Supporting Information

Highly Enantioselective Tandem Cycloisomerization/ Diels-Alder Reaction of 2-(1-Alkynyl)-2-alken-1-ones and Enals: Dual Catalysis with Platinum and Amine

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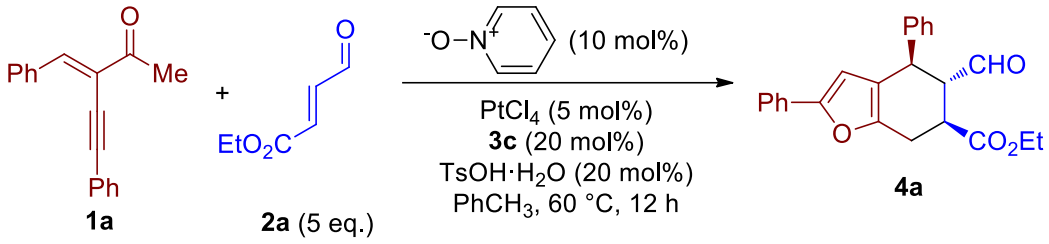
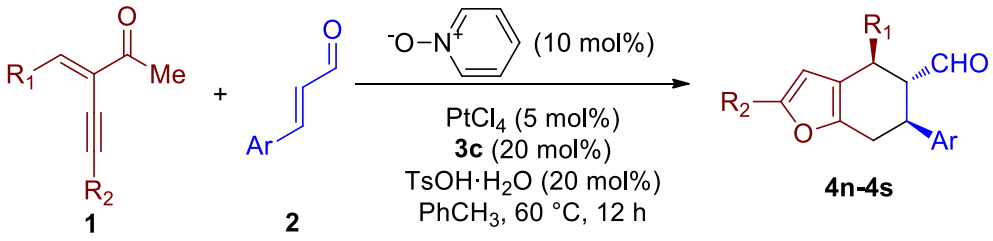
1. General information.

Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere; materials obtained from commercial suppliers were used directly without further purification. The $[\alpha]_D^{20}$ was recorded using PolAAr 3005 High Accuracy Polarimeter. Infrared (IR) spectra were obtained using a Bruker tensor 27 infrared spectrometer. 1H NMR spectra, 13C NMR spectra were recorded on a Bruker 400, 500 MHz spectrometer in chloroform-d3. All signals are reported in ppm with the internal TMS signal at 0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, hep = heptet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration). Enantiomer ratios were determined using chiral HPLC analysis by comparison with authentic racemic materials. Solid aldehydes were used directly. All other liquid aldehydes were freshly distilled prior to use.

2. General procedure for synthesis of 4.

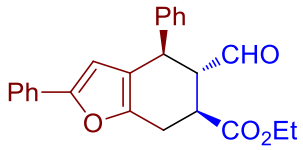


In a dried glass tube, a mixture of $PtCl_4$ (5 mol%), pyridine *N*-oxide (10 mol%), (2S)-2-[Bis[3,5-bis(trifluoromethyl)phenyl]-[(trimethylsilyl)oxy]methyl]pyrrolidine (**3c**, 20 mol%), TsOH•H_2O (20 mol%), **1a** (49.2 mg, 0.2 mmol) and **2a** ((E)-4-Oxo-2-butenoicacid ethyl 128 mg, 1.0 mmol) was mixed in $PhCH_3$ (2 mL), stirring at 60 °C until the reaction was complete (12 h). The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexanes/EtOAc = 25:1) to yield product (**4a**) as a solid (46.4 mg, 62%), which was confirmed by ^{1}H NMR, ^{13}C NMR spectrum, and enantio ratio was determined by chiral HPLC.



In a dried glass tube, a mixture of $PtCl_4$ (5 mol%), pyridine *N*-oxide (10 mol%), (2S)-2-[Bis[3,5-bis(trifluoromethyl)phenyl]-[(trimethylsilyl)oxy]methyl]pyrrolidine (20 mol%), TsOH•H_2O (20 mol%), **1** (0.4 mmol) and **2** (cinnamaldehyde derivatives, 0.2 mmol) was mixed in $PhCH_3$ (2 mL), stirring at 60 °C until the reaction was complete (24 h), the mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to yield product (**4n-4s**) as a solid.

1) (4R,5S,6S)-ethyl 5-formyl-2,4-diphenyl-4,5,6,7-tetrahydrobenzofuran-6-carboxylate (4a)



In a dried glass tube, a mixture of $PtCl_4$ (5 mol%), pyridine *N*-oxide (10 mol%), (2S)-2-[Bis[3,5-bis(trifluoromethyl)phenyl]-[(trimethylsilyl)oxy]methyl]pyrrolidine (**3c**, 20 mol%), $TsOH•H_2O$ (20 mol%), **1a** (49.2 mg, 0.2 mmol) and **2a** (128 mg, 1.0 mmol) was mixed in $PhCH_3$ (2 mL), stirring at 60 °C until the reaction was complete (12 h). The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by column chromatography. **4a** (46.4 mg, 62%) was obtained as a solid.

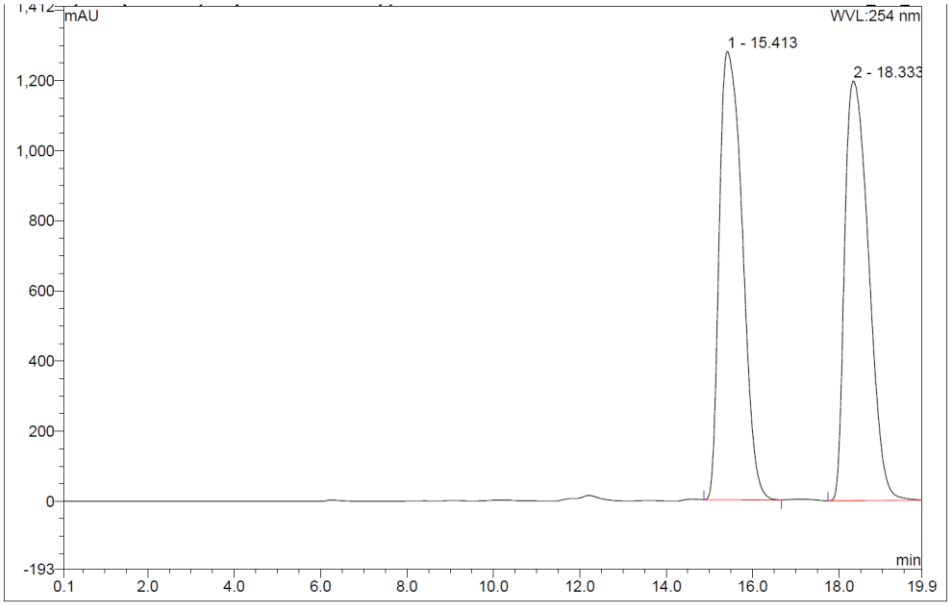
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 1H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.36-7.28 (m, 5H), 7.24-7.19 (m, 3H), 6.18 (s, 1H), 4.12-4.06 (m, 2H), 3.99-3.95 (m, 1H), 3.33-3.30 (m, 2H), 3.15-3.07 (m,2H), 1.19 (t, *J* = 7.2 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 173.3, 153.3, 148.0, 141.1, 130.7, 128.8, 128.6, 128.5, 127.4, 127.2, 123.4, 121.0, 105.0, 61.2, 55.8, 41.4, 40.9, 25.3, 14.0

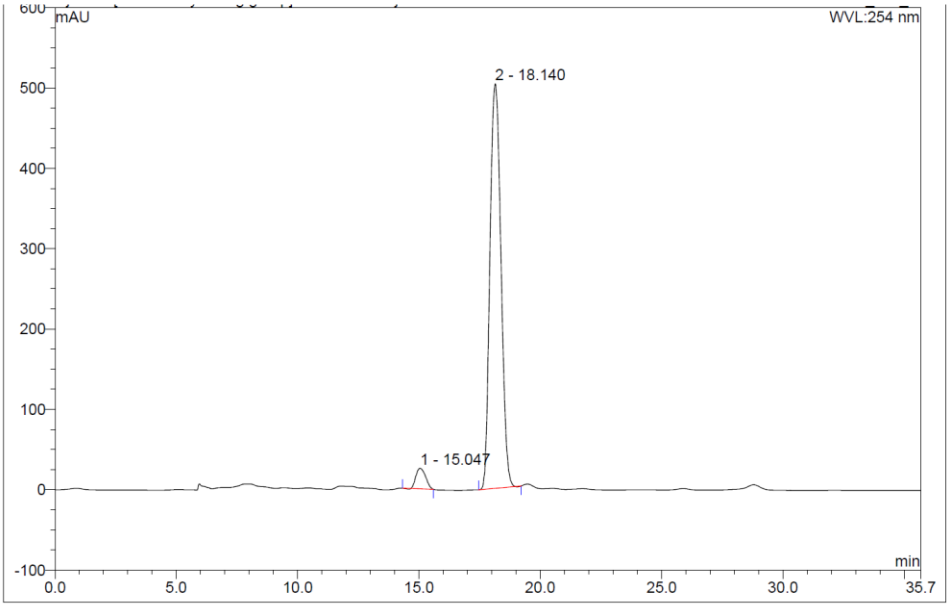
HRMS (ESI, m/z): $[M+Na]^+$ calcd.for $C_{24}H_{22}NaO_4$ 397.1410, found 397.1406

HPLC analysis: 92% ee (Chiralpak AD-H column, hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, UV detection at 254 nm), Rt (minor) = 15.05 min, Rt (major) = 18.14 min

$[\alpha]_D^{20}$= -16.4 (c = 0.50, $CHCl_3$)

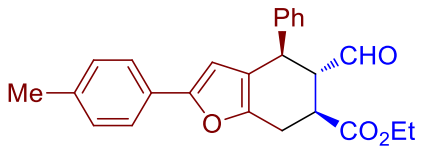


序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	15.41	n.a.	1278.692	787.537	50.60	n.a.	BMB*
2	18.33	n.a.	1196.930	768.721	49.40	n.a.	BMB
总和:			2475.622	1556.258	100.00	0.000	



序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	15.05	n.a.	25.366	11.600	4.21	n.a.	BMB*
2	18.14	n.a.	503.558	263.986	95.79	n.a.	BMB*
总和:			528.924	275.586	100.00	0.000	

2) (4R,5S,6S)-ethyl 5-formyl-4-phenyl-2-(p-tolyl)-4,5,6,7-tetrahydrobenzofuran-6-carboxylate (4b)



In a dried glass tube, a mixture of $PtCl_4$ (5 mol%), pyridine *N*-oxide (10 mol%), (2S)-2-[Bis[3,5-bis(trifluoromethyl)phenyl]-[(trimethylsilyl)oxy]methyl]pyrrolidine (**3c**, 20 mol%), TsOH•H_2O (20 mol%), **1b** (52.0 mg, 0.2 mmol) and **2a** (128 mg, 1.0 mmol) was mixed in $PhCH_3$ (2 mL), stirring at 60 °C until the reaction was complete (12 h). The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by column chromatography. **4b** (46.6 mg, 60%) was obtained as a solid.

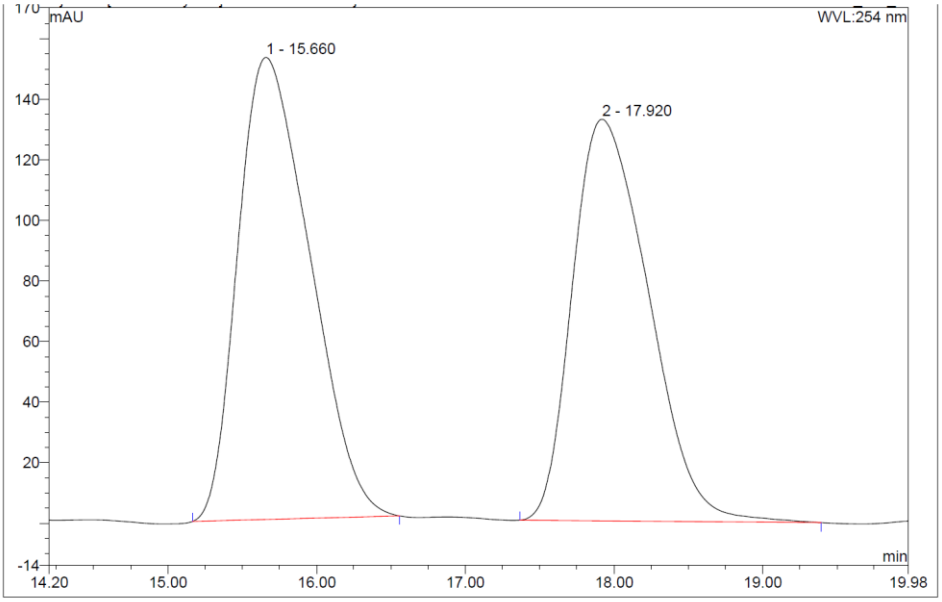
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.34-7.32 (m, *2*H), 7.30 – 7.26 (m, 1H), 7.25 – 7.19 (m, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.12 (s, 1H), 4.16 – 4.03 (m, 2H), 3.97 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.38 – 3.22 (m, 2H), 3.16 (dd, *J* = 16.4, 4.8 Hz, 1H), 3.04 (ddd, *J* = 16.2, 7.2, 3.2 Hz, 1H), 2.33 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1, 173.3, 153.5, 147.5, 141.1, 137.1, 129.3, 128.8, 128.5, 128.0, 127.4, 123.4, 120.8, 104.3, 61.2, 55.8, 41.5, 41.0, 25.3, 21.3, 14.0

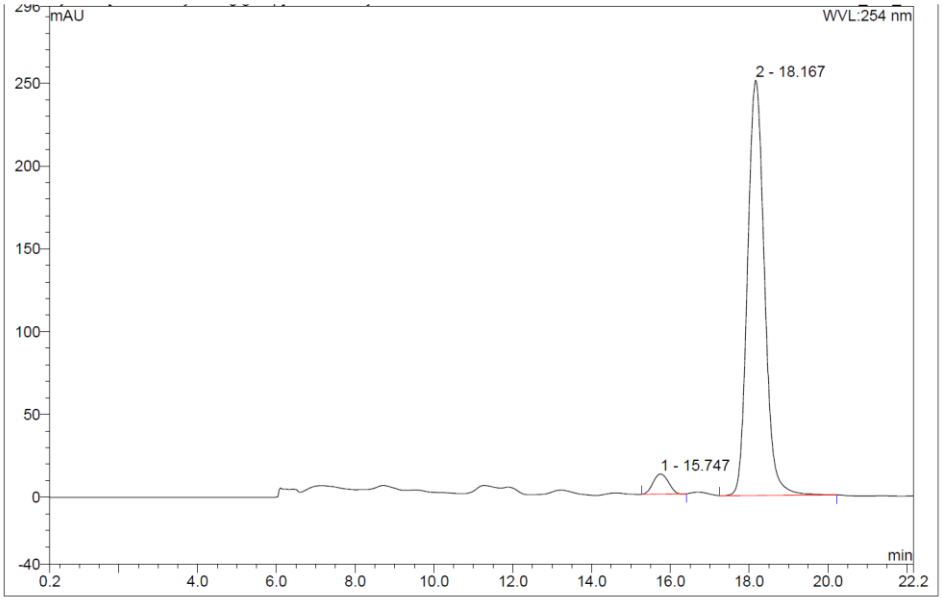
HRMS (ESI, m/z): $[M+Na]^+$ calcd.for $C_{25}H_{24}NaO_4$ 411.1567, found 411.1588

HPLC analysis: 92% ee (Chiralpak AD-H column, hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, UV detection at 254 nm), Rt (minor) = 15.75 min, Rt (major) = 18.17 min

$[\alpha]_D^{20}$= -10.7 (c = 0.50, $CHCl_3$,)

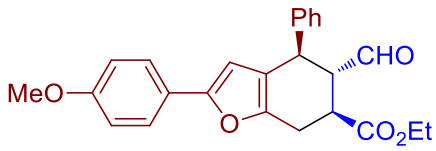


序号	保留时间 min		峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	15.66	n.a.		152.633	85.709	52.08	n.a.	BMB*
2	17.92	n.a.		132.671	78.874	47.92	n.a.	BMB*
总和:				285.304	164.583	100.00	0.000	



序号	保留时间 min		峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	15.75	n.a.		12.080	5.438	4.18	n.a.	BMB*
2	18.17	n.a.		250.643	124.587	95.82	n.a.	BMB*
总和:				262.723	130.025	100.00	0.000	

3) (4R,5S,6S)-ethyl 5-formyl-2-(4-methoxyphenyl)-4-phenyl-4,5,6,7-tetrahydrobenzofuran-6-carboxylate (4c)



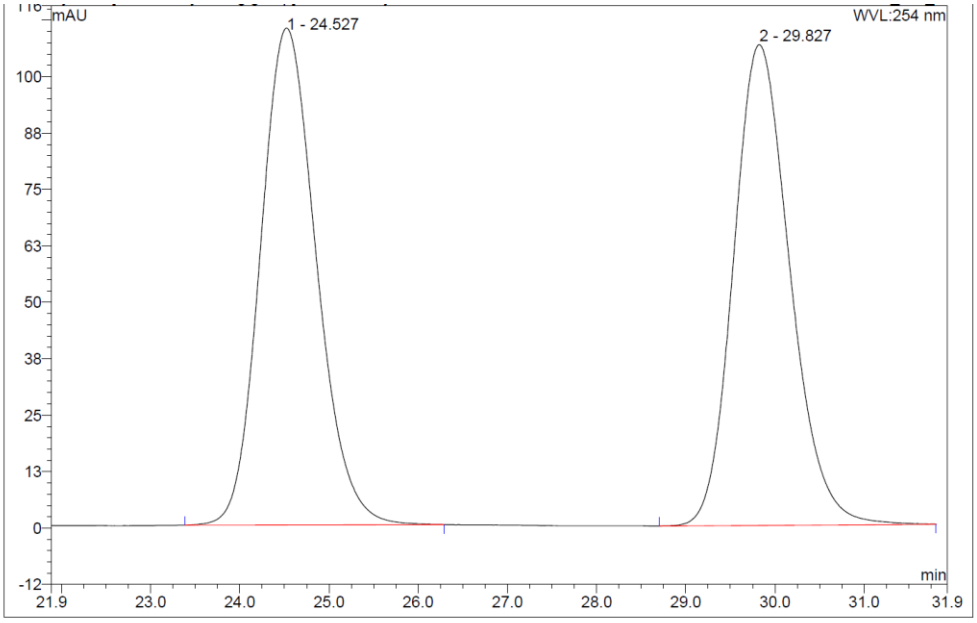
In a dried glass tube, a mixture of $PtCl_4$ (5 mol%), pyridine *N*-oxide (10 mol%), (2S)-2-[Bis[3,5-bis(trifluoromethyl)phenyl]-[(trimethylsilyl)oxy]methyl]pyrrolidine (**3c**, 20 mol%), TsOH•H_2O (20 mol%), **1c** (55.2 mg, 0.2 mmol) and **2a** (128 mg, 1.0 mmol) was mixed in $PhCH_3$ (2 mL), stirring at 60 °C until the reaction was complete (12 h). The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by column chromatography. **4c** (48.7mg, 60%) was obtained as a solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.37 – 7.30 (m, 2H), 7.30 – 7.26 (m, 1H), 7.25 – 7.20 (m, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.04 (s, 1H), 4.15 – 4.03 (m, 2H), 3.96 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.80 (s, 3H), 3.36 – 3.25 (m, 2H), 3.15 (dd, *J* = 16.4, 4.8 Hz, 1H), 3.08 – 2.99 (m, 1H), 1.19 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1, 173.3, 158.9, 153.4, 147.2, 141.2, 128.8, 128.5, 127.4, 124.9, 123.8, 120.8, 114.1, 103.4, 61.2, 55.8, 55.3, 41.5, 40.9, 25.2, 14.0

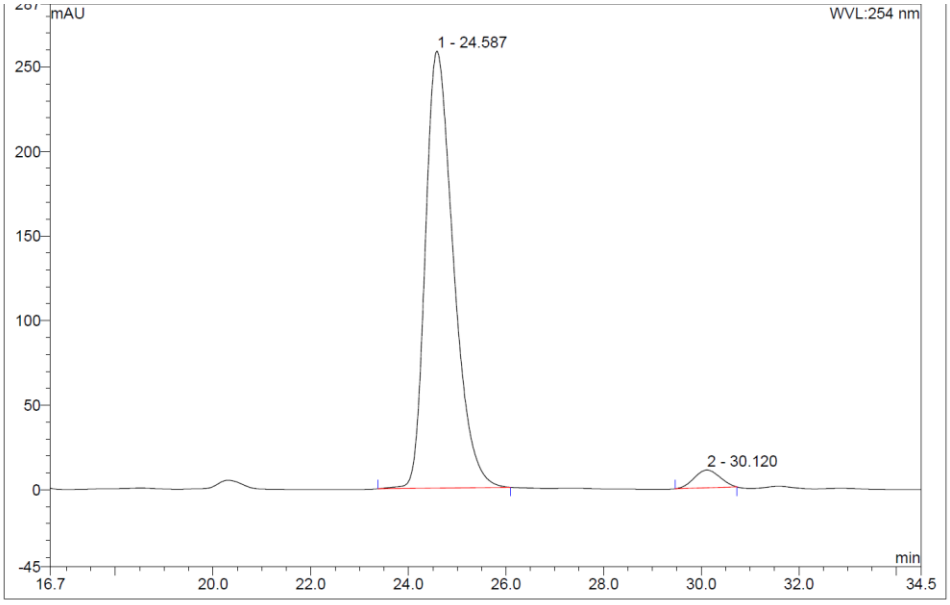
HRMS (ESI, m/z): $[M+Na]^+$ calcd.for $C_{25}H_{24}NaO_5$ 427.1516, found: 427.1529

HPLC analysis: 93% ee (Chiralpak AD-H column, hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, UV detection at 254 nm), Rt (major) = 24.59 min, Rt (minor) = 30.12 min

$[\alpha]_D^{20}$= -21.0 (c = 0.6, $CHCl_3$)

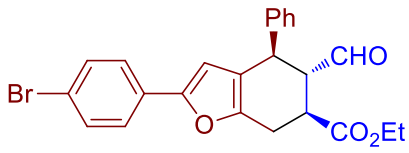


序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	24.53	n.a.	110.045	79.717	50.50	n.a.	BMB*
2	29.83	n.a.	106.471	78.138	49.50	n.a.	BMB*
总和:			216.515	157.856	100.00	0.000	



序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	24.59	n.a.	258.298	171.816	96.42	n.a.	BMB*
2	30.12	n.a.	10.493	6.380	3.58	n.a.	BMB*
总和:			268.791	178.196	100.00	0.000	

4) (4R,5S,6S)-ethyl 2-(4-bromophenyl)-5-formyl-4-phenyl-4,5,6,7-tetrahydrobenzofuran-6-carboxylate (4d)



In a dried glass tube, a mixture of $PtCl_4$ (5 mol%), pyridine *N*-oxide (10 mol%), (2S)-2-[Bis[3,5-bis(trifluoromethyl)phenyl]-[(trimethylsilyl)oxy]methyl]pyrrolidine (**3c**, 20 mol%), TsOH•H_2O (20 mol%), **1d** (64.8 mg, 0.2 mmol) and **2a** (128 mg, 1.0 mmol) was mixed in $PhCH_3$ (2 mL), stirring at 60 °C until the reaction was complete (12 h). The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by column chromatography. **4d** (43.4 mg, 48%) was obtained as a solid.

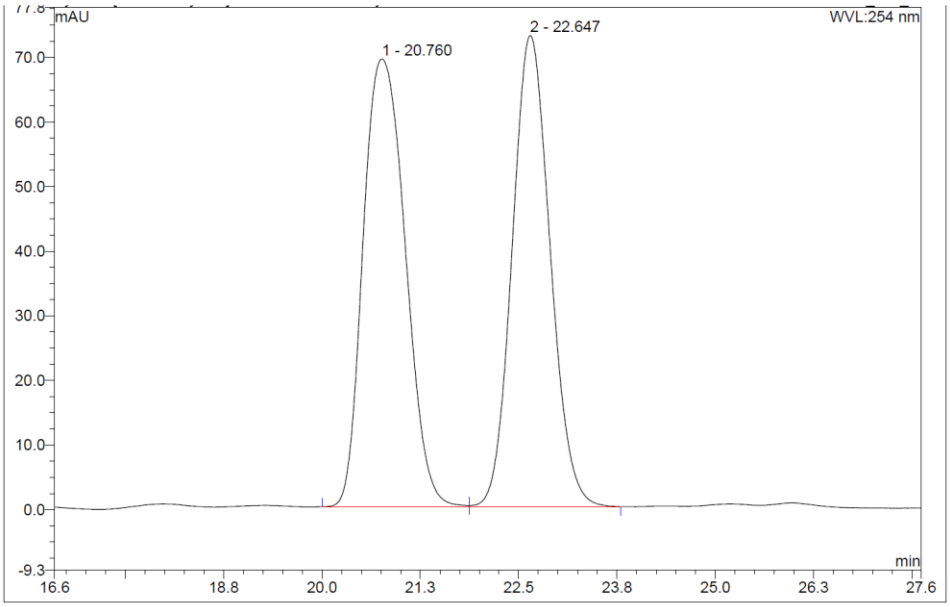
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 1H), 7.58 – 7.52 (m, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.16 (s, 1H), 4.16 – 4.06 (m, 2H), 3.99 (dq, *J* = 11.0, 7.0 Hz, 1H), 3.35 – 3.22 (m, 2H), 3.16 (dd, *J* = 16.0, 5.5 Hz, 1H), 3.10 – 3.00 (m, 1H), 1.20 (t, *J* = 7.0 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 202.5, 173.0, 153.5, 148.1, 140.2, 131.9, 130.5, 130.3, 128.7, 127.4, 123.5, 121.3, 120.4, 104.7, 61.4, 55.7, 41.0, 40.7, 25.2, 14.0

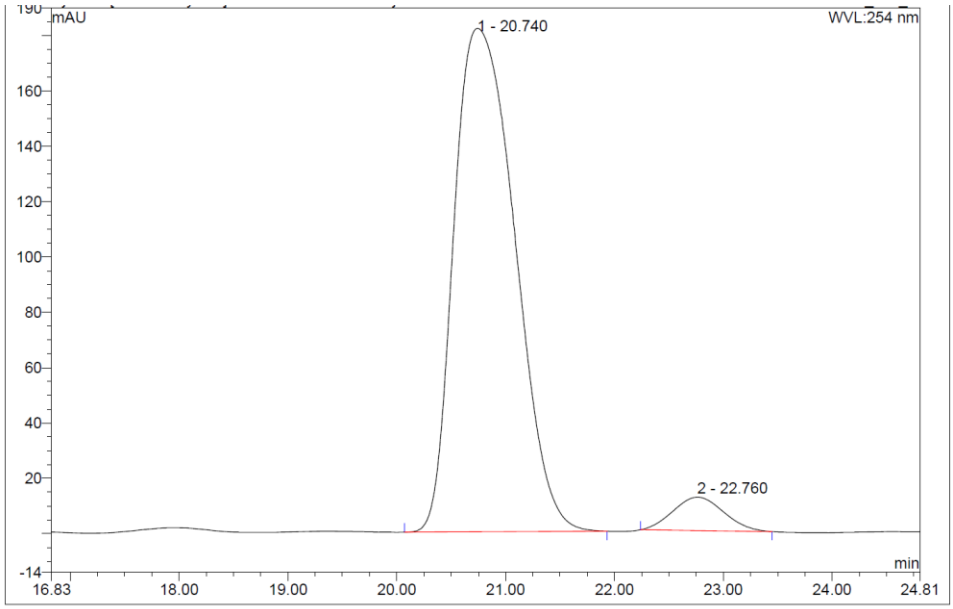
HRMS (ESI, m/z): $[M+H]^+$: calcd.for $C_{24}H_{22}BrO_4$ 453.0696, found: 453.0690

HPLC analysis: 90% ee (Chiralpak AD-H column, hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, UV detection at 254 nm), Rt (major) = 20.74 min; Rt (minor) = 22.76 min

$[\alpha]_D^{20}$= -7.4 (c = 0.50, $CHCl_3$)

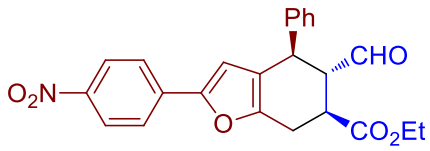


序号	保留时间 min		峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	20.76	n.a.		69.335	43.044	51.35	n.a.	BM *
2	22.65	n.a.		72.935	40.781	48.65	n.a.	MB*
总和:				142.269	83.825	100.00	0.000	



序号	保留时间 min		峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	20.74	n.a.		181.995	117.933	94.77	n.a.	BMB*
2	22.76	n.a.		12.079	6.512	5.23	n.a.	BMB*
总和:				194.075	124.445	100.00	0.000	

5) (4R,5S,6S)-ethyl 5-formyl-2-(4-nitrophenyl)-4-phenyl-4,5,6,7-tetrahydrobenzofuran-6-carboxylate (4e)



In a dried glass tube, a mixture of $PtCl_4$ (5 mol%), pyridine *N*-oxide (10 mol%), (2S)-2-[Bis[3,5-bis(trifluoromethyl)phenyl]-[(trimethylsilyl)oxy]methyl]pyrrolidine (**3c**, 20 mol%), TsOH•H_2O (20 mol%), **1e** (58.2 mg, 0.2 mmol) and **2a** (128 mg, 1.0 mmol) was mixed in $PhCH_3$ (2 mL), stirring at 60 °C until the reaction was complete (12 h). The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by column chromatography. **4e** (47.2 mg, 56%) was obtained as a solid.

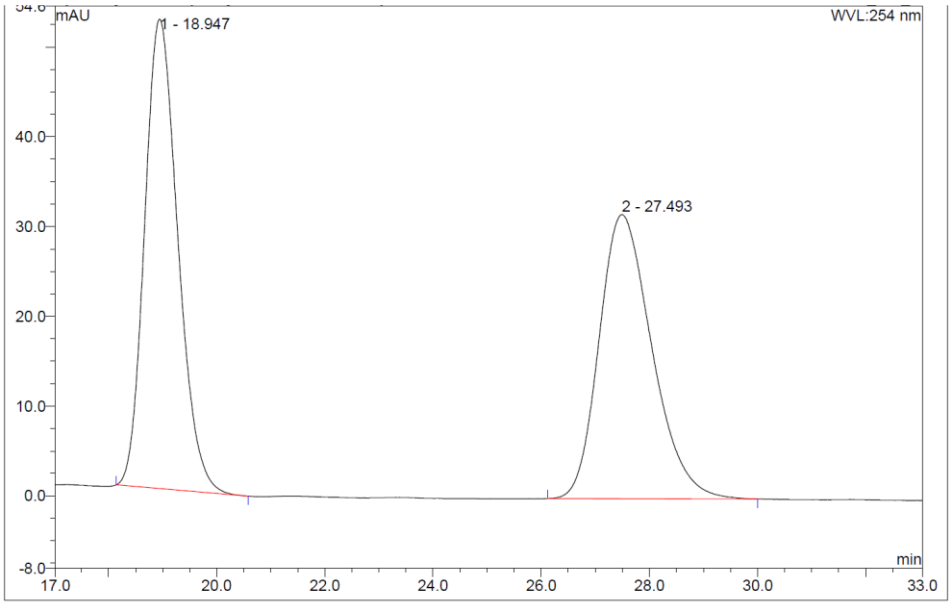
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (s, 1H), 8.20 (d, *J* = 9.2 Hz, 2H), 7.68 (d, *J* = 9.2 Hz, 2H), 7.41 – 7.28 (m, 3H), 7.25 – 7.18 (m, 2H), 6.43 (s, 1H), 4.19 – 4.04 (m, 2H), 3.95 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.42 – 3.26 (m, 2H), 3.19 (dd, *J* = 16.8, 5.2 Hz, 1H), 3.14 – 3.05 (m, 1H), 1.19 (t, *J* = 7.2 Hz, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.5, 172.9, 151.2, 150.6, 146.2, 140.6, 136.3, 129.0, 128.4, 127.7, 124.3, 123.5, 122.0, 109.2, 61.4, 55.5, 41.1, 40.7, 25.2, 14.0

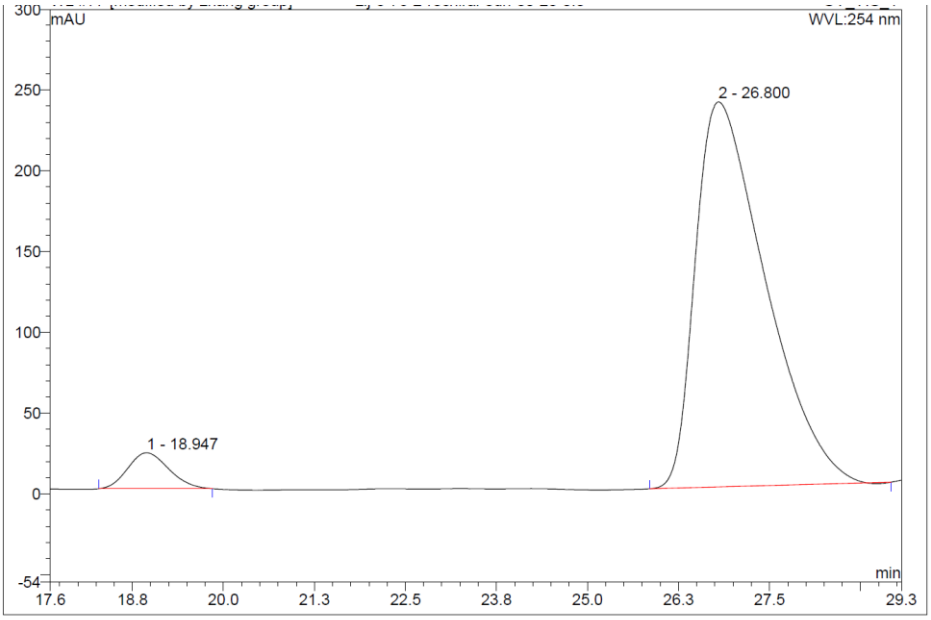
HRMS (ESI, m/z): $[M+Na]^+$ calcd.for $C_{24}H_{21}NNaO_6$ 442.1261, found 442.1262

HPLC analysis: 90% ee (Chiralpak OD-H column, hexane/*i*-PrOH = 80/20, flow rate 0.8 mL/min, UV detection at 254 nm), Rt (minor) = 18.95 min; Rt (major) = 26.80 min

$[\alpha]_D^{20}$= -36.0 (c = 0.50, $CHCl_3$)

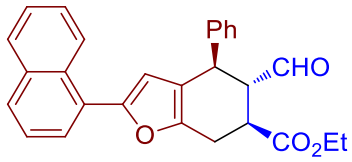


序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	18.95	n.a.	52.290	37.203	50.98	n.a.	BMB*
2	27.49	n.a.	31.642	35.771	49.02	n.a.	BMB*
总和:			83.932	72.974	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18.95	n.a.	22.241	14.482	5.17	n.a.	BMB*
2	26.80	n.a.	238.157	265.530	94.83	n.a.	BMB*
Total:			260.398	280.012	100.00	0.000	

6) (4R,5S,6S)-ethyl 5-formyl-2-(naphthalen-1-yl)-4-phenyl-4,5,6,7-tetrahydrobenzofuran-6-carboxylate (4f)



In a dried glass tube, a mixture of $PtCl_4$ (5 mol%), pyridine *N*-oxide (10 mol%), (2S)-2-[Bis[3,5-bis(trifluoromethyl)phenyl]-[(trimethylsilyl)oxy]methyl]pyrrolidine (**3c**, 20 mol%), TsOH•H_2O (20 mol%), **1f** (59.2 mg, 0.2 mmol) and **2a** (128 mg, 1.0 mmol) was mixed in $PhCH_3$ (2 mL), stirring at 60 °C until the reaction was complete (12 h). The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by column chromatography. **4f** (40.4 mg, 48%) was obtained as a solid.

