Supporting Information for

Catalytic Chemoselective [3+3] Cycloadditions of Azomethine Ylides with Quinone Monoimides Leading to the Construction of A Dihydrobenzoxazine Scaffold

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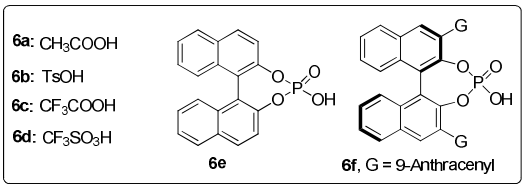
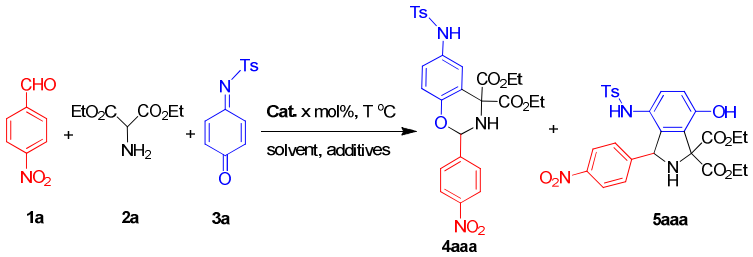
1. General information:

^{1}H and ^{13}C NMR spectra were measured respectively at 400 and 100 MHz, respectively. The solvents used for NMR spectroscopy were $CDCl_3$ and acetone-d_6, using tetramethylsilane as the internal reference. HRMS spectra were recorded on a LTQ-Orbitrap mass spectrometer. Analytical grade solvents for the column chromatography and commercially available reagents were used as received. Substrates **3** were synthesized according to the literature method.[1]

2. Screening of Catalysts and optimization of reaction conditions

Table 1. Screening of Catalysts and optimization of reaction conditions[a]





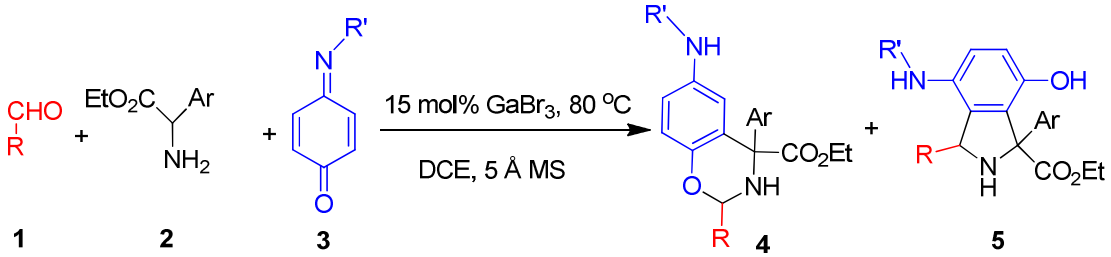
entry	**Cat.**	solvent	T (°C)	x	**1a**:**2a**:**3a**	additives	cr[b]	yield (%)[c]
1	**6a**	CH_2ClCH_2Cl	50	30	1.2:1:1.2	3 Å	>95:5	N.R.
2	**6b**	CH_2ClCH_2Cl	50	30	1.2:1:1.2	3 Å	>95:5	N.R.
3	**6c**	CH_2ClCH_2Cl	50	30	1.2:1:1.2	3 Å	>95:5	22
4	**6d**	CH_2ClCH_2Cl	50	30	1.2:1:1.2	3 Å	>95:5	54
5	**6e**	CH_2ClCH_2Cl	50	30	1.2:1:1.2	3 Å	>95:5	48
6[d]	**6f**	CH_2ClCH_2Cl	50	30	1.2:1:1.2	3 Å	66:34	45
7	**6d**	CCl_3CH_3	50	30	1.2:1:1.2	3 Å	>95:5	26
8	**6d**	$CHCl_2CH_2Cl$	50	30	1.2:1:1.2	3 Å	>95:5	23
9	**6d**	1,4-dioxane	50	30	1.2:1:1.2	3 Å	>95:5	44
10	**6d**	THF	50	30	1.2:1:1.2	3 Å	>95:5	41
11	**6d**	CH_3CN	50	30	1.2:1:1.2	3 Å	>95:5	38
12	**6d**	AcOEt	50	30	1.2:1:1.2	3 Å	>95:5	30
13	**6d**	toluene	50	30	1.2:1:1.2	3 Å	>95:5	N.R.
14	**6d**	CH_2ClCH_2Cl	65	30	1.2:1:1.2	3 Å	>95:5	61

1. A. B. Leduc, M. A. Kerr, *Eur. J. Org. Chem.* **2007**, 237.

15	**6d**	CH_2ClCH_2Cl	80	30	1.2:1:1.2	3 Å	>95:5	69
16	**6d**	CH_2ClCH_2Cl	80	30	1.2:1:2	3 Å	>95:5	46
17	**6d**	CH_2ClCH_2Cl	80	30	2.4:2:1	3 Å	>95:5	33
18	**6d**	CH_2ClCH_2Cl	80	30	1.2:1:1.2	4 Å	>95:5	54
19	**6d**	CH_2ClCH_2Cl	80	30	1.2:1:1.2	5 Å	>95:5	72
20	**6d**	CH_2ClCH_2Cl	80	30	1.2:1:1.2	Na_2SO_4	>95:5	41
21	$GaBr_3$	CH_2ClCH_2Cl	80	30	1.2:1:1.2	5 Å	>95:5	84
22	$Sc(OTf)_3$	CH_2ClCH_2Cl	80	30	1.2:1:1.2	5 Å	>95:5	58
23	$InCl_3$	CH_2ClCH_2Cl	80	30	1.2:1:1.2	5 Å	>95:5	N.R.
24	$Cu(OTf)_2$	CH_2ClCH_2Cl	80	30	1.2:1:1.2	5 Å	>95:5	N.R.
25	$GaBr_3$	CH_2ClCH_2Cl	80	50	1.2:1:1.2	5 Å	>95:5	22
26	$GaBr_3$	CH_2ClCH_2Cl	80	15	1.2:1:1.2	5 Å	>95:5	98
27	$GaBr_3$	CH_2ClCH_2Cl	80	15	1.2:1:1.2	-	>95:5	54

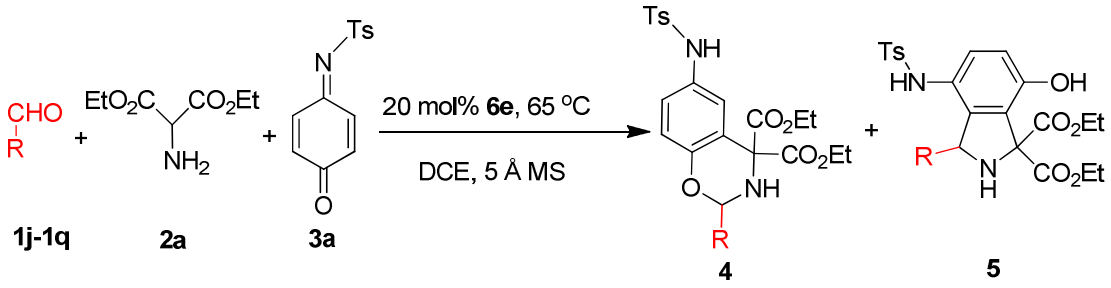
[a]Unless otherwise indicated, the reaction was carried out at the 0.1 mmol scale and catalyzed by x mol% **Cat.** with additives (100 mg) in a solvent at T °C for 48 h. [b]The *cr* value referred to the ratio of **4aaa**:**5aaa** and it was determined by ^{1}H NMR. [c]Isolated yield. [d]No chiral induction was observed (0% ee) in the presence of this chiral catalyst.

3. General procedure for the synthesis of compounds 4 and 8:

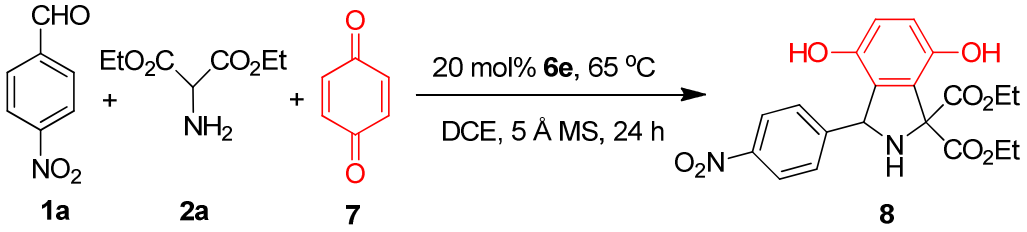


1 **2** **3** **4** **5**

Under an argon atmosphere, 1,2-dicholoroethane (0.5 mL) was added to the mixture of aldehydes **1** (0.12 mmol), amino-esters **2** (0.1 mmol), the catalyst $GaBr_3$ (0.015 mmol) and 5Å molecular sieves (100 mg). After being stirred at 30 °C for 30 min, the solution of quinone monoimides **3** (0.12 mmol) in 1,2-dicholoroethane (0.5 mL) was added to the reaction mixture, which was further stirred at 80 °C for 48 h. Then, the reaction mixture was filtered to remove molecular sieves and the solid powder was washed with ethyl acetate. The resultant solution was concentrated under the reduced pressure to give the residue, which was purified through flash column chromatography on silica gel (flushed by 10% Et_3N/petrol ether in advance) to afford pure products **4**.



For products **4jaa-4qaa**: 1,2-dicholoroethane (3 mL) was added to the mixture of aldehydes **1** (0.6 mmol), amino-esters **2** (0.5 mmol), the catalyst **6e** (0.1 mmol) and 5Å molecular sieves (300 mg). After being stirred at 50 °C for 3h, the solution of quinone monoimides **3** (0.6 mmol) in 1,2-dicholoroethane (5 mL) was added to the reaction mixture, which was further stirred at 65 °C for 24 h. Then, the reaction mixture was filtered to remove molecular sieves and the solid powder was washed with ethyl acetate. The resultant solution was concentrated under the reduced pressure to give the residue, which was purified through flash column chromatography on silica gel (flushed by 10% Et_3N/petrol ether in advance) to afford pure products **4**.



1,2-dicholoroethane (1 mL) was added to the mixture of aldehyde **1a** (0.24 mmol), amino-ester **2a** (0.2 mmol), the catalyst **6e** (0.04 mmol) and 5Å molecular sieves (150 mg). After being stirred at 50 °C for 3h, the solution of quinone **7** (0.24 mmol) in 1,2-dicholoroethane (1.5 mL) was added to the reaction mixture, which was further stirred at 65 °C for 24 h. Then, the reaction mixture was filtered to remove molecular sieves and the solid powder was washed with ethyl acetate. The resultant solution was concentrated under the reduced pressure to give the residue, which was purified through flash column chromatography on silica gel (flushed by 10% Et_3N/petrol ether in advance) to afford pure products **8**.

4. Characterization data of products 4, 5aaa and 8

Diethyl 6-(4-methylphenylsulfonamido)-2-(4-nitrophenyl)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (4aaa): Flash column chromatography eluent, petroleum ether /ethyl acetate = 4/1; Reaction time = 48h; yield: 98%; white solid; mp: 74-76 ^{o}C; >95:5 cr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 8.7 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 2.5 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 2H), 6.91 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 1H), 6.67 (s, 1H), 5.70 (d, *J* = 12.1 Hz, 1H), 4.36 – 4.24 (m, 3H), 4.23 – 4.15 (m, 1H), 3.54 (d, J = 12.1 Hz, 1H), 2.38 (s, 3H), 1.36 – 1.26 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 167.7, 152.3, 148.2, 144.2, 143.7, 135.9, 129.6, 127.5, 127.2, 125.4, 124.5, 123.6, 118.6, 118.1, 82.8, 66.5, 63.5, 62.8, 21.5,14.1,13.8; IR (KBr): 3263, 2925, 2855, 1728, 1599, 1523, 1495, 1462, 1397, 1347, 1295, 1159, 1090, 1040, 970, 906, 849, 816, 671 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{27}N_3O_9S\text{-}H)^-$ requires m/z 568.1390, found m/z 568.1408.

Diethyl 7-hydroxy-4-(4-methylphenylsulfonamido)-3-(4-nitrophenyl)isoindoline-1,1-dicarboxylate (5aaa): Flash column chromatography eluent, petroleum ether /ethyl acetate = 4/1; Reaction time = 48h; white solid; mp: 61-63 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.11 (d, *J* = 8.6 Hz, 2H), 7.41 – 3.37 (m, 4H), 7.20 (d, *J* = 8.1 Hz, 2H), 6.85 – 6.79 (m, 2H), 5.61 (d, *J* = 3.0 Hz, 1H), 5.45 (s, 1H), 4.41 – 4.23 (m, 4H), 3.55 (d, *J* = 4.1 Hz, 1H), 2.42 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.4, 152.6, 149.6, 147.6, 144.1, 141.2, 136.3, 130.0, 129.6, 129.3, 127.1, 123.9, 123.4, 123.0, 119.0, 77.7, 64.9, 63.7, 63.4, 21.6, 14.0, 13.9; IR (KBr): 3273, 2982, 2926, 1792, 1684, 1635, 1576, 1472, 1436, 1395, 1346, 1260, 1185, 1159, 1091, 1018, 945, 858, 815, 758 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{27}N_3O_9S+Na)^-$ requires m/z 592.1366, found m/z 592.1370.

Diethyl 6-(4-methylphenylsulfonamido)-2-(3-nitrophenyl)-2H-benzo[e][1,3]oxazine-4,4(3

H)-dicarboxylate (4baa): Flash column chromatography eluent, petroleum ether /ethyl acetate = 4/1; Reaction time = 48h; yield: 92%; white solid; mp: 72-73 ^{o}C; >95:5 cr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.28 – 8.22 (m, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.63 – 7.55 (m, 3H), 7.44 (d, *J* = 2.3 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 2H), 6.93 – 6.83 (m, 2H), 6.58 (s, 1H), 5.70 (d, *J* = 12.0 Hz, 1H), 4.40 – 4.25 (m, 3H), 4.24 – 4.15 (m, 1H), 3.55 (d, *J* = 12.0 Hz, 1H), 2.38 (s, 3H), 1.37 – 1.27 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 167.7, 152.3, 148.3, 143.7, 139.6, 135.9, 132.6, 129.6, 129.5, 127.2, 125.5, 124.6, 123.9, 121.7, 118.6, 82.6, 66.5, 63.5, 62.8, 21.5, 14.0, 13.8; IR (KBr): 3269, 2965, 1736, 1533, 1496, 1398, 1348, 1260, 1160, 1091, 1026, 905, 809, 732, 676, 605 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{27}N_3O_9S\text{-}H)^-$ requires m/z 568.1390, found m/z 568.1404.

Diethyl

6-(4-methylphenylsulfonamido)-2-(2-nitrophenyl)-2H-benzo[e][1,3]oxazine-4,4(3

H)-dicarboxylate (4caa): Flash column chromatography eluent, petroleum ether /ethyl acetate = 4/1; Reaction time = 48h; yield: 56%; white solid; mp: 64-66 ^{o}C; >95:5 cr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz, 1H), 7.89 (dd, *J* = 8.0, 0.7 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.55 – 7.50 (m, 1H), 7.38 (d, *J* = 2.5 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 2H), 6.92 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.81 (d, *J* = 8.8 Hz, 1H), 6.67 (s, 1H), 6.21 (d, *J* = 12.8 Hz, 1H), 4.41 – 4.25 (m, 3H), 4.18 – 4.10 (m, 1H), 3.61 (d, *J* = 12.9 Hz, 1H), 2.37 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 167.8, 152.7, 148.6, 143.7, 136.1, 132.9, 131.8, 129.7, 129.6, 129.6, 127.8, 127.3, 125.4, 124.6, 124.2, 118.7, 118.3, 80.1, 66.8, 63.4, 62.8, 21.5, 13.9, 13.8; IR (KBr): 3264, 2981, 2927, 1733, 1684, 1597, 1558, 1497, 1472, 1363, 1282, 1228, 1185, 1160, 1091, 1031, 980, 814 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{27}N_3O_9S\text{-}H)^-$ requires m/z 568.1390, found m/z 568.1417.

Diethyl

2-(4-cyanophenyl)-6-(4-methylphenylsulfonamido)-2H-benzo[e][1,3]oxazine-4,4(3

H)-dicarboxylate (4daa): Flash column chromatography eluent, petroleum ether

/ethyl acetate = 4/1; Reaction time = 48h; yield: 96%; white solid; mp: 138-140 ^{o}C; >95:5 cr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (q, *J* = 8.4 Hz, 4H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 2.6 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.90 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 6.69 (s, 1H), 5.65 (d, *J* = 12.0 Hz, 1H), 4.35 – 4.24 (m, 3H), 4.22 – 4.14 (m, 1H), 3.51 (d, *J* = 12.1 Hz, 1H), 2.38 (s, 3H), 1.34 – 1.26 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 167.7, 152.4, 143.7, 142.4, 136.0, 132.3, 129.7, 129.5, 127.8, 127.2, 125.4, 124.5, 118.6, 118.1, 112.8, 82.9, 66.5, 63.5, 62.7, 21.5, 14.0, 13.8; IR (KBr): 3283, 2984, 1742, 1593, 1498, 1399, 1333, 1297, 1239, 1160, 1094, 1017, 972, 877, 820, 708, 671 cm^{-1}; ESI FTMS exact mass calcd for $(C_{28}H_{27}N_3O_7S\text{-}H)^-$ requires m/z 548.1492, found m/z 548.1532.

Diethyl 2-(3-cyanophenyl)-6-(4-methylphenylsulfonamido)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (4eaa): Flash column chromatography eluent, petroleum ether /ethyl acetate = 4/1; Reaction time = 48h; yield: 88%; white solid; mp: 68-70 ^{o}C; >95:5 cr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 2.6 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 6.90 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 6.69 (s, 1H), 5.63 (d, *J* = 12.0 Hz, 1H), 4.38 – 4.25 (m, 3H), 4.23 – 4.15 (m, 1H), 3.51 (d, *J* = 12.0 Hz, 1H), 2.38 (s, 3H), 1.36 – 1.26 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 167.7, 152.3, 143.7, 139.1, 135.9, 132.5, 130.9, 130.2, 129.6, 129.4, 129.3, 127.2, 126.4, 125.4, 124.5, 118.6, 118.0, 112.6, 82.6, 66.5, 63.5, 62.8, 21.5, 14.0, 13.8; IR (KBr): 3265, 2982, 1735, 1595, 1497, 1395, 1330, 1230, 1160, 1091, 1026, 920, 813, 684 cm^{-1}; ESI FTMS exact mass calcd for $(C_{28}H_{27}N_3O_7S\text{-}H)^-$ requires m/z 548.1492, found m/z 548.1536.

Diethyl 6-(4-methylphenylsulfonamido)-2-(4-(trifluoromethyl)phenyl)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (4faa): Flash column chromatography eluent, petroleum ether /ethyl acetate = 4/1; Reaction time = 48h; yield: 92%; white solid; mp:

67-69 °C; >95:5 cr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 2.6 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 6.90 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 1H), 6.56 (s, 1H), 5.67 (d, *J* = 11.7 Hz, 1H), 4.36 – 4.25 (m, 3H), 4.22 – 4.15 (m, 1H), 3.53 (d, *J* = 11.9 Hz, 1H), 2.38 (s, 3H), 1.36 – 1.24 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 167.7, 152.6, 143.7, 136.1, 129.5, 129.3, 127.2, 126.8, 125.7, 125.5, 125.4, 124.6, 118.6, 118.1, 83.2, 66.6, 63.4, 62.7, 21.5, 14.0, 13.8; IR (KBr): 3267, 2984, 1737, 1498, 1398, 1369, 1327, 1259, 1163, 1066, 1024, 973, 813, 672 cm^{-1}; ESI FTMS exact mass calcd for $(C_{28}H_{27}F_3N_2O_7S\text{-}H)^-$ requires m/z 591.1413, found m/z 591.1451.

Diethyl 2-(4-chlorophenyl)-6-(4-methylphenylsulfonamido)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (4gaa): Flash column chromatography eluent, petroleum ether /ethyl acetate = 4/1; Reaction time = 48h; yield: 91%; white solid; mp: 68-70 °C; >95:5 cr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (t, *J* = 8.3 Hz, 4H), 7.41 – 7.37 (m, 3H), 7.22 (d, *J* = 8.2 Hz, 2H), 6.88 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.81 (d, *J* = 8.8 Hz, 1H), 6.43 (s, 1H), 5.59 (d, *J* = 11.5 Hz, 1H), 4.34 – 4.23 (m, 3H), 4.22 – 4.15 (m, 1H), 3.49 (d, *J* = 11.5 Hz, 1H), 2.38 (s, 3H), 1.34 – 1.26 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 167.8, 152.9, 143.6, 136.3, 136.0, 134.9, 129.5, 129.1, 128.7, 127.8, 127.2, 125.6, 124.8, 118.5, 118.0, 83.3, 66.6, 63.3, 62.6, 21.5, 14.4, 13.8; IR (KBr): 3265, 2965, 1736, 1496, 1399, 1368, 1260, 1160, 1109, 1024, 968, 868, 808, 673 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{27}ClN_2O_7S\text{-}H)^-$ requires m/z 557.1149, found m/z 557.1153.

Diethyl 2-(3,4-dichlorophenyl)-6-(4-methylphenylsulfonamido)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (4haa): Flash column chromatography eluent, petroleum ether /ethyl acetate = 4/1; Reaction time = 48h; yield: 89%; white solid; mp: 70-72 °C; >95:5 cr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 1.6 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.49 – 7.40 (m, 3H), 7.22 (d, *J* = 8.2 Hz, 2H), 6.88 (dd, *J* = 8.8, 2.6 Hz, 1H),

6.82 (d, J = 8.8 Hz, 1H), 6.44 (s, 1H), 5.57 (d, J = 11.7 Hz, 1H), 4.34 – 4.26 (m, 3H), 4.23 – 4.16 (m, 1H), 3.49 (d, J = 11.9 Hz, 1H), 2.38 (s, 3H), 1.34 – 1.24 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 167.7, 152.5, 143.7, 137.7, 135.9, 133.1, 132.7, 130.5, 129.5, 129.3, 128.5, 127.2, 125.8, 125.5, 124.7, 118.5, 118.0, 82.6, 66.5, 63.4, 62.7, 21.5, 14.0, 13.8; IR (KBr): 3262, 2964, 2925, 2856, 1736, 1497, 1446, 1397, 1369, 1330, 1261, 1160, 1092, 1027, 915, 869, 807, 672 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{26}Cl_2N_2O_7S\text{-}H)^-$ requires m/z 591.0760, found m/z 591.0761.

Diethyl 6-(4-methylphenylsulfonamido)-2-(3,4,5-trifluorophenyl)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (4iaa): Flash column chromatography eluent, petroleum ether /ethyl acetate = 4/1; Reaction time = 48h; yield: 83%; white solid; mp: 138-140 ^{o}C; >95:5 cr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 2.6 Hz, 1H), 7.28 (d, J = 7.6 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 6.88 (dd, J = 8.8, 2.6 Hz, 1H), 6.82 (d, J = 8.7 Hz, 1H), 6.36 (s, 1H), 5.54 (d, J = 11.9 Hz, 1H), 4.34 – 4.26 (m, 3H), 4.23 – 4.16 (m, 1H), 3.47 (d, J = 11.9 Hz, 1H), 2.38 (s, 3H), 1.34 – 1.27 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 167.6, 152.2, 143.7, 135.9, 129.5, 129.4, 127.2, 125.6, 124.5, 118.5, 118.0, 111.6, 111.0, 110.8, 82.1, 66.4, 63.5, 62.8, 21.5, 14.0, 13.8; IR (KBr): 3269, 2926, 1737, 1624, 1597, 1532, 1496, 1446, 1392, 1374, 1330, 1262, 1231, 1162, 1092, 1046 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{25}F_3N_2O_7S\text{-}H)^-$ requires m/z 577.5490, found m/z 577.5495.

