**Supporting information**

# Lewis Acid/Brønsted Acid Controlled Pd(II)-Catalysed Chemodivergent Functionalization of C($sp^2$)–H Bonds with *N*-(Arylthio)i(a)mides

*Manthena Chaitanya and Pazhamalai Anbarasan**

Department of Chemistry, Indian Institute of Technology Madras, Chennai-600036, India.

---

## Table of contents

## 1. General Comments:

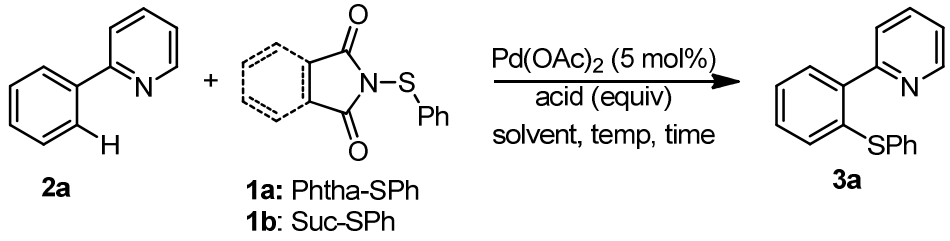
All reactions were carried out under an atmosphere of dry nitrogen using reaction tubes. Dry toluene was prepared by distilling over sodium ketyl and stored over molecular sieves 4Å under $N_2$ atmosphere. All the arylpyridine derivatives were synthesized from 2-bromopyridine derivatives and arylboronic acids employing literature procedure.[1] *N*-(phenylthio)pthalimide, *N*-(phenylthio)succinimide, *N*-(phenylthio)benzamide, 2-(phenylthio)-2,3-dihydrobenzo[*d*]isothiazole-1,1-dioxide, 1-(phenylthio)-1,2,3,4-tetrahydroquinoline and *N*,*N*-diisopropyl-*N*-(phenylthio)amine were prepared employing literature procedures.[2,3,4] $Pd(OAc)_2$ and $Cu(OAc)_2 \cdot H_2O$ were obtained from Aldrich and used as received. Column chromatography was performed using Rankem Silicagel (100-200 mesh) and the solvent system used unless otherwise specified, was ethyl acetate-hexanes with various percentage of polarity depending on the nature of the substrate.

## 2. Analytical Methods:

NMR data were recorded on Bruker DPX 400 and AVC 500 MHz spectrometers. $^{13}C$ and $^{1}H$ NMR spectra were referenced to signals of either deuterated solvents or residual protiated solvents. Infrared spectra were recorded on a Thermo Nicolet iS10 FT spectrometer. HRMS were recorded by electron spray ionization (ESI) method on a Q-TOF Micro with lock spray source.

[1] X. Rao, C. Liu, J. Qiu, Z. Jin, *Org. Biomol. Chem.* **2012**, *10*, 7875-7883.
[2] H. Shimada, S. Kikuchi, S. Okuda, K. Haraguchi, H. Tanaka, *Tetrahedron* **2009**, *65*, 6008-6016.
[3] P. Saravanan, P. Anbarasan, *Org. Lett*. **2014**, *16*, 848-851.
[4] N. Taniguchi, *Synlett* **2007**, *12*, 1917.

## 3. Optimization studies for the palladium catalyzed thiolation of C-H bonds:



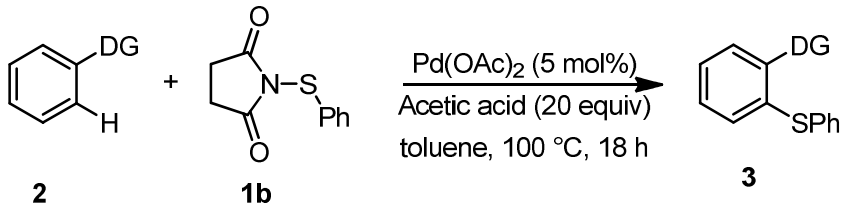

**2a** **1a:** Phtha-SPh **1b**: Suc-SPh **3a**

| Entry | 1a/1b | Acid (equiv) | Solvent | Temp (°C) | Time (h) | Yield (%) |
|---|---|---|---|---|---|---|
| 1 | **1a** | Acetic acid (20) | toluene | 100 | 18 | - |
| 2 | **1a** | TFA (20) | toluene | 100 | 18 | - |
| 3 | **1a** | - | Acetic acid | 80 | 18 | Trace |
| 4 | **1a** | - | Acetic acid | 100 | 18 | 53 |
| 5[a] | **1a** | - | Acetic acid | 100 | 18 | 13 |
| 6 | **1a** | - | Acetic acid | 120 | 18 | 63 |
| **7**[b] | **1a** | **-** | **Acetic acid** | **120** | **18** | **74** |
| 8 | **1a** | - | TFA | 100 | 18 | - |
| 9 | **1b** | - | Acetic acid | 100 | 12 | 43 |
| 10 | **1b** | - | Acetic acid | 80 | 12 | 20 |
| 11 | **1b** | - | Acetic acid | 120 | 12 | 47 |
| 12[a] | **1b** | - | Acetic acid | 120 | 12 | 63 |
| 13 | **1b** | Acetic acid (10) | Toluene | 120 | 12 | 67 |
| 14 | **1b** | Acetic acid (5) | Toluene | 120 | 12 | 54 |
| 15 | **1b** | Acetic acid (20) | Toluene | 120 | 12 | 70 |
| 16 | **1b** | TFA (20) | Toluene | 120 | 12 | 32 |
| 17 | **1b** | Acetic acid (20) | Toluene | 100 | 12 | 69 |
| 18[b] | **1b** | Acetic acid (20) | Toluene | 100 | 12 | 69 |
| 19 | **1b** | Acetic acid (20) | Xylene | 100 | 12 | 42 |
| 20 | **1b** | Acetic acid (20) | 1,4-dioxane | 100 | 12 | 24 |
| 21 | **1b** | Acetic acid (20) | $^{t}$AmOH | 100 | 12 | <10 |
| **22** | **1b** | **Acetic acid (20)** | **Toluene** | **100** | **18** | **80** |
| 23 | **1b** | Triflic acid (20) | Toluene | 100 | 18 | - |
| 24 | **1b** | Methane sulfonic acid (20) | Toluene | 100 | 18 | - |

| | | | | | | |
|---|---|---|---|---|---|---|
| 25 | **1b** | PTSA | Toluene | 100 | 18 | - |
| 26 | **1b** | Benzoic acid | Toluene | 100 | 18 | 22 |

Reaction conditions: 2-Phenyl pyridine **2a** (1 equiv), 2-(phenylthio)isoindoline-1,3-dione **1a** or 1-(phenylthio)pyrrolidine-2,5-dione **1b** (2 equiv), $Pd(OAc)_2$ (5 mol%), acid (equiv), solvent (1 mL), temp, time; [a] 3 equiv of 1-(phenylthio)pyrrolidine-2,5-dione **1a**; [b] 10 mol% of $Pd(OAc)_2$ was used.

## 4. General procedure for palladium catalyzed thiolation of C–H bonds:

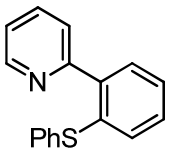



**2** **1b** **3**

A dry reaction tube (10 mL) was charged with arene **2** (0.2 mmol), *N*-(phenylthio)succinimide **1b** (0.4 mmol), $Pd(OAc)_2$ (5 mol%), acetic acid (20 equiv) and dry toluene (1 mL) under nitrogen atmosphere. The reaction tube was sealed under nitrogen atmosphere and kept at 100 °C for 18 h. After the completion of the reaction, as monitored by TLC, the reaction mixture was cooled to room temperature and purified by column chromatography using mixture of hexane and ethyl acetate as eluent to afford the analytically pure product **3**.

## 5. Properties of the isolated diarylsulfides:

**2-(2-(Phenylthio)phenyl)pyridine (3a)**




According to the general procedure the title compound **3a** was isolated in 80% yield (43 mg) as a yellow liquid using the mixture of hexane/ethyl acetate (90:10) as an eluent for column chromatography.

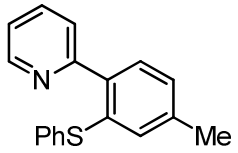
FTIR ($CHCl_3$): 2962, 2927, 1600, 1450, 1392, 1268, 1056, 710, 525 $cm^{-1}$.

$^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.73-8.64 (m, 1H), 7.70 (td, 1H, *J* = 7.5, 1.7 Hz), 7.56 (d, 1H, *J* = 7.8 Hz), 7.54-7.49 (m, 1H), 7.32-7.29 (m, 2H), 7.28-7.17 (m, 7H).

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.2 (C), 149.0 (CH), 141.1 (C), 136.0 (CH), 135.5 (C), 135.4 (C), 132.2 (CH), 131.3 (CH), 130.4 (CH), 129.2 (CH), 129.0 (CH), 127.3 (CH), 126.7 (CH), 124.3 (CH), 122.2 (CH).

HRMS: calcd. for $C_{17}H_{13}NS$+H: 264.0846; found: 264.0849.

**2-(4-Methyl-2-(phenylthio)phenyl)pyridine (3b)**




According to the general procedure the title compound **3b** was isolated in 63% yield (35 mg) as a yellow liquid using the mixture of hexane/ethyl acetate (90:10) as an eluent for column chromatography.

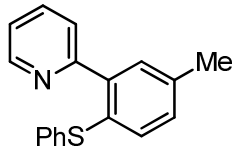
FTIR ($CHCl_3$): 3053, 2925, 1589, 1466, 1265, 909, 736, 650 $cm^{-1}$.

$^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.65 (ddd, 1H, *J* = 4.8, 1.7, 0.9 Hz), 7.66 (td, 1H, *J* = 7.7, 1.8 Hz), 7.54 (dt, 1H, *J* = 7.9, 1.0 Hz), 7.44 (d, 1H, *J* = 7.7 Hz), 7.28-7.17 (m, 6H), 7.15-7.09 (m, 2H), 2.27 (s, 3H).

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.4 (C), 149.0 (CH), 139.0 (C), 136.2 (C), 135.8 (CH), 134.4 (C), 132.6 (CH), 132.1 (C), 131.4 (CH), 130.4 (CH), 129.1 (CH), 128.1 (CH), 127.0 (CH), 124.4 (CH), 121.9 (CH), 21.2 ($CH_3$).

HRMS: calcd. for $C_{18}H_{15}NS$+H: 278.1003; found: 278.1011.

**2-(5-Methyl-2-(phenylthio)phenyl)pyridine (3c)**




According to the general procedure the title compound **3c** was isolated in 73% yield (40 mg) as a yellow liquid using the mixture of hexane/ethyl acetate (90:10) as an eluent for column chromatography.

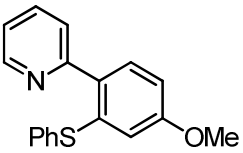
FTIR ($CHCl_3$): 2988, 2925, 2857, 1586, 1428, 1265, 909, 736, 650 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.65 (ddd, 1H, *J* = 4.8, 1.7, 0.9 Hz), 7.66 (td, 1H, *J* = 7.8, 1.8 Hz), 7.55 (dt, 1H, *J* = 7.9, 1.1 Hz), 7.40-7.38 (m, 1H), 7.26-7.23 (m, 1H), 7.22-7.18 (m, 5H), 7.17-7.09 (m, 2H), 2.37 (s, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.4 (C), 149.1 (CH), 142.4 (C), 137.6 (C), 137.0 (C), 135.7 (CH), 133.2 (CH), 131.4 (CH), 130.7 (CH), 130.6 (C), 130.0 (CH), 129.1 (CH), 126.6 (CH), 124.5 (CH), 122.1 (CH), 21.1 ($CH_3$).

HRMS: calcd. for $C_{18}H_{15}NS$+H: 278.1003; found: 278.1027.

**2-(4-Methoxy-2-(phenylthio)phenyl)pyridine (3d)**



According to the general procedure the title compound **3d** was isolated in 75% yield (44 mg) as a yellow liquid using the mixture of hexane/ethyl acetate (88:12) as an eluent for column chromatography.

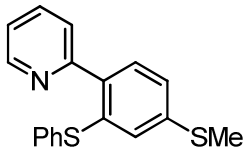
FTIR ($CHCl_3$): 3007, 2929, 2851, 1593, 1465, 1270, 1043, 782, 648 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.70-8.62 (m, 1H), 7.68 (td, 1H, *J* = 7.7, 1.7 Hz), 7.55 (dt, 1H, *J* = 7.8, 0.9 Hz), 7.47 (d, 1H, *J* = 8.4 Hz), 7.37-7.32 (m, 2H), 7.29-7.22 (m, 3H), 7.19 (ddd, 1H, *J* = 7.5, 4.9, 1.2 Hz), 6.83 (dd, 1H, *J* = 8.5, 2.6 Hz), 6.72 (d, 1H, *J* = 2.5 Hz), 3.69 (s, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 159.9 (C), 158.1 (C), 149.0 (CH), 137.0 (C), 135.9 (CH), 135.2 (C), 133.8 (C), 132.6 (CH), 131.5 (CH), 129.3 (CH), 127.6 (CH), 124.2 (CH), 121.8 (CH), 116.3 (CH), 112.4 (CH), 55.4 ($CH_3$).

HRMS: calcd. for $C_{18}H_{15}NOS+H$: 294.0953; found: 294.0965.

**2-(4-(Methylthio)-2-(phenylthio)phenyl)pyridine (3e)**




According to the general procedure the title compound **3e** was isolated in 58% yield (36 mg) as a yellow liquid using the mixture of hexane/ethyl acetate (90:10) as an eluent for column chromatography.

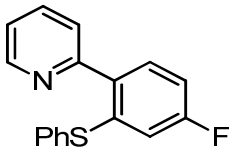
FTIR ($CHCl_3$): 3055, 2922, 2854, 1582, 1461, 1260, 1021, 786, 694 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.60 (ddd, 1H, *J* = 4.8, 1.8, 0.9 Hz), 7.62 (td, 1H, *J* = 7.7, 1.7 Hz), 7.49 (dt, 1H, *J* = 7.8, 1.0 Hz), 7.37 (d, 1H, *J* = 8.0 Hz), 7.27-7.23 (m, 2H), 7.22-7.11 (m, 4H), 7.08 (dd, 1H, *J* = 8.0, 1.8 Hz), 6.95 (d, 1H, *J* = 1.8 Hz), 2.24 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 157.8 (C), 149.1 (CH), 139.9 (C), 137.6 (C), 136.5 (C), 136.0 (CH), 135.0 (C), 132.6 (CH), 130.6 (CH), 129.3 (CH), 128.1 (CH), 127.7 (CH), 124.5 (CH), 124.2 (CH), 122.1 (CH), 15.5 ($CH_3$).

HRMS: calcd. for $C_{18}H_{15}NS_2$+H: 310.0724; found: 310.0704.

**2-(4-Fluoro-2-(phenylthio)phenyl)pyridine (3g)**




According to the general procedure the title compound **3g** was isolated in 31% yield (18 mg) as a yellow liquid using the mixture of hexane/ethyl acetate (90:10) as an eluent for column chromatography.

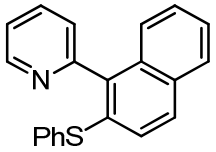
FTIR ($CHCl_3$): 3054, 2985, 2927, 1595, 1465, 1264, 908, 737, 650 $cm^{-1}$.

$^{1}H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.71 (d, 1H, $J$ = 3.8 Hz), 7.75 (td, 1H, $J$ = 7.4, 2.0 Hz), 7.57 (d, 1H, $J$ = 7.6 Hz), 7.51-7.44 (m, 1H), 7.44-7.37 (m, 2H), 7.37-7.29 (m, 3H), 7.29-7.24 (m, 1H), 6.94 (td, 1H, $J$ = 8.3, 2.4 Hz), 6.77 (dd, 1H, $J$ = 9.7, 2.7 Hz).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 162.9 (d, $J$ = 249.3 Hz, C), 157.5 (C), 149.2 (CH), 139.4 (d, $J$ = 7.9 Hz, C), 136.3 (CH), 136.1 (d, $J$ = 3.5 Hz, C), 133.8 (CH), 133.7 (C), 131.8 (d, $J$ = 8.7 Hz, CH), 129.6 (CH), 128.5 (CH), 124.2 (CH), 122.3 (CH), 116.3 (d, $J$ = 24.2 Hz, CH), 113.2 (d, $J$ = 21.6 Hz, CH).

HRMS: calcd. for $C_{17}H_{12}NFS$+H: 282.0753; found: 282.0759.

**2-(2-(Phenylthio)naphthalen-1-yl)pyridine (3i)**




According to the general procedure the title compound **3i** was isolated in 87% yield (54 mg) as a colorless liquid using the mixture of hexane/ethyl acetate (90:10) as an eluent for column chromatography.

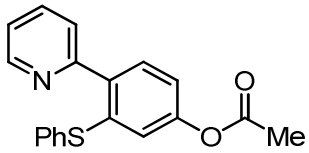
FTIR ($CHCl_3$): 3054, 2986, 2915, 1588, 1473, 1265, 812, 737, 650 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.68 (d, 1H, $J$ = 4.5 Hz), 7.76-7.57 (m, 3H), 7.37-7.30 (m, 2H), 7.30-7.25 (m, 3H), 7.25-7.16 (m, 3H), 7.16-7.02 (m, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 157.6 (C), 149.6 (CH), 139.3 (C), 136.2 (CH), 136.1 (C), 132.7 (C), 132.6 (C), 132.5 (C), 131.4 (CH), 129.1(9) (CH), 129.1(6) (CH), 128.8 (CH), 128.0 (CH), 127.0 (CH), 126.9 (CH), 126.0 (CH), 125.9 (CH), 125.8 (CH), 122.5 (CH).

HRMS: calcd. for $C_{21}H_{15}NS$+H: 314.1003; found: 314.1022.

**3-(Phenylthio)-4-(pyridin-2-yl)phenyl acetate (3j)**




According to the general procedure the title compound **3j** was isolated in 63% yield (40 mg) as a white solid using the mixture of hexane/ethyl acetate (82:18) as an eluent for column chromatography.

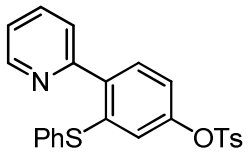
FTIR (KBr): 3058, 2925, 2855, 1723, 1592, 1466, 1268, 888, 790, 637 $cm^{-1}$.

$^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.61 (ddd, 1H, *J* = 4.8, 1.5, 0.8 Hz), 7.65 (td, 1H, *J* = 7.6, 1.7 Hz), 7.49 (dt, 1H, *J* = 7.8, 0.9 Hz), 7.44 (d, 1H, *J* = 8.3 Hz), 7.32-7.26 (m, 2H), 7.24-7.15 (m, 4H), 6.94 (dd, 1H, *J* = 8.4, 2.3 Hz), 6.78 (d, 1H, *J* = 2.2 Hz), 2.14 (s, 3H).

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 169.1 (C) , 157.5 (C), 151.0 (C), 149.1 (CH), 138.0 (C), 137.8 (C), 136.2 (CH), 134.4 (C), 133.0 (CH), 131.2 (CH), 129.5 (CH), 128.0 (CH), 124.3 (CH), 123.1 (CH), 122.3 (CH), 119.7 (CH), 21.1 ($CH_3$).

HRMS: calcd. for $C_{19}H_{15}NO_2S$+H: 322.0901; found: 322.0915.

**3-(Phenylthio)-4-(pyridin-2-yl)phenyl 4-methylbenzenesulfonate (3k)**




According to the general procedure the title compound **3k** was isolated in 50% yield (43 mg) as a colorless liquid using the mixture of hexane/ethyl acetate (80:20) as an eluent for column chromatography.

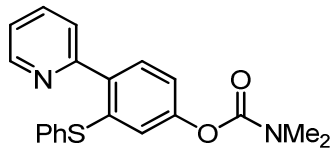
FTIR ($CHCl_3$): 3057, 2925, 2855, 1589, 1462, 1263, 817, 785, 661 $cm^{-1}$.

$^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.68 (s, 1H), 7.72 (s, 1H), 7.61 (s, 2H), 7.54 (s, 1H), 7.42 (t, 1H, *J* = 4.1 Hz), 7.30-7.22 (m, 8H), 6.93 (d, 1H, *J* = 6.2 Hz), 6.63 (s, 1H), 2.43 (s, 3H).

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 157.0 (C) , 149.9 (C), 149.1 (CH), 145.3 (C), 138.8 (C), 138.5 (C), 136.3 (CH), 133.5 (CH), 133.3 (C), 132.1 (C), 131.3 (CH), 129.8 (CH), 129.5 (CH), 128.5 (CH), 128.3 (CH), 124.1 (CH), 123.0 (CH), 122.5 (CH), 119.9 (CH), 21.8 ($CH_3$).

HRMS: calcd. for $C_{24}H_{19}NO_3S_2$+K: 472.0443; found: 472.0442.

**3-(Phenylthio)-4-(pyridin-2-yl)phenyl dimethylcarbamate (3l)**




According to the general procedure the title compound **3l** was isolated in 73% yield (51 mg) as a white solid using the mixture of hexane/ethyl acetate (82:18) as an eluent for column chromatography.

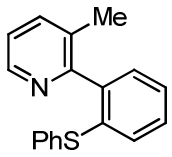
FTIR (KBr): 3055, 2925, 1724, 1586, 1465, 1264, 909, 736, 650 $cm^{-1}$.

$^{1}H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.67 (s, 1H), 7.70 (t, 1H, *J* = 7.2 Hz), 7.58-7.49 (m, 2H), 7.37-7.30 (m, 2H), 7.29-7.20 (m, 4H), 7.07 (d, 1H, *J* = 8.2 Hz), 6.95 (s, 1H), 3.02 (s, 3H), 2.95 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 157.7 (C), 154.4 (C), 151.8 (C), 149.0 (CH), 137.8 (C), 136.8 (C), 136.0 (CH), 134.8 (C), 132.4 (CH), 131.1 (CH), 129.3 (CH), 127.6 (CH), 124.3 (CH), 123.8 (CH), 122.1 (CH), 120.3 (CH), 36.7 ($CH_3$), 36.5 ($CH_3$).

HRMS: calcd. for $C_{20}H_{18}N_2O_2S$+H: 351.1167; found: 351.1172.

**3-Methyl-2-(2-(phenylthio)phenyl)pyridine (3m)**




According to the general procedure the title compound **3m** was isolated in 93% yield (52 mg) as a colorless liquid using the mixture of hexane/ethyl acetate (90:10) as an eluent for column chromatography.

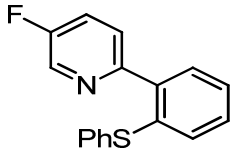
FTIR ($CHCl_3$): 3023, 2958, 2896, 1600, 1438, 1265, 1052, 732, 646 $cm^{-1}$.

$^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.38 (dd, 1H, *J* = 4.7, 0.8 Hz), 7.44 (dd, 1H, *J* = 7.7, 0.7 Hz), 7.20-7.07 (m, 10H), 2.08 (s, 3H).

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.1 (C), 146.5 (CH), 141.3 (C), 137.7 (CH), 135.6 (C), 134.9 (C), 132.1 (CH), 132.0 (C), 130.9 (CH), 129.5 (CH), 129.1 (CH), 128.7 (CH), 127.3 (CH), 126.8 (CH), 122.7 (CH), 19.2 ($CH_3$).

HRMS: calcd. for $C_{18}H_{15}NS$+H: 278.1003; found: 278.1013.

**5-Fluoro-2-(2-(phenylthio)phenyl)pyridine (3n)**




According to the general procedure the title compound **3n** was isolated in 70% yield (39 mg) as a yellow liquid using the mixture of hexane/ethyl acetate (90:10) as an eluent for column chromatography.

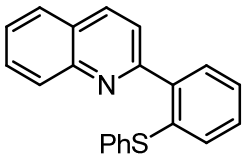
FTIR ($CHCl_3$): 3060, 2984, 2939, 1584, 1461, 1243, 1046, 914, 735, 601 $cm^{-1}$.

$^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.53 (d, 1H, *J* = 2.9 Hz), 7.57 (ddd, 1H, *J* = 8.6, 4.4, 0.5 Hz), 7.52-7.48 (m, 1H), 7.41 (td, 1H, *J* = 8.2, 2.8 Hz), 7.32-7.21 (m, 8H).

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.5 (d, *J* = 256.4 Hz, C), 154.3 (d, *J* = 4.1 Hz, C), 140.3 (C), 137.2 (d, *J* = 23.6 Hz, CH), 135.3 (C), 135.2 (C), 131.9 (CH), 131.6 (CH), 130.3 (CH), 129.2 (CH), 129.1 (CH), 127.3 (CH), 126.9 (CH), 126.2 (d, *J* = 4.1 Hz, CH), 122.8 (d, *J* = 18.4 Hz, CH).

HRMS: calcd. for $C_{17}H_{12}NFS$+H: 282.0753; found: 282.0761.

**2-(2-(Phenylthio)phenyl)quinoline (3p)**




According to the general procedure the title compound **3p** was isolated in 42% yield (26 mg) as a yellow liquid using the mixture of hexane/ethyl acetate (90:10) as an eluent for column chromatography.

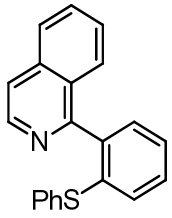
FTIR ($CHCl_3$): 3055, 2926, 2856, 1595, 1431, 1266, 1034, 832, 741 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.13-8.05 (m, 2H), 7.74 (dd, 1H, $J$ = 8.0, 0.9 Hz), 7.66-7.59 (m, 2H), 7.58-7.55 (m, 1H), 7.45 (ddd, 1H, $J$ = 8.0, 6.8, 1.0 Hz), 7.29-7.07 (m, 8H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.5 (C), 147.7 (C), 141.6 (C), 135.9 (CH), 135.8 (C), 132.2 (CH), 131.7 (CH), 130.5 (CH), 129.7 (CH), 129.6 (CH), 129.3 (CH), 129.2(7) (CH), 129.2 (3) (C), 127.6 (CH), 127.4 (CH), 127.0(8) (C), 127.0(0) (CH), 126.7 (CH), 122.3 (CH).

HRMS: calcd. for $C_{21}H_{15}NS$+H: 314.1003; found: 314.1002.

**1-(2-(Phenylthio)phenyl)isoquinoline (3q)**




According to the general procedure the title compound **3q** was isolated in 89% yield (55 mg) as a colorless liquid using the mixture of hexane/ethyl acetate (90:10) as an eluent for column chromatography.

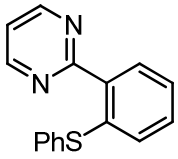
FTIR ($CHCl_3$): 3039, 2927, 1596, 1427, 1353, 1076, 1056, 721 $cm^{-1}$.

$^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.58 (d, 1H, *J* = 5.7 Hz), 7.84 (d, 1H, *J* = 8.0), 7.22-7.62 (m, 3H), 7.50-7.44 (m, 1H), 7.43-7.39 (m, 1H), 7.38-7.30 (m, 3H), 7.26-7.10 (m, 5H).

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 159.9 (C), 142.0 (CH), 140.2 (C), 136.7 (C), 136.3 (C), 135.1 (C), 132.3 (CH), 131.3 (CH), 130.5 (CH), 130.1 (CH), 129.2 (CH), 129.0 (CH), 127.5 (C), 127.4 (CH), 127.3 (CH), 127.2 (CH), 126.9 (CH), 126.6 (CH), 120.4 (CH).

HRMS: calcd. for $C_{21}H_{15}NS$+H: 314.1003; found: 314.0989.

**2-(2-(Phenylthio)phenyl)pyrimidine (3r)**




According to the general procedure the title compound **3r** was isolated in 47% yield (25 mg) as a yellow liquid using the mixture of hexane/ethyl acetate (90:10) as an eluent for column chromatography.

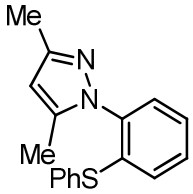
FTIR ($CHCl_3$): 3004, 2946, 2864, 1592, 1434, 1265, 910, 728 $cm^{-1}$.

$^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.88 (d, 2H, *J* = 4.8 Hz), 8.07-7.99 (m, 1H), 7.50-7.46 (m, 2H), 7.35-7.30 (m, 3H), 7.26-7.22 (m, 3H), 7.08-7.04 (m, 1H).

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 165.7 (C), 156.7 (CH), 139.0 (C), 137.1 (C), 135.0 (C), 134.2 (CH), 130.8 (CH), 130.1 (CH), 129.5 (CH), 129.4 (CH), 128.2 (CH), 125.5 (CH), 118.9 (CH).

HRMS: calcd. for $C_{16}H_{12}N_2S$+H: 265.0799; found: 265.0793.

**3,5-Dimethyl-1-(2-(phenylthio)phenyl)-1*H*-pyrazole (3s)**




According to the general procedure with 10 mol% $Pd(OAc)_2$ the title compound **3s** was isolated in 23% yield (13 mg) as a colorless liquid using the mixture of hexane/ethyl acetate (90:10) as an eluent for column chromatography.

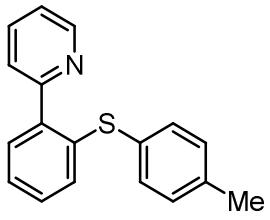
FTIR ($CHCl_3$): 3053, 2979, 2926, 1583, 1438, 1265, 1028, 896, 739 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.43-7.41 (m, 1H), 7.41-7.39 (m, 1H), 7.34-7.30 (m, 3H), 7.27-7.22 (m, 3H), 7.06-7.02 (m, 1H), 5.98 (s, 1H), 2.30 (s, 3H), 2.15 (s, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 149.2 (C), 140.9 (C), 138.0 (C), 137.8 (C), 134.1 (CH), 132.7 (C), 129.5(5) (CH), 129.5(2) (CH), 129.4 (CH), 128.8 (CH), 128.4 (CH), 126.5 (CH), 105.5 (CH), 13.7 ($CH_3$), 11.5 ($CH_3$).

HRMS: calcd. for $C_{17}H_{16}N_2S$+H: 281.1112; found: 281.1103.

**2-(2-(*p*-Tolylthio)phenyl)pyridine (3t)**




According to the general procedure the title compound **3t** was isolated in 70% yield (39 mg) as a colorless liquid using the mixture of hexane/ethyl acetate (90:10) as an eluent for column chromatography.

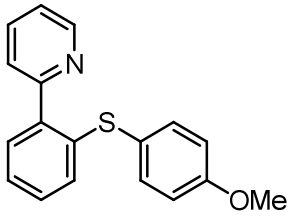
FTIR ($CHCl_3$): 3043, 2948, 1603, 1430, 1265, 1039, 745, 659 $cm^{-1}$.

$^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.71 (ddd, 1H, *J* = 4.9, 1.8, 0.9 Hz), 7.73 (td, 1H, *J* = 7.7, 1.8 Hz), 7.59 (dt, 1H, *J* = 7.8, 1.0 Hz), 7.51-7.47 (m, 1H), 7.28-7.22 (m, 5H), 7.14-7.07 (m, 3H), 2.32 (s, 3H).

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.4 (C), 149.1 (CH), 140.5 (C), 137.9 (C), 136.7 (C), 136.1 (CH), 133.2 (CH), 131.4 (C), 130.5 (CH), 130.3 (CH), 130.2 (CH), 128.9 (CH), 126.2 (CH), 124.3 (CH), 122.2 (CH).

HRMS: calcd. for $C_{18}H_{15}NS$+H: 278.1003; found: 278.1015.

**2-(2-((4-Methoxyphenyl)thio)phenyl)pyridine (3u)**




According to the general procedure the title compound **3u** was isolated in 72% yield (42 mg) as a colorless liquid using the mixture of hexane/ethyl acetate (90:10) as an eluent for column chromatography.

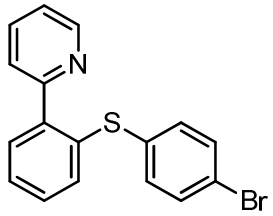
FTIR ($CHCl_3$): 3004, 2954, 1604, 1457, 1265, 1052, 732 $cm^{-1}$.

$^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.72 (ddd, 1H, *J* = 4.8, 1.7, 0.9 Hz), 7.76 (td, 1H, *J* = 7.7, 1.8 Hz), 7.60 (dt, 1H, *J* = 7.8, 0.9 Hz), 7.48-7.44 (m, 1H), 7.39-7.33 (m, 2H), 7.27 (ddd, 1H, *J* = 7.5, 4.9, 1.1 Hz), 7.23-7.17 (m, 2H), 7.02-6.97 (m, 1H), 6.88-6.84 (m, 2H), 3.80 (s, 3H).

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 160.0 (C), 158.5 (C), 149.1 (CH), 139.5 (C), 138.1 (C), 136.2 (CH), 136.1 (CH), 130.1 (CH), 128.9 (CH), 128.8 (CH), 125.6 (CH), 124.6 (C), 124.3 (CH), 122.2 (CH), 115.1 (CH), 55.4 ($OCH_3$).

HRMS: calcd. for $C_{18}H_{15}NOS$+H: 294.0953; found: 294.0966.

**2-(2-((4-Bromophenyl)thio)phenyl)pyridine (3v)**




According to the general procedure the title compound **3v** was isolated in 55% yield (38 mg) as a colorless liquid using the mixture of hexane/ethyl acetate (90:10) as an eluent for column chromatography.

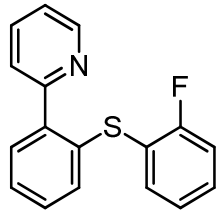
FTIR ($CHCl_3$): 3053, 2986, 2926, 1592, 1466, 1265, 896, 739 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.68 (ddd, 1H, $J$ = 4.8, 1.7, 0.9 Hz), 7.72 (td, 1H, $J$ = 7.6, 1.7 Hz), 7.57-7.51 (m, 2H), 7.38-7.30 (m, 3H), 7.29-7.23 (m, 3H), 7.15-7.09 (m, 2H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.2 (C), 149.1 (CH), 141.8 (C), 136.1 (CH), 135.4 (C), 134.5 (C), 133.2 (CH), 132.3 (CH), 132.1 (CH), 130.6 (CH), 129.2 (CH), 127.4 (CH), 124.3 (C), 122.3 (CH), 121.3 (C).

HRMS: calcd. for $C_{17}H_{12}NSBr$+H: 341.9952; found: 341.9978.

**2-(2-((2-Fluorophenyl)thio)phenyl)pyridine (3w)**




According to the general procedure the title compound **3w** was isolated in 80% yield (45 mg) as a yellow liquid using the mixture of hexane/ethyl acetate (90:10) as an eluent for column chromatography.

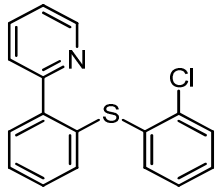
FTIR ($CHCl_3$): 3053, 2987, 2926, 1586, 1470, 1265, 908, 738, 651 $cm^{-1}$.

$^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.71-8.66 (m, 1H), 7.75-7.67 (m, 1H), 7.60 (d, 1H, *J* = 7.8 Hz), 7.53 (dd, 1H, *J* = 7.4, 1.6 Hz), 7.33-7.16 (m, 6H), 7.06-6.98 (m, 2H).

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 161.6 (d, *J* = 244.6 Hz, C), 158.1 (C), 149.0 (CH), 141.2 (C), 136.1 (CH), 135.0 (C), 134.7 (CH), 134.0 (C), 130.9 (CH), 130.4 (CH), 129.7 (d, *J* = 7.7 Hz, CH), 129.0 (CH), 126.9 (CH), 124.7 (d, *J* = 3.9 Hz, CH). 124.1 (CH), 122.2 (CH), 115.9 (d, *J* = 22.1 Hz, CH).

HRMS: calcd. for $C_{17}H_{12}NFS$+Na: 304.0572; found: 304.0573.

**2-(2-((2-Chlorophenyl)thio)phenyl)pyridine (3x)**




According to the general procedure the title compound **3x** was isolated in 56% yield (33 mg) as a yellow liquid using the mixture of hexane/ethyl acetate (90:10) as an eluent for column chromatography.

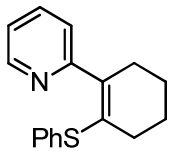
FTIR ($CHCl_3$): 3031, 2946, 2896, 1608, 1438, 1265, 1068, 910, 728 $cm^{-1}$.

$^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.65 (ddd, 1H, *J* = 4.8, 1.6, 0.9 Hz), 7.69 (td, 1H, *J* = 7.7, 1.8 Hz), 7.62-7.57 (m, 2H), 7.43-7.37 (m, 1H), 7.34-7.29 (m, 3H), 7.21 (ddd, 1H, *J* = 7.5, 4.8, 1.1 Hz), 7.12-7.07 (m, 3H).

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 158.0 (C), 149.2 (CH), 149.1 (C), 142.8 (C), 135.9 (CH), 134.5 (C), 133.3 (CH), 132.6 (C), 132.2 (CH), 130.9 (CH), 129.8 (CH), 129.3 (CH), 128.1 (CH), 127.8 (CH), 127.3 (CH), 124.3 (CH), 122.2 (CH).

HRMS: calcd. for $C_{17}H_{12}NSCl$+H: 298.0457; found: 298.0445.

**2-(2-(Phenylthio)cyclohex-1-en-1-yl)pyridine (6a)**




According to the general procedure the title compound **6a** was isolated in 77% yield (41 mg) as a yellow liquid using the mixture of hexane/ethyl acetate (92:8) as an eluent for column chromatography.

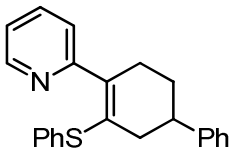
FTIR ($CHCl_3$): 3060, 2929, 2855, 1583, 1467, 1020, 742, 625, 536, 449 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.60-8.56 (m, 1H), 7.79 (td, 1H, $J$ = 7.6, 1.7 Hz), 7.33-7.20 (m, 1H), 7.28-7.22 (m, 4H), 7.17-7.10 (m, 2H), 2.62-2.58 (m, 2H), 2.31-2.26 (m, 2H), 1.83-1.77 (m, 2H), 1.77-1.70 (m, 2H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 160.4 (C), 148.9 (CH), 143.3 (C), 135.8 (CH), 135.7 (C), 129.9 (CH), 129.1 (C), 128.8 (CH), 126.1 (CH), 123.6 (CH), 121.8 (CH), 31.7 ($CH_2$), 31.3 ($CH_2$), 23.8 ($CH_2$), 22.6 ($CH_2$).

HRMS: calcd. for $C_{17}H_{17}NS$+H: 268.1160; found: 268.1189.

**2-(5-(Phenylthio)-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)pyridine (6c)**




According to the general procedure the title compound **6c** was isolated in 65% yield (45 mg) as a yellow liquid using the mixture of hexane/ethyl acetate (92:8) as an eluent for column chromatography.

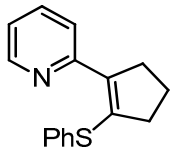
FTIR ($CHCl_3$): 3058, 2925, 2853, 1583, 1467, 1260, 1023, 743, 530, 410 $cm^{-1}$.

$^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.52 (d, 1H, *J* = 4.3 Hz), 7.53 (td, 1H, *J* = 7.7, 1.8 Hz), 7.29 (d, 1H, *J* = 7.7 Hz), 7.22-7.12 (m, 6H), 7.11-7.07 (m, 3H), 7.07-7.00 (m, 2H), 2.95-2.85 (m, 1H), 2.79 (dt, 1H, *J* = 18.1, 2.5 Hz), 2.71-2.58 (m, 1H), 2.55-2.45 (m, 1H), 2.41-2.31 (m, 1H), 2.08-1.98 (m, 1H), 1.94-1.81 (m, 1H).

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 160.0 (C), 149.0 (CH), 145.7 (C), 142.9 (C), 135.9 (CH), 135.2 (C), 130.0 (CH), 128.9 (CH), 128.8 (C), 128.5 (CH), 126.9 (CH), 126.3(6) (CH), 126.3(2) (CH), 123.8 (CH), 122.0 (CH), 41.3 (CH), 39.1 ($CH_2$), 32.4 ($CH_2$), 29.8 ($CH_2$).

HRMS: calcd. for $C_{23}H_{21}NS$+H: 344.1473; found: 344.1458.

**2-(2-(Phenylthio)cyclopent-1-en-1-yl)pyridine (6d)**




According to the general procedure the title compound **6d** was isolated in 50% yield (25 mg) as a yellow liquid using the mixture of hexane/ethyl acetate (92:8) as an eluent for column chromatography.

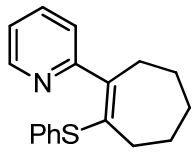
FTIR ($CHCl_3$): 2964, 2847, 1582, 1471, 1023, 781, 622, 409 $cm^{-1}$.

$^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.69 (ddd, 1H, *J* = 4.7, 1.7, 0.8 Hz), 7.64 (td, 1H, *J* = 7.8, 1.7 Hz), 7.57-7.51 (m, 2H), 7.40 (d, 1H, *J* = 8.0 Hz), 7.34-7.28 (m, 3H), 7.11-7.05 (m, 1H), 2.97-2.89 (m, 2H), 2.50-2.40 (m, 2H), 1.92 (q, 2H, *J* = 7.6 Hz).

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 155.3 (C), 148.7 (CH), 138.0 (C), 135.9 (CH), 134.1(9) (CH), 134.1(1) (C), 133.9 (C), 128.7 (CH), 128.1 (CH), 121.6 (CH), 120.6 (CH), 39.1 ($CH_2$), 35.6 ($CH_2$), 22.0 ($CH_2$).

HRMS: calcd. for $C_{16}H_{15}NS$+H: 254.1003; found: 254.1025.

**(2-(Phenylthio)cyclohept-1-en-1-yl)pyridine (6e)**




According to the general procedure the title compound **6e** was isolated in 53% yield (30 mg) as a white solid using the mixture of hexane/ethyl acetate (92:8) as an eluent for column chromatography.

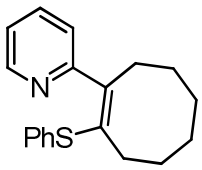
FTIR (KBr): 2922, 2849, 1585, 1462, 1022, 782, 689, 540, 477 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.61-8.57 (m, 1H), 7.57 (td, 1H, *J* = 7.6, 1.7 Hz), 7.32 (dt, 1H, *J* = 7.7, 1.9 Hz), 7.28-7.22 (m, 4H), 7.18-7.13 (m, 1H), 7.10 (ddd, 1H, *J* = 7.8, 4.5, 1.0 Hz), 2.78-2.70 (m, 2H), 2.57-2.50 (m, 2H), 1.86-1.78 (m, 2H), 1.76-1.68 (m, 2H), 1.64-1.55 (m, 2H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 161.8 (C), 149.0 (CH), 148.0 (C), 136.1 (C), 135.7 (CH), 134.8 (C), 130.0 (CH), 128.8 (CH), 126.1 (CH), 123.6 (CH), 121.6 (CH), 36.4($CH_2$), 35.3 ($CH_2$), 32.1 ($CH_2$), 26.8 ($CH_2$), 26.5 ($CH_2$).

HRMS: calcd. for $C_{18}H_{19}NS$+H: 282.1316; found: 282.1305.

**(*Z*)-2-(2-(Phenylthio)cyclooct-1-en-1-yl)pyridine (6f)**




According to the general procedure the title compound **6f** was isolated in 63% yield (37 mg) as a white solid using the mixture of hexane/ethyl acetate (92:8) as an eluent for column chromatography.

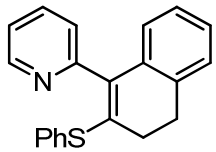
FTIR (KBr): 2925, 2851, 1581, 1466, 1022, 783, 691, 545, 422 $cm^{-1}$.

$^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.60 (ddd, 1H, *J* = 4.8, 1.6, 0.9 Hz), 7.59 (td, 1H, *J* = 7.6, 1.7 Hz), 7.28-7.19 (m, 5H), 7.16-7.09 (m, 2H), 2.82-2.73 (m, 2H), 2.53-2.45 (m, 2H), 1.72-1.53 (m, 8H).

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 160.7 (C), 149.1 (CH), 145.4 (C), 135.8 (C), 135.4 (CH), 132.1 (C), 130.3 (CH), 128.8 (CH), 126.2 (CH), 124.4 (CH), 121.7 (CH), 33.4 ($CH_2$), 31.8 ($CH_2$), 29.5 ($CH_2$), 29.4 ($CH_2$), 26.8 ($CH_2$), 26.6 ($CH_2$).

HRMS: calcd. for $C_{19}H_{21}NS$+H: 296.1473; found: 296.1473.

**2-(2-(Phenylthio)-3,4-dihydronaphthalen-1-yl)pyridine (6g)**




According to the general procedure the title compound **6g** was isolated in 68% yield (43 mg) as a brown liquid using the mixture of hexane/ethyl acetate (92:8) as an eluent for column chromatography.

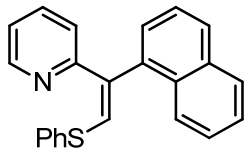
FTIR ($CHCl_3$): 3060, 2929, 1583, 1470, 1278, 1024, 791, 693, 449 $cm^{-1}$.

$^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.73 (ddd, 1H, *J* = 4.8, 1.7, 0.9 Hz), 7.74 (td, 1H, *J* = 7.7, 1.8 Hz), 7.40-7.34 (m, 3H), 7.29-7.23 (m, 3H), 7.23-7.18 (m, 1H), 7.14-7.08 (m, 2H), 7.07-7.01 (m, 1H), 6.61 (d, 1H, *J* = 7.4 Hz), 2.89 (t, 2H, *J* = 7.4 Hz), 2.57-2.50 (m, 2H).

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 157.8 (C), 149.6 (CH), 139.8 (C), 136.3 (CH), 135.3 (C), 135.1(9) (C), 135.1(3) (C), 133.9 (C), 131.2 (CH), 129.0 (CH), 127.4 (CH), 127.3 (CH), 127.0 (CH), 126.5 (CH), 125.8 (CH), 125.6 (CH), 122.3 (CH), 29.7 ($CH_2$), 29.4 ($CH_2$).

HRMS: calcd. for $C_{21}H_{17}NS$+H: 316.1160; found: 316.1136.

**(*Z*)-2-(1-(Naphthalen-1-yl)-2-(phenylthio)vinyl)pyridine (6h)**




According to the general procedure the title compound **6h** was isolated in 42% yield (29 mg) as a yellow liquid using the mixture of hexane/ethyl acetate (92:8) as an eluent for column chromatography.

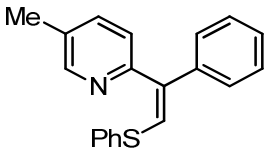
FTIR ($CHCl_3$): 2924, 2852, 1581, 1467, 1242, 1022, 796, 530, 480 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.84 (ddd, 1H, *J* = 4.8, 1.7, 0.9 Hz), 7.89-7.83 (m, 2H), 7.82-7.78 (m, 1H), 7.58-7.55 (m, 2H), 7.51-7.49 (m, 2H), 7.48-7.41 (m, 2H), 7.40-7.34 (m, 1H), 7.33-7.28 (m, 2H), 7.26-7.23 (m, 1H), 7.10 (ddd, 1H, *J* = 7.4, 4.8, 1.0 Hz), 6.95 (s, 1H), 6.75-6.69 (m, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 157.3 (C), 148.2 (CH), 139.1 (C), 138.7 (C), 136.1 (CH), 134.9 (CH), 133.9 (C), 133.6 (C), 132.8 (C), 130.9 (CH), 129.1 (CH), 128.3(9) (CH), 128.3(4) (CH), 128.0 (CH), 127.4 (CH), 126.4 (CH), 126.3 (CH), 126.0 (CH), 125.7 (CH), 123.0 (CH), 120.9 (CH).

HRMS: calcd. for $C_{23}H_{17}NS$+H: 340.1160; found: 340.1154.

**(*Z*)-5-Methyl-2-(1-phenyl-2-(phenylthio)vinyl)pyridine (6i)**



According to the general procedure the title compound **6i** was isolated in 35% yield (21 mg) as a yellow liquid using the mixture of hexane/ethyl acetate (92:8) as an eluent for column chromatography.

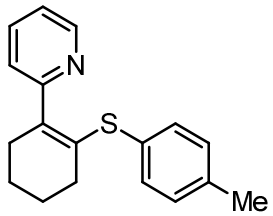
FTIR ($CHCl_3$): 2991, 2864, 2256, 1582, 1476, 1242, 1049, 742, 464 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.61 (dd, 1H, *J* = 1.5, 0.7 Hz), 7.54-7.51 (m, 2H), 7.43 (ddd, 1H, *J* = 8.1, 2.2, 0.6 Hz), 7.35-7.30 (m, 7H), 7.26-7.23 (m, 1H), 7.11 (d, 1H, *J* = 8.0 Hz), 6.86 (s, 1H), 2.35 (s, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 154.6 (C), 149.1 (CH), 141.2 (C), 138.4 (C), 137.2 (C), 136.6 (CH), 131.3 (C), 130.6 (CH), 130.4 (CH), 129.2 (CH), 128.6 (CH), 128.5 (CH), 127.4 (CH), 127.2 (CH), 123.3 (CH), 18.4 ($CH_3$).

HRMS: calcd. for $C_{20}H_{17}NS$+H: 304.1160; found: 304.1182.

**2-(2-(*p*-Tolylthio)cyclohex-1-en-1-yl)pyridine (6j)**




According to the general procedure the title compound **6j** was isolated in 86% yield (48 mg) as a yellow liquid using the mixture of hexane/ethyl acetate (92:8) as an eluent for column chromatography.

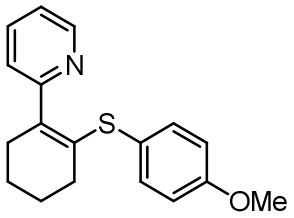
FTIR ($CHCl_3$): 3052, 2934, 2860, 1586, 1463, 1266, 1017, 736, 499 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.59 (ddd, 1H, *J* = 4.8, 1.7, 0.9 Hz), 7.61 (td, 1H, *J* = 7.7, 1.7 Hz), 7.33 (dt, 1H, *J* = 7.8, 1.0 Hz), 7.24-7.16 (m, 2H), 7.14 (ddd, 1H, *J* = 7.5, 4.9, 1.1 Hz), 7.11-7.04 (m, 2H), 2.62-2.56 (m, 2H), 2.30 (s, 3H), 2.26-2.22 (m, 2H), 1.81-1.70 (m, 4H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 160.5 (C), 148.9 (CH), 141.9 (C), 136.3 (C), 135.9 (CH), 131.7 (C), 130.7 (CH), 129.8 (C), 129.7 (CH), 123.7 (CH), 121.8 (CH), 31.7 ($CH_2$), 31.1 ($CH_2$), 23.8 ($CH_2$), 22.7 ($CH_2$), 21.1 ($CH_3$).

HRMS: calcd. for $C_{18}H_{19}NS$+H: 282.1316; found: 282.1309.

**2-(2-((4-Methoxyphenyl)thio)cyclohex-1-en-1-yl)pyridine (6k)**




According to the general procedure the title compound **6k** was isolated in 94% yield (56 mg) as a yellow liquid using the mixture of hexane/ethyl acetate (90:10) as an eluent for column chromatography.

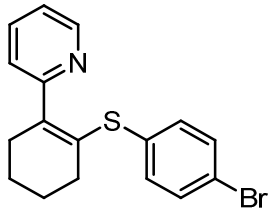
FTIR ($CHCl_3$): 3055, 2931, 2857, 1588, 1462, 1286, 1245, 1028, 827 $cm^{-1}$.

$^{1}H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.64-8.58 (m, 1H), 7.64 (td, 1H, *J* = 7.6, 1.6 Hz), 7.34 (dt, 1H, *J* = 7.9, 0.9 Hz), 7.30-7.23 (m, 2H), 7.15 (ddd, 1H, *J* = 7.4, 4.8, 0.7 Hz), 6.85-6.77 (m, 2H), 3.77 (s, 3H), 2.58-2.53 (m, 2H), 2.19-2.15 (m, 2H), 1.78-1.68 (m, 4H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 160.5 (C), 159.0 (C), 148.9 (CH), 139.4 (C), 135.9 (CH), 133.7 (CH), 131.0 (C), 125.2 (C), 123.8 (CH), 121.7 (CH), 114.4 (CH), 55.4 ($CH_3$), 31.6 ($CH_2$), 30.9 ($CH_2$), 23.7 ($CH_2$), 22.7 ($CH_2$).

HRMS: calcd. for $C_{18}H_{19}NOS$+H: 298.1266; found: 298.1274.

**2-(2-((4-Bromophenyl)thio)cyclohex-1-en-1-yl)pyridine (6l)**




According to the general procedure the title compound **6l** was isolated in 80% yield (55 mg) as a yellow liquid using the mixture of hexane/ethyl acetate (92:8) as an eluent for column chromatography.

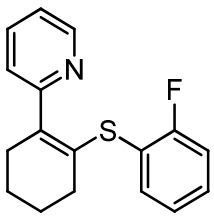
FTIR ($CHCl_3$): 3049, 2932, 2858, 1585, 1467, 1265, 1087, 738 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.58 (ddd, 1H, $J$ = 4.8, 1.7, 0.9 Hz), 7.61 (td, 1H, $J$ = 7.7, 1.8 Hz), 7.40-7.32 (m, 2H), 7.30-7.24 (m, 1H), 7.17-7.14 (m, 1H), 7.14-7.10 (m, 2H), 2.65-2.57 (m, 2H), 2.29-2.24 (m, 2H), 1.82-1.74 (m, 4H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 160.3 (C), 149.0 (CH), 144.3 (C), 135.9 (CH), 135.1 (C), 131.9 (CH), 131.3 (CH), 128.5 (C), 123.4 (CH), 122.0 (CH), 120.0 (C), 31.8 ($CH_2$), 31.4 ($CH_2$), 23.8 ($CH_2$), 22.6 ($CH_2$).

HRMS: calcd. for $C_{17}H_{16}BrNS$+H: 346.0265; found: 346.0239.

**2-(2-((2-Fluorophenyl)thio)cyclohex-1-en-1-yl)pyridine (6m)**




According to the general procedure the title compound **6m** was isolated in 87% yield (49 mg) as a colorless liquid using the mixture of hexane/ethyl acetate (92:8) as an eluent for column chromatography.

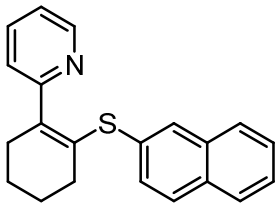
FTIR ($CHCl_3$): 3058, 2930, 2860, 1581, 1465, 1261, 1068, 754 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.63-8.55 (m, 1H), 7.62 (t, 1H, *J* = 7.6 Hz), 7.36 (d, 1H, *J* = 8.0 Hz), 7.30 (t, 1H, *J* = 7.4 Hz), 7.21-7.10 (m, 2H), 7.08-6.96 (m, 2H), 2.62-2.55 (m, 2H), 2.27-2.21 (m, 2H), 1.82-1.71 (m, 4H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 161.3 (d, *J* = 245.7 Hz, C), 160.1 (C), 148.8 (CH), 142.3 (C), 135.9 (CH), 132.5 (CH), 128.4 (C), 128.3 (CH), 124.4 (d, *J* = 3.7 Hz, CH), 123.5 (CH), 122.3 (d, *J* = 17.9 Hz, C), 121.8 (CH), 115.5 (d, *J* = 22.2 Hz, CH), 31.6 ($CH_2$), 31.0 ($CH_2$), 23.6 ($CH_2$), 22.5 ($CH_2$).

HRMS: calcd. for $C_{27}H_{16}NFS+H$: 286.1066; found: 286.1090.

**2-(2-(Naphthalen-2-ylthio)cyclohex-1-en-1-yl)pyridine (6n)**




According to the general procedure the title compound **6n** was isolated in 91% yield (58 mg) as a yellow liquid using the mixture of hexane/ethyl acetate (92:8) as an eluent for column chromatography.

FTIR ($CHCl_3$): 3053, 2932, 2858, 1587, 1464, 1266, 1050, 739 $cm^{-1}$.

