Supporting Information

Regio- and stereoselective C–H alkenylation of pyridines with silyl-substituted alkynes by half-sandwich scandium catalyst

Wei Zhou,[a] Shuya Wang,[b] Masayoshi Nishiura,[a,c] Xuefeng Cong*,[b], Zhaomin Hou *,[a,c]

[a]*Advanced Catalysis Research Group, RIKEN Center for Sustainable Resource Science, Wako, Saitama, Japan.*

[b]*Institute of Molecular Plus, Haihe Laboratory of Sustainable Chemical Transformations, Tianjin University, Tianjin, China.*

[c]*Organometallic Chemistry Laboratory, RIKEN Cluster for Pioneering Research, Wako, Saitama, Japan.*

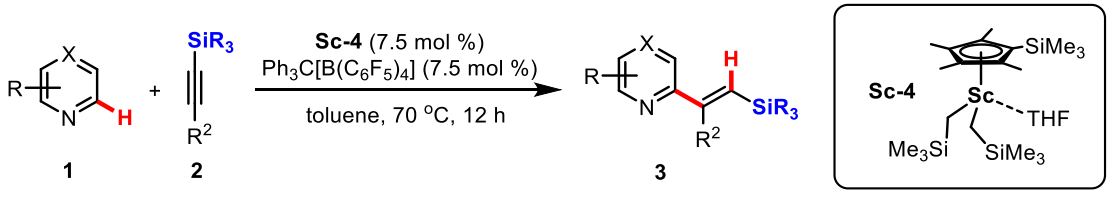
E-mail: xuefengcong@tju.edu.cn; houz@riken.jp

Table of Contents

I. General information

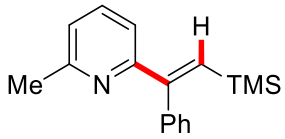
All manipulations of air- and moisture-sensitive compounds were performed under dry nitrogen atmosphere in an mBRAUN Labmaster glovebox. Nitrogen was purified by being passed through a dry column (4 Å molecular sieves, Nikka Seiko Co.) and a Gasclean GC-XR column (Nikka Seiko Co.). The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer (Mbraun) to ensure both were always below 0.1 ppm. Solvents (THF, Hexane and Toluene) (dehydrated, stabilizer-free) were obtained from Kanto Kagaku Co., purified by an mBRAUN SPS-800 solvent purification system, and dried over fresh Na chips in a glovebox. The commercially available alkynes and pyridines were obtained from Tokyo Chemical Industry Co., Ltd., dried with CaH_2 before use. Other silylated alkynes were prepared from corresponding literatures.[1] Half-sandwich complexes **Sc-1**~**Sc-4**, **Y-4** and **Lu-4** were also prepared according to the literature procedure.[2] Silica gel column chromatography was performed with Silica Gel 60 N (spherical, neutral, 40-50 μm) obtained from Kanato Chemical Co. All ^{1}H NMR and ^{13}C NMR spectra of organic products were recorded on Bruker AVANCE III HD 500 NMR (500 MHz) instrument. The ^{1}H NMR Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as standard. The ^{13}C NMR chemical shifts were given using $CDCl_3$ (77.16 ppm) as the internal standard. The data are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, coupling constant(s) in Hz, integration). High Resolution Mass Spectra were obtained on a Bruker microTOF-Q III (ESI^+).

II. General procedure for the Sc-catalyzed alkenylation of pyridines with silylated alkynes



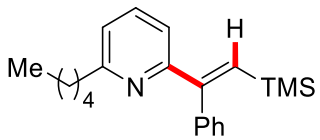
In a glovebox, $[Ph_3C][B(C_6F_5)_4]$ (13.8 mg, 0.015 mmol in 0.5 mL toluene) was added to a stirred toluene solution (1.5 mL) of **Sc-4** (7.2 mg, 0.015 mmol) in a Schlenk tube. After 10 min, to this tube was added pyridines **1** (0.2 mmol) and alkynes **2** (0.4 mmol). After that, the tube was sealed, taken outside, and stirred at 70 °C for 12 h. Then, the mixture was concentrated and purified by silica gel column chromatography (hexane/ethyl acetate = 4:1) to obtain the desired product **3**. The E/Z ratio (>19:1) and regioisomeric ratio (r.r.) (>19:1) were determined by NMR analysis of the crude reaction mixture.

III. Analytic data for synthesized compounds



(*E*)-2-Methyl-6-(1-phenyl-2-(trimethylsilyl)vinyl)pyridine (3a)

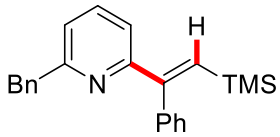
The title compound was prepared according to the general procedure as a white solid (52.5 mg, 98% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40–7.33 (m, 4H), 7.27 (s, 1H), 7.27–7.23 (m, 2H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 2.61 (s, 3H), -0.11 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.91, 157.03, 155.26, 141.56, 136.48, 132.68, 129.80, 127.98, 127.32, 121.86, 119.37, 24.82, -0.16; HRMS (ESI) m/z calcd. for $C_{17}H_{22}NSi$ $[M+H]^+$ = 268.1516, found = 268.1518.



(*E*)-2-Butyl-6-(1-phenyl-2-(trimethylsilyl)vinyl)pyridine (3b)

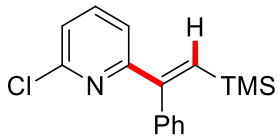
The title compound was prepared according to the general procedure as a white solid (55.6 mg, 86% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41–7.34 (m, 4H), 7.26–7.24 (m, 3H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 2.84 (t, *J* = 7.5 Hz, 2H), 1.82–1.76 (m, 2H), 1.40–1.38 (m, 4H), 0.92 (d, *J* = 7.0 Hz, 3H), -0.11 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.93, 156.96, 155.39, 141.67, 136.38, 132.62, 129.82,

127.95, 127.28, 121.18, 119.46, 38.49, 31.67, 29.29, 22.56, 14.05, -0.14; HRMS (ESI) m/z calcd. for $C_{21}H_{30}NSi$ $[M+H]^+$ = 324.2142, found = 324.2147.



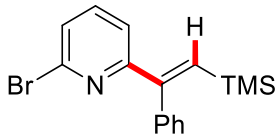
(*E*)-2-Benzyl-6-(1-phenyl-2-(trimethylsilyl)vinyl)pyridine (3c)

The title compound was prepared according to the general procedure as a white solid (66.4 mg, 94% yield) ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–7.34 (m, 4H), 7.32–7.30 (m, 5H), 7.25–7.21 (m, 3H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 4.22 (s, 3H), -0.10 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.40, 157.08, 155.21, 141.54, 139.62, 136.71, 133.03, 129.81, 129.35, 128.47, 127.98, 127.33, 126.28, 121.47, 119.71, 44.94, -0.15; HRMS (ESI) m/z calcd. for $C_{23}H_{26}NSi$ $[M+H]^+$ = 344.1829, found = 344.1832.



(*E*)-2-Chloro-6-(1-phenyl-2-(trimethylsilyl)vinyl)pyridine (3d)

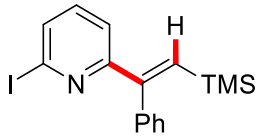
The title compound was prepared according to the general procedure as a white solid (54.0 mg, 94% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47–7.44 (m, 1H), 7.41–7.36 (m, 3H), 7.32 (s, 1H), 7.23–7.21 (m, 2H), 7.15 (d, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 7.5 Hz, 1H), – 0.1 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.45, 153.14, 151.02, 140.64, 138.95, 135.16, 129.72, 128.19, 127.63, 122.55, 120.49, -0.31; HRMS (ESI) m/z calcd. for $C_{16}H_{19}ClNSi$ $[M+H]^+$ = 288.0970, found = 288.0968.



(*E*)-2-Bromo-6-(1-phenyl-2-(trimethylsilyl)vinyl)pyridine (3e)

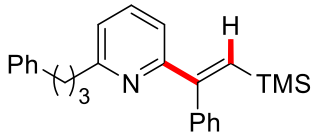
The title compound was prepared according to the general procedure as a white solid (60.2 mg, 91% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40–7.35 (m, 3H), 7.34–7.29 (m, 3H), 7.22–7.20 (m, 2H), 6.79 (d, *J* = 7.5 Hz, 1H), -0.12 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.00, 153.01, 141.93, 140.55, 138.64, 135.31, 129.71, 128.20,

127.64, 126.31, 120.81, -0.31; HRMS (ESI) m/z calcd. for $C_{16}H_{19}BrNSi$ $[M+H]^+$ = 332.0465, found = 332.0466.



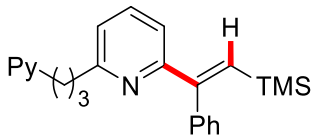
(*E*)-2-Iodo-6-(1-phenyl-2-(trimethylsilyl)vinyl)pyridine (3f)

The title compound was prepared according to the general procedure as a white solid (72.8 mg, 96% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.40–7.36 (m, 3H), 7.30 (s, 1H), 7.22–7.20 (m, 2H), 7.12–7.09 (m, 1H), 6.79 (d, *J* = 7.5 Hz, 1H), -0.11 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.56, 153.09, 140.48, 137.69, 135.20, 133.09, 129.71, 128.20, 127.62, 121.17, 118.27, -0.29; HRMS (ESI) m/z calcd. for $C_{16}H_{19}INSi$ $[M+H]^+$ = 380.0326, found = 380.0331.



(*E*)-2-(1-Phenyl-2-(trimethylsilyl)vinyl)-6-(3-phenylpropyl)pyridine (3g)

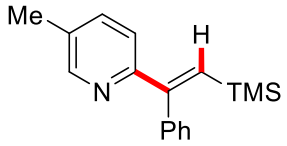
The title compound was prepared according to the general procedure as a white solid (69.0 mg, 93% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42–7.34 (m, 4H), 7.31–7.28 (m, 3H), 7.25–7.23 (m, 4H), 7.20–7.17 (m, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 7.5 Hz, 1H), 2.88 (t, *J* = 7.5 Hz, 2H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.17–2.11 (m, 2H), 0.92 (d, *J* = 7.0 Hz, 3H), -0.10 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.27, 157.07, 155.37, 142.37, 141.63, 136.45, 132.73, 129.81, 128.54, 128.27, 127.96, 127.30, 125.70, 121.31, 119.57, 37.81, 35.47, 31.04, -0.14; HRMS (ESI) m/z calcd. for $C_{25}H_{30}NSi$ $[M+H]^+$ = 372.2142, found = 372.2145.



(*E*)-2-(1-Phenyl-2-(trimethylsilyl)vinyl)-6-(3-(pyridin-2-yl)propyl)pyridine (3h)

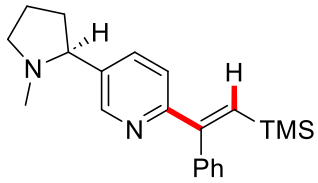
The title compound was prepared according to the general procedure as a white solid (58.8 mg, 79% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.53 (d, *J* = 4.5 Hz, 1H), 7.61–

7.57 (m, 1H), 7.42–7.34 (m, 4H), 7.27–7.23 (m, 3H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.12–7.09 (m, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 7.5 Hz, 1H), 2.92–2.89 (m, 4H), 2.27–2.21 (m, 2H), -0.10 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.95, 161.13, 157.03, 155.34, 149.18, 141.61, 136.48, 136.23, 132.67, 129.79, 127.94, 127.27, 122.95, 121.34, 120.95, 119.59, 37.85, 37.80, 29.51, -0.16; HRMS (ESI) m/z calcd. for $C_{24}H_{29}N_2Si$ $[M+H]^+$ = 373.2095, found = 373.2091.



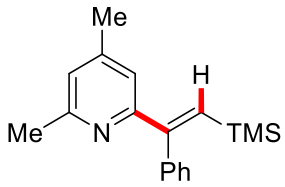
(*E*)-5-Methyl-2-(1-phenyl-2-(trimethylsilyl)vinyl)pyridine (3i)

The title compound was prepared according to the general procedure as a white solid (44.9 mg, 84% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.46 (s, 1H), 7.39–7.31 (m, 4H), 7.24–7.22 (m, 2H), 7.09 (s, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 2.31 (s, 3H), -0.11 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.63, 155.14, 149.68, 141.60, 136.73, 132.01, 131.71, 129.73, 128.00, 127.35, 121.76, 18.11, -0.20; HRMS (ESI) m/z calcd. for $C_{17}H_{22}NSi$ $[M+H]^+$ = 268.1516, found = 268.1518.



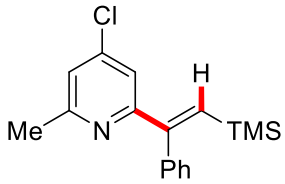
(*S*,*E*)-5-(1-Methylpyrrolidin-2-yl)-2-(1-phenyl-2-(trimethylsilyl)vinyl)pyridine (3j)

The title compound was prepared according to the general procedure as a white solid (49.7 mg, 74% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.55 (s, 1H), 7.54–7.52 (m, 1H), 7.40–7.34 (m, 3H), 7.25–7.24 (m, 2H), 7.16 (s, 2H), 6.92 (d, *J* = 8.0 Hz, 1H), 3.22 (t, *J* = 9.0 Hz, 1H), 3.08 (t, *J* = 8.0 Hz, 1H), 2.32–2.26 (m, 1H), 2.21–2.14 (m, 4H), 1.99–1.90 (m, 1H), 1.84–1.77 (m, 1H), 1.74–1.66 (m, 1H), -0.11 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.14, 155.08, 149.05, 141.48, 137.23, 135.16, 132.65, 129.73, 128.03, 127.39, 122.14, 68.65, 56.97, 40.31, 35.11, 22.51, -0.23; HRMS (ESI) m/z calcd. for $C_{21}H_{29}N_2Si$ $[M+H]^+$ = 337.2095, found = 337.2032.



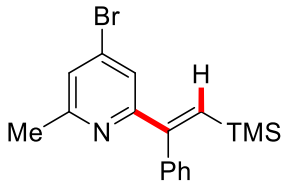
(*E*)-2,4-Dimethyl-6-(1-phenyl-2-(trimethylsilyl)vinyl)pyridine (3k)

The title compound was prepared according to the general procedure as a white solid (50.6 mg, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39–7.33 (m, 3H), 7.26–7.22 (m, 3H), 6.84 (s, 1H), 6.50 (s, 1H), 2.56 (s, 3H), 2.15 (s, 3H), -0.11 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.68, 157.11, 155.41, 147.42, 141.67, 132.67, 129.80, 127.93, 127.26, 122.84, 120.48, 24.57, 20.88, -0.16; HRMS (ESI) m/z calcd. for $C_{18}H_{24}NSi$ $[M+H]^+$ = 282.1673, found = 282.1677.



(*E*)-4-Chloro-2-methyl-6-(1-phenyl-2-(trimethylsilyl)vinyl)pyridine (3l)

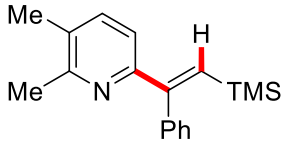
The title compound was prepared according to the general procedure as a white solid (57.2 mg, 95% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41–7.37 (m, 3H), 7.29 (s, 1H), 7.23–7.21 (m, 2H), 7.03 (s, 1H), 6.68 (s, 1H), 2.58 (s, 3H), -0.11 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.22, 158.67, 154.10, 144.38, 140.72, 134.75, 129.73, 128.19, 127.64, 121.78, 119.64, 24.60, -0.27; HRMS (ESI) m/z calcd. for $C_{17}H_{21}NClSi$ $[M+H]^+$ = 302.1126, found = 302.1128.



(*E*)-4-Bromo-2-methyl-6-(1-phenyl-2-(trimethylsilyl)vinyl)pyridine (3m)

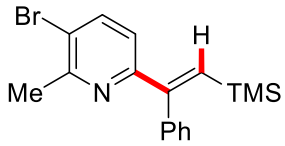
The title compound was prepared according to the general procedure as a white solid (66.2 mg, 96% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41–7.37 (m, 3H), 7.27 (s, 1H), 7.23–7.20 (m, 3H), 6.84 (s, 1H), 2.58 (s, 3H), -0.11 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.11, 158.54, 154.02, 140.68, 134.88, 133.28, 129.72, 128.19, 127.65,

124.80, 122.53, 24.51, -0.27; HRMS (ESI) m/z calcd. for $C_{17}H_{21}NBrSi$ $[M+H]^+$ = 346.0621, found = 346.0625.



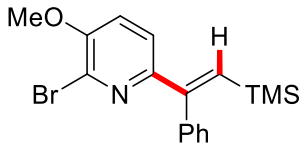
(*E*)-2,3-Dimethyl-6-(1-phenyl-2-(trimethylsilyl)vinyl)pyridine (3n)

The title compound was prepared according to the general procedure as a white solid (48.9 mg, 87% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32–7.38 (m, 3H), 7.25–7.19 (m, 4H), 6.60 (d, *J* = 8.0 Hz, 1H), 2.56 (s, 3H), 2.24 (s, 3H), -0.11 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.60, 155.22, 154.63, 141.71, 137.22, 131.32, 130.18, 129.79, 127.91, 127.22, 119.87, 23.07, 18.84, -0.13; HRMS (ESI) m/z calcd. for $C_{18}H_{24}NSi$ $[M+H]^+$ = 282.1673, found = 282.1677.



(*E*)-3-Bromo-2-methyl-6-(1-phenyl-2-(trimethylsilyl)vinyl)pyridine (3o)

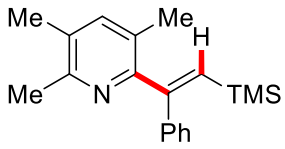
The title compound was prepared according to the general procedure as a white solid (55.2 mg, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.0 Hz, 1H), 7.39–7.35 (m, 3H), 7.25 (s, 1H), 7.22–7.21 (m, 2H), 6.57 (d, *J* = 8.0 Hz, 1H), 2.71 (s, 3H), -0.11 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.51, 155.87, 154.18, 141.05, 139.86, 133.70, 129.70, 128.11, 127.53, 121.02, 120.13, 25.31, -0.26; HRMS (ESI) m/z calcd. for $C_{17}H_{21}NBrSi$ $[M+H]^+$ = 346.0621, found = 346.0625.



(*E*)-2-Bromo-3-methoxy-6-(1-phenyl-2-(trimethylsilyl)vinyl)pyridine (3p)

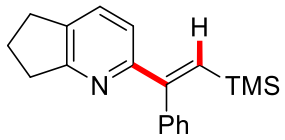
The title compound was prepared according to the general procedure as a white solid (57.8 mg, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39–7.34 (m, 3H), 7.21–7.20 (m, 1H), 7.14 (s, 1H), 6.91 (d, *J* = 8.5 Hz, 1H), 6.74 (d, *J* = 7.5 Hz, 1H), 3.86 (s, 3H), -0.13 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.59, 151.61, 150.72, 140.99, 132.40,

132.25, 129.69, 128.12, 127.50, 121.86, 118.23, 56.27, -0.22; HRMS (ESI) m/z calcd. for $C_{17}H_{21}NOBrSi$ $[M+H]^+$ = 362.0570, found = 362.0571.



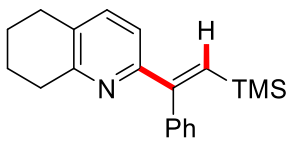
(*E*)-2,3,5-Trimethyl-6-(1-phenyl-2-(trimethylsilyl)vinyl)pyridine (3q)

The title compound was prepared according to the general procedure as a white solid (41.8 mg, 72% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.09–7.08 (m, 2H), 7.05–7.00 (m, 3H), 6.92 (s, 1H), 2.23 (s, 3H), 1.99 (s, 3H), 1.83 (s, 3H), -0.23 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.64, 156.94, 153.41, 142.04, 139.58, 133.81, 129.56, 128.77, 127.64, 127.35, 127.29, 22.19, 19.02, 18.65, -0.21; HRMS (ESI) m/z calcd. for $C_9H_{25}NSi$ $[M+H]^+$ = 295.1756, found = 295.1758.



(*E*)-2-(1-Phenyl-2-(trimethylsilyl)vinyl)-6,7-dihydro-5H-cyclopenta[b]pyridine (3r)

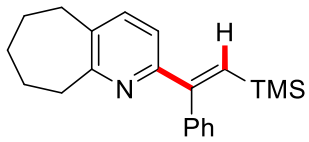
The title compound was prepared according to the general procedure as a white solid (53.1 mg, 91% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–7.34 (m, 3H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.25–7.23 (m, 2H), 7.19 (s, 1H), 3.06 (s, *J* = 7.5 Hz, 2H), 2.89 (s, *J* = 7.5 Hz, 2H), 2.18–2.10 (m, 2H), -0.11 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.59, 156.23, 155.42, 141.91, 135.79, 131.93, 131.46, 129.77, 127.94, 127.23, 120.11, 34.43, 30.42, 23.35, -0.13; HRMS (ESI) m/z calcd. for $C_{19}H_{23}NSi$ $[M+H]^+$ = 293.1600, found = 293.1601.



(*E*)-2-(1-Phenyl-2-(trimethylsilyl)vinyl)-5,6,7,8-tetrahydroquinoline (3s)

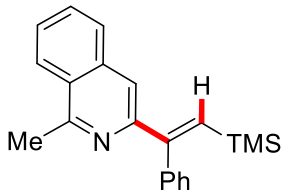
The title compound was prepared according to the general procedure as a white solid (54.9 mg, 94% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–7.33 (m, 3H), 7.24–7.23

(m, 2H), 7.17–7.16 (m, 2H), 6.61 (d, *J* = 8.0 Hz, 1H), 2.98 (t, *J* = 6.5 Hz, 2H), 2.73 (t, *J* = 6.5 Hz, 2H), 1.93–1.88 (m, 2H), 1.83–1.78 (m, 2H), -0.11 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.91, 155.32, 154.93, 141.74, 136.89, 131.63, 131.13, 129.80, 127.93, 127.24, 119.73, 32.97, 28.53, 23.18, 22.79, -0.12; HRMS (ESI) m/z calcd. for $C_{20}H_{25}NSi$ [M+H] $^+$ = 293.1600, found = 293.1601.



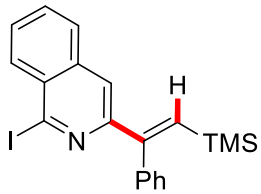
(*E*)-2-(1-Phenyl-2-(trimethylsilyl)vinyl)-6,7,8,9-tetrahydro-5H-cyclohepta[b]pyridine (3t)

The title compound was prepared according to the general procedure as a white solid (59.0 mg, 92% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–7.32 (m, 3H), 7.25–7.24 (m, 3H), 7.17 (d, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 3.11 (t, *J* = 5.0 Hz, 2H), 2.73 (t, *J* = 4.0 Hz, 2H), 1.89–1.85 (m, 2H), 1.75–1.73 (m, 2H), 1.65–1.64 (m, 2H), -0.12 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.73, 155.25, 154.25, 141.75, 136.92, 136.68, 131.42, 129.81, 127.91, 127.21, 119.79, 39.86, 35.02, 32.54, 28.12, 26.73, -0.11; HRMS (ESI) m/z calcd. for $C_{21}H_{27}NSi$ [M+H] $^+$ = 321.1913, found = 321.1914.



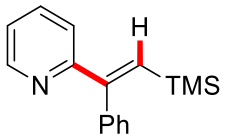
(*E*)-1-Methyl-3-(1-phenyl-2-(trimethylsilyl)vinyl)isoquinoline (3u)

The title compound was prepared according to the general procedure as a white solid (56.2 mg, 89% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.59–7.50 (m, 4H), 7.46–7.40 (m, 3H), 7.34–7.32 (m, 2H), 7.02 (s, 1H), 3.04 (s, 3H), -0.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.15, 155.20, 149.99, 141.67, 136.39, 131.94, 129.97, 129.83, 128.00, 127.92, 127.30, 126.86, 126.64, 125.52, 117.64, 22.83, -0.10; HRMS (ESI) m/z calcd. for $C_{21}H_{23}NSi$ [M+H] $^+$ = 317.1600, found = 317.1608.



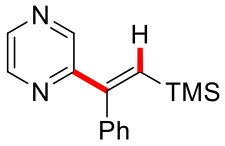
(*E*)-1-Iodo-3-(1-phenyl-2-(trimethylsilyl)vinyl)isoquinoline (3v)

The title compound was prepared according to the general procedure as a white solid (77.0 mg, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07–8.06 (m, 1H), 7.60–7.57 (m, 2H), 7.49–7.43 (m, 5H), 7.30–7.29 (m, 2H), 7.02 (s, 1H), -0.08 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.03, 152.44, 140.80, 136.63, 134.01, 132.84, 130.95, 130.79, 129.87, 128.63, 128.21, 127.88, 127.58, 119.04, -0.19; HRMS (ESI) m/z calcd. for $C_{20}H_{20}INSi$ $[M+H]^+$ = 429.0410, found = 429.0411.



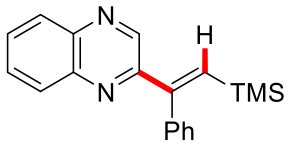
(*E*)-2-(1-Phenyl-2-(trimethylsilyl)vinyl)pyridine (3w)

The title compound was prepared according to the general procedure as a white solid (36.0 mg, 71% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.63 (d, *J* = 4.5 Hz, 1H), 7.54–7.51 (m, 1H), 7.40–7.36 (m, 3H), 7.26–7.23 (m, 2H), 7.17 (s, 1H), 7.15–7.12 (m, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), – 0.1 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.11, 155.18, 149.19, 141.37, 136.35, 133.33, 129.76, 128.07, 127.46, 122.23, 122.16, -2.3; HRMS (ESI) m/z calcd. for $C_{16}H_{20}NSi$ $[M+H]^+$ = 254.0360, found = 254.1363.



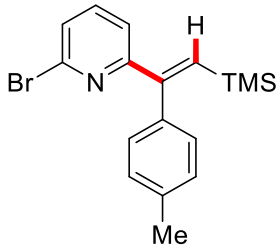
(*E*)-2-(1-Phenyl-2-(trimethylsilyl)vinyl)pyrazine (3x)

The title compound was prepared according to the general procedure as a white solid (27.4 mg, 54% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.56 (br, 1H), 8.41 (d, *J* = 7.0 Hz, 1H), 8.29 (s, 1H), 7.43–7.37 (m, 3H), 7.25–7.24 (m, 2H), 7.18 (s, 1H), -0.08 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.52, 152.55, 143.70, 143.49, 142.91, 139.97, 136.54, 129.57, 128.36, 127.94, -0.35; HRMS (ESI) m/z calcd. for $C_{15}H_{19}N_2Si$ $[M+H]^+$ = 255.1312, found = 255.1315.



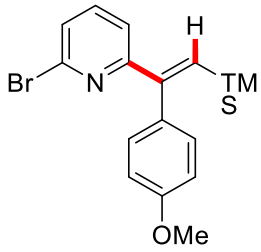
(*E*)-2-(1-Phenyl-2-(trimethylsilyl)vinyl)quinoxaline (3y)

The title compound was prepared according to the general procedure as a white solid (29.1 mg, 48% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (s, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.77–7.70 (m, 2H), 7.45–7.39 (m, 3H), 7.32–7.31 (m, 3H), -0.03 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.38, 153.03, 144.52, 141.94, 141.48, 140.11, 138.26, 130.11, 129.73, 129.69, 129.57, 128.96, 128.40, 128.02, -0.23; $C_{19}H_{21}N_2Si$ $[M+H]^+$ = 305.1469, found = 305.1474



(*E*)-2-Bromo-6-(1-(p-tolyl)-2-(trimethylsilyl)vinyl)pyridine (3z)

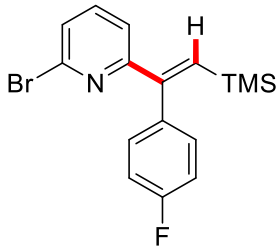
The title compound was prepared according to the general procedure as a white solid (64.9 mg, 94% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35–7.32 (m, 1H), 7.30–7.28 (m, 2H), 7.19 (d, *J* = 7.5 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 7.5 Hz, 1H), 2.40 (s, 3H), -0.10 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.27, 153.10, 141.87, 138.59, 137.53, 137.28, 135.09, 126.22, 120.80, 21.25, -0.23; HRMS (ESI) m/z calcd. for $C_{17}H_{21}BrNSi$ $[M+H]^+$ = 346.0621, found = 346.0627.



(*E*)-2-Bromo-6-(1-(4-methoxyphenyl)-2-(trimethylsilyl)vinyl)pyridine (3aa)

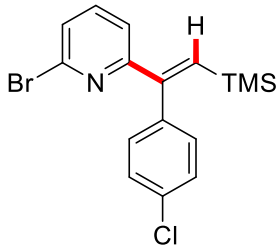
The title compound was prepared according to the general procedure as a white solid (65.7 mg, 91% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36–7.33 (m, 1H), 7.29 (d, *J* =

7.5 Hz, 1H), 7.25 (s, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 7.5 Hz, 1H), 3.85 (s, 3H), -0.10 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.47, 159.14, 152.77, 141.87, 138.60, 135.28, 132.83, 130.83, 126.23, 120.78, 113.54, 55.22, -0.21; HRMS (ESI) m/z calcd. for $C_{17}H_{21}BrNOSi$ $[M+H]^+$ = 362.0570, found = 362.0571.



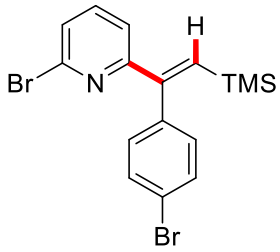
(*E*)-2-Bromo-6-(1-(4-fluorophenyl)-2-(trimethylsilyl)vinyl)pyridine (3ab)

The title compound was prepared according to the general procedure as a white solid (52.3 mg, 75% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–7.35 (m, 1H), 7.32–7.30 (m, 2H), 7.22–7.17 (m, 2H), 7.10–7.07 (m, 2H), 6.78 (d, *J* = 7.5 Hz, 1H), -0.10 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.40 (d, *J* = 245.38 Hz), 158.93, 151.99, 142.01, 138.70, 136.49 (d, *J* = 3.50 Hz), 136.06, 131.37 (d, *J* = 8.00 Hz), 126.46, 120.62, 115.21 (d, *J* = 21.38 Hz), -0.28; HRMS (ESI) m/z calcd. for $C_{16}H_{18}BrFNSi$ $[M+H]^+$ = 350.0370, found = 350.0373.



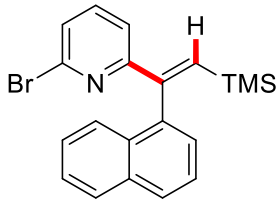
(*E*)-2-Bromo-6-(1-(4-chlorophenyl)-2-(trimethylsilyl)vinyl)pyridine (3ac)

The title compound was prepared according to the general procedure as a white solid (60.6 mg, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–7.35 (m, 3H), 7.32–7.30 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.77 (d, *J* = 7.5 Hz, 1H), -0.09 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.66, 151.84, 142.02, 139.03, 138.71, 136.14, 133.69, 131.11, 128.47, 126.52, 120.60, -0.24; HRMS (ESI) m/z calcd. for $C_{16}H_{18}BrClNSi$ $[M+H]^+$ = 366.0075, found = 366.0076.



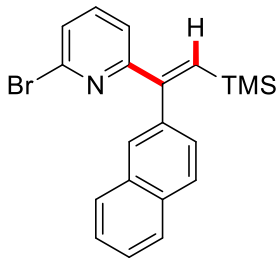
(*E*)-2-Bromo-6-(1-(4-bromophenyl)-2-(trimethylsilyl)vinyl)pyridine (3ad)

The title compound was prepared according to the general procedure as a white solid (74.3 mg, 92% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.38–7.35 (m, 1H), 7.32–7.29 (m, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.77 (d, *J* = 7.5 Hz, 1H), -0.09 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.57, 151.83, 142.02, 139.51, 138.71, 136.12, 131.43, 126.54, 121.80, 120.60, -0.23; HRMS (ESI) m/z calcd. for $C_{16}H_{18}Br_2NSi$ $[M+H]^+$ = 405.9571, found = 405.9578.



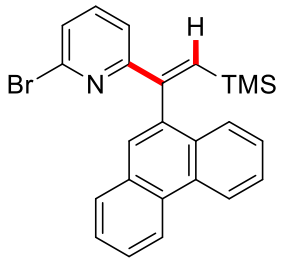
(*E*)-2-Bromo-6-(1-(naphthalen-1-yl)-2-(trimethylsilyl)vinyl)pyridine (3ae)

The title compound was prepared according to the general procedure as a white solid (68.6 mg, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89–7.86 (m, 2H), 7.70–7.67 (m, 2H), 7.52–7.44 (m, 2H), 7.37–7.34 (m, 2H), 7.28–7.25 (m, 1H), 7.22–7.18 (m, 1H), 6.54 (d, *J* = 7.5 Hz, 1H), -0.30 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.52, 150.93, 142.00, 138.89, 137.90, 137.06, 133.50, 132.50, 128.20, 127.67, 126.37, 126.19, 126.16, 125.99, 125.28, 120.66, -0.70; HRMS (ESI) m/z calcd. for $C_{20}H_{21}BrNSi$ $[M+H]^+$ = 382.0621, found = 382.0623.



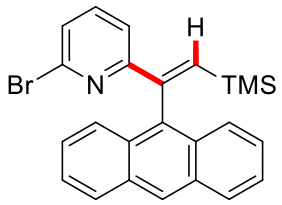
(*E*)-2-Bromo-6-(1-(naphthalen-2-yl)-2-(trimethylsilyl)vinyl)pyridine (3af)

The title compound was prepared according to the general procedure as a white solid (70.9 mg, 93% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90–7.83 (m, 3H), 7.73 (s, 1H), 7.54–7.52 (m, 2H), 7.39 (s, 1H), 7.32–7.30 (m, 3H), 6.82–6.78 (m, 1H), -0.12 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.01, 153.06, 142.00, 138.65, 138.11, 135.88, 133.10, 132.72, 128.73, 127.92, 127.82, 127.79, 127.71, 126.40, 126.36, 126.17, 120.98, -0.18; HRMS (ESI) m/z calcd. for $C_{20}H_{21}BrNSi$ $[M+H]^+$ = 382.0621, found = 382.0623.



(*E*)-2-Bromo-6-(1-(phenanthren-9-yl)-2-(trimethylsilyl)vinyl)pyridine (3ag)

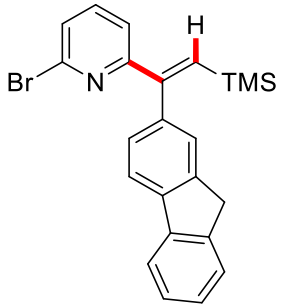
The title compound was prepared according to the general procedure as a white solid (65.5 mg, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.73 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.71–7.68 (m, 2H), 7.65–7.62 (m, 3H), 7.48–7.45 (m, 1H), 7.28–7.25 (m, 1H), 7.19–7.16 (m, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), -0.25 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.39, 151.20, 142.04, 138.90, 137.36, 136.52, 131.48, 131.31, 130.34, 130.30, 128.63, 128.54, 127.11, 126.91, 126.75, 126.73, 126.46, 122.86, 122.66, 120.69, -0.51; HRMS (ESI) m/z calcd. for $C_{24}H_{23}BrNSi$ $[M+H]^+$ = 432.0778, found = 432.0780.



(*E*)-2-(1-(Anthracen-9-yl)-2-(trimethylsilyl)vinyl)-6-bromopyridine (3ah)

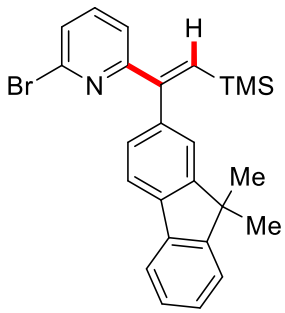
The title compound was prepared according to the general procedure as a white solid (74.1 mg, 86% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.50 (s, 1H), 8.04–8.03 (m, 3H), 7.93 (d, *J* = 8.5 Hz, 2H), 7.47–7.44 (m, 2H), 7.39–7.36 (m, 2H), 7.28–7.26 (m, 1H), 7.13–7.10 (m, 1H), 6.30 (d, *J* = 7.5 Hz, 1H), -0.56 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.21, 148.37, 142.13, 139.20, 139.05, 134.44, 131.35, 130.42, 128.47, 126.96,

126.53, 125.76, 125.36, 120.54, -1.27; HRMS (ESI) m/z calcd. for $C_{24}H_{23}BrNSi$ [M+H] $^{+}$ = 432.0778, found = 432.0780.



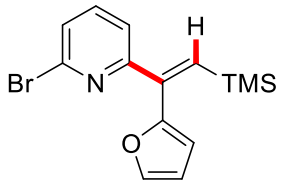
(*E*)-2-(1-(9H-Fluoren-2-yl)-2-(trimethylsilyl)vinyl)-6-bromopyridine (3ai)

The title compound was prepared according to the general procedure as a white solid (79.8 mg, 95% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83–7.79 (m, 2H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.42–7.38 (m, 2H), 7.35–7.29 (m, 4H), 7.22 (d, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), -0.10 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.29, 153.39, 143.36, 143.16, 141.96, 141.36, 141.17, 139.15, 138.65, 135.36, 128.42, 126.86, 126.39, 126.33, 125.10, 120.93, 119.95, 119.58, 36.92, -0.15; HRMS (ESI) m/z calcd. for $C_{24}H_{23}BrNSi$ [M+H] $^{+}$ = 420.0778, found = 432.0780.



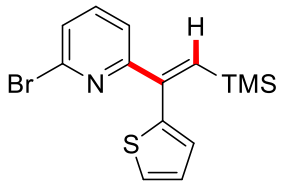
(*E*)-2-Bromo-6-(1-(9,9-dimethyl-9H-fluoren-2-yl)-2-(trimethylsilyl)vinyl)pyridine (3aj)

The title compound was prepared according to the general procedure as a white solid (86.0 mg, 96% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77–7.73 (m, 2H), 7.46 (d, *J* = 7.0 Hz, 1H), 7.38–7.30 (m, 6H), 7.18 (d, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 1.51 (s, 6H), -0.09 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.23, 153.70, 153.64, 153.49, 141.96, 139.61, 138.84, 138.69, 138.62, 135.38, 128.47, 127.37, 127.05, 126.33, 124.21, 122.66, 120.90, 120.02, 119.69, 46.86, 27.06, -0.20; HRMS (ESI) m/z calcd. for $C_{25}H_{27}BrNSi$ [M+H] $^{+}$ = 448.1091, found = 448.1094.



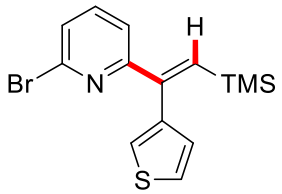
(*Z*)-2-Bromo-6-(1-(furan-2-yl)-2-(trimethylsilyl)vinyl)pyridine (3ak)

The title compound was prepared according to the general procedure as a white solid (59.2 mg, 92% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50–7.47 (m, 2H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 6.65 (s, 1H), 6.47–6.46 (m, 1H), 6.36 (d, *J* = 3.0 Hz, 1H), 0.13 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.71, 152.83, 142.74, 141.90, 141.52, 138.67, 137.09, 126.82, 121.14, 111.48, 110.84, 0.03; HRMS (ESI) m/z calcd. for $C_{14}H_{17}BrNOSi$ $[M+H]^+$ = 322.0257, found = 322.0258.



(*Z*)-2-Bromo-6-(1-(thiophen-2-yl)-2-(trimethylsilyl)vinyl)pyridine (3al)

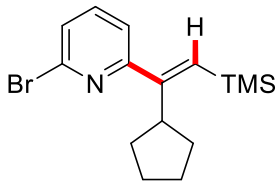
The title compound was prepared according to the general procedure as a white solid (64.9 mg, 96% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41–7.38 (m, 1H), 7.36–7.35 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.06–7.01 (m, 2H), 6.96–6.95 (m, 1H), -0.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.04, 145.41, 141.72, 141.09, 139.68, 138.76, 128.22, 126.75, 126.56, 126.01, 120.56, -0.50; HRMS (ESI) m/z calcd. for $C_{14}H_{17}BrNSSi$ $[M+H]^+$ = 338.0029, found = 338.0030.



(*E*)-2-Bromo-6-(1-(thiophen-3-yl)-2-(trimethylsilyl)vinyl)pyridine (3am)

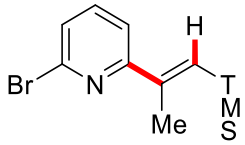
The title compound was prepared according to the general procedure as a white solid (64.2 mg, 95% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39–7.34 (m, 2H), 7.32–7.30 (m, 2H), 7.16–7.15 (m, 1H), 6.95 (d, *J* = 4.5 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), -0.06 (s,

9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.77, 147.93, 141.90, 140.68, 138.74, 136.72, 129.22, 126.45, 125.50, 124.35, 120.46, -0.40; HRMS (ESI) m/z calcd. for $C_{14}H_{17}BrNSSi$ $[M+H]^+$ = 338.0029, found = 338.0030.



