Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Enantioselective Indium(I)-catalyzed [4+2] Annulation of Alkoxyallenes and β,γ-Unsaturated α-Keto Esters

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Supporting Information

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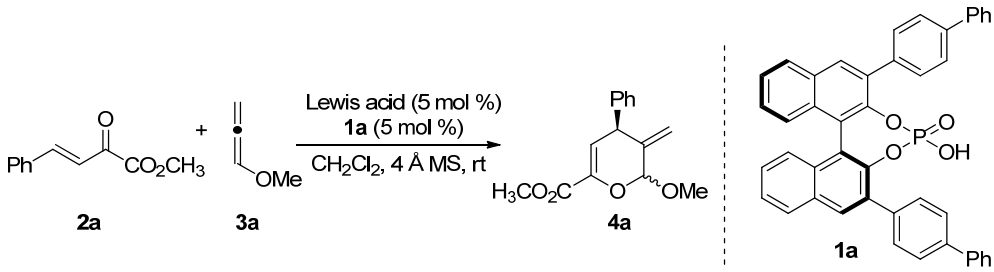
General Information: Commercial reagents were used as received, unless otherwise indicated. ^{1}H and ^{13}C NMR spectra were measured on a NMR instrument (400 and 500 MHz for ^{1}H NMR, 100 and 125 MHz for ^{13}C NMR). Tetramethylsilane (TMS) served as the internal standard for ^{1}H NMR, and $CDCl_3$ served as the internal standard for ^{13}C NMR. The following abbreviations were used to express the multiplicities: s = singlet; d= doublet; t = triplet; q = quartet; m = multiplet; br = broad. HPLC analysis was performed using Daicel Chiralpak columns. Optical rotations were measured using a 2 mL cell with a 1 dm path length on a Perkin-Elmer 341 digital polarimeter and reported as follows: $[\alpha]_D^{25}$ (c = g/100 mL, solvent). HRMS was recorded on a commercial apparatus (ESI Source or APCI Source).

Table S1. Different Lewis Acid in Asymmetric [4+2] Annulation of β,γ–Unsaturated α-Keto Ester 2a with Methoxyallene 3a.[a]

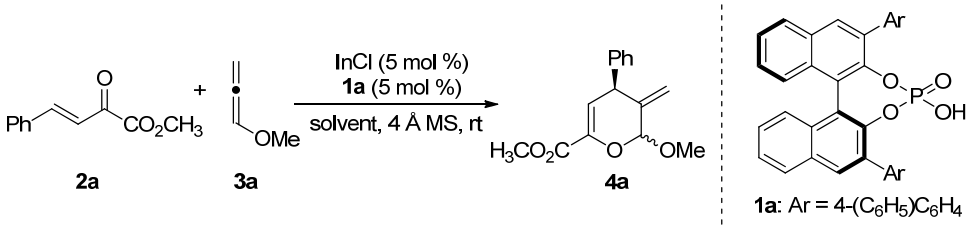


2a 3a 4a 1a

entry	LA	solvent	yield [b] (%)	ee [c] (%)
1	none	CH_2Cl_2	NR	–
2	$InBr_3$	CH_2Cl_2	29 (66:34)	80 (20)
3	$InCl_3$	CH_2Cl_2	30 (77:23)	94 (67)
4	InI_3	CH_2Cl_2	40 (50:50)	71 (23)
5	InF_3	CH_2Cl_2	NR	–
6	$In(OTf)_3$	CH_2Cl_2	NR	–
7	$Sc(OTf)_3$	CH_2Cl_2	NR	–
8	YCl_3	CH_2Cl_2	25 (56:44)	57 (10)
9	$FeCl_3$	CH_2Cl_2	NR	–
10	$MgCl_2$	CH_2Cl_2	14 (>95:5)	45
11	$Mg(OTf)_2$	CH_2Cl_2	NR	–
12	$Hf(OTf)_4$	CH_2Cl_2	NR	–
13	$HfCl_4$	CH_2Cl_2	38 (58:42)	47 (36)
14	InCl	CH_2Cl_2	64 (72:28)	95 (67)
15	InI	CH_2Cl_2	NR	–
16	InBArF	CH_2Cl_2	30 (50:50)	50 (11)

[a] General conditions: **2a** (0.10 mmol), **3a** (0.40 mmol), **1a** (5 mol %), Lewis acid (5 mol %), and 4 Å MS (20 mg), at room temperature in CH_2Cl_2 (0.2 mL) for 6 h. [b] Determined by ^1H NMR analysis with an internal standard, 1,3,5-trimethyloxyl benzene, diastereoselectivies (dr = exo/endo) are shown in parentheses. [c] Determined by chiral HPLC, enantioselectivity of endo-product is shown in parentheses. MS = molecular sieve, rt = room temperature, NR = no reaction.

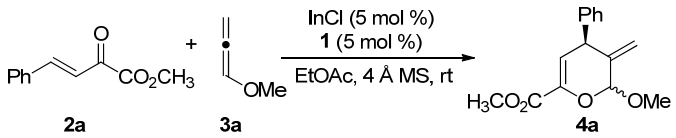
Table S2. Different Solvents in Asymmetric [4+2] Annulation of β,γ–Unsaturated α-Keto Ester 2a with Methoxyallene 3a. [a]



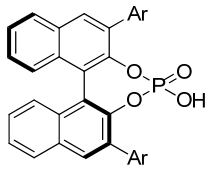
entry	solvent	yield [b] (%, dr)	ee [c] (%)
1	$CHCl_3$	73 (77:23)	94 (57)
2	Toluene	71 (76:24)	92 (83)
3	Et_2O	60 (74:26)	98 (95)
4	Acetone	72 (82:18)	97 (78)
5	CH_3CN	64 (78:22)	93 (53)
6	EtOAc	94 (82:18)	98 (90)
7	THF	NR	–
8	1,4-Dioxane	NR	–
9	DMF	NR	–
10	Cyclohexane	NR	–

[a] General conditions: **2a** (0.10 mmol), **3a** (0.40 mmol), **1a** (5 mol %), InCl (5 mol %), and 4 Å MS (20 mg), at room temperature in solvent (0.2 mL) for 6 h. [b] Determined by ^{1}H NMR analysis with an internal standard, 1,3,5-trimethyloxylbenzene, diastereoselectivities (dr = exo/endo) are shown in parentheses. [c] Determined by chiral HPLC, enantioselectivity of endo-product is shown in parentheses. MS = molecular sieve, rt = room temperature, NR = no reaction, EtOAc = ethyl acetate, THF = tetrahydrofuran, DMF = N,N-dimethylformamide.

Table S3. Different Chiral Ligands in Asymmetric [4+2] Annulation of β,γ–Unsaturated α-Keto Ester 2a with Methoxyallene 3a. [a]



2a **3a** **4a**



1a: Ar = 4-$(C_6H_5)C_6H_4$
1b: Ar = 4-$(C_6F_5)C_6H_4$
1c: Ar = 4-BrC_6H_4
1d: Ar = 4-$MeOC_6H_4$
1e: Ar = 2,4,6-$(CH_3)_3C_6H_2$
1f: Ar = C_6H_4
1g: Ar = 4-(2,4,6-$(CH_3)_3C_6H_2)C_6H_4$
1h: Ar = $Si(C_6H_5)_3$
1i: Ar = $CH(C_6H_5)_2$
1j: Ar = C_6F_5

entry	ligand	yield [b] (%, dr)	ee [c] (%)
1	**1a**	94 (82:18)	98 (90)
2	**1b**	76 (86:14)	96 (88)
3	**1c**	88 (58:42)	97 (91)
4	**1d**	92 (79:21)	98 (95)
5	**1e**	trace	–
6	**1f**	trace	–
7	**1g**	56 (86:14)	84 (54)
8	**1h**	trace	–
9	**1i**	trace	–
10	**1j**	trace	–
11	Ag[**1a**]	35 (60:40)	89 (47)
12	Li[**1a**]	27 (59:41)	83 (20)
13	none	NR	–
14 [d]	**1a**	23 (74:26)	93 (80)
15 [e]	**1a**	85 (80:20)	97 (88)

[a] General conditions: **2a** (0.10 mmol), **3a** (0.40 mmol), **1** (5 mol %), InCl (5 mol %), and 4 Å MS (20 mg), at room temperature in EtOAc (0.2 mL) for 6 h. [b] Determined by ^{1}H NMR analysis with an internal standard, 1,3,5-trimethyloxylbenzene, diastereoselectivities (dr = exo/endo) are shown in parentheses. [c] Determined by chiral HPLC, enantioselectivity of endo-product is shown in parentheses. [d] **1a** (2.5 mol%), [e] **1a** (10 mol%). MS = molecular sieve, rt = room temperature, NR = no reaction, EtOAc = ethyl acetate.

Experimental Section

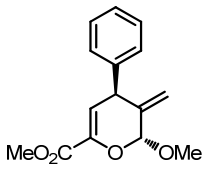
General Procedure I: Enantioselective [4+2] cycloaddition of β,γ-unsaturated α-keto esters 2 with alkoxyallenes 3:

To a dry reaction tube was added chiral phosphoric acid (0.005 mmol, 5 mol%), InCl (0.005 mmol, 5 mol%), 4Å M.S. (20 mg) and **2** (0.1 mmol), the mixture was stirred for 0.5 h at ambient tempature, then EtOAc (0.2 mL) and **3** (0.4 mmol) was added to the mixture. The mixture was stirred for 6 h at room temperature. The mixture was purified by column chromatography on silica gel with petroleum-ethyl acetate (20:1 to 4:1) to give the desired cycloaddition product **4**. Product **4a** is a known compound.[1]

Procedure for a large scale:

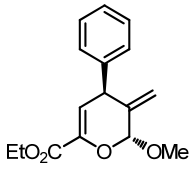
To a dry reaction tube was added chiral phosphoric acid (0.05 mmol, 5 mol%), InCl (0.05 mmol, 5 mol%), 4Å M.S. (200 mg) and **2g** (1 mmol), the mixture was stirred for 0.5 h at ambient temperature, then EtOAc (2 mL) and **3b** (4 mmol) was added to the mixture. The mixture was stirred for 6 h at room temperature. The reaction solution was concentrated and the residure was purified by column chromatography on silica gel with petroleum-ethyl acetate (10:1 to 4:1) to give the desired cycloaddition product **4p** in 71% yield and with >95:5 dr and 98% ee.

Characterization:



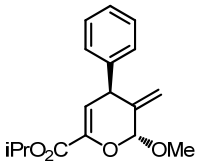
4a

4a: Pale yellow oil as an inseparable diastereoisomeric mixture, 96% yield, 25.2 mg, 82:18 *dr*, 98% ee for exo-**4a**. $[\alpha]_D^{25}$ = -203.44 (*c* 0.66, $CHCl_3$). HPLC analysis: Daicel Chiralpak OD-H, iso-propanol/hexane = 2:98, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 9.40 min (major), 10.95 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 3H), 7.21 – 7.18 (m, 2H), 6.35 (d, *J* = 4.5 Hz, 0.18H), 6.22 (d, *J* = 3.0 Hz, 0.82H), 5.35 (s, 1H), 5.18 (d, *J* = 3.0 Hz, 1H), 4.45 (d, *J* = 2.5 Hz, 0.82H), 4.38 (q, *J* = 2.5 Hz, 0.82H), 4.21 (d, *J* = 4.0 Hz, 0.18H), 3.83 (d, *J* = 5.5 Hz, 3H), 3.58 (s, 2.46H), 3.43 (s, 0.54H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 142.3, 140.7, 139.8, 129.4, 128.8, 128.6, 128.4, 127.4, 127.0, 116.3, 115.6, 115.4, 115.1, 102.2, 101.5, 56.0, 55.9, 52.4, 43.4, 41.9. IR (thin film, cm^{-1}):2920, 2849, 1735, 1647, 1437, 1308, 1223, 1113, 1090, 1008, 928, 702. HRMS (ESI) calcd for $C_{15}H_{16}O_4Na^+$: 283.0941, found: 283.0944.



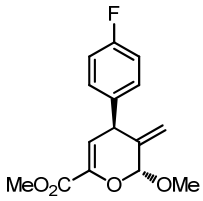
4b

4b: Yellow oil as an inseparable diastereoisomeric mixture, 86% yield, 23.6 mg, 86:14 *dr*, 95% ee for exo-**4b**. $[\alpha]_D^{25}$ = -75.52 (*c* 1.62, $CHCl_3$). HPLC analysis: Daicel Chiralpak OD-H, iso-propanol/hexane = 2:98, flow rate = 1.0 mL/min, λ = 239 nm, retention time: 7.83 min (major), 8.61 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.5 Hz, 2H), 7.32 – 7.28 (m, 1H), 7.20 (d, *J* = 7.0 Hz, 2H), 6.34 (d, *J* = 4.0 Hz, 0.14H), 6.21 (d, *J* = 3.0 Hz, 0.86H), 5.35 (d, *J* = 4.5 Hz, 1H), 5.32 (s, 0.14H), 5.18 (d, *J* = 2.5 Hz, 1H), 4.45 (d, *J* = 2.5 Hz, 1H), 4.38 (d, *J* = 3.0 Hz, 1H), 4.38-4.20 (m, 2H), 3.58 (s, 2,58H), 3.43 (s, 0.42H), 1.32 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7, 142.3, 142.0, 141.6, 141.0, 140.8, 139.8, 129.4, 128.7, 128.5, 128.3, 127.4, 127.0, 116.3, 115.3, 115.1, 115.0, 102.1, 101.4, 61.4, 55.9, 55.8, 43.3, 41.9, 14.3. IR (thin film, cm^{-1}): 2981, 2929, 1730, 1663, 1446, 1371, 1304, 1224, 1111, 1089, 764, 702. HRMS (ESI) calcd for $C_{16}H_{18}O_4Na^+$: 297.1097, found: 297.1103.



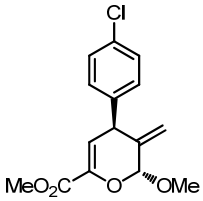
4c

4c: Yellow oil as an inseparable diastereoisomeric mixture, 80% yield, 23.1 mg, 77:23 *dr*, 89% ee for exo-**4c**. $[\alpha]_D^{25}$ = -68.06 (*c* 1.86, $CHCl_3$). HPLC analysis: Daicel Chiralpak OD-H, iso-propanol/hexane = 2:98, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.12 min (major), 6.96 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.19 (m, 5H), 6.31 (d, *J* = 4.0 Hz, 0.23H), 6.18 (d, *J* = 3.0 Hz, 0.77H), 5.35-5,31 (m,1.23H), 5.17 – 5.12 (m, 2H), 4.45 (d, *J* = 2.5 Hz, 0.77H), 4.37 (d, *J* = 3.0 Hz, 0.77H), 4.20 (d, *J* = 4.0 Hz, 0.23H), 3.57 (s, 2.31H), 3.44 (s, 0.69H), 1.31 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2, 142.4, 142.0, 141.7, 141.2, 141.0, 139.9, 129.4, 128.7, 128.5, 128.4, 127.3, 126.9, 116.3, 115.0, 114.9, 114.8, 102.0, 101.3, 69.0, 55.9, 55.8, 43.3, 41.9, 21.9, 21.9. IR (thin film, cm^{-1}): 2982, 2936, 1728, 1375, 1302, 1225, 1105, 1007, 764, 702. HRMS (ESI) calcd for $C_{17}H_{20}O_4Na^+$: 311.1254, found: 311.1260.



4d

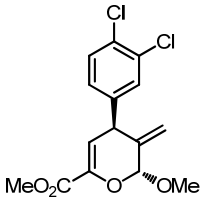
4d: Pale Yellow oil as an inseparable diastereoisomeric mixture, 85% yield, 23.7 mg, 84:16 *dr*, 95% ee for exo-**4d**. $[\alpha]_D^{25}$ = -163.45 (*c* 0.70, $CHCl_3$). HPLC analysis: Daicel Chiralpak AD-H, iso-propanol/hexane = 1:99, flow rate = 0.5 mL/min, λ = 239 nm, retention time: 46.18 min (minor), 52.45 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 6.96 (m, 4H), 6.31 (d, *J* = 4.0 Hz, 0.16H), 6.16 (d, *J* = 2.5 Hz, 0.84H), 5.34 (s, 1H), 5.31 (s, 0.16H), 5.18 (d, *J* = 2.5 Hz, 1H), 4.43 (d, *J* = 2.5 Hz, 0.84H), 4.37 (q, *J* = 2.5 Hz, 0.84H), 4.18 (d, *J* = 4.0 Hz, 0.16H), 3.84 (s, 0.48H), 3.83 (s, 2.52H), 3.57 (s, 2.52H), 3.43 (s, 0.48H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 163.1, 161.0, 142.3, 140.8, 135.5, 135.5, 131.0, 130.9, 129.9, 129.8, 116.5, 115.8, 115.6, 115.4, 115.3, 115.2, 115.1, 115.0, 102.1, 101.4, 56.0, 55.9, 52.4, 42.6, 41.2. IR (thin film, cm^{-1}): 2920, 2849, 1735, 1648, 1510, 1314, 1223, 1114, 1090, 1007, 838. HRMS (ESI) calcd for $C_{15}H_{15}O_4FNa^+$: 301.0847, found: 301.0852.



4e

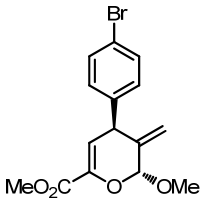
4e: Yellow oil as an inseparable diastereoisomeric mixture, 85% yield, 25.0 mg, 85:15 *dr*, 97% ee for exo-**4e**. $[\alpha]_D^{25}$ = -154.52 (*c* 0.83, $CHCl_3$). HPLC analysis: Daicel Chiralpak OD-H, iso-propanol/hexane = 1:99, flow rate = 0.5 mL/min, λ = 210 nm, retention time: 26.56 min (minor), 29.49 min (major). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.5 Hz, 1.70H), 7.26 (d, *J* = 1.5 Hz, 0.60H), 7.13 (d, *J* = 8.5 Hz, 1.70H), 6.30 (d, *J* = 4.0 Hz, 0.15H), 6.15 (d, *J* = 3.0 Hz, 0.85H), 5.34 (s, 1H), 5.30 (s, 0.15H), 5.19 (dd, *J* = 6.5, 2.0 Hz, 1H), 4.44 (d, *J* = 2.5 Hz, 0.85H), 4.36 (q, *J* = 3.0 Hz, 0.85H), 4.17 (d, *J* = 4.0 Hz, 0.15H), 3.84 (s, 0.45H), 3.83 (s, 2.55H), 3.57 (s, 2.55H), 3.42 (s, 0.45H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 142.0, 140.9, 138.3, 133.3, 130.7, 129.7, 129.0, 128.7, 116.6, 115.1, 114.9, 114.6, 102.1, 101.4, 56.0, 55.9, 52.5, 42.7,

41.3. IR (thin film, cm^{-1}): 2921, 2849, 1735, 1648, 1491, 1313, 1222, 1114, 1091, 1007, 928, 830. HRMS (ESI) calcd for $C_{15}H_{15}O_4ClNa^+$: 317.0551, found: 317.0554.



4f

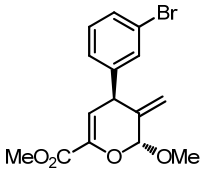
4f: Yellow oil as an inseparable diastereoisomeric mixture, 96% yield, 31.6 mg, 84:16 *dr*, 96% ee for exo-**4f**. $[\alpha]_D^{25}$ = -111.98 (*c* 0.89, $CHCl_3$). HPLC analysis: Daicel Chiralpak OD-H, iso-propanol/hexane = 5:95, flow rate = 1.0 mL/min, λ = 239 nm, retention time: 8.37 min (major), 9.01 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 0.16H), 7.29 (d, *J* = 2.0 Hz, 0.84H), 7.16 (dd, *J* = 8.0, 2.0 Hz, 0.16H), 7.04 (dd, *J* = 8.0, 2.0 Hz, 0.84H), 6.28 (d, *J* = 4.0 Hz, 0.16H), 6.11 (d, *J* = 3.0 Hz, 0.84H), 5.37 (s, 0.16H), 5.34 (s, 0.84H), 5.24 (d, *J* = 1.0 Hz, 0.16H), 5.22 (d, *J* = 2.5 Hz, 0.84H), 4.46 (d, *J* = 2.5 Hz, 0.84H), 4.35 (q, *J* = 2.5 Hz, 0.84H), 4.14 (d, *J* = 4.0 Hz, 0.16H), 3.85 (s, 0.48H), 3.84 (s, 2.52H), 3.57 (s, 2.52H), 3.42 (s, 0.48H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0, 141.7, 141.4, 141.3, 141.1, 140.9, 140.1, 132.9, 132.5, 131.6, 131.3, 131.0, 130.8, 130.4, 130.3, 128.8, 127.7, 117.2, 115.4, 114.0, 113.6, 102.0, 101.3, 56.1, 55.9, 52.6, 52.6, 42.2, 41.1. IR (thin film, cm^{-1}): 2923, 2850, 1733, 1648, 1471, 1438, 1308, 1114, 1091, 1007, 929, 768. HRMS (APCI) calcd for $C_{15}H_{13}O_4Cl_2^-$: 327.0198, found: 327.0196.



4g

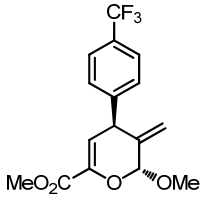
4g: Yellow oil as an inseparable diastereoisomeric mixture, 77% yield, 26.2 mg, 86:14 *dr*, 96% ee for exo-**4g**. $[\alpha]_D^{25}$ = -129.42 (*c* 3.69, $CHCl_3$). HPLC analysis: Daicel Chiralpak AD-H, iso-propanol/hexane = 1:99, flow rate = 0.5 mL/min, λ = 239 nm, retention time: 27.05 min (minor), 29.53 min (major). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.5 Hz, 1.72H), 7.42 (d, *J* = 8.5 Hz, 0.28H), 7.20 (d, *J* = 8.5 Hz, 0.28H), 7.07 (d, *J* = 8.5 Hz, 1.72H), 6.30 (d, *J* = 4.0 Hz, 0.14H), 6.14 (d, *J* = 3.0 Hz, 0.86H),

5.34 (d, J = 4.5 Hz, 1H), 5.20 (dd, J = 7.0, 2.0 Hz, 1H), 4.44 (d, J = 2.5 Hz, 0.86H), 4.35 (q, J = 3.0 Hz, 0.86H), 4.15 (d, J = 4.0 Hz, 0.14H), 3.84 (s, 0.42H), 3.83 (s, 2.58H), 3.57 (s, 2.58H), 3.41 (s, 0.42H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1, 141.8, 141.4, 141.1, 140.9, 140.6, 138.8, 131.9, 131.6, 131.1, 130.1, 121.4, 121.0, 116.7, 115.2, 114.8, 114.5, 102.1, 101.4, 56.0, 55.9, 52.5, 42.7, 41.4. IR (thin film, cm^{-1}): 2998, 2952, 1734, 1488, 1437, 1313, 1223, 1114, 1090, 1010, 928, 827, 761. HRMS (ESI) calcd for $C_{15}H_{15}O_4BrNa^+$: 361.0046, found: 361.0046.



4h

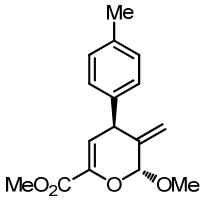
4h: Yellow oil as an inseparable diastereoisomeric mixture, 83% yield, 28.2 mg, 82:18 *dr*, 97% ee for exo-**4h**. $[\alpha]_D^{25}$ = -157.85 (*c* 0.65, $CHCl_3$). HPLC analysis: Daicel Chiralpak OD-H, iso-propanol/hexane = 1:99, flow rate = 0.5 mL/min, λ = 239 nm, retention time: 26.92 min (major), 30.58 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 1H), 7.34 (t, J = 2.0 Hz, 1H), 7.23 (t, J = 8.0 Hz, 1H), 7.20 – 7.10 (m, 1H), 6.31 (d, J = 4.0 Hz, 0.18H), 6.15 (d, J = 3.0 Hz, 0.82H), 5.35 (d, J = 12.0 Hz, 1H), 5.22 (dd, J = 11.0, 2.0 Hz, 1H), 4.46 (d, J = 2.5 Hz, 0.82H), 4.35 (q, J = 3.0 Hz, 0.82H), 4.16 (d, J = 4.0 Hz, 0.18H), 3.85 (s, 0.54H), 3.84 (s, 2.46H), 3.57 (s, 2.46H), 3.42 (s, 0.54H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0, 143.8, 142.1, 141.7, 141.2, 141.1, 140.9, 132.3, 131.4, 130.6, 130.3, 130.1, 130.1, 128.2, 126.9, 122.8, 122.6, 117.0, 115.3, 114.6, 114.3, 102.0, 101.3, 56.0, 55.9, 52.5, 42.8, 41.6. IR (thin film, cm^{-1}): 2922, 2849, 1733, 1649, 1437, 1310, 1222, 1114, 1090, 1007, 928. HRMS (ESI) calcd for $C_{15}H_{15}O_4BrNa^+$: 361.0046, found: 361.0047.



4i

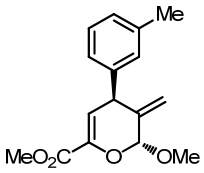
4i: Yellow oil as an inseparable diastereoisomeric mixture, 64% yield, 21.0 mg, 88:12 *dr*, 96% ee for exo-**4i**. $[\alpha]_D^{25}$ = -108.53 (*c* 1.40, $CHCl_3$). HPLC analysis: Daicel

Chiralpak OD-H, iso-propanol/hexane = 2:98, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 8.50 min (minor), 9,85 min (major). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 1.76H), 7.55 (d, *J* = 8.0 Hz, 0.24H), 7.44 (d, *J* = 8.0 Hz, 0.24H), 7.32 (d, *J* = 8.0 Hz, 1.76H), 6.32 (d, *J* = 4.0 Hz, 0.12H), 6.15 (d, *J* = 3.0 Hz, 0.88H), 5.37 (s, 0.12H), 5.35 (s, 0.88H), 5.24 (d, *J* = 1.5 Hz, 0.12H), 5.20 (d, *J* = 3.0 Hz, 0.88H), 4.45 (d, *J* = 3.0 Hz, 0.88H), 4.39 (d, *J* = 2.5 Hz, 0.88H), 4.24 (d, *J* = 4.0 Hz, 0.12H), 3.84 (s, 0.36H), 3.83 (s, 2.64H), 3.57 (s, 2.64H), 3.41 (s, 0.36H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0, 145.5, 143.9, 141.7, 141.2, 141.0, 129.9, 129.8, 129.7, 128.6, 125.8, 125.8, 125.8, 125.7, 125.5, 125.5, 125.3, 123.1, 117.1, 115.3, 114.3, 114.0, 102.0, 101.4, 56.0, 55.9, 52.5, 42.9, 41.7. IR (thin film, cm^{-1}): 2955, 1735, 1325, 1166, 1111, 1069, 930, 840. HRMS (ESI) calcd for $C_{16}H_{15}O_4F_3Na^+$: 351.0815, found: 351.0819.



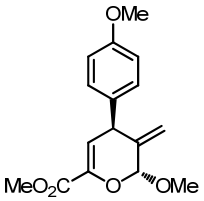
4j

4j: Yellow oil as an inseparable diastereoisomeric mixture, 72% yield, 19.7 mg, 93:7 *dr*, 96% ee for exo-**4j**. $[\alpha]_D^{25}$ = -111.54 (*c* 0.26, $CHCl_3$). HPLC analysis: Daicel Chiralpak OJ-H, iso-propanol/hexane = 10:90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 10.74 min (major), 27.55 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.34 (d, *J* = 4.0 Hz, 0.07H), 6.20 (d, *J* = 3.0 Hz, 0.93H), 5.34 (s, 1H), 5.17 (d, *J* = 3.0 Hz, 1H), 4.48 (d, *J* = 2.5 Hz, 1H), 4.34 (q, *J* = 3.0 Hz, 1H), 3.83 (s, 0.21H), 3.82 (s, 2.79H), 3.57 (s, 2.79H), 3.43 (s, 0.21H), 2.35 (s, 2.79H), 2.32 (s, 0.21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 142.4, 140.6, 137.0, 136.7, 129.5, 129.3, 115.9, 115.0, 102.2, 56.0, 52.4, 41.5, 21.2. IR (thin film, cm^{-1}): 3360, 2925, 2854, 1735, 1653, 1514, 1437, 1306, 1223, 1114, 953, 927. HRMS (ESI) calcd for $C_{16}H_{18}O_4Na^+$: 297.1097, found: 297.1097.



4k

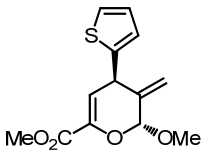
4k: Yellow oil as an inseparable diastereoisomeric mixture, 70% yield, 19.2 mg, 92:8 *dr*, 96% ee for exo-**4k**. $[\alpha]_D^{25}$ = -134.21 (*c* 0.19, $CHCl_3$). HPLC analysis: Daicel Chiralpak OD-H, iso-propanol/hexane = 2:98, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 8.01 min (major), 9.18 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (s, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.01 – 6.95 (m, 2H), 6.34 (d, *J* = 4.0 Hz, 0.08H), 6.21 (d, *J* = 3.0 Hz, 0.92H), 5.34 (s, 1H), 5.18 (d, *J* = 2.8 Hz, 1H), 4.48 (s, 1H), 4.34 (d, *J* = 3.0 Hz, 1H), 3.84 (s, 0.24H), 3.83 (s, 2.76H), 3.57 (s, 2.76H), 3.49 (s, 0.24H), 2.34 (s, 2.76H), 2.33(s, 0.24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 142.3, 140.6, 139.7, 138.5, 130.1, 128.6, 128.2, 126.5, 115.8, 115.0, 102.2, 56.0, 52.4, 41.9, 21.5. HRMS (ESI) calcd for $C_{16}H_{18}O_4Na^+$: 297.1097, found: 297.1099.



4l

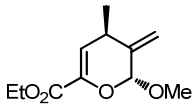
4l: Yellow oil as an inseparable diastereoisomeric mixture, 81% yield, 23.5 mg, 87:13 *dr*, 96% ee for exo-**4l**. $[\alpha]_D^{25}$ = -191.14 (*c* 0.66, $CHCl_3$). HPLC analysis: Daicel Chiralpak IC-H, iso-propanol/hexane = 10:90, flow rate = 1.0 mL/min, λ = 239 nm, retention time: 9.45 min (minor), 12.60 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.5 Hz, 0.26H), 7.10 (d, *J* = 8.5 Hz, 1.74H), 6.88 (d, *J* = 8.5 Hz, 1.74H), 6.83 (d, *J* = 8.5 Hz, 0.26H), 6.32 (d, *J* = 4.0 Hz, 0.13H), 6.18 (d, *J* = 3.0 Hz, 0.87H), 5.33 (s, 0.87H), 5.32 (s, 0.13H), 5.16 (d, *J* = 3.0 Hz, 1H), 4.47 (d, *J* = 2.5 Hz, 0.87H), 4.33 (d, *J* = 3.0 Hz, 0.87H), 4.16 (d, *J* = 4.0 Hz, 0.13H), 3.86 – 3.76 (m, 6H), 3.56 (s, 2.61H), 3.43 (s, 0.39H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 159.0, 142.6, 140.5, 133.7, 131.7, 130.4, 129.4, 116.0, 115.8, 114.9, 114.2, 114.0, 102.2, 101.5, 56.0, 55.9, 55.4, 55.4, 52.4, 42.7, 41.1. IR (thin film, cm^{-1}): 2920, 2849, 1733, 1647, 1512, 1304, 1252, 1112, 1090, 1007, 833. HRMS (ESI) calcd for $C_{16}H_{18}O_5Na^+$: 313.1046, found:

313.1050.



4m

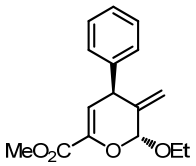
4m: Brown oil as an inseparable diastereoisomeric mixture, 99% yield, 26.4 mg, 88:12 *dr*, 99% ee for exo-**4m**. $[\alpha]_D^{25}$ = -194.01 (*c* 1.39, $CHCl_3$). HPLC analysis: Daicel Chiralpak OD-H, iso-propanol/hexane = 2:98, flow rate = 1.0 mL/min, λ = 239 nm, retention time: 12.83 min (major), 13.73 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 0.98H), 7.16 (d, *J* = 2.0 Hz, 0.12H), 7.00 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.95 – 6.89 (m, 1H), 6.37 (d, *J* = 4.0 Hz, 0.12H), 6.23 (d, *J* = 2.5 Hz, 0.88H), 5.39 (s, 0.12H), 5.34 (d, *J* = 8.5 Hz, 1H), 5.30 (s, 0.12H), 5.24 (d, *J* = 2.5 Hz, 0.88H), 4.74 (dd, *J* = 17.0, 2.5 Hz, 1.86H), 4.45 (d, *J* = 4.0 Hz, 0.12H), 3.83 (s, 0.36H), 3.82 (s, 2.64H), 3.57 (s, 2.64H), 3.43 (s, 0.36H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 144.7, 142.2, 141.3, 141.2, 140.5, 140.3, 127.0, 126.8, 126.7, 125.2, 125.1, 124.5, 116.9, 114.9, 114.8, 114.6, 101.8, 101.2, 56.1, 55.8, 52.4, 38.3, 37.1. IR (thin film, cm^{-1}): 2921, 2849, 1735, 1647, 1437, 1305, 1256, 1112, 1090, 1005, 948, 702. HRMS (ESI) calcd for $C_{13}H_{14}O_4SNa^+$: 289.0505, found: 289.0506.



4n

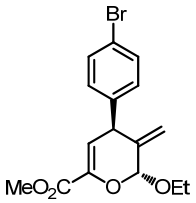
4n: Yellow oil as an inseparable diastereoisomeric mixture, 97% yield, 20.6 mg, 75:25 *dr*, 94% ee for exo-**4n**. $[\alpha]_D^{25}$ = -84.08 (*c* 1.95, $CHCl_3$). HPLC analysis: Daicel Chiralpak AD-H, iso-propanol/hexane = 1:99, flow rate = 1.0 mL/min, λ = 239 nm, retention time: 9.33 min (minor), 12.89 min (major). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.11 (d, *J* = 4.0 Hz, 0.25H), 5.98 (d, *J* = 2.5 Hz, 0.75H), 5.24 (d, *J* = 7.0Hz, 1H), 5.22 – 5.08 (m, 1H), 5.01 (d, *J* = 2.5 Hz, 1H), 4.25 (q, *J* = 7.0 Hz, 2H), 3.48 (d, *J* = 18.0 Hz, 3H), 3.23 (dddd, *J* = 10.0, 7.0 4.5, 3.0 Hz, 0.75H), 2.98 (qd, *J* = 7.5, 4.0 Hz, 0.25H), 1.30 (td, *J* = 7.5, 3.5 Hz, 4H), 1.23 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.8, 143.6, 142.8, 139.9, 139.4, 117.8, 117.6, 114.2, 111.5, 102.1, 101.8, 61.2, 61.2, 55.9, 55.8, 32.8, 29.0, 22.0, 16.3, 14.3. IR (thin film, cm^{-1}): 2967, 2920, 1730,

1371, 1313, 1242, 1098, 1023, 964, 767. HRMS (ESI) calcd for $C_{11}H_{16}O_4Na^+$: 235.0941, found: 235.0942.



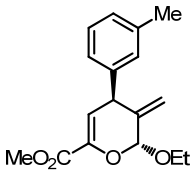
4o

4o: Pale yellow oil, 69% yield, 18.9 mg, >19:1 *dr*, 94% ee. $[\alpha]_D^{25}$ = -197.48 (*c* 0.74, $CHCl_3$). HPLC analysis: Daicel Chiralpak OD-H, iso-propanol/hexane = 5:95, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.43 min (major), 6.27 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.0 Hz, 2H), 7.32 – 7.27 (m, 1H), 7.24 – 7.16 (m, 2H), 6.21 (d, *J* = 2.5 Hz, 1H), 5.45 (s, 1H), 5.17 (d, *J* = 3.0 Hz, 1H), 4.49 – 4.36 (m, 2H), 3.94 (dq, *J* = 10.0, 7.0 Hz, 1H), 3.82 (s, 3H), 3.73 (dq, *J* = 10.0, 7.0 Hz, 1H), 1.28 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 142.6, 140.7, 140.0, 129.4, 128.8, 127.4, 115.5, 114.7, 100.9, 64.3, 52.4, 42.0, 15.3, 1.2. IR (thin film, cm^{-1}): 2920, 2849, 1735, 1647, 1437, 1308, 1259, 1222, 1091, 994, 928, 798, 702. HRMS (ESI) calcd for $C_{16}H_{18}O_4Na^+$: 297.1108, found: 297.1104.



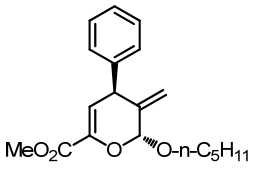
4p

4p: Pale yellow oil, 75% yield, 26.5 mg, >19:1 *dr*, 98% ee. $[\alpha]_D^{25}$ = -164.91 (*c* 0.80, $CHCl_3$). HPLC analysis: Daicel Chiralpak AD-H, iso-propanol/hexane = 2:98, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.34 min (minor), 8.37 min (major). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 6.14 (d, *J* = 2.5 Hz, 1H), 5.44 (s, 1H), 5.18 (d, *J* = 2.5 Hz, 1H), 4.40 (dd, *J* = 22.0, 2.5 Hz, 2H), 3.93 (dq, *J* = 10.0, 7.0 Hz, 1H), 3.82 (s, 3H), 3.73 (dq, *J* = 10.0, 7.0 Hz, 1H), 1.27 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 142.1, 140.9, 139.0, 131.9, 131.2, 121.3, 114.9, 114.7, 100.8, 64.3, 52.5, 41.4, 15.2. IR (thin film, cm^{-1}): 3358, 2920, 2894, 1736, 1488, 1312, 1114, 1090, 992, 922, 826. HRMS (ESI) calcd for $C_{16}H_{17}O_4BrNa^+$: 375.0202, found: 375.0206.



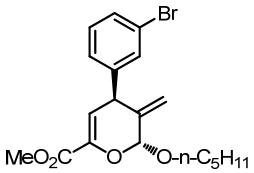
4q

4q: Yellow oil, 64% yield, 18.5 mg, >19:1 *dr*, 97% ee. $[\alpha]_D^{25}$ = -125.79 (*c* 0.70, $CHCl_3$). HPLC analysis: Daicel Chiralpak IC-H, iso-propanol/hexane = 10:90, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.58 min (minor), 7.29 min (major). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (t, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 2H), 6.20 (d, *J* = 3.0 Hz, 1H), 5.45 (s, 1H), 5.17 (d, *J* = 3.0 Hz, 1H), 4.47 (d, *J* = 2.5 Hz, 1H), 4.37 (d, *J* = 3.0 Hz, 1H), 3.94 (dq, *J* = 10.0, 7.0 Hz, 1H), 3.82 (s, 3H), 3.73 (dq, *J* = 10.0, 7.0 Hz, 1H), 2.34 (s, 3H), 1.27 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.3, 142.5, 140.6, 139.8, 138.4, 130.1, 128.6, 128.1, 126.5, 115.7, 114.7, 100.9, 64.2, 52.4, 41.9, 21.5, 15.3. IR (thin film, cm^{-1}): 2976, 2924, 1734, 1647, 1438, 1308, 1253, 1114, 1090, 992, 772, 706. HRMS (ESI) calcd for $C_{17}H_{20}O_4Na^+$: 311.1254, found: 311.1257.



