Highly Diastereo- and Enantiselective Michael Addition of 3-Substituted Benzofuran-2(3H)-ones to 4-oxo-enoates Catalyzed by Lanthanide(III)-*N,N'*-dioxide Complexes

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Contents:

(A) General Information:

^{1}H NMR spectra were recorded at 400 MHz. The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constants (Hz), integration. ^{13}C NMR data were collected at 100 MHz with complete proton decoupling.

Enantiomeric excesses (*ee*'s) were determined by chiral HPLC analysis on Daicel Chiralcel IA, IB, IC, OD-H and AD-H columns in comparison with the authentic racemates. Optical rotations were reported as follows: $[\alpha]_D^T$ (c: g/100 mL, in solvent). ESI-HRMS spectra were recorded on a commercial apparatus and methanol or acetonitrile was used to dissolve the sample. All reactions were performed in sealed oven-dried glass tubes under an atmosphere of air. THF was distilled from sodium benzophenone ketyl. CH_2Cl_2 was distilled over CaH_2. EtOH was used without further purification. 4 Å MS was powdered <50 μm, which was activated at 400 ^{o}C for 2 h.

(B) Typical experimental procedure for the asymmetric Michael additions of benzonfuran-2(3H)-ones to 4-oxo-enoates:

The procedure for scandium-catalyzed Michael additions of benzonfuran-2(3H)-ones (Procedure A): *N,N'*-dioxide **L7** (3.4 mg, 0.006 mmol), scandium triflate (2.5 mg, 0.005 mmol), benzofuran-2(3H)-ones (0.10 mmol), 4 Å molecular sieves (20 mg) and 1.0 mL EtOH were stirred in a dry reaction tube under air at room temperature for 20 min, then the mixture was cooled to 0 ^{o}C or kept at room temperature. After that, 4-oxo-enoates (0.11 mmol) was added to the mixture. The sealed tube was stirred at 0 ^{o}C for 5-20 h or at room temperature (23-25 ^{o}C) for 12 h. The d.r. value was determined by the ^{1}H NMR analysis of crude products which was further purified by flash chromatography (petroleum ether: ethyl acetate = 15:1 to 5:1) on silica gel to afford the desired product (**3a**, 98% yield, 88/12 d.r., 91% *ee* for major isomer). The pure major isomer of products could be isolated by flash chromatography.

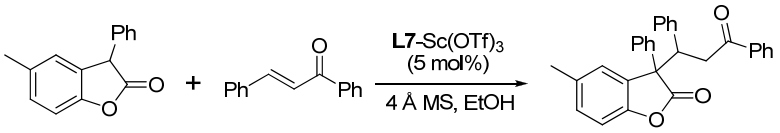
The procedure for the scale-up reaction with 2 mol% catalyst loading: *N,N'*-dioxide **L7** (33.9 mg), scandium triflate (24.6 mg), benzofuran-2(3H)-one **1d** (560.0 mg, 2.5 mmol), 4 Å molecular sieves (200 mg) and 10.0 mL EtOH were stirred in a dry reaction tube under air at room temperature for 20 min, then the mixture was cooled to 0 ^{o}C. After that, 4-oxo-enoate **2e** (609.0 mg, 2.63 mmol) was added to the mixture. The sealed tube was stirred at 0 ^{o}C for 24 h. The d.r. value was determined by the ^{1}H NMR analysis of crude products which was further purified by flash chromatography (petroleum ether: ethyl acetate = 15:1 to 5:1) on silica gel to afford the desired product (**3z**, 1.12g, 98% yield, >95/5 d.r., 94% *ee* for major isomer).

The procedure for yttrium-catalyzed Michael additions of 3-(phenylthio)

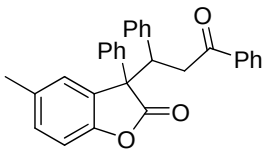
benzofuran-2(3H)-one (Procedure B): *N,N'*-dioxide **L8** (4.4 mg, 0.006 mmol), yttrium triflate (2.7 mg, 0.005 mmol), 4-oxo-enoates (0.11 mmol), 4 Å molecular sieves (20 mg) and 0.6 mL acidic $CHCl_3$ were stirred in a dry reaction tube under air at room temperature for 20 min. The mixture was cooled to 0 ^oC. Then 0.10 mmol 3-(phenylthio)benzofuran-2(3H)-one **1i** (in 0.4 mL acidic $CHCl_3$) was added to the mixture and the sealed tube was stirred at 0 ^oC for 20 h. After that the d.r. value was determined by the ^1H NMR analysis of crude products which was further purified by flash chromatography (petroleum ether: ethyl acetate = 15:1 to 5:1) on silica gel to afford the desired product (**4a**, 92% yield, >95/5 d.r., 92% *ee* for major isomer).

The preparation of acidic chloroform: 300 μL saturated aqueous solution of hydrochloric acid (36 %~38 %) was added to EtOH to form 5.0 mL ethanol solution. Finally, 50 μL such ethanol solution was dissolved in the 5.0 mL distilled chloroform to form the acidic chloroform.

The scandium-catalyzed Michael addition of benzonfuran-2(3H)-one 1b to chalcone: *N,N'*-dioxide **L7** (3.4 mg, 0.006 mmol), scandium triflate (2.5 mg, 0.005 mmol), benzofuran-2(3H)-one **1b** (0.10 mmol), 4 Å molecular sieves (20 mg) and 1.0 mL EtOH were stirred in a dry reaction tube under air at room temperature for 20 min. Then chalcone (0.11 mmol) was added to the mixture and the sealed tube was stirred at 30 ^oC for 20 h. After that, the crude mixture was purified by flash chromatography (petroleum ether: ethyl acetate = 15:1) on silica gel to afford the desired product 4.0 mg (9% yield) with 86/14 d.r., 69% *ee* for major isomer.

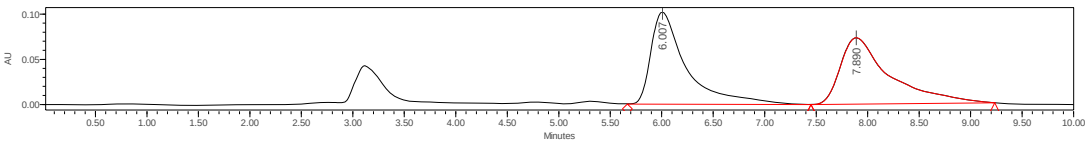


0 ^oC, 24 h: trace
30 ^oC, 20 h: 9% yield
86/14 dr, 69% ee (major)

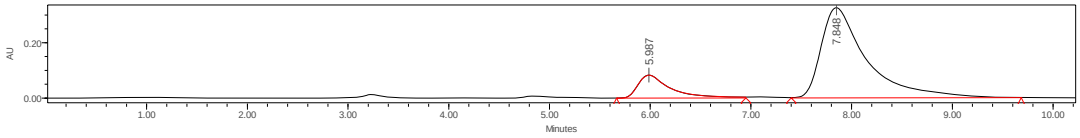


The compound as know compound (ref. **5a** in manuscript):. 9% yield, 86/14 d.r., 69% *ee* of major isomer. HPLC (chiral OD-H column), hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm, major diastereomer: *t*r (major) = 7.85 min, *t*r (minor) = 5.99 min.

Major isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.58 (m, 4H), 7.56 – 7.45 (m, 2H), 7.44 – 7.26 (m, 5H), 7.23 – 7.17 (m, 1H), 7.12 – 6.97 (m, 3H), 6.85 (t, *J* = 7.2 Hz, 3H), 4.73 (dd, *J* = 11.2, 2.0 Hz, 1H), 3.71 (dd, *J* = 16.8, 11.6 Hz, 1H), 3.23 (dd, *J* = 16.8, 2.4 Hz, 1H), 2.57 (s, 3H).

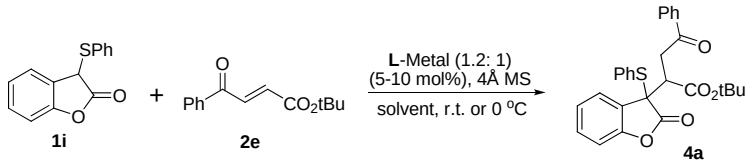


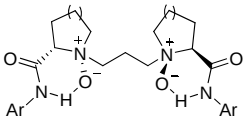
	Retention Time	Area	% Area
1	6.007	2439902	49.95
2	7.890	2445088	50.05



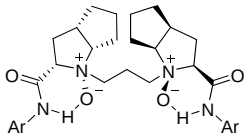
	Retention Time	Area	% Area
1	5.987	1883778	15.57
2	7.848	10212653	84.43

(C) Optimization of Michael reaction of 3-(phenylthio) benzofuran-2(3H)-one to 4-oxo-enoates:





L4: Ar = 2,6-*i*-$Pr_2C_6H_3$, n = 2
L10: Ar = 2,6-*i*-$Pr_2C_6H_3$, n = 1
L7: Ar = 2,4,6-$Me_3C_6H_2$, n = 2
L8: Ar = 2,4,6-*i*-$Pr_3C_6H_2$, n = 2

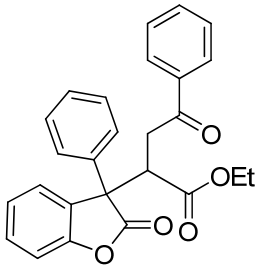


L9: Ar = 2,4,6-*i*-$Pr_3C_6H_2$

Entry	Metal	L	X mol%	Solvent	*T* [°C]	Time [h]	Yield [%] [b]	d.r. [%] [c]	*ee* [%] [c]
1	***Sc(OTf)$_3$***	***L7***	***5***	***EtOH***	***0***	***24***	***96***	***69/31***	***51***
2	Sc(OTf)$_3$	**L4**	10	CH_2Cl_2	25	5	97	73/27	37
3	Y(OTf)$_3$	**L4**	10	CH_2Cl_2	25	5	96	85/15	58
4	Y(OTf)$_3$	**L10**	10	CH_2Cl_2	25	5	93	94/6	28
5	Y(OTf)$_3$	**L9**	10	CH_2Cl_2	25	5	92	89/11	11
6	Y(OTf)$_3$	**L8**	10	CH_2Cl_2	25	5	98	93/7	69
7	Y(OTf)$_3$	**L8**	10	EtOAc	25	5	98	95/5	44
8	Y(OTf)$_3$	**L8**	10	THF	25	5	99	92/8	62
9	Y(OTf)$_3$	**L8**	5	EtOH	0	6	93	98/2	78
10	Y(OTf)$_3$	**L8**	5	$CHCl_3$[d]	0	24	89	96/4	86
11	Y(OTf)$_3$	**L8**	5	$CHCl_3$[e]	0	24	25	92/8	58
12	Y(OTf)$_3$	**L8**	5	$CHCl_3$[f]	0	20	91	93/7	82
13	***Y(OTf)$_3$***	***L8***	***5***	***$CHCl_3$[g]***	***0***	***20***	***91***	***>95/5[h]***	***92***

[a] Unless otherwise noted, reactions were carried out with **L** (12 or 6 mol%), metal (10 or 5 mol%), 4 Å MS (20 mg), **1a** (0.10 mmol), and **2a** (0.11 mmol) in solvent (1.0 mL). [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] Using unpurified $CHCl_3$ as solvent. [e] Using distilled $CHCl_3$ as solvent. [f] Using 1.0 mL distilled $CHCl_3$ and 20μL EtOH as solvent. [g] Using 1.0 mL acidic $CHCl_3$ as solvent. [h] The d.r. was determined to be > 95/5 by ^{1}H NMR analysis of crude products.

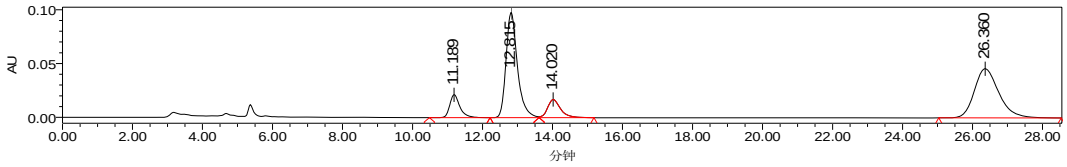
(D) The analytical and spectral characterization data for the product:



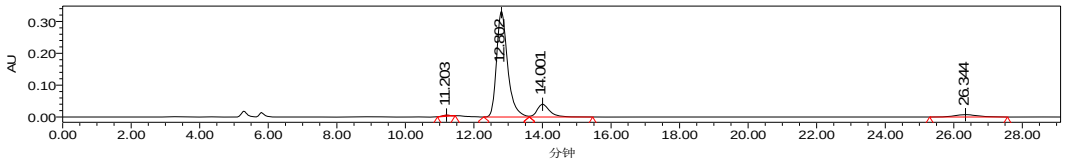
Compound **3a**: Prepared according to the general procedure A at 0 °C for 5 h. 98% yield, 88/12 d.r., 91% *ee* of major isomer, 90% *ee* of minor isomer. HPLC (chiral AD-H column), hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 12.80 min, *t*r (minor) = 26.34 min. minor diastereomer: *t*r (major) = 14.00 min, *t*r (minor) = 11.19 min.

Pure of major isomer: $[\alpha]_D^{20} = -77.57$ (c = 0.70 in CH_2Cl_2).

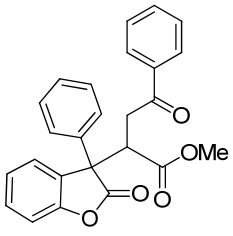
Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 7.2 Hz, 2H), 7.61 (d, J = 7.6 Hz, 1H), 7.52 (t, J = 6.8 Hz, 3H), 7.43 – 7.20 (m, 7H), 7.17 (d, J = 8.0 Hz, 1H), 4.34 (dd, J = 10.8, 2.8 Hz, 1H), 3.84 (q, J = 6.8 Hz, 2H), 3.62 (dd, J = 18.0, 10.8 Hz, 1H), 3.06 (dd, J = 18.0, 2.8 Hz, 1H), 0.84 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 176.4, 171.9, 152.9, 136.2, 136.2, 133.6, 129.7, 129.1, 128.7, 128.4, 128.4, 128.2, 127.1, 126.4, 124.5, 111.2, 61.2, 56.6, 48.2, 37.6, 13.6. ESI-HRMS: calcd for $C_{26}H_{22}NaO_5^+$ ([M + Na]$^+$) 437.1365, found 437.1364; calcd for $C_{26}H_{23}O_5^+$ ([M + H]$^+$) 415.1545, found 415.1541.



	Retention Time	Area	% Area
1	11.189	427688	8.08
2	12.815	2214133	41.81
3	14.020	432859	8.17
4	26.360	2220917	41.94



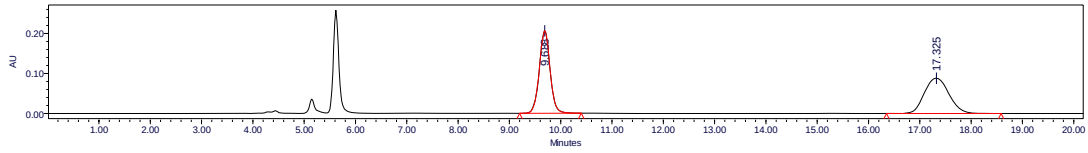
	Retention Time	Area	% Area
1	11.203	55253	0.62
2	12.802	7422555	83.95
3	14.001	1018747	11.52
4	26.344	344702	3.90



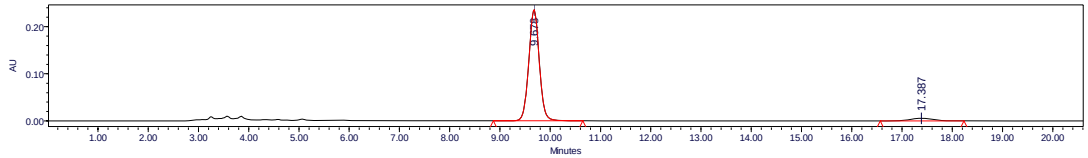
Compound **3b**: Prepared according to the general procedure A at 0 °C for 5 h. 94% yield, 78/22 d.r., 90% *ee* of major isomer. HPLC (chiral IA column), hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 9.68 min, *t*r (minor) = 17.39 min.

Pure of major isomer: $[\alpha]_D^{20} = -87.76$ (c = 0.48 in CH_2Cl_2).

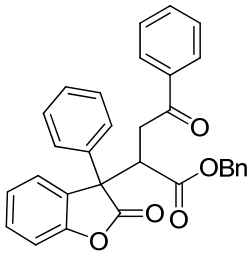
Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ7.92 – 7.72 (m, 2H), 7.70 – 7.58 (m, 1H), 7.58 – 7.45 (m, 3H), 7.45 – 7.25 (m, 6H), 7.25 – 7.20 (m, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 4.37 (dd, *J* = 10.4, 2.8 Hz, 1H), 3.62 (dd, *J* = 18.0, 10.4 Hz, 1H), 3.36 (s, 3H), 3.09 (dd, *J* = 18.0, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 176.4, 172.6, 152.9, 136.1, 133.6, 129.7, 129.2, 128.7, 128.4, 128.4, 128.2, 127.0, 126.3, 124.5, 111.2, 56.6, 52.2, 48.2, 37.7. ESI-HRMS: calcd for $C_{25}H_{20}NaO_5^+$ ([M + Na]$^+$) 423.1208, found 423.1205; calcd for $C_{25}H_{21}O_5^+$ ([M + H]$^+$) 401.1389, found 401.1393.



	Retention Time	Area	% Area
1	9.688	3009938	50.60
2	17.325	2938326	49.40

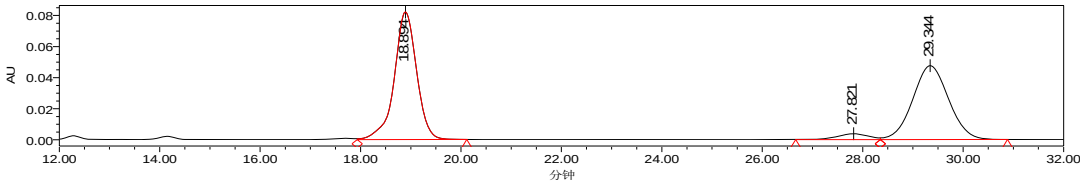


	Retention Time	Area	% Area
1	9.678	3431530	94.98
2	17.387	181554	5.02

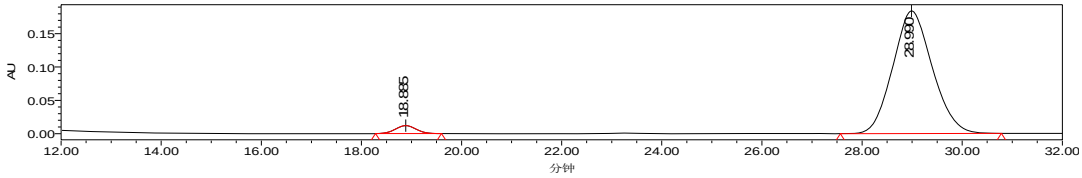


Compound **3c**: Prepared according to the general procedure A at 0 ^{o}C for 5 h. 96% yield, 86/14 d.r., 93% *ee* of major isomer. HPLC (chiral IE column), hexane/ *i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 28.99 min, *t*r (minor) = 18.89 min.
Pure of major isomer: $[\alpha]_D^{20} = -57.95$ (*c* = 0.83 in CH_2Cl_2).

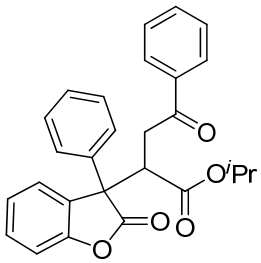
Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.2 Hz, 2H), 7.58 – 7.44 (m, 4H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.35 – 7.18 (m, 7H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.05 – 6.85 (m, 2H), 4.82 (dd, *J* = 32.4, 12.0 Hz, 2H), 4.43 (dd, *J* = 10.8, 2.8 Hz, 1H), 3.61 (dd, *J* = 17.6, 10.8 Hz, 1H), 3.06 (dd, *J* = 17.6, 2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 176.4, 171.9, 152.9, 136.2, 136.1, 135.1, 133.5, 129.7, 129.1, 128.7, 128.4, 128.2, 128.2, 128.1, 127.1, 126.4, 124.5, 111.2, 67.2, 56.6, 48.0, 37.7. ESI-HRMS: calcd for $C_{31}H_{24}NaO_5^+$ ([M + Na]$^+$) 499.1521, found 499.1522; calcd for $C_{31}H_{25}O_5^+$ ([M + H]$^+$) 477.1702, found 477.1704.



	Retention Time	Area	% Area
1	18.894	2534594	50.14
2	27.821	161848	3.20
3	29.344	2358735	46.66

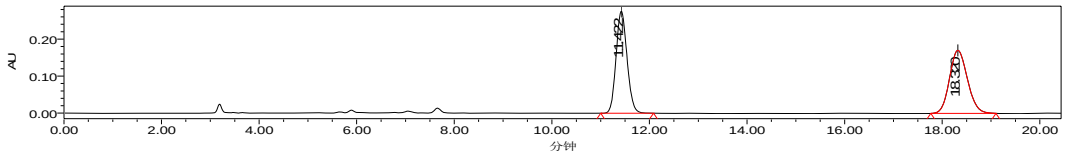


	Retention Time	Area	% Area
1	18.885	348484	3.35
2	28.990	10064480	96.65



Compound **3d**: Prepared according to the general procedure A at 0 °C for 5 h. 98% yield, 93/7 d.r., 94% *ee* of major isomer. HPLC (chiral IE column), hexane/ *i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 17.71 min, *t*r (minor) = 11.13 min. Pure of major isomer: $[\alpha]_D^{20} = -89.47$ (*c* = 0.57 in CH_2Cl_2).

Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.2 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 3H), 7.45 – 7.30 (m, 5H), 7.30 – 7.20 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 1H), 4.78 – 4.59 (m, 1H), 4.30 (dd, *J* = 10.8, 2.8 Hz, 1H), 3.63 (dd, *J* = 17.6, 10.4 Hz, 1H), 3.03 (dd, *J* = 17.6, 2.4 Hz, 1H), 1.04 (d, *J* = 6.4 Hz, 3H), 0.72 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 176.4, 171.3, 152.9, 136.3, 133.5, 129.6, 129.1, 128.7, 128.5, 128.4, 128.2, 127.2, 126.5, 124.4, 111.2, 68.9, 56.6, 48.4, 37.6, 21.4, 21.0. ESI-HRMS: calcd for $C_{27}H_{24}NaO_5^+$ ([M + Na]$^+$) 451.1521, found 451.1521.



	Retention Time	Area	% Area
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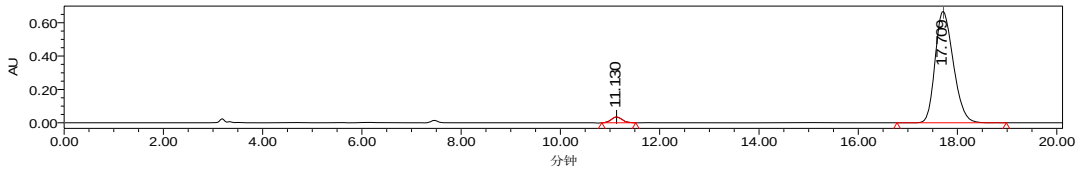
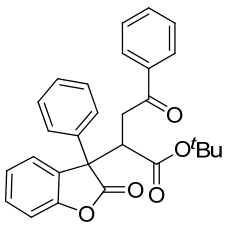
2	18.320	4322751	50.07

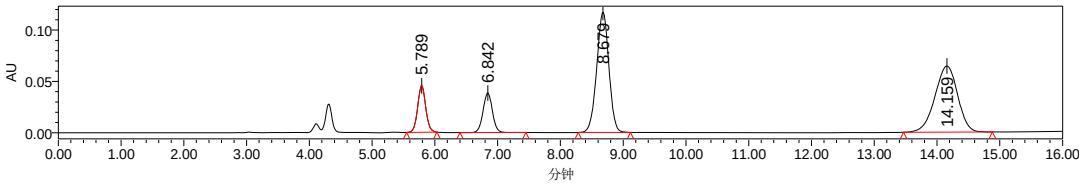


	Retention Time	Area	% Area
1	11.130	526652	3.01
2	17.709	16986487	96.99

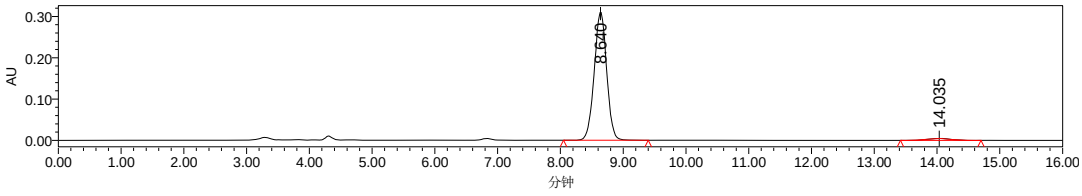


Compound **3e**: Prepared according to the general procedure A at 0 °C for 5 h. 97% yield, > 95/5 d.r., 96% *ee* of major isomer. HPLC (chiral IA column), hexane/ *i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 8.64 min, *t*r (minor) = 14.04 min.
Pure of major isomer: $[\alpha]_D^{20} = -89.34$ (*c* = 0.88 in CH_2Cl_2).

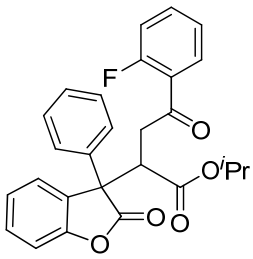
Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.2 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.56 – 7.49 (m, 3H), 7.45 – 7.21 (m, 5H), 7.30 – 7.21 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 1H), 4.21 (dd, *J* = 10.8, 2.8 Hz, 1H), 3.62 (dd, *J* = 17.6, 10.8 Hz, 1H), 2.99 (dd, *J* = 17.6, 2.8 Hz, 1H), 1.09 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 176.4, 170.8, 152.9, 136.4, 136.4, 133.4, 129.6, 129.0, 128.7, 128.6, 128.3, 128.2, 127.3, 126.5, 124.4, 111.1, 81.8, 56.6, 49.1, 37.5, 27.4. ESI-HRMS: calcd for $C_{28}H_{26}NaO_5^+$ ([M + Na]$^+$) 465.1678, found 465.1677.



	Retention Time	Area	% Area
1	5.789	408018	10.18
2	6.842	400889	10.00
3	8.679	1580358	39.43
4	14.159	1619025	40.39



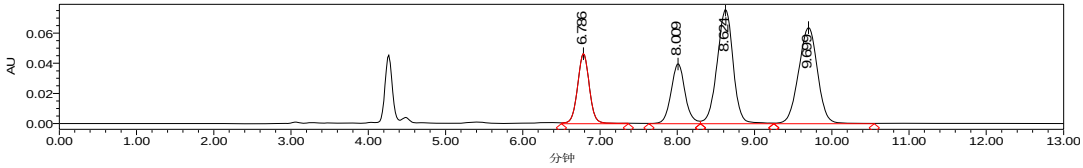
	Retention Time	Area	% Area
1	8.640	4291396	97.39
2	14.035	115182	2.61



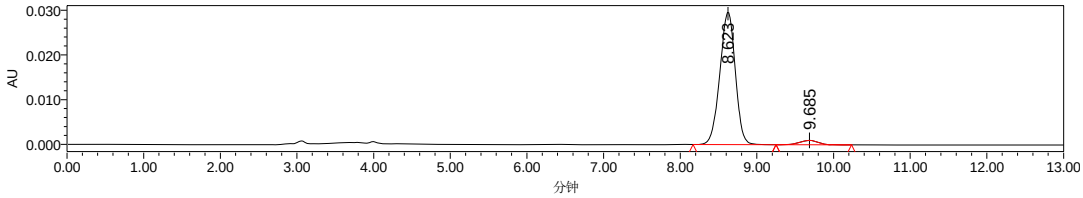
Compound **3f**: Prepared according to the general procedure A at 0 °C for 5 h. 98% yield, 93/7 d.r., 92% *ee* of major isomer. HPLC (chiral IA column), hexane/ *i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 8.62 min, *t*r (minor) = 9.69 min.
Pure of major isomer: $[\alpha]_D^{20} = -235.33$ (*c* = 0.27 in CH_2Cl_2).

Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (td, *J* = 7.6, 1.6 Hz, 1H), 7.72 – 7.61 (m, 1H), 7.61 – 7.51 (m, 2H), 7.50 – 7.42 (m, 1H), 7.42 – 7.26 (m, 4H), 7.26 – 7.21 (m, 1H), 7.17 (dd, *J* = 7.6, 5.2 Hz, 2H), 7.05 (dd, *J* = 10.8, 8.4 Hz, 1H), 4.72 (dt, *J* = 12.6, 6.4 Hz, 1H), 4.26 (dd, *J* = 10.8, 2.8 Hz, 1H), 3.51 (ddd, *J* = 18.4, 10.8, 2.8 Hz, 1H), 3.03 (dt, *J* = 18.8, 2.8 Hz, 1H), 1.07 (d, *J*

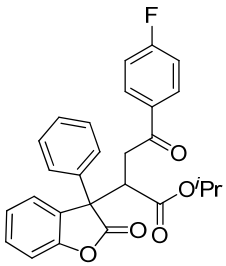
= 6.0 Hz, 3H), 0.72 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 195.4, 176.3, 171.3, 163.3, 160.7, 153.0, 136.0, 135.4, 135.0, 130.6, 130.6, 130.0, 128.9, 128.4, 127.8, 127.4, 126.9, 125.0, 124.9, 124.5, 124.5, 124.4, 116.9, 116.7, 111.1, 68.8, 56.4, 48.3, 42.6, 42.5, 21.4, 21.0. ESI-HRMS: calcd for $C_{27}H_{23}FNaO_5^+$ ([M + Na]$^+$) 469.1427, found 469.1422; calcd for $C_{27}H_{24}FO_5^+$ ([M + H]$^+$) 447.1608, found 447.1606.



	Retention Time	Area	% Area
1	6.786	496196	15.64
2	8.009	499628	15.75
3	8.624	1090072	34.36
4	9.699	1086408	34.25

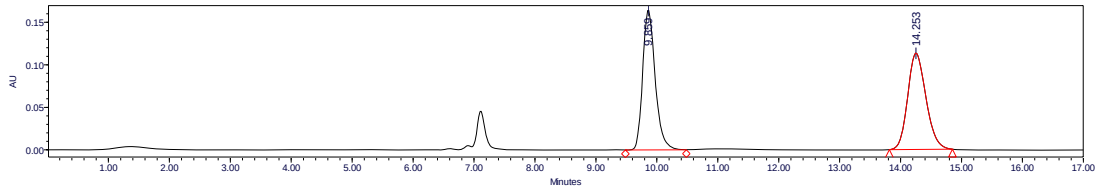


	Retention Time	Area	% Area
1	8.623	414114	96.21
2	9.685	16330	3.79

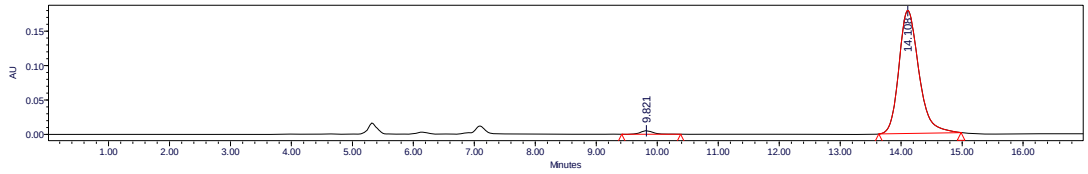


Compound **3g**: Prepared according to the general procedure A at 0 ^{o}C for 5 h. 97% yield, 92/8 d.r., 96% *ee* of major isomer. HPLC (chiral IE column), hexane/*i*-PrOH = 70/30, flow rate 0.8 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 14.11 min, *t*r (minor) = 9.82 min.
Pure of major isomer: $[\alpha]_D^{20} = -97.70$ (*c* = 0.87 in CH_2Cl_2).

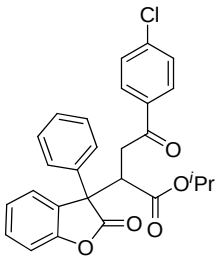
Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.4, 6.0 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.40 – 7.30 (m, 3H), 7.30 – 7.21 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.06 (t, *J* = 8.4 Hz, 2H), 4.76 – 4.63 (m, 1H), 4.29 (dd, *J* = 10.8, 2.8 Hz, 1H), 3.60 (dd, *J* = 17.6, 10.4 Hz, 1H), 3.01 (dd, *J* = 17.6, 2.4 Hz, 1H), 1.04 (d, *J* = 6.4 Hz, 3H), 0.72 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 176.4, 171.2, 167.3, 164.7, 152.9, 136.2, 132.7, 132.7, 130.9, 130.9, 129.7, 129.1, 128.4, 127.2, 126.4, 124.5, 115.9, 115.7, 111.2, 68.9, 56.5, 48.3, 37.45, 21.4, 21.0. ESI-HRMS: calcd for $C_{27}H_{23}FNaO_5^+$ ([M + Na]$^+$) 469.1427, found 469.1427; calcd for $C_{27}H_{24}FO_5^+$ ([M + H]$^+$) 447.1608, found 447.1606.



	Retention Time	Area	% Area
1	9.859	2350787	49.94
2	14.253	2356534	50.06

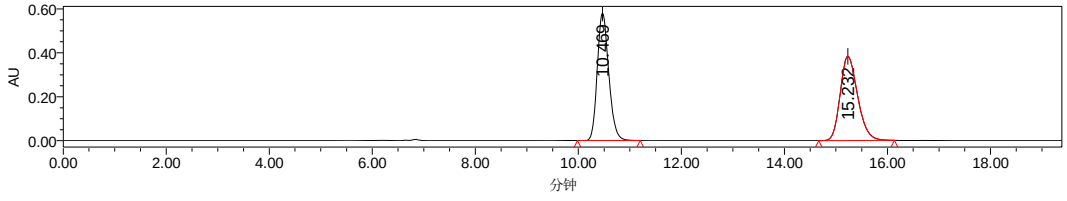


	Retention Time	Area	% Area
1	9.821	71720	1.74
2	14.108	4050421	98.26

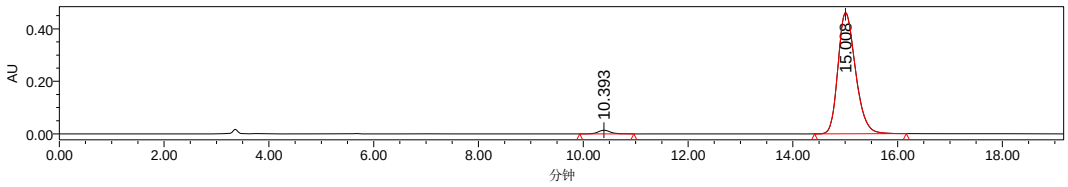


Compound **3h**: Prepared according to the general procedure A at 0 °C for 5 h. 98% yield, 94/6 d.r., 96% *ee* of major isomer. HPLC (chiral IE column), hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 15.01 min, *t*r (minor) = 10.39 min.
Pure of major isomer: $[\alpha]_D^{20} = -85.78$ (*c* = 0.63 in CH_2Cl_2).

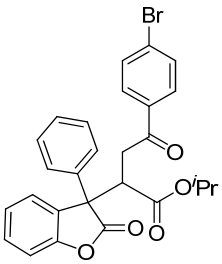
Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.43 – 7.26 (m, 6H), 7.26 – 7.20 (m, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 4.70 (hept, *J* = 6.2 Hz, 1H), 4.28 (dd, *J* = 10.4, 2.8 Hz, 1H), 3.59 (dd, *J* = 17.6, 10.4 Hz, 1H), 3.01 (dd, *J* = 17.6, 2.8 Hz, 1H), 1.04 (d, *J* = 6.0 Hz, 3H), 0.71 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 176.4, 171.2, 152.9, 140.0, 136.2, 134.6, 129.69, 129.7, 129.1, 129.0, 128.5, 127.2, 126.4, 124.5, 111.2, 69.0, 56.5, 48.3, 37.5, 21.4, 21.0. ESI-HRMS: calcd for $C_{27}H_{23}ClNaO_5^+$ ([M + Na]$^+$) 485.1132 (487.1102 for Cl^{37}), found 485.1138 (487.1097 for Cl^{37}).



	Retention Time	Area	% Area
1	10.469	9029136	50.02
2	15.232	9020255	49.98

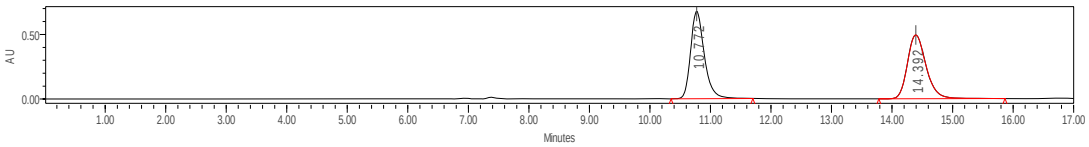


	Retention Time	Area	% Area
1	10.393	213815	1.96
2	15.008	10670195	98.04

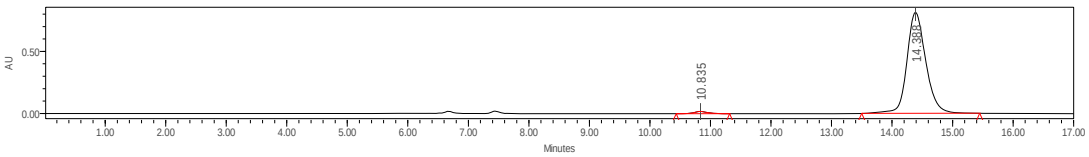


Compound **3i**: Prepared according to the general procedure A at 0 °C for 5 h. 98% yield, 93/7 d.r., 97% *ee* of major isomer. HPLC (chiral IE column), hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 14.39 min, *t*r (minor) = 10.84 min.
Pure of major isomer: $[\alpha]_D^{20} = -99.78$ (*c* = 0.99 in CH_2Cl_2).

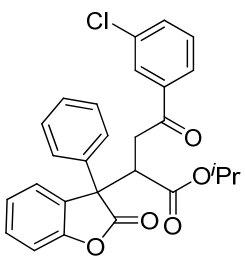
Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.64 (m, 2H), 7.60 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.58 – 7.45 (m, 4H), 7.40 – 7.26 (m, 4H), 7.23 (td, *J* = 7.6, 0.9 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 4.70 (hept, *J* = 6.0 Hz, 1H), 4.27 (dd, *J* = 10.4, 2.8 Hz, 1H), 3.58 (dd, *J* = 18.0, 10.8 Hz, 1H), 3.00 (dd, *J* = 18.0, 3.2 Hz, 1H), 1.03 (d, *J* = 6.4 Hz, 3H), 0.71 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 176.3, 171.2, 152.9, 136.2, 135.0, 132.0, 129.7, 129.7, 129.1, 128.7, 128.4, 128.4, 127.1, 126.4, 124.5, 111.2, 68.9, 56.5, 48.3, 37.5, 21.4, 21.0. ESI-HRMS: calcd for $C_{27}H_{23}BrNaO_5^+$ ($[M + Na]^+$) 529.0627 (531.0606 for Br^{81}), found 529.0626 (531.0612 for Br^{81}).



