Supporting Information

Chemo- and regioselective synthesis of polysubstituted 2-aminothiophenes by the cyclization of *gem*-dibromo or *gem*-dichoroalkenes with β-keto tertiary thioamides

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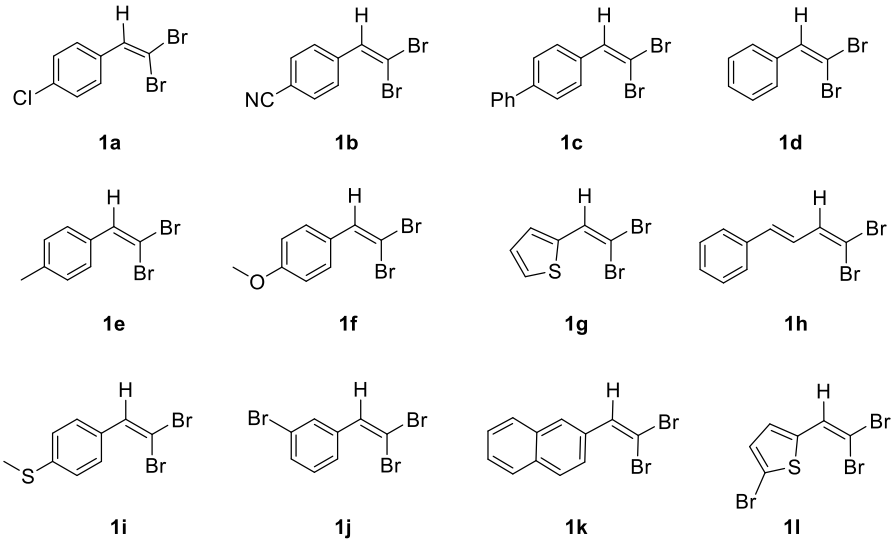
1. General information

All reagents were of analytical grade, and obtained from commercial suppliers and used without further purification. DMSO and other solvents were dried by standard method prior to use. Melting points were measured in an open capillary using Büchi melting point B-540 apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C NMR, respectively) using TMS as internal standard. The GC and GC-MS were recorded on HP 5973 MSD with 6890 GC. High resolution mass spectra (HRMS) were recorded under electron impact conditions using a MicroMass GCT CA 055 instrument and recorded on a MicroMass LCTTM spectrometer. Silica gel (300−400 mesh size) was used for column chromatography. TLC analysis of reaction mixtures was performed using silica gel plates.

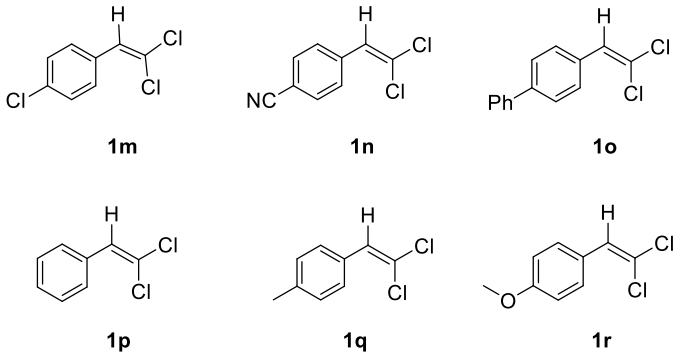
2. The *gem*-dibromoalkenes (1a–l), *gem*-dichloroalkenes (1m–r) and β-keto tertiary thioamides (2a–g) used in this reaction

(1) The *gem*-dibromoalkenes (1a–l) used in this reaction



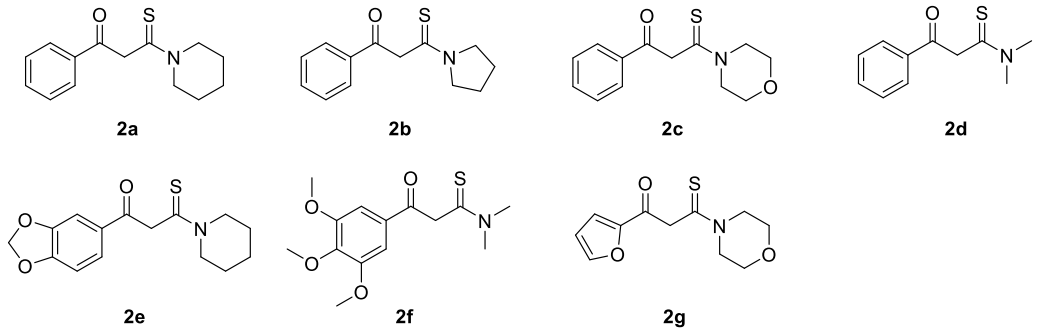
The *gem*-dibromoalkenes (**1a**–**l**) were prepared according to the reported procedure (J. Liu, F. Dai, Z. Yang, S. Wang, K. Xie, A. Wang, X. Chen and Z. Tan, *Tetrahedron Lett*., 2012, **53**, 5678–5683).

(2) The *gem*-dichloroalkenes (1m–r) used in this reaction



The *gem*-dichloroalkenes (**1m**–**r**) were prepared according to the reported procedure (S. G. Newman, C. S. Bryan, D. Perez and M. Lautens, *Synthesis*, 2011, 342).

(3) The β-keto tertiary thioamides (2a–g) used in this reaction

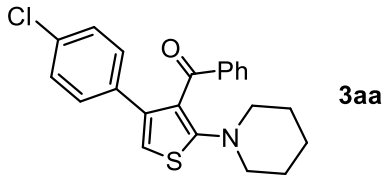


The β-keto tertiary thioamides (**2a–g**) were prepared according to the reported procedures (Q. Liu and T. Rovis, *Org. Lett.*, 2009, **11**, 2856; G. C. Nandi, M. S. Singh, H. Ila and H. Junjappa, *Eur. J. Org. Chem.*, 2012, 967).

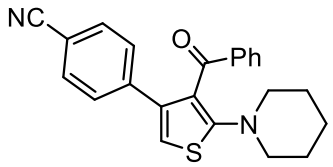
3. General procedure for the synthesis of compounds 3

A 25 mL of dried round-bottom flask was charged with 1,1-dihaloalkene **1** (1.0 mmol), β-ketothioamide **2** (1.2 mmol), K_2CO_3 (2.5 mmol, 345.0 mg), and DMSO (5 mL) under argon atmosphere. The mixture was stirred at 120 °C for 4 h (monitored by TLC). After the reaction completed, the reaction mixture was quenched with H_2O (20 mL) and extracted with EtOAc (3×10 mL). The combined organic layer was washed with brine (2×10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude residue was then purified by column chromatography on silica gel to afford the pure target compounds **3**.

4. Characterization data of compounds 3

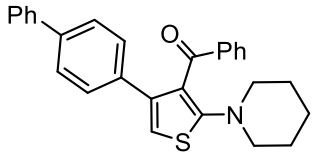


(4-(4-Chlorophenyl)-2-(piperidin-1-yl)thiophen-3-yl)(phenyl)methanone (3aa=3ma): Yellow solid; yield: 90% (**3aa**), 82% (**3ma**); mp: 97.0−97.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.6 Hz, 2H), 7.53–7.49 (m, 1H), 7.41–7.37 (m, 2H), 7.20–7.15 (m, 4H), 6.70 (s, 1H), 2.91 (t, *J* = 5.0 Hz, 4H), 1.35–1.27 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.0, 162.9, 141.0, 137.9, 135.2, 133.0, 132.9, 129.9, 129.6, 128.3, 128.1, 124.9, 113.1, 55.7, 25.3, 23.5. HRMS (EI) calcd for $C_{22}H_{20}ClNOS$ $[M]^+$: 381.0952, found: 381.0953.



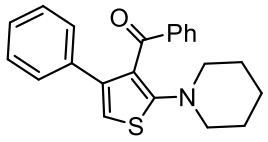
3ba

4-(4-Benzoyl-5-(piperidin-1-yl)thiophen-3-yl)benzonitrile (3ba): Yellow solid; yield: 92%; mp: 94.8−95.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.55–7.49 (m, 3H), 7.42–7.38 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.76 (s, 1H), 2.92 (t, *J* = 5.2 Hz, 4H), 1.28–1.26 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.5, 163.6, 141.4, 140.5, 137.7, 133.1, 132.0, 129.9, 129.0, 128.2, 124.2, 118.9, 114.3, 110.6, 55.6, 25.3, 23.4. HRMS (EI) calcd for $C_{23}H_{20}N_2OS$ $[M]^+$: 372.1296, found: 372.1298.



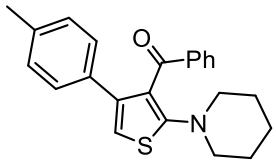
3ca

(4-([1,1'-Biphenyl]-4-yl)-2-(piperidin-1-yl)thiophen-3-yl)(phenyl)methanone (3ca=3oa): Yellow solid; yield: 88% (**3ca**), 78% (**3oa**); mp: 135.6−136.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92–7.90 (m, 2H), 7.57–7.47 (m, 5H), 7.43–7.39 (m, 4H), 7.35–7.30 (m, 3H), 6.79 (s, 1H), 2.95 (t, *J* = 5.2 Hz, 4H), 1.37–1.31 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.2, 162.7, 141.8, 140.8, 139.8, 138.1, 135.7, 132.8, 130.0, 128.7, 128.1, 127.2, 127.0, 126.9, 125.4, 113.1, 55.7, 25.4, 23.5. HRMS (EI) calcd for $C_{28}H_{25}NOS$ $[M]^+$: 424.1683, found: 424.1685.



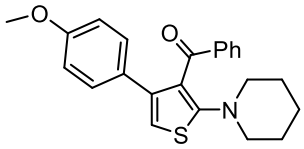
3da

Phenyl(4-phenyl-2-(piperidin-1-yl)thiophen-3-yl)methanone (3da=3pa): Yellow oil; yield: 80% (**3da**), 72% (**3pa**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.2 Hz, 2H), 7.49–7.45 (m, 1H), 7.38–7.34 (m, 2H), 7.24–7.16 (m, 5H), 6.71 (s, 1H), 2.91 (t, *J* = 4.8 Hz, 4H), 1.34–1.29 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.2, 162.6, 142.2, 138.1, 136.7, 132.7, 129.9, 128.3, 128.2, 128.1, 127.0, 125.4, 112.9, 55.7, 25.4, 23.5. HRMS (EI) calcd for $C_{22}H_{21}NOS$ $[M]^+$: 347.1347, found: 347.1346.



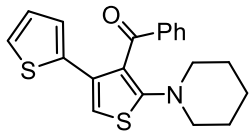
3ea

Phenyl(2-(piperidin-1-yl)-4-(*p*-tolyl)thiophen-3-yl)methanone (3ea=3qa): Yellow solid; yield: 80% (**3ea**), 80% (**3qa**); mp: 85.0−86.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 7.6 Hz, 2H), 7.53–7.50 (m, 1H), 7.42–7.38 (m, 2H), 7.15 (d, *J* = 7.6 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.72 (s, 1H), 2.93 (t, *J* = 4.8 Hz, 4H), 2.29 (s, 3H), 1.34–1.29 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.3, 162.3, 142.1, 138.1, 136.7, 133.8, 132.7, 129.9, 128.9, 128.2, 128.0, 125.6, 112.6, 55.7, 25.4, 23.5, 21.2. HRMS (EI) calcd for $C_{23}H_{23}NOS$ $[M]^+$: 361.1506, found: 361.1504.



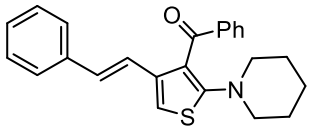
3fa

(4-(4-Methoxyphenyl)-2-(piperidin-1-yl)thiophen-3-yl)(phenyl)methanone (3fa=3ra): Yellow solid; yield: 75% (**3fa**), 50% (**3ra**); mp: 68.5−69.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.2 Hz, 2H), 7.52–7.49 (m, 1H), 7.41–7.37 (m, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.68 (s, 1H), 3.75 (s, 3H), 2.92 (t, *J* = 5.0 Hz, 4H), 1.31–1.28 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.4, 162.3, 158.7, 141.7, 138.1, 132.7, 129.9, 129.4, 129.3, 128.1, 125.5, 113.6, 112.2, 55.7, 55.2, 25.4, 23.5. HRMS (EI) calcd for $C_{23}H_{23}NO_2S$ $[M]^+$: 377.1451, found: 377.1452.



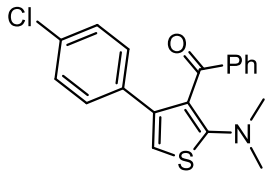
3ga

Phenyl(5'-(piperidin-1-yl)-[2,3'-bithiophen]-4'-yl)methanone (3ga): Yellow oil; yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.2 Hz, 2H), 7.53–7.49 (m, 1H), 7.41–7.38 (m, 2H), 7.12–7.10 (m, 1H), 6.92–6.91 (m, 1H), 6.87–6.85 (m, 2H), 2.93 (t, *J* = 4.8 Hz, 4H), 1.35–1.31 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.4, 161.8, 138.0, 137.9, 133.7, 132.9, 129.8, 128.1, 127.2, 125.7, 125.2, 124.6, 113.4, 55.6, 25.4, 23.5. HRMS (EI) calcd for $C_{20}H_{19}NOS_2$ $[M]^+$: 353.0912, found: 353.0910.



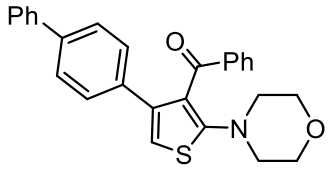
3ha

(*E*)-Phenyl(2-(piperidin-1-yl)-4-styrylthiophen-3-yl)methanone (3ha): Yellow oil; yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.52–7.49 (m, 1H), 7.42–7.37 (m, 4H), 7.27–7.23 (m, 2H), 7.18–7.15 (m, 1H), 7.11 (d, *J* = 16.4 Hz, 1H)， 6.91 (d, *J* = 16.0 Hz, 1H), 6.90 (s, 1H)， 2.85 (t, *J* = 5.2 Hz, 4H), 1.27–1.26 (m, 2H), 1.17–1.12 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.8, 163.8, 138.8, 138.2, 137.5, 132.7, 130.0, 129.6, 128.6, 128.1, 127.5, 126.5, 123.6, 122.8, 109.7, 55.7, 25.2, 23.4. HRMS (EI) calcd for $C_{24}H_{23}NOS$ $[M]^+$: 373.1500, found: 373.1501.



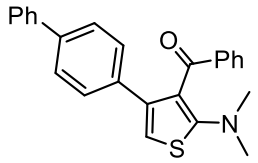
3ad

(4-(4-Chlorophenyl)-2-(dimethylamino)thiophen-3-yl)(phenyl)methanone (3ad=3md): Yellow oil; yield: 86% (**3ad**), 75% (**3md**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76–7.74 (m, 2H), 7.44–7.40 (m, 1H), 7.31–7.27 (m, 2H), 7.10 (s, 4H), 6.51 (s, 1H), 2.80 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.3, 162.4, 141.3, 138.6, 135.5, 132.8, 132.7, 129.8, 129.6, 128.2, 120.7, 109.8, 45.6. HRMS (EI) calcd for $C_{19}H_{16}ClNOS$ $[M]^+$: 341.0639, found: 341.0641.



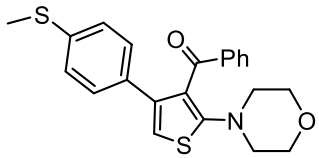
3cc

(4-([1,1'-Biphenyl]-4-yl)-2-morpholinothiophen-3-yl)(phenyl)methanone (3cc=3oc): Yellow solid; yield: 88% (**3cc**), 76% (**3oc**); mp: 134.5−135.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–7.82 (m, 2H), 7.52–7.43 (m, 5H), 7.40–7.34 (m, 4H), 7.31–7.29 (m, 3H), 6.87 (s, 1H), 3.46 (t, *J* = 4.8 Hz, 4H), 2.98 (t, *J* = 4.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.3, 160.6, 141.6, 140.6, 139.9, 138.0, 135.2, 133.0, 129.8, 128.7, 128.6, 128.2, 127.3, 127.2, 127.0, 126.9, 114.1, 66.4, 54.4. HRMS (EI) calcd for $C_{27}H_{23}NO_2S$ $[M]^+$: 425.1450, found: 425.1452.



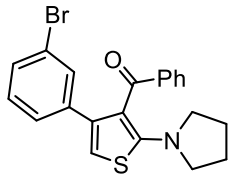
3cd

(4-([1,1'-Biphenyl]-4-yl)-2-(dimethylamino)thiophen-3-yl)(phenyl)methanone (3cd=3od): Yellow solid; yield: 90% (**3cd**), 81% (**3od**); mp: 127.1−128.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79–7.77 (m, 2H), 7.48–7.46 (m, 2H), 7.37–7.34 (m, 5H), 7.28–7.22 (m, 5H), 6.57 (s, 1H), 2.79 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.6, 162.2, 142.1, 140.7, 139.6, 138.8, 136.0, 132.7, 129.9, 128.7, 128.2, 127.2, 127.0, 126.8, 121.4, 109.9, 45.7. HRMS (EI) calcd for $C_{25}H_{21}NOS$ $[M]^+$: 383.1344, found: 383.1346.



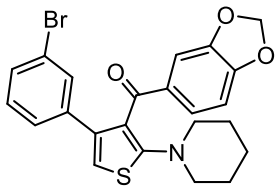
3ic

(4-(4-(Methylthio)phenyl)-2-morpholinothiophen-3-yl)(phenyl)methanone (3ic): Yellow oil; yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81–7.79 (m, 2H), 7.50–7.48 (m, 1H), 7.39–7.35 (m, 2H), 7.17–7.08 (m, 4H), 6.81 (s, 1H), 3.46 (t, *J* = 4.6 Hz, 4H), 2.96 (t, *J* = 4.6 Hz, 4H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.3, 160.5, 141.4, 137.9, 137.5, 133.3, 129.7, 128.6, 128.2, 127.1, 126.4, 113.8, 66.4, 54.4, 15.7. HRMS (EI) calcd for $C_{22}H_{21}NO_2S_2$ $[M]^+$: 395.1014, found: 395.1015.



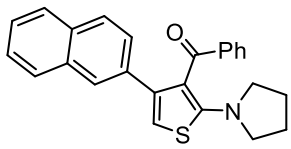
3jb

(4-(3-Bromophenyl)-2-(pyrrolidin-1-yl)thiophen-3-yl)(phenyl)methanone (3jb): Yellow oil; yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65–7.63 (m, 2H), 7.30–7.26 (m, 2H), 7.19–7.16 (m, 2H), 7.12–7.09 (m, 1H), 7.01–6.99 (m, 1H), 6.89–6.85 (m, 1H), 6.26 (s, 1H), 3.19 (t, *J* = 6.6 Hz, 4H), 1.98–1.94 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.8, 159.7, 141.3, 139.8, 139.6, 132.0, 131.4, 129.7, 129.5, 129.2, 127.8, 127.0, 121.8, 114.8, 106.2, 53.3, 26.1. HRMS (EI) calcd for $C_{21}H_{18}BrNOS$ $[M]^+$: 413.0272, found: 413.0279.



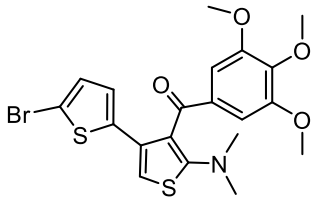
3je

Benzo[*d*][1,3]dioxol-5-yl(4-(3-bromophenyl)-2-(piperidin-1-yl)thiophen-3-yl)methanone (3je): Yellow oil; yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.41 (m, 2H), 7.35–7.34 (m, 1H), 7.31–7.29 (m, 1H), 7.11–7.03 (m, 2H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.71 (s, 1H), 6.01 (s, 2H), 2.94 (s, 4H), 1.40 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.3, 161.8, 151.7, 147.9, 140.3, 138.7, 132.7, 131.1, 130.0, 129.6, 126.9, 126.8, 124.9, 122.2, 113.3, 109.2, 107.7, 101.8, 55.5, 25.5, 23.6. HRMS (EI) calcd for $C_{23}H_{20}BrNO_3S$ $[M]^+$: 471.0327, found: 471.0332.



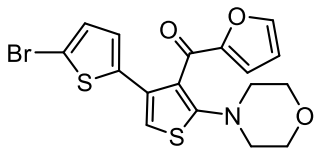
3kb

(4-(Naphthalen-2-yl)-2-(pyrrolidin-1-yl)thiophen-3-yl)(phenyl)methanone (3kb): Yellow solid; yield: 78%; mp: 109.6−110.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70–7.61 (m, 5H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.37–7.30 (m, 2H), 7.24–7.21 (m, 1H), 7.11–7.01 (m, 3H), 6.35 (s, 1H), 3.19 (t, *J* = 6.6 Hz, 4H), 1.95–1.92 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.4, 159.4, 143.0, 139.8, 135.2, 133.0, 132.1, 131.9, 129.8, 127.8, 127.7, 127.5, 127.3, 127.0, 126.8, 125.9, 125.5, 115.3, 106.2, 53.3, 26.1. HRMS (EI) calcd for $C_{25}H_{21}NOS$ $[M]^+$: 383.1344, found: 383.1346.



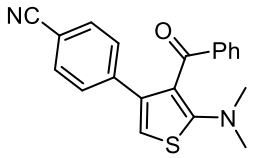
3lf

(5-Bromo-5'-(dimethylamino)-[2,3'-bithiophen]-4'-yl)(3,4,5-trimethoxyphenyl)methanone (3lf): Yellow oil; yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08 (s, 2H), 6.75 (d, *J* = 4.0 Hz, 1H), 6.62 (s, 1H), 6.52 (d, *J* = 3.6 Hz, 1H), 3.89 (s, 3H), 3.83 (s, 6H), 2.82 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.1, 161.2, 152.8, 142.6, 139.7, 133.5, 133.4, 130.1, 126.0, 119.9, 110.9, 110.4, 107.3, 60.9, 56.3, 45.5. HRMS (EI) calcd for $C_{20}H_{20}BrNO_4S_2$ $[M]^+$: 482.9997, found: 483.0000.



3lg

(5-Bromo-5'-morpholino-[2,3'-bithiophen]-4'-yl)(furan-2-yl)methanone (3lg): Yellow oil; yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 4.0 Hz, 1H), 7.00 (d, *J* = 3.6 Hz, 1H), 6.86 (s, 1H), 6.83 (d, *J* = 4.0 Hz, 1H), 6.67 (d, *J* = 3.6 Hz, 1H), 6.48 (dd, *J* = 3.2, 1.6 Hz, 1H), 3.65 (t, *J* = 4.6 Hz, 4H), 3.05–3.03 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.9, 160.7, 153.1, 147.2, 139.1, 132.6, 130.3, 125.9, 125.3, 120.2, 114.3, 112.4, 111.3, 66.5, 54.4. HRMS (EI) calcd for $C_{17}H_{14}BrNO_3S_2$ $[M]^+$: 424.9578, found: 424.9577.