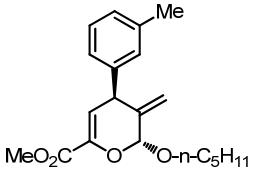
4r

4r: Yellow oil, 96% yield, 30.4 mg, >19:1 *dr*, 99% ee. $[\alpha]_D^{25}$ = -177.91 (*c* 0.89, $CHCl_3$). HPLC analysis: Daicel Chiralpak IC, iso-propanol/hexane = 10:90, flow rate = 1.0 mL/min, λ = 239 nm, retention time: 5.09 min (minor), 5.67 min (major). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.25 (m, 1H), 7.20 (d, *J* = 7.0 Hz, 2H), 6.21 (d, *J* = 3.0 Hz, 1H), 5.43 (s, 1H), 5.16 (d, *J* = 3.0 Hz, 1H), 4.42 (dd, *J* = 15.0, 3.0 Hz, 2H), 3.87 (dt, *J* = 10.0, 7.0 Hz, 1H), 3.82 (s, 3H), 3.66 (dt, *J* = 10.0, 6.5 Hz, 1H), 1.64 (t, *J* = 6.5 Hz, 2H), 1.33 (q, *J* = 4.0 Hz, 4H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3, 142.6, 140.7, 139.9, 129.4, 128.7, 127.3, 115.6, 114.6, 101.1, 68.8, 52.4, 42.0, 29.4, 28.3, 22.6, 14.2. IR (thin film, cm^{-1}): 2954, 2930, 1737, 1307, 1222, 1114, 1090, 993, 763, 702. HRMS (ESI) calcd for $C_{19}H_{24}O_4Na^+$: 339.1567, found: 339.1571.



4s

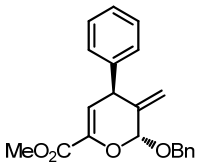
4s: Pale yellow oil, 84% yield, 33.2 mg, >19:1 *dr*, 99% ee. $[\alpha]_D^{25}$ = -212.67 (*c* 0.94, $CHCl_3$). HPLC analysis: Daicel Chiralpak AD-H, iso-propanol/hexane = 2:98, flow rate = 1.0 mL/min, λ = 239 nm, retention time: 6.51 min (minor), 8.65 min (major). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 2.0 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 6.14 (d, *J* = 3.0 Hz, 1H), 5.42 (s, 1H), 5.18 (d, *J* = 3.0 Hz, 1H), 4.44 (d, *J* = 2.5 Hz, 1H), 4.38 (d, *J* = 3.0 Hz, 1H), 3.86 (dt, *J* = 10.0, 7.0 Hz, 1H), 3.83 (s, 3H), 3.66 (dt, *J* = 10.0, 6.5 Hz, 1H), 1.63 (t, *J* = 6.5 Hz, 2H), 1.39 – 1.28 (m, 4H), 0.90 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 142.3, 142.0, 141.1, 132.4, 130.6, 130.3, 128.2, 122.8, 114.8, 114.4, 101.0, 68.8, 52.5, 41.7, 29.3, 28.3, 22.5, 14.2. IR (thin film, cm^{-1}): 2954, 2931, 2871, 1737, 1311, 1115, 1091, 928, 764. HRMS (ESI) calcd for $C_{19}H_{23}O_4BrNa^+$: 417.0672, found: 417.0677.



4t

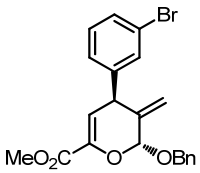
4t: Yellow oil, 72% yield, 23.8 mg, >19:1 *dr*, 96% ee. $[\alpha]_D^{25}$ = -200.41 (*c* 0.85, $CHCl_3$). HPLC analysis: Daicel Chiralpak AD-H, iso-propanol/hexane = 2:98, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 11.60 min (minor), 13.76 min (major). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 15.0, 8.0 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.20 (d, *J* = 3.0 Hz, 1H), 5.43 (s, 1H), 5.15 (d, *J* = 2.5 Hz, 1H), 4.45 (d, *J* = 2.5 Hz, 1H), 4.36 (d, *J* = 3.0 Hz, 1H), 3.87 (dt, *J* = 10.0, 7.0 Hz, 1H), 3.82 (s, 3H), 3.66 (dt, *J* = 10.0, 6.5 Hz, 1H), 2.34 (s, 3H), 1.64 (t, *J* = 6.5 Hz, 2H), 1.33 (q, *J* = 4.0 Hz, 4H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 142.6, 140.6, 139.8, 138.4, 130.1, 128.6, 128.1, 126.5, 115.7, 114.5, 101.1, 68.8, 52.3, 41.9, 29.4, 28.3, 22.5, 21.5, 14.2. IR (thin film, cm^{-1}): 2954, 2930, 1736,

1313, 1114, 1090, 996, 774, 705. HRMS (ESI) calcd for $C_{20}H_{26}O_4Na^+$: 353.1723, found: 353.1725.



4u

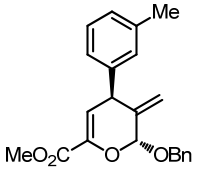
4u: Yellow oil, 72% yield, 24.2 mg, >19:1 *dr*, 91% ee. $[\alpha]_D^{25}$ = -154.38 (*c* 1.01, $CHCl_3$). HPLC analysis: Daicel Chiralpak IC, iso-propanol/hexane = 10:90, flow rate = 1.0 mL/min, λ = 239 nm, retention time: 6.81 min (minor), 8.56 min (major). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.26 (m, 8H), 7.19 (d, *J* = 7.0 Hz, 2H), 6.23 (d, *J* = 3.0 Hz, 1H), 5.53 (s, 1H), 5.15 (d, *J* = 2.5 Hz, 1H), 4.92 (d, *J* = 12.0 Hz, 1H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.45 (q, *J* = 3.0 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 142.2, 140.6, 139.8, 137.3, 129.4, 128.8, 128.6, 128.0, 128.0, 127.4, 115.8, 115.1, 100.2, 70.0, 52.4, 41.9. IR (thin film, cm^{-1}): 3030, 2951, 1733, 1437, 1307, 1222, 1114, 1087, 998, 761, 701. HRMS (ESI) calcd for $C_{21}H_{20}O_4Na^+$: 359.1254, found: 359.1257.



4v

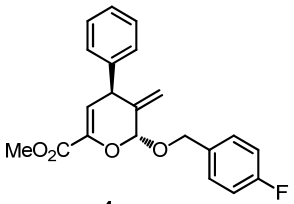
4v: Pale yellow oil, 74% yield, 30.7 mg, >19:1 *dr*, 97% ee. $[\alpha]_D^{25}$ = -216.30 (*c* 0.27, $CHCl_3$). HPLC analysis: Daicel Chiralpak AD-H, iso-propanol/hexane = 2:98, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 13.17 min (minor), 16.96 min (major). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.33 (m, 5H), 7.31 (ddt, *J* = 8.5, 5.5, 3.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.17 (d, *J* = 3.0 Hz, 1H), 5.52 (s, 1H), 5.17 (d, *J* = 3.0 Hz, 1H), 4.91 (d, *J* = 12.0 Hz, 1H), 4.76 (d, *J* = 12.0 Hz, 1H), 4.48 – 4.39 (m, 2H), 3.82 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.0, 142.2, 141.7, 141.0, 137.2, 132.4, 130.6, 130.3, 128.6, 128.2, 128.0, 122.8, 115.3, 114.7, 100.1, 70.1, 52.5, 41.6. IR (thin film, cm^{-1}): 3359, 2920, 2850, 1733, 1647, 1471, 1438, 1311, 1221, 1114, 1088, 998, 930, 698. HRMS (ESI) calcd for

$C_{21}H_{19}O_4BrNa^+$: 437.0359, found: 437.0363.



4w

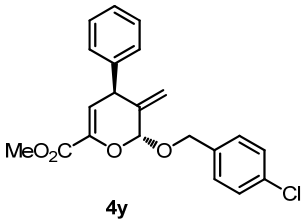
4w: Pale yellow oil, 73% yield, 25.6 mg, >19:1 *dr*, 98% ee. $[\alpha]_D^{25}$ = -219.30 (*c* 0.29, $CHCl_3$). HPLC analysis: Daicel Chiralpak IC, iso-propanol/hexane = 10:90, flow rate = 1.0 mL/min, λ = 239 nm, retention time: 6.26 min (minor), 7.60 min (major). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (q, *J* = 8.0 Hz, 4H), 7.31 (d, *J* = 7.0 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 2H), 6.23 (d, *J* = 3.0 Hz, 1H), 5.52 (s, 1H), 5.15 (d, *J* = 3.0 Hz, 1H), 4.91 (d, *J* = 12.0 Hz, 1H), 4.76 (d, *J* = 12.0 Hz, 1H), 4.47 (d, *J* = 2.5 Hz, 1H), 4.41 (d, *J* = 3.0 Hz, 1H), 3.81 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3, 142.2, 140.5, 139.7, 138.4, 137.4, 130.1, 128.6, 128.6, 128.1, 128.0, 128.0, 126.5, 116.0, 115.1, 100.3, 70.0, 52.4, 41.9, 29.9, 21.5. IR (thin film, cm^{-1}): 3361, 2920, 2850, 1733, 1647, 1436, 1314, 1252, 1233, 1113, 1087, 996, 702. HRMS (ESI) calcd for $C_{22}H_{22}O_4Na^+$: 373.1410, found: 373.1415.



4x

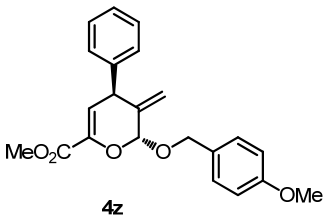
4x: Yellow oil, 76% yield, 26.9 mg, >19:1 *dr*, 98% ee. $[\alpha]_D^{25}$ = -114.68 (*c* 0.76, $CHCl_3$). HPLC analysis: Daicel Chiralpak OD-H, iso-propanol/hexane = 2:98, flow rate = 1.0 mL/min, λ = 239 nm, retention time: 10.68 min (major), 11.71 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 4H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.0 Hz, 2H), 7.04 (t, *J* = 8.5 Hz, 2H), 6.23 (d, *J* = 3.0 Hz, 1H), 5.50 (s, 1H), 5.15 (d, *J* = 2.5 Hz, 1H), 4.87 (d, *J* = 12.0 Hz, 1H), 4.73 (d, *J* = 12.0 Hz, 1H), 4.50 – 4.38 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.6, 163.1, 161.6, 142.1, 140.6, 139.7, 133.1, 133.1, 129.9, 129.8, 129.4, 128.8, 127.4, 115.9, 115.5, 115.4, 115.2, 100.1, 69.4, 52.4, 41.9. IR (thin film, cm^{-1}): 3359, 2921, 2851, 1735, 1511, 1308, 1222, 1114, 1082, 1000, 771, 702. HRMS (ESI) calcd for $C_{21}H_{19}O_4FNa^+$: 377.1160,

found: 377.1160.



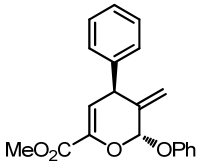
4y

4y: Pale yellow oil, 94% yield, 34.8 mg, >19:1 *dr*, 97% ee. $[\alpha]_D^{25}$ = -213.68 (*c* 0.29, $CHCl_3$). HPLC analysis: Daicel Chiralpak IC, iso-propanol/hexane = 10:90, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.35 min (minor), 7.73 min (major). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 7H), 7.19 (d, *J* = 7.0 Hz, 2H), 6.23 (d, *J* = 3.0 Hz, 1H), 5.50 (s, 1H), 5.16 (d, *J* = 3.0 Hz, 1H), 4.86 (d, *J* = 12.0 Hz, 1H), 4.74 (d, *J* = 12.0 Hz, 1H), 4.44 (dd, *J* = 13.5, 3.0 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1, 142.0, 140.5, 139.7, 135.9, 133.8, 129.5, 129.4, 128.8, 128.8, 127.5, 115.9, 115.3, 100.3, 69.3, 52.5, 41.9. IR (thin film, cm^{-1}): 2919, 2849, 1733, 1492, 1436, 1307, 1221, 1113, 1085, 996, 930, 701. HRMS (ESI) calcd for $C_{21}H_{19}O_4ClNa^+$: 393.0864, found: 393.0868.



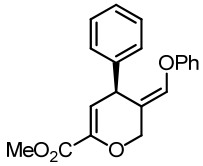
4z

4z: Yellow oil, 53% yield, 19.4 mg, >19:1 *dr*, 92% ee. $[\alpha]_D^{25}$ = -87.14 (*c* 0.56, $CHCl_3$). HPLC analysis: Daicel Chiralpak IC, iso-propanol/hexane = 5:95, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 13.36 min (minor), 21.21 min (major). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 5H), 7.18 (d, *J* = 6.5 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 6.22 (d, *J* = 2.5 Hz, 1H), 5.50 (s, 1H), 5.13 (d, *J* = 2.5 Hz, 1H), 4.84 (d, *J* = 11.5 Hz, 1H), 4.69 (d, *J* = 11.5 Hz, 1H), 4.43 (d, *J* = 4.5 Hz, 2H), 3.82 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 159.5, 142.3, 140.6, 139.8, 129.8, 129.5, 129.3, 128.8, 127.4, 115.8, 115.0, 114.0, 99.9, 69.7, 55.4, 52.4, 41.9. IR (thin film, cm^{-1}): 3359, 2920, 2859, 1734, 1514, 1304, 1250, 1113, 1081, 764, 702. HRMS (ESI) calcd for $C_{22}H_{22}O_5Na^+$: 389.1359, found: 389.1359.



exo-5

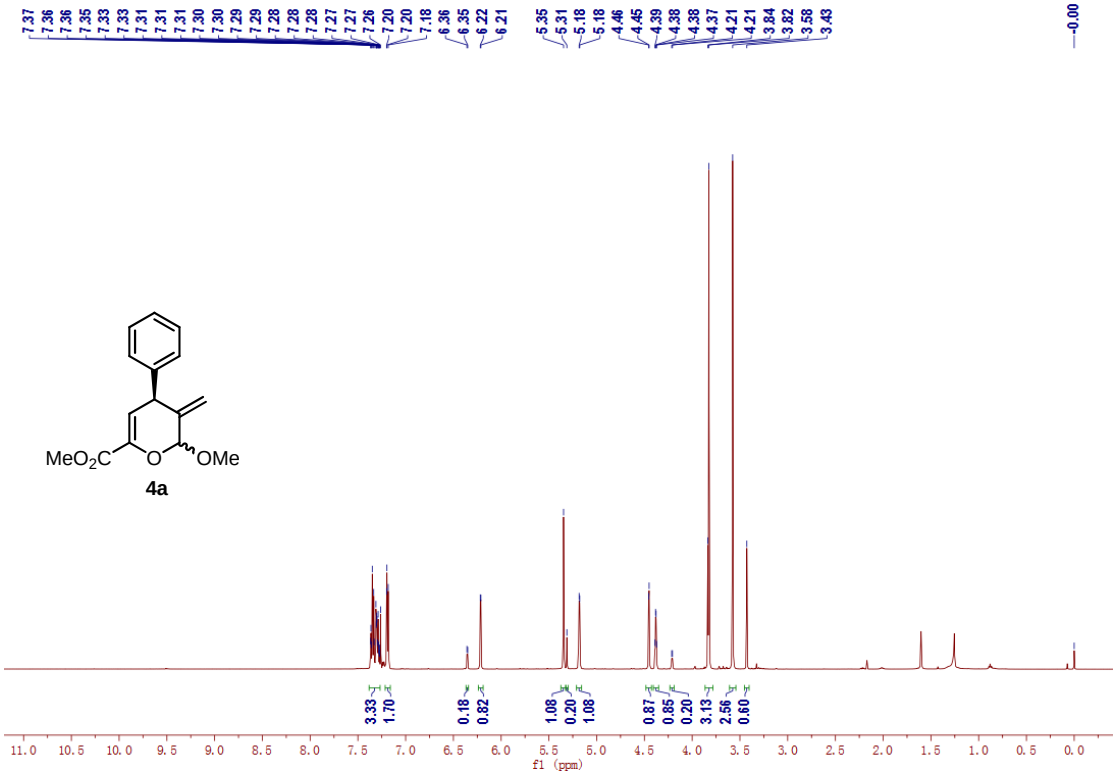
exo-**5**: Pale yellow oil, 40% yield, 12.8 mg, 91% ee. $[\alpha]_D^{25}$ = -327.53 (*c* 0.47, $CHCl_3$). HPLC analysis: Daicel Chiralpak IC, iso-propanol/hexane = 10:90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 6.26 min (minor), 6.62 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dq, *J* = 15.5, 7.5 Hz, 5H), 7.25 (t, *J* = 3.5 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.29 (d, *J* = 2.5 Hz, 1H), 6.04 (s, 1H), 5.27 (d, *J* = 2.5 Hz, 1H), 4.60 (d, *J* = 2.5 Hz, 1H), 4.55 (d, *J* = 2.5 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 156.7, 141.5, 140.8, 139.6, 129.8, 129.5, 128.9, 127.5, 123.0, 117.5, 115.6, 115.6, 99.5, 52.4, 41.8. IR (thin film, cm^{-1}): 2951, 2920, 2849, 1735, 1494, 1228, 1108, 1005, 754, 702. HRMS (ESI) calcd for $C_{20}H_{18}O_4Na^+$: 345.1100, found: 345.1097.

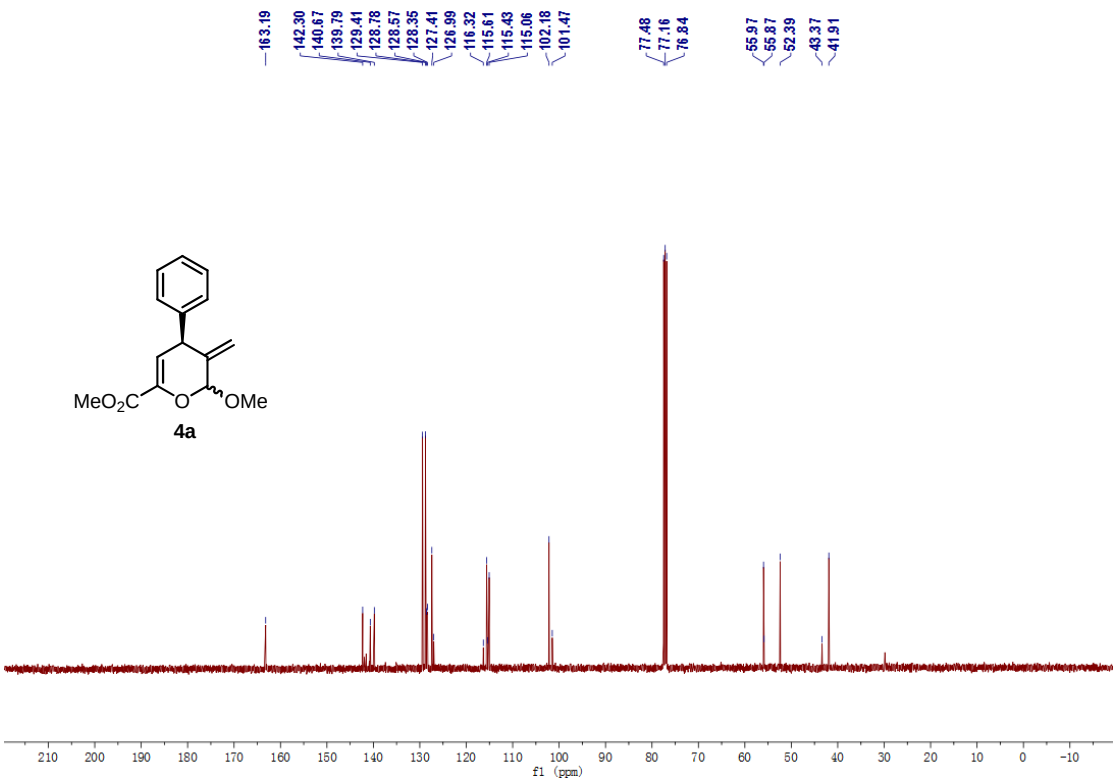


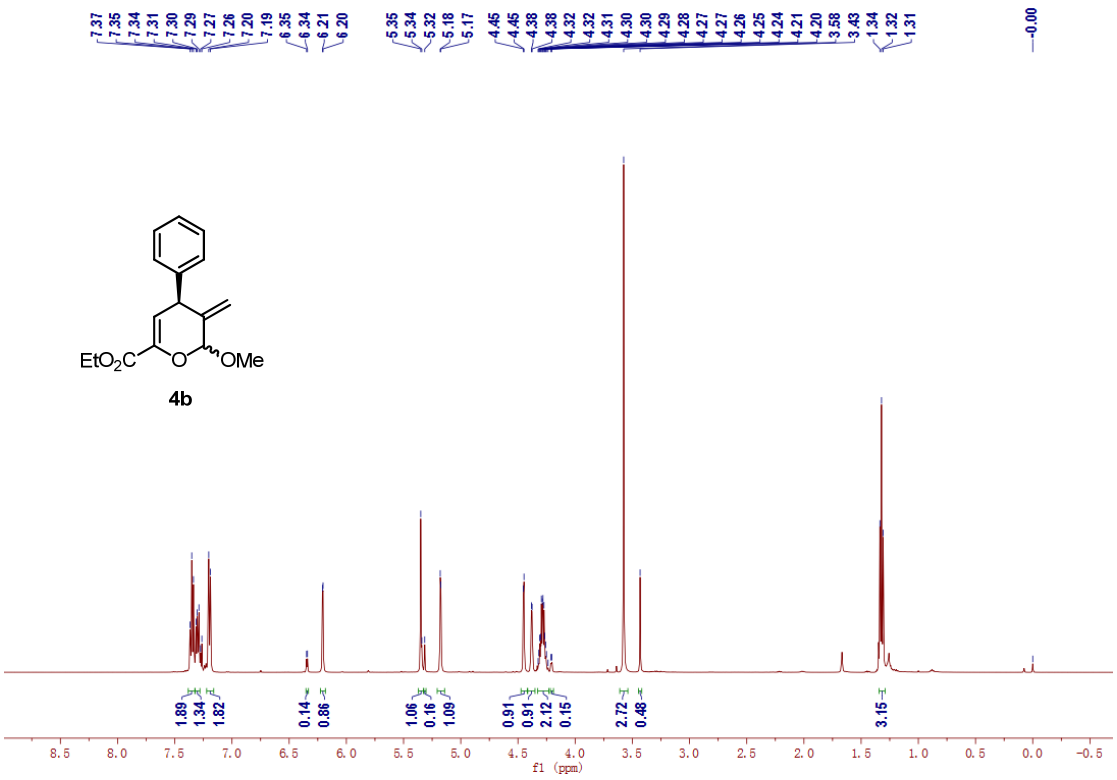
***E*-5'**

***E*-5'**: Pale yellow oil, 29% yield, 9.3 mg, 99% ee. $[\alpha]_D^{25}$ = -377.39 (*c* 0.46, $CHCl_3$). HPLC analysis: Daicel Chiralpak IC, iso-propanol/hexane = 10:90, flow rate = 1.0 mL/min, λ = 210 nm, retention time: 11.29 min (major), 34.30 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$, for *E*-**4ah'**) δ 7.41 (d, *J* = 7.5 Hz, 2H), 7.34 (q, *J* = 7.5 Hz, 4H), 7.25 (d, *J* = 3.0 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.63 (s, 1H), 6.28 (d, *J* = 5.0 Hz, 1H), 4.76 (d, *J* = 5.0 Hz, 1H), 4.44 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 157.0, 145.1, 142.4, 139.1, 129.9, 128.7, 128.1, 127.0, 123.6 , 116.9, 116.5, 112.2 , 65.2, 52.5, 37.1. IR (thin film, cm^{-1}): 2951, 2921, 2853, 1732, 1491, 1277, 1223, 1113, 757, 701. HRMS (ESI) calcd for $C_{20}H_{18}O_4Na^+$: 345.1100, found: 345.1097.