	Retention Time	Area	% Area
1	10.772	10667706	50.26
2	14.392	10558947	49.74

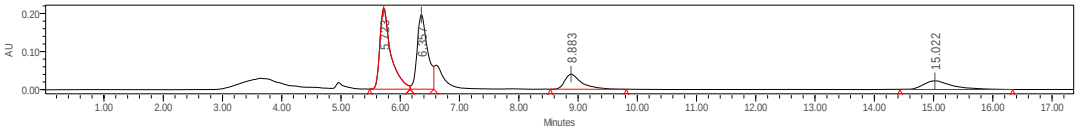


	Retention Time	Area	% Area
1	10.835	252705	1.42
2	14.388	17584416	98.58

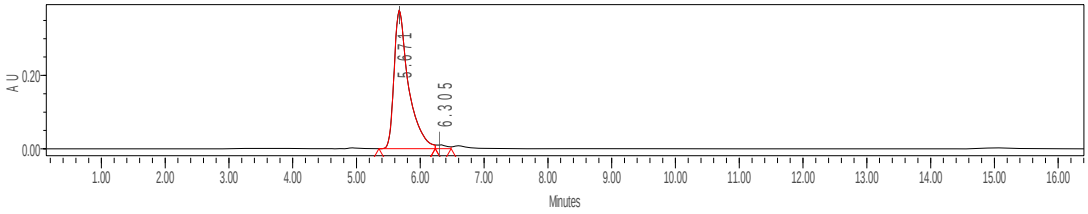


Compound **3j**: Prepared according to the general procedure A at 0 °C for 5 h. 98% yield, 94/6 d.r., 96% *ee* of major isomer. HPLC (chiral IC column), hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 5.67 min, *t*r (minor) = 6.31 min.
Pure of major isomer: $[\alpha]_D^{20} = -94.26$ (*c* = 0.92 in CH_2Cl_2).

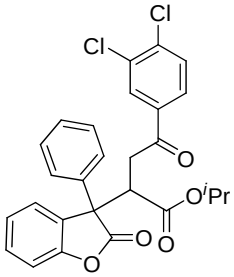
Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.56 – 7.42 (m, 3H), 7.40 – 7.25 (m, 5H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 4.78 – 4.52 (m, 1H), 4.28 (dd, *J* = 10.4, 2.8 Hz, 1H), 3.60 (dd, *J* = 17.6, 10.8 Hz, 1H), 3.01 (dd, *J* = 18.0, 2.8 Hz, 1H), 1.04 (d, *J* = 6.0 Hz, 3H), 0.72 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 176.3, 171.1, 152.9, 137.8, 136.2, 135.0, 133.4, 130.0, 129.7, 129.1, 128.4, 128.4, 128.2, 127.1, 126.4, 126.4, 124.5, 111.2, 69.0, 56.5, 48.3, 37.7, 21.4, 21.0. ESI-HRMS: calcd for $C_{27}H_{23}ClNaO_5^+$ ($[M + Na]^+$) 485.1132 (487.1102 for Cl^{37}), found 485.1127 (487.1106 for Cl^{37}).



	Retention Time	Area	% Area
1	5.723	2732979	40.82
2	6.357	2390448	35.70
3	8.883	786275	11.74
4	15.022	785345	11.73



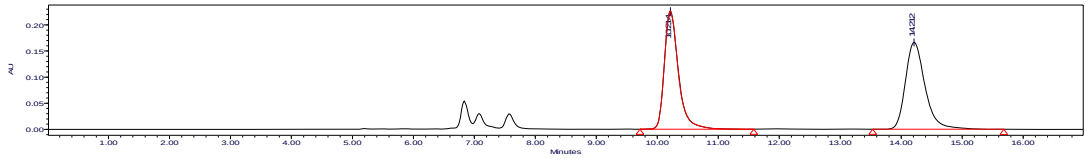
	Retention Time	Area	% Area
1	5.671	5947981	97.91
2	6.305	127267	2.09



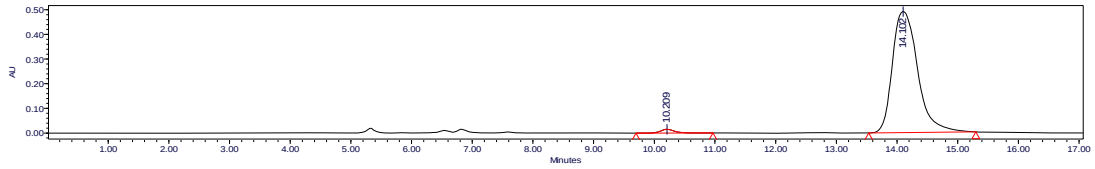
Compound **3k**: Prepared according to the general procedure A at 0 °C for 5 h. 96% yield, >95/5 d.r., 97% *ee* of major isomer. HPLC (chiral IE column), hexane/*i*-PrOH = 70/30, flow rate 0.8 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 14.10 min, *t*r (minor) = 10.21 min.
Pure of major isomer: $[\alpha]_D^{20} = -95.18$ (*c* = 0.95 in CH_2Cl_2).

Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.63 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.60 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.55 – 7.43 (m, 3H), 7.40 – 7.26 (m, 4H), 7.25 – 7.20 (m, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 4.79 – 4.58 (m, 1H), 4.27 (dd, *J* = 10.4, 2.8 Hz, 1H), 3.57 (dd, *J* = 18.0, 10.8 Hz, 1H), 3.00

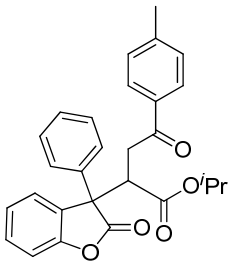
(dd, J = 17.6, 2.8 Hz, 1H), 1.04 (d, J = 6.4 Hz, 3H), 0.72 (d, J = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 176.3, 171.1, 152.9, 137.8, 136.2, 135.0, 133.4, 130.0, 129.7, 129.1, 128.4, 128.4, 128.2, 127.1, 126.4, 126.4, 124.5, 111.2, 68.98, 56.5, 48.3, 37.7, 21.4, 21.0. ESI-HRMS: calcd for $C_{27}H_{22}Cl_2NaO_5^+$ ([M + Na]$^+$) 519.0742 (521.0712 for Cl^{37}), found 519.0742 (521.0710 for Cl^{37}).



	Retention Time	Area	% Area
1	10.214	3633295	49.52
2	14.212	3704402	50.48

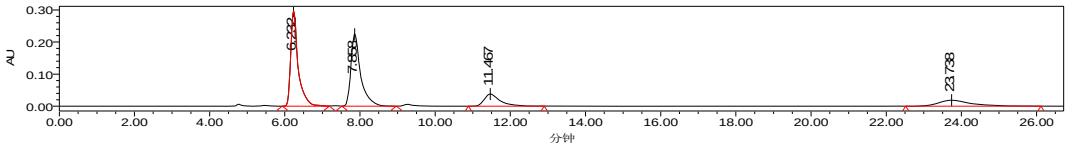


	Retention Time	Area	% Area
1	10.209	230364	1.59
2	14.102	14233864	98.41



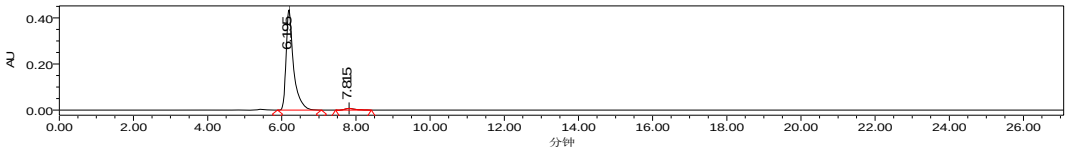
Compound **3l**: Prepared according to the general procedure A at 0 °C for 12 h. 98% yield, 89/11 d.r., 96% *ee* of major isomer. HPLC (chiral IC column), hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 6.20 min, *t*r (minor) = 7.82 min.
Pure of major isomer: $[\alpha]_D^{20} = -77.17$ (c = 0.76 in CH_2Cl_2).

Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 7.6 Hz, 1H), 7.52 (d, J = 7.6 Hz, 2H), 7.40 – 7.30 (m, 3H), 7.30 – 7.12 (m, 5H), 4.85 – 4.60 (m, 1H), 4.29 (dd, J = 10.8, 2.8 Hz, 1H), 3.59 (dd, J = 17.6, 10.4 Hz, 1H), 3.01 (dd, J = 17.6, 2.8 Hz, 1H), 2.37 (s, 3H), 1.03 (d, J = 6.0 Hz, 3H), 0.71 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 176.4, 171.4, 152.9, 144.3, 136.4, 133.9, 129.6, 129.3, 129.1, 128.5, 128.4, 128.3, 127.2, 126.5, 124.4, 111.1, 68.8, 56.6, 48.4, 37.5, 21.8, 21.4, 21.0. ESI-HRMS: calcd for $C_{28}H_{26}NaO_5^+$ ([M + Na]$^+$) 465.1678, found 465.1679; ESI-HRMS: calcd for $C_{28}H_{27}O_5^+$ ([M + H]$^+$) 443.1858, found 443.1853.

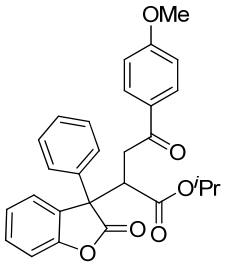


	Retention Time	Area	% Area
1	6.232	4078531	39.35

2	7.858	4058348	39.16
3	11.467	1115485	10.76
4	23.738	1112242	10.73

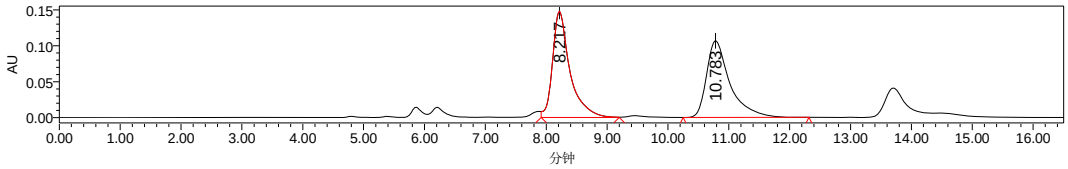


	Retention Time	Area	% Area
1	6.195	6062309	97.90
2	7.815	130059	2.10

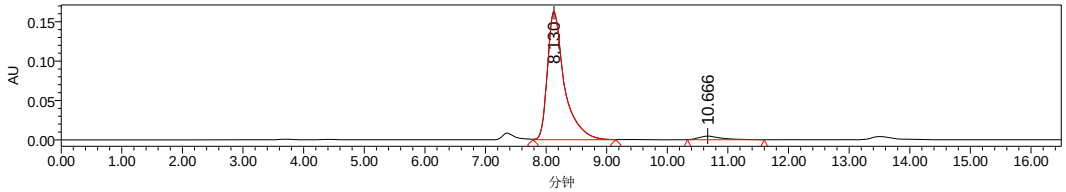


Compound **3m**: Prepared according to the general procedure A at 25 °C for 12 h. 95% yield, 91/9 d.r., 93% *ee* of major isomer. HPLC (chiral IC column), hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 8.13 min, *t*r (minor) = 10.67 min.
Pure of major isomer: $[\alpha]_D^{20} = -85.98$ (*c* = 0.74 in CH_2Cl_2).

Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.2 Hz, 2H), 7.61 (d, *J* = 6.8 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.42 – 7.26 (m, 4H), 7.25 – 7.20 (m, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 4.83 – 4.60 (m, 1H), 4.28 (dd, *J* = 10.8, 2.8 Hz, 1H), 3.84 (s, 3H), 3.57 (dd, *J* = 17.2, 10.8 Hz, 1H), 2.98 (dd, *J* = 17.2, 2.8 Hz, 1H), 1.03 (d, *J* = 6.0 Hz, 3H), 0.71 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 176.5, 171.4, 163.8, 152.9, 136.4, 130.6, 129.6, 129.4, 129.1, 128.5, 128.4, 127.2, 126.5, 124.4, 113.8, 111.1, 68.8, 56.6, 55.6, 48.4, 37.2, 21.4, 21.0. ESI-HRMS: calcd for $C_{28}H_{26}NaO_6^+$ ($[M + Na]^+$) 481.1627, found 481.1622; ESI-HRMS: calcd for $C_{28}H_{27}O_6^+$ ($[M + H]^+$) 459.1808, found 459.1805.

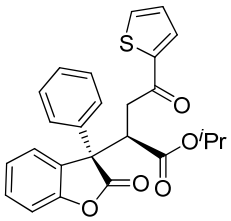


	Retention Time	Area	% Area
1	8.217	2918303	50.70
2	10.783	2837841	49.30

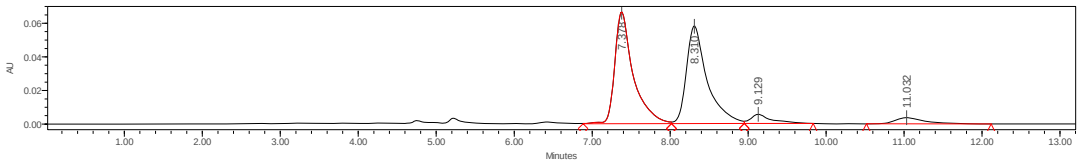


	Retention Time	Area	% Area
1	8.130	3139349	96.51

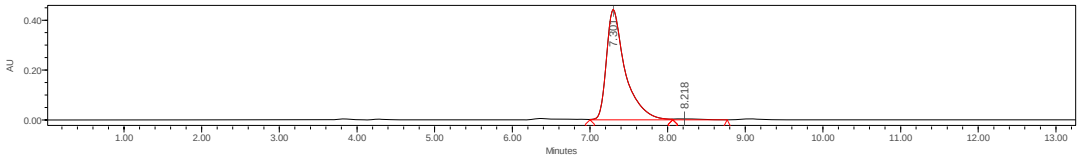
2	10.666	113538	3.49



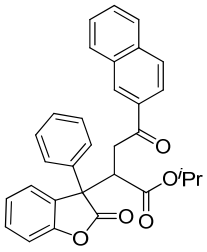
Compound **3n**: Prepared according to the general procedure A at 0 °C for 5 h. 97% yield, 94/6 d.r., 98% *ee* of major isomer. HPLC (chiral IC column), hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 7.30 min, *t*r (minor) = 8.22 min.
Pure of major isomer: $[\alpha]_D^{20} = -89.52$ (c = 0.75 in CH_2Cl_2).
M.p.: 154-156 °C.
Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ7.75 – 7.55 (m, 3H), 7.52 (d, J = 7.6 Hz, 2H), 7.40 – 7.30 (m, 3H), 7.30 – 7.26 (m, 1H), 7.25 – 7.18 (m, 1H), 7.15 (d, J = 8.0 Hz, 1H), 7.05 (dd, J = 4.8, 4.0 Hz, 1H), 4.80 – 4.60 (m, 1H), 4.28 (dd, J = 11.2, 3.2 Hz, 1H), 3.54 (dd, J = 17.2, 10.8 Hz, 1H), 2.99 (dd, J = 17.2, 3.2 Hz, 1H), 1.00 (d, J = 6.0 Hz, 3H), 0.73 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 176.4, 171.1, 152.9, 143.4, 136.2, 134.2, 132.6, 129.6, 129.1, 128.6, 128.4, 128.2, 127.1, 126.3, 124.4, 111.1, 69.0, 56.5, 48.5, 38.0, 21.3, 21.0. ESI-HRMS: calcd for $C_{25}H_{22}NaO_5S^+$ ([M + Na]$^+$) 457.1086, found 457.1085; ESI-HRMS: calcd for $C_{25}H_{23}O_5S^+$ ([M + H]$^+$) 435.1266, found 435.1269.



	Retention Time	Area	% Area
1	7.378	1087113	46.14
2	8.310	1069479	45.39
3	9.129	102376	4.34
4	11.032	97323	4.13



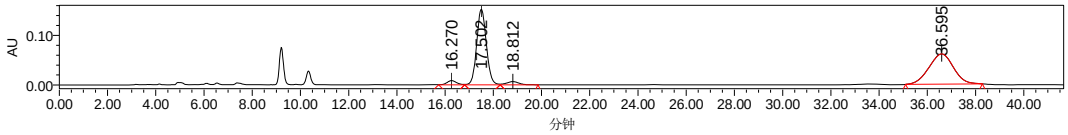
	Retention Time	Area	% Area
1	7.301	7389398	99.01
2	8.218	73514	0.99



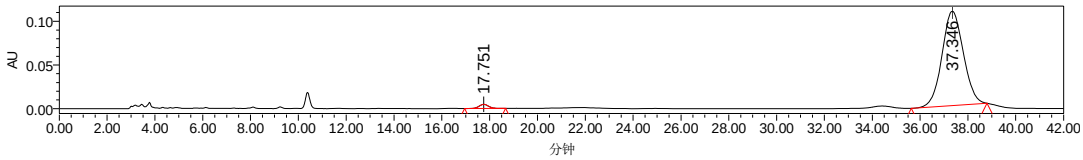
Compound **3o**: Prepared according to the general procedure A at 0 °C for 5 h. 98% yield, 93/7 d.r., 96% *ee* of major isomer. HPLC (chiral IE column), hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 37.35 min, *t*r (minor) = 17.75 min.
Pure of major isomer: $[\alpha]_D^{20} = -103.72$ (c = 0.94 in CH_2Cl_2).

Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.90 (d, J = 8.4 Hz, 2H), 7.82

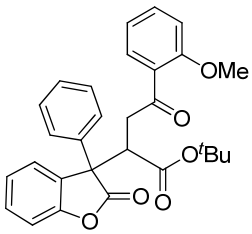
(d, J = 8.4 Hz, 2H), 7.64 (d, J = 7.2 Hz, 1H), 7.61 – 7.49 (m, 4H), 7.39 – 7.30 (m, 3H), 7.30 – 7.20 (m, 2H), 7.17 (d, J = 8.0 Hz, 1H), 4.79 – 4.62 (m, 1H), 4.37 (dd, J = 10.4, 2.8 Hz, 1H), 3.77 (dd, J = 17.6, 10.8 Hz, 1H), 3.20 (dd, J = 17.6, 2.8 Hz, 1H), 1.04 (d, J = 6.4 Hz, 3H), 0.73 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 176.5, 171.4, 152.9, 136.4, 135.8, 133.6, 132.5, 130.0, 129.7, 129.6, 129.1, 128.7, 128.7, 128.5, 128.4, 127.8, 127.1, 126.9, 126.4, 124.5, 123.8, 111.2, 68.9, 56.6, 48.5, 37.6, 21.4, 21.0. ESI-HRMS: calcd for $C_{31}H_{26}NaO_5^+$ ([M + Na]$^+$) 501.1678, found 501.1681; ESI-HRMS: calcd for $C_{31}H_{27}O_5^+$ ([M + H]$^+$) 479.1858, found 479.1855.



	Retention Time	Area	% Area
1	16.270	233116	2.59
2	17.502	4239326	47.05
3	18.812	226404	2.51
4	36.595	4311699	47.85

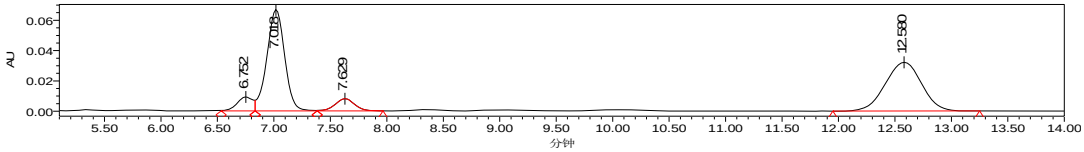


	Retention Time	Area	% Area
1	17.751	129929	1.90
2	37.346	6697972	98.10

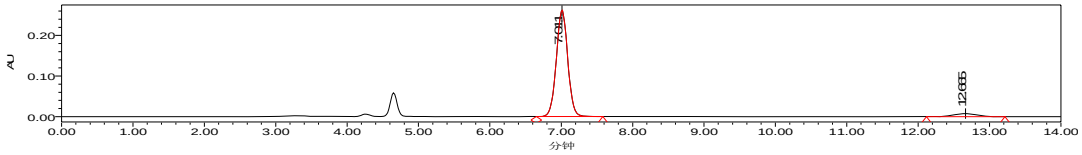


Compound **3p**: Prepared according to the general procedure A at 25 ^{o}C for 8 h. 98% yield, 90/10 d.r., 89% *ee* of major isomer. HPLC (chiral IA column), hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 7.01 min, *t*r (minor) = 12.67 min.
Pure of major isomer: $[\alpha]_D^{20} = -32.23$ (c = 0.94 in CH_2Cl_2).

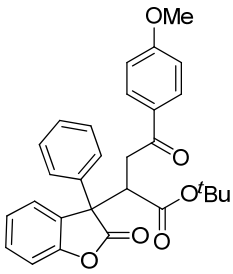
Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.6 Hz, 1H), 7.63 (dd, J = 7.6, 1.6 Hz, 1H), 7.56 (d, J = 7.2 Hz, 2H), 7.45 – 7.21 (m, 6H), 7.16 (d, J = 8.0 Hz, 1H), 6.93 (t, J = 7.6 Hz, 1H), 6.87 (d, J = 8.4 Hz, 1H), 4.12 (dd, J = 11.2, 2.8 Hz, 1H), 3.71 (s, 3H), 3.44 (dd, J = 18.4, 11.2 Hz, 1H), 3.03 (dd, J = 18.0, 2.8 Hz, 1H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 176.5, 171.1, 158.9, 153.1, 136.1, 134.0, 130.5, 129.5, 128.7, 128.2, 127.9, 127.7, 127.4, 127.2, 124.2, 120.6, 111.6, 110.9, 81.4, 56.7, 55.3, 49.3, 43.1, 27.4. ESI-HRMS: calcd for $C_{29}H_{28}NaO_6^+$ ([M + Na]$^+$) 495.1784, found 495.1783; ESI-HRMS: calcd for $C_{29}H_{29}O_6^+$ ([M + H]$^+$) 473.1964, found 473.1960.



	Retention Time	Area	% Area
1	6.752	92278	5.59
2	7.018	735391	44.55
3	7.629	102826	6.23
4	12.580	720223	43.63

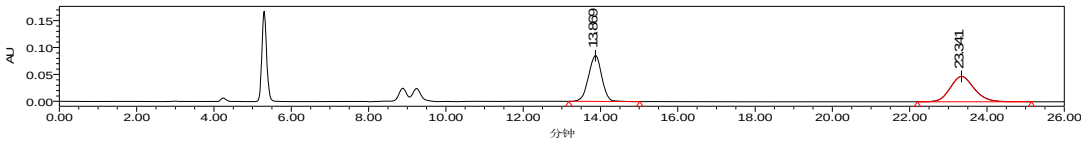


	Retention Time	Area	% Area
1	7.011	2929195	94.50
2	12.665	170353	5.50

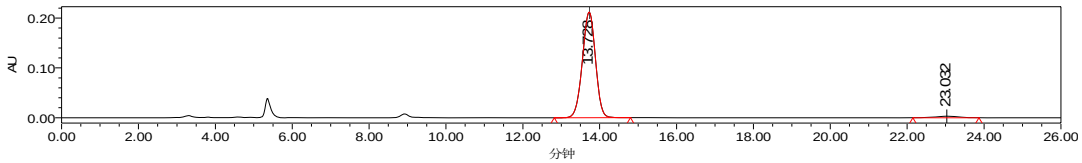


Compound **3q**: Prepared according to the general procedure A at 25 ^{o}C for 8 h. 98% yield, >95/5 d.r., 95% *ee* of major isomer. HPLC (chiral IA column), hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 13.73 min, *t*r (minor) = 23.03 min.
Pure of major isomer: $[\alpha]_D^{20} = -91.08$ (*c* = 0.94 in CH_2Cl_2).

Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.41 – 7.30 (m, 3H), 7.30 – 7.21 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 4.20 (dd, *J* = 10.8, 2.8 Hz, 1H), 3.83 (s, 3H), 3.56 (dd, *J* = 17.6, 10.8 Hz, 1H), 2.94 (dd, *J* = 17.6, 2.8 Hz, 1H), 1.08 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 176.5, 170.9, 163.7, 152.9, 136.5, 130.5, 129.5, 129.5, 129.0, 128.6, 128.3, 127.3, 126.6, 124.3, 113.8, 111.1, 81.7, 56.6, 55.6, 49.1, 37.1, 27.4. ESI-HRMS: calcd for $C_{29}H_{28}NaO_6^+$ ([M + Na]$^+$) 495.1784, found 495.1783; ESI-HRMS: calcd for $C_{29}H_{29}O_6^+$ ([M + H]$^+$) 473.1964, found 473.1960.

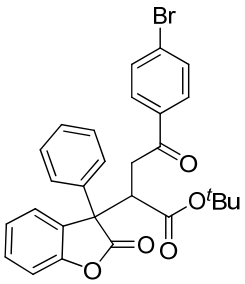


	Retention Time	Area	% Area
1	13.869	2017502	50.00
2	23.341	2017815	50.00



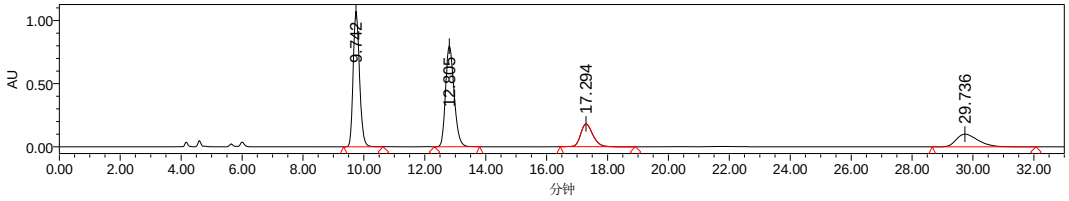
	Retention Time	Area	% Area
1	13.728	4994916	97.49

2	23.032	128424	2.51

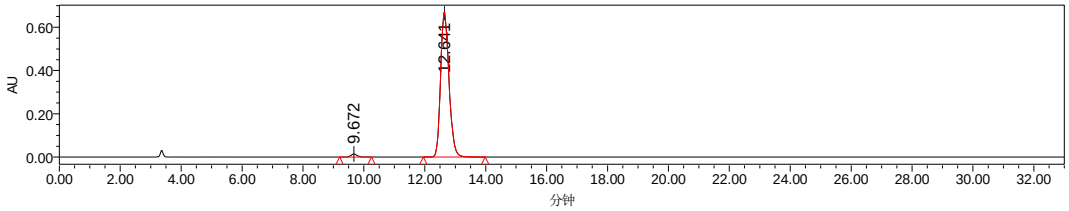


Compound **3r**: Prepared according to the general procedure A at 0 °C for 5 h. 99% yield, >95/5 d.r., 97% *ee* of major isomer. HPLC (chiral IE column), hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 12.64 min, *t*r (minor) = 9.67 min.
Pure of major isomer: $[\alpha]_D^{20} = -86.83$ (*c* = 1.01 in CH_2Cl_2).

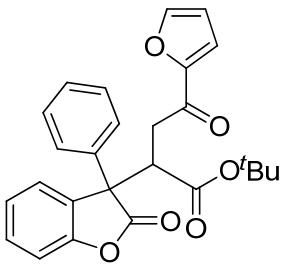
Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 6.8, 1.6 Hz, 2H), 7.59 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.58 – 7.48 (m, 4H), 7.41 – 7.27 (m, 4H), 7.26 – 7.20 (m, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 4.19 (dd, *J* = 10.8, 2.8 Hz, 1H), 3.57 (dd, *J* = 17.6, 10.8 Hz, 1H), 2.95 (dd, *J* = 17.6, 2.8 Hz, 1H), 1.09 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 176.3, 170.6, 152.9, 136.4, 135.1, 132.0, 129.7, 129.6, 129.1, 128.6, 128.5, 128.4, 127.2, 126.5, 124.4, 111.2, 81.9, 56.6, 49.0, 37.4, 27.4. ESI-HRMS: calcd for $C_{28}H_{25}BrNaO_5^+$ ($[M + Na]^+$) 543.0783 (545.0763 for Br^{81}), found 543.0781 (545.0763 for Br^{81}).



	Retention Time	Area	% Area
1	9.742	15579802	37.87
2	12.805	15590978	37.90
3	17.294	4986428	12.12
4	29.736	4983469	12.11



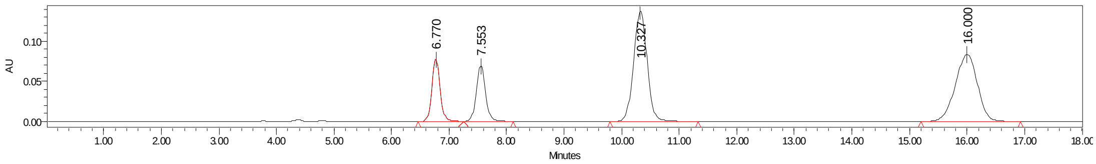
	Retention Time	Area	% Area
1	9.672	202928	1.56
2	12.641	12833892	98.44



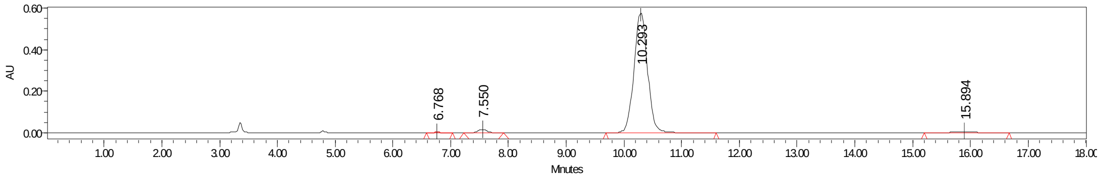
Compound **3s**: Prepared according to the general procedure A at 0 °C for 5 h. 97% yield, >95/5 d.r., 97% *ee* of major isomer. HPLC (chiral IA column), hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 10.29 min, *t*r (minor) = 15.89 min.
Pure of major isomer: $[\alpha]_D^{20} = -79.53$ (*c* = 0.86 in CH_2Cl_2).

Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.6,

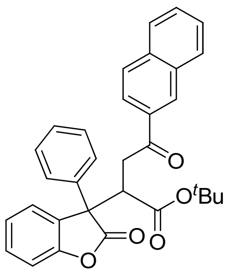
1.2 Hz, 1H), 7.57 – 7.44 (m, 3H), 7.41 – 7.27 (m, 4H), 7.22 (td, *J* = 7.6, 0.8 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 3.6 Hz, 1H), 6.47 (dd, *J* = 3.6, 2.0 Hz, 1H), 4.17 (dd, *J* = 11.2, 2.8 Hz, 1H), 3.43 (dd, *J* = 17.2, 10.8 Hz, 1H), 2.87 (dd, *J* = 17.2, 3.2 Hz, 1H), 1.09 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.2, 176.3, 170.6, 152.9, 152.1, 146.7, 136.3, 129.6, 129.0, 128.5, 128.3, 127.3, 126.4, 124.3, 117.8, 112.4, 111.1, 81.9, 56.5, 48.8, 37.1, 27.4. ESI-HRMS: calcd for $C_{26}H_{24}NaO_6^+$ ($[M + Na]^+$) 455.1471, found 455.1472.



	Retention Time	Area	% Area
1	6.770	769853	12.83
2	7.553	764959	12.75
3	10.327	2236176	37.27
4	16.000	2229423	37.15

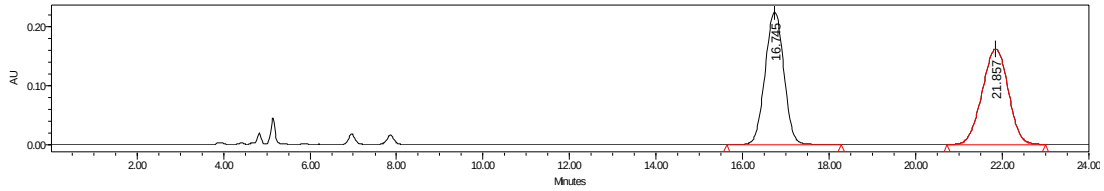


	Retention Time	Area	% Area
1	6.768	23304	0.24
2	7.550	168850	1.73
3	10.293	9415597	96.47
4	15.894	151987	1.56

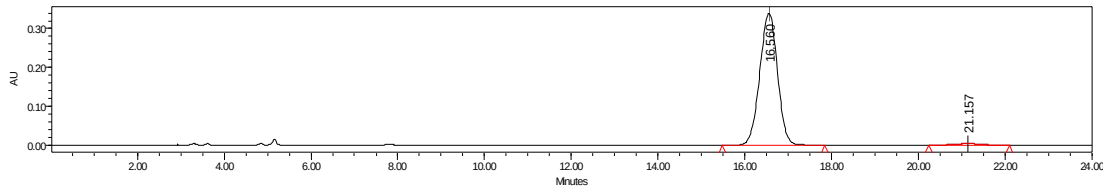


Compound **3t**: Prepared according to the general procedure A at 0 ^{o}C for 5 h. 95% yield, >95/5 d.r., 97% *ee* of major isomer. HPLC (chiral IA column), hexane/ *i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 16.56 min, *t*r (minor) = 21.16 min.
Pure of major isomer: $[\alpha]_D^{20} = -98.82$ (*c* = 0.93 in CH_2Cl_2).

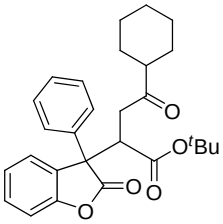
Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.60 – 7.45 (m, 4H), 7.45 – 7.30 (m, 3H), 7.30 – 7.20 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 1H), 4.29 (dd, *J* = 10.8, 2.8 Hz, 1H), 3.76 (dd, *J* = 17.6, 10.8 Hz, 1H), 3.16 (dd, *J* = 17.2, 2.8 Hz, 1H), 1.10 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 176.5, 170.8, 152.9, 136.6, 135.8, 133.8, 132.5, 130.0, 129.7, 129.6, 129.1, 128.8, 128.7, 128.5, 128.4, 127.8, 127.2, 126.9, 126.4, 124.4, 123.8, 111.2, 81.9, 56.7, 49.3, 37.5, 27.4. ESI-HRMS: calcd for $C_{32}H_{28}NaO_5^+$ ($[M + Na]^+$) 515.1834, found 515.1829.



	Retention Time	Area	% Area
1	16.745	6809603	49.75
2	21.857	6877781	50.25

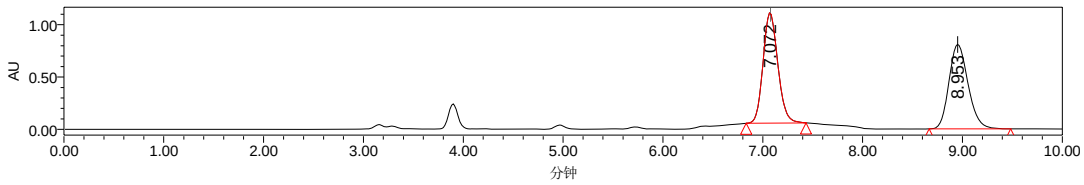


	Retention Time	Area	% Area
1	16.560	9648131	98.39
2	21.157	158023	1.61

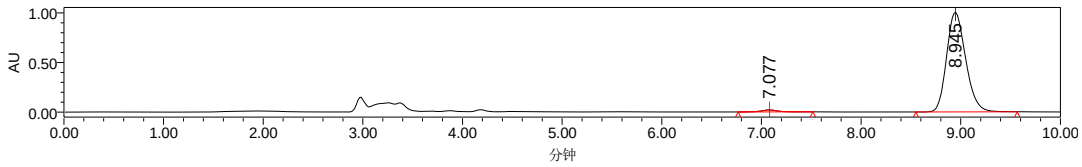


Compound **3u**: Prepared according to the general procedure A at 0 ^{o}C for 12 h. 85% yield, > 95/5 d.r., 97% *ee* of major isomer. HPLC (chiral IE column), hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 210 nm, major diastereomer: *t*r (major) = 8.95 min, *t*r (minor) = 7.08 min.
Pure of major isomer: $[\alpha]_D^{20} = -57.99$ (*c* = 0.78 in CH_2Cl_2).

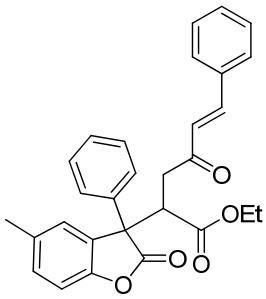
Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.38 – 7.25 (m, 4H), 7.25 – 7.18 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 4.04 (dd, *J* = 10.4, 2.8 Hz, 1H), 2.99 (dd, *J* = 18.0, 10.8 Hz, 1H), 2.47 (dd, *J* = 18.0, 2.8 Hz, 1H), 2.26 – 2.11 (m, 1H), 1.85 – 1.50 (m, 6H), 1.32 – 1.11 (m, 6H), 1.09 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.0, 176.4, 170.9, 152.9, 136.4, 129.5, 128.9, 128.4, 128.3, 127.3, 126.6, 124.3, 111.1, 81.6, 56.5, 50.7, 48.5, 39.4, 28.4, 28.2, 27.4, 25.8, 25.6, 25.6. ESI-HRMS: calcd for $C_{28}H_{32}NaO_5^+$ ([M + Na]$^+$) 471.2147, found 471.2145.



	Retention Time	Area	% Area
1	7.072	10855473	50.33
2	8.953	10712875	49.67



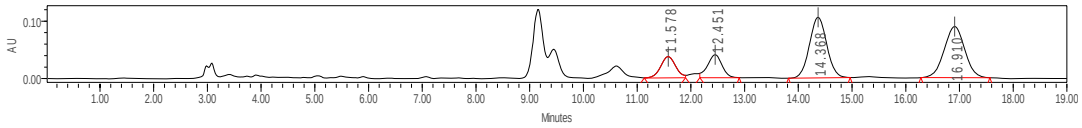
	Retention Time	Area	% Area
1	7.077	203111	1.51
2	8.945	13289707	98.49



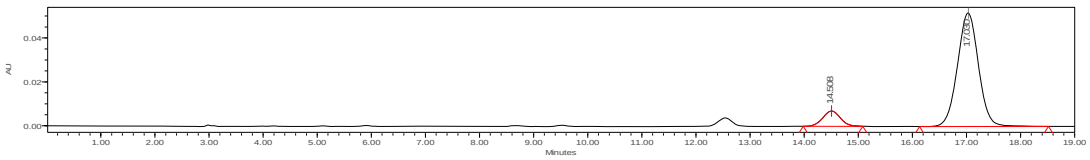
Compound **3v**: Prepared according to the general procedure A with 1.1 e.q. of **2v** at 0 °C for 24 h. 93% yield, 77/23 d.r., 80% *ee* of major isomer. HPLC (chiral IA column), hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 17.03 min, *t*r (minor) = 14.51 min.