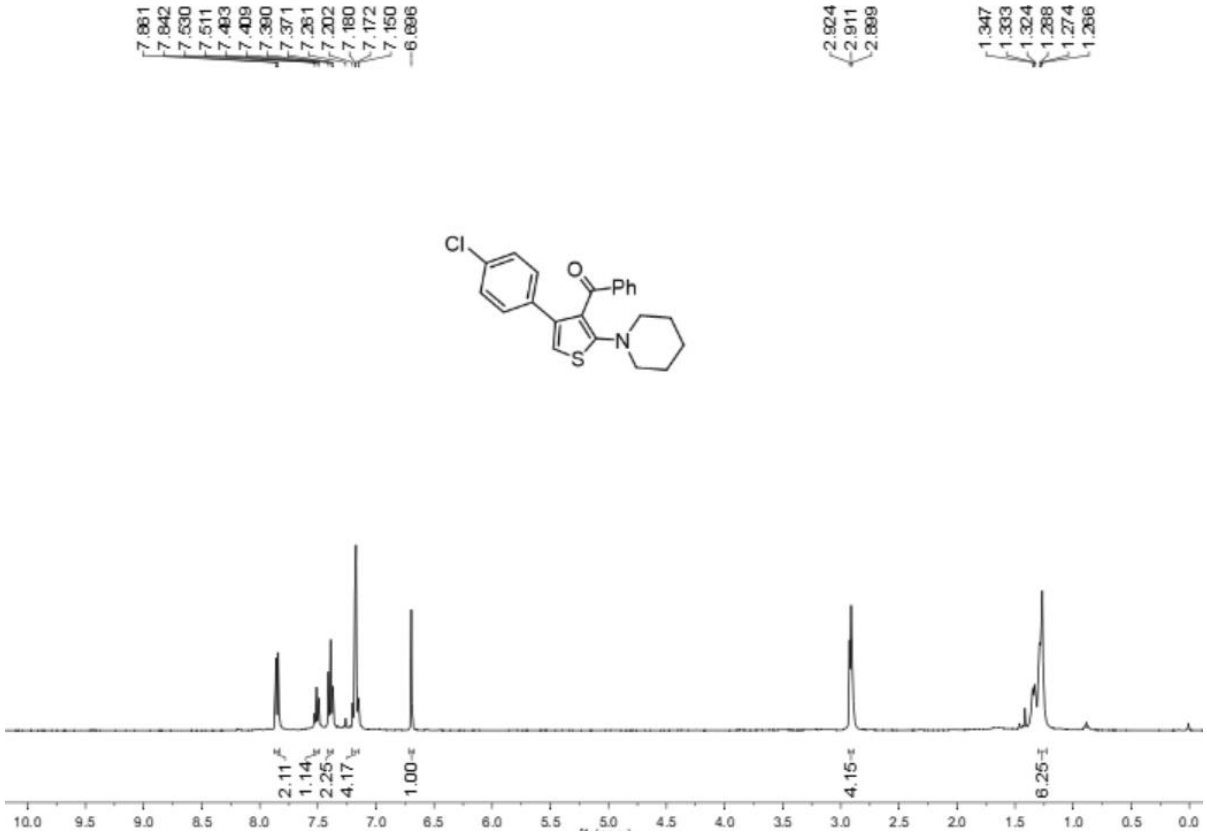


3nd

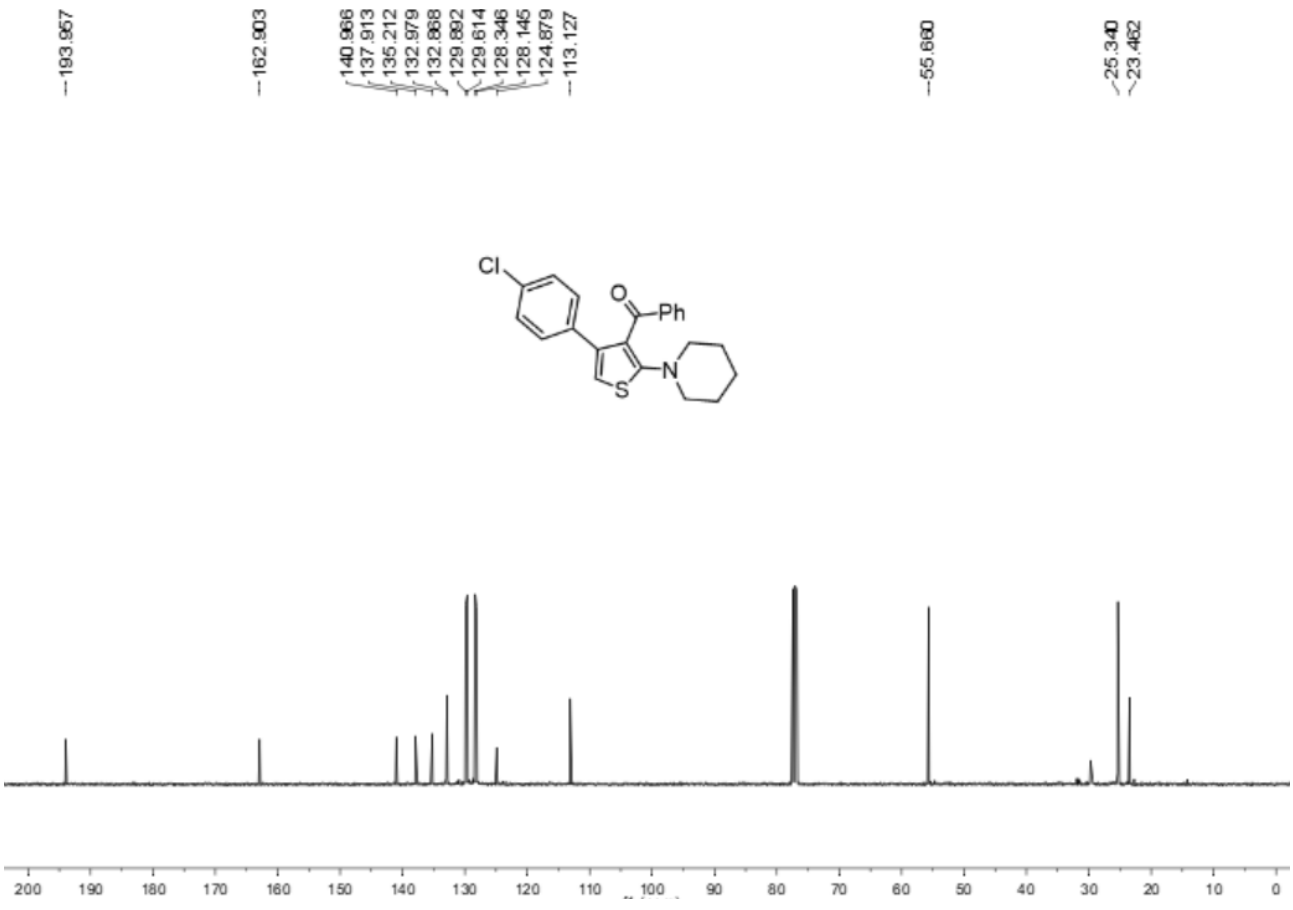
4-(4-Benzoyl-5-(dimethylamino)thiophen-3-yl)benzonitrile (3nd): Yellow oil; yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.42–7.40 (m, 3H), 7.31–7.25 (m, 4H), 6.56 (s, 1H), 2.82 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.7, 163.0, 141.7, 140.8, 138.6, 133.0, 131.8, 129.7, 128.9, 128.3, 119.7, 118.9, 110.8, 110.4, 45.5. HRMS (EI) calcd for $C_{20}H_{16}N_2OS$ $[M]^+$: 332.0436, found: 332.0431.

5. ^{1}H, ^{13}C NMR and HRMS (EI) spectra of compounds 3

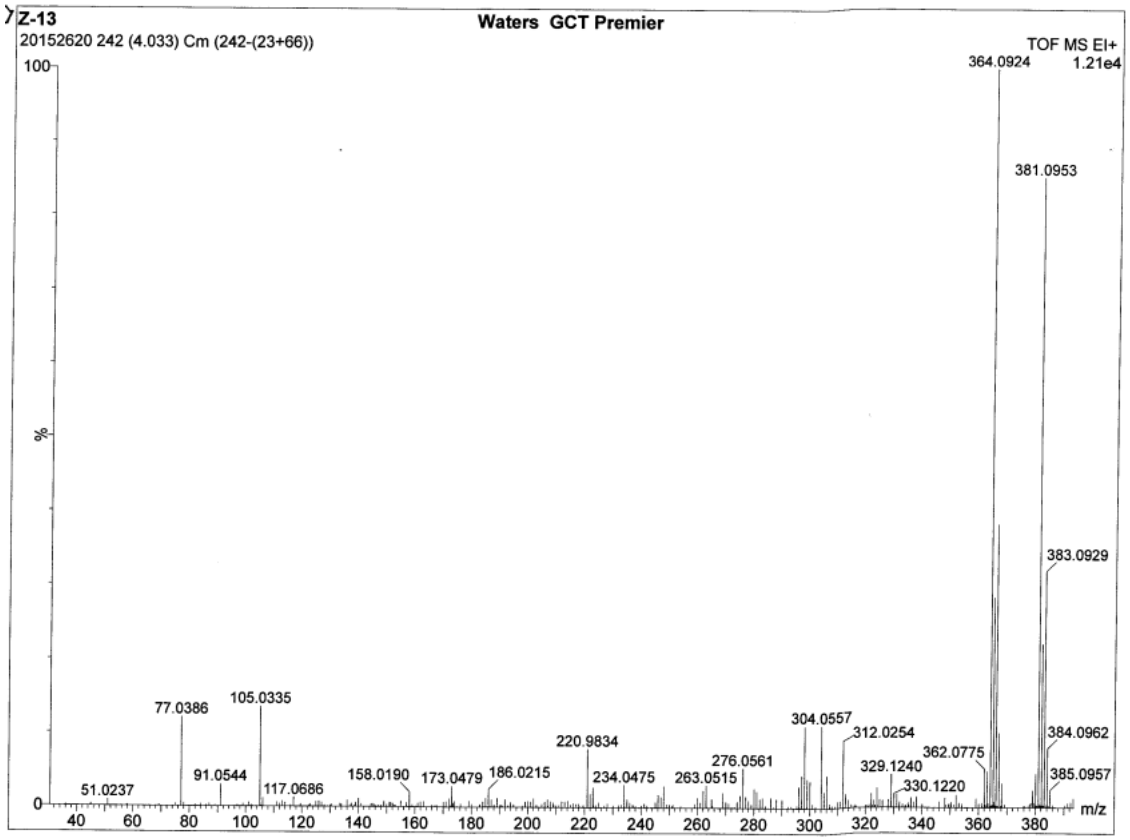
^{1}H NMR spectrum of 3aa (3ma)



^{13}C NMR spectrum of 3aa (3ma)

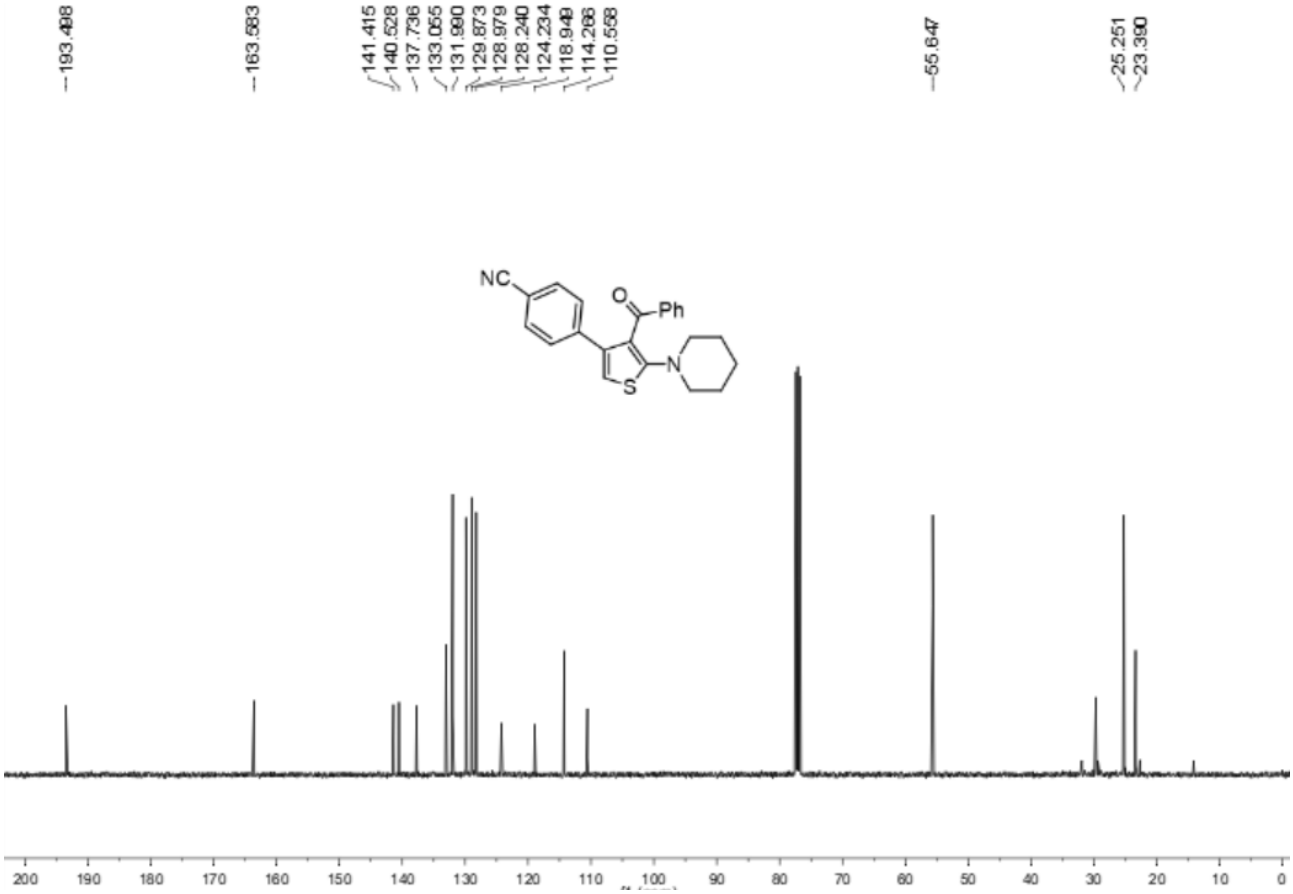


HRMS (EI) of 3aa (3ma)

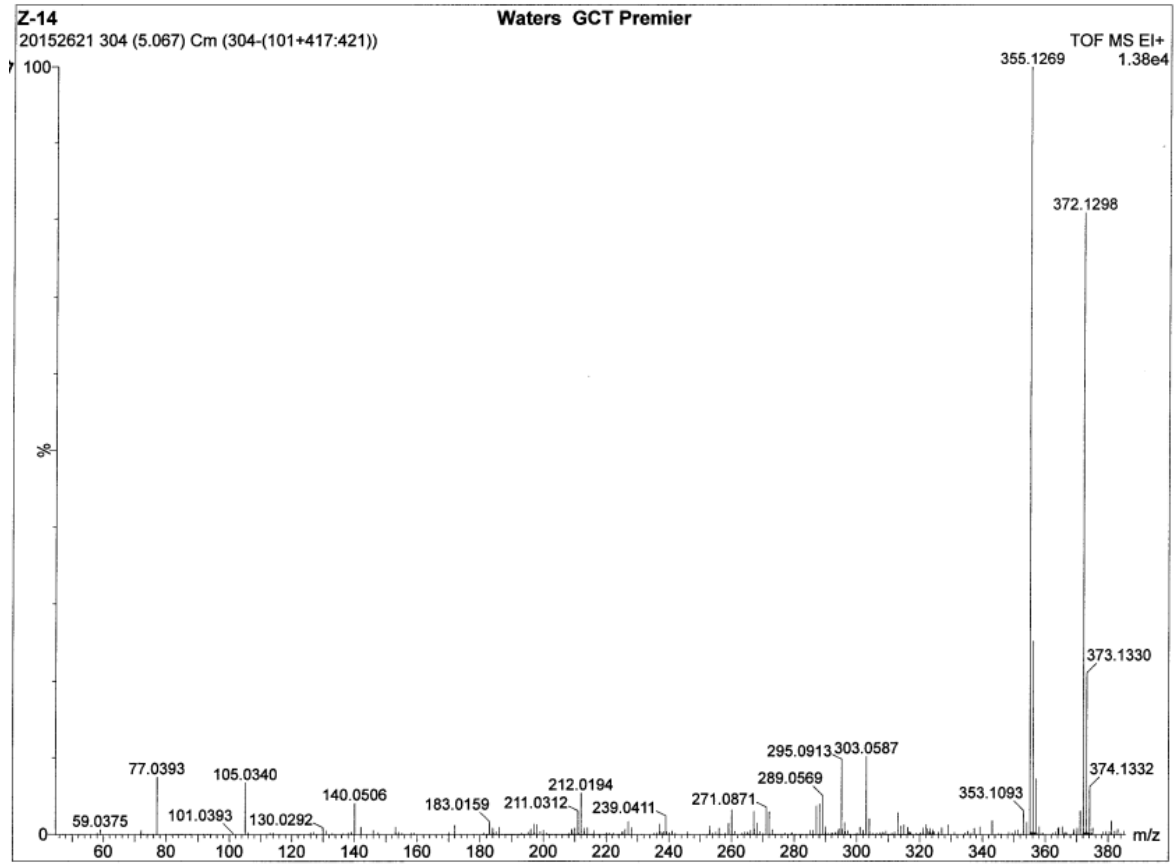


^{1}H NMR spectrum of 3ba

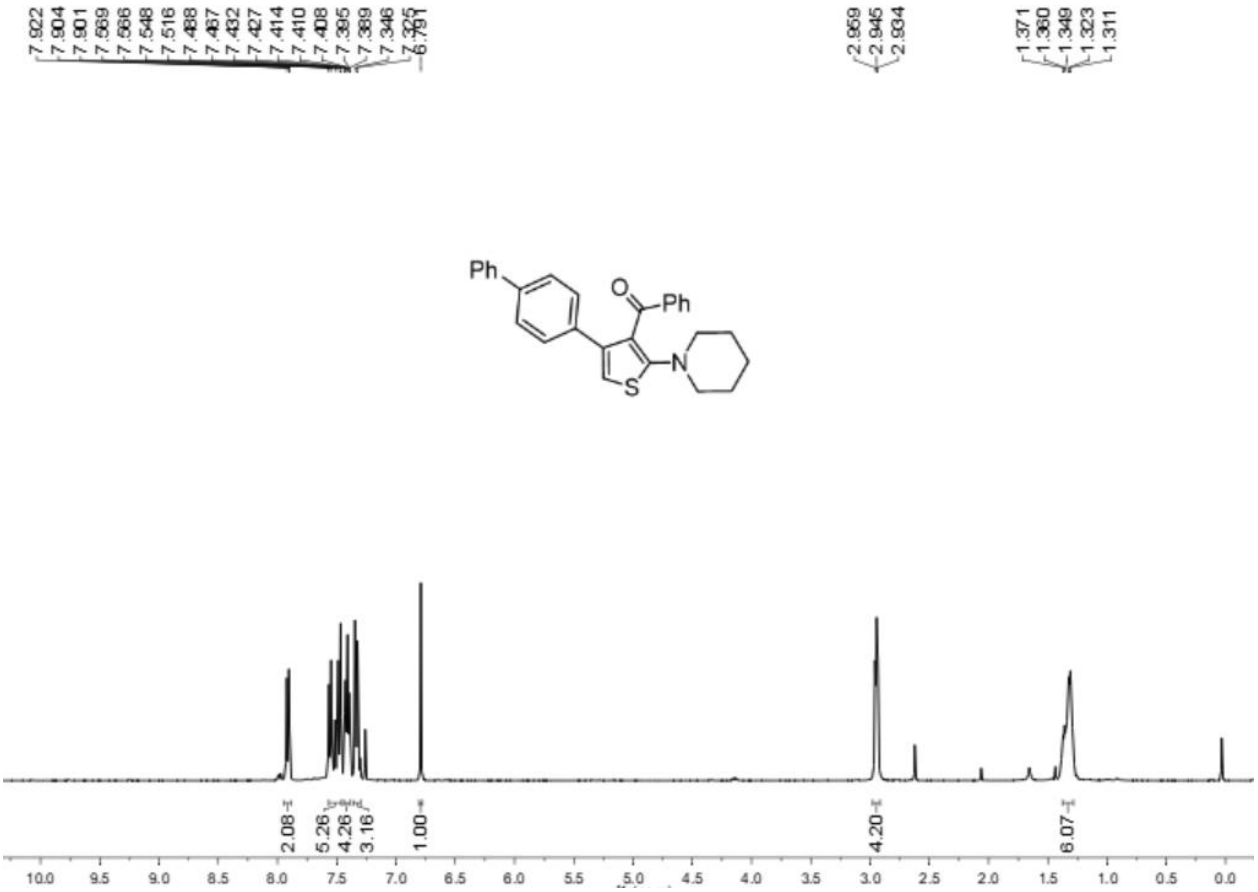
^{13}C NMR spectrum of 3ba



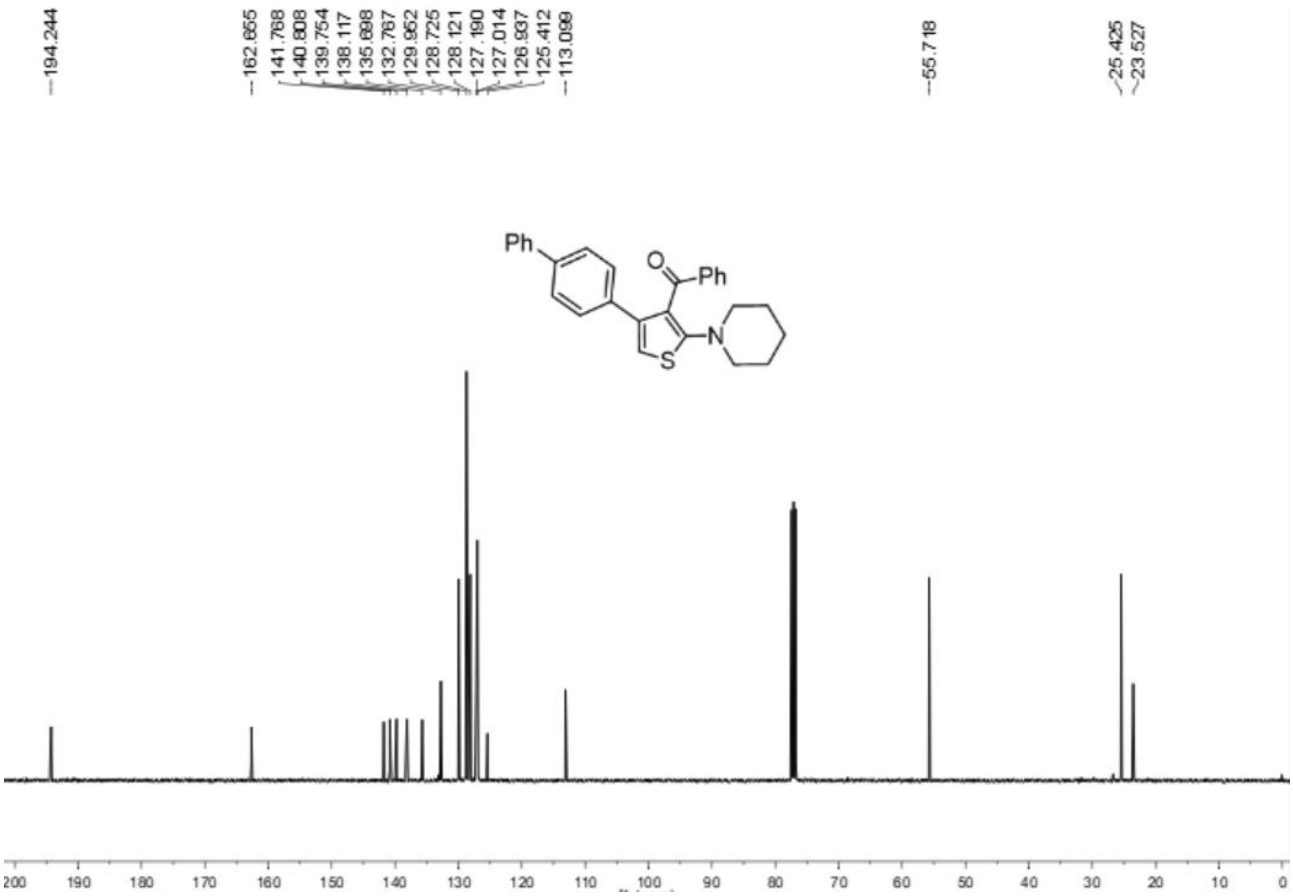
HRMS (EI) of 3ba



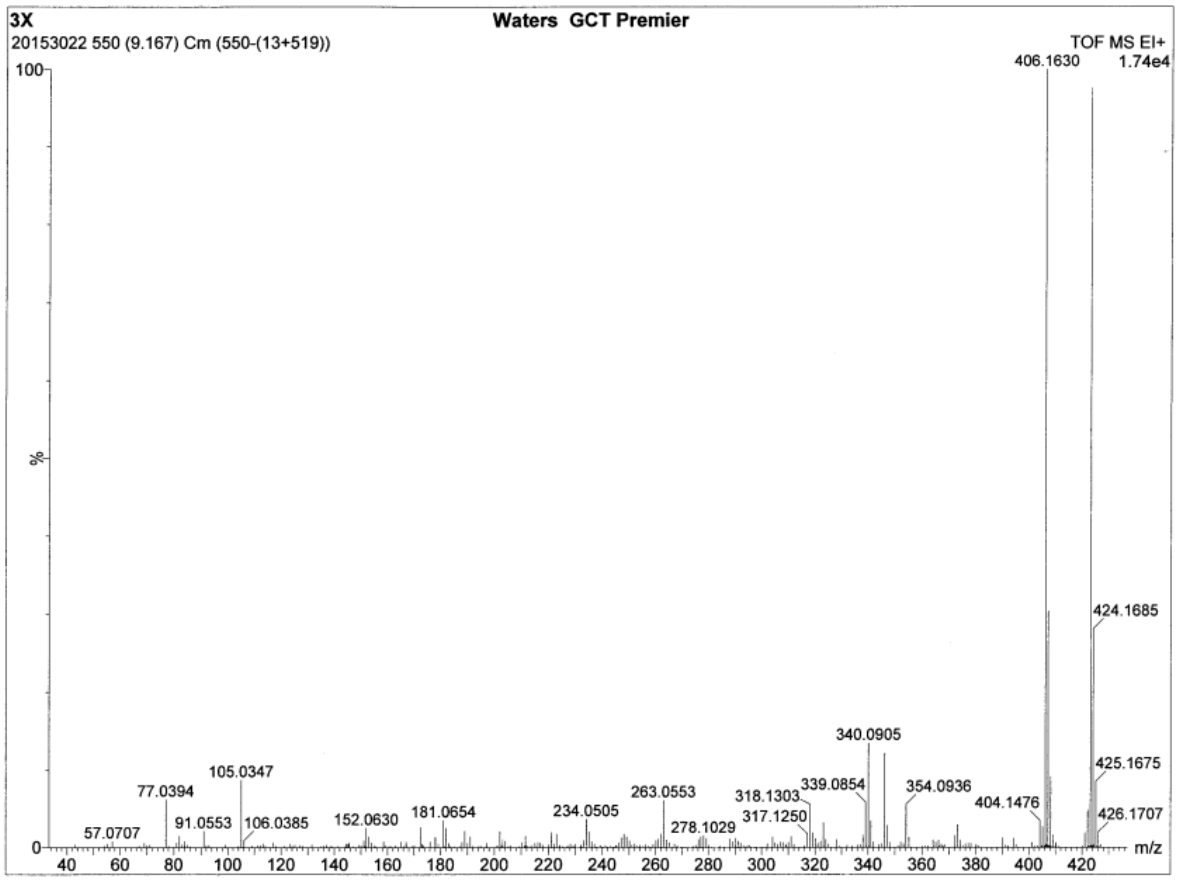
^{1}H NMR spectrum of 3ca (3oa)



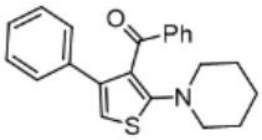
^{13}C NMR spectrum of 3ca (3oa)

