Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Iridium-catalyzed oxidative Ar–H/Ar–H cross-coupling of primary benzamides with thiophenes

*Guangying Tan, Chunhao Ran and Jingsong You**

Key Laboratory of Green Chemistry and Technology of Ministry of Education, College of Chemistry, Sichuan University, 29 Wangjiang Road, Chengdu 610064, P.R. China

E-mail: jsyou@scu.edu.cn

Table of Contents

I. General remarks

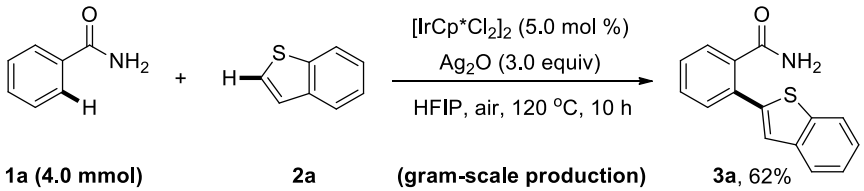
NMR spectra were obtained on an Agilent 400-MR DD2 spectrometer. The ^{1}H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$ or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 7.26; DMSO-d_6: δ = 2.50). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ or DMSO-d_6 as the internal standard ($CDCl_3$: δ = 77.16; DMSO-d_6: δ = 39.52). High-resolution mass spectra (HRMS) were obtained with a Shimadzu LCMS-IT-TOF (ESI). Melting points were determined with XRC-1 and are uncorrected.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. $IrCl_3 \cdot H_2O$ were purchased from Shanxi Kaida Chemical Engineering (China) CO., Ltd. Various primary benzamides and thiophenes were purchased from Adamas-beta Ltd.

II. General procedure for the heteroarylation of primary benzamides

A Schlenk tube with a magnetic stir bar was charged with $[IrCp^*Cl_2]_2$ (8.0 mg, 10 μmol), Ag_2O (139.0 mg, 0.6 mmol), primary benzamides **1** (0.2 mmol, 1.0 equiv), and thiophenes **2** (0.6 mmol, 3.0 equiv) in HFIP (0.5 mL) under an air atmosphere. The resulting mixture was stirred at 120 ^{o}C for 6 h and then diluted with 3 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired product **3** or **4**.

III. Procedure for the synthesis of 3a on 4 mmol scale

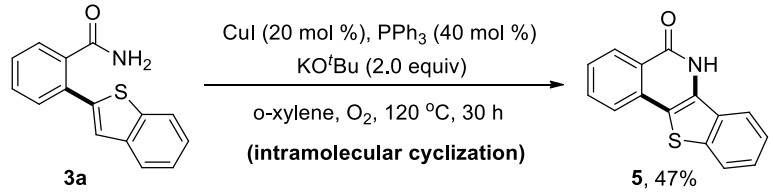


1a (4.0 mmol) **2a** **(gram-scale production)** **3a**, 62%

A Schlenk tube with a magnetic stir bar was charged with $[IrCp^*Cl_2]_2$ (160 mg, 0.2 mmol), Ag_2O (2780 mg, 12 mmol), benzamide **1a** (484 mg, 4.0 mmol, 1.0 equiv), and benzothiophene **2a** (1608 mg, 12.0 mmol, 3.0 equiv) in HFIP (5.0 mL) under an air atmosphere. The resulting mixture was stirred at 120 ^{o}C for 10 h and then diluted with 10 mL of dichloromethane. The solution was filtered through a celite pad and washed

with 10-20 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired product **3a** (627 mg, 62% yield).

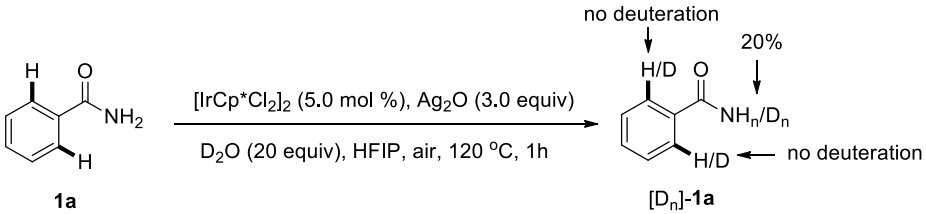
IV. Intramolecular annulation of 3a[1]



A Schlenk tube with a magnetic stir bar was charged with CuI (7.6 mg, 20 mol %), PPh_3 (21.0, 40 mol %), KO^{t}Bu (44.9, 2.0 equiv), and 2-(benzo[*b*]thiophen-2-yl)benzamide **3a** (50.6 mg, 0.2 mmol) in *o*-xylene (1.0 mL) under an O_2 atmosphere (1 atm). The resulting mixture was stirred at 120 ^{o}C for 30 h and then diluted with 10 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired product **5** (23 mg, 47% yield) as a yellow solid. M.p.: > 250 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.49-7.55 (m, 2H), 7.60-7.64 (m, 1H), 7.82-7.88 (m, 2H), 8.06-8.10 (m, 1H), 8.35 (d, J = 7.6 Hz, 1H), 8.43-8.47 (m, 1H), 12.62 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 114.1, 121.8, 123.4, 123.7, 124.9, 125.1, 126.8, 127.4, 128.3, 130.1, 132.6, 133.1, 133.5, 137.4, 161.9 ppm. HRMS (ESI): calcd for $C_{15}H_{10}NOS$ $[M+H]^+$ 252.0483, found 252.0490.

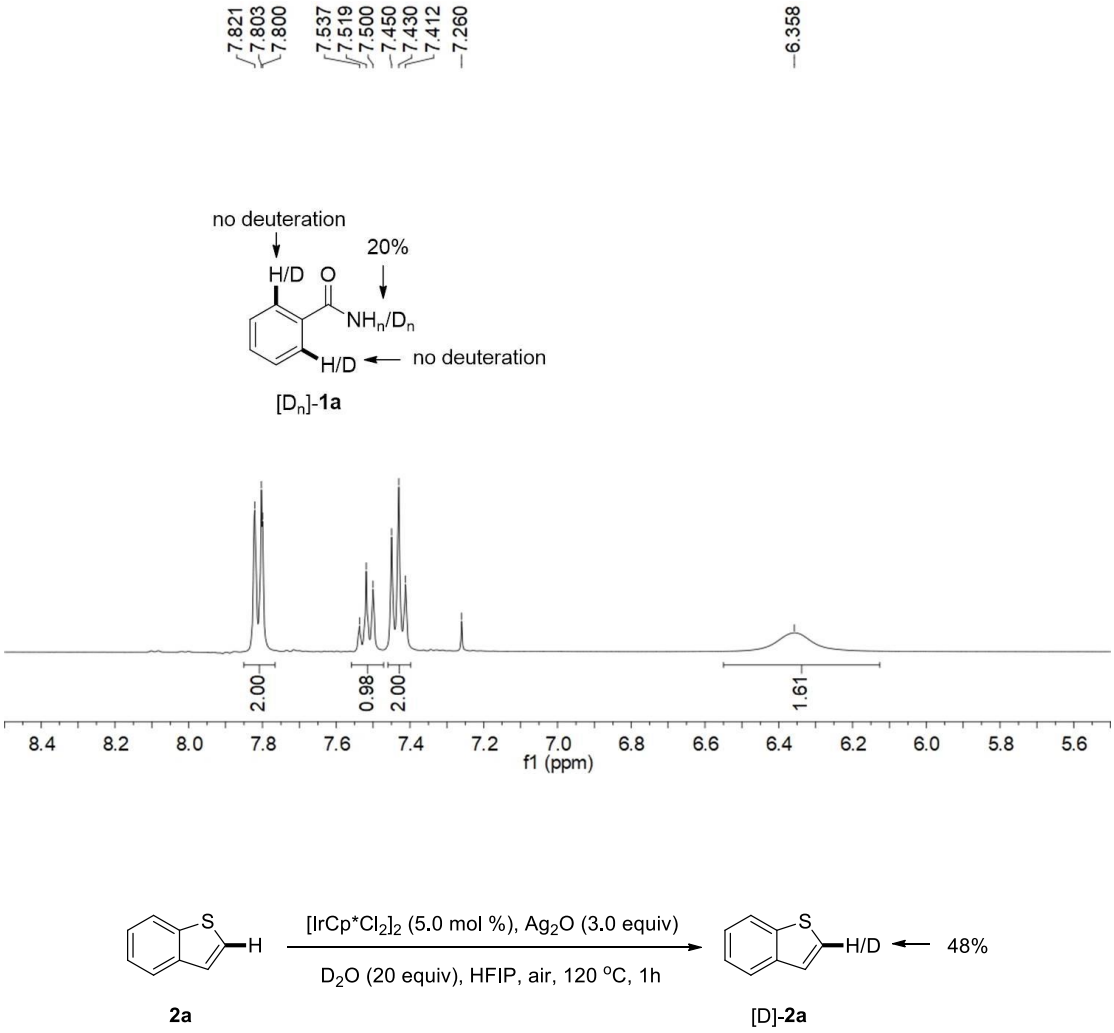
V. Mechanistic study

(i) H/D exchange experiments



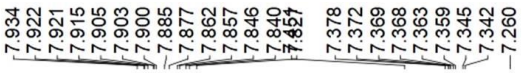
A Schlenk tube with a magnetic stir bar was charged with $[IrCp^*Cl_2]_2$ (8.0 mg, 10 μmol), Ag_2O (139.0 mg, 0.6 mmol), benzamide **1a** (24.2 mg, 0.2 mmol), and D_2O (72 μL, 4.0 mmol) in HFIP (0.5 mL) under an air atmosphere. The resulting mixture was

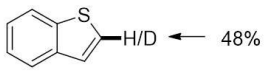
stirred at 120 °C for 1 h and then diluted with 3 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 10/1, v/v) to provide [D_n]-**1a**. The deuterated ratio was calculated from ^{1}H NMR analysis.



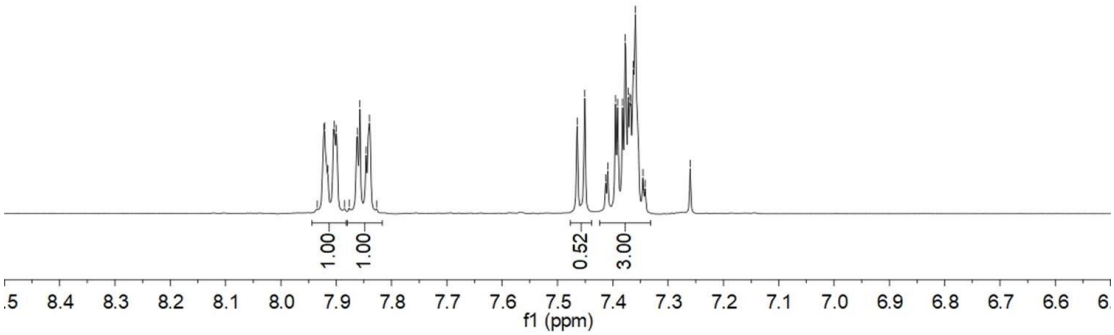
2a [D]-**2a**

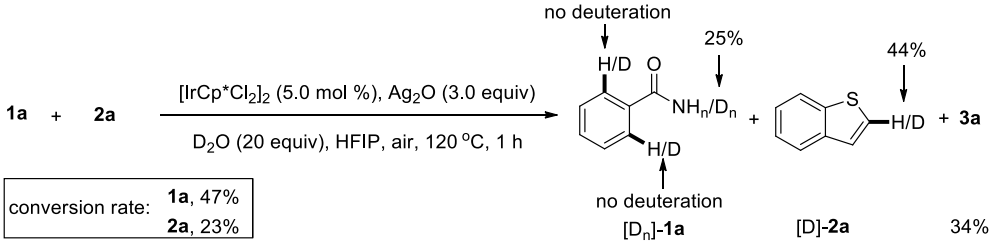
A Schlenk tube with a magnetic stir bar was charged with [$IrCp^*Cl_2]_2$ (8.0 mg, 10 μmol), Ag_2O (139.0 mg, 0.6 mmol), benzothiophene **2a** (26.8 mg, 0.2 mmol), and D_2O (72 μL, 4.0 mmol) in HFIP (0.5 mL) under an air atmosphere. The resulting mixture was stirred at 120 °C for 1 h and then diluted with 3 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 10/1, v/v) to provide [D]-**2a**. The deuterated ratio was calculated from ^{1}H NMR analysis.



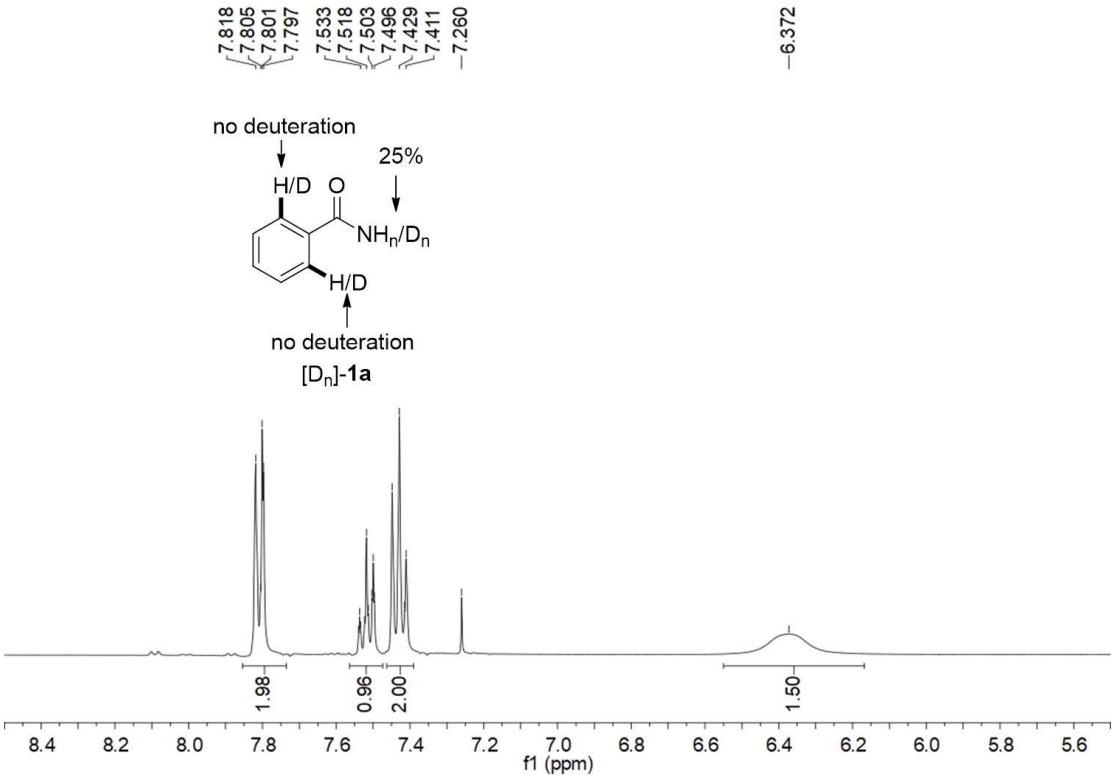


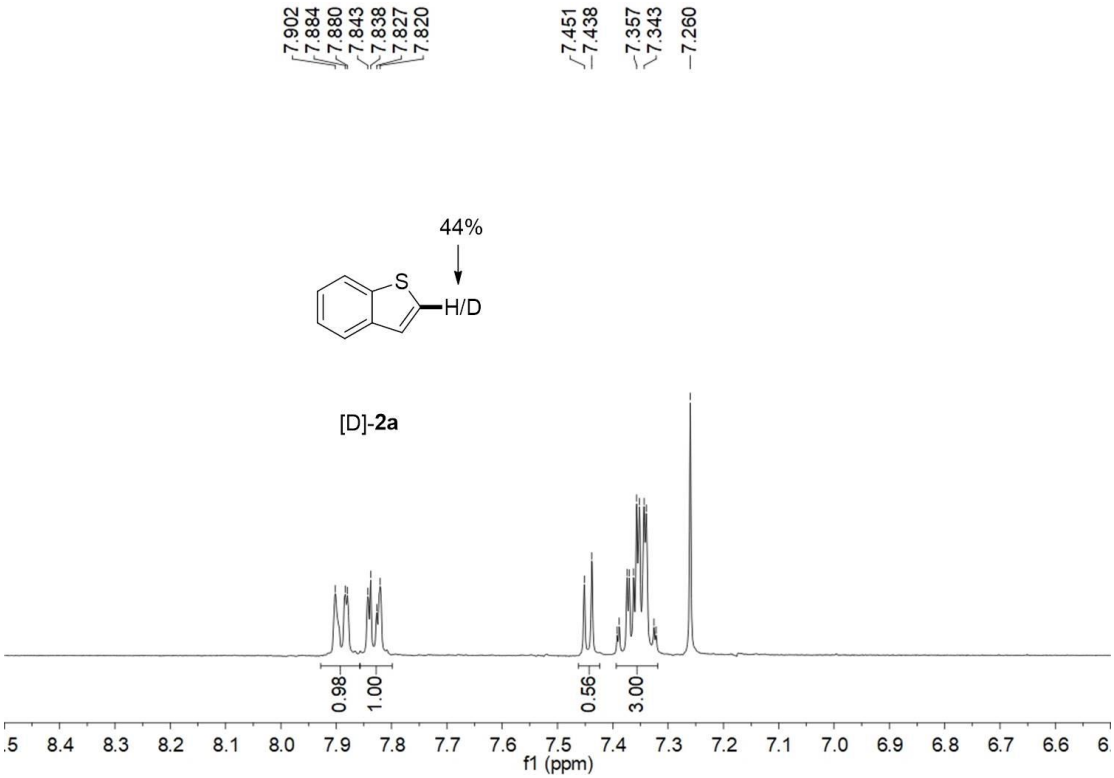
[D]-**2a**



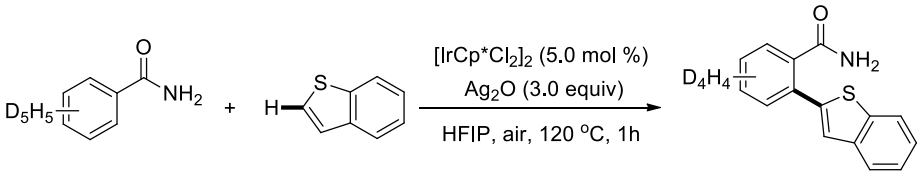


A Schlenk tube with a magnetic stir bar was charged with $[IrCp^*Cl_2]_2$ (8.0 mg, 10 μmol), Ag_2O (139.0 mg, 0.6 mmol), benzamide **1a** (24.2 mg), benzothiophene **2a** (80.4 mg, 0.6 mmol), and D_2O (72 μL, 4.0 mmol) in HFIP (0.5 mL) under an air atmosphere. The resulting mixture was stirred at 120 ^oC for 1 h and then diluted with 3 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 10/1, v/v) to provide $[D_n]$-**1a**, [D]-**2a** and **3a**. The conversion of **1a** and **2a** were 47% and 23%, respectively and the yield of **3a** was 34%. The deuterated ratio was calculated from ^1H NMR analysis.


7.818
7.805
7.801
7.797
7.533
7.518
7.503
7.496
7.429
7.411
7.260
6.372
no deuteration
25%
H/D
O
NHn/Dn
H/D
no deuteration
[Dn]-1a
1.98
0.96
2.00
1.50
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
f1 (ppm)

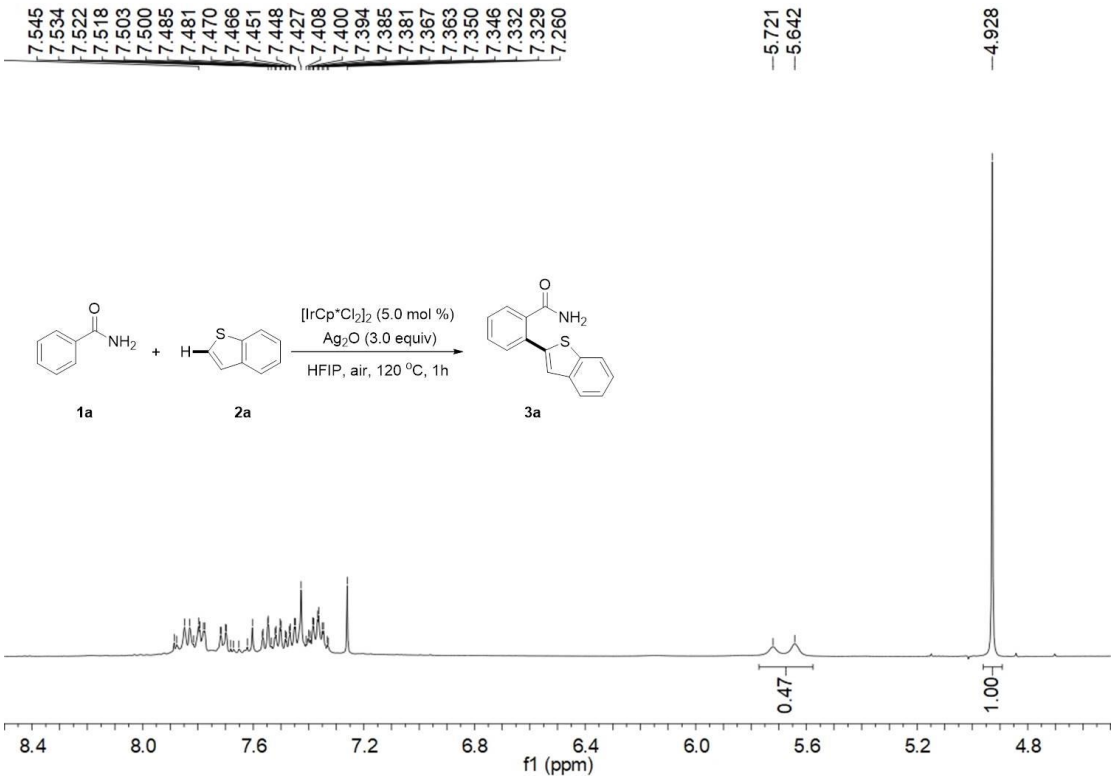

7.902
7.884
7.880
7.843
7.838
7.827
7.820
7.451
7.438
7.357
7.343
7.260
44%
S
H/D
[D]-2a
0.98
1.00
0.56
3.00
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
f1 (ppm)

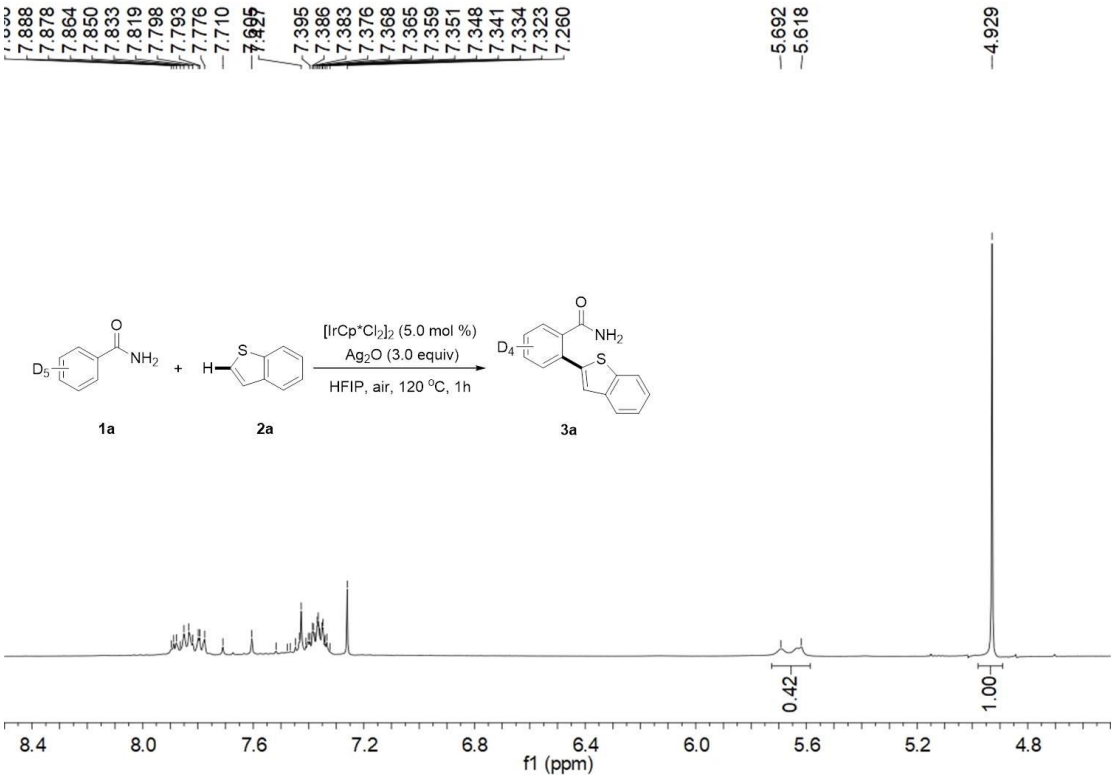
(ii) Kinetic isotope experiments

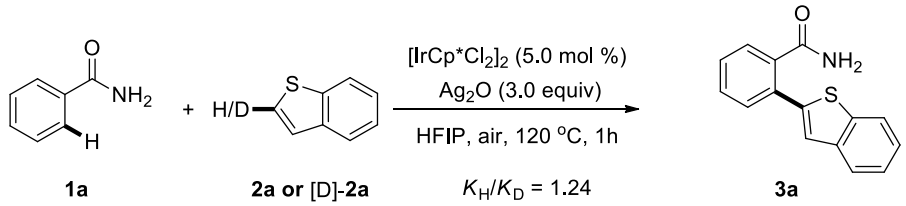


1a or [D_5]-**1a** **2a** K_H/K_D = 1.12 **3a** or [D_4]-**3a**

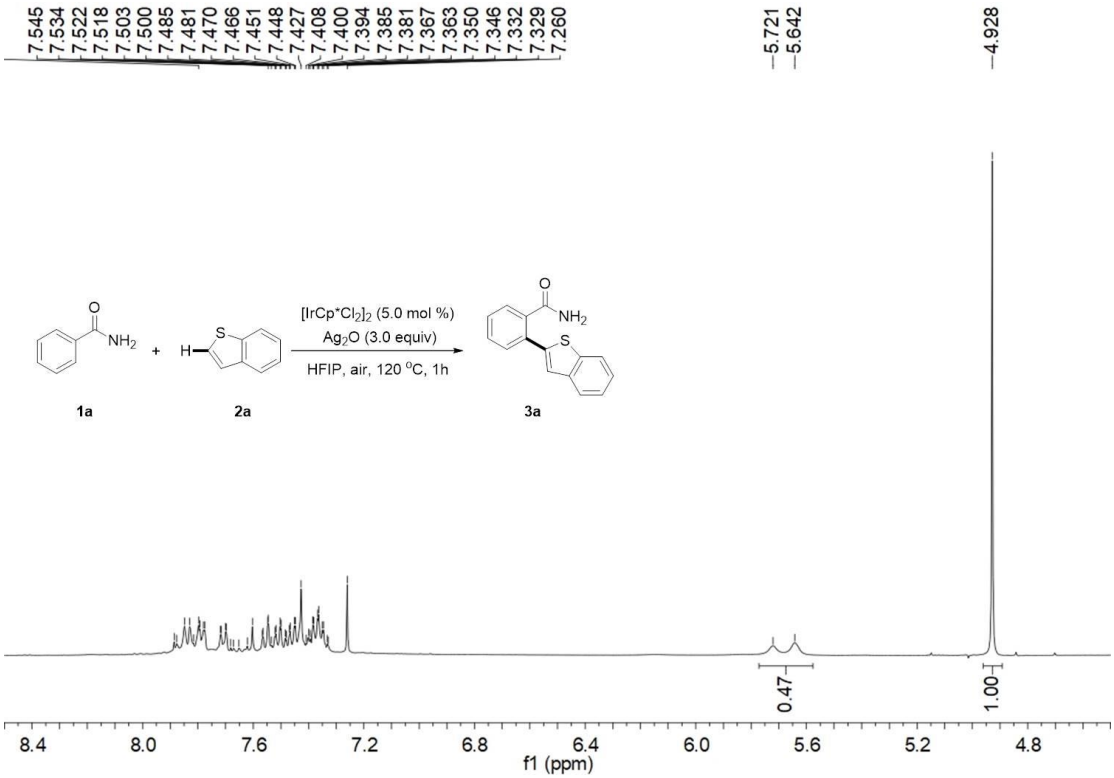
A Schlenk tube with a magnetic stir bar was charged with [IrCp*Cl_2]$_2$ (8.0 mg, 10 μmol), Ag_2O (139.0 mg, 0.6 mmol), benzamide **1a** (24.2 mg) or deuterated benzamide [D_5]-**1a** (25.2 mg), and benzothiophene **2a** (80.4 mg, 0.6 mmol) in HFIP (0.5 mL) under an air atmosphere. The resulting mixture was stirred at 120 °C for 1 h and then diluted with 3 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The deuterated ratio was calculated from ^{1}H NMR analysis. The yield of **3a** was determined by ^{1}H NMR analysis of the crude product using dibromomethane (0.2 mmol, 14 μL) as internal standard. A kinetic isotope effect (KIE) value (k_H/k_D = 1.12) was obtained.