NMR Spectrum



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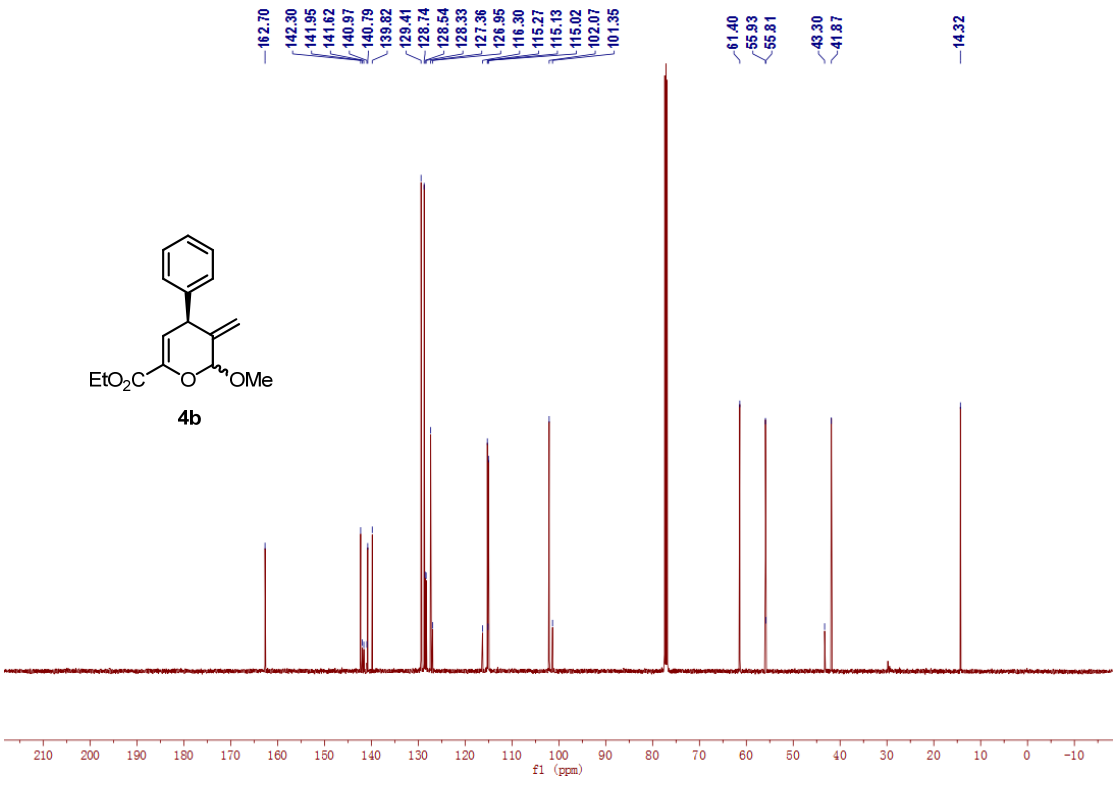
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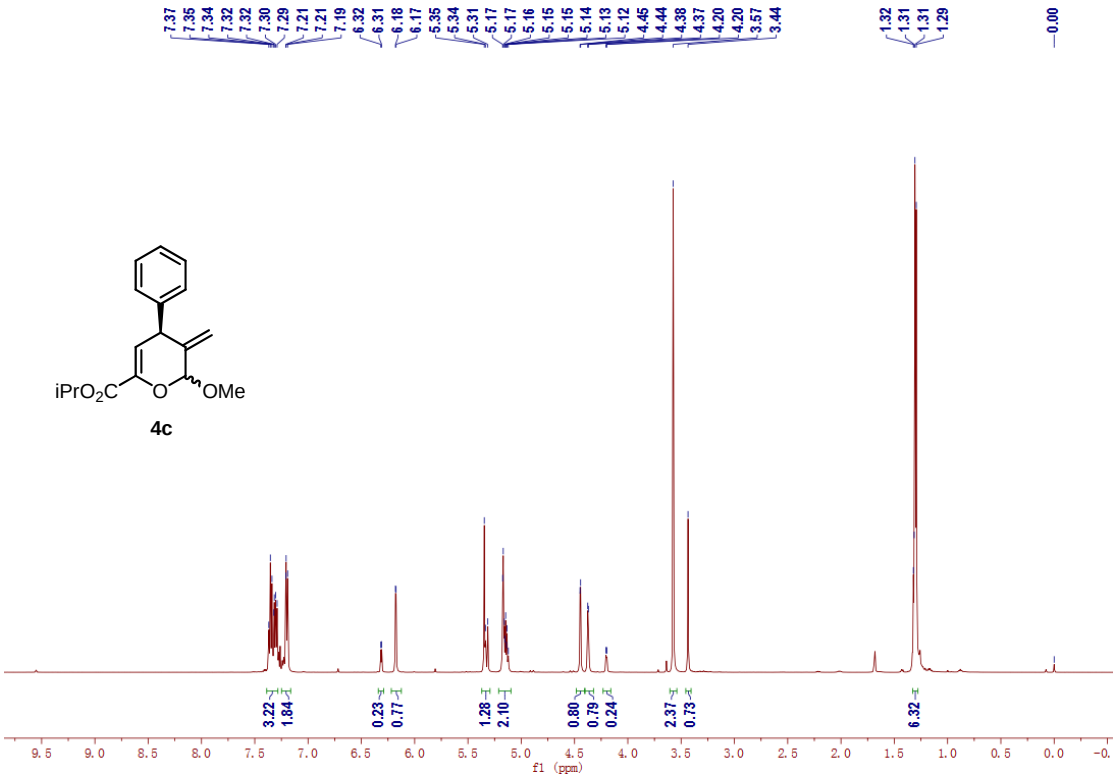
4b
f1 (ppm)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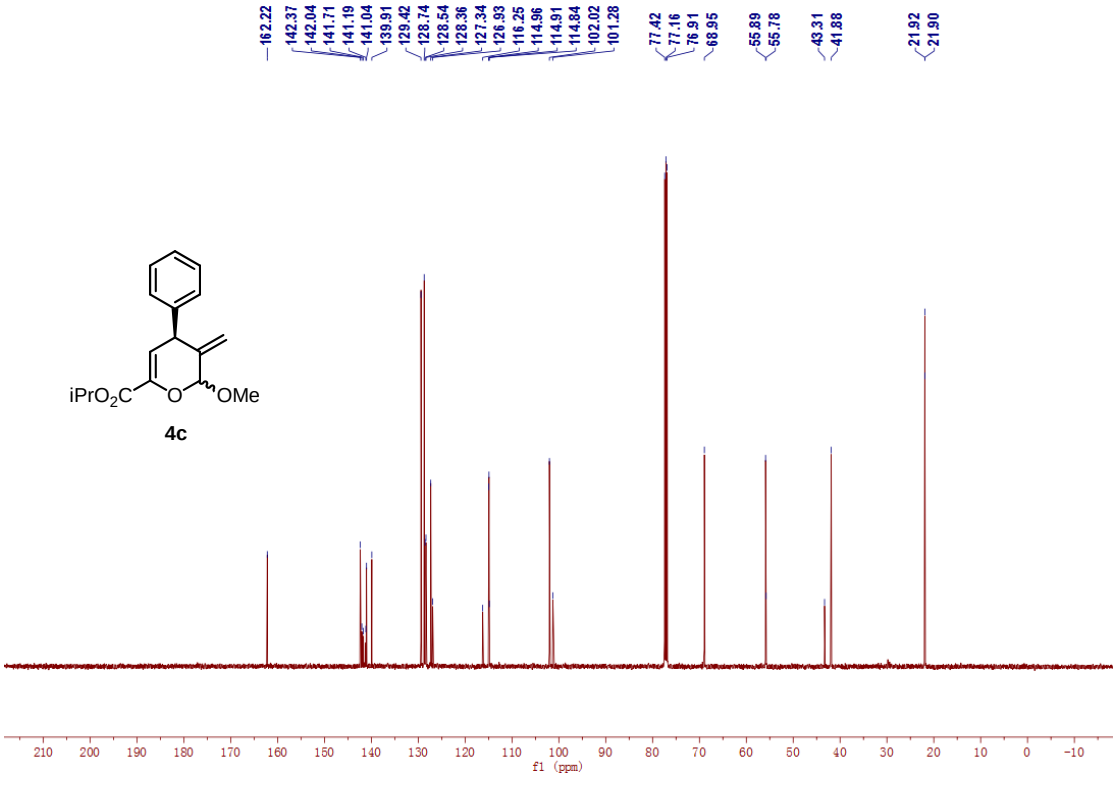
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77.16
76.91
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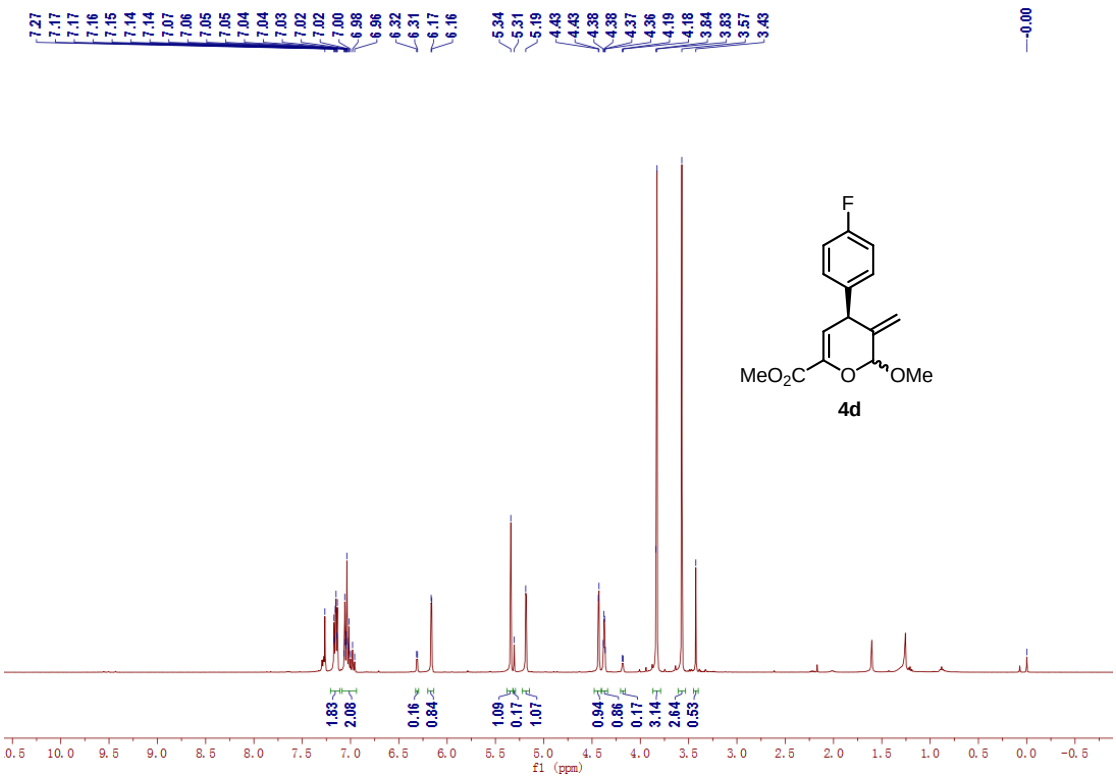
21.90
iPrO2C
O
OMe
4c
f1 (ppm)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0.00
F
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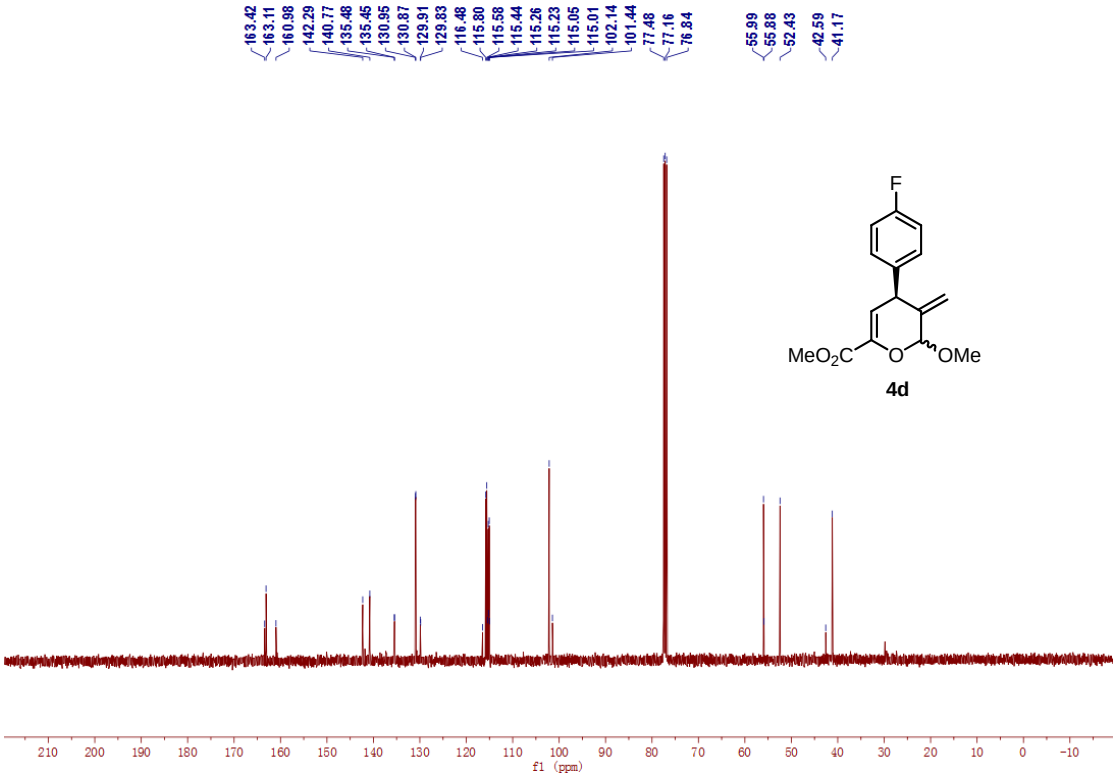
f1 (ppm)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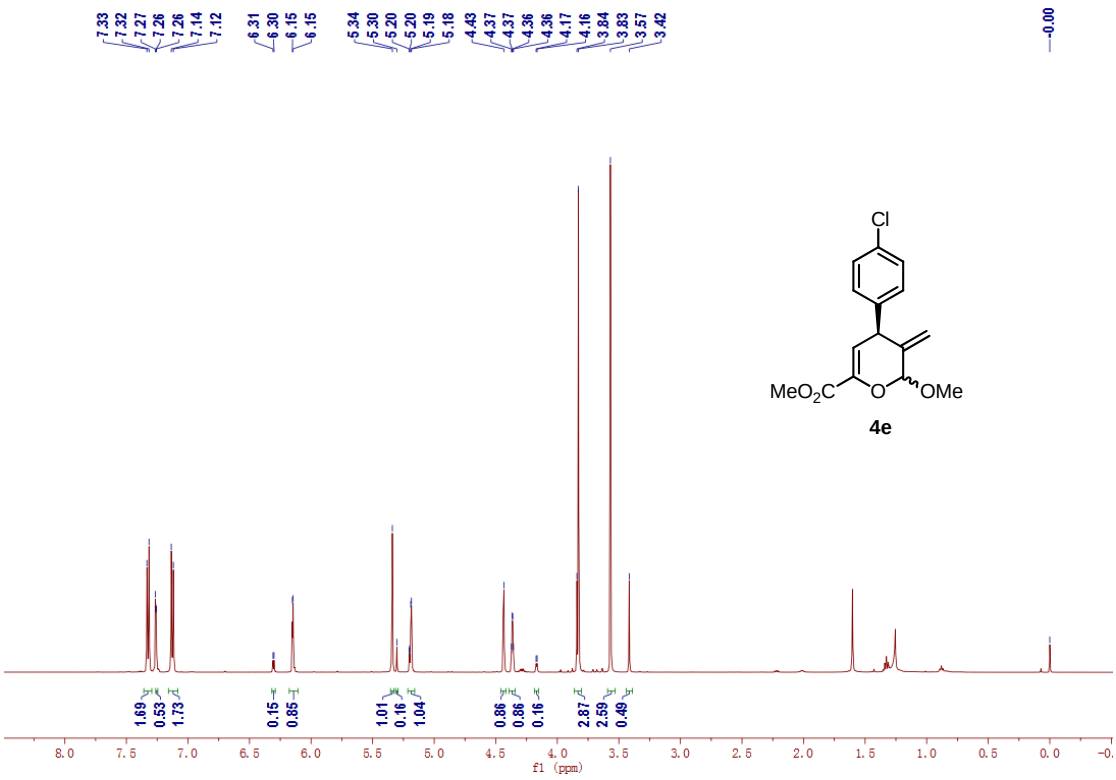
F
MeO2C
O
OMe
4d
f1 (ppm)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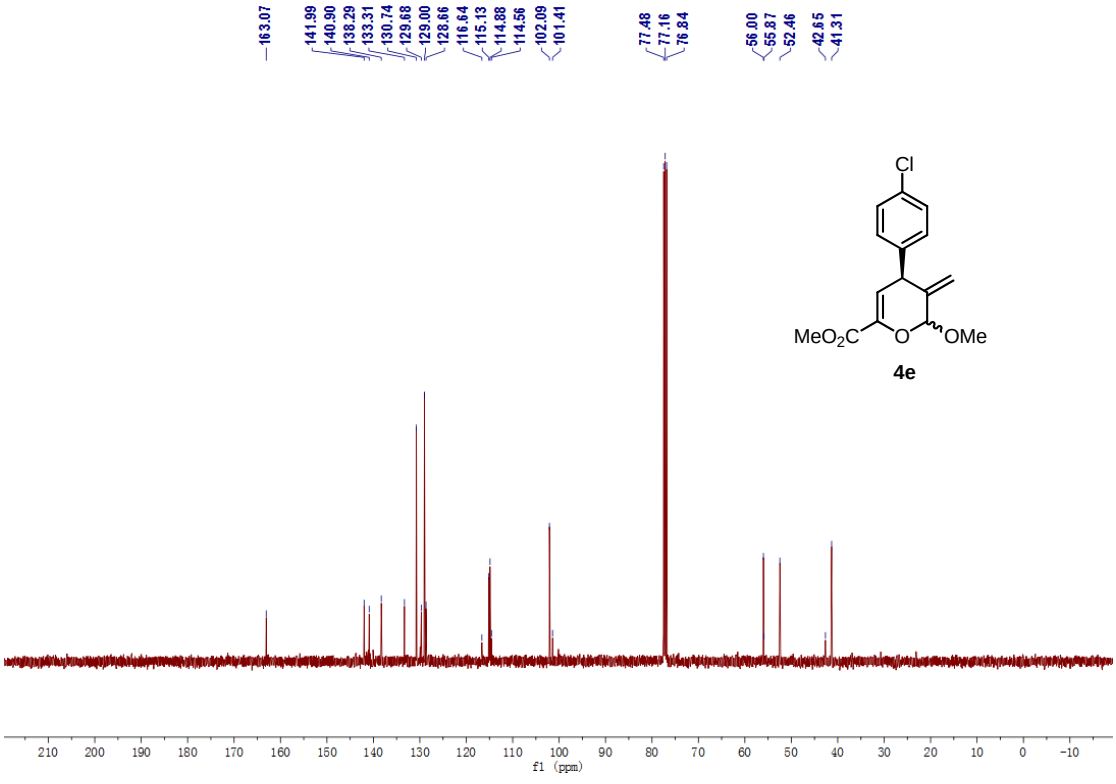
0.53
1.73
0.15
0.85
1.01
0.16
1.04
0.86
0.86
0.16
2.87
2.59
0.49
f1 (ppm)
Cl
MeO2C
O
OMe
4e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102.09
101.41
77.48
77.16
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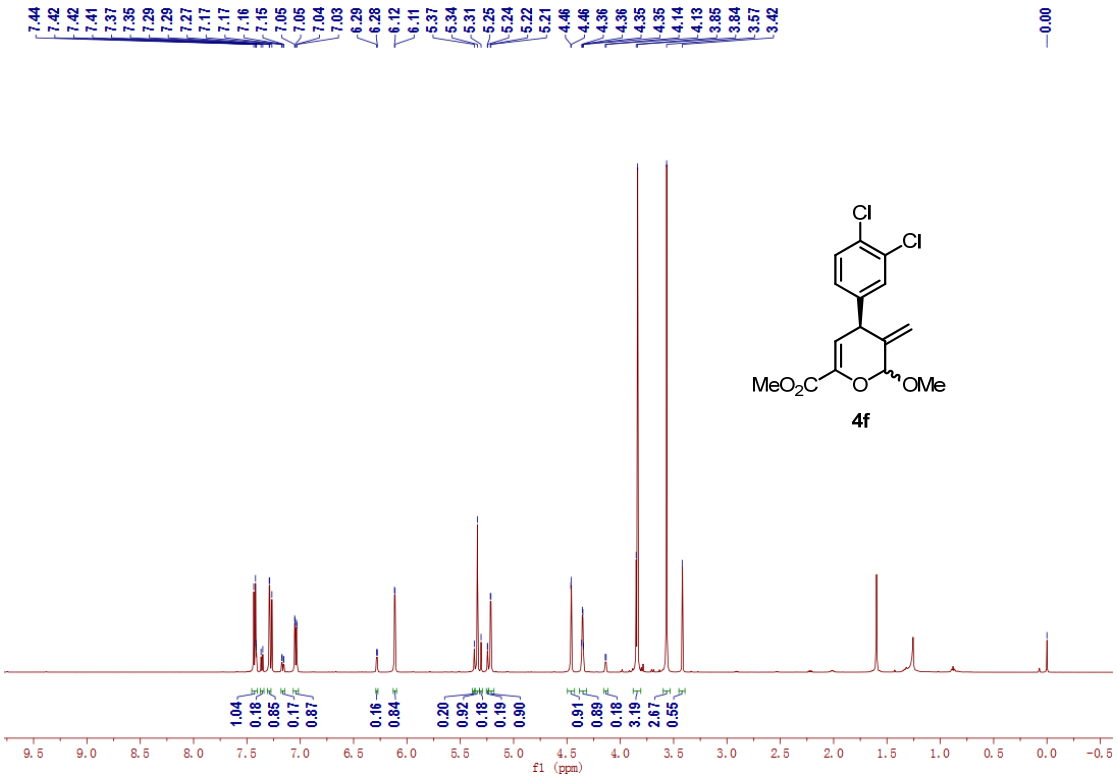
42.65
41.31
f1 (ppm)
Cl
MeO2C
O
OMe
4e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7.04
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6.11
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5.31
5.25
5.24
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4.46
4.36
4.36
4.35
4.35
4.14
4.13
3.85
3.84
3.57
3.42
0.00
Cl
Cl
MeO2C
O
OMe
4f
1.04
0.18
0.85
0.17
0.87
0.16
0.84
0.20
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0.91
0.89
0.18
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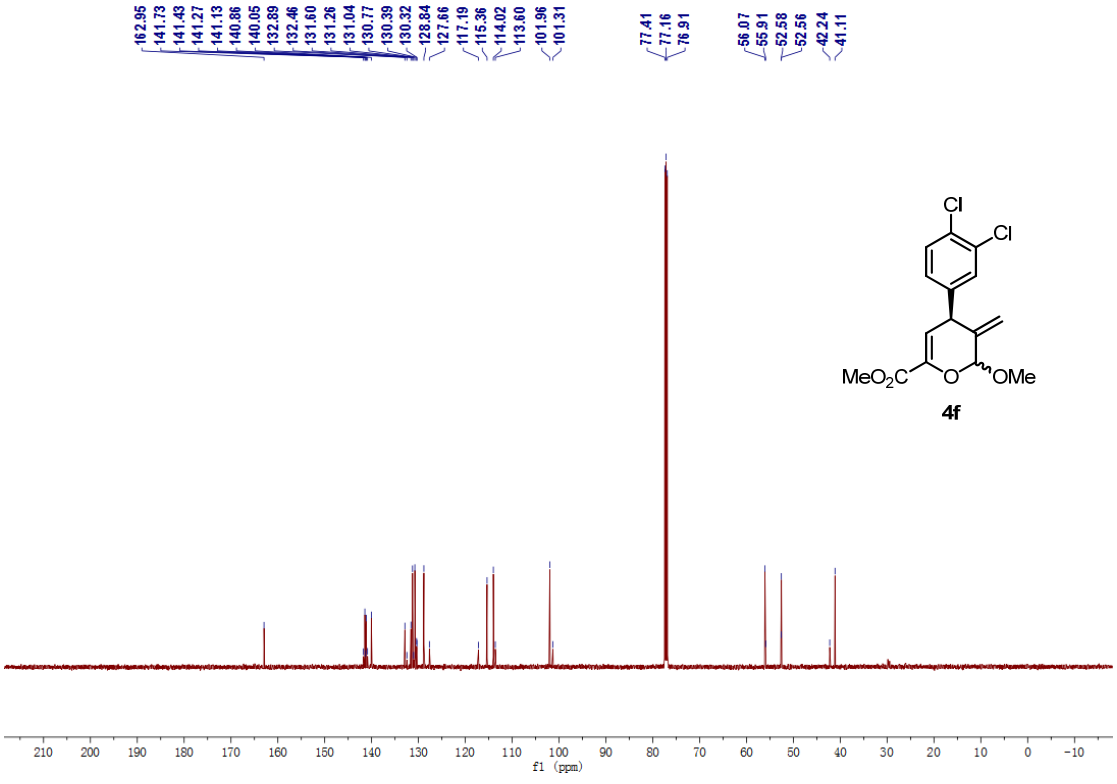
f1 (ppm)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101.31
77.41
77.16
76.91
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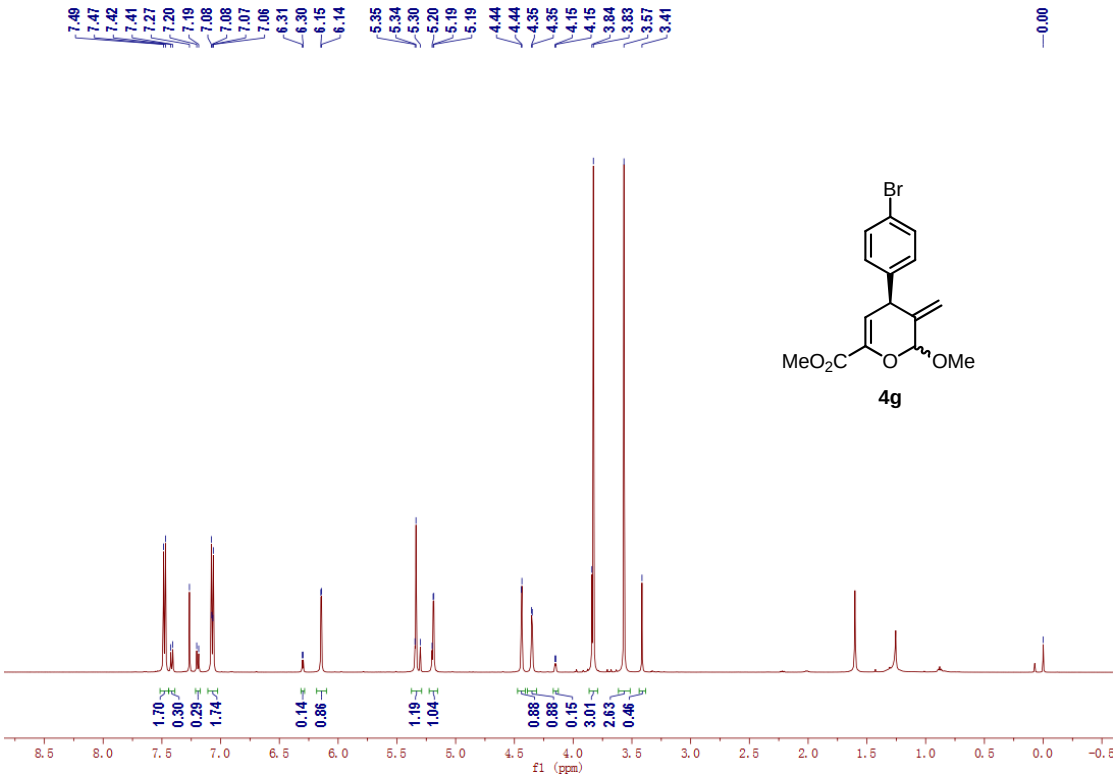
52.56
42.24
41.11
Cl
Cl
MeO2C
O
OMe
4f
f1 (ppm)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6.15
6.14
5.35
5.34
5.30
5.20
5.19
5.19
4.44
4.44
4.35
4.35
4.15
4.15
3.84
3.83
3.57
3.41
0.00
Br
MeO2C
O
OMe
4g
1.70
0.30
0.29
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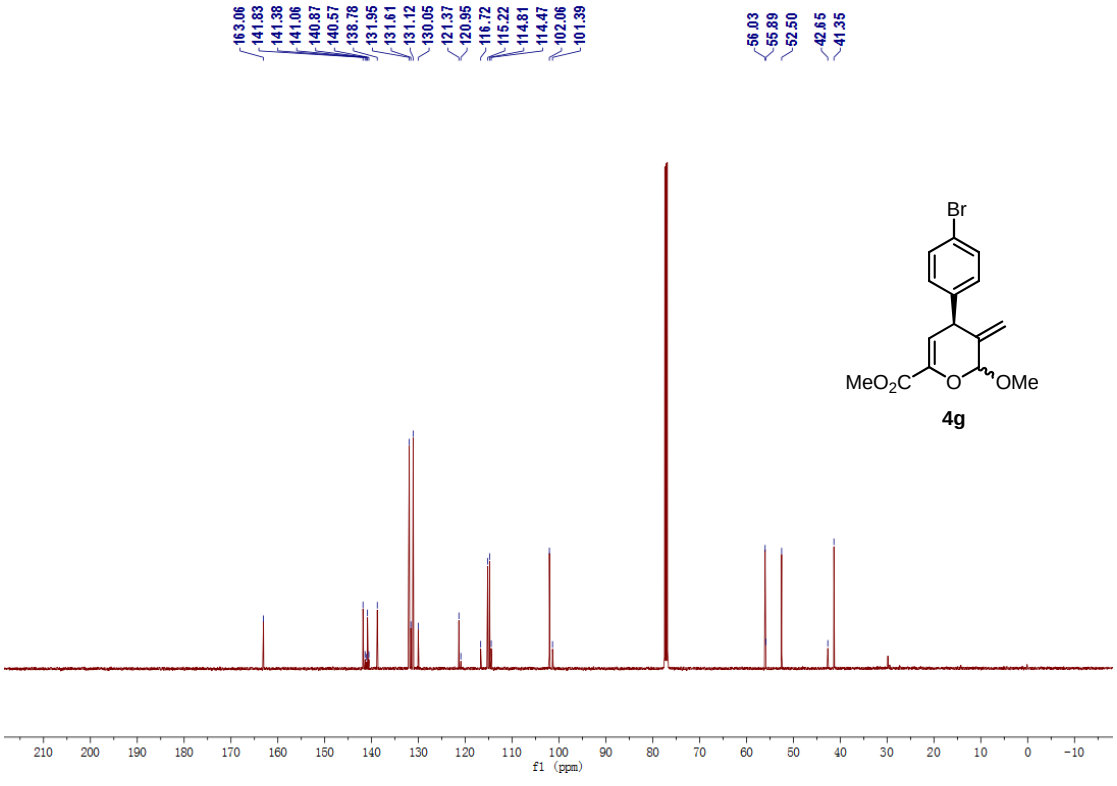
0.88
0.88
0.15
3.01
2.63
0.46
f1 (ppm)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115.22
114.81
114.47
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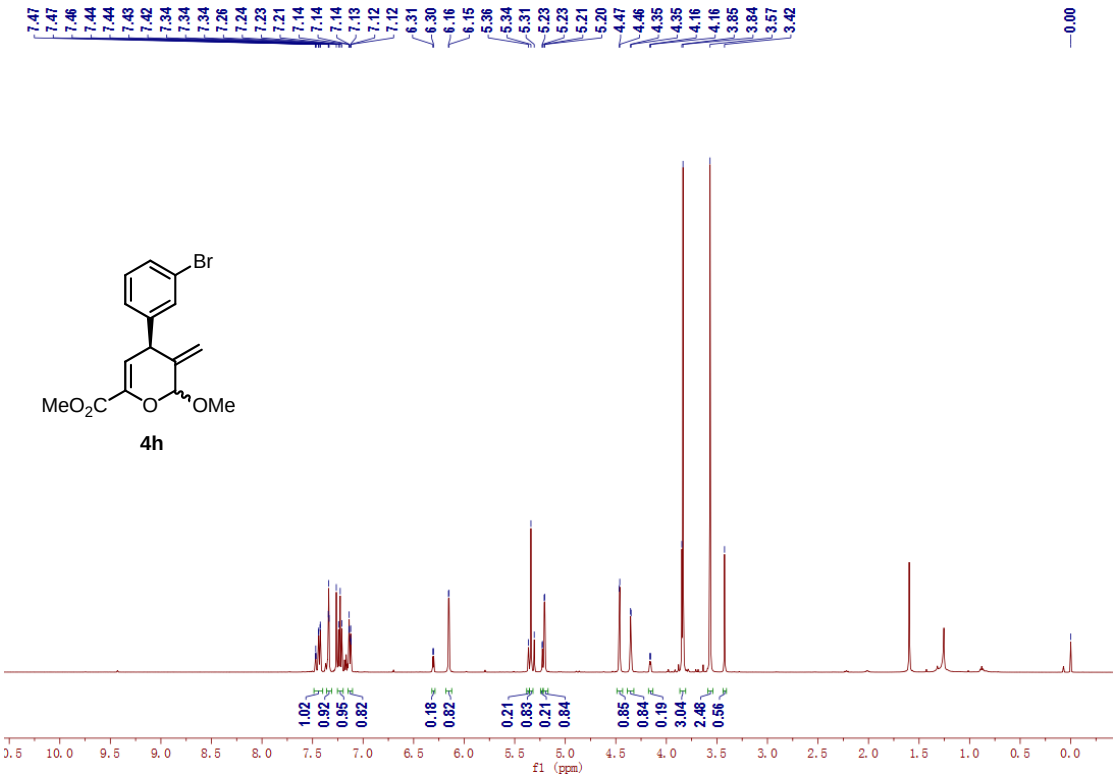
42.65
41.35
Br
MeO2C
O
OMe
4g
f1 (ppm)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Br
MeO2C
O
OMe
4h
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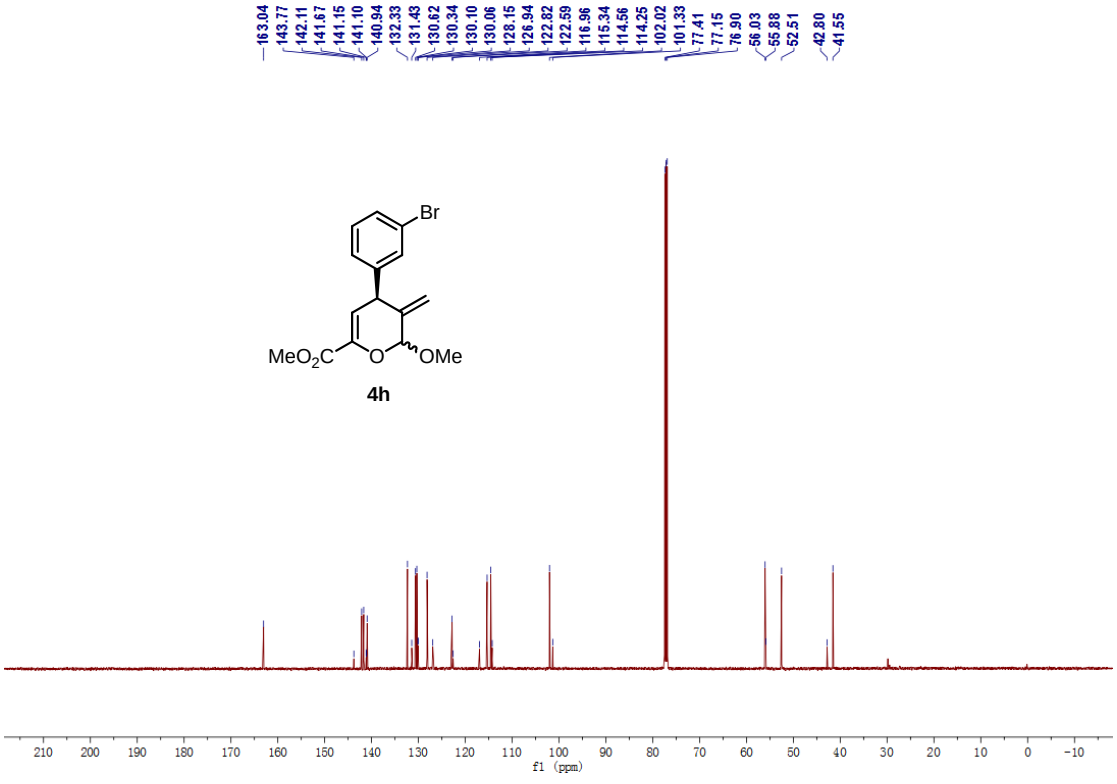
f1 (ppm)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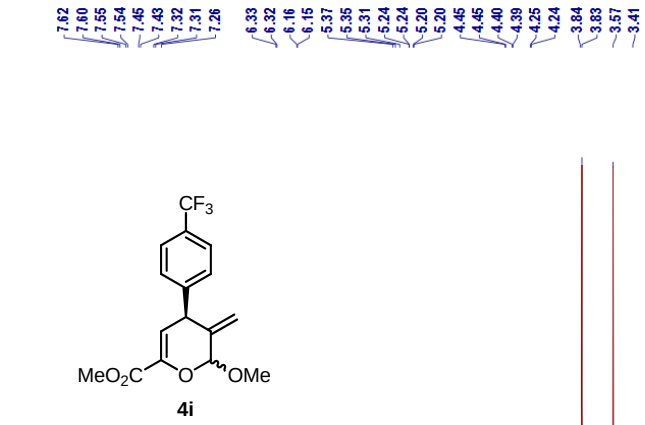
Br
MeO2C
O
OMe
4h
f1 (ppm)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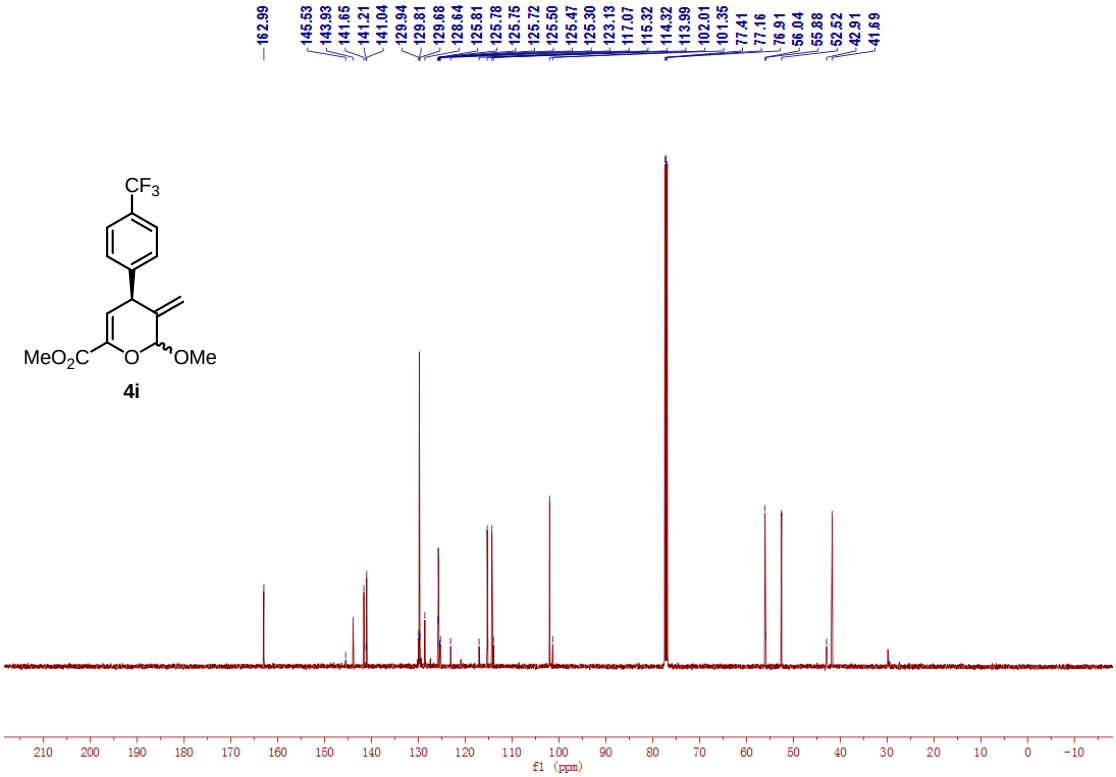
6.33
6.32
6.16
6.15
5.37
5.35
5.31
5.24
5.24
5.20
5.20
4.45
4.45
4.40
4.39
4.25
4.24
3.84
3.83
3.57
3.41
CF3
MeO2C
O
OMe
4i
1.84
0.26
0.28
1.83
0.12
0.88
0.16
0.90
0.14
0.93
0.92
0.93
0.13
3.16
2.76
0.41
f1 (ppm)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125.50
125.47
125.30
123.13
117.07
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114.32
113.99
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101.35
77.41
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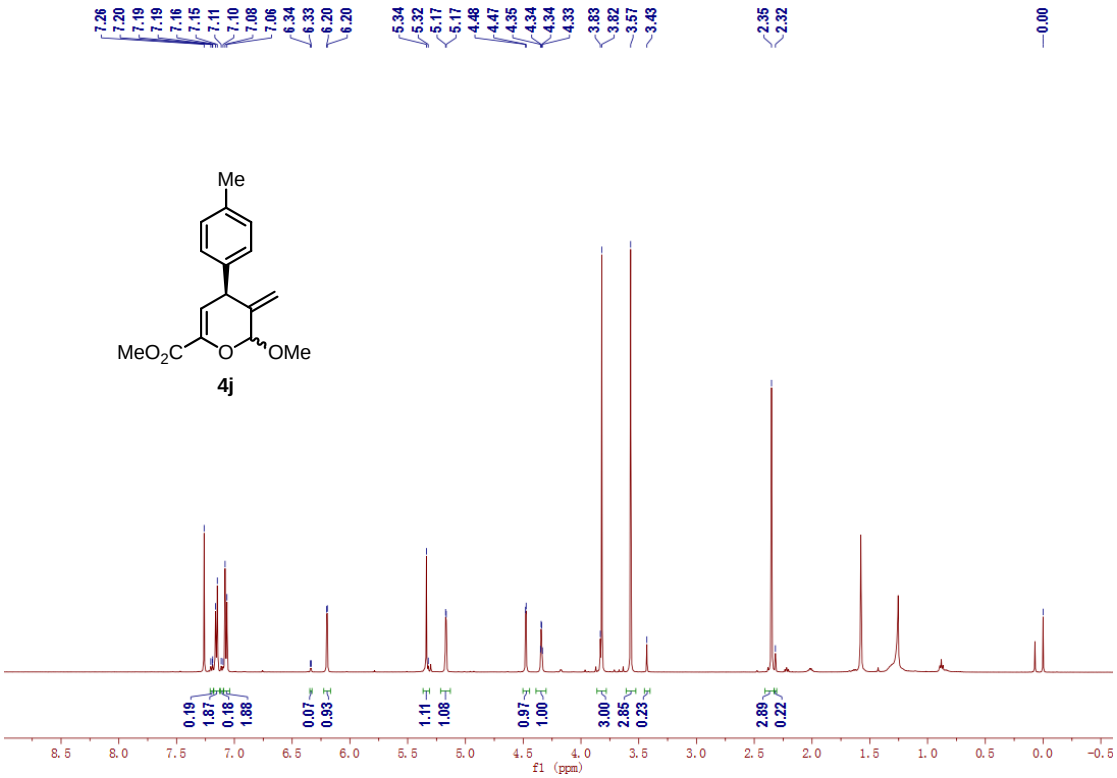
42.91
41.69
CF3
MeO2C
O
OMe
4i
f1 (ppm)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6.20
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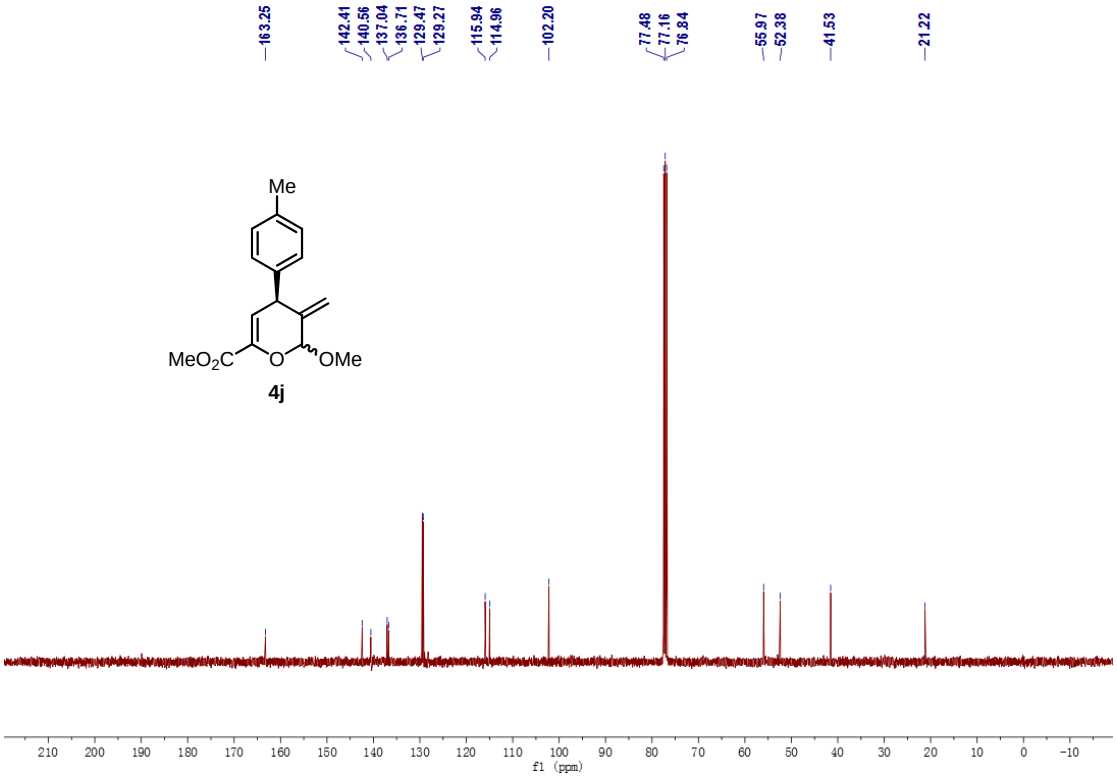
5.34
5.32
5.17
5.17
4.48
4.47
4.35
4.34
4.34
4.33
3.83
3.82
3.57
3.43
2.35
2.32
0.00
Me
MeO2C
O
OMe
4j
0.19
1.87
0.18
1.88
0.07
0.93
1.11
1.08
0.97
1.00
3.00
2.85
0.23
2.89
0.22
f1 (ppm)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102.20
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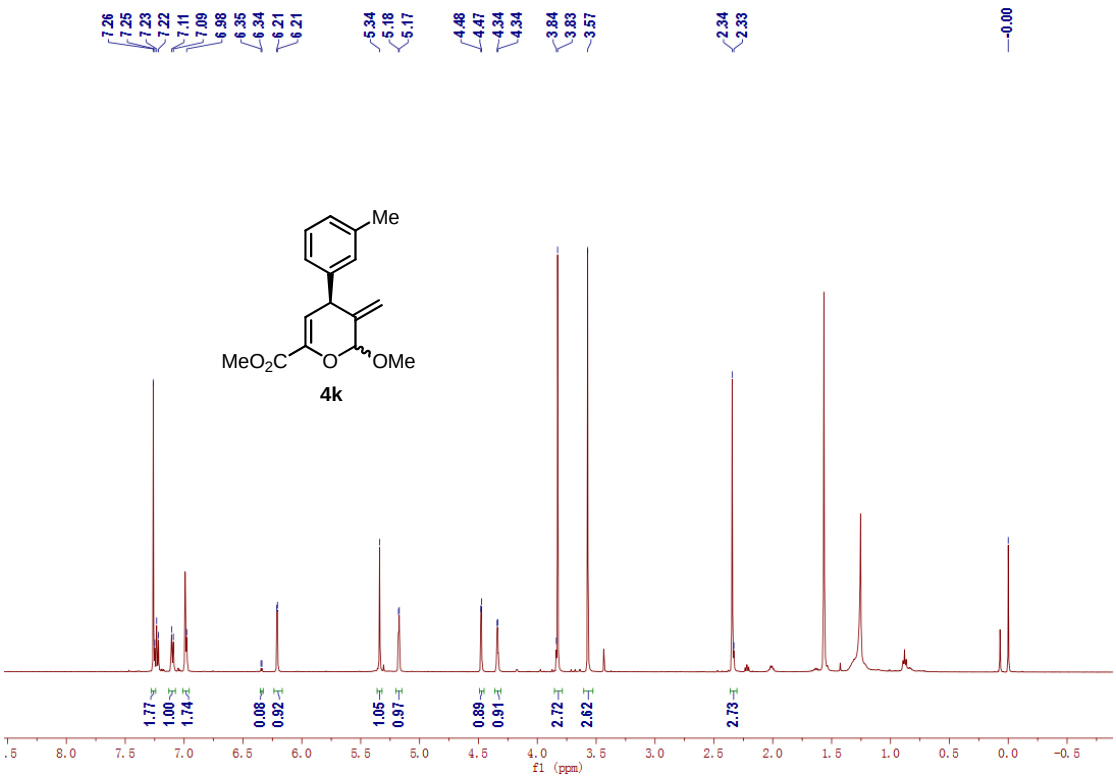
O
OMe
4j
f1 (ppm)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5.18
5.17
4.48
4.47
4.34
4.34
3.84
3.83
3.57
2.34
2.33
0.00
Me
MeO2C
O
OMe
4k
1.77
1.00
1.74
0.08
0.92
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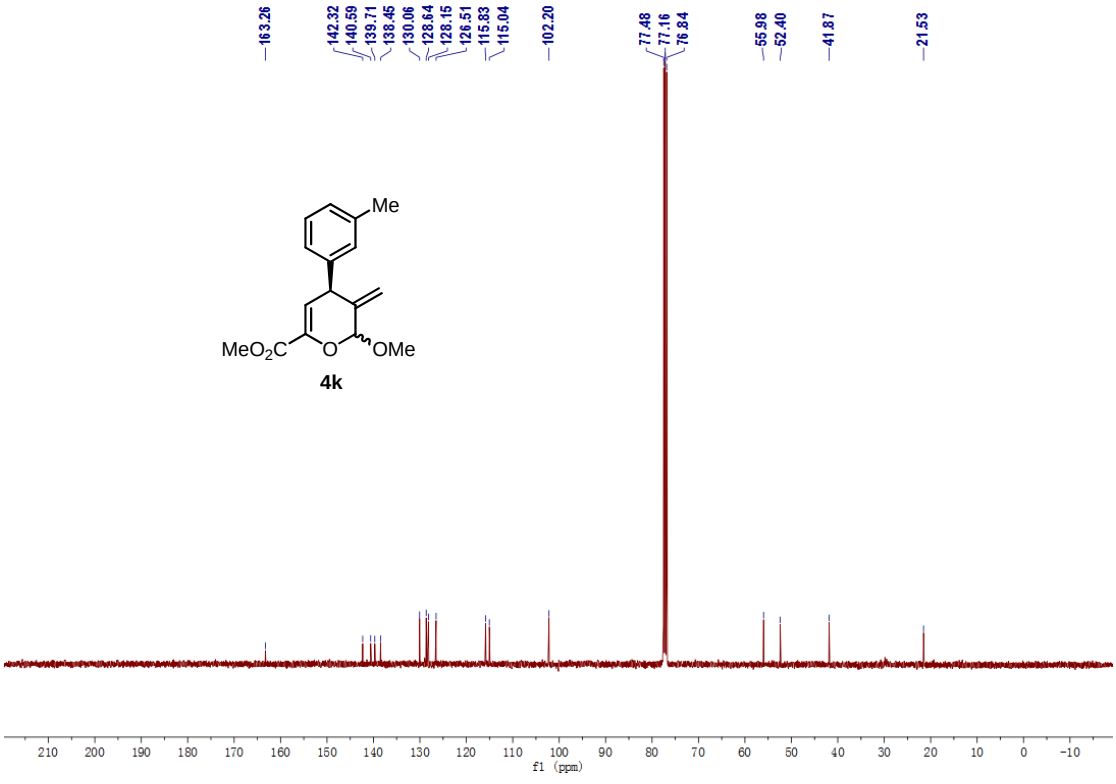
0.97
0.89
0.91
2.72
2.62
2.73
f1 (ppm)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115.83
115.04
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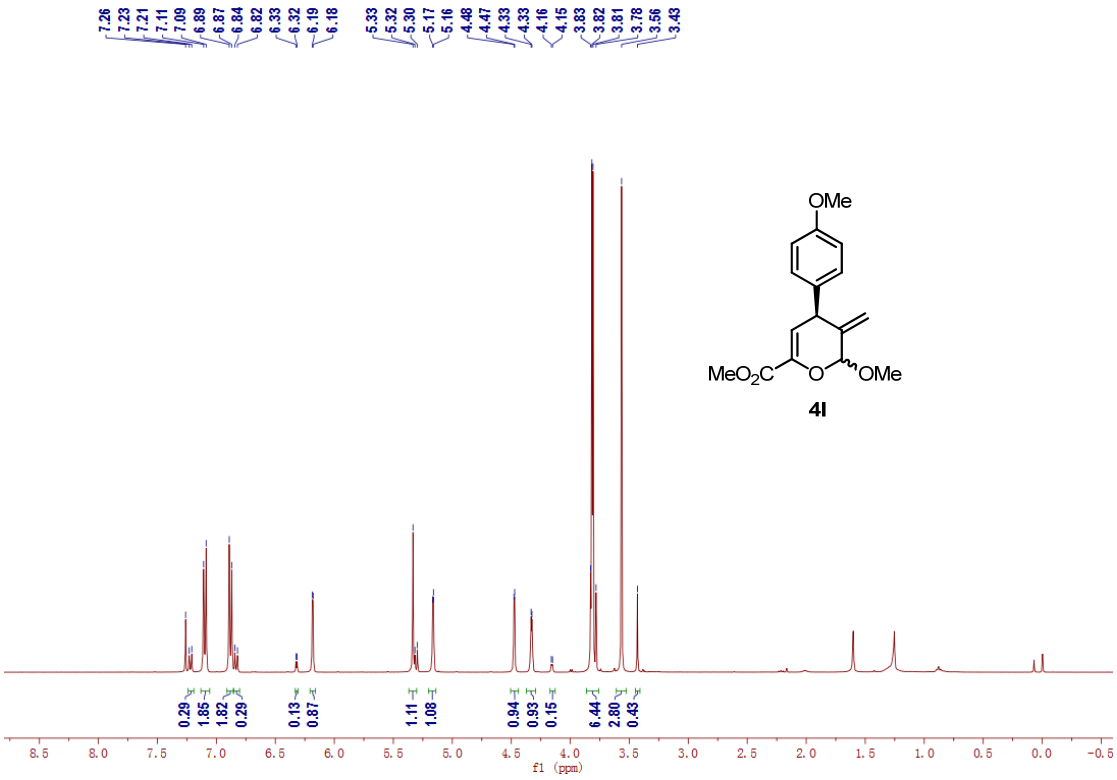
76.84
55.98
52.40
41.87
21.53
Me
MeO2C
O
OMe
4k
f1 (ppm)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6.18