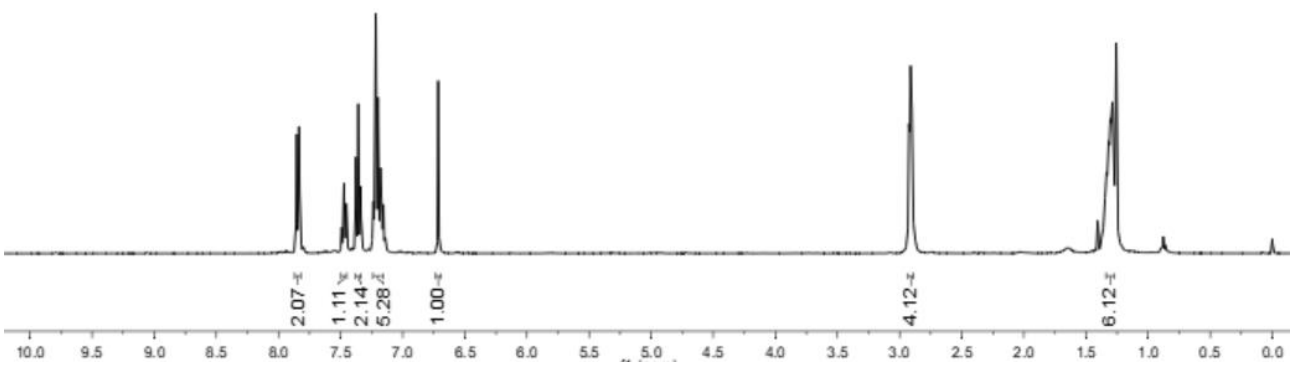


HRMS (EI) of 3ca (3oa)

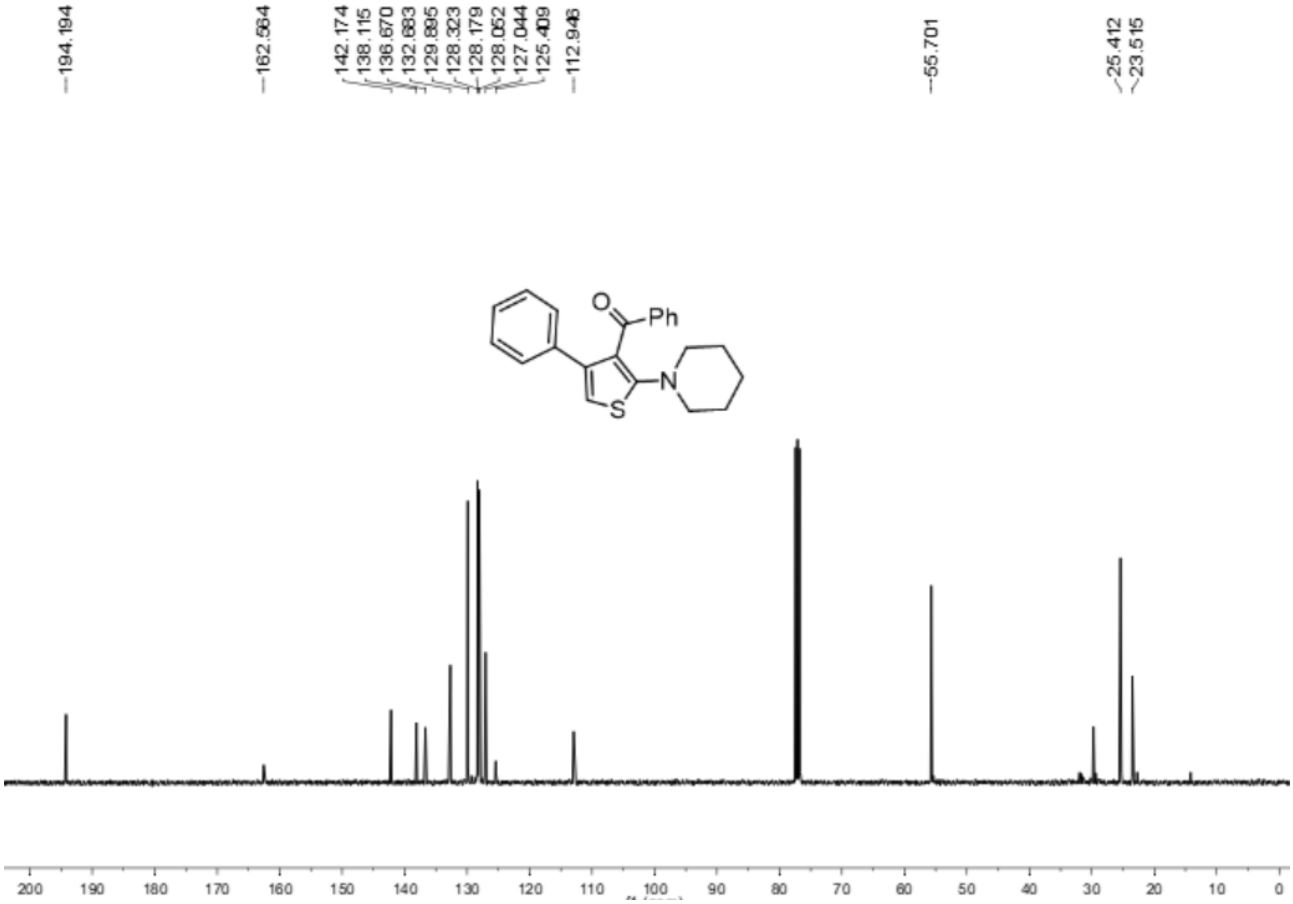


^{1}H NMR spectrum of 3da (3pa)

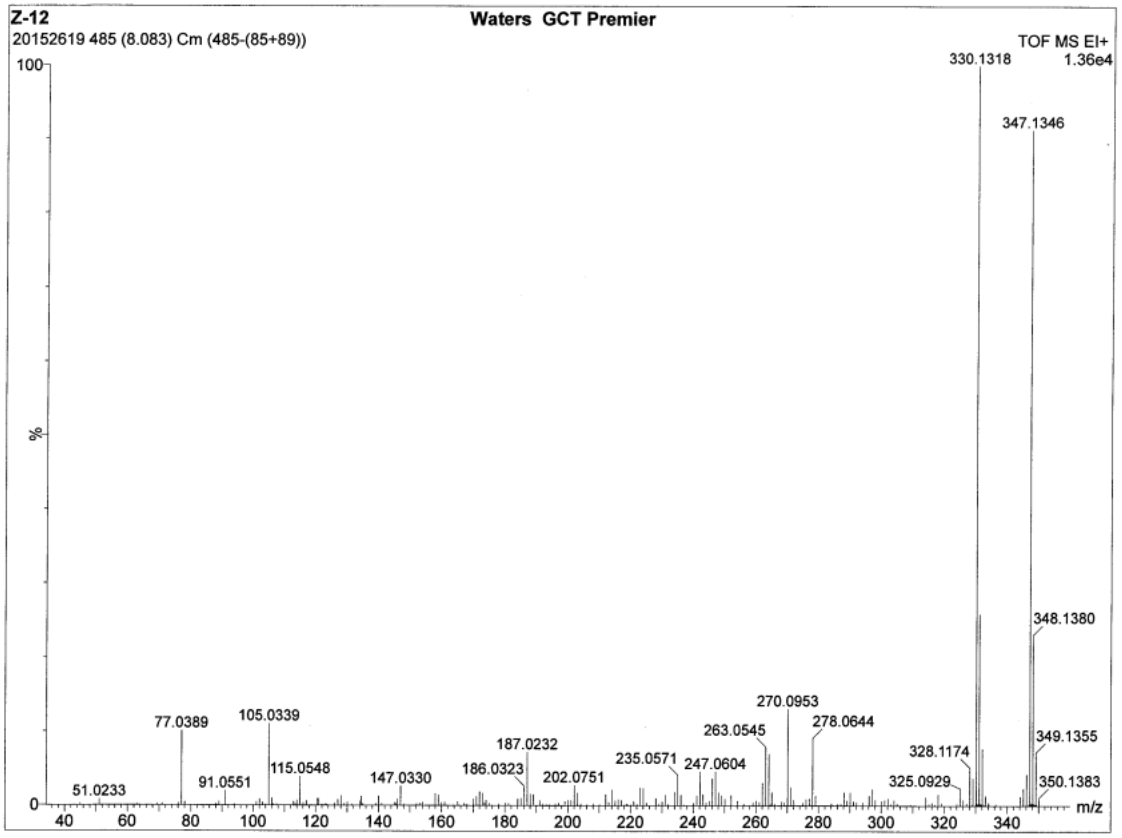




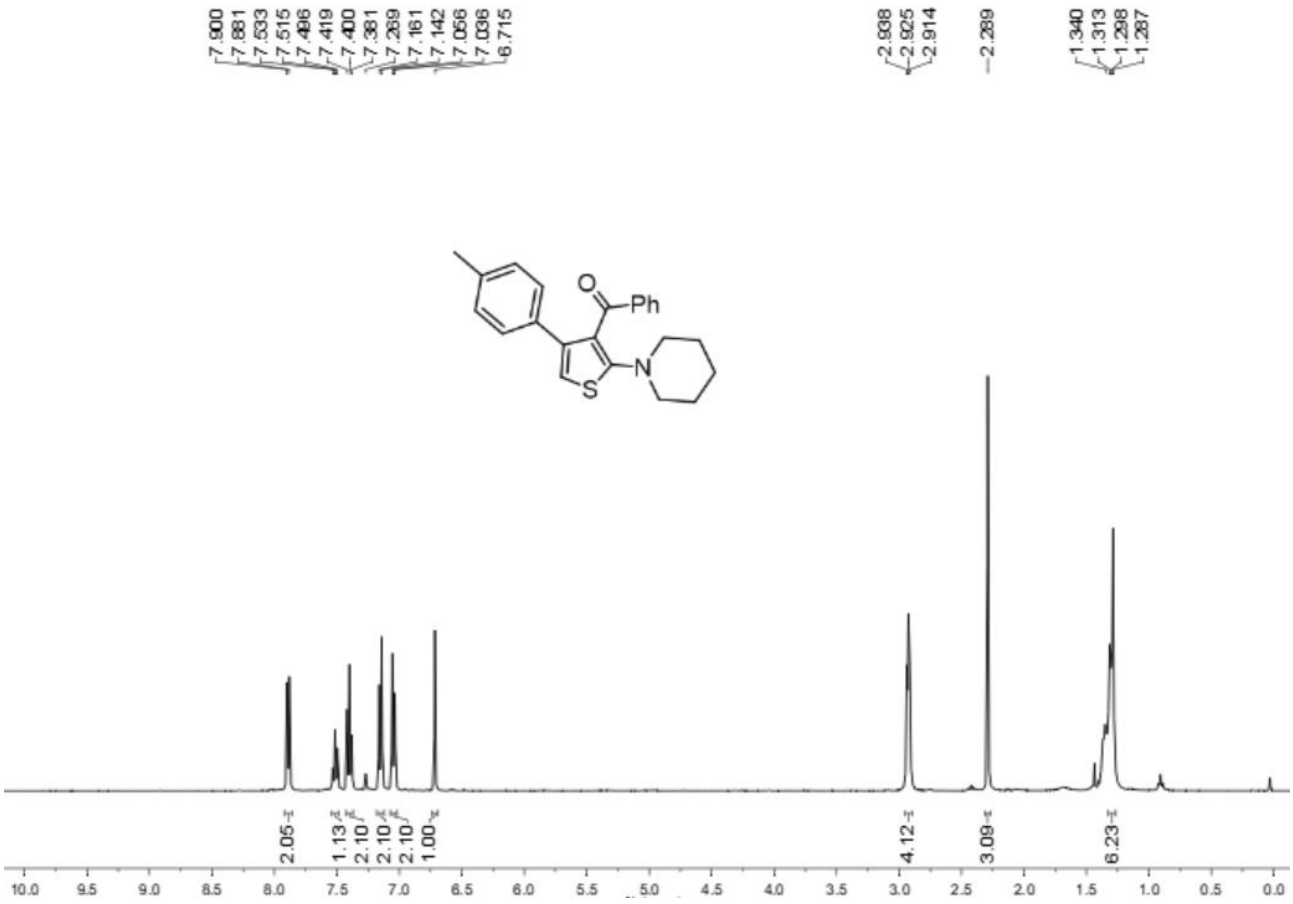
^{13}C NMR spectrum of 3da (3pa)



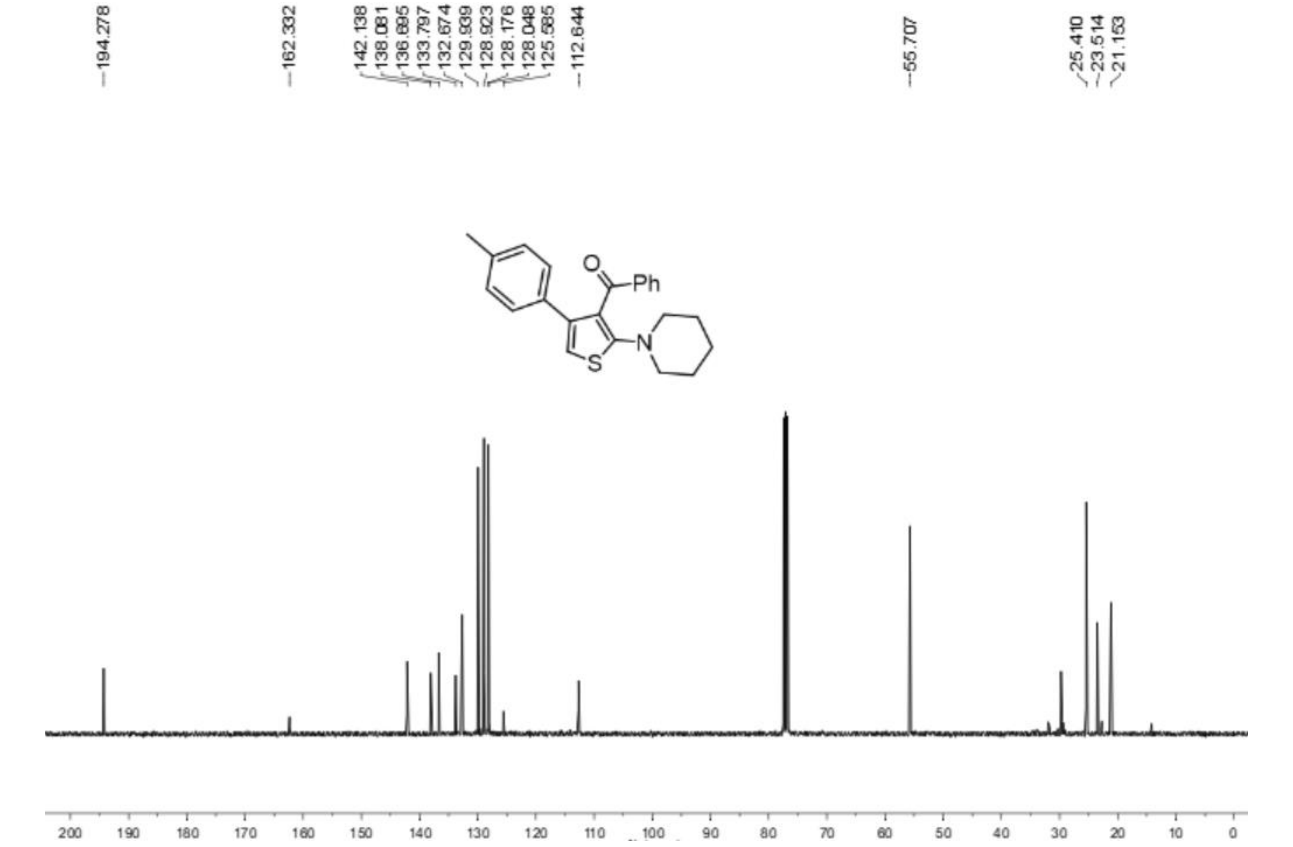
HRMS (EI) of 3da (3pa)



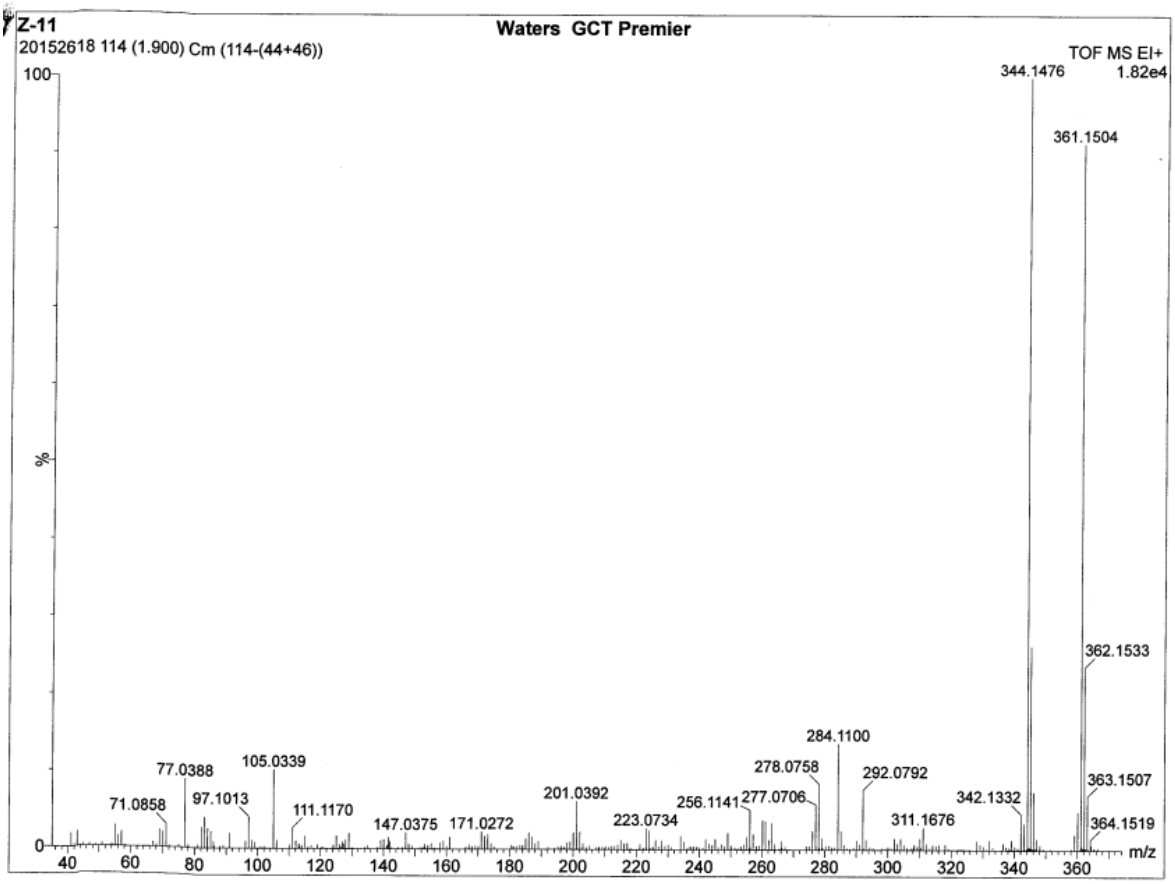
^{1}H NMR spectrum of 3ea (3qa)



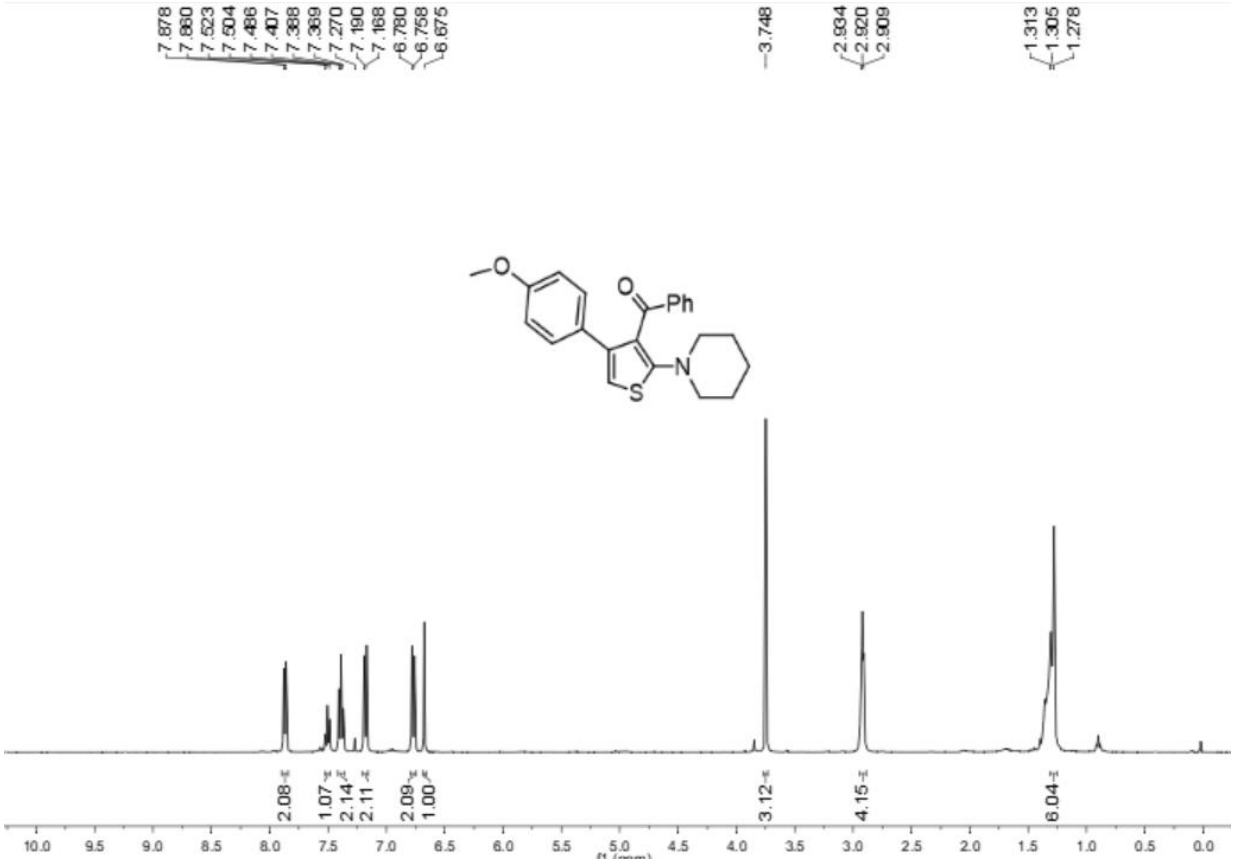
^{13}C NMR spectrum of 3ea (3qa)



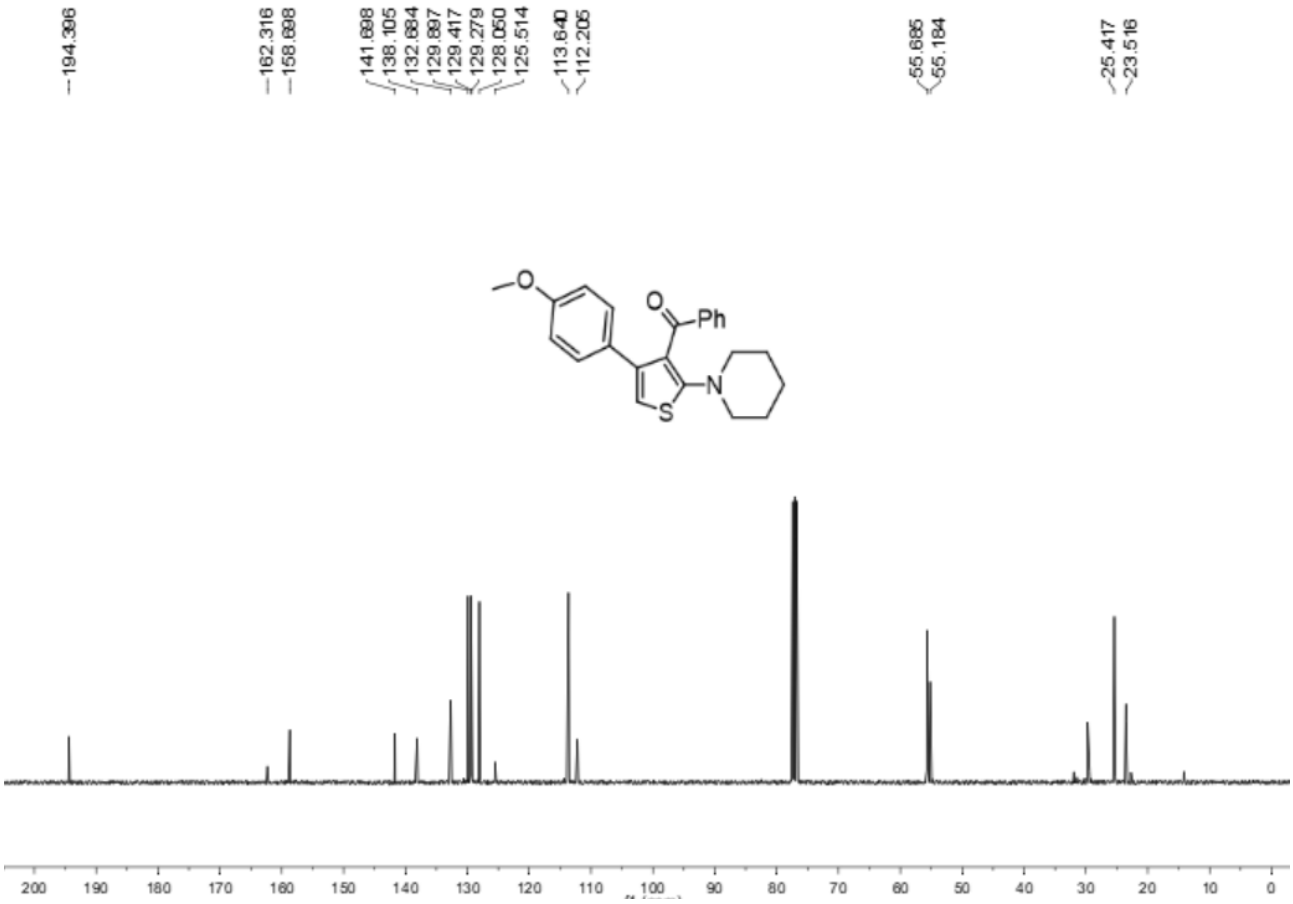
HRMS (EI) of 3ea (3qa)