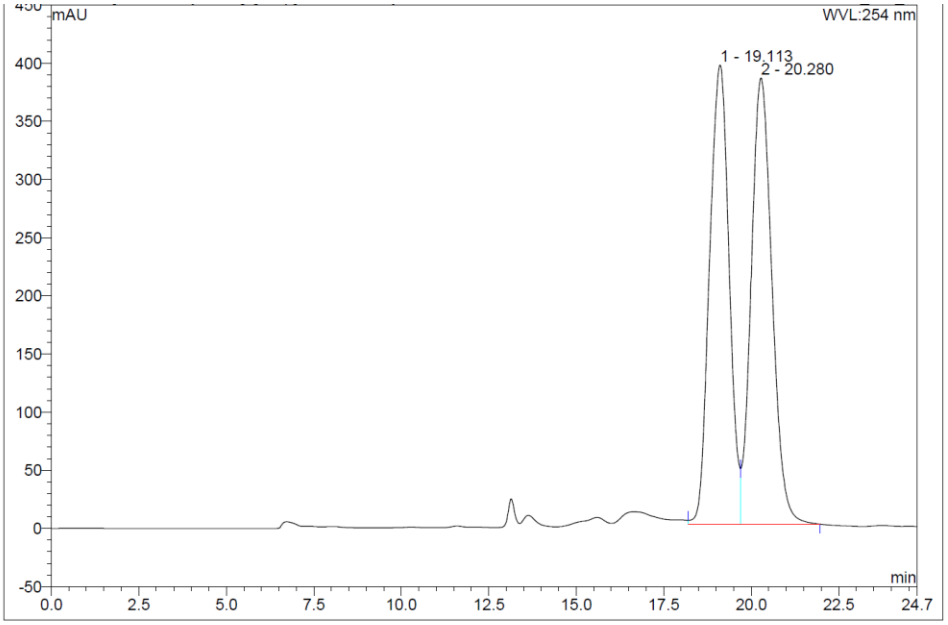
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (s, 1H), 8.39 – 8.28 (m, 1H), 7.85 (dd, *J* = 6.8, 2.8 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.72 – 7.64 (m, 1H), 7.51 – 7.43 (m, 3H), 7.39 – 7.31 (m, 2H), 7.32 – 7.21 (m, 3H), 6.27 (s, 1H), 4.21 – 4.05 (m, 2H), 3.98 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.43 – 3.30 (m, 2H), 3.24 (dd, *J* = 17.6, 4.8 Hz, 1H), 3.12 (ddd, *J* = 9.6, 8.8, 5.6 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1, 173.3, 152.8, 148.3, 141.1, 134.0, 130.1, 128.8, 128.6, 128.5, 128.3, 127.5, 126.6, 125.9, 125.8, 125.4, 125.3, 120.7, 109.3, 61.3, 55.9, 41.5, 41.0, 25.4, 14.0

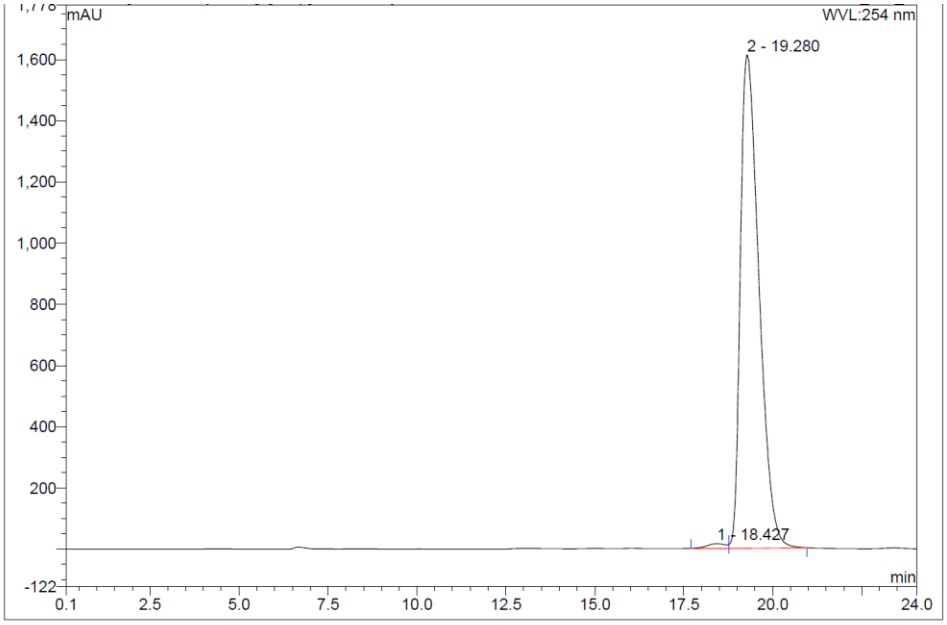
HRMS (ESI, m/z): $[M+Na]^+$ calcd.for $C_{28}H_{24}NaO_4$ 447.1567, found 447.1567

HPLC analysis: 98% ee (Chiralpak IC column, hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, UV detection at 254 nm), Rt (minor) = 18.43 min; Rt (major) = 19.28 min

$[\alpha]_D^{20}$= -21.8 (c =1.0, $CHCl_3$)

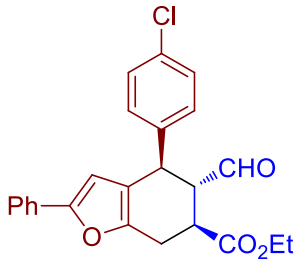


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	19.11	n.a.	394.604	255.021	49.05	n.a.	M *
2	20.28	n.a.	383.666	264.898	50.95	n.a.	MB*
Total:			778.270	519.919	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18.43	n.a.	15.343	9.441	0.96	n.a.	BM *
2	19.28	n.a.	1612.982	976.853	99.04	n.a.	MB*
Total:			1628.325	986.294	100.00	0.000	

7) (4R,5S,6S)-ethyl 4-(4-chlorophenyl)-5-formyl-2-phenyl-4,5,6,7-tetrahydrobenzofuran-6-carboxylate (4g)



In a dried glass tube, a mixture of $PtCl_4$ (5 mol%), pyridine *N*-oxide (10 mol%), (2S)-2-[Bis[3,5-bis(trifluoromethyl)phenyl]-[(trimethylsilyl)oxy]methyl]pyrrolidine (**3c**, 20 mol%), TsOH•H_2O (20 mol%), **1g** (56.0 mg, 0.2 mmol) and **2a** (128 mg, 1.0 mmol) was mixed in $PhCH_3$ (2 mL), stirring at 60 °C until the reaction was complete (12 h). The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by column chromatography. **4g** (38.6 mg, 47 %) was obtained as a solid.

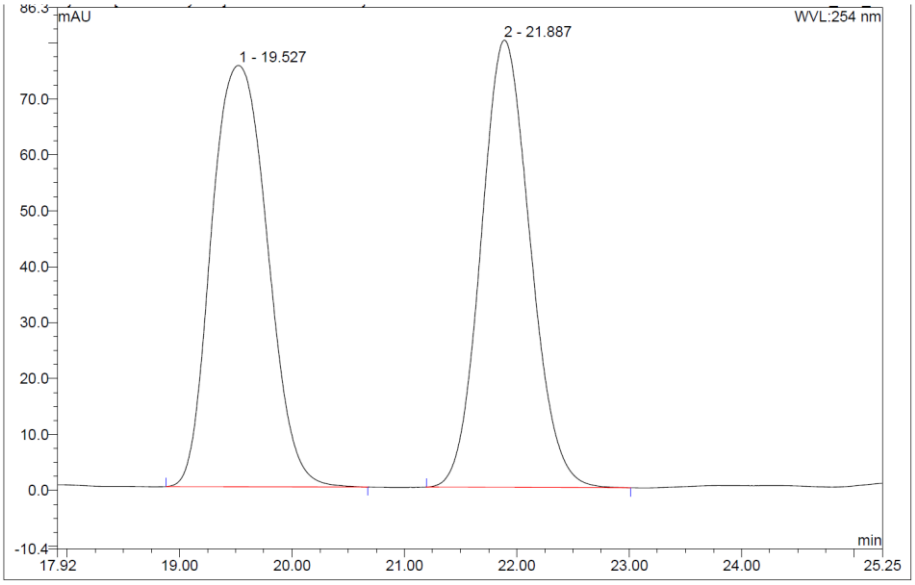
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (d, *J* = 0.8 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.37 – 7.28 (m, 4H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.15 (s, 1H), 4.16 – 4.04 (m, 2H), 3.99 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.36 – 3.20 (m, 2H), 3.21 – 3.12 (m, 1H), 3.10 – 3.00 (m, 1H), 1.20 (t, *J* = 7.1 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 202.5, 173.0, 153.5, 148.0, 139.7, 133.2, 130.6, 129.9, 129.0, 128.7, 127.4, 123.5, 120.5, 104.8, 61.3, 55.7, 41.0, 40.7, 25.2, 14.0

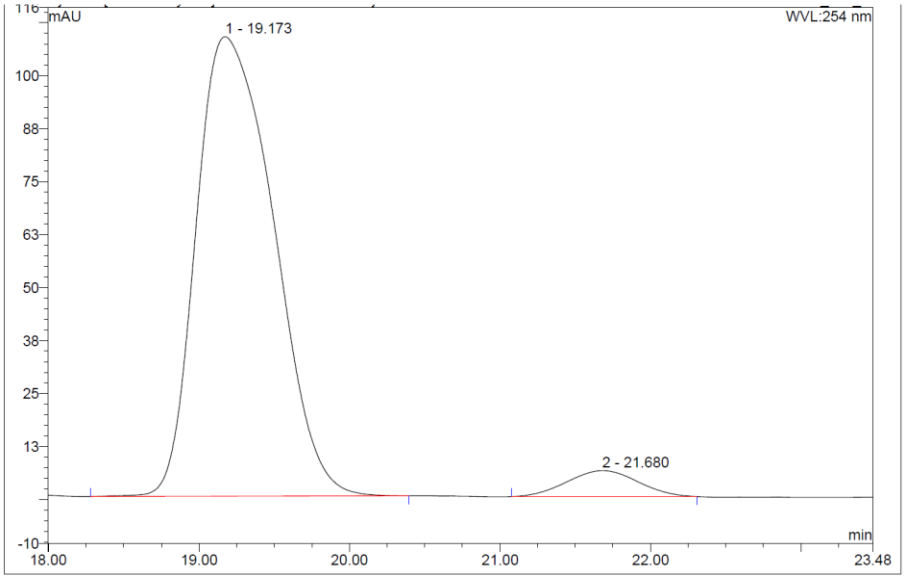
HRMS (ESI, m/z): $[M+Na]^+$ calcd.for $C_{24}H_{21}ClNaO_4$ 431.1021, found 431.1028

HPLC analysis: 90% ee (Chiralpak AD-H column, hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, UV detection at 254 nm), Rt (major) = 19.17 min, Rt (minor) = 21.68 min

$[\alpha]_D^{20}$= -13.7 (c = 0.50, $CHCl_3$)

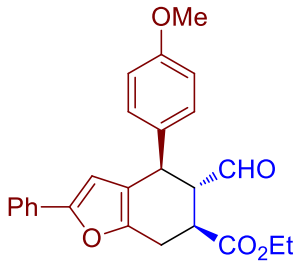


序号	保留时间 min		峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	19.53	n.a.		75.322	43.517	51.70	n.a.	BMB*
2	21.89	n.a.		79.945	40.659	48.30	n.a.	BMB*
总和:				155.266	84.176	100.00	0.000	



序号	保留时间 min		峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	19.17	n.a.		108.436	64.687	95.09	n.a.	BMB
2	21.68	n.a.		6.113	3.338	4.91	n.a.	BMB*
总和:				114.548	68.026	100.00	0.000	

8) (4R,5S,6S)-ethyl 5-formyl-4-(4-methoxyphenyl)-2-phenyl-4,5,6,7-tetrahydrobenzofuran-6-carboxylate (4h)



In a dried glass tube, a mixture of $PtCl_4$ (5 mol%), pyridine *N*-oxide (10 mol%), (2S)-2-[Bis[3,5-bis(trifluoromethyl)phenyl]-[(trimethylsilyl)oxy]methyl]pyrrolidine (**3c**, 20 mol%), TsOH•H_2O (20 mol%), **1h** (55.2 mg, 0.2 mmol) and **2a** (128 mg, 1.0 mmol) was mixed in $PhCH_3$ (2 mL), stirring at 60 °C until the reaction was complete (12 h). The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by column chromatography. **4h** (53.2 mg, 65 %) was obtained as a solid.

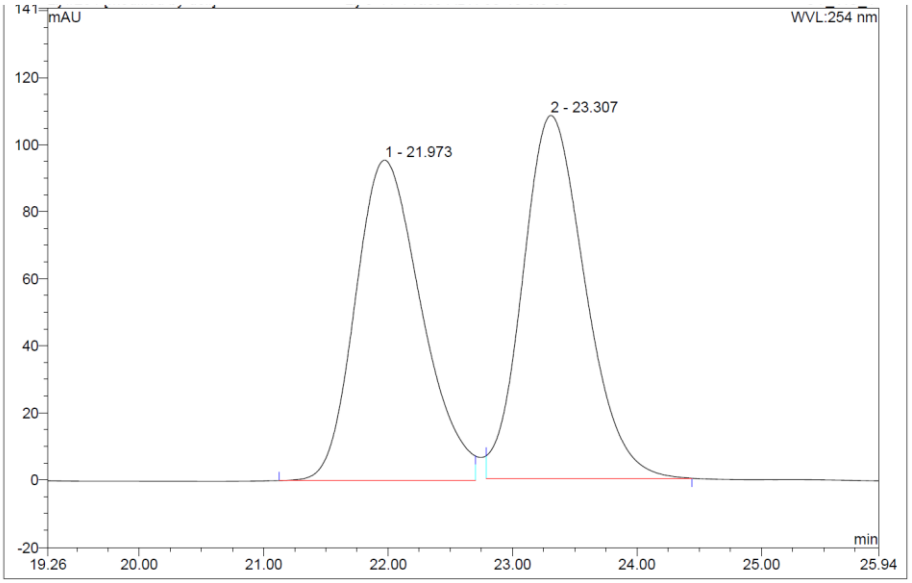
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.71 (d, *J* = 0.5 Hz, 1H), 7.56-7.54 (m, 2H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.23 – 7.18 (m, 1H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.18 (s, 1H), 4.17 – 4.09 (m, 1H), 4.06 – 3.97 (m, 2H), 3.80 (s, 3H), 3.32 – 3.23 (m, 2H), 3.20 – 3.11 (m, 1H), 3.03 (ddd, *J* = 12.0, 1.0, 3.5 Hz, 1H), 1.21 (t, *J* = 7.0 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 203.3, 173.3, 158.9, 153.3, 147.8, 132.9, 130.7, 129.5, 128.6, 127.2, 123.4, 121.4, 114.2, 105.0, 61.2, 56.0, 55.3, 41.1, 40.7, 25.4, 14.0

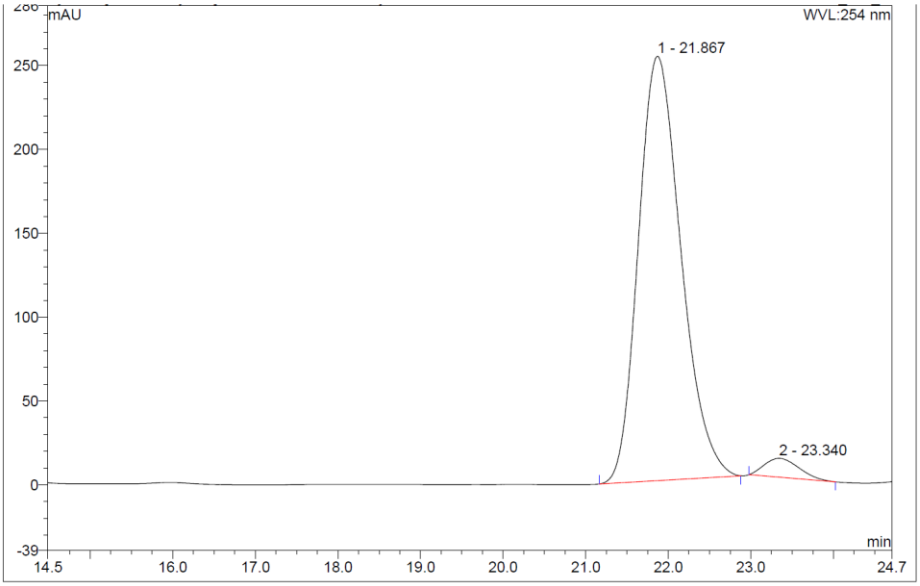
HRMS (ESI, m/z): $[M+H]^+$ calcd.for $C_{25}H_{25}O_5$ 405.1697, found 405.1696

HPLC analysis: 93% ee (Chiralpak AD-H column, hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, UV detection at 254 nm), Rt (major) = 21.87 min; Rt (minor) = 23.34 min

$[\alpha]_D^{20}$= - 10.4 (c = 1.0, $CHCl_3$)

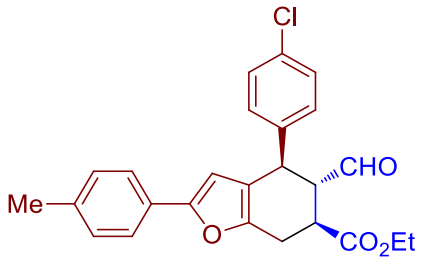


序号	保留时间 min		峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	21.97	n.a.		95.586	58.738	48.29	n.a.	BM *
2	23.31	n.a.		108.277	62.908	51.71	n.a.	MB*
总和:				203.862	121.646	100.00	0.000	



序号	保留时间 min		峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	21.87	n.a.		253.015	151.336	96.54	n.a.	BMB*
2	23.34	n.a.		11.173	5.430	3.46	n.a.	BMB*
总和:				264.188	156.765	100.00	0.000	

9) (4R,5S,6S)-ethyl 4-(4-chlorophenyl)-5-formyl-2-(p-tolyl)-4,5,6,7-tetrahydrobenzofuran-6-carboxylate (4i)



In a dried glass tube, a mixture of $PtCl_4$ (5 mol%), pyridine *N*-oxide (10 mol%), (2S)-2-[Bis[3,5-bis(trifluoromethyl)phenyl]-[(trimethylsilyl)oxy]methyl]pyrrolidine (**3c**, 20 mol%), TsOH•H_2O (20 mol%), **1i** (58.8 mg, 0.2 mmol) and **2a** (128 mg, 1.0 mmol) was mixed in $PhCH_3$ (2 mL), stirring at 60 °C until the reaction was complete (12 h). The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by column chromatography. **4i** (52.4 mg, 62%) was obtained as a solid.

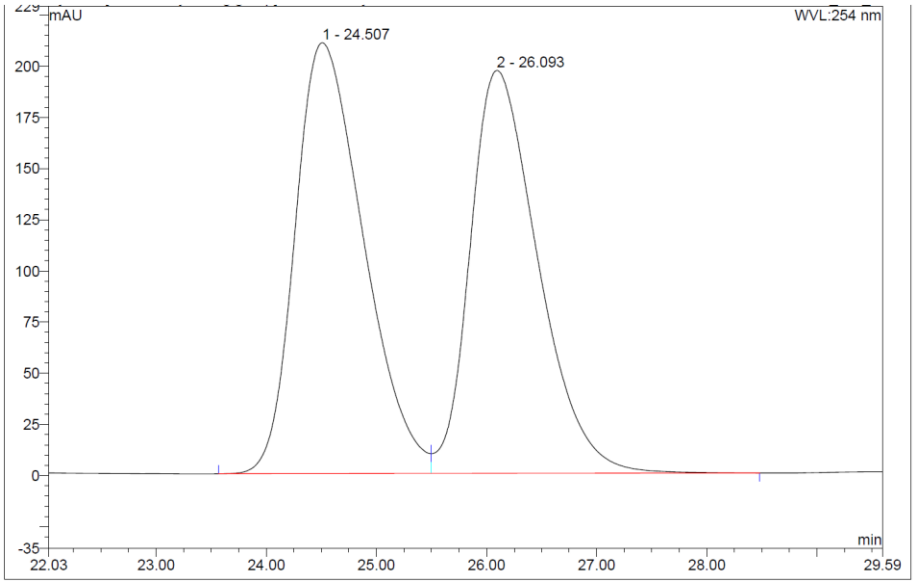
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.71 (d, *J* = 1.0 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.17-7.14 (m, 4H), 6.09 (s, 1H), 4.18 – 4.05 (m, 2H), 3.99 (dq, *J* = 11.0, 7.0 Hz, 1H), 3.35 – 3.20 (m, 2H), 3.19 – 3.10 (m, 1H), 3.04 (ddd, *J* = 11.5, 9.0, 2.5 Hz, 1H), 2.34 (s, 3H), 1.20 (t, *J* = 7.0 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 202.6, 173.1, 153.7, 147.6, 139.7, 137.2, 133.2, 129.9, 129.3, 128.9, 127.9, 123.4, 120.3, 104.0, 61.3, 55.7, 41.0, 40.7, 25.2, 21.2, 14.0

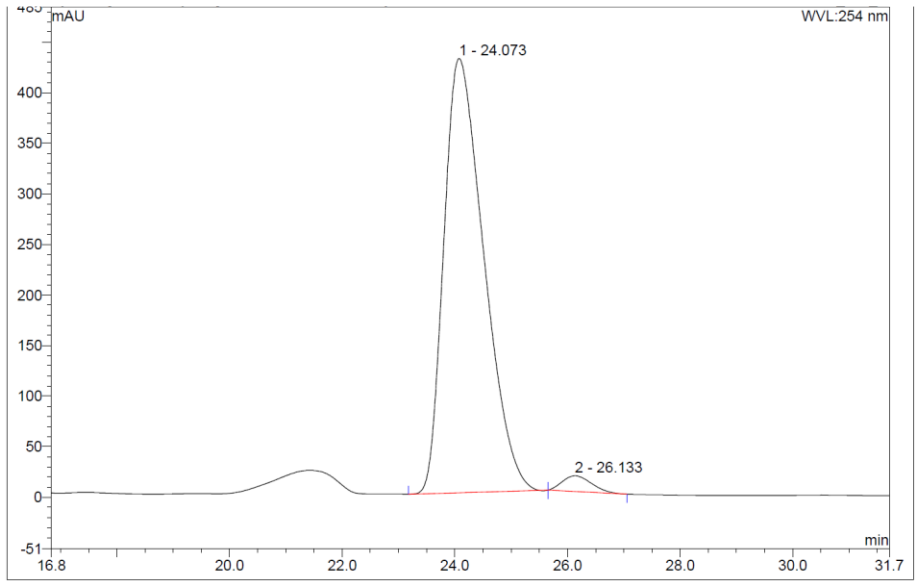
HRMS: calcd.for $C_{25}H_{23}ClO_4$ 422.1285, found: 422.1292

HPLC analysis: 95% ee (Chiralpak AD-H column, hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, UV detection at 254 nm), Rt (major) = 24.07 min; Rt (minor) = 26.13 min

$[\alpha]_D^{20}$= - 20.0 (c = 0.60, $CHCl_3$)

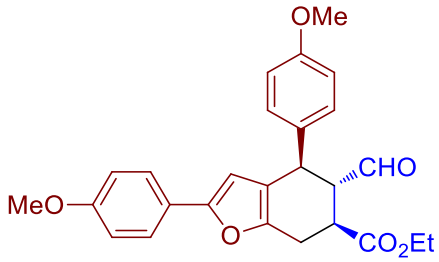


序号	保留时间		峰名称	峰高	峰面积	相对峰面积	样品量	类型
	min			mAU	mAU*min	%		
1	24.51	n.a.		210.547	151.508	51.84	n.a.	BM
2	26.09	n.a.		196.927	140.777	48.16	n.a.	MB
总和:				407.473	292.285	100.00	0.000	



序号	保留时间		峰名称	峰高	峰面积	相对峰面积	样品量	类型
	min			mAU	mAU*min	%		
1	24.07	n.a.		429.388	353.064	97.42	n.a.	BMb*
2	26.13	n.a.		15.508	9.338	2.58	n.a.	bMB*
总和:				444.896	362.402	100.00	0.000	

10) (4R,5S,6S)-ethyl 5-formyl-2,4-bis(4-methoxyphenyl)-4,5,6,7-tetrahydrobenzofuran-6-carboxylate (4j)



In a dried glass tube, a mixture of $PtCl_4$ (5 mol%), pyridine *N*-oxide (10 mol%), (2S)-2-[Bis[3,5-bis(trifluoromethyl)phenyl]-[(trimethylsilyl)oxy]methyl]pyrrolidine (**3c**, 20 mol%), TsOH•H_2O (20 mol%), **1j** (61.2 mg, 0.2 mmol) and **2a** (128 mg, 1.0 mmol) was mixed in $PhCH_3$ (2 mL), stirring at 60 °C until the reaction was complete (12 h). The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by column chromatography. **4j** (48.3 mg, 56%) was obtained as a solid.

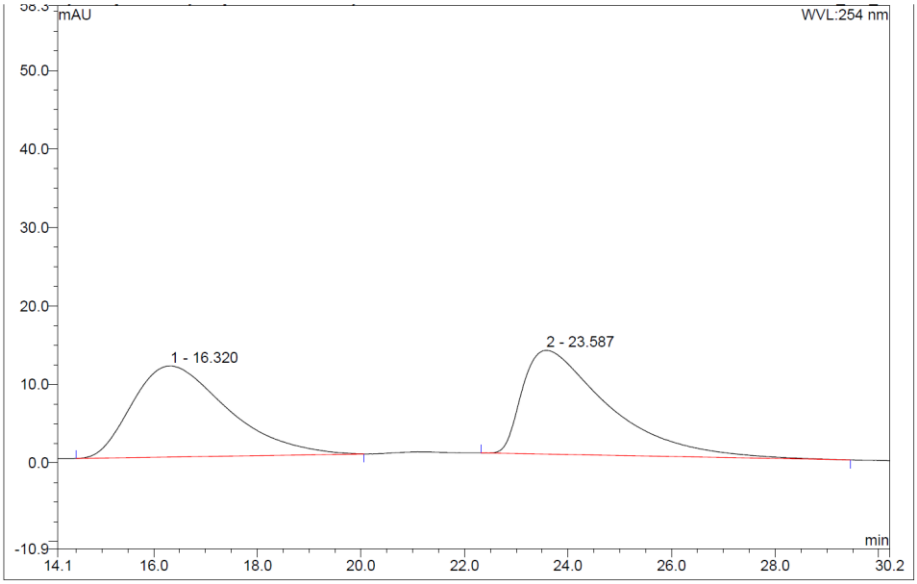
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.48 (d, *J* = 9.0 Hz, 2H), 7.14 (d, *J* = 9.0 Hz, 2H), 6.92 – 6.78 (m, 4H), 6.04 (s, 1H), 4.11 (dq, *J* = 11.0, 7.0 Hz, 1H), 4.02 (dq, *J* = 11.0, 7.0 Hz, 2H), 3.81 (s, 3H), 3.81 (s, 3H), 3.32 – 3.23 (m, 2H), 3.19 – 3.12 (m, 1H), 3.02 (ddd, *J* = 16.0, 8.5, 6.0 Hz, 1H), 1.21 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 203.4, 173.4, 158.9, 158.8, 153.3, 147.0, 133.0, 129.5, 124.88, 123.8, 121.2, 114.1, 114.1, 103.4, 61.2, 56.0, 55.3, 41.1, 40.8, 25.4, 14.0

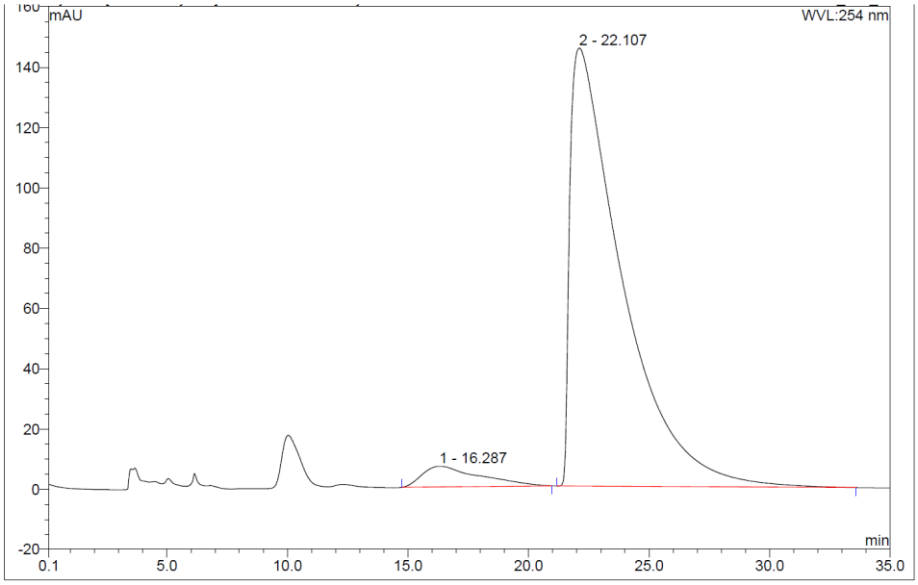
MS (EI) m/z (%): 434 (M^+, 3.36); 135 (100); **HRMS**: calcd.for $C_{26}H_{26}O_6$ 434.1729, found 434.1730

HPLC analysis: 90% ee (Chiralpak AS-H column, hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, UV detection at 254 nm), Rt (minor) = 16.29 min; Rt (major) = 22.11 min

$[\alpha]_D^{20}$= -10.7 (c = 0.60, $CHCl_3$)

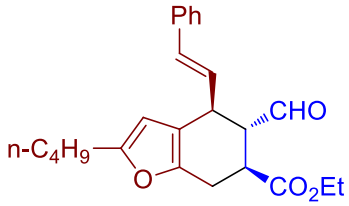


序号	保留时间 min		峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	16.32	n.a.		11.609	24.806	49.46	n.a.	BMB*
2	23.59	n.a.		13.242	25.352	50.54	n.a.	BMB*
总和:				24.851	50.158	100.00	0.000	



序号	保留时间 min		峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	16.29	n.a.		6.860	18.863	4.95	n.a.	BMB*
2	22.11	n.a.		145.311	362.504	95.05	n.a.	BMB*
总和:				152.171	381.368	100.00	0.000	

11) (4S,5S,6S)-ethyl 2-butyl-5-formyl-4-((E)-styryl)-4,5,6,7-tetrahydrobenzofuran-6-carboxylate (4k)



In a dried glass tube, a mixture of $PtCl_4$ (5 mol%), pyridine *N*-oxide (10 mol%), (2S)-2-[Bis[3,5-bis(trifluoromethyl)phenyl]-[(trimethylsilyl)oxy]methyl]pyrrolidine (**3c**, 20 mol%), TsOH•H_2O (20 mol%), **1k** (50.4 mg, 0.2 mmol) and **2a** (128 mg, 1.0 mmol) was mixed in $PhCH_3$ (2 mL), stirring at 60 °C until the reaction was complete (12 h). The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by column chromatography. **4k** (35.1 mg, 46%) was obtained as a solid.

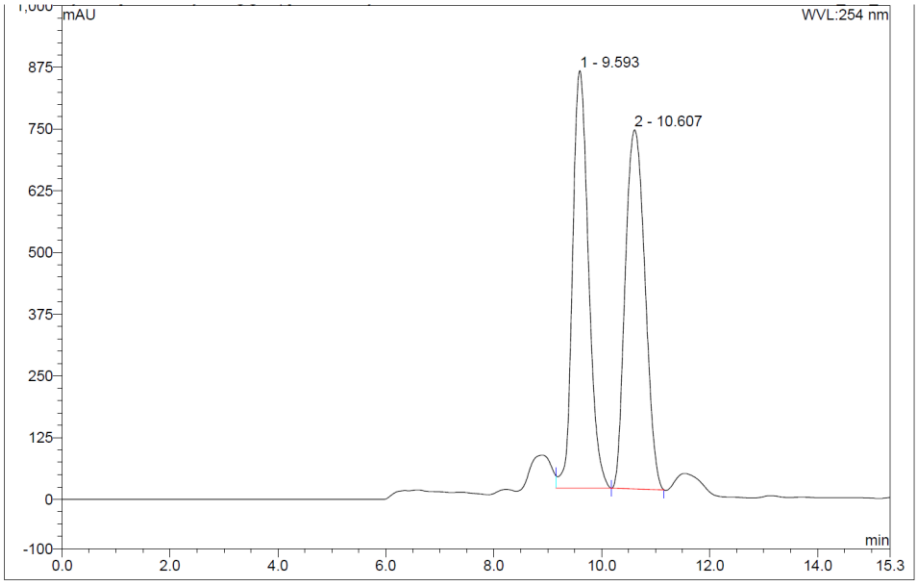
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.87 (d, *J* = 1.5 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.31 (dd, *J* = 8.0, 7.0 Hz, 2H), 7.25 – 7.21 (m, 1H), 6.50 (d, *J* = 15.5 Hz, 1H), 6.15 (dd, *J* = 15.5, 8.5 Hz, 1H), 5.80 (s, 1H), 4.22 – 3.99 (m, 2H), 3.60 (t, *J* = 9.0 Hz, 1H), 3.18 (td, *J* = 1.0, 6.0 Hz, 1H), 3.10 – 3.04 (m, 1H), 2.98 (dd, *J* = 16.5, 6.0 Hz, 1H), 2.84 (ddd, *J* = 16.5, 9.5, 2.5 Hz, 1H), 2.55 (t, *J* = 7.5 Hz, 2H), 1.62 – 1.52 (m, 2H), 1.36 (dq, *J* = 14.5, 7.5 Hz, 2H), 1.23 (t, *J* = 7.0 Hz, 3H), 0.91 (t, *J* = 7.5 Hz, 3H)

^{13}C NMR (126 MHz, $CDCl_3$) δ 203.1, 173.6, 156.0, 145.5, 136. 6, 132.5, 129.6, 128.6, 127.7, 126.4, 118.0, 104.6, 61.2, 53.5, 40.5, 39.0, 30.2, 27.8, 25.1, 22.3, 14.1, 13.8

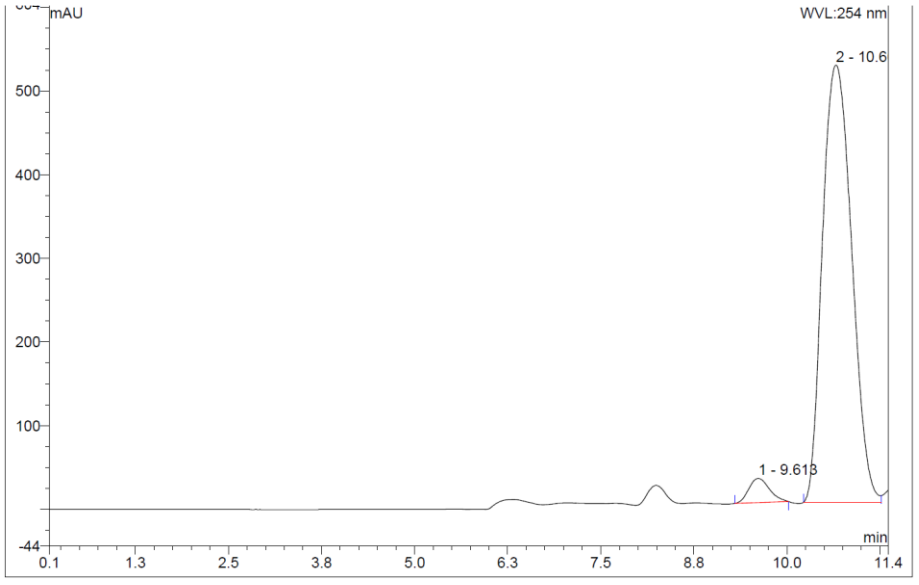
MS (EI) m/z (%): 380 (M^+, 70.93); 289 (100); **HRMS**: calcd.for $C_{24}H_{28}O_4$ 380.1988, found: 380.1984.

