Copper-Catalyzed Selective Difunctionalization of N‑Heteroarenes through Halogen Atom Transfer Radical Process

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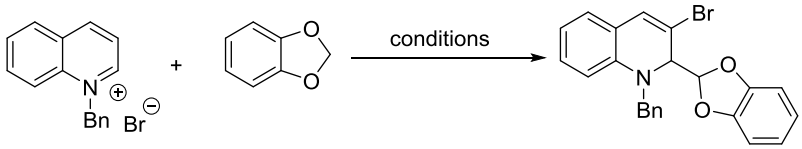
Supporting Information

Content

General Information:

Unless otherwise noted, all reactants or reagents including dry solvents were obtained from commercial suppliers and used as received. Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates (Merck silica gel 60 F254). The developed chromatogram was analyzed by UV lamp (254 nm). ^{1}H NMR and ^{13}C NMR spectra were obtained on a Variance 400M. Chemical shifts (δ) are expressed in parts per million and are internally referenced. High-resolution mass spectra (HRMS) were obtained on AB 5800 MALDI-TOF/TOF and are reported as m/z (relative intensity).

Table S1 Optimization of reaction conditions



1a **2a** **3a**

entry	cat.	oxidant	time (min)	solvent	yield (%)[b]
1	CuBr	TBHP	10	free	45
2	$CuCl_2$	TBHP	10	free	38
3	$CuBr_2$	TBHP	10	free	40
4	$Co(acac)_2$	TBHP	10	free	51
5	$Fe(acac)_2$	TBHP	10	free	19
6	$Fe(acac)_3$	TBHP	10	free	21
7	$Cu(acac)_2$	BQ	10	free	trace
8	$Cu(acac)_2$	Oxone	10	free	trace
9	$Cu(acac)_2$	DCP	10	free	trace
10	$Cu(acac)_2$	^{m}CPBA	10	free	trace
11	$Cu(acac)_2$	CHP	10	free	trace
12	$Cu(acac)_2$	^{t}BuOCl	10	free	trace
13	$Cu(acac)_2$	TBHP	60	free	55
14	$Cu(acac)_2$	TBHP	10	$PhCH_3$	32
15	$Cu(acac)_2$	TBHP	10	EtOH	28
16	$Cu(acac)_2$	TBHP	10	CH_3CN	51
17	$Cu(acac)_2$	TBHP	10	cyclohexane	44

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (3 mmol, 10 equiv), catalysts (5 mol%), rt. [b]Isolated yield.

Experiment section:

General Procedure for the Preparation of 3, 5 and 6.

Quinolinium salts (0.3 mmol), ether (3 mmol), CuCN (0.0015 mmol), TBHP (3 equiv., 70% aqueous solution) were added to a tube under air. The mixture was stirred RT for 10 mins. The reaction mixture was quenched with saturated $Na_2S_3O_3$ solution, extracted repeatedly with ethyl acetate, dried over $MgSO_4$. It was then removal of the organic solvent in vacuum and followed by flash silica gel column chromatographic purification afforded products with petroleum/ethyl acetate mixtures.

General Procedure for the Preparation of 11.

3a (0.084 g, 0.2 mmol), **10** (0.037 g, 0.24 mmol), $Pd(PPh_3)_4$ (11.2 mg, 0.01 mmol), K_2CO_3 (55.2 mg, 0.4 mmol) in DME and H_2O (V = 3:1) were added to a schlenk tube under Ar. The mixture was stirred at 100 ^oC for 12 h. The reaction mixture was extracted repeatedly with ethyl acetate, dried over $MgSO_4$. It was then removal of the organic solvent in vacuum and followed by flash silica gel column chromatographic purification afforded products with petroleum/ethyl acetate mixtures.

Experimental

General Procedure for the Preparation of 3, 5 and 6.

Quinolinium salts (0.3 mmol), ether (3 mmol), CuCN (0.0015 mmol), TBHP (3 equiv., 70% aqueous solution) were added to a tube under air. The mixture was stirred RT for 10 mins. The reaction mixture was quenched with saturated $Na_2S_2O_3$ solution, extracted repeatedly with ethyl acetate, dried over $MgSO_4$. It was then removal of the organic solvent in vacuum and followed by flash silica gel column chromatographic purification afforded products with 15−30% ethyl acetate in petroleum as the eluent.

General Procedure for the Preparation of 11.

3a (0.084 g, 0.2 mmol), **10** (0.037 g, 0.24 mmol), $Pd(PPh_3)_4$ (11.2 mg, 0.01 mmol), K_2CO_3 (55.2 mg, 0.4 mmol) in DME and H_2O (V = 3:1) were added to a schlenk tube under Ar. The mixture was stirred at 100 ^oC for 12 h. The reaction mixture was extracted repeatedly with ethyl acetate, dried over $MgSO_4$. It was then removal of the organic solvent in vacuum and followed by flash silica gel column chromatographic purification afforded products with 15% ethyl acetate in petroleum as the eluent.

2-(Benzo[*d*][1,3]dioxol-2-yl)-1-benzyl-3-bromo-1,2-dihydroquinoline (3a): colorless oil, 0.0993 g, 79%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.40-7.34 (m, 4H, ArH), 7.28-7.25 (m, 1H, ArH), 7.17 (d, *J* = 7.5 Hz, 1H, ArH), 7.10 (s, 1H, CH), 7.03-6.99 (m, 1H, ArH), 6.83-6.79 (m, 1H, ArH), 6.77-6.75 (m, 1H, ArH), 6.72-6.67 (m, 4H, ArH), 6.33 (d, *J* = 2.0 Hz, 1H, CH), 4.93-4.80 (m, 2H, CH_2), 4.37 (d, *J* = 1.9 Hz, 1H, CH); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 147.9, 147.7, 139.2, 138.5, 136.9, 130.7, 128.9, 128.4, 127.5, 126.7, 121.6, 116.5, 112.9, 111.4, 108.3, 108.2, 85.6, 53.1, 49.7. HRMS (ESI) Calcd. for $C_{23}H_{19}BrNO_2$ ($[M+H]^+$): 420.0594, found: 420.0592, 422.0573.

2-(Benzo[*d*][1,3]dioxol-2-yl)-3-bromo-1-(4-methylbenzyl)-1,2-dihydroquinoline (3b): colorless oil, 0.1052 g, 81%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.40-7.37 (m, 3H, ArH), 7.32 (d, *J* = 7.1 Hz, 2H, ArH), 7.28-7.24 (m, 1H, ArH), 7.12 (s, 1H, CH), 6.99-6.95 (m, 1H, ArH), 6.78-6.74 (m, 2H, ArH), 6.68-6.65 (m, 3H, ArH), 6.59 (d, *J* = 8.1 Hz, 1H, ArH), 6.20 (s, 1H, CH), 4.90-4.79 (m, 2H, CH_2), 1.77 (s, 3H, CH_3); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 148.0, 147.8, 138.9, 138.4, 136.6, 129.3, 129.0, 128.3, 127.4, 126.6, 121.5, 121.3, 120.7, 114.0, 112.9, 108.2, 108.1, 94.3, 53.2, 46.41, 24.3. HRMS (ESI) Calcd. for $C_{24}H_{21}BrNO_2$ ($[M+H]^+$): 434.0750, found: 434.0745, 436.0730.

2-(Benzo[*d*][1,3]dioxol-2-yl)-3-bromo-1-(4-methoxybenzyl)-1,2-dihydroquinoline (3c): colorless oil, 0.0996 g, 74%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.26 (d, *J* = 8.4 Hz, 2H, ArH), 7.16 (d, *J* = 7.3 Hz, 1H, ArH), 7.08 (s, 1H, CH), 7.02-7.00 (m, 1H, ArH), 6.94 (d, *J* = 8.4 Hz, 2H, ArH), 6.82-6.78 (m, 1H, ArH), 6.76 (d, *J* = 5.5 Hz, 1H, ArH), 6.71-6.69 (m, 4H, ArH), 6.30 (d, *J* = 1.5 Hz, 1H, CH), 4.84-4.71 (m, 2H, CH_2), 4.35 (s, 1H, CH), 3,74 (s, 3H, CH_3); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 158.8, 147.9, 147.7, 139.2, 136.8, 130.7, 130.1, 128.39, 128.0, 121.6, 121.5, 116.5, 114.4, 113.0, 111.4, 108.3, 108.2, 85.4, 55.5, 52.61, 49.7. HRMS (ESI) Calcd. for $C_{24}H_{21}BrNO_3$ ($[M+H]^+$): 450.0699, found: 450.0695, 452.0679.

2-(Benzo[*d*][1,3]dioxol-2-yl)-3-bromo-1-(3,5-dimethoxybenzyl)-1,2-dihydroquinoline (3d): colorless oil, 0.1034 g, 72%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.16 (d, *J* = 7.5 Hz, 1H, ArH), 7.06 (s, 1H, CH), 7.04-7.00 (m, 1H, ArH),6.82-6.78 (m, 2H, ArH), 6.71-6.63 (m, 4H, ArH), 6.52 (d, *J* = 1.9 Hz, 2H, ArH), 6.41 (s, 1H, ArH), 6.32 (d, *J* = 1.8 Hz, 1H, CH)), 4.82-4.71 (m, 2H, CH_2), 4.35 (d, *J* = 1.4 Hz, 1H, CH), 3,74 (s, 6H, OCH_3); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 161.2, 147.9, 147.8, 141.0, 139.2, 136.9, 130.6, 128.5, 121.6, 121.5,

116.4, 112.8, 111.5, 108.3, 108.1, 105.1, 98.2, 85.5, 55.6, 53.21, 49.7. HRMS (ESI) Calcd. for $C_{25}H_{23}BrNO_4$ ([M+H]$^+$): 480.0805, found: 480.0803, 482.0784.

2-(Benzo[*d*][1,3]dioxol-2-yl)-3-bromo-1-(4-fluorobenzyl)-1,2-dihydroquinoline (3e): colorless oil, 0.0773 g, 59%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.39-7.36 (m, 2H, ArH), 7.25-7.21 (m, 2H, ArH), 7.17 (d, *J* = 7.6 Hz, 1H, ArH), 7.10 (s, 1H, CH), 7.04-7.00 (m, 1H, ArH), 6.83-6.80 (m, 1H, ArH), 6.81-6.75 (m, 1H, ArH), 6.71-6.66 (m, 4H, ArH), 6.32 (d, *J* = 2.0 Hz, 1H, CH), 4.92-4.77 (m, 2H, CH_2), 4.36 (d, *J* = 1.7 Hz, 1H, CH); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 147.8, 147.7, 139.0, 136.8, 134.6, 130.4, 128.6, 128.6, 128.5, 121.6, 116.5, 115.8, 115.6, 112.9, 111.4, 108.3, 108.2, 85.7, 52.4, 49.6. HRMS (ESI) Calcd. for $C_{23}H_{18}BrFNO_2$ ([M+H]$^+$): 438.0499, found: 438.0495, 440.0477.

2-(Benzo[*d*][1,3]dioxol-2-yl)-3-bromo-1-(4-(trifluoromethyl)benzyl)-1,2-dihydroquinoline (3f): colorless oil, 0.0891 g, 61%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.77 (d, *J* = 8.1 Hz, 2H, ArH), 7.55 (d, *J* = 8.0 Hz, 2H, ArH), 7.19 (d, *J* = 7.4 Hz, 1H, ArH), 7.14 (s, 1H, CH), 7.04-7.00 (m, 1H, ArH), 6.85-6.81 (m, 1H, ArH), 6.79-6.76 (m, 1H, ArH), 6.71-6.64 (m, 4H, ArH), 6.34 (d, *J* = 1.8 Hz, 1H, CH), 5.04-4.90 (m, 2H, CH_2), 4.38 (d, *J* = 1.6 Hz, 1H, CH); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 147.8, 147.7, 143.6, 138.9, 136.7, 130.8, 128.6, 127.4, 125.9, 121.8, 121.6, 116.6, 112.8, 111.4, 110.0, 108.3, 108.2, 86.0, 52.7, 49.6. HRMS (ESI) Calcd. for $C_{24}H_{18}BrF_3NO_2$ ([M+H]$^+$): 488.0468, found: 488.0466, 490.0447.

2-(Benzo[*d*][1,3]dioxol-2-yl)-3-bromo-1-(4-nitrobenzyl)-1,2-dihydroquinoline (3g): colorless oil, 0.0863 g, 62%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 8.26 (d, *J* = 8.7 Hz, 2H, ArH), 7.59 (d, *J* = 8.6 Hz, 2H, ArH), 7.20 (d, *J* = 6.7 Hz, 1H, ArH), 7.15 (s, 1H, CH), 7.03-6.99 (m, 1H, ArH), 6.85-6.78 (m, 2H, ArH), 6.75-6.68 (m, 3H, ArH), 6.62 (d, *J* = 8.3 Hz, 1H, ArH), 6.35 (d, *J* = 2.0 Hz, 1H, CH), 5.10-4.96 (m, 2H, CH_2), 4.39 (d, *J* = 2.0 Hz, 1H, CH); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 147.8, 147.7, 147.2, 146.9, 138.9, 136.6, 130.8, 128.6, 127.8, 124.2, 121.9, 121.7, 116.6, 112.7, 111.4, 108.3, 108.3, 86.2, 52.7, 49.5. HRMS (ESI) Calcd. for $C_{23}H_{18}BrN_2O_4$ ([M+H]$^+$): 465.0444, found: 465.0443, 467.0425.

2-(Benzo[*d*][1,3]dioxol-2-yl)-3-bromo-1-(naphthalen-1-ylmethyl)-1,2-dihydroquinoline (3h): colorless oil, 0.1027 g, 73%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 8.13 (d, *J* = 8.0 Hz, 1H, ArH), 7.99 (d, *J* = 7.7 Hz, 1H, ArH), 7.86 (d, *J* = 8.1 Hz, 1H, ArH), 7.64-7.57 (m, 2H, ArH), 7.53-7.49 (m, 1H, ArH), 7.40 (d, *J* = 7.1 Hz, 1H, ArH), 7.23 (d, *J* = 7.5 Hz, 1H, ArH),

7.10 (s, 1H, CH), 7.00-6.96 (m, 1H, ArH), 6.85-6.81 (m, 1H, ArH), 6.78-6.69 (m, 4H, ArH), 6.59 (d, *J* = 8.3 Hz, 1H, ArH), 6.38 (d, *J* = 1.9 Hz, 1H, CH), 5.46 (d, *J* = 17.7 Hz, 1H, CH_2), 5.25 (d, *J* = 17.8 Hz, 1H, CH_2), 4.44 (d, *J* = 1.8 Hz, 1H, CH),; ^{13}C NMR (100 MHz, d_6-DMSO) δ: 147.9, 147.7, 139.5, 136.7, 133.8, 133.2, 130.7, 130.7, 129.1, 128.6, 127.8, 126.7, 126.4, 125.9, 123.4, 123.3, 121.7, 116.3, 112.7, 111.5, 108.3, 108.3, 85.9, 51.0, 49.7. HRMS (ESI) Calcd. for $C_{27}H_{21}BrNO_2$ ($[M+H]^+$): 470.0750, found: 470.0751, 472.0733.

2-(Benzo[*d*][1,3]dioxol-2-yl)-3-bromo-1-butyl-1,2-dihydroquinoline (3i): colorless oil, 0.1004 g, 87%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.13 (t, *J* = 7.4 Hz, 2H, ArH), 6.90-6.81 (m, 3H, ArH), 6.70-6.63 (m, 4H, ArH), 6.24 (d, *J* = 2.2 Hz, 1H, CH), 4.24 (d, *J* = 1.9 Hz, 1H, CH), 3.76-3.69 (m, 1H, CH), 3.47-3.40 (m, 1H, CH), 1.59-1.44 (m, 2H, CH_2), 1.42-1.35 (m, 2H, CH_2), 0.93 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 147.9, 147.7, 139.1, 136.3, 130.8, 128.5, 121.5, 121.3, 116.6, 112.3, 111.4, 108.1, 84.8, 49.9, 49.2, 30.2, 19.6, 14.2. HRMS (ESI) Calcd. for $C_{20}H_{21}BrNO_2$ ($[M+H]^+$): 386.0750, found: 386.0754, 388.0730.

2-(Benzo[*d*][1,3]dioxol-2-yl)-3-bromo-1-phenethyl-1,2-dihydroquinoline (3j): colorless oil, 0.1052 g, 81%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.33-7.30 (m, 4H, ArH), 7.23-7.15 (m, 3H, ArH), 7.03 (d, *J* = 8.3 Hz, 1H, ArH), 6.88-6.86 (m, 2H, ArH), 6.75 (d, *J* = 6.7 Hz, 1H, ArH), 6.72-6.66 (m, 3H, ArH), 6.19 (d, *J* = 2.6 Hz, 1H, CH), 4.25 (d, *J* = 2.4 Hz, 1H, CH), 3.89-3.83 (m, 1H, CH_2), 3.76-3.71 (m, 1H, CH_2), 2.88-2.80 (m, 2H, CH_2); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 147.4, 147.2, 138.5, 135.5, 130.4, 128.9, 128.4, 128.2, 126.3, 121.2, 121.1, 121.0, 116.4, 112.0, 110.8, 107.8, 107.7, 85.2, 50.5, 49.3, 33.7. HRMS (ESI) Calcd. for $C_{24}H_{21}BrNO_2$ ($[M+H]^+$): 434.0750, found: 434.0748, 436.0730.

2-(Benzo[*d*][1,3]dioxol-2-yl)-3-bromo-1-(3-phenylpropyl)-1,2-dihydroquinoline (3k): colorless oil, 0.1153 g, 86%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.32-7.28 (m, 2H, ArH), 7.22-7.18 (m, 3H, ArH), 7.15-7.10 (m, 2H, ArH), 6.87-6.82 (m, 3H, ArH), 6.65-6.62 (m, 3H, ArH), 6.57-6.54 (m, 1H, ArH), 6.26 (d, *J* = 2.2 Hz, 1H, ArH), 4.27 (d, *J* = 2.0 Hz, 1H, CH), 3.81-3.74 (m, 1H, CH_2), 3.49-3.41 (m, 1H, CH_2), 2.74-2.60 (m, 2H, CH_2), 1.94-1.77 (m, 2H, CH_2); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 147.8, 147.7, 142.0, 139.1, 136.2, 130.8, 128.8, 128.7, 128.5, 126.3, 121.5, 121.4, 116.8, 112.4, 111.5, 108.1, 108.0, 85.1, 49.9, 49.0, 32.4, 29.9. HRMS (ESI) Calcd. for $C_{25}H_{23}BrNO_2$ ($[M+H]^+$): 448.0907, found: 448.0910, 450.0886.

Ethyl 2-(2-(benzo[d][1,3]dioxol-2-yl)-3-bromoquinolin-1(2H)-yl)acetate (3l): colorless oil, 0.0784 g, 63%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.18 (d, *J* = 7.5 Hz, 1H, ArH), 7.13 (t, *J* = 7.7 Hz, 1H, ArH), 6.93 (s, 1H, CH), 6.88 (t, *J* = 7.4 Hz, 1H, ArH), 6.79 (d, *J* = 7.0 Hz, 1H, ArH), 6.74-6.67 (m, 4H, ArH), 6.27 (d, *J* = 2.1 Hz, 1H, CH), 4.52-4.46 (m, 2H, CH_2), 4.29 (d, *J* = 1.6 Hz, 1H, CH), 4.15-4.11 (m, 2H, CH_2), 1.19 (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 169.3, 147.3, 147.1, 139.1, 135.9, 130.3, 128.1, 121.3, 121.2, 121.2, 116.3, 111.7, 110.9, 108.0, 107.9, 86.2, 60.7, 50.3, 49.2, 14.0. HRMS (ESI) Calcd. for $C_{20}H_{19}BrNO_4$ ([M+H]$^+$): 416.0492, found: 416.0490, 418.0477.

Methyl 4-(2-(benzo[d][1,3]dioxol-2-yl)-3-bromoquinolin-1(2H)-yl)butanoate (3m): colorless oil, 0.0991 g, 77%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.32-7.28 (m, 2H, ArH), 7.22-7.18 (m, 3H, ArH), 7.15-7.10 (m, 2H, ArH), 6.87-6.82 (m, 3H, ArH), 6.65-6.62 (m, 3H, ArH), 6.57-6.54 (m, 1H, ArH), 6.26 (d, *J* = 2.2 Hz, 1H, ArH), 4.27 (d, *J* = 2.0 Hz, 1H, CH), 3.81-3.74 (m, 1H, CH_2), 3.49-3.41 (m, 1H, CH_2), 2.74-2.60 (m, 2H, CH_2), 1.94-1.77 (m, 2H, CH_2); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 147.8, 147.7, 142.0, 139.1, 136.2, 130.8, 128.8, 128.7, 128.5, 126.3, 121.5, 121.4, 116.8, 112.4, 111.5, 108.1, 108.0, 85.1, 49.9, 49.0, 32.4, 29.9. HRMS (ESI) Calcd. for $C_{21}H_{21}BrNO_4$ ([M+H]$^+$): 430.0648, found: 430.0646, 432.0628.

2-(Benzo[*d*][1,3]dioxol-2-yl)-1-benzyl-3-bromo-4-methyl-1,2-dihydroquinoline (3n): colorless oil, 0.0805 g, 63%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.40-7.37 (m, 3H, ArH), 7.32 (d, *J* = 7.1 Hz, 2H, ArH), 7.28-7.24 (m, 1H, ArH), 7.12 (s, 1H, CH), 6.99-6.95 (m, 1H, ArH), 6.78-6.74 (m, 2H, ArH), 6.68-6.65 (m, 3H, ArH), 6.59 (d, *J* = 8.1 Hz, 1H, ArH), 6.20 (s, 1H, CH), 4.90-4.79 (m, 2H, CH_2), 1.77 (s, 3H, CH_3); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 148.0, 147.8, 138.9, 138.4, 136.6, 129.3, 129.0, 128.3, 127.4, 126.6, 121.5, 121.3, 120.7, 114.0, 112.9, 108.2, 108.1, 94.3, 53.2, 46.41, 24.3. HRMS (ESI) Calcd. for $C_{24}H_{21}BrNO_2$ ([M+H]$^+$): 434.0750, found: 434.0745, 436.0730.

2-(Benzo[*d*][1,3]dioxol-2-yl)-1-benzyl-3-bromo-6-methyl-1,2-dihydroquinoline (3o): colorless oil, 0.1013 g, 78%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.39-7.32 (m, 4H, ArH), 7.27-7.24 (m, 1H, ArH), 7.06 (s, 1H, CH), 6.99 (s, 1H, ArH), 6.81 (d, *J* = 8.6 Hz, 1H, ArH), 6.75 (d, *J* = 6.2 Hz, 1H, ArH), 6.71-6.66 (m, 3H, ArH), 6.56 (d, *J* = 8.4 Hz, 1H, ArH), 6.32 (d, *J* = 1.9 Hz, 1H, ArH), 4.90-4.77 (m, 2H, CH_2), 4.30 (d, *J* = 1.7 Hz, 1H, CH), 2.09 (s, 3H, CH_3); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 148.0, 147.8, 138.6, 136.9, 136.9, 131.0, 130.4,

128.9, 128.9, 127.4, 126.7, 121.6, 116.5, 112.9, 111.5, 108.2, 108.0, 84.9, 53.0, 49.73, 20.5. HRMS (ESI) Calcd. for $C_{24}H_{21}BrNO_2$ ([M+H]$^+$): 434.0750, found: 434.0746, 436.0731.

2-(Benzo[*d*][1,3]dioxol-2-yl)-1-benzyl-3-bromo-6-fluoro-1,2-dihydroquinoline (3p): colorless oil, 0.1022 g, 78%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.41-7.37 (m, 2H, ArH), 7.34-7.32 (m, 2H, ArH), 7.29-7.25 (m, 1H, ArH), 7.11 (s, 1H, CH), 7.05-7.02 (m, 1H, ArH), 6.93-6.82 (m, 2H, ArH), 6.78-6.76 (m, 1H, ArH), 6.72-6.64 (m, 3H, ArH), 6.38 (d, *J* = 1.8 Hz, 1H, CH), 4.91-4.80 (m, 2H, CH_2), 4.40 (d, *J* = 1.7 Hz, 1H, CH); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 147.8, 147.6, 138.3, 136.9, 135.9, 129.0, 127.5, 126.7, 122.1, 121.7, 118.1, 118.0, 117.0, 116.8, 115.2, 115.0, 114.2, 114.1, 111.0, 109.0, 108.3, 108.1, 84.6, 53.4, 49.6. HRMS (ESI) Calcd. for $C_{23}H_{18}BrFNO_2$ ([M+H]$^+$): 438.0499, found: 438.0495.

2-(Benzo[*d*][1,3]dioxol-2-yl)-1-benzyl-3-bromo-6-chloro-1,2-dihydroquinoline (3q): colorless oil, 0.0938 g, 69%, ^{1}H NMR (400 MHz, d_6-DMSO) δ7.41-7.37 (m, 2H, ArH), 7.33-7.31 (m, 2H, ArH), 7.29-7.25 (m, 1H, ArH), 7.23 (s, *J* = 2.4 Hz, 1H, ArH), 7.11 (s, 1H, CH), 7.05-7.02 (m, 1H, ArH), 6.77-6.75 (m, 1H, ArH), 6.72-6.65 (m, 4H, ArH), 6.36 (d, *J* = 1.8 Hz, 1H, CH), 4.91-4.80 (m, 2H, CH_2), 4.41 (d, *J* = 1.7 Hz, 1H, CH); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 13C NMR (101 MHz, dmso) δ 147.8, 147.6, 138.2, 138.0, 136.7, 130.2, 129.0, 128.2, 127.6, 126.6, 124.8, 121.7, 118.2, 114.5, 111.0, 108.3, 108.1, 85.7, 53.2, 49.3. HRMS (ESI) Calcd. for $C_{23}H_{18}BrClNO_2$ ([M+H]$^+$): 454.0204, found: 454.0202.

2-(Benzo[*d*][1,3]dioxol-2-yl)-1-benzyl-3,6-dibromo-1,2-dihydroquinoline (3r): colorless oil, 0.1125 g, 75%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.41-7.25 (m, 6H, ArH), 7.16-7.14 (m, 1H, ArH), 7.12 (s, 1H, CH), 6.77-6.76 (m, 1H, ArH), 6.73-6.65 (m, 3H, ArH), 6.60 (d, *J* = 8.9 Hz, 1H, ArH), 6.36 (d, *J* = 1.8 Hz, 1H, CH), 4.90-4.80 (m, 2H, CH_2), 4.41 (s, 1H, CH); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 147.8, 147.6, 138.6, 138.0, 136.7, 133.0, 131.0, 129.0, 127.6, 126.6, 121.7, 118.6, 114.9, 112.5, 111.0, 108.3, 108.1, 85.9, 53.2, 49.2. HRMS (ESI) Calcd. for $C_{23}H_{18}Br_2NO_2$ ([M+H]$^+$): 499.9678, found: 499.9679.

2-(Benzo[*d*][1,3]dioxol-2-yl)-1-benzyl-3-chloro-1,2-dihydroquinoline (3s): colorless oil, 0.0574 g, 51%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.46 (d, *J* = 7.8 Hz, 1H, ArH), 7.38-7.36 (m, 2H, ArH),7.30 (d, *J* = 7.6 Hz, 2H, ArH), 7.26-7.23 (m, 1H, ArH), 6.98-6.95 (m, 1H, ArH), 6.77-6.75 (m, 3H, ArH), 6.69 (t, *J* = 7.5 Hz, 1H, ArH), 6.66 (d, *J* = 8.2 Hz, 1H, ArH), 6.63 (d, *J* = 8.3 Hz, 1H, ArH), 6.60 (s, 2H, ArH), 4.81 (s, 2H, CH_2), 4.36 (d, *J* = 8.2 Hz, 1H,

CH); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 147.6, 147.2, 139.6, 138.2, 137.0, 128.5, 128.3, 128.0, 126.8, 126.0, 121.5, 121.4, 120.2, 116.8, 112.9, 111.4, 108.0, 107.8, 87.8, 52.8, 50.3. HRMS (ESI) Calcd. for $C_{23}H_{19}ClNO_2$ ($[M+H]^+$): 376.1099, found: 376.1092.

2-(Benzo[*d*][1,3]dioxol-2-yl)-3-chloro-1-(4-methylbenzyl)-1,2-dihydroquinoline (3t): colorless oil, 0.0724 g, 62%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.14 (d, *J* = 6.2 Hz, 4H, ArH), 6.93 (t, *J* = 7.3 Hz, 1H, ArH), 6.82-6.79 (m, 3H, ArH), 6.74 (t, *J* = 3.3 Hz, 2H, ArH), 6.67-6.63 (m, 2H, ArH), 6.57 (s, 2H, ArH), 4.73 (s, 2H, CH_2), 4.32 (d, *J* = 8.2 Hz, 1H, CH), 2.25 (s, 3H, CH_3); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 148.0, 147.6, 140.0, 137.5, 136.4, 135.5, 129.5, 128.7, 128.4, 126.4, 121.9, 121.8, 120.6, 117.2, 113.4, 111.9, 108.5, 108.3, 88.1, 53.2, 50.7, 21.1. HRMS (ESI) Calcd. for $C_{24}H_{21}ClNO_2$ ($[M+H]^+$): 390.1255, found: 390.1256.

2-(Benzo[*d*][1,3]dioxol-2-yl)-3-chloro-1-(4-fluorobenzyl)-1,2-dihydroquinoline (3u): colorless oil, 0.0519 g, 44%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.43 (d, *J* = 7.4 Hz, 1H, ArH), 7.31-7.28 (m, 2H, ArH), 7.22-7.18 (m, 2H, ArH), 6.95 (t, *J* = 7.8 Hz, 1H, ArH), 6.75-6.72 (m, 3H, ArH), 6.69-6.65 (m, 1H, ArH), 6.63 (s, 2H, ArH), 6.61-6.59 (m, 1H, ArH), 6.57 (s, 2H, ArH), 4.77 (s, 2H, CH_2), 4.34 (d, *J* = 8.2 Hz, 1H, CH); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 148.0, 147.6, 139.9, 137.3, 134.7, 128.8, 128.5, 128.4, 128.3, 121.9, 121.9, 120.8, 117.3, 115.8, 115.6, 113.3, 111.8, 108.5, 108.3, 88.5, 52.6, 50.7. HRMS (ESI) Calcd. for $C_{23}H_{18}ClFNO_2$ ($[M+H]^+$): 394.1005, found: 394.1008.

2-(Benzo[*d*][1,3]dioxol-2-yl)-3-benzyl-6-bromo-2,3-dihydrobenzo[*d*]thiazole (**5a**): colorless oil, 0.0921 g, 72%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.33-7.23 (m, 6H, ArH), 7.00-6.98 (m, 1H, ArH), 6.90-6.83 (m, 2H, ArH), 6.82-6.79 (m, 2H, ArH), 6.38 (d, *J* = 8.4 Hz, 1H, ArH), 6.30 (d, *J* = 3.3 Hz, 1H, CH), 5.66 (d, *J* = 3.3 Hz, 1H, CH), 4.68 (d, *J* = 16.2 Hz, 1H, CH_2), 4.47 (d, *J* = 16.4 Hz, 1H, CH_2). ^{13}C NMR (100 MHz, d_6-DMSO) δ: 147.4, 147.3, 147.2, 137.6, 129.2, 129.0, 128.2, 127.7, 127.6, 124.0, 122.1, 110.8, 110.2, 109.6, 108.6, 108.5, 71.8, 53.4. HRMS (ESI) Calcd. for $C_{21}H_{17}BrNO_2S$ ($[M+H]^+$): 426.0158, found: 426.0158.