5.33
5.32
5.30
5.17
5.16
4.48
4.47
4.33
4.33
4.16
4.15
3.83
3.82
3.81
3.78
3.56
3.43
OMe
MeO2C
O
OMe
4l
0.29
1.85
1.82
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0.13
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1.11
1.08
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0.93
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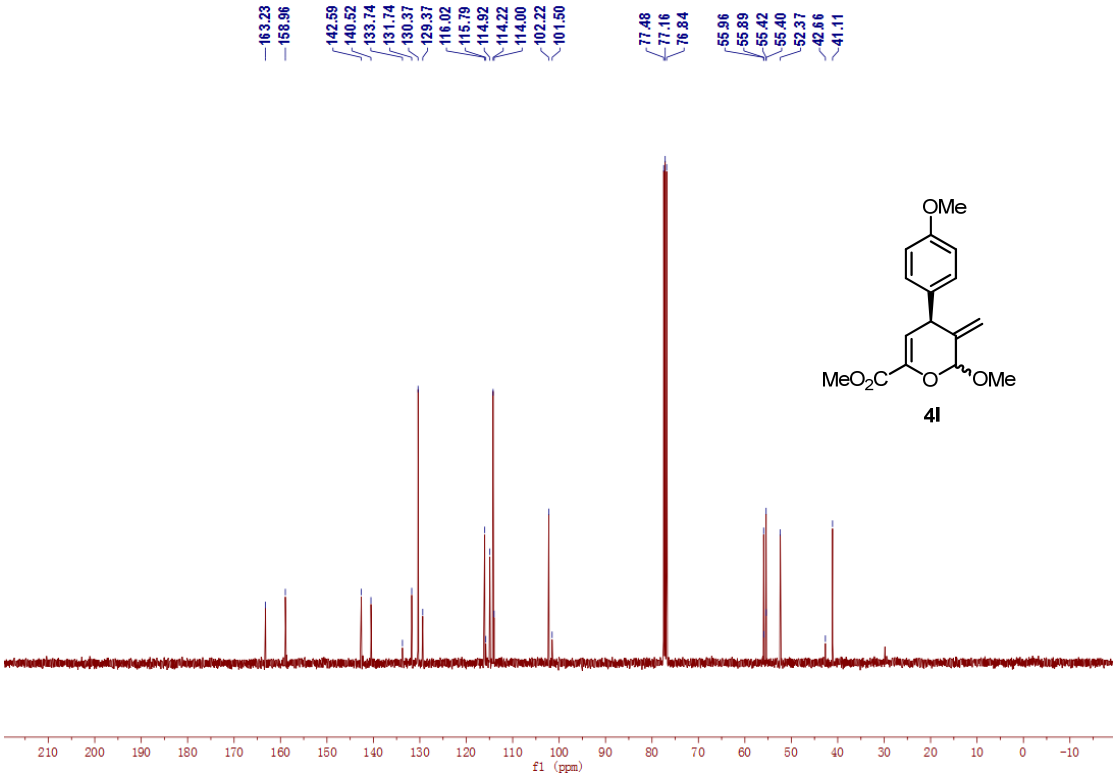
0.43
f1 (ppm)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114.00
102.22
101.50
77.48
77.16
76.84
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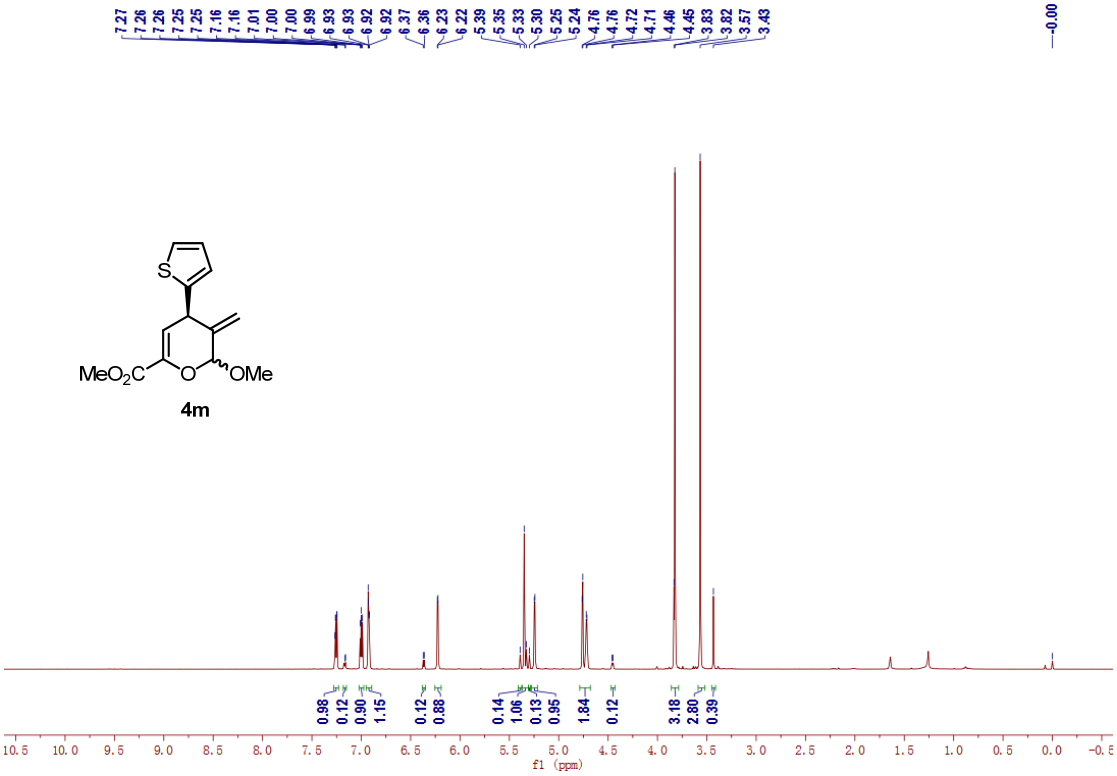
55.40
52.37
42.66
41.11
OMe
MeO2C
O
OMe
4l
f1 (ppm)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7.00
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6.92
6.92
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6.36
6.23
6.22
5.39
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5.33
5.30
5.25
5.24
4.76
4.76
4.72
4.71
4.46
4.45
3.83
3.82
3.57
3.43
0.00
S
MeO2C
O
OMe
4m
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0.12
0.90
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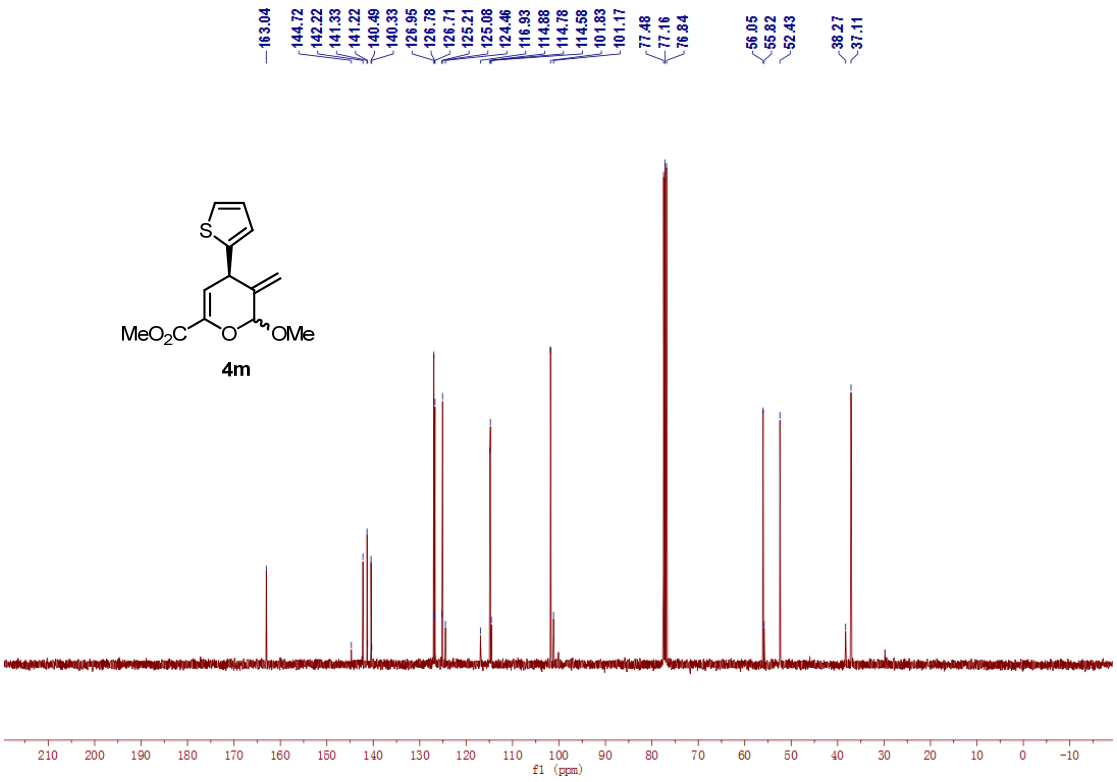
1.06
0.13
0.95
1.84
0.12
3.18
2.80
0.39
f1 (ppm)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125.08
124.46
116.93
114.88
114.78
114.58
101.83
101.17
77.48
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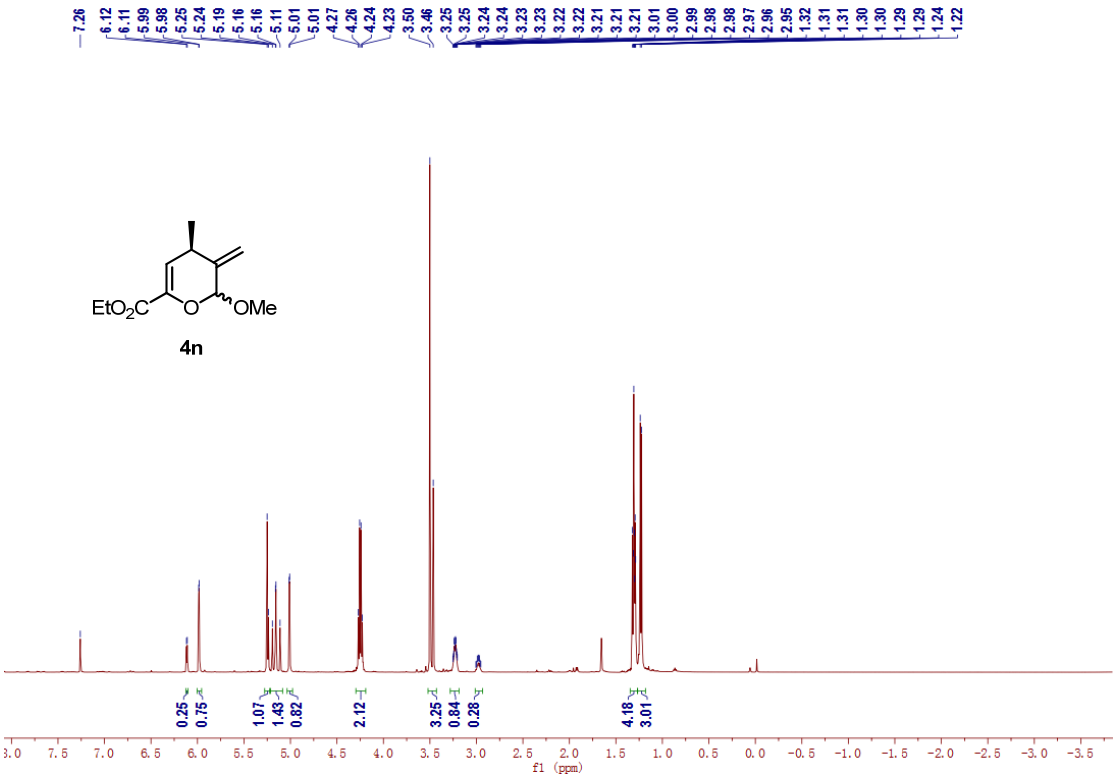
55.82
52.43
38.27
37.11
S
MeO2C
O
OMe
4m
f1 (ppm)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5.01
5.01
4.27
4.26
4.24
4.23
3.50
3.46
3.25
3.25
3.24
3.24
3.23
3.23
3.22
3.22
3.21
3.21
3.21
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2.97
2.96
2.95
1.32
1.31
1.31
1.30
1.30
1.29
1.29
1.24
1.22
EtO2C
O
OMe
4n
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2.12
3.25
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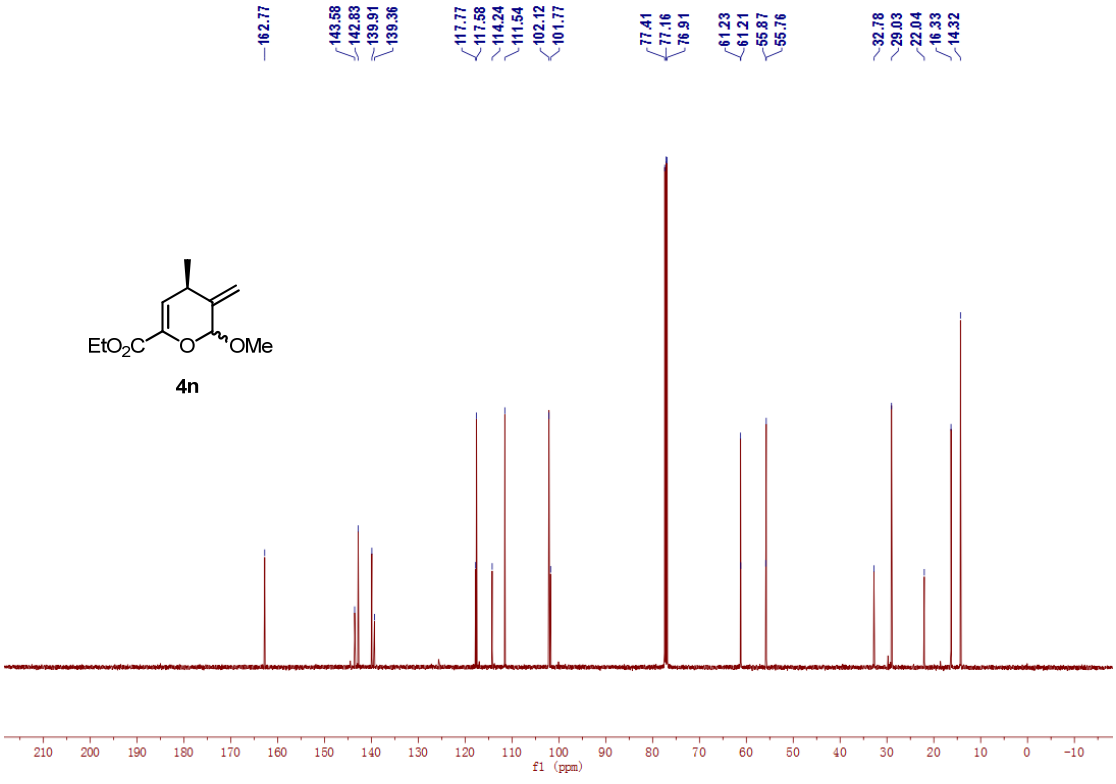
0.28
4.18
3.01
f1 (ppm)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61.23
61.21
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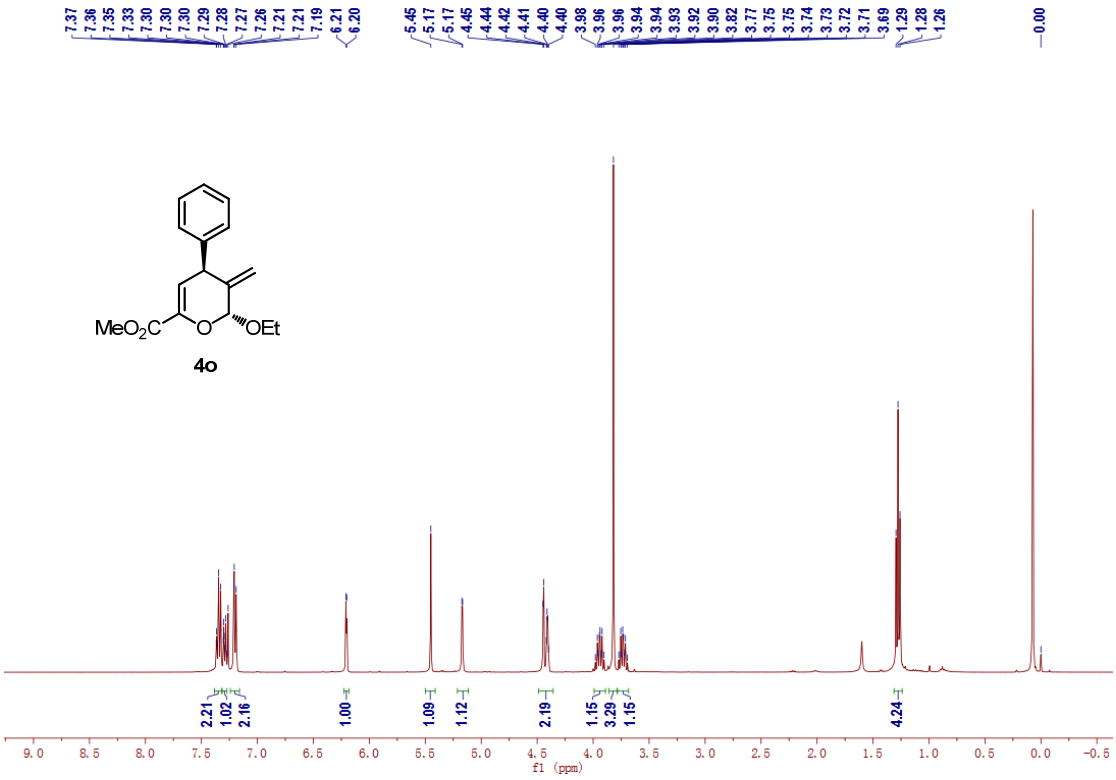
32.78
29.03
22.04
16.33
14.32
EtO2C
O
OMe
4n
f1 (ppm)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6.20
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5.17
5.17
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4.44
4.42
4.41
4.40
4.40
3.98
3.96
3.96
3.94
3.94
3.93
3.92
3.90
3.82
3.77
3.75
3.75
3.74
3.73
3.72
3.71
3.69
1.29
1.28
1.26
0.00
MeO2C
OEt
4o
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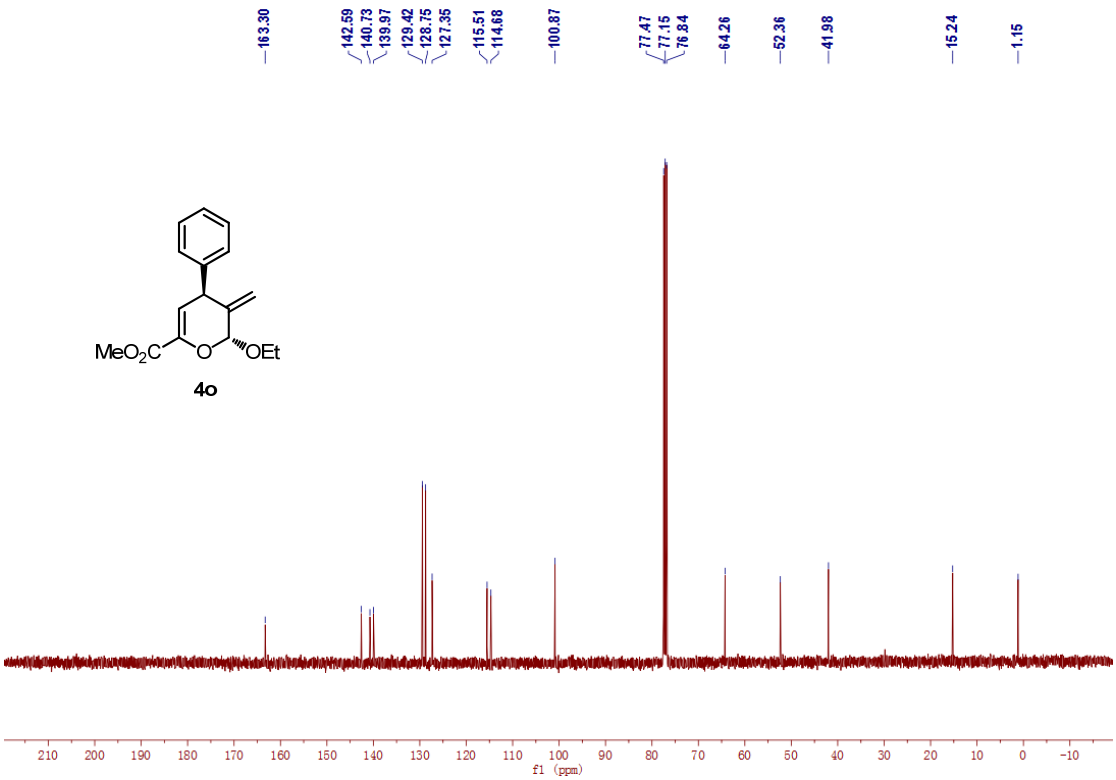
1.00
1.09
1.12
2.19
1.15
3.29
1.15
4.24
f1 (ppm)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100.87
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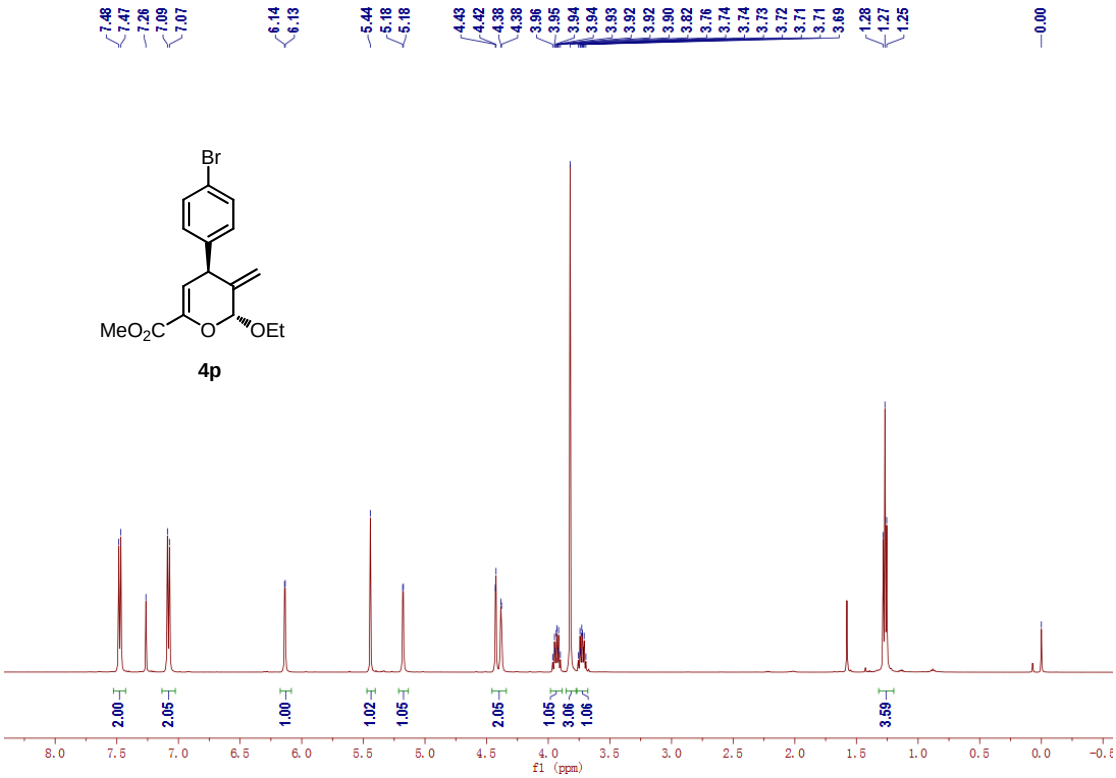
64.26
52.36
41.98
15.24
1.15
MeO2C
OEt
4o
f1 (ppm)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5.18
4.43
4.42
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4.38
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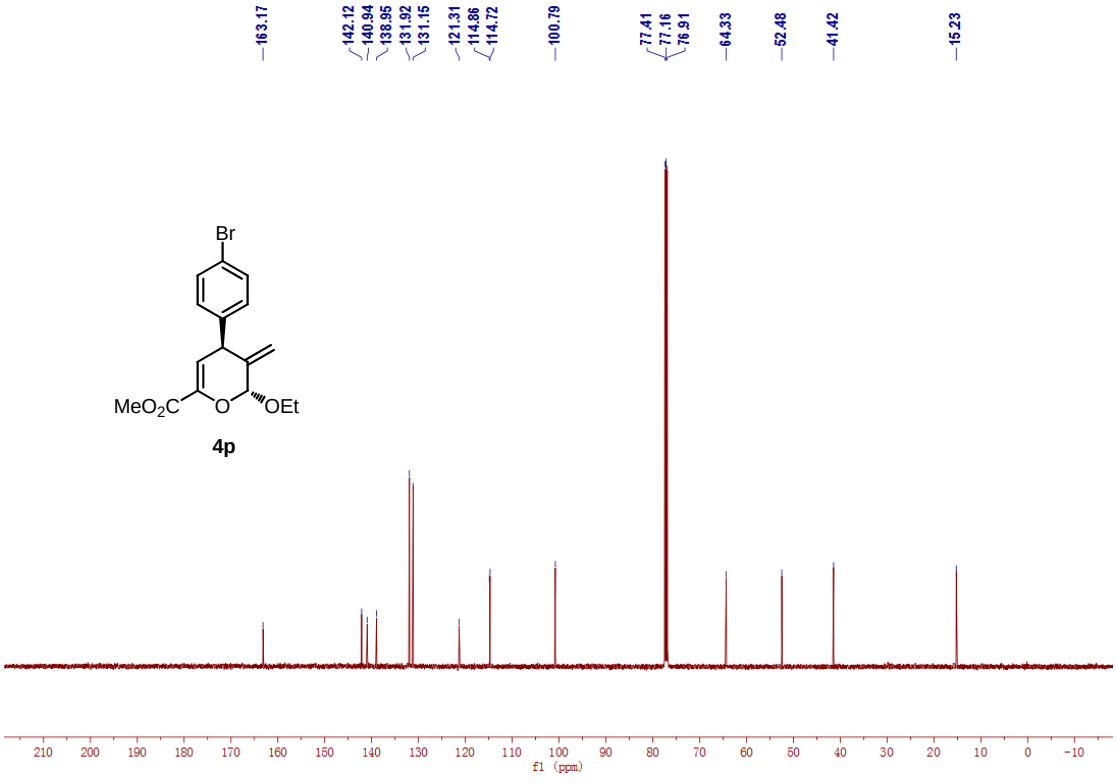
3.95
3.94
3.94
3.93
3.92
3.92
3.90
3.82
3.76
3.74
3.74
3.73
3.72
3.71
3.71
3.69
1.28
1.27
1.25
0.00
Br
MeO2C
O
OEt
4p
2.00
2.05
1.00
1.02
1.05
2.05
1.05
3.06
1.06
3.59
f1 (ppm)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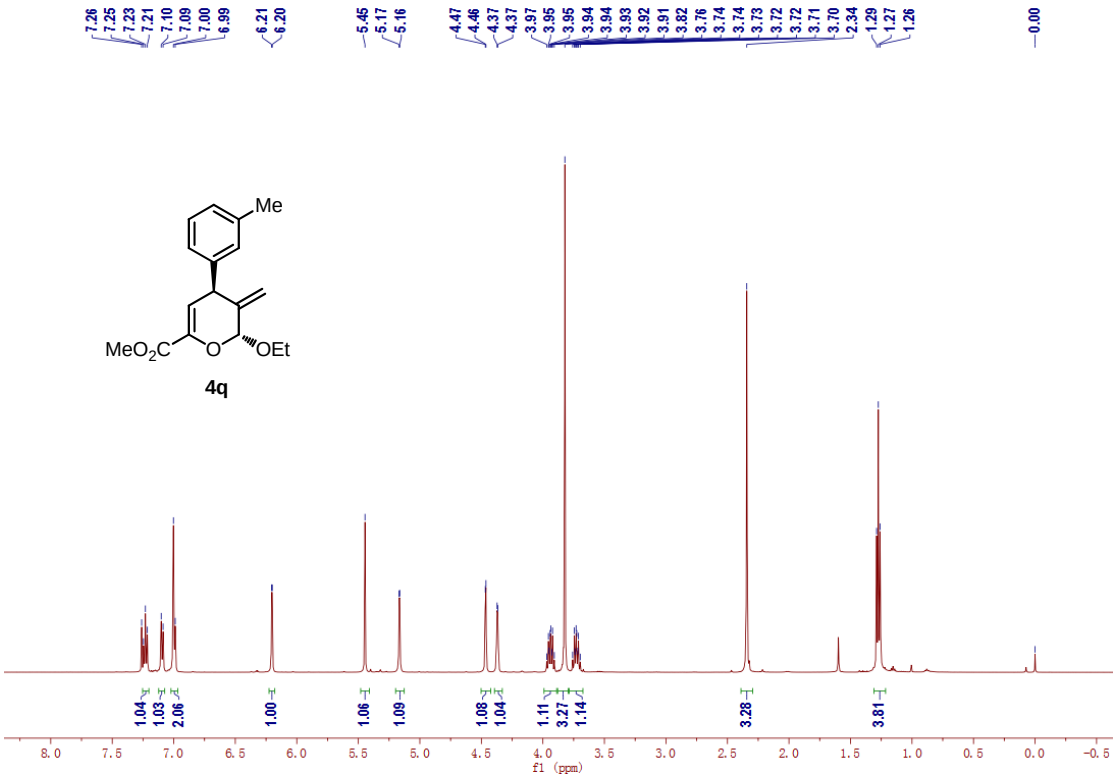
64.33
52.48
41.42
15.23
Br
MeO2C
O
OEt
4p
f1 (ppm)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4.46
4.37
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3.97
3.95
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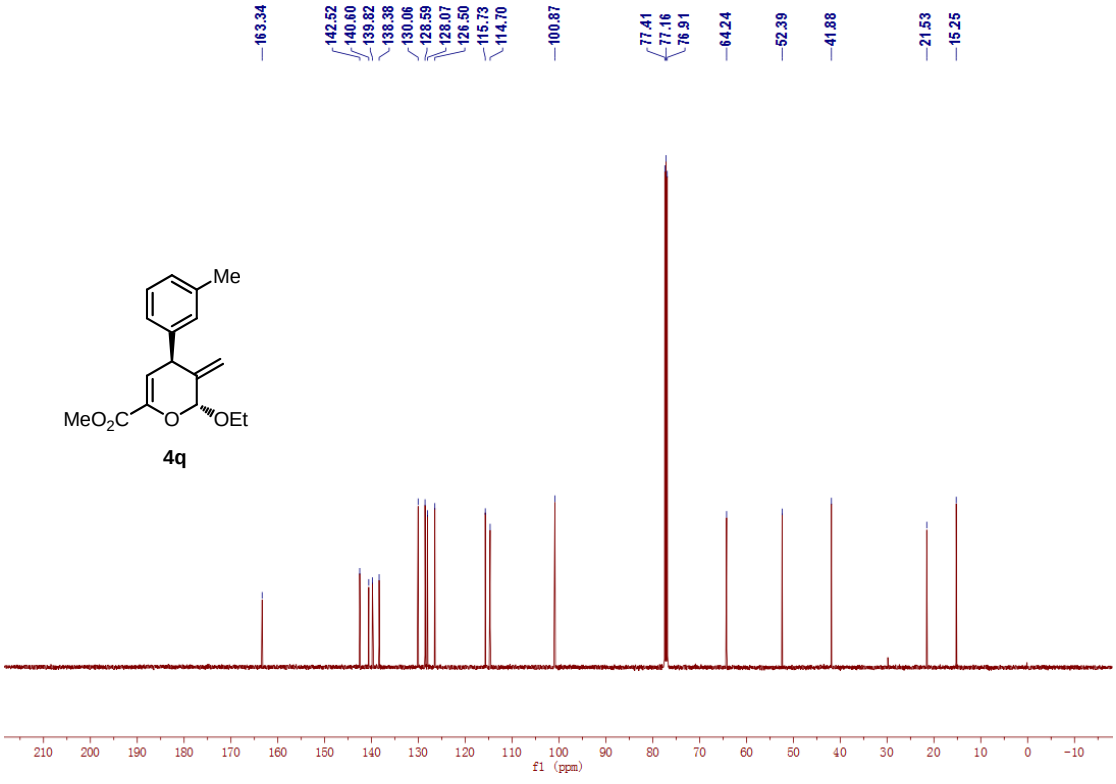
3.94
3.94
3.93
3.92
3.91
3.82
3.76
3.74
3.74
3.73
3.72
3.72
3.71
3.70
2.34
1.29
1.27
1.26
0.00
Me
MeO2C
O
OEt
4q
1.04
1.03
2.06
1.00
1.06
1.09
1.08
1.04
1.11
3.27
1.14
3.28
3.81
f1 (ppm)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139.82
138.38
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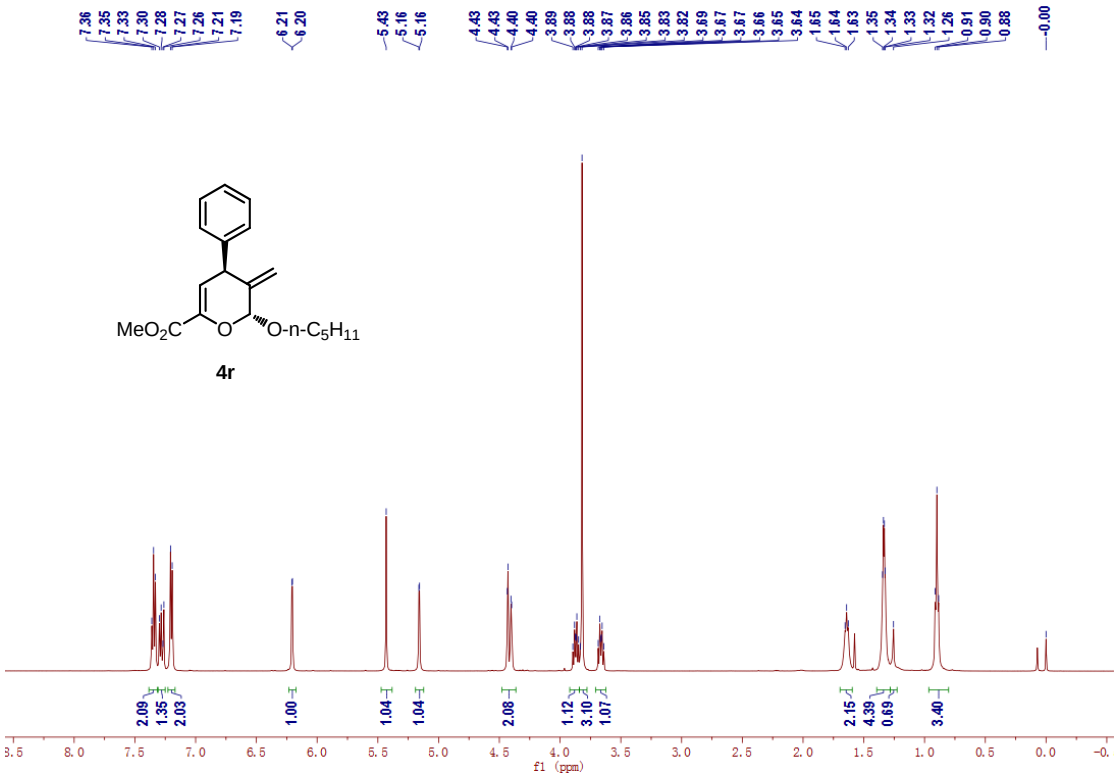
128.59
128.07
126.50
115.73
114.70
100.87
77.41
77.16
76.91
64.24
52.39
41.88
21.53
15.25
Me
MeO2C
O
OEt
4q
f1 (ppm)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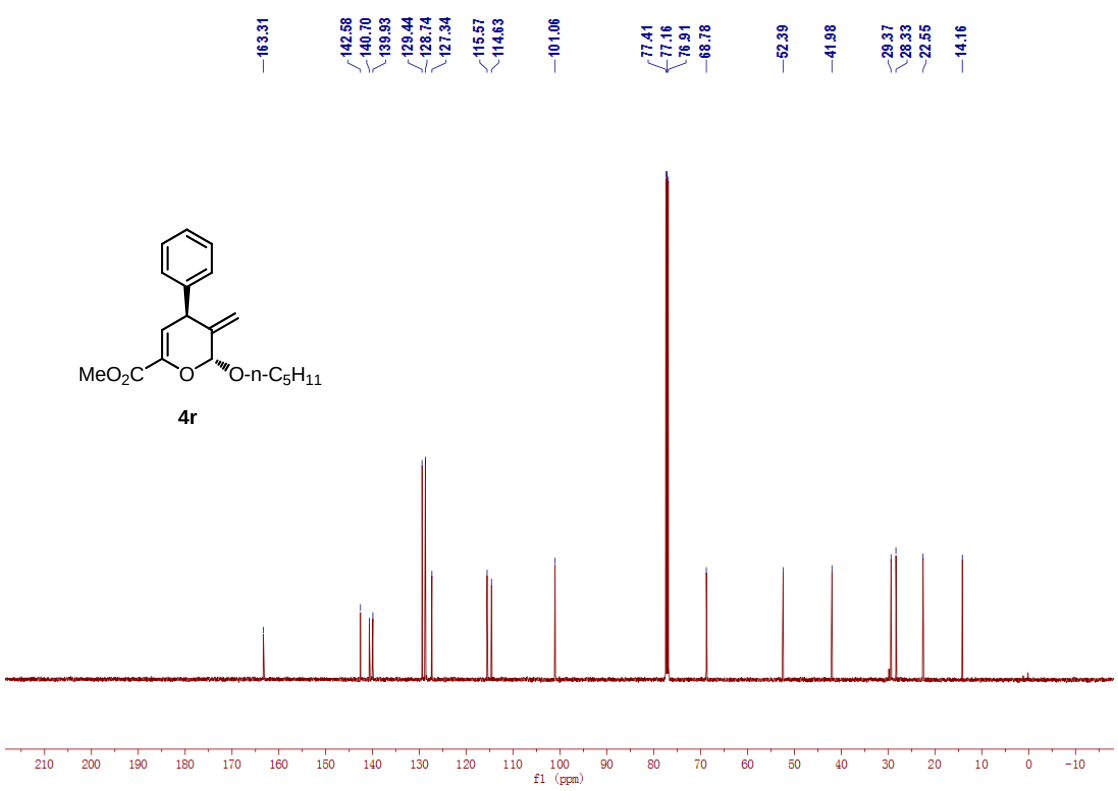
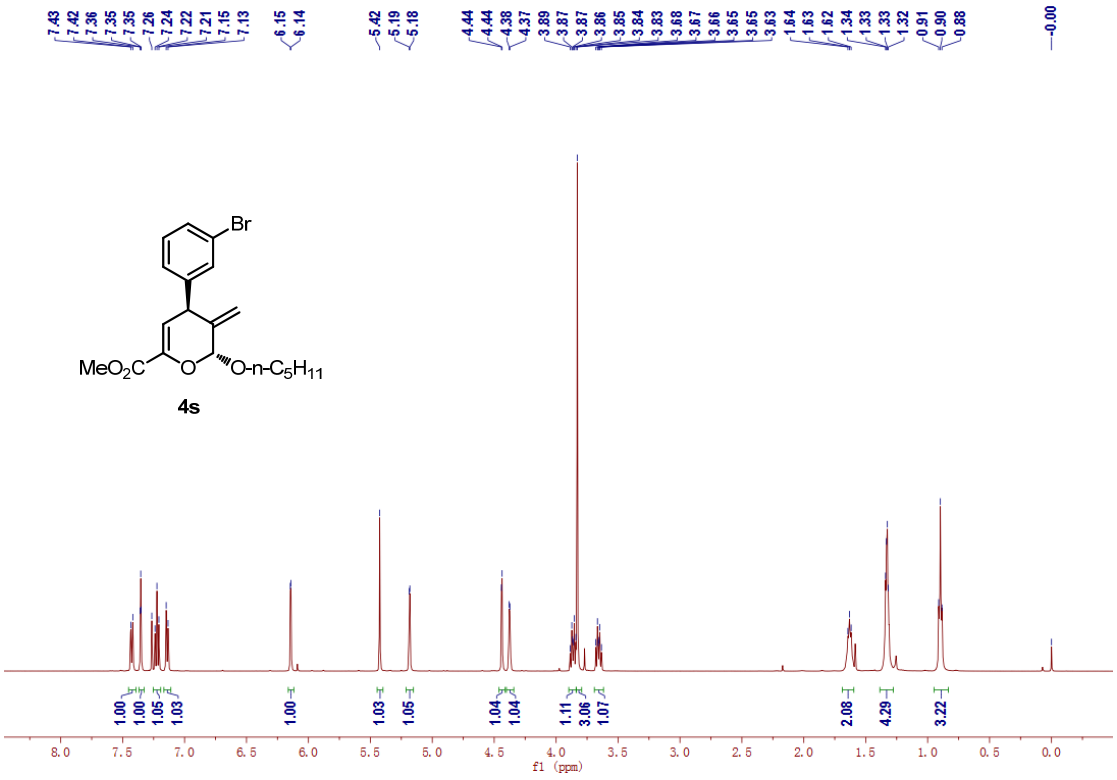
6.21 6.20
5.43 5.16 5.16
4.43 4.43 4.40 4.40 3.89 3.88 3.88 3.87 3.86 3.85 3.83 3.82 3.69 3.67 3.67 3.66 3.65 3.64
1.65 1.64 1.63 1.35 1.34 1.33 1.32 1.26 0.91 0.90 0.88
0.00
MeO2C
O
O-n-C5H11
4r
2.09 1.35 2.03 1.00 1.04 1.04 2.08 1.12 3.10 1.07 2.15 4.39 0.69 3.40
f1 (ppm)