Diethyl 6-(4-methylphenylsulfonamido)-2-phenyl-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (4jaa): Flash column chromatography eluent, petroleum ether /ethyl acetate = 4/1; Reaction time = 24h; yield: 90%; white solid; mp: 64-66 ^{o}C; >95:5 cr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.57 (m, 4H), 7.47 – 7.40 (m, 4H), 7.24 (d, J = 8.0 Hz, 2H), 6.91 (dd, J = 8.8, 2.6 Hz, 1H), 6.84 (d, J = 8.7 Hz, 1H), 6.45 (s, 1H), 5.64 (d, J = 11.5 Hz, 1H), 4.37 – 4.27 (m, 3H), 4.26 – 4.17 (m, 1H), 3.56 (d, J = 11.5 Hz, 1H), 2.41 (s, 3H), 1.35 (t, J = 4.4 Hz, 3H), 1.30 (t, J = 4.4 Hz, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 169.3, 167.9, 153.2, 143.6, 137.5, 136.0, 129.5, 129.0, 128.9, 128.5, 127.2, 126.3, 125.6, 124.8, 118.6, 118.0, 84.09, 66.8, 63.2, 62.6, 21.5, 14.0, 13.8; IR (KBr): 3267, 2964, 1737, 1497, 1398, 1261, 1160, 1093, 1024, 866, 805, 701, 601 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{28}N_2O_7S\text{-}H)^-$ requires m/z 523.1539, found m/z 523.1544.

Diethyl 6-(4-methylphenylsulfonamido)-2-(m-tolyl)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (4kaa): Flash column chromatography eluent, petroleum ether /ethyl acetate = 4/1; Reaction time = 24h; yield: 77%; white solid; mp: 80-82 ^oC; >95:5 cr; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.37 (m, 3H), 7.32 – 7.28 (m, 1H), 7.23 – 7.19 (m, 3H), 6.88 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.82 (d, *J* = 8.7 Hz, 1H), 6.41 (s, 1H), 5.57 (d, *J* = 11.2 Hz, 1H), 4.35 – 4.23 (m, 3H), 4.23 – 4.16 (m, 1H), 3.53 (d, *J* = 11.2 Hz, 1H), 2.38 (s, 3H), 2.37 (s, 3H), 1.31 (t, *J* = 5.2 Hz, 3H), 1.28 (t, *J* = 5.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 167.9, 153.2, 143.6, 138.3, 137.5, 136.0, 129.8, 129.5, 128.8, 128.5, 127.2, 126.8, 125.6, 124.9, 123.3, 118.6, 118.0, 84.2, 66.8, 63.2, 62.6, 21.5, 21.4, 14.0, 13.8; IR (KBr): 3264, 2964, 1736, 1497, 1399, 1368, 1330, 1261, 1160, 1092, 1023, 867, 804, 701 cm^{-1}; ESI FTMS exact mass calcd for $(C_{28}H_{30}N_2O_7S\text{-}H)^-$ requires m/z 537.1696, found m/z 537.1717.

Diethyl 6-(4-methylphenylsulfonamido)-2-(p-tolyl)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (4laa): Flash column chromatography eluent, petroleum ether /ethyl acetate = 4/1; Reaction time = 24h; yield: 41%; white solid; mp: 78-80 ^oC; >95:5 cr; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 2.5 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 4H), 6.89 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.80 (d, *J* = 8.7 Hz, 1H), 6.66 (s, 1H), 5.58 (d, *J* = 11.2 Hz, 1H), 4.33 – 4.26 (m, 3H), 4.22 – 4.16 (m, 1H), 3.52 (d, *J* = 11.2 Hz, 1H), 2.38 (s, 3H), 2.37 (s, 3H), 1.31 (t, *J* = 4.4 Hz, 3H), 1.28 (t, *J* = 4.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 167.9, 153.2, 143.6, 138.9, 136.0, 134.7, 129.5, 129.2, 128.9, 127.2, 126.2, 125.4, 124.7, 118.6, 117.9,

84.0, 66.8, 63.2, 62.6, 21.5, 21.3, 14.0, 13.8; IR (KBr): 3263, 2981, 1736, 1497, 1399, 1368, 1330, 1261, 1161, 1091, 1028, 926, 813, 731, 670 cm^{-1}; ESI FTMS exact mass calcd for $(C_{28}H_{30}N_2O_7S\text{-}H)^-$ requires m/z 537.1696, found m/z 537.1719.

Diethyl 6-(4-methylphenylsulfonamido)-2-(thiophen-2-yl)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (4maa): Flash column chromatography eluent, petroleum ether /ethyl acetate = 4/1; Reaction time = 24h; yield: 62%; white solid; inseparable chemoselective isomers; 59:41 cr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.52 (m, 5H), 7.43 (d, *J* = 2.5 Hz, 1H), 7.37 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.26 – 7.18 (m, 4H), 7.05 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.94 – 6.81 (m, 4H), 6.68 – 6.54 (m, 2H), 6.04 (d, *J* = 6.6 Hz, 0.7H), 5.88 (d, *J* = 11.1 Hz, 1H), 5.44 (d, *J* = 6.6 Hz, 0.7H), 4.34 – 4.15 (m, 6.8H), 3.74 (d, *J* = 11.2 Hz, 1H), 2.40 (s, 2.1H), 2.39 (s, 3H), 1.33 – 1.24 (m, 10.2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 169.2, 167.7, 156.1, 152.6, 143.7, 143.7, 140.3, 135.9, 129.6, 129.5, 129.4, 129.2, 129.0, 128.3, 127.4, 127.2, 127.1, 126.8, 126.1, 125.9, 125.8, 125.4, 124.6, 124.5, 118.5, 118.4, 117.8, 81.2, 66.5, 63.3, 63.2, 62.7, 62.5, 62.1, 21.5, 14.4, 14.0, 13.9, 13.8; IR (KBr): 3267, 2982, 1737, 1498, 1398, 1370, 1257, 1159, 1091, 1025, 912, 814, 710 cm^{-1}; ESI FTMS exact mass calcd for $(C_{25}H_{26}N_2O_7S_2\text{-}H)^-$ requires m/z 529.1103, found m/z 529.1103.

Diethyl 6-(4-methylphenylsulfonamido)-2-(thiophen-3-yl)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (4naa): Flash column chromatography eluent, petroleum ether /ethyl acetate = 5/1; Reaction time = 24h; yield: 71%; white solid; mp: 138-140 ^{o}C; >95:5 cr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.51 – 7.49 (m, 1H), 7.41 (d, *J* = 2.6 Hz, 1H), 7.34 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.25 – 7.23 (m, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.91 – 6.88 (m, 2H), 6.79 (d, *J* = 8.7 Hz, 1H), 5.68 (s, 1H), 4.32 – 4.24 (m, 3H), 4.21 – 4.15 (m, 1H), 3.62 (s, 1H), 2.37 (s, 3H), 1.33 – 1.26 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 167.9, 152.8, 143.7, 139.1, 136.0, 129.6, 129.3, 127.3, 126.3, 125.9, 125.4, 124.5, 123.3, 118.5, 118.0, 81.3, 66.5, 63.3, 62.7, 21.5, 14.0,

13.9; IR (KBr): 3255, 2981, 2932, 1735, 1691, 1606, 1507, 1398, 1327, 1231, 1157, 1091, 1052, 915, 867, 811, 672 cm^{-1}; ESI FTMS exact mass calcd for $(C_{25}H_{26}N_2O_7S_2\text{-}H)^-$ requires m/z 529.1103, found m/z 529.1109.

Diethyl 6-(4-methylphenylsulfonamido)-2-(m-tolyl)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (4oaa): Flash column chromatography eluent, petroleum ether /ethyl acetate = 4/1; Reaction time = 24h; yield: 56%; white solid; mp: 116-118 ^oC; >95:5 cr; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.86 (s, 1H), 6.80 (d, *J* = 2.2 Hz, 1H), 6.75 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.48 (d, *J* = 8.4 Hz, 1H), 5.09 (d, *J* = 12.8 Hz, 1H), 4.32 (d, *J* = 8.2 Hz, 1H), 4.28 – 4.15 (m, 4H), 3.10 (dd, *J* = 12.8, 8.2 Hz, 1H), 2.36 (s, 3H), 1.80 – 1.73 (m, 1H), 1.69 – 1.51 (m, 6H), 1.30 – 1.21 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 168.0, 154.9, 143.5, 136.5, 135.9, 129.4, 128.8, 127.5, 124.8, 120.3, 110.4, 100.0, 62.3, 62.1, 61.9, 47.5, 37.4, 25.2, 22.7, 22.6, 21.5, 14.1, 14.0; IR (KBr): 3268, 2933, 1742, 1483, 1400, 1306, 1233, 1160, 1091, 1024, 864, 814, 704 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{34}N_2O_7S\text{-}H)^-$ requires m/z 529.2009, found m/z 529.2018.

Diethyl 2-(heptan-3-yl)-6-(4-methylphenylsulfonamido)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (4paa): Flash column chromatography eluent, petroleum ether /ethyl acetate = 5/1; Reaction time = 24h; yield: 74%; white solid; inseparable chemoselective isomers; 58:42 cr; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.50 (m, 4.8H), 7.31 (d, *J* = 2.5 Hz, 1.4H), 7.20 – 7.17 (m, 4.8H), 6.84 (dd, *J* = 8.8, 2.6 Hz, 1.4H), 6.76 – 6.73 (m, 2.4H), 6.70 – 6.64 (m, 3.4H), 6.48 (d, *J* = 8.4 Hz, 1H), 5.05 (dd, *J* = 13.1, 10.5 Hz, 1H), 4.51 – 4.42 (m, 1.4H), 4.34 (d, *J* = 7.7 Hz, 1H), 4.30 – 4.07 (m, 11H), 3.23 – 3.18 (m, 2.4H), 2.36 – 2.35 (s, 7.2H), 1.71 – 1.47 (m, 9H), 1.34 – 1.23 (m, 23H), 0.98 – 0.81 (m, 13H), 0.77 – 0.68 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 168.9, 168.3, 168.0, 155.5, 153.7, 143.5, 143.5, 136.1, 135.8, 129.5, 129.4, 128.5, 127.4, 127.3, 125.4, 124.8, 124.4, 120.7, 118.4, 118.2, 110.0, 109.9, 101.4,

101.2, 85.2, 85.1, 66.7, 63.2, 62.3, 62.2, 61.9, 50.0, 49.9, 43.4, 43.3, 28.2, 27.7, 26.1, 25.2, 23.2, 23.0, 21.8, 21.5, 21.2, 14.0, 13.9, 13.8, 11.4, 11.3, 8.4, 8.1; IR (KBr): 3266, 2964, 2869, 1738, 1603, 1490, 1390, 1249, 1159, 1095, 1026, 933, 867, 813, 672 cm^{-1}; ESI FTMS exact mass calcd for $(C_{28}H_{38}N_2O_7S\text{-}H)^-$ requires m/z 545.2322, found m/z 545.2333.

Diethyl 2-cyclopentyl-6-(4-methylphenylsulfonamido)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (4qaa): Flash column chromatography eluent, petroleum ether /ethyl acetate = 5/1; Reaction time = 24h; yield: 81%; white solid; mp: 114 - 116 ^oC; 41:59 cr; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 2.4 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 6.83 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.69 (d, *J* = 8.7 Hz, 1H), 6.42 (s, 1H), 4.34 – 4.13 (m, 6H), 3.21 (s, 1H), 2.37 (s, 3H), 1.86 – 1.79 (m, 2H), 1.65 – 1.49 (m, 4H), 1.32 – 1.24 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 168.1, 153.5, 143.5, 136.1, 129.5, 128.4, 127.3, 125.6, 124.8, 118.3, 118.1, 86.8, 66.7, 63.2, 62.4, 43.7, 28.2, 27.8, 25.7, 25.6, 21.5, 14.0, 13.9; IR (KBr): 3272, 2961, 2868, 1741, 1635, 1502, 1461, 1390, 1259, 1159, 1095, 1027, 957, 869, 671 cm^{-1}; ESI FTMS exact mass calcd for $(C_{26}H_{32}N_2O_7S\text{-}H)^-$ requires m/z 515.1852, found m/z 515.1860.

Methyl 4-(3-chlorophenyl)-6-(4-methylphenylsulfonamido)-2-(4-nitrophenyl)-3,4-dihydro-2H-benzo[e][1,3]oxazine-4-carboxylate (4aba): Flash column chromatography eluent, petroleum ether /ethyl acetate = 4/1; Reaction time = 48 h; yield: 87%; inseparable diastereomers; 83:17 dr; white solid; mp: 102-104 ^oC; >95:5 cr; ^1H NMR (400 MHz, $CDCl_3$) δ 8.26(m, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.30 (m, 4H), 7.28 – 7.17 (m, 3H), 7.03 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 6.54 (s, 1H), 5.39 (d, *J* = 14.1 Hz, 1H), 3.78 (s, 3H), 3.71 (d, *J* = 14.1 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 155.5, 144.8, 143.9, 135.9, 129.8, 128.5, 127.3, 126.5, 125.8, 123.5, 119.7, 119.4, 81.3, 65.7, 53.7, 21.6; IR (KBr): 3268, 2921, 1738, 1524, 1495, 1345, 1252, 1160, 1090, 1021, 913,

808, 732 cm^{-1}; ESI FTMS exact mass calcd for $(C_{29}H_{24}ClN_3O_7S\text{-}H)^-$ requires m/z 592.0945, found m/z 592.0955.

Methyl 4-(4-chlorophenyl)-6-(4-methylphenylsulfonamido)-2-(4-nitrophenyl)-3,4-dihydro-2H-benzo[e][1,3]oxazine-4-carboxylate (4aca): Flash column chromatography eluent, petroleum ether /ethyl acetate = 4/1; Reaction time = 48 h; yield: 82%; inseparable diastereomers; 80:20 dr; white solid; mp: 102-104 °C; >95:5 cr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.7 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.27 (m, 3H), 7.23 – 7.18 (m, 3H), 7.05 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.56 (s, 1H), 5.35 (d, *J* = 14.1 Hz, 1H), 3.74 (s, 3H), 3.68 (d, *J* = 14.1 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 152.3, 148.1, 144.8, 143.9, 140.4, 135.8, 134.3, 129.7, 129.5, 129.0, 128.6, 127.3, 127.2, 125.8, 123.5, 123.1, 119.9, 119.4, 81.3, 65.6, 53.7, 21.6; IR (KBr): 3265, 2958, 2852, 1736, 1614, 1524, 1493, 1456, 1345, 1255, 1160, 1092, 1019, 807 cm^{-1}; ESI FTMS exact mass calcd for $(C_{29}H_{24}ClN_3O_7S\text{-}H)^-$ requires m/z 592.0945, found m/z 592.0959.

Methyl 4-(4-fluorophenyl)-6-(4-methylphenylsulfonamido)-2-(4-nitrophenyl)-3,4-dihydro-2H-benzo[e][1,3]oxazine-4-carboxylate (4ada): Flash column chromatography eluent, petroleum ether /ethyl acetate = 4/1; Reaction time = 48 h; yield: 77%; inseparable diastereomers; 80:20 dr; white solid; mp: 108-110 °C; >95:5 cr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.7, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.25 – 7.20 (m, 4H), 7.07 – 6.99 (m, 3H), 6.95 (d, *J* = 8.7, 2H), 6.51 (s, 1H), 5.36 (d, *J* = 14.1 Hz, 1H), 3.74 (s, 3H), 3.68 (d, *J* = 14.1 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 152.3, 148.1, 144.9, 143.9, 137.7, 135.9, 130.2, 130.1, 129.7, 127.6, 127.3, 127.3, 125.7, 123.5, 123.1, 119.3, 115.4, 115.2, 81.2, 65.5, 53.6, 21.6; IR (KBr): 3268, 2961, 1737, 1498, 1345, 1260, 1159, 1093, 1021, 804, 735 cm^{-1}; ESI FTMS exact mass calcd for $(C_{29}H_{24}FN_3O_7S\text{-}H)^-$ requires m/z 576.1241, found m/z 576.1261.

Methyl 6-(4-methylphenylsulfonamido)-2-(4-nitrophenyl)-4-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazine-4-carboxylate (4aea): Flash column chromatography eluent, petroleum ether /ethyl acetate = 4/1; Reaction time = 48 h; yield: 84%; inseparable diastereomers; 80:20 dr; white solid; mp: 84-86 ^{o}C; >95:5 cr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.73 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.30 (m, 3H), 7.25 – 7.19 (m, 4H), 7.08 – 7.00 (m, 2H), 6.94 (d, *J* = 8.8 Hz, 1H), 6.49 (s, 1H), 5.38 (d, *J* = 14.0 Hz, 1H), 3.73 (s, 3H), 3.68 (d, *J* = 14.0 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 152.4, 148.0, 145.1, 143.8, 141.8, 135.9, 129.7, 128.9, 128.4, 128.3, 128.3, 127.3, 127.3, 125.7, 123.5, 123.3, 120.3, 119.2, 81.3, 66.0, 53.5, 21.6; IR (KBr): 3277, 2961, 2921, 2852, 1736, 1614, 1524, 1494, 1453, 1345, 1259, 1160, 1093, 1022, 912, 857, 804, 698 cm^{-1}; ESI FTMS exact mass calcd for $(C_{29}H_{25}N_3O_7S\text{-}H)^-$ requires m/z 558.1335, found m/z 558.1363.

Methyl 4-(4-chlorophenyl)-6-(4-chlorophenylsulfonamido)-2-(4-nitrophenyl)-3,4-dihydro-2H-benzo[e][1,3]oxazine-4-carboxylate (4acf): Flash column chromatography eluent, petroleum ether /ethyl acetate = 5/1; Reaction time = 24h; yield: 56%; white solid; mp: 88-90 ^{o}C; 83:17 dr; >95:5 cr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.0 Hz, 2H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.66 – 7.63 (m, 2H), 7.43 (dd, *J* = 5.4, 3.7 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.20 – 7.15 (m, 3H), 7.09 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.98 – 6.95 (m, 1H), 6.87 (s, 1H), 5.35 (d, *J* = 14.1 Hz, 1H), 3.74 (s, 3H), 3.68 (d, *J* = 14.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 152.5, 148.1, 144.7, 140.4, 139.6, 137.2, 134.4, 129.6, 129.4, 128.8, 128.8, 128.7, 128.7, 127.6, 127.3, 125.9, 123.6, 123.5, 123.1, 120.0, 119.5, 81.3, 65.6, 53.7.; IR (KBr): 3312, 3087, 2955, 1735, 1654, 1608, 1586, 1522, 1491, 1397, 1346, 1245, 1164, 1045, 1013, 972, 856, 754, 704 cm^{-1}; ESI FTMS exact mass calcd for $(C_{28}H_{21}Cl_2N_3O_7S\text{-}H)^-$ requires m/z 612.0399, found m/z 612.0375.

Diethyl 6-(2-methylphenylsulfonamido)-2-(4-nitrophenyl)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (4aab): Flash column chromatography eluent, petroleum ether /ethyl acetate = 4/1; Reaction time = 48h; yield: 87%; white solid; mp: 68-70 ^{o}C; >95:5 cr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.8 Hz, 2H), 7.88 – 7.84 (m, 1H), 7.80 (d, *J* = 8.6 Hz, 2H), 7.43 (td, *J* = 7.5, 1.2 Hz, 1H), 7.39 (d, *J* = 2.5 Hz, 1H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 1H), 6.62 (s, 1H), 5.67 (d, *J* = 12.1 Hz, 1H), 4.36 – 4.25 (m, 3H), 4.25 – 4.17 (m, 1H), 3.52 (d, *J* = 12.1 Hz, 1H), 2.60 (s, 3H), 1.36 – 1.28 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 167.6, 152.4, 148.4, 144.2, 137.3, 137.2, 133.1, 132.5, 129.9, 129.3, 127.6, 126.3, 125.2, 124.4, 123.7, 118.7, 118.1, 82.8, 66.5, 63.6, 62.8, 20.5, 14.1, 13.9; IR (KBr): 3280, 2927, 1728, 1525, 1396, 1349, 1262, 1160, 1131, 1021, 976, 850, 802, 758, 692 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{27}N_3O_9S\text{-}H)^-$ requires m/z 568.1390, found m/z 568.1414.

Diethyl 6-(4-methoxyphenylsulfonamido)-2-(4-nitrophenyl)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (4aac): Flash column chromatography eluent, petroleum ether /ethyl acetate = 4/1; Reaction time = 48h; yield: 97%; white solid; mp: 71-73 ^{o}C; >95:5 cr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.8 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.65 – 7.59 (m, 2H), 7.41 (d, *J* = 2.5 Hz, 1H), 6.95 – 6.83 (m, 4H), 6.60 (s, 1H), 5.70 (d, *J* = 12.1 Hz, 1H), 4.36 – 4.25 (m, 3H), 4.25 – 4.17 (m, 1H), 3.83 (s, 3H), 3.54 (d, *J* = 12.1 Hz, 1H), 1.33 (t, *J* = 5.0 Hz, 3H), 1.30 (t, *J* = 5.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 167.7, 163.0, 152.4, 148.3, 144.2, 130.5, 129.7, 129.4, 127.6, 125.7, 124.7, 123.7, 118.6, 118.1, 114.1, 82.8, 66.6, 63.6, 62.8, 55.6, 14.1, 13.9; IR (KBr): 3270, 2970, 1736, 1597, 1526, 1497, 1463, 1347, 1260, 1156, 1093, 1024, 975, 832, 802, 727 cm^{-1}; ESI FTMS exact mass calcd for $(C_{27}H_{27}N_3O_{10}S\text{-}H)^-$ requires m/z 584.1339, found m/z 584.1382.

Diethyl 6-(4-(tert-butyl)phenylsulfonamido)-2-(4-nitrophenyl)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (4aad): Flash column chromatography eluent, petroleum ether /ethyl acetate = 4/1; Reaction time = 48h; yield: 95%; white solid; mp: 80-82 ^{o}C; >95:5 cr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 8.27 (m, 2H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.68 – 7.63 (m, 2H), 7.50 (d, *J* = 2.6 Hz, 1H), 7.48 – 7.44 (m, 2H), 6.96 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 1H), 6.74 (s, 1H), 5.73 (d, *J* = 12.1 Hz, 1H), 4.41 – 4.27 (m, 3H), 4.28 – 4.17 (m, 1H), 3.57 (d, *J* = 12.1 Hz, 1H), 1.39 – 1.30 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 167.7, 156.7, 152.3, 148.2, 144.2, 136.1, 129.7, 127.6, 127.0, 126.1, 125.3, 124.4, 123.7, 118.6, 118.2, 82.8, 66.6, 63.5, 62.8, 35.2, 31.1, 14.1, 13.9; IR (KBr): 3269, 2965, 1736, 1597, 1526, 1496, 1398, 1346, 1261, 1163, 1090, 1024, 977, 803, 752 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{33}N_3O_9S\text{-}H)^-$ requires m/z 610.1860, found m/z 610.1854.