Pure of major isomer: $[\alpha]_D^{20} = -46.46$ ($c = 0.82$ in CH_2Cl_2).

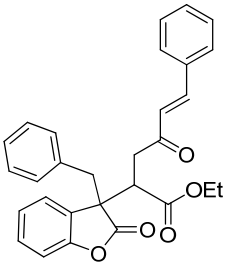
Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.43 (m, 5 H), 7.43 – 7.26 (m, 7 H), 7.14 (dd, J = 8.0, 1.2 Hz, 1H), 7.04 (d, J = 8.0 Hz, 1H), 6.62 (d, J = 16.4 Hz, 1H), 4.26 (dd, J = 10.8, 2.8 Hz, 1H), 4.00 – 3.75 (m, 2H), 3.29 (dd, J = 18.0, 10.8 Hz, 1H), 2.78 (dd, J = 18.0, 2.8 Hz, 1H), 2.40 (s, 3H), 0.87 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 176.8, 171.95, 150.8, 143.5, 136.5, 134.3, 134.1, 130.8, 130.1, 129.1, 129.1, 128.5, 128.4, 128.3, 127.1, 126.8, 125.5, 110.7, 61.2, 56.7, 48.0, 39.7, 21.4, 13.7. ESI-HRMS: calcd for $C_{29}H_{26}NaO_5^+$ ([M + Na]$^+$) 477.1678, found 477.1675.



	Retention Time	Area	% Area
1	11.578	719974	11.67
2	12.451	746363	12.10
3	14.368	2353517	38.15
4	16.910	2349946	38.09



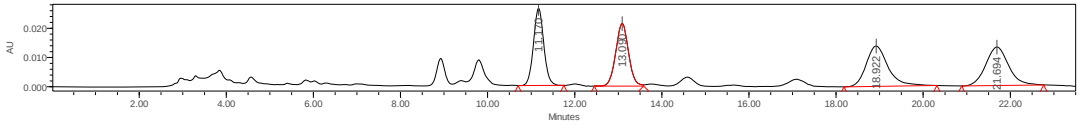
	Retention Time	Area	% Area
1	14.508	155440	10.04
2	17.030	1392297	89.96



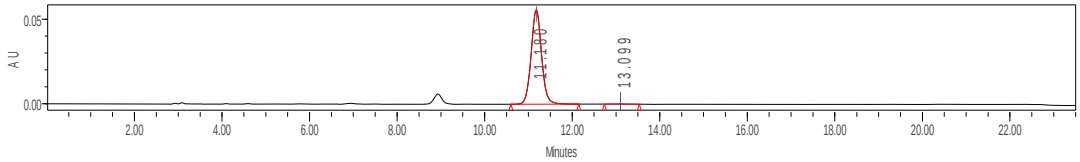
Compound **3w**: Prepared according to the general procedure A with 1.3 e.q. of **1h** at 23 °C for 24 h. 80% yield, 77/23 d.r., 99% *ee* of major isomer. HPLC (chiral IA column), hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 11.18 min, *t*r (minor) = 13.10 min.

Pure of major isomer: $[\alpha]_D^{20} = 7.74$ (*c* = 0.59 in CH_2Cl_2).

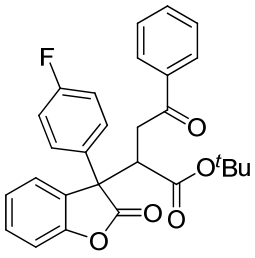
Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.34 (m, 7H), 7.26 – 7.20 (m, 2H), 7.19 – 6.99 (m, 3H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.76 (d, *J* = 6.8 Hz, 2H), 6.69 (d, *J* = 16.4 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.79 (dd, *J* = 10.0, 3.6 Hz, 1H), 3.37 (d, *J* = 13.2 Hz, 1H), 3.20 – 3.05 (m, 2H), 3.02 (dd, *J* = 18.0, 4.0 Hz, 1H), 1.16 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.79, 177.43, 172.19, 153.18, 143.70, 134.30, 134.04, 130.88, 130.05, 129.56, 129.11, 128.56, 128.16, 127.32, 127.10, 125.50, 125.34, 124.18, 110.66, 61.44, 54.63, 46.96, 42.60, 39.52, 14.09. ESI-HRMS: calcd for $C_{29}H_{26}NaO_5^+$ ([M + Na]$^+$) 477.1678, found 477.1675.



	Retention Time	Area	% Area
1	11.170	434851	23.81
2	13.090	434839	23.81
3	18.922	478759	26.22
4	21.694	477510	26.15



	Retention Time	Area	% Area
1	11.180	919961	99.57
2	13.099	4001	0.43

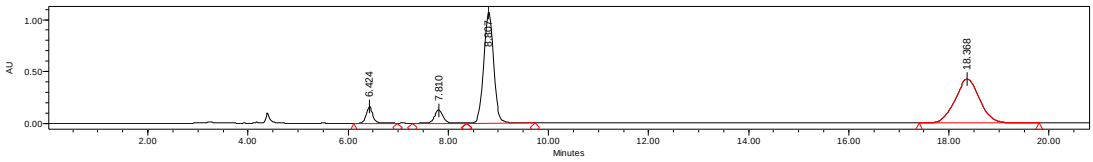


Compound **3x**: Prepared according to the general procedure A at 0 °C for 5 h. 98% yield, >95/5 d.r., 96% *ee* of major isomer. HPLC (chiral IA column), hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 8.82 min, *t*r (minor) = 18.58 min.

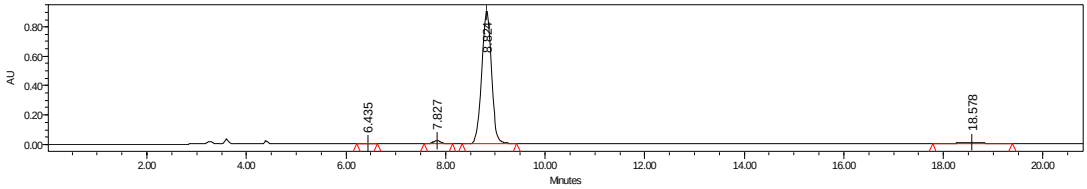
Pure of major isomer: $[\alpha]_D^{20} = -58.43$ (*c* = 0.90 in CH_2Cl_2).

Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.55 – 7.49 (m, 3H), 7.39 (t, *J* = 7.6 Hz, 3H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.03 (t, *J* = 8.4 Hz, 2H), 4.16 (dd, *J* = 10.8, 2.8 Hz, 1H), 3.50 (dd, *J* = 17.6, 10.8 Hz, 1H), 2.95 (dd, *J* = 17.6, 2.8 Hz, 1H), 1.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 176.4, 170.6, 163.8, 161.4, 153.0, 136.4, 133.5, 132.1, 132.0, 129.9, 129.4, 129.3, 128.7,

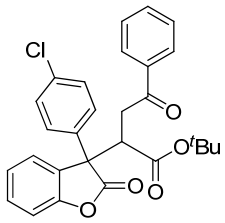
128.2, 127.9, 126.8, 124.5, 115.9, 115.7, 111.3, 81.9, 56.0, 49.2, 37.6, 27.5. ESI-HRMS: calcd for $C_{28}H_{25}FNaO_5^+$ ([M + Na]$^+$) 483.1584, found 483.1583.



	Retention Time	Area	% Area
1	6.424	1517133	4.73
2	7.810	1532165	4.78
3	8.807	14519534	45.27
4	18.368	14507130	45.23

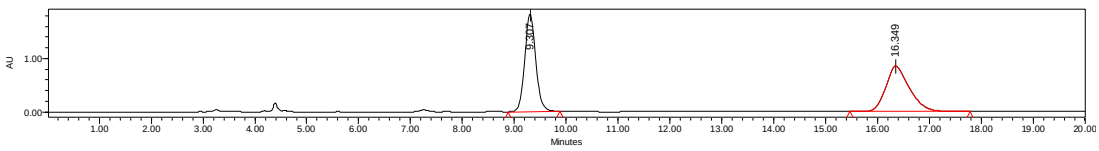


	Retention Time	Area	% Area
1	6.435	23321	0.19
2	7.827	240953	1.91
3	8.824	12095998	96.04
4	18.578	234369	1.86



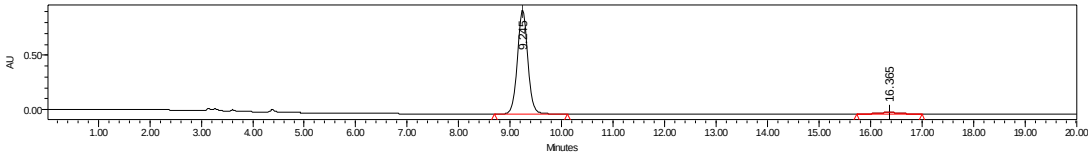
Compound **3y**: Prepared according to the general procedure A at 0 ^{o}C for 5 h. 96% yield, >95/5 d.r., 94% *ee* of major isomer. HPLC (chiral IA column), hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 9.25 min, *t*r (minor) = 16.37 min.
Pure of major isomer: $[\alpha]_D^{20} = -63.38$ (c = 0.85 in CH_2Cl_2).

Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.6 Hz, 2H), 7.59 (d, J = 7.2 Hz, 1H), 7.55 – 7.45 (m, 3H), 7.45 – 7.35 (m, 3H), 7.31 (d, J = 8.4 Hz, 2H), 7.26 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 8.0 Hz, 1H), 4.16 (dd, J = 10.8, 3.2 Hz, 1H), 3.53 (dd, J = 17.6, 10.8 Hz, 1H), 2.95 (dd, J = 17.6, 2.8 Hz, 1H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 176.1, 170.5, 153.0, 136.3, 134.9, 134.5, 133.5, 129.9, 129.1, 128.9, 128.7, 128.2, 127.8, 126.6, 124.5, 111.3, 82.0, 56.1, 49.1, 37.5, 27.5. ESI-HRMS: calcd for $C_{28}H_{25}ClNaO_5^+$ ([M + Na]$^+$) 499.1288 (501.1259 for Cl^{37}), found 499.1285 (501.1263 for Cl^{37}).

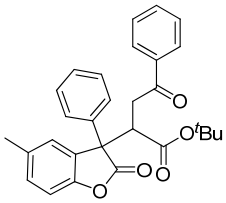


	Retention Time	Area	% Area

1	9.307	26919819	50.10
2	16.349	26816197	49.90

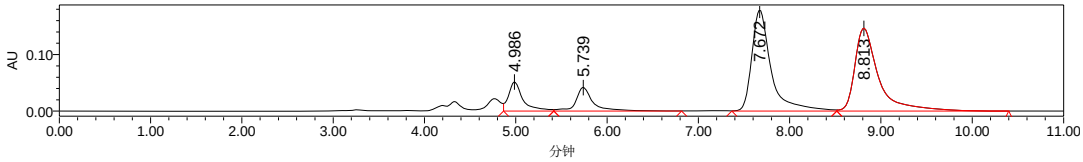


	Retention Time	Area	% Area
1	9.245	13303162	97.22
2	16.365	380322	2.78

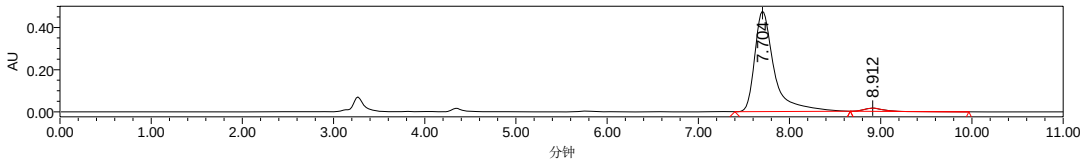


Compound **3z**: Prepared according to the general procedure A at 0 ^{o}C for 5 h. 95% yield, >95/5 d.r., 94% *ee* of major isomer. HPLC (chiral IA column), hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 7.70 min, *t*r (minor) = 8.91 min.
Pure of major isomer: $[\alpha]_D^{20} = -88.30$ (*c* = 0.91 in CH_2Cl_2).

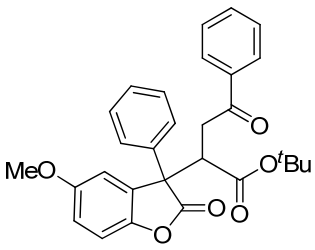
Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.77 (m, 2H), 7.58 – 7.47 (m, 3H), 7.43 – 7.31 (m, 5H), 7.30 – 7.25 (m, 1H), 7.14 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 4.20 (dd, *J* = 11.2, 2.8 Hz, 1H), 3.65 (dd, *J* = 18.0, 11.2 Hz, 1H), 3.00 (dd, *J* = 18.0, 3.2 Hz, 1H), 2.39 (s, 3H), 1.10 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 176.7, 170.8, 150.8, 136.7, 136.4, 134.0, 133.4, 130.0, 129.0, 128.6, 128.5, 128.3, 128.2, 127.2, 126.8, 110.7, 81.7, 56.8, 49.0, 37.5, 27.4, 21.4. ESI-HRMS: calcd for $C_{29}H_{28}NaO_5^+$ ($[M + Na]^+$) 479.1834, found 479.1834.



	Retention Time	Area	% Area
1	4.986	570301	8.89
2	5.739	564399	8.80
3	7.672	2626562	40.96
4	8.813	2650950	41.34



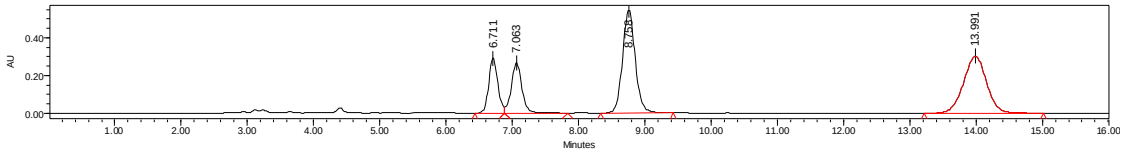
	Retention Time	Area	% Area
1	7.704	7058472	96.89
2	8.912	226261	3.11



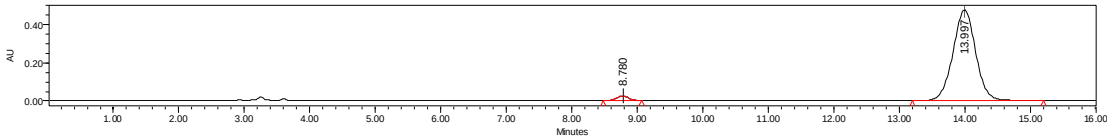
Compound **3aa**: Prepared according to the general procedure A at 0 °C for 12 h. 77% yield, >95/5 d.r., 94% *ee* of major isomer. HPLC (chiral IA column), hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 14.00 min, *t*r (minor) = 8.78 min.

Pure of major isomer: $[\alpha]_D^{20} = -70.5$ ($c = 0.60$ in CH_2Cl_2).

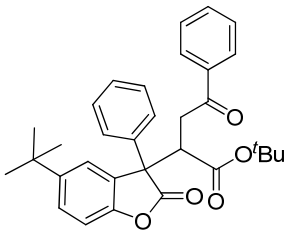
Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 7.6 Hz, 2H), 7.61 – 7.45 (m, 3H), 7.45 – 7.35 (m, 2H), 7.35 – 7.25 (m, 2H), 7.30 – 7.24 (m, 1H), 7.15 (d, J = 2.8 Hz, 1H), 7.08 (d, J = 8.8 Hz, 1H), 6.88 (dd, J = 8.8, 2.4 Hz, 1H), 4.21 (dd, J = 10.8, 2.8 Hz, 1H), 3.82 (s, 3H), 3.61 (dd, J = 17.6, 10.8 Hz, 1H), 2.98 (dd, J = 18.0, 2.8 Hz, 1H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 176.8, 170.7, 156.7, 146.8, 136.5, 136.5, 133.4, 129.4, 129.0, 128.7, 128.3, 128.2, 127.3, 114.9, 112.4, 111.6, 81.7, 57.3, 56.1, 48.8, 37.6, 27.5. ESI-HRMS: calcd for $C_{29}H_{28}NaO_6^+$ ($[M + Na]^+$) 495.1784, found 495.1783.



	Retention Time	Area	% Area
1	6.711	2783913	13.75
2	7.063	2956361	14.61
3	8.758	7243897	35.79
4	13.991	7256755	35.85



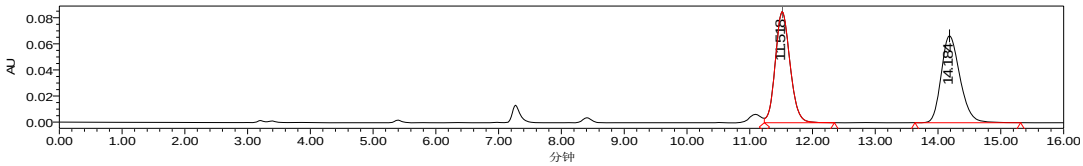
	Retention Time	Area	% Area
1	8.780	320642	2.73
2	13.997	11441728	97.27



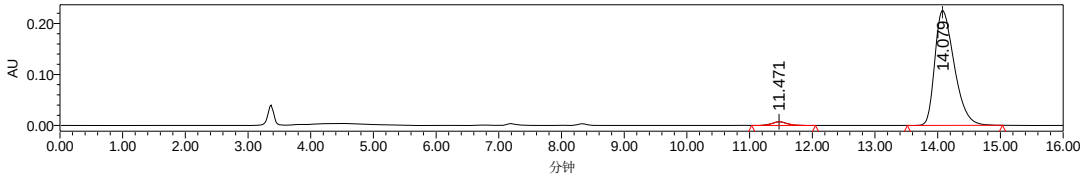
Compound **3ab**: Prepared according to the general procedure A at 0 °C for 8 h. 86% yield, >95/5 d.r., 95% *ee* of major isomer. HPLC (chiral IE column), hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 14.08 min, *t*r (minor) = 11.47 min.

Pure of major isomer: $[\alpha]_D^{20} = -75.12$ ($c = 0.86$ in CH_2Cl_2).

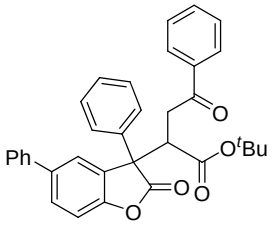
Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.77 (m, 2H), 7.62 – 7.47 (m, 4H), 7.43 – 7.30 (m, 5H), 7.30 – 7.25 (m, 1H), 7.06 (d, J = 8.8 Hz, 1H), 4.22 (dd, J = 10.8, 2.8 Hz, 1H), 3.68 (dd, J = 17.6, 10.8 Hz, 1H), 3.04 (dd, J = 18.0, 2.8 Hz, 1H), 1.34 (s, 9H), 1.08 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 176.8, 170.9, 150.7, 147.5, 136.9, 136.5, 133.4, 129.1, 128.6, 128.26, 128.21, 127.16, 126.39, 123.05, 110.33, 81.65, 56.85, 49.17, 37.30, 34.92, 31.74, 27.41. ESI-HRMS: calcd for $C_{32}H_{34}NaO_5^+$ ($[M + Na]^+$) 521.2304, found 521.2309.



	Retention Time	Area	% Area
1	11.518	1387333	50.03
2	14.184	1385911	49.97

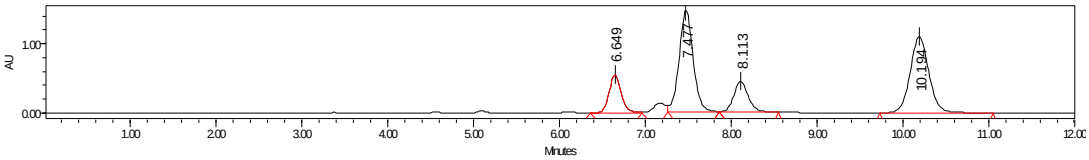


	Retention Time	Area	% Area
1	11.471	118061	2.38
2	14.079	4833536	97.62

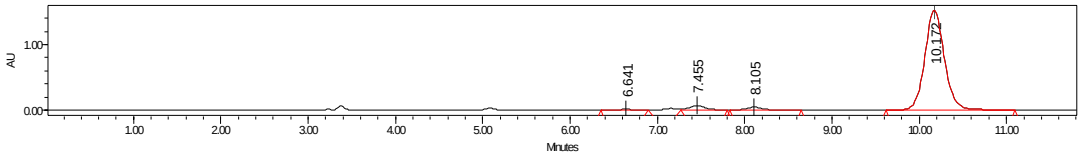


Compound **3ac**: Prepared according to the general procedure A at 0 °C for 8 h. 93% yield, >95/5 d.r., 93% *ee* of major isomer. HPLC (chiral IE column), hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 10.17 min, *t*r (minor) = 7.46 min.
Pure of major isomer: $[\alpha]_D^{20} = -37.19$ (*c* = 0.80 in CH_2Cl_2).

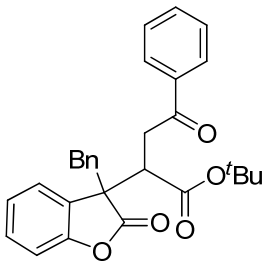
Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.79 (d, *J* = 1.6 Hz, 1H), 7.64 – 7.49 (m, 6H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.43 – 7.30 (m, 5H), 7.31 – 7.21 (m, 2H), 4.27 (dd, *J* = 10.8, 2.4 Hz, 1H), 3.73 (dd, *J* = 18.0, 10.8 Hz, 1H), 3.06 (dd, *J* = 17.6, 2.4 Hz, 1H), 1.09 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 176.4, 170.9, 152.3, 140.5, 137.9, 136.5, 136.4, 133.4, 129.4, 129.2, 129.1, 128.7, 128.4, 128.4, 128.3, 127.6, 127.2, 127.2, 125.1, 111.3, 81.8, 56.8, 49.1, 37.4, 27.5. ESI-HRMS: calcd for $C_{34}H_{30}NaO_5^+$ ($[M + Na]^+$) 541.1991, found 541.1987.



	Retention Time	Area	% Area
1	6.649	5282466	11.98
2	7.477	16932525	38.40
3	8.113	5249306	11.90
4	10.194	16635958	37.72



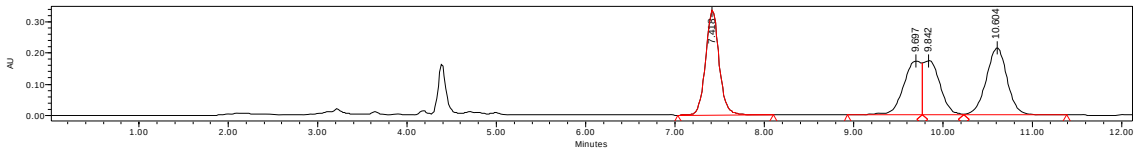
	Retention Time	Area	% Area
1	6.641	78614	0.31
2	7.455	862386	3.45
3	8.105	502433	2.01
4	10.172	23554794	94.23



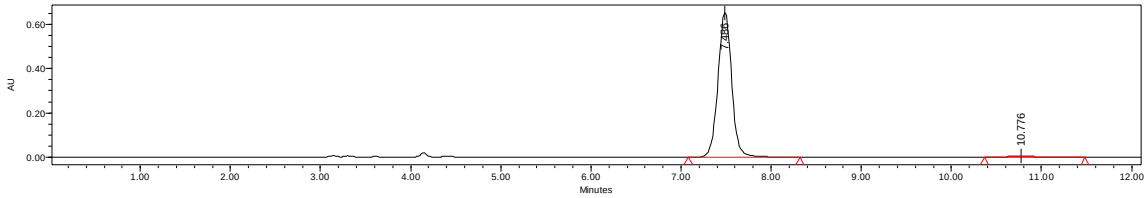
Compound **3ad**: Prepared according to the general procedure A with 1.3 e.q. of **1h** at 23 °C for 24 h. 93% yield, >95/5 d.r.,97 % *ee* of major isomer. HPLC (chiral IA column), hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 7.49 min, *t*r (minor) = 10.78 min.

Pure of major isomer: $[\alpha]_D^{20}$ = + 18.78 (*c* = 0.41 in CH_2Cl_2).

Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (t, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.51 – 7.35 (m, 3H), 7.26 – 7.15 (m, 2H), 7.15 – 6.96 (m, 3H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.78 (d, *J* = 7.2 Hz, 2H), 3.76 (dd, *J* = 9.6, 4.4 Hz, 1H), 3.51 (dd, *J* = 17.6, 9.2 Hz, 1H), 3.41 (dd, *J* = 17.6, 4.0 Hz, 1H), 3.35 (d, *J* = 13.2 Hz, 1H), 3.17 (d, *J* = 13.2 Hz, 1H), 1.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 177.4, 171.1, 153.2, 136.5, 134.1, 133.6, 130.1, 129.5, 128.8, 128.3, 128.1, 127.6, 127.3, 125.4, 124.0, 110.6, 82.1, 54.5, 48.2, 42.6, 37.1, 27.7. ESI-HRMS: calcd for $C_{29}H_{28}NaO_5^+$ ($[M + Na]^+$) 479.1834, found 479.1831.

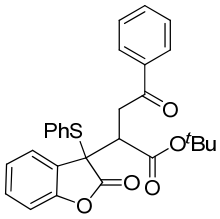


	Retention Time	Area	% Area
1	7.418	3564489	30.23
2	9.697	2395397	20.32
3	9.842	2311390	19.60
4	10.604	3519452	29.85



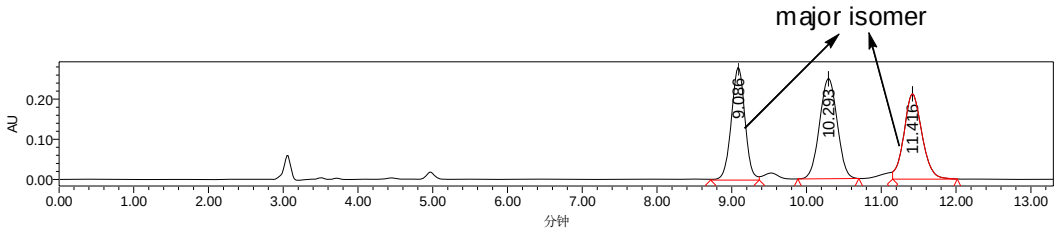
	Retention Time	Area	% Area
1	7.486	6934904	98.67

2	10.776	93292	1.33

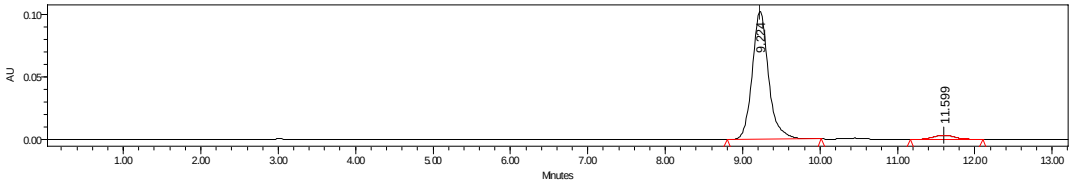


Compound **4a**: Prepared according to the general procedure B at 0 °C for 20 h. 91% yield, >95/5 d.r., 92% *ee* of major isomer. HPLC (chiral IA column), hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 9.22 min, *t*r (minor) = 11.60 min.
Pure of major isomer: $[\alpha]_D^{20} = -28.40$ (*c* = 0.84 in CH_2Cl_2).

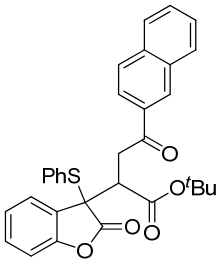
Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 7.91 (m, 2H), 7.66 – 7.55 (m, 1H), 7.55 – 7.43 (m, 2H), 7.32 – 7.24 (m, 2H), 7.25 – 7.18 (m, 1H), 7.19 – 7.03 (m, 5H), 6.80 (d, *J* = 7.7 Hz, 1H), 4.03 – 3.90 (m, 2H), 3.90 – 3.78 (m, 1H), 1.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 174.3, 169.9, 152.6, 137.2, 136.6, 133.6, 130.4, 129.9, 129.0, 128.8, 128.5, 127.8, 127.4, 125.5, 124.2, 110.5, 82.4, 58.5, 47.6, 37.1, 27.4. ESI-HRMS: calcd for $C_{28}H_{26}NaO_5S^+$ ($[M + Na]^+$) 497.1399, found 497.1398.



	Retention Time	Area	% Area
1	9.086	3562562	31.78
2	10.293	4086274	36.45
3	11.416	3562879	31.78



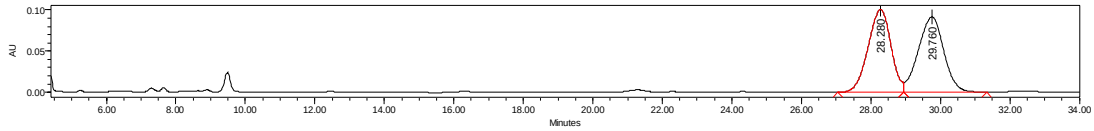
	Retention Time	Area	% Area
1	9.224	1498668	95.92
2	11.599	63767	4.08



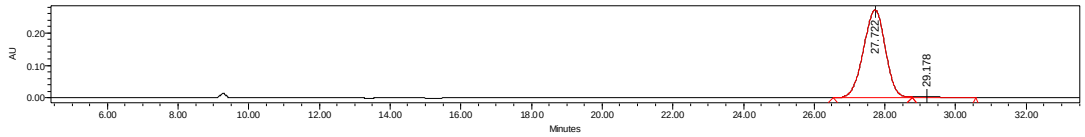
Compound **4b**: Prepared according to the general procedure B at 0 °C for 20 h. 95% yield, >95/5 d.r., 97% *ee* of major isomer. HPLC (chiral IA column), hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 7.49 min, *t*r (minor) = 10.78 min.
Pure of major isomer: $[\alpha]_D^{20} = -53.72$ (*c* =1.05 in CH_2Cl_2).

Pure of major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.11 (dd, *J* = 8.4, 1.6 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.65 – 7.55 (m, 2H),

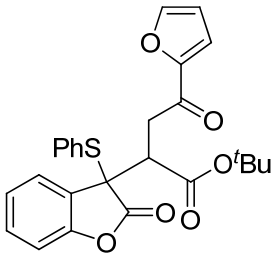
7.34 – 7.27 (m, 2H), 7.22 (dt, *J* = 8.0, 4.0 Hz, 1H), 7.19 – 7.07 (m, 5H), 6.82 (d, *J* = 8.0 Hz, 1H), 4.18 – 4.08 (m, 1H), 4.05 – 3.95 (m, 2H), 1.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 174.4, 169.9, 152.6, 137.2, 135.9, 133.9, 132.7, 130.5, 130.3, 129.9, 129.9, 129.0, 128.8, 128.7, 127.9, 127.8, 127.5, 127.0, 125.5, 124.2, 124.1, 110.5, 82.5, 58.6, 47.8, 37.2, 27.5. ESI-HRMS: calcd for $C_{32}H_{28}NaO_5S^+$ ($[M + Na]^+$) 547.1555, found 547.1552.



	Retention Time	Area	% Area
1	28.280	4589235	49.64
2	29.760	4655038	50.36

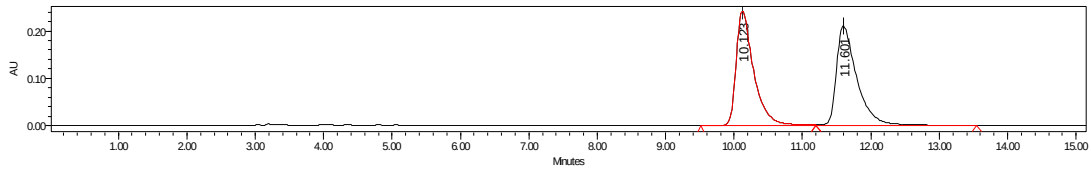


	Retention Time	Area	% Area
1	27.722	11771621	98.50
2	29.178	179789	1.50

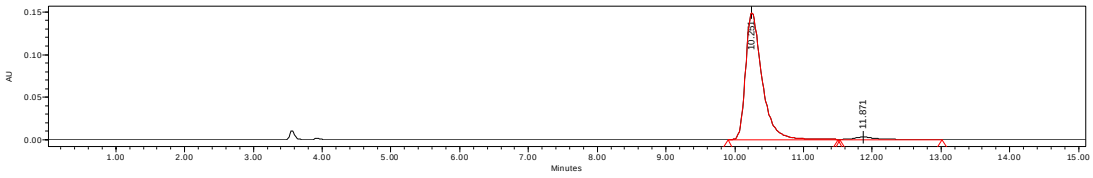


Compound **4c**: Prepared according to the general procedure B at 0 °C for 20 h. 91% yield, >95/5 d.r., 95% *ee* of major isomer. HPLC (chiral IB column), hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm, major diastereomer: *t*r (major) = 10.25 min, *t*r (minor) = 11.87 min. Pure of major isomer: $[\alpha]_D^{20} = -29.54$ (*c* = 0.87 in CH_2Cl_2).

Pure of major isomer:^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 0.8 Hz, 1H), 7.36 – 7.27 (m, 2H), 7.26 – 7.01 (m, 9H), 6.88 – 6.71 (m, 1H), 6.57 (dd, *J* = 3.2, 1.6 Hz, 1H), 3.88 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.82 (dd, *J* = 17.6, 3.6 Hz, 1H), 3.70 (dd, *J* = 17.6, 10.4 Hz, 1H), 1.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.2, 174.2, 169.7, 152.6, 152.3, 146.9, 137.2, 130.5, 129.9, 129.0, 127.8, 127.4, 125.3, 124.1, 118.1, 112.5, 110.5, 82.6, 58.4, 47.4, 36.8, 27.4. ESI-HRMS: calcd for $C_{26}H_{24}NaO_6S^+$ ($[M + Na]^+$) 487.1191, found 487.1191.