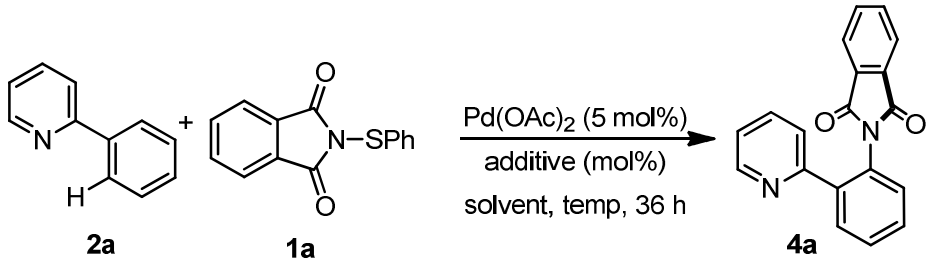
$^1H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.65-8.55 (m, 1H), 7.81-7.66 (m, 4H), 7.63-7.54 (m, 1H), 7.48-7.38 (m, 2H), 7.36 (d, 2H, *J* = 7.9 Hz), 7.17-7.08 (m, 1H), 2.69-2.61 (m, 2H), 2.35-2.28 (m, 2H), 1.85-1.72 (m, 4H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 160.4 (C), 149.0 (CH), 143.4 (C), 135.9 (CH), 133.7 (C), 133.2 (C), 131.9 (C), 129.1 (C), 128.4 (CH), 128.2 (CH), 128.0 (CH), 127.7 (CH), 127.2

(CH), 126.5 (CH), 125.7 (CH), 123.6 (CH), 121.9 (CH), 31.8 ($CH_2$), 31.4 ($CH_2$), 23.8 ($CH_2$), 22.7 ($CH_2$).

HRMS: calcd. for $C_{21}H_{19}NS$+H: 318.1316; found: 318.1335.

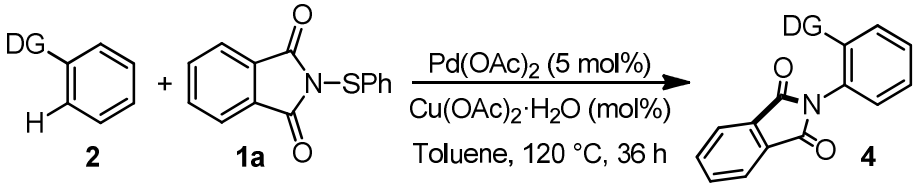
## 6. Optimization studies for the palladium catalyzed i(a)midation of C–H bonds:




| Entry | Additive (mol%) | Solvent | Temp (°C) | Yield (%) |
|---|---|---|---|---|
| 1 | - | Toluene | 100 | - |
| 2 | CuI (50) | Toluene | 100 | 20 |
| 3 | CuI (100) | Toluene | 100 | 16 |
| 4 | AgOAc (50) | Toluene | 100 | - |
| 5 | AgOAc (100) | Toluene | 100 | - |
| 6 | $AgOCOCF_3$ (100) | Toluene | 100 | - |
| 7 | $Ag_2CO_3$ (100) | Toluene | 100 | - |
| 8 | CuI (50) | Toluene | 120 | 41 |
| 9 | CuBr (50) | Toluene | 120 | 53 |
| 10 | CuCl (50) | Toluene | 120 | - |
| 11 | $CuBr_2$ (50) | Toluene | 120 | 13 |
| 12 | $CuCl_2$ (50) | Toluene | 120 | - |
| **13** | **$Cu(OAc)_2·H_2O$ (50)** | **Toluene** | **120** | **77** |
| 14 | $Cu(OAc)_2·H_2O$ (50) | 1,4-dioxane | 120 | 17 |
| 15 | $Cu(OAc)_2·H_2O$ (50) | Chlorobenzene | 100 | 57 |
| 16 | $Cu(OAc)_2·H_2O$ (50) | $^t$AmOH | 100 | 61 |
| 17[a] | $Cu(OAc)_2·H_2O$ (50) | Toluene | 120 | 57 |
| 18[b] | $Cu(OAc)_2·H_2O$ (50) | Toluene | 120 | - |
| 19 | $FeCl_3$ (50) | Toluene | 120 | - |
| 20 | $BF_3·Et_2O$ (50) | Toluene | 120 | - |

Reaction conditions: 2-Phenylpyridine **2a** (1 equiv), *N*-(phenylthio)pthalimide **1a** (2 equiv), $Pd(OAc)_2$ (5 mol%), additive (mol%), solvent (1 mL), temp, time. [a] $Pd(OAc)_2$ (8 mol%). [b] without $Pd(OAc)_2$.

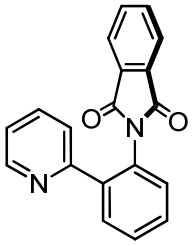
## 7. General procedure for palladium catalyzed i(a)midation of C-H bonds:




A dry reaction tube (10 mL) was charged with arene **2** (0.2 mmol), 2-(phenylthio)isoindoline-1,3-dione **1a** (0.4 mmol), $Pd(OAc)_2$ (5 mol%), $Cu(OAc)_2 \cdot H_2O$ (50 mol%) and dry toluene (2 mL) under nitrogen atmosphere. The reaction tube was sealed under nitrogen atmosphere and kept at 120 °C for 36 h. After the completion of the reaction, as monitored by TLC the reaction mixture was cooled to room temperature and purified by column chromatography using mixture of hexane and ethyl acetate as eluent to afford the pure product.

## 8. Properties of the isolated imidation products:

**2-(2-(Pyridin-2-yl)phenyl)isoindoline-1,3-dione (4a)**




According to the general procedure the title compound **4a** was isolated in 77% yield (46 mg) as a white solid using the mixture of hexane/ethyl acetate (80:20) as an eluent for column chromatography.

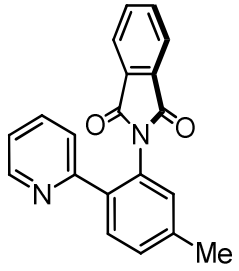
FTIR (KBr): 3199, 2923, 1716, 1584, 1496, 1380, 889, 754, 624 $cm^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.28 (dd, 1H, *J* = 4.7, 0.7 Hz), 7.85-7.82 (m, 2H), 7.74-7.70 (m, 3H), 7.63 (td, 1H, *J* = 7.7, 1.7 Hz), 7.59-7.51 (m, 2H), 7.46 (d, 1H, *J* = 7.9 Hz), 7.44-7.37 (m, 1H), 7.05 (ddd, 1H, *J* = 7.4, 4.8, 1.0 Hz).

$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 167.7 (C), 149.3 (CH), 136.7 (CH), 134.3 (C), 134.1 (CH), 132.2 (C), 130.5 (CH), 130.2 (CH), 129.7 (C), 129.6 (CH), 129.5 (CH), 123.6(8) (CH), 123.6(4) (C), 122.9 (CH), 122.1 (CH).

HRMS: calcd. for $C_{19}H_{12}N_2O_2$+H: 301.0977; found: 301.0984.

**2-(5-Methyl-2-(pyridin-2-yl)phenyl)isoindoline-1,3-dione (4b)**




According to the general procedure the title compound **4b** was isolated in 63% yield (40 mg) as a white solid using the mixture of hexane/ethyl acetate (80:20) as an eluent for column chromatography.

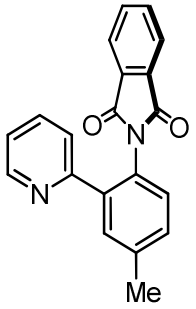
FTIR (KBr): 3043, 2946, 2213, 1739, 1465, 1087, 725 $cm^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.28-8.21 (m, 1H), 7.82 (dd, 2H, *J* = 5.4, 3.1 Hz), 7.70 (dd, 2H, *J* = 5.4, 3.1 Hz), 7.64-7.57 (m, 2H), 7.44 (d, 1H, *J* = 7.9 Hz), 7.36 (dd, 1H, *J* = 7.9, 0.9 Hz), 7.21 (d, 1H, *J* = 0.6 Hz), 7.02 (ddd, 1H, *J* = 7.5, 4.8, 1.0 Hz), 2.44 (s, 3H).

$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 167.9 (C), 157.0 (C), 149.2 (CH), 139.8 (C), 136.6 (CH), 135.6 (C), 134.0 (CH), 132.2 (C), 130.7 (CH), 130.4 (CH), 130.3 (CH), 129.4 (C), 123.6 (CH), 122.7 (CH), 121.9 (CH), 21.1 ($CH_3$).

HRMS: calcd. for $C_{20}H_{14}N_2O_2$+H: 315.1134; found: 315.1132.

**2-(4-Methyl-2-(pyridin-2-yl)phenyl)isoindoline-1,3-dione (4c)**




According to the general procedure the title compound **4c** was isolated in 72% yield (45 mg) as a white solid using the mixture of hexane/ethyl acetate (80:20) as an eluent for column chromatography.

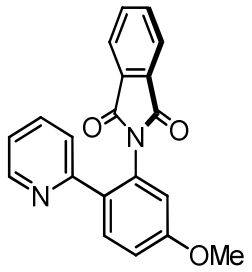
FTIR (KBr): 3040, 2924, 2863, 1721, 1587, 1468, 890, 791, 531 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.22 (dd, 1H, *J* = 4.1 Hz), 7.73(dd, 2H, *J* = 5.4, 3.0 Hz), 7.62 (dd, 2H, *J* = 5.4, 3.0 Hz), 7.52 (td, 1H, *J* = 7.7, 1.7 Hz), 7.45 (s, 1H), 7.35 (d, 1H, *J* = 7.9 Hz), 7.27 (d, 1H, *J* = 8.1 Hz), 7.19 (d, 1H, *J* = 8.1 Hz), 7.00-6.94 (m, 1H), 2.37 (s, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 167.9 (C), 157.0 (C), 149.3 (CH), 139.7 (C), 138.3 (C), 136.6 (CH), 134.0 (CH), 132.1 (C), 131.2 (CH), 130.2 (CH), 129.8 (CH), 127.0 (C), 123.6 (CH), 122.7 (CH), 122.1 (CH), 21.3 ($CH_3$).

HRMS: calcd. for $C_{20}H_{14}N_2O_2$+H: 315.1134; found: 315.1130.

**2-(5-Methoxy-2-(pyridin-2-yl)phenyl)isoindoline-1,3-dione (4d)**




According to the general procedure the title compound **4d** was isolated in 69% yield (46 mg) as a light yellow solid using the mixture of hexane/ethyl acetate (78:22) as an eluent for column chromatography.

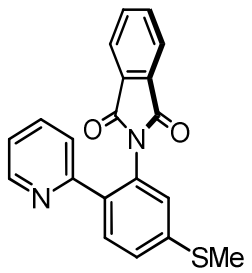
FTIR (KBr): 3007, 2928, 2848, 1721, 1587, 1427, 1279, 1048, 910, 730, 530 $cm^{-1}$.

$^{1}H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.22 (ddd, 1H, *J* = 4.8, 1.7, 0.8 Hz), 7.83 (dd, 2H, *J* = 5.3, 3.1 Hz), 7.71 (dd, 2H, *J* = 5.5, 3.0 Hz), 7.65 (d, 1H, *J* = 8.6 Hz), 7.59 (td, 1H, *J* = 7.7, 1.8 Hz), 7.41 (dt, 1H, *J* = 7.9, 0.9 Hz), 7.09 (dd, 1H, *J* = 8.7, 2.6 Hz), 7.00 (ddd, 1H, *J* = 7.5, 4.8, 1.0 Hz), 6.93 (d, 1H, *J* = 2.6 Hz), 3.86 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 167.7 (C), 160.4 (C), 156.8 (C), 149.2 (CH), 136.6 (CH), 134.0 (CH), 132.2 (C), 131.4 (CH), 131.0 (C), 130.8 (C), 123.6 (CH), 122.5 (CH), 121.6 (CH), 115.5(9) (CH), 115.5(4) (CH), 55.6 ($CH_3$).

HRMS: calcd. for $C_{20}H_{14}N_2O_3$+H: 331.1083; found: 331.1098.

**2-(5-(Methylthio)-2-(pyridin-2-yl)phenyl)isoindoline-1,3-dione (4e)**



According to the general procedure the title compound **4e** was isolated in 73% yield (50 mg) as a white solid using the mixture of hexane/ethyl acetate (77:23) as an eluent for column chromatography.

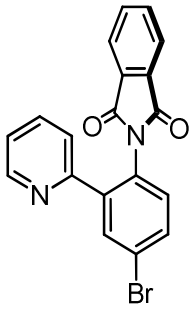
FTIR (KBr): 3048, 2921, 2881, 1718, 1592, 1466, 894, 719 $cm^{-1}$.

$^{1}H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.26-8.20 (m, 1H), 7.83 (dd, 2H, *J* = 5.4, 3.1 Hz), 7.71 (dd, 2H, *J* = 5.4, 3.1 Hz), 7.63 (d, 1H, *J* = 8.2 Hz), 7.60 (dd, 1H, *J* = 7.5, 1.6 Hz), 7.46-7.38 (m, 2H), 7.23 (d, 1H, *J* = 1.9 Hz), 7.06-7.01 (m, 1H), 2.51 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 167.6 (C), 156.5 (C), 149.3 (CH), 140.9 (C), 136.7 (CH), 134.9 (C), 134.1 (CH), 132.1 (C), 130.6 (CH), 130.2 (C), 127.4 (CH), 127.2 (CH), 123.6 (CH), 122.6 (CH), 122.0 (CH), 15.5 ($CH_3$).

HRMS: calcd. for $C_{20}H_{14}N_2O_2S$+Na: 369.0674; found: 369.0680.

**2-(4-Bromo-2-(pyridin-2-yl)phenyl)isoindoline-1,3-dione (4f)**




According to the general procedure the title compound **4f** was isolated in 29% yield (22 mg) as a white solid using the mixture of hexane/ethyl acetate (80:20) as an eluent for column chromatography.

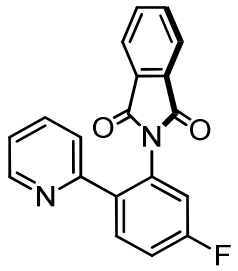
FTIR (KBr): 3055, 2984, 2926, 1720, 1586, 1428, 1087, 890, 738 $cm^{-1}$.

$^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.23 (ddd, 1H, *J* = 4.8, 1.7, 0.8 Hz), 7.80 (d, 1H, *J* = 2.2 Hz), 7.75 (dd, 2H, *J* = 5.5, 3.0 Hz), 7.65 (dd, 2H, *J* = 5.4, 3.0 Hz), 7.62-7.56 (m, 2H), 7.37 (td, 1H, *J* = 7.9, 0.8 Hz), 7.21 (d, 1H, *J* = 8.4 Hz), 7.02 (ddd, 1H, *J* = 7.5, 4.9, 1.1 Hz).

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 167.4 (C), 155.7 (C), 149.4 (CH), 140.2 (C), 137.0 (CH), 134.2 (CH), 133.6 (CH), 132.6 (CH), 132.1 (C), 131.7 (CH), 128.8 (C), 123.8 (CH), 123.5 (C), 122.9 (CH), 122.7 (CH).

HRMS: calcd. for $C_{19}H_{11}N_2O_2Br$+H: 379.0082; found: 379.0090.

**2-(5-Fluoro-2-(pyridin-2-yl)phenyl)isoindoline-1,3-dione (4g)**




According to the general procedure the title compound **4g** was isolated in 62% yield (40 mg) as a white solid using the mixture of hexane/ethyl acetate (80:20) as an eluent for column chromatography.

FTIR (KBr): 3047, 2967, 2856, 1723, 1466, 1267, 1085, 874, 718, 530 $cm^{-1}$.

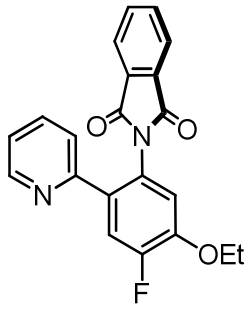
$^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.26 (d, 1H, *J* = 4.2 Hz), 7.83 (dd, 2H, *J* = 5.5, 3.0 Hz), 7.73 (dd, 2H, *J* = 5.5, 3.0 Hz), 7.71-7.67 (m, 1H), 7.634 (td, 1H, *J* = 7.7, 1.8 Hz), 7.42 (d, 1H, *J* = 7.9 Hz), 7.30-7.25 (m, 1H), 7.16 (dd, 1H, *J* = 8.7, 2.5 Hz), 7.06 (ddd, 1H, *J* = 7.7, 4.6, 1.2 Hz).

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 167.3 (C), 162.7 (d, *J* = 249.0 Hz, C), 156.3 (C), 149.4 (CH), 136.9 (CH), 134.9 (d, *J* = 3.6 Hz, C), 134.3 (CH), 131.9 (d, *J* = 9.0 Hz, CH), 131.2

(d, $J$ = 10.7 Hz, C), 123.8 (CH), 123.6 (C), 122.7 (CH), 122.2 (CH), 117.6 (d, $J$ = 23.3 Hz, CH), 116.7 (d, $J$ = 21.3 Hz, CH).

HRMS: calcd. for $C_{19}H_{11}N_2O_2F$+Na: 341.0702; found: 341.0717.

**2-(5-Ethoxy-4-fluoro-2-(pyridin-2-yl)phenyl)isoindoline-1,3-dione (4h)**




According to the general procedure the title compound **4h** was isolated in 45% yield (32 mg) as a white solid using the mixture of hexane/ethyl acetate (80:20) as an eluent for column chromatography.

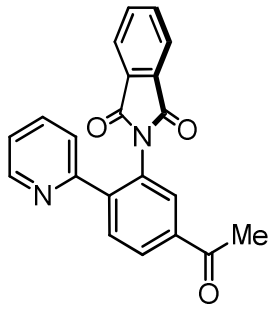
FTIR (KBr): 3051, 2987, 2929, 1723, 1470, 1264, 1045, 909, 737, 650 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.24 (ddd, 1H, $J$ = 4.7, 1.7, 0.8 Hz), 7.85-7.82 (m, 2H), 7.74-7.71 (m, 2H), 7.61 (td, 1H, $J$ = 7.6, 1.5 Hz), 7.47 (d, 1H, $J$ = 11.7 Hz), 7.38 (dd, 1H, $J$ = 7.9, 0.8 Hz), 7.03 (ddd, 1H, $J$ = 7.5, 4.9, 0.8 Hz), 6.96 (d, 1H, $J$ = 7.7 Hz), 4.16 (q, 2H, $J$ = 7.0 Hz), 1.47 (t, 3H, $J$ = 7.0 Hz).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 167.8 (C), 155.7 (C), 152.6 (d, $J$ = 246.4 Hz, C), 149.3 (CH), 147.7 (d, $J$ = 11.9 Hz, C), 136.8 (CH), 134.2 (CH), 132.1 (CH), 131.3 (d, $J$ = 6.6 Hz, C), 125.9 (C), 125.5 (d, $J$ = 3.3 Hz, C), 123.7 (CH), 122.3 (d, $J$ = 32.1 Hz, CH), 117.7 (d, $J$ = 21.0 Hz, CH), 116.3 (CH), 65.3 ($CH_2$), 14.7 ($CH_3$).

HRMS: calcd. for $C_{21}H_{15}N_2O_3F$+H: 363.1145; found: 363.1151.

**2-(5-Acetyl-2-(pyridin-2-yl)phenyl)isoindoline-1,3-dione (4i)**




According to the general procedure the title compound **4i** was isolated in 51% yield (35 mg) as a light yellow solid using the mixture of hexane/ethyl acetate (78:22) as an eluent for column chromatography.

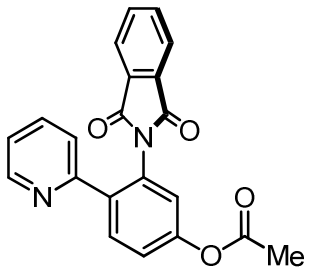
FTIR (KBr): 3077, 3027, 1689, 1589, 1446, 1257, 948, 728 $cm^{-1}$.

$^{1}H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.30 (d, 1H, *J* = 4.4 Hz), 8.14 (dd, 1H, *J* = 8.1, 1.5 Hz), 7.99 (d, 1H, *J* = 1.6 Hz), 7.86-7.82 (m, 3H), 7.74 (dd, 2H, *J* = 5.3, 3.0 Hz), 7.67 (td, 1H, *J* = 7.7, 1.7 Hz), 7.50 (d, 1H, *J* = 7.9 Hz), 7.14-7.09 (m, 1H), 2.65 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 196.6 (C), 167.5 (C), 156.0 (C), 149.5 (CH), 142.7 (C), 137.9 (C), 137.0 (CH), 134.3 (CH), 132.0 (C), 130.9 (CH), 130.5 (CH), 129.8 (C), 129.2 (CH), 123.8 (CH), 123.0 (CH), 122.8 (CH), 26.8 ($CH_3$).

HRMS: calcd. for $C_{21}H_{14}N_2O_3$+H: 343.1083; found: 343.1093.

**3-(1,3-Dioxoisoindolin-2-yl)-4-(pyridin-2-yl)phenyl acetate (4j)**



According to the general procedure the title compound **4j** was isolated in 52% yield (37 mg) as a white solid using the mixture of hexane/ethyl acetate (78:22) as an eluent for column chromatography.

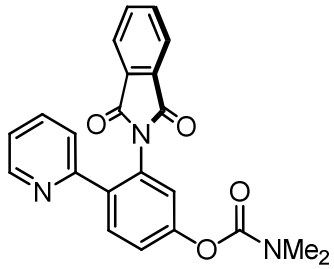
FTIR (KBr): 3058, 2925, 1772, 1723, 1592, 1466, 1268, 961, 720 $cm^{-1}$.

$^{1}H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.29 (d, 1H, *J* = 3.9 Hz), 7.82 (dd, 2H, *J* = 5.3, 3.1 Hz), 7.74-7.70 (m, 3H), 7.65 (td, 1H, *J* = 7.7, 1.6 Hz), 7.44 (d, 1H, *J* = 7.8 Hz), 7.35 (dd, 1H, *J* = 8.5, 2.3 Hz), 7.23 (d, 1H, *J* = 2.3 Hz), 7.10-7.06 (m, 1H), 2.32 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 168.8 (C), 167.3 (C), 156.4 (C), 151.1 (C), 149.3 (CH), 137.0 (CH), 135.9 (C), 134.2 (CH), 132.0 (C), 131.3 (CH), 123.8 (CH), 123.2 (C), 122.9 (CH), 122.7 (CH), 122.3 (CH), 117.3 (CH), 21.2 ($CH_3$).

HRMS: calcd. for $C_{21}H_{14}N_2O_4$+H: 359.1031; found: 359.1025.

**3-(1,3-Dioxoisoindolin-2-yl)-4-(pyridin-2-yl)phenyl dimethylcarbamate (4k)**




According to the general procedure the title compound **4k** was isolated in 59% yield (46 mg) as a white solid using the mixture of hexane/ethyl acetate (55:45) as an eluent for column chromatography.

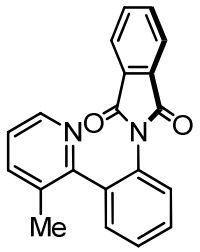
FTIR (KBr): 3055, 2925, 1724, 1586, 1465, 1264, 880, 719 $cm^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.26 (d, 1H, *J* = 4.1 Hz), 7.85-7.80 (m, 2H), 7.74-7.68 (m, 3H), 7.63 (t, 1H, *J* = 7.7Hz), 7.45 (d, 1H, *J* = 7.8 Hz), 7.39 (dd, 1H, *J* = 8.6, 1.9 Hz), 7.24 (d, 1H, *J* = 1.7 Hz), 7.05 (dd, 1H, 6.5, 5.3 Hz), 3.11 (s, 3H), 3.02 (s, 3H).

$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 167.4 (C), 156.6 (C), 154.2 (C), 152.0 (C), 149.3 (CH), 136.8 (CH), 135.3 (C), 134.1 (CH), 132.1 (C), 131.1 (CH), 130.4 (C), 123.7 (CH), 123.2 (CH), 122.9 (CH), 122.7 (CH), 122.1 (CH), 36.8 ($CH_3$), 36.6 ($CH_3$).

HRMS: calcd. for $C_{22}H_{17}N_3O_4$+H: 388.1297; found: 388.1293.

**2-(2-(3-Methylpyridin-2-yl)phenyl)isoindoline-1,3-dione (4l)**




According to the general procedure the title compound **4l** was isolated in 49% yield (31 mg) as a white solid using the mixture of hexane/ethyl acetate (80:20) as an eluent for column chromatography.

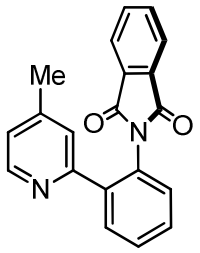
FTIR (KBr): 3054, 2986, 1724, 1438, 1265, 908, 735, 646 $cm^{-1}$.

$^1$H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.16 (dd, 1H, *J* = 4.7, 1.1 Hz), 7.84 (dd, 1H, *J* = 5.5, 3.0 Hz), 7.76 (dd, 2H, *J* = 5.5, 3.0 Hz), 7.66 (dd, 1H, *J* = 5.4, 3.0 Hz), 7.55-7.48 (m, 4H), 7.45-7.42 (m, 1H), 6.97 (dd, 1H, *J* = 7.7, 4.7 Hz), 2.32 (s, 3H).

$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 167.2 (C), 156.2 (C), 146.4 (CH), 138.9 (C), 138.3 (CH), 134.3 (C), 134.0 (CH), 132.1 (C), 131.9 (C), 130.5 (CH), 129.7 (CH), 129.0 (CH), 128.8 (CH), 123.5 (CH), 122.3 (CH), 19.5 ($CH_3$).

HRMS: calcd. for $C_{20}H_{14}N_2O_2$+Na: 337.0953; found: 337.0951.

**2-(2-(4-Methylpyridin-2-yl)phenyl)isoindoline-1,3-dione (4m)**




According to the general procedure the title compound **4m** was isolated in 59% yield (37 mg) as a white solid using the mixture of hexane/ethyl acetate (80:20) as an eluent for column chromatography.

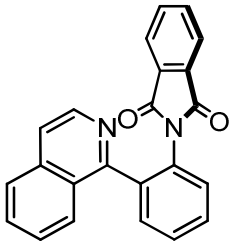
FTIR (KBr): 3048, 29864, 1729, 1438, 1265, 908, 742, 646 $cm^{-1}$

$^1H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.12 (s, 1H), 7.83 (dd, 2H, *J* = 5.3, 3.0 Hz), 7.74-7.69 (m, 3H), 7.60-7.47 (m, 2H), 7.43-7.37 (m, 1H), 7.30 (s, 1H), 6.88 (d, 1H, *J* = 3.8 Hz), 2.27 (s, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 167.8 (C), 156.7 (C), 148.7 (CH), 148.1 (C), 138.4 (C), 134.3 (CH), 134.0 (CH), 132.2 (CH), 130.5 (CH), 130.2 (CH), 129.8 (C), 129.5 (CH), 129.4 (CH), 123.6 (CH), 123.2 (C), 21.2 ($CH_3$).

HRMS: calcd. for $C_{20}H_{14}N_2O_2$+Na: 337.0953; found: 337.0937.

**2-(2-(Isoquinolin-1-yl)phenyl)isoindoline-1,3-dione (4n)**




According to the general procedure the title compound **4n** was isolated in 32% yield (22 mg) as a white solid using the mixture of hexane/ethyl acetate (80:20) as an eluent for column chromatography.

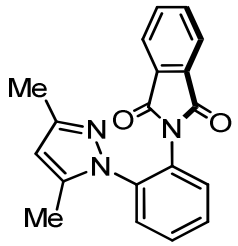
FTIR (KBr): 3057, 2924, 2855, 1723, 1586, 1452, 1293, 1169, 830, 717, 583 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.35 (d, 1H, *J* = 5.6 Hz), 7.99 (d, 1H, *J* = 8.4 Hz), 7.76-7.67 (m, 3H), 7.67-7.55 (m, 6H), 7.54-7.46 (m, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 167.1 (C), 157.8 (C), 142.0 (CH), 137.7 (C), 136.6 (C), 134.3 (C), 134.0 (CH), 131.9 (CH), 131.7 (C), 130.8 (C), 130.1 (CH), 129.8 (CH), 129.5 (CH), 128.8 (CH), 127.3 (CH), 127.2 (CH), 126.8 (CH), 123.5 (CH), 120.1 (CH).

HRMS: calcd. for $C_{23}H_{14}N_2O_2$+H: 351.1134; found: 351.1148.

**2-(2-(3,5-Dimethyl-1H-pyrazol-1-yl)phenyl)isoindoline-1,3-dione (4o)**




According to the general procedure the title compound **4o** was isolated in 37% yield (24 mg) as a white solid using the mixture of hexane/ethyl acetate (80:20) as an eluent for column chromatography.

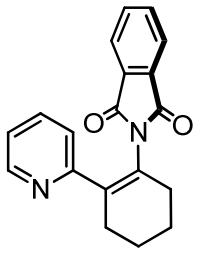
FTIR (KBr): 2922, 2849, 1717, 1601, 1463, 1215, 1083, 892, 719, 528 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.83 (dd, 2H, *J* = 5.5, 3.0 Hz), 7.71 (dd, 2H, *J* = 5.4, 3.0 Hz), 7.55-7.48 (m, 3H), 7.47-7.38 (m, 1H), 5.78 (s, 1H), 2.26 (s, 3H), 1.75 (s, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 166.9 (C), 149.5 (C), 140.6 (C), 137.0 (C), 134.0 (CH), 130.9 (CH), 129.4 (CH), 128.7 (CH), 127.4 (CH), 123.6 (CH), 106.1 (CH), 13.0 ($CH_3$), 11.8 ($CH_3$).

HRMS: calcd. for $C_{19}H_{15}N_3O_2$+H: 318.1242; found: 318.1256.

**2-(6-(Pyridin-2-yl)cyclohex-1-en-1-yl)isoindoline-1,3-dione (4p)**



According to the general procedure the title compound **4p** was isolated in 30% yield (18 mg) as a white solid using the mixture of hexane/ethyl acetate (80:20) as an eluent for column chromatography.

FTIR (KBr): 3423, 2928, 1712, 1585, 1466, 1429, 1264, 1078, 909 $cm^{-1}$.

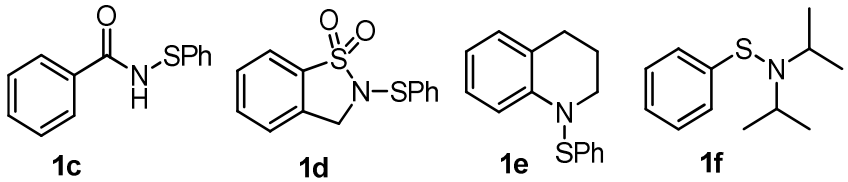
$^1H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.38 (d, 1H, *J* = 3.9 Hz), 7.78-7.72 (m, 2H), 7.68-7.62 (m, 2H), 7.44 (t, 1H, *J* = 7.7 Hz), 7.14 (d, 1H, *J* = 7.7 Hz), 7.01-6.94 (m, 1H), 2.67 (s, 2H), 2.39 (s, 2H), 1.90 (s, 4H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 167.4 (C), 158.1 (C), 149.3 (CH), 139.2 (C), 136.2 (CH), 133.9 (CH), 132.1 (C), 127.2 (C), 123.4 (CH), 122.0 (CH), 121.7 (CH), 29.3 ($CH_2$), 29.0 ($CH_2$), 22.5 ($CH_2$), 22.3 ($CH_2$).

HRMS: calcd. for $C_{19}H_{16}N_2O_2$+H: 305.1290; found: 305.1298.

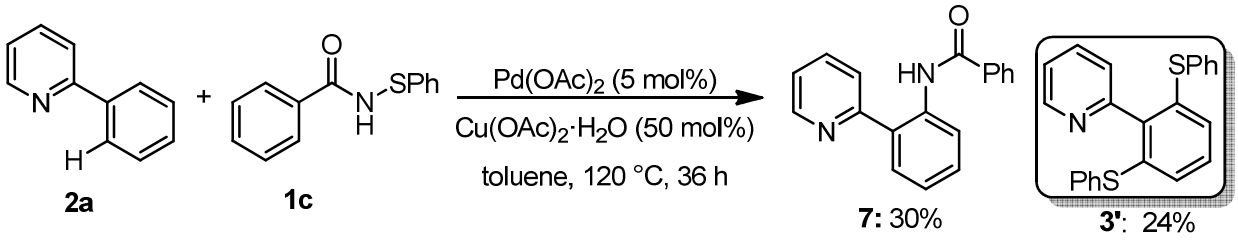
## 9. Palladium catalyzed amidation or amination of C–H bonds:

To extend the palladium catalyzed imidation of C-H bonds to amidation or amination, various N–S reagents **1c-1f** were synthesized[3,4] and subjected under the optimized imidation reaction conditions.



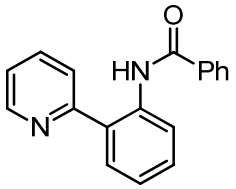

**1c** **1d** **1e** **1f**

The reaction of **2a** (0.2 mmol) with **1d** (2 equiv.) under the optimized conditions with $Pd(OAc)_2$ and $Cu(OAc)_2 \cdot H_2O$ gave the thiolated product **3a** in 27% yield and no corresponding amidation product was observed. Interestingly, the reaction of **2a** (0.2 mmol) with *N*-(phenylthio)benzamide **1c** (2 equiv.) in the presence of 5 mol% of $Pd(OAc)_2$ and 50 mol% of $Cu(OAc)_2 \cdot H_2O$ in toluene at 120 °C for 36 h provided the corresponding amidation product **7** in 30% yield (16 mg) along with the dithiolation product **3'** in 24% yield (18 mg).




On the other hand, palladium catalyzed amination with N-S reagents **1e** and **1f** didn't afford the expected amination of C–H bond, instead rapid decomposition of the N–S reagent was observed under the reaction conditions.

**2-(6-(Pyridin-2-yl)cyclohex-1-en-1-yl)isoindoline-1,3-dione (7)**




The title compound **7** was isolated in 30% yield (16 mg) as a white solid using the mixture of hexane/ethyl acetate (90:10) as an eluent for column chromatography.

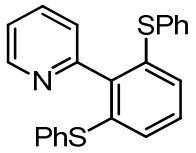
FTIR (KBr): 3448, 3056, 2922, 1731, 1667, 1587, 1473, 1434, 1266, 1047, 749 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 13.3 (s, 1H), 8.79 (dd, 1H, $J$ = 8.3, 1.1 Hz), 8.68 (ddd, 1H, $J$ = 4.9, 1.8, 0.9 Hz), 8.08-7.99 (m, 2H), 7.88-7.78 (m, 2H), 7.73 (dd, 1H, $J$ = 7.9, 1.5 Hz), 7.55-7.45 (m, 4H), 7.29 (ddd, 1H, $J$ = 7.2, 4.9, 1.3 Hz), 7.24-7.18 (m, 1H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 165.6 (C), 158.4 (C), 147.4 (CH), 138.2 (C), 138.0 (CH), 135.8 (C), 131.6 (CH), 130.4 (CH), 128.9 (CH), 128.7 (CH), 127.5 (CH), 125.7 (C), 123.7 (CH), 123.1 (CH), 122.1 (CH), 122.0 (CH).

HRMS: calcd. for $C_{18}H_{14}N_2O$+H: 275.1184; found: 275.1182.

**2-(2,6-Bis(phenylthio)phenyl)pyridine (3')**




The title compound **3'** was synthesized in 24% yield (18 mg) as a white solid using the mixture of hexane/ethyl acetate (92:8) as an eluent for column chromatography.

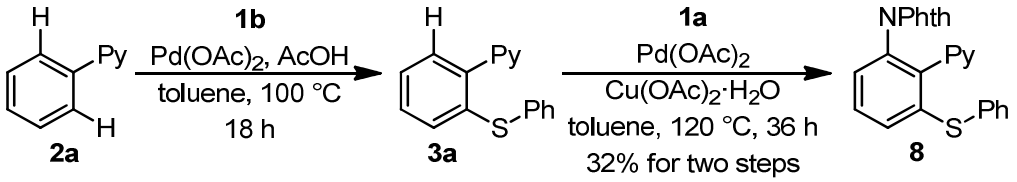
FTIR (KBr): 2965, 2927, 1602, 1450, 1392, 1267, 1056, 710, 529 $cm^{-1}$.

$^{1}H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.70 (d, 1H, $J$ = 4.7 Hz), 7.70 (td, 1H, $J$ = 7.6, 1.2 Hz), 7.35 (d, 1H, $J$ = 7.6 Hz), 7.33-7.22 (m, 11H), 7.09 (d, 1H, $J$ = 7.7 Hz), 7.06-6.91 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 157.0 (C), 149.5 (CH), 140.8 (C), 137.7 (CH), 136.1 (CH), 134.6 (CH), 132.7 (CH), 129.3 (CH), 129.2 (C), 128.4 (CH), 127.7 (CH), 125.4 (CH), 122.7 (CH).

HRMS: calcd. for $C_{23}H_{17}NS_2$+H: 372.0880; found: 372.0885.

## 10. Orthogonal functionalization of 2-phenylpyridine: Synthesis of 2-(3-(phenylthio)-2-(pyridin-2-yl)phenyl)isoindoline-1,3-dione (8)




Following the palladium catalyzed optimized conditions for the thiolation with **1b** followed by imidation with **1a** gave the orthogonally functionalized **8** in 31% overall yield (25 mg) for two-steps.

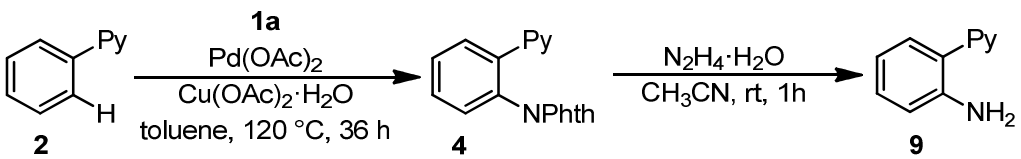
FTIR (KBr): 3056, 2925, 2853, 1720, 1586, 1108, 884, 718 $cm^{-1}$.

$^{1}H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.47-8.40 (m, 1H), 7.87 (dd, 1H, *J* = 5.4, 3.1 Hz), 7.77 (dd, 3H, *J* = 5.4, 3.1 Hz), 7.67 (dd, 2H, *J* = 5.4, 3.0 Hz), 7.59 (td, 1H, *J* = 7.7, 1.7 Hz), 7.44 (d, 1H, *J* = 7.7 Hz), 7.38-7.36 (m, 2H), 7.31-7.26 (m, 3H), 7.21 (dd, 1H, *J* = 7.7, 1.0 Hz), 7.06 (ddd, 1H, *J* = 7.5, 4.9, 1.0 Hz).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 167.1 (C), 155.1 (C), 149.3 (CH), 139.9 (C), 138.6 (C), 135.8 (CH), 134.4 (CH), 134.1 (CH), 133.0 (CH), 131.8 (C), 131.4 (CH), 131.2 (C), 129.5 (CH), 128.0 (CH), 127.6 (CH), 125.5 (CH), 123.7 (CH), 123.6 (C), 122.5 (CH).

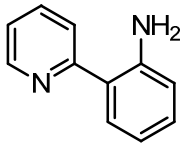
HRMS: calcd. for $C_{25}H_{16}N_2O_2S$+H: 409.1011; found: 409.1024.

## 11. Direct amination of C–H bonds *via* imidation:



Following the palladium-catalyzed imidation of C-H bond with **1a**, imidated product **4** was synthesized. A dry reaction tube was charged with **4** (0.15 mmol, obtained from imidation reaction), $N_2H_4 \cdot H_2O$ (1.5 mmol) and 8 mL acetonitrile. The reaction mixture was stirred at room temperature for 1 h. After completion of the reaction, as monitored by TLC, the reaction mixture was cooled to room temperature and purified by column chromatography using mixture of hexane and ethyl acetate as eluent afforded the pure product **9.**

**2-(pyridin-2-yl)aniline (9a)**




According to the general procedure the title compound **9a** was isolated in 80% yield (20 mg) as a light yellow liquid using the mixture of hexane/ethyl acetate (90:10) as an eluent for column chromatography.

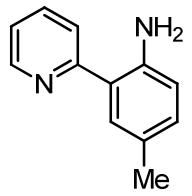
FTIR (KBr): 3400, 3325, 3051, 2986, 2928, 1592, 1476, 1265, 908, 737, 650 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.60 (ddd, 1H, *J* = 4.9, 1.8, 0.8 Hz), 7.79-7.71 (m, 1H,), 7.65 (td, 1H, *J* = 8.1, 0.9 Hz), 7.51 (dd, 1H, *J* = 7.7, 1.5 Hz), 7.21-7.14 (m, 2H), 6.82-6.74 (m, 2H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 24 °C): δ 159.5 (C), 147.9 (CH), 146.6 (C), 137.0 (CH), 130.0 (CH), 129.5 (CH), 122.3(8) (C), 122.3 (CH), 121.0 (CH), 117.7 (CH), 117.3 (CH).

HRMS: calcd. for $C_{11}H_{10}N_2$+H: 171.0922; found: 171.0935.

**4-Methyl-2-(pyridin-2-yl)aniline (9b)**




According to the general procedure the title compound **9b** was isolated in 78% yield (22 mg) as a light yellow liquid using the mixture of hexane/ethyl acetate (90:10) as an eluent for column chromatography.

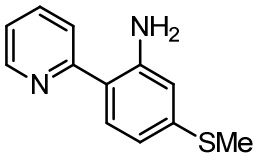
FTIR (KBr): 3455, 3335, 3054, 2985, 2922, 1589, 1473, 1265, 909, 746, 650 $cm^{-1}$.

$^{1}H$ NMR (500 MHz, $CDCl_3$, 24 °C): δ 8.60 (ddd, 1H, *J* = 4.9, 1.8, 0.8 Hz), 7.74 (td, 1H, *J* = 8.0, 1.9 Hz), 7.64 (d, 1H, *J* = 8.0 Hz), 7.31 (d, 1H, *J* = 1.4 Hz), 7.16 (ddd, 1H, *J* = 7.4, 4.9, 1.0 Hz), 7.03-6.97 (m, 1H), 6.69 (d, 1H, *J* = 8.0 Hz), 5.51 (bs, 2H), 2.30 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, 24 °C): δ 159.5 (C), 148.0 (CH), 144.0 (C), 136.9 (CH), 130.7 (CH), 129.9 (CH), 126.8 (C), 122.6 (C), 122.3 (CH), 121.0 (CH), 117.4 (CH), 20.6 ($CH_3$).

HRMS: calcd. for $C_{12}H_{12}N_2$+H: 185.1079; found: 185.1042.

**5-(Methylthio)-2-(pyridin-2-yl)aniline (9c)**




According to the general procedure the title compound **9c** was isolated in 79% yield (26 mg) as a yellow solid using the mixture of hexane/ethyl acetate (90:10) as an eluent for column chromatography.

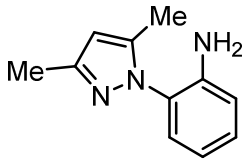
FTIR (KBr): 3449, 3299, 3054, 2921, 1588, 1467, 1253, 1097, 908, 776, 630 $cm^{-1}$.

$^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C): δ 8.62-8.53 (m, 1H), 7.72 (td, 1H, *J* = 8.0, 1.9 Hz), 7.62 (d, 1H, *J* = 8.1 Hz), 7.44 (d, 1H, *J* = 8.2 Hz), 7.13 (ddd, 1H, *J* = 7.3, 4.8, 1.0 Hz), 6.66 (dd, 1H, *J* = 8.3, 1.9 Hz), 6.60 (d, 1H, *J* = 1.9 Hz), 5.89 (bs, 2H), 2.48 (s, 3H).

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 159.1 (C), 147.8 (CH), 147.1 (C), 140.6 (C), 136.9 (CH), 129.6 (CH), 121.7 (CH), 120.7 (CH), 119.0 (C), 115.5 (CH), 114.0 (CH), 15.4 ($CH_3$).

HRMS: calcd. for $C_{12}H_{12}N_2S$+H: 217.0799; found: 217.0827.

**2-(2,4-Dimethyl-1*H*-imidazol-1-yl)aniline (9d)**




According to the general procedure the title compound **9e** was isolated in 99% yield (27 mg) as a colorless solid using the mixture of hexane/ethyl acetate (90:10) as an eluent for column chromatography.

FTIR (KBr): 3457, 3381, 3051, 2980, 2925, 1621, 1554, 1509, 1422, 908, 740 $cm^{-1}$.

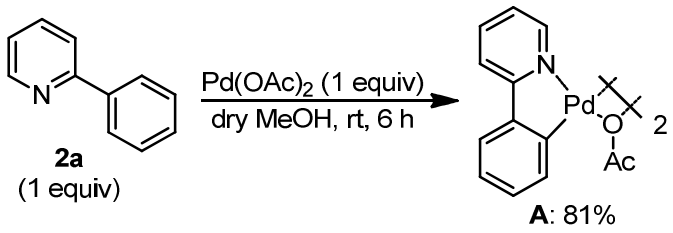
$^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.17 (t, 1H, *J* = 7.3 Hz), 7.06 (d, 1H), 6.95-6.65 (m, 2H), 5.97 (s, 1H), 3.94 (s, 2H), 2.28 (s, 3H), 2.15 (s, 3H).

$^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 149.5 (C), 143.5 (C), 140.8 (C), 129.5 (CH), 127.7 (CH), 125.6 (C), 118.1 (CH), 116.7 (CH), 105.7 (CH), 13.7 ($CH_3$), 11.6 ($CH_3$).

HRMS: calcd. for $C_{11}H_{13}N_3$+H: 188.1182; found: 188.1183.

## 12.Mechanistic studies:

### i) Synthesis of palladium complex A:

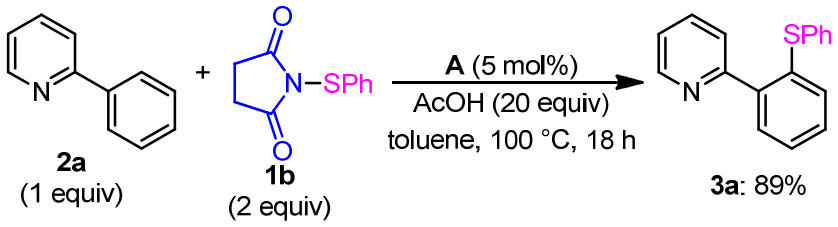



The complex **A** was synthesized from **2a** according to the literature procedure.[5]To a mixture of 2-phenylpyridine **2a** (0.9 mmol) and $Pd(OAc)_2$ (0.9 mmol), dry methanol (14 mL) was added and stirred at rt under $N_2$ atmposphere for 6h. During this time a yellow precipitate was observed in the reaction mixture. After the completion of reaction, it was filtered through a small pad of celite using hexane, followed by the yellow residue was washed with DCM and the DCM solvent was concentrated in *vacuo* afforded the pure product **A** as a yellow solid in 81% yield.

$^1$H NMR (400 MHz, $CDCl_3$, 24 °C): δ 7.90-7.84 (m, 2H), 7.36 (td, 2H, $J$ = 7.9, 1.6 Hz), 7.08 (d, 2H, $J$ = 7.9 Hz), 6.94-6.77 (m, 8H), 6.55-6.32 (m, 2H), 2.26 (s, 6H).

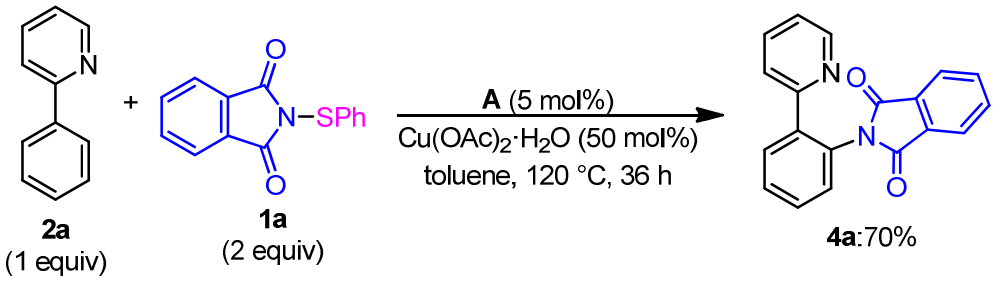
$^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$, 24 °C): δ 181.8 (C), 164.3 (C), 152.0 (C), 150.2 (CH), 144.5 (C), 137.5 (CH), 131.9 (CH), 128.5 (CH), 123.9 (CH), 122.4 (CH), 121.1 (CH), 117.1 (CH), 24.9 ($CH_3$).

### ii) Palladium complex A catalyzed thiolation and amidation of 2a:



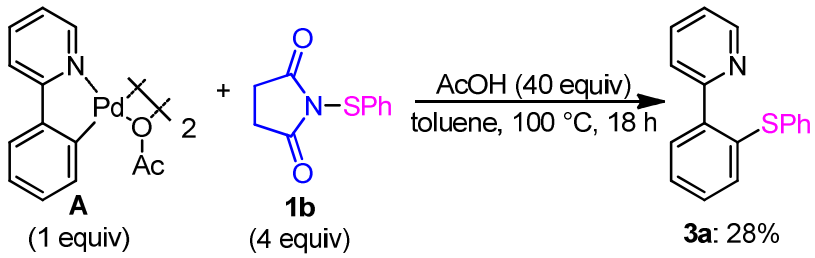

[5] X. Peng, Y. Zhu, T. A. Ramirez, B. Zhao, Y. Shi, *Org. Lett.* **2011**, *13*, 5244-5247.

A dry reaction tube (10 mL) was charged with **2a** (0.3 mmol), *N*-(phenylthio)succinimide **1b** (0.6 mmol), **A** (5 mol%), acetic acid (20 equiv) and dry toluene (1.5 mL) under nitrogen atmosphere. The reaction tube was sealed under nitrogen atmosphere and kept at 100 °C for 18 h. After the completion of the reaction, as monitored by TLC, the reaction mixture was cooled to room temperature and purified by column chromatography afforded the product **3a** in 89% yield.



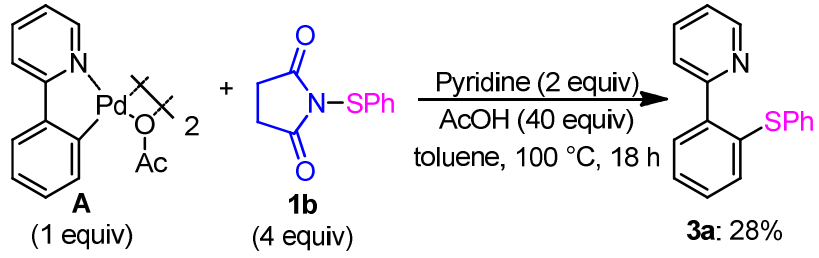

A dry reaction tube (10 mL) was charged with **2a** (0.3 mmol), *N*-(phenylthio)pthalimide **1a** (0.6 mmol), **A** (5 mol%), $Cu(OAc)_2 \cdot H_2O$ (50 mol%) and dry toluene (2 mL) under nitrogen atmosphere. The reaction tube was sealed under nitrogen atmosphere and kept at 120 °C for 36 h. After the completion of the reaction, as monitored by TLC the reaction mixture was cooled to room temperature and purified by column chromatography afforded the product **4a** in 70% yield.

### iii) Stoichiometric reaction of palladacycle A:

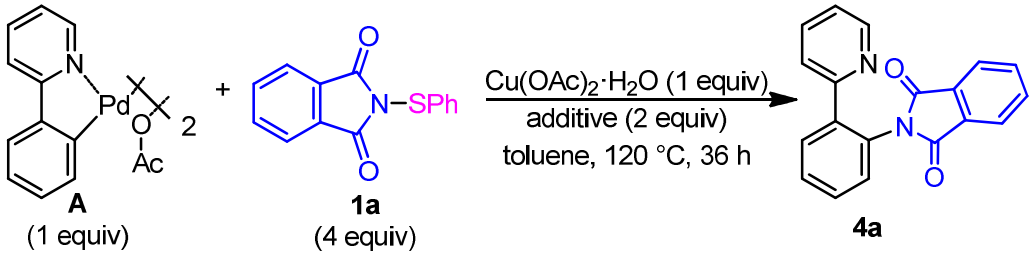



In a dry reaction tube (10 mL) palladacycle **A** (0.05 mmol), *N*-(phenylthio)succinimide **1b** (0.2 mmol), acetic acid (40 equiv) was taken and dry toluene (0.75 mL) was added and stirred at 100 °C under nitrogen atmosphere for 18 h. After the completion of the reaction, the reaction

mixture was cooled to room temperature and purified by column chromatography afforded the product **3a** in 28% yield.




In a dry reaction tube (10 mL) palladacycle **A** (0.05 mmol), *N*-(phenylthio)succinimide **1b** (0.2 mmol), acetic acid (40 equiv) and pyridine (2 equiv) was taken and dry toluene (0.75 mL) was added and stirred at 100 °C under nitrogen atmosphere for 18 h. After the completion of the reaction, the reaction mixture was cooled to room temperature and purified by column chromatography afforded the product **3a** in 28% yield.



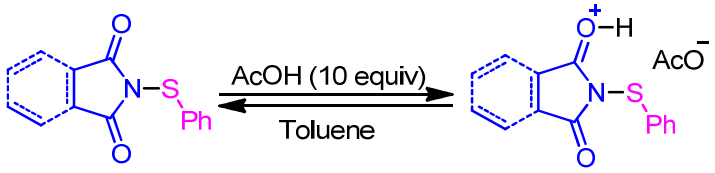

| Entry | Additive | Yield (%) |
|---|---|---|
| 1 | - | - |
| 2 | $PPh_3$ | - |
| 3 | Pyridine | - |
| 4 | 2l | 26[a] |

a) mixture of **4a** and **4l**

In a dry reaction tube (10 mL) palladacycle **A** (0.05 mmol), *N*-(phenylthio)pthalimide **1a** (0.2 mmol), $Cu(OAc)_2 \cdot H_2O$ (1 equiv) and additive (2 equiv) was taken and dry toluene (1 mL) was

added and stirred at 120 °C under nitrogen atmosphere for 36 h. After the completion of the reaction, the reaction mixture was cooled to room temperature and purified by column chromatography.

**iv) Variable temperature FTIR and NMR study of mixture of 1a/1b and acetic acid:**




The reaction of **2a** with **1a**/**1b** in the presence of acetic acid provided the thiolation of C–H bond. We anticipated that, in the presence of acetic acid, amide oxygen would get protonated, which makes the i(a)mide as good leaving group, consequently, arylthio moiety could get transferred to form the C–S bond. To get the insight information about the hypothesis, variable temperatures FTIR and NMR was studied. In FTIR, the compound **1b** in toluene shows carbonyl stretching frequency at 1731 $cm^{-1}$ (Figure S1). In the presence of acetic acid at room temperature the carbonyl stretching frequency is shifted to lower frequency (1717 $cm^{-1}$). Next, increasing the temperature to 50 °C didn't show any further reduction in the stretching frequency (1718 $cm^{-1}$). This lowering in carbonyl stretching frequency of **1b** in the presence of acetic acid indicates the weakening of the C=O bond possible through protonation of carbonyl oxygen. Similar trend was also observed with **1a** in the presence of acetic acid, where the original band (1743 $cm^{-1}$) is shifted to 1717 $cm^{-1}$ at room temperature and 1715 $cm^{-1}$ at 50 °C (Figure S2).