2-(Benzo[*d*][1,3]dioxol-2-yl)-6-bromo-3-(4-methylbenzyl)-2,3-dihydrobenzo[*d*]thiazole (**5b**); colorless oil, 0.1017 g, 77%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.25 (d, *J* = 1.9 Hz, 1H, ArH), 7.17-7.15 (m, 2H, ArH), 7.12-7.10 (m, 2H, ArH), 7.00-6.98 (m, 1H, ArH), 6.87-

6.85 (m, 1H, ArH), 6.81-6.80 (m, 3H, ArH), 6.38 (d, *J* = 8.5 Hz, 1H, ArH), 6.29 (d, *J* = 3.3 Hz, 1H, CH), 5.53 (d, *J* = 3.2 Hz, 1H, CH), 4.61 (d, *J* = 16.1 Hz, 1H, CH_2), 4.41 (d, *J* = 16.1 Hz, 1H, CH_2), 2.25 (s, 3H, CH_3). ^{13}C NMR (100 MHz, d_6-DMSO) δ: 147.4, 147.3, 147.2, 136.9, 134.4, 129.6, 129.2, 128.2, 127.7, 123.9, 122.1, 110.9, 110.1, 109.6, 108.6, 108.5, 71.8, 53.2, 21.1. HRMS (ESI) Calcd. for $C_{22}H_{19}BrNO_2S$ ($[M+H]^+$): 440.0314, found: 440.0315.

2-(Benzo[*d*][1,3]dioxol-2-yl)-6-bromo-3-(4-methoxybenzyl)-2,3-dihydrobenzo[*d*]thiazole (**5c**); colorless oil, 0.0863 g, 63%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.25 (d, *J* = 2.0 Hz, 1H, ArH), 7.20-7.18 (m, 2H, ArH), 7.01-6.99 (m, 1H, ArH), 6.88-6.86 (m, 3H, ArH), 6.81-6.80 (m, 3H, ArH), 6.43 (d, *J* = 8.5 Hz, 1H, ArH), 6.28 (d, *J* = 3.3 Hz, 1H, CH), 5.62 (d, *J* = 3.2 Hz, 1H, CH), 4.58 (d, *J* = 16.1 Hz, 1H, CH_2), 4.37 (d, *J* = 15.8 Hz, 1H, CH_2), 3.71 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, d_6-DMSO) δ: 158.5, 147.0, 146.9, 146.8, 128.9, 128.8, 128.7, 127.7, 123.5, 121.6, 113.9, 110.7, 109.7, 109.1, 108.1, 108.0, 71.2, 55.0, 52.4. HRMS (ESI) Calcd. for $C_{22}H_{19}BrNO_3S$ ($[M+H]^+$): 456.0264, found: 456.0266.

2-(Benzo[*d*][1,3]dioxol-2-yl)-6-bromo-3-(3,5-dimethoxybenzyl)-2,3-dihydrobenzo[*d*]thiazole (**5d**): colorless oil, 0.0861 g, 59%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.28 (d, *J* = 2.0 Hz, 1H, ArH), 7.01-6.99 (m, 1H, ArH), 6.86-6.82 (m, 5H, ArH), 6.44 (d, *J* = 2.1 Hz, 1H, ArH), 6.39-6.36 (m, 2H, ArH), 6.31 (d, *J* = 3.2 Hz, 1H, CH), 5.70 (d, *J* = 3.2 Hz, 1H, CH), 4.62 (d, *J* = 16.5 Hz, 1H, CH_2), 4.41 (d, *J* = 16.6 Hz, 1H, CH_2), 3.68 (s, 6H, OCH_3). ^{13}C NMR (100 MHz, d_6-DMSO) δ: 161.0, 147.5, 147.4, 147.2, 140.1, 129.2, 128.2, 124.0, 122.1, 122.1, 110.9, 110.2, 109.5, 108.6, 108.5, 105.4, 99.2, 72.0, 55.5, 53.5. HRMS (ESI) Calcd. for $C_{23}H_{21}BrNO_4S$ ($[M+H]^+$): 487.3875, found: 487.3873.

2-(Benzo[*d*][1,3]dioxol-2-yl)-6-bromo-3-(4-fluorobenzyl)-2,3-dihydrobenzo[*d*]thiazole (**5e**): colorless oil, 0.1026 g, 77%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.30-7.27 (m, 2H, ArH), 7.16-7.12 (m, 2H, ArH), 7.02-6.99 (m, 1H, ArH), 6.87-6.83 (m, 1H, ArH), 6.81-6.80 (m, 3H, ArH), 6.39 (d, *J* = 8.5 Hz, 1H, ArH), 6.29 (d, *J* = 3.3 Hz, 1H, CH), 5.67 (d, *J* = 3.3 Hz, 1H, CH), 4.64 (d, *J* = 16.2 Hz, 1H, CH_2), 4.45 (d, *J* = 16.3 Hz, 1H, CH_2). ^{13}C NMR (100 MHz, d_6-DMSO) δ: 147.4, 147.3, 147.0, 133.8, 129.7, 129.6, 129.4, 128.2, 124.0, 122.1, 115.8, 115.6, 111.1, 110.4, 109.5, 108.6, 108.5, 71.8, 52.8. HRMS (ESI) Calcd. for $C_{21}H_{16}BrFNO_2S$ ($[M+H]^+$): 444.0064, found: 444.0064, 446.0043.

2-(Benzo[*d*][1,3]dioxol-2-yl)-6-bromo-3-(4-chlorobenzyl)-2,3-dihydrobenzo[*d*]thiazole (**5f**): colorless oil, 0.1050 g, 76%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.37 (d, *J* = 8.5 Hz, 1H, ArH), 7.30-7.27 (m, 3H, ArH), 7.01-6.98 (m, 1H, ArH), 6.85-6.80 (m, 4H, ArH), 6.36 (d, *J* = 8.4 Hz, 1H, ArH), 6.30 (d, *J* = 3.3 Hz, 1H, CH), 5.69 (d, *J* = 3.2 Hz, 1H, CH), 4.65 (d, *J* = 16.5 Hz, 1H, CH_2), 4.47 (d, *J* = 16.5 Hz, 1H, CH_2). ^{13}C NMR (100 MHz, d_6-DMSO) δ: 147.4, 147.3, 147.0, 136.8, 132.3, 129.5, 129.3, 128.9, 128.3, 124.0, 122.1, 111.0, 110.4, 109.5, 108.6, 108.5, 71.9, 52.9. HRMS (ESI) Calcd. for $C_{21}H_{16}BrClNO_2S$ ($[M+H]^+$): 459.9768, found: 459.9767, 461.9748.

2-(Benzo[*d*][1,3]dioxol-2-yl)-6-bromo-3-(4-(trifluoromethyl)benzyl)-2,3-dihydrobenzo[*d*]thiazole (**5g**): colorless oil, 0.1201 g, 81%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.67 (d, *J* = 8.1 Hz, 1H, ArH), 7.48 (d, *J* = 8.1 Hz, 1H, ArH), 7.30 (d, *J* = 2.0 Hz, 1H, ArH), 7.01-6.99 (m, 1H, ArH), 6.83-6.78 (m, 4H, ArH), 6.35-6.31 (m, 2H, ArH, CH), 5.75 (d, *J* = 3.3 Hz, 1H, CH), 4.77 (d, *J* = 17.0 Hz, 1H, CH_2), 4.60 (d, *J* = 17.1 Hz, 1H, CH_2). ^{13}C NMR (100 MHz, d_6-DMSO) δ: 147.4, 147.3, 146.9, 142.8, 129.2, 128.3, 128.2, 125.8, 125.8, 124.1, 122.1, 110.7, 110.5, 109.6, 108.6, 72.0, 53.1. HRMS (ESI) Calcd. for $C_{22}H_{16}BrF_3NO_2S$ ($[M+H]^+$): 494.0032, found: 494.0038, 496.0011.

Ethyl 2-(2-(benzo[*d*][1,3]dioxol-2-yl)-6-bromobenzo[*d*]thiazol-3(2*H*)-yl)acetate (**5h**): colorless oil, 0.1201 g, 81%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.26 (d, *J* = 2.0 Hz, 1H, ArH), 7.04-7.02 (m, 1H, ArH), 6.87-6.80 (m, 5H, ArH), 6.44 (d, *J* = 8.5 Hz, 2H, ArH), 6.32 (d, *J* = 3.9 Hz, 1H, CH), 5.67 (d, *J* = 3.9 Hz, 1H, CH), 4.36 (d, *J* = 18.4 Hz, 1H, CH_2), 4.17-4.05 (m, 3H, CH_2, CH_2CH_3), 4.36 (d, *J* = 18.4 Hz, 1H, CH_2), 1.17 (t, *J* = 7.1 Hz, 1H, CH_3). ^{13}C NMR (100 MHz, d_6-DMSO) δ: 169.7, 147.3, 147.3, 147.0, 128.7, 128.2, 123.8, 122.2, 110.4, 109.4, 108.6, 71.8, 61.0, 50.8, 14.5. HRMS (ESI) Calcd. for $C_{18}H_{17}BrNO_4S$ ($[M+H]^+$): 422.0056, found: 422.0058, 424.0036.

1-Benzyl-3-bromo-2-(5-chlorobenzo[*d*][1,3]dioxol-2-yl)-1,2-dihydroquinoline (6a): colorless oil, 0.0992 g, 73%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.40-7.37 (m, 2H, ArH), 7.33 (d, *J* = 8.1 Hz, 2H, ArH), 7.29-7.25 (m, 1H, ArH), 7.16 (d, *J* = 7.3 Hz, 1H, ArH), 7.11 (d, *J* = 2.6 Hz, 1H, ArH), 7.04-7.01 (m, 1H, ArH), 6.84-6.63 (m, 5H, ArH), 6.44 (t, *J* = 2.0 Hz, 1H, CH), 4.93-4.79 (m, 2H, CH_2), 4.37 (d, *J* = 1.7 Hz, 1H, CH); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 149.0, 148.8, 147.3, 147.1, 139.2, 138.5, 137.1, 130.7, 128.9, 128.6, 127.5,

126.8, 126.7, 124.8, 121.6, 121.1, 116.1, 113.0, 108.8, 108.7, 85.1, 53.1, 49.7. HRMS (ESI) Calcd. for $C_{23}H_{18}BrClNO_2$ ([M+H]$^+$): 454.0204, found: 454.0202, 456.0183.

1-Benzyl-3-bromo-2-(5-bromobenzo[*d*][1,3]dioxol-2-yl)-1,2-dihydroquinoline (6b): colorless oil, 0.1032 g, 69%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.40-7.36 (m, 2H, ArH), 7.32 (d, *J* = 7.9 Hz, 2H, ArH), 7.31-7.25 (m, 1H, ArH), 7.16 (d, *J* = 6.7 Hz, 1H, ArH), 7.11 (d, *J* = 3.3 Hz, 1H, ArH), 7.05-7.01 (m, 1H, ArH), 6.91-6.80 (m, 3H, ArH), 6.71-6.60 (m, 2H, ArH), 6.43 (t, *J* = 1.6 Hz, 1H, CH), 4.93-4.78 (m, 2H, CH_2), 4.38 (d, *J* = 1.4 Hz, 1H, CH); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 149.3, 149.1, 147.7, 147.5, 139.2, 138.5, 137.0, 130.7, 128.9, 128.6, 127.5, 126.8, 126.7, 124.1, 121.6, 116.1, 113.0, 112.7, 112.0, 111.4, 111.3, 109.4, 85.1, 53.1, 49.7. HRMS (ESI) Calcd. for $C_{23}H_{18}Br_2NO_2$ ([M+H]$^+$): 499.9678, found: 499.9677.

1-Benzyl-3-bromo-2-(1,3-dioxolan-2-yl)-1,2-dihydroquinoline (6c): colorless oil, 0.0389 g, 35%, dr = 1:1, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.31-7.19 (m, 10H, ArH), 7.08-6.97 (m, 6H, ArH), 6.67-6.57 (m, 4H, ArH), 5.00 (s, 1H, CH), 4.88-4.80 (m, 3H, CH), 4.74 (d, *J* = 11.8 Hz, 2H, CH_2), 4.64-4.50 (m, 3H, CH), 4.38 (d, *J* = 6.9 Hz, 1H, CH), 4.22-4.18 (m, 1H, CH), 4.07-4.02 (m, 1H, CH), 3.92-3.80 (m, 3H, CH), 3.70-3.67 (m, 1H, CH); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 142.4, 141.8, 138.7, 138.5, 130.5, 129.9, 129.7, 129.5, 128.9, 127.4, 127.3, 127.2, 127.1, 123.3, 122.6, 117.9, 114.0, 113.9, 111.9, 110.5, 95.0, 94.6, 77.2, 76.6, 66.6, 66.3, 66.2, 65.9, 54.9, 54.6. HRMS (ESI) Calcd. for $C_{19}H_{19}BrNO_2$ ([M+H]$^+$): 372.0594, found: 372.0598, 374.0576.

1-Benzyl-3-bromo-2-(tetrahydrofuran-2-yl)-1,2-dihydroquinoline (6d): colorless oil, 0.0343 g, 31%, dr = 3:2, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.34-7.19 (m, 7H, ArH), 7.09-6.94 (m, 4H, ArH), 6.89-6.69 (m, 2H, ArH), 6.63-6.51 (m, 1H, ArH), 4.81-4.74 (m, 2H, CH_2), 4.56-4.51 (m, 1H, CH), 4.16-4.09 (m, 1H, CH), 3.99-3.79 (m, 2H, CH_2), 3.65-3.47 (m, 2H, CH_2), 1.99-1.53 (m, 5H, CH_2), 1.44-1.37 (m, 1H, CH), 1.19 (s, 2H, CH_2),; ^{13}C NMR (100 MHz, d_6-DMSO) δ: 138.5, 134.7, 130.8, 129.6, 129.0, 128.9, 128.8, 127.9, 127.5, 127.4, 127.2, 126.9, 121.4, 117.3, 112.7, 110.0, 81.1, 80.7, 79.9, 68.1, 67.9, 67.5, 54.9, 54.3, 53.0, 49.2, 30.8, 29.4, 28.9, 26.9, 26.5, 25.9, 25.7. HRMS (ESI) Calcd. for $C_{20}H_{21}BrNO$ ([M+H]$^+$): 370.0801, found: 370.0800, 372.0781.

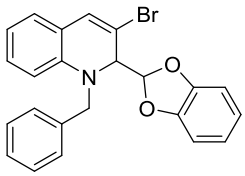
1-Benzyl-3-bromo-2-(tetrahydro-2*H*-pyran-2-yl)-1,2-dihydroquinoline (6e): colorless oil, 0.0310 g, 27%, dr = 3:2 ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.35-7.18 (m, 6H, ArH), 7.07-6.84 (m, 4H, ArH), 6.73-6.51 (m, 2H, ArH), 4.88-4.82 (m, 1H, CH), 4.77-4.73 (m, 1H, CH_2), 4.54-4.37 (m, 1H, CH_2), 4.19 (d, *J* = 6.7 Hz, 1H, CH), 3.98-3.85 (m, 1H, CH_2), 3.52-3.45 (m, 1H, CH_2), 1.76-1.64 (m, 2H, CH_2), 1.53-1.39 (m, 2H, CH_2), 1.21-1.16 (m, 2H, CH_2),; ^{13}C NMR (100 MHz, d_6-DMSO) δ: 141.5, 138.5, 134.7, 128.4, 128.4, 126.9, 126.7, 126.5, 120.9, 120.6, 116.9, 116.7, 113.2, 112.2, 104.5, 80.8, 78.8, 69.1, 68.6, 68.2, 67.6, 54.7, 53.7, 50.4, 45.7, 30.4, 28.9, 28.0, 27.4, 25.9, 25.5, 22.6, 22.6. HRMS (ESI) Calcd. for $C_{21}H_{23}BrNO$ ($[M+H]^+$): 384.0958, found: 384.0955, 386.0937.

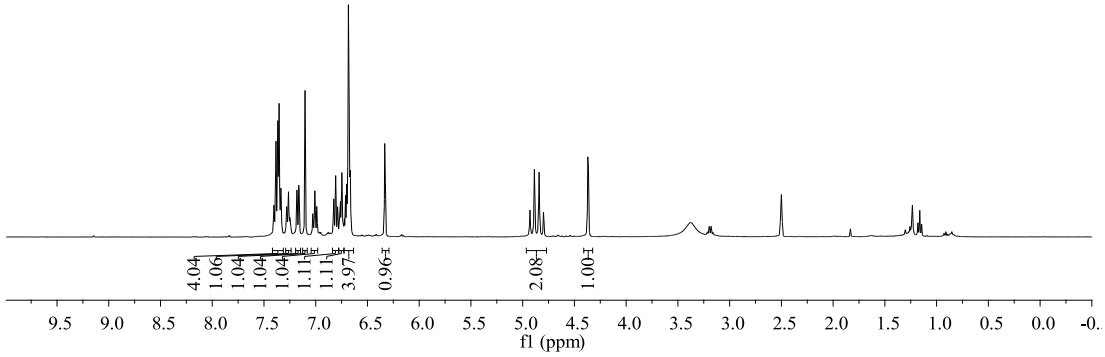
2,8-Bis(benzo[*d*][1,3]dioxol-2-yl)-1-benzyl-3-methyl-1,2-dihydroquinoline (9): colorless oil, 0.0841 g, 59%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.28-7.22 (m, 5H, ArH), 7.19-7.15 (m, 1H, ArH), 7.08 (d, *J* = 7.8 Hz, 1H, ArH), 7.03-7.01 (m, 1H, ArH), 6.92-6.87 (m, 4H, ArH), 6.81-6.77 (m, 1H, ArH), 6.75-6.72 (m, 1H, ArH), 6.63 (d, *J* = 7.5 Hz, 1H, ArH), 6.43-6.39 (m, 2H, ArH), 6.19 (d, *J* = 4.7 Hz, 1H, CH), 4.67 (d, *J* = 16.1 Hz, 1H, CH_2), 4.49 (d, *J* = 16.0 Hz, 1H, CH_2), 4.25 (d, *J* = 4.7 Hz, 1H, CH), 2.12 (s, 3H, CH_3); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 147.9, 147.4, 147.0, 143.1, 138.5, 135.4, 128.8, 128.3, 127.5, 127.4, 125.7, 124.3, 122.5, 122.4, 122.0, 122.0, 121.3, 117.1, 113.4, 109.9, 109.6, 109.3, 108.8, 108.7, 107.5, 65.5, 54.3, 18.6. HRMS (ESI) Calcd. for $C_{31}H_{25}NNaO_4$ ($[M+Na]^+$): 498.1676, found: 498.1675.

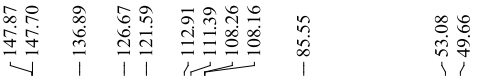
2-(Benzo[*d*][1,3]dioxol-2-yl)-1-benzyl-3-(4-methoxyphenyl)-1,2-dihydroquinoline (11): colorless oil, 0.0814 g, 91%, ^{1}H NMR (400 MHz, d_6-DMSO) δ: 7.46-7.35 (m, 6H, ArH), 7.28-7.24 (m, 2H, ArH), 7.21 (s, 1H, ArH), 7.02-6.98 (m, 1H, ArH), 6.88-6.82 (m, 2H, ArH), 6.81-6.78 (m, 1H, ArH), 6.69-6.59 (m, 4H, ArH), 6.51-6.49 (m, 1H, ArH), 6.12 (d, *J* = 2.8 Hz, 1H, ArH), 5.01-4.91 (m, 2H, CH_2), 4.69 (d, *J* = 2.7 Hz, 1H, CH), 3.74 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, d_6-DMSO) δ: 157.4, 147.9, 147.7, 140.3, 138.8, 132.6, 131.6, 131.2, 128.9, 128.0, 127.4, 126.9, 125.3, 121.4, 121.0, 117.8, 114.3, 112.3, 111.8, 108.1, 108.0, 103.3, 55.5, 53.8, 44.0.. HRMS (ESI) Calcd. for $C_{30}H_{26}NO_3$ ($[M+H]^+$): 448.1907, found: 448.1911.

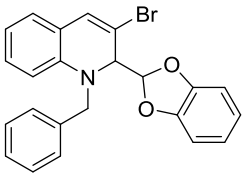
Spectroscopic Data for Products

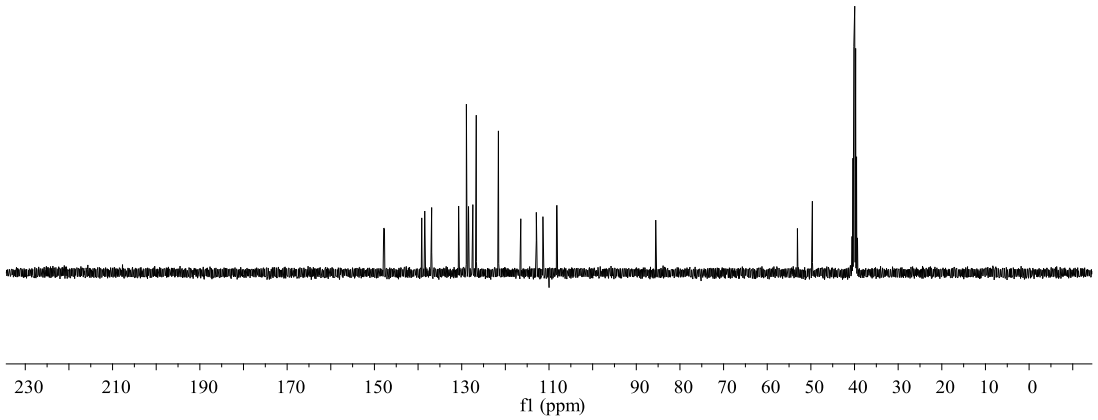
3a











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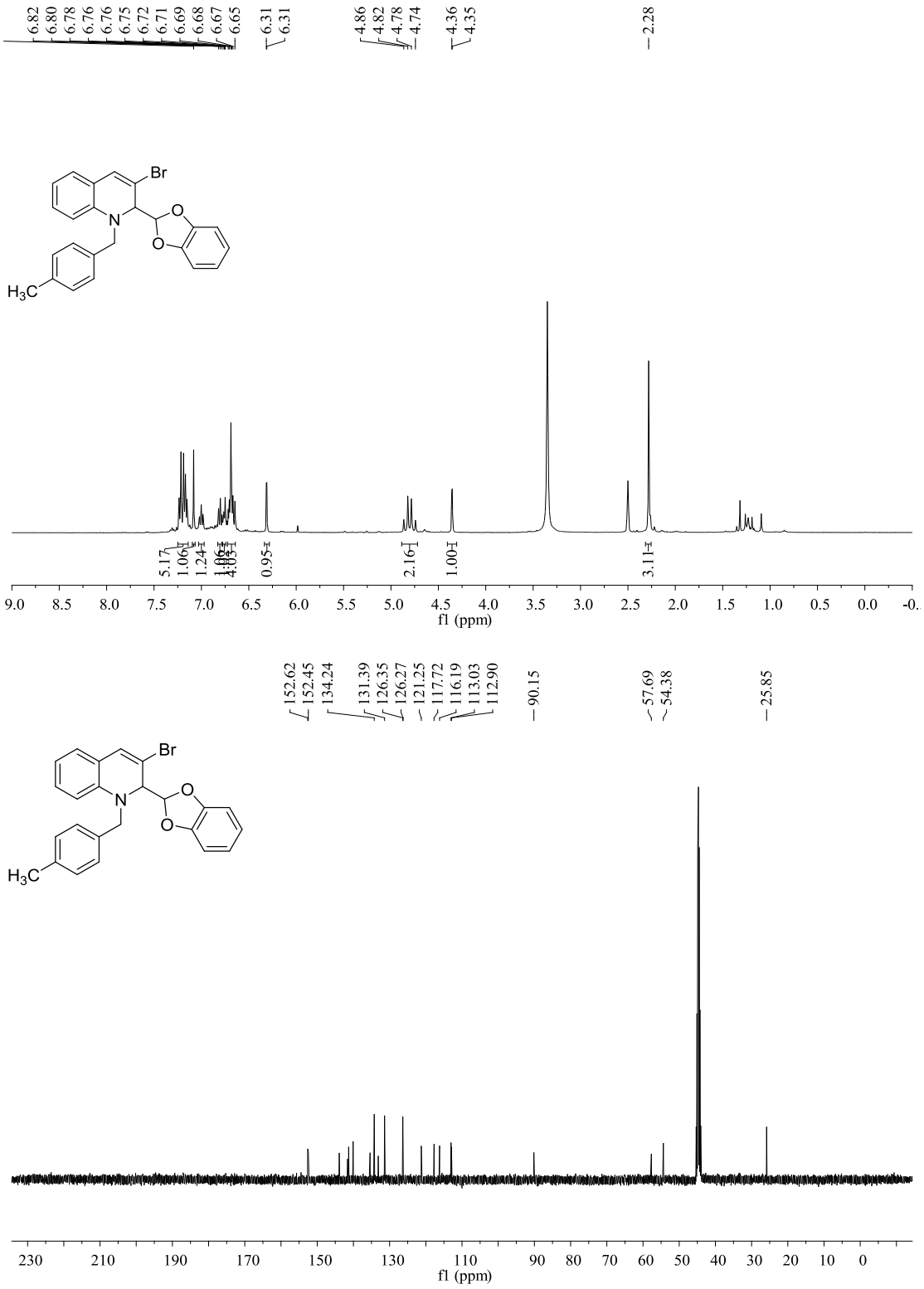
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4.78
4.74
4.36
4.35
2.28
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O
O
H3C
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1.06
1.24
0.95
2.16
1.00
3.11
fl (ppm)
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152.45
134.24
131.39
126.35
126.27
121.25
117.72
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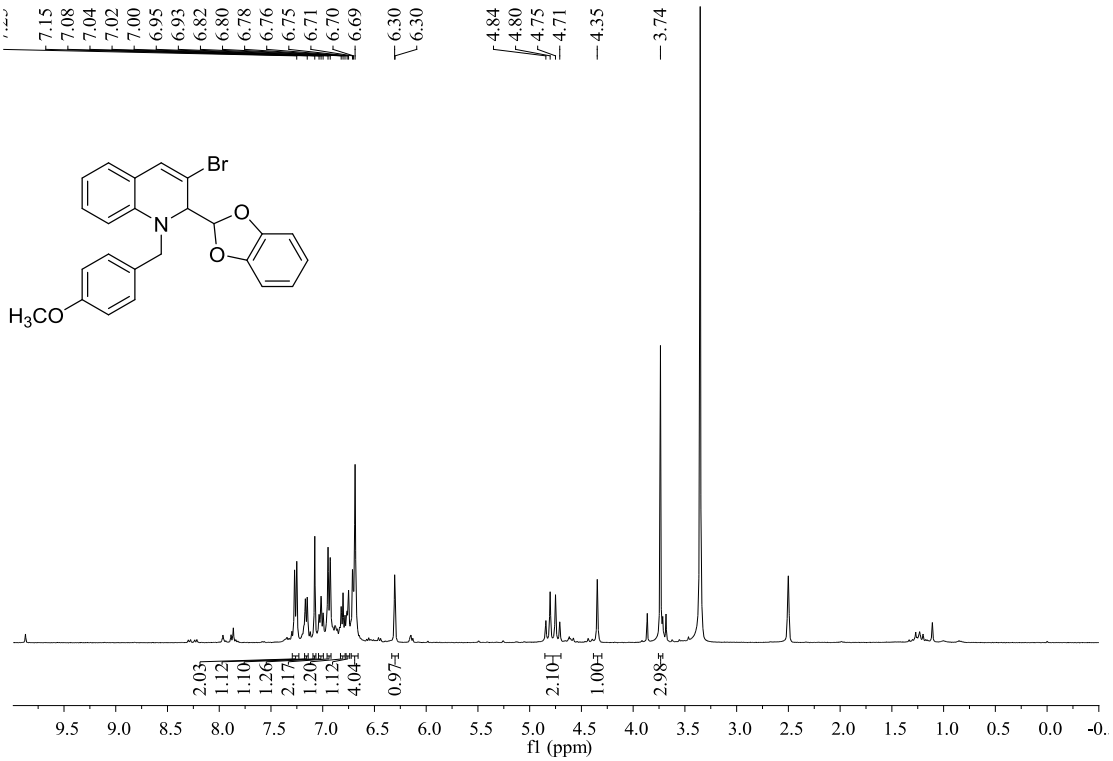
O
H3C
fl (ppm)