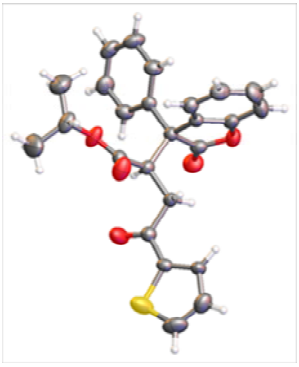


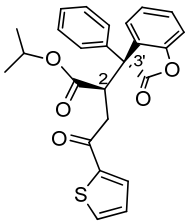
	Retention Time	Area	% Area
1	10.123	4334106	49.86
2	11.601	4358244	50.14



	Retention Time	Area	% Area
1	10.251	2462437	97.66
2	11.871	58904	2.34

(E) X-ray structure for 3n





product **3n** (*2R, 3'R*)

Table 1 Crystal data and structure refinement for 3n (CCDC983289)

Identification code	130909_s1_wz
Empirical formula	$C_{25}H_{22}O_5S$
Formula weight	434.48
Temperature/K	293.15
Crystal system	monoclinic
Space group	$P2_1$
a/Å	7.7042(4)
b/Å	15.7653(7)
c/Å	9.1879(4)
α/°	90
β/°	104.370(5)
γ/°	90
Volume/Å^3	1081.03(9)
Z	2
ρ_{calc}mg/mm^3	1.335
m/mm^{-1}	0.184
F(000)	456.0
Crystal size/mm^3	0.3 × 0.25 × 0.2

2Θ range for data collection	6.04 to 52.73°
Index ranges	$-8 \le h \le 9$, $-19 \le k \le 19$, $-10 \le l \le 11$
Reflections collected	4739
Independent reflections	3432[R(int) = 0.0221]
Data/restraints/parameters	3432/1/282
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	$R_1 = 0.0548$, $wR_2 = 0.1238$
Final R indexes [all data]	$R_1 = 0.0726$, $wR_2 = 0.1396$
Largest diff. peak/hole / e $Å^{-3}$	0.20/-0.37
Flack parameter	0.13(11)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3n. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	10132(3)	7307.0(11)	10340.5(16)	77.3(6)
O1	9011(4)	5210(2)	2931(3)	45.9(9)
O2	10961(5)	4629(3)	4889(4)	56.1(10)
O3	9562(6)	5550(2)	9166(4)	62.1(11)
O4	5350(5)	5264(2)	7230(4)	60.2(10)
O5	6105(5)	3901(2)	7222(4)	49.7(9)
C1	9895(10)	8345(4)	9849(8)	70.8(18)
C2	9195(8)	8448(4)	8370(7)	59.5(16)
C3	8842(6)	7692(3)	7558(5)	40.5(11)
C4	9276(6)	6987(3)	8533(5)	38.1(11)
C5	9129(6)	6078(3)	8186(5)	37.7(11)
C6	8420(7)	5832(3)	6571(5)	40.0(11)
C7	7965(6)	4879(3)	6405(5)	34.8(10)
C8	7725(6)	4548(3)	4764(5)	31.5(10)
C9	9430(7)	4779(3)	4265(5)	40.6(11)
C10	6334(6)	5010(3)	3583(4)	33.8(10)
C11	7158(7)	5340(3)	2534(5)	41.6(11)
C12	6258(8)	5735(4)	1236(5)	54.4(15)
C13	4413(8)	5815(4)	1009(6)	60.7(16)
C14	3551(8)	5511(3)	2047(6)	53.5(14)
C15	4499(7)	5104(3)	3335(5)	41.7(11)
C16	7549(6)	3575(3)	4623(5)	34.7(10)
C17	6281(7)	3188(3)	3491(6)	47.8(13)
C18	6201(8)	2306(4)	3371(6)	56.2(14)

C19	7360(8)	1809(3)	4369(7)	54.4(14)
C20	8654(8)	2182(3)	5500(6)	50.9(13)
C21	8762(7)	3053(3)	5617(5)	44.5(12)
C22	6315(6)	4715(3)	7001(5)	38.0(11)
C23	4497(7)	3617(4)	7678(6)	55.1(14)
C24	3937(10)	2817(5)	6834(8)	82(2)
C25	4984(10)	3506(6)	9345(7)	90(2)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3n. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka×b×U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	111.6(15)	57.6(9)	49.8(9)	-12.0(8)	-4.1(9)	-1.5(10)
O1	49(2)	46(2)	48.5(18)	5.9(18)	23.0(15)	-4.4(18)
O2	39(2)	67(3)	63(2)	-3(2)	12.7(17)	-6.5(19)
O3	91(3)	42(2)	42.5(18)	1.6(19)	-4.7(18)	2(2)
O4	63(2)	43(2)	84(3)	11(2)	37(2)	13(2)
O5	52(2)	32.0(17)	75(2)	6.2(19)	34.8(18)	-1.0(17)
C1	80(5)	52(4)	80(4)	-32(4)	20(3)	-12(3)
C2	73(4)	39(3)	70(4)	5(3)	25(3)	-3(3)
C3	54(3)	32(2)	33(2)	-5(2)	7(2)	-6(2)
C4	41(3)	37(2)	34(2)	-6(2)	6.3(19)	-5(2)
C5	39(3)	36(3)	35(2)	0(2)	5.5(19)	-3(2)
C6	56(3)	30(2)	35(2)	-1(2)	13(2)	-9(2)
C7	42(3)	27(2)	34(2)	1(2)	7.5(18)	-2(2)
C8	32(2)	30(2)	32(2)	-1(2)	8.9(17)	-0.9(19)
C9	41(3)	36(3)	44(2)	-7(2)	10(2)	-5(2)
C10	42(3)	28(2)	32(2)	-3(2)	11.1(19)	-3(2)
C11	53(3)	35(2)	40(2)	-5(2)	16(2)	-8(2)
C12	71(4)	53(3)	43(3)	8(3)	20(3)	3(3)
C13	75(4)	54(3)	47(3)	13(3)	3(3)	14(3)
C14	51(3)	44(3)	59(3)	0(3)	2(3)	6(3)
C15	43(3)	38(3)	43(3)	1(2)	10(2)	-1(2)
C16	39(3)	32(2)	36(2)	-3(2)	13.1(19)	0(2)
C17	45(3)	46(3)	49(3)	-6(3)	4(2)	0(3)
C18	59(3)	37(3)	68(3)	-15(3)	7(3)	-9(3)
C19	62(4)	30(3)	76(4)	-3(3)	26(3)	-4(3)
C20	63(4)	33(3)	58(3)	1(3)	18(3)	10(3)
C21	46(3)	40(3)	42(3)	-7(3)	3(2)	1(2)

C22	43(3)	37(3)	33(2)	3(2)	7.4(19)	1(2)
C23	46(3)	49(3)	77(4)	12(3)	28(3)	-4(3)
C24	82(5)	80(5)	81(4)	-4(4)	16(4)	-36(4)
C25	91(5)	118(6)	72(4)	-2(5)	43(4)	-38(5)

Table 4 Bond Lengths for 3n.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C1	1.696(7)	C8	C9	1.539(6)
S1	C4	1.704(5)	C8	C10	1.510(6)
O1	C9	1.368(6)	C8	C16	1.542(6)
O1	C11	1.398(6)	C10	C11	1.381(6)
O2	C9	1.200(6)	C10	C15	1.383(6)
O3	C5	1.210(5)	C11	C12	1.370(7)
O4	C22	1.193(6)	C12	C13	1.390(8)
O5	C22	1.316(6)	C13	C14	1.376(8)
O5	C23	1.472(6)	C14	C15	1.386(7)
C1	C2	1.342(9)	C16	C17	1.380(6)
C2	C3	1.398(7)	C16	C21	1.400(7)
C3	C4	1.414(7)	C17	C18	1.395(7)
C4	C5	1.467(7)	C18	C19	1.359(8)
C5	C6	1.499(6)	C19	C20	1.380(7)
C6	C7	1.542(6)	C20	C21	1.379(7)
C7	C8	1.563(6)	C23	C24	1.487(9)
C7	C22	1.525(6)	C23	C25	1.494(8)

Table 5 Bond Angles for 3n.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	S1	C4	92.1(3)	C11	C10	C8	108.5(4)
C9	O1	C11	107.8(3)	C11	C10	C15	118.3(4)
C22	O5	C23	119.0(4)	C15	C10	C8	133.1(4)
C2	C1	S1	112.1(5)	C10	C11	O1	112.3(4)
C1	C2	C3	114.4(6)	C12	C11	O1	123.9(4)
C2	C3	C4	110.4(4)	C12	C11	C10	123.9(5)
C3	C4	S1	111.0(4)	C11	C12	C13	116.7(5)
C3	C4	C5	129.6(4)	C14	C13	C12	121.0(5)
C5	C4	S1	119.4(4)	C13	C14	C15	120.7(5)

O3	C5	C4	121.2(4)	C10	C15	C14	119.4(4)
O3	C5	C6	121.6(4)	C17	C16	C8	122.3(4)
C4	C5	C6	117.2(4)	C17	C16	C21	117.7(4)
C5	C6	C7	111.6(4)	C21	C16	C8	119.9(4)
C6	C7	C8	113.0(3)	C16	C17	C18	120.6(5)
C22	C7	C6	108.6(4)	C19	C18	C17	120.9(5)
C22	C7	C8	112.3(4)	C18	C19	C20	119.5(5)
C9	C8	C7	107.6(3)	C21	C20	C19	120.1(5)
C9	C8	C16	105.9(4)	C20	C21	C16	121.1(5)
C10	C8	C7	115.2(4)	O4	C22	O5	125.0(5)
C10	C8	C9	100.2(3)	O4	C22	C7	123.5(4)
C10	C8	C16	112.8(4)	O5	C22	C7	111.5(4)
C16	C8	C7	113.6(4)	O5	C23	C24	105.4(5)
O1	C9	C8	110.8(4)	O5	C23	C25	108.2(5)
O2	C9	O1	120.8(5)	C24	C23	C25	113.6(6)
O2	C9	C8	128.4(5)				

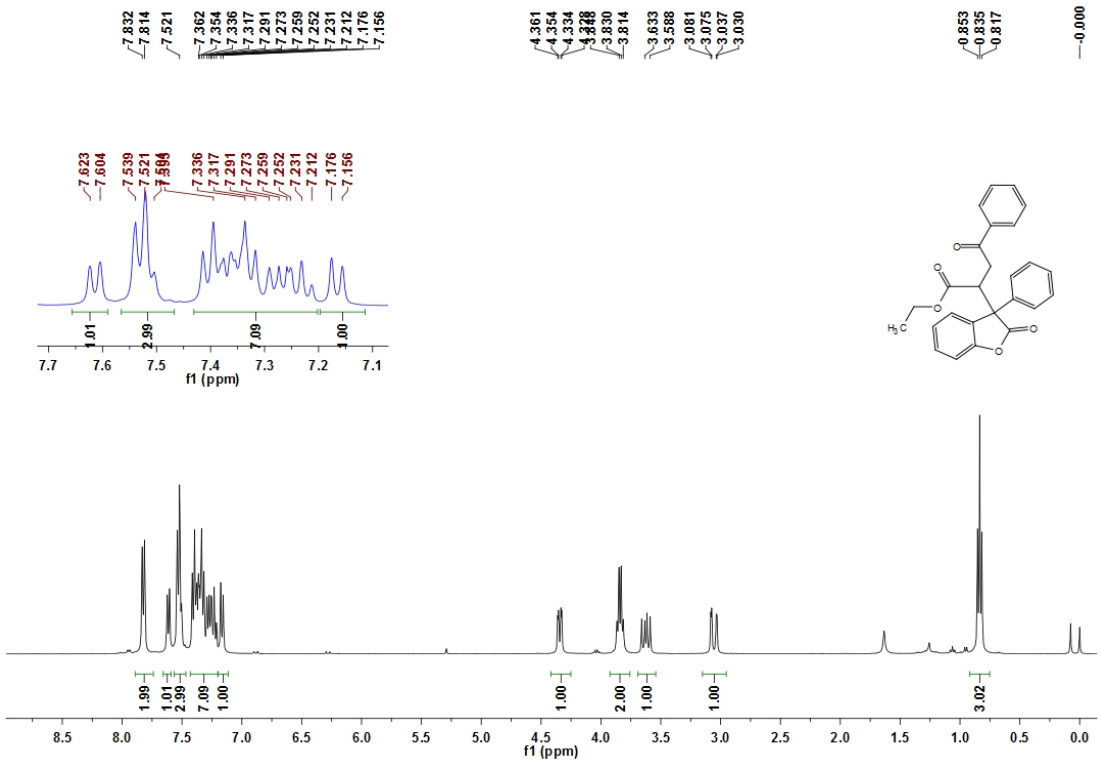
Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3n.

Atom	*x*	*y*	*z*	U(eq)
H1	10213	8791	10526	85
H2	8965	8979	7922	71
H3	8385	7656	6523	49
H6A	9308	5965	6020	48
H6B	7352	6161	6140	48
H7	8969	4569	7049	42
H12	6852	5939	542	65
H13	3751	6078	142	73
H14	2318	5581	1881	64
H15	3907	4895	4028	50
H17	5472	3518	2801	57
H18	5343	2055	2598	67
H19	7282	1221	4291	65
H20	9454	1845	6184	61
H21	9657	3298	6369	53
H23	3547	4043	7388	66
H24A	3737	2923	5776	123
H24B	2851	2613	7045	123

H24C	4862	2399	7136	123
H25A	5954	3109	9627	135
H25B	3966	3296	9660	135
H25C	5345	4042	9820	135

(F) Copies of the NMR spectra

3a



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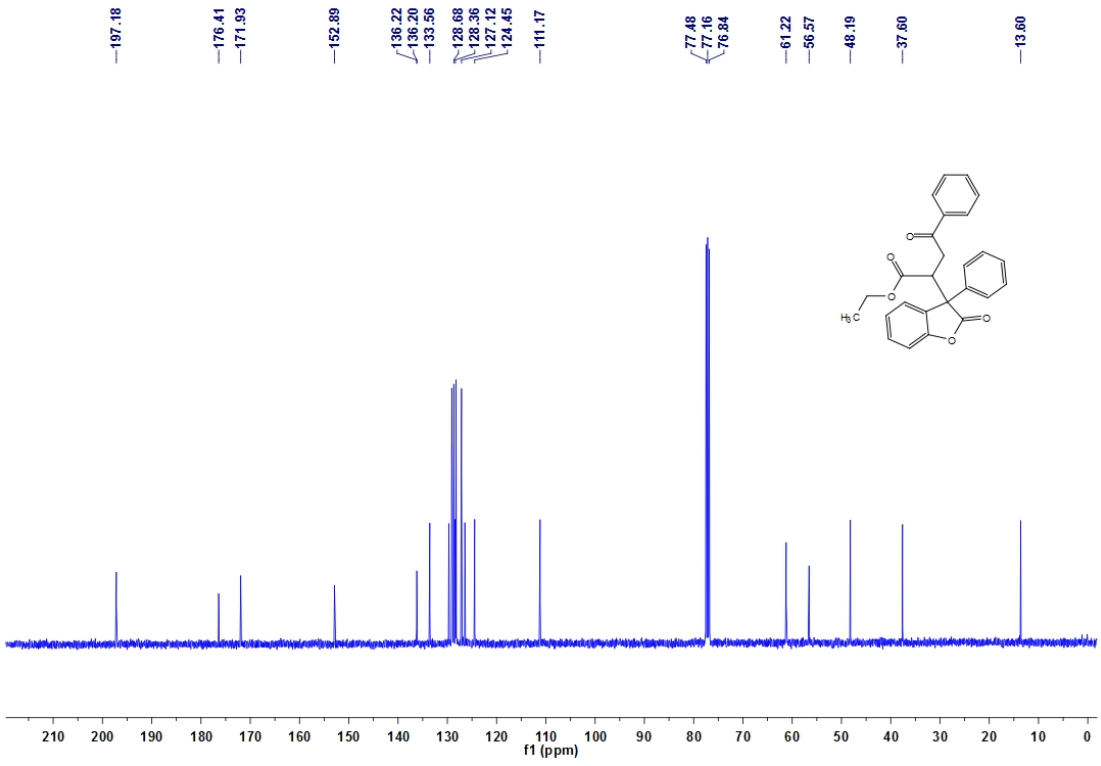

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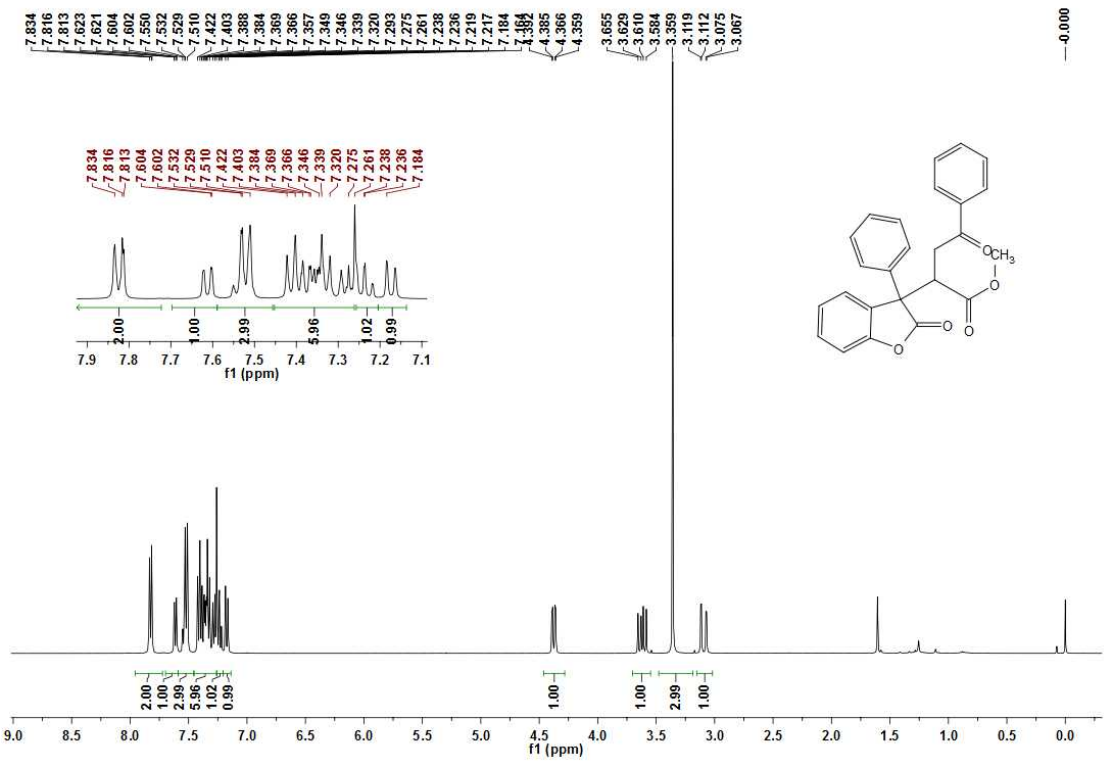

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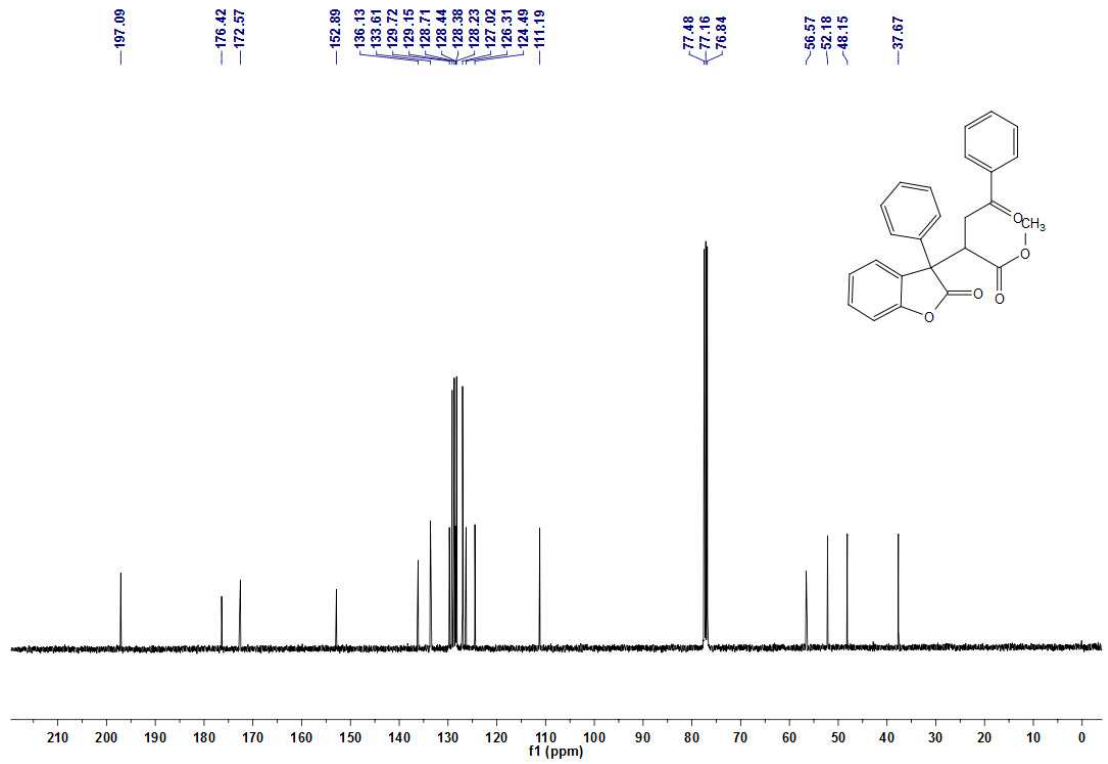

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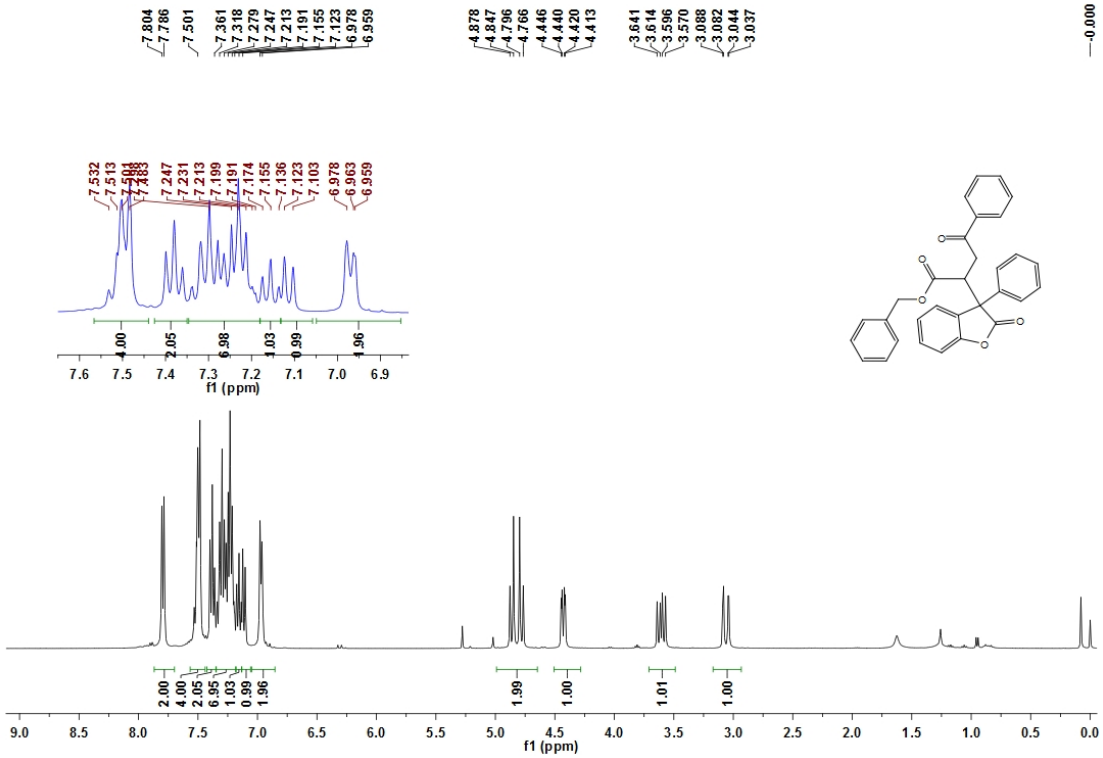
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7.213
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6.959
4.878
4.847
4.796
4.766
4.446
4.440
4.420
4.413
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3.596
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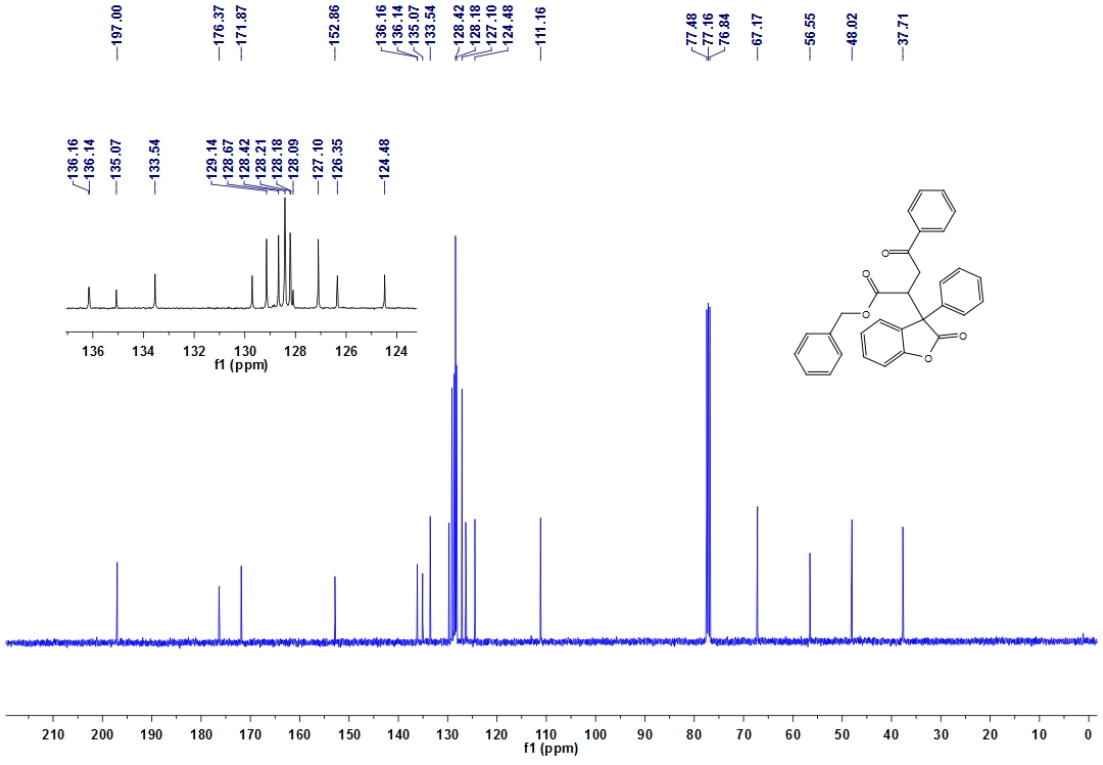
f1 (ppm)

3c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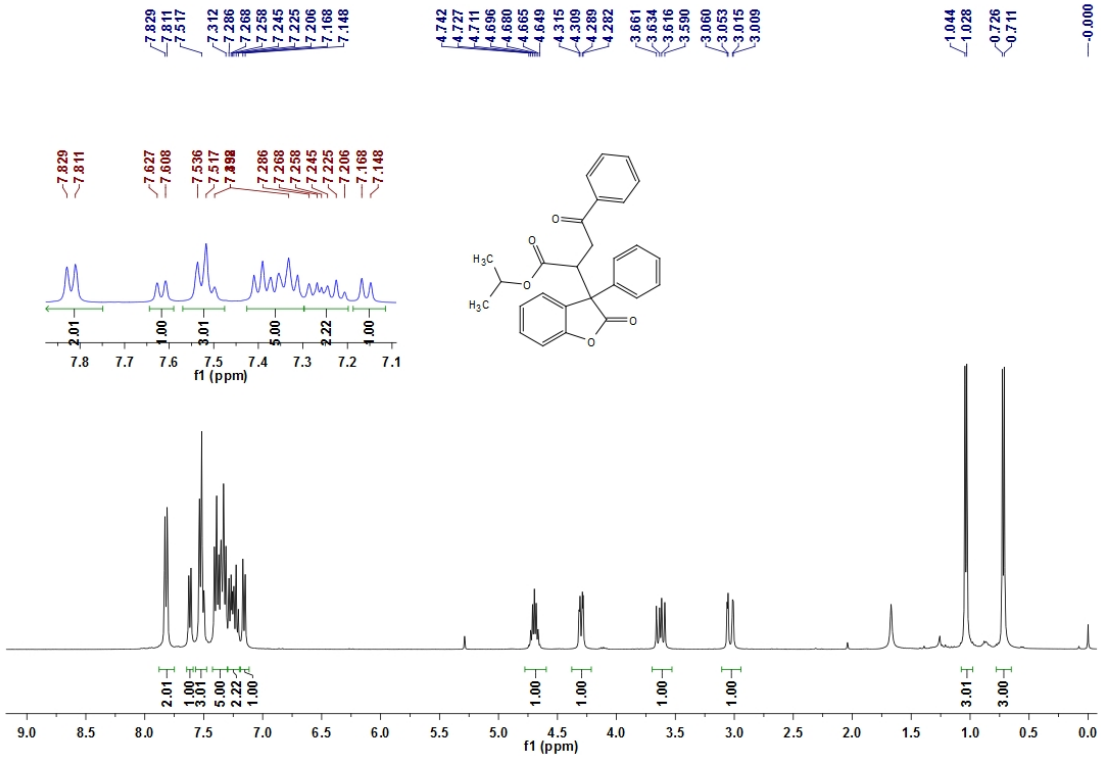
f1 (ppm)

3d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4.315
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4.289
4.282
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3.634
3.616
3.590
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3.015
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1.044
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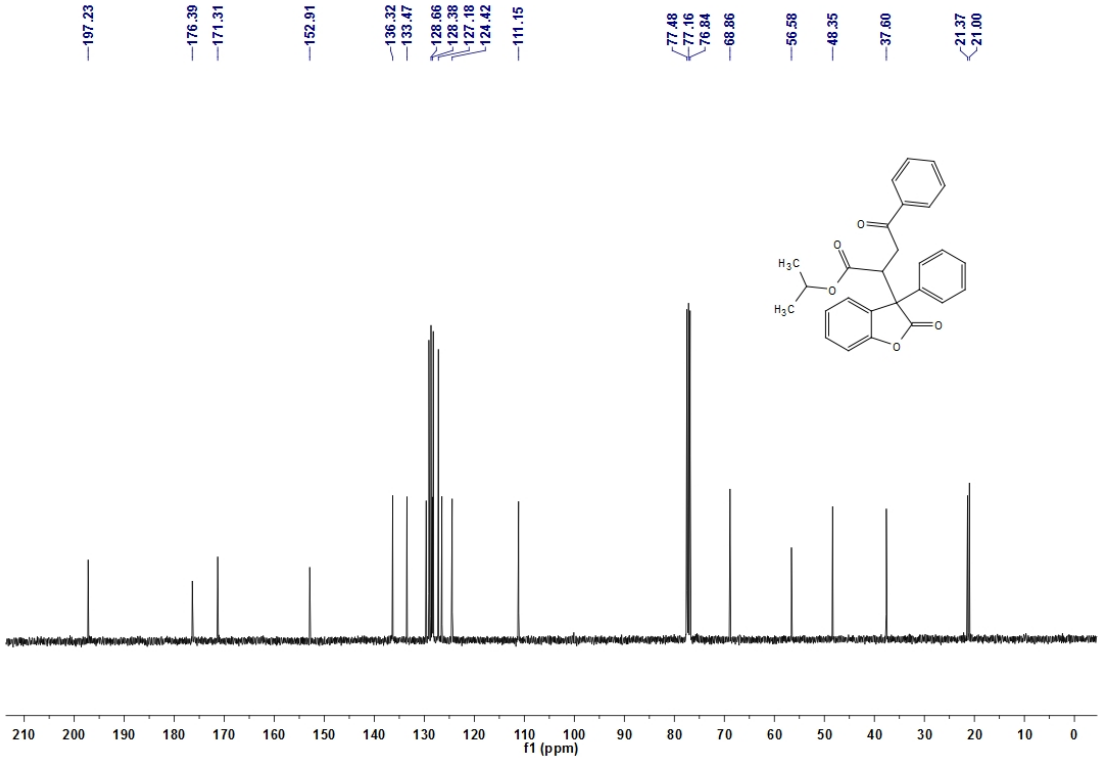
3d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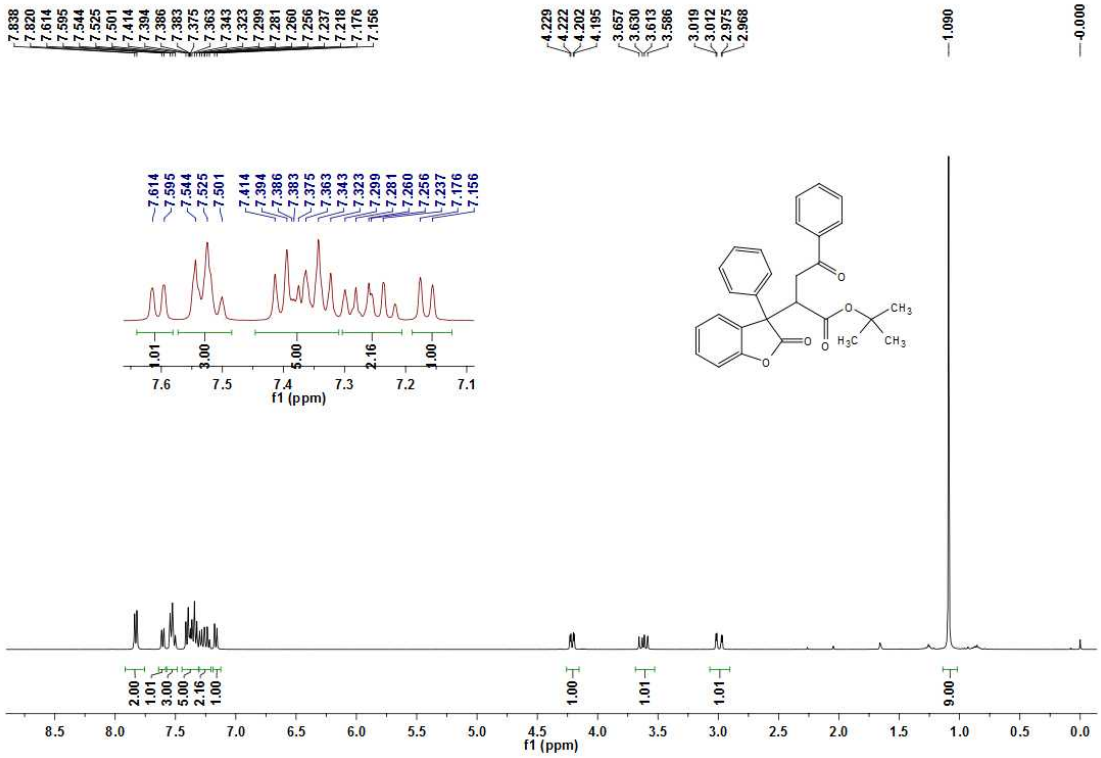
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7.383
7.375
7.363
7.343
7.323
7.299
7.281
7.260
7.256
7.237
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4.222
4.202
4.195
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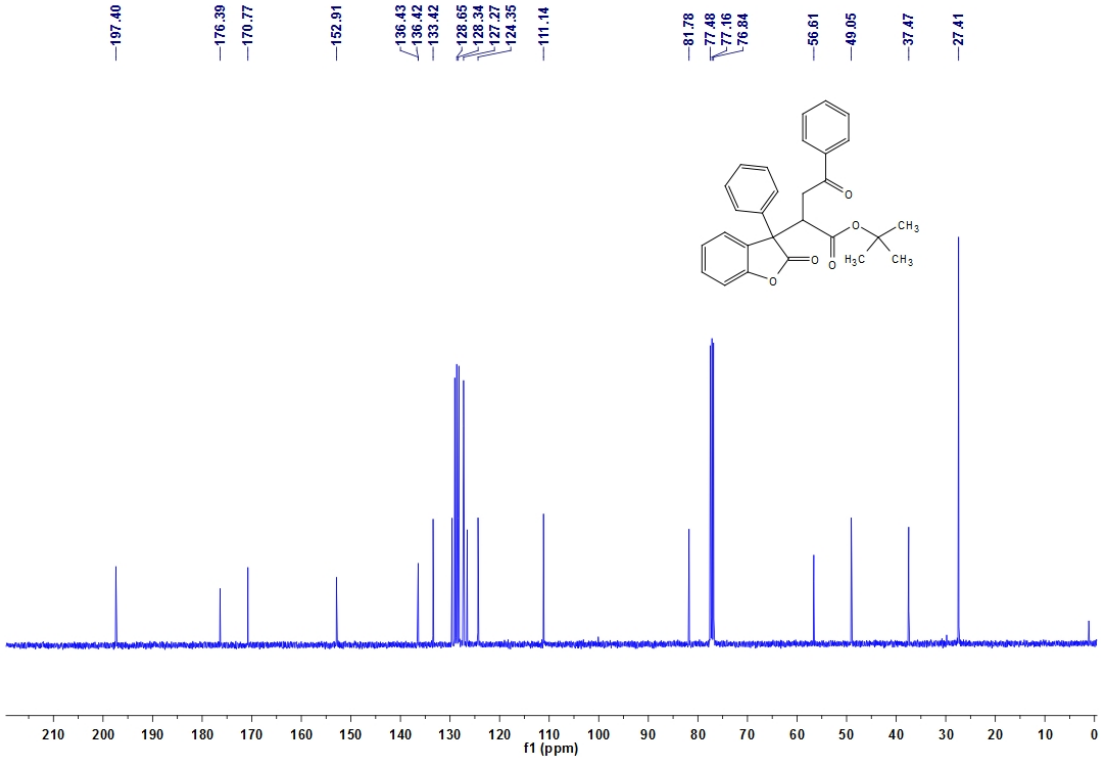
f1 (ppm)

3e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127.27
124.35
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77.48
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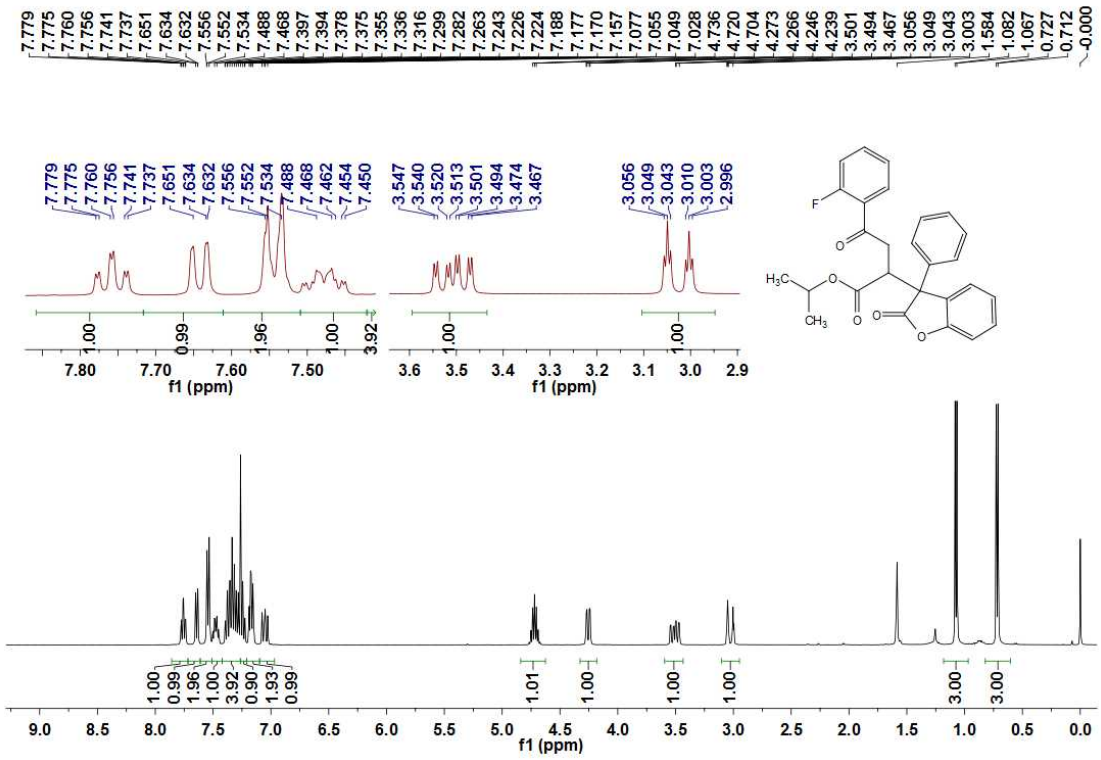
49.05
37.47
27.41
f1 (ppm)

3f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7.468
7.462
7.454
7.450
3.547
3.540
3.520
3.513
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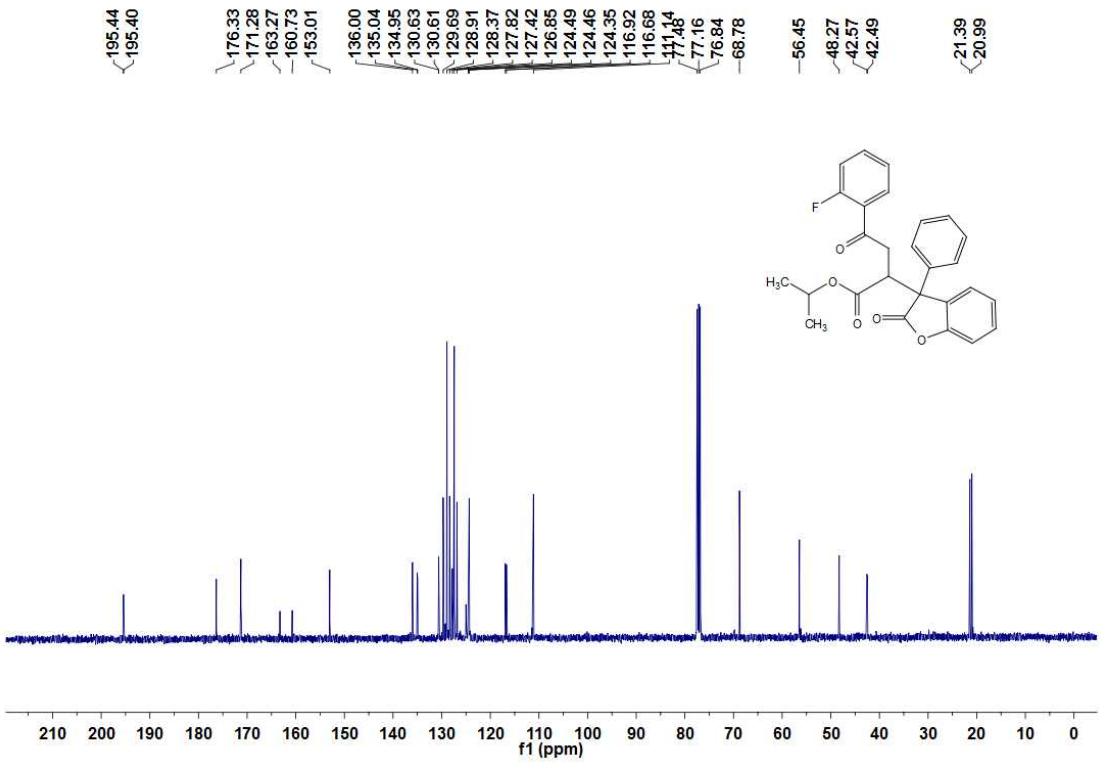
f1 (ppm)