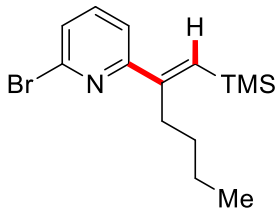
(*E*)-2-Bromo-6-(1-cyclopentyl-2-(trimethylsilyl)vinyl)pyridine (3an)

The title compound was prepared according to the general procedure as a white solid (59.6 mg, 92% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45–7.42 (m, 1H), 7.30–7.27 (m, 2H), 5.89 (s, 1H), 3.10–3.03 (s, 1H), 1.86–1.77 (m, 6H), 1.60–1.57 (m, 2H), 0.19 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.74, 158.68, 140.21, 138.16, 133.25, 125.65, 121.33, 46.34, 31.95, 26.40, 0.24; HRMS (ESI) m/z calcd. for $C_{15}H_{23}BrNSi$ $[M+H]^+$ = 324.0778, found = 324.0780.



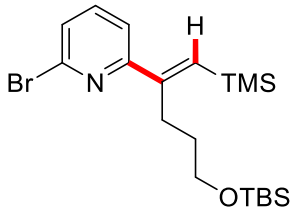
(*E*)-2-Bromo-6-(1-(trimethylsilyl)prop-1-en-2-yl)pyridine (3ao)

The title compound was prepared according to the general procedure as a white solid (58.4 mg, 93% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50–7.47 (m, 1H), 7.43–7.41 (m, 1H), 7.33–7.32 (m, 1H), 6.57 (s, 1H), 2.24 (s, 3H), 0.21 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.06, 149.05, 141.31, 138.57, 132.25, 126.15, 118.33, 19.24, -0.19; HRMS (ESI) m/z calcd. for $C_{14}H_{25}BrNSi$ $[M+H]^+$ = 314.0934, found = 314.0933.



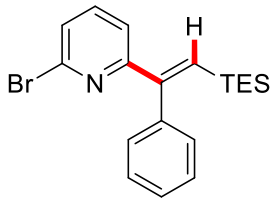
(*E*)-2-Bromo-6-(1-(trimethylsilyl)hex-1-en-2-yl)pyridine (3ap)

The title compound was prepared according to the general procedure as a white solid (54.3 mg, 87% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49–7.46 (m, 1H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 6.32 (s, 1H), 2.69–2.66 (m, 2H), 1.36–1.35 (m, 4H), 0.90 (t, *J* = 6.5 Hz, 3H), 0.20 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.18, 155.06, 141.31, 138.54, 132.25, 126.04, 119.21, 33.04, 31.75, 22.94, 13.97, 0.11; HRMS (ESI) m/z calcd. for $C_{14}H_{23}BrNSi$ $[M+H]^+$ = 312.0778, found = 312.0782.



(*E*)-2-Bromo-6-(5-((tert-butyldimethylsilyl)oxy)-1-(trimethylsilyl)pent-1-en-2-yl) pyridine (3aq)

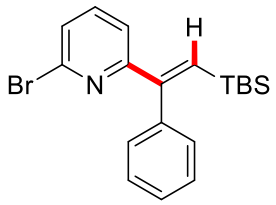
The title compound was prepared according to the general procedure as a white solid (77.0 mg, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48–7.45 (m, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 6.40 (s, 1H), 3.64 (t, *J* = 6.5 Hz, 2H), 2.75–2.72 (m, 2H), 1.63–1.59 (m, 2H), 0.90 (s, 9H), 0.21 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.70, 154.26, 141.35, 138.56, 132.57, 126.12, 119.20, 63.15, 32.64, 29.78, 25.98, 18.35, 0.06, -5.32; HRMS (ESI) m/z calcd. for $C_{19}H_{35}BrNSi_2$ $[M+H]^+$ = 428.1435, found = 428.1437.



(*E*)-2-Bromo-6-(1-phenyl-2-(triethylsilyl)vinyl)pyridine (3ar)

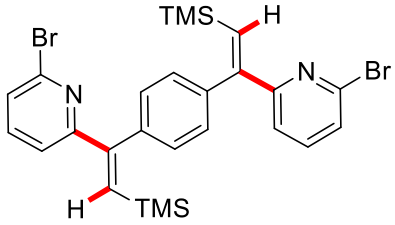
The title compound was prepared according to the general procedure as a white solid (67.3 mg, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37–7.36 (m, 3H), 7.35–7.32 (m, 1H), 7.29–7.28 (m, 1H), 7.26 (s, 1H), 7.22–7.21 (m, 2H), 6.77 (d, *J* = 7.5 Hz, 1H), 0.85 (t, *J* = 8.0 Hz, 9H), 0.36 (q, *J* = 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.13, 153.77, 141.90, 140.86, 138.58, 132.64, 129.56, 128.08, 127.65, 126.25,

120.74, 7.52, 4.11; HRMS (ESI) m/z calcd. for $C_{19}H_{25}BrNSi_2$ $[M+H]^+$ = 374.0934, found = 374.0936.



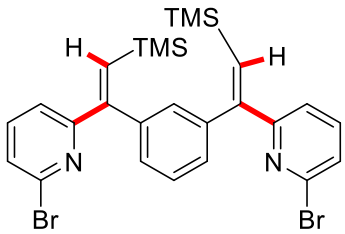
(*E*)-2-Bromo-6-(2-(tert-butyldimethylsilyl)-1-phenylvinyl)pyridine (3as)

The title compound was prepared according to the general procedure as a white solid (52.3 mg, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39–7.31 (m, 5H), 7.29–7.28 (m, 1H), 7.21–7.20 (m, 2H), 6.76 (d, *J* = 7.0 Hz, 1H), 0.93 (s, 9H), -0.30 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.14, 153.74, 141.90, 140.67, 138.58, 132.31, 129.85, 128.11, 127.52, 126.26, 120.70, 26.73, 17.03, -5.14; HRMS (ESI) m/z calcd. for $C_{19}H_{25}BrNSi_2$ $[M+H]^+$ = 374.0934, found = 374.0936.



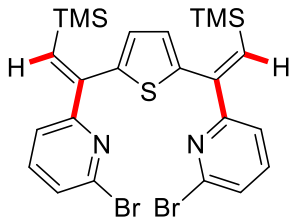
1,4-Bis((*E*)-1-(6-bromopyridin-2-yl)-2-(trimethylsilyl)vinyl)benzene (3at)

The title compound was prepared according to the general procedure as a white solid (104.1 mg, 89% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34–7.31 (m, 2H), 7.28–7.27 (m, 4H), 7.20 (br, 4H), 6.77 (d, *J* = 7.5 Hz, 2H), - 0.08 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.04, 152.70, 142.00, 140.13, 138.69, 135.55, 129.74, 126.43, 120.59, -0.07; HRMS (ESI) m/z calcd. for $C_{26}H_{31}Br_2N_2Si_2$ $[M+H]^+$ = 585.0387, found = 585.0388.



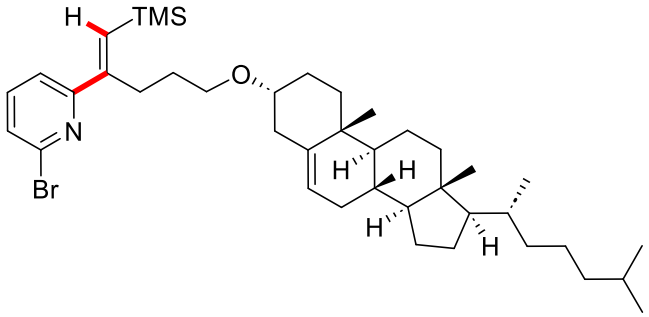
1,3-Bis((*E*)-1-(6-bromopyridin-2-yl)-2-(trimethylsilyl)vinyl)benzene (3au)

The title compound was prepared according to the general procedure as a white solid (79.6 mg, 68% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46–7.43 (m, 1H), 7.37–7.34 (m, 2H), 7.31–7.30 (m, 2H), 7.26–7.25 (m, 3H), 7.22 (s, 2H), 7.03 (s, 1H), 6.89 (d, *J* = 7.5 Hz, 2H), -0.07 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.25, 152.98, 141.92, 140.86, 138.53, 135.51, 130.59, 129.27, 128.26, 126.46, 120.84, 0.01; HRMS (ESI) m/z calcd. for $C_{26}H_{31}Br_2N_2Si_2$ $[M+H]^+$ = 585.0387, found = 585.0388.



2,5-Bis((*Z*)-1-(6-bromopyridin-2-yl)-2-(trimethylsilyl)vinyl)thiophene (3av)

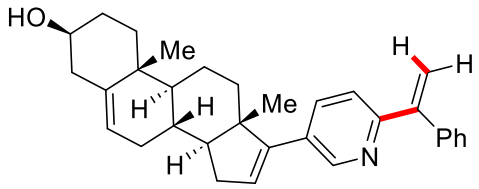
The title compound was prepared according to the general procedure as a white solid (113.9 mg, 64% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44–7.41 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.29 (s, 2H), 7.16 (d, *J* = 7.5 Hz, 2H), 6.93 (s, 2H), 0.09 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.22, 145.45, 142.39, 141.74, 139.55, 138.70, 128.05, 126.69, 120.43, -0.17; HRMS (ESI) m/z calcd. for $C_{24}H_{29}Br_2N_2Si_2$ $[M+H]^+$ = 590.9951, found = 890.9954.



2-Bromo-6-((*E*)-5-(((*3R,8S,9S,10R,13R,14S,17R*)-10,13-dimethyl-17-((*R*)-6-methyl heptan-2-Yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a] phenanthren-3-yl)oxy)-1-(trimethylsilyl)pent-1-en-2-yl)pyridine (3aw)

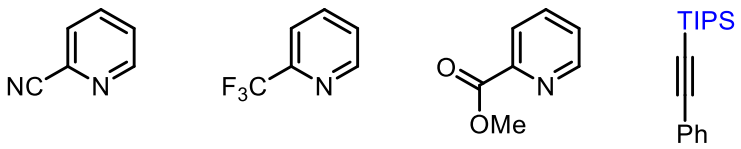
The title compound was prepared according to the general procedure as a white solid (117.3 mg, 86% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48–7.45 (m, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 6.36 (s, 1H), 5.34–5.33 (m, 1H), 3.47 (t, *J* = 6.5 Hz, 2H), 3.15–3.10 (m, 1H), 2.76–2.73 (m, 2H), 2.36–2.33 (m, 1H), 2.20–2.15 (m, 3H),

2.02–1.95 (m, 2H), 1.90–1.79 (m, 3H), 1.67–1.25 (m, 15H), 1.16–0.86 (m, 20H), 0.68 (s, 3H), 0.21 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.87, 154.36, 141.31, 141.08, 138.57, 132.71, 126.11, 121.44, 119.30, 78.96, 67.62, 56.79, 56.16, 50.21, 42.32, 39.79, 39.51, 39.19, 37.25, 36.90, 36.19, 35.78, 31.96, 31.90, 30.91, 30.06, 29.85, 28.46, 28.23, 28.00, 24.29, 23.82, 22.81, 22.55, 21.07, 19.38, 18.71, 11.85, 0.09; HRMS (ESI) m/z calcd. for $C_{40}H_{65}BrNSi$ $[M+H]^+$ = 682.4013, found = 682.4015.



(*3S,8R,9S,10R,13S,14S*)-10,13-Dimethyl-17-(6-(1-phenylvinyl)pyridin-3-yl)-2,3,4,7,8,9,10,11,12,13,14,15-dodecahydro-1H-cyclopenta[*a*]phenanthren-3-ol (3ax)

The title compound was prepared according to the general procedure as a white solid (68.7 mg, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.67 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.37–7.33 (m, 5H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.03 (br, 1H), 6.01 (s, 1H), 5.56 (s, 1H), 5.39 (d, *J* = 5.0 Hz, 1H), 3.54 (br, 1H), 2.35–2.24 (m, 3H), 2.10–2.05 (m, 3H), 1.87–1.85 (m, 2H), 1.79–1.74 (m, 3H), 1.71–1.63 (m, 3H), 1.53–1.47 (m, 3H), 1.13–1.04 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.39, 151.51, 148.95, 147.40, 141.13, 140.50, 133.78, 131.64, 129.18, 128.50, 128.25, 127.78, 122.14, 121.35, 117.26, 71.71, 57.52, 50.34, 47.29, 42.29, 37.17, 36.69, 35.29, 31.82, 31.62, 31.51, 30.43, 20.89, 19.33, 16.59; HRMS (ESI) m/z calcd. for $C_{32}H_{38}NO$ $[M+H]^+$ = 452.2948, found = 452.2951.

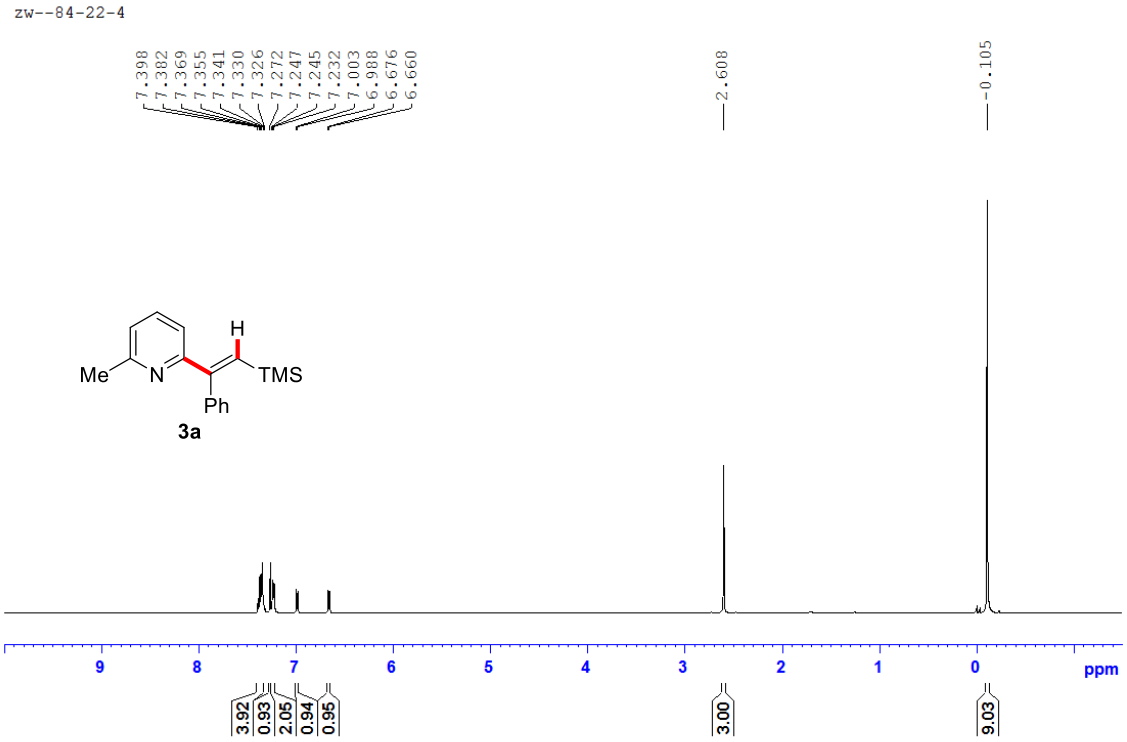


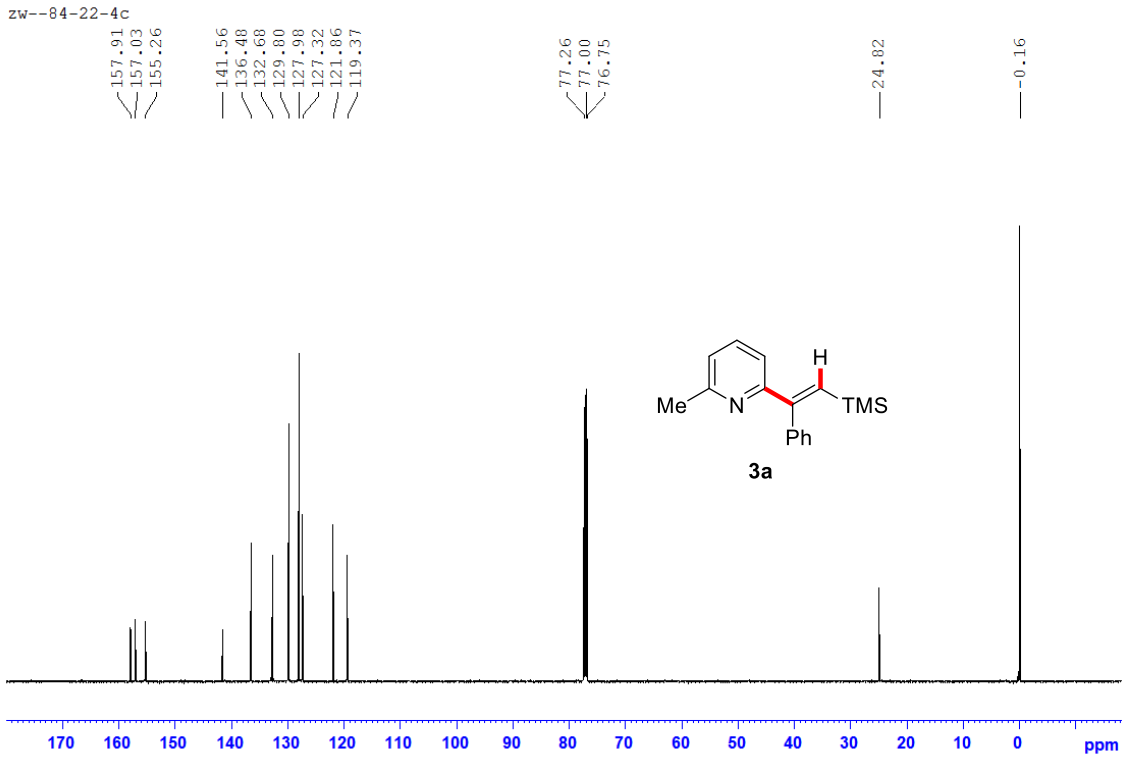
Scheme S1. Ineffect substrates for the present C–H alkenylation by **Sc-4**.

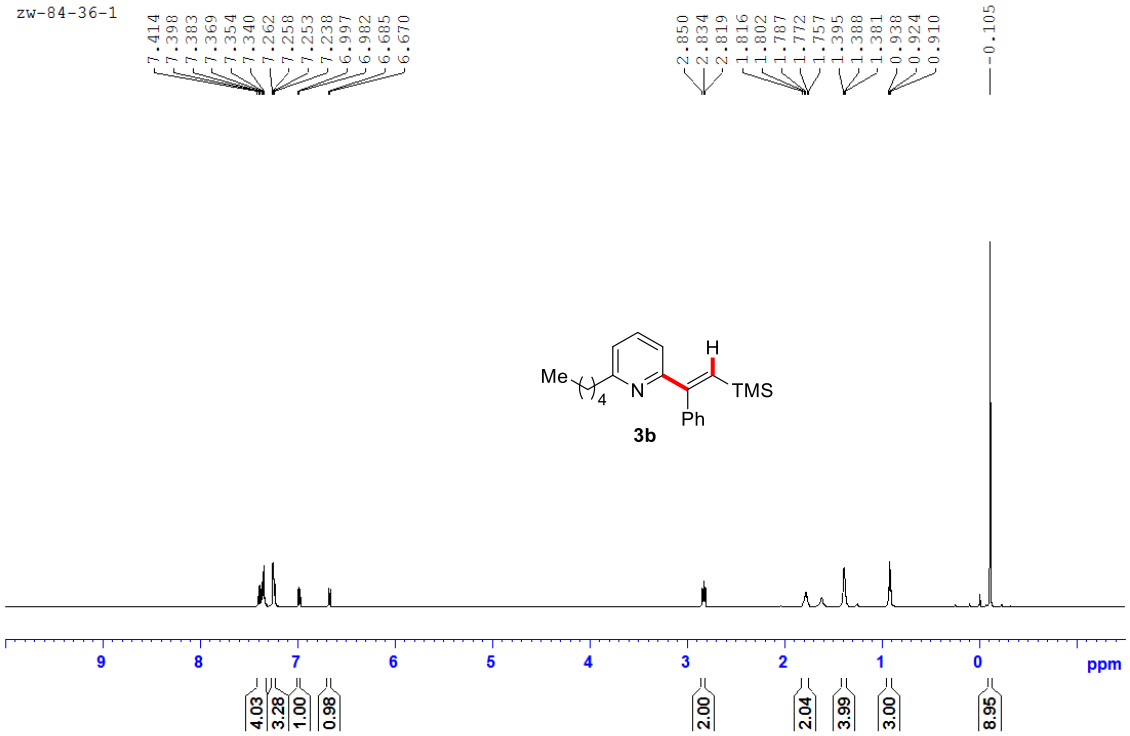
References

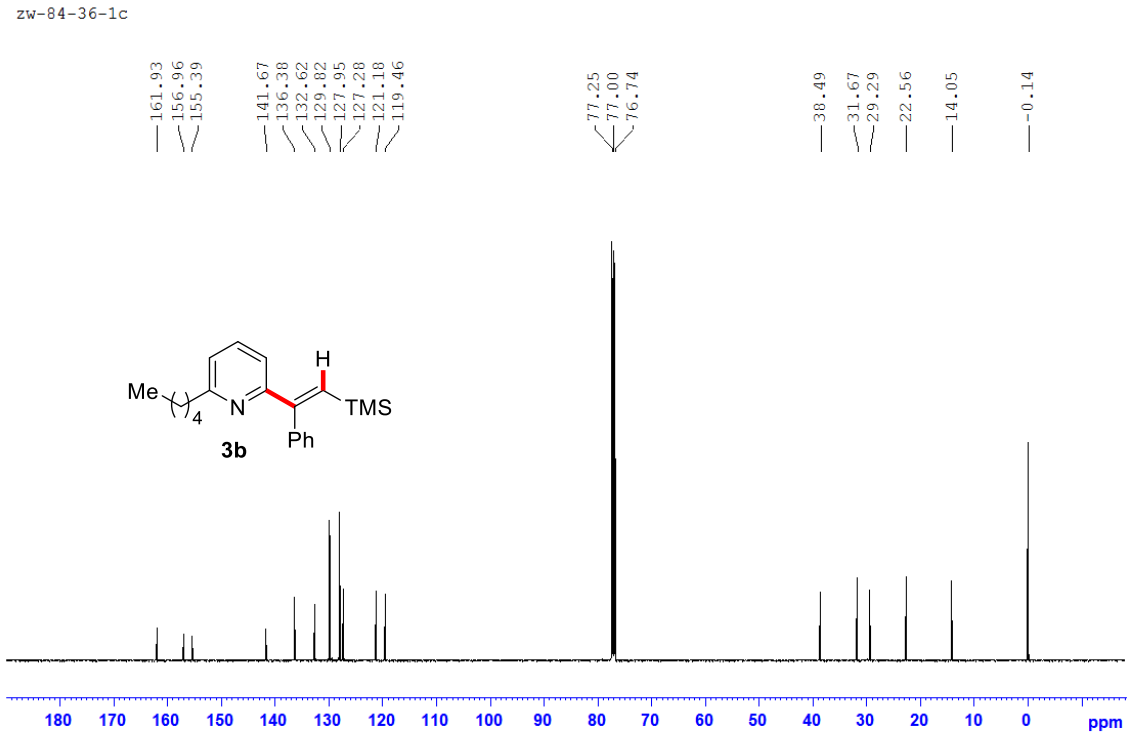
1. (a) X.-Y. Jin, C.-S. Wu, A.-D. Liu, L. Liu, L. Cheng, *Synthesis*, **2022**, *54*, 1643. (b) T. X. Neenan, G. M. Whitesides, *J. Org. Chem.*, **1988**, *53*, 2489.
2. (a) L. E. Manzer, *J. Am. Chem. Soc.*, **1978**, *100*, 8068. (b) M. Nishiura, J. Baldamus, T. Shima, K. Mori, Z. Hou, *Chem. Eur. J.*, **2011**, *17*, 5033. (c) T. Shima, M. Nishiura, Z. Hou, *Organometallics*, **2011**, *30*, 2513. (d) X. Li, M. Nishiura, K. Mori, T. Mashiko, Z. Hou, *Chem. Commun.*, **2007**, 4137.

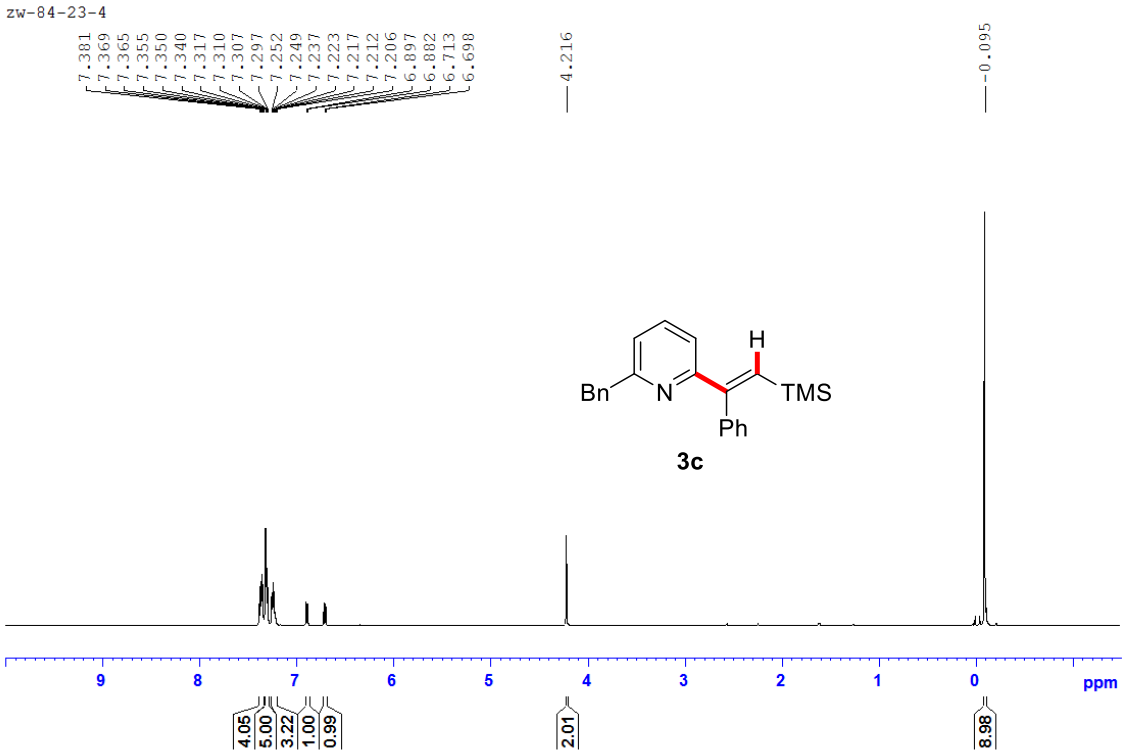
IV NMR spectra

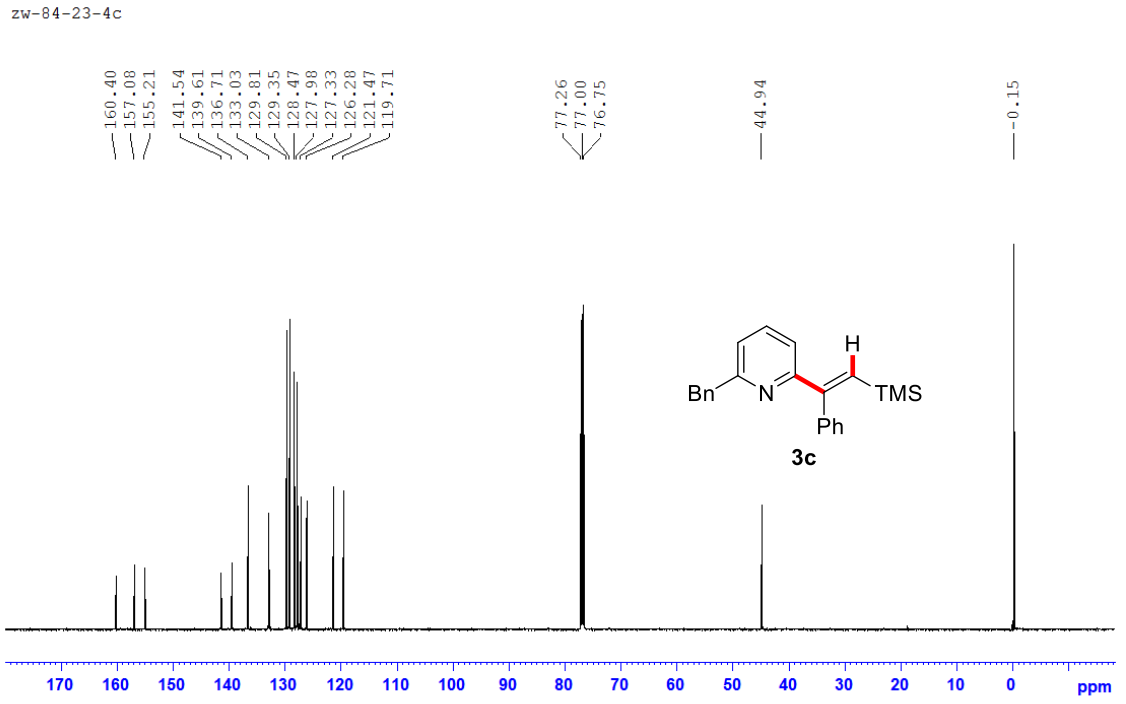




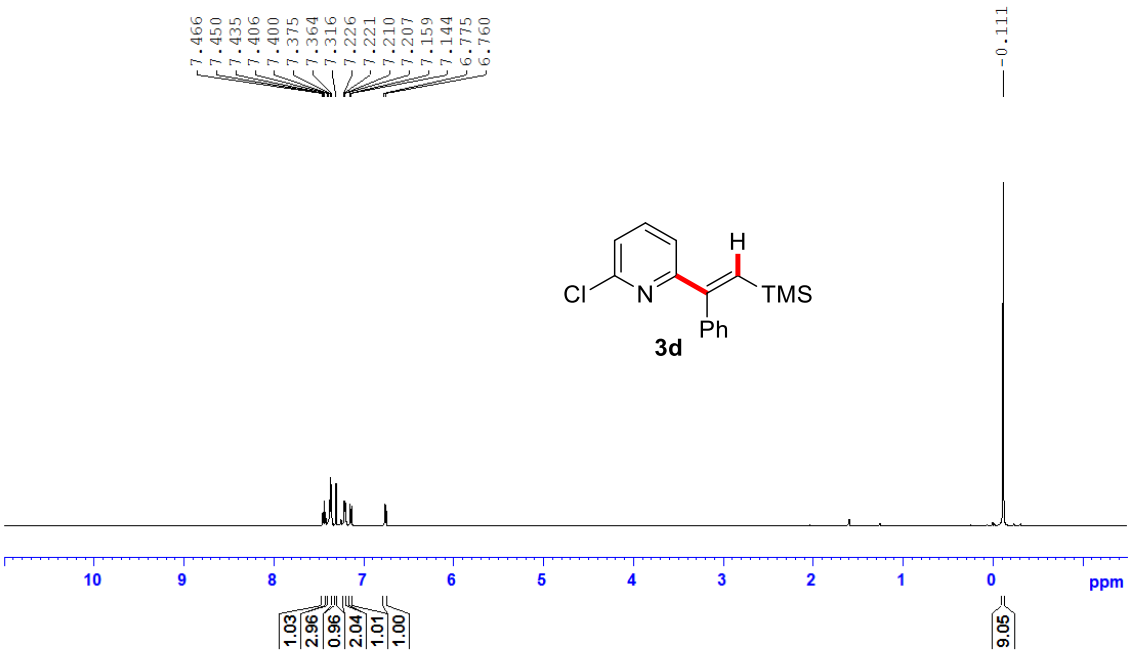

zw-84-36-1
7.414
7.398
7.383
7.369
7.354
7.340
7.262
7.258
7.253
7.238
6.997
6.982
6.685
6.670
2.850
2.834
2.819
1.816
1.802
1.787
1.772
1.757
1.395
1.388
1.381
0.938
0.924
0.910
0.105
Me
4
N
H
TMS
Ph
3b
9
8
7
6
5
4
3
2
1
0
ppm
4.03
3.28
1.00
0.98
2.00
2.04
3.99
3.00
8.95


zw-84-36-1c
161.93
156.96
155.39
141.67
136.38
132.62
129.82
127.95
127.28
121.18
119.46
77.25
77.00
76.74
38.49
31.67
29.29
22.56
14.05
-0.14
Me
4
N
H
TMS
Ph
3b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

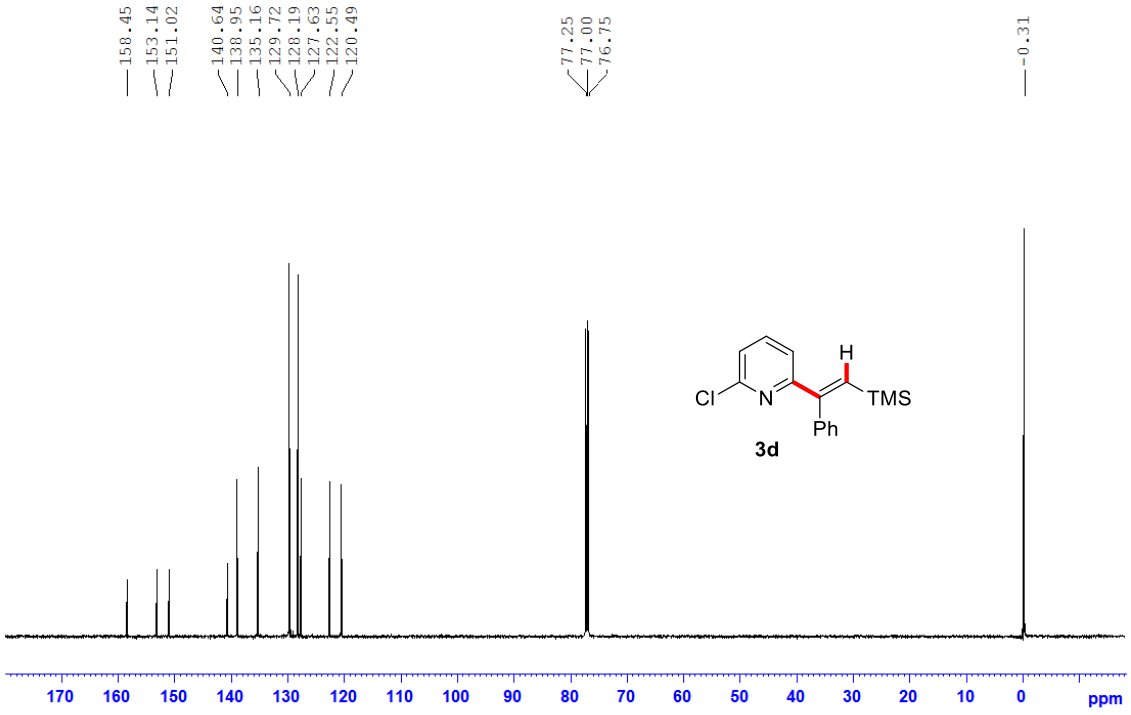

zw-84-23-4
7.381
7.369
7.365
7.355
7.350
7.340
7.317
7.310
7.307
7.297
7.252
7.249
7.237
7.223
7.217
7.212
7.206
6.897
6.882
6.713
6.698
4.216
0.095
H
Bn
N
TMS
Ph
3c
9
8
7
6
5
4
3
2
1
0
ppm
4.05
5.00
3.22
1.00
0.99
2.01
8.98


zw-84-23-4c
160.40
157.08
155.21
141.54
139.61
136.71
133.03
129.81
129.35
128.47
127.98
127.33
126.28
121.47
119.71
77.26
77.00
76.75
44.94
0.15
H
Bn
N
TMS
Ph
3c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

