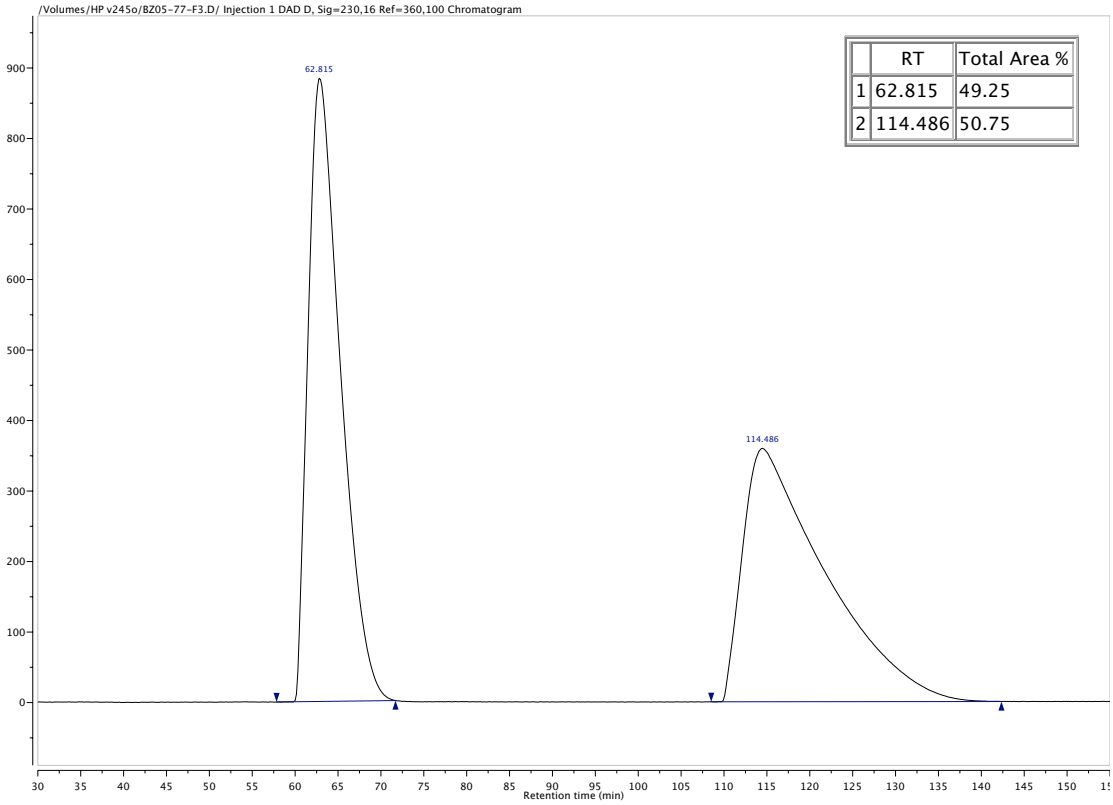
Racemic **2d**:




Enantioenriched **2d**:

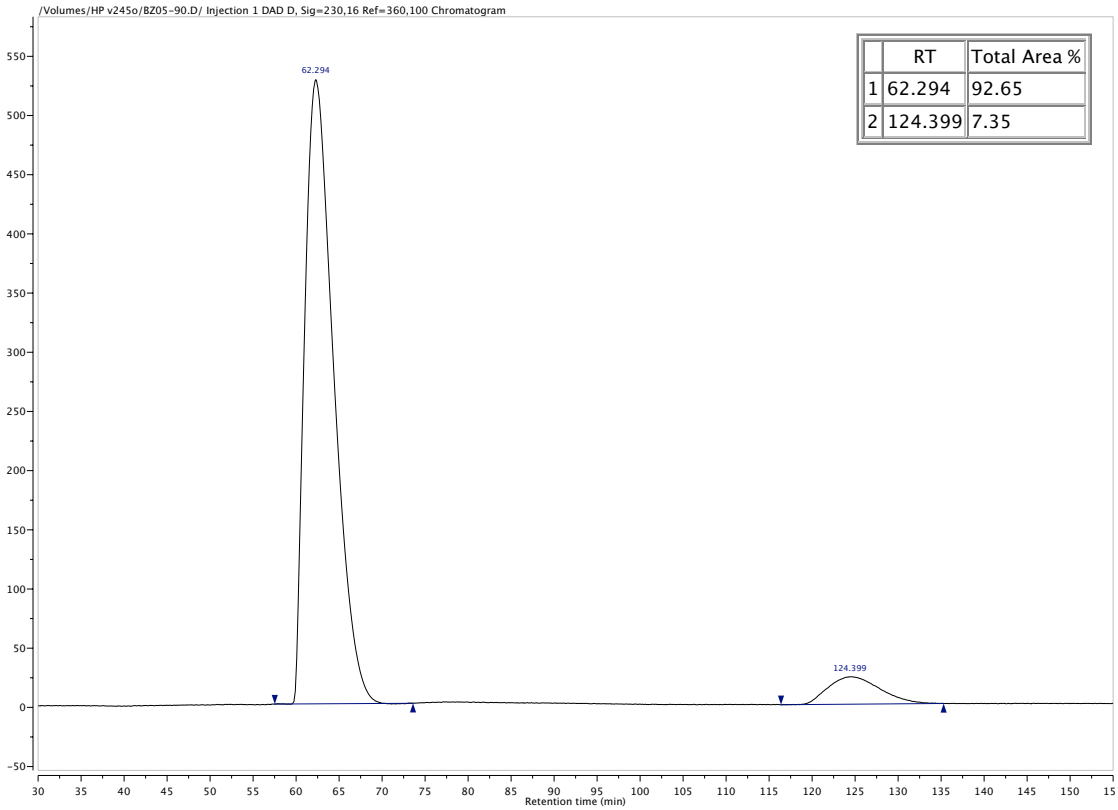


Racemic **2e**:



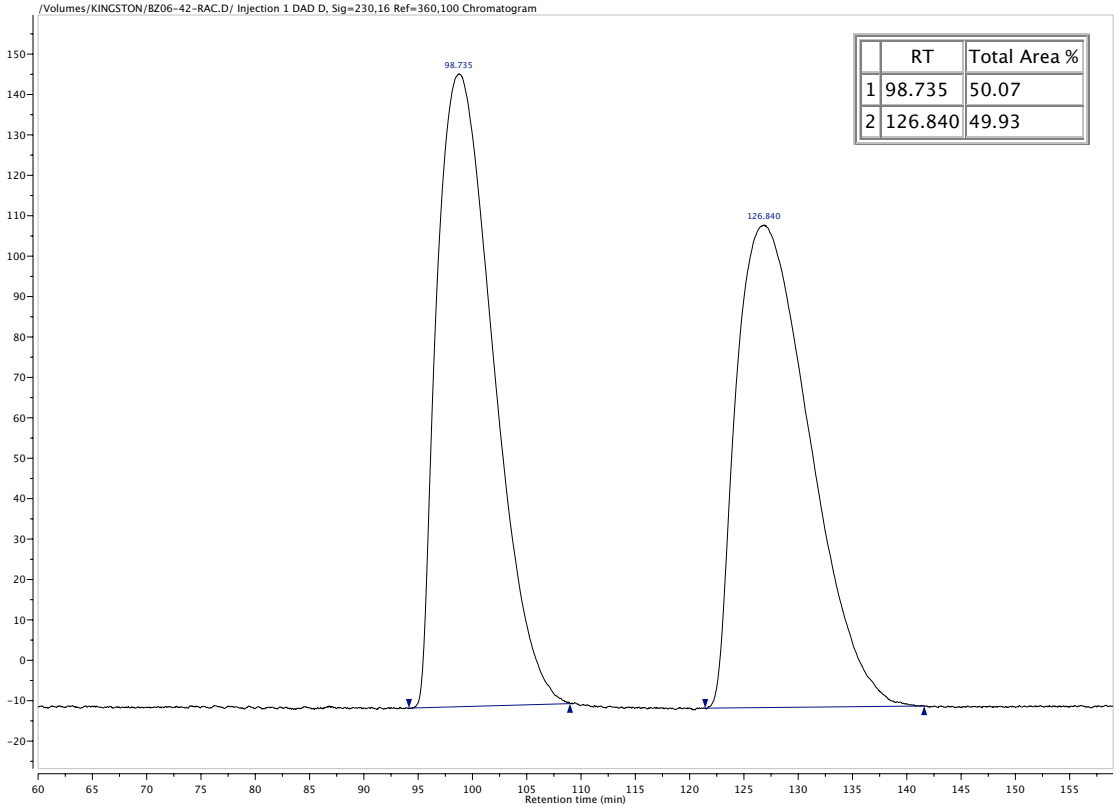

| | RT | Total Area % |
|---|---|---|
| 1 | 62.815 | 49.25 |
| 2 | 114.486 | 50.75 |

Enantioenriched **2e**:



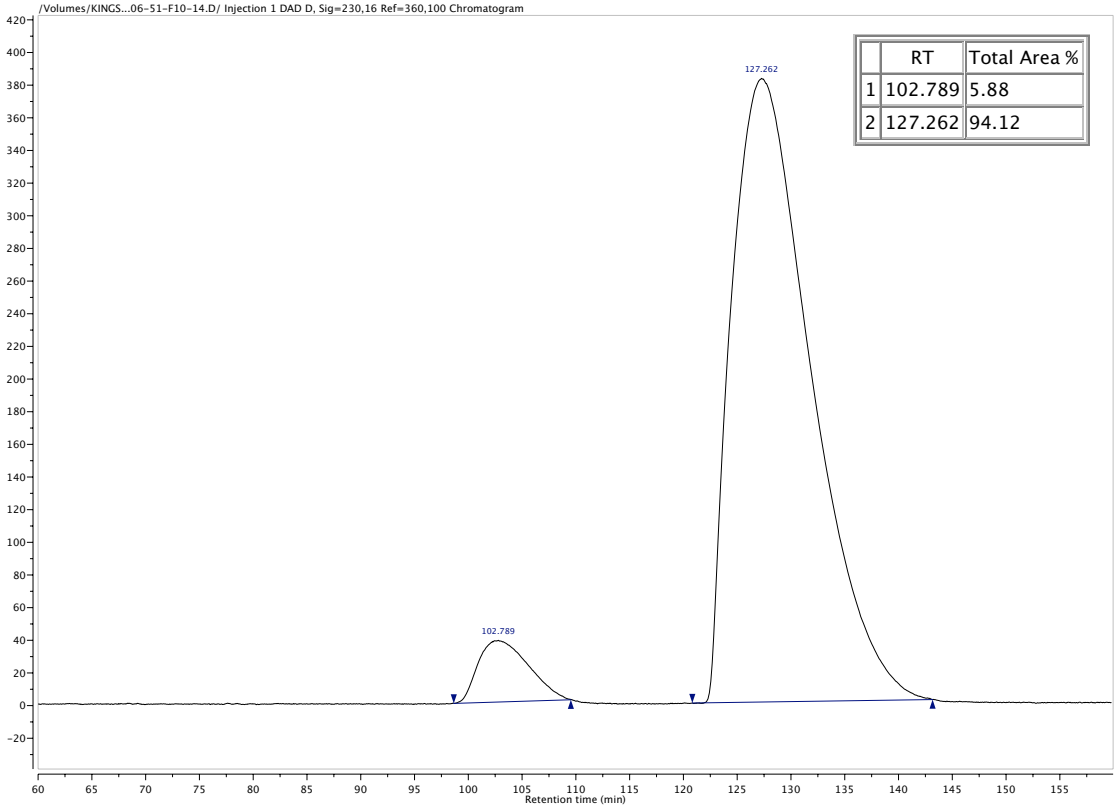

| | RT | Total Area % |
|---|---|---|
| 1 | 62.294 | 92.65 |
| 2 | 124.399 | 7.35 |

Racemic **2f**:



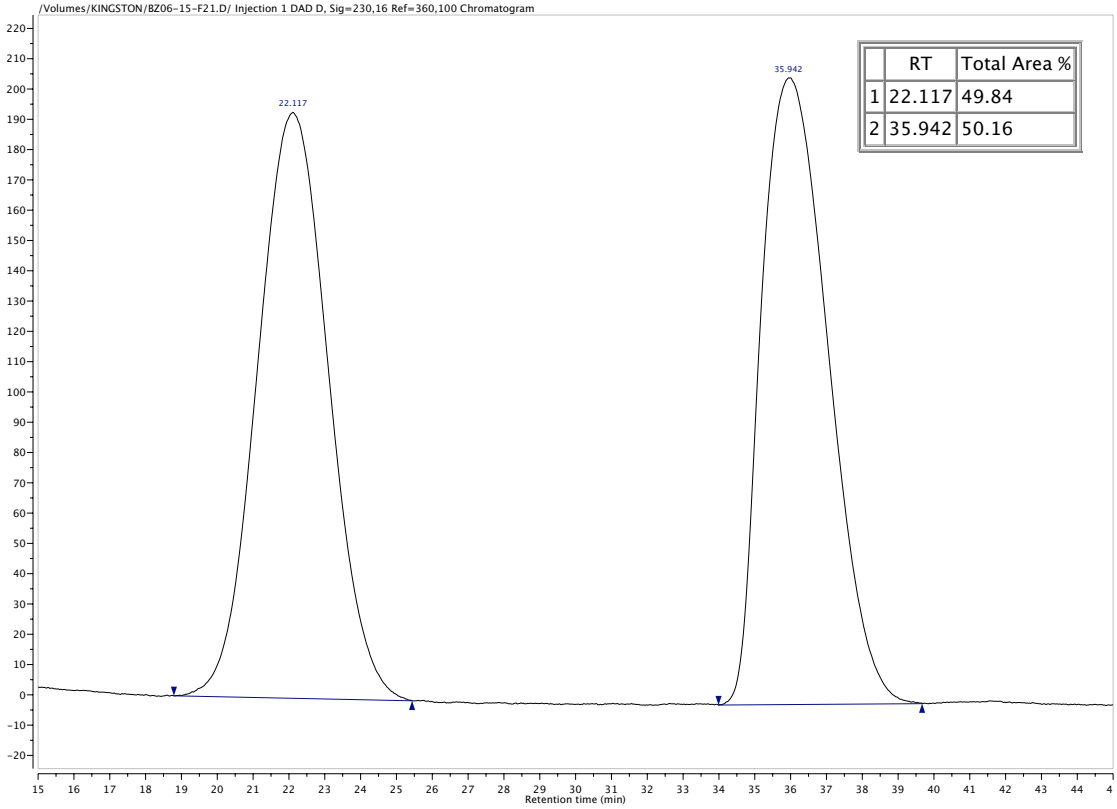

| | RT | Total Area % |
|---|---|---|
| 1 | 98.735 | 50.07 |
| 2 | 126.840 | 49.93 |

Enantioenriched **2f**:

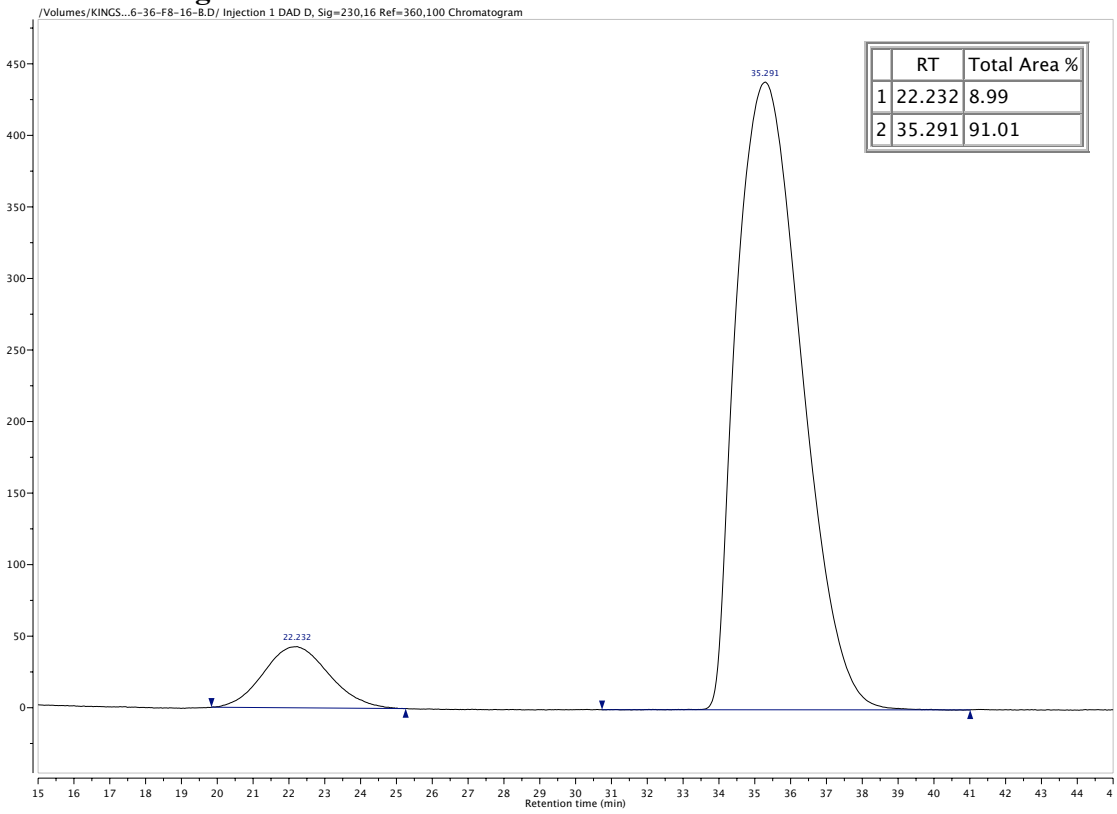



| | RT | Total Area % |
|---|---|---|
| 1 | 102.789 | 5.88 |
| 2 | 127.262 | 94.12 |

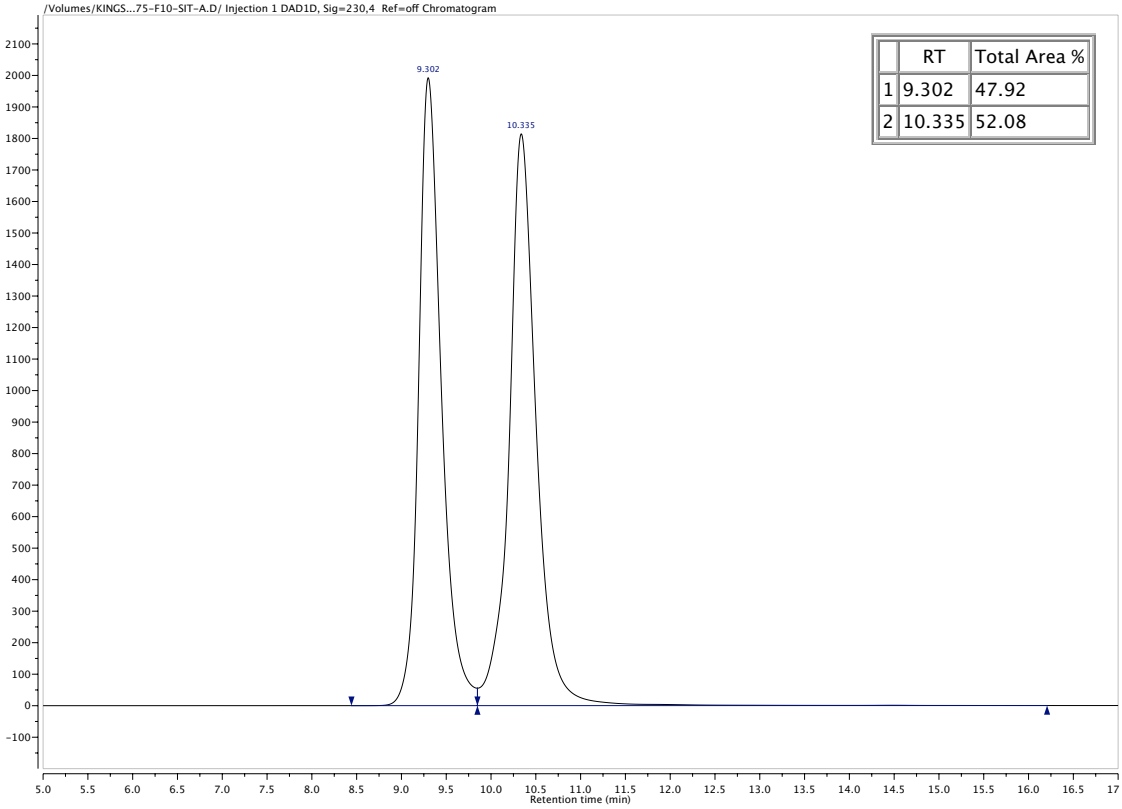
Racemic **2g**:




Enantioenriched **2g**:

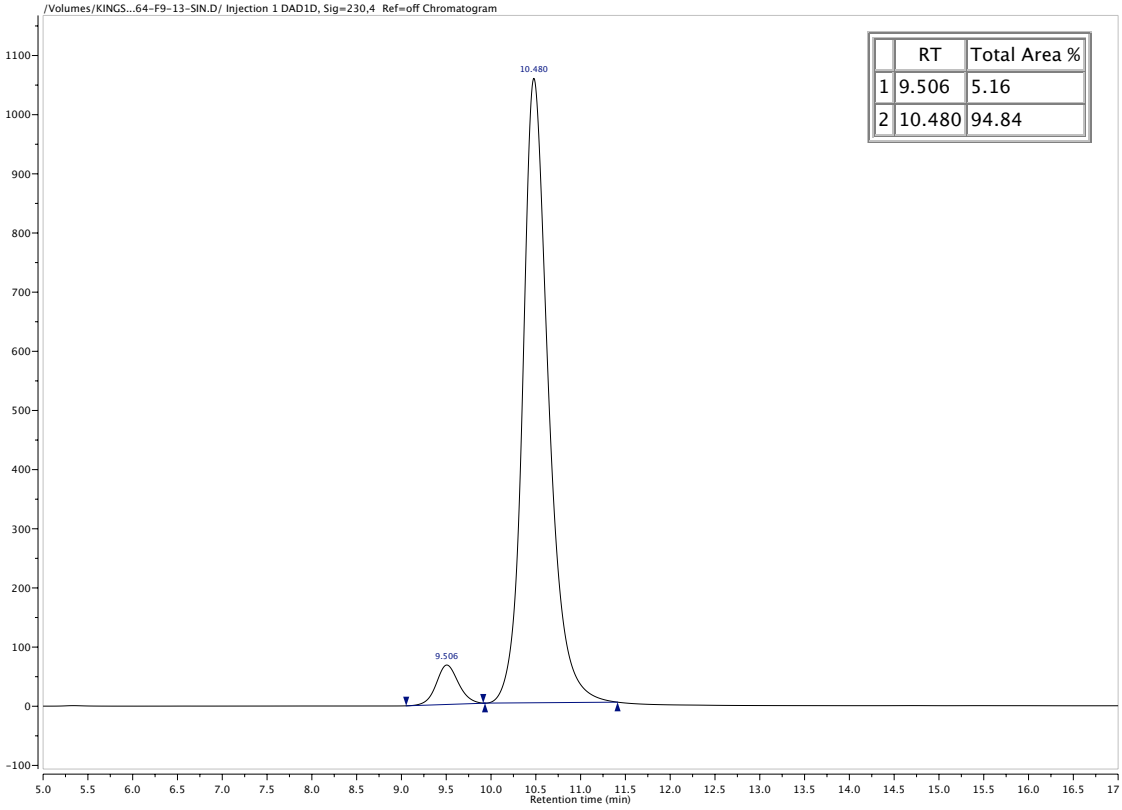


Racemic **2h**:



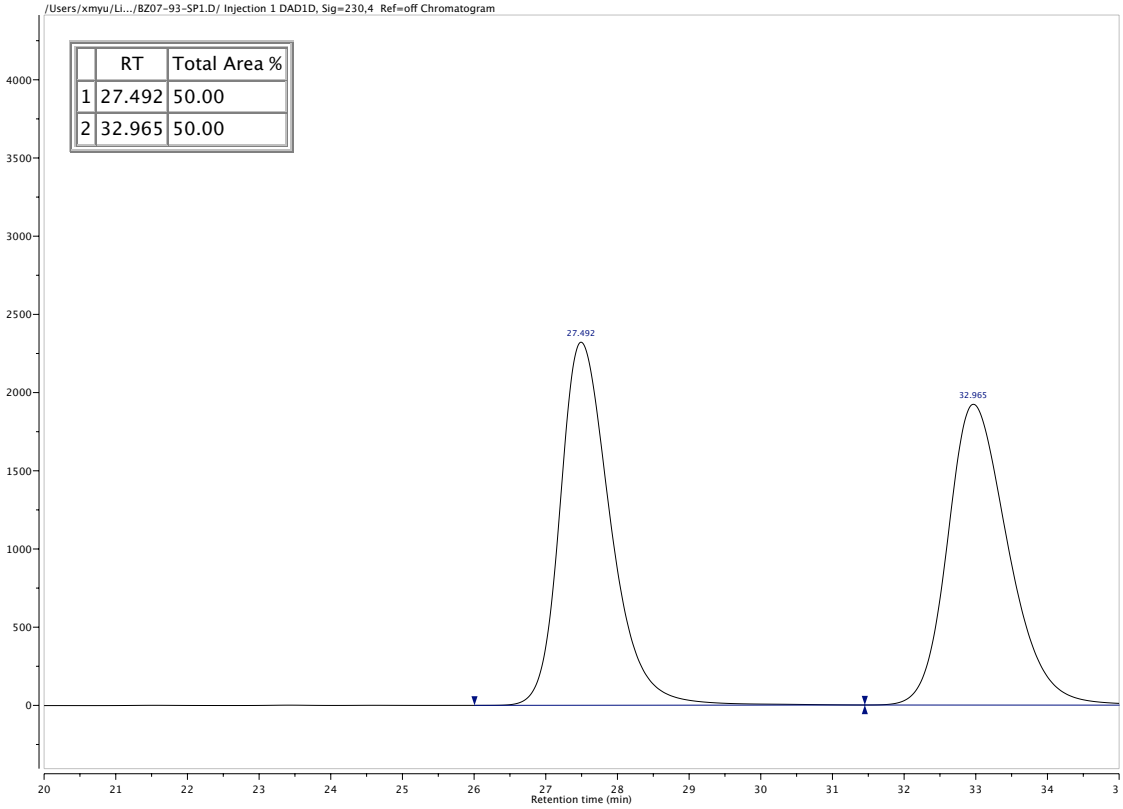

| | RT | Total Area % |
|---|---|---|
| 1 | 9.302 | 47.92 |
| 2 | 10.335 | 52.08 |

Enantioenriched **2h:**

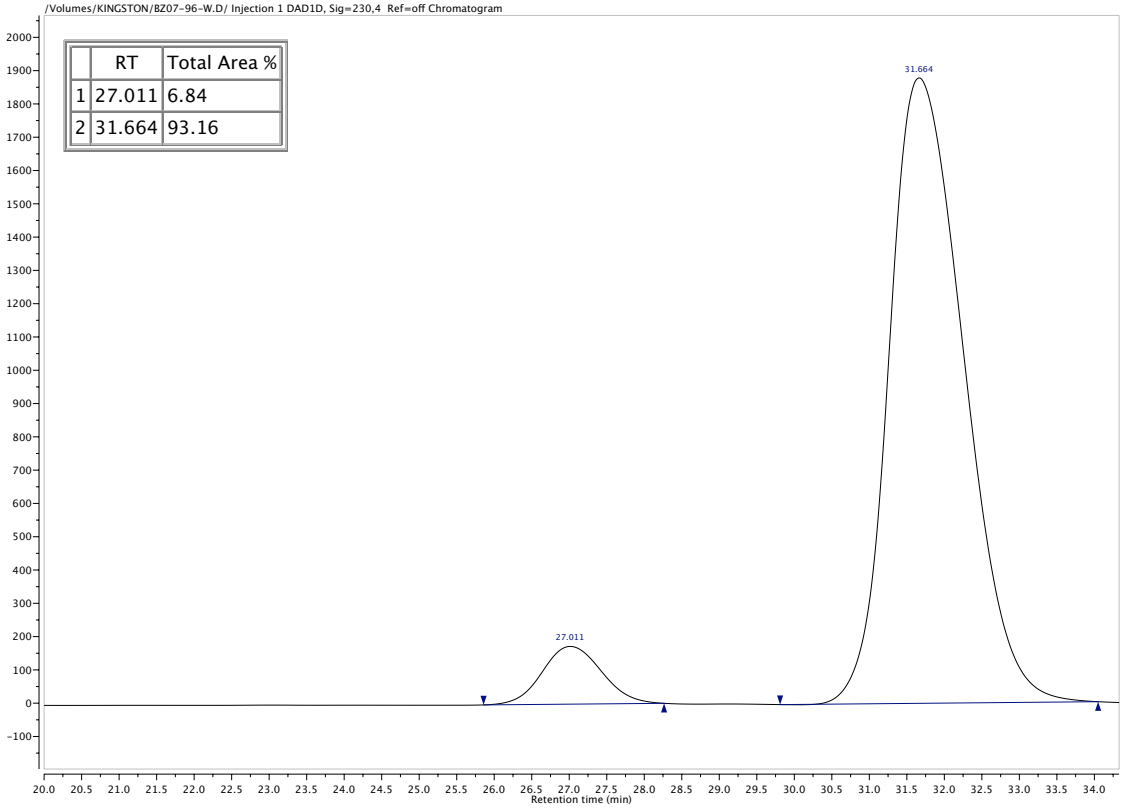



| | RT | Total Area % |
|---|---|---|
| 1 | 9.506 | 5.16 |
| 2 | 10.480 | 94.84 |