3f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128.91
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127.42
126.85
124.49
124.46
124.35
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116.68
111.14
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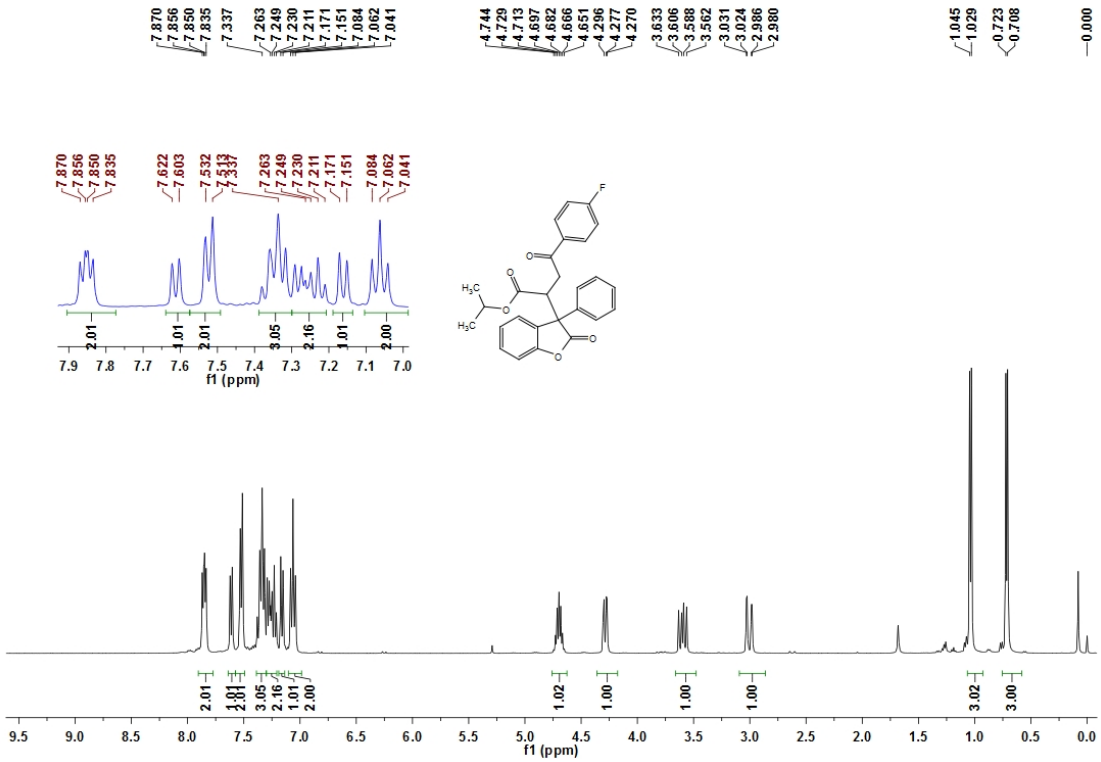
f1 (ppm)

3g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7.171
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7.084
7.062
7.041
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4.729
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4.682
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4.651
4.296
4.277
4.270
3.633
3.606
3.588
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3.031
3.024
2.986
2.980
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1.029
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0.708
0.000
F
O
O
O
O
H3C
H3C
2.01
1.01
2.01
3.05
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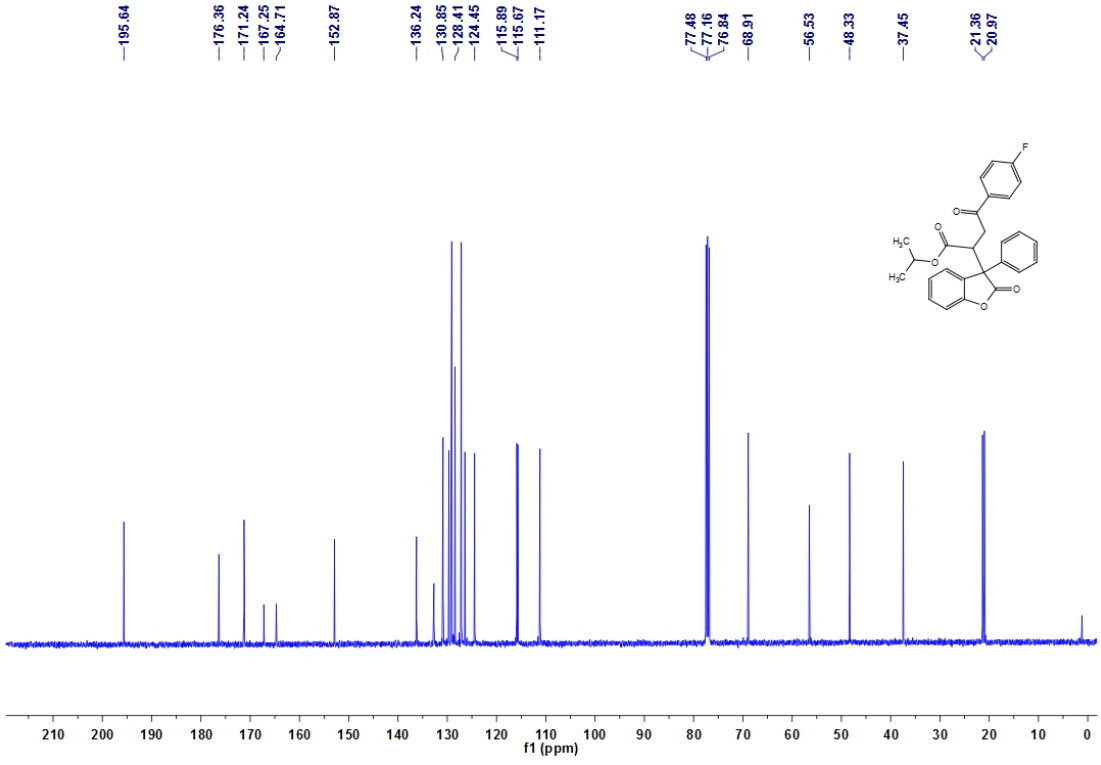
2.00
1.02
1.00
1.00
1.00
3.02
3.00
f1 (ppm)

3g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77.48
77.16
76.84
68.91
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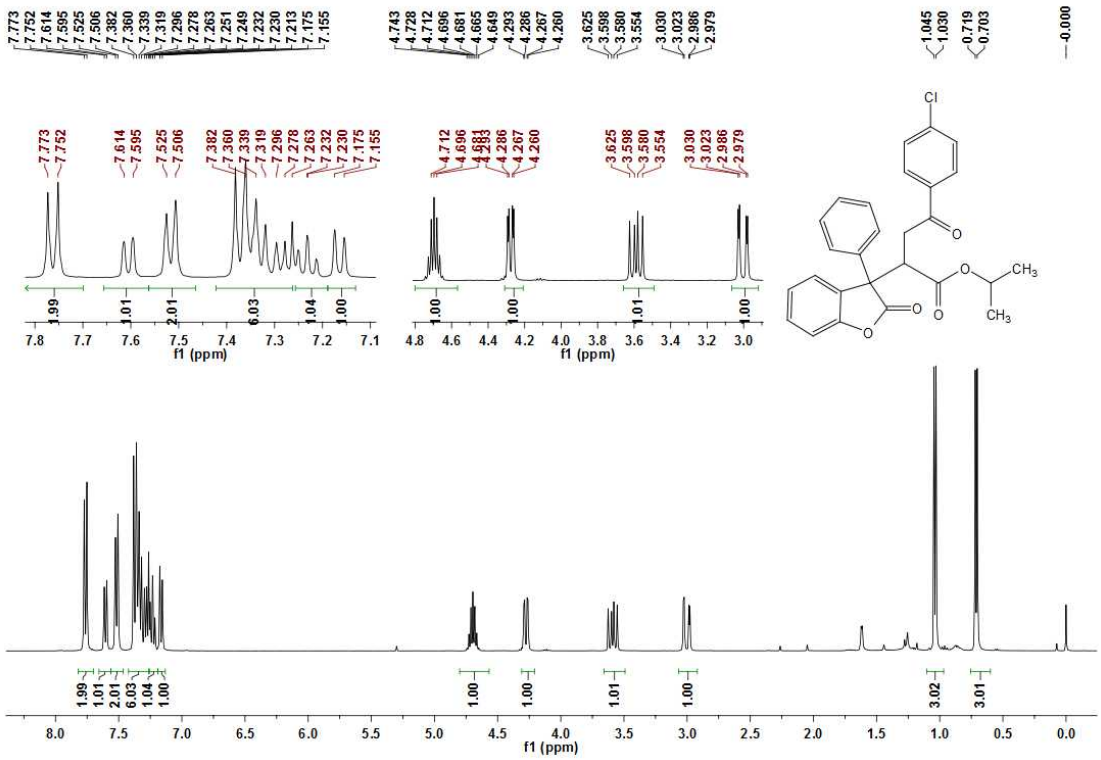
O
O
O
H3C
H3C
f1 (ppm)

3h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7.175
7.155
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4.286
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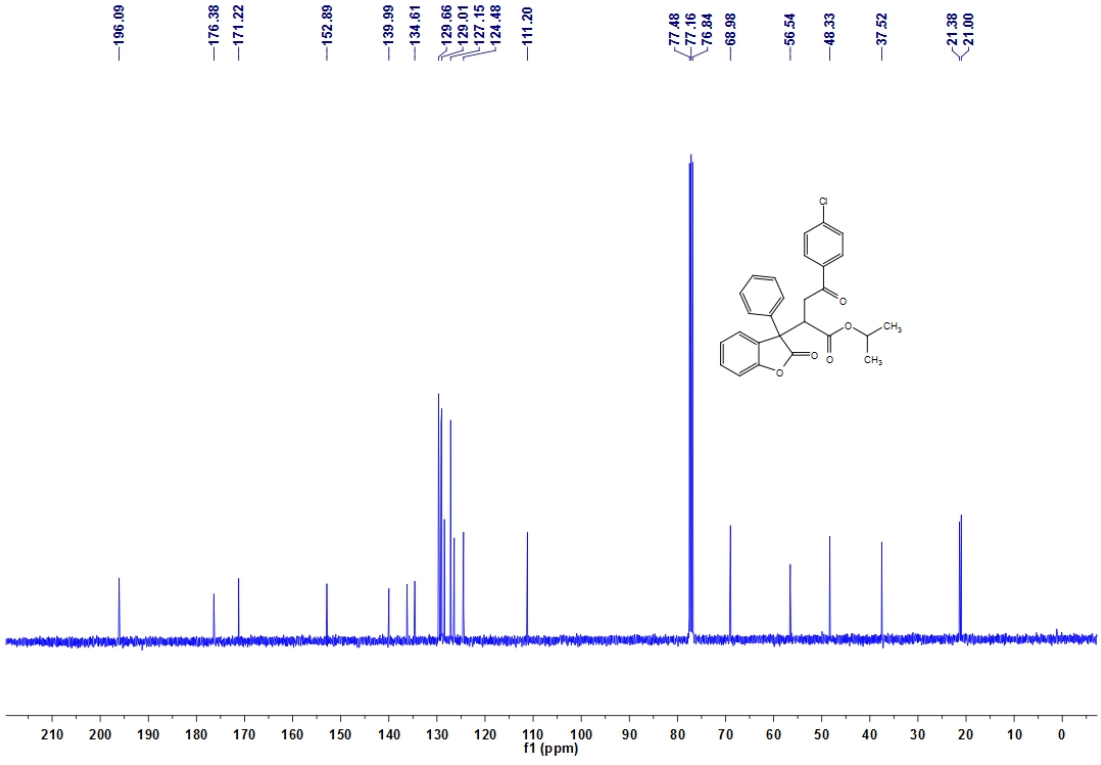
3.625
3.598
3.580
3.554
3.030
3.023
2.986
2.979
1.045
1.030
0.719
0.703
-0.000
Cl
O
O
O
O
CH3
CH3
1.99
1.01
2.01
6.03
1.04
1.00
1.00
1.00
1.01
1.00
3.02
3.01
f1 (ppm)

3h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127.15
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111.20
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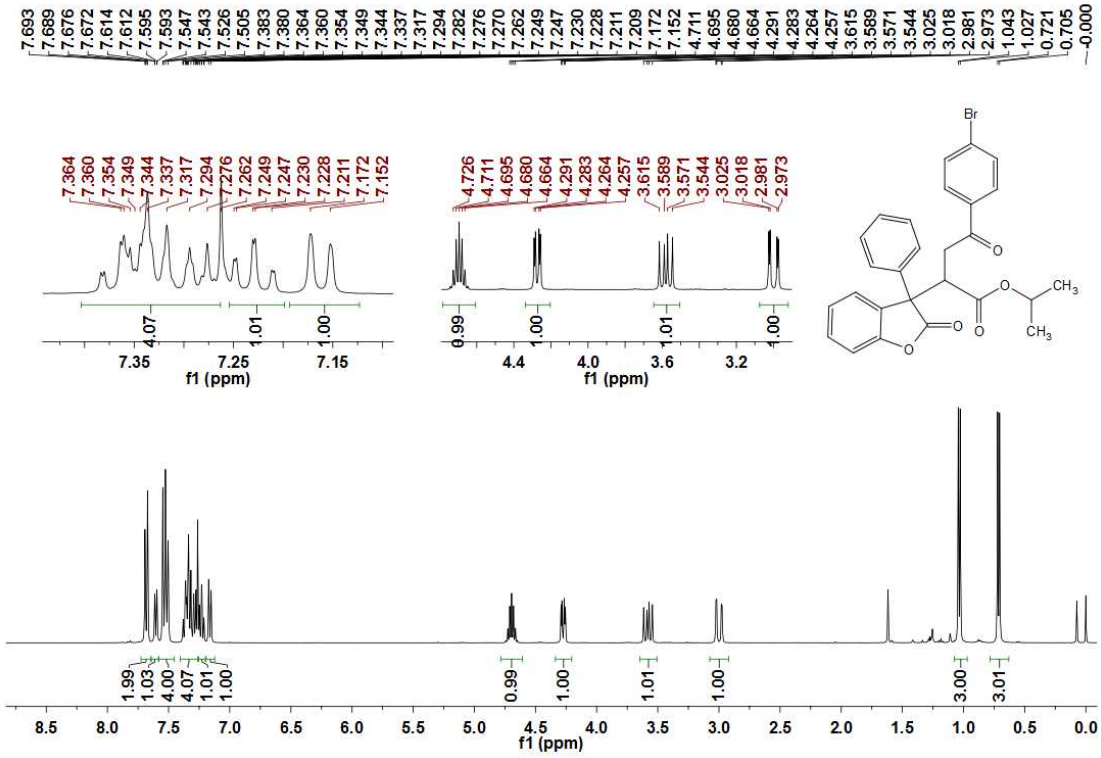
77.16
76.84
68.98
56.54
48.33
37.52
21.38
21.00
Cl
O
O
O
O
CH3
CH3
f1 (ppm)

3i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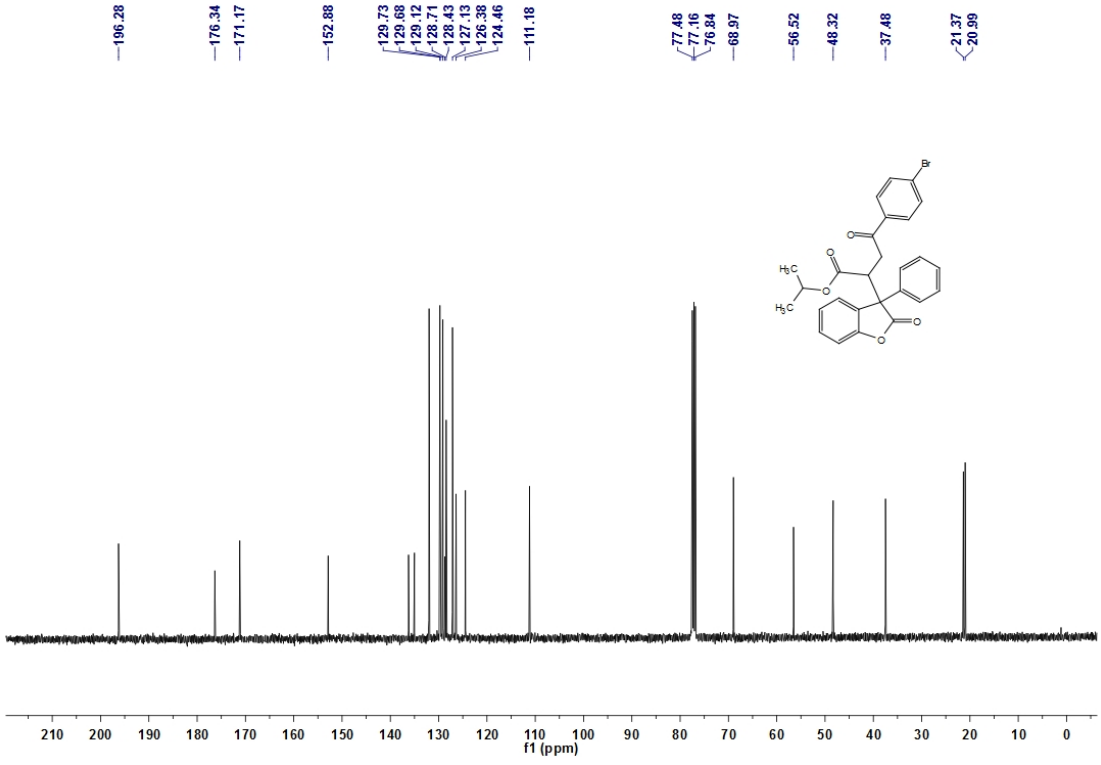
7.364 7.360 7.354 7.349 7.344 7.337 7.317 7.294 7.276 7.262 7.249 7.247 7.230 7.228 7.211 7.172 7.152
4.07 1.01 1.00
7.35 7.25 7.15
f1 (ppm)
4.726 4.711 4.695 4.680 4.664 4.291 4.283 4.264 4.257 3.615 3.589 3.571 3.544 3.025 3.018 2.981 2.973
0.99 1.00 1.01 1.00
4.4 4.0 3.6 3.2
f1 (ppm)
Br
O
O
O
O
O
CH3
CH3
1.99 1.03 4.00 4.07 1.01 1.00 0.99 1.00 1.01 1.00 3.00 3.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3i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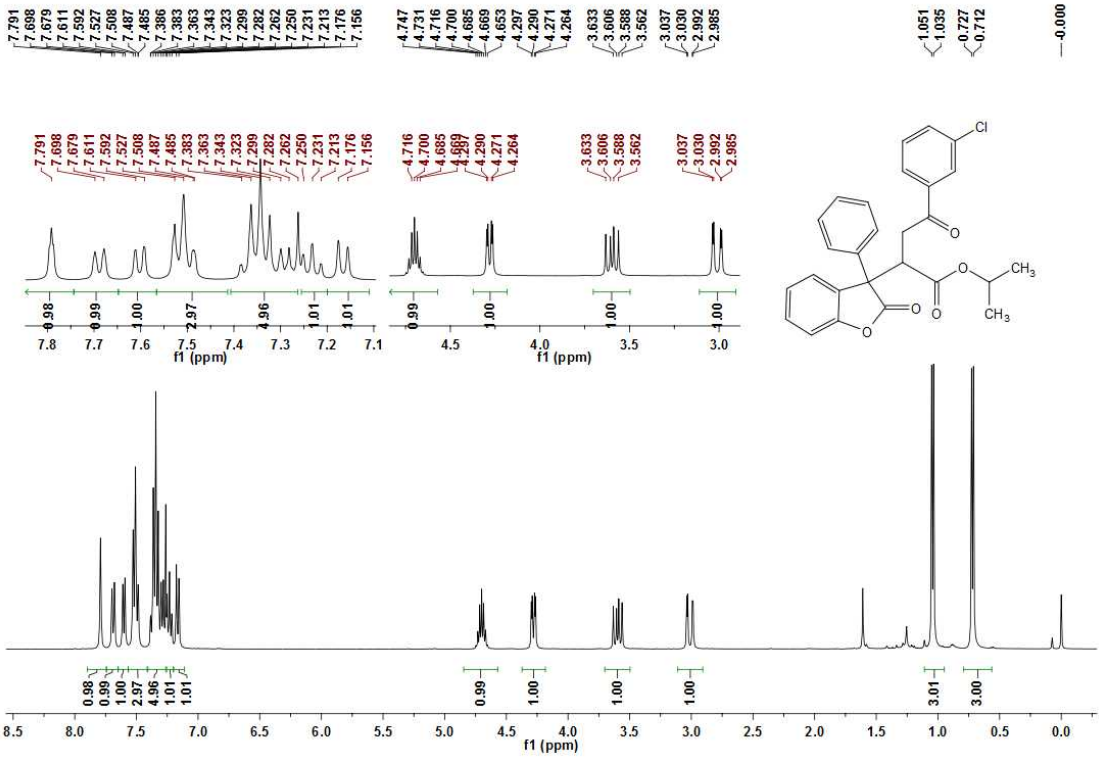
Br
H3C
H3C
O
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3j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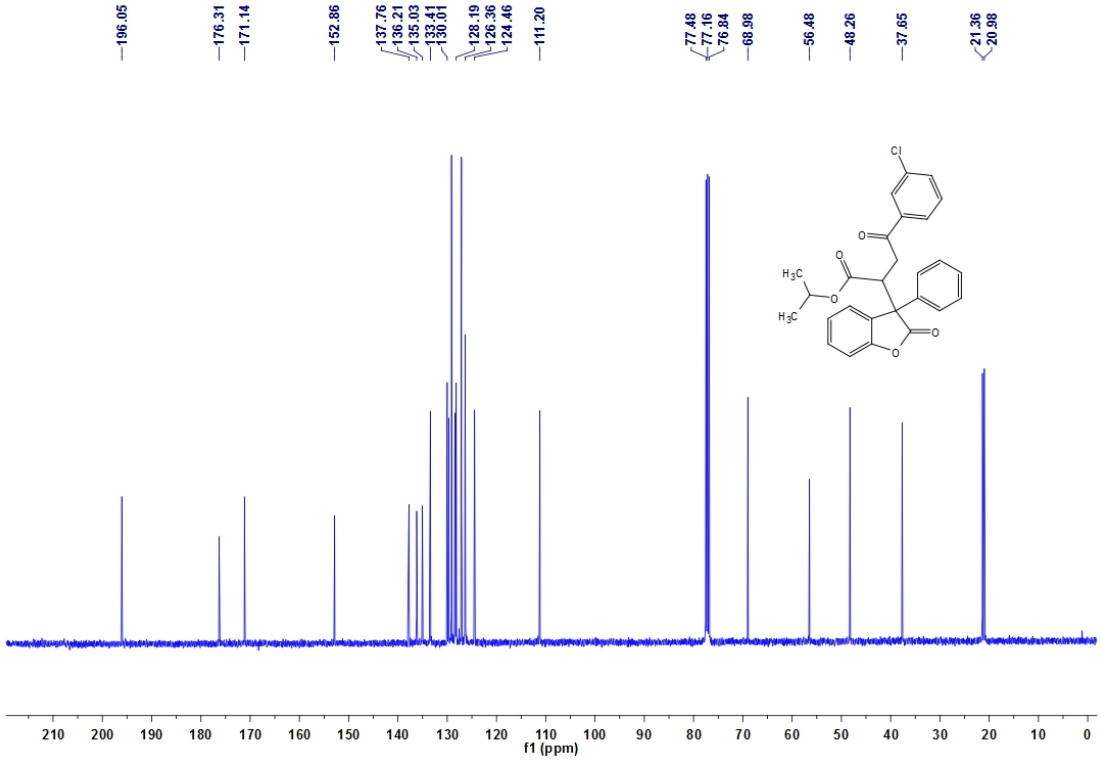
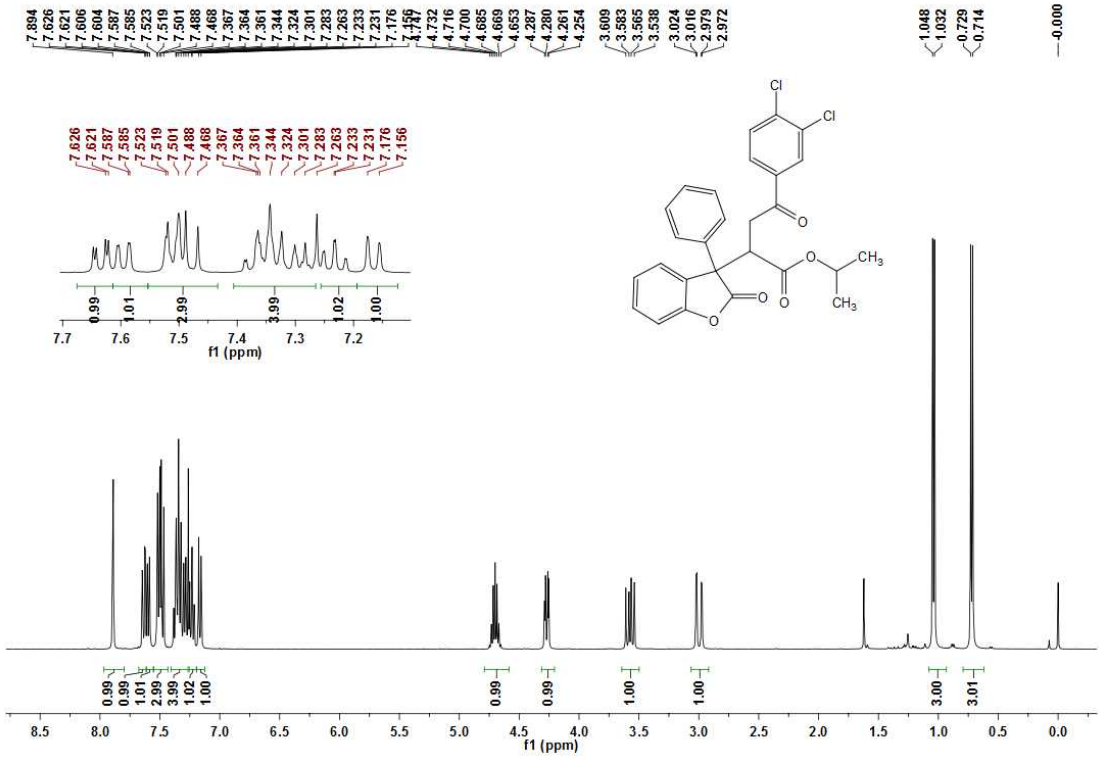
7.323
7.299
7.282
7.262
7.250
7.231
7.213
7.176
7.156
4.747
4.731
4.716
4.700
4.685
4.669
4.653
4.297
4.290
4.271
4.264
3.633
3.606
3.588
3.562
3.037
3.030
2.992
2.985
1.051
1.035
0.727
0.712
-0.000
0.98
0.99
1.00
2.97
4.96
1.01
1.01
0.99
1.00
1.00
1.00
3.01
3.00
f1 (ppm)
Cl
O
O
O
O
CH3
CH3

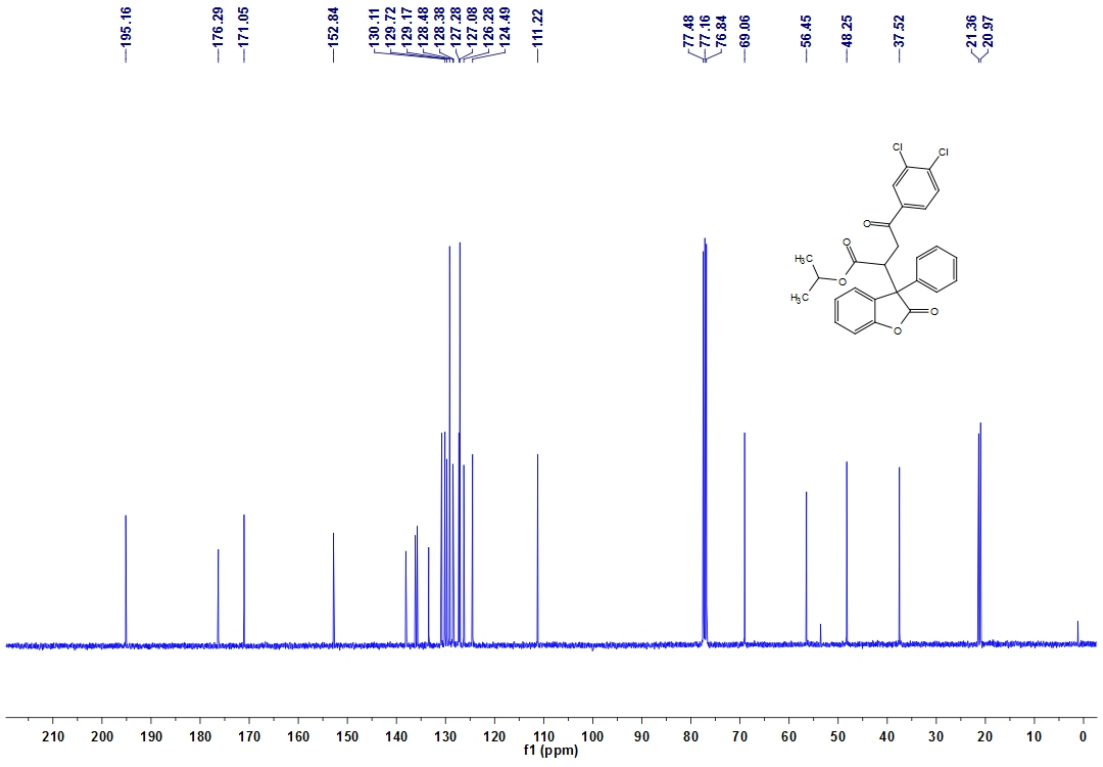
3j


196.05
176.31
171.14
152.86
137.76
136.21
135.03
133.41
130.01
128.19
126.36
124.46
111.20
77.48
77.16
76.84
68.98
56.48
48.26
37.65
21.36
20.98
f1 (ppm)
Cl
O
O
O
O
H3C
H3C

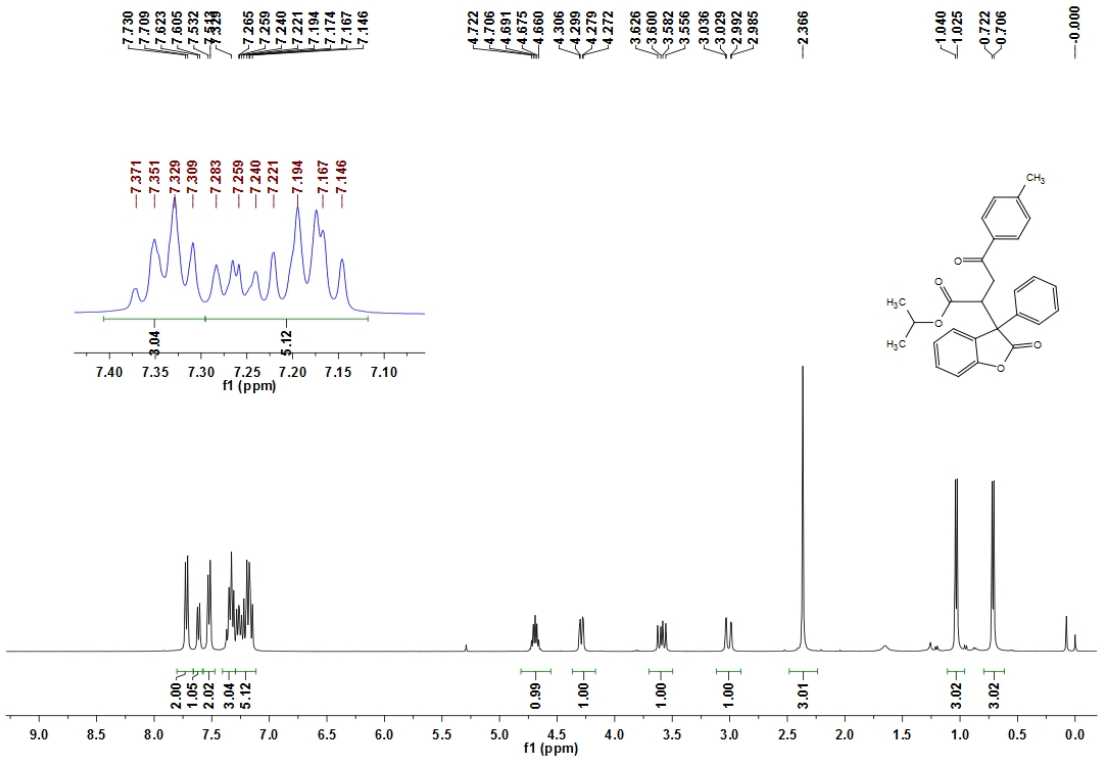
3k



3k



3l



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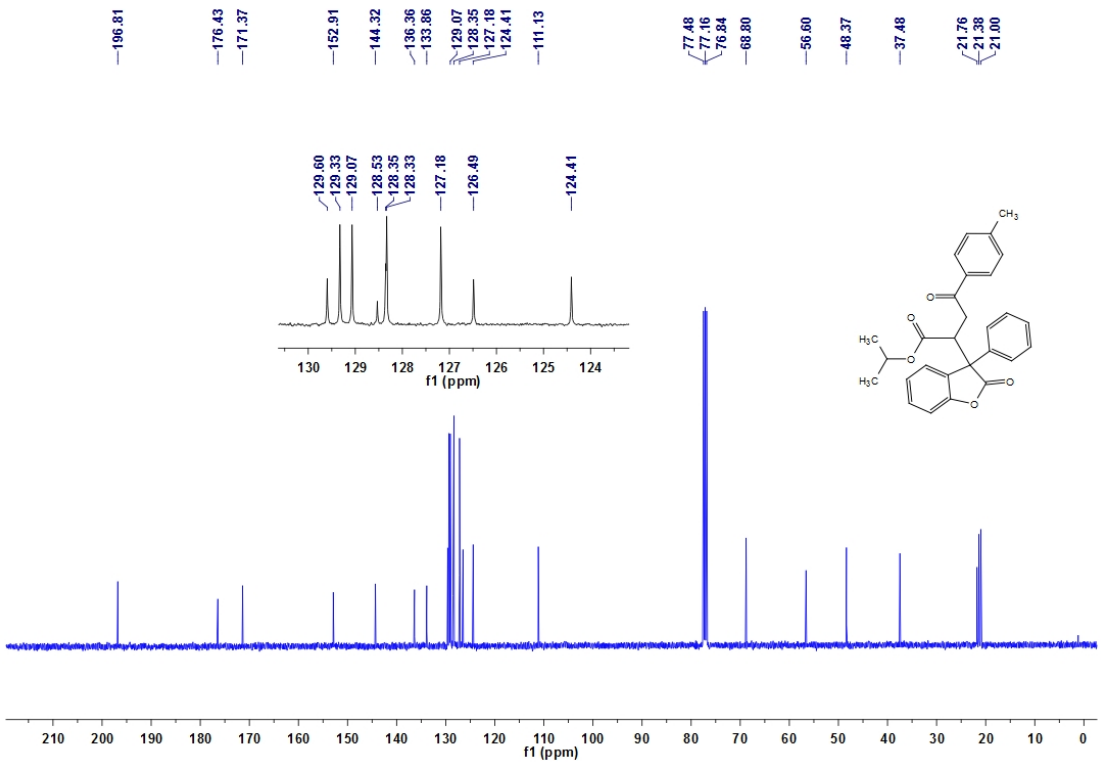
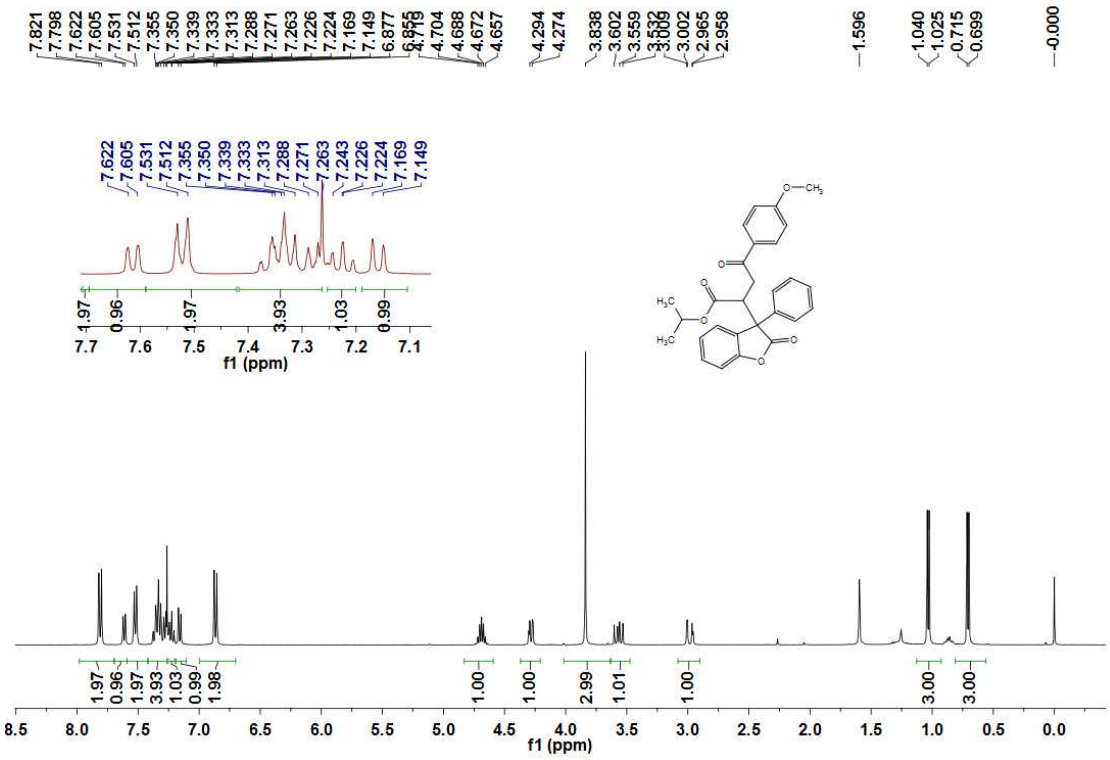