Diethyl 2-(4-nitrophenyl)-6-(phenylsulfonamido)-2H-benzo[e][1,3]oxazine-4,4(3H)-dicarboxylate (4aae): Flash column chromatography eluent, petroleum ether /ethyl acetate = 4/1; Reaction time = 48h; yield: 94%; white solid; mp: 138-140 ^{o}C; >95:5 cr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.8 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.71 – 7.68 (m, 2H), 7.58 – 7.52 (m, 1H), 7.48 – 7.41 (m, 3H), 6.91 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.87 – 6.82 (m, 1H), 6.62 (s, 1H), 5.70 (d, *J* = 12.1 Hz, 1H), 4.38 – 4.25 (m, 3H), 4.25 – 4.17 (m, 1H), 3.54 (d, *J* = 12.1 Hz, 1H), 1.33 (t, *J* = 6.0 Hz, 3H), 1.29 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 167.7, 152.5, 148.3, 144.2, 138.9, 132.9, 129.3, 129.0, 127.6, 127.2, 125.7, 124.8, 123.7, 118.7, 118.2, 82.8, 66.6, 63.6, 62.9, 14.1, 13.9; IR (KBr): 3263, 2981, 1737, 1525, 1395, 1346, 1235, 1162, 1093, 1027, 971, 852, 752, 724, 690 cm^{-1}; ESI FTMS exact mass calcd for $(C_{26}H_{25}N_3O_9S\text{-}H)^-$ requires m/z 554.1234, found m/z 554.1281.

Diethyl 6-(4-chlorophenylsulfonamido)-2-(4-nitrophenyl)-2H-benzo[e][1,3]oxazine-4,4(3

H)-dicarboxylate (4aaf): Flash column chromatography eluent, petroleum ether /ethyl acetate = 4/1; Reaction time = 48h; yield: 90%; white solid; mp: 72-74 ^{o}C; >95:5 cr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.26 (m, 2H), 7.82 (d, *J* = 8.6 Hz, 2H), 7.66 – 7.60 (m, 2H), 7.44 – 7.37 (m, 3H), 6.94 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 1H), 6.64 (s, 1H), 5.70 (d, *J* = 12.0 Hz, 1H), 4.37 – 4.25 (m, 3H), 4.25 – 4.18 (m, 1H), 3.54 (d, *J* = 12.0 Hz, 1H), 1.33 (t, *J* = 6.0, 3H), 1.29 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 167.6, 152.7, 148.2, 144.10, 139.5, 137.3, 129.3, 128.9, 128.7, 127.7, 126.0, 125.0, 123.7, 118.8, 118.2, 82.9, 66.6, 63.6, 62.9, 14.1, 13.9; IR (KBr): 3268, 2981, 1736, 1525, 1496, 1398, 1346, 1236, 1164, 1091, 1022, 975, 853, 755, 609 cm^{-1}; ESI FTMS exact mass calcd for $(C_{26}H_{24}ClN_3O_9S\text{-}H)^-$ requires m/z 588.0844, found m/z 588.0873.

Diethyl

6-(3-bromophenylsulfonamido)-2-(4-nitrophenyl)-2H-benzo[e][1,3]oxazine-4,4(3

H)-dicarboxylate (4aag): Flash column chromatography eluent, petroleum ether /ethyl acetate = 4/1; Reaction time = 48h; yield: 79%; white solid; mp: 135-137 ^{o}C; >95:5 cr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.7 Hz,2H), 7.89 (s, 1H), 7.82 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.43 (d, *J* = 1.5 Hz, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 6.96 – 6.84 (m, 2H), 6.53 (s, 1H), 5.71 (d, *J* = 12.0 Hz, 1H), 4.37 – 4.29 (m, 3H), 4.26 – 4.20 (m, 1H), 3.56 (d, *J* = 12.1 Hz, 1H), 1.34 (t, *J* = 6.1 Hz, 3H), 1.31 (t, *J* = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 167.6, 152.8, 148.3, 144.1, 140.8, 136.0, 130.5, 130.0, 128.8, 127.6, 125.9, 125.1, 123.7, 123.0, 118.9, 118.3, 82.9, 66.5, 63.6, 62.9, 14.1, 13.9; IR (KBr): 3266, 2988, 1738, 1526, 1497, 1399, 1370, 1259, 1161, 1091, 913, 868, 733, 696 cm^{-1}; ESI FTMS exact mass calcd for $(C_{26}H_{24}BrN_3O_9S\text{-}H)^-$ requires m/z 632.0339, found m/z 632.0338.

Diethyl

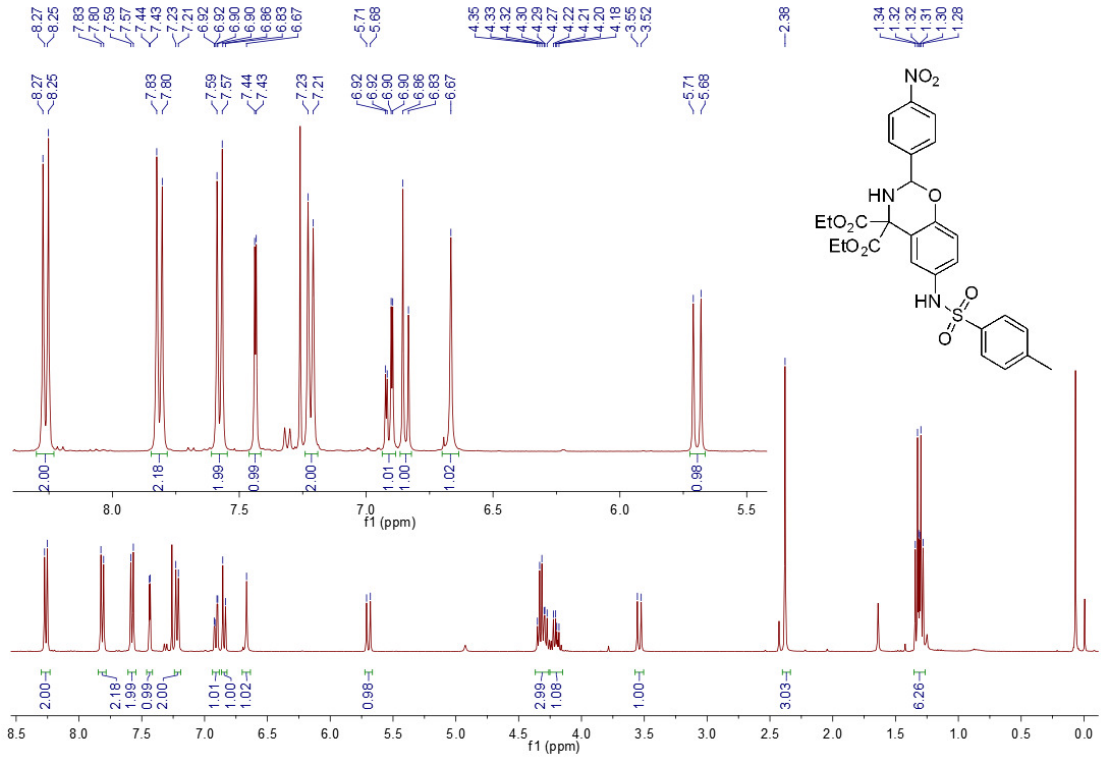
2-cyclopentyl-6-(4-methylphenylsulfonamido)-2H-benzo[e][1,3]oxazine-4,4(3H)-d

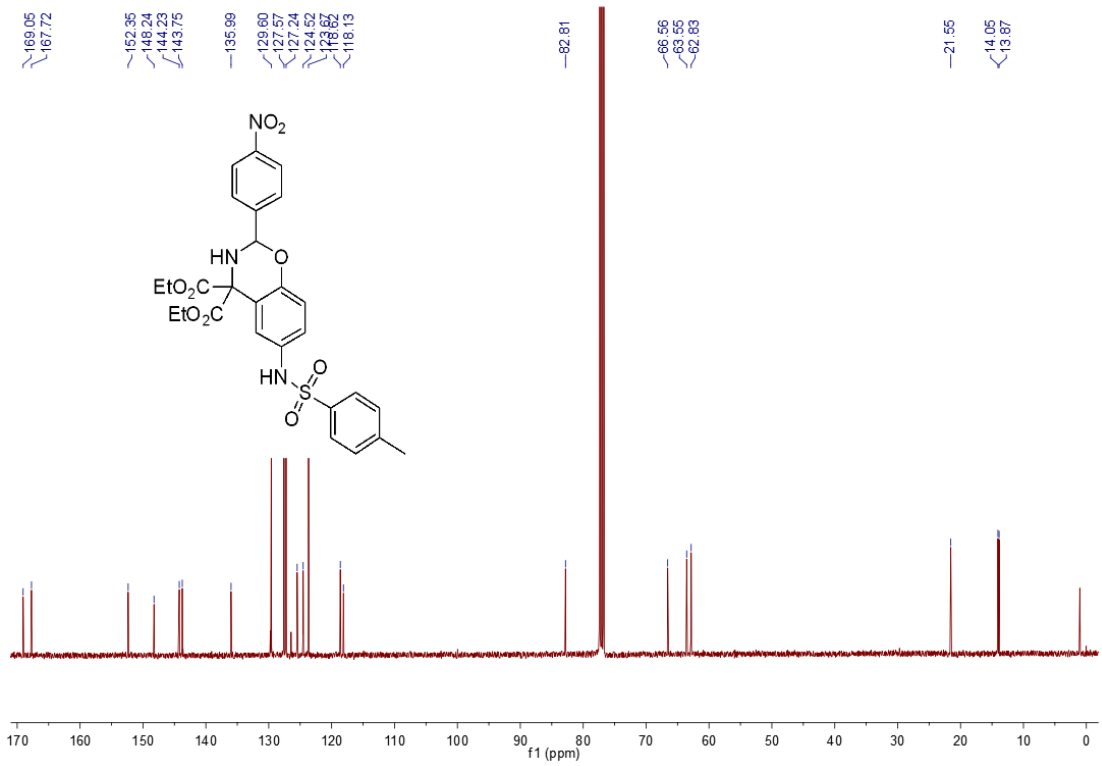
icarboxylate (8): Flash column chromatography eluent, petroleum ether /ethyl acetate

= 5/1; Reaction time = 24h; yield: 66%; white solid; mp: 110-112 ^{o}C; ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.17 – 8.14 (m, 2H), 7.96 (s, 1H), 7.75 (s, 1H), 7.66 – 7.63 (m, 2H), 6.72 – 6.67 (m, 2H), 5.85 (d, J = 5.6 Hz, 1H), 4.37 – 4.25 (m, 4H), 4.21 (d, J = 5.6 Hz, 1H), 1.30 – 1.26 (m, 6H); ^{13}C NMR (100 MHz, Acetone-d_6) δ 171.0, 170.8, 152.0, 147.0, 146.5, 145.8, 130.5, 129.4, 122.7, 117.7, 117.6, 115.7, 77.7, 64.7, 64.6, 62.4, 62.1, 13.4; IR (KBr): 3685, 3645, 3373, 2965, 2859, 1733, 1603, 1516, 1462, 1348, 1264, 1099, 1022, 860, 819, 753, 702 cm^{-1}; ESI FTMS exact mass calcd for $(C_{20}H_{20}N_2O_8\text{-}H)^-$ requires m/z 415.1142, found m/z 415.1149.

5. NMR Spectra of products 4, 5aaa and 8

4aaa





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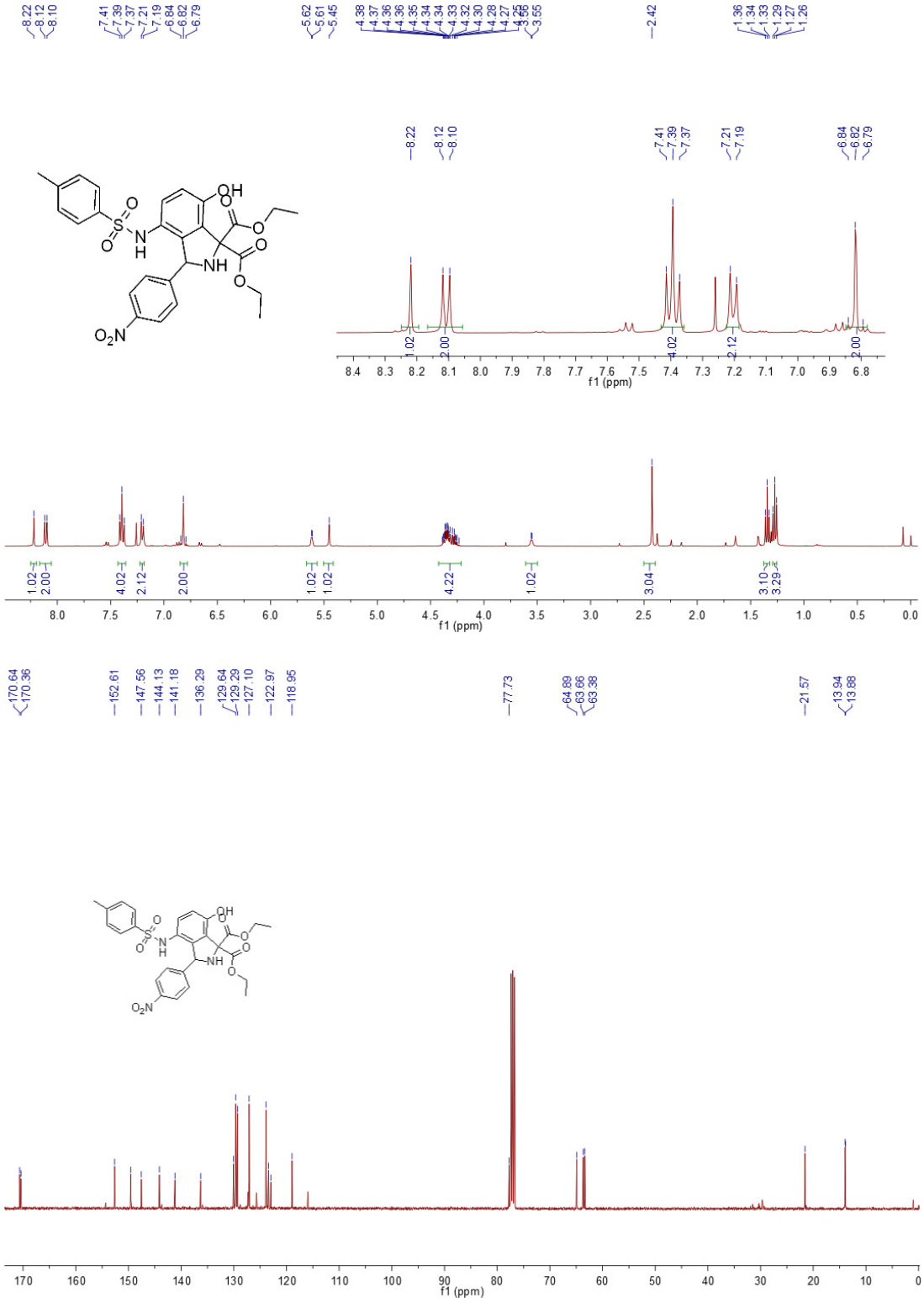
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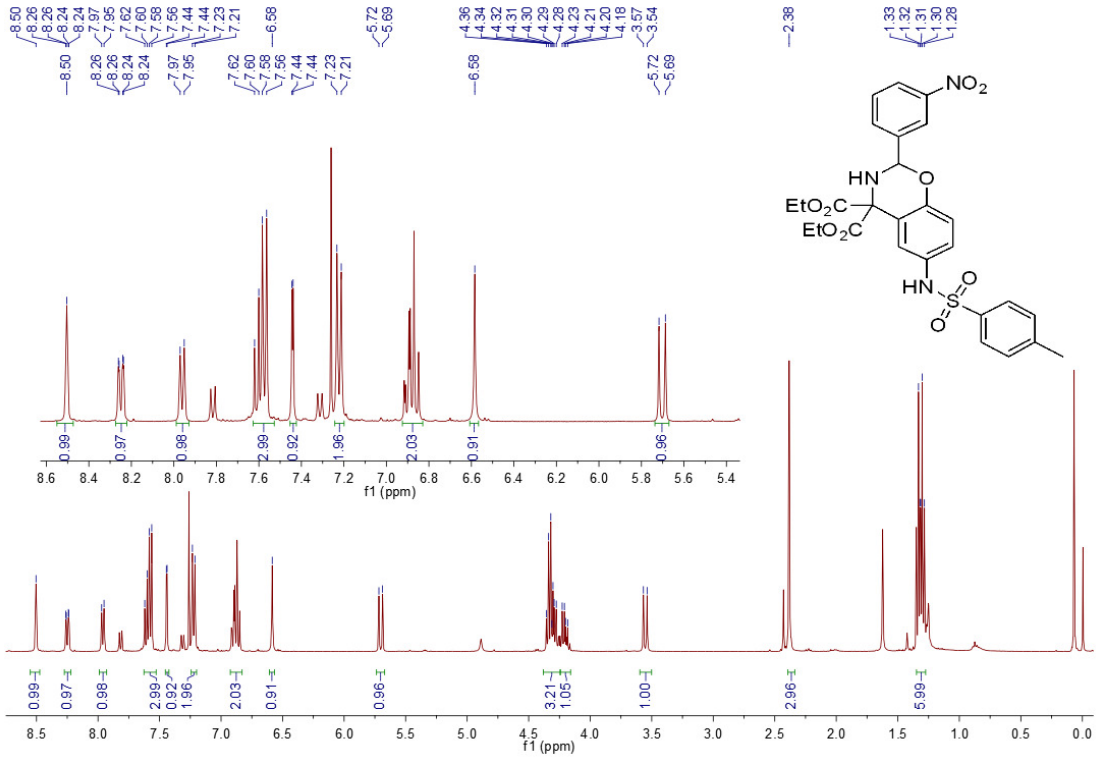
13.88

4baa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S
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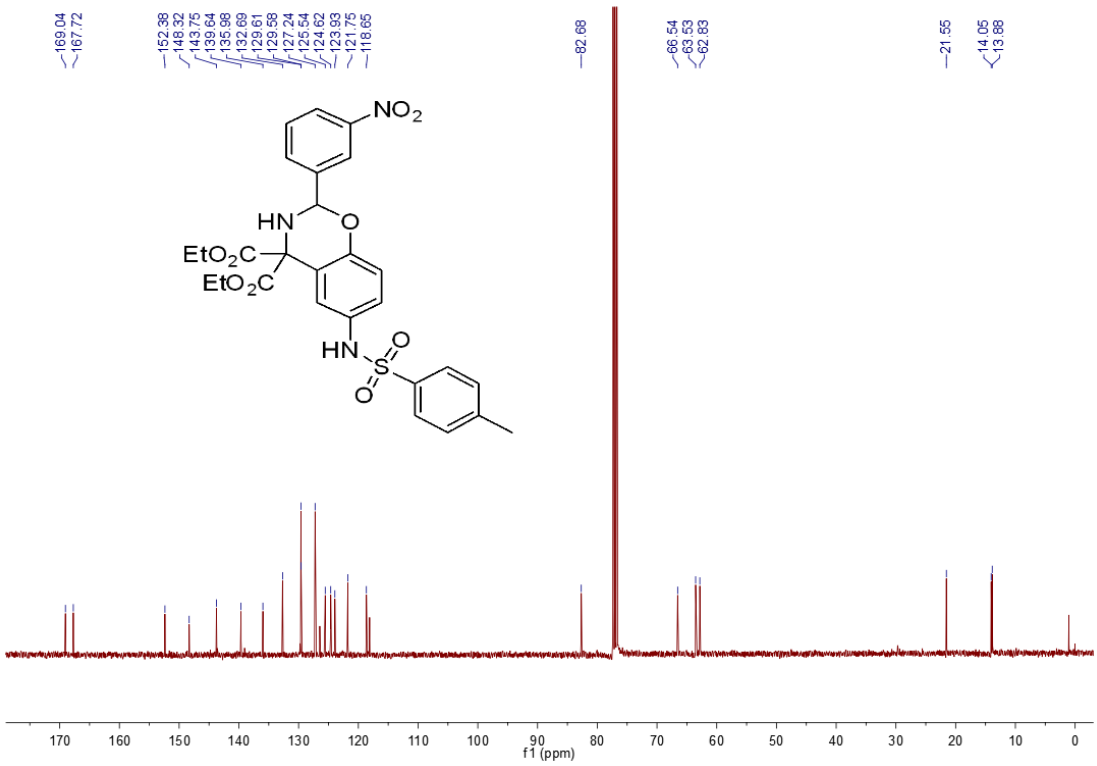
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S
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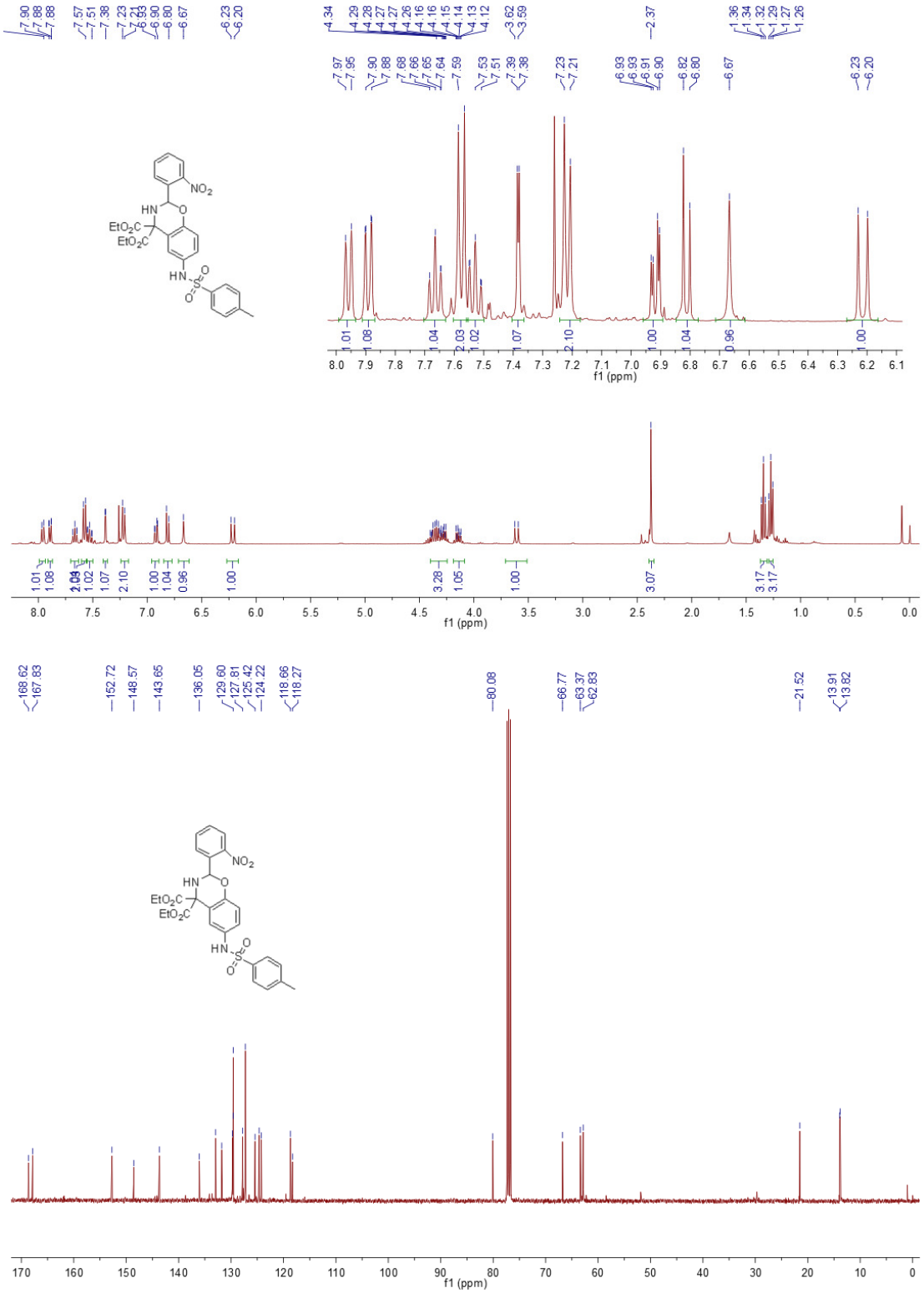
f1 (ppm)

