Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Chiral Ion-Pair Photoredox Organocatalyst: Enantioselective Anti-Markovnikov Hydroetherification of Alkenols

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General Information.

All commercial reagents were used without further purification unless otherwise noted. Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on Bruker UltraShield 300MHz or 400MHz spectrometer with solvent resonance as the internal standard (^{1}H NMR: $CDCl_3$ at 7.26 ppm; ^{13}C NMR: $CDCl_3$ at 77.16 ppm).. ^{1}H NMR data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, td = triplet of doublet, dt = doublet of triplet, dd = doublet of doublet), coupling constants (Hz), and integration. Infrared Spectroscopy was conducted on Thermo Fisher Nicolet 6700. High resolution mass spectra were obtained using electrospray ionization (ESI) mass spectrometer. Silica gel (300 – 400 mesh) was for column chromatography. Irradiation of photochemical reactions were carried out using 32×0.2 W blue LED floodlamp, with Pyrex glass schlenk tube purchased from Synthware. Stern-Volmer Analyses was performed using the commercially available LP920 system by Edinburgh Instruments, Inc., and laser excitation was provided by a pulsed Nd:YAG laser in combination with an optical parametric oscillator (OPO) for wavelength selection. The enantiomeric excesses were determined by HPLC analysis on Chiral Daicel Chiralpak OD-H, AD-H, AS-H. Optical rotations were measured on a commercial polarimeter and reported as follows: $[\alpha]_D^{25}$ (c = g/100 mL, solvent). NOTE: A couple of racemic and chiral samples were determined by ^{1}H NMR and ^{13}C NMR. For several samples, the slight deviation of retention time in HPLC most possibly due to the low polarity of eluent.

Materials.

Compound **1a**[1], **S7 – S11**[2] were prepared according to reported process. Substrate **2a** – **2n** were prepared through method I. Solvents were freshly dried according to *the purification handbook Purification of Laboratory Chemicals* before using. 1,2-dichloroethane (DCE) was degassed by "pump-freeze-thaw" cycles (×2) before using. Other reagents were obtained from commercial sources and used without further purification. Unless otherwise noted, the reactions were taken under argon.

Optimization of Solvent, H-atom Donor and Catalyst on Substrate 2a

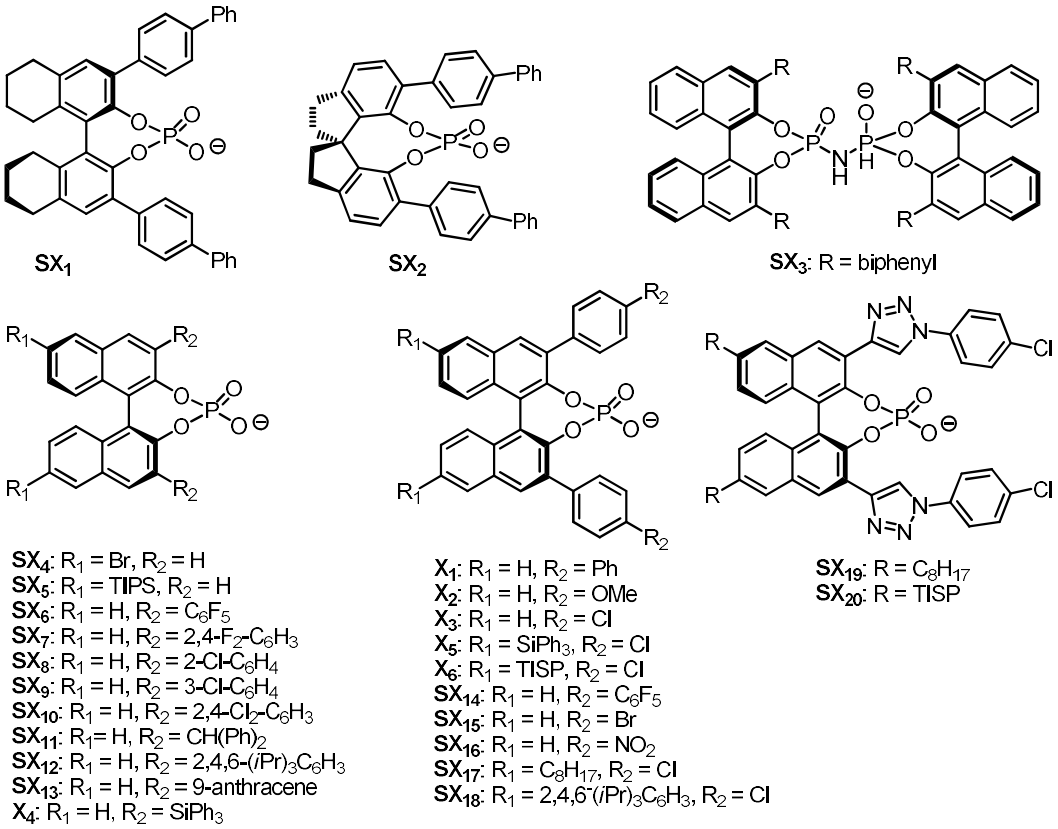
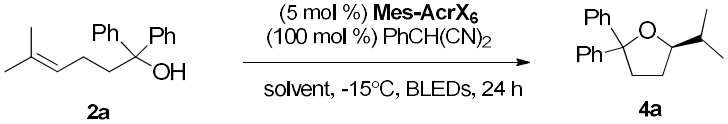


Table S1. Solvent Optimization on Substrate 2a.

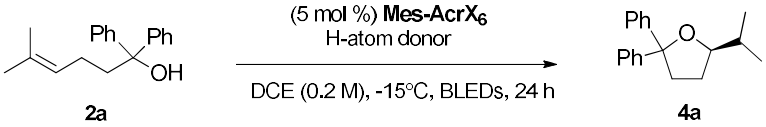


2a 4a

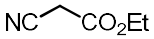
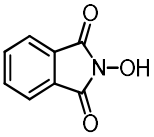
Entry	Solvent (concentration)	Yield[a] (%)	*ee*[b] (%)
1	DCM (0.2)	83	53
2	CH_3CN (0.2)	23	30
3	Toluene (0.2)	38	31
4	$CHCl_3$ (0.2)	90	20
5	PhCl (0.2)	68	41
6	Ethyl acetate (0.2)	83	50
7	THF (0.2)	< 5	--
8	Et_2O 0.2)	85	47
9	Hexane (0.2)	38	19
10	DCE (0.2)	83	56
11	DCE (0.4)	83	56
12	DCE (0.05)	< 5	--

[a] Determined by isolation after chromatographic purification.. [b] Determined by HPLC analysis.

Table S2. H-atom Donor Optimization on Substrate 2a.

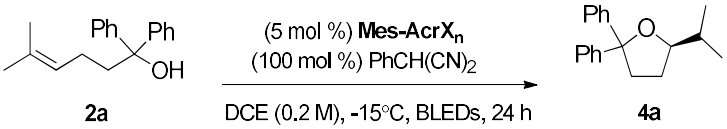


2a **4a**

Entry	H-atom donor (mmol %)	Yield[a] (%)	*ee*[b] (%)
1	$PhCH(CN)_2$ (100)	83	56
2	$(PhS)_2$ (10)	83	56
3	Ph_3SiH (100)	< 5	--
4		70	49
5		< 5	--

[a] Determined by isolation after chromatographic purification.. [b] Determined by HPLC analysis.

Table S3. Catalyst Optimization on Substrate 2a.

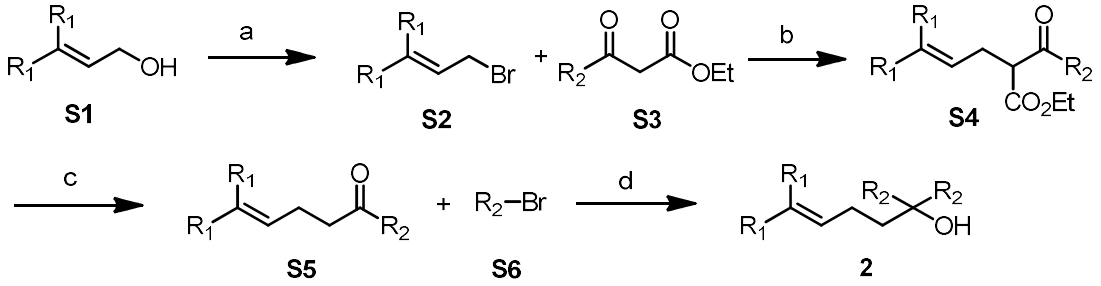


2a **4a**

Entry	Chiral anion $\mathbf{X_n}$	Yield[a] (%)	*ee*[b] (%)
1	$\mathbf{X_1}$	78	22
2	$\mathbf{X_2}$	83	18
3	$\mathbf{X_3}$	83	38
4	$\mathbf{X_4}$	< 5	--
5	$\mathbf{X_5}$	83	41
6	$\mathbf{X_6}$	83	56
7	$\mathbf{SX_1}$	78	11
8	$\mathbf{SX_2}$	83	12
9	$\mathbf{SX_3}$	83	20
10	$\mathbf{SX_4}$	78	4
11	$\mathbf{SX_5}$	80	15
12	$\mathbf{SX_6}$	< 5	--
13	$\mathbf{SX_7}$	10	--
14	$\mathbf{SX_8}$	77	35
15	$\mathbf{SX_9}$	83	37
16	$\mathbf{SX_{10}}$	77	30
17	$\mathbf{SX_{11}}$	35	9
18	$\mathbf{SX_{12}}$	< 5	--
19	$\mathbf{SX_{13}}$	50	13
20	$\mathbf{SX_{14}}$	60	20
21	$\mathbf{SX_{15}}$	77	33
22	$\mathbf{SX_{16}}$	< 5	--
23	$\mathbf{SX_{17}}$	83	41
24	$\mathbf{SX_{18}}$	83	50
25	$\mathbf{SX_{19}}$	83	33
26	$\mathbf{SX_{20}}$	83	49

[a] Determined by isolation after chromatographic purification.. [b] Determined by HPLC analysis.

Experimental Section.



a) PBr_3, Et_2O, 0°C, 30 min. b) NaH, THF, 0°C - RT, 4 h. c) KOH (aq.), EtOH, reflux, 2 h.
d) *n*BuLi, THF, -78°C - RT, overnight.

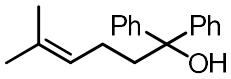
Method I: To a solution of allylic alcohol **S1** (1.0 eq.) dry Et_2O at 0 ºC was added PBr_3 (1.2 eq., in 5 mL of Et_2O) and the mixture was stirred at this temperature for 30 min. The reaction mixture was quenched with saturated $NaHCO_3$ carefully at 0 ºC. It was partitioned between EtOAc and water. The organic phase was separated. The aqueous phase was extracted three times with EtOAc. The combined EtOAc extract was successively washed with saturated $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated in *vacuo* to allylic bromide **S2**, which was used in the next step without further purification.

To a solution of β-ketocarbonyl **S3** (1.0 eq.) in dry THF at 0 ºC was added NaH (1.5 eq.) and the mixture was stirred at this temperature for 30 min. A solution of allylic bromide **S2** (1.0 eq., in 5 mL of THF) was added via cannula. The resulting solution was warmed to room temperature and stirred overnight, which was quenched with saturated NH_4Cl at 0 ºC. The mixture was partitioned between EtOAc and water. The organic phase was separated and the aqueous phase was extracted three times with EtOAc. The combined EtOAc extract was washed with brine, dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by silica gel chromatography to give the desired product β-ketocarbonyl **S4**.

To a solution of β-ketocarbonyl **S4** (1.0 eq.) in EtOH at room temperature was added aqueous KOH (4.0 eq., 7.0 M in H_2O) and the mixture was heated to reflux (92 ºC) for 2 h. The resulting solution was cooled to room temperature and removed most EtOH in *vacuo*. It was partitioned between EtOAc and water. The organic phase was separated. The aqueous phase was extracted three times with EtOAc. The combined EtOAc extract was successively washed with brine, dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by silica gel chromatography to give the desired product ketone **S5**.

To a solution of aryl bromide **S6** (2.0 eq.) in dry THF at -78 ºC was slowly added *n*BuLi (2.0 eq., 2.4 M in hexane) and the mixture was stirred at this temperature for 1 h. A solution of ketone **S5** (1.0 eq., in 5 mL of THF) was added via cannula. The resulting solution was stirred at -78 ºC for further 1 h and slowly warmed to room temperature overnight. The resulting solution was quenched with saturated NH_4Cl. The mixture was partitioned between EtOAc and water. The organic phase was separated and the aqueous phase was extracted three times with EtOAc. The combined EtOAc extract was washed with brine, dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by silica gel chromatography to give the desired substrate **2**.

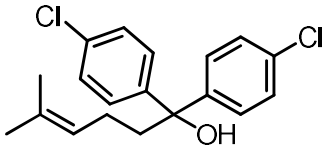
5-methyl-1,1-diphenylhex-4-en-1-ol (**2a**)



2a

2a: following general method I, compound **2a** (45% for 4 steps) was prepared as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.33 (m, 4H), 7.22 (t, J = 7.6 Hz, 4H), 7.15 – 7.11 (m, 2H), 5.09 (t, J = 7.1 Hz, 1H), 2.28 (s, 1H), 2.26 – 2.23 (m, 2H), 1.94 – 1.91 (m, 2H), 1.59 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.15, 132.69, 128.26, 126.86, 126.11, 124.25, 78.64, 41.87, 25.86, 22.95, 17.75. IR (thin film, cm^{-1}): 3475, 2956, 2925, 2854, 1447, 699. HRMS (ESI^-): calcd for $[C_{19}H_{21}OCl]^-$ 265.1598, found 265.1596.

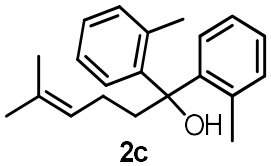
1,1-bis(4-chlorophenyl)-5-methylhex-4-en-1-ol (**2b**)



2b

2b: following general method I, compound **2b** (40% for 4 steps) was prepared as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 8H), 5.15 (t, J = 7.1 Hz, 1H), 2.43 (s, 1H), 2.28 – 2.25 (m, 2H), 2.00 - 1.93 (m, 2H), 1.67 (s, 3H), 1.46 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.28, 133.26, 132.94, 128.47, 127.51, 123.77, 78.04, 41.61, 25.84, 22.83, 17.80. IR (thin film, cm^{-1}): 3471, 2957, 2926, 2854, 1655, 1489, 821. HRMS (ESI^-): calcd for $[C_{19}H_{19}OCl_2]^-$ 333.0818, found 333.0818.

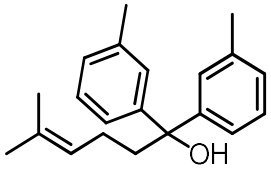
5-methyl-1,1-di-o-tolylhex-4-en-1-ol (**2c**)



2c

2c: following general method I, compound **2c** (48% for 4 steps) was prepared as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, J = 7.7, 1.2 Hz, 2H), 7.21 – 7.13 (m, 4H), 7.03 (d, J = 7.1 Hz, 2H), 5.15 (t, J = 7.2 Hz, 1H), 2.37 – 2.33 (m, 2H), 1.98 – 1.90 (m, 9H), 1.67 (s, 3H), 1.51 (s, 3H). ^{13} 13C NMR (101 MHz, $CDCl_3$) δ 143.97, 136.25, 132.40, 132.30, 127.21, 127.11, 125.33, 124.46, 78.76, 40.93, 25.84, 22.88, 21.52, 17.76. IR (thin film, cm^{-1}): 3359, 2957, 2921, 2851, 1659, 1633, 1457, 1377, 754. HRMS (ESI^-): calcd for $[C_{21}H_{25}O]^-$ 293.1911, found 293.1908.

5-methyl-1,1-di-m-tolylhex-4-en-1-ol (**2d**)

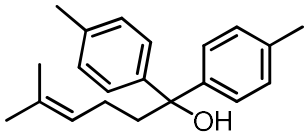


2d

2d: following general method I, compound **2d** (46% for 4 steps) was prepared as colorless oil. ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.18 (m, 6H), 7.02 (d, J = 3.8 Hz, 2H), 5.17 (t, J = 7.3 Hz, 1H), 2.36 – 2.27 (m, 9H), 2.01 – 1.97 (m, 2H), 1.67 (s, 3H), 1.48 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.16, 137.76, 132.53, 128.09, 127.56, 126.71, 124.37, 123.17, 78.54, 41.95, 25.86, 22.97, 21.77, 17.74. IR (thin film, cm^{-1}): 3476, 3020, 2956, 2924, 2855, 1605, 1456, 789. HRMS (ESI^-): calcd for $[C_{21}H_{25}O]^-$ 293.1911, found 293.1908.

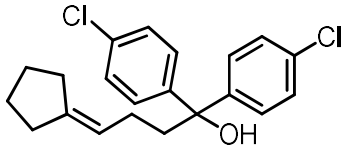
5-methyl-1,1-di-p-tolylhex-4-en-1-ol (**2e**)



2e

2e: following general method I, compound **2e** (50% for 4 steps) was prepared as colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, J = 7.9 Hz, 4H), 7.11 (d, J = 7.9 Hz, 4H), 5.17 (t, J = 7.0 Hz, 1H), 2.35 – 2.26 (m, 9H), 2.02 – 1.97 (m, 2H), 1.68 (s, 3H), 1.49 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.46, 136.34, 132.50, 128.93, 125.99, 124.38, 78.42, 41.94, 25.86, 23.01, 21.11, 17.80. IR (thin film, cm^{-1}): 3473, 3023, 2970, 2923, 2856, 1510, 1448, 817. HRMS (ESI^-): calcd for $[C_{21}H_{25}O]^-$ 293.1911, found 293.1908.

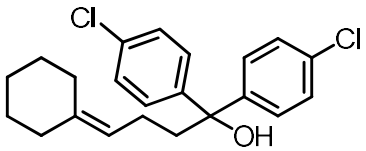
1,1-bis(4-chlorophenyl)-4-cyclopentylidenebutan-1-ol (**2f**)



2f

2f: following general method I, compound **2f** (40% for 4 steps) was prepared as colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.29 (m, 4H), 7.24 – 7.21 (m, 4H), 5.23 (d, J = 6.9 Hz, 1H), 2.49 (s, 1H), 2.27 – 2.24 (m, 2H), 2.17 – 2.15 (m, 2H), 1.97 – 1.92 (m, 4H), 1.61 – 1.52 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.28, 145.15, 132.88, 128.43, 127.48, 119.17, 78.08, 41.38, 33.75, 28.72, 26.42, 26.35, 24.42. IR (thin film, cm^{-1}): 3478, 2954, 2927, 2855, 1671, 1489, 1400, 1093, 1013, 819. HRMS (ESI^-): calcd for $[C_{21}H_{21}OCl_2]^-$ 359.0975, found 359.0971.

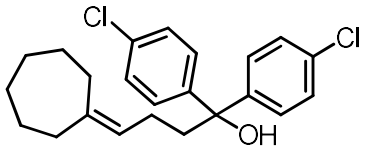
1,1-bis(4-chlorophenyl)-4-cyclohexylidenebutan-1-ol (**2g**)



2g

2g: following general method I, compound **2g** (45% for 4 steps) was prepared as colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.28 (m, 4H), 7.25 – 7.22 (m, 4H), 5.08 (t, J = 7.3 Hz, 1H), 2.48 (s, 1H), 2.24 (dd, J = 8.7, 6.5 Hz, 2H), 2.02 – 1.89 (m, 6H), 1.48 – 1.39 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.31, 141.48, 132.92, 128.46, 127.51, 120.52, 78.22, 41.91, 37.26, 28.76, 28.64, 27.83, 26.91, 21.98. IR (thin film, cm^{-1}): 3578, 3489, 2927, 2853, 1593, 1489, 1093, 822. HRMS (ESI^-): calcd for $[C_{22}H_{23}OCl_2]^-$ 373.1131, found 373.1127.

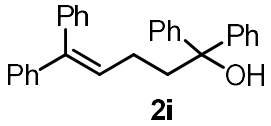
1,1-bis(4-chlorophenyl)-4-cycloheptylidenebutan-1-ol (**2h**)



2h

2h: following general method I, compound **2h** (40% for 4 steps) was prepared as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.6 Hz, 4H), 7.23 (d, J = 8.7 Hz, 4H), 5.12 (t, J = 7.1 Hz, 1H), 2.40 (s, 1H), 2.24 (dd, J = 8.9, 6.6 Hz, 2H), 2.15 – 2.12 (m, 2H), 2.01 – 1.91 (m, 4H), 1.49 – 1.43 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.31, 143.12, 132.95, 128.48, 127.53, 123.96, 78.13, 41.65, 37.95, 30.12, 29.97, 29.40, 29.29, 27.10, 22.43. IR (thin film, cm^{-1}): 3727, 2956, 2923, 2852, 1489, 1094, 821. HRMS (ESI^-): calcd for $[C_{23}H_{25}OCl_2]^-$ 387.1288, found 387.1284.

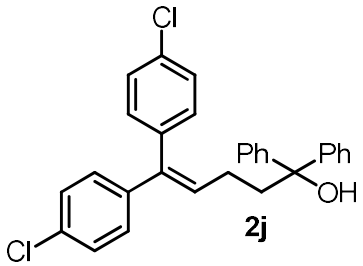
1,1,5,5-tetraphenylpent-4-en-1-ol (**2i**)



2i

2i: following general method I, compound **2i** (50% for 4 steps) was prepared as colorless viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.08 (m, 18H), 7.10 (dd, J = 7.7, 1.6 Hz, 2H), 6.11 (t, J = 7.7 Hz, 1H), 2.43 – 2.39 (m, 2H), 2.18 – 2.12 (m, 2H), 2.07 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.91, 142.70, 142.39, 140.01, 129.87, 129.24, 128.35, 128.28, 128.21, 127.28, 127.05, 127.02, 126.93, 126.07, 78.35, 42.10, 24.61. IR (thin film, cm^{-1}): 3559, 3359, 2921, 2851, 1659, 1633, 1598, 1494, 1446, 761, 699. HRMS (ESI^-): calcd for $[C_{29}H_{25}O]^-$ 389.1911, found 389.1915.

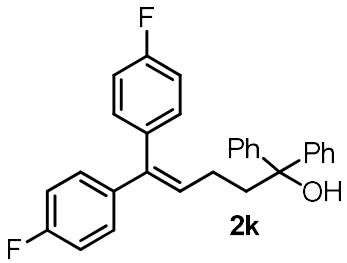
5,5-bis(4-chlorophenyl)-1,1-diphenylpent-4-en-1-ol (**2j**)



2j

2j: following general method I, compound **2j** (30% for 4 steps) was prepared as colorless viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.19 (m, 14H), 7.06 (d, J = 8.6 Hz, 2H), 6.97 (d, J = 8.3 Hz, 2H), 6.08 (t, J = 7.7 Hz, 1H), 2.39 – 2.36 (m, 2H), 2.14 – 2.06 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.71, 140.73, 140.10, 137.90, 133.16, 133.06, 131.16, 130.43, 128.70, 128.49, 128.43, 128.34, 127.07, 126.03, 78.29, 41.87, 24.61. IR (thin film, cm^{-1}): 3059, 3027, 2957, 2926, 2854, 1722, 1491, 1447, 1288, 1091, 829, 700. HRMS (ESI^-): calcd for $[C_{29}H_{23}OCl_2]^-$ 457.1131, found 457.1128.

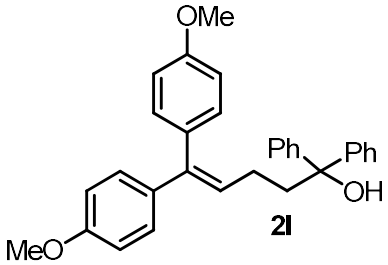
5,5-bis(4-fluorophenyl)-1,1-diphenylpent-4-en-1-ol (**2k**)



2k

2k: following general method I, compound **2k** (25% for 4 steps) was prepared as colorless viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.31 (m, 4H), 7.27 – 7.24 (m, 4H), 7.20 (t, J = 7.2 Hz, 2H), 7.10 (dd, J = 8.6, 5.5 Hz, 2H), 7.25 – 6.90 (m, 6H), 6.02 (t, J = 7.7 Hz, 1H), 2.40 – 2.37 (m, 2H), 2.13 – 2.09 (m, 2H), 2.05 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.18, 162.99, 161.22, 161.04, 146.79, 140.30, 138.71, 138.68, 135.65, 135.62, 131.42, 131.36, 129.55, 128.81, 128.75, 128.32, 127.04, 126.04, 115.44, 115.27, 115.16, 114.99, 78.32, 41.97, 24.60. IR (thin film, cm^{-1}): 3359, 2921, 2851, 1601, 1508, 1223, 835, 700. HRMS (ESI^-): calcd for $[C_{29}H_{23}OF_2]^-$ 425.1722, found 425.1718.

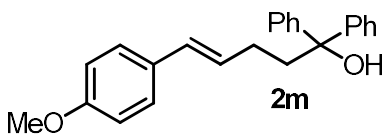
5,5-bis(4-methoxyphenyl)-1,1-diphenylpent-4-en-1-ol (**2l**)



2l

2l: following general method I, compound **2l** (30% for 4 steps) was prepared as light yellow viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.33 (m, 4H), 7.28 – 7.24 (m, 4H), 7.21 – 7.17 (m, 2H), 7.12 – 7.10 (m, 2H), 7.01 – 6.98 (m, 2H), 6.85 – 6.77 (m, 4H), 5.97 (t, J = 7.6 Hz, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 2.42 – 2.38 (m, 2H), 2.17 – 2.12 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.84, 158.60, 146.97, 141.41, 135.80, 132.51, 130.96, 128.42, 128.26, 127.28, 126.89, 126.08, 113.71, 113.56, 78.40, 55.41, 55.37, 42.20, 24.55. IR (thin film, cm^{-1}): 3559, 2921, 2850, 1660, 1633, 1606, 1511, 1245, 1033, 831, 701. HRMS (ESI^-): calcd for $[C_{31}H_{29}O_3]^-$ 449.2122, found 449.2119.

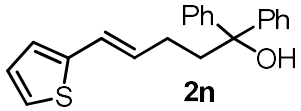
(*E*)-5-(4-methoxyphenyl)-1,1-diphenylpent-4-en-1-ol (**2m**)



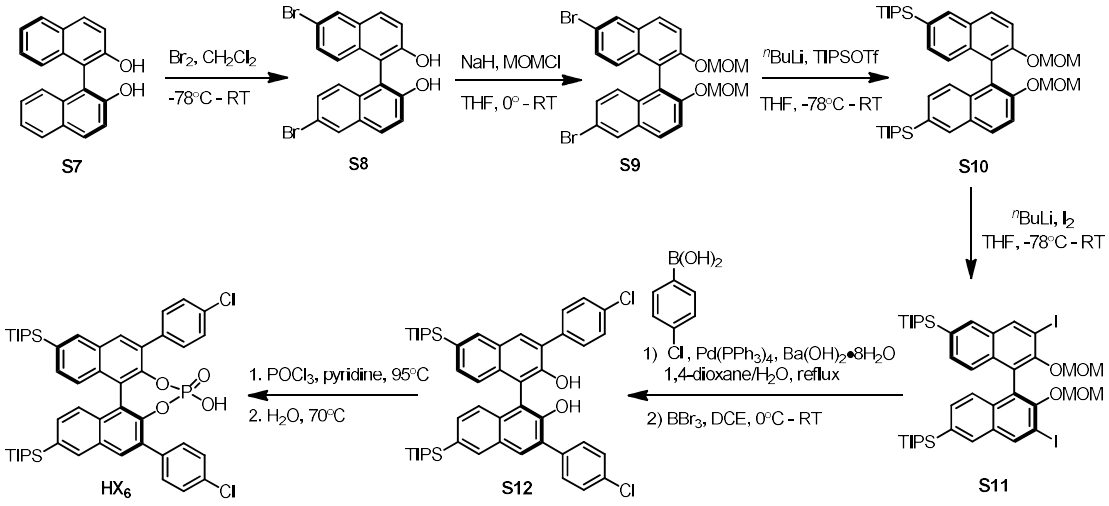
2m

2m: following general method I, compound **2m** (40% for 4 steps) was prepared as slight yellow viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.8 Hz, 4H), 7.26 (t, J = 7.7 Hz, 4H), 7.19 – 7.15 (m, 4H), 6.76 (d, J = 8.6 Hz, 2H), 6.23 (d, J = 15.8 Hz, 1H), 6.06 – 6.00 (m, 1H), 3.73 (s, 3H), 2.42 – 2.38 (m, 2H), 2.17 – 2.13 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.84, 147.01, 130.59, 129.64, 128.38, 128.33, 127.14, 127.01, 126.16, 114.05, 78.41, 55.40, 41.70, 27.70. IR (thin film, cm^{-1}): 3445, 2920, 2849, 1634, 1608, 1510, 1246, 700. HRMS (ESI^-): calcd for $[C_{24}H_{23}O_2]^-$ 343.1704, found 343.1708.