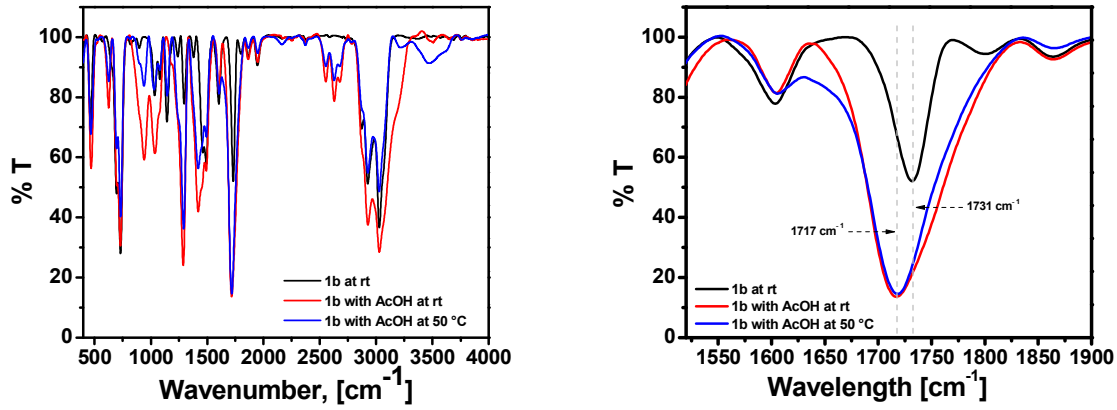



**Figure S1**. FTIR spectrum of **1b** with acetic acid at various temperatures

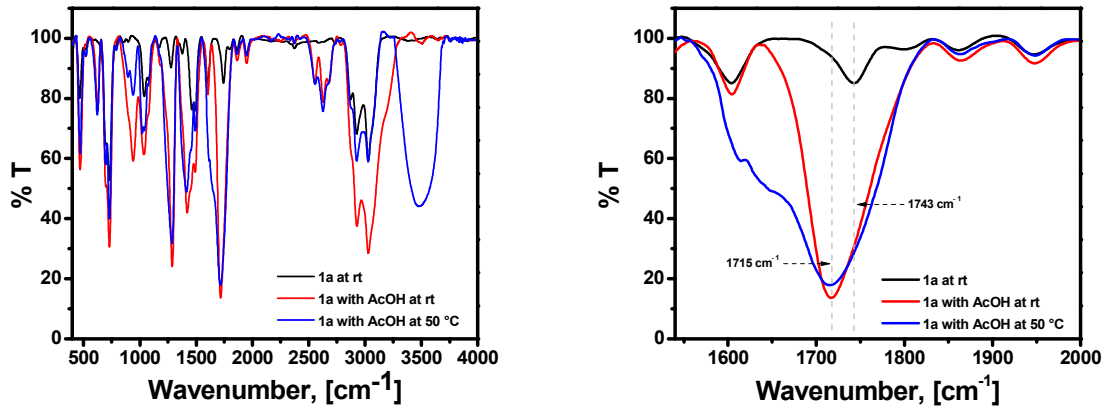



**Figure S2**. FTIR spectrum of **1a** with acetic acid at various temperatures

Subsequently, $^{1}$H NMR study of **1b** with acetic acid in toluene-d8 at variable temperature clearly shows the significant shift of methylene proton attached to carbonyl of imide towards downfield (1.56 ppm to 1.65 ppm, Figure S3). Similarly, most of the aromatic carbons in $^{13}$C NMR also shifted to downfield. Specifically, the significant shift was observed for carbonyl carbon of **1b** from δ 175.28 at room temperature to 175.70 at 100 °C (Figure S4). Similar trend was observed in **1a**, where the carbonyl carbon shifted from δ 167.08 at room temperature to 167.41 at 100 °C (Figure S6). Downfield shift both in $^{1}$H and $^{13}$C NMR suggests decrease in electron density on overall molecules, which is possibly due to protonation of amide oxygen.

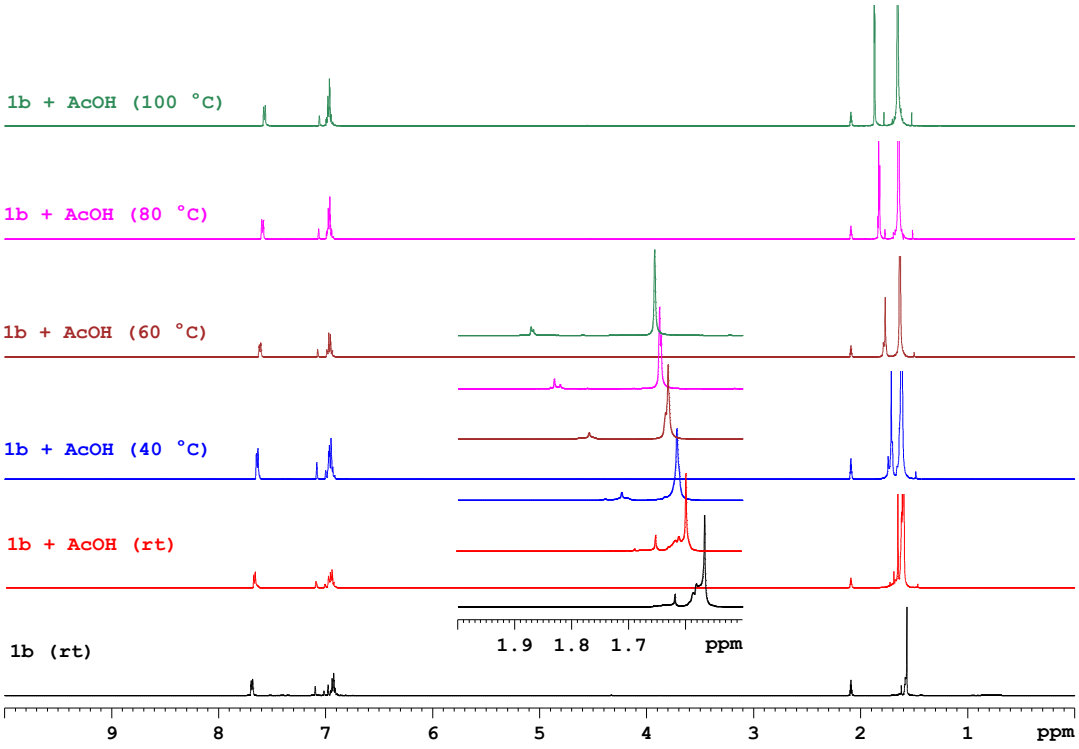



**Figure S3**. $^{1}$H-NMR of **1b** with acetic acid at various temperatures

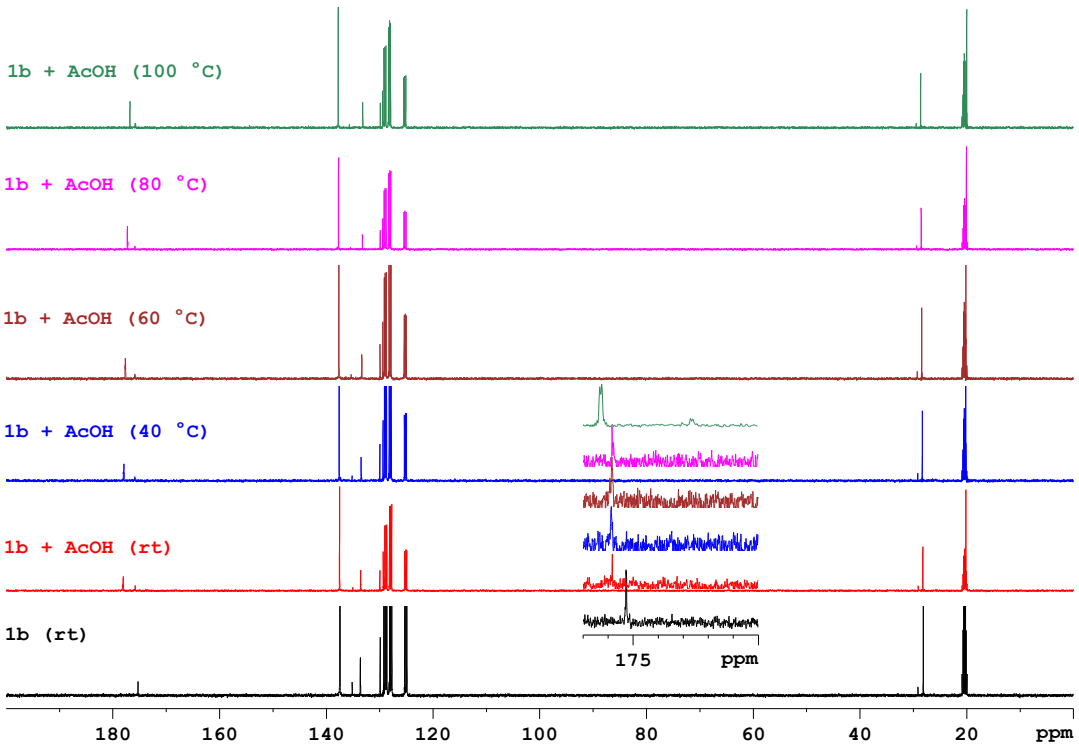



**Figure S4**. $^{13}$C-NMR of **1b** with acetic acid at various temperatures

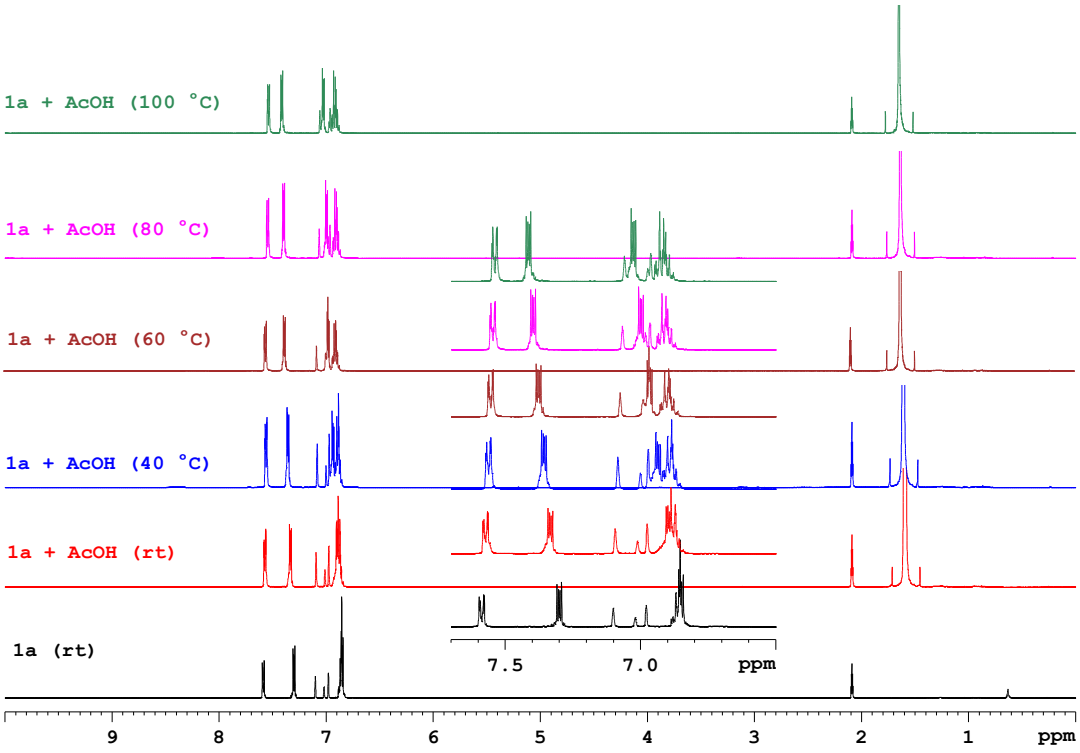



**Figure S5**. [1]H-NMR of **1a** with acetic acid at various temperatures

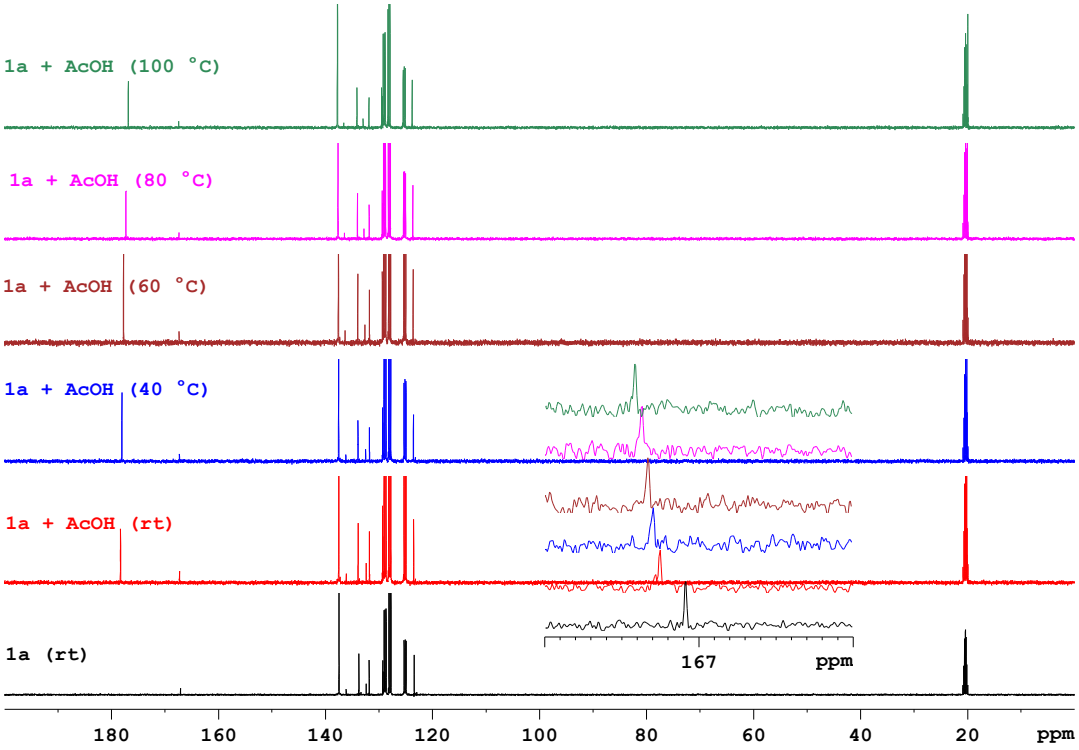
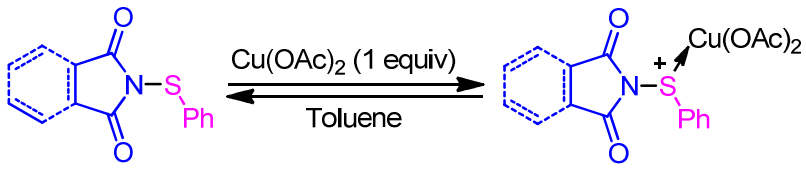



**Figure S6**. [13]C-NMR of **1a** with acetic acid at various temperatures

**v) Variable temperature FTIR and NMR study of mixture of 1a and $Cu(OAc)_2$:**




As anticipated, the reaction **2a** with **1a** in presence of $Cu(OAc)_2$ afforded the formation of imidation product **4a**, which is possibly through the coordination of sulphur with $Cu(OAc)_2$ making the arylthio moiety as good leaving group and as a consequence, the imide moiety could get transferred to form C–N bond. To validate the assumption variable temperature FTIR and NMR was investigated. At room temperature in FTIR, the compound **1a** shows carbonyl stretching frequency at 1743 $cm^{-1}$. In presence of 1 equivalent of $Cu(OAc)_2$ at various temperatures (rt, 50 °C and 100 °C) showed no change in the stretching frequency of carbonyl group even after 12 h (Figure S7), whereas in the presence of acetic acid significant lowering of stretching frequency of carbonyl group was observed (Figure S2). This result reveals that $Cu(OAc)_2$ is not coordinating with carbonyl group of the imide moiety.

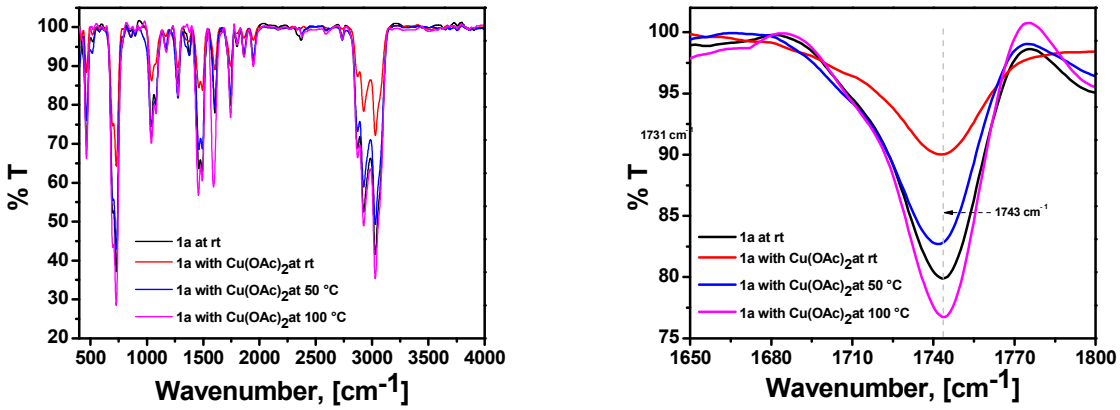



**Figure S7**. IR spectrum of **1a** with $Cu(OAc)_2$ at various temperatures

Next, to demonstrate the interaction of $Cu(OAc)_2$ with sulfur of **1a**, variable temperature $^1H$ and $^{13}C$ NMR was examined with equimolar mixture of **1a** and $Cu(OAc)_2$ in toluene-$d_8$. In $^1H$ NMR,

a significant downfield shift of protons of arylthio moiety (6.74-6.93 ppm to 6.83- 7.01 ppm) was observed. In particular, ortho protons have showed major downfield (Figure S8). On the other hand, only selected carbons are shifted to downfield in $^{13}C$ NMR. The carbonyl carbon of **1a** that was observed in toluene-$d_8$ at δ 167.08 at rt only marginally shifted to δ 167.17 in presence of $Cu(OAc)_2$ at 100 °C, which is for less downfield shift compared to the shift observed in the presence of AcOH. Interestingly, the quaternary carbon which is attached to the sulfur was significantly shifted from δ 136.12 to 136.63, when temperature was raised from room temperature to 100 °C (Figure S9 and S10). These observations suggested that the imide moiety in **1a** is not interacting with $Cu(OAc)_2$, on the other hand, significant shift in the sulfur attached quaternary carbon reveals the possible co-ordination of sulfur with $Cu(OAc)_2$.

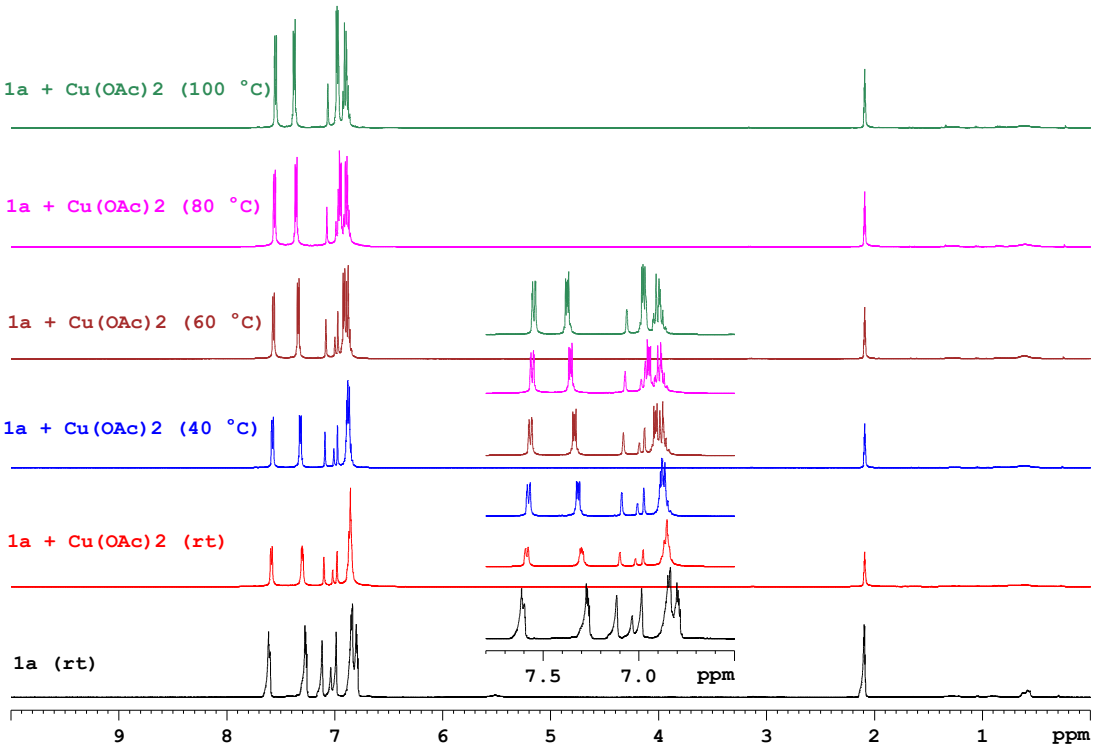



**Figure S8**. $^1H$-NMR of **1a** with $Cu(OAc)_2$ at various temperatures

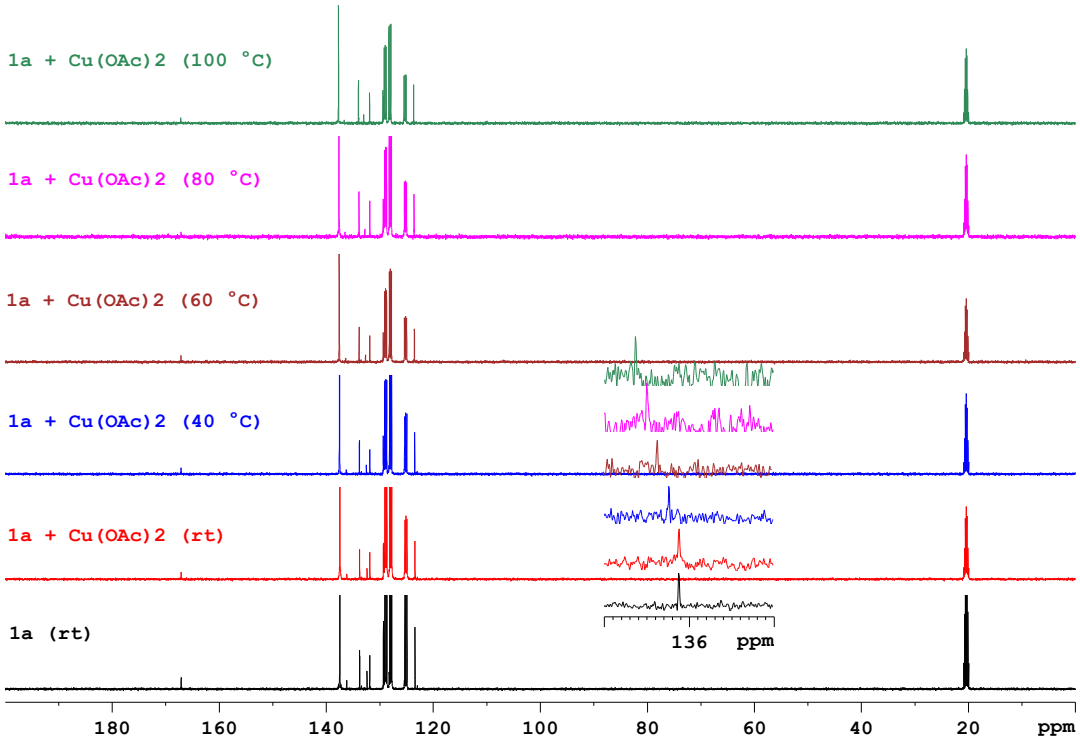
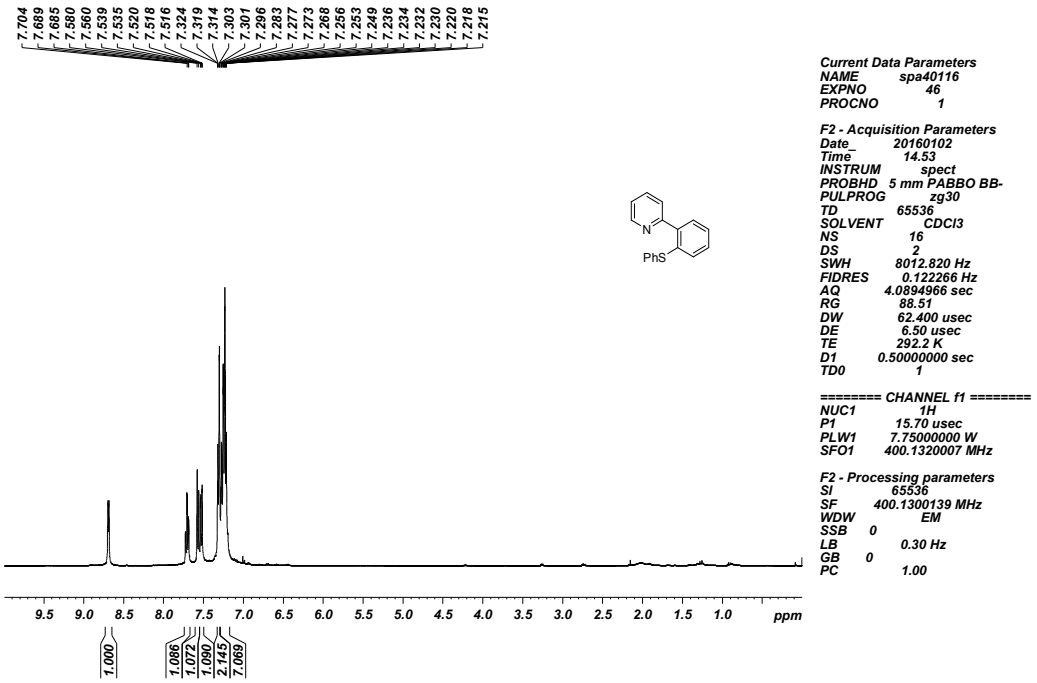



**Figure S9**. $^{13}$C-NMR of **1a** with $Cu(OAc)_2$ at various temperatures

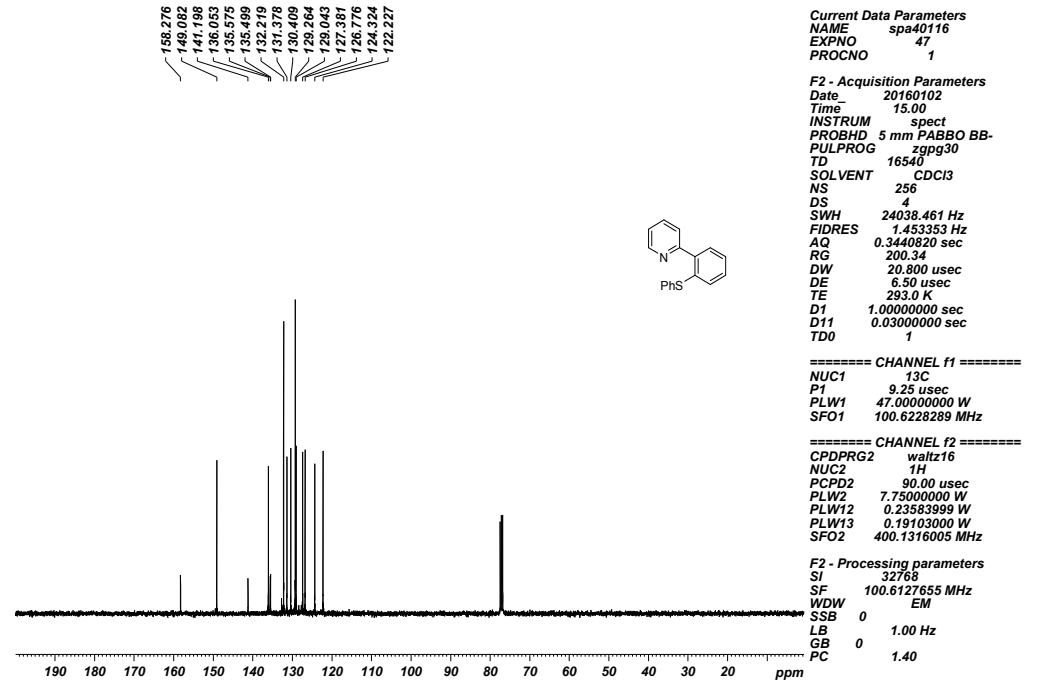
# 13. NMR spectra of isolated compounds:

## 2-(2-(Phenylthio)phenyl)pyridine (3a)

### $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

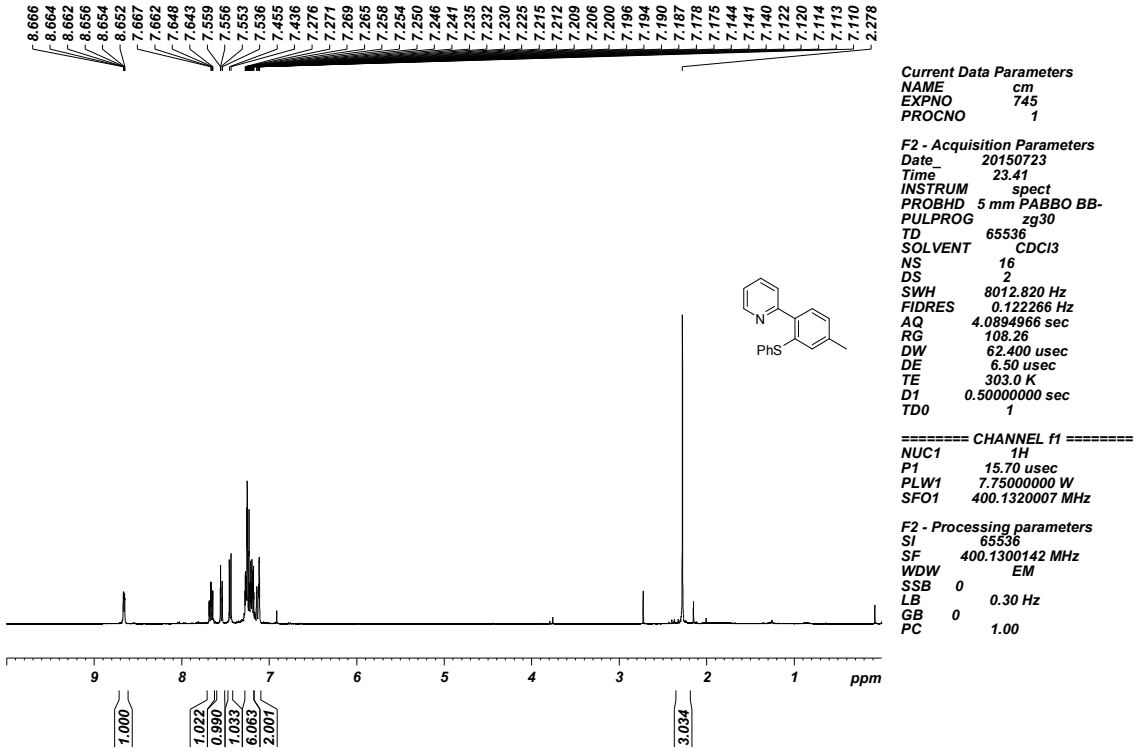



### $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

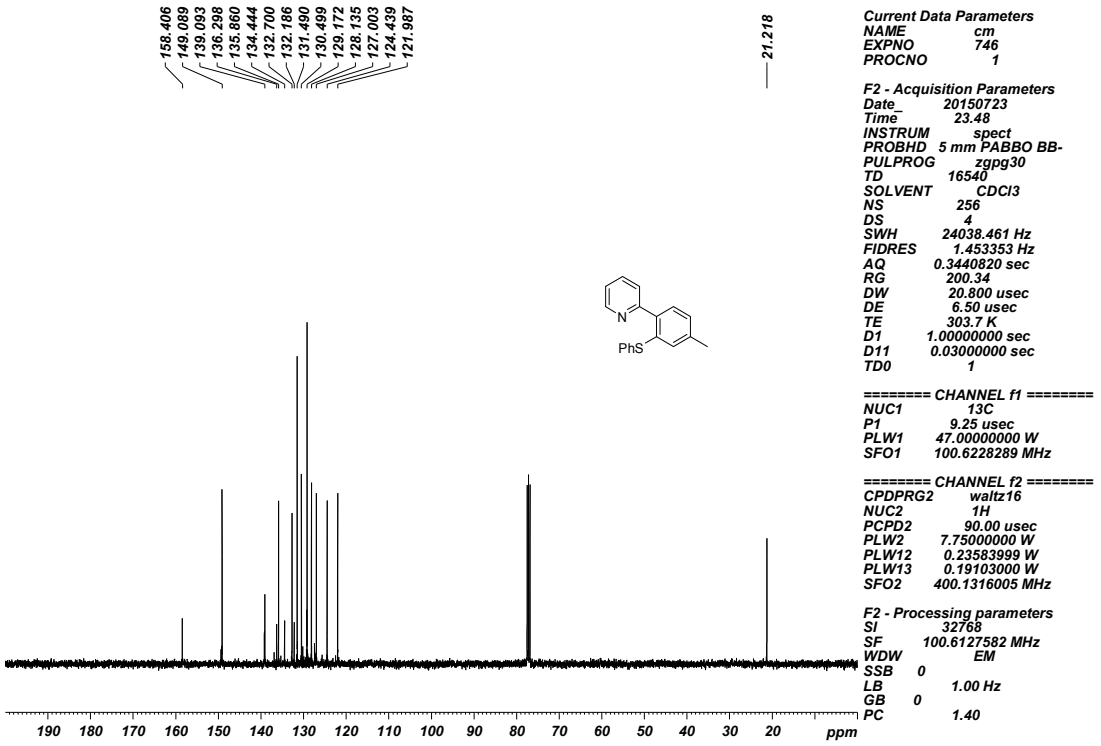


## 2-(4-Methyl-2-(phenylthio)phenyl)pyridine (3b)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

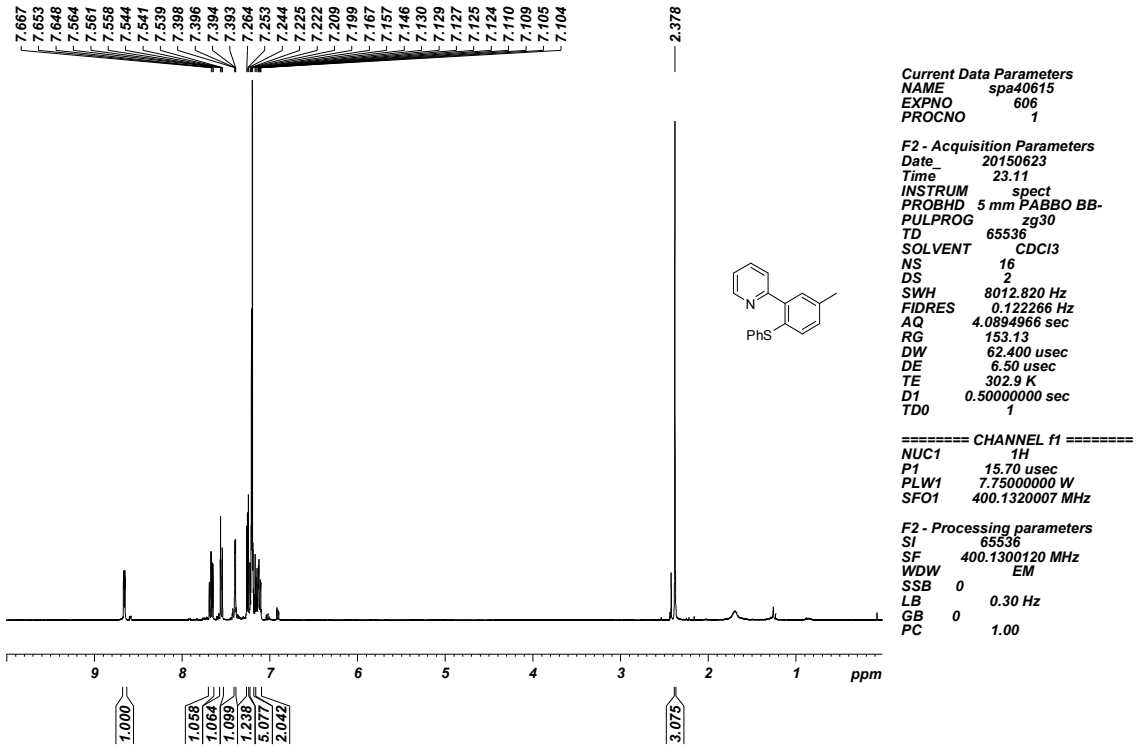



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

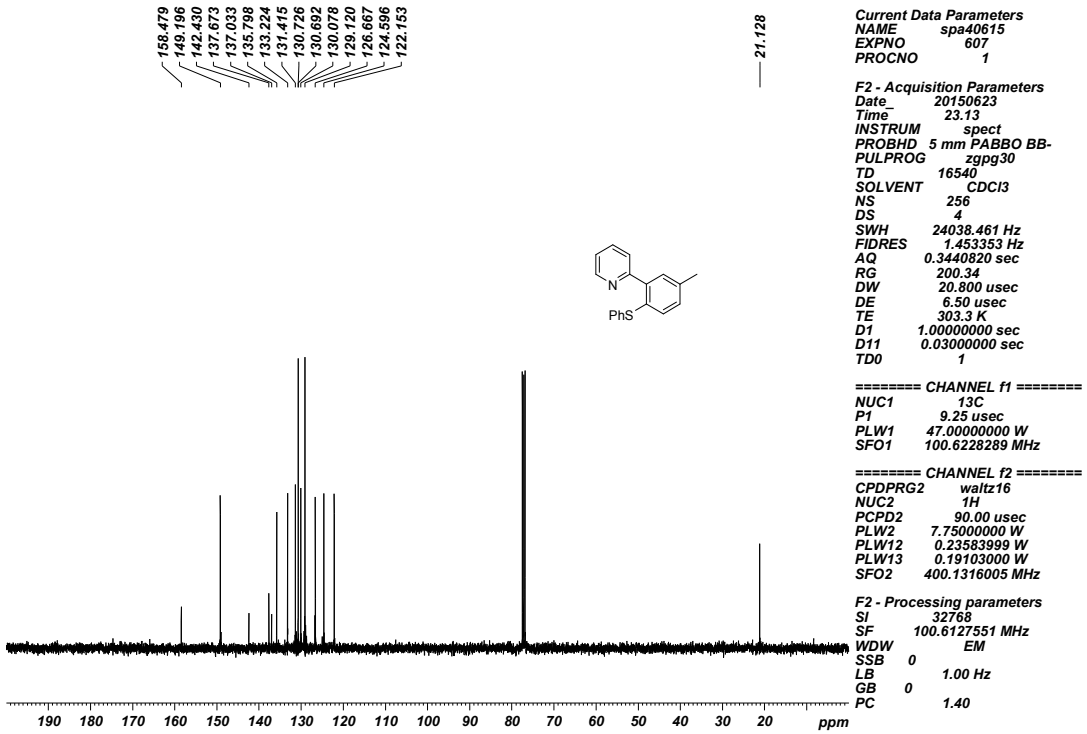


## 2-(5-Methyl-2-(phenylthio)phenyl)pyridine (3c)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

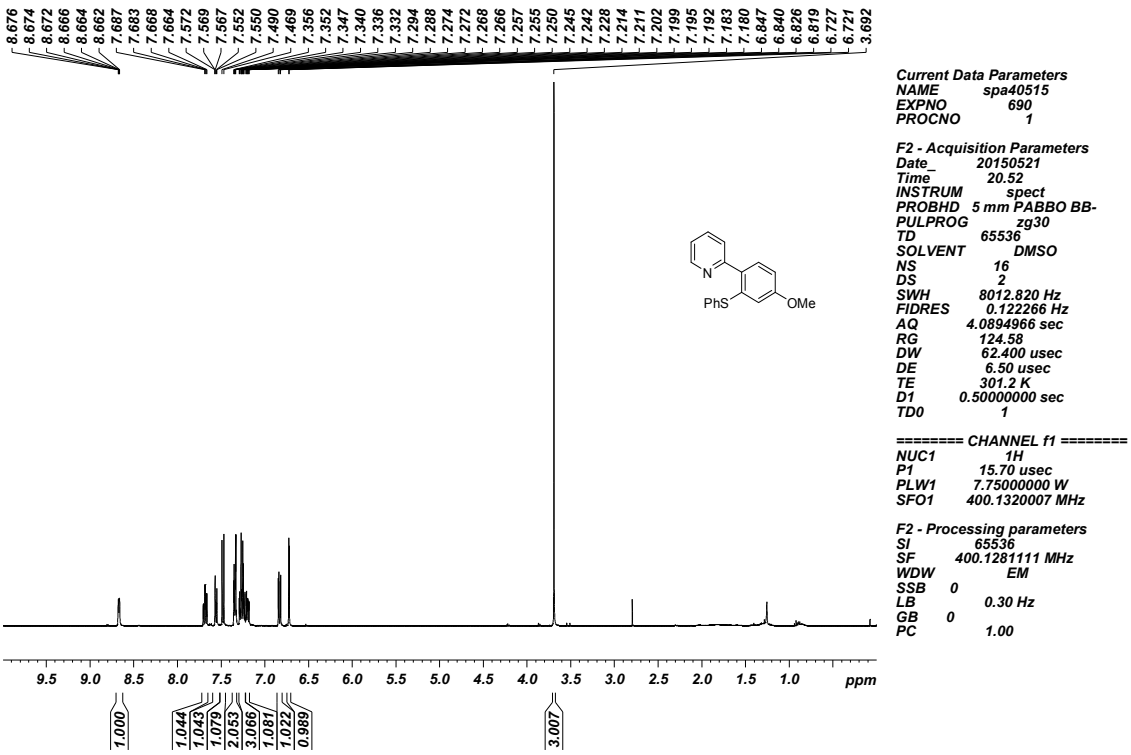



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)



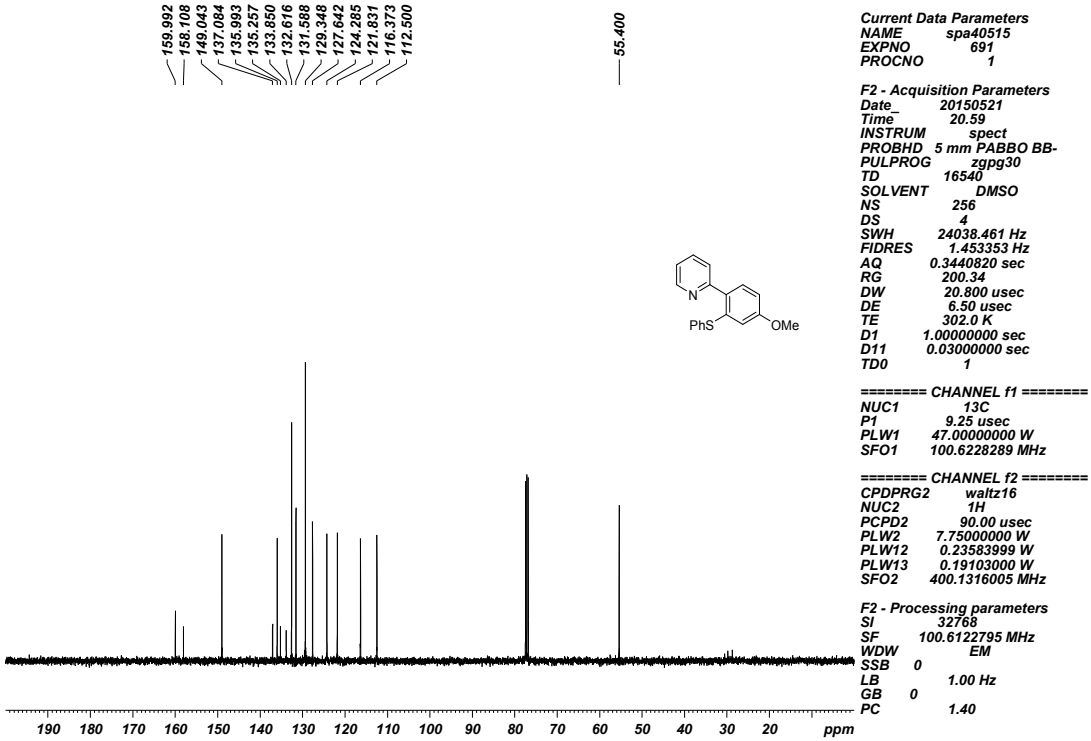
## 2-(4-Methoxy-2-(phenylthio)phenyl)pyridine (3d)

### $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)




```
Current Data Parameters
NAME          spa40515
EXPNO              690
PROCNO               1

F2 - Acquisition Parameters
Date_         20150521
Time             20.52
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD              65536
SOLVENT          DMSO
NS                  16
DS                   2
SWH           8012.820 Hz
FIDRES           0.122266 Hz
AQ            4.0894966 sec
RG                 124.58
DW                62.400 usec
DE                 6.50 usec
TE                301.2 K
D1            0.50000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1                15.70 usec
PLW1          7.75000000 W
SFO1          400.1320007 MHz

F2 - Processing parameters
SI                 65536
SF            400.1281111 MHz
WDW                  EM
SSB          0
LB                0.30 Hz
GB           0
PC                1.00
```

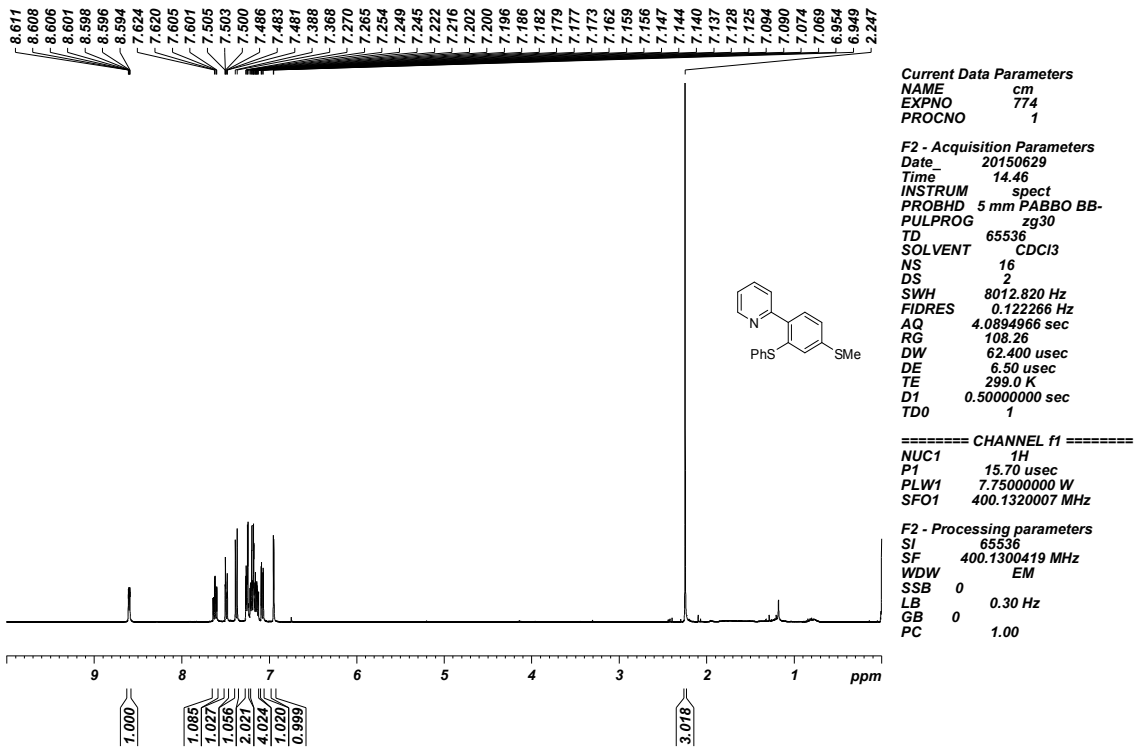
### $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)



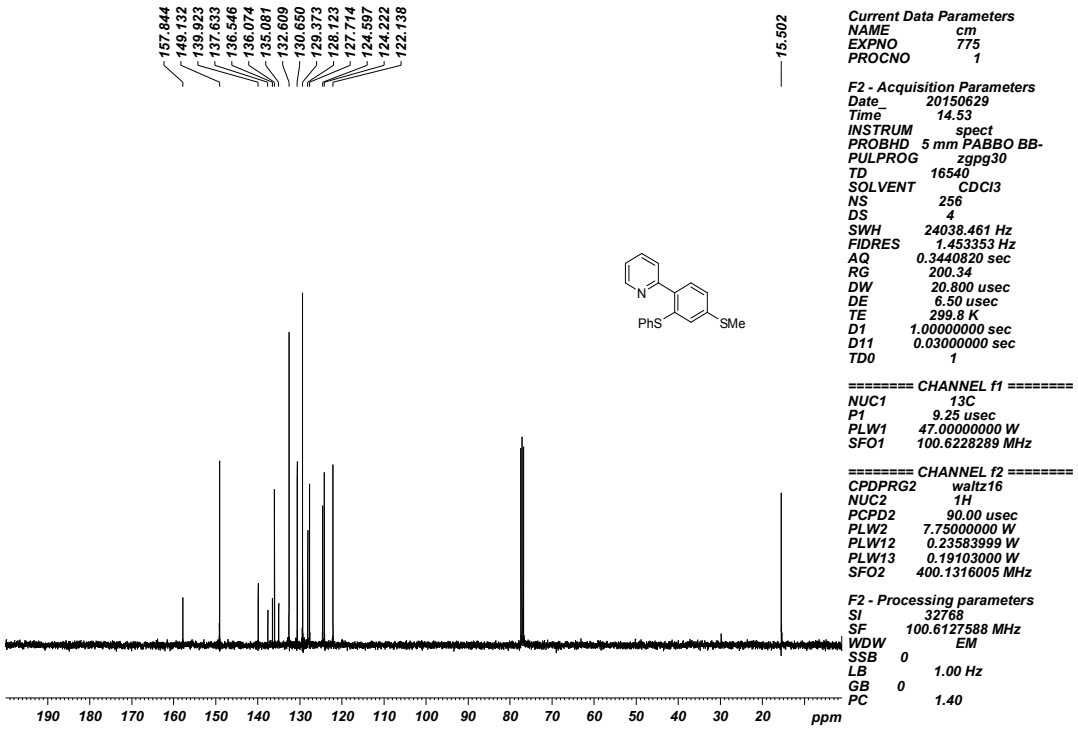

```
Current Data Parameters
NAME          spa40515
EXPNO              691
PROCNO               1

F2 - Acquisition Parameters
Date_         20150521
Time             20.59
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG        zgpg30
TD              16540
SOLVENT          DMSO
NS                 256
DS                   4
SWH           24038.461 Hz
FIDRES            1.453353 Hz
AQ            0.3440820 sec
RG                 200.34
DW                20.800 usec
DE                 6.50 usec
TE                302.0 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1                9.25 usec
PLW1         47.00000000 W
SFO1         100.6228289 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            90.00 usec
PLW2          7.75000000 W
PLW12         0.23583999 W
PLW13         0.19103000 W
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF            100.6122795 MHz
WDW                  EM
SSB          0
LB                1.00 Hz
GB           0
PC                1.40
```