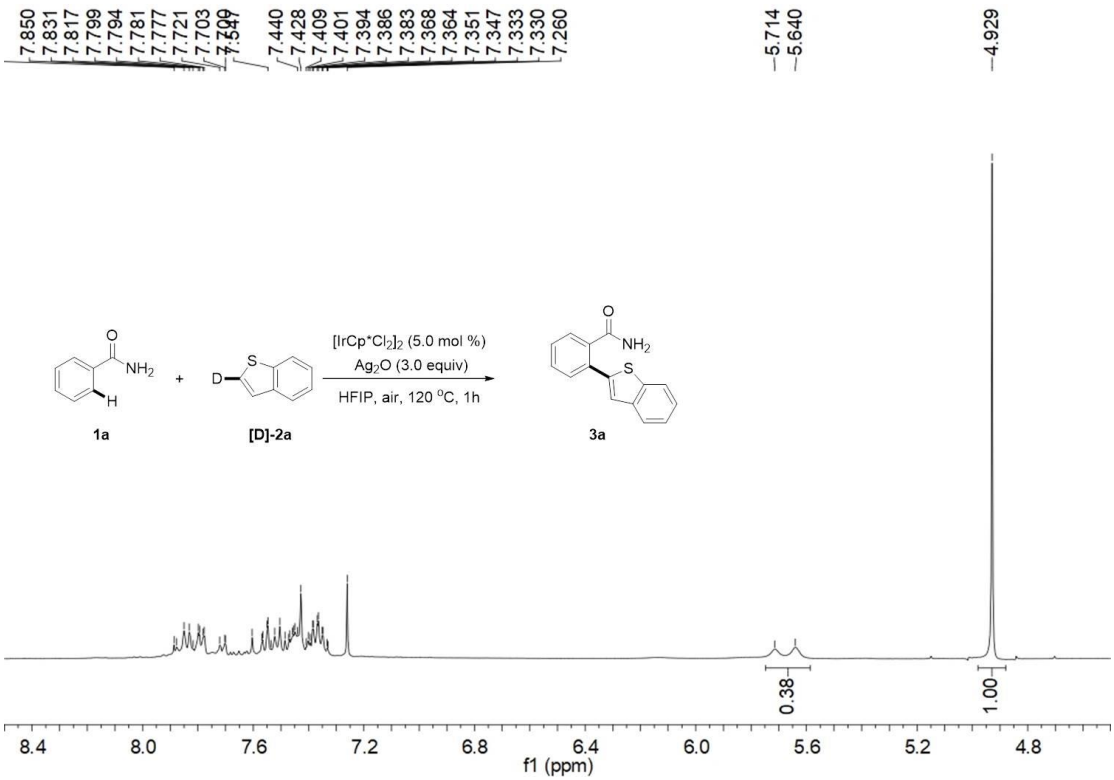




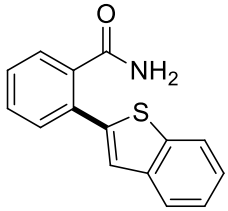


A Schlenk tube with a magnetic stir bar was charged with $[IrCp^*Cl_2]_2$ (8.0 mg, 10 μmol), Ag_2O (139.0 mg, 0.6 mmol), benzamide **1a** (24.2 mg), and benzothiophene **2a** (80.4 mg, 0.6 mmol) or deuterated benzothiophene [D]-**2a** (81.0 mg, 0.6 mmol) in HFIP (0.5 mL) under an air atmosphere. The resulting mixture was stirred at 120 °C for 1 h and then diluted with 3 mL of dichloromethane. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The deuterated ratio was calculated from ^1H NMR analysis. The yield of **3a** was determined by ^1H NMR analysis of the crude product using dibromomethane (0.2 mmol, 14 μL) as internal standard. A kinetic isotope effect (KIE) value (k_H/k_D = 1.24) was obtained.


7.545
7.534
7.522
7.518
7.503
7.500
7.485
7.481
7.470
7.466
7.451
7.448
7.427
7.408
7.400
7.394
7.385
7.381
7.367
7.363
7.350
7.346
7.332
7.329
7.260
5.721
5.642
4.928
[IrCp*Cl2]2 (5.0 mol %)
Ag2O (3.0 equiv)
HFIP, air, 120 °C, 1h
1a
2a
3a
0.47
1.00
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
f1 (ppm)

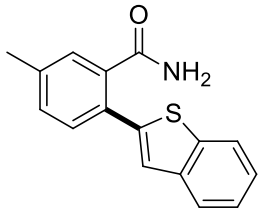

7.850
7.831
7.817
7.799
7.794
7.781
7.777
7.721
7.703
7.440
7.428
7.409
7.401
7.394
7.386
7.383
7.368
7.364
7.351
7.347
7.333
7.330
7.260
5.714
5.640
4.929
[IrCp*Cl2]2 (5.0 mol %)
Ag2O (3.0 equiv)
HFIP, air, 120 °C, 1h
1a
[D]-2a
3a
0.38
1.00
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
f1 (ppm)

VI. Experimental data for the described substances



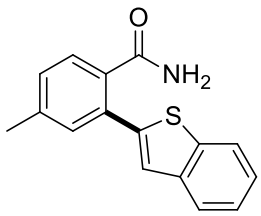
2-(Benzo[*b*]thiophen-2-yl)benzamide (3a)

Following the general procedure. Benzamide **1a** (24.2 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **3a** as a yellow solid (35 mg, 70% yield). M.p.: 138-139 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.71 (d, J = 48.4 Hz, 2H), 7.33-7.40 (m, 2H), 7.42-7.52 (m, 3H), 7.54-7.57 (m, 1H), 7.70 (dd, J = 7.6 Hz, 1.6 Hz, 1H), 7.78-7.80 (m, 1H), 7.84 (d, J = 7.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.3, 124.0, 124.1, 124.82, 124.83, 128.8, 128.9, 130.5, 131.0, 132.0, 135.5, 140.3, 140.4, 141.2, 171.3 ppm. HRMS (ESI): calcd for $C_{15}H_{12}NOS$ $[M+H]^+$ 254.0640, found 254.0643.



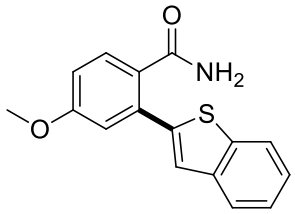
2-(Benzo[*b*]thiophen-2-yl)-5-methylbenzamide (3b)

Following the general procedure. 3-Methylbenzamide **1b** (27.0 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **3b** as a yellow solid (36 mg, 68% yield). M.p.: 223-224 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.43 (s, 3H), 5.62 (d, J = 5.2 Hz, 2H), 7.30-7.29 (m, 4H), 7.44 (d, J = 8.0 Hz, 1H), 7.54 (s, 1H), 7.77-7.79 (m, 1H), 7.83 (d, J = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4, 122.3, 123.9, 124.0, 124.7, 124.8, 129.2, 129.5, 131.7, 132.0, 132.6, 140.2, 140.4, 140.9, 141.4, 171.2 ppm. HRMS (ESI): calcd for $C_{16}H_{14}NOS$ $[M+H]^+$ 268.0796, found 268.0798.



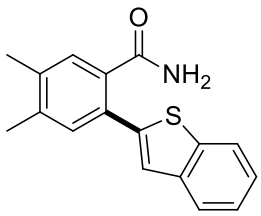
2-(Benzo[*b*]thiophen-2-yl)-4-methylbenzamide (3c)

Following the general procedure. 4-Methylbenzamide **1c** (27.0 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **3c** as a yellow soild (35 mg, 65% yield). M.p.: 185-186 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3H), 5.67 (d, *J* = 40 Hz, 2H), 7.25-7.27 (m, 1H), 7.33-7.39 (m, 4H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.2 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4, 122.3, 123.9, 124.0, 124.7, 124.8, 129.2, 129.5, 131.7, 132.0, 132.6, 140.2, 140.4, 140.9, 141.4, 171.2 ppm. HRMS (ESI): calcd for $C_{16}H_{14}NOS$ $[M+H]^+$ 268.0796, found 268.0798.



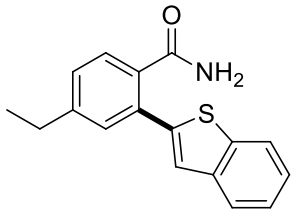
2-(Benzo[*b*]thiophen-2-yl)-4-methoxybenzamide (3d)

Following the general procedure. 4-Methoxybenzamide **1d** (30.2 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **3d** as a yellow soild (41 mg, 72% yield). M.p.: 187-188 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.87 (s, 3H), 5.63 (d, *J* = 21.2 Hz, 2H), 6.97 (dd, *J* = 6.0 Hz, 2.4 Hz, 1H), 7.02 (d, *J* = 2.8 Hz, 1H), 7.34-7.41 (m, 3H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.79 (dd, *J* = 7.2 Hz, 2.0 Hz, 1H), 7.83-7.85 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.7, 114.2, 116.4, 122.3, 124.1, 124.2, 124.90, 124.92, 127.6, 131.3, 134.0, 140.1, 140.4, 141.3, 161.0, 170.6 ppm. HRMS (ESI): calcd for $C_{16}H_{14}NO_2S$ $[M+H]^+$ 284.0745, found 284.0743.



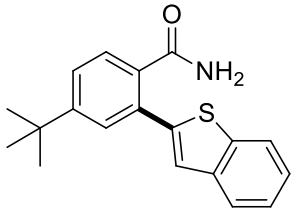
2-(Benzo[*b*]thiophen-2-yl)-4,5-dimethylbenzamide (3e)

Following the general procedure. 3,4-Dimethylbenzamide **1e** (29.8 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **3e** as a yellow soild (42 mg, 74% yield). M.p.: 198-199 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33 (m, 6H), 5.65 (d, *J* = 38.8 Hz, 2H), 7.30 (s, 1H), 7.32-7.39 (m, 3H), 7.53 (s, 1H), 7.77 (dd, *J* = 6.8 Hz, 1.6 Hz, 1H), 7.82-7.84 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.6, 19.8, 122.2, 123.7, 123.9, 124.6, 124.8, 129.4, 130.3, 132.2, 132.6, 137.8, 139.6, 140.3, 140.4, 141.6, 171.3 ppm. HRMS (ESI): calcd for $C_{17}H_{16}NOS$ $[M+H]^+$ 282.0953, found 282.0958.



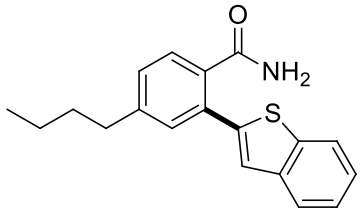
2-(Benzo[*b*]thiophen-2-yl)-4-ethylbenzamide (3f)

Following the general procedure. 4-Ethylbenzamide **1f** (29.8 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **3f** as a yellow soild (39 mg, 70% yield). M.p.: 152-153 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (t, *J* = 7.6 Hz, 3H), 2.69-2.75 (m, 2H), 5.67 (d, *J* = 41.2 Hz, 2H), 7.29 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.33-7.40 (m, 4H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.77-7.79 (m, 1H), 7.84 (d, *J* = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.4, 28.8, 122.3, 123.9, 124.0, 124.7, 124.8, 128.4, 129.2, 130.6, 132.1, 132.8, 140.3, 140.4, 141.6, 147.1, 171.2 ppm. HRMS (ESI): calcd for $C_{17}H_{16}NOS$ $[M+H]^+$ 282.0953, found 282.0949.



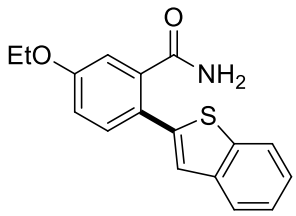
2-(Benzo[*b*]thiophen-2-yl)-4-(*tert*-butyl)benzamide (3g)

Following the general procedure. 4-(*tert*-Butyl)benzamide **1g** (35.4 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **3g** as a yellow soild (48 mg, 78% yield). M.p.: 162-163 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35 (s, 9H), 5.71 (d, *J* = 59.6 Hz, 2H), 7.33-7.41 (m, 3H), 7.48 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 7.53 (d, *J* = 1.6 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.79 (dd, *J* = 7.2 Hz, 1.6 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.2, 35.0, 122.3, 123.9, 124.0, 124.7, 124.8, 126.0, 128.2, 129.0, 131.8, 132.6, 140.3, 140.4, 141.9, 154.0, 171.2 ppm. HRMS (ESI): calcd for $C_{19}H_{20}NOS$ $[M+H]^+$ 310.1266, found 310.1263.



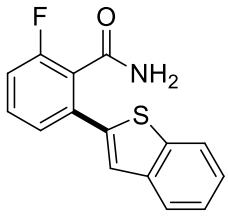
2-(Benzo[*b*]thiophen-2-yl)-4-butylbenzamide (3h)

Following the general procedure. 4-Butylbenzamide **1h** (35.4 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **3h** as a yellow soild (46 mg, 74% yield). M.p.: 145-146 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 7.2 Hz, 3H), 1.33-1.42 (m, 2H), 1.59-1.67 (m, 2H), 2.67 (t, *J* = 7.6 Hz, 2H), 5.66 (d, *J* = 30.4 Hz, 2H), 7.27 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.33-7.40 (m, 4H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.78 (dd, *J* = 6.8 Hz, 1.6 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 22.4, 33.4, 35.5, 122.3, 123.9, 124.0, 124.7, 124.8, 128.9, 129.1, 131.1, 132.0, 132.7, 140.3, 140.4, 141.6, 145.8, 171.3 ppm. HRMS (ESI): calcd for $C_{19}H_{20}NOS$ $[M+H]^+$ 310.1266, found 310.1267.



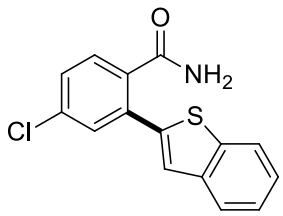
2-(Benzo[*b*]thiophen-2-yl)-5-ethoxybenzamide (3i)

Following the general procedure. 3-Ethoxybenzamide **1i** (33.0 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **3i** as a yellow soild (40 mg, 68% yield). M.p.: 195-196 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44 (t, *J* = 7.2 Hz, 3H), 4.08-4.13 (m, 2H), 5.68 (d, *J* = 27.6 Hz, 2H), 7.01 (dd, *J* = 8.4 Hz, 2.8 Hz, 1H), 7.23 (d, *J* = 2.8 Hz, 1H), 7.31-7.39 (m, 3H), 7.45 (d, *J* = 8.8 Hz, 1H), 7.75-7.77 (m, 1H), 7.82 (d, *J* = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.9, 64.0, 114.2, 117.3, 122.2, 123.5, 123.9, 124.1, 124.6, 124.8, 132.4, 136.5, 140.3, 140.4, 141.3, 159.3, 170.1 ppm. HRMS (ESI): calcd for $C_{17}H_{16}NO_2S$ $[M+H]^+$ 298.0902, found 298.0904.



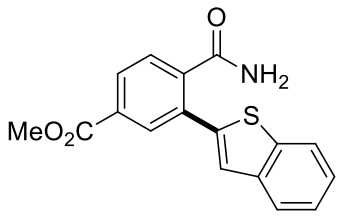
2-(Benzo[*b*]thiophen-2-yl)-6-fluorobenzamide (3j)

Following the general procedure. 2-Fluorobenzamide **1j** (27.8 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **3j** as a yellow soild (34 mg, 63% yield). M.p.: 122-123 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.89 (d, *J* = 90 Hz, 2H), 7.12-7.16 (m, 1H), 7.32-7.46 (m, 4H), 7.54 (s, 1H), 7.77-7.83 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 115.7 (d, *J* = 22 Hz), 122.2, 124.0 (d, *J* = 18 Hz), 124.1, 124.3, 124.8, 125.0, 126.2 (d, *J* = 3 Hz), 131.1 (d, *J* = 9 Hz), 134.0 (d, *J* = 3 Hz), 139.6 (d, *J* = 2 Hz), 140.2, 140.3, 159.4 (d, *J* = 248 Hz), 166.9 ppm. HRMS (ESI): calcd for $C_{15}H_{11}FNOS$ $[M+H]^+$ 272.0545, found 272.0544.



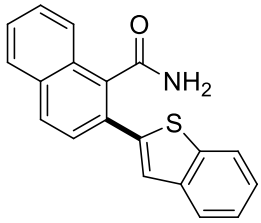
2-(Benzo[*b*]thiophen-2-yl)-4-chlorobenzamide (3k)

Following the general procedure. 4-Chlorobenzamide **1k** (31.0 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **3k** as a yellow soild (37 mg, 65% yield). M.p.: 179-180 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.65 (d, *J* = 34.8 Hz, 2H), 7.36-7.44 (m, 4H), 7.54 (d, *J* = 2.0 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.80 (dd, *J* = 6.8 Hz, 2.8 Hz, 1H), 7.84-7.86 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.4, 124.3, 124.7, 125.0, 125.2, 128.9, 130.5, 130.9, 133.7, 133.8, 136.5, 139.6, 140.1, 140.5, 170.1 ppm. HRMS (ESI): calcd for $C_{15}H_{11}ClNOS$ $[M+H]^+$ 288.0250, found 288.0242.



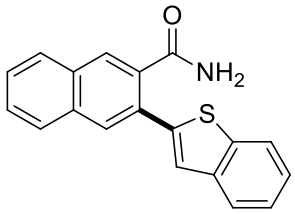
Methyl 3-(benzo[*b*]thiophen-2-yl)-4-carbamoylbenzoate (3l)

Following the general procedure. Methyl 4-carbamoylbenzoate **1l** (35.8 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **3l** as a yellow soild (45 mg, 73% yield). M.p.: 173-174 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.95 (s, 3H), 5.81 (d, *J* = 54.8 Hz, 2H), 7.34-7.38 (m, 2H), 7.46 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.78-7.81 (m, 1H), 7.83-7.85 (m, 1H), 8.07 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 8.22 (d, *J* = 1.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 52.7, 122.3, 124.2, 124.5, 124.9, 125.1, 129.0, 129.6, 131.9, 132.0, 132.3, 139.3, 140.0, 140.2, 140.5, 166.0, 170.5 ppm. HRMS (ESI): calcd for $C_{17}H_{14}NO_3S$ $[M+H]^+$ 312.0694, found 312.0692.



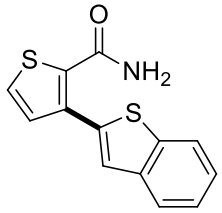
2-(Benzo[*b*]thiophen-2-yl)-1-naphthamide (3m)

Following the general procedure. 1-Naphthamide **1m** (34.2 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **3m** as a yellow soild (40 mg, 66% yield). M.p.: 216-217 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.82 (d, J = 65.2 Hz, 2H), 7.34-7.42 (m, 2H), 7.54-7.62 (m, 2H), 7.65-7.69 (m, 2H), 7.82-7.90 (m, 3H), 7.94 (d, J = 8.8 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 110.2, 122.2, 124.2, 124.3, 124.8, 125.8, 127.1, 127.4, 127.9, 128.2, 128.8, 129.8, 130.1, 133.0, 133.2, 140.5, 141.3, 171.4 ppm. HRMS (ESI): calcd for $C_{19}H_{14}NOS$ $[M+H]^+$ 304.0796, found 304.0793.



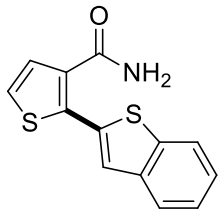
3-(Benzo[*b*]thiophen-2-yl)-2-naphthamide (3n)

Following the general procedure. 2-Naphthamide **1n** (34.2 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **3n** as a yellow soild (44 mg, 72% yield). M.p.: > 250 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.36-7.43 (m, 2H), 7.60-7.63 (m, 4H), 7.86-7.88 (m, 1H), 8.00-8.09 (m, 5H), 8.17 (s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 132.2, 132.7, 133.8, 134.5, 134.7, 137.1, 137.4, 137.5, 137.9, 138.0, 139.0, 139.2, 141.8, 142.7, 145.5, 149.4, 150.1, 152.0, 180.8 ppm. HRMS (ESI): calcd for $C_{19}H_{14}NOS$ $[M+H]^+$ 304.0796, found 304.0796.



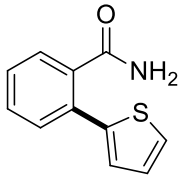
3-(Benzo[*b*]thiophen-2-yl)thiophene-2-carboxamide (3o)

Following the general procedure. Thiophene-2-carboxamide **1o** (25.4 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **3o** as a yellow soild (30 mg, 59% yield). M.p.: 157-158 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.18 (s, 2H), 7.15 (dd, J = 5.2 Hz, 0.8 Hz, 1H), 7.38-7.44 (m, 2H), 7.46 (s, 1H), 7.52 (d, J = 5.2 Hz, 1H), 7.80-7.87 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.4, 124.2, 125.0, 125.1, 125.3, 129.6, 131.8, 134.8, 135.7, 136.3, 139.7, 140.6, 163.8 ppm. HRMS (ESI): calcd for $C_{13}H_{10}NOS_2$ $[M+H]^+$ 260.0204, found 260.0193.



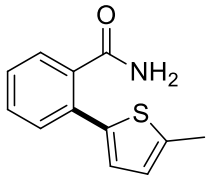
2-(Benzo[*b*]thiophen-2-yl)thiophene-3-carboxamide (3p)

Following the general procedure. Thiophene-3-carboxamide **1p** (25.4 mg, 0.2 mmol) and benzothiophene **2a** (80.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3p** as a yellow soild (23 mg, 44% yield). M.p.: 177-178 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.82 (d, J = 54.0 Hz, 2H), 7.34 (d, J = 5.2 Hz, 1H), 7.36-7.43 (m, 2H), 7.48 (d, J = 5.6 Hz, 1H), 7.55 (s, 1H), 7.80-7.84 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.3, 124.3, 125.1, 125.5, 125.9, 126.2, 130.0, 133.6, 140.0, 137.0, 139.7, 140.9, 165.4 ppm. HRMS (ESI): calcd for $C_{13}H_{10}NOS_2$ $[M+H]^+$ 260.0204, found 260.0200.



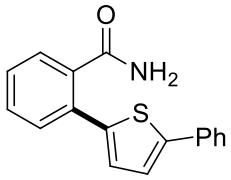
2-(Thiophen-2-yl)benzamide (4a)

Following the general procedure. Benzamide **1a** (24.2 mg, 0.2 mmol) and thiophene **2a** (50.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **4a** as a yellow soild (27 mg, 67% yield). M.p.: 131-132 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.65 (d, J = 76.0 Hz, 2H), 7.07-7.09 (m, 1H), 7.20 (d, J = 2.8 Hz, 1H), 7.37-7.44 (m, 2H), 7.47 (d, J = 4.0 Hz, 2H), 7.69 (d, J = 7.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 126.7, 127.3, 128.0, 128.3, 128.9, 130.5, 131.0, 132.1, 135.1, 141.1, 171.4 ppm. HRMS (ESI): calcd for $C_{11}H_{10}NOS$ $[M+H]^+$ 204.0483, found 204.0479.



2-(5-Methylthiophen-2-yl)benzamide (4b)

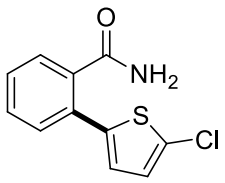
Following the general procedure. Benzamide **1a** (24.2 mg, 0.2 mmol) and 2-methylthiophene **2b** (58.8 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **4b** as a yellow soild (31 mg, 71% yield). M.p.: 116-117 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.51 (s, 3H), 5.71 (d, J = 64.4 Hz, 2H), 6.73 (d, J = 2.8 Hz, 1H), 6.98 (d, J = 3.6 Hz, 1H), 7.35-7.46 (m, 3H), 7.67 (d, J = 7.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.5, 126.2, 127.3, 127.9, 128.9, 130.4, 130.7, 132.4, 134.8, 138.6, 141.5, 171.6 ppm. HRMS (ESI): calcd for $C_{12}H_{12}NOS$ $[M+H]^+$ 218.0640, found 218.0638.



2-(5-Phenylthiophen-2-yl)benzamide (4c)

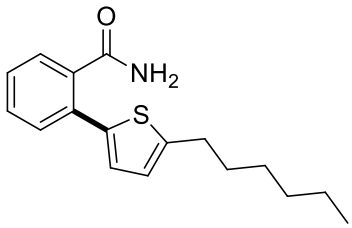
Following the general procedure. Benzamide **1a** (24.2 mg, 0.2 mmol) and 2-phenylthiophene **2c** (96.0 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **4c** as a yellow soild (34 mg, 61% yield). M.p.: 147-148 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ =

5.76 (d, *J* = 62.8 Hz, 2H), 7.18 (d, *J* = 3.6 Hz, 1H), 7.28-7.32 (m, 2H), 7.37-7.43 (m, 3H), 7.44-7.53 (m, 2H), 7.61-7.62 (m, 2H), 7.67-7.69 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.9, 125.8, 127.9, 128.2, 128.3, 128.9, 129.1, 130.5, 130.6, 131.9, 134.0, 135.0, 140.3, 145.6, 171.6 ppm. HRMS (ESI): calcd for $C_{17}H_{14}NOS$ $[M+H]^+$ 280.0796, found 280.0798.



2-(5-Chlorothiophen-2-yl)benzamide (4d)

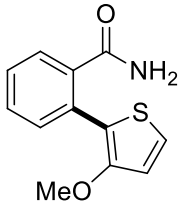
Following the general procedure. Benzamide **1a** (24.2 mg, 0.2 mmol) and 2-chlorothiophene **2d** (70.8 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **4d** as a yellow soild (27 mg, 58% yield). M.p.: 126-127 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.74 (d, *J* = 85.2 Hz, 2H), 6.89 (d, *J* = 4.0 Hz, 1H), 6.98 (d, *J* = 4.0 Hz, 1H), 7.39-7.48 (m, 3H), 7.62-7.64 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 126.6, 127.0, 128.6, 128.7, 130.6, 130.7, 131.0, 131.2, 135.2, 139.6, 171.2 ppm. HRMS (ESI): calcd for $C_{11}H_9ClNOS$ $[M+H]^+$ 238.0093, found 238.0095.



2-(5-Hexylthiophen-2-yl)benzamide (4e)

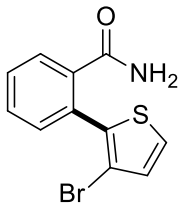
Following the general procedure. Benzamide **1a** (24.2 mg, 0.2 mmol) and 2-hexylthiophene **2e** (100.8 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **4e** as a yellow soild (42 mg, 73% yield). M.p.: 67-68 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.2 Hz, 3H), 1.25-1.39 (m, 6H), 1.65-1.73 (m, 2H), 2.81 (t, *J* = 7.6 Hz, 2H), 5.72 (d, *J* = 71.2 Hz, 2H), 6.74 (d, *J* = 3.2 Hz, 1H), 6.99 (d, *J* = 3.2 Hz, 1H), 7.34-7.38 (m, 1H), 7.43 (d, *J* = 4.0 Hz, 1H), 7.67 (d, *J* = 3.6 Hz, 1H) ppm. ^{13}C NMR

(100 MHz, $CDCl_3$): δ = 14.2, 22.7, 29.0, 30.3, 31.68, 31.71, 124.9, 127.0, 127.9, 128.9, 130.4, 130.7, 132.5, 134.8, 138.2, 147.7, 171.6 ppm. HRMS (ESI): calcd for $C_{17}H_{22}NOS$ $[M+H]^+$ 288.1422, found 288.1413.



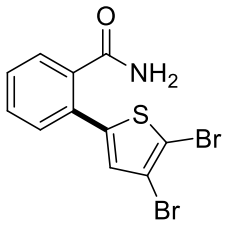
2-(3-Methoxythiophen-2-yl)benzamide (4f)

Following the general procedure. Benzamide **1a** (24.2 mg, 0.2 mmol) and 3-methoxylthiophene **2f** (68.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **4f** as yellow oil (35 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.81 (s, 3H), 5.90 (d, *J* = 33.2 Hz, 2H), 6.89 (d, *J* = 5.6 Hz, 1H), 7.28 (d, *J* = 5.2 Hz, 1H), 7.36-7.41 (m, 2H), 7.44-7.48 (m, 1H), 7.78-7.80 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 58.6, 116.6, 117.3, 124.5, 128.1, 129.4, 129.9, 130.6, 132.0, 135.7, 154.1 ppm. HRMS (ESI): calcd for $C_{12}H_{12}NO_2S$ $[M+H]^+$ 234.0589, found 234.0596.



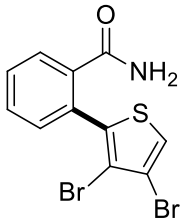
2-(3-Bromothiophen-2-yl)benzamide (4g)

Following the general procedure. Benzamide **1a** (24.2 mg, 0.2 mmol) and 3-bromolthiophene **2g** (68.4 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **4g** as a yellow soild (35 mg, 63% yield). M.p.: 111-112 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.68 (d, *J* = 104.8 Hz, 2H), 7.06 (d, *J* = 5.2 Hz, 1H), 7.38-7.42 (m, 2H), 7.47-7.54 (m, 2H), 7.83-7.85 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 110.9, 126.9, 129.3, 129.5, 130.4, 130.67, 130.68, 132.2, 136.1, 136.4, 170.1 ppm. HRMS (ESI): calcd for $C_{11}H_9BrNOS$ $[M+H]^+$ 281.9588, found 281.9582.



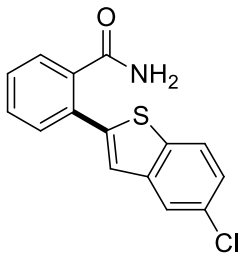
2-(4,5-Dibromothiophen-2-yl)benzamide (4h)

Following the general procedure. Benzamide **1a** (24.2 mg, 0.2 mmol) and 2,3-dibromothiophene **2h** (144.0 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **4h** as a yellow soild (36 mg, 51% yield). M.p.: 172-173 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.73 (d, J = 64.4 Hz, 2H), 7.04 (s, 1H), 7.39-7.48 (m, 3H), 7.61 (dd, J = 7.6 Hz, 1.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 112.0, 114.5, 128.5, 129.1, 129.5, 130.4, 130.5, 130.7, 135.3, 142.4, 170.8 ppm. HRMS (ESI): calcd for $C_{11}H_8Br_2NOS$ $[M+H]^+$ 359.8693, found 359.8696.