3m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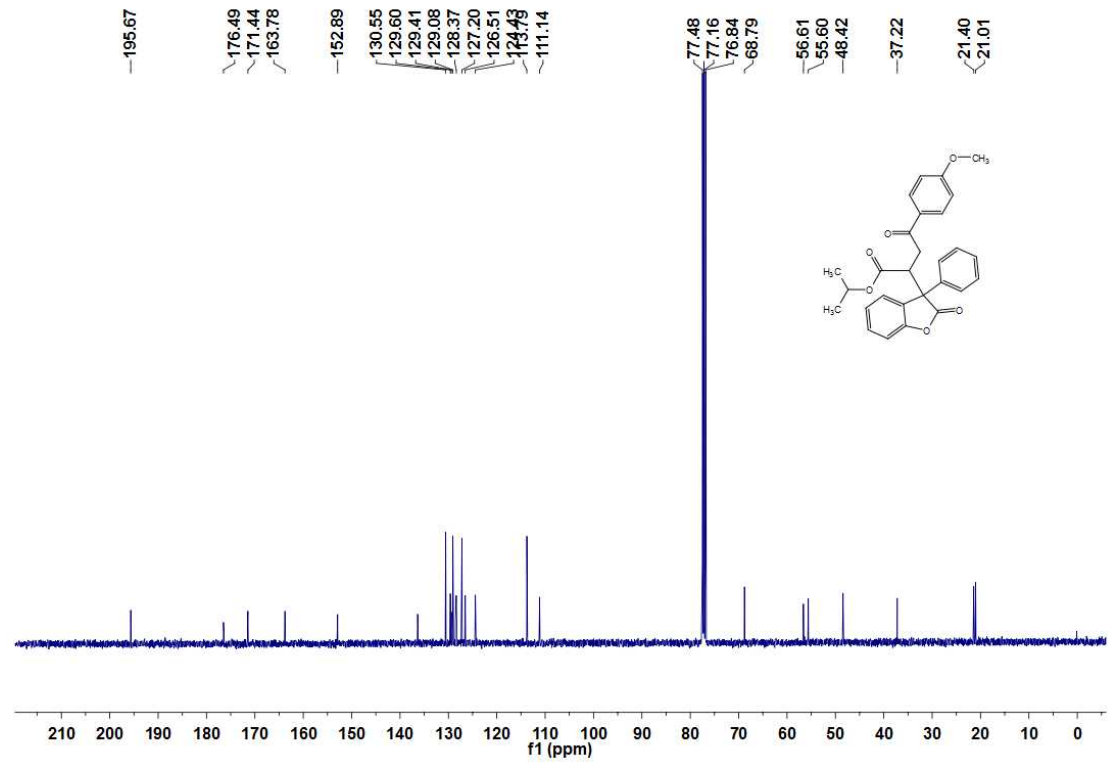
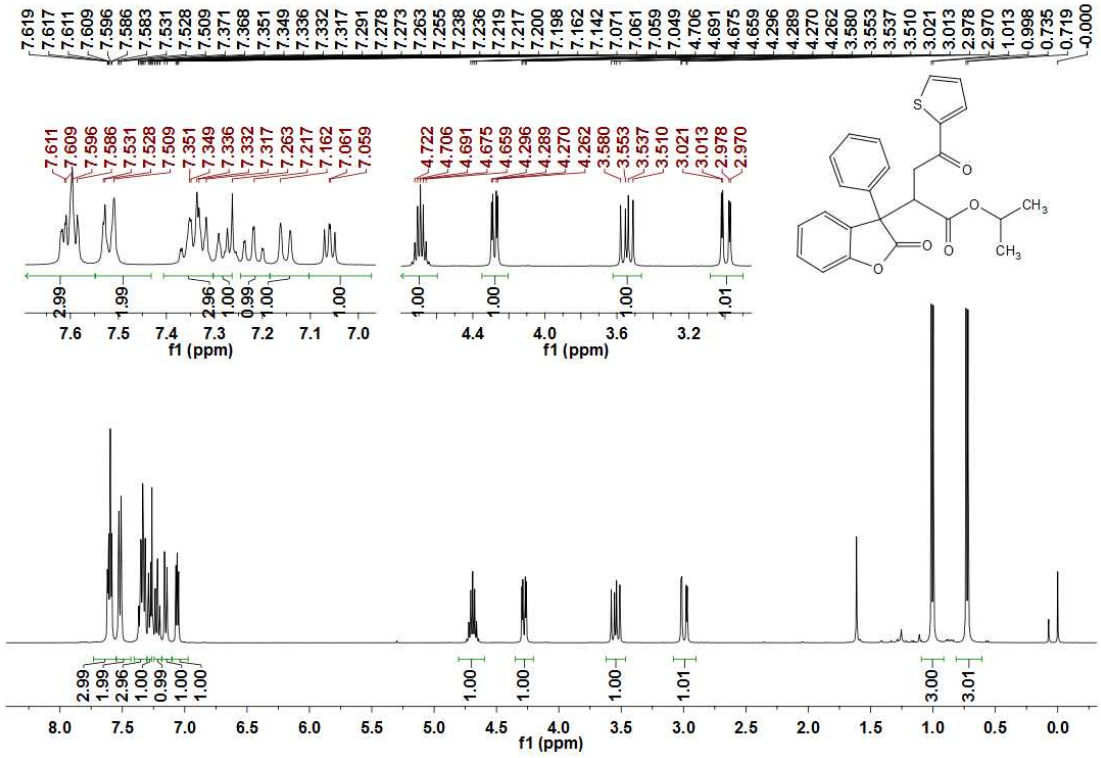
7.798
7.622
7.605
7.531
7.512
7.355
7.350
7.339
7.333
7.313
7.288
7.271
7.263
7.226
7.224
7.169
7.149
6.877
4.704
4.688
4.672
4.657
4.294
4.274
3.838
3.602
3.559
3.002
2.965
2.958
1.596
1.040
1.025
0.715
0.699
0.000
1.97
0.96
1.97
3.93
1.03
0.99
1.00
1.00
2.99
1.01
1.00
3.00
3.00
f1 (ppm)

3m


195.67
176.49
171.44
163.78
152.89
130.55
129.60
129.41
129.08
128.37
127.20
126.51
111.14
77.48
77.16
76.84
68.79
56.61
55.60
48.42
37.22
21.40
21.01
f1 (ppm)

3n



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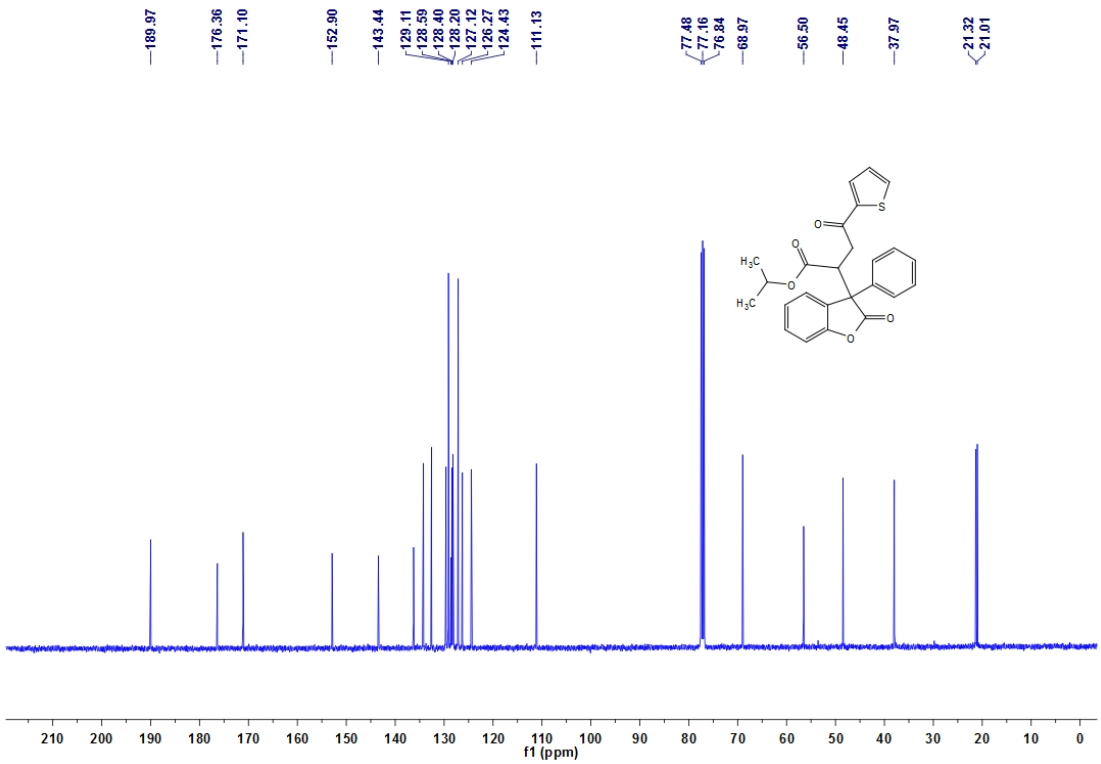
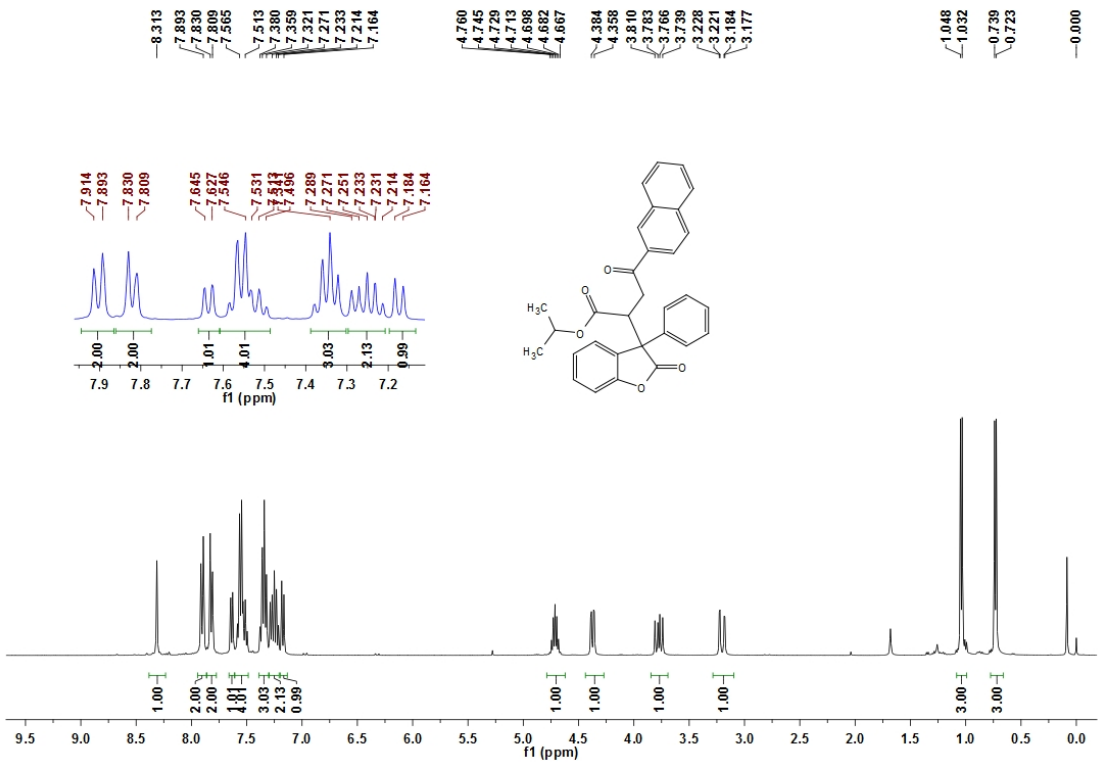
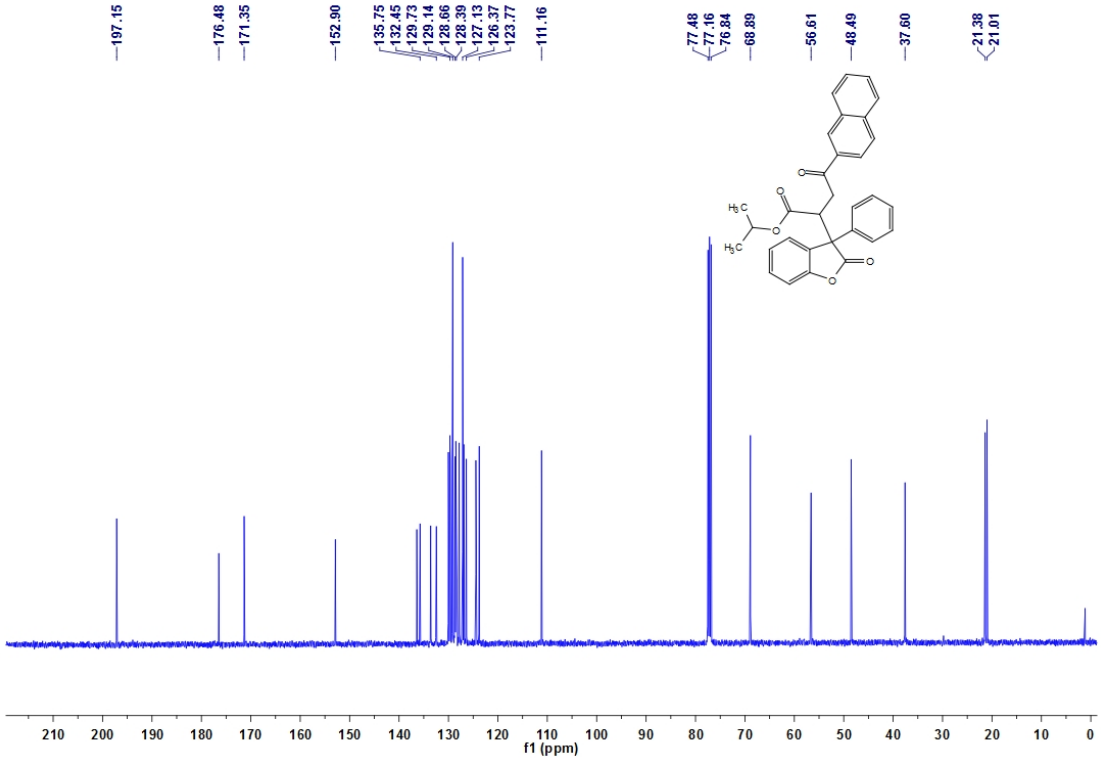


3o


8.313
7.893
7.830
7.809
7.565
7.513
7.380
7.359
7.321
7.271
7.233
7.214
7.164
4.760
4.745
4.729
4.713
4.698
4.682
4.667
4.384
4.358
3.810
3.783
3.766
3.739
3.228
3.221
3.184
3.177
1.048
1.032
0.739
0.723
0.000
f1 (ppm)

3o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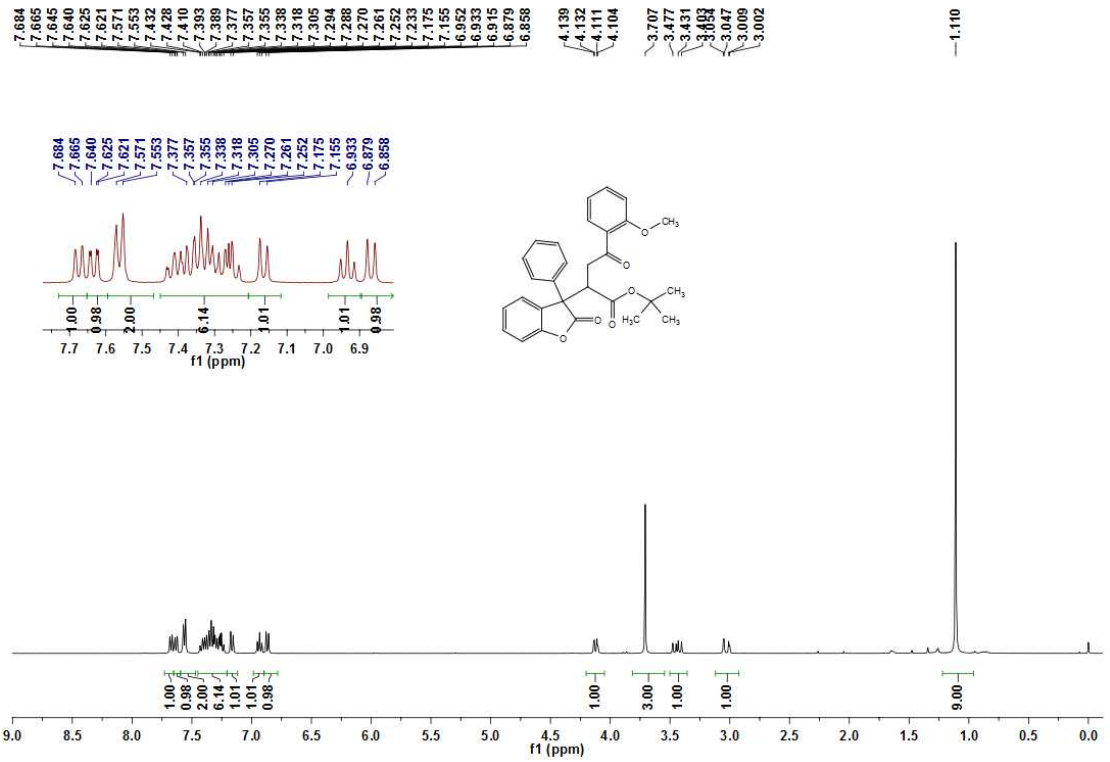
176.48
171.35
152.90
135.75
132.45
129.73
129.14
128.66
128.39
127.13
126.37
123.77
111.16
77.48
77.16
76.84
68.89
56.61
48.49
37.60
21.38
21.01
f1 (ppm)

3p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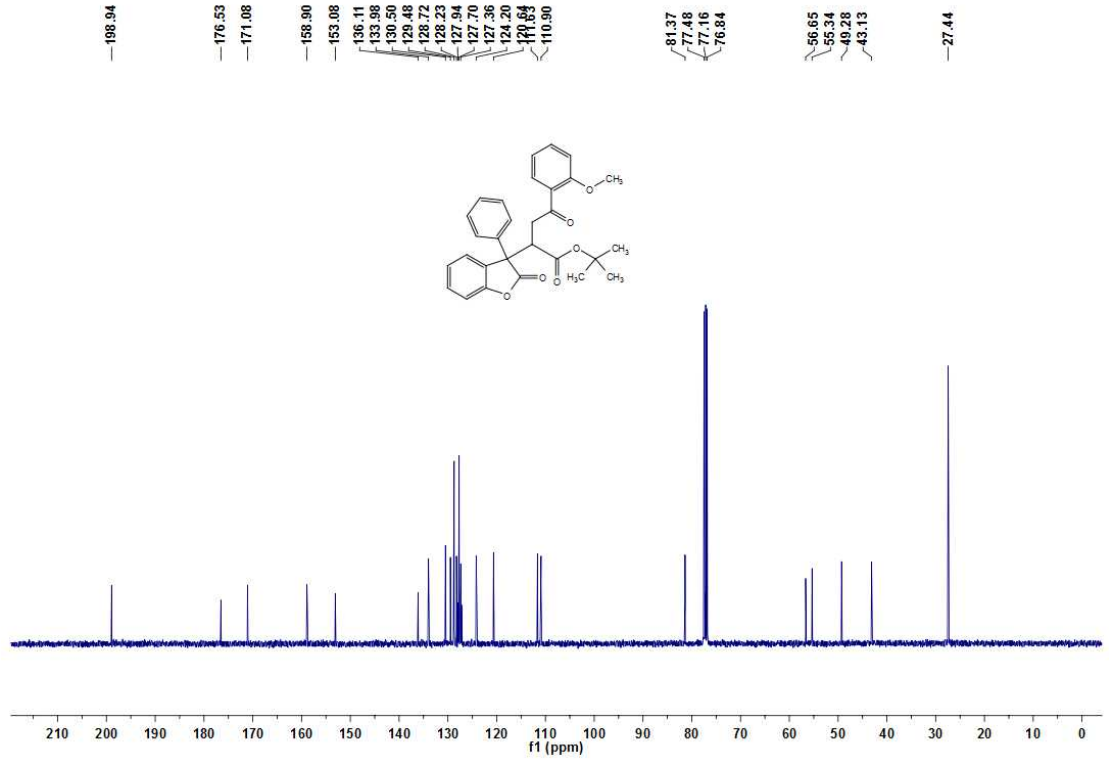
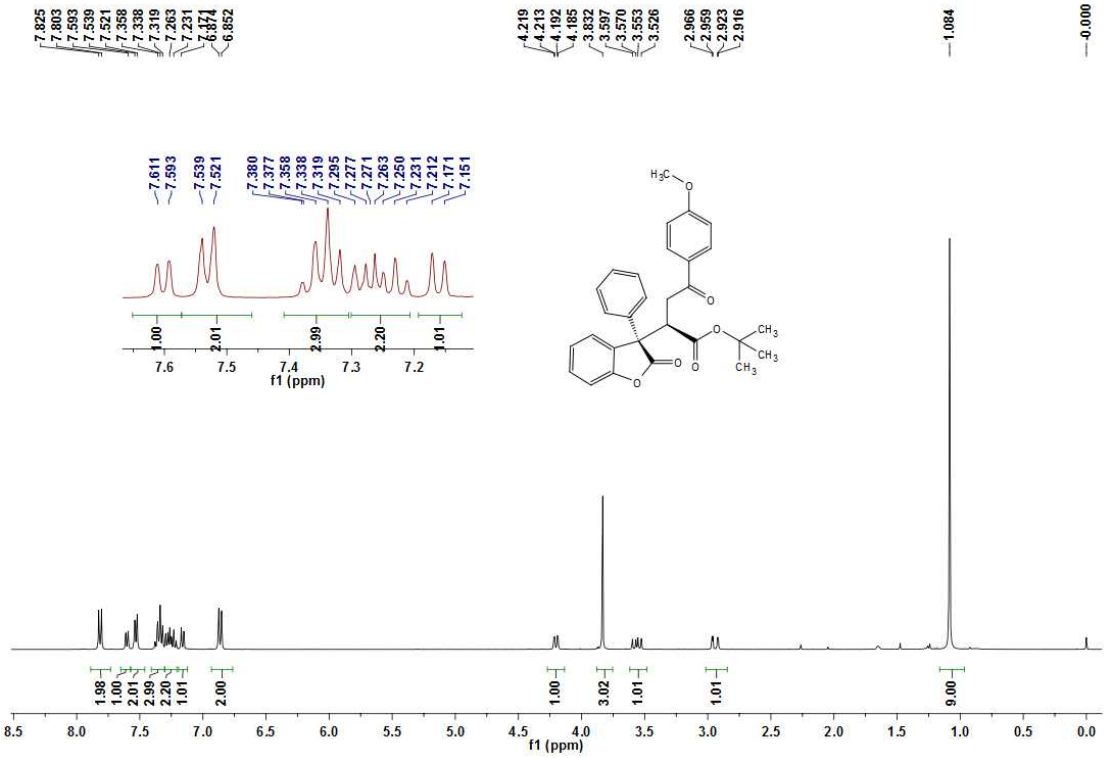
7.665
7.645
7.640
7.625
7.621
7.571
7.553
7.432
7.428
7.410
7.393
7.389
7.377
7.357
7.355
7.338
7.318
7.305
7.294
7.288
7.270
7.261
7.252
7.233
7.175
7.155
6.952
6.933
6.915
6.879
6.858
4.139
4.132
4.111
4.104
3.707
3.477
3.431
3.047
3.009
3.002
1.110
1.00
0.98
2.00
6.14
1.01
1.01
0.98
1.00
3.00
1.00
1.00
9.00
f1 (ppm)

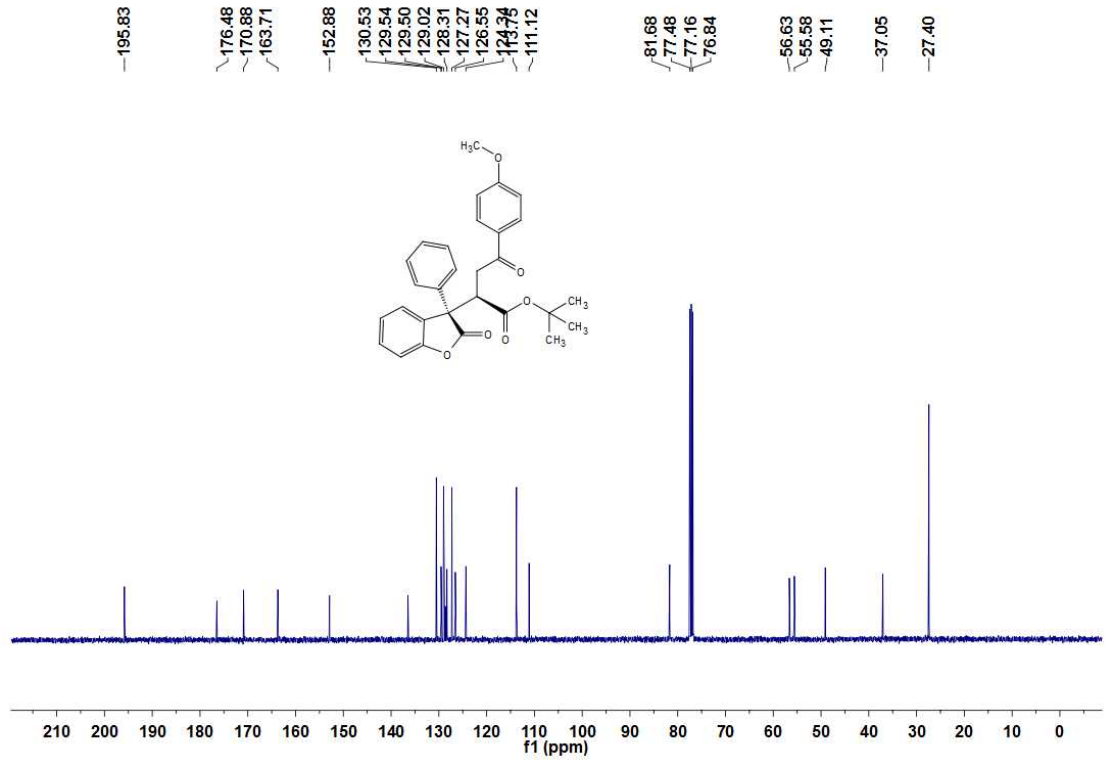
3p


198.94
176.53
171.08
158.90
153.08
136.11
133.98
130.50
129.48
128.72
128.23
127.94
127.70
127.36
124.20
120.64
111.63
110.90
81.37
77.48
77.16
76.84
56.65
55.34
49.28
43.13
27.44
f1 (ppm)

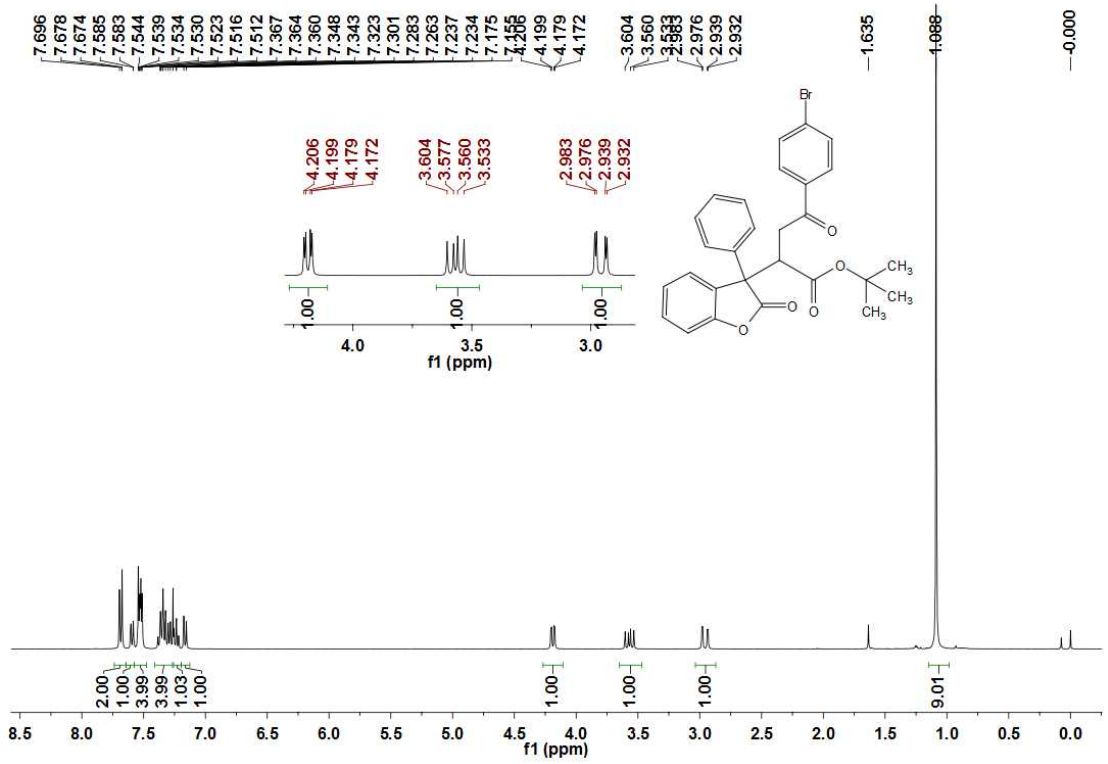
3q



3q



3r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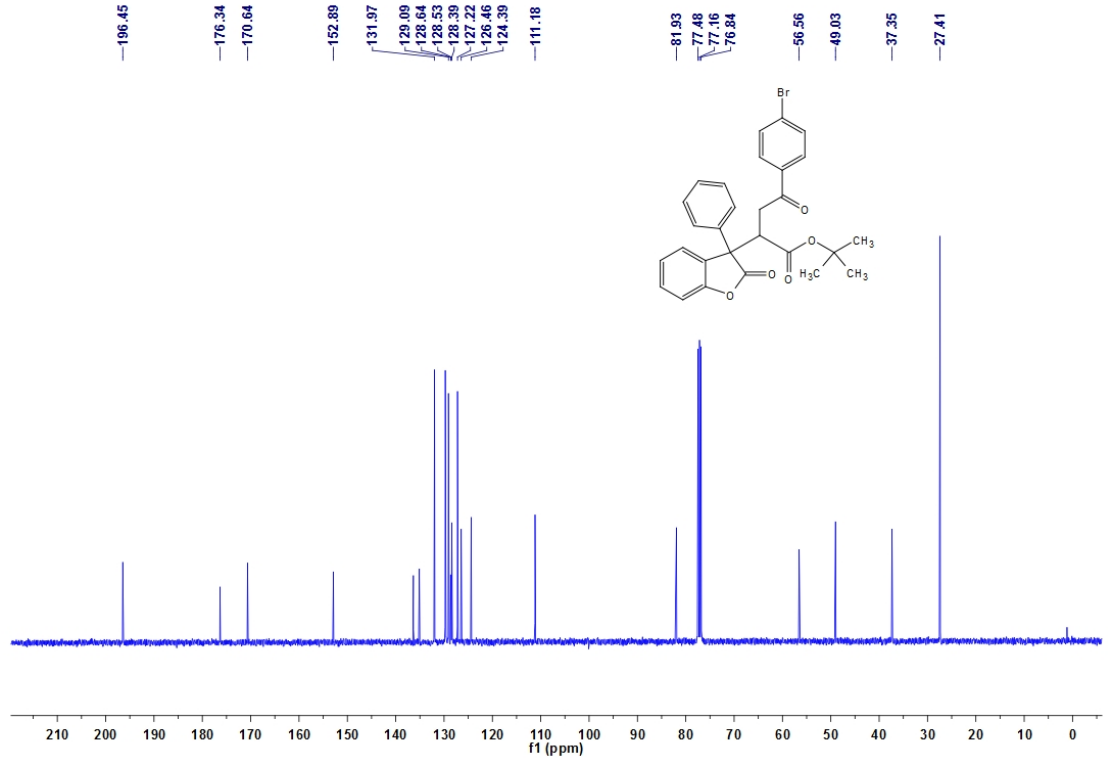
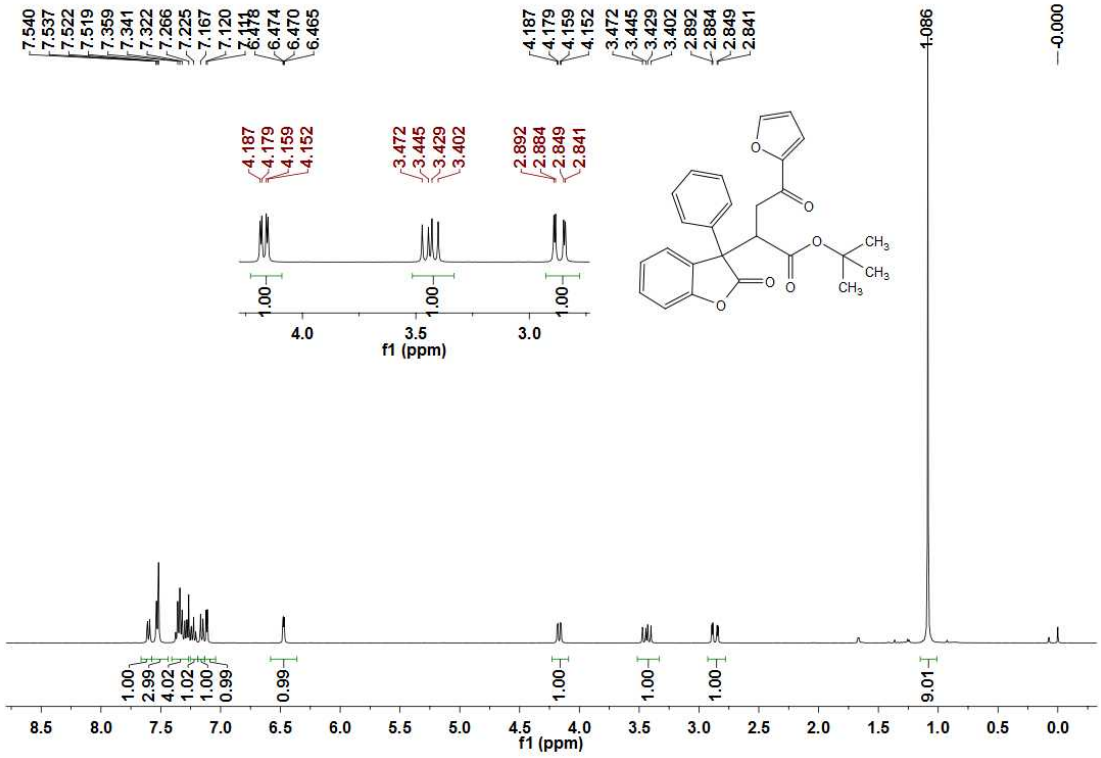
7.583
7.544
7.539
7.534
7.530
7.523
7.516
7.512
7.367
7.364
7.360
7.348
7.343
7.323
7.301
7.283
7.263
7.237
7.234
7.175
4.206
4.199
4.179
4.172
3.604
3.560
2.983
2.976
2.939
2.932
1.635
1.088
0.000
Br
O
O
O
O
O
CH3
CH3
CH3
1.00
1.00
1.00
4.0
3.5
3.0
f1 (ppm)
2.00
1.00
3.99
3.99
1.03
1.00
1.00
1.00
1.00
9.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3r


196.45
176.34
170.64
152.89
131.97
129.09
128.64
128.53
128.39
127.22
126.46
124.39
111.18
81.93
77.48
77.16
76.84
56.56
49.03
37.35
27.41
Br
O
O
O
O
O
CH3
CH3
H3C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3s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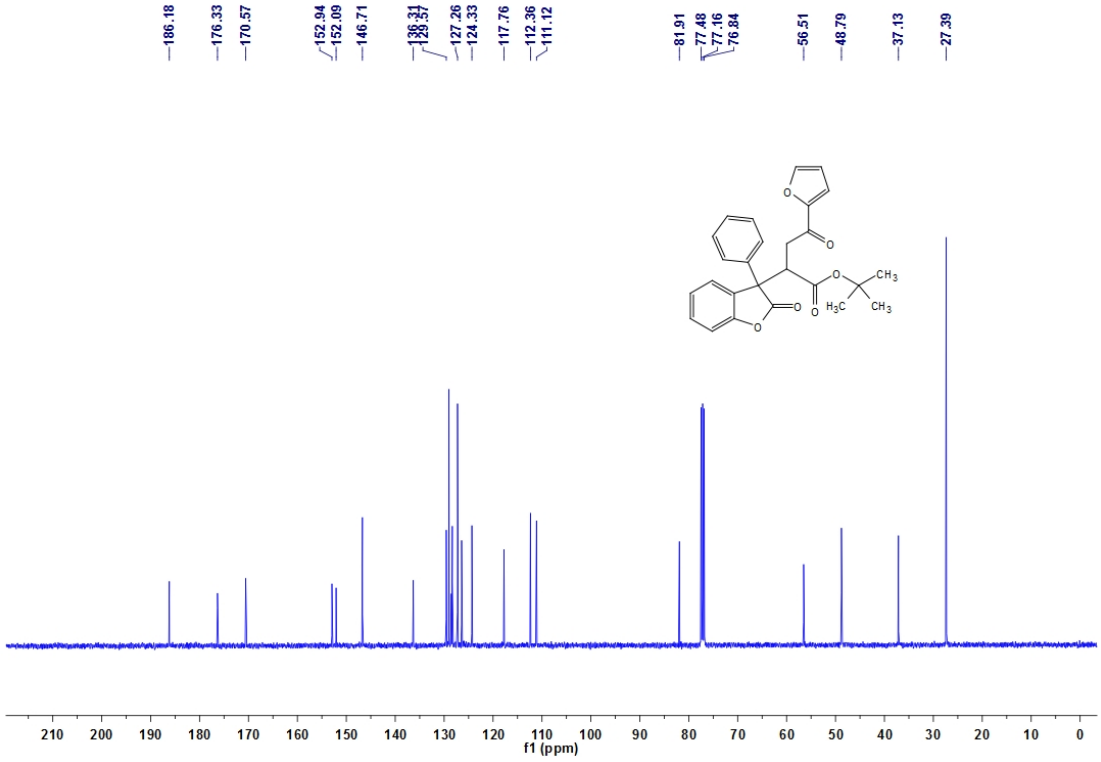
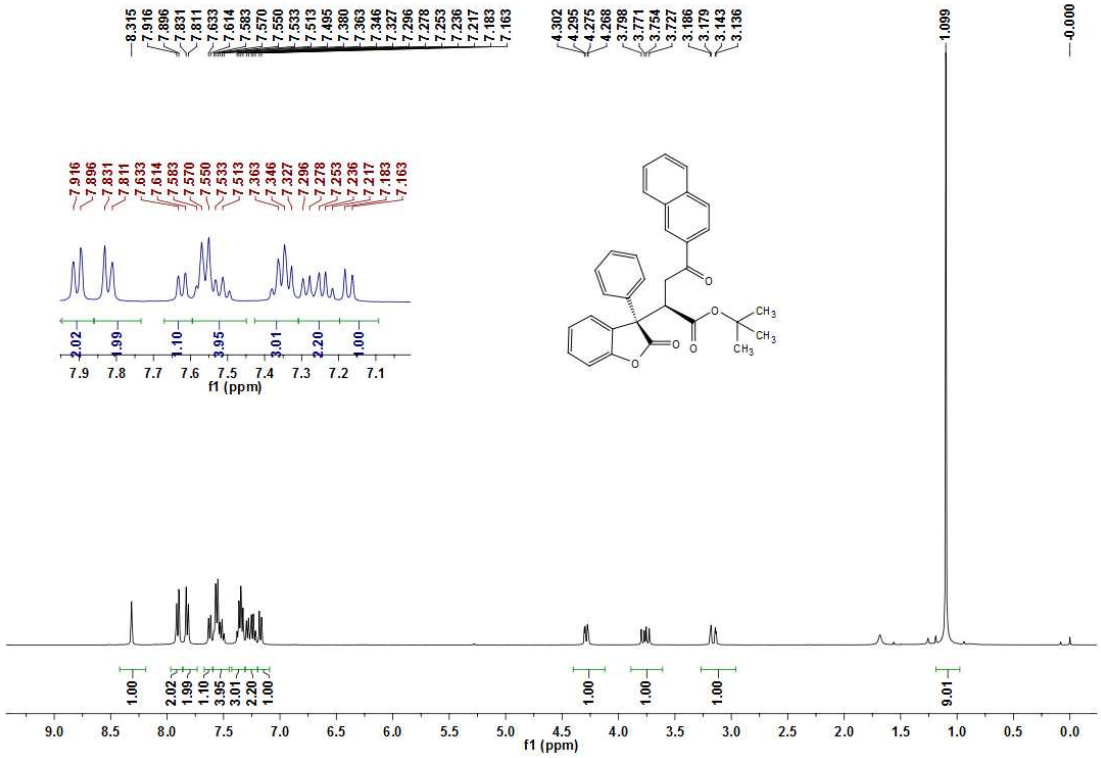
7.537
7.522
7.519
7.359
7.341
7.322
7.266
7.225
7.167
7.120
6.474
6.470
6.465
4.187
4.179
4.159
4.152
3.472
3.445
3.429
3.402
2.892
2.884
2.849
2.841
1.086
0.000
f1 (ppm)