3c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3.74
Br
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O
O
H3CO
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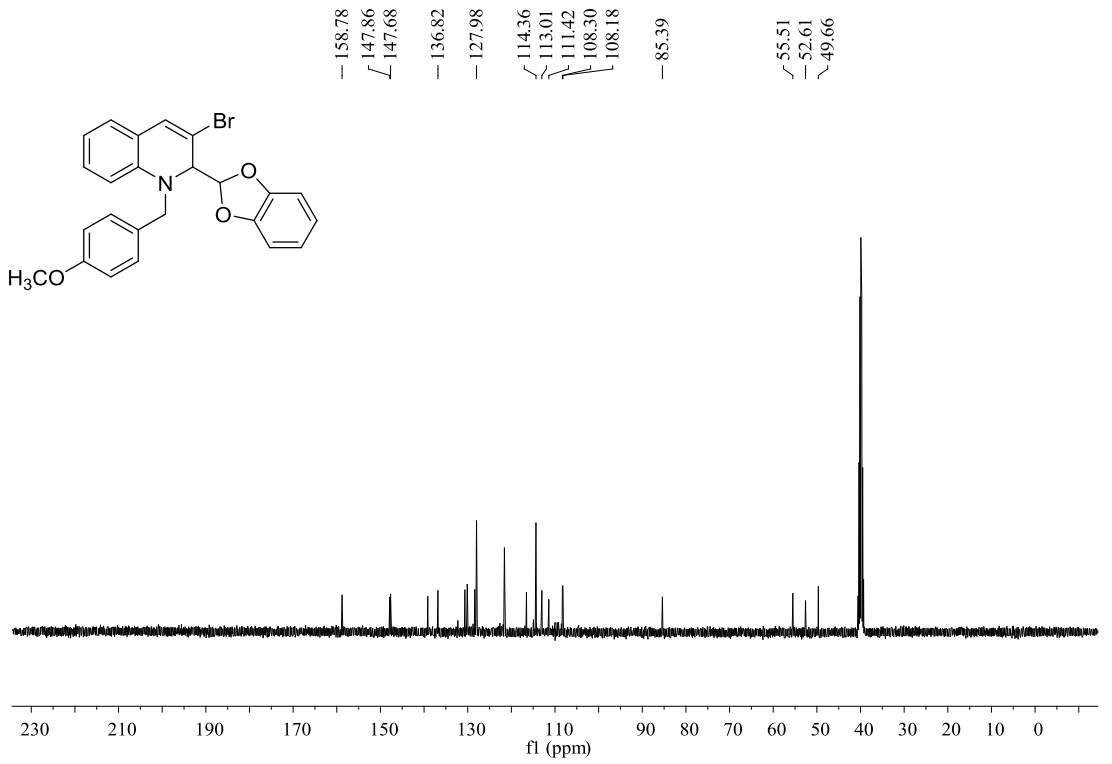
fl (ppm)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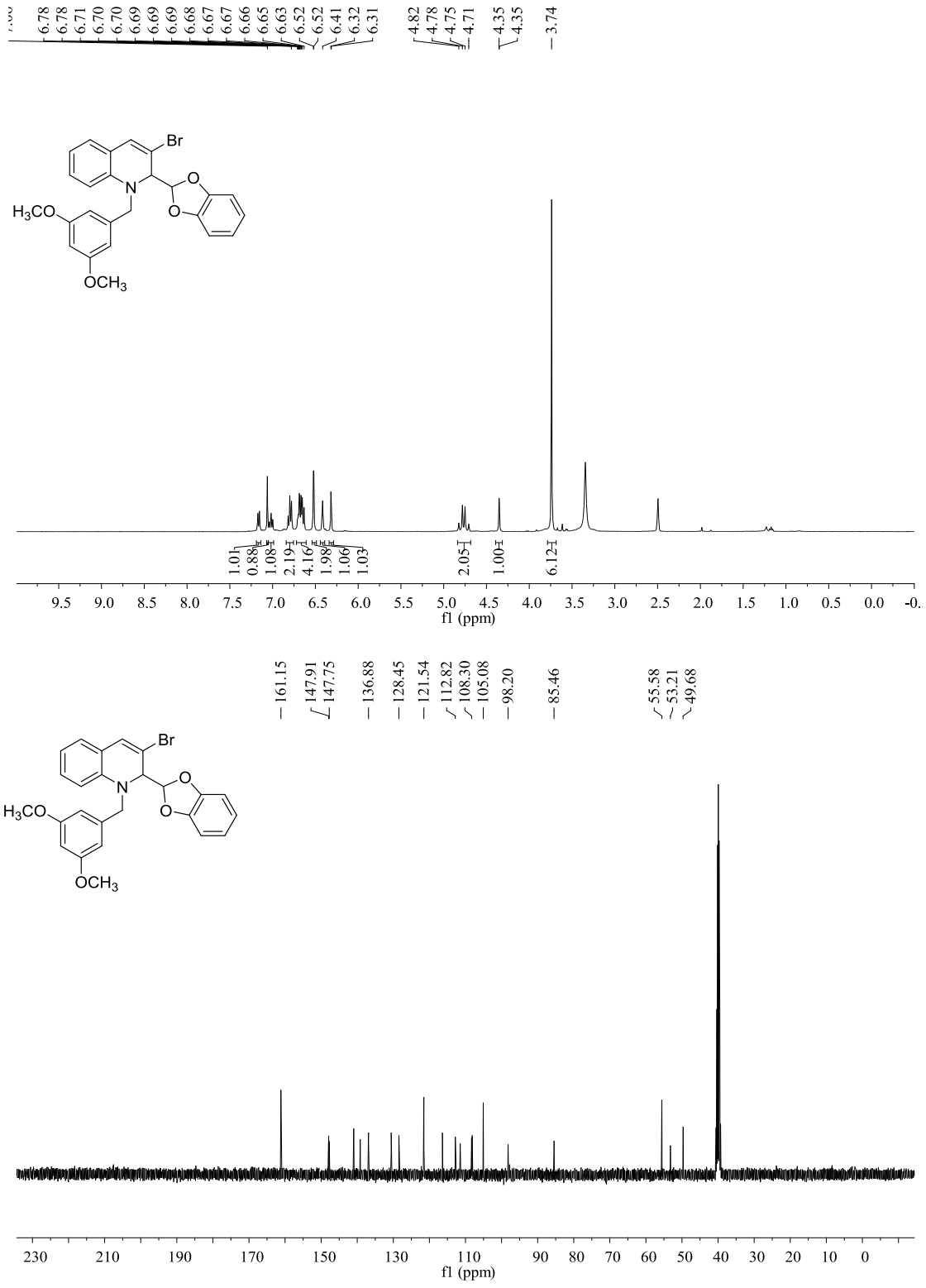
O
O
H3CO
fl (ppm)

3d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4.35
4.35
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O
O
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OCH3
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1.08
2.19
4.16
1.98
1.06
1.03
2.05
1.00
6.12
fl (ppm)
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147.91
147.75
136.88
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108.30
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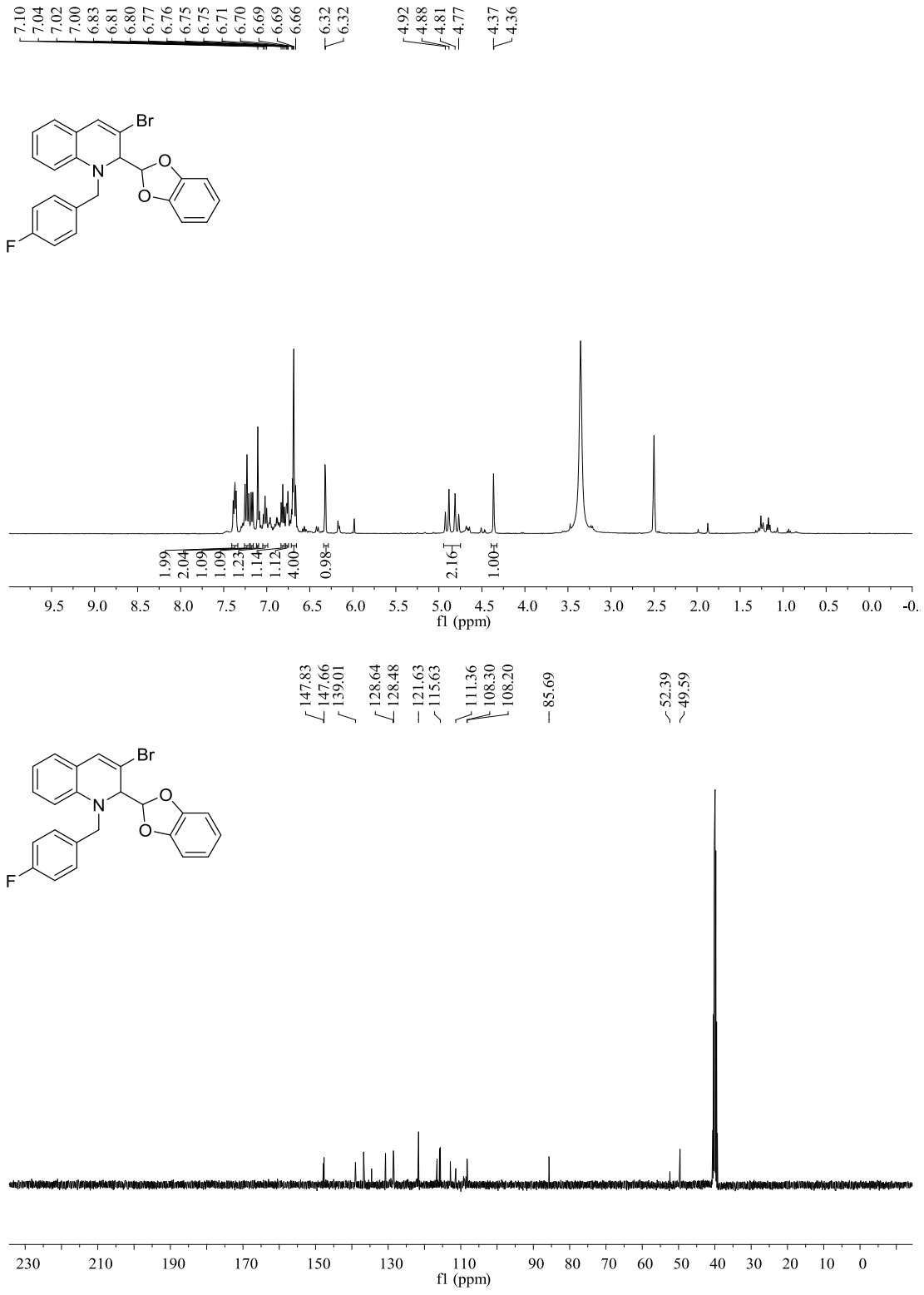
fl (ppm)

3e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6.69
6.66
6.32
6.32
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4.88
4.81
4.77
4.37
4.36
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N
O
O
F
1.99
2.04
1.09
1.09
1.23
1.14
1.12
4.00
0.98
2.16
1.00
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f1 (ppm)
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147.66
139.01
128.64
128.48
121.63
115.63
111.36
108.30
108.20
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52.39
49.59
Br
N
O
O
F
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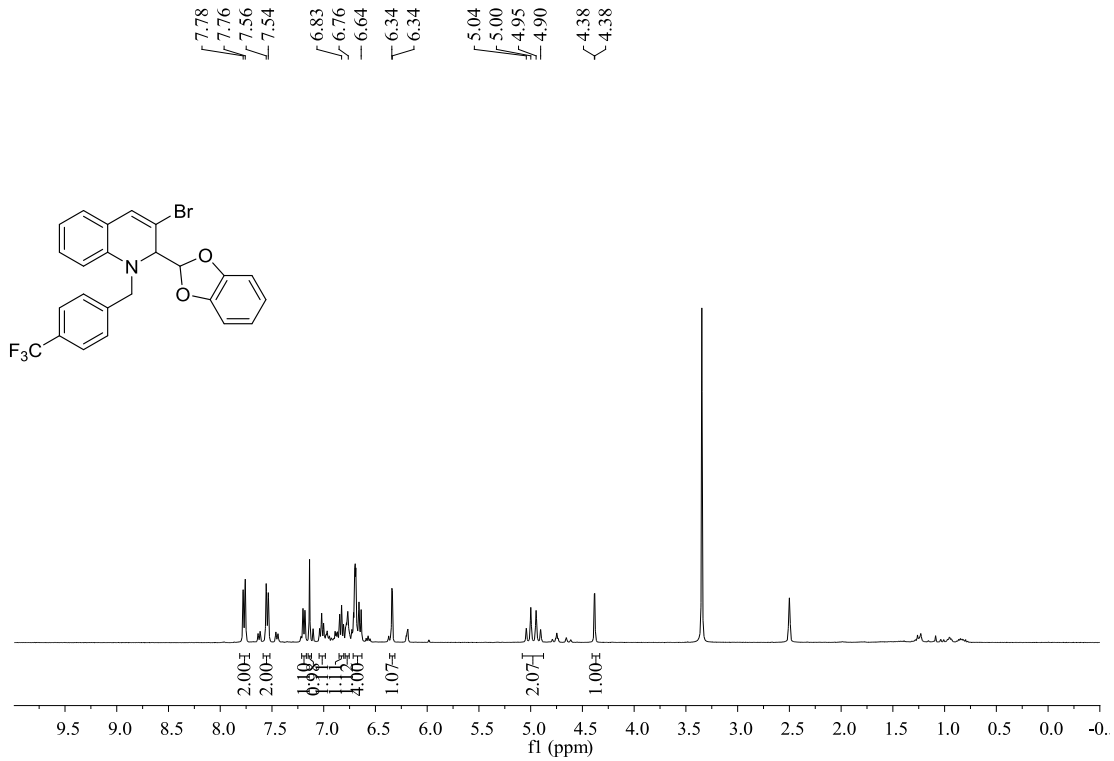
f1 (ppm)

3f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N
O
O
F3C
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2.00
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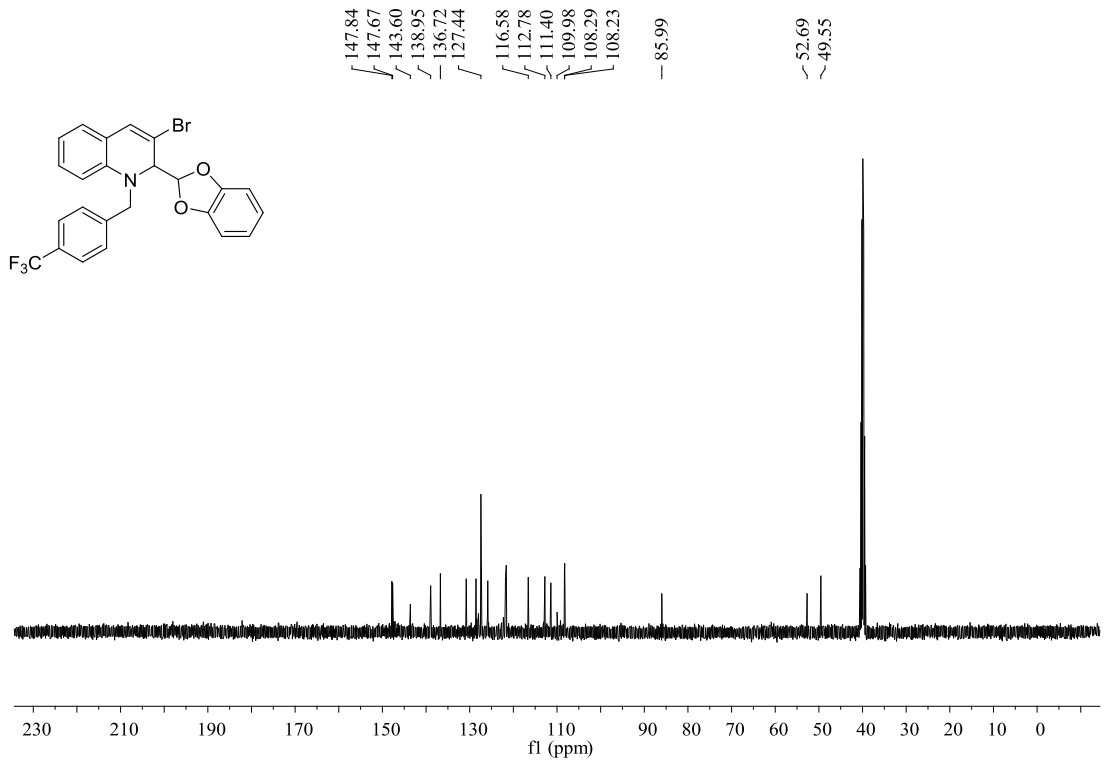
1.00
fl (ppm)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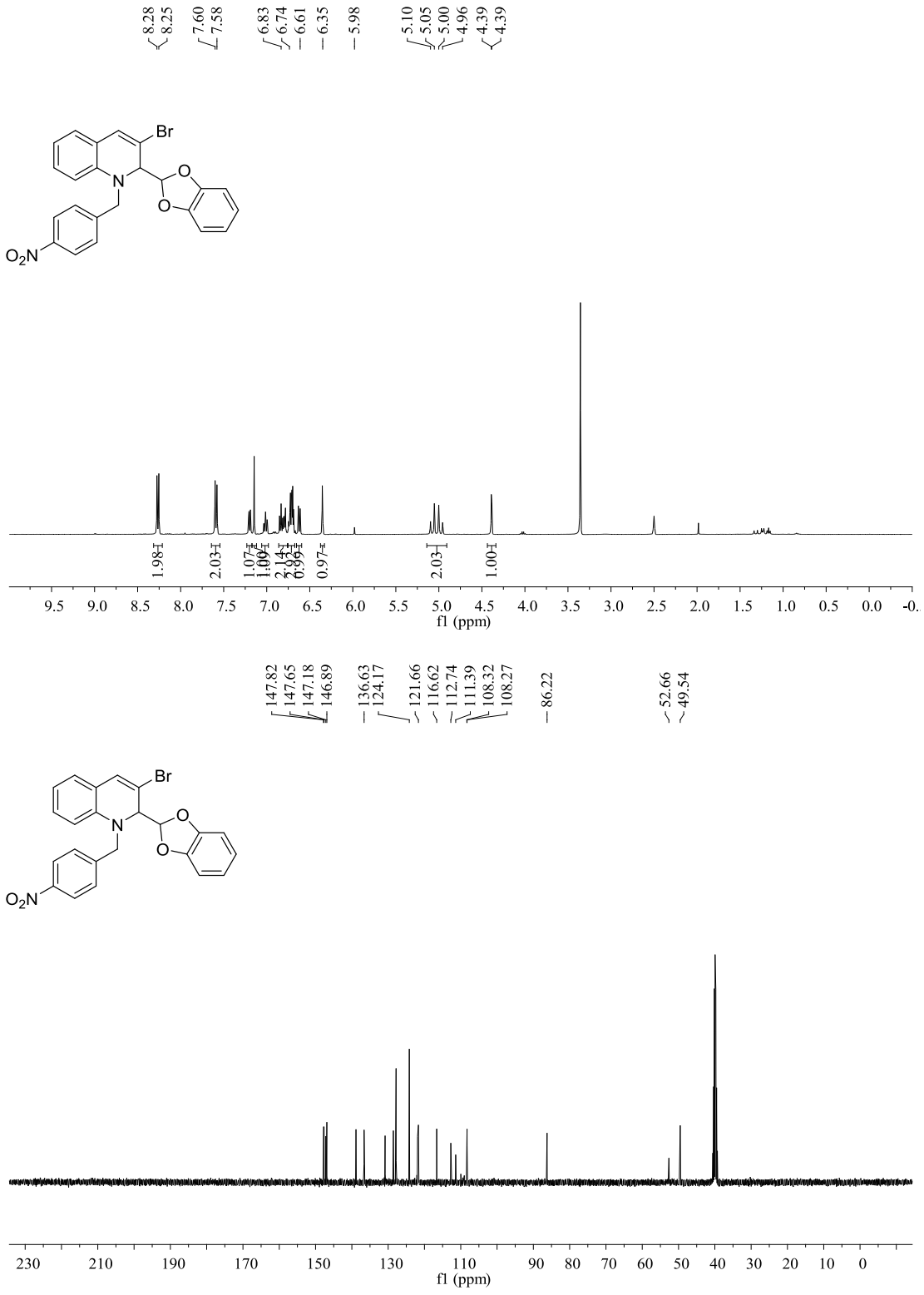
52.69
49.55
Br
N
O
O
F3C
fl (ppm)

3g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5.05
5.00
4.96
4.39
4.39
Br
N
O
O
O2N
1.98
2.03
1.07
1.00
2.14
2.04
0.96
0.97
2.03
1.00
9.5 9.0 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)
147.82
147.65
147.18
146.89
136.63
124.17
121.66
116.62
112.74
111.39
108.32
108.27
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Br
N
O
O
O2N
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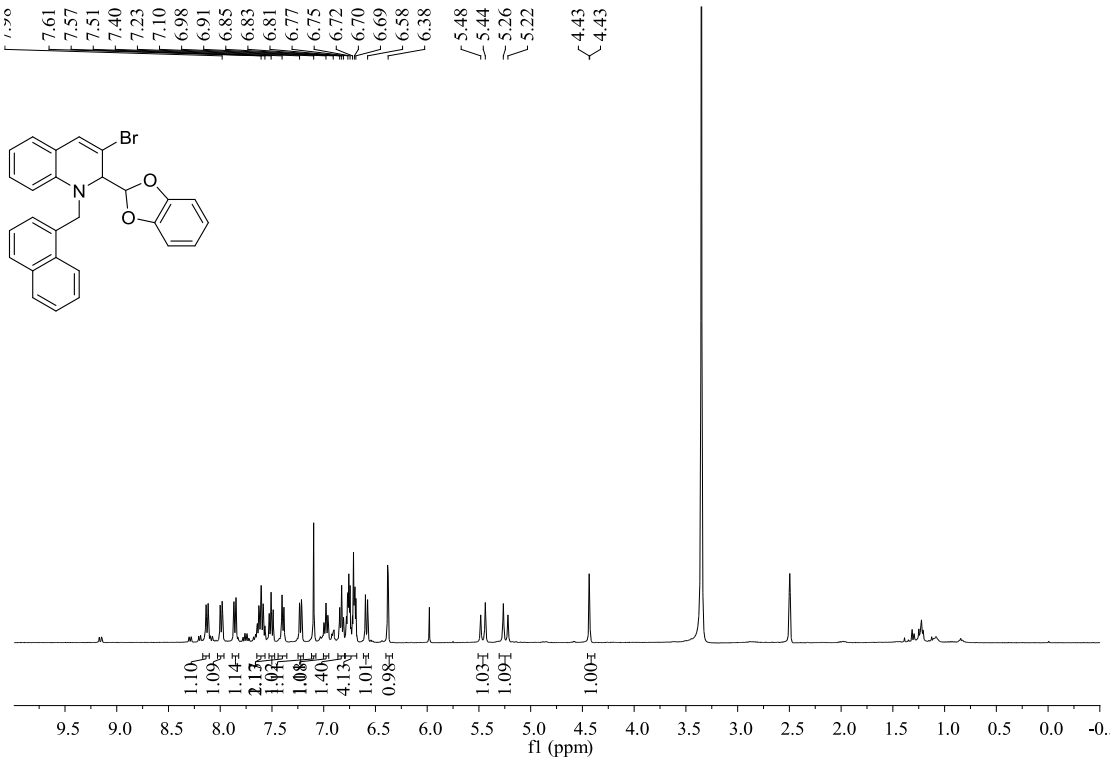
f1 (ppm)

3h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5.44
5.26
5.22
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4.43
Br
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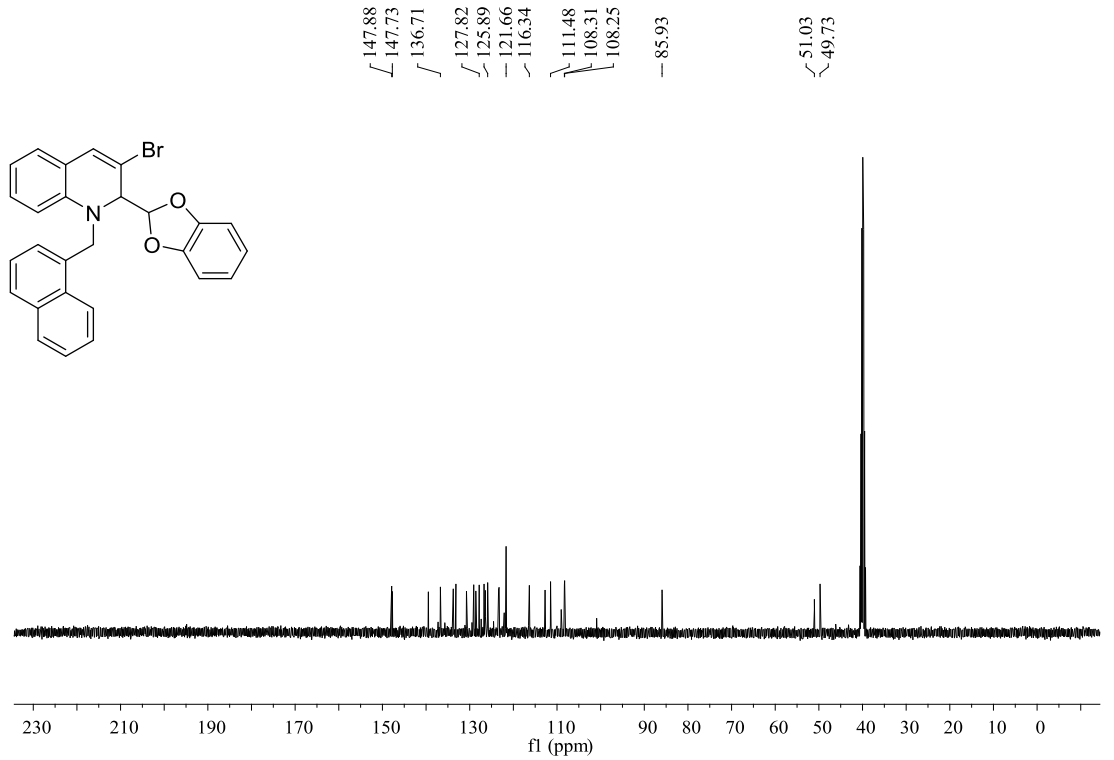
O
N
1.10
1.09
1.14
1.01
0.98
1.03
1.09
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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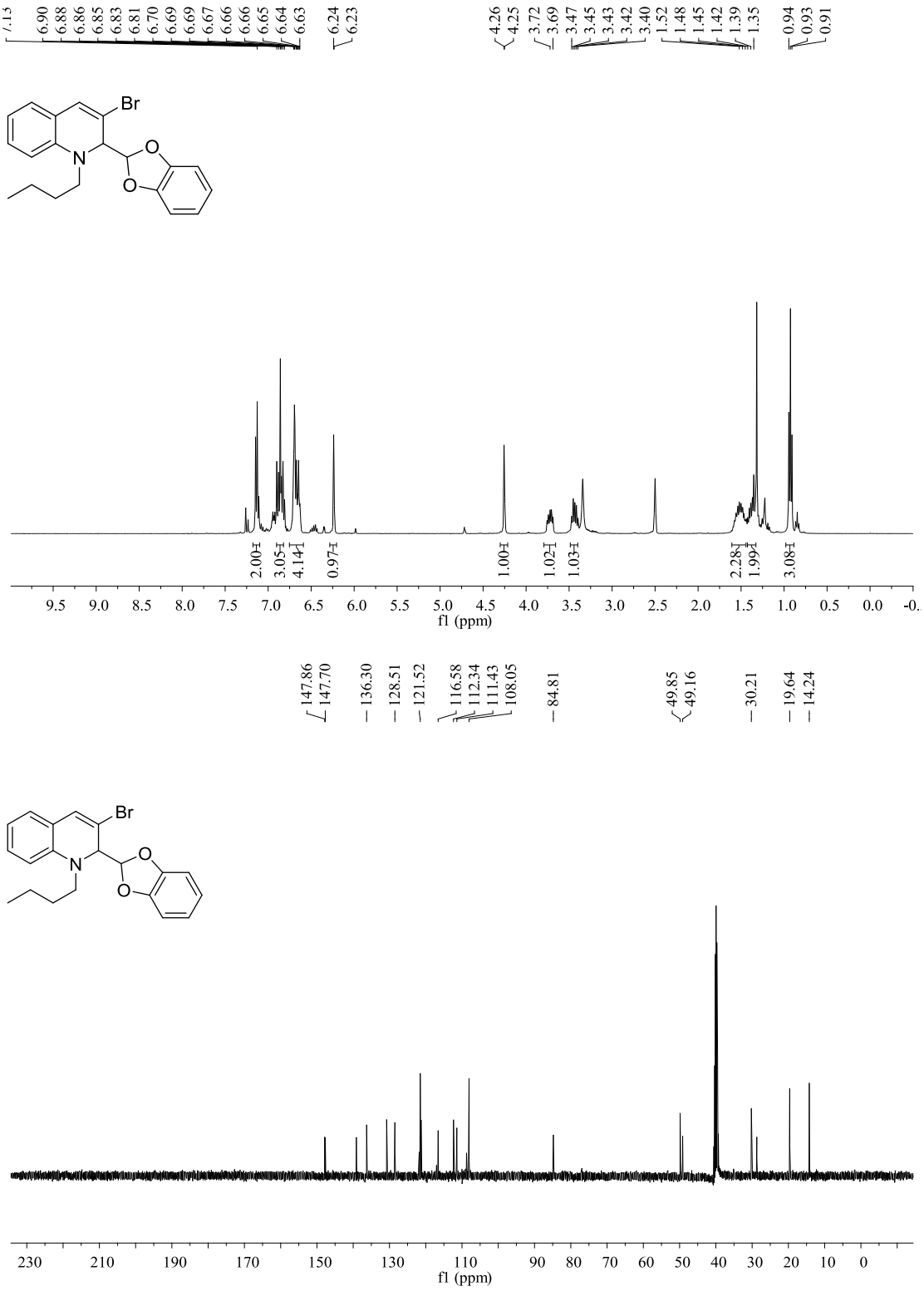
f1 (ppm)

3i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1.48
1.45
1.42
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O
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3.05
4.14
0.97
1.00
1.02
1.03
2.28
1.99
3.08
9.5 9.0 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)
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O
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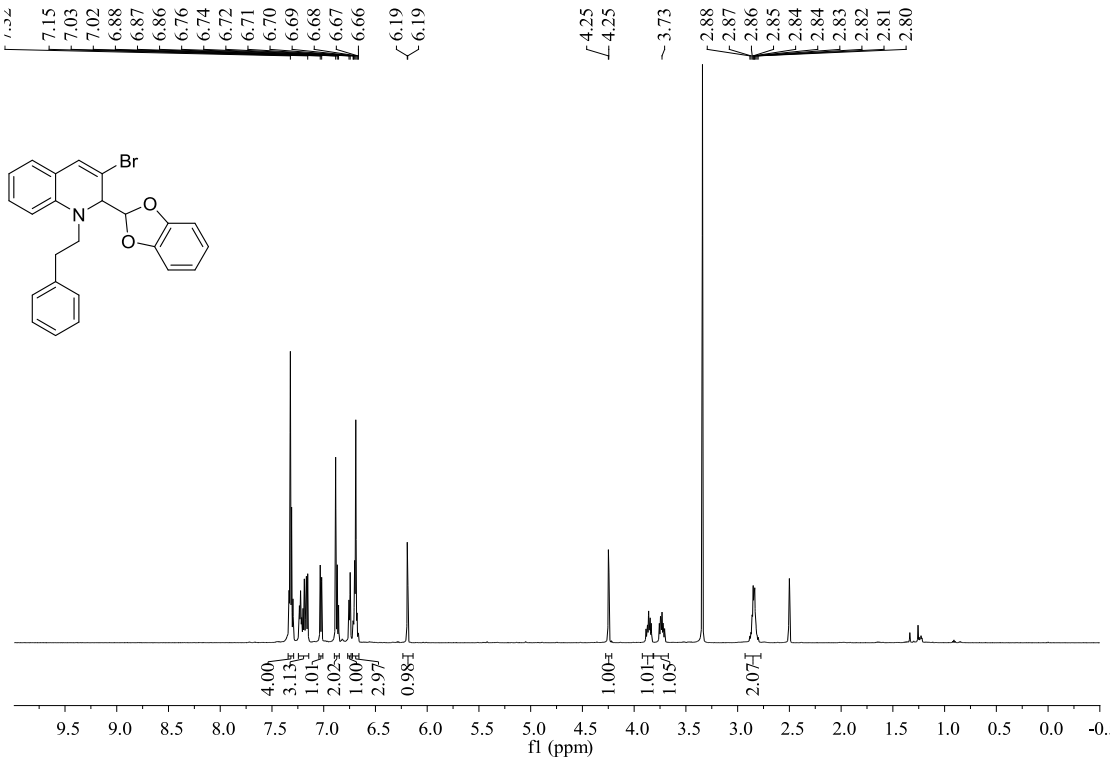
f1 (ppm)