4caa



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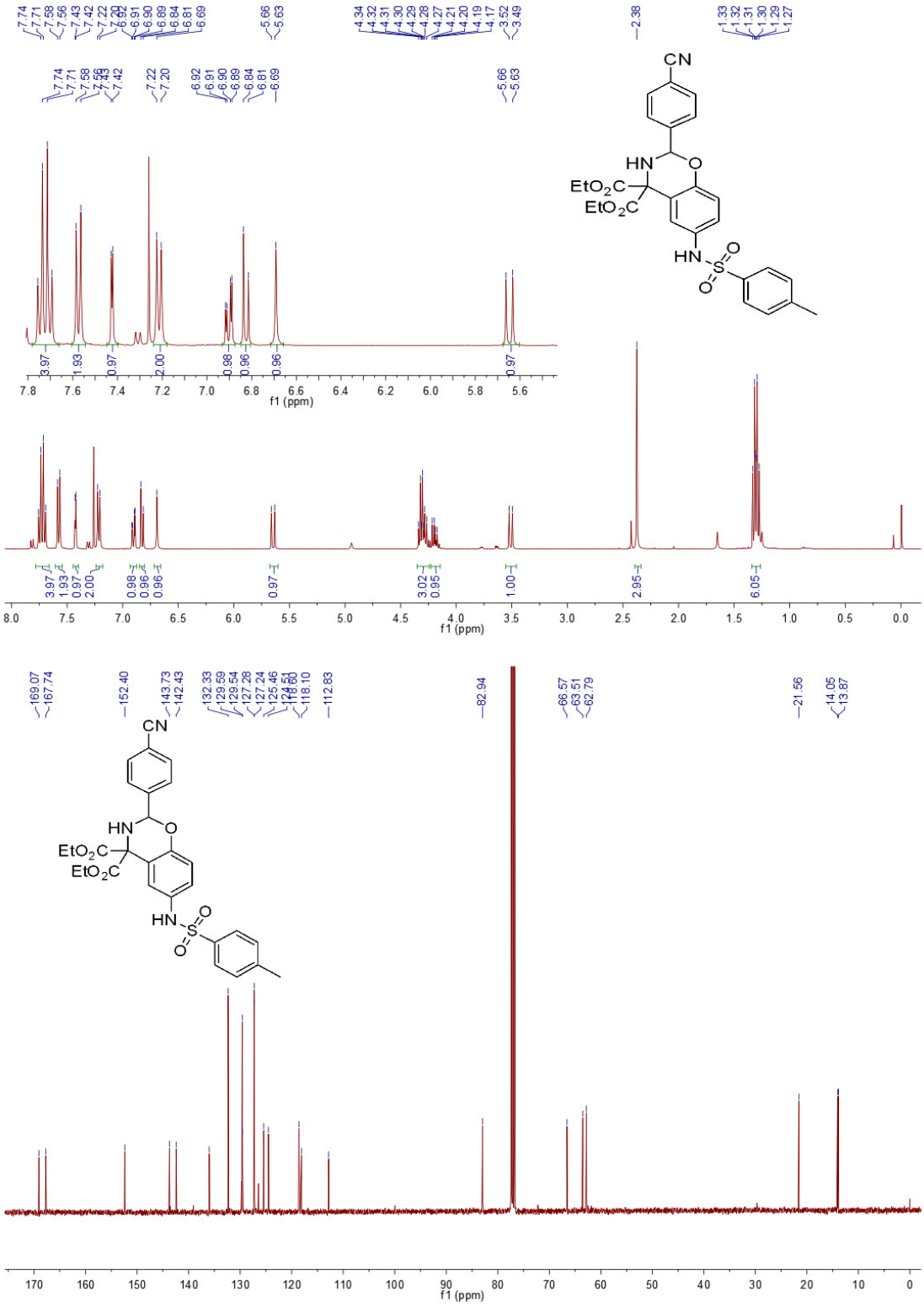

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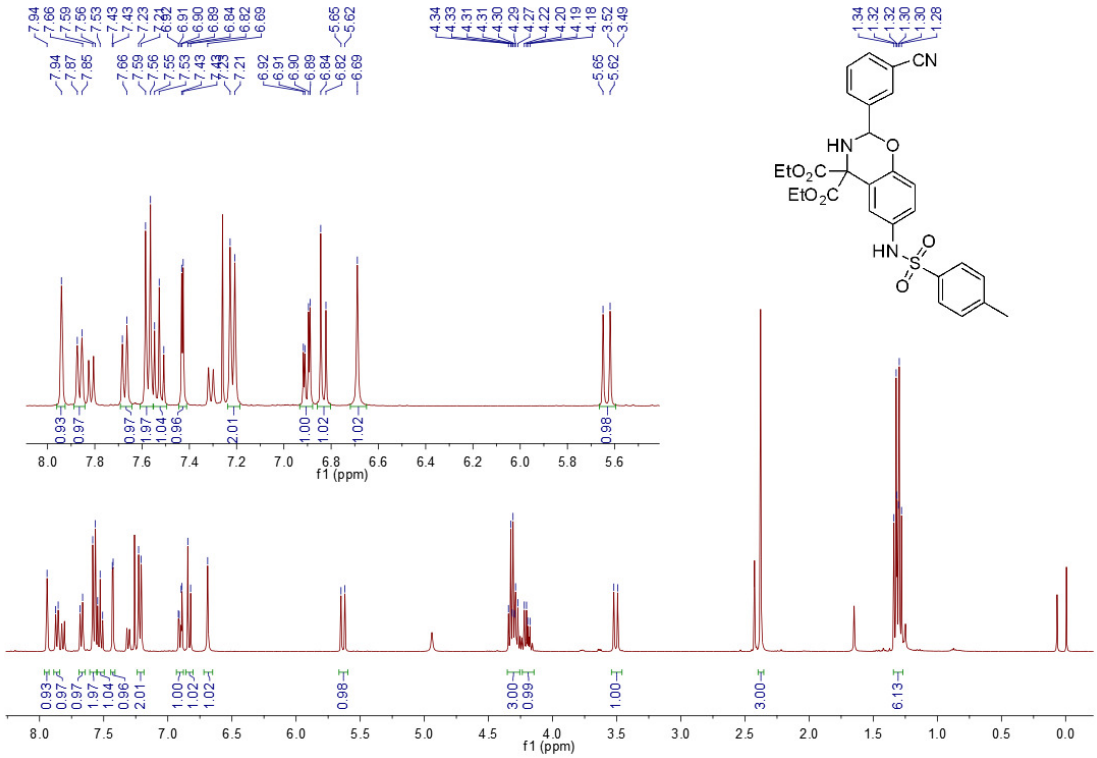
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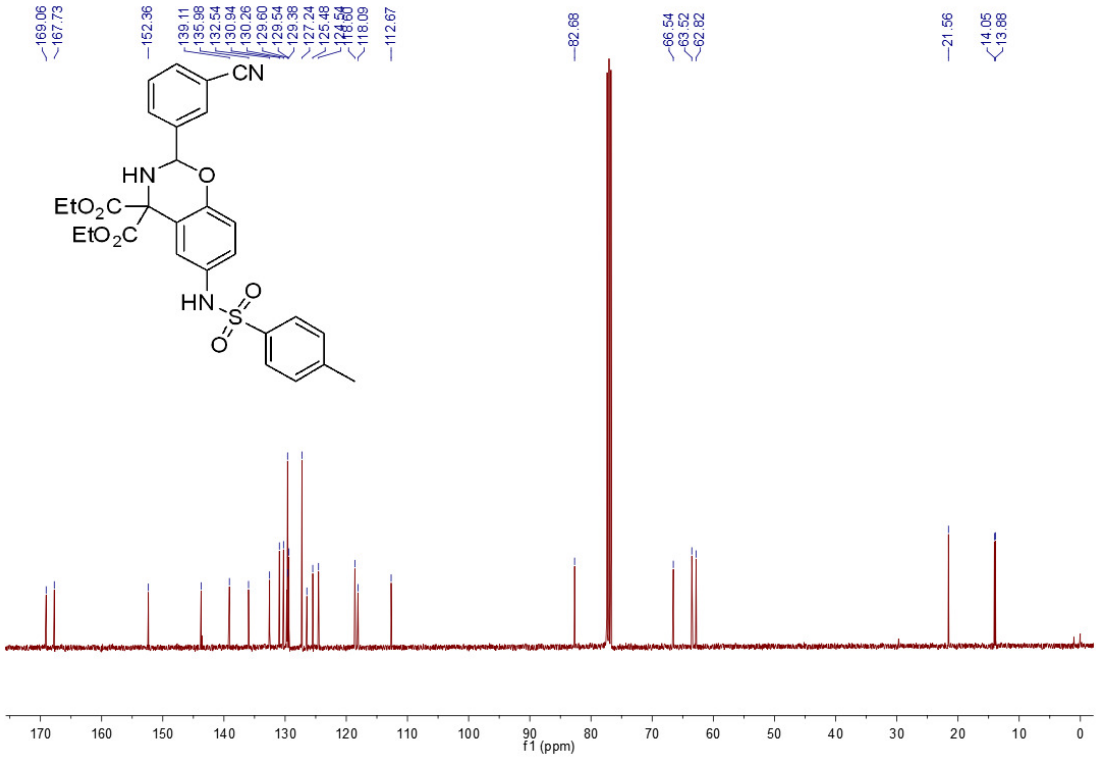
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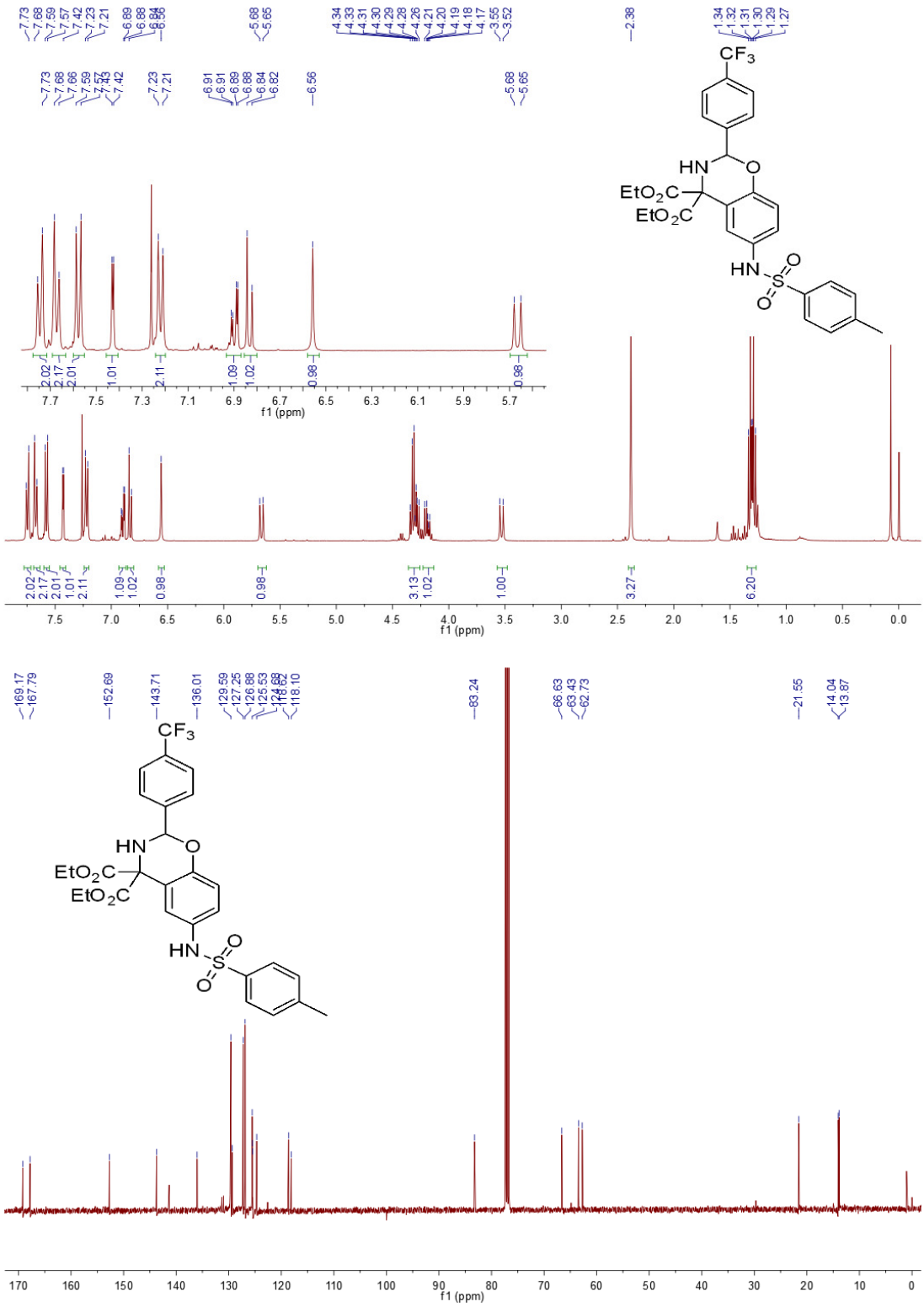
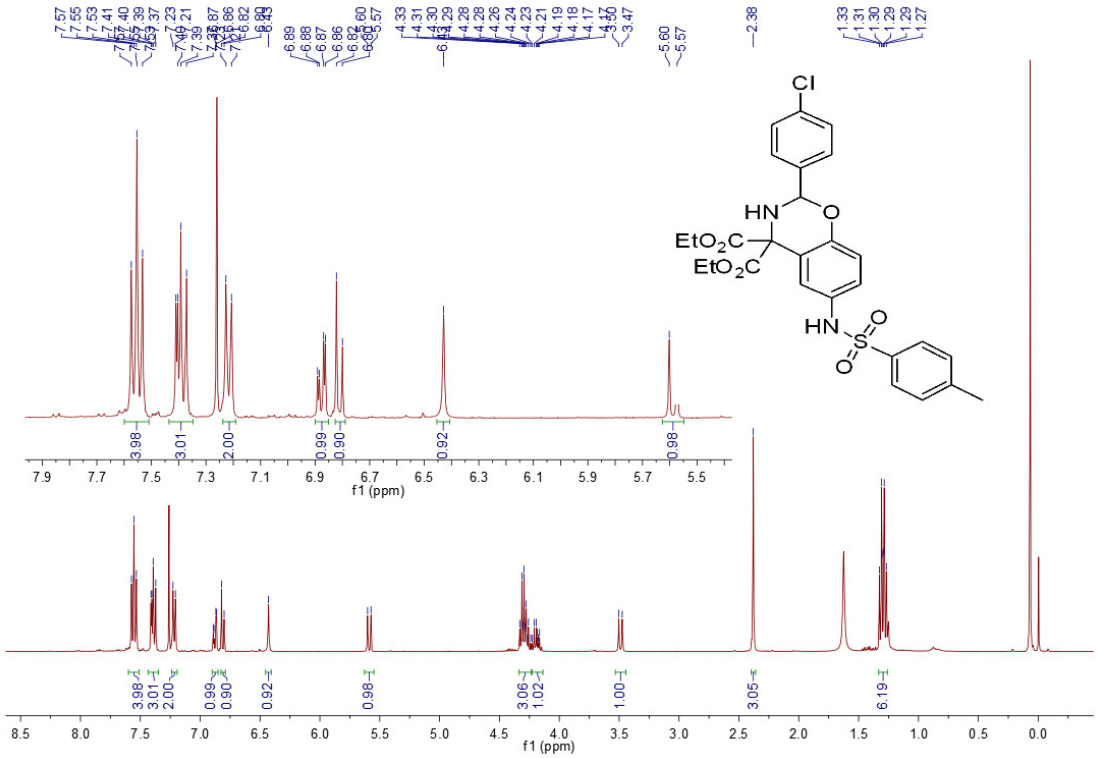
f1 (ppm)

4faa



4gaa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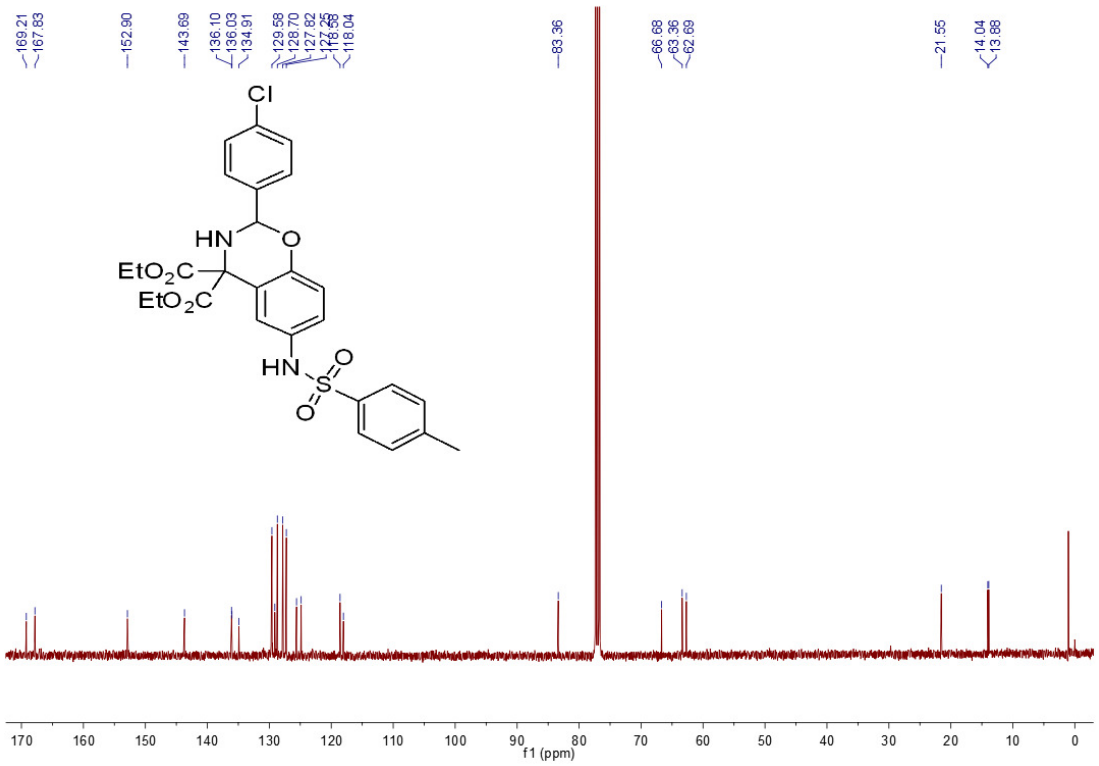
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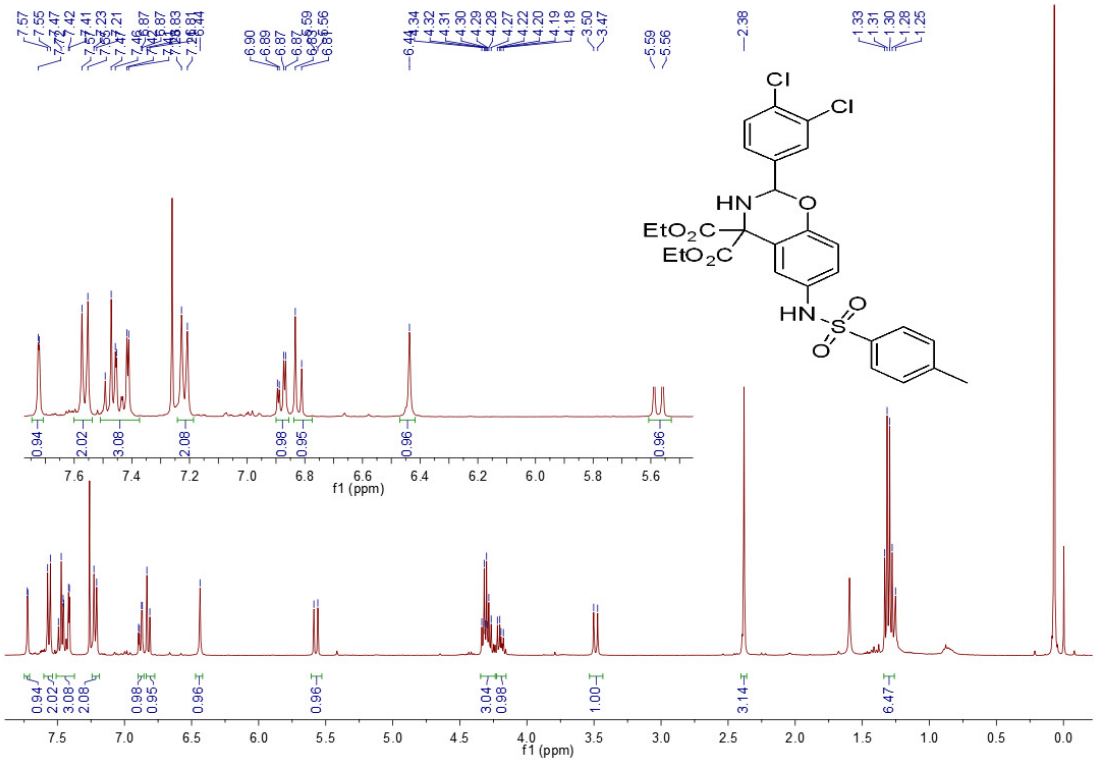
O
EtO2C
EtO2C
HN
O=S=O
f1 (ppm)