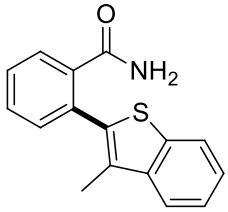
2-(3,4-Dibromothiophen-2-yl)benzamide (4i)

Following the general procedure. Benzamide **1a** (24.2 mg, 0.2 mmol) and 3,4-dibromothiophene **2i** (144.0 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **4i** as yellow oil (37 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.68 (d, J = 91.2 Hz, 2H), 7.36-7.39 (m, 1H), 7.45 (s, 1H), 7.50-7.56 (m, 2H), 7.78-7.82 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 114.0, 114.4, 123.9, 129.0, 129.9, 130.6, 130.8, 132.1, 136.2, 137.6, 170.0 ppm. HRMS (ESI): calcd for $C_{11}H_8Br_2NOS$ $[M+H]^+$ 359.8693, found 359.8697.



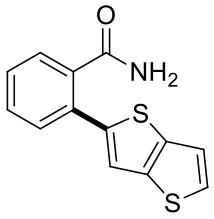
2-(5-Chlorobenzo[*b*]thiophen-2-yl)benzamide (4j)

Following the general procedure. Benzamide **1a** (24.2 mg, 0.2 mmol) and 5-chlorobenzothiophene **2j** (100.8 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **4j** as a yellow soild (35 mg, 61% yield). M.p.: 124-125 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.71 (d, J = 58.8 Hz, 2H), 7.31 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.36 (s, 1H), 7.41-7.60 (m, 4H), 7.67-7.69 (m, 1H), 7.73-7.81 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.1, 123.3, 123.5, 125.2, 127.5, 128.8, 129.0, 130.6, 131.0, 131.6, 135.6, 138.5, 141.3, 143.3, 171.2 ppm. HRMS (ESI): calcd for $C_{15}H_{11}ClNOS$ $[M+H]^+$ 288.0250, found 288.0255.



2-(3-Methylbenzo[*b*]thiophen-2-yl)benzamide (4k)

Following the general procedure. Benzamide **1a** (24.2 mg, 0.2 mmol) and 3-methylbenzothiophene **2k** (88.8 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **4k** as a yellow soild (36 mg, 67% yield). M.p.: 143-144 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.27 (s, 3H), 5.57 (d, J = 24.4 Hz, 2H), 7.38-7.47 (m, 3H), 7.50-7.58 (m, 2H), 7.73 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.96-7.98 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.4, 122.4, 122.6, 124.8, 125.1, 129.1, 130.0, 130.8, 130.9, 131.9, 132.1, 135.0, 135.6, 139.5, 140.4, 170.0 ppm. HRMS (ESI): calcd for $C_{16}H_{14}NOS$ $[M+H]^+$ 268.0796, found 268.0805.



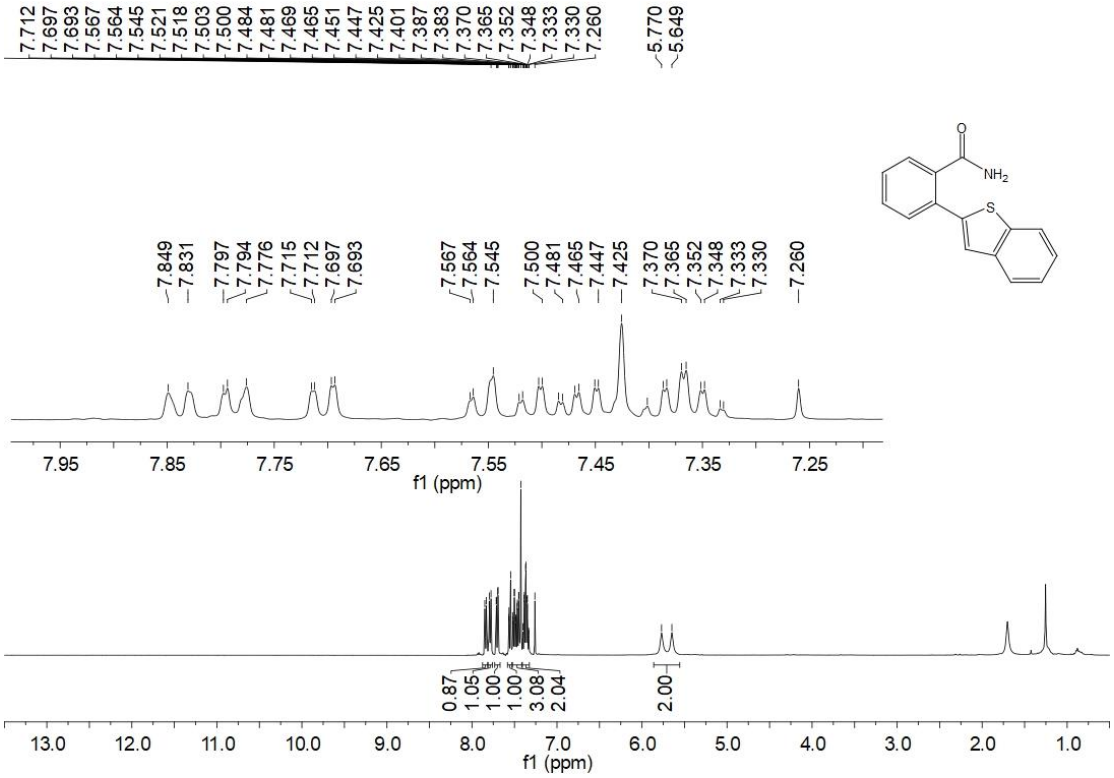
2-(Thieno[3,2-*b*]thiophen-2-yl)benzamide (4l)

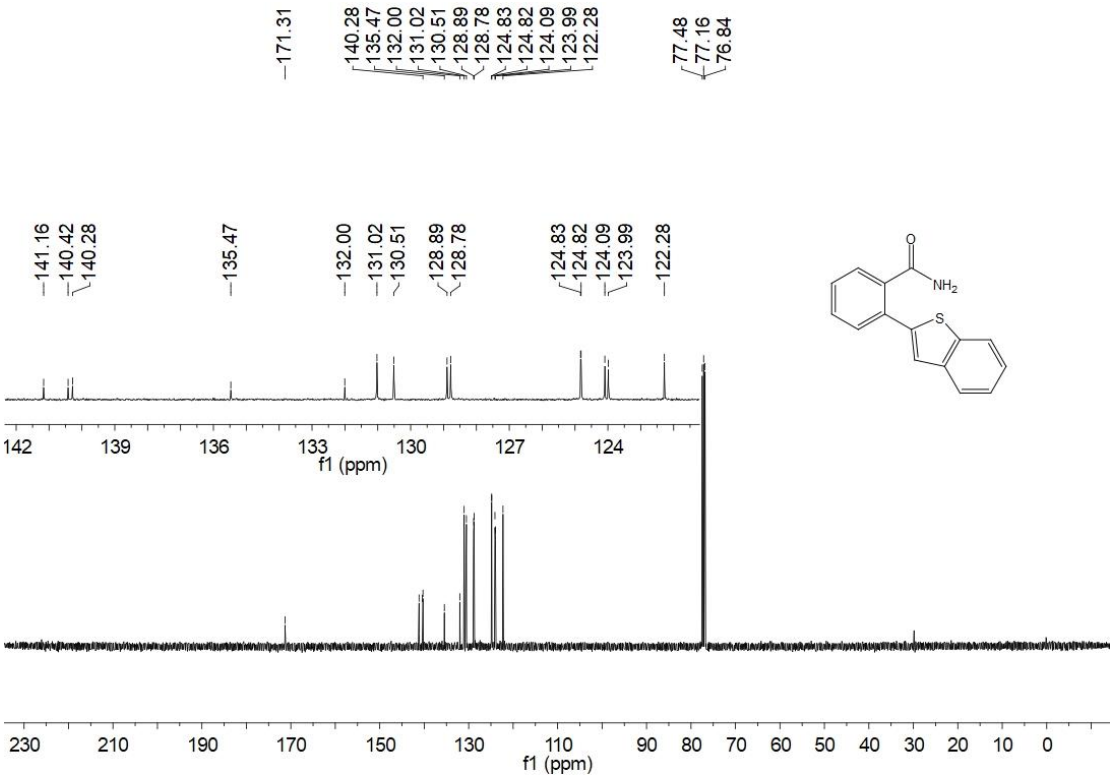
Following the general procedure. Benzamide **1a** (24.2 mg, 0.2 mmol) and thieno[3,2-*b*]thiophene **2l** (84.0 mg, 0.6 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **4l** as a yellow soild (29 mg, 56% yield). M.p.: 147-148 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.73 (d, J = 61.6 Hz, 2H), 7.26-7.28 (m, 1H), 7.39-7.42 (m, 2H), 7.43-7.53 (m, 3H), 7.68 (dd, J = 8.0 Hz, 1.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 119.5, 119.6, 127.6, 128.5, 128.8, 130.5, 130.9, 132.2, 135.3, 139.8, 142.7, 171.4 ppm. HRMS (ESI): calcd for $C_{13}H_{10}NOS_2$ $[M+H]^+$ 260.0204, found 260.0191.

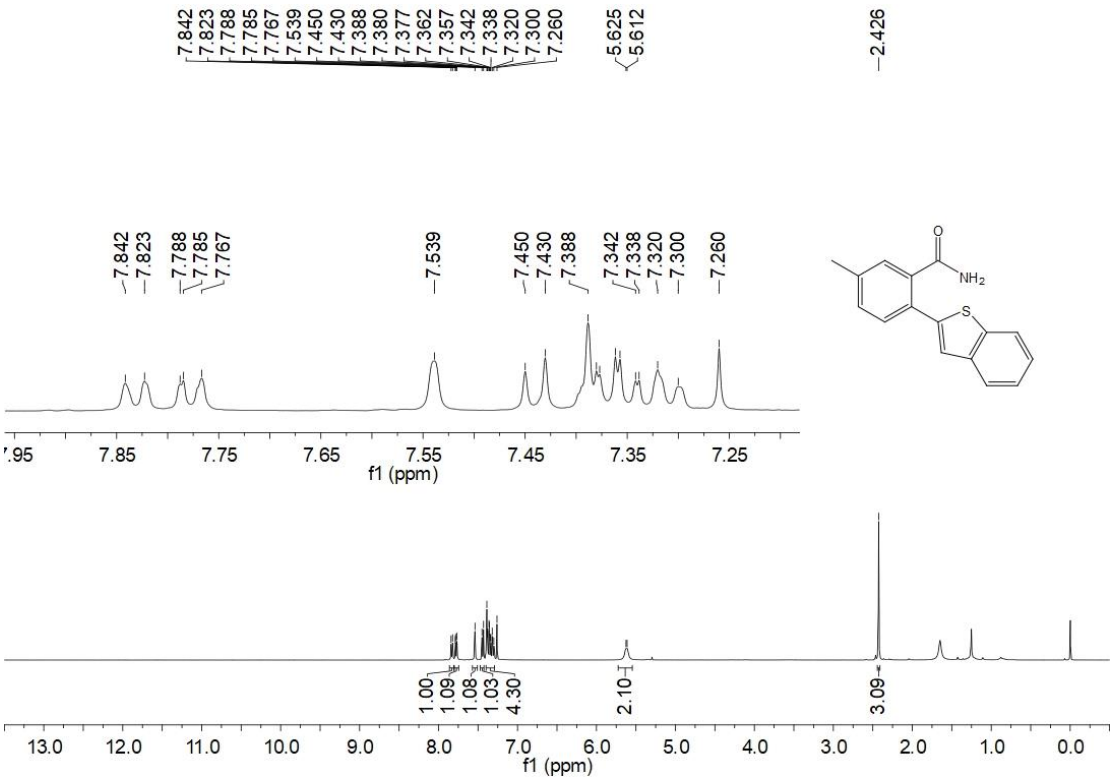
VII. References

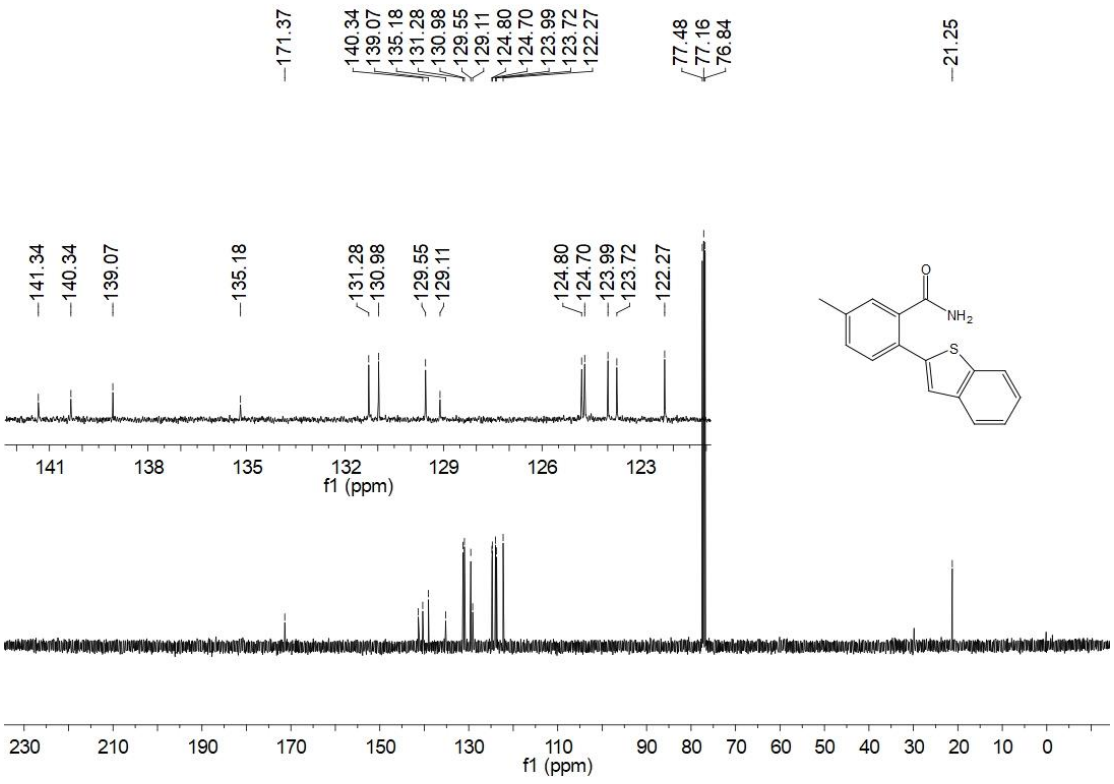
(1) Q. Gui, Z. Yang, X. Chen, J. Liu, Z. Tan, R. Guo and W. Yu, *Synlett* 2013, **24**, 1016.

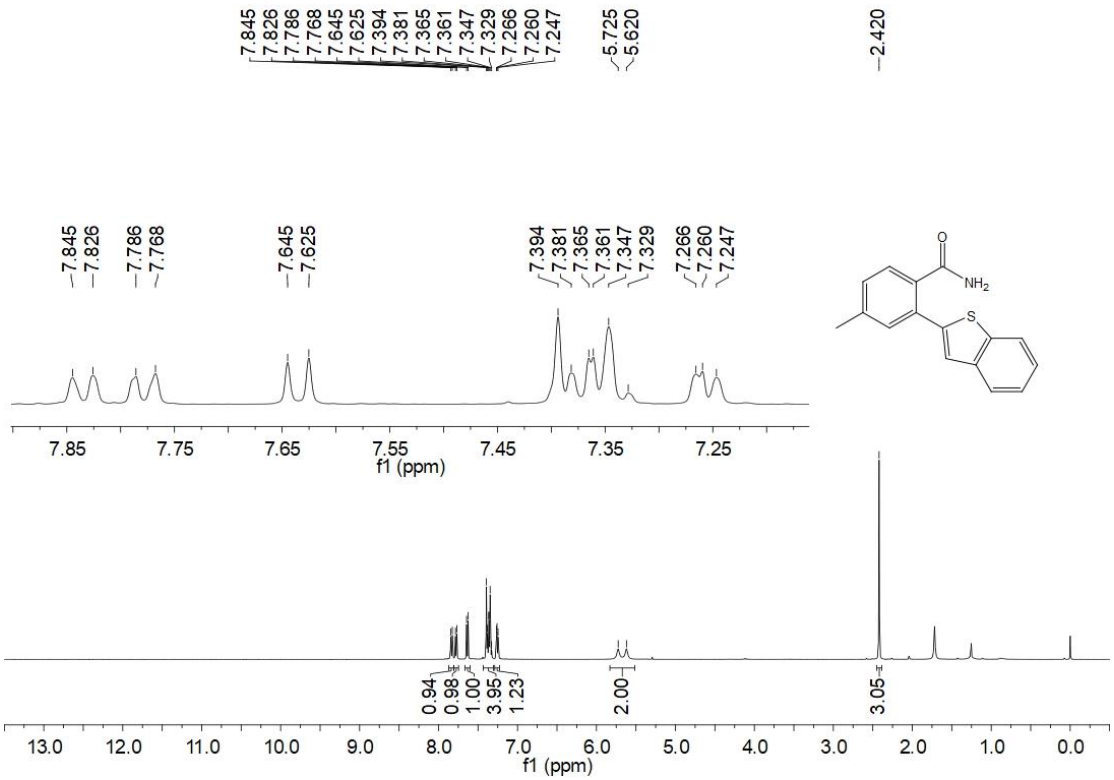
VIII. Copies of ^{1}H and ^{13}C NMR spectra

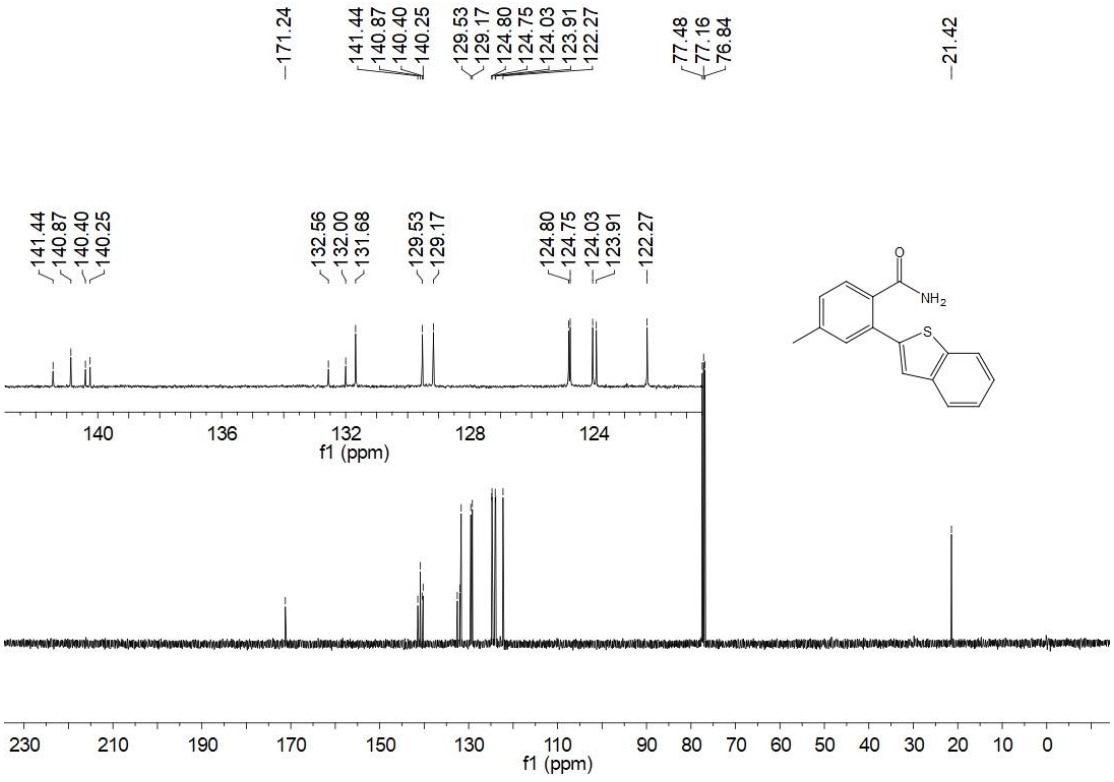


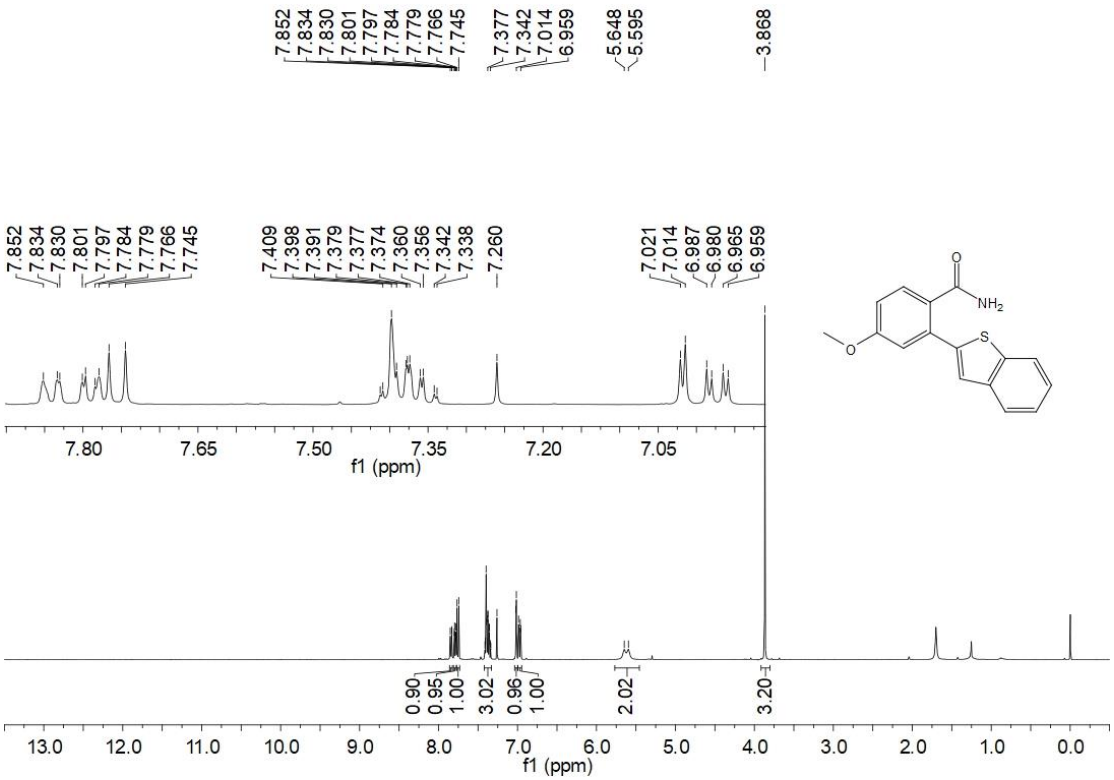


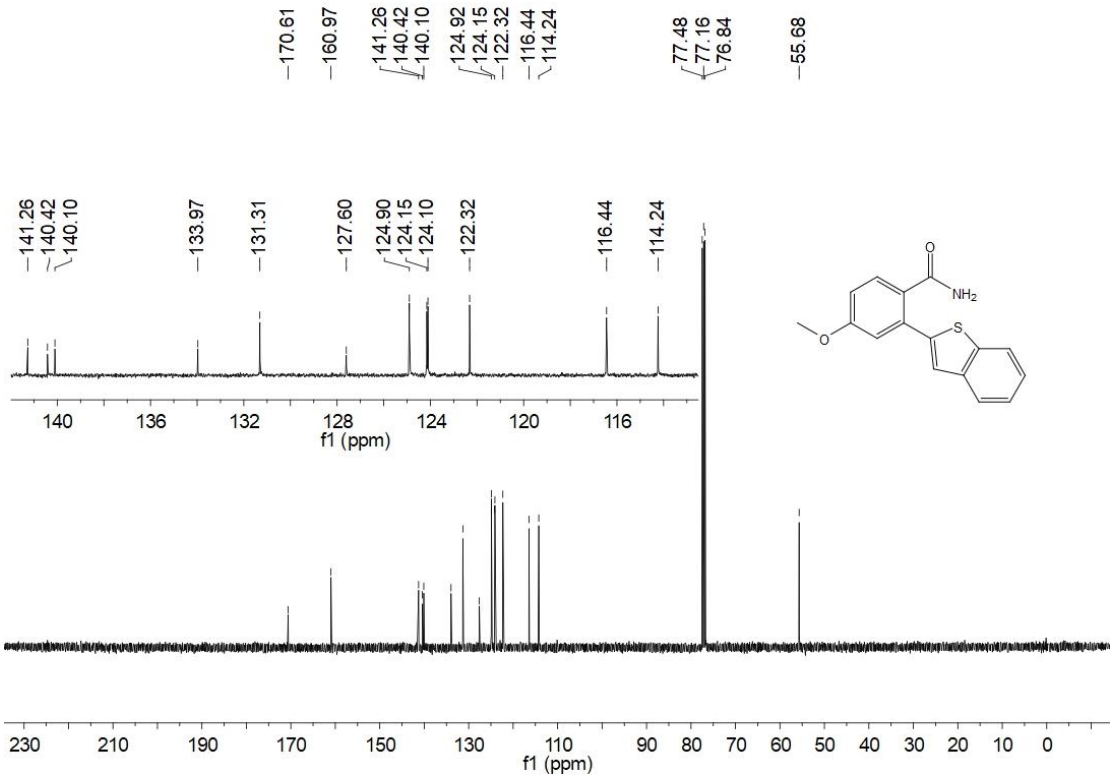

7.842
7.823
7.788
7.785
7.767
7.539
7.450
7.430
7.388
7.380
7.377
7.362
7.357
7.342
7.338
7.320
7.300
7.260
5.625
5.612
2.426
NH2
S
f1 (ppm)
1.00
1.09
1.08
1.03
4.30
2.10
3.09

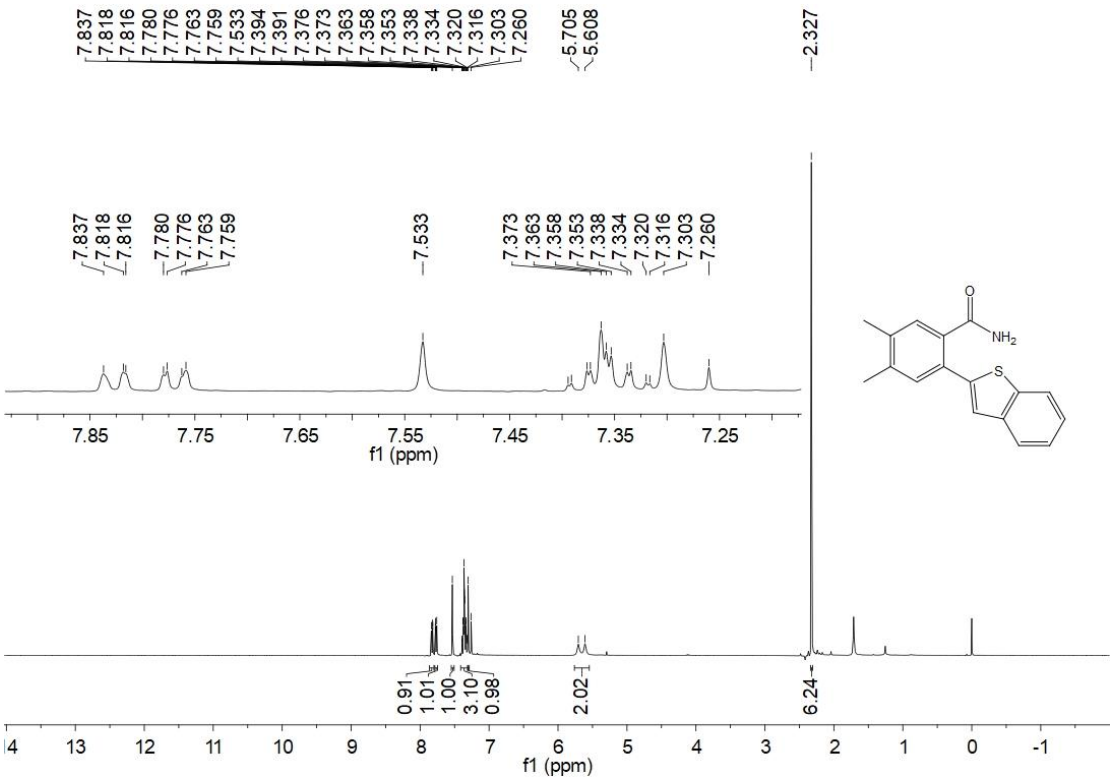

171.37
140.34
139.07
135.18
131.28
130.98
129.55
129.11
124.80
124.70
123.99
123.72
122.27
77.48
77.16
76.84
21.25
NH2
S
f1 (ppm)