3j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2.02
1.00
2.97
0.98
1.00
1.01
1.05
2.07
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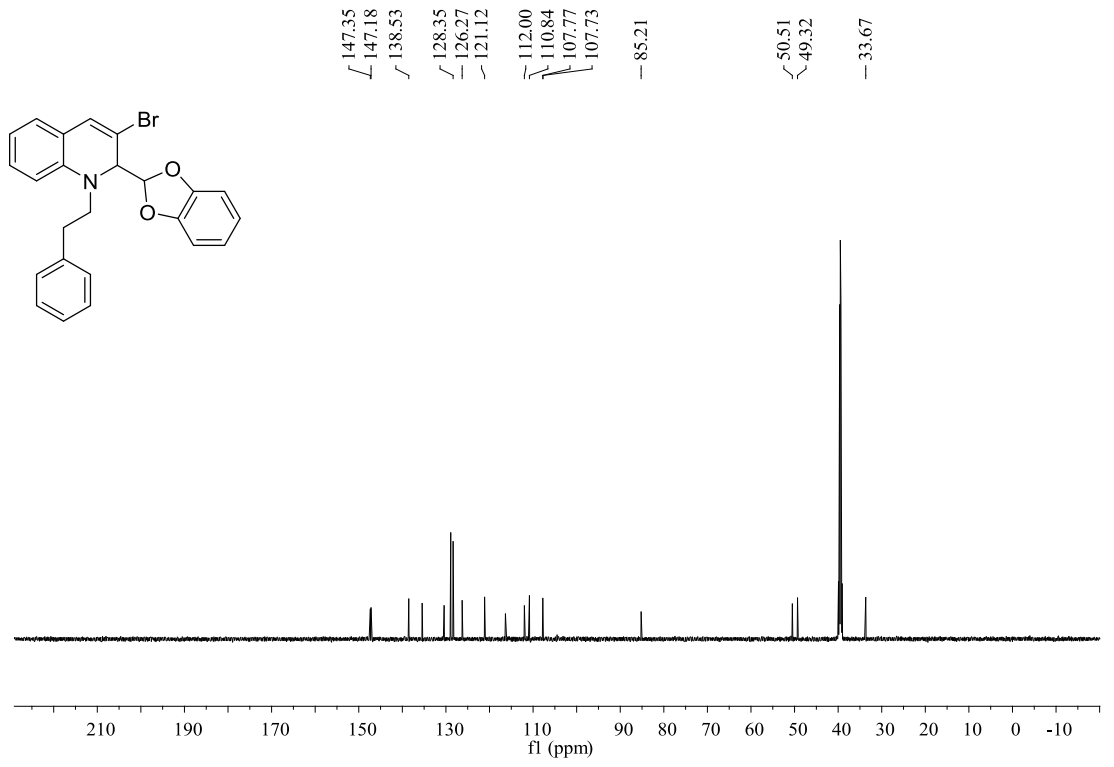
f1 (ppm)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33.67
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O
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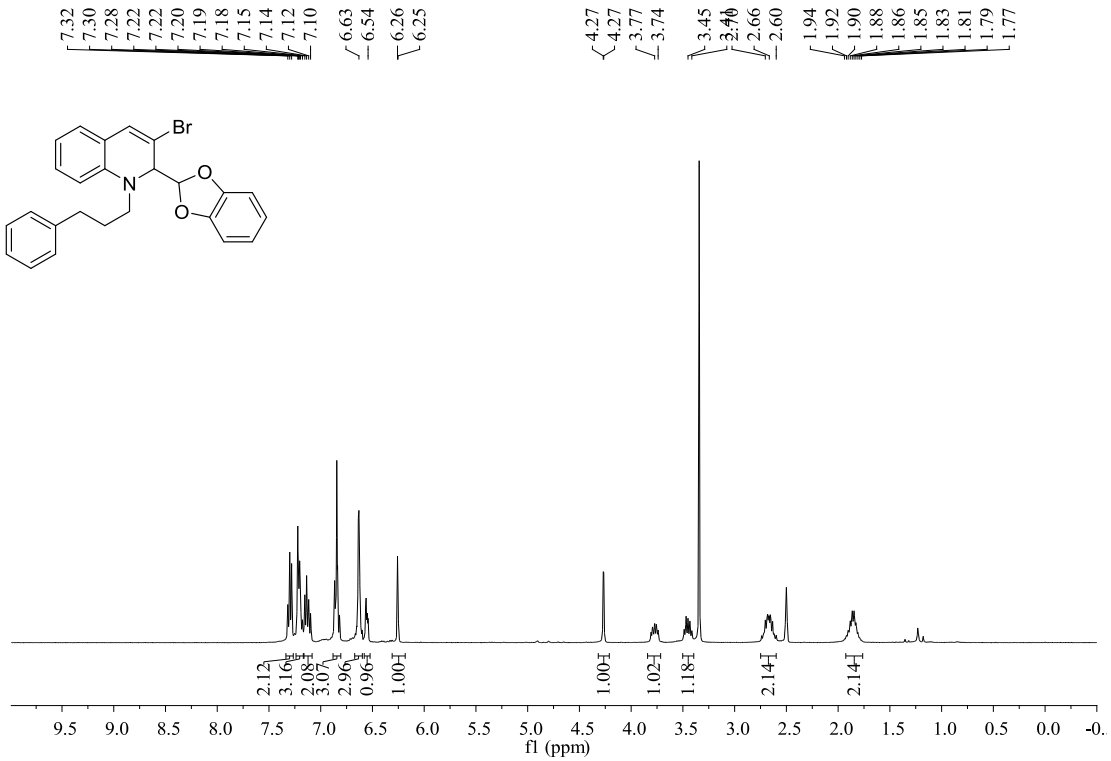
f1 (ppm)

3k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1.85
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1.81
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O
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3.16
2.08
3.07
2.96
0.96
1.00
1.00
1.02
1.18
2.14
2.14
9.5 9.0 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
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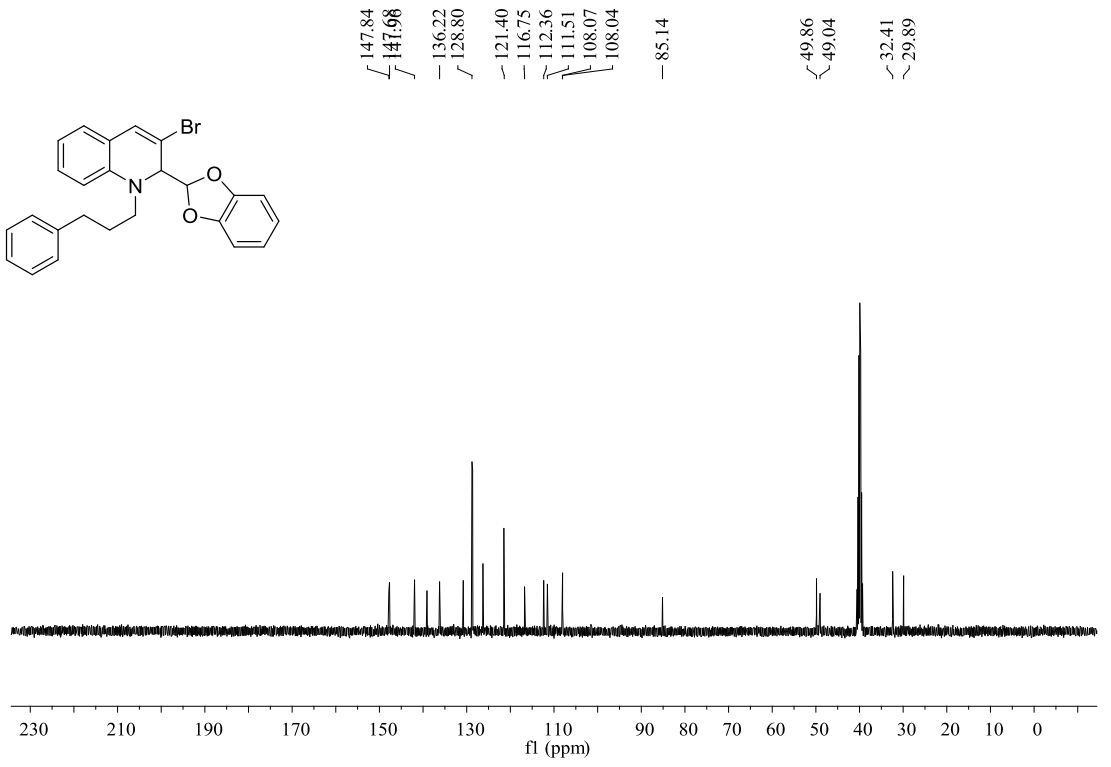
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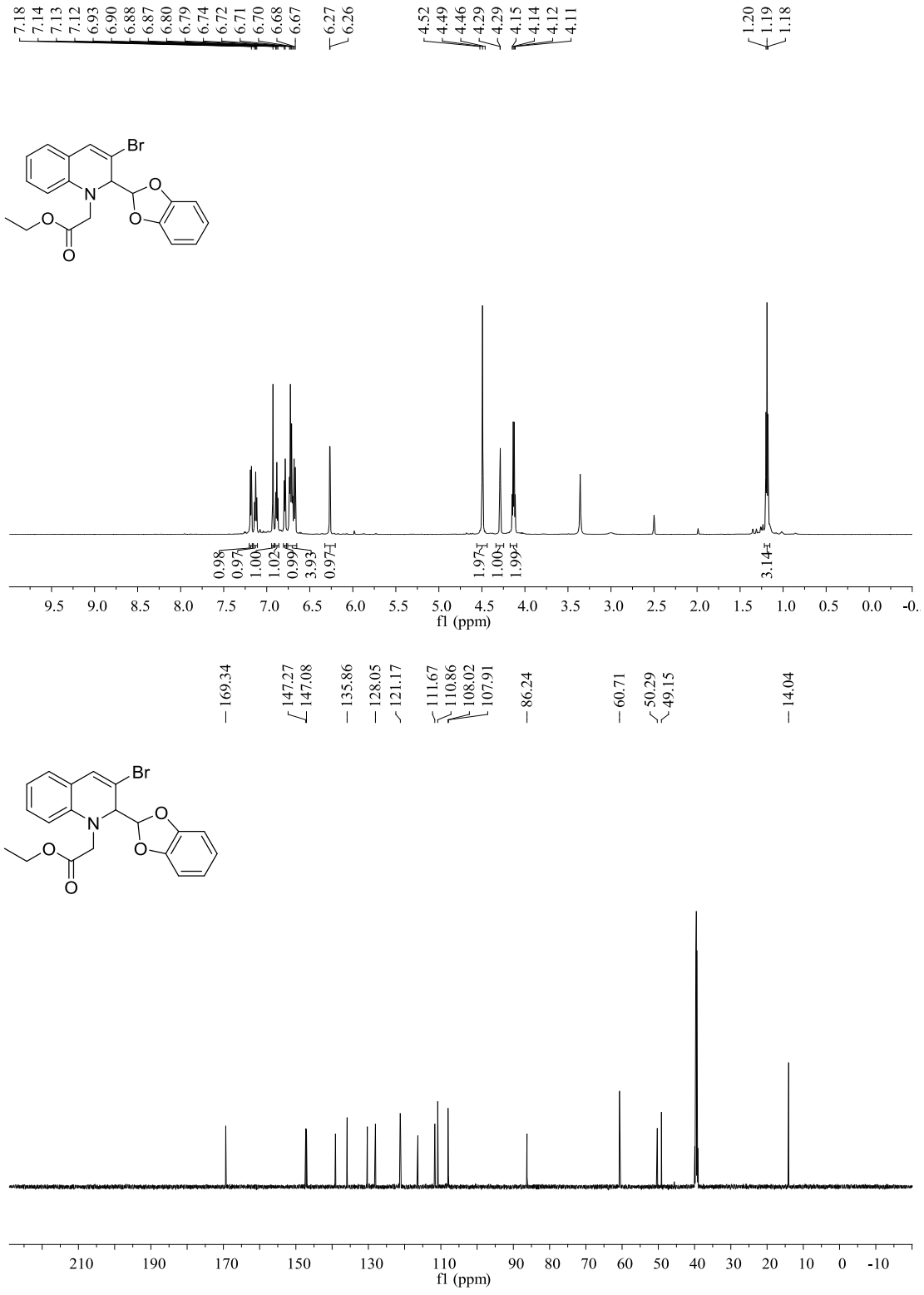
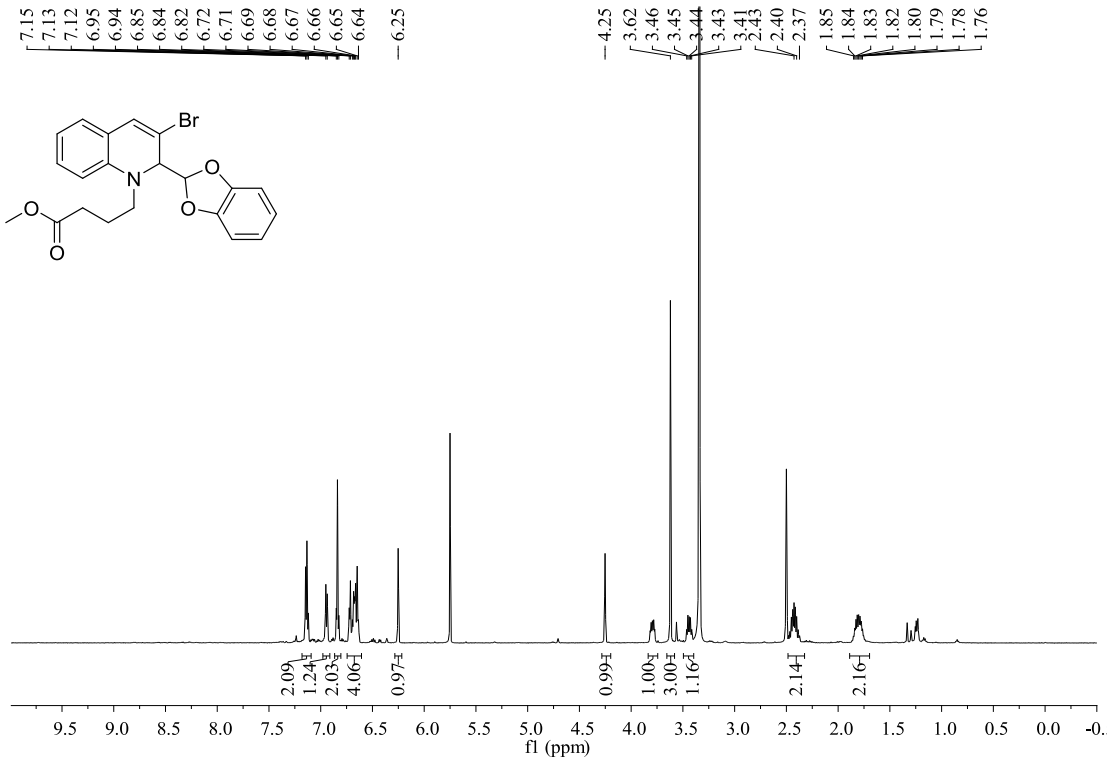
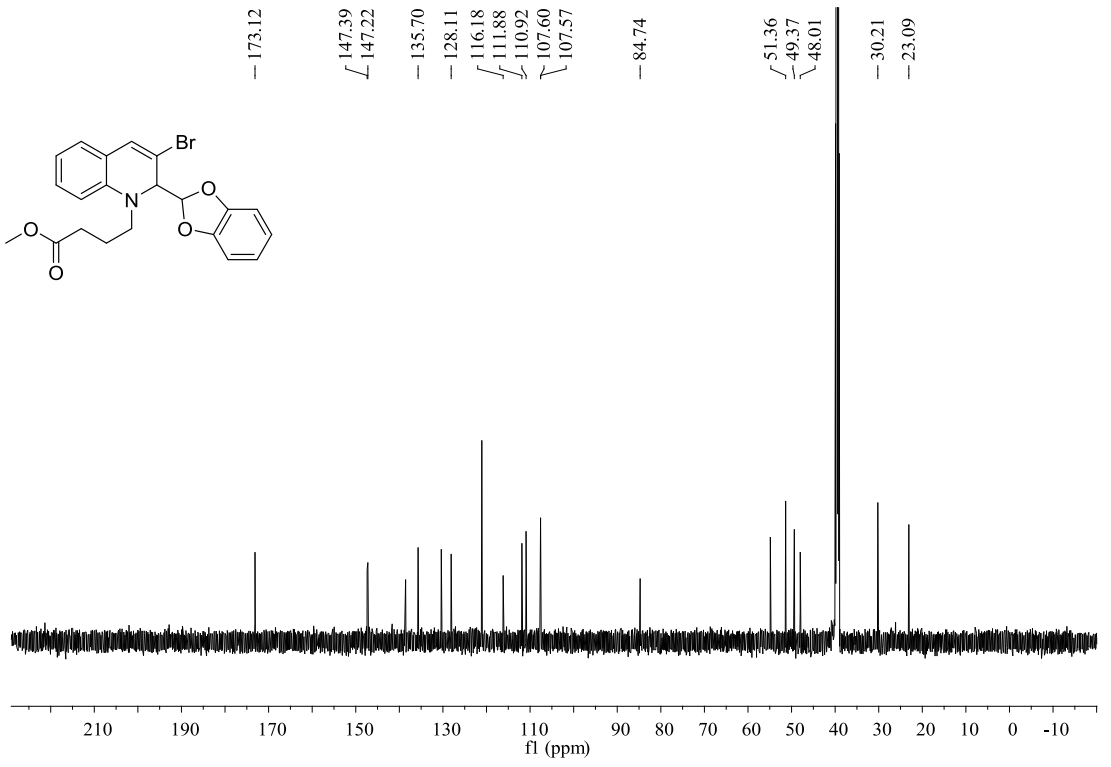
O
O
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3l

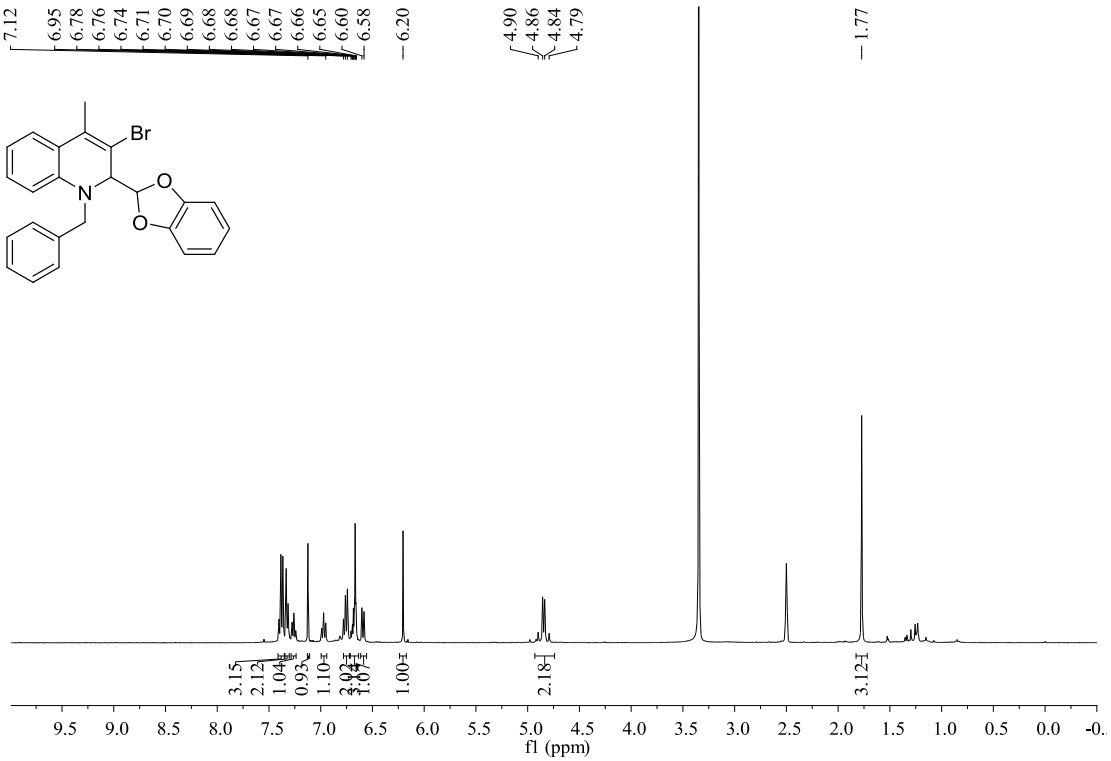

7.18
7.14
7.13
7.12
6.93
6.90
6.88
6.87
6.80
6.79
6.74
6.72
6.71
6.70
6.68
6.67
6.27
6.26
4.52
4.49
4.46
4.29
4.29
4.15
4.14
4.12
4.11
1.20
1.19
1.18
Br
N
O
O
O
O
O
0.98
0.97
1.00
1.02
0.99
3.93
0.97
1.97
1.00
1.99
3.14
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
169.34
147.27
147.08
135.86
128.05
121.17
111.67
110.86
108.02
107.91
86.24
60.71
50.29
49.15
14.04
Br
N
O
O
O
O
O
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

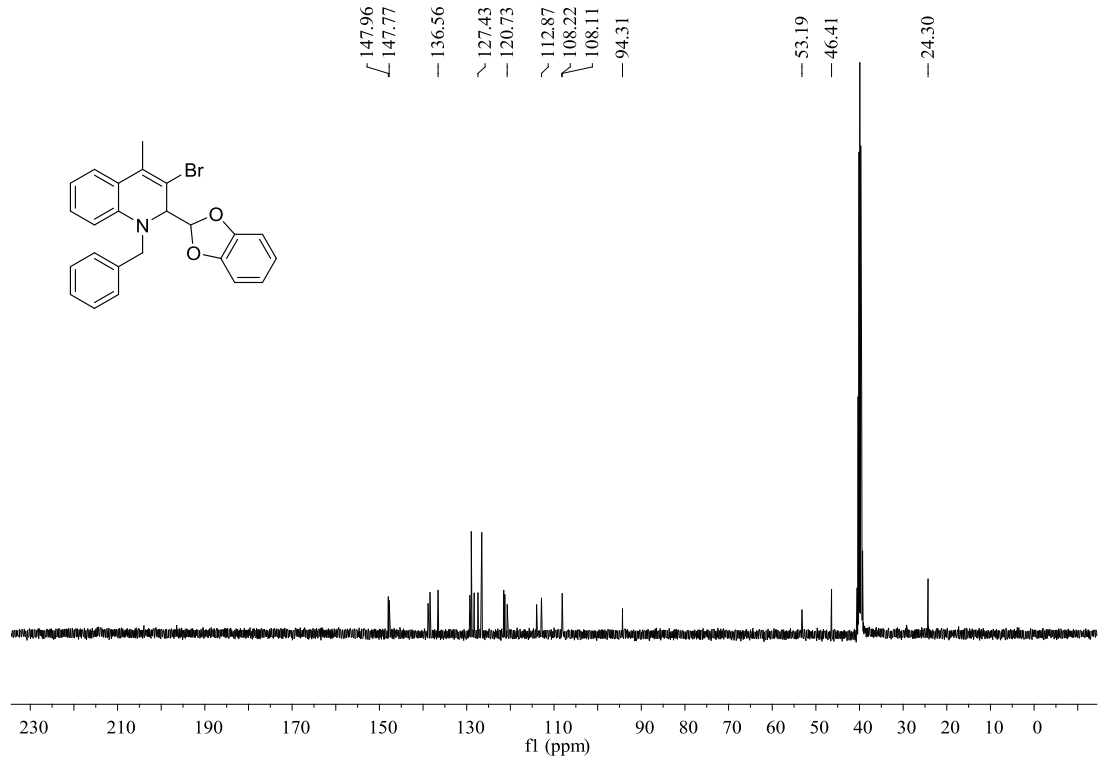
3m


7.15
7.13
7.12
6.95
6.94
6.85
6.84
6.82
6.72
6.71
6.69
6.68
6.67
6.66
6.65
6.64
6.25
4.25
3.62
3.46
3.45
3.44
3.43
3.41
2.43
2.40
2.37
1.85
1.84
1.83
1.82
1.80
1.79
1.78
1.76
Br
O
N
O
O
O
O
2.09
1.24
2.03
4.06
0.97
0.99
1.00
3.00
1.16
2.14
2.16
9.5 9.0 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)

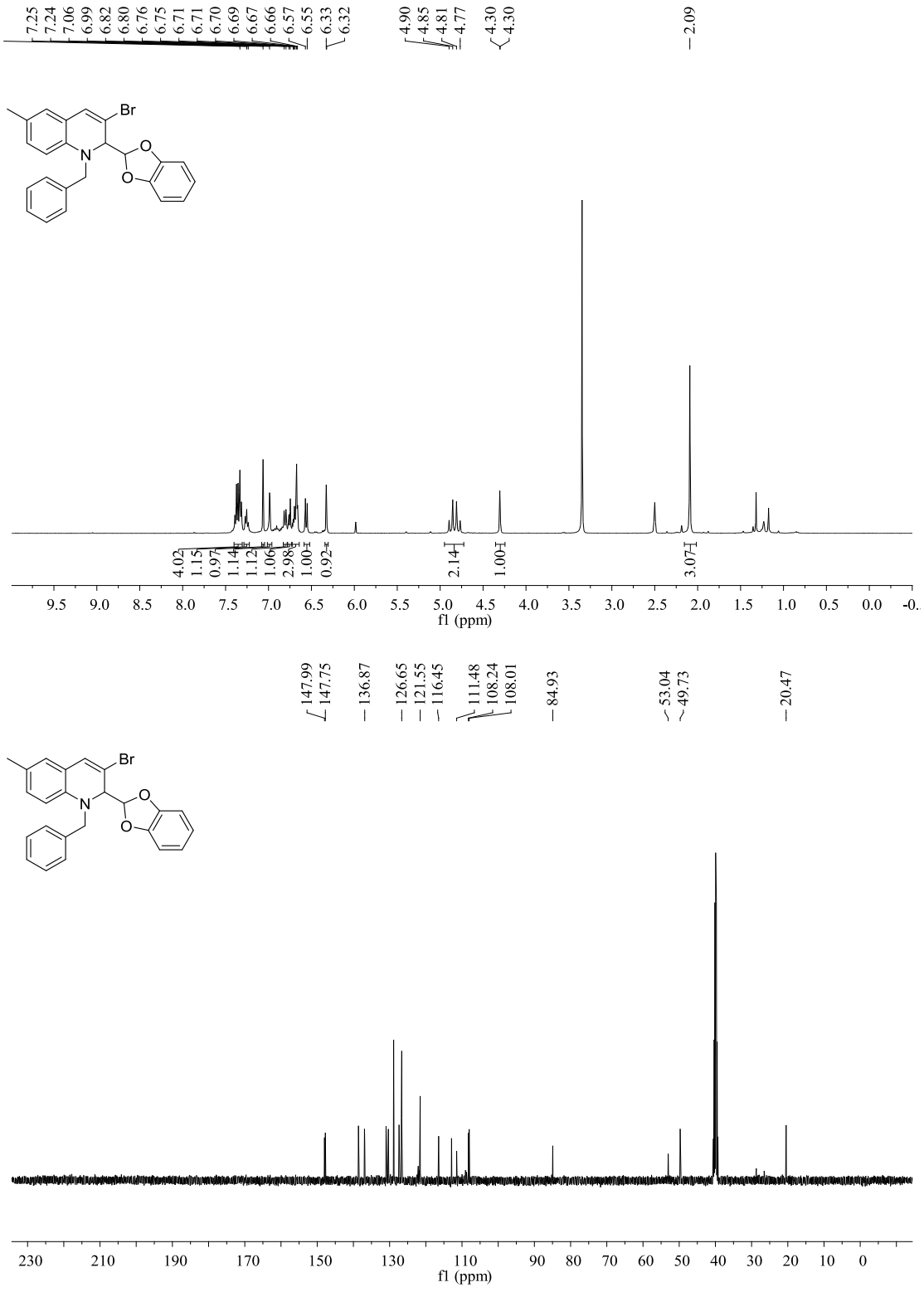

173.12
147.39
147.22
135.70
128.11
116.18
111.88
110.92
107.60
107.57
84.74
51.36
49.37
48.01
30.21
23.09
Br
O
N
O
O
O
O
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3n

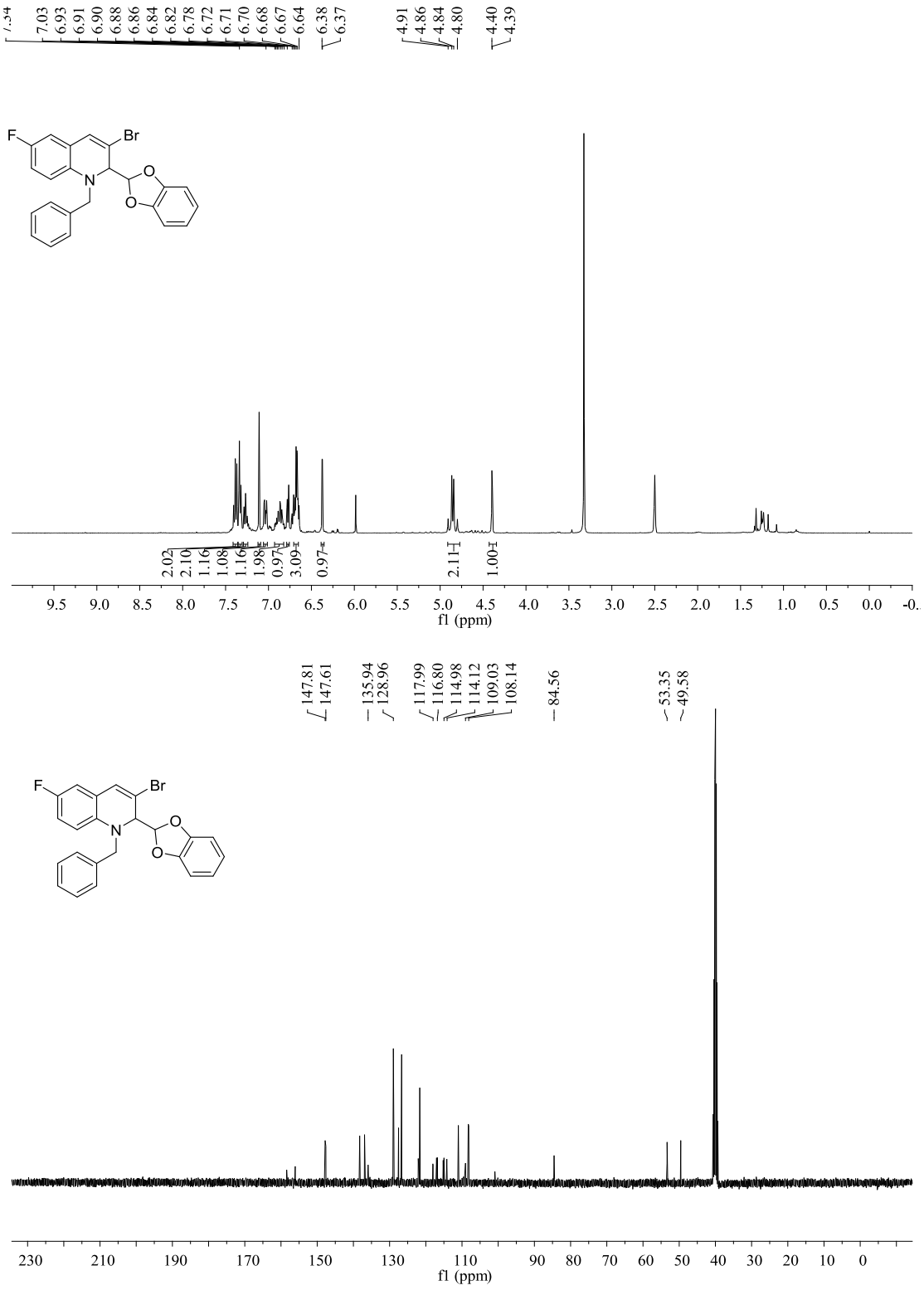

7.12
6.95
6.78
6.76
6.74
6.71
6.70
6.69
6.68
6.68
6.67
6.67
6.66
6.65
6.60
6.58
6.20
4.90
4.86
4.84
4.79
1.77
Br
N
O
O
3.15
2.12
1.04
0.93
1.10
2.02
1.07
1.00
2.18
3.12
fl (ppm)