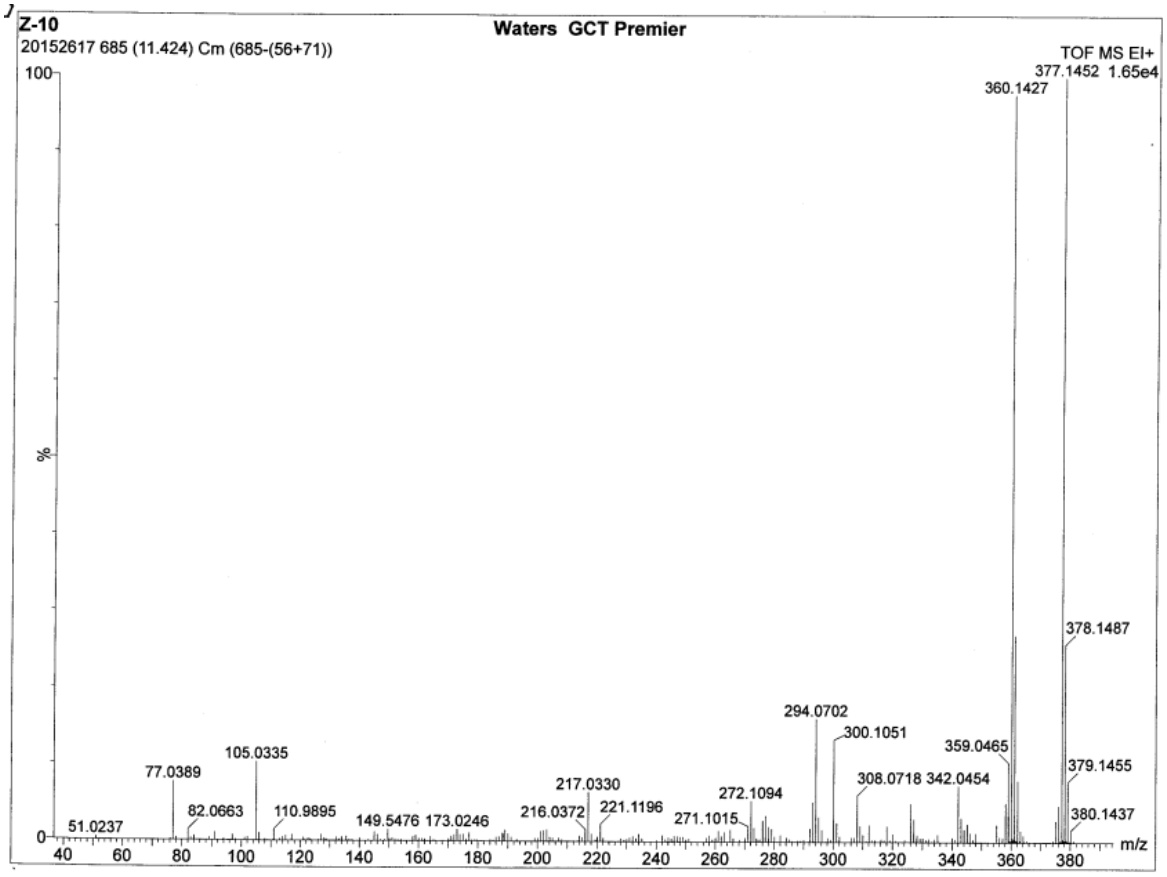
^{1}H NMR spectrum of 3fa (3ra)



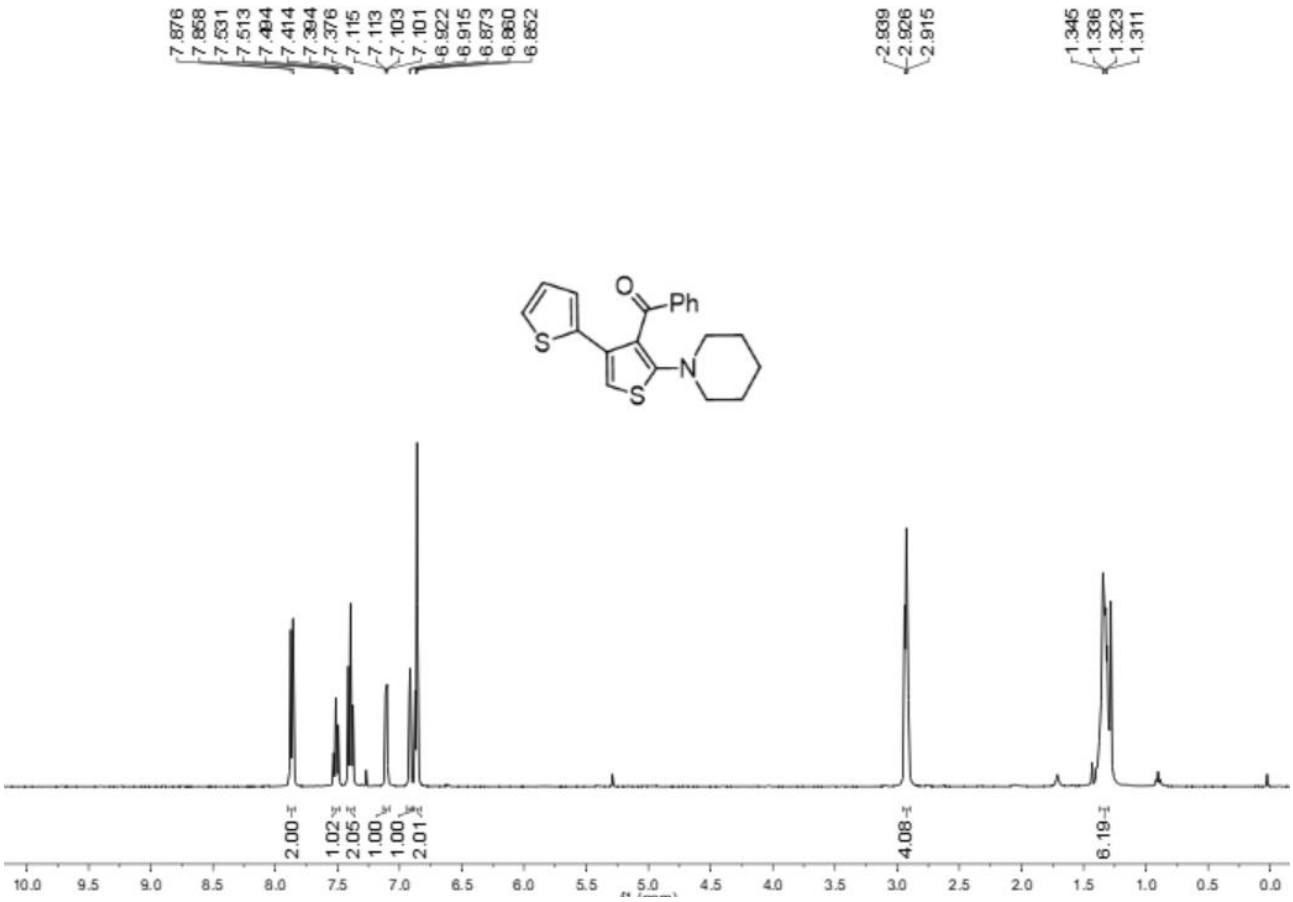
^{13}C NMR spectrum of 3fa (3ra)



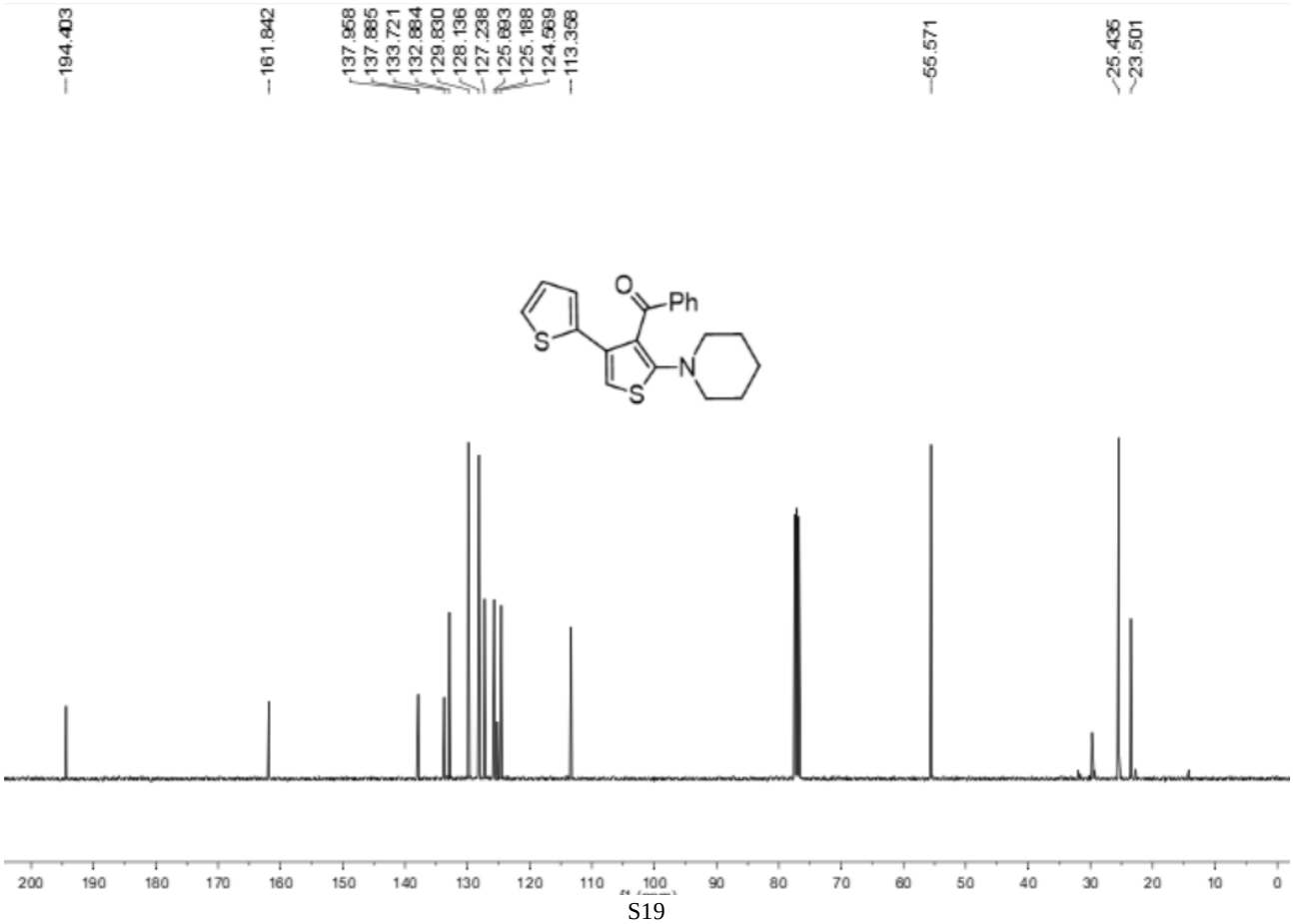
HRMS (EI) of 3fa (3ra)