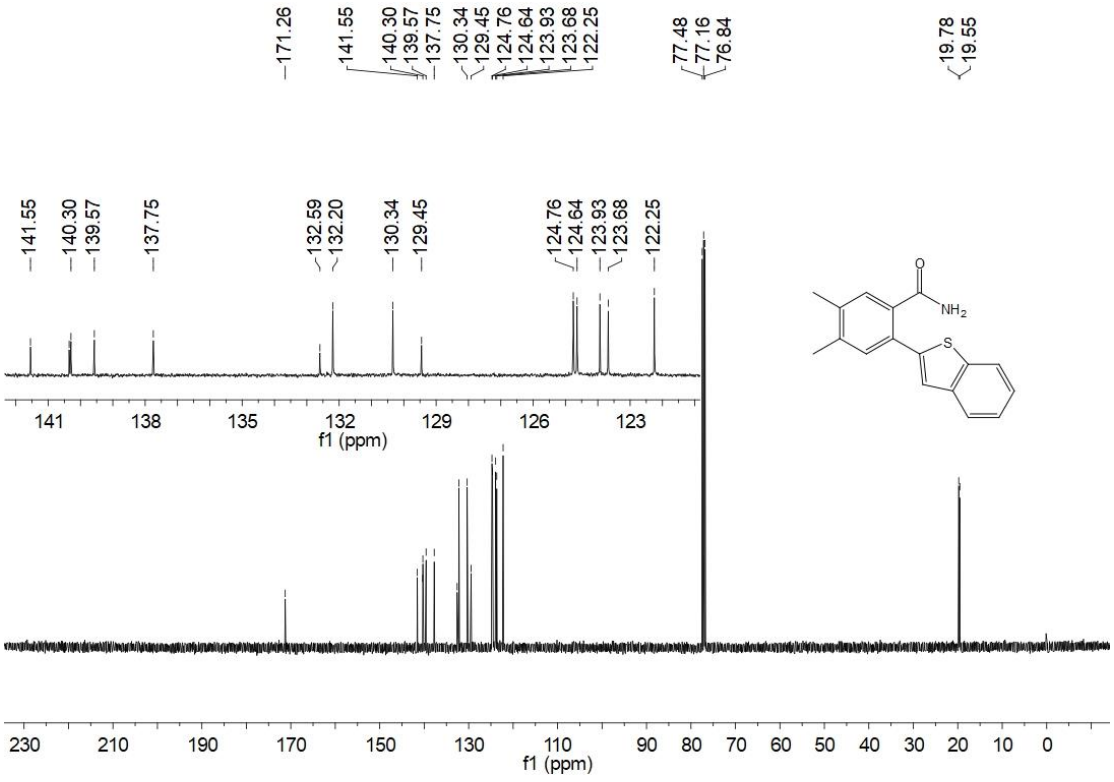

7.845
7.826
7.786
7.768
7.645
7.625
7.394
7.381
7.365
7.361
7.347
7.329
7.266
7.260
7.247
5.725
5.620
2.420
O
NH2
S
7.85
7.75
7.65
7.55
7.45
7.35
7.25
f1 (ppm)
0.94
0.98
1.00
3.95
1.23
2.00
3.05
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

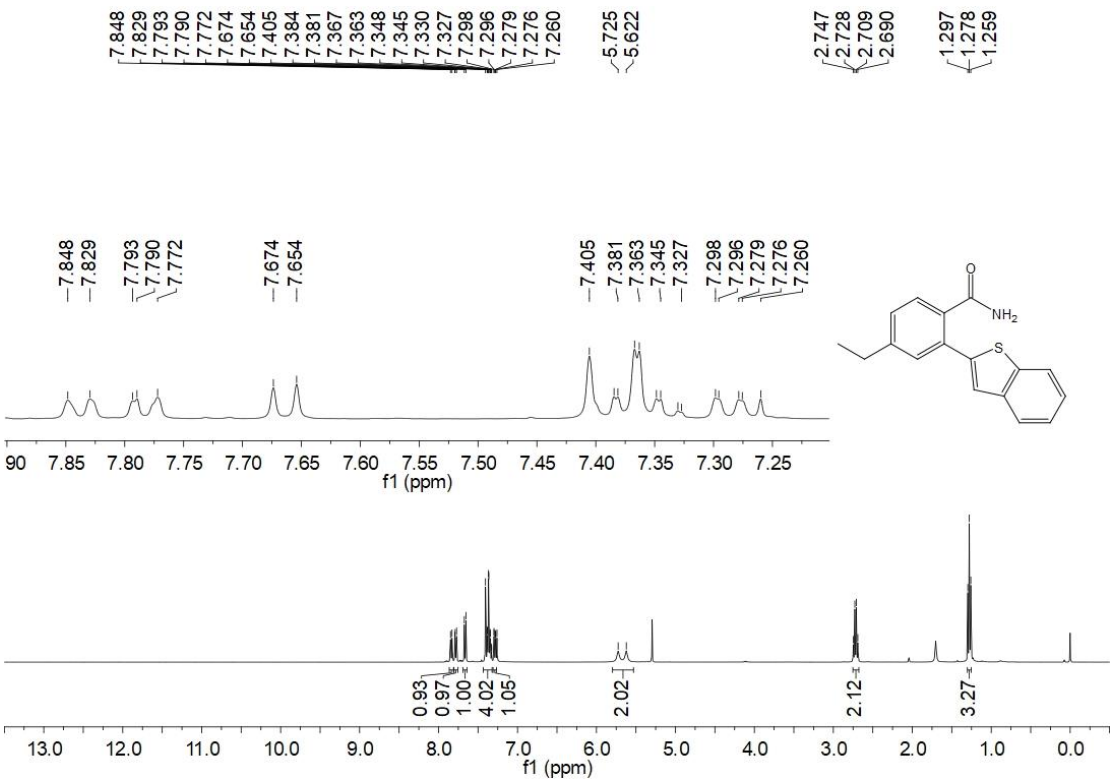

171.24
141.44
140.87
140.40
140.25
129.53
129.17
124.80
124.75
124.03
123.91
122.27
77.48
77.16
76.84
21.42
132.56
132.00
131.68
O
NH2
S
140
136
132
128
124
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

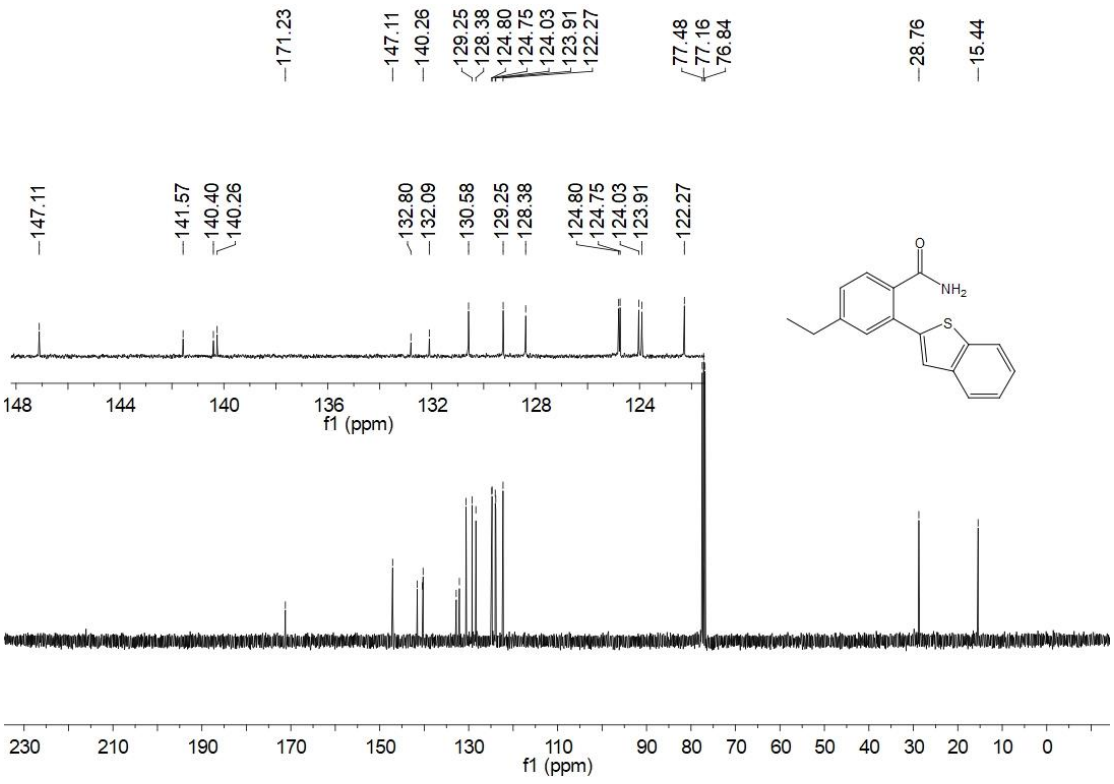

7.852
7.834
7.830
7.801
7.797
7.784
7.779
7.766
7.745
7.409
7.398
7.391
7.379
7.377
7.374
7.360
7.356
7.342
7.338
7.260
7.021
7.014
6.987
6.980
6.965
6.959
5.648
5.595
3.868
NH2
O
S
f1 (ppm)
0.90
0.95
1.00
3.02
0.96
1.00
2.02
3.20

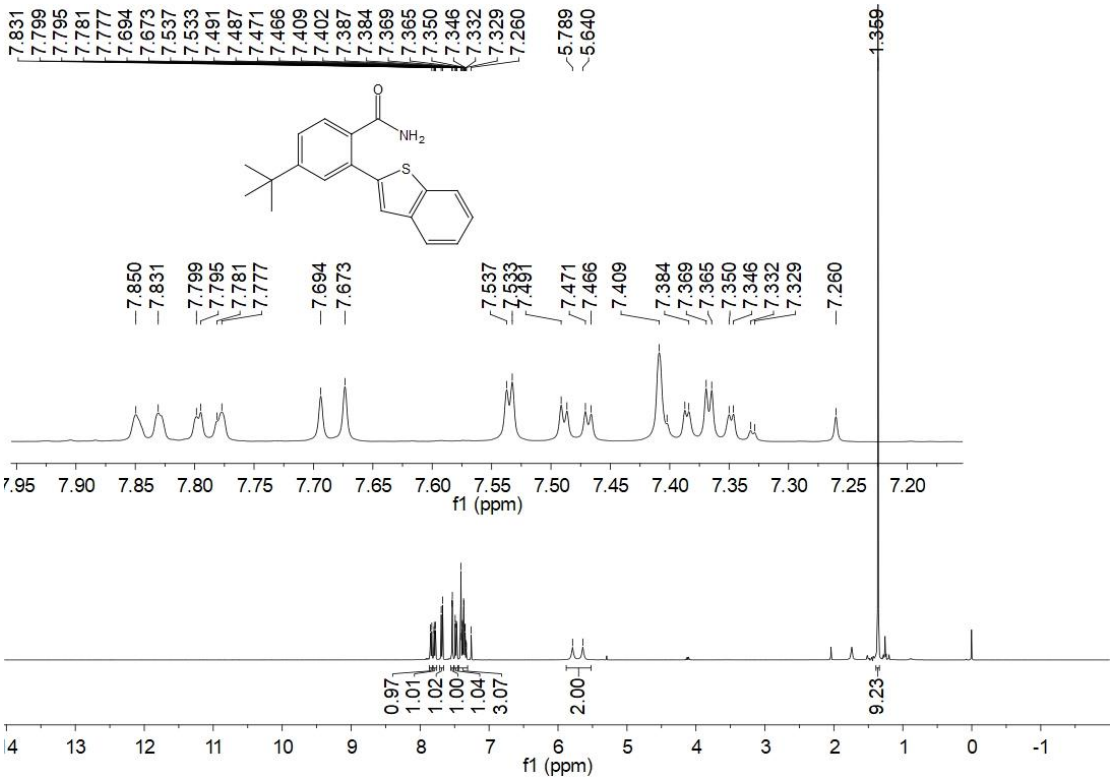

170.61
160.97
141.26
140.42
140.10
124.92
124.15
122.32
116.44
114.24
77.48
77.16
76.84
55.68
133.97
131.31
127.60
NH2
O
S
f1 (ppm)

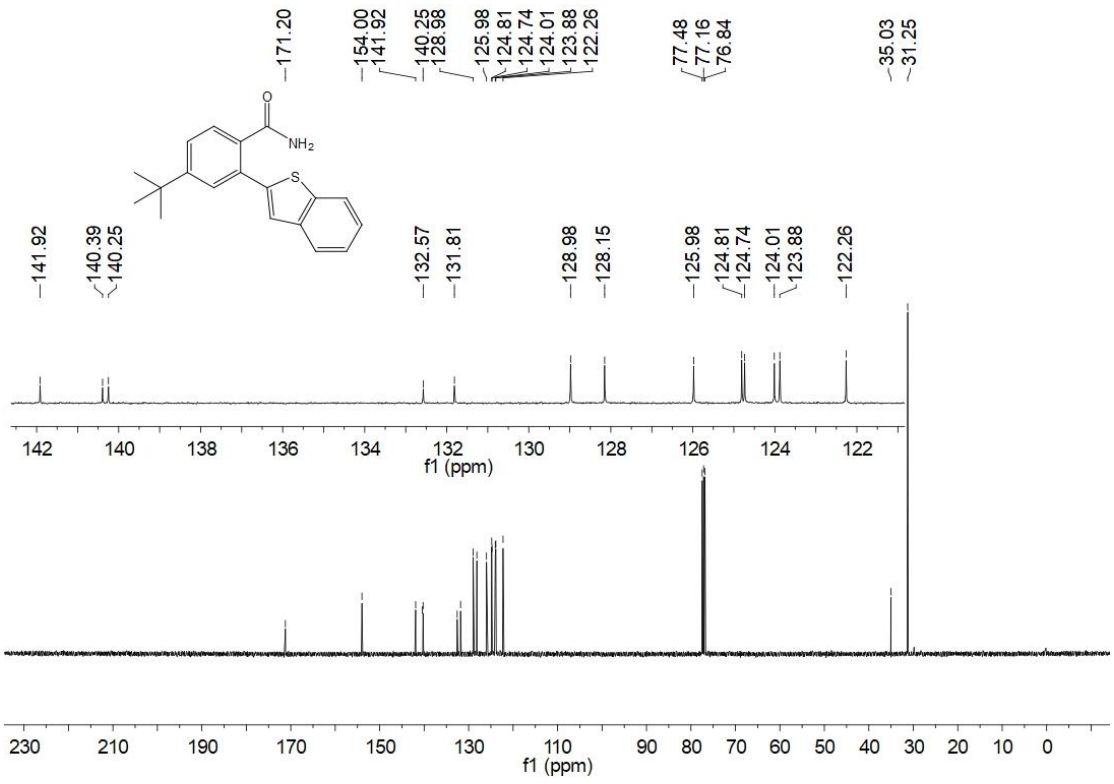

7.837
7.818
7.816
7.780
7.776
7.763
7.759
7.533
7.394
7.391
7.376
7.373
7.363
7.358
7.353
7.338
7.334
7.320
7.316
7.303
7.260
5.705
5.608
2.327
7.85
7.75
7.65
7.55
7.45
7.35
7.25
f1 (ppm)
0.91
1.01
1.00
3.10
0.98
2.02
6.24
f1 (ppm)
O
NH2
S

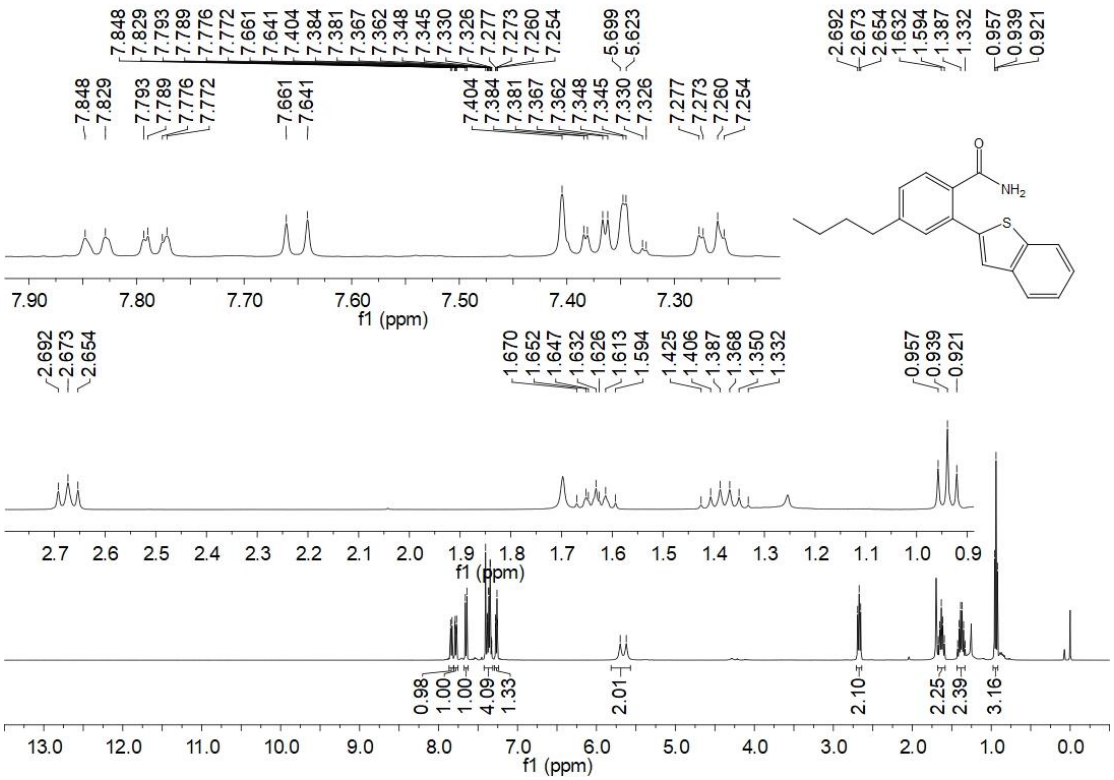

171.26
141.55
140.30
139.57
137.75
130.34
129.45
124.76
124.64
123.93
123.68
122.25
77.48
77.16
76.84
19.78
19.55
141
138
135
132
129
126
123
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O
NH2
S

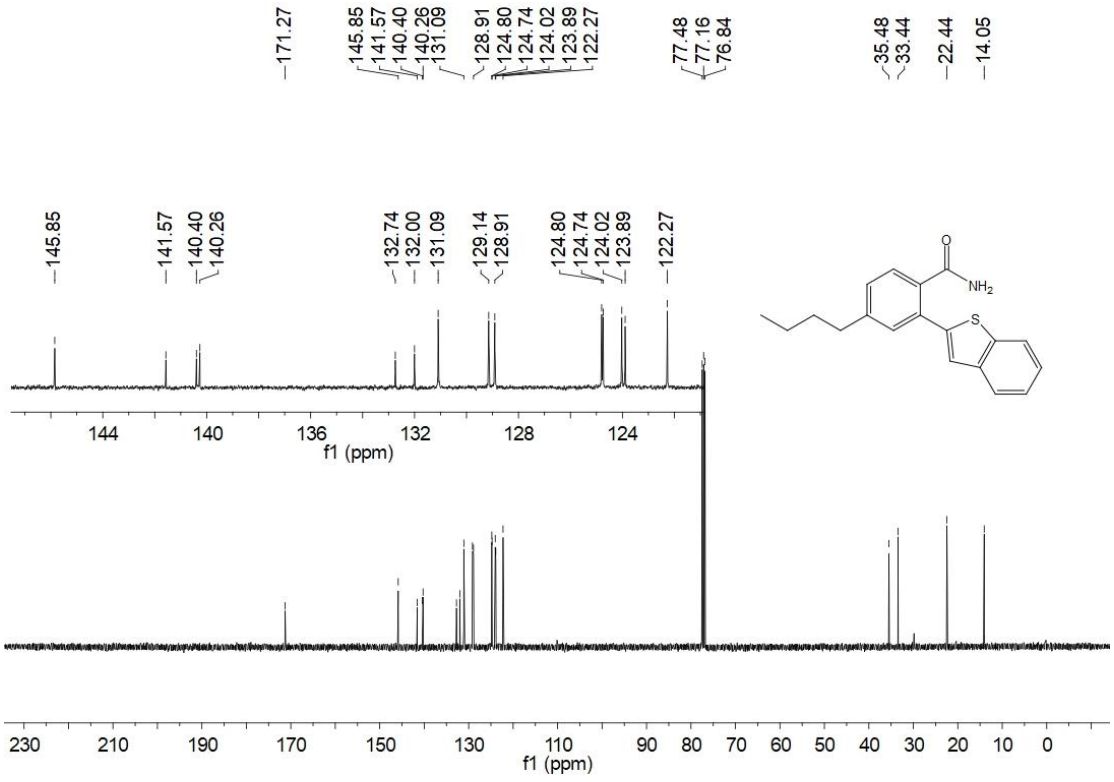

7.848
7.829
7.793
7.790
7.772
7.674
7.654
7.405
7.384
7.381
7.367
7.363
7.348
7.345
7.330
7.327
7.298
7.296
7.279
7.276
7.260
5.725
5.622
2.747
2.728
2.709
2.690
1.297
1.278
1.259
NH2
S
f1 (ppm)
0.93
0.97
1.00
4.02
1.05
2.02
2.12
3.27

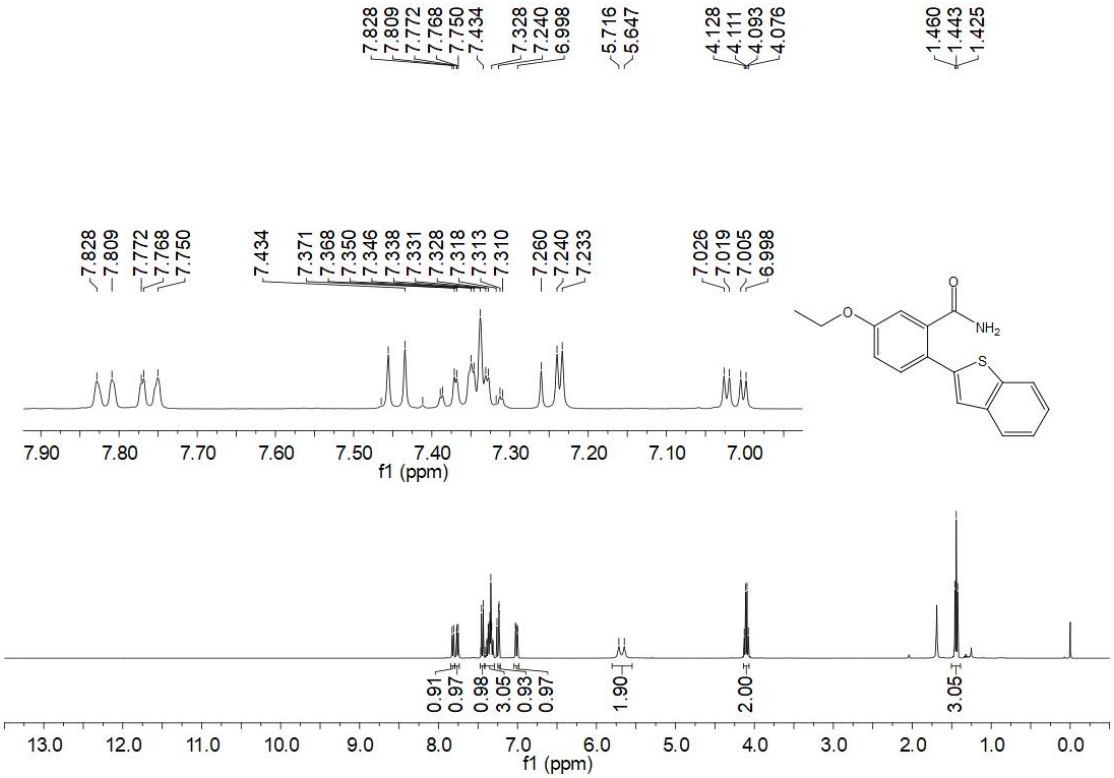

171.23
147.11
140.26
129.25
128.38
124.80
124.75
124.03
123.91
122.27
77.48
77.16
76.84
28.76
15.44
141.57
140.40
132.80
132.09
130.58
NH2
S
f1 (ppm)

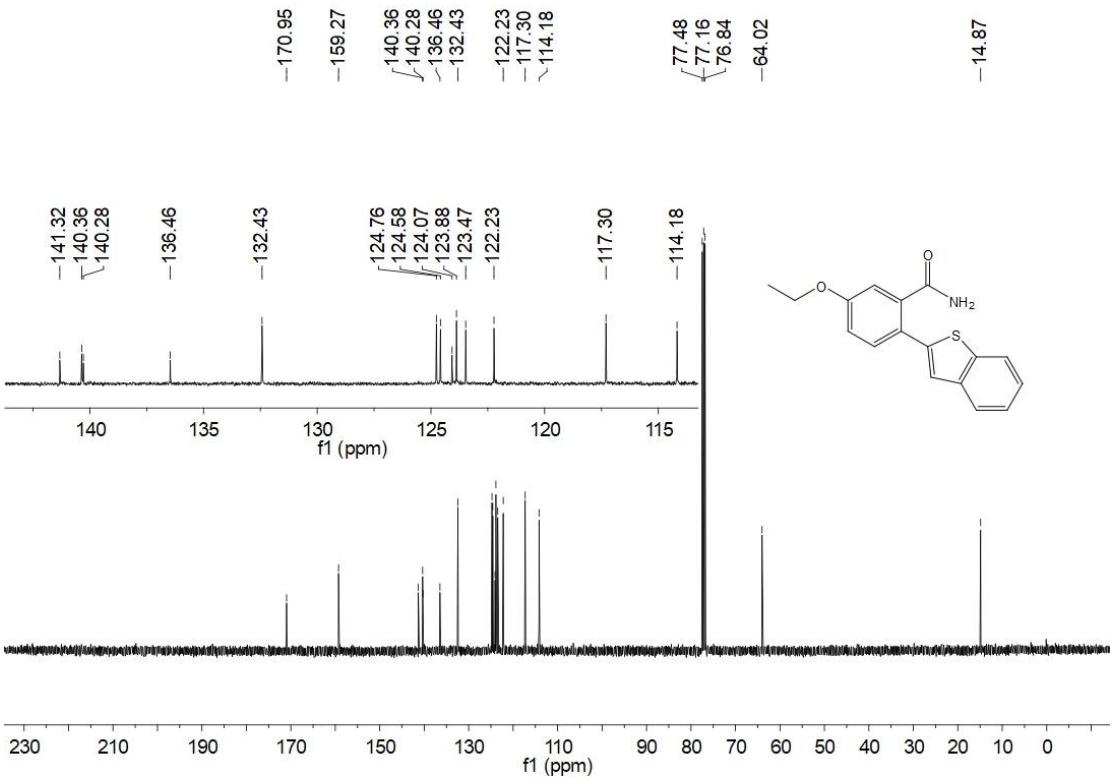

7.831
7.799
7.795
7.781
7.777
7.694
7.673
7.537
7.533
7.491
7.487
7.471
7.466
7.409
7.402
7.387
7.384
7.369
7.365
7.350
7.346
7.332
7.329
7.260
5.789
5.640
1.360
O
NH2
S
7.850
7.831
7.799
7.795
7.781
7.777
7.694
7.673
7.537
7.533
7.491
7.471
7.466
7.409
7.384
7.369
7.365
7.350
7.346
7.332
7.329
7.260
f1 (ppm)
0.97
1.01
1.02
1.00
1.04
3.07
2.00
9.23
f1 (ppm)

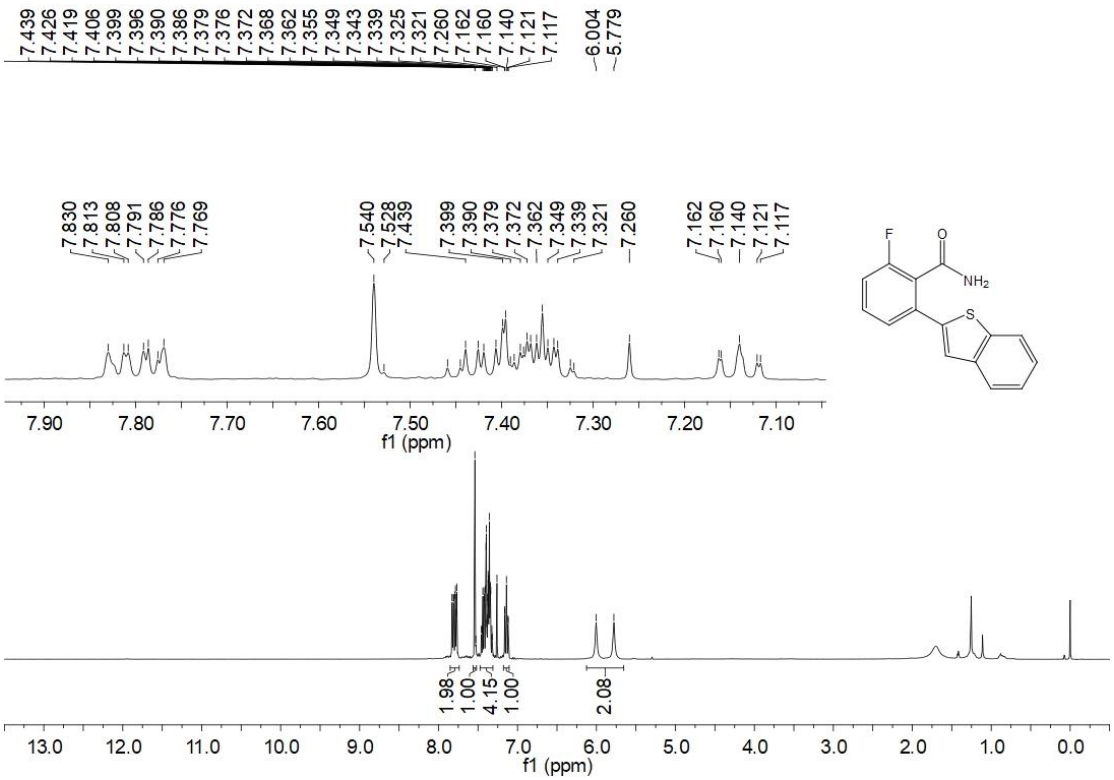

171.20
154.00
141.92
140.25
128.98
125.98
124.81
124.74
124.01
123.88
122.26
77.48
77.16
76.84
35.03
31.25
O
NH2
S
141.92
140.39
140.25
132.57
131.81
128.98
128.15
125.98
124.81
124.74
124.01
123.88
122.26
f1 (ppm)
f1 (ppm)