147.96
147.77
136.56
127.43
120.73
112.87
108.22
108.11
94.31
53.19
46.41
24.30
Br
N
O
O
fl (ppm)

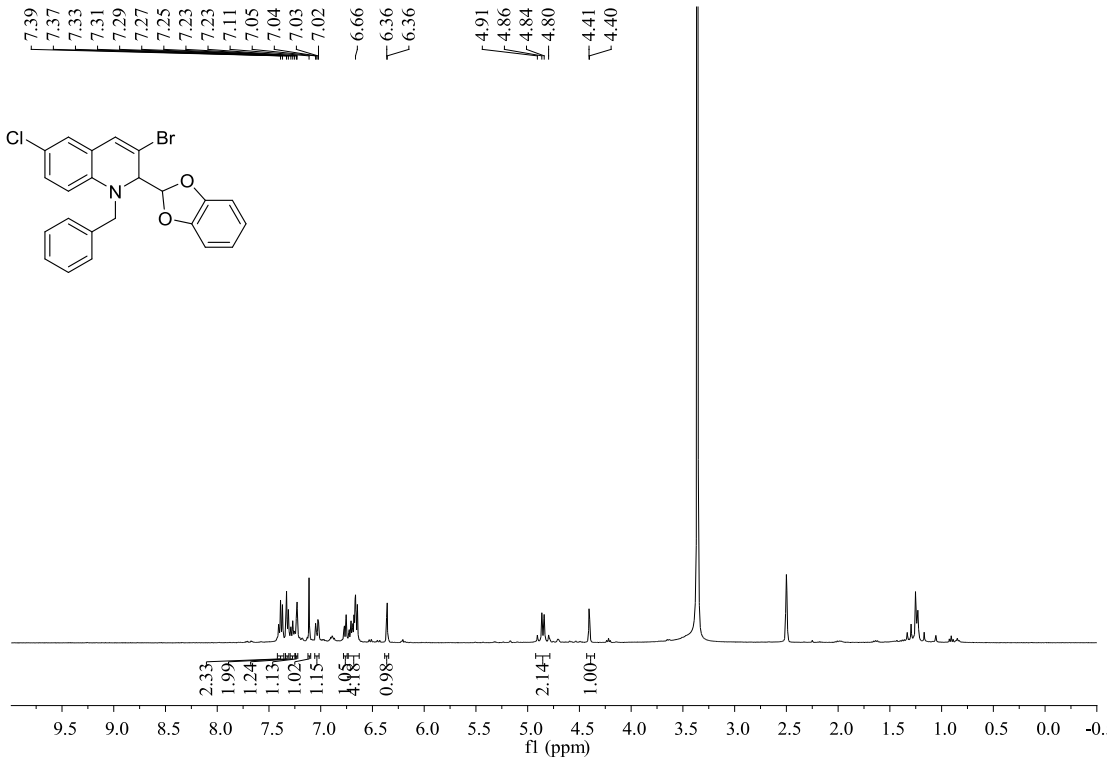
3o

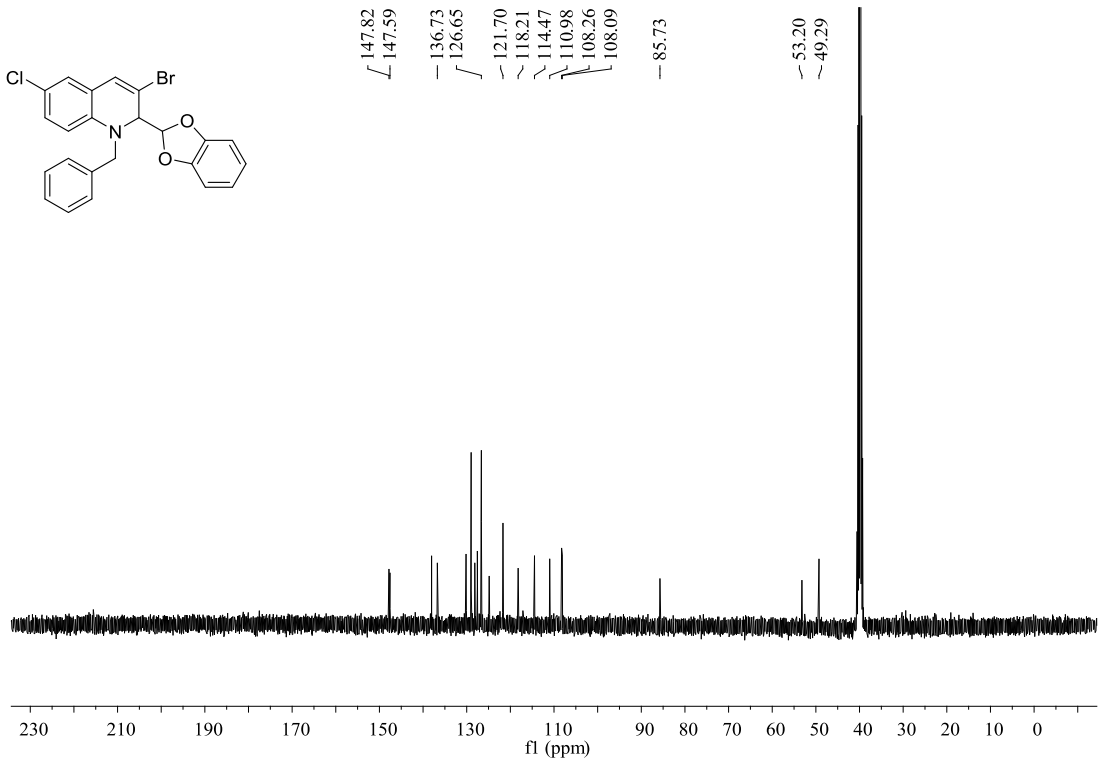

7.25
7.24
7.06
6.99
6.82
6.80
6.76
6.75
6.71
6.71
6.70
6.69
6.67
6.66
6.57
6.55
6.33
6.32
4.90
4.85
4.81
4.77
4.30
4.30
2.09
Br
N
O
O
4.02
1.15
0.97
1.14
1.12
1.06
2.98
1.00
0.92
2.14
1.00
3.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
147.99
147.75
136.87
126.65
121.55
116.45
111.48
108.24
108.01
84.93
53.04
49.73
20.47
Br
N
O
O
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3p

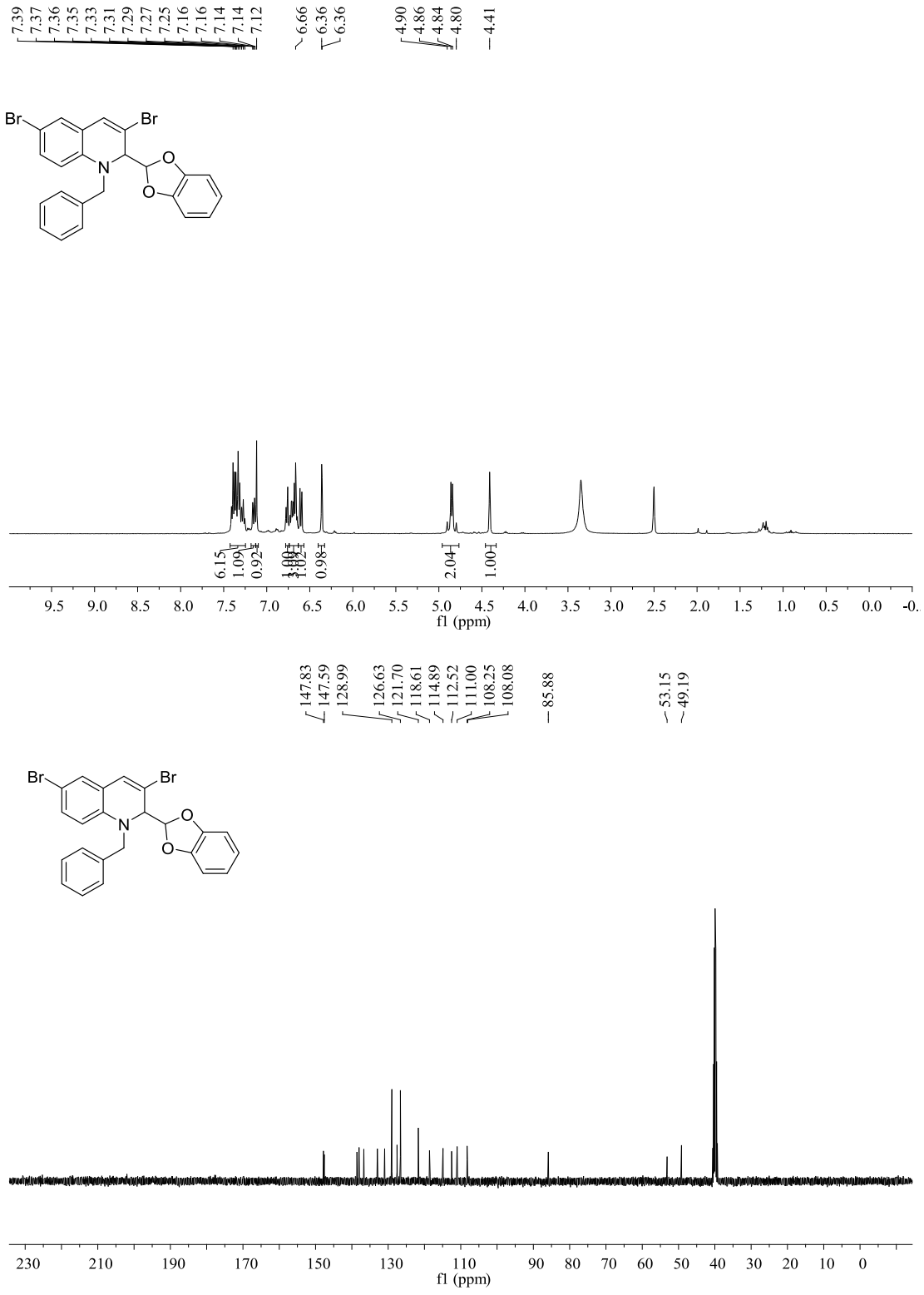

7.03
6.93
6.91
6.90
6.88
6.86
6.84
6.82
6.78
6.72
6.71
6.70
6.68
6.67
6.64
6.38
6.37
4.91
4.86
4.84
4.80
4.40
4.39
F
Br
N
O
O
2.02
2.10
1.16
1.08
1.16
1.98
0.97
3.09
0.97
2.11
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
147.81
147.61
135.94
128.96
117.99
116.80
114.98
114.12
109.03
108.14
84.56
53.35
49.58
F
Br
N
O
O
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3q

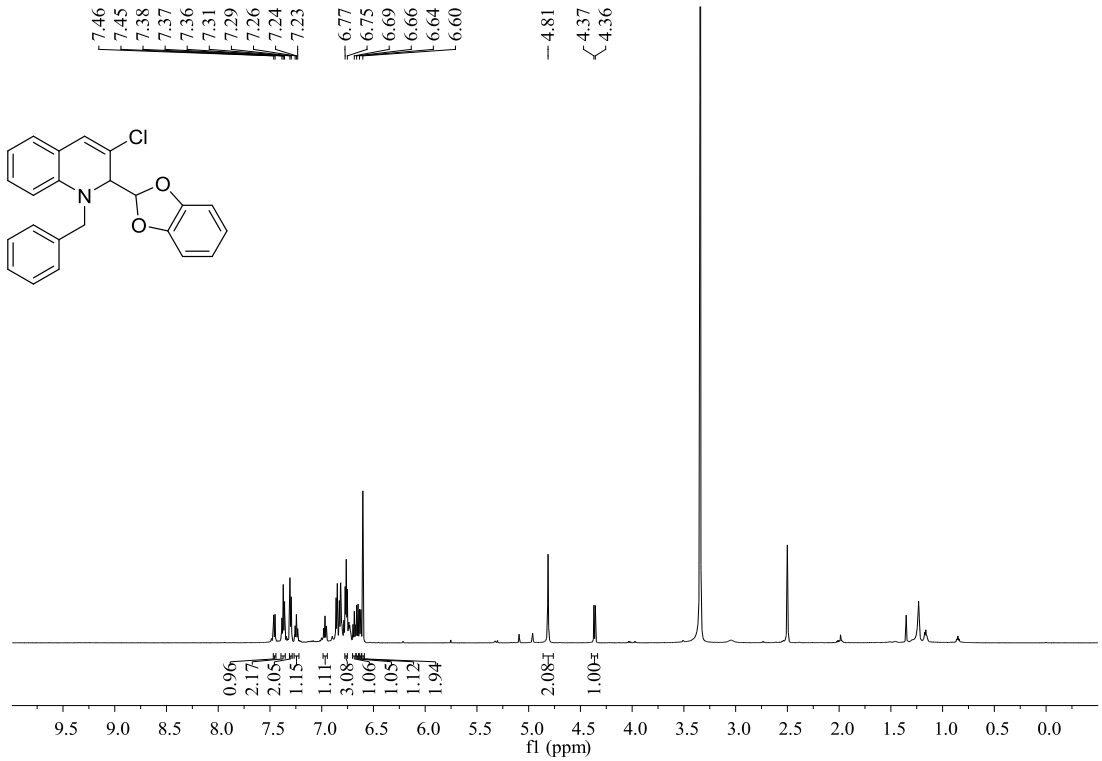

7.39
7.37
7.33
7.31
7.29
7.27
7.25
7.23
7.23
7.11
7.05
7.04
7.03
7.02
6.66
6.36
6.36
4.91
4.86
4.84
4.80
4.41
4.40
Cl
Br
N
O
O
2.33
1.99
1.24
1.13
1.02
1.15
0.98
2.14
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

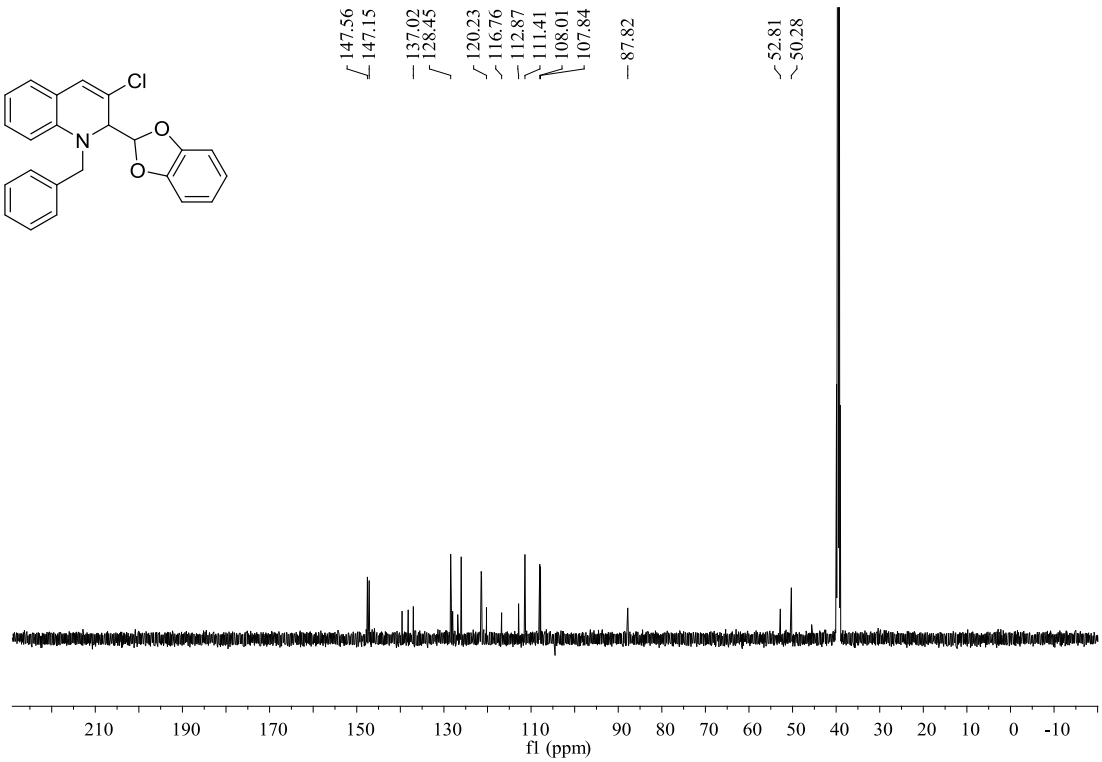

147.82
147.59
136.73
126.65
121.70
118.21
114.47
110.98
108.26
108.09
85.73
53.20
49.29
Cl
Br
N
O
O
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3r

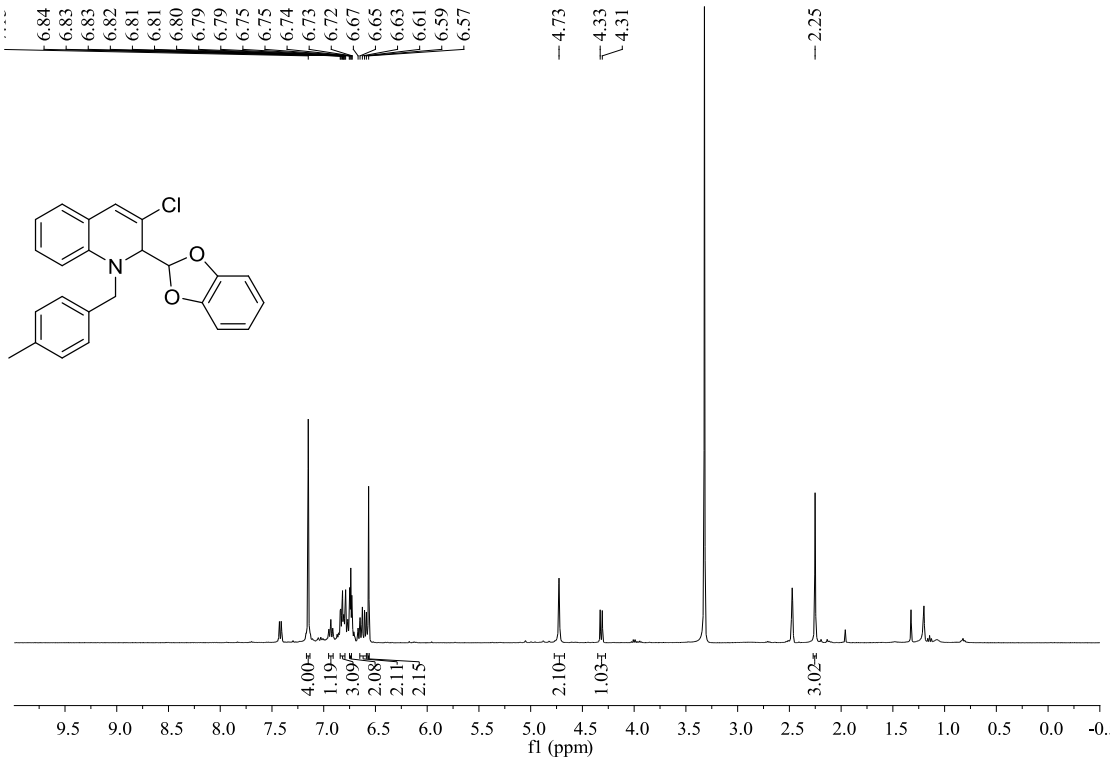

7.39
7.37
7.36
7.35
7.33
7.31
7.29
7.27
7.25
7.16
7.16
7.14
7.14
7.12
6.66
6.36
6.36
4.90
4.86
4.84
4.80
4.41
Br
Br
N
O
O
6.15
1.09
0.92
1.00
1.02
0.98
2.04
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
147.83
147.59
128.99
126.63
121.70
118.61
114.89
112.52
111.00
108.25
108.08
85.88
53.15
49.19
Br
Br
N
O
O
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

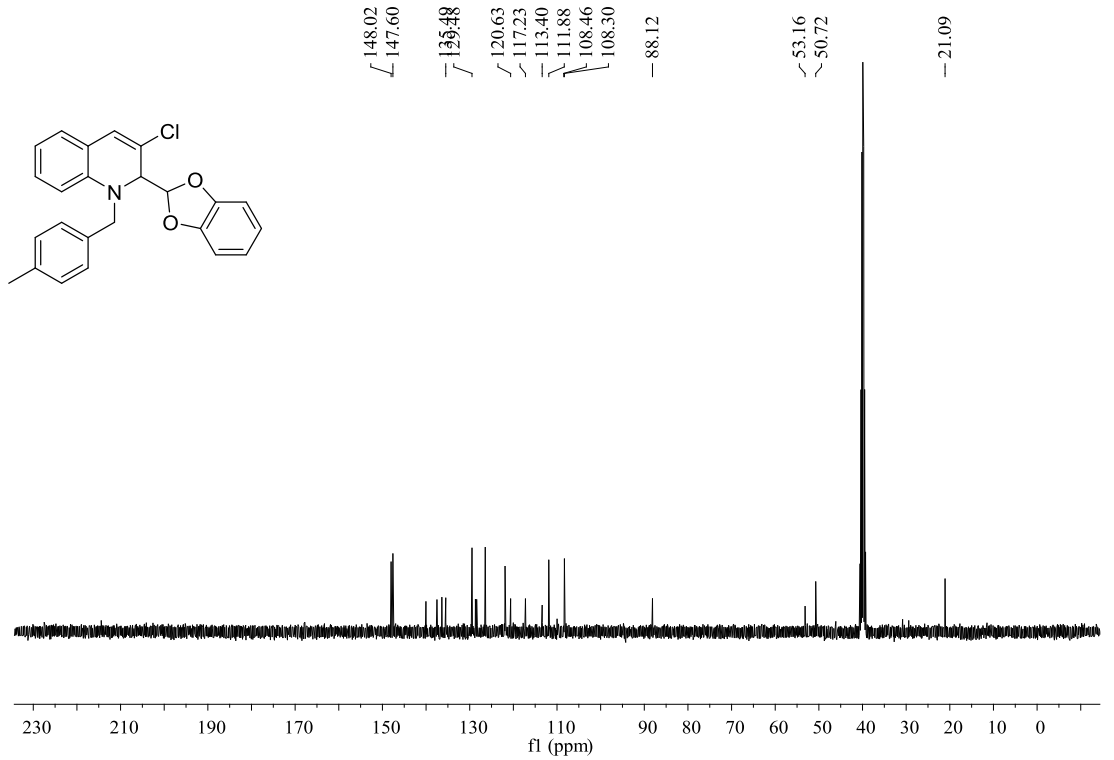
3s


7.46
7.45
7.38
7.37
7.36
7.31
7.29
7.26
7.24
7.23
6.77
6.75
6.69
6.66
6.64
6.60
4.81
4.37
4.36
Cl
N
O
O
0.96
2.17
2.05
1.15
1.11
3.08
1.06
1.05
1.12
1.94
2.08
1.00
9.5 9.0 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)

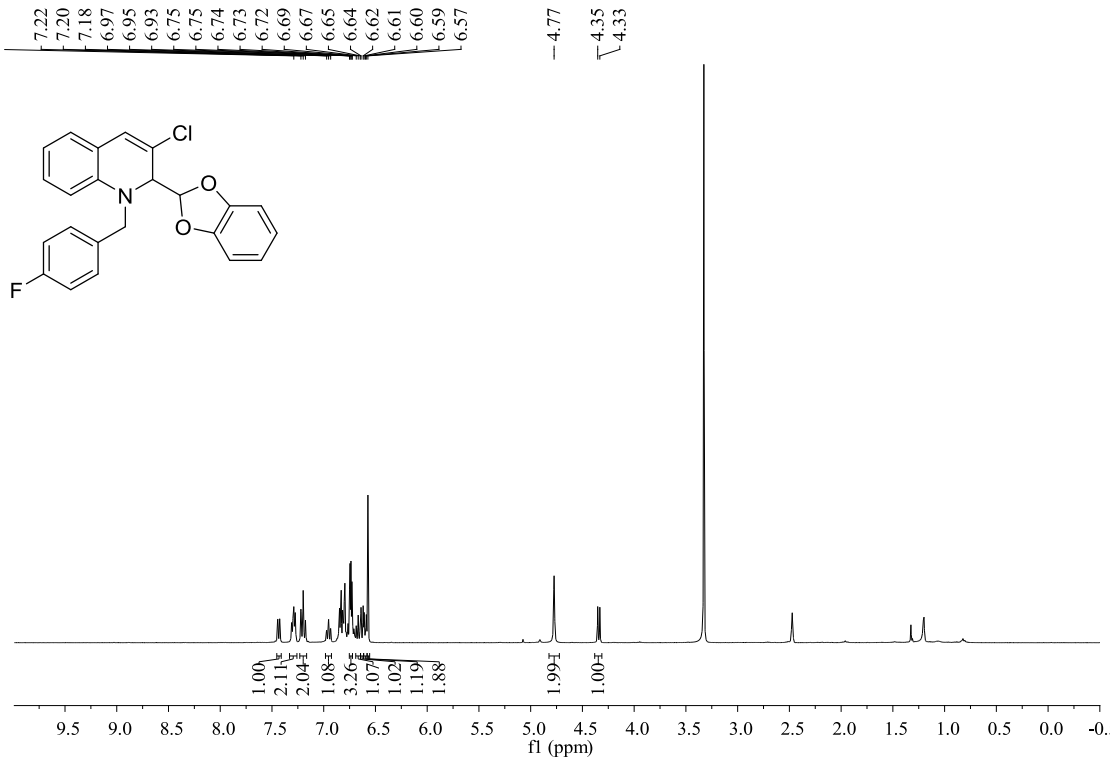

147.56
147.15
137.02
128.45
120.23
116.76
112.87
111.41
108.01
107.84
87.82
52.81
50.28
Cl
N
O
O
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

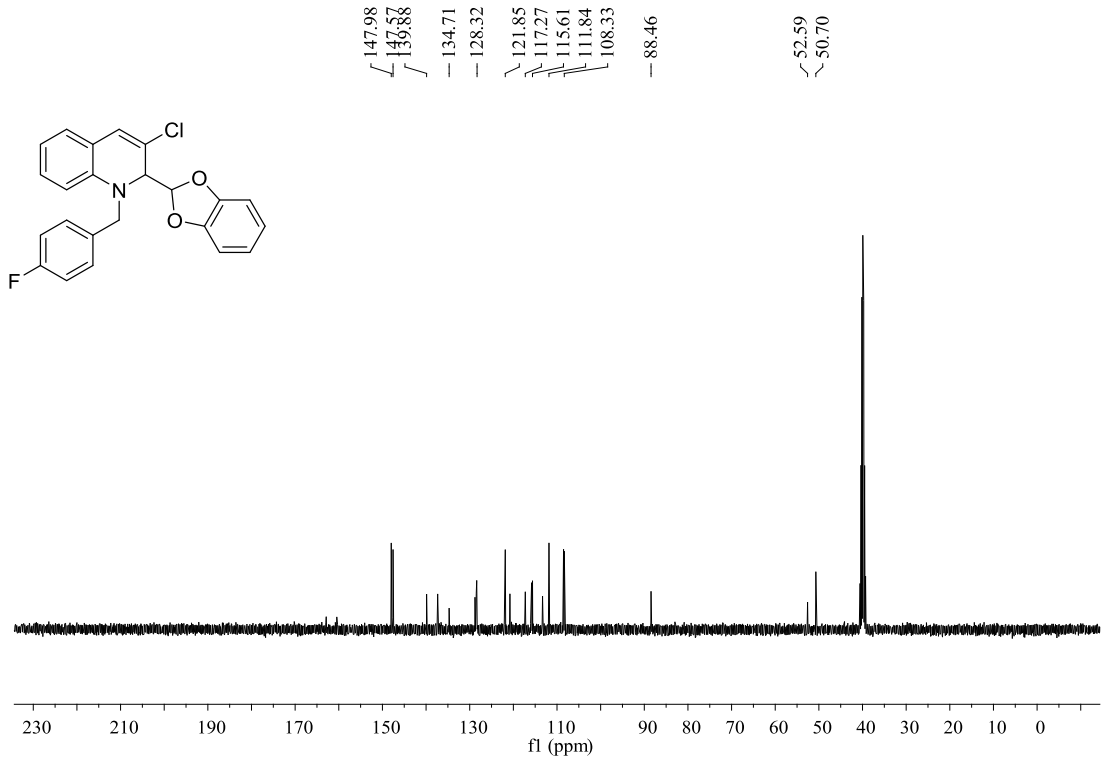
3t


6.84
6.83
6.83
6.82
6.81
6.81
6.80
6.79
6.79
6.75
6.75
6.74
6.73
6.72
6.67
6.65
6.63
6.61
6.59
6.57
4.73
4.33
4.31
2.25
Cl
N
O
O
4.00
1.19
3.09
2.08
2.11
2.15
2.10
1.03
3.02
9.5 9.0 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)

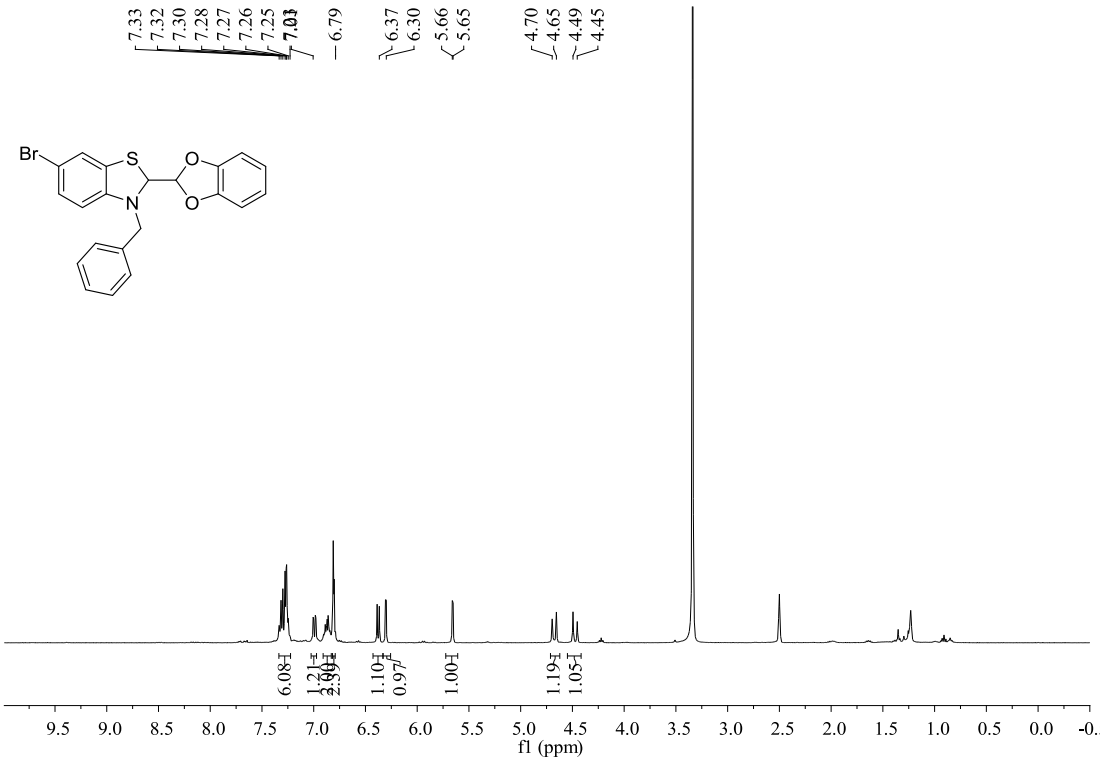

148.02
147.60
135.48
129.48
120.63
117.23
113.40
111.88
108.46
108.30
88.12
53.16
50.72
21.09
Cl
N
O
O
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