## 2-(4-(Methylthio)-2-(phenylthio)phenyl)pyridine (3e)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

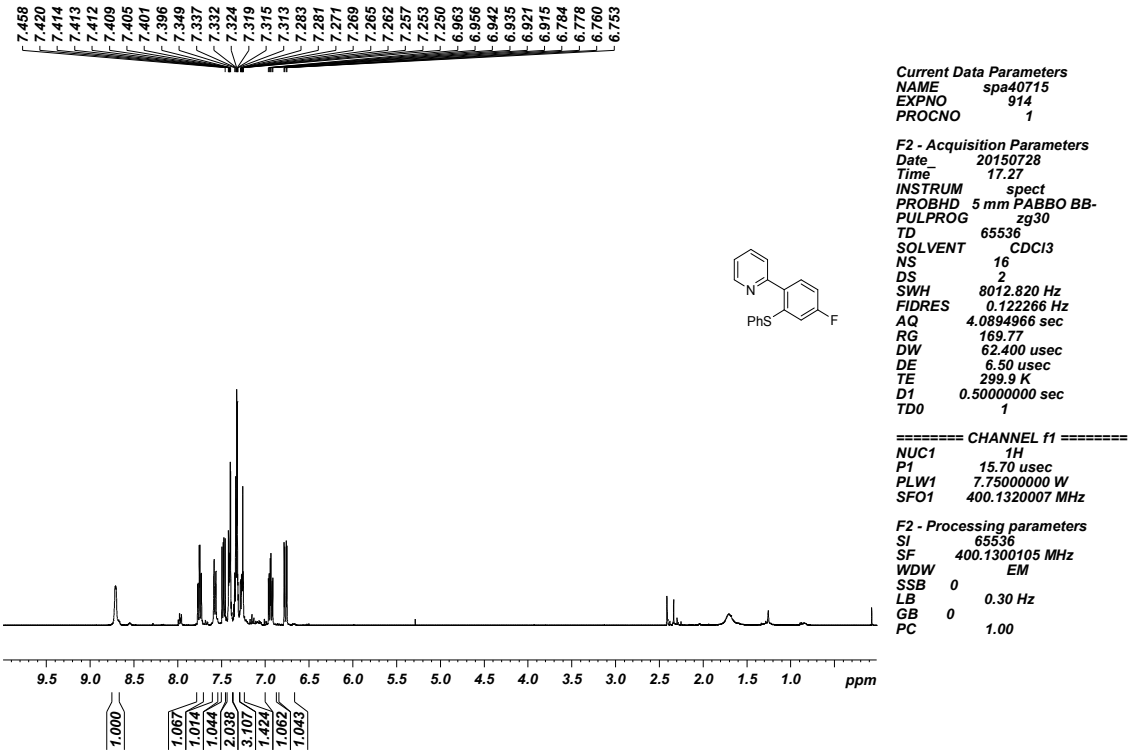



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

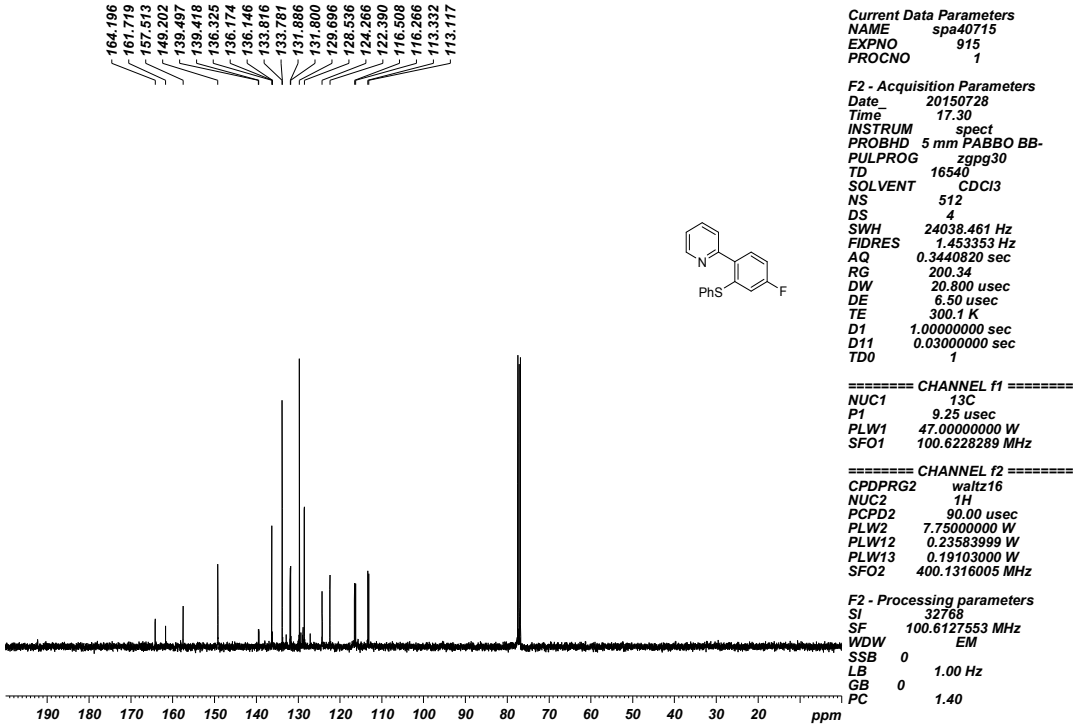


## 2-(4-Fluoro-2-(phenylthio)phenyl)pyridine (3g)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

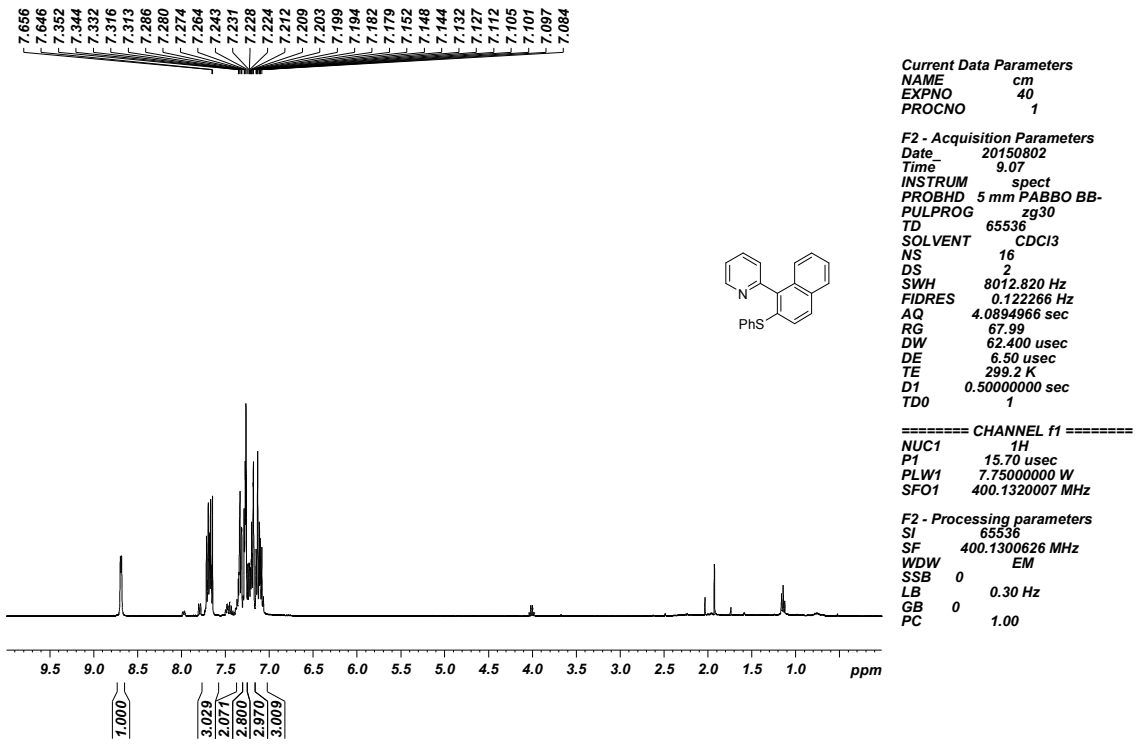



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

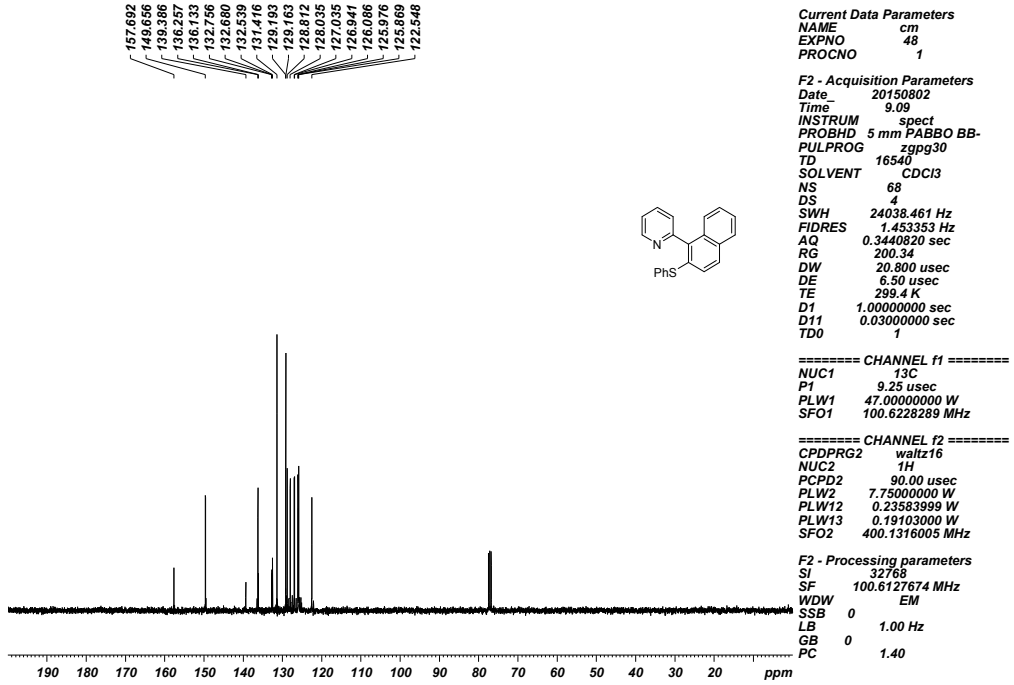


## 2-(2-(Phenylthio)naphthalen-1-yl)pyridine (3i)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

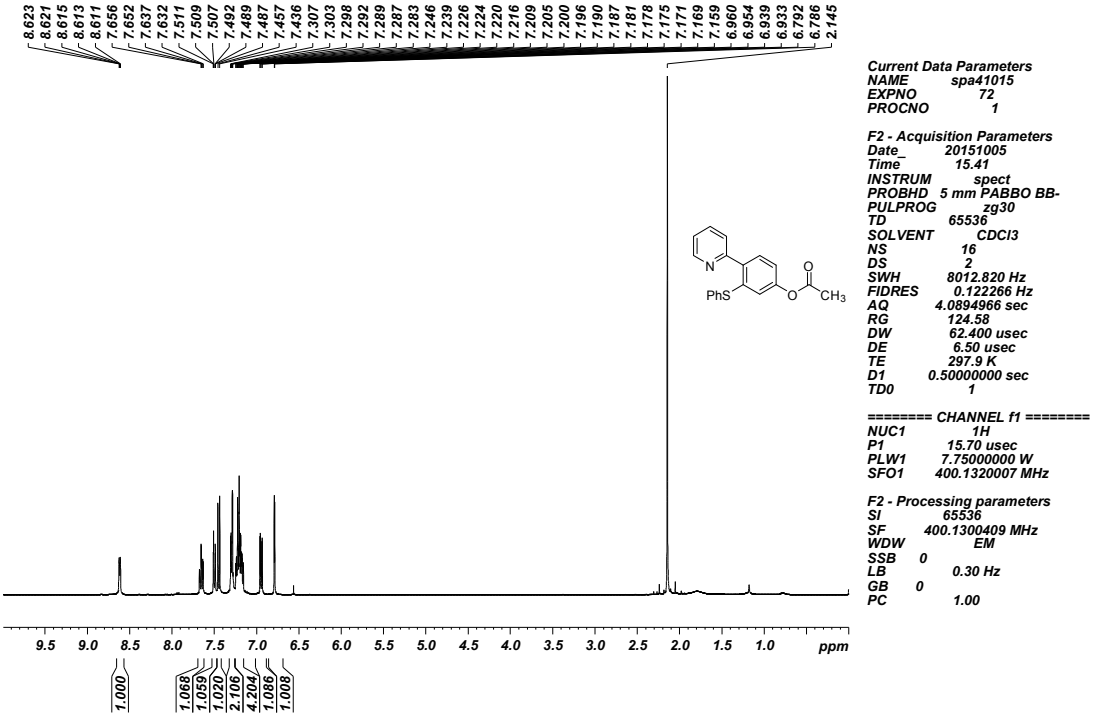



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

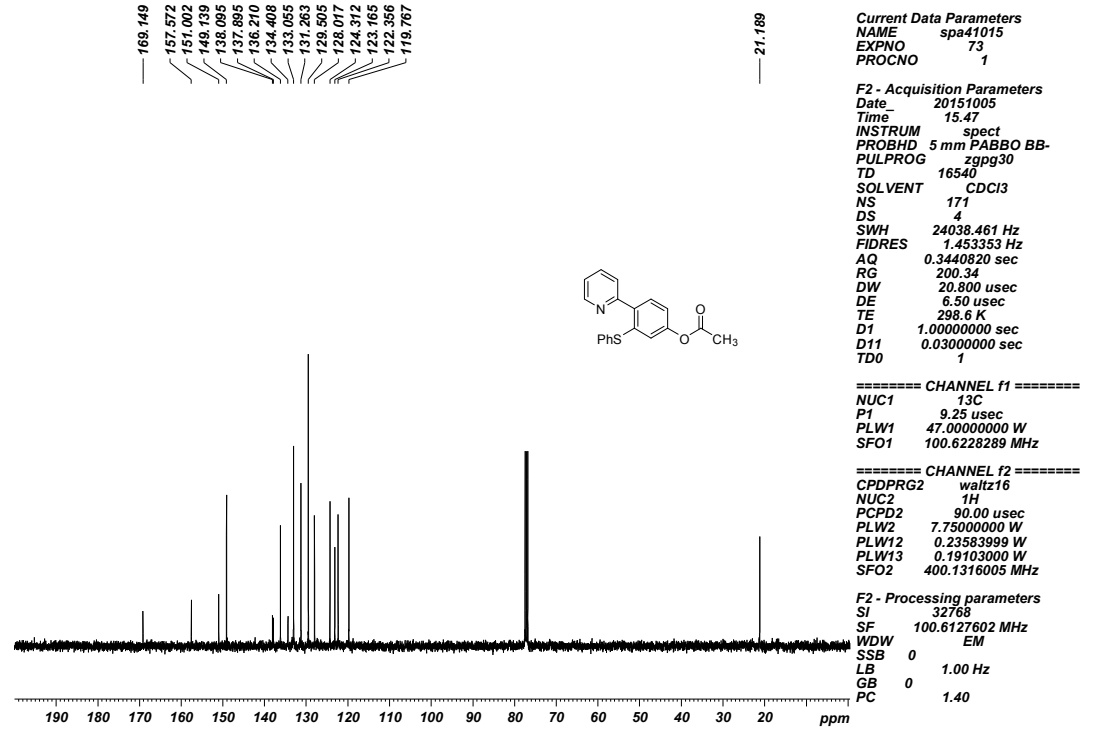


## 3-(Phenylthio)-4-(pyridin-2-yl)phenyl acetate (3j)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

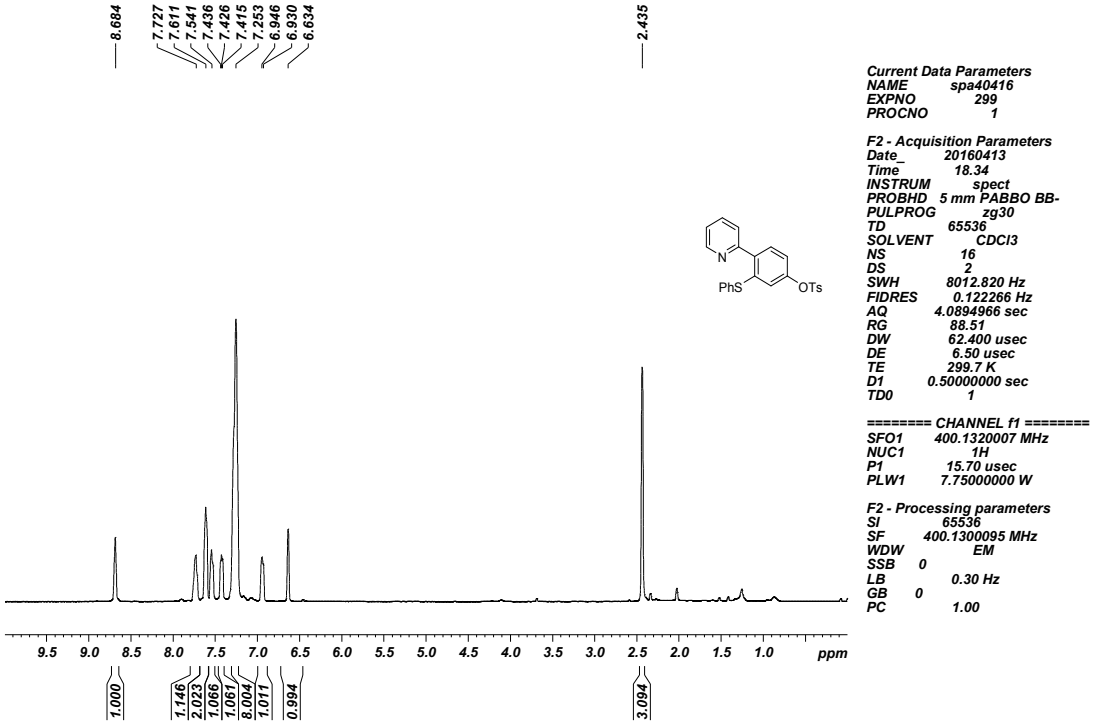



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)



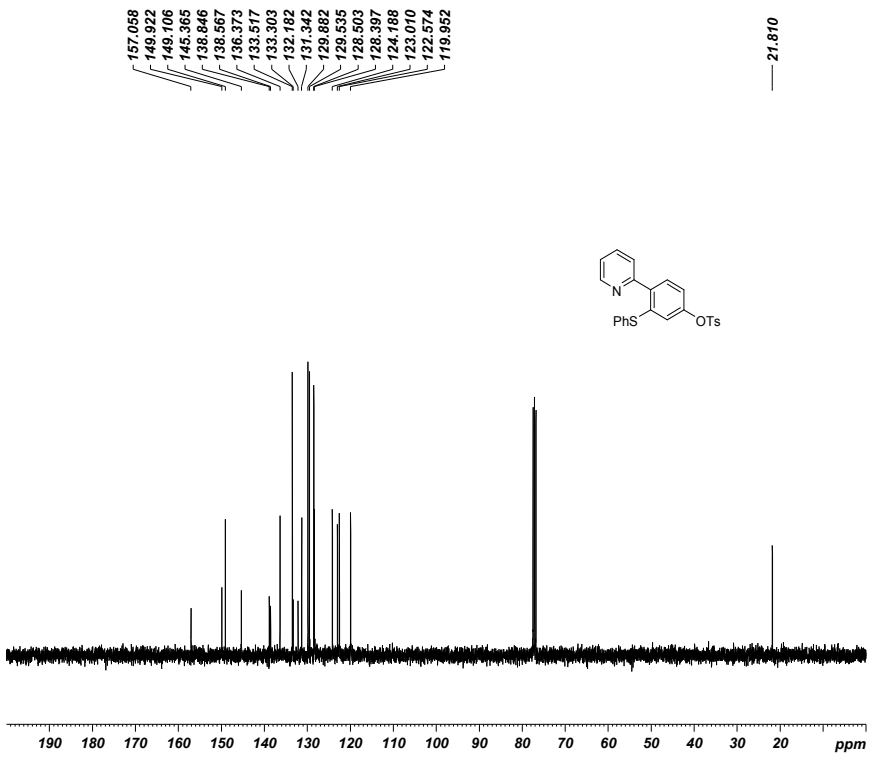
## 3-(Phenylthio)-4-(pyridin-2-yl)phenyl 4-methylbenzenesulfonate (3k)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)



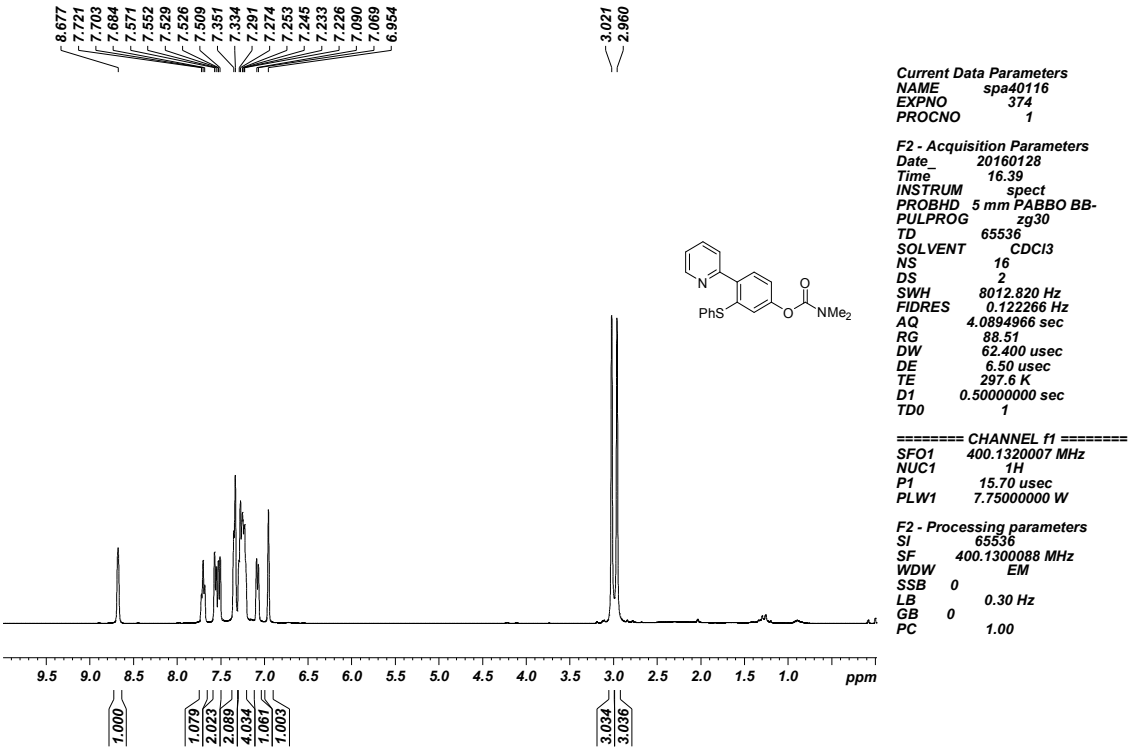

```
Current Data Parameters
NAME          spa40416
EXPNO              299
PROCNO               1

F2 - Acquisition Parameters
Date_         20160413
Time             18.34
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD              65536
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           8012.820 Hz
FIDRES           0.122266 Hz
AQ            4.0894966 sec
RG                88.51
DW                62.400 usec
DE                 6.50 usec
TE                299.7 K
D1           0.50000000 sec
TD0                  1

======== CHANNEL f1 ========
SFO1         400.1320007 MHz
NUC1                1H
P1                15.70 usec
PLW1         7.75000000 W

F2 - Processing parameters
SI                65536
SF           400.1300095 MHz
WDW                 EM
SSB      0
LB               0.30 Hz
GB       0
PC                1.00
```

## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

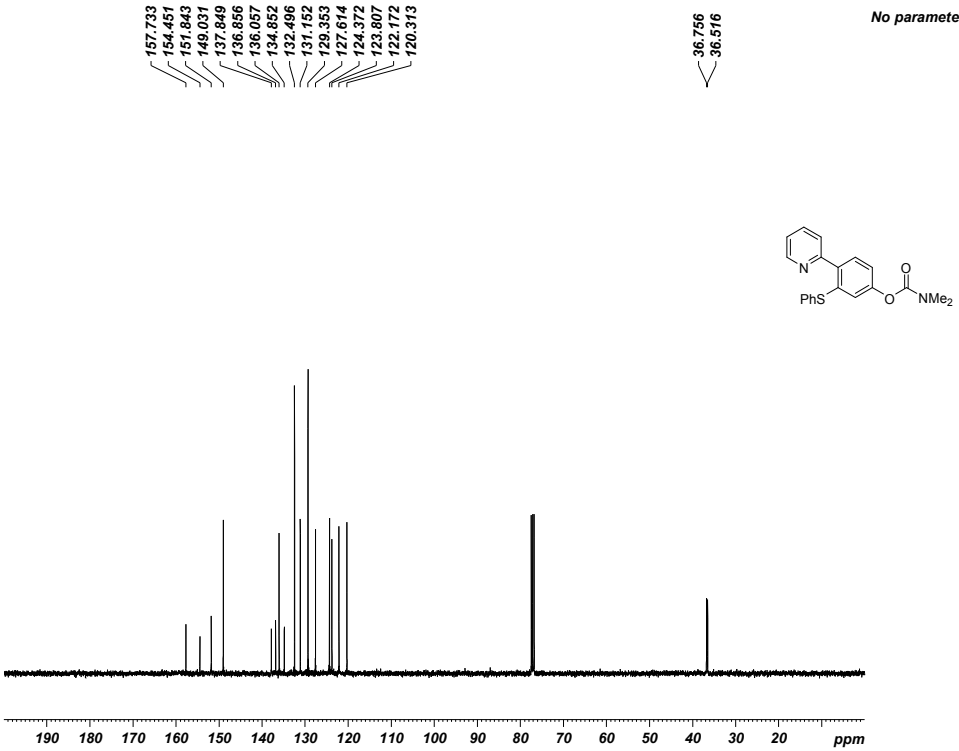


## 3-(Phenylthio)-4-(pyridin-2-yl)phenyl dimethylcarbamate (3l)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

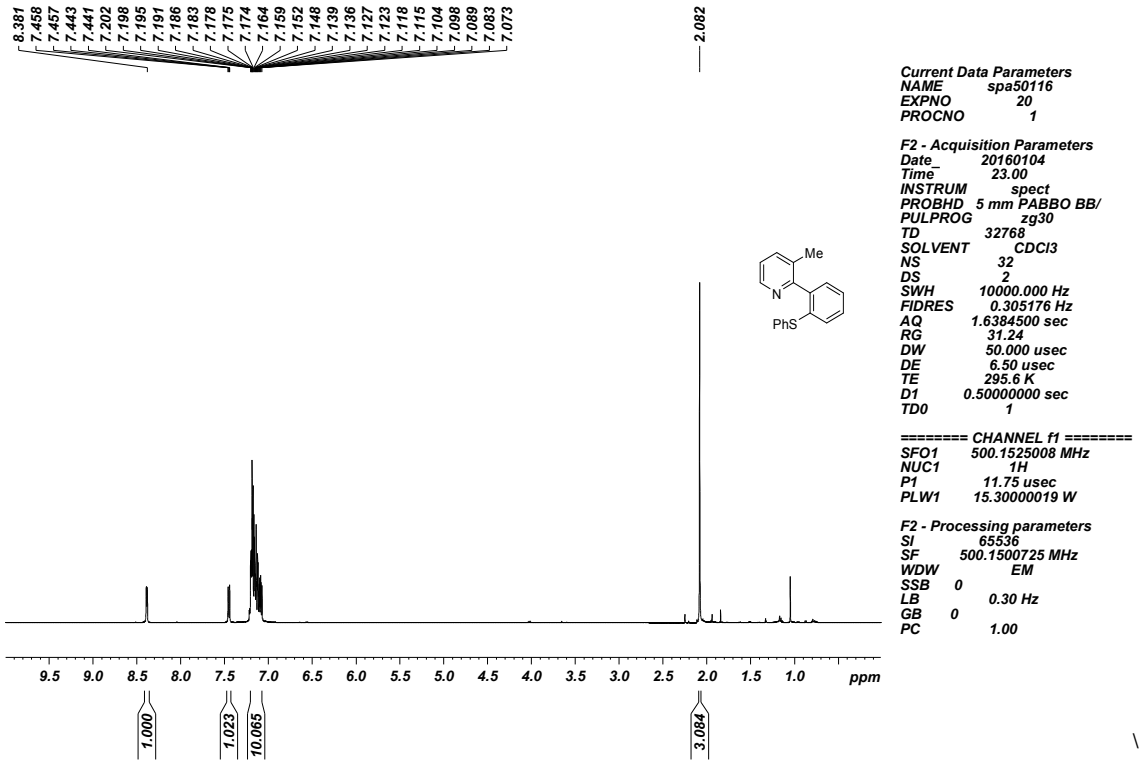



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

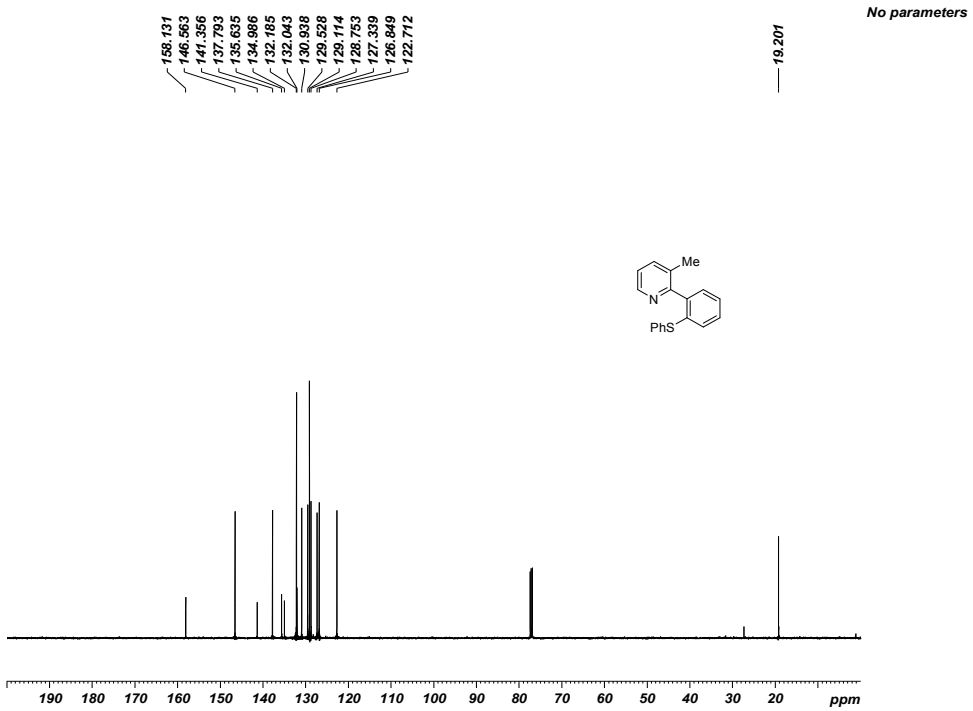


## 3-Methyl-2-(2-(phenylthio)phenyl)pyridine (3m)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

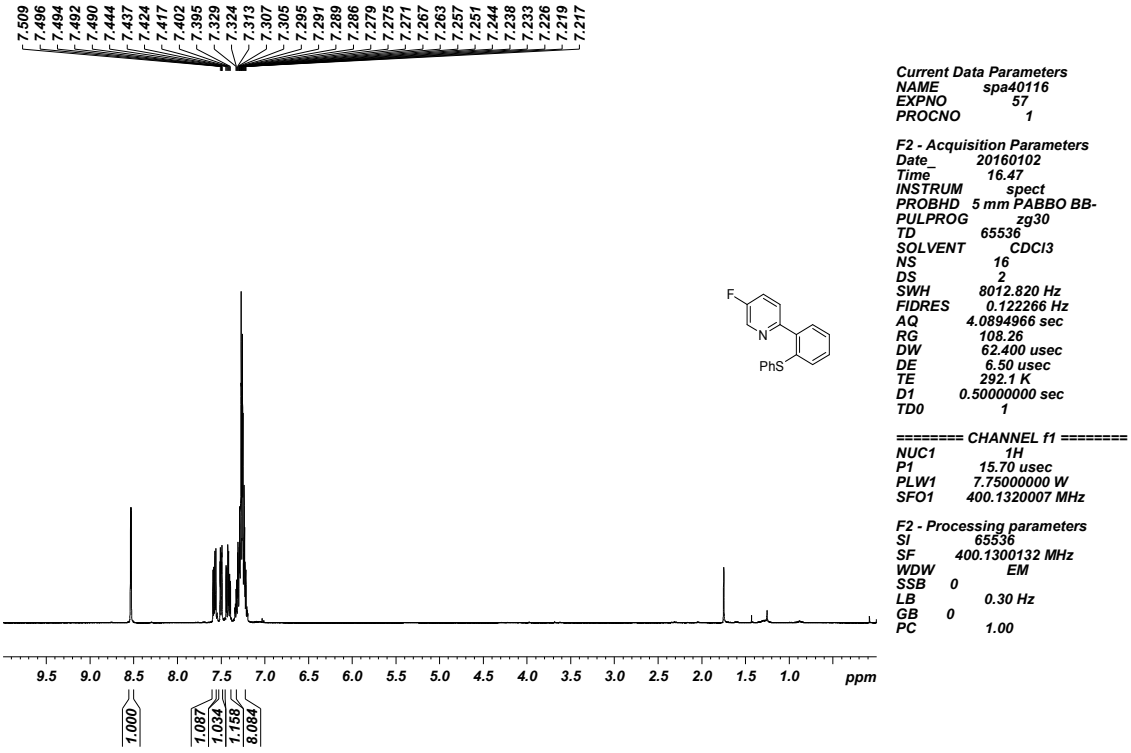



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)



## 5-Fluoro-2-(2-(phenylthio)phenyl)pyridine (3n)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)



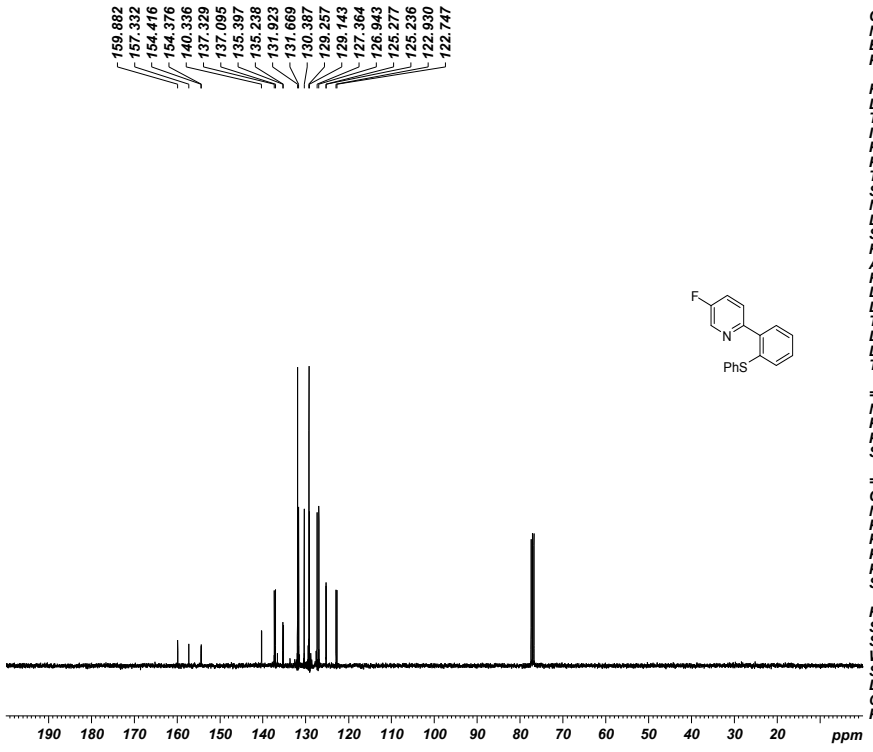

*Current Data Parameters*
*NAME spa40116*
*EXPNO 57*
*PROCNO 1*

*F2 - Acquisition Parameters*
*Date_ 20160102*
*Time 16.47*
*INSTRUM spect*
*PROBHD 5 mm PABBO BB-*
*PULPROG zg30*
*TD 65536*
*SOLVENT CDCl3*
*NS 16*
*DS 2*
*SWH 8012.820 Hz*
*FIDRES 0.122266 Hz*
*AQ 4.0894966 sec*
*RG 108.26*
*DW 62.400 usec*
*DE 6.50 usec*
*TE 292.1 K*
*D1 0.50000000 sec*
*TD0 1*

*======== CHANNEL f1 ========*
*NUC1 1H*
*P1 15.70 usec*
*PLW1 7.75000000 W*
*SFO1 400.1320007 MHz*

*F2 - Processing parameters*
*SI 65536*
*SF 400.1300132 MHz*
*WDW EM*
*SSB 0*
*LB 0.30 Hz*
*GB 0*
*PC 1.00*

## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)




*Current Data Parameters*
*NAME spa40116*
*EXPNO 55*
*PROCNO 1*

*F2 - Acquisition Parameters*
*Date_ 20160102*
*Time 19.37*
*INSTRUM spect*
*PROBHD 5 mm PABBO BB-*
*PULPROG zgpg30*
*TD 16540*
*SOLVENT CDCl3*
*NS 256*
*DS 4*
*SWH 24038.461 Hz*
*FIDRES 1.453353 Hz*
*AQ 0.3440820 sec*
*RG 200.34*
*DW 20.800 usec*
*DE 6.50 usec*
*TE 292.5 K*
*D1 1.00000000 sec*
*D11 0.03000000 sec*
*TD0 1*

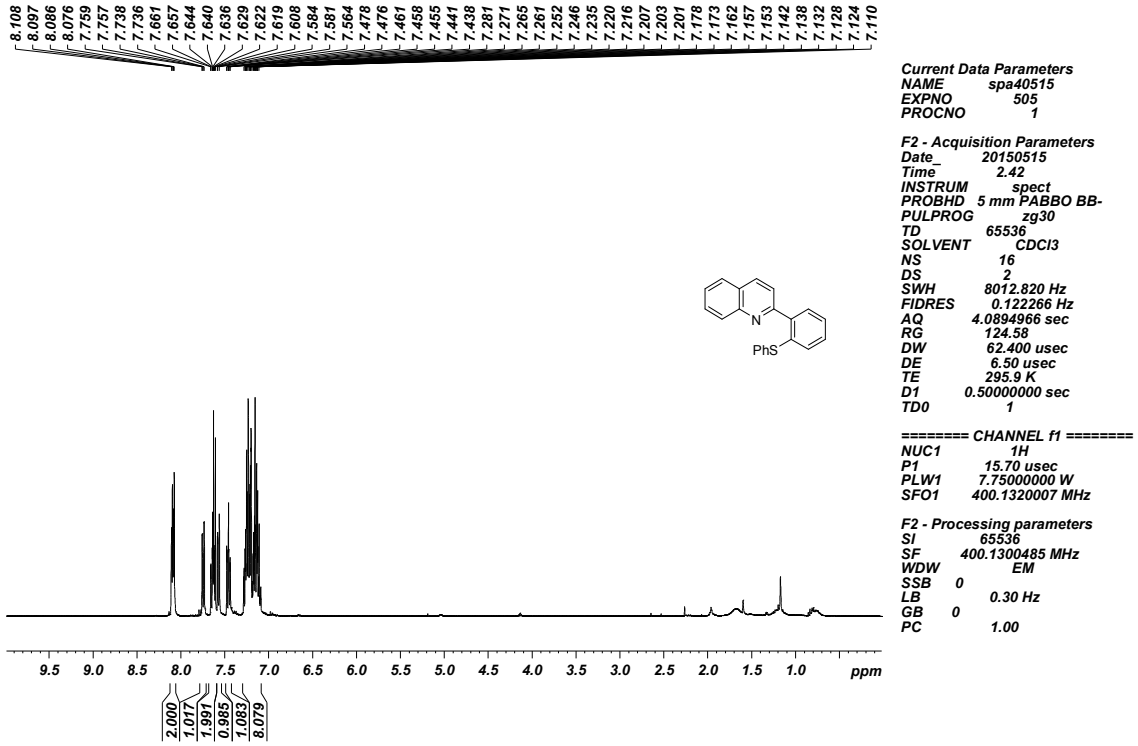
*======== CHANNEL f1 ========*
*NUC1 13C*
*P1 9.25 usec*
*PLW1 47.00000000 W*
*SFO1 100.6228289 MHz*

*======== CHANNEL f2 ========*
*CPDPRG2 waltz16*
*NUC2 1H*
*PCPD2 90.00 usec*
*PLW2 7.75000000 W*
*PLW12 0.23583999 W*
*PLW13 0.19103000 W*
*SFO2 400.1316005 MHz*

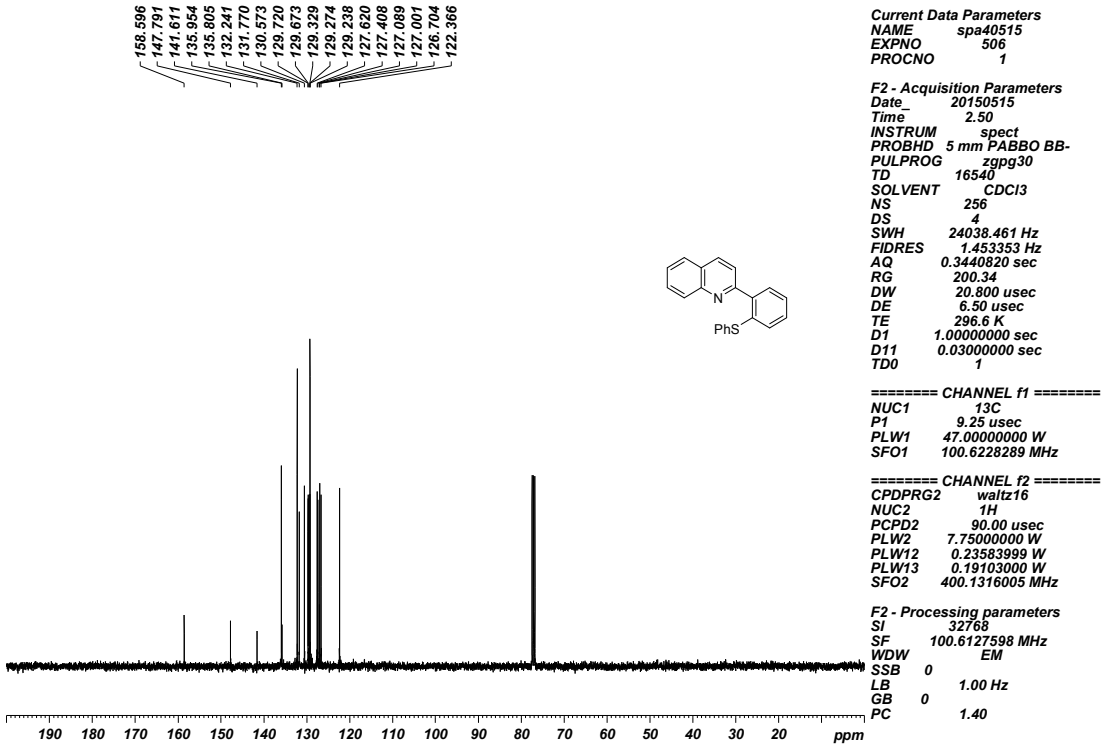
*F2 - Processing parameters*
*SI 32768*
*SF 100.6127690 MHz*
*WDW EM*
*SSB 0*
*LB 1.00 Hz*
*GB 0*
*PC 1.40*

## 2-(2-(Phenylthio)phenyl)quinolone (3p)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

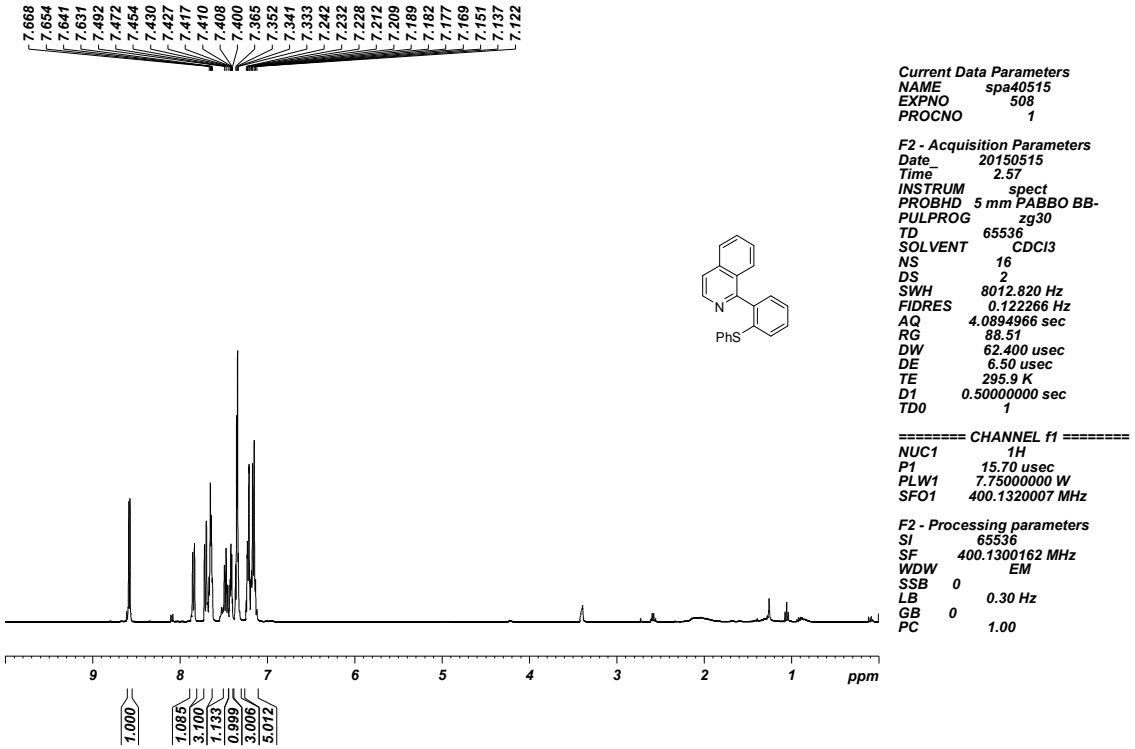



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

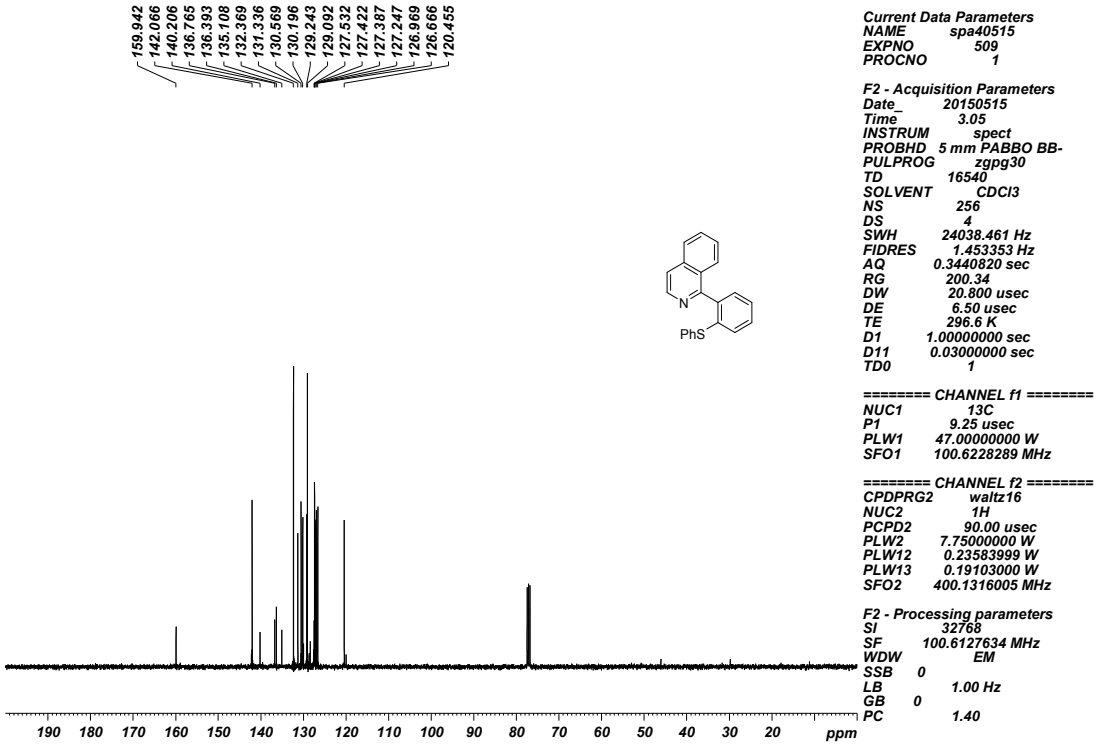


## 1-(2-(Phenylthio)phenyl)isoquinoline (3q)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

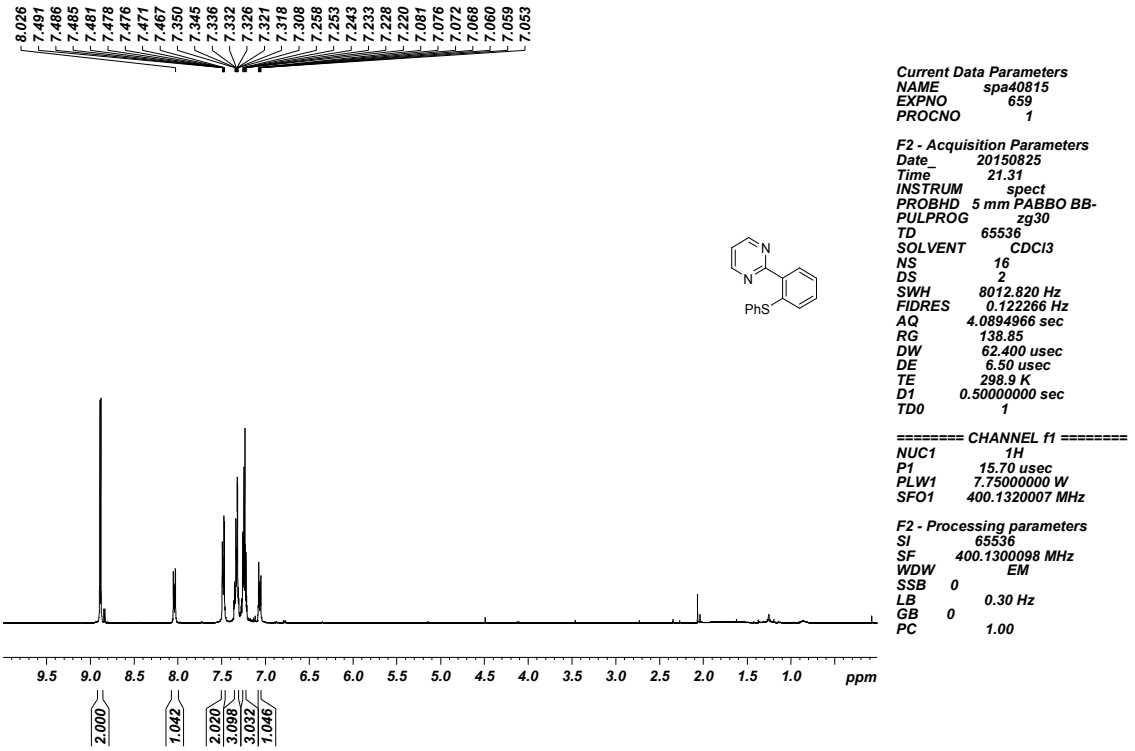



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

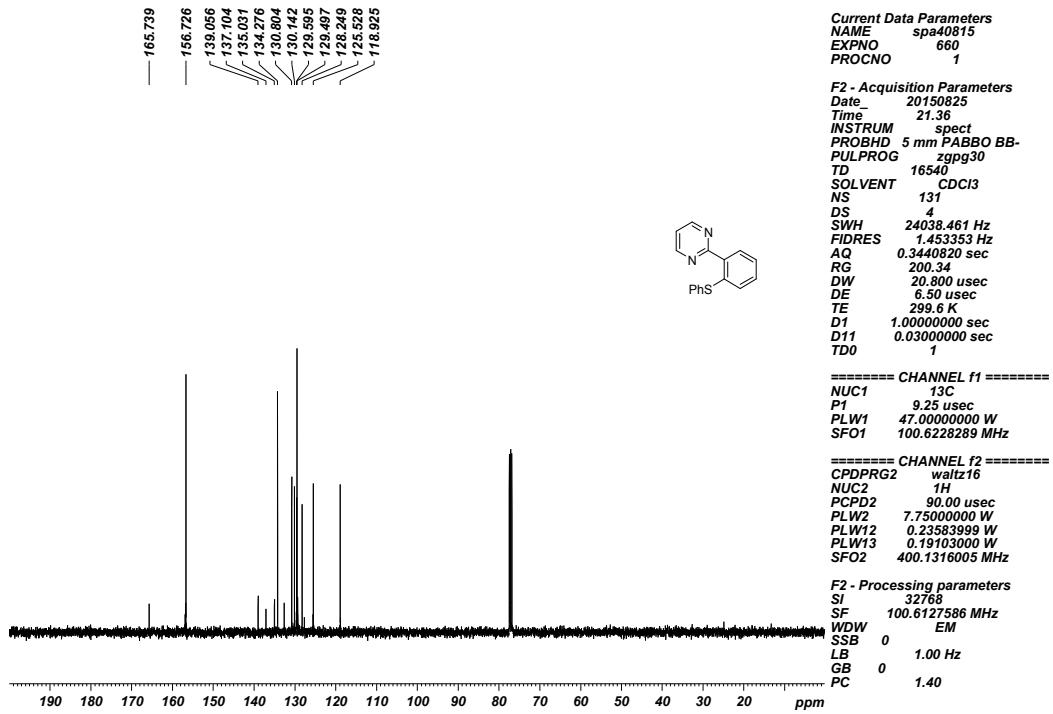


## 2-(2-(Phenylthio)phenyl)pyrimidine (3r)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

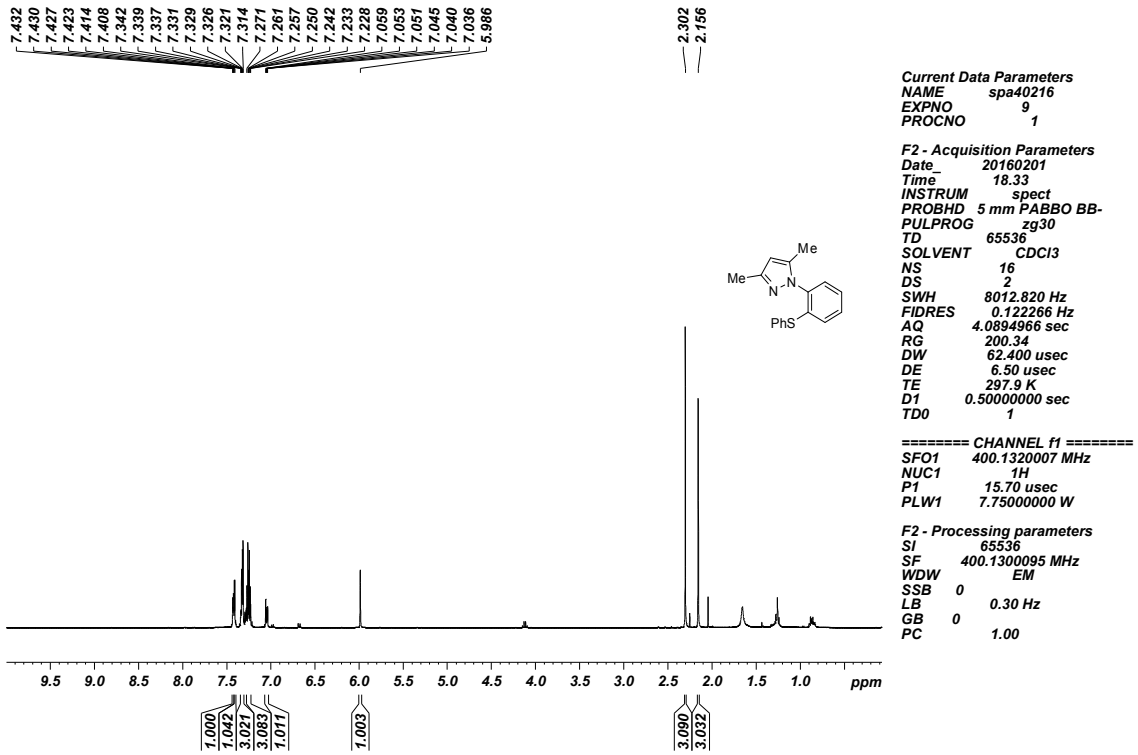



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

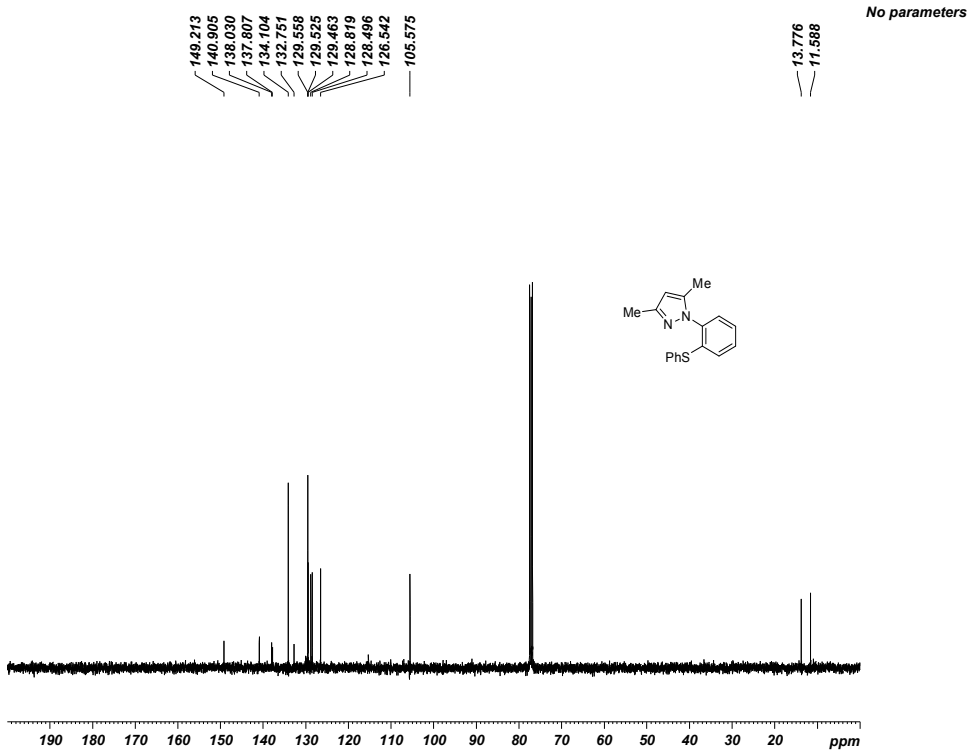


## 3,5-Dimethyl-1-(2-(phenylthio)phenyl)-1*H*-pyrazole (3s)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

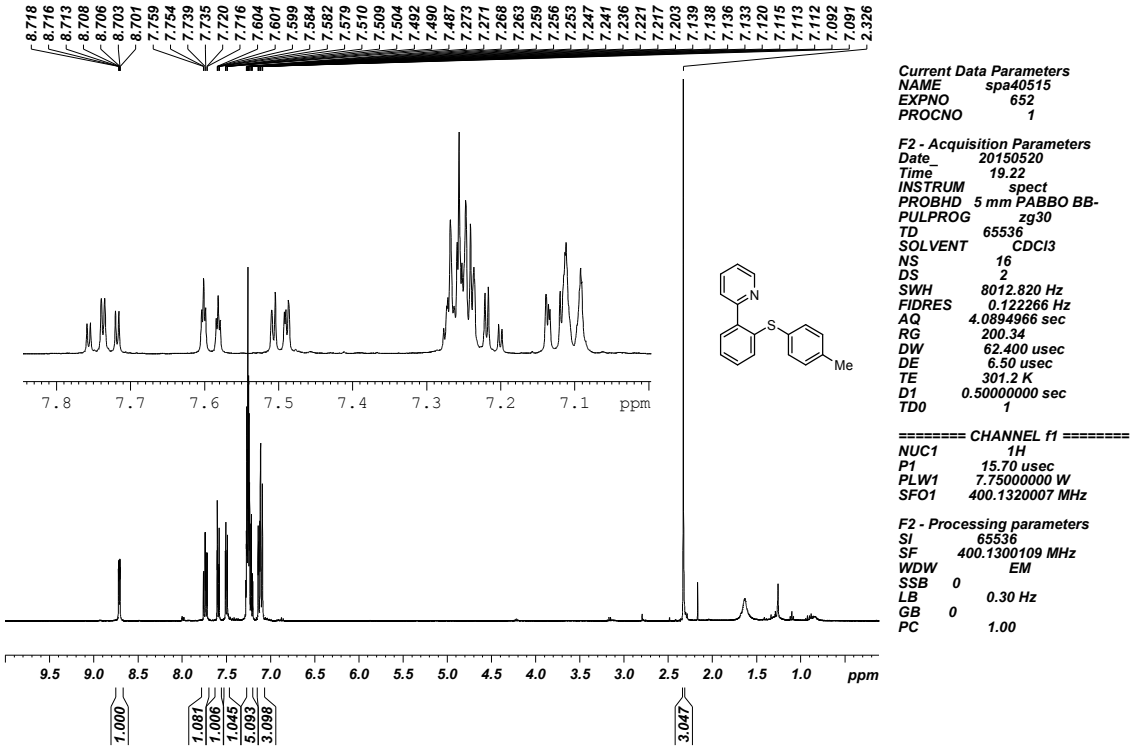



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

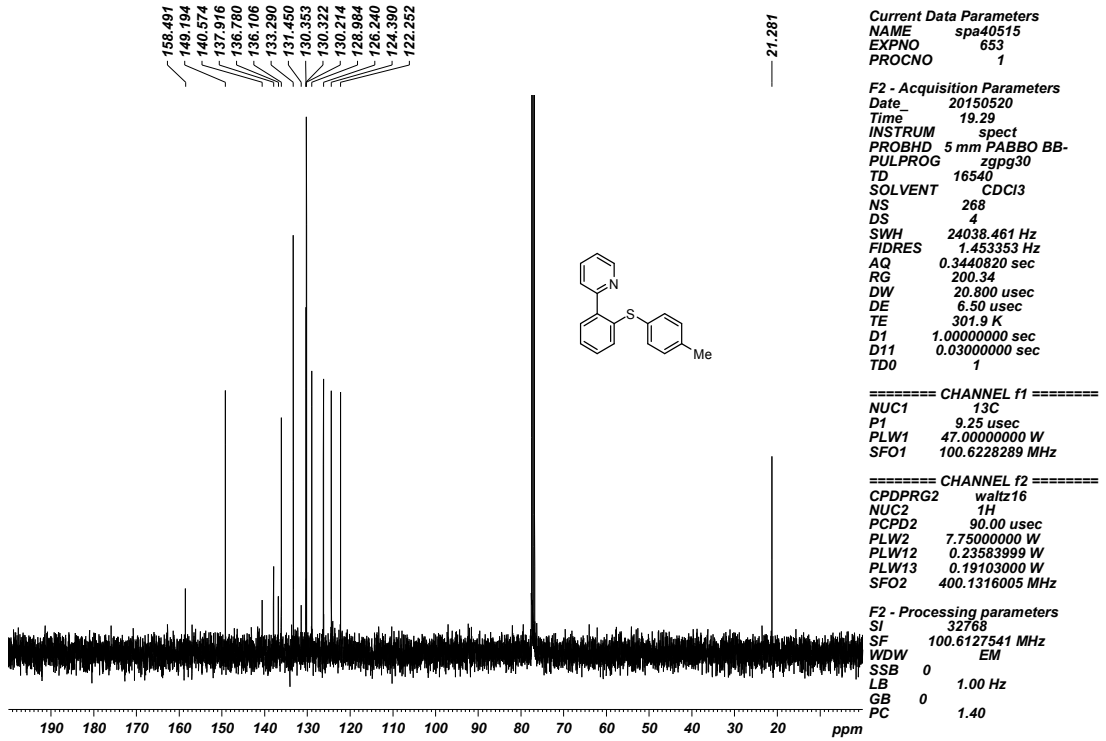


## 2-(2-(*p*-Tolylthio)phenyl)pyridine (3t)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

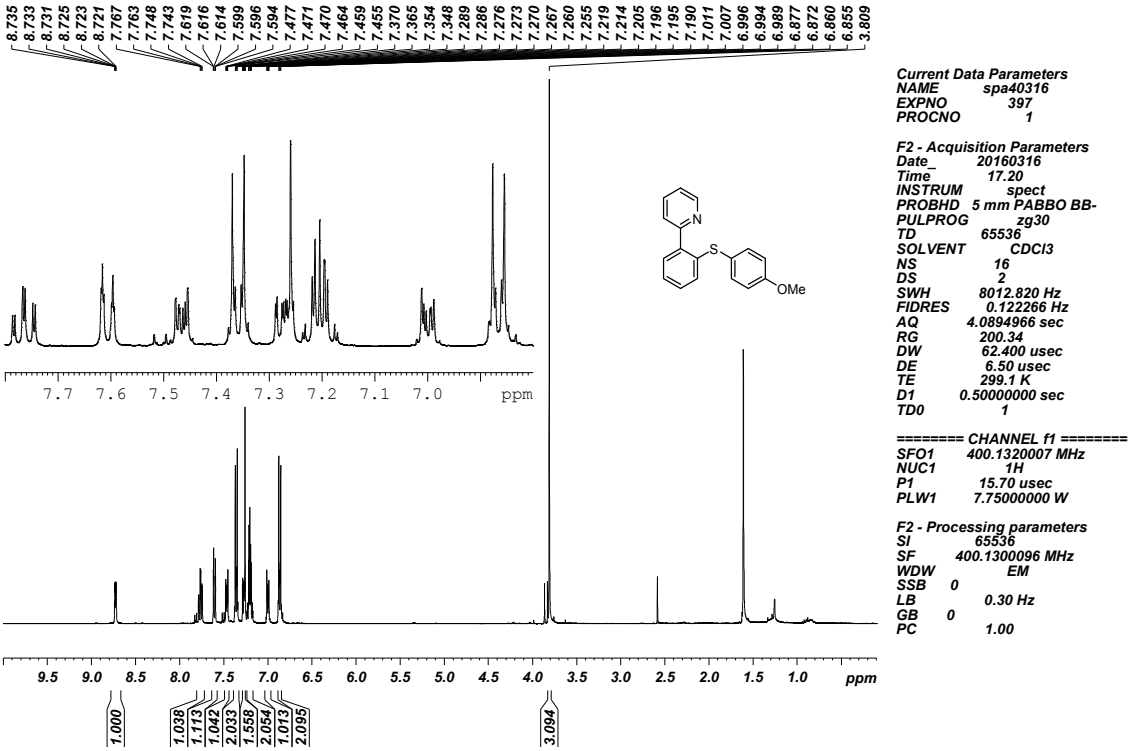



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)