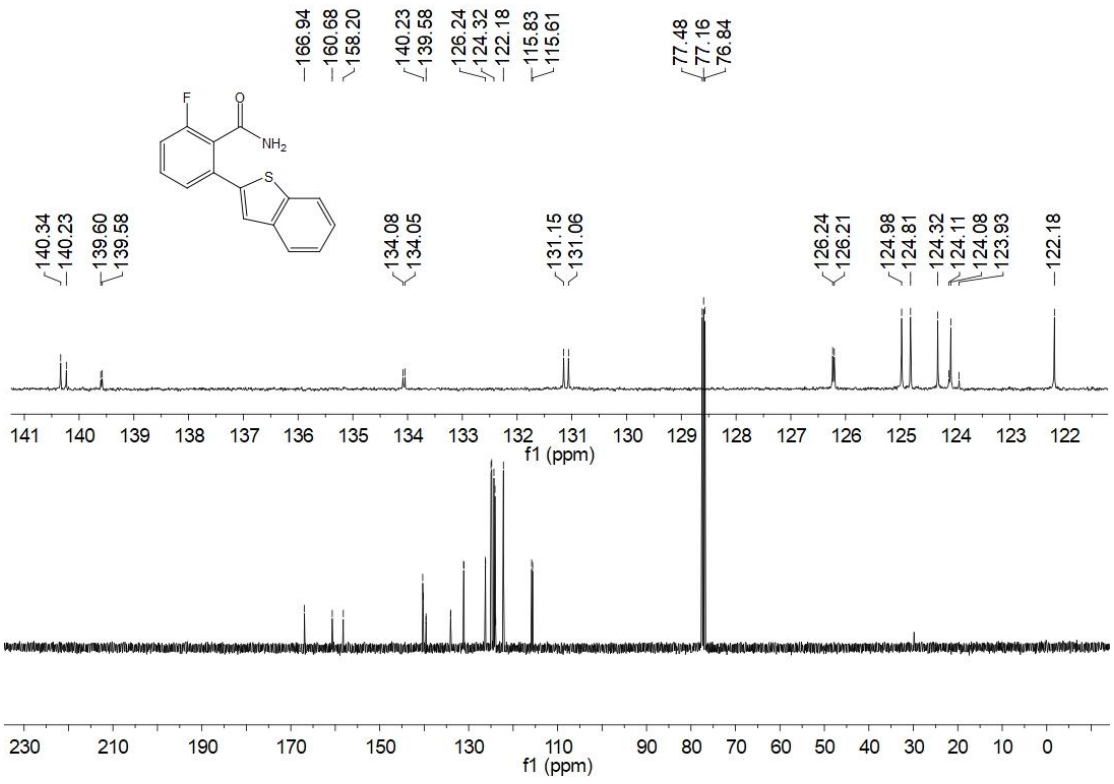

7.848
7.829
7.793
7.789
7.776
7.772
7.661
7.641
7.404
7.384
7.381
7.367
7.362
7.348
7.345
7.330
7.326
7.277
7.273
7.260
7.254
5.699
5.623
2.692
2.673
2.654
1.670
1.652
1.647
1.632
1.626
1.613
1.594
1.425
1.406
1.387
1.368
1.350
1.332
0.957
0.939
0.921
f1 (ppm)
0.98
1.00
1.00
4.09
1.33
2.01
2.10
2.25
2.39
3.16
NH2
O
S


171.27
145.85
141.57
140.40
140.26
131.09
128.91
124.80
124.74
124.02
123.89
122.27
77.48
77.16
76.84
35.48
33.44
22.44
14.05
f1 (ppm)
NH2
O
S

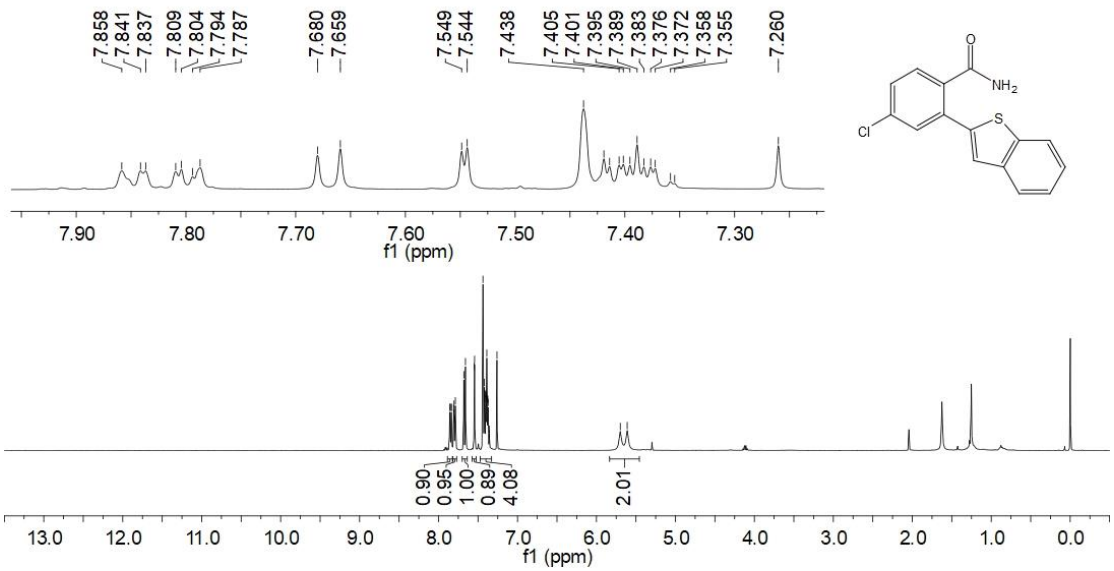

7.828
7.809
7.772
7.768
7.750
7.434
7.328
7.240
6.998
5.716
5.647
4.128
4.111
4.093
4.076
1.460
1.443
1.425
7.434
7.371
7.368
7.350
7.346
7.338
7.331
7.328
7.318
7.313
7.310
7.260
7.240
7.233
7.026
7.019
7.005
6.998
O
NH2
S
7.90 7.80 7.70 7.60 7.50 7.40 7.30 7.20 7.10 7.00
f1 (ppm)
0.91
0.97
0.98
3.05
0.93
0.97
1.90
2.00
3.05
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

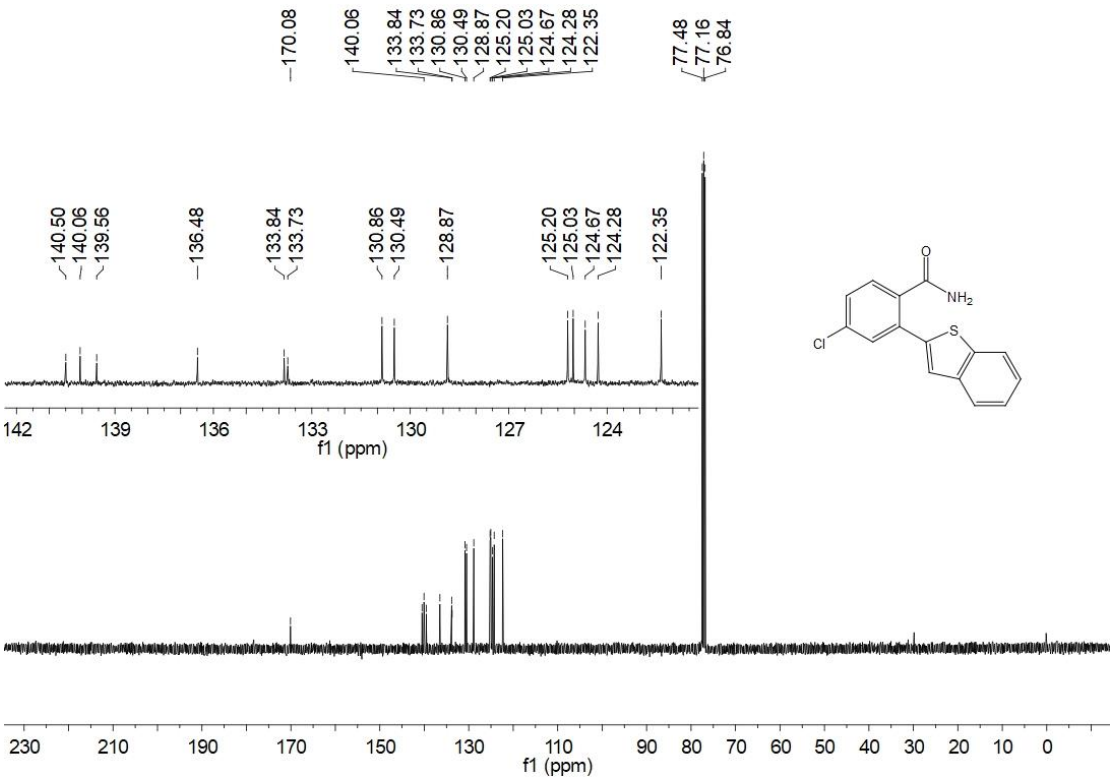

170.95
159.27
140.36
140.28
136.46
132.43
122.23
117.30
114.18
77.48
77.16
76.84
64.02
14.87
141.32
140.36
140.28
136.46
132.43
124.76
124.58
124.07
123.88
123.47
122.23
117.30
114.18
O
NH2
S
140 135 130 125 120 115
f1 (ppm)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

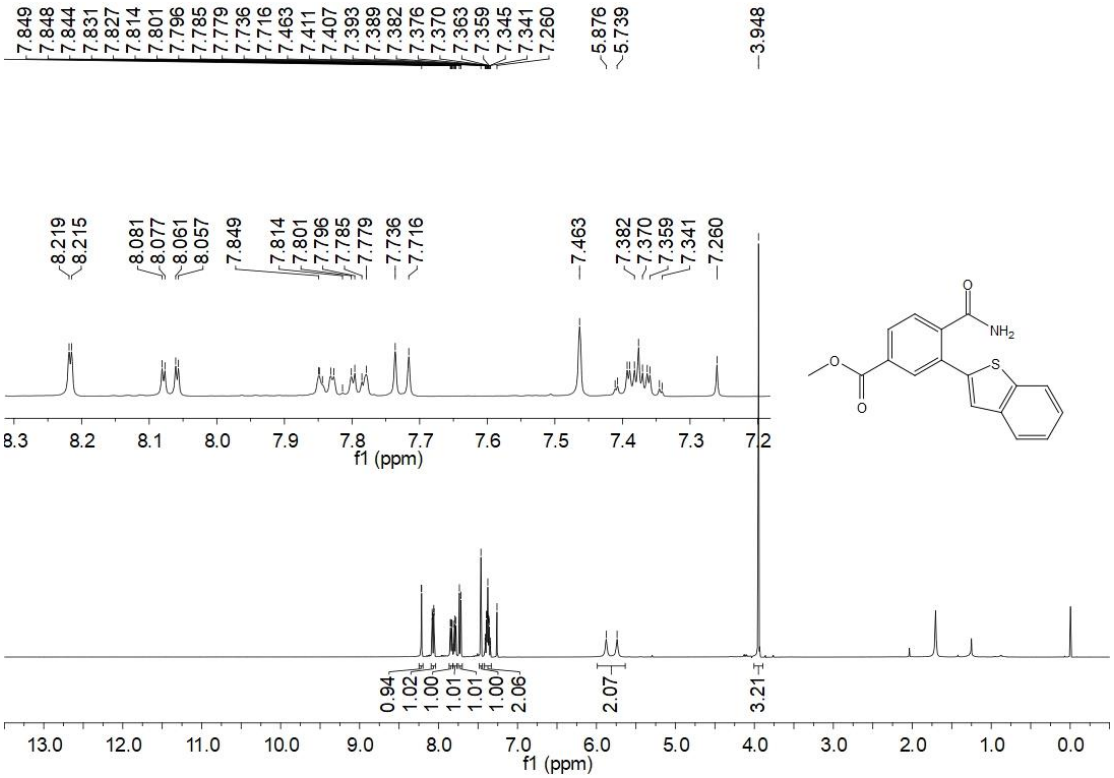

7.439
7.426
7.419
7.406
7.399
7.396
7.390
7.386
7.379
7.376
7.372
7.368
7.362
7.355
7.349
7.343
7.339
7.325
7.321
7.260
7.162
7.160
7.140
7.121
7.117
6.004
5.779
7.830
7.813
7.808
7.791
7.786
7.776
7.769
7.540
7.528
7.439
7.399
7.390
7.379
7.372
7.362
7.349
7.339
7.321
7.260
7.162
7.160
7.140
7.121
7.117
F
O
NH2
S
7.90
7.80
7.70
7.60
7.50
7.40
7.30
7.20
7.10
f1 (ppm)
1.98
1.00
4.15
1.00
2.08
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

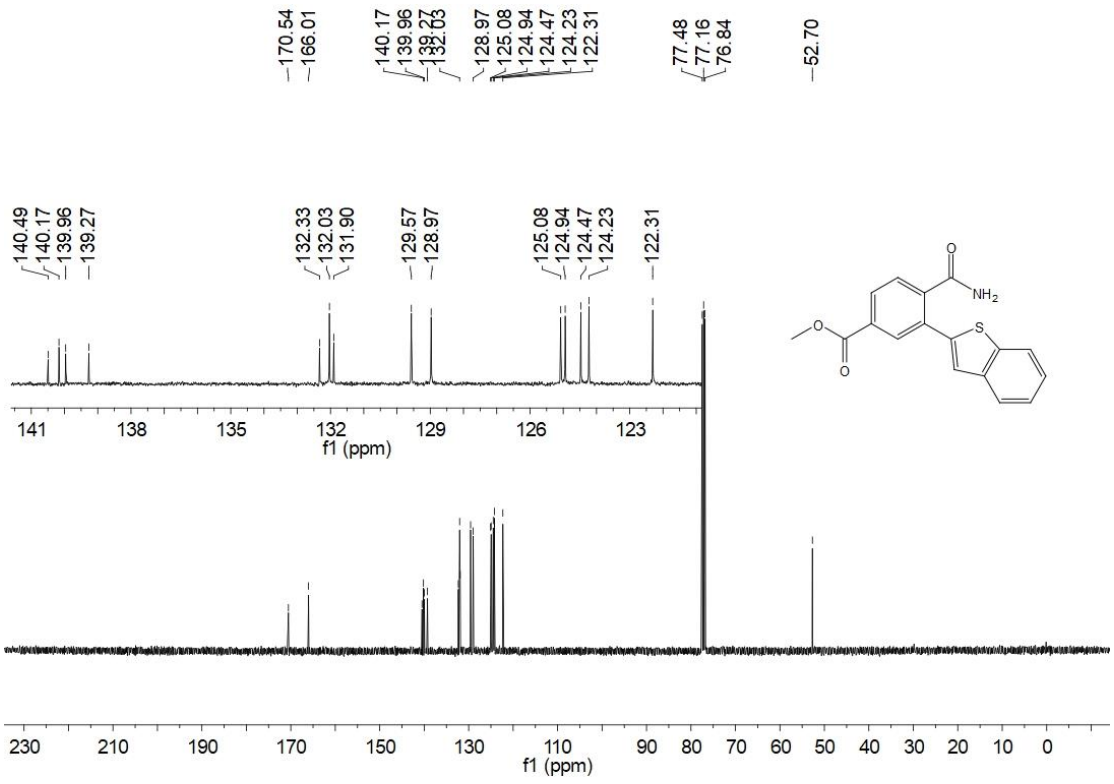

166.94
160.68
158.20
140.23
139.58
126.24
124.32
122.18
115.83
115.61
77.48
77.16
76.84
F
O
NH2
S
140.34
140.23
139.60
139.58
134.08
134.05
131.15
131.06
126.24
126.21
124.98
124.81
124.32
124.11
124.08
123.93
122.18
141
140
139
138
137
136
135
134
133
132
131
130
129
128
127
126
125
124
123
122
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

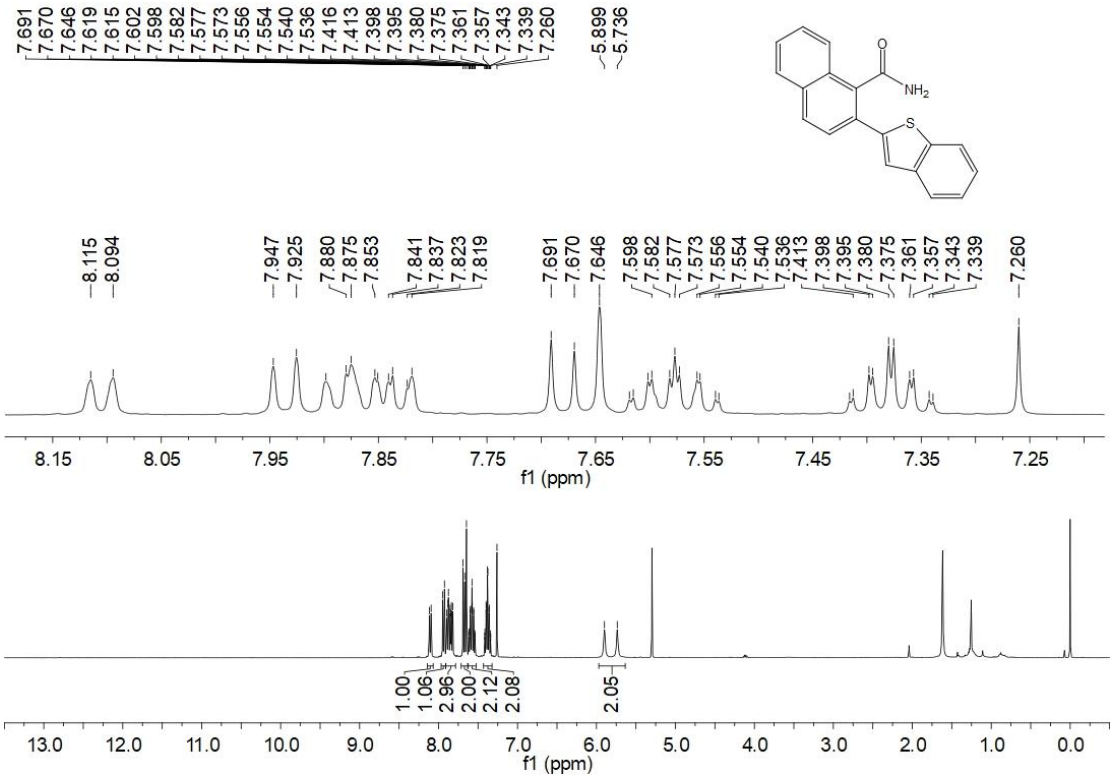

7.858
7.841
7.837
7.809
7.804
7.794
7.787
7.680
7.659
7.549
7.544
7.438
7.419
7.414
7.405
7.401
7.395
7.389
7.383
7.376
7.372
7.358
7.355
7.260
5.698
5.611

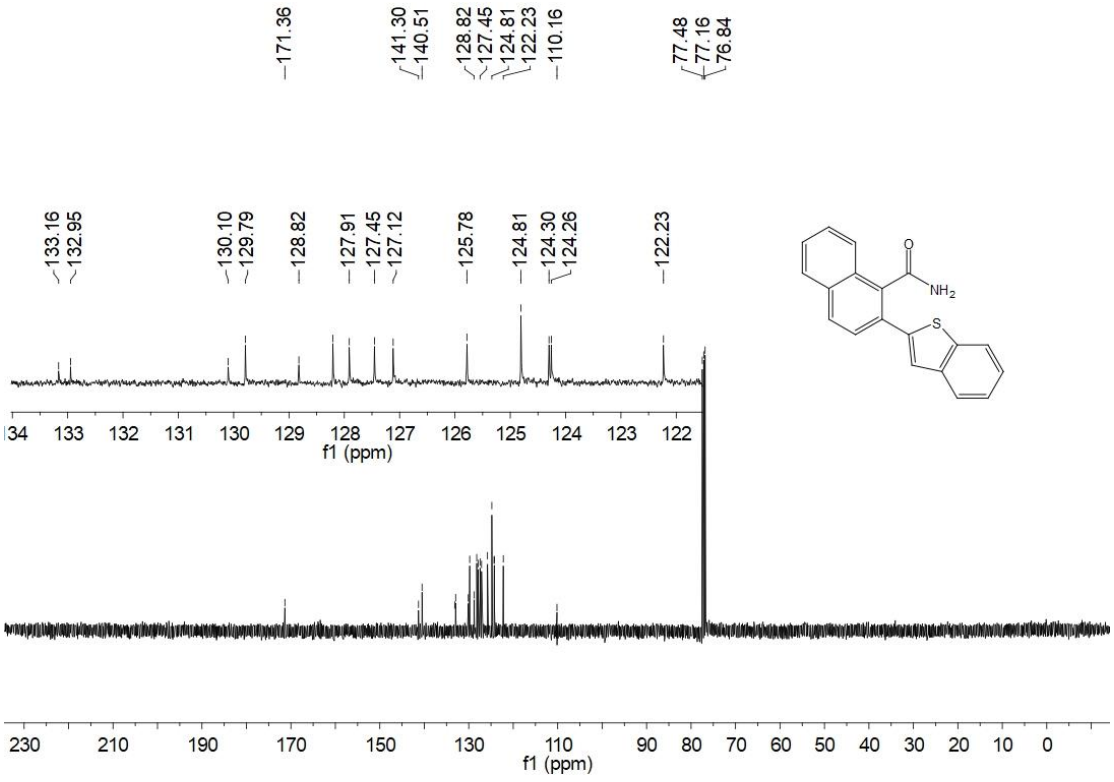

7.858
7.841
7.837
7.809
7.804
7.794
7.787
7.680
7.659
7.549
7.544
7.438
7.405
7.401
7.395
7.389
7.383
7.376
7.372
7.358
7.355
7.260
O
NH2
Cl
S
7.90
7.80
7.70
7.60
7.50
7.40
7.30
f1 (ppm)
0.90
0.95
1.00
0.89
4.08
2.01
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

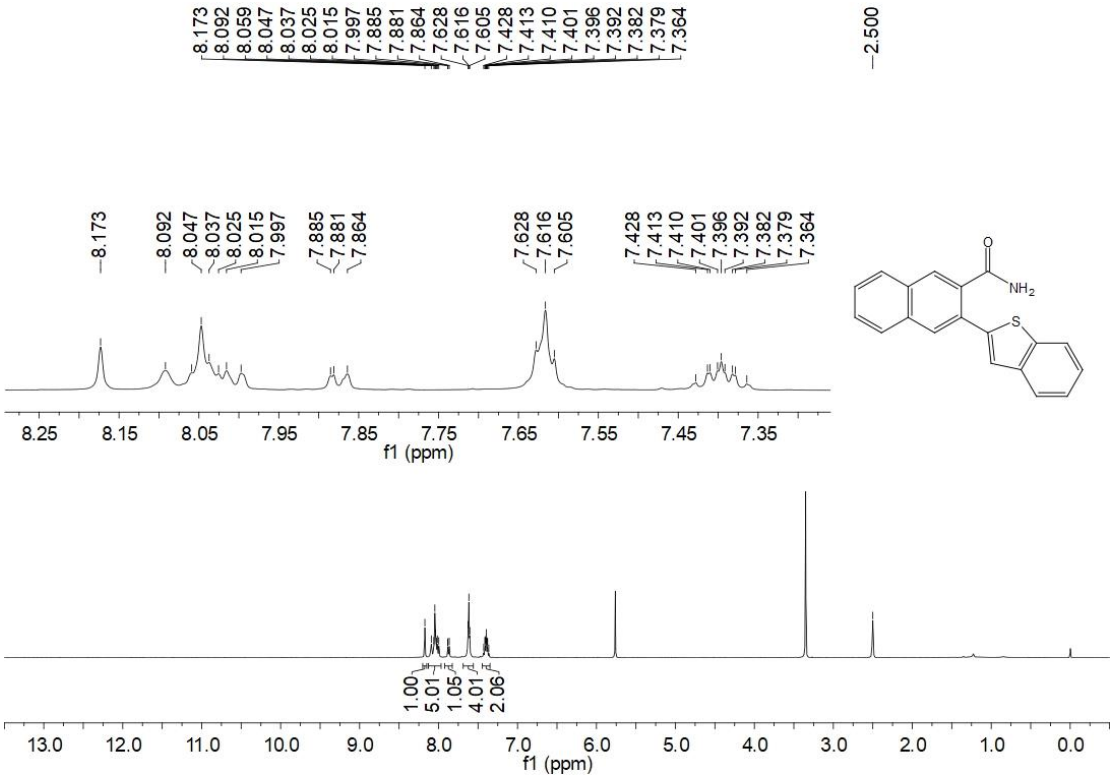

170.08
140.06
133.84
133.73
130.86
130.49
128.87
125.20
125.03
124.67
124.28
122.35
77.48
77.16
76.84
140.50
140.06
139.56
136.48
133.84
133.73
130.86
130.49
128.87
125.20
125.03
124.67
124.28
122.35
O
NH2
Cl
S
142
139
136
133
130
127
124
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

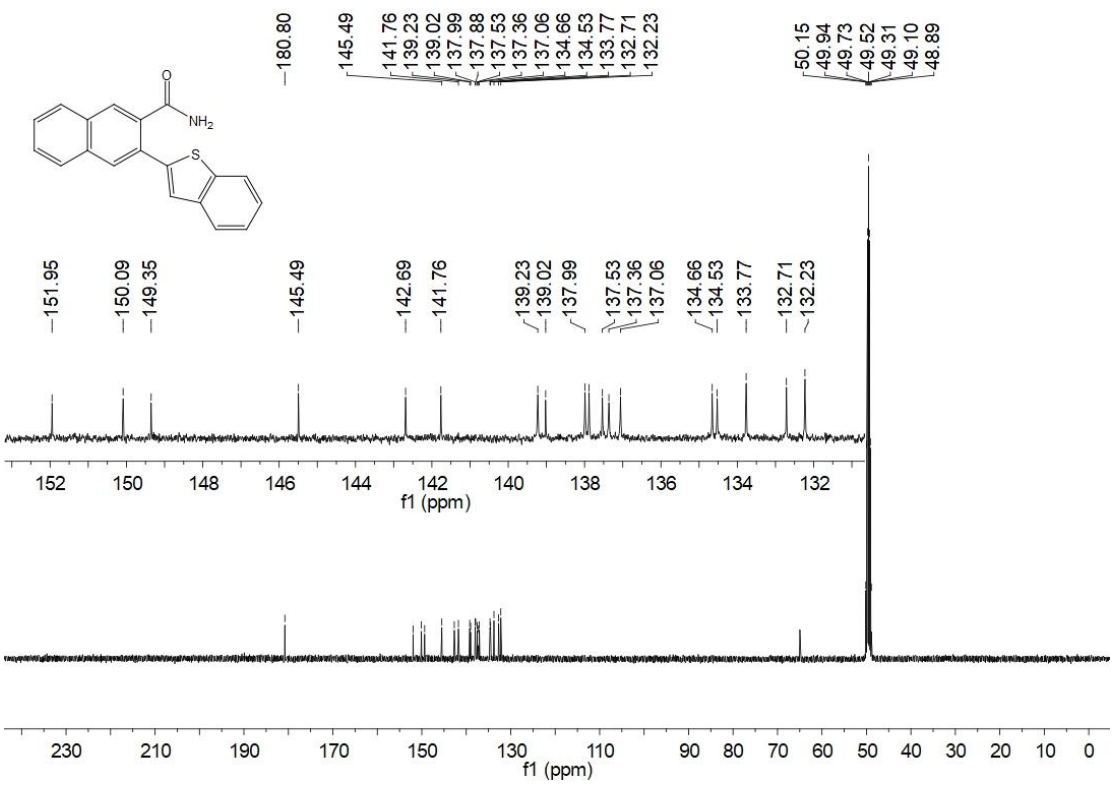

7.849
7.848
7.844
7.831
7.827
7.814
7.801
7.796
7.785
7.779
7.736
7.716
7.463
7.411
7.407
7.393
7.389
7.382
7.376
7.370
7.363
7.359
7.345
7.341
7.260
5.876
5.739
3.948
8.219
8.215
8.081
8.077
8.061
8.057
7.849
7.814
7.801
7.796
7.785
7.779
7.736
7.716
7.463
7.382
7.370
7.359
7.341
7.260
f1 (ppm)
0.94
1.02
1.00
1.01
1.01
1.00
2.06
2.07
3.21
f1 (ppm)