HPLC analysis: 92% ee (Chiralpak AD-H column, hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, UV detection at 254 nm), Rt (minor) = 9.61 min; Rt (major) = 10.66 min

$[\alpha]_D^{20}$= -15.6 (c = 0.50, $CHCl_3$)

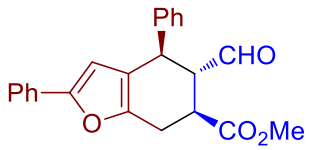


序号	保留时间 min		峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	9.59	n.a.		845.987	289.717	48.47	n.a.	Mb*
2	10.61	n.a.		727.405	307.982	51.53	n.a.	bMB*
总和:				1573.392	597.700	100.00	0.000	



序号	保留时间 min		峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	9.61	n.a.		28.970	9.303	3.76	n.a.	BMB*
2	10.66	n.a.		522.724	238.191	96.24	n.a.	BM *
总和:				551.694	247.493	100.00	0.000	

12) (4R,5S,6S)-methyl 5-formyl-2,4-diphenyl-4,5,6,7-tetrahydrobenzofuran-6-carboxylate (4l)



In a dried glass tube, a mixture of $PtCl_4$ (5 mol%), pyridine *N*-oxide (10 mol%), (2S)-2-[Bis[3,5-bis(trifluoromethyl)phenyl]-[(trimethylsilyl)oxy]methyl]pyrrolidine (**3c**, 20 mol%), $TsOH•H_2O$ (20 mol%), **1a** (49.2 mg, 0.2 mmol) and **2b** (114 mg, 1.0 mmol) was mixed in $PhCH_3$ (2 mL), stirring at 60 °C until the reaction was complete (24 h). The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by column chromatography. **4l** (34.7 mg, 48%) was obtained as a solid.

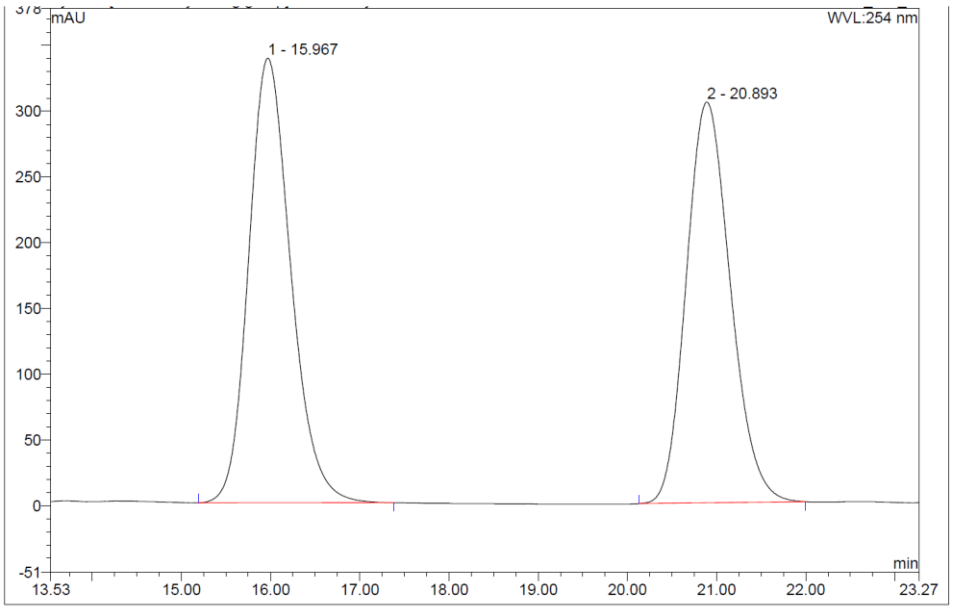
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.56 (dd, *J* = 8.4, 1.1 Hz, 2H), 7.38 – 7.30 (m, 4H), 7.29 (dt, *J* = 9.5, 4.3 Hz, 1H), 7.23 (dd, *J* = 5.1, 3.5 Hz, 3H), 6.19 (s, 1H), 4.10 (dd, *J* = 6.8, 2.2 Hz, 1H), 3.58 (s, 3H), 3.39 – 3.26 (m, 2H), 3.16 (dd, *J* = 17.4, 4.9 Hz, 1H), 3.10 – 3.00 (m, 1H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 203.0, 173.8, 153.4, 147.9, 141.0, 130.7, 128.8, 128.6, 128.5, 127.4, 127.3, 123.5, 120.9, 105.0, 55.8, 52.2, 41.3, 40.6, 25.2

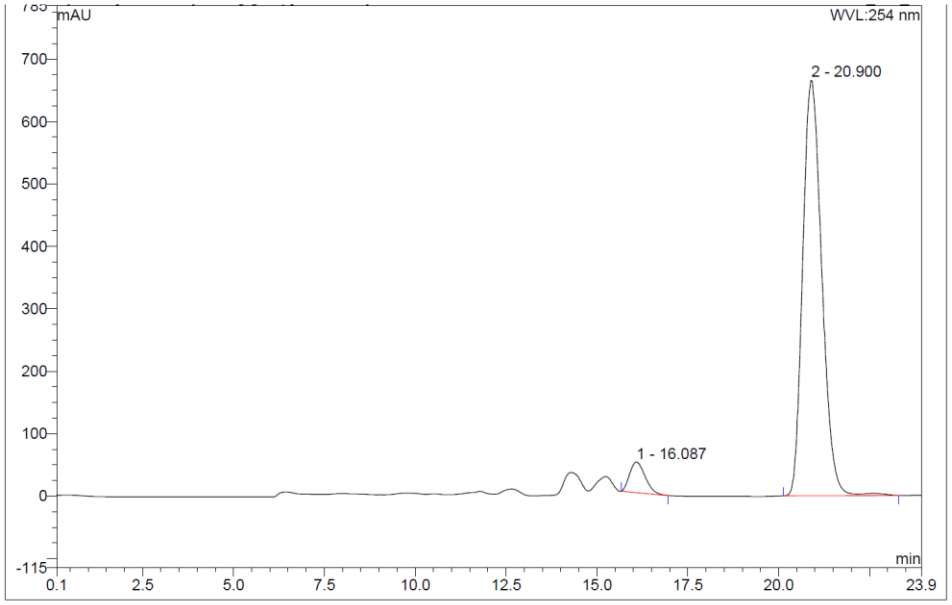
MS(EI): m/z (%): 360 (M^+, 57.69); 105 (100); **HRMS**: calcd.for $C_{23}H_{20}O_4$ 360.1362, found 360.1359.

HPLC analysis: 90% ee (Chiralpak AD-H column, hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, UV detection at 254 nm), Rt (minor) = 16.09 min; Rt (major) = 20.9 min

$[\alpha]_D^{20}$= -4.2 (c = 1.0, $CHCl_3$)



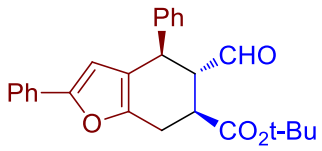
序号	保留时间 min		峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	15.97	n.a.		338.187	185.318	51.43	n.a.	BMB*
2	20.89	n.a.		304.893	175.012	48.57	n.a.	BMB*
总和:				643.080	360.331	100.00	0.000	



序号	保留时间 min		峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	16.09	n.a.		48.836	24.162	5.62	n.a.	BMB*
2	20.90	n.a.		665.712	405.659	94.38	n.a.	BMB*
总和:				714.548	429.821	100.00	0.000	

13) (4R,5S,6S)-tert-butyl

5-formyl-2,4-diphenyl-4,5,6,7-tetrahydrobenzofuran-6-carboxylate (4m)



In a dried glass tube, a mixture of $PtCl_4$ (5 mol%), pyridine *N*-oxide (10 mol%), (2S)-2-[Bis[3,5-bis(trifluoromethyl)phenyl]-[(trimethylsilyl)oxy]methyl]pyrrolidine (**3c**, 20 mol%), $TsOH•H_2O$ (20 mol%), **1a** (49.2 mg, 0.2 mmol) and **2c** (156 mg, 1.0 mmol) was mixed in $PhCH_3$ (2 mL), stirring at 60 °C until the reaction was complete (24 h). The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by column chromatography. **4m** (42.1 mg, 52%) was obtained as a solid.

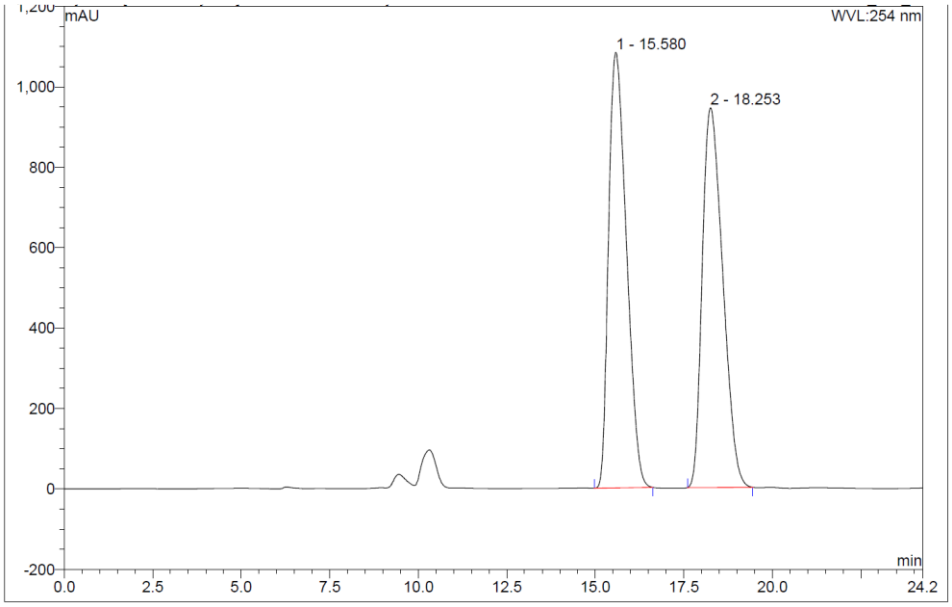
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.60 – 7.48 (m, 2H), 7.37 – 7.27 (m, 5H), 7.24 – 7.16 (m, 3H), 6.13 (s, 1H), 4.07 – 3.96 (m, 1H), 3.28 – 3.14 (m, 3H), 3.05 – 2.92 (m, 1H), 1.43 (s, 9H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 203.2, 172.5, 153.2, 148.0, 141.1, 130.7, 128.9, 128.6, 128.6, 127.5, 127.2, 123.4, 121.4, 105.0, 81.8, 56.0, 42.7, 41.9, 27.9, 26.0

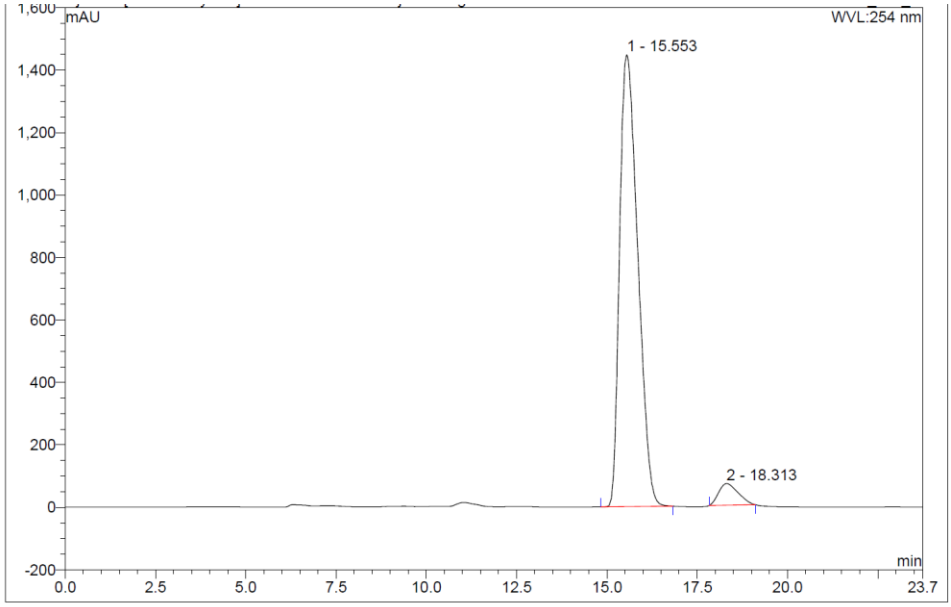
MS(EI): m/z (%): 402 (M^+, 67.74); 317 (100); **HRMS**: calcd.for $C_{26}H_{26}O_4$ 402.1831, found 402.1826

HPLC analysis: 90% ee (Chiralpak AD-H column, hexane/*i*-PrOH = 95/5, flow rate 0.5 mL/min, UV detection at 254 nm), Rt (major) = 15.55 min; Rt (minor) = 18.31 min

$[\alpha]_D^{20}$= 11.0 (c = 0.50, $CHCl_3$)

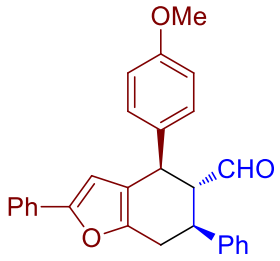


序号	保留时间 min		峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	15.58	n.a.		1082.653	632.055	49.96	n.a.	BMB*
2	18.25	n.a.		944.148	633.113	50.04	n.a.	BMB*
总和:				2026.801	1265.167	100.00	0.000	



序号	保留时间 min		峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	15.55	n.a.		1446.754	841.811	95.13	n.a.	BMB*
2	18.31	n.a.		68.954	43.129	4.87	n.a.	BMB*
总和:				1515.708	884.940	100.00	0.000	

14) (4R,5R,6S)-4-(4-methoxyphenyl)-2,6-diphenyl-4,5,6,7-tetrahydrobenzofuran-5-carbaldehyde (4n)



In a dried glass tube, a mixture of $PtCl_4$ (5 mol%), pyridine *N*-oxide (10 mol%), (2S)-2-[Bis[3,5-bis(trifluoromethyl)phenyl]-[(trimethylsilyl)oxy]methyl]pyrrolidine (**3c**, 20 mol%), TsOH•H_2O (20 mol%), **1h** (110.4 mg, 0.4 mmol) and **2d** (26.4 mg, 0.2 mmol) was mixed in $PhCH_3$ (2 mL), stirring at 60 °C until the reaction was complete (24 h). The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by column chromatography. **4n** (45.8 mg, 56%) was obtained as a solid.

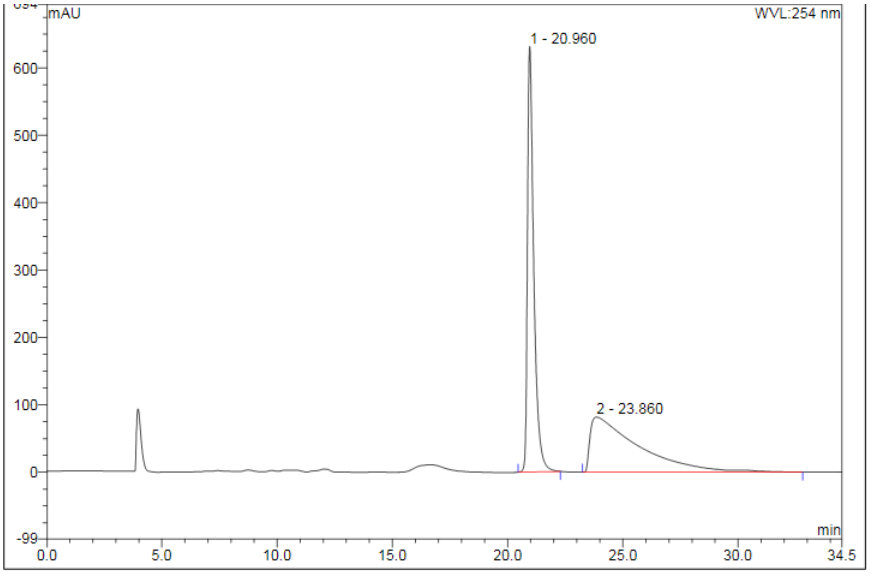
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.37 (d, *J*= 3.4 Hz, 1H), 7.64 –7.52 (m, 2H), 7.36 –7.28 (m, 6H), 7.27 –7.22 (m, 1H), 7.22 –7.18 (m, 1H), 7.13 (d, *J*= 8.7 Hz, 2H), 6.84 (d, *J*= 8.7 Hz, 2H), 6.21 (s, 1H), 4.27 (d, *J*= 10.0 Hz, 1H), 3.79 (s, 3H), 3.45 (td, *J*= 11.3, 5.8 Hz, 1H), 3.21 (ddd, *J*= 11.6, 10.1, 3.4 Hz, 1H), 3.17 –2.94 (m, 2H).

^{13}C NMR (125MHz, $CDCl_3$) δ 203.7, 158.6, 152.8, 149.1, 141.2, 133.6, 130.9, 129.6, 129.0, 128.6, 127.7, 127.4, 127.1, 123.4, 121.7, 114.0, 105.4, 60.8, 55.2, 43.8, 41.0, 32.2

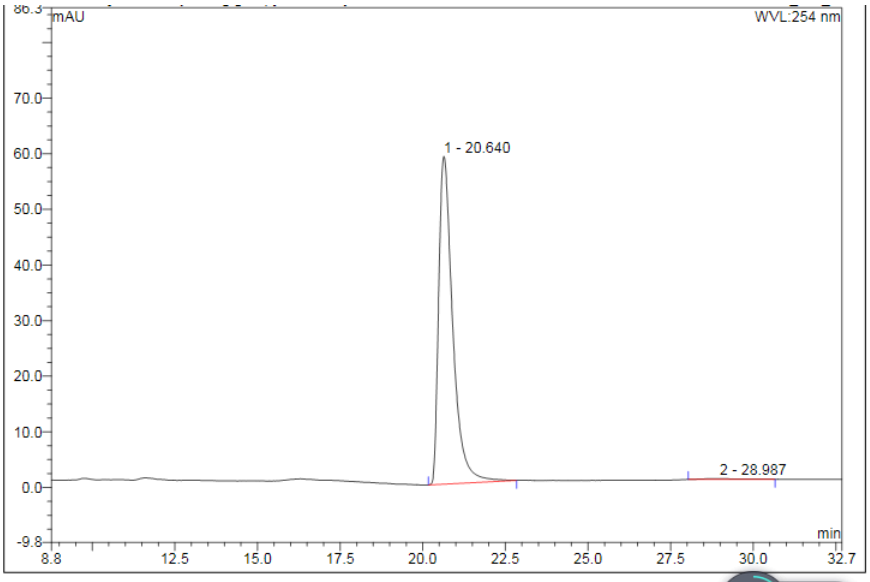
HRMS (ESI, m/z): $[M+H]^+$ calcd.for $C_{28}H_{25}O_3$ 409.1798, found 409.1796

HPLC analysis: 99% ee (Chiralpak OD-H column, hexane/*i*-PrOH = 95/5, flow rate 0.8 mL/min, UV detection at 254 nm), Rt (major) = 20.64 min; Rt (minor) = 28.99 min

$[\alpha]_D^{20}$= -20.6 (c = 1.0, $CHCl_3$)

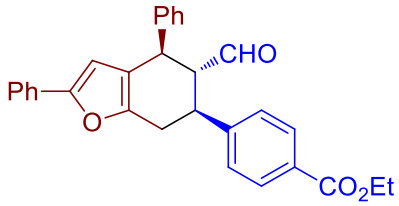


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.96	n.a.	631.829	201.804	50.41	n.a.	BMB*
2	23.86	n.a.	81.633	198.556	49.59	n.a.	BMB*
Total:			713.462	400.360	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	20.64	n.a.	58.962	29.034	99.44	n.a.	BMB*
2	28.99	n.a.	0.123	0.163	0.56	n.a.	BMB*
Total:			59.085	29.197	100.00	0.000	

15) ethyl 4-((4R,5R,6S)-5-formyl-2,4-diphenyl-4,5,6,7-tetrahydrobenzofuran-6-yl)benzoate (4o)



In a dried glass tube, a mixture of $PtCl_4$ (5 mol%), pyridine *N*-oxide (10 mol%), (2S)-2-[Bis[3,5-bis(trifluoromethyl)phenyl]-[(trimethylsilyl)oxy]methyl]pyrrolidine (**3c**, 20 mol%), TsOH•H_2O (20 mol%), **1a** (98.4 mg, 0.4 mmol) and **2e** (40.8 mg, 0.2 mmol) was mixed in $PhCH_3$ (2 mL), stirring at 60 °C until the reaction was complete (24 h). The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by column chromatography. **4o** (48.7 mg, 54%) was obtained as a solid.

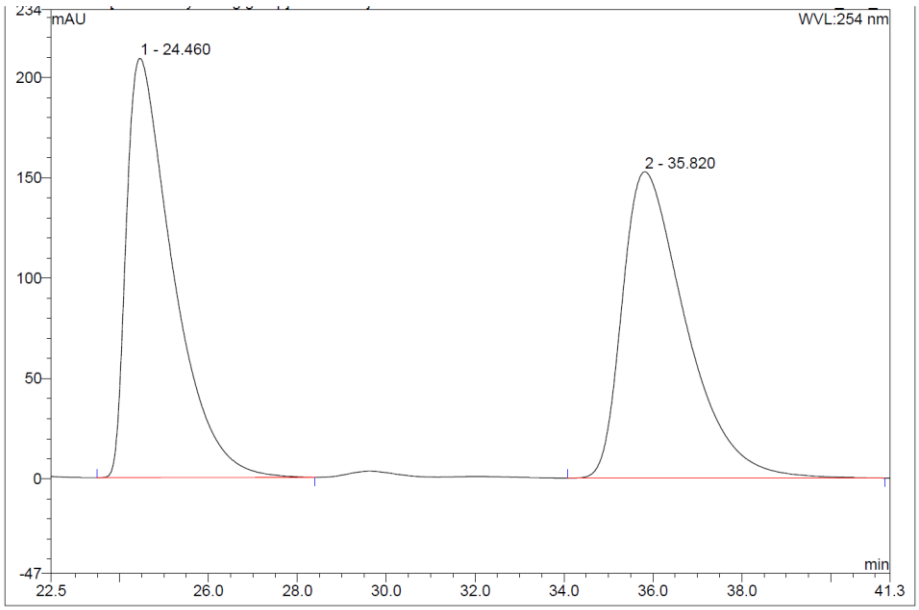
^{1}H NMR (500 MHz, $CDCl_3$) δ) δ 9.38 (d, *J*= 3.1 Hz, 1H), 8.01 (d, *J*= 8.3 Hz, 2H), 7.57 (d, *J*= 7.2 Hz, 2H), 7.39-7.34(m, 3H), 7.33 –7.26 (m, 4H), 7.24 –7.17 (m, 3H), 6.20 (s, 1H), 4.37 (q, *J*= 7.2 Hz, 2H), 4.30 (d, *J*= 10.0 Hz, 1H), 3.54 (td, *J*= 11.0, 6.1 Hz, 1H), 3.29 (ddd, *J*= 11.6, 10.1, 3.1 Hz, 1H), 3.19 –3.00 (m, 2H), 1.38 (t, *J*= 7.1 Hz, 3H)

^{13}C NMR (125MHz, $CDCl_3$) δ 203.1, 166.2, 153.0, 148.7, 146.4, 141.4, 130.8, 130.3, 129.7, 128.8, 128.6, 128.6, 127.7, 127.3, 127.2, 123.4, 121.4, 105.2, 61.0, 60.3, 43.6, 42.1, 31.9, 14.3.

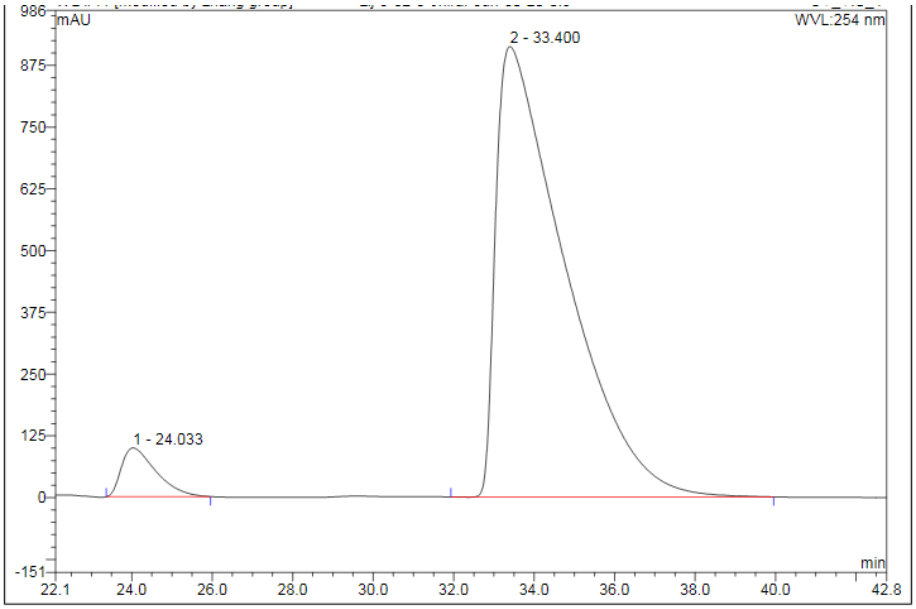
MS(EI): m/z (%): 450 (M^+, 45.19); 246 (100); **HRMS**: calcd.for $C_{30}H_{26}O_4$ 450.1833, found 450.1831

HPLC analysis: 90% ee (Chiralpak OD-H column, hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, UV detection at 254 nm), Rt (minor) = 24.03 min; Rt (major) = 33.40 min

$[\alpha]_D^{20}$= -24.3 (c = 0.60, $CHCl_3$)

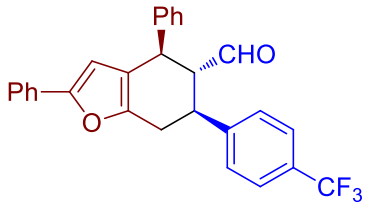


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	24.46	n.a.	208.992	252.592	49.98	n.a.	BMB*
2	35.82	n.a.	152.677	252.800	50.02	n.a.	BMB*
Total:			361.669	505.392	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	24.03	n.a.	98.651	98.351	5.13	n.a.	BMB*
2	33.40	n.a.	911.489	1818.195	94.87	n.a.	BMB*
Total:			1010.141	1916.546	100.00	0.000	

16) (4R,5R,6S)-2,4-diphenyl-6-(4-(trifluoromethyl)phenyl)-4,5,6,7-tetrahydroben zofuran-5-carbaldehyde (4p)



In a dried glass tube, a mixture of $PtCl_4$ (5 mol%), pyridine *N*-oxide (10 mol%), (2S)-2-[Bis[3,5-bis(trifluoromethyl)phenyl]-[(trimethylsilyl)oxy]methyl]pyrrolidine (**3c**, 20 mol%), $TsOH•H_2O$ (20 mol%), **1a** (98.4 mg, 0.4 mmol) and **2f** (40.0 mg, 0.2 mmol) was mixed in $PhCH_3$ (2 mL), stirring at 60 °C until the reaction was complete (24 h). The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by column chromatography. **4p** (44.8 mg, 50%) was obtained as a solid.

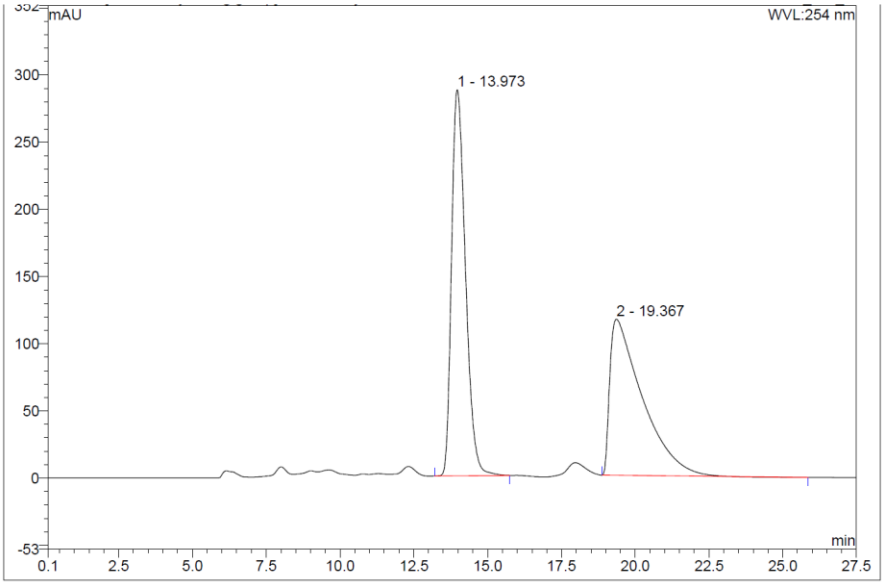
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (d, *J* = 3.2 Hz, 1H), 7.61 – 7.54 (m, 4H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.25 (m, 5H), 7.24 – 7.20 (m, 3H), 6.21 (s, 1H), 4.30 (d, *J* = 10.1 Hz, 1H), 3.56 (td, *J* = 11.3, 5.7 Hz, 1H), 3.30 (ddd, *J* = 11.5, 10.1, 3.1 Hz, 1H), 3.18 – 3.11 (m, 1H), 3.06 (ddd, *J* = 16.7, 11.2, 2.9 Hz, 1H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.1, 153.1, 148.6, 145.5, 141.2, 130.7, 129.7 (q, *J* = 32.6 Hz), 128.8, 128.7, 128.5, 128.1, 127.4, 127.2, 126.0 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 270.0 Hz), 123.5, 121.4, 105.2, 60.2, 43.2, 42.2, 31.9

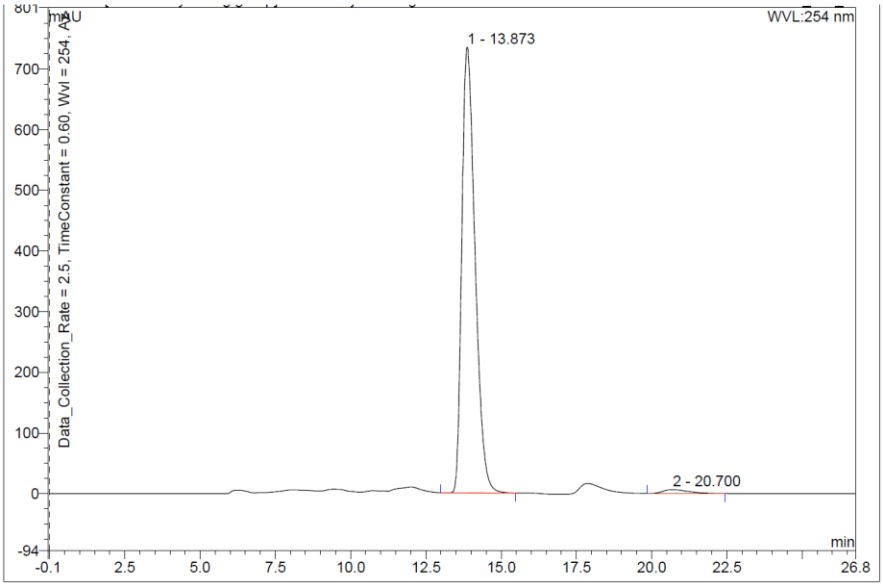
MS(EI): m/z (%): 446 (M^+, 77.54); 246 (100); **HRMS**: calcd.for $C_{28}H_{21}F_3O_2$ 446.1494, found 446.1497

HPLC analysis: 97% ee (Chiralpak OD-H column, hexane/*i*-PrOH = 80/20, flow rate 0.5 mL/min, UV detection at 254 nm), Rt (major) = 13.87 min; Rt (minor) = 20.70 min

$[\alpha]_D^{20}$= -18.7 (c = 0.6, $CHCl_3$)

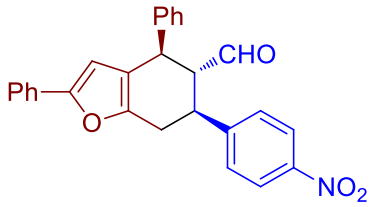


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.97	n.a.	287.439	157.212	51.47	n.a.	BMB*
2	19.37	n.a.	116.160	148.224	48.53	n.a.	BMB*
Total:			403.599	305.436	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	13.87	n.a.	734.694	374.152	98.35	n.a.	BMB*
2	20.70	n.a.	6.333	6.288	1.65	n.a.	BMB*
Total:			741.026	380.439	100.00	0.000	

17) (4R,5R,6S)-6-(4-nitrophenyl)-2,4-diphenyl-4,5,6,7-tetrahydrobenzofuran-5-carbaldehyde (4q)



In a dried glass tube, a mixture of $PtCl_4$ (5 mol%), pyridine *N*-oxide (10 mol%), (2S)-2-[Bis[3,5-bis(trifluoromethyl)phenyl]-[(trimethylsilyl)oxy]methyl]pyrrolidine (**3c**, 20 mol%), TsOH•H_2O (20 mol%), **1a** (98.4 mg, 0.4 mmol) and **2g** (35.4 mg, 0.2 mmol) was mixed in $PhCH_3$ (2 mL), stirring at 60 °C until the reaction was complete (24 h). The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by column chromatography. **4q** (47.6 mg, 56%) was obtained as a solid.