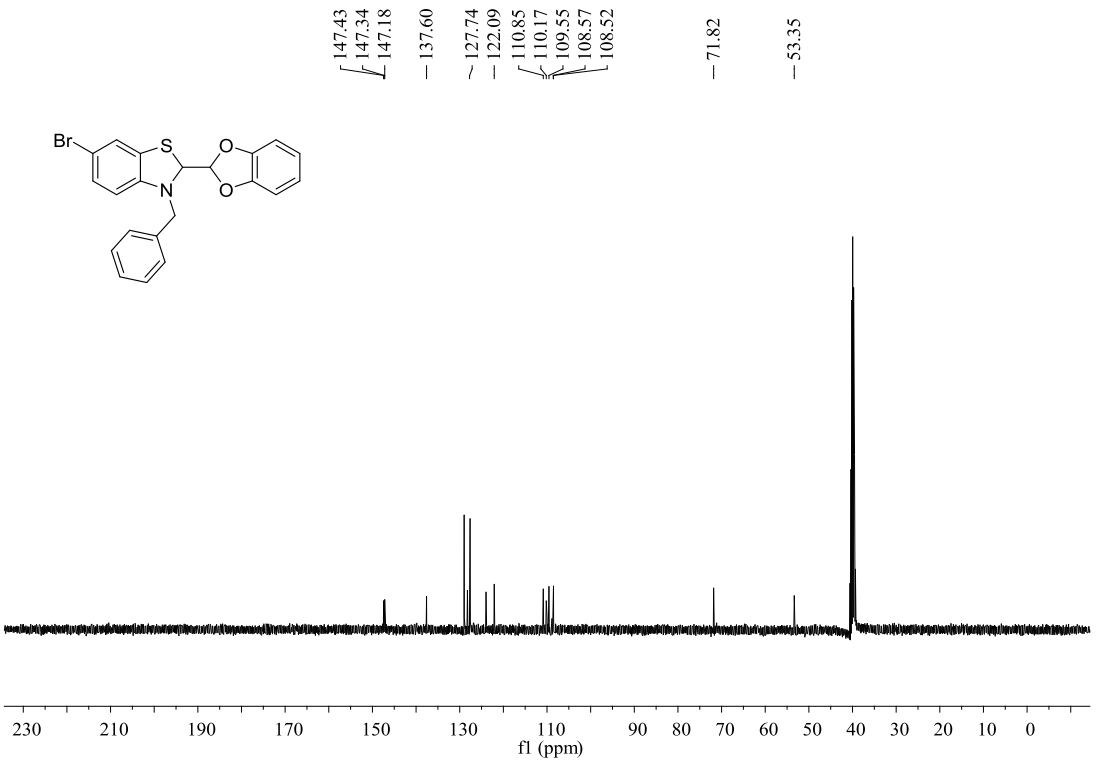
3u


7.22
7.20
7.18
6.97
6.95
6.93
6.75
6.75
6.74
6.73
6.72
6.69
6.67
6.65
6.64
6.62
6.61
6.60
6.59
6.57
4.77
4.35
4.33
Cl
N
O
O
F
1.00
2.11
2.04
1.08
3.26
1.07
1.02
1.19
1.88
1.99
1.00
9.5 9.0 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)

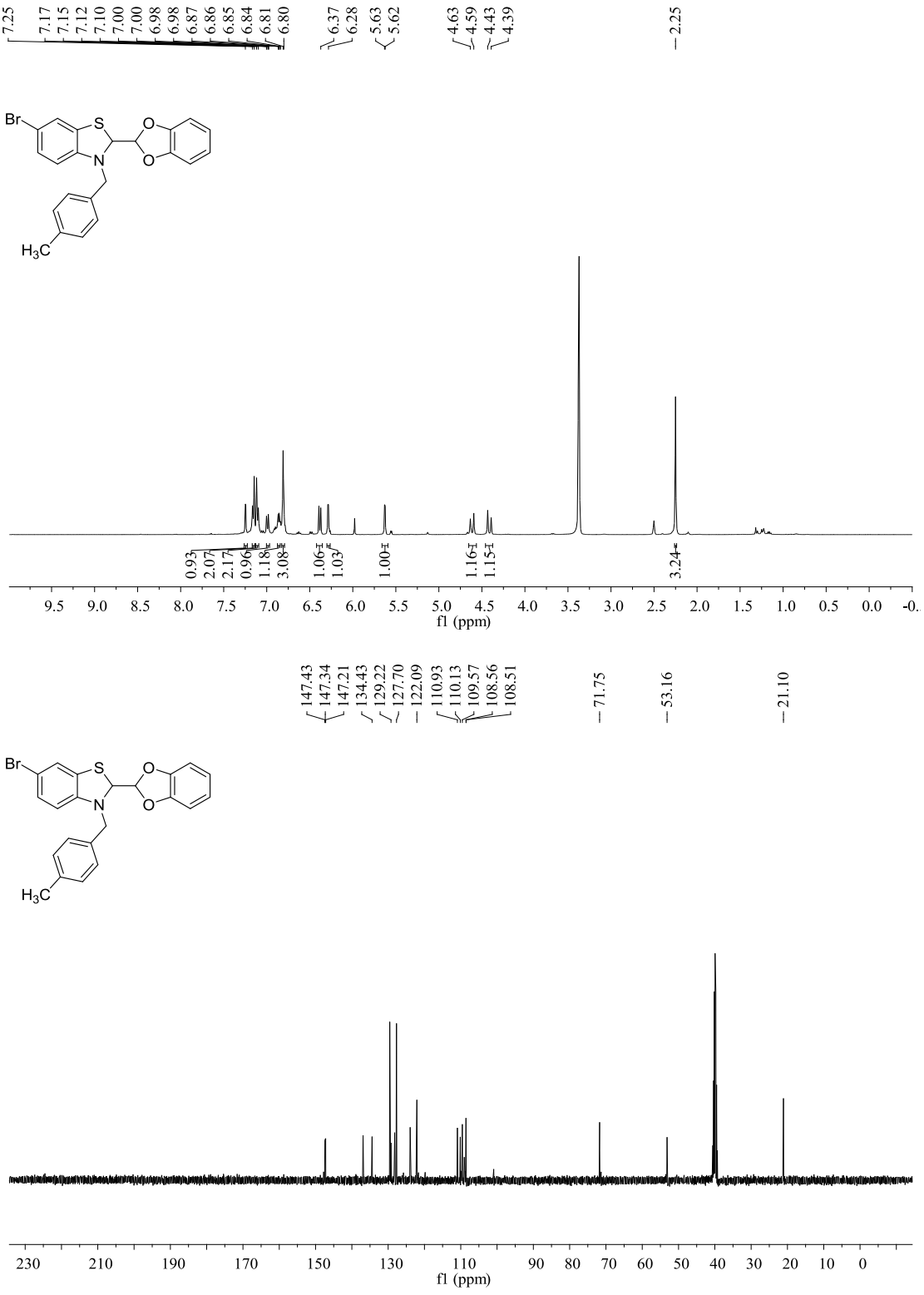

147.98
147.57
139.88
134.71
128.32
121.85
117.27
115.61
111.84
108.33
88.46
52.59
50.70
Cl
N
O
O
F
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

5a

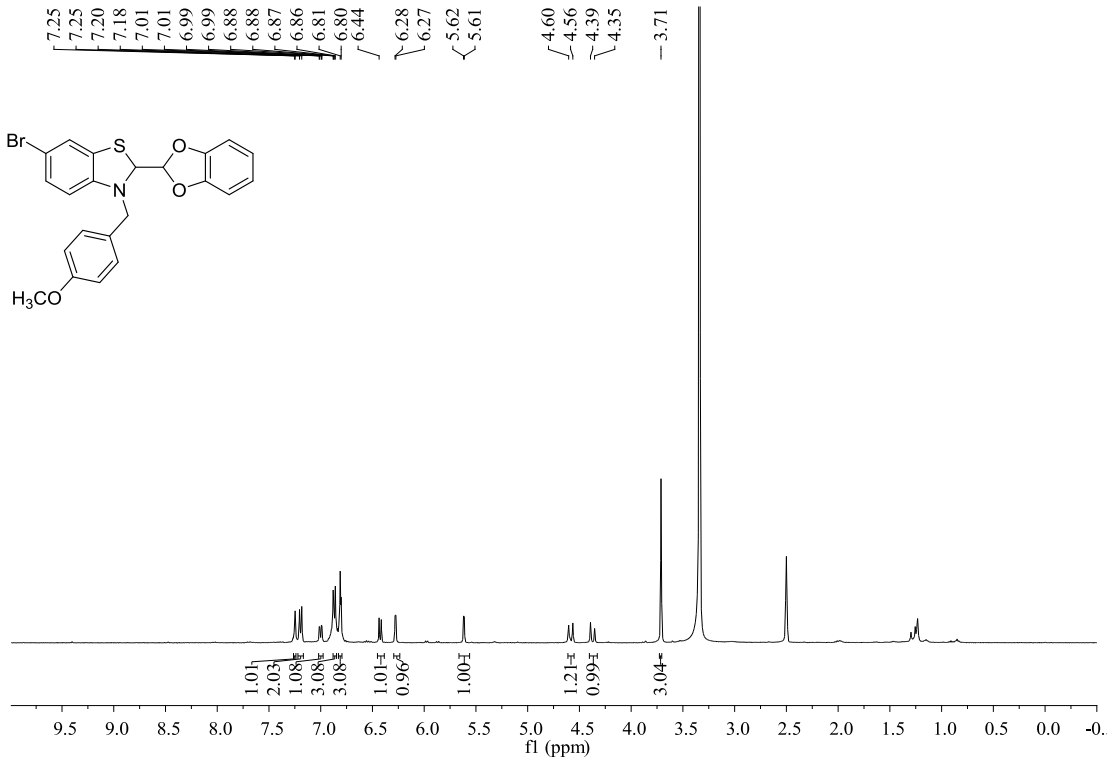

7.33
7.32
7.30
7.28
7.27
7.26
7.25
6.79
6.37
6.30
5.66
5.65
4.70
4.65
4.49
4.45
Br
S
O
N
O
6.08
1.21
2.90
1.10
0.97
1.00
1.19
1.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

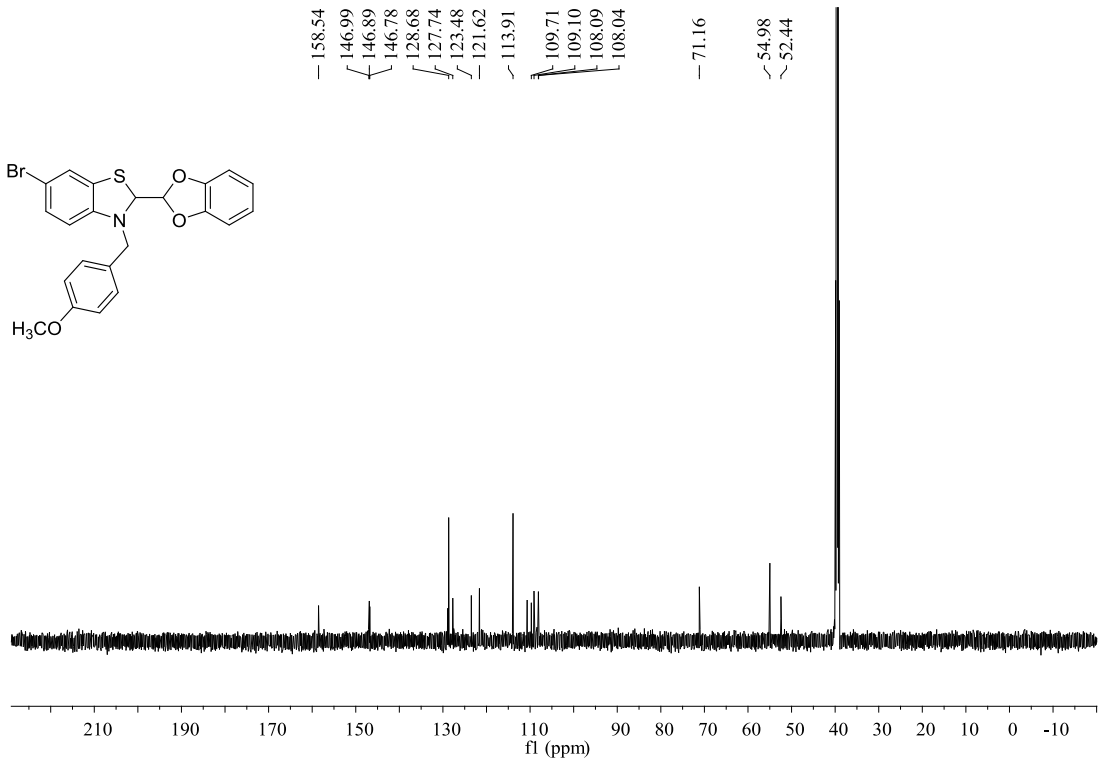

147.43
147.34
147.18
137.60
127.74
122.09
110.85
110.17
109.55
108.57
108.52
71.82
53.35
Br
S
O
N
O
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

5b

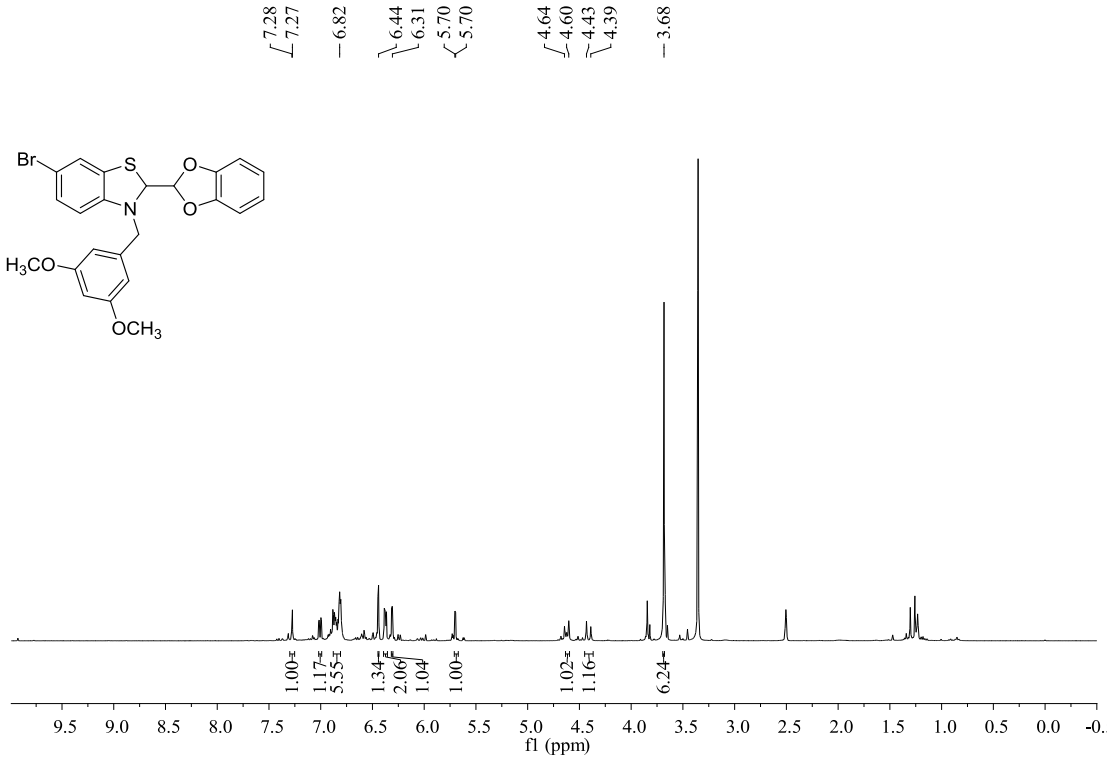

7.25
7.17
7.15
7.12
7.10
7.00
7.00
6.98
6.98
6.87
6.86
6.85
6.84
6.81
6.80
6.37
6.28
5.63
5.62
4.63
4.59
4.43
4.39
2.25
Br
S
O
O
N
H3C
0.93
2.07
2.17
0.96
1.18
3.08
1.06
1.03
1.00
1.16
1.15
3.24
fl (ppm)
147.43
147.34
147.21
134.43
129.22
127.70
122.09
110.93
110.13
109.57
108.56
108.51
71.75
53.16
21.10
fl (ppm)

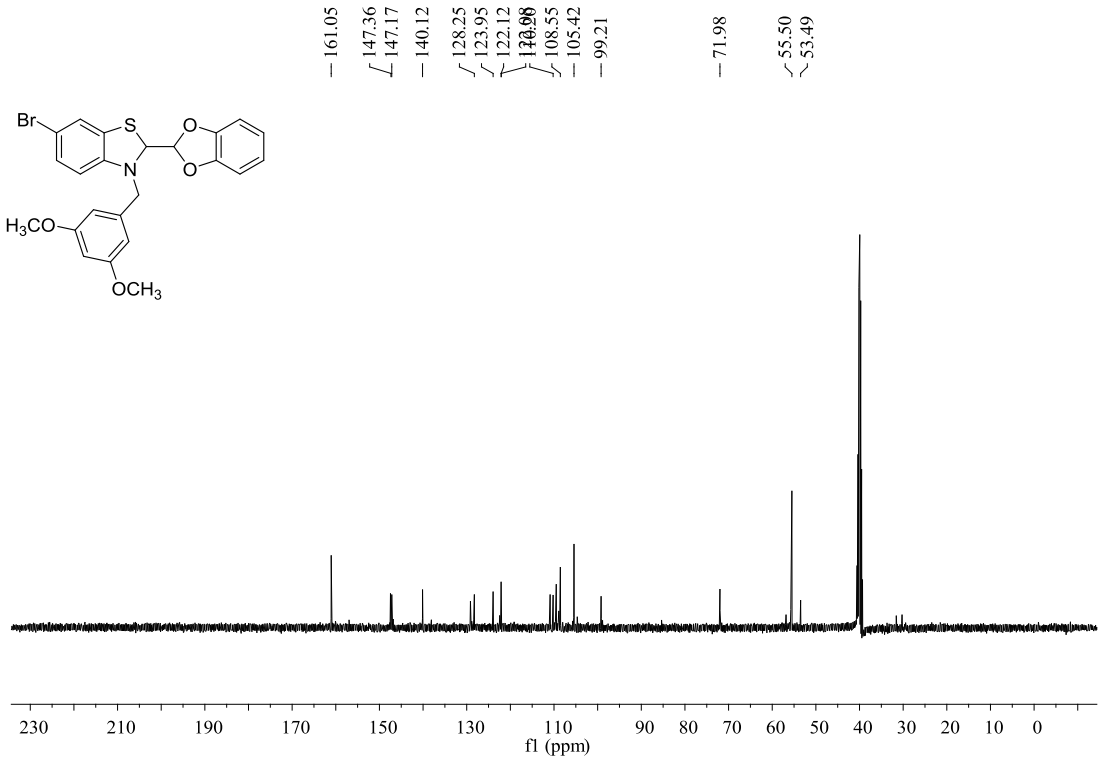
5c


7.25
7.25
7.20
7.18
7.01
7.01
6.99
6.99
6.88
6.88
6.87
6.86
6.81
6.80
6.44
6.28
6.27
5.62
5.61
4.60
4.56
4.39
4.35
3.71
Br
S
O
O
N
H3CO
1.01
2.03
1.08
3.08
3.08
1.01
0.96
1.00
1.21
0.99
3.04
9.5 9.0 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)

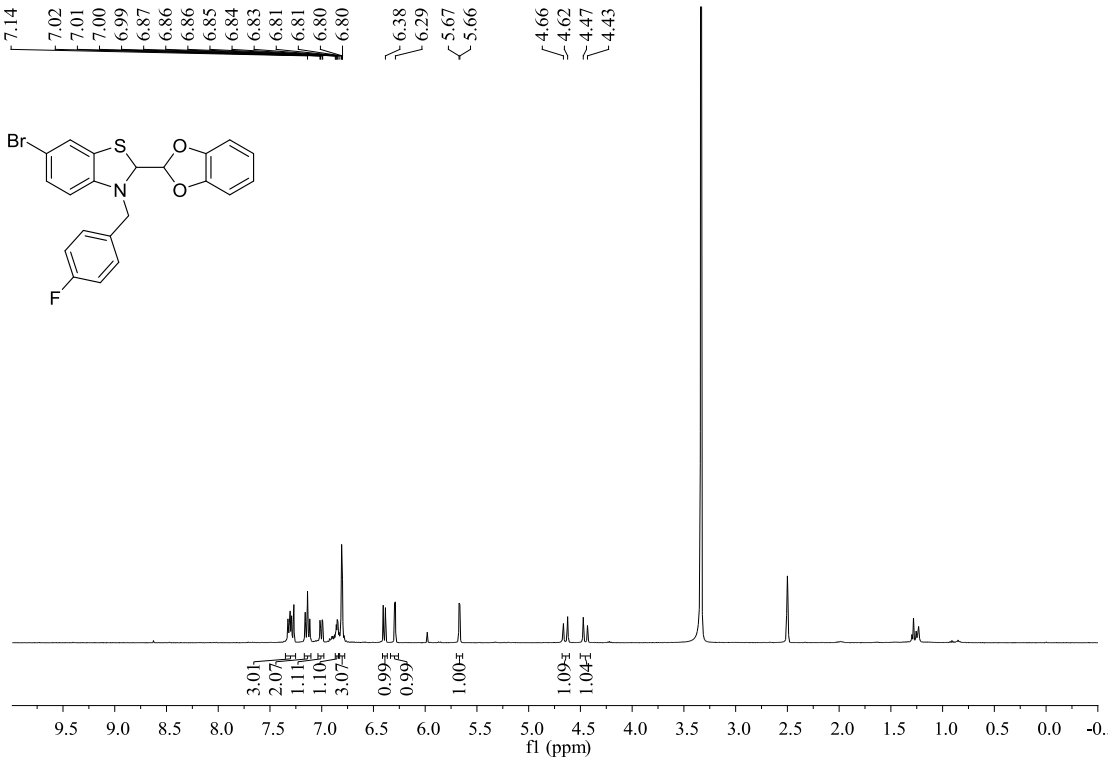

158.54
146.99
146.89
146.78
128.68
127.74
123.48
121.62
113.91
109.71
109.10
108.09
108.04
71.16
54.98
52.44
Br
S
O
O
N
H3CO
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

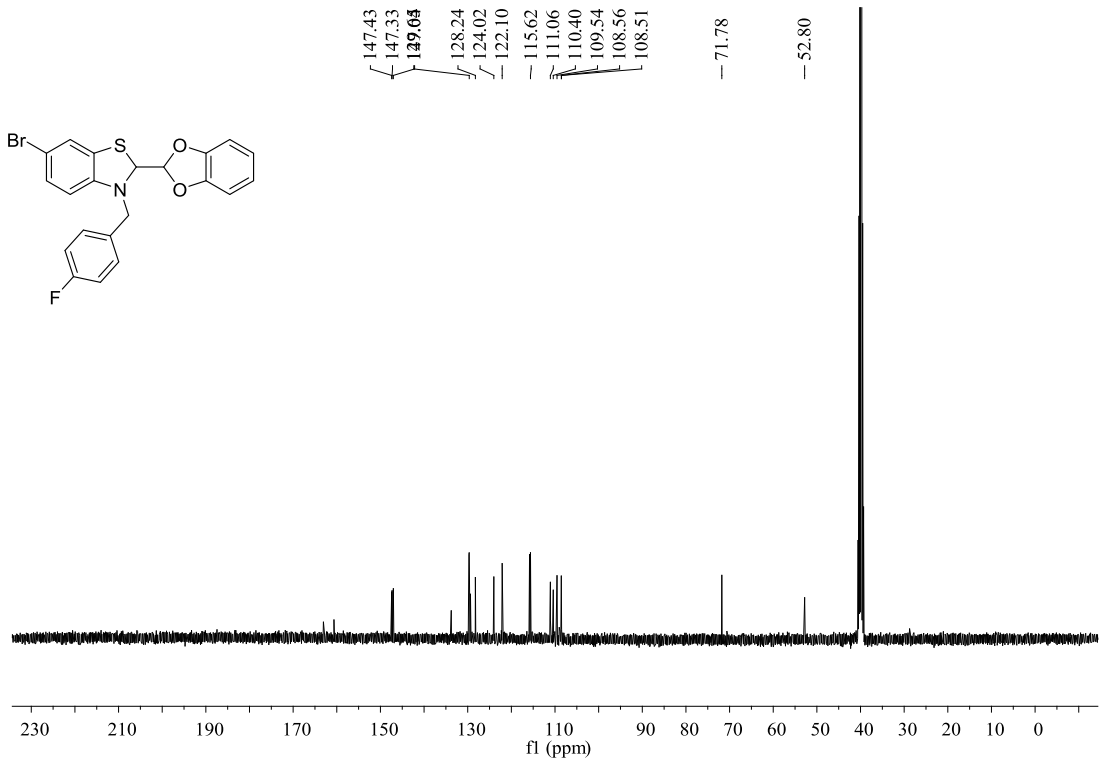
5d


7.28
7.27
6.82
6.44
6.31
5.70
5.70
4.64
4.60
4.43
4.39
3.68
Br
S
O
O
N
H3CO
OCH3
1.00
1.17
5.55
1.34
2.06
1.04
1.00
1.02
1.16
6.24
9.5 9.0 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)

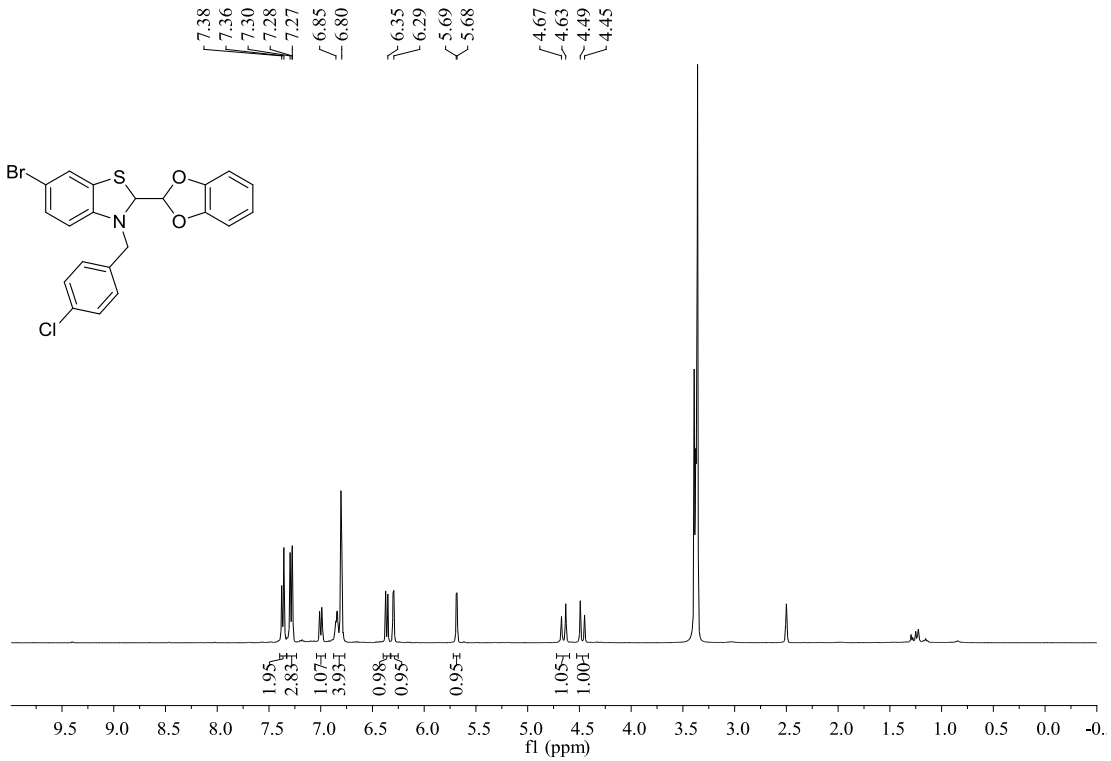

161.05
147.36
147.17
140.12
128.25
123.95
122.12
108.55
105.42
99.21
71.98
55.50
53.49
Br
S
O
O
N
H3CO
OCH3
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

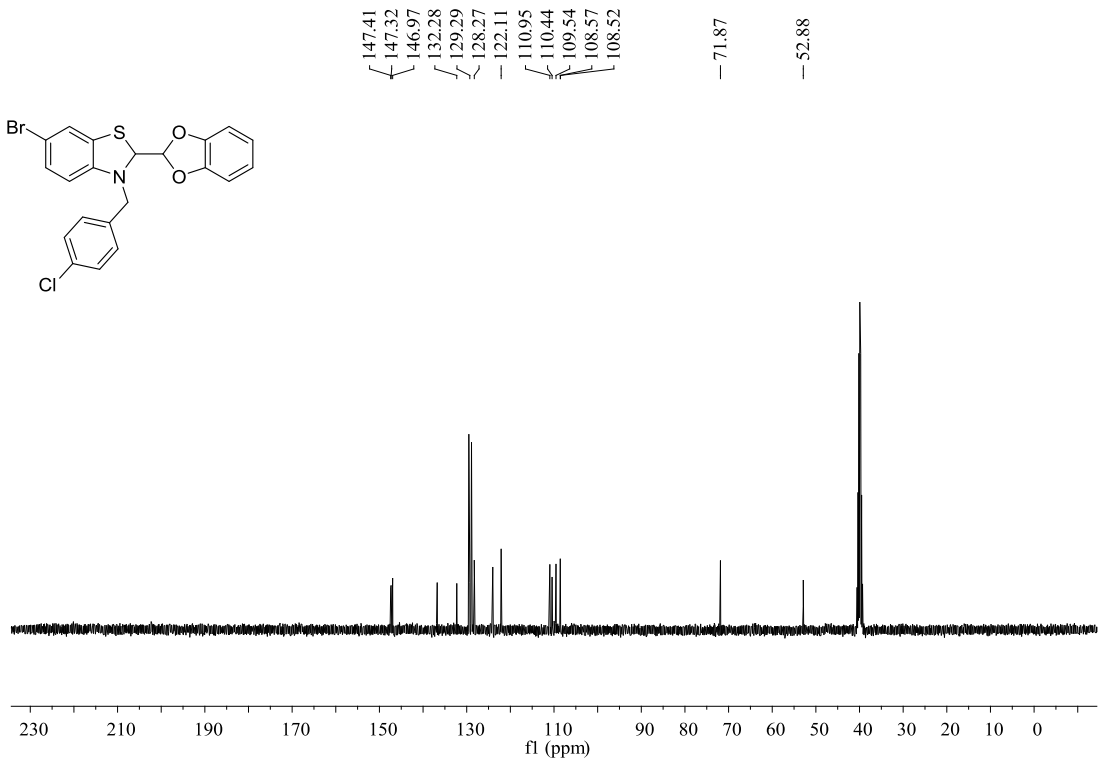
5e


7.14
7.02
7.01
7.00
6.99
6.87
6.86
6.86
6.85
6.84
6.83
6.81
6.81
6.80
6.80
6.38
6.29
5.67
5.66
4.66
4.62
4.47
4.43
Br
S
O
O
N
F
3.01
2.07
1.11
1.10
3.07
0.99
0.99
1.00
1.09
1.04
9.5 9.0 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)