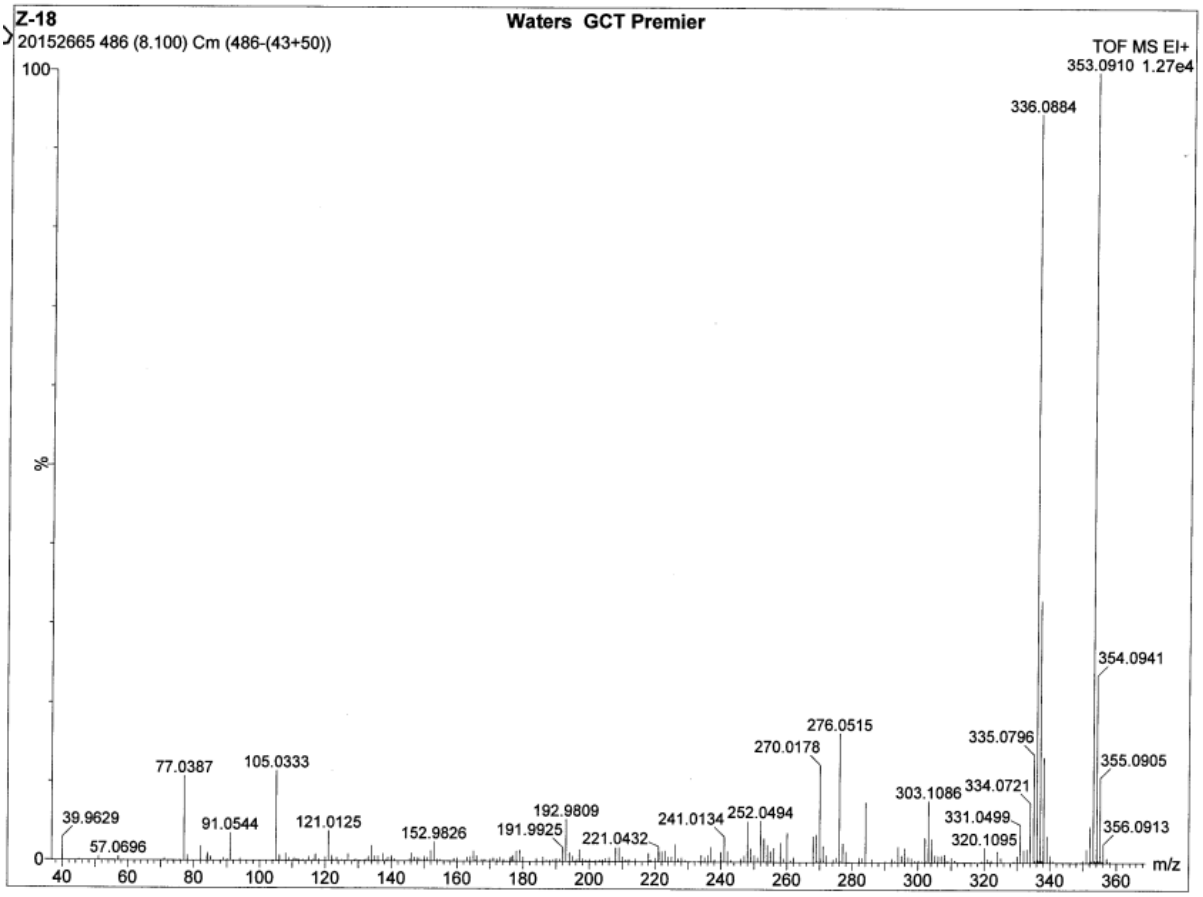
^{1}H NMR spectrum of 3ga



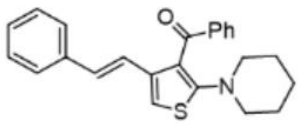
^{13}C NMR spectrum of 3ga

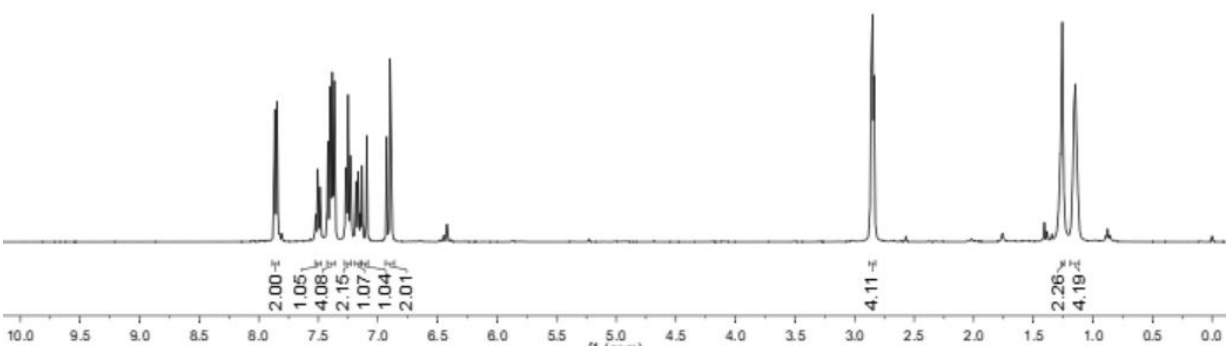


HRMS (EI) of 3ga

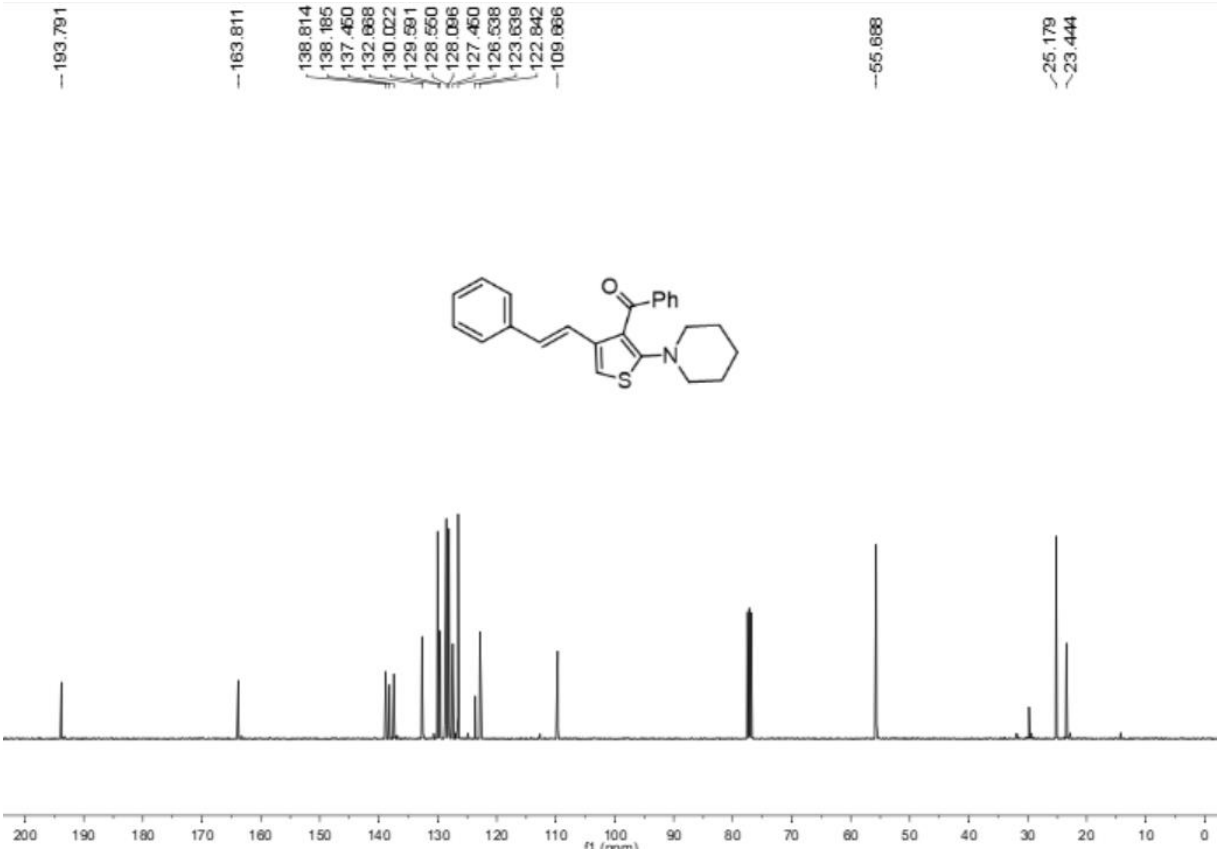


^{1}H NMR spectrum of 3ha

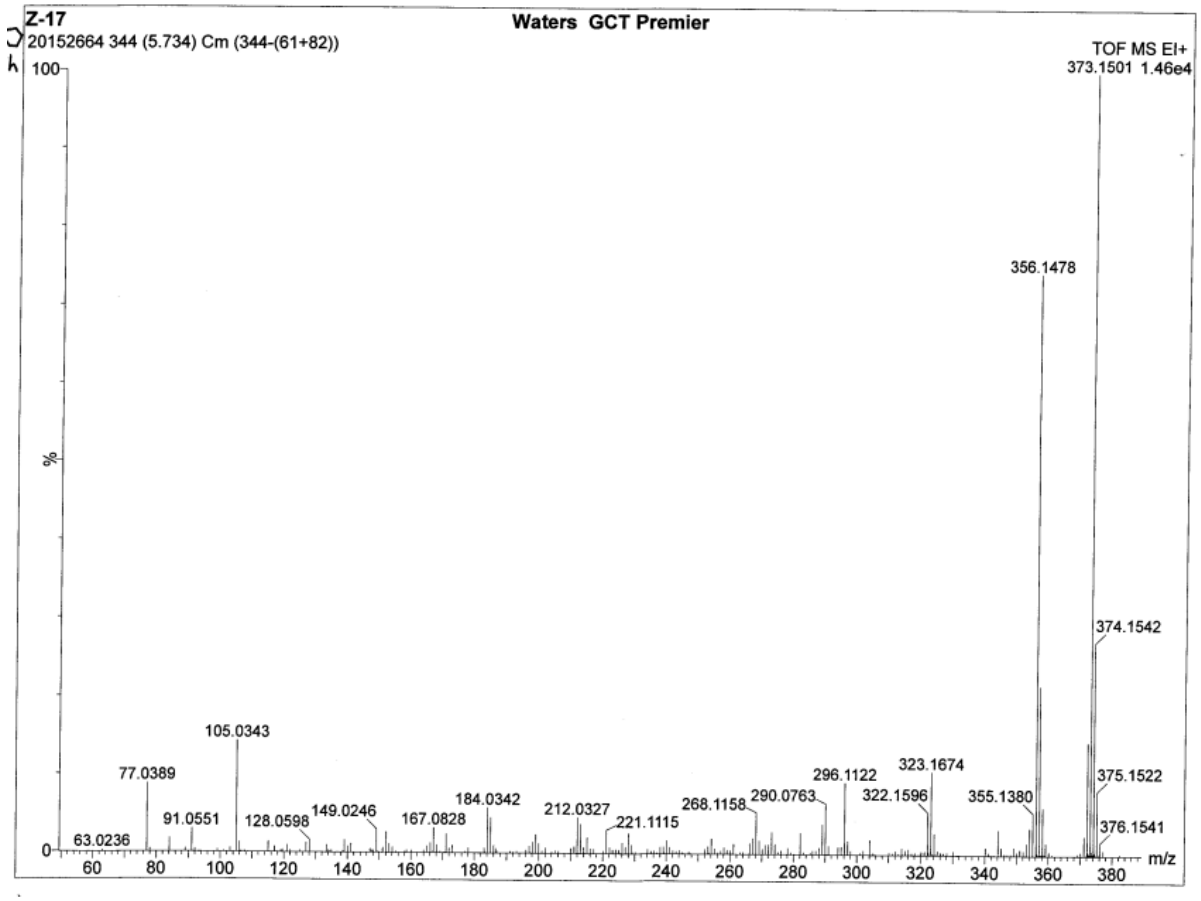




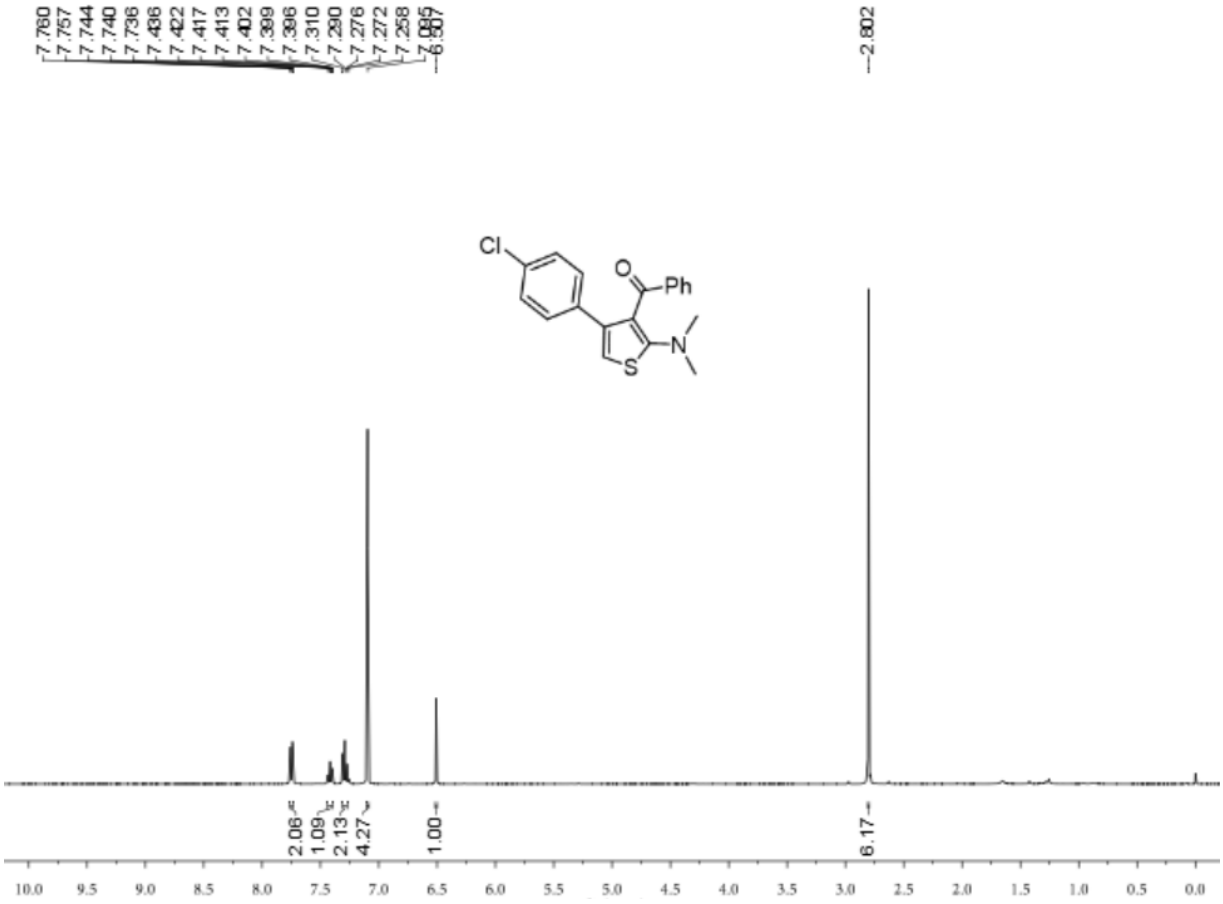
^{13}C NMR spectrum of 3ha



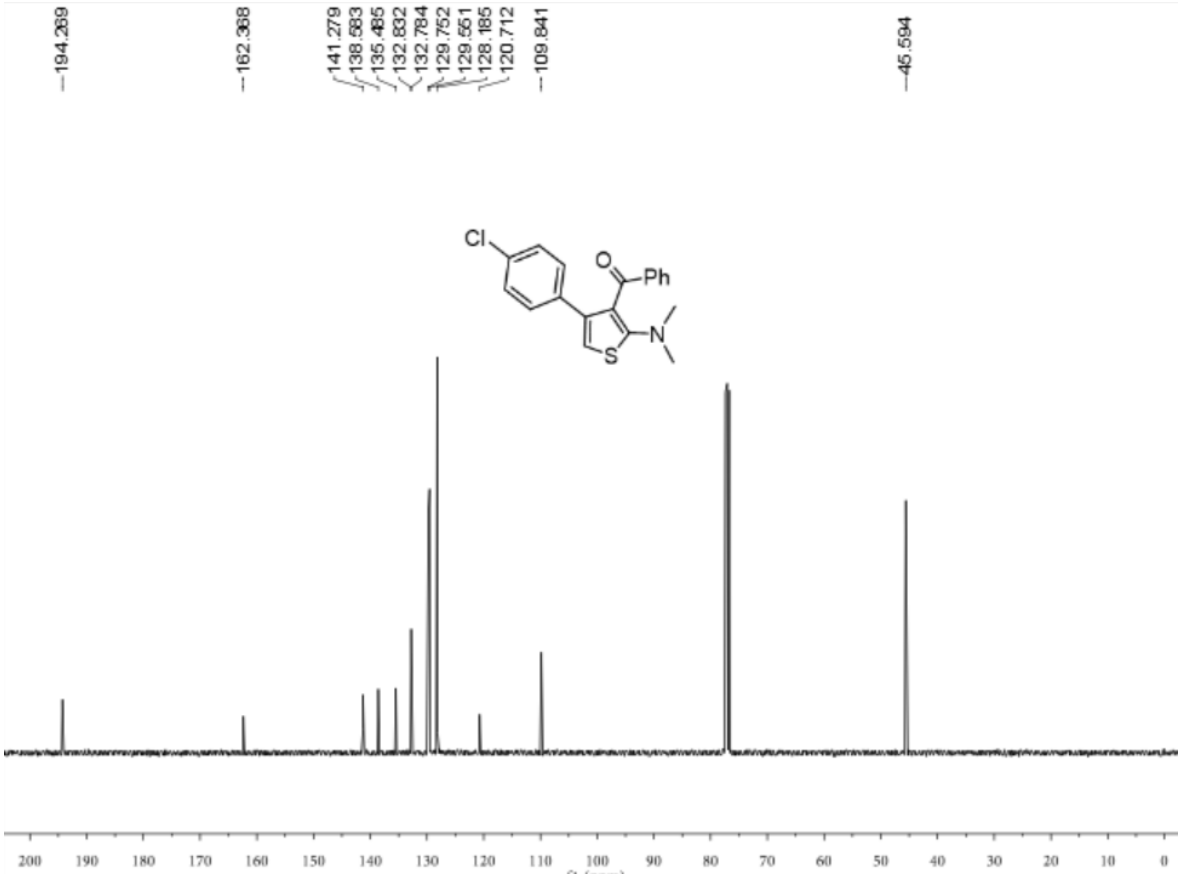
HRMS (EI) of 3ha



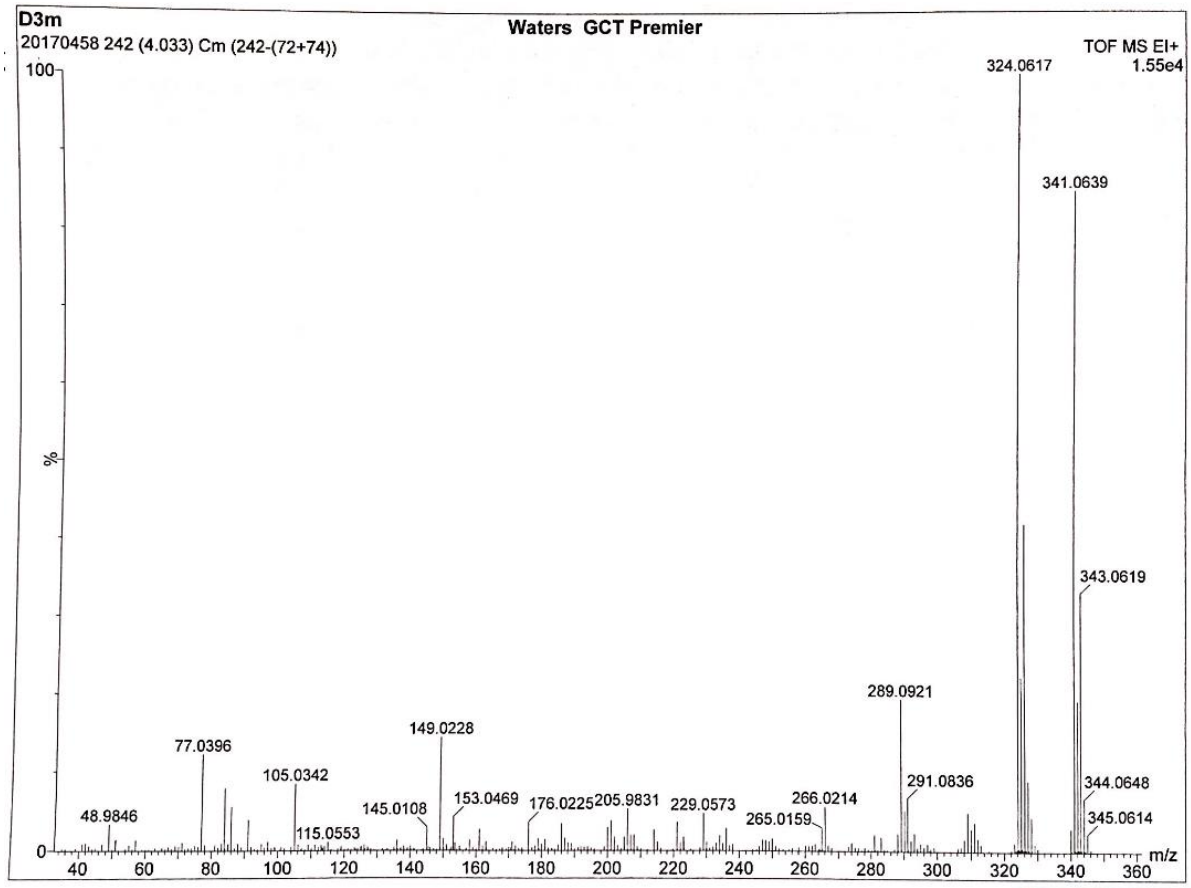
^{1}H NMR spectrum of 3ad (3md)



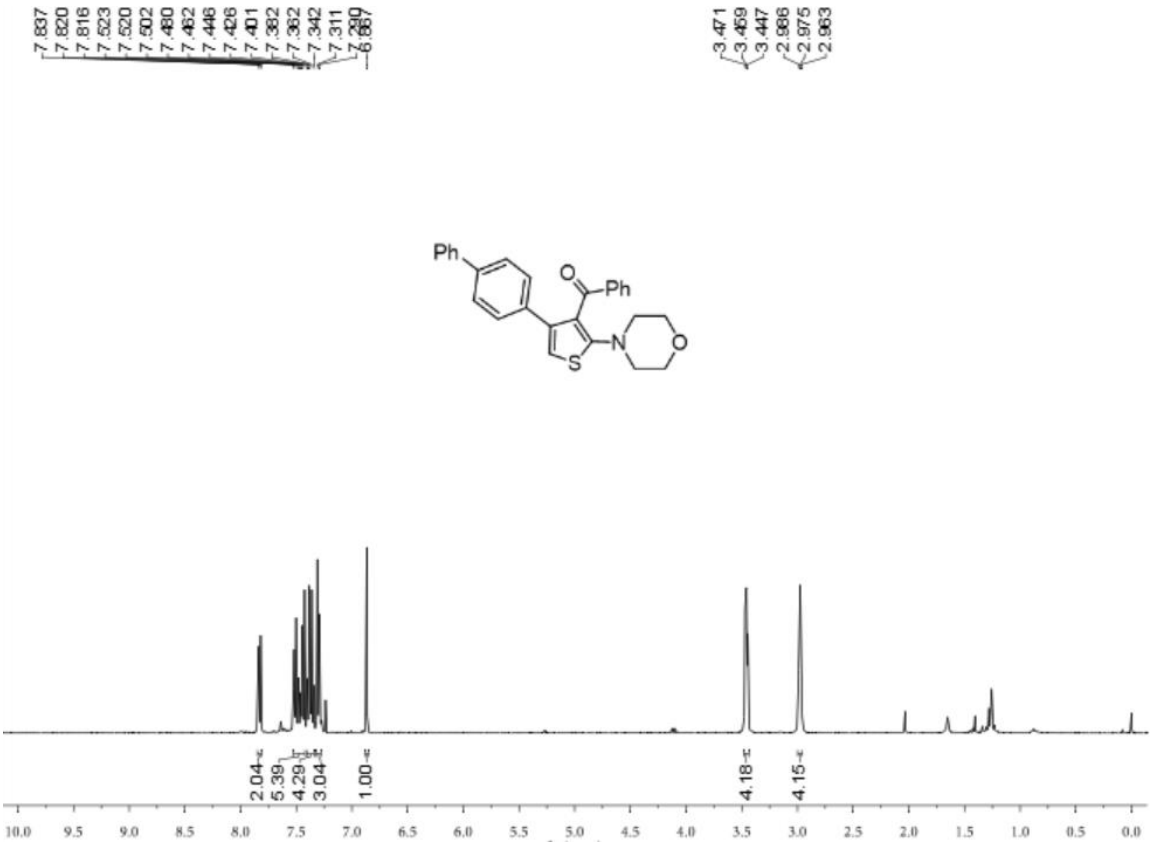
^{13}C NMR spectrum of 3ad (3md)



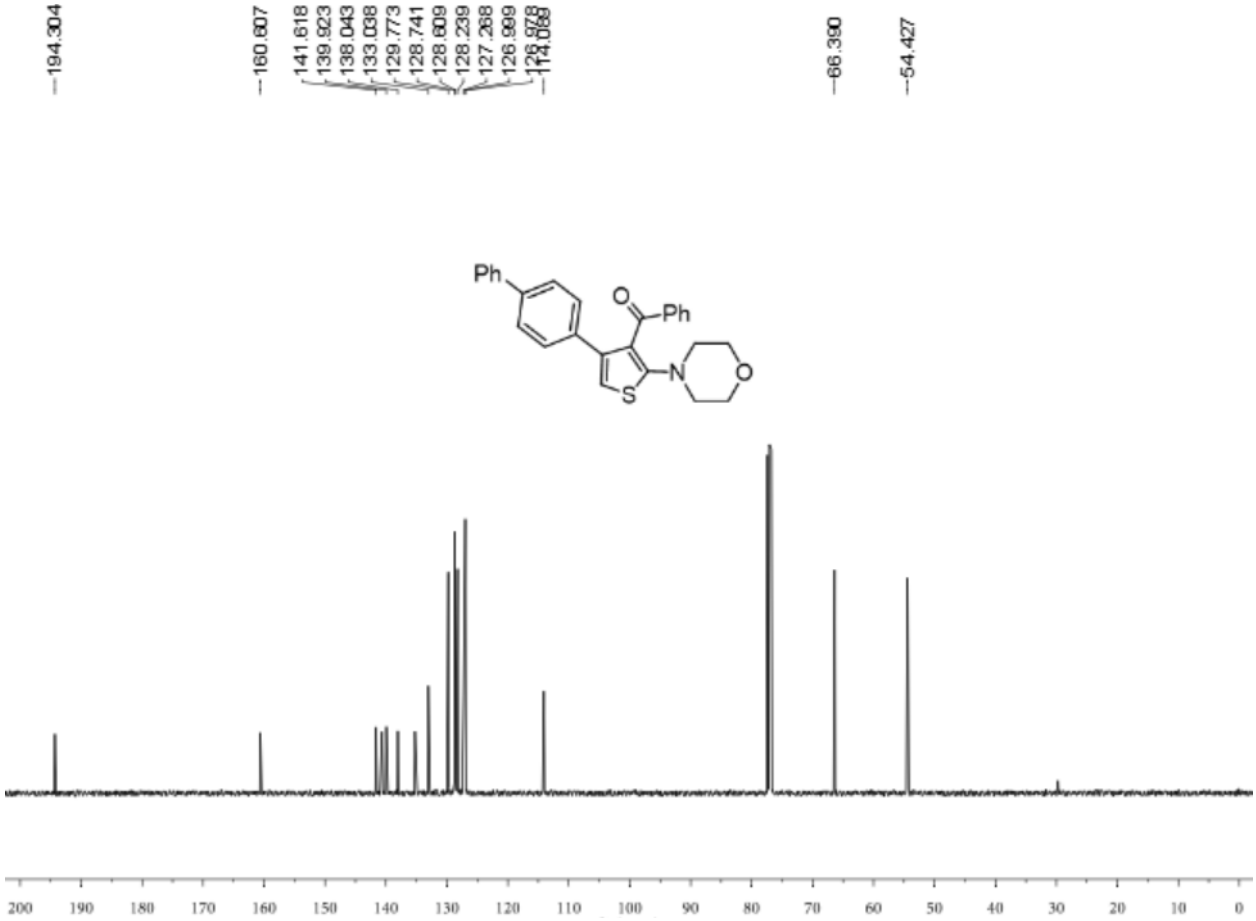
HRMS (EI) of 3ad (3md)



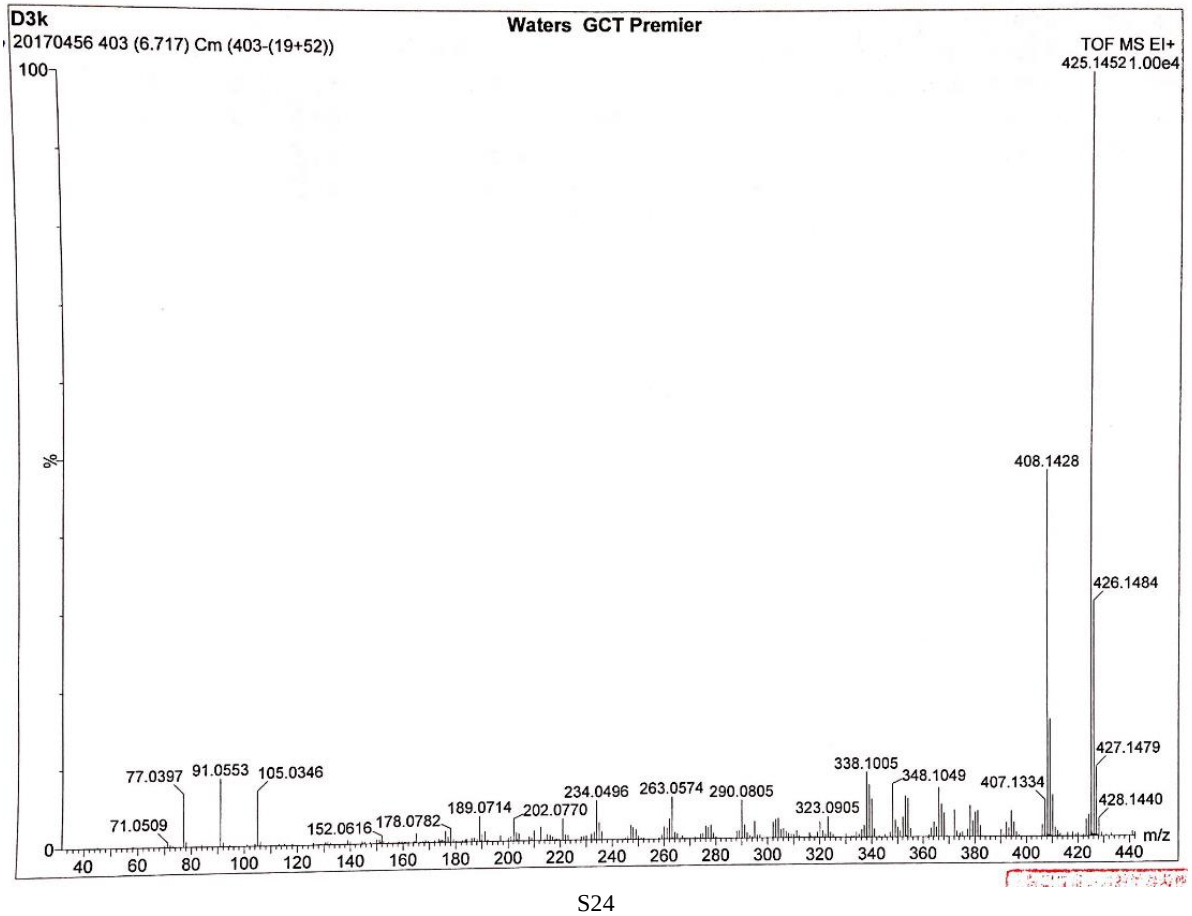
^{1}H NMR spectrum of 3cc (3oc)



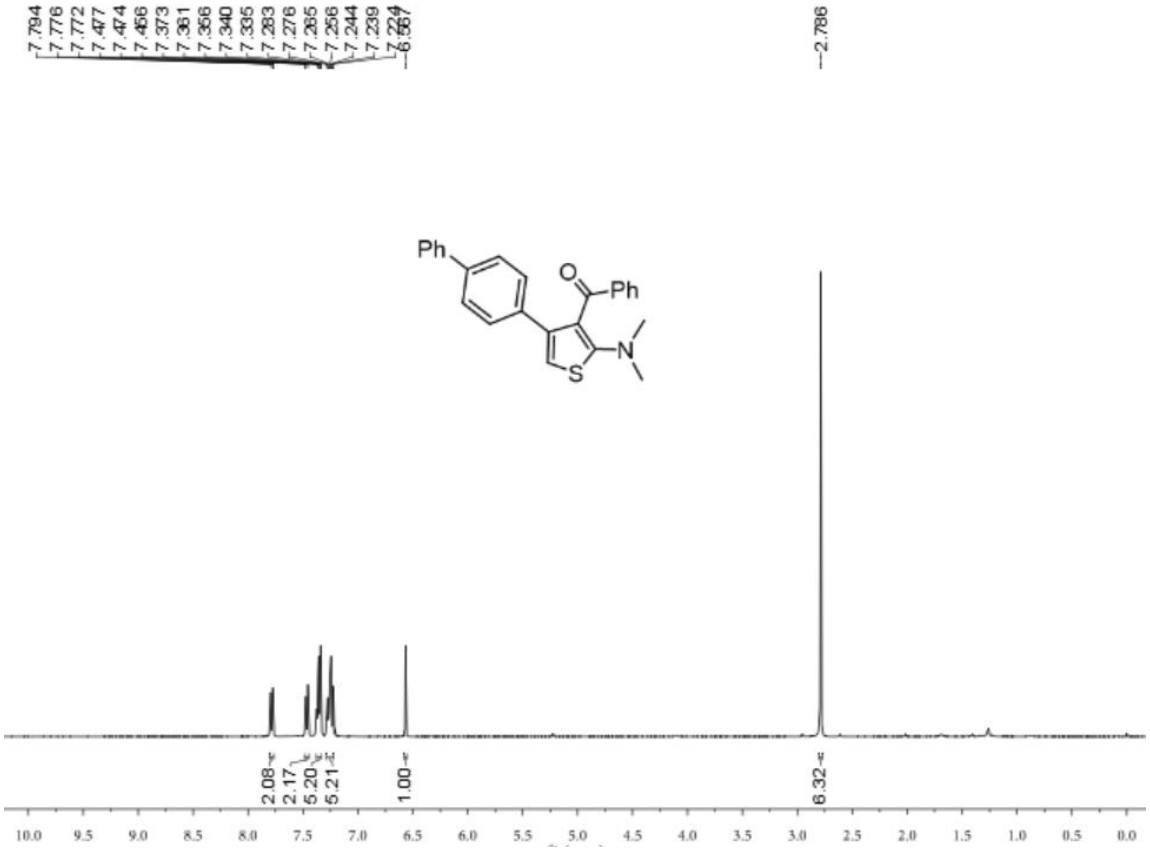
^{13}C NMR spectrum of 3cc (3oc)



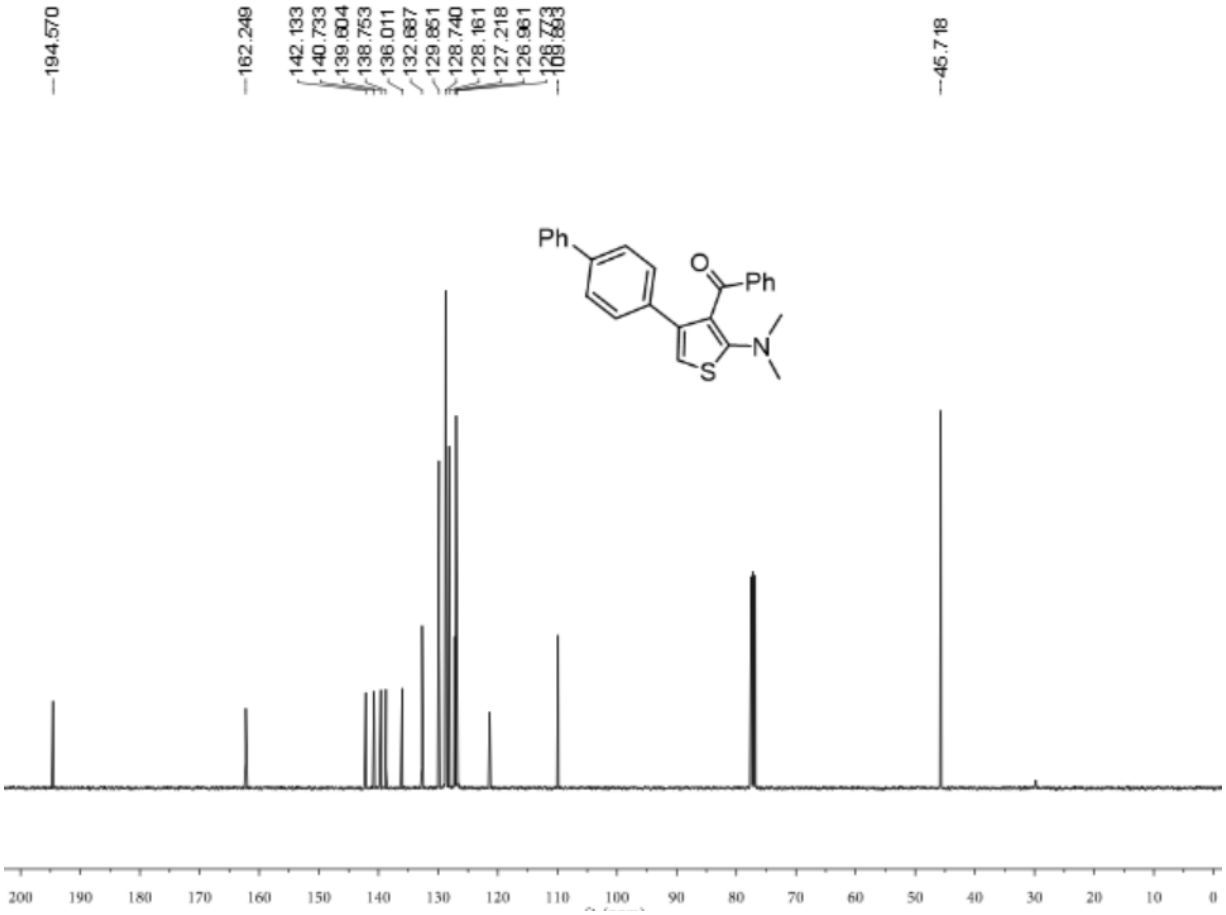
HRMS (EI) of 3cc (3oc)