163.31
142.58 140.70 139.93 129.44 128.74 127.34 115.57 114.63 101.06 77.41 77.16 76.91 68.78 52.39 41.98 29.37 28.33 22.55 14.16
MeO2C
O
O-n-C5H11
4r
f1 (ppm)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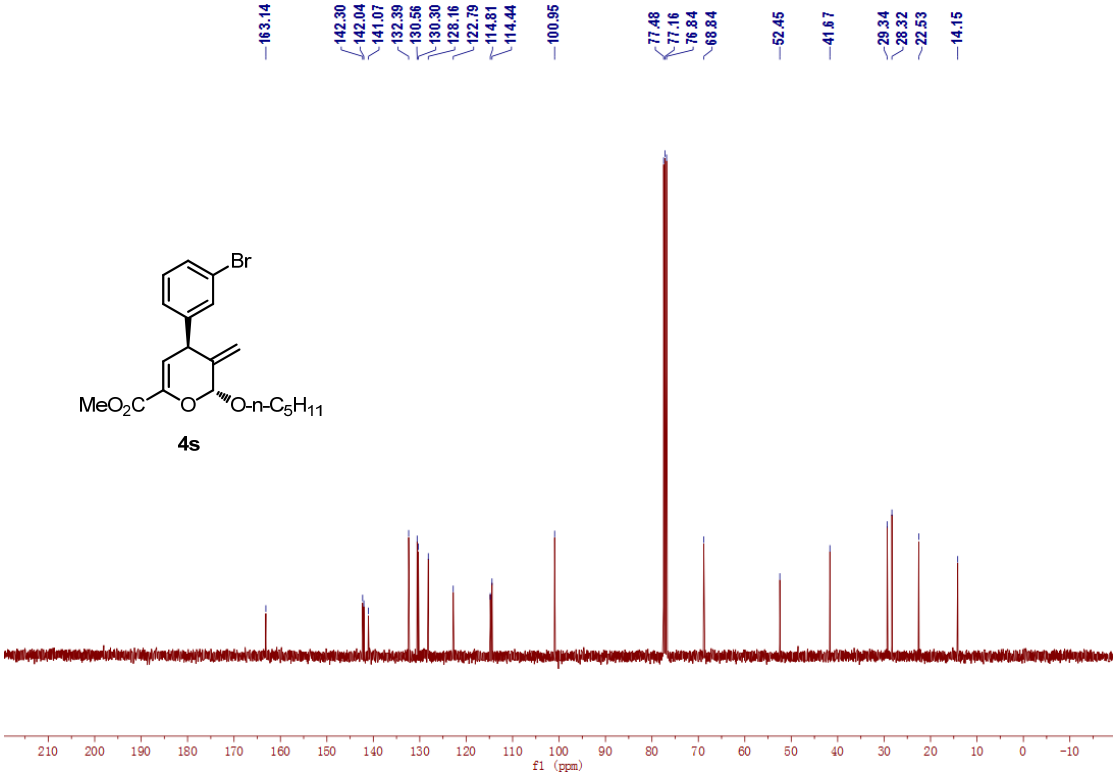
6.15
6.14
5.42
5.19
5.18
4.44
4.44
4.38
4.37
3.89
3.87
3.87
3.86
3.85
3.84
3.83
3.68
3.67
3.66
3.65
3.63
1.64
1.63
1.62
1.34
1.33
1.33
1.32
0.91
0.90
0.88
0.00
Br
MeO2C
O
O-n-C5H11
4s
1.00
1.00
1.05
1.03
1.00
1.03
1.05
1.04
1.04
1.11
3.06
1.07
2.08
4.29
3.22
f1 (ppm)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130.56
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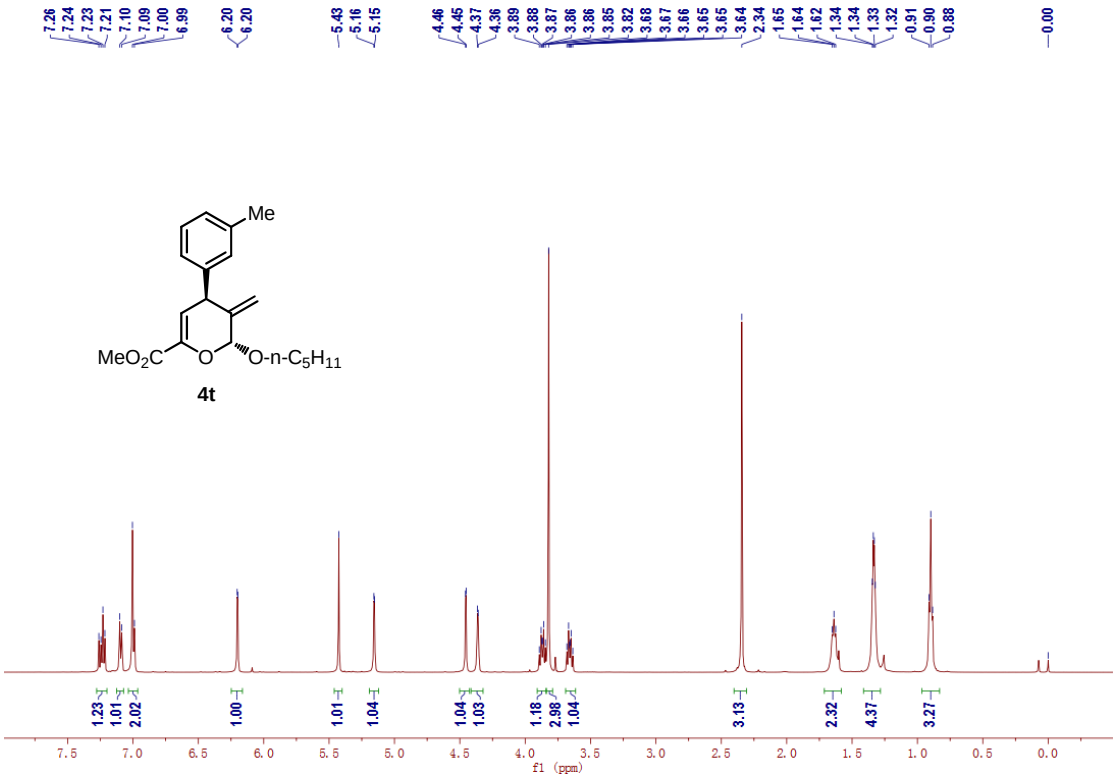
128.16
122.79
114.81
114.44
100.95
77.48
77.16
76.84
68.84
52.45
41.67
29.34
28.32
22.53
14.15
Br
MeO2C
O
O-n-C5H11
4s
f1 (ppm)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6.20
6.20
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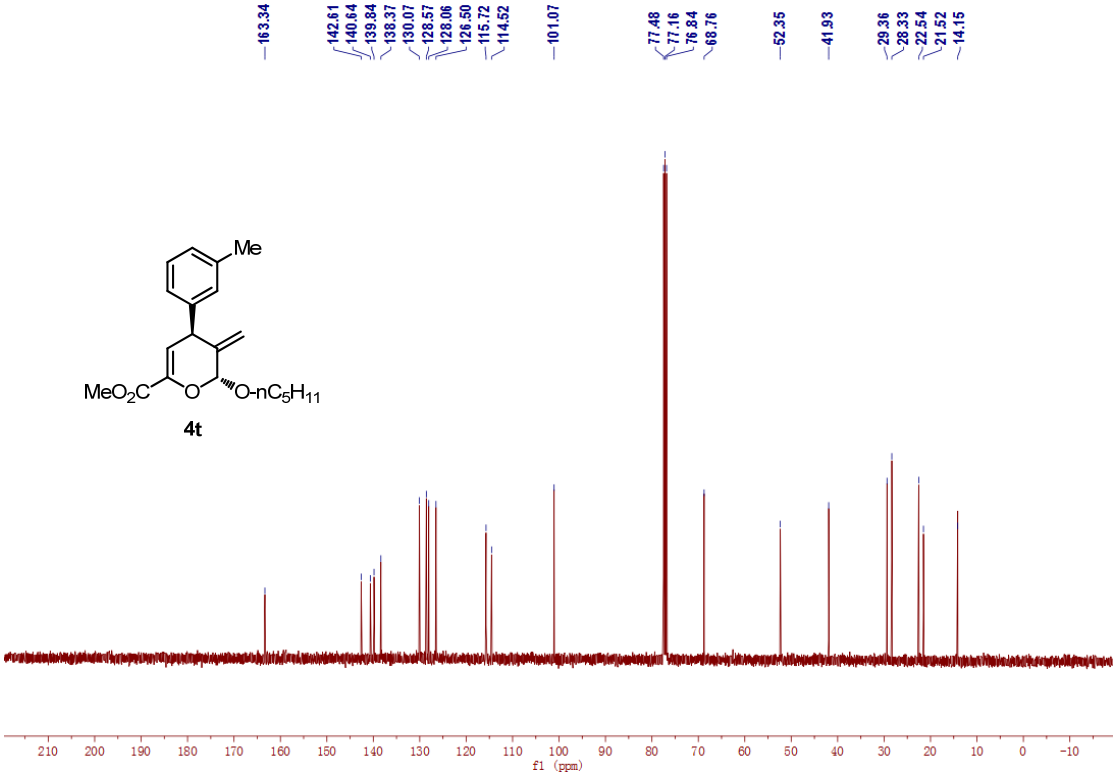
5.16
5.15
4.46
4.45
4.37
4.36
3.89
3.88
3.87
3.86
3.86
3.85
3.82
3.68
3.67
3.66
3.65
3.65
3.64
2.34
1.65
1.64
1.62
1.34
1.34
1.33
1.32
0.91
0.90
0.88
0.00
Me
MeO2C
O
O-n-C5H11
4t
1.23
1.01
2.02
1.00
1.01
1.04
1.04
1.03
1.18
2.98
1.04
3.13
2.32
4.37
3.27
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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138.37
130.07
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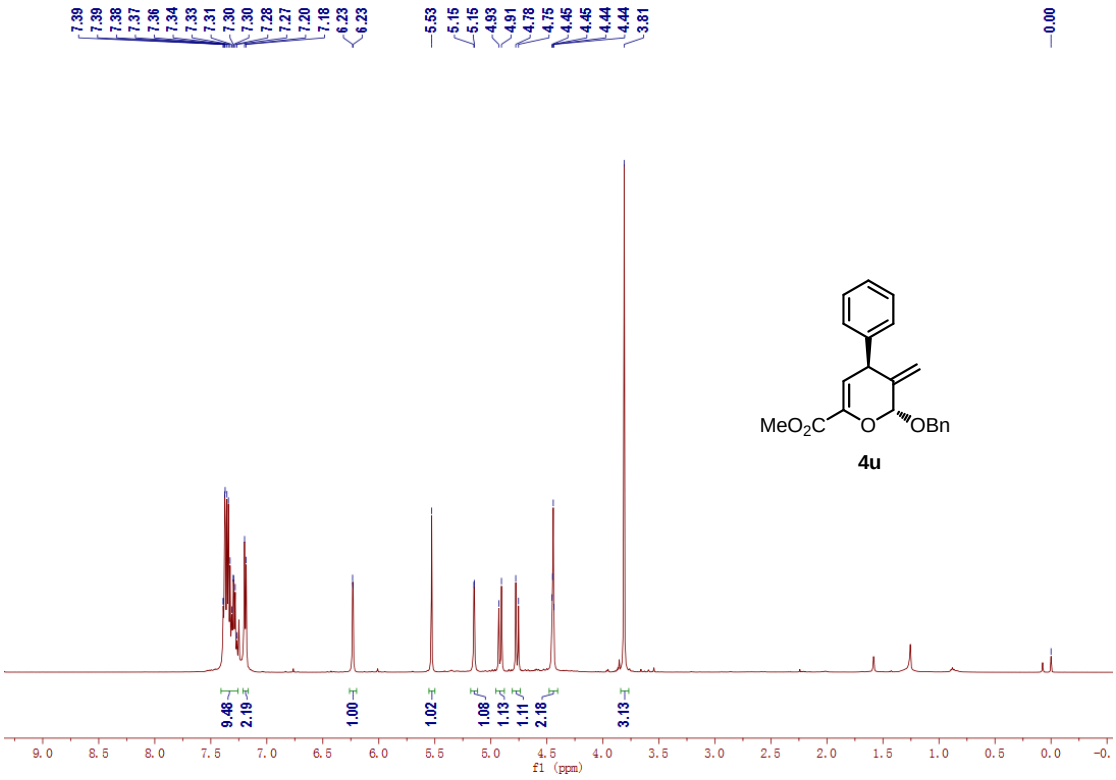
126.50
115.72
114.52
101.07
77.48
77.16
76.84
68.76
52.35
41.93
29.36
28.33
22.54
21.52
14.15
Me
MeO2C
O
O-nC5H11
4t
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.33
7.31
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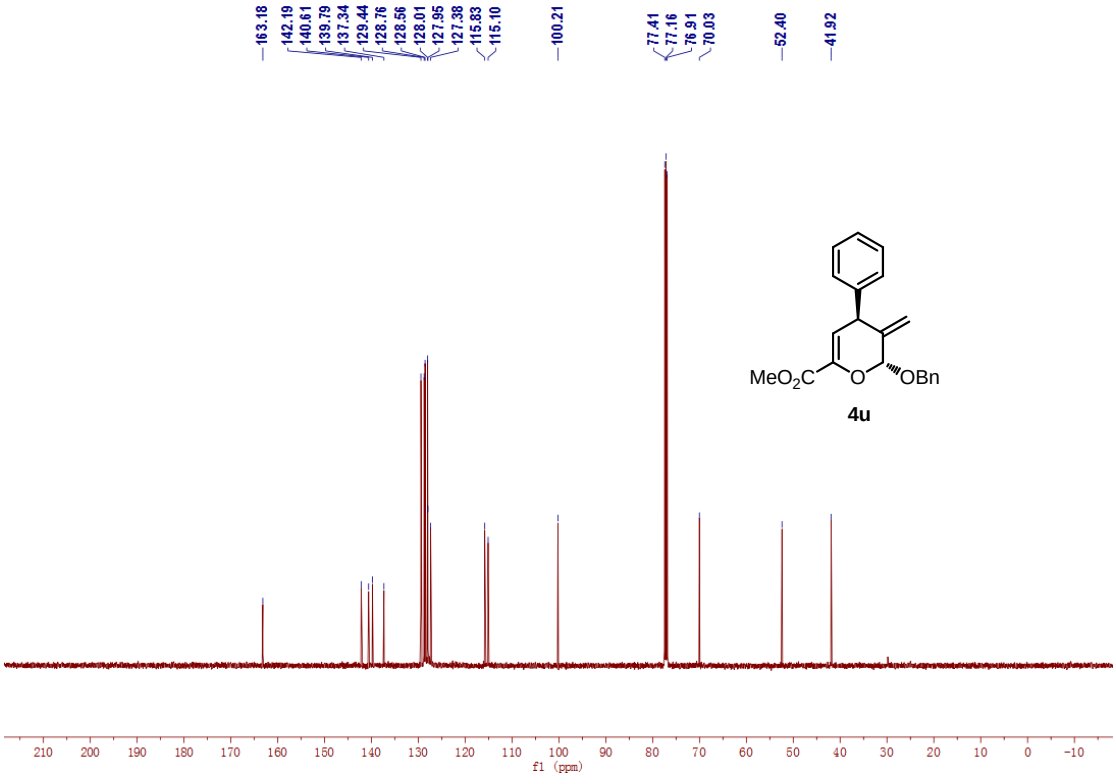
7.30
7.28
7.27
7.20
7.18
6.23
6.23
5.53
5.15
5.15
4.93
4.91
4.78
4.75
4.45
4.45
4.44
4.44
3.81
0.00
MeO2C
O
OBn
4u
9.48
2.19
1.00
1.02
1.08
1.13
1.11
2.18
3.13
f1 (ppm)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137.34
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127.95
127.38
115.83
115.10
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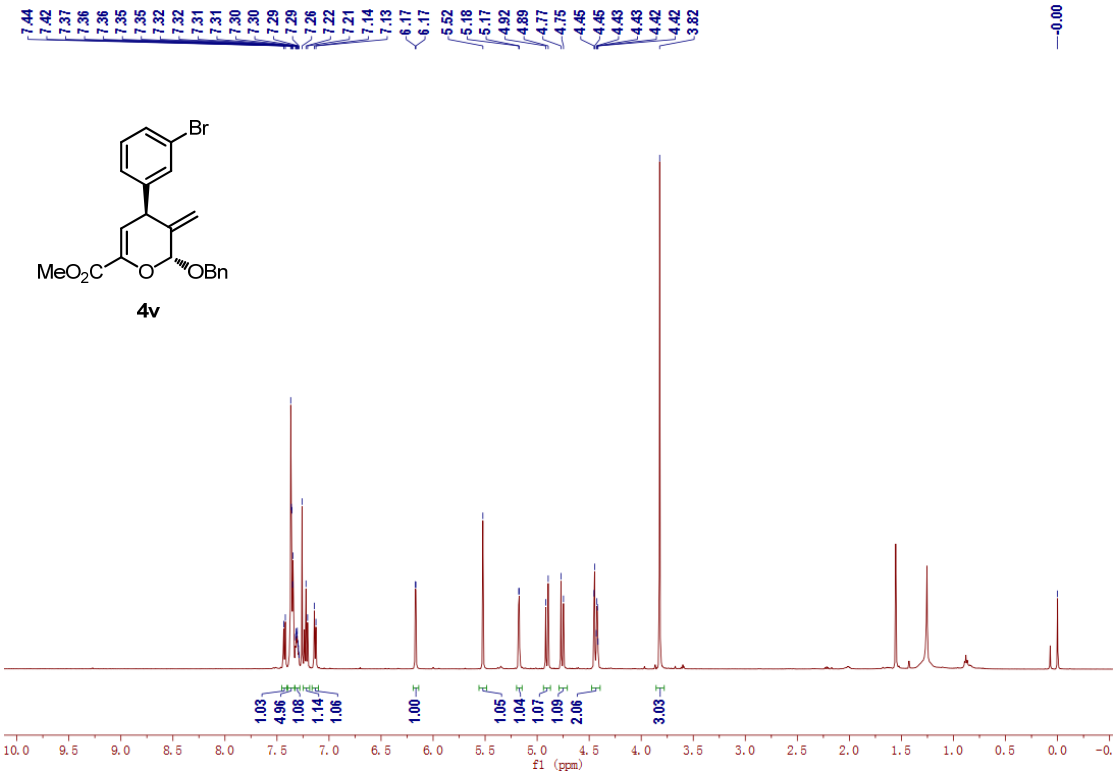
77.16
76.91
70.03
52.40
41.92
MeO2C
O
OBn
4u
f1 (ppm)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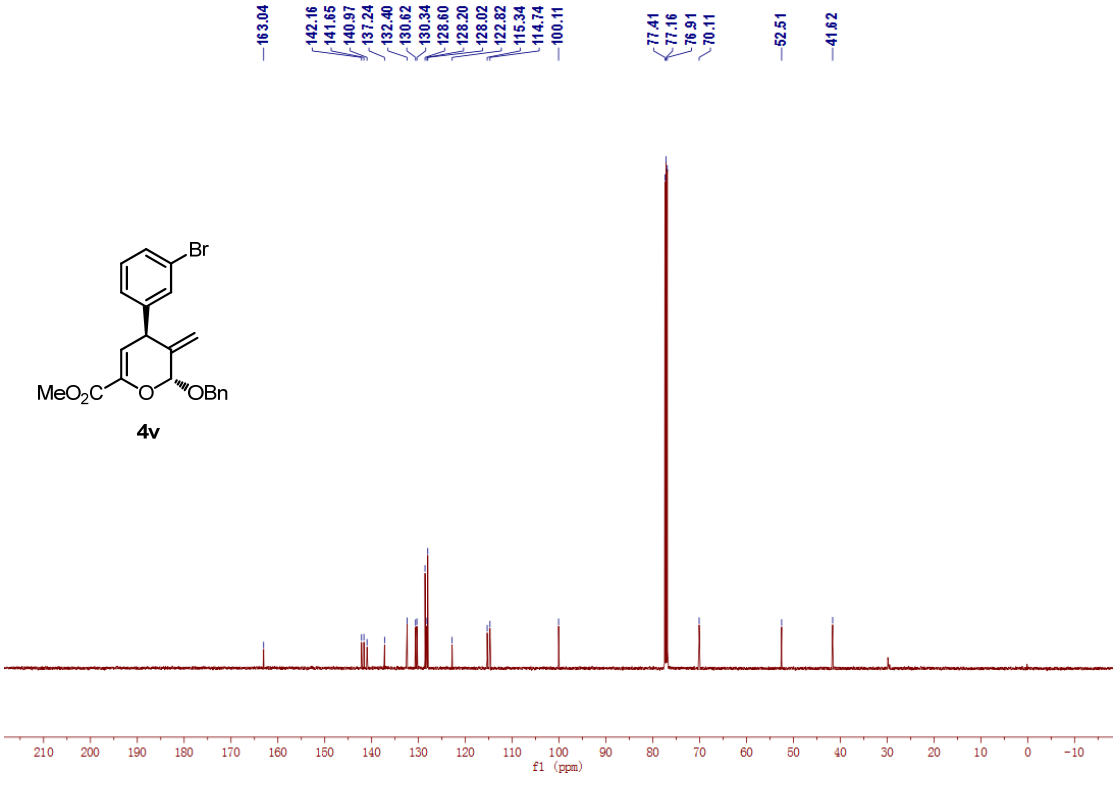
7.31
7.30
7.30
7.29
7.29
7.26
7.22
7.21
7.14
7.13
6.17
6.17
5.52
5.18
5.17
4.92
4.89
4.77
4.75
4.45
4.45
4.43
4.43
4.42
4.42
3.82
0.00
Br
MeO2C
O
OBn
4v
1.03
4.96
1.08
1.14
1.06
1.00
1.05
1.04
1.07
1.09
2.06
3.03
f1 (ppm)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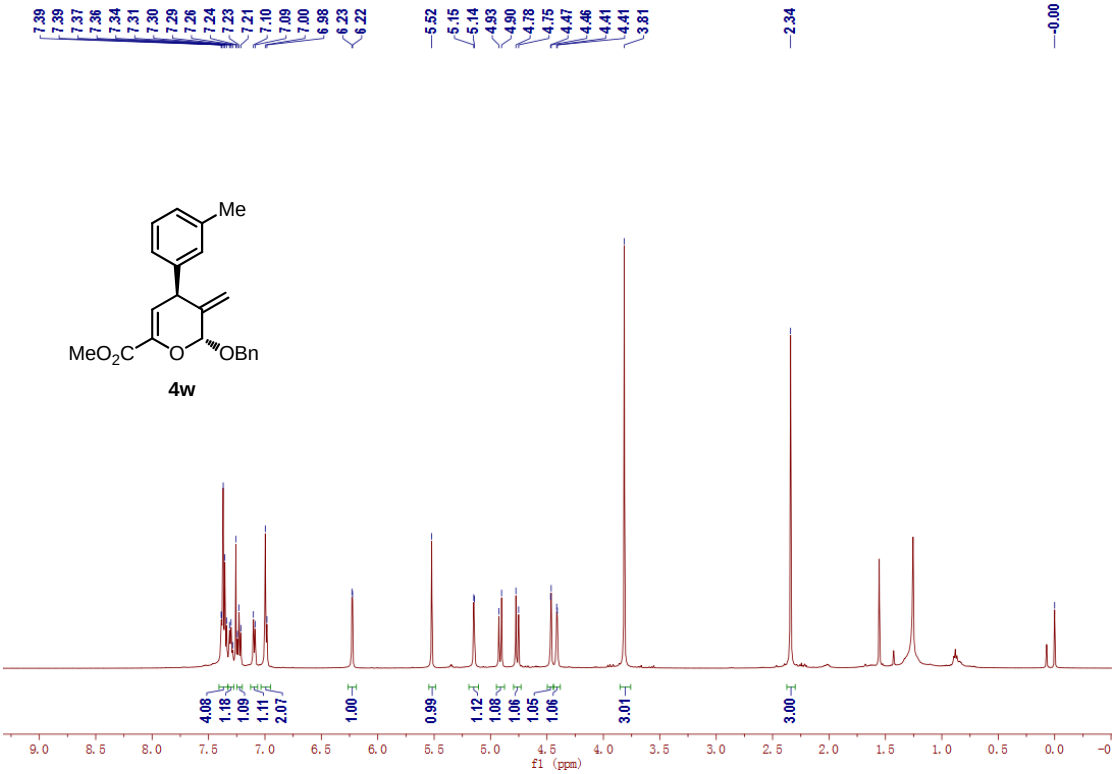
142.16
141.65
140.97
137.24
132.40
130.62
130.34
128.80
128.20
128.02
122.82
115.34
114.74
100.11
77.41
77.16
76.91
70.11
52.51
41.62
Br
MeO2C
O
OBn
4v
f1 (ppm)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7.39
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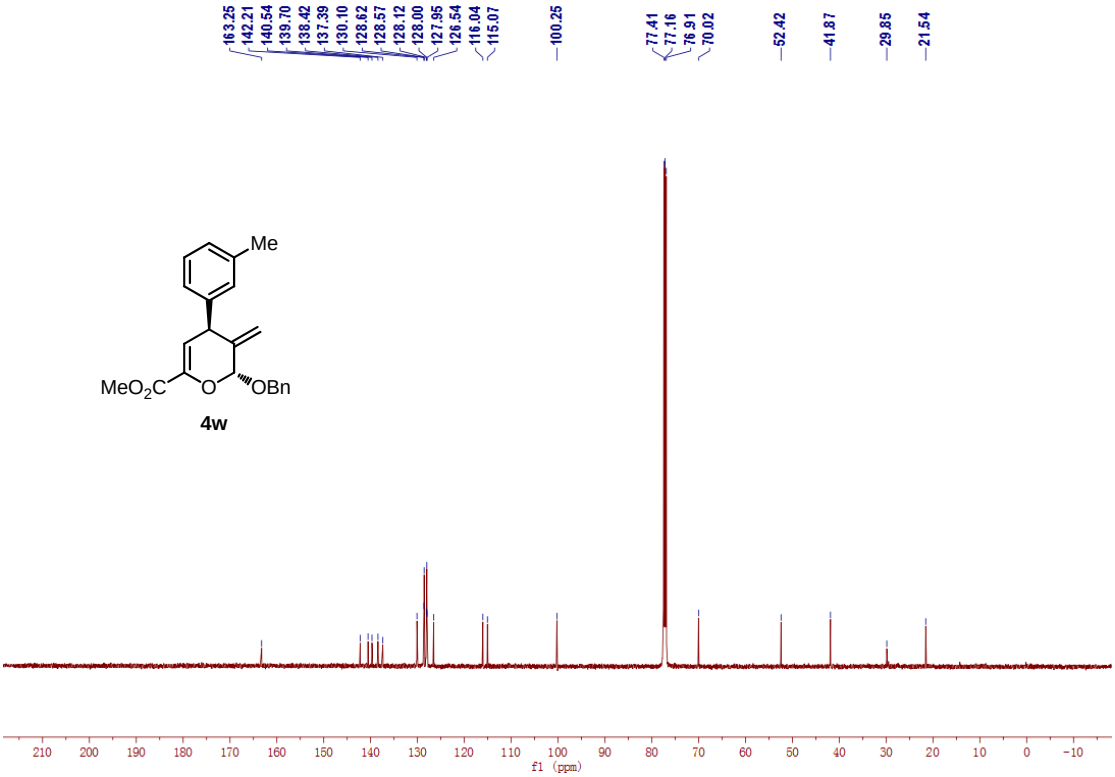
7.36
7.34
7.31
7.30
7.29
7.26
7.24
7.23
7.21
7.10
7.09
7.00
6.98
6.23
6.22
5.52
5.15
5.14
4.93
4.90
4.78
4.75
4.47
4.46
4.41
4.41
3.81
2.34
0.00
Me
MeO2C
O
OBn
4w
4.08
1.18
1.09
1.11
2.07
1.00
0.99
1.12
1.08
1.06
1.05
1.06
3.01
3.00
f1 (ppm)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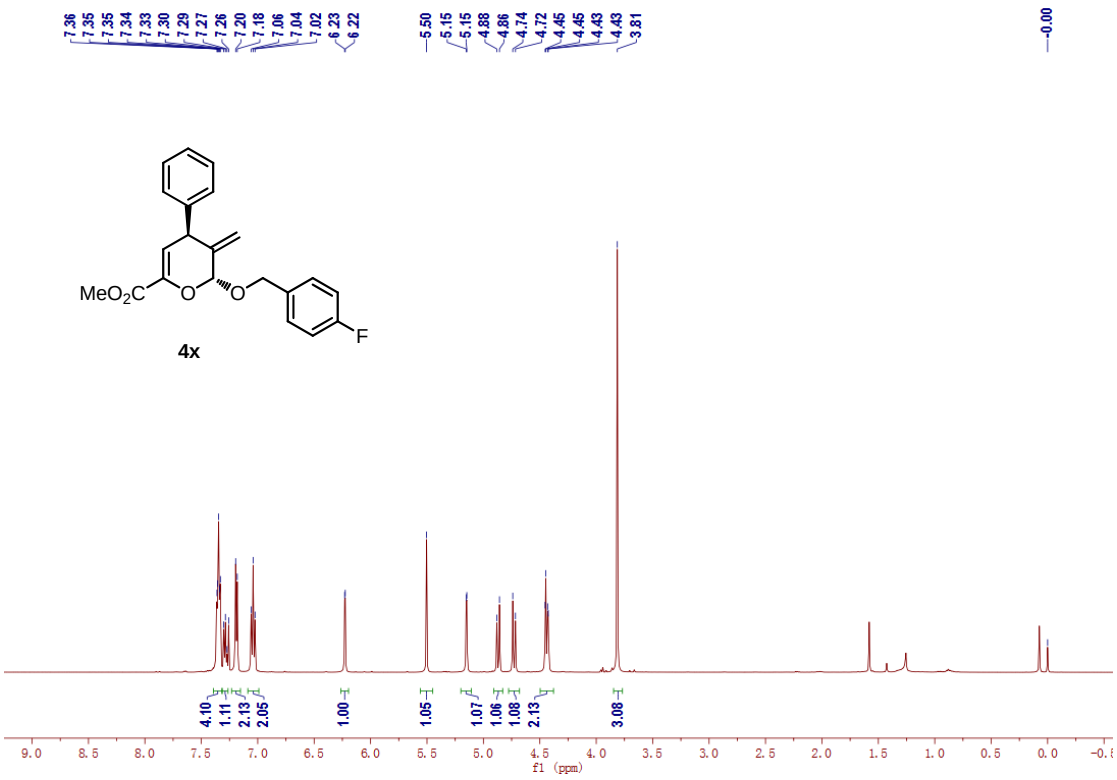
137.39
130.10
128.82
128.57
128.12
128.00
127.95
126.54
116.04
115.07
100.25
77.41
77.16
76.91
70.02
52.42
41.87
29.85
21.54
Me
MeO2C
O
OBn
4w
f1 (ppm)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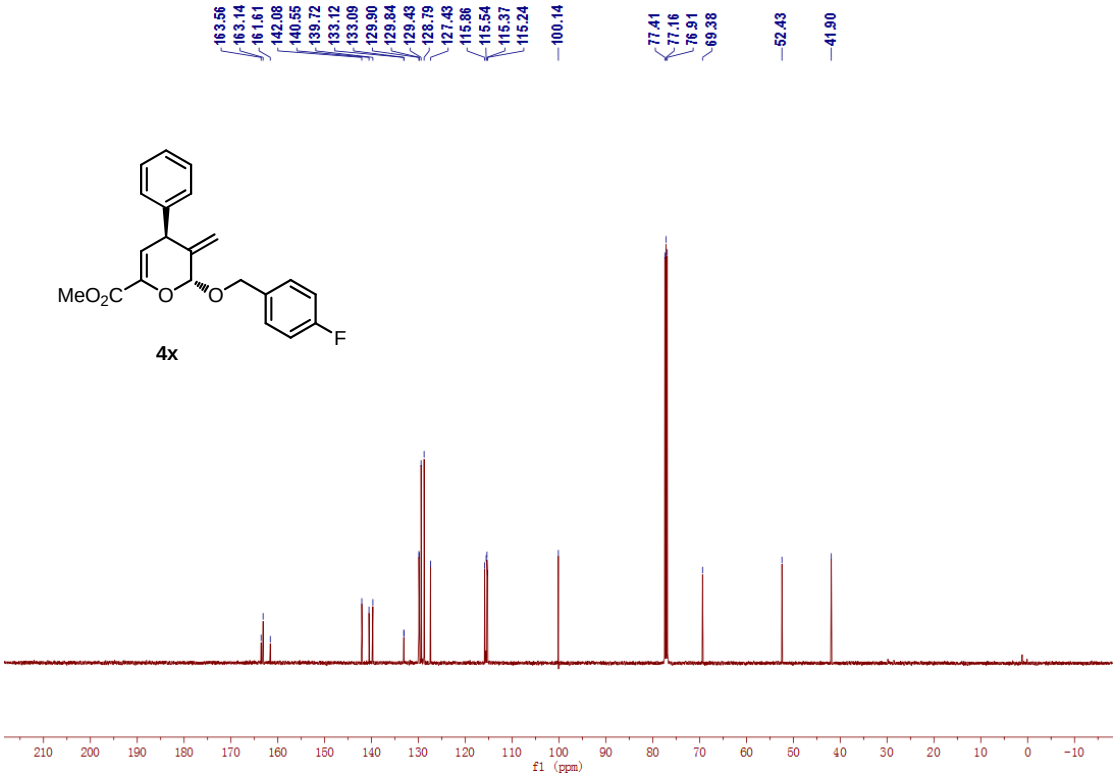
7.29
7.27
7.26
7.20
7.18
7.06
7.04
7.02
6.23
6.22
5.50
5.15
5.15
4.88
4.86
4.74
4.72
4.45
4.45
4.43
4.43
3.81
0.00
MeO2C
O
O
F
4x
4.10
1.11
2.13
2.05
1.00
1.05
1.07
1.06
1.08
2.13
3.08
f1 (ppm)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161.61
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139.72
133.12
133.09
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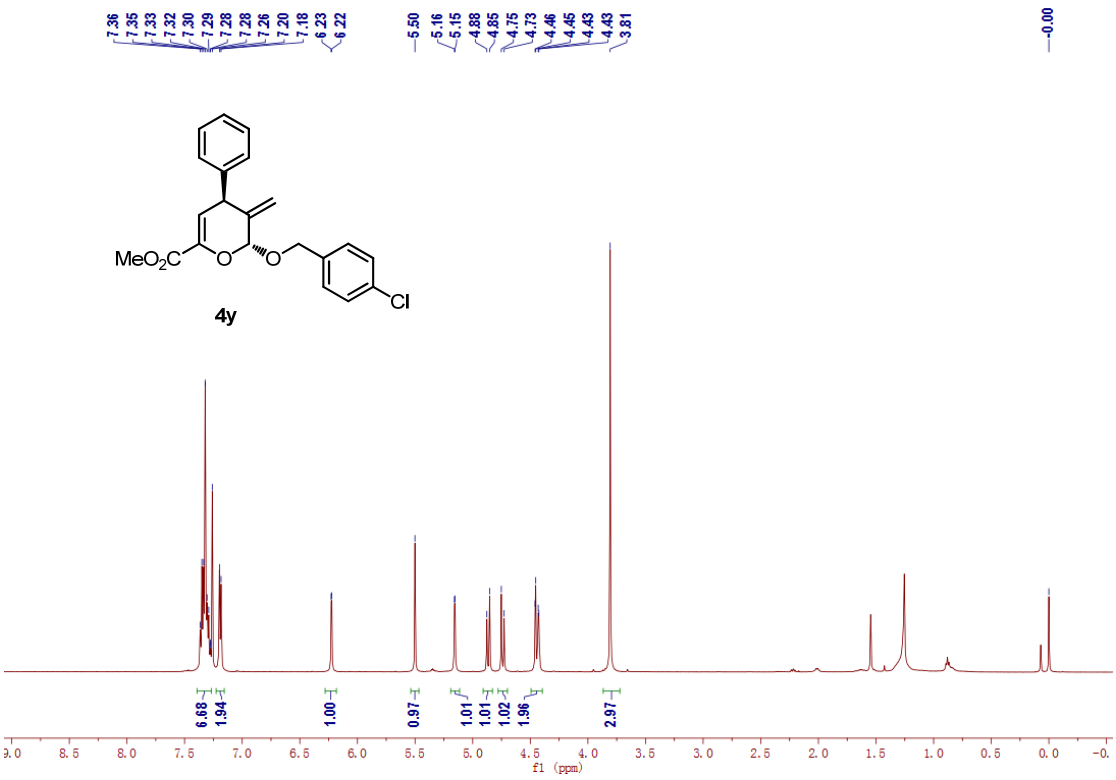
129.84
129.43
128.79
127.43
115.86
115.54
115.37
115.24
100.14
77.41
77.16
76.91
69.38
52.43
41.90
MeO2C
O
O
F
4x
f1 (ppm)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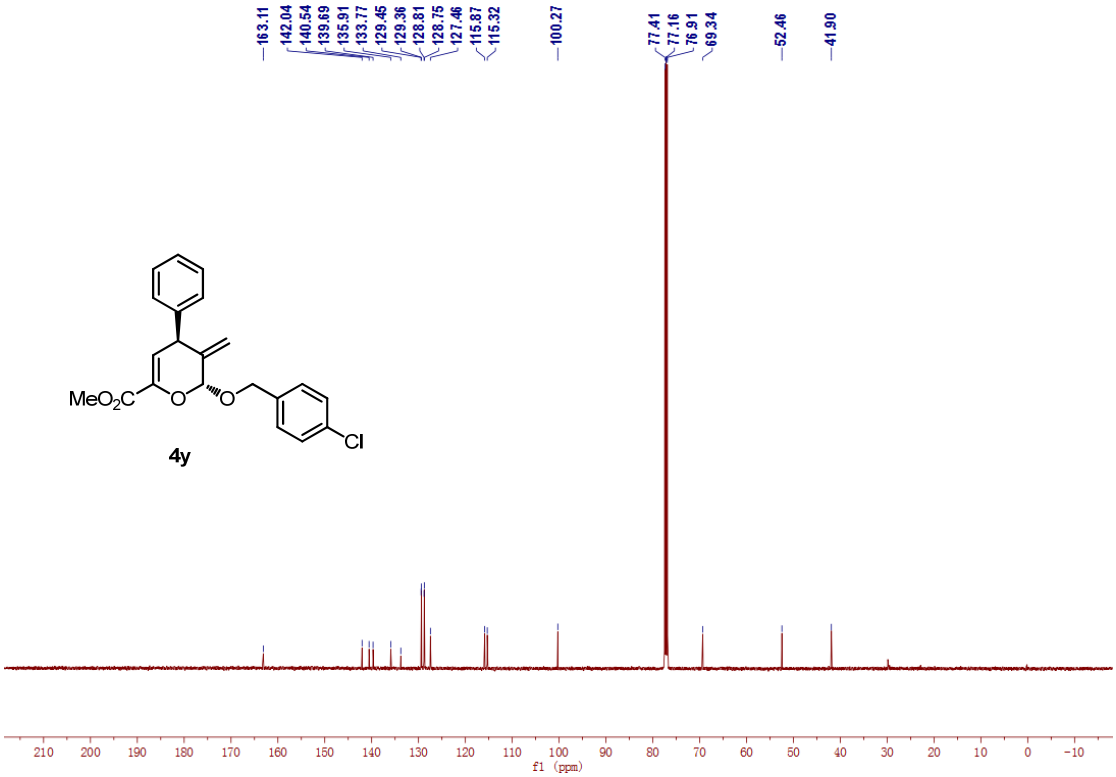
7.20
7.18
6.23
6.22
5.50
5.16
5.15
4.88
4.85
4.75
4.73
4.46
4.45
4.43
4.43
3.81
0.00
MeO2C
O
O
Cl
4y
6.68
1.94
1.00
0.97
1.01
1.01
1.02
1.96
2.97
f1 (ppm)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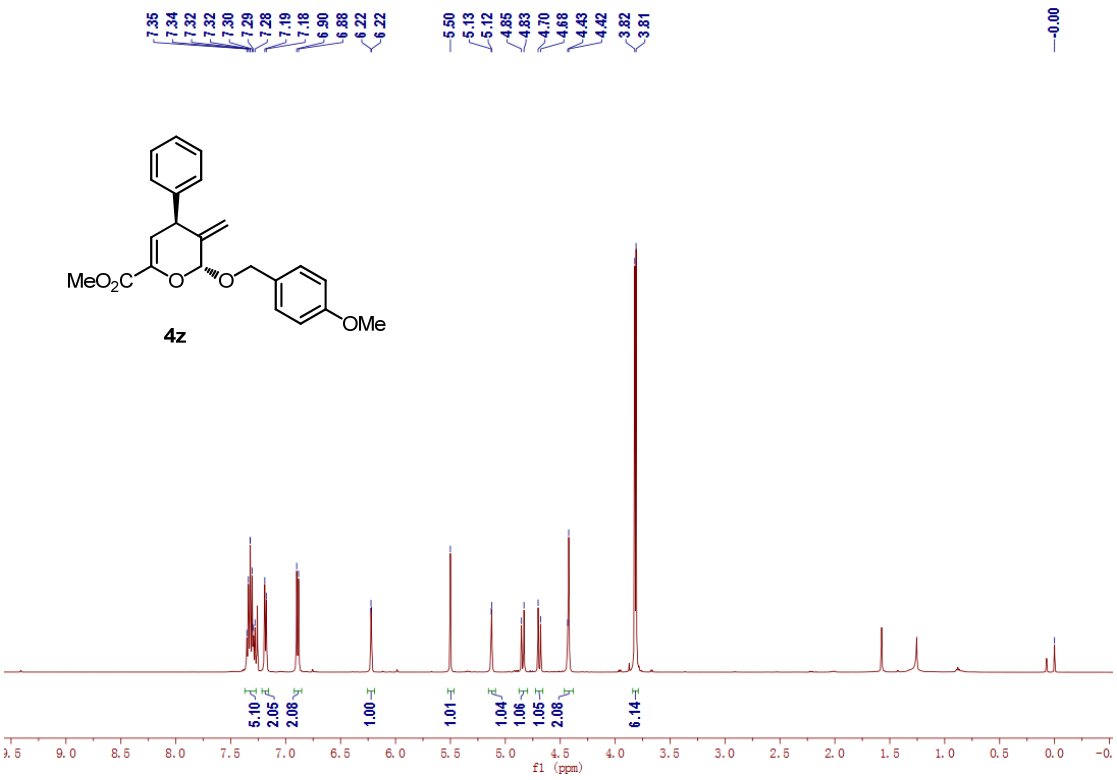
135.91
133.77
129.45
129.36
128.81
128.75
127.46
115.87
115.32
100.27
77.41
77.16
76.91
69.34
52.46
41.90
MeO2C
O
O
Cl
4y
f1 (ppm)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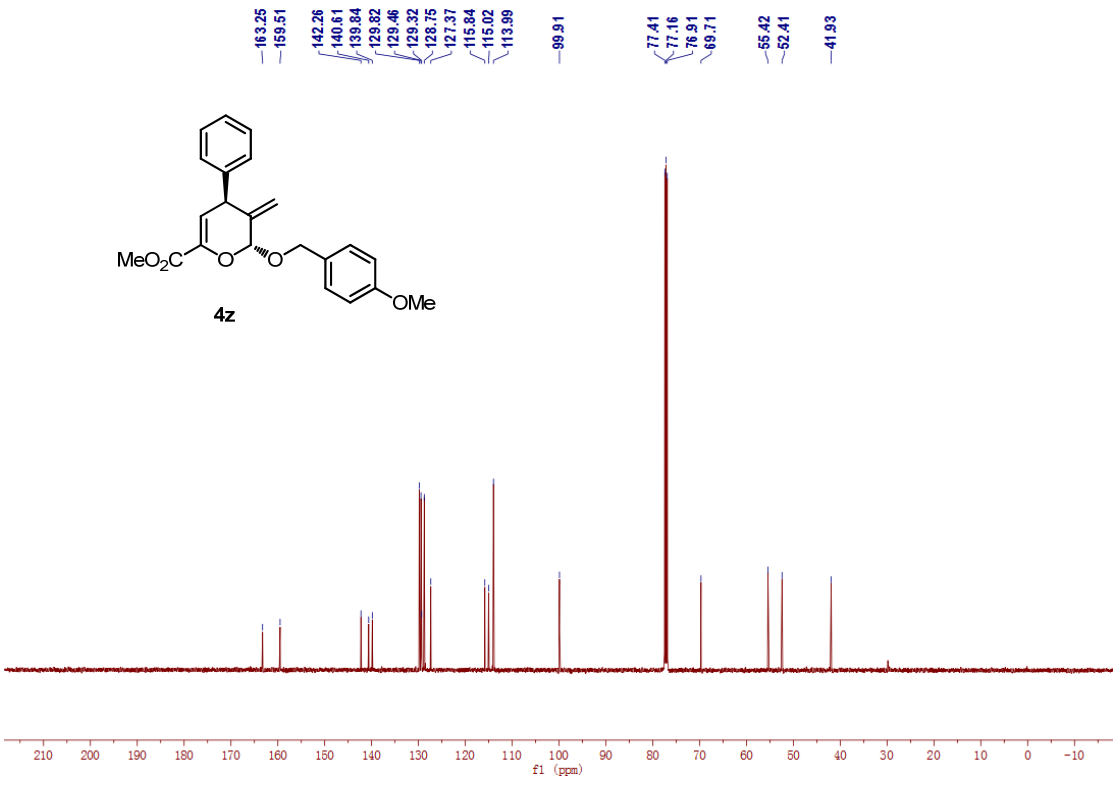
7.32
7.30
7.29
7.28
7.19
7.18
6.90
6.88
6.22
6.22
5.50
5.13
5.12
4.85
4.83
4.70
4.68
4.43
4.42
3.82
3.81
0.00
MeO2C
O
O
OMe
4z
5.10
2.05
2.08
1.00
1.01
1.04
1.06
1.05
2.08
6.14
f1 (ppm)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159.51
142.26
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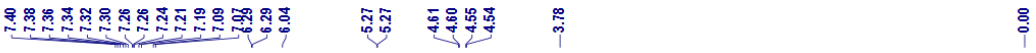
139.84
129.82
129.46
129.32
128.75
127.37
115.84
115.02
113.99
99.91
77.41
77.16
76.91
69.71
55.42
52.41
41.93
MeO2C
O
O
OMe
4z
f1 (ppm)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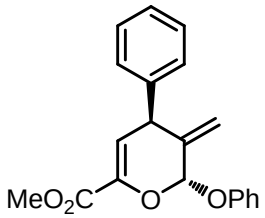
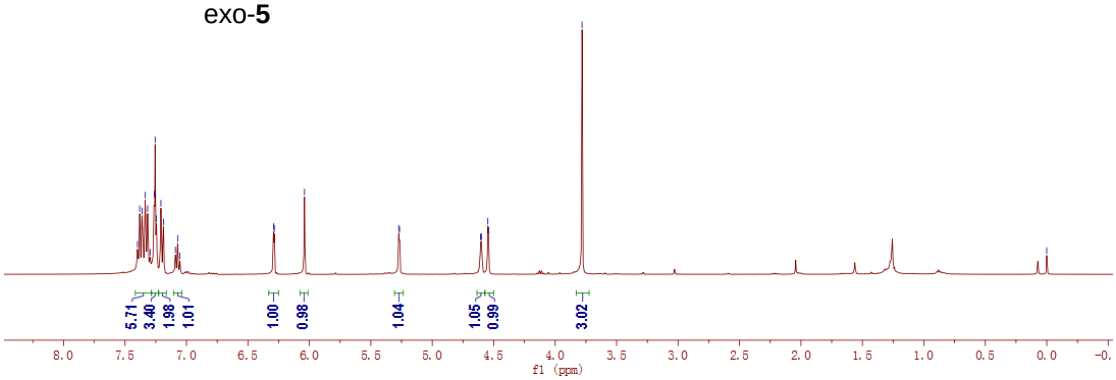
7.34
7.32
7.30
7.26
7.26
7.24
7.21
7.19
7.09
6.29
6.04
5.27
5.27
4.61
4.60
4.55
4.54
3.78
0.00