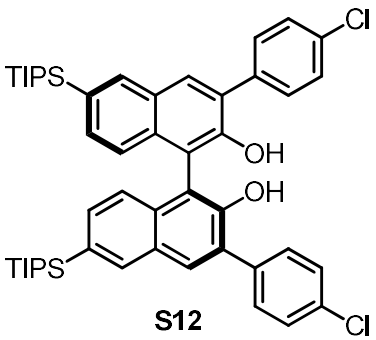
(*E*)-1,1-diphenyl-5-(thiophen-2-yl)pent-4-en-1-ol (**2n**)



2n: following general method I, compound **2n** (28% for 4 steps) was prepared as colorless viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 7.5 Hz, 4H), 7.32 (t, J = 7.7 Hz, 4H), 7.25 – 7.22 (m, 2H), 7.07 (d, J = 5.0 Hz, 1H), 6.91 (dd, J = 5.0, 3.6 Hz, 1H), 6.83 (d, J = 3.4 Hz, 1H), 6.47 (d, J = 15.7 Hz, 1H), 6.06 (dt, J = 15.5, 6.9 Hz, 1H), 2.46 – 2.43 (m, 2H), 2.21 – 2.16 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.93, 143.01, 130.57, 128.38, 127.34, 127.09, 126.17, 124.48, 123.53, 123.38, 78.33, 41.53, 27.55. IR (thin film, cm^{-1}): 3359, 3024, 2955, 2922, 2851, 1717, 1447, 1287, 697. HRMS (ESI^-): calcd for $[C_{21}H_{19}OS]^-$ 319.1162, found 319.1158.



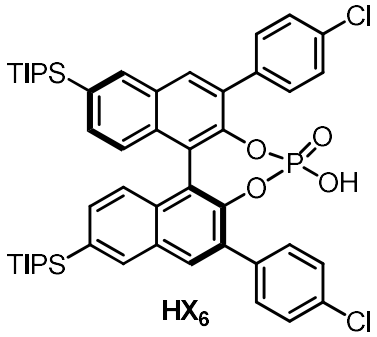
(*S*)-(3,3'-bis(4-chlorophenyl)-2,2'-bis(methoxymethoxy)-[1,1'-binaphthalene]-6,6'-diyl)bis(triisopropylsilane) (**S12**)



In a flask, **S11** (1.0 g, 1.07 mmol), (4-chlorophenyl)boronic acid (0.40 g, 2.57 mmol), $Pd(PPh_3)_4$ (0.185 g, 0.16 mmol), and $Ba(OH)_2$ (1.69 g, 5.35 mmol) were combined and purged with nitrogen. A mixture of 3:1 dioxane : H_2O (16 mL) was added and then stirred with reflux for 24 h. The resulting reaction was cooled to room temperature, then diluted with 1M HCl and DCM until a homogeneous biphasic solution resulted. The aqueous layer was extracted twice with DCE. The combined organic layers were washed with water and brine. The organic layer was then dried over

Na_2SO_4 and concentrated under vacuum form the reaction residue, which was dissolved in DCE (16 mL). 12M HCl (5.0 mL) was added into above mixture at room temperature. The reaction was heated to reflux for 6 h, then cooled to room temperature. The mixture was partitioned between DCE and water. The organic phase was separated and the aqueous phase was extracted three times with DCE. The combined DCE extract was washed with saturated aqueous $NaHCO_3$, dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by silica gel chromatography to give the desired product **S12** (0.526 g, 60%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 20.0 Hz, 4H), 7.72 – 7.70 (m, 4H), 7.46 – 7.44 (m, 6H), 7.25 (d, J = 8.4 Hz, 2H), 5.35 (s, 2H), 1.47 (dt, J = 14.9, 7.5 Hz, 6H), 1.11 (dd, J = 7.5, 3.8 Hz, 36H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.54, 136.59, 136.24, 133.84, 133.81, 133.01, 132.03, 131.18, 131.11, 129.32, 129.15, 128.65, 122.88, 111.86, 18.79, 18.77, 11.05. HRMS (ESI$^-$): calcd for $[C_{50}H_{59}O_2Cl_2Si_2]^-$ 817.3436, found 817.3427.

(4*R*,11b*S*)-2,6-bis(4-chlorophenyl)-4-hydroxy-9,14-bis(triisopropylsilyl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-oxide (**HX_6**)

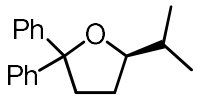


HX_6

To a solution of **S12** (0.5 g, 0.61 mmol) in pyridine (5.0 mL) was added dropwise freshly distilled $POCl_3$ (170 μL, 1.83 mmol) over 1 min. The resultant mixture was stirred at 95 °C for 12 h, upon which H_2O (5.0 mL) was cautiously added. Heating was continued at 70 °C for an additional 12 h. The reaction mixture was then cooled to ambient temperature and poured into chilled 6 M aqueous HCl. The reaction mixture was extracted with DCE. The organic phase was separated and the aqueous phase was extracted three times with DCE. The combined DCE extract was washed with brine, dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by silica gel chromatography to give the desired product **HX_6** (0.484 g, 90%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 2H), 7.99 (s, 2H), 7.55 – 7.26 (m, 12H), 1.50 (dt, J = 14.9, 7.4 Hz, 6H), 1.12 (dd, J = 7.4, 1.6 Hz, 36H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.29, 136.34, 135.36, 133.89, 133.49, 132.72, 132.61, 132.59, 132.22, 131.71, 131.18, 131.08, 128.49, 125.80, 122.44, 18.72, 18.70, 10.98. HRMS (ESI$^-$): calcd for $[C_{50}H_{58}O_4Cl_2PSi_2]^-$ 879.2994, found 879.2984.

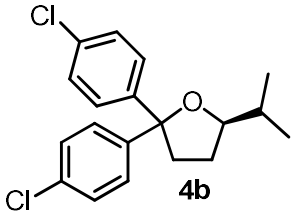
General procedure I for photoinduced enantioselective anti-Markovnikov hydroetherification of 2a. To a flame-dried Schlenk tube equipped with a magnetic stir bar was added **Mes-AcrBF$_4$** (5 mol %) and **NaX_6** (5 mol %). The mixture was diluted with 0.5 mL of anhydrous chloroform. After stirring for 15 min under dark, the solvent was removed in *vacuo*. Then **2a** (0.05 mmol) and 2-phenylmalononitrile (100 mol %) was added. Following the mixture diluted with 0.25 mL DCE in glove box, the reaction was irradiated with Blue LEDs in -15 °C for 24 h. Upon completion, the reaction mixture was concentrated in *vacuo*. The residue was purified by silica gel chromatography (1% EtOAc in Petroleum ether) to give **4a** (11.0 mg, 83% yield, 56% *ee.*

Reaction temperature was -25 °C, 70% yield, 60% *ee*).



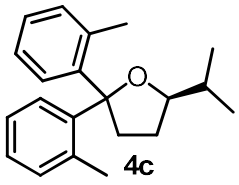
4a

5-isopropyl-2,2-diphenyltetrahydrofuran (**4a**): $[\alpha]_D^{25}$ = -2.6° (c = 0.35, $CHCl_3$, 60% *ee*). HPLC analysis: Daicel Chiralpak OD-H, 0.1% *iso*-propanol/hexane, flow rate = 0.5 mL/min, λ = 216 nm, retention time: 15.5 min (minor), 22.1 min (major). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.44 (m, 4H), 7.31 – 7.25 (m, 4H), 7.21 - 7.16 (m, 2H), 3.75 (q, J = 7.2 Hz, 1H), 2.68 – 2.62 (m, 1H), 2.50 - 2.44 (m, 1H), 1.96 – 1.89 (m, 1H), 1.81 - 1.77 (m, 1H), 1.72 - 1.65 (m, 1H), 1.08 (d, J = 6.6 Hz, 3H), 0.89 (d, J = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.62, 147.04, 128.25, 128.08, 126.64, 126.55, 126.05, 125.91, 87.65, 84.45, 39.23, 33.65, 29.20, 19.68, 18.69. IR (thin film, cm^{-1}): 3444, 2956, 2922, 2851, 1633, 1470, 1055, 701. HRMS (APCI$^+$): calcd for $[C_{19}H_{23}O]^+$ 267.1743, found 267.1738.



4b

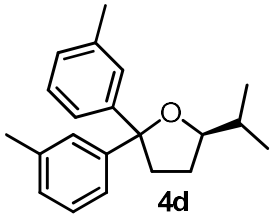
2,2-bis(4-chlorophenyl)-5-isopropyltetrahydrofuran (**4b**): the product **4b** (82% yield, 53% *ee*) was synthesized according to the general procedure I. $[\alpha]_D^{25}$ = -4.0° (c = 0.85, $CHCl_3$). HPLC analysis: Daicel Chiralpak OD-H, 0.1% *iso*-propanol/hexane, flow rate = 0.3 mL/min, λ = 221 nm, retention time: 19.1 min (major), 20.0 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 4H), 7.27 – 7.22 (m, 4H), 3.72 (q, J = 7.3 Hz, 1H), 2.59 – 2.54 (m, 1H), 2.44 – 2.39 (m, 1H), 1.92 (td, J = 13.4, 6.9 Hz, 1H), 1.76 – 1.65 (m, 2H), 1.05 (d, J = 6.6 Hz, 3H), 0.87 (d, J = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.70, 145.22, 132.71, 132.60, 128.51, 128.32, 127.40, 127.26, 86.87, 84.78, 39.13, 33.61, 29.19, 19.57, 18.67.. IR (thin film, cm^{-1}): 2962, 2923, 2876, 2848, 1488, 1091, 1055, 1008, 825. HRMS (APCI$^+$): calcd for $[C_{19}H_{21}OCl_2]^+$ 335.0964, found 355.0968.



4c

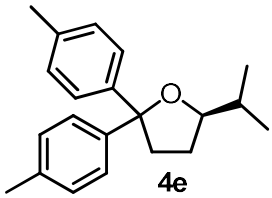
5-isopropyl-2,2-di-o-tolyltetrahydrofuran (**4c**): the product **4c** (54% yield, 33% *ee*) was synthesized according to the general procedure I. $[\alpha]_D^{25}$ = -11.0° (c = 0.4, $CHCl_3$). HPLC analysis: Daicel Chiralpak OD-H, 0.1% *iso*-propanol/hexane, flow rate = 0.2 mL/min, λ = 218 nm, retention time: 29.4 min (major), 31.4 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, J = 7.7 Hz, 1H), 7.58 (d, J = 7.5 Hz, 1H), 7.16 – 7.11 (m, 4H), 7.04 – 7.00 (m, 2H), 3.62 (q, J = 7.4 Hz, 1H), 2.69 – 2.63 (m, 1H), 2.50 – 2.44 (m, 1H), 2.05 – 1.98 (m, 7H), 1.79 – 1.69 (m, 2H), 0.99 (d, J = 6.6 Hz, 3H), 0.84 (d, J = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.02, 143.44, 136.85, 136.32, 132.32, 132.07, 127.02, 126.98, 126.80, 126.38, 124.99, 124.86, 88.37, 84.08, 36.65, 33.69, 29.50, 21.77,

21.67, 19.67, 18.87.. IR (thin film, cm^{-1}): 2958, 2927, 2871, 1460, 1046, 753. HRMS ($APCI^+$): calcd for $[C_{21}H_{27}O_3]^+$ 295.2056, found 295.2054.



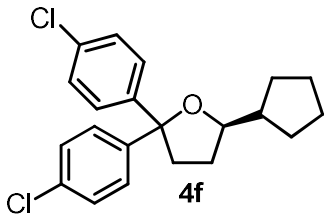
4d

5-isopropyl-2,2-di-m-tolyltetrahydrofuran (**4d**): the product **4d** (50% yield, 59% *ee*) was synthesized according to the general procedure I. $[\alpha]_D^{25}$ = -4.3° (c = 0.30, $CHCl_3$). HPLC analysis: Daicel Chiralpak OD-H, 0.2% *iso*-propanol/hexane, flow rate = 0.5 mL/min, λ = 214 nm, retention time: 7.9 min (minor), 8.2 min (major). ^1H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 4H), 7.16 (dtd, J = 10.3, 7.5, 2.7 Hz, 2H), 7.00 – 6.97 (m, 2H), 3.74 (q, J = 7.4 Hz, 1H), 2.63 – 2.61 (m, 1H), 2.45 – 2.42 (m, 1H), 2.32 (d, J = 6.5 Hz, 6H), 1.92 – 1.89 (m, 1H), 1.80 – 1.78 (m, 1H), 1.68 – 1.66 (m, 1H), 1.08 (d, J = 3.7 Hz, 3H), 0.88 (d, J = 3.7 Hz, 3H).. ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.64, 147.05, 137.74, 137.52, 128.08, 127.91, 127.38, 127.28, 126.73, 126.59, 123.09, 122.97, 87.63, 84.33, 39.15, 33.60, 29.85, 29.07, 21.80, 19.71, 18.63. IR (thin film, cm^{-1}): 2922, 2851, 1727, 1467, 1284, 1121, 1073. HRMS ($APCI^+$): calcd for $[C_{21}H_{27}O]^+$ 295.2056, found 295.2059.



4e

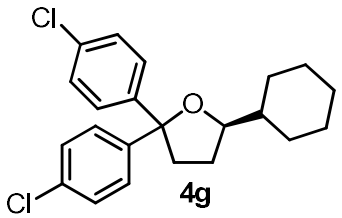
5-isopropyl-2,2-di-p-tolyltetrahydrofuran (**4e**): the product **4e** (77% yield, 50% *ee*) was synthesized according to the general procedure I. $[\alpha]_D^{25}$ = -5.0° (c = 0.30, $CHCl_3$). HPLC analysis: Daicel Chiralpak AD-H x 2, 0.5% *iso*-propanol/hexane, flow rate = 0.5 mL/min, λ = 223 nm, retention time: 16.4 min (minor), 17.0 min (major). ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 4H), 7.08 (dd, J = 17.4, 7.1 Hz, 4H), 3.72 (dd, J = 14.3, 7.2 Hz, 1H), 2.63 – 2.58 (m, 1H), 2.44 – 2.38 (m, 1H), 2.29 (d, J = 8.7 Hz, 6H), 1.92 – 1.88 (m, 1H), 1.79 – 1.76 (m, 1H), 1.68 – 1.65 (m, 1H), 1.06 (dd, J = 6.6, 1.6 Hz, 3H), 0.87 (dd, J = 6.7, 1.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.93, 144.24, 136.09, 135.99, 128.94, 128.75, 125.96, 125.80, 87.47, 84.29, 39.20, 33.63, 29.85, 29.19, 21.12, 19.68, 18.66. IR (thin film, cm^{-1}): 3358, 3192, 2956, 2851, 1659, 1633, 1470. HRMS ($APCI^+$): calcd for $[C_{15}H_{27}O]^+$ 295.2056, found 295.2051.



4f

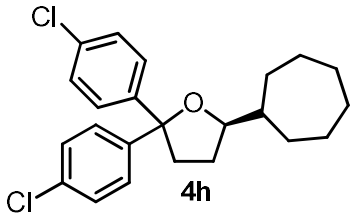
2,2-bis(4-chlorophenyl)-5-cyclopentyltetrahydrofuran (**4f**): the product **4f** (80% yield, 50% *ee*) was synthesized according to the general procedure I. $[\alpha]_D^{25}$ = -9.1° (c = 0.55, $CHCl_3$). HPLC analysis:

Daicel Chiralpak OD-H, 0.1% *iso*-propanol/hexane, flow rate = 0.3 mL/min, λ = 223 nm, retention time: 19.8 min (major), 20.9 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 4H), 7.26 – 7.22 (m, 4H), 3.85 (dd, J = 14.8, 7.3 Hz, 1H), 2.60 - 2.53 (m, 1H), 2.48 – 2.41 (m, 1H), 2.02 – 1.89 (m, 3H), 1.68 – 1.61 (m, 4H), 1.53 - 1.47 (m, 2H), 1.21 – 1.16 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.84, 145.30, 132.70, 132.59, 128.49, 128.31, 127.43, 127.30, 86.90, 83.77, 45.51, 39.21, 30.55, 30.12, 29.16, 25.77, 25.72. IR (thin film, cm^{-1}): 2951, 2920, 2873, 2854, 1489, 1089, 1055, 819. HRMS (APCI$^+$): calcd for $[C_{21}H_{23}OCl_2]^+$ 366.1121, found 366.1117.



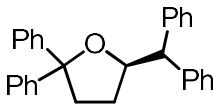
4g

2,2-bis(4-chlorophenyl)-5-cyclohexyltetrahydrofuran (**4g**): the product **4g** (85% yield, 64% *ee*) was synthesized according to the general procedure I. $[\alpha]_D^{25}$ = -5.4° (c = 0.65, $CHCl_3$). HPLC analysis: Daicel Chiralpak OD-H, 0.1% *iso*-propanol/hexane, flow rate = 1.0 mL/min, λ = 207 nm, retention time: 6.1 min (major), 6.7 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 4H), 7.27 – 7.23 (m, 4H), 3.74 (q, J = 7.4 Hz, 1H), 2.56 (dt, J = 12.5, 7.4 Hz, 1H), 2.41 (ddd, J = 12.5, 8.3, 6.2 Hz, 1H), 2.11 – 1.89 (m, 3H), 1.75 – 1.66 (m, 6H), 1.47 – 1.43 (m, 1H), 1.21 – 0.97 (m, 3H). ^{13} C NMR (101 MHz, $CDCl_3$) δ 145.78, 145.29, 132.71, 132.60, 128.51, 128.33, 127.41, 127.27, 86.67, 83.79, 43.41, 39.05, 30.07, 29.24, 29.15, 26.73, 26.15, 26.10. IR (thin film, cm^{-1}): 3359, 2923, 2852, 1633, 1489, 1092, 1013, 822. HRMS (APCI$^+$): calcd for $[C_{22}H_{25}OCl_2]^+$ 375.1277, found 375.1272.



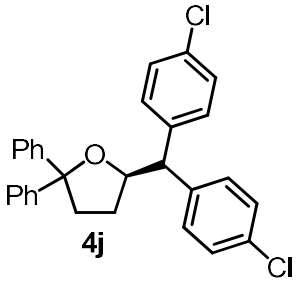
4h

2,2-bis(4-chlorophenyl)-5-cycloheptyltetrahydrofuran (**4h**): the product **4h** (80% yield, 54% *ee*) was synthesized according to the general procedure I. $[\alpha]_D^{25}$ = -2.4° (c = 0. 50, $CHCl_3$). HPLC analysis: Daicel Chiralpak OD-H, 0.1% *iso*-propanol/hexane, flow rate = 0.3 mL/min, λ = 213 nm, retention time: 17.9 min (major), 19.0 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 4H), 7.26 – 7.22 (m, 4H), 3.79 (q, J = 7.2 Hz, 1H), 2.57 (dt, J = 12.6, 7.5 Hz, 1H), 2.44 – 2.39 (m, 1H), 2.03 – 2.01 (m, 1H), 1.92 (dd, J = 12.7, 6.2 Hz, 1H), 1.72 - 1.62 (m, 6H), 1.52 – 1.34 (m, 6H), 1.19 – 1.17 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.75, 145.23, 132.71, 132.58, 128.52, 128.32, 127.43, 127.26, 86.69, 83.73, 44.74, 39.21, 30.86, 30.49, 29.36, 28.74, 28.55, 26.99, 26.89. IR (thin film, cm^{-1}): 2920, 2851, 1663, 1631, 1489, 1457, 1394, 1096, 824. HRMS (APCI$^+$): calcd for $[C_{23}H_{27}OCl]^+$ 389.1434, found 389.1428.



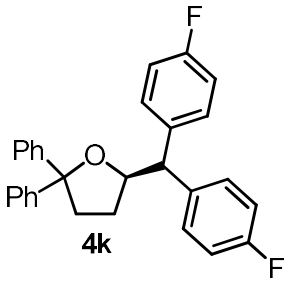
4i

5-benzhydryl-2,2-diphenyltetrahydrofuran (**4i**): the product **4i** (80% yield, 13% *ee*) was synthesized according to the general procedure I. $[\alpha]_D^{25}$ = -2.4° (c = 0.25, $CHCl_3$). HPLC analysis: Daicel Chiralpak AD-H, 0.5% *iso*-propanol/hexane, flow rate = 1.0 mL/min, λ = 218 nm, retention time: 6.0 min (minor), 6.4 min (major). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.15 (m, 20H), 4.84 (q, J = 7.5 Hz, 1H), 4.05 (d, J = 8.4 Hz, 1H), 2.64 – 2.59 (m, 1H), 2.40 – 2.34 (m, 1H), 1.88 (dd, J = 12.8, 6.5 Hz, 1H), 1.76 (dd, J = 12.9, 6.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.35, 146.95, 143.06, 143.00, 129.03, 128.77, 128.53, 128.31, 128.24, 128.05, 126.72, 126.58, 126.52, 126.26, 125.89, 125.84, 88.58, 80.82, 57.40, 38.71, 30.90. IR (thin film, cm^{-1}): 3650, 3567, 1721, 1505, 1644, 1541. HRMS ($APCI^+$): calcd for $[C_{29}H_{27}O]^+$ 391.2056, found 391.2052.



4j

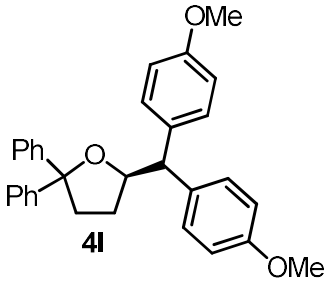
5-(bis(4-chlorophenyl)methyl)-2,2-diphenyltetrahydrofuran (**4j**): the product **4j** (80% yield, 9% *ee*) was synthesized according to the general procedure I. $[\alpha]_D^{25}$ = -2.0° (c = 0.35, $CHCl_3$). HPLC analysis: Daicel Chiralpak OD-H, 1.0% *iso*-propanol/hexane, flow rate = 1.0 mL/min, λ = 223 nm, retention time: 7.0 min (minor), 8.2 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.8 Hz, 2H), 7.32 – 7.14 (m, 16H), 4.74 (q, J = 7.1 Hz, 1H), 3.98 (d, J = 8.2 Hz, 1H), 2.62 (dt, J = 12.7, 7.2 Hz, 1H), 2.36 (ddd, J = 12.5, 8.2, 6.7 Hz, 1H), 1.90 (td, J = 13.9, 7.0 Hz, 1H), 1.72 (dt, J = 15.1, 7.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.99, 146.62, 141.05, 140.86, 132.60, 132.32, 130.38, 130.00, 128.80, 128.47, 128.40, 128.14, 126.86, 126.75, 125.76, 125.73, 88.82, 80.44, 56.02, 38.45, 30.78. IR (thin film, cm^{-1}): 3360, 2920, 2850, 1659, 1633, 1490, 1471, 1091. HRMS ($APCI^+$): calcd for $[C_{29}H_{25}OCl_2]^+$ 459.1278, found 459.1273.



4k

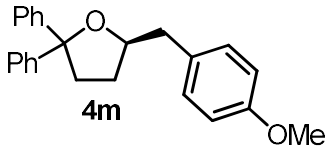
5-(bis(4-fluorophenyl)methyl)-2,2-diphenyltetrahydrofuran (**4k**): the product **4k** (77% yield, 10% *ee*) was synthesized according to the general procedure I. $[\alpha]_D^{25}$ = -0.9° (c = 0.45, $CHCl_3$). HPLC analysis: Daicel Chiralpak OD-H, 1.0% *iso*-propanol/hexane, flow rate = 1.0 mL/min, λ = 227 nm, retention time: 7.5 min (minor), 8.8 min (major). ^{1}H NMR (500 MHz, CDCl3) δ 7.41 (d, J = 7.7 Hz, 2H), 7.33 – 7.14 (m, 12H), 6.95 (dt, J = 15.3, 8.7 Hz, 4H), 4.74 (q, J = 7.2 Hz, 1H), 4.01 (d, J = 8.1

Hz, 1H), 2.64 – 2.58 (m, 1H), 2.35 – 2.30 (m, 1H), 1.89 (dq, J = 14.0, 7.0 Hz, 1H), 1.73 (dt, J = 14.9, 7.0 Hz, 1H). ^{13}C NMR (126 MHz, CDCl3) δ 162.64, 160.69, 147.08, 146.72, 138.64, 138.31, 130.47, 130.41, 130.13, 130.07, 128.38, 128.12, 126.83, 126.71, 125.78, 125.77, 115.50, 115.33, 115.14, 114.97, 88.75, 80.76, 55.68, 38.48, 30.77. IR (thin film, cm^{-1}): 3839, 3649, 1603, 1507, 1224, 824. HRMS (APCI$^+$): calcd for $[C_{29}H_{25}OF_2]^+$ 427.1868, found 427.1863.



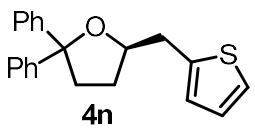
4l

5-(bis(4-methoxyphenyl)methyl)-2,2-diphenyltetrahydrofuran (**4l**): the product **4l** (90% yield, 8% *ee*) was synthesized according to the general procedure I. $[\alpha]_D^{25}$ = 0.5° (c = 0.65, $CHCl_3$). HPLC analysis: Daicel Chiralpak AS-H, 2.5% *iso*-propanol/hexane, flow rate = 1.0 mL/min, λ = 190 nm, retention time: 7.7 min (major), 9.1 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 7.8 Hz, 2H), 7.35 (d, J = 7.8 Hz, 2H), 7.30 – 7.13 (m, 10H), 6.82 (d, J = 8.5 Hz, 2H), 6.77 (d, J = 8.5 Hz, 2H), 4.74 (q, J = 7.3 Hz, 1H), 3.96 (d, J = 8.3 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 2.62 – 2.57 (m, 1H), 2.37 – 2.31 (m, 1H), 1.87 (dd, J = 12.8, 6.6 Hz, 1H), 1.74 (dd, J = 12.5, 7.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.13, 157.97, 147.39, 147.00, 135.68, 135.53, 129.88, 129.62, 128.30, 128.03, 126.69, 126.56, 125.90, 125.88, 113.86, 113.59, 88.55, 81.14, 55.58, 55.33, 38.68, 30.85. IR (thin film, cm^{-1}): 2921, 2834, 1608, 1509, 1463, 1447, 1246, 1176, 1033, 703. HRMS (APCI$^+$): calcd for $[C_{31}H_{31}O_3]^+$ 451.2268, found 451.2261.



4m

5-(4-methoxybenzyl)-2,2-diphenyltetrahydrofuran (**4m**): the product **4m** (88% yield, 3% *ee*) was synthesized according to the general procedure I. $[\alpha]_D^{25}$ = -0.6° (c = 0.50, $CHCl_3$). HPLC analysis: Daicel Chiralpak AS-H, 1.0% *iso*-propanol/hexane, flow rate = 1.0 mL/min, λ = 214 nm, retention time: 6.4 min (minor), 7.4 min (major). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (t, J = 8.6 Hz, 4H), 7.29 – 7.25 (m, 4H), 7.20 – 7.15 (m, 4H), 6.82 (d, J = 8.4 Hz, 2H), 4.32 (p, J = 6.7 Hz, 1H), 3.78 (s, 3H), 3.07 (dd, J = 13.6, 5.9 Hz, 1H), 2.73 (dd, J = 13.6, 7.2 Hz, 1H), 2.63 – 2.58 (m, 1H), 2.50 – 2.45 (m, 1H), 1.91 (dd, J = 12.5, 6.8 Hz, 1H), 1.72 (dd, J = 12.4, 7.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.17, 147.41, 146.87, 131.07, 130.45, 128.26, 128.11, 126.70, 126.67, 126.03, 125.99, 113.80, 88.36, 80.20, 55.38, 41.75, 38.77, 30.90. IR (thin film, cm^{-1}): 3445, 2920, 2849, 1634, 1608, 1510, 1246, 700. HRMS (APCI$^+$): calcd for $[C_{24}H_{25}O_2]^+$ 345.1849, found 345.1844.



4n

2,2-diphenyl-5-(thiophen-2-ylmethyl)tetrahydrofuran (**4n**): the product **4n** (75% yield, 2% *ee*) was synthesized according to the general procedure I. $[\alpha]_D^{25}$ = -3.1° (c = 0.35, $CHCl_3$). HPLC analysis: Daicel Chiralpak OD-H, 1.0% *iso*-propanol/hexane, flow rate = 1.0 mL/min, λ = 231 nm, retention time: 6.6 min (minor), 7.4 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 4H), 7.31 – 7.26 (m, 4H), 7.20 – 7.14 (m, 3H), 6.94 (dd, J = 5.1, 3.4 Hz, 1H), 6.88 - 6.87 (m, 1H), 4.37 (p, J = 6.6 Hz, 1H), 3.27 (dd, J = 14.7, 6.1 Hz, 1H), 3.05 (dd, J = 14.7, 6.7 Hz, 1H), 2.69 – 2.63 (m, 1H), 2.54 – 2.47 (m, 1H), 2.02 (tt, J = 14.3, 7.1 Hz, 1H), 1.81 – 1.75 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.18, 146.60, 141.06, 128.32, 128.17, 126.77, 126.77, 126.73, 125.94, 125.94, 125.71, 123.97, 88.64, 79.46, 38.63, 36.83, 31.03, 0.15. IR (thin film, cm^{-1}): 3359, 2920, 2850, 1659, 1633, 1471, 1447, 1049, 696. HRMS (APCI$^+$): calcd for $[C_{21}H_{21}OS]^+$ 321.1308, found 321.1303.

^{1}H NMR Investigation

Figure 2b: To a solution of **X_6Na** (0.01 mmol) in CD_2Cl_2 (0.5 mL) at room temperature was added **Mes-AcrBF$_4$** (0.01 mmol). The mixture was stirred under dark for 15 min. The reaction mixture was conducted to ^{1}H NMR detection without further purification.