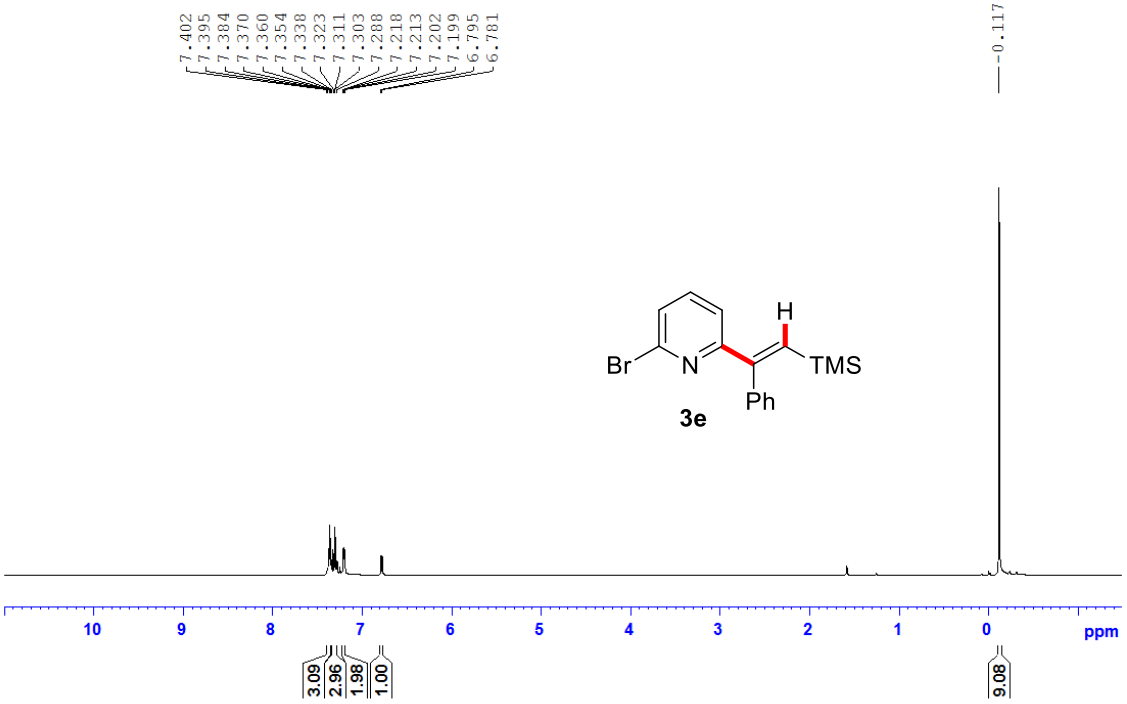
zw-84-22-2



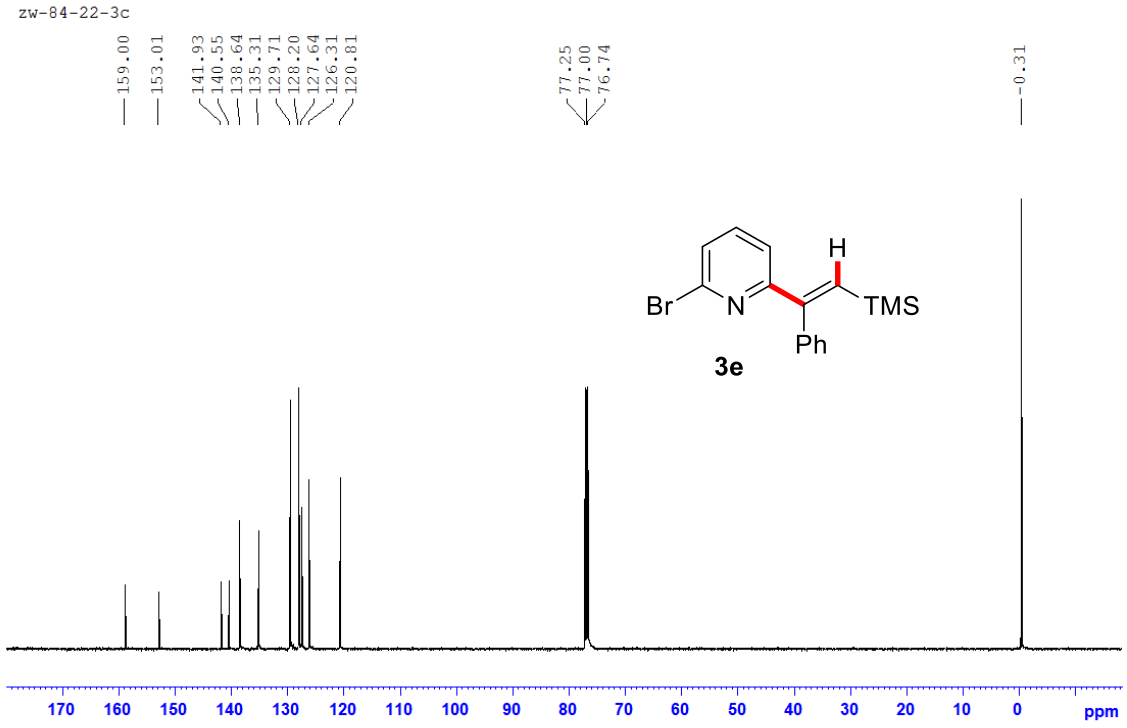
zw-84-22-2c

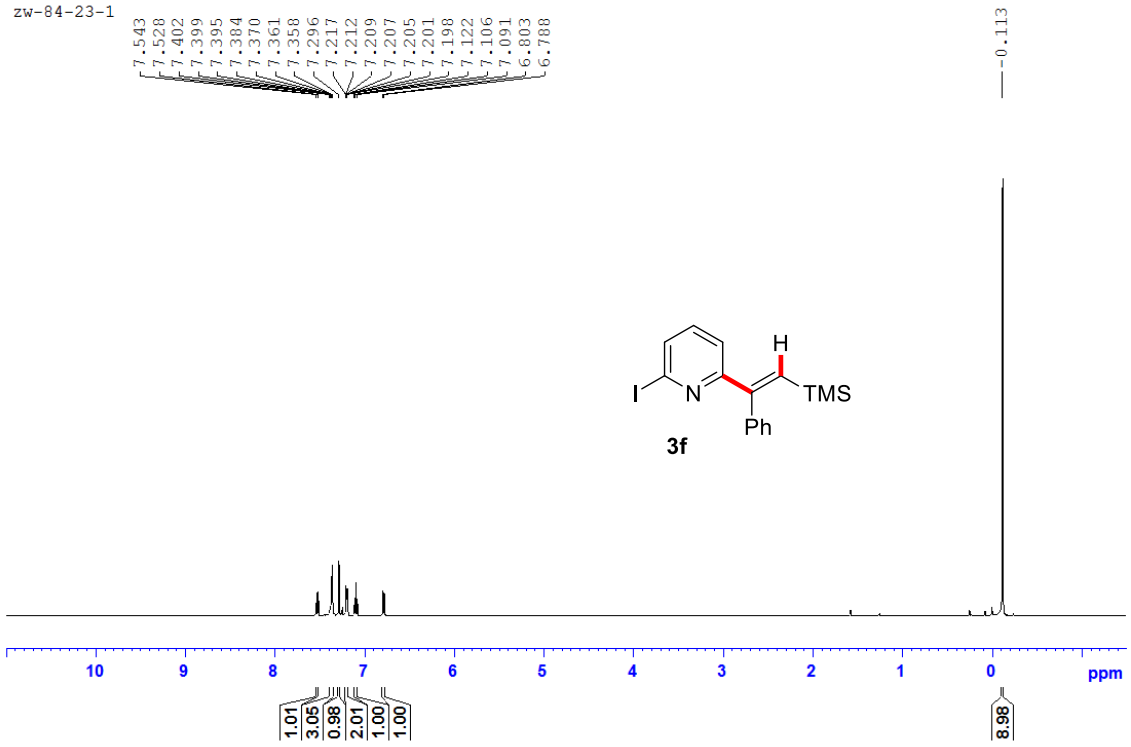


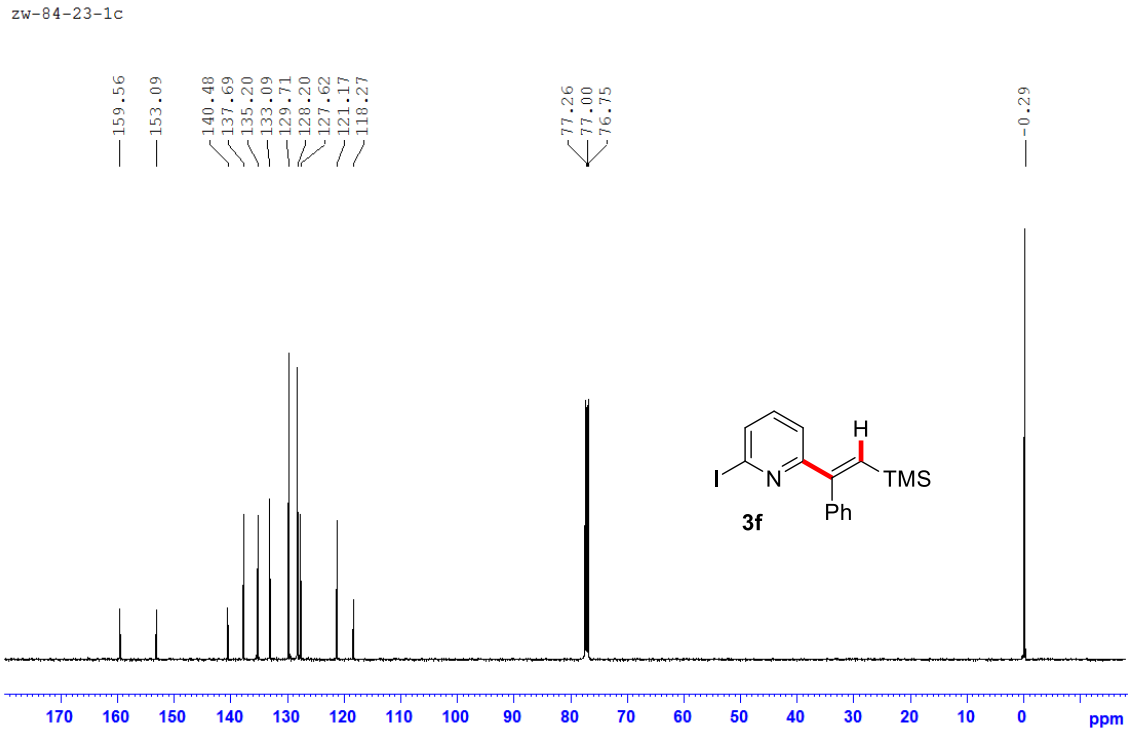
zw-84-22-3

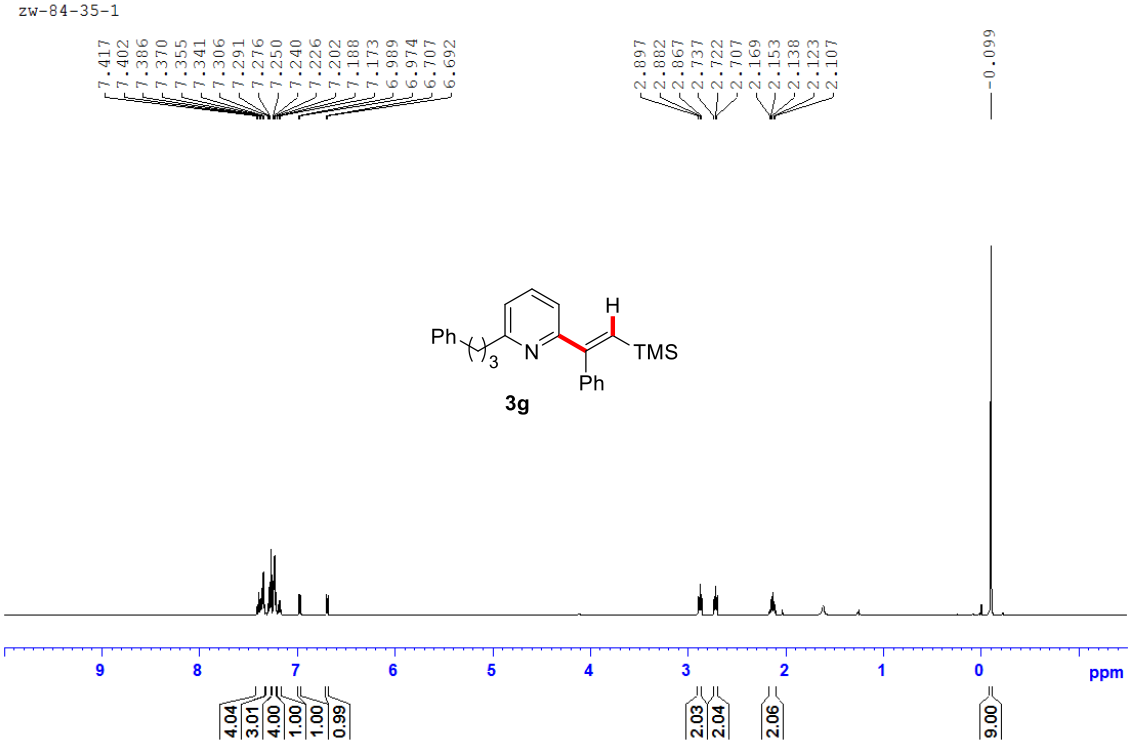


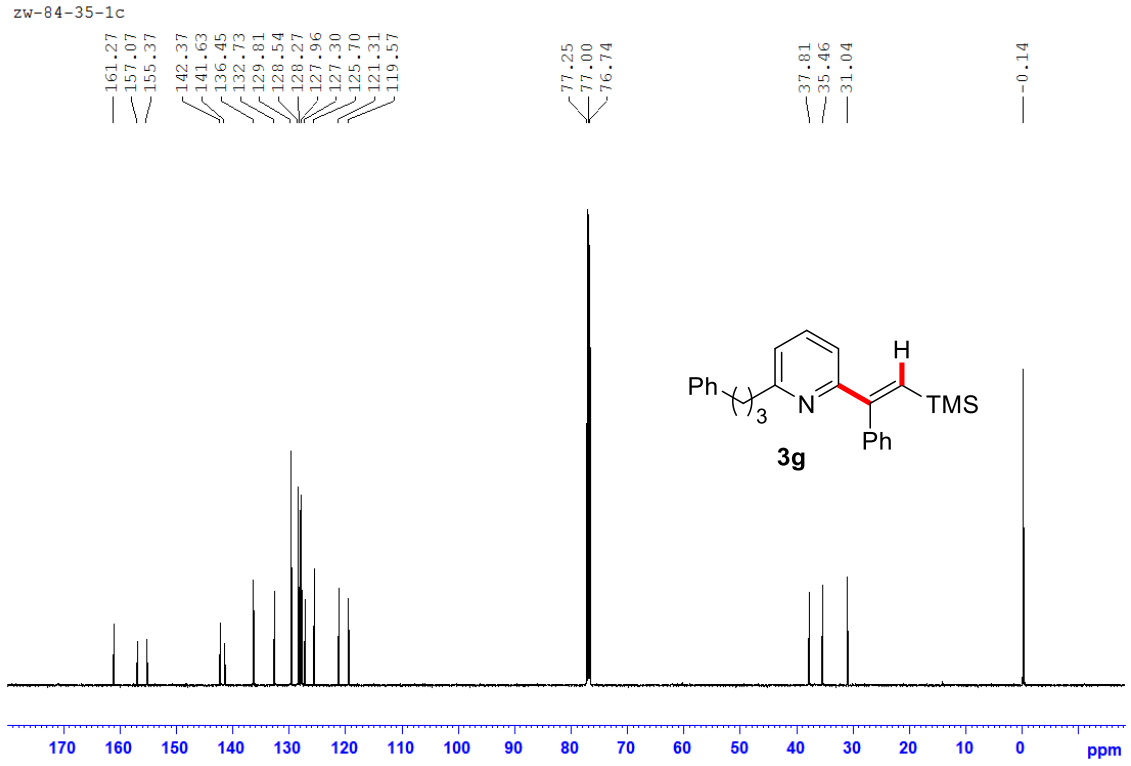
zw-84-22-3c



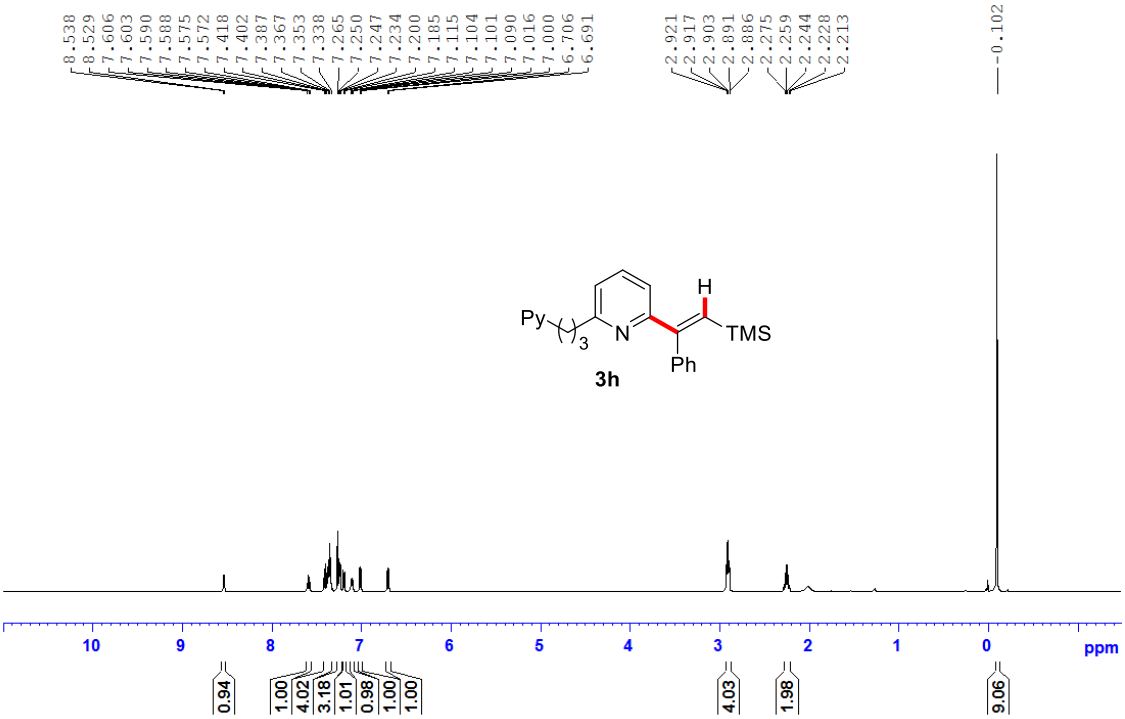

zw-84-23-1
7.543
7.528
7.402
7.399
7.395
7.384
7.370
7.361
7.358
7.296
7.217
7.212
7.209
7.207
7.205
7.201
7.198
7.122
7.106
7.091
6.803
6.788
-0.113
H
I
N
TMS
Ph
3f
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
3.05
0.98
2.01
1.00
1.00
8.98


zw-84-23-1c
159.56
153.09
140.48
137.69
135.20
133.09
129.71
128.20
127.62
121.17
118.27
77.26
77.00
76.75
-0.29
H
I
N
TMS
Ph
3f
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

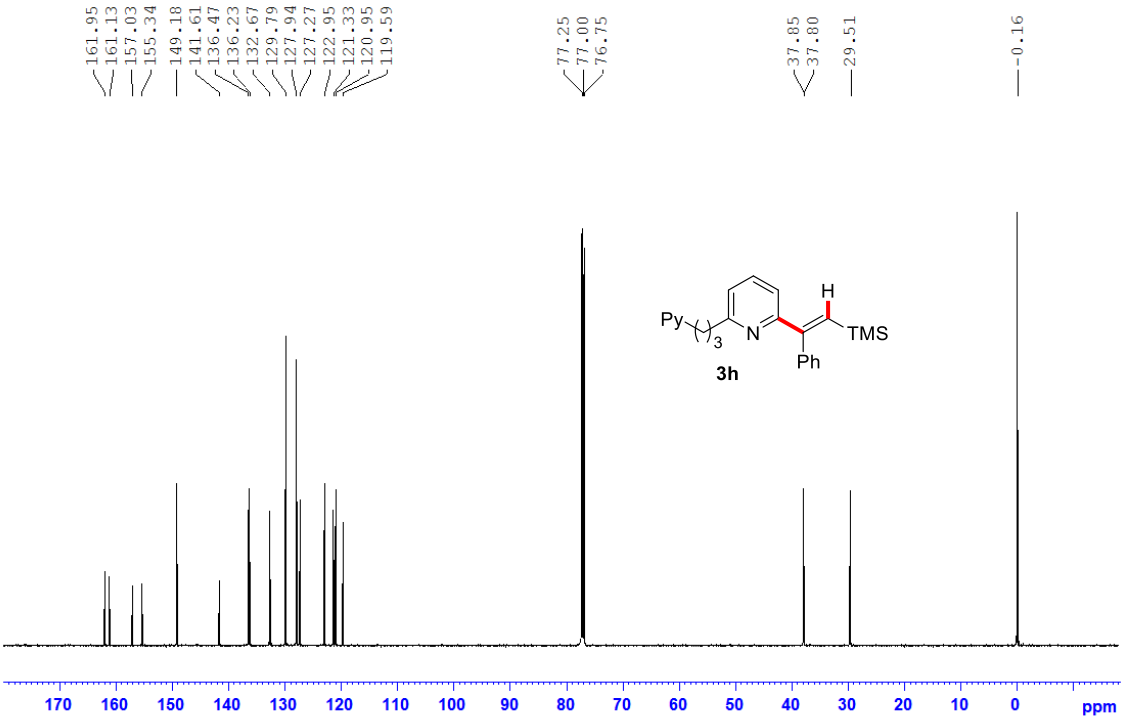

zw-84-35-1
7.417
7.402
7.386
7.370
7.355
7.341
7.306
7.291
7.276
7.250
7.240
7.226
7.202
7.188
7.173
6.989
6.974
6.707
6.692
2.897
2.882
2.867
2.737
2.722
2.707
2.169
2.153
2.138
2.123
2.107
0.099
Ph
3
N
H
TMS
Ph
3g
9
8
7
6
5
4
3
2
1
0
ppm
4.04
3.01
4.00
1.00
1.00
0.99
2.03
2.04
2.06
9.00


zw-84-35-1c
161.27
157.07
155.37
142.37
141.63
136.45
132.73
129.81
128.54
128.27
127.96
127.30
125.70
121.31
119.57
77.25
77.00
76.74
37.81
35.46
31.04
0.14
Ph
3
N
H
TMS
Ph
3g
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

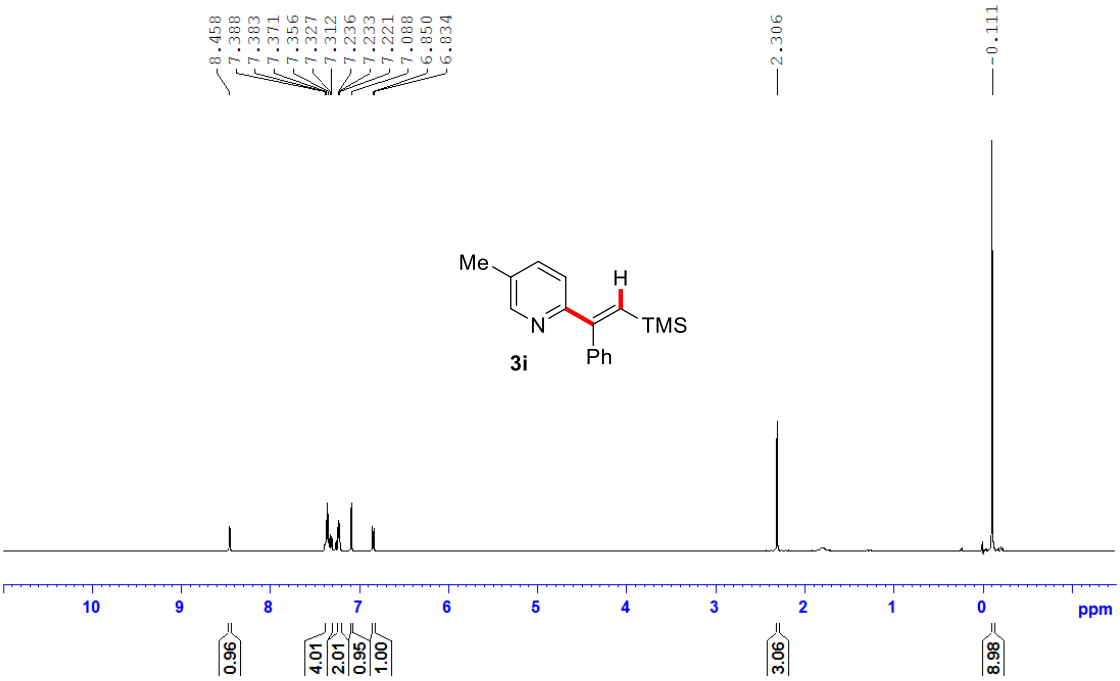
zw-84-32-2



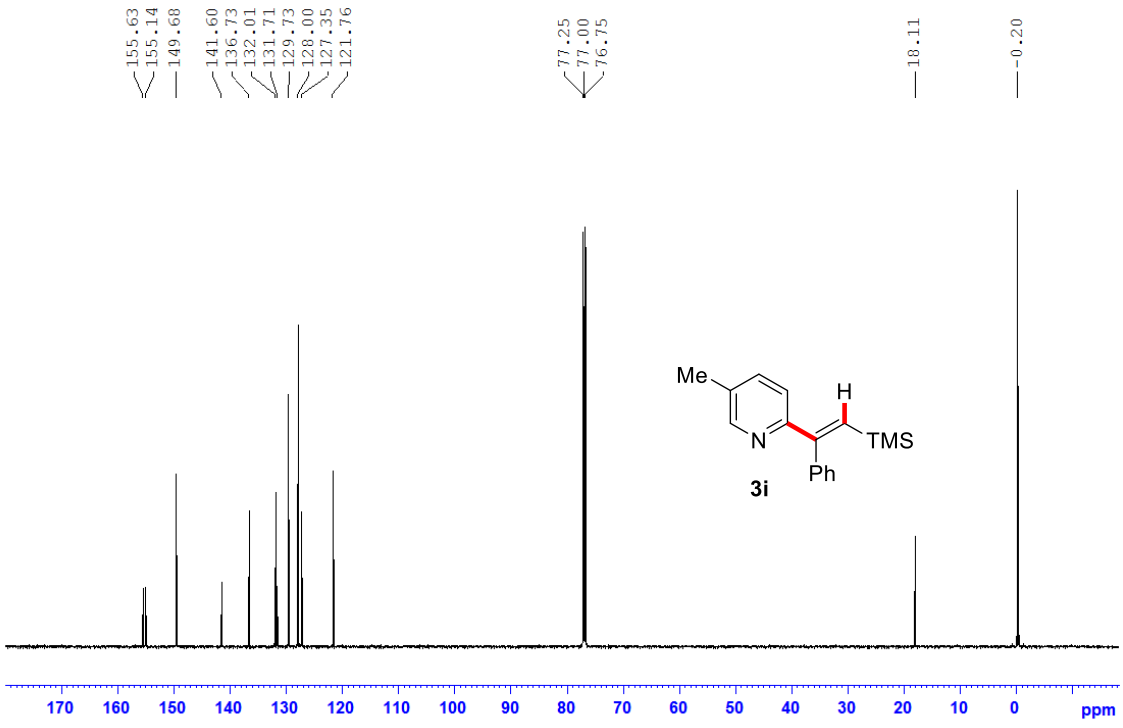
zw-84-32-2c

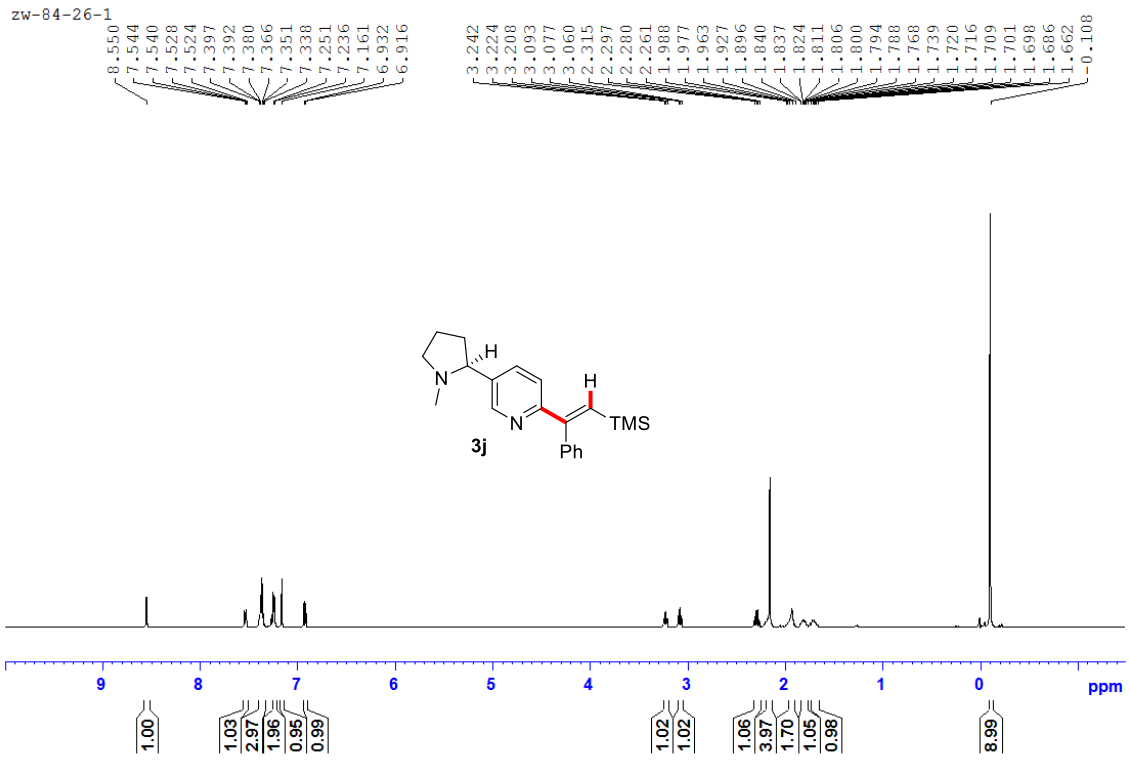


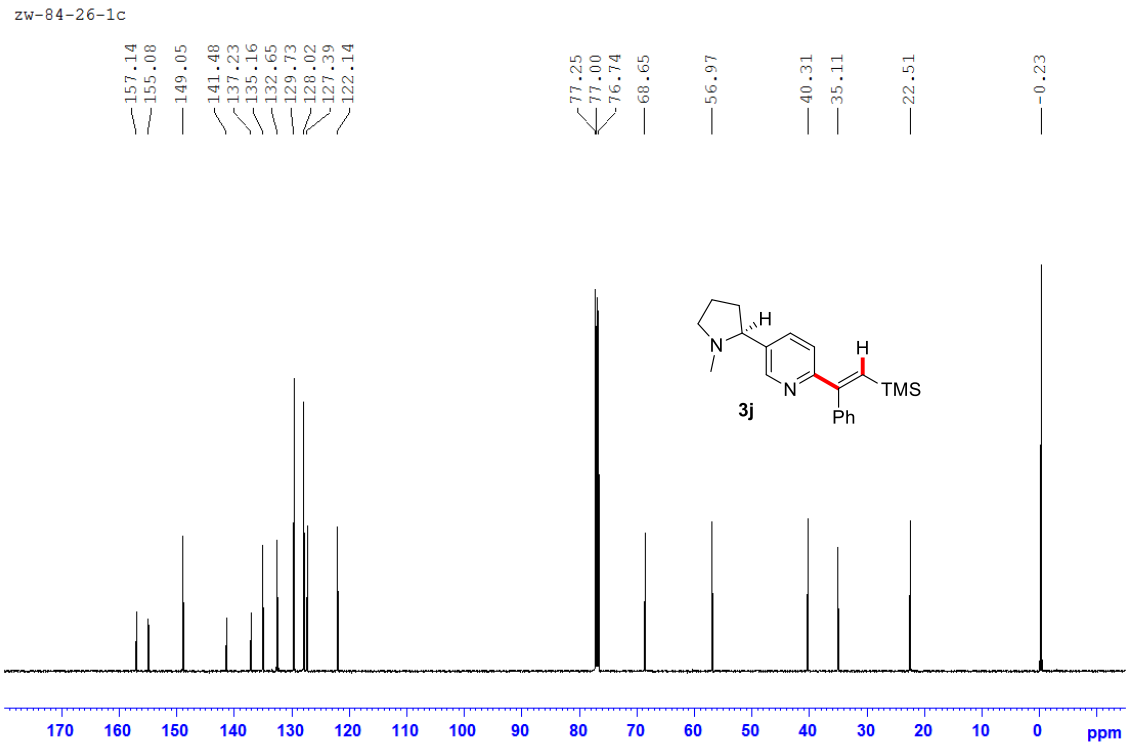
zw-84-29-2



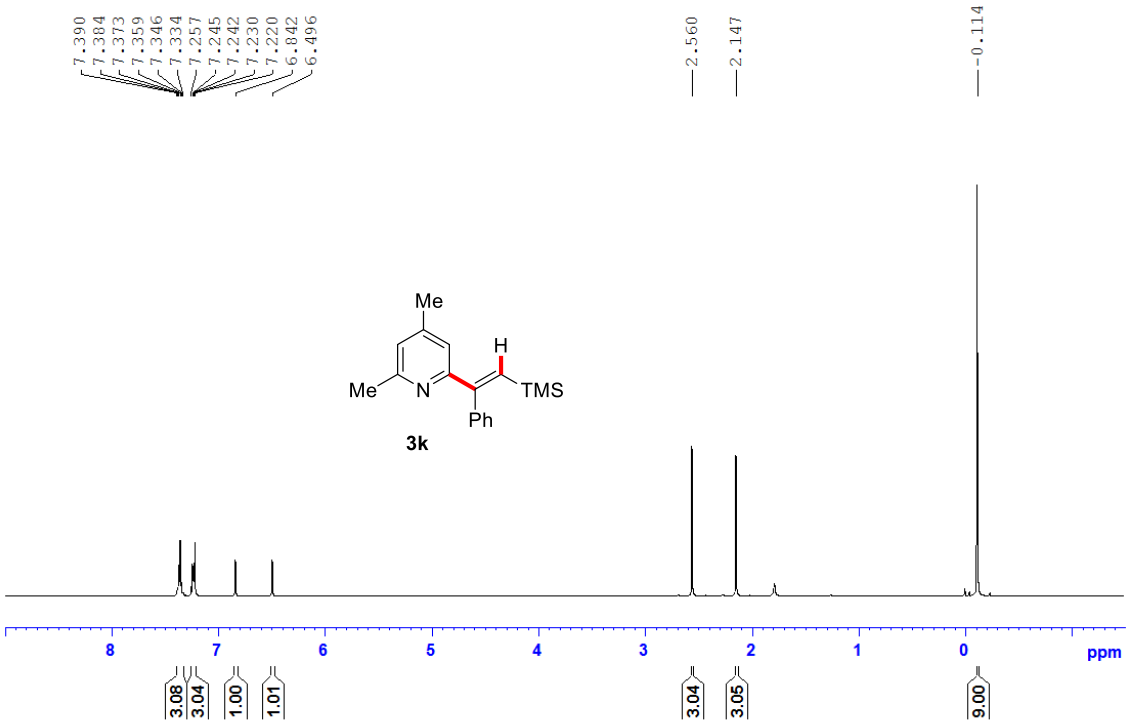
zw-84-29-2c



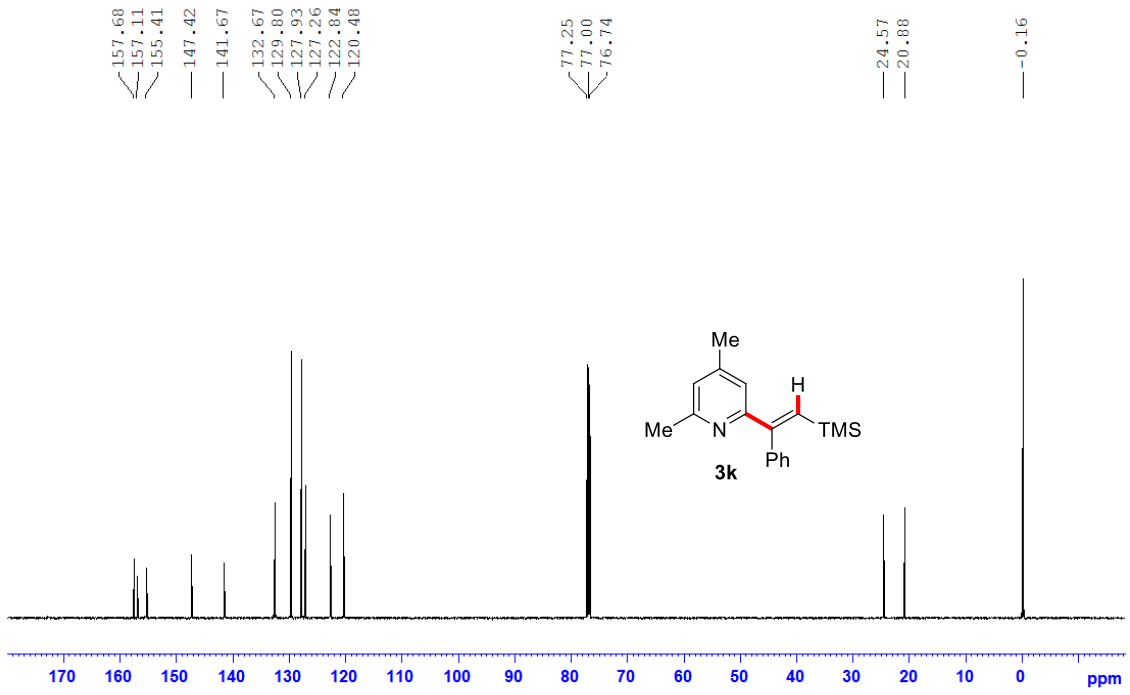

zw-84-26-1
8.550
7.544
7.540
7.528
7.524
7.397
7.392
7.380
7.366
7.351
7.338
7.251
7.236
7.161
6.932
6.916
3.242
3.224
3.208
3.093
3.077
3.060
2.315
2.297
2.280
2.261
1.988
1.977
1.963
1.927
1.896
1.840
1.837
1.824
1.811
1.806
1.800
1.794
1.788
1.768
1.739
1.720
1.716
1.709
1.701
1.698
1.686
1.662
-0.108
H
N
H
N
TMS
Ph
3j
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.03
2.97
1.96
0.95
0.99
1.02
1.02
1.06
3.97
1.70
1.05
0.98
8.99


zw-84-26-1c
157.14
155.08
149.05
141.48
137.23
135.16
132.65
129.73
128.02
127.39
122.14
77.25
77.00
76.74
68.65
56.97
40.31
35.11
22.51
-0.23
H
N
H
N
TMS
Ph
3j
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