4haa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Cl
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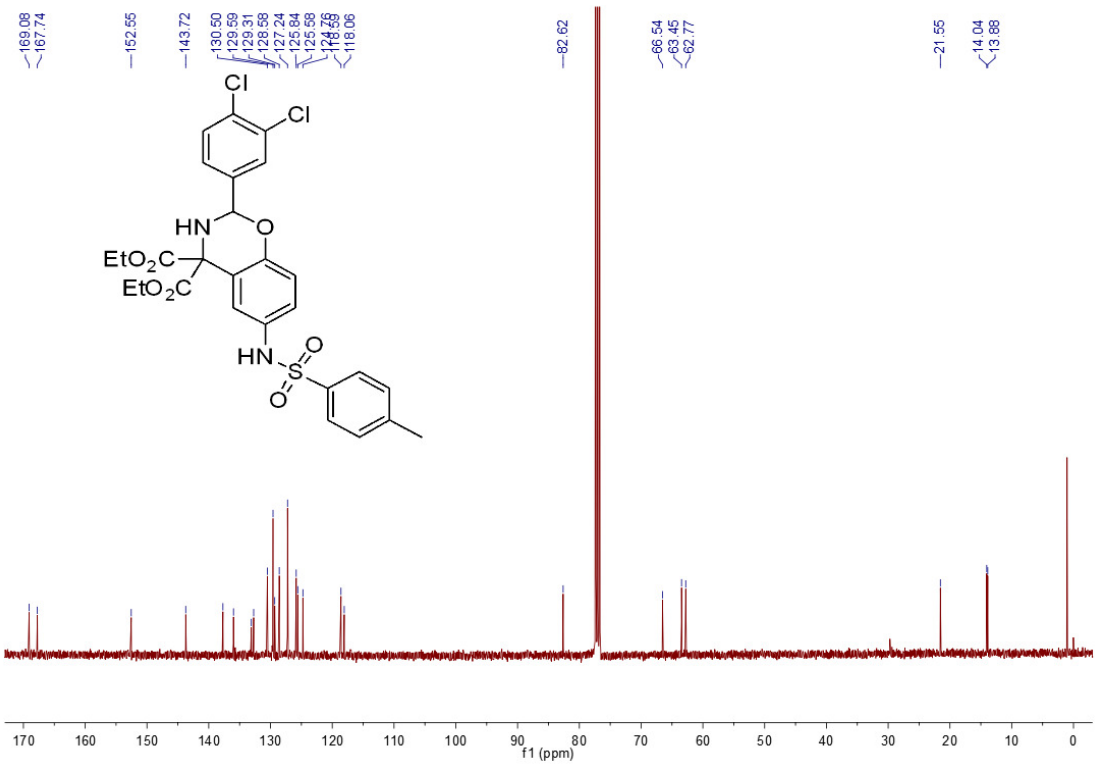
O
EtO2C
EtO2C
HN
S
O
O
f1 (ppm)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EtO2C
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HN
S
O
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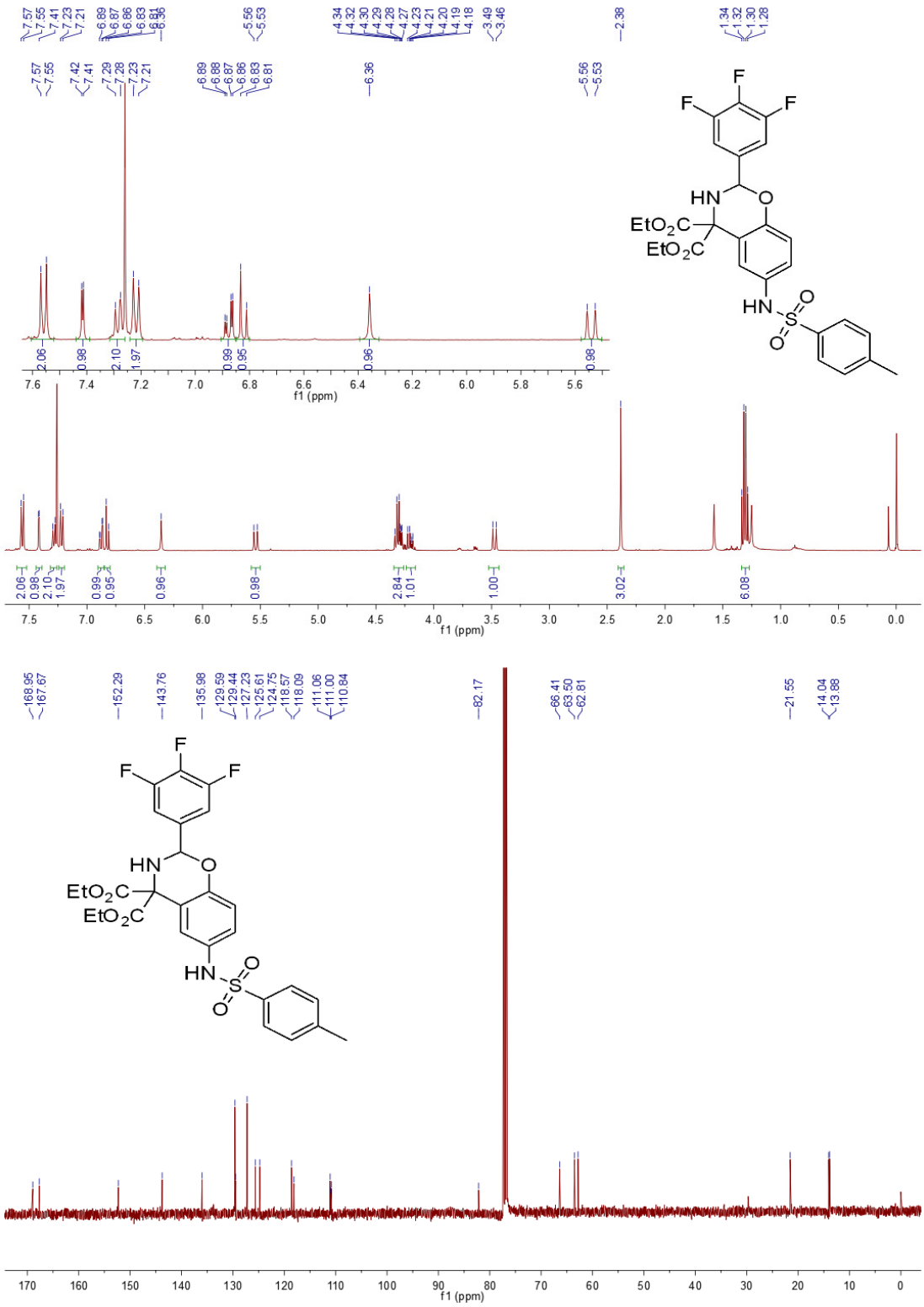
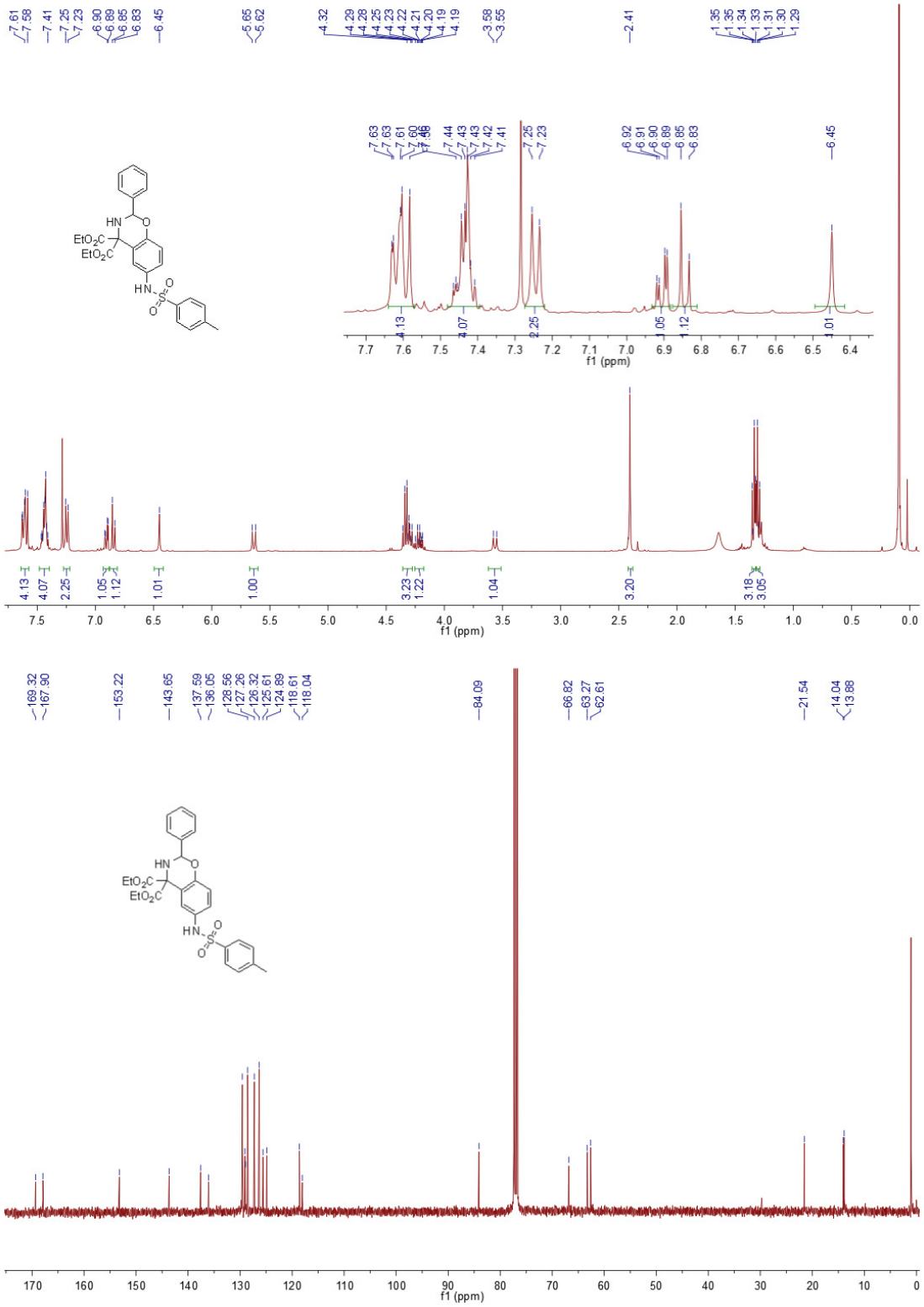
f1 (ppm)

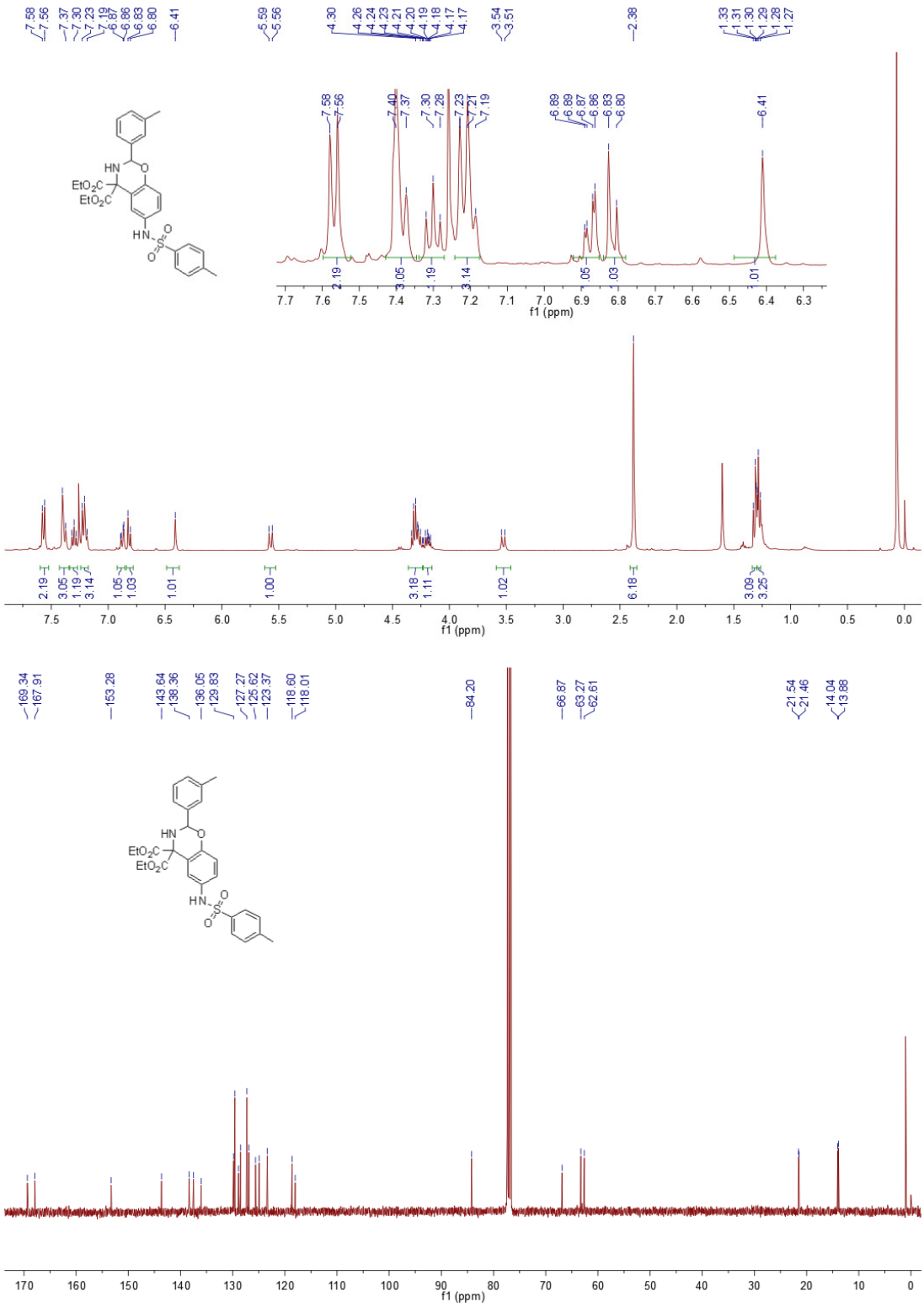
4iaa



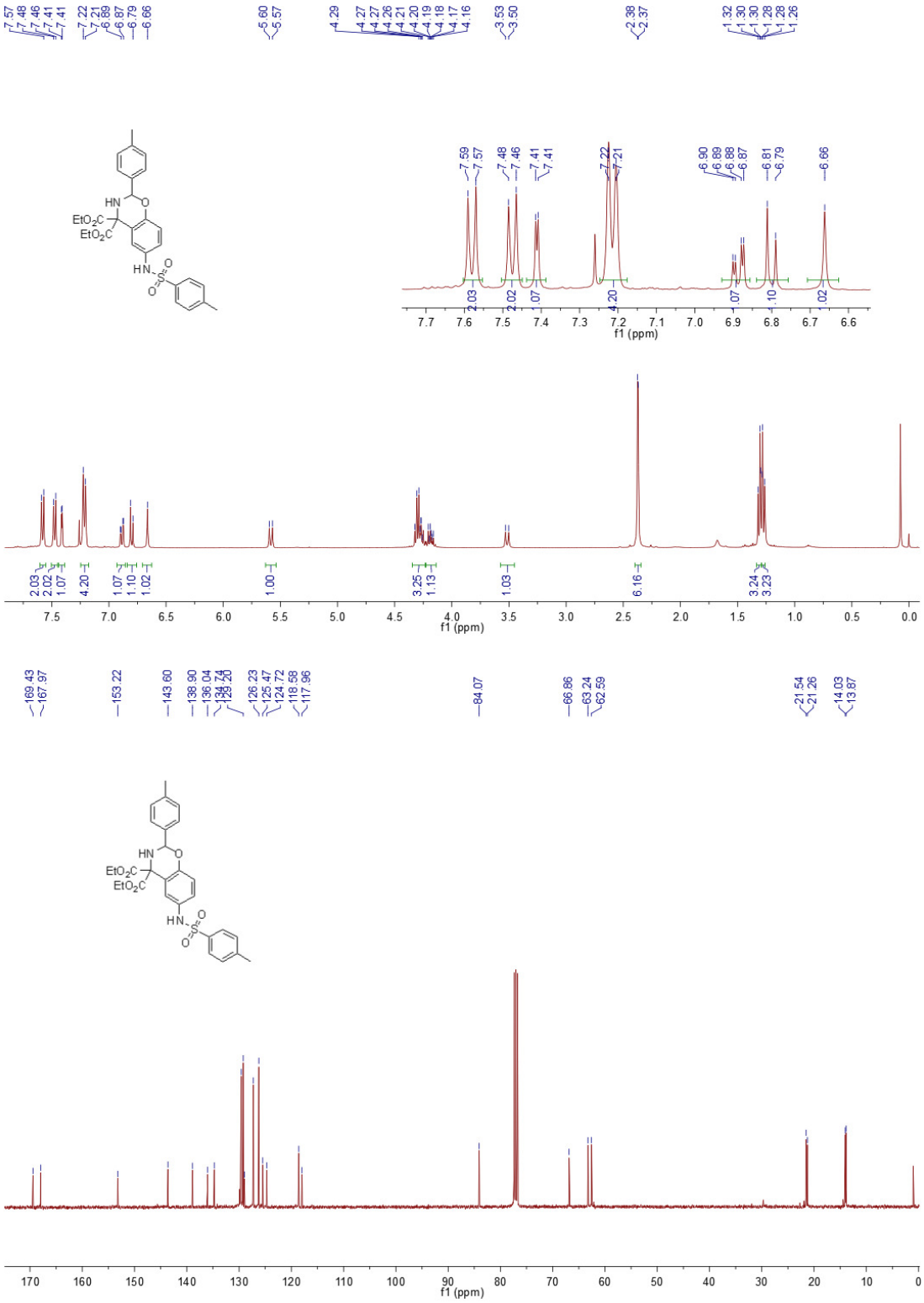
4jaa



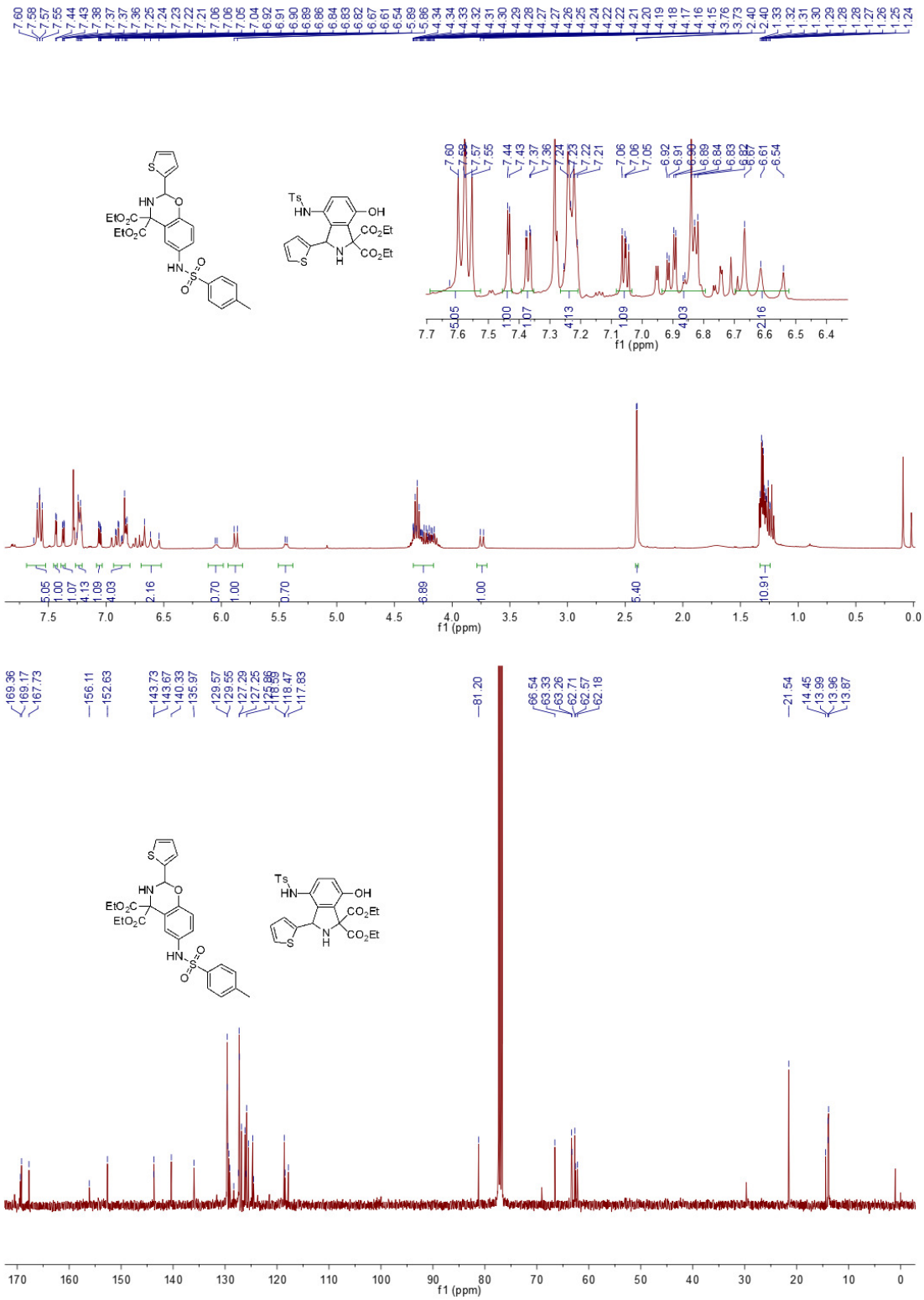
4kaa


7.58
7.56
7.37
7.30
7.23
7.19
6.87
6.86
6.83
6.80
6.41
5.59
5.56
4.30
4.26
4.24
4.23
4.21
4.20
4.19
4.18
4.17
4.17
3.54
3.51
2.38
1.33
1.31
1.30
1.29
1.28
1.27
HN
EtO2C
EtO2C
HN
O
S
O
2.19
3.05
1.19
3.14
1.05
1.03
1.01
1.00
3.18
1.11
1.02
6.18
3.09
3.25
f1 (ppm)
169.34
167.91
153.28
143.64
138.36
136.05
129.83
127.27
125.62
123.37
118.60
118.01
84.20
66.87
63.27
62.61
21.54
21.46
14.04
13.88