Figure 2c: To a solution of **HX_6** (0.01 mmol) in CD_2Cl_2 (0.5 mL) at room temperature was added **Mes-AcrBF$_4$** (0.01 mmol). The mixture was stirred under dark for 15 min. The reaction mixture was conducted to ^{1}H NMR detection without further purification.

Laser Flash Photolysis Studies.

Laser Flash Photolysis/Transient Absorption was performed using the commercially available LP920 system by Edinburgh Instruments, Inc. Laser excitation was provided by a pulsed Nd:YAG laser in combination with an optical parametric oscillator (OPO) for wavelength selection. Probe light was generated by a 450 W Xe lamp. Typical experiments employed laser excitation at 435 nm with single wavelength transient absorption monitored at the indicated wavelengths (1.0 nm bandwidths) with a photomultiplier tube (PMT) and transient spectra recorded using a gated CCD at the indicated time delays (10 ns gate width) unless otherwise indicated. Laser Flash photolysis experiments were performed on a 50 μM solution of **Mes-AcrBF$_4$** and chiral photocatalyst **Mes-AcrX$_6$** in DCE. Pure argon was bubbled through the solution for 20 min before test. Transient absorption kinetics were conducted at 480 nm corresponding to the the transient absorption spectrum for triplet **Mes-Acr$^+$**. Transient absorption kinetics were fit in Origin.

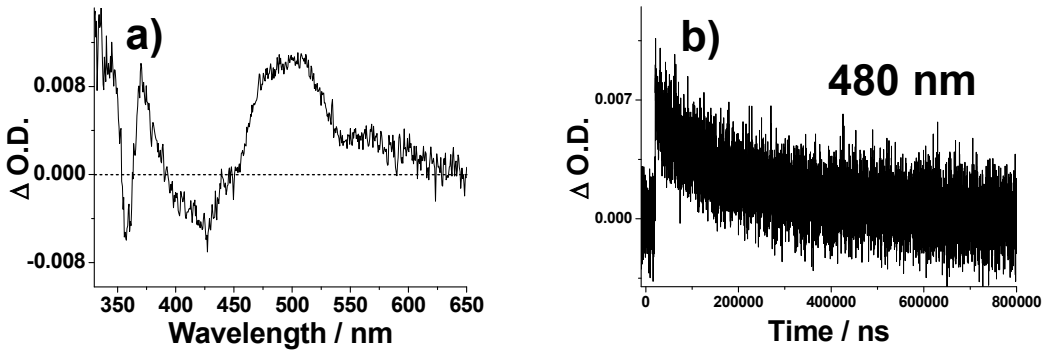


Figure 3. a) Transient absorption spectrum for **Mes-AcrX$_6$** taken at 10 ns. b) Transient absorption kinetics for **Mes-AcrX$_6$** measured at 480 nm. Conditions: [**Mes-AcrX$_6$**]= 50 μM in DCE; λ_{ex} = 435 nm; Ar atmosphere.

Stern-Volmer Analyses.

Stern-Volmer experiments[3] were conducted with detection at 510 nm, where the solutions in DCE contained **Mes-AcrBF$_4$** (1.6×10^{-5} M) or **Mes-AcrX$_6$** (1.6×10^{-5} M) and the quencher **2a** ranging from 3.0×10^{-4} to 1.6×10^{-3} M in concentration. Stern-Volmer analysis was conducted according to the following relationship:

$$\frac{\tau_0}{\tau} = 1 + K_{SV}[Q] = 1 + k_q\tau_0[Q]$$

where τ_o and τ are the fluorescence lifetime in the absence and presence of quencher Q, K_{SV} is the Stern-Volmer constant, k_q is the bimolecular quenching constant, and [Q] is the concentration of quencher.

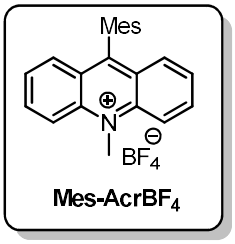
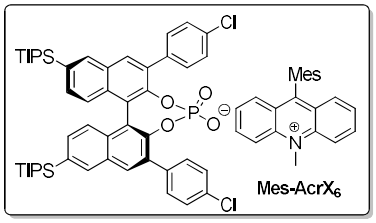
[*Q*] [**2a**] (mM)	k_{obs} (ns^{-1})	[*Q*] [**2a**] (mM)	k_{obs} (ns^{-1})
			
0	0.1107	0	0.1106
0.300	0.1109	0.657	0.1135
0.900	0.1142	1.201	0.1143
1.500	0.1172	1.562	0.1166

Table S4. Fluorescence lifetime of **Mes-AcrBF$_4$** (16 μM in DCE) and **Mes-AcrX$_6$** (16 μM in DCE) measured at 510 nm at the concentrations of quencher **2a**. Pseudo-first-order rate constants $k_{obs} = 1/\tau$.

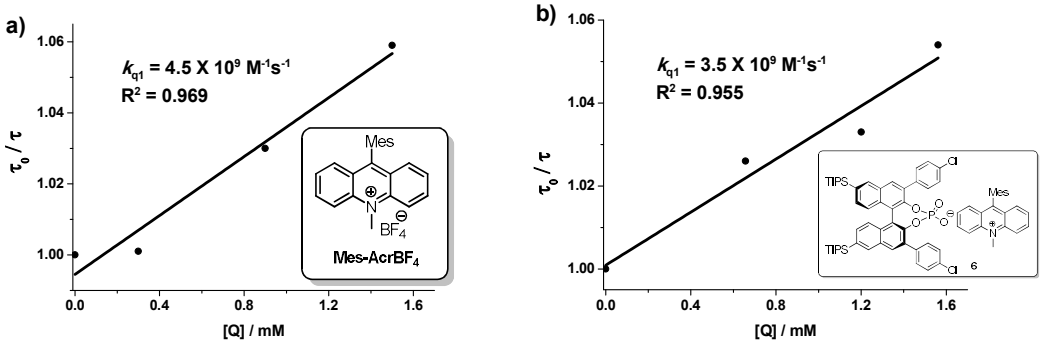


Figure S1. Stern–Volmer plots of quenching of **Mes-Acr**$^+$ (in DCE) fluorescence lifetime for quencher **2a** studied. **Mes-Acr**$^+$ fluorescence lifetime was measured with the laser flash photolysis spectrometer at 510 nm. a) Stern-Volmer plots for **Mes-AcrBF$_4$**; b) Stern-Volmer plots for **Mes-AcrX$_6$**. The Stern–Volmer quenching constant, K_{SV}, was determined by the slope of the linear regression, where the bimolecular quenching constant, k_q, is equal to K_{SV}/τ_0. Conditions: [**Mes-Acr**$^+$] = 16 μm; λ_{ex} = 435 nm; Ar atmosphere.

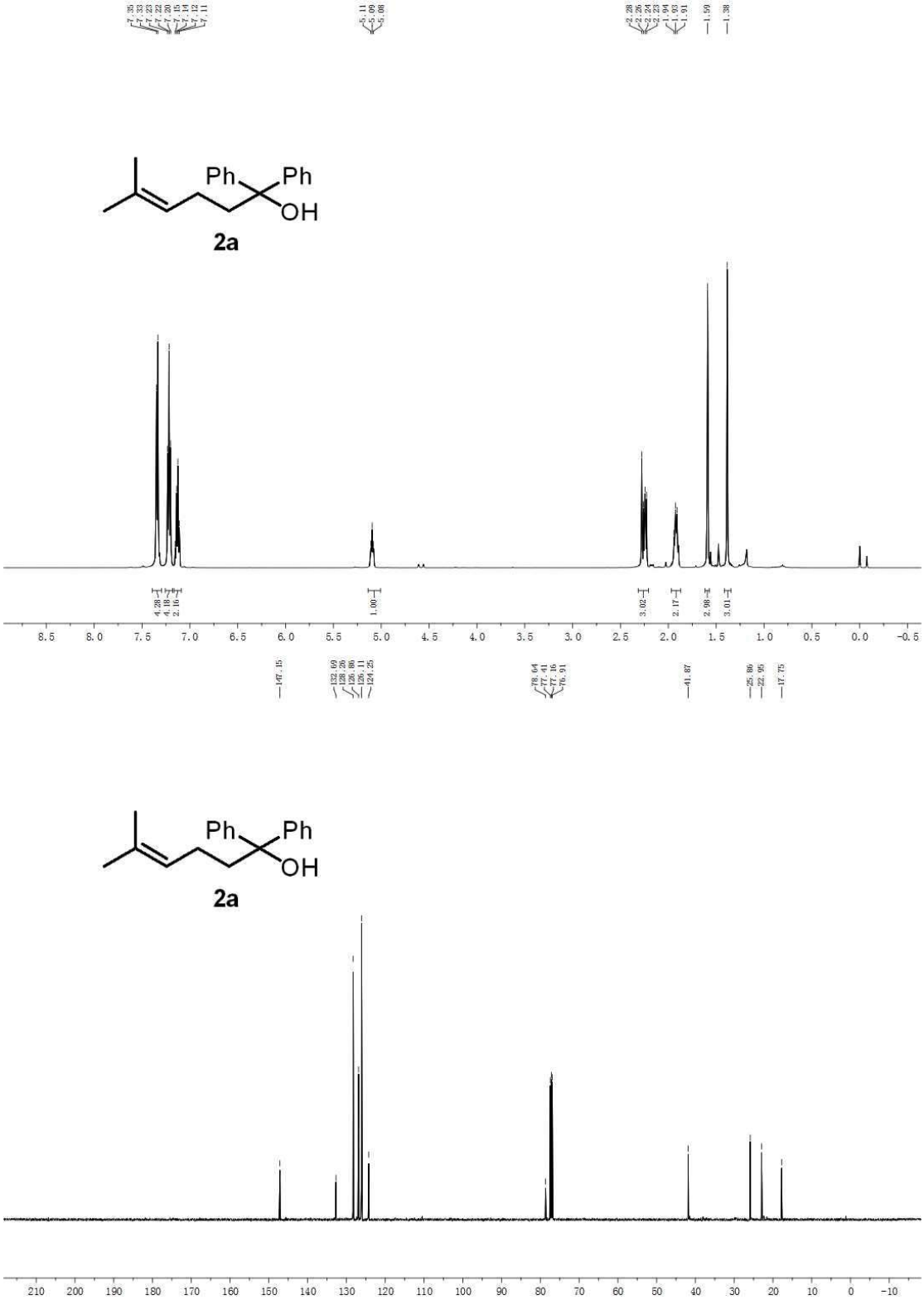
References.

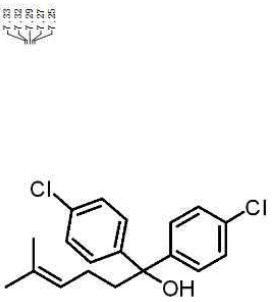
[1] D. S. Hamilton; D. A. Nicewicz. *J. Am. Chem. Soc.* **2012**, *134*, 18577.

[2] F. Romanov-Michailidis; L. Guénée; A. Alexakis. *Org. Lett.* **2013**, *15*, 5890.

[3] N. Romero,; D. A. Nicewicz, *J. Am. Chem. Soc*, **2014**, *136*, 17024.

NMR Spectrums.





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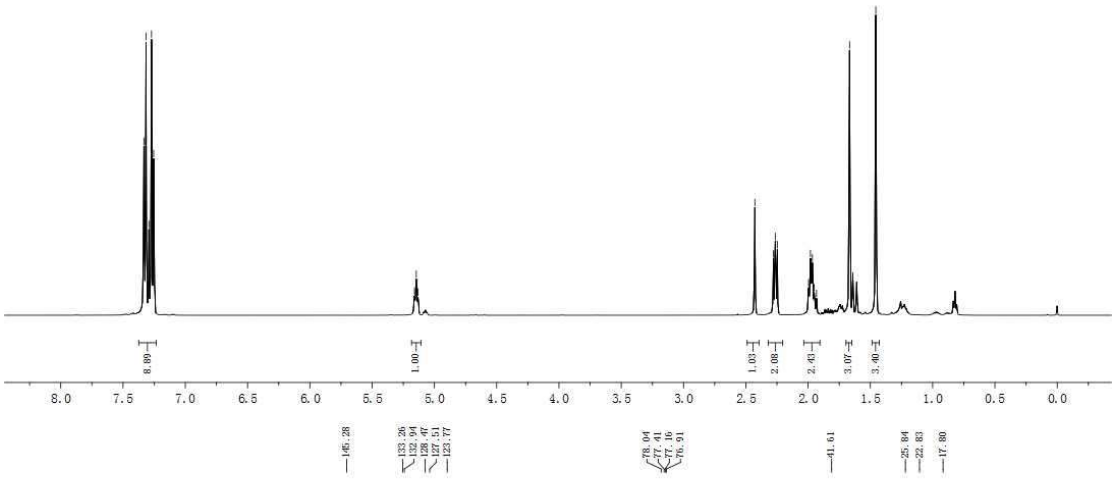

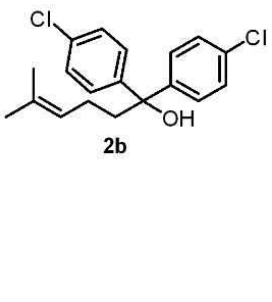

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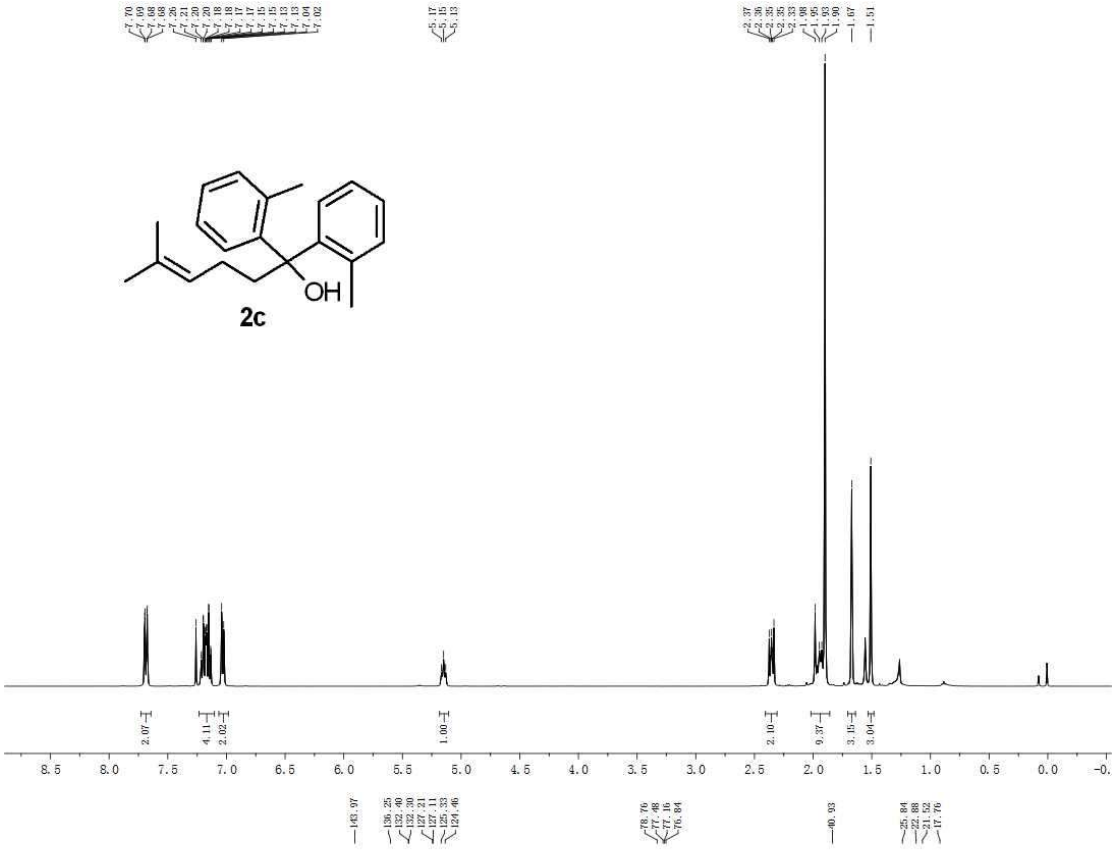
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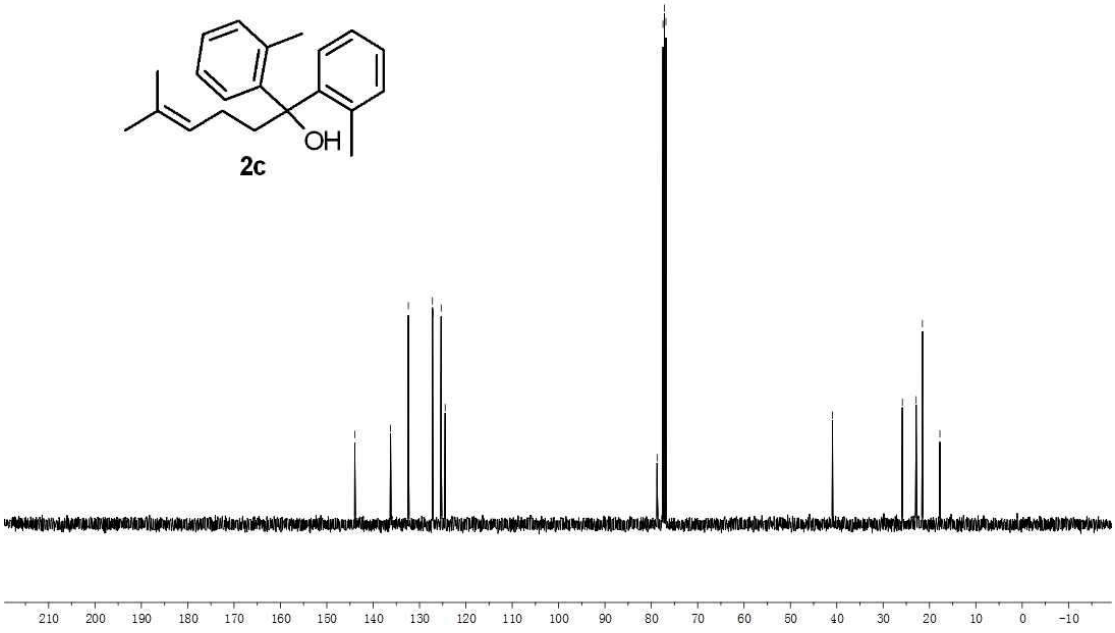
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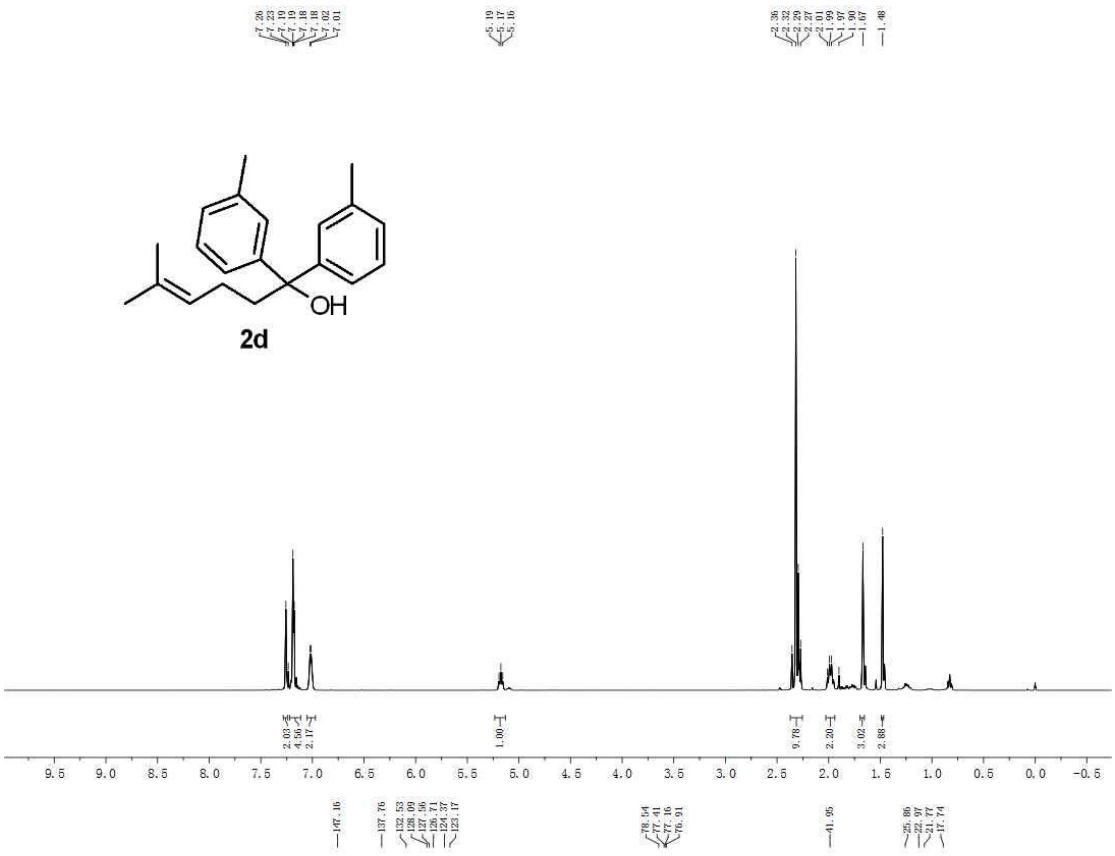
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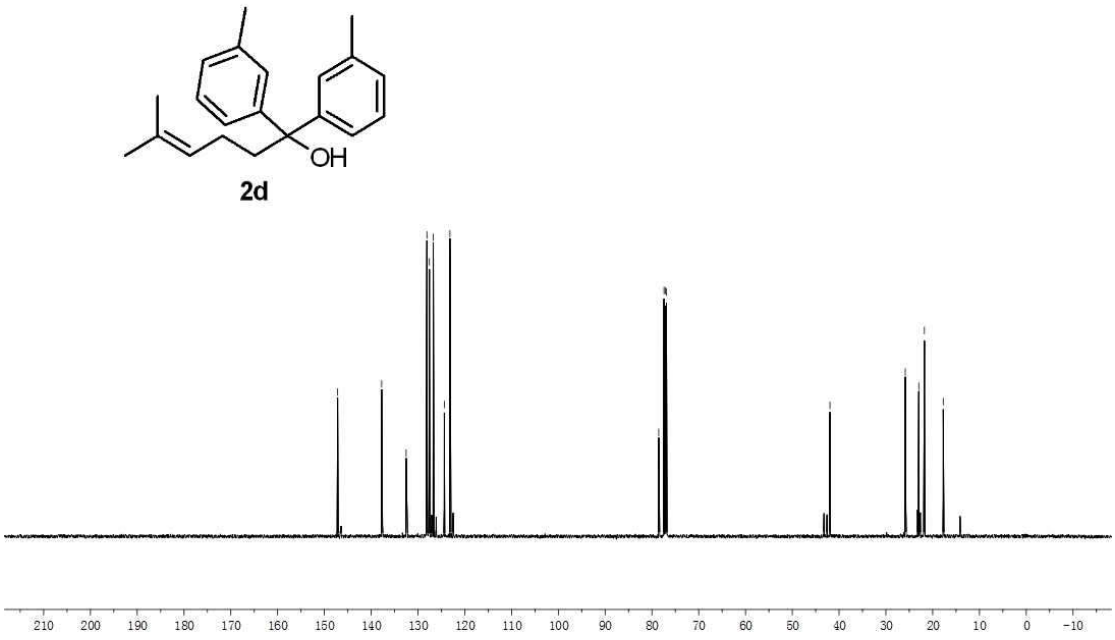
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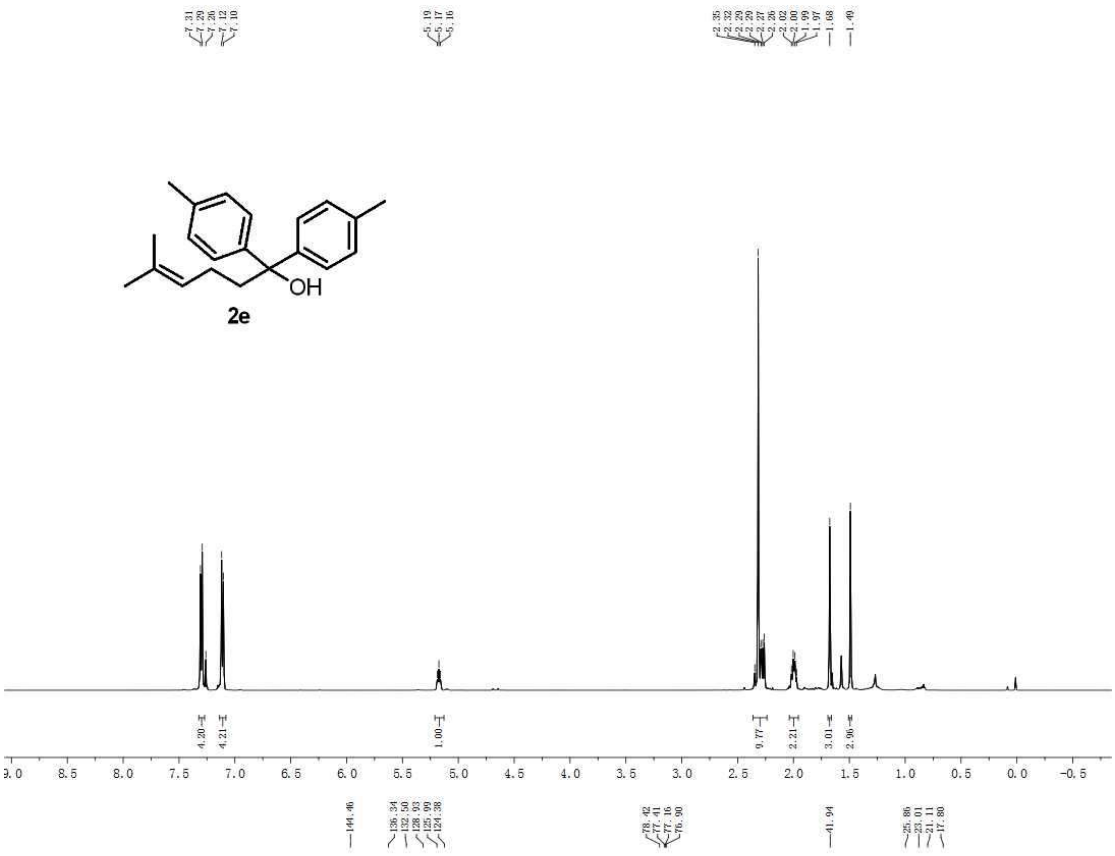
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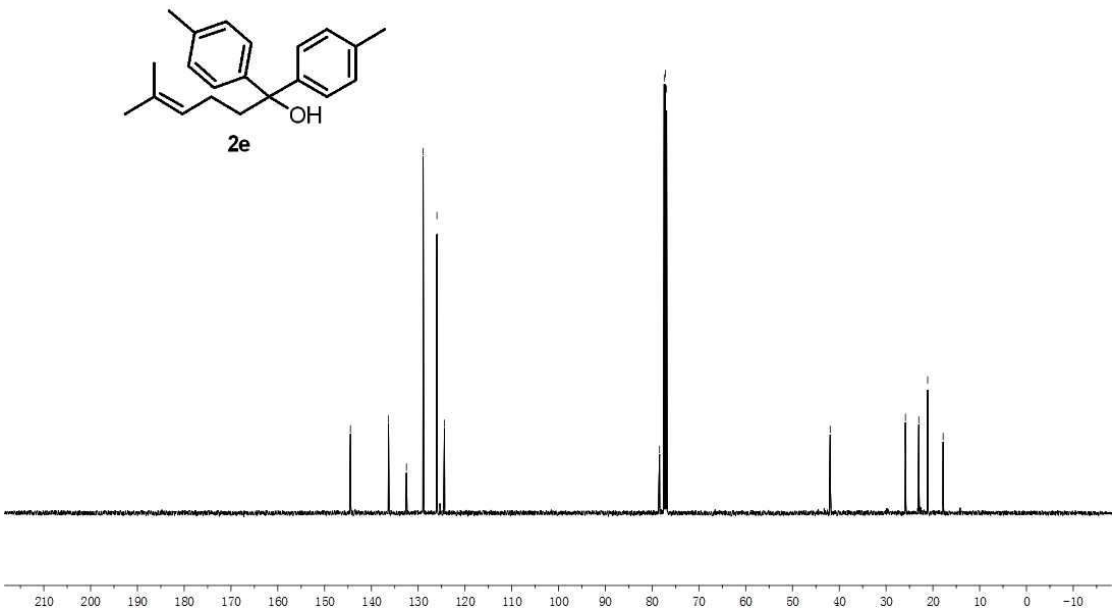
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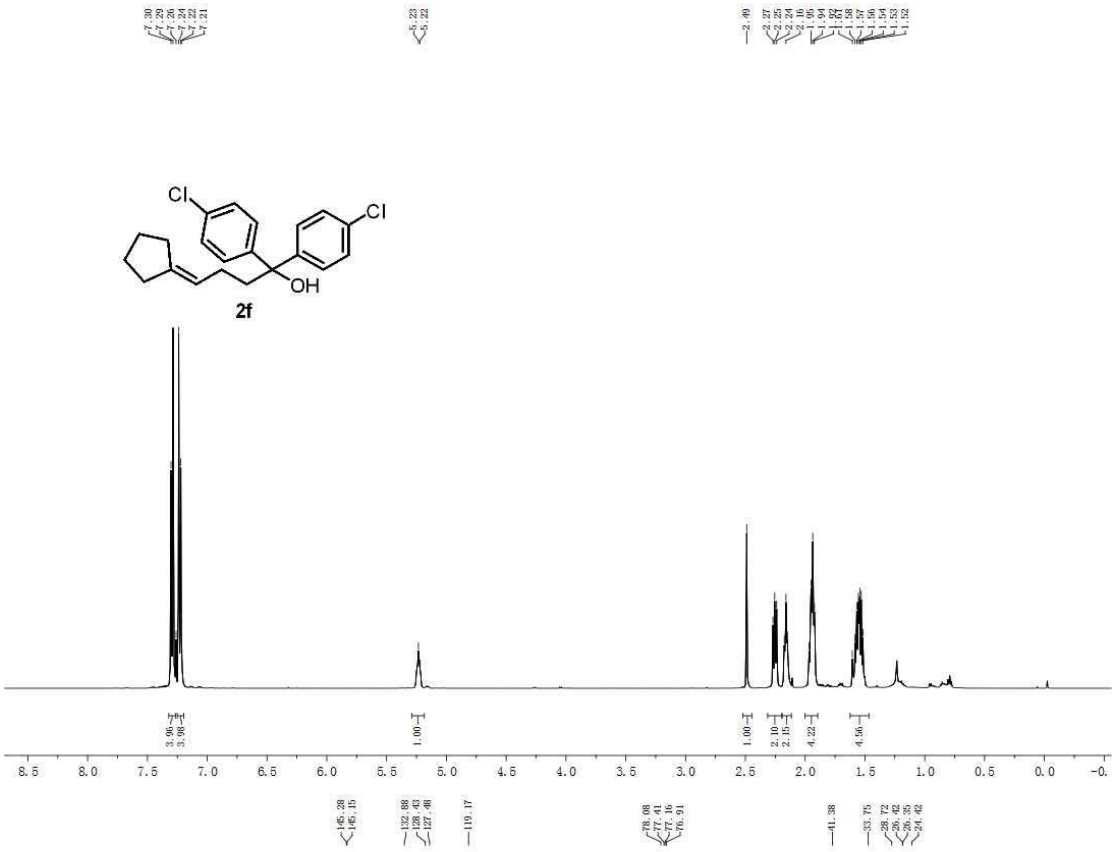
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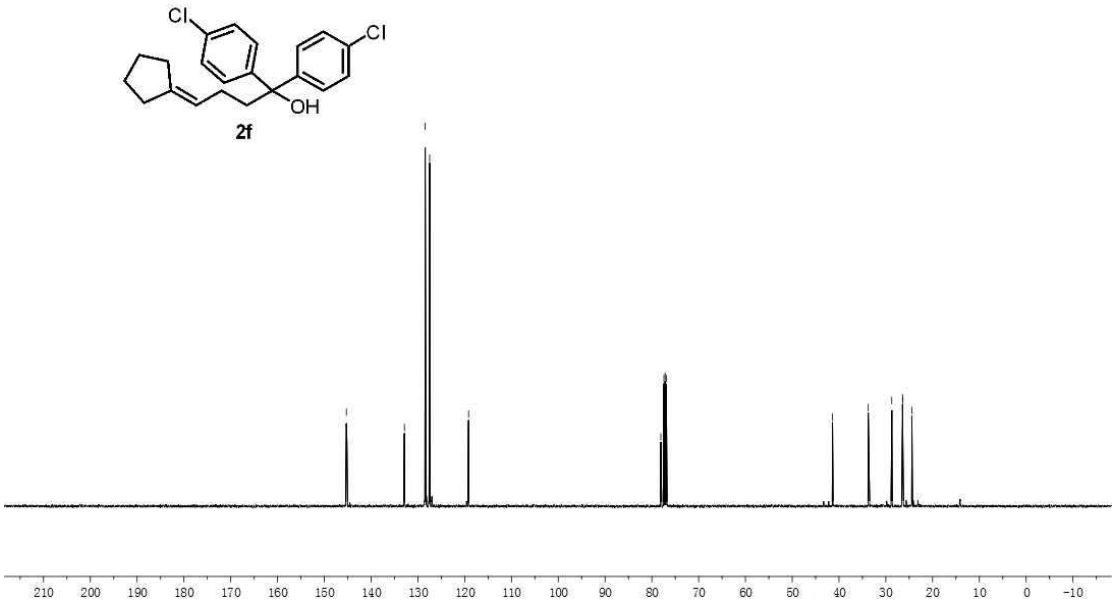
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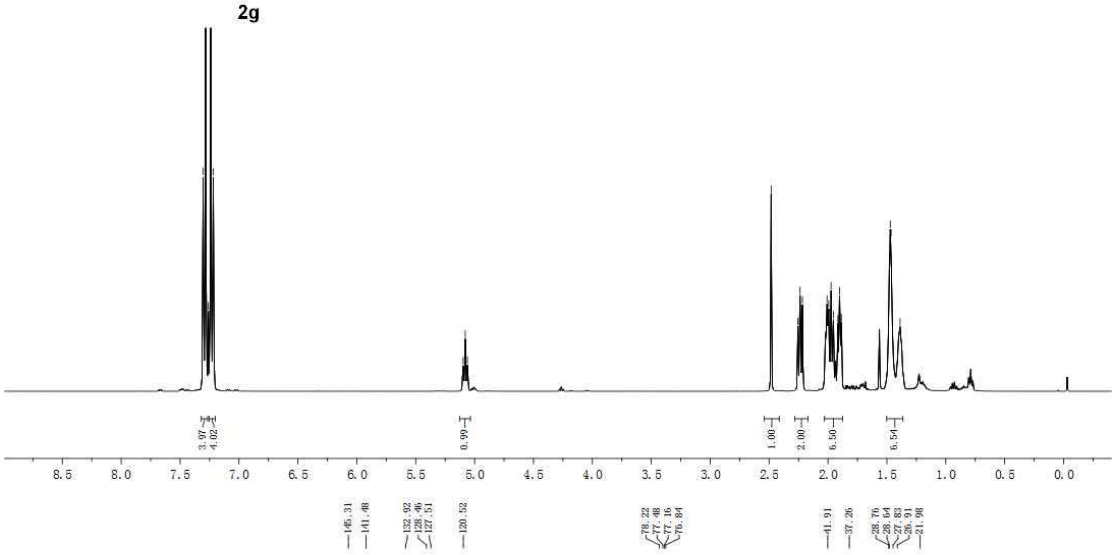
2g