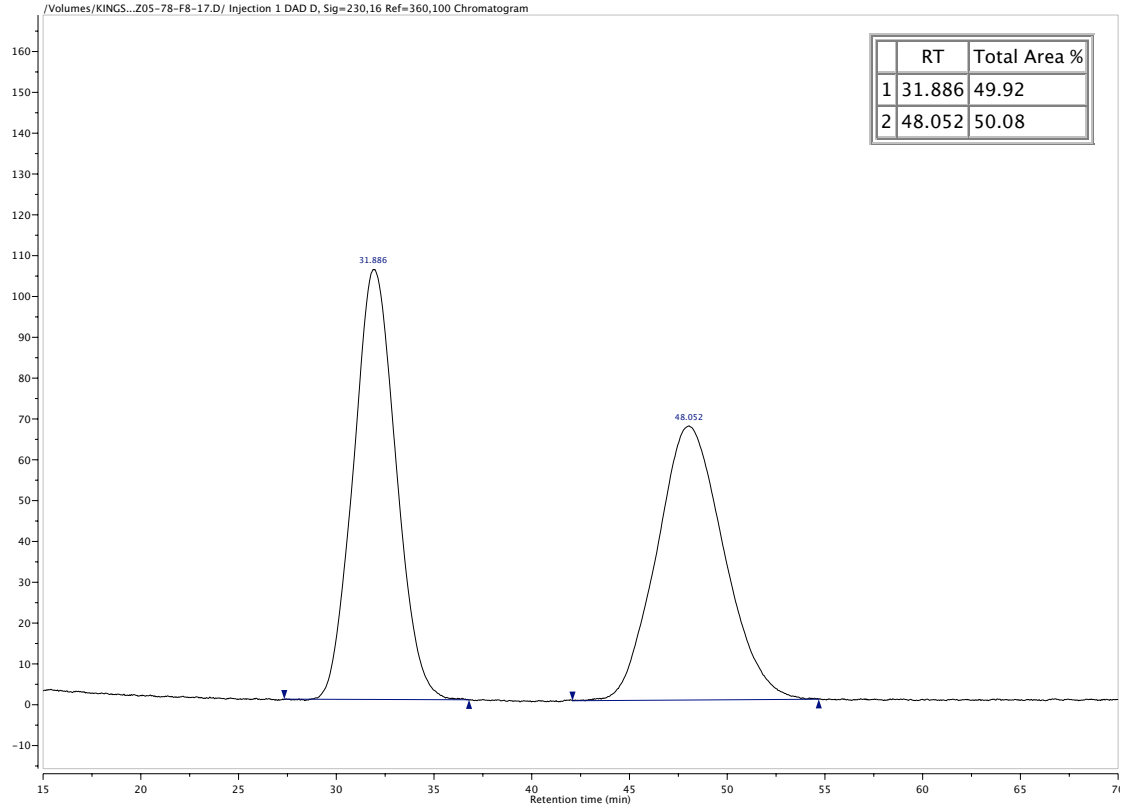
Racemic **2i**:



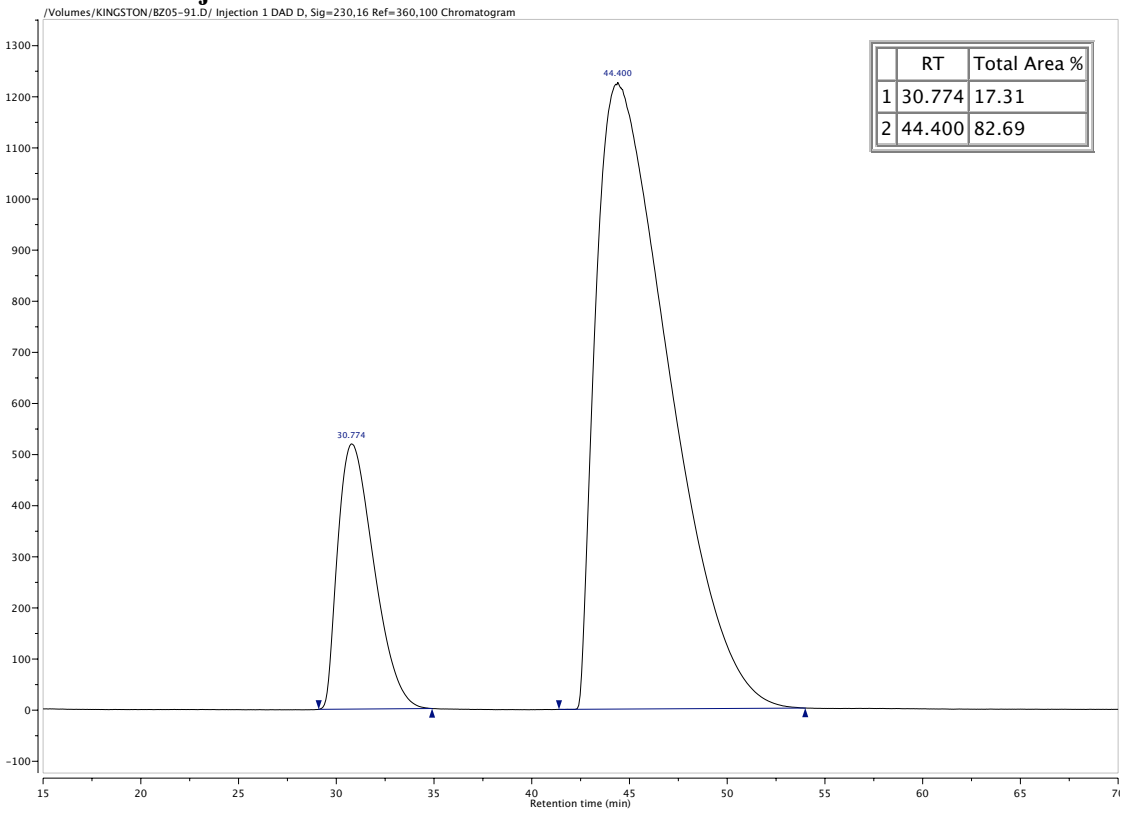

Enantioenriched **2i:**



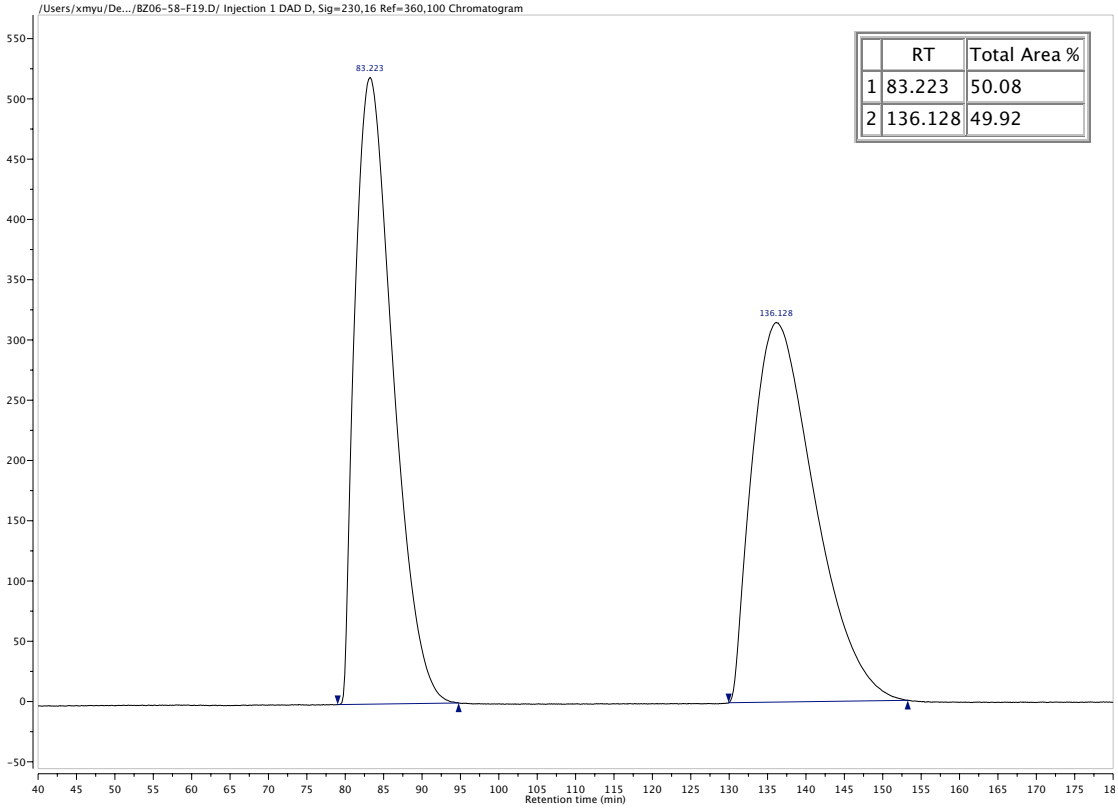
Racemic **2j**:




Enantioenriched **2j:**

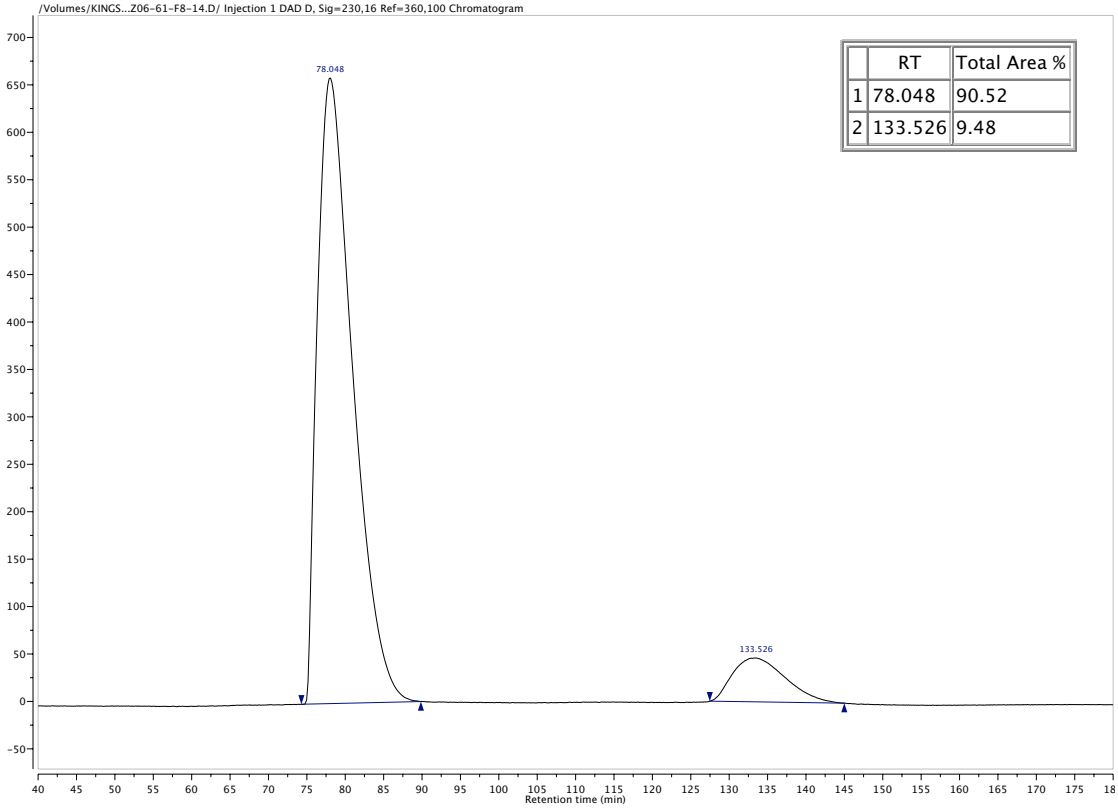


Racemic **2k**:



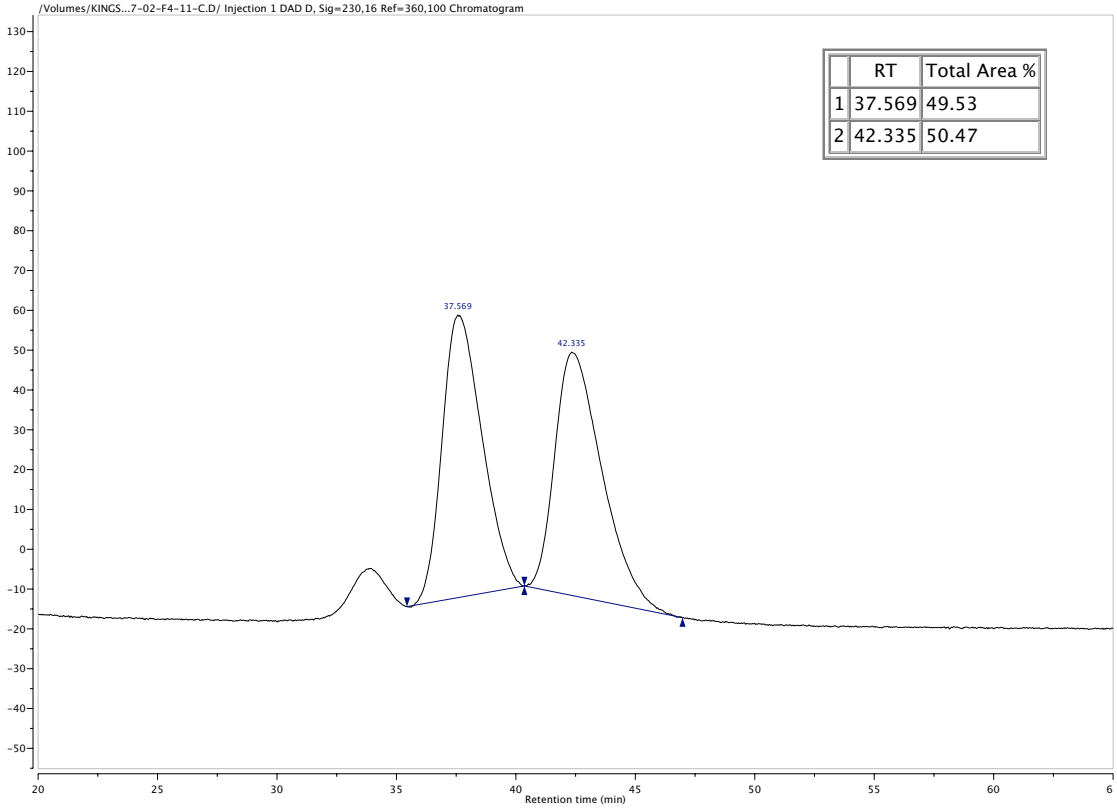

| | RT | Total Area % |
|---|---|---|
| 1 | 83.223 | 50.08 |
| 2 | 136.128 | 49.92 |

Enantioenriched **2k:**

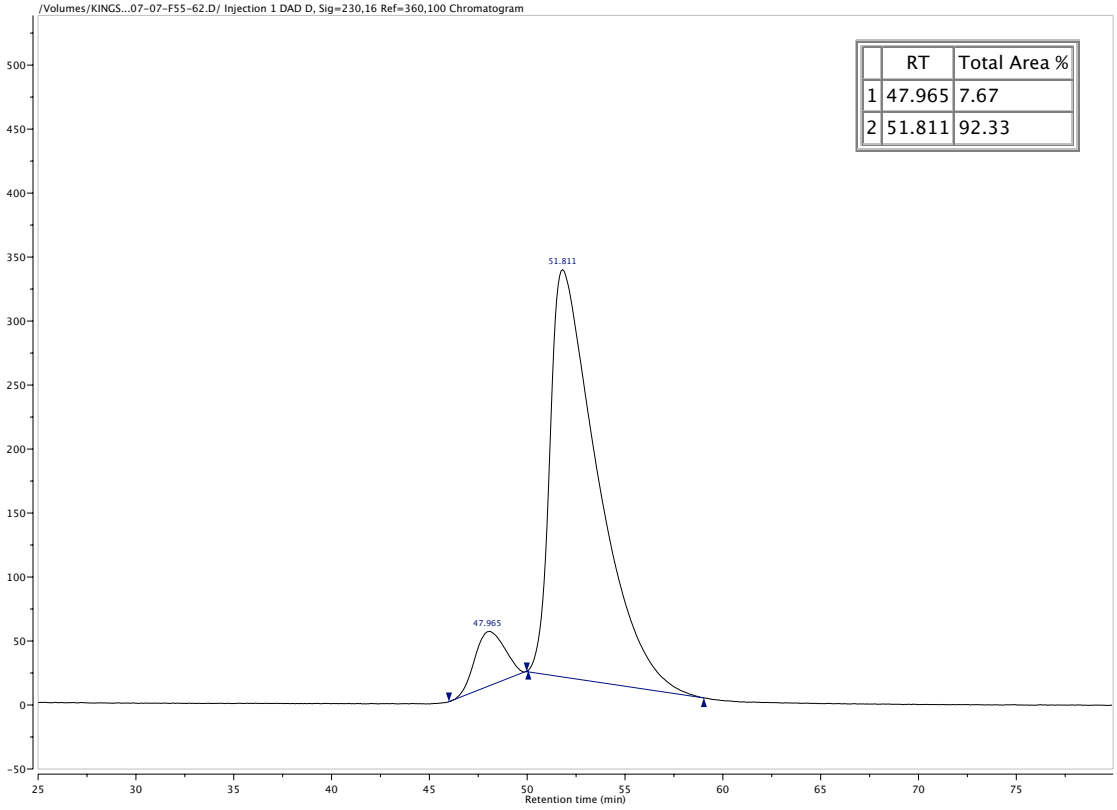



| | RT | Total Area % |
|---|---|---|
| 1 | 78.048 | 90.52 |
| 2 | 133.526 | 9.48 |

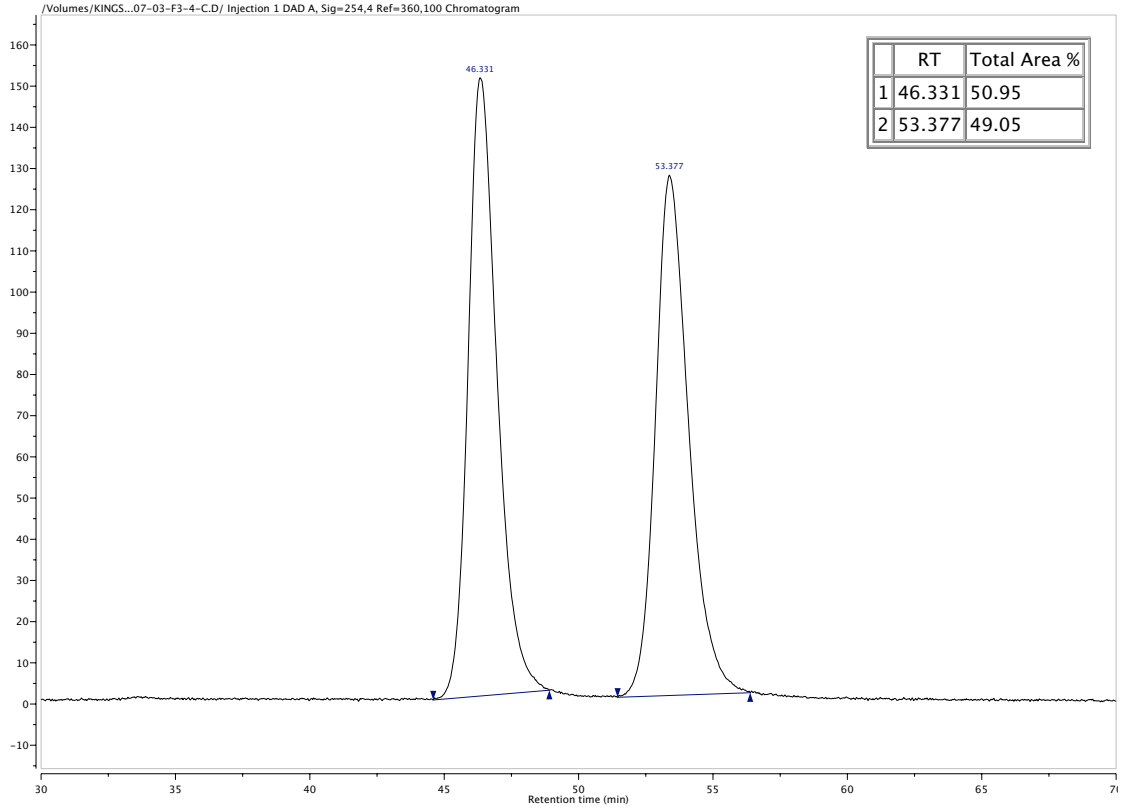
Racemic **2l**:




Enantioenriched **2l:**

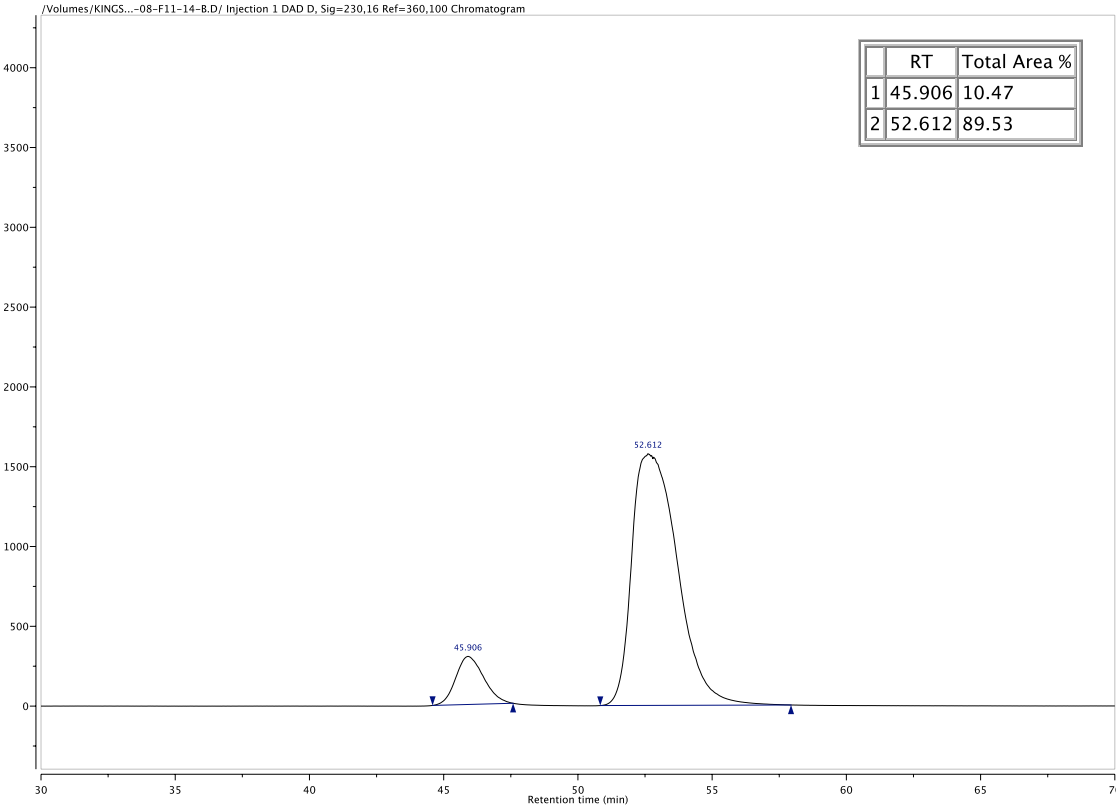


Racemic **2m**:



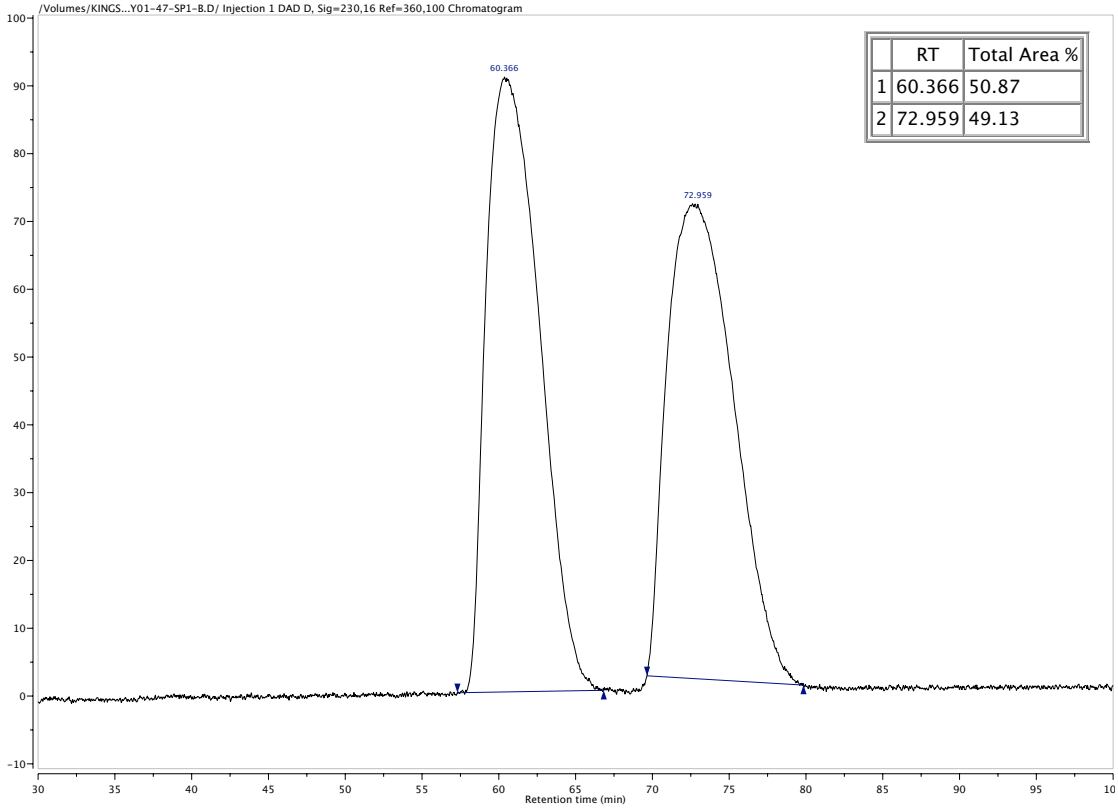

| | RT | Total Area % |
|---|---|---|
| 1 | 46.331 | 50.95 |
| 2 | 53.377 | 49.05 |

Enantioenriched **2m:**

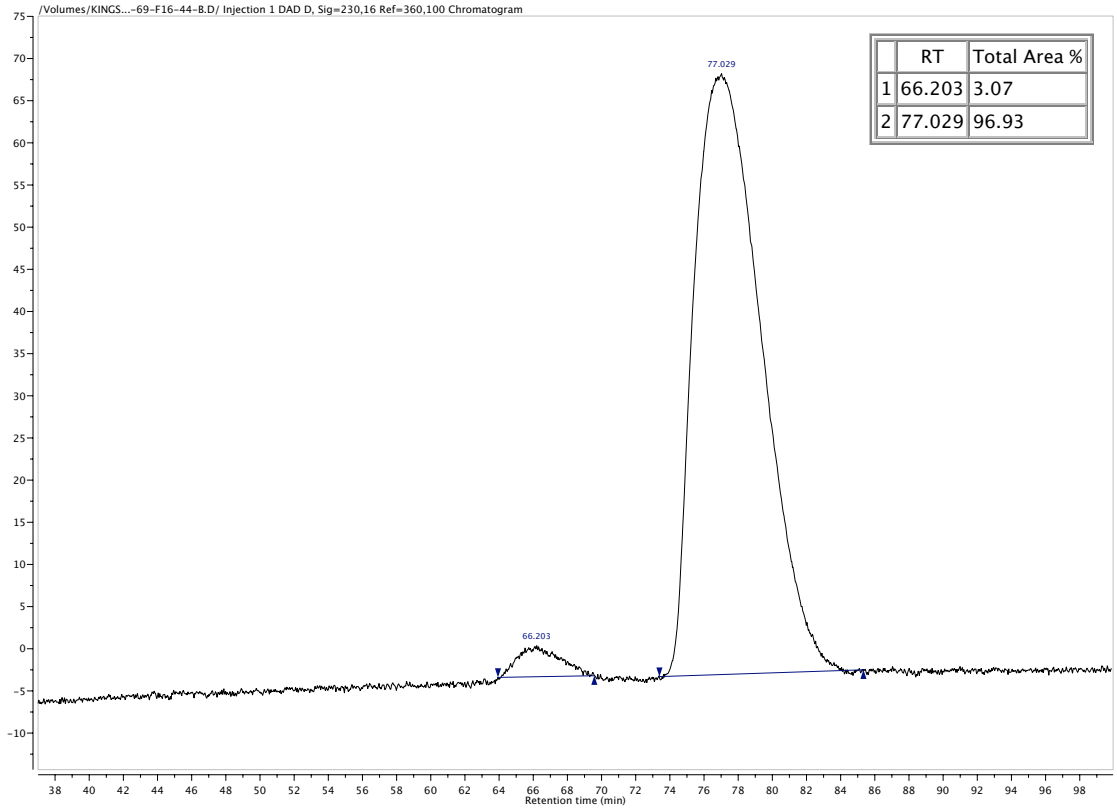



| | RT | Total Area % |
|---|---|---|
| 1 | 45.906 | 10.47 |
| 2 | 52.612 | 89.53 |

