Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Phosphine-mediated Enantioselective [4+1] Annulations between ortho-Quinone Methides and Morita-Baylis-Hillman Carbonates

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Supporting Information

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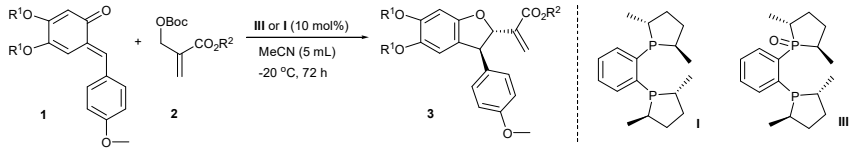
Experimental section

General

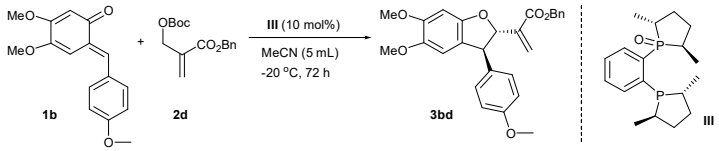
All reactions were carried out with dry, freshly distilled solvents in anhydrous conditions. All chemicals were used without further purification as commercially available unless otherwise noted. All reactions were performed under an atmosphere of dry nitrogen. Thin-layer chromatography (TLC) was performed on silica gel plates (60F-254) using UV-light (254 and 365 nm). Flash chromatography was conducted on silica gel (300–400 mesh). NMR (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR) spectra were recorded in $CDCl_3$ with TMS as the internal standard. Chemical shifts are reported in ppm and coupling constants are given in Hz. Data for ^{1}H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; m, multiplet), coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High resolution mass spectral (HRMS) analyses were measured using ESI techniques.

General procedure for the [4+1] annulation between *o*-QMs (1) and MBH carbonates (2)



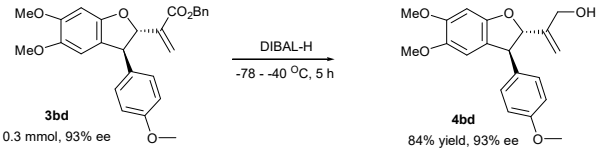
Under nitrogen atmosphere, a mixture of *o*-QMs **1** (0.20 mmol), MBH carbonate **2** (0.50 mmol), catalyst **III** or **I** (0.02 mmol) in MeCN (5.0 mL) was stirred at -20 °C in a sealed tube for 72 h. After removal of the solvent, the crude residue was purified by column chromatography (petroleum ether/ethyl acetate) on silica gel to give the corresponding products **3**.

Procedure for scaling up the [4+1] annulation between *o*-QMs 1b and MBH carbonate 2d



Under nitrogen atmosphere, a mixture of *o*-QMs **1b** (2.25 mmol), MBH carbonate **2d** (7.50 mmol), catalyst **III** (0.225 mmol) in MeCN (50.0 mL) was stirred at -20 °C in a sealed tube for 72 h. After removal of the solvent, the crude residue was purified by column chromatography (petroleum ether/ethyl acetate) on silica gel to give the corresponding products **3bd** (447.6 mg) in 45% yield with 93% ee.

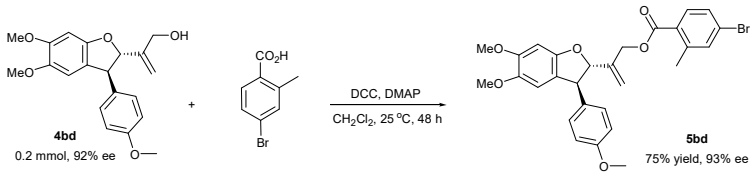
Procedure for transformation of ester group to hydroxy group



To a solution of **3bd** (0.3 mmol) in CH_2Cl_2 (5.0 mL) at -78 °C, DIBAL-H (0.75 mmol, 1M in hexane) was added dropwise. The mixture was stirred at -78 °C for 30 min and then at -40 °C for 4 h. The mixture was diluted with Et_2O. Rocelle's salt was added. The mixture was stirred at room temperature overnight. The mixture was extracted with Et_2O three times. The combined organic layer was washed with 1 M HCl, sat $NaHCO_3$, and bine, dried by Na_2SO_4 and filtered. Solvent

was removed under *vacuo*. The crude alcohol was purified by column chromatography (petroleum ether/ethyl acetate) on silica gel to give the corresponding products **4bd** (87.7 mg) in 84% yield with 93% ee.

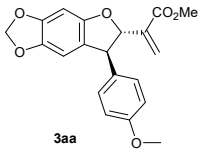
Procedure for esterification of alcohol 4bd



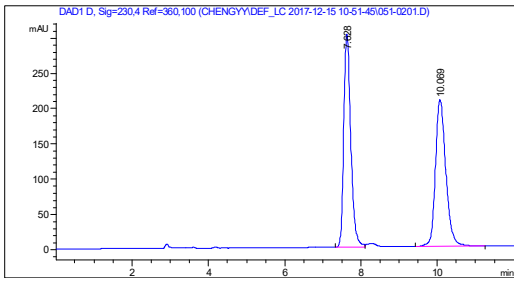
To a solution of **4bd** (0.2 mmol), 4-bromo-2-methylbenzoic acid (0.22 mmol), DCC (0.22 mmol) in CH_2Cl_2 (5.0 mL) with catalytic amount of 4-dimethylaminopyridine (DMAP) were stirred at room temperature overnight. The mixture was diluted with CH_2Cl_2 (20.0 mL), which was washed with 1 M HCl, sat $NaHCO_3$, and bine, dried by Na_2SO_4 and filtered. Solvent was removed under *vacuo*. The crude product was purified by column chromatography (petroleum ether/ethyl acetate) on silica gel to give the corresponding products **5bd** (80.7 mg) in 75% yield with 93% ee.

Compounds characterization

Methyl 2-((6S,7S)-6,7-dihydro-7-(4-methoxyphenyl)benzofuro[5,6-d][1,3]dioxol-6-yl)acrylate

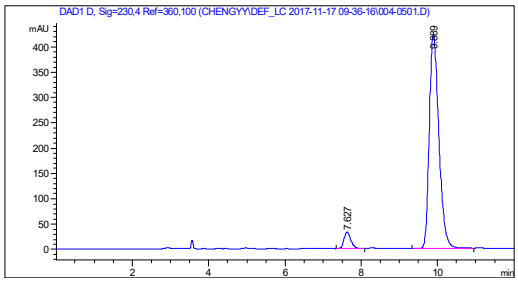


(3aa), ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.10 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 9.0 Hz, 2H), 6.51 (s, 1H), 6.43 (s, 1H), 6.30 (s, 1H), 5.89-5.87 (m, 3H), 5.31 (d, J = 5.0 Hz, 1H), 4.30 (d, J = 5.0 Hz, 1H), 3.78 (s, 3H), 3.74 (s, 3H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 166.0, 158.7, 154.0, 147.9, 142.3, 139.3, 135.5, 128.8, 125.5, 120.8, 114.1, 105.6, 101.4, 93.0, 89.6, 55.4, 54.4, 52.0. HRMS: exact mass calculated for $[M+H]^+$ ($C_{20}H_{19}O_6$) requires m/z 355.11761, found m/z 355.11679. HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 230 nm.



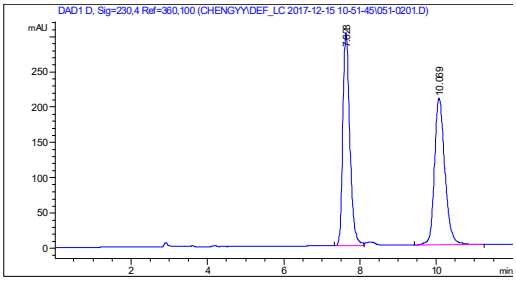
Racemic

#	Time	Area	Height	Width	Area%	Symmetry
1	7.628	3836.8	301.8	0.1943	49.440	0.718
2	10.069	3923.8	207.9	0.2882	50.560	0.731



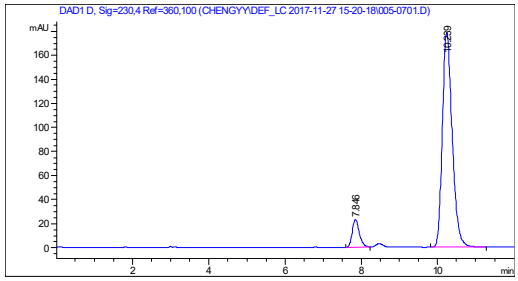
Chiral (Catalyst **III**, 89% ee, 56% yield)

#	Time	Area	Height	Width	Area%	Symmetry
1	7.627	420.7	33.2	0.1959	5.409	0.772
2	9.889	7358	423.8	0.2686	94.591	0.69



Racemic

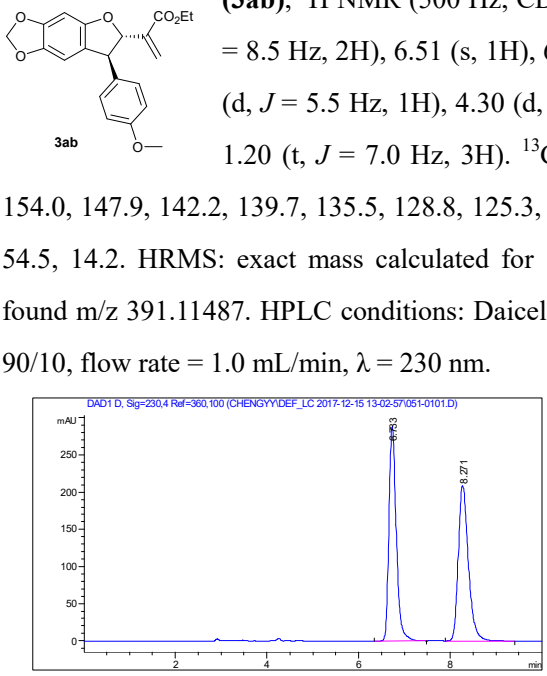
#	Time	Area	Height	Width	Area%	Symmetry
1	7.628	3836.8	301.8	0.1943	49.440	0.718
2	10.069	3923.8	207.9	0.2882	50.560	0.731



Chiral (Catalyst **I**, 83% ee, 82% yield)

#	Time	Area	Height	Width	Area%	Symmetry
1	7.846	297.8	23.1	0.1985	8.487	0.784
2	10.239	3211.5	178.6	0.2758	91.513	0.729

Ethyl 2-((6S,7S)-6,7-dihydro-7-(4-methoxyphenyl)benzofuro[5,6-d][1,3]dioxol-6-yl)acrylate (3ab), ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.11 (d, J = 8.5 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 6.51 (s, 1H), 6.43 (s, 1H), 6.30 (s, 1H), 5.88-5.84 (m, 3H), 5.33 (d, J = 5.5 Hz, 1H), 4.30 (d, J = 5.5 Hz, 1H), 4.22-4.16 (m, 2H), 3.78 (s, 3H), 1.20 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 165.5, 158.7, 154.0, 147.9, 142.2, 139.7, 135.5, 128.8, 125.3, 120.9, 114.1, 105.5, 101.4, 93.0, 89.6, 61.0, 55.4, 54.5, 14.2. HRMS: exact mass calculated for $[M+Na]^+$ ($C_{21}H_{20}O_6Na$) requires m/z 391.11521, found m/z 391.11487. HPLC conditions: Daicel Chiralpak OD-H column, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 230 nm.



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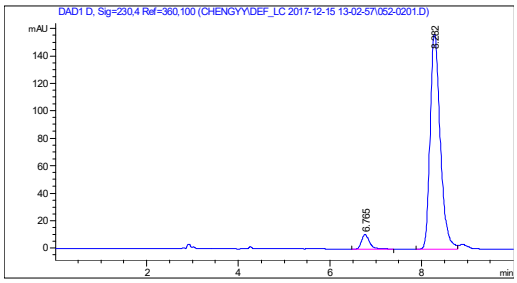
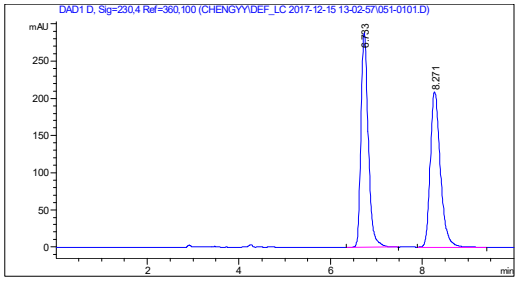


Chiral (Catalyst **III**, 89% ee, 32% yield)

#	Time	Area	Height	Width	Area%	Symmetry
1	6.733	3209.6	289	0.1696	50.003	0.725
2	8.271	3209.3	209.1	0.2331	49.997	0.7

#	Time	Area	Height	Width	Area%	Symmetry
1	6.765	137.7	11	0.1879	5.400	0.68
2	8.282	2413	156.8	0.2355	94.600	0.709



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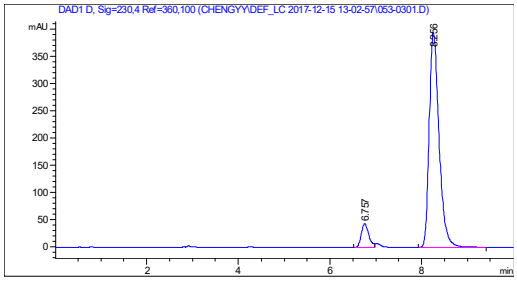


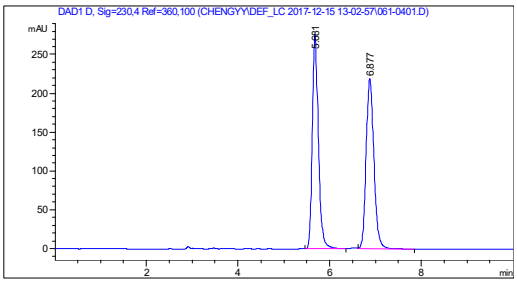
Chiral (Catalyst **I**, 84% ee, 76% yield)

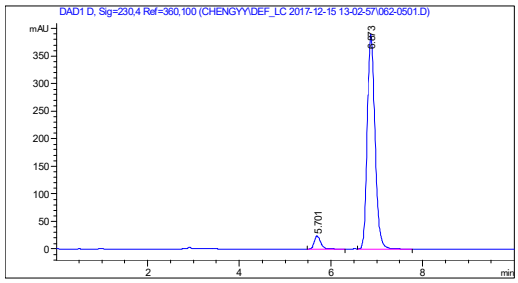
#	Time	Area	Height	Width	Area%	Symmetry
1	6.733	3209.6	289	0.1696	50.003	0.725
2	8.271	3209.3	209.1	0.2331	49.997	0.7

#	Time	Area	Height	Width	Area%	Symmetry
1	6.757	501.3	44.4	0.1738	7.829	0.769
2	8.256	5902.7	395.3	0.2282	92.171	0.666

Isobutyl 2-((6S,7S)-6,7-dihydro-7-(4-methoxyphenyl)benzofuro[5,6-d][1,3]dioxol-6-yl) acrylate (3ac), ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.11 (d, J = 8.5 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 6.51 (s, 1H), 6.43 (s, 1H), 6.31 (s, 1H), 5.88-5.84 (m, 3H), 5.32 (d, J = 5.5 Hz, 1H), 4.32 (d, J = 5.5 Hz, 1H), 3.98-3.89 (m, 2H), 3.78 (s, 3H), 1.91-1.83 (m, 1H), 0.87 (t, J = 6.5 Hz, 6H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 165.6, 158.8, 154.1, 147.9, 142.2, 139.6, 135.4, 128.8, 125.5, 120.9, 114.1, 105.5, 101.4, 93.0, 89.8, 71.1, 55.4, 54.4, 27.8, 19.2, 19.1. HRMS: exact mass calculated for $[M+H]^+$ ($C_{23}H_{25}O_6$) requires m/z 397.16456, found m/z 397.16400. HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 230 nm.

3ac



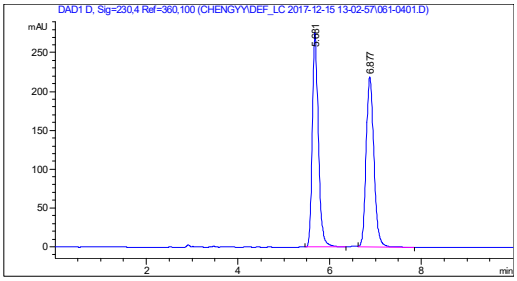


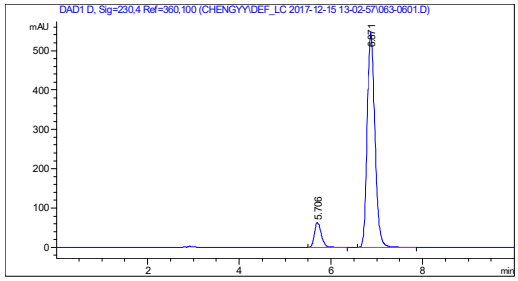
Racemic

#	Time	Area	Height	Width	Area%	Symmetry
1	5.681	2586.9	276.7	0.1431	49.870	0.738
2	6.877	2600.4	219.4	0.1823	50.130	0.808

Chiral (Catalyst **III**, 90% ee, 32% yield)

#	Time	Area	Height	Width	Area%	Symmetry
1	5.701	247	24.5	0.1537	5.107	0.726
2	6.873	4590.2	389.9	0.1813	94.893	0.793





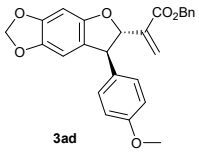
Racemic

#	Time	Area	Height	Width	Area%	Symmetry
1	5.681	2586.9	276.7	0.1431	49.870	0.738
2	6.877	2600.4	219.4	0.1823	50.130	0.808

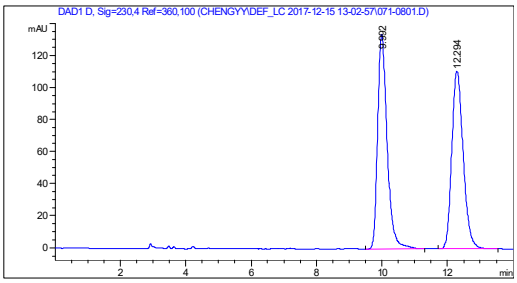
Chiral (Catalyst **I**, 81% ee, 78% yield)

#	Time	Area	Height	Width	Area%	Symmetry
1	5.706	681.5	64	0.1642	9.596	0.7
2	6.871	6420.4	547	0.1809	90.404	0.779

Benzyl 2-((6S,7S)-6,7-dihydro-7-(4-methoxyphenyl)benzofuro[5,6-d][1,3]dioxol-6-yl)acrylate



(3ad), ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.35-7.31 (m, 3H), 7.27-7.24 (m, 2H), 7.04 (d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 6.50 (s, 1H), 6.41 (s, 1H), 6.35 (s, 1H), 5.88-5.87 (m, 3H), 5.33 (d, *J* = 5.5 Hz, 1H), 5.21-5.15 (m, 2H), 4.29 (d, *J* = 5.5 Hz, 1H), 3.77 (s, 3H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 165.4, 158.7, 154.0, 147.9, 142.3, 139.4, 135.6, 135.4, 128.8, 128.6, 128.4, 126.1, 120.8, 114.1, 105.5, 101.4, 93.0, 89.6, 66.8, 55.3, 54.4. HRMS: exact mass calculated for $[M+H]^+$ ($C_{26}H_{23}O_6$) requires m/z 431.14891, found m/z 431.14902. HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 230 nm.



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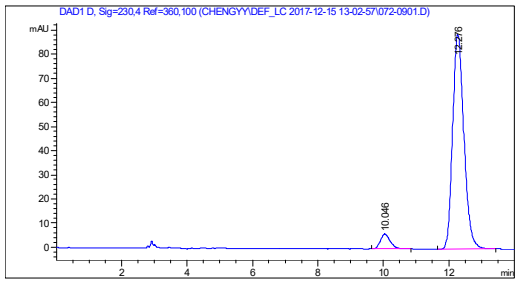
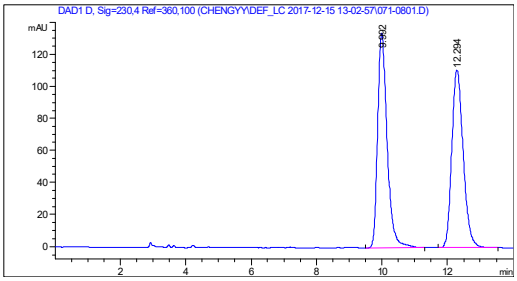


Chiral (Catalyst **III**, 88% ee, 42% yield)

#	Time	Area	Height	Width	Area%	Symmetry
1	9.992	2718	134.3	0.3081	50.238	0.674
2	12.294	2692.3	111.1	0.3727	49.762	0.766

#	Time	Area	Height	Width	Area%	Symmetry
1	10.046	131.4	6.2	0.3261	5.789	0.762
2	12.276	2139.2	89.2	0.3699	94.211	0.778



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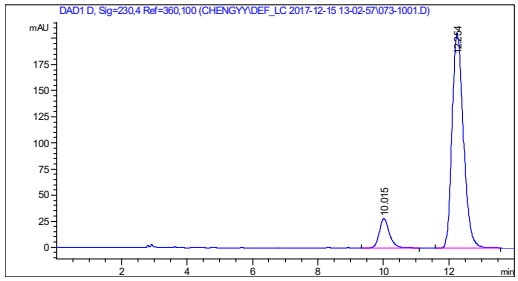
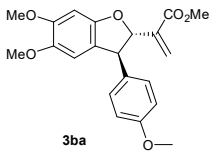


Chiral (Catalyst **I**, 79% ee, 90% yield)

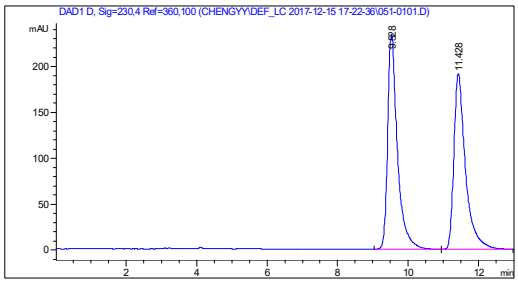
#	Time	Area	Height	Width	Area%	Symmetry
1	9.992	2718	134.3	0.3081	50.238	0.674
2	12.294	2692.3	111.1	0.3727	49.762	0.766

#	Time	Area	Height	Width	Area%	Symmetry
1	10.015	629.9	28.4	0.3331	11.265	0.758
2	12.254	4961.4	206	0.371	88.735	0.742

Methyl 2-((2S,3S)-2,3-dihydro-5,6-dimethoxy-3-(4-methoxyphenyl)benzofuran-2-yl)acrylate

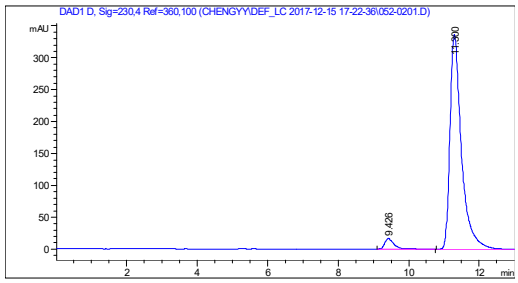


(3ba), ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.10 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 9.0 Hz, 2H), 6.59 (s, 1H), 6.54 (s, 1H), 6.30 (s, 1H), 5.88 (s, 1H), 5.29 (d, J = 5.0 Hz, 1H), 4.36 (d, J = 5.0 Hz, 1H), 3.88 (s, 3H), 3.79 (s, 3H), 3.74 (s, 3H), 3.73 (s, 3H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 166.0, 158.7, 153.6, 149.9, 144.2, 139.4, 135.6, 128.9, 125.5, 119.5, 114.1, 109.0, 94.7, 89.4, 56.7, 56.2, 55.3, 54.7, 52.0. HRMS: exact mass calculated for $[M+H]^+$ ($C_{21}H_{23}O_6$) requires m/z 371.14891, found m/z 371.14825. HPLC conditions: Daicel Chiralpak AD-H column, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 230 nm.