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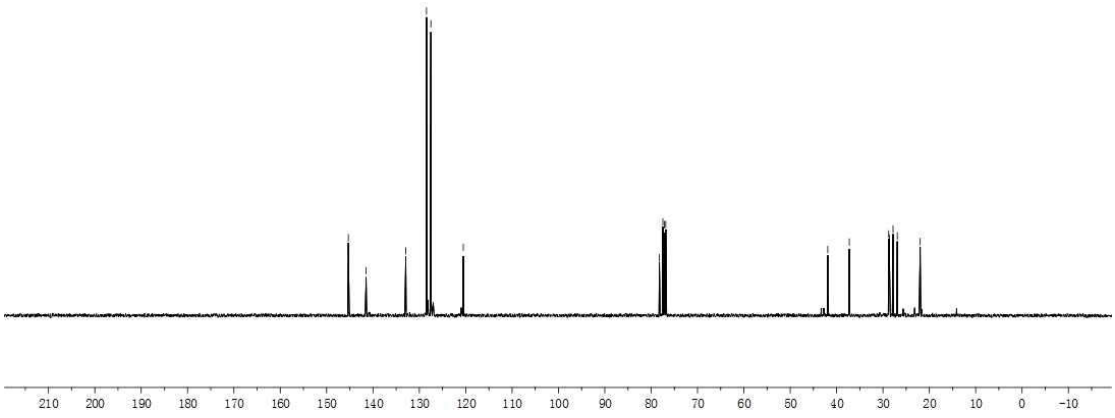

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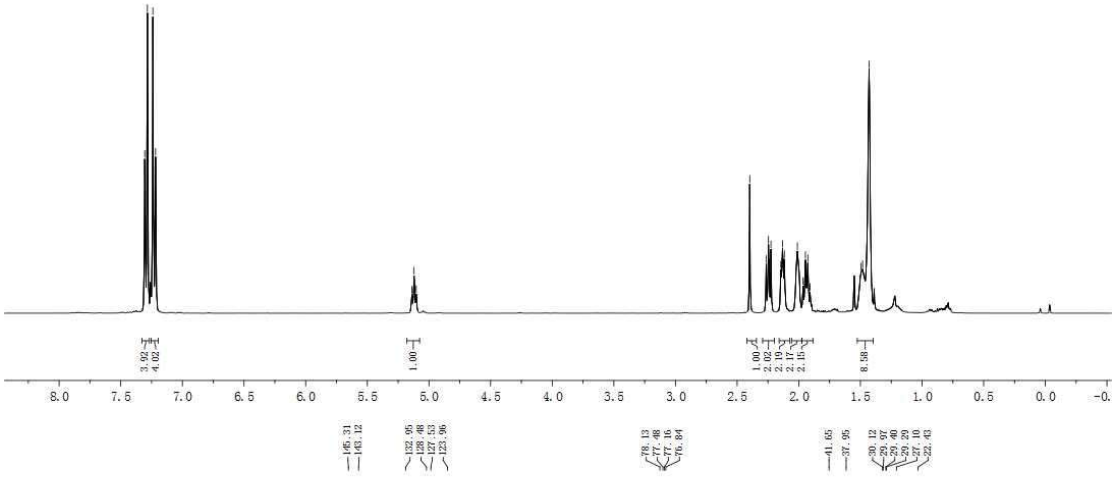
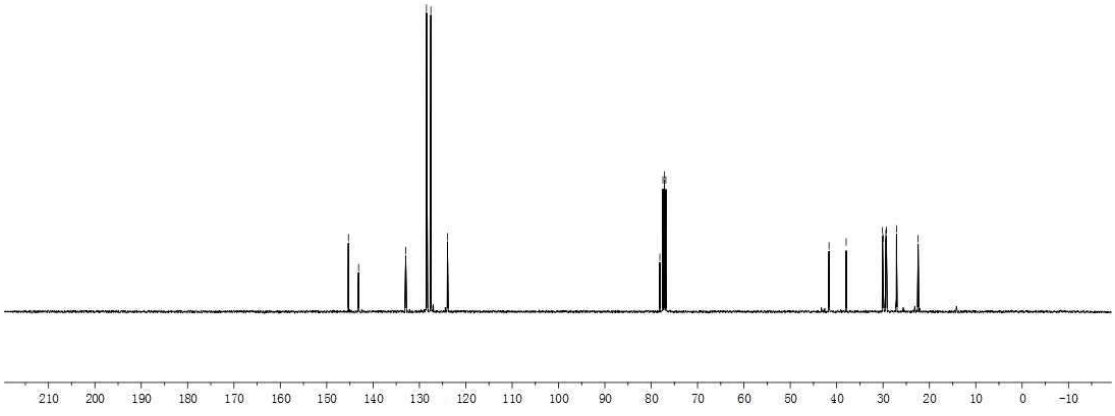
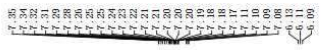
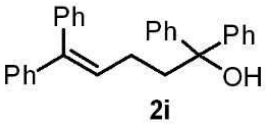


2h







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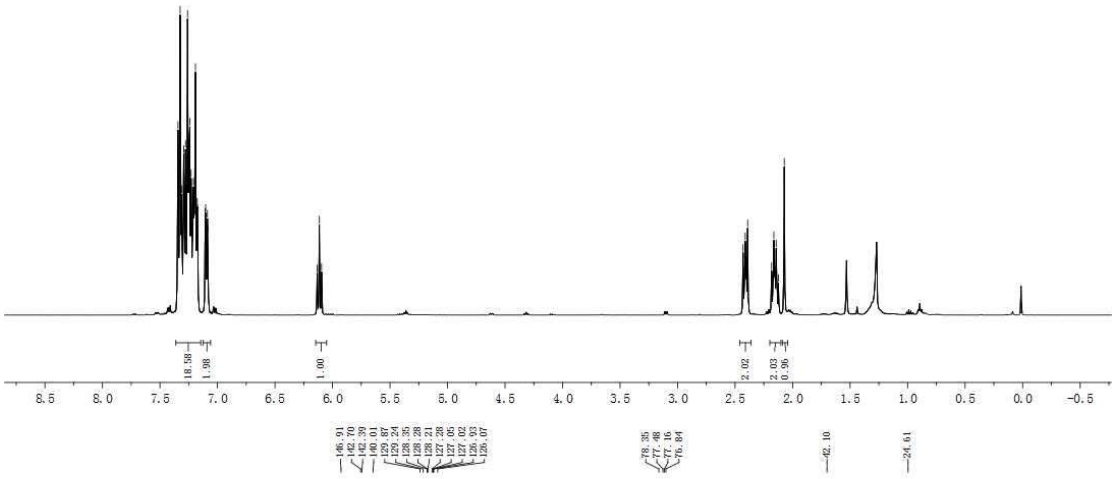

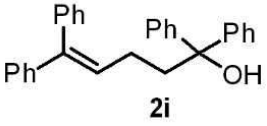

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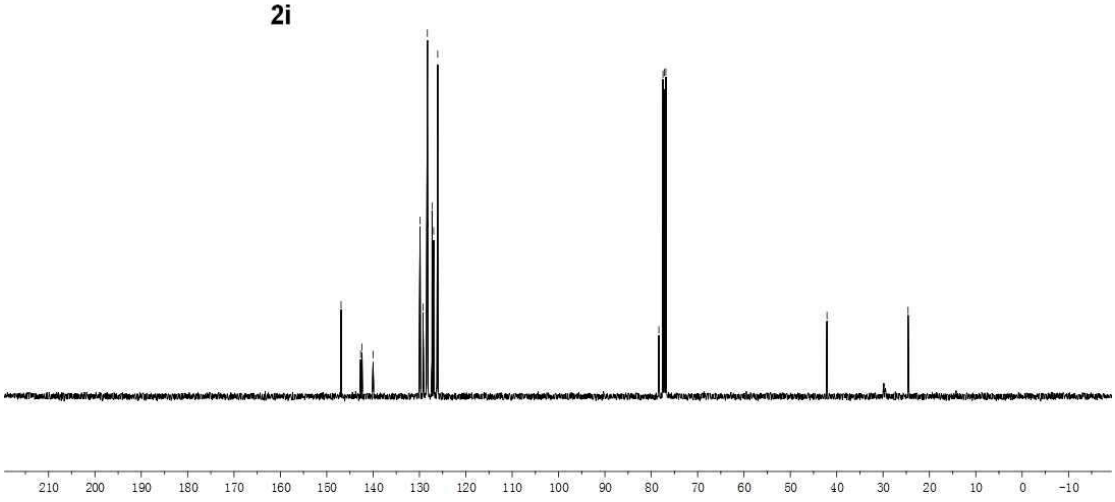

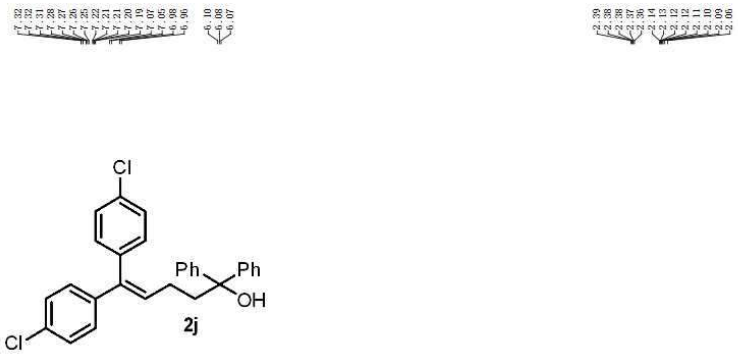
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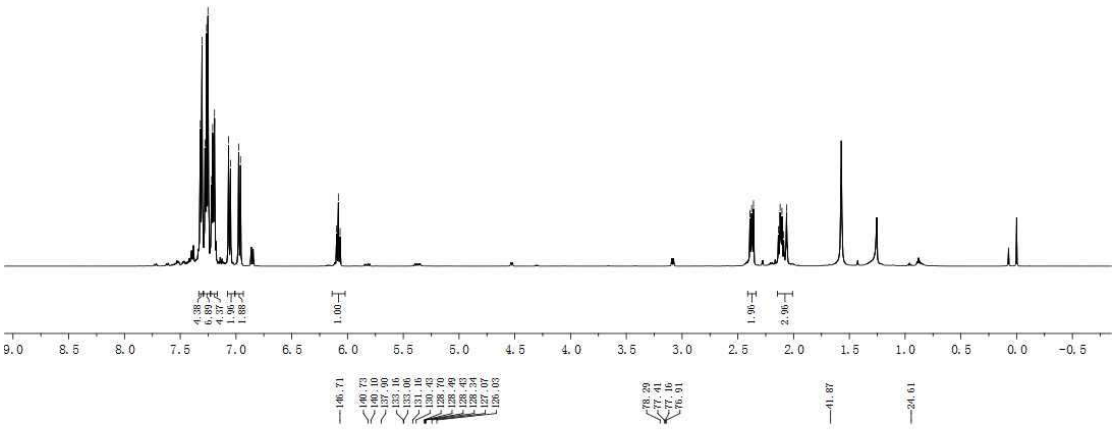

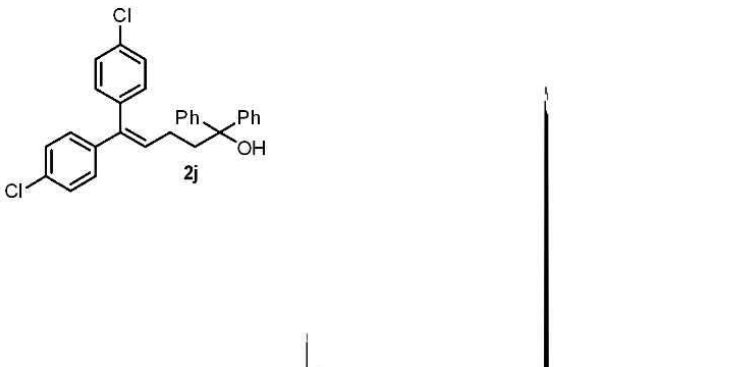
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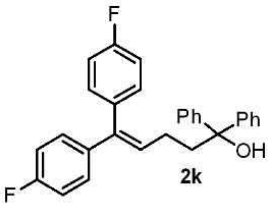

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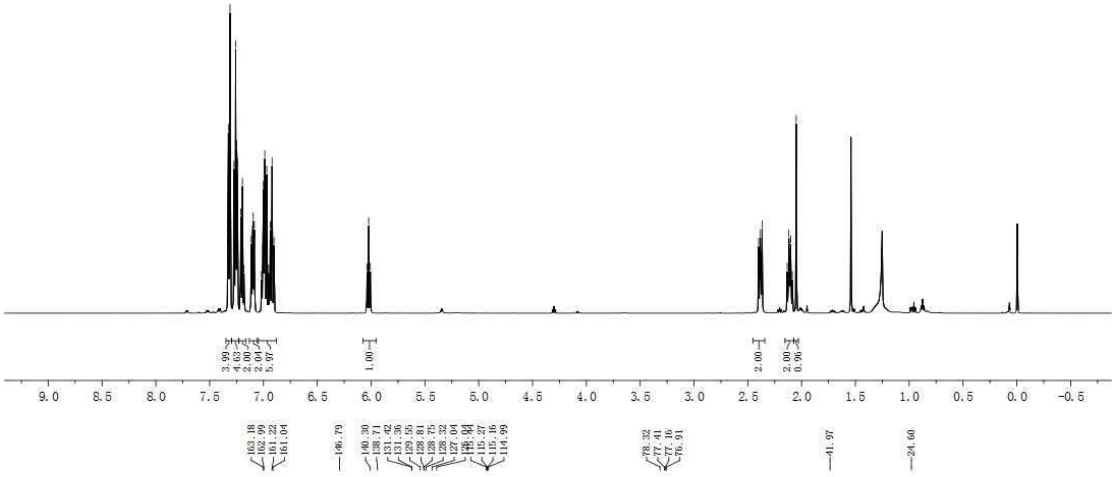

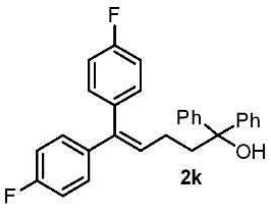

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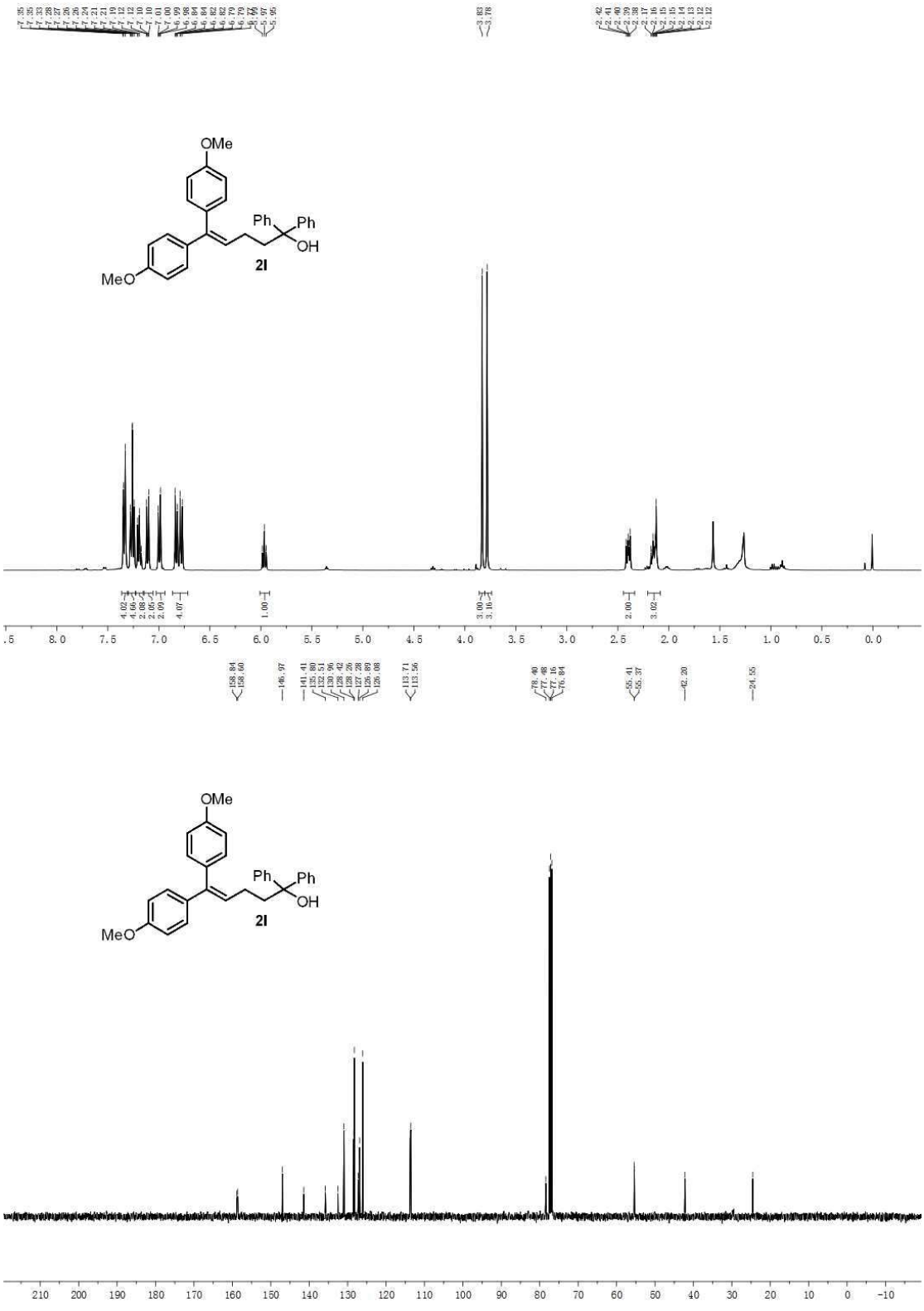
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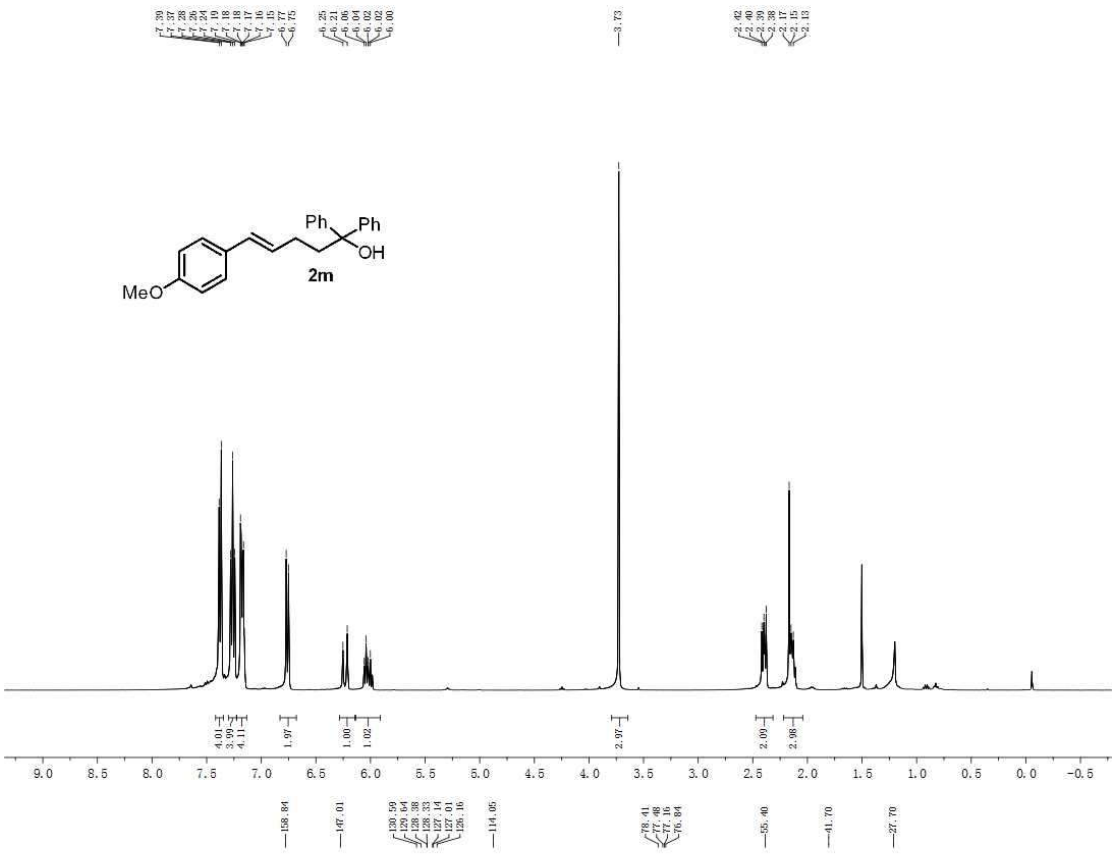
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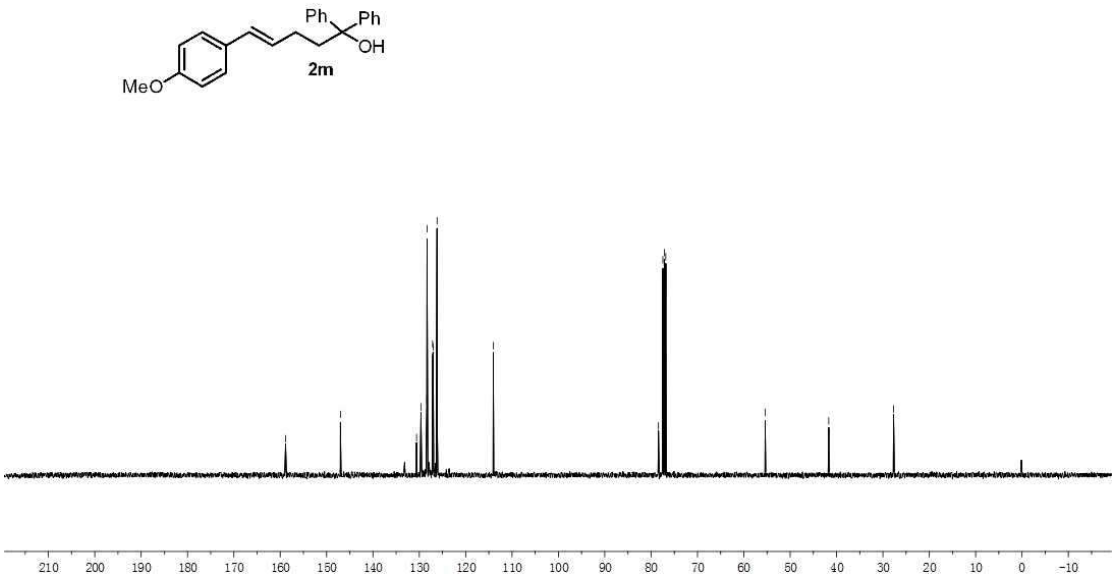
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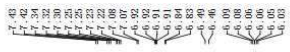