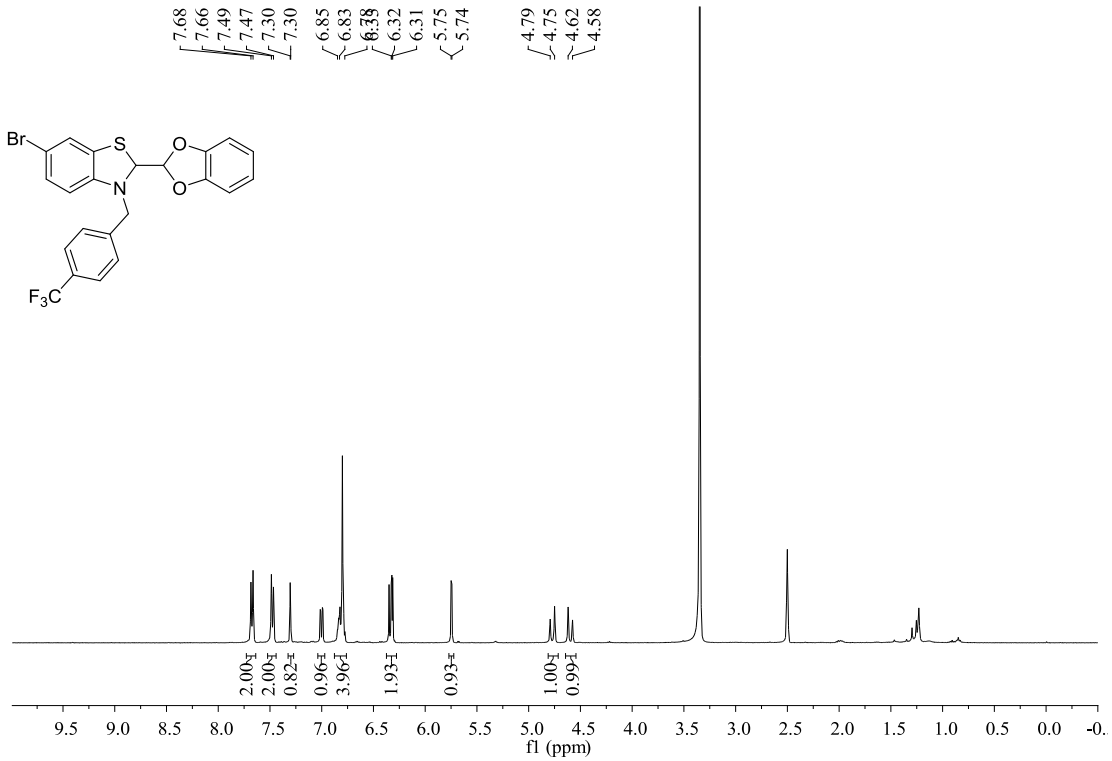

147.43
147.33
128.24
124.02
122.10
115.62
111.06
110.40
109.54
108.56
108.51
71.78
52.80
Br
S
O
O
N
F
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

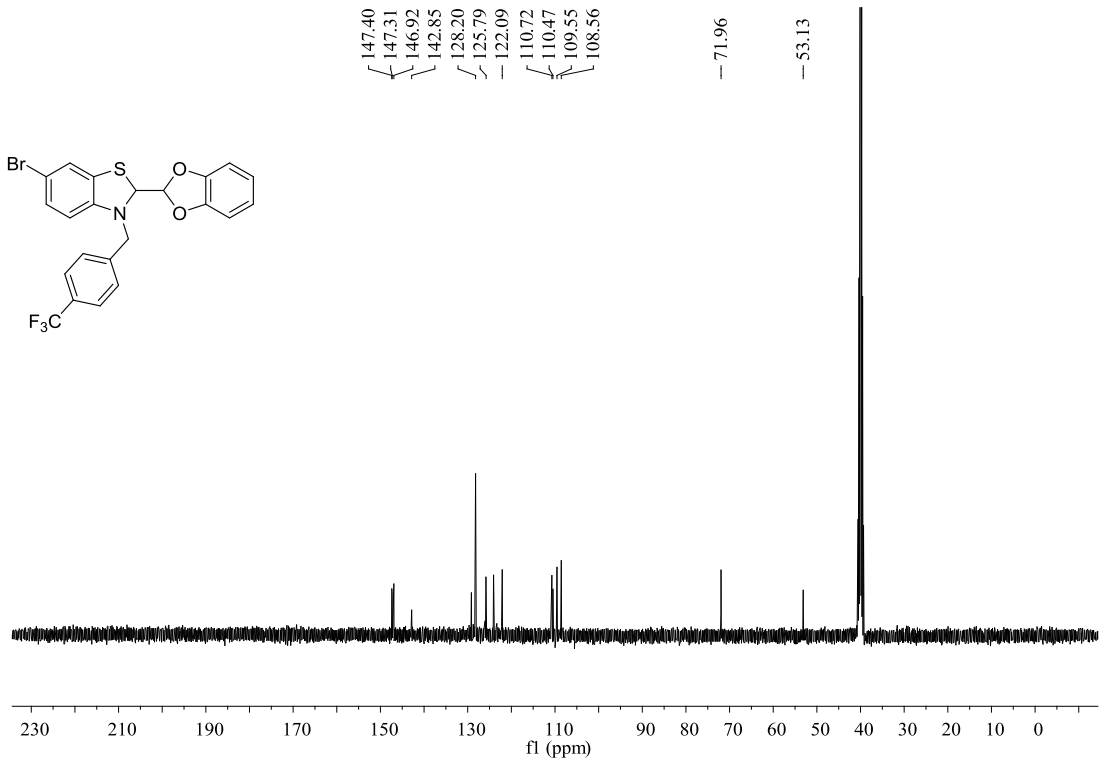
5f


7.38
7.36
7.30
7.28
7.27
6.85
6.80
6.35
6.29
5.69
5.68
4.67
4.63
4.49
4.45
Br
S
O
O
N
Cl
1.95
2.83
1.07
3.93
0.98
0.95
0.95
1.05
1.00
9.5 9.0 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)

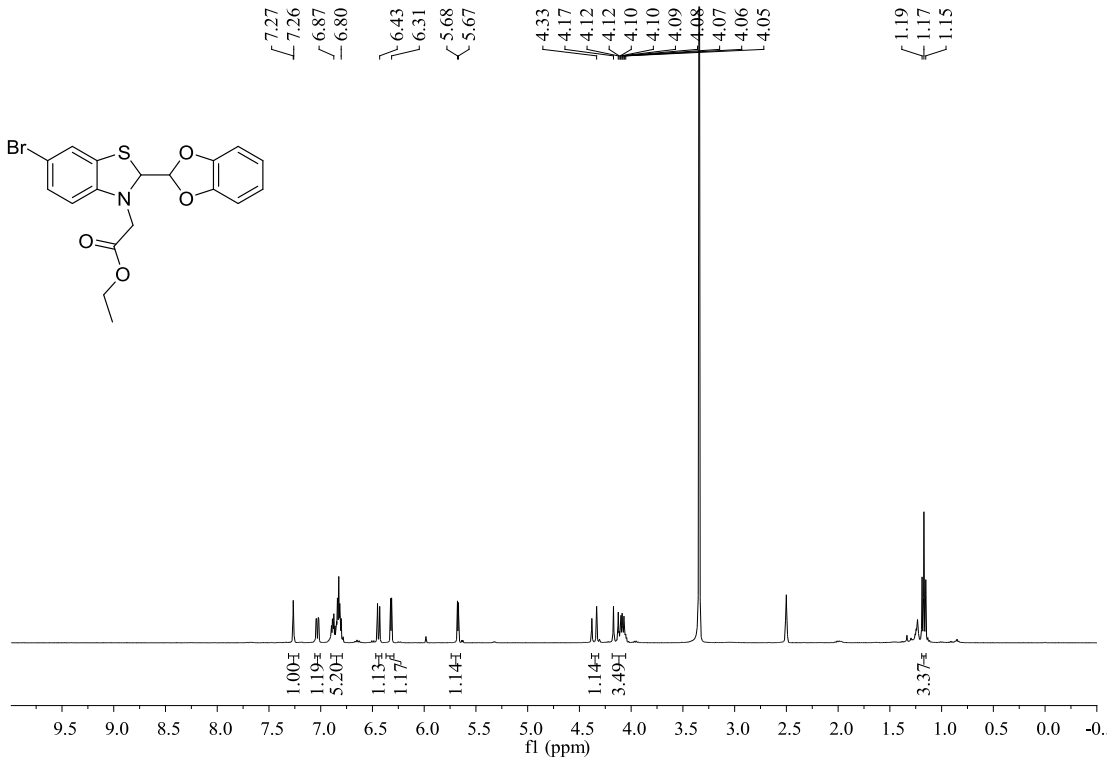

147.41
147.32
146.97
132.28
129.29
128.27
122.11
110.95
110.44
109.54
108.57
108.52
71.87
52.88
Br
S
O
O
N
Cl
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

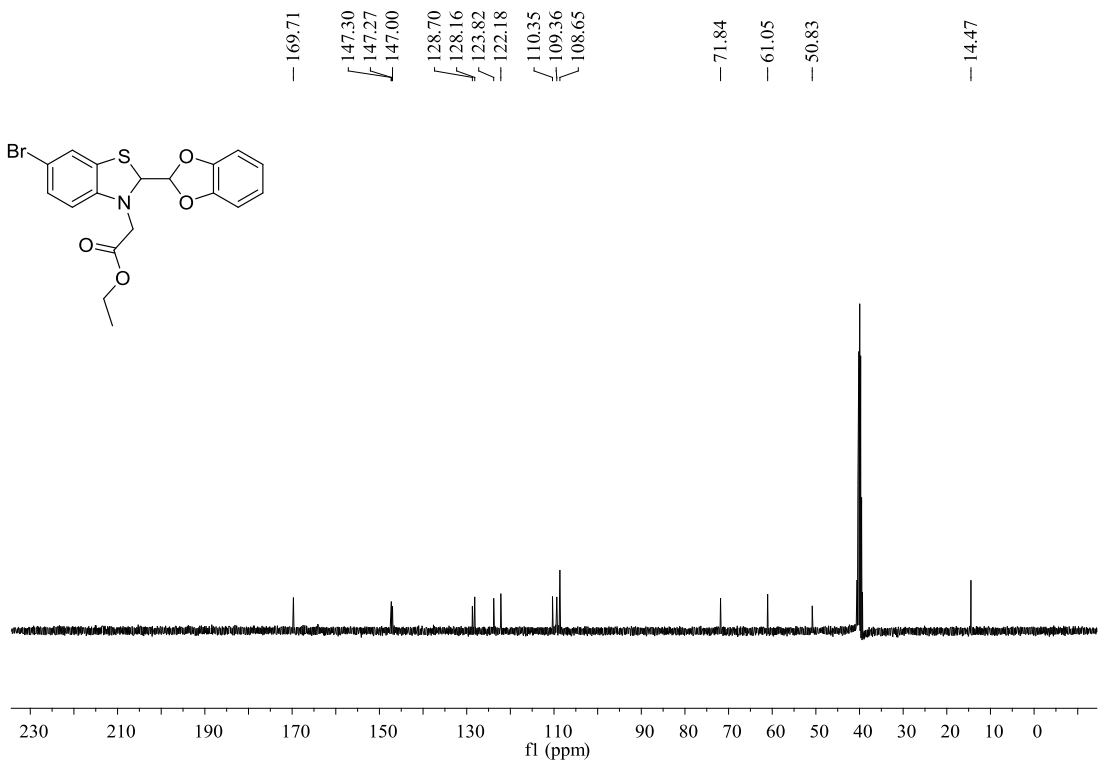
5g


7.68
7.66
7.49
7.47
7.30
7.30
6.85
6.83
6.32
6.31
5.75
5.74
4.79
4.75
4.62
4.58
Br
S
O
O
N
F3C
2.00
2.00
0.82
0.96
3.96
1.93
0.93
1.00
0.99
fl (ppm)


147.40
147.31
146.92
142.85
128.20
125.79
122.09
110.72
110.47
109.55
108.56
71.96
53.13
Br
S
O
O
N
F3C
fl (ppm)

5h


7.27
7.26
6.87
6.80
6.43
6.31
5.68
5.67
4.33
4.17
4.12
4.12
4.10
4.10
4.09
4.08
4.07
4.06
4.05
1.19
1.17
1.15
Br
S
O
O
N
O
O
1.00
1.19
5.20
1.13
1.17
1.14
1.14
3.49
3.37
fl (ppm)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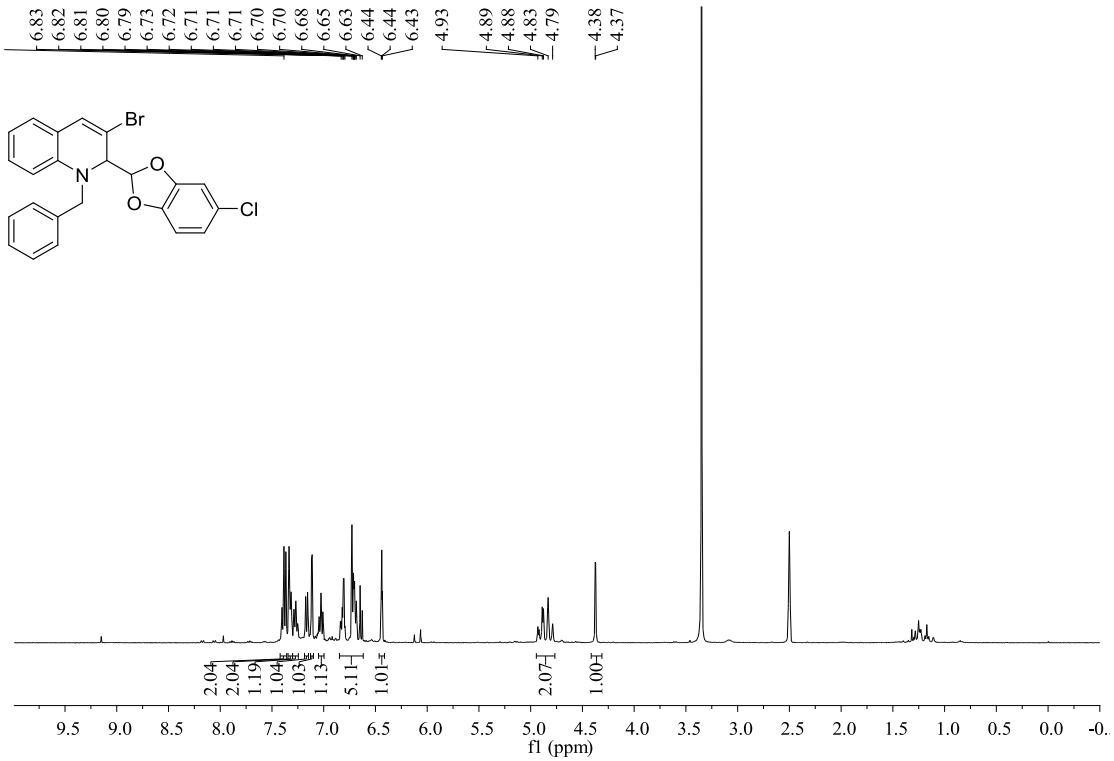
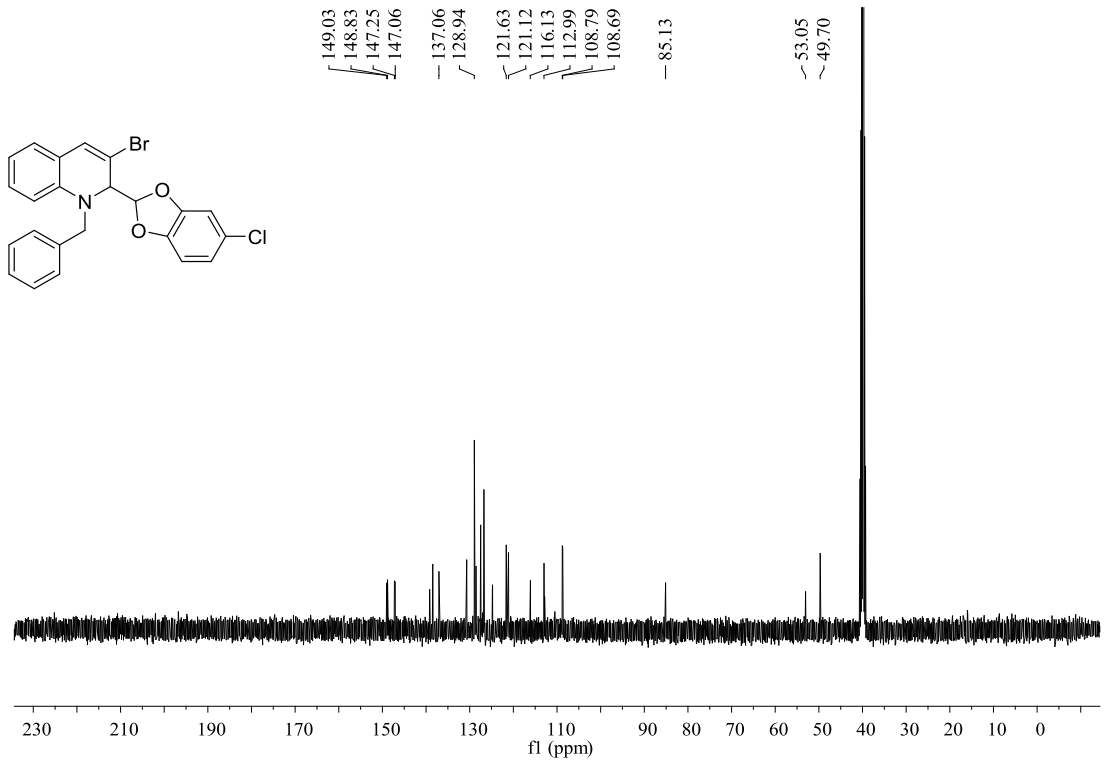
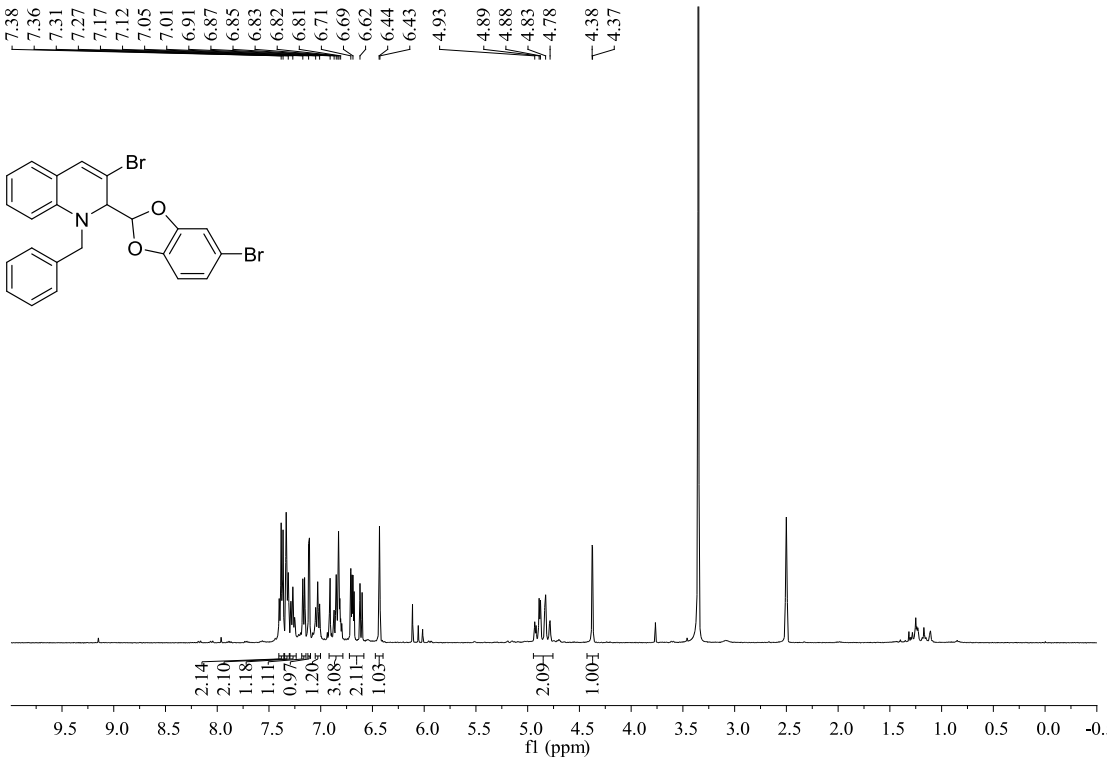
147.30
147.27
147.00
128.70
128.16
123.82
122.18
110.35
109.36
108.65
71.84
61.05
50.83
14.47
Br
S
O
O
N
O
O
fl (ppm)

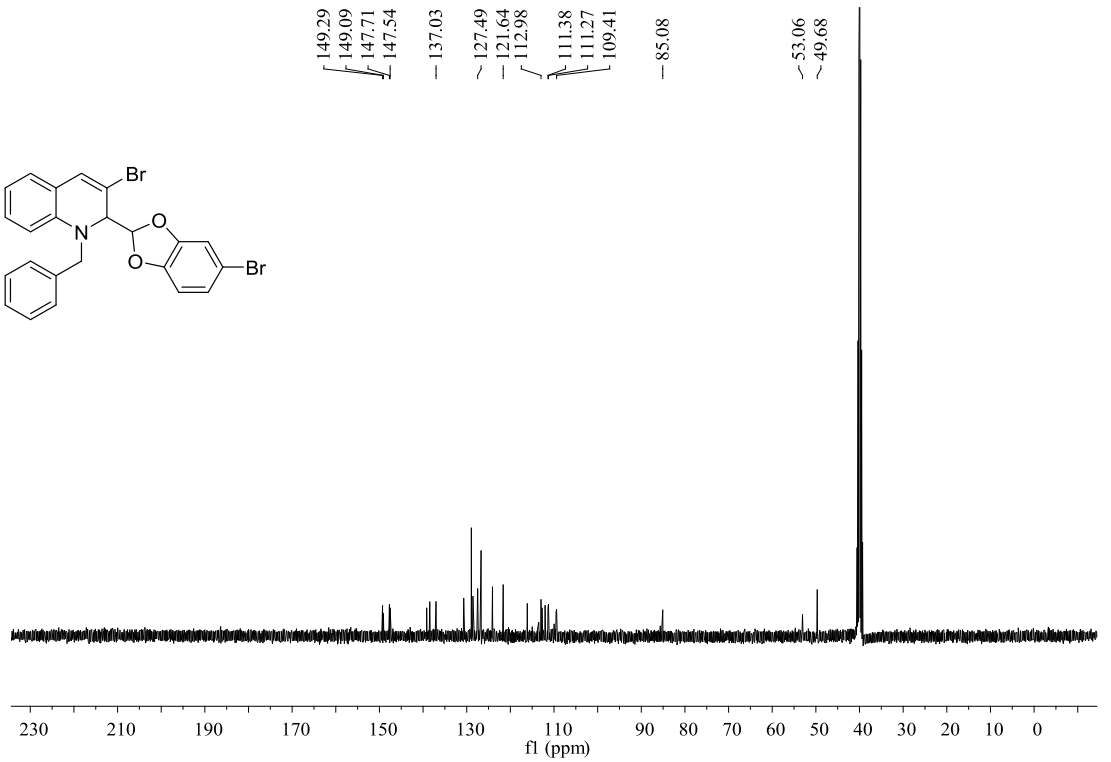
6a


6.83
6.82
6.81
6.80
6.79
6.73
6.72
6.71
6.71
6.71
6.70
6.70
6.68
6.65
6.63
6.44
6.44
6.43
4.93
4.89
4.88
4.83
4.79
4.38
4.37
Br
N
O
O
Cl
2.04
2.04
1.19
1.04
1.03
1.13
5.11
1.01
2.07
1.00
9.5 9.0 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)

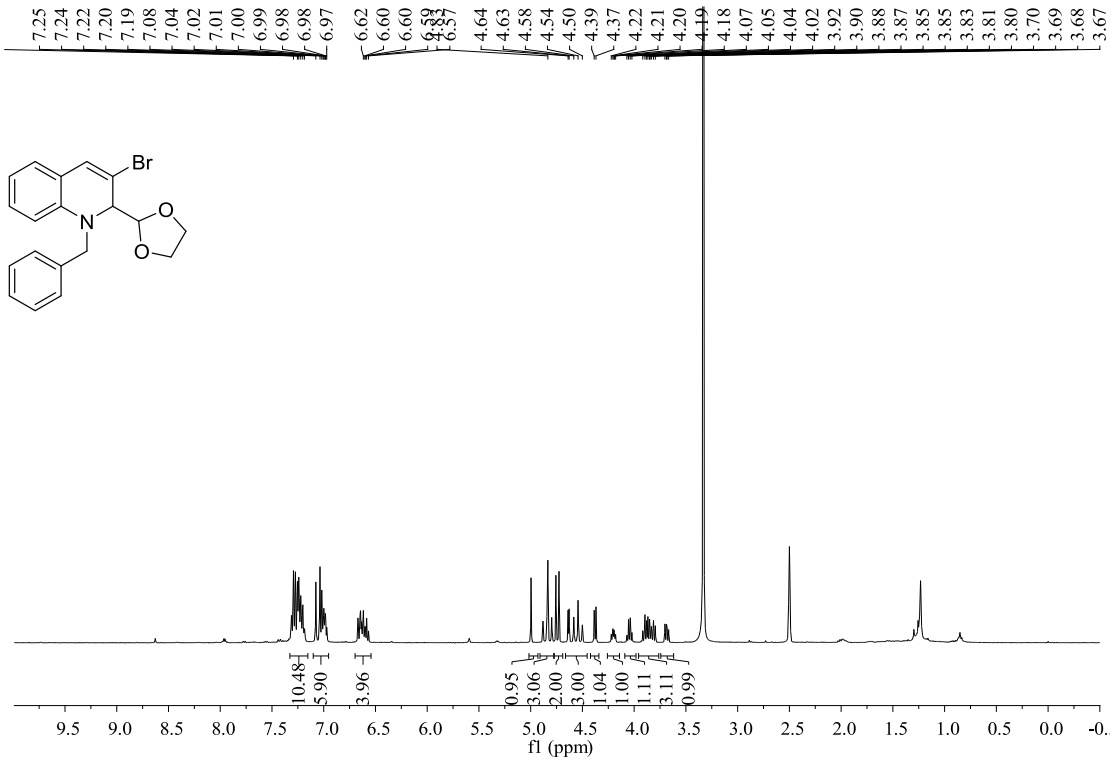

149.03
148.83
147.25
147.06
137.06
128.94
121.63
121.12
116.13
112.99
108.79
108.69
85.13
53.05
49.70
Br
N
O
O
Cl
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

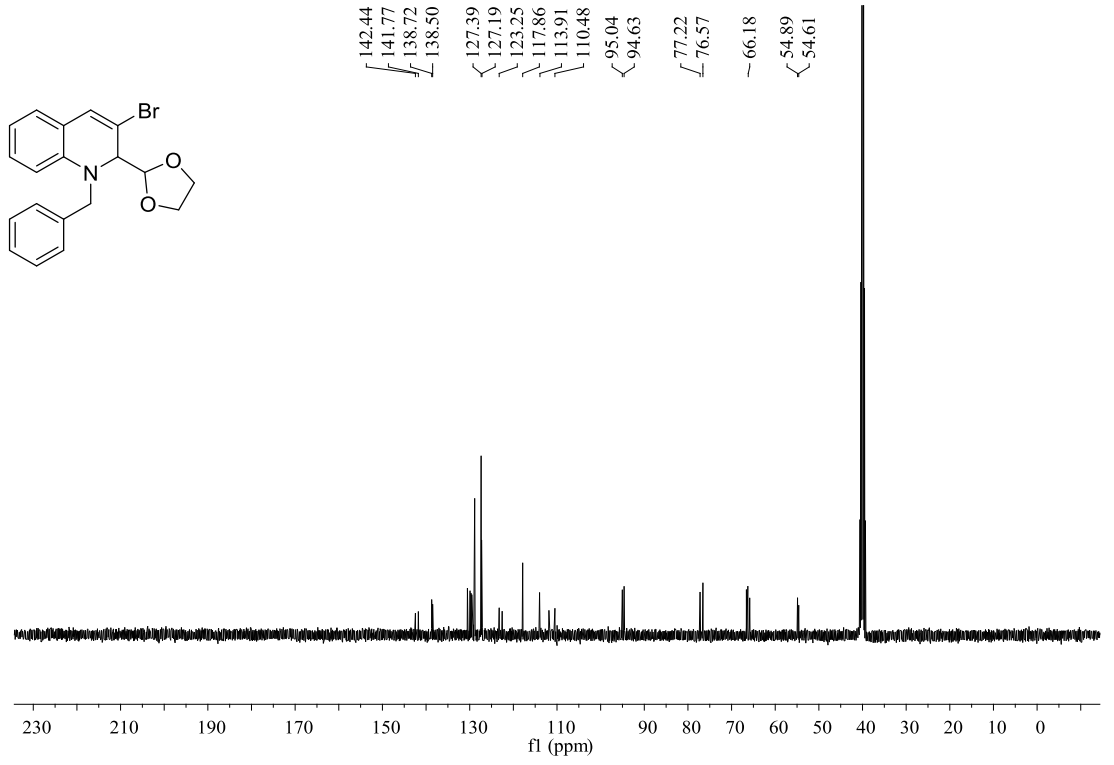
6b


7.38
7.36
7.31
7.27
7.17
7.12
7.05
7.01
6.91
6.87
6.85
6.83
6.82
6.81
6.71
6.69
6.62
6.44
6.43
4.93
4.89
4.88
4.83
4.78
4.38
4.37
Br
N
O
O
Br
2.14
2.10
1.18
1.11
0.97
1.20
3.08
2.11
1.03
2.09
1.00
9.5 9.0 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)