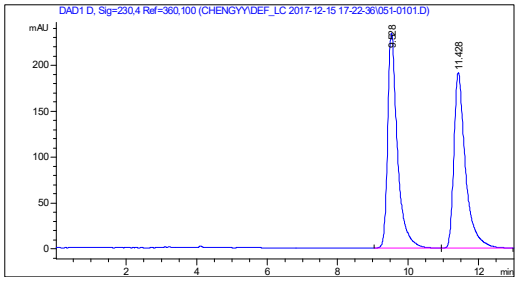
Racemic

#	Time	Area	Height	Width	Area%	Symmetry
1	9.528	593.7	30.8	0.2831	50.641	0.568
2	11.428	578.6	25.2	0.3382	49.359	0.56



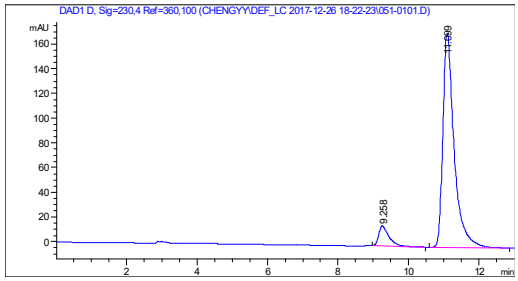
Chiral (Catalyst **III**, 92% ee, 51% yield)

#	Time	Area	Height	Width	Area%	Symmetry
1	9.426	317.7	16.8	0.2791	3.985	0.546
2	11.3	7655	337.4	0.3347	96.015	0.56



Racemic

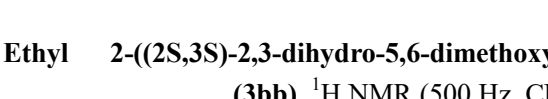
#	Time	Area	Height	Width	Area%	Symmetry
1	9.528	593.7	30.8	0.2831	50.641	0.568
2	11.428	578.6	25.2	0.3382	49.359	0.56

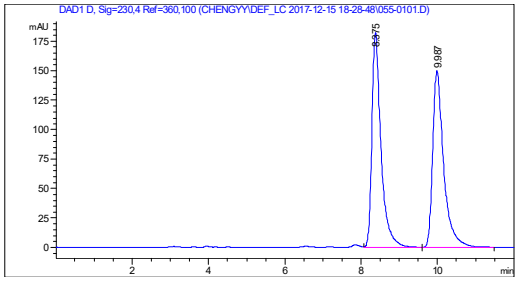


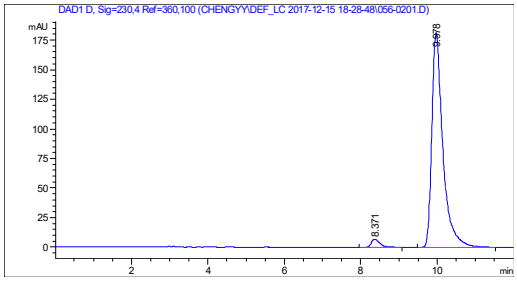
Chiral (Catalyst **I**, 85% ee, 65% yield)

#	Time	Area	Height	Width	Area%	Symmetry
1	9.258	319.3	16.1	0.2854	7.607	0.503
2	11.099	3878.7	173.6	0.3286	92.393	0.564

Ethyl 2-((2S,3S)-2,3-dihydro-5,6-dimethoxy-3-(4-methoxyphenyl)benzofuran-2-yl)acrylate (3bb), ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.11 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 6.59 (s, 1H), 6.53 (s, 1H), 6.30 (s, 1H), 5.85 (s, 1H), 5.31 (d, J = 5.5 Hz, 1H), 4.36 (d, J = 5.0 Hz, 1H), 4.23-4.16 (m, 2H), 3.88 (s, 3H), 3.79 (s, 3H), 3.73 (s, 3H), 1.21 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 165.6, 158.7, 153.6, 149.9, 144.1, 139.8, 135.6, 128.9, 125.3, 119.6, 114.1, 109.0, 94.7, 89.5, 61.1, 56.7, 56.2, 55.3, 54.8, 14.2. HRMS: exact mass calculated for $[M+H]^+$ ($C_{22}H_{25}O_6$) requires m/z 385.16456, found m/z 385.16345. HPLC conditions: Daicel Chiralpak AD-H column, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 230 nm.





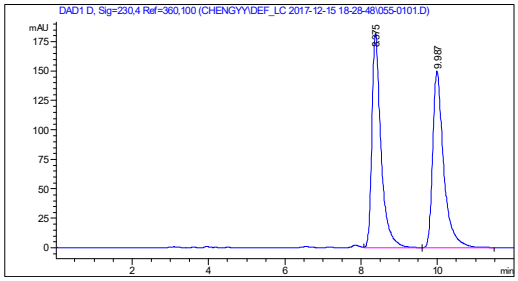


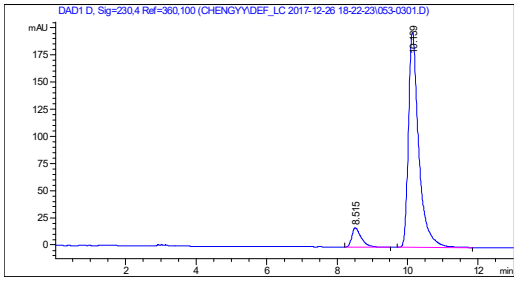
Racemic

#	Time	Area	Height	Width	Area%	Symmetry
1	8.375	3036.4	182.7	0.2439	50.339	0.57
2	9.987	2995.5	149.9	0.2951	49.661	0.567

Chiral (Catalyst **III**, 94% ee, 54% yield)

#	Time	Area	Height	Width	Area%	Symmetry
1	8.371	120.6	7.2	0.2468	3.181	0.579
2	9.978	3670.1	182.1	0.2971	96.819	0.562





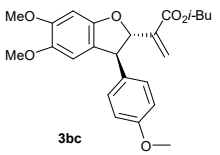
Racemic

#	Time	Area	Height	Width	Area%	Symmetry
1	8.375	3036.4	182.7	0.2439	50.339	0.57
2	9.987	2995.5	149.9	0.2951	49.661	0.567

Chiral(Catalyst **I**, 85% ee, 80% yield)

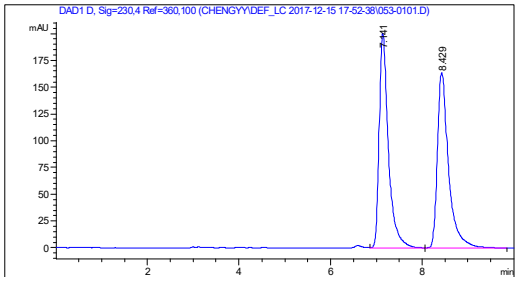
#	Time	Area	Height	Width	Area%	Symmetry
1	8.515	336.8	17.9	0.2741	7.708	0.506
2	10.139	4032.9	198	0.2997	92.292	0.563

Isobutyl 2-((2S,3S)-2,3-dihydro-5,6-dimethoxy-3-(4-methoxyphenyl)benzofuran-2-yl)acrylate

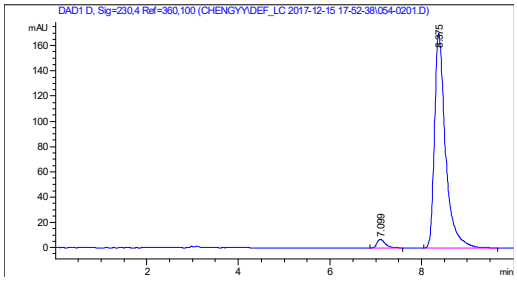


3bc

(3bc), ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.12 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 6.58 (s, 1H), 6.54 (s, 1H), 6.31 (s, 1H), 5.85 (s, 1H), 5.31 (d, J = 5.5 Hz, 1H), 4.39 (d, J = 5.5 Hz, 1H), 3.99-3.89 (m, 2H), 3.88 (s, 3H), 3.79 (s, 3H), 3.73 (s, 3H), 1.91-1.83 (m, 1H), 0.89-0.86 (m, 6H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 165.6, 158.7, 153.7, 149.9, 144.1, 139.7, 135.5, 128.9, 125.5, 119.6, 114.1, 109.0, 94.8, 89.6, 71.1, 56.7, 56.2, 55.3, 54.7, 27.8, 19.2, 19.1. HRMS: exact mass calculated for $[M+H]^+$ ($C_{24}H_{29}O_6$) requires m/z 413.19587, found m/z 413.19513. HPLC conditions: Daicel Chiralpak AD-H column, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 230 nm.



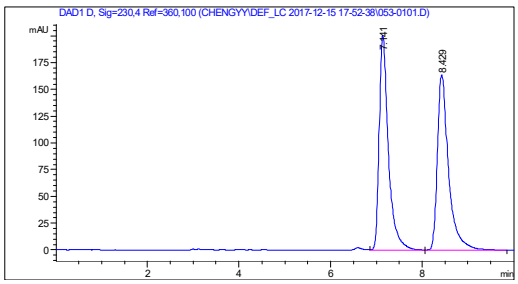
Racemic



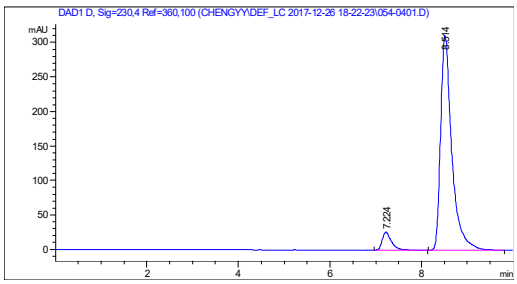
Chiral (Catalyst **III**, 94% ee, 55% yield)

#	Time	Area	Height	Width	Area%	Symmetry
1	7.141	2803.1	200.9	0.2068	50.148	0.577
2	8.429	2786.5	163.8	0.2504	49.852	0.566

#	Time	Area	Height	Width	Area%	Symmetry
1	7.099	93	7.1	0.1959	3.159	0.628
2	8.375	2852.5	170.4	0.2473	96.841	0.571



Racemic

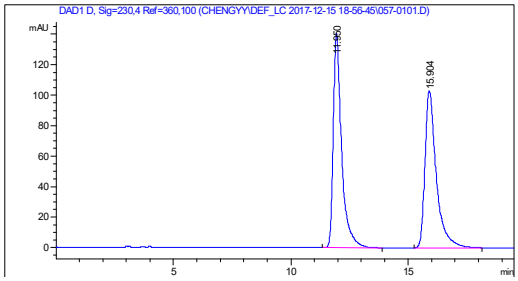


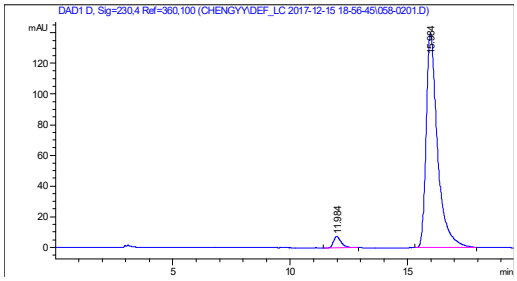
Chiral (Catalyst **I**, 87% ee, 75% yield)

#	Time	Area	Height	Width	Area%	Symmetry
1	7.141	2803.1	200.9	0.2068	50.148	0.577
2	8.429	2786.5	163.8	0.2504	49.852	0.566

#	Time	Area	Height	Width	Area%	Symmetry
1	7.224	380.6	26.3	0.2145	6.668	0.585
2	8.514	5327.5	312.1	0.2511	93.332	0.566

Benzyl 2-((2S,3S)-2,3-dihydro-5,6-dimethoxy-3-(4-methoxyphenyl)benzofuran-2-yl)acrylate (3bd), ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.33-7.32 (m, 3H), 7.27-7.25 (m, 2H), 7.04 (d, J = 8.5 Hz, 2H), 6.80 (d, J = 8.5 Hz, 2H), 6.57 (s, 1H), 6.51 (s, 1H), 6.35 (s, 1H), 5.87 (s, 1H), 5.31 (d, J = 5.0 Hz, 1H), 5.22-5.16 (m, 2H), 4.36 (d, J = 5.5 Hz, 1H), 3.88 (s, 3H), 3.78 (s, 3H), 3.73 (s, 3H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 165.4, 158.7, 153.6, 149.9, 144.2, 139.5, 135.6, 135.5, 128.9, 128.6, 128.4, 128.3, 126.1, 119.5, 114.1, 109.0, 94.7, 89.5, 66.8, 56.7, 56.2, 55.3, 54.7. HRMS: exact mass calculated for $[M+H]^+$ ($C_{27}H_{27}O_6$) requires m/z 447.18022, found m/z 447.17957. HPLC conditions: Daicel Chiralpak AD-H column, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 230 nm.



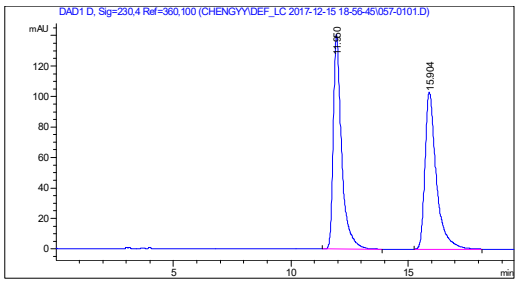


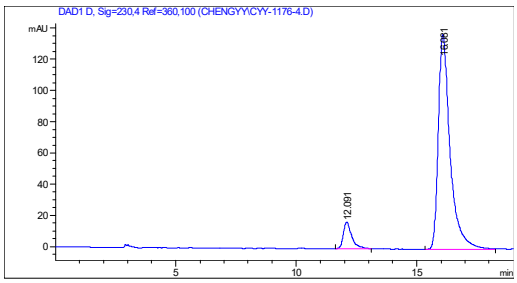
Racemic

Chiral (Catalyst **III**, 93% ee, 67% yield)

#	Time	Area	Height	Width	Area%	Symmetry
1	11.95	3502.4	141.1	0.3657	50.111	0.564
2	15.904	3486.9	103.2	0.4982	49.889	0.567

#	Time	Area	Height	Width	Area%	Symmetry
1	11.984	178.8	7.6	0.3522	3.655	0.632
2	15.984	4712.8	140	0.4986	96.345	0.575





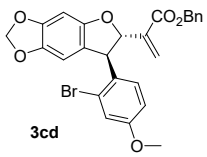
Racemic

Chiral (Catalyst **I**, 84% ee, 74% yield)

#	Time	Area	Height	Width	Area%	Symmetry
1	11.95	3502.4	141.1	0.3657	50.111	0.564
2	15.904	3486.9	103.2	0.4982	49.889	0.567

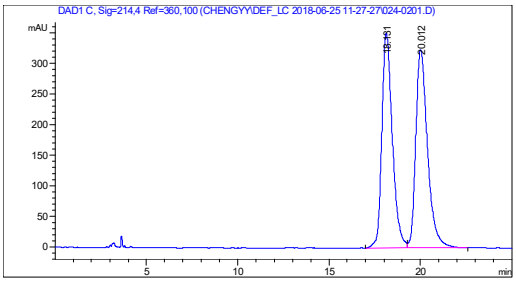
#	Time	Area	Height	Width	Area%	Symmetry
1	12.091	410.2	17	0.3576	8.032	0.612
2	16.081	4696.7	138	0.5032	91.968	0.57

benzyl 2-((6S,7R)-7-(2-bromo-4-methoxyphenyl)-6,7-dihydrobenzofuro[5,6-d][1,3]dioxol-6-yl)acrylate (3cd)

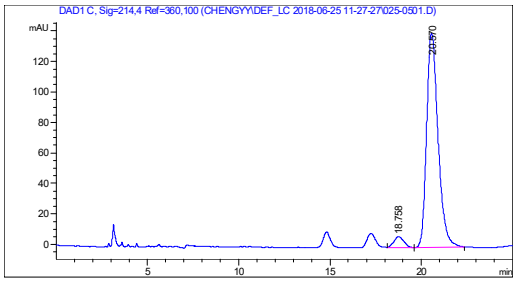


3cd

^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.27-7.26 (m, 3H), 7.19-7.17 (m, 2H), 7.09 (d, J = 9.0 Hz, 1H), 7.01 (d, J = 2.5 Hz, 1H), 6.79 (dd, J = 2.5, 9.0 Hz, 1H), 6.47 (s, 1H), 6.42 (s, 1H), 6.39 (s, 1H), 5.93 (s, 1H), 5.87 (s, 2H), 5.43 (d, J = 6.0 Hz, 1H), 5.24 (d, J = 12.5 Hz, 1H), 5.08 (d, J = 12.5 Hz, 1H), 4.92 (d, J = 6.0 Hz, 1H), 3.75 (s, 3H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 165.2, 158.9, 153.8, 148.0, 142.3, 139.5, 135.5, 134.7, 129.7, 128.5, 128.2, 128.1, 126.2, 124.0, 121.0, 117.5, 114.8, 105.1, 101.4, 93.0, 89.2, 66.8, 55.6, 53.1. HRMS: exact mass calculated for $[M+H]^+$ ($C_{26}H_{22}O_6Br$) requires m/z 509.05943, found m/z 509.05939. HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/2-propanol = 97/3, flow rate = 1.0 mL/min, λ = 214 or 254 nm.



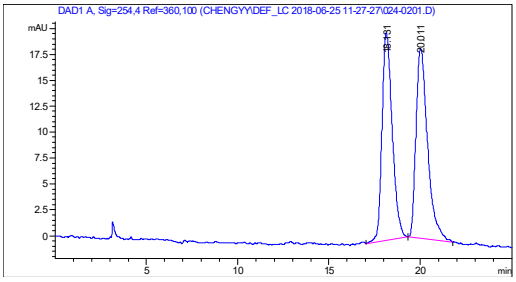
Racemic



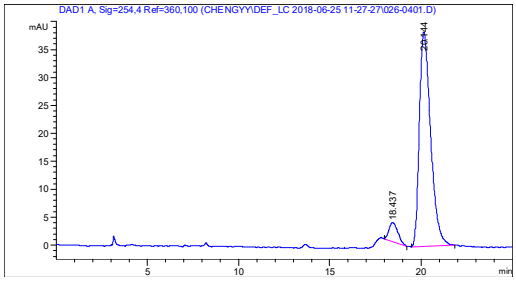
Chiral (Catalyst **III**, 92% ee, 23% yield)

#	Time	Area	Height	Width	Area%	Symmetry
1	18.131	14072.3	351	0.6117	49.280	0.69
2	20.012	14483.5	323.8	0.6778	50.720	0.643

#	Time	Area	Height	Width	Area%	Symmetry
1	18.758	265.1	6.9	0.5934	4.151	0.805
2	20.57	6121.7	140.6	0.6618	95.849	0.72



Racemic

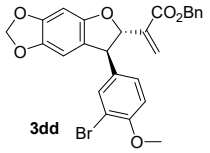


Chiral (Catalyst **I**, 87% ee, 79% yield)

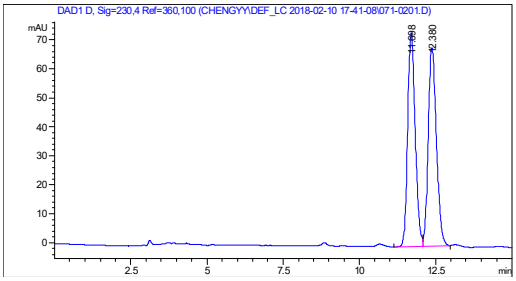
#	Time	Area	Height	Width	Area%	Symmetry
1	18.131	782.8	20.1	0.5993	49.262	0.695
2	20.011	806.3	18.3	0.6673	50.738	0.615

#	Time	Area	Height	Width	Area%	Symmetry
1	18.437	114.5	3.4	0.4922	6.507	0.671
2	20.144	1645.4	38.4	0.6522	93.493	0.614

benzyl 2-((6S,7S)-7-(3-bromo-4-methoxyphenyl)-6,7-dihydrobenzofuro[5,6-d][1,3]dioxol-6-yl)acrylate (3dd)

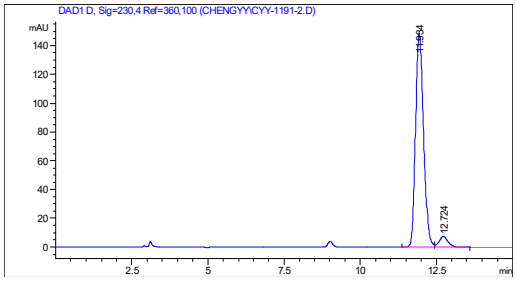


^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.34-7.32 (m, 4H), 7.28-7.26 (m, 2H), 7.03 (d, J = 8.5 Hz, 1H), 6.76 (d, J = 8.5 Hz, 1H), 6.50 (s, 1H), 6.39 (s, 1H), 6.36 (s, 1H), 5.90-5.87 (m, 3H), 5.33 (d, J = 5.0 Hz, 1H), 5.22-5.16 (m, 2H), 4.25 (d, J = 4.5 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 165.4, 155.1, 154.1, 148.3, 142.5, 139.3, 137.1, 135.6, 132.6, 128.8, 128.5, 128.4, 128.0, 126.3, 120.2, 112.1, 112.0, 105.5, 101.6, 93.2, 89.4, 66.9, 56.4, 54.2. HRMS: exact mass calculated for $[M+H]^+$ ($C_{26}H_{22}O_6Br$) requires m/z 509.05943, found m/z 509.05854. HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/2-propanol = 95/5, flow rate = 1.0 mL/min, λ = 230 nm.