MeO2C
O
OPh

exo-**5**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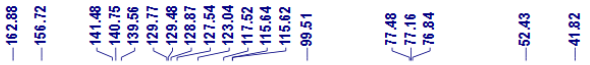
3.40
1.98
1.01
1.00
0.98
1.04
1.05
0.99
3.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


162.88
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140.75
139.56
129.77
129.48
128.87
127.54
123.04
117.52
115.64
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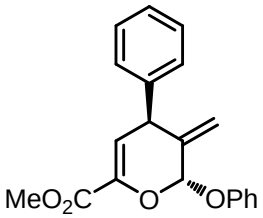
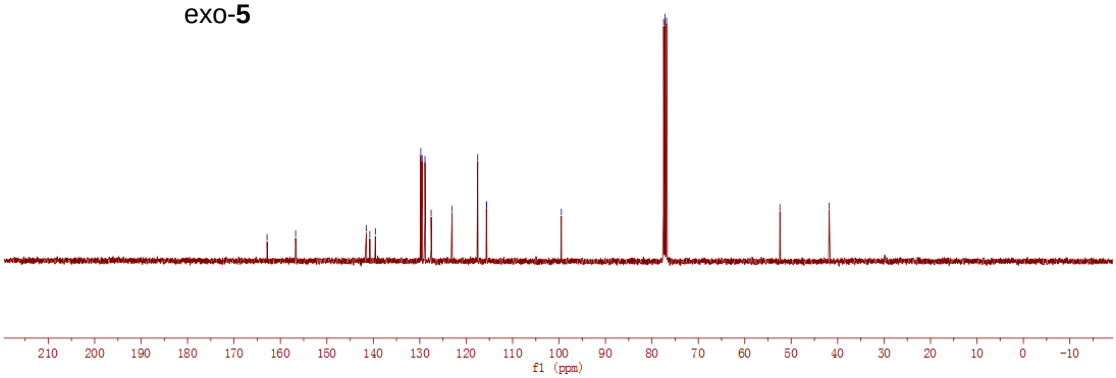
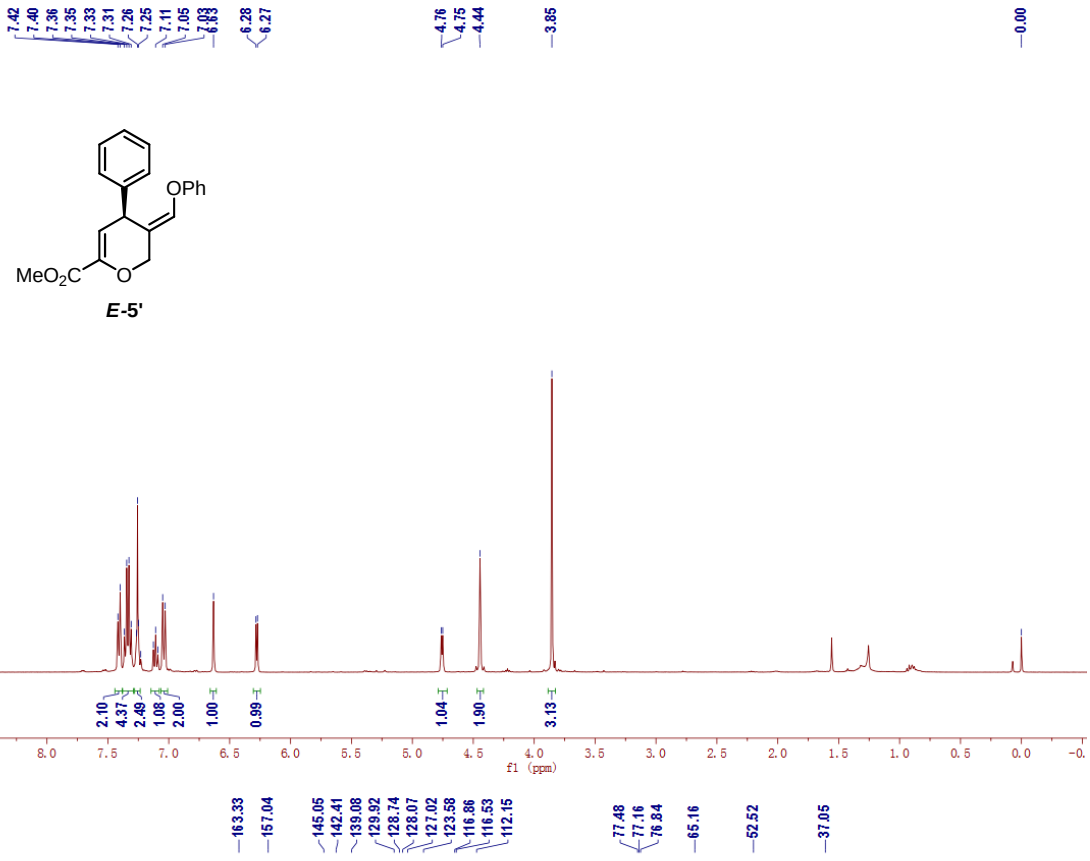
99.51
77.48
77.16
76.84
52.43
41.82


MeO2C
O
OPh

exo-**5**


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.42
7.40
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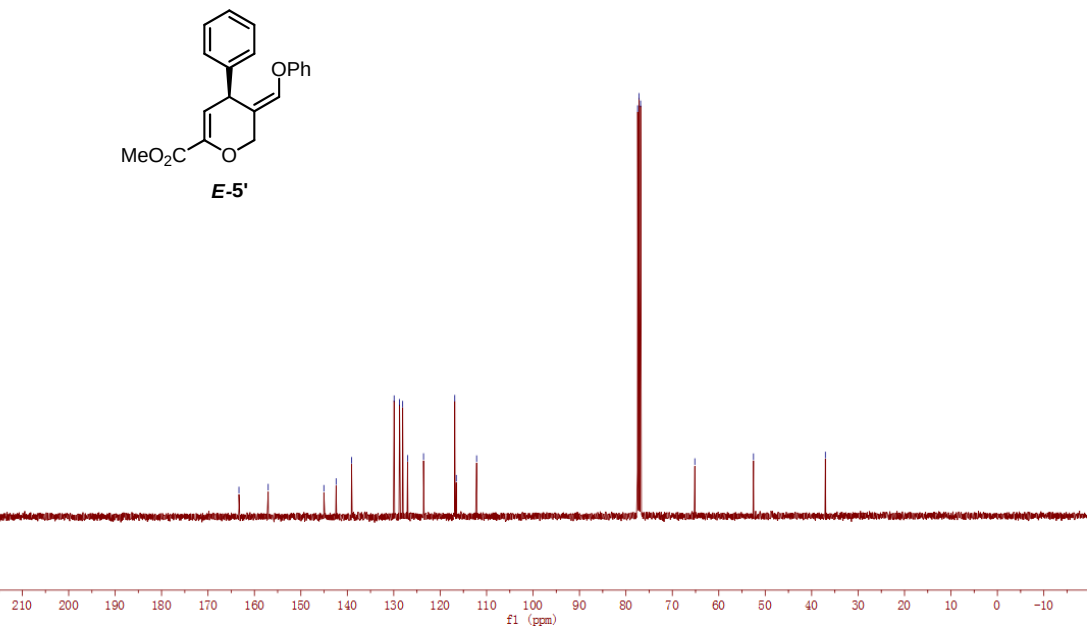
7.35
7.33
7.31
7.26
7.25
7.11
7.05
6.28
6.27
4.76
4.75
4.44
3.85
0.00
OPh
MeO2C
O
2.10
4.37
2.49
1.08
2.00
1.00
0.99
1.04
1.90
3.13
f1 (ppm)

***E*-5'**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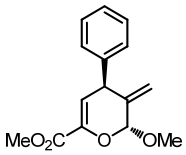
157.04
145.05
142.41
139.08
129.92
128.74
128.07
127.02
123.58
116.86
116.53
112.15
77.48
77.16
76.84
65.16
52.52
37.05
OPh
MeO2C
O
f1 (ppm)

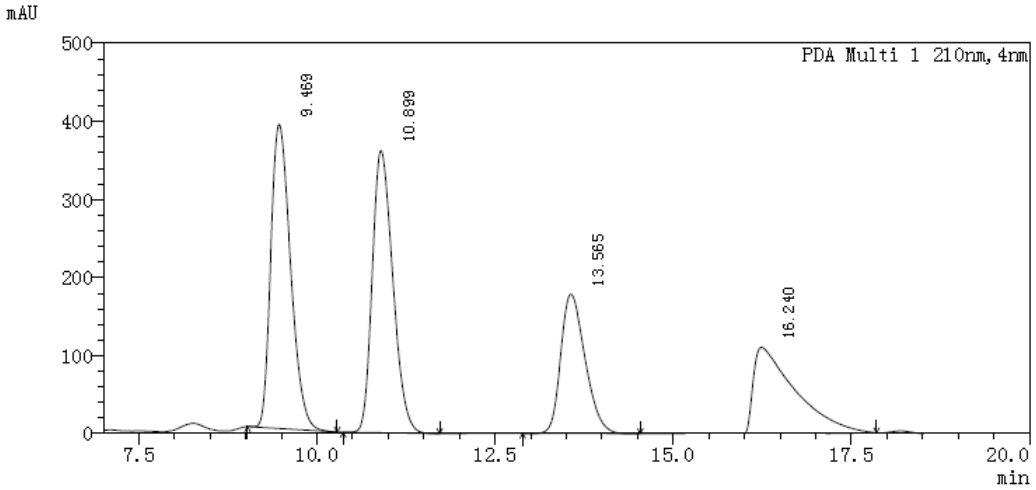
***E*-5'**

HPLC Spectrum



4a

<Chromatogram>

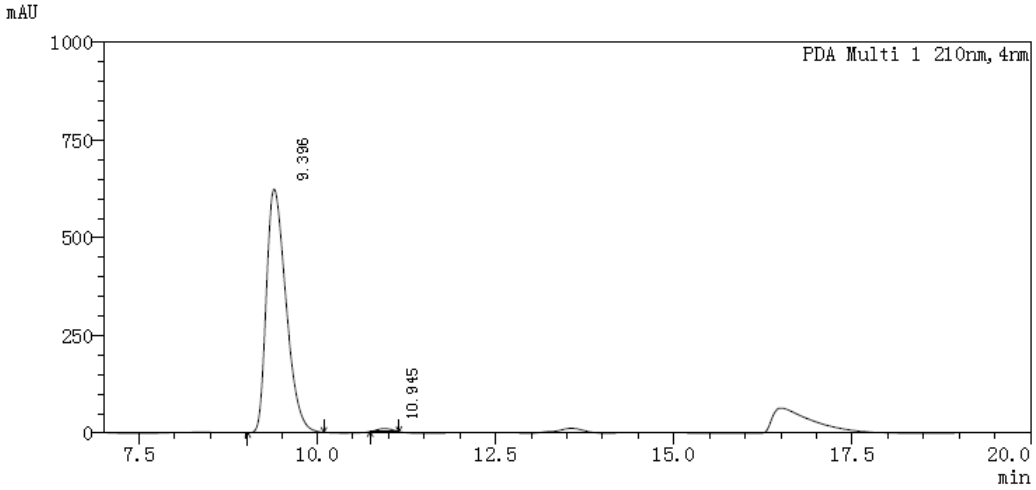


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	9.469	389569	7524643	31.839
2	10.899	361493	7272327	30.772
3	13.565	178528	4242478	17.951
4	16.240	111920	4593771	19.438

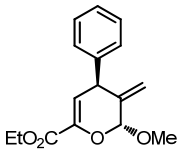
<Chromatogram>



<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	9.396	623223	11948952	99.088
2	10.945	7777	109943	0.912



4b

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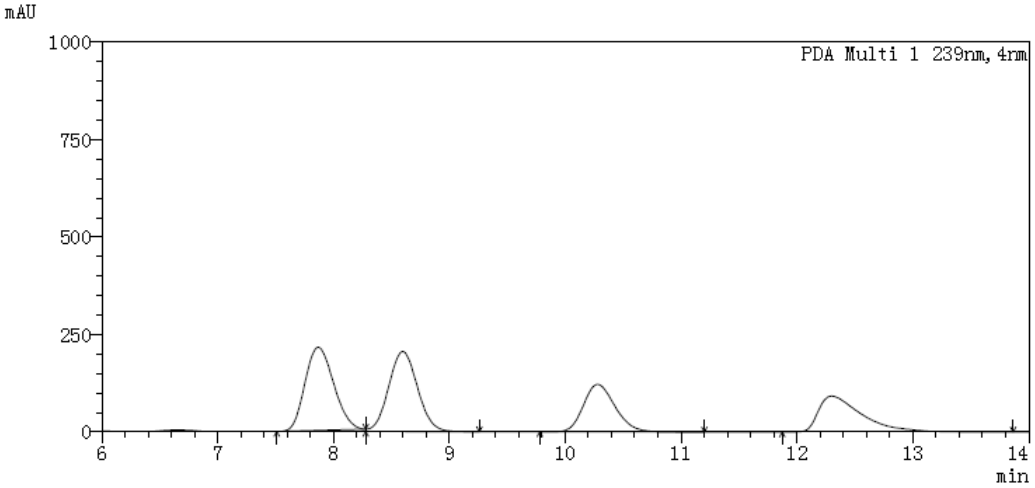
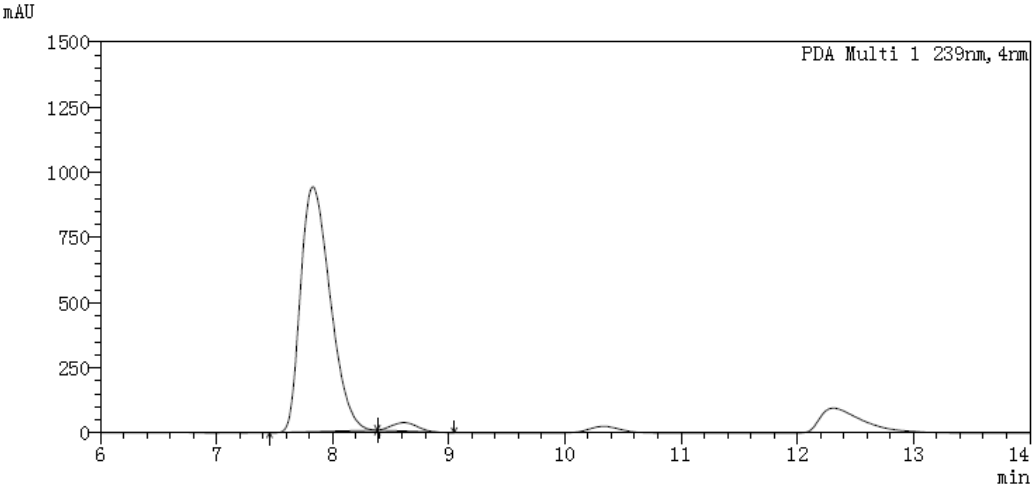


<Peak Results>

PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	7.868	213133	3662201	30.761
2	8.597	205467	3562308	29.922
3	10.279	121722	2305556	19.366
4	12.300	92006	2375389	19.952

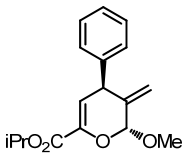
<Chromatogram>



<Peak Results>

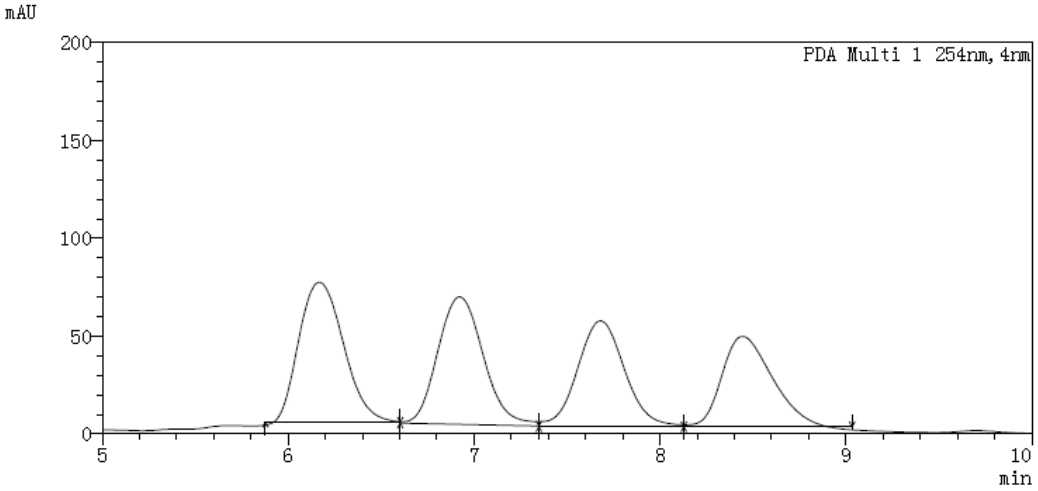
PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	7.830	939591	16699549	97.219
2	8.612	32189	477781	2.781



4c

〈Chromatogram〉

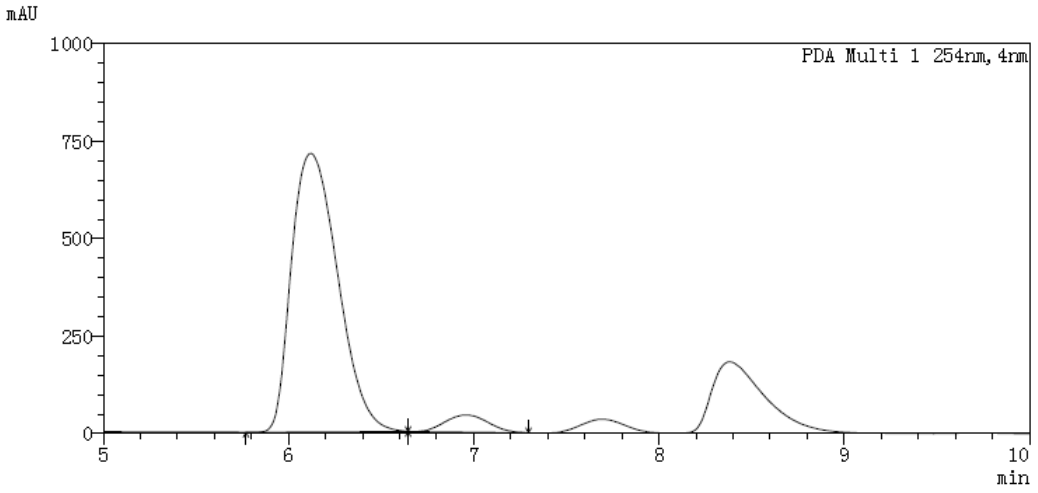


〈Peak Results〉

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	6.167	71514	1186788	28.854
2	6.922	65157	1107002	26.914
3	7.680	54240	954676	23.211
4	8.444	46285	864653	21.022

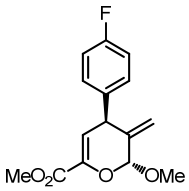
〈Chromatogram〉



〈Peak Results〉

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	6.120	715127	12436052	94.614
2	6.959	43916	707938	5.386



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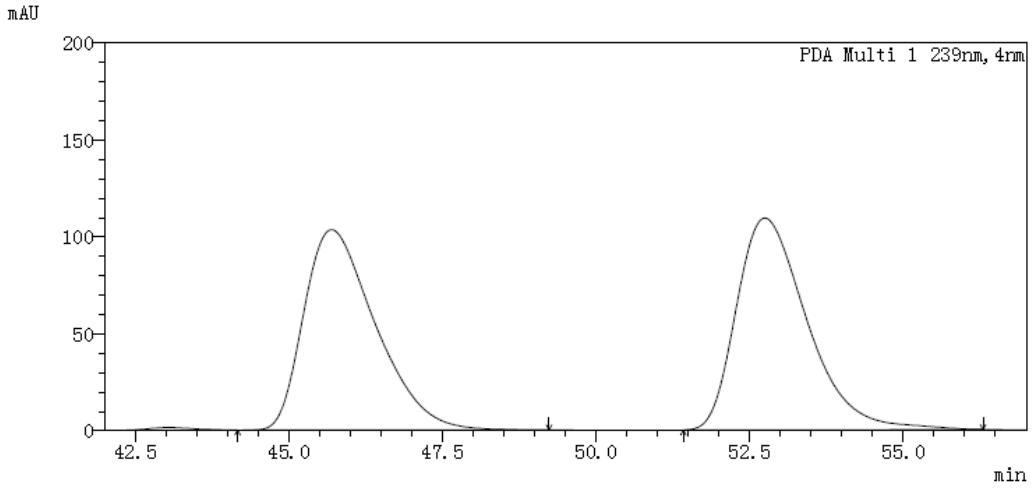
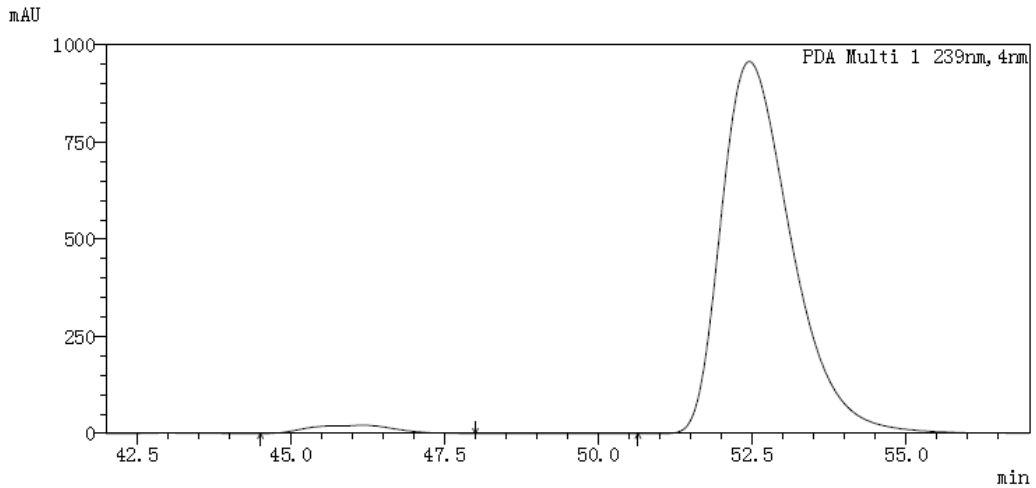


<Peak Results>

PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	45.700	103352	8364762	48.896
2	52.747	109328	8742428	51.104

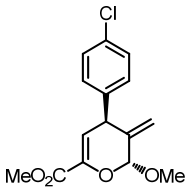
<Chromatogram>



<Peak Results>

PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	46.184	21191	2043815	2.619
2	52.453	958147	75999450	97.381



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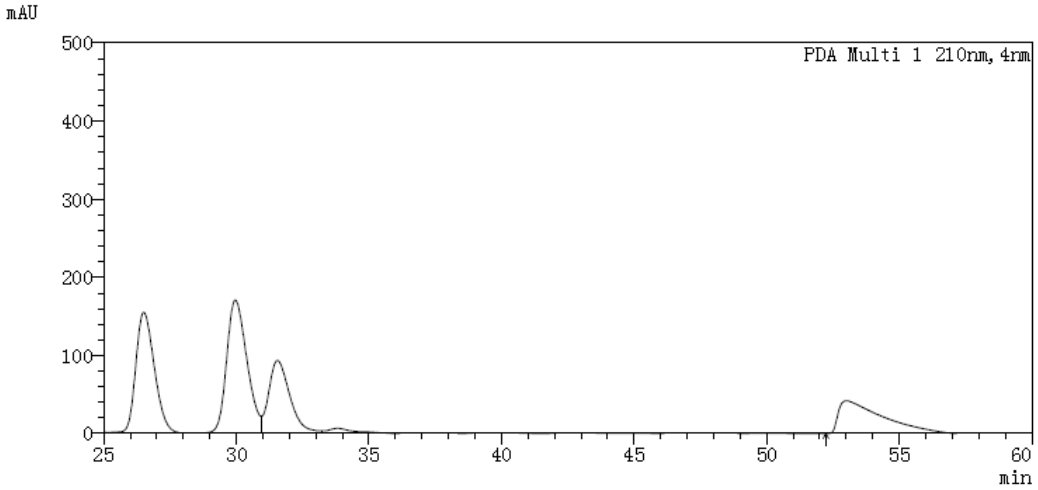
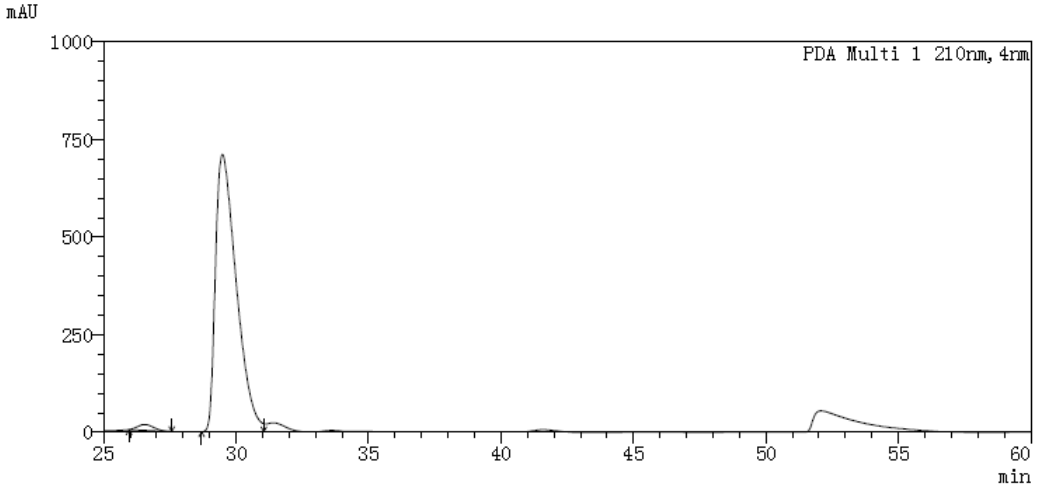


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	26.516	156119	7816827	28.315
2	29.968	171929	9304789	33.704
3	31.558	94624	5364479	19.432
4	53.011	42152	5120951	18.549

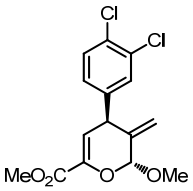
<Chromatogram>



<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	26.556	14971	629305	1.595
2	29.491	710220	38836002	98.405



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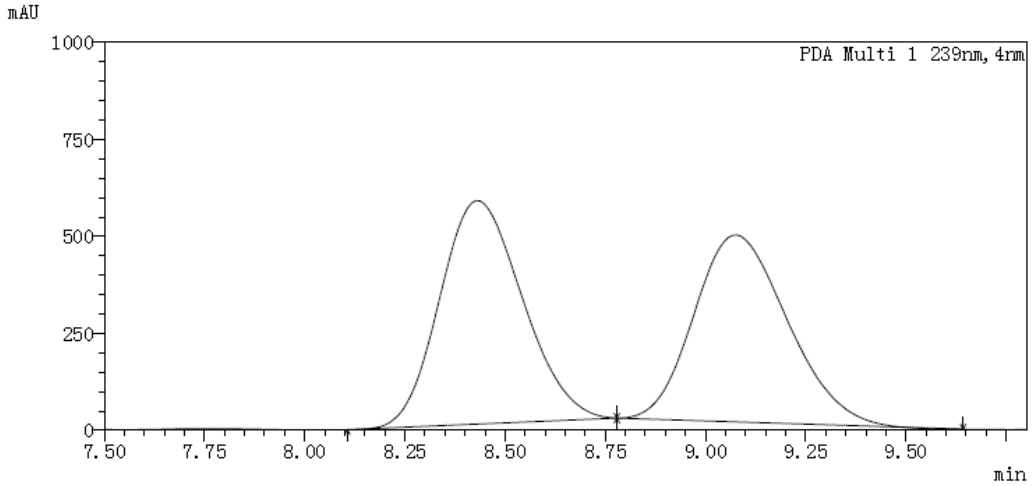
〈Chromatogram〉

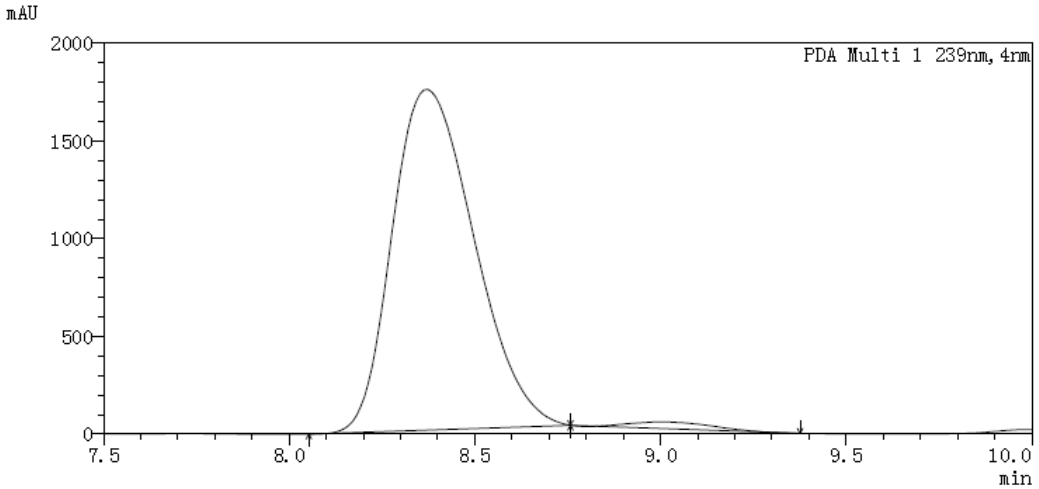


〈Peak Results〉

PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	8.431	576127	8275413	51.491
2	9.075	481943	7796294	48.509