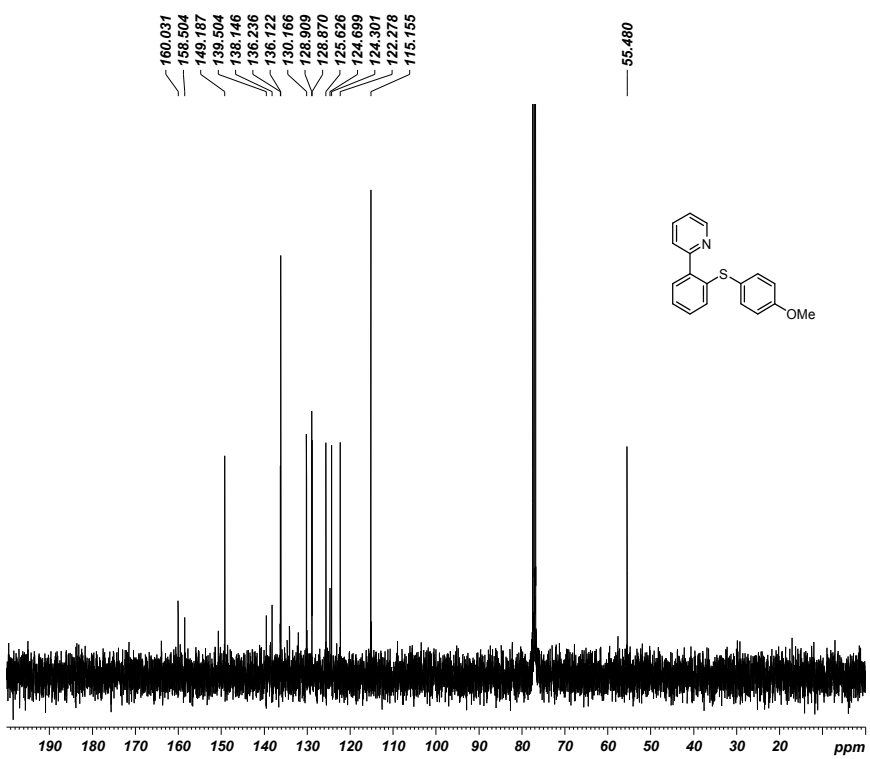
## 2-(2-((4-Methoxyphenyl)thio)phenyl)pyridine (3u)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)



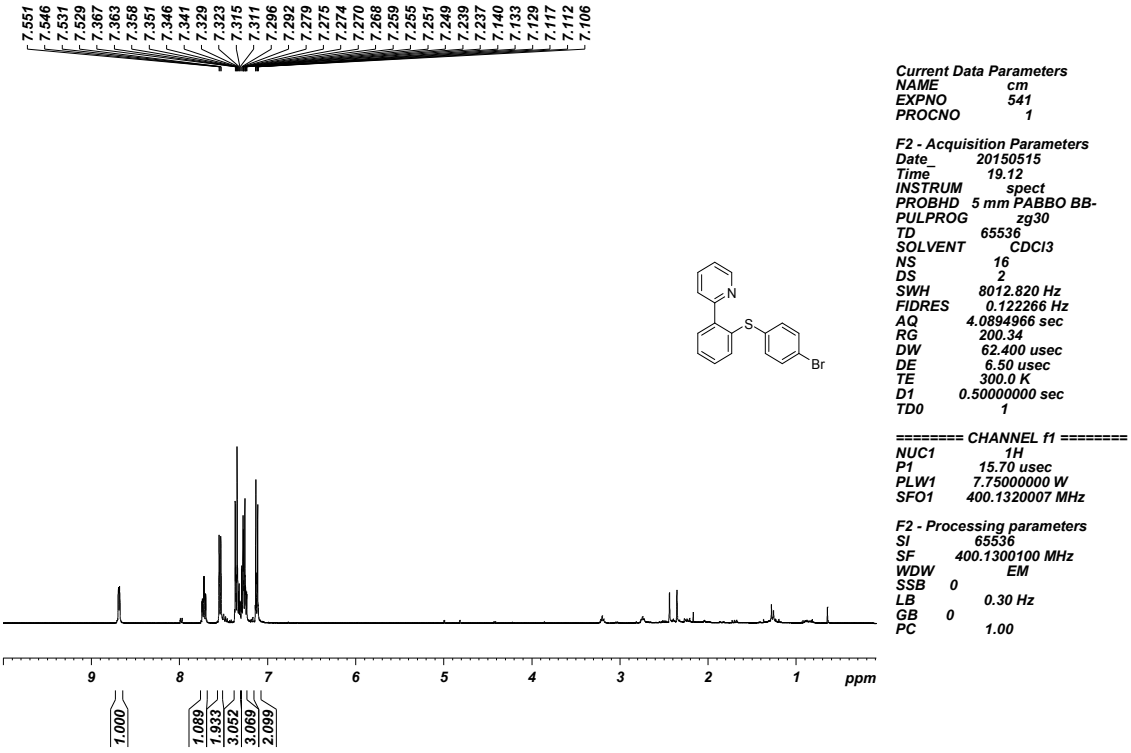

```
Current Data Parameters
NAME          spa40316
EXPNO              397
PROCNO               1

F2 - Acquisition Parameters
Date_        20160316
Time            17.20
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD              65536
SOLVENT          CDCl3
NS                 16
DS                  2
SWH          8012.820 Hz
FIDRES       0.122266 Hz
AQ           4.0894966 sec
RG              200.34
DW              62.400 usec
DE               6.50 usec
TE              299.1 K
D1           0.50000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1       400.1320007 MHz
NUC1               1H
P1              15.70 usec
PLW1        7.75000000 W

F2 - Processing parameters
SI              65536
SF         400.1300096 MHz
WDW                EM
SSB     0
LB              0.30 Hz
GB      0
PC              1.00
```

## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

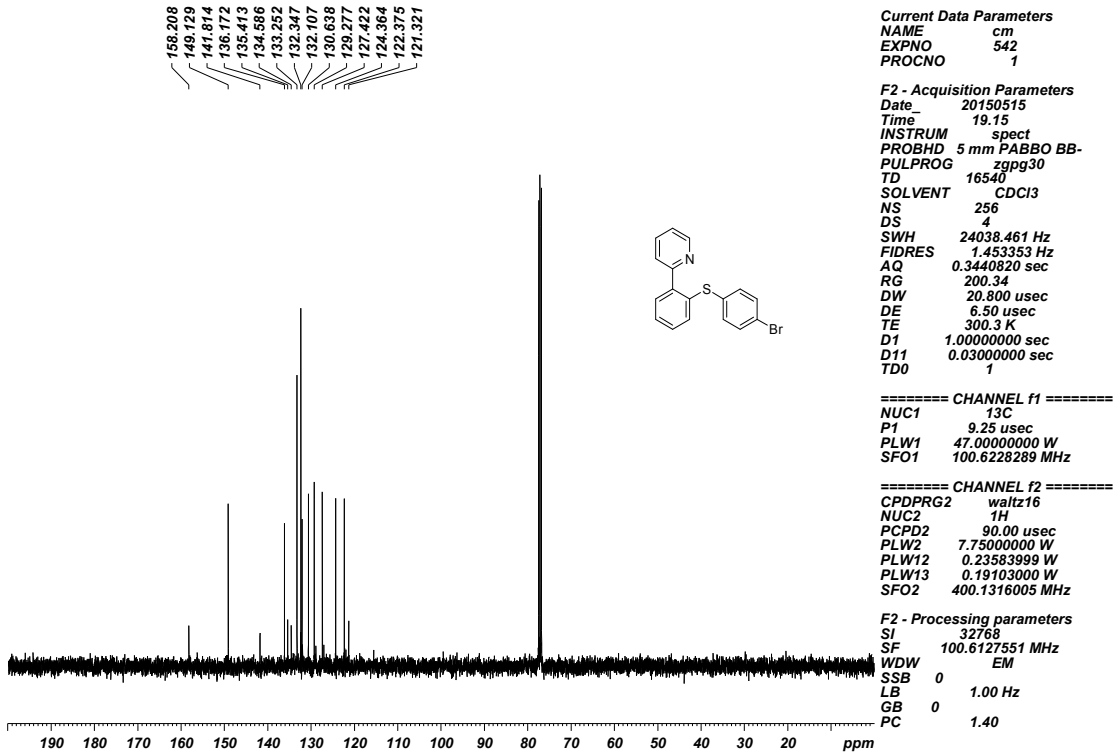


## 2-(2-((4-Bromophenyl)thio)phenyl)pyridine (3v)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

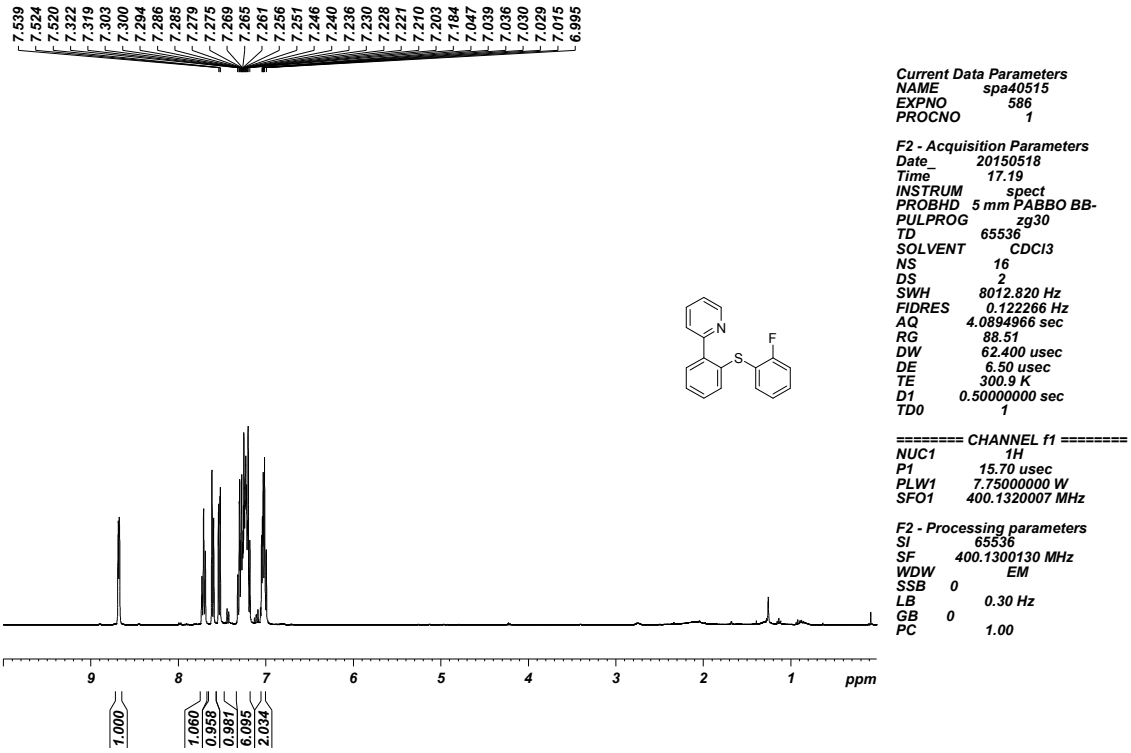



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

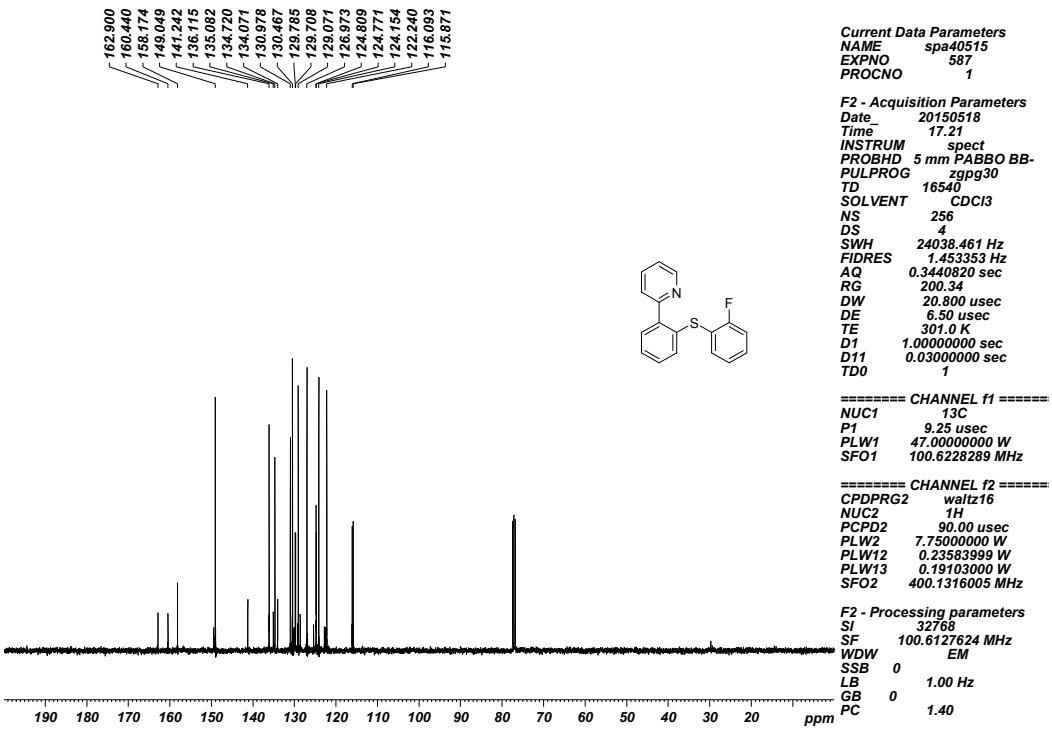


## 2-(2-((2-Fluorophenyl)thio)phenyl)pyridine (3w)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C

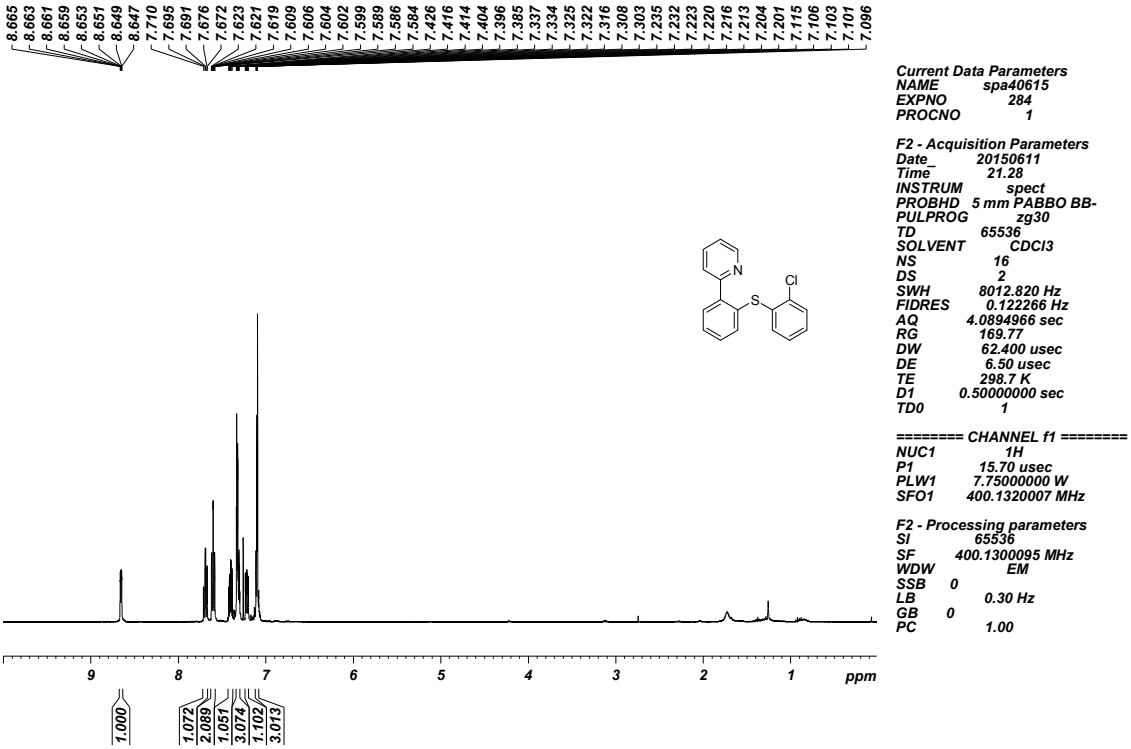



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

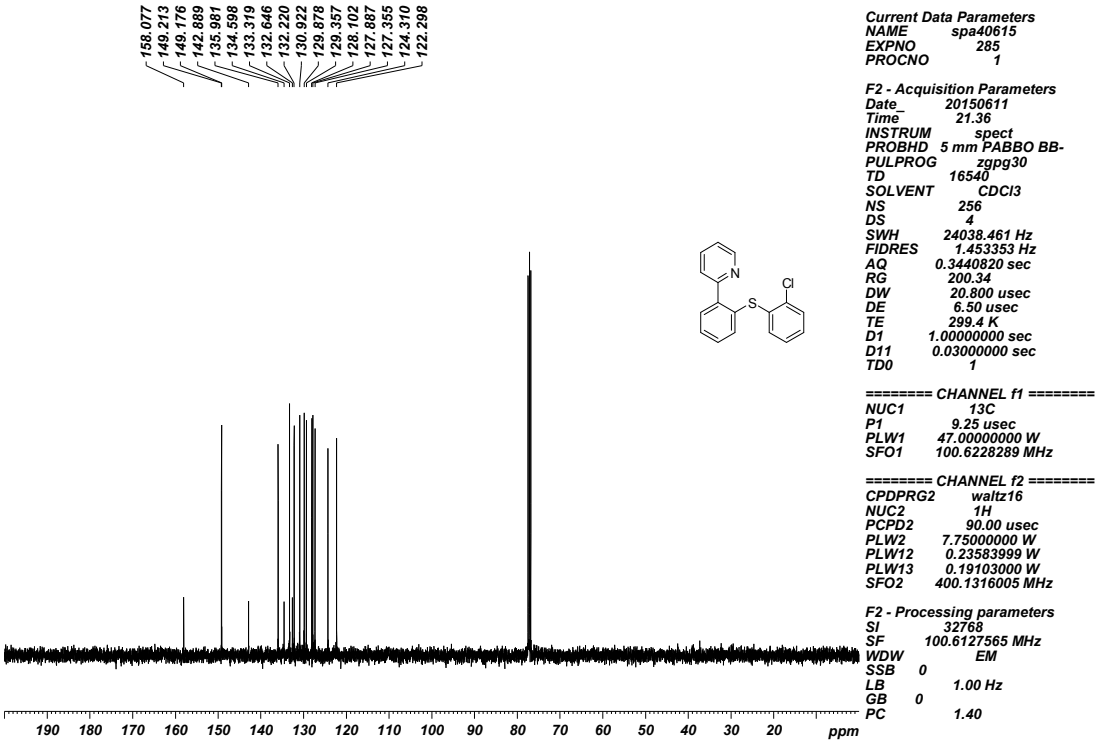


## 2-(2-((2-Chlorophenyl)thio)phenyl)pyridine (3x)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

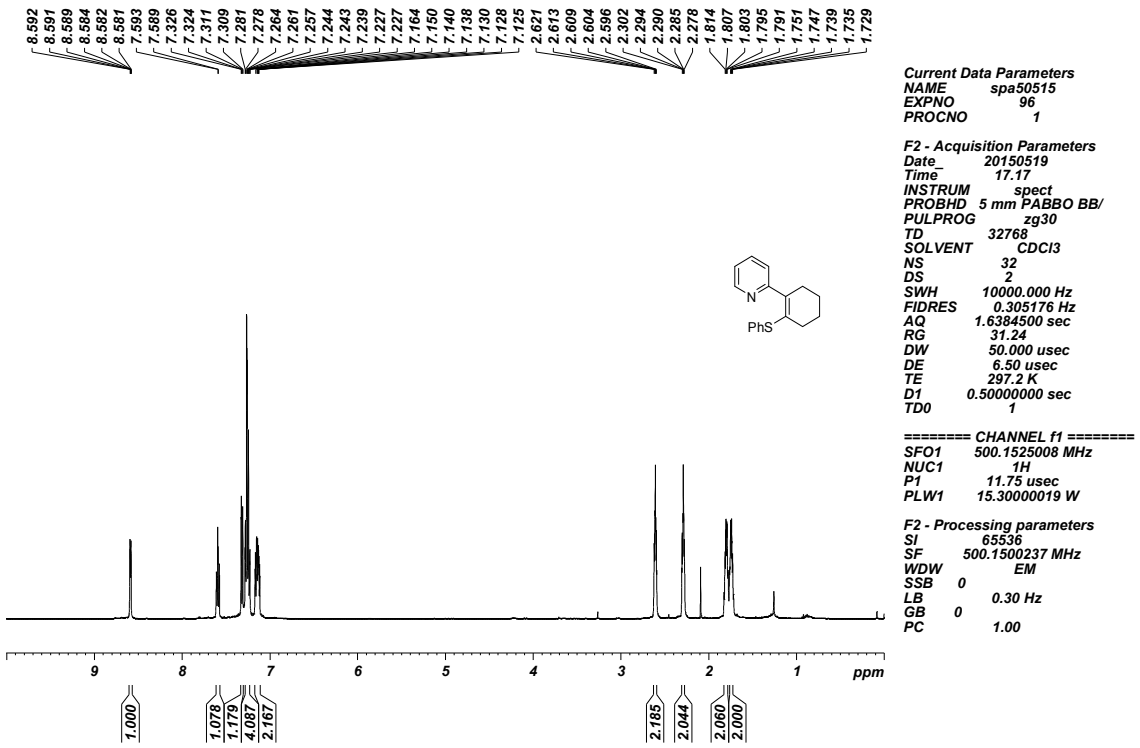



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

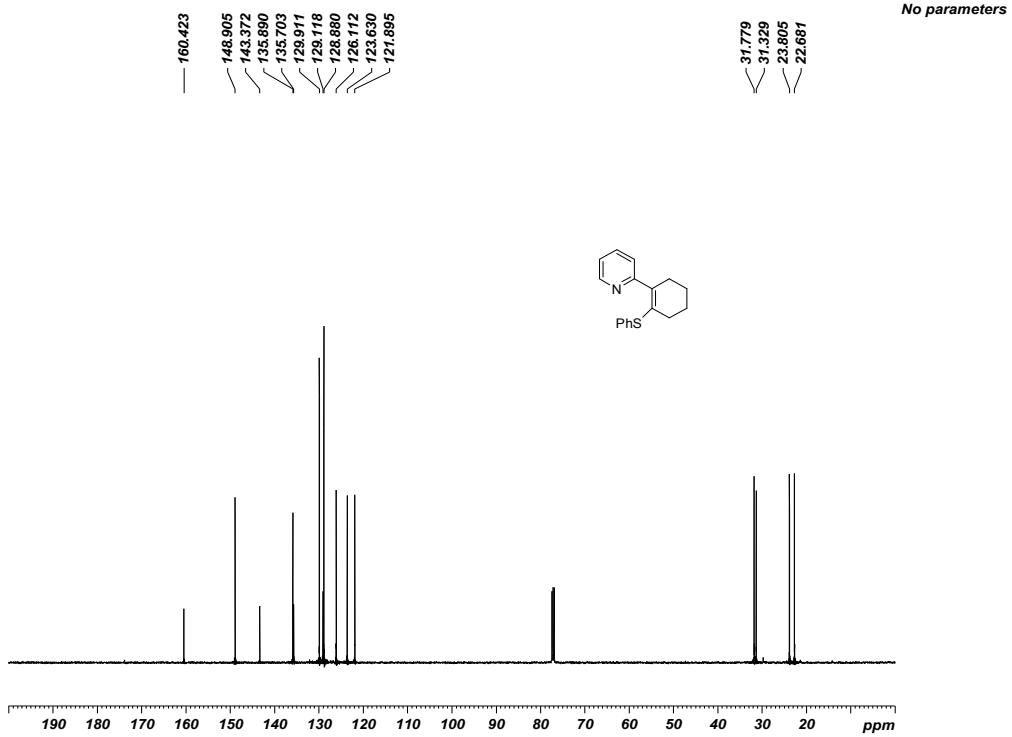


## 2-(2-(Phenylthio)cyclohex-1-en-1-yl)pyridine (6a)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

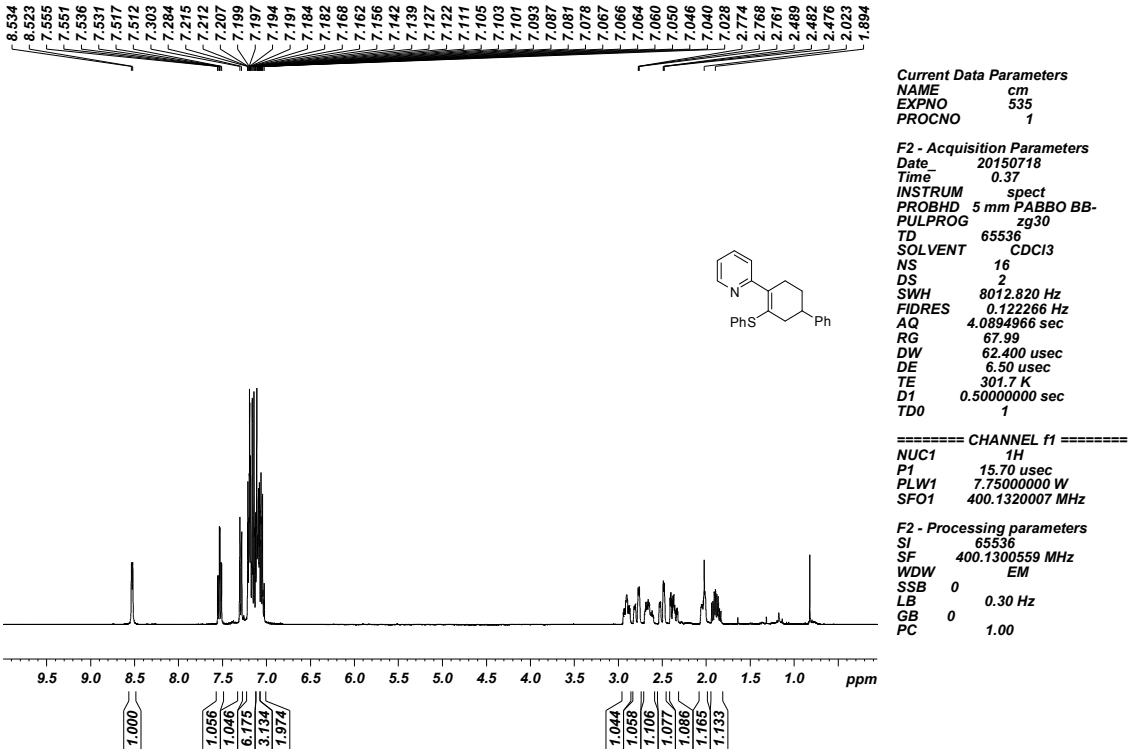



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)



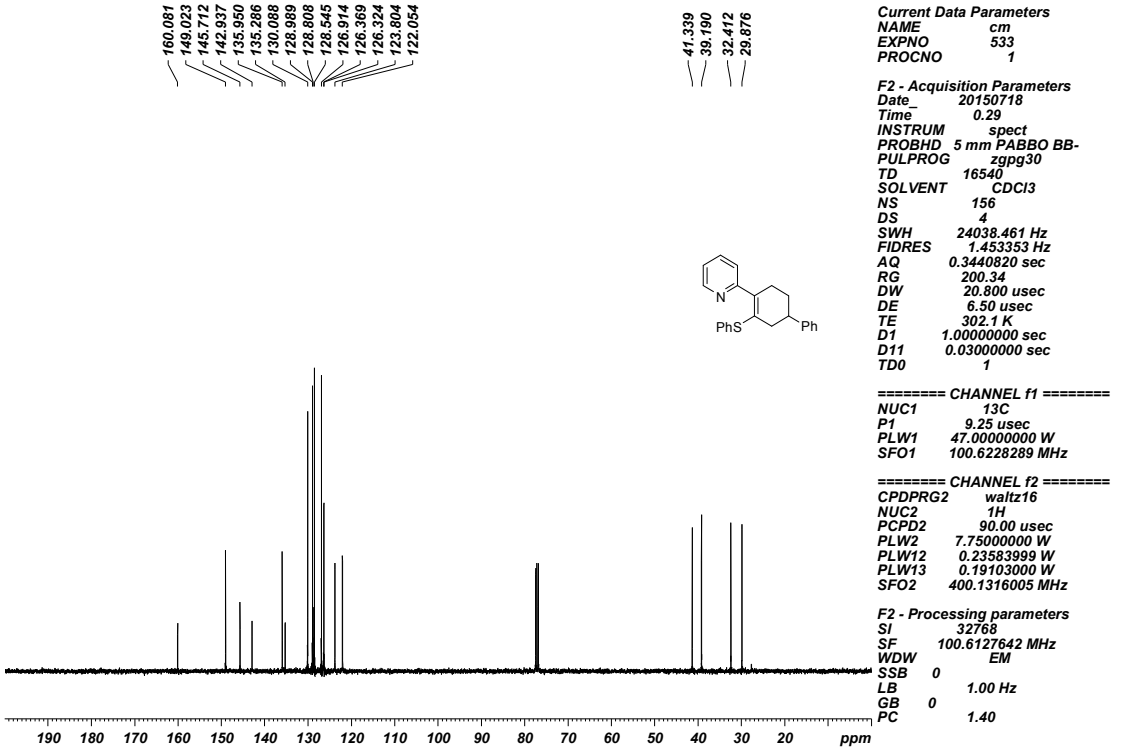
## 2-(5-(Phenylthio)-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)pyridine (6c)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)




```
Current Data Parameters
NAME            cm
EXPNO           535
PROCNO          1

F2 - Acquisition Parameters
Date_           20150718
Time            0.37
INSTRUM         spect
PROBHD   5 mm PABBO BB-
PULPROG         zg30
TD              65536
SOLVENT         CDCl3
NS              16
DS              2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ              4.0894966 sec
RG              67.99
DW              62.400 usec
DE              6.50 usec
TE              301.7 K
D1              0.50000000 sec
TD0             1

======== CHANNEL f1 ========
NUC1            1H
P1              15.70 usec
PLW1            7.75000000 W
SFO1            400.1320007 MHz

F2 - Processing parameters
SI              65536
SF              400.1300559 MHz
WDW             EM
SSB     0
LB              0.30 Hz
GB      0
PC              1.00
```

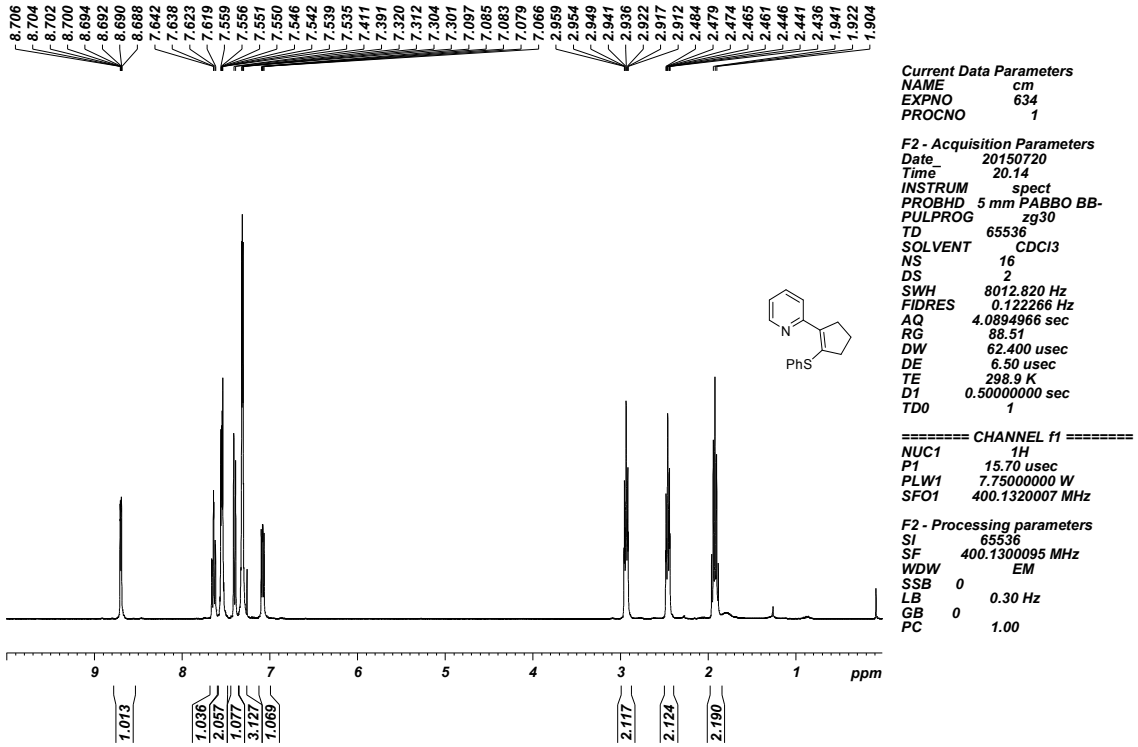
## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)



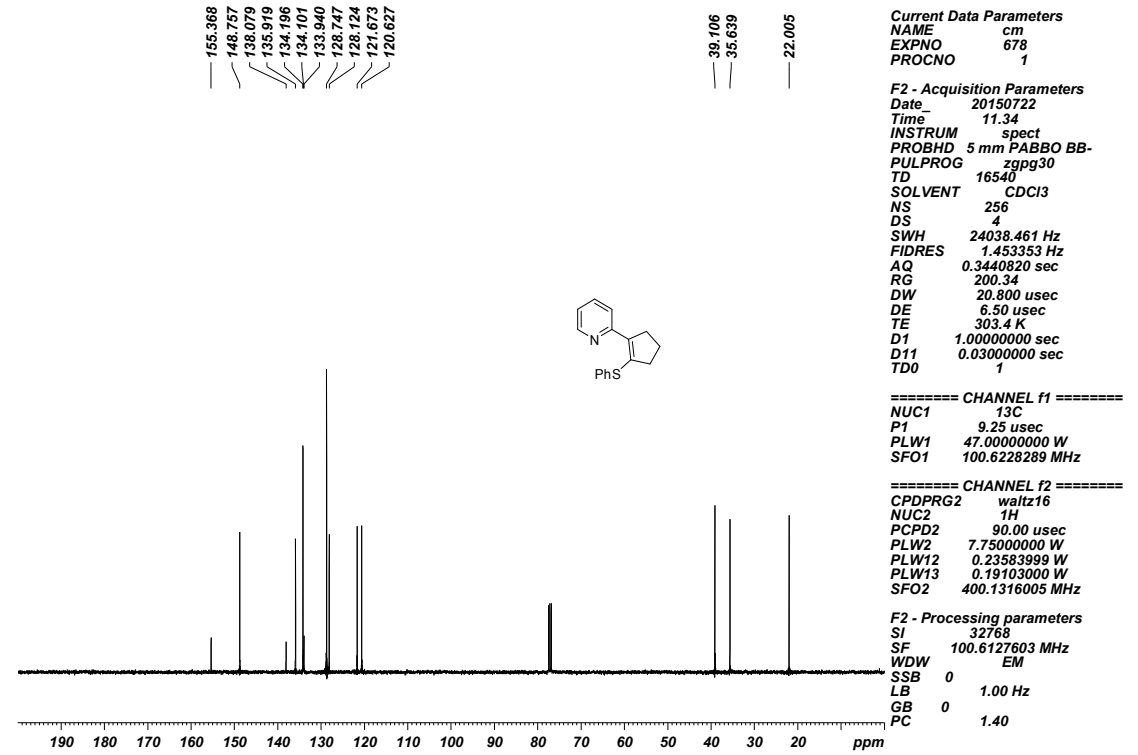

```
Current Data Parameters
NAME            cm
EXPNO           533
PROCNO          1

F2 - Acquisition Parameters
Date_           20150718
Time            0.29
INSTRUM         spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD              16540
SOLVENT         CDCl3
NS              156
DS              4
SWH             24038.461 Hz
FIDRES          1.453353 Hz
AQ              0.3440820 sec
RG              200.34
DW              20.800 usec
DE              6.50 usec
TE              302.1 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0             1

======== CHANNEL f1 ========
NUC1            13C
P1              9.25 usec
PLW1            47.00000000 W
SFO1            100.6228289 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2            1H
PCPD2           90.00 usec
PLW2            7.75000000 W
PLW12           0.23583999 W
PLW13           0.19103000 W
SFO2            400.1316005 MHz

F2 - Processing parameters
SI              32768
SF              100.6127642 MHz
WDW             EM
SSB     0
LB              1.00 Hz
GB      0
PC              1.40
```

## 2-(2-(Phenylthio)cyclopent-1-en-1-yl)pyridine (6d)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

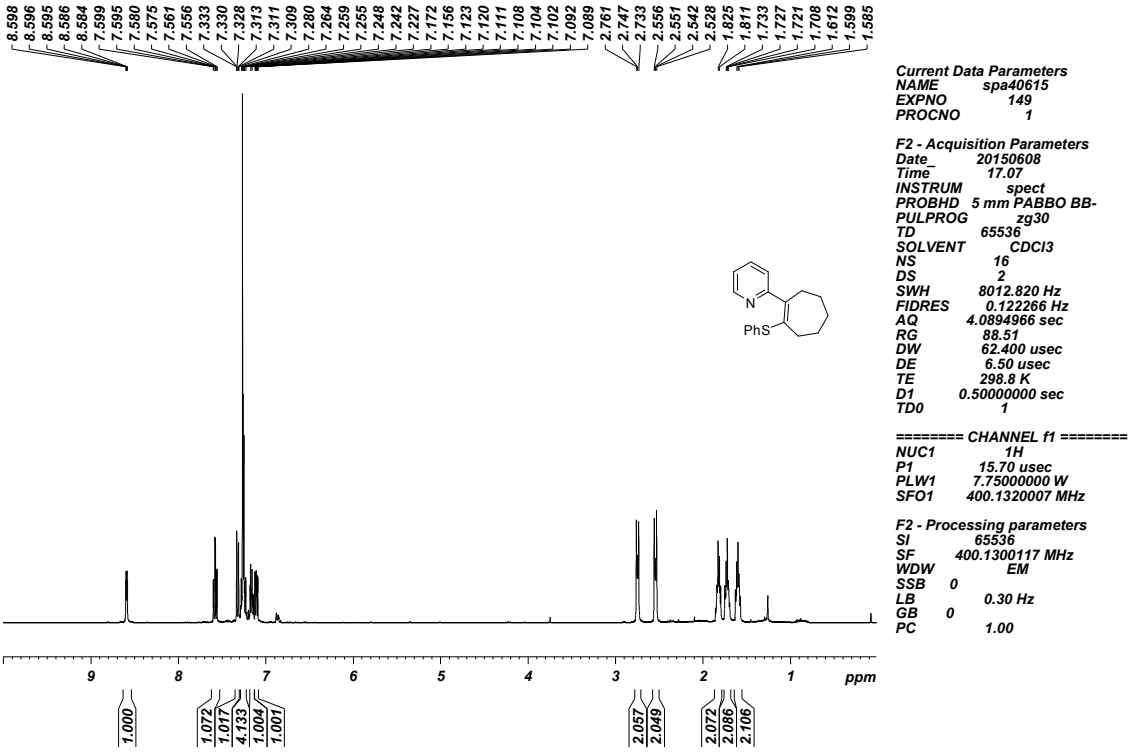



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

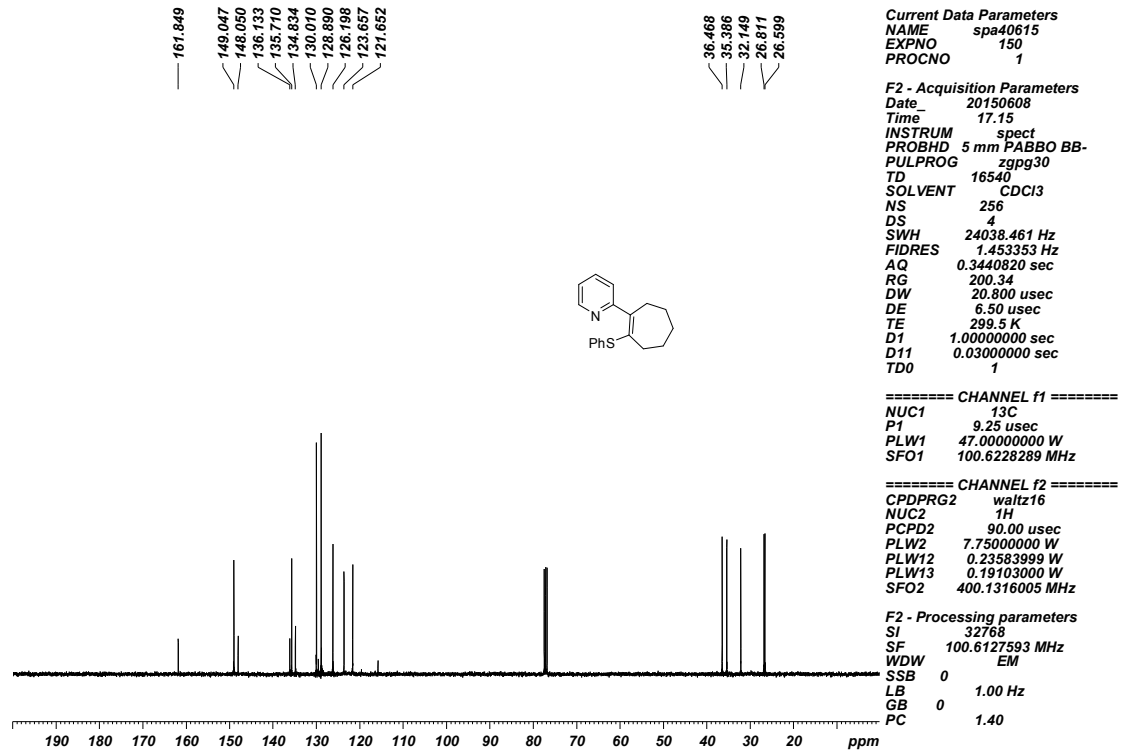


## 2-(2-(Phenylthio)cyclohept-1-en-1-yl)pyridine (6e)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

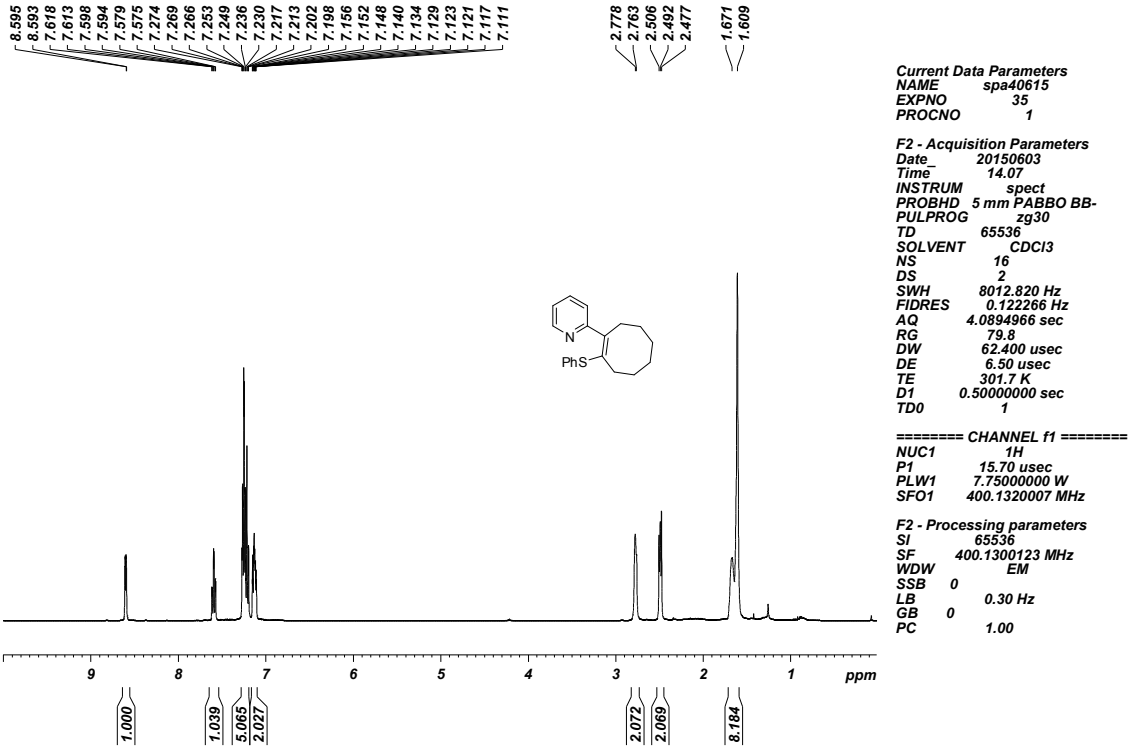



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

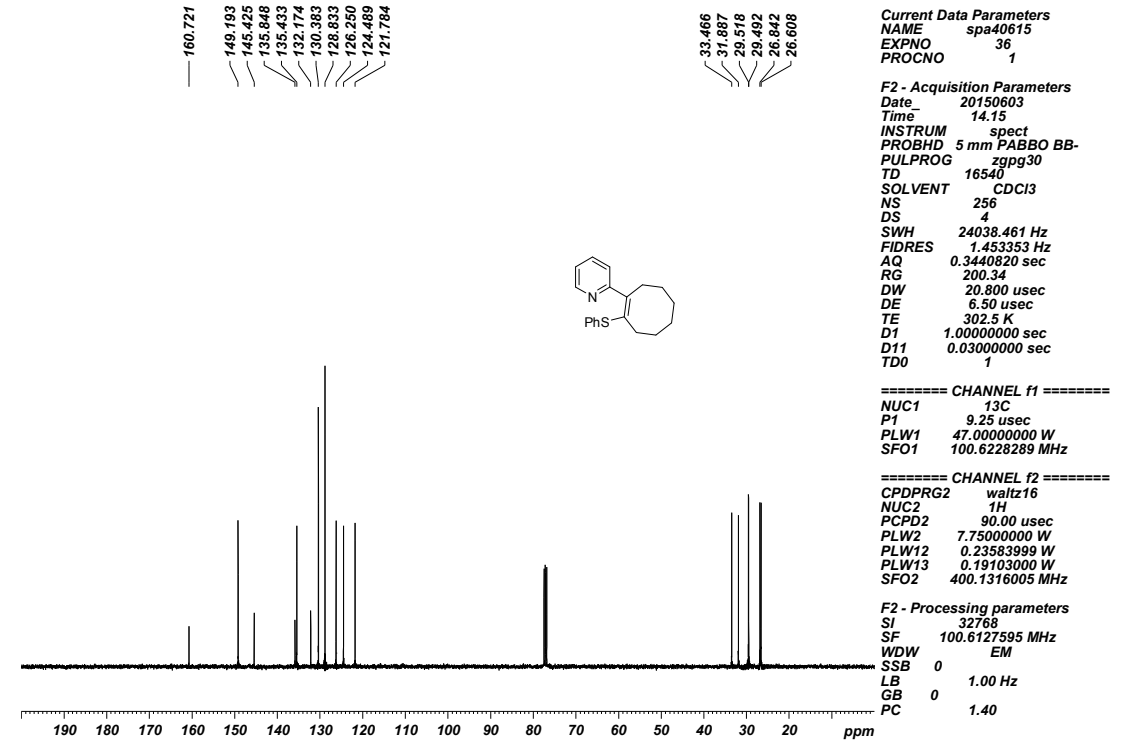


## (*Z*)-2-(2-(Phenylthio)cyclooct-1-en-1-yl)pyridine (6f)

### $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

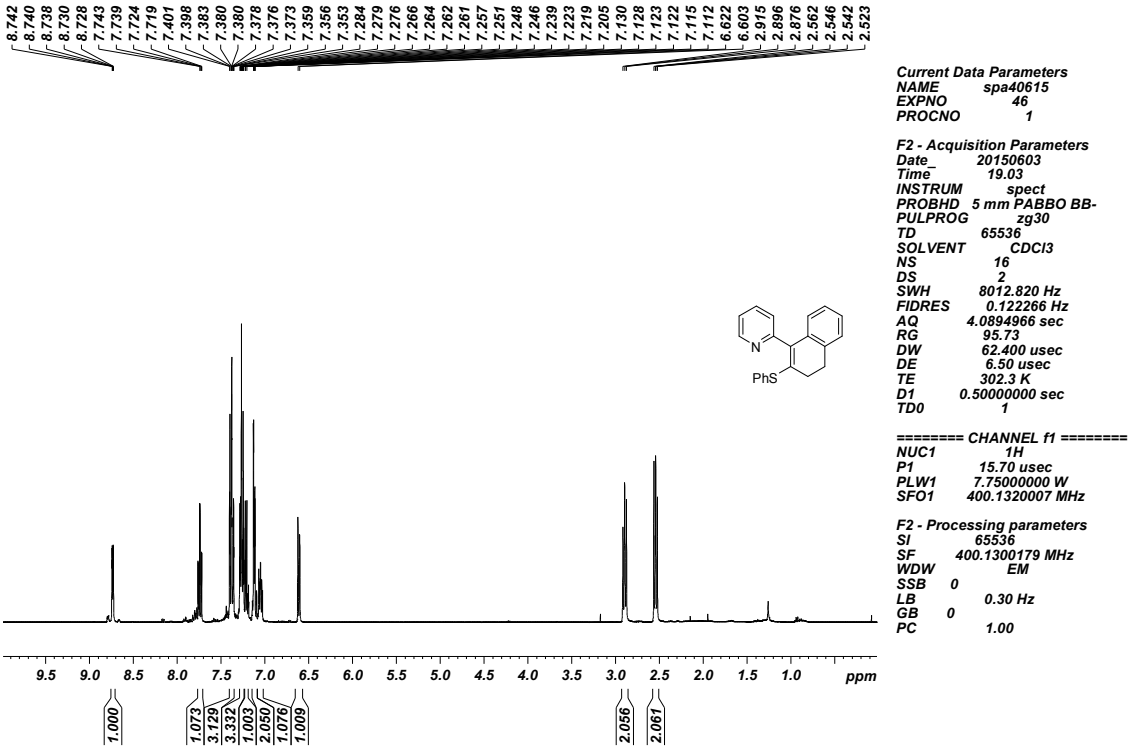



### $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)



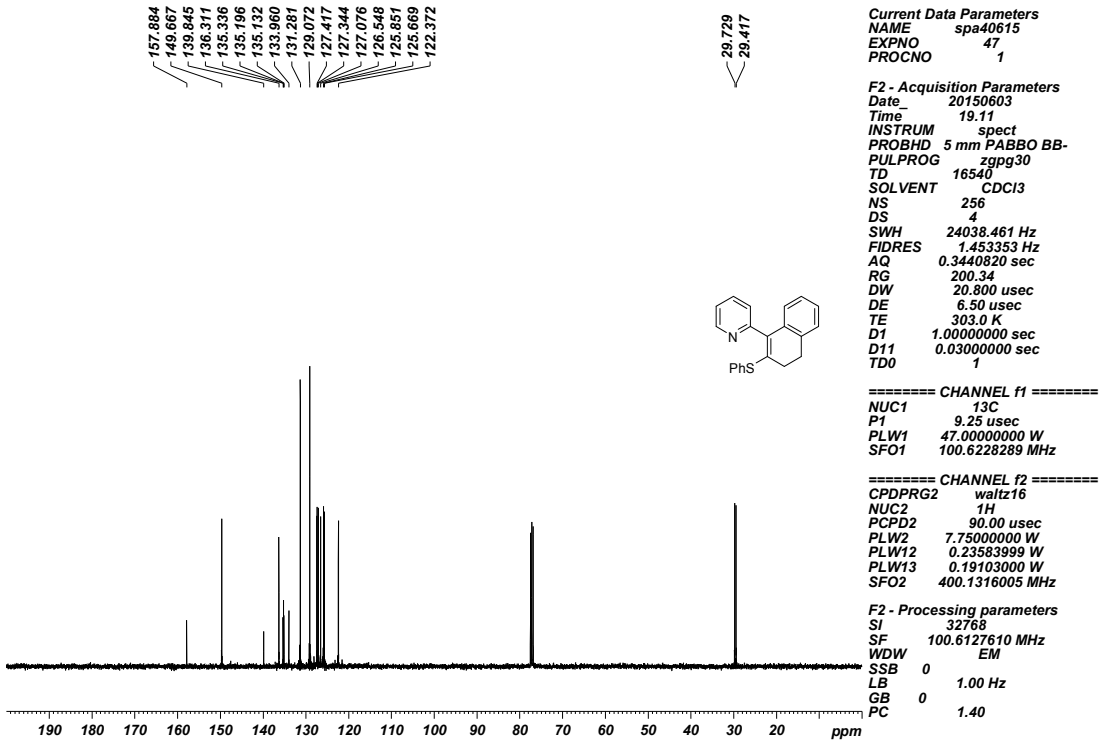
## 2-(2-(Phenylthio)-3,4-dihydronaphthalen-1-yl)pyridine (6g)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)




```
Current Data Parameters
NAME          spa40615
EXPNO            46
PROCNO            1

F2 - Acquisition Parameters
Date_         20150603
Time             19.03
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD              65536
SOLVENT          CDCl3
NS                 16
DS                  2
SWH           8012.820 Hz
FIDRES           0.122266 Hz
AQ            4.0894966 sec
RG                95.73
DW                62.400 usec
DE                 6.50 usec
TE               302.3 K
D1            0.50000000 sec
TD0                1

======== CHANNEL f1 ========
NUC1               1H
P1                15.70 usec
PLW1           7.75000000 W
SFO1         400.1320007 MHz

F2 - Processing parameters
SI              65536
SF          400.1300179 MHz
WDW                EM
SSB     0
LB               0.30 Hz
GB      0
PC               1.00
```