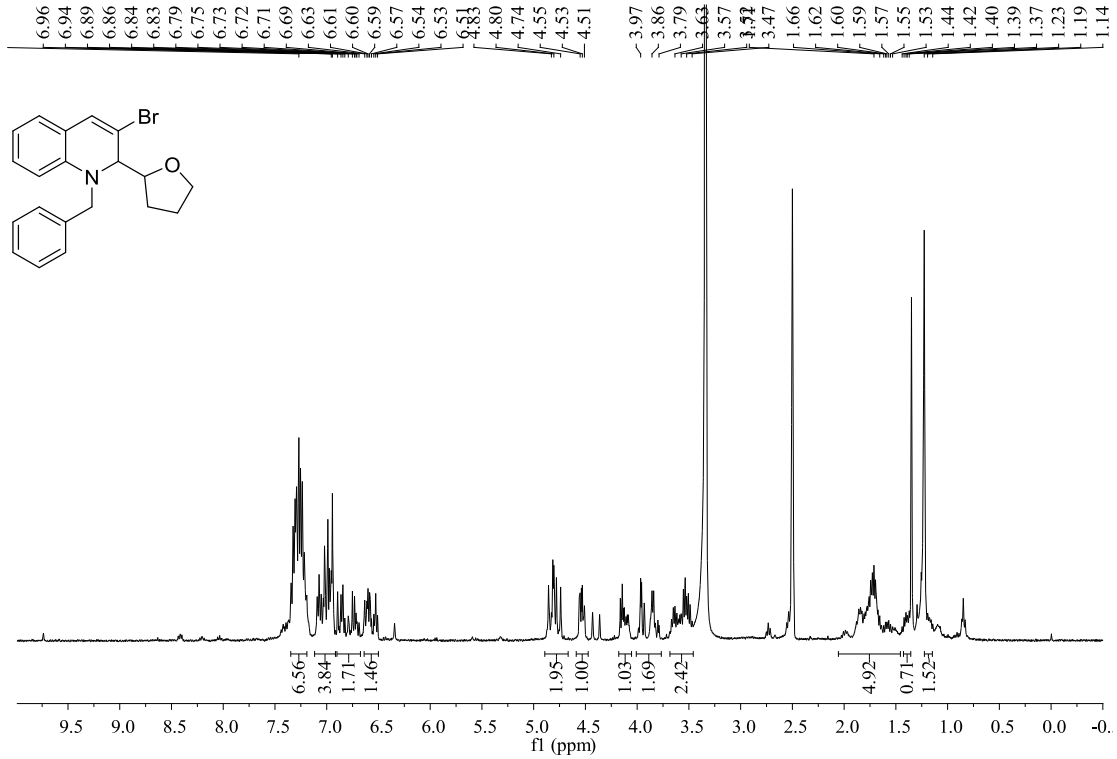

149.29
149.09
147.71
147.54
137.03
127.49
121.64
112.98
111.38
111.27
109.41
85.08
53.06
49.68
Br
N
O
O
Br
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

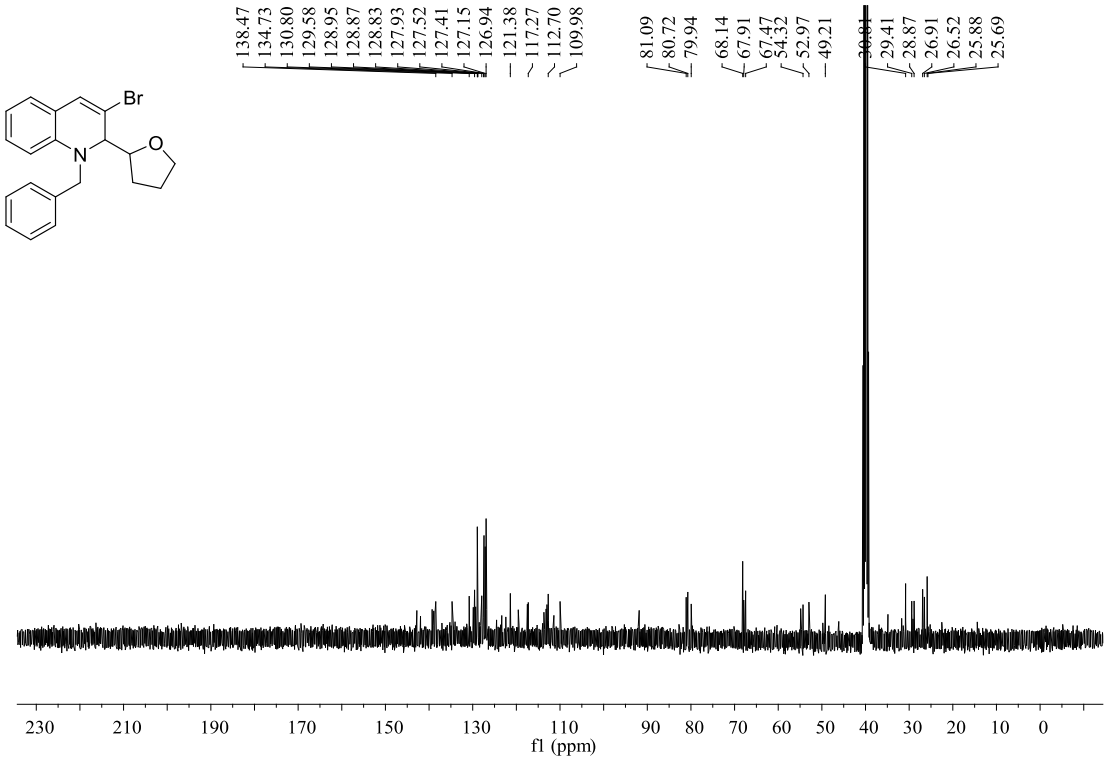
6c


Br
N
O
O
7.25 7.24 7.22 7.20 7.19 7.08 7.04 7.02 7.01 7.00 6.99 6.98 6.97
6.62 6.60 6.60 4.64 4.63 4.58 4.54 4.50 4.39 4.37 4.22 4.21 4.20 4.19 4.18 4.07 4.05 4.04 4.02 3.92 3.90 3.88 3.87 3.85 3.85 3.83 3.81 3.80 3.70 3.69 3.68 3.67
10.48 5.90 3.96 0.95 3.06 2.00 3.00 1.04 1.00 1.11 3.11 0.99
9.5 9.0 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)

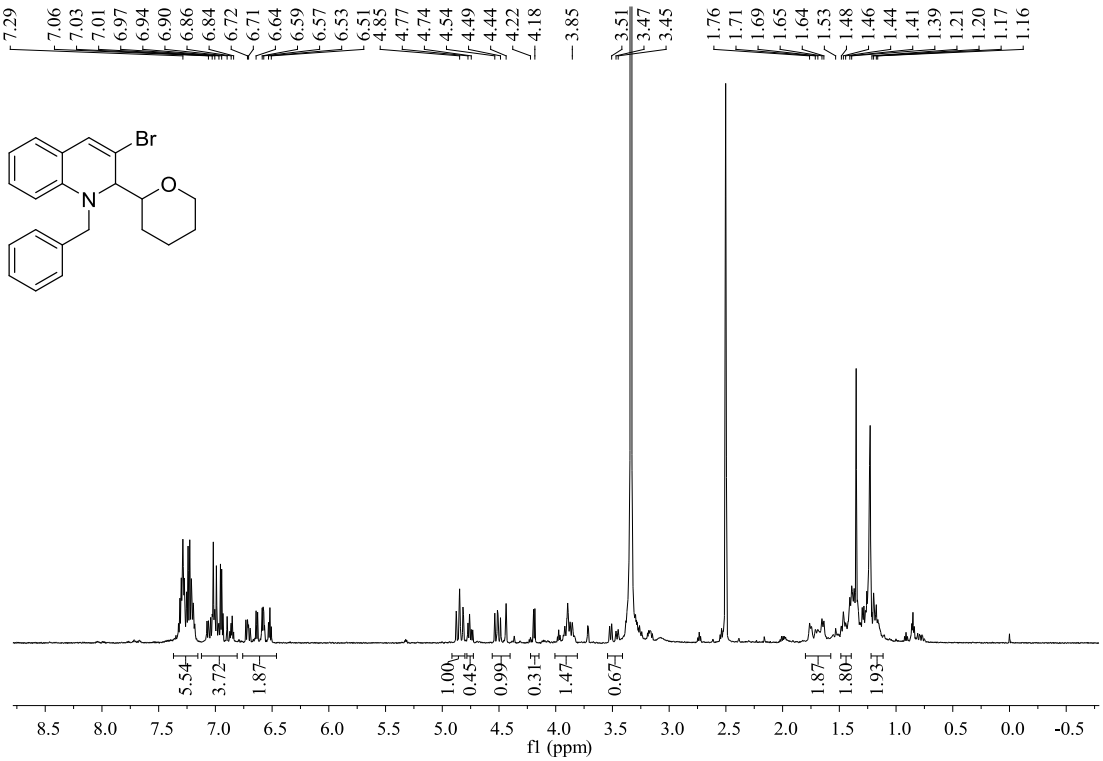

Br
N
O
O
142.44 141.77 138.72 138.50 127.39 127.19 123.25 117.86 113.91 110.48 95.04 94.63 77.22 76.57 66.18 54.89 54.61
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

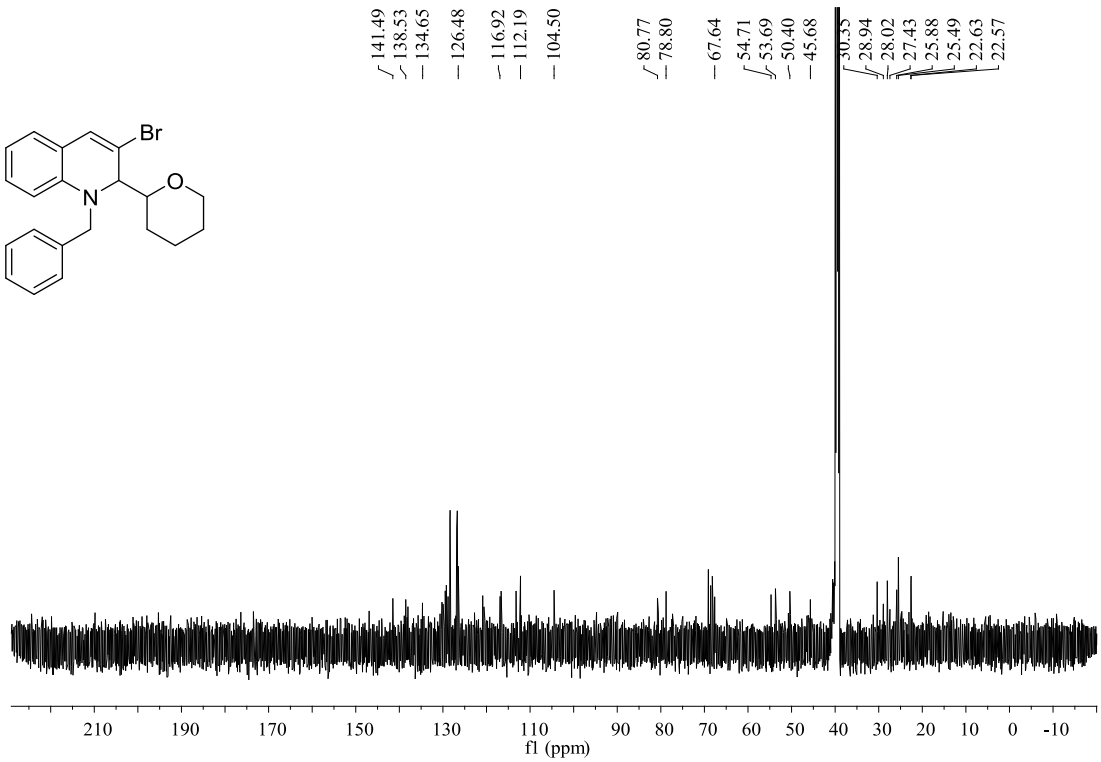
6d


6.96
6.94
6.89
6.86
6.84
6.83
6.79
6.75
6.73
6.72
6.71
6.69
6.63
6.61
6.60
6.59
6.57
6.54
6.53
6.51
4.83
4.80
4.74
4.55
4.53
4.51
3.97
3.86
3.79
3.63
3.57
3.47
1.66
1.62
1.60
1.59
1.57
1.55
1.53
1.44
1.42
1.40
1.39
1.37
1.23
1.19
1.14
Br
N
O
6.56
3.84
1.71
1.46
1.95
1.00
1.03
1.69
2.42
4.92
0.71
1.52
fl (ppm)

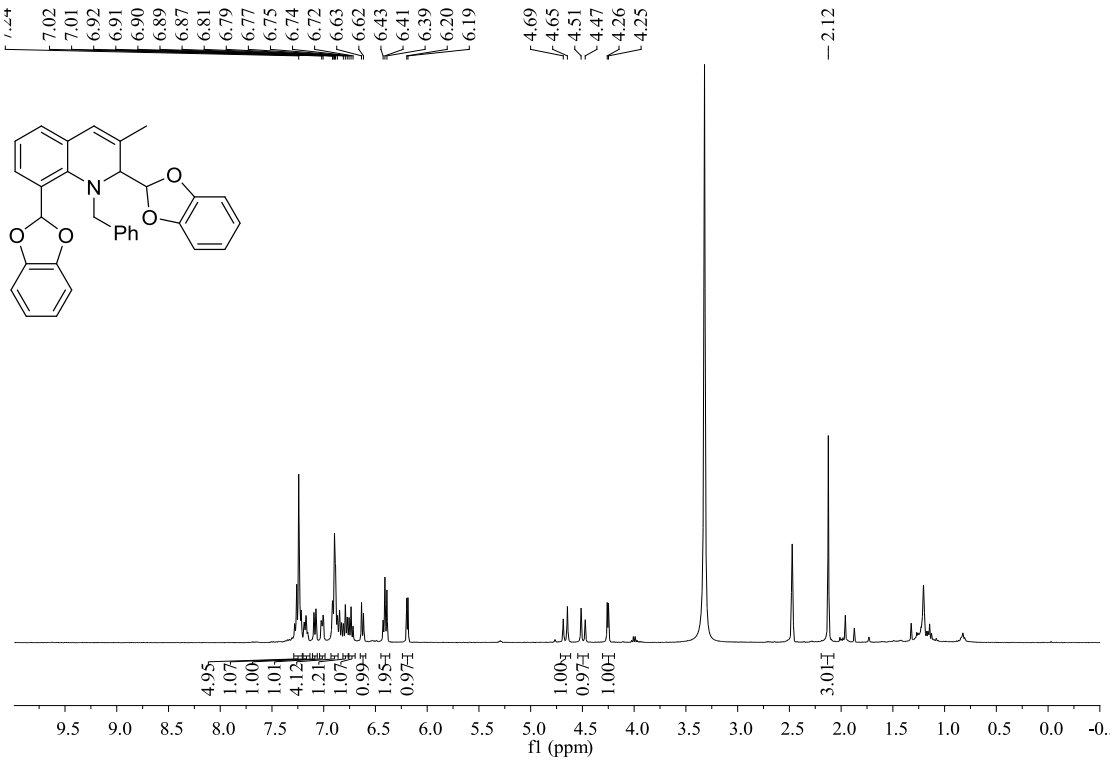

138.47
134.73
130.80
129.58
128.95
128.87
128.83
127.93
127.52
127.41
127.15
126.94
121.38
117.27
112.70
109.98
81.09
80.72
79.94
68.14
67.91
67.47
54.32
52.97
49.21
30.81
29.41
28.87
26.91
26.52
25.88
25.69
Br
N
O
fl (ppm)

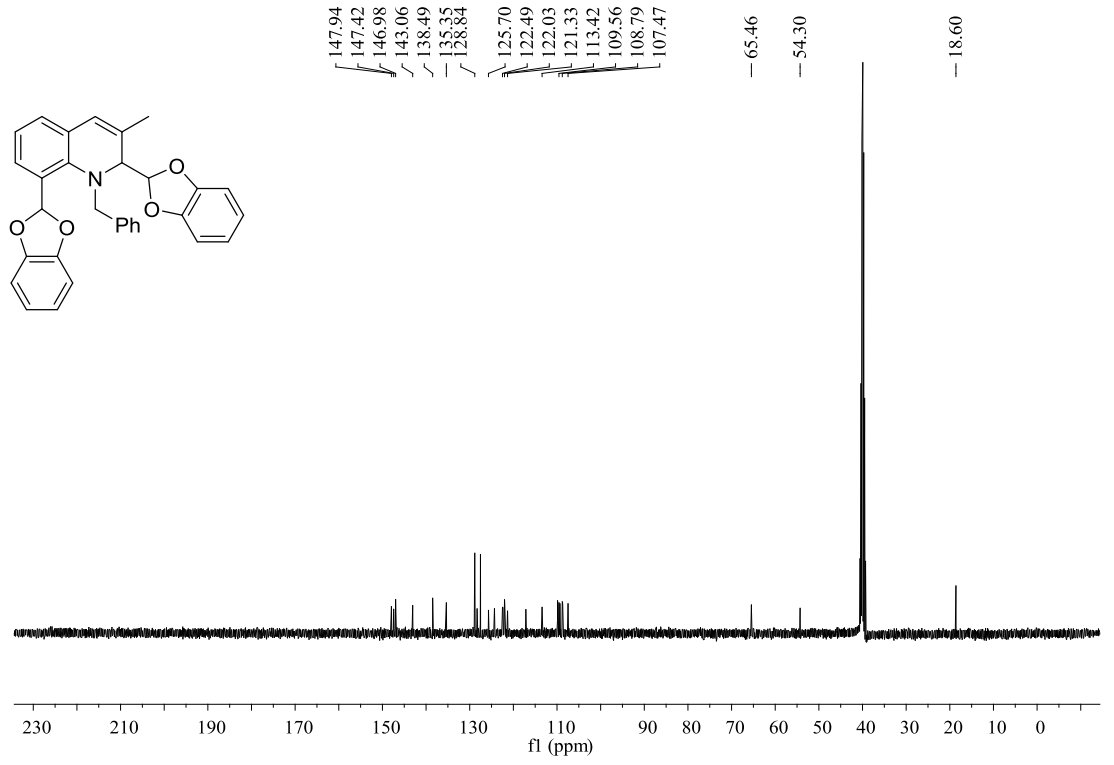
6e


7.29
7.06
7.03
7.01
6.97
6.94
6.90
6.86
6.84
6.72
6.71
6.64
6.59
6.57
6.53
6.51
4.85
4.77
4.74
4.54
4.49
4.44
4.22
4.18
3.85
3.51
3.47
3.45
1.76
1.71
1.69
1.65
1.64
1.53
1.48
1.46
1.44
1.41
1.39
1.21
1.20
1.17
1.16
Br
N
O
5.54
3.72
1.87
1.00
0.45
0.99
0.31
1.47
0.67
1.87
1.80
1.93
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
-0.5
f1 (ppm)


141.49
138.53
134.65
126.48
116.92
112.19
104.50
80.77
78.80
67.64
54.71
53.69
50.40
45.68
30.35
28.94
28.02
27.43
25.88
25.49
22.63
22.57
Br
N
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

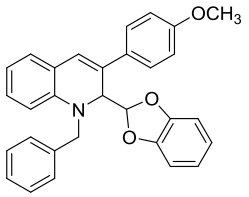
9

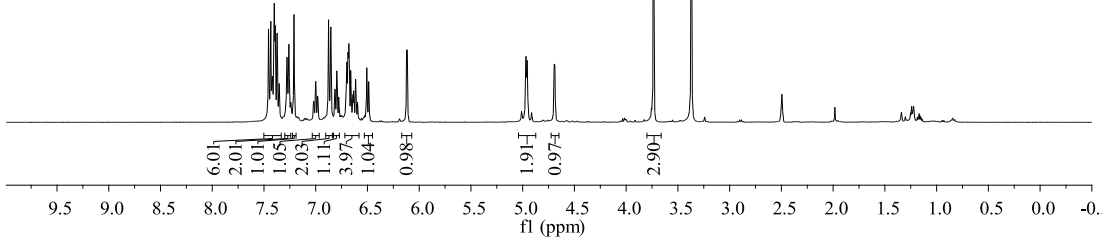

7.02
7.01
6.92
6.91
6.90
6.89
6.87
6.81
6.79
6.77
6.75
6.74
6.72
6.63
6.62
6.43
6.41
6.39
6.20
6.19
4.69
4.65
4.51
4.47
4.26
4.25
2.12
Ph
4.95
1.00
1.01
4.12
1.07
0.99
1.95
0.97
1.00
0.97
1.00
3.01
fl (ppm)

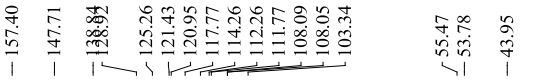

147.94
147.42
146.98
143.06
138.49
135.35
128.84
125.70
122.49
122.03
121.33
113.42
109.56
108.79
107.47
65.46
54.30
18.60
Ph
fl (ppm)

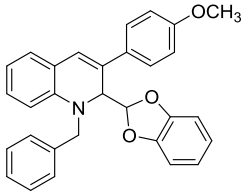
11

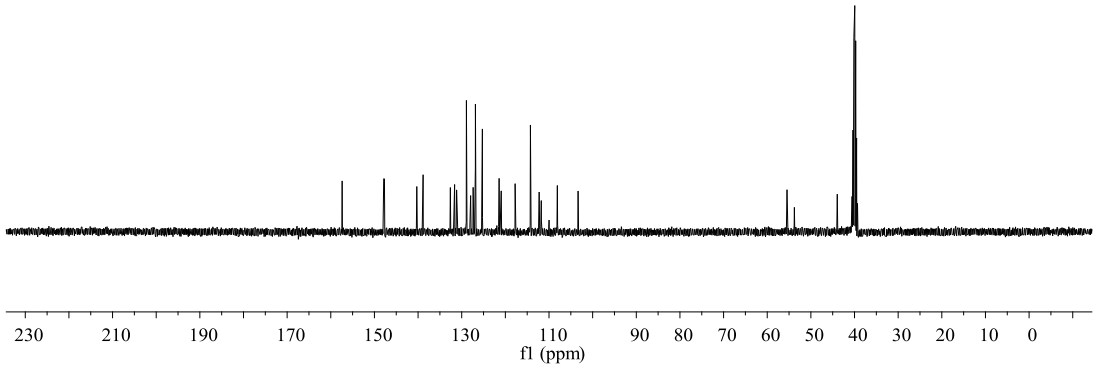

7.35
7.26
7.21
7.02
6.98
6.88
6.81
6.78
6.69
6.68
6.66
6.64
6.63
6.61
6.59
6.49
6.12
6.12
5.01
4.97
4.96
4.91
4.70
4.69
3.74


OCH3
N
O
O

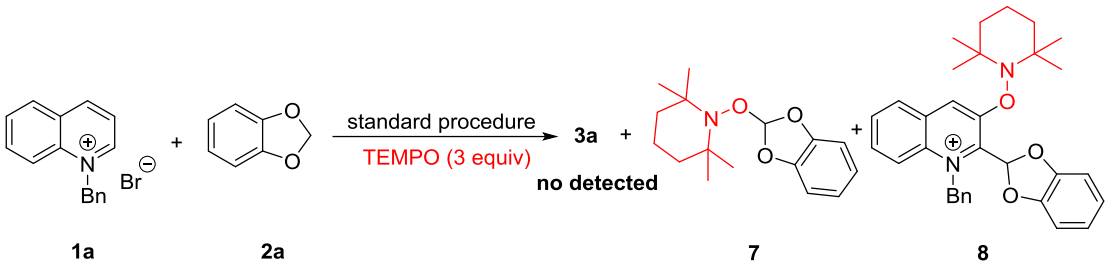

6.01
2.01
1.01
1.05
2.03
1.11
3.97
1.04
0.98
1.91
0.97
2.90
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


157.40
147.71
138.84
128.92
125.26
121.43
120.95
117.77
114.26
112.26
111.77
108.09
108.05
103.34
55.47
53.78
43.95


OCH3
N
O
O


230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

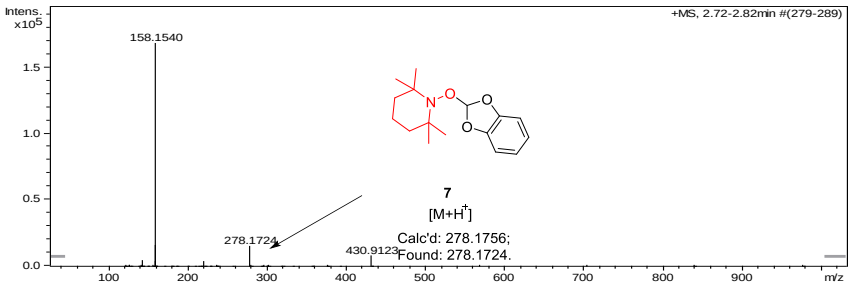
Adducts detected by HRMS

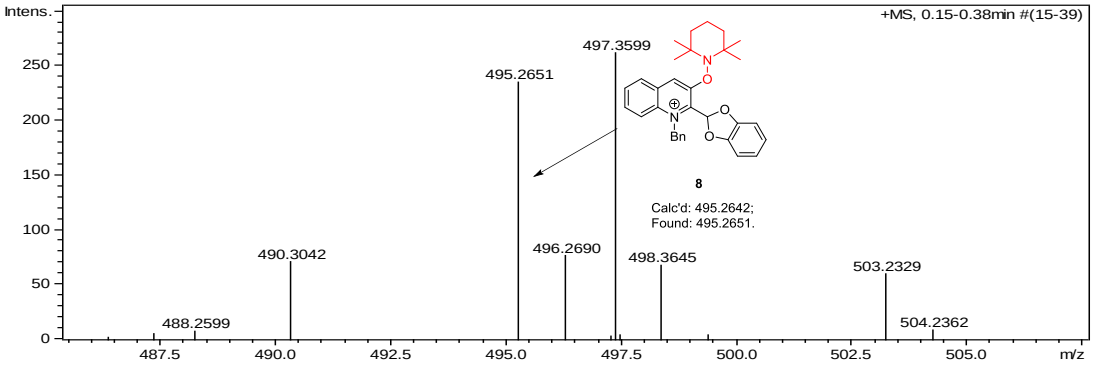


1a 2a 7 8

[M+H+]
Calc'd: 278.1751
Found: 278.1724

Calc'd: 495.2642
Found: 495.2651





DFT data

Cartesian coordinates of the radical adduct **A**

C	-4.76497400	0.02276800	1.54156900
C	-3.44459400	0.39755000	1.45086500
C	-2.67729700	0.01780000	0.31677000
C	-3.30095800	-0.74875500	-0.72665200
C	-4.65314800	-1.09601300	-0.60171100
C	-5.38160100	-0.72097400	0.51171000
H	-5.33633000	0.29552000	2.42285400
H	-2.98558000	0.93820300	2.26916700
C	-2.53471500	-1.09289400	-1.89775900
H	-5.12144600	-1.66352200	-1.40065900
H	-6.42700800	-0.99828100	0.59818600
C	-1.20652000	-0.87878900	-1.92036200
C	-0.51409800	-0.33147900	-0.72796600
H	-3.04942700	-1.53510800	-2.74593100
H	-0.58518200	-1.18111900	-2.75652400
N	-1.37353500	0.39081000	0.17185900
C	2.17252100	-1.32408900	0.85486300
C	2.25147600	-1.98730600	-0.35952700
C	3.45411100	-2.32165600	-0.94514500
C	4.60382800	-1.95427200	-0.23427000
C	4.52561000	-1.29849200	0.99669500
C	3.29324200	-0.96792000	1.57545800
C	0.10742800	-1.58739400	0.06682400
H	3.50095600	-2.84788300	-1.89185700
H	5.57737500	-2.19469800	-0.64826900
H	5.43901500	-1.04394400	1.52380400
H	3.22243500	-0.47877200	2.54108900
O	0.97405200	-2.25673500	-0.80249300
O	0.84126400	-1.14951200	1.17912900
C	-0.77200700	1.41981000	1.05751400
H	-0.39394500	0.92777400	1.96161300
H	-1.58185500	2.09718900	1.33465900
C	0.32056300	2.19839900	0.37014700
C	1.64209300	2.09294700	0.80000900
C	0.00767200	3.03180900	-0.70903700
C	2.65095600	2.80636500	0.15210800
H	1.88200600	1.45622300	1.64704500
C	1.01333200	3.74155600	-1.35801700
H	-1.02512300	3.12473800	-1.04105400
C	2.33733300	3.62680100	-0.92854200

H	3.67800000	2.71918100	0.49343600
H	0.76563800	4.38876400	-2.19364800
H	3.12116500	4.18208600	-1.43420900
H	0.34669400	0.28937100	-0.99217800
H	-0.71668100	-2.23603300	0.38310800

E(UM062X/6-31+G(d)) = -1092.39382036
Sum of electronic and zero-point Energies= -1092.024825
Sum of electronic and thermal Energies= -1092.005213
Sum of electronic and thermal Enthalpies= -1092.004269
Sum of electronic and thermal Free Energies= -1092.075177

Frequencies：

25.1745	28.4756	35.2302
57.7188	65.3384	71.5121
96.4876	133.1393	167.8355
183.8173	206.6513	233.0721
262.4712	273.6035	316.4179
346.3709	355.1006	396.5128
416.9996	424.4770	431.5524
456.0147	478.6335	484.4483
508.6908	520.0826	553.2404
563.9362	569.5163	573.2701
578.7872	630.5458	632.7420
633.9184	699.6430	721.7859
727.9099	731.1438	764.7720
771.5156	781.0593	786.9187
807.4630	820.8775	835.1880
846.2864	866.3343	871.1070
877.3850	881.0084	885.1648
896.8715	953.7108	963.7184
972.0628	996.8465	1012.0122
1013.5723	1016.2913	1020.9602
1035.2796	1038.0776	1039.7338
1044.8612	1057.4516	1067.8440
1068.8566	1094.7070	1124.3588
1129.5207	1137.4370	1162.7387
1181.0693	1182.8176	1184.4944
1194.4259	1204.1156	1209.0711
1212.3628	1241.7088	1253.5941
1258.7271	1271.7472	1283.7985
1309.8346	1314.3229	1328.5202
1348.9807	1366.9173	1370.7010
1381.3404	1385.5681	1395.1658

1419.8558	1432.7427	1468.0278
1487.3189	1508.6301	1511.8342
1526.1373	1531.8320	1535.6692
1555.1553	1597.6410	1660.8085
1679.7682	1688.1687	1691.4780
1695.1705	1718.7824	3101.3268
3132.4364	3147.7192	3166.1479
3191.4410	3221.4821	3229.8040
3230.3422	3232.3771	3232.8805
3237.0549	3239.6422	3245.6574
3248.0073	3249.9596	3251.9872
3257.7584	3259.9493	3271.5381