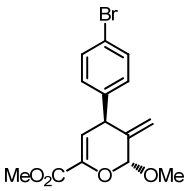
〈Chromatogram〉



〈Peak Results〉

PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	8.370	1744186	26784638	98.190
2	9.005	33477	493682	1.810



4g

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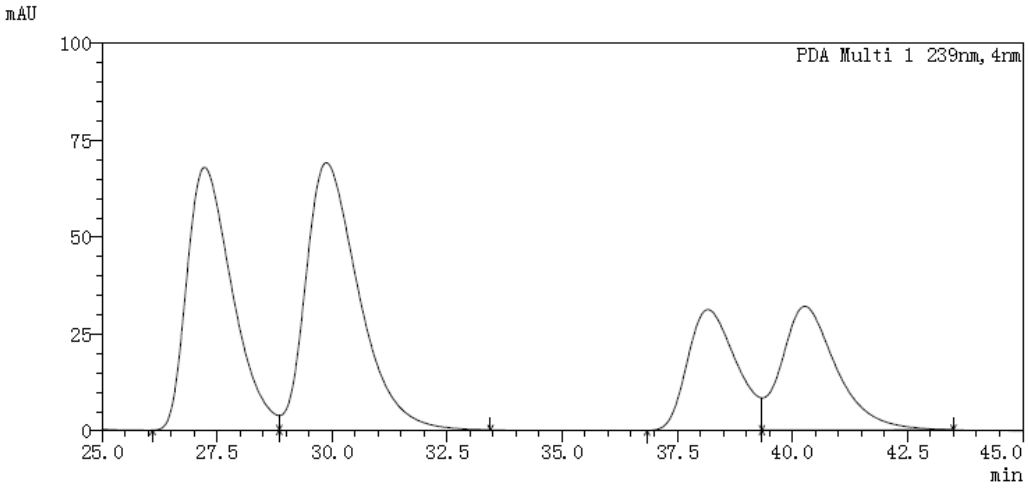

<Peak Results>

PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	27.230	67813	4639335	30.759
2	29.874	69021	5492802	36.418
3	38.165	31165	2298186	15.237
4	40.273	31979	2652529	17.586

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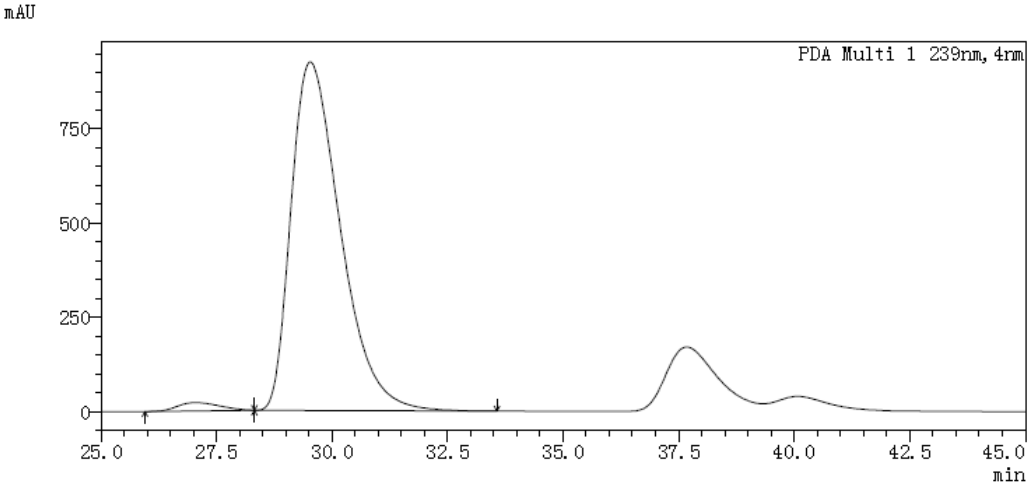
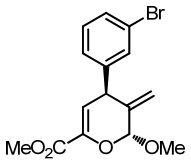


<Peak Results>

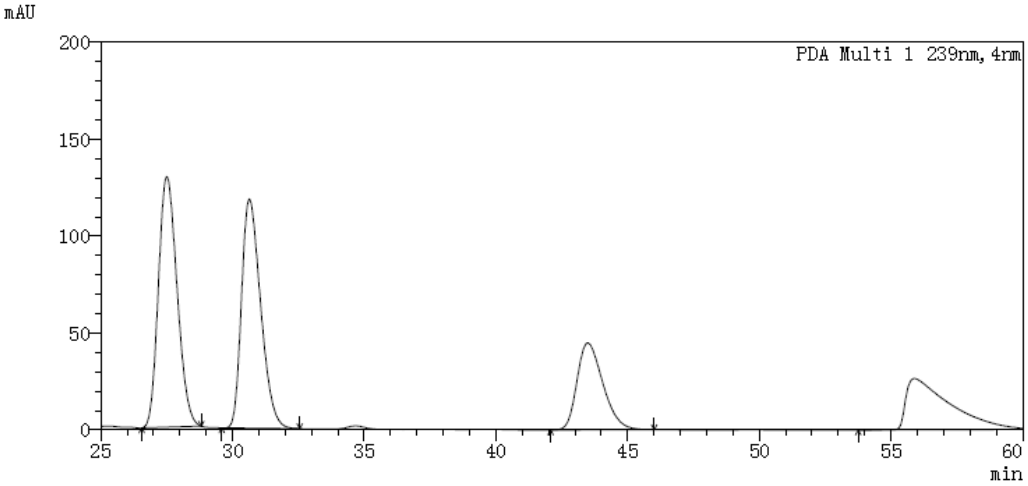
PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	27.045	22409	1403000	2.003
2	29.528	924379	68634834	97.997



4h

〈Chromatogram〉

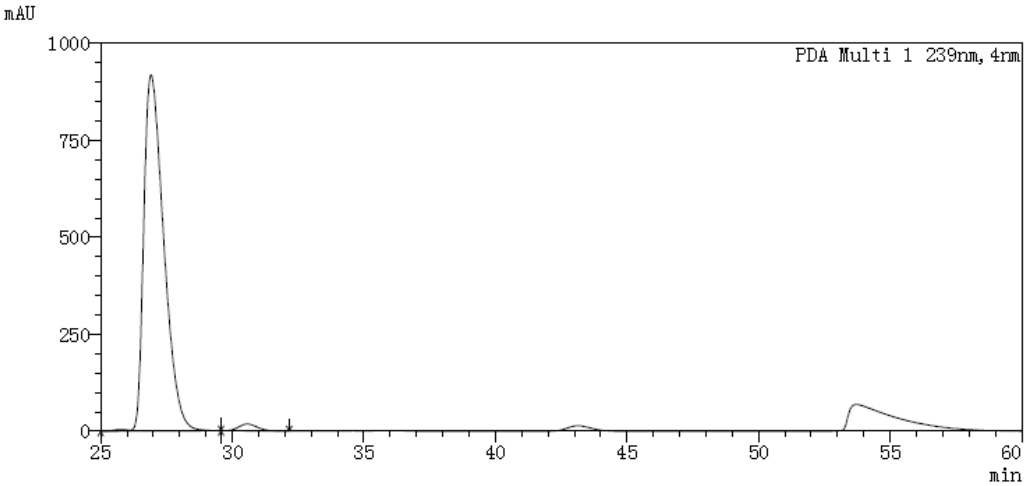


〈Peak Results〉

PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	27.512	129378	6379450	34.524
2	30.646	118182	5966543	32.289
3	43.494	44792	3051677	16.515
4	55.899	26435	3080615	16.672

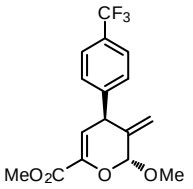
〈Chromatogram〉



〈Peak Results〉

PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	26.918	918089	48455031	98.285
2	30.576	17477	845487	1.715



4i

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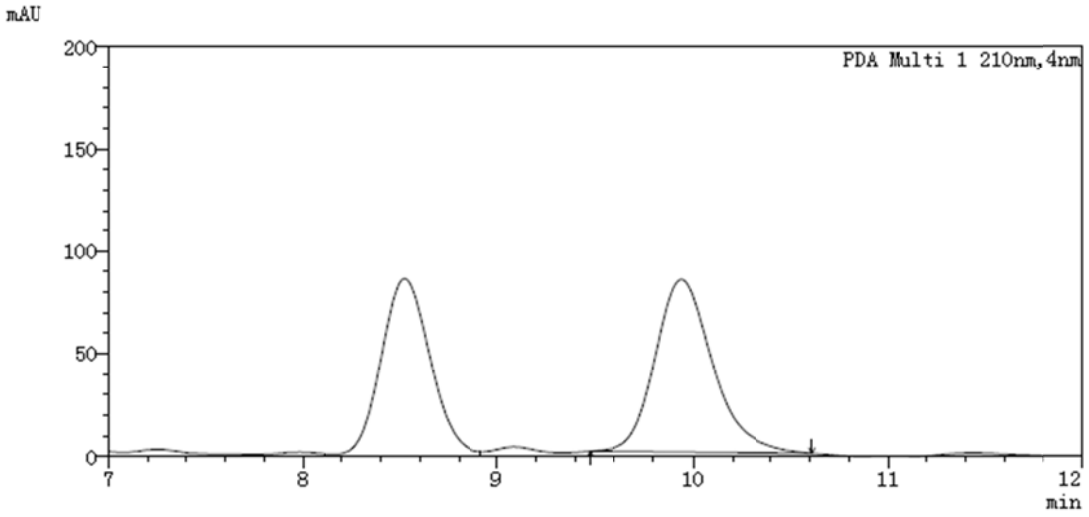

<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	8.518	89004	1622288	48.681
2	9.940	84184	1710170	51.319

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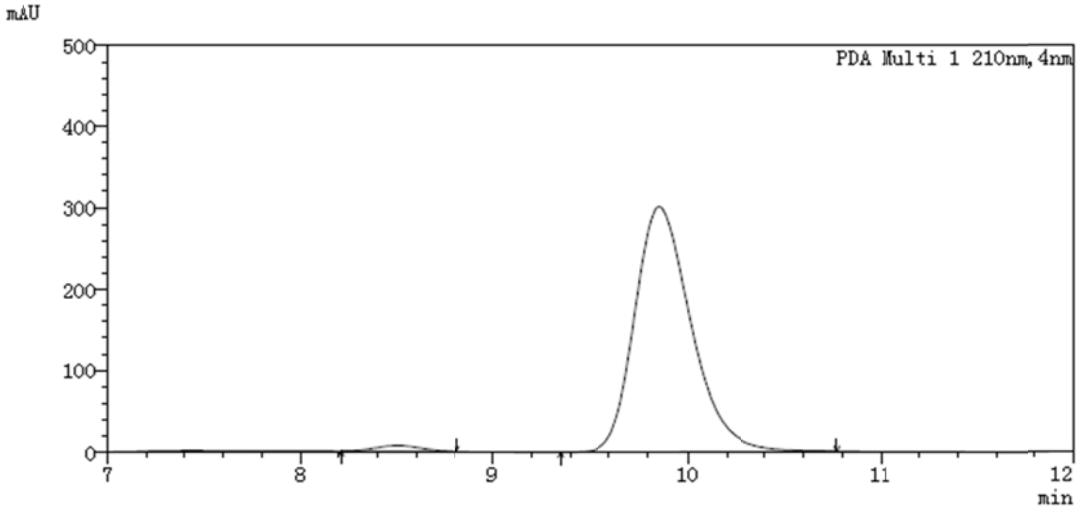
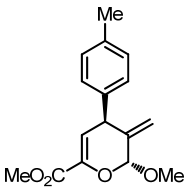


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	8.500	7092	114806	1.873
2	9.855	300575	6015966	98.127



4j

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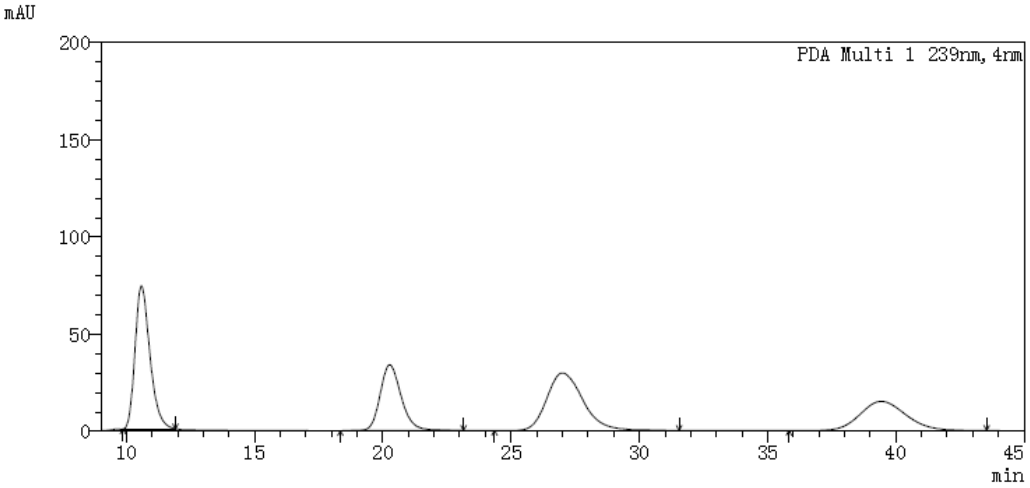

<Peak Results>

PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	10.585	73585	2967650	30.789
2	20.264	33806	1922197	19.943
3	27.000	29626	2892308	30.008
4	39.432	14996	1856446	19.261

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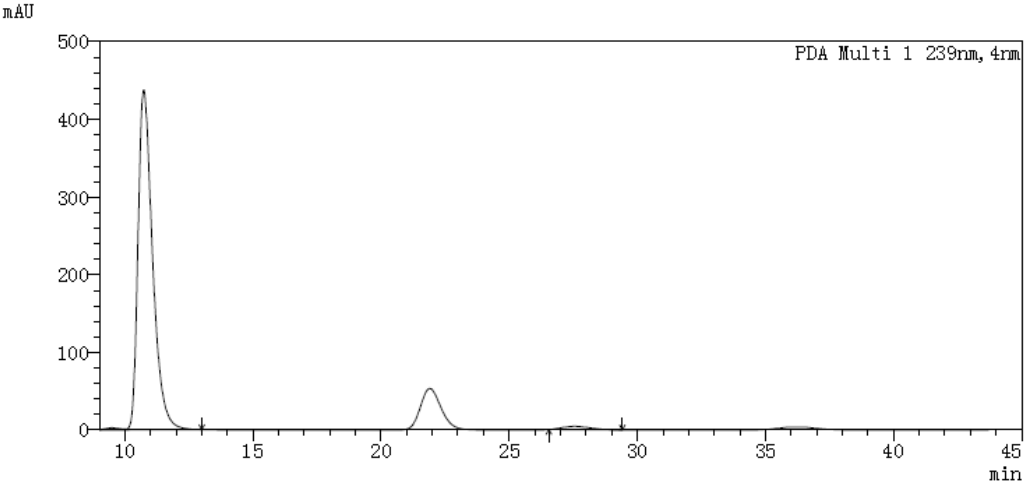
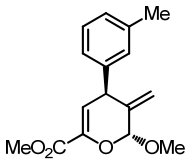


<Peak Results>

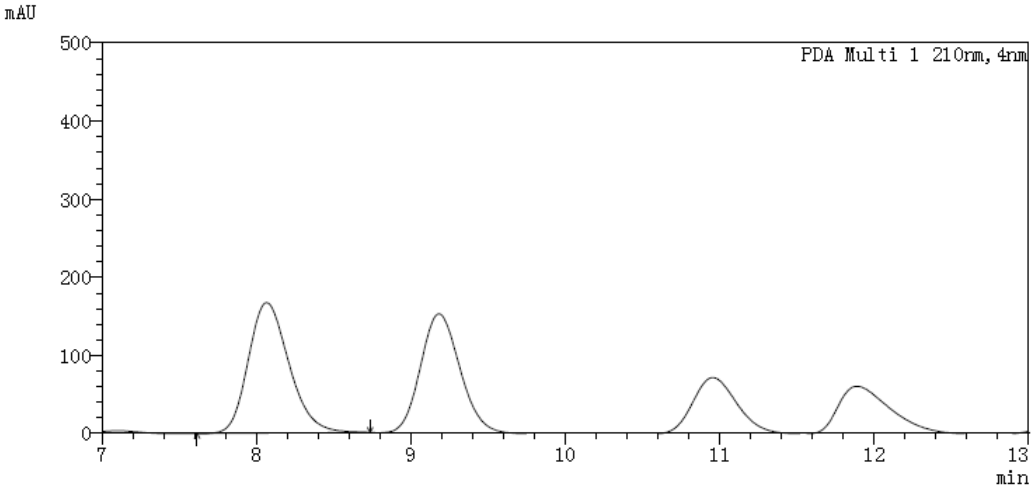
PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	10.735	437682	17353388	98.206
2	27.544	4087	317020	1.794



4k

〈Chromatogram〉

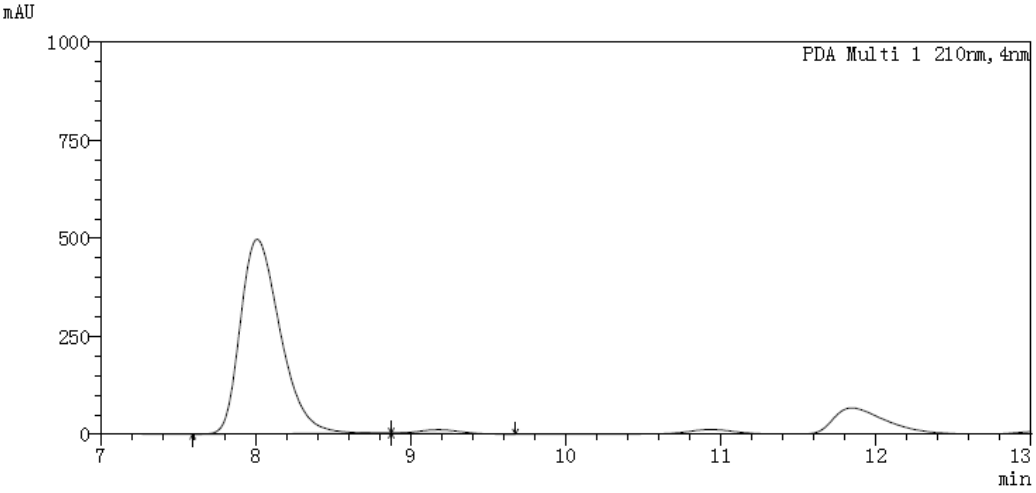


〈Peak Results〉

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	8.067	167021	3059286	34.774
2	9.182	155308	2866150	32.579
3	10.955	72339	1436256	16.326
4	11.888	61149	1435849	16.321

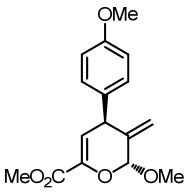
〈Chromatogram〉



〈Peak Results〉

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	8.010	496543	8873787	98.063
2	9.178	10005	175325	1.937



4l

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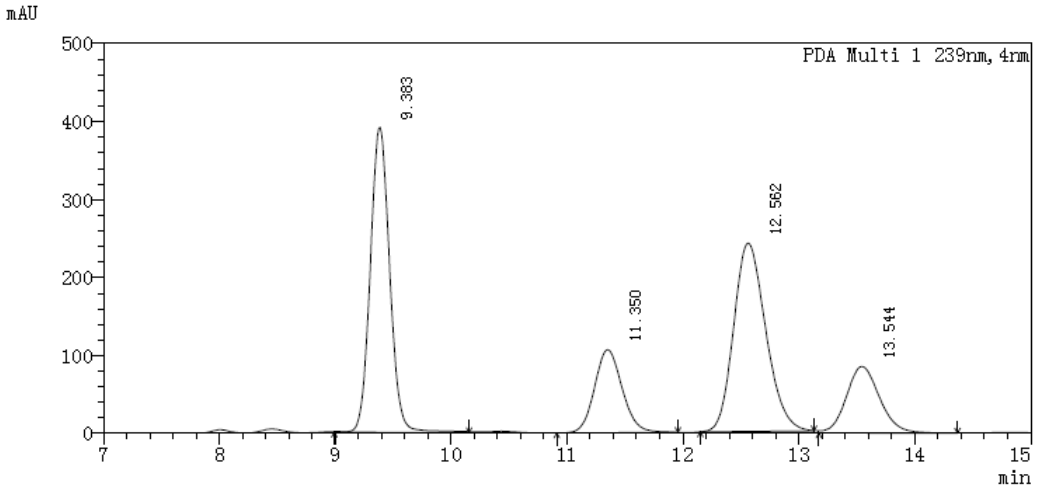

<Peak Results>

PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	9.383	390946	4559526	35.931
2	11.350	106512	1763704	13.899
3	12.562	241617	4656378	36.694
4	13.544	85378	1709974	13.475

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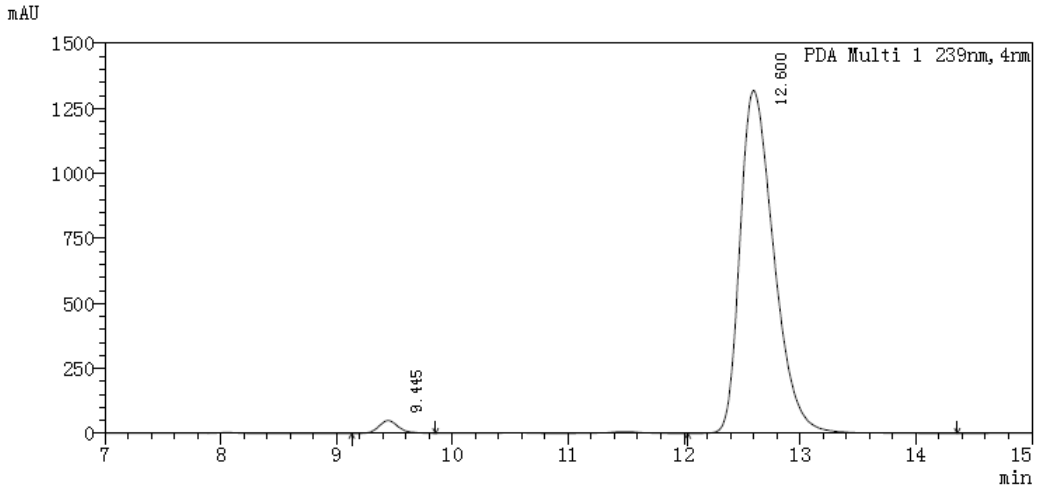
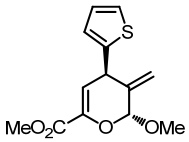


<Peak Results>

PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	9.445	49099	586172	2.144
2	12.600	1318345	26751347	97.856



4m

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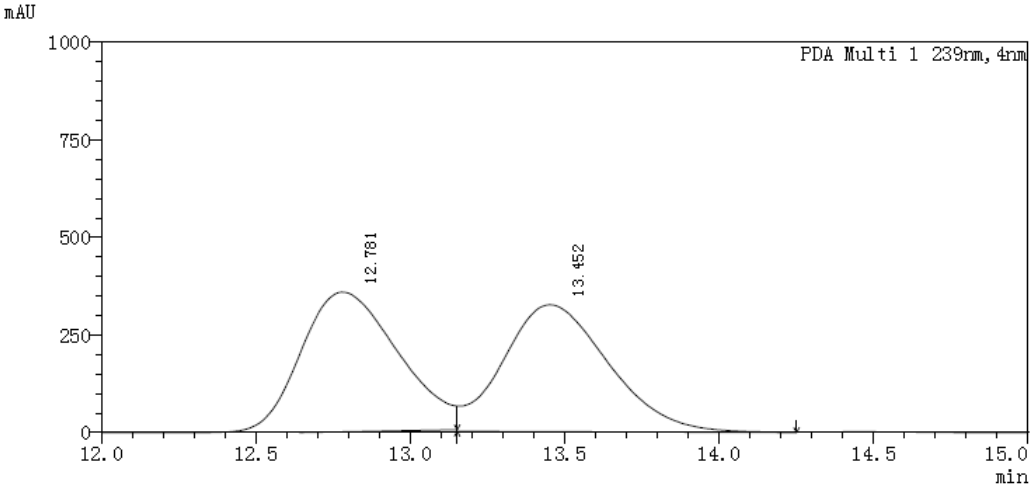
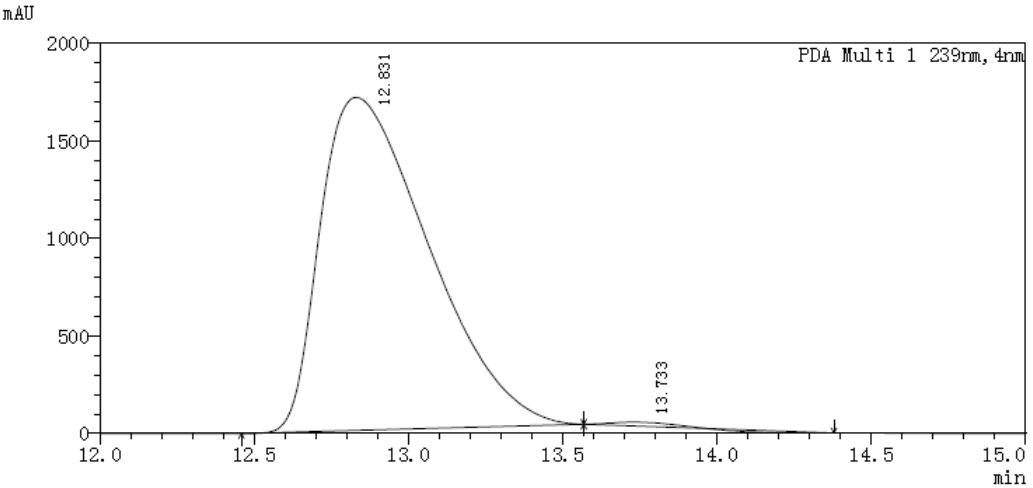


<Peak Results>

PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	12.781	358309	7901085	50.557
2	13.452	325381	7726951	49.443

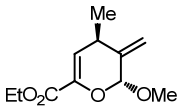
<Chromatogram>



<Peak Results>

PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	12.831	1708413	41747156	99.741
2	13.733	19181	108198	0.259



4n

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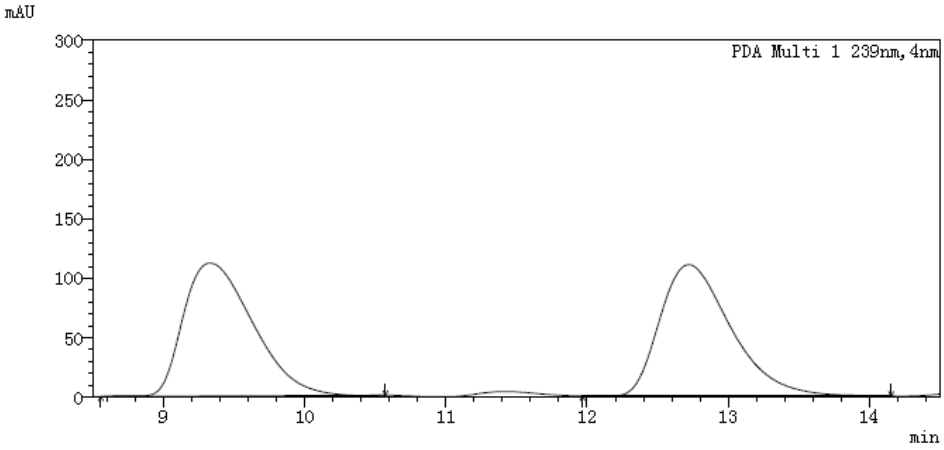
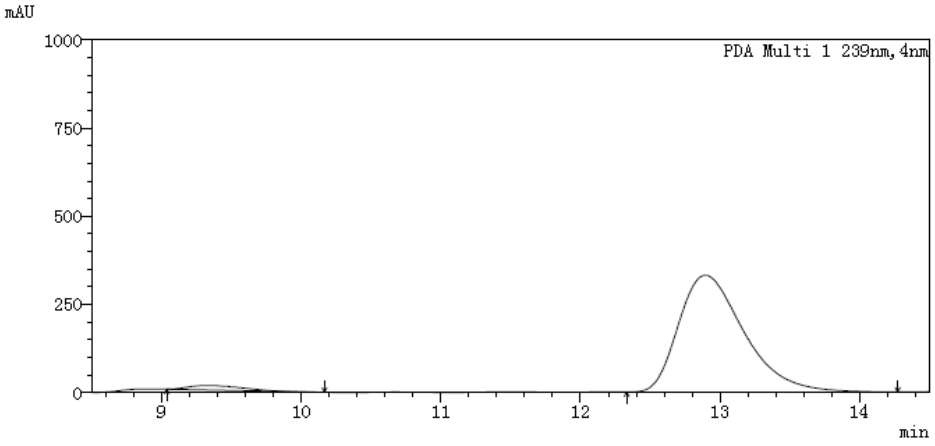


<Peak Results>

PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	9.328	111865	3813362	49.676
2	12.720	110528	3863044	50.324

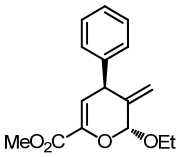
<Chromatogram>



<Peak Results>

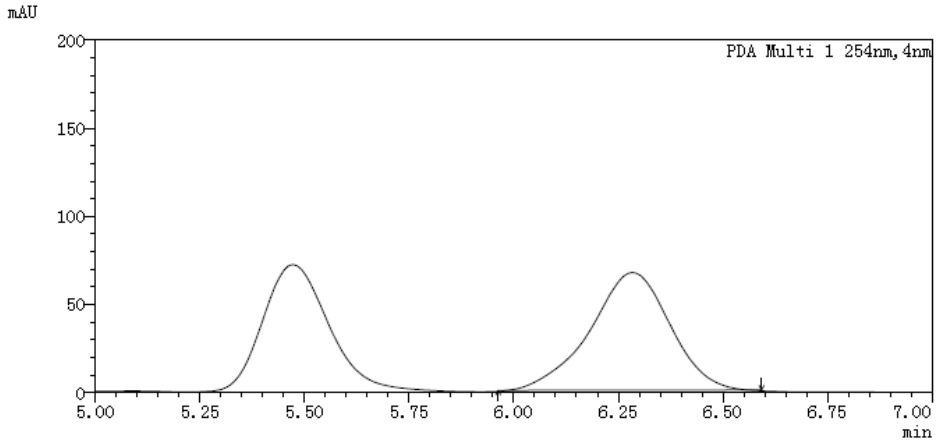
PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	9.329	12767	342406	3.079
2	12.894	331402	10779339	96.921



4o

<Chromatogram>

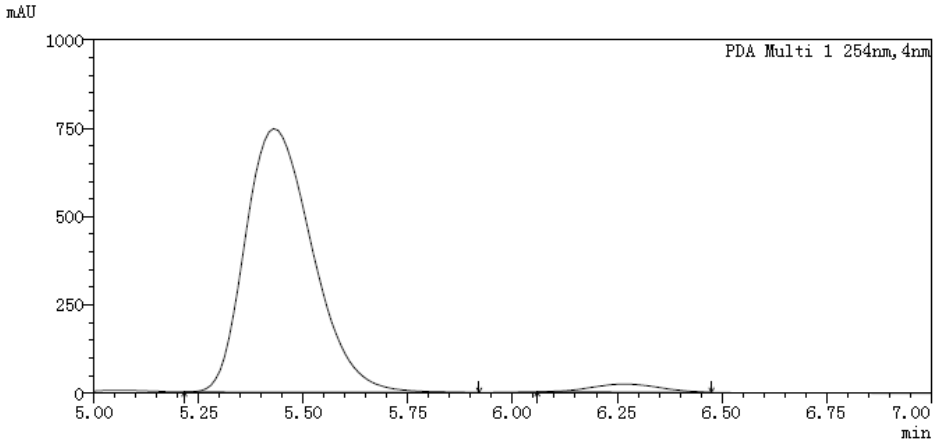


<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	5.472	74568	887276	50.093
2	6.284	66858	883999	49.907

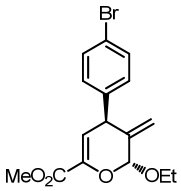
<Chromatogram>



<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	5.431	746134	8306052	97.014
2	6.268	22869	255665	2.986



4p

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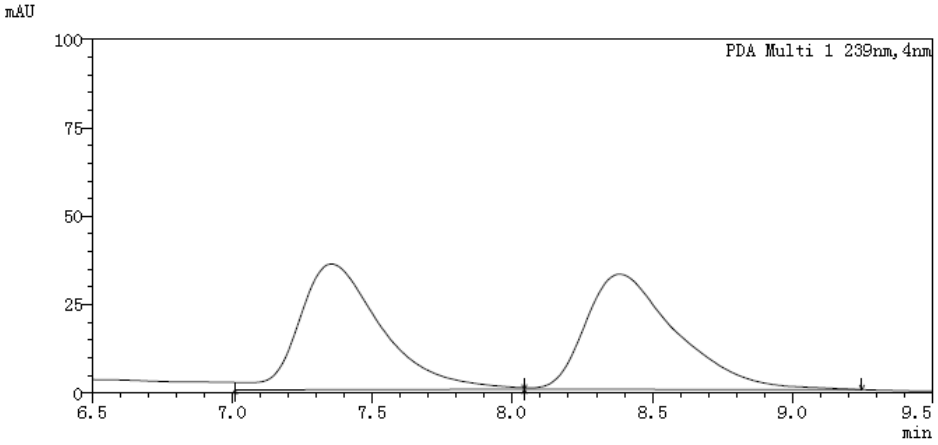
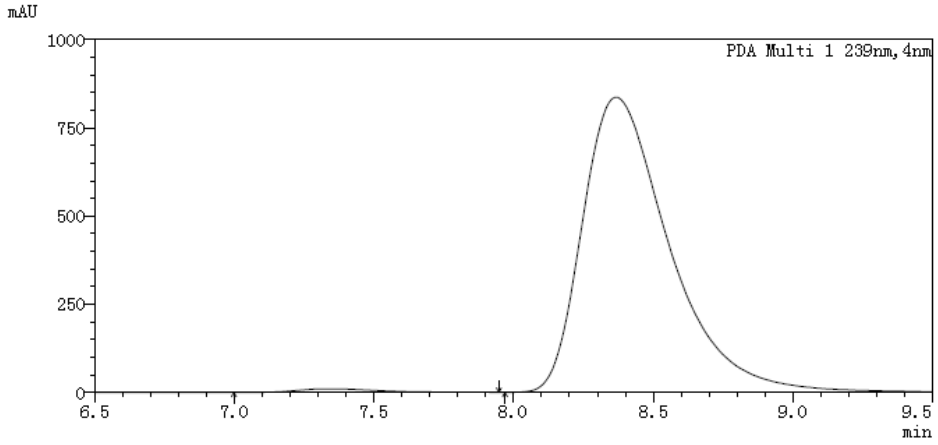


<Peak Results>

PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	7.353	35585	732708	49.915
2	8.383	32653	735208	50.085

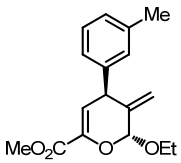
<Chromatogram>



<Peak Results>

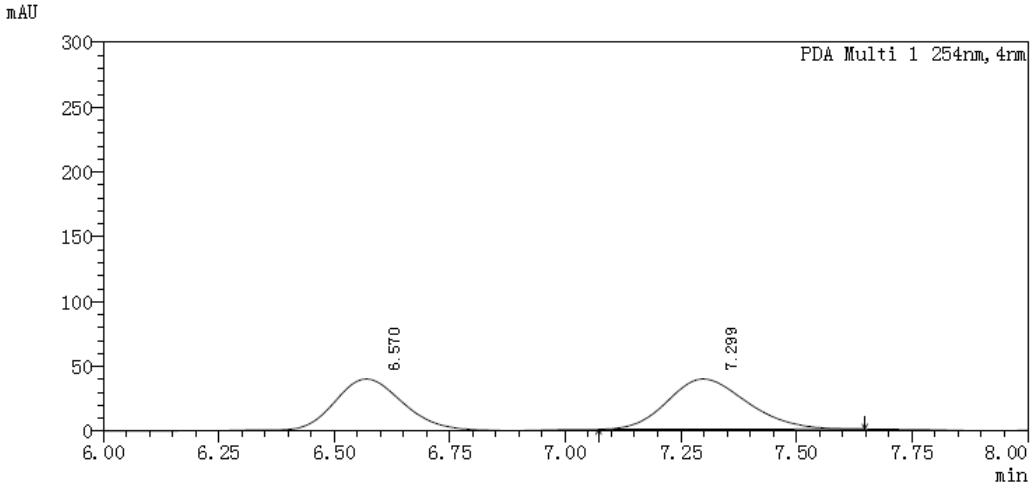
PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	7.340	10185	193011	1.053
2	8.367	837107	18130410	98.947



4q

〈Chromatogram〉

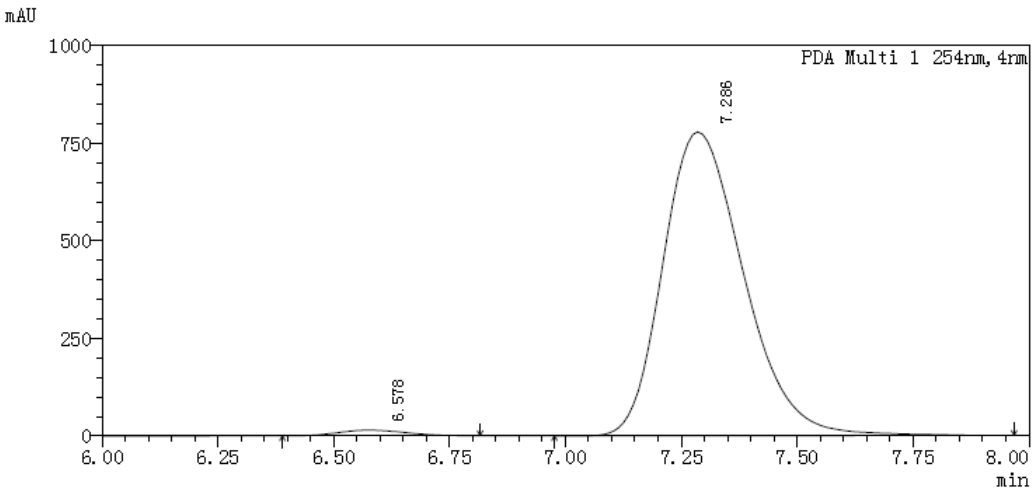


〈Peak Results〉

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	6.570	40953	448385	49.085
2	7.299	38825	465106	50.915