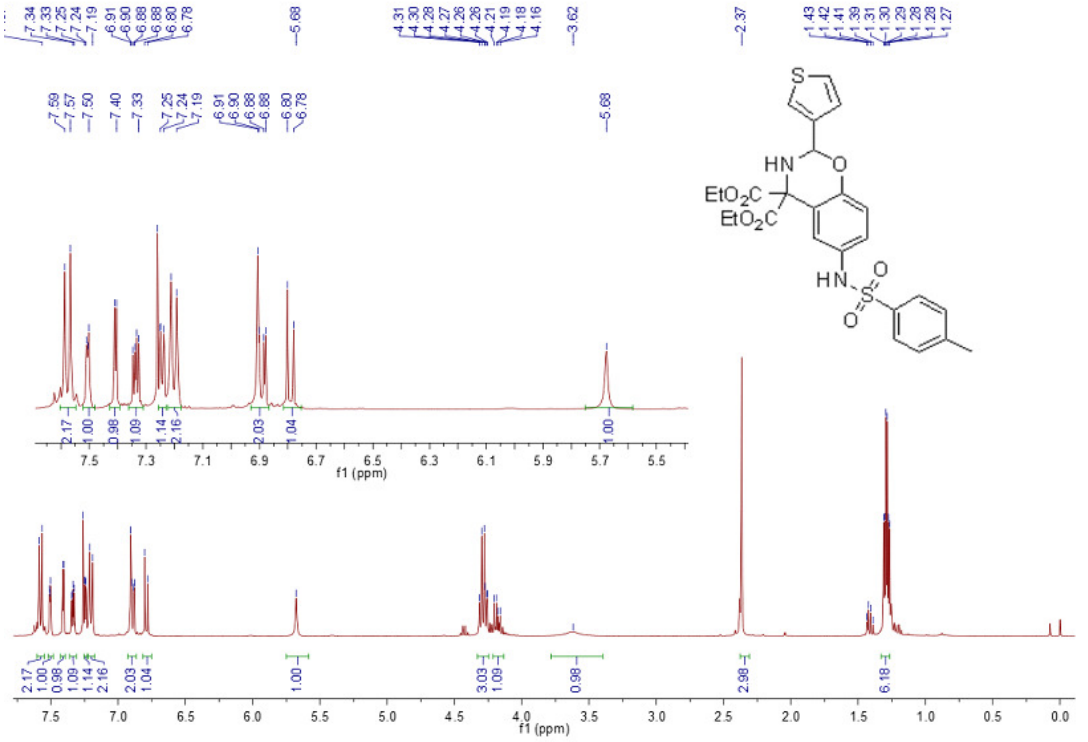
4laa

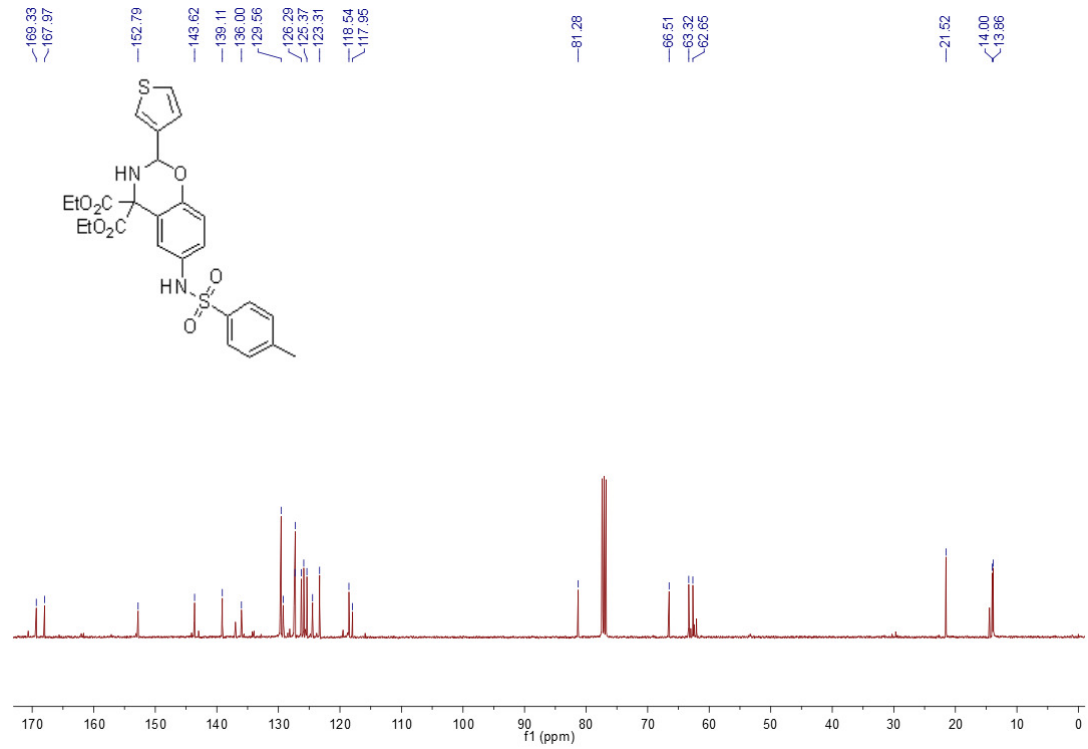


4maa (inseparable chemoselective isomers)

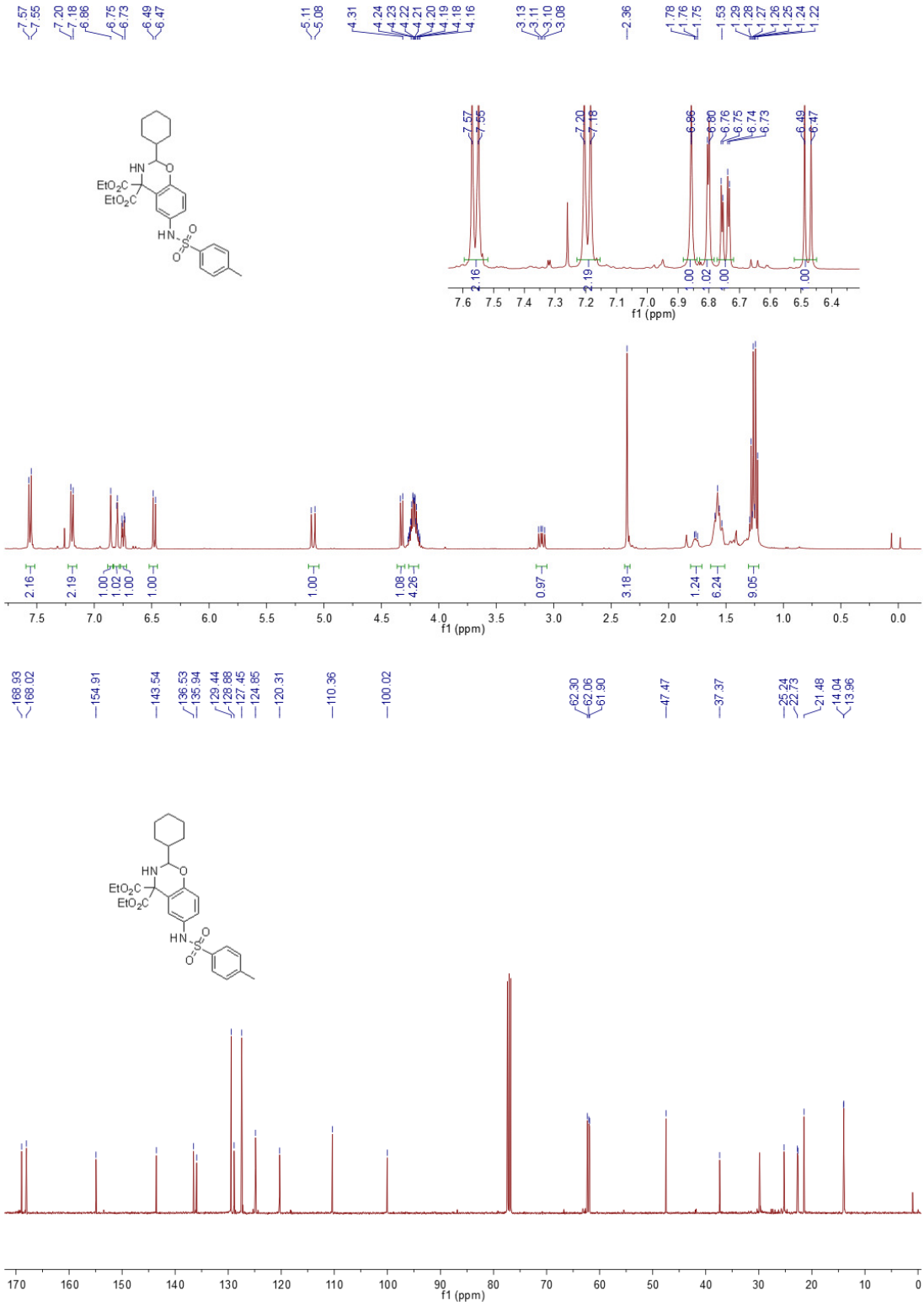


4naa

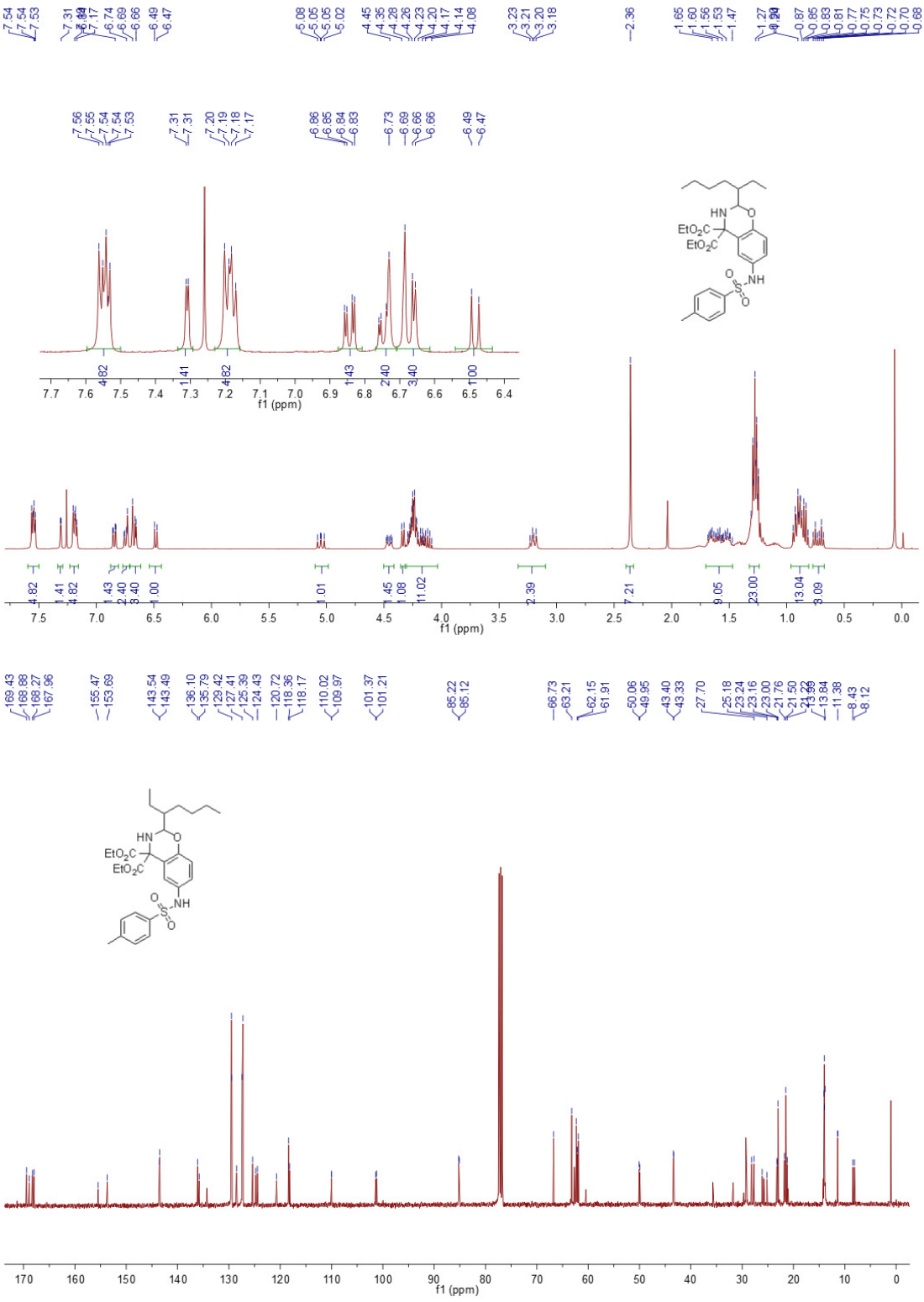




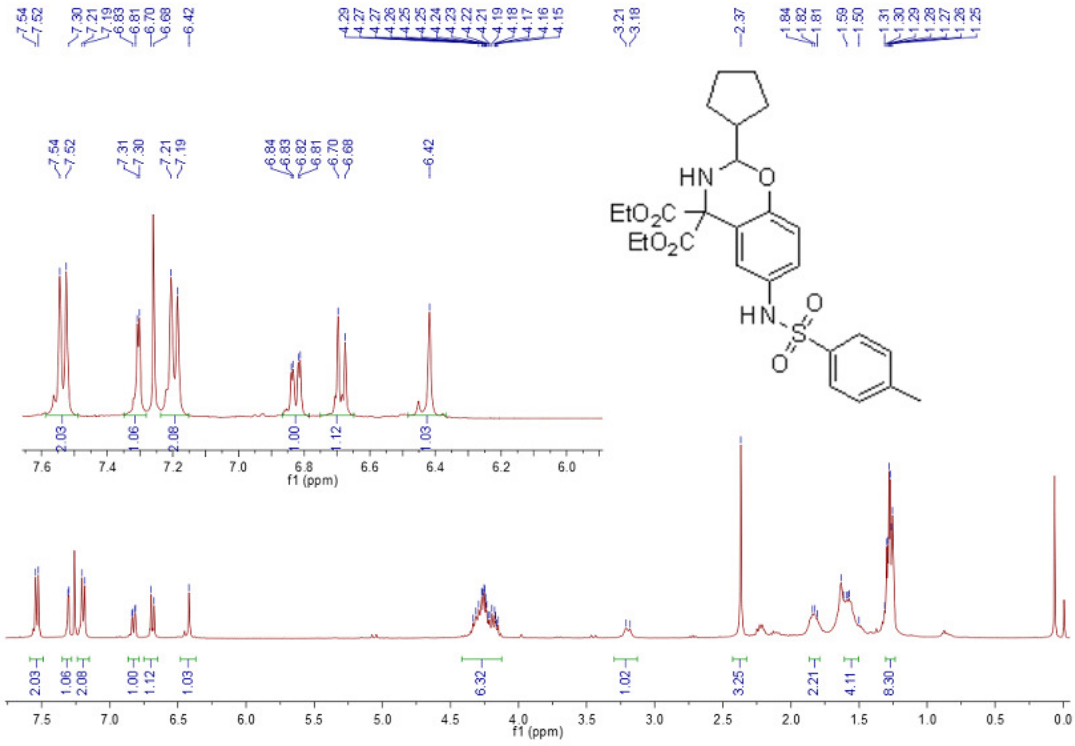
4oaa

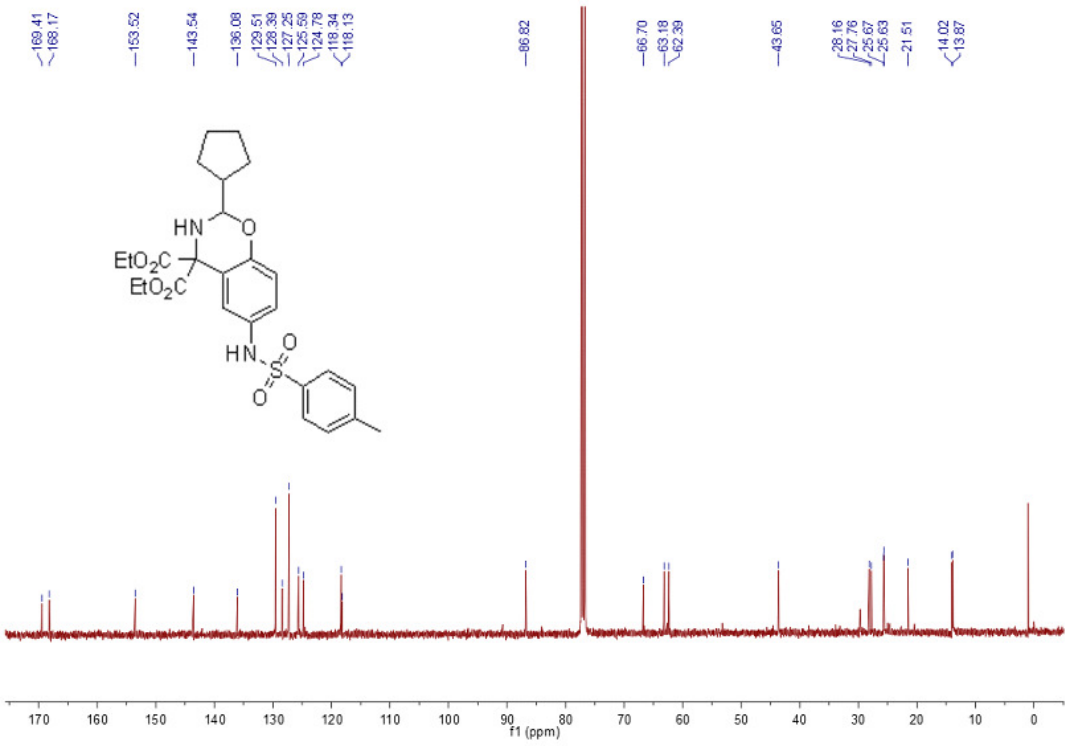


4paa (inseparable chemoselective isomers)

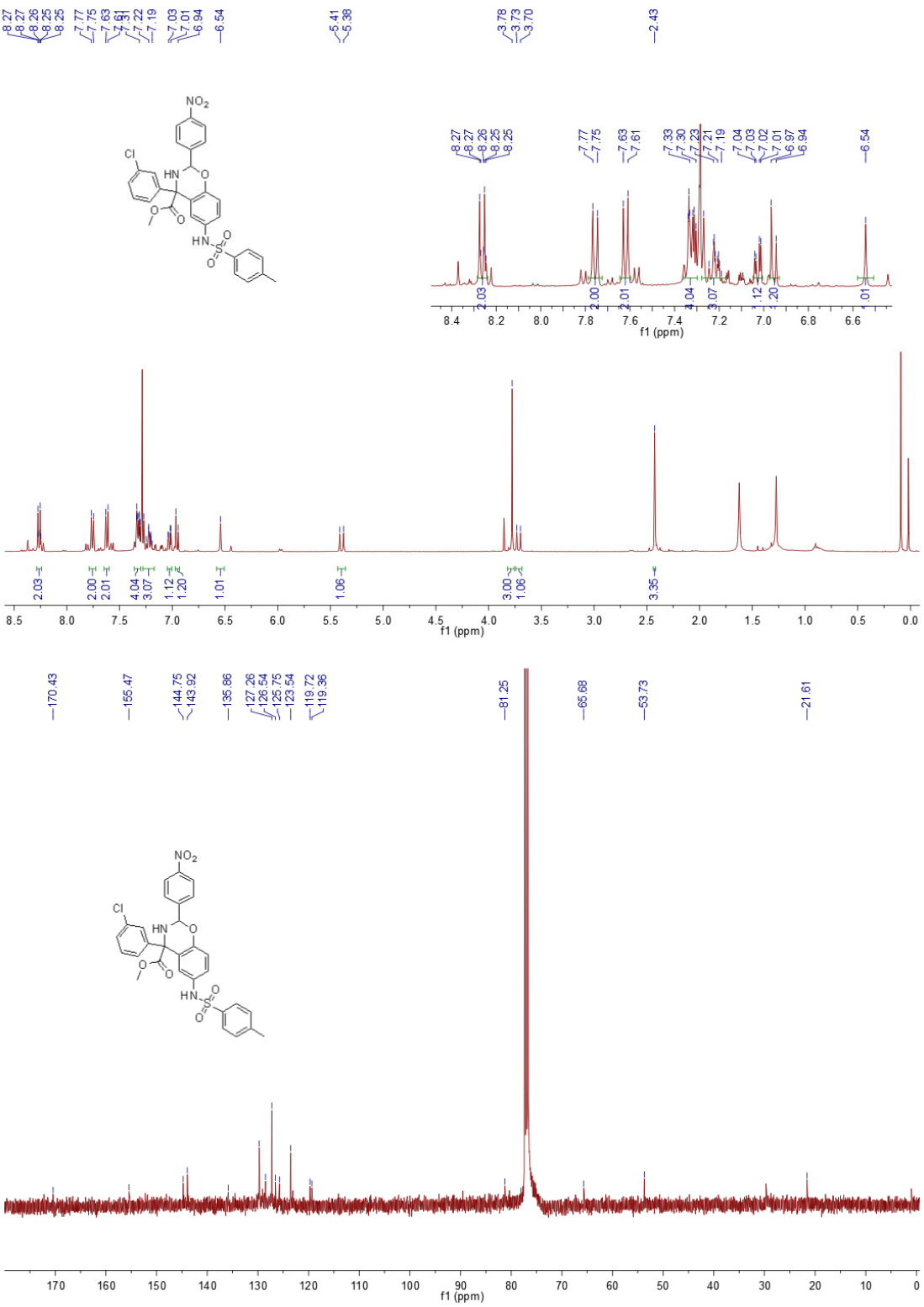


4qaa

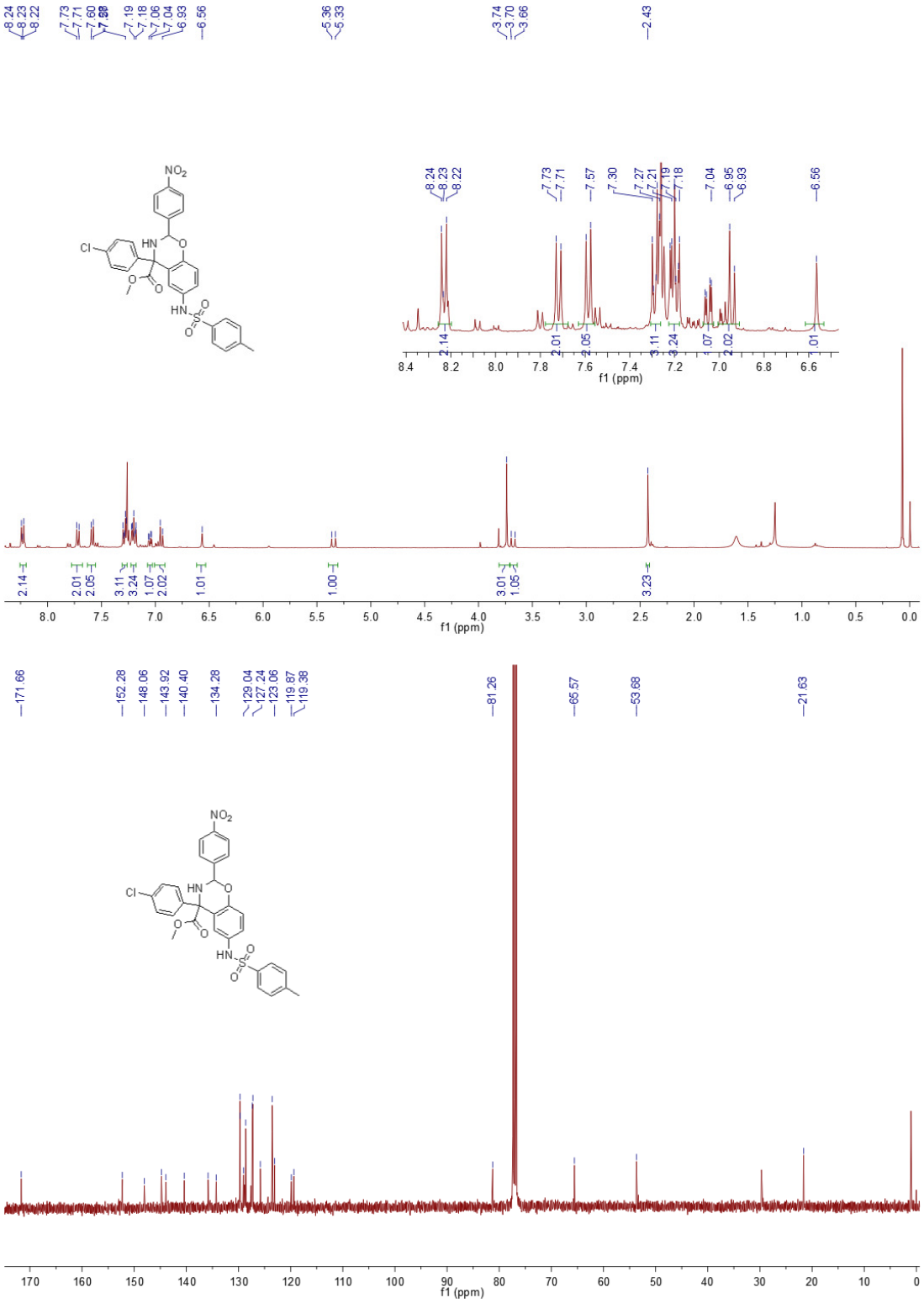




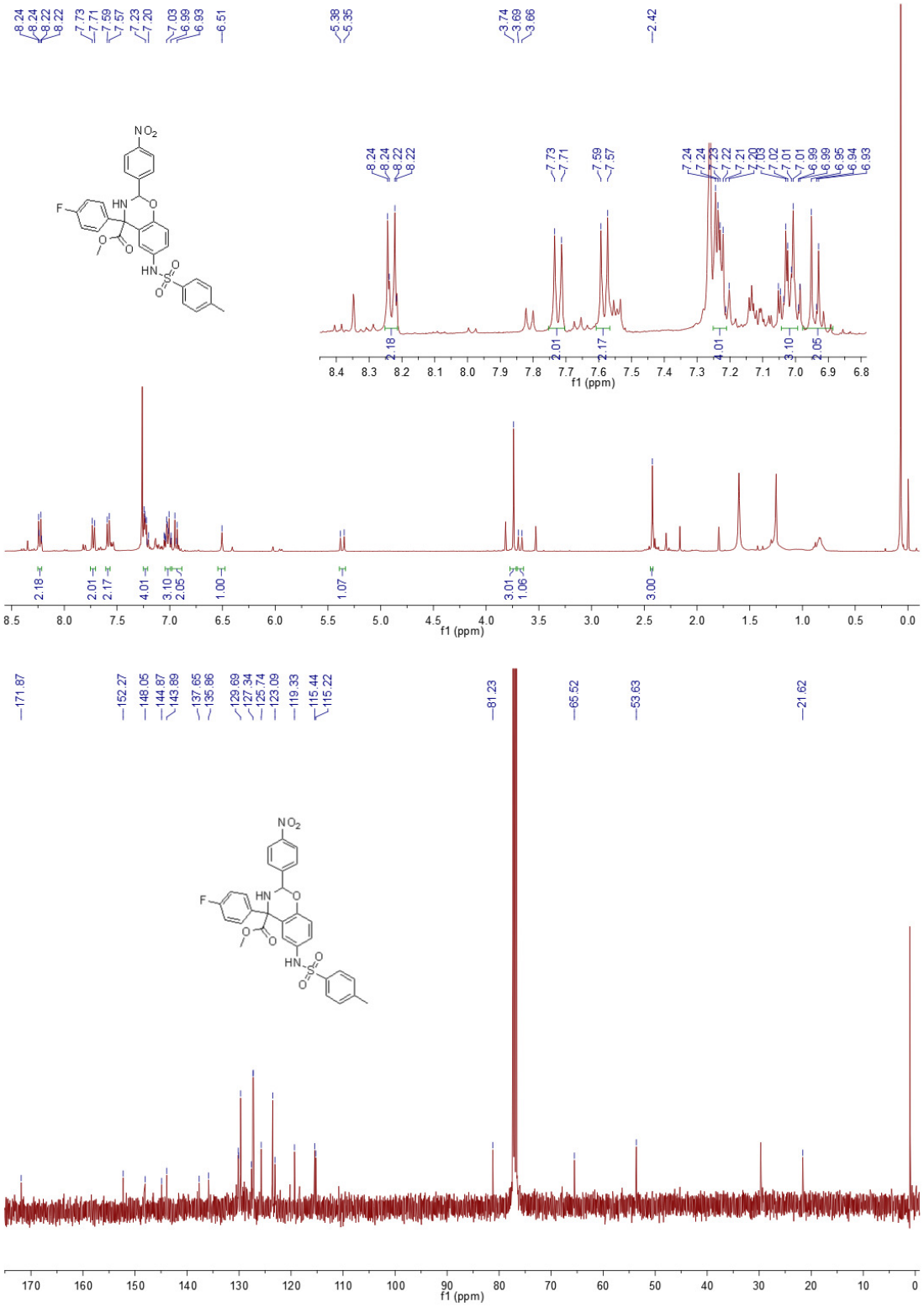
4aba (inseparable diastereomers)