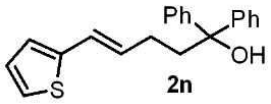

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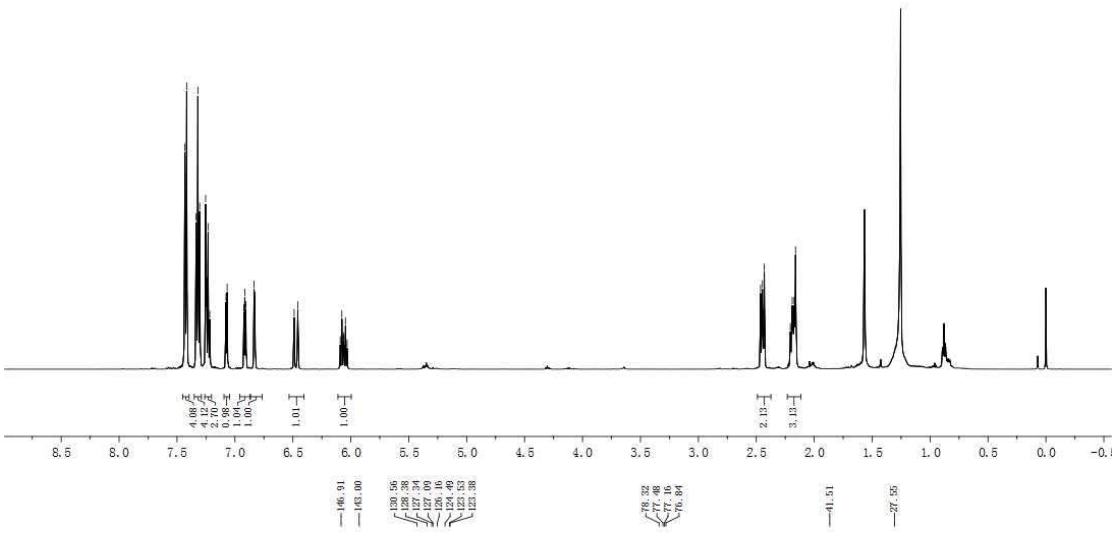

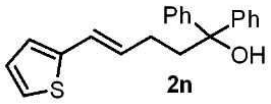

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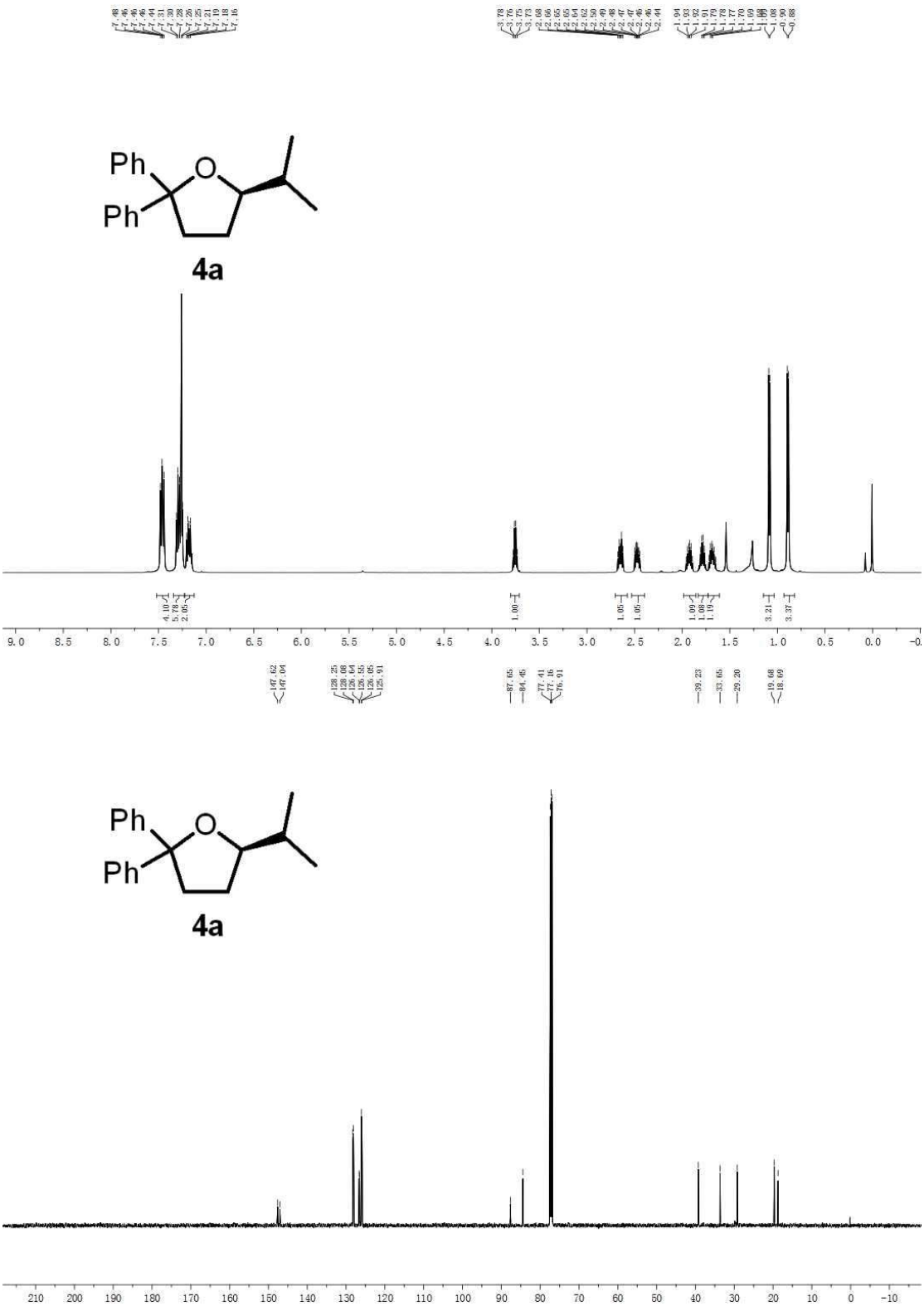
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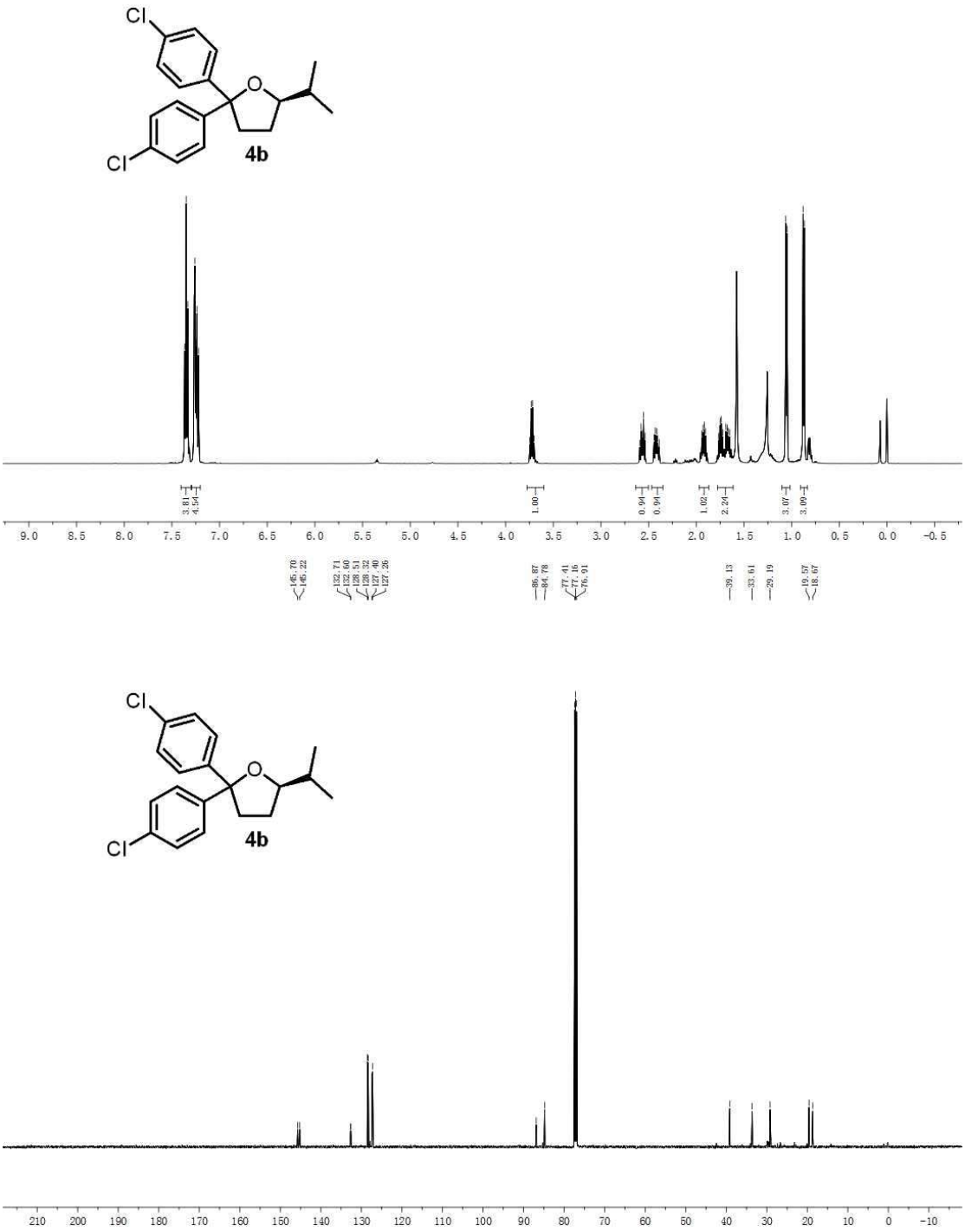
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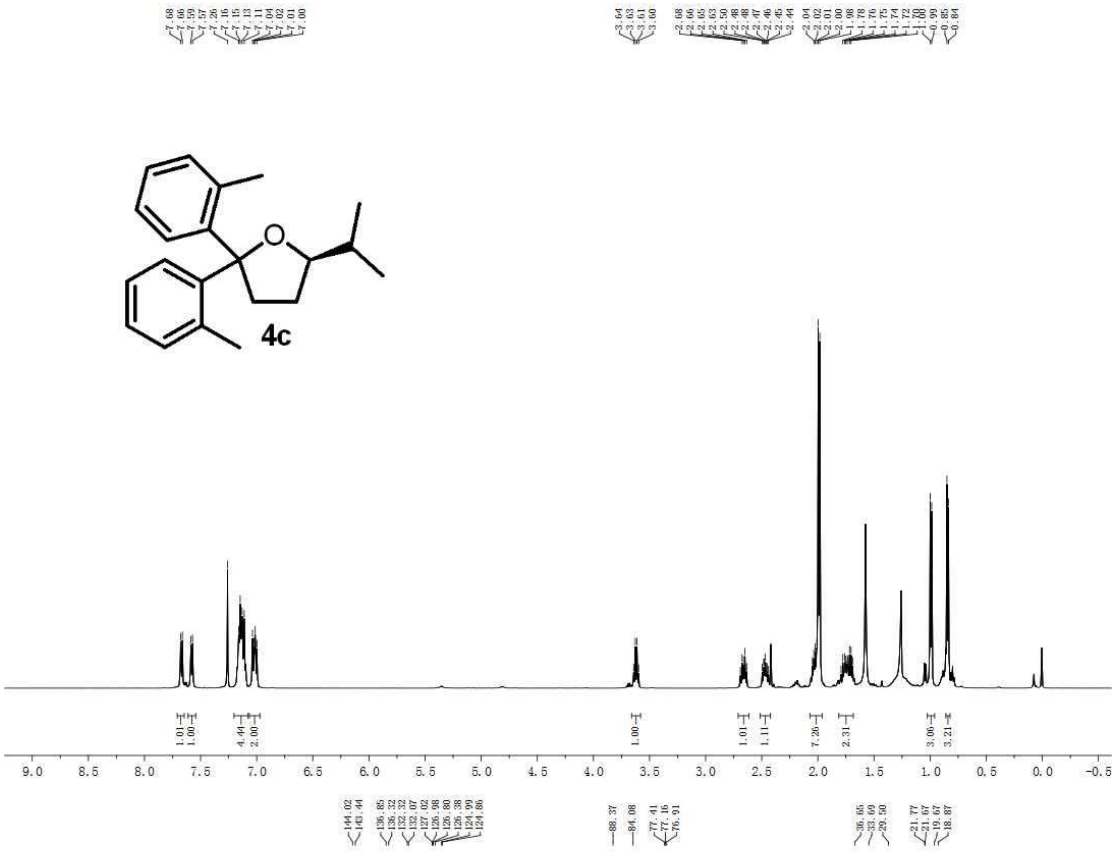
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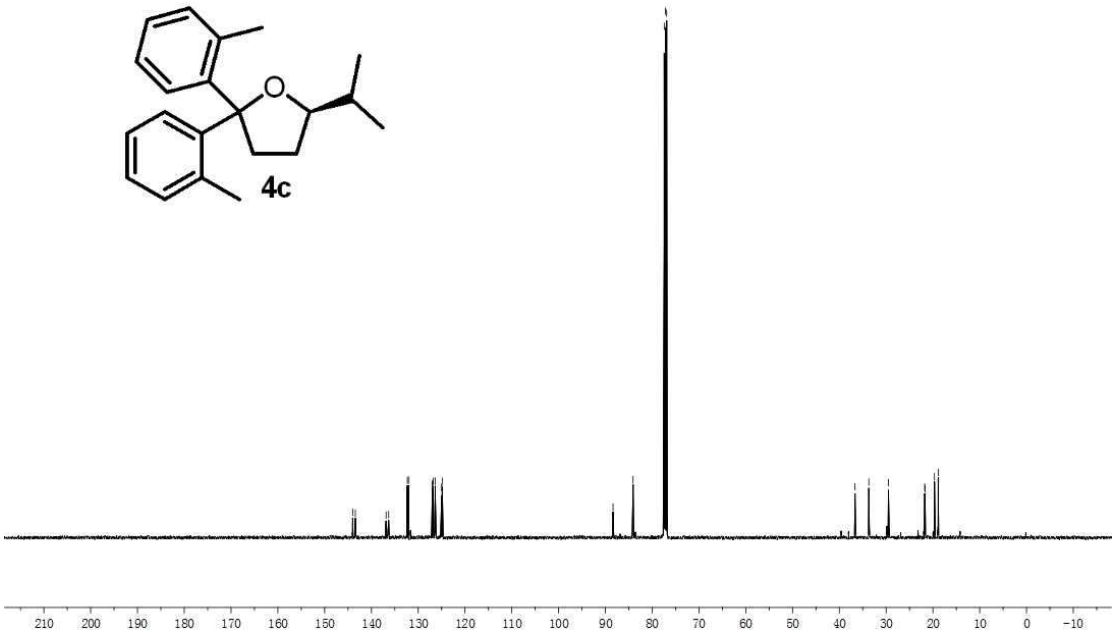
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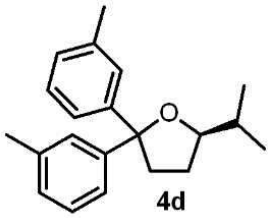
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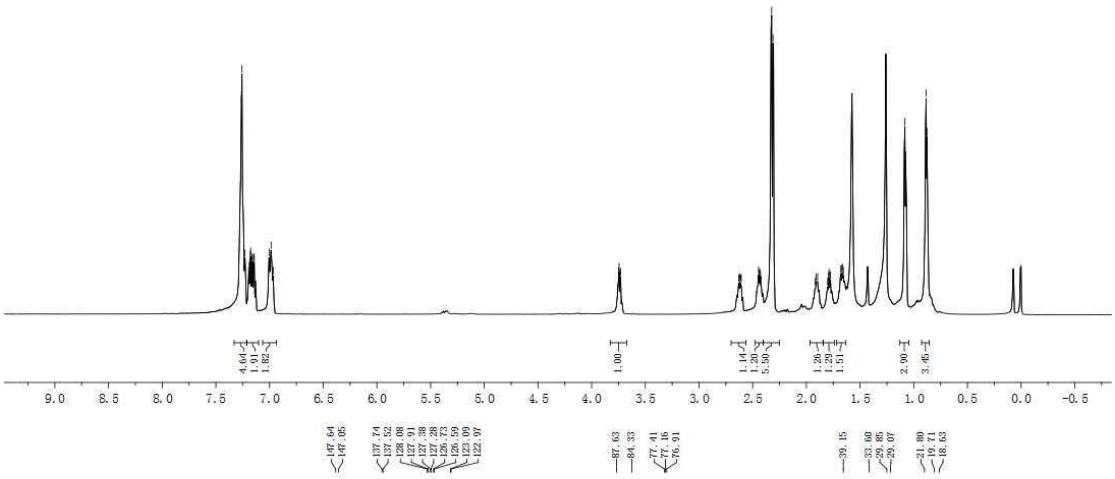

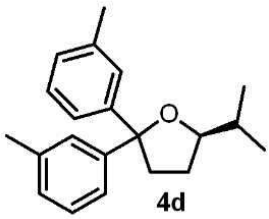
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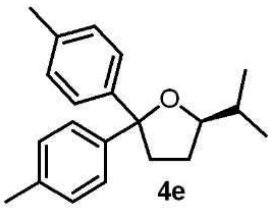
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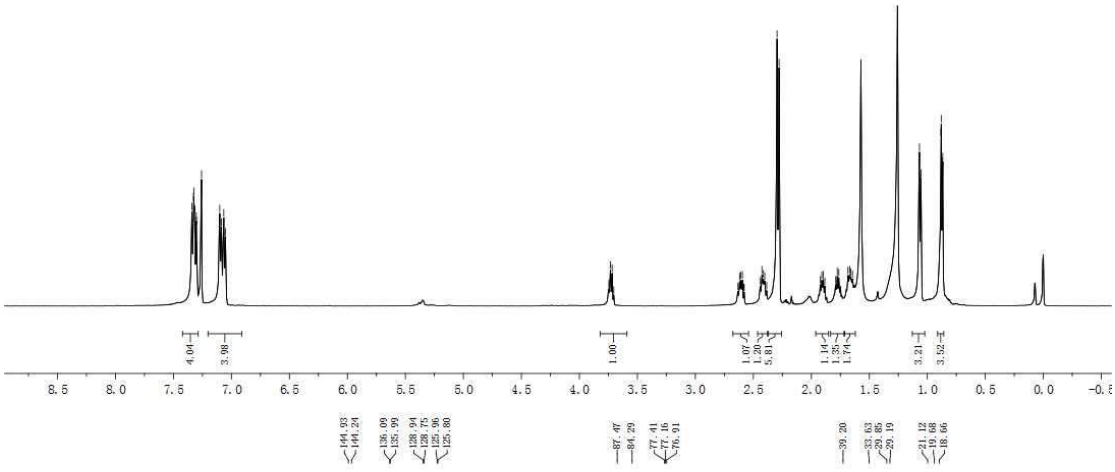

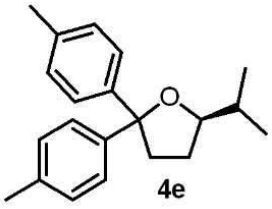
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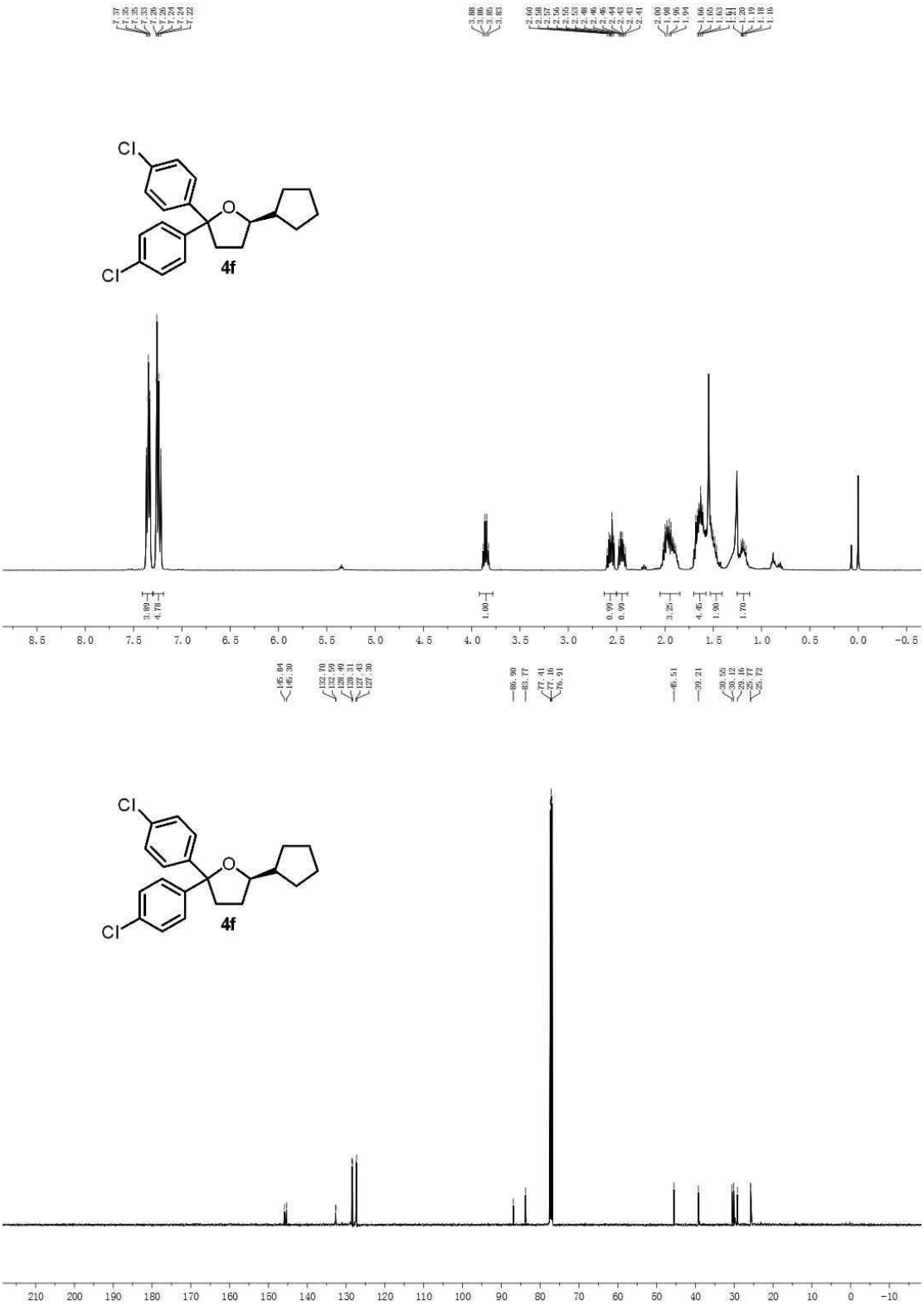
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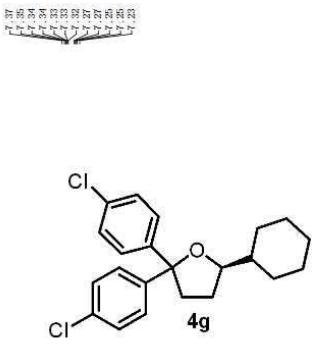
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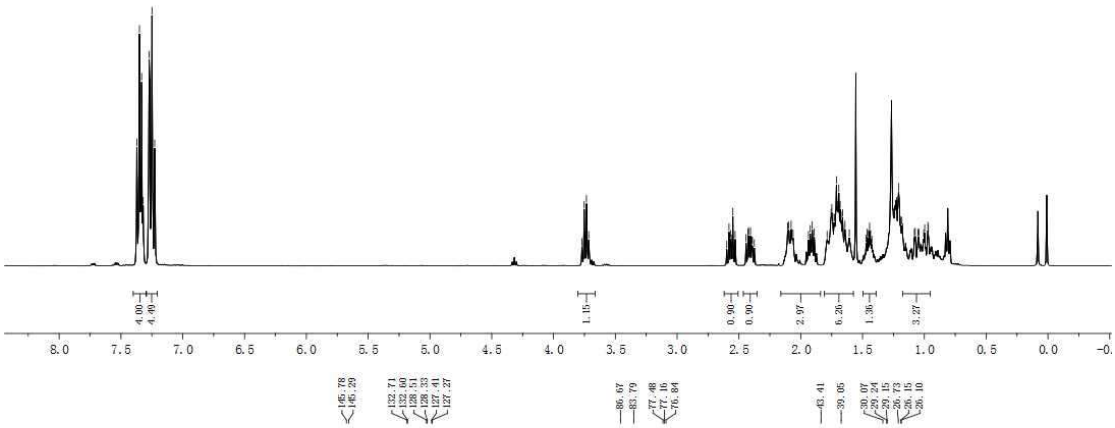

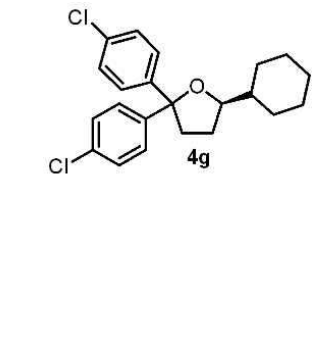
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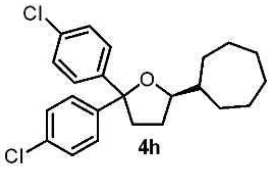
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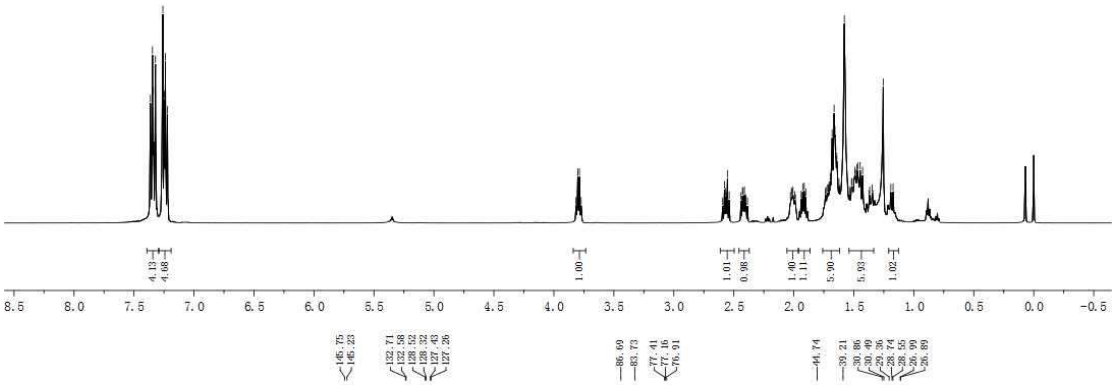
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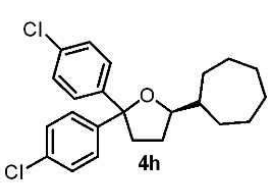
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4h

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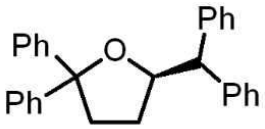

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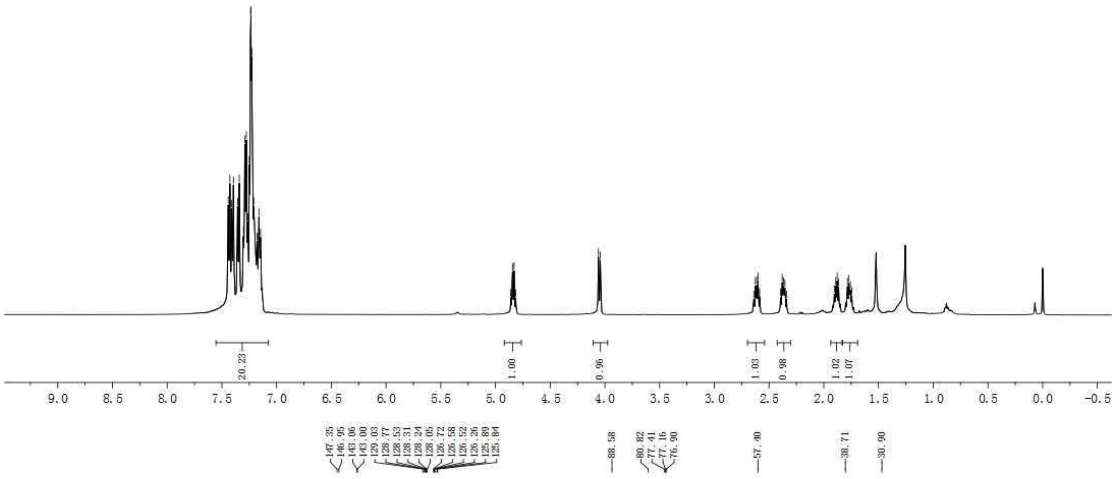