3s


186.18
176.33
170.57
152.94
152.09
146.71
136.31
128.57
127.26
124.33
117.76
112.36
111.12
81.91
77.48
77.16
76.84
56.51
48.79
37.13
27.39
f1 (ppm)

3t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7.896
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7.811
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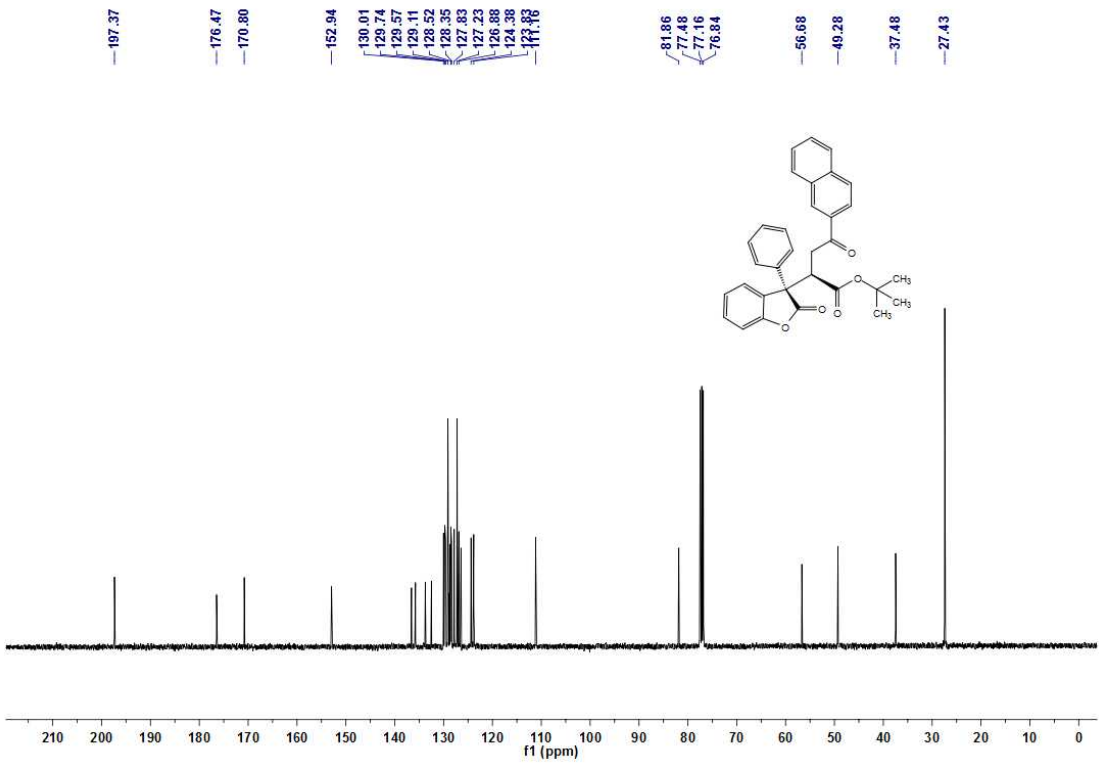
7.614
7.583
7.570
7.550
7.533
7.513
7.495
7.380
7.363
7.346
7.327
7.296
7.278
7.253
7.236
7.217
7.183
7.163
4.302
4.295
4.275
4.268
3.798
3.771
3.754
3.727
3.186
3.179
3.143
3.136
1.099
-0.000
2.02
1.99
1.10
3.95
3.01
2.20
1.00
f1 (ppm)

3t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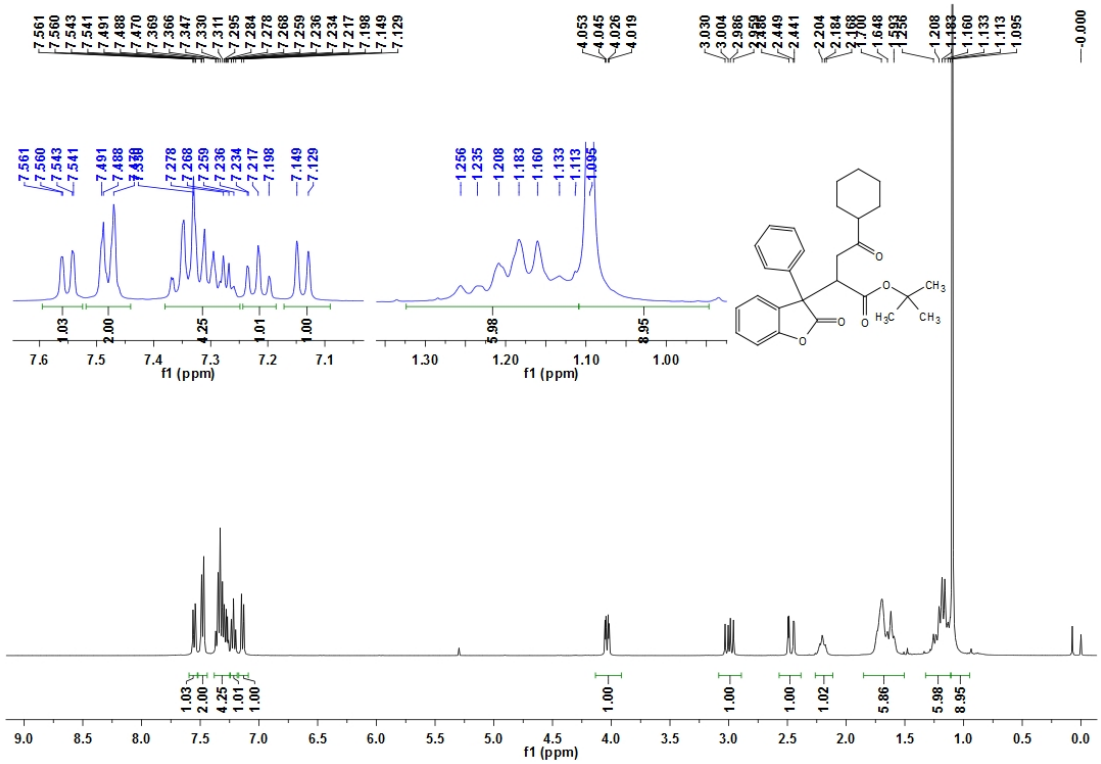
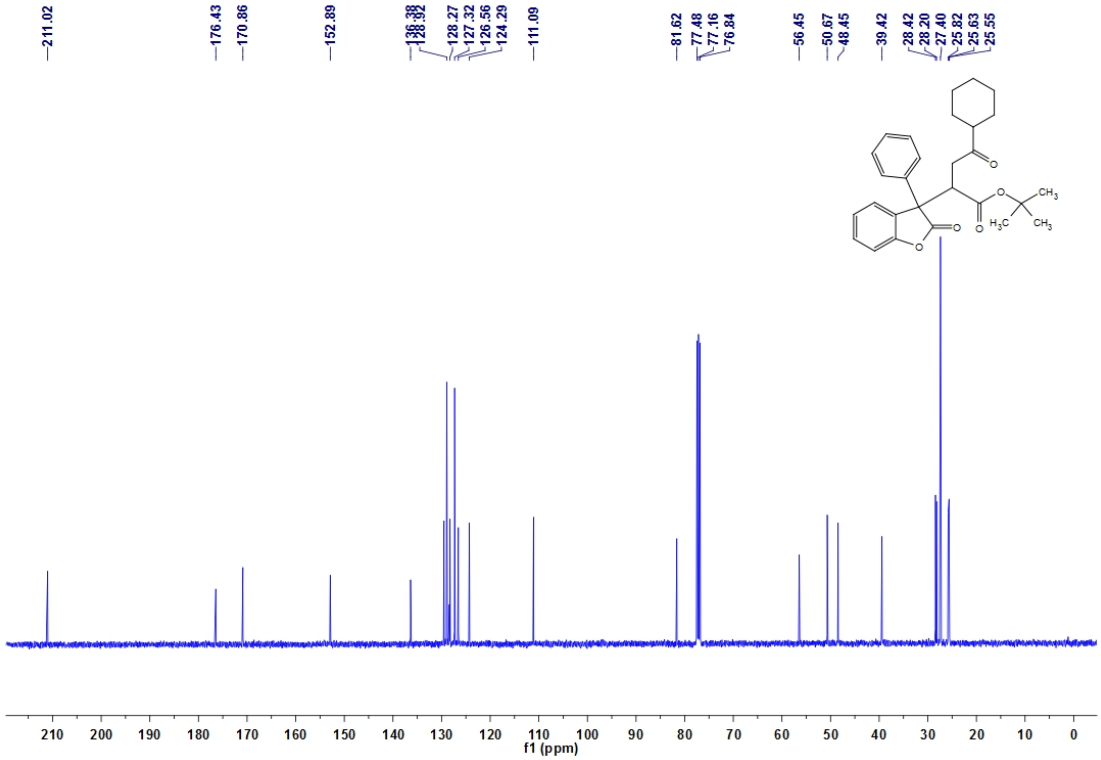
176.47
170.80
152.94
130.01
129.74
129.57
129.11
128.52
128.35
127.83
127.23
126.88
124.38
81.86
77.48
77.16
76.84
56.68
49.28
37.48
27.43
f1 (ppm)

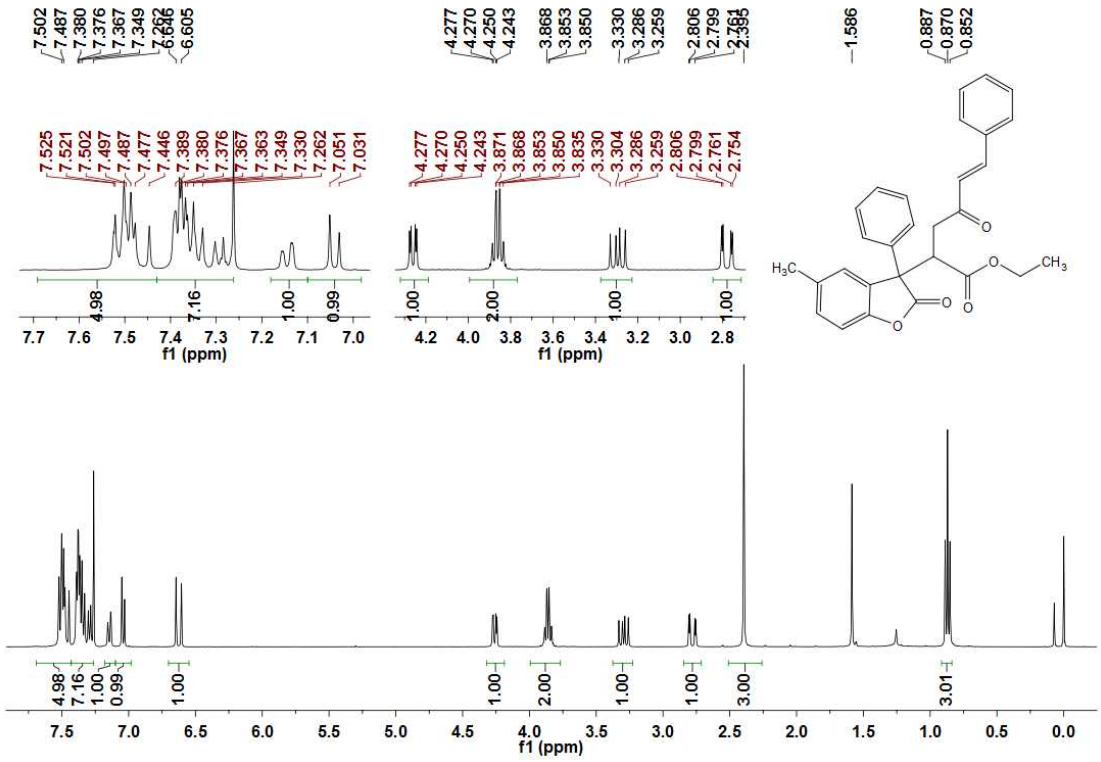
3u



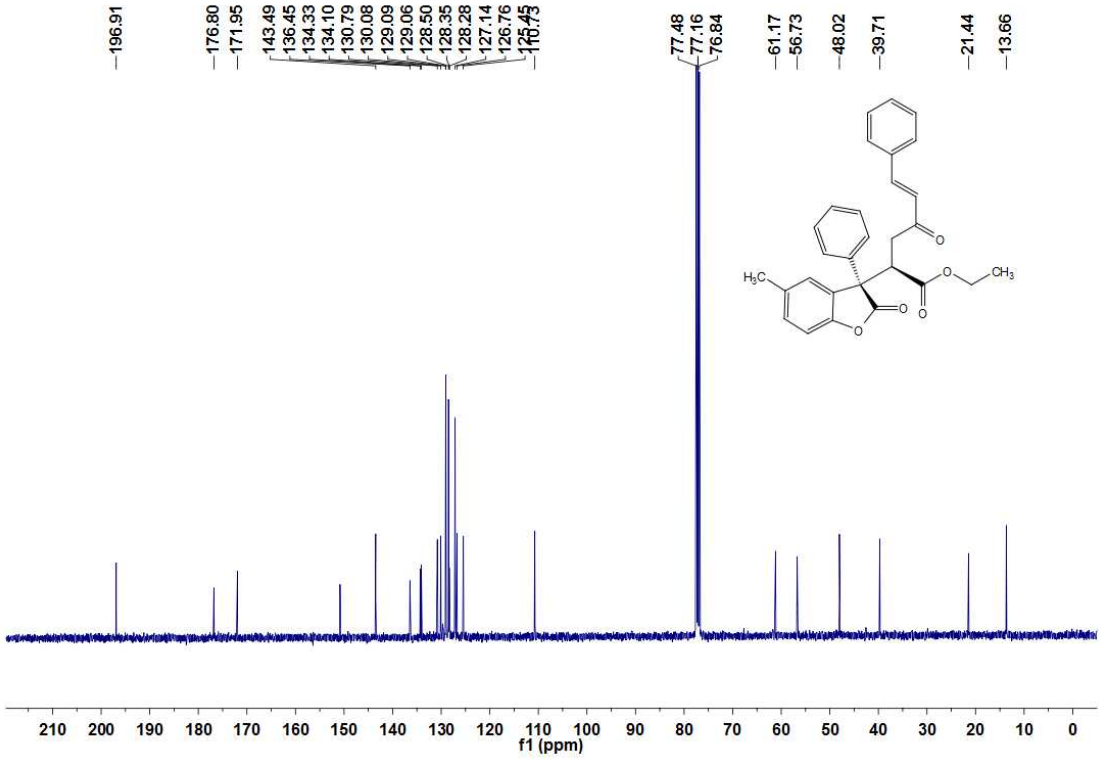
3u



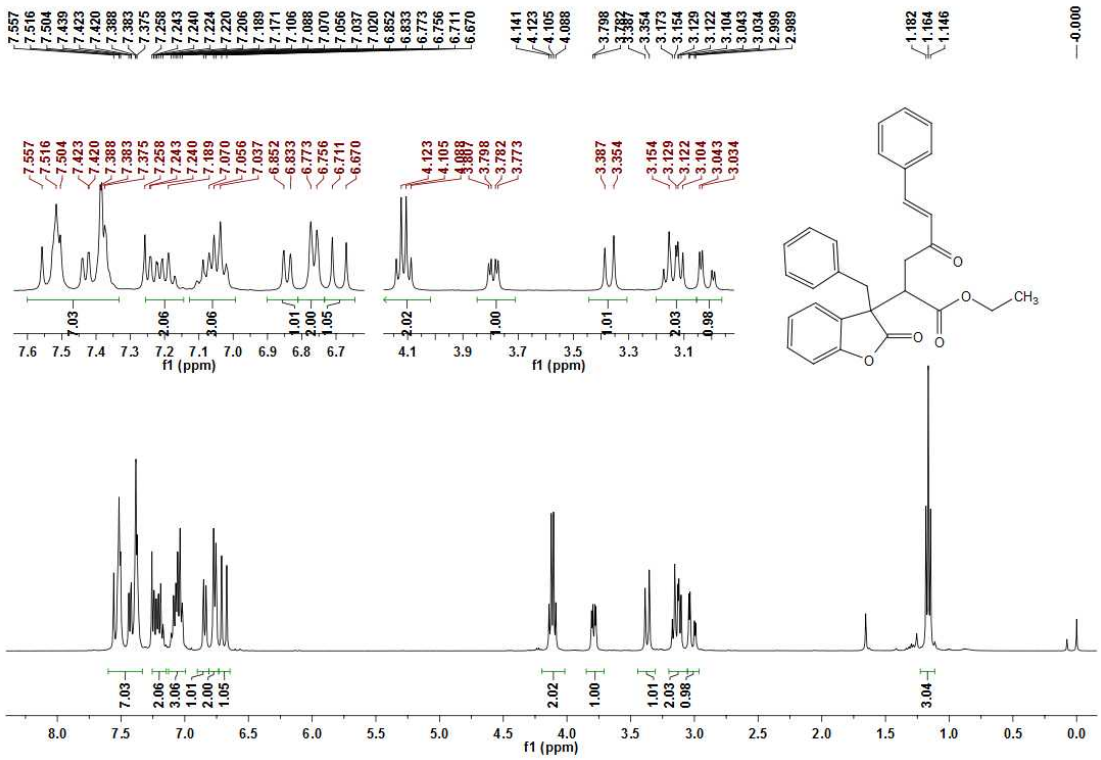
3v



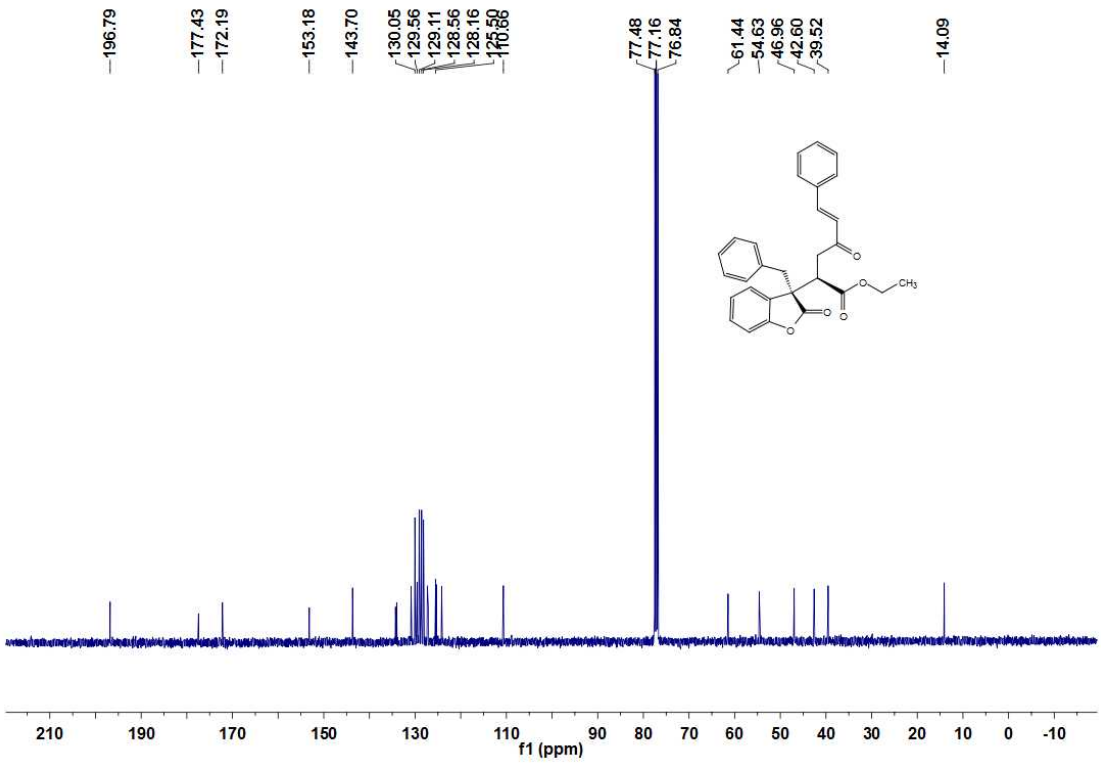
3v



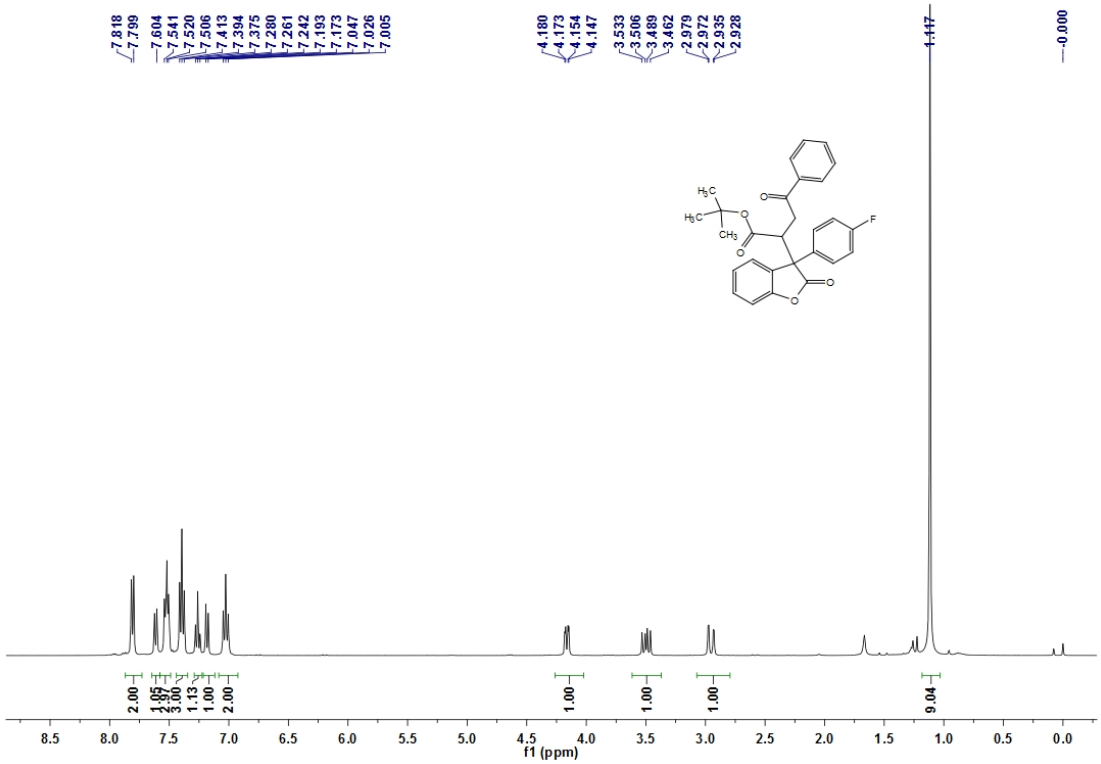
3w



3w



3x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7.394
7.375
7.280
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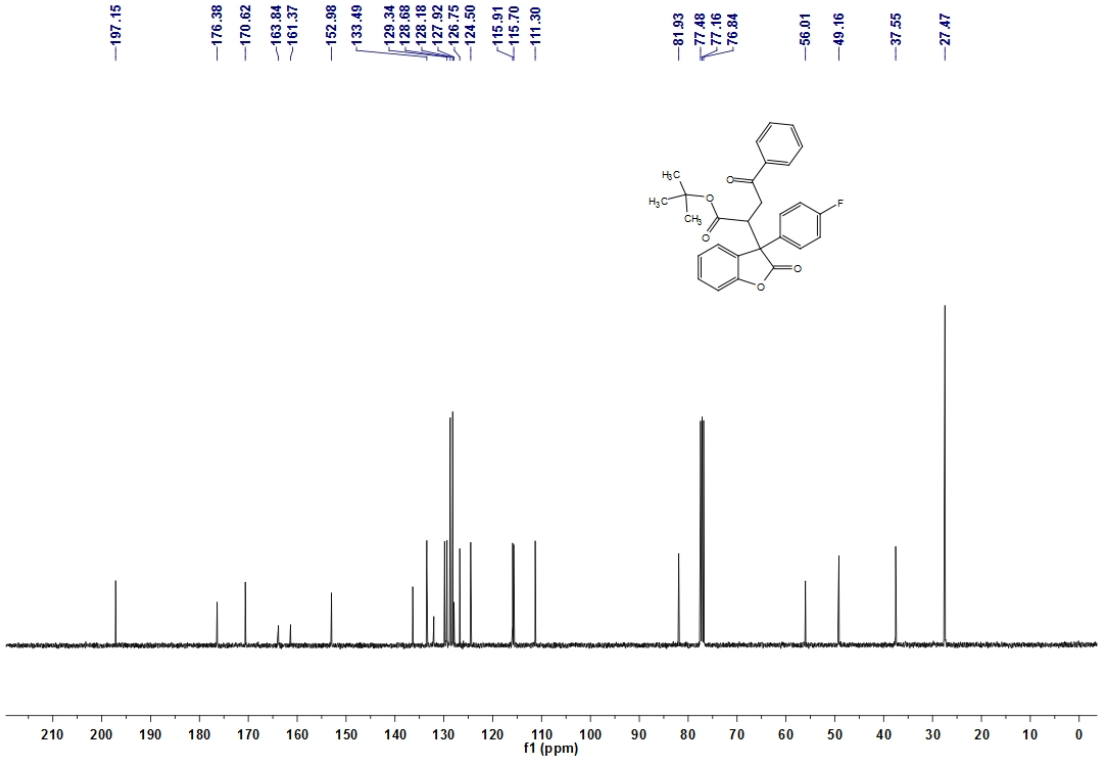
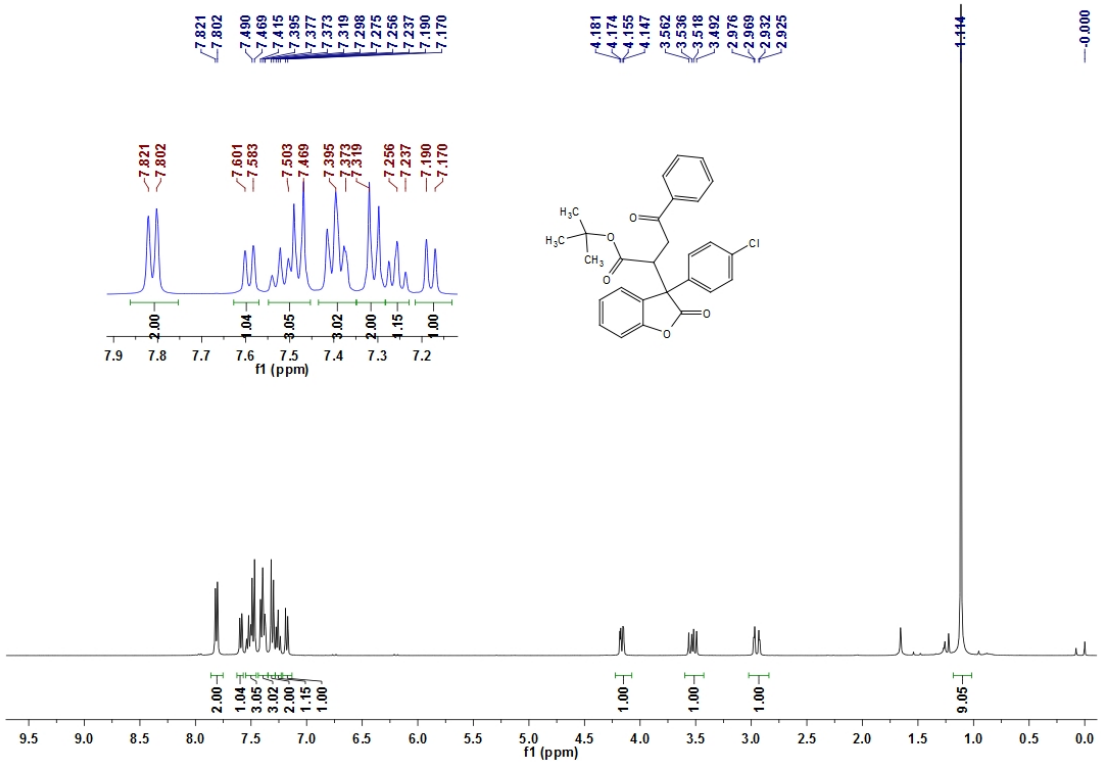
7.242
7.193
7.173
7.047
7.026
7.005
4.180
4.173
4.154
4.147
3.533
3.506
3.489
3.462
2.979
2.972
2.935
2.928
1.147
-0.000
2.00
1.05
2.07
3.00
1.13
1.00
2.00
1.00
1.00
1.00
9.04
f1 (ppm)

3x


197.15
176.38
170.62
163.84
161.37
152.98
133.49
129.34
128.68
128.18
127.92
126.75
124.50
115.91
115.70
111.30
81.93
77.48
77.16
76.84
56.01
49.16
37.55
27.47
f1 (ppm)

3y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7.415
7.395
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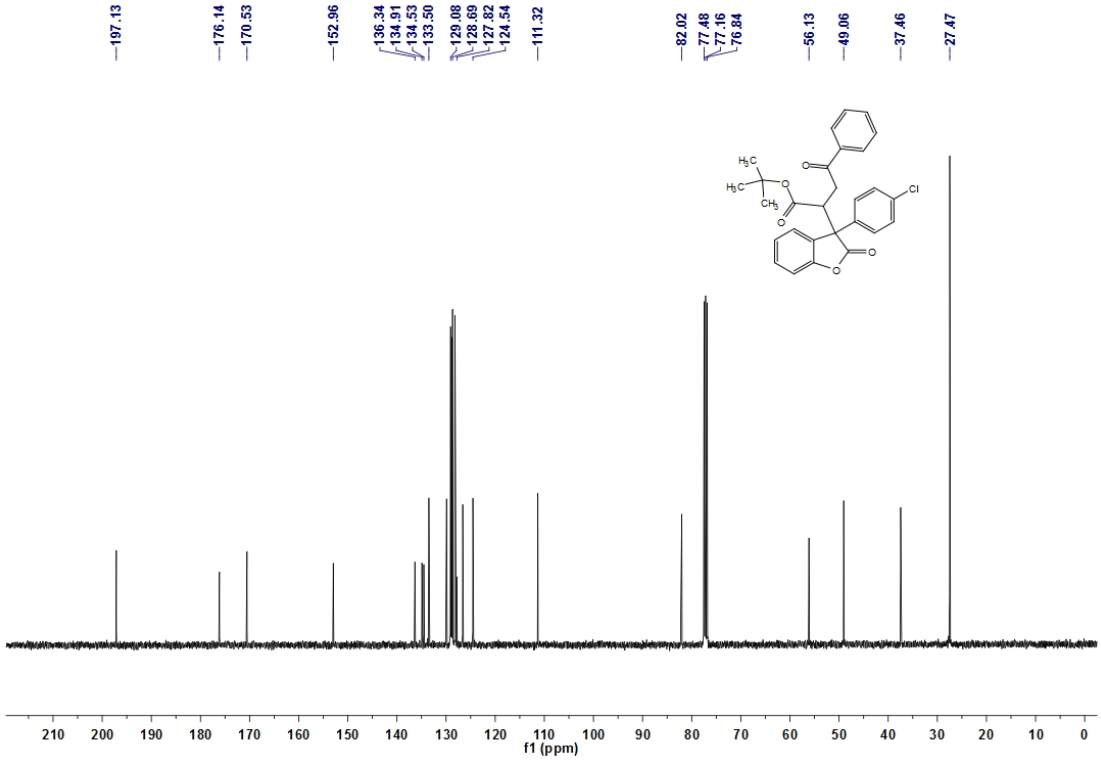
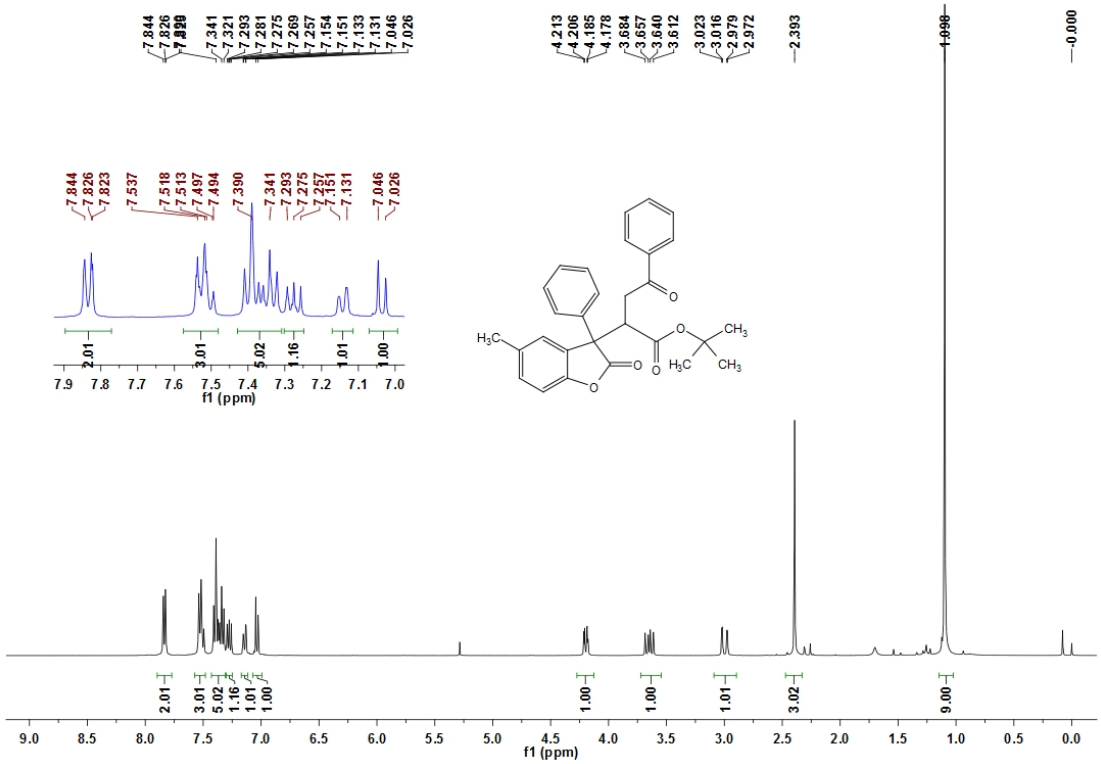
7.373
7.319
7.298
7.275
7.256
7.237
7.190
7.170
4.181
4.174
4.155
4.147
3.562
3.536
3.518
3.492
2.976
2.969
2.932
2.925
1.414
0.000
f1 (ppm)

3y


197.13
176.14
170.53
152.96
136.34
134.91
134.53
133.50
129.08
128.69
127.82
124.54
111.32
82.02
77.48
77.16
76.84
56.13
49.06
37.46
27.47
f1 (ppm)

3z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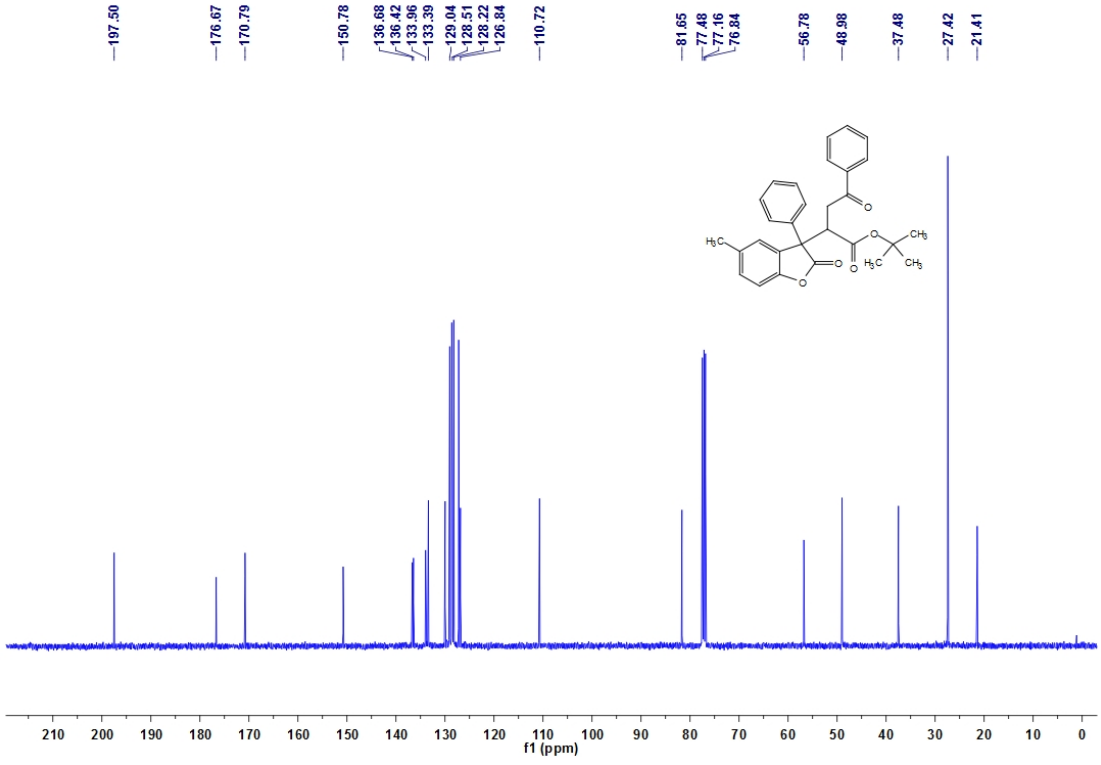
7.518
7.513
7.497
7.494
7.390
7.341
7.293
7.275
7.257
7.154
7.151
7.131
7.046
7.026
4.213
4.206
4.185
4.178
3.684
3.657
3.640
3.612
3.023
3.016
2.979
2.972
2.393
1.000
0.000
2.01
3.01
5.02
1.16
1.01
1.00
f1 (ppm)