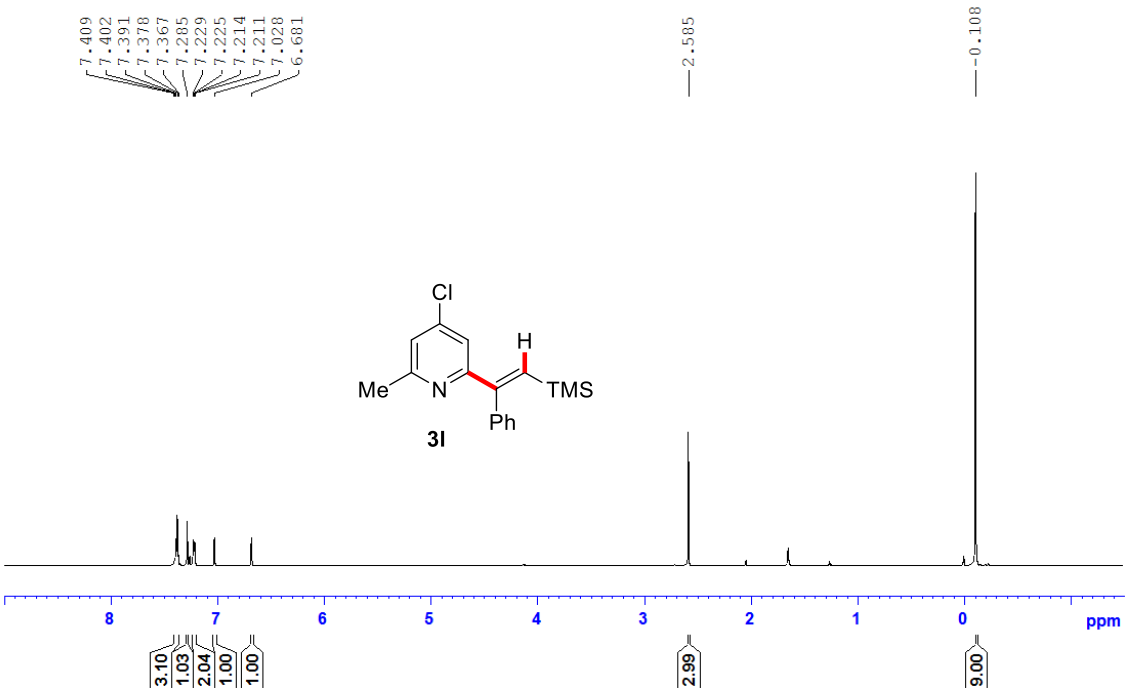
zw-84-23-3



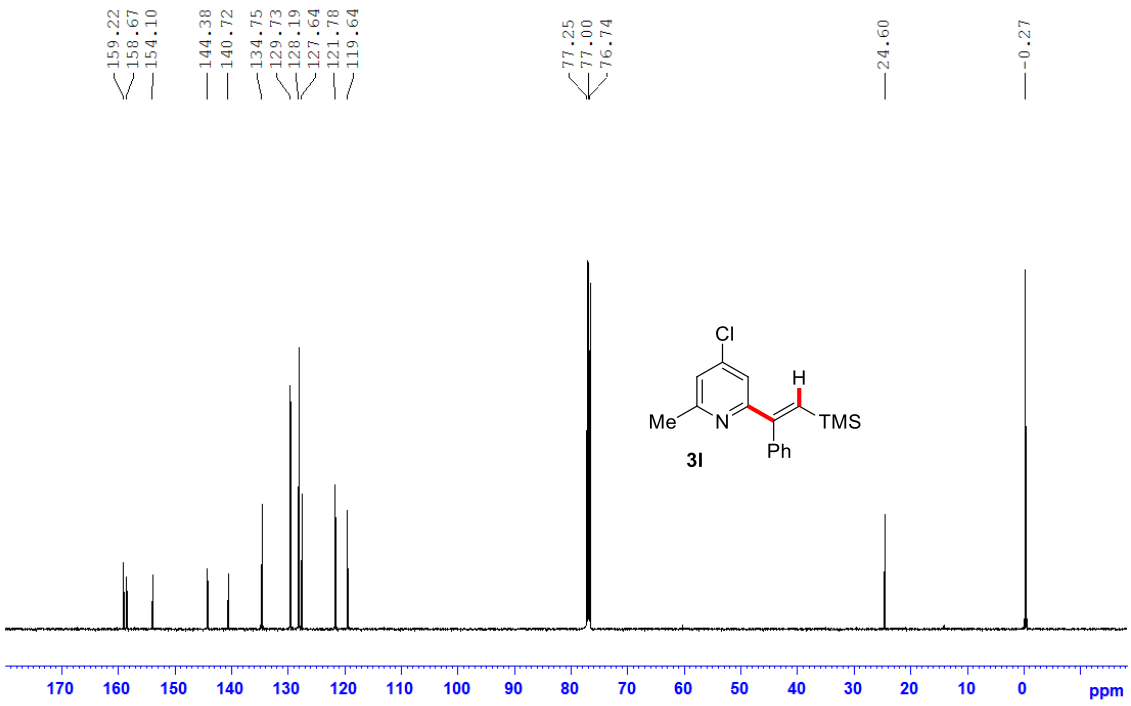
zw-84-23-3c

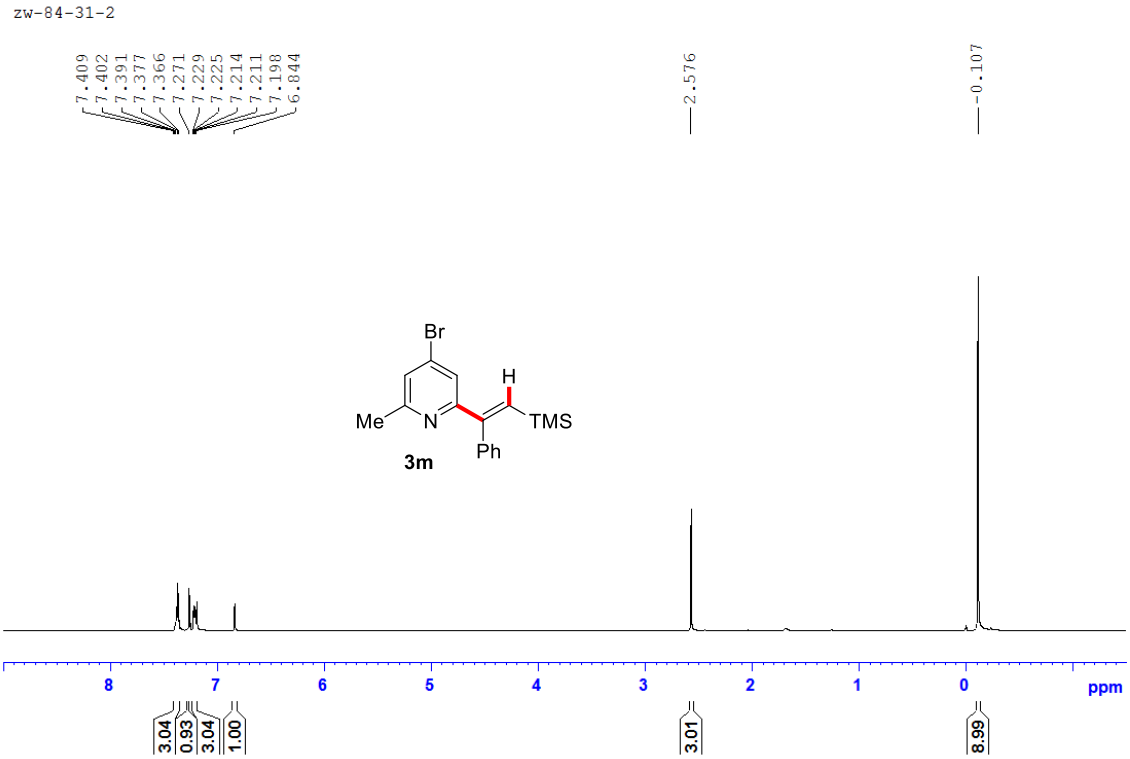


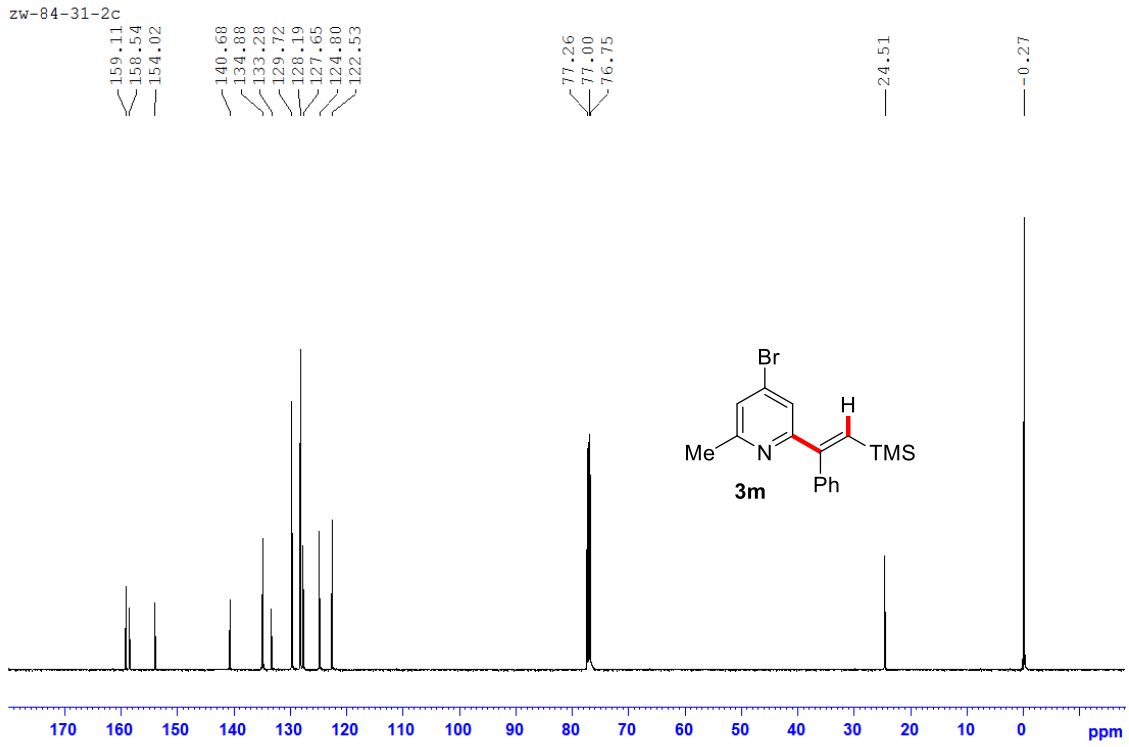
zw-84-31-1



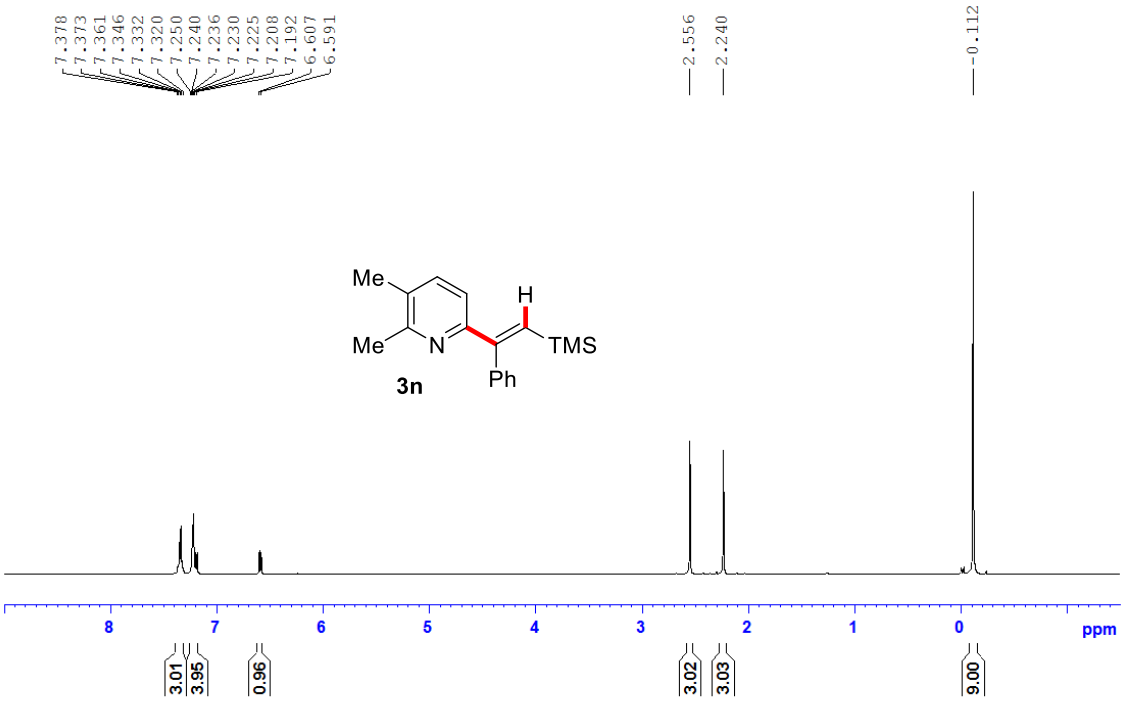
zw-84-31-1c



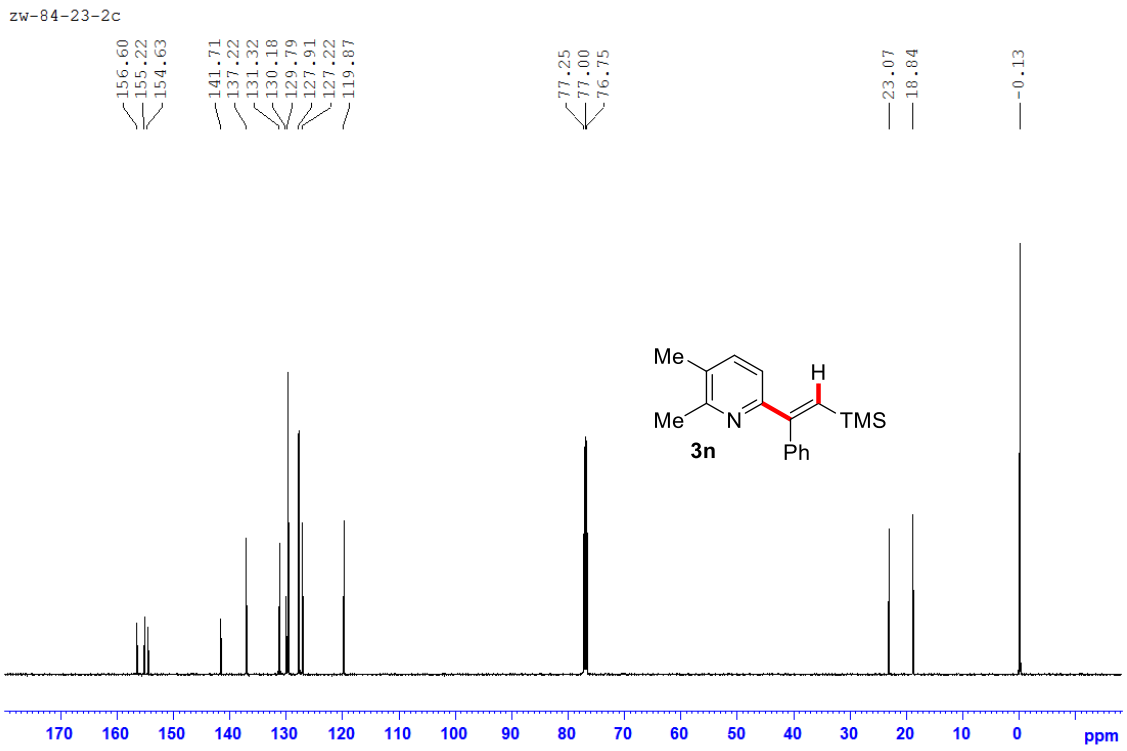

zw-84-31-2
7.409
7.402
7.391
7.377
7.366
7.271
7.229
7.225
7.214
7.211
7.198
6.844
2.576
0.107
Br
H
Me
N
TMS
Ph
3m
8
7
6
5
4
3
2
1
0
ppm
3.04
0.93
3.04
1.00
3.01
8.99

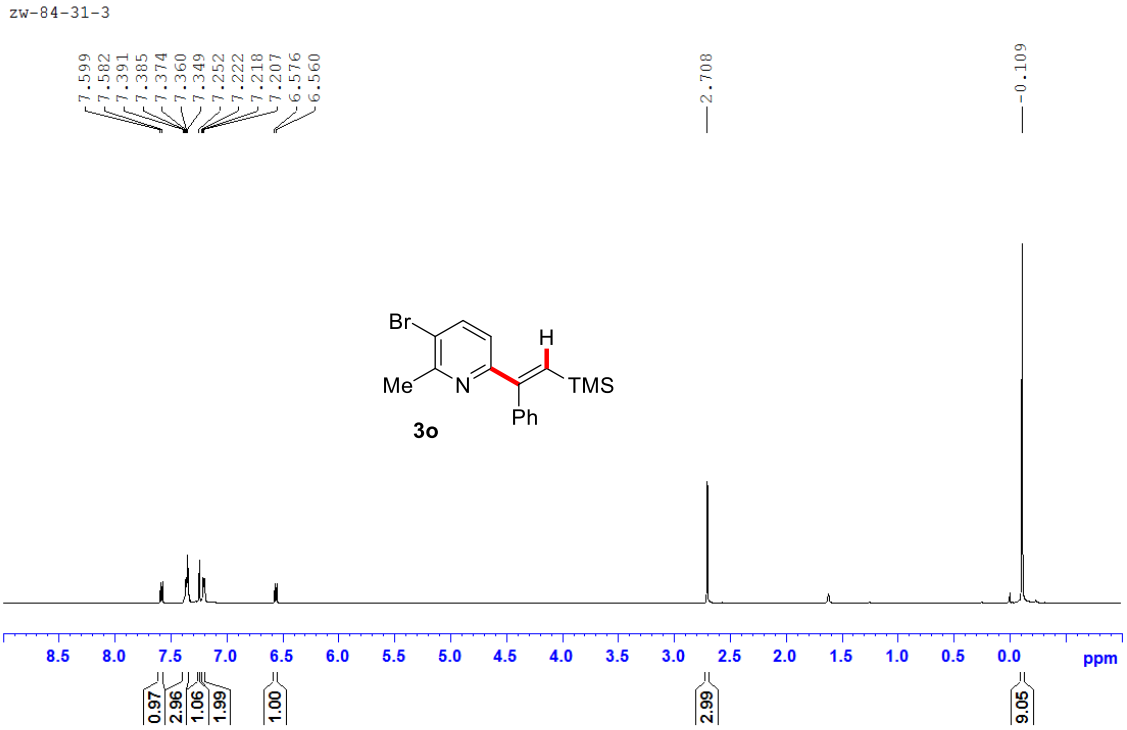

zw-84-31-2c
159.11
158.54
154.02
140.68
134.88
133.28
129.72
128.19
127.65
124.80
122.53
77.26
77.00
76.75
24.51
0.27
Br
H
Me
N
TMS
Ph
3m
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

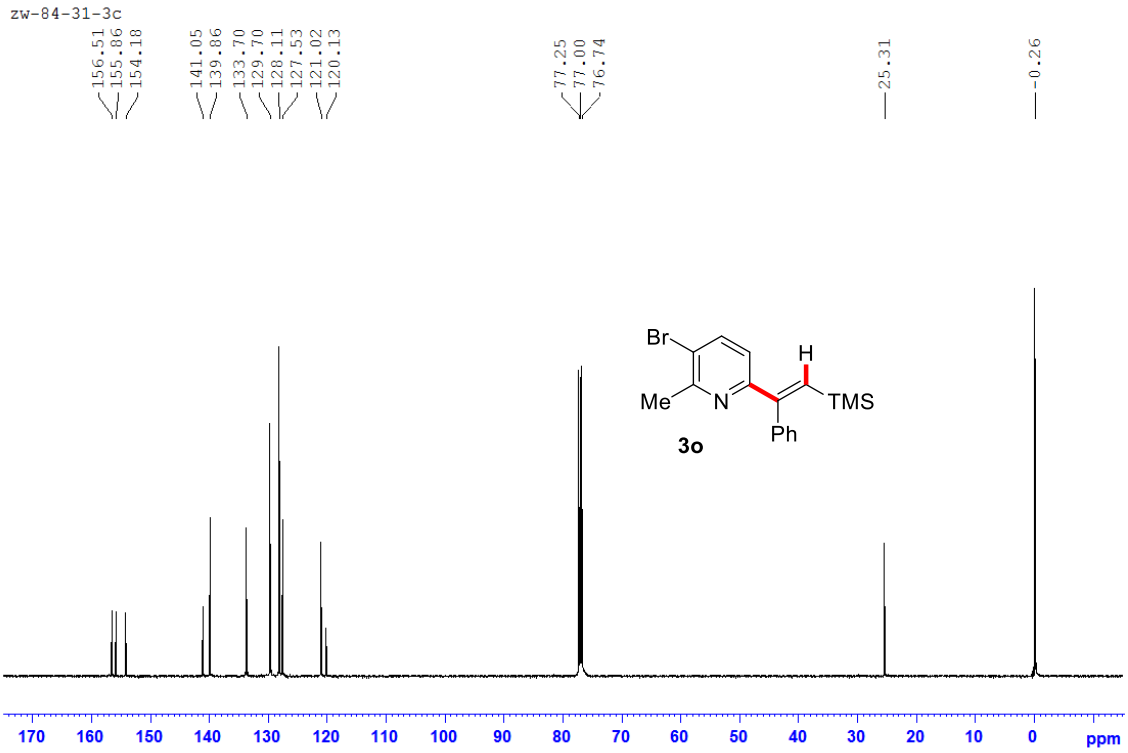
zw-84-23-2

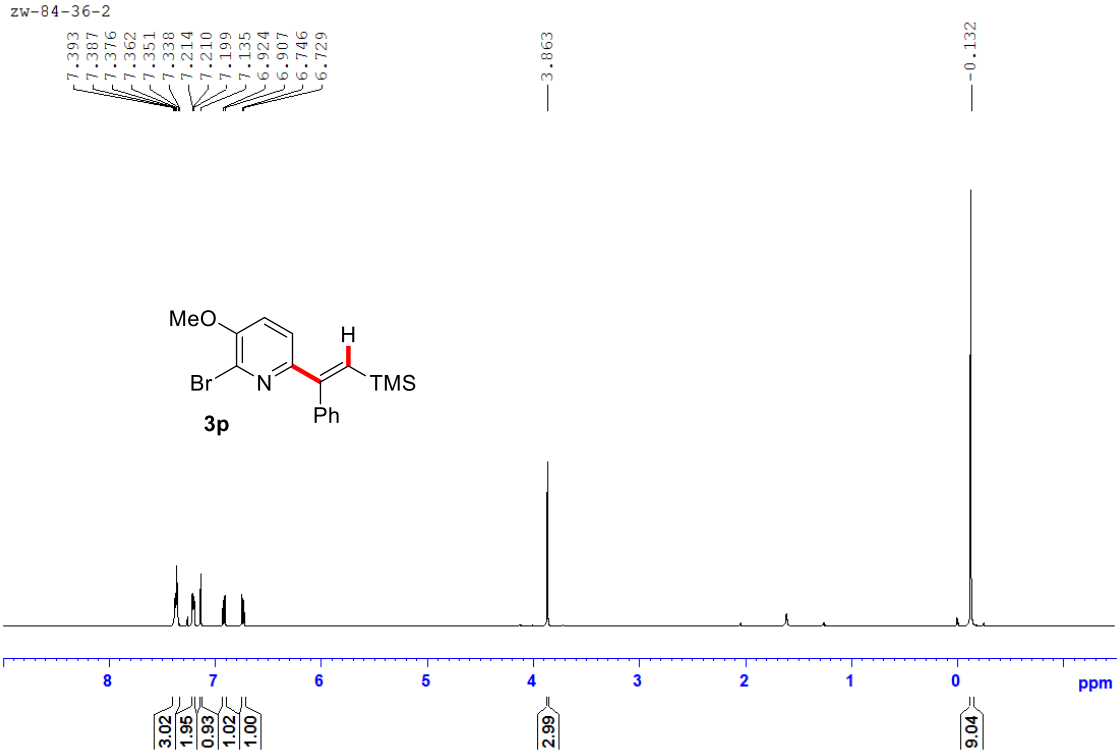


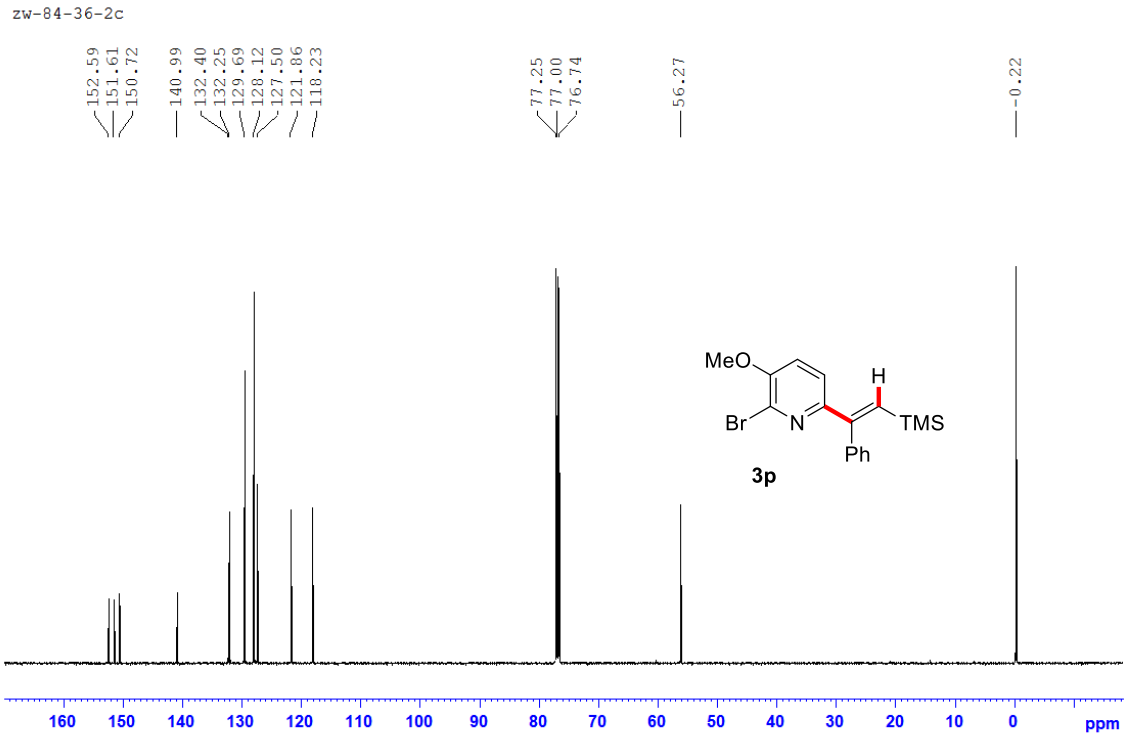
zw-84-23-2c

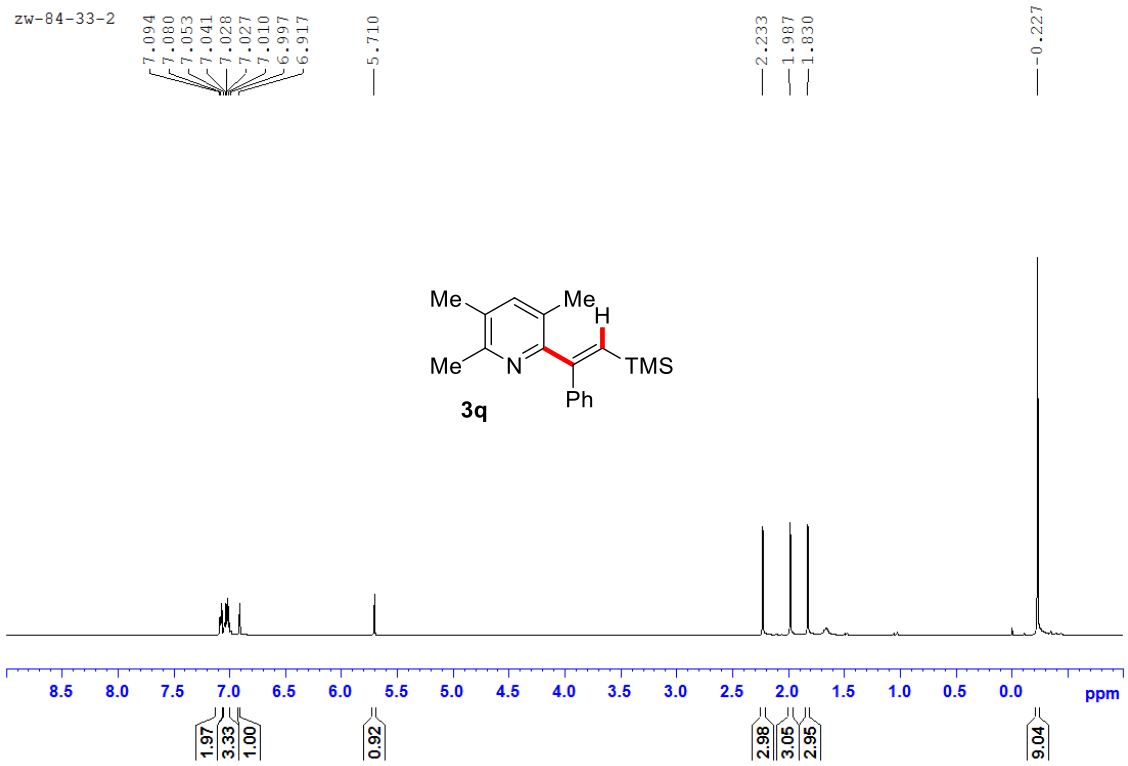


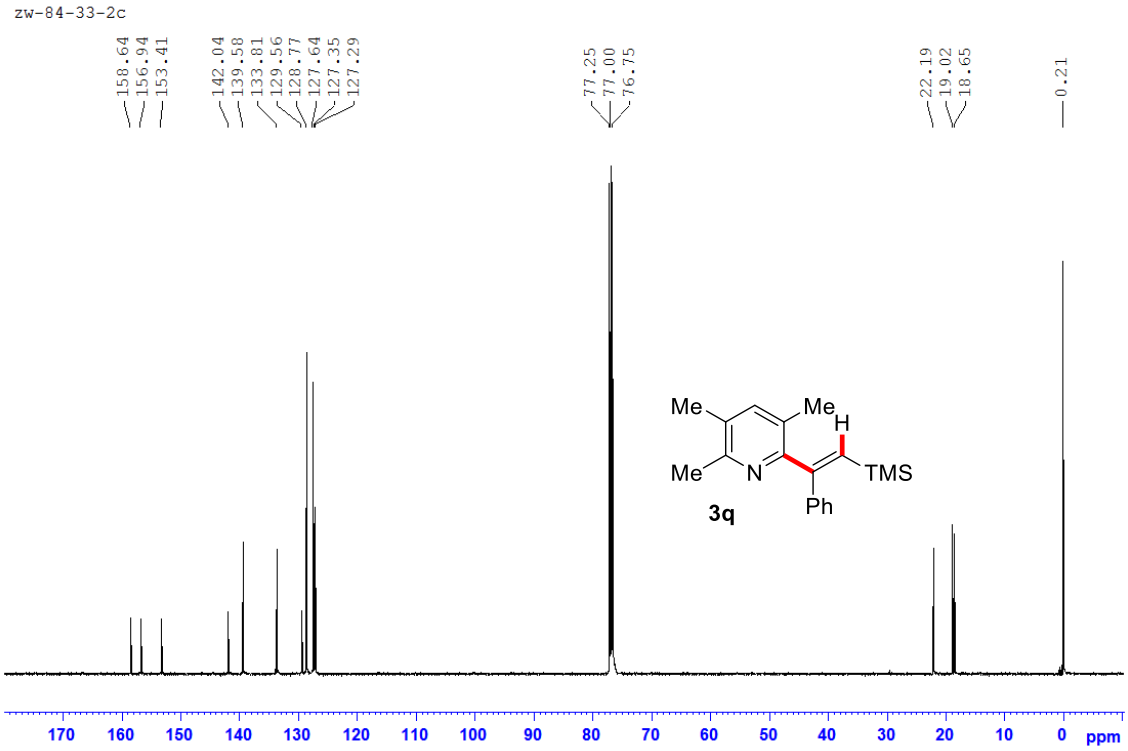

zw-84-31-3
7.599
7.582
7.391
7.385
7.374
7.360
7.349
7.252
7.222
7.218
7.207
6.576
6.560
2.708
0.109
Br
H
Me
N
TMS
Ph
3o
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.97
2.96
1.06
1.99
1.00
2.99
9.05


zw-84-31-3c
156.51
155.86
154.18
141.05
139.86
133.70
129.70
128.11
127.53
121.02
120.13
77.25
77.00
76.74
25.31
-0.26
Br
H
Me
N
TMS
Ph
3o
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

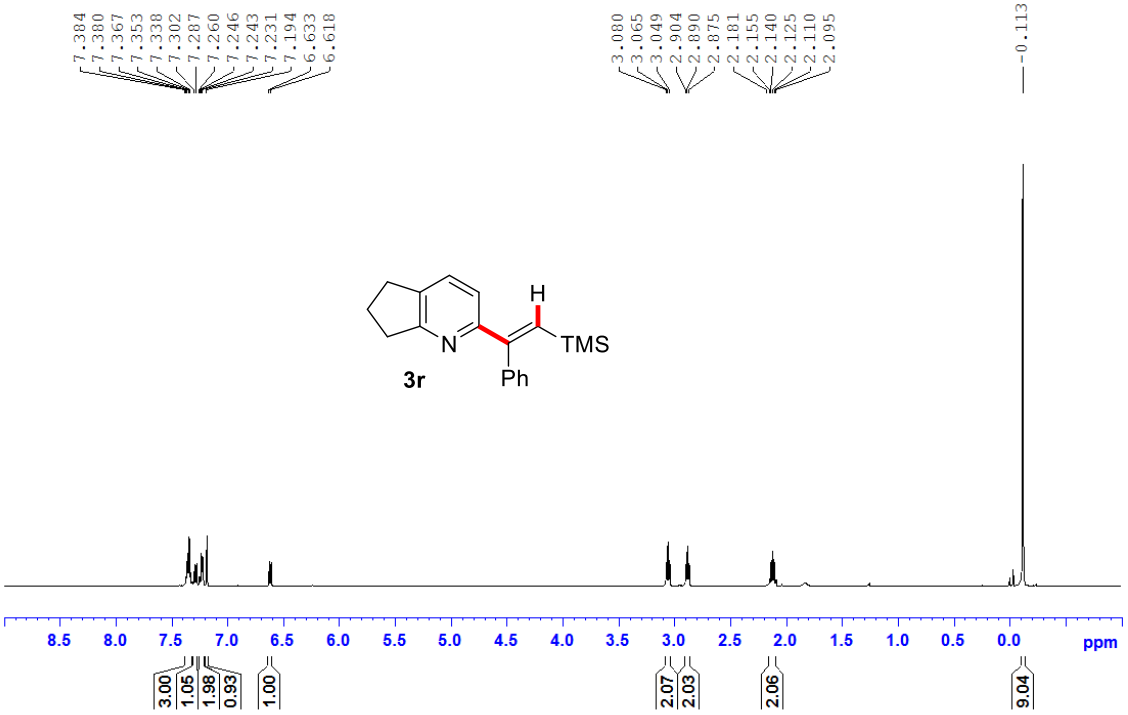

zw-84-36-2
7.393
7.387
7.376
7.362
7.351
7.338
7.214
7.210
7.199
7.135
6.924
6.907
6.746
6.729
3.863
0.132
MeO
Br
N
H
TMS
Ph
3p
8
7
6
5
4
3
2
1
0
ppm
3.02
1.95
0.93
1.02
1.00
2.99
9.04


zw-84-36-2c
152.59
151.61
150.72
140.99
132.40
132.25
129.69
128.12
127.50
121.86
118.23
77.25
77.00
76.74
56.27
0.22
MeO
Br
N
H
TMS
Ph
3p
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

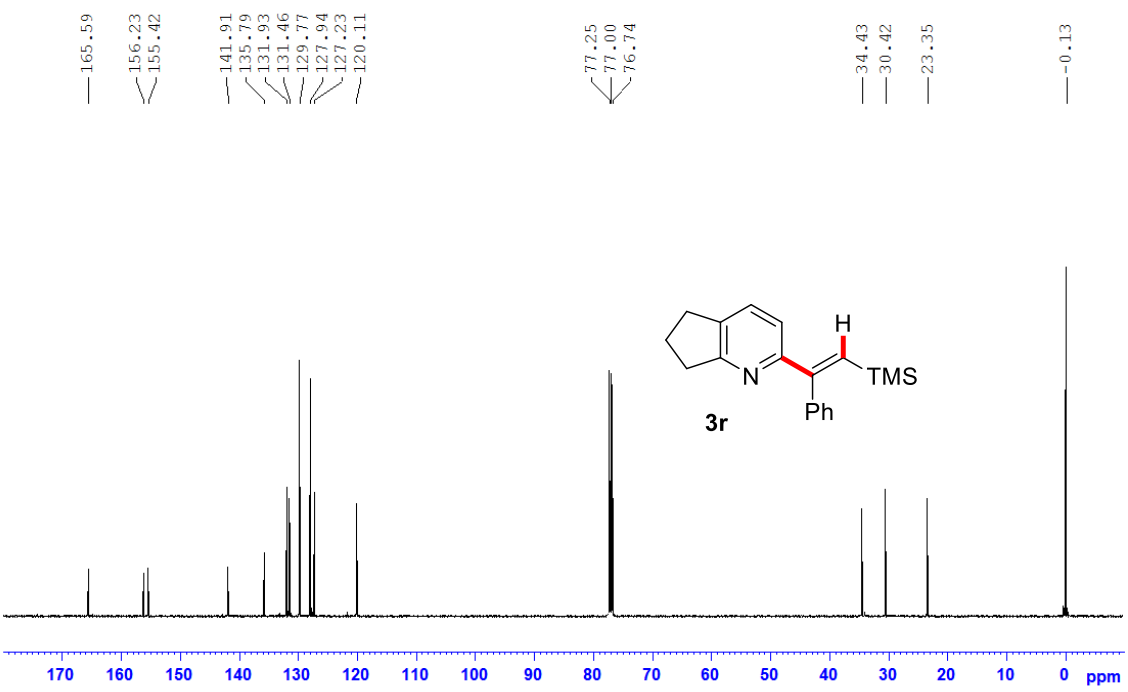

zw-84-33-2
7.094
7.080
7.053
7.041
7.028
7.027
7.010
6.997
6.917
5.710
2.233
1.987
1.830
0.227
Me
Me
H
Me
N
TMS
Ph
3q
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.97
3.33
1.00
0.92
2.98
3.05
2.95
9.04

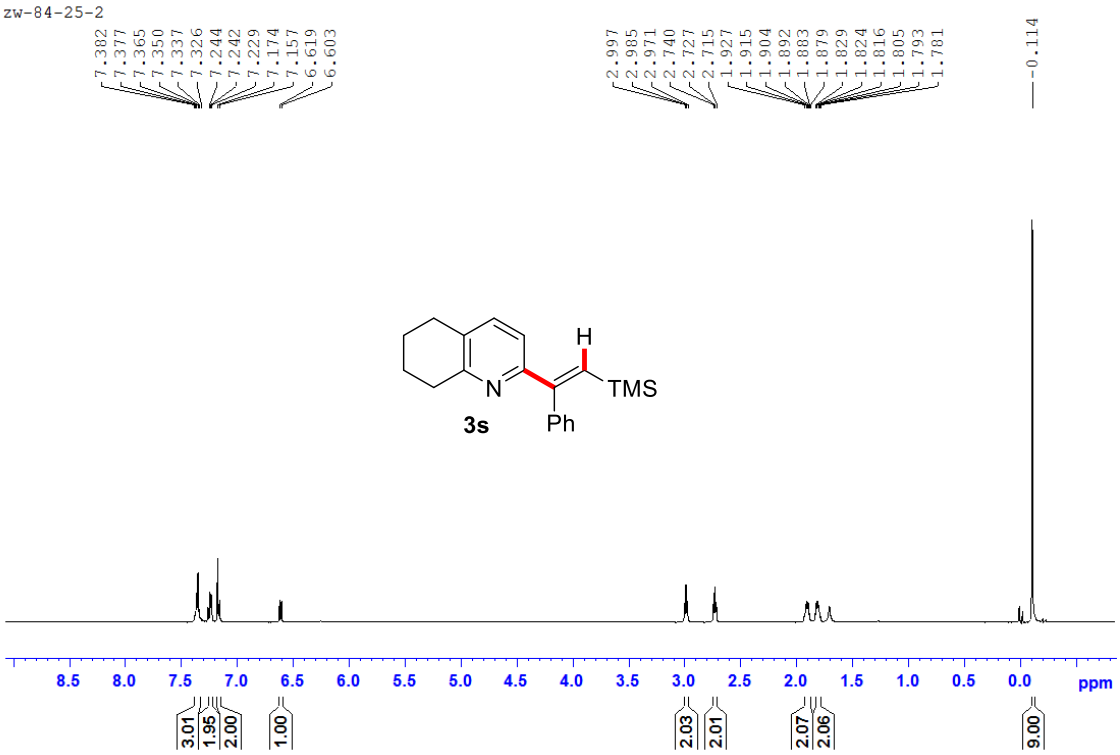

zw-84-33-2c
158.64
156.94
153.41
142.04
139.58
133.81
129.56
128.77
127.64
127.35
127.29
77.25
77.00
76.75
22.19
19.02
18.65
0.21
Me
Me
H
Me
N
TMS
Ph
3q
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

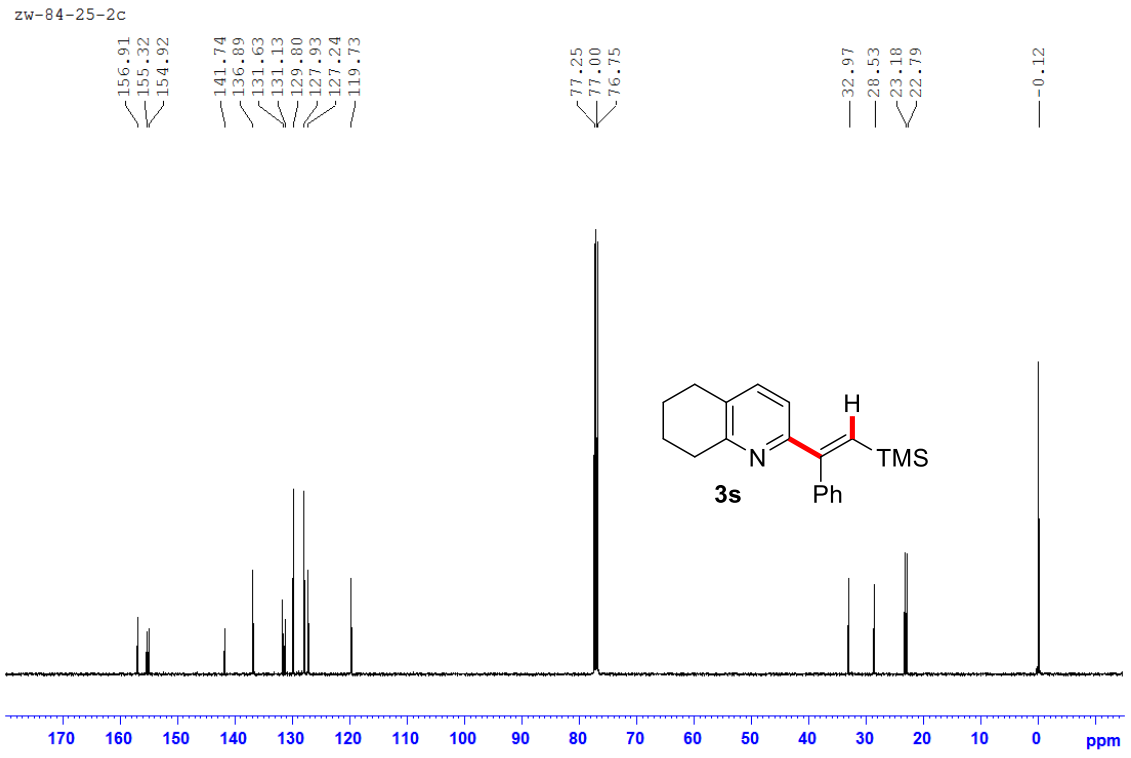
zw-84-25-1

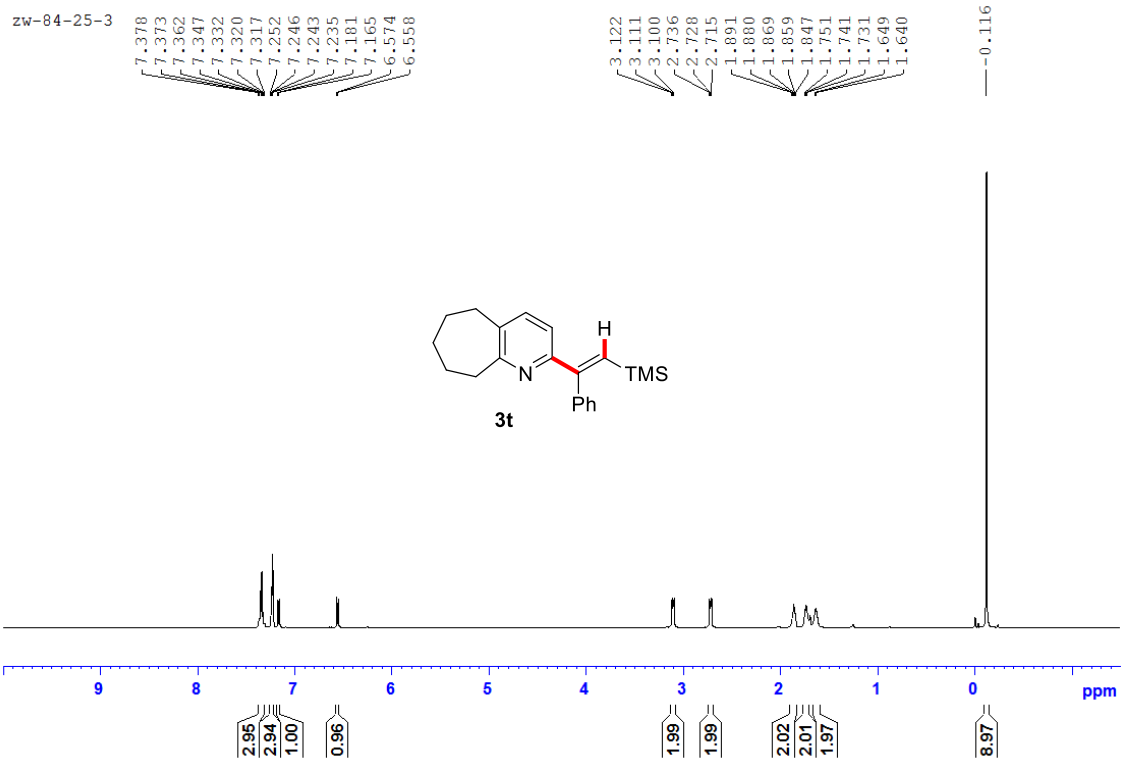


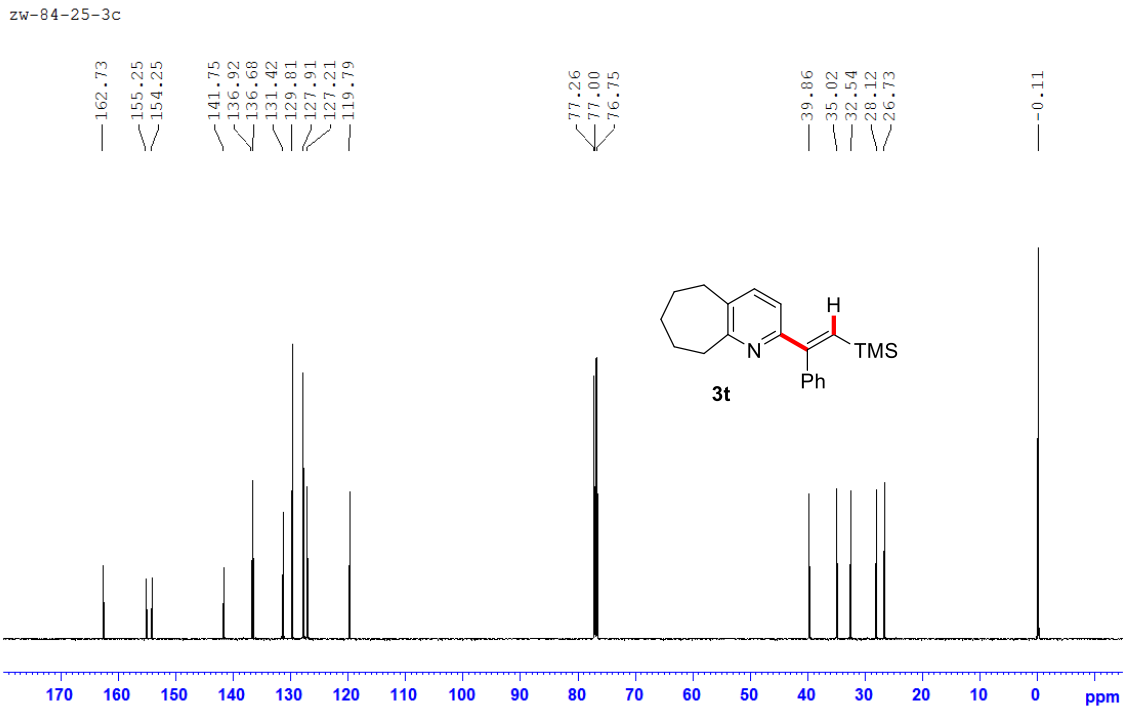
zw-84-25-1c



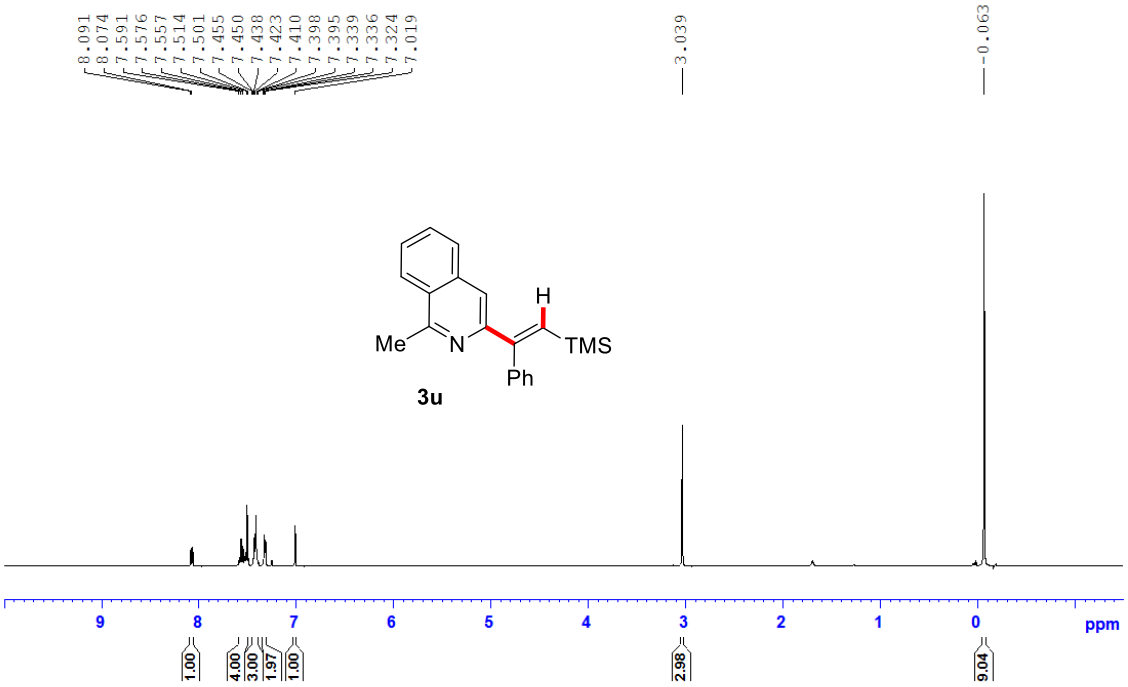

zw-84-25-2
7.382
7.377
7.365
7.350
7.337
7.326
7.244
7.242
7.229
7.174
7.157
6.619
6.603
2.997
2.985
2.971
2.740
2.727
2.715
1.927
1.915
1.904
1.892
1.883
1.879
1.829
1.824
1.816
1.805
1.793
1.781
-0.114
H
N
TMS
Ph
3s
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
3.01
1.95
2.00
1.00
2.03
2.01
2.07
2.06
9.00


zw-84-25-2c
156.91
155.32
154.92
141.74
136.89
131.63
131.13
129.80
127.93
127.24
119.73
77.25
77.00
76.75
32.97
28.53
23.18
22.79
-0.12
H
N
TMS
Ph
3s
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