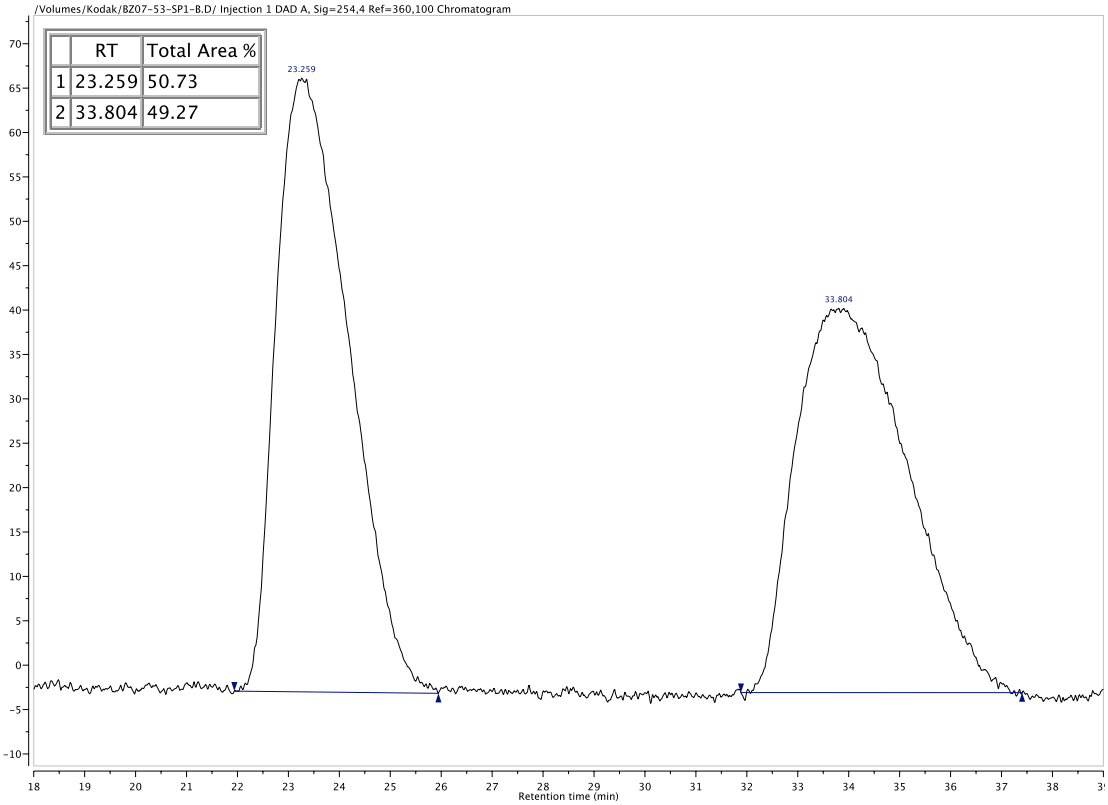
Racemic **2n**:



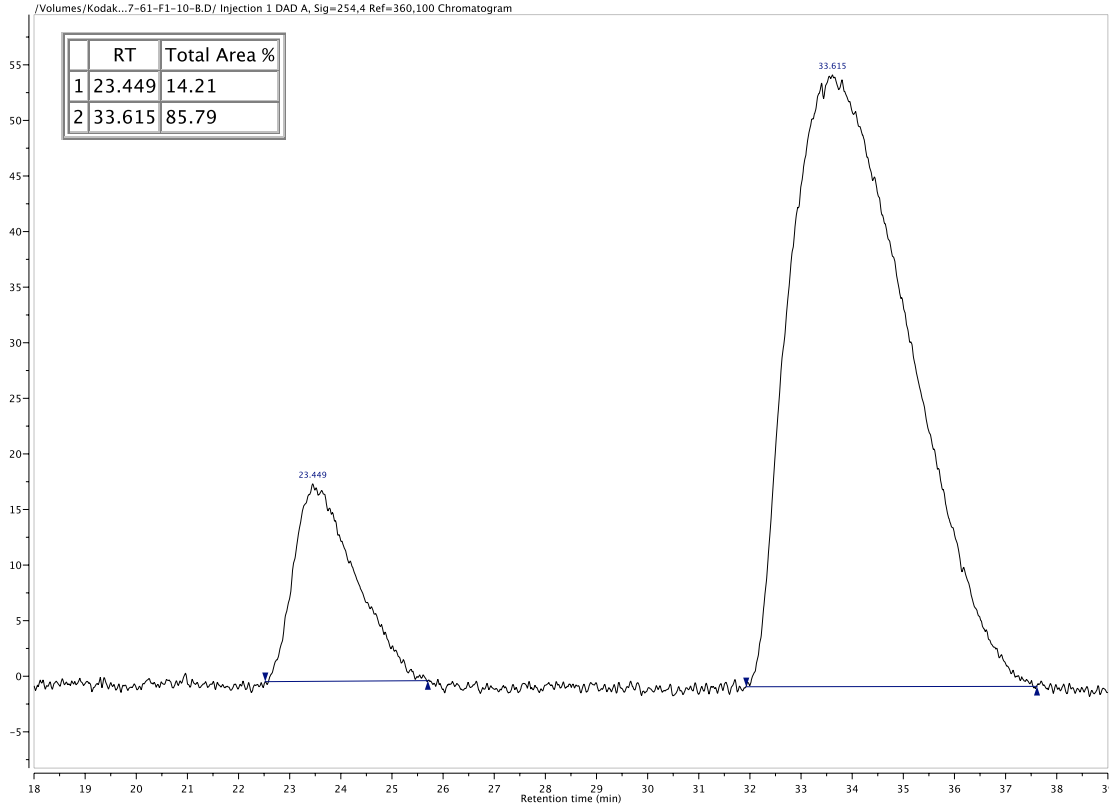

Enantioenriched **2n:**



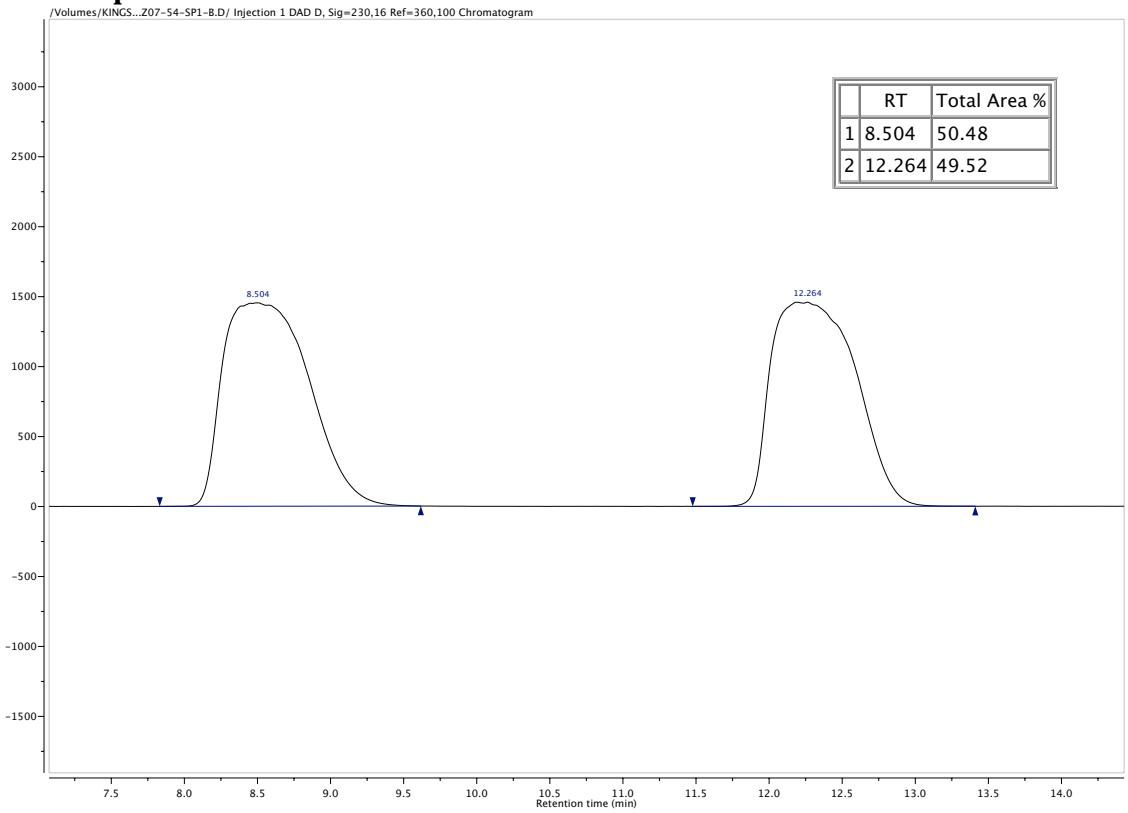
Racemic **2o:**



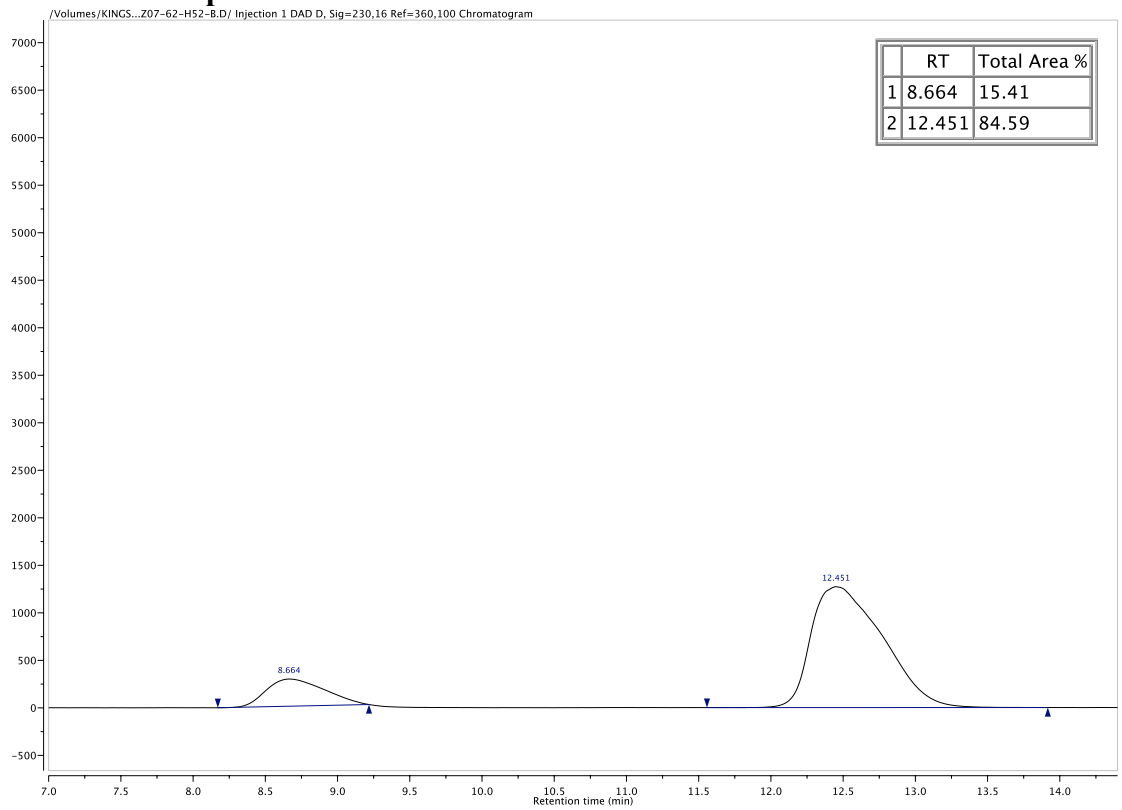

Enantioenriched **2o:**



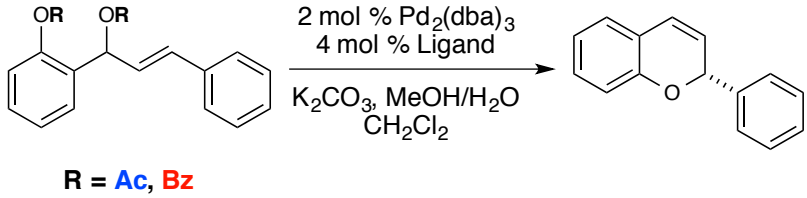
Racemic **2p**:




Enantioenriched **2p:**

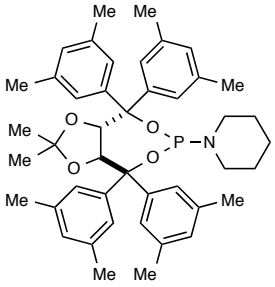


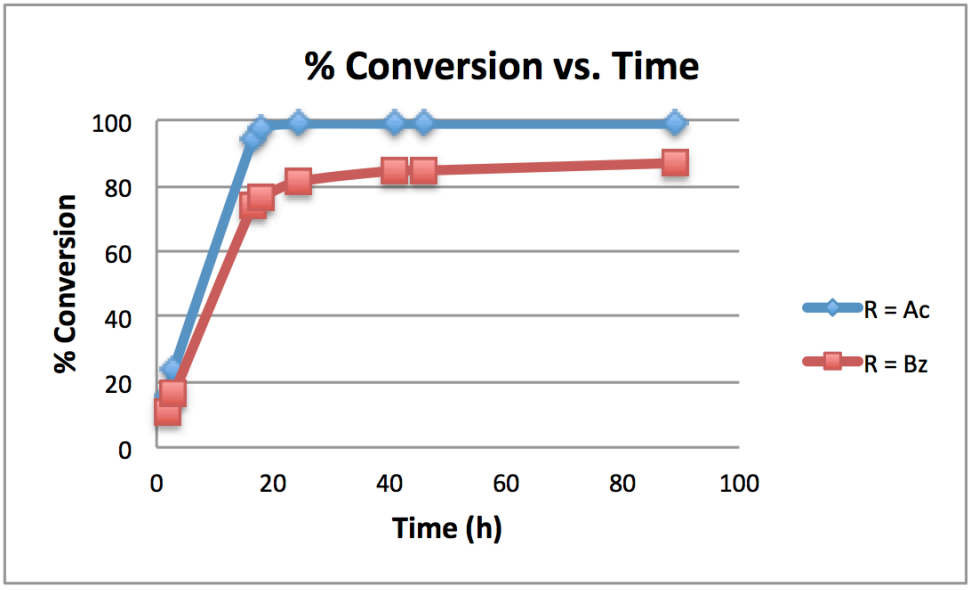
**Bis-Benzoylated vs. Bis-Acetated Substrates**

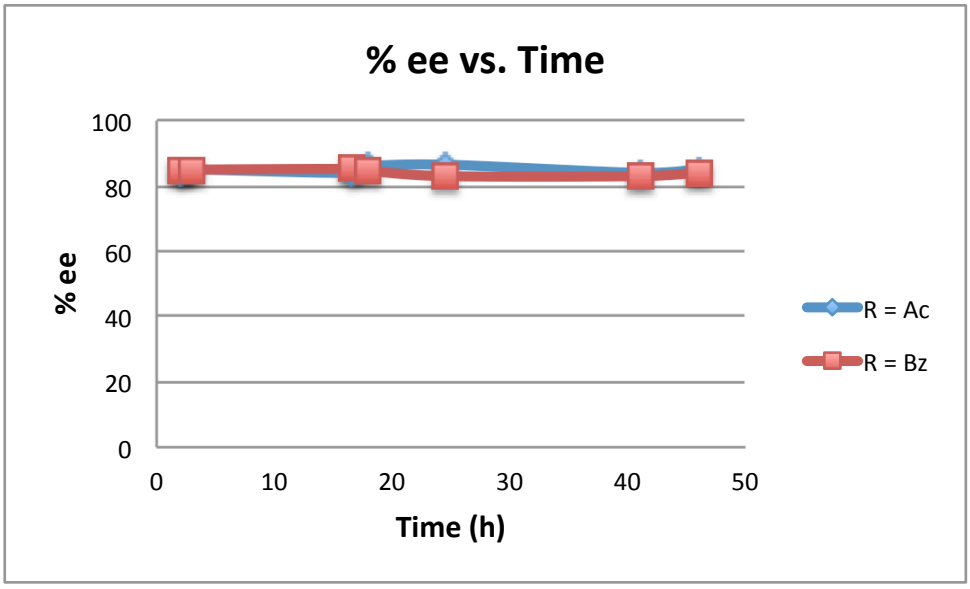



R = Ac, Bz

Ligand:

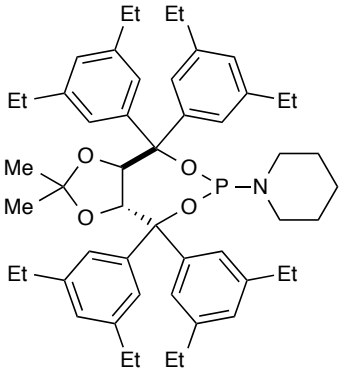


**Determination of Absolute Stereochemistry of L3k**

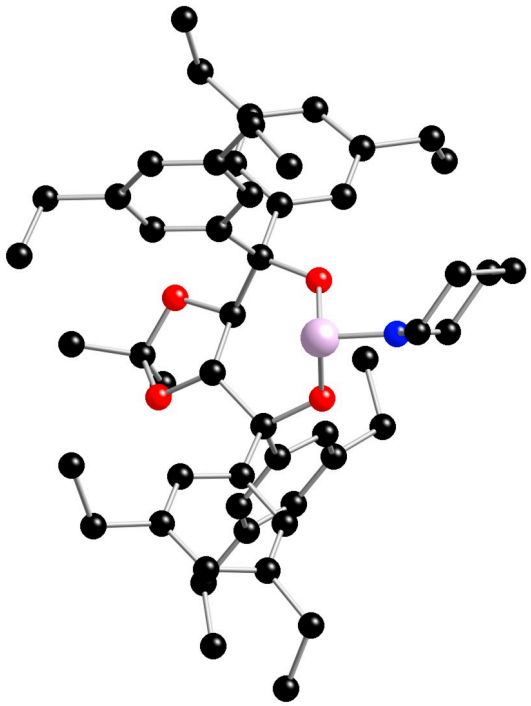
The absolute stereochemistry of **L3k** was determined by the X-ray diffraction. Recrystallized from ethanol.




**L3k**

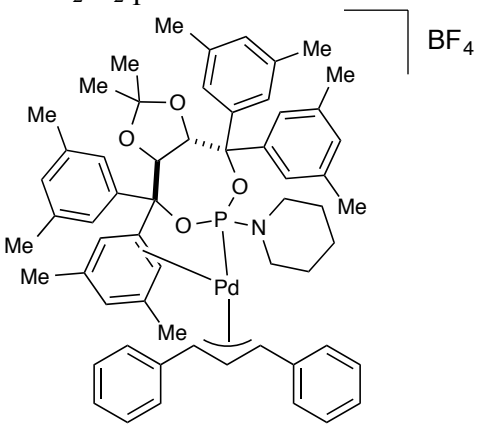
X-ray crystal structure of 1-((3a*R*,8a*R*)-4,4,8,8-tetrakis(3,5-diethylphenyl)-2,2-dimethyltetrahydro-[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-yl)piperidine:

X-ray diffraction was performed at 100 K and raw frame data were processed using SAINT. Molecular structures was solved using direct methods and refined on F2 by full-matrix least-square techniques. The GOF = 1.033 for 1065 variables refined to R1 = 0.0349 for 15189 reflections with I>2α(I). A multi-scan absorption correction was performed and the Flack parameter was 0.014(3). Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 984483.



**Determination of Structure of [Pd($\eta^3$-1,3-diphenylallyl){(*S*,*S*)-L3g}]$BF_4$**

The structure of [Pd($\eta^3$-1,3-diphenylallyl){(*S*,*S*)-**L3g**}]$BF_4$ was determined by the X-ray diffraction. Recrystallized from $CH_2Cl_2$:pentane.




X-ray crystal structure of [Pd($\eta^3$-1,3-diphenylallyl){(*S*,*S*)-**L3g**}]$BF_4$:

X-ray diffraction was performed at 100 K and raw frame data were processed using SAINT. Molecular structures was solved using direct methods and refined on F2 by full-matrix least-square techniques. The GOF = 0.919 for 677 variables refined to R1 = 0.0234 for 8799 reflections with I>2α(I). A multi-scan absorption correction was performed and the Flack parameter was -0.009(3). Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 969569.