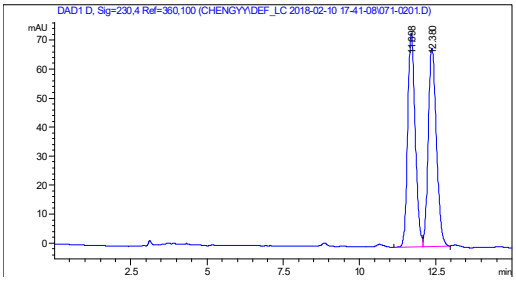
Racemic

#	Time	Area	Height	Width	Area%	Symmetry
1	11.698	1272.7	73.8	0.2672	50.006	0.81
2	12.38	1272.4	68.4	0.2891	49.994	0.778



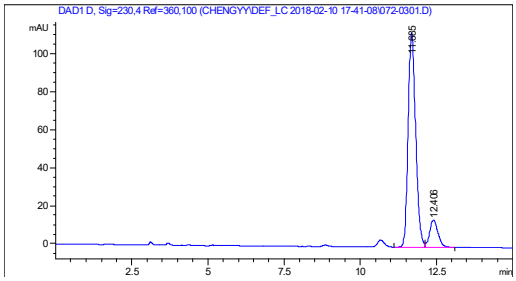
Chiral (Catalyst **III**, 90% ee, 31% yield)

#	Time	Area	Height	Width	Area%	Symmetry
1	11.934	2730.1	149.2	0.2834	94.825	0.776
2	12.724	149	7.3	0.3112	5.175	0.807



Racemic

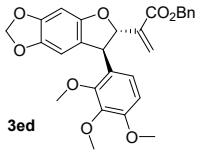
#	Time	Area	Height	Width	Area%	Symmetry
1	11.698	1272.7	73.8	0.2672	50.006	0.81
2	12.38	1272.4	68.4	0.2891	49.994	0.778



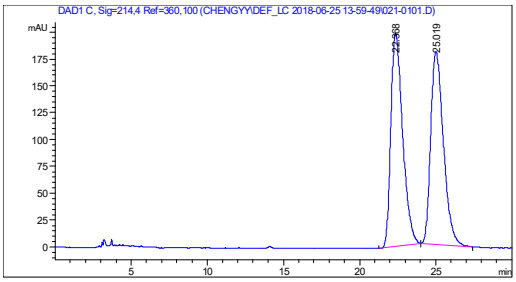
Chiral (Catalyst **I**, 76% ee, 70% yield)

#	Time	Area	Height	Width	Area%	Symmetry
1	11.685	1946.4	112.5	0.2678	87.820	0.79
2	12.406	269.9	14.3	0.2902	12.180	0.822

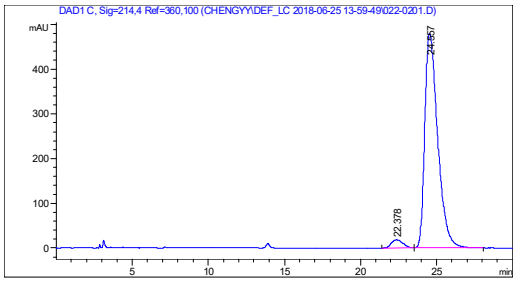
benzyl 2-((6S,7R)-6,7-dihydro-7-(2,3,4-trimethoxyphenyl)benzofuro[5,6-d][1,3]dioxol-6-yl)acrylate (3ed)



^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.29-7.282 (m, 3H), 7.21-7.19 (m, 2H), 6.82 (d, J = 8.5 Hz, 1H), 6.59 (d, J = 8.5 Hz, 1H), 6.47 (s, 1H), 6.40 (s, 1H), 6.36 (s, 1H), 5.92 (s, 1H), 5.85 (s, 2H), 5.47 (d, J = 6.0 Hz, 1H), 5.22 (d, J = 12.5 Hz, 1H), 5.09 (q, J = 12.5 Hz, 1H), 4.63 (d, J = 6.5 Hz, 1H), 3.83 (s, 6H), 3.33 (s, 3H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 165.3, 153.9, 152.8, 151.7, 147.6, 142.2, 142.0, 139.9, 135.7, 129.1, 128.5, 128.2, 128.0, 125.9, 123.1, 121.5, 107.5, 105.1, 101.3, 92.9, 88.9, 66.6, 61.0, 60.7, 56.0, 49.2. HRMS: exact mass calculated for $[M+H]^+$ ($C_{28}H_{27}O_8$) requires m/z 491.17004, found m/z 491.16968. HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/2-propanol = 97/3, flow rate = 1.0 mL/min, λ = 214 nm.



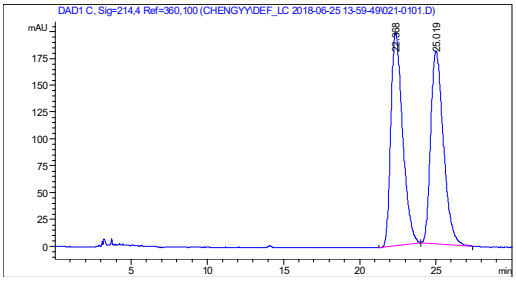
Racemic



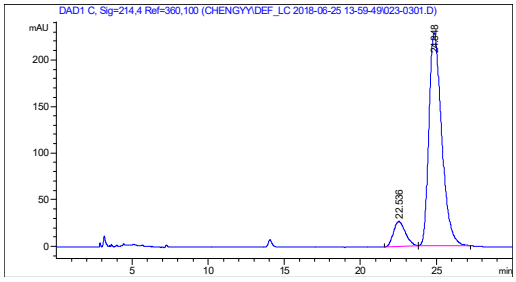
Chiral (Catalyst **III**, 93% ee, 44% yield)

#	Time	Area	Height	Width	Area%	Symmetry
1	22.368	10688.9	198.8	0.8153	50.625	0.633
2	25.019	10424.8	179.6	0.8852	49.375	0.658

#	Time	Area	Height	Width	Area%	Symmetry
1	22.378	990.4	18.9	0.7906	3.383	0.849
2	24.557	28287.6	480.1	0.8994	96.617	0.572



Racemic

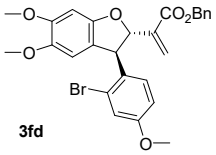


Chiral (Catalyst **I**, 80% ee, 42% yield)

#	Time	Area	Height	Width	Area%	Symmetry
1	22.368	10688.9	198.8	0.8153	50.625	0.633
2	25.019	10424.8	179.6	0.8852	49.375	0.658

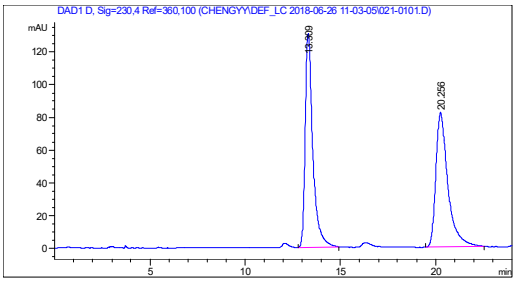
#	Time	Area	Height	Width	Area%	Symmetry
1	22.536	1466.5	26.7	0.8224	9.925	0.819
2	24.848	13309	228.6	0.8971	90.075	0.638

benzyl 2-((2S,3R)-3-(2-bromo-4-methoxyphenyl)-2,3-dihydro-5,6-dimethoxybenzofuran-2-yl)acrylate (3fd)



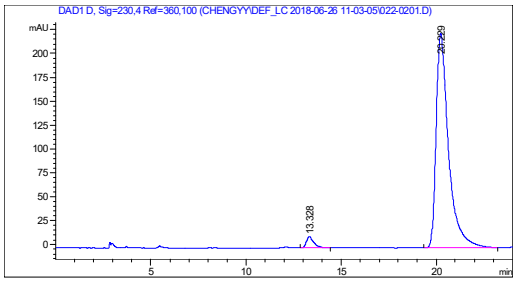
3fd

^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.27-7.26 (m, 3H), 7.19-7.17 (m, 2H), 7.07 (d, J = 8.5 Hz, 1H), 7.02 (d, J = 7.5 Hz, 1H), 6.79 (dd, J = 5.5, 8.5 Hz, 1H), 6.55 (s, 1H), 6.50 (s, 1H), 6.40 (s, 1H), 5.94 (s, 1H), 5.40 (d, J = 6.0 Hz, 1H), 5.25 (d, J = 7.5 Hz, 1H), 5.09 (d, J = 12.5 Hz, 1H), 4.99 (d, J = 6.0 Hz, 1H), 3.86 (s, 3H), 3.75 (s, 3H), 3.72 (s, 3H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 165.2, 158.8, 153.4, 149.9, 144.2, 139.6, 135.5, 134.8, 129.8, 128.5, 128.1, 126.2, 124.1, 119.7, 117.5, 114.7, 108.5, 94.8, 89.1, 66.8, 56.7, 56.1, 55.5, 53.4. HRMS: exact mass calculated for $[M+H]^+$ ($C_{27}H_{26}O_6Br$) requires m/z 525.09073, found m/z 525.09058. HPLC conditions: Daicel Chiralpak AD-H column, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 230 nm.



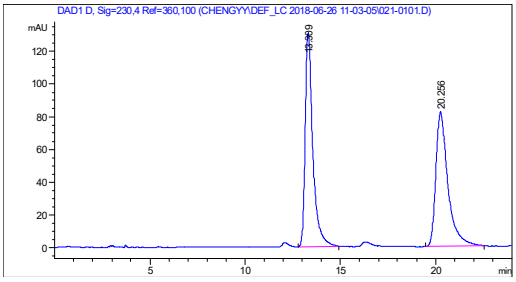
Racemic

#	Time	Area	Height	Width	Area%	Symmetry
1	13.309	3638.7	130.6	0.4131	50.388	0.582
2	20.256	3582.7	81.8	0.6468	49.612	0.574



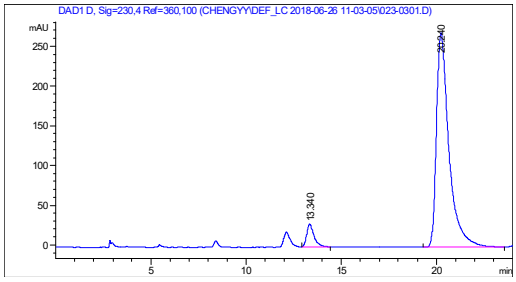
Chiral (Catalyst **III**, 94% ee, 37% yield)

#	Time	Area	Height	Width	Area%	Symmetry
1	13.328	325.3	11.8	0.4034	3.110	0.603
2	20.229	10135.8	224.8	0.6661	96.890	0.524



Racemic

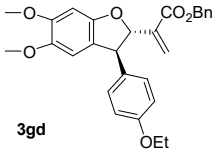
#	Time	Area	Height	Width	Area%	Symmetry
1	13.309	3638.7	130.6	0.4131	50.388	0.582
2	20.256	3582.7	81.8	0.6468	49.612	0.574



Chiral (Catalyst **I**, 89% ee, 47% yield)

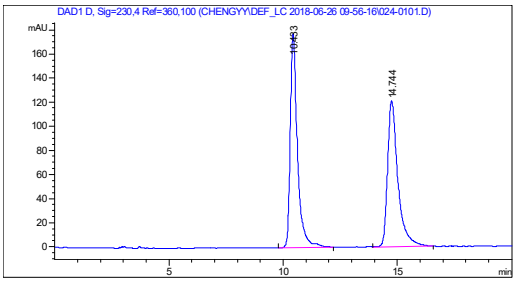
#	Time	Area	Height	Width	Area%	Symmetry
1	13.34	752.2	28.4	0.4009	5.775	0.614
2	20.24	12272.5	270.3	0.6618	94.225	0.517

benzyl 2-((2S,3S)-3-(4-ethoxyphenyl)-2,3-dihydro-5,6-dimethoxybenzofuran-2-yl)acrylate (3gd)



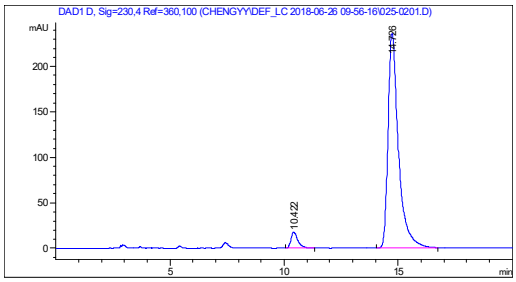
3gd

^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.33-7.32 (m, 3H), 7.27-7.25 (m, 2H), 7.02 (d, J = 8.5 Hz, 2H), 6.78 (d, J = 8.5 Hz, 2H), 6.57 (s, 1H), 6.51 (s, 1H), 6.35 (s, 1H), 5.87 (s, 1H), 5.31 (d, J = 5.0 Hz, 1H), 5.22-5.16 (m, 2H), 4.36 (d, J = 5.0 Hz, 1H), 3.99 (q, J = 7.0 Hz, 2H), 3.87 (s, 3H), 3.72 (s, 3H), 1.40 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 165.4, 158.1, 153.6, 149.9, 144.1, 139.5, 135.6, 135.3, 128.9, 128.6, 128.3, 126.1, 119.5, 114.6, 109.0, 94.7, 89.5, 66.8, 63.5, 56.7, 56.2, 54.7, 15.0. HRMS: exact mass calculated for $[M+H]^+$ ($C_{28}H_{29}O_6$) requires m/z 461.19587, found m/z 461.19540. HPLC conditions: Daicel Chiralpak AD-H column, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 230 nm.



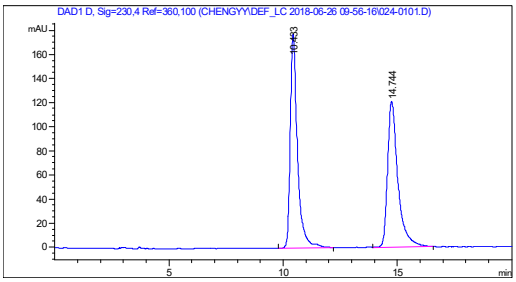
Racemic

#	Time	Area	Height	Width	Area%	Symmetry
1	10.433	3873.5	177.8	0.3202	50.542	0.584
2	14.744	3790.4	120.8	0.466	49.458	0.589



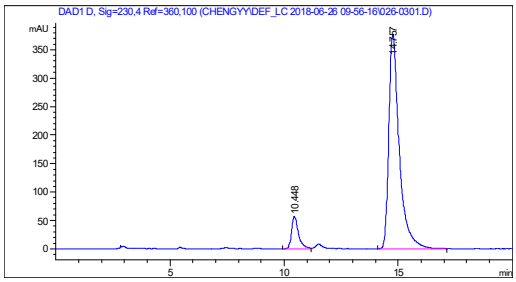
Chiral (Catalyst **III**, 90% ee, 37% yield)

#	Time	Area	Height	Width	Area%	Symmetry
1	10.422	376.6	17.9	0.3137	4.806	0.609
2	14.726	7460.1	236.1	0.4707	95.194	0.57



Racemic

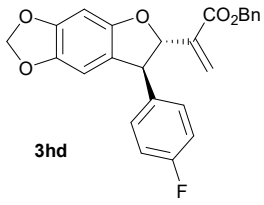
#	Time	Area	Height	Width	Area%	Symmetry
1	10.433	3873.5	177.8	0.3202	50.542	0.584
2	14.744	3790.4	120.8	0.466	49.458	0.589



Chiral (Catalyst **I**, 82% ee, 57% yield)

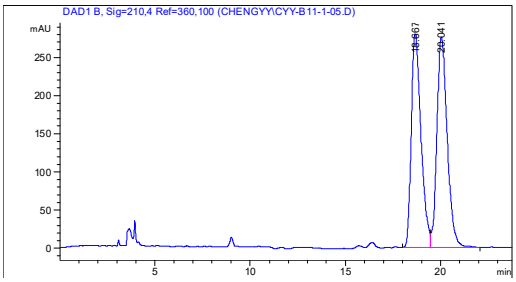
#	Time	Area	Height	Width	Area%	Symmetry
1	10.448	1216.5	56.7	0.3202	9.185	0.619
2	14.757	12028.4	377.7	0.4696	90.815	0.558

Benzyl 2-((6S,7S)-6,7-dihydro-7-(4-fulorophenyl)benzofuro[5,6-d][1,3]dioxol-6-yl)acrylate (3hd)

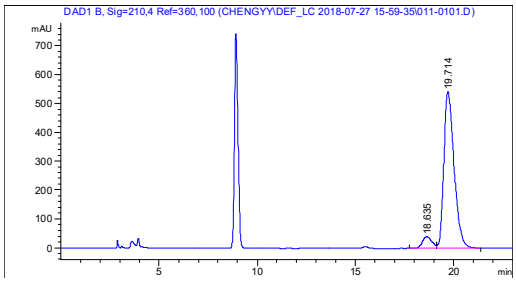


3hd

^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.36-7.33 (m, 3H), 7.28-7.25 (m, 2H), 7.08-7.05 (m, 2H), 6.92 (t, J = 8.7 Hz, 2H), 6.51 (s, 1H), 6.39 (s, 1H), 6.36 (s, 1H), 5.89-5.88 (m, 3H), 5.33 (d, J = 5.0 Hz, 1H), 5.19 (s, 2H), 4.30 (d, J = 5.0 Hz, 1H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 165.3, 162.0 (J = 245.8 H), 154.1, 148.2, 142.4, 139.2, 139.0, 135.5, 129.3 (J = 8.1 Hz), 128.7, 128.5, 128.4, 126.1, 120.3, 115.6 (J = 21.7 Hz), 105.5, 101.5, 93.1, 89.3, 66.9, 54.5. HRMS: exact mass calculated for $[M+H]^+$ ($C_{25}H_{20}O_5F$) requires m/z 419.12893, found m/z 419.12738. HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/2-propanol = 99.2/0.8, flow rate = 1.0 mL/min, λ = 210 nm.



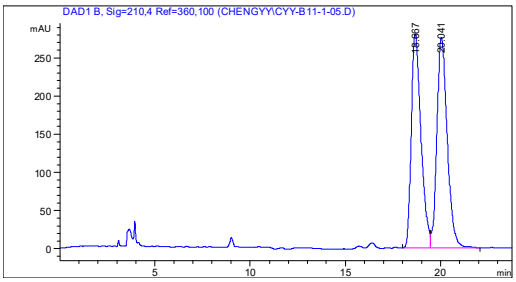
Racemic



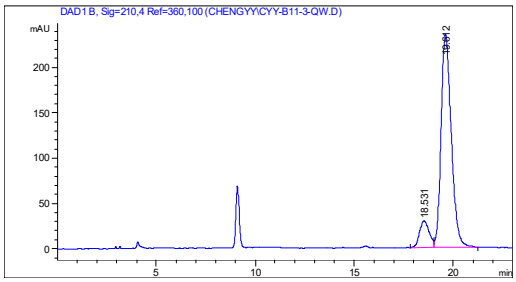
Chiral (Catalyst **III**, 87% ee, 38% yield)

#	Time	Area	Height	Width	Area%	Symmetry
1	18.667	9956	280.1	0.5447	48.992	0.632
2	20.041	10365.8	275.3	0.5753	51.008	0.703

#	Time	Area	Height	Width	Area%	Symmetry
1	18.635	1395.6	40.8	0.5267	6.596	0.835
2	19.714	19763.4	542.4	0.5591	93.404	0.637



Racemic

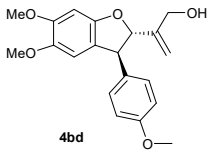


Chiral (Catalyst **I**, 79% ee, 75% yield)

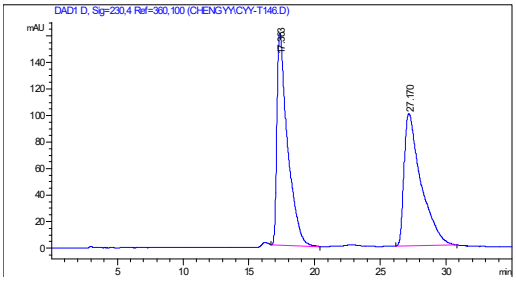
#	Time	Area	Height	Width	Area%	Symmetry
1	18.667	9956	280.1	0.5447	48.992	0.632
2	20.041	10365.8	275.3	0.5753	51.008	0.703

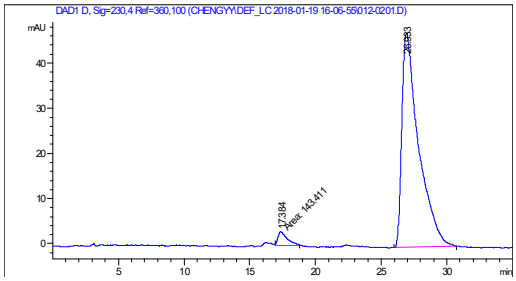
#	Time	Area	Height	Width	Area%	Symmetry
1	18.531	1001.5	29.3	0.5187	10.651	0.851
2	19.612	8401.7	235.2	0.5508	89.349	0.705

2-((2S,3S)-2,3-dihydro-5,6-dimethoxy-3-(4-methoxyphenyl)benzofuran-2-yl)prop-2-en-1-ol



(4bd), 87.7 mg, 84% yield. ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.13 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.53 (s, 1H), 6.48 (s, 1H), 5.25 (s, 1H), 5.11 (s, 1H), 5.02 (d, *J* = 8.5 Hz, 1H), 4.47 (d, *J* = 8.5 Hz, 1H), 4.33-4.21 (m, 2H), 3.87 (s, 3H), 3.80 (s, 3H), 3.73 (s, 3H), 1.98 (s, 1H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 158.9, 153.6, 149.8, 146.3, 144.1, 134.1, 129.3, 120.1, 114.3, 113.3, 108.8, 94.9, 93.8, 62.8, 56.8, 56.2, 55.4, 53.9. HRMS: exact mass calculated for $[M-H]^-$ ($C_{20}H_{21}O_5$) requires m/z 341.13945, found m/z 341.13980. HPLC conditions: Daicel Chiralpak AD-H column, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 230 nm, retention time: t_R (minor) = 17.384 min, t_R (major) = 26.933 min, 93% ee.