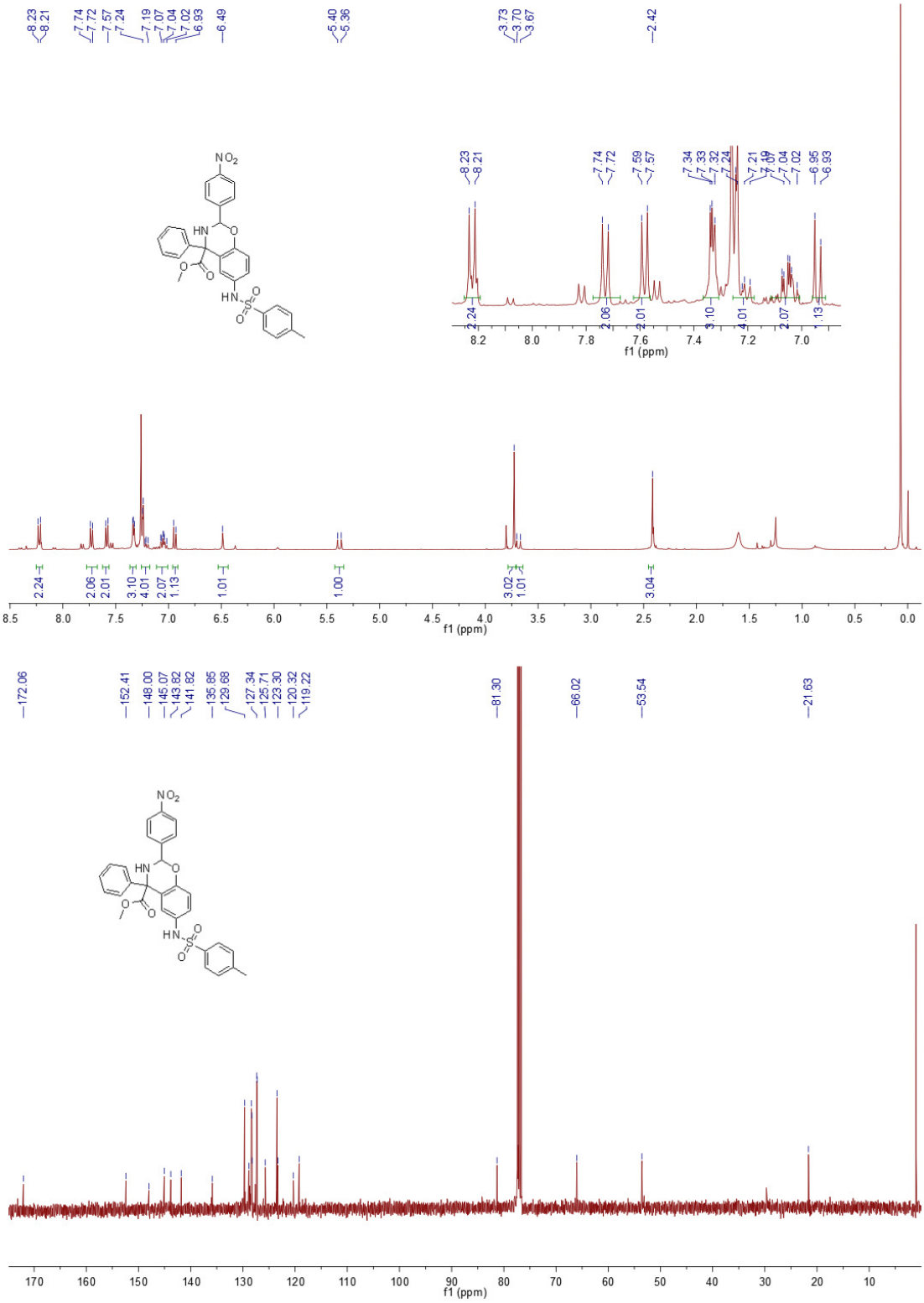
4aca (inseparable diastereomers)



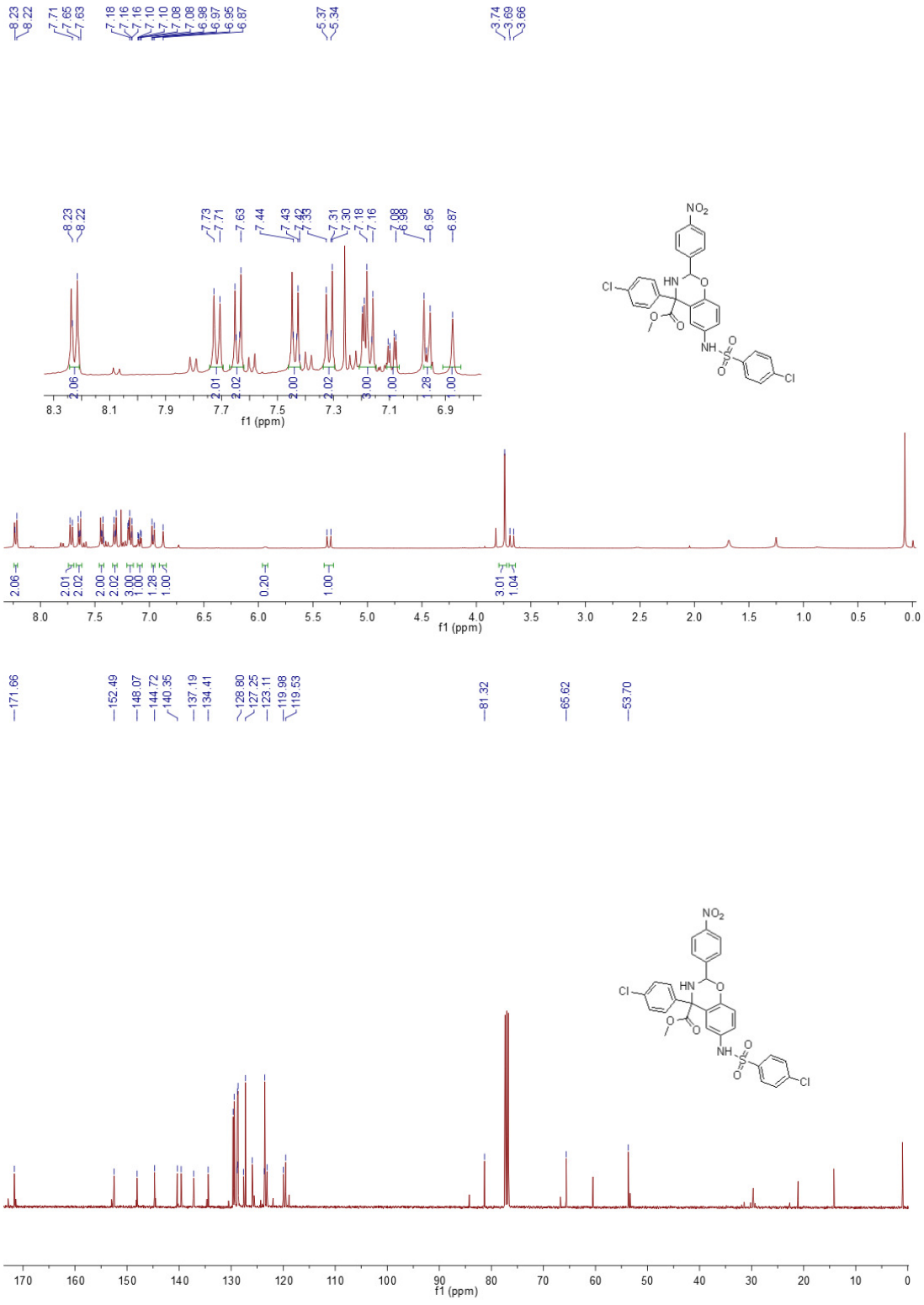
4ada (inseparable diastereomers)



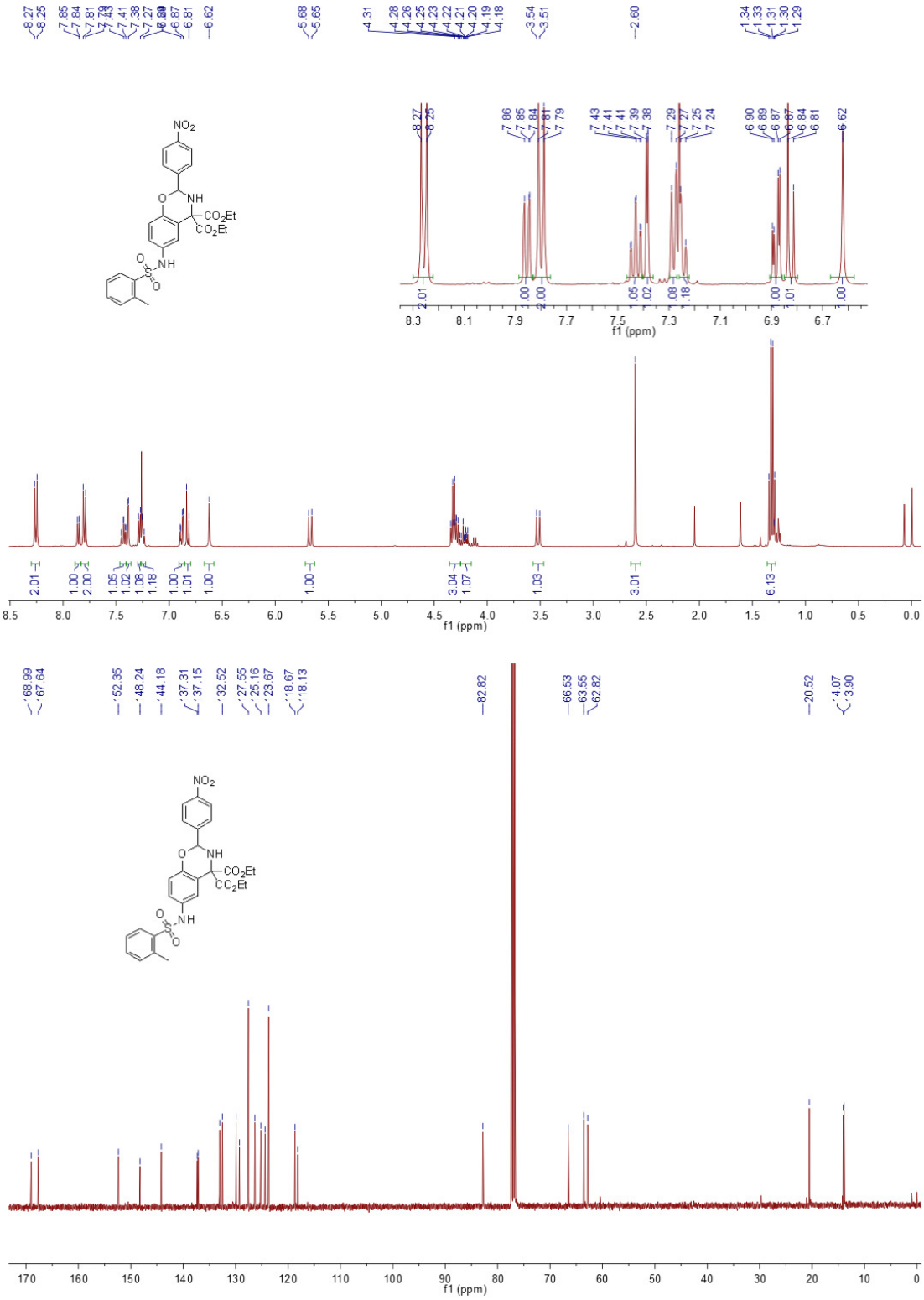
4aea (inseparable diastereomers)



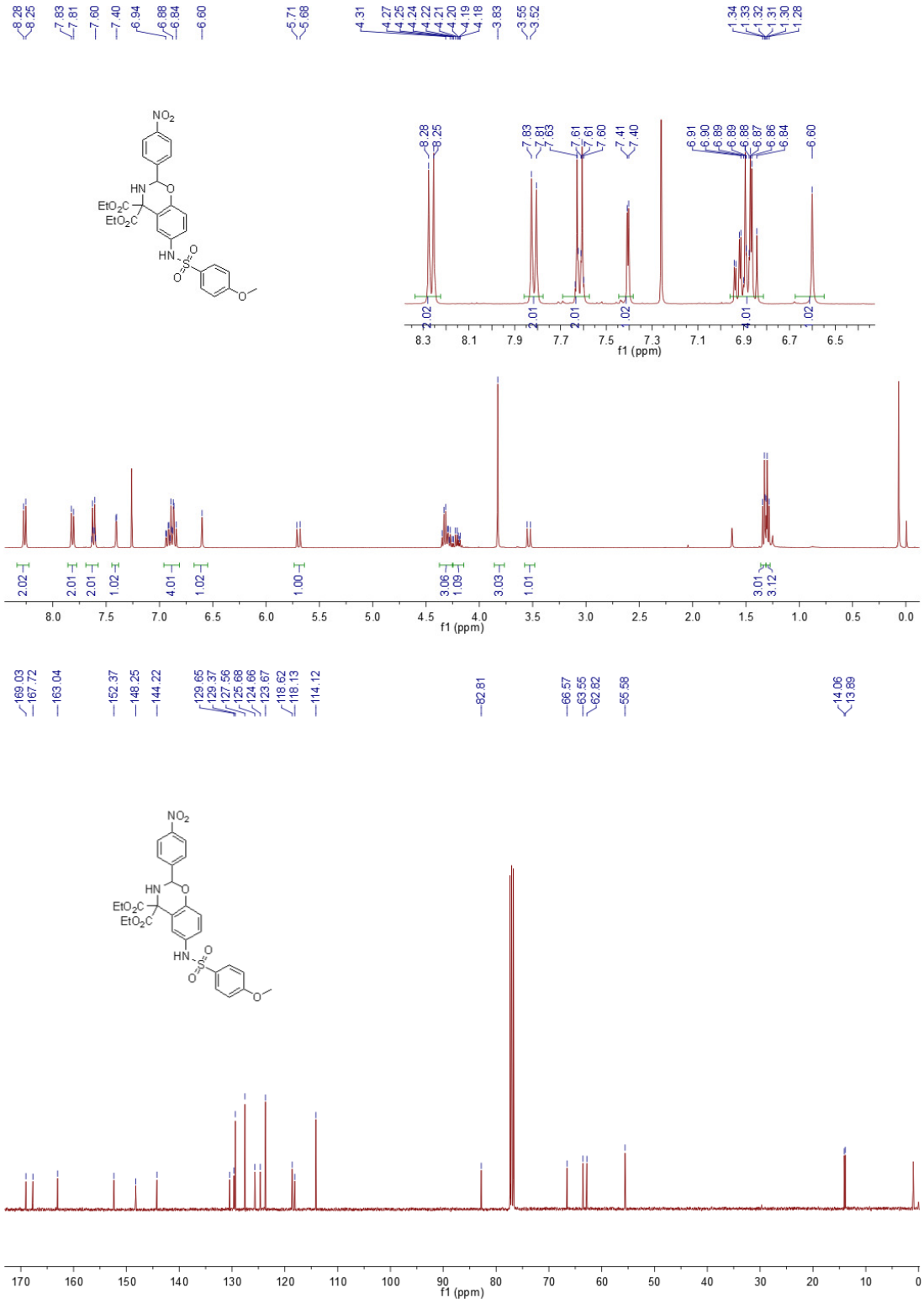
4acf (the mixture of two diastereomers)



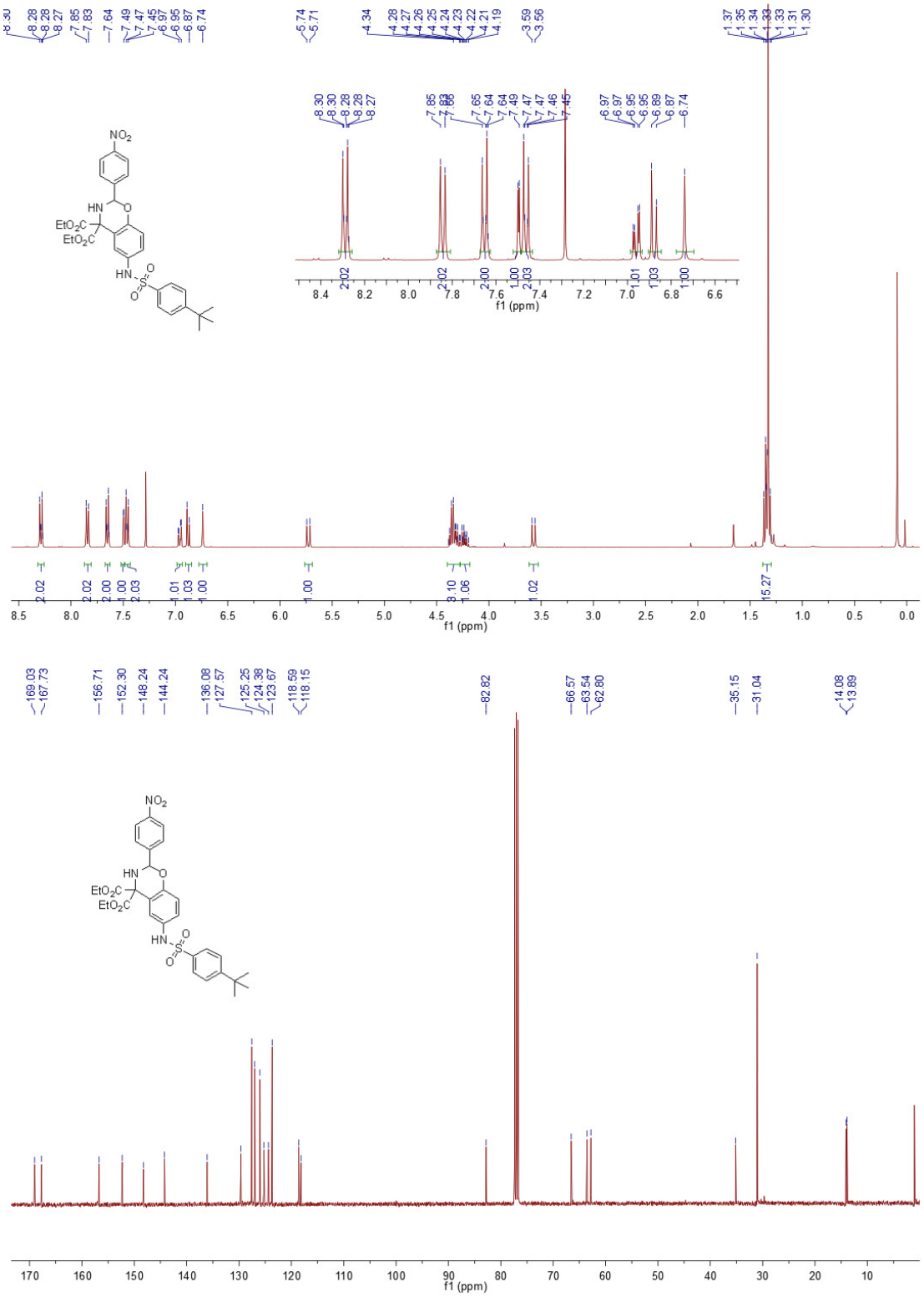
4aab



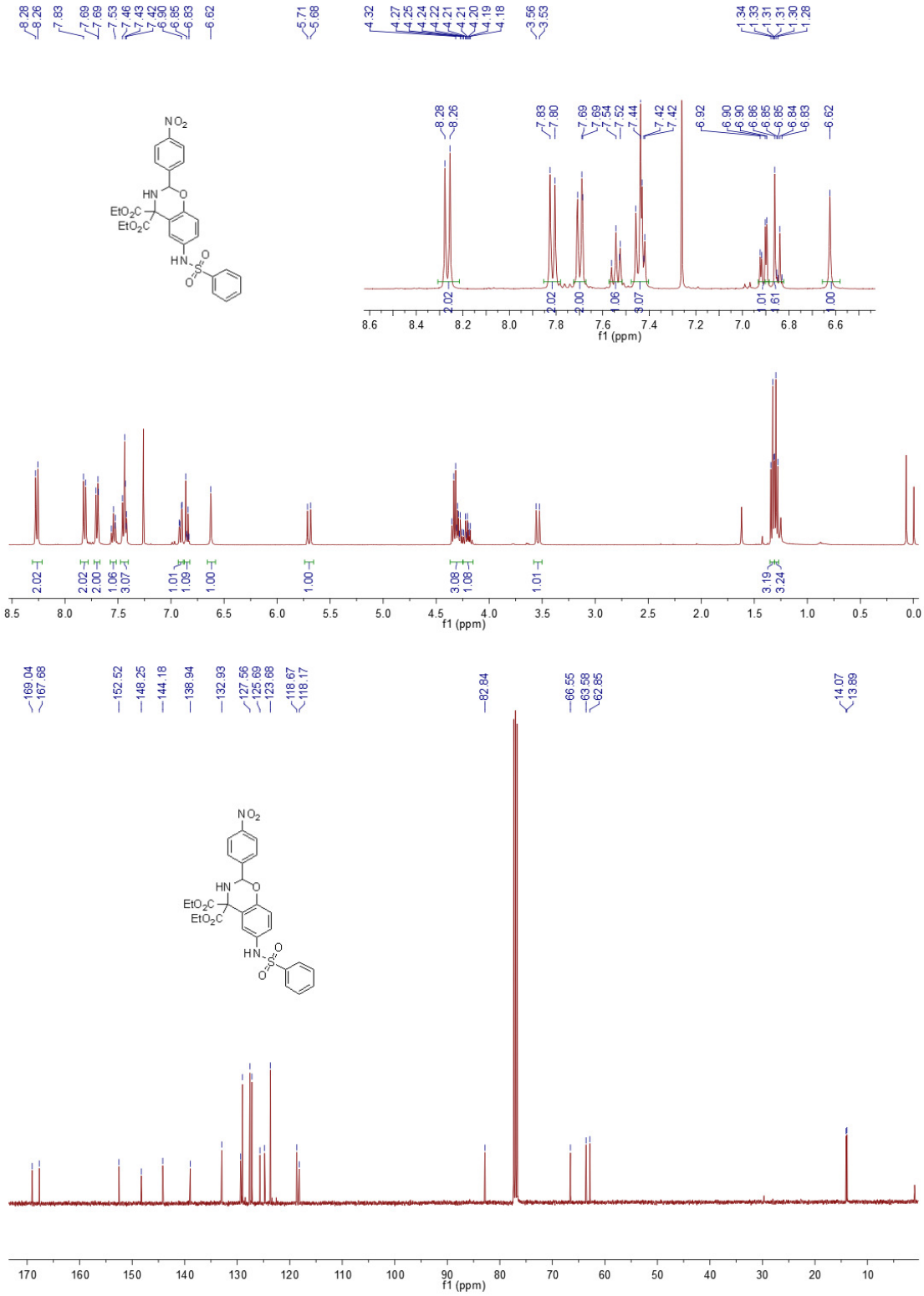
4aac


8.28
8.25
7.83
7.81
7.60
7.40
6.94
6.88
6.84
6.60
5.71
5.68
4.31
4.27
4.25
4.24
4.22
4.21
4.20
4.19
4.18
3.83
3.55
3.52
1.34
1.33
1.32
1.31
1.30
1.28
NO2
HN
O
EtO2C
EtO2C
HN
O
S
O
O
f1 (ppm)
f1 (ppm)
169.03
167.72
163.04
152.37
148.25
144.22
129.65
129.37
127.56
125.68
124.66
123.67
118.62
118.13
114.12
82.81
66.57
63.55
62.82
55.58
14.06
13.89
f1 (ppm)