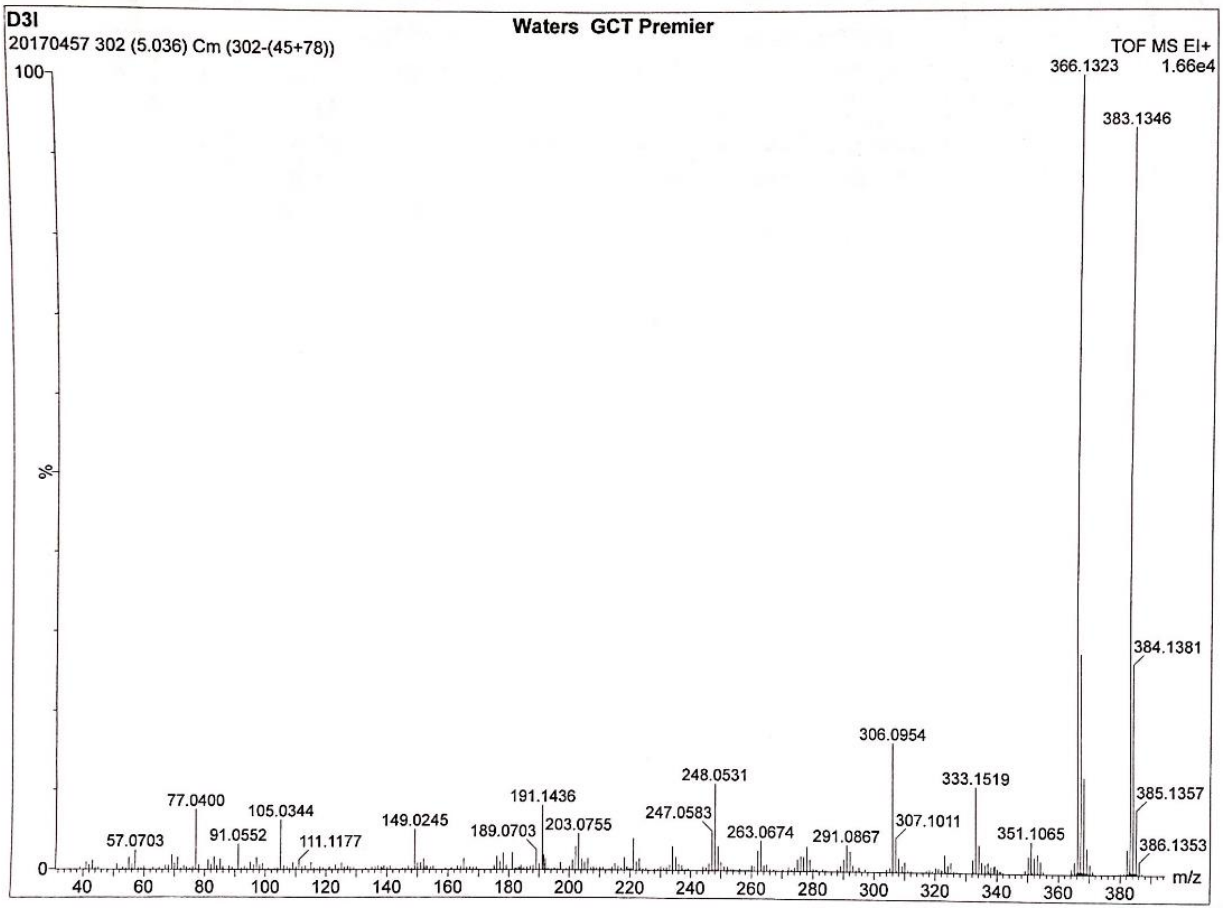
[1]H NMR spectrum of 3cd (3od)



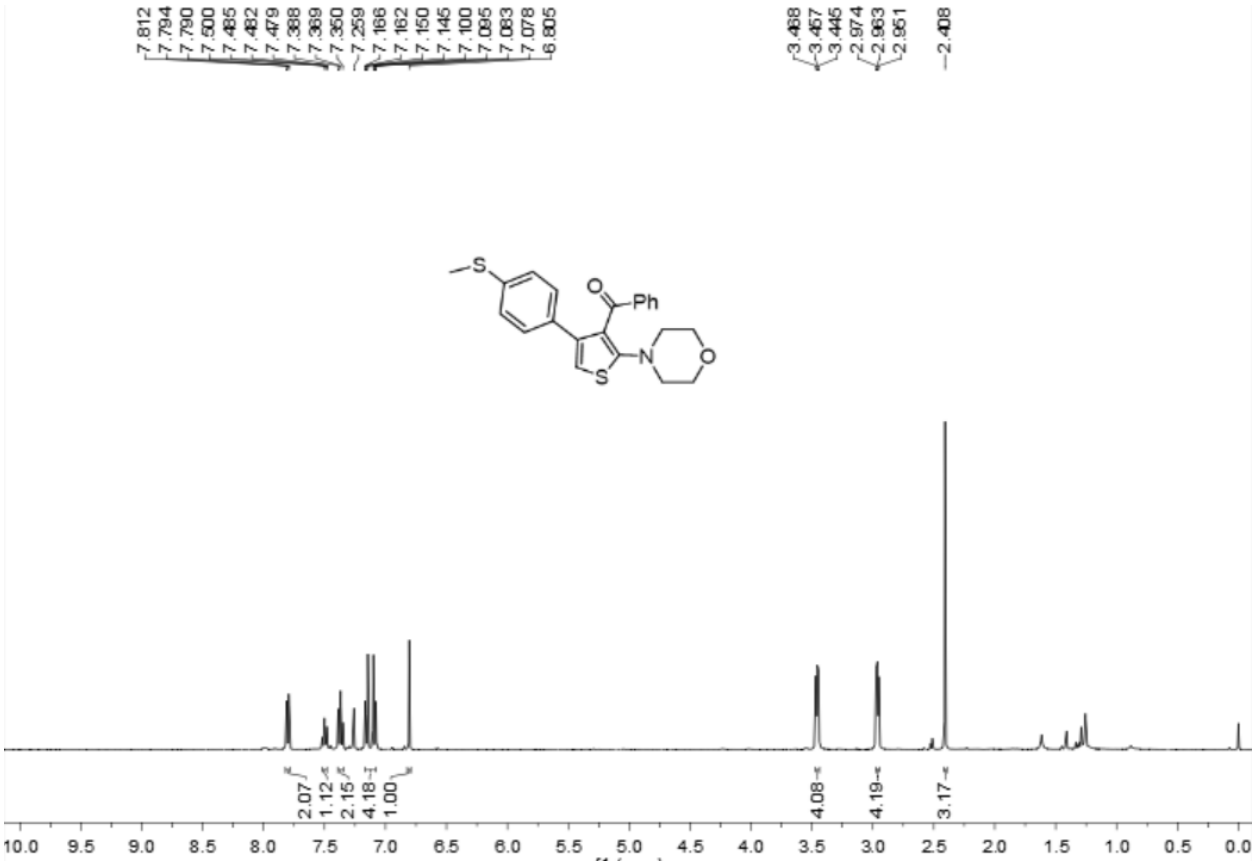
[13]C NMR spectrum of 3cd (3od)



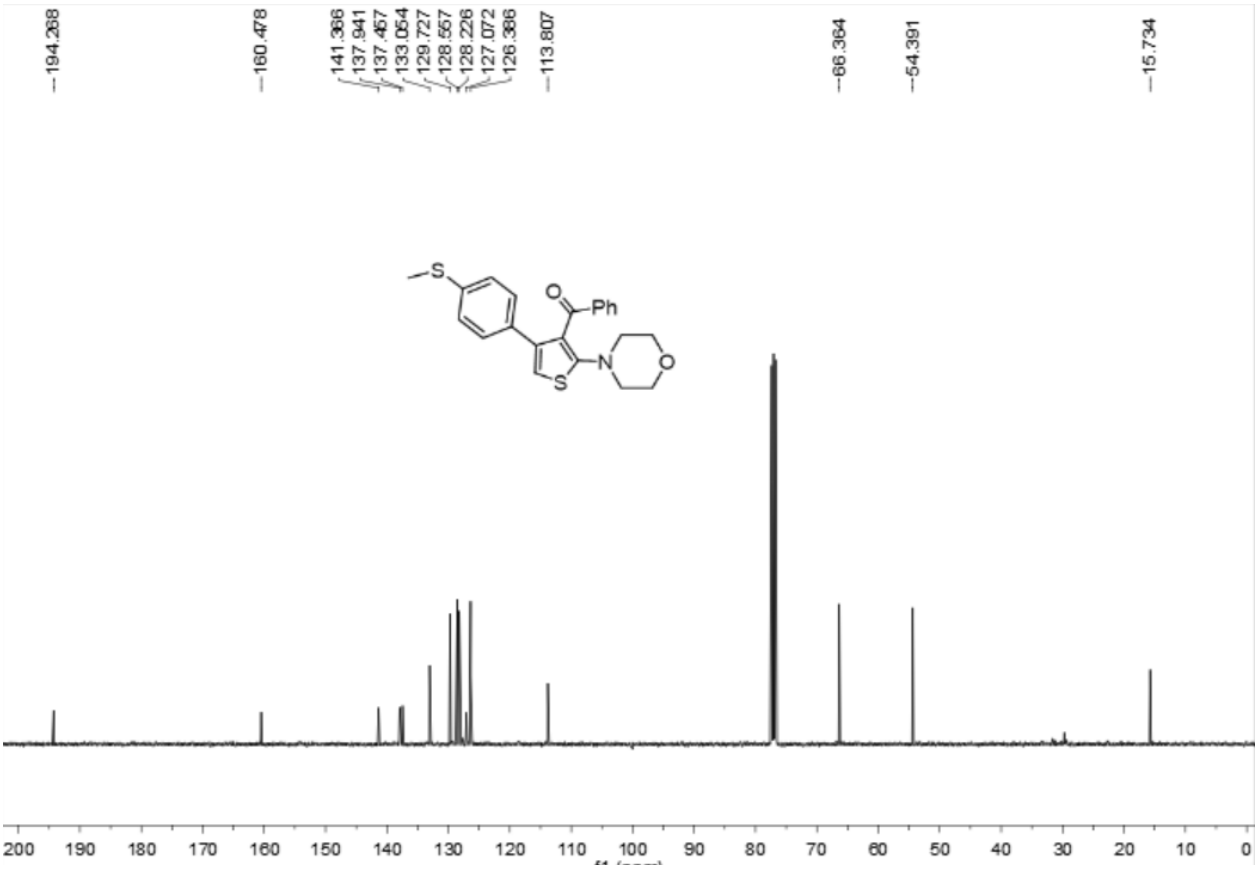
HRMS (EI) of 3cd (3od)