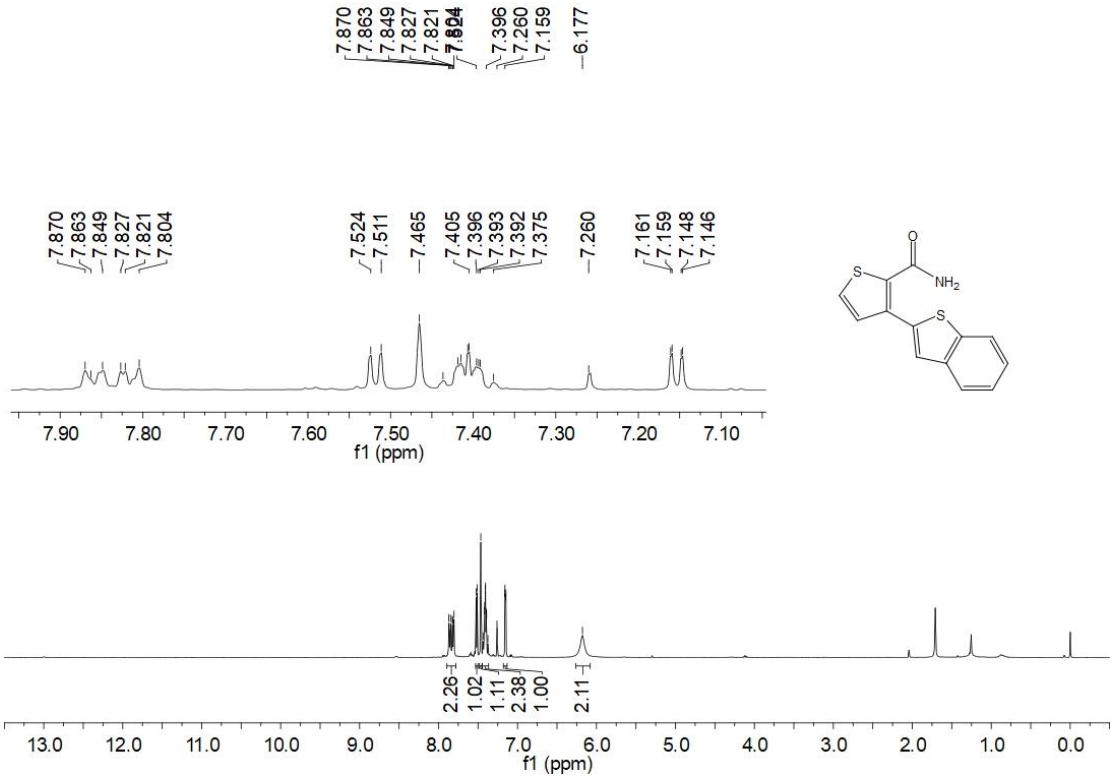

170.54
166.01
140.17
139.96
139.27
132.03
128.97
125.08
124.94
124.47
124.23
122.31
77.48
77.16
76.84
52.70
140.49
140.17
139.96
139.27
132.33
132.03
131.90
129.57
128.97
125.08
124.94
124.47
124.23
122.31
f1 (ppm)
f1 (ppm)

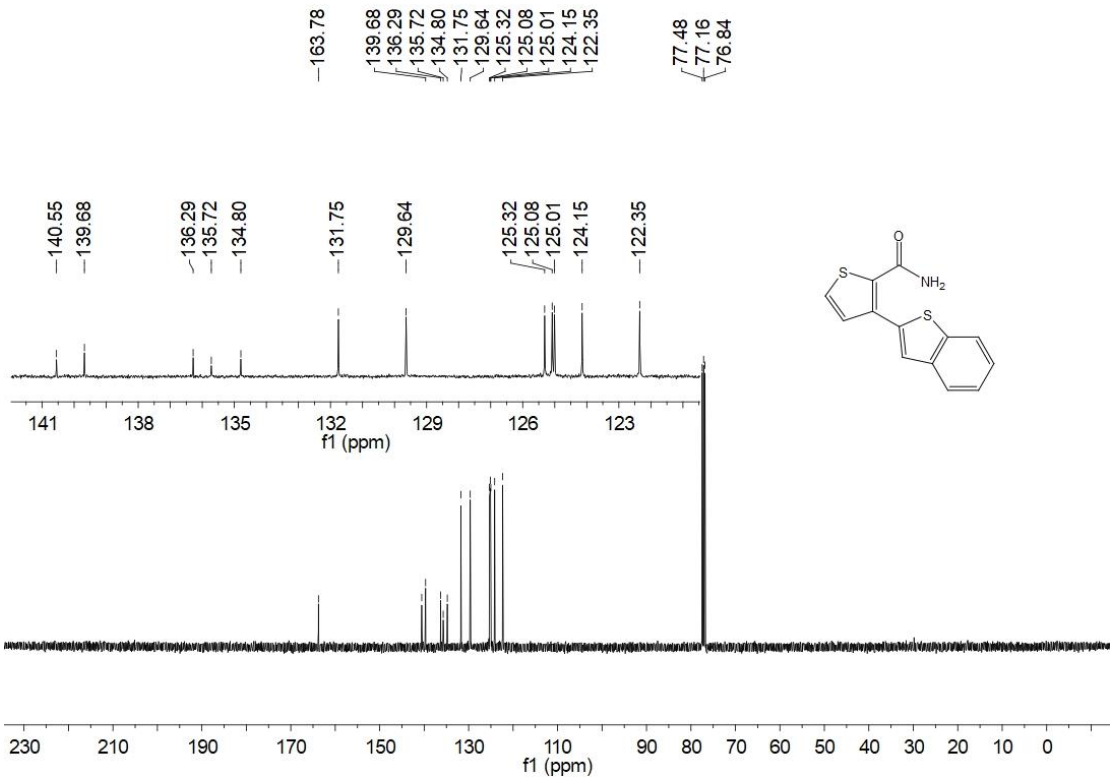

7.691
7.670
7.646
7.619
7.615
7.602
7.598
7.582
7.577
7.573
7.556
7.554
7.540
7.536
7.416
7.413
7.398
7.395
7.380
7.375
7.361
7.357
7.343
7.339
7.260
5.899
5.736
O
NH2
S
8.115
8.094
7.947
7.925
7.880
7.875
7.853
7.841
7.837
7.823
7.819
7.691
7.670
7.646
7.598
7.582
7.577
7.573
7.556
7.554
7.540
7.536
7.413
7.398
7.395
7.380
7.375
7.361
7.357
7.343
7.339
7.260
8.15
8.05
7.95
7.85
7.75
7.65
7.55
7.45
7.35
7.25
f1 (ppm)
1.00
1.06
2.96
2.00
2.12
2.08
2.05
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

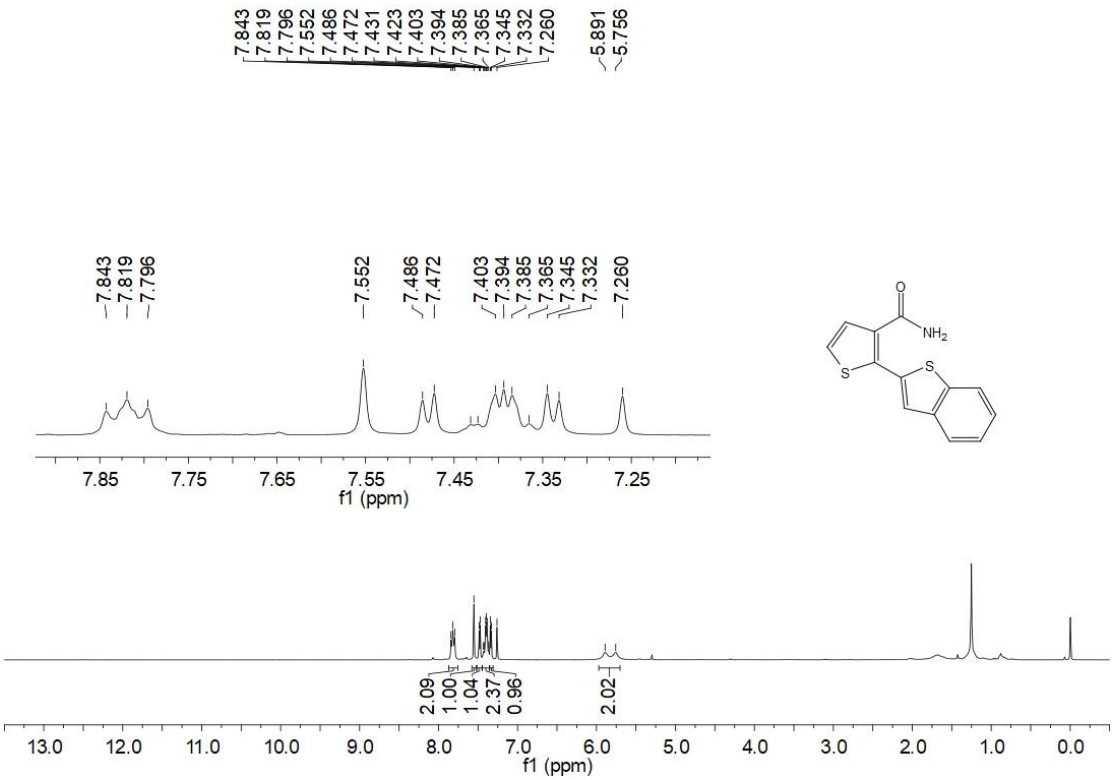

171.36
141.30
140.51
128.82
127.45
124.81
122.23
110.16
77.48
77.16
76.84
133.16
132.95
130.10
129.79
128.82
127.91
127.45
127.12
125.78
124.81
124.30
124.26
122.23
O
NH2
S
34
133
132
131
130
129
128
127
126
125
124
123
122
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

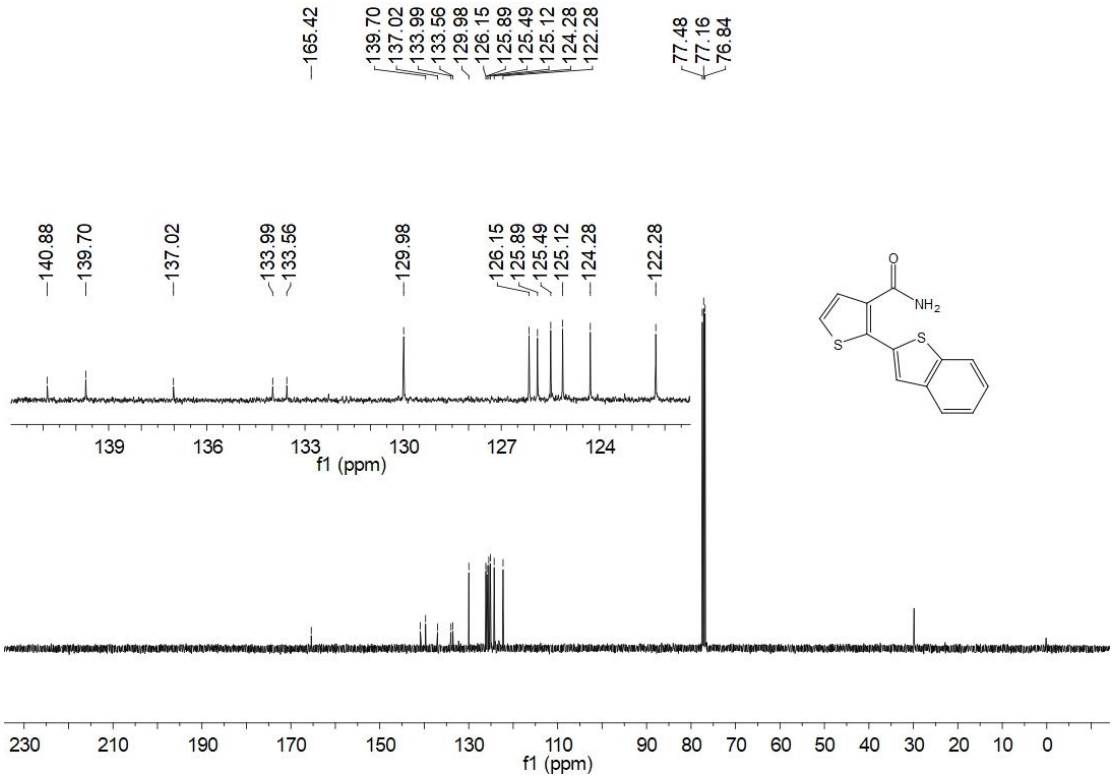

8.173
8.092
8.059
8.047
8.037
8.025
8.015
7.997
7.885
7.881
7.864
7.628
7.616
7.605
7.428
7.413
7.410
7.401
7.396
7.392
7.382
7.379
7.364
2.500
O
NH2
S
f1 (ppm)
1.00
5.01
1.05
4.01
2.06

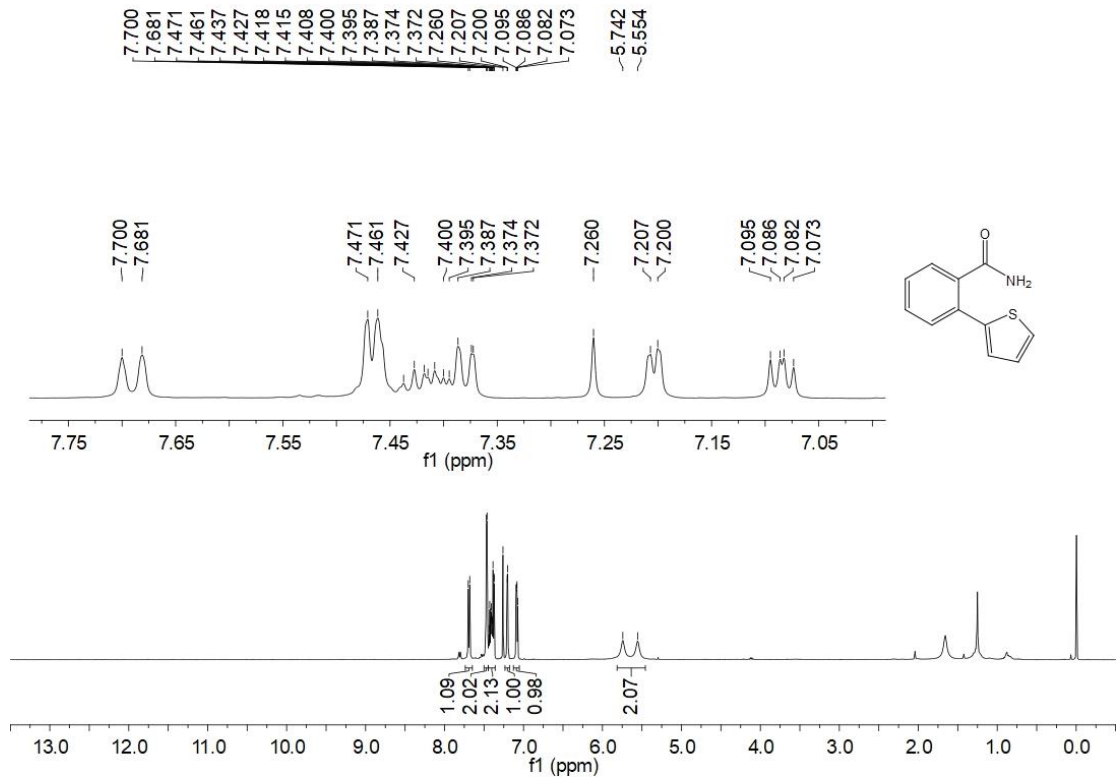

180.80
145.49
141.76
139.23
139.02
137.99
137.88
137.53
137.36
137.06
134.66
134.53
133.77
132.71
132.23
50.15
49.94
49.73
49.52
49.31
49.10
48.89
O
NH2
S
151.95
150.09
149.35
145.49
142.69
141.76
139.23
139.02
137.99
137.53
137.36
137.06
134.66
134.53
133.77
132.71
132.23
f1 (ppm)

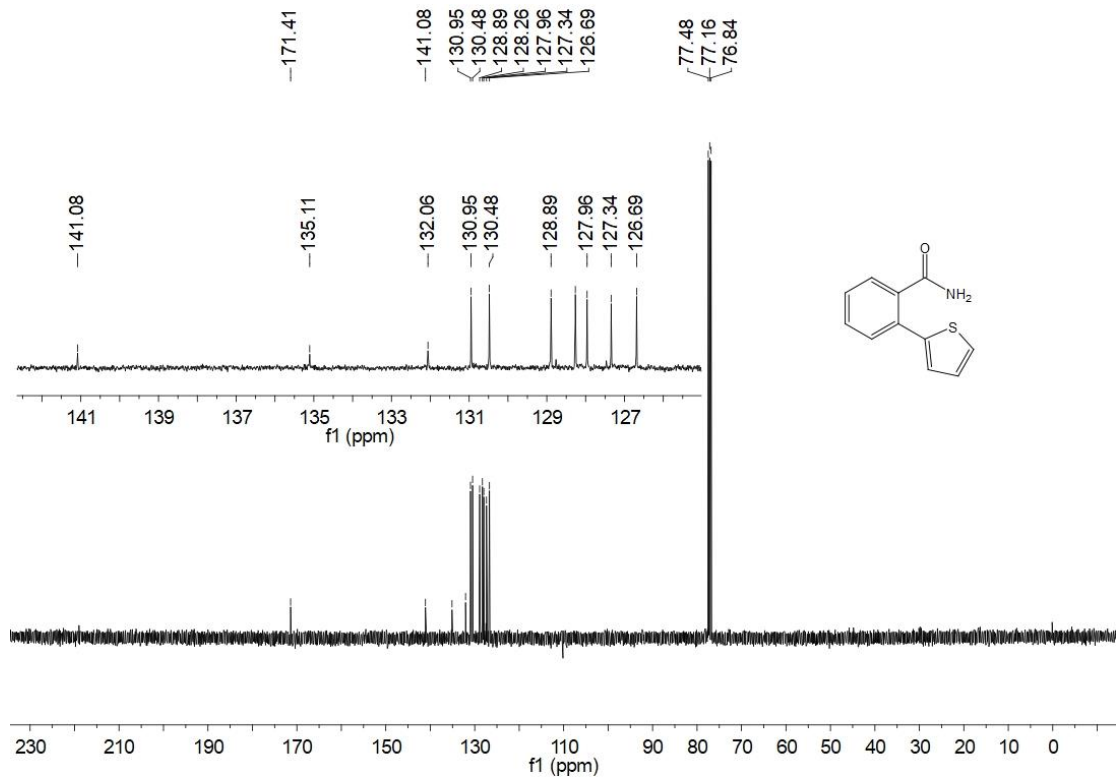

7.870
7.863
7.849
7.827
7.821
7.804
7.524
7.511
7.465
7.405
7.396
7.393
7.392
7.375
7.260
7.161
7.159
7.148
7.146
6.177
f1 (ppm)
2.26
1.02
1.11
2.38
1.00
2.11
f1 (ppm)

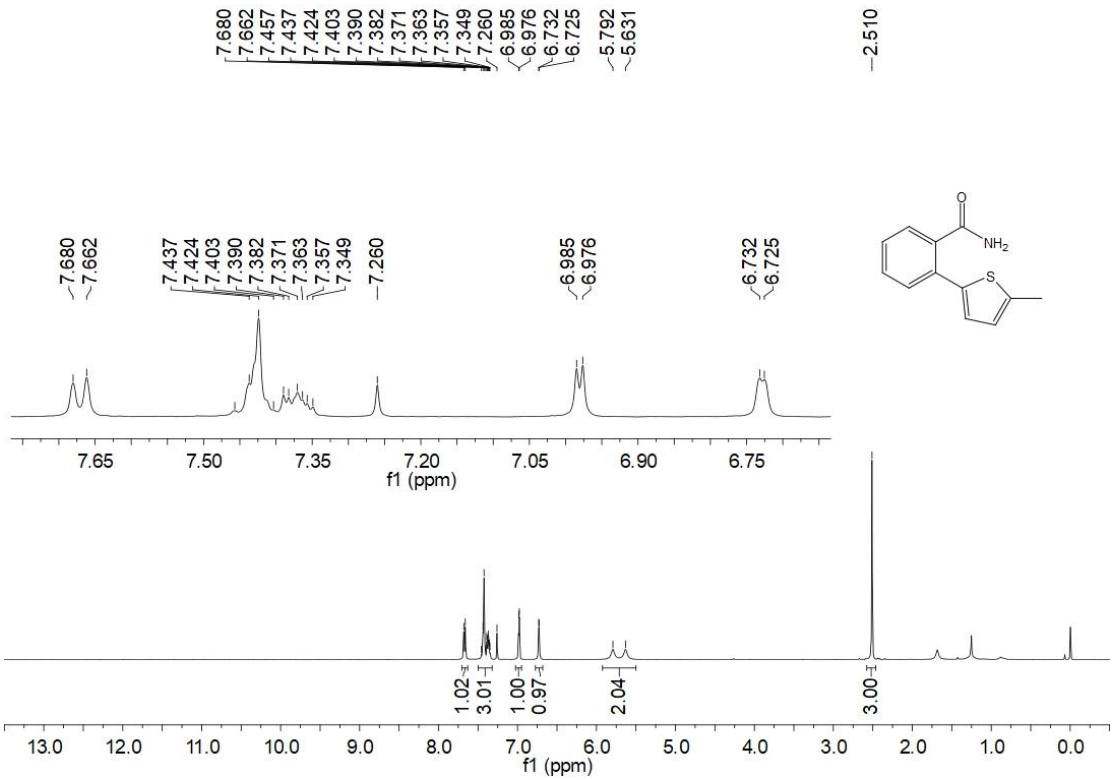

163.78
139.68
136.29
135.72
134.80
131.75
129.64
125.32
125.08
125.01
124.15
122.35
77.48
77.16
76.84
f1 (ppm)
f1 (ppm)

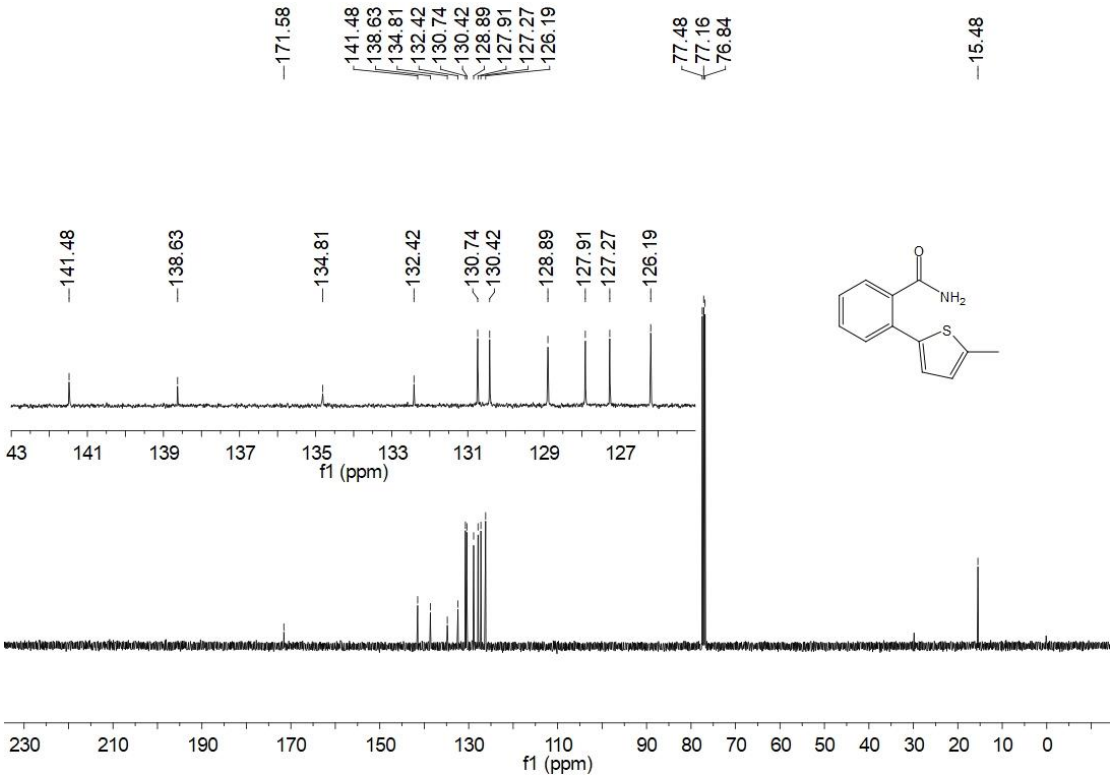

7.843
7.819
7.796
7.552
7.486
7.472
7.431
7.423
7.403
7.394
7.385
7.365
7.345
7.332
7.260
5.891
5.756
7.85
7.75
7.65
7.55
7.45
7.35
7.25
f1 (ppm)
O
NH2
S
S
2.09
1.00
1.04
2.37
0.96
2.02
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

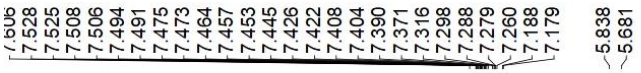

165.42
139.70
137.02
133.99
133.56
129.98
126.15
125.89
125.49
125.12
124.28
122.28
77.48
77.16
76.84
140.88
139.70
137.02
133.99
133.56
129.98
126.15
125.89
125.49
125.12
124.28
122.28
139
136
133
130
127
124
f1 (ppm)
O
NH2
S
S
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

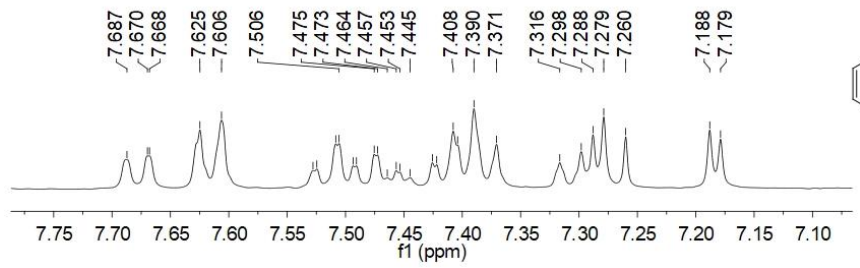

7.700
7.681
7.471
7.461
7.437
7.427
7.418
7.415
7.408
7.400
7.395
7.387
7.374
7.372
7.260
7.207
7.200
7.095
7.086
7.082
7.073
5.742
5.554
NH2
S
f1 (ppm)
1.09
2.02
2.13
1.00
0.98
2.07

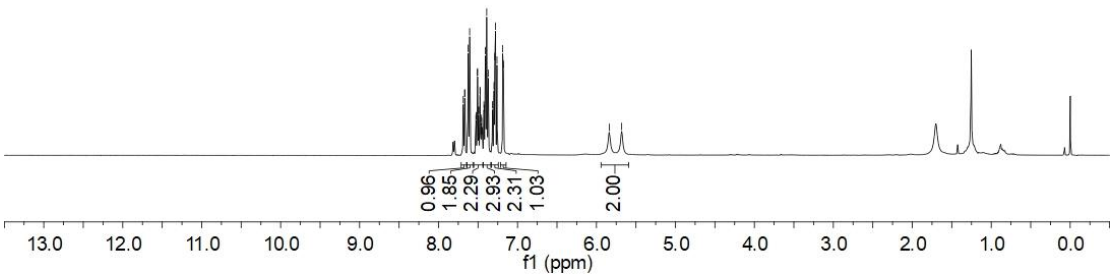

171.41
141.08
130.95
130.48
128.89
128.26
127.96
127.34
126.69
77.48
77.16
76.84
135.11
132.06
NH2
S
f1 (ppm)

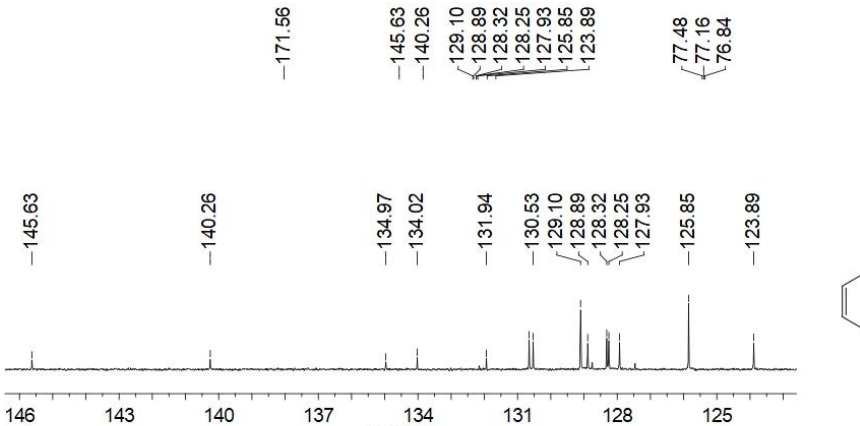

7.680
7.662
7.457
7.437
7.424
7.403
7.390
7.382
7.371
7.363
7.357
7.349
7.260
6.985
6.976
6.732
6.725
5.792
5.631
2.510
O
NH2
S
7.65
7.50
7.35
7.20
7.05
6.90
6.75
f1 (ppm)
1.02
3.01
1.00
0.97
2.04
3.00
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


171.58
141.48
138.63
134.81
132.42
130.74
130.42
128.89
127.91
127.27
126.19
77.48
77.16
76.84
15.48
O
NH2
S
43
141
139
137
135
133
131
129
127
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

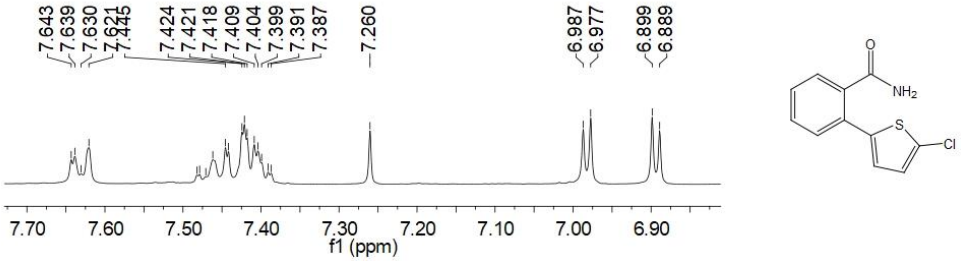

7.528
7.525
7.508
7.506
7.494
7.491
7.475
7.473
7.464
7.457
7.453
7.445
7.426
7.422
7.408
7.404
7.390
7.371
7.316
7.298
7.288
7.279
7.260
7.188
7.179
5.838
5.681