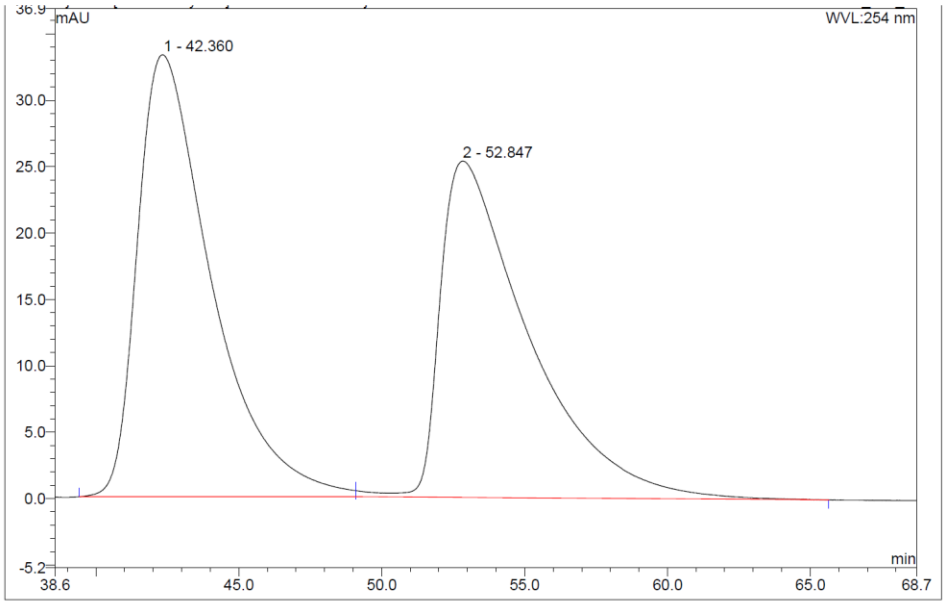
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.42 (d, *J* = 3.0 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.36 – 7.29 (m, 4H), 7.28 – 7.19 (m, 4H), 6.21 (s, 1H), 4.28 (d, *J* = 10.0 Hz, 1H), 3.63 (td, *J* = 11.5, 5.5 Hz, 1H), 3.37 – 3.26 (m, 1H), 3.16 (dd, *J* = 16.5, 5.0 Hz, 1H), 3.05 (ddd, *J* = 16.5, 11.0, 3.0 Hz, 1H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 202.8, 153.2, 149.1, 148.2, 147.2, 140.9, 130.6, 128.9, 128.7, 128.6, 128.5, 127.5, 127.3, 124.3, 123.5, 121.4, 105.1, 60.1, 43.0, 42.4, 31.6

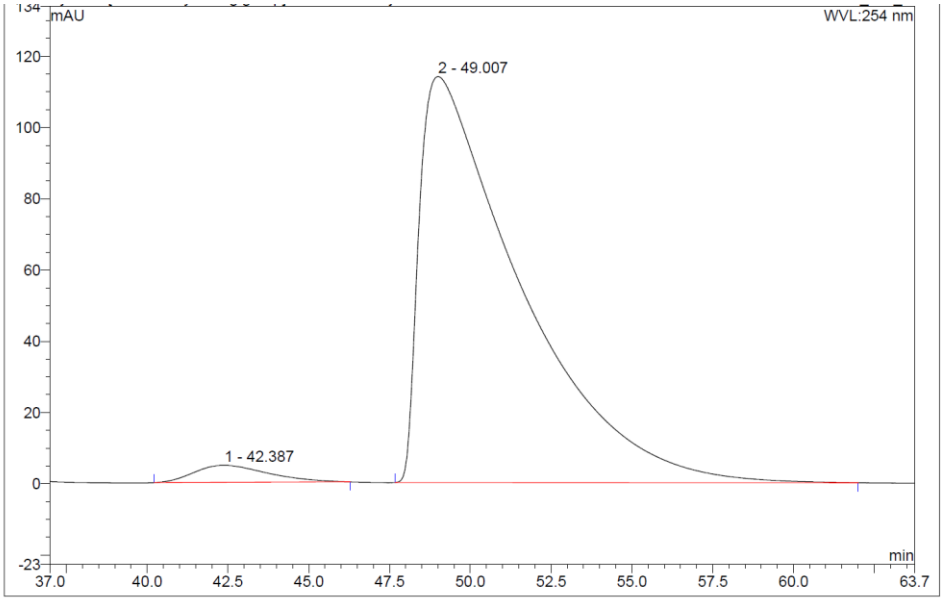
HRMS (ESI, m/z): $[M+H]^+$ calcd.for $C_{27}H_{22}NO_4$ 424.1543, found 424.1544.

HPLC analysis: 94% ee (Chiralpak OD-H column, hexane/*i*-PrOH = 80/20, flow rate 0.8 mL/min, UV detection at 254 nm), Rt (minor) = 42.39 min; Rt (major) = 49.01 min

$[\alpha]_D^{20}$= -50.3 (c = 1.0, $CHCl_3$)

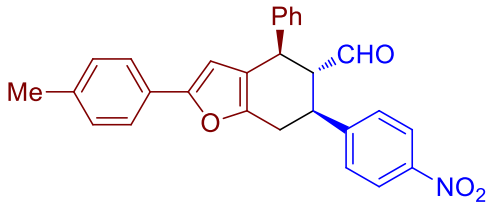


序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	42.36	n.a.	33.280	99.889	52.31	n.a.	BM *
2	52.85	n.a.	25.338	91.063	47.69	n.a.	MB*
总和:			58.618	190.952	100.00	0.000	



序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	42.39	n.a.	4.794	12.613	2.96	n.a.	BMB*
2	49.01	n.a.	113.979	413.241	97.04	n.a.	BMB*
总和:			118.772	425.854	100.00	0.000	

18) (4R,5R,6S)-6-(4-nitrophenyl)-4-phenyl-2-(p-tolyl)-4,5,6,7-tetrahydrobenzofuran-5-carbaldehyde (4r)



In a dried glass tube, a mixture of $PtCl_4$ (5 mol%), pyridine *N*-oxide (10 mol%), (2S)-2-[Bis[3,5-bis(trifluoromethyl)phenyl]-[(trimethylsilyl)oxy]methyl]pyrrolidine (**3c**, 20 mol%), TsOH•H_2O (20 mol%), **1b** (104.0 mg, 0.4 mmol) and **2g** (35.4 mg, 0.2 mmol) was mixed in $PhCH_3$ (2 mL), stirring at 60 °C until the reaction was complete (24 h). The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by column chromatography. **4r** (50.8 mg, 58%) was obtained as a solid.

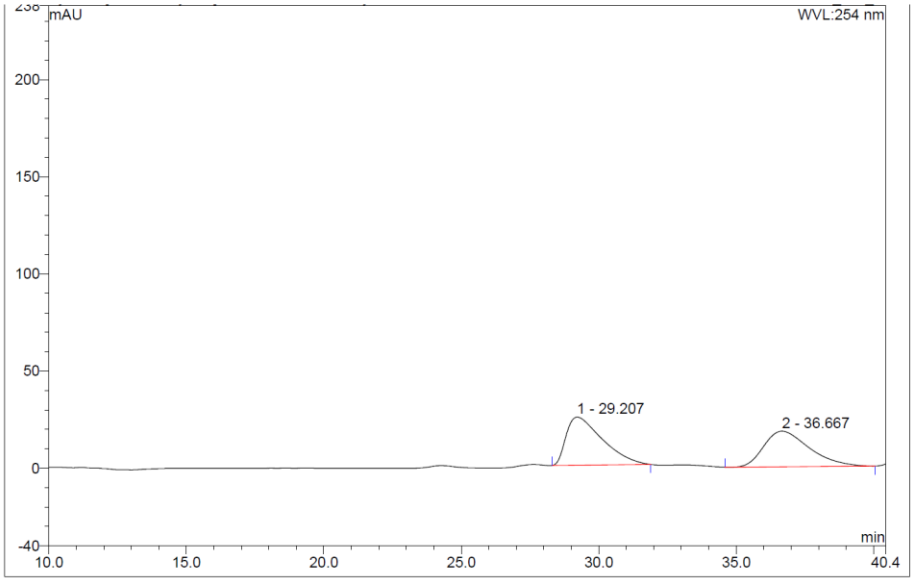
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.41 (d, *J* = 3.0 Hz, 1H), 8.18 (d, *J* = 8.8 Hz, 2H), 7.46 (dd, *J* = 8.4, 1.5 Hz, 4H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.29 – 7.26 (m, 1H), 7.24 – 7.20 (m, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 6.15 (s, 1H), 4.27 (d, *J* = 9.9 Hz, 1H), 3.62 (td, *J* = 11.3, 5.6 Hz, 1H), 3.31 (ddd, *J* = 11.4, 10.0, 3.0 Hz, 1H), 3.18 – 3.11 (m, 1H), 3.04 (ddd, *J* = 16.7, 11.1, 2.9 Hz, 1H), 2.33 (s, 3H)

^{13}C NMR (126 MHz, $CDCl_3$) δ 202.9, 153.4, 149.2, 147.7, 147.1, 141.0, 137.2, 129.4, 128.9, 128.6, 128.5, 128.0, 127.5, 124.2, 123.4, 121.3, 104.4, 60.1, 43.0, 42.4, 31.6, 21.2

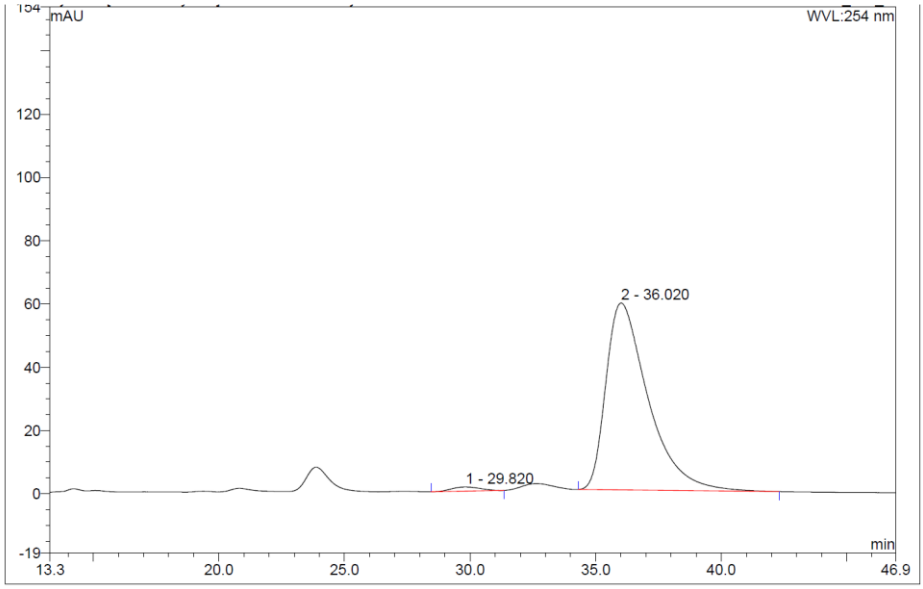
MS(EI): m/z (%): 437 (M^+, 48.98); 260 (100), **HRMS**: calcd.for $C_{28}H_{23}NO_4$ 437.1627, found 437.1629.

HPLC analysis: 97% ee (Chiralpak OD-3 column, hexane/*i*-PrOH = 80/20, flow rate 0.8 mL/min, UV detection at 254 nm), Rt (minor) = 29.82 min; Rt (major) = 36.02 min

$[\alpha]_D^{20}$= -19.0 (c = 1.0, $CHCl_3$)

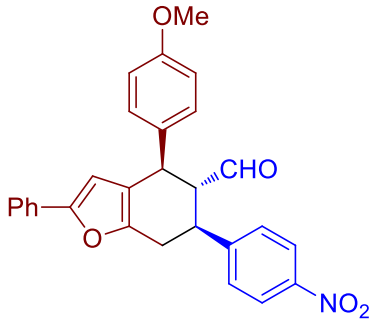


序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	29.21	n.a.	24.735	37.767	51.80	n.a.	BMB*
2	36.67	n.a.	18.345	35.145	48.20	n.a.	BMB*
总和:			43.079	72.912	100.00	0.000	



序号	保留时间 min	峰名称	峰高 mAU	峰面积 mAU*min	相对峰面积 %	样品量	类型
1	29.82	n.a.	1.339	1.760	1.50	n.a.	BMB*
2	36.02	n.a.	59.096	115.171	98.50	n.a.	BMB*
总和:			60.436	116.931	100.00	0.000	

19) (4R,5R,6S)-4-(4-methoxyphenyl)-6-(4-nitrophenyl)-2-phenyl-4,5,6,7-tetrahydr obenzofuran-5-carbaldehyde (4s)



In a dried glass tube, a mixture of $PtCl_4$ (5 mol%), pyridine *N*-oxide (10 mol%), (2S)-2-[Bis[3,5-bis(trifluoromethyl)phenyl]-[(trimethylsilyl)oxy]methyl]pyrrolidine (**3c**, 20 mol%), TsOH•H_2O (20 mol%), **1h** (110.4 mg, 0.4 mmol) and **2g** (35.4 mg, 0.2 mmol) was mixed in $PhCH_3$ (2 mL), stirring at 60 °C until the reaction was complete (24 h). The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by column chromatography. **4s** (54.5 mg, 60%) was obtained as a solid.

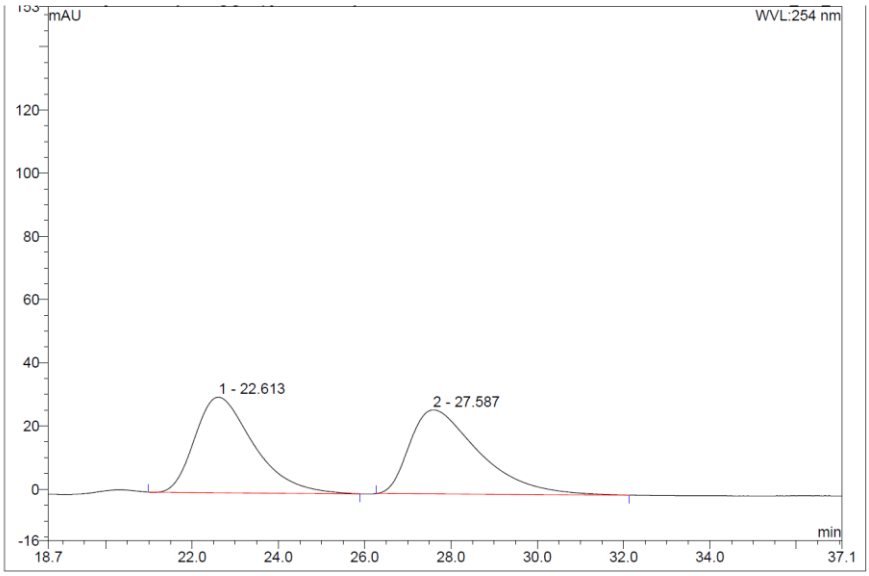
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.42 (d, *J* = 3.1 Hz, 1H), 8.19 (d, *J* = 8.7 Hz, 2H), 7.68 – 7.54 (m, 2H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.22 (s, 1H), 4.23 (d, *J* = 9.9 Hz, 1H), 3.79 (s, 3H), 3.62 (td, *J* = 11.4, 5.7 Hz, 1H), 3.27 (ddd, *J* = 11.5, 10.1, 3.1 Hz, 1H), 3.15 (dd, *J* = 16.4, 5.3 Hz, 1H), 3.03 (ddd, *J* = 16.7, 11.3, 2.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 203.0, 158.9, 153.1, 149.2, 148.1, 147.2, 132.8, 130.7, 129.4, 128.7, 128.6, 127.3, 124.3, 123.4, 121.8, 114.2, 105.1, 60.3, 55.3, 43.0, 41.6, 31.7

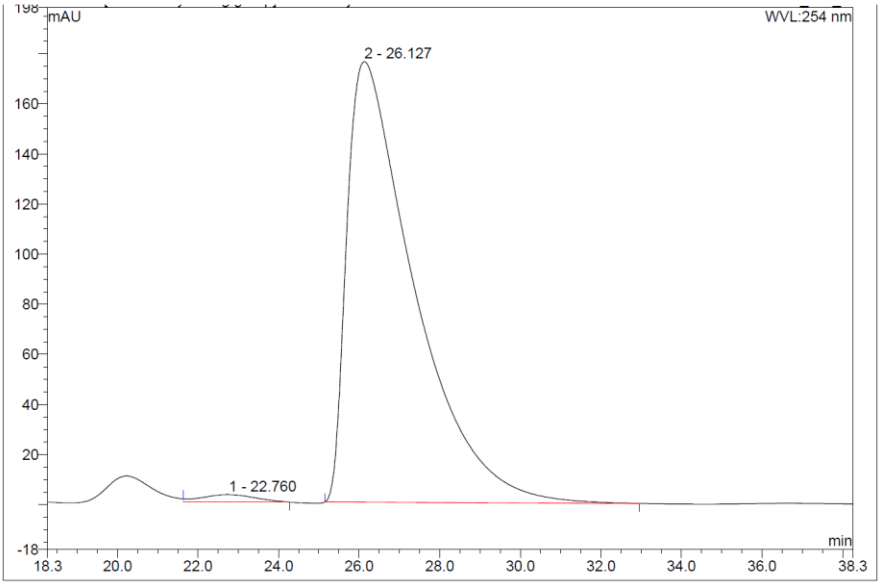
HRMS (ESI, m/z): $[M+H]^+$ calcd.for $C_{28}H_{24}NO_5$ 454.1649, found 454.1653.

HPLC analysis: 97% ee (Chiralpak OD-H column, hexane/*i*-PrOH =60/40, flow rate 1.0 mL/min, UV detection at 254 nm), Rt (minor) = 22.76 min; Rt (major) = 26.13 min

$[\alpha]_D^{20}$= -27.6 (c = 0.60, $CHCl_3$)

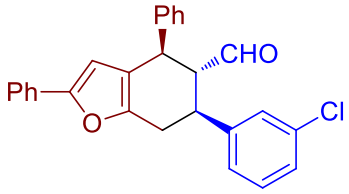


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	22.61	n.a.	30.252	47.655	49.15	n.a.	BMB*
2	27.59	n.a.	26.598	49.296	50.85	n.a.	BMB*
Total:			56.850	96.950	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	22.76	n.a.	2.989	4.571	1.33	n.a.	MB*
2	26.13	n.a.	175.914	340.106	98.67	n.a.	BMB*
Total:			178.903	344.677	100.00	0.000	

20) (4R,5R,6S)-6-(3-chlorophenyl)-2,4-diphenyl-4,5,6,7-tetrahydrobenzofuran-5-carbaldehyde (4t)



In a dried glass tube, a mixture of $PtCl_4$ (5 mol%), pyridine *N*-oxide (10 mol%), (2S)-2-[Bis[3,5-bis(trifluoromethyl)phenyl]-[(trimethylsilyl)oxy]methyl]pyrrolidine (**3c**, 20 mol%), TsOH•H_2O (20 mol%), **1a** (98.4 mg, 0.4 mmol) and **2h** (33.2 mg, 0.2 mmol) was mixed in $PhCH_3$ (2 mL), stirring at 60 °C until the reaction was complete (24 h). The mixture was passed through a short silica gel column and then concentrated under reduced pressure. The residue was purified by column chromatography. **4r** (40.4 mg, 49%) was obtained as a solid.

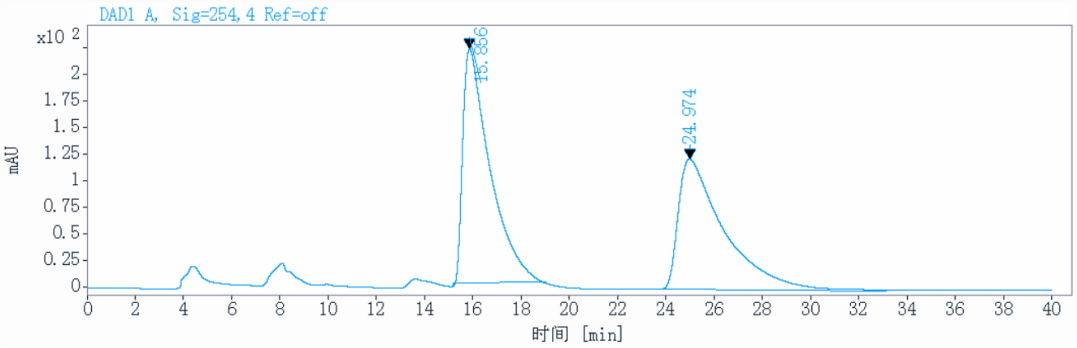
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.41 (d, *J* = 3.2 Hz, 1H), 7.61 – 7.52 (m, 2H), 7.38 – 7.28 (m, 6H), 7.26 – 7.15 (m, 6H), 6.21 (s, 1H), 4.30 (d, *J* = 9.8 Hz, 1H), 3.46 (td, *J* = 11.3, 5.7 Hz, 1H), 3.25 (ddd, *J* = 11.6, 10.1, 3.2 Hz, 1H), 3.18 – 3.10 (m, 1H), 3.05 (ddd, *J* = 16.7, 11.1, 2.8 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 203.18, 152.98, 148.69, 143.36, 141.39, 134.85, 130.77, 130.33, 128.74, 128.63, 128.56, 127.78, 127.68, 127.31, 127.17, 125.93, 123.43, 121.37, 105.24, 60.31, 43.28, 42.01, 31.97.

HRMS (ESI, m/z): $[M+H]^+$ calcd.for $C_{27}H_{22}ClO_2$ 413.1303, found 413.1300.

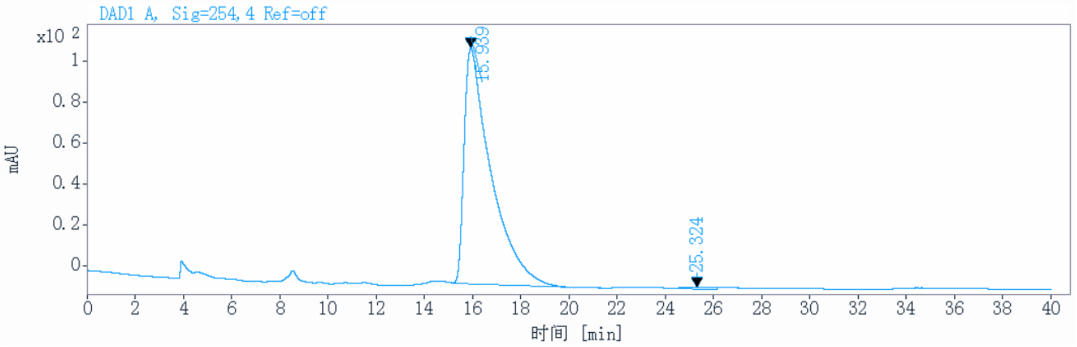
HPLC analysis: 98% ee (Chiralpak AD-H column, hexane/*i*-PrOH = 95/5, flow rate 0.75 mL/min, UV detection at 254 nm), Rt (major) = 15.94 min, Rt (minor) = 25.32 min.

$[\alpha]_D^{20}$= -23.2 (c = 1.0, $CHCl_3$)



信号: DAD1 A, Sig=254,4 Ref=off

RT	Area	Height	Area%	Height%
15.856	17220.5586	220.1901	51.6415	64.31
24.974	16125.7891	122.2174	48.3585	35.69
? ?	33346.3477			

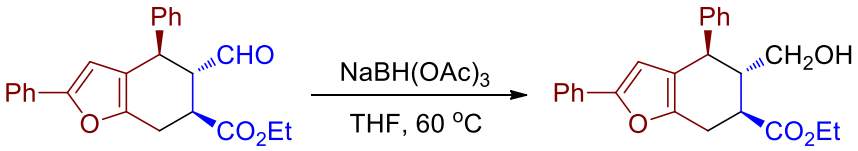


信号: DAD1 A, Sig=254,4 Ref=off

RT	Area	Height	Area%	Height%
15.939	8865.0576	114.9247	99.1018	99.23
25.324	80.3469	0.8954	0.8982	0.77
? ?	8945.4045			

3. Transformations of 4a

1) (4R,5S,6S)-ethyl 5-(hydroxymethyl)-2,4-diphenyl-4,5,6,7-tetrahydrobenzofuran-6-carboxylate (5)



4a, 96% ee **5**, 82% yield, 96% ee

Under N_2, a stirred solution of **4a** (0.2 mmol) in THF (2 mL) was added $NaBH(OAc)_3$ (0.6 mmol). The mixture was stirred at 60 °C for 3 h. After completion of the reaction, the reaction mixture was directly applied to a silica gel chromatography column to afford the desired **5** in 82% (61.7 mg) yield without loss of enantiopurity.

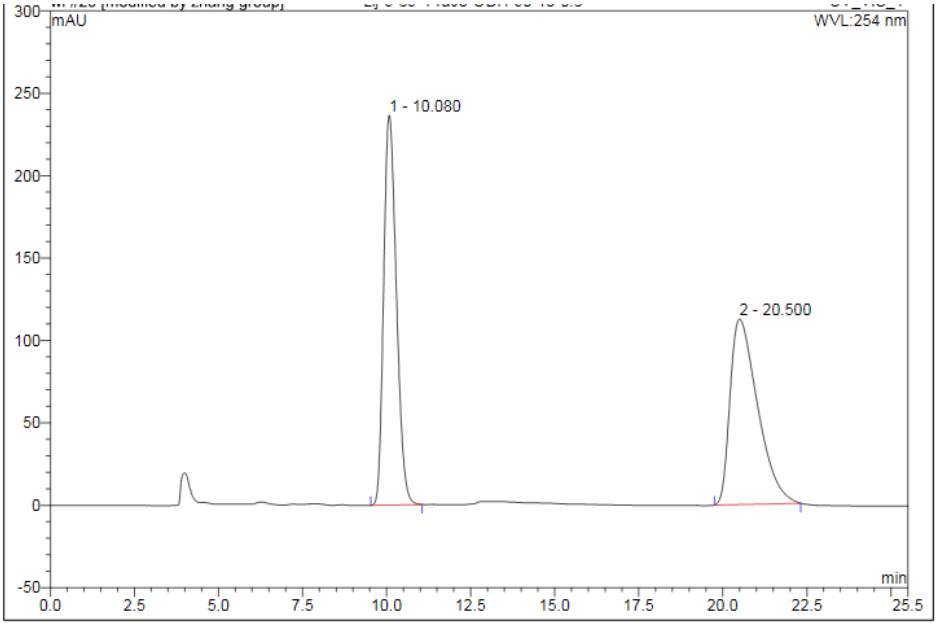
^{1}H NMR (500 MHz, CDCl3) δ 7.54 (dd, J = 8.4, 1.1 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.27 – 7.25 (m, 1H), 7.24 – 7.22 (m, 2H), 7.20 – 7.17 (m, 1H), 6.12 (s, 1H), 4.18 (qq, J = 10.8, 7.1 Hz, 2H), 4.01 – 3.92 (m, 1H), 3.59 (d, J = 11.9 Hz, 1H), 3.55 – 3.45 (m, 1H), 3.21 (ddd, J = 15.5, 10.0, 2.8 Hz, 1H), 3.13 – 3.00 (m, 2H), 2.13 (tt, J = 10.2, 3.2 Hz, 1H), 1.81 (s, 1H), 1.28 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.6, 152.8, 147.9, 142.8, 130.9, 128.9, 128.6, 128.5, 126.9, 126.9, 123.3, 122.3, 105.8, 61.3, 61.1, 47.3, 42.8, 41.3, 26.1, 14.2

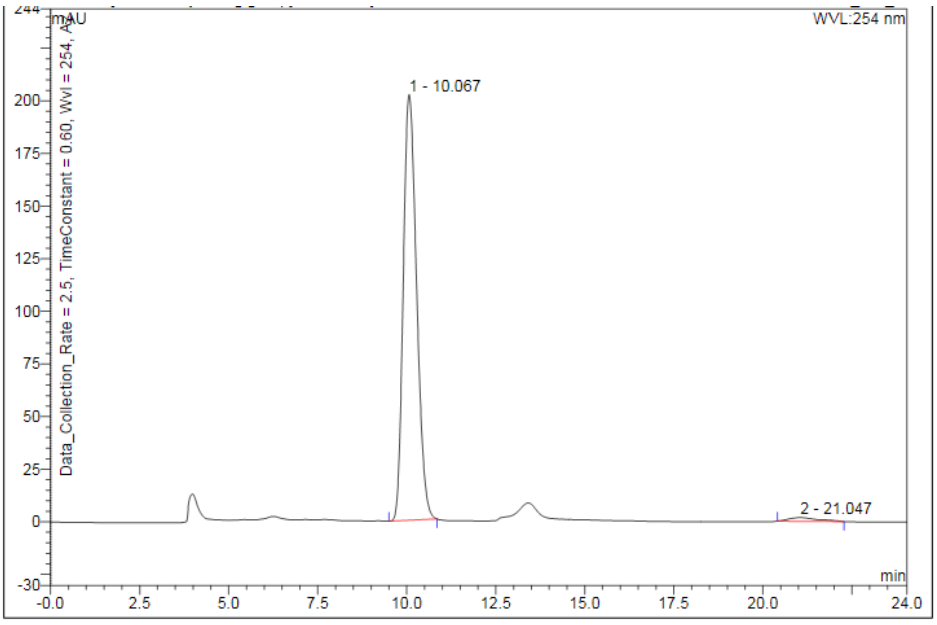
HRMS (ESI, m/z): $[M+H]^+$ calcd.for $C_{24}H_{25}O_4$ 377.1747, found 377.1749

HPLC analysis: 96% ee (Chiralpak OD-H column, hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, UV detection at 254 nm), Rt (major) = 10.07 min; Rt (minor) = 21.05 min

$[\alpha]_D^{20}$= -10.6 (c = 1.0, $CHCl_3$)

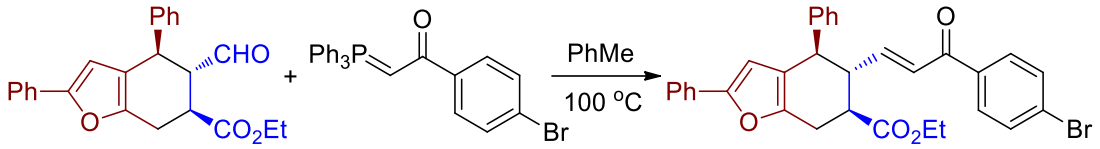


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.08	n.a.	236.616	103.769	49.24	n.a.	BMB*
2	20.50	n.a.	112.576	106.955	50.76	n.a.	BMB*
Total:			349.192	210.724	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.07	n.a.	202.298	87.537	98.19	n.a.	BMB*
2	21.05	n.a.	1.687	1.615	1.81	n.a.	BMB*
Total:			203.985	89.152	100.00	0.000	

2) (4R,5S,6S)-ethyl 5-((E)-3-(4-bromophenyl)-3-oxoprop-1-en-1-yl)-2,4-diphenyl-4,5,6,7-tetrahydrobenzofuran-6-carboxylate (6)



4a, 96% ee

6, 75% yield, 96% ee

A stirred solution of **4a** (0.2 mmol) in toluene (2 mL) was added 1-(4-bromophenyl)-2-(triphenylphosphoranylidene)ethanone (0.4 mmol). The mixture was stirred at 100 °C for 12 h. After completion of the reaction, the reaction mixture was directly applied to a silica gel chromatography column to afford the desired **6** in 75% (83.1 mg) yield without loss of enantiopurity.

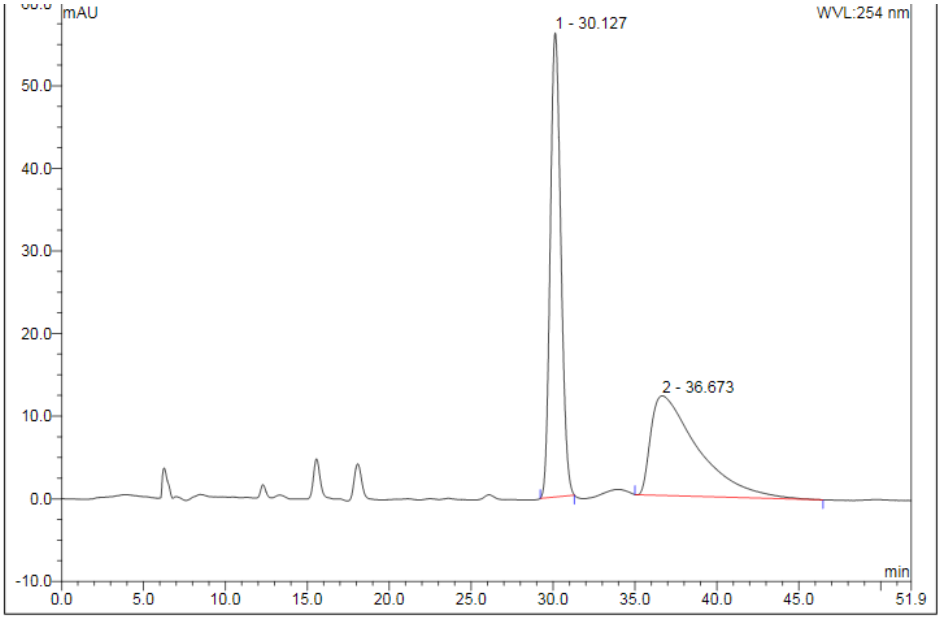
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.2 Hz, 2H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.36 – 7.27 (m, 4H), 7.22 (dt, *J* = 13.6, 5.5 Hz, 2H), 7.17 – 7.10 (m, 2H), 6.84 (dd, *J* = 15.4, 9.8 Hz, 1H), 6.35 (d, *J* = 15.3 Hz, 1H), 6.15 (s, 1H), 4.08 (q, *J* = 7.0 Hz, 2H), 3.83 – 3.76 (m, 1H), 3.23 – 3.17 (m, 1H), 3.15 – 3.06 (m, 2H), 2.90 (q, *J* = 10.0 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 188.9, 173.4, 153.1, 148.0, 147.1, 141.7, 136.2, 131.8, 130.8, 130.0, 128.8, 128.6, 128.5, 128.3, 128.0, 127.1, 127.1, 123.4, 121.3, 105.4, 61.0, 50.1, 45.8, 45.7, 26.2, 14.1.