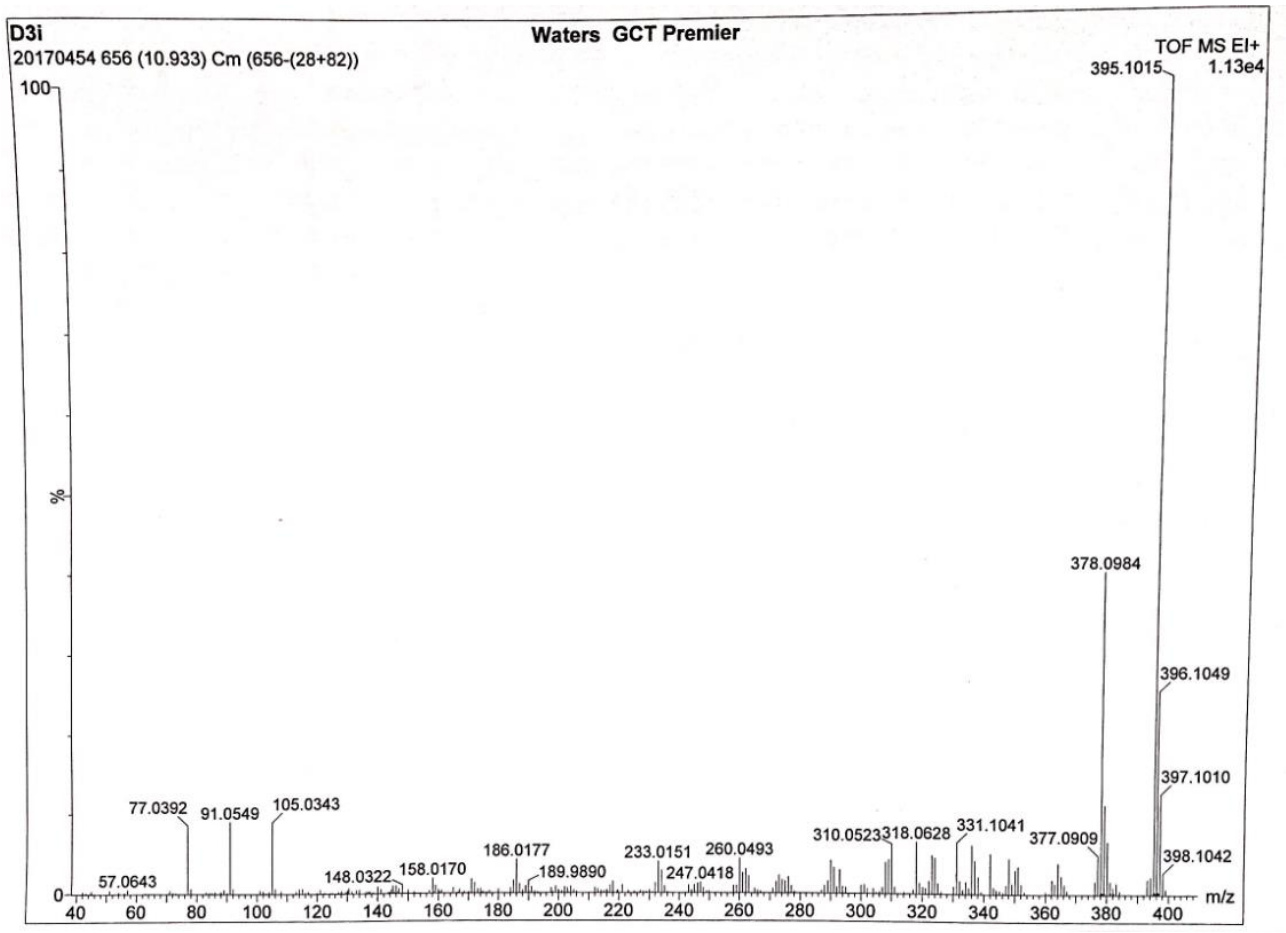
^{1}H NMR spectrum of 3ic



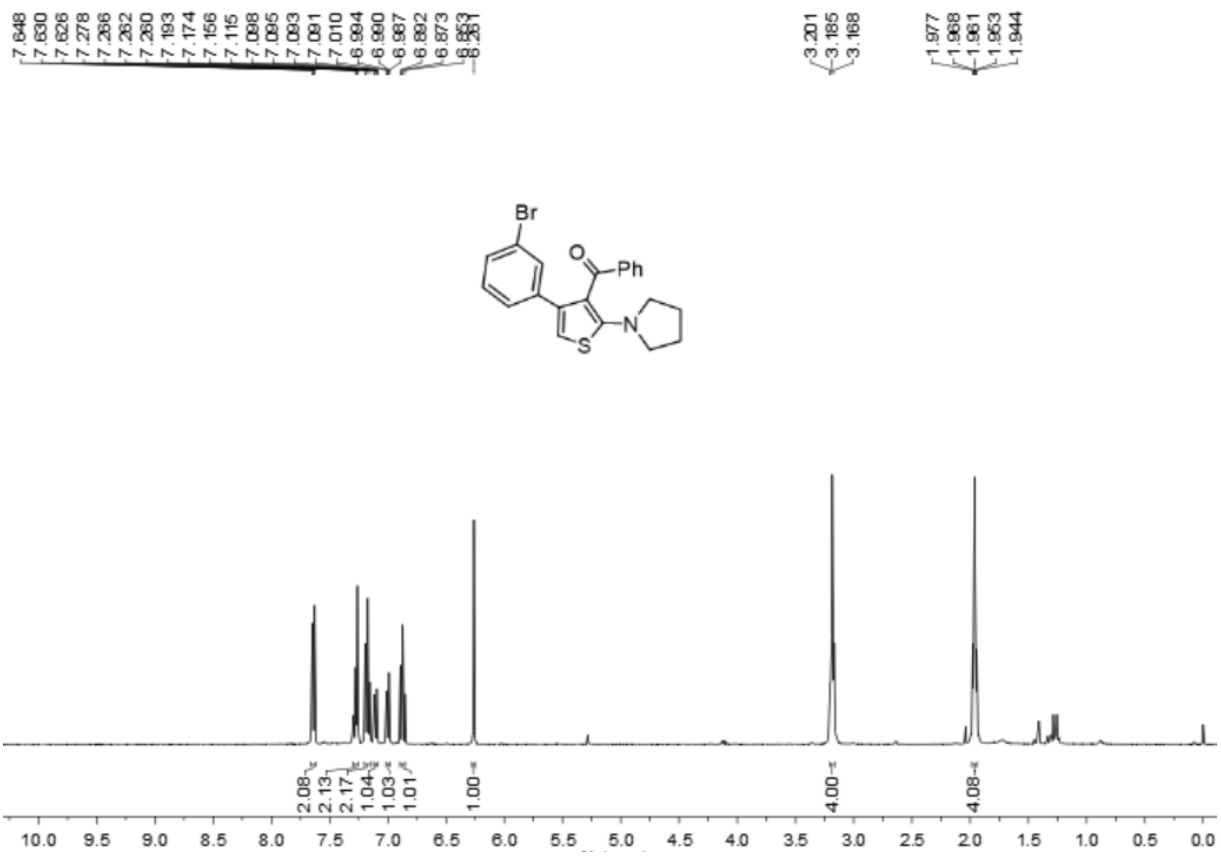
^{13}C NMR spectrum of 3ic



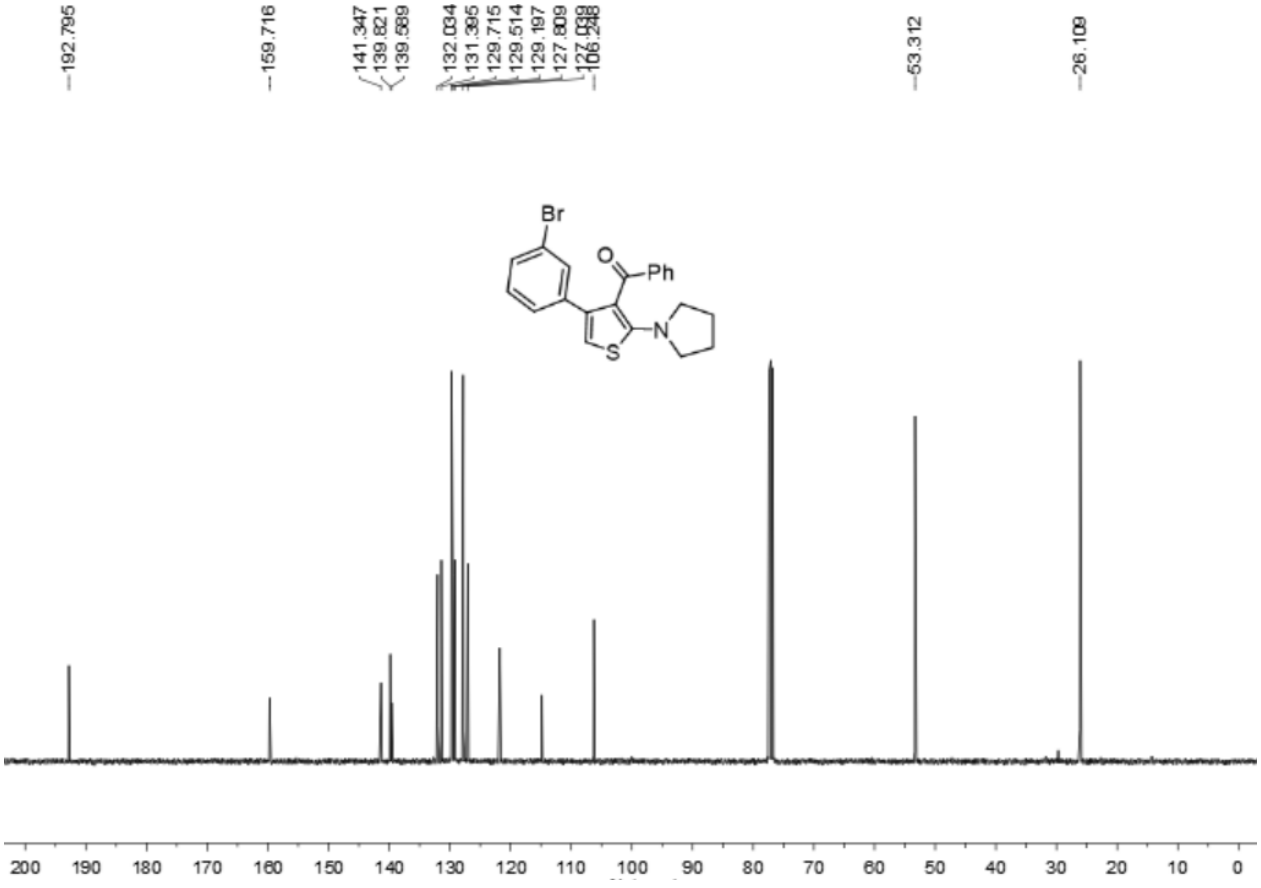
HRMS (EI) of 3ic



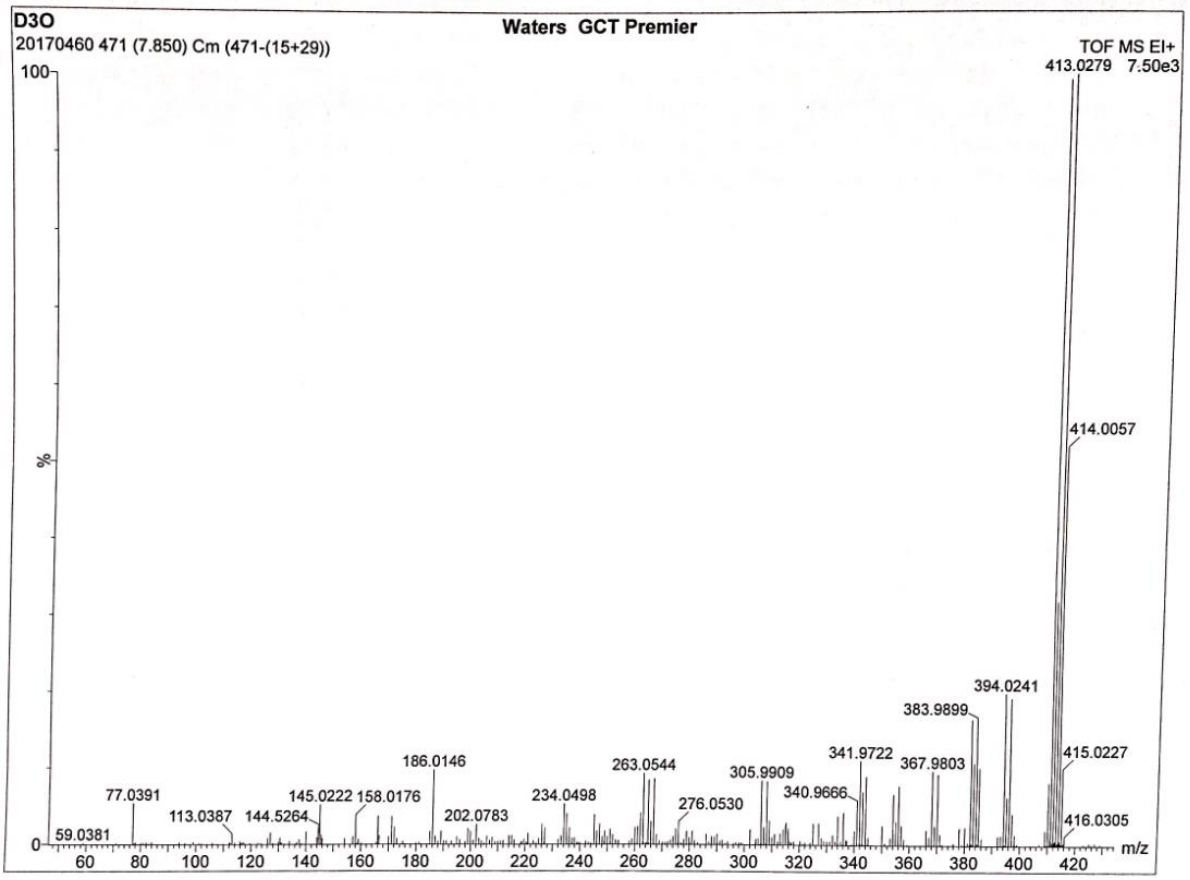
^{1}H NMR spectrum of 3jb



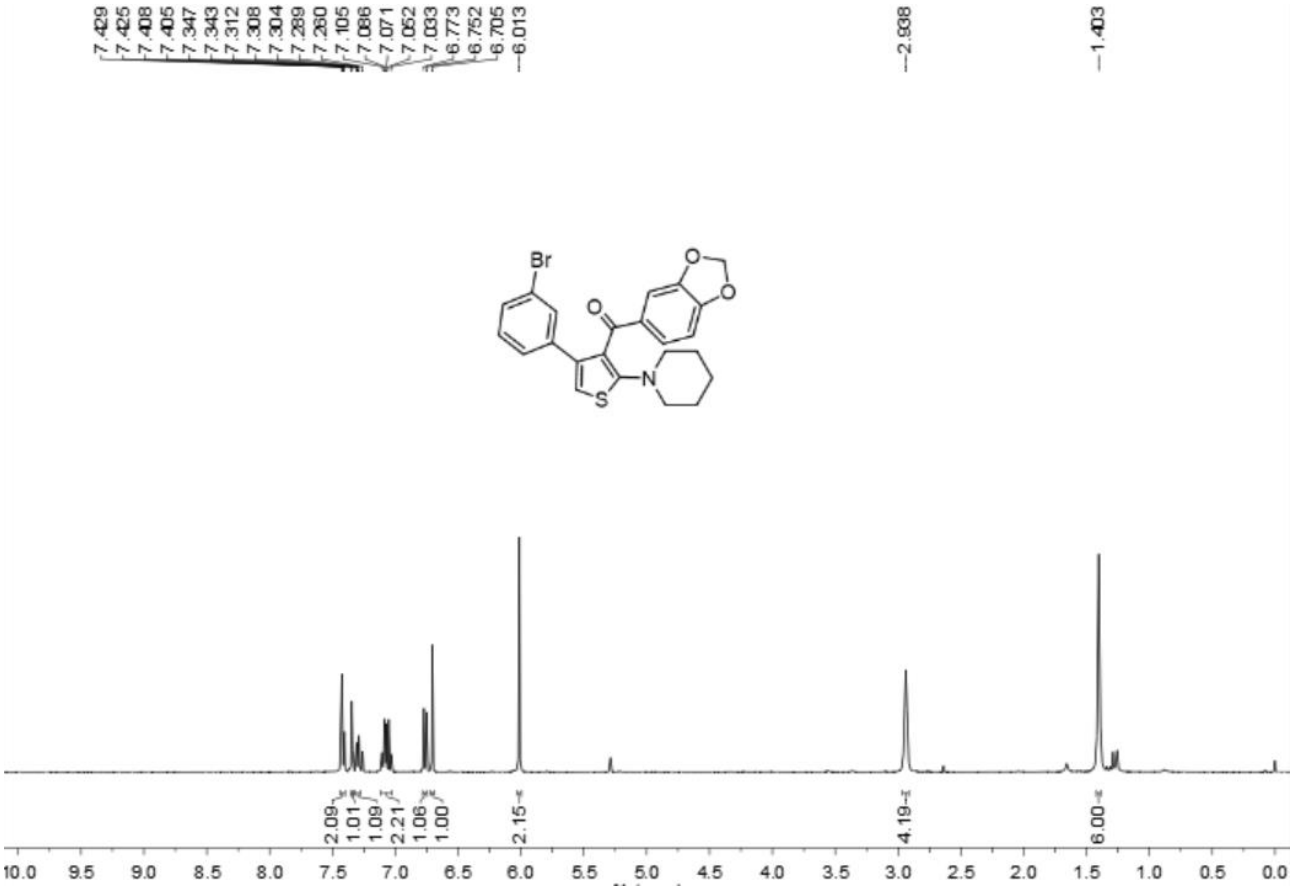
^{13}C NMR spectrum of 3jb



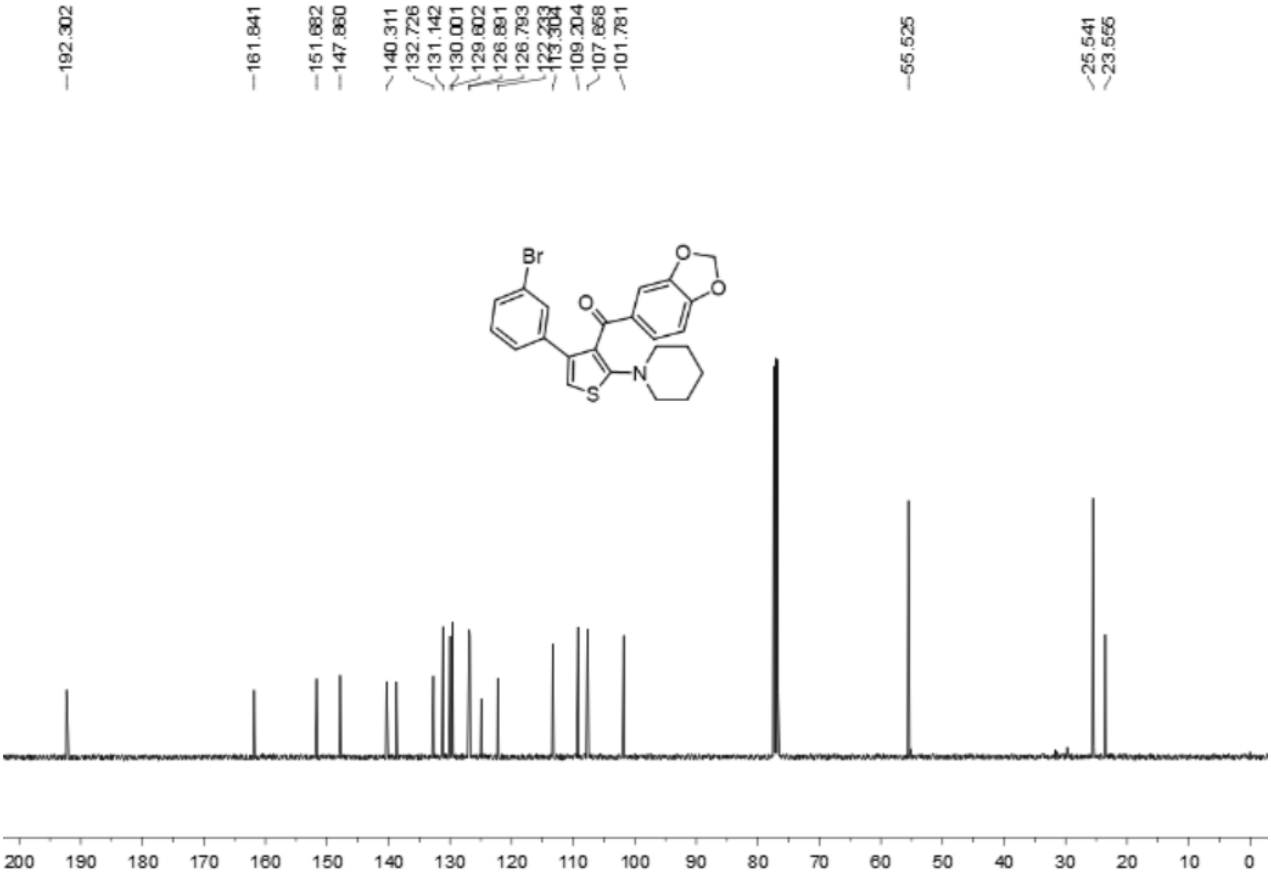
HRMS (EI) of 3jb



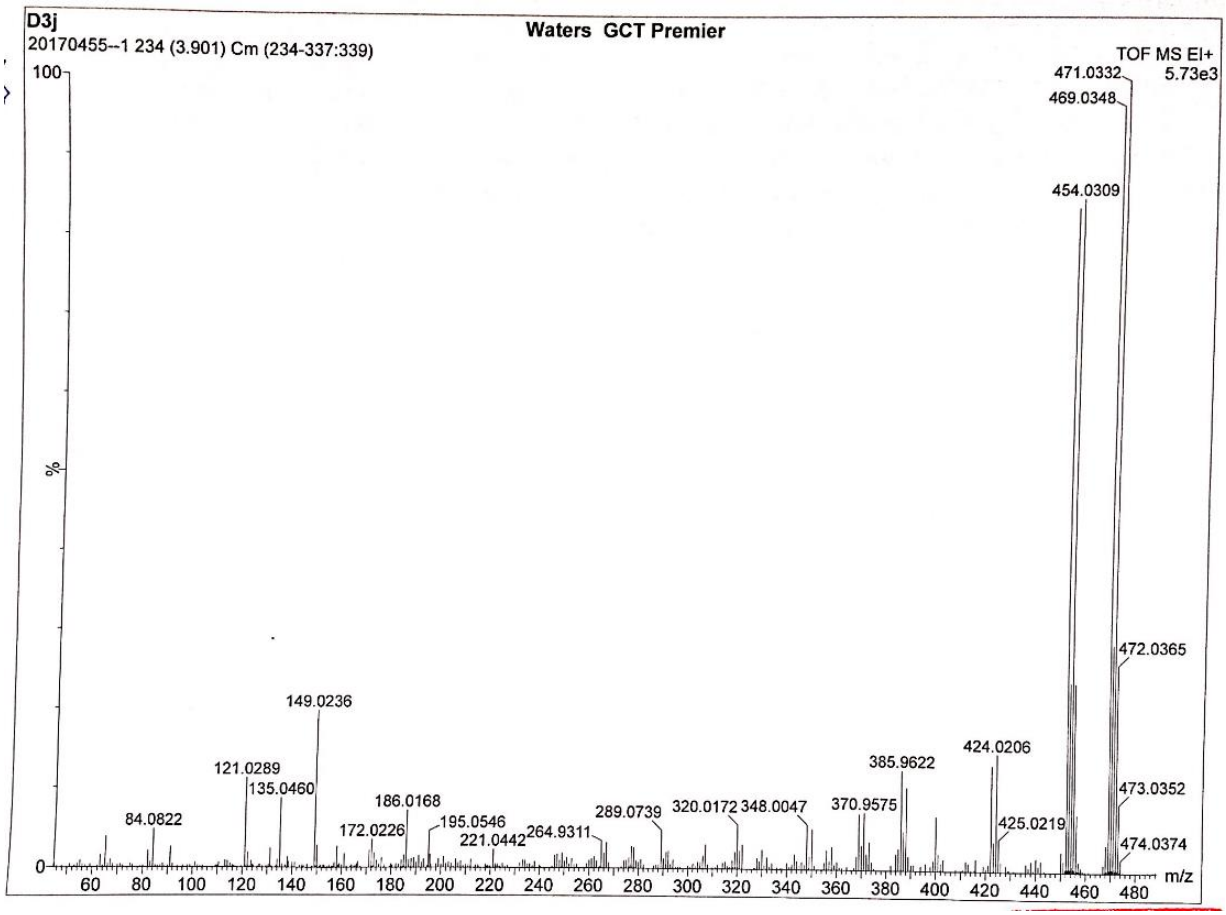
^{1}H NMR spectrum of 3je



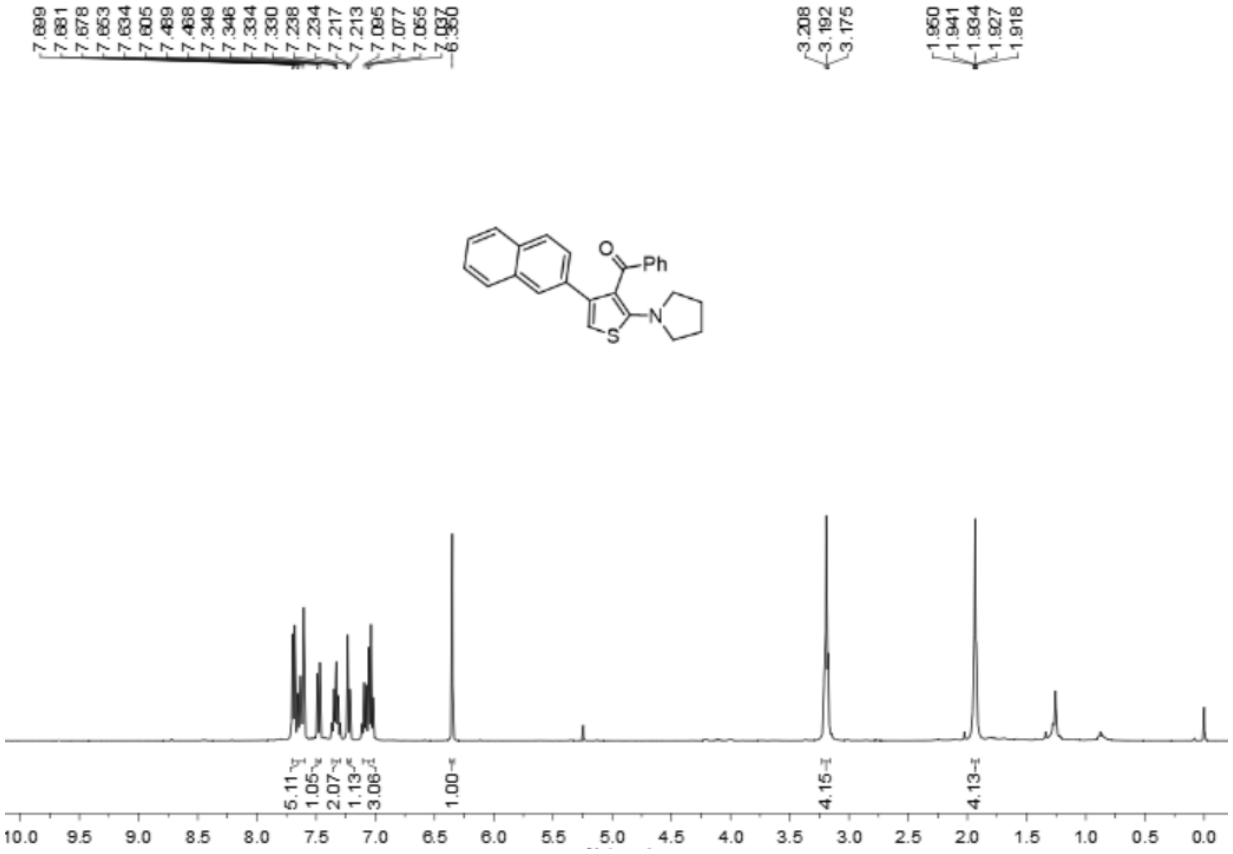
^{13}C NMR spectrum of 3je



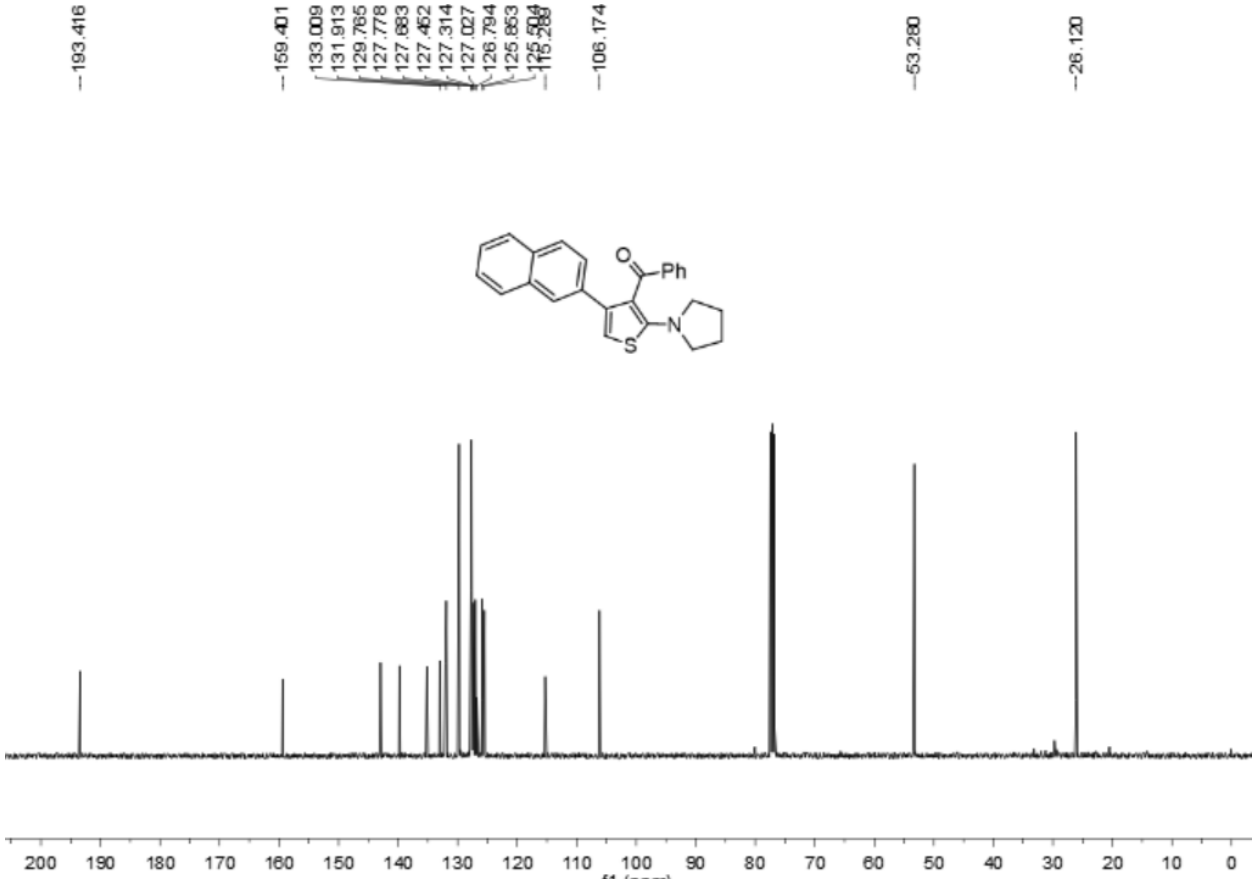
HRMS (EI) of 3je



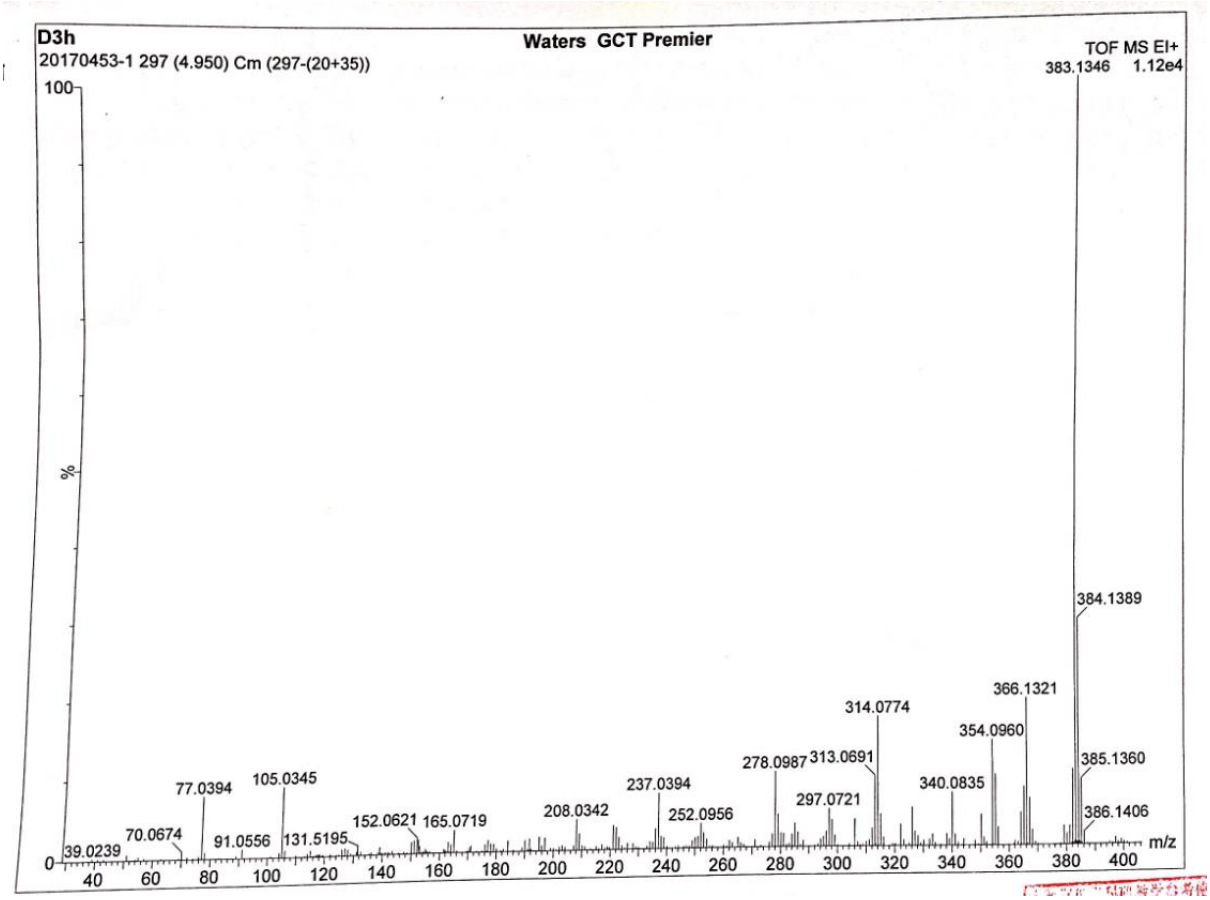
^{1}H NMR spectrum of 3kb



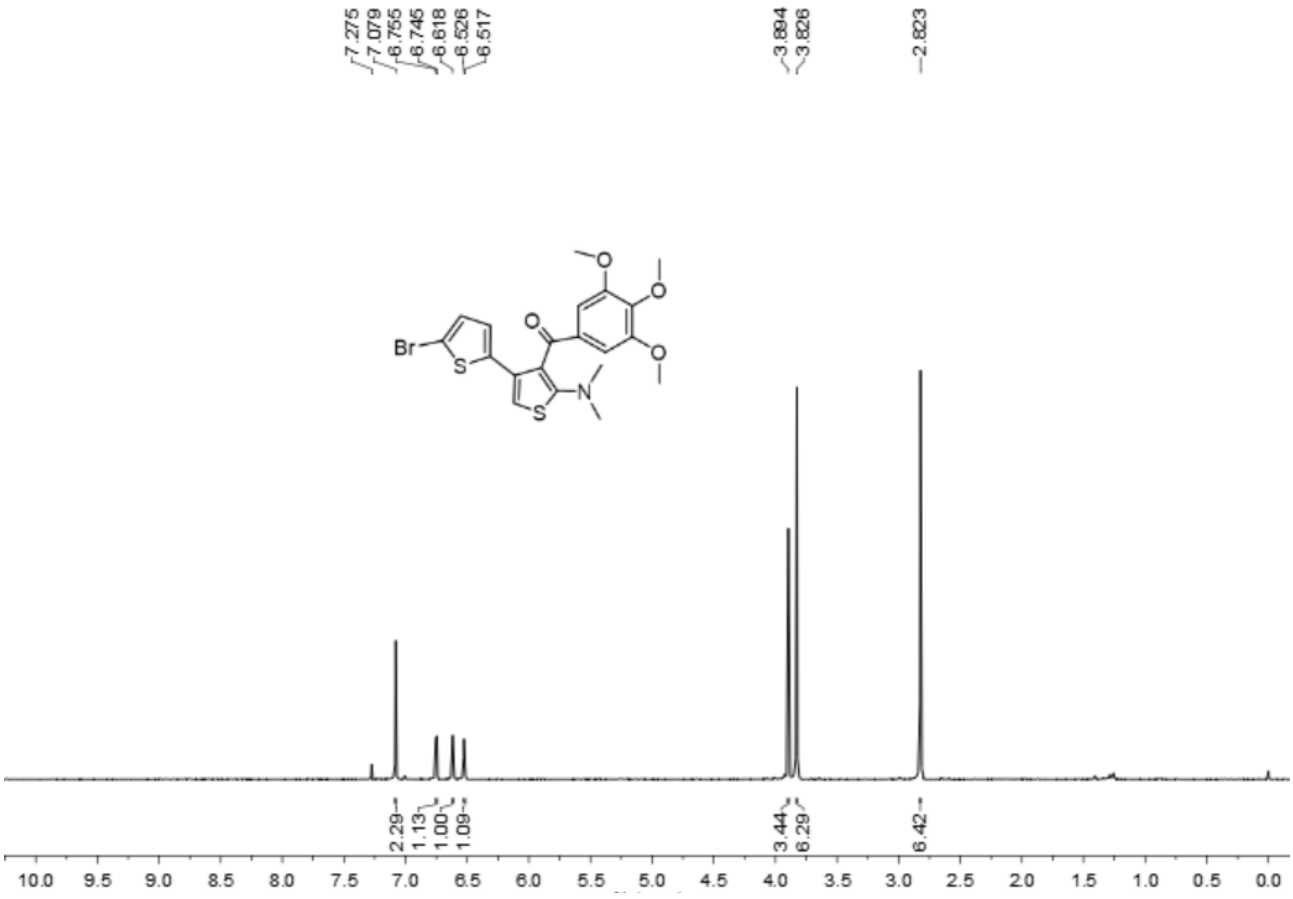
^{13}C NMR spectrum of 3kb



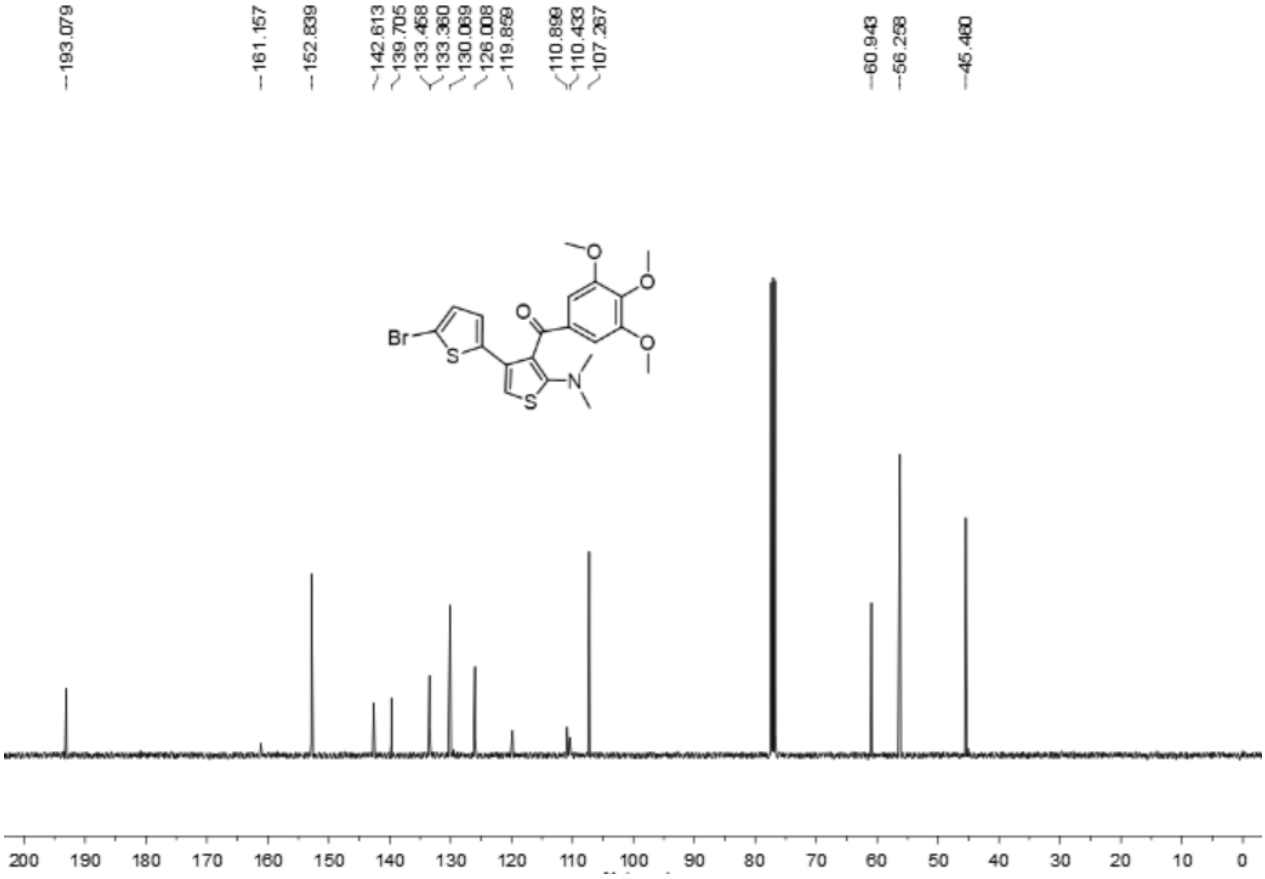
HRMS (EI) of 3kb



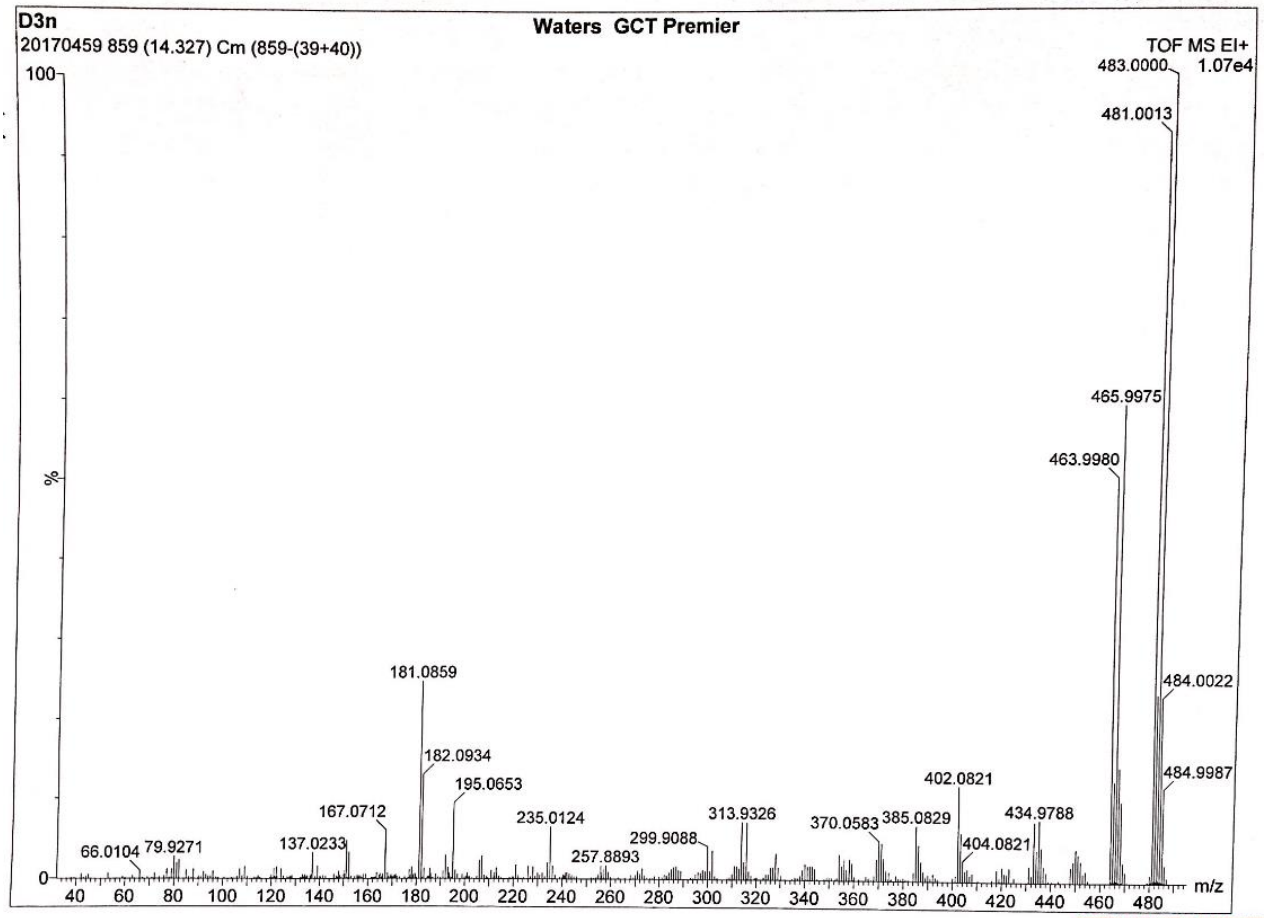
^{1}H NMR spectrum of 3lf



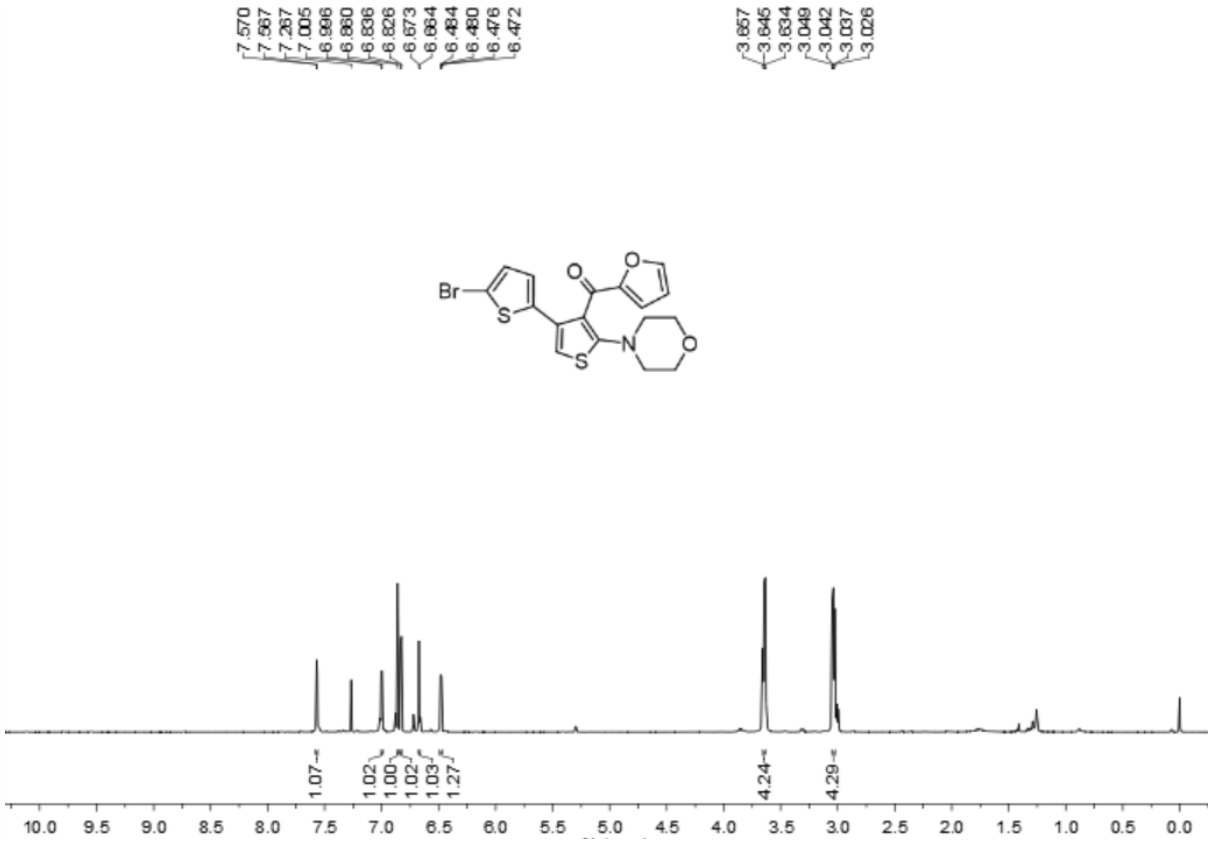
^{13}C NMR spectrum of 3lf



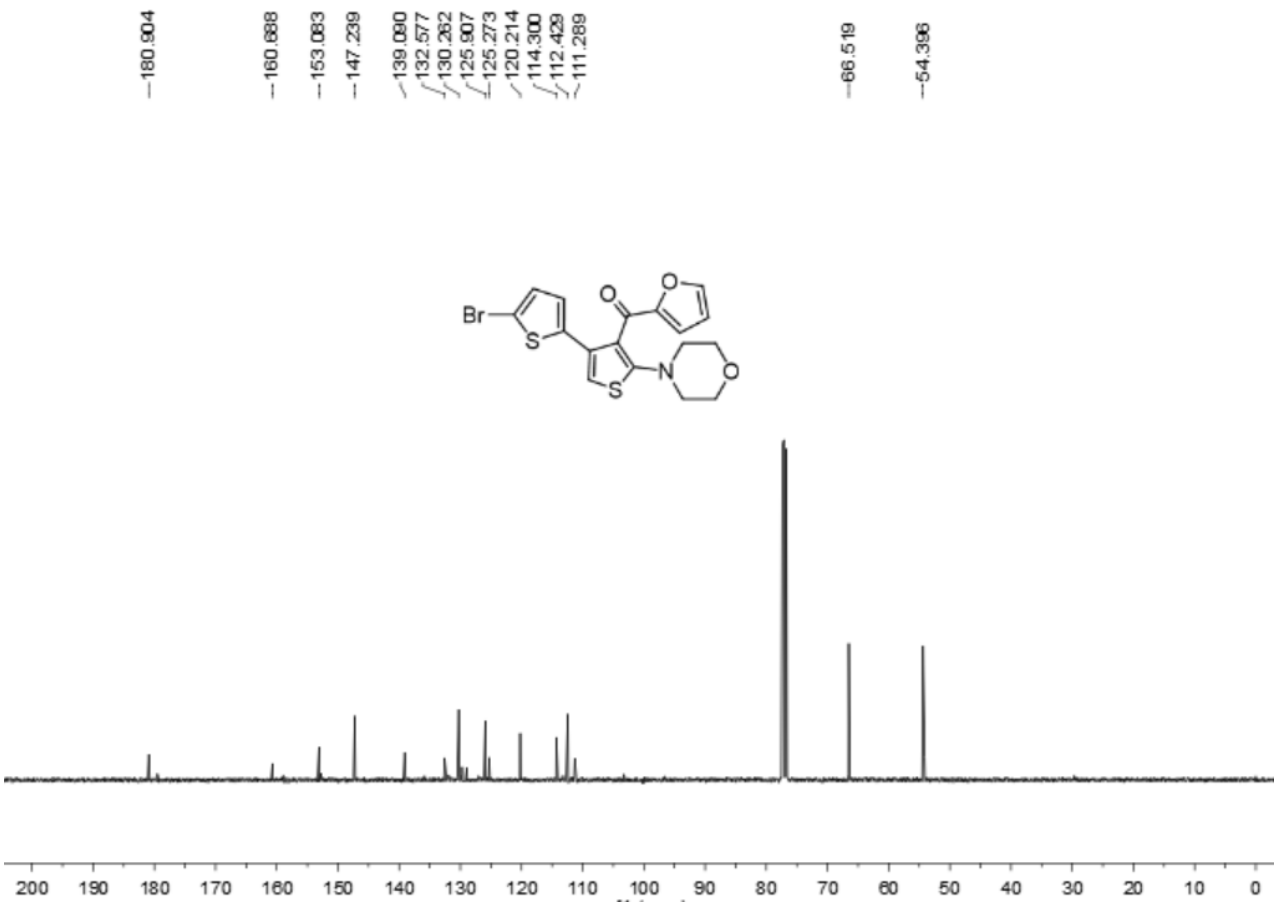
HRMS (EI) of 3lf



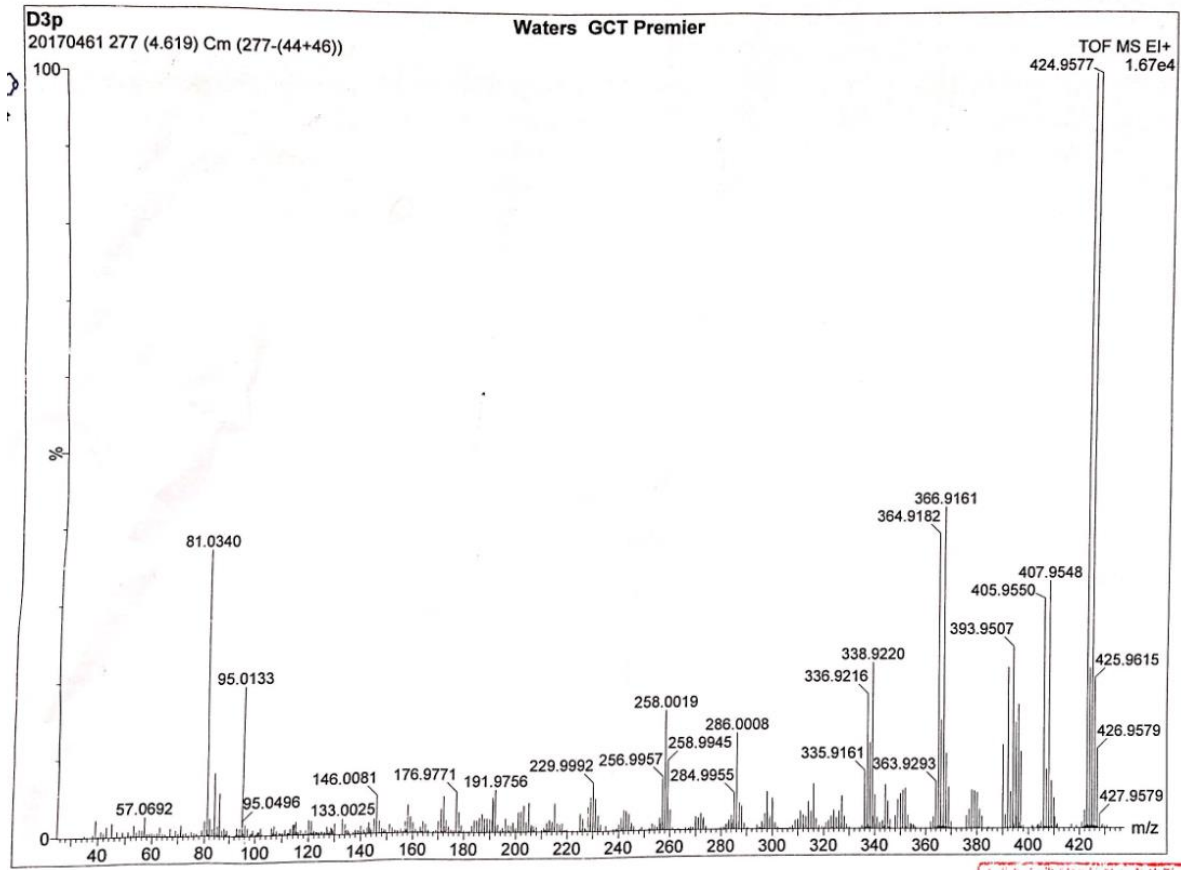
^{1}H NMR spectrum of 3lg



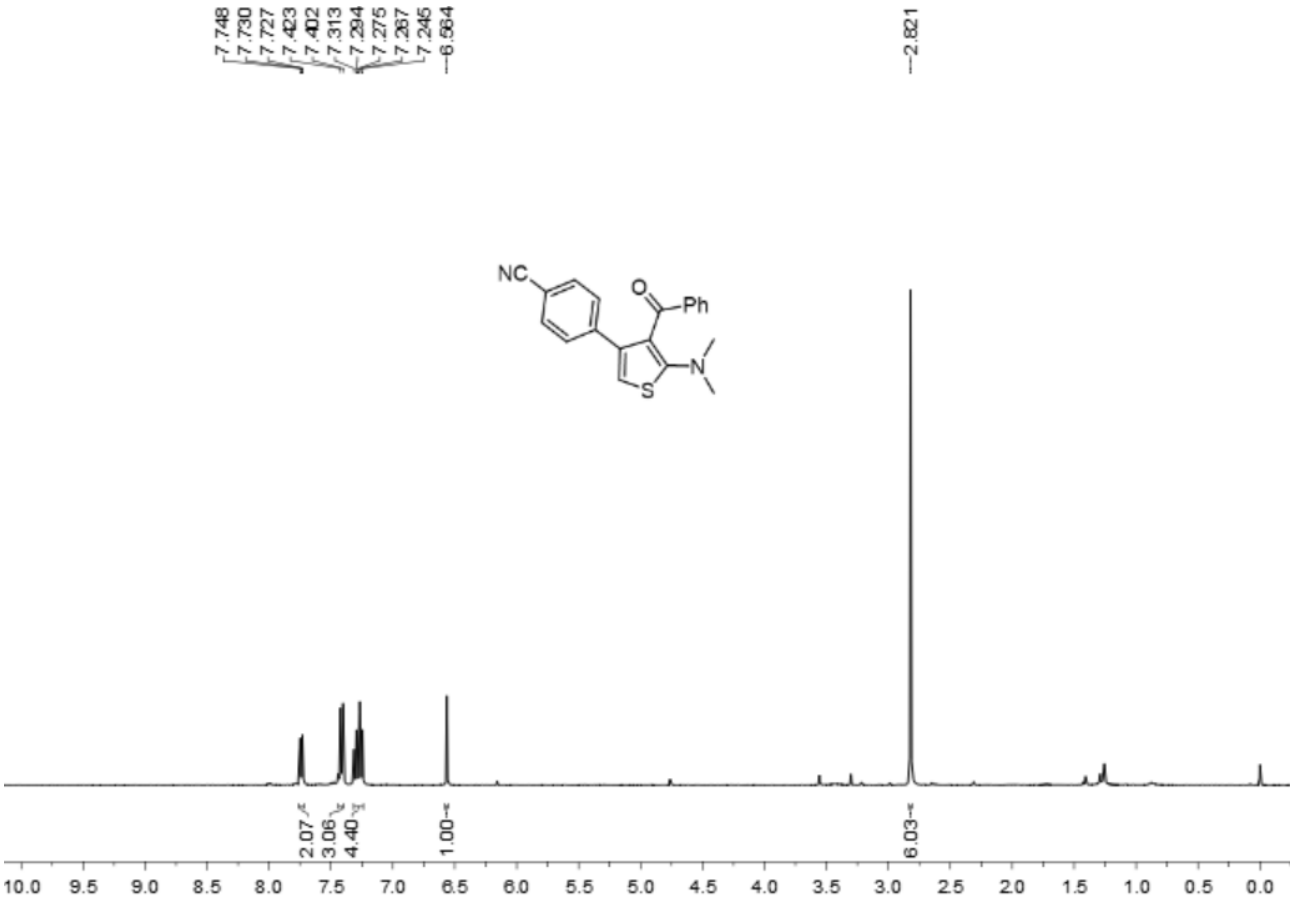
^{13}C NMR spectrum of 3lg



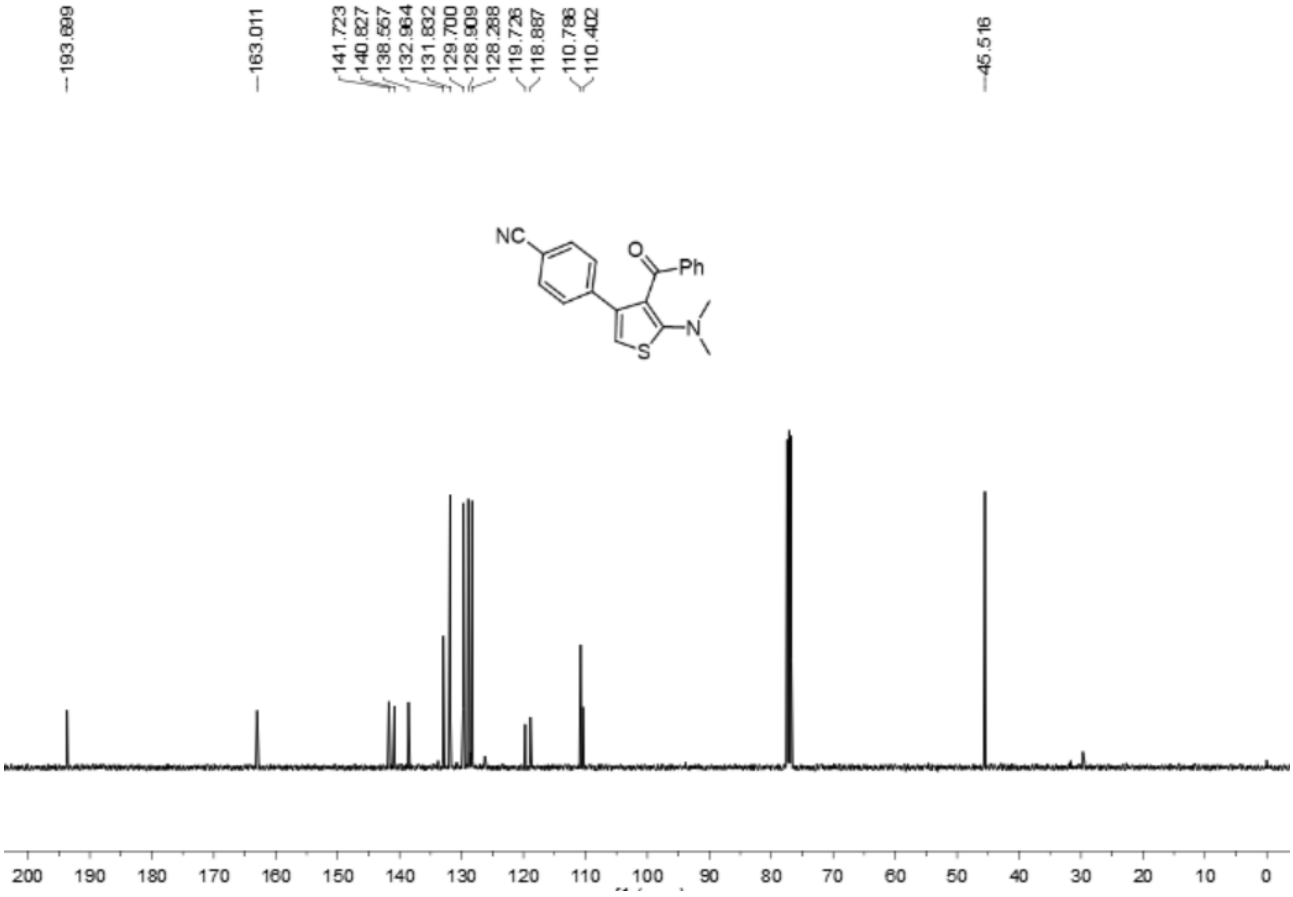
HRMS (EI) of 3lg



^{1}H NMR spectrum of 3nd



^{13}C NMR spectrum of 3nd



6. X-ray crystal structure of compound 3ba

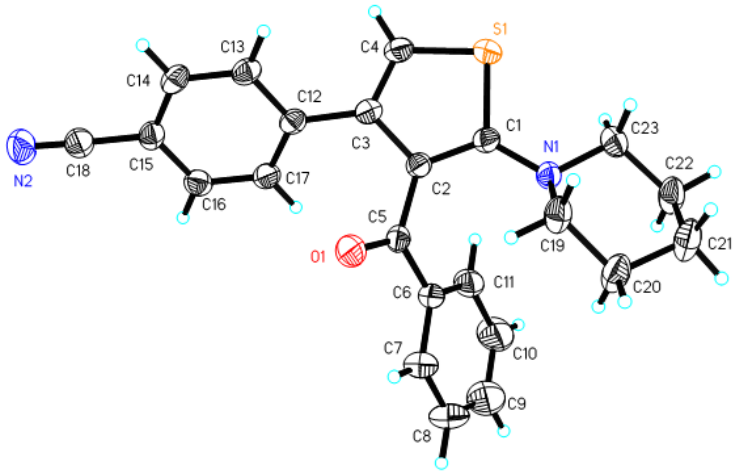