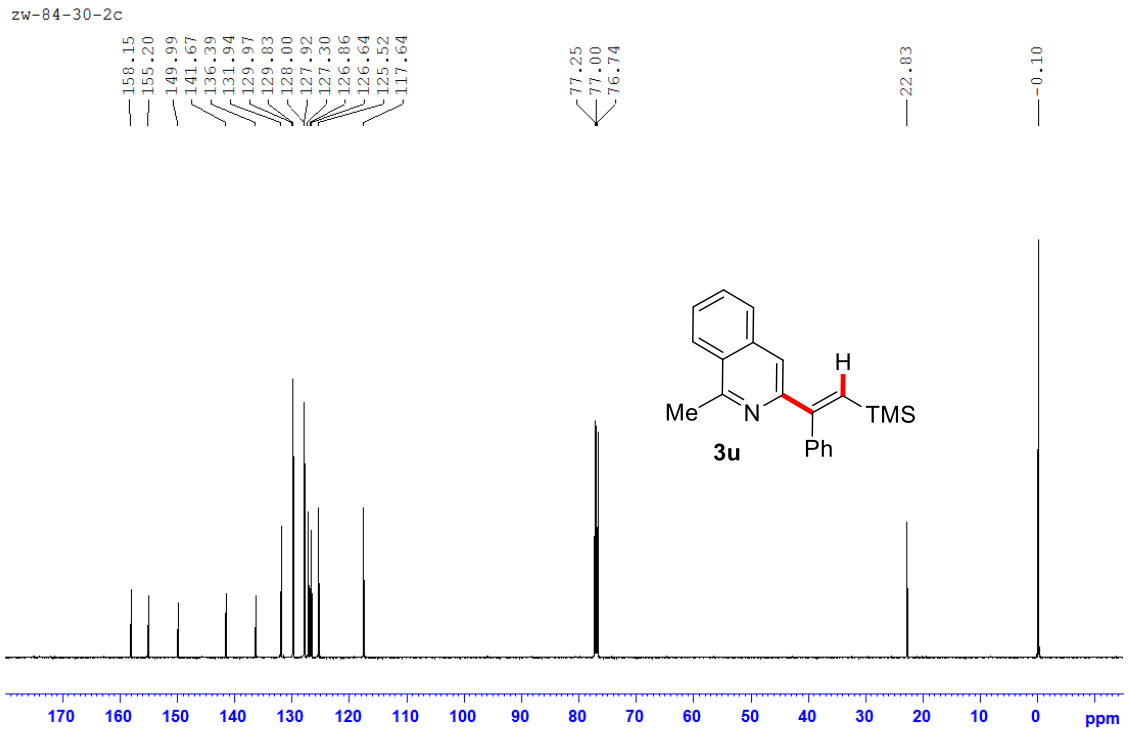

zw-84-25-3
7.378
7.373
7.362
7.347
7.332
7.320
7.317
7.252
7.246
7.243
7.235
7.181
7.165
6.574
6.558
3.122
3.111
3.100
2.736
2.728
2.715
1.891
1.880
1.869
1.859
1.847
1.751
1.741
1.731
1.649
1.640
0.116
H
N
TMS
Ph
3t
9
8
7
6
5
4
3
2
1
0
ppm
2.95
2.94
1.00
0.96
1.99
1.99
2.02
2.01
1.97
8.97


zw-84-25-3c
162.73
155.25
154.25
141.75
136.92
136.68
131.42
129.81
127.91
127.21
119.79
77.26
77.00
76.75
39.86
35.02
32.54
28.12
26.73
0.11
H
N
TMS
Ph
3t
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

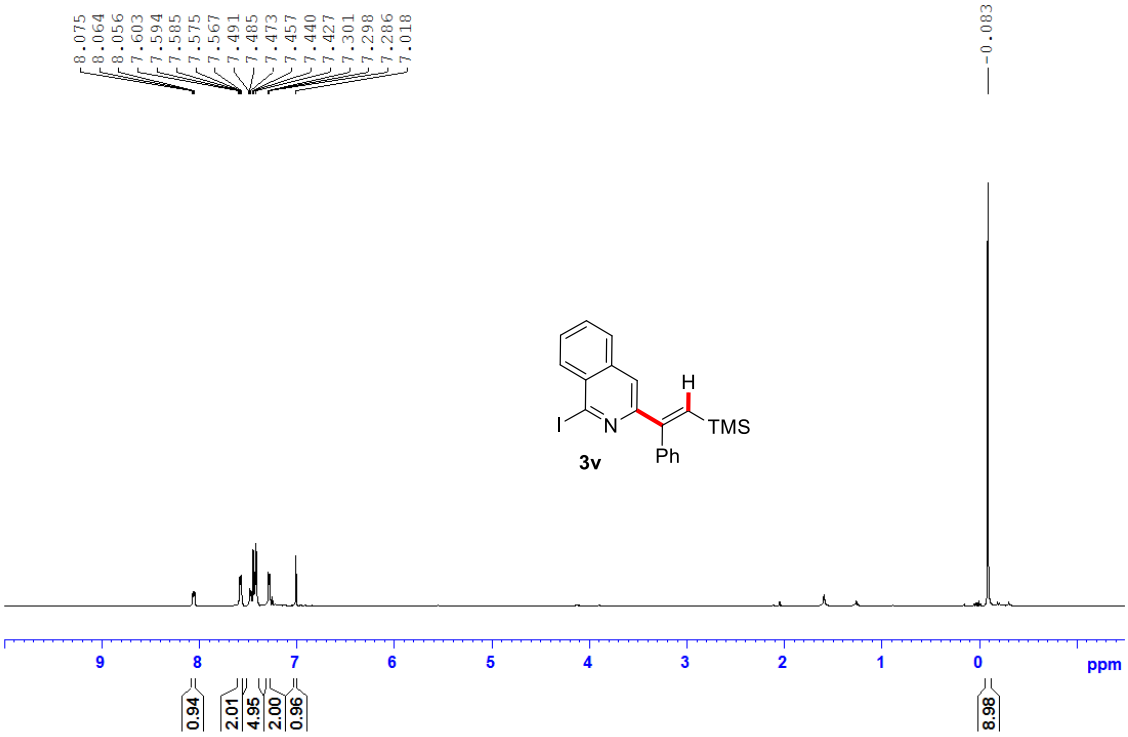
zw-84-30-2



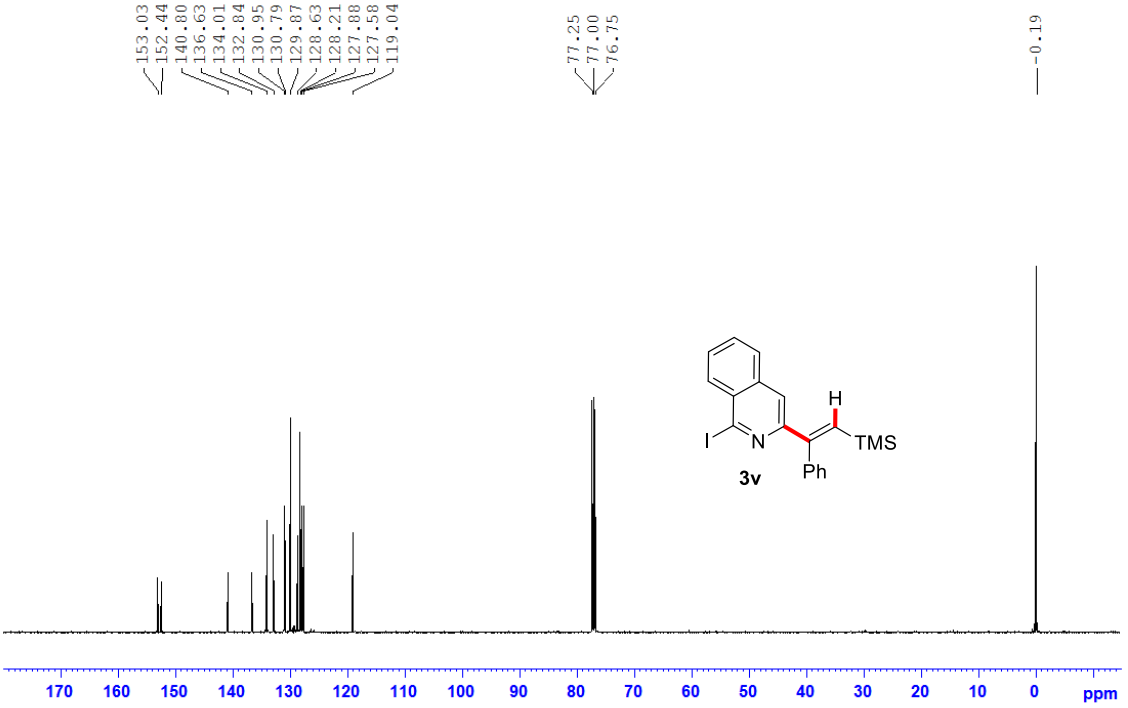
zw-84-30-2c

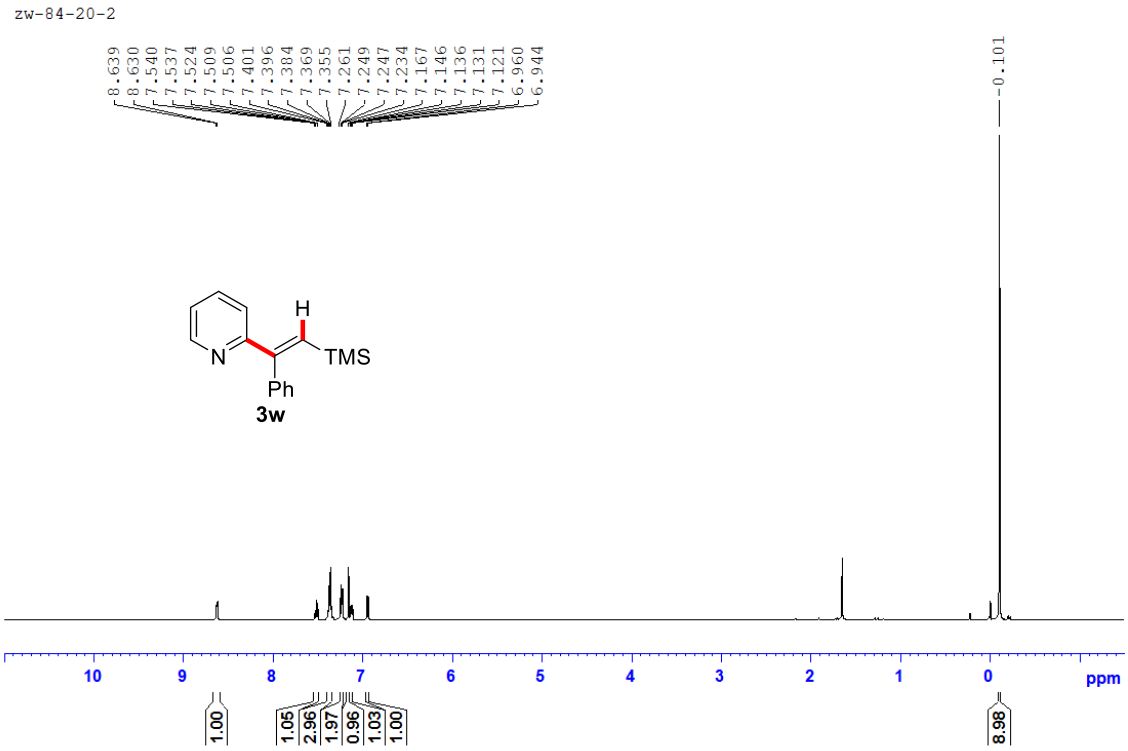


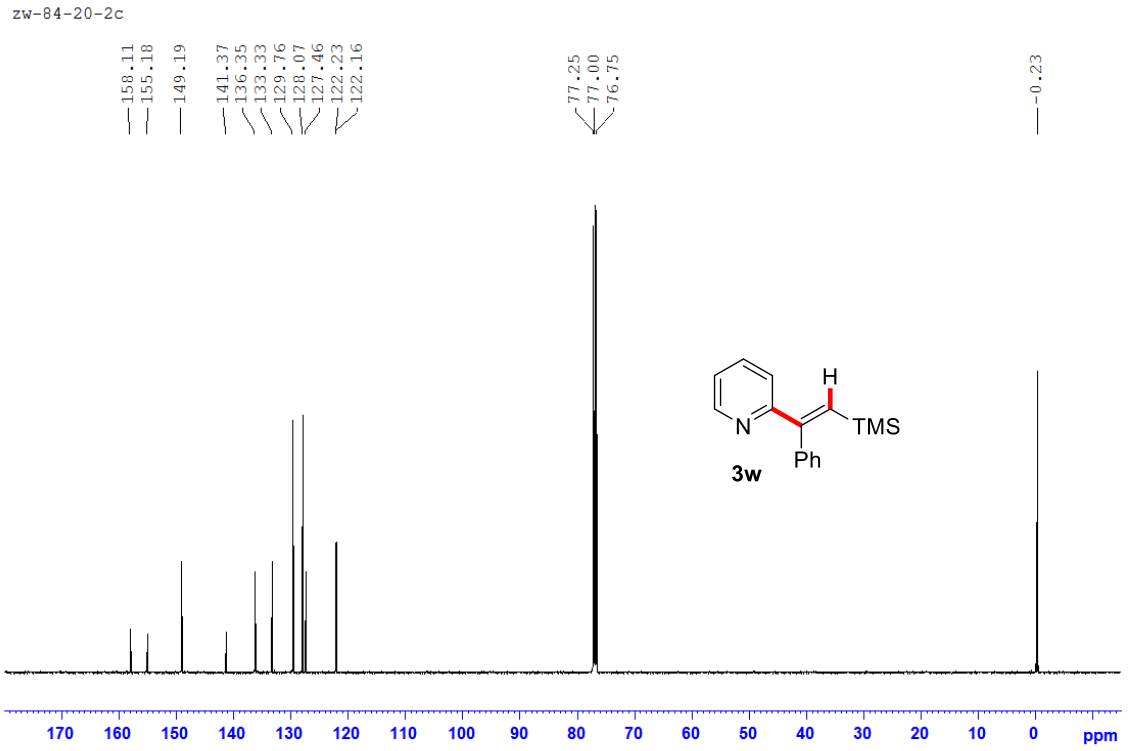
zw-84-30-3



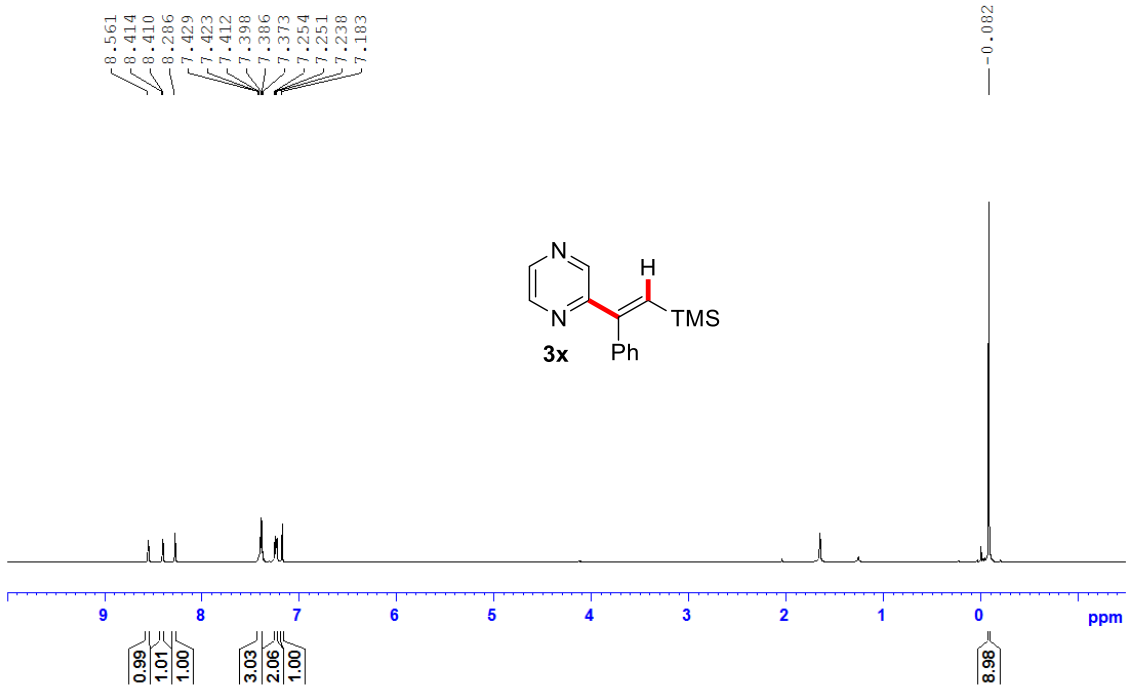
zw-84-30-3c



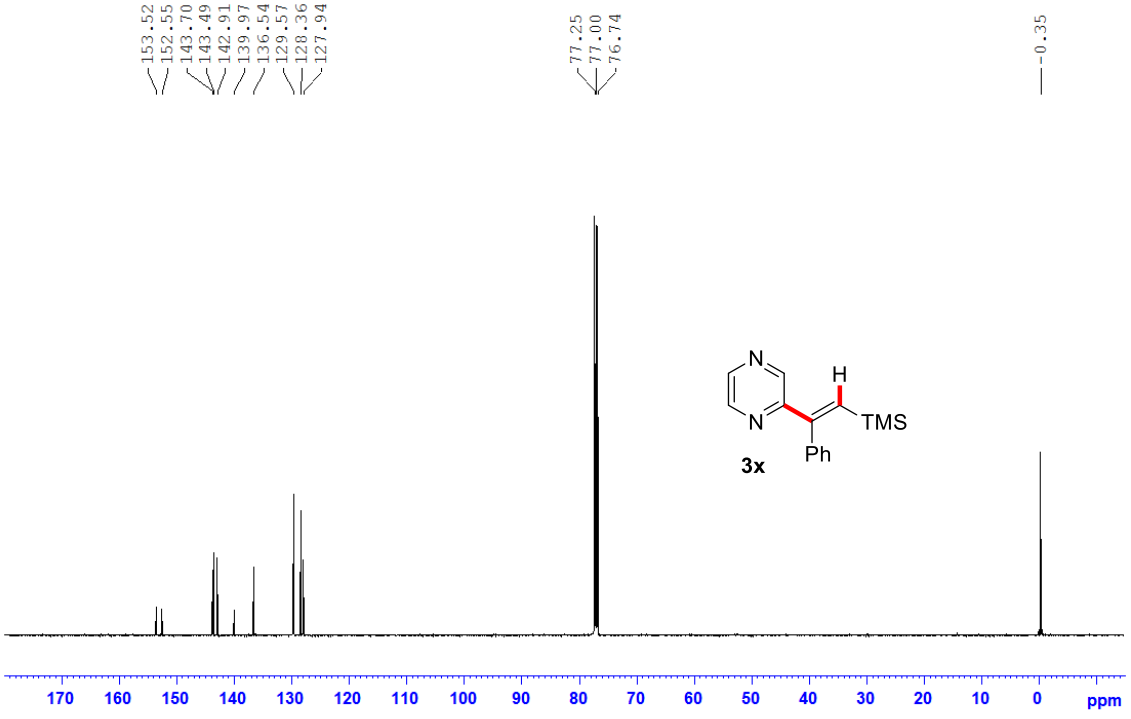

zw-84-20-2
8.639
8.630
7.540
7.537
7.524
7.509
7.506
7.401
7.396
7.384
7.369
7.355
7.261
7.249
7.247
7.234
7.167
7.146
7.136
7.131
7.121
6.960
6.944
0.101
H
N
TMS
Ph
3w
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.05
2.96
1.97
0.96
1.03
1.00
8.98


zw-84-20-2c
158.11
155.18
149.19
141.37
136.35
133.33
129.76
128.07
127.46
122.23
122.16
77.25
77.00
76.75
-0.23
H
N
TMS
Ph
3w
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

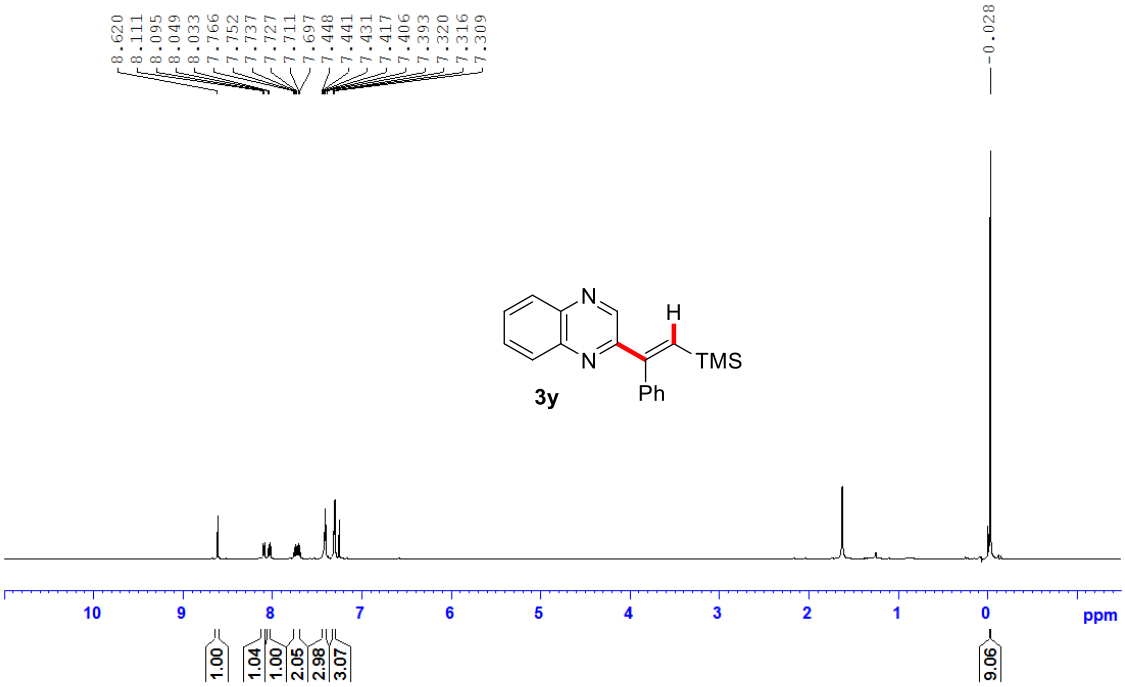
zw-84-28-1



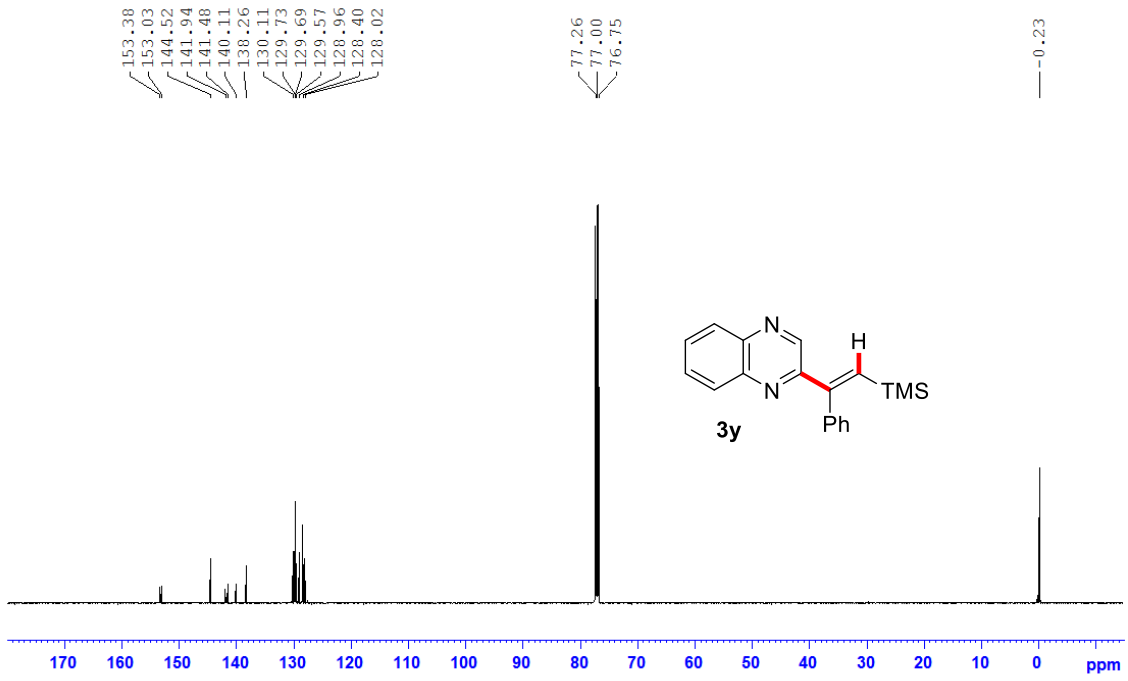
zw-84-28-1c

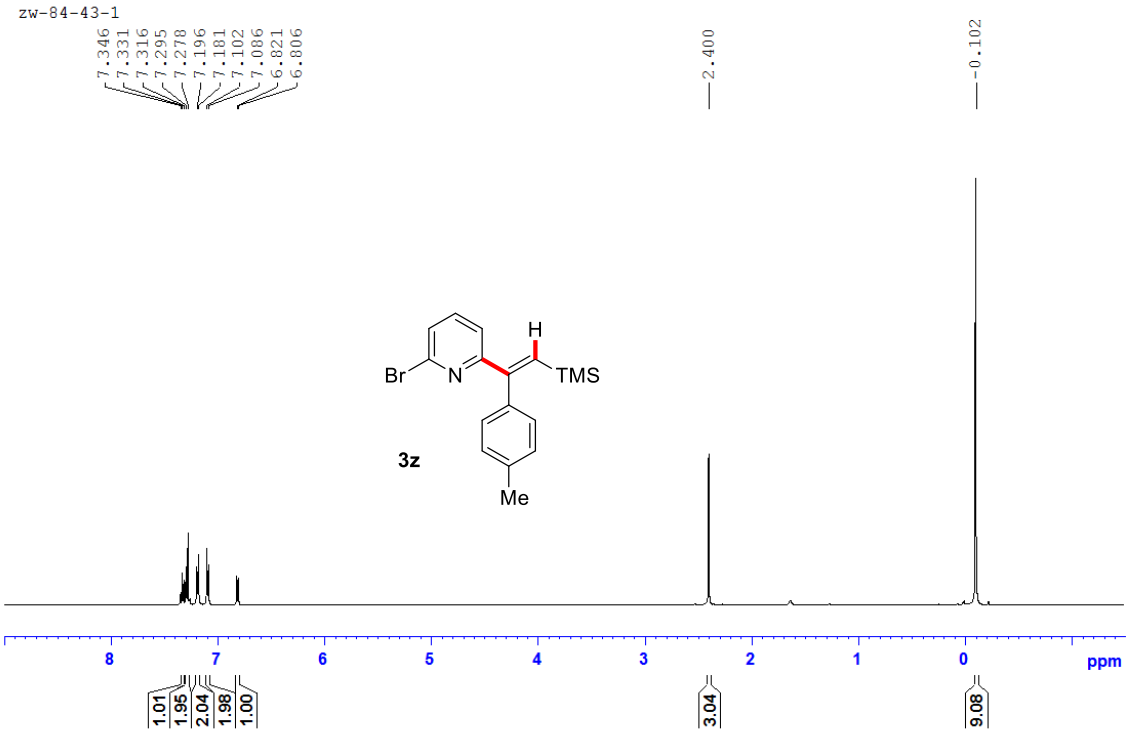


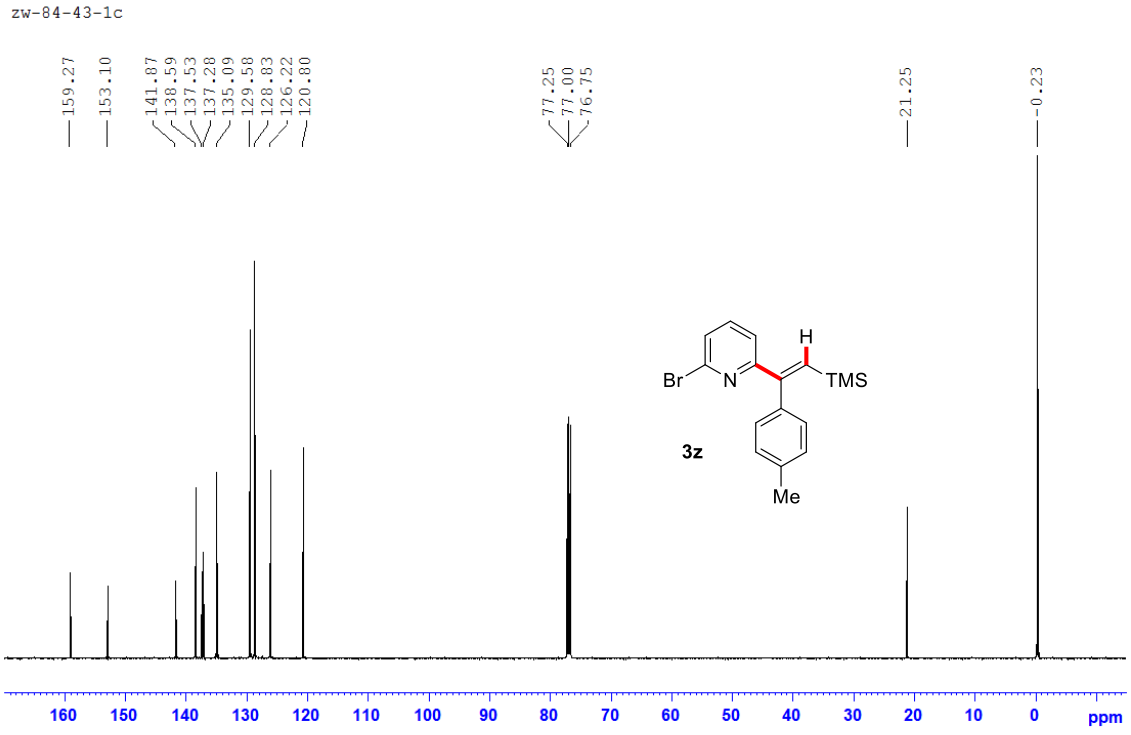
zw-84-30-1

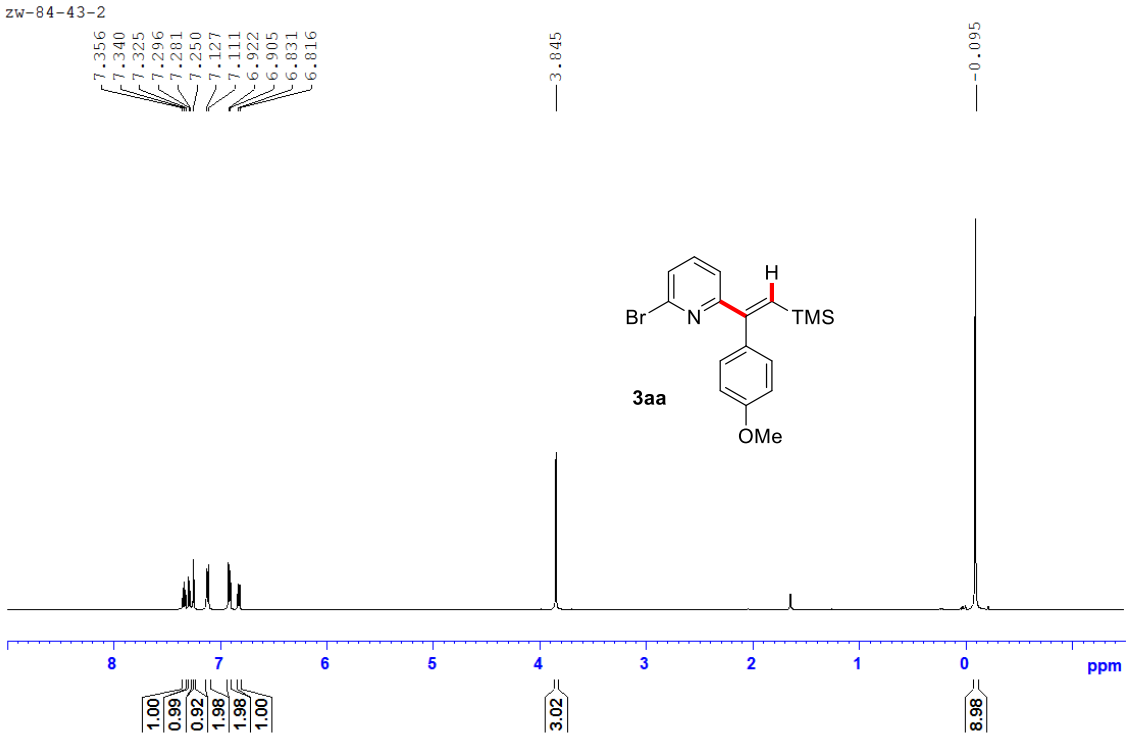


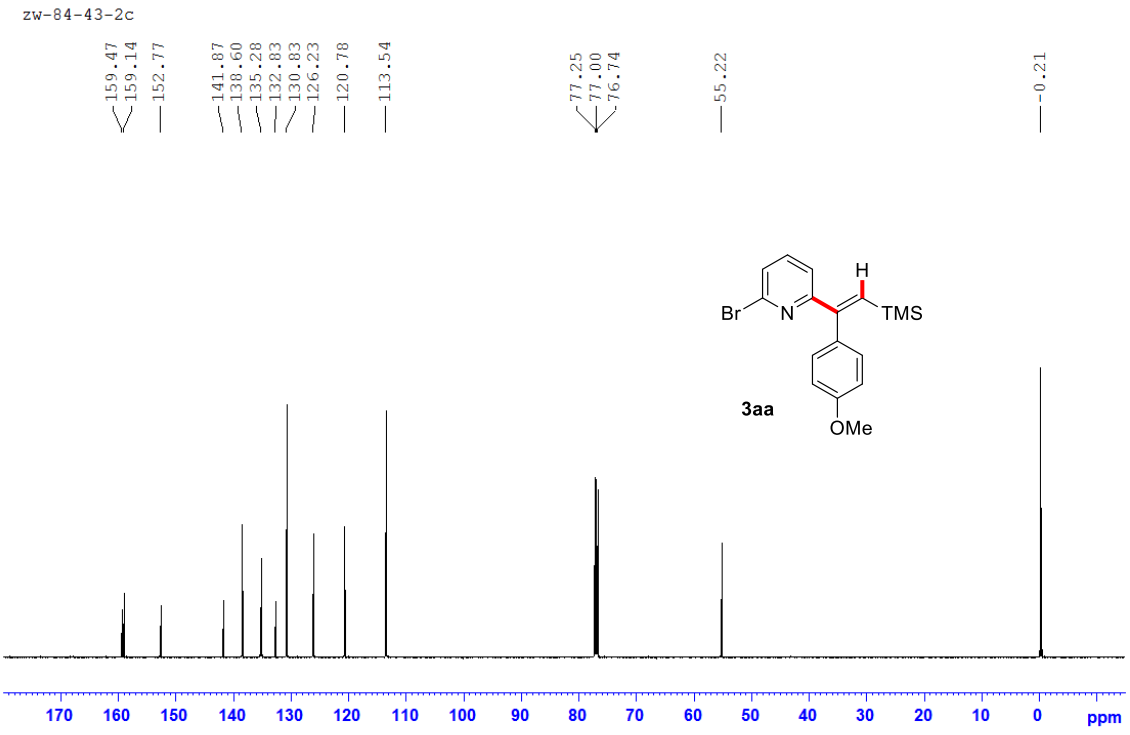
zw-84-30-1c



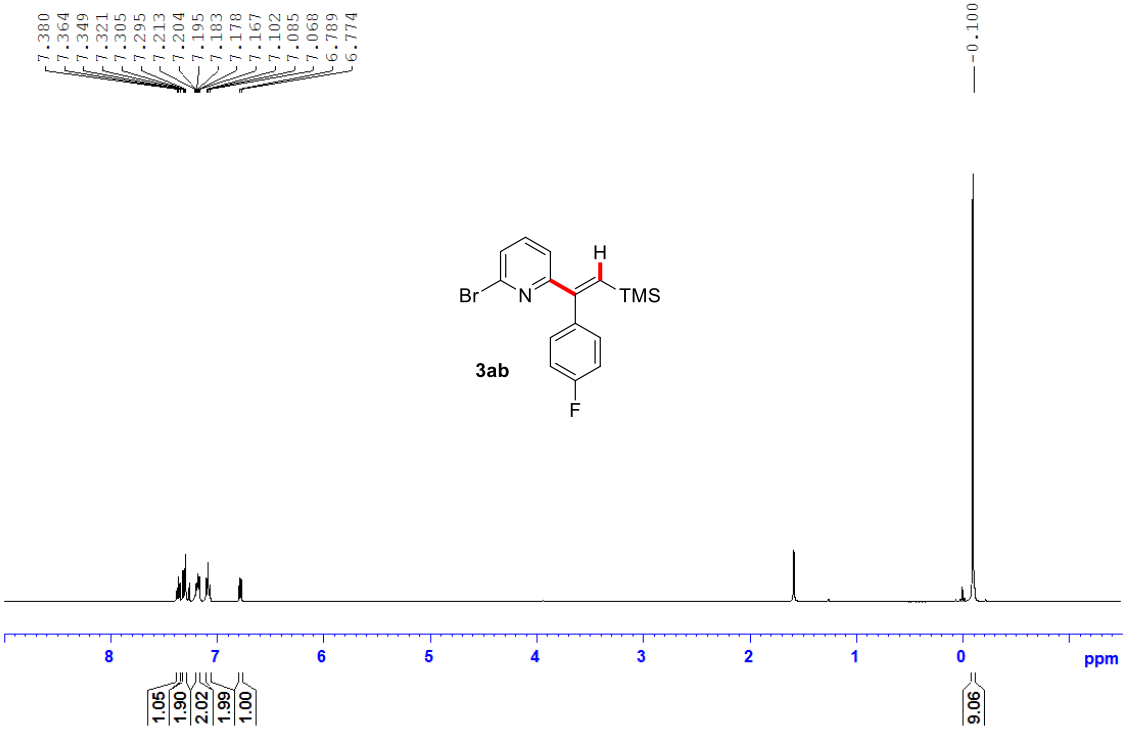

zw-84-43-1
7.346
7.331
7.316
7.295
7.278
7.196
7.181
7.102
7.086
6.821
6.806
2.400
0.102
H
Br
N
TMS
3z
Me
8
7
6
5
4
3
2
1
0
ppm
1.01
1.95
2.04
1.98
1.00
3.04
9.08


zw-84-43-1c
159.27
153.10
141.87
138.59
137.53
137.28
135.09
129.58
128.83
126.22
120.80
77.25
77.00
76.75
21.25
0.23
H
Br
N
TMS
3z
Me
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