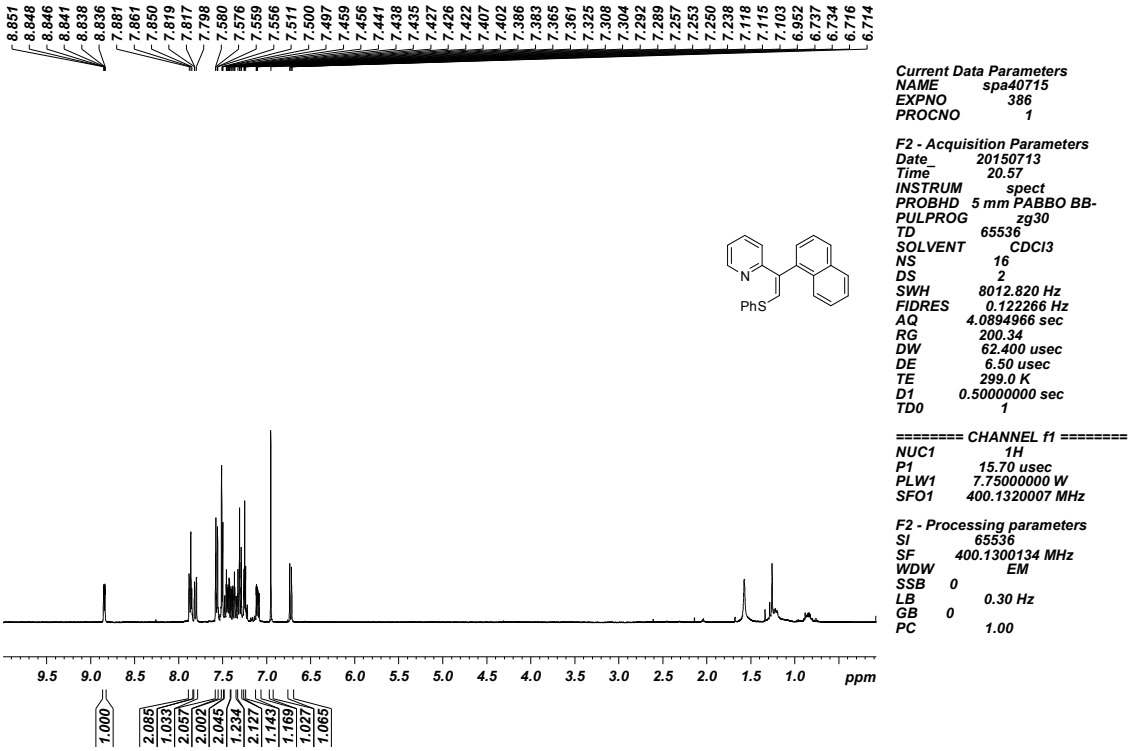
## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)




```
Current Data Parameters
NAME          spa40615
EXPNO            47
PROCNO            1

F2 - Acquisition Parameters
Date_         20150603
Time             19.11
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG        zgpg30
TD              16540
SOLVENT          CDCl3
NS                256
DS                  4
SWH          24038.461 Hz
FIDRES           1.453353 Hz
AQ           0.3440820 sec
RG                200.34
DW                20.800 usec
DE                 6.50 usec
TE               303.0 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                1

======== CHANNEL f1 ========
NUC1              13C
P1                9.25 usec
PLW1         47.00000000 W
SFO1        100.6228289 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2               1H
PCPD2            90.00 usec
PLW2          7.75000000 W
PLW12         0.23583999 W
PLW13         0.19103000 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI              32768
SF          100.6127610 MHz
WDW                EM
SSB     0
LB               1.00 Hz
GB      0
PC               1.40
```

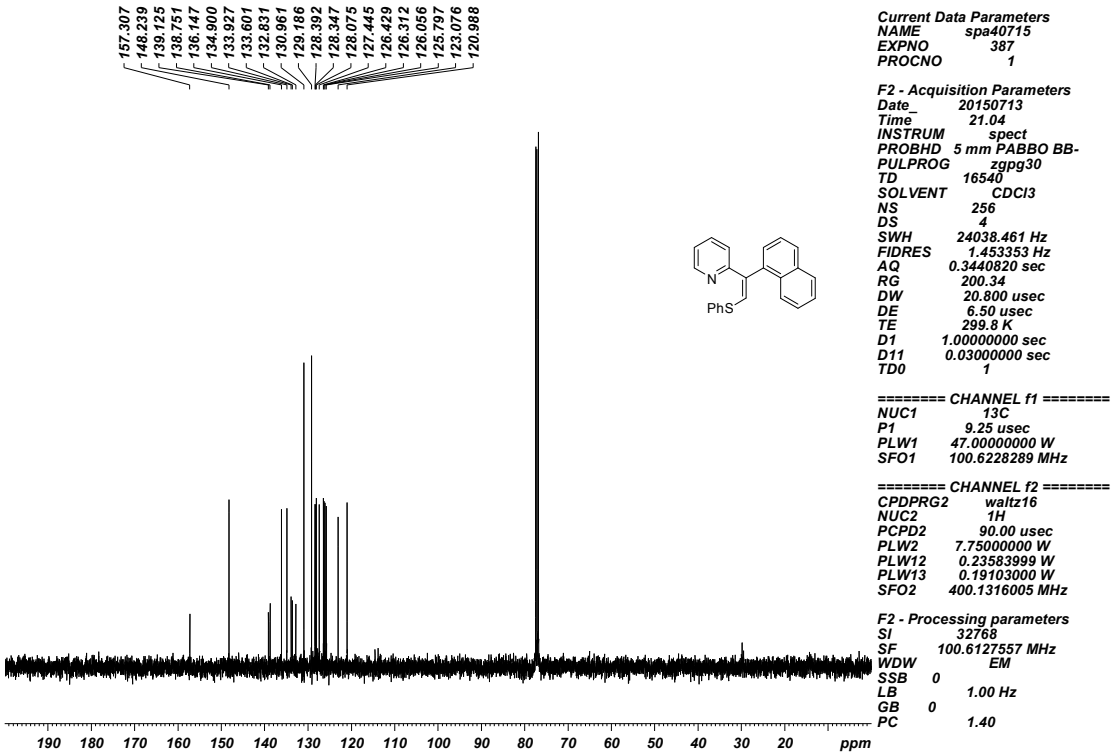
## (*Z*)-2-(1-(Naphthalen-1-yl)-2-(phenylthio)vinyl)pyridine (6h)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)




```
Current Data Parameters
NAME          spa40715
EXPNO              386
PROCNO               1

F2 - Acquisition Parameters
Date_         20150713
Time             20.57
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG          zg30
TD              65536
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           8012.820 Hz
FIDRES           0.122266 Hz
AQ            4.0894966 sec
RG                200.34
DW                62.400 usec
DE                 6.50 usec
TE                299.0 K
D1            0.50000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                 1H
P1                15.70 usec
PLW1          7.75000000 W
SFO1          400.1320007 MHz

F2 - Processing parameters
SI                65536
SF            400.1300134 MHz
WDW                  EM
SSB      0
LB                0.30 Hz
GB       0
PC                1.00
```

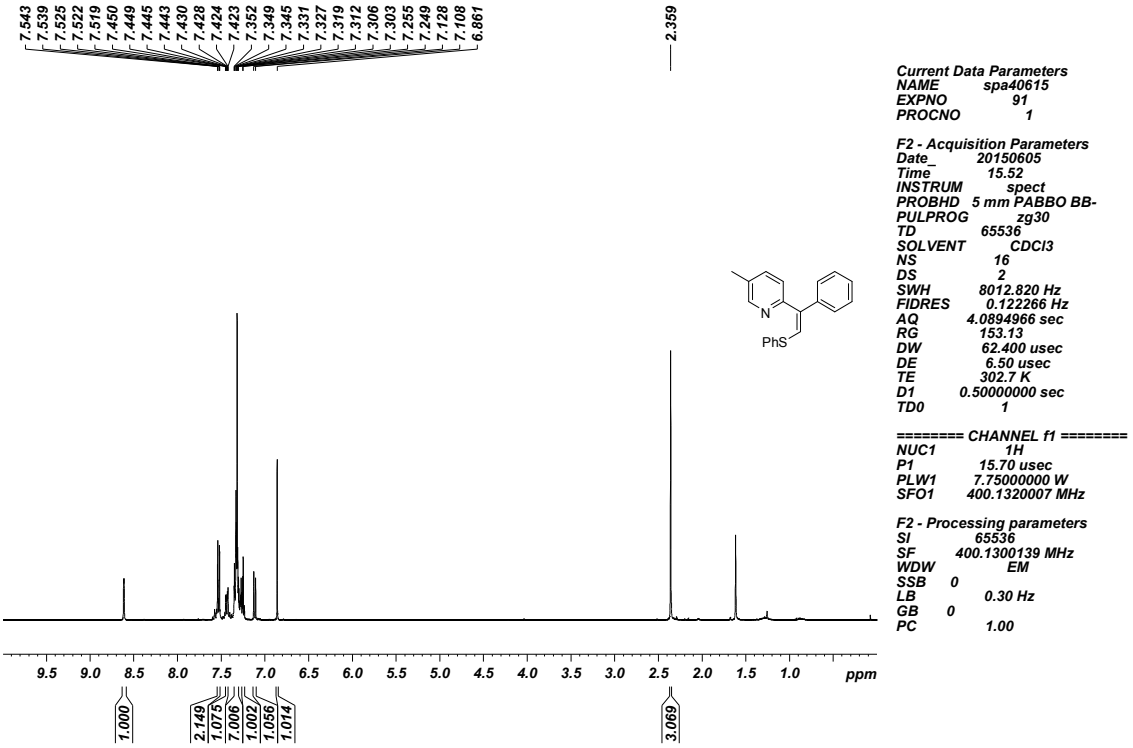
## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)



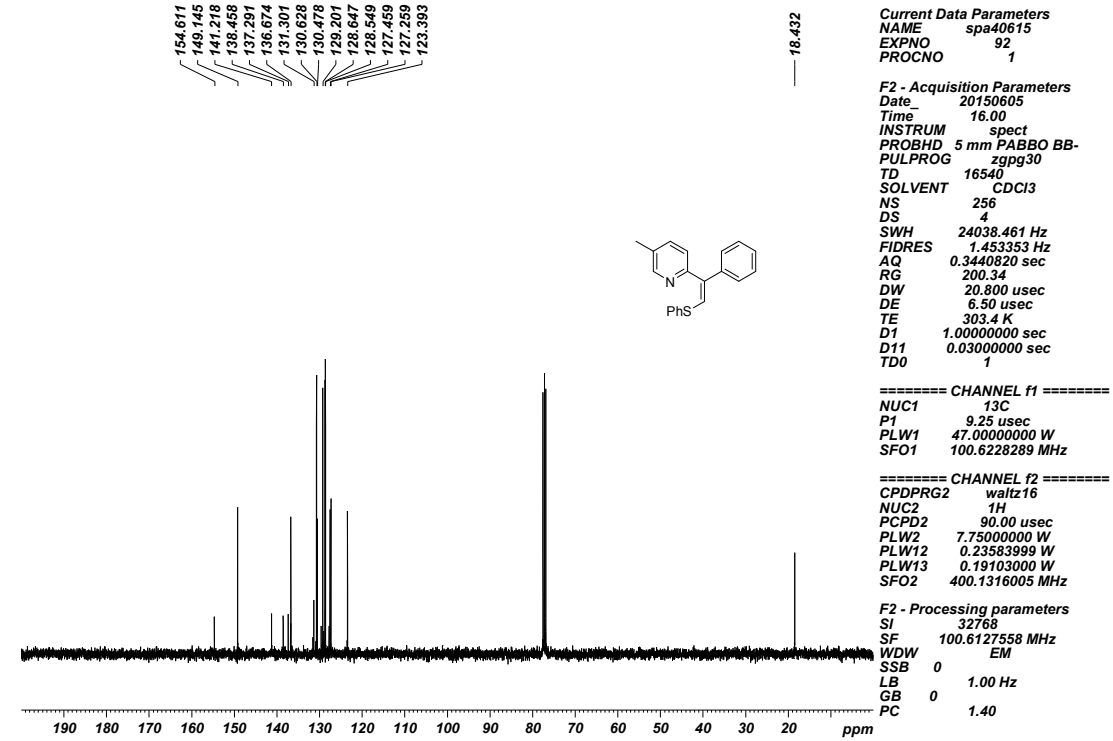

```
Current Data Parameters
NAME          spa40715
EXPNO              387
PROCNO               1

F2 - Acquisition Parameters
Date_         20150713
Time             21.04
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD              16540
SOLVENT          CDCl3
NS                 256
DS                   4
SWH          24038.461 Hz
FIDRES           1.453353 Hz
AQ           0.3440820 sec
RG                200.34
DW                20.800 usec
DE                 6.50 usec
TE                299.8 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.25 usec
PLW1         47.00000000 W
SFO1         100.6228289 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             90.00 usec
PLW2          7.75000000 W
PLW12         0.23583999 W
PLW13         0.19103000 W
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                32768
SF            100.6127557 MHz
WDW                  EM
SSB      0
LB                1.00 Hz
GB       0
PC                1.40
```