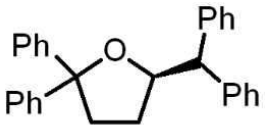

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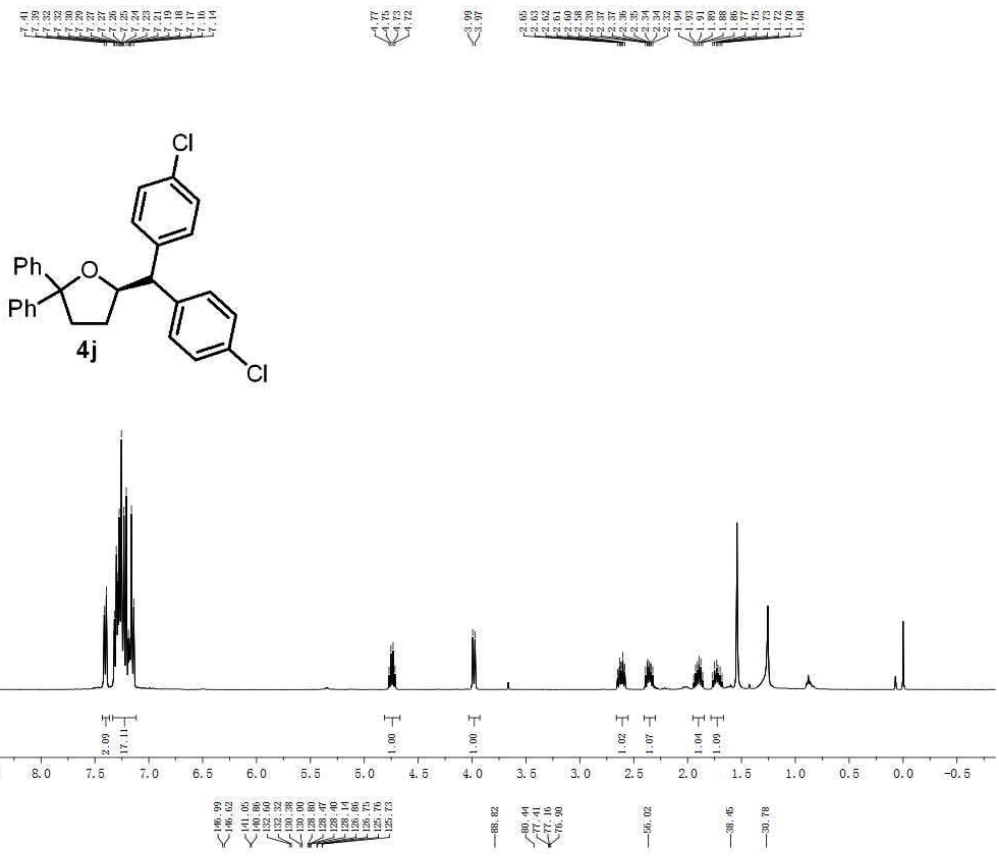
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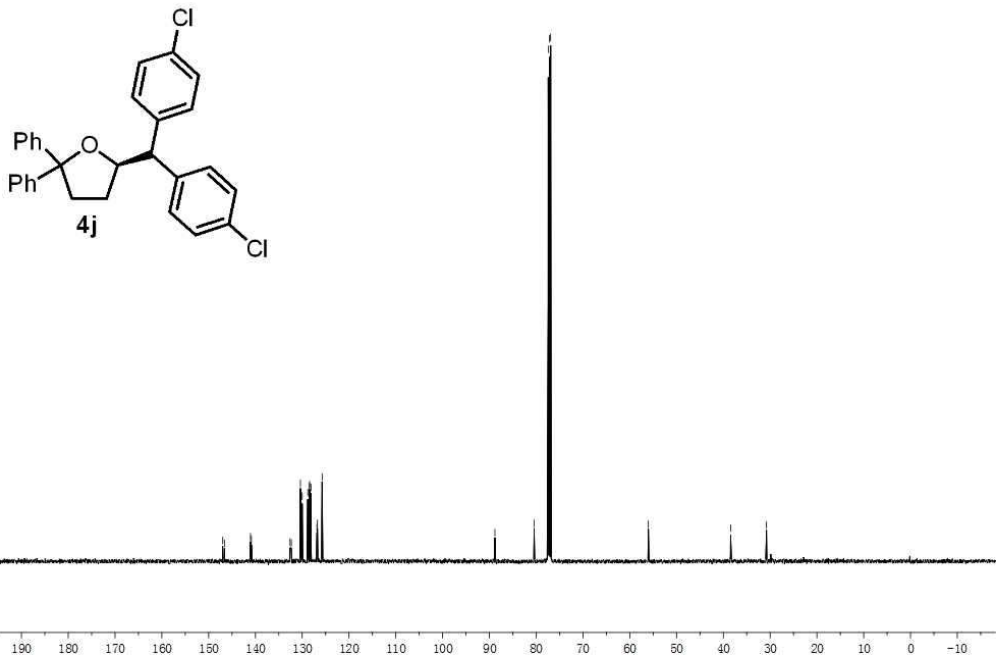
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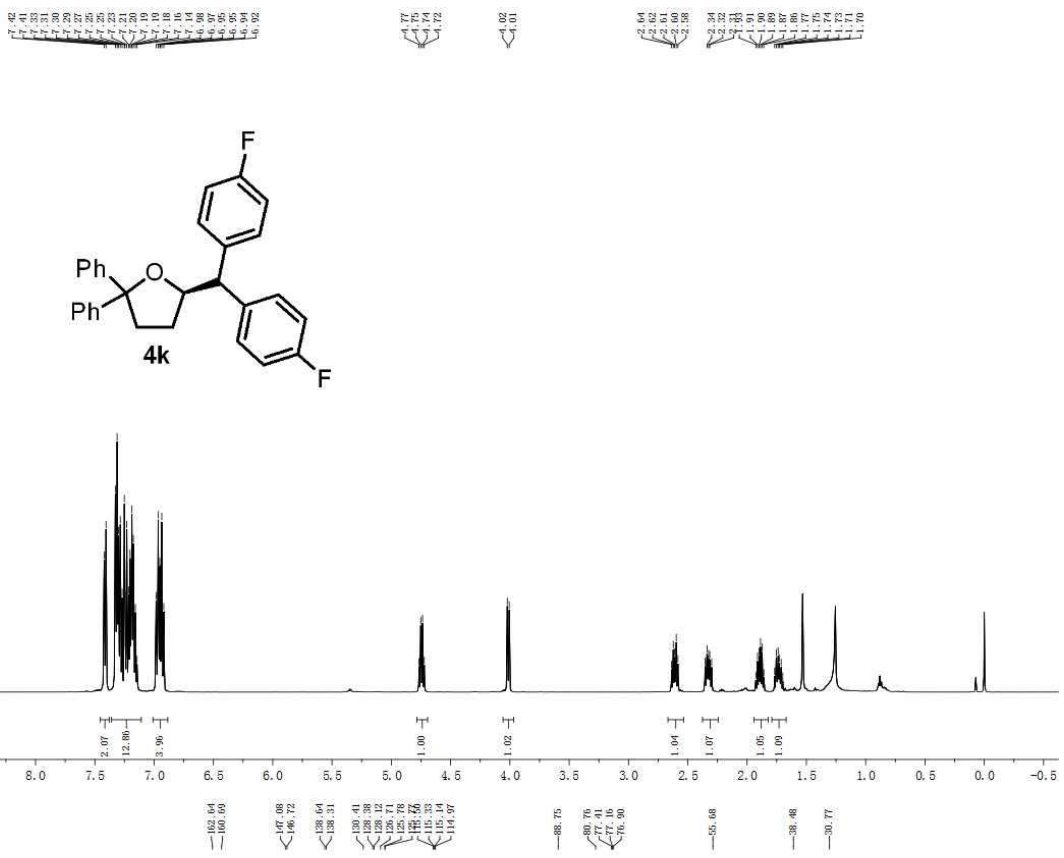
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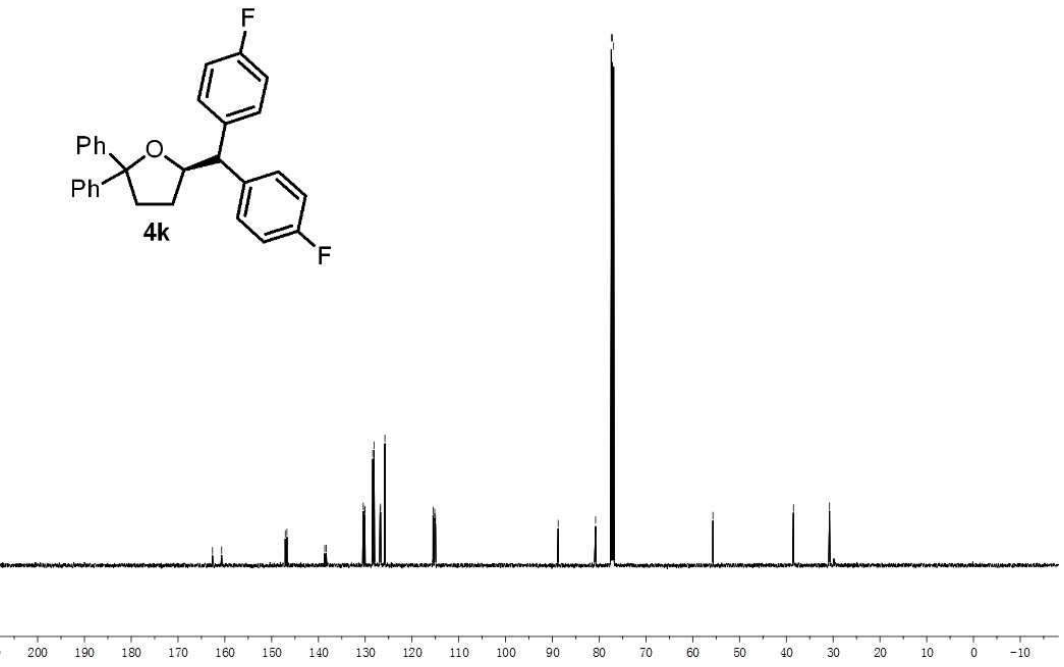
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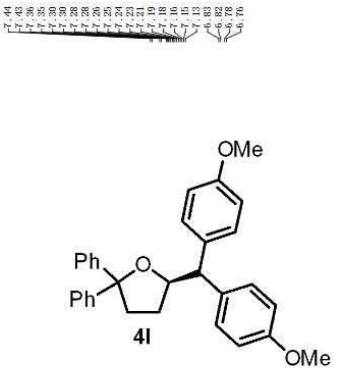
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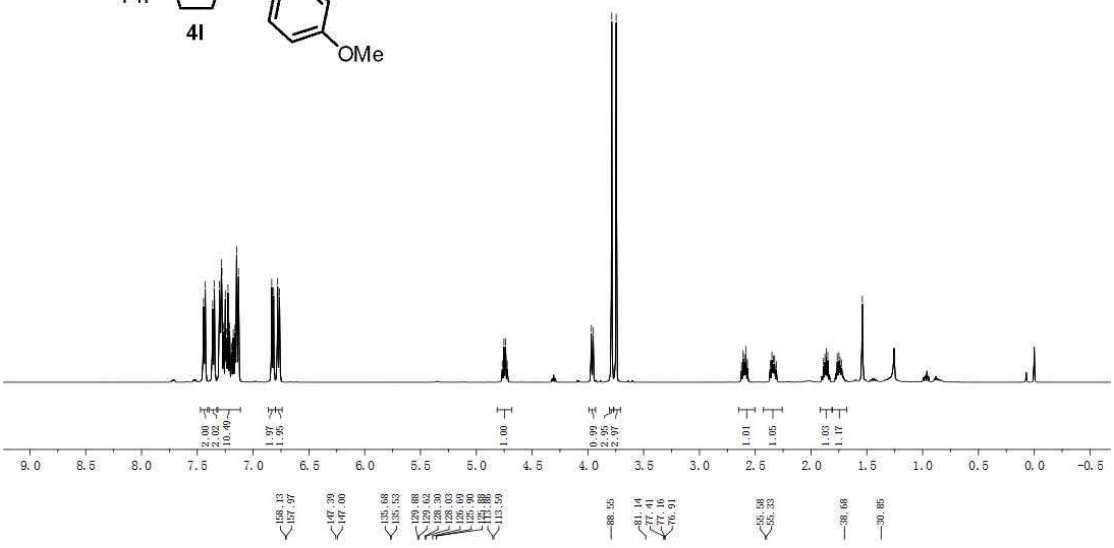

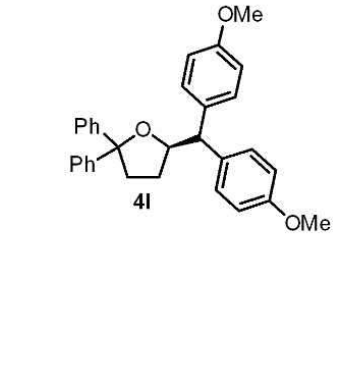
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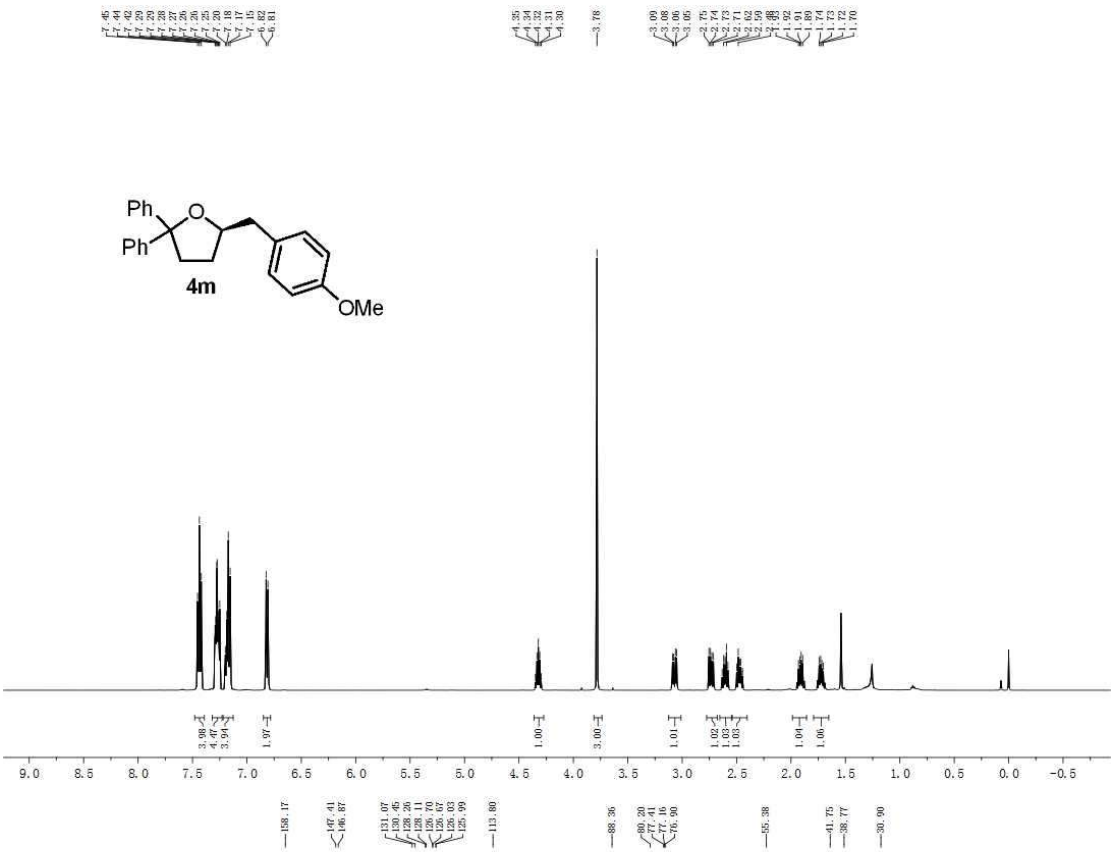
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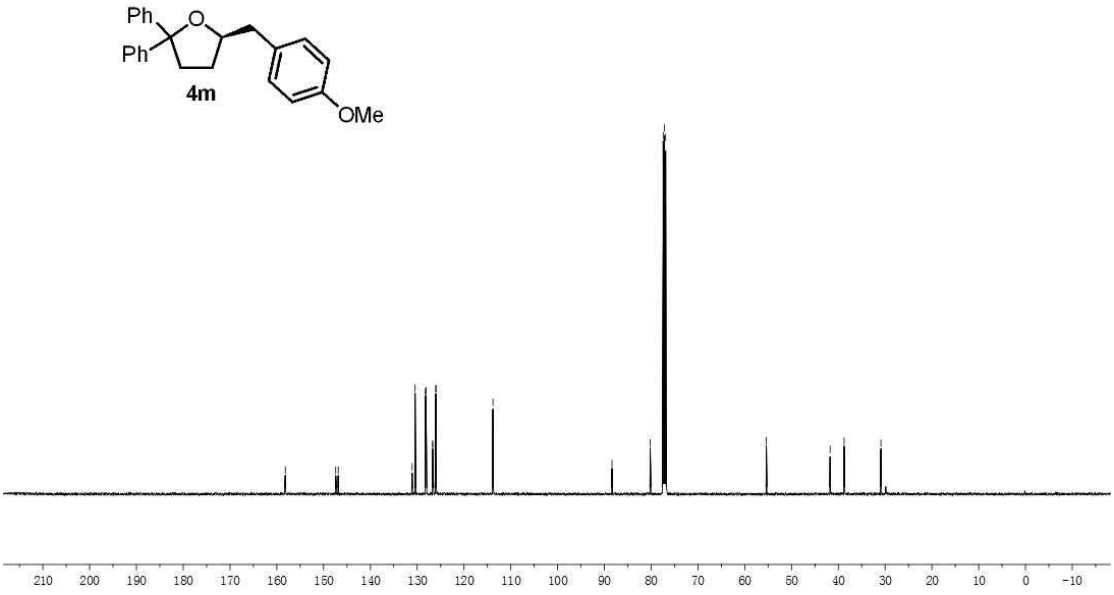
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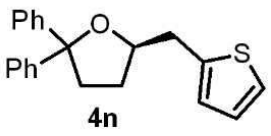

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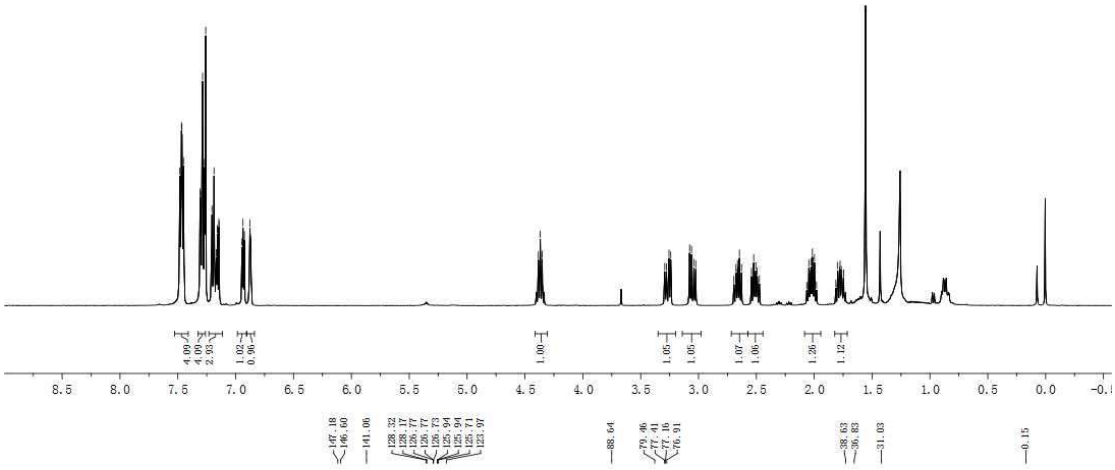

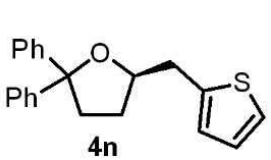

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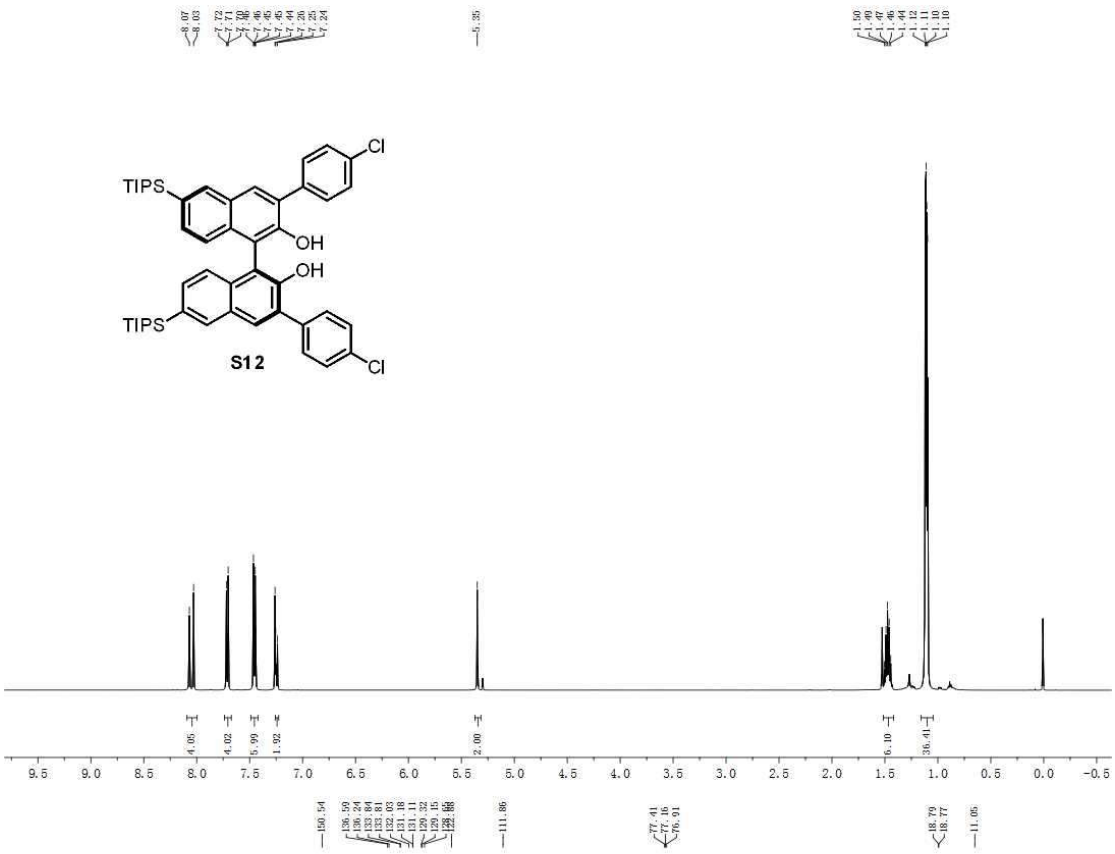
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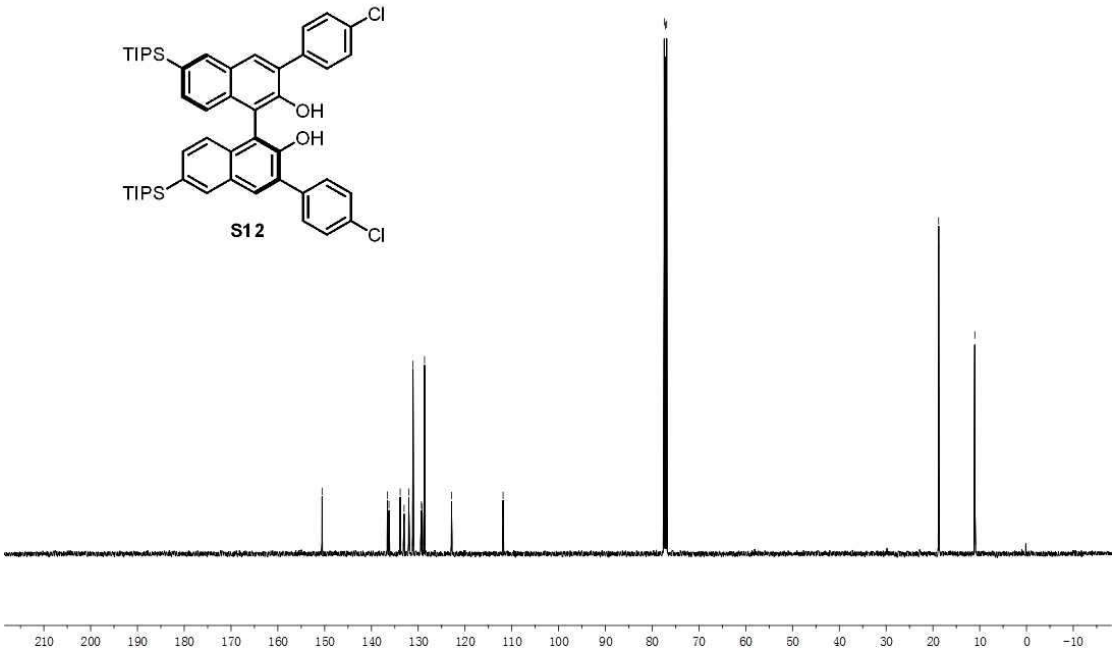
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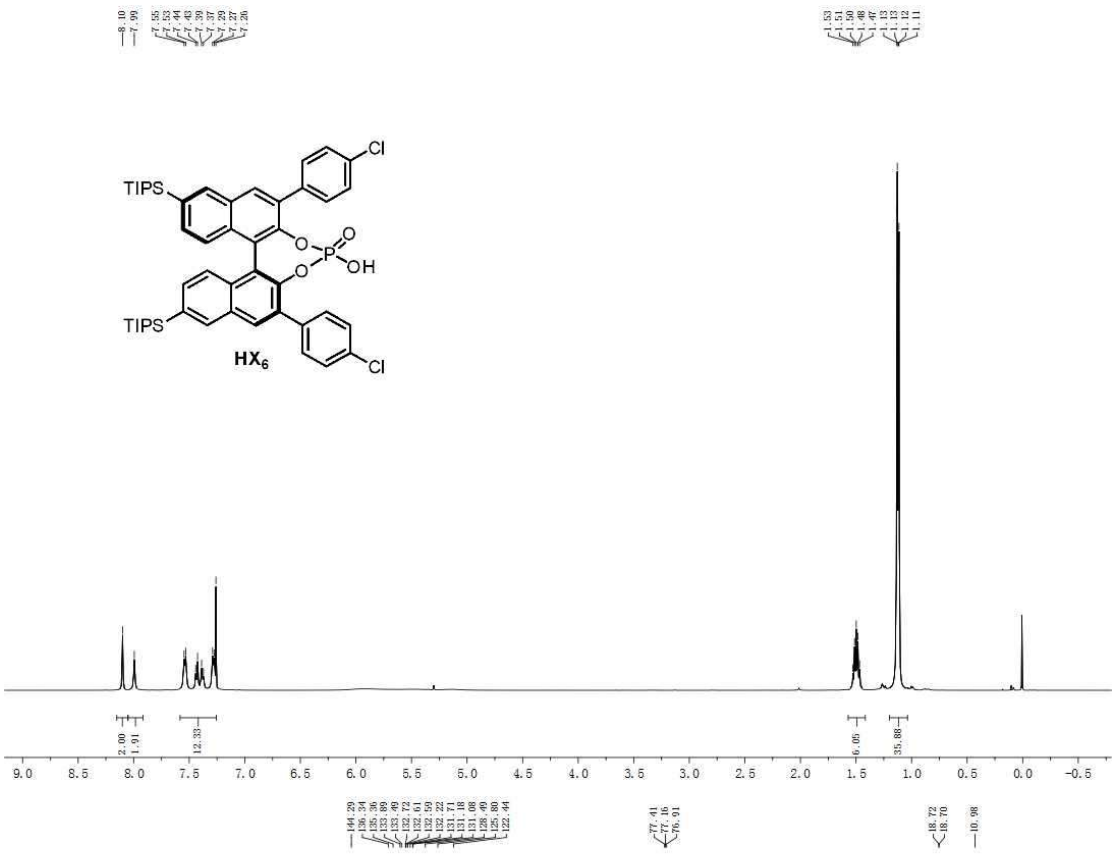
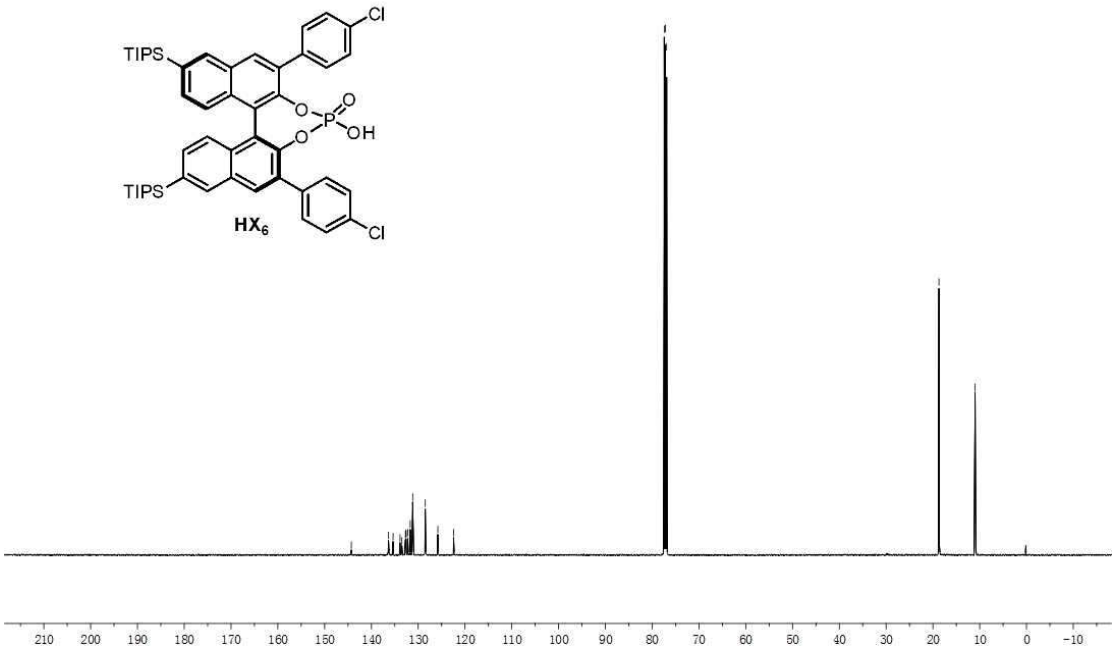
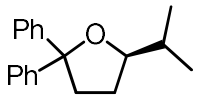
Cl
S12