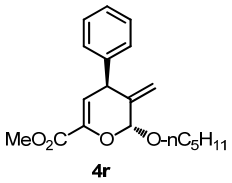
〈Chromatogram〉



〈Peak Results〉

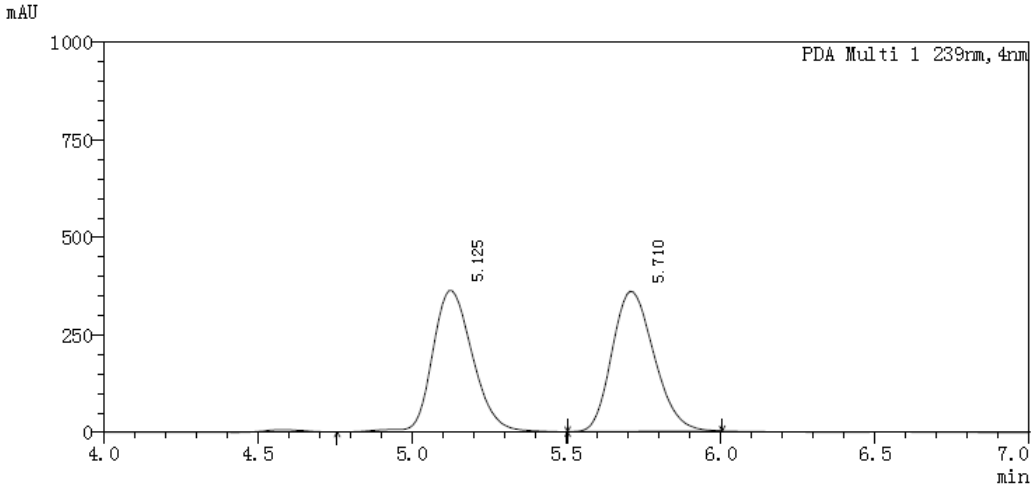
PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	6.578	14603	144243	1.506
2	7.286	778957	9434660	98.494



4r

〈Chromatogram〉

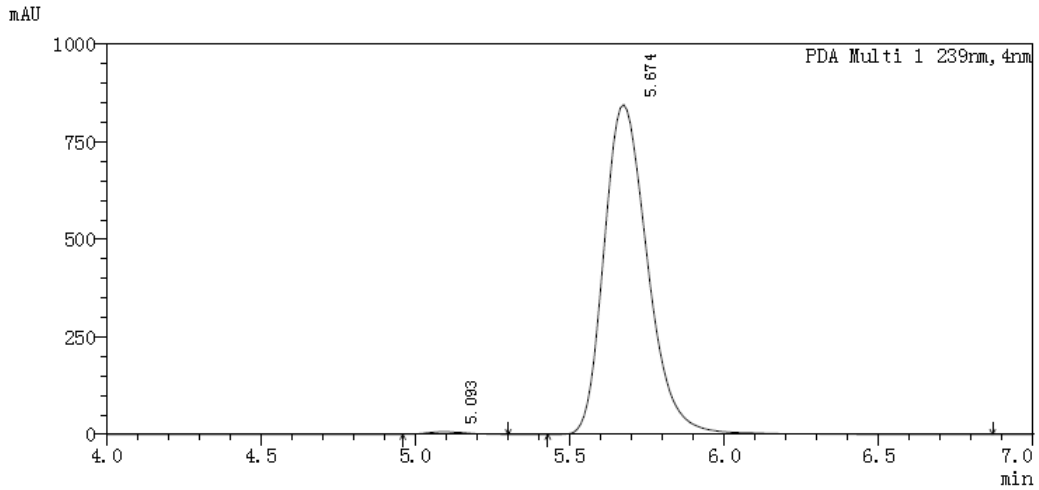


〈Peak Results〉

PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	5.125	362295	3282364	49.071
2	5.710	359678	3406684	50.929

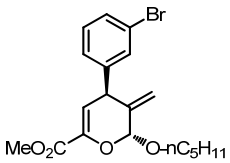
〈Chromatogram〉



〈Peak Results〉

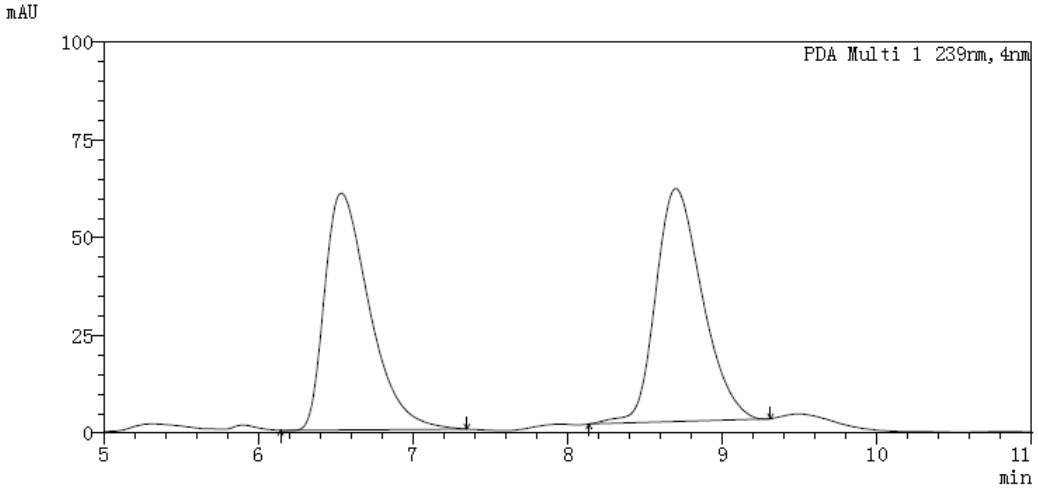
PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	5.093	6394	56085	0.671
2	5.674	845977	8302725	99.329



4s

〈Chromatogram〉

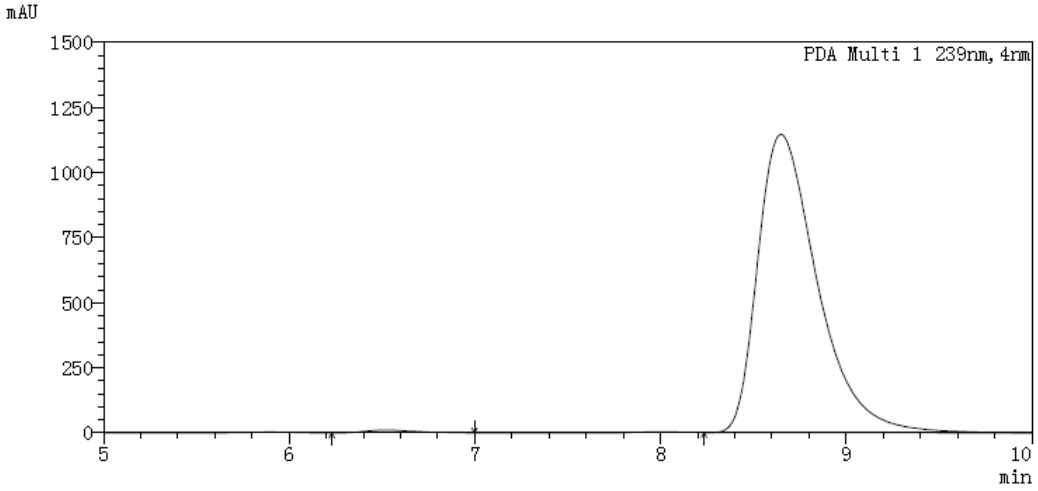


〈Peak Results〉

PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	6.537	60631	1220534	49.411
2	8.699	59636	1249655	50.589

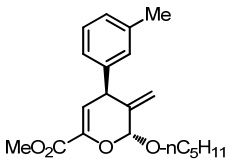
〈Chromatogram〉



〈Peak Results〉

PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	6.515	10153	191829	0.744
2	8.649	1146448	25604135	99.256



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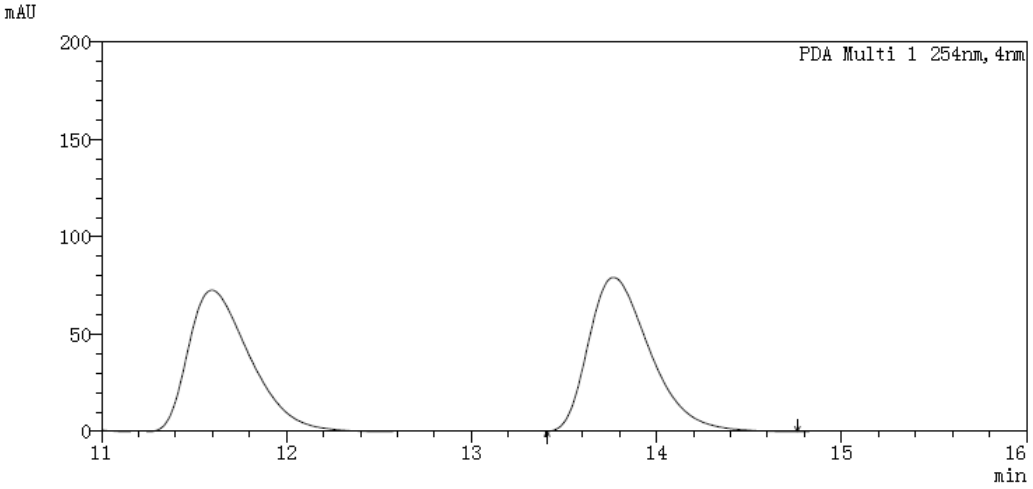
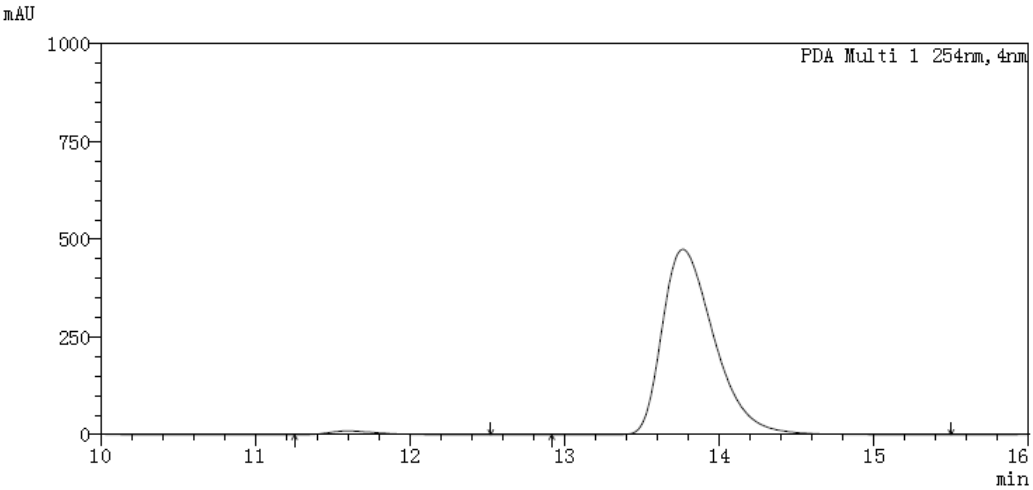


<Peak Results>

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	11.596	73216	1726549	48.525
2	13.768	79272	1831524	51.475

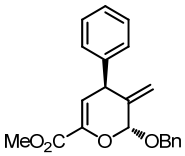
<Chromatogram>



<Peak Results>

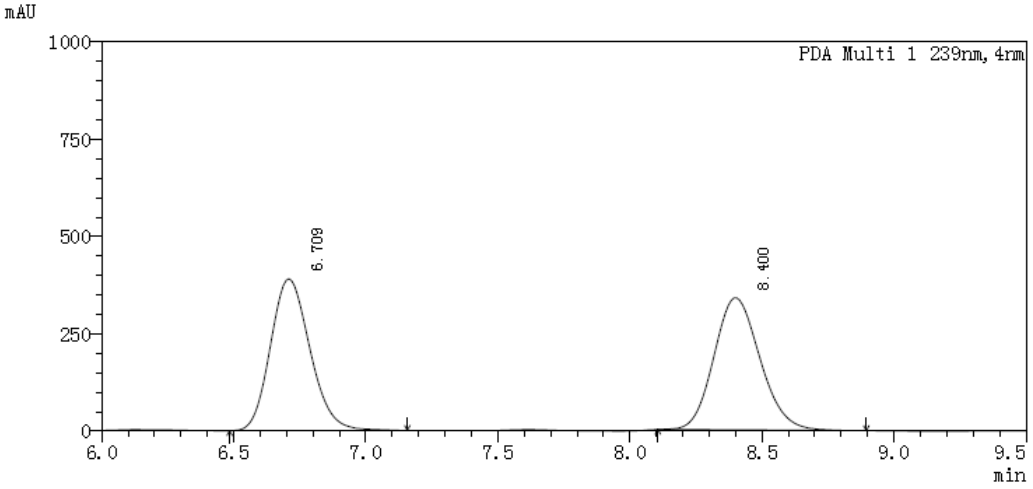
PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	11.599	9501	213702	1.884
2	13.764	474885	11129614	98.116



4u

〈Chromatogram〉

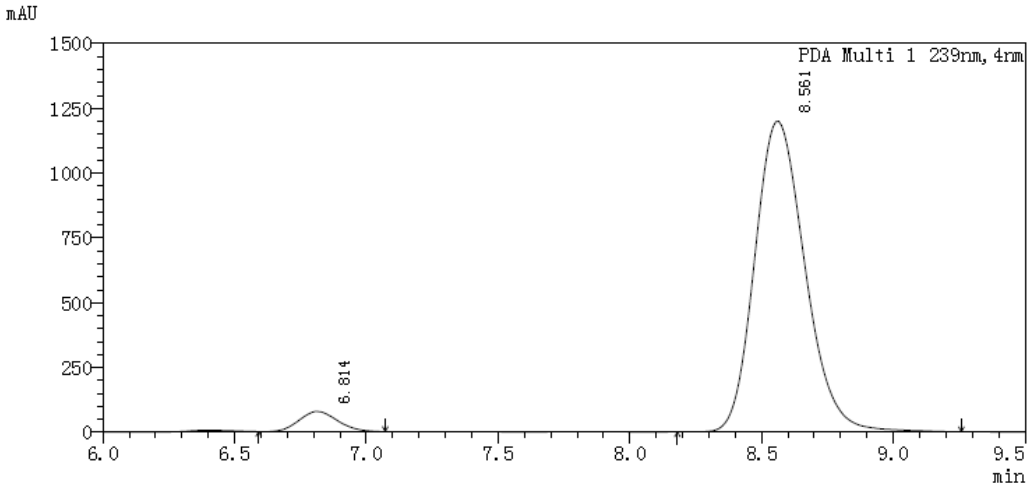


〈Peak Results〉

PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	6.709	390678	4063099	49.649
2	8.400	339230	4120483	50.351

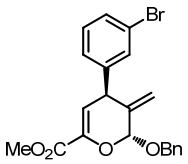
〈Chromatogram〉



〈Peak Results〉

PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	6.814	77356	778762	4.675
2	8.561	1198522	15877955	95.325



4v

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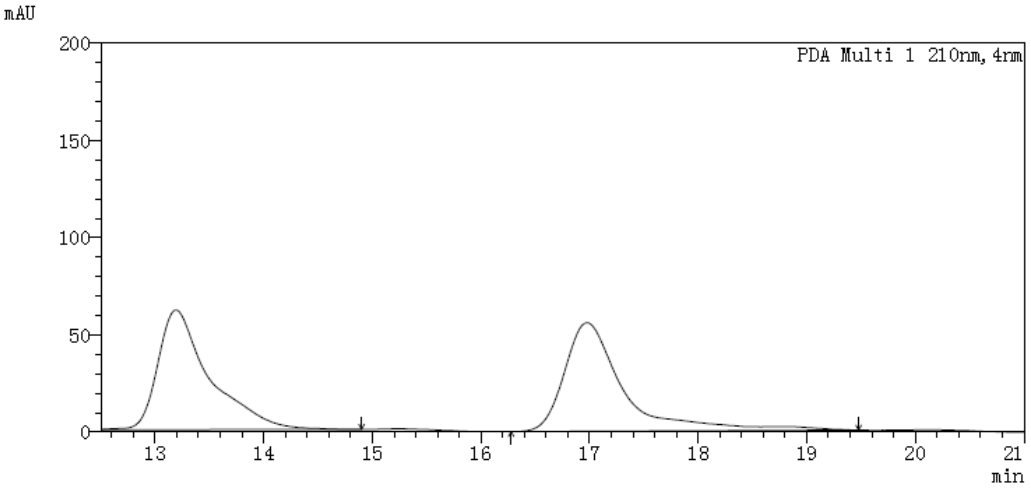
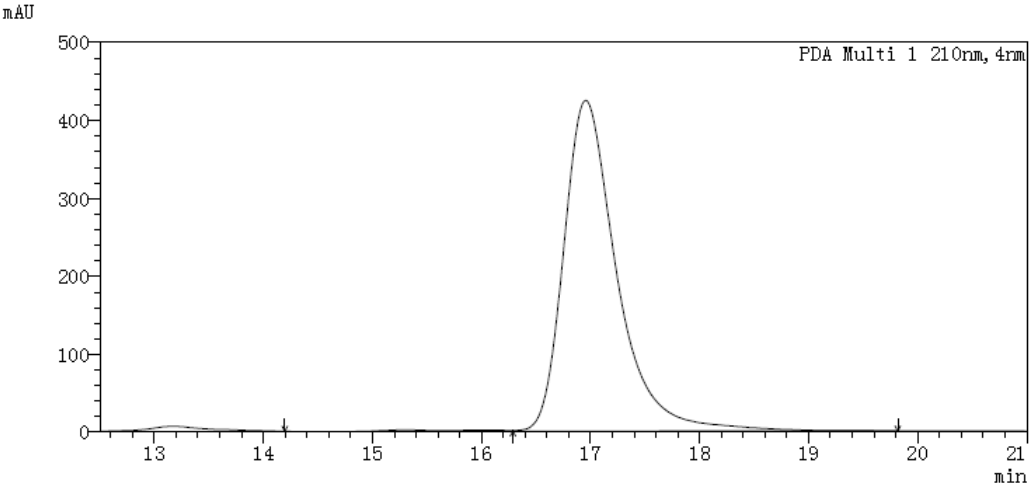


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	13.192	61557	2035474	49.135
2	16.978	55881	2107103	50.865

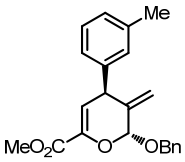
<Chromatogram>



<Peak Results>

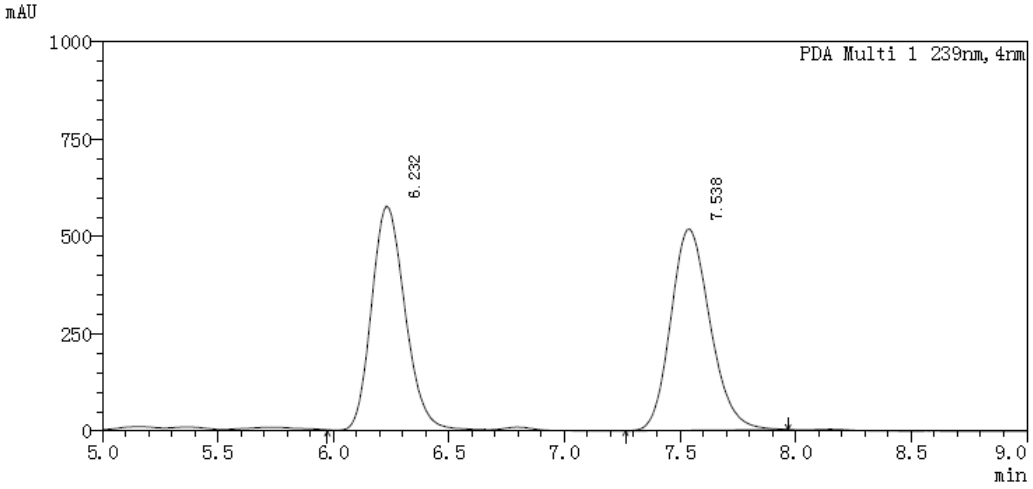
PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	13.167	6303	230223	1.575
2	16.956	424482	14385475	98.425



4w

〈Chromatogram〉

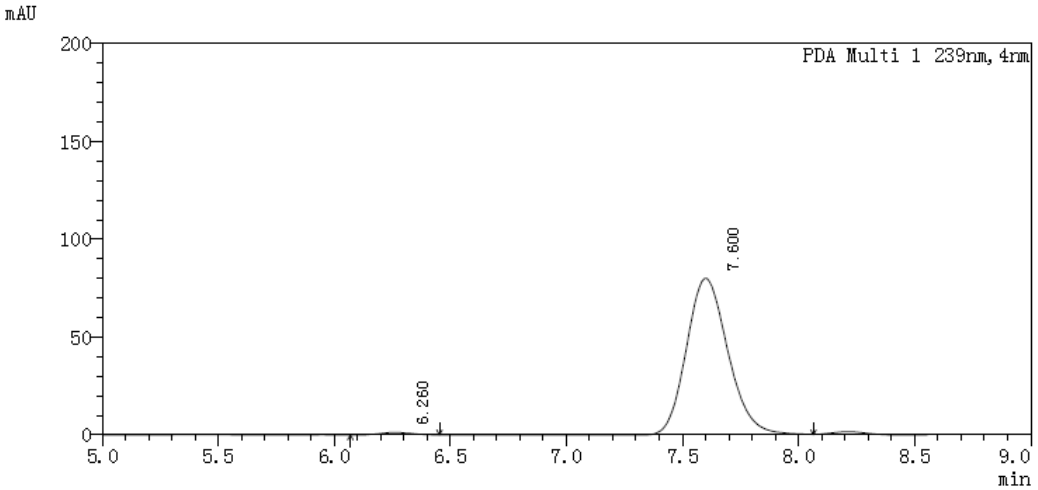


〈Peak Results〉

PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	6.232	579069	5950375	49.216
2	7.538	517697	6140054	50.784

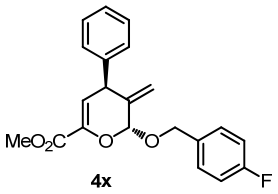
〈Chromatogram〉



〈Peak Results〉

PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	6.260	1248	12264	1.205
2	7.600	80138	1005793	98.795



4x

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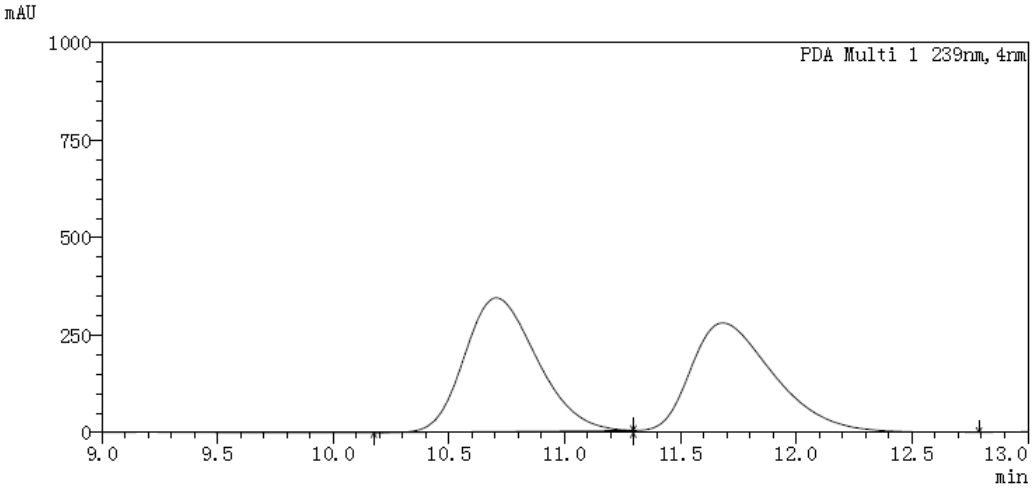
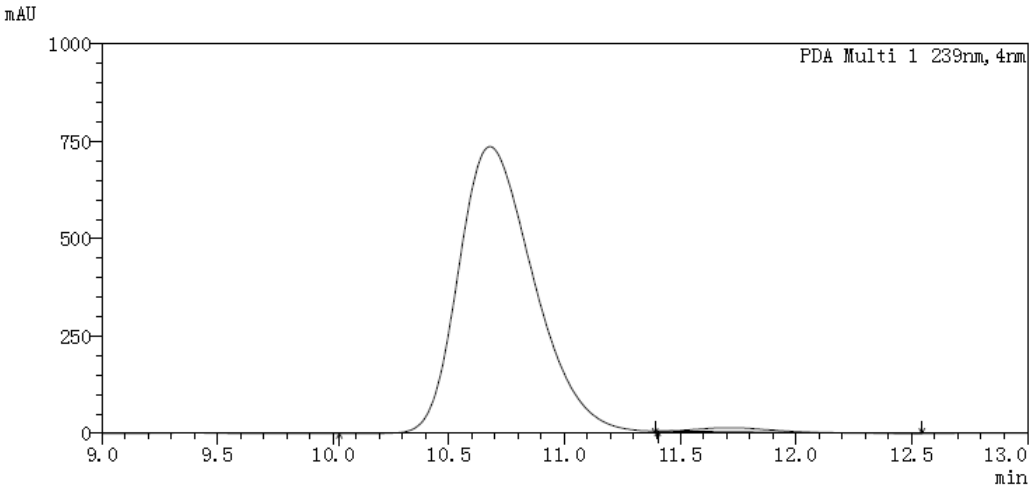


<Peak Results>

PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	10.705	342914	7440032	51.022
2	11.683	281950	7142025	48.978

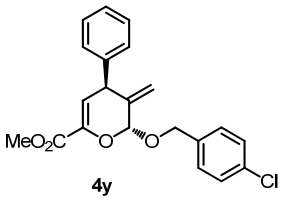
<Chromatogram>



<Peak Results>

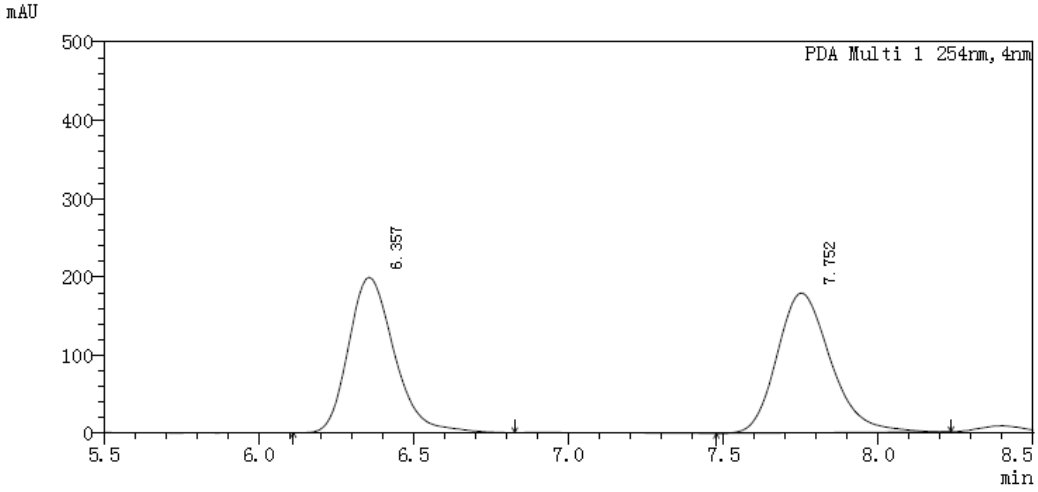
PDA Ch1 239nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	10.678	737341	16727055	98.859
2	11.709	10264	193095	1.141



4y

〈Chromatogram〉

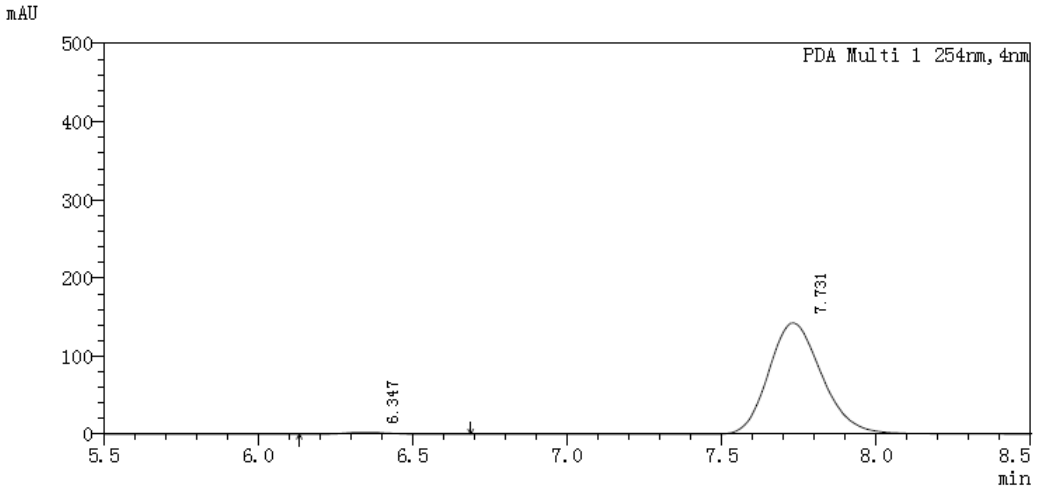


〈Peak Results〉

PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	6.357	198564	2034555	48.666
2	7.752	178526	2146065	51.334

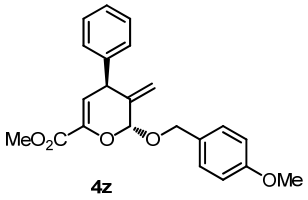
〈Chromatogram〉



〈Peak Results〉

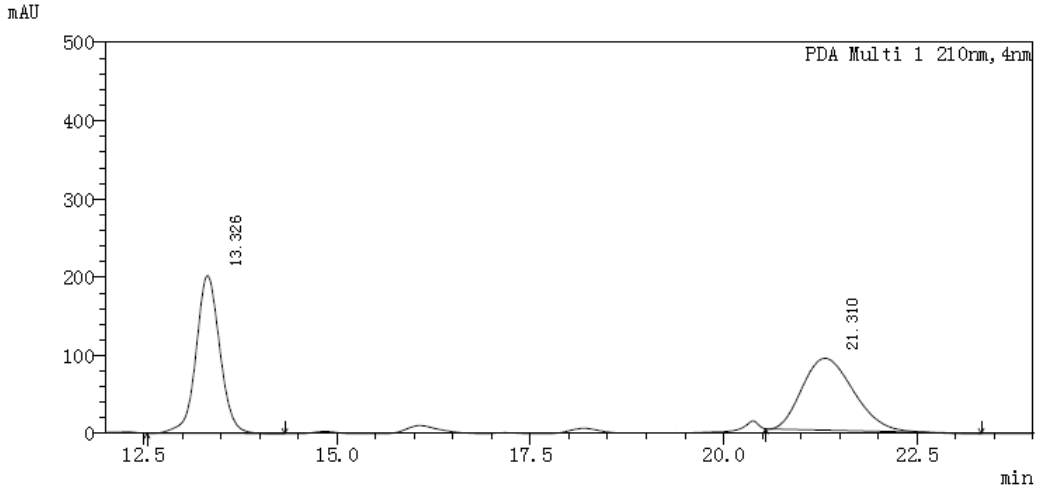
PDA Ch1 254nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	6.347	2767	27723	1.580
2	7.731	142672	1727060	98.420



4z

〈Chromatogram〉

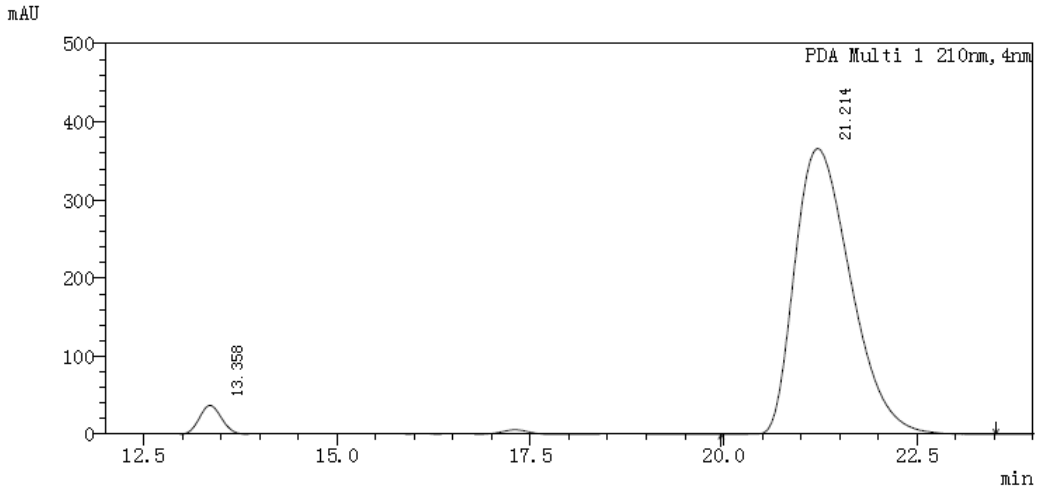


〈Peak Results〉

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	13.326	201863	4323089	50.326
2	21.310	92144	4267041	49.674

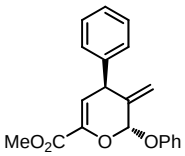
〈Chromatogram〉



〈Peak Results〉

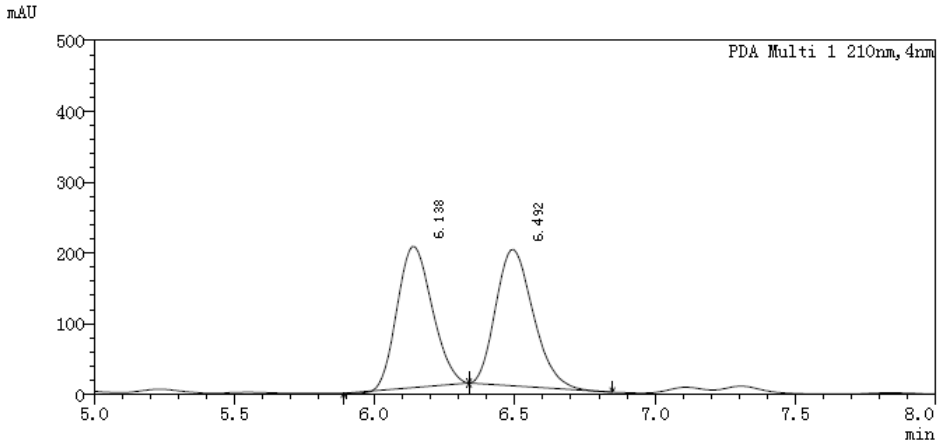
PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	13.358	37897	789722	4.105
2	21.214	365889	18447131	95.895



exo-5

〈Chromatogram〉

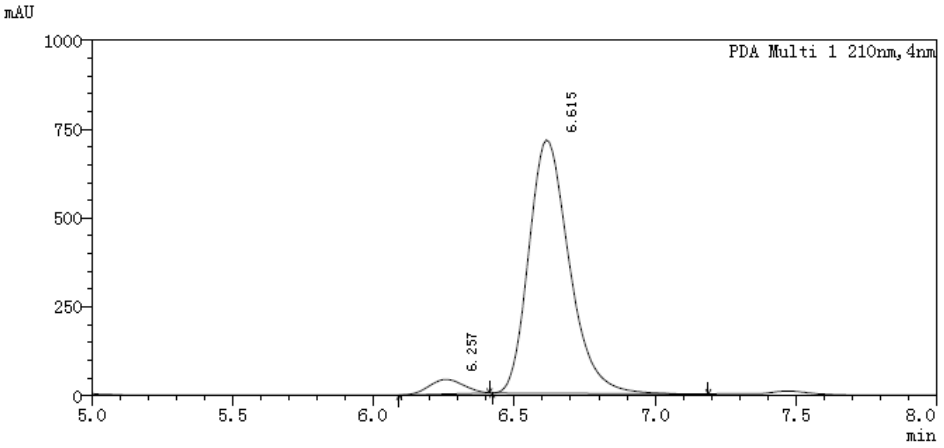


〈Peak Results〉

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	6.138	199373	1737750	49.188
2	6.492	192511	1795118	50.812

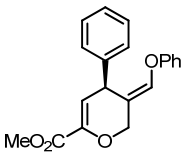
〈Chromatogram〉



〈Peak Results〉

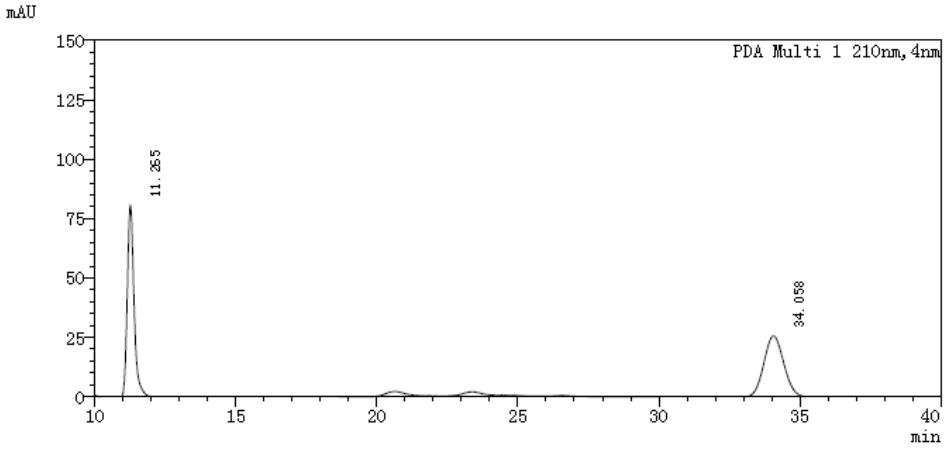
PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	6.257	40979	349237	4.661
2	6.615	713973	7143230	95.339



E-5'

<Chromatogram>

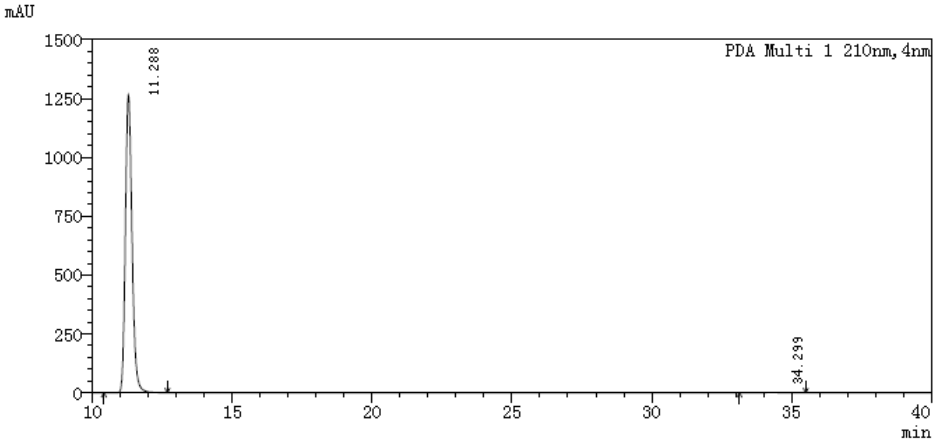


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	11.265	80886	1361867	50.179
2	34.058	26190	1352175	49.821

<Chromatogram>

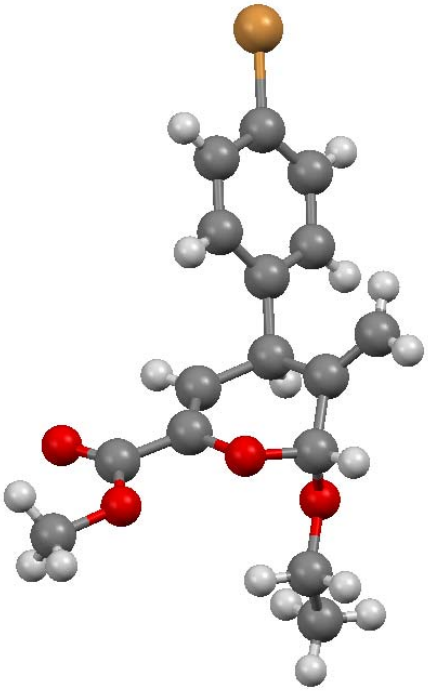


<Peak Results>

PDA Ch1 210nm

Index	Time/min	Height/mAU	Quantity/Area	Area %/%
1	11.288	1264537	20989916	99.523
2	34.299	1905	100530	0.477

X-ray Crystallographic study for 4p



Reference

1. K. D. Robarge, D. L. Boger, *J. Org. Chem.*, **1988**, *53*, 3373.