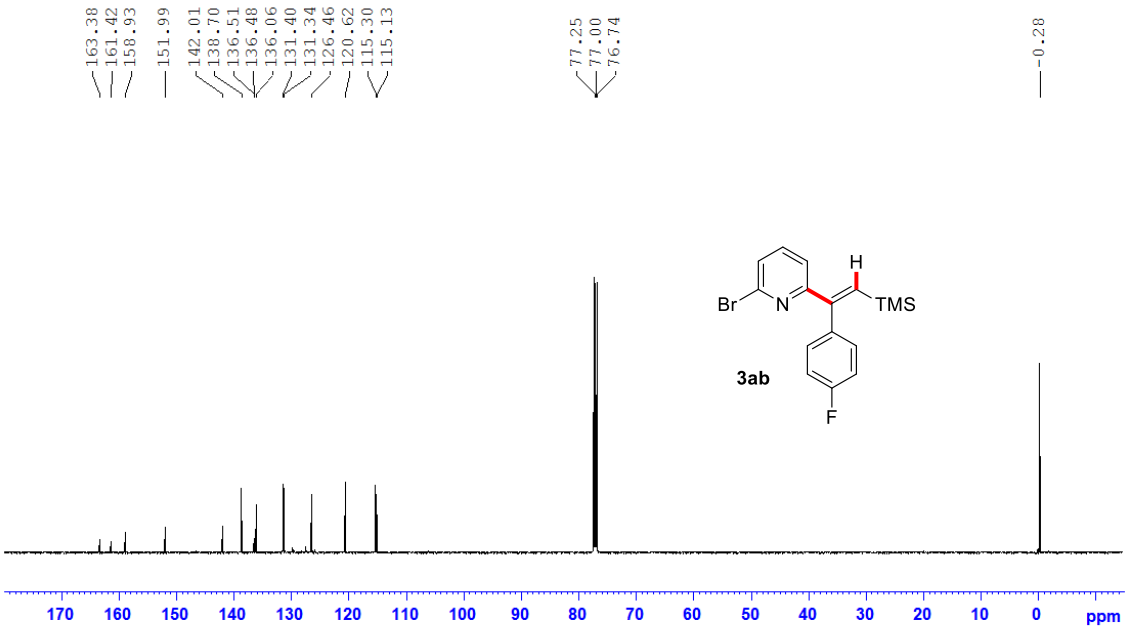

zw-84-43-2
7.356
7.340
7.325
7.296
7.281
7.250
7.127
7.111
6.922
6.905
6.831
6.816
3.845
0.095
Br
N
H
TMS
OMe
3aa
8
7
6
5
4
3
2
1
0
ppm
1.00
0.99
0.92
1.98
1.98
1.00
3.02
8.98

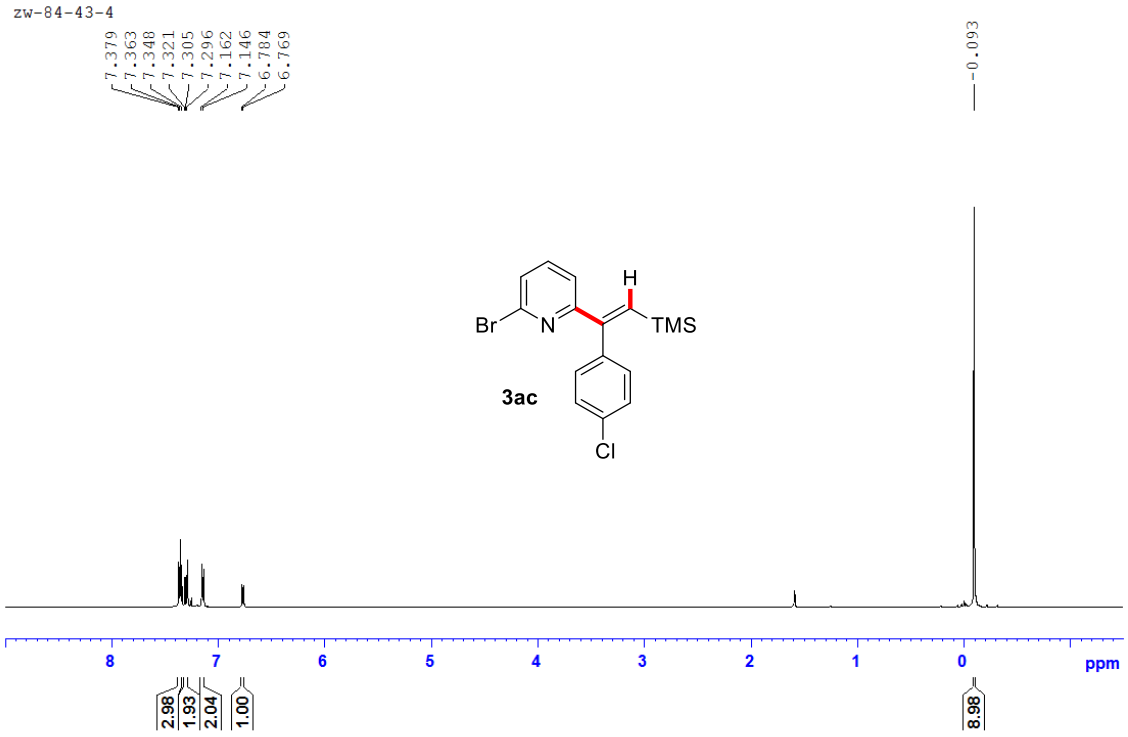

zw-84-43-2c
159.47
159.14
152.77
141.87
138.60
135.28
132.83
130.83
126.23
120.78
113.54
77.25
77.00
76.74
55.22
0.21
Br
N
H
TMS
OMe
3aa
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

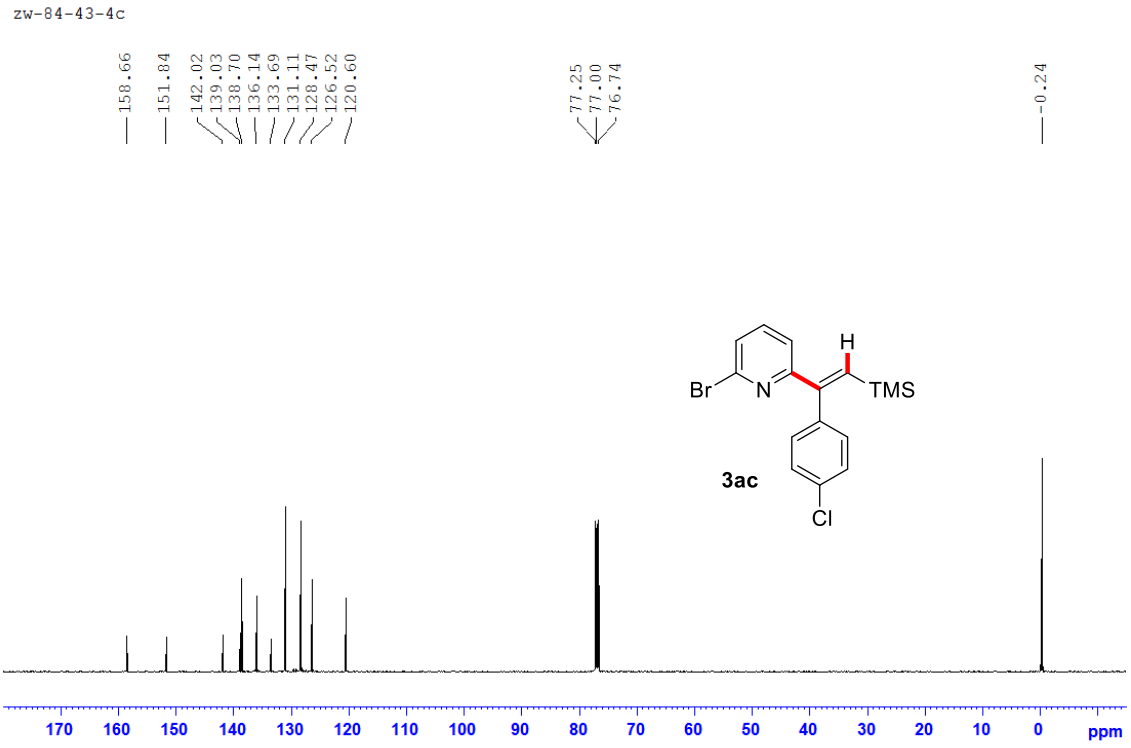
zw-84-43-3



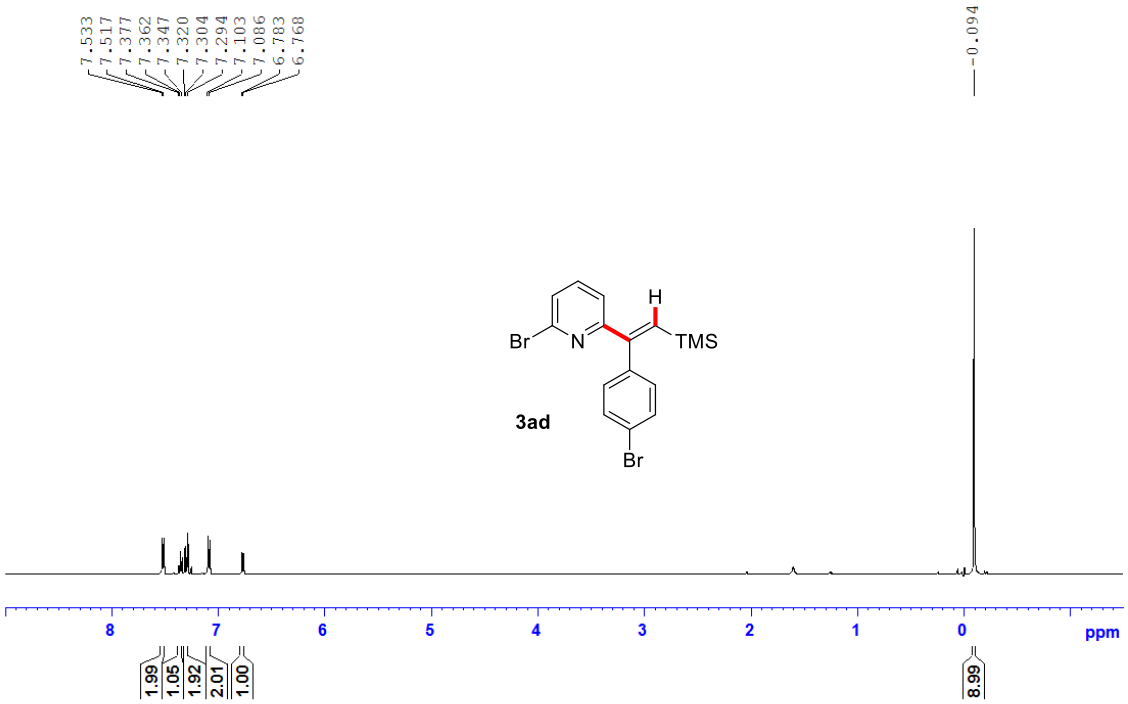
zw-84-43-3c



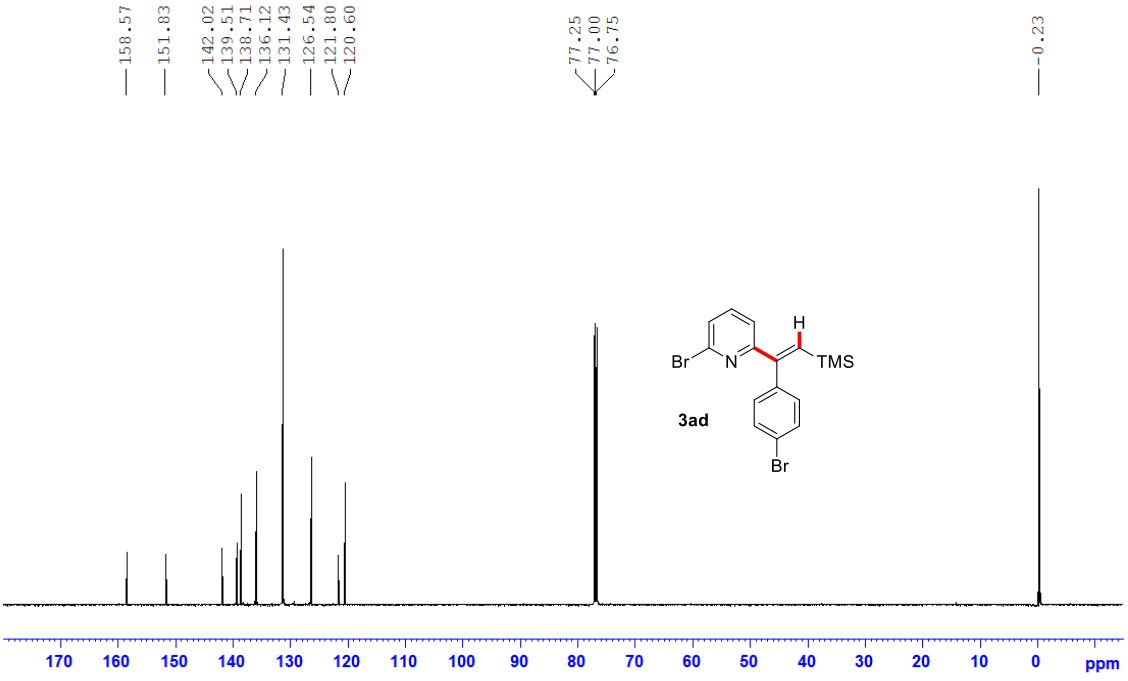

zw-84-43-4
7.379
7.363
7.348
7.321
7.305
7.296
7.162
7.146
6.784
6.769
-0.093
H
Br
N
TMS
3ac
Cl
8
7
6
5
4
3
2
1
0
ppm
2.98
1.93
2.04
1.00
8.98

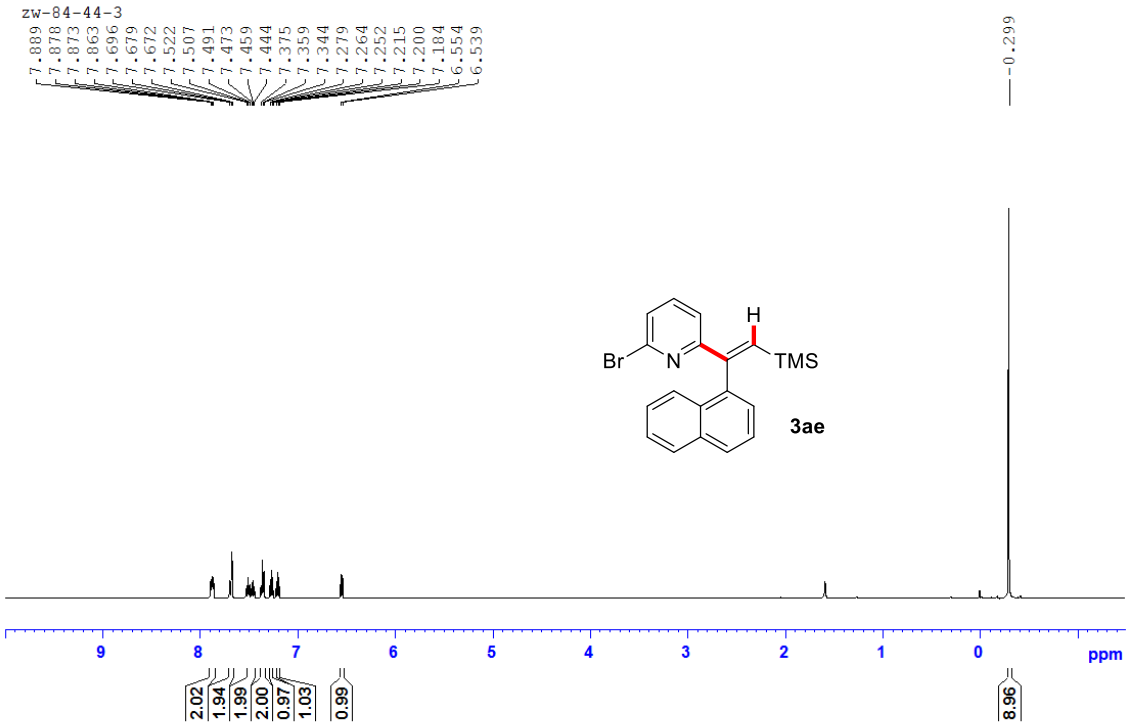

zw-84-43-4c
158.66
151.84
142.02
139.03
138.70
136.14
133.69
131.11
128.47
126.52
120.60
77.25
77.00
76.74
-0.24
H
Br
N
TMS
3ac
Cl
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

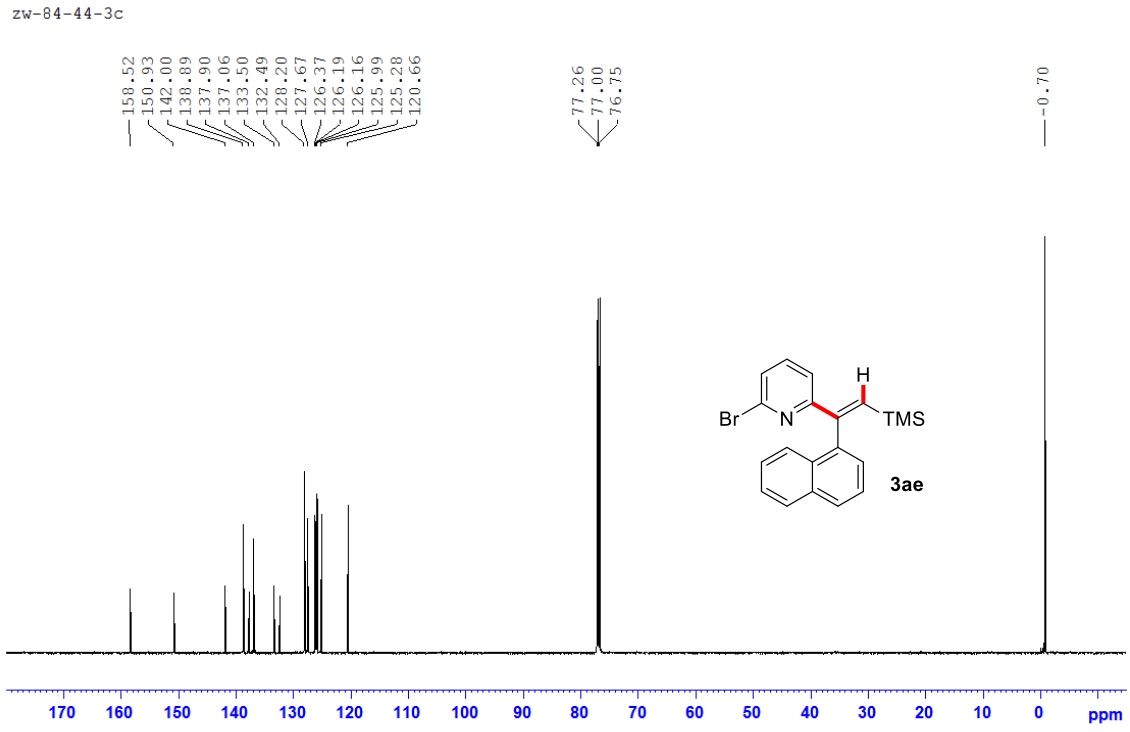
zw-84-44-1



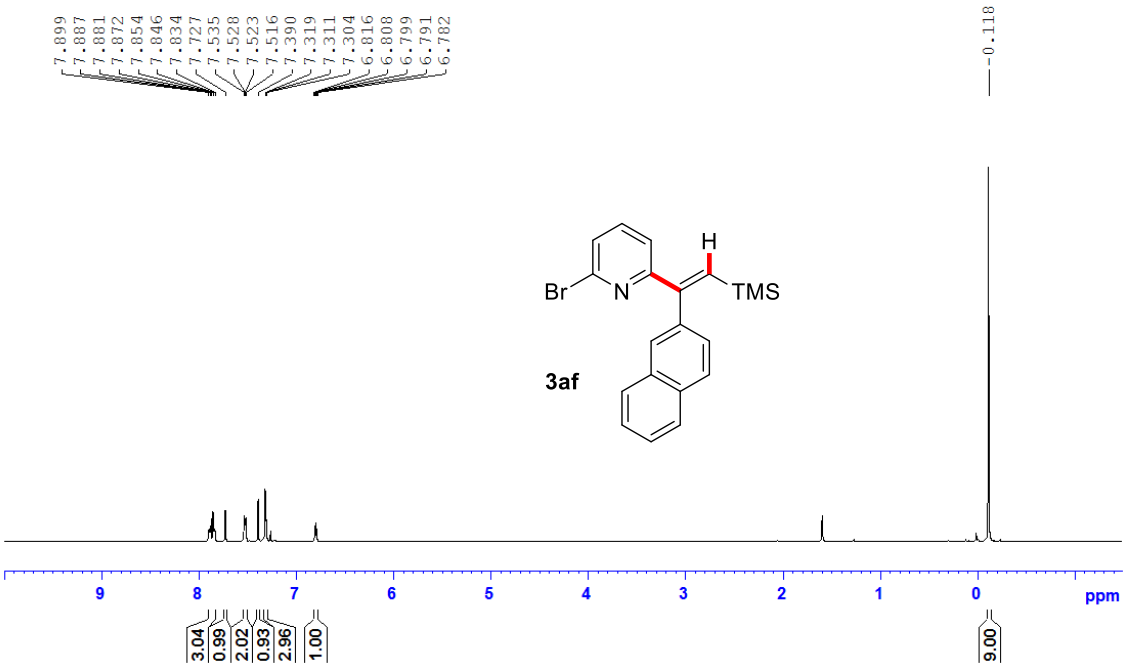
zw-84-44-1c



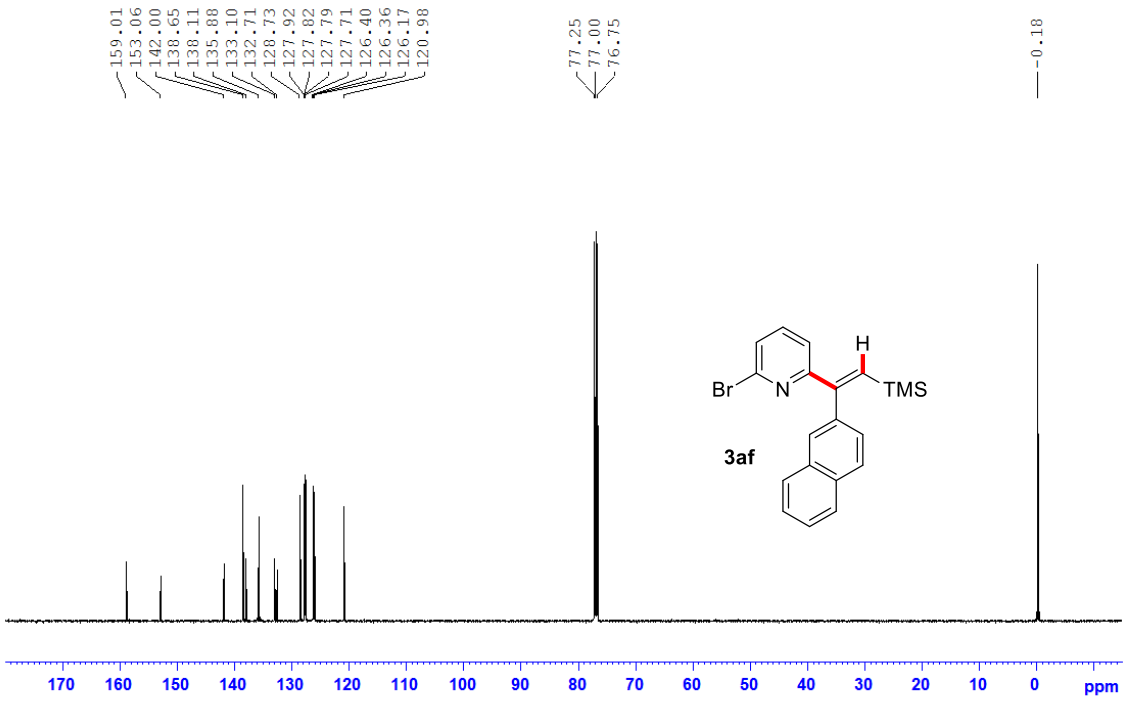

zw-84-44-3
7.889
7.878
7.873
7.863
7.696
7.679
7.672
7.522
7.507
7.491
7.473
7.459
7.444
7.375
7.359
7.344
7.279
7.264
7.252
7.215
7.200
7.184
6.554
6.539
0.299
Br
N
H
TMS
3ae
9
8
7
6
5
4
3
2
1
0
ppm
2.02
1.94
1.99
2.00
0.97
1.03
0.99
8.96


zw-84-44-3c
158.52
150.93
142.00
138.89
137.90
137.06
133.50
132.49
128.20
127.67
126.37
126.19
126.16
125.99
125.28
120.66
77.26
77.00
76.75
0.70
Br
N
H
TMS
3ae
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