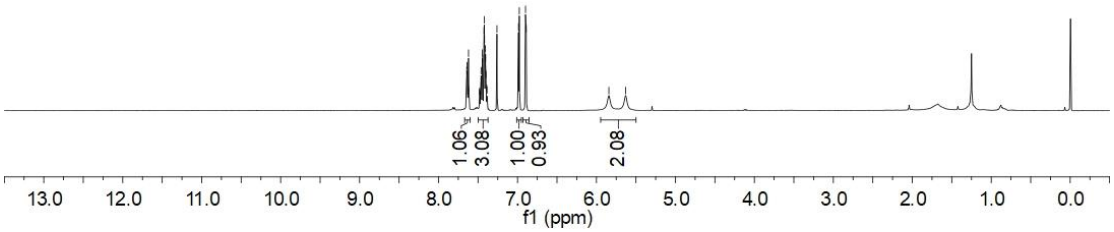

7.687
7.670
7.668
7.625
7.606
7.506
7.475
7.473
7.464
7.457
7.453
7.445
7.408
7.390
7.371
7.316
7.298
7.288
7.279
7.260
7.188
7.179
O
NH2
S
7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10
f1 (ppm)


0.96
1.85
2.29
2.93
2.31
1.03
2.00
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

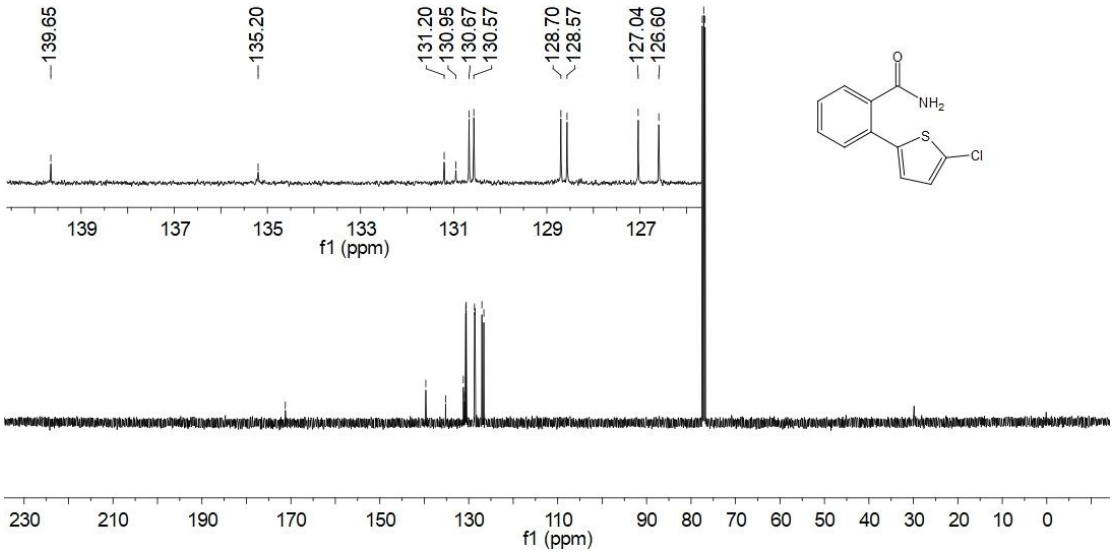

171.56
145.63
140.26
129.10
128.89
128.32
128.25
127.93
125.85
123.89
77.48
77.16
76.84
145.63
140.26
134.97
134.02
131.94
130.53
129.10
128.89
128.32
128.25
127.93
125.85
123.89
O
NH2
S
146 143 140 137 134 131 128 125
f1 (ppm)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

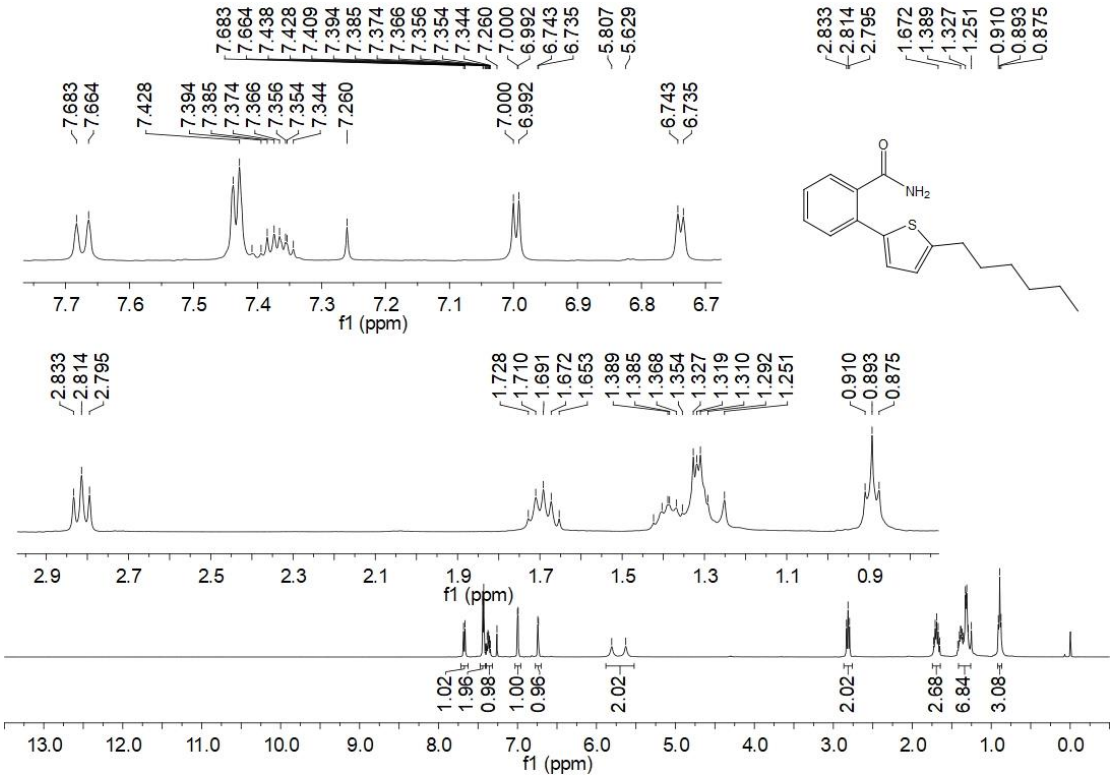

7.643
7.639
7.630
7.621
7.482
7.479
7.471
7.462
7.445
7.442
7.424
7.421
7.418
7.409
7.404
7.399
7.391
7.387
7.260
6.987
6.977
6.899
6.889
5.843
5.630

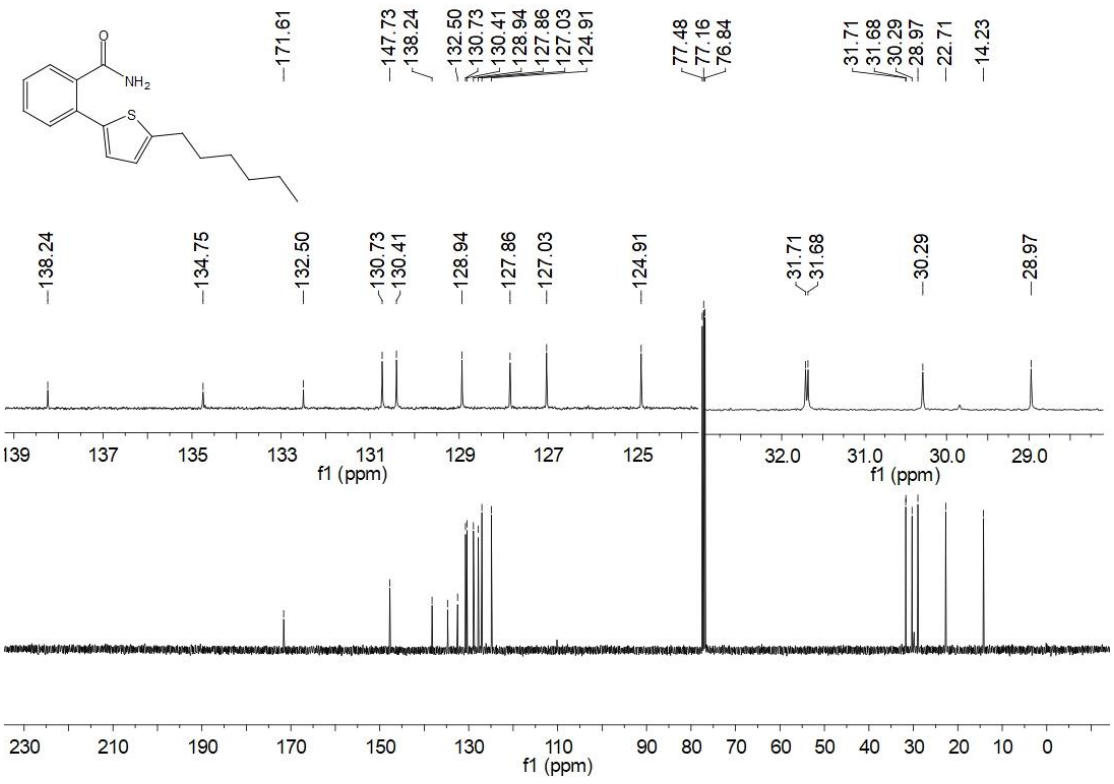

7.643
7.639
7.630
7.621
7.445
7.424
7.421
7.418
7.409
7.404
7.399
7.391
7.387
7.260
6.987
6.977
6.899
6.889
O
NH2
S
Cl
7.70
7.60
7.50
7.40
7.30
7.20
7.10
7.00
6.90
f1 (ppm)

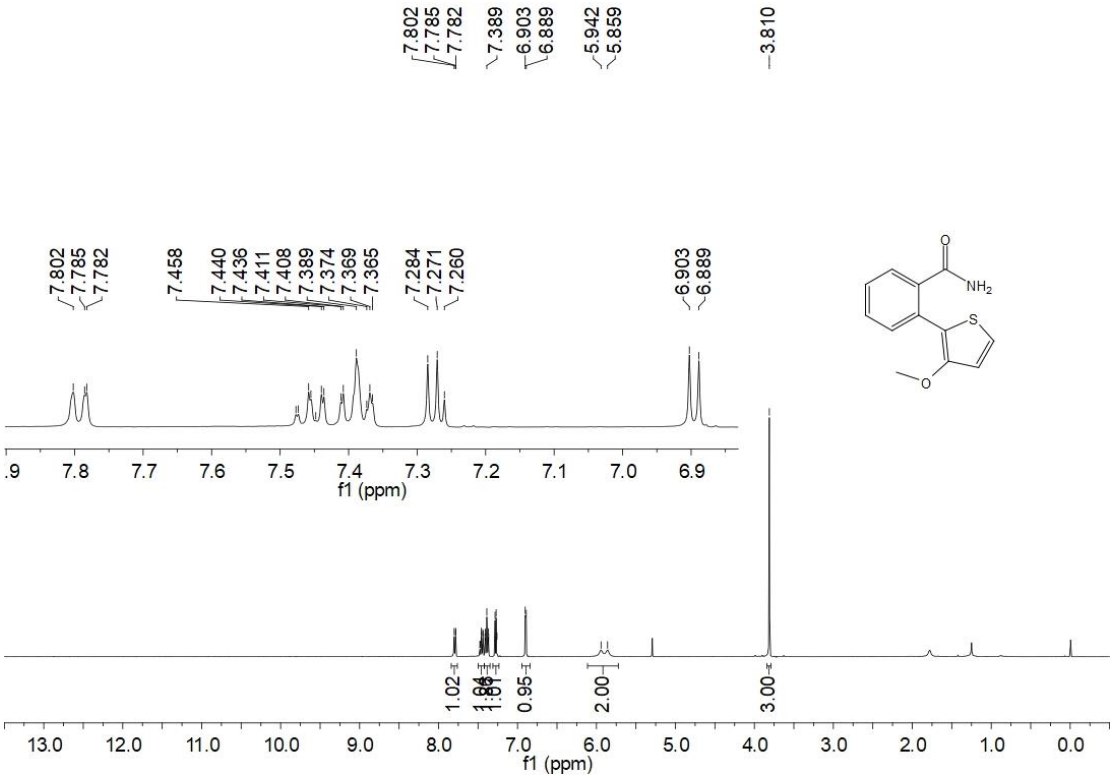

1.06
3.08
1.00
0.93
2.08
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

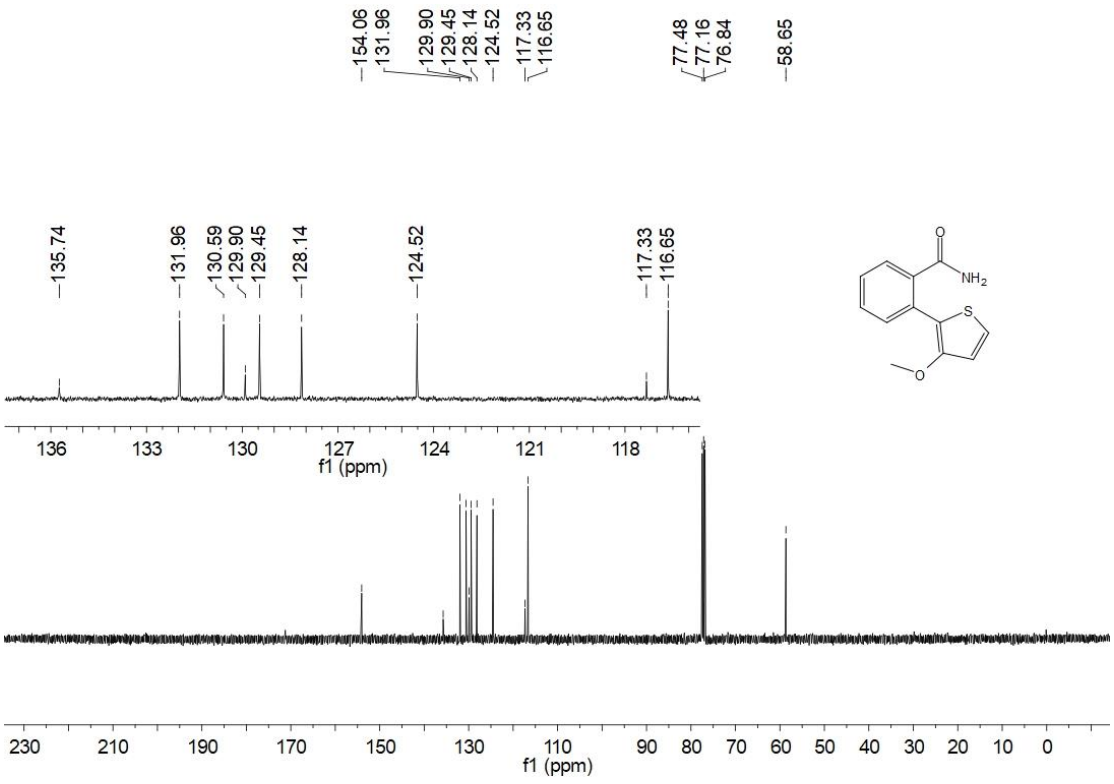

171.24
139.65
135.20
131.20
130.95
130.67
130.57
128.70
128.57
127.04
126.60
77.48
77.16
76.84

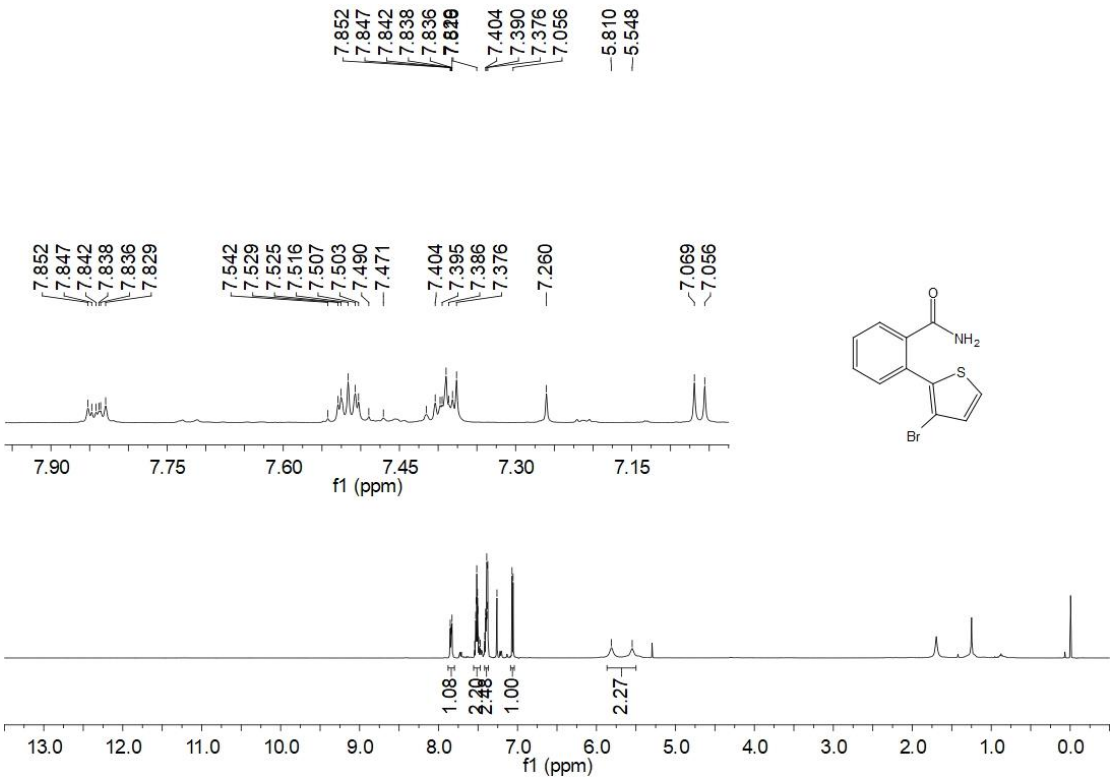

139.65
135.20
131.20
130.95
130.67
130.57
128.70
128.57
127.04
126.60
O
NH2
S
Cl
139
137
135
133
131
129
127
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

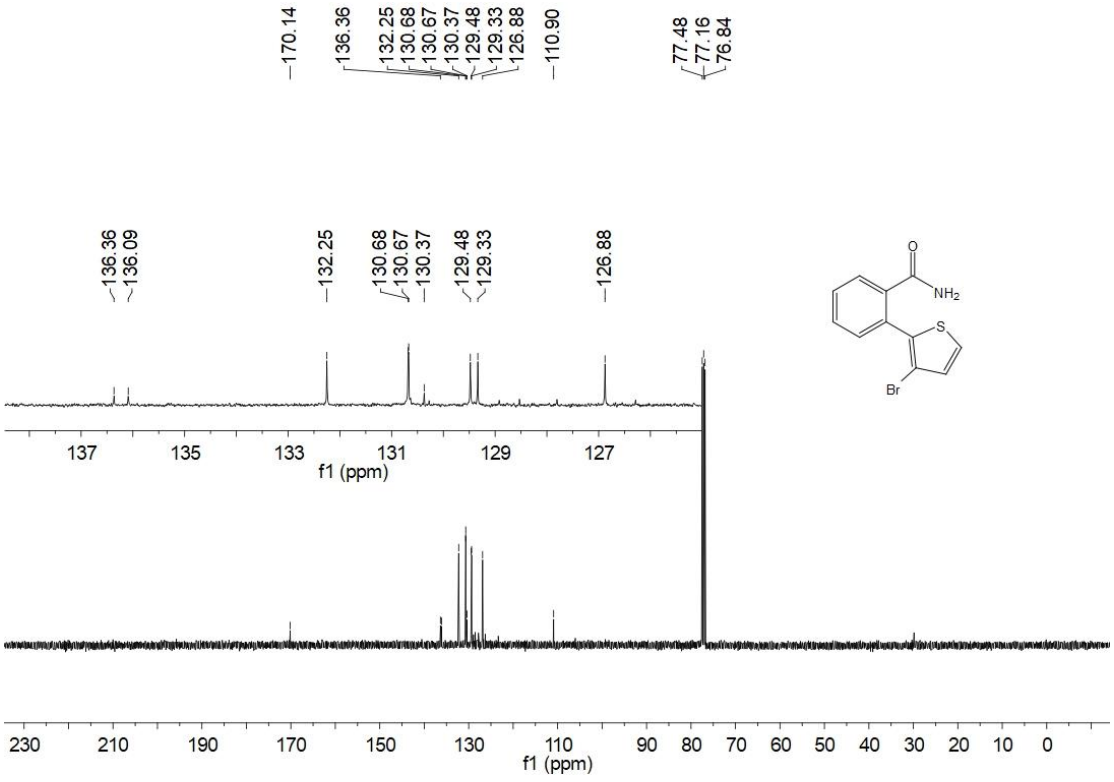

7.683
7.664
7.438
7.428
7.409
7.394
7.385
7.374
7.366
7.356
7.354
7.344
7.260
7.000
6.992
6.743
6.735
5.807
5.629
2.833
2.814
2.795
1.672
1.389
1.327
1.251
0.910
0.893
0.875
NH2
S
f1 (ppm)
1.728
1.710
1.691
1.672
1.653
1.389
1.385
1.368
1.354
1.327
1.319
1.310
1.292
1.251
1.02
1.96
0.98
1.00
0.96
2.02
2.02
2.68
6.84
3.08

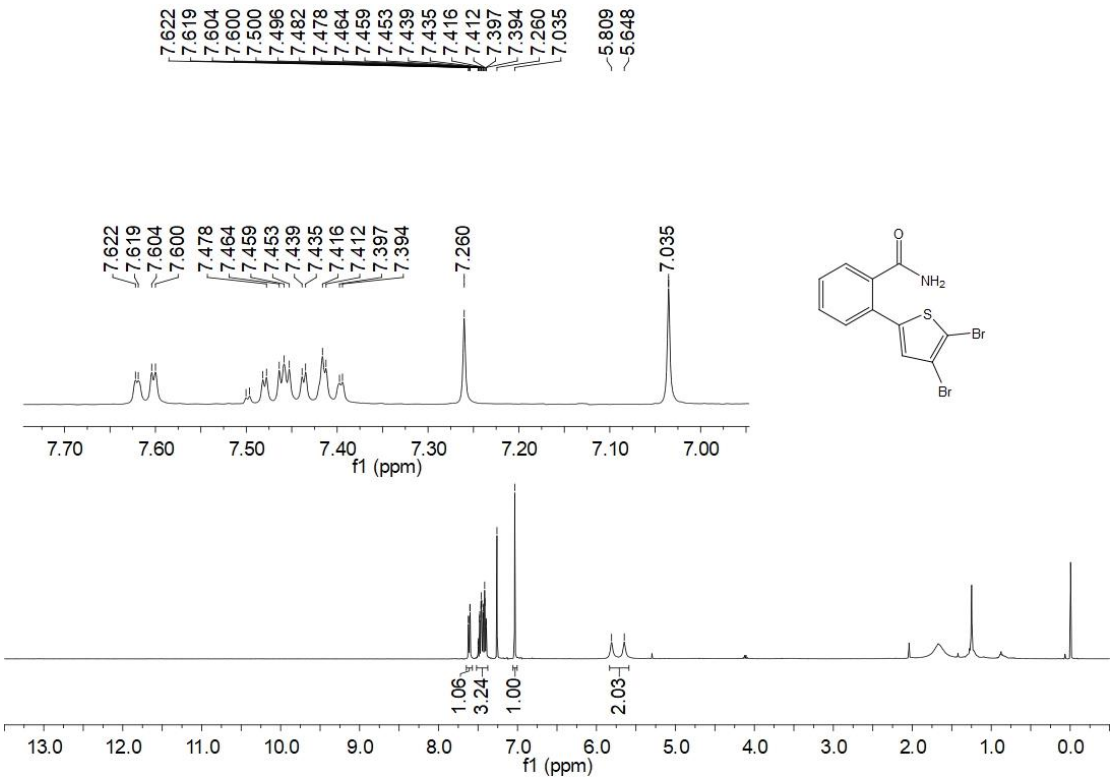

171.61
147.73
138.24
132.50
130.73
130.41
128.94
127.86
127.03
124.91
77.48
77.16
76.84
31.71
31.68
30.29
28.97
22.71
14.23
NH2
S
f1 (ppm)

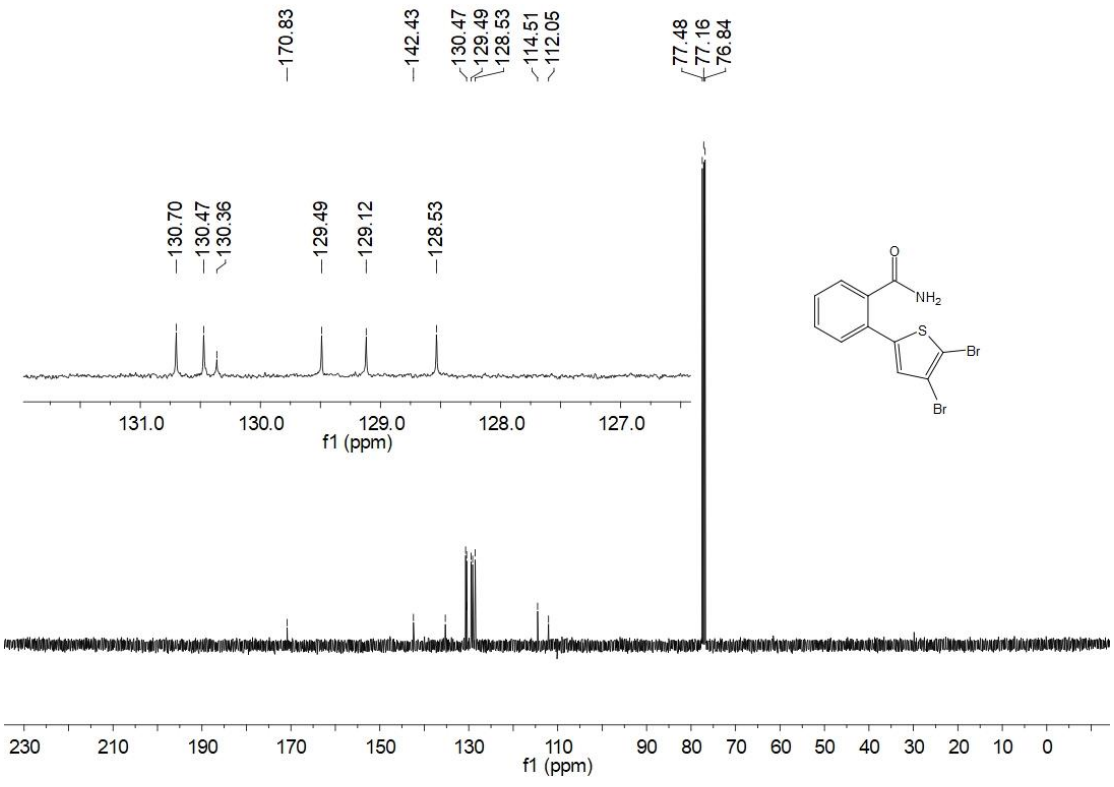

7.802
7.785
7.782
7.458
7.440
7.436
7.411
7.408
7.389
7.374
7.369
7.365
7.284
7.271
7.260
6.903
6.889
7.389
5.942
5.859
3.810
NH2
O
S
f1 (ppm)
1.02
0.95
2.00
3.00

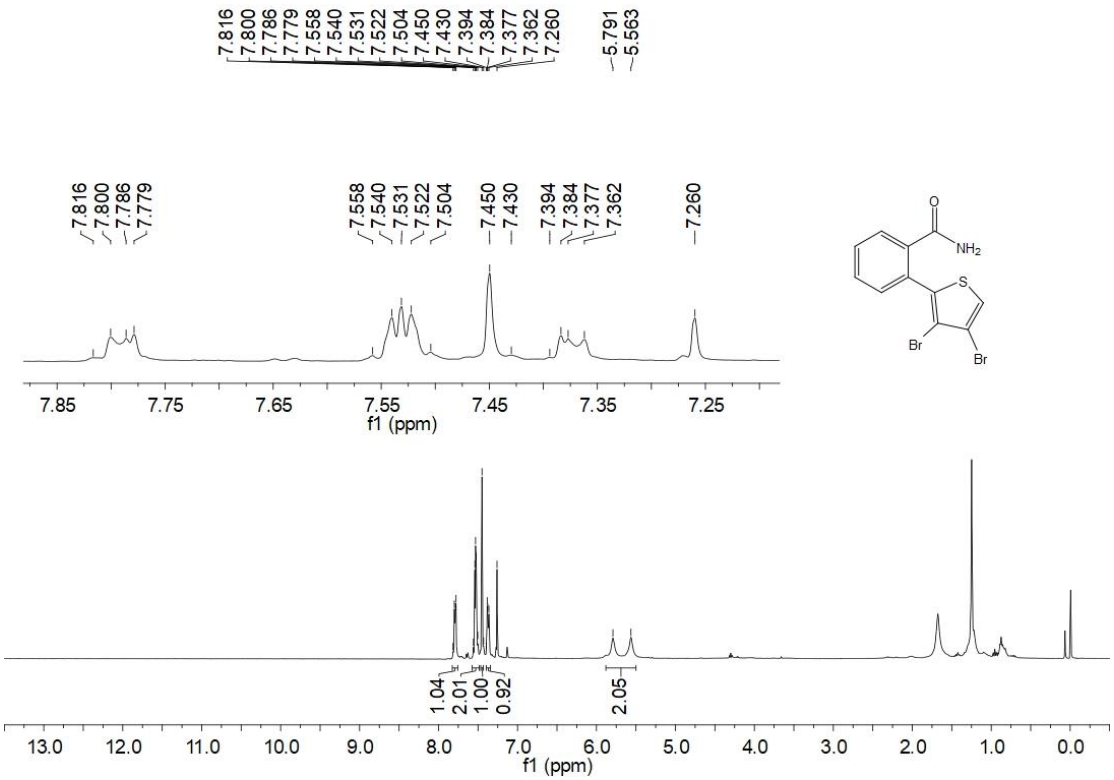

154.06
131.96
129.90
129.45
128.14
124.52
117.33
116.65
77.48
77.16
76.84
58.65
NH2
O
S
f1 (ppm)