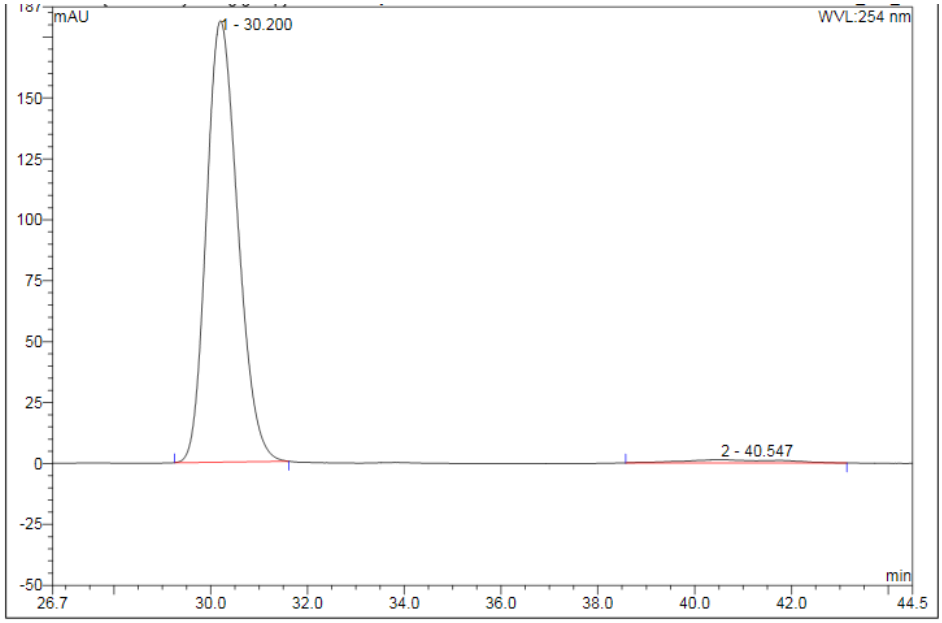
HRMS (ESI, m/z): [M+NH_4^+] calcd. for $C_{32}H_{31}BrNO_4$ 572.1431, found 572.1424.

HPLC analysis: 96% ee (Chiralpak AD-H column, hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, UV detection at 254 nm), Rt (major) = 30.20 min; Rt (minor) = 40.55 min

$[\alpha]_D^{20}$= -6.7 (c = 0.50, $CHCl_3$)

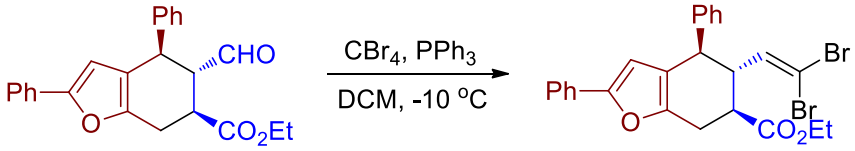


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	30.13	n.a.	56.196	42.163	51.29	n.a.	BMB*
2	36.67	n.a.	12.036	40.043	48.71	n.a.	BMB*
Total:			68.232	82.206	100.00	0.000	



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	30.20	n.a.	181.052	136.225	97.84	n.a.	BMB*
2	40.55	n.a.	1.320	3.001	2.16	n.a.	BMB*
Total:			182.372	139.226	100.00	0.000	

3) (4R,5S,6S)-ethyl 5-(2,2-dibromovinyl)-2,4-diphenyl-4,5,6,7-tetrahydrobenzofuran-6-carboxylate (7)



4a, 96% ee

7, 89% yield, 96% ee

To a solution of **4a** (0.2 mmol) and CBr_4 (0.3 mmol) in DCM (2 mL) at -10 ºC was added dropwise a solution of PPh_3 (0.6 mmol)) in DCM (2 mL) by syringe. The addition rate was controlled so that the internal temperature was subzero. After addition, the mixture was stirred for another 0.5 h before warmed to rt and stirred for another 1 h. Then the reaction mixture was directly applied to a silica gel chromatography column to afford the desired **7** in 89% (94.1 mg) yield without loss of enantiopurity.

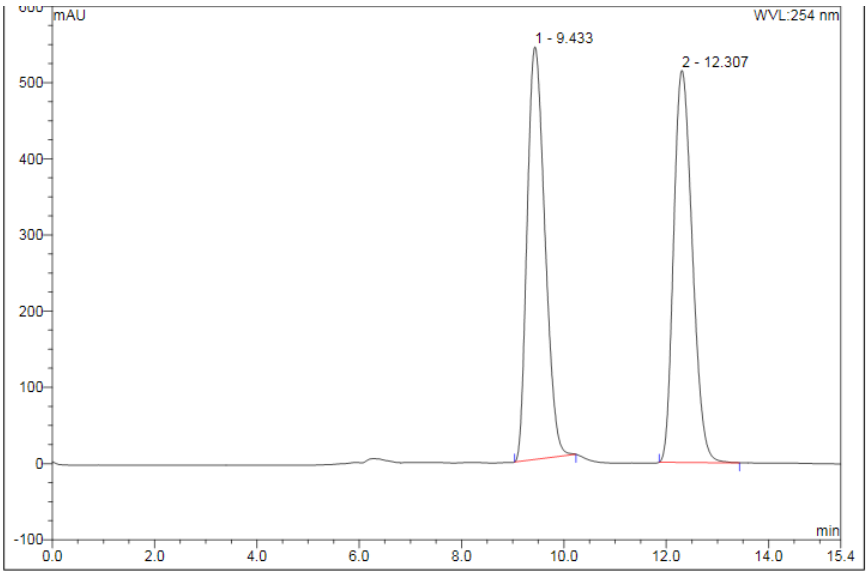
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.36 – 7.26 (m, 5H), 7.23 – 7.18 (m, 1H), 7.18 – 7.14 (m, 2H), 6.32 (d, *J* = 10.2 Hz, 1H), 6.18 (s, 1H), 4.19 – 4.06 (m, 2H), 3.68 (d, *J* = 9.1 Hz, 1H), 3.25 (ddd, *J* = 16.4, 10.5, 2.8 Hz, 1H), 3.12 – 3.00 (m, 2H), 2.94 (td, *J* = 10.6, 5.5 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.8, 153.0, 148.2, 140.9, 137.7, 130.8, 128.9, 128.6, 128.3, 127.1, 123.4, 120.9, 105.4, 92.1, 61.1, 50.2, 45.3, 45.2, 25.8, 14.2

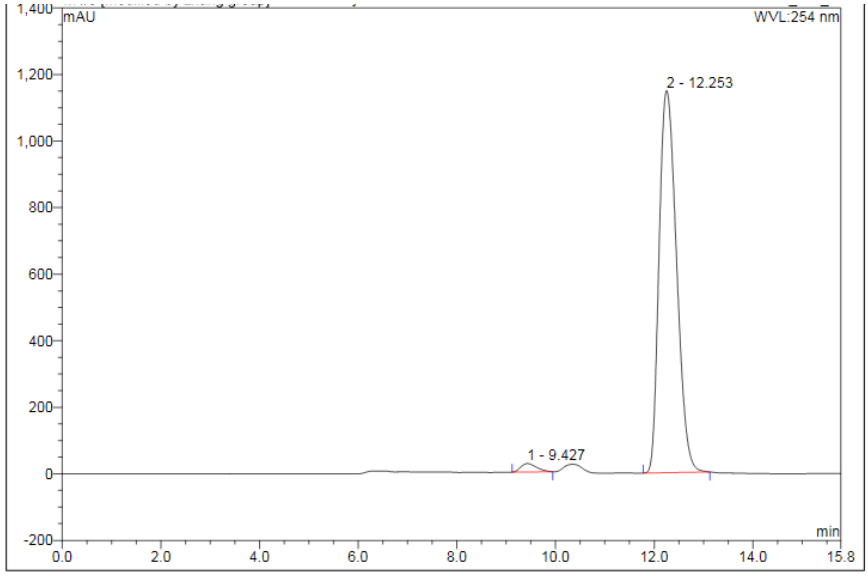
HRMS (ESI, m/z): $[M+H]^+$ calcd.for $C_{25}H_{23}Br_2O_3$ 529.0008, found 529.0020

HPLC analysis: 96% ee (Chiralpak AD-H column, hexane/*i*-PrOH = 90/10, flow rate 0.5 mL/min, UV detection at 254 nm), Rt (minor) = 9.43 min; Rt (major) = 12.25 min

$[\alpha]_D^{20}$= -9.8 (c = 0.50, $CHCl_3$)



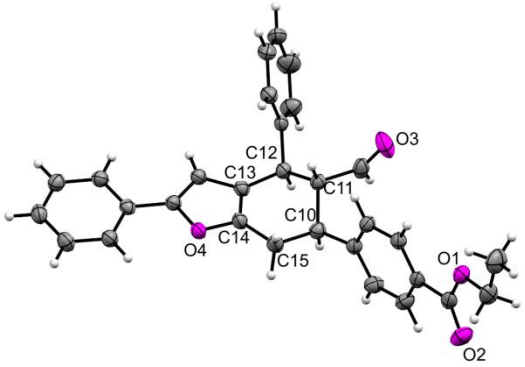
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.43	n.a.	541.504	216.962	49.94	n.a.	BMB*
2	12.31	n.a.	514.474	217.524	50.06	n.a.	BMB*
Total:			1055.978	434.486	100.00	0.000	

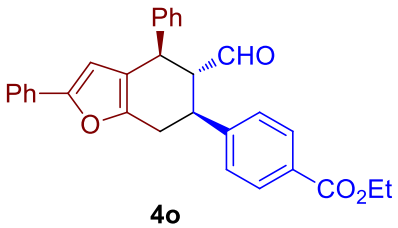


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.43	n.a.	25.446	9.488	1.98	n.a.	BMB*
2	12.25	n.a.	1148.766	469.428	98.02	n.a.	BMB*
Total:			1174.212	478.916	100.00	0.000	

4. X-ray crystallographic analysis

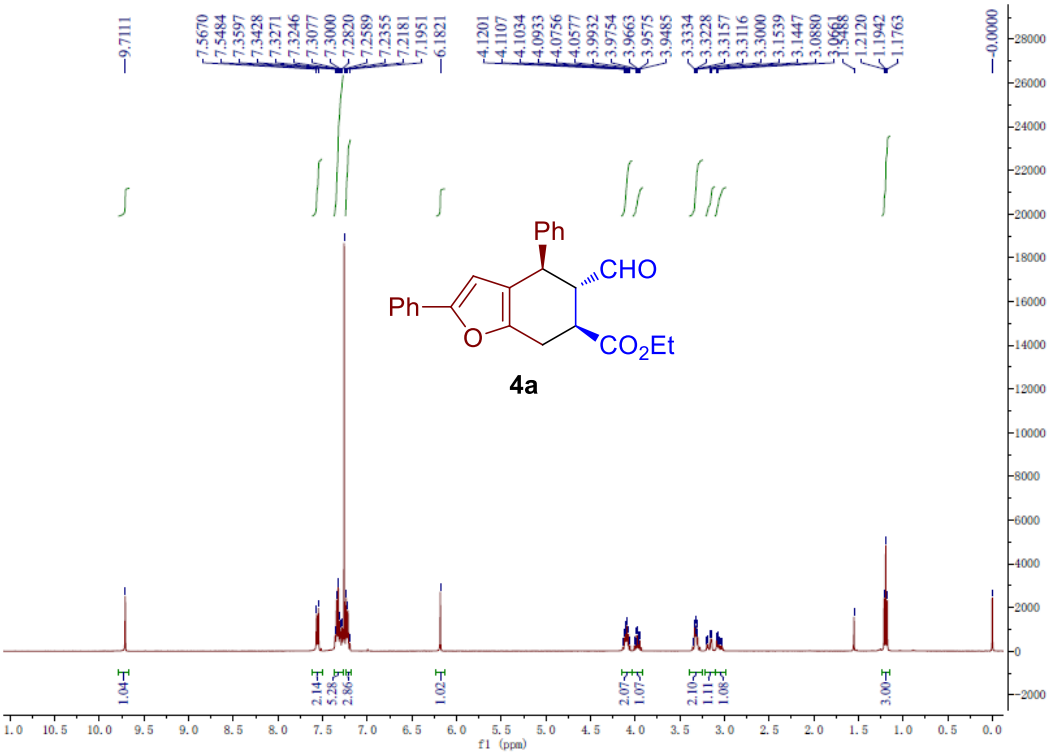
Product **4o** was crystallized as a colorless crystal *via* vaporization of a petrollium ether/EA solution, and its relative configuration was determined by x-ray structure analysis. The CCDC number was 1994848. The supplementary crystallographic data that could be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data request/cif.

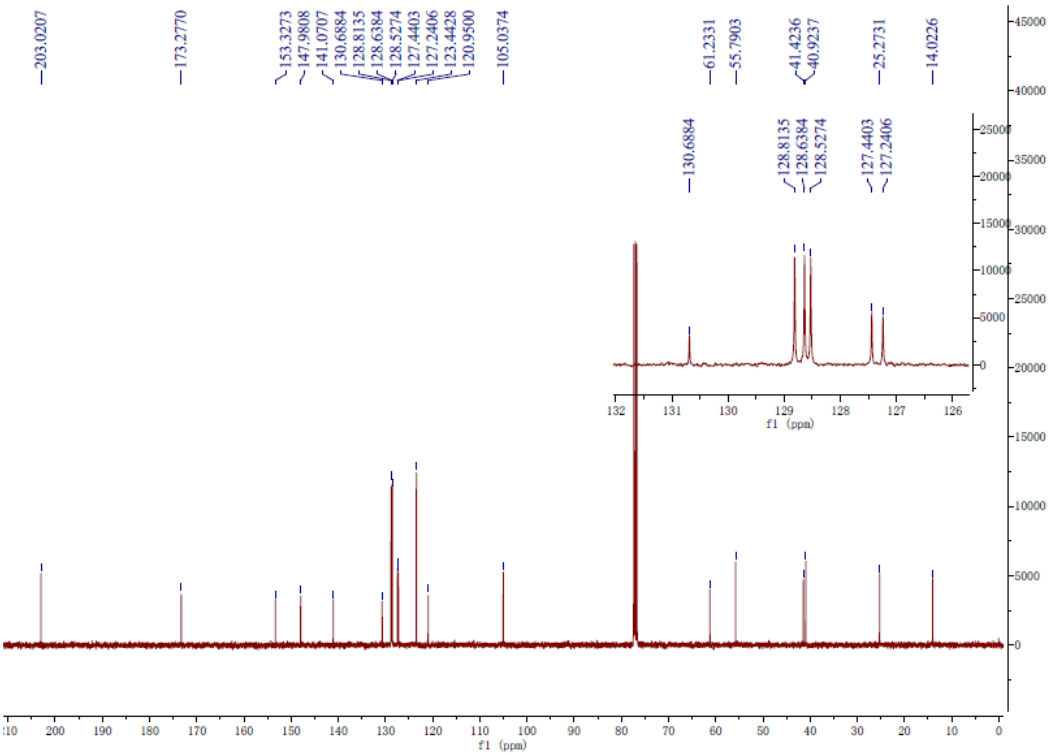


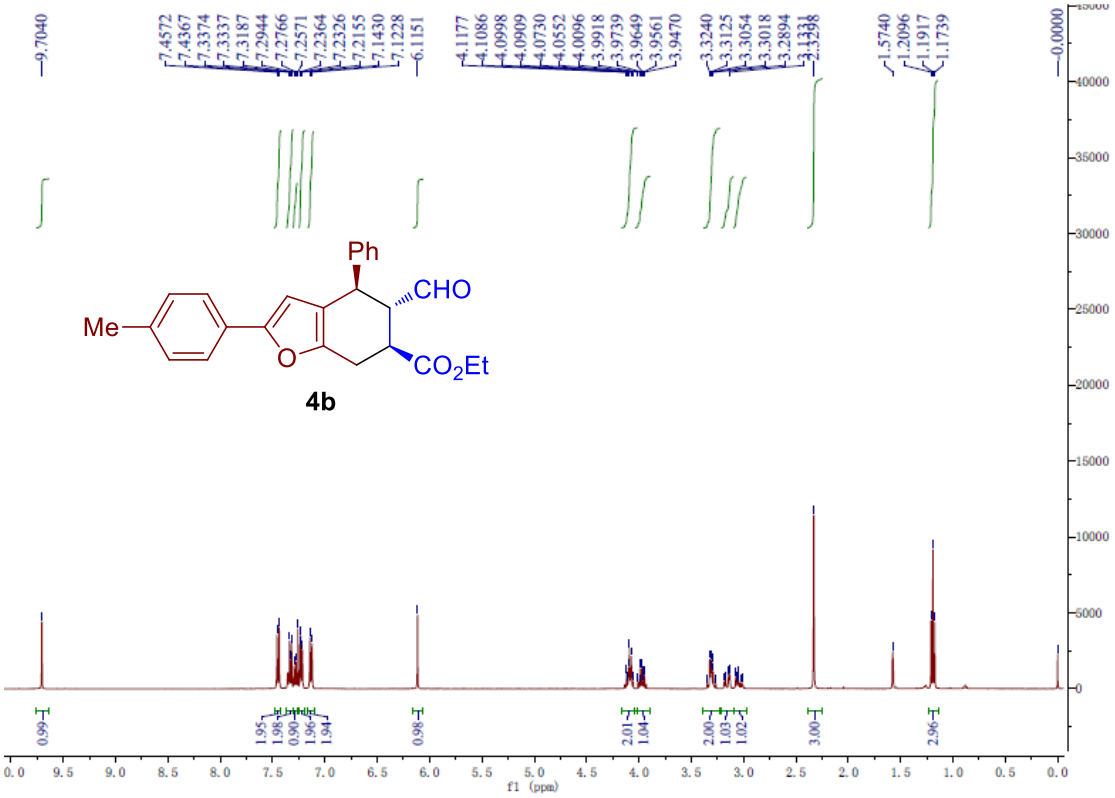


4o

5. ^{1}H, ^{13}C NMR spectra







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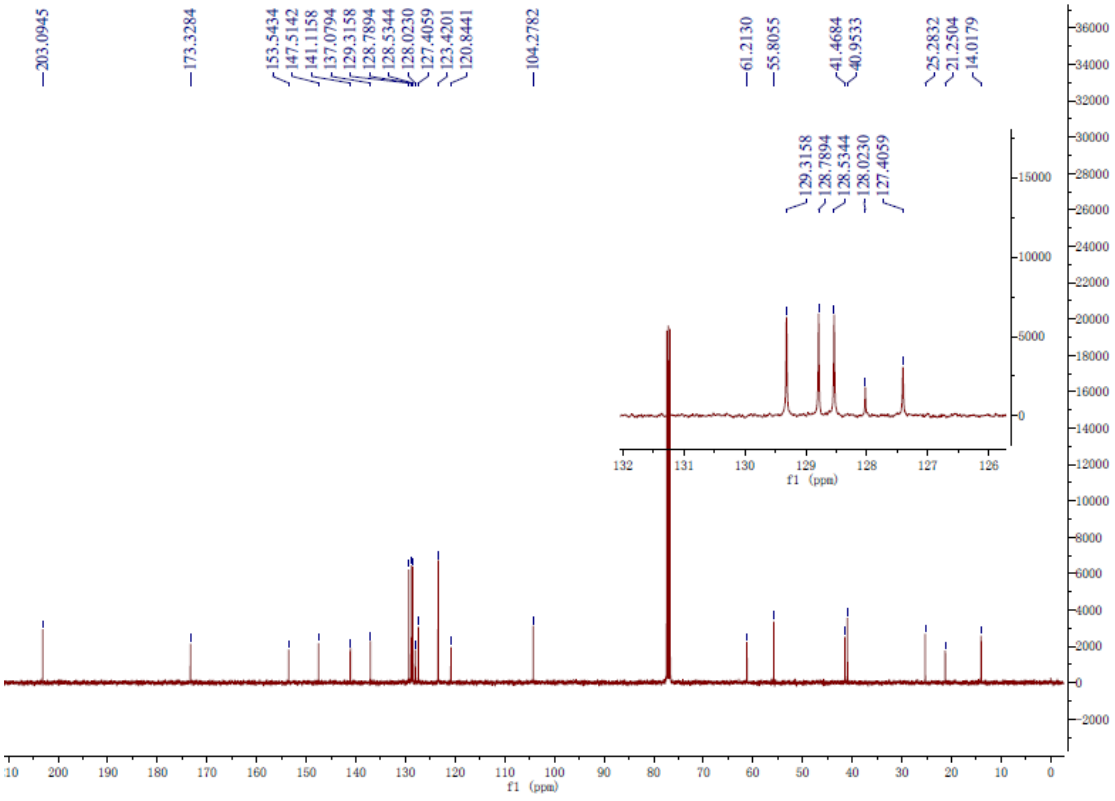

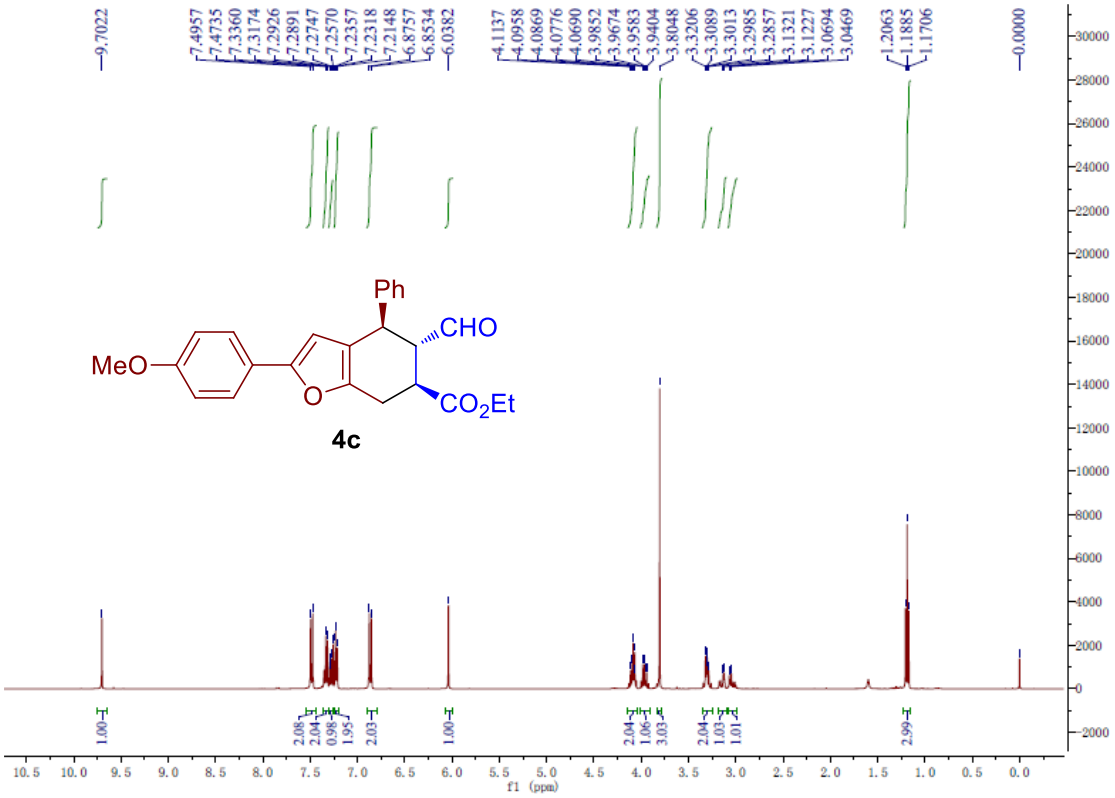
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7.2318
7.2148
6.8757
6.8534
6.0382
4.1137
4.0958
4.0869
4.0776
4.0690
3.9852
3.9674
3.9583
3.9404
3.8048
3.3206
3.3089
3.3013
3.2985
3.2857
3.1321
3.1227
3.0694
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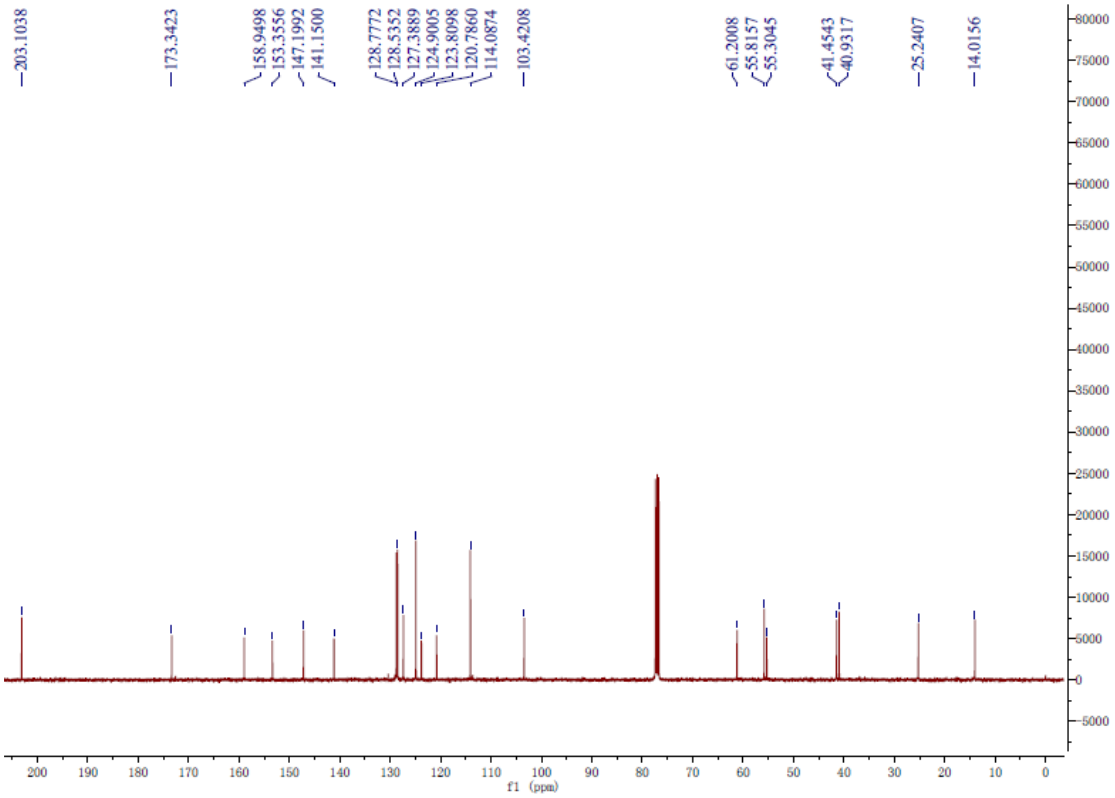
0.0000
Ph
CHO
MeO
O
CO2Et
4c
f1 (ppm)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123.8098
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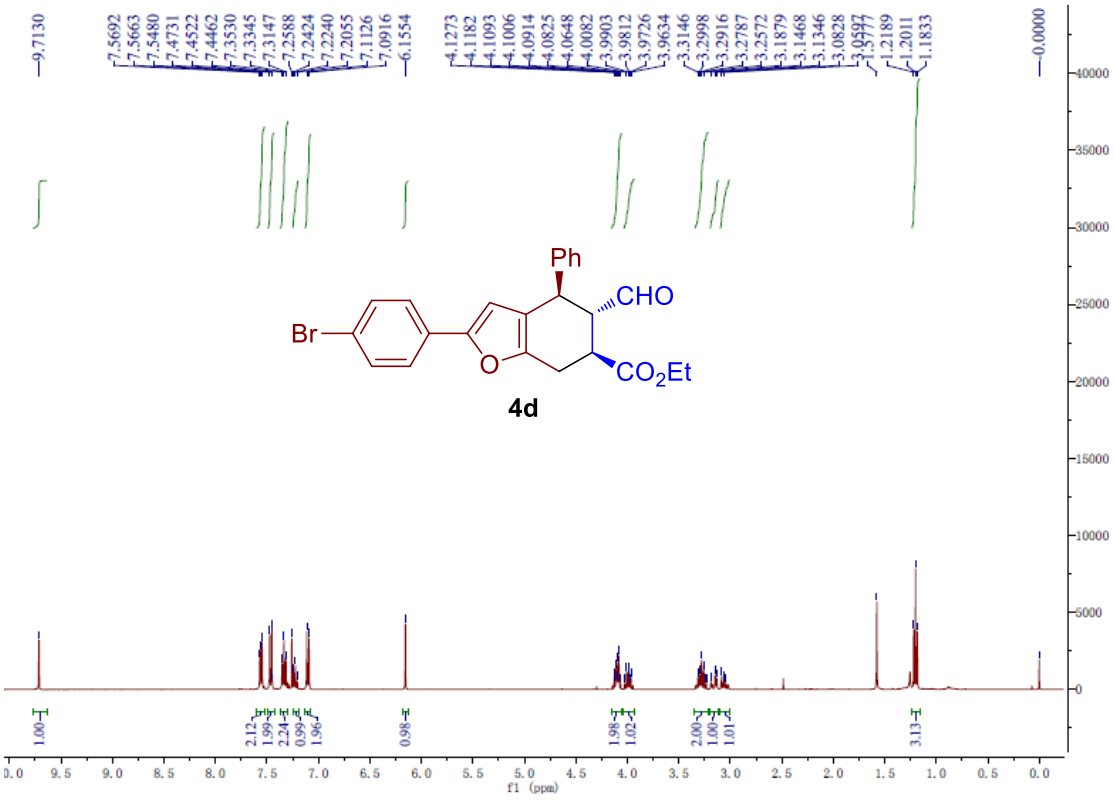
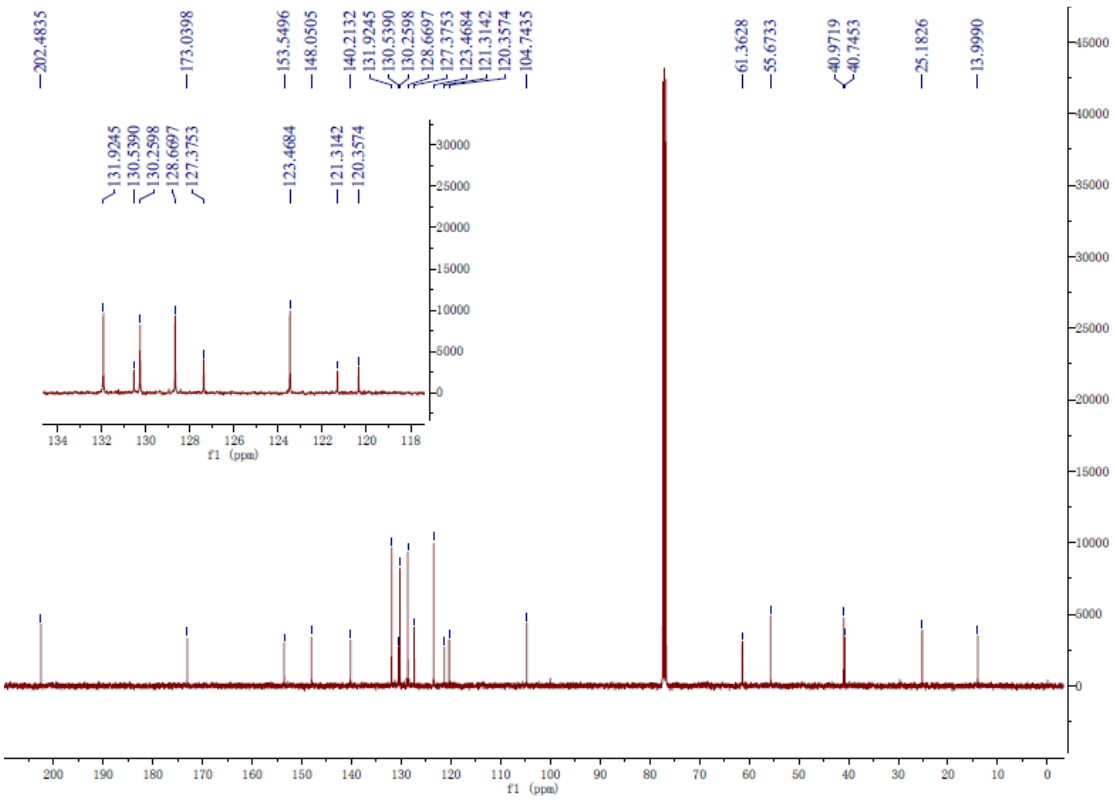
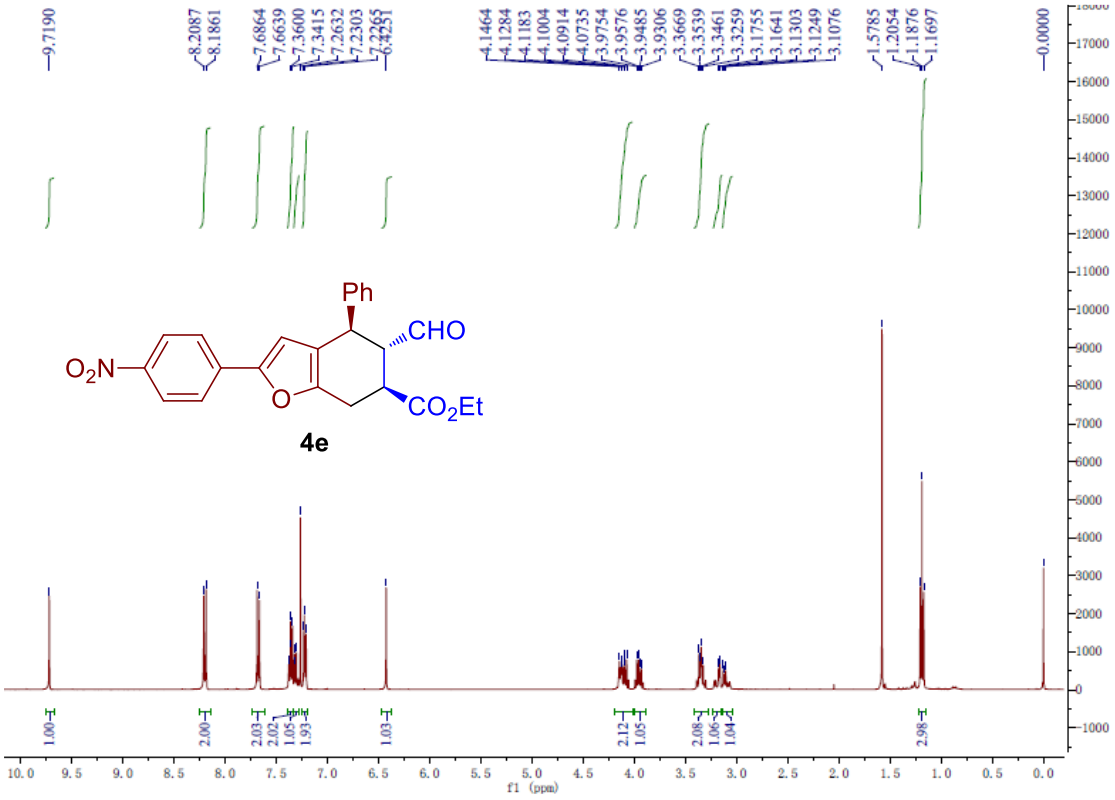
f1 (ppm)