3z


197.50
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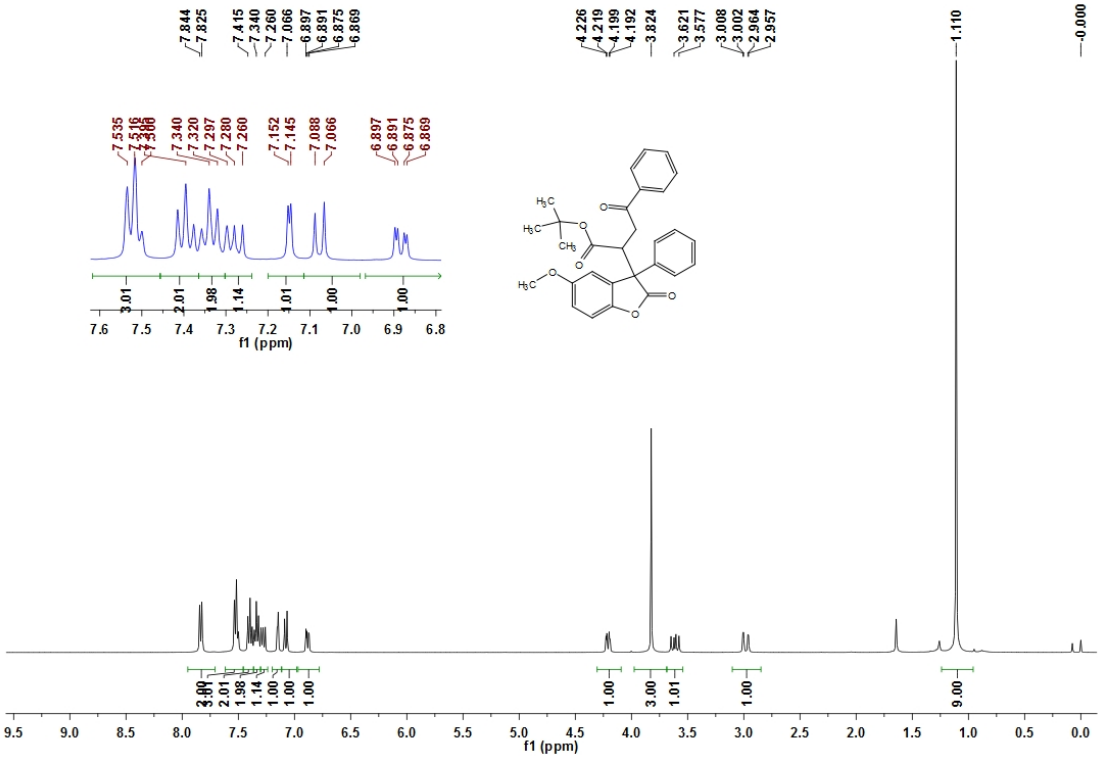
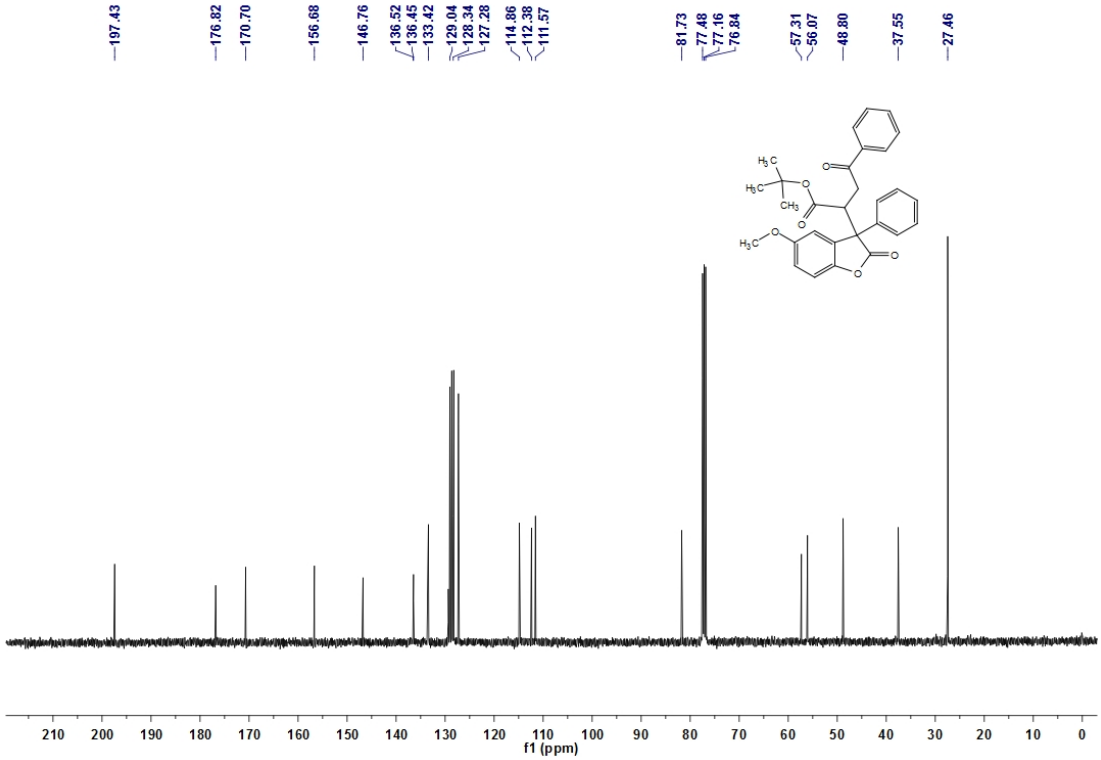
150.78
136.68
136.42
133.96
133.39
129.04
128.51
128.22
126.84
110.72
81.65
77.48
77.16
76.84
56.78
48.98
37.48
27.42
21.41
f1 (ppm)

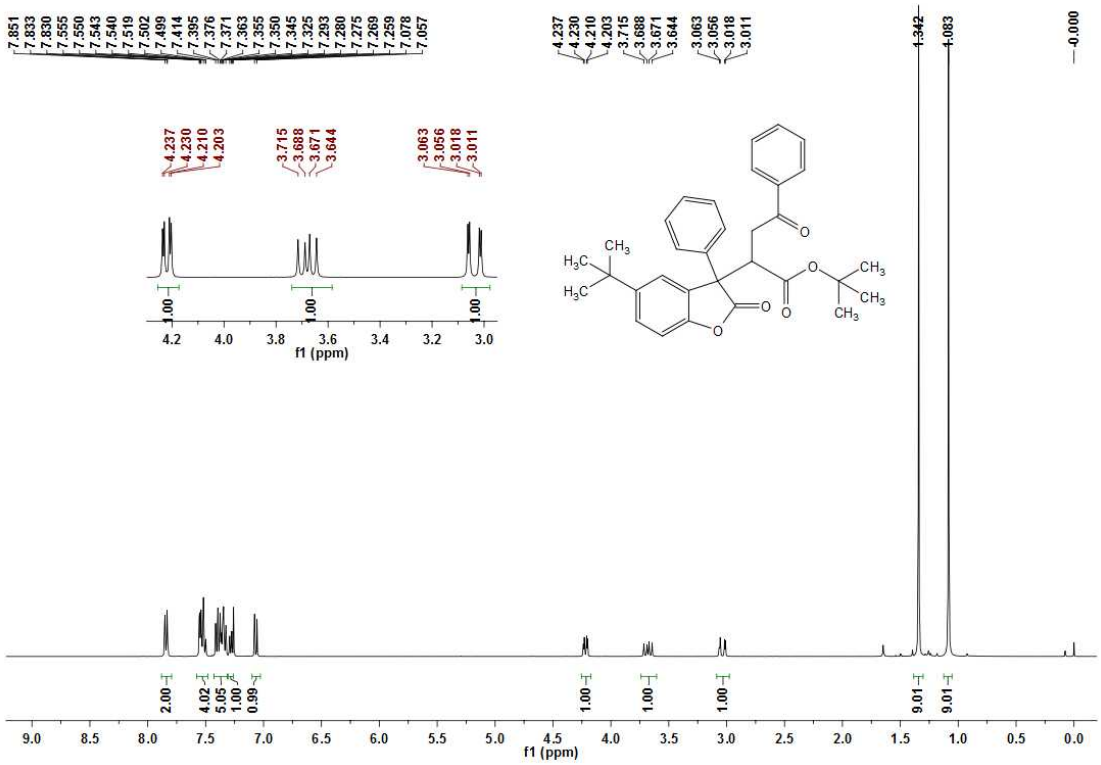
3aa


7.844
7.825
7.415
7.340
7.260
7.066
6.897
6.891
6.875
6.869
4.226
4.219
4.199
4.192
3.824
3.621
3.577
3.008
3.002
2.964
2.957
1.110
-0.000
f1 (ppm)

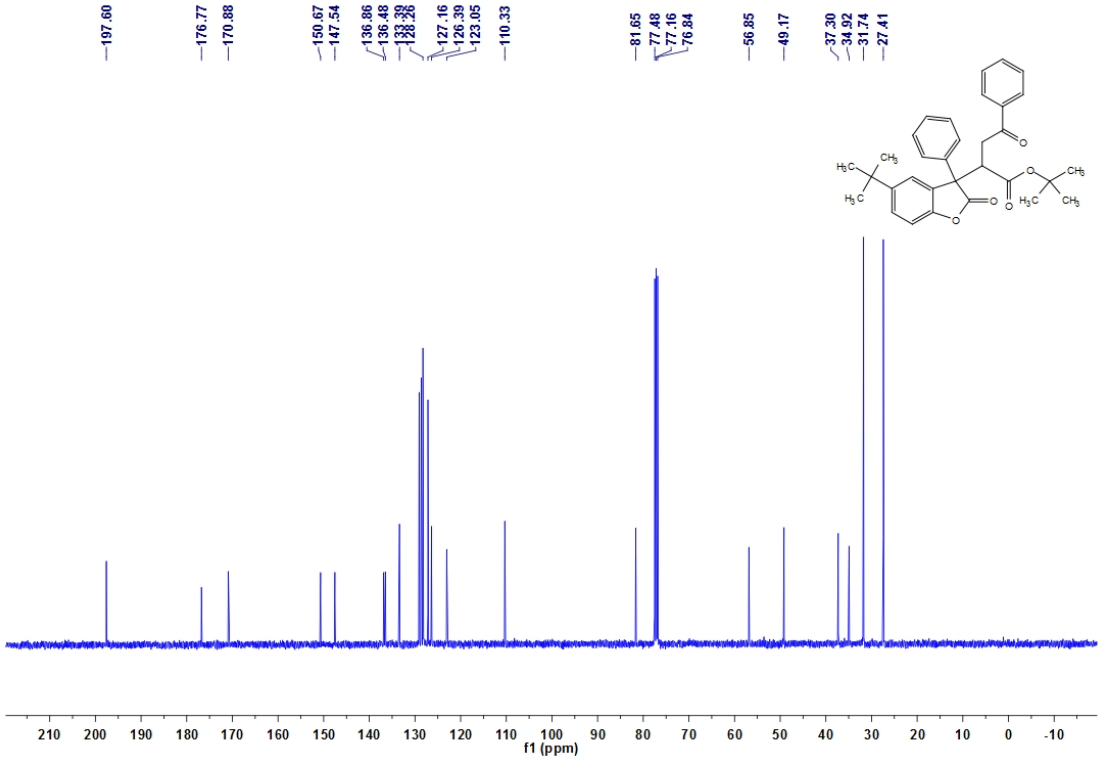
3aa


197.43
176.82
170.70
156.68
146.76
136.52
136.45
133.42
129.04
128.34
127.28
114.86
112.38
111.57
81.73
77.48
77.16
76.84
57.31
56.07
48.80
37.55
27.46
f1 (ppm)

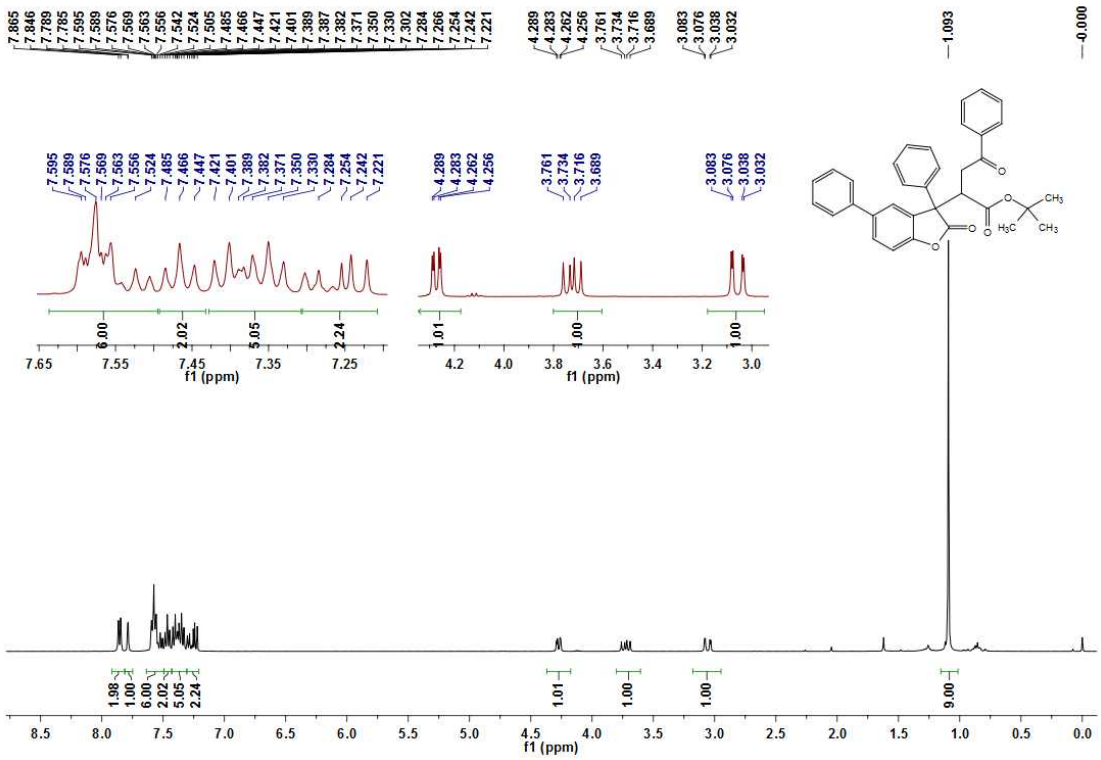
3ab


7.851
7.833
7.830
7.555
7.550
7.543
7.540
7.519
7.502
7.499
7.414
7.395
7.376
7.371
7.363
7.355
7.350
7.345
7.325
7.293
7.280
7.275
7.269
7.259
7.078
7.057
4.237
4.230
4.210
4.203
3.715
3.688
3.671
3.644
3.063
3.056
3.018
3.011
1.342
1.083
0.000
2.00
4.02
5.05
1.00
0.99
1.00
1.00
1.00
9.01
9.01
f1 (ppm)

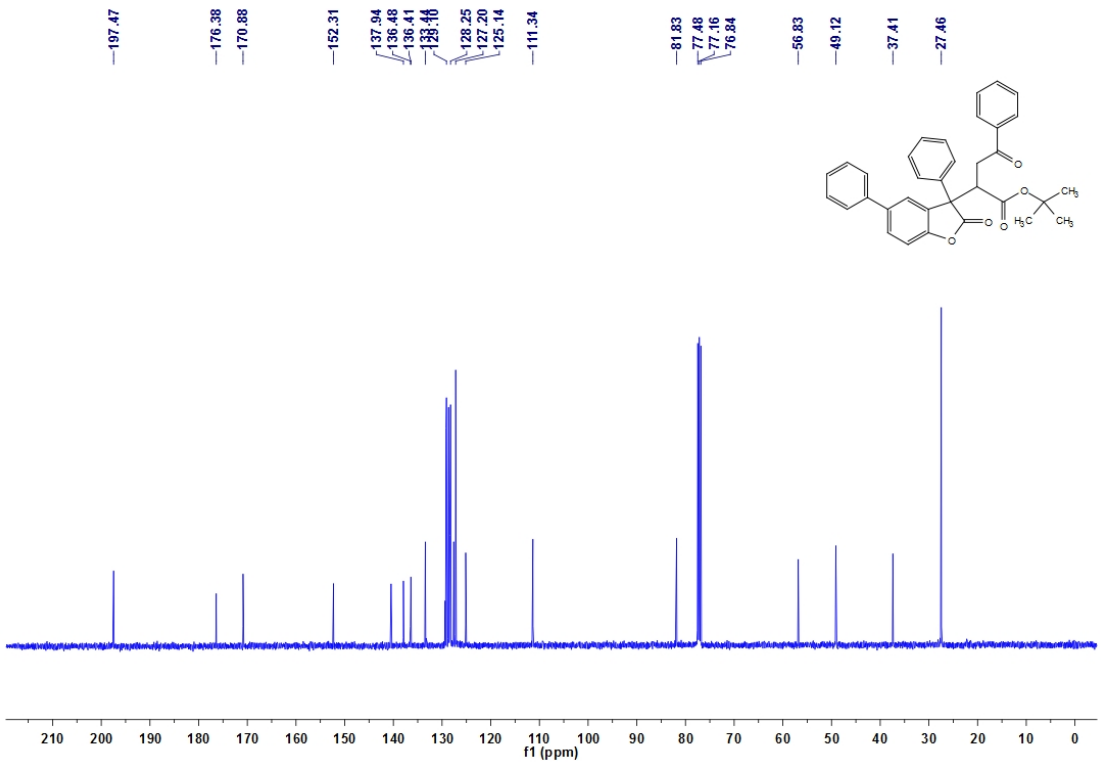
3ab


197.60
176.77
170.88
150.67
147.54
136.86
136.48
127.16
126.39
123.05
110.33
81.65
77.48
77.16
76.84
56.85
49.17
37.30
34.92
31.74
27.41
f1 (ppm)

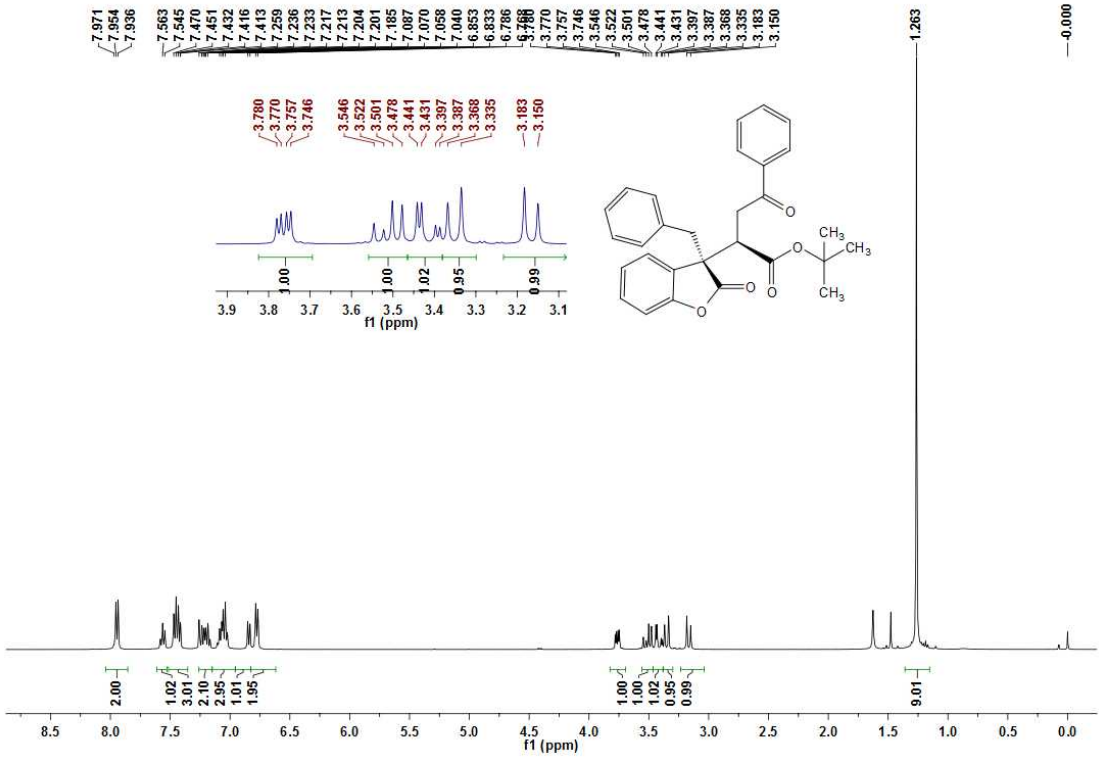
3ac



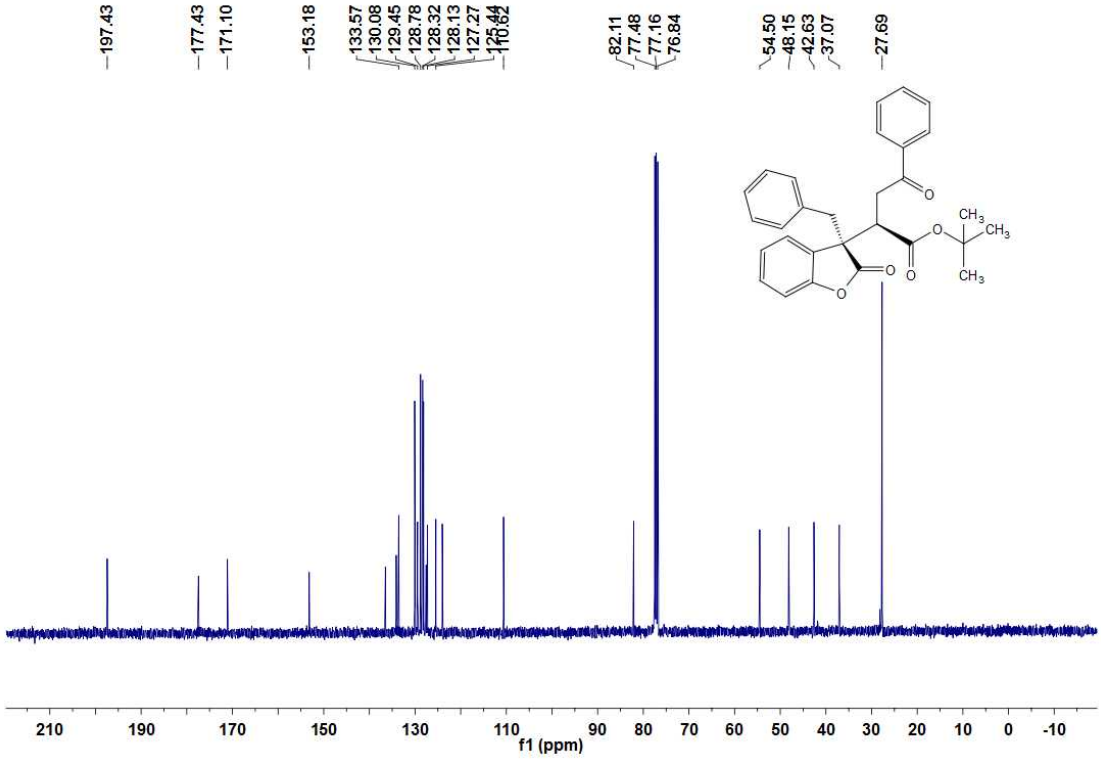
3ac



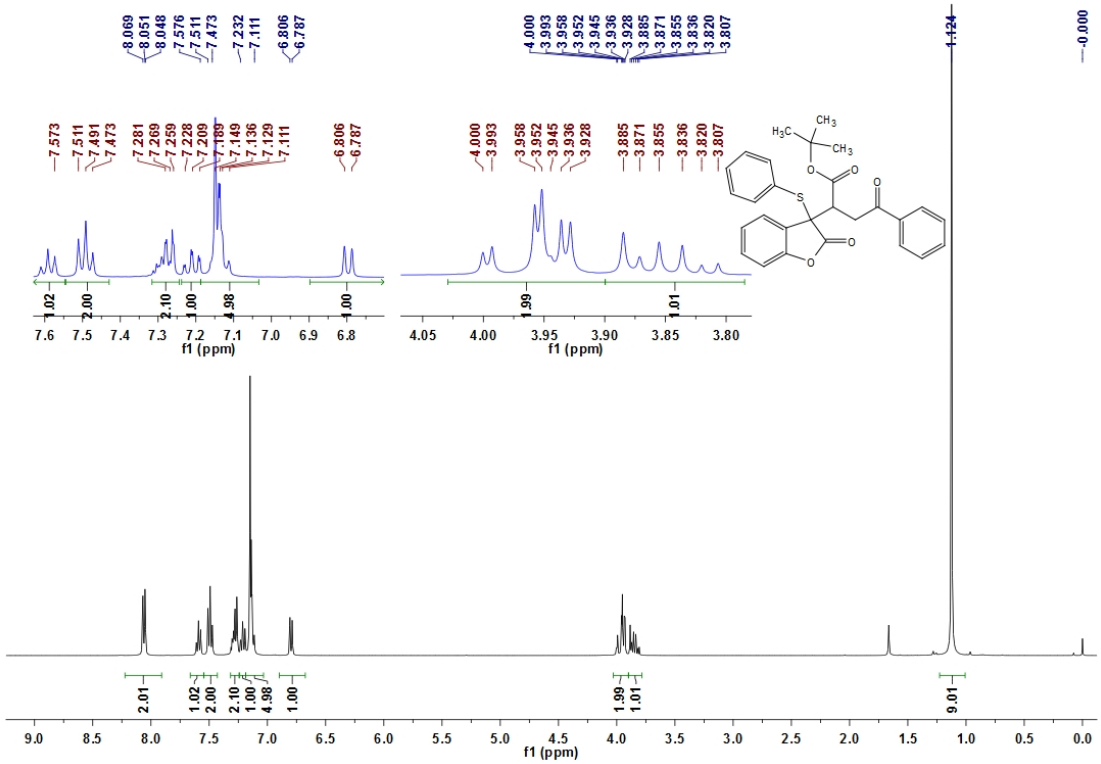
3ad


7.971
7.954
7.936
7.563
7.545
7.470
7.451
7.432
7.416
7.413
7.259
7.236
7.233
7.217
7.213
7.204
7.201
7.185
7.087
7.070
7.058
7.040
6.853
6.833
6.786
3.780
3.770
3.757
3.746
3.546
3.522
3.501
3.478
3.441
3.431
3.397
3.387
3.368
3.335
3.183
3.150
1.263
-0.000
f1 (ppm)
f1 (ppm)

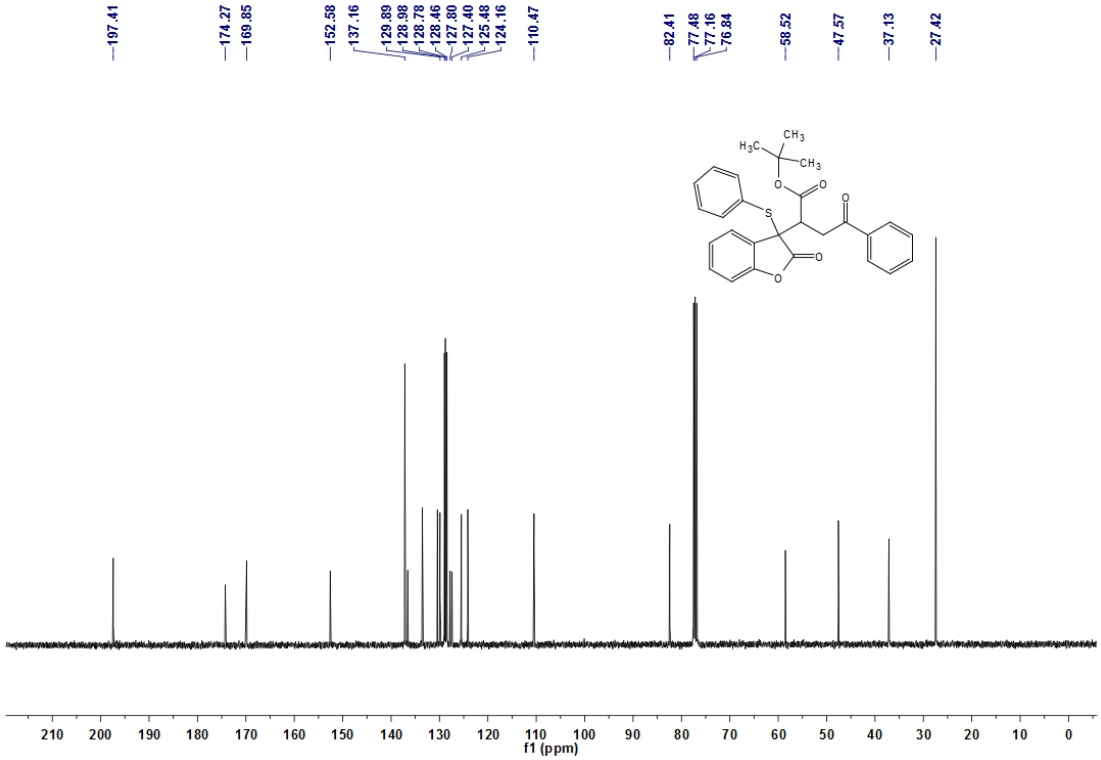
3ad


197.43
177.43
171.10
153.18
133.57
130.08
129.45
128.78
128.32
128.13
127.27
82.11
77.48
77.16
76.84
54.50
48.15
42.63
37.07
27.69
f1 (ppm)
f1 (ppm)

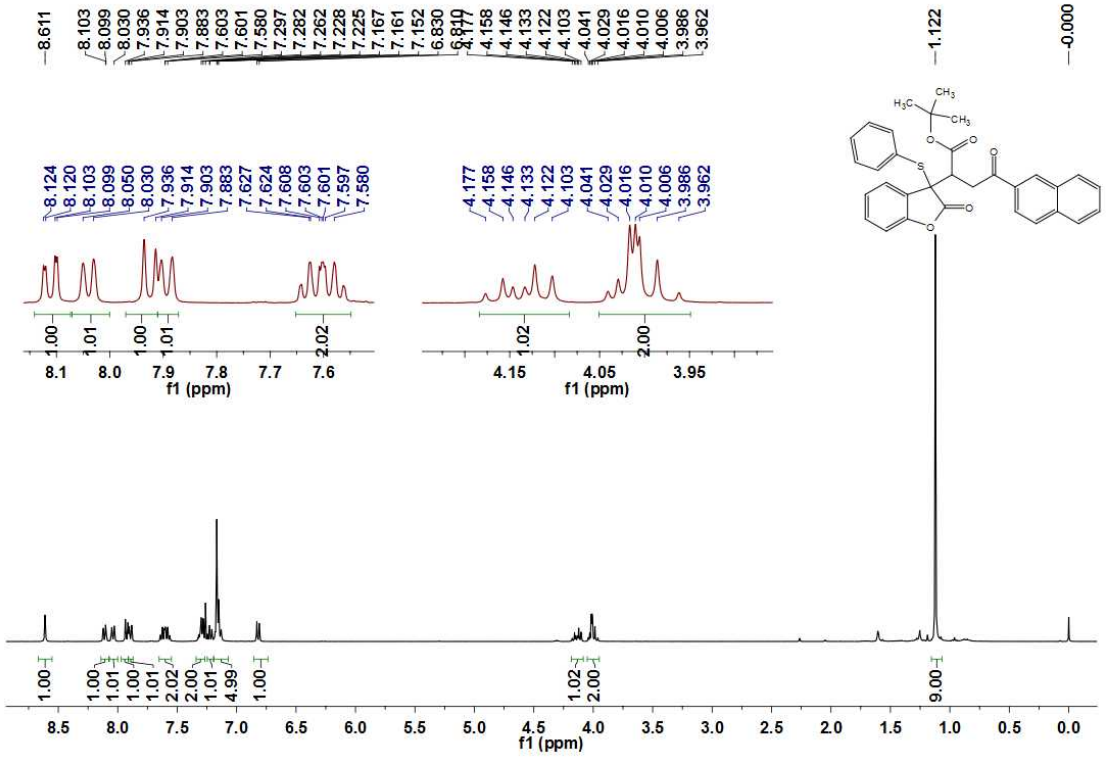
4a


8.069
8.051
8.048
7.576
7.511
7.473
7.232
7.111
6.806
6.787
4.000
3.993
3.958
3.952
3.945
3.936
3.928
3.885
3.871
3.855
3.836
3.820
3.807
1.124
-0.000
f1 (ppm)

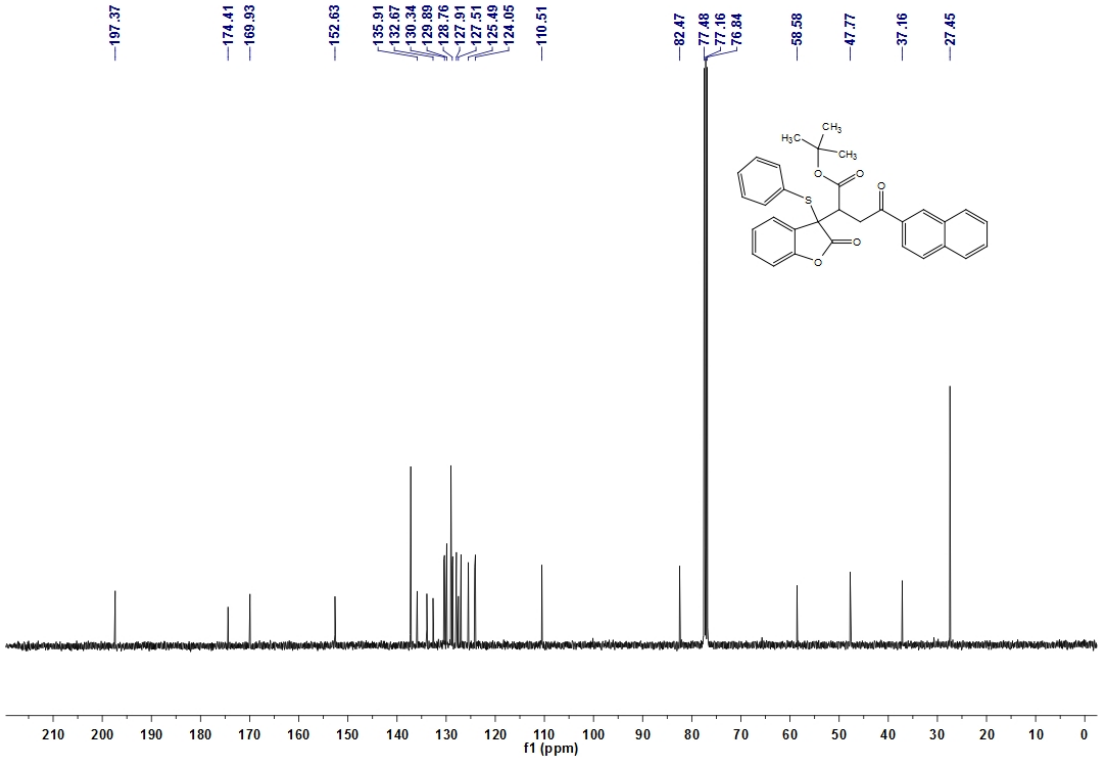
4a


197.41
174.27
169.85
152.58
137.16
129.89
128.98
128.78
128.46
127.80
127.40
125.48
124.16
110.47
82.41
77.48
77.16
76.84
58.52
47.57
37.13
27.42
f1 (ppm)

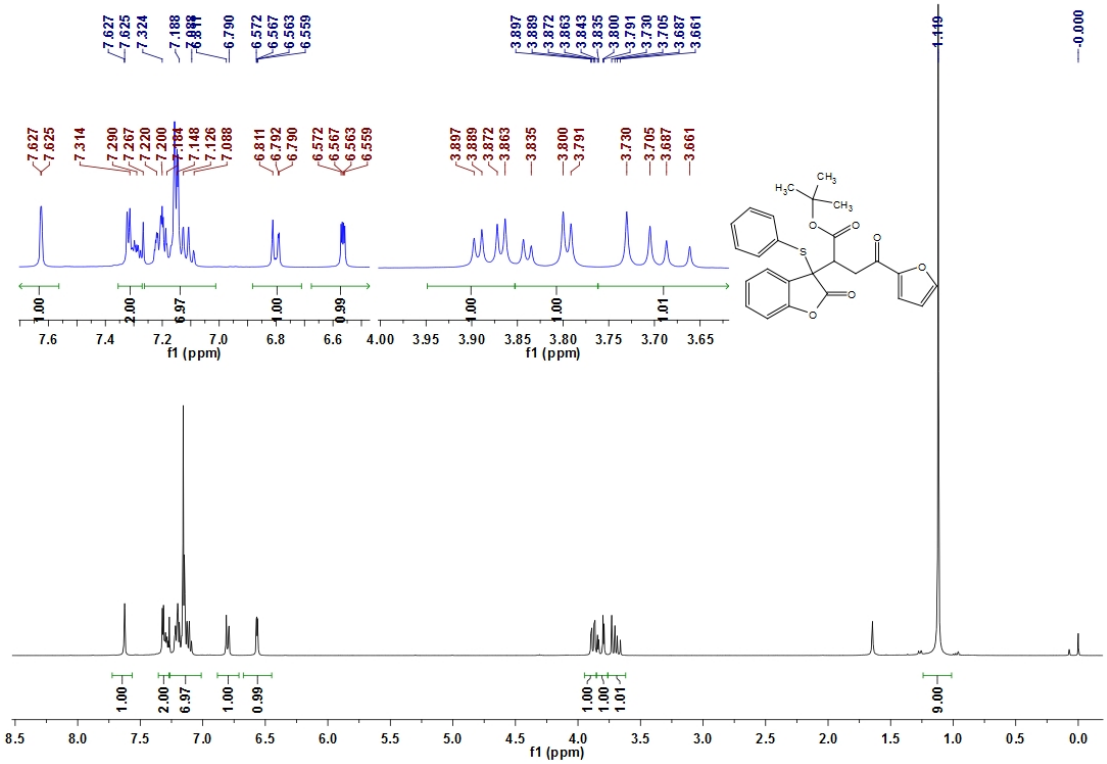
4b


8.611
8.103
8.099
8.030
7.936
7.914
7.903
7.883
7.603
7.601
7.580
7.297
7.282
7.262
7.228
7.225
7.167
7.161
7.152
6.830
4.158
4.146
4.133
4.122
4.103
4.041
4.029
4.016
4.010
4.006
3.986
3.962
1.122
0.000
f1 (ppm)

4b


197.37
174.41
169.93
152.63
135.91
132.67
130.34
129.89
128.76
127.91
127.51
125.49
124.05
110.51
82.47
77.48
77.16
76.84
58.58
47.77
37.16
27.45
f1 (ppm)

4c



4c