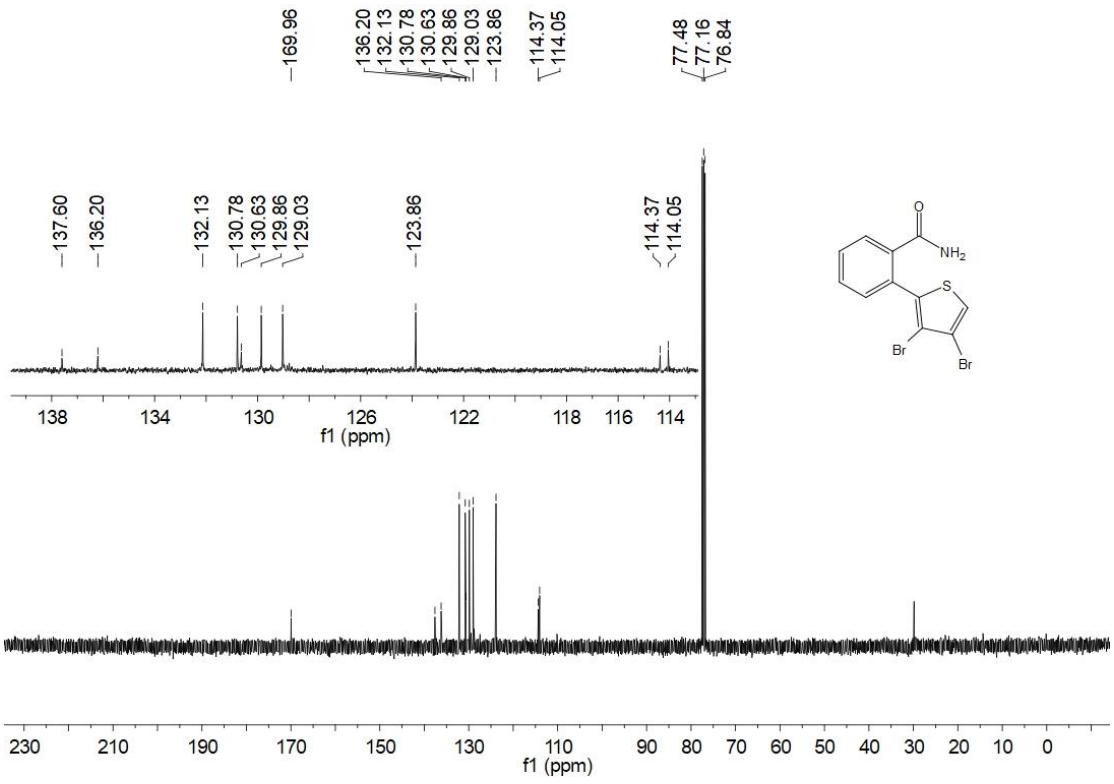

7.852
7.847
7.842
7.838
7.836
7.404
7.390
7.376
7.056
5.810
5.548
7.542
7.529
7.525
7.516
7.507
7.503
7.490
7.471
7.395
7.386
7.260
7.069
7.056
O
NH2
S
Br
7.90
7.75
7.60
7.45
7.30
7.15
f1 (ppm)
1.08
2.27
1.00
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


170.14
136.36
132.25
130.68
130.67
130.37
129.48
129.33
126.88
110.90
77.48
77.16
76.84
136.36
136.09
132.25
130.68
130.67
130.37
129.48
129.33
126.88
O
NH2
S
Br
137
135
133
131
129
127
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

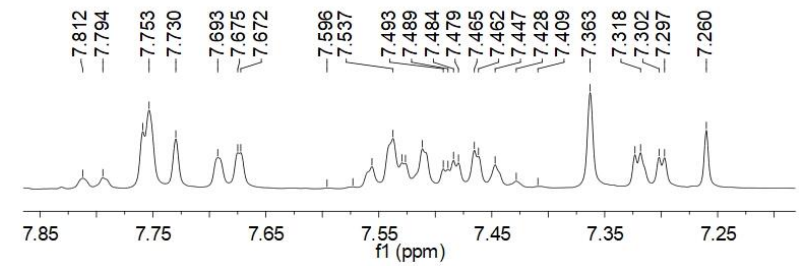

7.622
7.619
7.604
7.600
7.500
7.496
7.482
7.478
7.464
7.459
7.453
7.439
7.435
7.416
7.412
7.397
7.394
7.260
7.035
5.809
5.648
7.70
7.60
7.50
7.40
7.30
7.20
7.10
7.00
f1 (ppm)
O
NH2
S
Br
Br
1.06
3.24
1.00
2.03
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

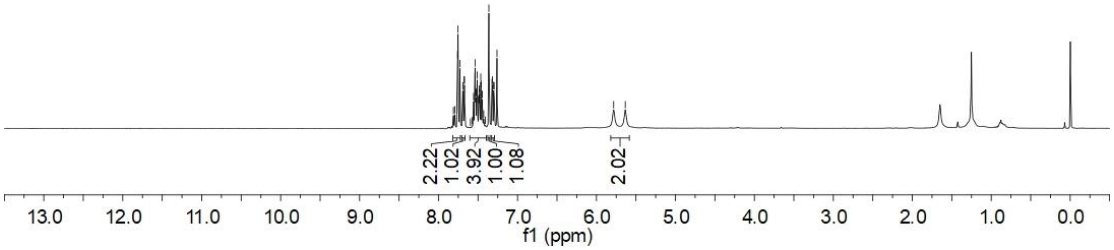

170.83
142.43
130.47
129.49
128.53
114.51
112.05
77.48
77.16
76.84
130.70
130.47
130.36
129.49
129.12
128.53
131.0
130.0
129.0
128.0
127.0
f1 (ppm)
O
NH2
S
Br
Br
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

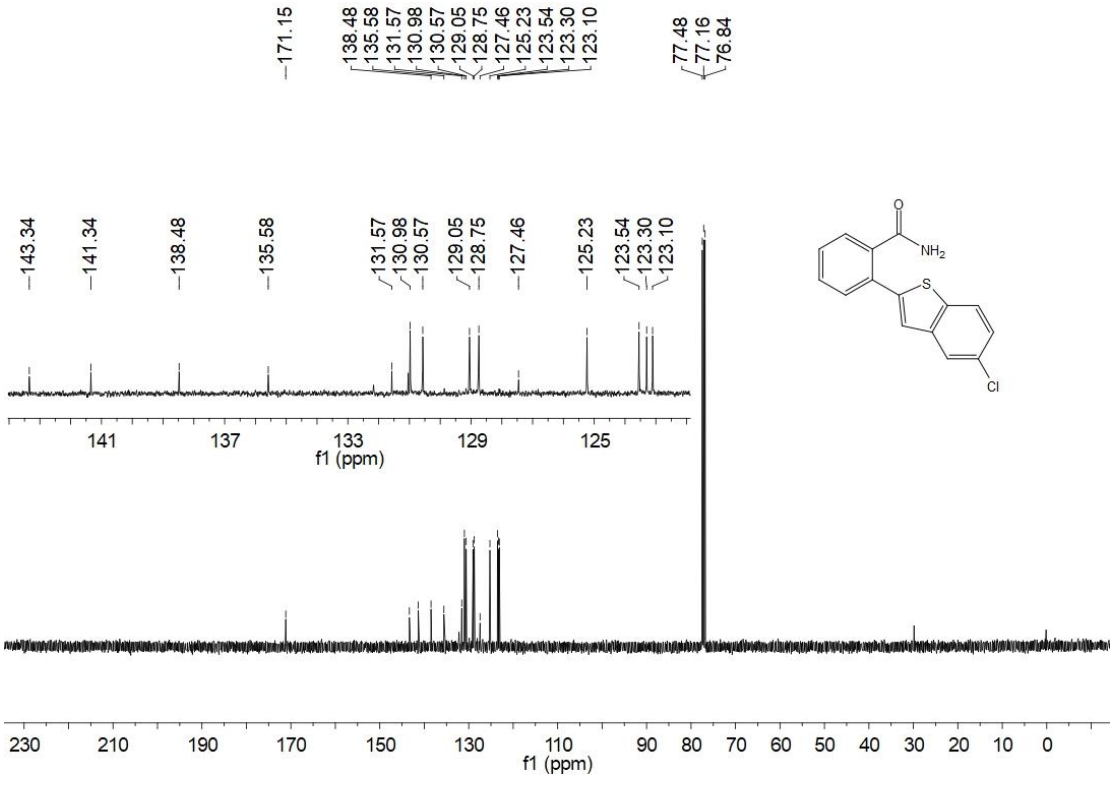

7.816
7.800
7.786
7.779
7.558
7.540
7.531
7.522
7.504
7.450
7.430
7.394
7.384
7.377
7.362
7.260
5.791
5.563
NH2
S
Br
Br
f1 (ppm)
1.04
2.01
1.00
0.92
2.05
f1 (ppm)

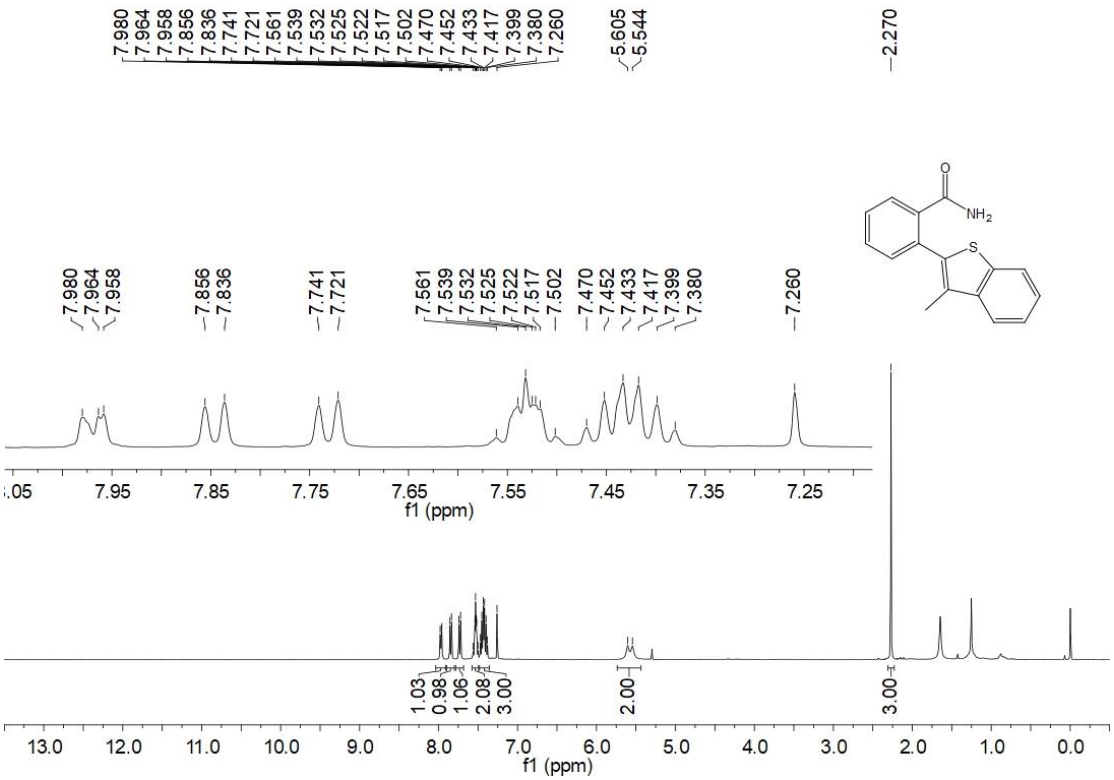

169.96
136.20
132.13
130.78
130.63
129.86
129.03
123.86
114.37
114.05
77.48
77.16
76.84
NH2
S
Br
Br
f1 (ppm)
f1 (ppm)

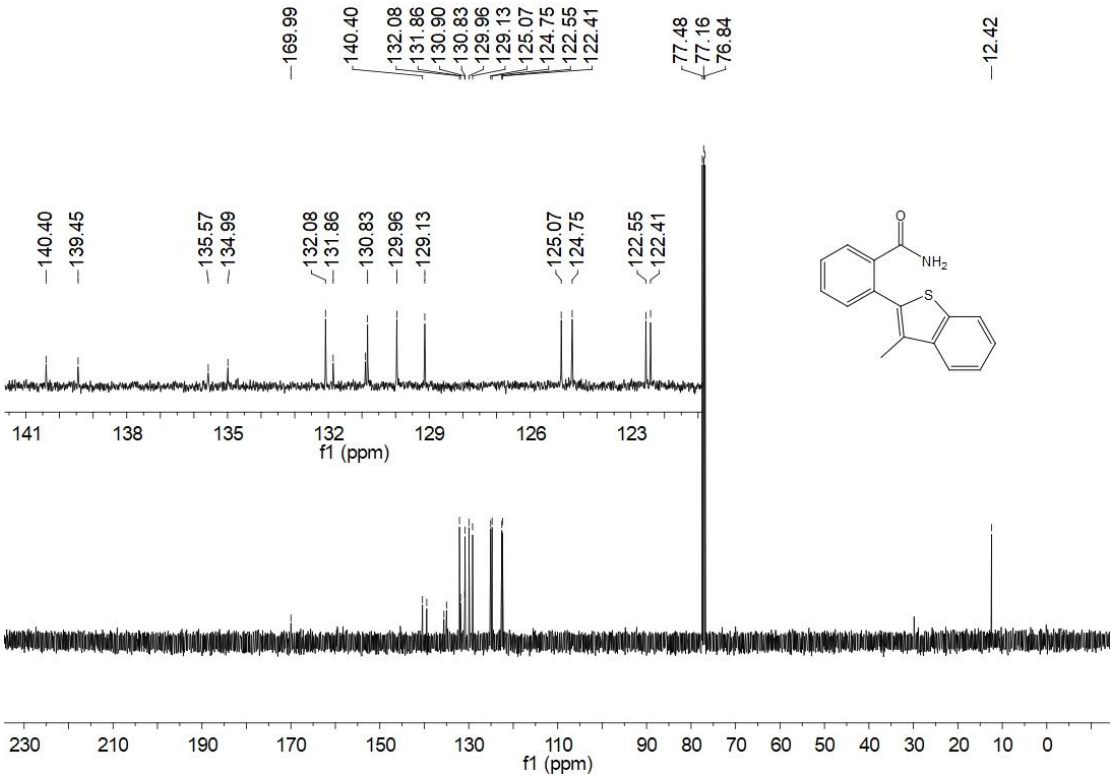

7.693
7.675
7.672
7.596
7.573
7.556
7.537
7.529
7.526
7.511
7.493
7.489
7.484
7.479
7.465
7.462
7.447
7.428
7.409
7.363
7.323
7.318
7.302
7.297
7.260
5.782
5.635

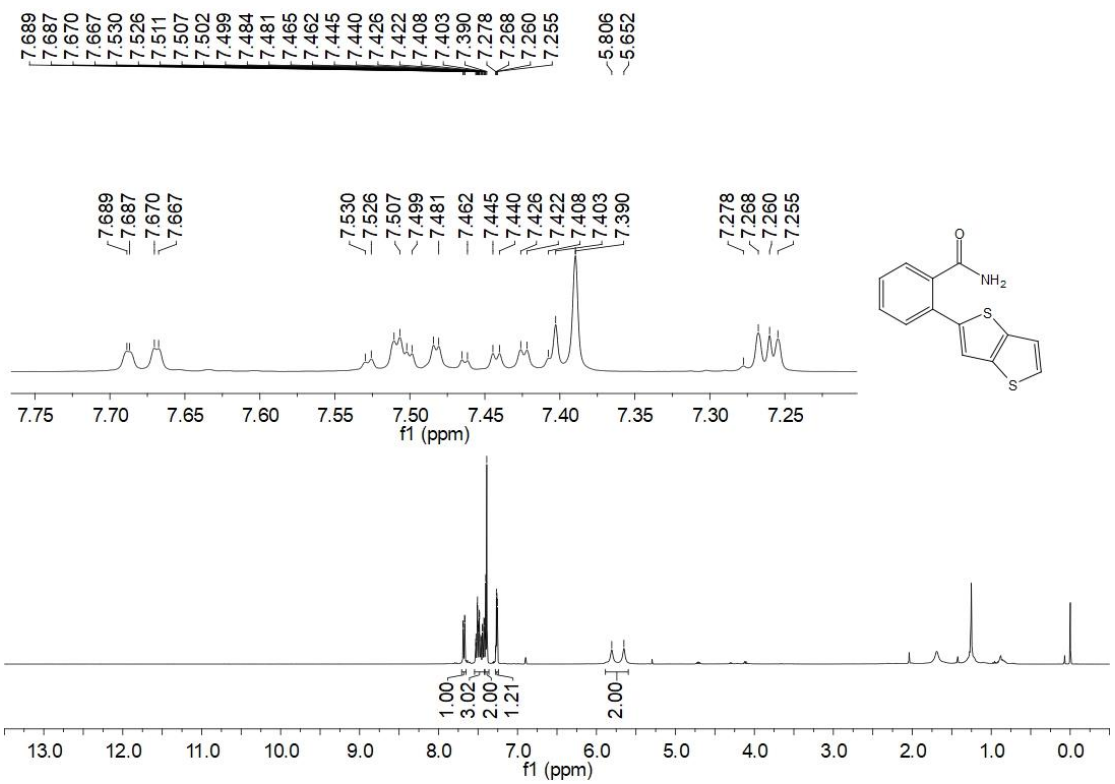

7.812
7.794
7.753
7.730
7.693
7.675
7.672
7.596
7.537
7.493
7.489
7.484
7.479
7.465
7.462
7.447
7.428
7.409
7.363
7.318
7.302
7.297
7.260
7.85
7.75
7.65
7.55
7.45
7.35
7.25
f1 (ppm)

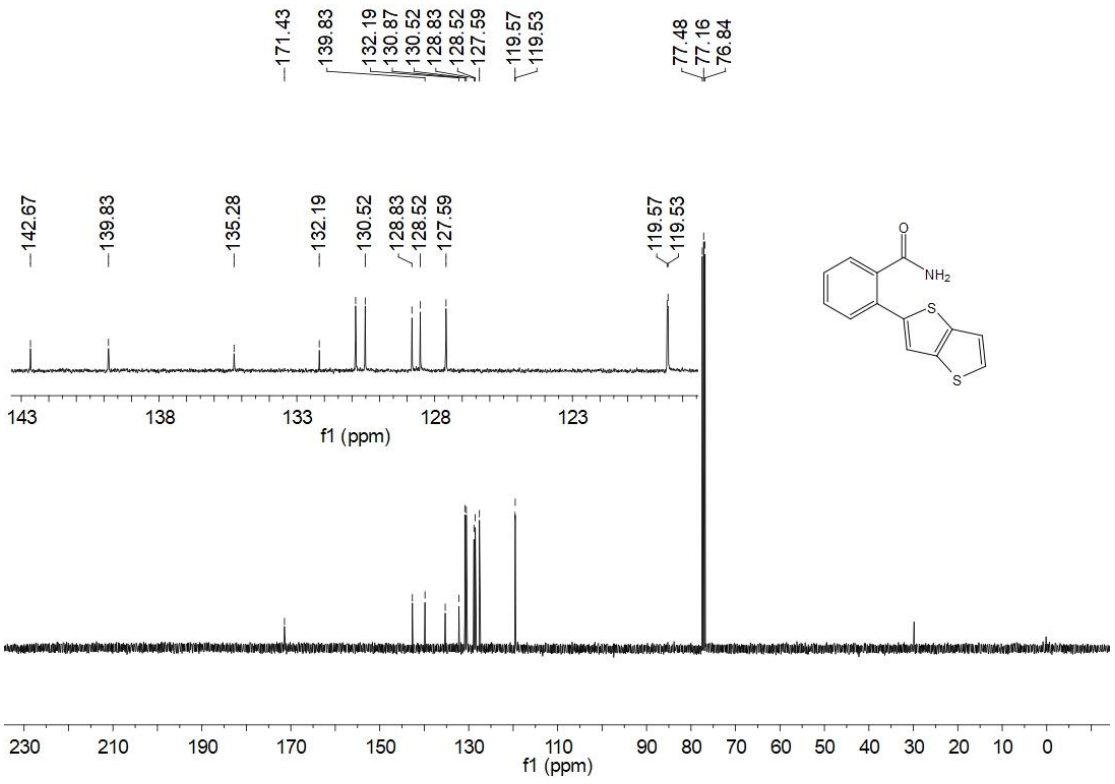

2.22
1.02
3.92
1.00
1.08
2.02
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

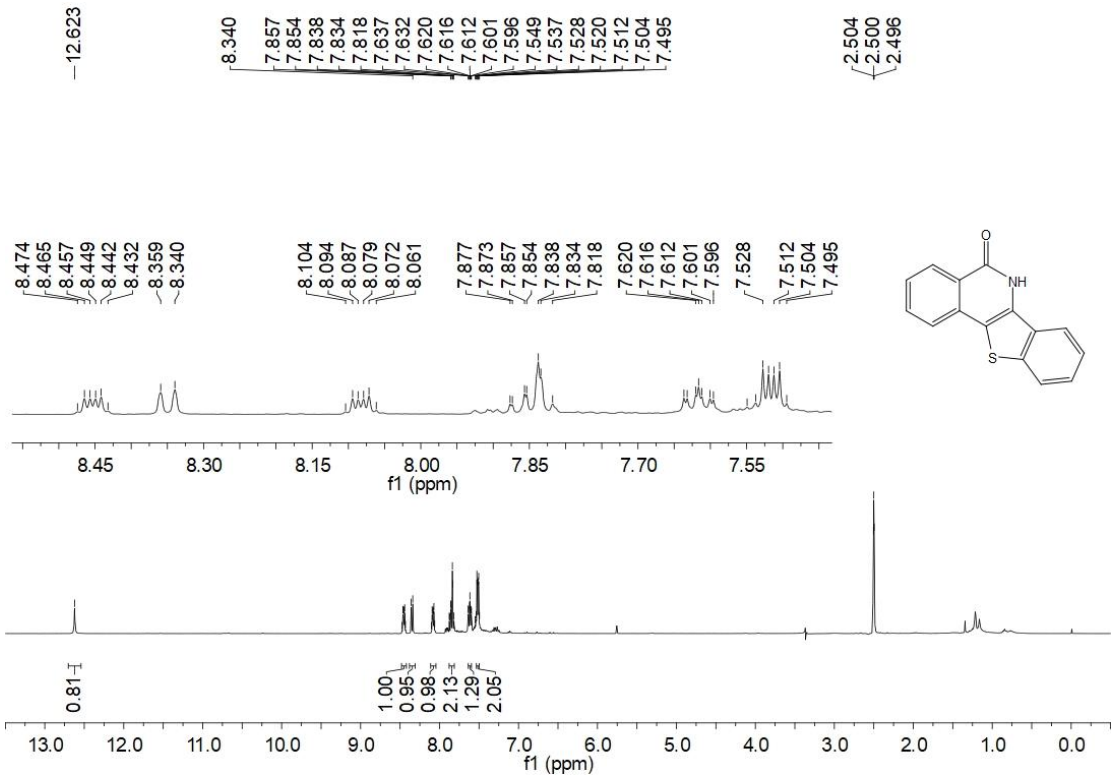

171.15
138.48
135.58
131.57
130.98
130.57
129.05
128.75
127.46
125.23
123.54
123.30
123.10
77.48
77.16
76.84
143.34
141.34
138.48
135.58
131.57
130.98
130.57
129.05
128.75
127.46
125.23
123.54
123.30
123.10
141
137
133
129
125
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

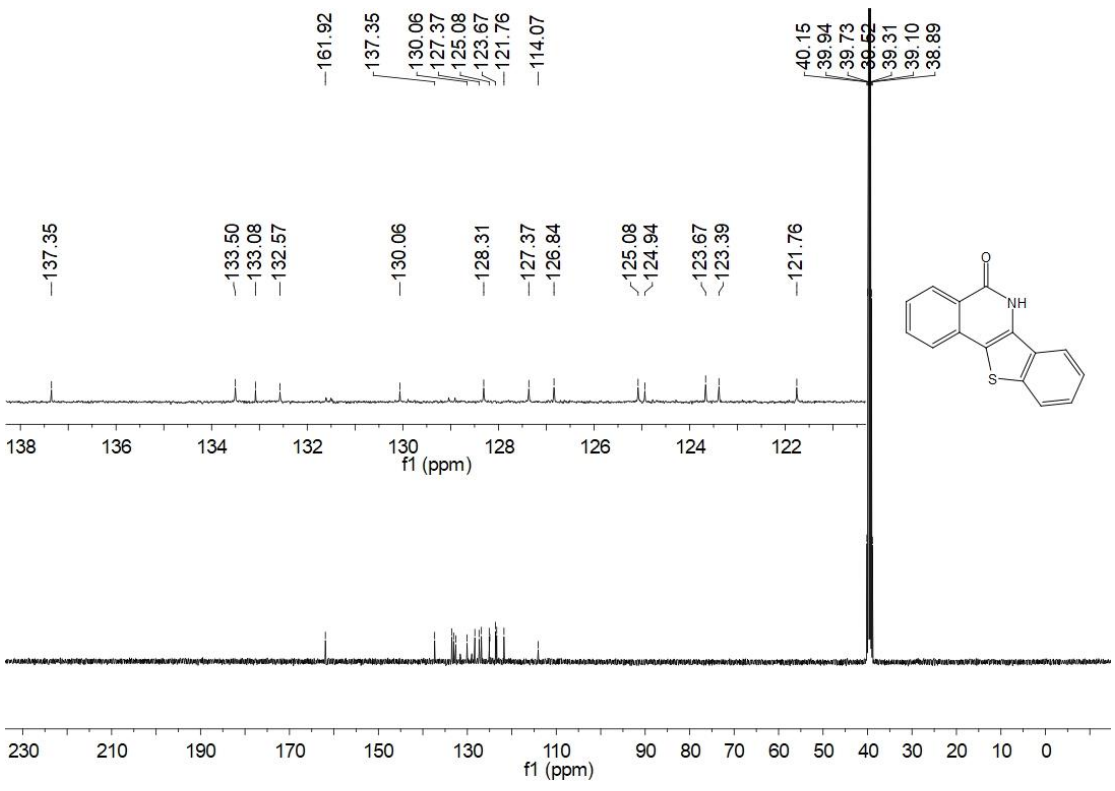

7.980
7.964
7.958
7.856
7.836
7.741
7.721
7.561
7.539
7.532
7.525
7.522
7.517
7.502
7.470
7.452
7.433
7.417
7.399
7.380
7.260
5.605
5.544
2.270
NH2
S
f1 (ppm)
1.03
0.98
1.06
2.08
3.00
2.00
3.00


169.99
140.40
132.08
131.86
130.90
130.83
129.96
129.13
125.07
124.75
122.55
122.41
77.48
77.16
76.84
12.42
NH2
S
f1 (ppm)


7.689
7.687
7.670
7.667
7.530
7.526
7.511
7.507
7.502
7.499
7.484
7.481
7.465
7.462
7.445
7.440
7.426
7.422
7.408
7.403
7.390
7.278
7.268
7.260
7.255
5.806
5.652
f1 (ppm)
1.00
3.02
2.00
1.21
2.00


171.43
139.83
132.19
130.87
130.52
128.83
128.52
127.59
119.57
119.53
77.48
77.16
76.84
142.67
139.83
135.28
132.19
130.52
128.83
128.52
127.59
119.57
119.53
f1 (ppm)


12.623
8.340
7.857
7.854
7.838
7.834
7.818
7.637
7.632
7.620
7.616
7.612
7.601
7.596
7.549
7.537
7.528
7.520
7.512
7.504
7.495
2.504
2.500
2.496
8.474
8.465
8.457
8.449
8.442
8.432
8.359
8.340
8.104
8.094
8.087
8.079
8.072
8.061
7.877
7.873
7.857
7.854
7.838
7.834
7.818
7.620
7.616
7.612
7.601
7.596
7.528
7.512
7.504
7.495
O
NH
S
8.45
8.30
8.15
8.00
7.85
7.70
7.55
f1 (ppm)
0.81
1.00
0.95
0.98
2.13
1.29
2.05
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


161.92
137.35
130.06
127.37
125.08
123.67
121.76
114.07
40.15
39.94
39.73
39.52
39.31
39.10
38.89
137.35
133.50
133.08
132.57
130.06
128.31
127.37
126.84
125.08
124.94
123.67
123.39
121.76
O
NH
S
138
136
134
132
130
128
126
124
122
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)