Figure S1. X-ray crystal structure of **3ba**.

Single crystals of **3ba** (yellowish prisms) suitable for diffraction study were obtained by slow diffusion of hexane into a dichloromethane solution of compound **3ba**. X-ray crystallographic data for compound **3ba** (CCDC 1434924) has been deposited in the Cambridge Crystallographic Data Center. The data can be obtained free of charge via http://www.ccdc.ac.ck./data_request/cif. The X-ray crystallography data of **3ba** are listed below.

Empirical formula	C23 H20 N2 O S	
Formula weight	372.47	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 7.7469(8) Å	a= 90°.
	b = 17.4348(19) Å	b= 92.609(2)°.
	c = 14.3624(16) Å	g = 90°.
Volume	1937.9(4) $Å^3$	
Z	4	
Density (calculated)	1.277 Mg/m^3	
Absorption coefficient	0.182 mm^{-1}	
F(000)	784	
Crystal size	0.220 x 0.170 x 0.130 mm^3	
Theta range for data collection	1.838 to 25.998°.	
Index ranges	-9<=h<=9, -21<=k<=20, -17<=l<=9	
Reflections collected	11485	
Independent reflections	3825 [R(int) = 0.0353]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.7457 and 0.6382
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3825 / 0 / 244
Goodness-of-fit on F^2	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0540, wR2 = 0.1297
R indices (all data)	R1 = 0.0731, wR2 = 0.1401
Extinction coefficient	n/a
Largest diff. peak and hole	0.246 and -0.191 e.$Å^{-3}$