TIPS
TIPS
Cl
Cl
O
P
OH
HX6


TIPS
TIPS
Cl
Cl
O
P
OH
HX6

HPLC Charts



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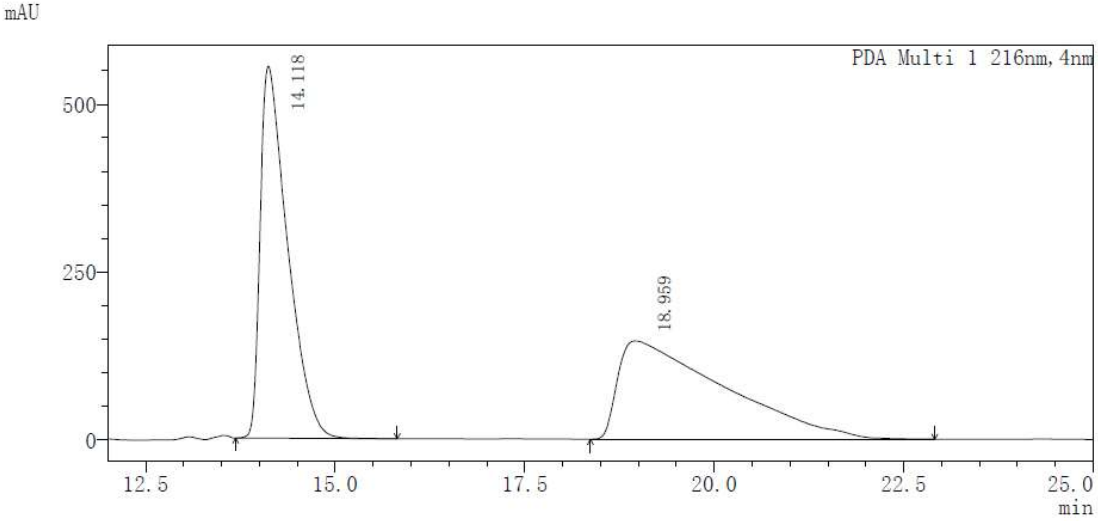
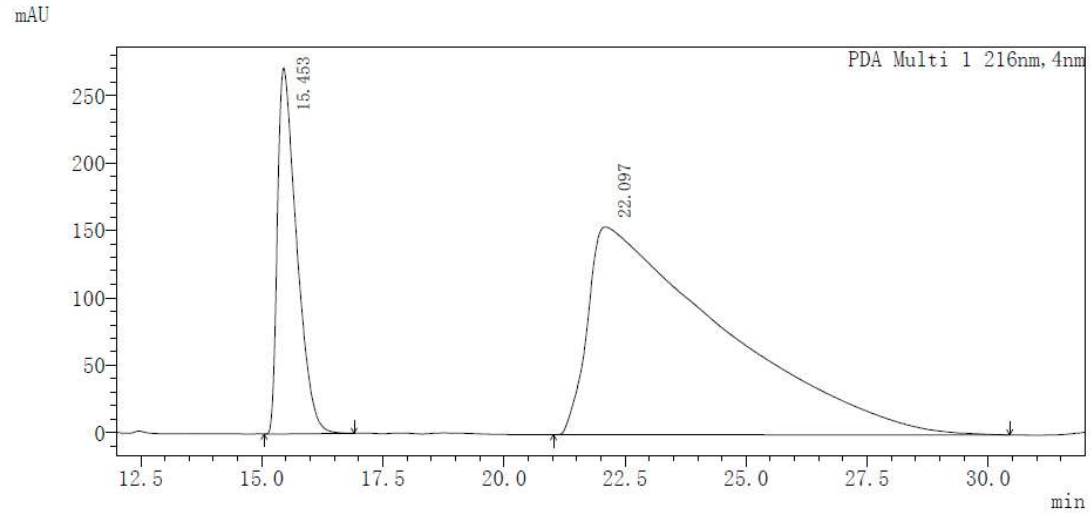


〈Peak Results〉

PDA Ch1 216nm

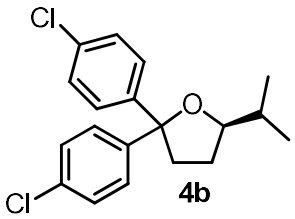
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	14.118	554136	13973099	49.522
2	18.959	146446	14243116	50.478



〈Peak Results〉

PDA Ch1 216nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	15.453	271368	7477985	20.051
2	22.097	153954	29816818	79.949



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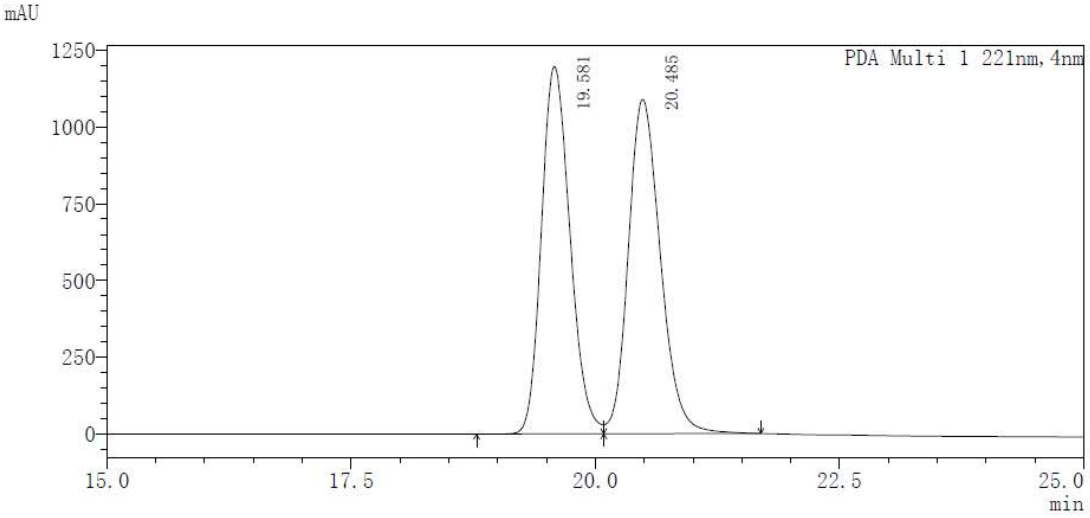
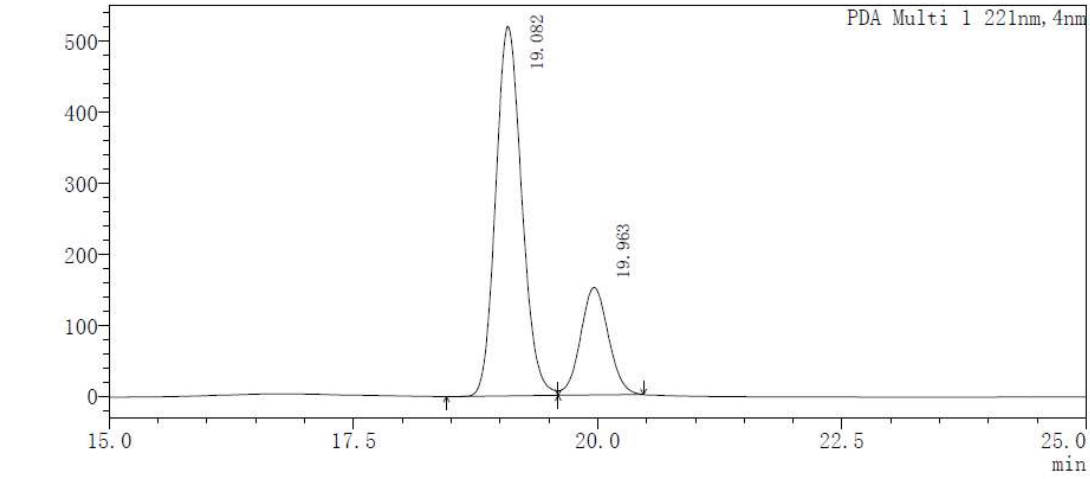


〈Peak Results〉

PDA Ch1 221nm

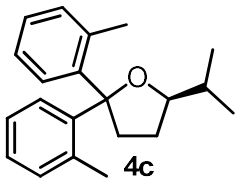
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	19.581	1196793	24361433	49.424
2	20.485	1089015	24929696	50.576



〈Peak Results〉

PDA Ch1 221nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	19.082	519821	9650532	76.231
2	19.963	151511	3008984	23.769



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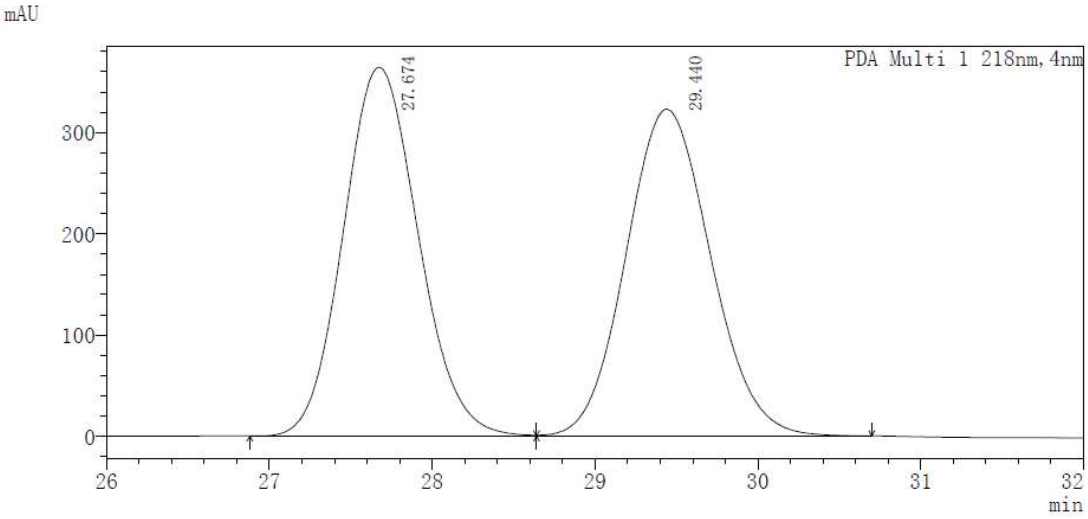
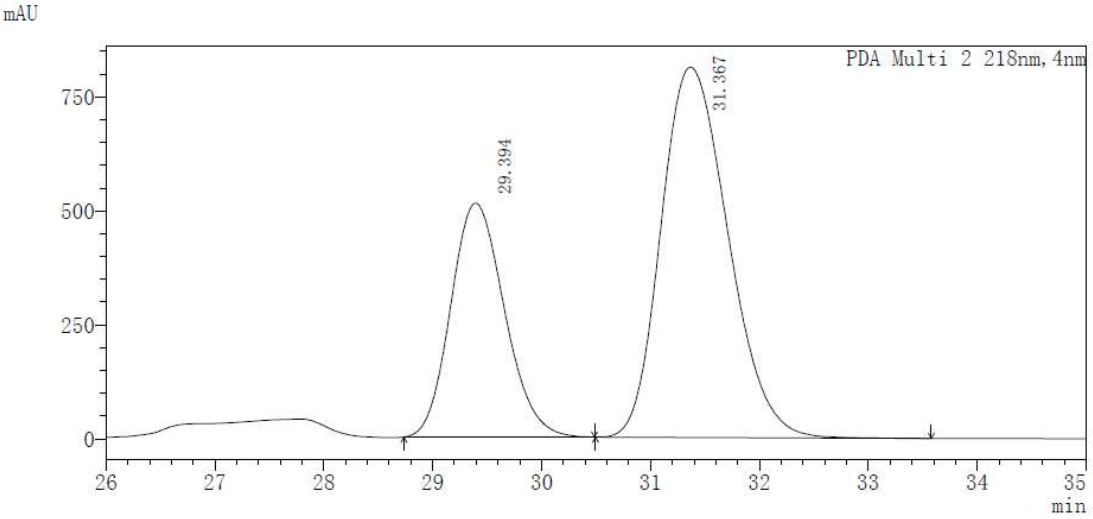


〈Peak Results〉

PDA Ch1 218nm

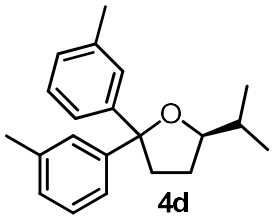
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	27.674	363887	11644395	49.935
2	29.440	322545	11674498	50.065



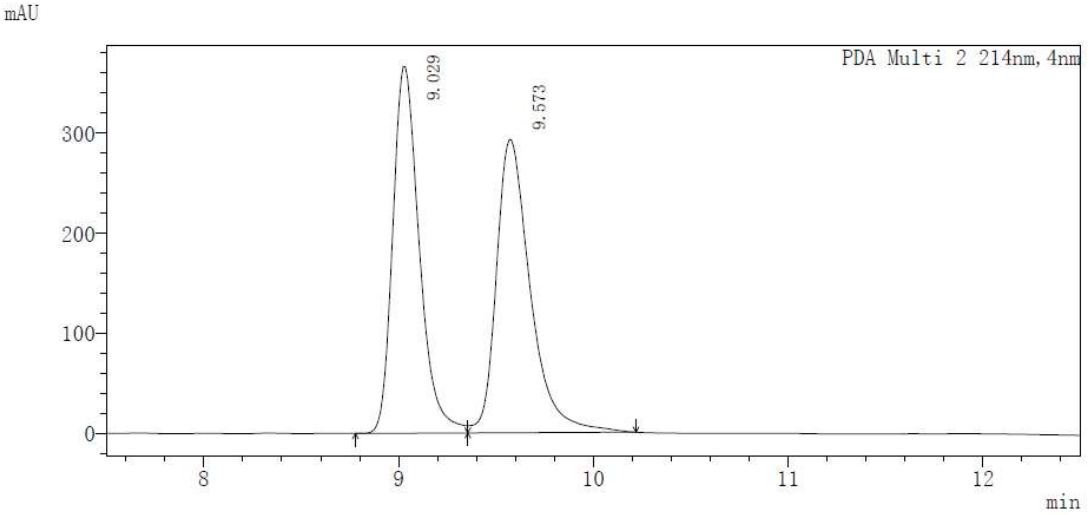
〈Peak Results〉

PDA Ch2 218nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	29.394	512944	17592214	33.605
2	31.367	812325	34757314	66.395



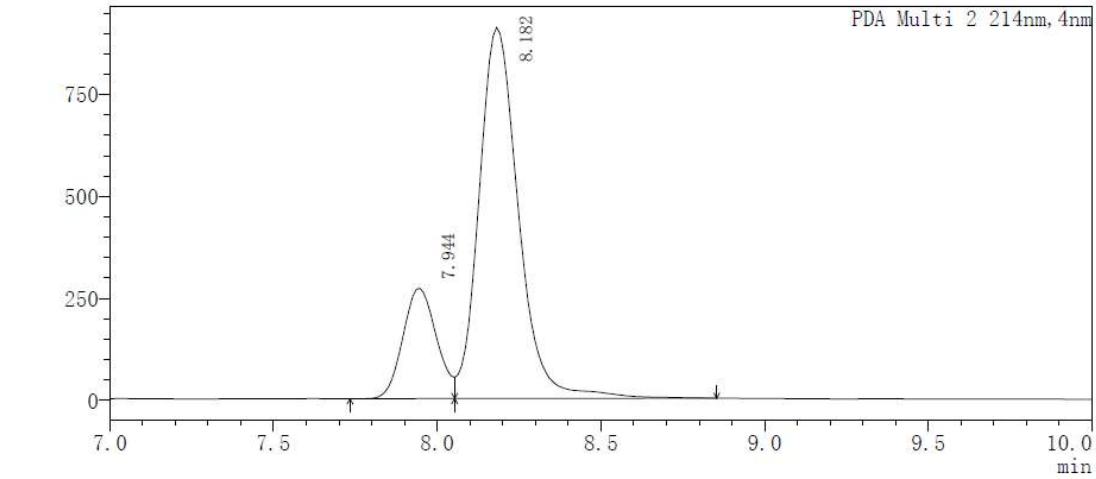
4d



〈Peak Results〉

PDA Ch2 214nm

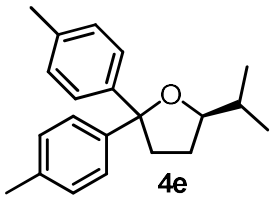
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	9.029	366243	3476329	49.463
2	9.573	292822	3551773	50.537



〈Peak Results〉

PDA Ch2 214nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	7.944	271139	1944982	20.382
2	8.182	909439	7597646	79.618



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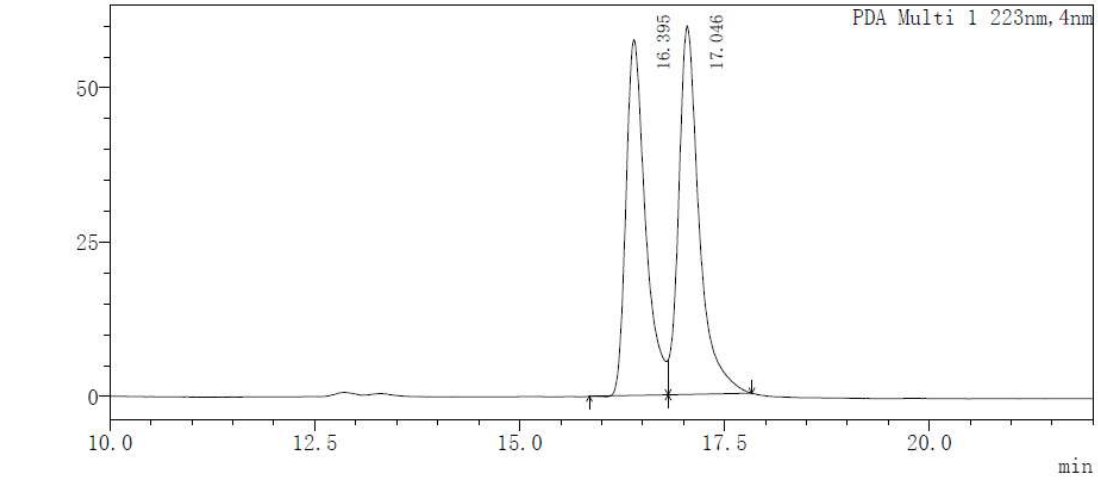
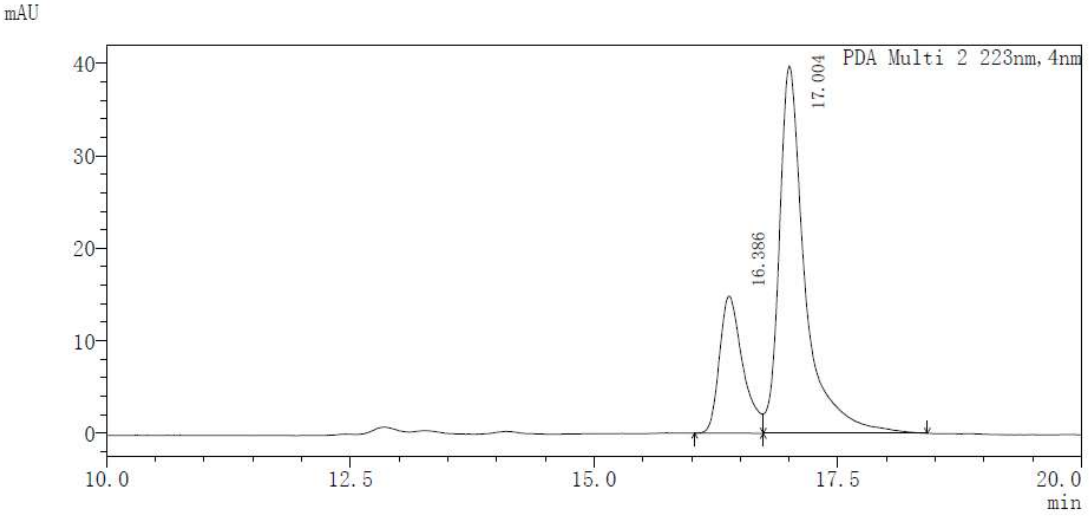


〈Peak Results〉

PDA Ch1 223nm

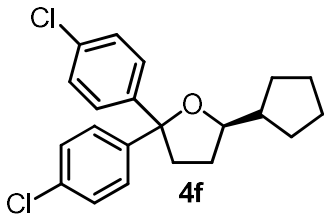
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	16.395	57607	957056	47.961
2	17.046	59666	1038435	52.039



〈Peak Results〉

PDA Ch2 223nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	16.386	14836	246173	25.223
2	17.004	39690	729796	74.777



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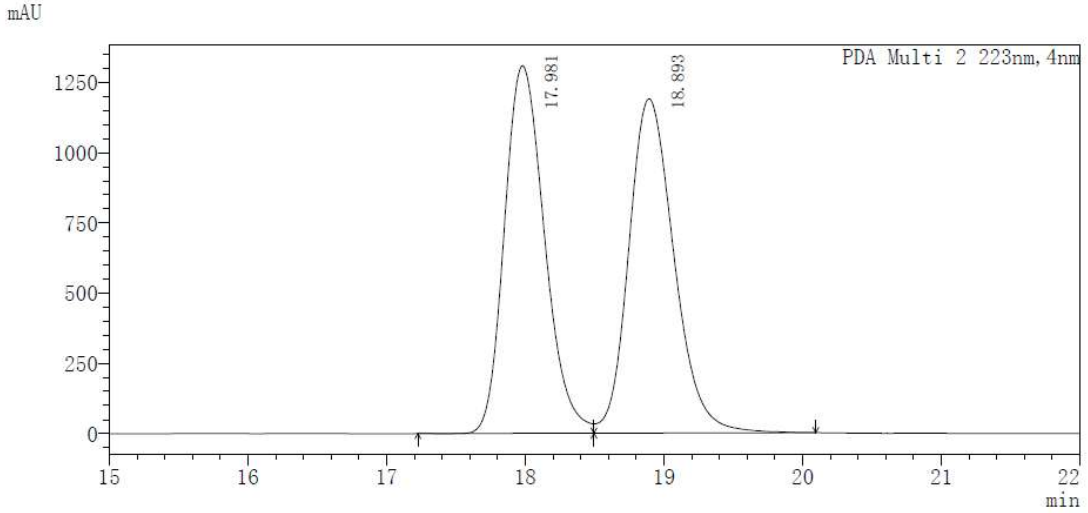
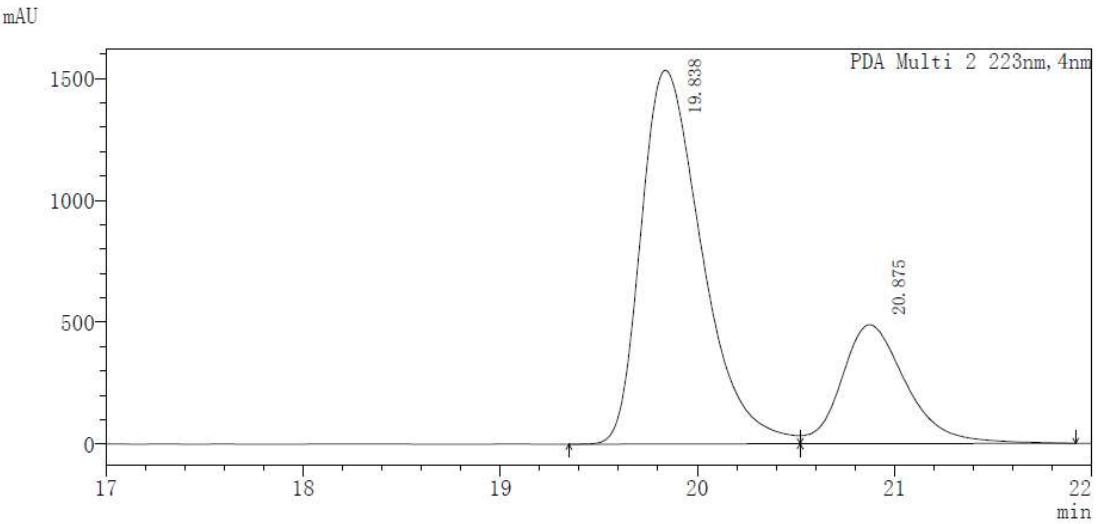


〈Peak Results〉

PDA Ch2 223nm

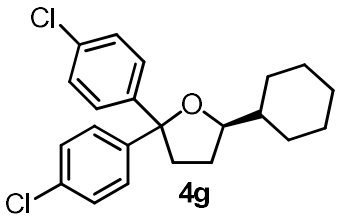
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	17.981	1309002	26280953	49.337
2	18.893	1190602	26986929	50.663



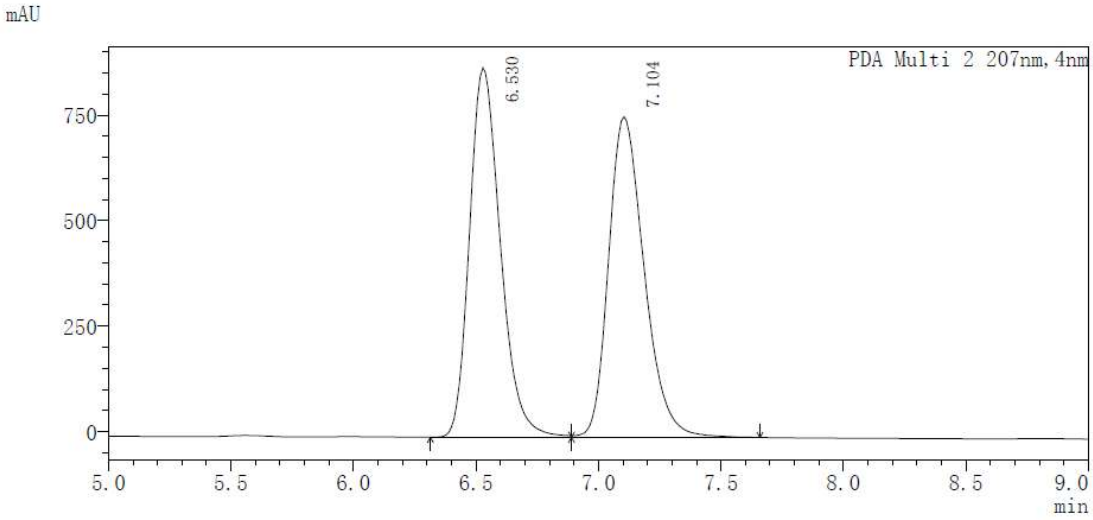
〈Peak Results〉

PDA Ch2 223nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	19.838	1532511	32923453	74.761
2	20.875	487556	11115091	25.239



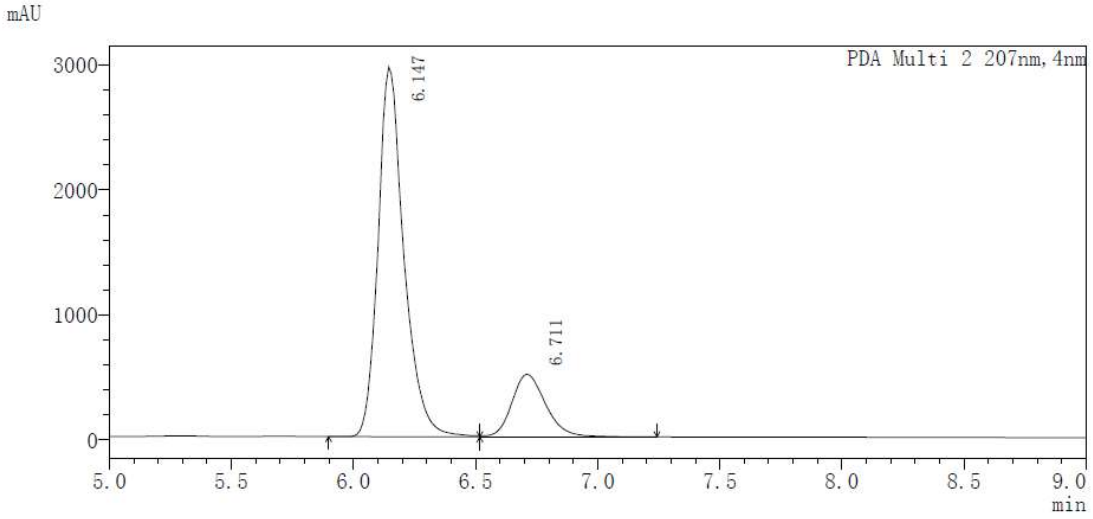
4g



〈Peak Results〉

PDA Ch2 207nm

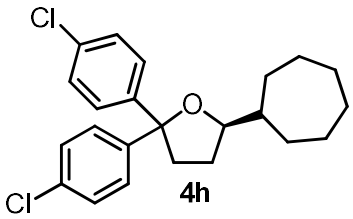
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	6.530	874914	7680842	49.994
2	7.104	759638	7682567	50.006