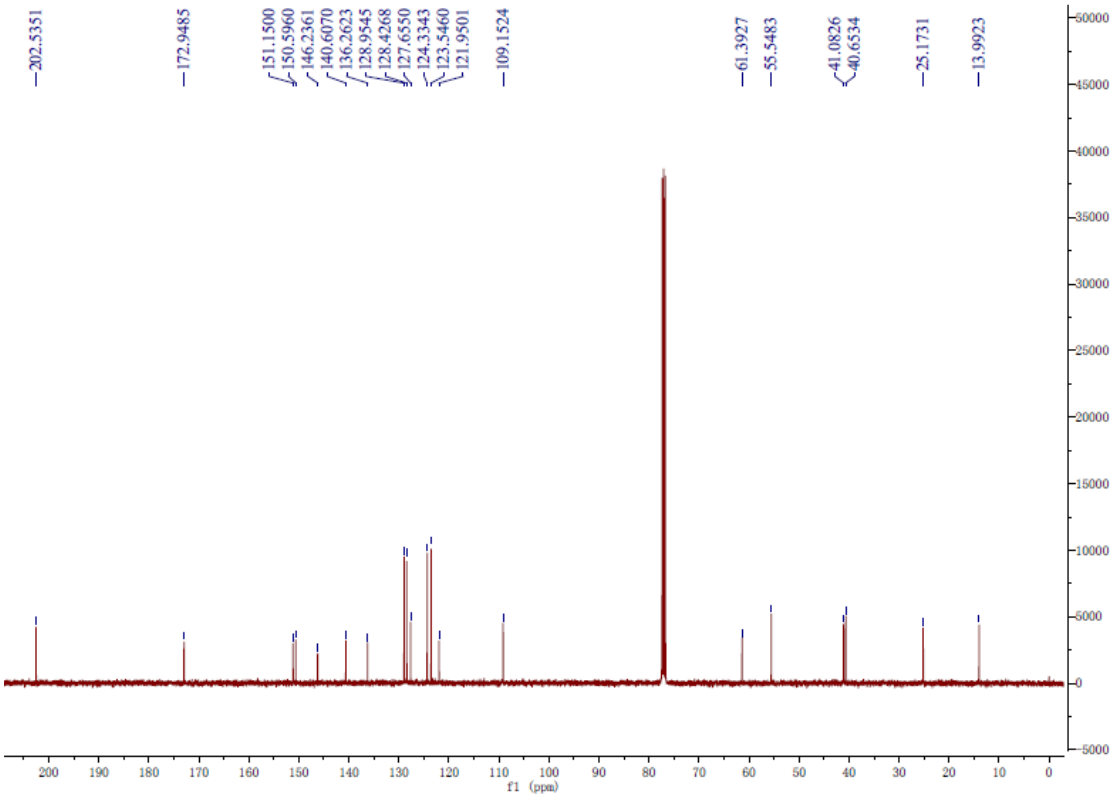


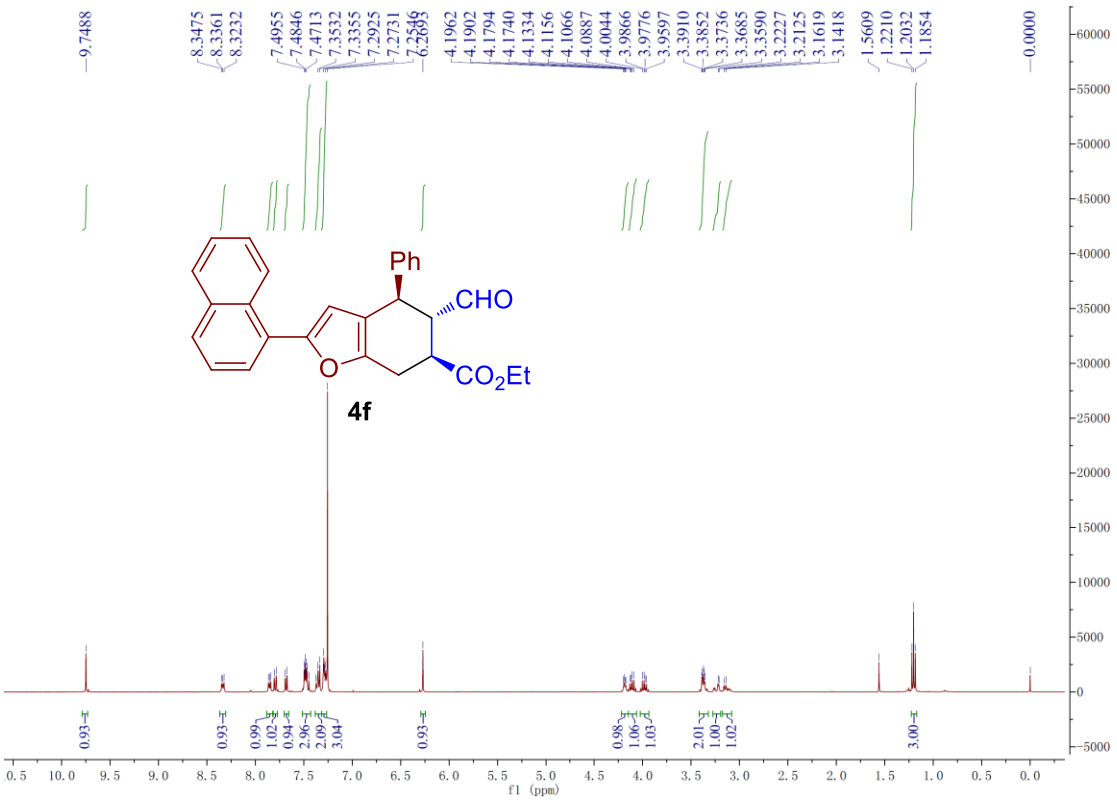
4d





4e

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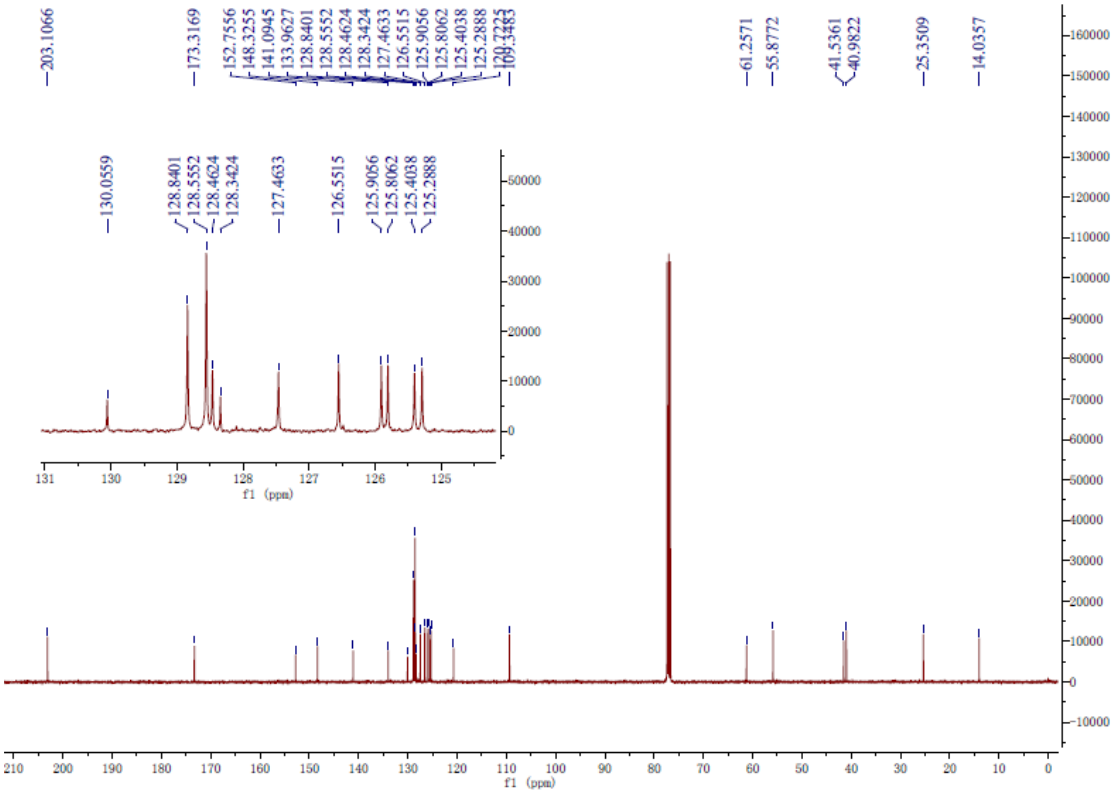
CHO
CO2Et
O
4f
f1 (ppm)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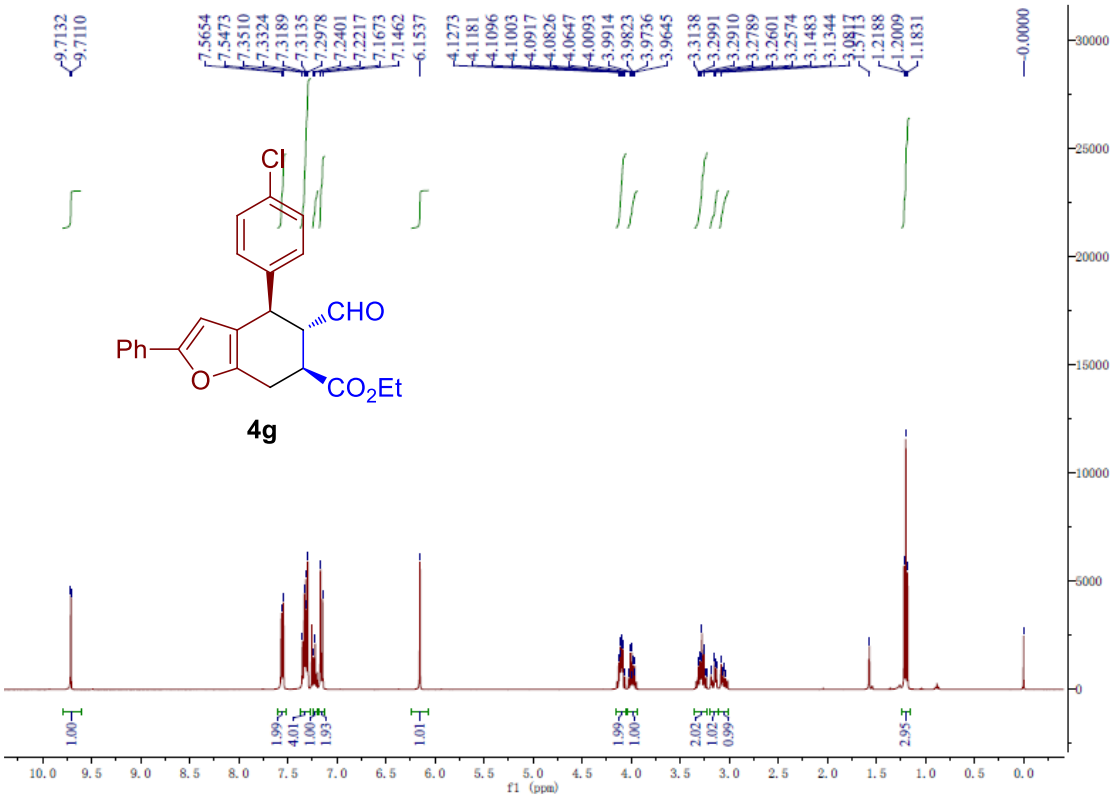
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O
CO2Et
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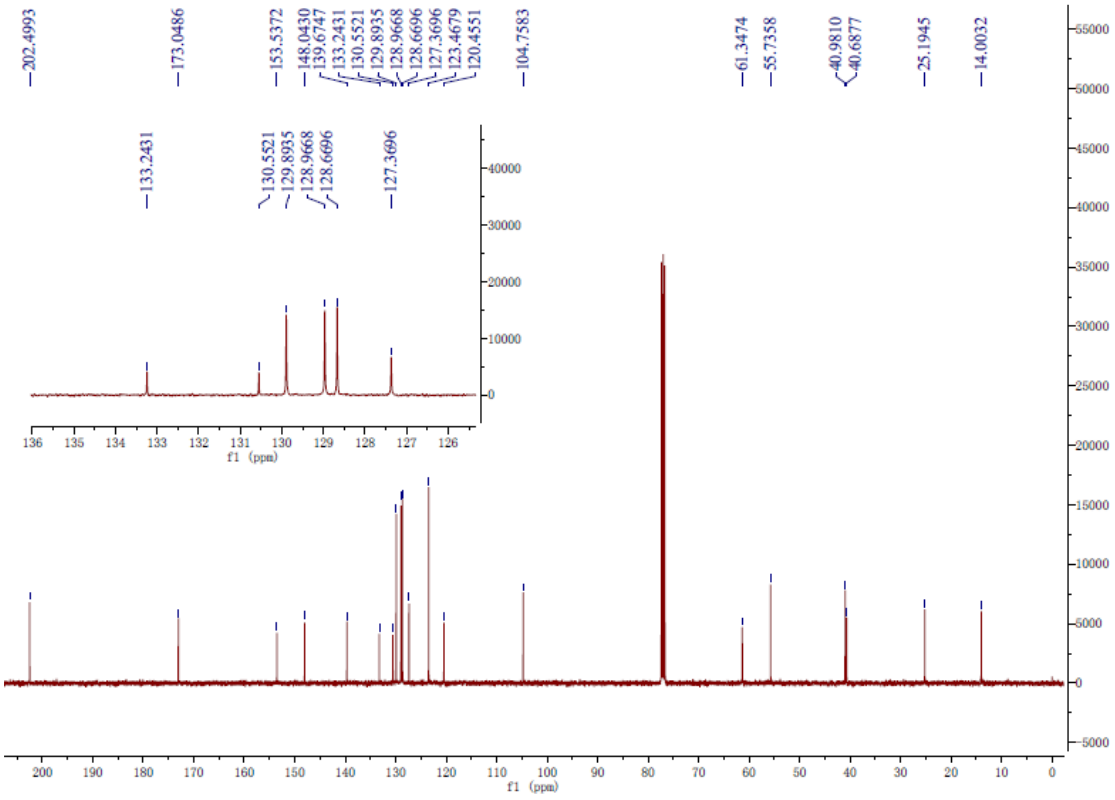

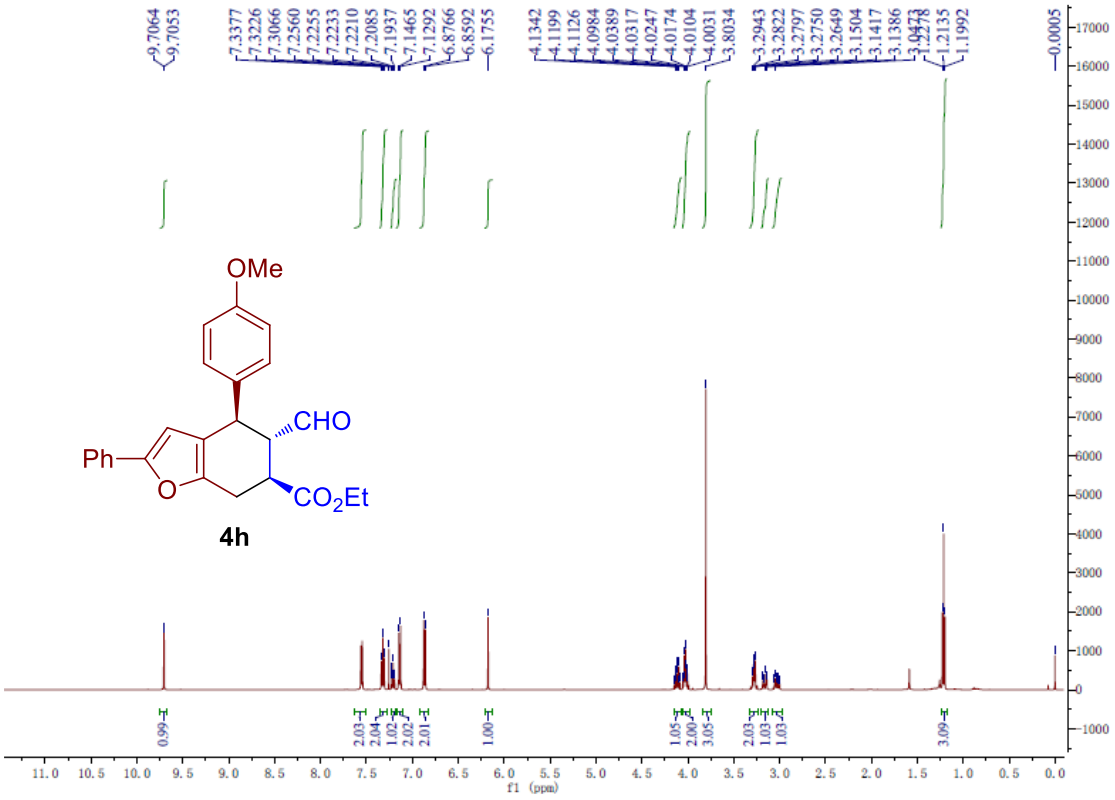
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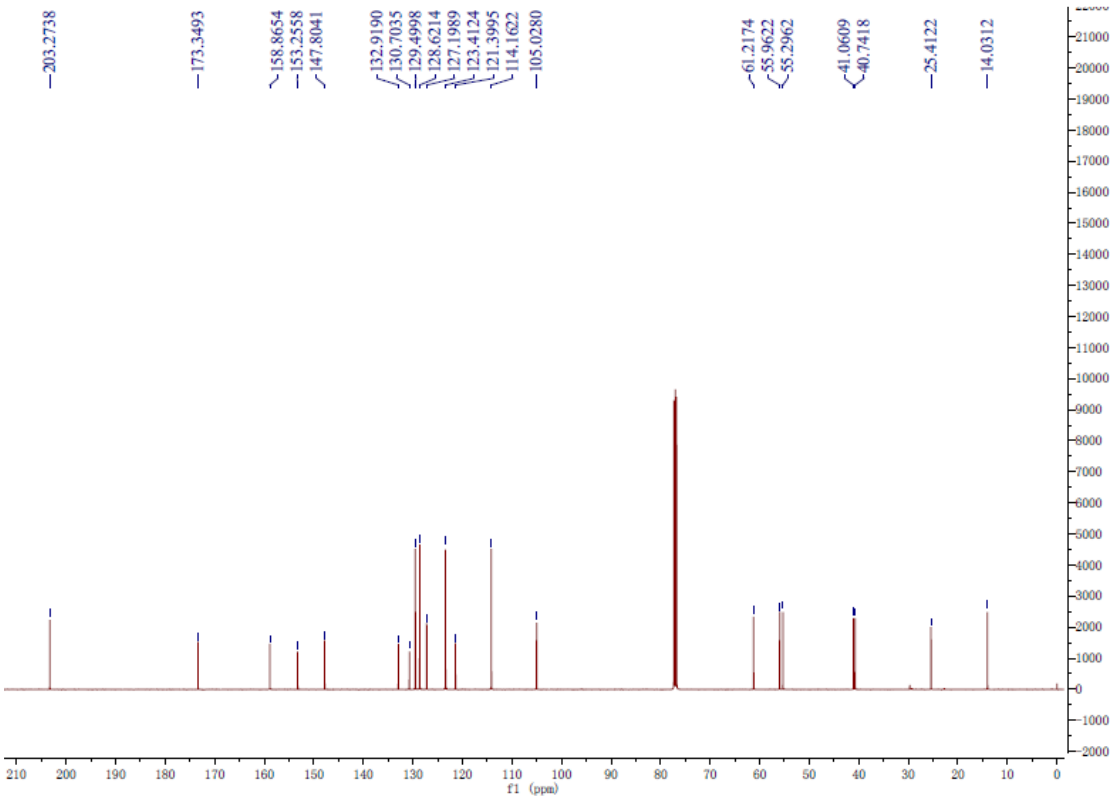
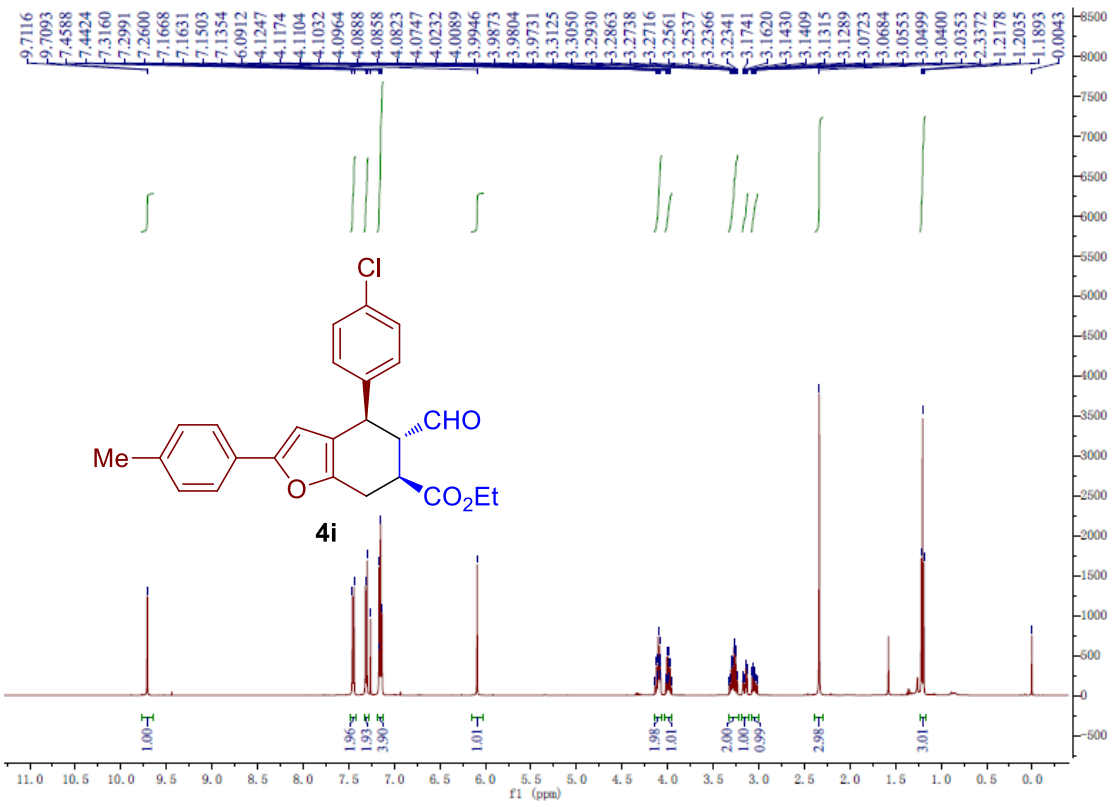
CHO
Ph
O
CO2Et
4h

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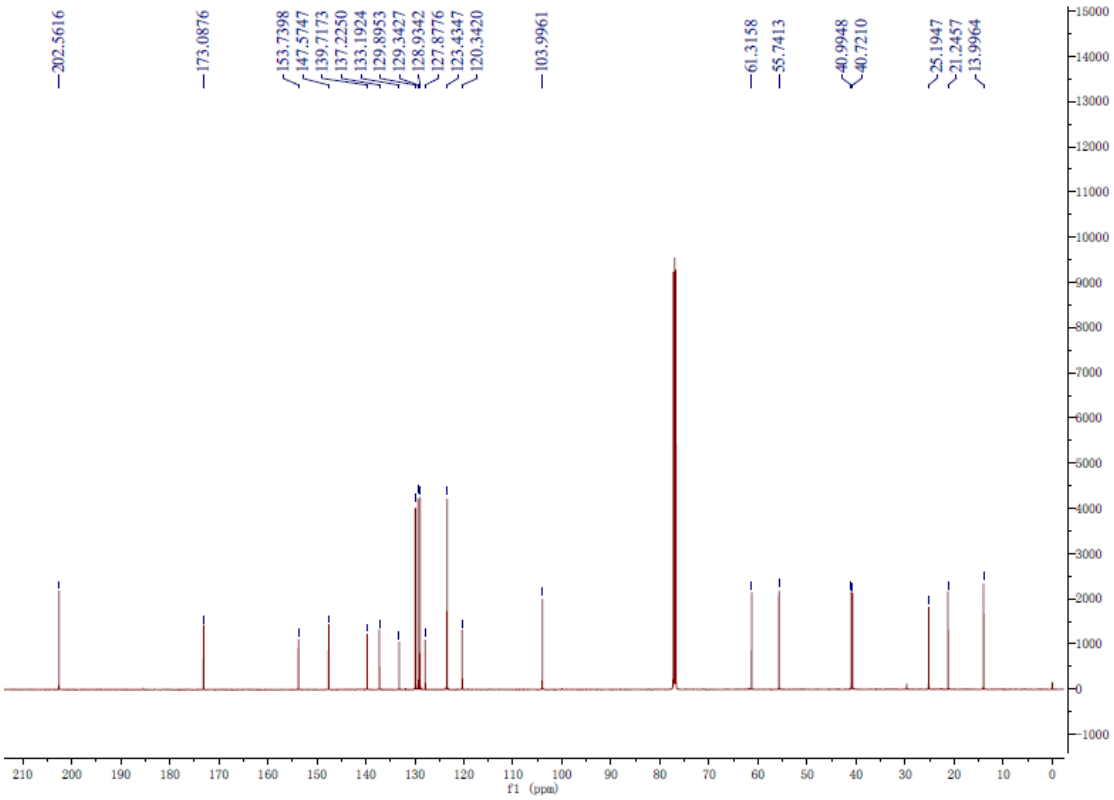
CHO
Me
O
CO_2Et
4i
f1 (ppm)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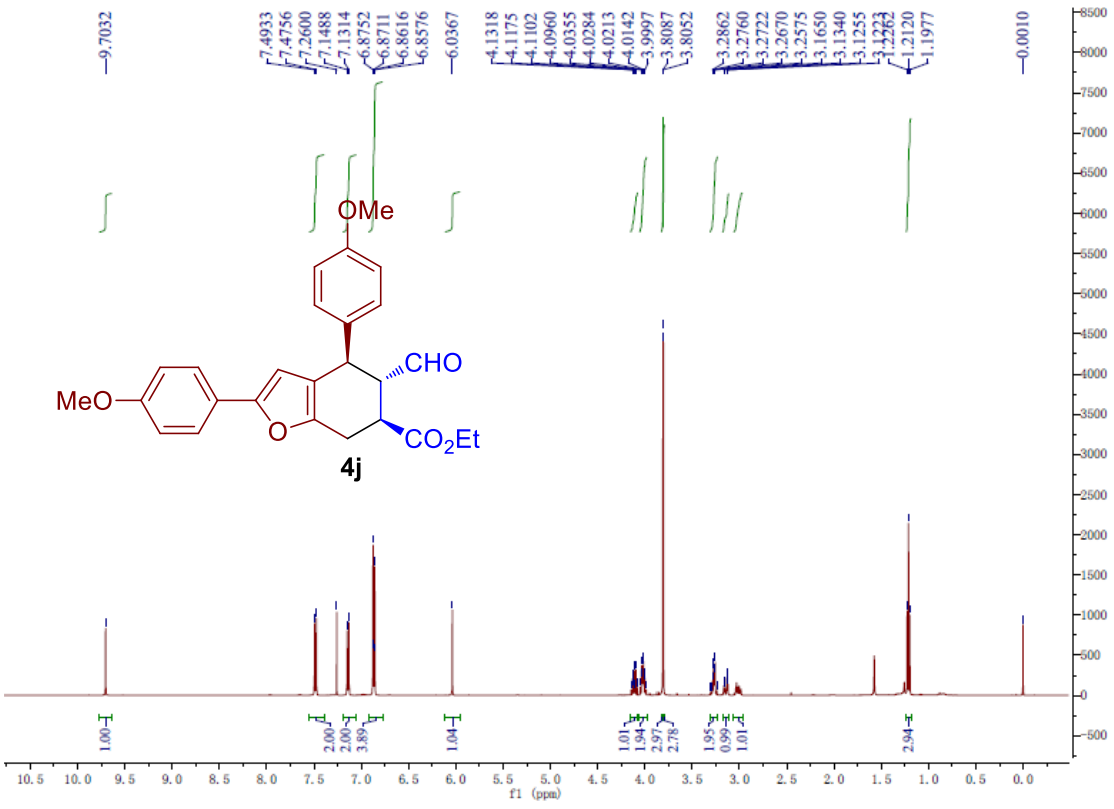
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O
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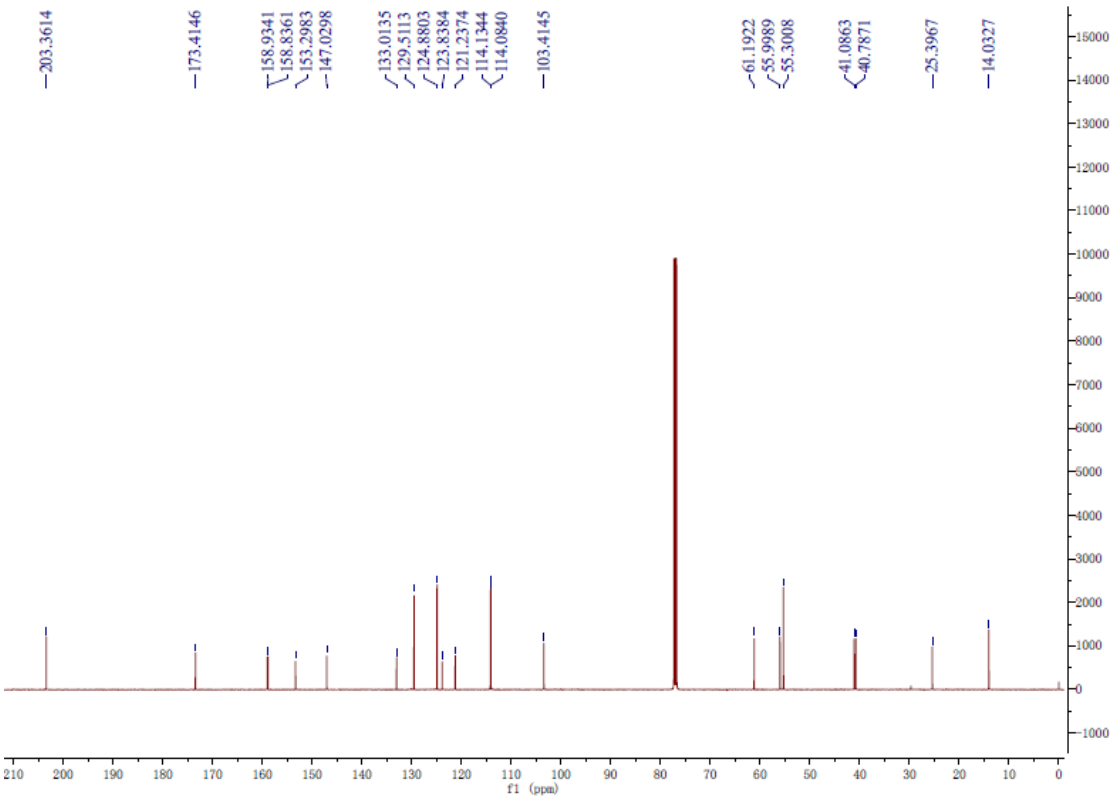
4j
f1 (ppm)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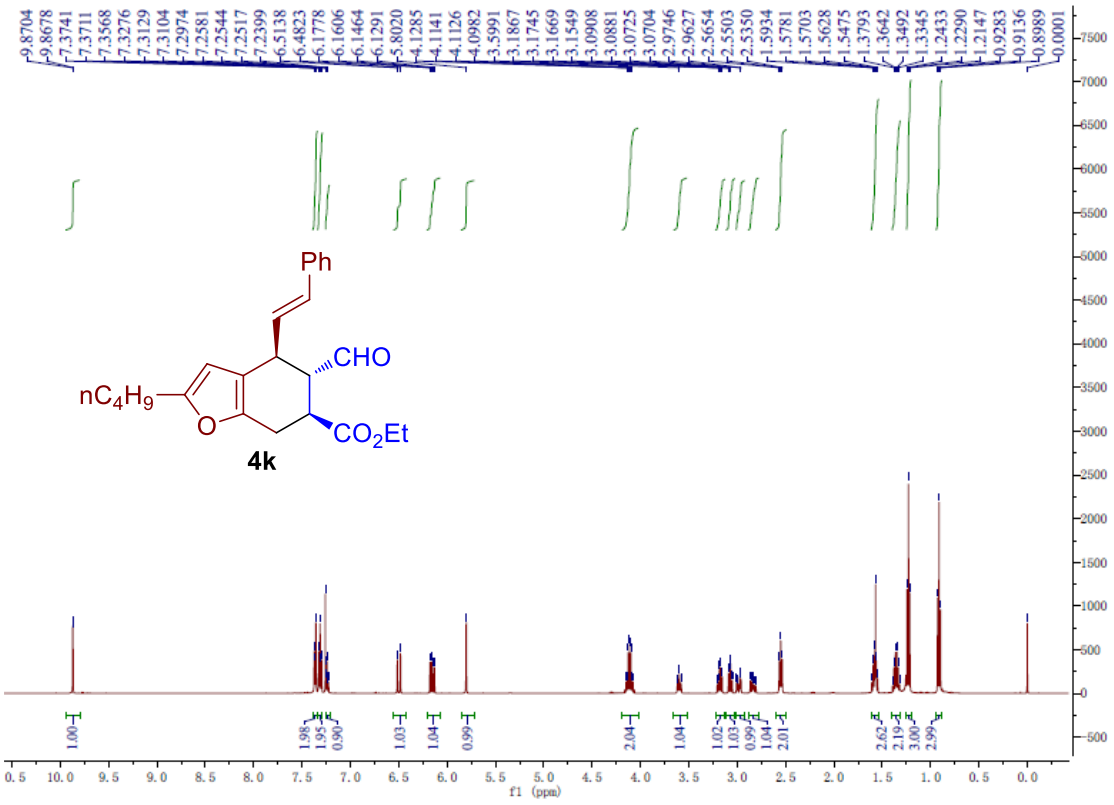
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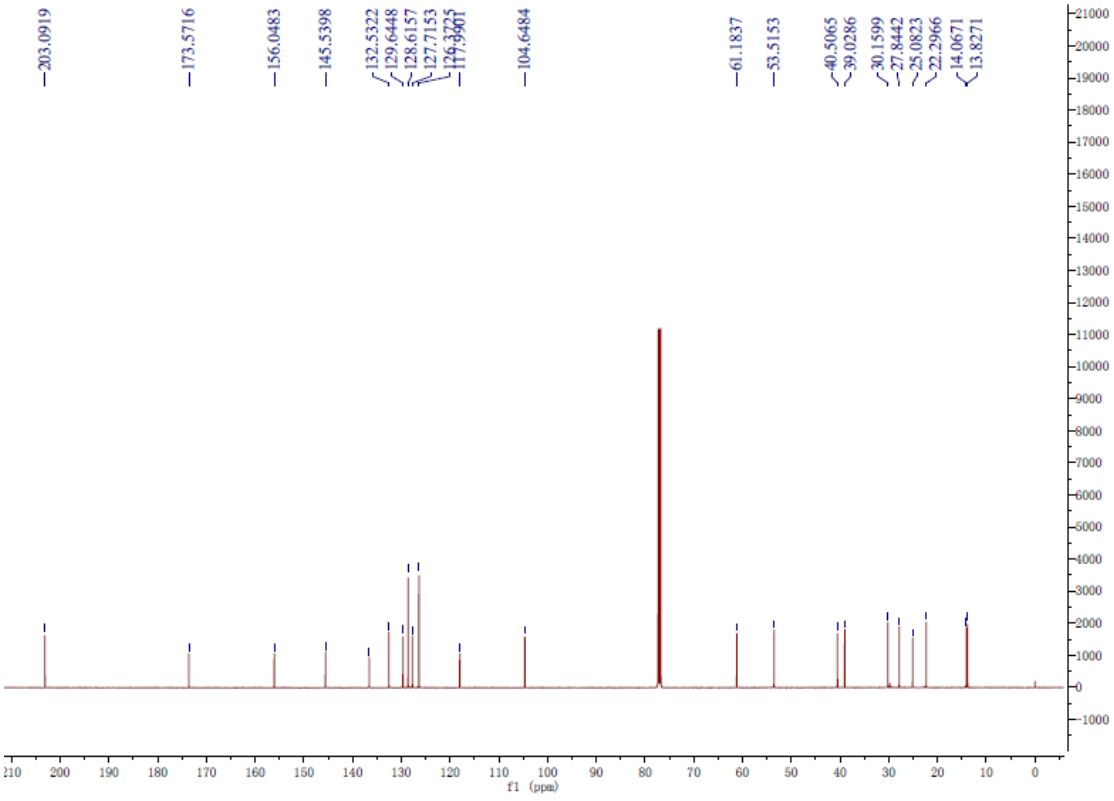
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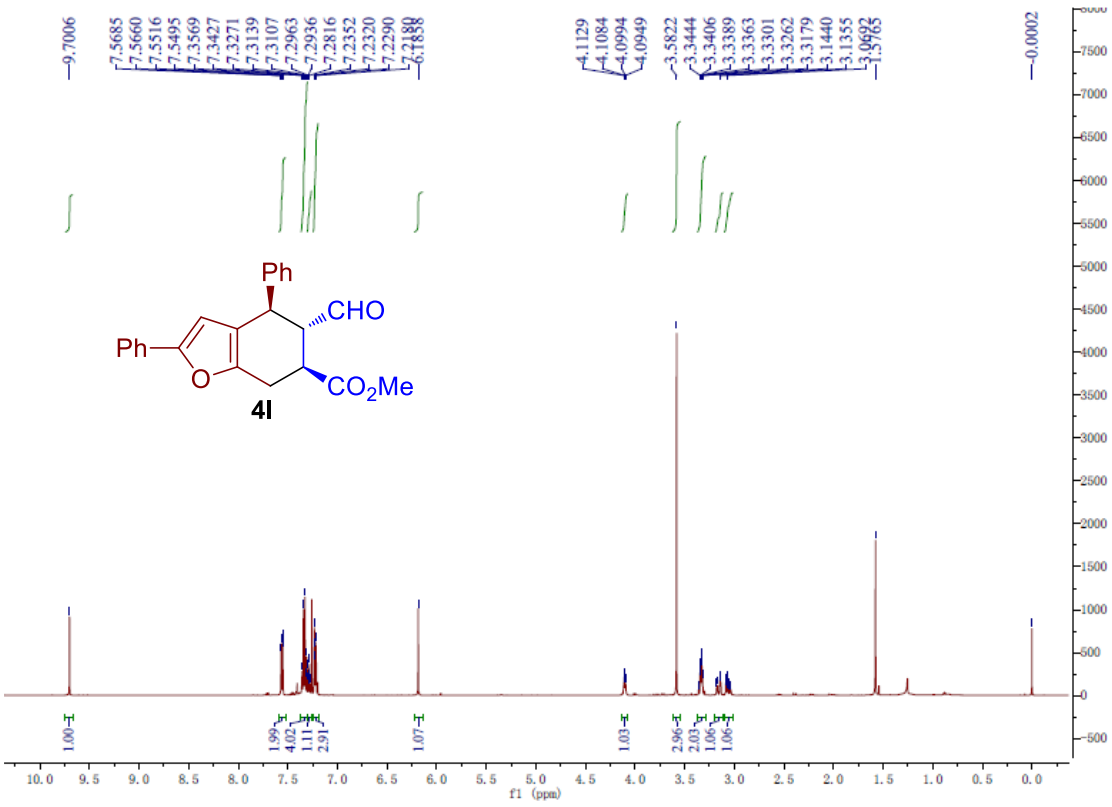
f1 (ppm)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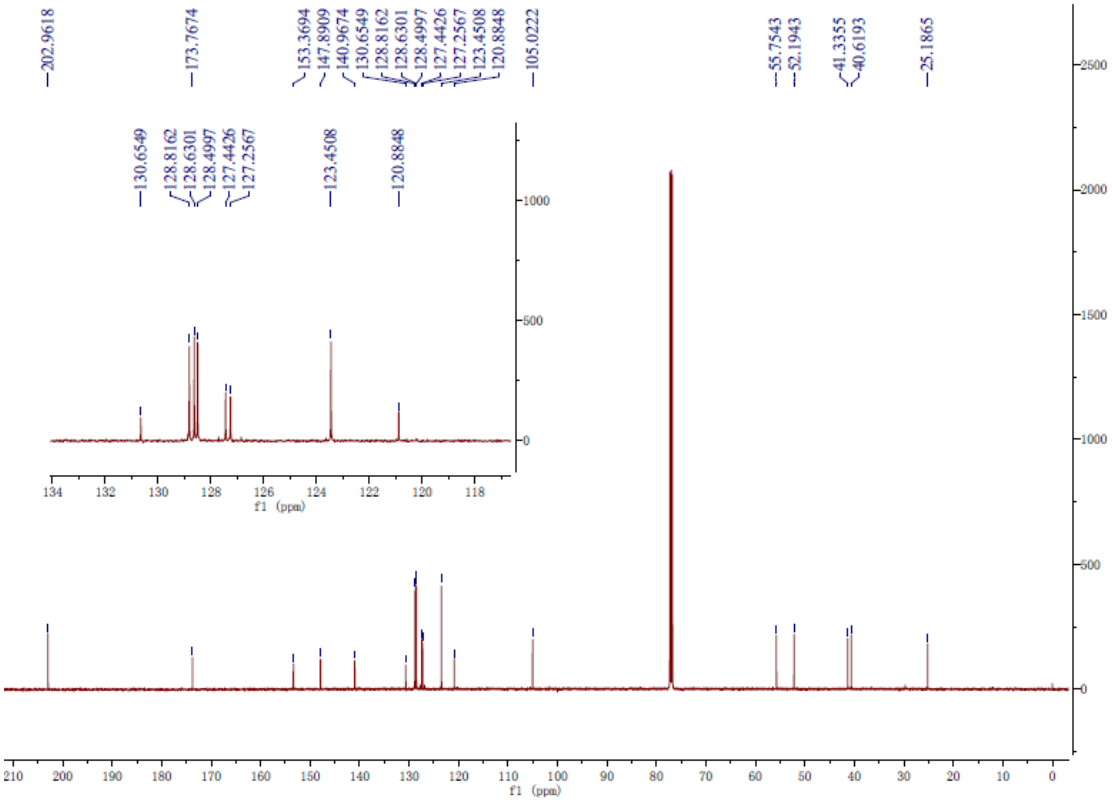