## (Z)-5-Methyl-2-(1-phenyl-2-(phenylthio)vinyl)pyridine (6i)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

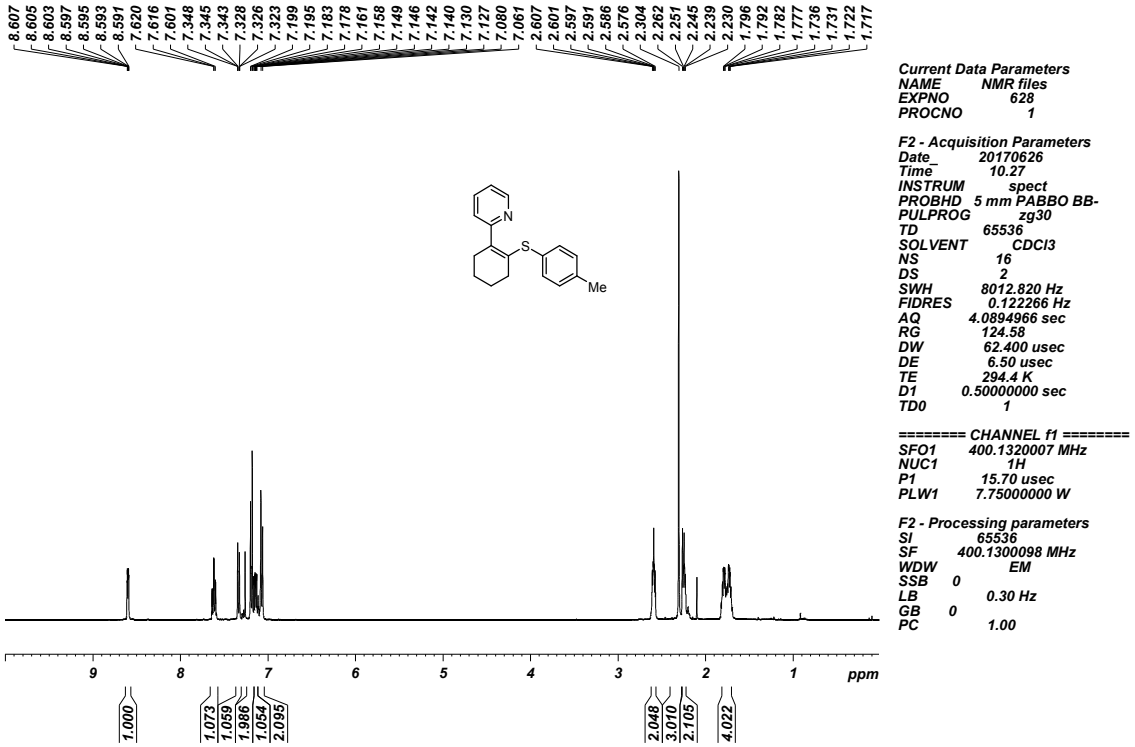



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

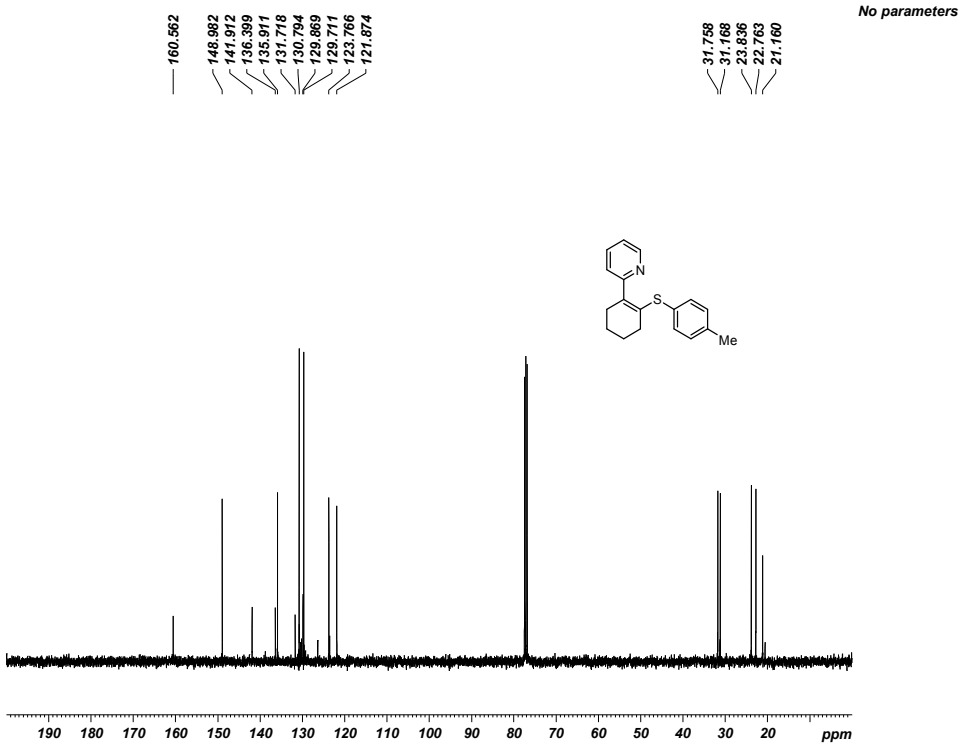


## 2-(2-(*p*-Tolylthio)cyclohex-1-en-1-yl)pyridine (6j)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

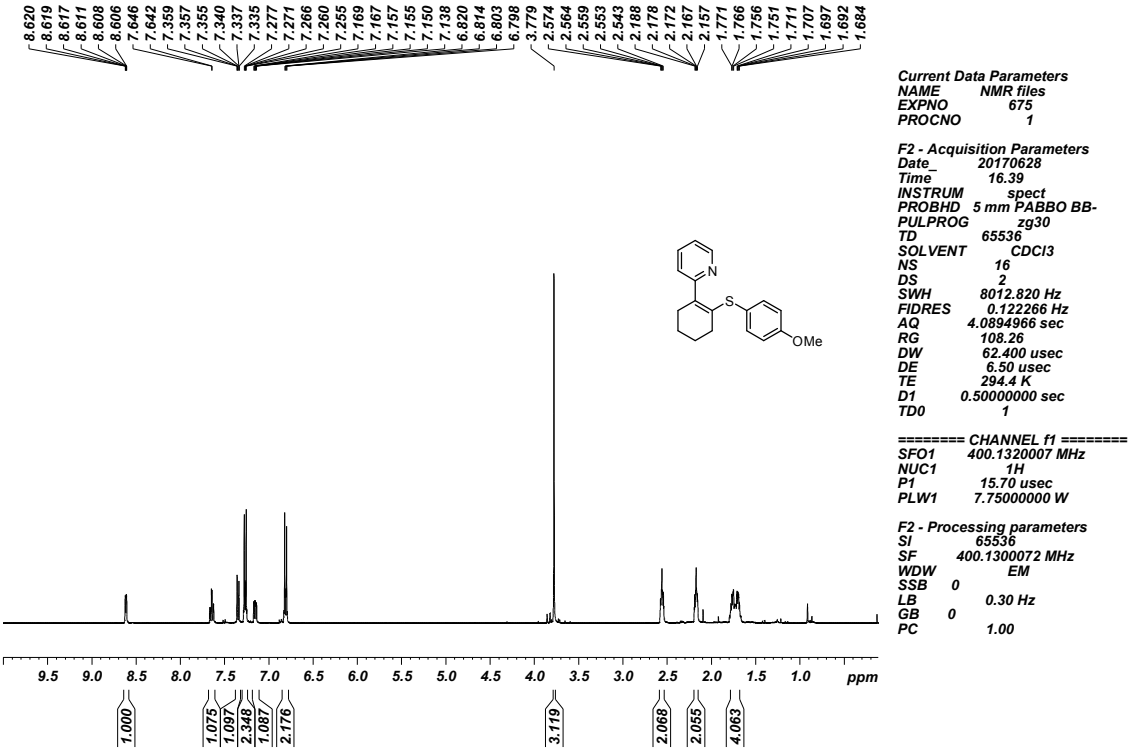



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

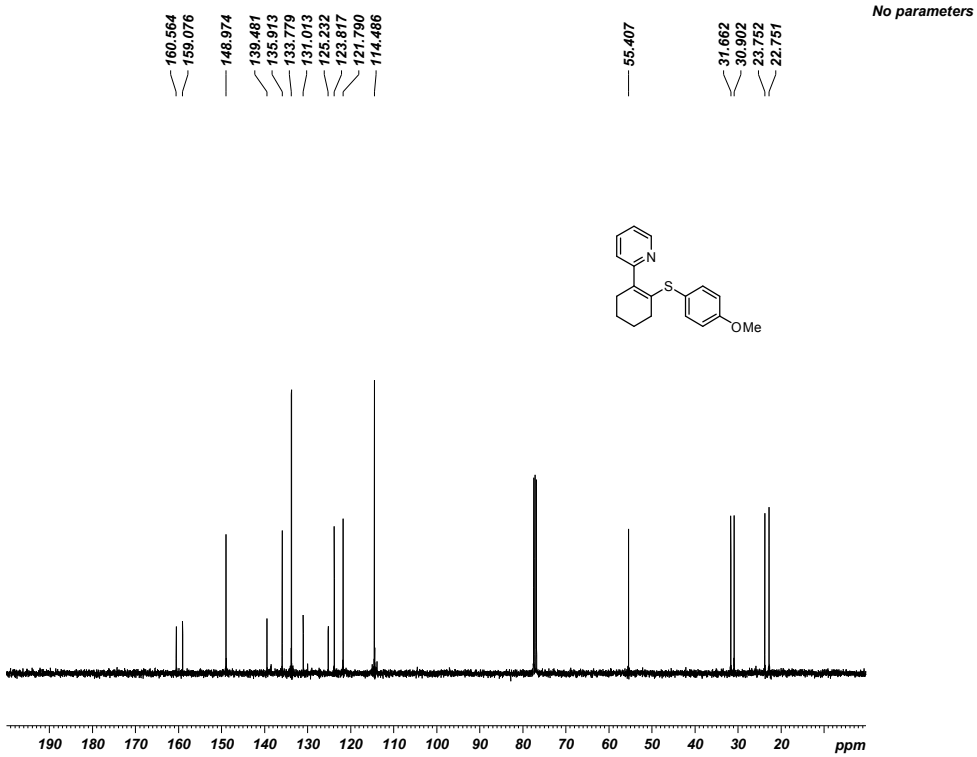


## 2-(2-((4-methoxyphenyl)thio)cyclohex-1-en-1-yl)pyridine (6k)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

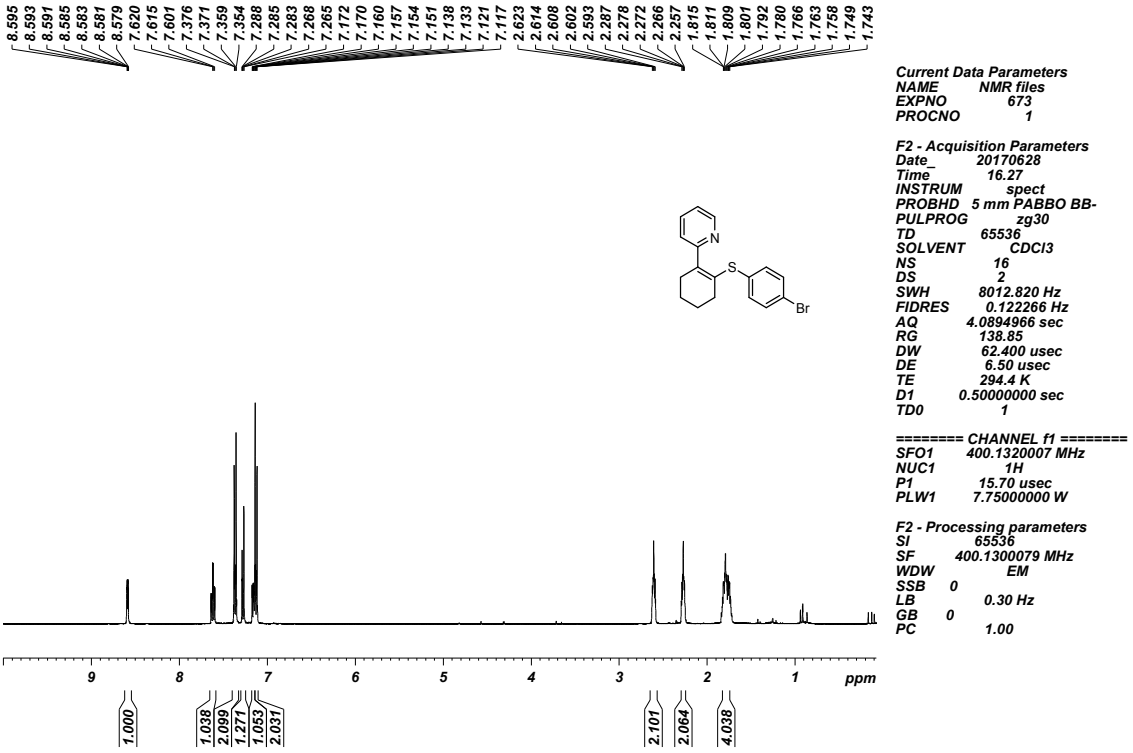



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

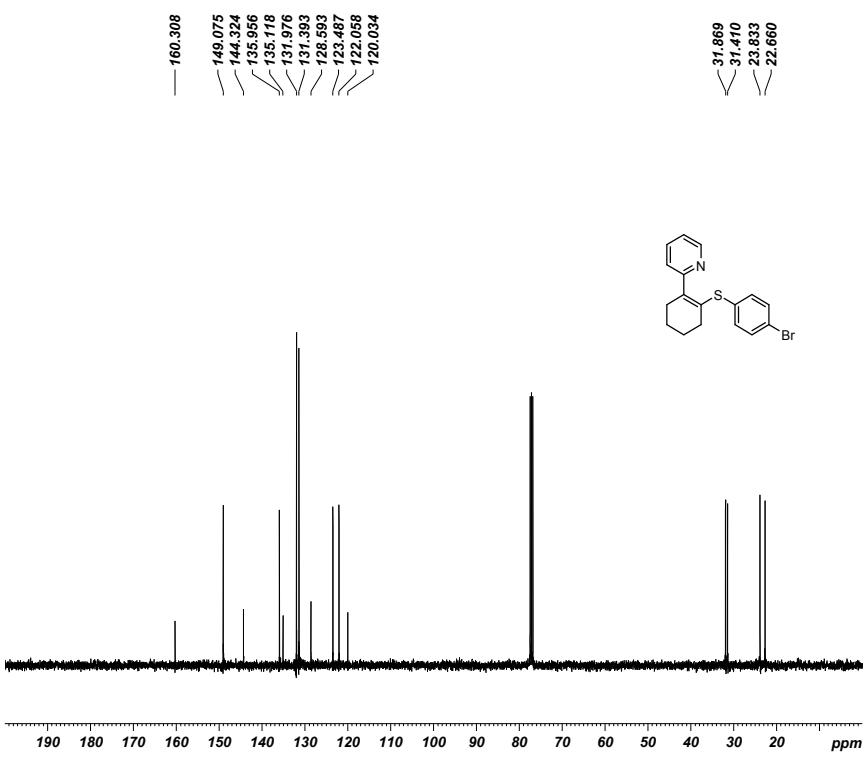


## 2-(2-((4-Bromophenyl)thio)cyclohex-1-en-1-yl)pyridine (6l)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

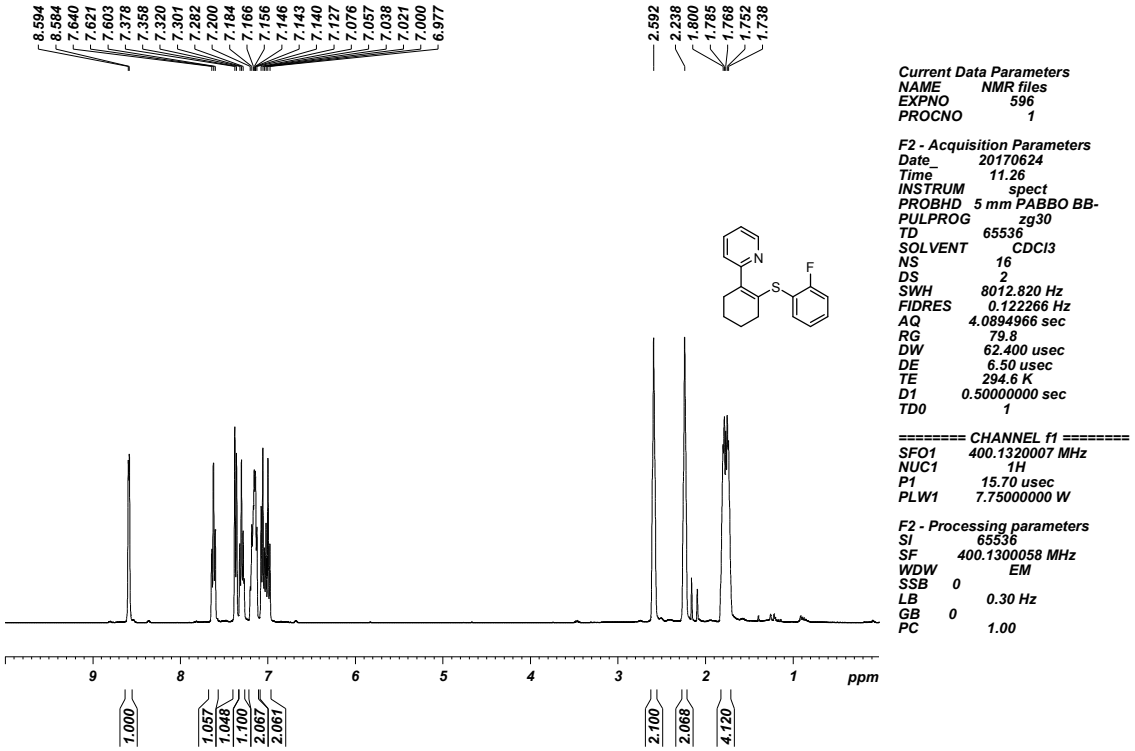



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

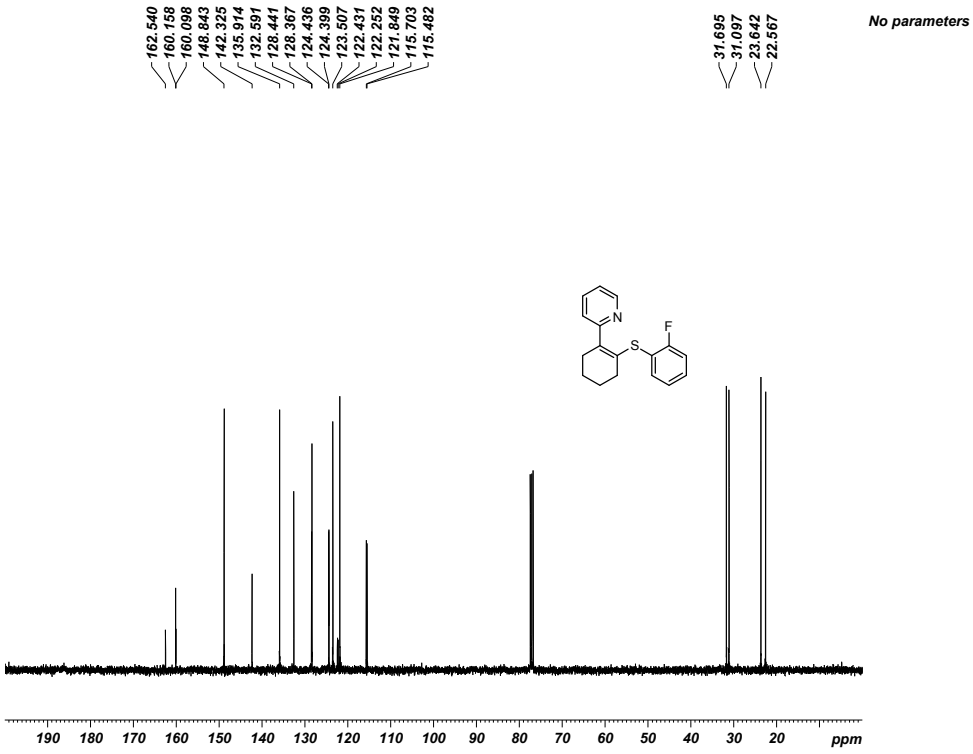


## 2-(2-((2-Fluorophenyl)thio)cyclohex-1-en-1-yl)pyridine (6m)

### $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

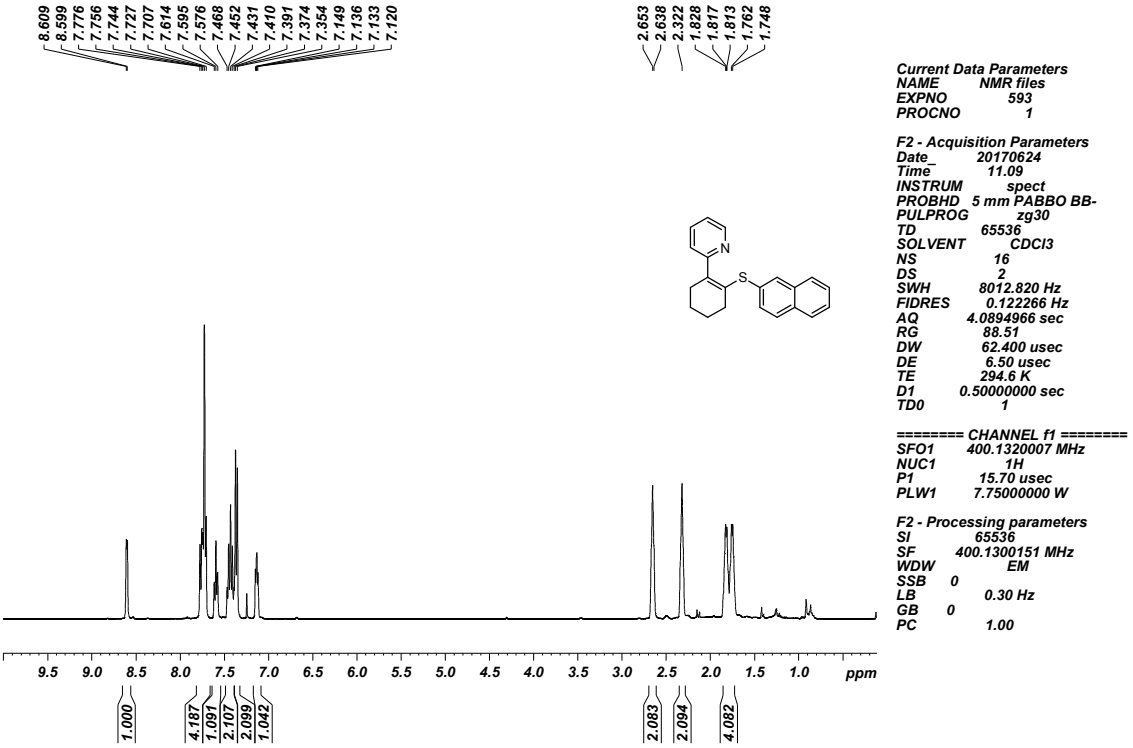



### $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

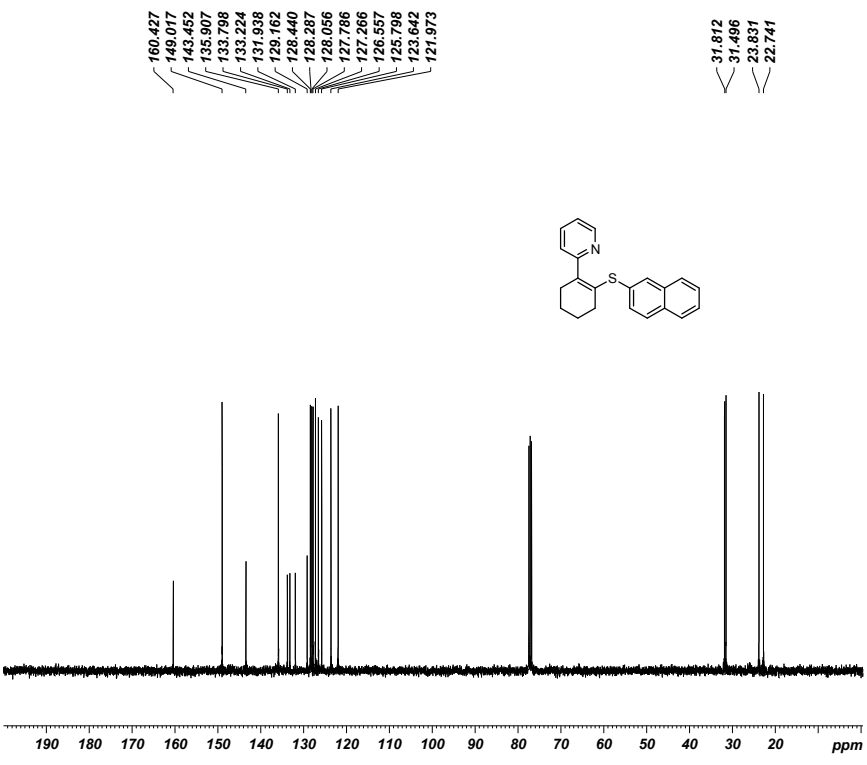


## 2-(2-(Naphthalen-2-ylthio)cyclohex-1-en-1-yl)pyridine (6n)

### $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

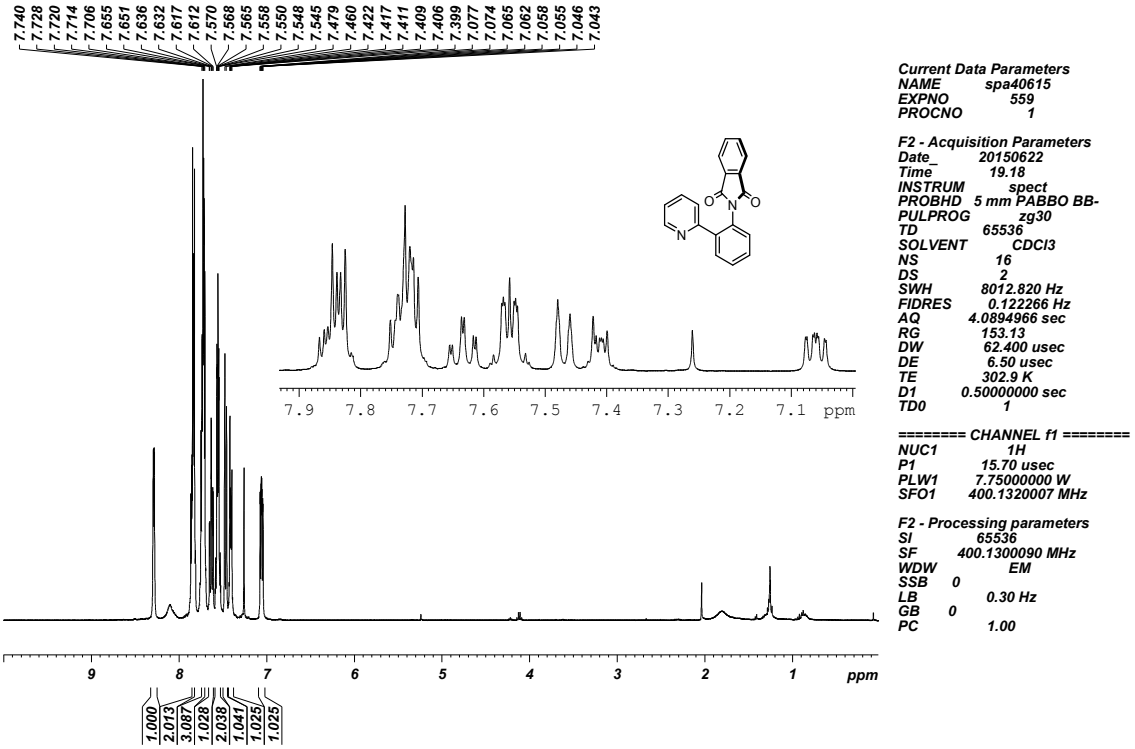



### $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

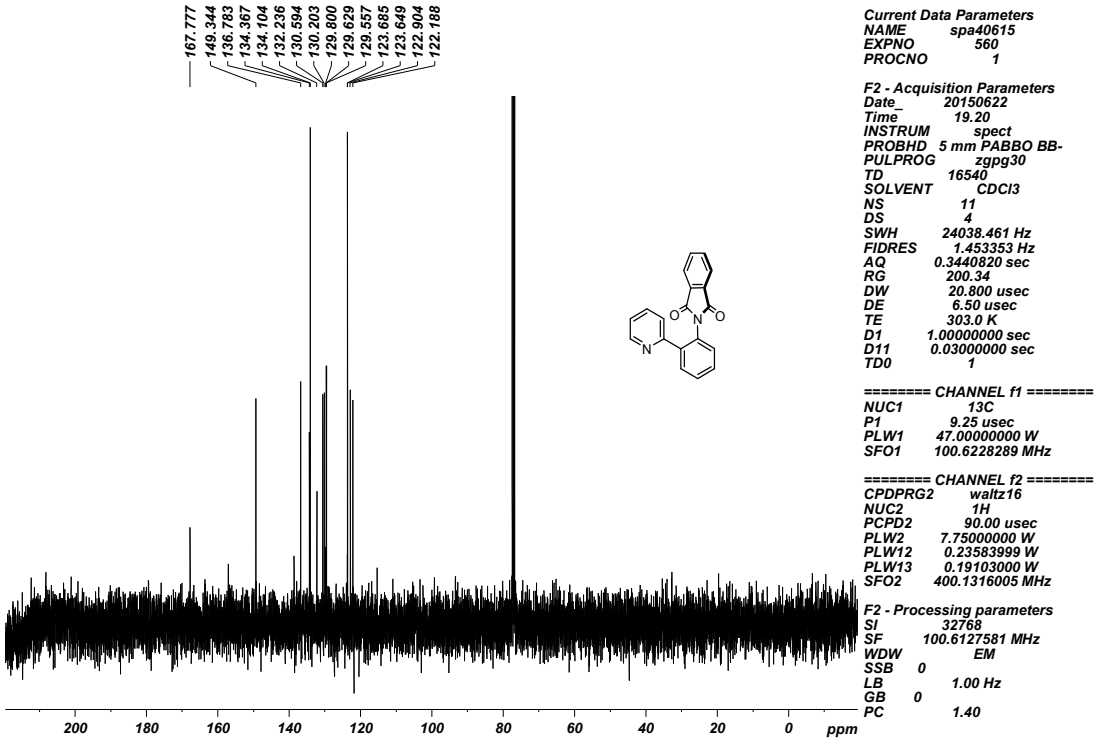


## 2-(2-(Pyridin-2-yl)phenyl)isoindoline-1,3-dione (4a)

### $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

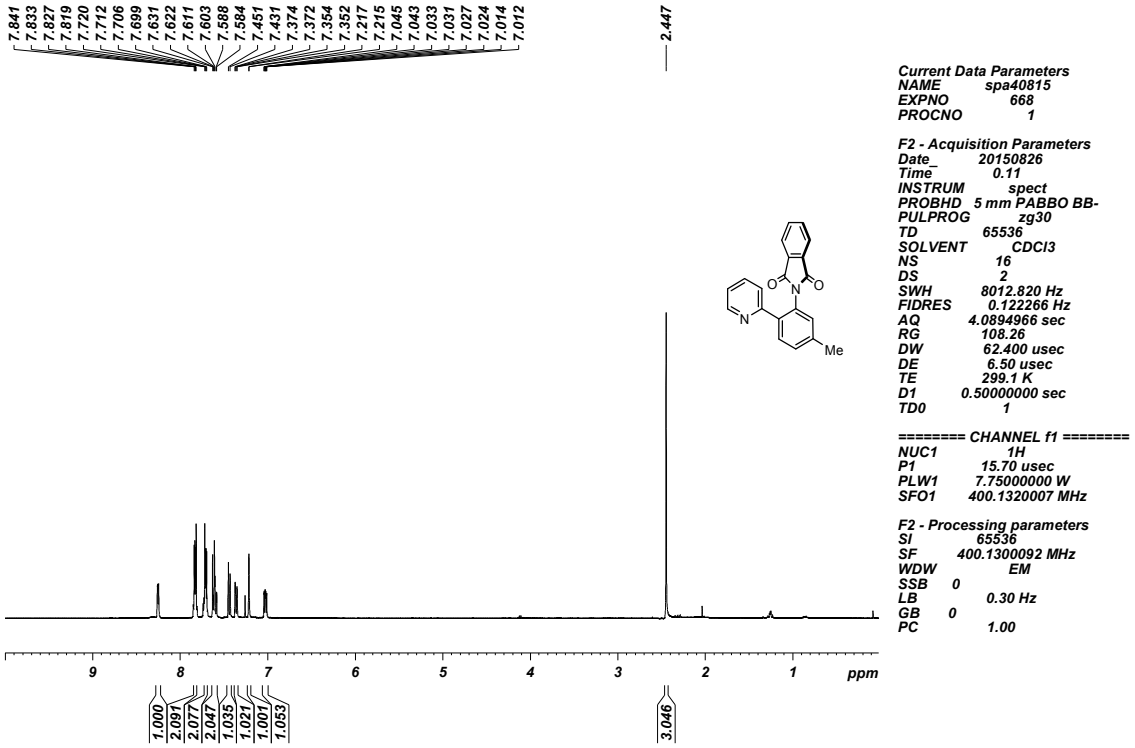



### $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

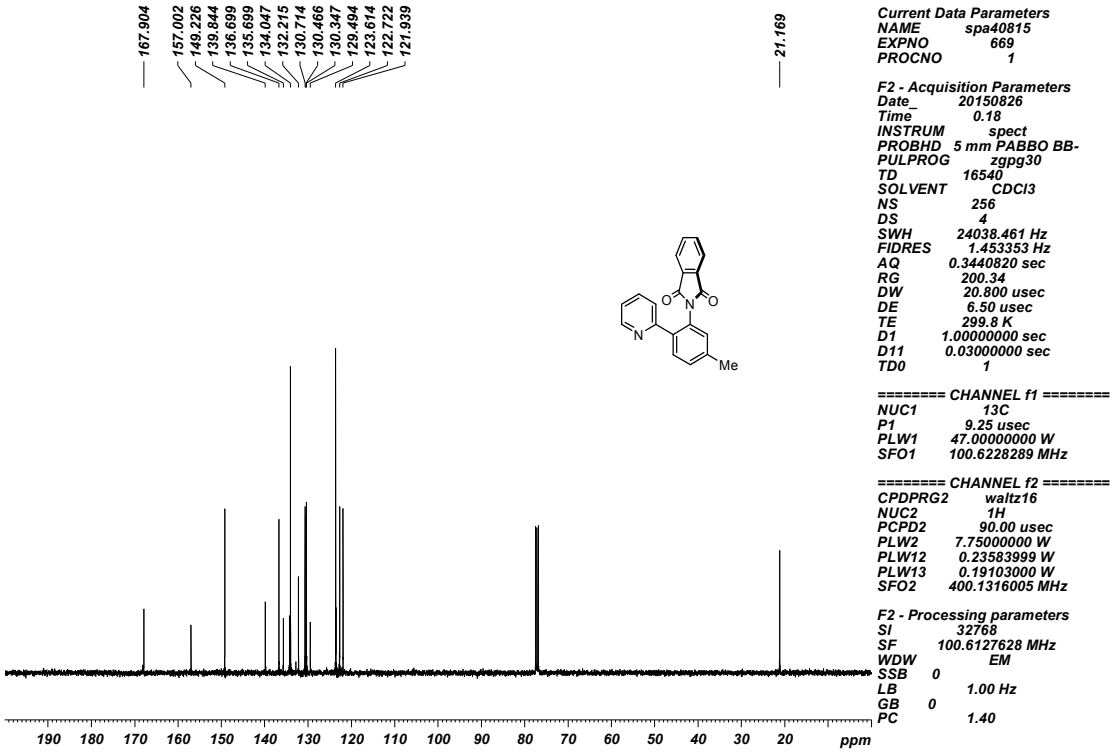


## 2-(5-Methyl-2-(pyridin-2-yl)phenyl)isoindoline-1,3-dione (4b)

### $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

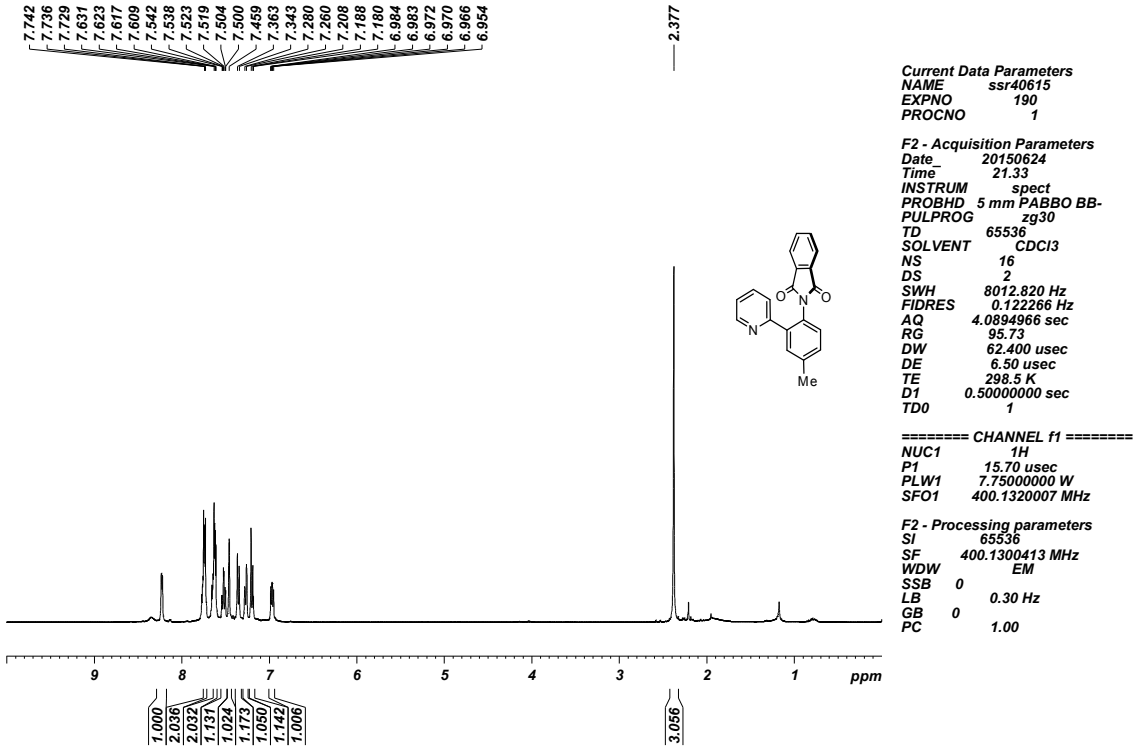



### $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

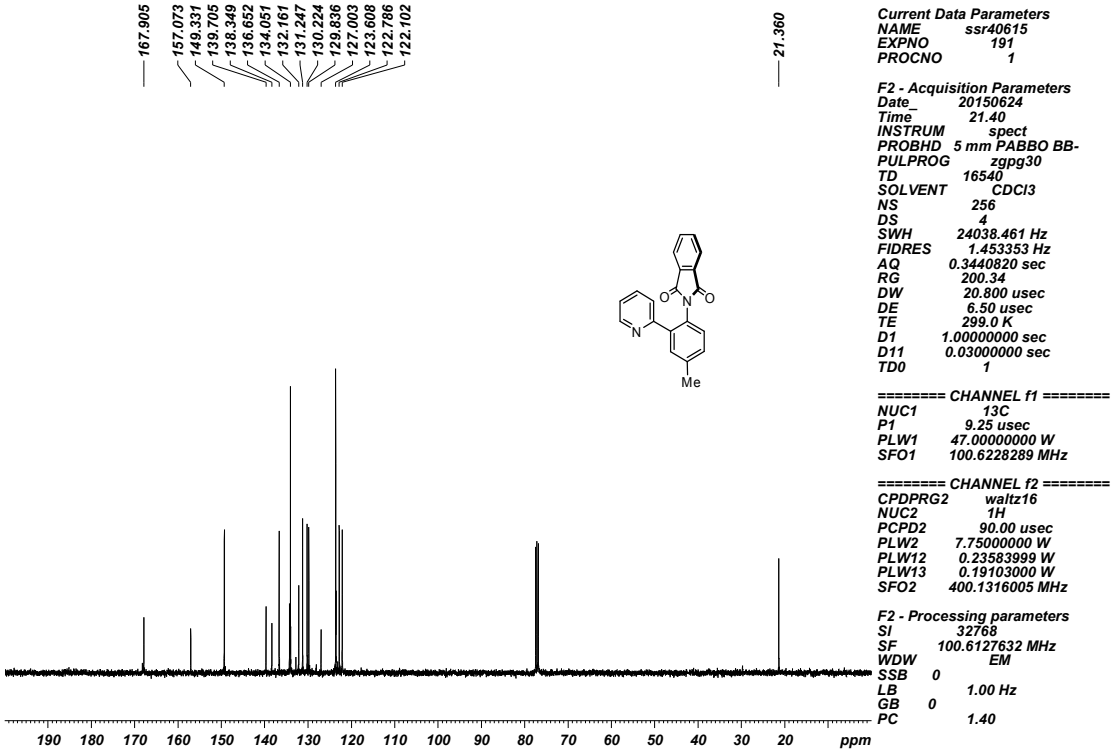


## 2-(4-Methyl-2-(pyridin-2-yl)phenyl)isoindoline-1,3-dione (4c)

### $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

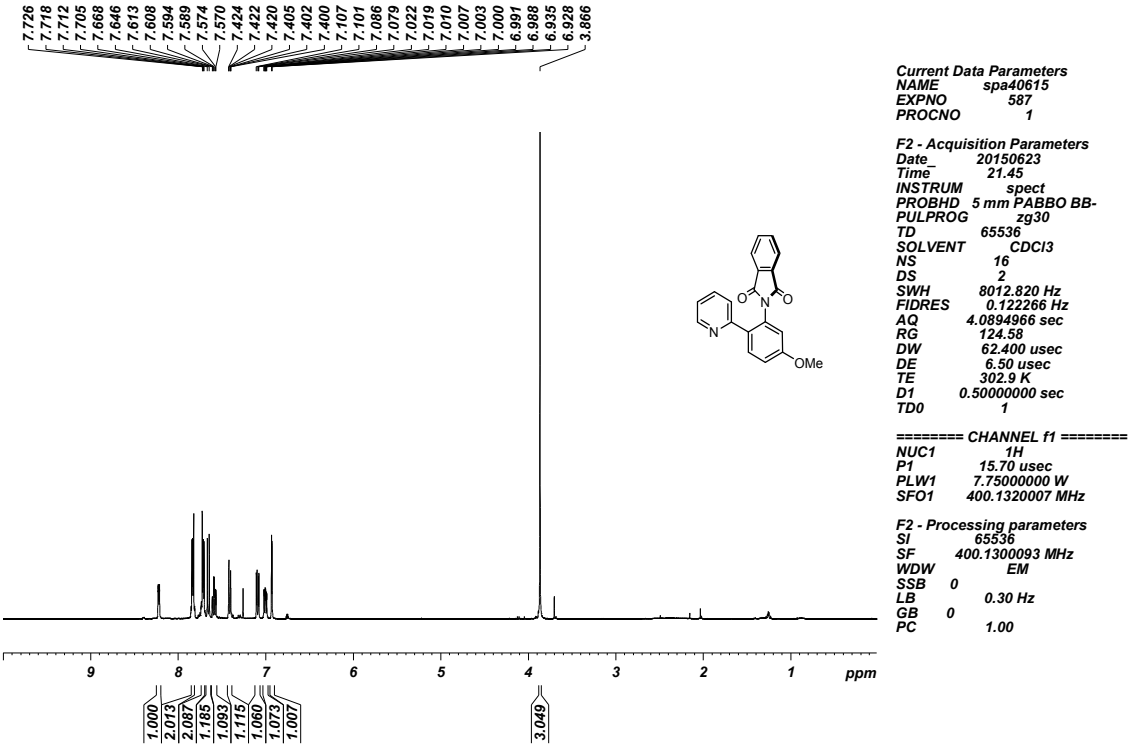



### $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

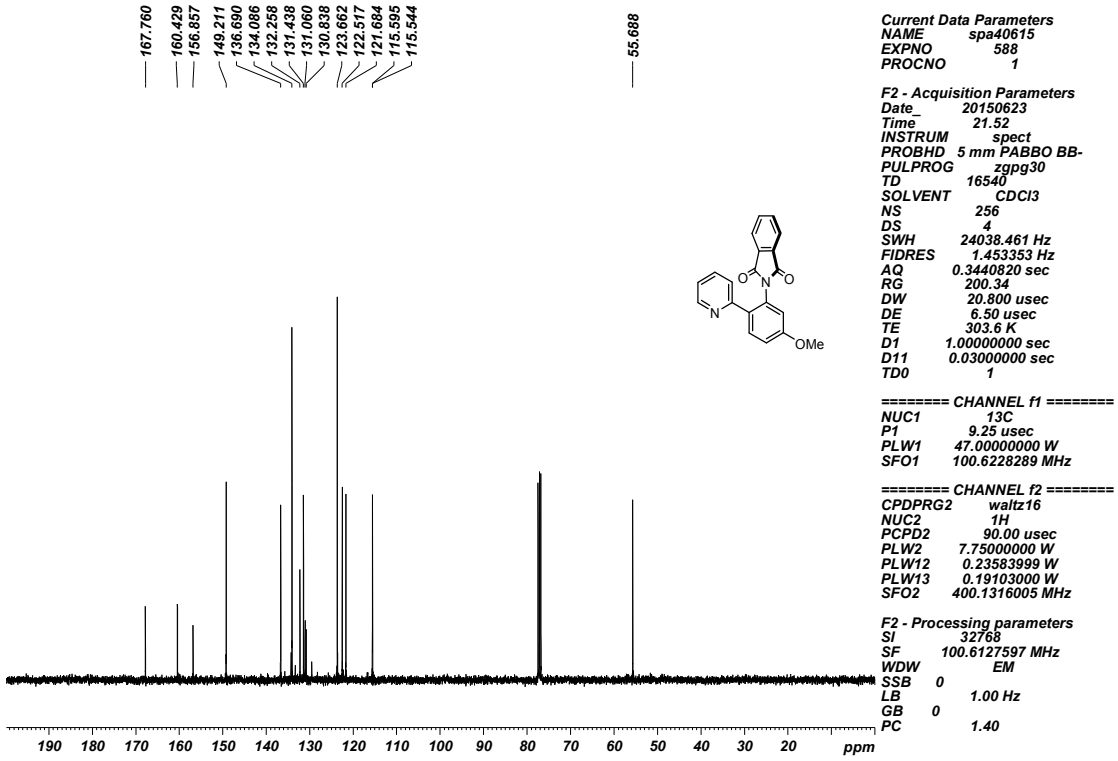


## 2-(5-Methoxy-2-(pyridin-2-yl)phenyl)isoindoline-1,3-dione (4d)

### $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

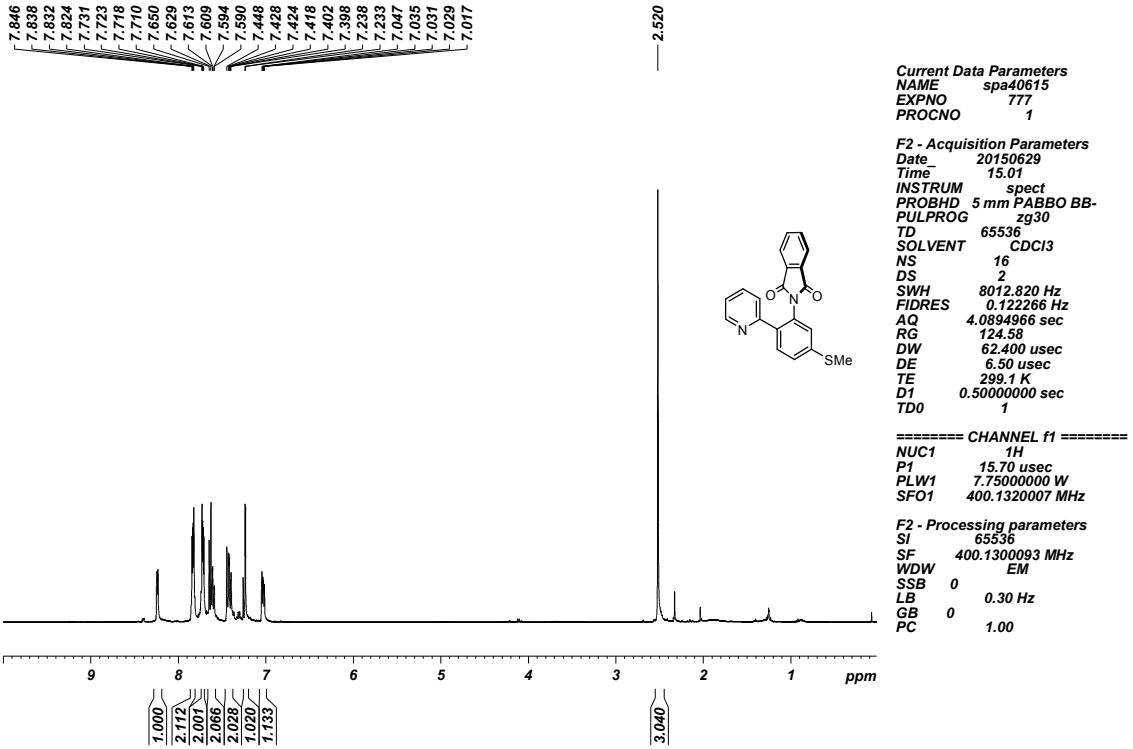



### $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

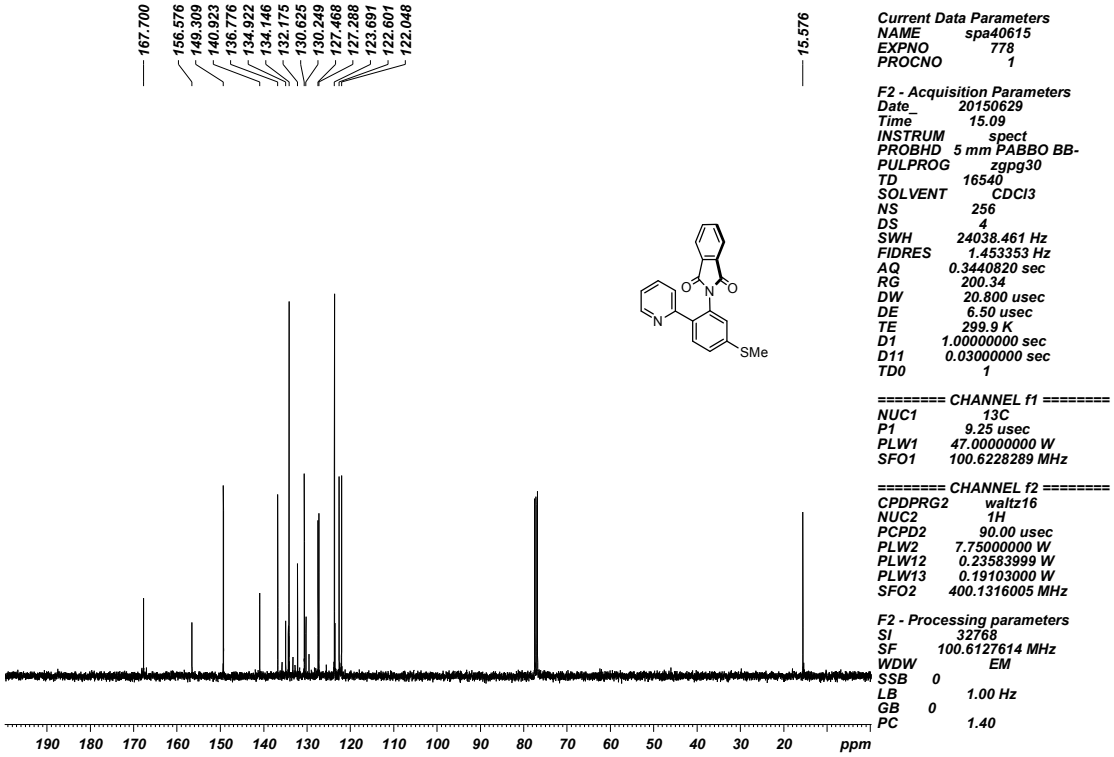


## 2-(5-(Methylthio)-2-(pyridin-2-yl)phenyl)isoindoline-1,3-dione (4e)

### $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

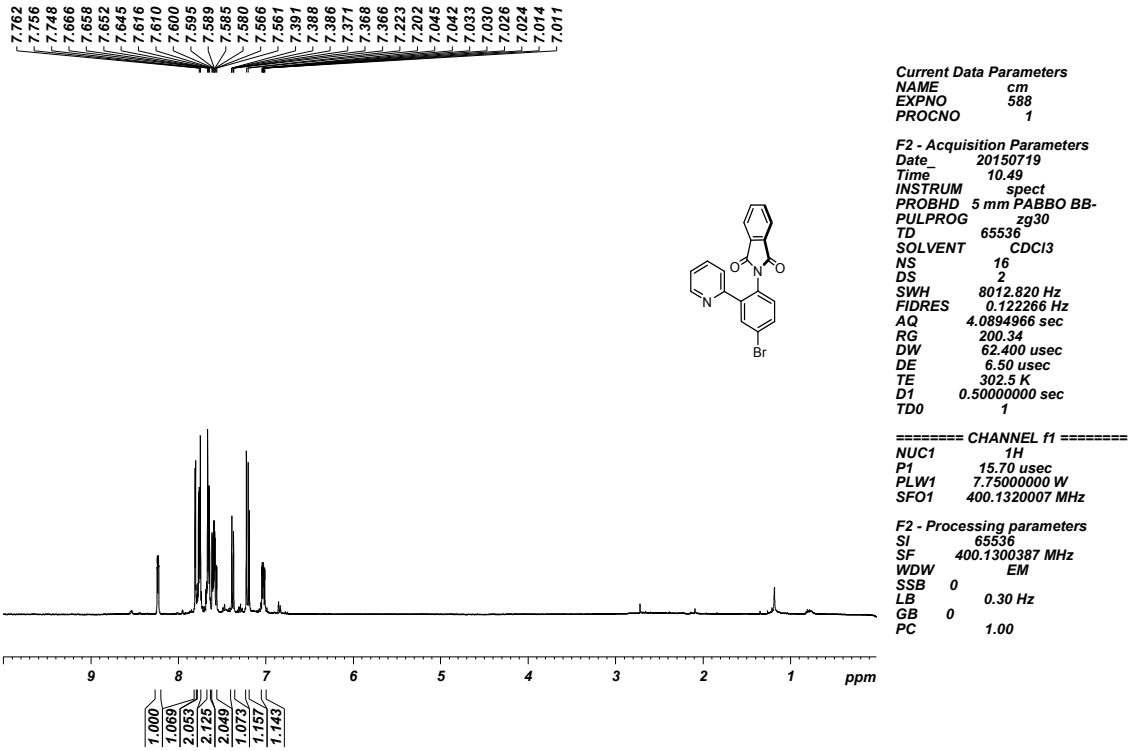



### $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

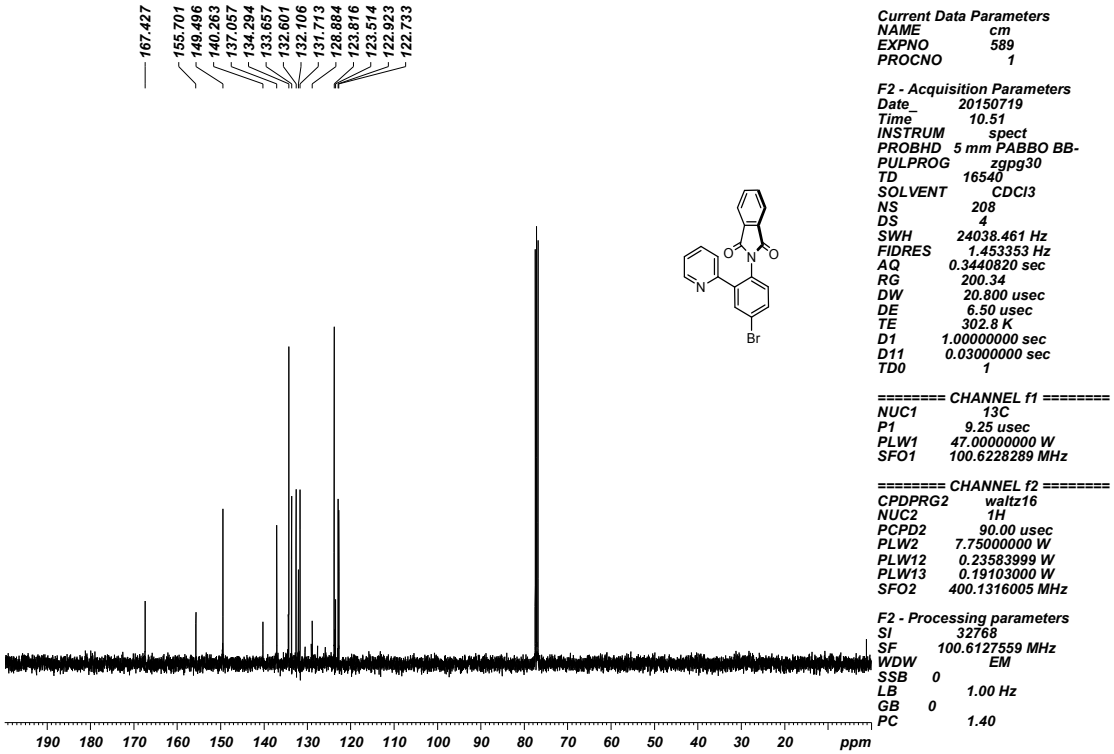


## 2-(4-Bromo-2-(pyridin-2-yl)phenyl)isoindoline-1,3-dione (4f)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

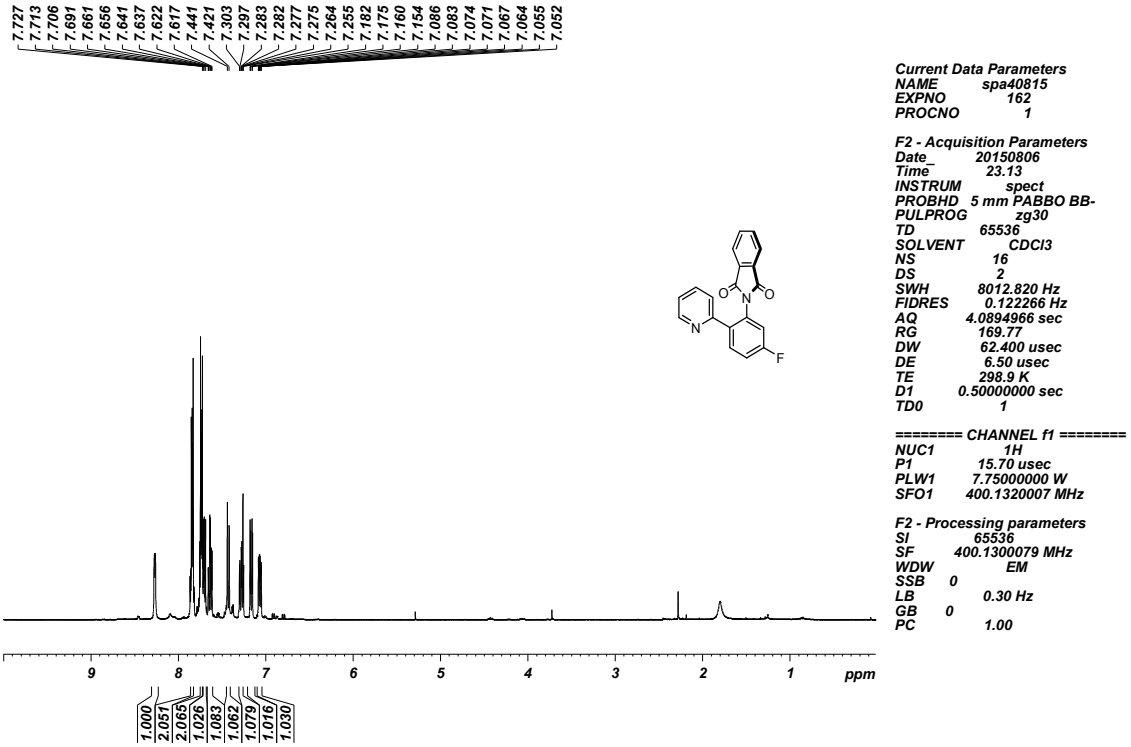



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

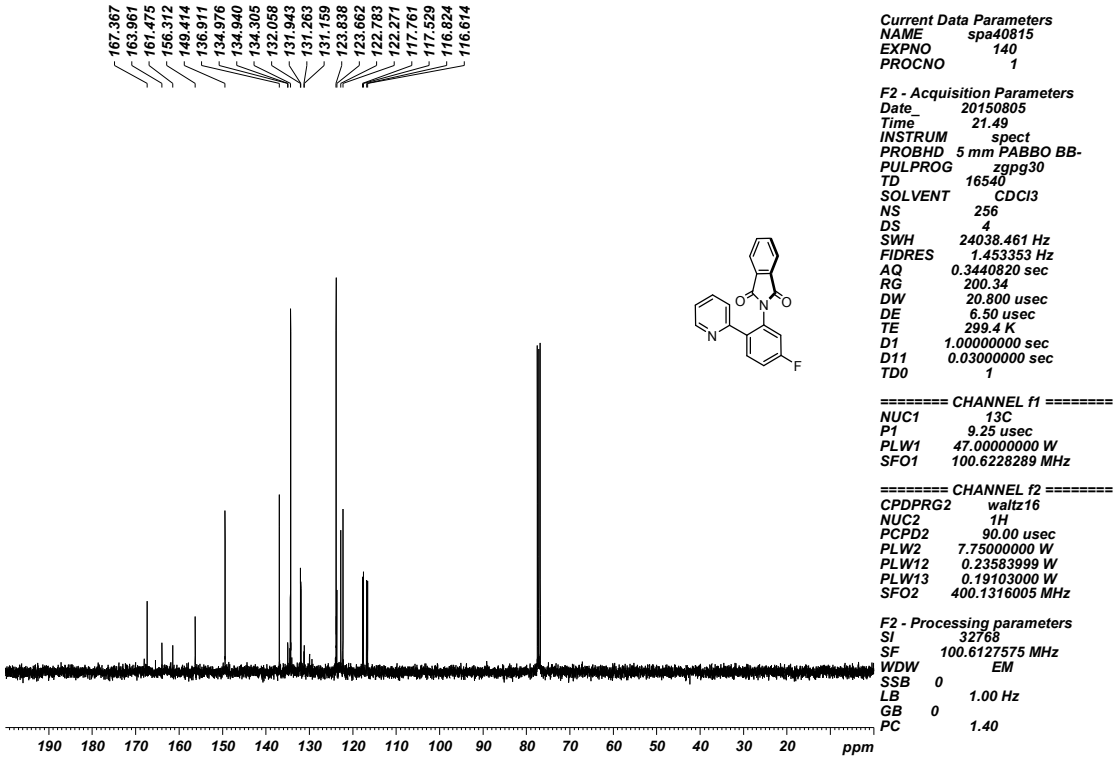


## 2-(5-Fluoro-2-(pyridin-2-yl)phenyl)isoindoline-1,3-dione (4g)

### $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

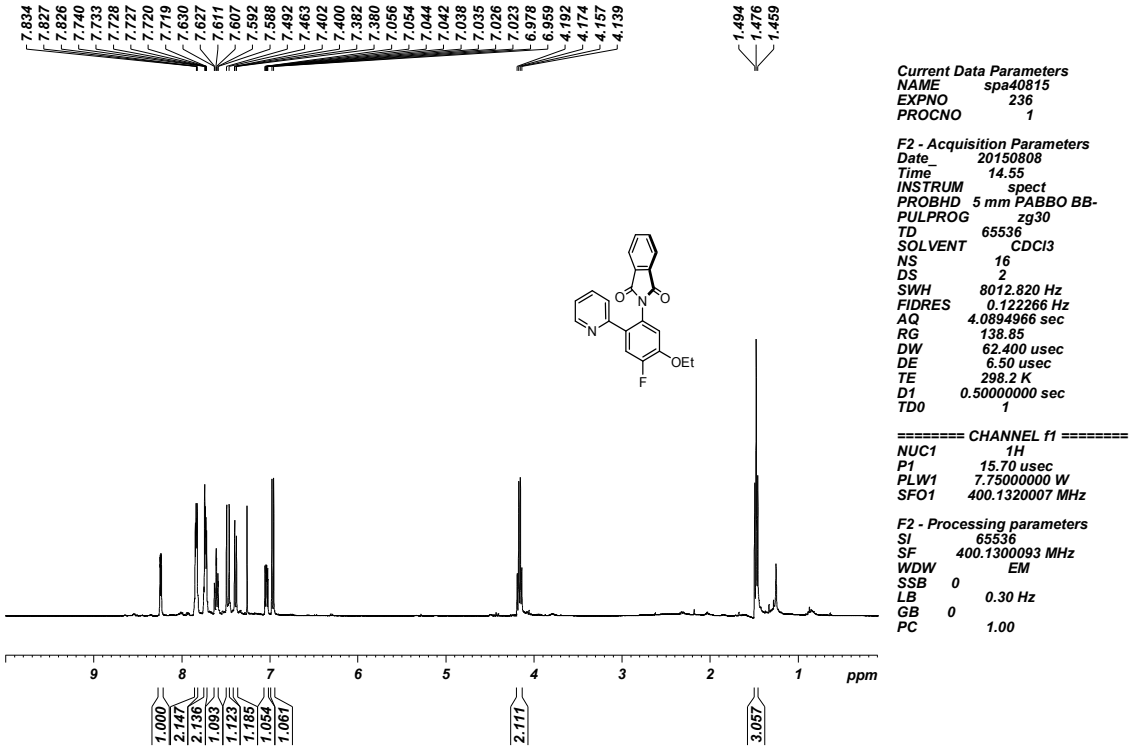



### $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

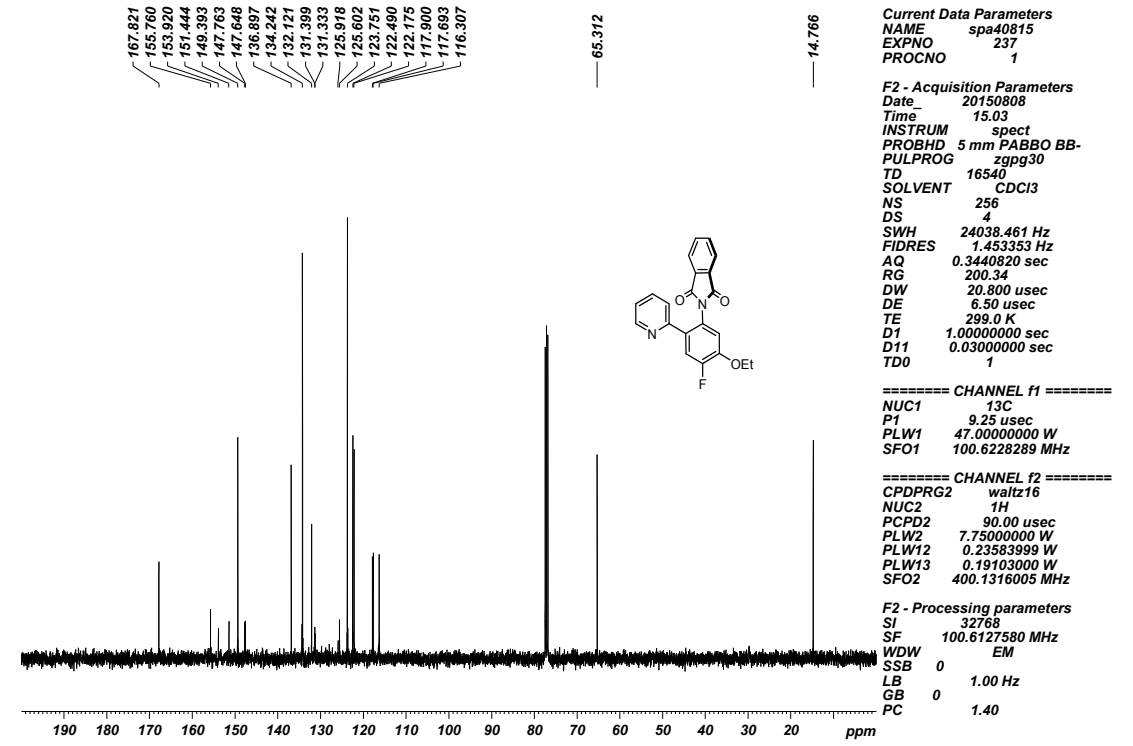


## 2-(5-Ethoxy-4-fluoro-2-(pyridin-2-yl)phenyl)isoindoline-1,3-dione (4h)

### $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

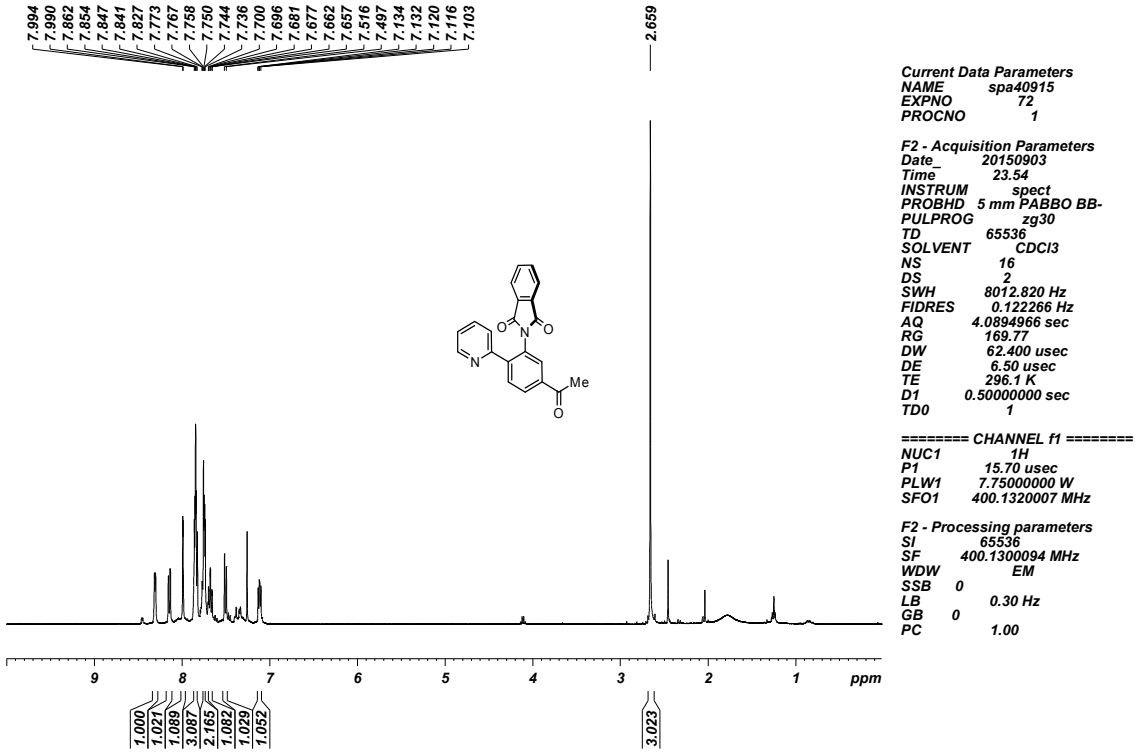



### $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

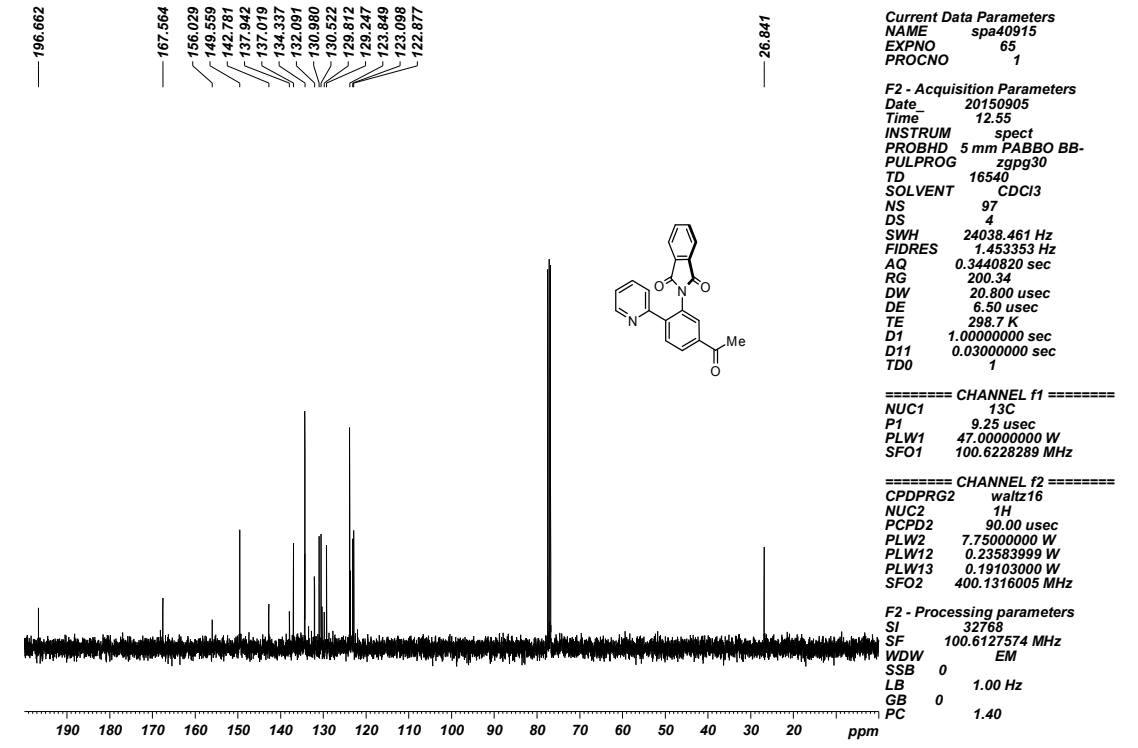


## 2-(5-Acetyl-2-(pyridin-2-yl)phenyl)isoindoline-1,3-dione (4i)

### $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

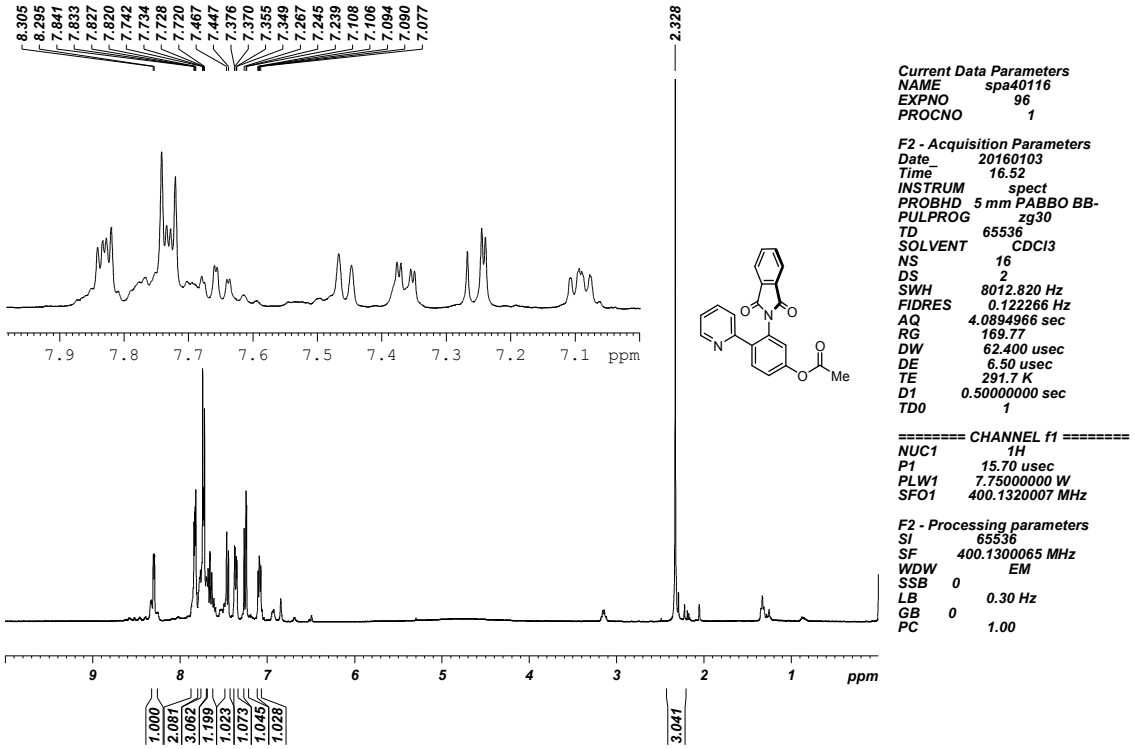



### $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

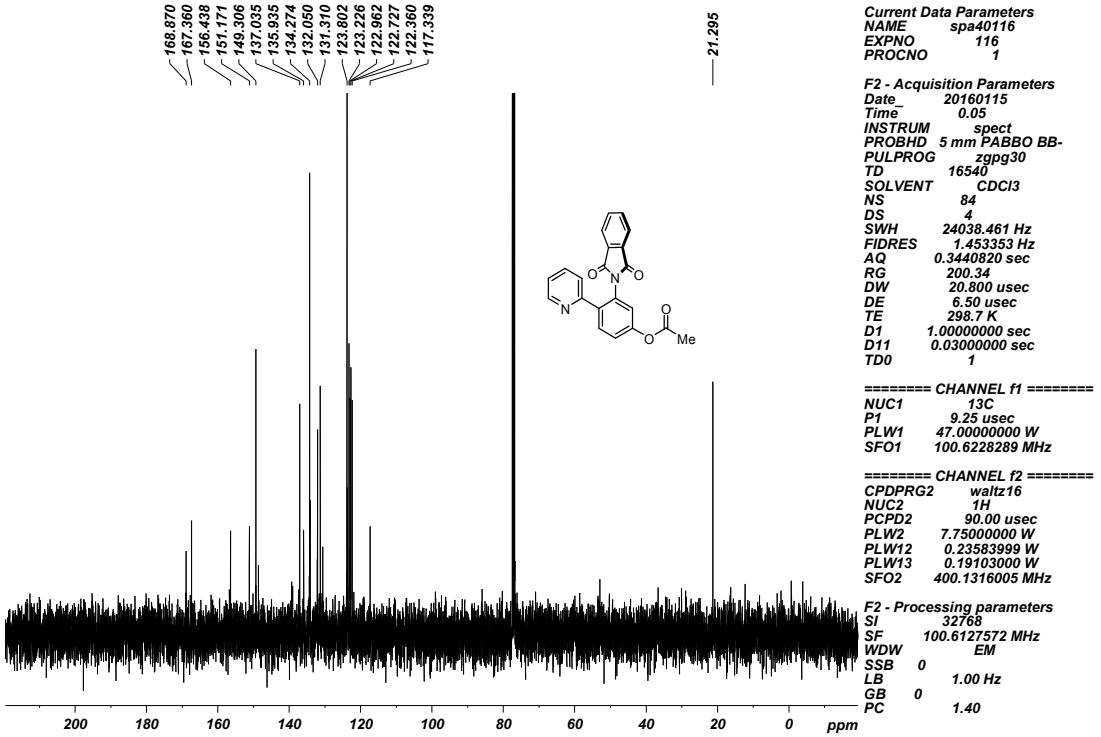


## 3-(1,3-Dioxoisoindolin-2-yl)-4-(pyridin-2-yl)phenyl acetate (4j)

### $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

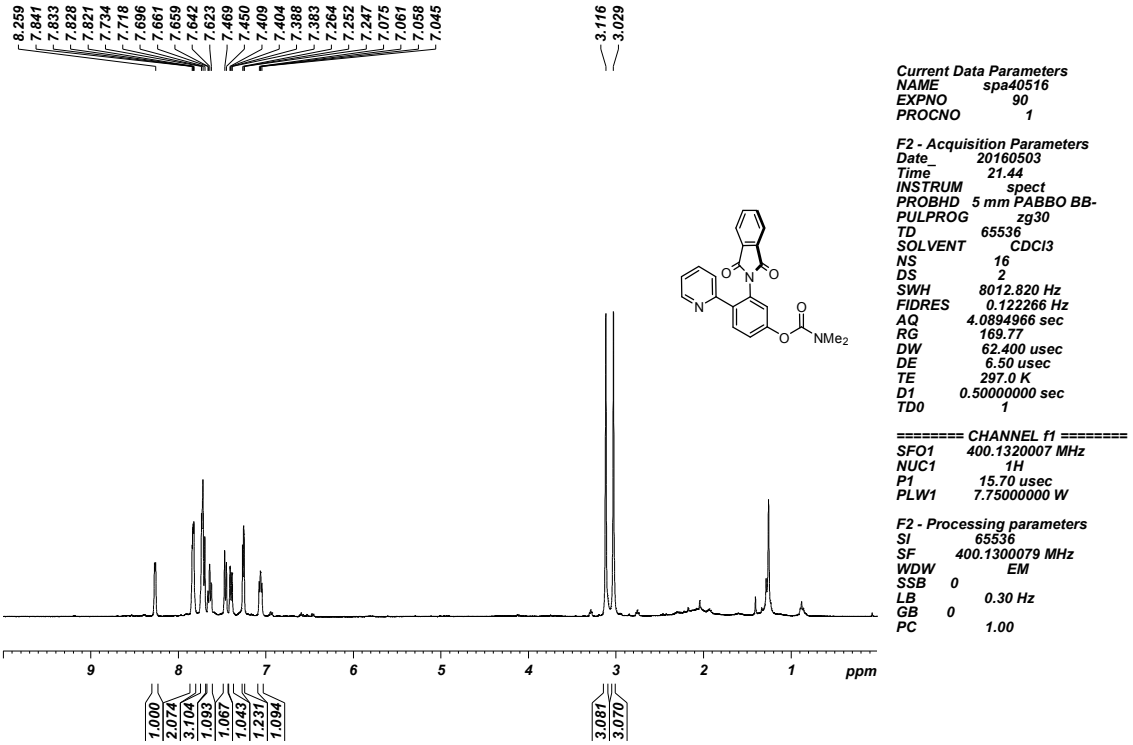



### $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

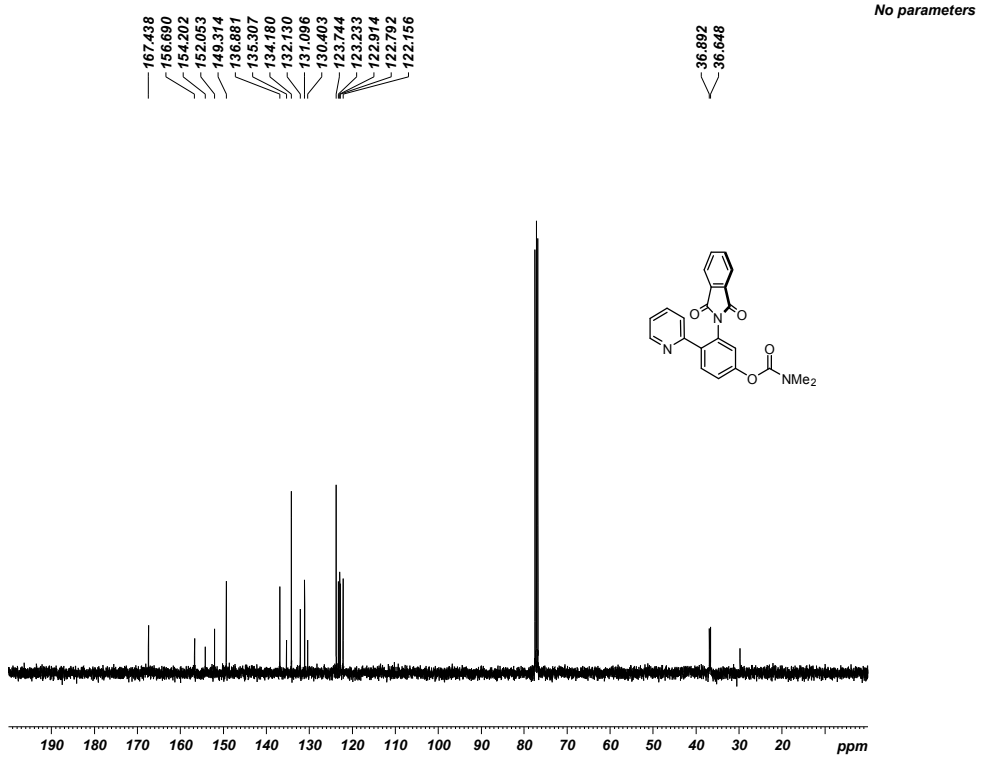


## 3-(1,3-Dioxoisoindolin-2-yl)-4-(pyridin-2-yl)phenyl dimethylcarbamate (4k)

### $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

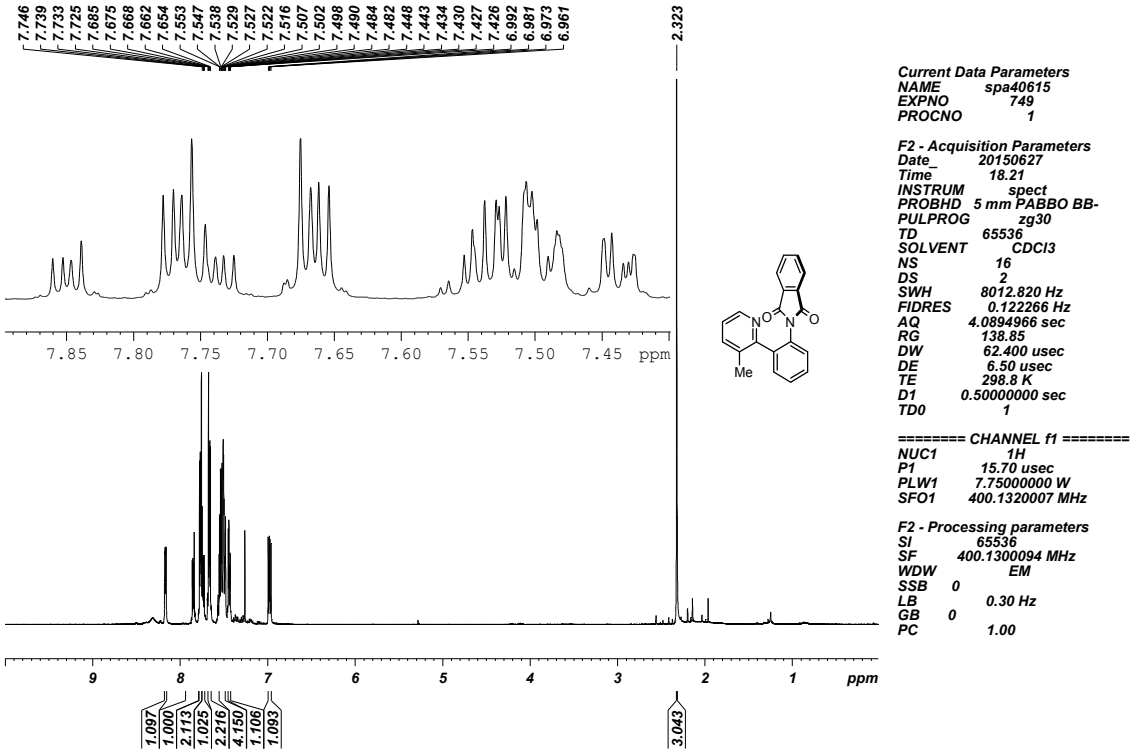



### $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

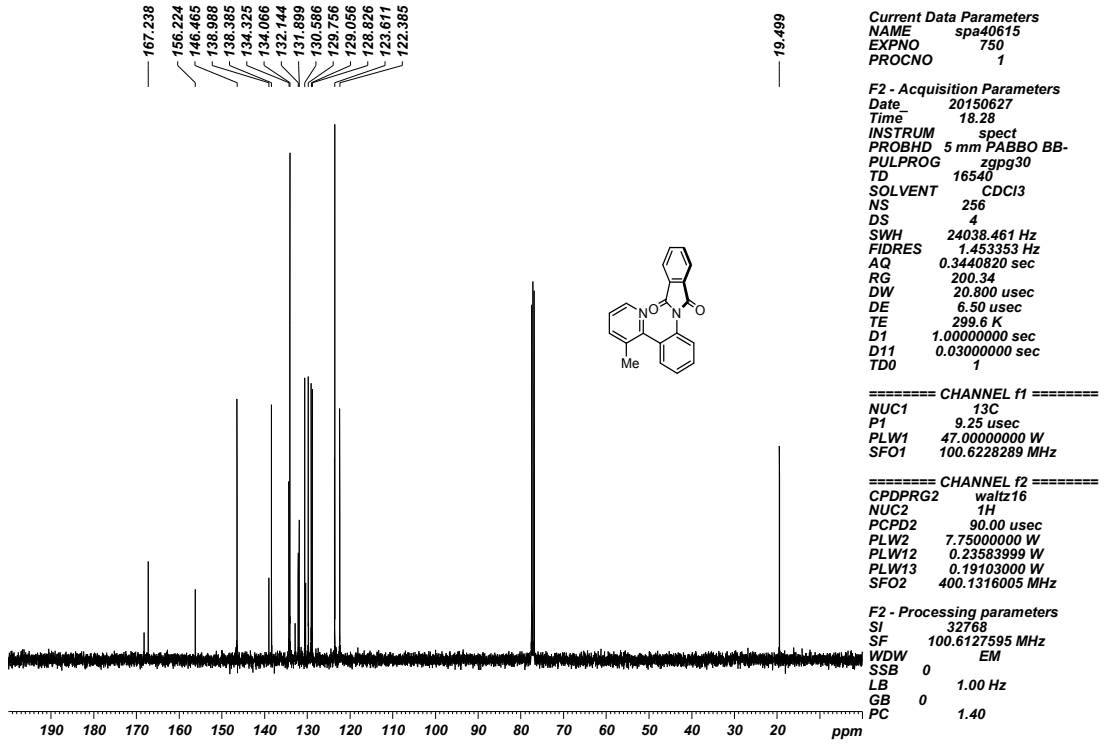