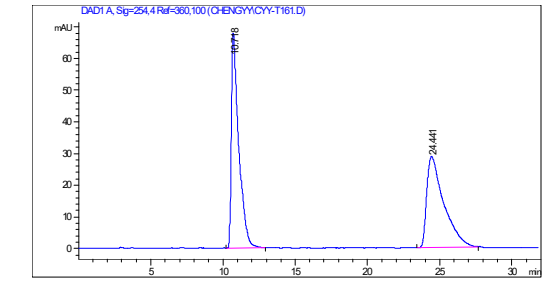
Racemic

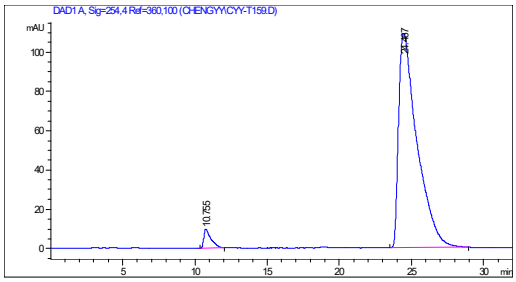
#	Time	Area	Height	Width	Area%	Symmetry
1	17.363	8954.4	159.8	0.7956	50.134	0.345
2	27.17	8906.5	99.7	1.2703	49.866	0.352

Chiral

#	Time	Area	Height	Width	Area%	Symmetry
1	17.384	143.4	3	0.8092	3.317	0.46
2	26.933	4180.6	47.5	1.2374	96.683	0.347

2-((2S,3S)-2,3-dihydro-5,6-dimethoxy-3-(4-methoxyphenyl)benzofuran-2-yl)allyl 4-bromo-2-methylbenzoate (5bd), 80.7 mg, 75% yield. ^{1}H NMR (500 Hz, $CDCl_3$): δ (ppm) 7.62 (d, J = 8.5 Hz, 1H), 7.40 (s, 1H), 7.32 (d, J = 8.5 Hz, 1H), 7.12 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 8.5 Hz, 2H), 6.51 (s, 1H), 6.45 (s, 1H), 5.31 (s, 1H), 5.25 (s, 1H), 5.07 (d, J = 8.0 Hz, 1H), 4.98-4.88 (m, 2H), 4.53 (d, J = 8.5 Hz, 1H), 3.86 (s, 3H), 3.78 (s, 3H), 3.71 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (126 Hz, $CDCl_3$): δ (ppm) 166.1, 158.9, 153.7, 149.8, 144.1, 142.7, 142.2, 134.6, 134.4, 132.2, 129.2, 129.0, 128.0, 126.9, 119.9, 115.1, 114.3, 108.7, 94.8, 93.1, 63.9, 56.7, 56.2, 55.3, 54.0, 21.7. HRMS: exact mass calculated for $[M+H]^+$ ($C_{28}H_{28}O_6Br$) requires m/z 539.10638, found m/z 539.10632. HPLC conditions: Daicel Chiralpak AD-3 column, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_R (minor) = 10.755 min, t_R (major) = 24.467 min, 93% ee.





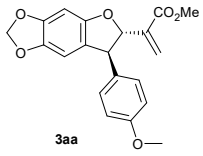
Racemic

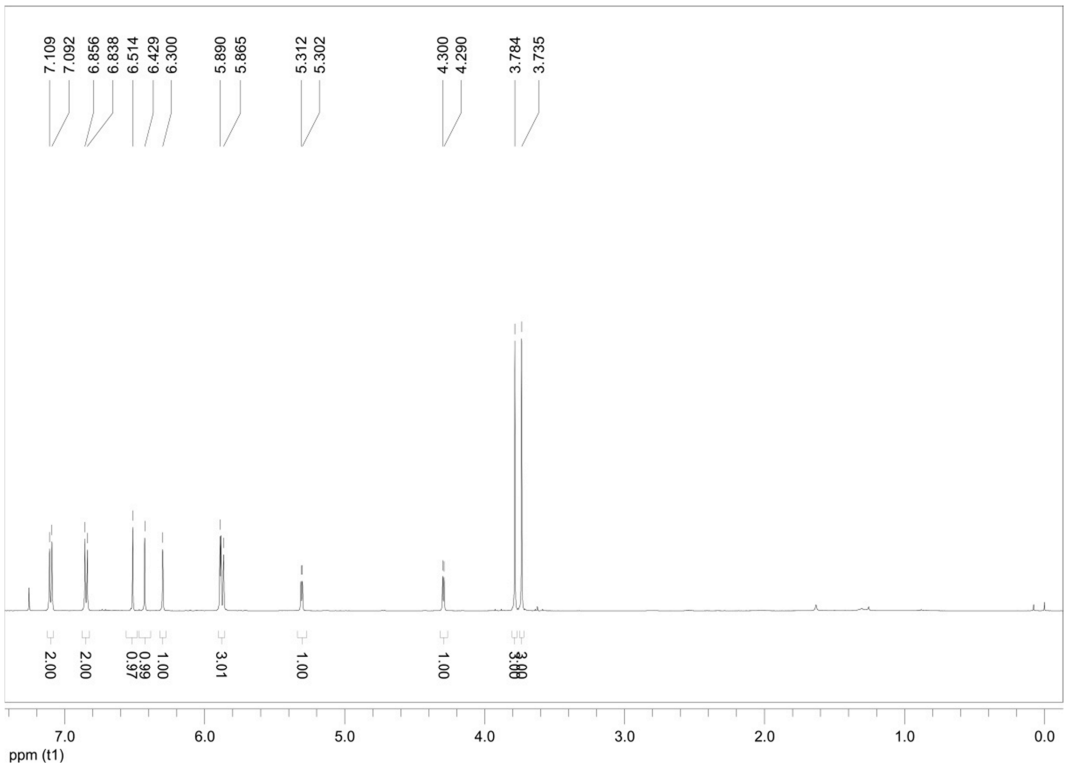
#	Time	Area	Height	Width	Area%	Symmetry
1	10.718	2417.8	68	0.5051	50.554	0.341
2	24.441	2364.8	28.9	1.1755	49.446	0.359

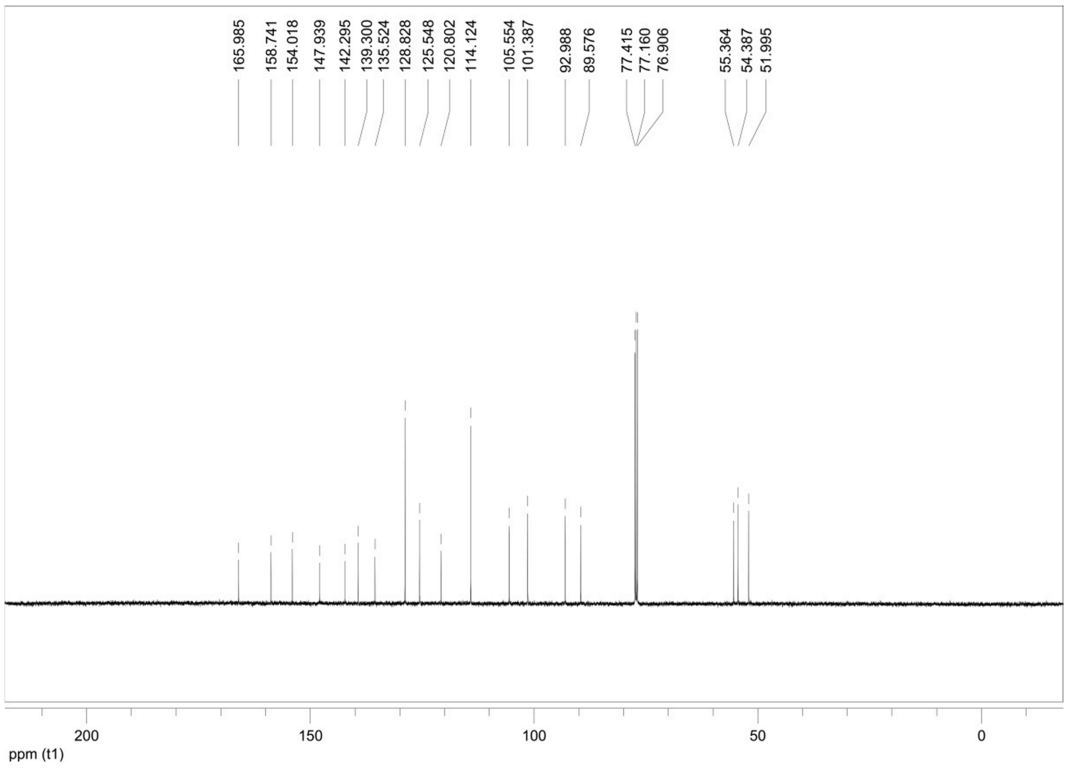
Chiral

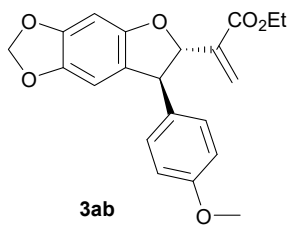
#	Time	Area	Height	Width	Area%	Symmetry
1	10.755	339.7	9.9	0.4908	3.400	0.355
2	24.467	9652.4	109.2	1.277	96.600	0.346

Copies of NMR spectra

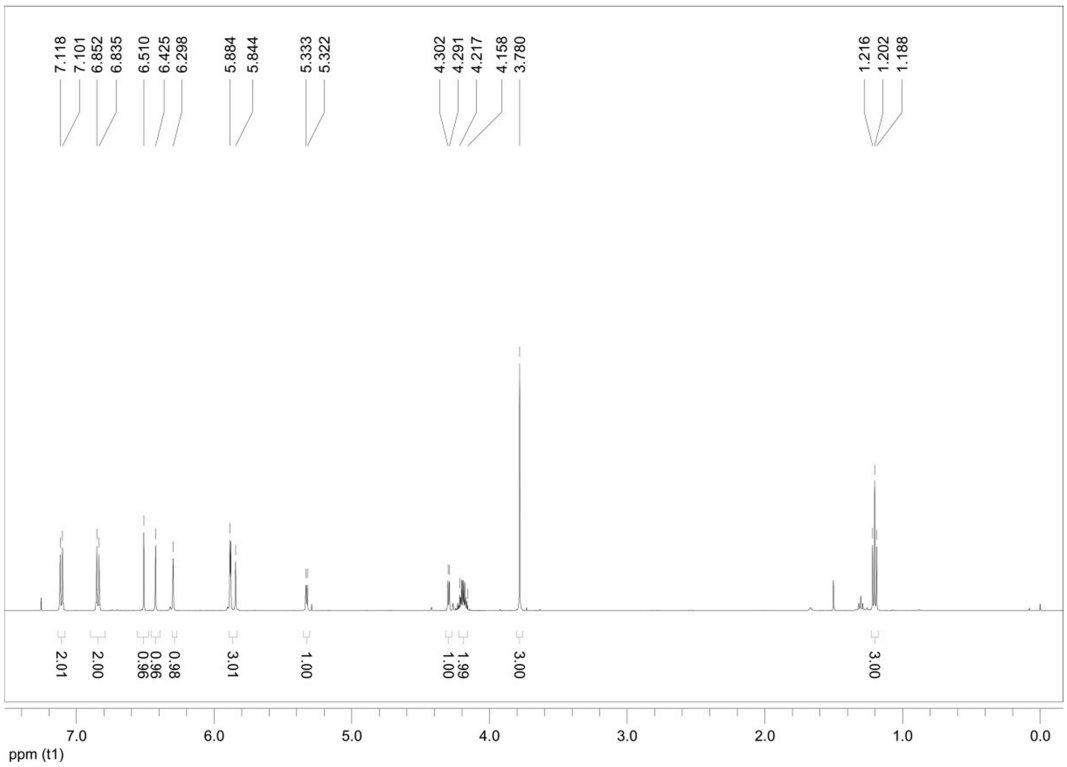


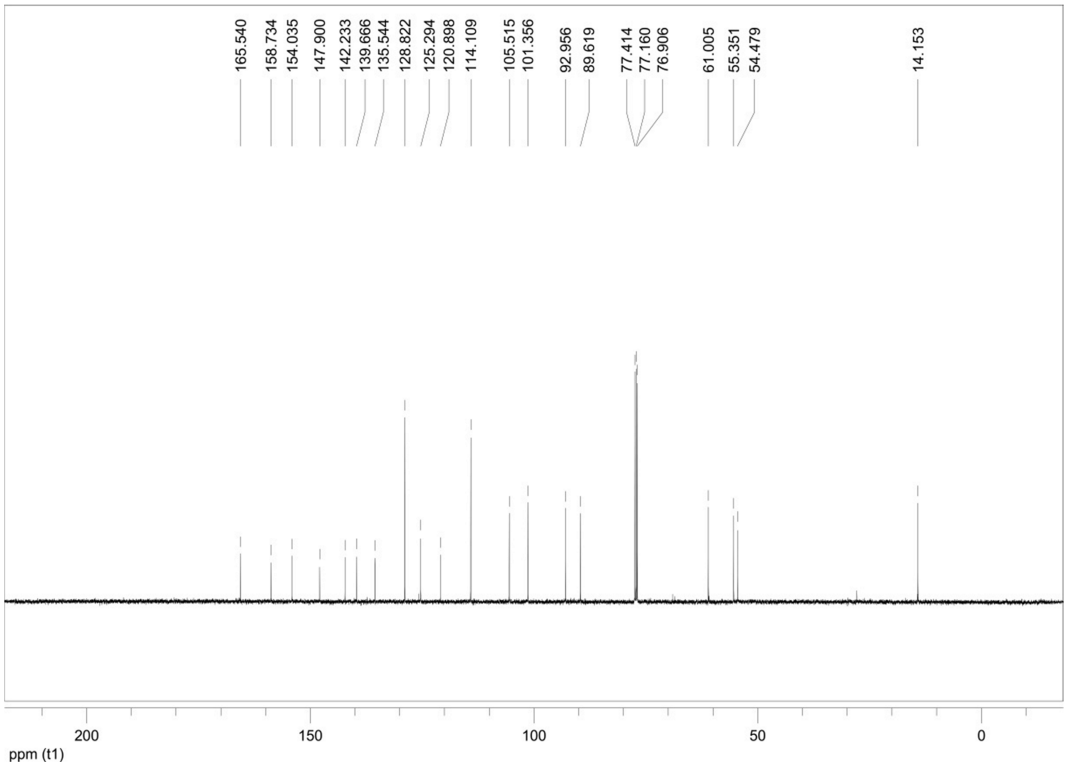


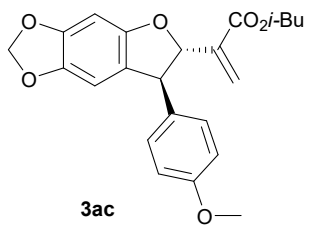



O
O
O
O
CO2Et
O

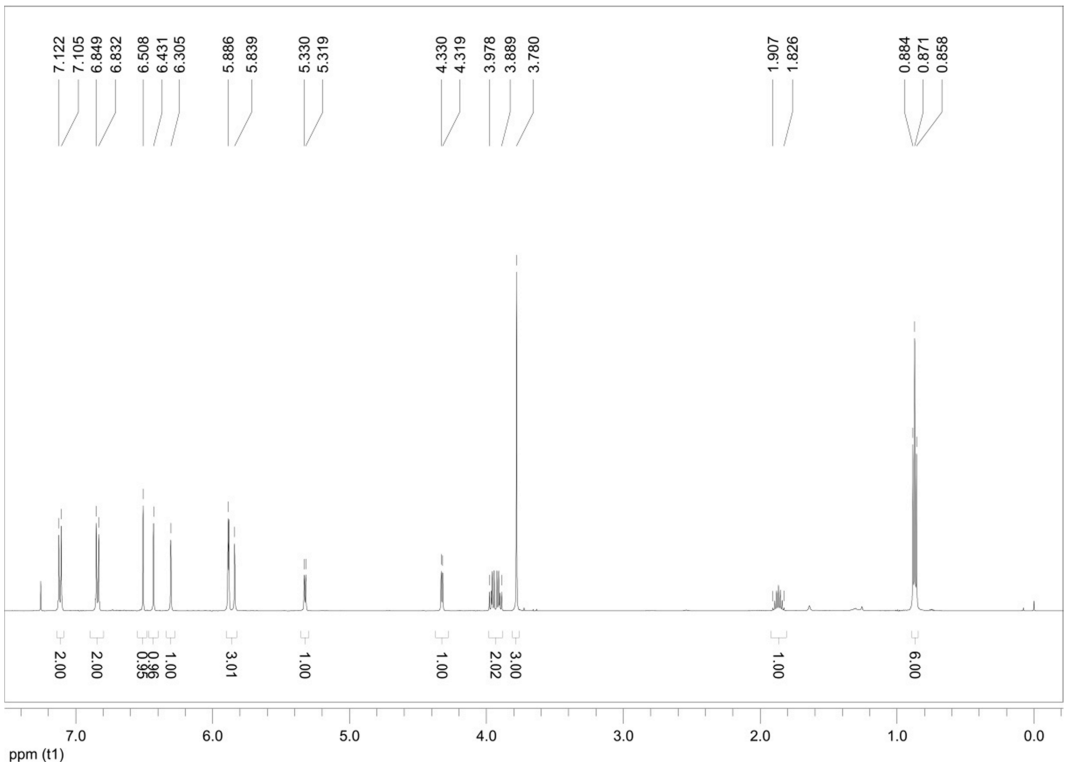
3ab


7.118
7.101
6.852
6.835
6.510
6.425
6.298
5.884
5.844
5.333
5.322
4.302
4.291
4.217
4.158
3.780
1.216
1.202
1.188
2.01
2.00
0.96
0.96
0.98
1.01
1.00
1.00
1.99
3.00
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


165.540
158.734
154.035
147.900
142.233
139.666
135.544
128.822
125.294
120.898
114.109
105.515
101.356
92.956
89.619
77.414
77.160
76.906
61.005
55.351
54.479
14.153
200
150
100
50
0
ppm (t1)