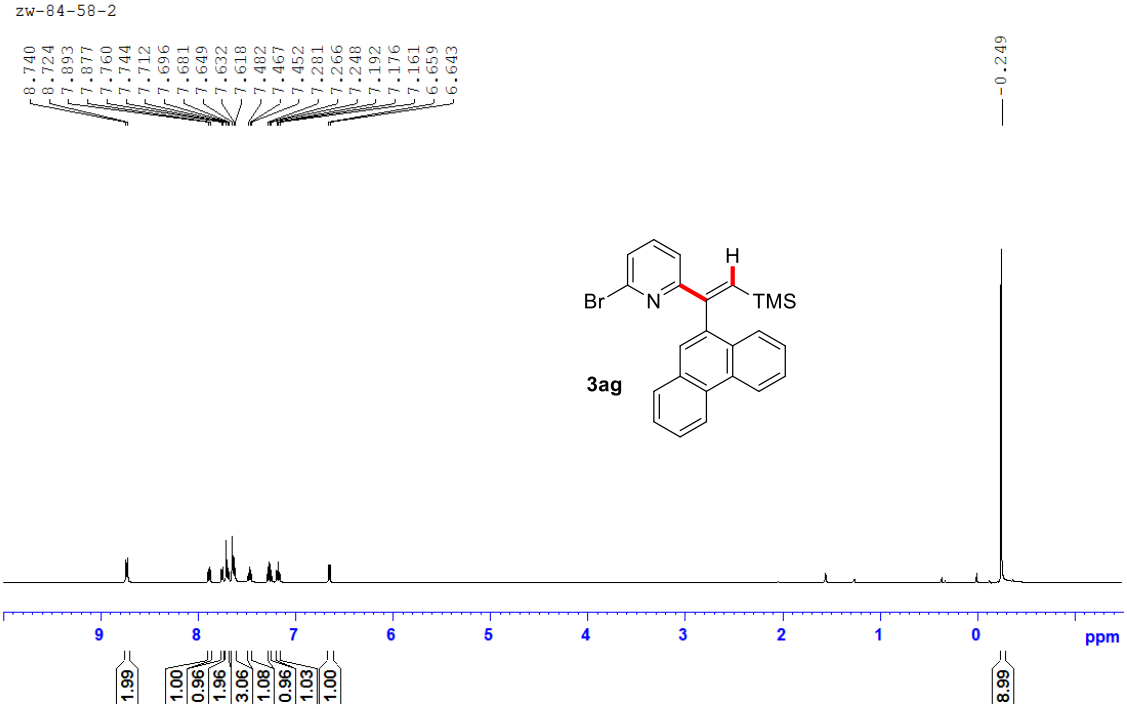
zw-84-44-4



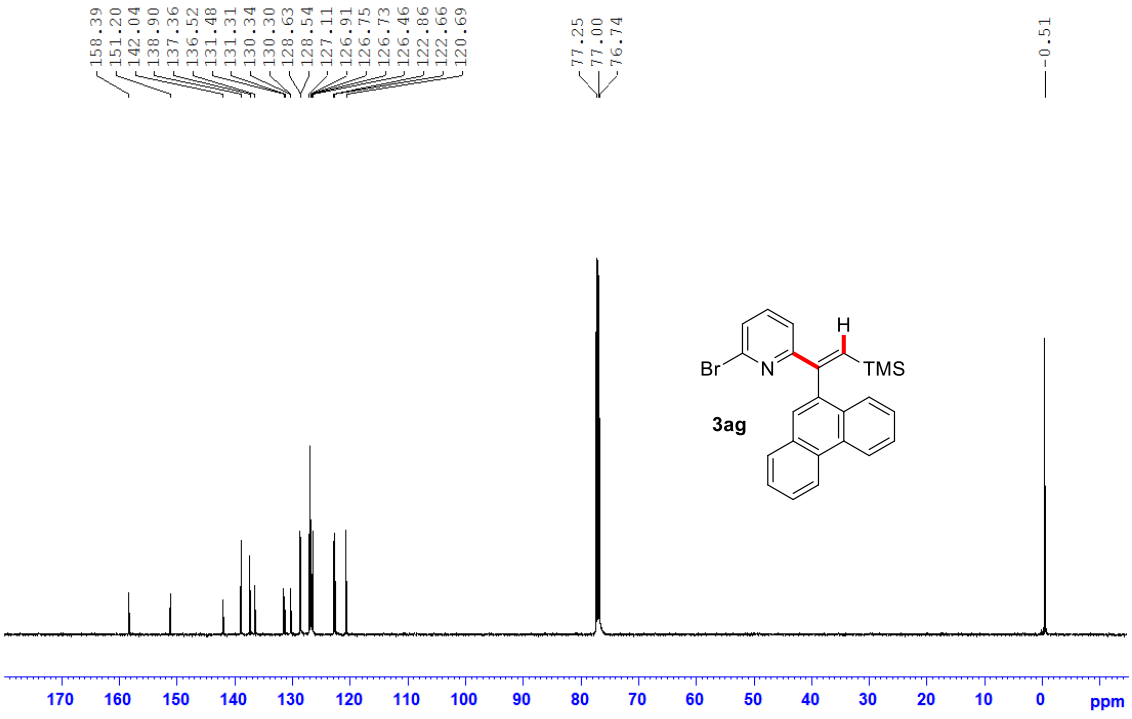
zw-84-44-4c



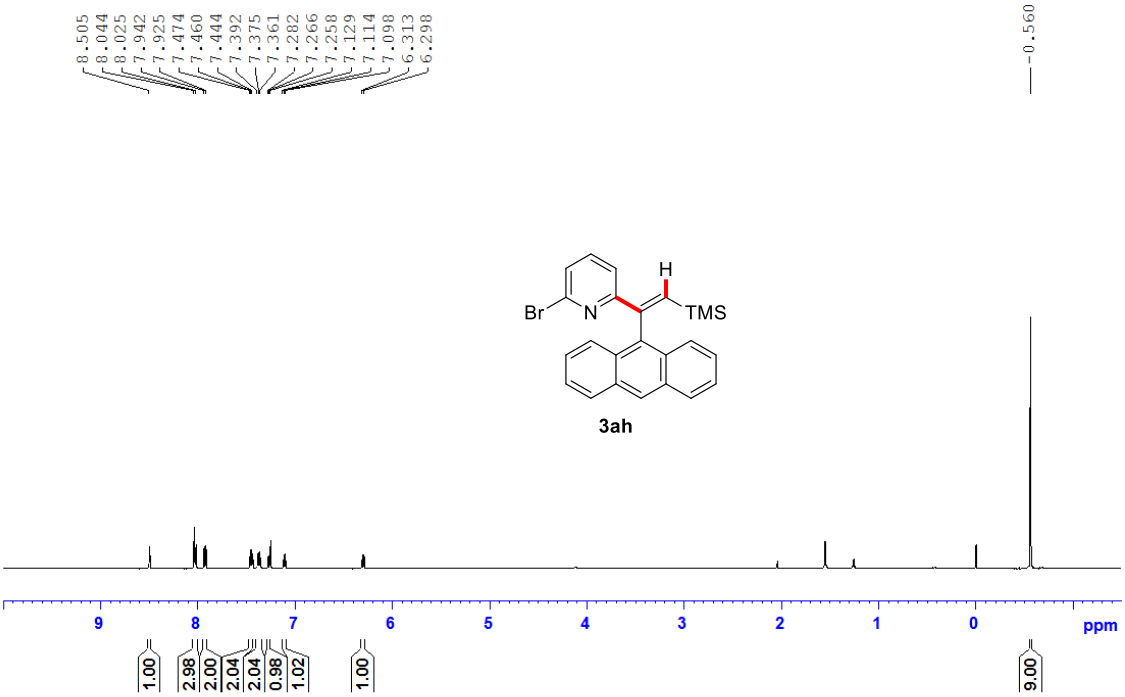
zw-84-58-2



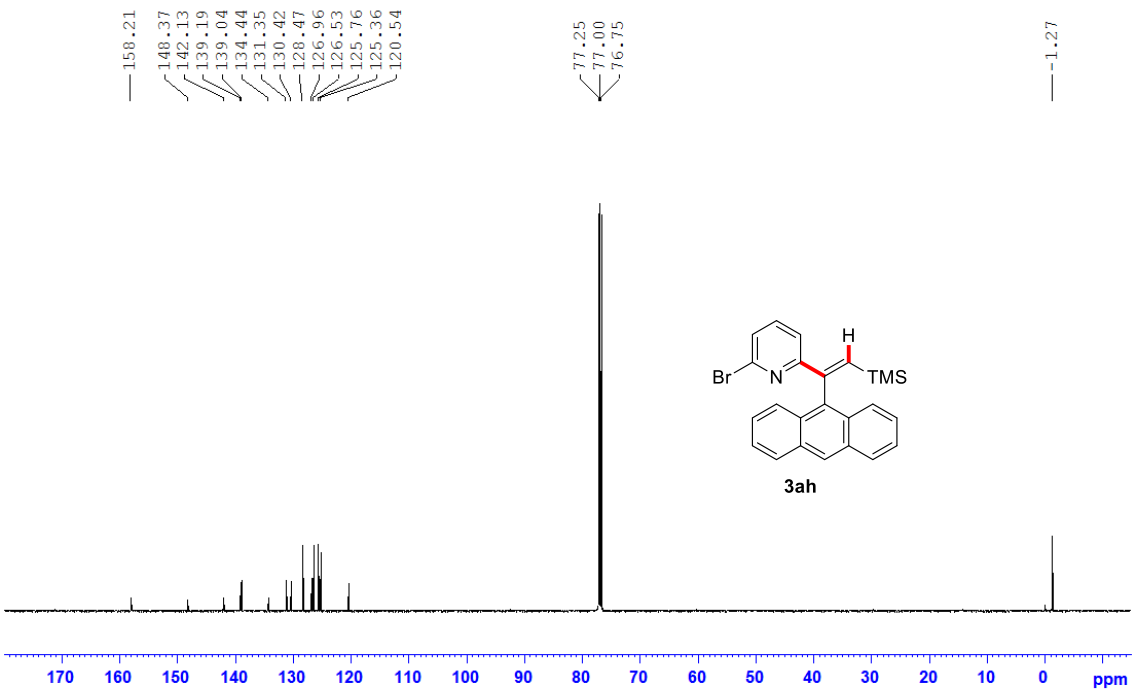
zw-84-58-2c

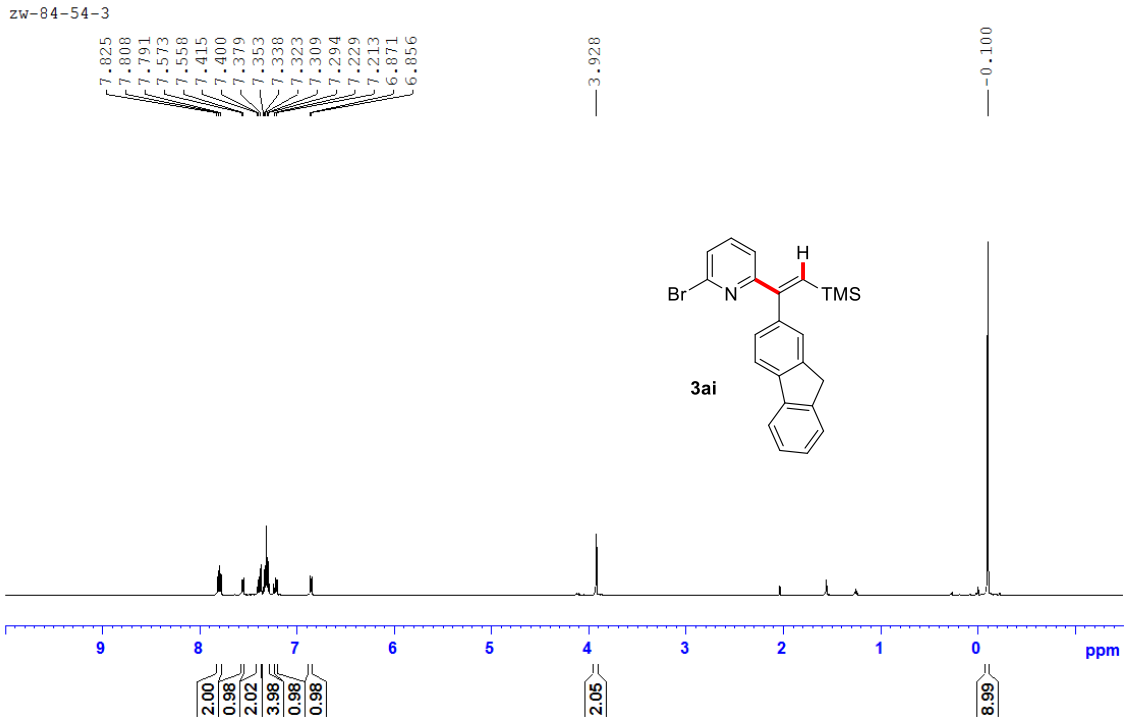


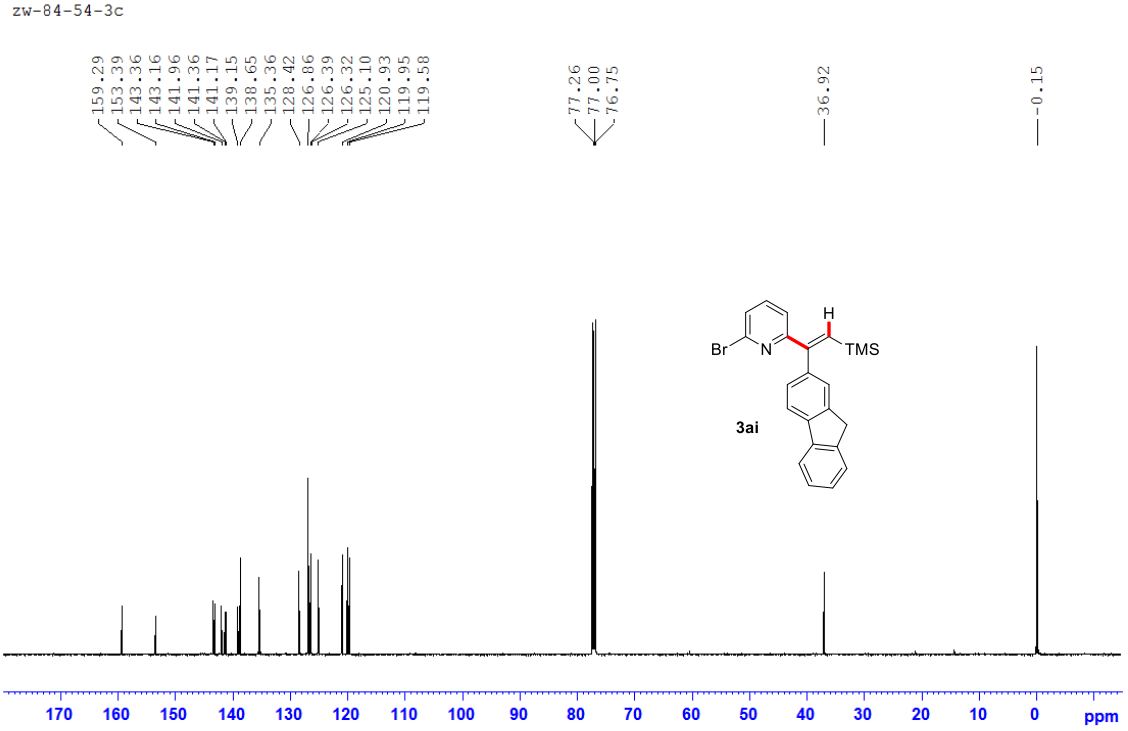
zw-84-58-1



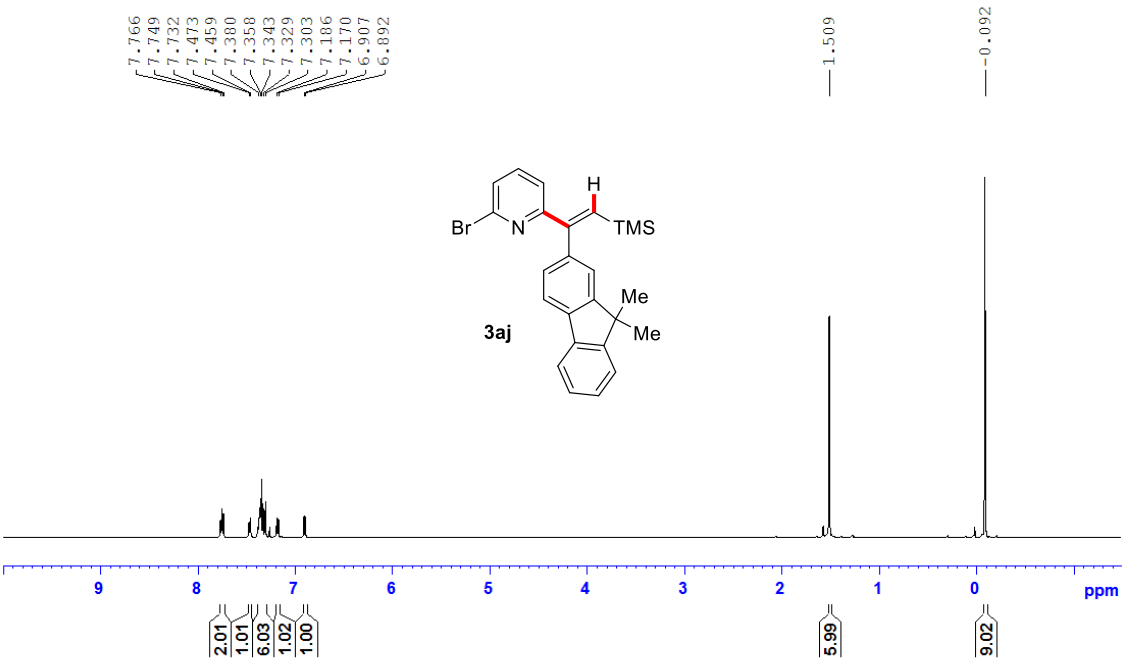
zw-84-58-1c



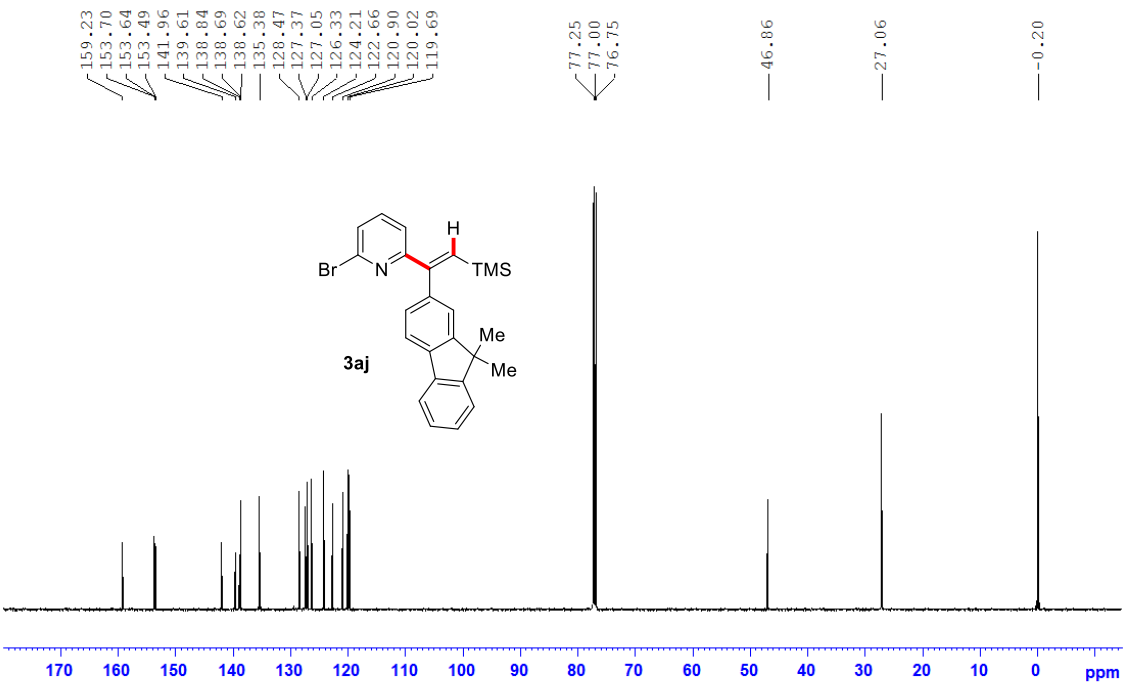

zw-84-54-3
7.825
7.808
7.791
7.573
7.558
7.415
7.400
7.379
7.353
7.338
7.323
7.309
7.294
7.229
7.213
6.871
6.856
3.928
0.100
Br
N
H
TMS
3ai
9
8
7
6
5
4
3
2
1
0
ppm
2.00
0.98
2.02
3.98
0.98
0.98
2.05
8.99


zw-84-54-3c
159.29
153.39
143.36
143.16
141.96
141.36
141.17
139.15
138.65
135.36
128.42
126.86
126.39
126.32
125.10
120.93
119.95
119.58
77.26
77.00
76.75
36.92
0.15
Br
N
H
TMS
3ai
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