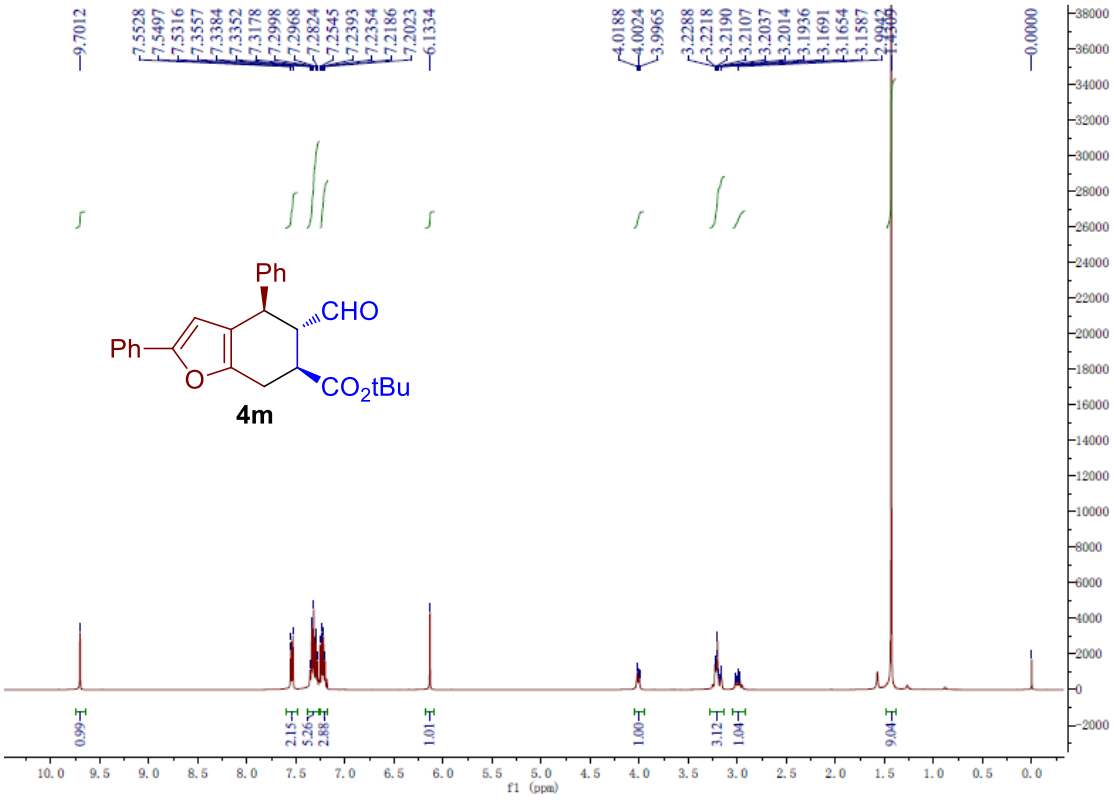
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Ph
O
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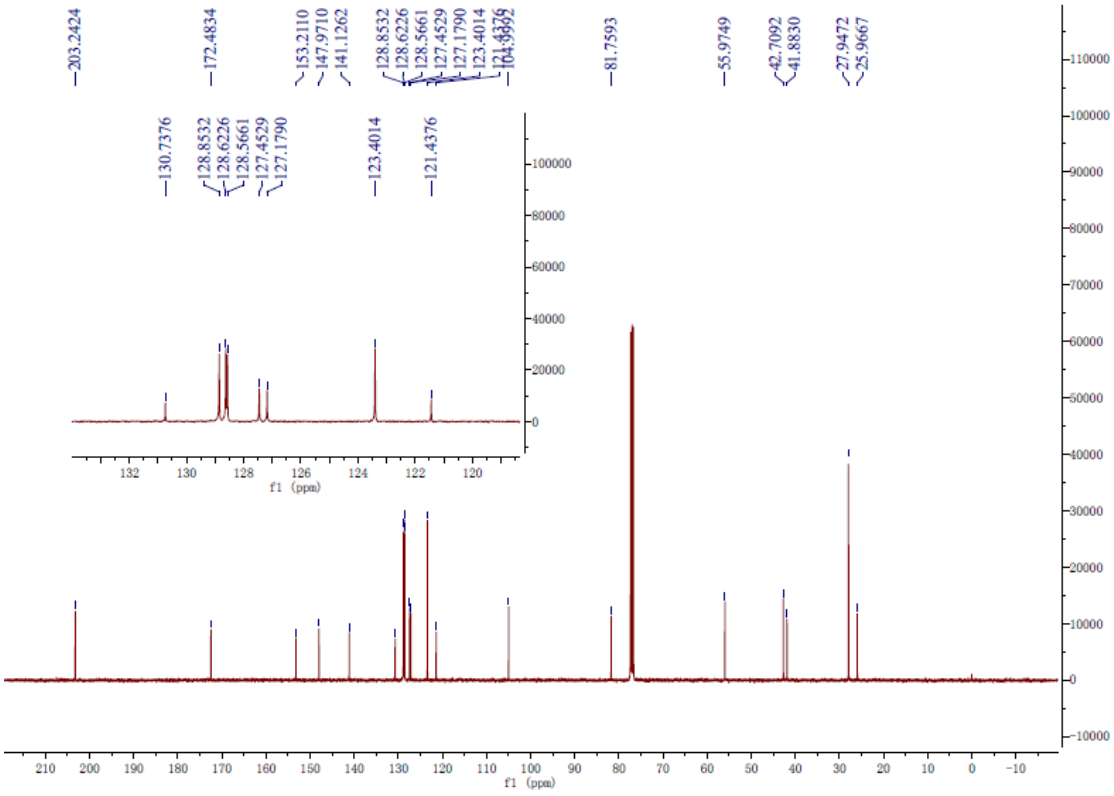

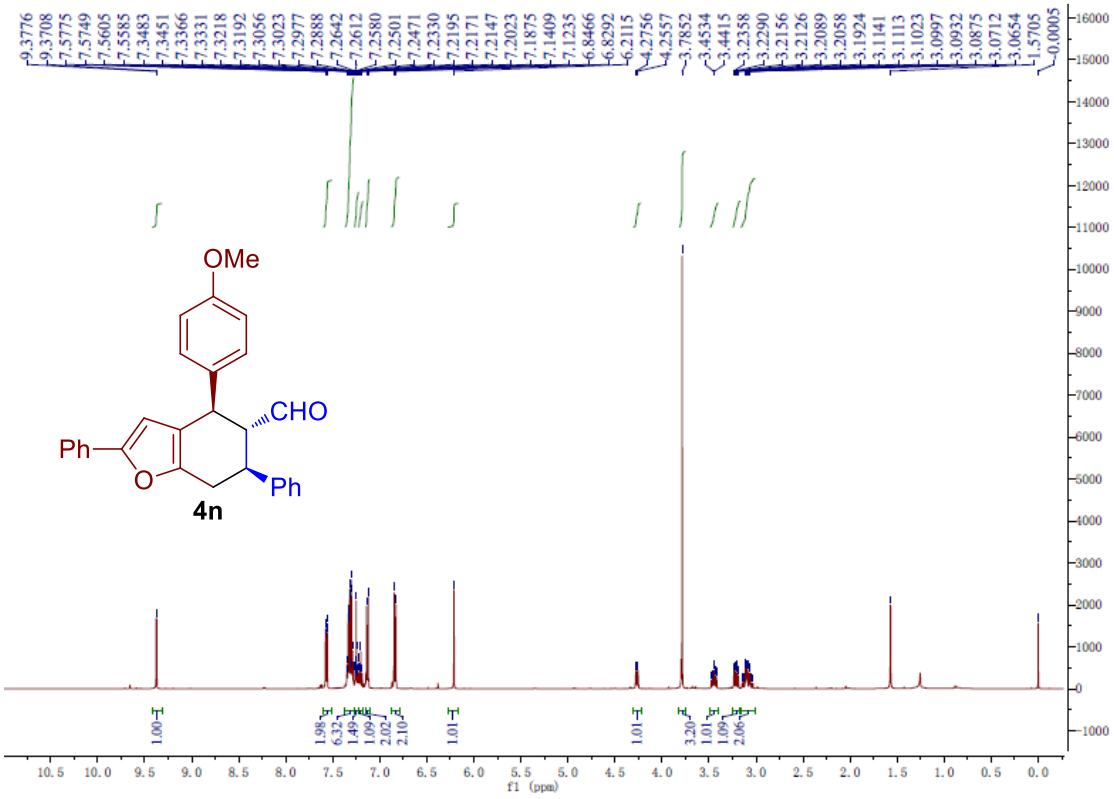
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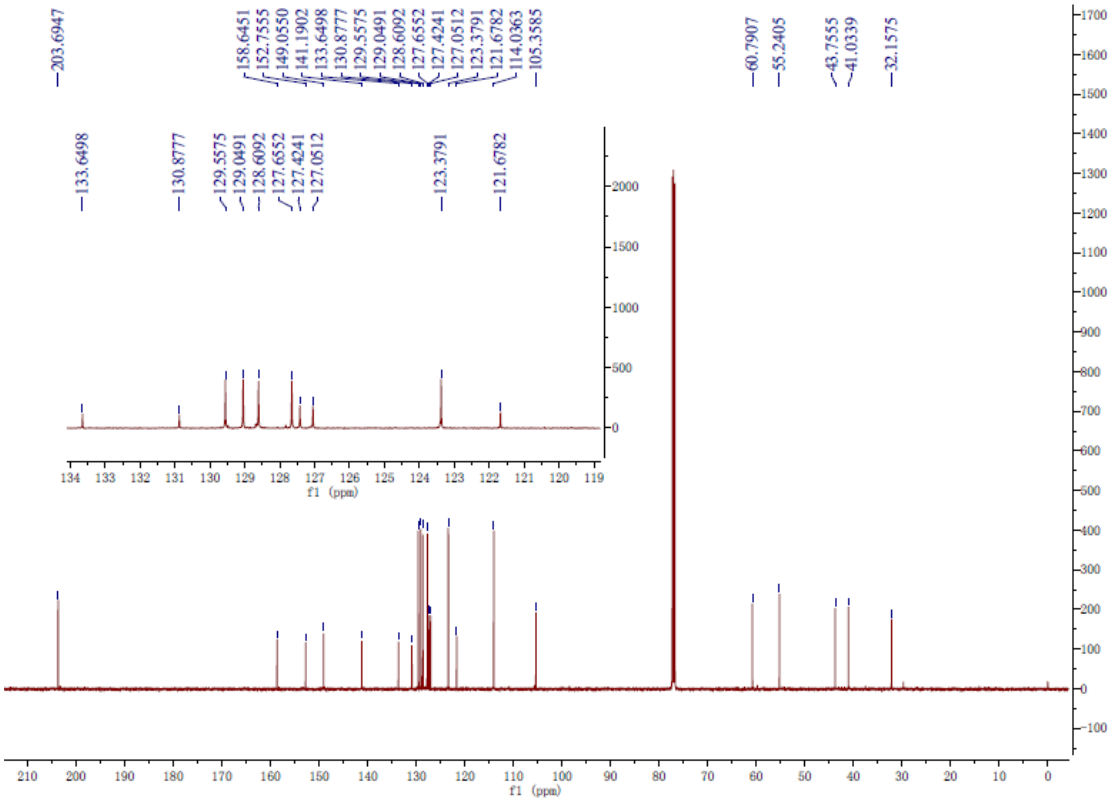

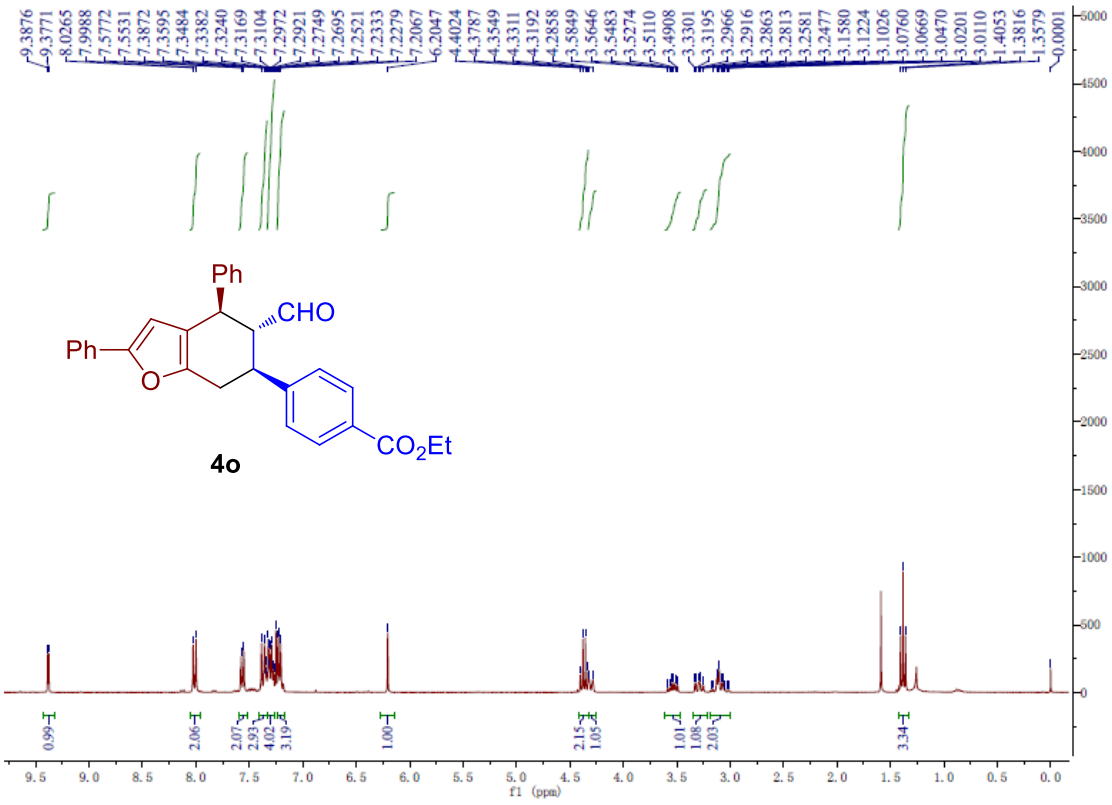

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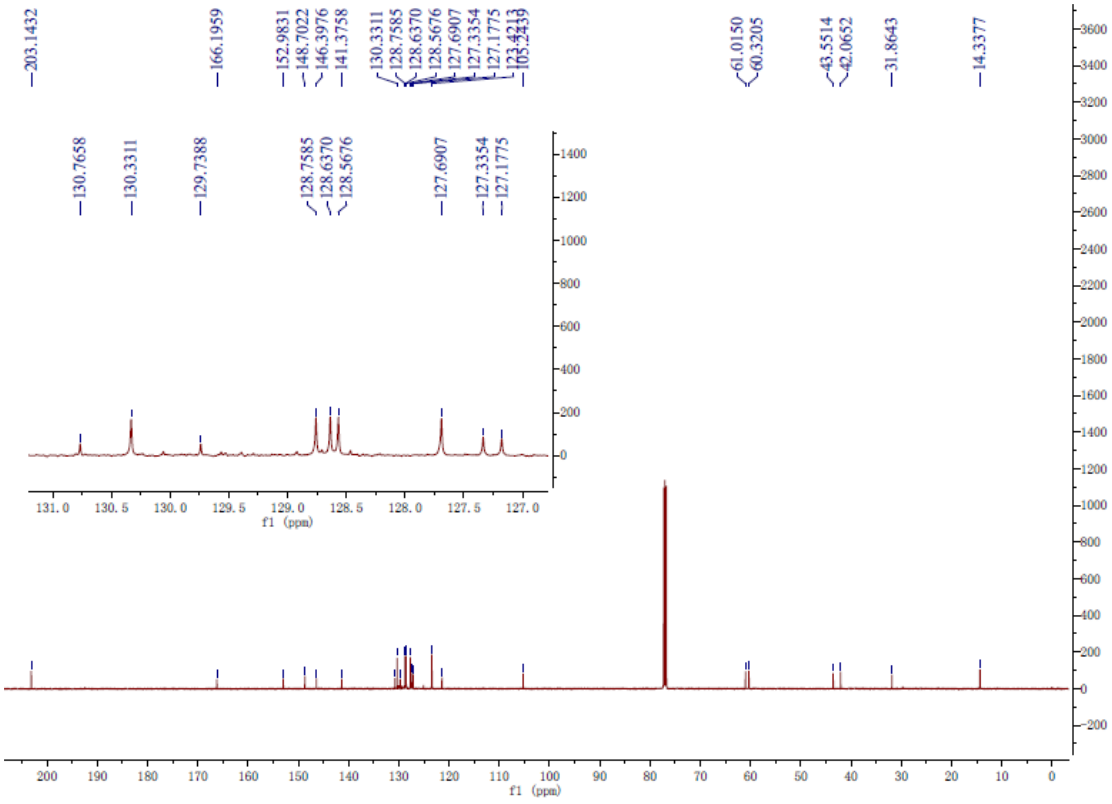

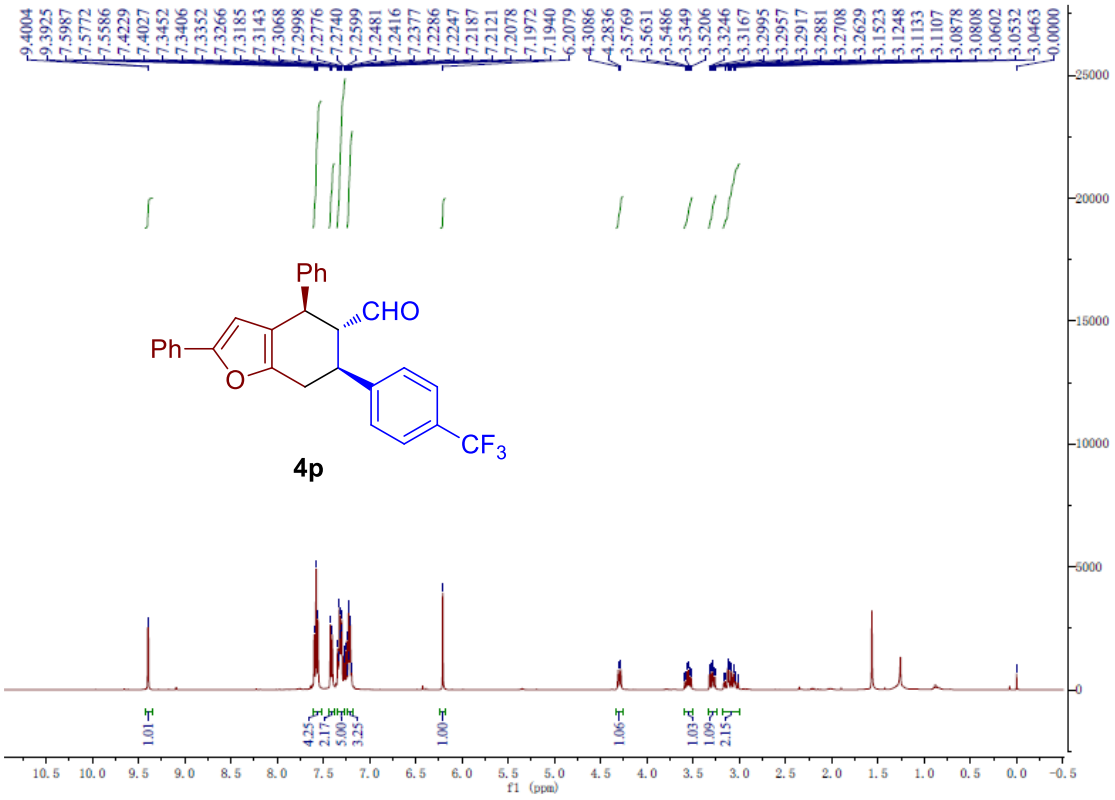
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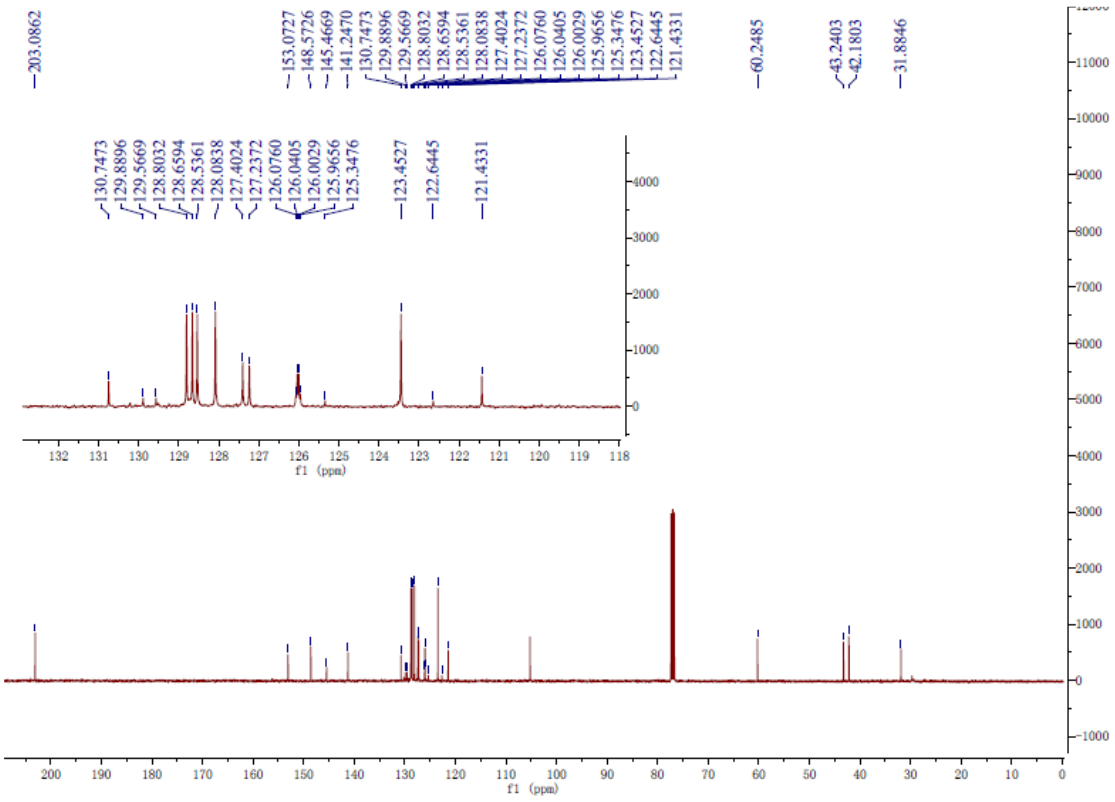
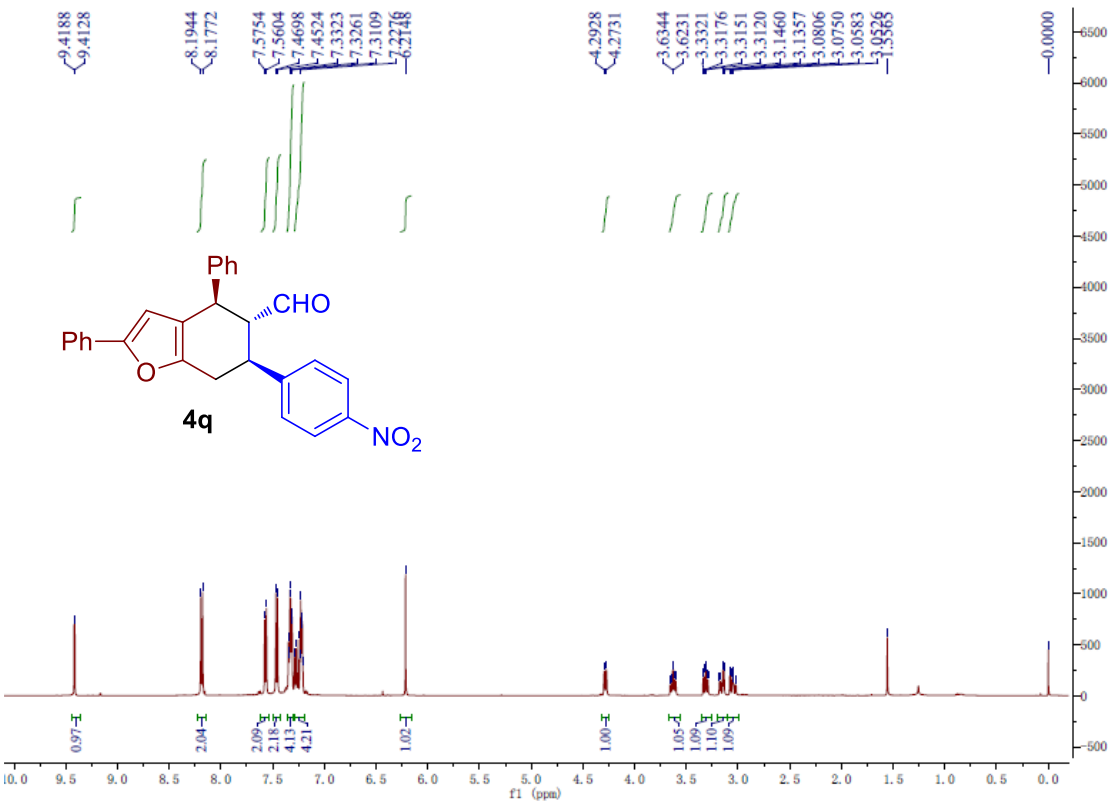
Ph
O
CF3
4p

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Ph
O
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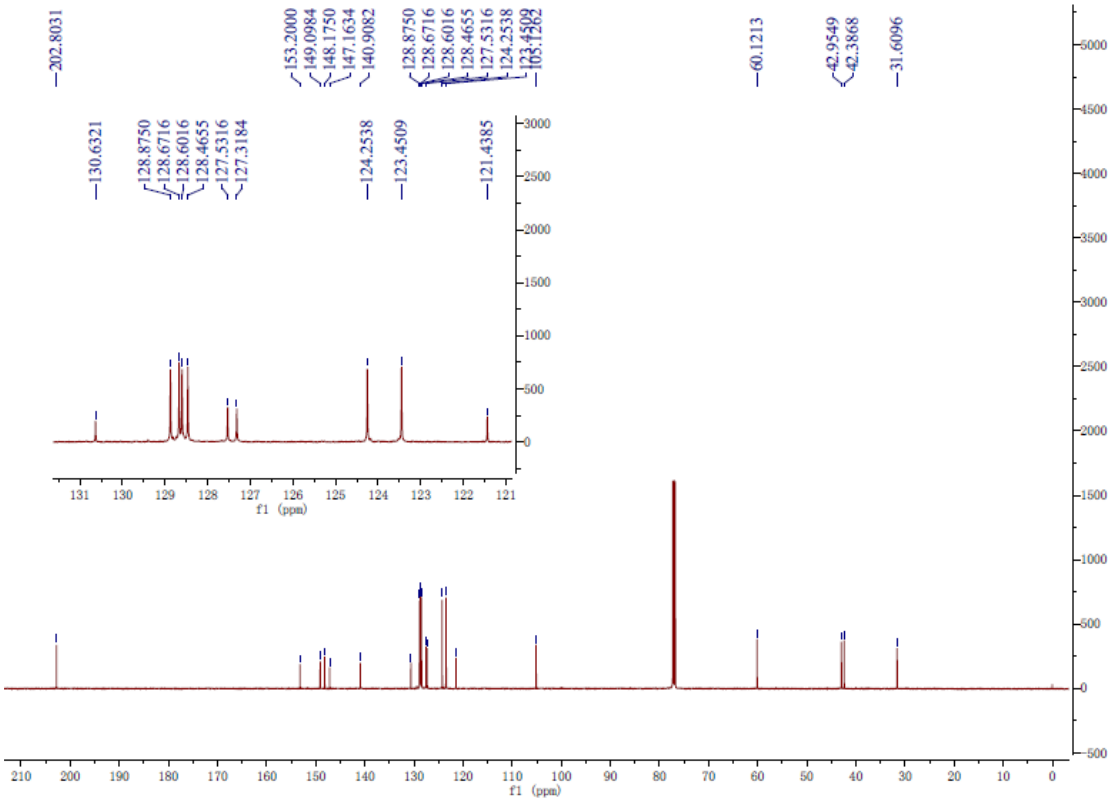
NO2
f1 (ppm)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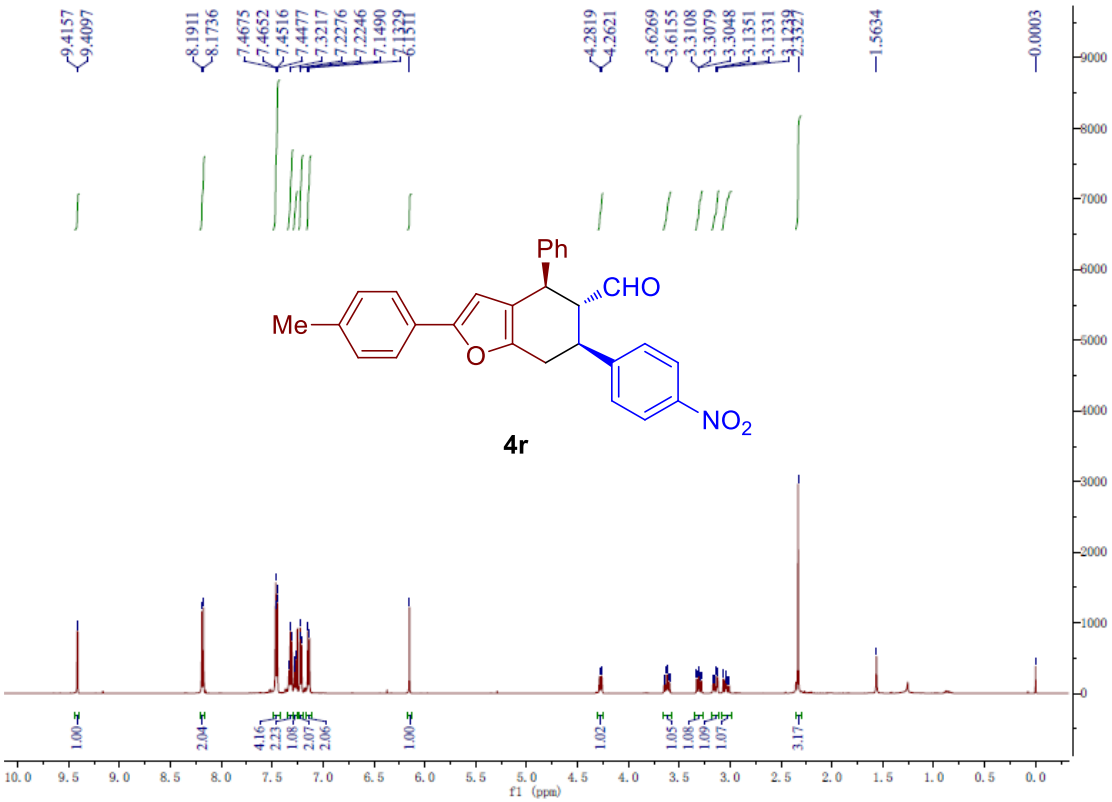
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7.1329
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3.6155
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3.3079
3.3048
3.1351
3.1331
3.1329
2.3527
1.5634
0.0003
Ph
CHO
Me
O
NO2
4r
1.00
2.04
4.16
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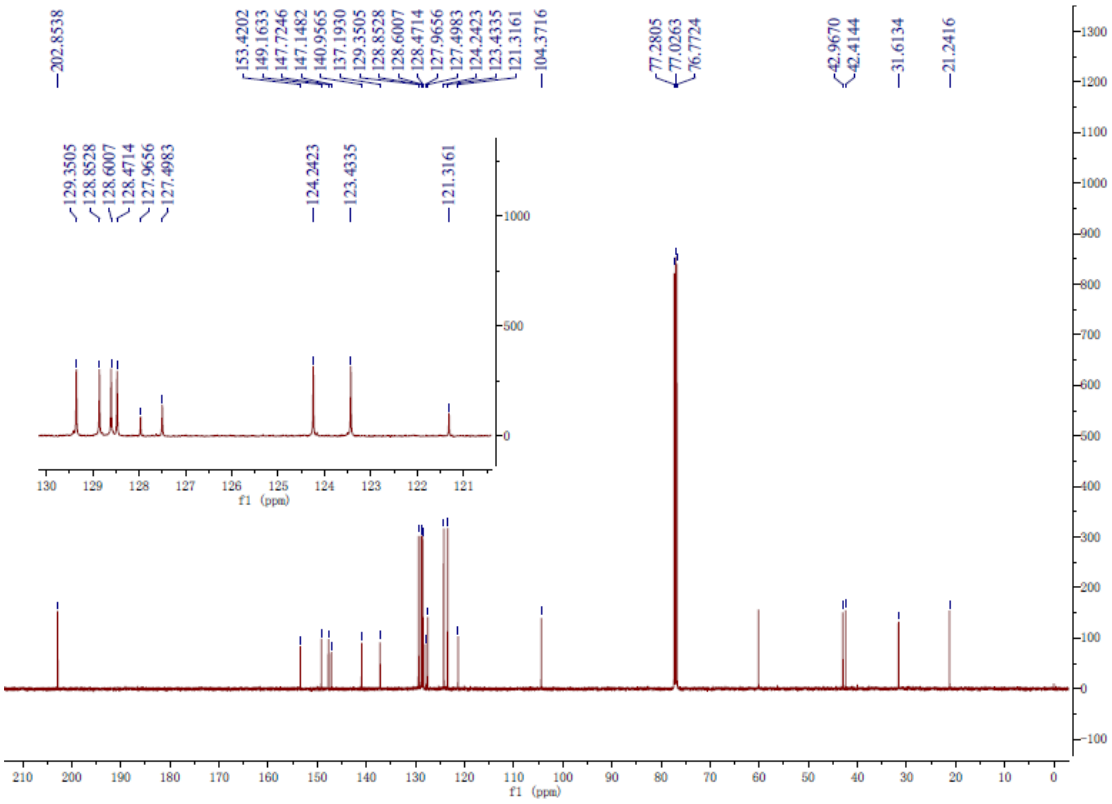
2.06
1.00
1.02
1.05
1.08
1.09
1.07
3.17
f1 (ppm)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127.9656
127.4983
124.2423
123.4335
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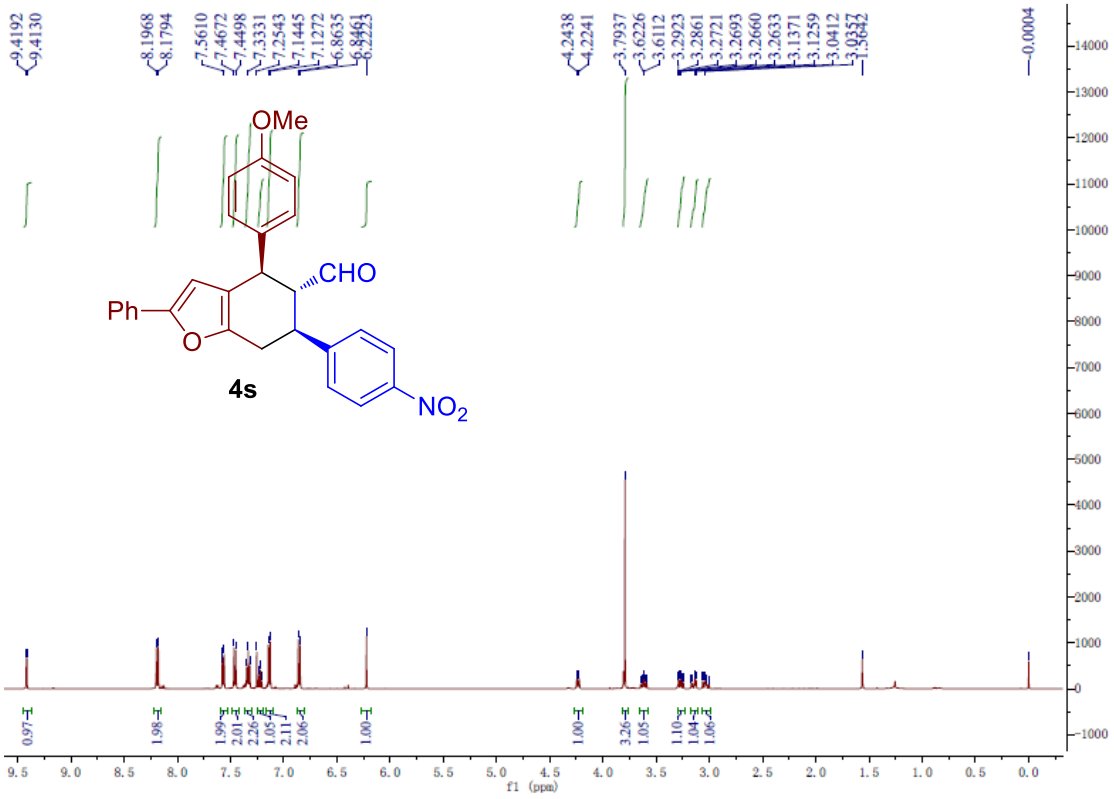
21.2416
f1 (ppm)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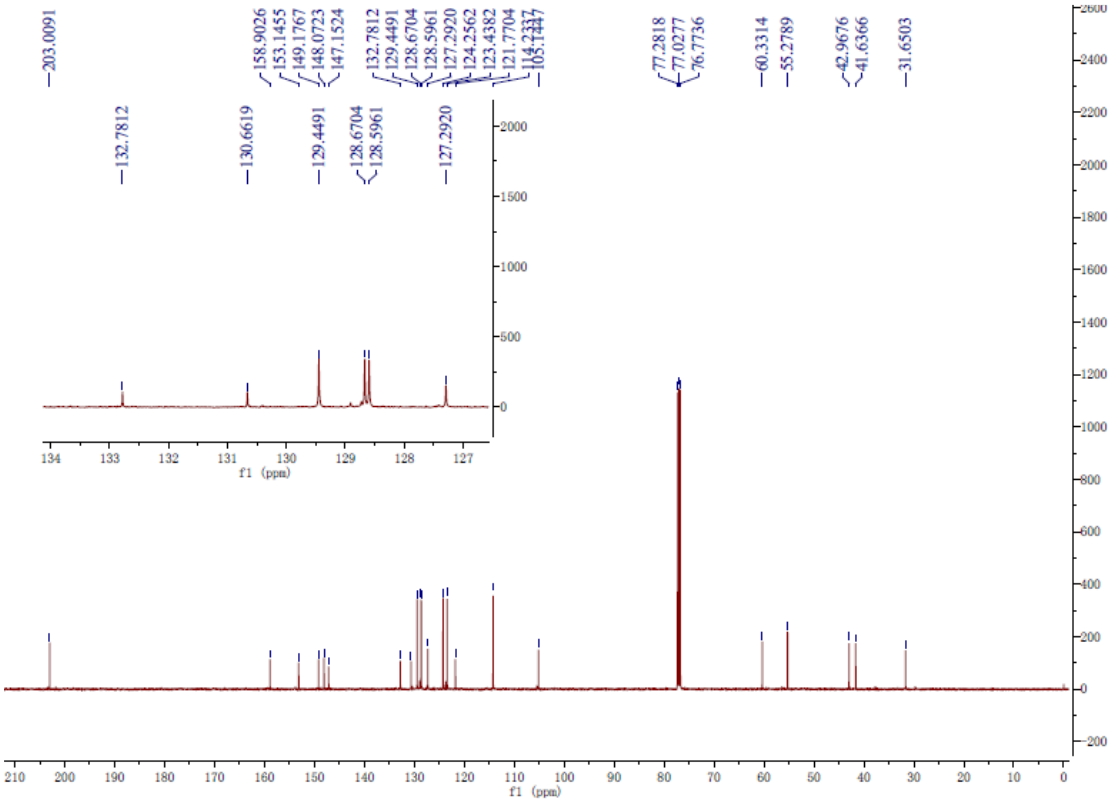
CHO
Ph
O
4s
NO2
f1 (ppm)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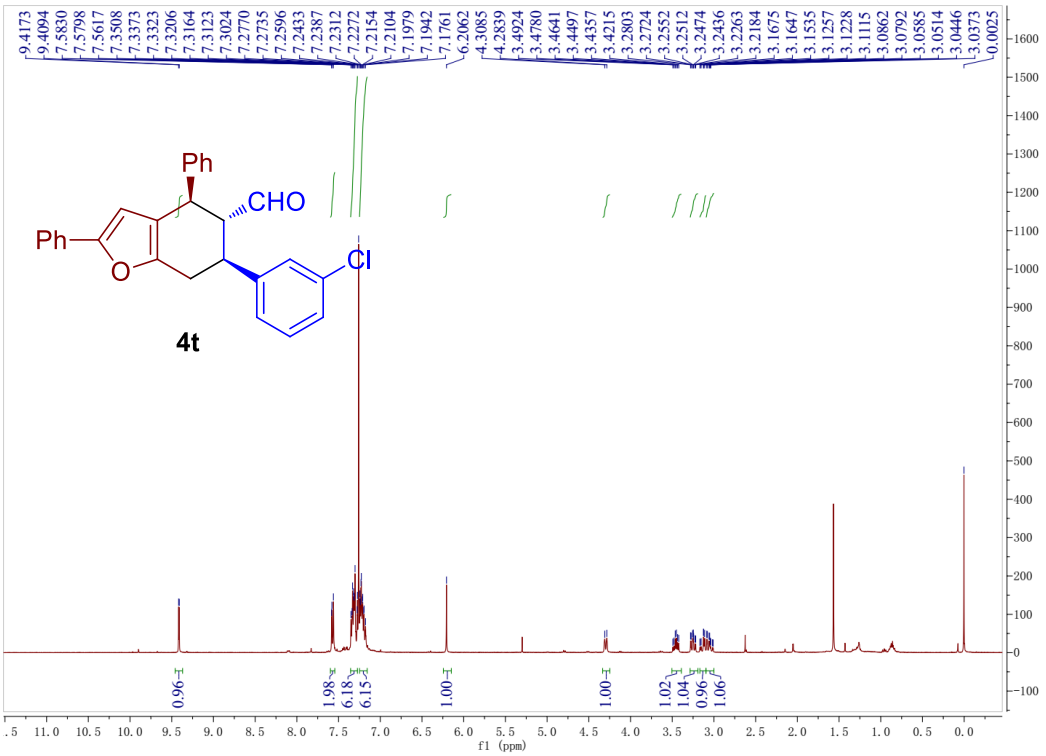
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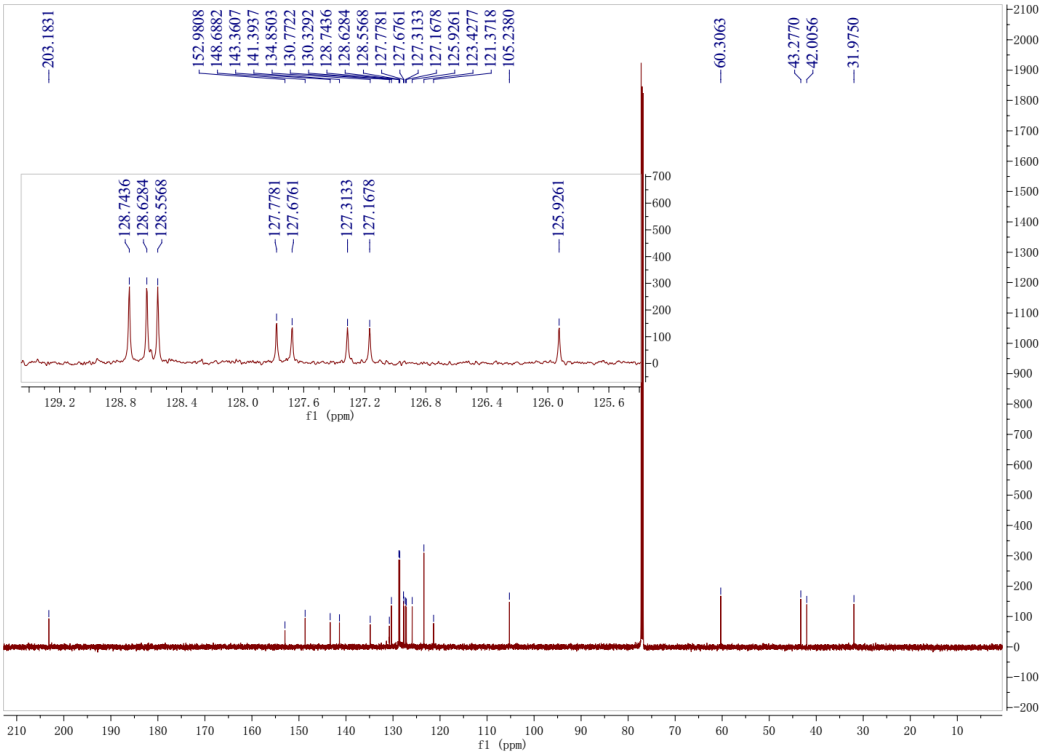
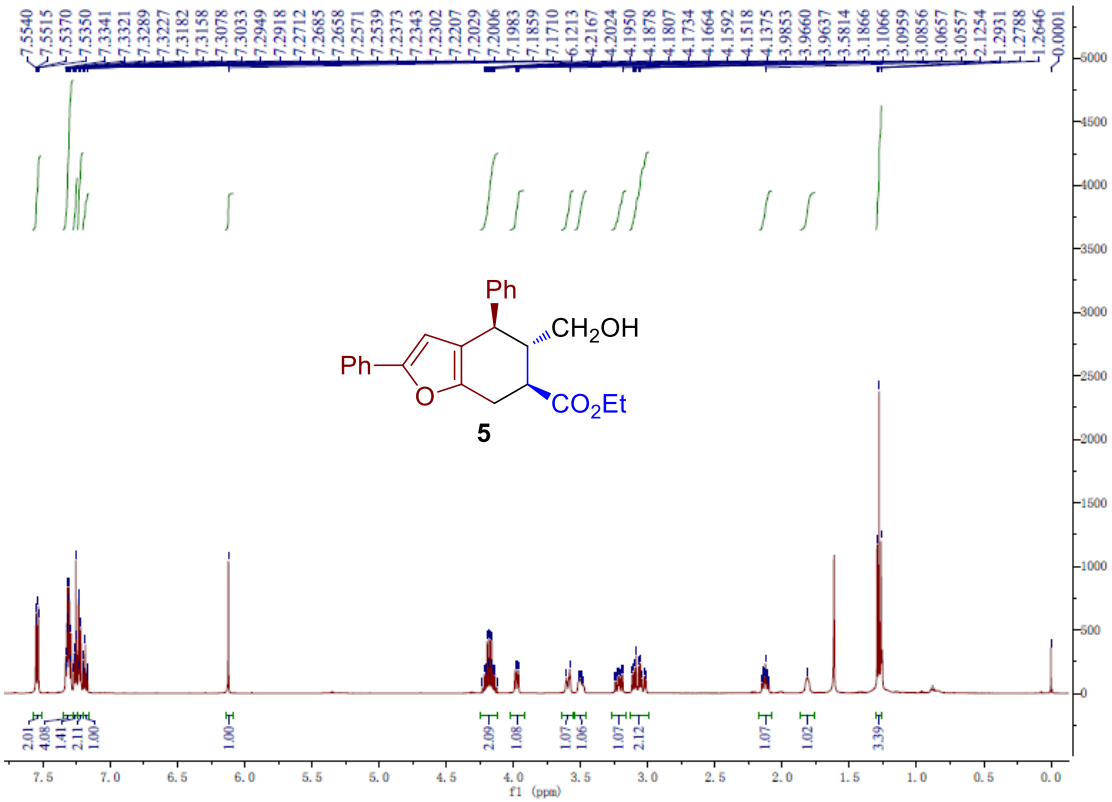
CHO
Ph
O
Cl
4t
f1 (ppm)


f1 (ppm)
f1 (ppm)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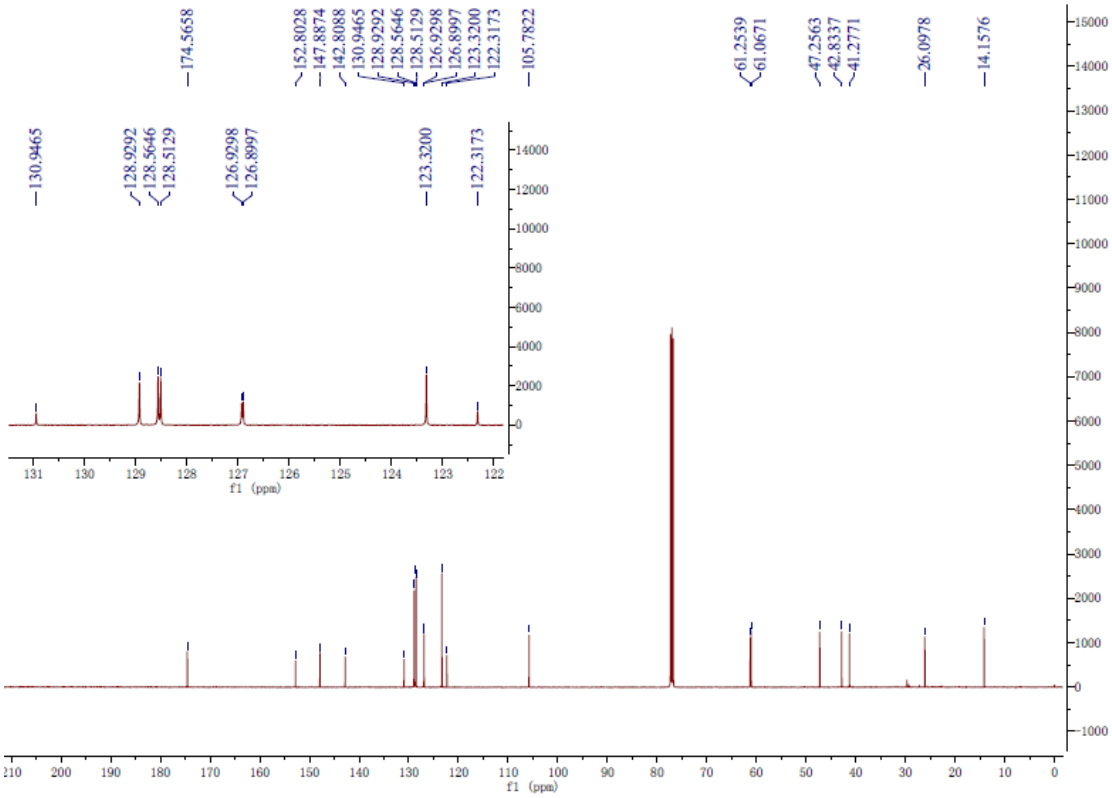
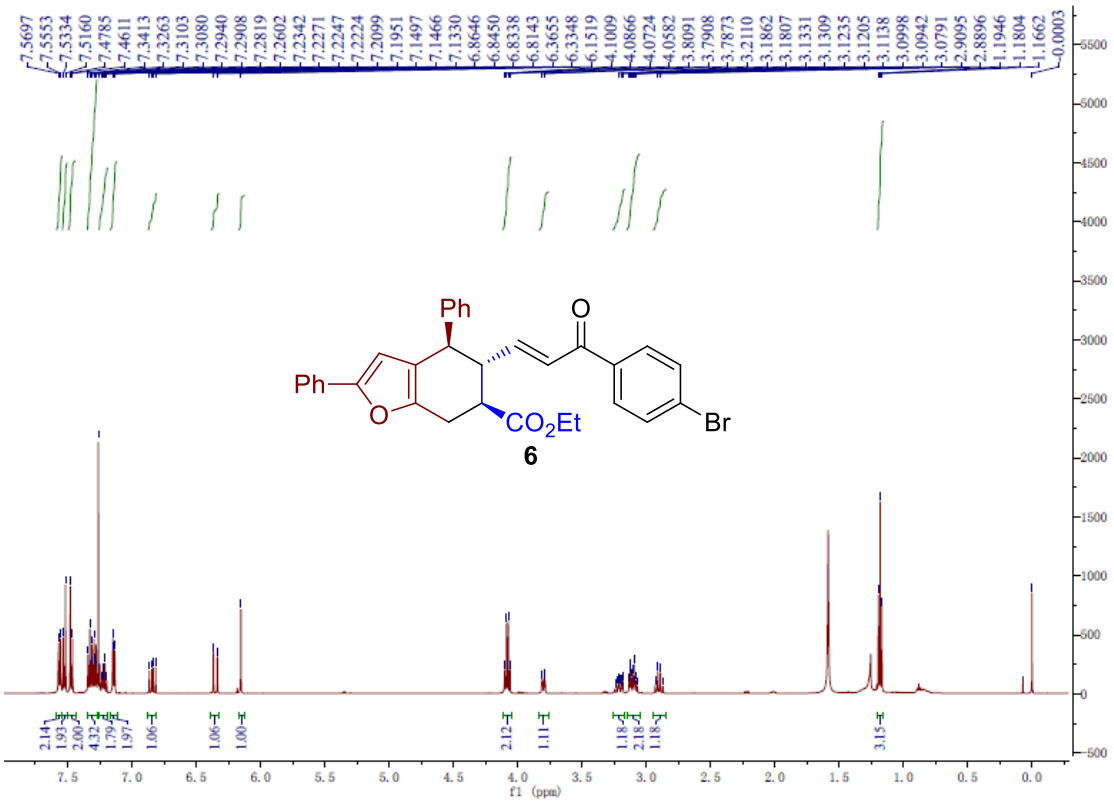
Ph
O
CO2Et
5

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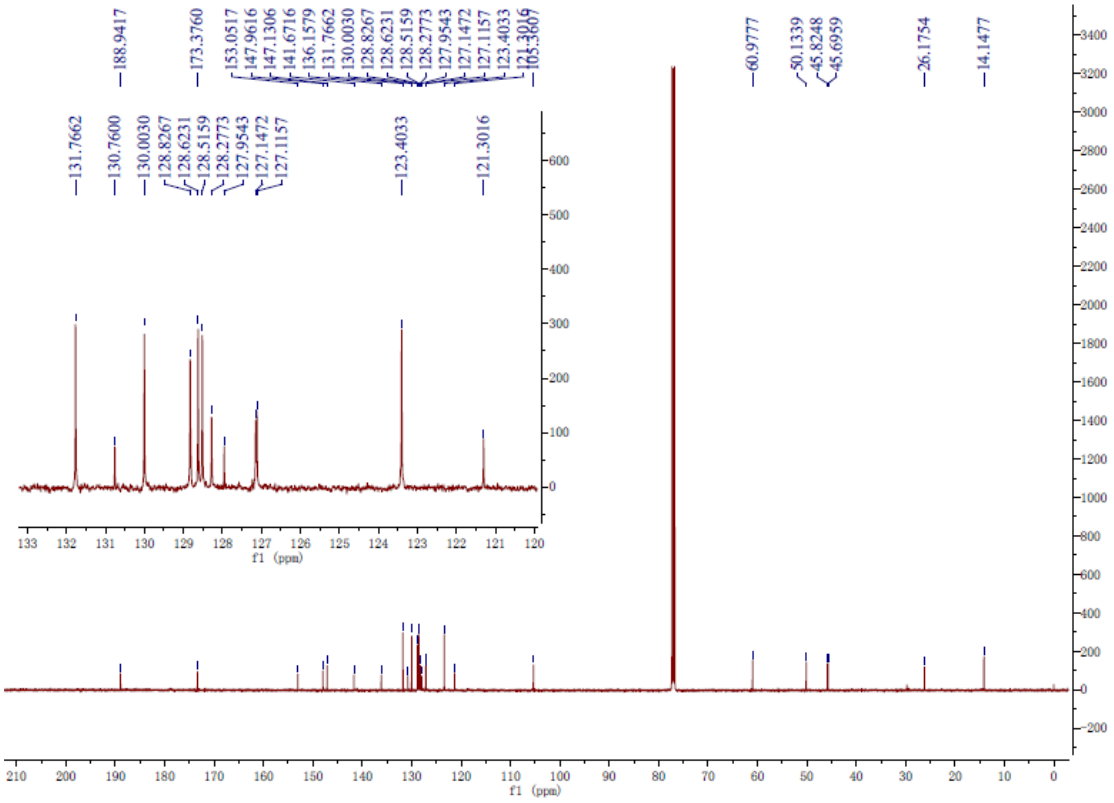
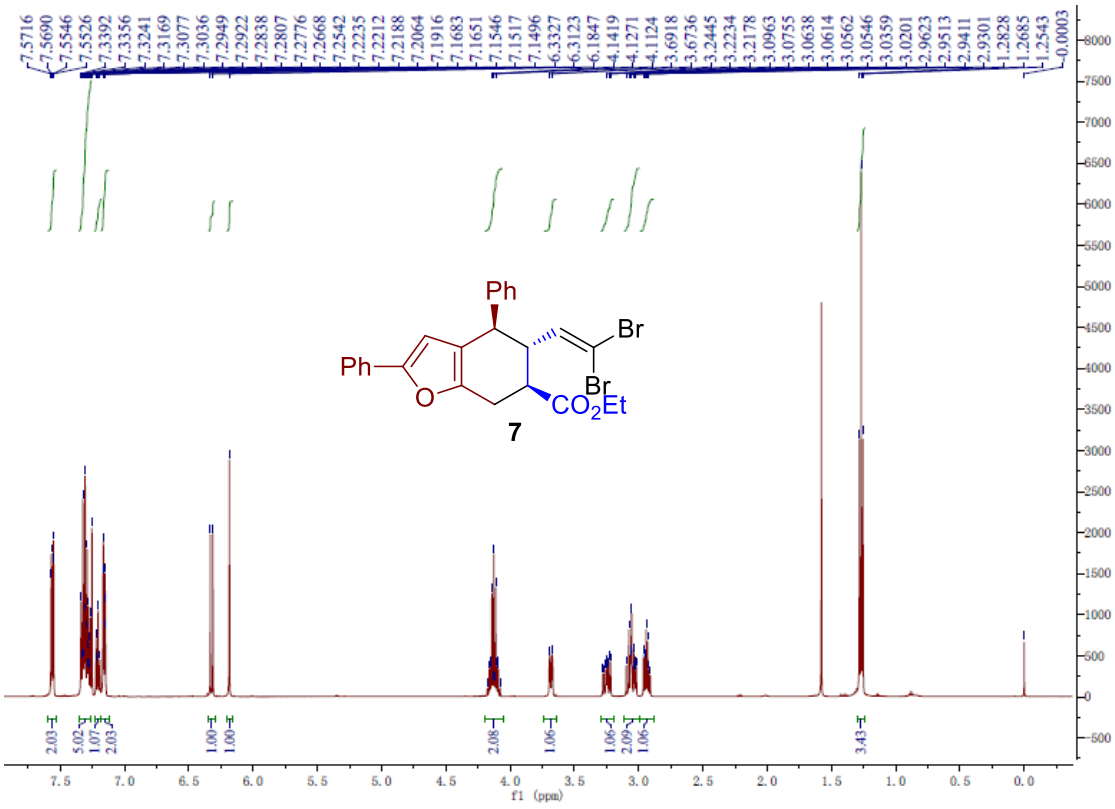
Ph
O
CO2Et
Br
6

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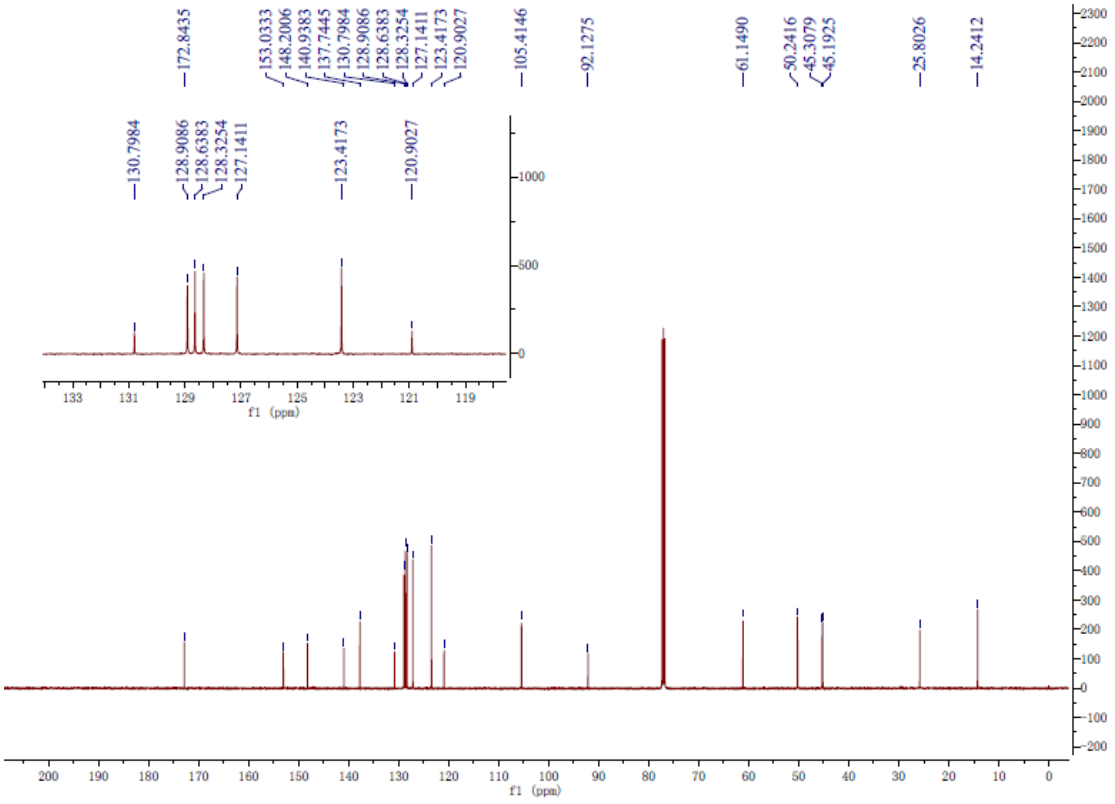
Br
Ph
O
Br
CO2Et
7
f1 (ppm)


f1 (ppm)