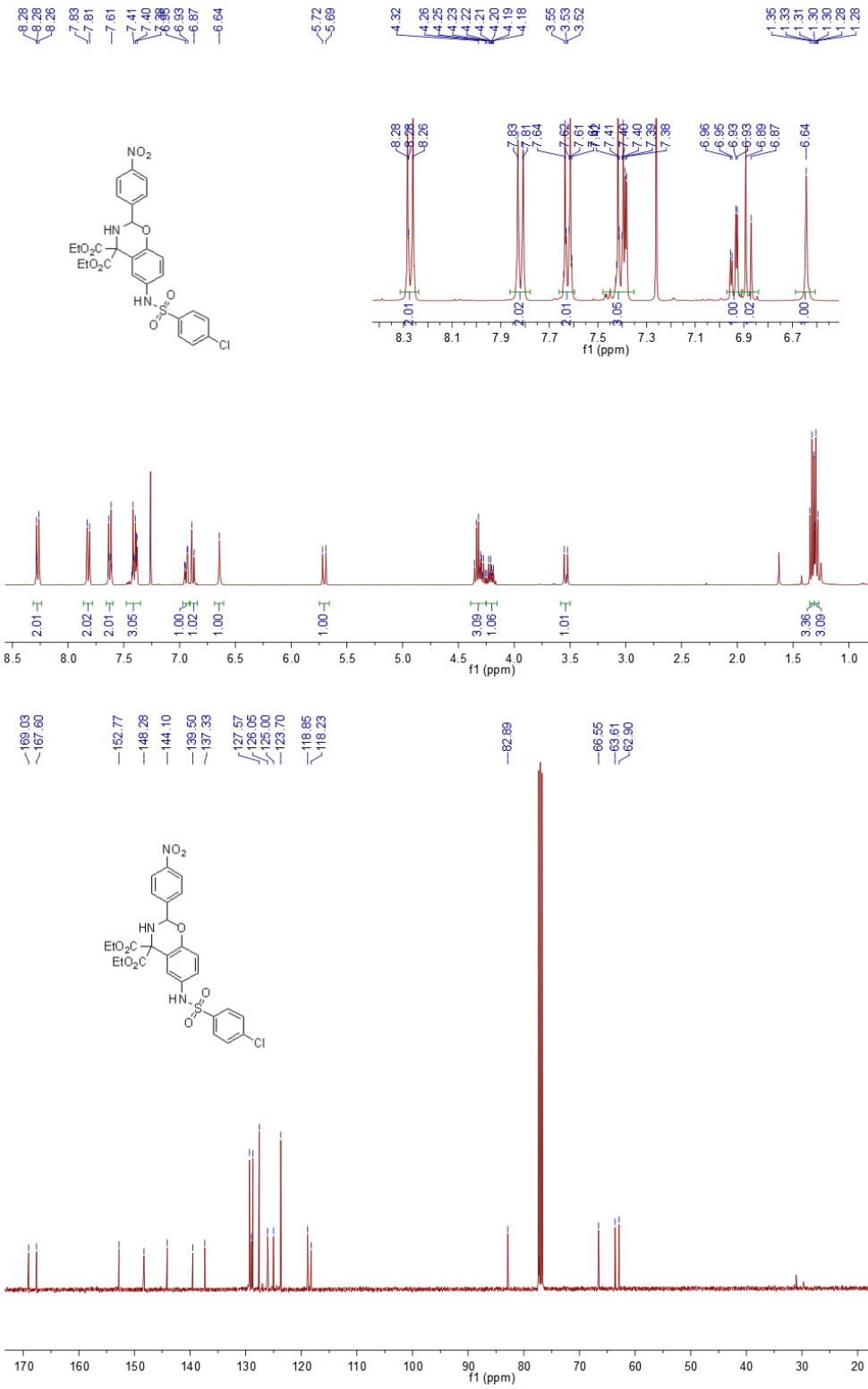
4aad



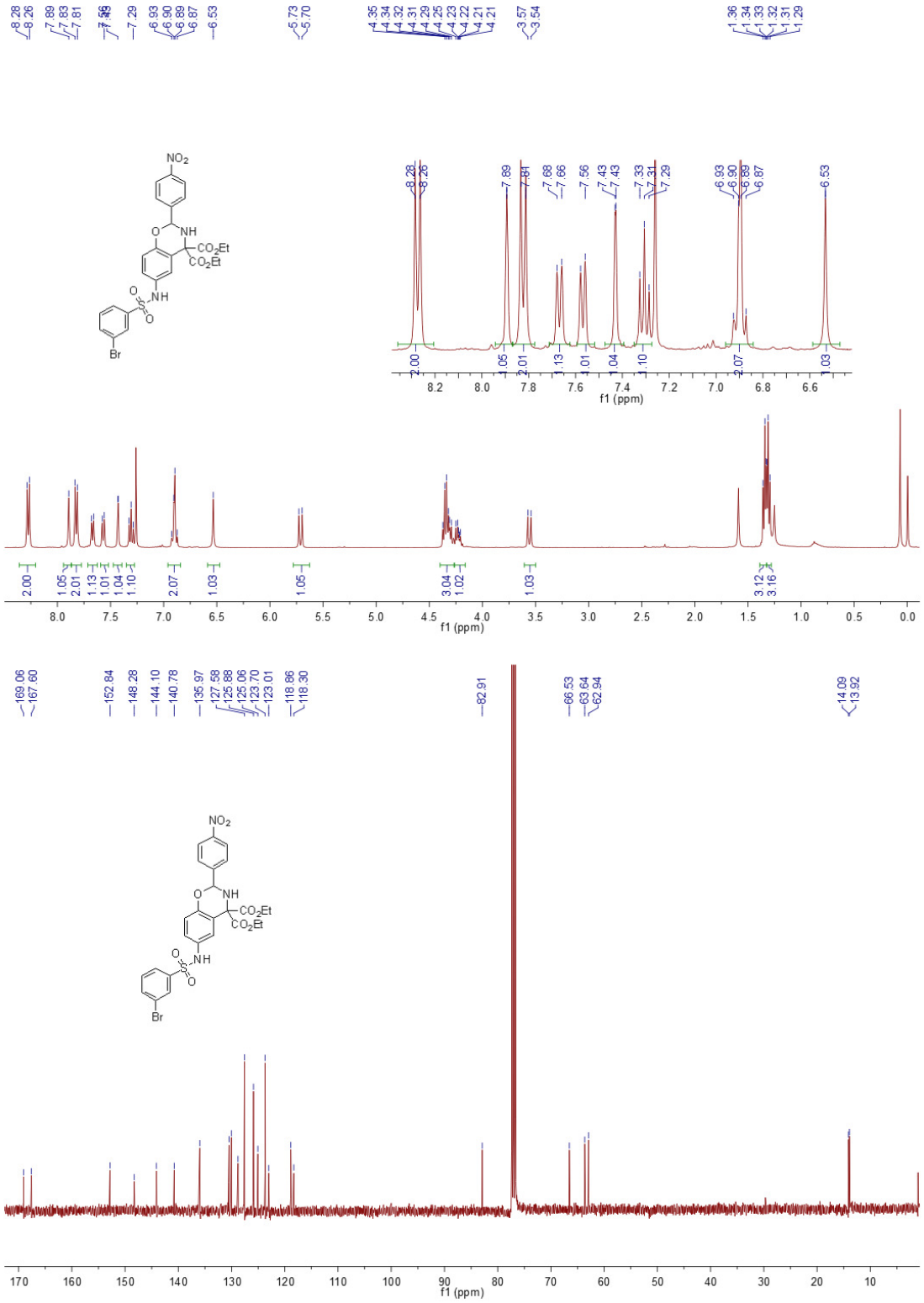
4aae



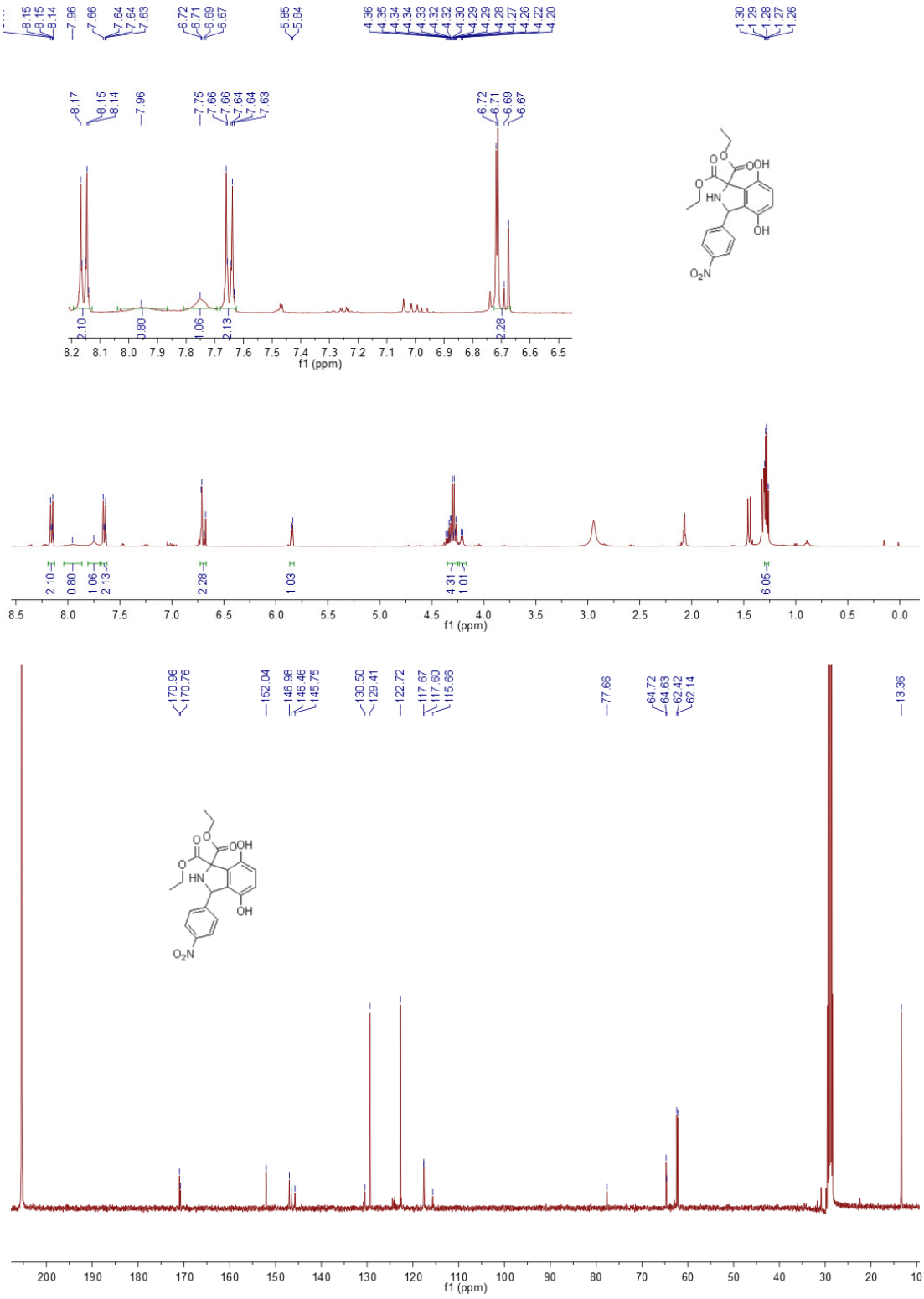
4aaf


8.28
8.28
8.26
7.83
7.81
7.61
7.41
7.40
6.93
6.87
6.64
5.72
5.69
4.32
4.26
4.25
4.23
4.22
4.21
4.20
4.19
4.18
3.55
3.53
3.52
1.35
1.33
1.31
1.30
1.30
1.28
1.28
NO2
HN
O
EtO2C
EtO2C
HN
S
O
O
Cl
f1 (ppm)
f1 (ppm)
169.03
167.60
152.77
148.28
144.10
139.50
137.33
127.57
126.05
125.00
123.70
118.85
118.23
82.89
66.55
63.61
62.90
14.06
13.88
f1 (ppm)

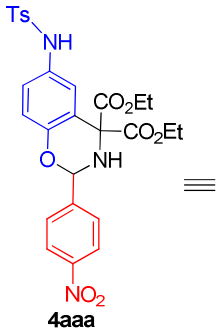
4aag



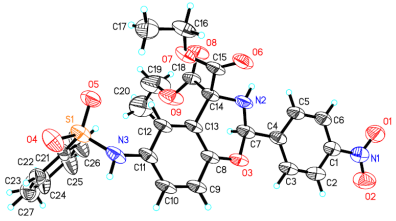
Compound 8


8.15
8.15
8.14
7.96
7.66
7.64
7.64
7.63
6.72
6.71
6.69
6.67
5.85
5.84
4.36
4.35
4.34
4.34
4.33
4.32
4.32
4.30
4.29
4.29
4.28
4.27
4.26
4.22
4.20
1.30
1.29
1.28
1.27
1.26
8.17
8.15
8.14
7.96
7.75
7.66
7.66
7.64
7.64
7.63
6.72
6.71
6.69
6.67
2.10
0.80
1.06
2.13
2.28
f1 (ppm)
OH
HN
OH
O2N
2.10
0.80
1.06
2.13
2.28
1.03
4.31
1.01
6.05
f1 (ppm)
170.96
170.76
152.04
146.98
146.46
145.75
130.50
129.41
122.72
117.67
117.60
115.66
77.66
64.72
64.63
62.42
62.14
13.36
f1 (ppm)

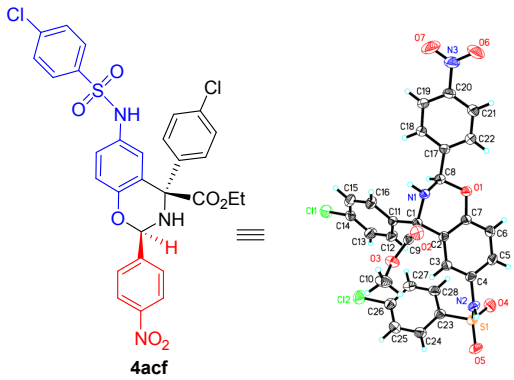
6. X-ray single crystal data for compound 4aaa and 4acf



4aaa

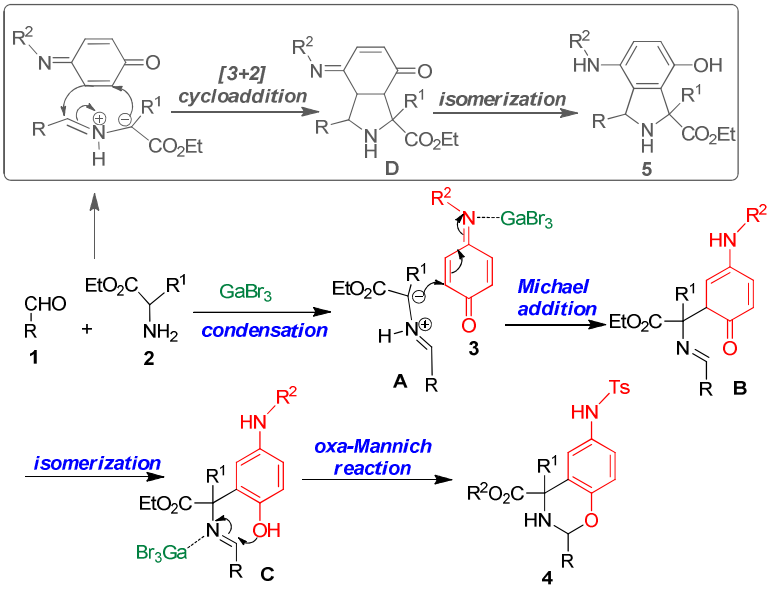


Empirical formula	C27 H27 N3 O9 S	
Formula weight	569.57	
Temperature	296 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.3006(6) Å	α= 86.352(4)°.
	b = 9.3862(7) Å	β= 87.532(4)°.
	c = 17.7170(15) Å	γ = 77.772(4)°.
Volume	1345.68(18) $Å^3$	
Z	2	
Density (calculated)	1.406 Mg/m^3	
Absorption coefficient	0.180 mm^{-1}	
F(000)	596	
Crystal size	0.39 x 0.32 x 0.3 mm^3	
Theta range for data collection	2.224 to 25.929°.	
Index ranges	-10<=h<=10, -11<=k<=11, -21<=l<=21	
Reflections collected	20031	
Independent reflections	5190 [R(int) = 0.0272]	
Completeness to theta = 26.000°	98.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.1631	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5190 / 0 / 405	
Goodness-of-fit on F^2	1.066	
Final R indices [I>2sigma(I)]	R1 = 0.0693, wR2 = 0.2010	
R indices (all data)	R1 = 0.0938, wR2 = 0.2277	
Extinction coefficient	0.004(2)	
Largest diff. peak and hole	0.577 and -0.402 e.$Å^{-3}$	



Empirical formula	C28 H21 Cl2 N3 O7 S	
Formula weight	614.44	
Temperature	173.1500 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.4575(2) Å	α= 80.3987(13)°.
	b = 12.5061(3) Å	β= 85.8752(13)°.
	c = 13.4396(3) Å	γ = 78.3825(13)°.
Volume	1371.80(6) $Å^3$	
Z	2	
Density (calculated)	1.488 Mg/m^3	
Absorption coefficient	0.366 mm^{-1}	
F(000)	632	
Crystal size	0.39 x 0.32 x 0.3 mm^3	
Theta range for data collection	2.096 to 27.533°.	
Index ranges	-10<=h<=10, -16<=k<=14, -15<=l<=17	
Reflections collected	23016	
Independent reflections	6251 [R(int) = 0.0269]	
Completeness to theta = 26.000°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6233	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6251 / 0 / 371	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0497, wR2 = 0.1327	
R indices (all data)	R1 = 0.0809, wR2 = 0.1534	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.496 and -0.548 $e.Å^{-3}$	

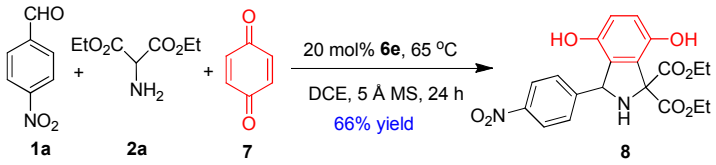
7. Disscussion on the possible reaction pathway:



Based on the experiment results and previous investigations on 1,3-DCs of azomethine ylide, we suggested a possible reaction pathway to explain the formation of [3+3] cycloaddition products **4**. Initially, the condensation of aldehydes **1** with amino-esters **2** in the presence of $GaBr_3$ afforded azomethine ylides **A**, which underwent Michael addition with QMIs **3** at the C3-postion, thus generating transient intermediates **B**. The intermediates **B** rapidly isomerized into their phenol forms **C**, which subsequently carried out the intramolecular *oxa*-Mannich reaction to give [3+3] cycloaddition products **4**. Instead, the formation of [3+2] cycloaddition products **5** might include a concerted 1,3-DC of azomethine ylides **A** with the electron-deficient C=C bond of QMIs **3** to generate intermediates **D**, which could also quickly isomerize into the final products **5**. So, the experimentally observed excellent chemoselectivity may largely be ascribed to the action of catalyst $GaBr_3$ or **6e** in activating the substrates and stabilizing the possible transition states, thus benefiting a stepwise [3+3] reaction pathway rather than a concerted [3+2] reaction process.

8. The reaction using quinone instead of QMIs:

At last, we tried the reaction using quinone **7** instead of QMIs **3** under the optimal conditions (eq. 7). As expected, this reaction exclusively afforded the [3+2] cycloaddition product **8** in 66% yield, which was in accord with the literature.[2]



[2] For some examples: a) C. Wang, X.-H. Chen, S.-M. Zhou, L.-Z. Gong, *Chem. Commun.* **2010**, *46*, 1275; b) Z. He, T. Liu, H. Tao, C.-J. Wang, *Org. Lett.* **2012**, *14*, 6230; c) K. Liu, H.-L. Teng, L. Yao, H.-Y. Tao, C.-J. Wang, *Org. Lett.* **2013**, *15*, 2250.