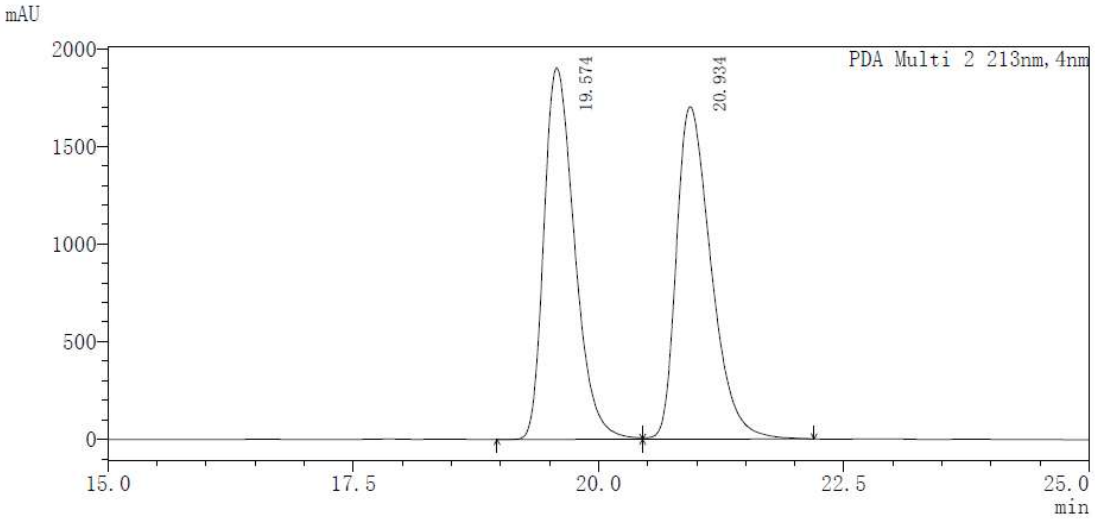
〈Peak Results〉

PDA Ch2 207nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	6.147	2960635	21863060	81.929
2	6.711	501686	4822224	18.071



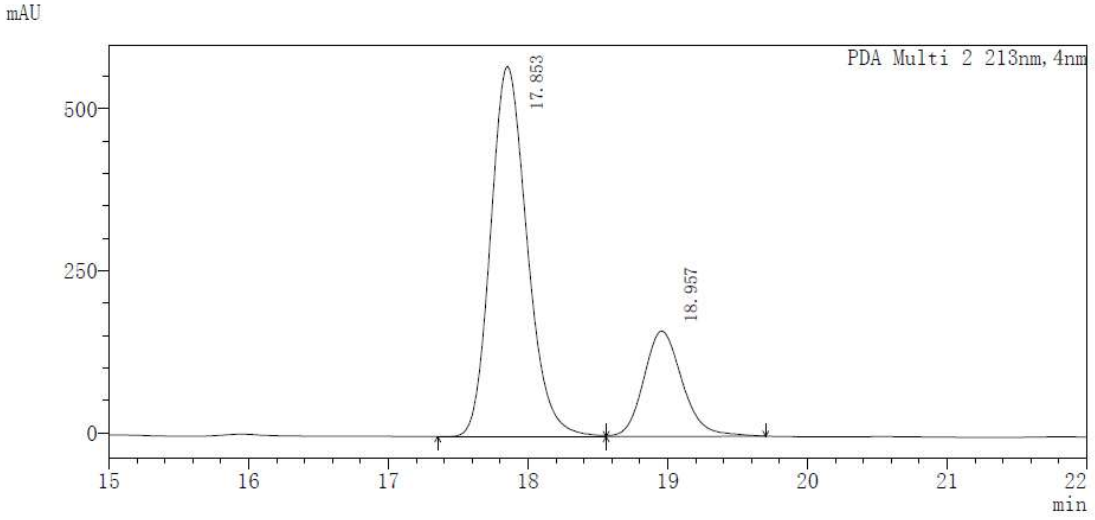
4h



〈Peak Results〉

PDA Ch2 213nm

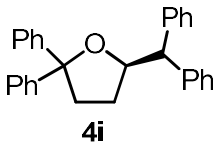
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	19.574	1902640	41360332	49.631
2	20.934	1702383	41975472	50.369



〈Peak Results〉

PDA Ch2 213nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	17.853	571290	10358754	76.891
2	18.957	162485	3113177	23.109



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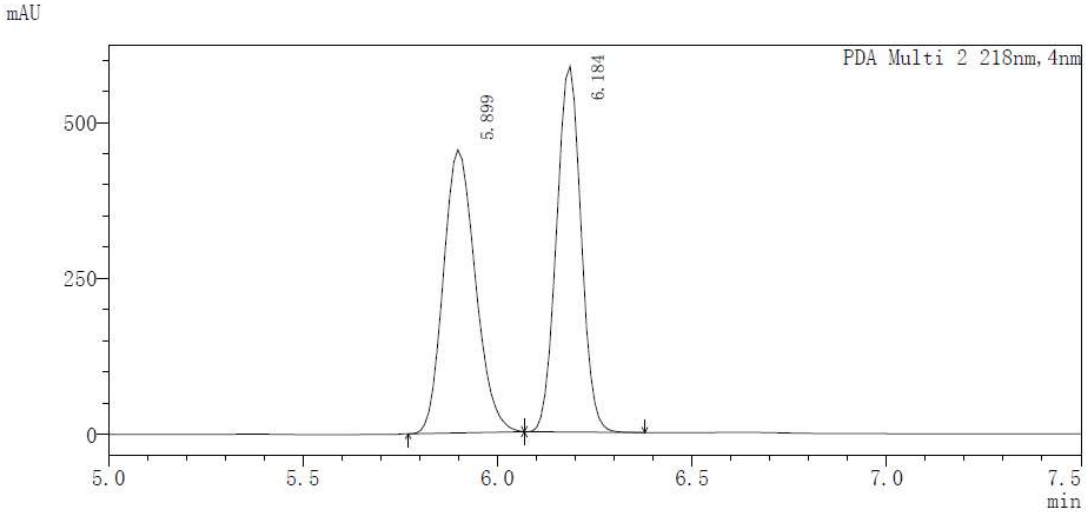
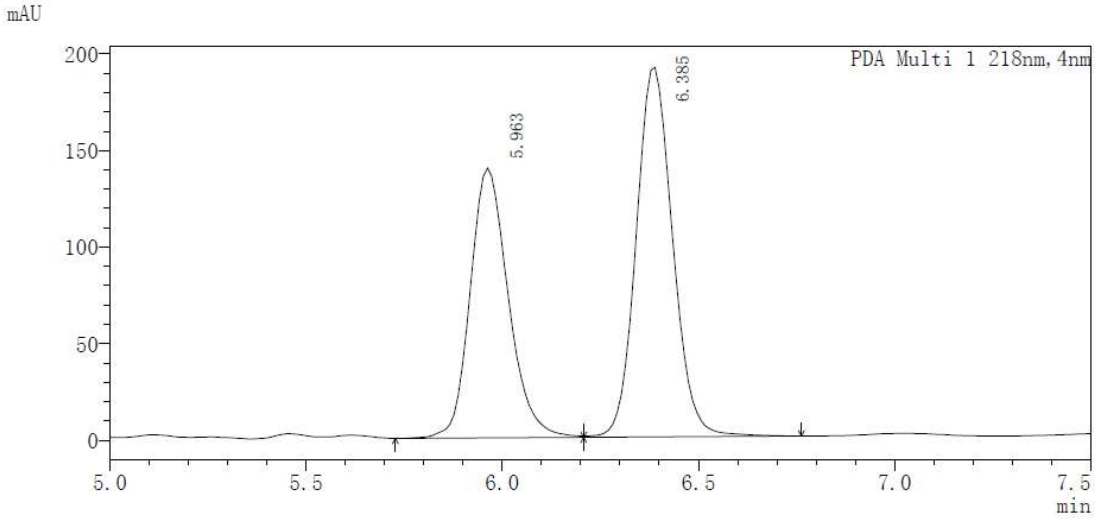


〈Peak Results〉

PDA Ch2 218nm

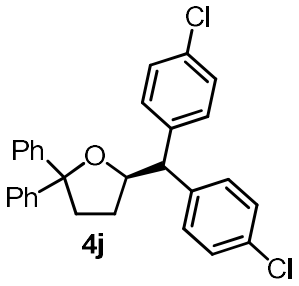
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	5.899	454043	2595308	50.162
2	6.184	586516	2578594	49.838



〈Peak Results〉

PDA Ch1 218nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	5.963	139622	945553	43.319
2	6.385	191274	1237218	56.681



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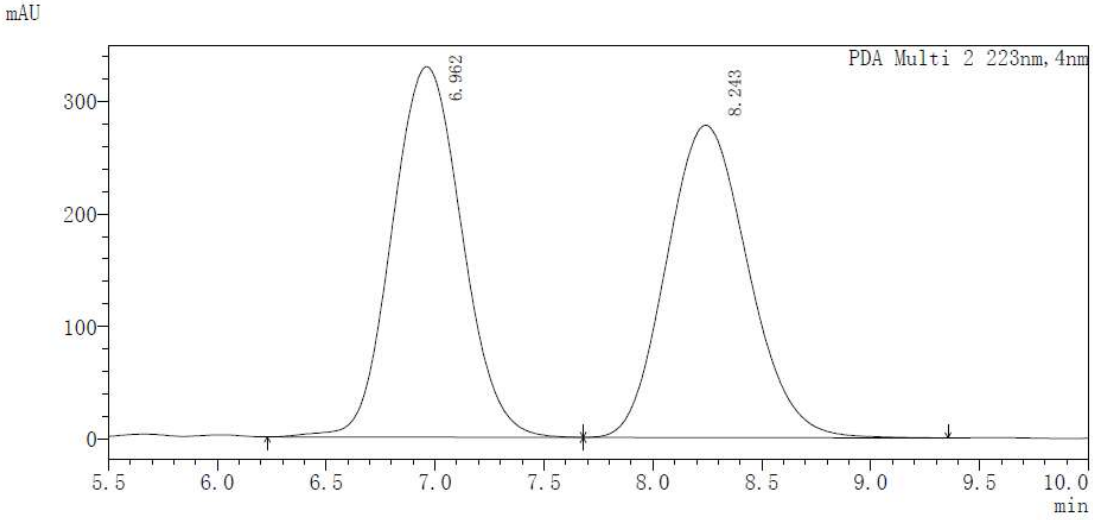
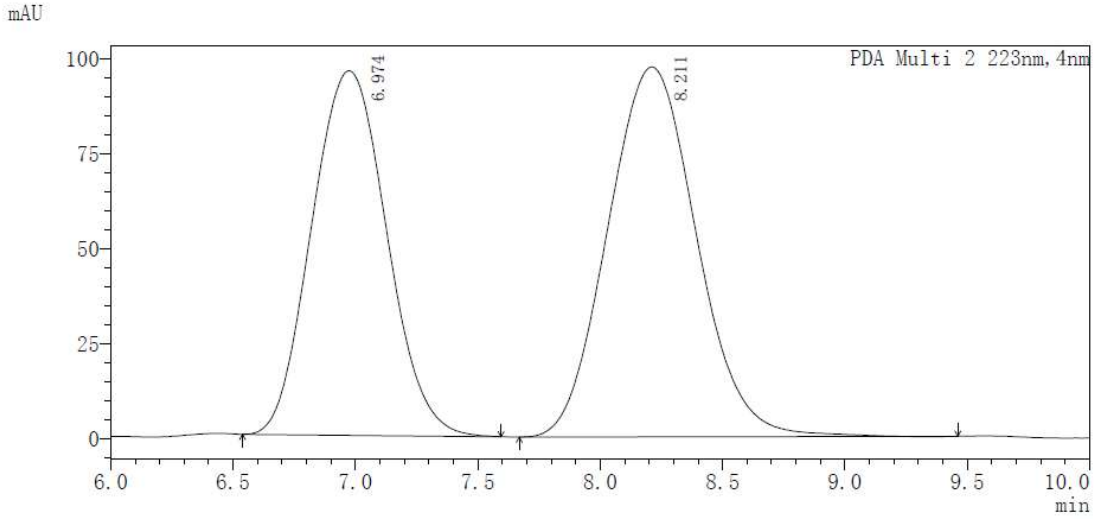


〈Peak Results〉

PDA Ch2 223nm

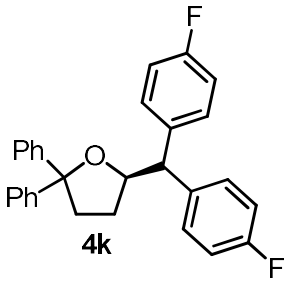
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	6.962	329616	7371687	50.447
2	8.243	277970	7240953	49.553



〈Peak Results〉

PDA Ch2 223nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	6.974	95959	2042472	45.429
2	8.211	97341	2453477	54.571



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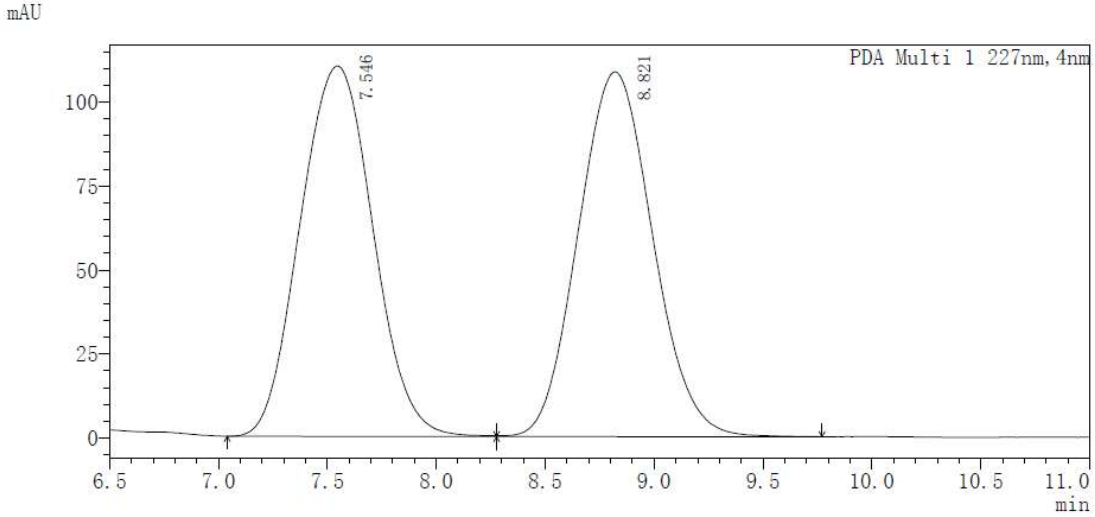
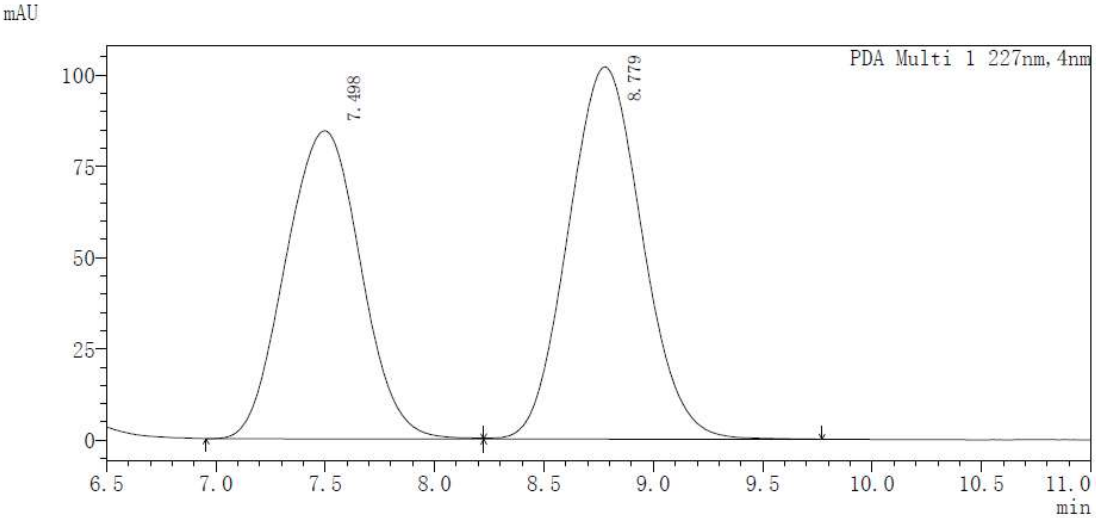


〈Peak Results〉

PDA Ch1 227nm

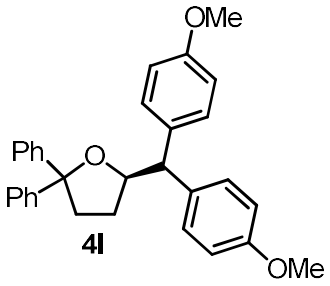
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	7.546	110212	2566586	49.889
2	8.821	108570	2577982	50.111



〈Peak Results〉

PDA Ch1 227nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	7.498	84434	2020158	45.714
2	8.779	101989	2398964	54.286



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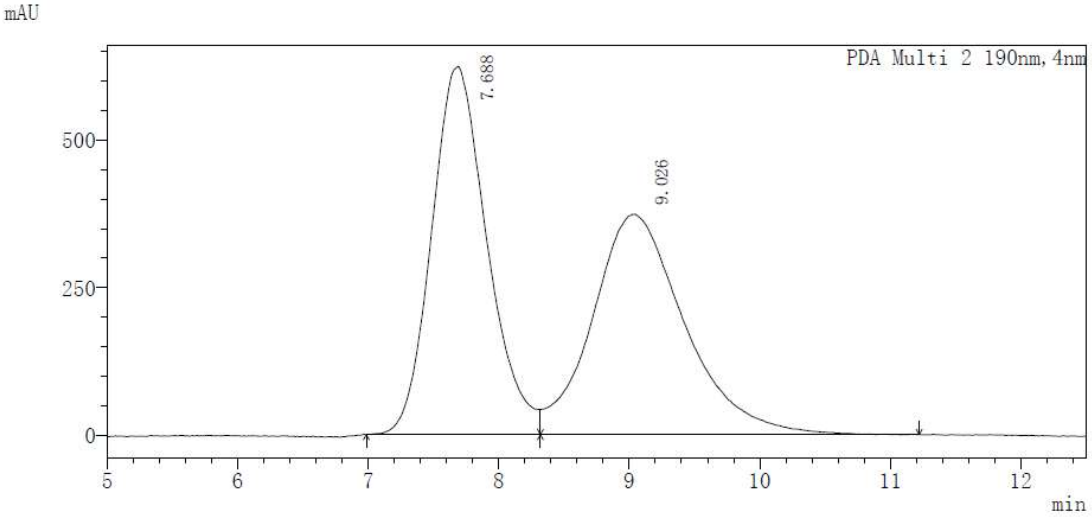
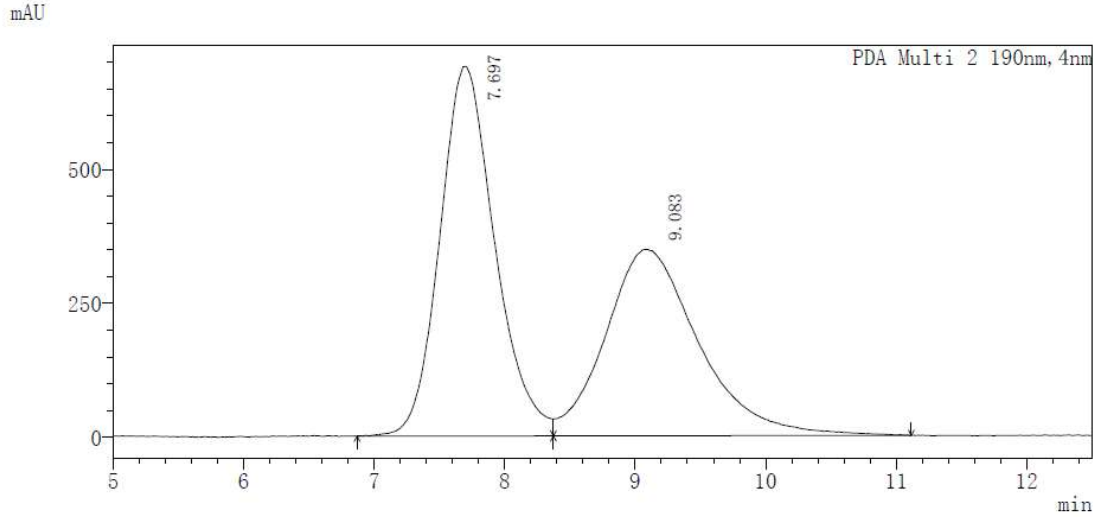


〈Peak Results〉

PDA Ch2 190nm

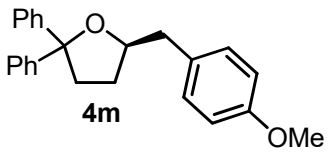
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	7.688	622840	18398018	50.195
2	9.026	372805	18254966	49.805



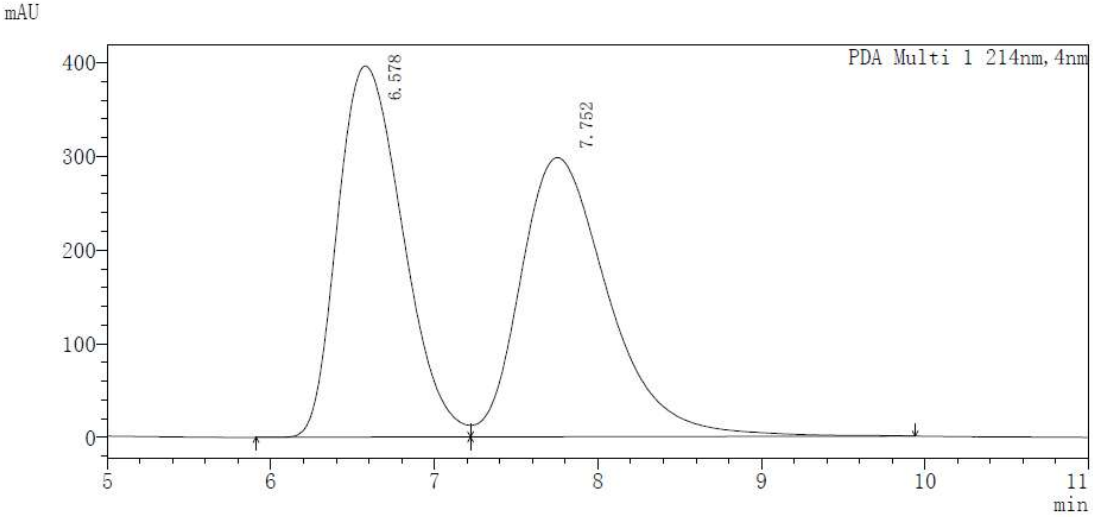
〈Peak Results〉

PDA Ch2 190nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	7.697	689380	20218739	53.948
2	9.083	347484	17259520	46.052



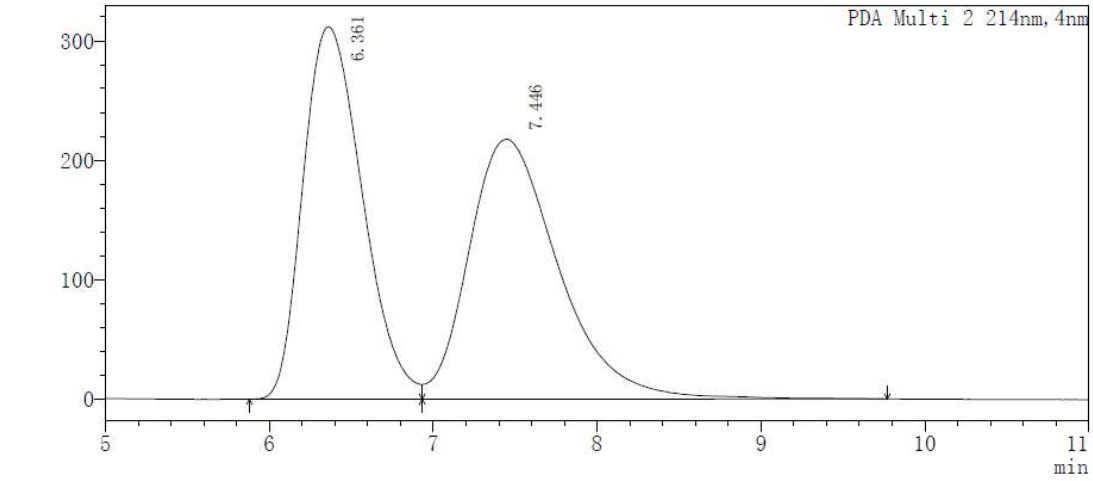
4m



〈Peak Results〉

PDA Ch1 214nm

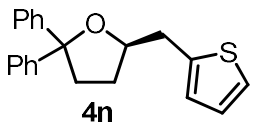
Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	6.578	396131	10963077	49.645
2	7.752	298017	11119955	50.355



〈Peak Results〉

PDA Ch2 214nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	6.361	311641	7854614	48.721
2	7.446	217515	8267050	51.279



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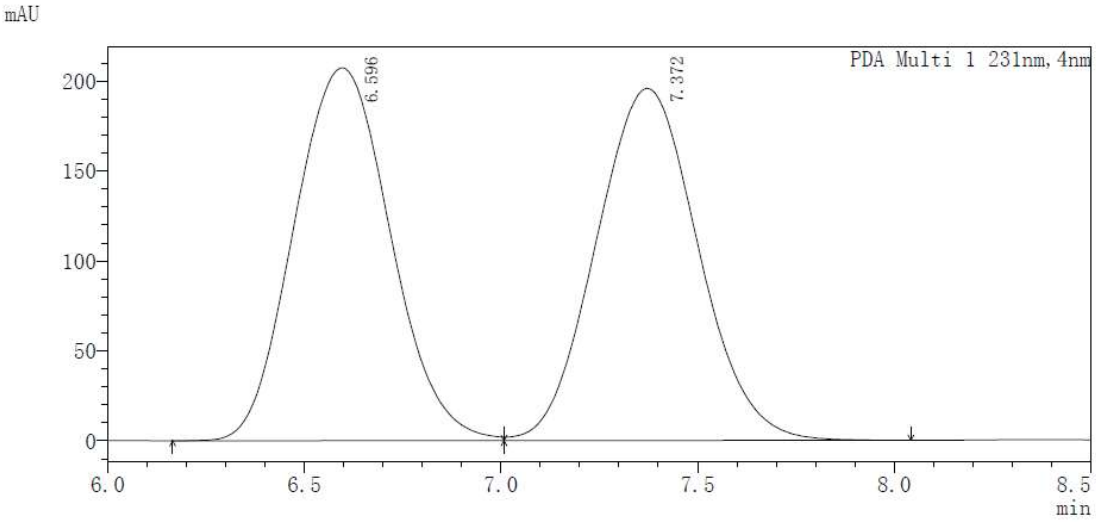
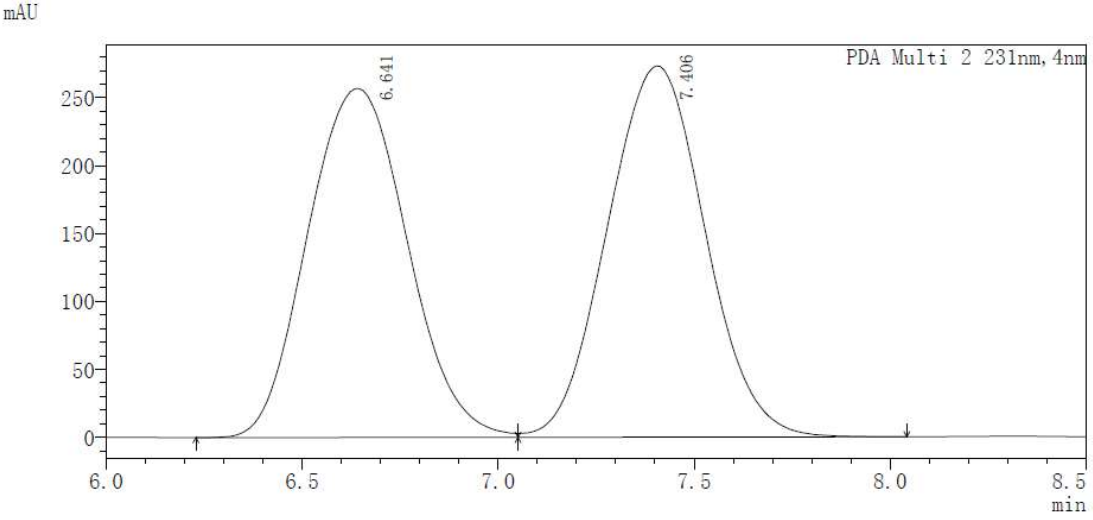


〈Peak Results〉

PDA Ch1 231nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	6.596	207107	3531754	50.015
2	7.372	195759	3529678	49.985



〈Peak Results〉

PDA Ch2 231nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	6.641	256789	4540435	48.918
2	7.406	273140	4741239	51.082