O
O
O
O
CO2i-Bu
O

3ac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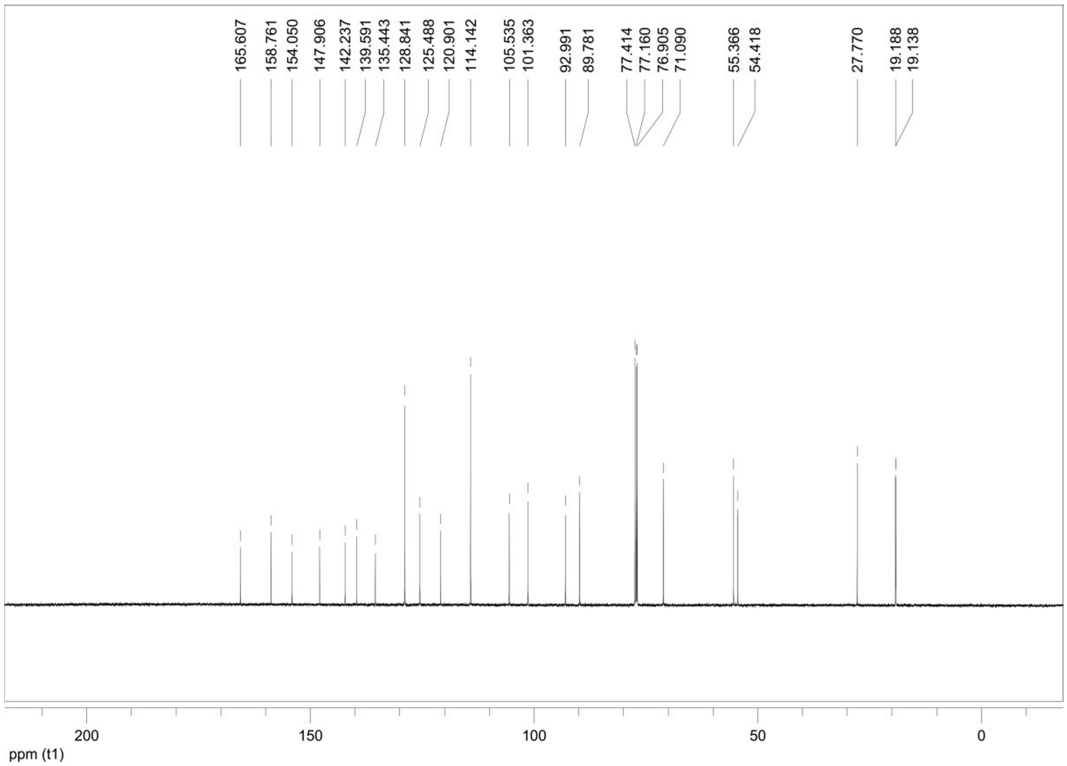
7.105
6.849
6.832
6.508
6.431
6.305
5.886
5.839
5.330
5.319
4.330
4.319
3.978
3.889
3.780
1.907
1.826
0.884
0.871
0.858
2.00
2.00
0.95
0.98
1.00
3.01
1.00
1.00
2.02
3.00
1.00
6.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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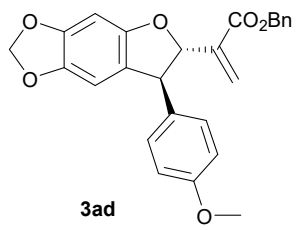
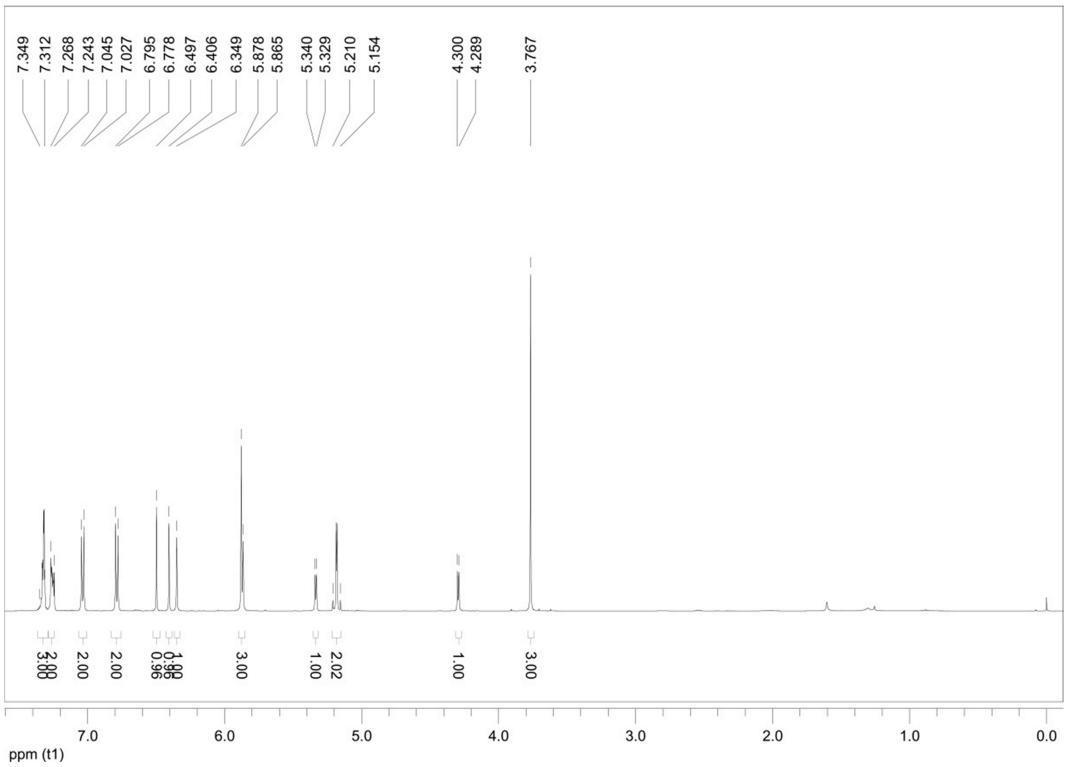
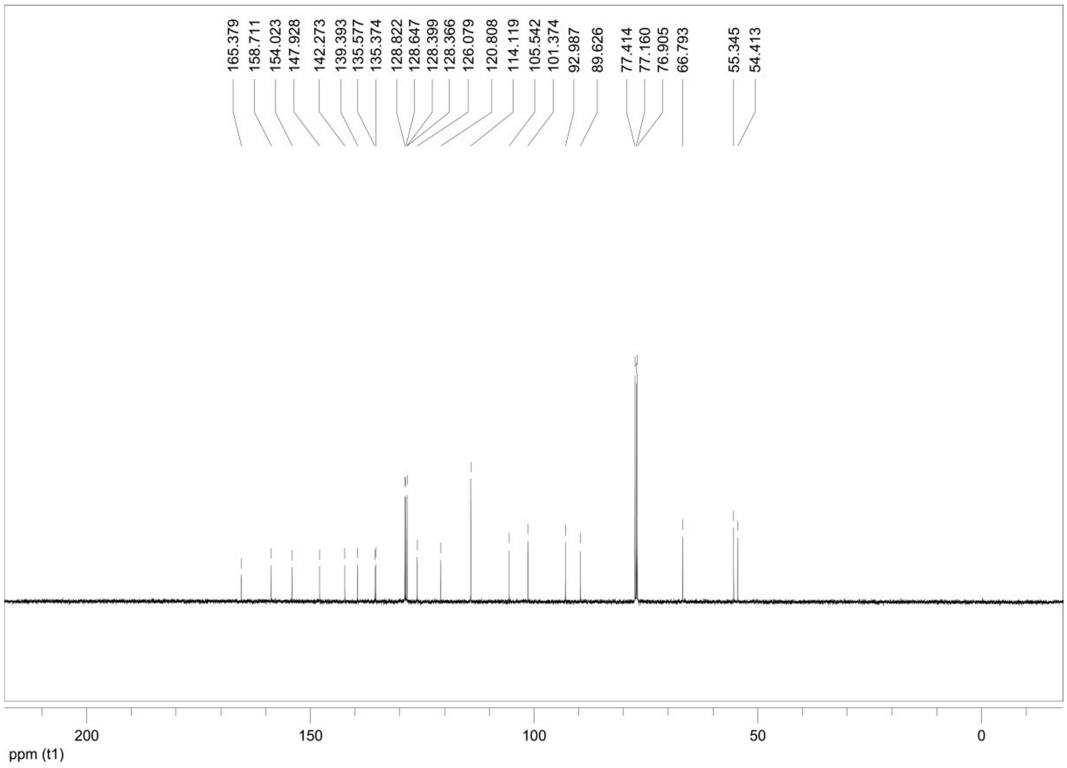
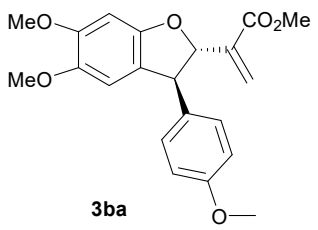
158.761
154.050
147.906
142.237
139.591
135.443
128.841
125.488
120.901
114.142
105.535
101.363
92.991
89.781
77.414
77.160
76.905
71.090
55.366
54.418
27.770
19.188
19.138
200
150
100
50
0
ppm (t1)


O
O
O
O
CO2Bn
O

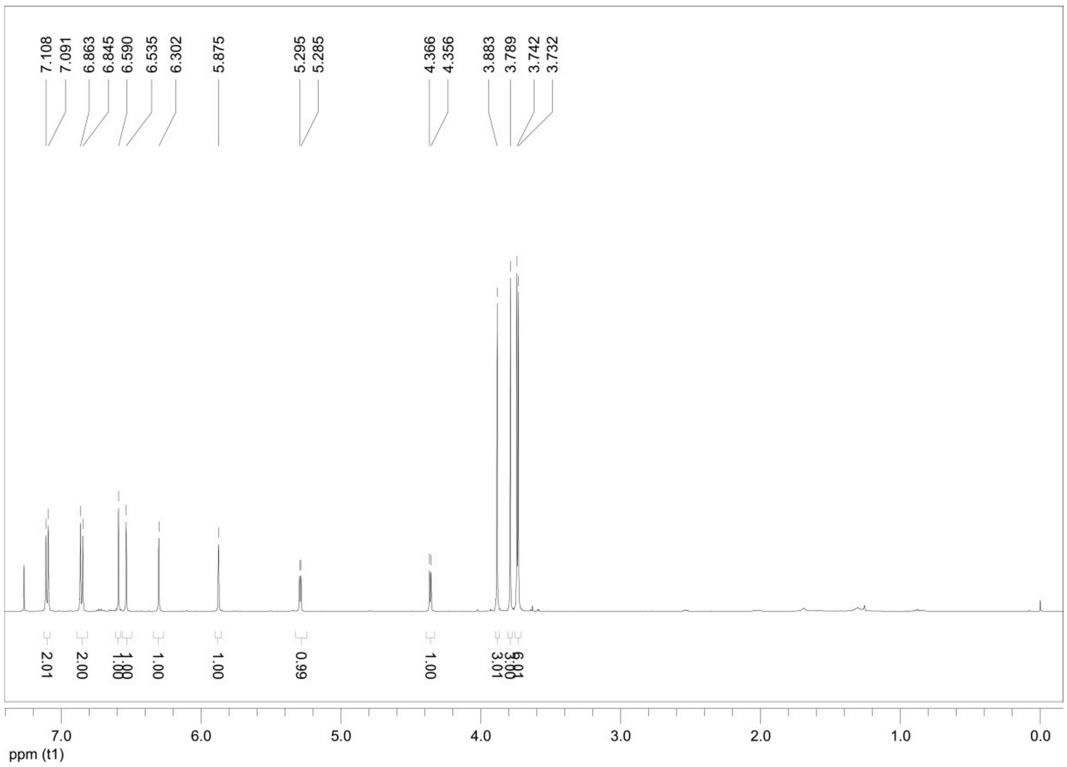
3ad

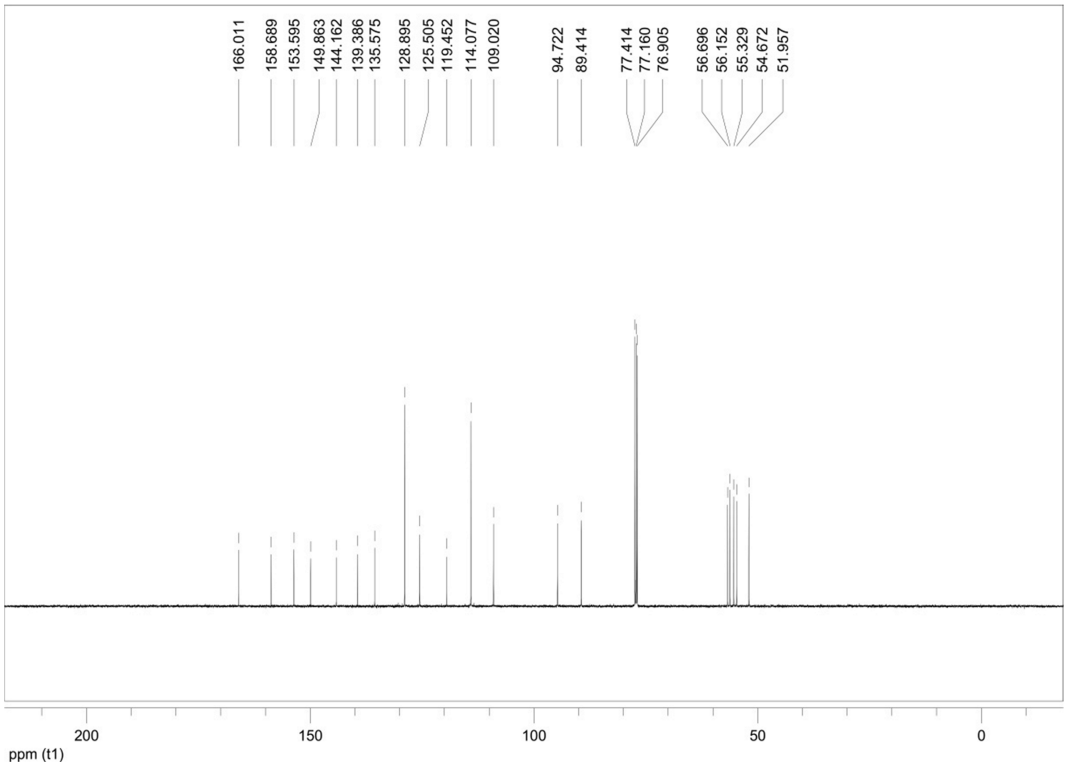

7.349
7.312
7.268
7.243
7.045
7.027
6.795
6.778
6.497
6.406
6.349
5.878
5.865
5.340
5.329
5.210
5.154
4.300
4.289
3.767
2.00
2.00
0.96
0.98
3.00
1.00
2.02
1.00
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

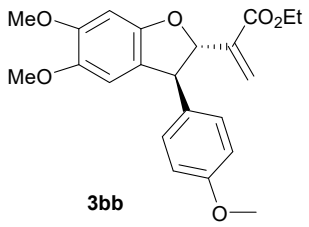

165.379
158.711
154.023
147.928
142.273
139.393
135.577
135.374
128.822
128.647
128.399
128.366
126.079
120.808
114.119
105.542
101.374
92.987
89.626
77.414
77.160
76.905
66.793
55.345
54.413
200
150
100
50
0
ppm (t1)


MeO
MeO
O
CO2Me
O

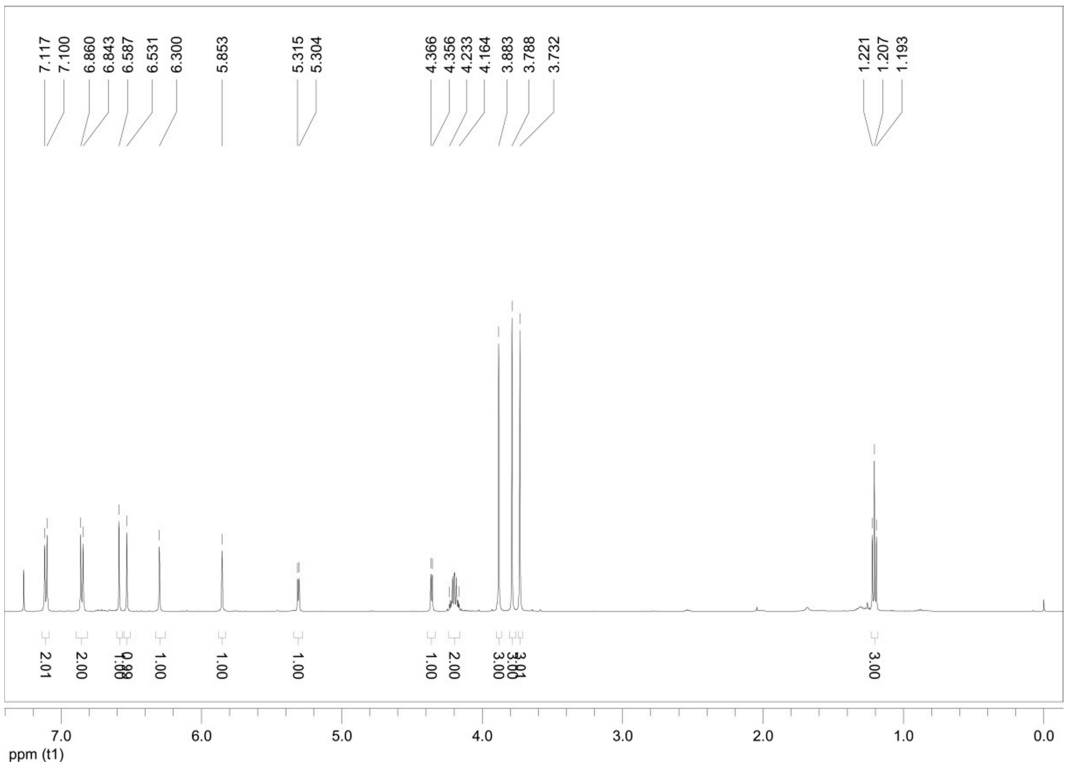
3ba

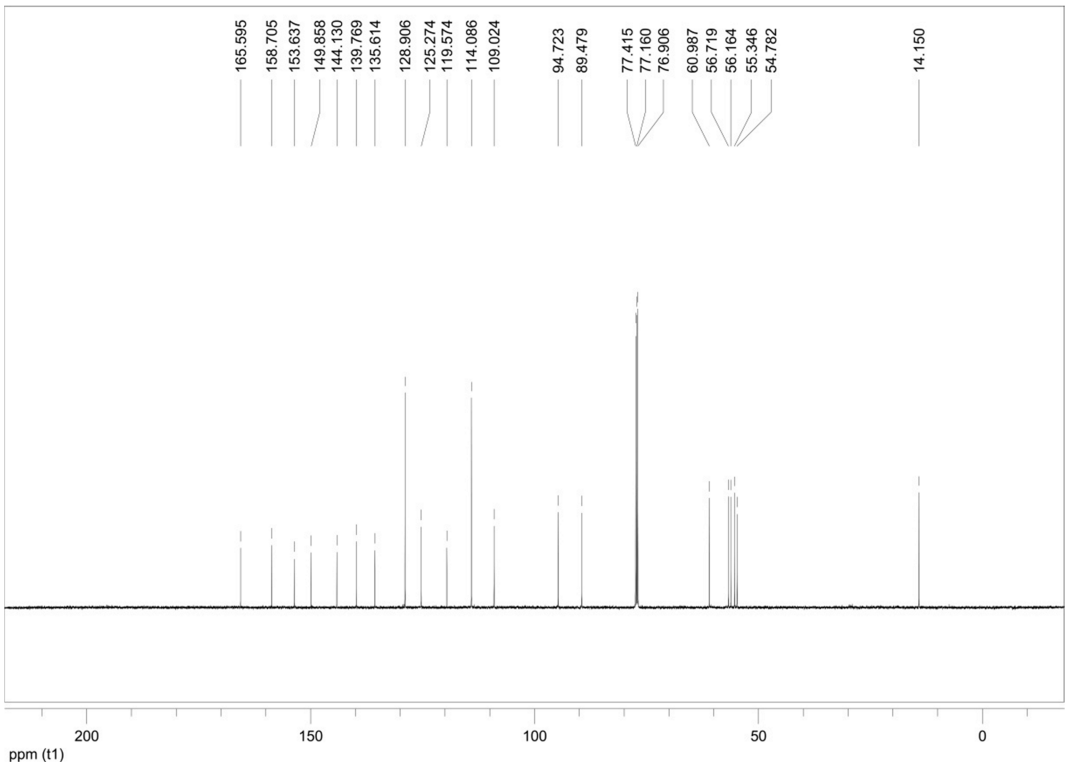

7.108
7.091
6.863
6.845
6.590
6.535
6.302
5.875
5.295
5.285
4.366
4.356
3.883
3.789
3.742
3.732
2.01
2.00
1.00
1.00
0.99
1.00
3.01
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


166.011
158.689
153.595
149.863
144.162
139.386
135.575
128.895
125.505
119.452
114.077
109.020
94.722
89.414
77.414
77.160
76.905
56.696
56.152
55.329
54.672
51.957
200
150
100
50
0
ppm (t1)


MeO
MeO
O
CO2Et
O

3bb


7.117
7.100
6.860
6.843
6.587
6.531
6.300
5.853
5.315
5.304
4.366
4.356
4.233
4.164
3.883
3.788
3.732
1.221
1.207
1.193
2.01
2.00
1.00
1.00
1.00
1.00
2.00
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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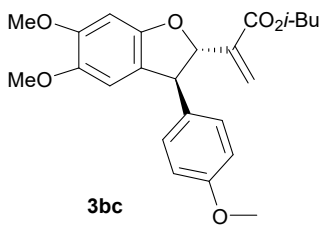
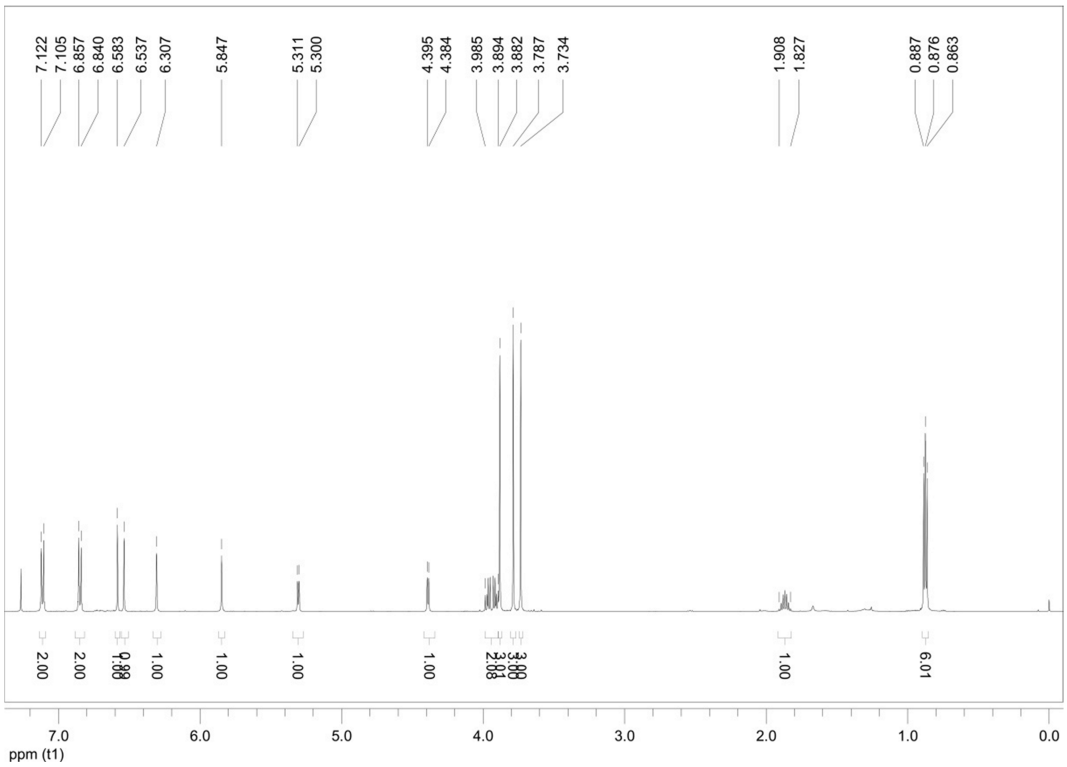
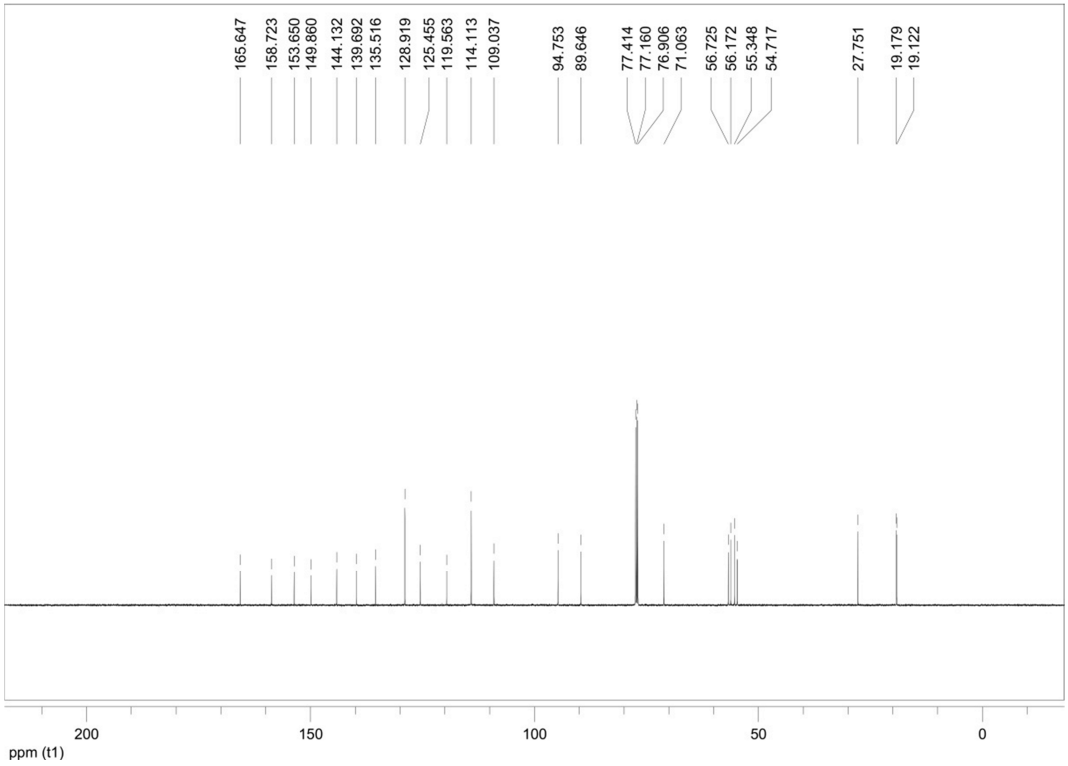
158.705
153.637
149.858
144.130
139.769
135.614
128.906
125.274
119.574
114.086
109.024
94.723
89.479
77.415
77.160
76.906
60.987
56.719
56.164
55.346
54.782
14.150
200
150
100
50
0
ppm (t1)


MeO
MeO
O
CO2i-Bu
O—

3bc


7.122
7.105
6.857
6.840
6.583
6.537
6.307
5.847
5.311
5.300
4.395
4.384
3.985
3.894
3.882
3.787
3.734
1.908
1.827
0.887
0.876
0.863
2.00
2.00
0.88
1.00
1.00
1.00
1.00
3.03
1.00
9.01
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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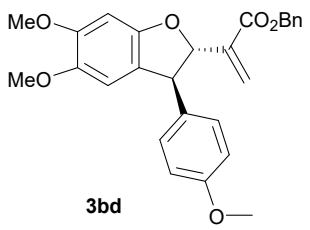
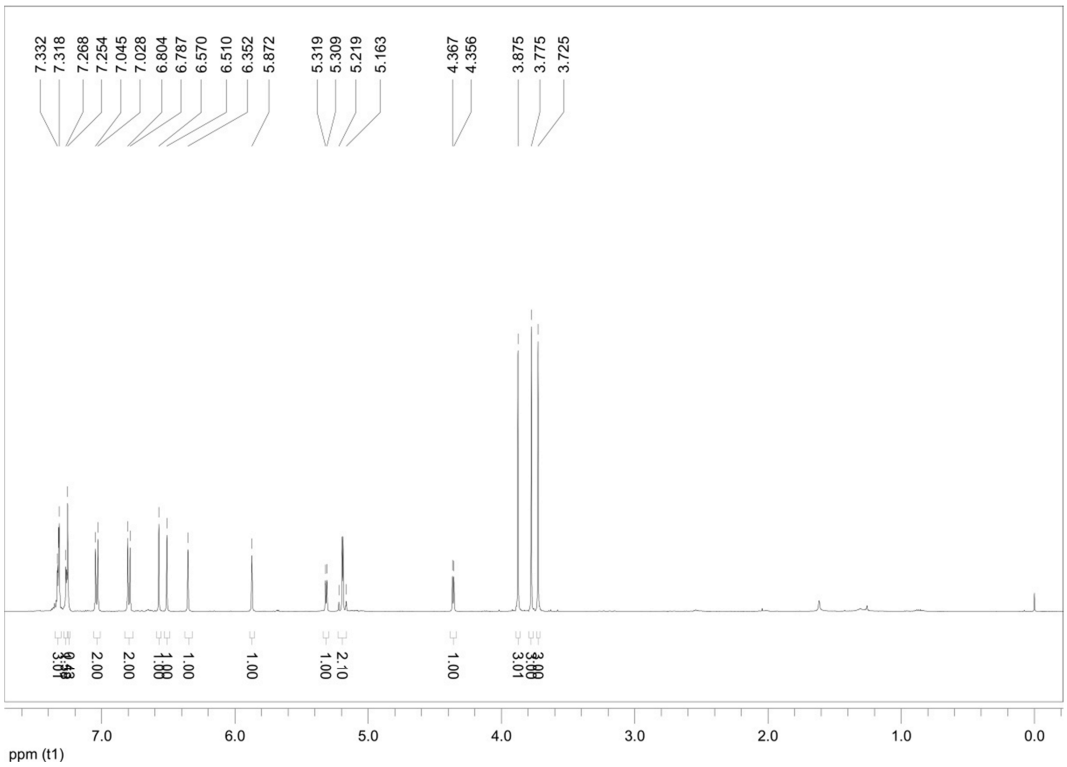
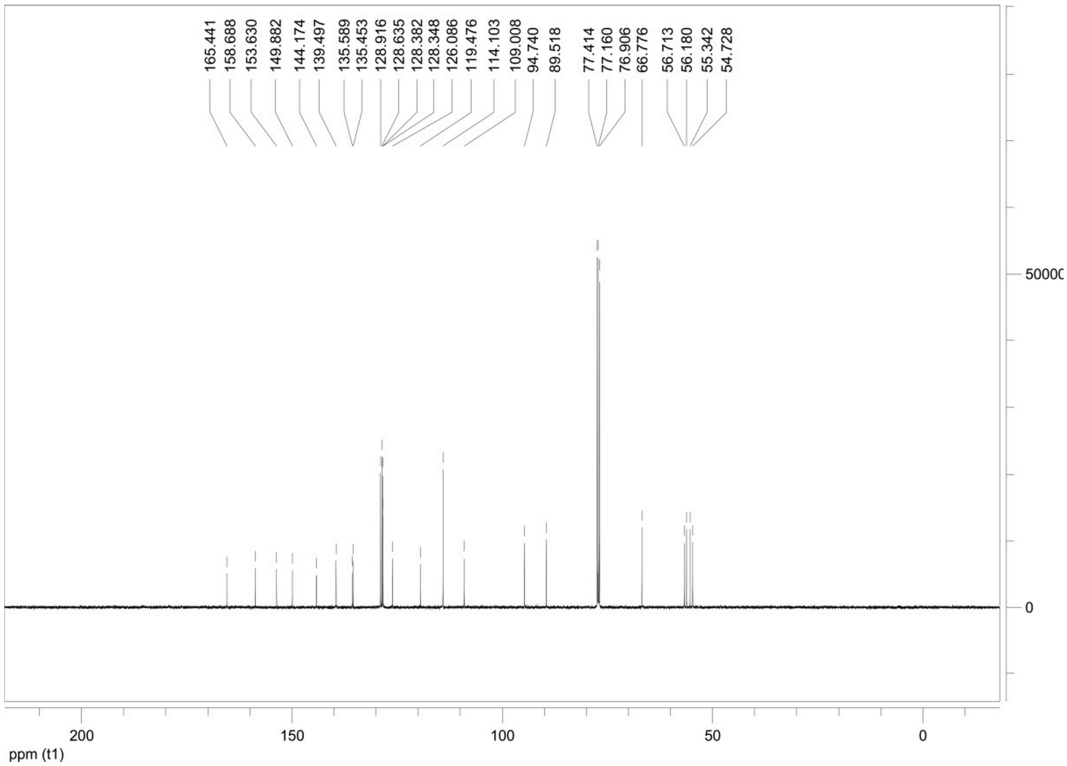
158.723
153.650
149.860
144.132
139.692
135.516
128.919
125.455
119.563
114.113
109.037
94.753
89.646
77.414
77.160
76.906
71.063
56.725
56.172
55.348
54.717
27.751
19.179
19.122
200
150
100
50
0
ppm (t1)


MeO
MeO
O
CO2Bn
O

3bd


7.332
7.318
7.268
7.254
7.045
7.028
6.804
6.787
6.570
6.510
6.352
5.872
5.319
5.309
5.219
5.163
4.367
4.356
3.875
3.775
3.725
2.00
2.00
1.00
1.00
2.10
1.00
10.33
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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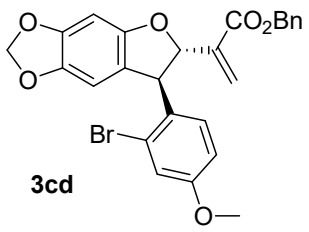
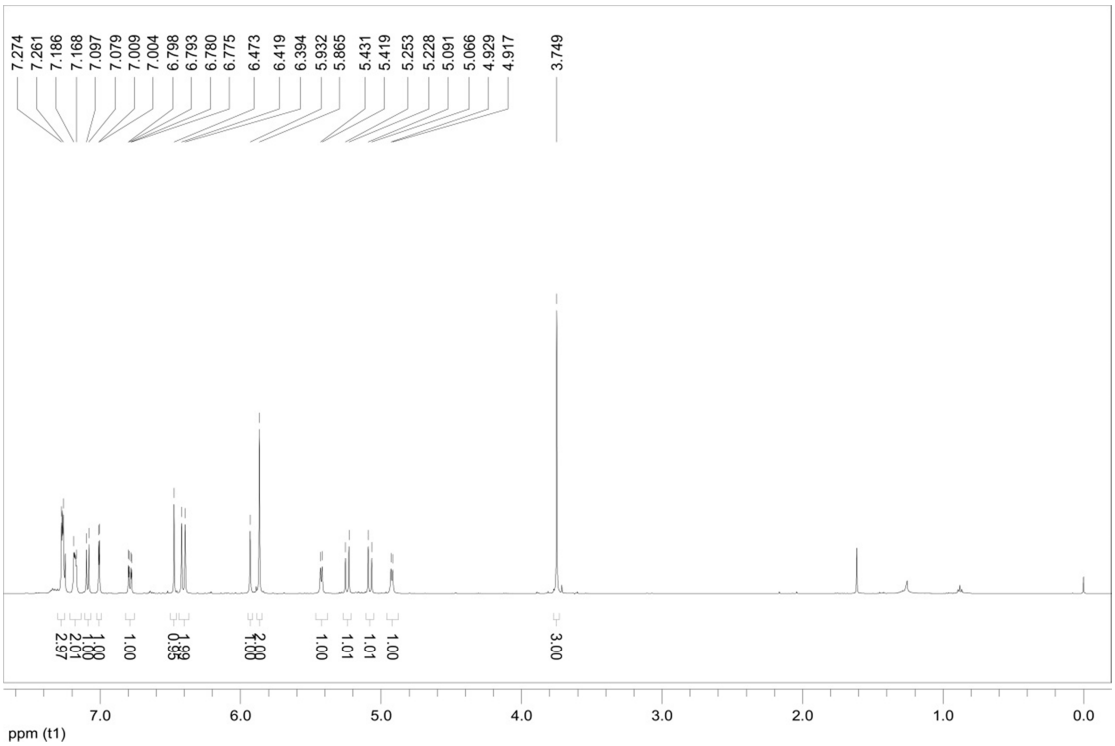
158.688
153.630
149.882
144.174
139.497
135.589
135.453
128.916
128.635
128.382
128.348
126.086
119.476
114.103
109.008
94.740
89.518
77.414
77.160
76.906
66.776
56.713
56.180
55.342
54.728
50000
0
200
150
100
50
0
ppm (t1)


O
O
O
O
CO2Bn
Br
O—

3cd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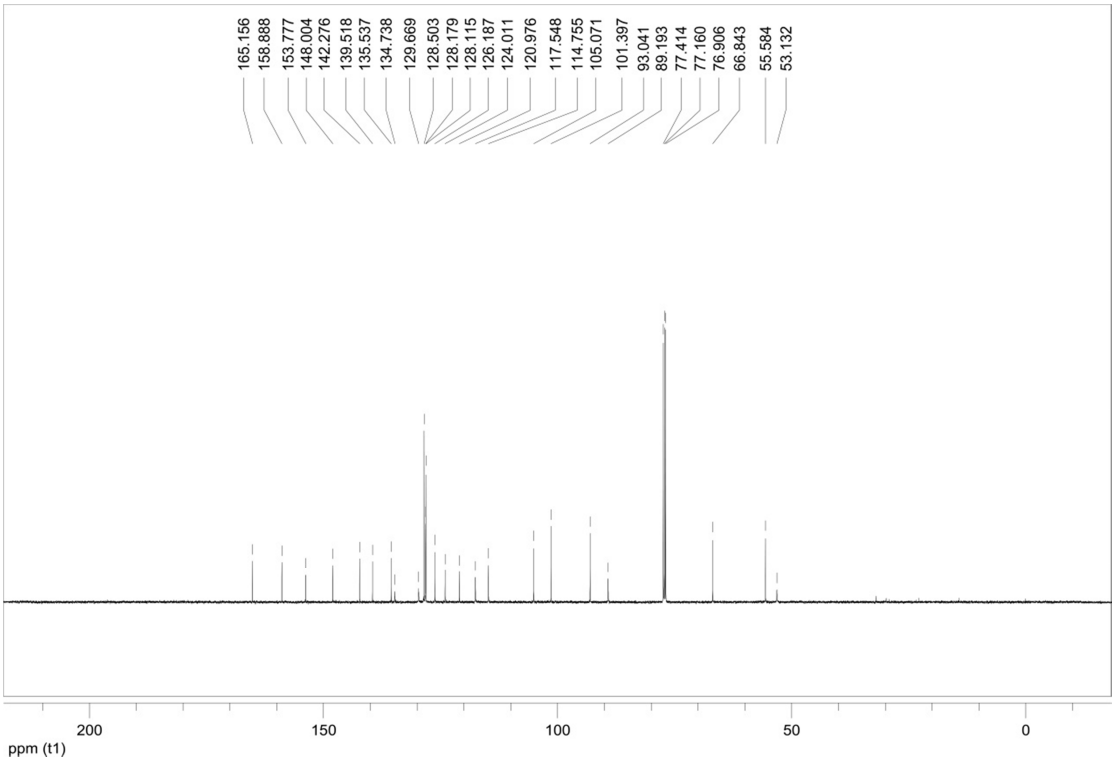
7.261
7.186
7.168
7.097
7.079
7.009
7.004
6.798
6.793
6.780
6.775
6.473
6.419
6.394
5.932
5.865
5.431
5.419
5.253
5.228
5.091
5.066
4.929
4.917
3.749
2.97
2.01
1.08
1.00
0.98
1.00
1.00
1.01
1.01
1.00
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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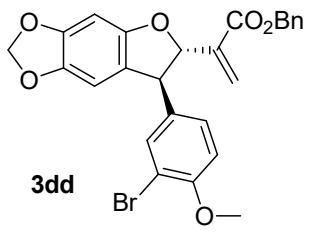
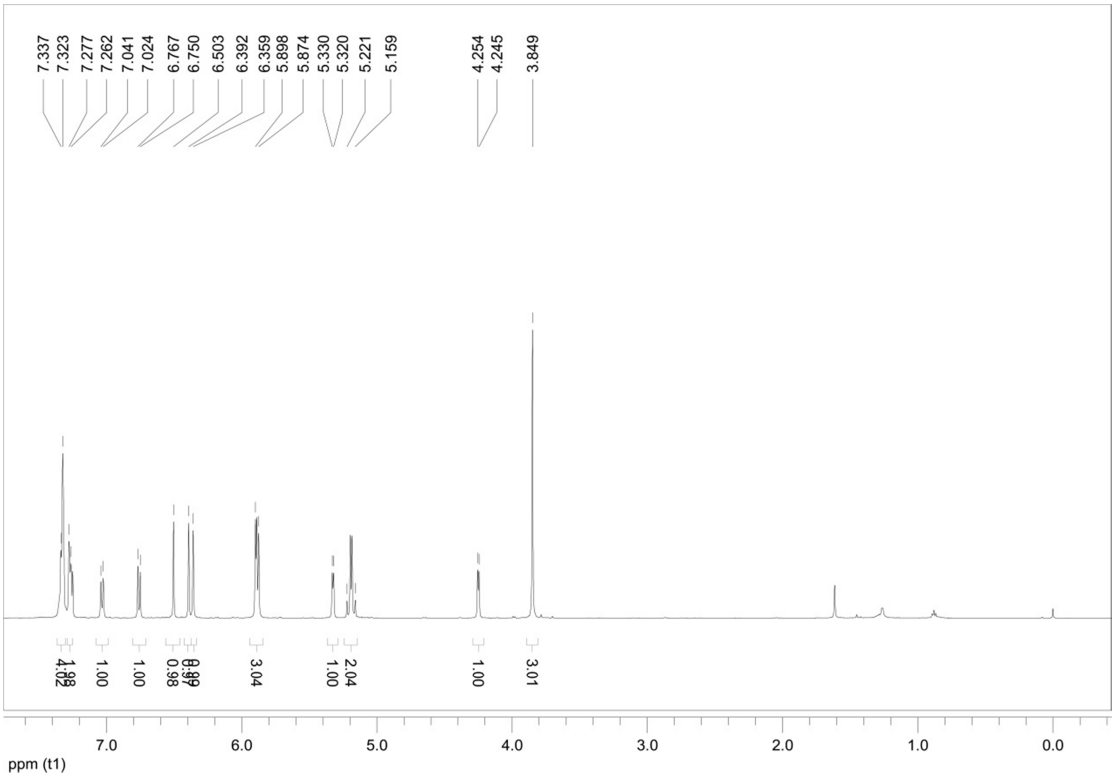
153.777
148.004
142.276
139.518
135.537
134.738
129.669
128.503
128.179
128.115
126.187
124.011
120.976
117.548
114.755
105.071
101.397
93.041
89.193
77.414
77.160
76.906
66.843
55.584
53.132
200
150
100
50
0
ppm (t1)


O
O
O
O
CO2Bn
Br
O—

3dd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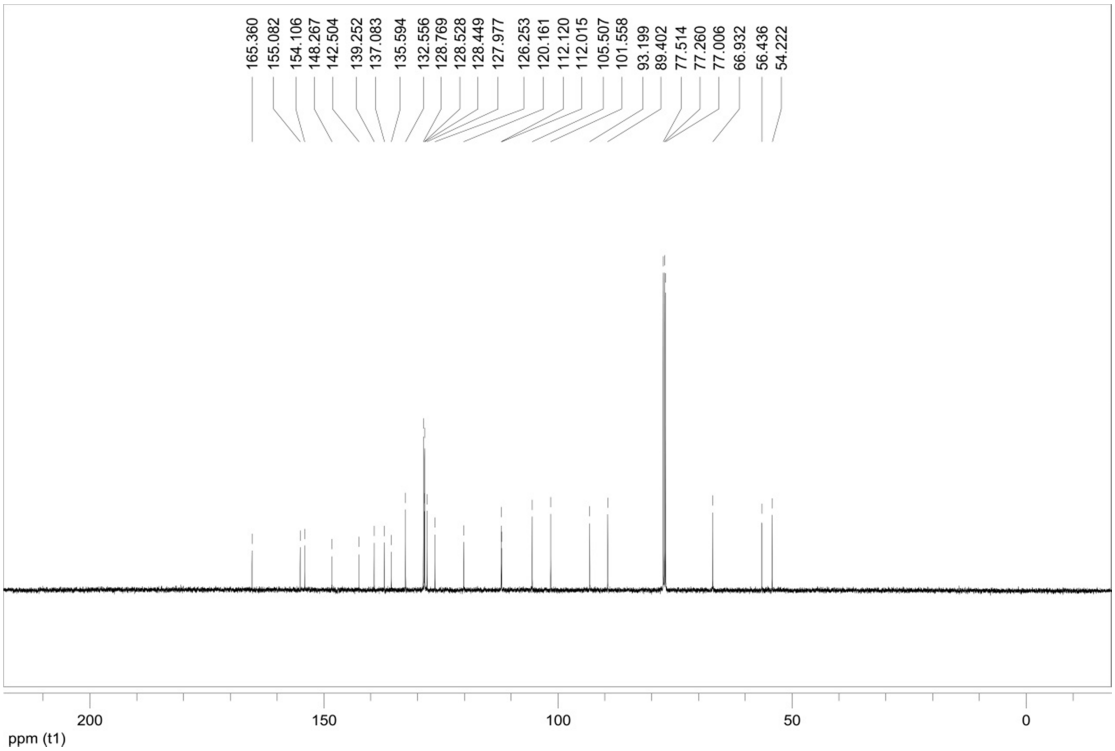
7.323
7.277
7.262
7.041
7.024
6.767
6.750
6.503
6.392
6.359
5.898
5.874
5.330
5.320
5.221
5.159
4.254
4.245
3.849
1.00
1.00
0.98
3.04
1.00
2.04
1.00
3.01
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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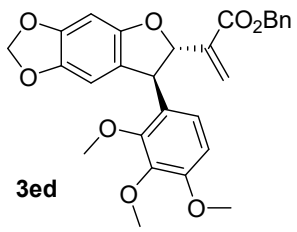
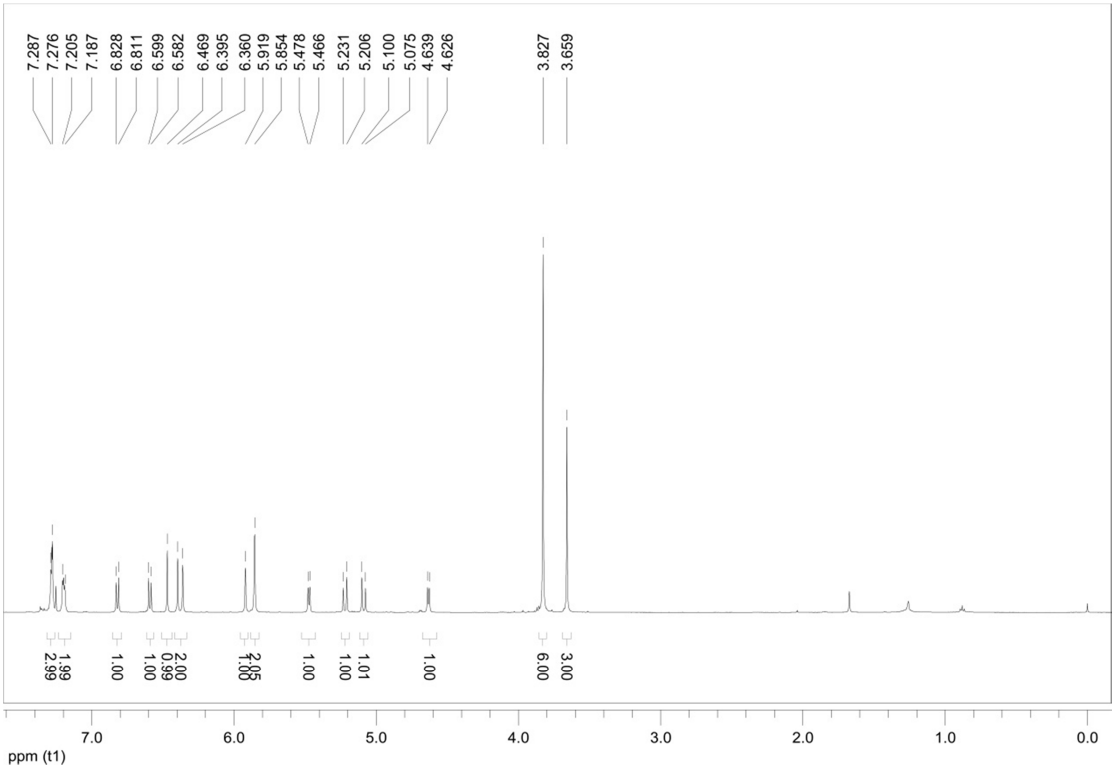
154.106
148.267
142.504
139.252
137.083
135.594
132.556
128.769
128.528
128.449
127.977
126.253
120.161
112.120
112.015
105.507
101.558
93.199
89.402
77.514
77.260
77.006
66.932
56.436
54.222
200
150
100
50
0
ppm (t1)


O
O
O
O
CO2Bn
O
O
O

3ed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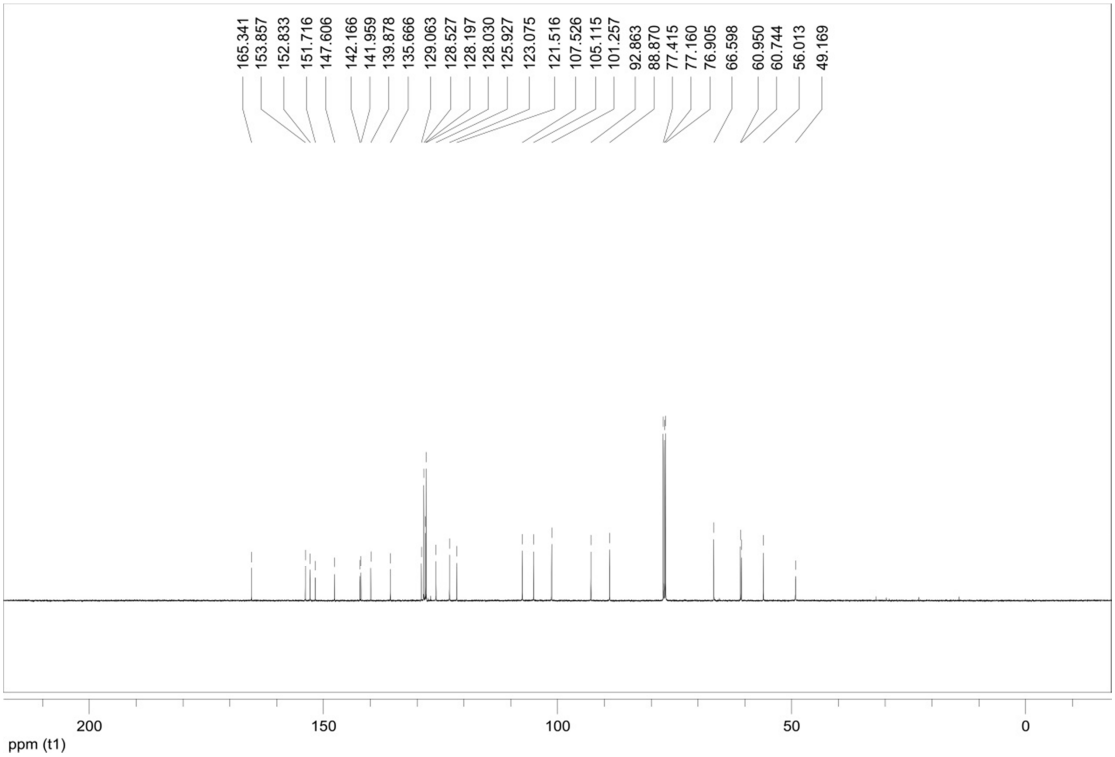
7.276
7.205
7.187
6.828
6.811
6.599
6.582
6.469
6.395
6.360
5.919
5.854
5.478
5.466
5.231
5.206
5.100
5.075
4.639
4.626
3.827
3.659
2.99
1.99
1.00
1.00
0.99
2.00
2.05
2.08
1.00
1.00
1.01
1.00
6.00
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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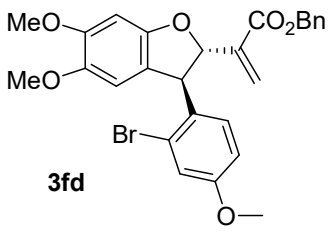
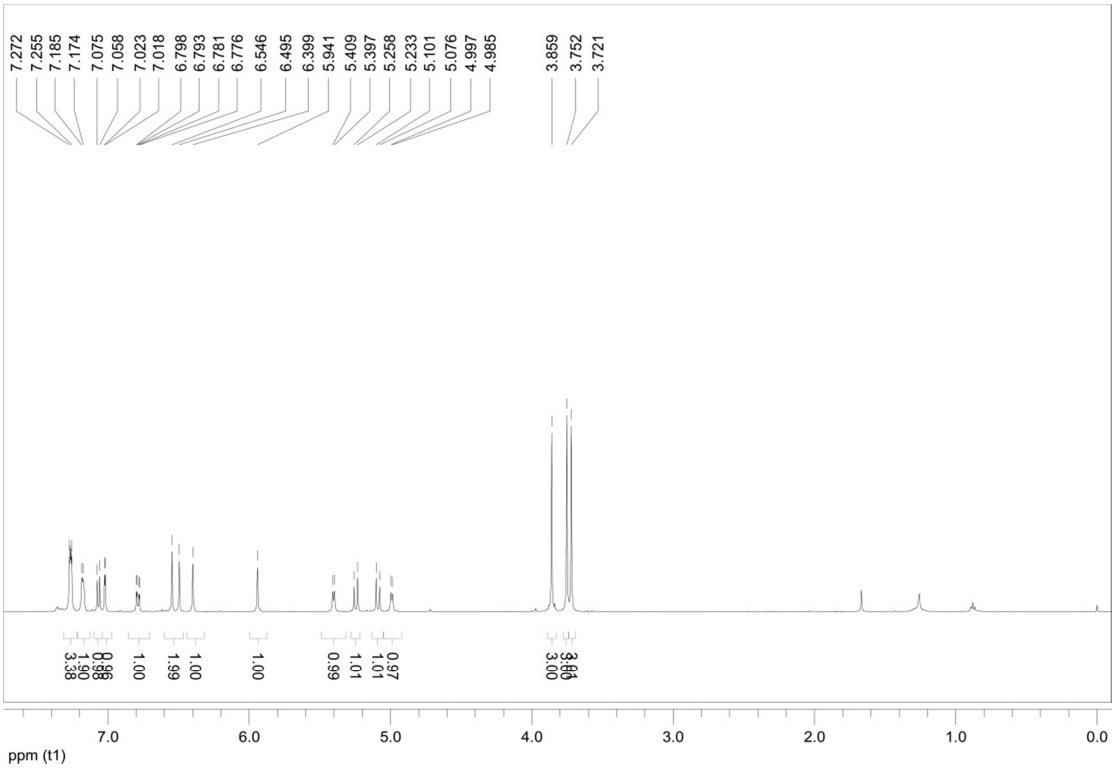
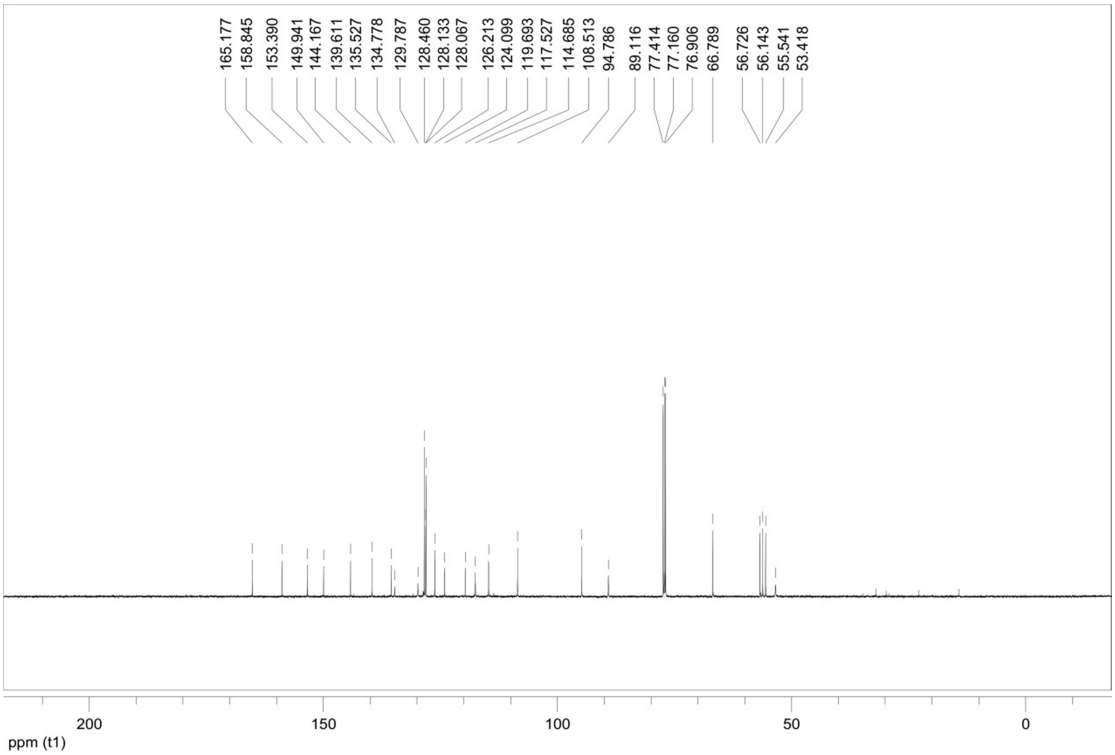
153.857
152.833
151.716
147.606
142.166
141.959
139.878
135.666
129.063
128.527
128.197
128.030
125.927
123.075
121.516
107.526
105.115
101.257
92.863
88.870
77.415
77.160
76.905
66.598
60.950
60.744
56.013
49.169
200
150
100
50
0
ppm (t1)


MeO
MeO
O
CO2Bn
Br
O

3fd


7.272
7.255
7.185
7.174
7.075
7.058
7.023
7.018
6.798
6.793
6.781
6.776
6.546
6.495
6.399
5.941
5.409
5.397
5.258
5.233
5.101
5.076
4.997
4.985
3.859
3.752
3.721
3.38
1.90
1.00
1.99
1.00
1.00
0.99
1.01
0.97
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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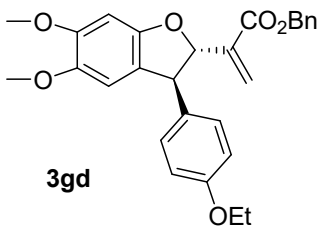
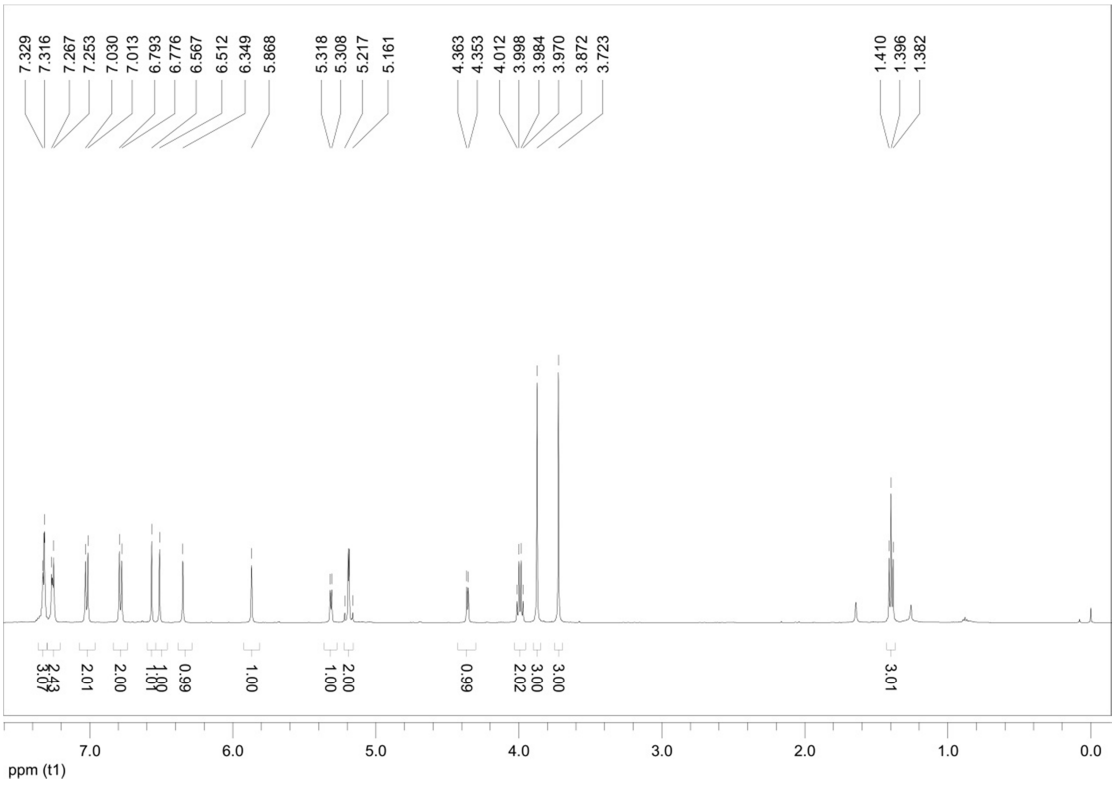
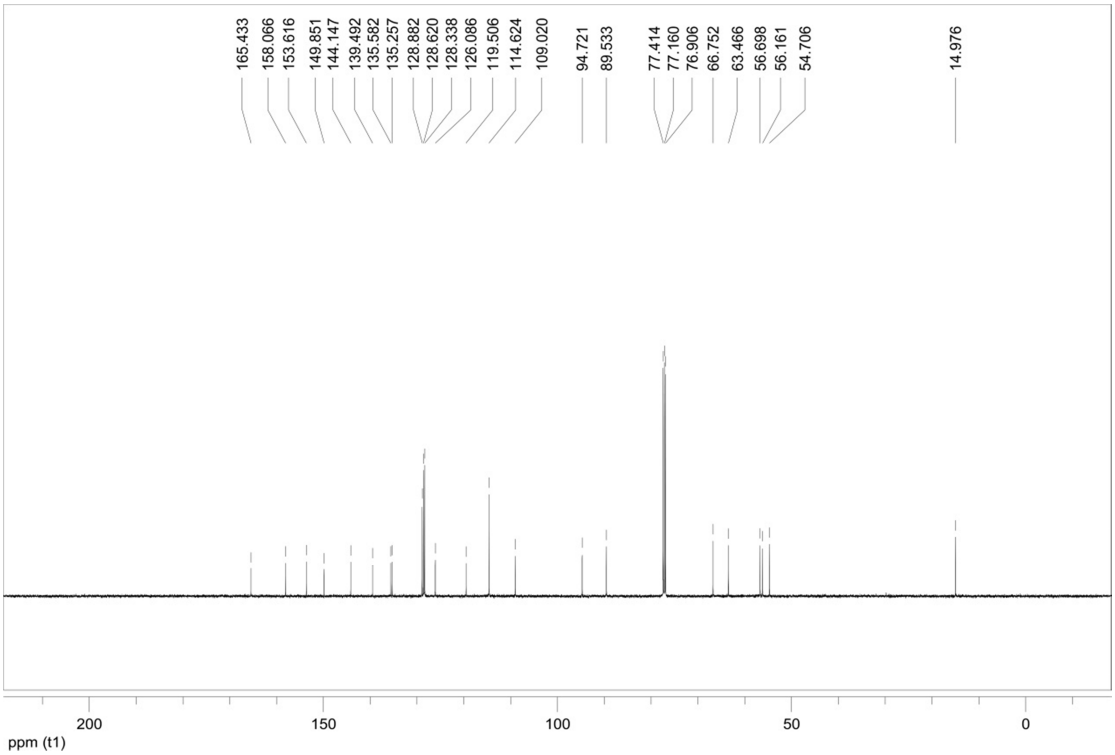
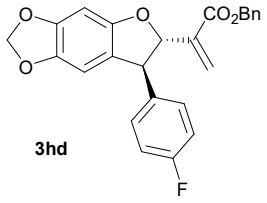
158.845
153.390
149.941
144.167
139.611
135.527
134.778
129.787
128.460
128.133
128.067
126.213
124.099
119.693
117.527
114.685
108.513
94.786
89.116
77.414
77.160
76.906
66.789
56.726
56.143
55.541
53.418
200
150
100
50
0
ppm (t1)


CO2Bn
OEt

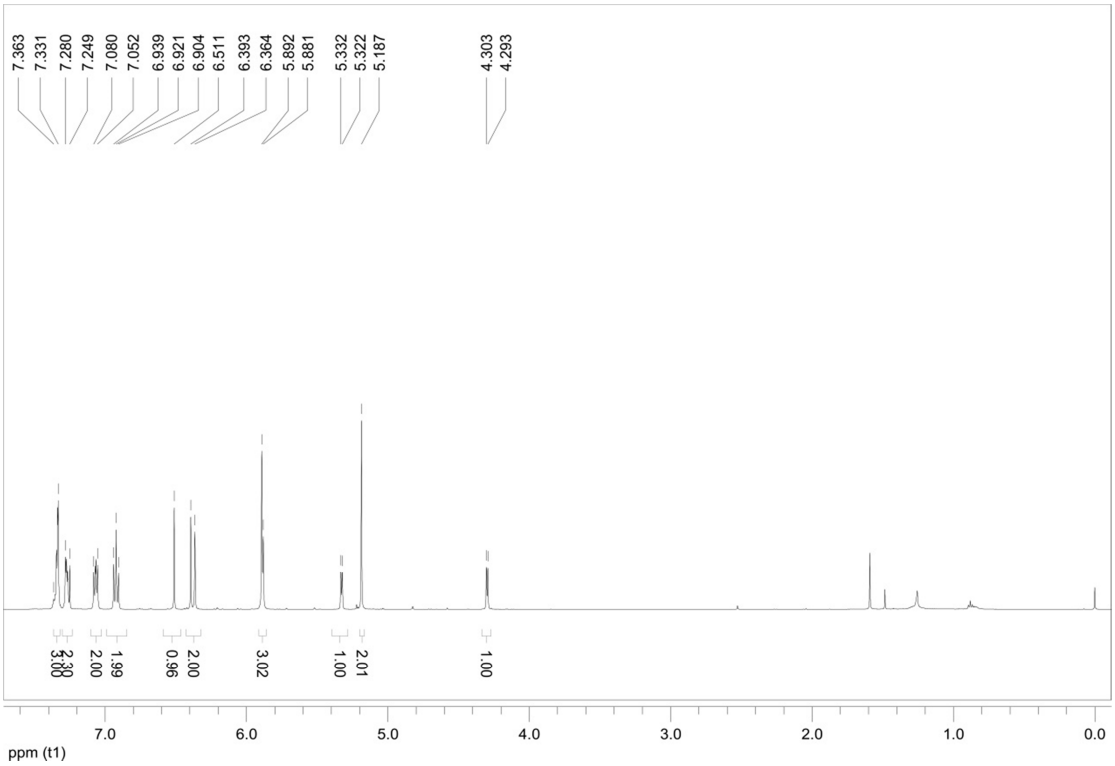
3gd

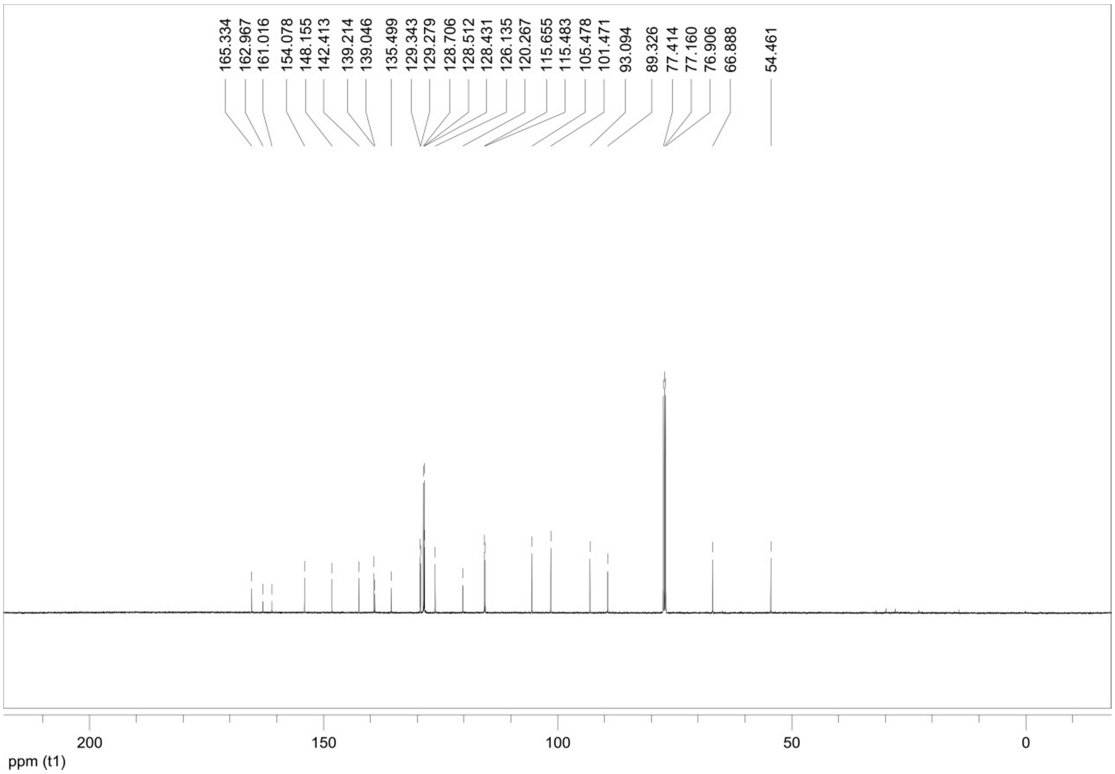

7.329
7.316
7.267
7.253
7.030
7.013
6.793
6.776
6.567
6.512
6.349
5.868
5.318
5.308
5.217
5.161
4.363
4.353
4.012
3.998
3.984
3.970
3.872
3.723
1.410
1.396
1.382
3.07
2.43
2.01
2.00
1.00
1.00
0.99
1.00
1.00
2.00
0.99
2.02
3.00
3.00
3.01
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

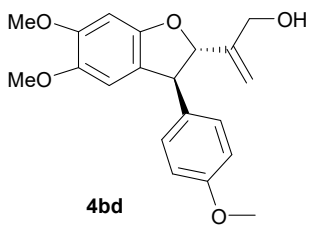

165.433
158.066
153.616
149.851
144.147
139.492
135.582
135.257
128.882
128.620
128.338
126.086
119.506
114.624
109.020
94.721
89.533
77.414
77.160
76.906
66.752
63.466
56.698
56.161
54.706
14.976
200
150
100
50
0
ppm (t1)


O
O
O
O
CO2Bn
F

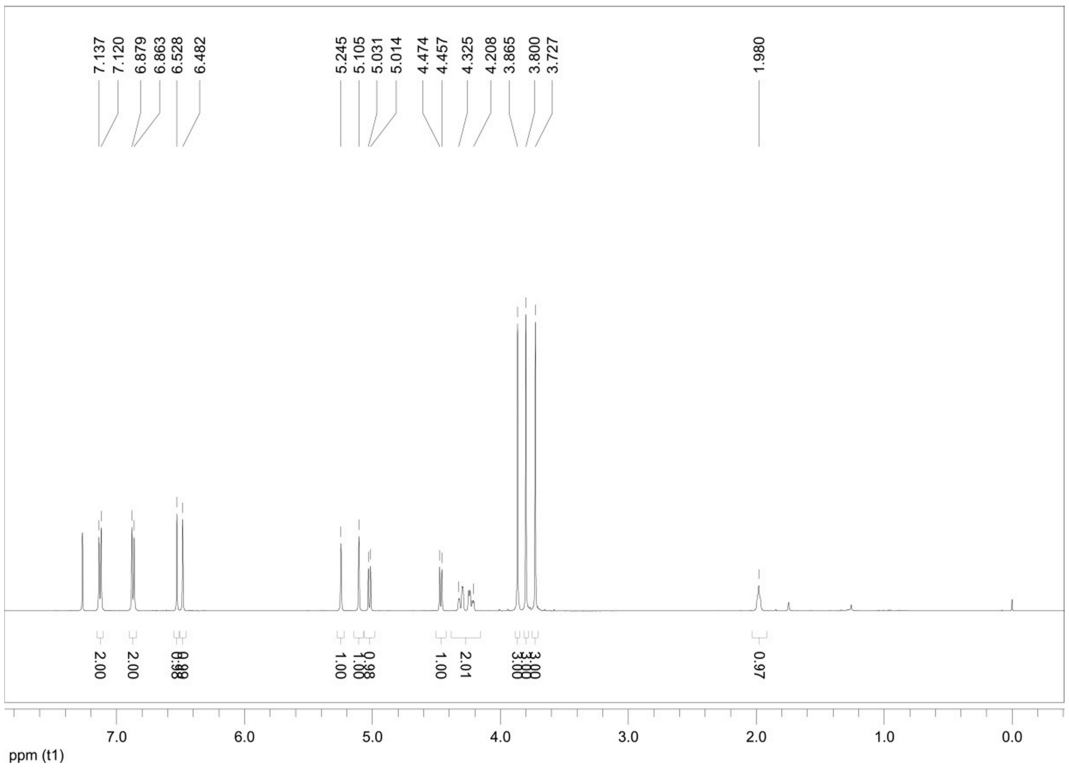
3hd

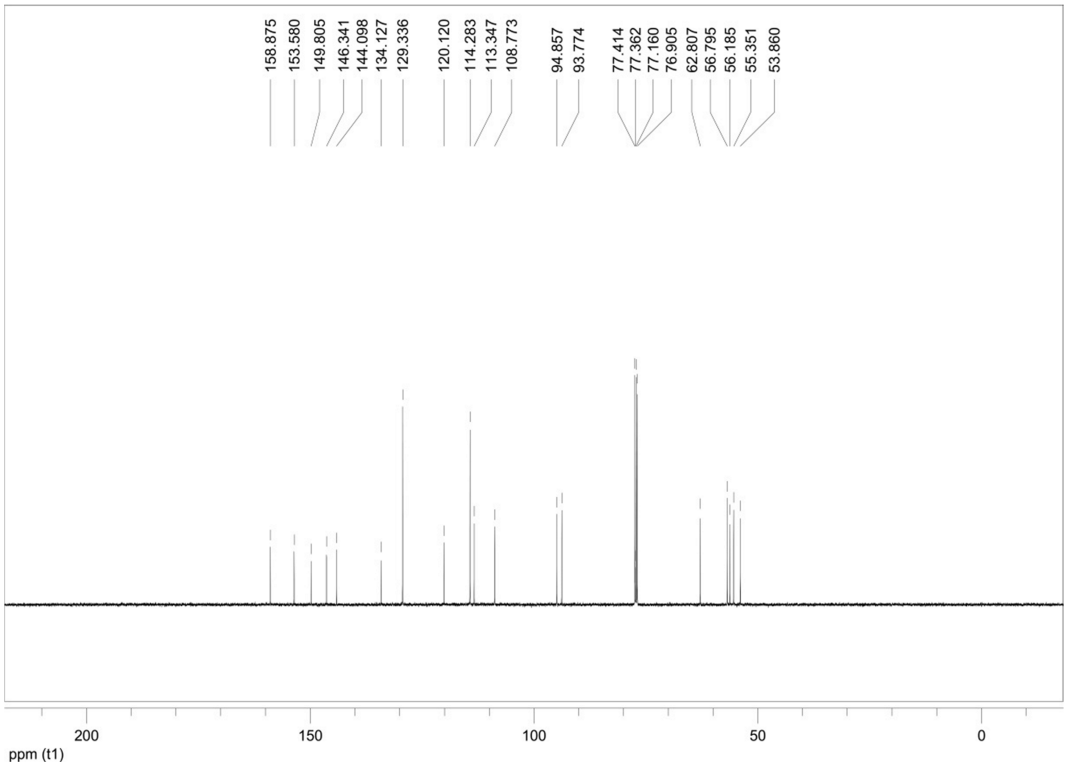

7.363
7.331
7.280
7.249
7.080
7.052
6.939
6.921
6.904
6.511
6.393
6.364
5.892
5.881
5.332
5.322
5.187
4.303
4.293
3.00
2.00
1.99
0.96
2.00
3.02
1.00
2.01
1.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

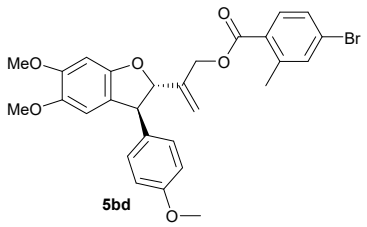

165.334
162.967
161.016
154.078
148.155
142.413
139.214
139.046
135.499
129.343
129.279
128.706
128.512
128.431
126.135
120.267
115.655
115.483
105.478
101.471
93.094
89.326
77.414
77.160
76.906
66.888
54.461
200
150
100
50
0
ppm (t1)


MeO
MeO
O
OH
O

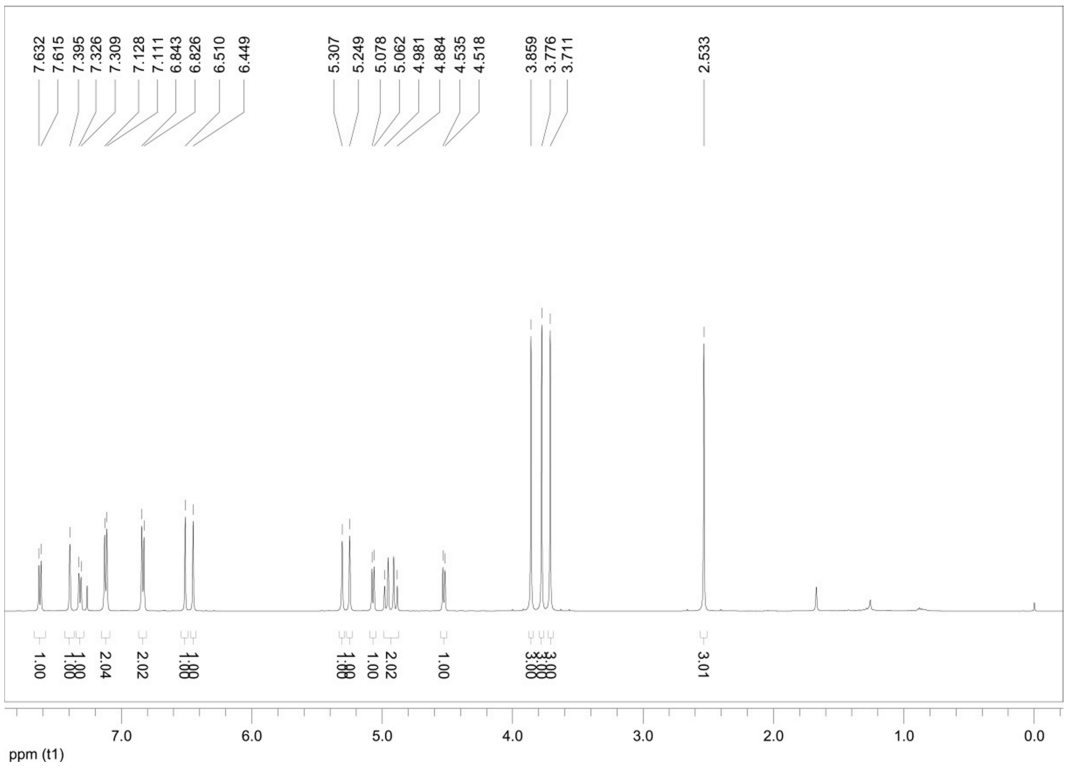
4bd

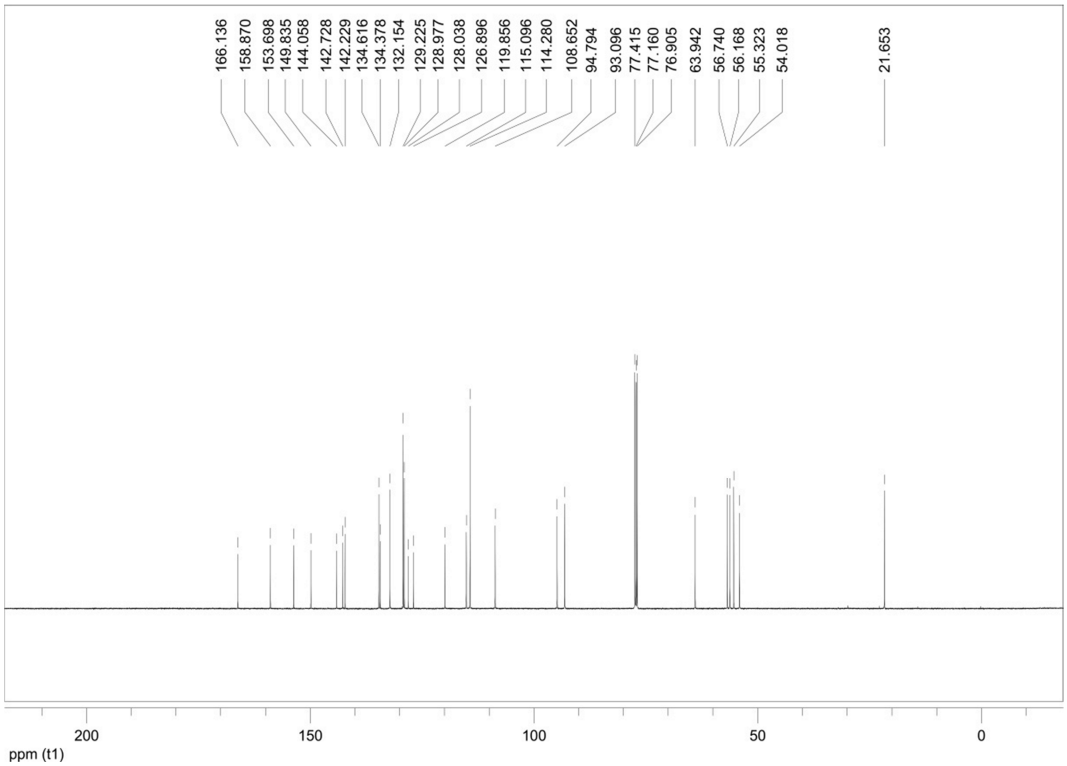

7.137
7.120
6.879
6.863
6.528
6.482
5.245
5.105
5.031
5.014
4.474
4.457
4.325
4.208
3.865
3.800
3.727
1.980
2.00
2.00
0.98
1.00
0.98
1.00
2.01
3.00
3.00
3.00
0.97
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


158.875
153.580
149.805
146.341
144.098
134.127
129.336
120.120
114.283
113.347
108.773
94.857
93.774
77.414
77.362
77.160
76.905
62.807
56.795
56.185
55.351
53.860
200
150
100
50
0
ppm (t1)

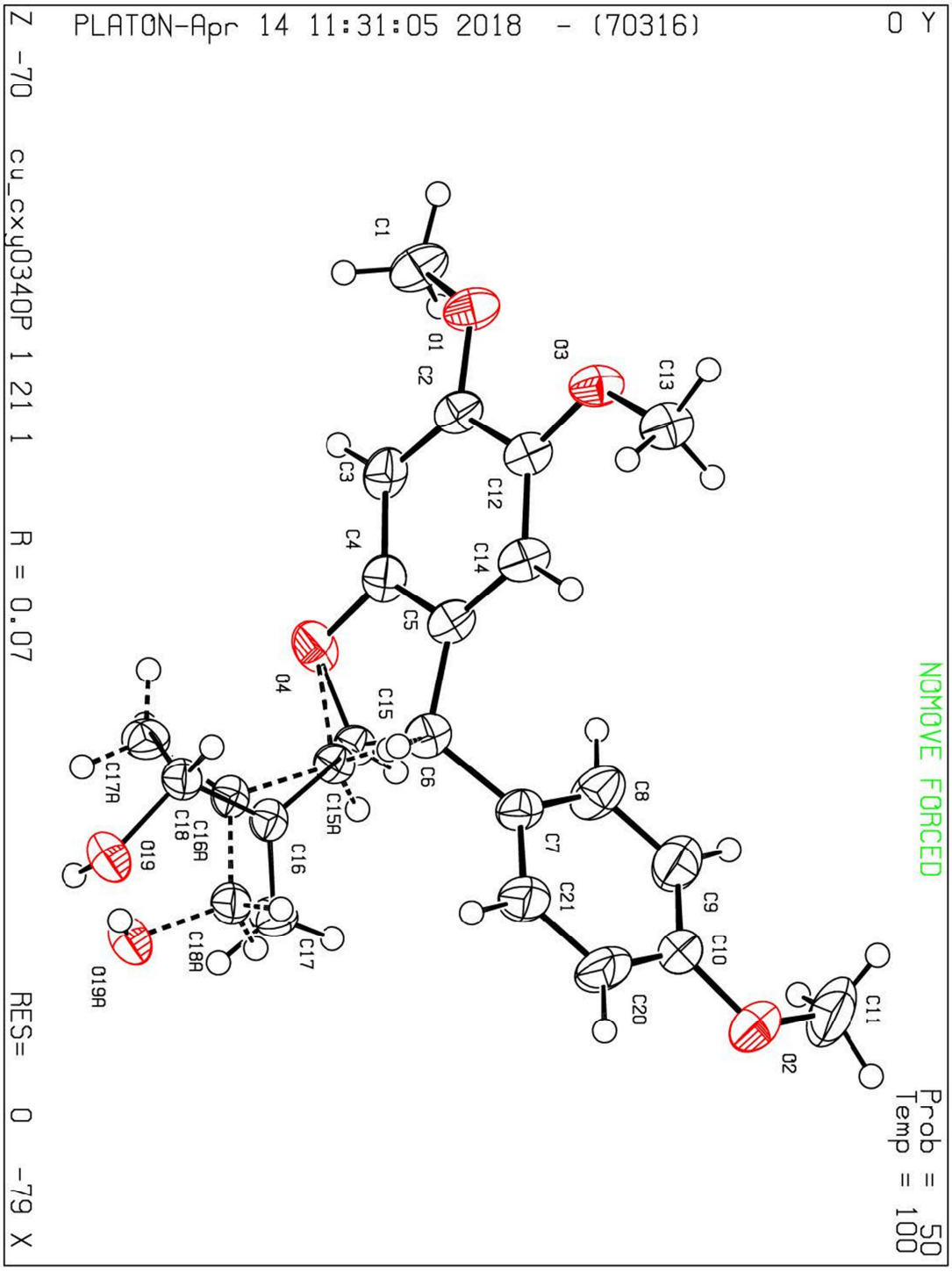

MeO
MeO
O
O
O
Br
O

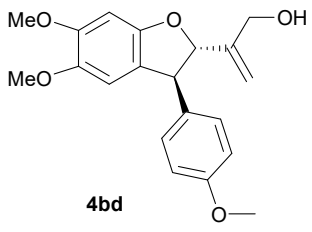
5bd


7.632
7.615
7.395
7.326
7.309
7.128
7.111
6.843
6.826
6.510
6.449
5.307
5.249
5.078
5.062
4.981
4.884
4.535
4.518
3.859
3.776
3.711
2.533
1.00
1.08
1.11
2.04
2.02
1.88
1.88
1.00
2.02
1.00
3.33
3.30
3.30
3.01
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


166.136
158.870
153.698
149.835
144.058
142.728
142.229
134.616
134.378
132.154
129.225
128.977
128.038
126.896
119.856
115.096
114.280
108.652
94.794
93.096
77.415
77.160
76.905
63.942
56.740
56.168
55.323
54.018
21.653
200
150
100
50
0
ppm (t1)

Crystal Structure and data for compound 4bd





4bd