## 2-(2-(3-Methylpyridin-2-yl)phenyl)isoindoline-1,3-dione (4l)

### $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

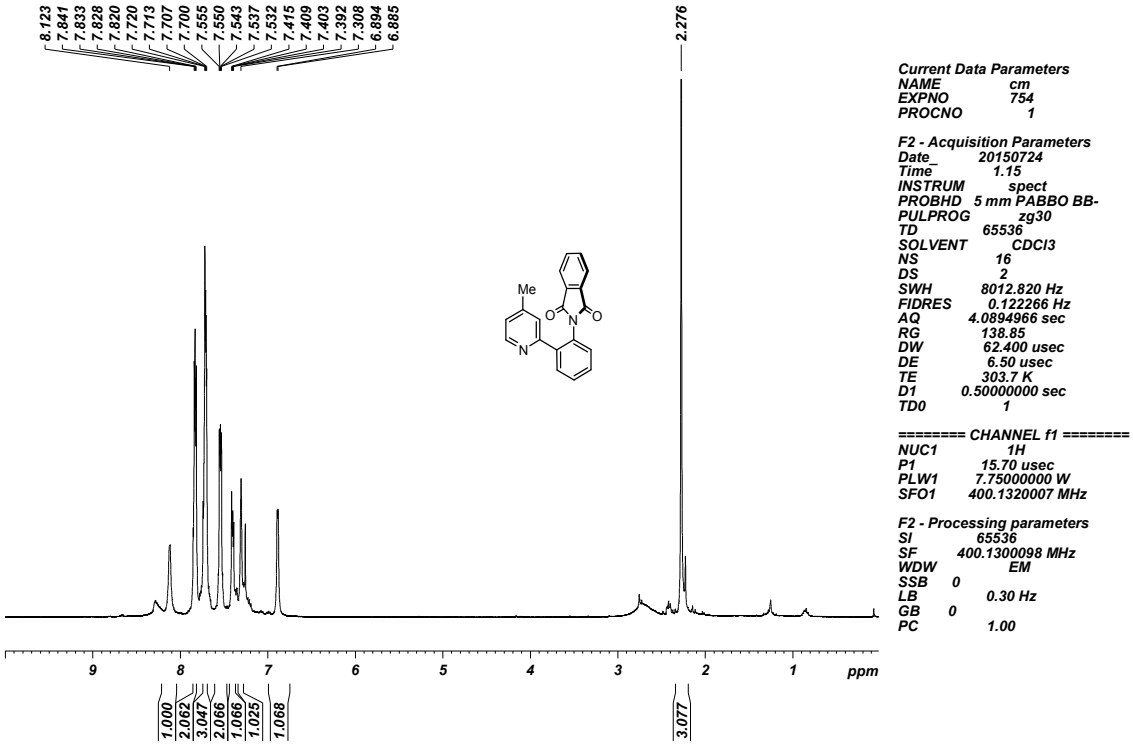



### $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

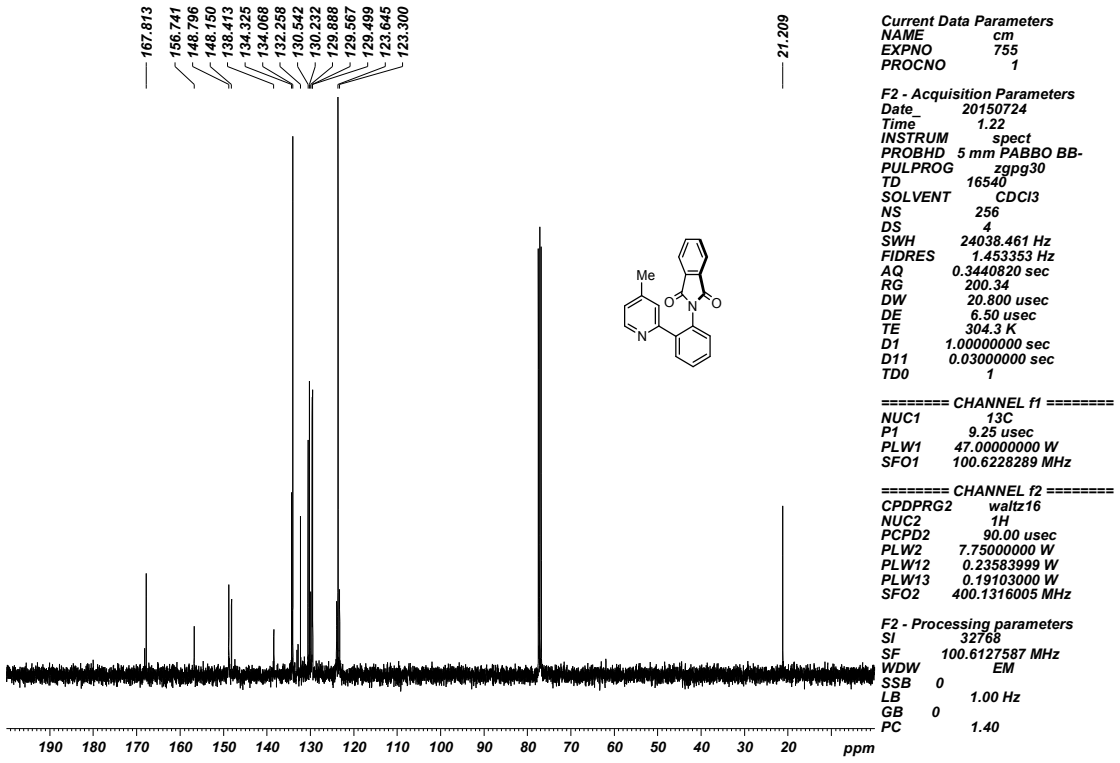


## 2-(2-(4-Methylpyridin-2-yl)phenyl)isoindoline-1,3-dione (4m)

### $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

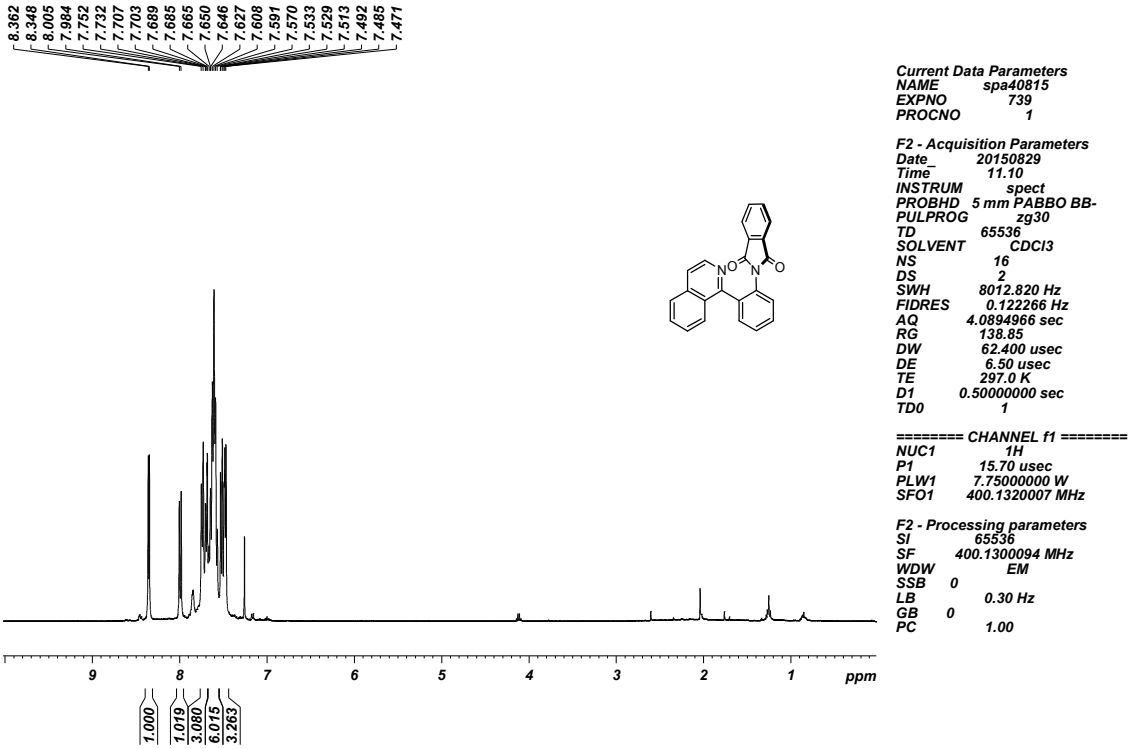



### $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

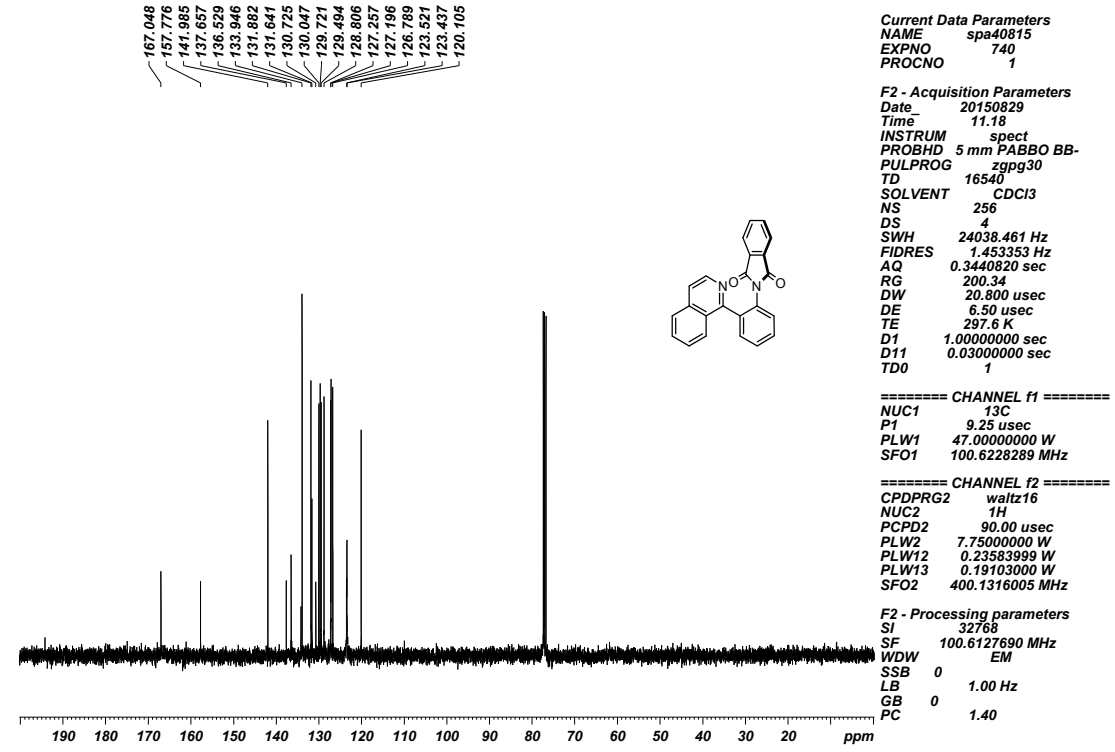


## 2-(2-(Isoquinolin-1-yl)phenyl)isoindoline-1,3-dione (4n)

### $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

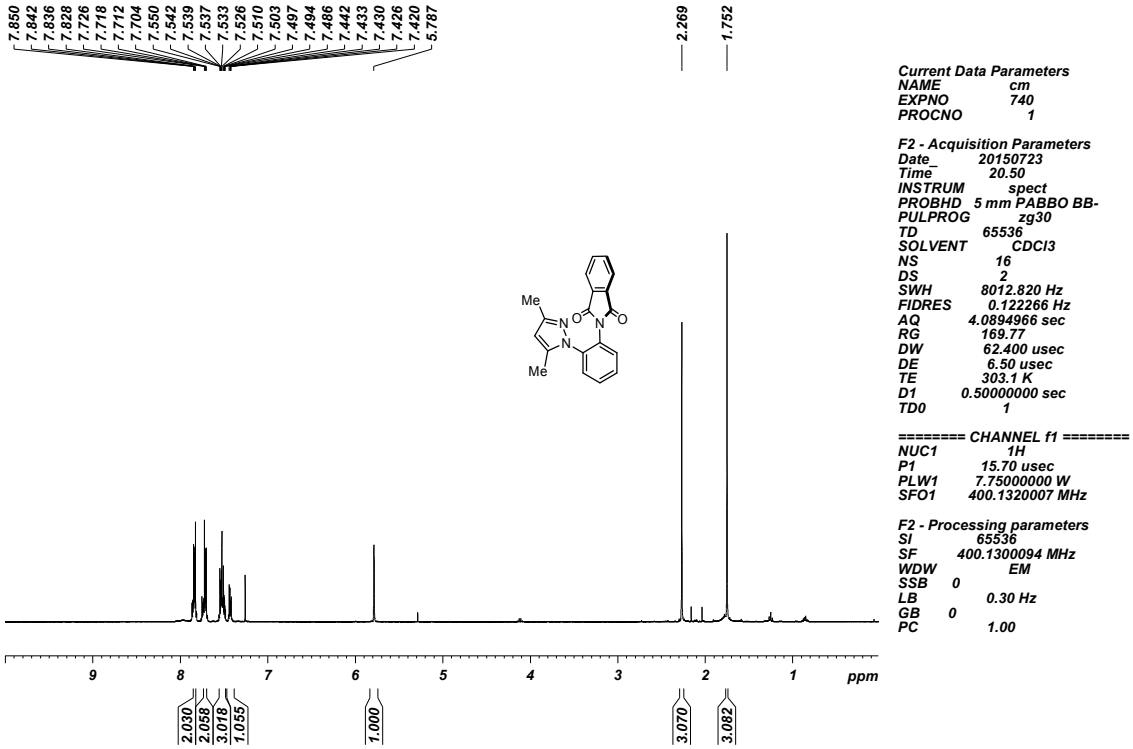



### $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

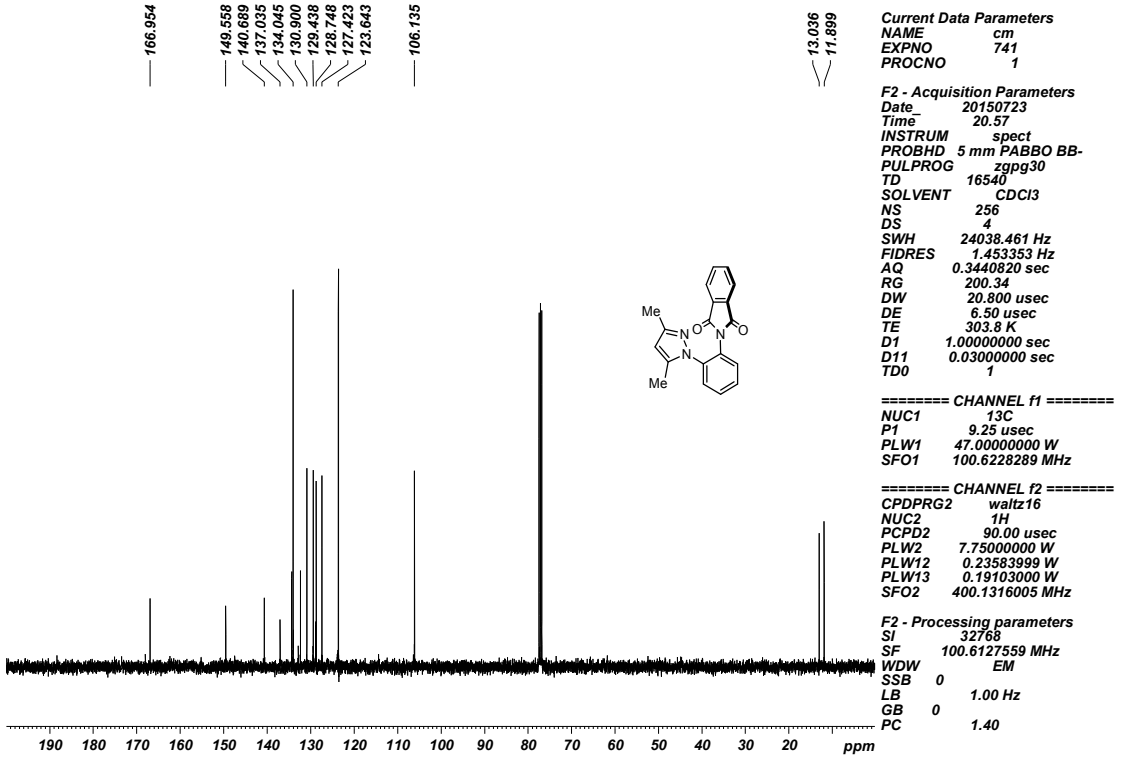


## 2-(2-(3,5-Dimethyl-1*H*-pyrazol-1-yl)phenyl)isoindoline-1,3-dione (4o)

### $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

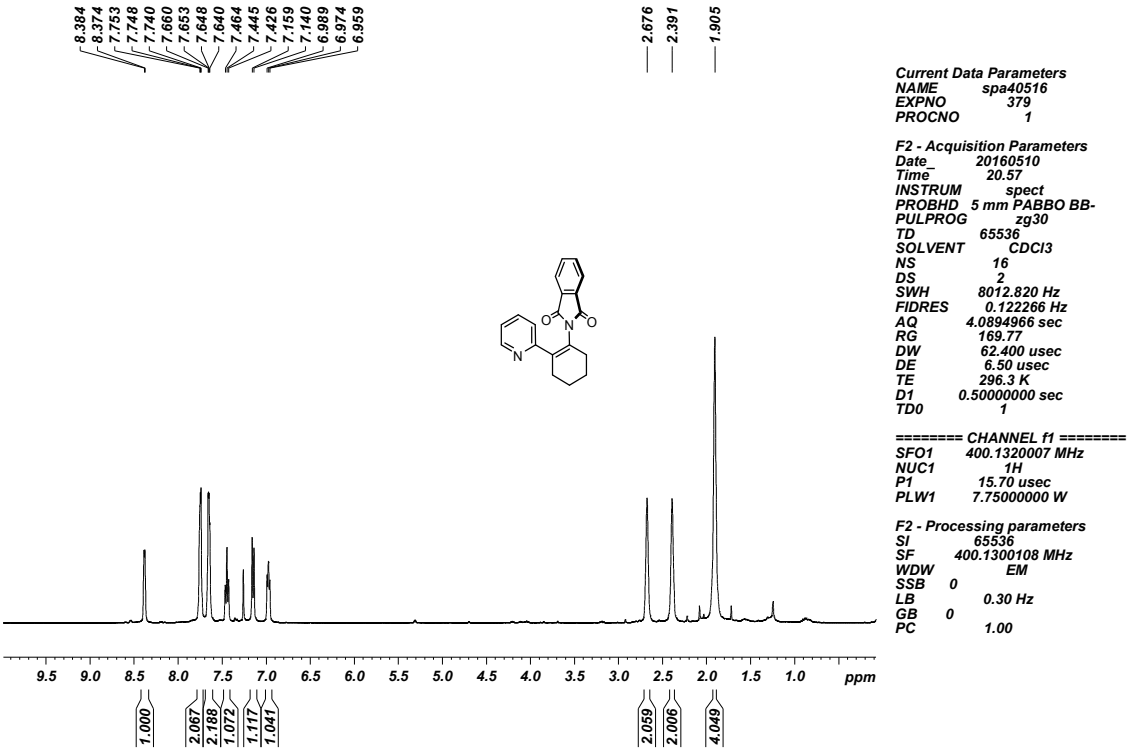



### $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

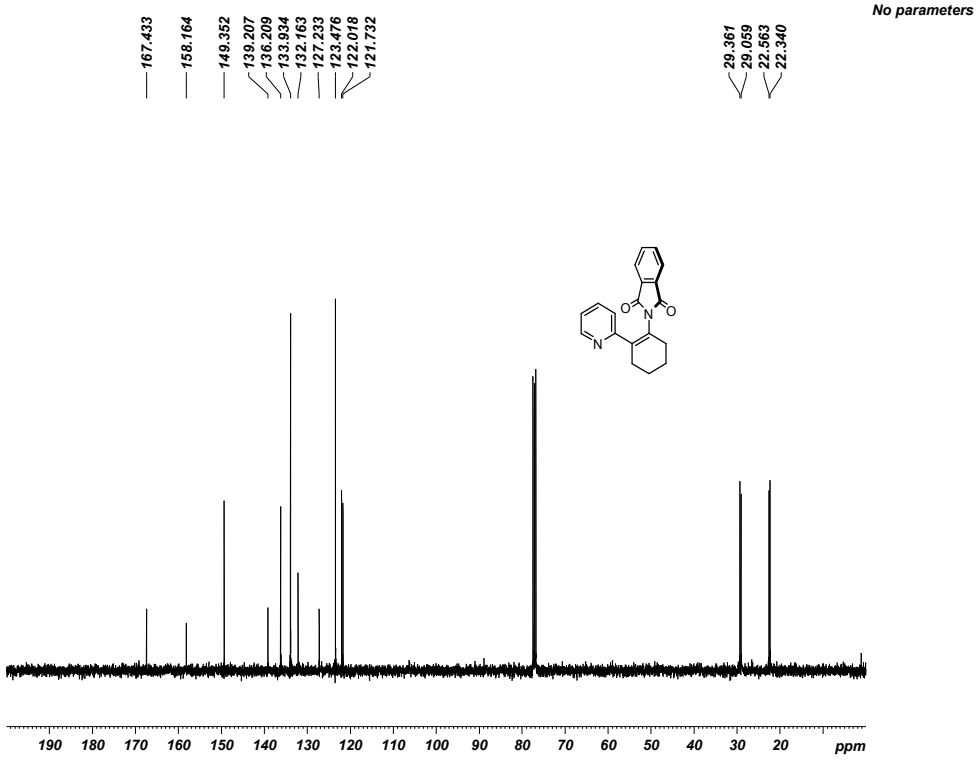


## 2-(6-(Pyridin-2-yl)cyclohex-1-en-1-yl)isoindoline-1,3-dione (4p)

### $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

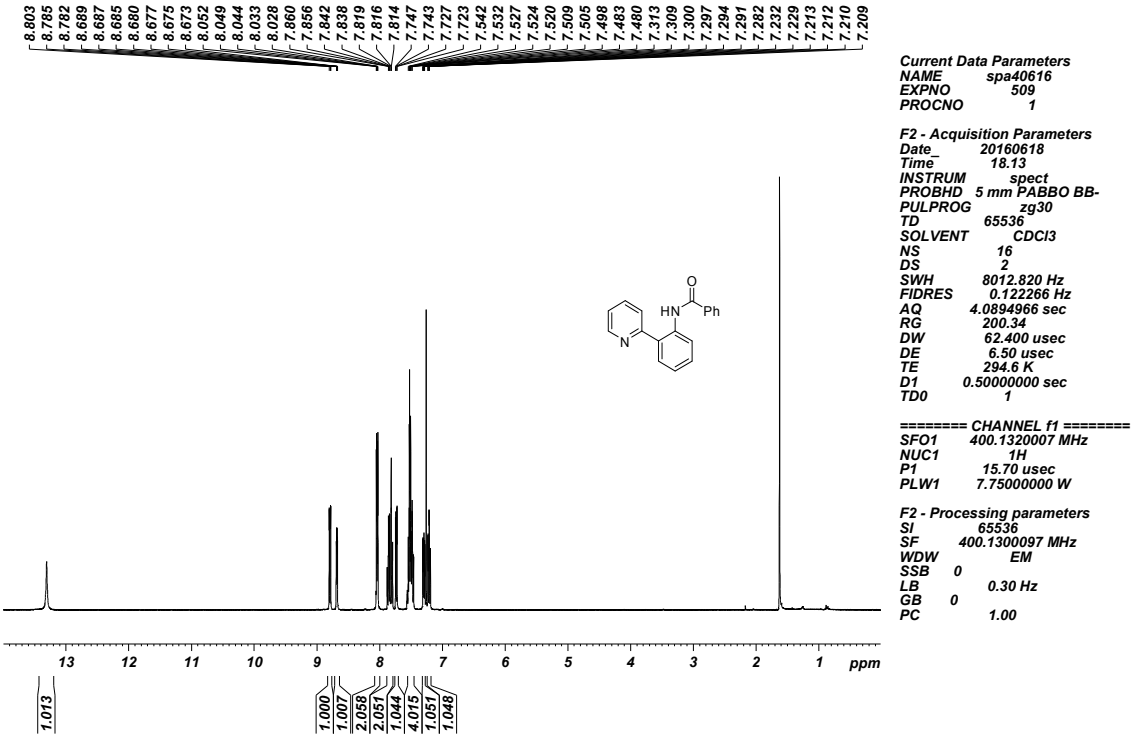



### $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

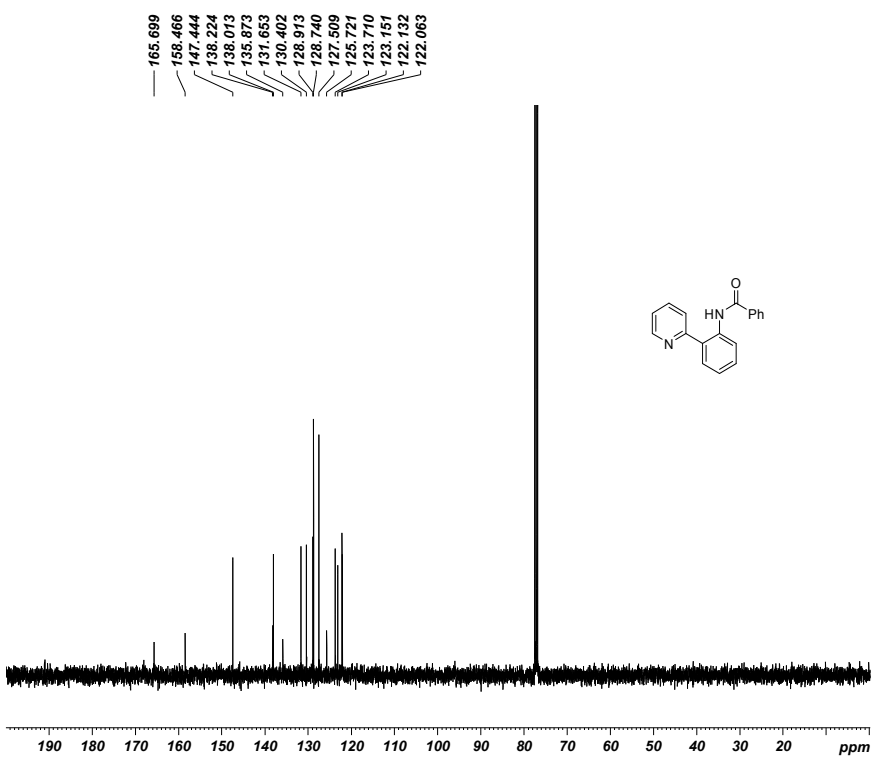


## 2-(6-(Pyridin-2-yl)cyclohex-1-en-1-yl)isoindoline-1,3-dione (7)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

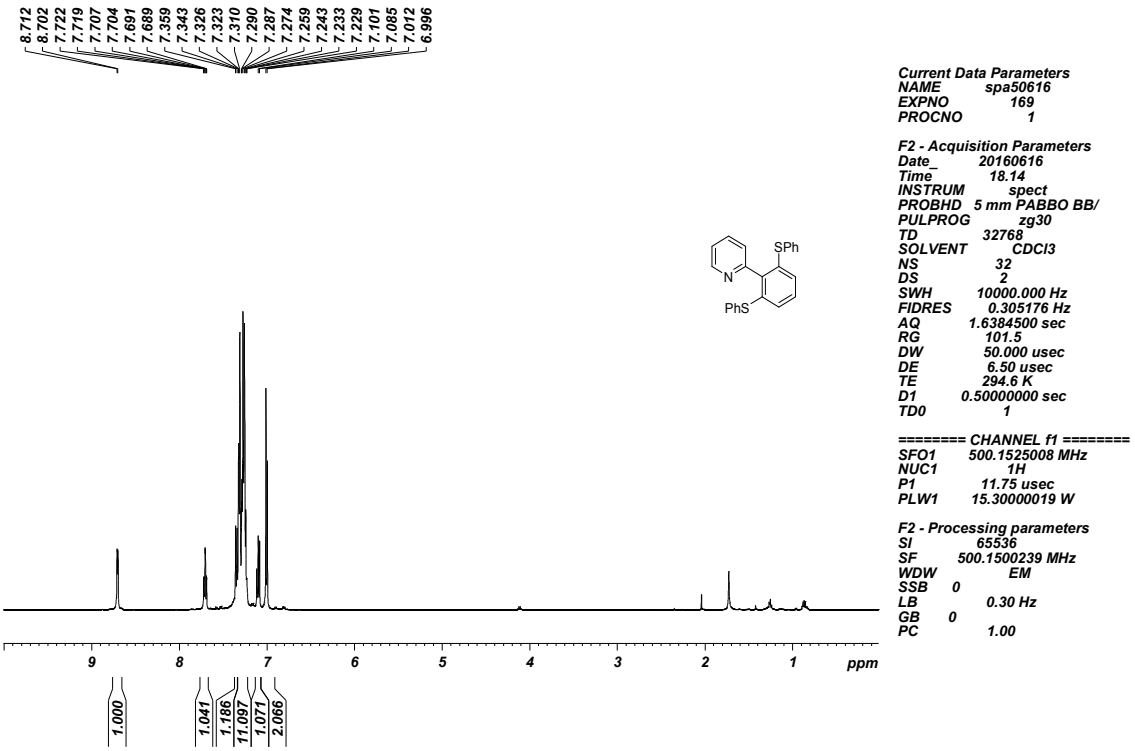



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

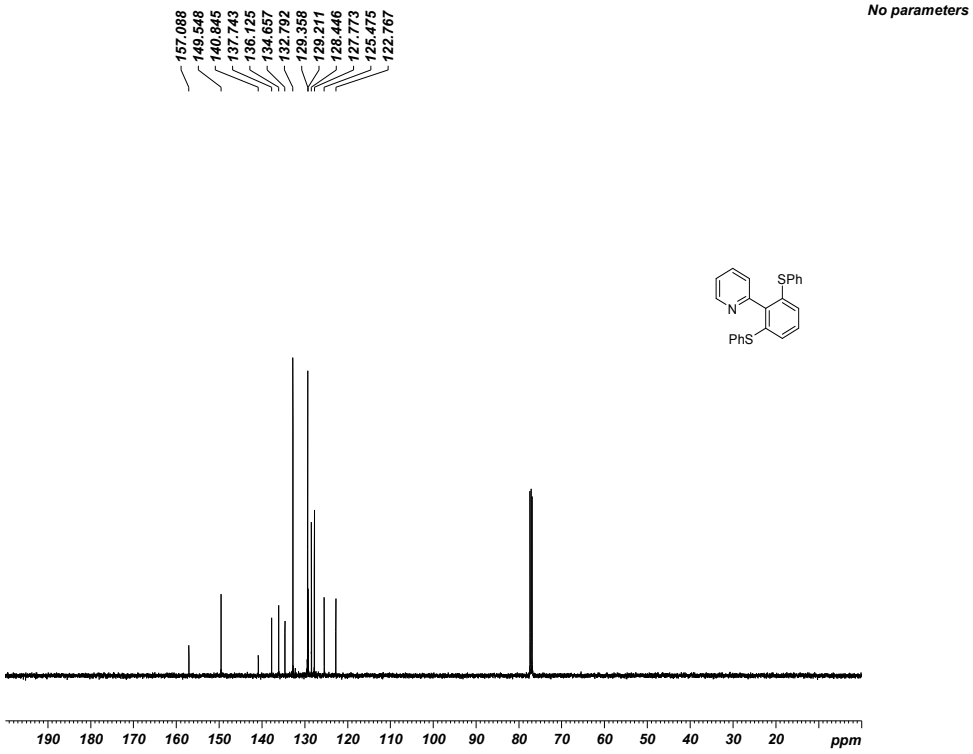


## 2-(2,6-Bis(phenylthio)phenyl)pyridine (3')

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

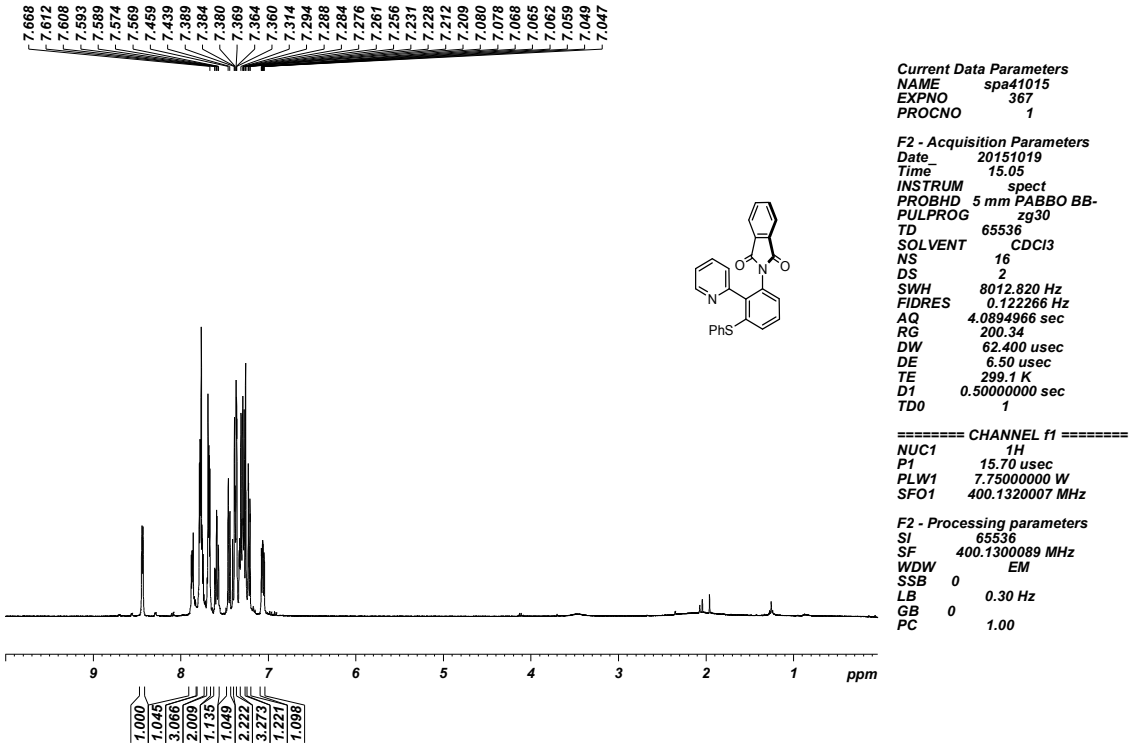



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

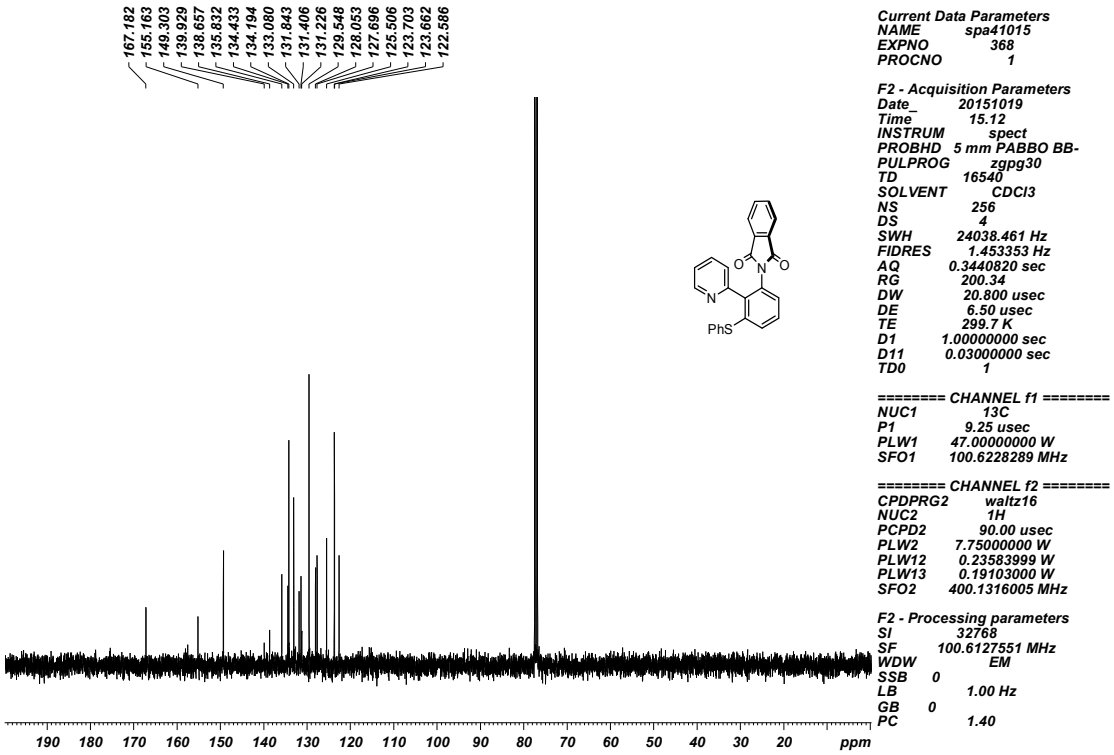


## 2-(3-(Phenylthio)-2-(pyridin-2-yl)phenyl)isoindoline-1,3-dione (8)

### $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

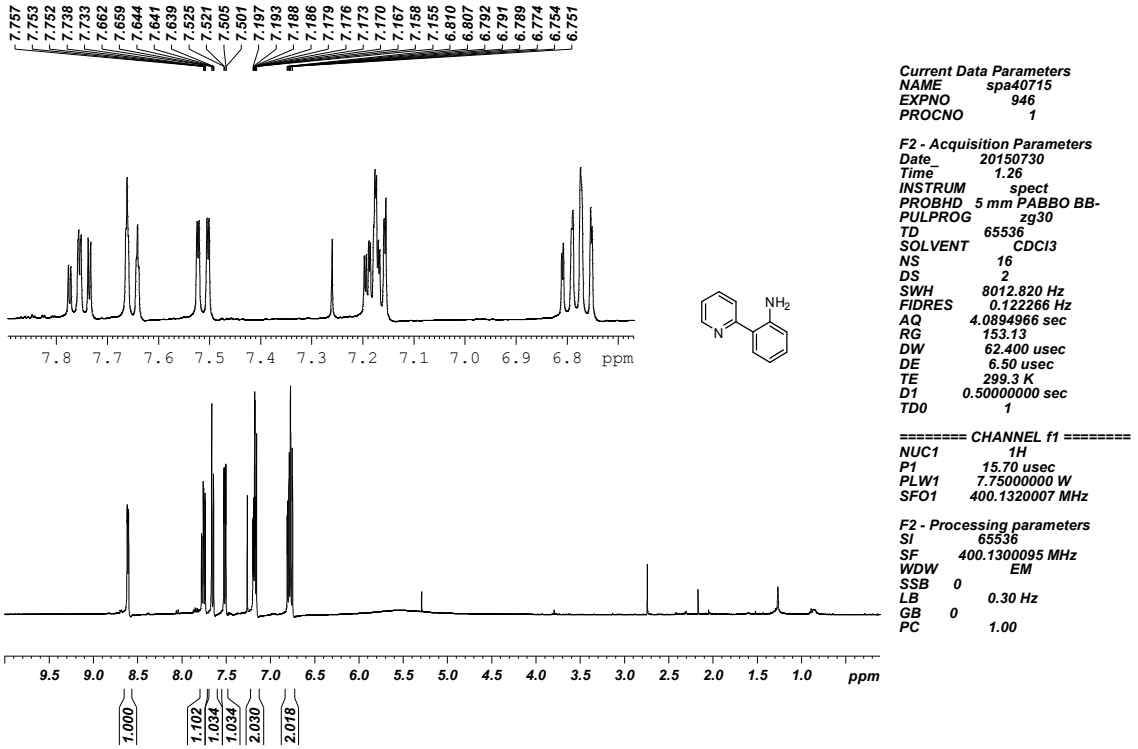



### $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)



## 2-(Pyridin-2-yl)aniline (9a)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)



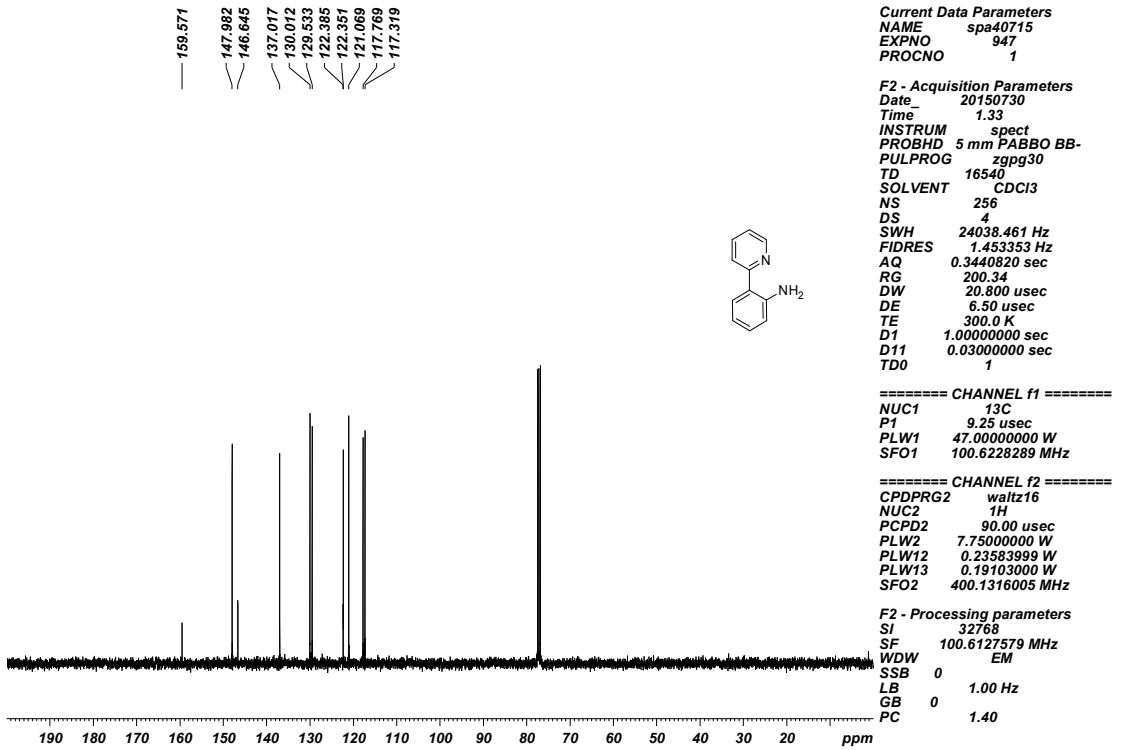

*Current Data Parameters*
*NAME spa40715*
*EXPNO 946*
*PROCNO 1*

*F2 - Acquisition Parameters*
*Date_ 20150730*
*Time 1.26*
*INSTRUM spect*
*PROBHD 5 mm PABBO BB-*
*PULPROG zg30*
*TD 65536*
*SOLVENT CDCl3*
*NS 16*
*DS 2*
*SWH 8012.820 Hz*
*FIDRES 0.122266 Hz*
*AQ 4.0894966 sec*
*RG 153.13*
*DW 62.400 usec*
*DE 6.50 usec*
*TE 299.3 K*
*D1 0.50000000 sec*
*TD0 1*

*======== CHANNEL f1 ========*
*NUC1 1H*
*P1 15.70 usec*
*PLW1 7.75000000 W*
*SFO1 400.1320007 MHz*

*F2 - Processing parameters*
*SI 65536*
*SF 400.1300095 MHz*
*WDW EM*
*SSB 0*
*LB 0.30 Hz*
*GB 0*
*PC 1.00*

## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)




*Current Data Parameters*
*NAME spa40715*
*EXPNO 947*
*PROCNO 1*

*F2 - Acquisition Parameters*
*Date_ 20150730*
*Time 1.33*
*INSTRUM spect*
*PROBHD 5 mm PABBO BB-*
*PULPROG zgpg30*
*TD 16540*
*SOLVENT CDCl3*
*NS 256*
*DS 4*
*SWH 24038.461 Hz*
*FIDRES 1.453353 Hz*
*AQ 0.3440820 sec*
*RG 200.34*
*DW 20.800 usec*
*DE 6.50 usec*
*TE 300.0 K*
*D1 1.00000000 sec*
*D11 0.03000000 sec*
*TD0 1*

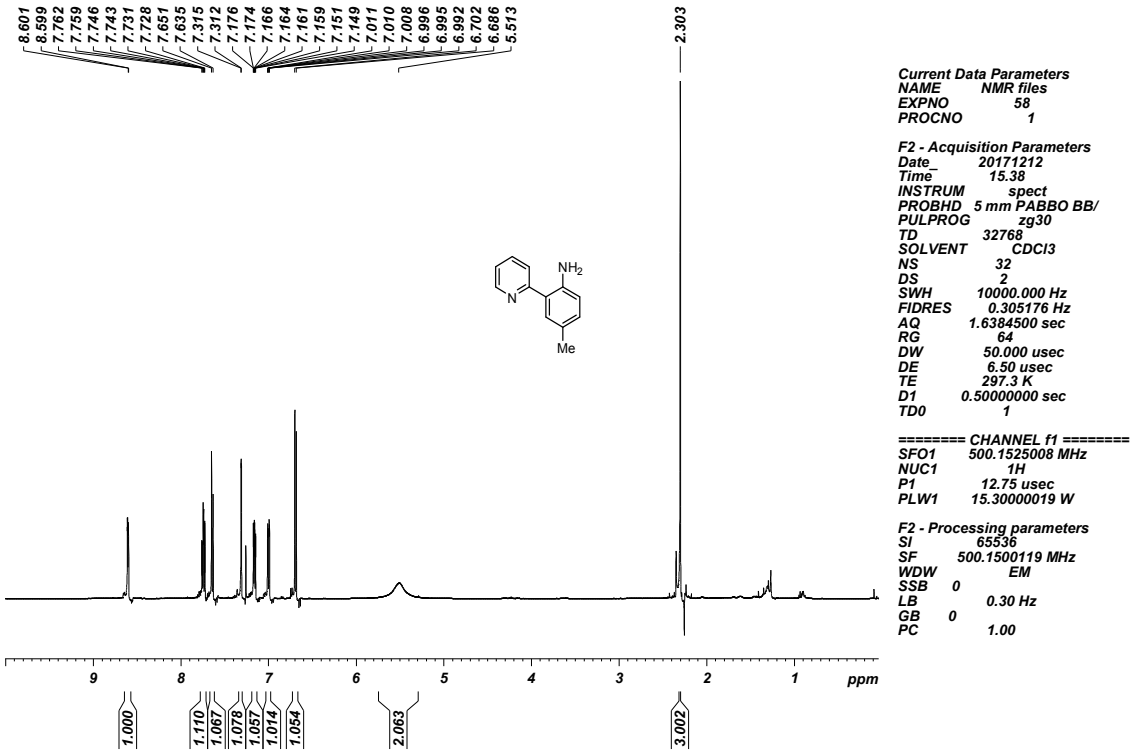
*======== CHANNEL f1 ========*
*NUC1 13C*
*P1 9.25 usec*
*PLW1 47.00000000 W*
*SFO1 100.6228289 MHz*

*======== CHANNEL f2 ========*
*CPDPRG2 waltz16*
*NUC2 1H*
*PCPD2 90.00 usec*
*PLW2 7.75000000 W*
*PLW12 0.23583999 W*
*PLW13 0.19103000 W*
*SFO2 400.1316005 MHz*

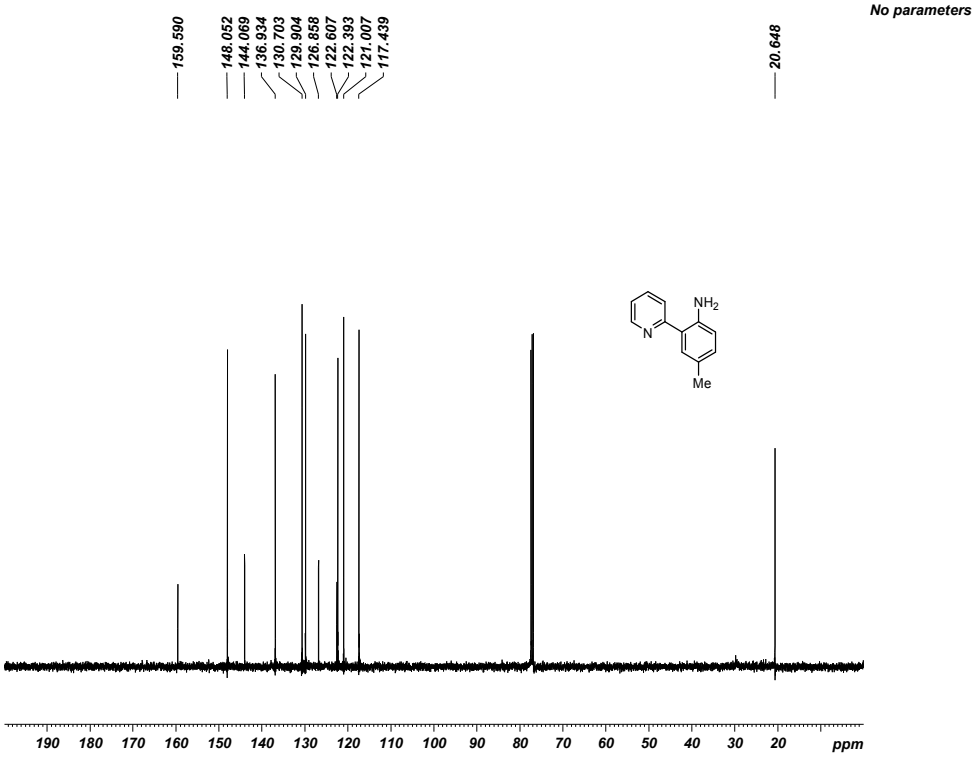
*F2 - Processing parameters*
*SI 32768*
*SF 100.6127579 MHz*
*WDW EM*
*SSB 0*
*LB 1.00 Hz*
*GB 0*
*PC 1.40*

**4-Methyl-2-(pyridin-2-yl)aniline (9b)**

**$^{1}$H NMR (500 MHz, $CDCl_3$, 24 °C)**

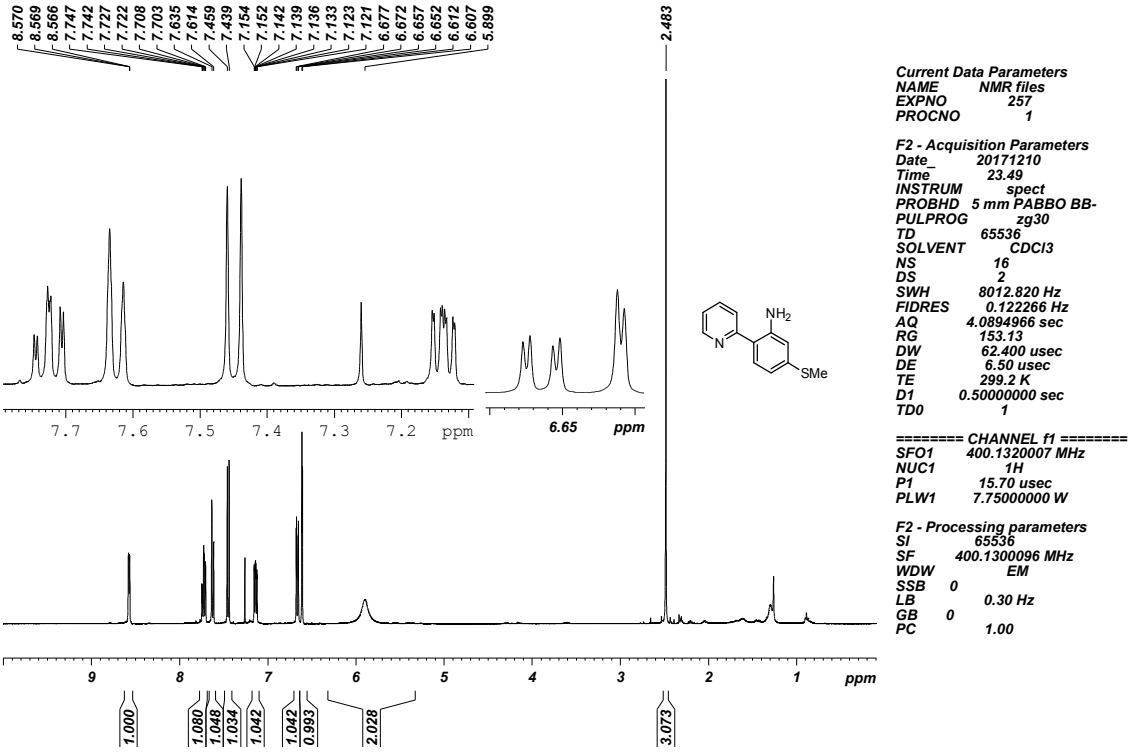



**$^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$, 24 °C)**

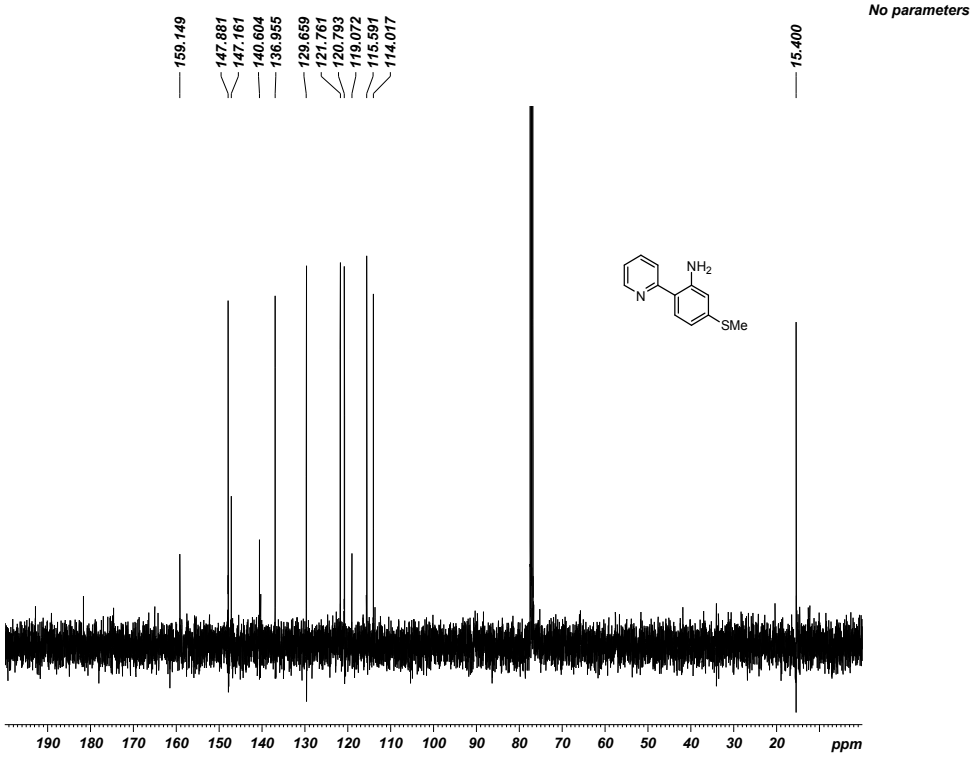


## 5-(Methylthio)-2-(pyridin-2-yl)aniline (9c)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

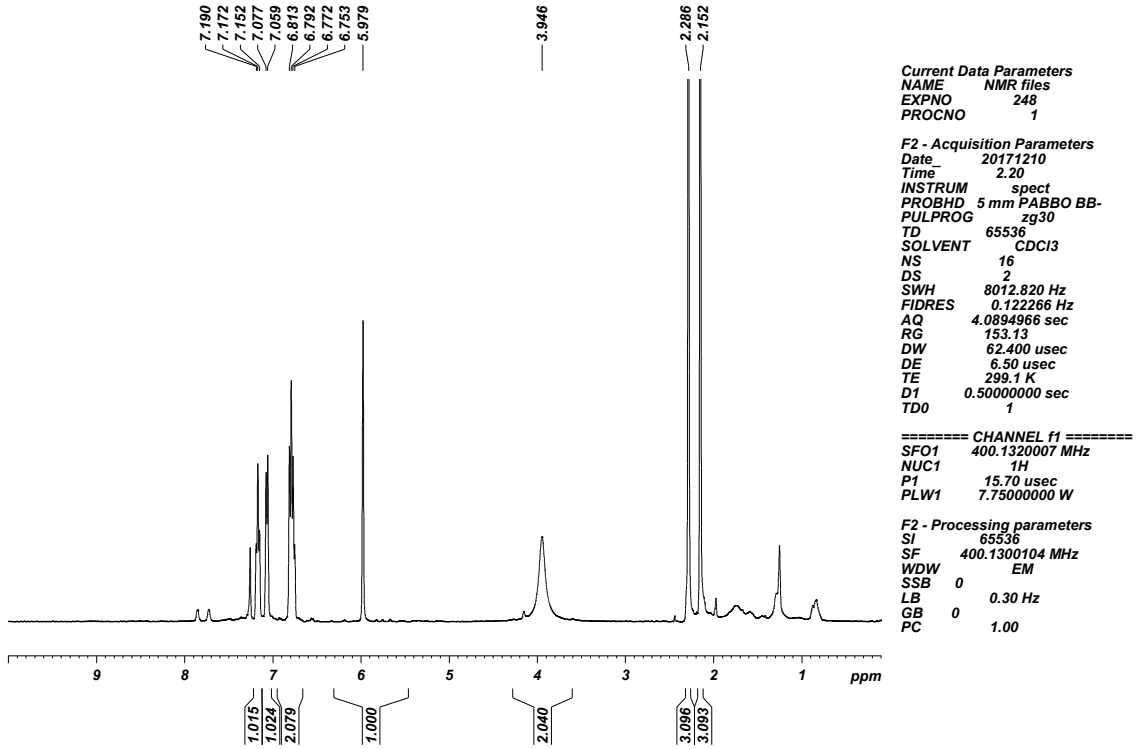



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)

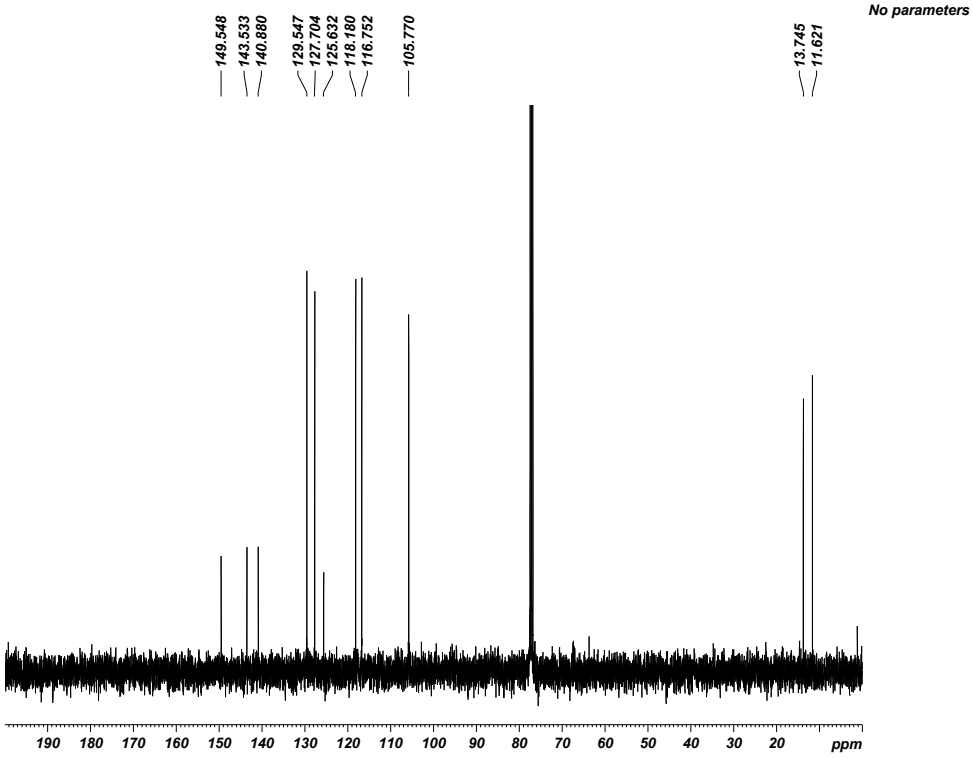


## 2-(2,4-Dimethyl-1*H*-imidazol-1-yl)aniline (9d)

## $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)

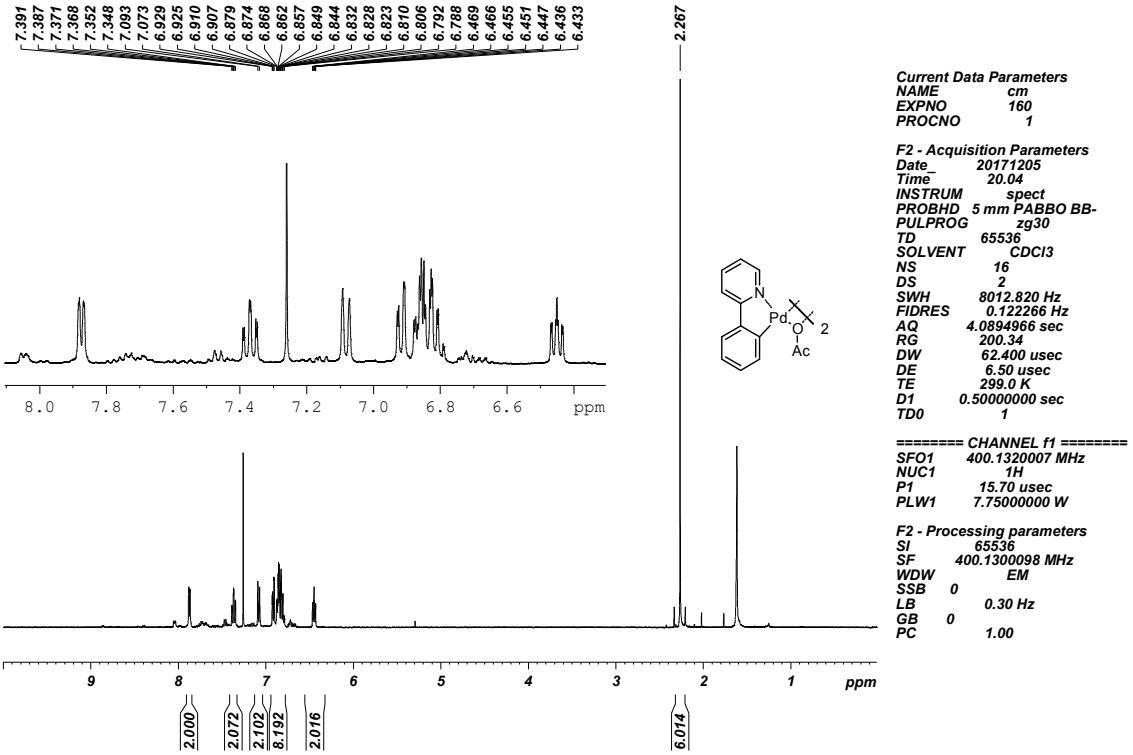



## $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)



## Palladacycle (A)

### $^{1}$H NMR (400 MHz, $CDCl_3$, 24 °C)




### $^{13}$C{$^{1}$H} NMR (100 MHz, $CDCl_3$, 24 °C)