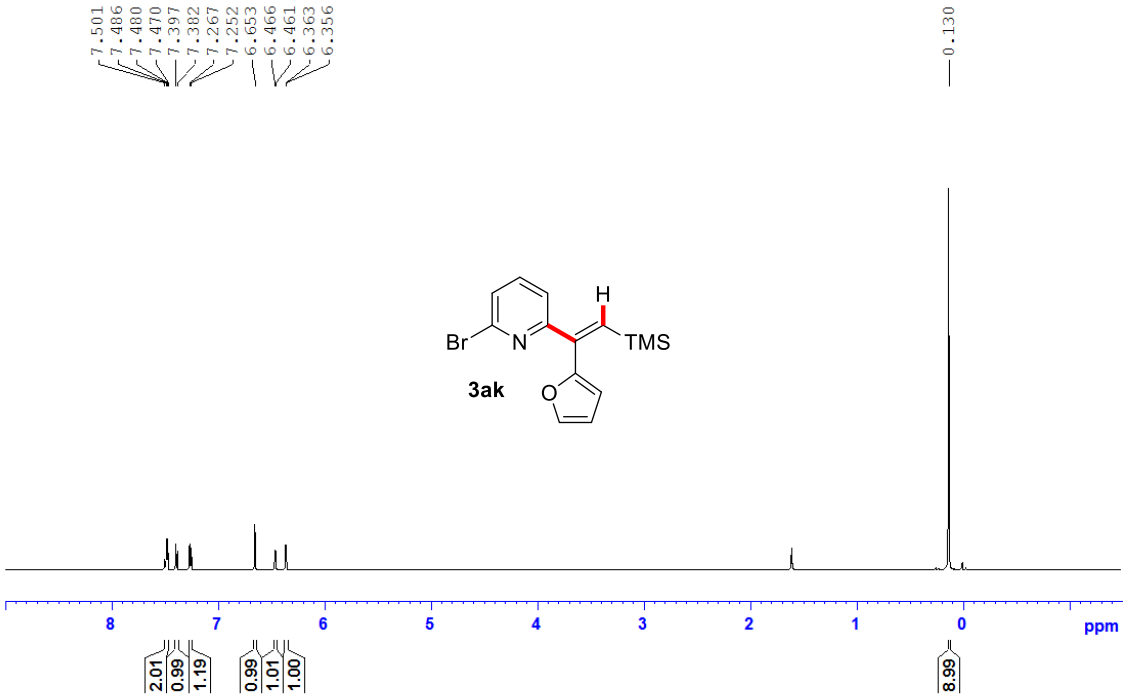
zw-84-54-4



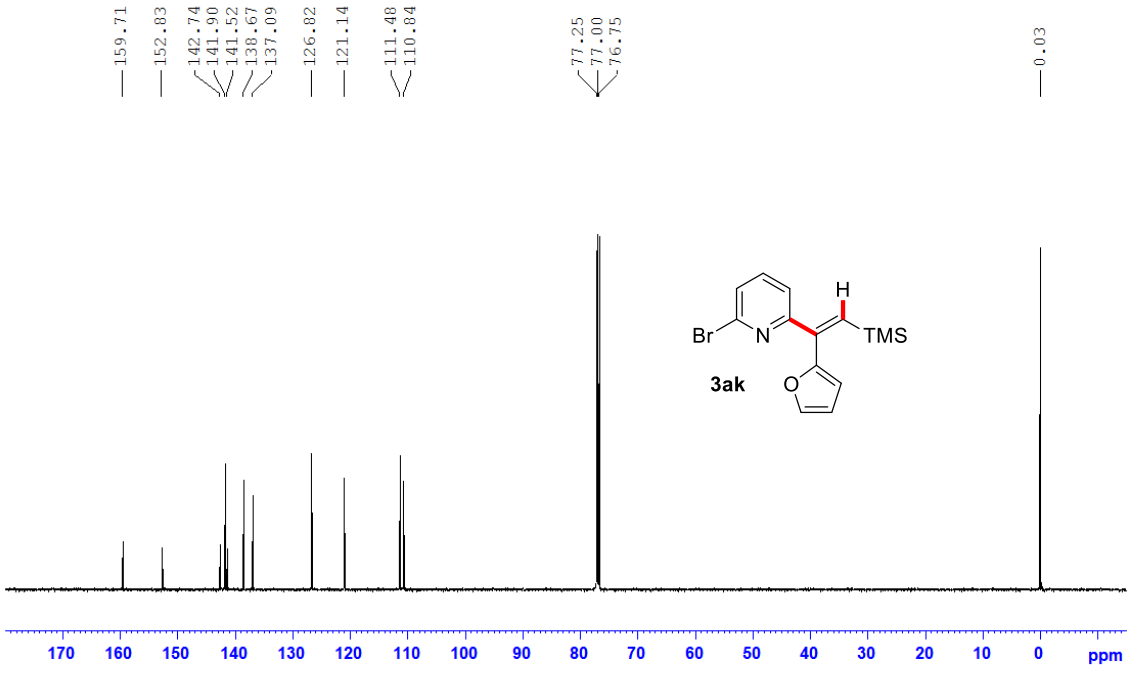
zw-84-54-4c



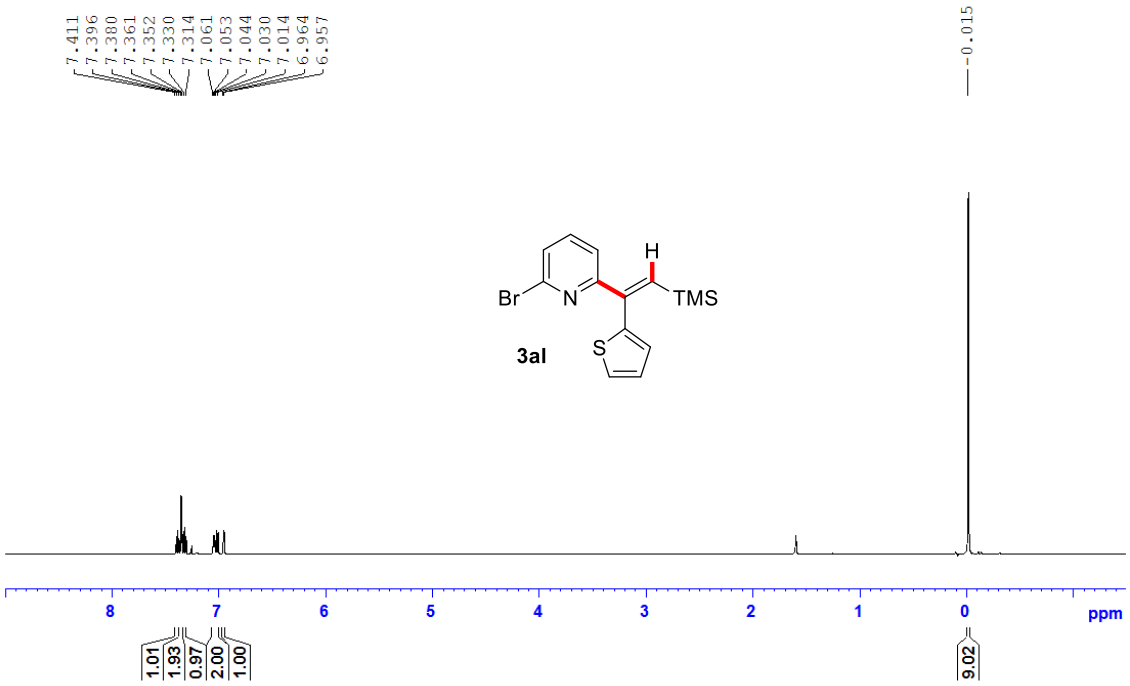
zw-84-45-1



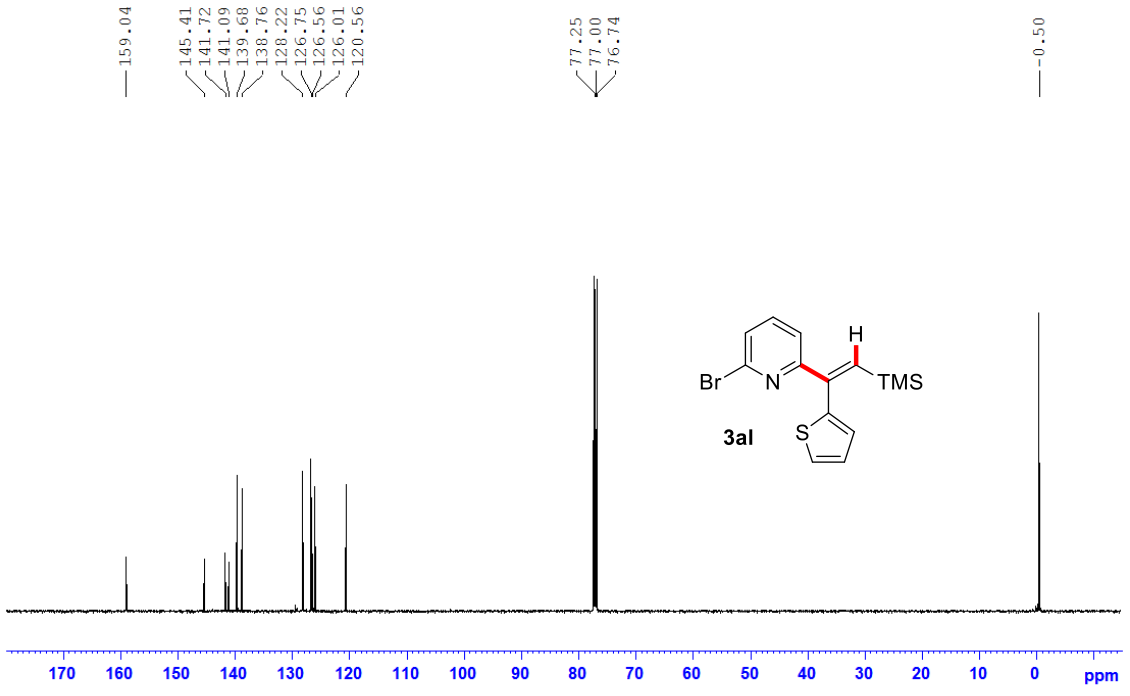
zw-84-45-1



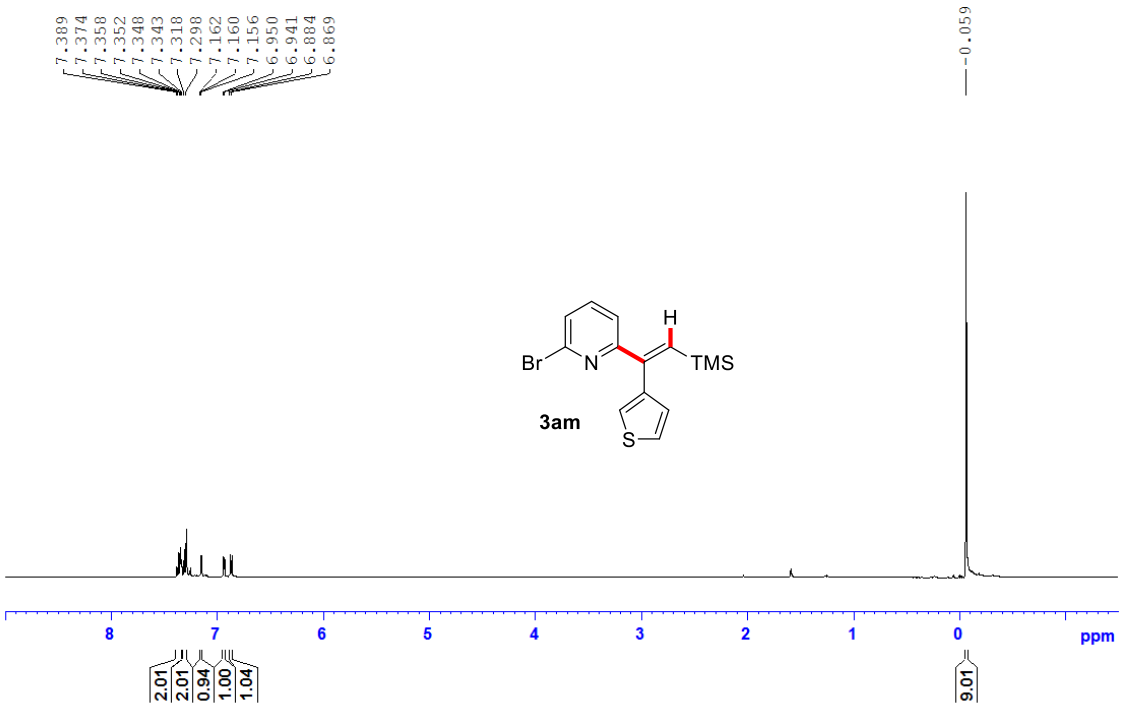
zw-84-45-2



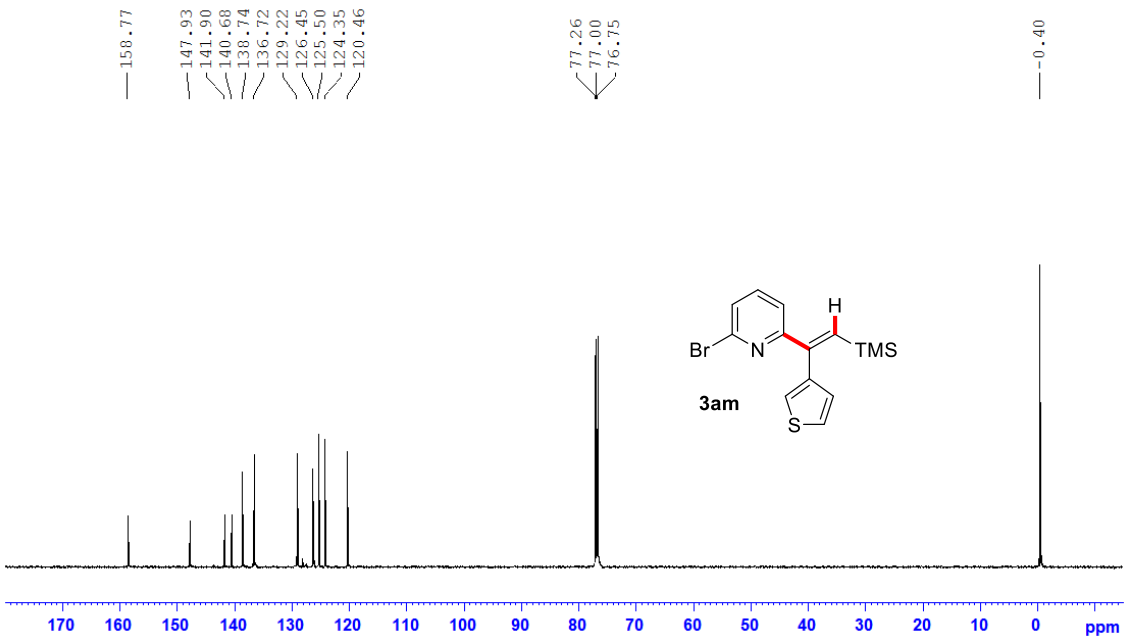
zw-84-45-2c



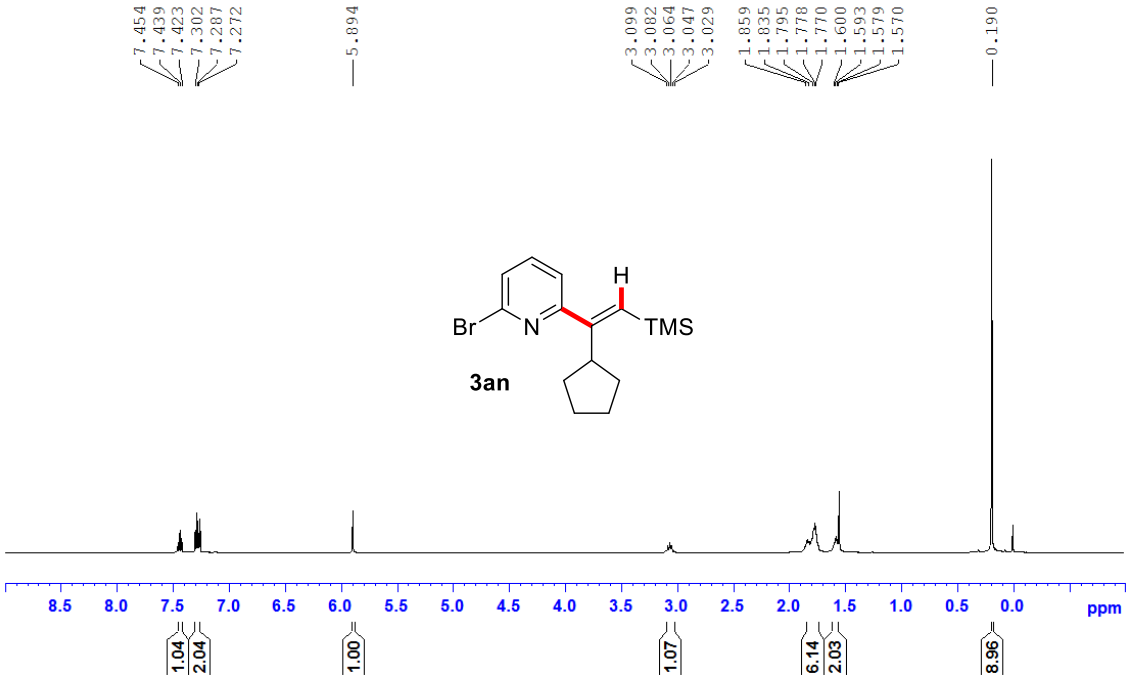
zw-84-54-1



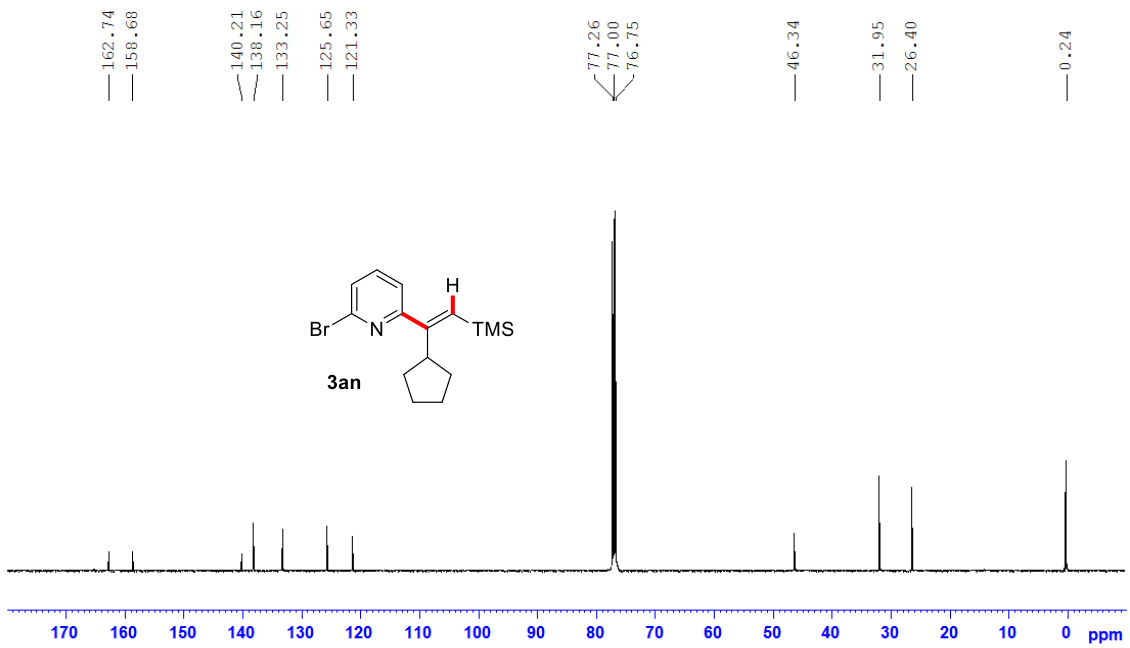
zw-84-54-1c



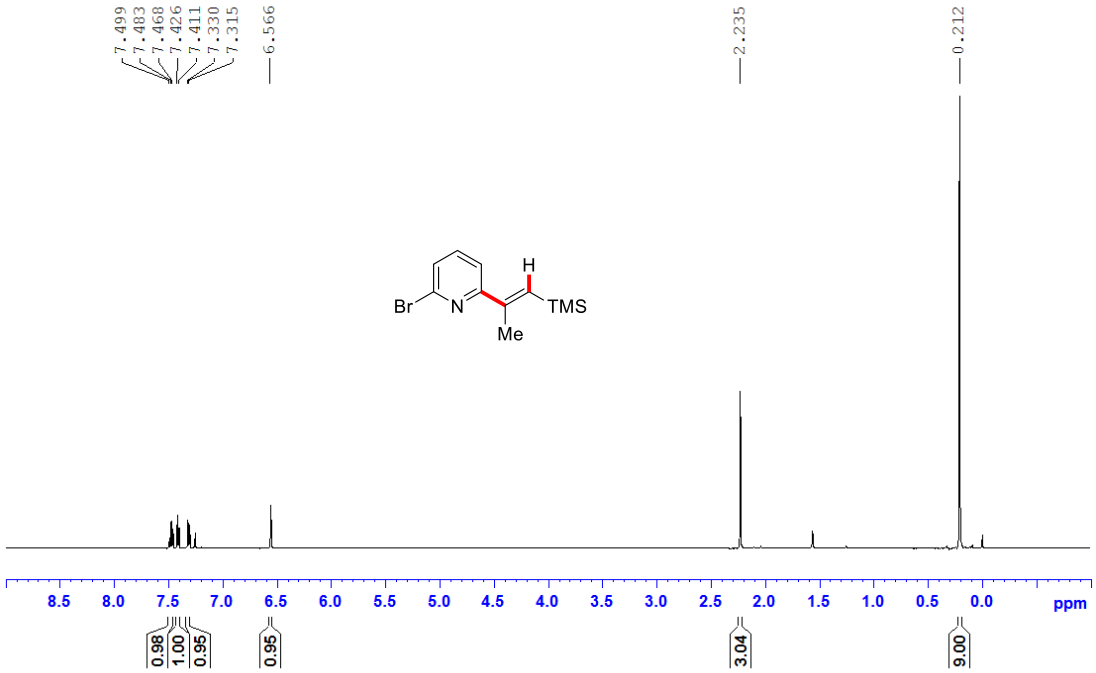
zw-84-58-3s



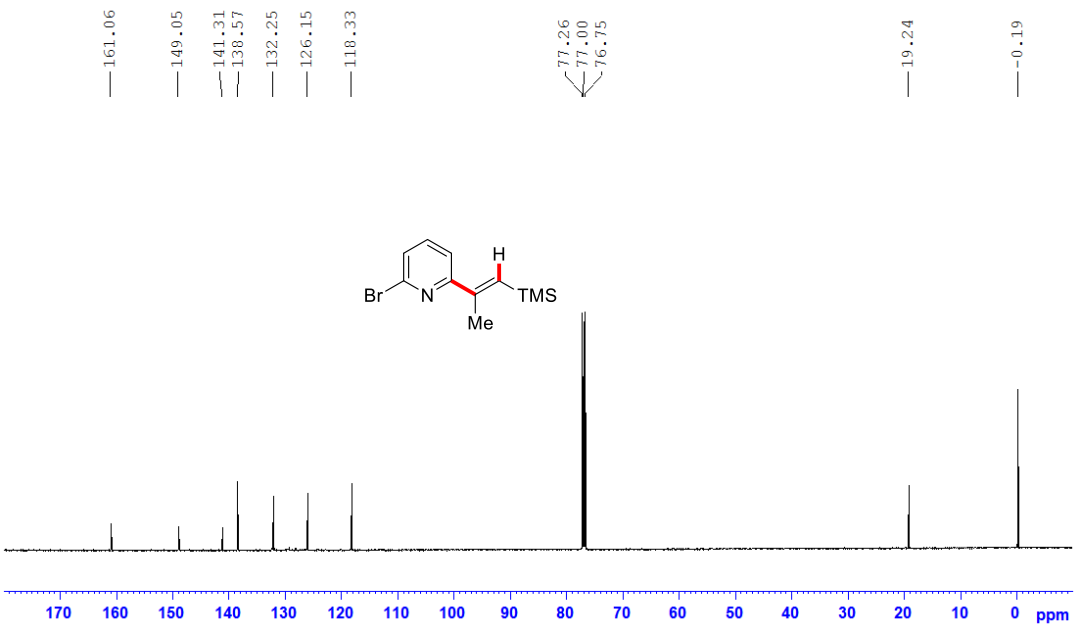
zw-84-58-3cs



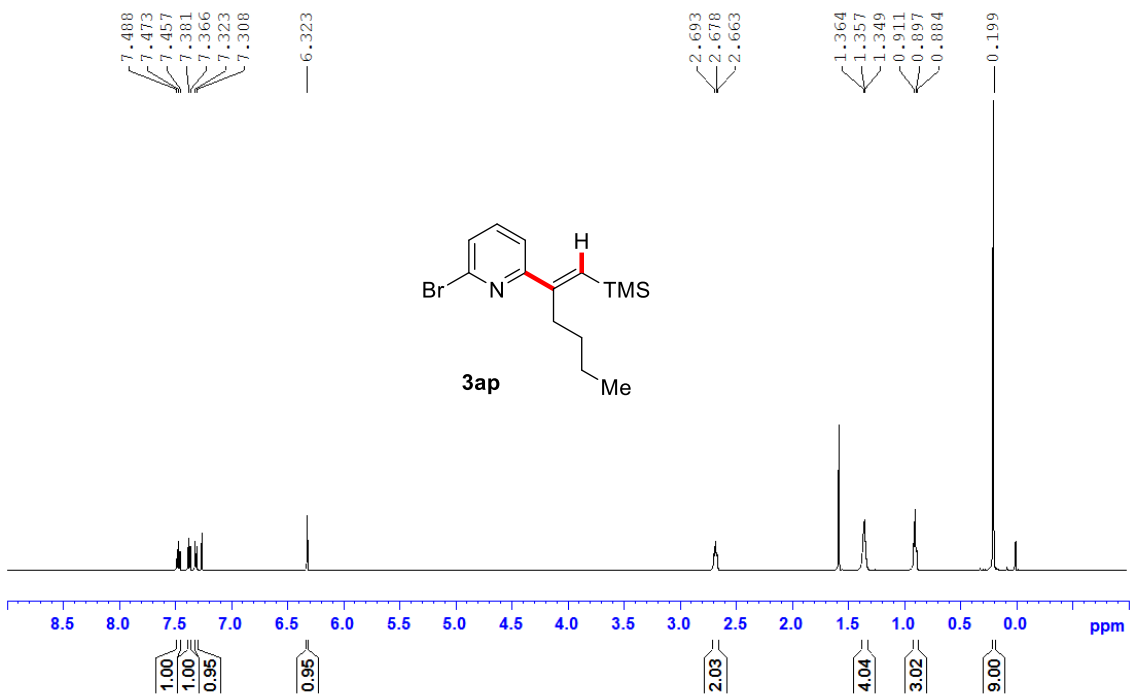
zw-84-58-4



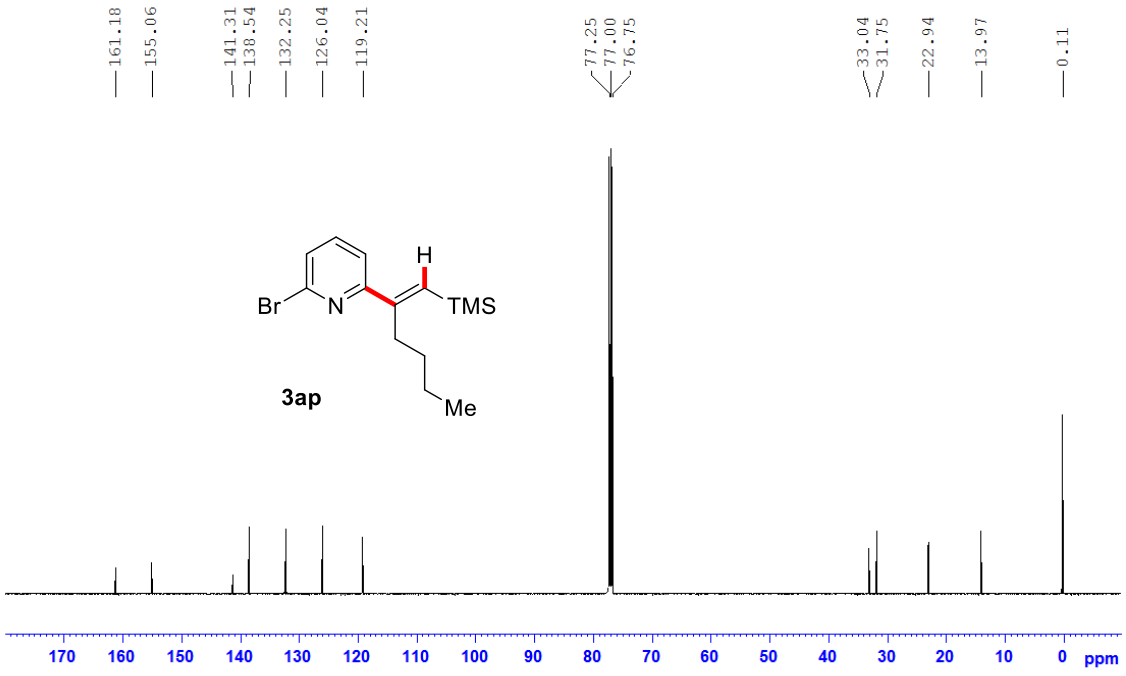
zw-84-58-4c



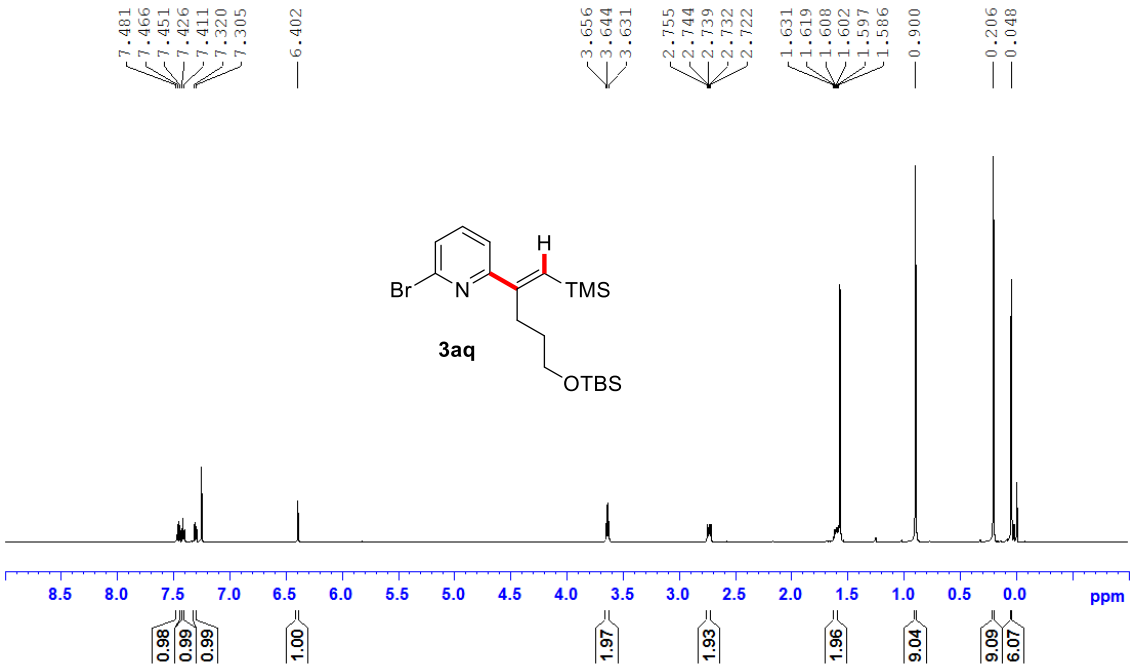
zw-84-46-1t



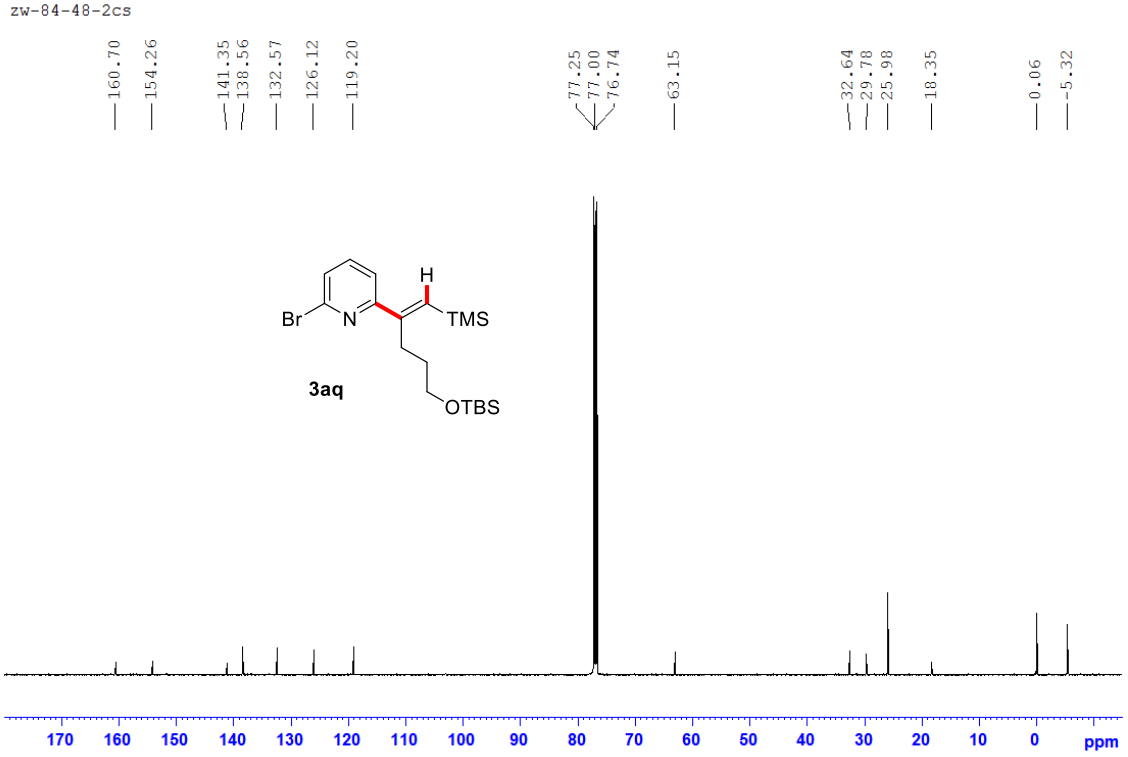
zw-84-46-1tc

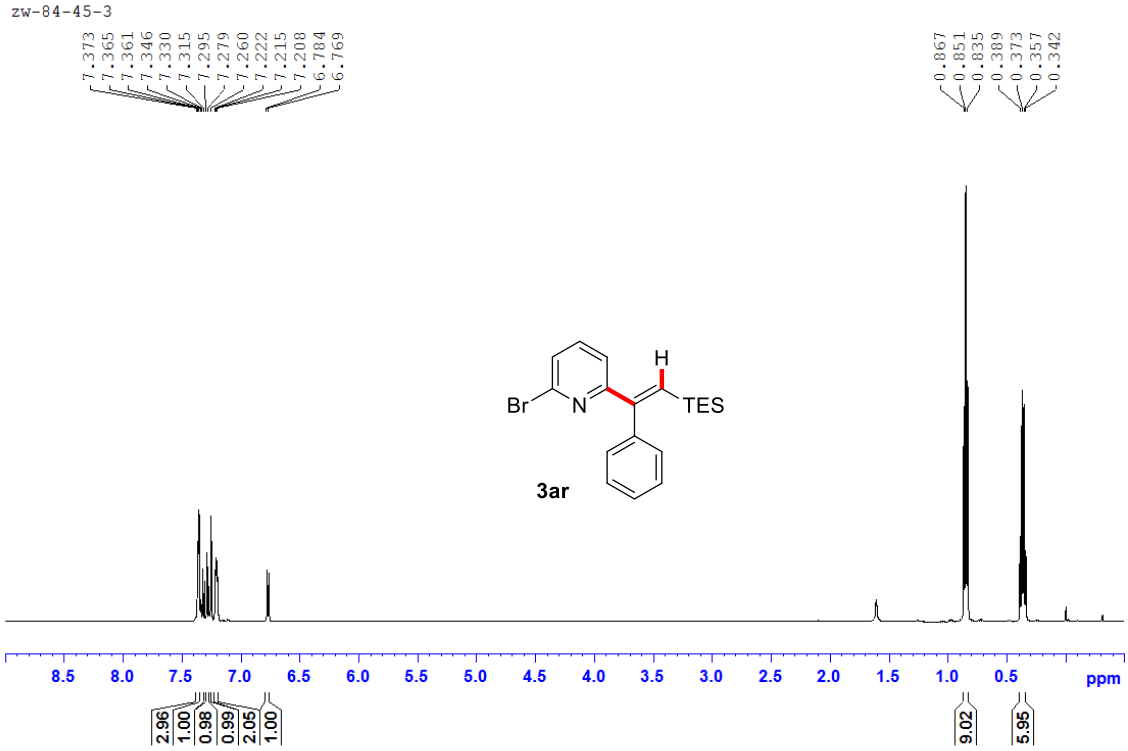


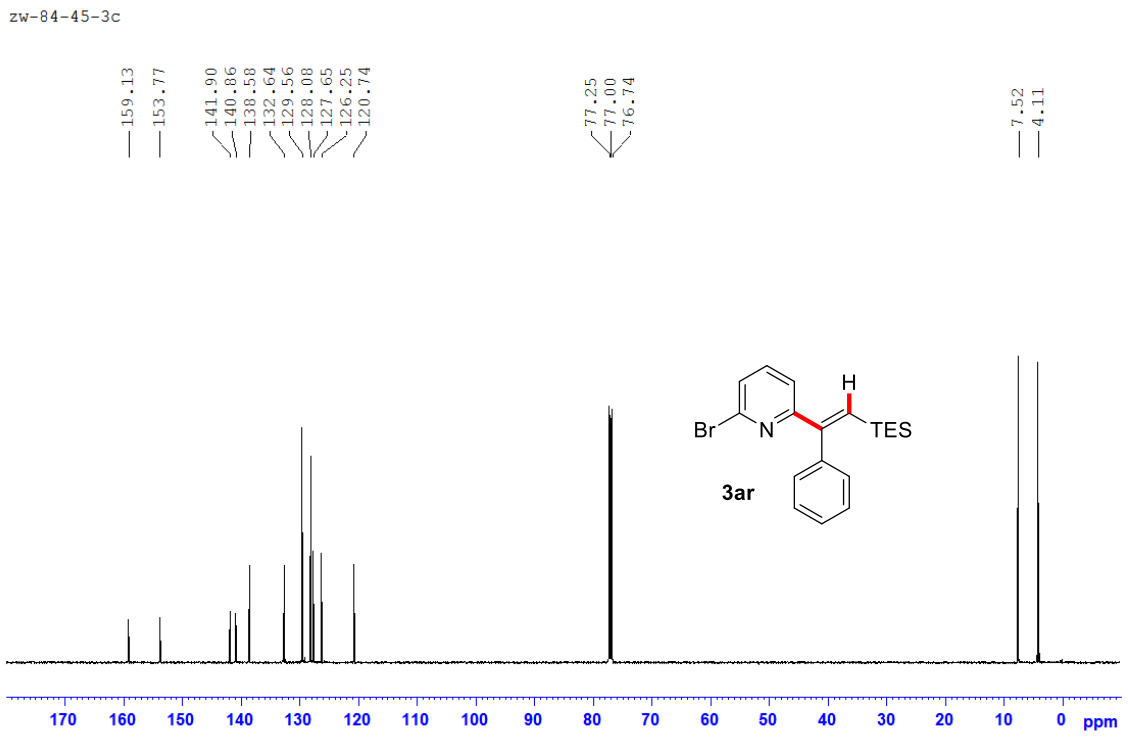
zw-84-48-2s

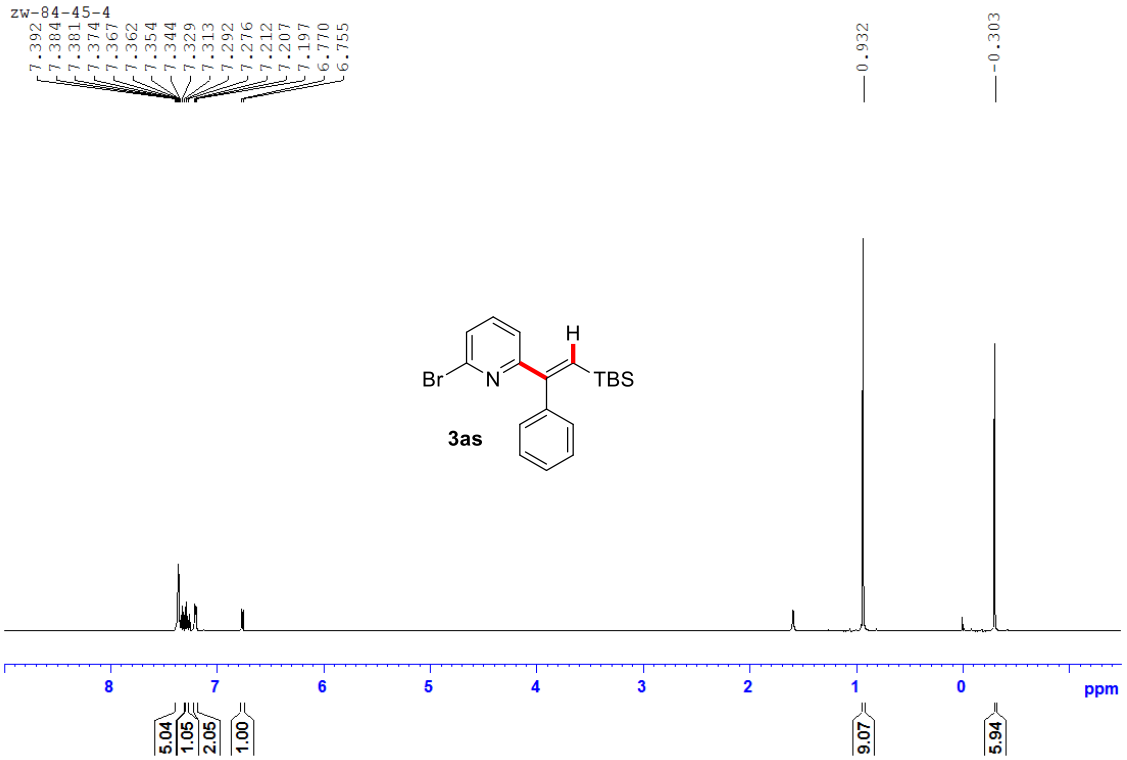


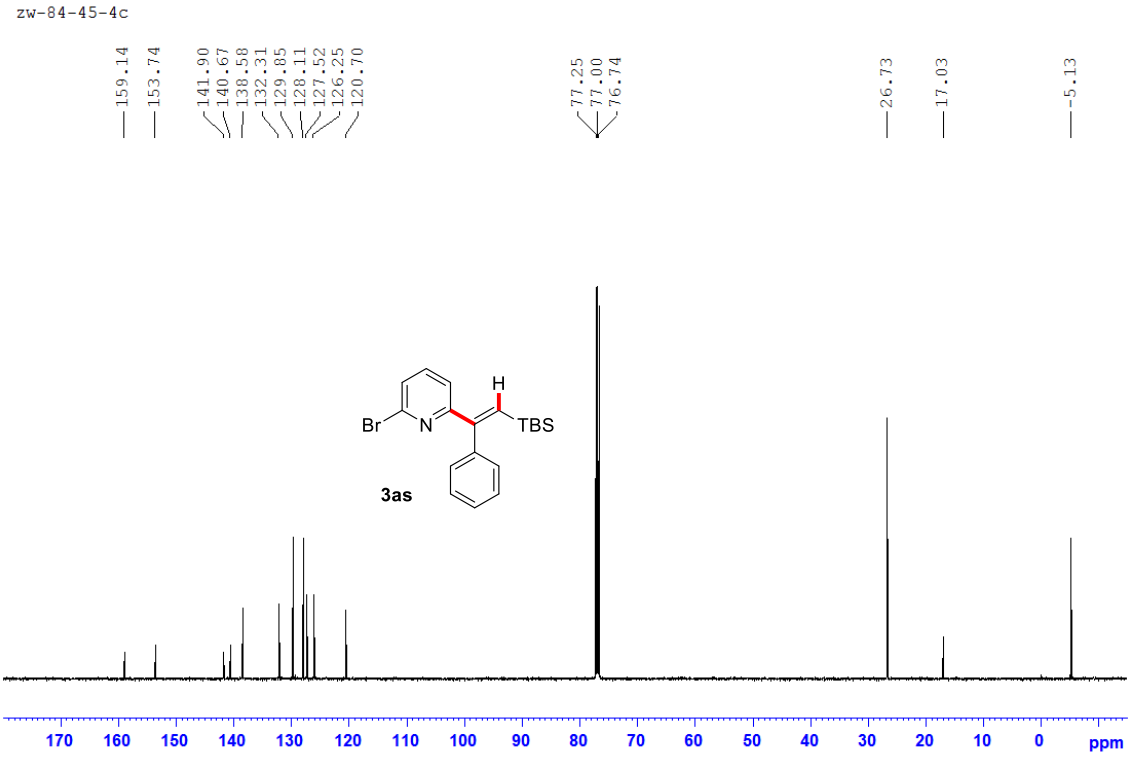
zw-84-48-2cs

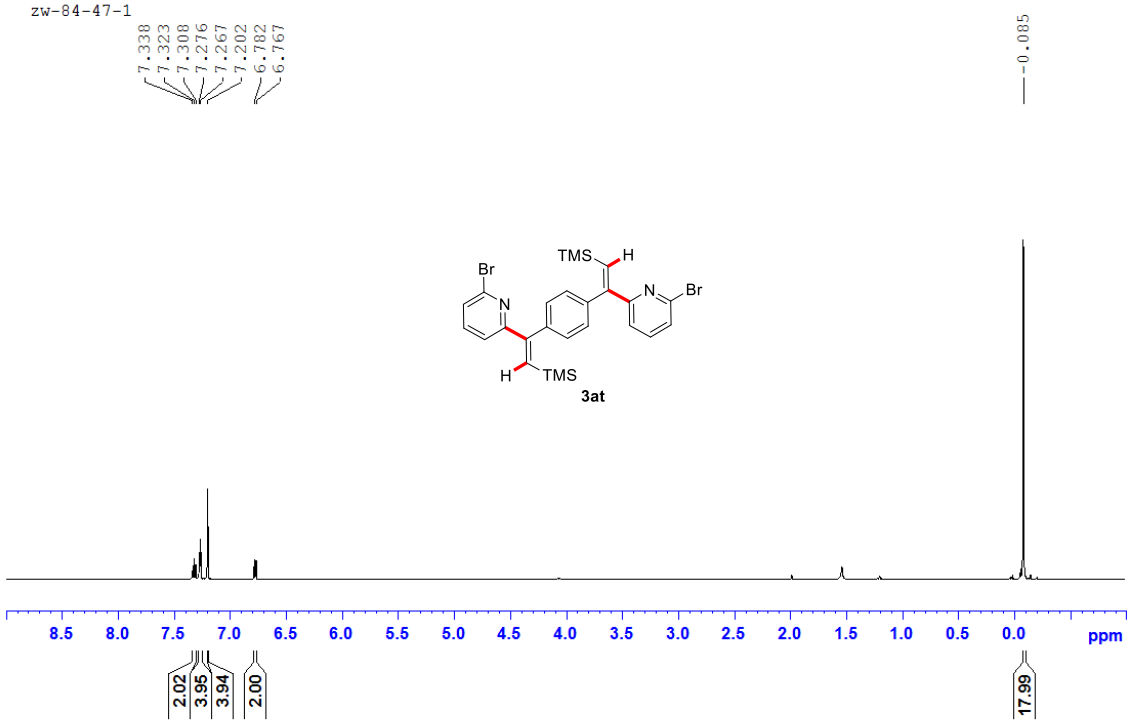


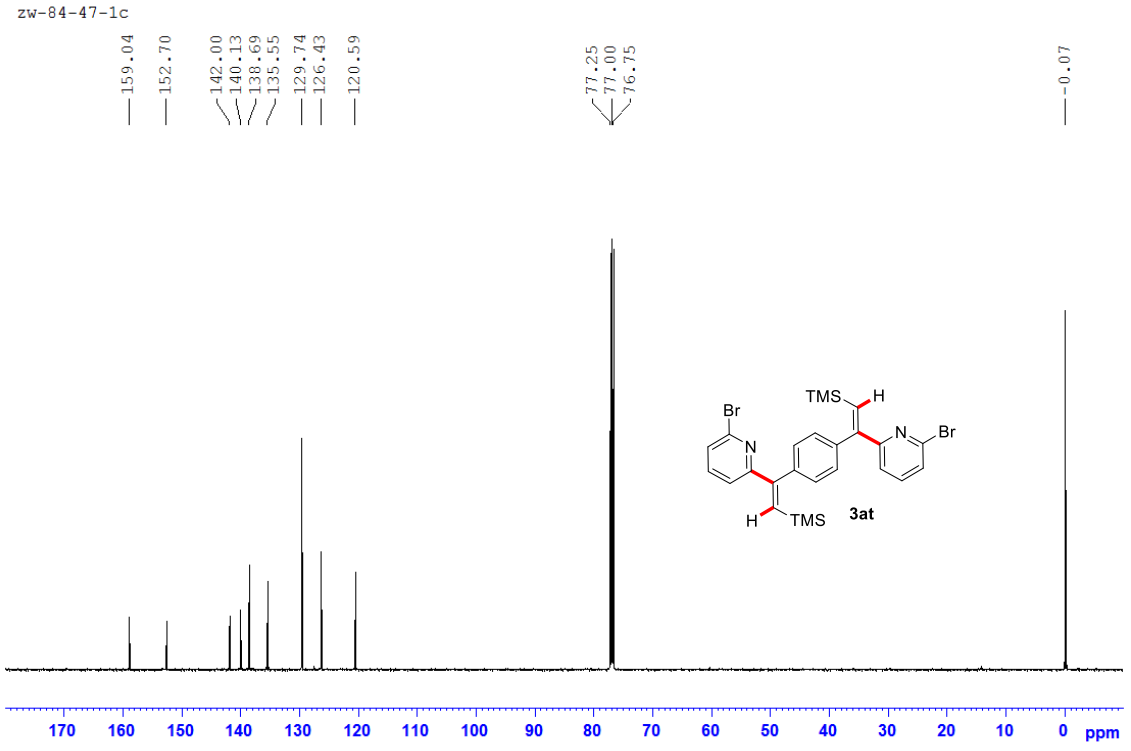

zw-84-45-3
7.373
7.365
7.361
7.346
7.330
7.315
7.295
7.279
7.260
7.222
7.215
7.208
6.784
6.769
0.867
0.851
0.835
0.389
0.373
0.357
0.342
Br
N
H
TES
3ar
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.96
1.00
0.98
0.99
2.05
1.00
9.02
5.95

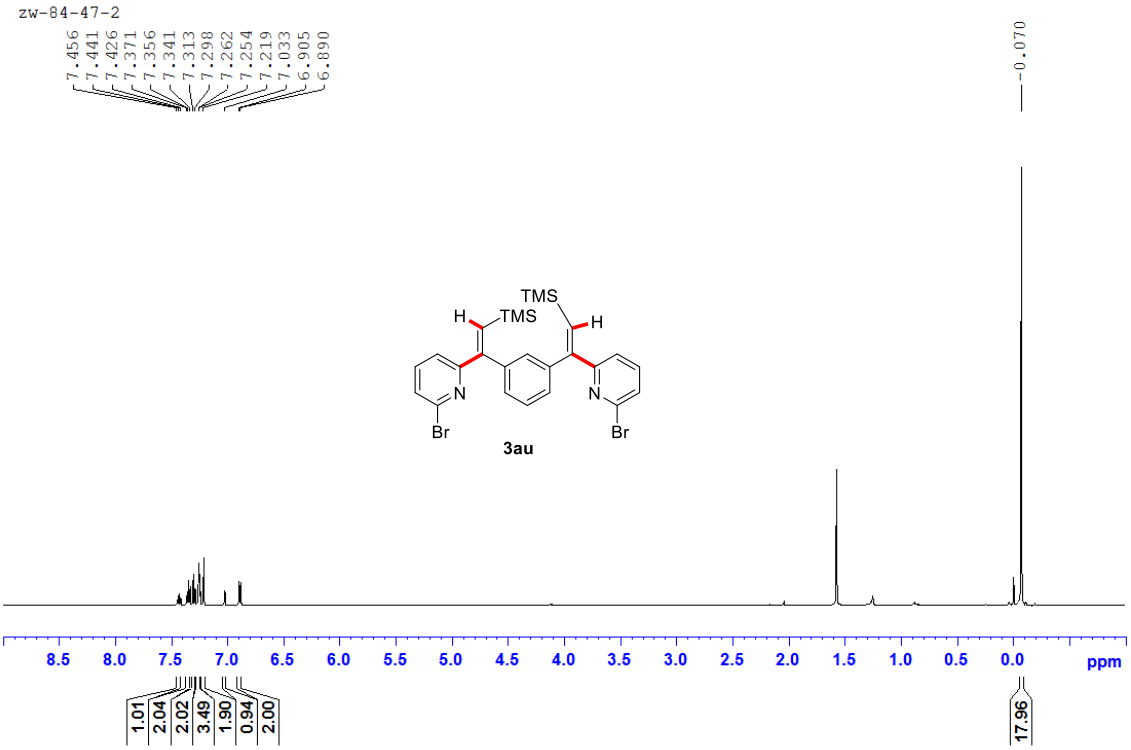

zw-84-45-3c
159.13
153.77
141.90
140.86
138.58
132.64
129.56
128.08
127.65
126.25
120.74
77.25
77.00
76.74
7.52
4.11
Br
N
H
TES
3ar
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

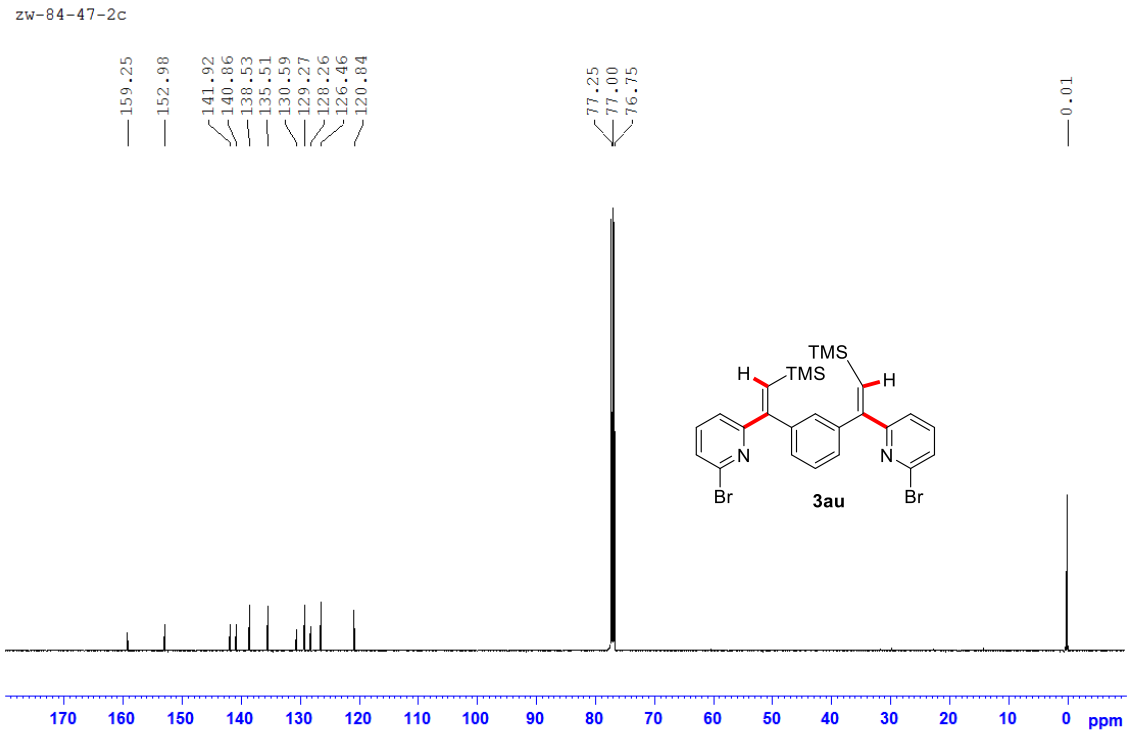

zw-84-45-4
7.392
7.384
7.381
7.374
7.367
7.362
7.354
7.344
7.329
7.313
7.292
7.276
7.212
7.207
7.197
6.770
6.755
0.932
-0.303
Br
N
H
TBS
3as
8
7
6
5
4
3
2
1
0
ppm
5.04
1.05
2.05
1.00
9.07
5.94

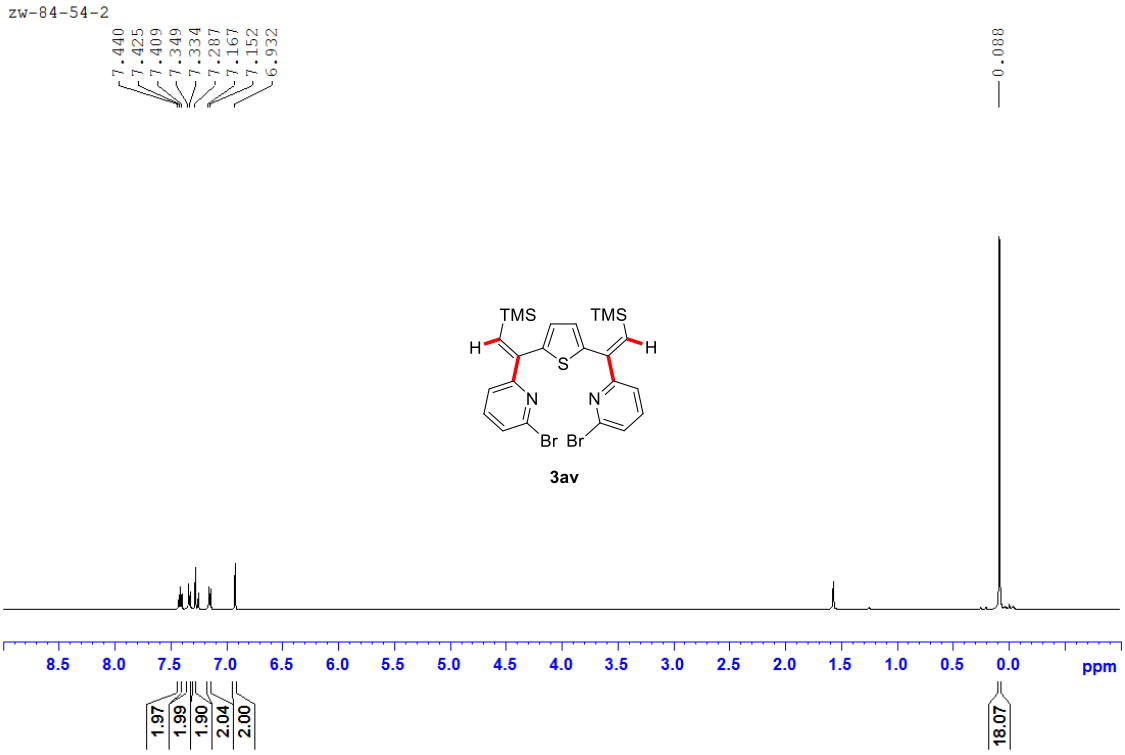

zw-84-45-4c
159.14
153.74
141.90
140.67
138.58
132.31
129.85
128.11
127.52
126.25
120.70
77.25
77.00
76.74
26.73
17.03
-5.13
Br
N
H
TBS
3as
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

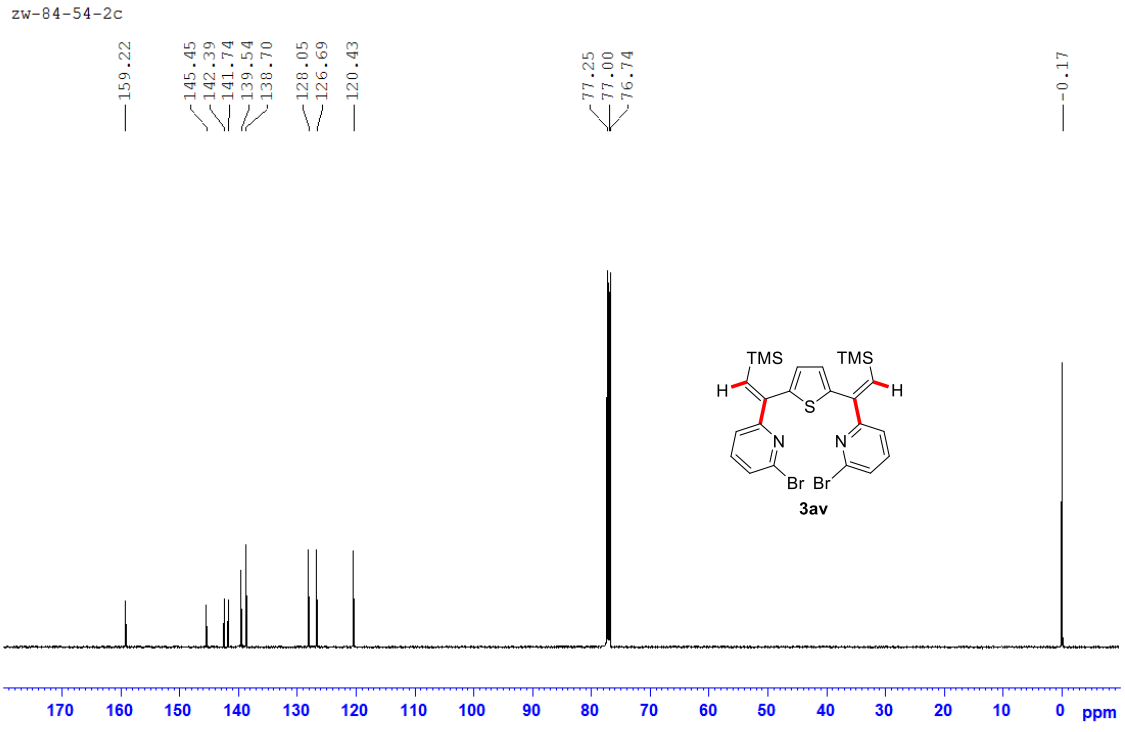

zw-84-47-1
7.338
7.323
7.308
7.276
7.267
7.202
6.782
6.767
0.085
TMS
H
Br
N
N
Br
H
TMS
3at
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.02
3.95
3.94
2.00
17.99


zw-84-47-1c
159.04
152.70
142.00
140.13
138.69
135.55
129.74
126.43
120.59
77.25
77.00
76.75
0.07
TMS
H
Br
N
N
Br
H
TMS
3at
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

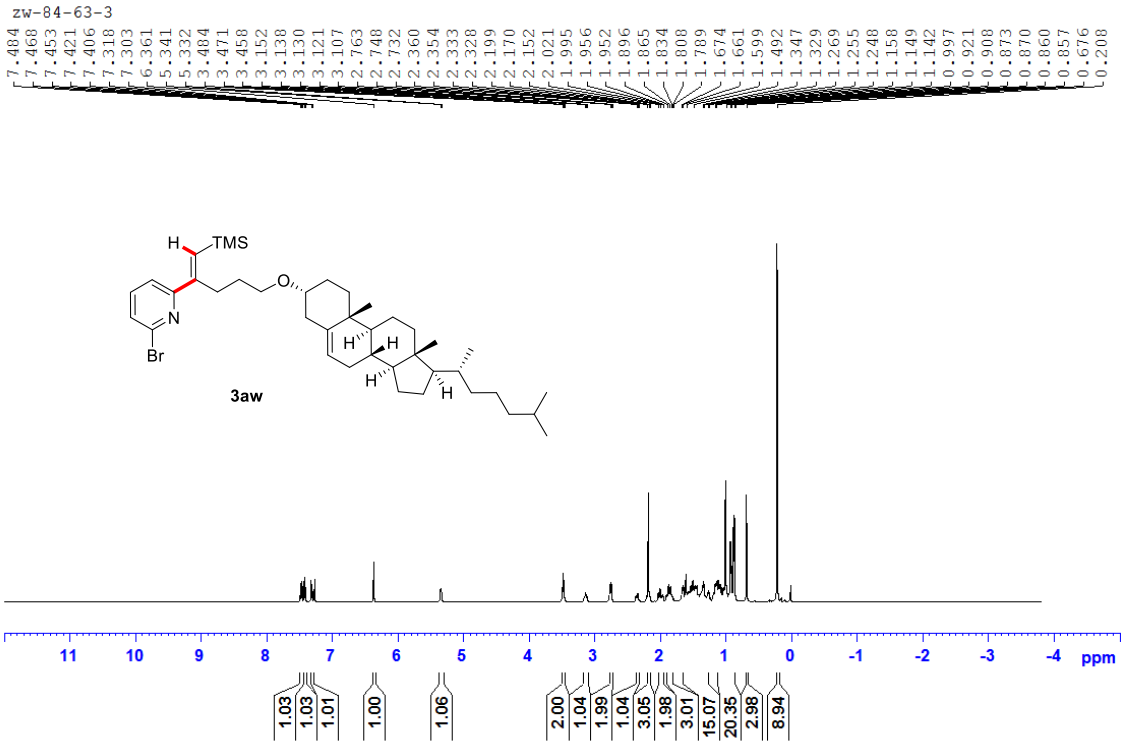

zw-84-47-2
7.456
7.441
7.426
7.371
7.356
7.341
7.313
7.298
7.262
7.254
7.219
7.033
6.905
6.890
-0.070
TMS
H
TMS
H
N
N
Br
Br
3au
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.01
2.04
2.02
3.49
1.90
0.94
2.00
17.96


zw-84-47-2c
159.25
152.98
141.92
140.86
138.53
135.51
130.59
129.27
128.26
126.46
120.84
77.25
77.00
76.75
0.01
TMS
H
TMS
H
N
N
Br
Br
3au
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

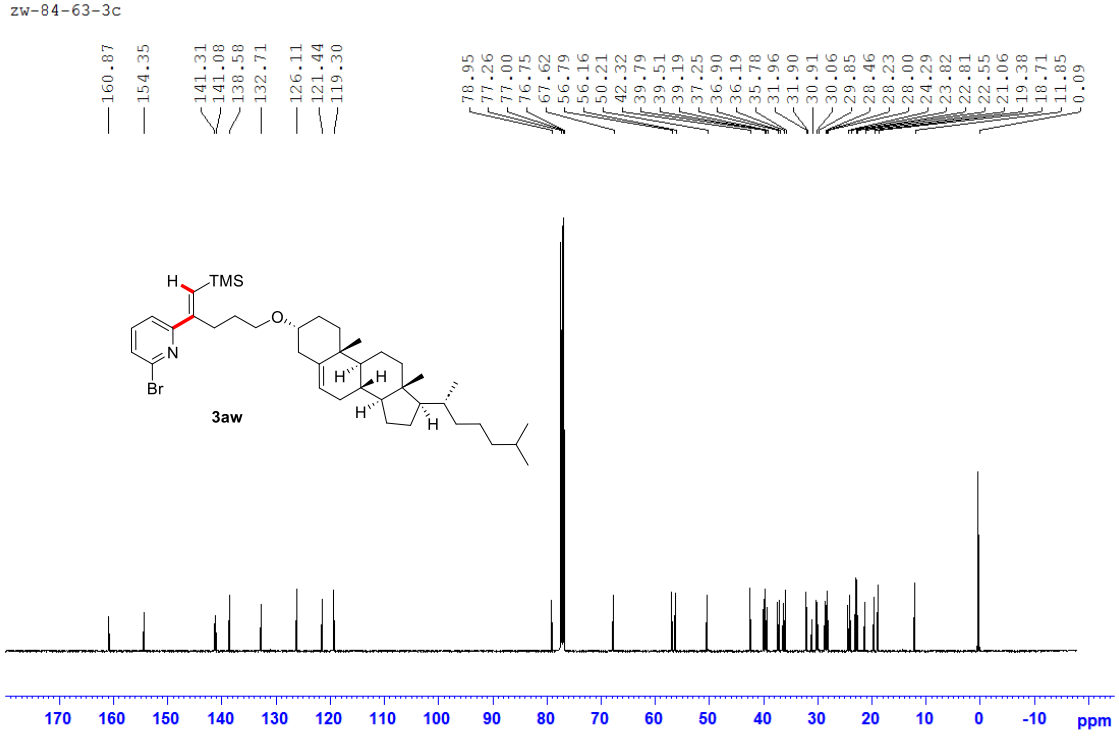

zw-84-54-2
7.440
7.425
7.409
7.349
7.334
7.287
7.167
7.152
6.932
0.088
TMS
TMS
H
H
S
N
N
Br Br
3av
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.97
1.99
1.90
2.04
2.00
18.07

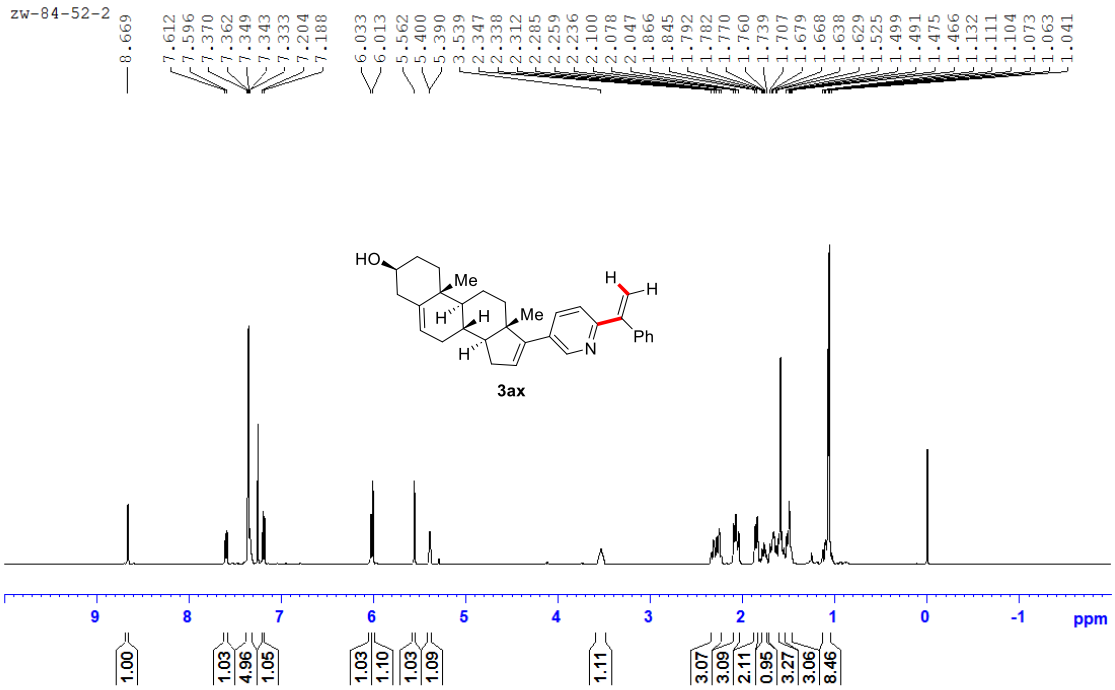

zw-84-54-2c
159.22
145.45
142.39
141.74
139.54
138.70
128.05
126.69
120.43
77.25
77.00
76.74
0.17
TMS
TMS
H
H
S
N
N
Br Br
3av
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

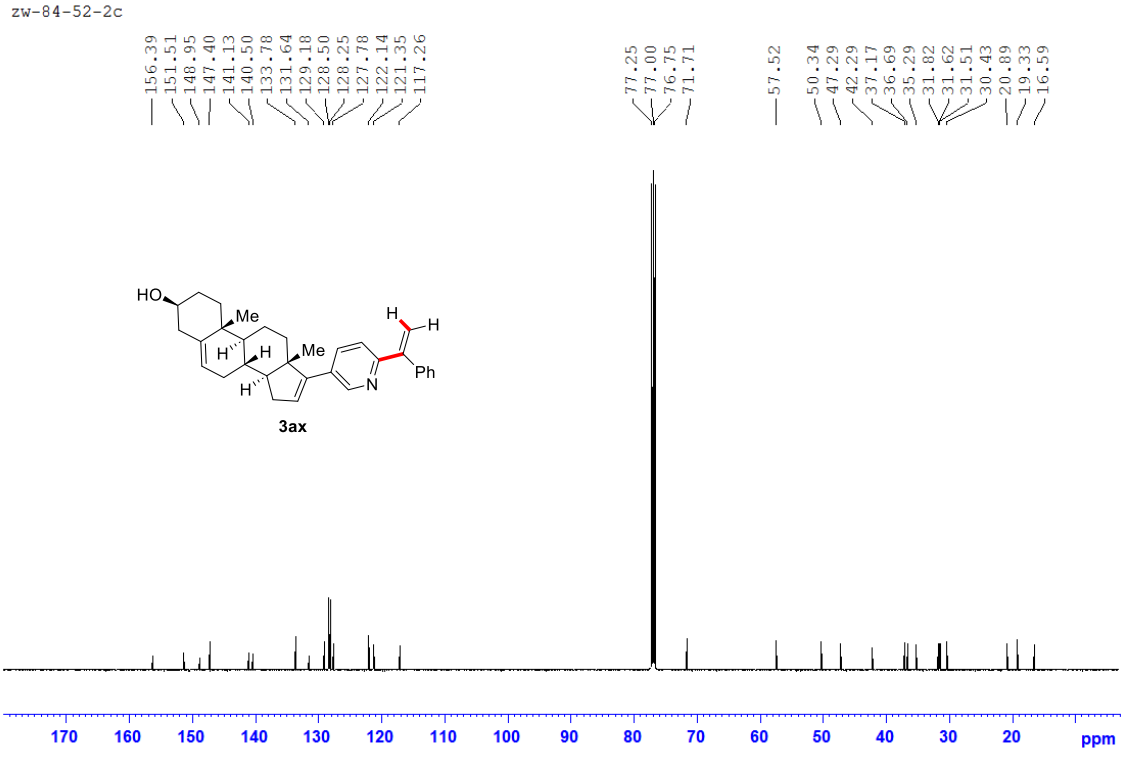
zw-84-63-3



zw-84-63-3c




zw-84-52-2
8.669
7.612
7.596
7.370
7.362
7.349
7.343
7.333
7.204
7.188
6.033
6.013
5.562
5.400
5.390
3.539
2.347
2.338
2.312
2.285
2.259
2.236
2.100
2.078
2.047
1.866
1.845
1.792
1.782
1.770
1.760
1.739
1.707
1.679
1.668
1.638
1.629
1.525
1.499
1.491
1.475
1.466
1.132
1.111
1.104
1.073
1.063
1.041
HO
Me
H
H
Me
H
H
N
Ph
3ax
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.00
1.03
4.96
1.05
1.03
1.10
1.03
1.09
1.11
3.07
3.09
2.11
0.95
3.27
3.06
8.46


zw-84-52-2c
156.39
151.51
148.95
147.40
141.13
140.50
133.78
131.64
129.18
128.50
128.25
127.78
122.14
121.35
117.26
77.25
77.00
76.75
71.71
57.52
50.34
47.29
42.29
37.17
36.69
35.29
31.82
31.62
31.51
30.43
20.89
19.33
16.59
HO
Me
H
H
Me
H
H
N
Ph
3ax
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm