Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Rhodium-Catalyzed Denitrogenative *gem*-Difunctionalization of Pyridotriazoles with Thioesters: Formal Carbene Insertion into C(O)–S Bonds

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General Experimental Section

Analytic methods. All the reactions were carried out under argon atmosphere using standard Schlenk technique. ^{1}H NMR (400 MHz), ^{19}F (376 MHz) and $^{13}C\{^{1}H\}$ NMR (100 MHz) were recorded on a Bruker AV400 NMR spectrometer. Chemical shifts of ^{1}H, ^{19}F, and $^{13}C\{^{1}H\}$ NMR spectra are reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton ($CDCl_3$: δ = 7.26 ppm, DMSO-d_6: δ = 2.50), carbon ($CDCl_3$: δ = 77.00, DMSO-d_6: δ = 39.50). All coupling constants (*J* values) were reported in Hertz (Hz). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplets (dt), triplet (t), triplet of doublets (td), quartet (q), and multiplet (m). Column chromatography was performed on silica gel 200-300 mesh. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). HRMS were done on Agilent 6520 Q-TOF LC/MS or Varian 7.0T FTMS.

General preparation for chemicals. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. The substrates pyridotriazoles (**1**)[1] and thioesters (**2**)[2] were prepared according to the literature procedures.

X-ray Crystallographic Analysis. All intensity data were collected with a Bruker SMART CCD diffractometer equipped with graphite mono-chromated Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least squares on F^2.[3] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were considered in calculated positions. Single crystals of complexes **3aa** and **3zb** suitable for X-ray diffraction were obtained from hexane/CH_2Cl_2 solution. The crystal data and summary of X-ray data collection are presented in Tables S1.

Single crystal X-ray structure of complex 3aa and 3zb

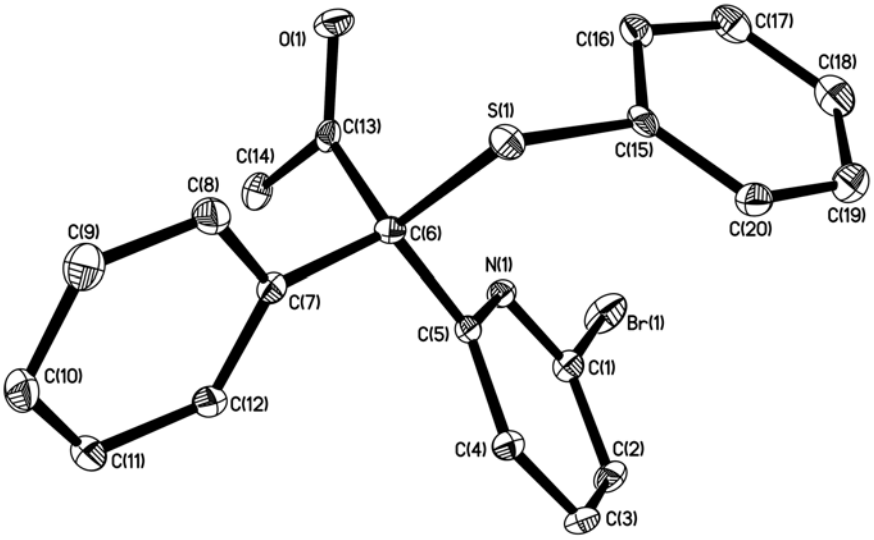


Figure S1. ORTEP diagram of complex **3aa**. Thermal ellipsoids are shown at the 30% level. All hydrogen atoms have been omitted for clarity.

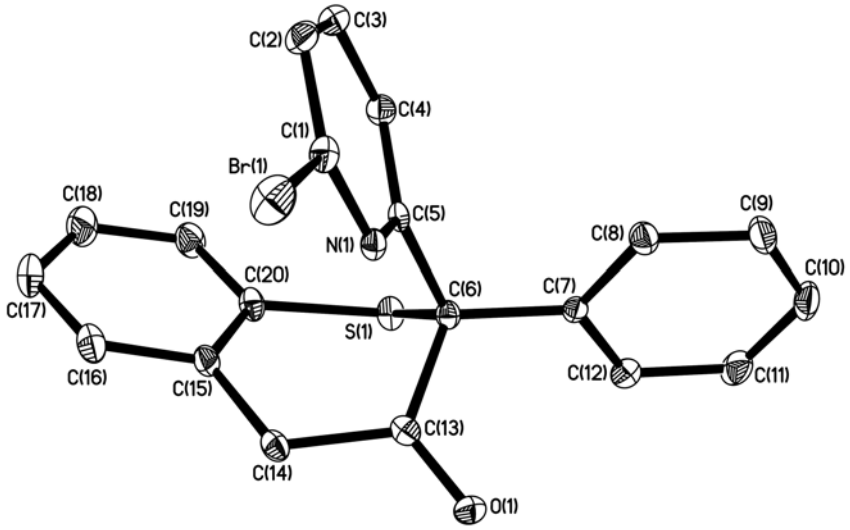


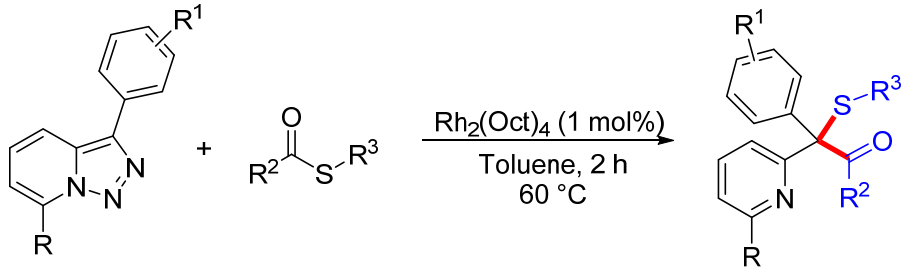
Figure S2. ORTEP diagram of complex **3zb**. Thermal ellipsoids are shown at the 30% level. All hydrogen atoms have been omitted for clarity.

Table S1. Crystal Data and Summary of X-ray Data Collection for 3aa and 3zb

complex	**3aa**	**3zb**
formula	$C_{20}H_{16}BrNOS$	$C_{20}H_{14}BrNOS$
fw	398.30	396.29
crystal system	triclinic	Monoclinic
space group	P-1	C2/c
a (Å)	8.0631(16)	21.028(4)
b (Å)	9.1192(18)	11.443(2)
c (Å)	12.401(3)	15.478(3)
α (°)	106.20(3)	90
β (°)	95.56(3)	113.67(3)
γ (°)	96.77(3)	90
V (Å^3)	861.4(4)	3411.3(14)
Z	2	8
ρ_{calcd} (g cm^{-3})	1.536	1.543
μ (mm^{-1})	2.513	2.538
F(000)	404.0	1600
cryst size (mm)	0.20×0.18×0.12	0.20×0.18×0.12
max. 2ϑ(°)	55.62	88.71
no. of reflns collected	10421	20089
no. of indep reflns/R_{int}	4063 / 0.0448	4058 / 0.0562
no. of params	218	218
goodness-of-fit on F^2	0.997	1.029
R_1, wR_2 [$I > 2\sigma(I)$]	0.0318, 0.0677	0.0358, 0.0700
R_1, wR_2 (all data)	0.0505, 0.0715	0.0529, 0.0749

Preparation and Characterization of Products 3

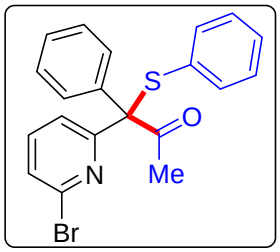
General Procedure A: Rh-Catalyzed denitrogenative thiocarbonylation of pyridotriazoles with thioesters



1 **2** **3**

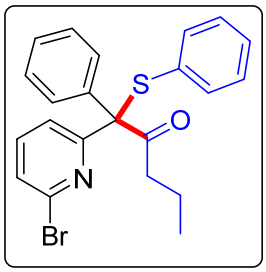
A mixture of pyridotriazole (**1**) (0.40 mmol, 2.0 equiv), $Rh_2(Oct)_4$ (0.002 mmol, 1.0 mol %), and thioester (**2**) (0.20 mmol, 1.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry Toluene (2.0 mL) was added and the resulting mixture was stirred at 60 °C for 2 h using heating modular of parallel reactor under Ar atmosphere. The reaction was then cooled to room temperature and transferred to a 100 mL round-bottomed flask using CH_2Cl_2. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel with petroleum ether/EtOAc.

1-(6-bromopyridin-2-yl)-1-phenyl-1-(phenylthio)propan-2-one (3aa)



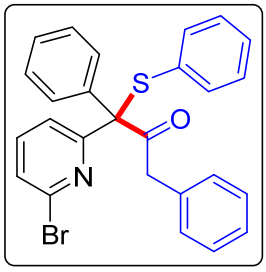
The title compound was isolated by column chromatography (eluent: EtOAc/ petroleum ether = 1/50) as a white solid in 97% yield (77.1 mg); M.p.: 151-153 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.58 (d, *J* = 6.9 Hz, 2H), 7.40-7.30 (m, 5H), 7.22-7.18 (m, 1H), 7.10-7.05 (m, 5H), 2.18 (s, 3H); **$^{13}C\{^1H\}$ NMR (DMSO-d_6, 100 MHz):** δ 199.7, 159.4, 139.7, 139.6, 137.0, 135.2, 130.7, 129.2, 129.0, 128.5, 128.4, 128.0, 126.9, 123.4, 76.9, 27.4; **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}BrNOS$ 398.0209, Found: 398.0208.

1-(6-bromopyridin-2-yl)-1-phenyl-1-(phenylthio)pentan-2-one (3ab)



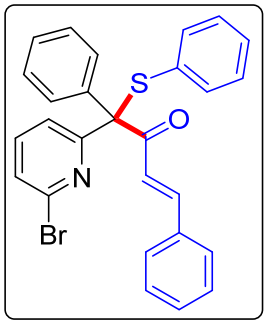
The title compound was isolated by column chromatography (eluent: EtOAc /petroleum ether = 1/50) as a pale yellow solid in 86% yield (73.4 mg); M.p.: 51-53 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.60 (d, *J* = 6.9, 2H), 7.36-7.28 (m, 5H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.08-6.98 (m, 5H), 2.57-2.49 (m, 1H), 2.25-2.18 (m, 1H), 1.66-1.56 (m, 1H), 1.53-1.42 (m, 1H), 0.74 (t, *J* = 7.4 Hz, 3H); **$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz):** δ 203.4, 160.1, 140.5, 137.8, 137.3, 135.6, 131.6, 129.6, 128.6, 128.3, 128.2, 128.0, 126.4, 123.2, 77.7, 42.0, 18.5, 13.6; **HRMS (ESI)** m/z**:** $[M+H]^+$ Calcd for $C_{22}H_{21}BrNOS$ 426.0522, Found: 426.0530.

1-(6-bromopyridin-2-yl)-1,3-diphenyl-1-(phenylthio)propan-2-one (3ac)



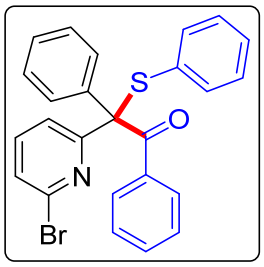
The title compound was isolated by column chromatography (eluent: EtOAc /petroleum ether = 1/50) as a pale yellow solid in 89% yield (84.6 mg); M.p.: 122-124 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.62-7.60 (m, 2H), 7.40-7.31 (m, 5H), 7.23-7.17 (m, 4H), 7.10 (dd, *J* = 7.6, 0.6 Hz, 1H), 7.08-7.00 (m, 6H), 3.90 (d, *J* = 16.1 Hz, 1H), 3.60 (d, *J* = 16.1 Hz, 1H); **$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz):** δ 200.5, 160.0, 140.6, 138.0, 137.2, 135.7, 134.9, 131.4, 129.6, 128.7, 128.5, 128.3, 128.2, 128.0, 126.6, 126.5, 123.6, 77.4, 46.3 (one signal missing due to overlap); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{26}H_{21}BrNOS$ 474.0522, Found: 474.0530.

(*E*)-1-(6-bromopyridin-2-yl)-1,4-diphenyl-1-(phenylthio)but-3-en-2-one (3ad)



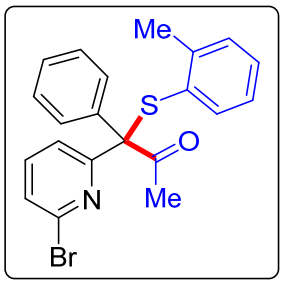
The title compound was isolated by column chromatography (eluent: EtOAc /petroleum ether = 1/50) as a pale yellow oil in 97% yield (94.4 mg); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.69 (d, *J* = 15.7 Hz, 1H), 7.51-7.48 (m, 2H), 7.47-7.44 (m, 2H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.36-7.26 (m, 8H), 7.24-7.20 (m, 1H) 7.17-7.05 (m, 5H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 191.4, 160.0, 142.3, 140.7, 138.3, 135.8, 134.7, 131.0, 130.2, 129.5, 129.0, 128.7, 128.4, 128.3, 128.1, 127.7, 126.6, 124.3, 123.5, 75.0 (one signal missing due to overlap); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{27}H_{21}BrNOS$ 486.0522, Found: 486.0527.

2-(6-bromopyridin-2-yl)-1,2-diphenyl-2-(phenylthio)ethan-1-one (3ae)



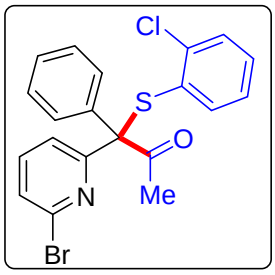
The title compound was isolated by column chromatography (eluent: EtOAc /petroleum ether = 1/50) as a pale yellow oil in 37% yield (34.2mg); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.73 (d, *J* = 7.4 Hz, 2H), 7.54 (dd, *J* = 8.3, 1.5 Hz, 2H), 7.40-7.31 (m, 3H), 7.28-7.17 (m, 7H), 7.08-6.99 (m, 4H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 194.5, 160.4, 140.4, 138.7, 138.2, 136.2, 135.8, 132.0, 131.4, 130.6, 129.6, 128.9, 128.2, 128.0, 127.7, 127.6, 126.3, 123.6, 75.5; **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{25}H_{19}BrNOS$ 460.0365, Found: 460.0375.

1-(6-bromopyridin-2-yl)-1-phenyl-1-(*o*-tolylthio)propan-2-one (3af)



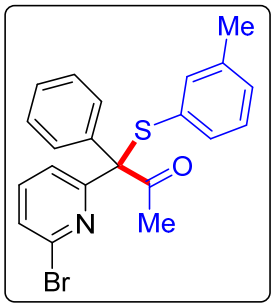
The title compound was isolated by column chromatography (eluent: EtOAc/ petroleum ether = 1/50) as a pale yellow solid in 93% yield (76.2 mg); M.p.: 113-115 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.56 (dd, *J* = 8.1, 2.2 Hz, 2H), 7.36-7.30 (m, 5H), 7.09 (td, *J* = 7.2, 1.5 Hz, 1H), 7.03-6.99 (m, 2H), 6.89 (dd, *J* = 6.9, 1.0 Hz, 1H), 6.86 (dd, *J* = 7.1, 1.4 Hz, 1H), 2.18 (s, 3H), 1.94 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 201.0, 159.8, 142.8, 140.6, 137.8, 137.4, 135.2, 131.0, 130.2, 129.7, 128.6, 128.2, 127.9, 126.5, 125.9, 122.8, 77.1, 27.6, 20.5; **HRMS (ESI):** $[M+Na]^+$ Calcd for $C_{21}H_{18}BrNNaOS^+$ 434.0185, Found: 434.0184.

1-(6-bromopyridin-2-yl)-1-((4-chlorophenyl)thio)-1-phenylpropan-2-one (3ag)



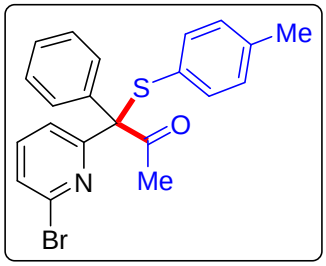
The title compound was isolated by column chromatography (eluent: EtOAc /petroleum ether = 1/50) as a pale yellow solid in 76% yield (65.7 mg); M.p.: 126-128 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.58-7.56 (m, 2H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.37-7.31 (m, 4H), 7.24 (dd, *J* = 8.8, 1.2 Hz, 1H), 7.15 (dd, *J* = 7.6, 0.9 Hz 1H), 7.11-7.06 (m, 2H), 6.97-6.92 (m, 1H), 2.22 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 200.7, 159.8, 140.5, 138.4, 137.6, 137.1, 135.1, 131.5, 129.6, 129.4, 129.0, 128.5, 128.1, 126.8, 126.6, 123.0, 76.8, 27.9; **HRMS (ESI):** $[M+Na]^+$ Calcd for $C_{20}H_{15}BrClNNaOS^+$ 453.9638, Found: 453.9641.

1-(6-bromopyridin-2-yl)-1-phenyl-1-(*m*-tolylthio)propan-2-one (3ah)



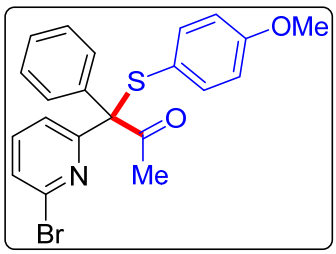
The title compound was isolated by column chromatography (eluent: EtOAc /petroleum ether = 1/50) as a white solid in 88% yield (72.7 mg); M.p.: 113-115 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.58-7.55 (m, 2H), 7.40-7.29 (m, 5H), 7.10 (dd, *J* = 7.7, 0.7 Hz, 1H), 7.01-6.95 (m, 2H), 6.88 (d, *J* = 7.2 Hz, 1H), 6.82 (s, 1H), 2.18 (s, 3H), 2.15 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 200.8, 160.3, 140.5, 138.1, 137.9, 137.7, 136.2, 132.5, 131.1, 129.6, 129.5, 128.3, 128.1, 128.0, 126.4, 123.3, 77.2, 27.9, 21.1**;** **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{21}H_{18}BrNNaOS$ 434.0185, Found: 434.0174.

1-(6-bromopyridin-2-yl)-1-phenyl-1-(*p*-tolylthio)propan-2-one (3ai)



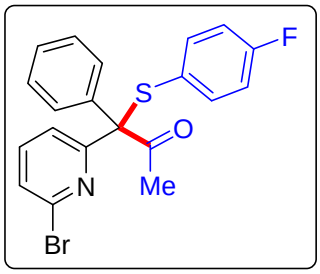
The title compound was isolated by column chromatography (eluent: EtOAc /petroleum ether = 1/50) as a yellow solid in 82% yield (67.8 mg); M.p.: 149-151 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.60-7.58 (m, 2H), 7.40-7.29 (m, 5H), 7.10 (dd, *J* = 7.7, 0.8 Hz, 1H), 6.95-6.88 (m, 4H), 2.25 (s, 3H), 2.17 (s, 3H), **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** 200.6, 160.4, 140.6, 139.2, 138.0, 137.9, 135.8, 129.6, 129.2, 128.3, 127.9, 127.7, 126.4, 123.1, 77.1, 27.8, 21.1; **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{21}H_{18}BrNNaOS$ 434.0185, Found: 434.0178.

1-(6-bromopyridin-2-yl)-1-((4-methoxyphenyl)thio)-1-phenylpropan-2-one (3aj)



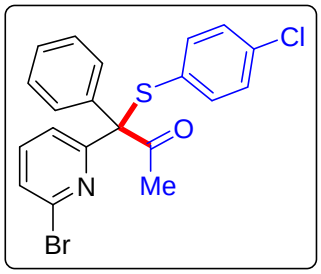
The title compound was isolated by column chromatography (eluent: EtOAc /petroleum ether = 1/50 to EtOAc /petroleum ether = 1/20) as a pale yellow solid in 92% yield (78.2 mg); M.p.: 191-193 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.59-7.56 (m, 2H), 7.41-7.29 (m, 5H), 7.06 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.99-6.96 (m, 2H), 6.63-6.60 (m, 2H), 3.72 (s, 3H), 2.16 (s, 3H); **^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz):** δ 199.6, 160.2, 159.5, 139.7, 139.4, 137.6, 137.1, 129.2, 128.3, 127.8, 126.6, 123.4, 120.7, 114.1, 76.9, 55.1, 27.4; **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{21}H_{18}BrNNaO_2S$ 450.0134, Found: 450.0135.

1-(6-bromopyridin-2-yl)-1-((4-fluorophenyl)thio)-1-phenylpropan-2-one (3ak)



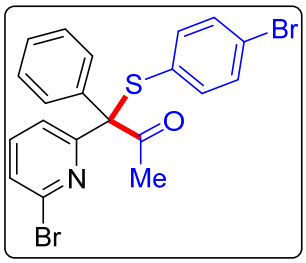
The title compound was isolated by column chromatography (eluent: EtOAc /petroleum ether = 1/50) as a pale yellow solid in 85% yield (70.6 mg); M.p.: 151-153 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.57-7.55 (m, 2H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.37-7.29 (m, 4H), 7.11 (d, *J* = 7.7 Hz, 1H), 7.06-7.02 (m, 2H), 6.77 (t, *J* = 8.6, 2H), 2.15 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 200.6, 163.3 (d, J_{C-F} = 250.0 Hz) , 160.0, 140.7, 138.2 (d, J_{C-F} = 8.6 Hz), 138.1, 137.4, 129.4, 128.5, 128.1, 126.5, 123.2, 115.4 (d, J_{C-F} = 21.7 Hz), 77.5, 27.8 (one signal missing due to overlap); **^{19}F NMR ($CDCl_3$, 376 MHz):** δ -111.5 (s); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}BrFNOS$ 416.0115, Found: 416.0115.

1-(6-bromopyridin-2-yl)-1-((4-chlorophenyl)thio)-1-phenylpropan-2-one (3al)



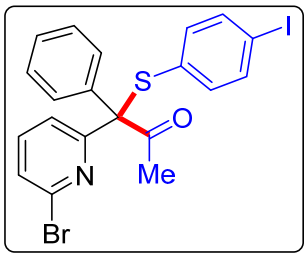
The title compound was isolated by column chromatography (eluent: EtOAc /petroleum ether = 1/50) as a pale yellow solid in 82% yield (71.0 mg); M.p.: 147-149 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.57-7.55 (m, 2H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.38-7.31 (m, 4H), 7.12 (dd, *J* = 7.7, 0.6 Hz, 1H), 7.07-7.03 (m, 2H), 7.00-6.96 (m, 2H), 2.15 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 200.5, 160.0, 140.7, 138.1, 137.4, 136.9, 135.3, 130.1, 129.4, 128.54, 128.52, 128.2, 126.6, 123.1, 77.5, 27.8; **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}BrClNOS$ 431.9819, Found: 431.9821.

1-((4-bromophenyl)thio)-1-(6-bromopyridin-2-yl)-1-phenylpropan-2-one (3am)



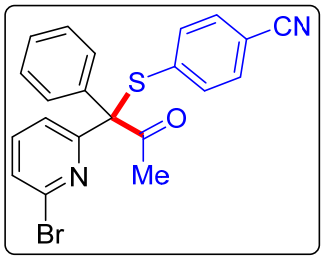
The title compound was isolated by column chromatography (eluent: EtOAc /petroleum ether = 1/50) as a white solid in 97% yield (92.1 mg); M.p.: 148-150 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.57-7.54 (m, 2H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.38-7.30 (m, 4H), 7.22-7.19 (m, 2H), 7.12 (dd, *J* = 7.7, 0.7 Hz, 1H), 6.93-6.90 (m, 2H), 2.15 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 200.4, 159.8, 140.6, 138.2, 137.2, 137.0, 131.4, 130.6, 129.3, 128.5, 128.2, 126.6, 123.5, 123.0, 77.4, 27.7; **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}Br_2NOS$ 475.9314, Found: 475.9316.

1-(6-bromopyridin-2-yl)-1-((4-iodophenyl)thio)-1-phenylpropan-2-one (3an)



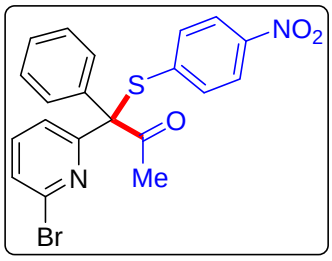
The title compound was isolated by column chromatography (eluent: EtOAc /petroleum ether = 1/50) as an orange solid in 97% yield (101.6 mg); M.p.: 126-128 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.57-7.54 (m, 2H), 7.44-7.38 (m, 3H), 7.37-7.31 (m, 4H), 7.12 (dd, *J* = 7.6, 0.5 Hz, 1H), 6.78-6.75 (m, 2H), 2.15 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 200.5, 159.9, 140.7, 138.2, 137.5, 137.3, 137.0, 131.5, 129.4, 128.6, 128.2, 126.7, 123.1, 95.4, 77.4, 27.8; **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}BrINOS$ 523.9175, Found: 523.9178.

4-((1-(6-bromopyridin-2-yl)-2-oxo-1-phenylpropyl)thio)benzonitrile (3ao)



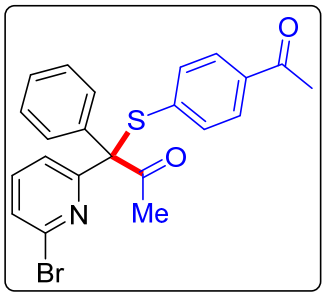
The title compound was isolated by column chromatography (eluent: EtOAc /petroleum ether = 1/50 to EtOAc /petroleum ether = 1/20) as a pale yellow solid in 76% yield (64.2 mg); M.p.: 135-137 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.52 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.39-7.33 (m, 6H), 7.27-7.25 (m, 1H), 7.17 (d, *J* = 8.3 Hz, 2H), 2.17 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 200.4, 159.6, 140.6, 139.2, 138.5, 136.8, 133.9, 131.6, 129.0, 128.8, 128.5, 126.9, 123.1, 118.3, 111.3, 77.4, 27.9; **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{21}H_{16}BrN_2OS$ 423.0161, Found: 423.0165.

1-(6-bromopyridin-2-yl)-1-((4-nitrophenyl)thio)-1-phenylpropan-2-one(3ap)



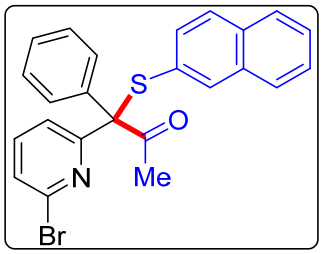
The title compound was isolated by column chromatography (eluent: EtOAc /petroleum ether = 1/50 to EtOAc /petroleum ether = 1/10) as a pale orange solid in 86% yield (76.6 mg); M.p.: 89-91 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.94-7.90 (m, 2H), 7.53 (dd, *J* = 8.3, 1.8 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.39-7.33 (m, 4H), 7.29 (dd, *J* = 7.7, 0.5 Hz, 1H), 7.24-7.20 (m, 2H), 2.19 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 200.4, 159.6, 146.9, 141.9, 140.6, 138.7, 136.8, 133.3, 128.93, 128.88, 128.6, 127.0, 123.14, 123.08, 77.4, 28.0; **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}BrN_2O_3S$ 443.0060, Found: 443.0062.

1-((4-acetylphenyl)thio)-1-(6-bromopyridin-2-yl)-1-phenylpropan-2-one (3aq)



The title compound was isolated by column chromatography (eluent: EtOAc /petroleum ether = 1/50 to EtOAc /petroleum ether = 1/10) as a pale yellow oil in 93% yield (82.1 mg); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.67-7.64 (m, 2H), 7.57-7.55 (m, 2H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.38-7.30 (m, 4H), 7.22 (dd, *J* = 7.7, 0.7 Hz, 1H), 7.16-7.13 (m, 2H), 2.51 (s, 3H), 2.18 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 200.4, 197.4, 159.9, 140.5, 138.7, 138.4, 137.1, 136.1, 133.5, 129.1, 128.6, 128.3, 128.0, 126.7, 123.0, 77.1, 27.9, 26.5; **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{22}H_{18}BrNNaO_2S$ 462.0134, Found: 462.0142.

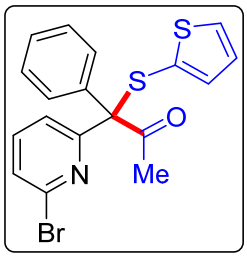
1-(6-bromopyridin-2-yl)-1-(naphthalen-2-ylthio)-1-phenylpropan-2-one (3ar)



The title compound was isolated by column chromatography (eluent: EtOAc /petroleum ether = 1/50 to EtOAc /petroleum ether = 1/10) as a pale orange solid in 98% yield (88.3 mg); M.p.: 115-117 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 6.8 Hz, 2H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 4.1 Hz, 2H), 7.46-7.39 (m, 2H), 7.37-7.32 (m, 3H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.28 (br s, 1H), 7.11 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.05 (dd, *J* = 6.8, 1.1 Hz, 1H), 2.21 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 200.8, 160.0, 140.6, 138.0, 137.6, 135.6, 133.0, 132.9, 131.7, 131.0, 129.5, 128.9, 128.4,

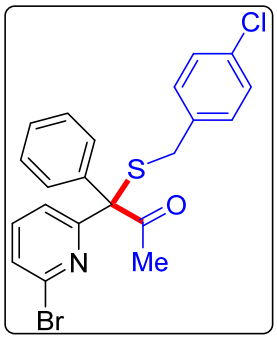
128.1, 127.7, 127.4, 126.7, 126.5, 126.1, 123.1, 77.5, 27.8; **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{24}H_{18}BrNNaOS$ 470.0185, Found: 470.0189.

1-(6-bromopyridin-2-yl)-1-phenyl-1-(thiophen-2-ylthio)propan-2-one (3as)



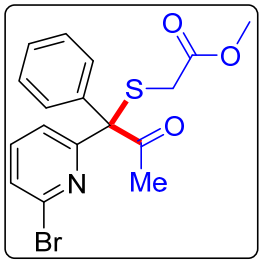
The title compound was isolated by column chromatography (eluent: EtOAc /petroleum ether = 1/50) as a white solid in 95% yield (76.7 mg); M.p.: 116-118 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.57 (dd, *J* = 8.2, 1.6 Hz, 2H), 7.43-7.32 (m, 5H), 7.27-7.26 (m, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.82-6.79 (m, 1H), 6.73 (dd, *J* = 3.5, 1.0 Hz, 1H), 2.17 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 201.1, 159.6, 140.8, 138.0, 137.8, 136.9, 131.8, 129.6, 129.5, 128.6, 128.3, 126.9, 126.7, 123.0, 79.2, 27.7; **HRMS (ESI)**: $[M+H]^+$ Calcd for $C_{18}H_{15}BrNOS_2$ 403.9773, Found: 403.9777.

1-(6-bromopyridin-2-yl)-1-phenyl-1-(thiophen-2-ylthio)propan-2-one (3at)



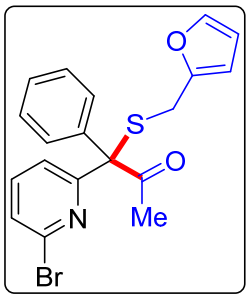
The title compound was isolated by column chromatography (eluent: EtOAc /petroleum ether = 1/50) as a yellow oil in 85% yield (76.0 mg); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.60-7.58 (m, 2H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.39 (dd, *J* = 7.5, 0.6 Hz, 1H), 7.38-7.34 (m, 3H) 7.31-7.29 (m, 1H), 7.23-7.20 (m, 2H), 7.15-7.12 (m, 2H), 3.57 (d, *J* = 12.1 Hz, 1H), 3.40 (d, *J* = 12.2 Hz, 1H), 2.22 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 200.0, 161.1, 140.7, 138.8, 137.5, 134.9, 132.9, 130.5, 129.0, 128.6, 128.0, 126.7, 122.3, 72.7, 34.9, 27.8 (one signal missing due to overlap); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}BrClNOS$ 445.9976, Found: 445.9977.

methyl 2-((1-(6-bromopyridin-2-yl)-2-oxo-1-phenylpropyl)thio)acetate (3au)



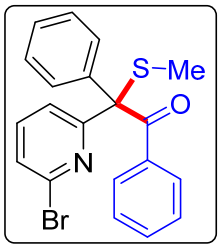
The title compound was isolated by column chromatography (eluent: EtOAc /petroleum ether = 1/10) as a pale yellow oil in 67% yield (52.6 mg); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.55 (t, *J* = 1.5 Hz, 1H), 7.53-7.51 (m, 2H), 7.43 (dd, *J* = 7.7, 0.5 Hz, 1H), 7.38 (dd, *J* = 7.8, 0.5 Hz, 1H), 7.36-7.33 (m, 2H), 7.31-7.28 (m, 1H), 3.61 (s, 3H), 3.26 (d, *J* = 15.6 Hz, 1H), 3.11 (d, *J* = 15.6 Hz, 1H), 2.18 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 200.3, 169.6, 160.7, 140.8, 138.9, 137.0, 129.1, 128.6, 128.1, 126.9, 122.4, 72.3, 52.4, 33.1, 27.7; **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{17}H_{16}BrNNaO_3S$ 415.9926, Found: 415.9933.

1-(6-bromopyridin-2-yl)-1-((furan-2-ylmethyl)thio)-1-phenylpropan-2-one (3av)



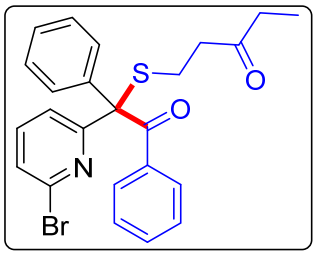
The title compound was isolated by column chromatography (eluent: EtOAc /petroleum ether = 1/50) as an orange oil in 55% yield (43.8 mg); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.59 (d, *J* = 7.8 Hz, 2H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.37-7.28 (m, 5H), 6.25-6.23 (m, 1H), 6.06 (d, *J* = 2.9 Hz, 1H), 3.67 (d, *J* = 13.9 Hz, 1H), 3.51 (d, *J* = 13.9 Hz, 1H), 2.22 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 200.3, 161.1, 149.8, 142.2, 140.7, 138.8, 137.5, 129.1, 128.6, 127.9, 126.7, 122.2, 110.5, 108.1, 72.4, 27.8, 27.7; **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{19}H_{17}BrNO_2S$ 402.0158, Found: 402.0160.

2-(6-bromopyridin-2-yl)-2-(methylthio)-1,2-diphenylethan-1-one (3aw)



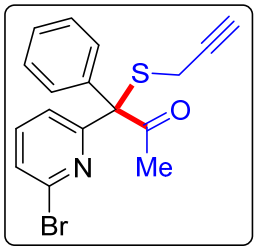
The title compound was isolated by column chromatography (eluent: CH_2Cl_2 /petroleum ether = 1/5) as an orange oil in 84% yield (67.2 mg); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.77 (d, *J* = 7.4 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.43-7.41 (m, 2H), 7.39-7.28 (m, 4H), 7.25-7.20 (m, 3H), 1.96 (s, 3H) **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 193.5, 161.6, 140.7, 138.7, 138.6, 136.2, 131.7, 130.3, 129.2, 128.3, 127.5, 126.3, 122.0, 70.0, 14.3 (one signal missing due to overlap); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}BrNOS$ 398.0209, Found: 398.0213.

1-((1-(6-bromopyridin-2-yl)-2-oxo-1,2-diphenylethyl)thio)pentan-3-one (3ax)



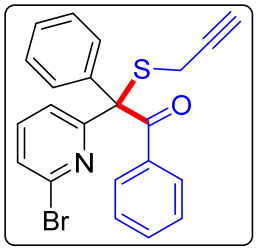
The title compound was isolated by column chromatography (eluent: EtOAc /petroleum ether = 1/50 to EtOAc /petroleum ether = 1/20) as a pale yellow solid in 88% yield (82.9 mg); M.p.: 78-80 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.77 (dd, *J* = 8.6, 1.3 Hz, 2H), 7.58 (dd, *J* = 8.7, 1.3 Hz, 2H), 7.44-7.27 (m, 6H), 7.26-7.20 (m, 3H), 2.69-2.63 (m, 2H), 2.61-2.56 (m, 2H), 2.30 (q, *J* = 7.3 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 209.3, 194.6, 161.7, 140.6, 139.1, 138.7, 136.0, 131.8, 130.4, 129.2, 128.3, 127.7, 127.6, 126.4, 122.2, 70.7, 41.3, 35.7, 25.4, 7.6; **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{24}H_{23}BrNO_2S$ 468.0627, Found: 468.0633.

1-(6-bromopyridin-2-yl)-1-phenyl-1-(prop-2-yn-1-ylthio)propan-2-one (3ay)



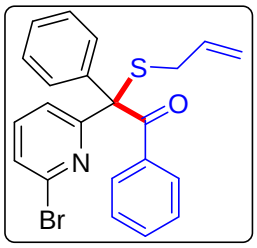
The title compound was isolated by column chromatography (eluent: EtOAc /petroleum ether = 1/50) as a orange oil in 86% yield (61.7 mg); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.56-7.50 (m, 3H), 7.42 (dd, *J* = 7.7, 0.6 Hz, 1H), 7.40-7.34 (m, 3H), 7.32-7.29 (m,1H), 3.17 (dd, *J* = 16.0, 2.7 Hz, 1H), 3.00 (dd, *J* = 16.0, 2.7 Hz, 1H), 2.22 (s, 3H), 2.12 (t, *J* = 2.7 Hz, 1H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 200.4, 160.7, 140.8, 138.9, 137.0, 129.0, 128.6, 128.1, 126.9, 122.5, 78.7, 72.5, 71.7, 27.8, 18.9; **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{17}H_{15}BrNOS$ 360.0052, Found: 360.0046.

2-(6-bromopyridin-2-yl)-1,2-diphenyl-2-(prop-2-yn-1-ylthio)ethan-1-one (3az)



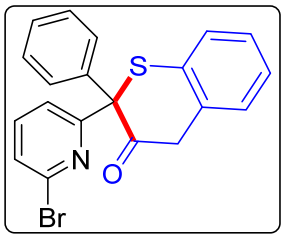
The title compound was isolated by column chromatography (eluent: EtOAc /petroleum ether = 1/50) as an pale orange oil in 97% yield (82.3 mg); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.73 (dd, *J* = 8.4, 1.1 Hz, 2H), 7.60-7.58 (m, 2H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.40-7.27 (m, 6H), 7.25-7.20 (m, 2H), 3.20 (d, *J* = 2.7 Hz, 2H), 2.10 (t, *J* = 2.7 Hz, 1H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 194.6, 161.0, 140.7, 138.7, 138.1, 135.8, 132.0, 130.3, 129.1, 128.5, 127.9, 127.7, 126.6, 122.5, 78.6, 71.9, 71.1, 19.7; **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}BrNOS$ 422.0209, Found: 422.0204.

2-(allylthio)-2-(6-bromopyridin-2-yl)-1,2-diphenylethan-1-one (3za)



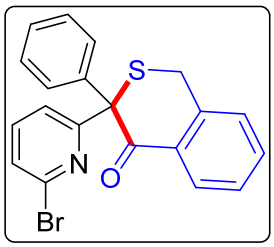
The title compound was isolated by column chromatography (eluent: EtOAc /petroleum ether = 1/50) as a pale pale yellow oil in 72% yield (60.5 mg); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.78 (d, *J* = 8.6 Hz, 2H), 7.61 (dd, *J* = 8.9, 1.4 Hz, 2H) 7.42 (t, *J* = 7.6 Hz, 1H), 7.39-7.28 (m, 5H), 7.27-7.21 (m, 3H), 5.78-5.68 (m, 1H), 5.11 (dd, *J* = 16.9, 1.3 Hz, 1H), 5.02 (d, *J* = 10.0 Hz, 1H), 3.15-3.05 (m, 2H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 194.4, 161.8, 140.7, 139.0, 138.6, 136.2, 132.5, 131.8, 130.3, 129.2, 128.4, 127.7, 127.6, 126.4, 122.2, 118.5, 70.7, 34.9; **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{22}H_{19}BrNOS$ 424.0365, Found: 424.0371.

2-(allylthio)-2-(6-bromopyridin-2-yl)-1,2-diphenylethan-1-one (3zb)



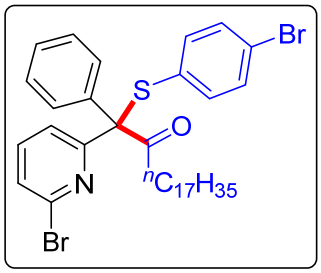
The title compound was isolated by column chromatography (eluent: EtOAc /petroleum ether = 1/50) as a pale yellow solid in 86% yield (67.9 mg); M.p.: 149-151 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.38 (t, *J* = 7.7 Hz, 1H), 7.31-7.21 (m, 8H), 7.10-7.02 (m, 3H), 4.11 (d, *J* = 20.3 Hz, 1H), 3.93 (d, *J* = 20.3 Hz, 1H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 200.7, 160.6, 139.8, 138.6, 137.1, 135.4, 131.4, 129.2, 128.4, 128.3, 128.13, 128.10, 127.3, 126.9, 126.7, 123.0, 67.3, 45.3; **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{15}BrNOS$ 396.0052, Found: 396.0054.

3-(6-bromopyridin-2-yl)-3-phenylisothiochroman-4-one (3zc)



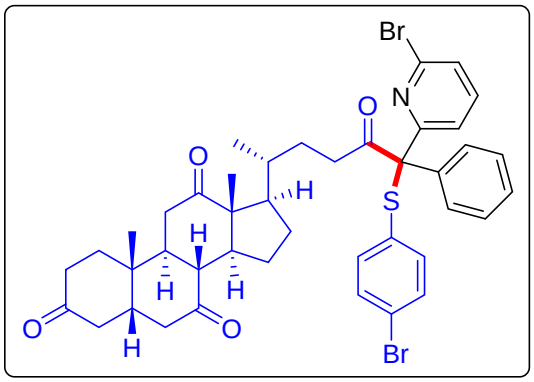
The title compound was isolated by column chromatography (eluent: EtOAc /petroleum ether = 1/50) as a pale pink solid in 62% yield (48.6 mg); M.p.: 186-188 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 8.17 (d, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.38-7.29 (m, 8H), 7.03 (d, *J* = 7.4 Hz, 2H), 3.69 (d, *J* = 16.9 Hz, 1H), 3.61 (d, *J* = 16.9 Hz, 1H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 191.0, 160.2, 140.9, 140.5, 138.1, 137.4, 133.5, 132.2, 129.8, 128.7, 128.6, 128.2, 127.5, 127.4, 126.8, 124.2, 64.8, 28.9; **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{15}BrNOS$ 396.0052, Found: 396.0059.

1-((4-bromophenyl)thio)-1-(6-bromopyridin-2-yl)-1-phenylnonadecan-2-one (3zd)



The title compound was isolated by column chromatography (eluent: EtOAc/ petroleum ether = 1/50 to EtOAc/ petroleum ether = 1/20) as a yellow solid in 99% yield (140.0 mg); M.p.: 51-53 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.56 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.42-7.29 (m, 5H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 2H), 2.55-2.47 (m, 1H), 2.23-2.15 (m, 1H), 1.62-1.51 (m, 1H), 1.48-1.37 (m, 1H), 1.32-1.07 (m, 28H), 0.88 (t, *J* = 6.6 Hz, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 203.3, 160.0, 140.6, 138.0, 137.12, 137.08, 131.3, 130.9, 129.4, 128.5, 128.2, 126.5, 123.4, 123.2, 77.8, 40.1, 31.8, 29.8, 29.63, 29.59, 29.5, 29.33, 29.29, 29.2, 28.9, 25.1, 22.6, 14.1 (five signals missing due to overlap); **HRMS (ESI):** $[M+Na]^+$ Calcd for $C_{36}H_{47}Br_2NNaOS$ 722.1637, Found: 722.1644.

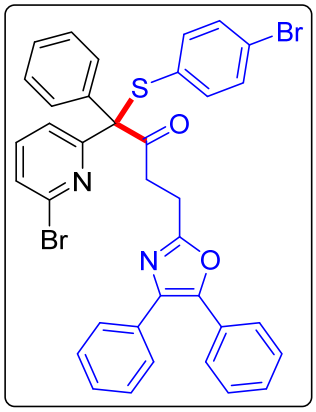
(5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-17-(6-((4-bromophenyl)thio)-6-(6-bromopyridin-2-yl)-5-oxo-6-phenylhexan-2-yl)-10,13-dimethyldodecahydro-3*H*-cyclopenta[*a*]phenanthrene-3,7,12(2*H*,4*H*)-trione (3ze)



The title compound was isolated by column chromatography (eluent: EtOAc/ petroleum ether = 1/20 to EtOAc/ petroleum ether = 1/2) as a yellow oil in 83% yield (136.1 mg, mixture of two diastereoisomers, *d.r.* = 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.59-7.55 (m, 2H), 7.42-7.30 (m, 5H), 7.17 (dd, *J* = 8.5, 1.9 Hz, 2H), 7.04 (d, *J* = 7.5 Hz) + 6.99 (d, *J* = 7.2 Hz) (1H), 6.85 (dd, *J* = 8.5, 2.6 Hz, 2H), 2.92-2.76 (m, 3H), 2.66-1.55(m, 21H), 1.37 (s, 3H), 1.00 (s) + 0.95 (s) (3H), 0.64 (d, *J* = 6.5 Hz) + 0.53 (d, *J* = 6.6 Hz) (3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 212.0, 211.9, 208.9, 208.6, 203.7, 160.1, 159.9, 140.71, 140.68, 138.0, 137.14, 137.10, 137.0, 131.4, 130.94, 130.88, 129.5, 128.62, 128.59, 128.32, 128.27, 126.6, 123.48, 123.43, 123.29, 123.23, 78.2, 78.0, 56.84, 56.78, 51.7, 51.6, 49.0, 46.8, 45.6, 45.5, 44.9, 42.7, 38.6, 37.1, 37.0, 36.4, 36.0, 35.2, 35.1, 30.7, 30.6, 27.39, 27.36, 25.08, 25.05,

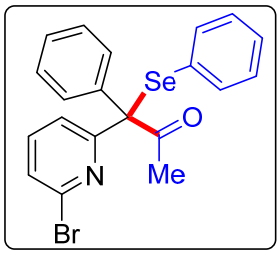
21.9, 18.9, 18.7, 11.9, 11.8 (20 signals missing due to overlap); **HRMS (ESI):** $[M+Na]^+$ Calcd for $C_{42}H_{45}Br_2NNaO_4S^+$ 840.1328, Found: 840.1332.

1-((4-bromophenyl)thio)-1-(6-bromopyridin-2-yl)-4-(4,5-diphenyloxazol-2-yl)-1-phenylbutan-2-one (3zf)



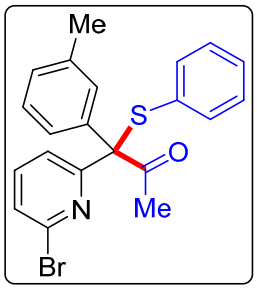
The title compound was isolated by column chromatography (eluent: EtOAc/ petroleum ether = 1/20 to EtOAc/ petroleum ether = 1/2) as a yellow solid in 94% yield (133.7 mg); M.p.: 146-148 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.58-7.52 (m, 6H), 7.42-7.28 (m, 11H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 2H), 3.23-3.10 (m, 3H), 2.84-2.74 (m, 1H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 201.3, 162.2, 159.8, 145.0, 140.6, 138.2, 137.0, 136.7, 134.9, 132.4, 131.4, 130.6, 129.2, 128.8, 128.7, 128.5, 128.39, 128.36, 128.2, 127.9, 127.8, 126.7, 126.3, 123.5, 123.3, 77.2, 37.1, 23.7; **HRMS (ESI):** $[M+Na]^+$ Calcd for $C_{36}H_{26}Br_2N_2NaO_2S$ 730.9974, Found: 730.9978.

1-(6-bromopyridin-2-yl)-1-phenyl-1-(phenylselanyl)propan-2-one (3zg)



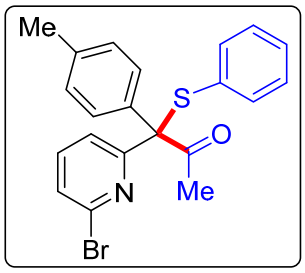
The title compound was isolated by column chromatography (eluent: EtOAc/ petroleum ether = 1/50) as a pale yellow solid in 68% yield (60.1 mg); M.p.: 125-127 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.54 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.36-7.21 (m, 6H), 7.11-7.05 (m, 4H), 6.84 (dd, *J* = 6.8, 1.7 Hz, 1H), 2.17 (s, 3H); **^{13}C{^{1}H} NMR (DMSO-*d_6*, 100 MHz):** δ 200.9, 161.0, 140.59, 140.57, 137.99, 137.95, 137.3, 130.0, 129.0, 128.4, 128.3, 127.8, 126.3, 122.8, 75.1, 27.7; **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}BrNOSe$ 445.9653, Found: 445.9658.

1-(6-bromopyridin-2-yl)-1-phenyl-1-(*m*-tolylthio)propan-2-one (3ba)



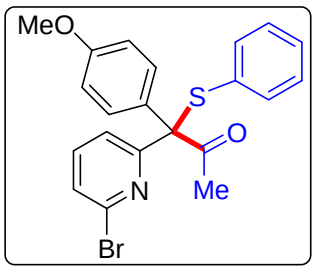
The title compound was isolated by column chromatography (eluent: EtOAc/ petroleum ether = 1/50) as a yellow solid in 98% yield (80.7 mg); M.p.: 110-112 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.40 (s, 1H), 7.39-7.34 (m, 2H), 7.29 (dd, *J* = 7.8, 0.5 Hz, 1H), 7.25-7.17 (m, 2H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.10-7.05 (m, 5H), 2.33 (s, 3H), 2.17 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 200.9, 160.2, 140.5, 138.1, 137.9, 137.4, 135.6, 131.5, 130.0, 128.8, 128.7, 128.3, 126.4, 123.2, 77.5, 27.8, 21.5 (two signals missing due to overlap); **HRMS (ESI)** $[M+H]^+$ m/z: Calcd for $C_{21}H_{19}BrNOS$ 412.0365, Found: 412.0367.

1-(6-bromopyridin-2-yl)-1-phenyl-1-(*p*-tolylthio)propan-2-one (3ca)



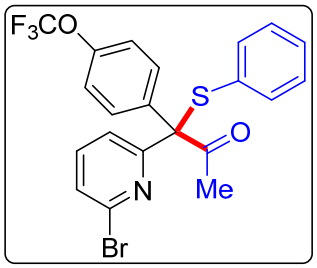
The title compound was isolated by column chromatography (eluent: EtOAc/ petroleum ether = 1/50) as a pale yellow solid in 94% yield (77.7 mg); M.p.: 126-128 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.21-7.14 (m, 3H), 7.10-7.04 (m, 5H), 2.35 (s, 3H), 2.16 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 200.9, 160.3, 140.5, 137.9, 135.5, 134.4, 131.6, 129.3, 129.1, 128.7, 128.3, 126.3, 123.0, 77.3, 27.7, 21.0 (one signals missing due to overlap); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{21}H_{19}BrNOS$ 412.0365, Found: 412.0366.

1-(6-bromopyridin-2-yl)-1-((4-methoxyphenyl)thio)-1-phenylpropan-2-one (3da)



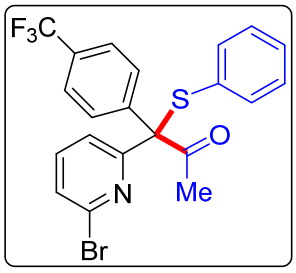
The title compound was isolated by column chromatography (eluent: EtOAc/ petroleum ether = 1/20) as a pale yellow solid in 98% yield (84.6 mg); M.p.: 169-171 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.50 (d, *J* = 8.8 Hz, 2H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.20 (t, *J* = 7.0 Hz, 1H), 7.10-7.03 (m, 5H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 2.16 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 200.8, 160.3, 159.1, 140.5, 138.0, 135.5, 131.5, 130.7, 129.2, 128.7, 128.3, 126.4, 122.9, 113.7, 76.9, 55.2, 27.6; **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{21}H_{19}BrNO_2S$ 428.0314, Found: 428.0323.

1-(6-bromopyridin-2-yl)-1-phenyl-1-((4-(trifluoromethoxy)phenyl)thio)propan-2-one (3ea)



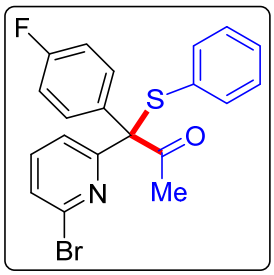
The title compound was isolated by column chromatography (eluent: EtOAc/ petroleum ether = 1/50) as a yellow solid in 92% yield (88.4 mg); M.p.: 141-143 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.55 (d, *J* = 8.9 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.25-7.21 (m, 2H), 7.14-7.09 (m, 4H), 7.04 (d, *J* = 7.2 Hz, 2H), 2.22 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 200.1, 159.9, 148.5, 140.9, 138.5, 136.6, 135.3, 131.3, 130.9, 129.1, 128.6, 126.9, 122.7, 120.34 (q, J_{C-F} = 257.6 Hz), 120.28, 75.7, 27.8; **^{19}F NMR ($CDCl_3$, 376 MHz):** δ -57.7 (s); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{21}H_{16}BrF_3NO_2S$ 482.0032, Found: 482.0036.

1-(6-bromopyridin-2-yl)-1-phenyl-1-((4-(trifluoromethyl)phenyl)thio)propan-2-one (3fa)



The title compound was isolated by column chromatography (eluent: EtOAc/ petroleum ether = 1/50) as a yellow oil in 91% yield (84.3 mg); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.4 Hz, 2H), 7.12 (t, *J* = 7.8 Hz, 2H), 7.05 (d, *J* = 7.5 Hz, 2H), 2.24 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 199.7, 159.6, 142.0, 141.0, 138.6, 135.1, 130.7, 130.1, 129.7 (d, J_{C-F} = 32.7 Hz), 129.1, 128.7, 127.1, 125.0 (q, J_{C-F} = 3.6 Hz), 123.9 (d, J_{C-F} = 272.3 Hz), 122.7, 75.9, 27.8; **^{19}F NMR ($CDCl_3$, 376 MHz):** δ -62.6 (s); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{21}H_{16}BrF_3NOS$ 466.0083, Found: 466.0089.

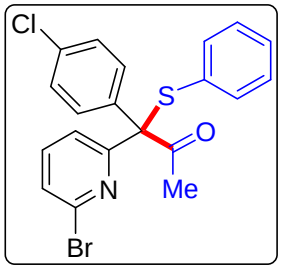
1-(6-bromopyridin-2-yl)-1-((4-fluorophenyl)thio)-1-phenylpropan-2-one (3ga)



The title compound was isolated by column chromatography (eluent: EtOAc/ petroleum ether = 1/50) as a pale yellow solid in 97% yield (80.5 mg); M.p.: 141-143 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.55-7.52 (m, 2H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.14-7.09 (m, 3H), 7.05-6.98 (m, 4H), 2.19 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 200.3, 162.1 (d, J_{C-F} = 248.7 Hz), 160.1, 140.8, 138.3, 135.4, 133.6 (d, J_{C-F} = 3.4 Hz), 131.5 (d, J_{C-F} = 8.1 Hz), 131.1, 129.0, 128.5, 126.7, 122.7, 115.1 (d, J_{C-F} = 21.4

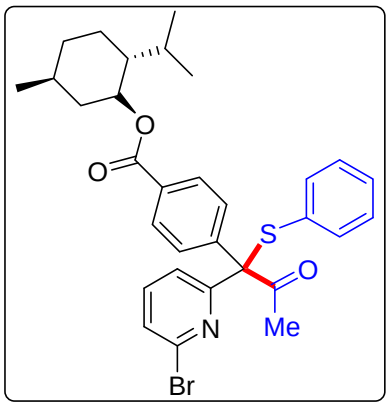
Hz), 76.0, 27.7; **^{19}F NMR ($CDCl_3$, 376 MHz):** δ -102.0 (s); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}BrFNOS$ 416.0115, Found: 416.0124.

1-(6-bromopyridin-2-yl)-1-((4-chlorophenyl)thio)-1-phenylpropan-2-one (3ha)



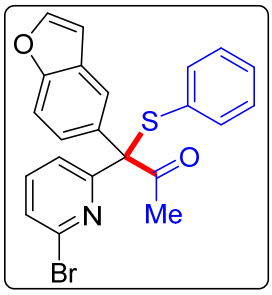
The title compound was isolated by column chromatography (eluent: EtOAc/ petroleum ether = 1/50) as a pale yellow solid in 71% yield (61.7 mg); M.p.: 127-129 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.51 (d, *J* = 8.6 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 8.6 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.14-7.09 (m, 3H), 7.04 (d, *J* = 7.4 Hz, 2H), 2.20 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 200.0, 159.9, 140.8, 138.4, 136.4, 135.3, 133.9, 131.1, 130.9, 129.0, 128.6, 128.3, 126.8, 122.7, 76.0, 27.7; **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{16}BrClNOS$ 431.9819, Found: 431.9816.

(1*R*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl-4-(1-(6-bromopyridin-2-yl)-2-oxo-1-(phenylthio) propyl)benzoate (3ia)



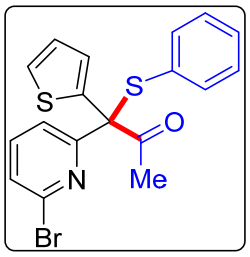
The title compound was isolated by column chromatography (eluent: EtOAc/ petroleum ether = 1/50) as a yellow oil in 96% yield (112.0 mg, mixture of two diastereoisomers, *d.r.* = 1:1); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.98 (d, *J* = 8.6 Hz, 2H), 7.68-7.64 (m, 2H), 7.42 (td, *J* = 7.8, 2.2 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.24-7.19 (m, 1H), 7.16-7.03 (m, 5H), 4.96-4.89 (m, 1H), 2.21+2.20 (s+s, 3H), 2.12-2.09 (m, 1H), 1.98-1.91 (m, 1H), 1.74-1.71 (m, 2H), 1.57-1.51 (m, 2H), 1.14-1.07 (m, 2H), 0.93-0.90 (m, 7H), 0.80-0.78 (s+s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 199.9, 199.8, 165.5, 159.7, 159.6, 142.6, 142.5, 140.8, 138.4, 138.3, 135.2, 135.1, 130.9, 130.8, 130.14, 130.11, 129.6, 129.3, 129.0, 128.56, 128.55, 126.8, 122.8, 122.7, 76.6, 76.4, 74.9, 47.12, 47.10, 40.8, 34.2, 31.3, 27.83, 27.79, 26.3, 23.5, 22.0, 20.7, 16.40, 16.39 (14 signals missing due to overlap); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{31}H_{35}BrNO_3S$ 580.1516, Found: 580.1520.

1-(benzofuran-7-yl)-1-(6-bromopyridin-2-yl)-1-(phenylthio)propan-2-one (3ja)



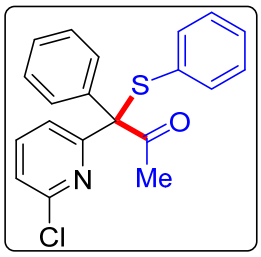
The title compound was isolated by column chromatography (eluent: EtOAc/ petroleum ether = 1/50) as a white solid in 71% yield (62.7 mg); M.p.: 127-129 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.87 (s, 1H), 7.64 (s, 1H), 7.54 (d, *J* = 8.8 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.20-7.17 (m, 1H), 7.11 (d, *J* = 7.7 Hz, 1H), 7.06 (d, *J* = 4.0 Hz, 4H), 6.74 (s, 1H), 2.18 (s, 3H); **^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz):** δ 199.8, 159.8, 153.5, 146.7, 139.6, 139.5, 135.1, 131.7, 131.0, 128.9, 128.4, 127.2, 126.7, 125.6, 123.4, 122.2, 111.2, 107.0, 76.9, 27.4; **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}BrNO_2S$ 438.0158, Found: 438.0164.

1-(6-bromopyridin-2-yl)-1-((4-chlorophenyl)thio)-1-(thiophen-2-yl)propan-2-one (3ka)



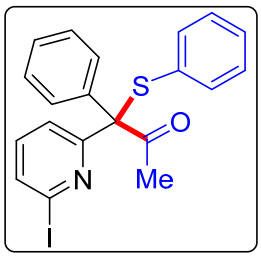
The title compound was isolated by column chromatography (eluent: EtOAc/ petroleum ether = 1/50) as an orange solid in 50% yield (40.3 mg); M.p.: 102-104 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.46 (t, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.27-7.22 (m, 3H), 7.13 (t, *J* = 7.7 Hz, 2H), 7.06-7.03 (m, 3H), 6.96-6.93 (m, 1H), 2.20 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 199.0, 159.9, 141.3, 140.9, 138.6, 136.2, 130.5, 129.4, 129.3, 128.5, 127.3, 127.2, 126.3, 122.2, 72.7, 26.7; **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{18}H_{15}BrClNOS_2$ 403.9773, Found: 403.9765.

1-(6-chloropyridin-2-yl)-1-phenyl-1-(phenylthio)propan-2-one (3la)



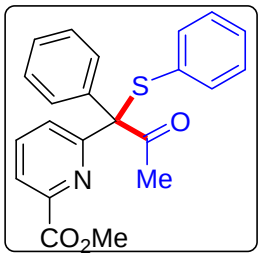
The title compound was isolated by column chromatography (eluent: EtOAc/ petroleum ether = 1/50 to EtOAc/ petroleum ether = 1/20) as a white solid in 88% yield (62.2 mg); M.p.: 149-151 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.59 (d, *J* = 7.3 Hz, 2H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.36-7.30 (m, 3H), 7.20 (t, *J* = 6.6 Hz, 1H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.10-7.05 (m, 5H), 2.18 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 200.7, 159.8, 150.2, 138.3, 137.7, 135.5, 131.5, 129.6, 128.8, 128.4, 128.0, 122.8, 122.7, 77.2, 27.9 (one signal missing due to overlap); **HRMS (ESI)** m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}ClNOS$ 354.0714, Found: 354.0722.

1-(6-iodopyridin-2-yl)-1-phenyl-1-(phenylthio)propan-2-one (3ma)



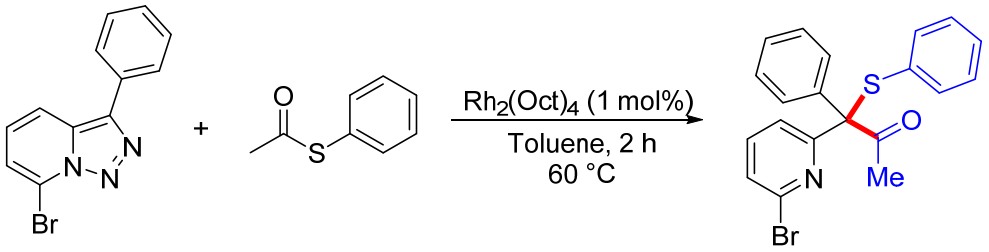
The title compound was isolated by column chromatography (eluent: EtOAc/ petroleum ether = 1/50 to EtOAc/ petroleum ether = 1/20) as a white solid in 84% yield (74.8 mg); M.p.: 135-137 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.59-7.57 (m, 2H), 7.53 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.37-7.30 (m, 3H), 7.21-7.17 (m, 1H), 7.14 (d, *J* = 7.7 Hz, 1H), 7.10-7.05 (m, 5H), 2.16 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 200.8, 160.7, 137.6, 137.1, 135.5, 133.2, 131.5, 129.4, 128.7, 128.4, 128.3, 128.0, 123.5, 116.0, 77.4, 27.7; **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{20}H_{16}INNaOS$ 467.9889, Found: 467.9893.

methyl 6-(2-oxo-1-phenyl-1-(phenylthio)propyl)picolinate (3na)



The title compound was isolated by column chromatography (eluent: EtOAc/ petroleum ether = 1/20 to DCM/ EtOAc = 1/10) as colorless oil in 81% yield (60.9 mg); **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.94 (d, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 7.9 Hz, 1H), 7.57 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.35-7.30 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.19-7.13 (m, 1H), 7.07-7.02 (m, 4H), 3.94 (s, 3H), 2.21 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 201.3, 165.5, 159.4, 147.1, 137.9, 136.7, 135.4, 131.8, 129.5, 128.6, 128.41, 128.35, 128.0, 127.5, 123.4, 77.8, 52.7, 28.1; **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd for $C_{22}H_{19}NNaO_3S$ 400.0978, Found: 400.0982.

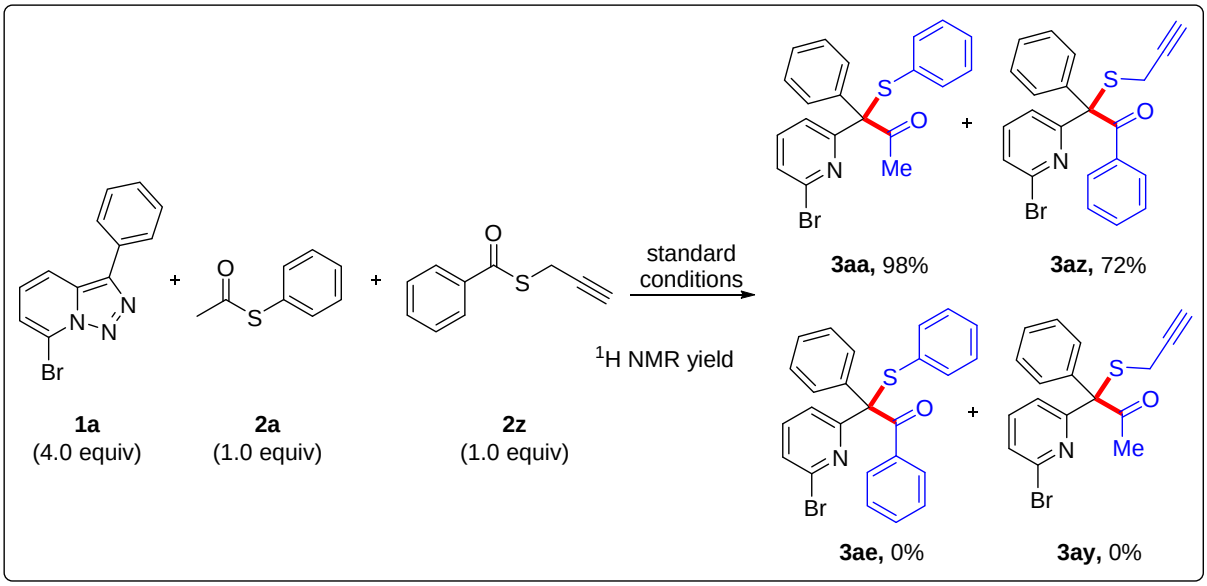
Scale up preparation of 3aa



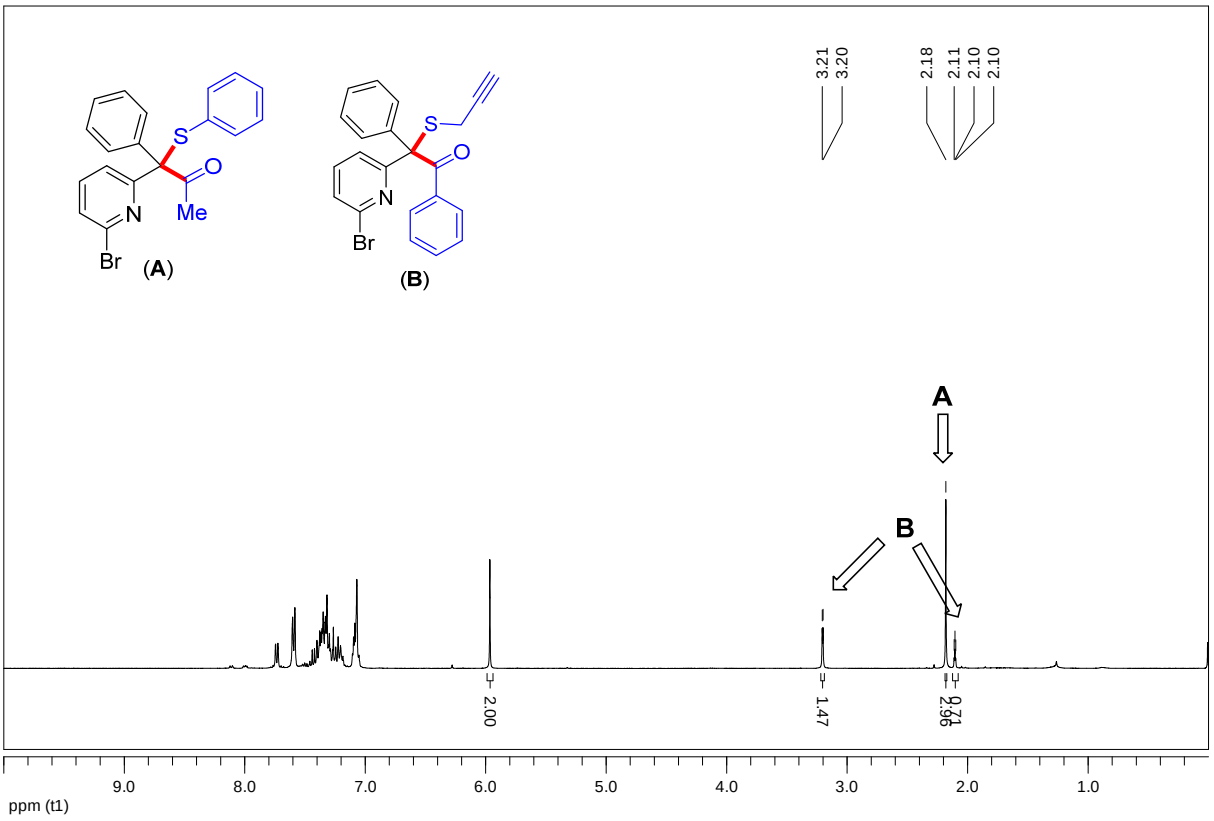
1a **2a** **3aa,** 92%

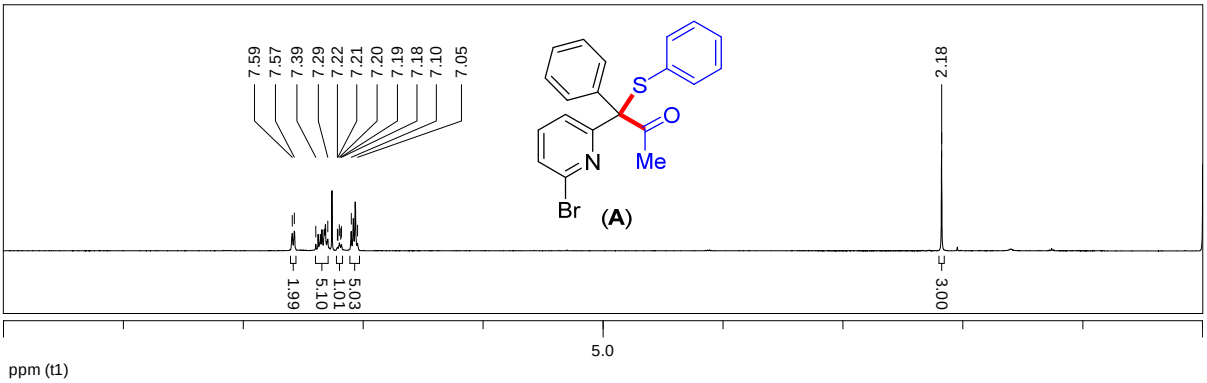
A mixture of pyridotriazole **1a** (4.0 mmol, 2.0 equiv), $Rh_2(Oct)_4$ (0.02 mmol, 1.0 mol %) were weighted in a Schlenk tube equipped with a stir bar. Thioester **2a** (2.0 mmol, 1.0 equiv) and dry Toluene (20 mL) was added and the mixture was stirred at 60 °C for 2 h using heating modular of parallel reactor under Ar atmosphere. Afterwards, the reaction was cooled to room temperature and transferred to a 100 mL round-bottomed flask using CH_2Cl_2. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel. The desired product **3aa** was obtained in 92% isolated yield (731.1 mg).

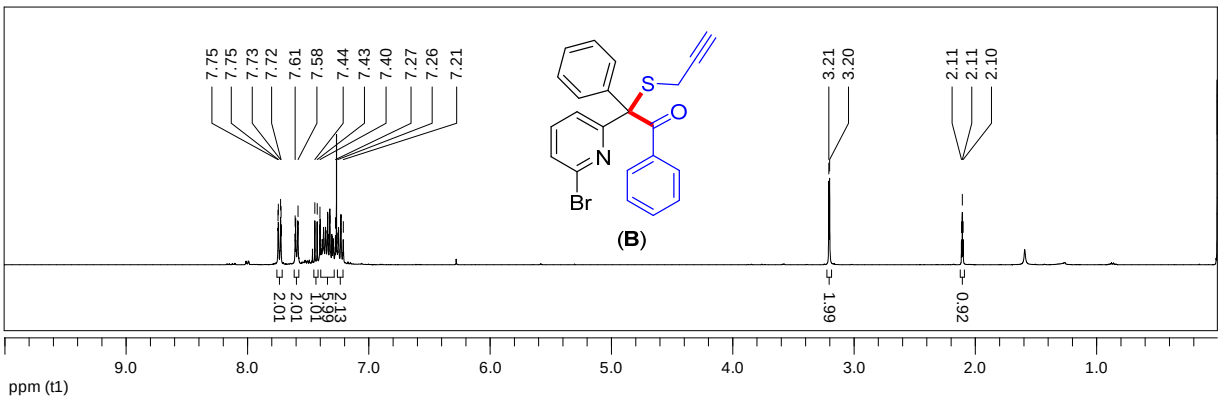
Intermolecular competation reaction

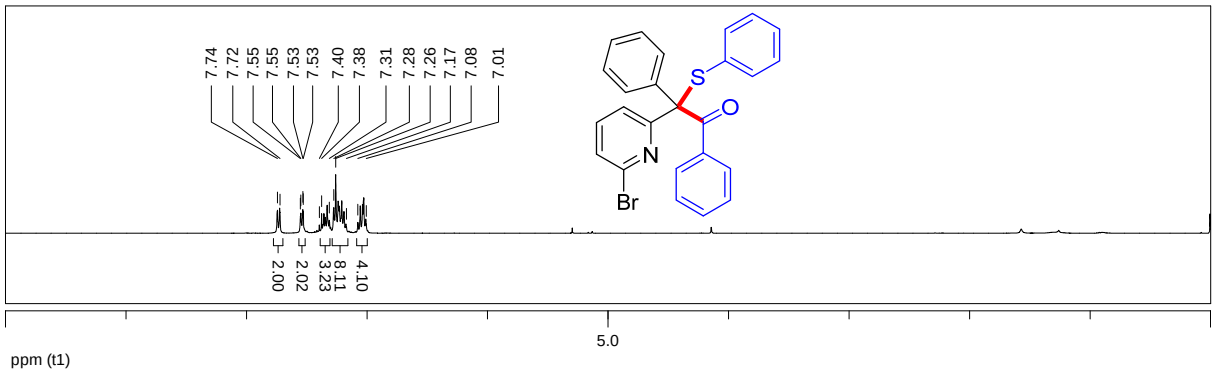


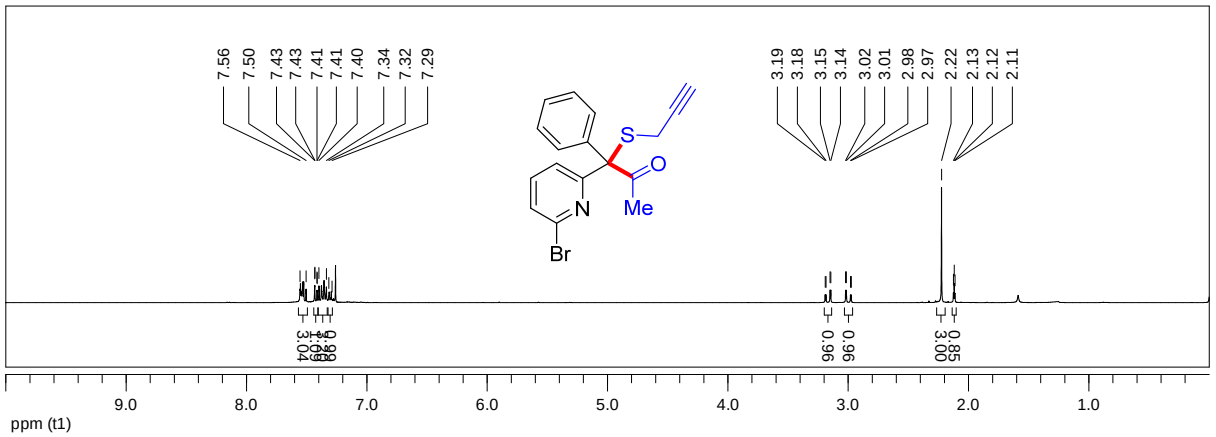
A mixture of pyridotriazoles (**1a**) (0.4 mmol, 4.0 equiv), $Rh_2(Oct)_4$ (0.002 mmol, 2.0 mol %) were weighted in a Schlenk tube equipped with a stir bar. Thioesters (**2a**) (0.1 mmol, 1.0 equiv), **2z** (0.1 mmol, 1.0 equiv) and dry Toluene (2.0 mL) were added and the mixture was stirred at 60 °C for 2 h using heating modular of parallel reactor under Ar atmosphere. Afterwards, the reaction was cooled to room temperature and transferred to a 100 mL round-bottomed flask using CH_2Cl_2. Solvent was evaporated under reduced pressure. Only the corresponding products **3aa** and **3az** were observed from the ^{1}H NMR of crude reaction mixture, and cross-over products **3ae** and **3ay** were not detected. The yield of **3aa** (98%) and **3az** (73%) were determined by integration of ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard.


3.21
3.20
2.18
2.11
2.10
2.10
S
O
N
Me
Br
(A)
S
O
N
Br
(B)
A
B
2.00
1.47
0.96
0.21
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

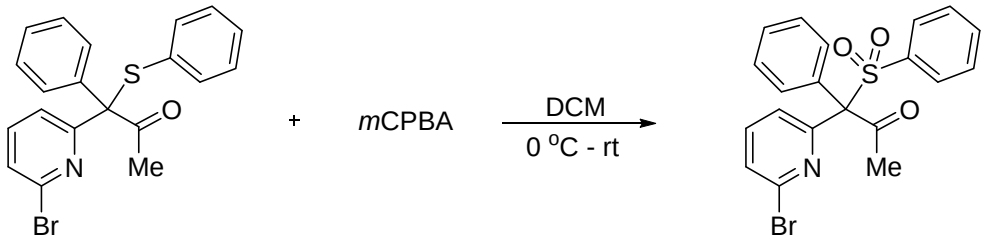

7.59
7.57
7.39
7.29
7.22
7.21
7.20
7.19
7.18
7.10
7.05
S
O
N
Me
Br
(A)
2.18
1.99
5.10
1.01
5.03
3.00
5.0
ppm (t1)


7.75
7.75
7.73
7.72
7.61
7.58
7.44
7.43
7.40
7.27
7.26
7.21
S
O
N
Br
(B)
3.21
3.20
2.11
2.11
2.10
2.01
2.01
5.99
1.01
2.13
1.99
0.92
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


7.74
7.72
7.55
7.55
7.53
7.53
7.40
7.38
7.31
7.28
7.26
7.17
7.08
7.01
2.00
2.02
3.23
8.11
4.10
S
O
N
Br
5.0
ppm (t1)

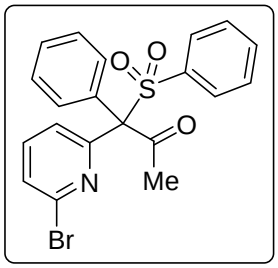

7.56
7.50
7.43
7.43
7.41
7.41
7.40
7.34
7.32
7.29
3.19
3.18
3.15
3.14
3.02
3.01
2.98
2.97
2.22
2.13
2.12
2.11
3.04
0.96
0.96
3.00
0.85
S
O
N
Me
Br
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

Oxidation reaction of 3aa



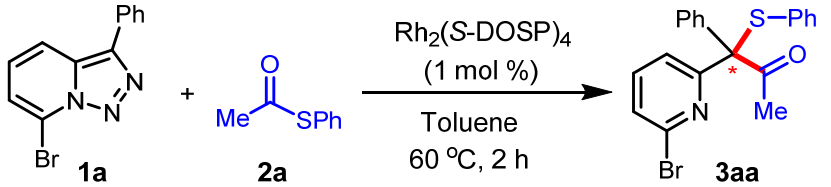
3aa **4**, 83%

3aa (0.2 mmol, 1.0 equiv) was weighted in a round bottom flask equipped with a stir bar and dry dichloromethane (1.0 mL) was added. Then *m*CPBA (1.2 mmol, 6.0 equiv) solution in dichloromethane (1.5 mL) was added dropwise at 0 °C. The mixture was stirred at room temperature overnight. Afterwards, sodium hydroxide solution was added to neutralize the system and extracted by CH_2Cl_2. Drying by Anhydrous magnesium sulfate. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel.



The title compound was isolated by column chromatography (eluent: EtOAc/ petroleum ether = 1/50 to EtOAc/ petroleum ether = 1/20) as a white solid in 83% yield (71.3 mg); M.p.: 221-223 °C; **^{1}H NMR ($CDCl_3$, 400 MHz):** δ 7.89 (d, *J* = 7.7 Hz, 2H), 7.68-7.64 (m, 1H), 7.58-7.57 (m, 4H), 7.48-7.35 (m, 5H), 7.28-7.24 (m, 2H), 2.04 (s, 3H); **^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz):** δ 198.8, 154.1, 140.8, 138.6, 137.7, 133.4, 131.3, 131.0, 130.5, 129.5, 128.6, 128.3, 127.7, 125.9, 91.1, 29.6; **HRMS (ESI):** $[M+H]^+$ Calcd for $C_{20}H_{17}BrNO_3S^+$ 430.0107, Found: 430.0104.

Asymmetric synthesis

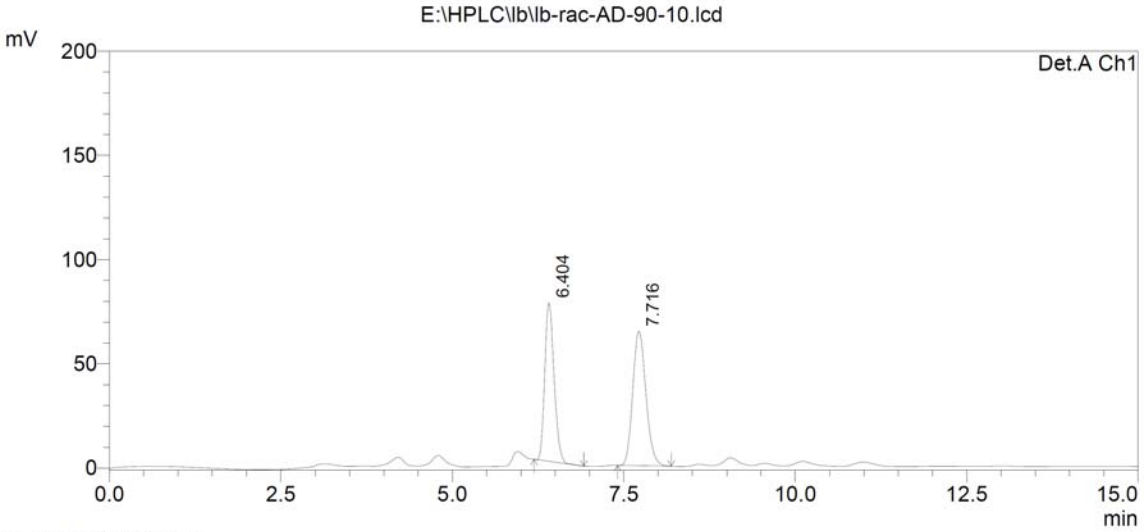


91% yield, 79% e.e.

Rh_2(S-DOSP)$_4$: dirhodium(II) tetrakis[(*S*)-*N*-(*p*-dodecylphenylsulfonyl)prolinate]

A mixture of pyridotriazole **1a** (0.4 mmol, 2.0 equiv), Rh_2(*S*-DOSP)$_4$ (0.002 mmol, 1.0 mol %) were weighted in a Schlenk tube equipped with a stir bar. Thioester **2a** (0.2 mmol, 1.0 equiv) and dry Toluene (2 mL) was added and the mixture was stirred at 60 °C for 2 h using heating modular of parallel reactor under Ar atmosphere. Afterwards, the reaction was cooled to room temperature and transferred to a 100 mL round-bottomed flask using CH_2Cl_2. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel. The desired product **3aa** was obtained in 91% isolated yield (72.5 mg).

The enantiomeric excess of **3aa** was determined by HPLC with a Chiralpak OD-H column, n-hexane/2-propanol= 90:10, flow rate= 1 mL/min, 254 nm UV detector.

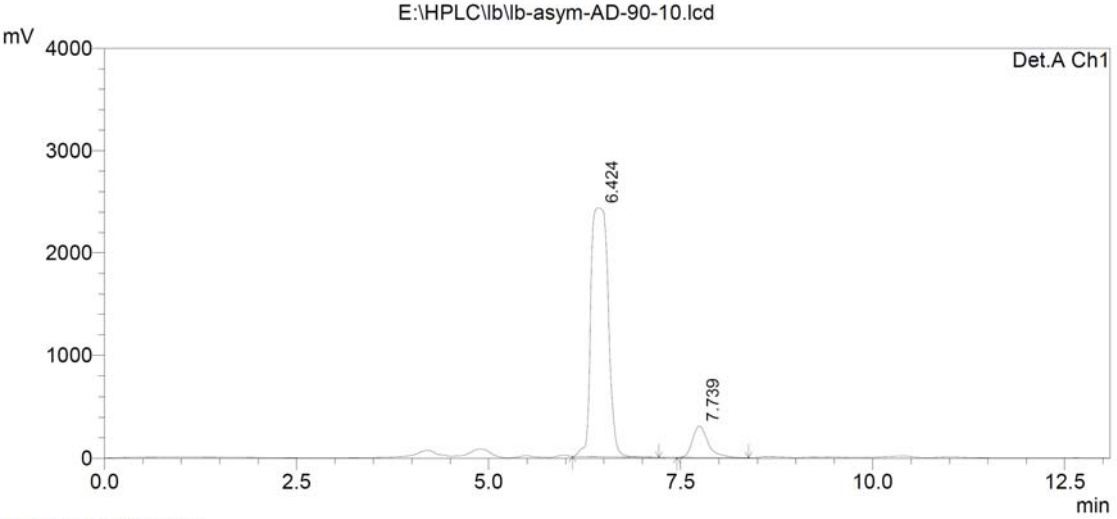


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.404	716602	76101	45.396	54.128
2	7.716	861955	64493	54.604	45.872
Total		1578557	140595	100.000	100.000



1 Det.A Ch1/254nm

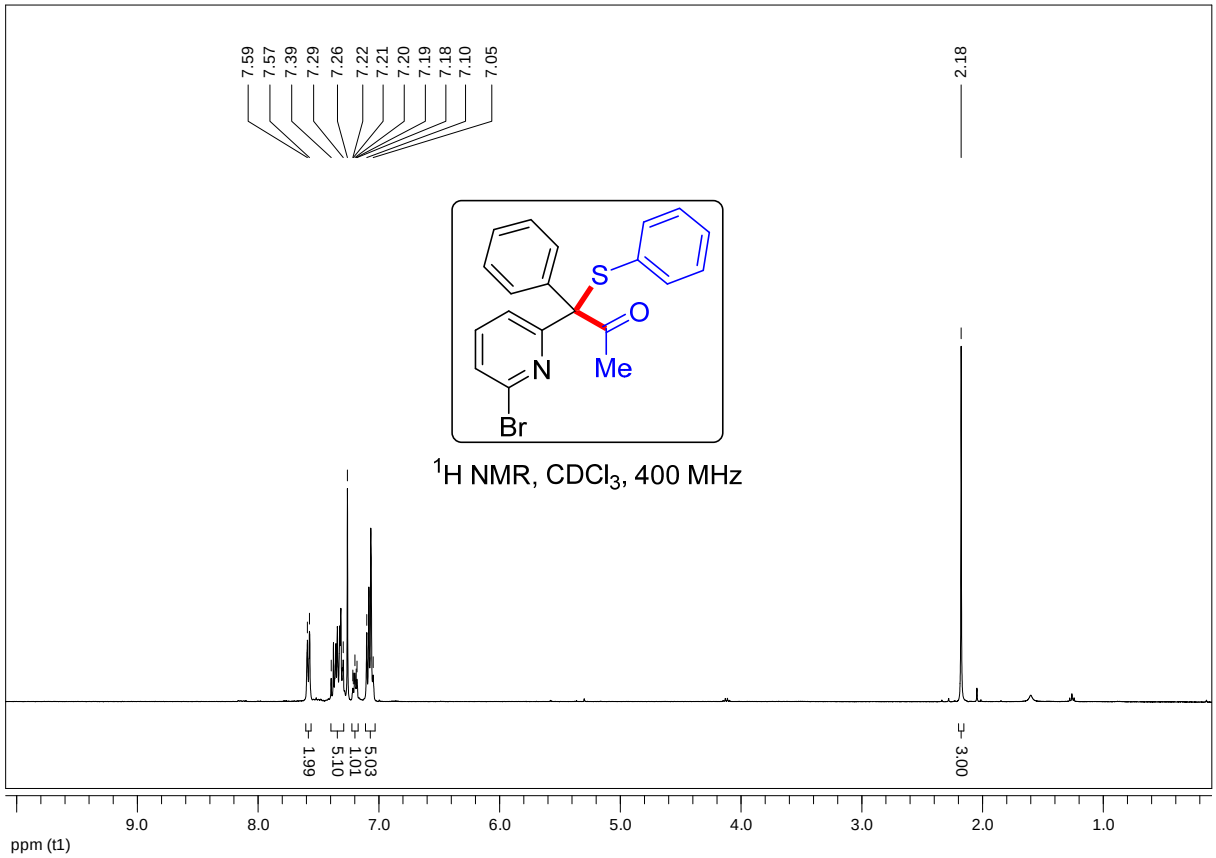
PeakTable

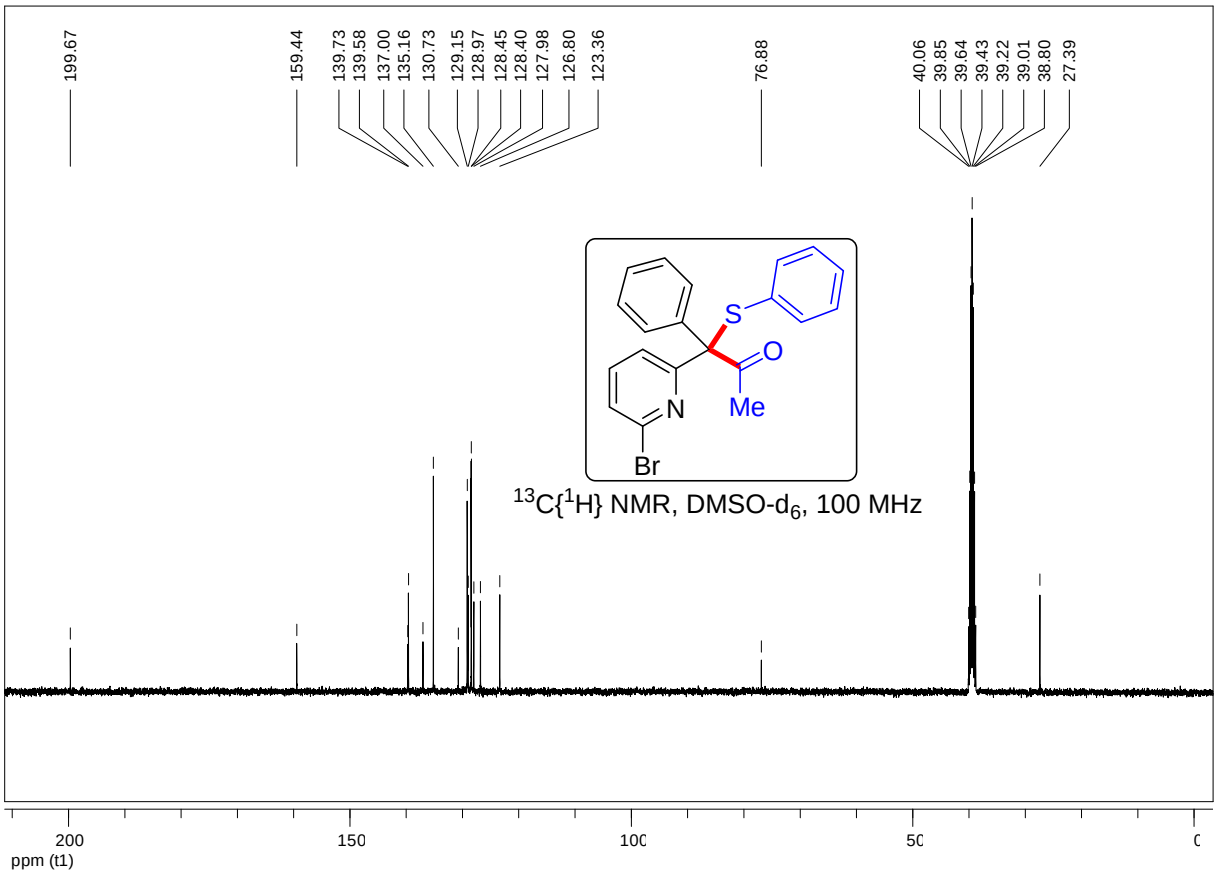
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.424	38007036	2427823	89.762	88.734
2	7.739	4334929	308254	10.238	11.266
Total		42341965	2736078	100.000	100.000

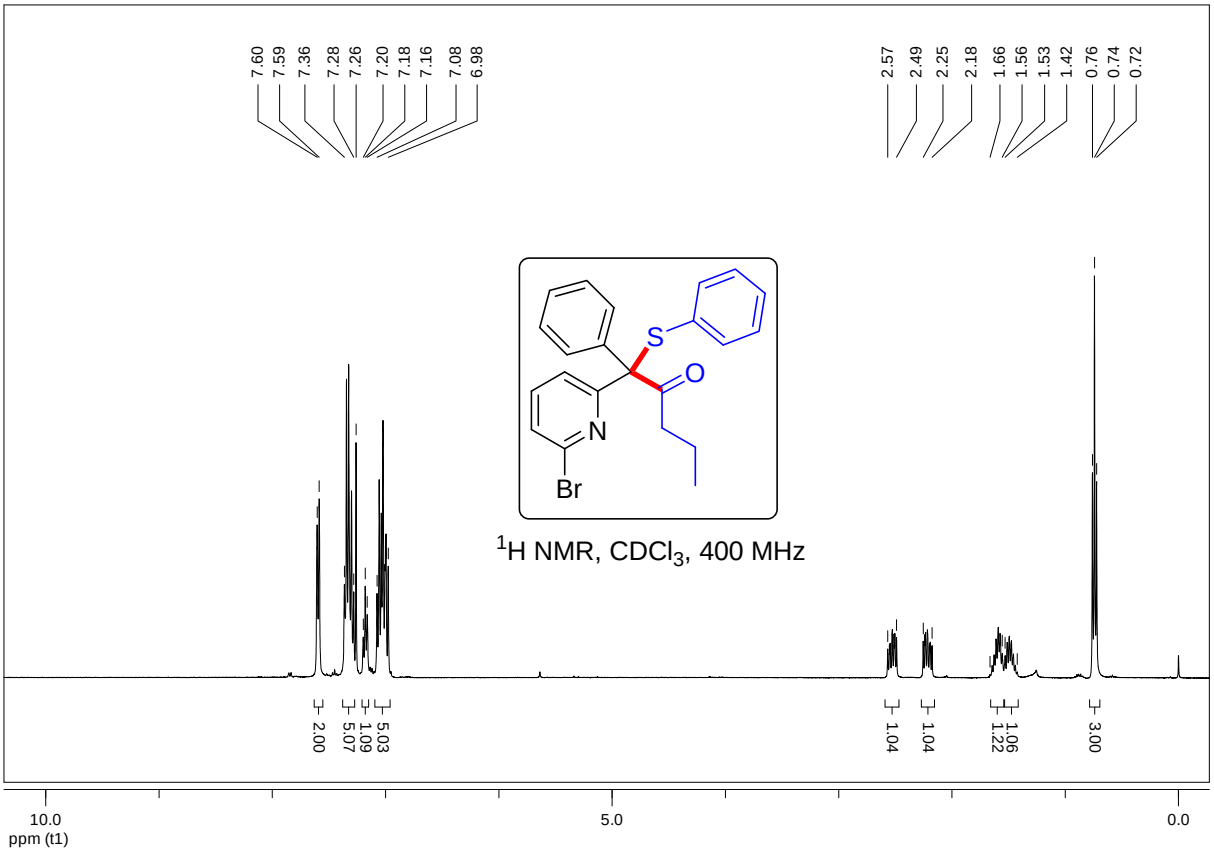
Spectral Copies of ^{1}H, ^{13}C, and ^{19}F NMR of Compounds Obtained in this Study

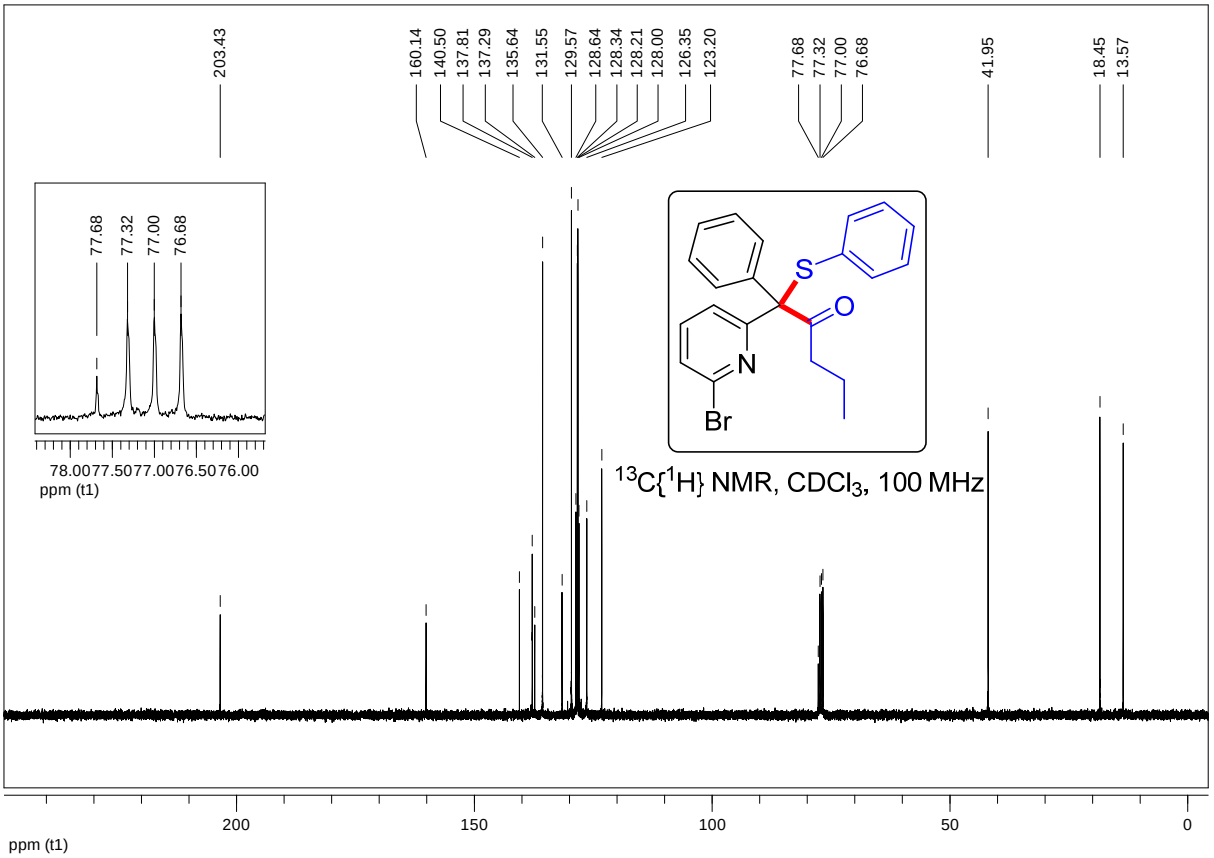
1-(6-bromopyridin-2-yl)-1-phenyl-1-(phenylthio)propan-2-one (3aa)



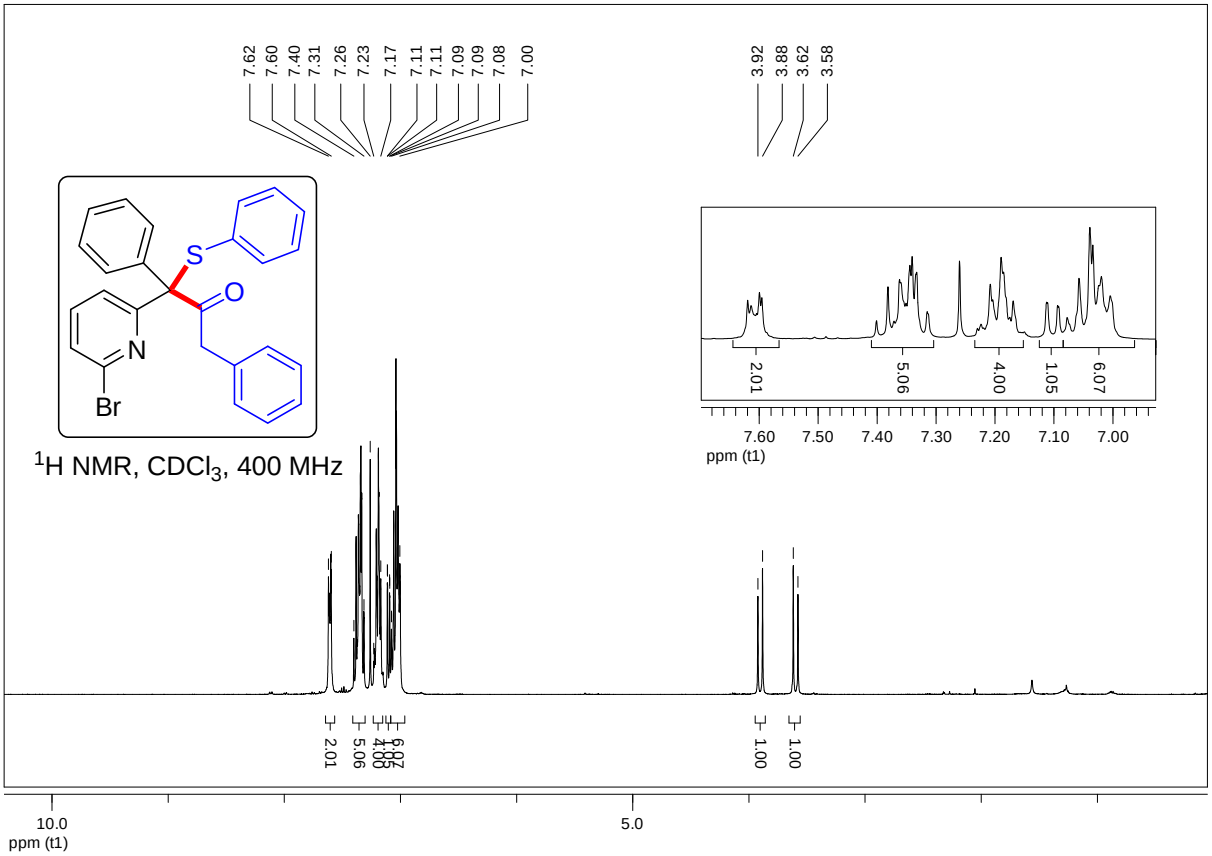


1-(6-bromopyridin-2-yl)-1-phenyl-1-(phenylthio)pentan-2-one (3ab)

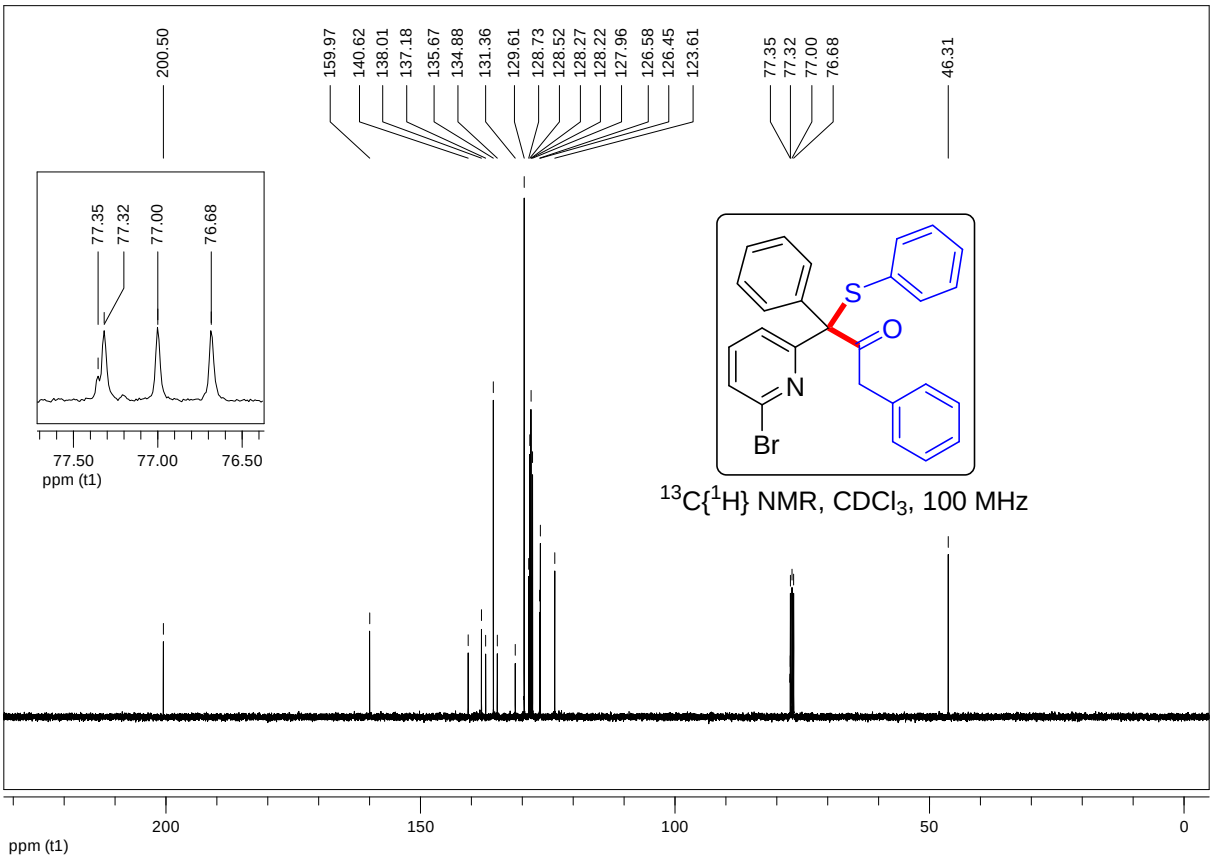




1-(6-bromopyridin-2-yl)-1,3-diphenyl-1-(phenylthio)propan-2-one (3ac)

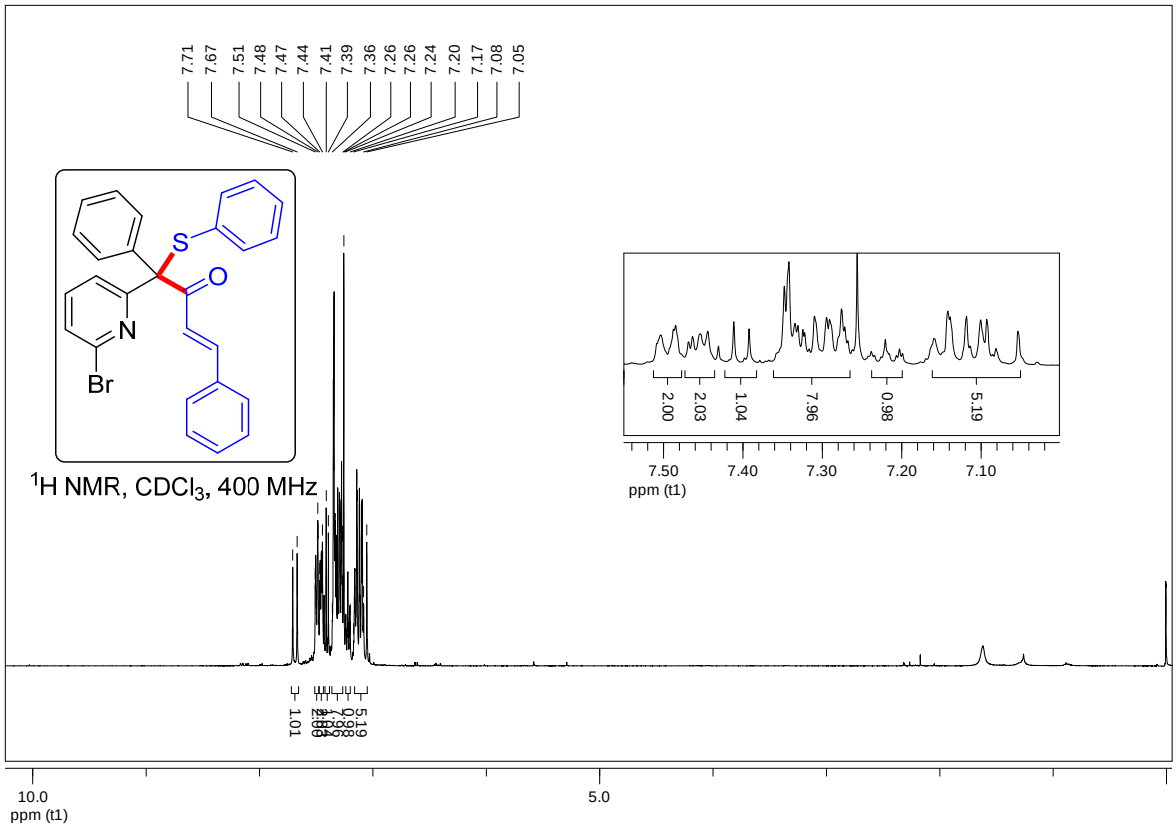


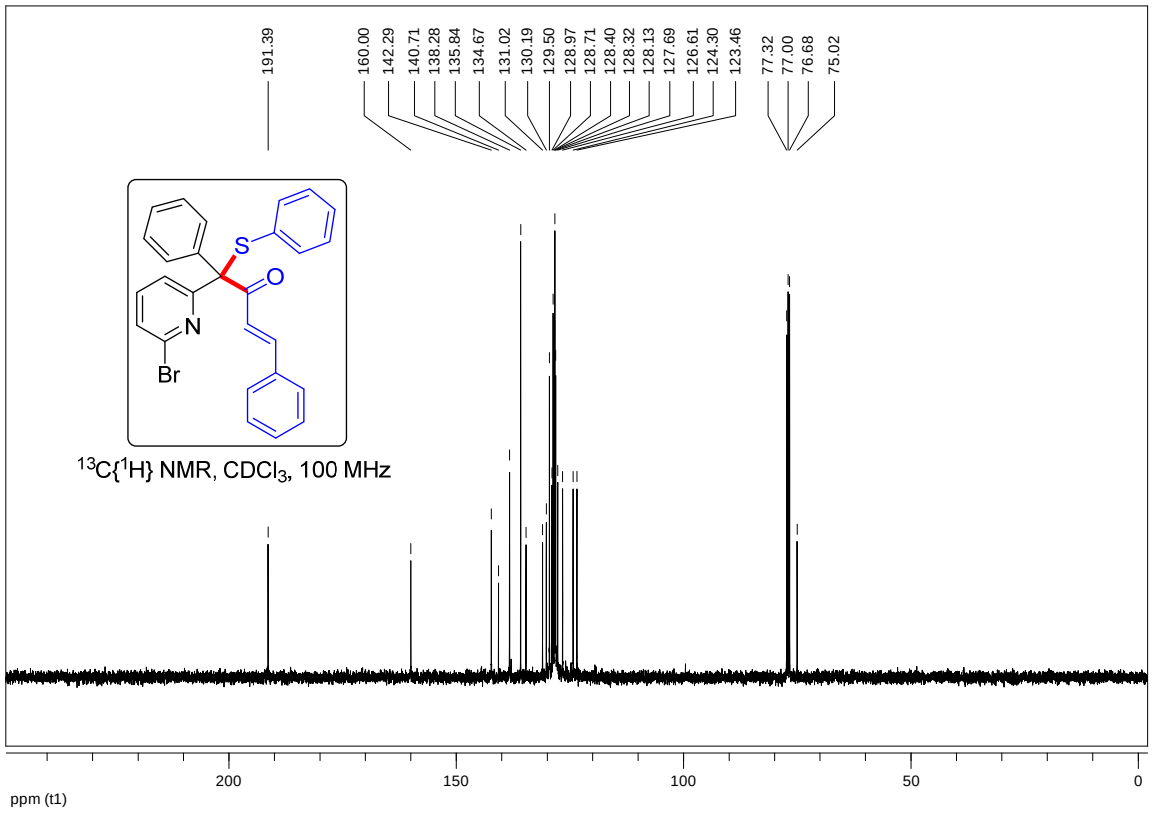
^{1}H NMR, $CDCl_3$, 400 MHz



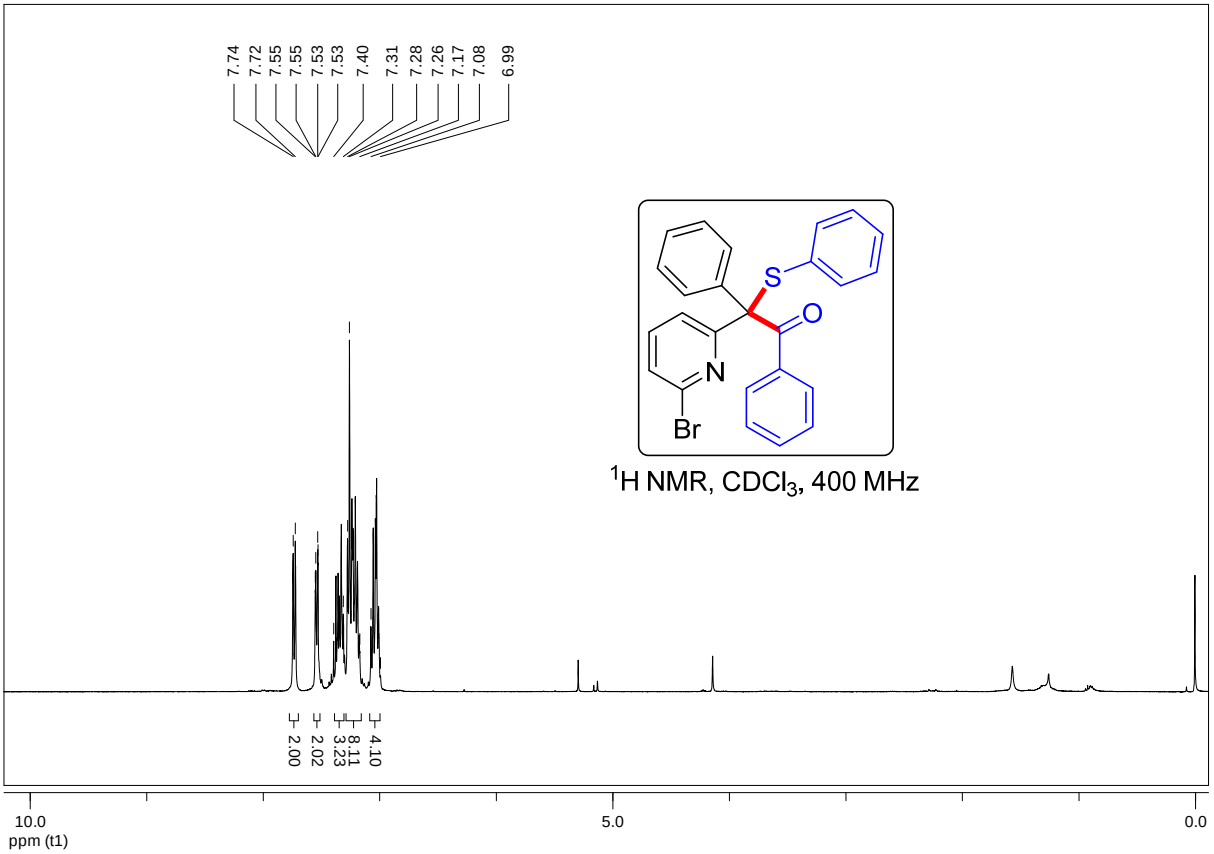
^{13}C{^{1}H} NMR, $CDCl_3$, 100 MHz

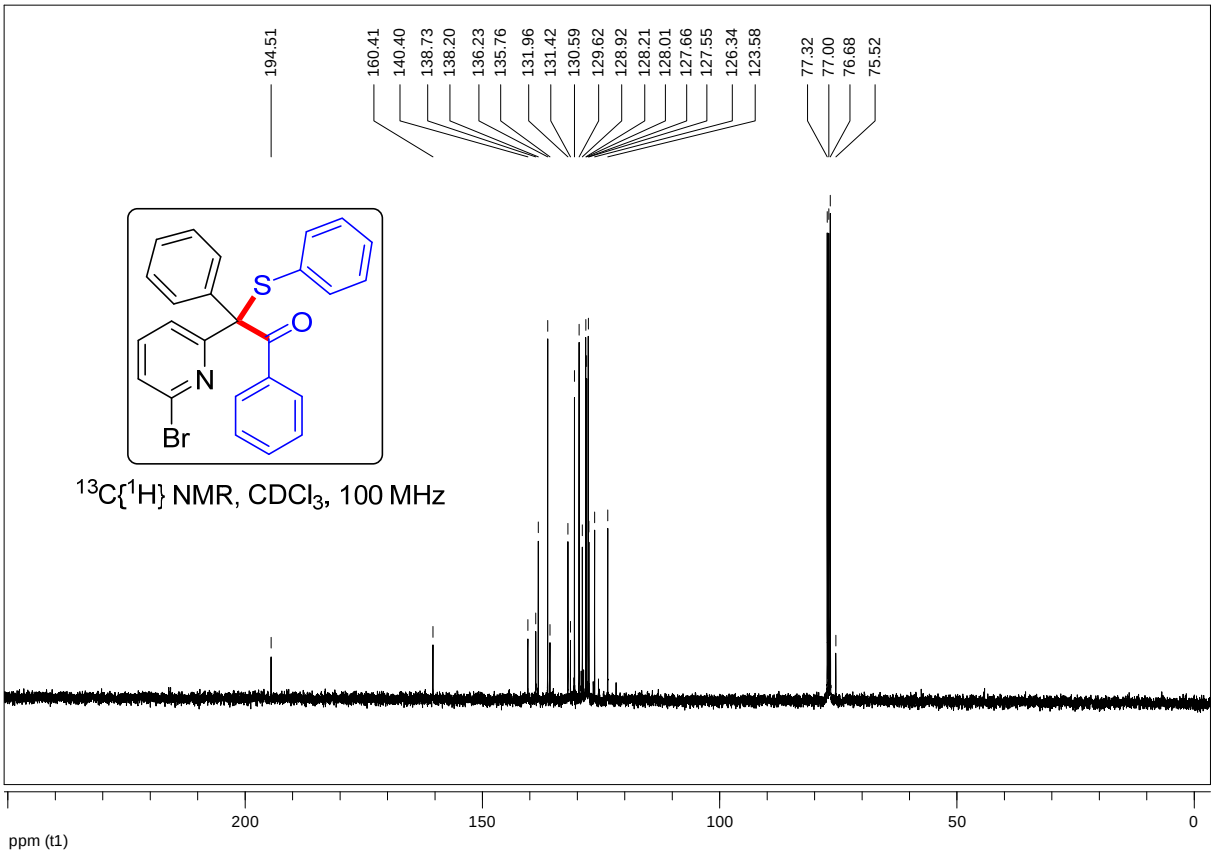
(*E*)-1-(6-bromopyridin-2-yl)-1,4-diphenyl-1-(phenylthio)but-3-en-2-one (3ad)



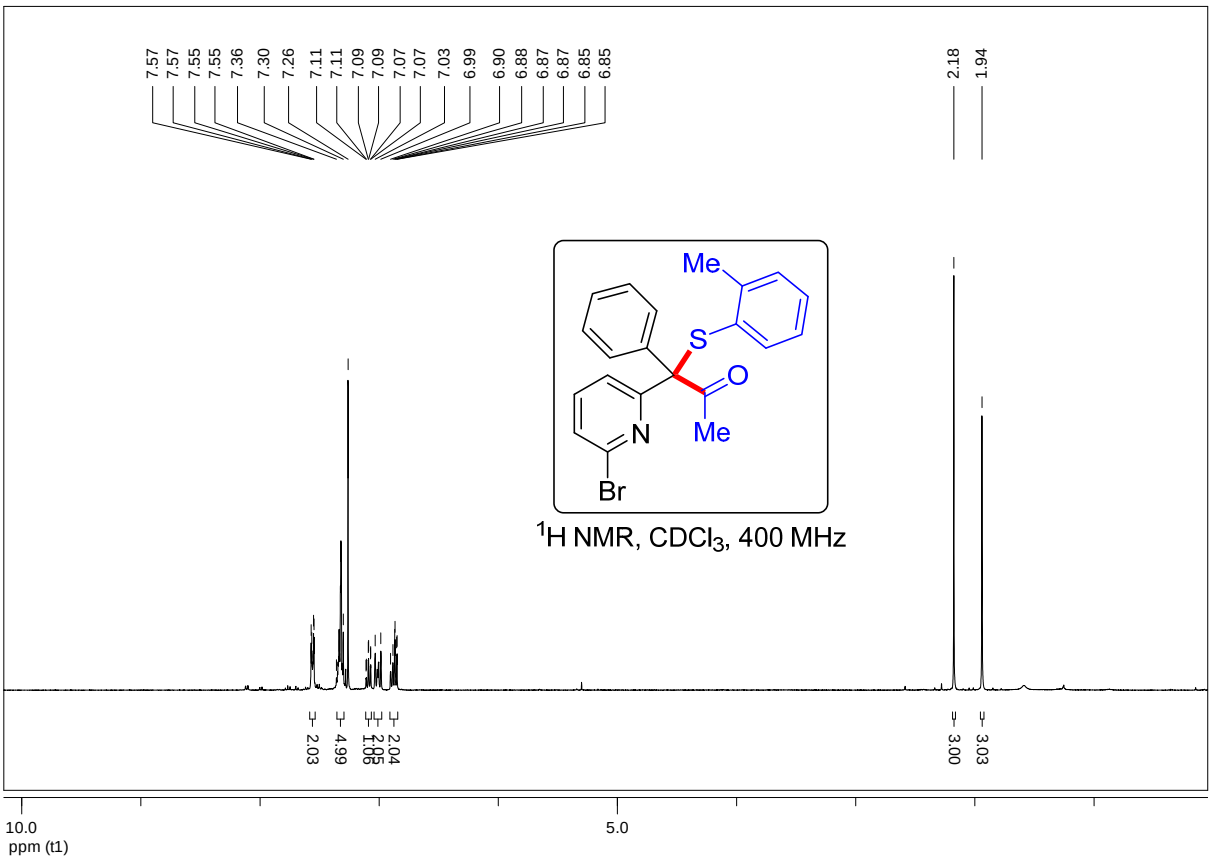


2-(6-bromopyridin-2-yl)-1,2-diphenyl-2-(phenylthio)ethan-1-one (3ae)

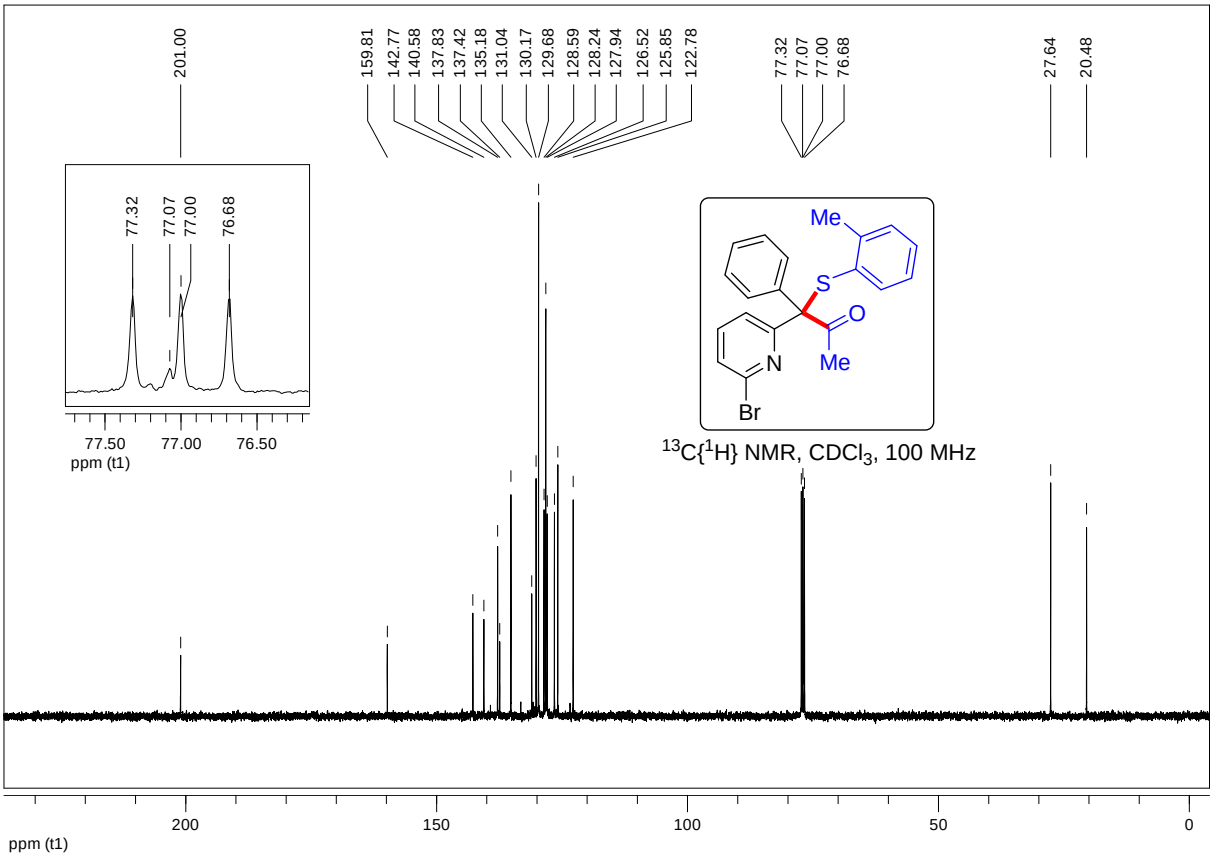




1-(6-bromopyridin-2-yl)-1-phenyl-1-(o-tolylthio)propan-2-one (3af)

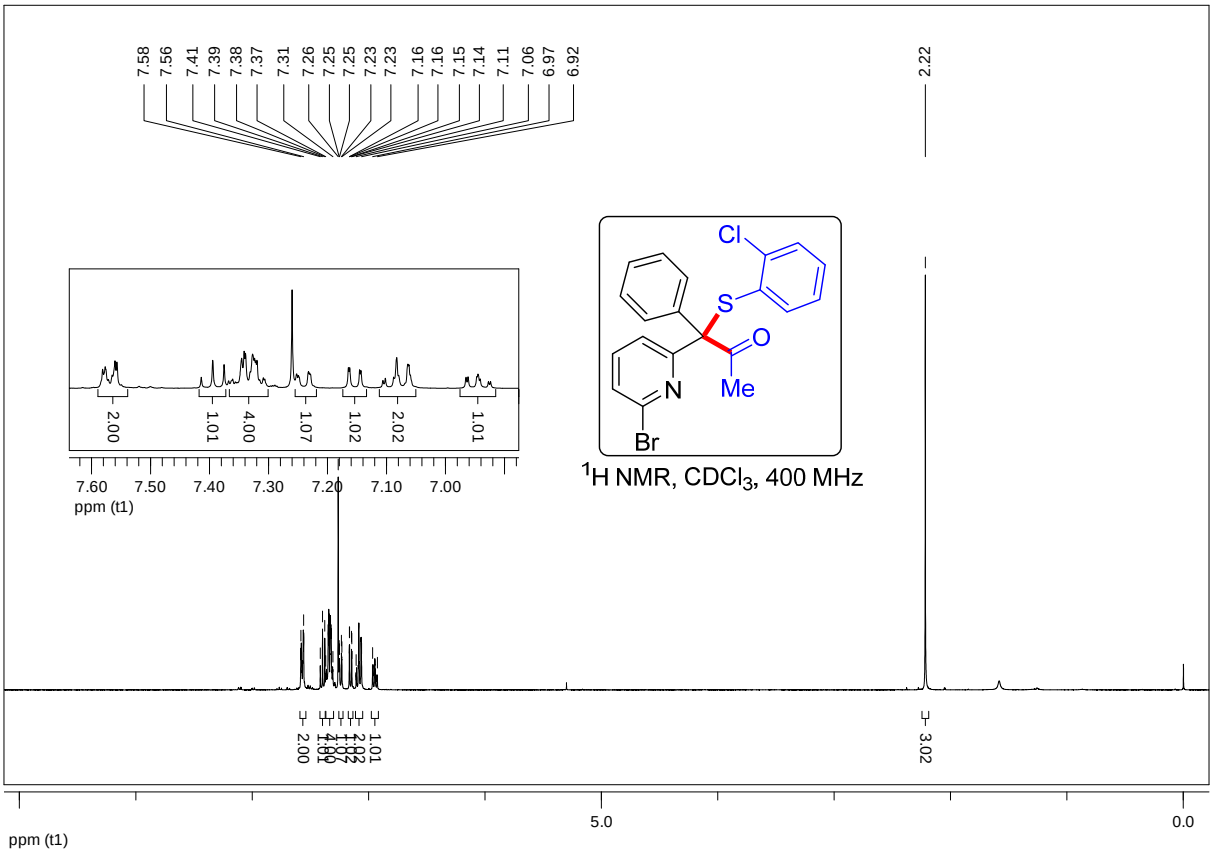


^{1}H NMR, $CDCl_3$, 400 MHz

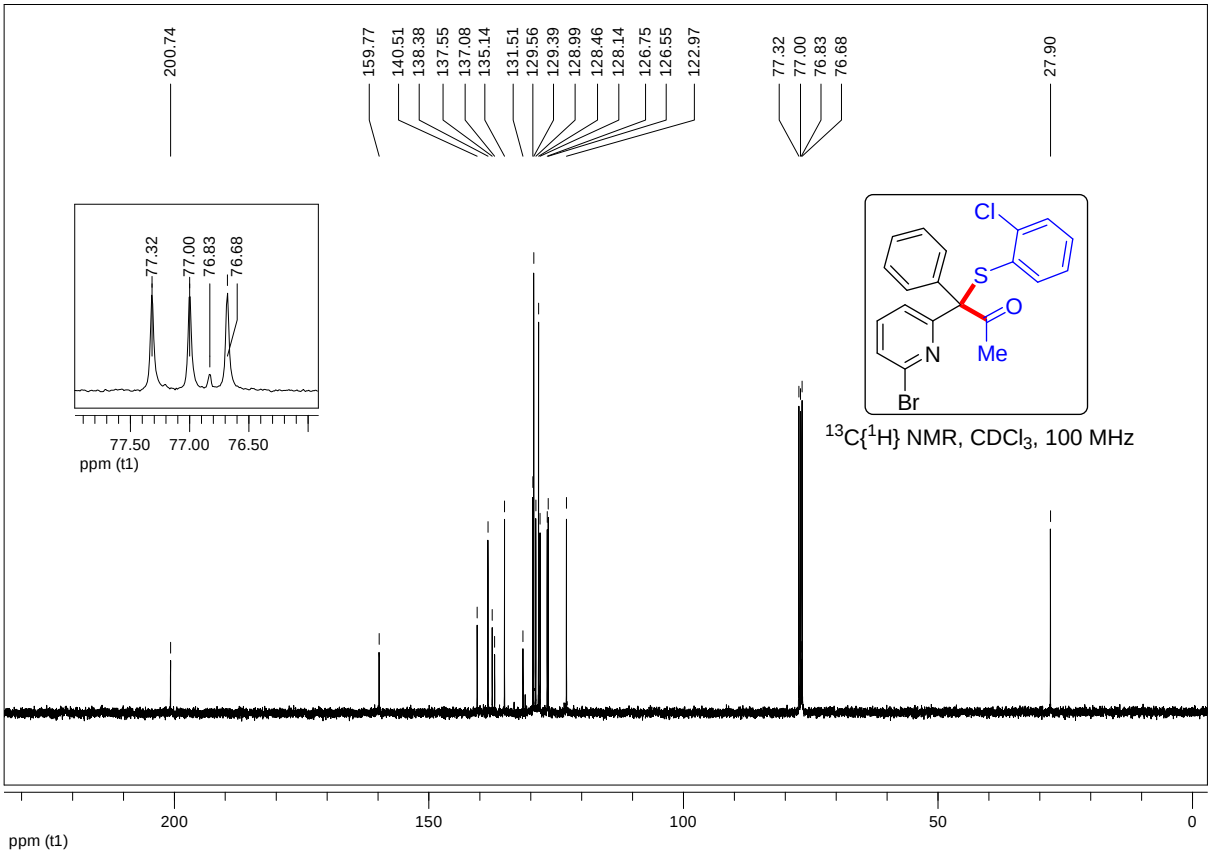


$^{13}C\{^{1}H\}$ NMR, $CDCl_3$, 100 MHz

1-(6-bromopyridin-2-yl)-1-phenyl-1-(m-tolylthio)propan-2-one (3ag)

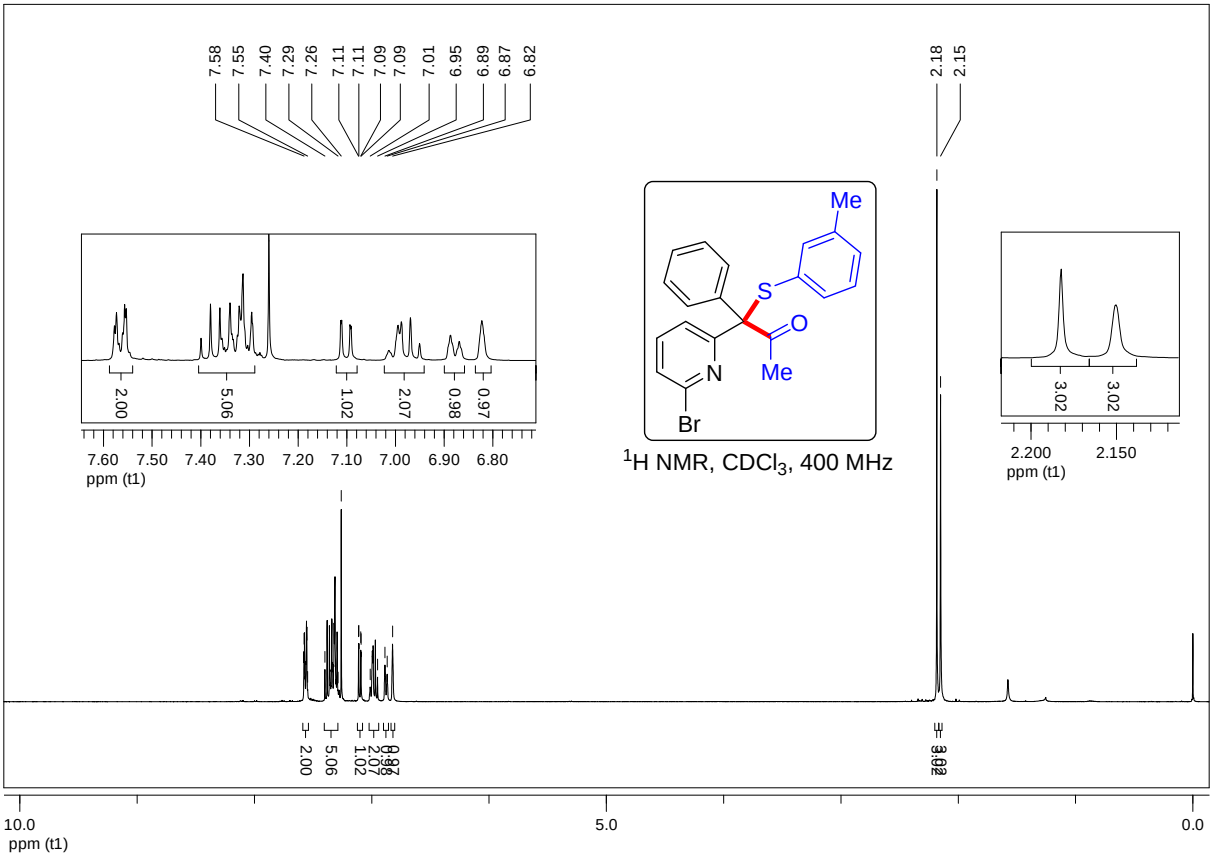


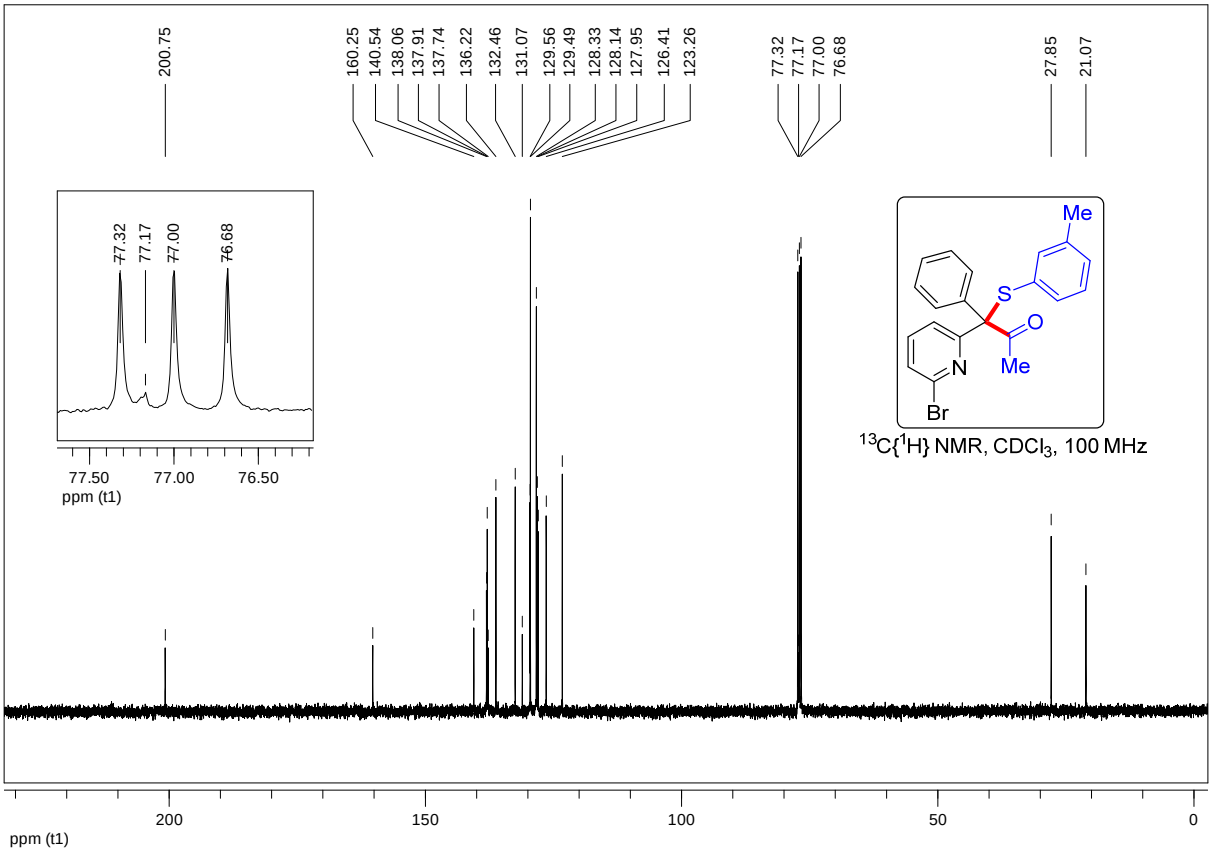
^{1}H NMR, $CDCl_3$, 400 MHz



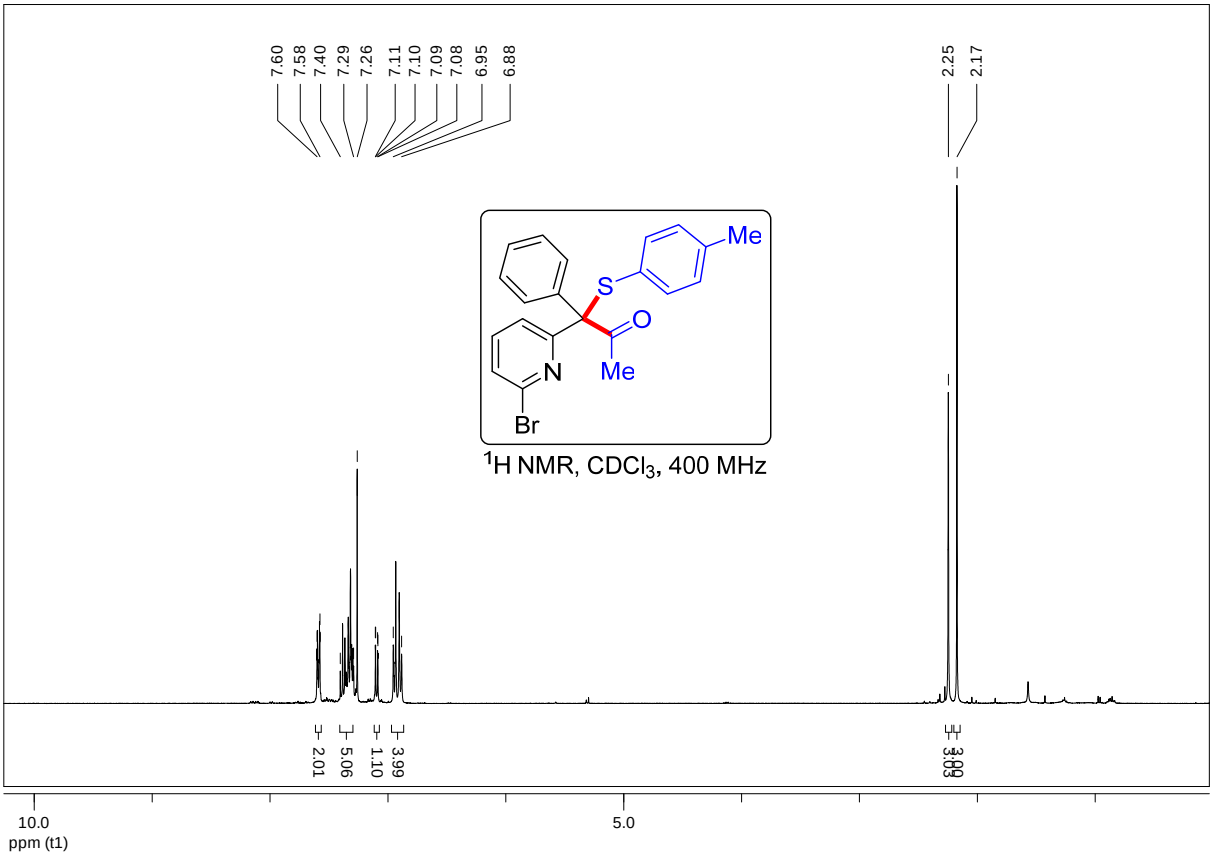
$^{13}C\{^{1}H\}$ NMR, $CDCl_3$, 100 MHz

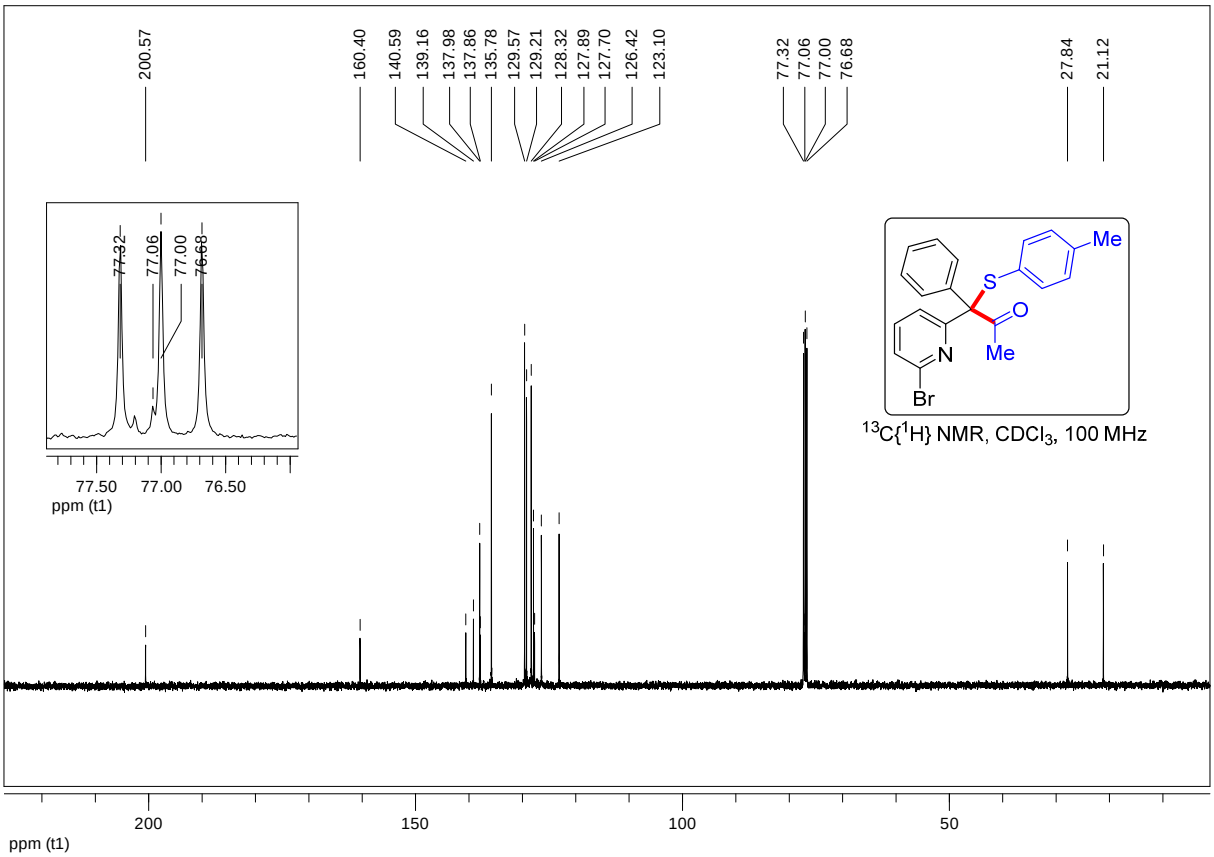
1-(6-bromopyridin-2-yl)-1-phenyl-1-(m-tolylthio)propan-2-one (3ah)





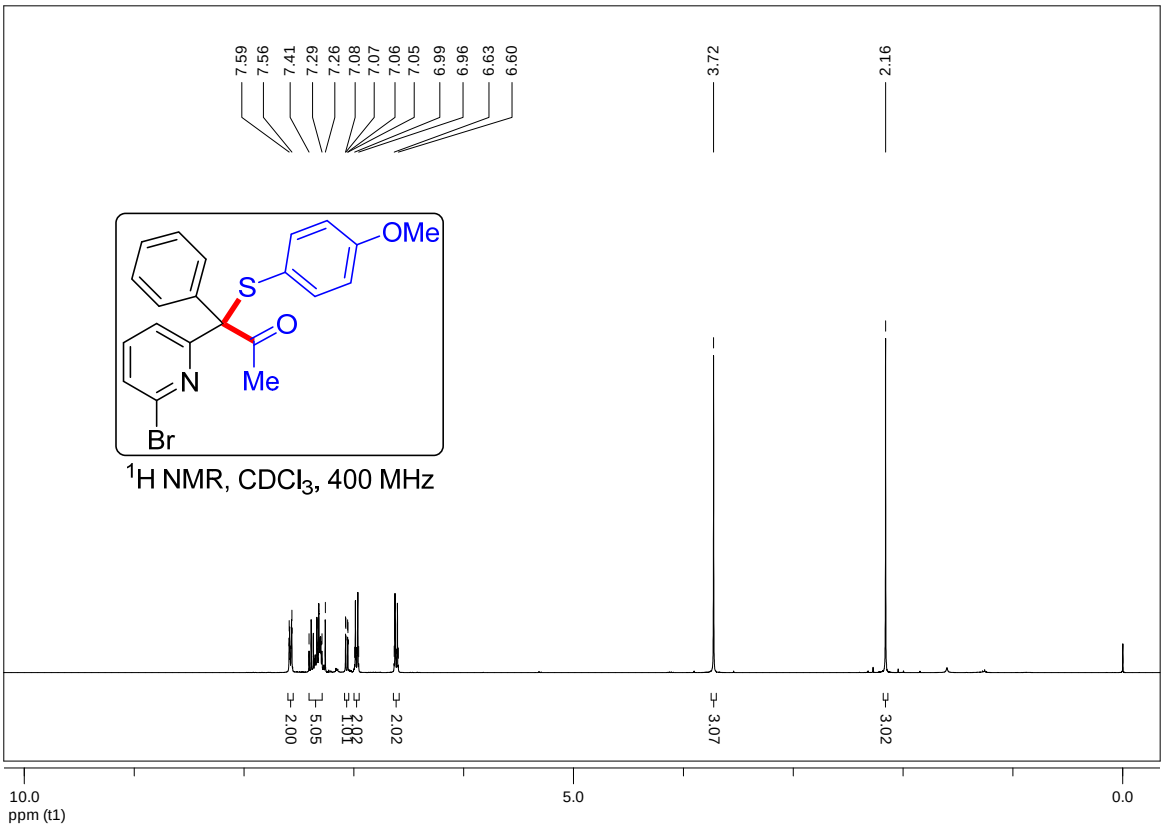
1-(6-bromopyridin-2-yl)-1-phenyl-1-(p-tolylthio)propan-2-one (3ai)

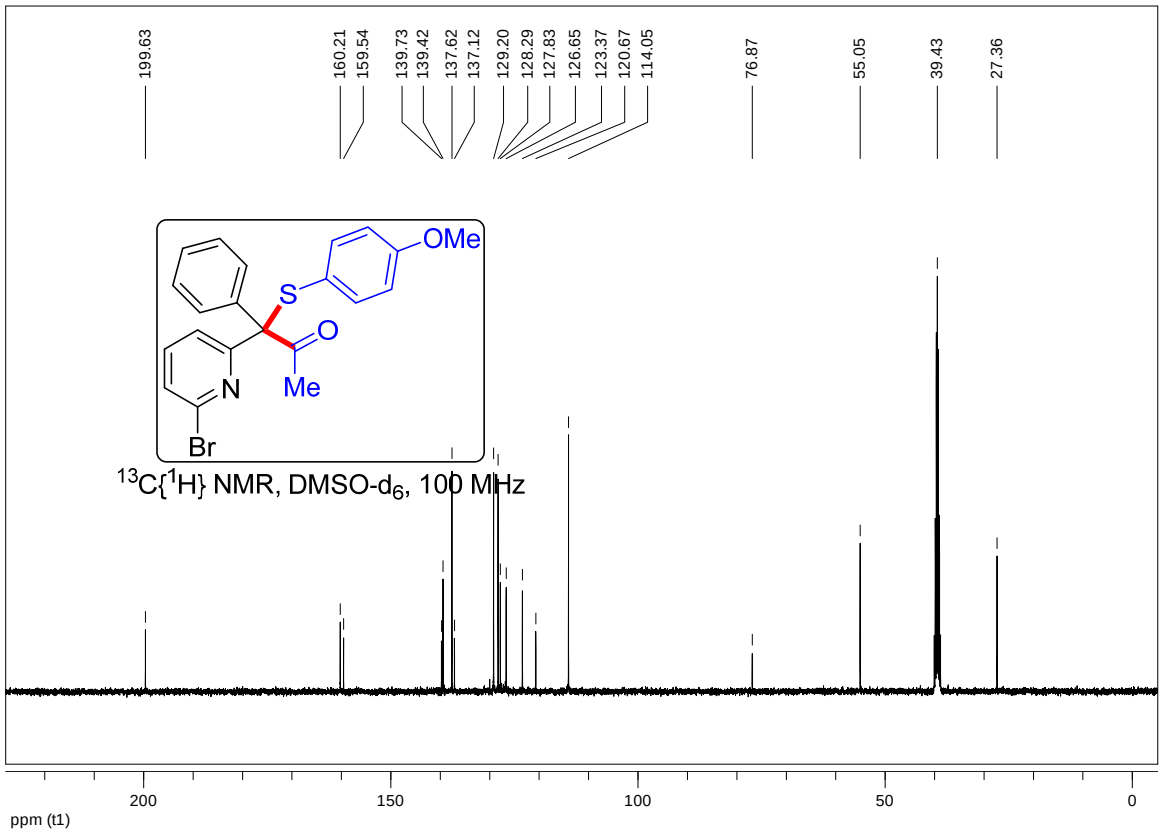




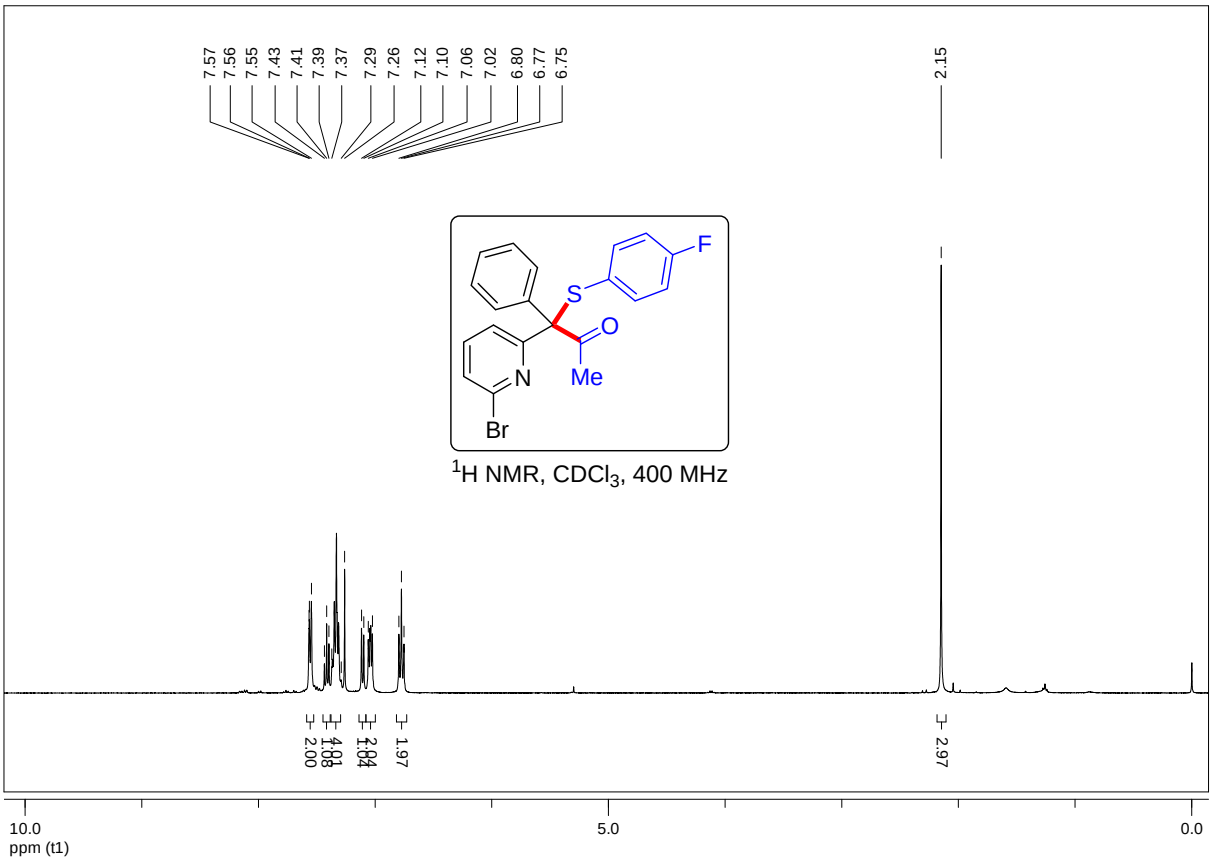
1-(6-bromopyridin-2-yl)-1-((4-methoxyphenyl)thio)-1-phenylpropan-2-one

(3aj)

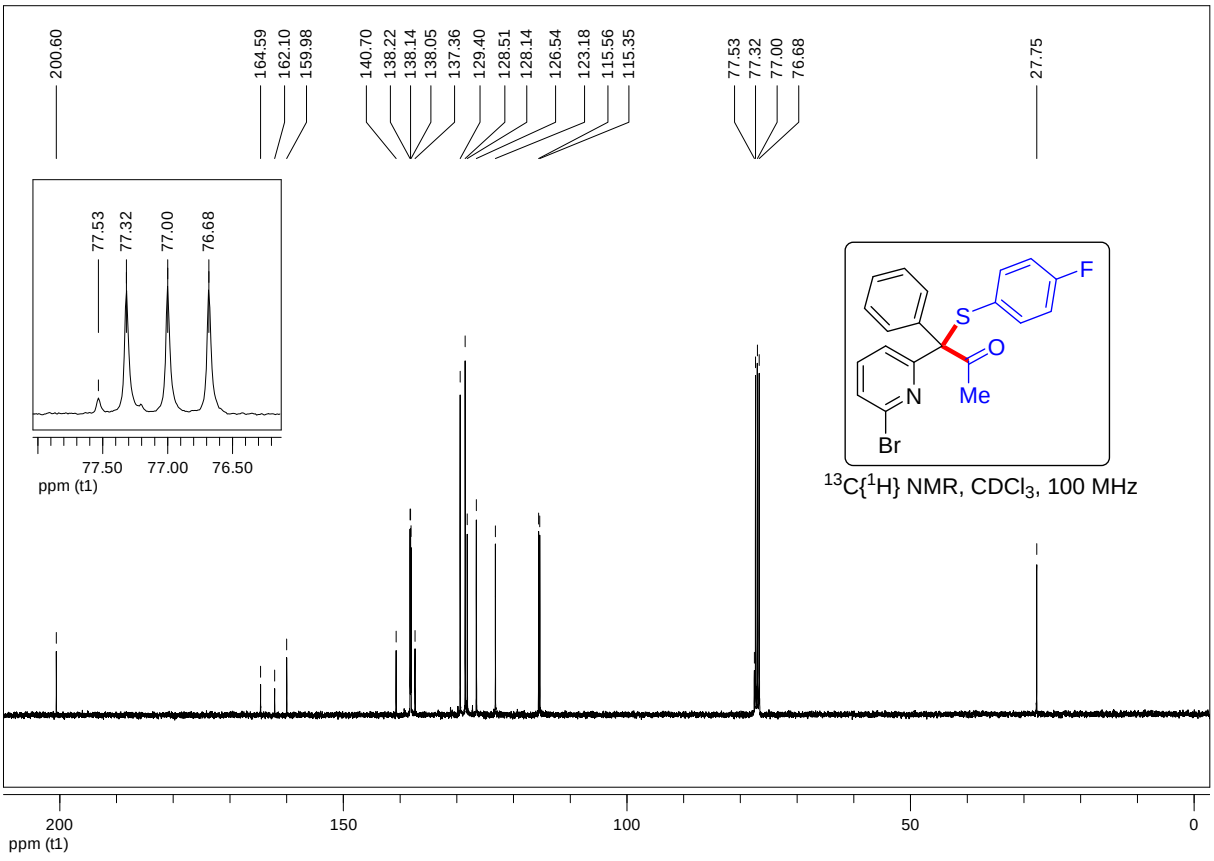




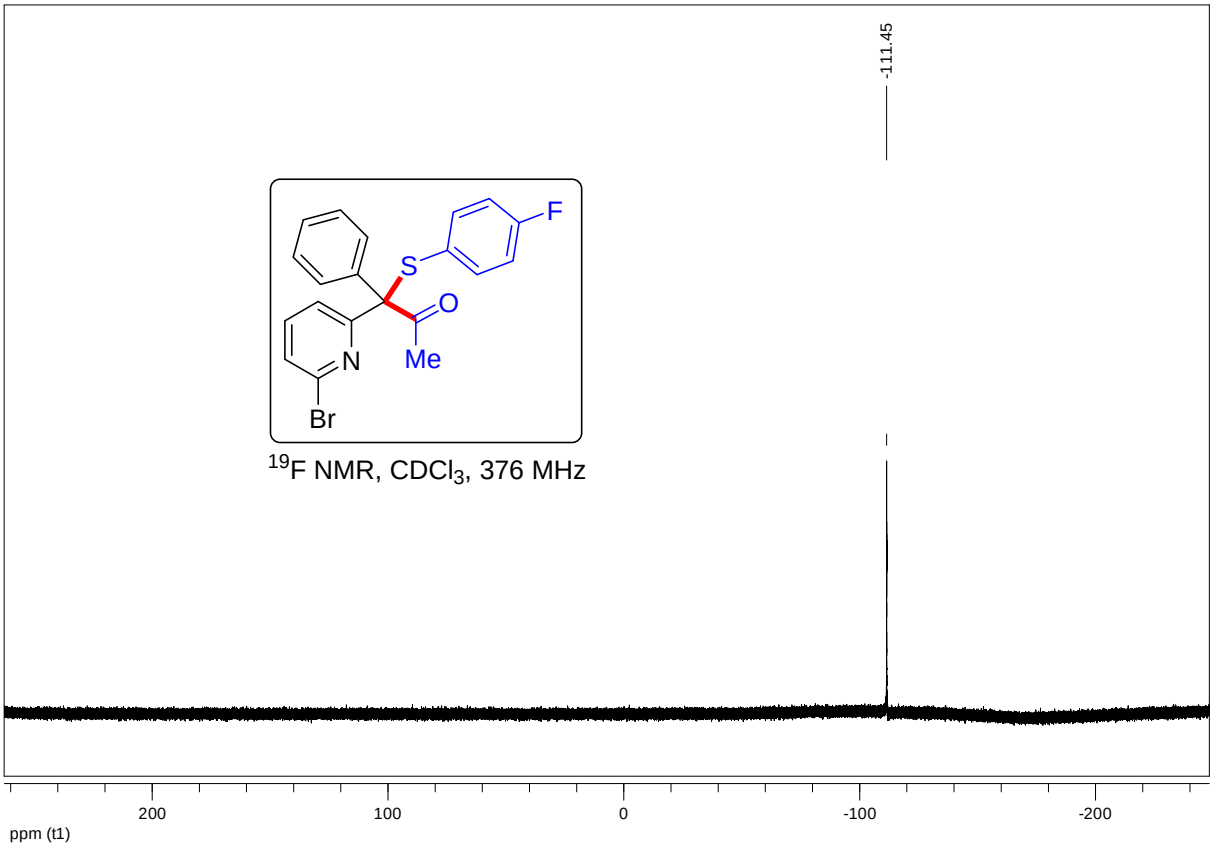
1-(6-bromopyridin-2-yl)-1-((4-fluorophenyl)thio)-1-phenylpropan-2-one (3ak)



^{1}H NMR, $CDCl_3$, 400 MHz

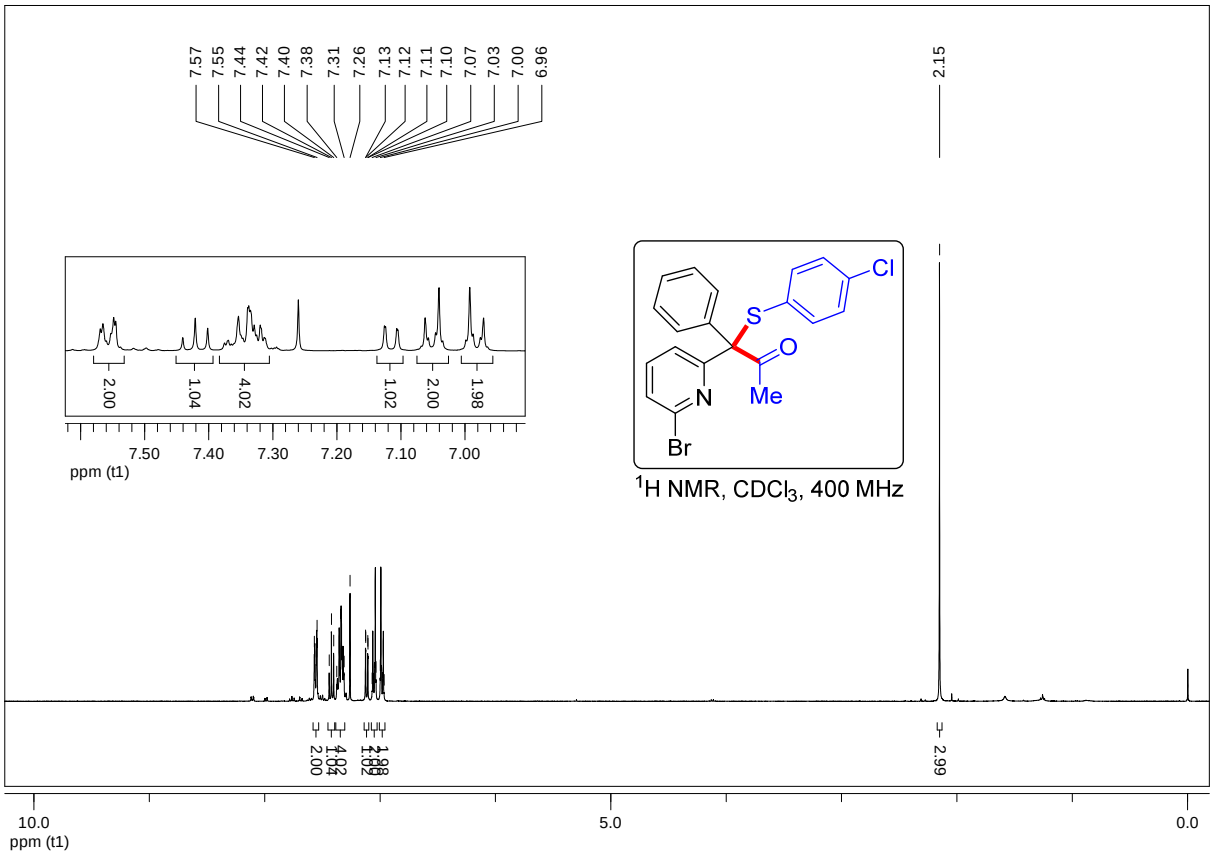


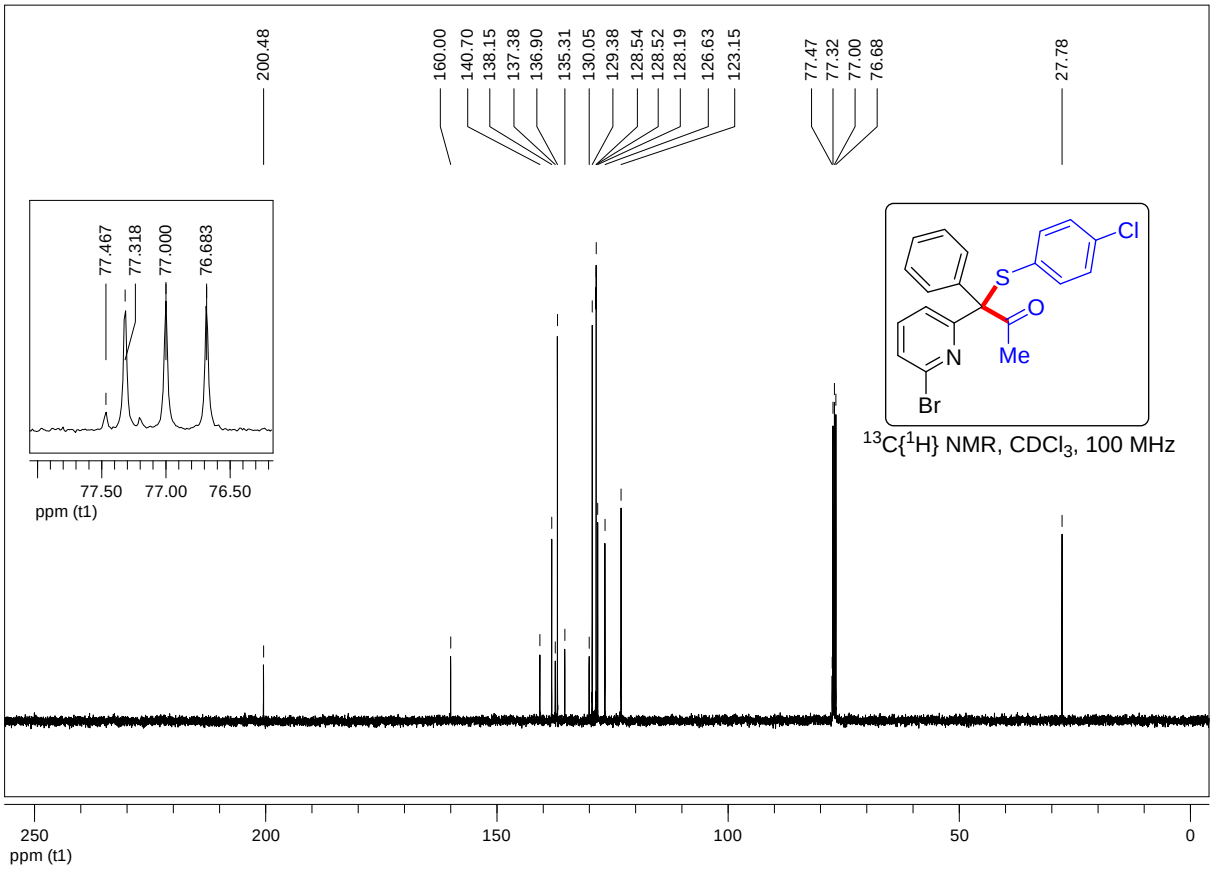
^{13}C{^{1}H} NMR, $CDCl_3$, 100 MHz



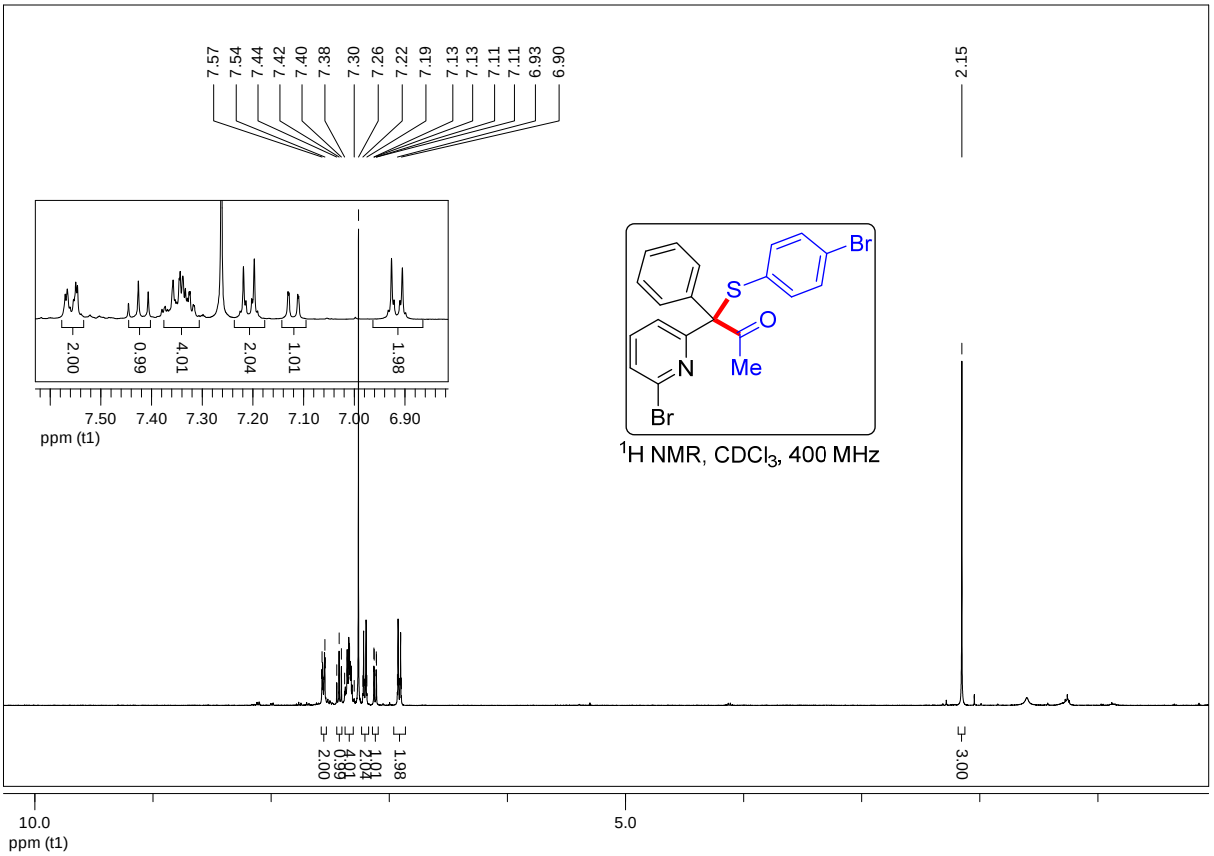
^{19}F NMR, $CDCl_3$, 376 MHz

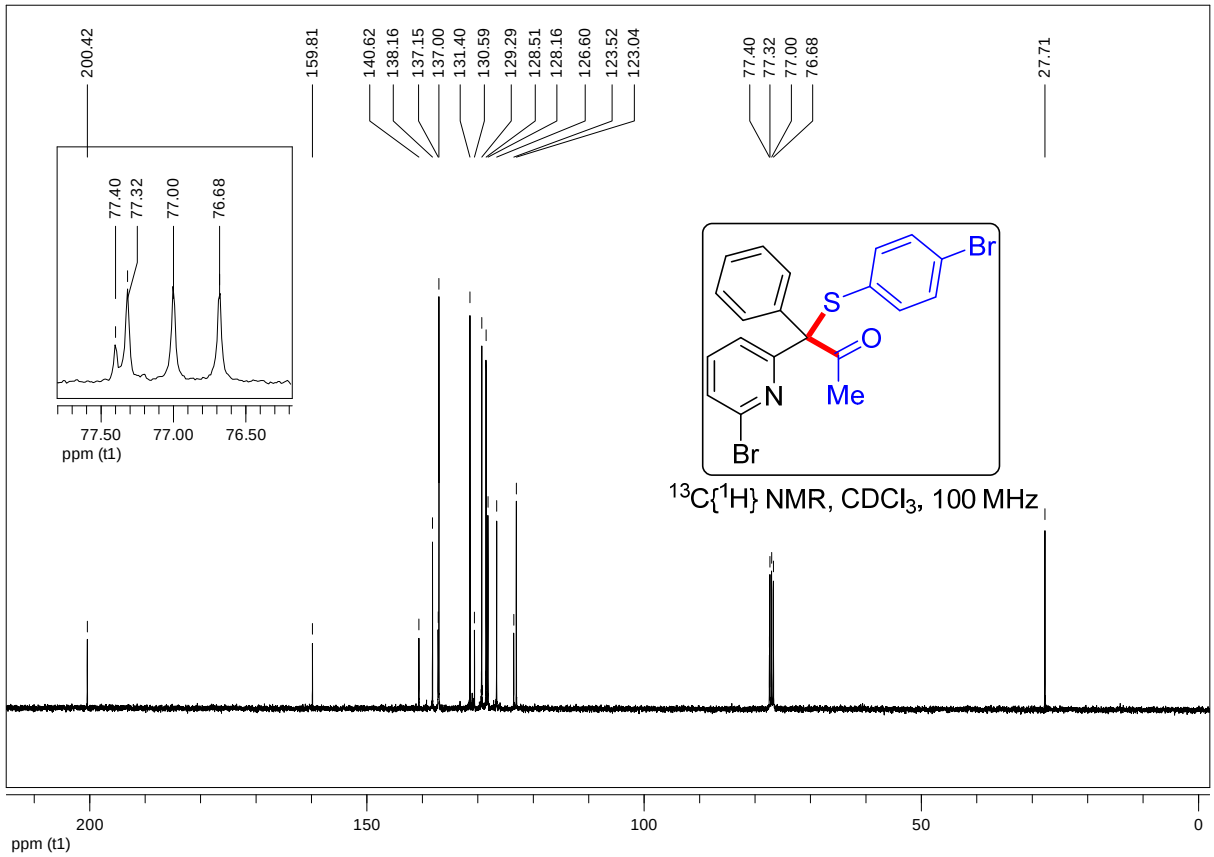
1-(6-bromopyridin-2-yl)-1-((4-chlorophenyl)thio)-1-phenylpropan-2-one (3al)



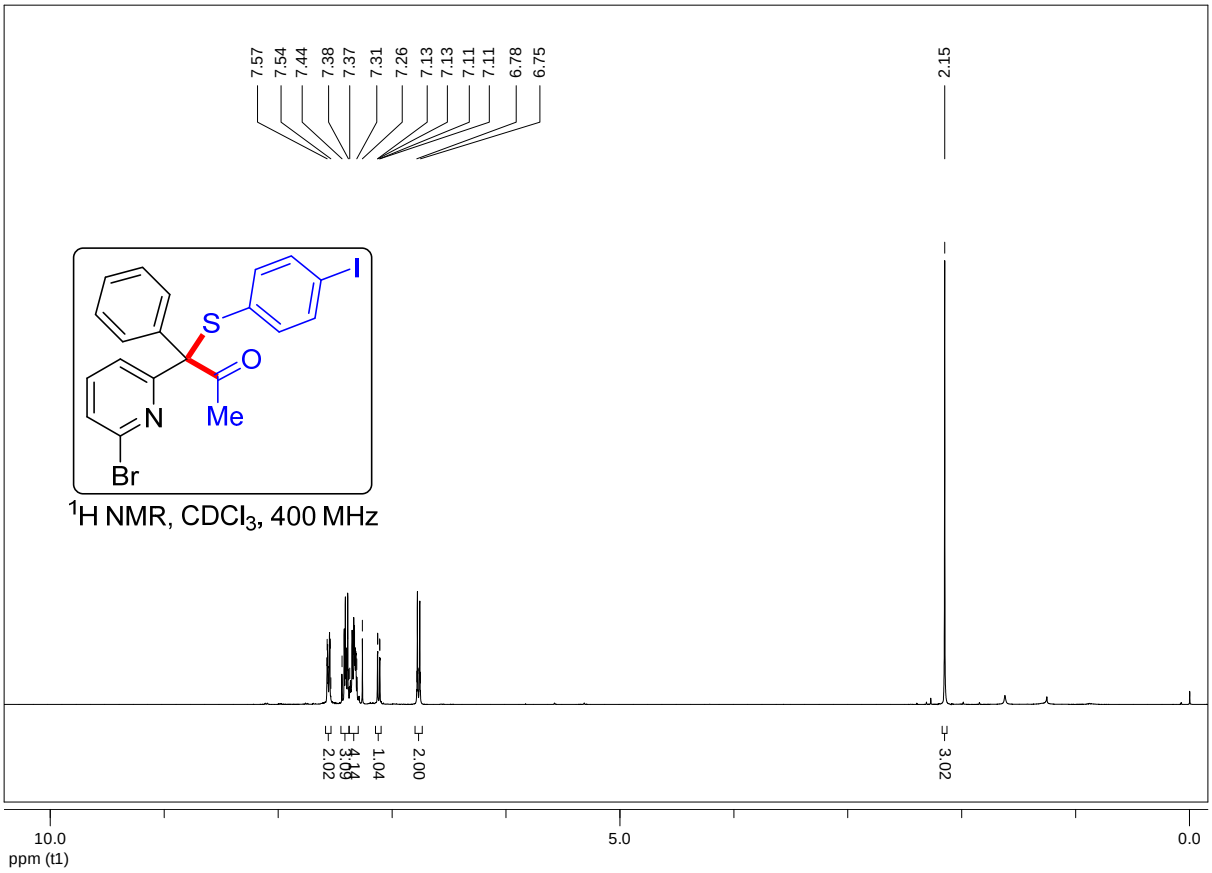


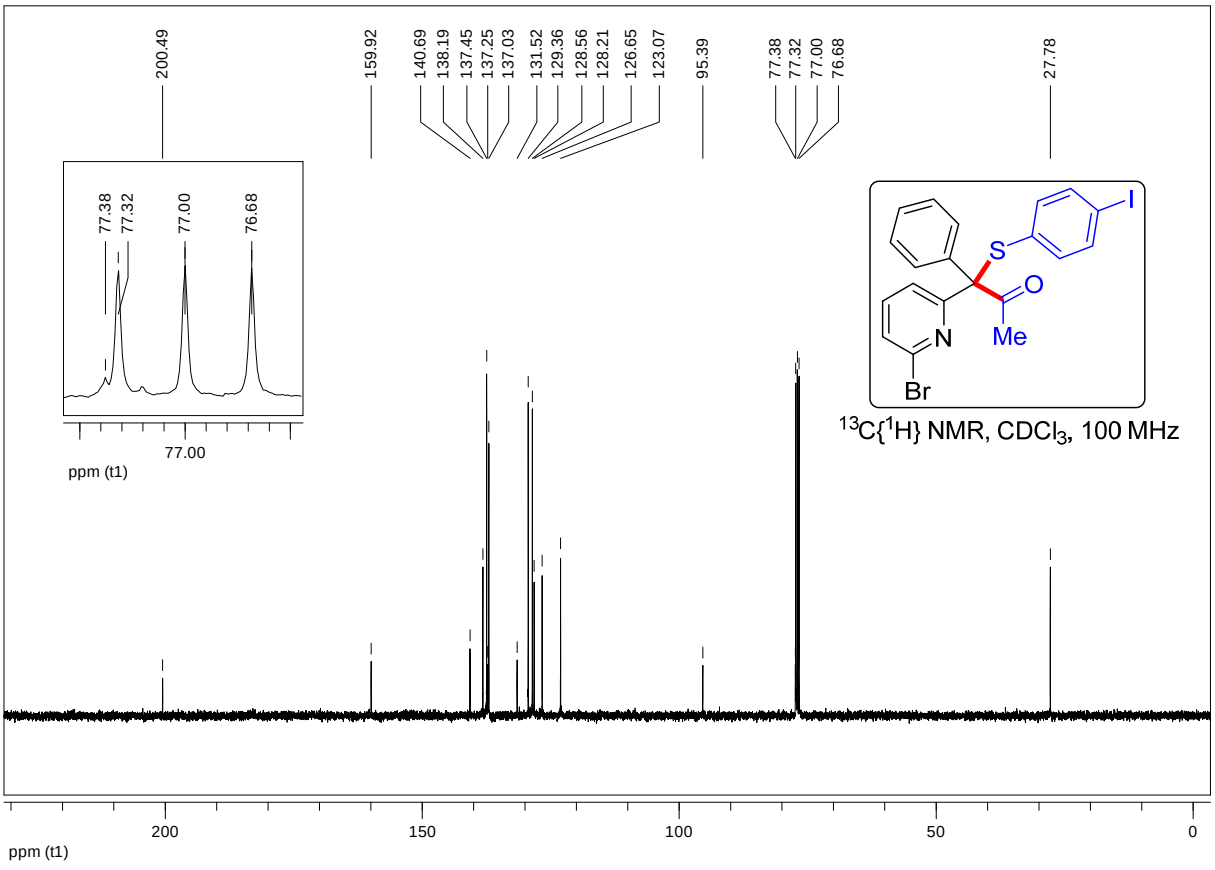
1-((4-bromophenyl)thio)-1-(6-bromopyridin-2-yl)-1-phenylpropan-2-one(3am)



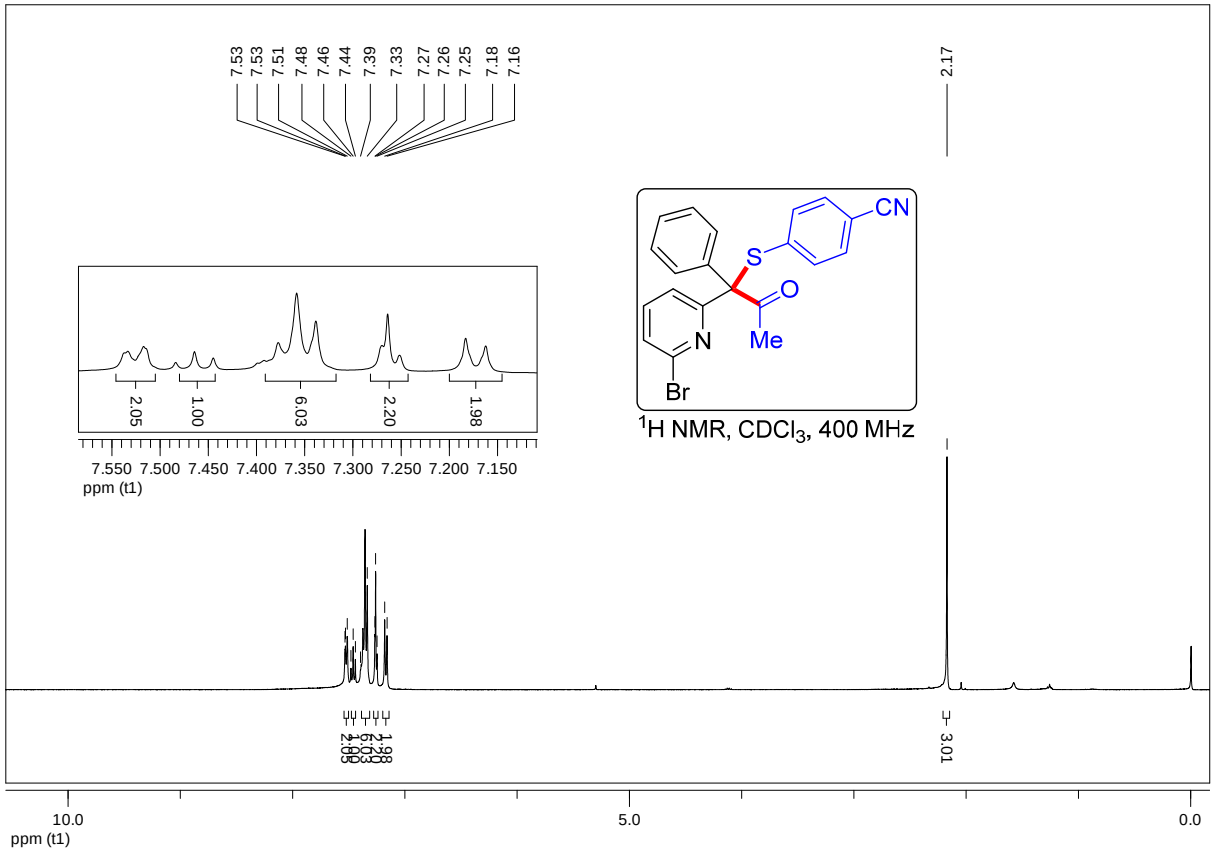


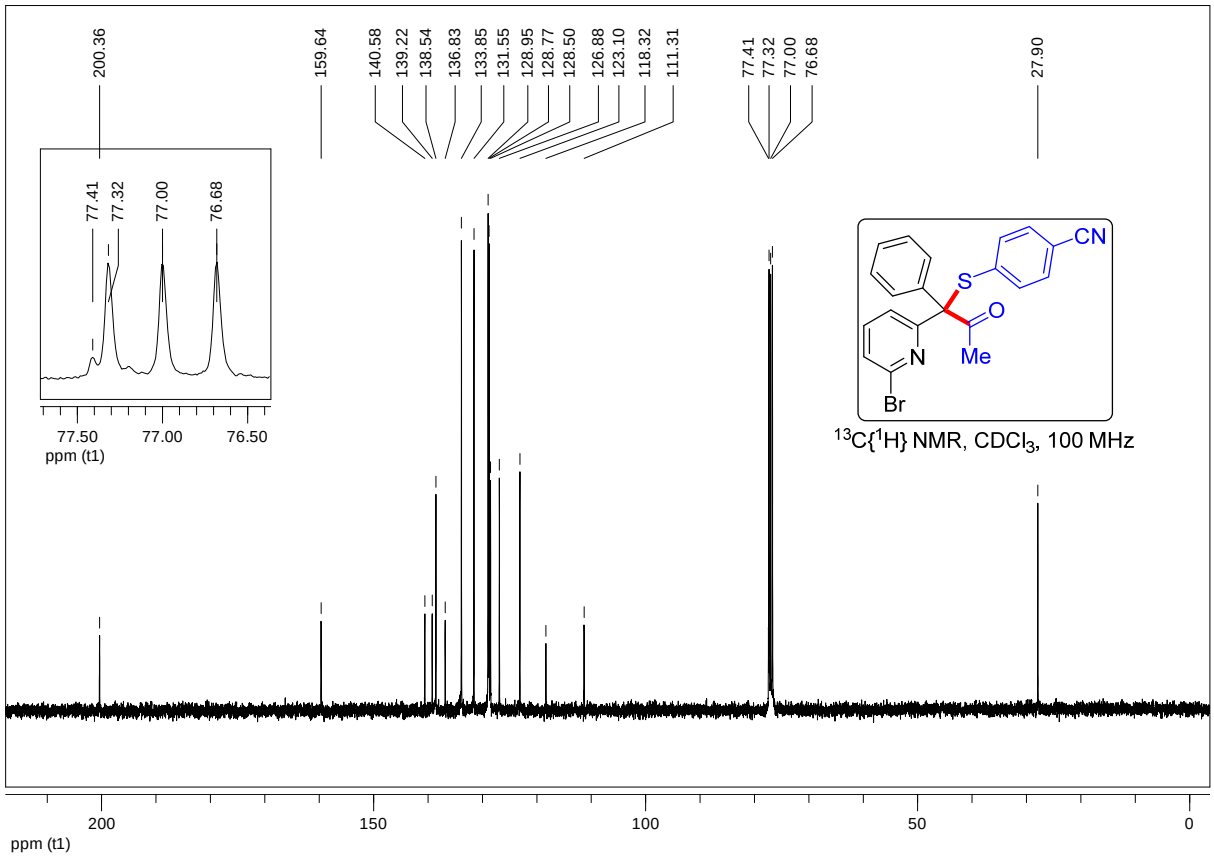
1-(6-bromopyridin-2-yl)-1-((4-iodophenyl)thio)-1-phenylpropan-2-one (3an)



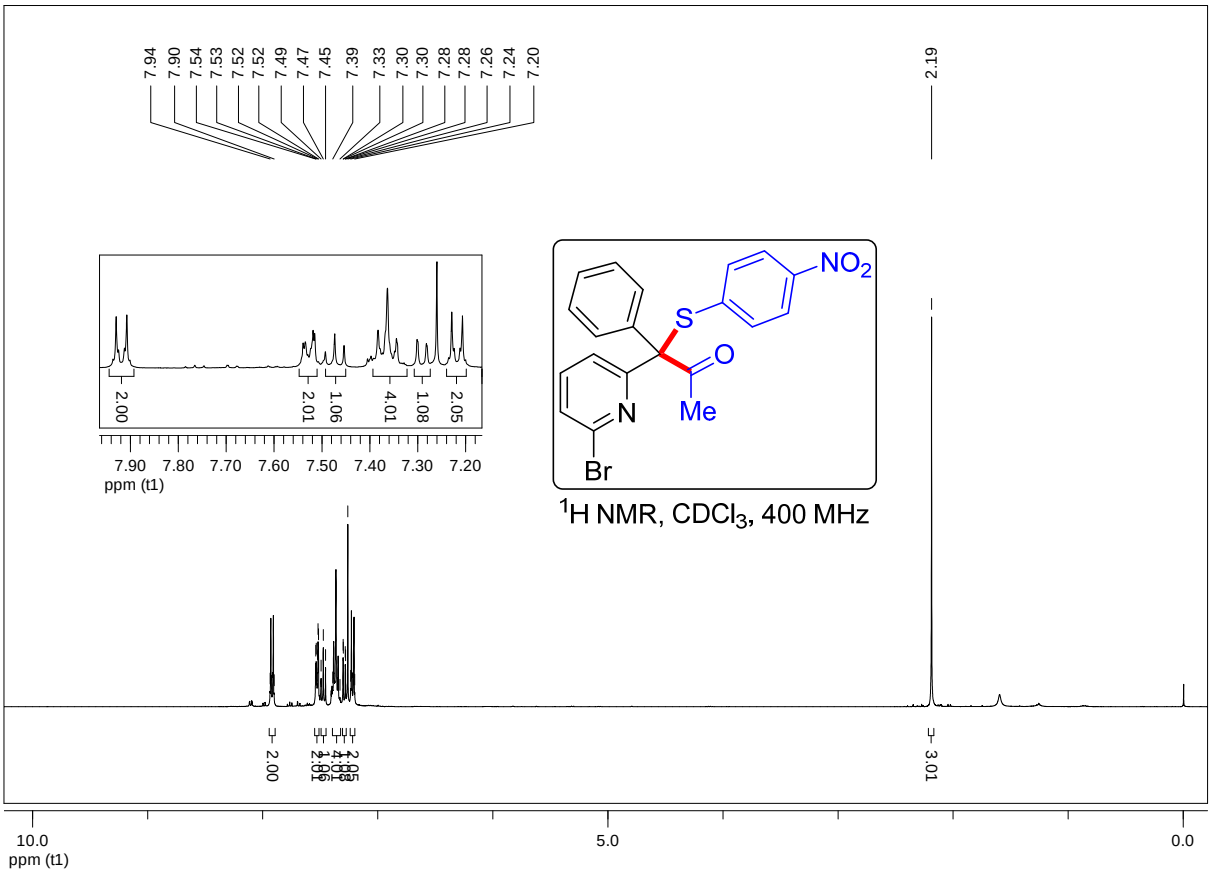


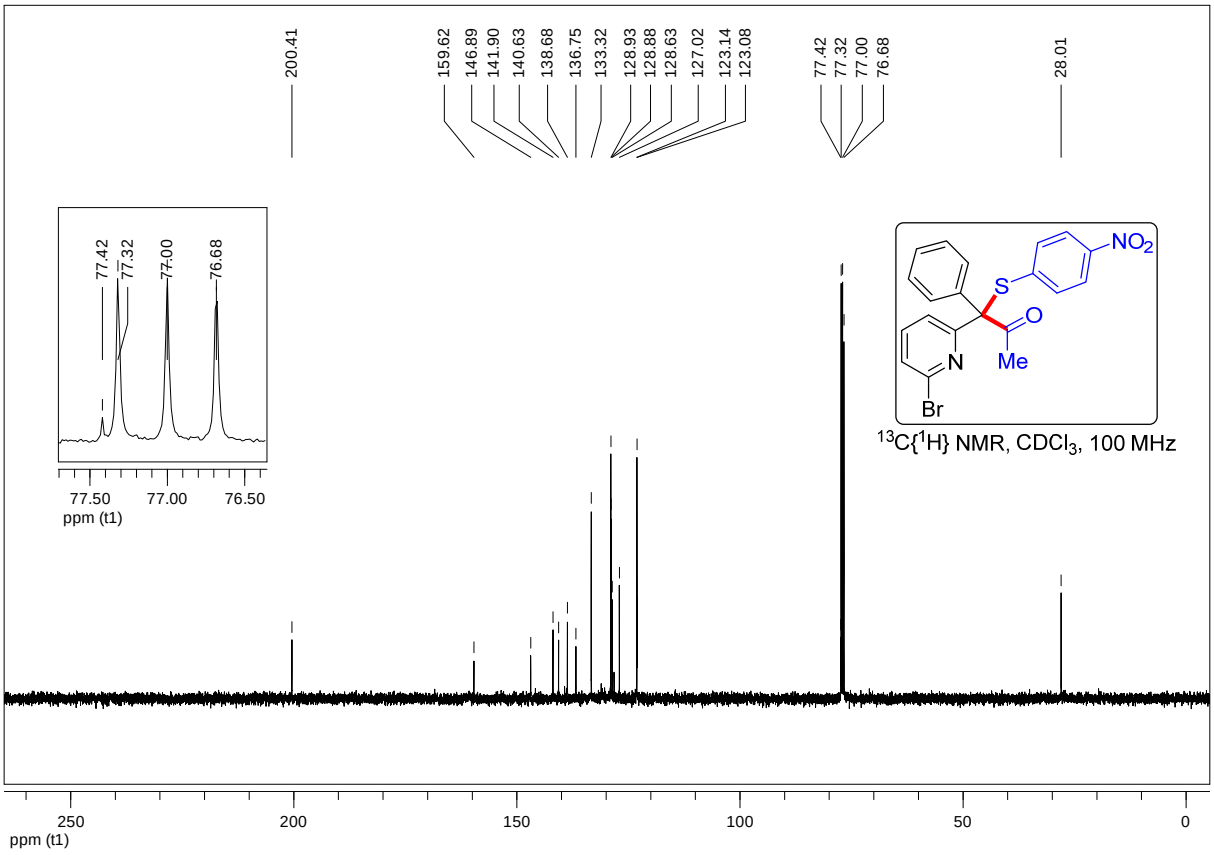
4-((1-(6-bromopyridin-2-yl)-2-oxo-1-phenylpropyl)thio)benzonitrile (3ao)



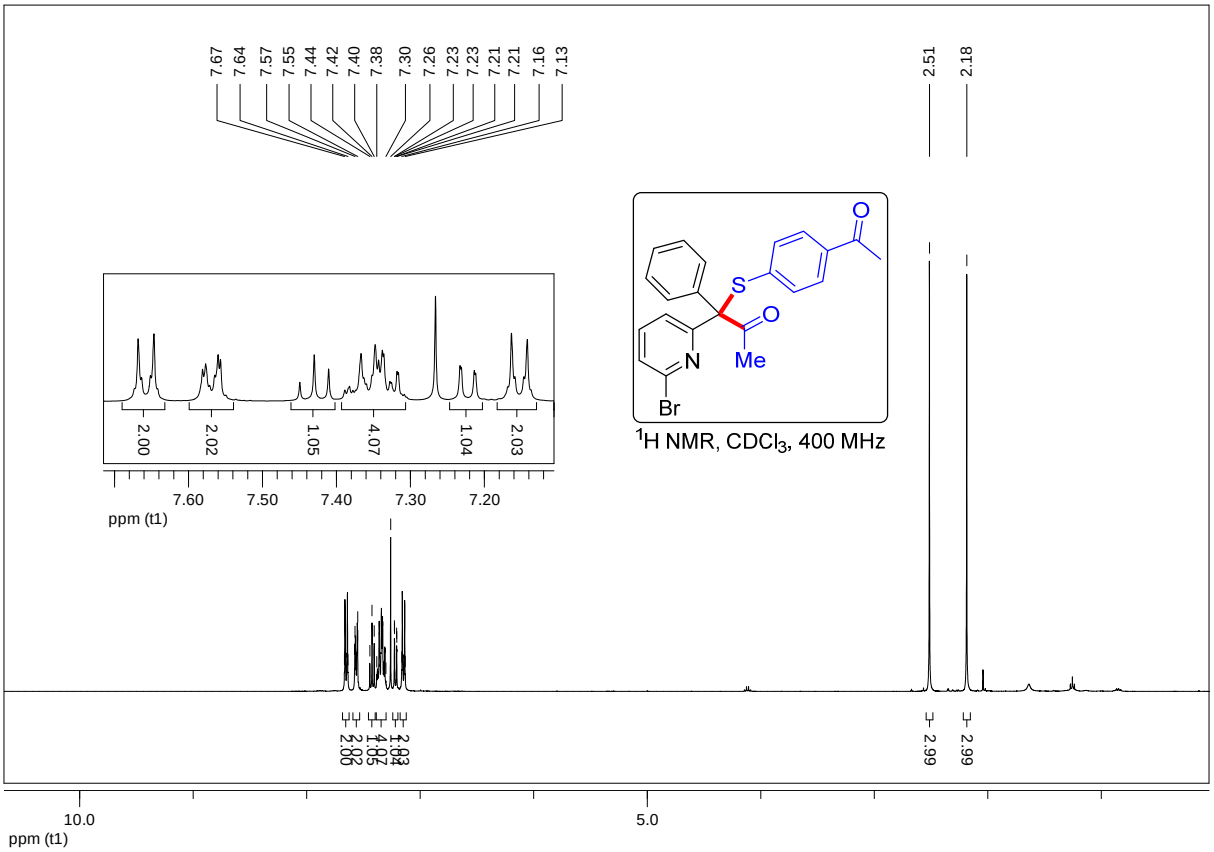


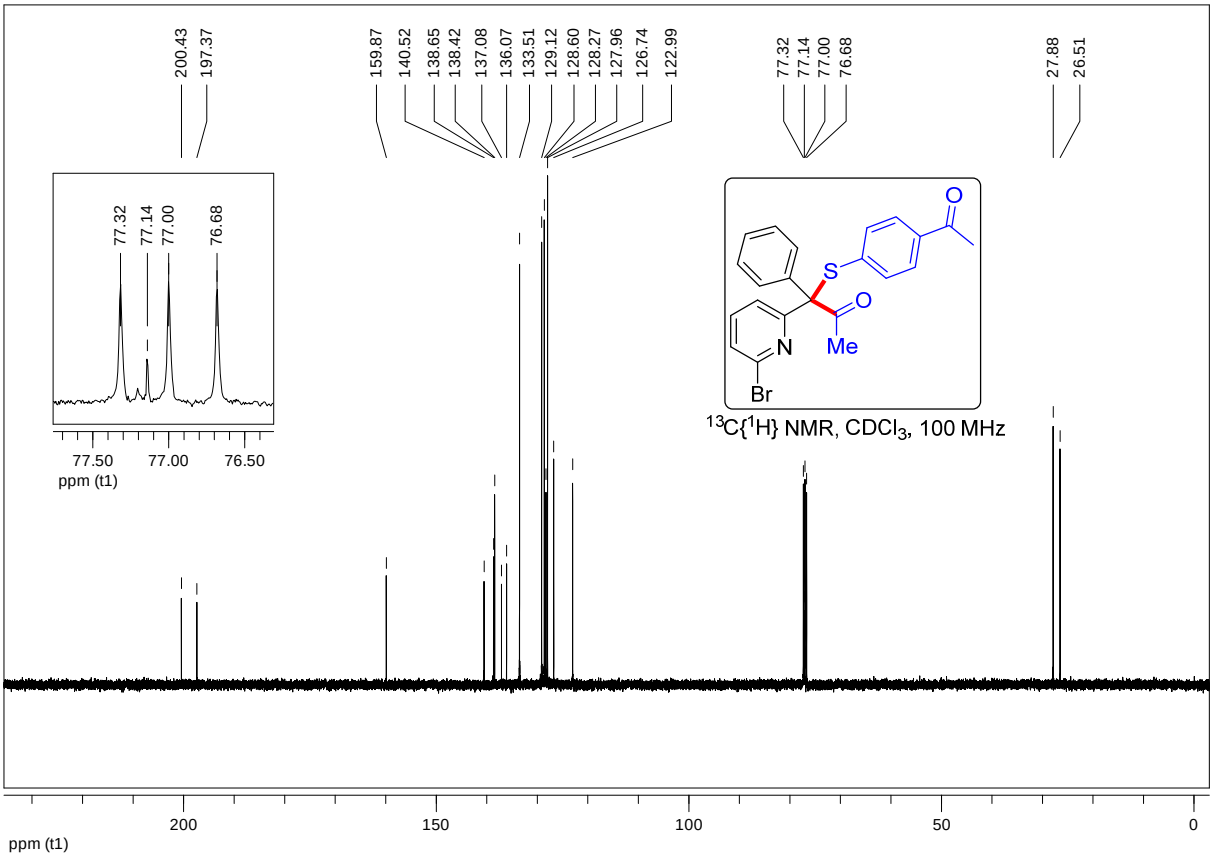
1-(6-bromopyridin-2-yl)-1-((4-nitrophenyl)thio)-1-phenylpropan-2-one (3ap)



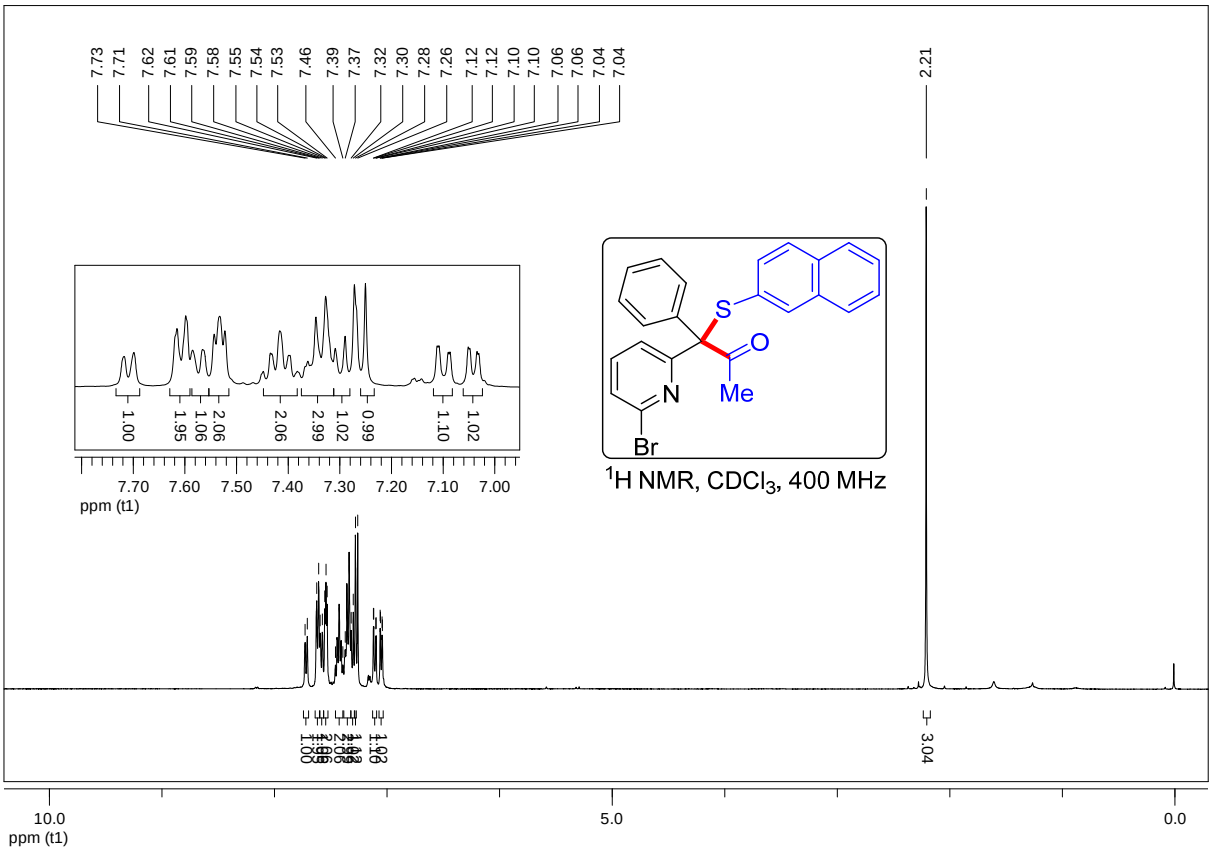


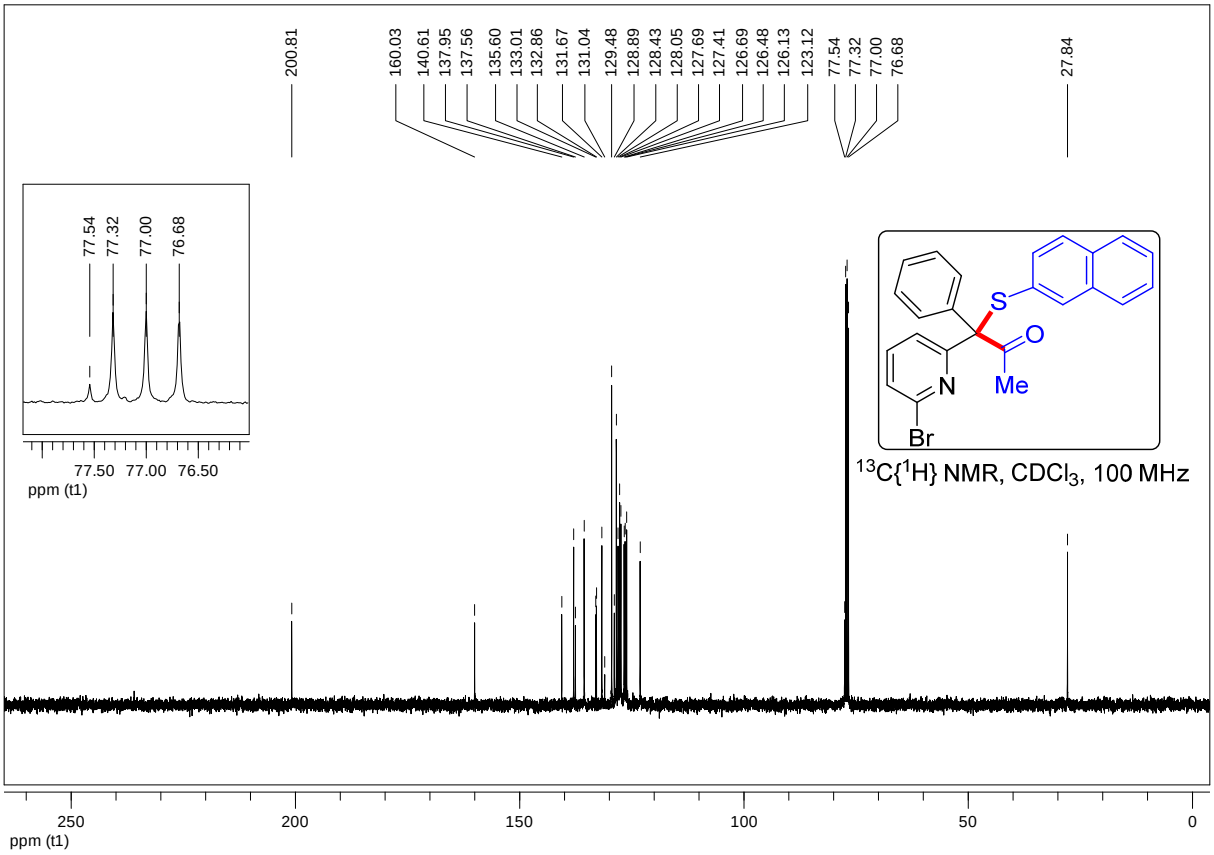
1-((4-acetylphenyl)thio)-1-(6-bromopyridin-2-yl)-1-phenylpropan-2-one (3aq)



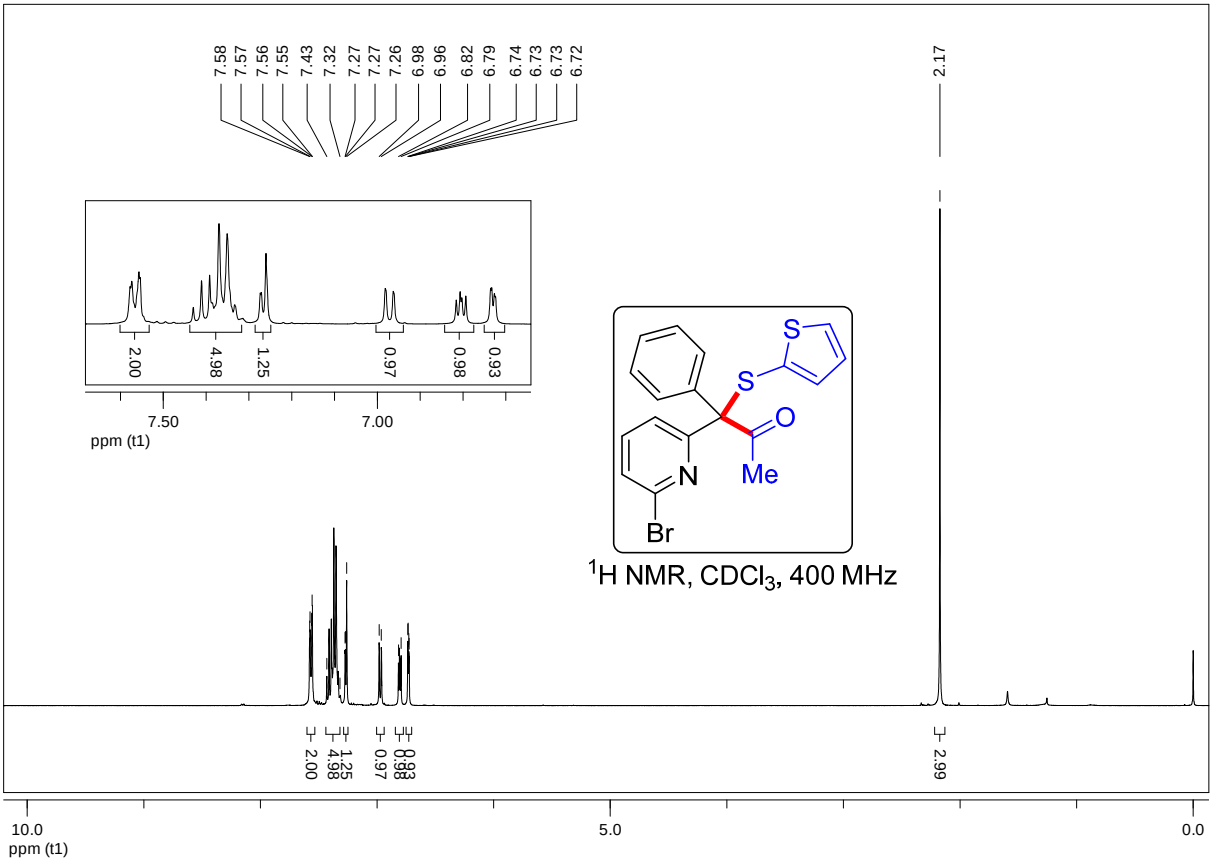


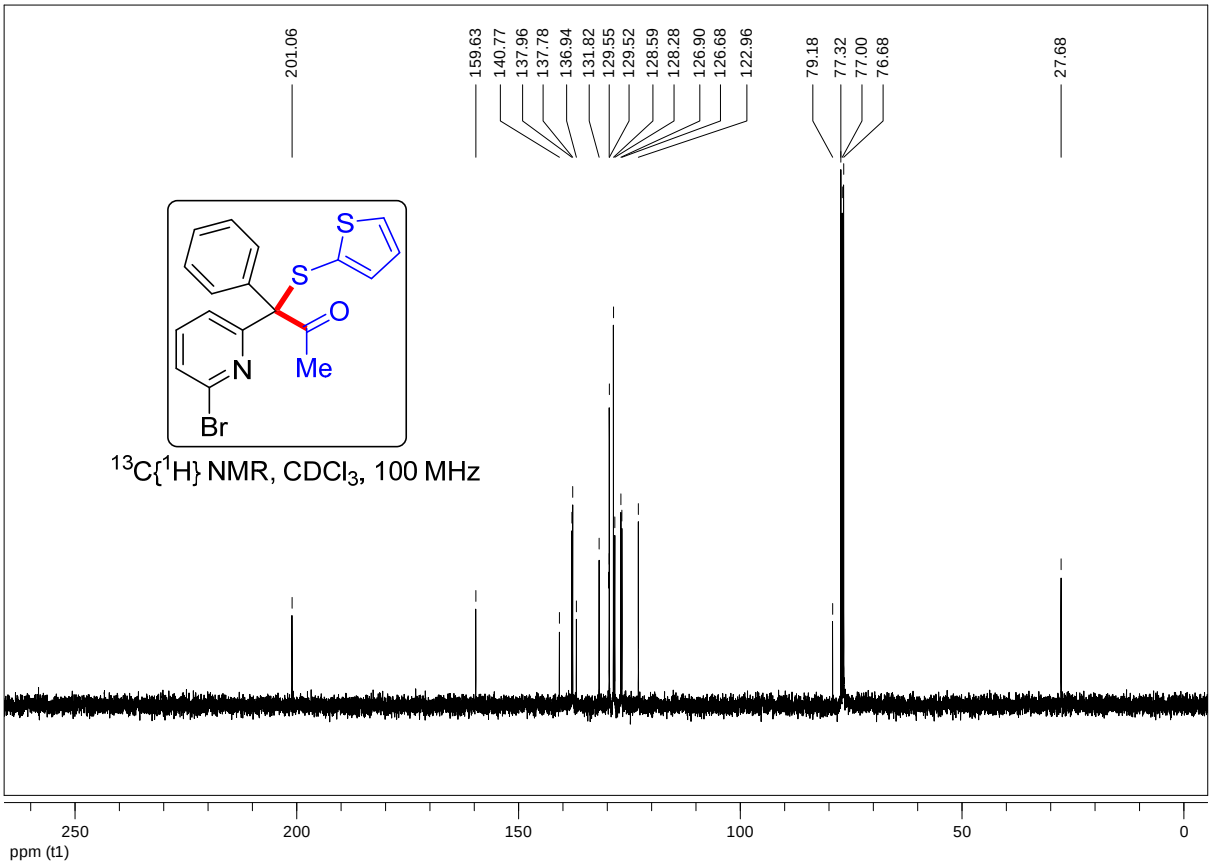
1-(6-bromopyridin-2-yl)-1-(naphthalen-2-ylthio)-1-phenylpropan-2-one (3ar)



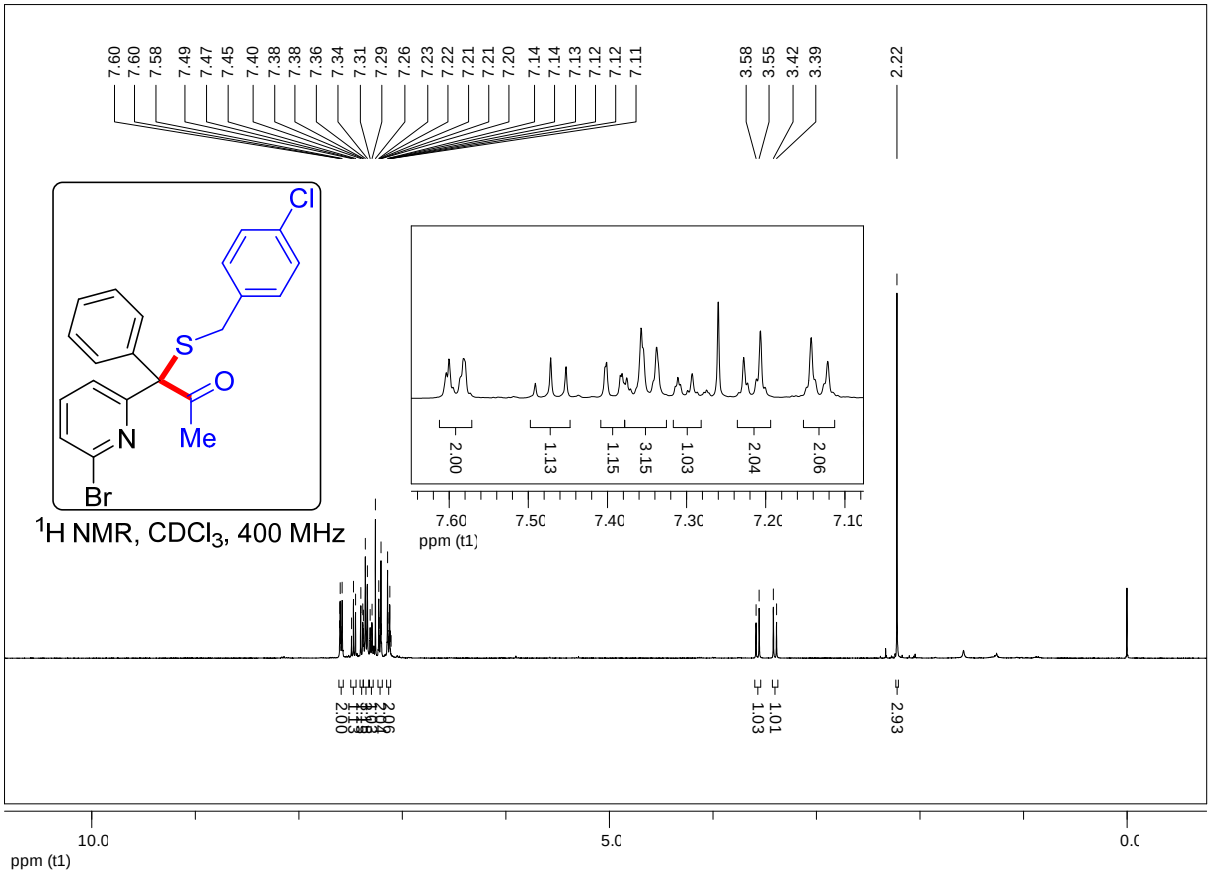


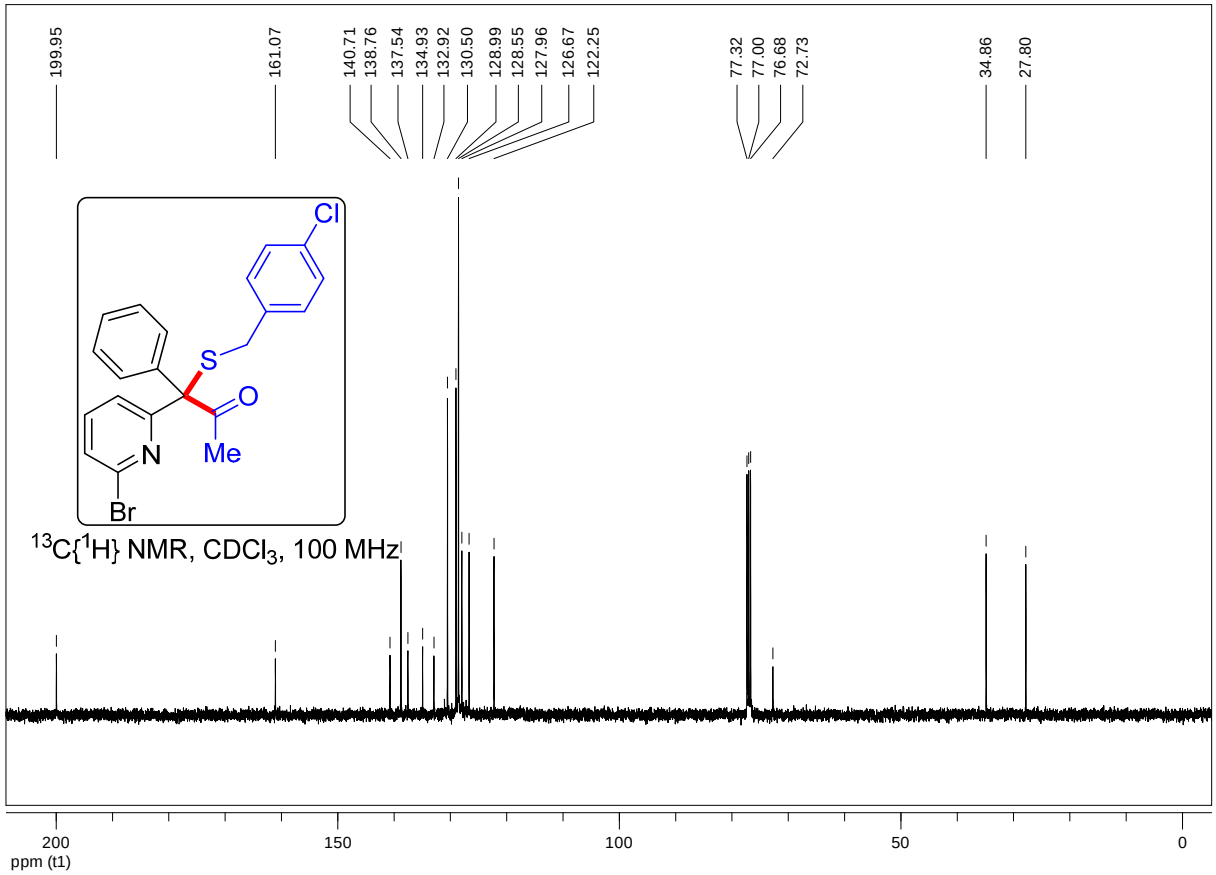
1-(6-bromopyridin-2-yl)-1-phenyl-1-(thiophen-2-ylthio)propan-2-one (3as)



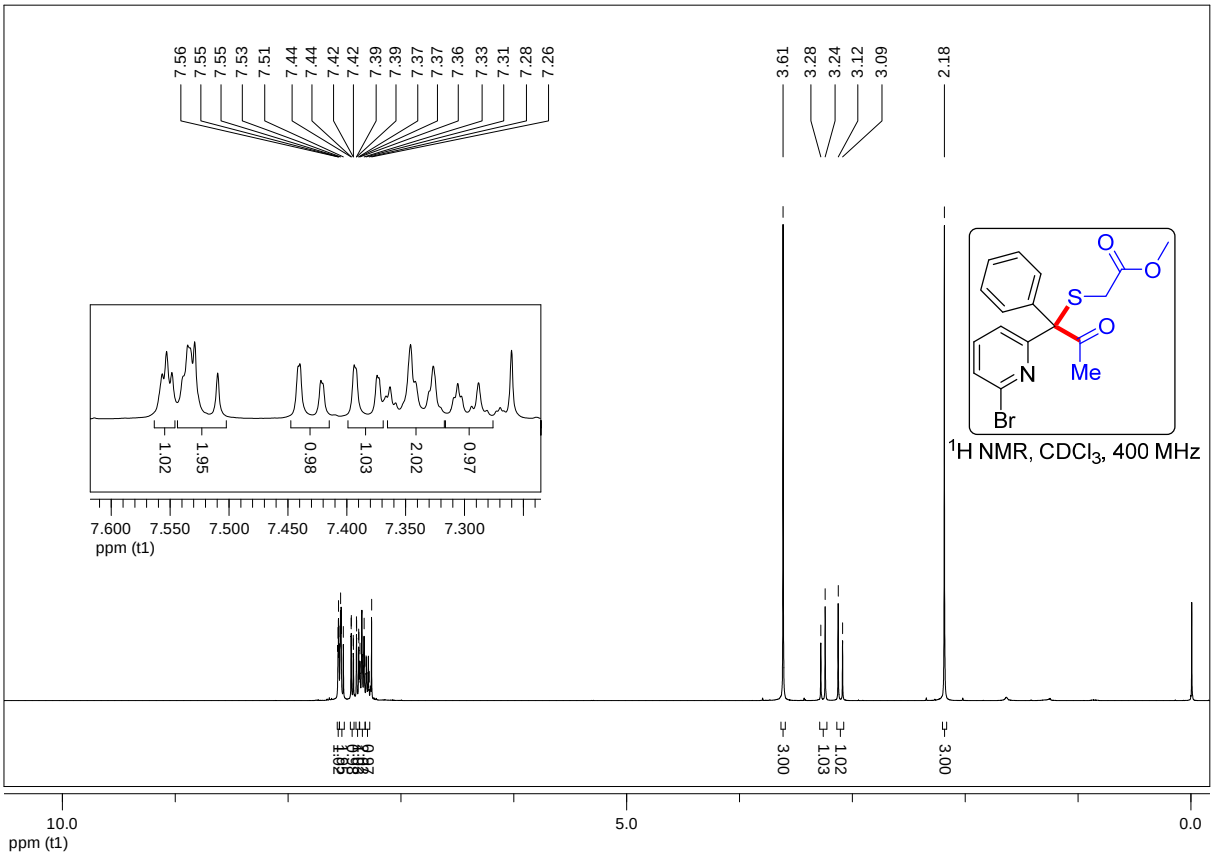


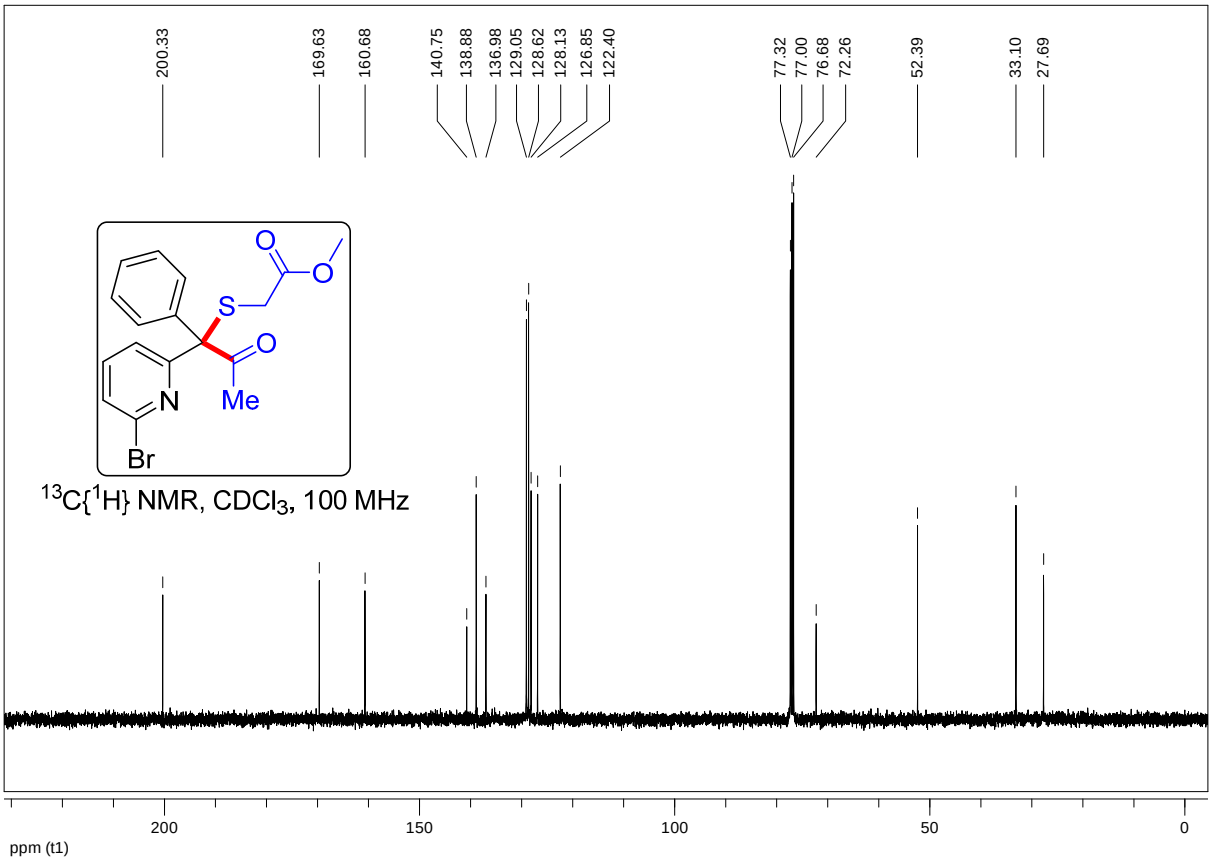
1-(6-bromopyridin-2-yl)-1-((4-chlorobenzyl)thio)-1-phenylpropan-2-one (3at)





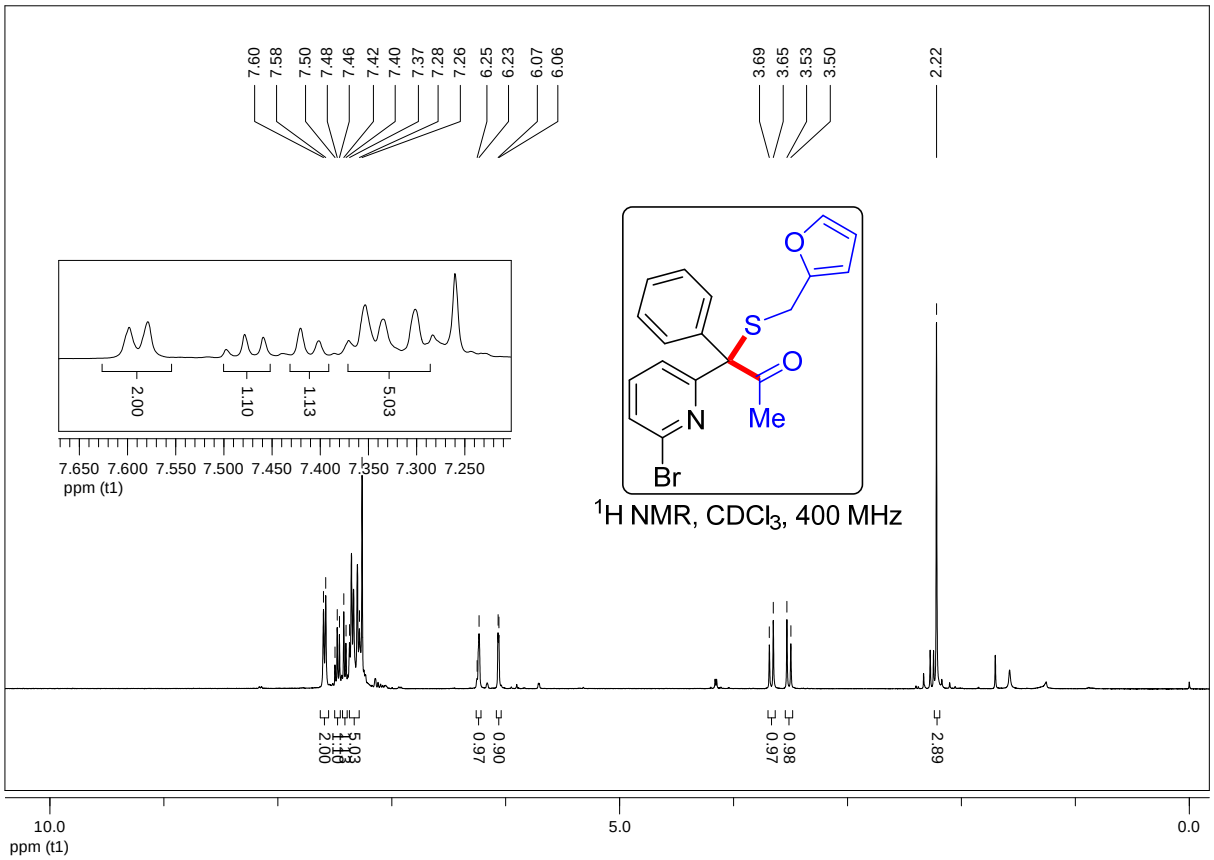
methyl 2-((1-(6-bromopyridin-2-yl)-2-oxo-1-phenylpropyl)thio)acetate (3au)

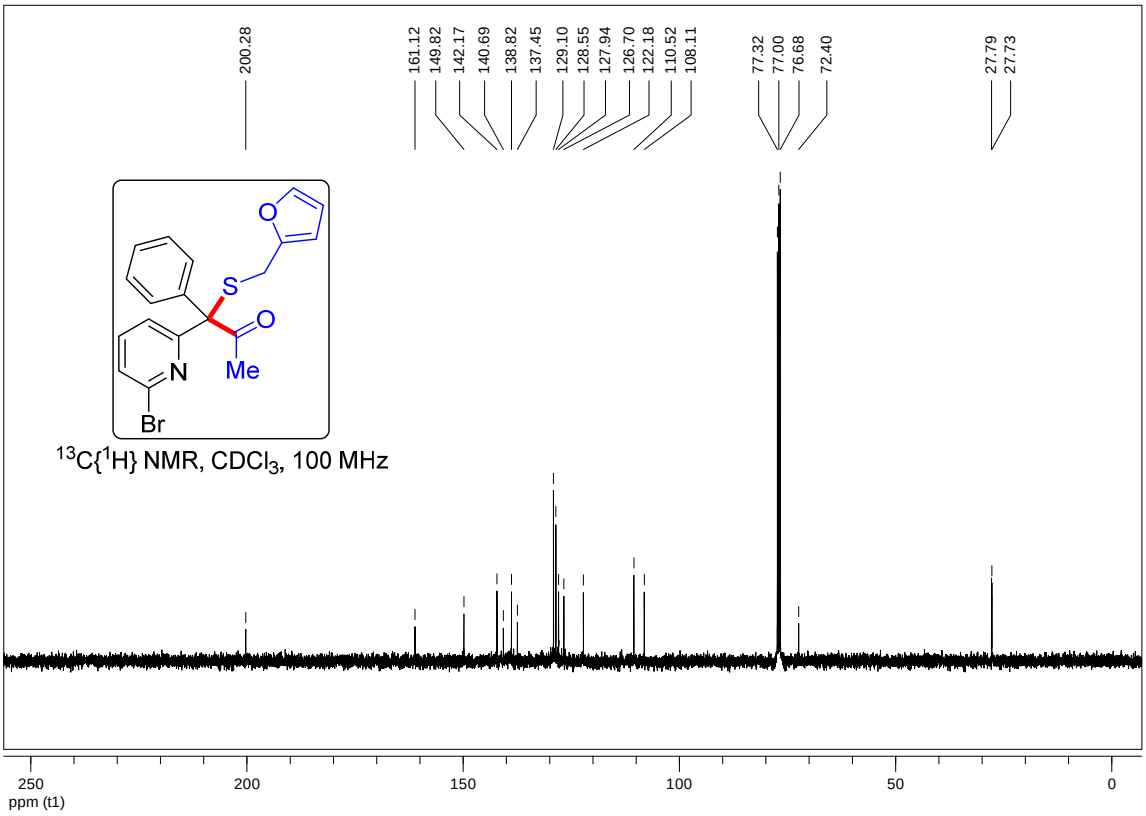




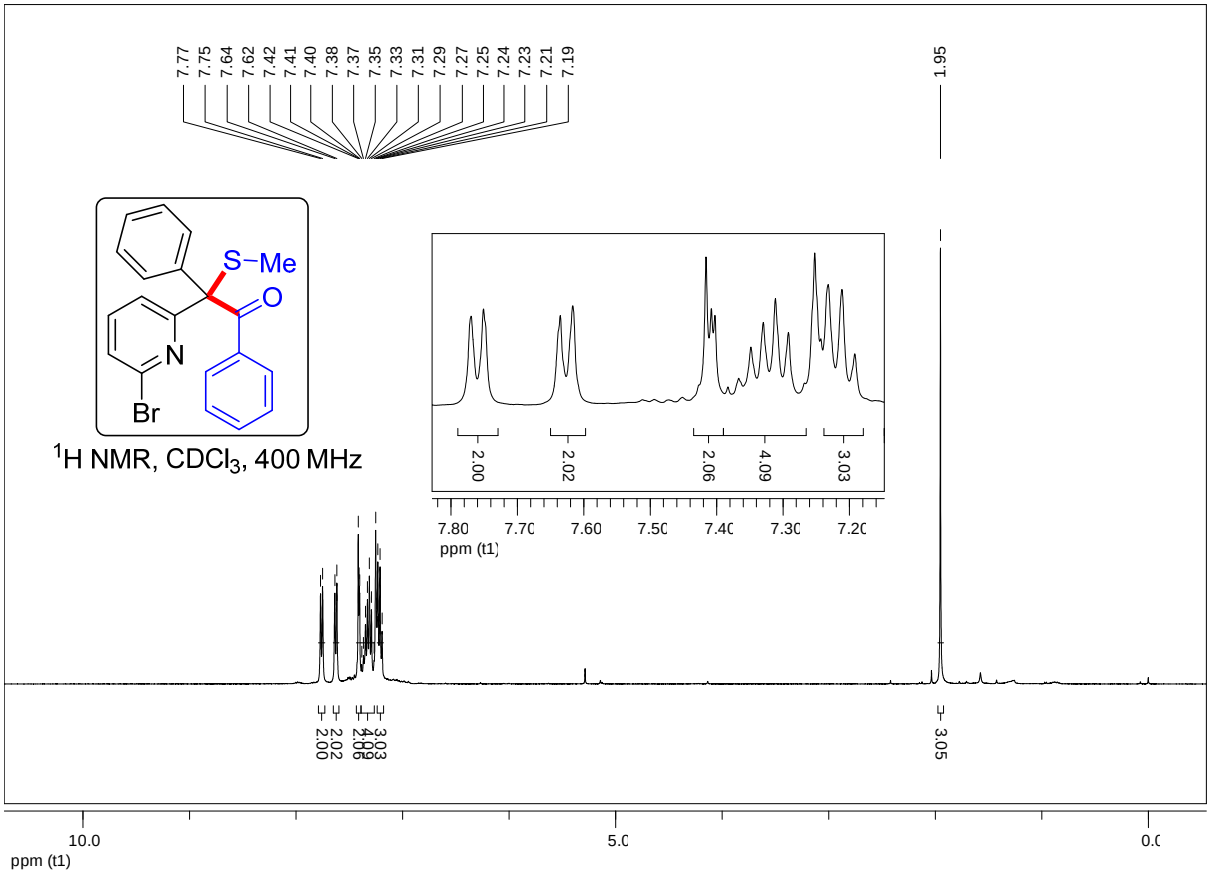
1-(6-bromopyridin-2-yl)-1-((furan-2-ylmethyl)thio)-1-phenylpropan-2-one

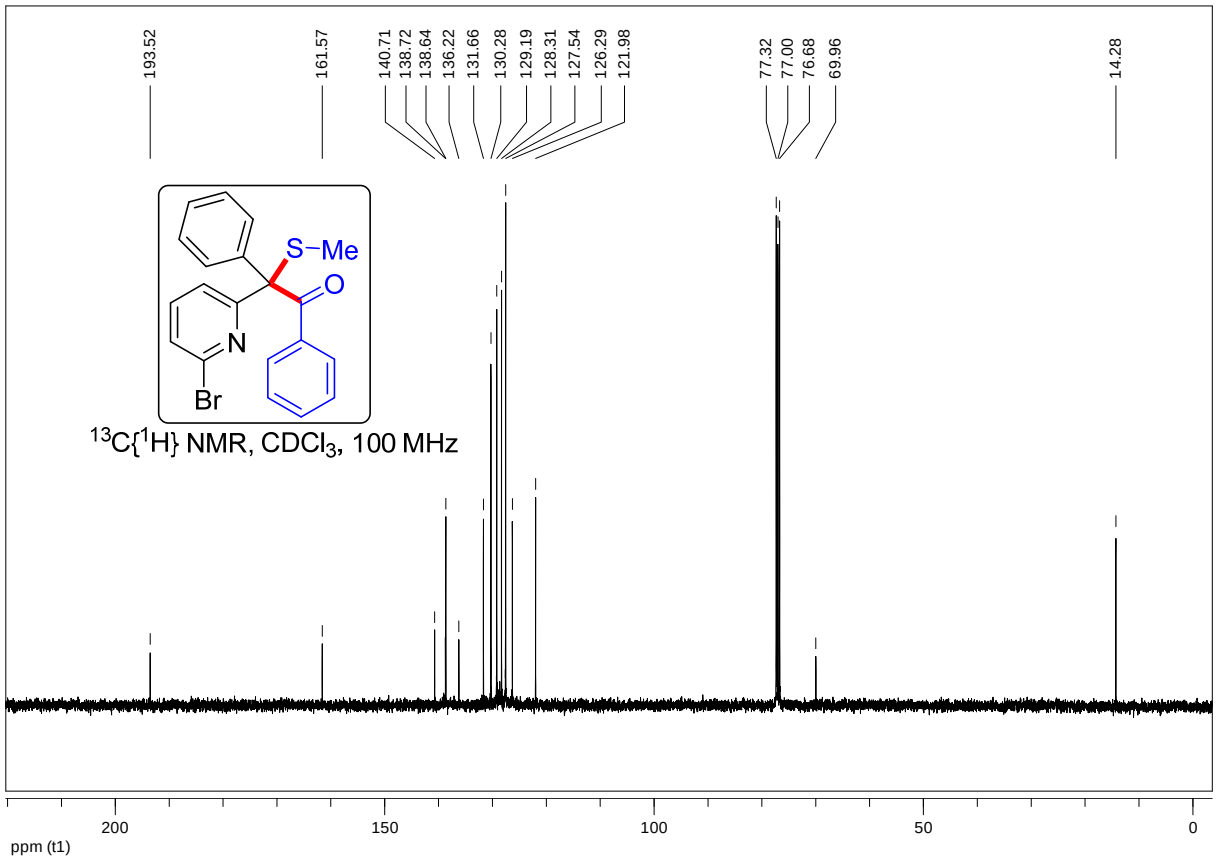
(3av)



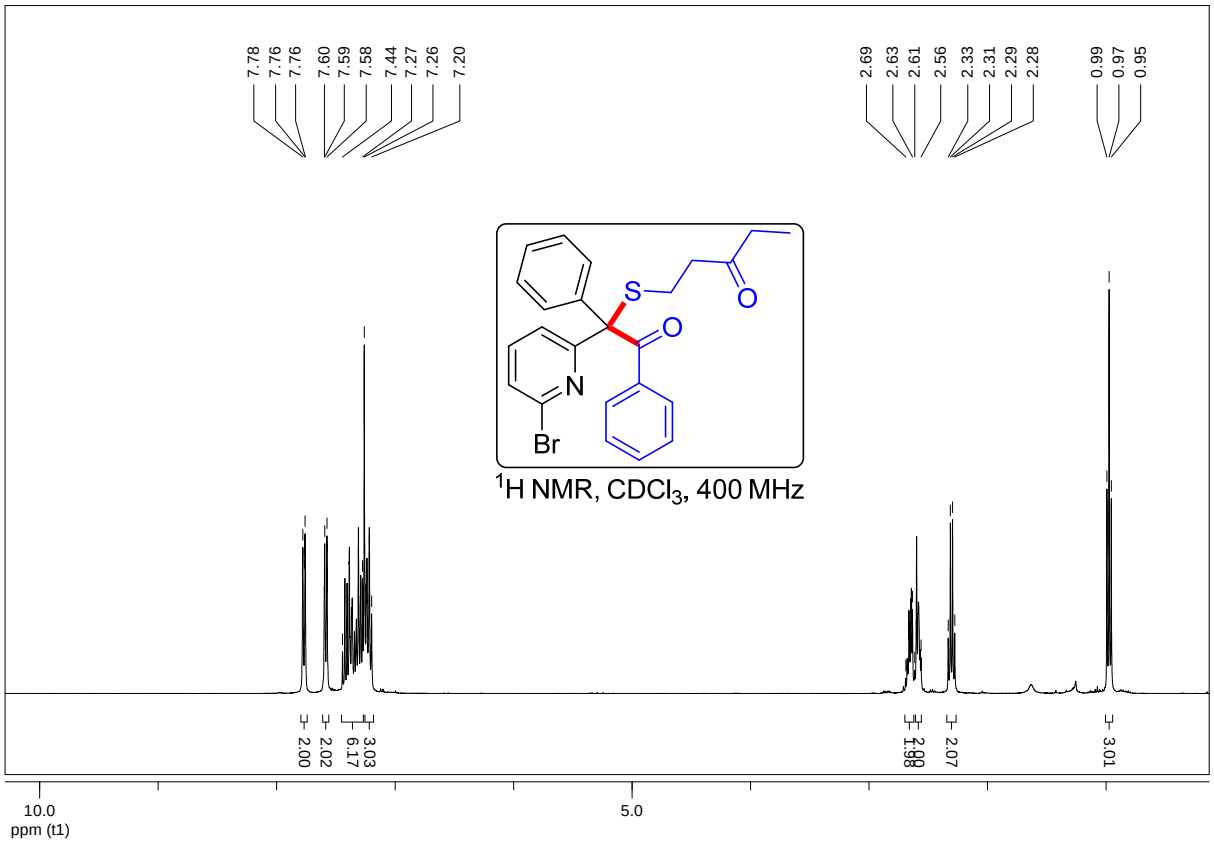


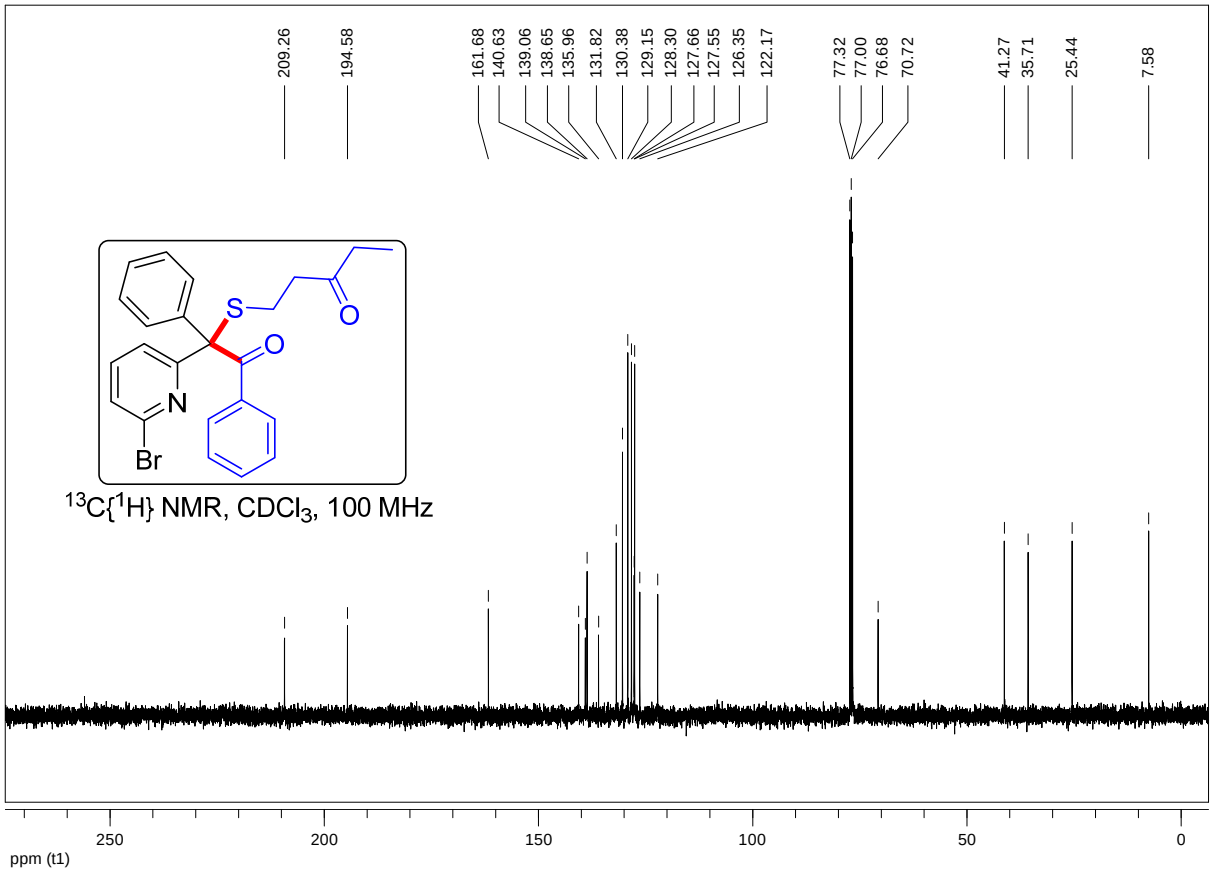
2-(6-bromopyridin-2-yl)-2-(methylthio)-1,2-diphenylethan-1-one (3aw)



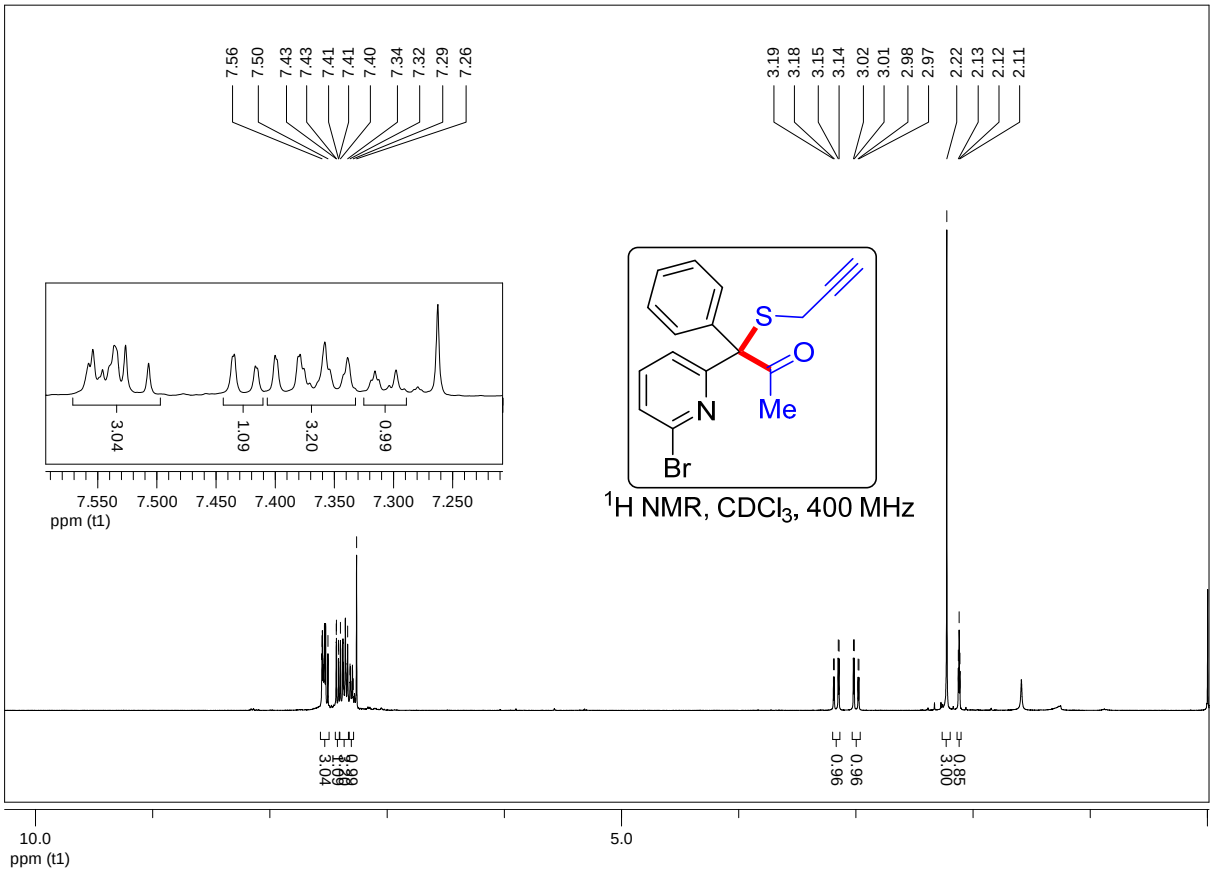


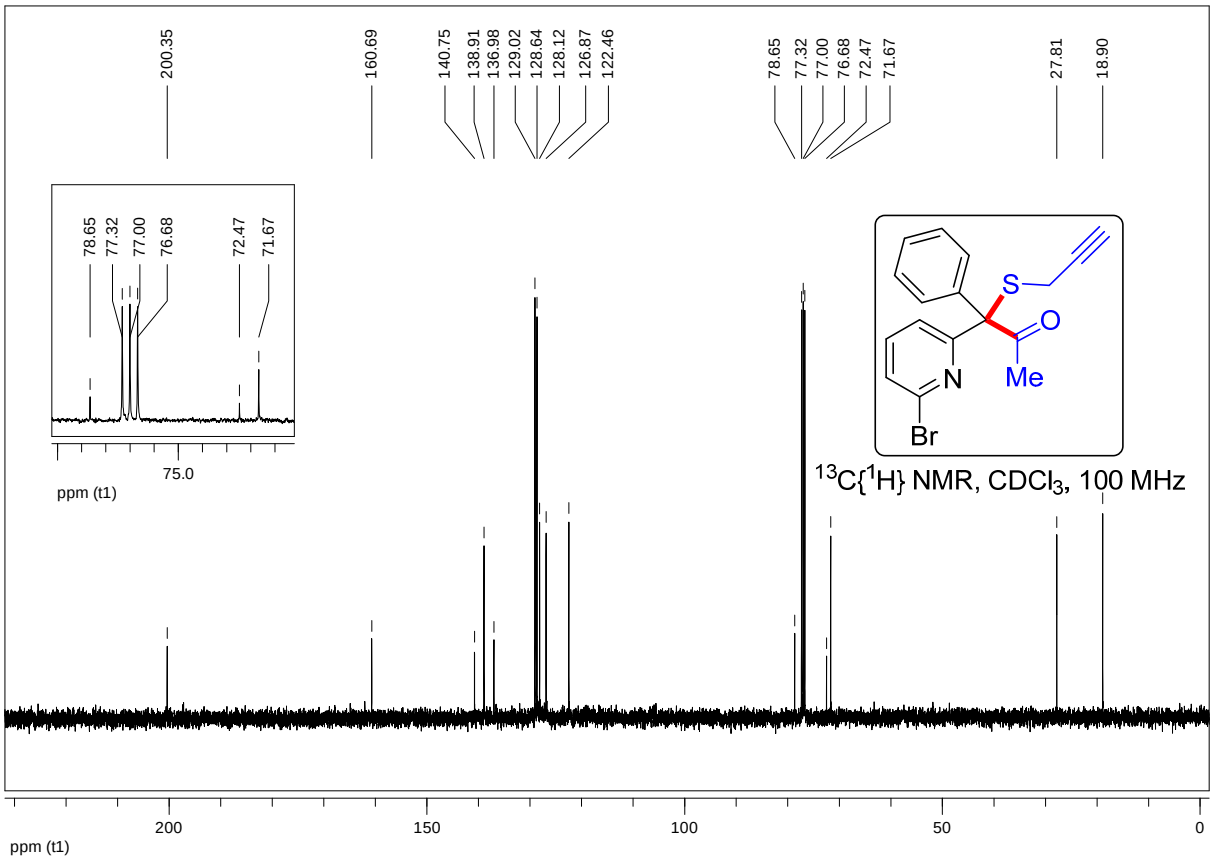
1-((1-(6-bromopyridin-2-yl)-2-oxo-1,2-diphenylethyl)thio)pentan-3-one (3ax)



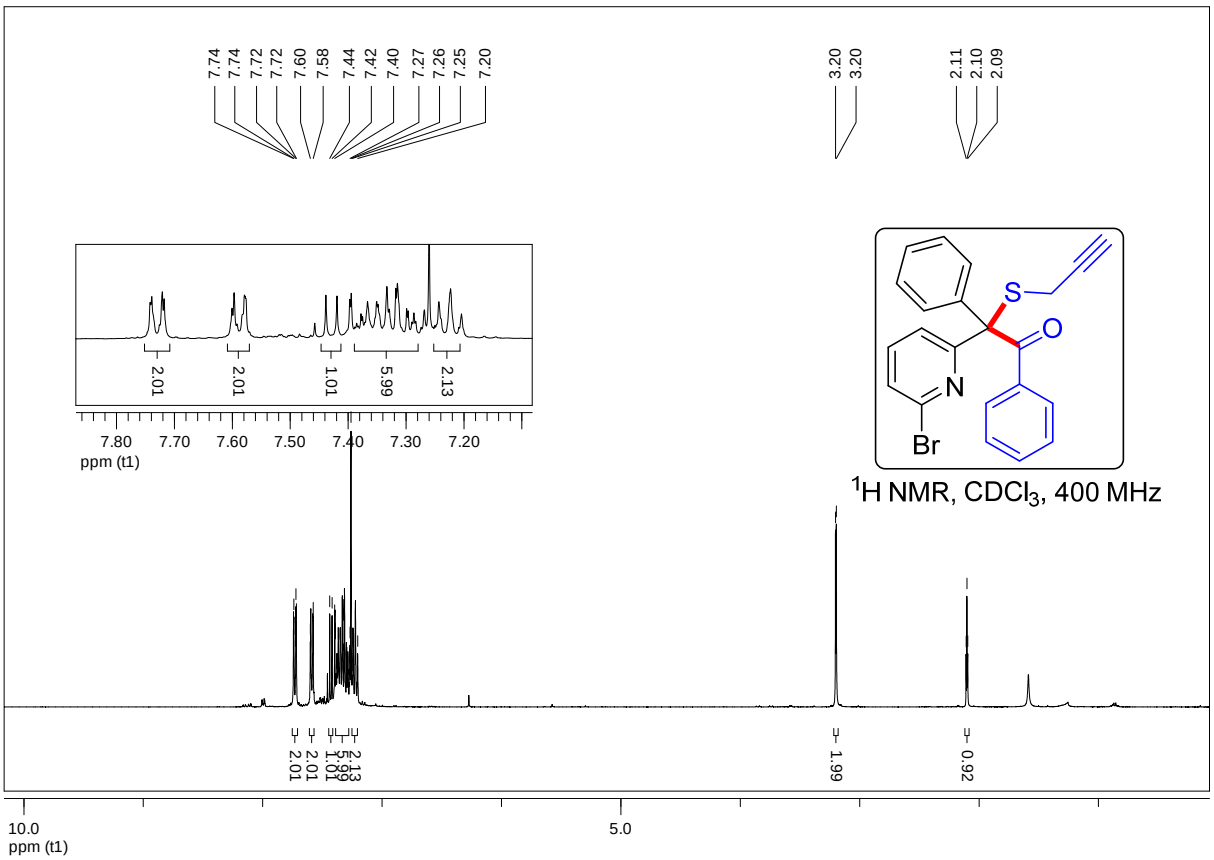


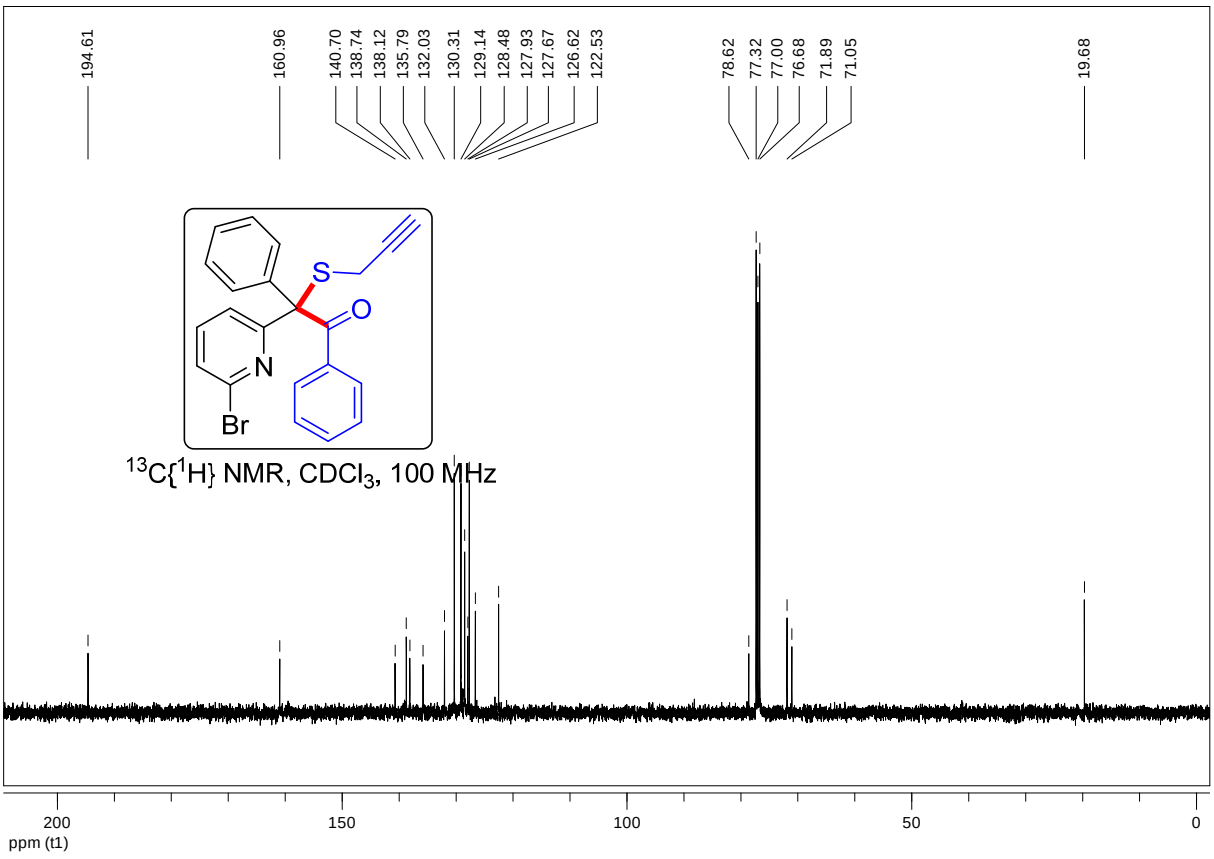
1-(6-bromopyridin-2-yl)-1-phenyl-1-(prop-2-yn-1-ylthio)propan-2-one (3ay)



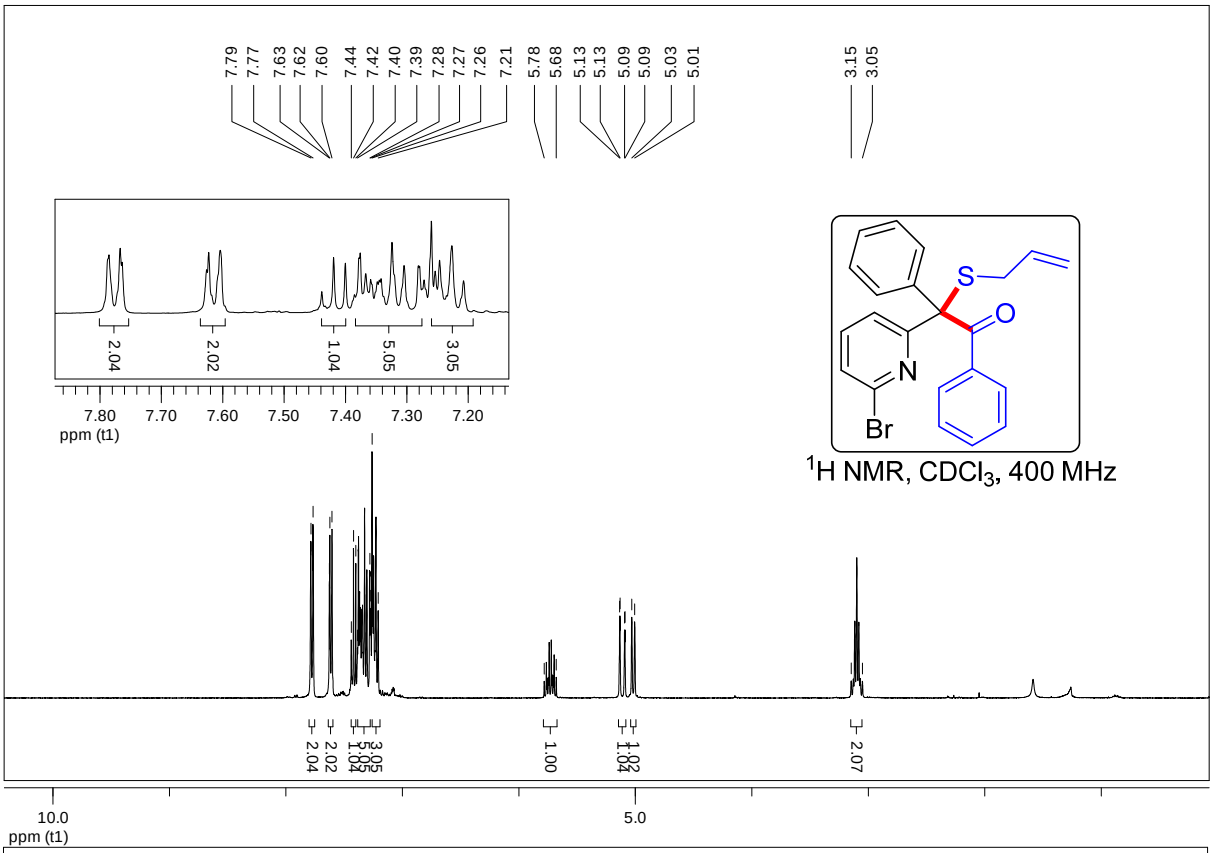


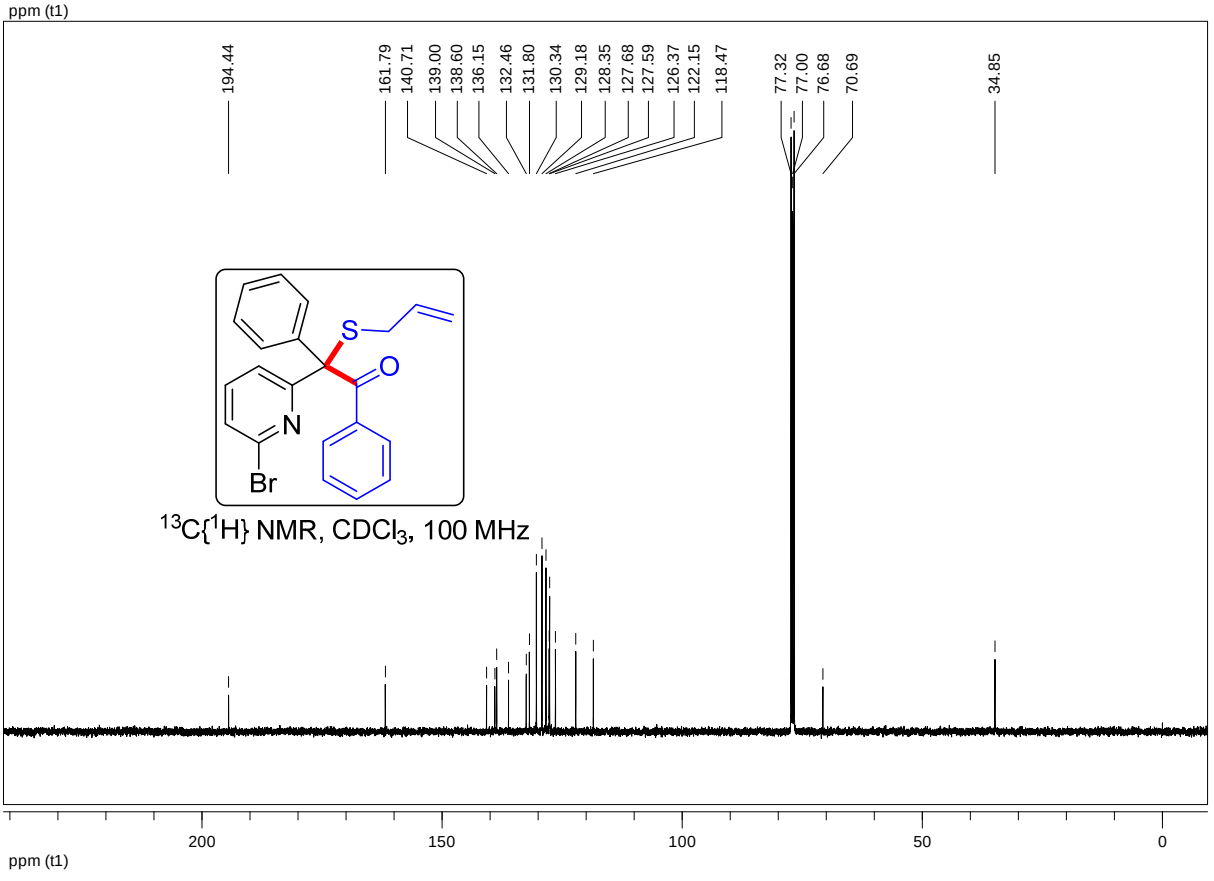
2-(6-bromopyridin-2-yl)-1,2-diphenyl-2-(prop-2-yn-1-ylthio)ethan-1-one (3az)



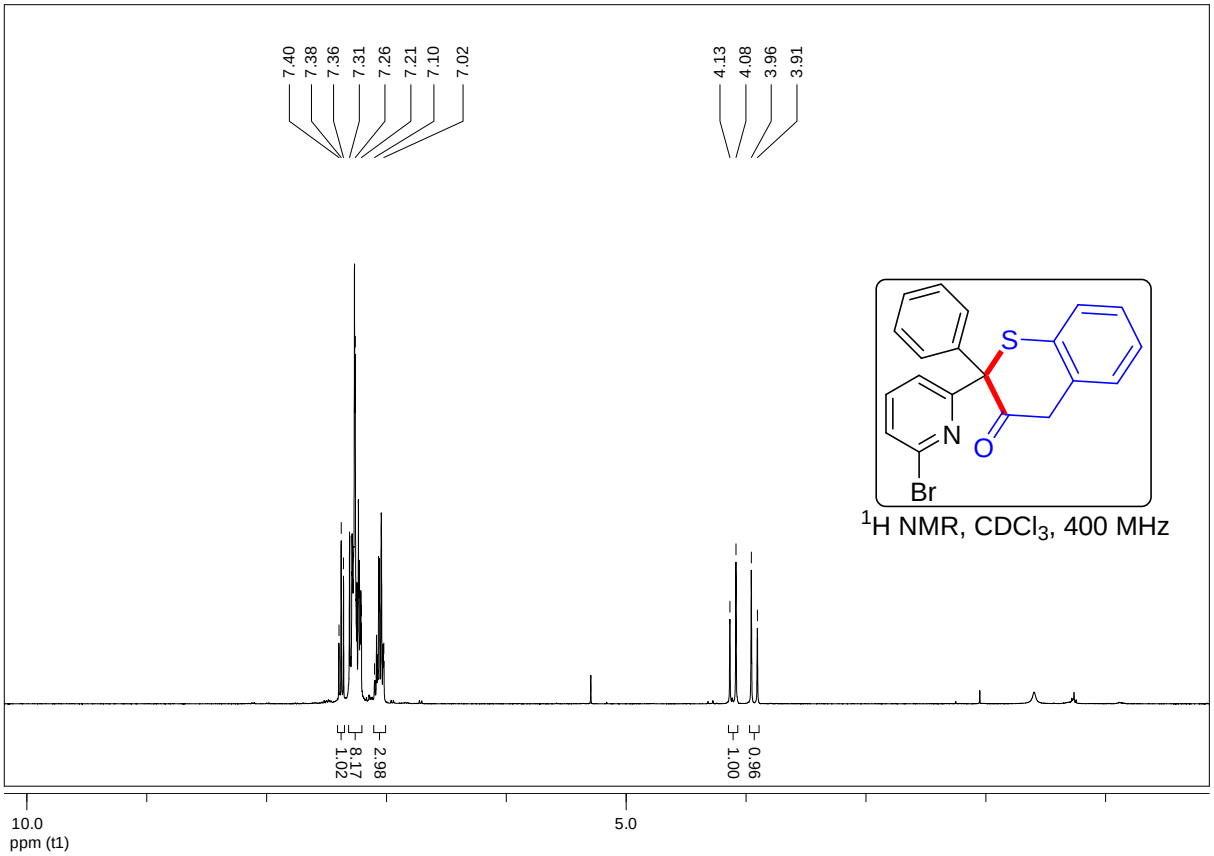


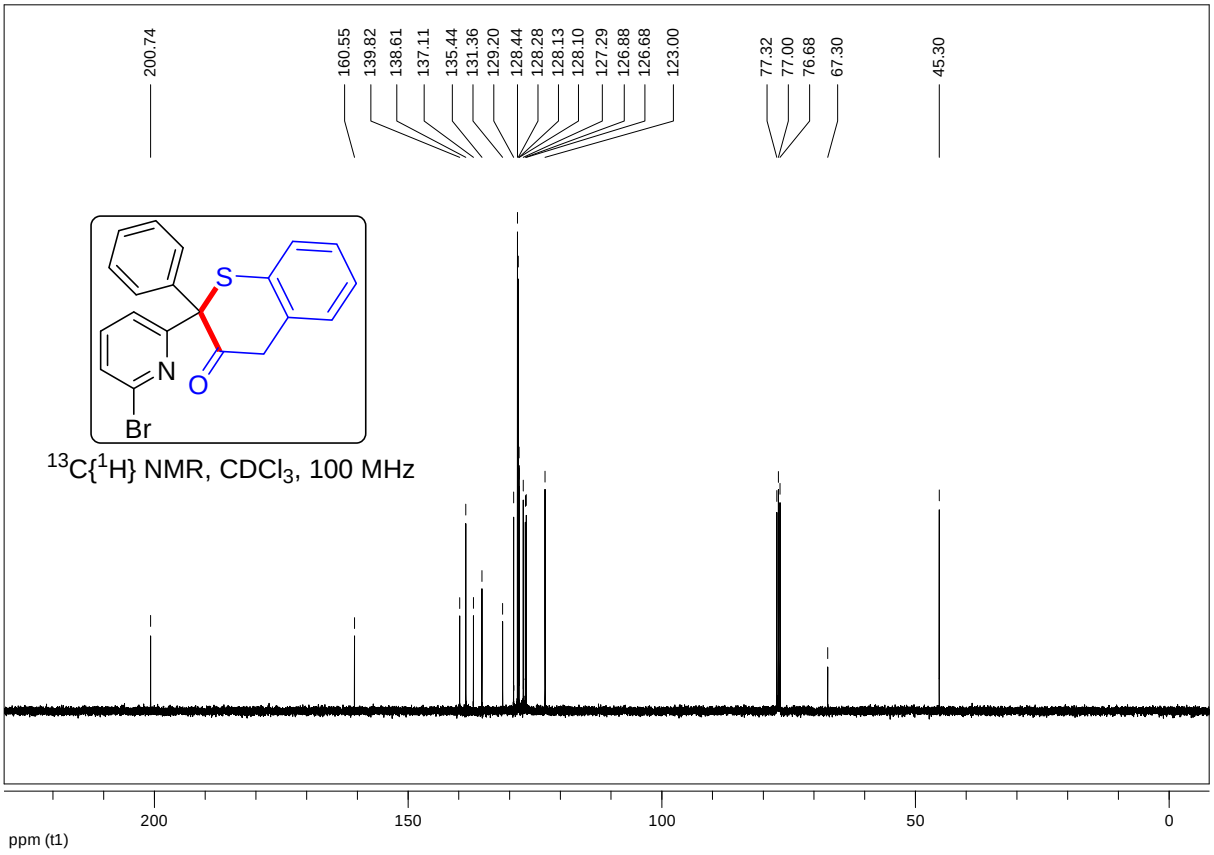
2-(allylthio)-2-(6-bromopyridin-2-yl)-1,2-diphenylethan-1-one (3za)



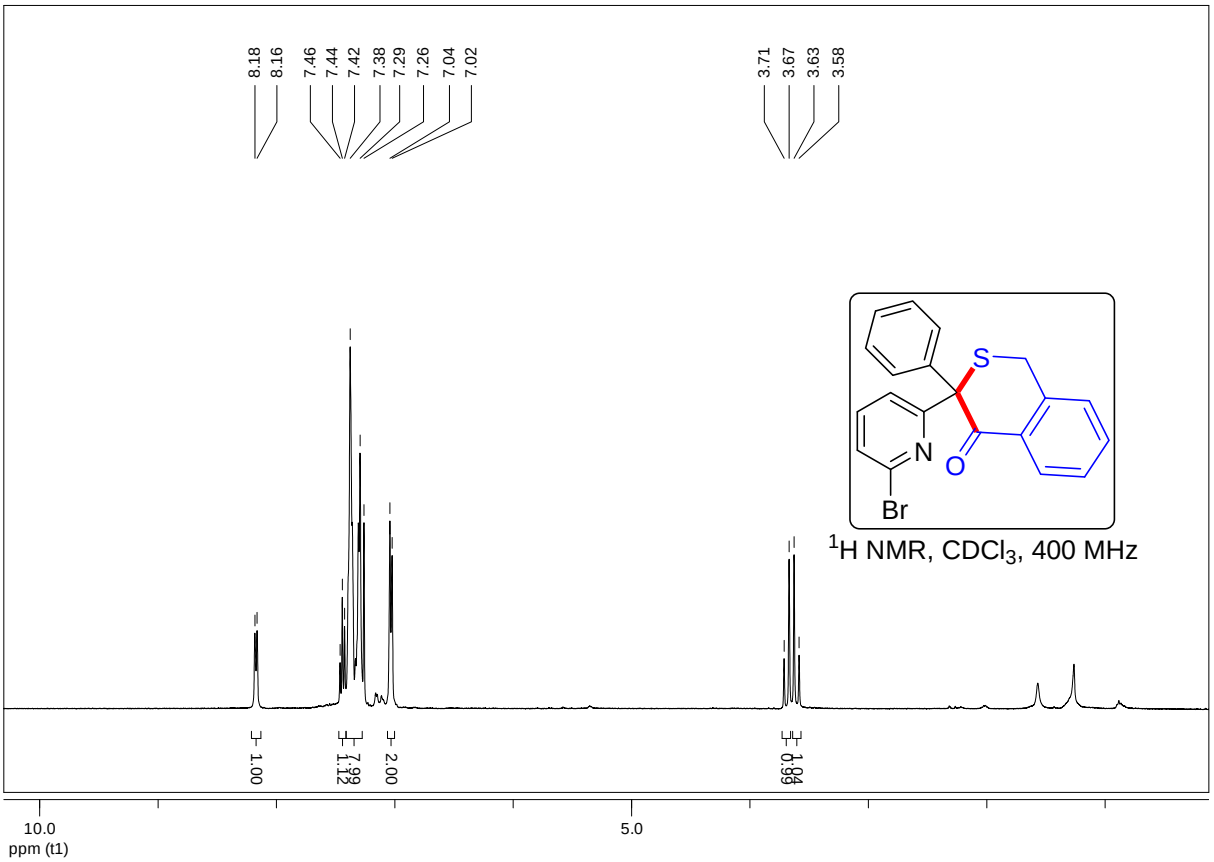


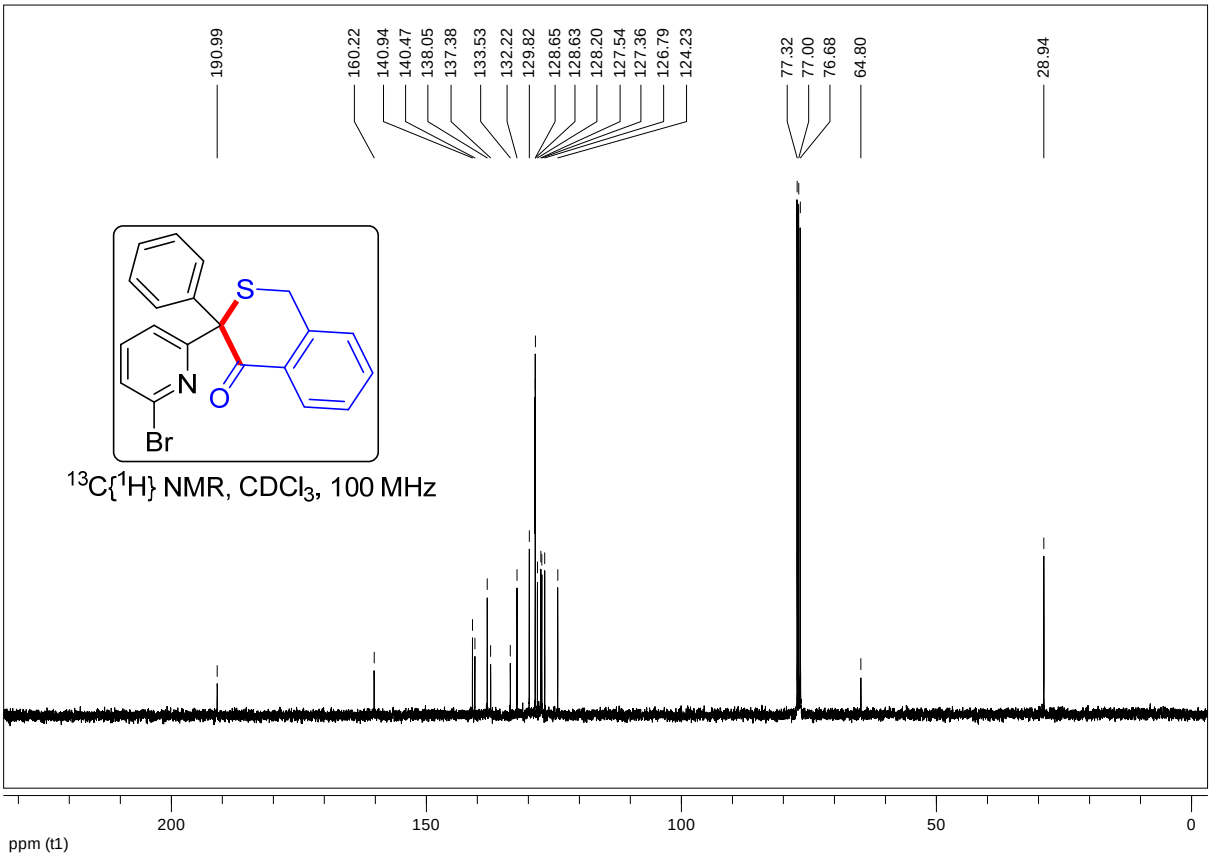
2-(allylthio)-2-(6-bromopyridin-2-yl)-1,2-diphenylethan-1-one (3zb)



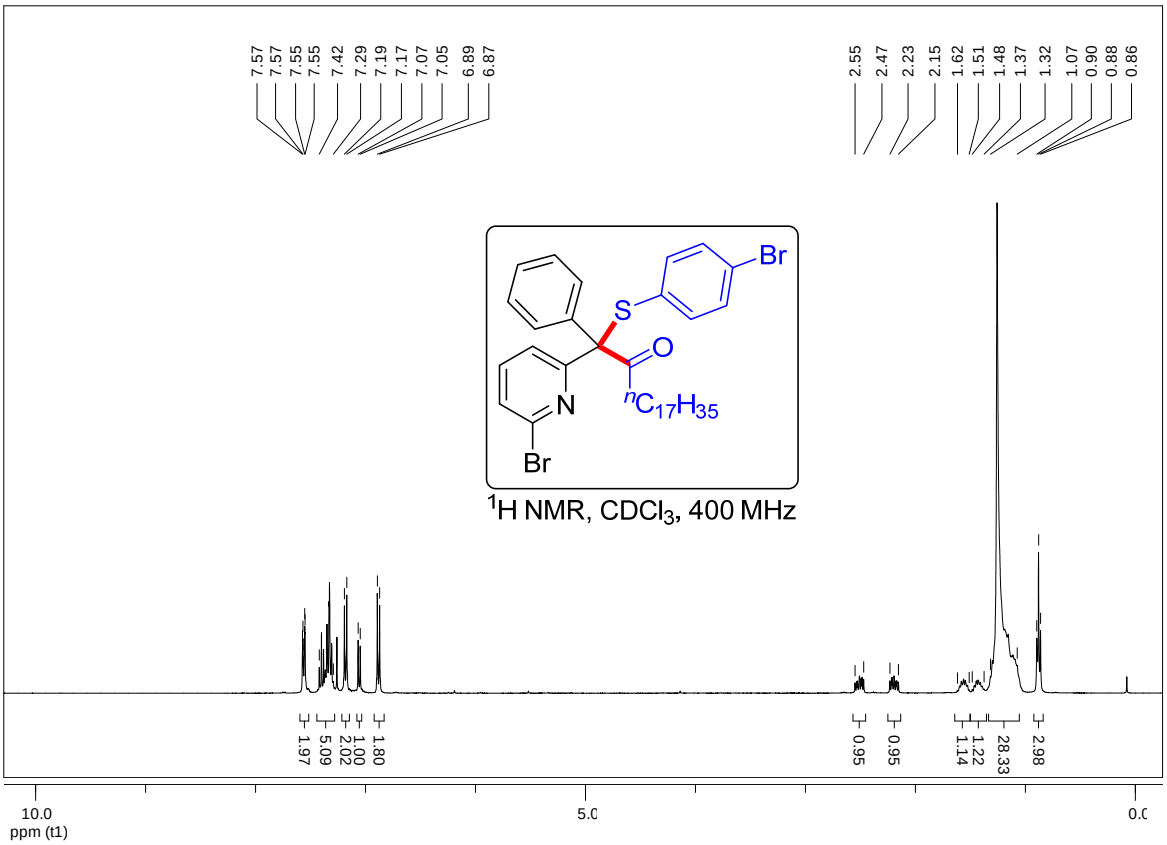


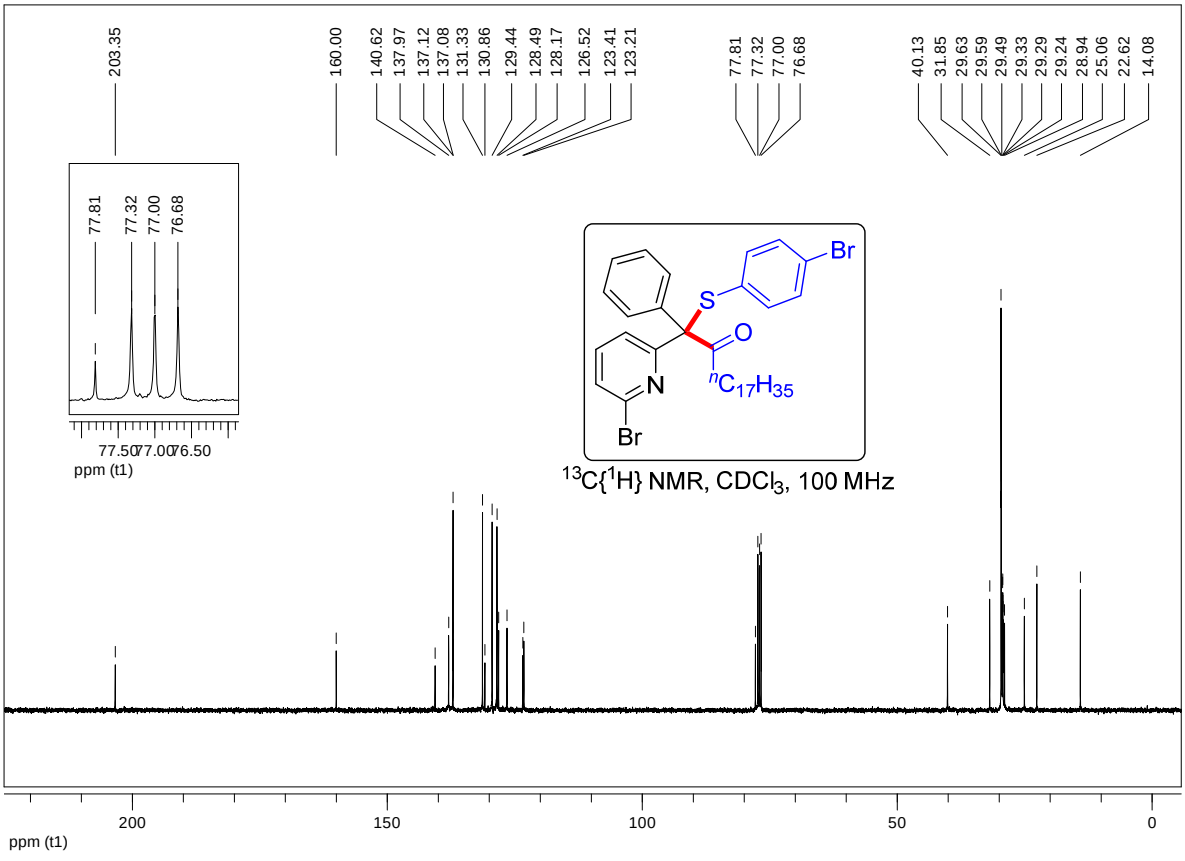
3-(6-bromopyridin-2-yl)-3-phenylisothiochroman-4-one (3zc)



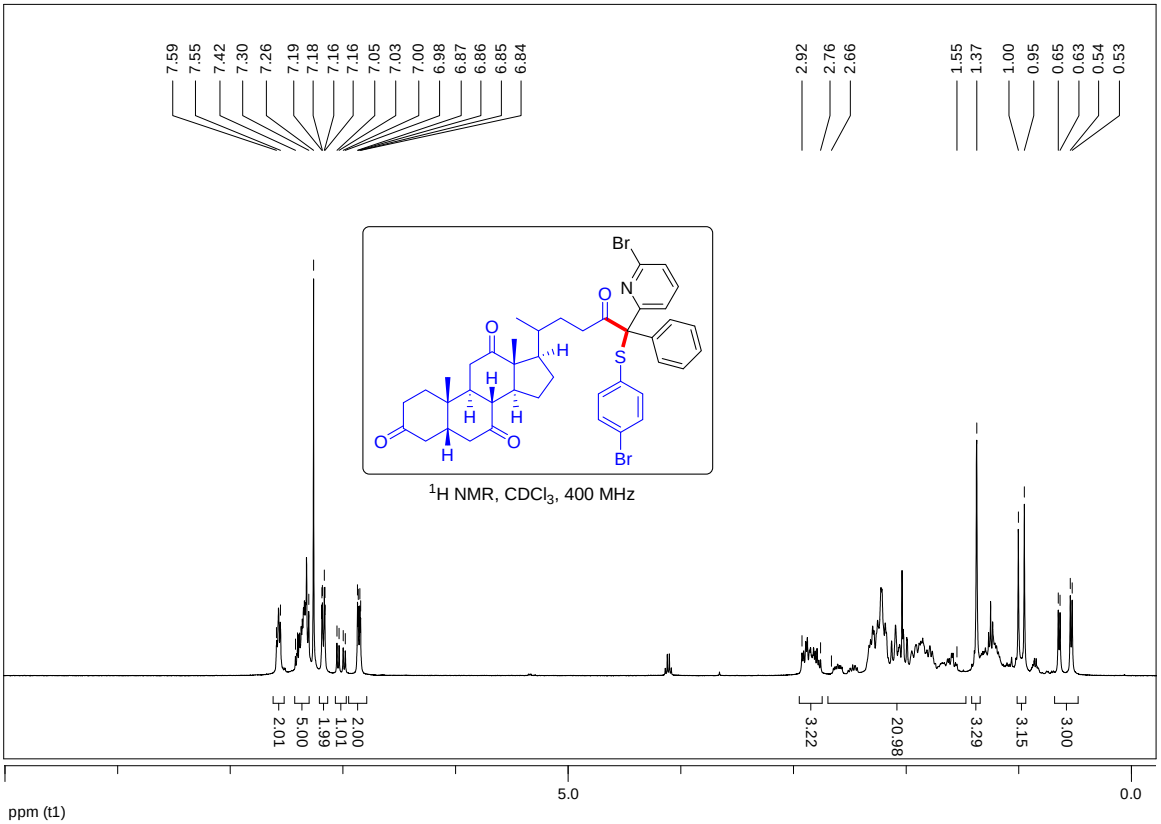


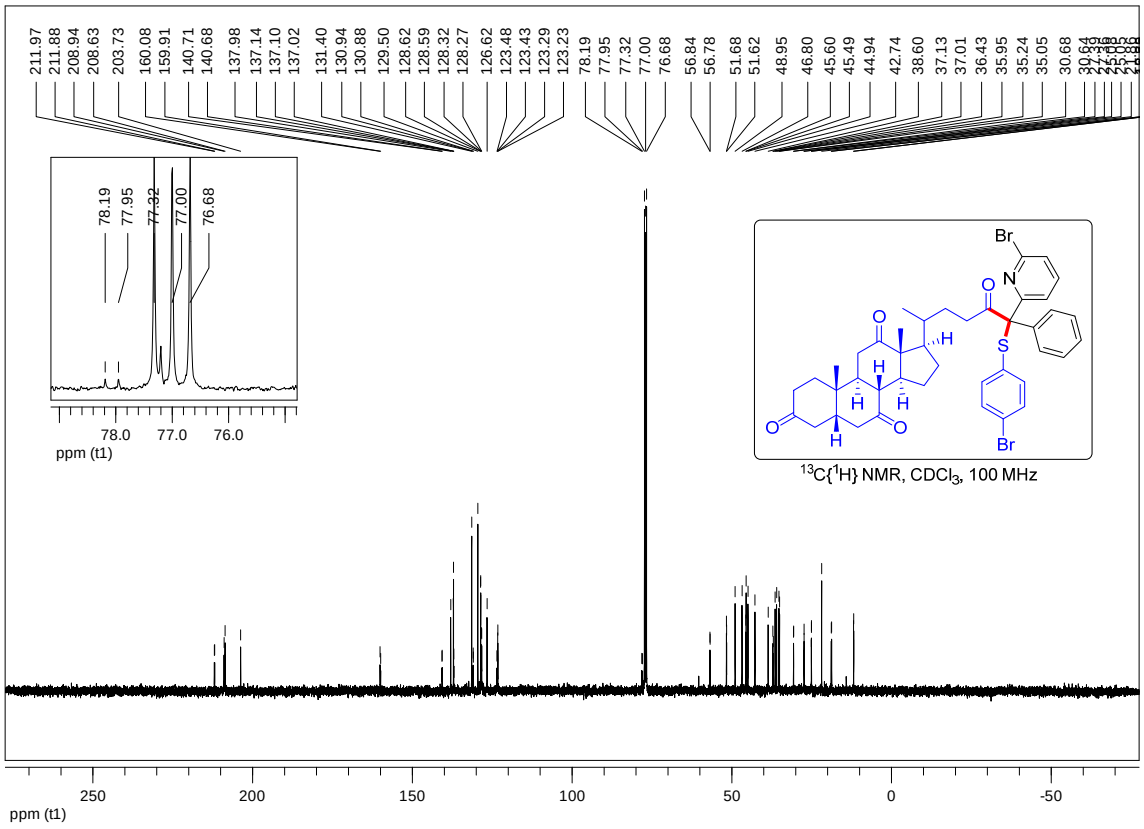
1-((4-bromophenyl)thio)-1-(6-bromopyridin-2-yl)-1-phenylnonadecan-2-one (3zd)



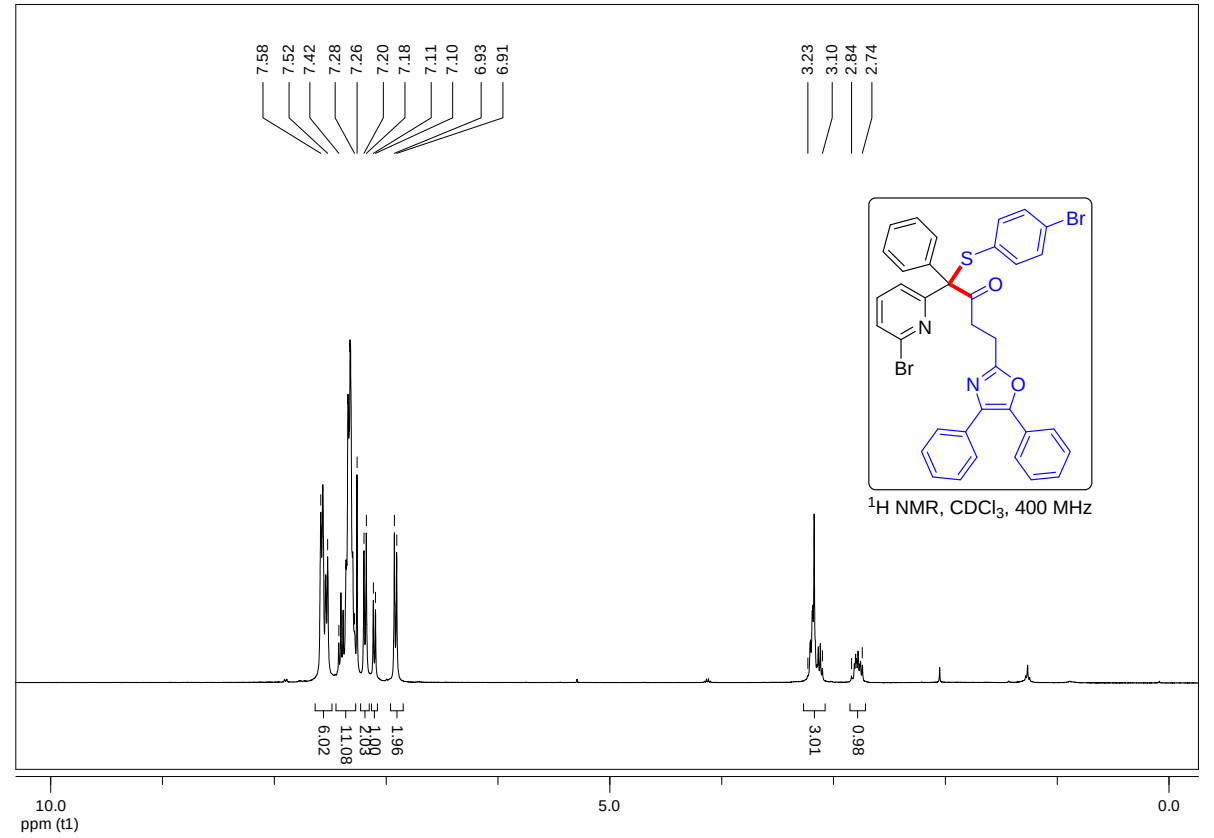


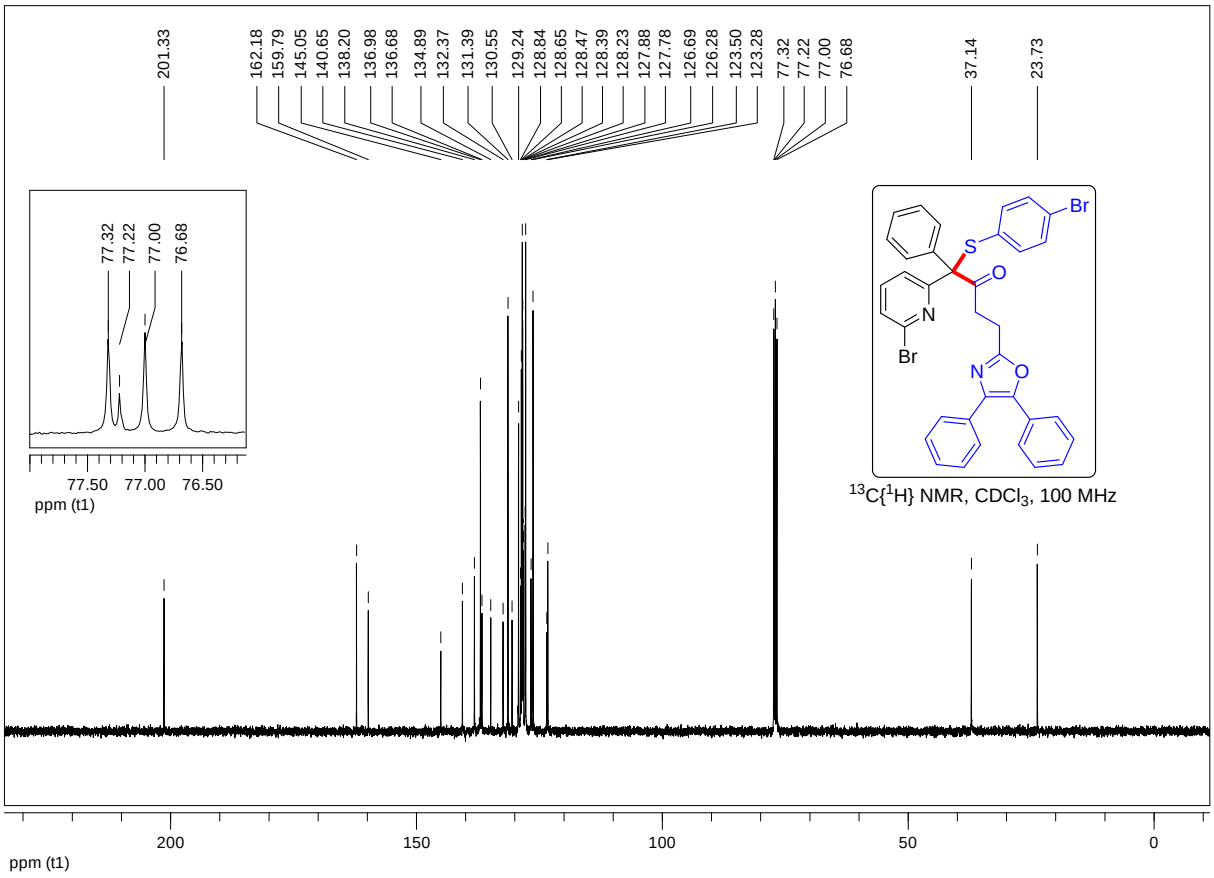
(5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-17-(6-((4-bromophenyl)thio)-6-(6-bromopyridin-2-yl)-5-oxo-6-phenylhexan-2-yl)-10,13-dimethyldodecahydro-3*H*-cyclopenta[*a*]phenanthrene-3,7,12(2*H*,4*H*)-trione (3ze)



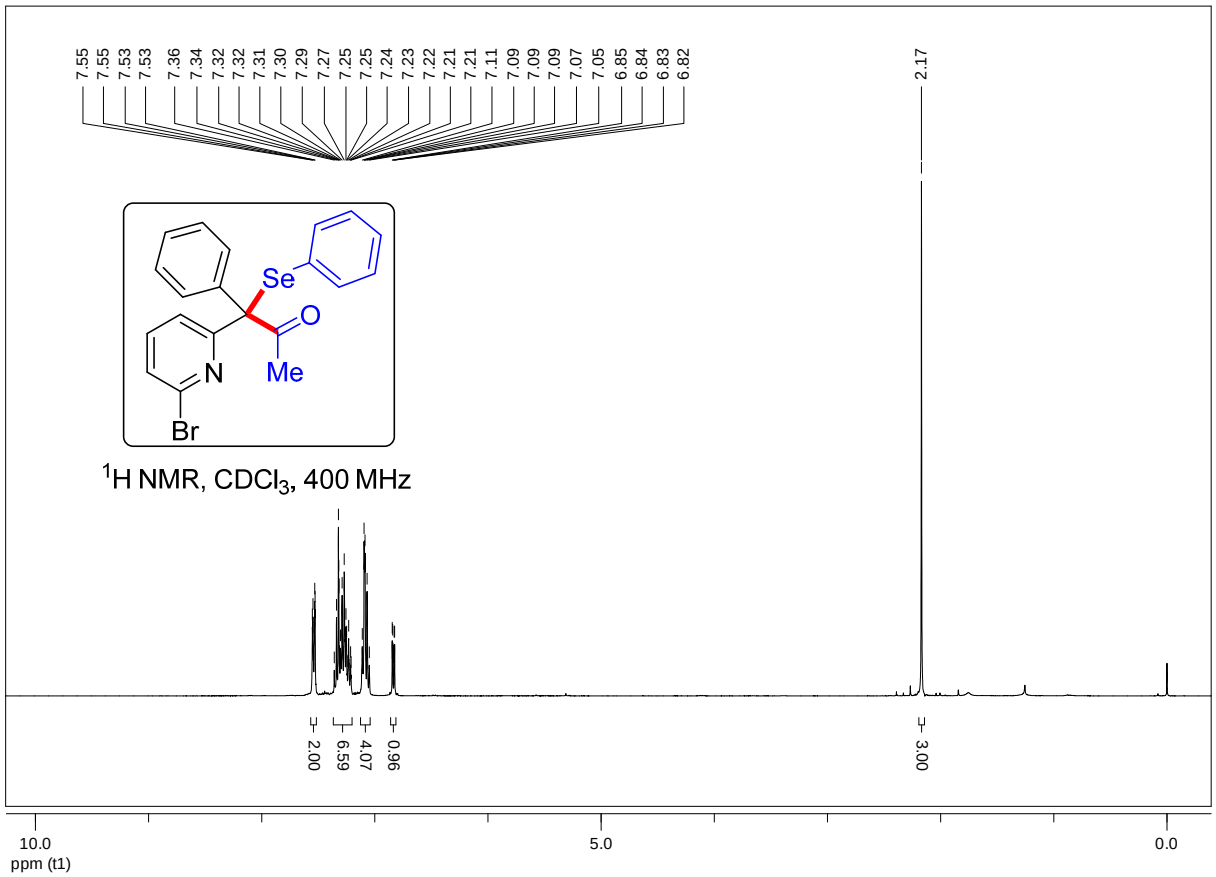


1-((4-bromophenyl)thio)-1-(6-bromopyridin-2-yl)-4-(4,5-diphenyloxazol-2-yl)-1-phenylbutan-2-one (3zf)

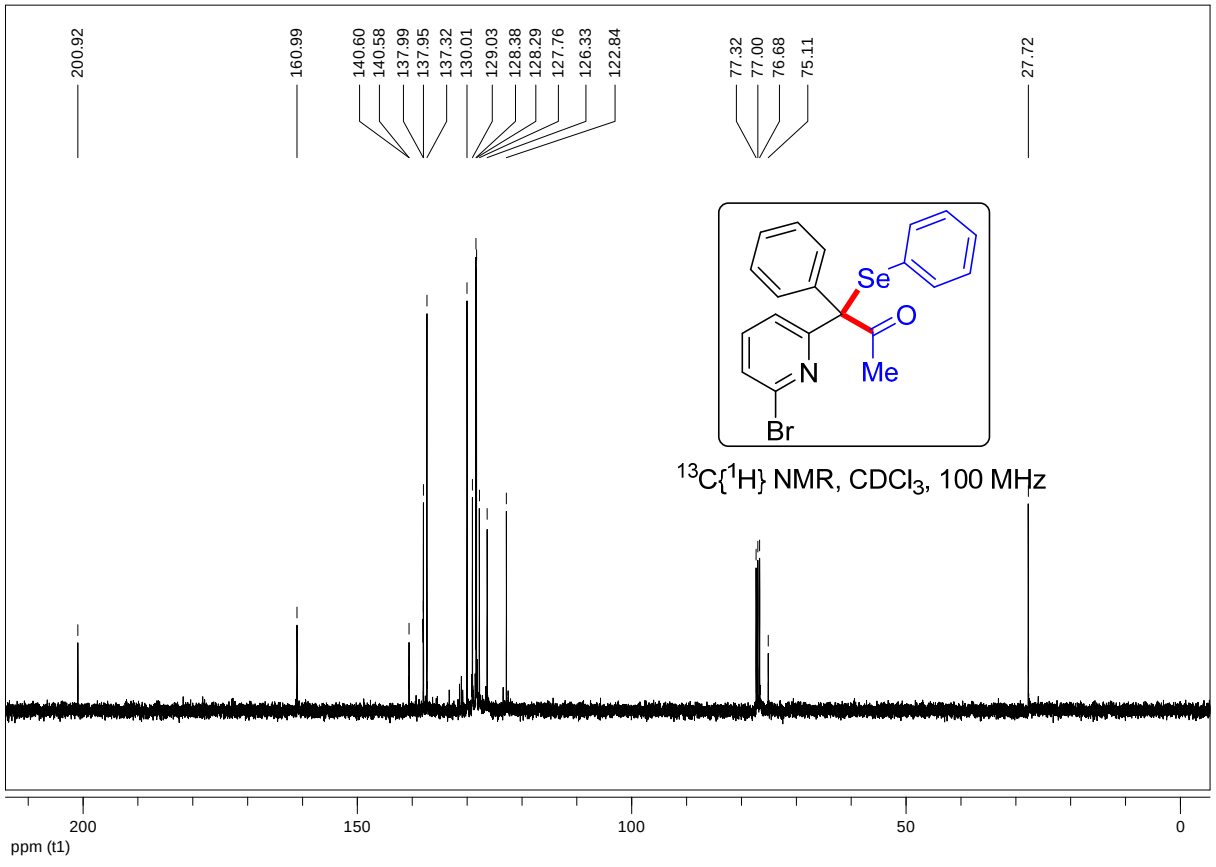




1-(6-bromopyridin-2-yl)-1-phenyl-1-(phenylselanyl)propan-2-one (3zg)

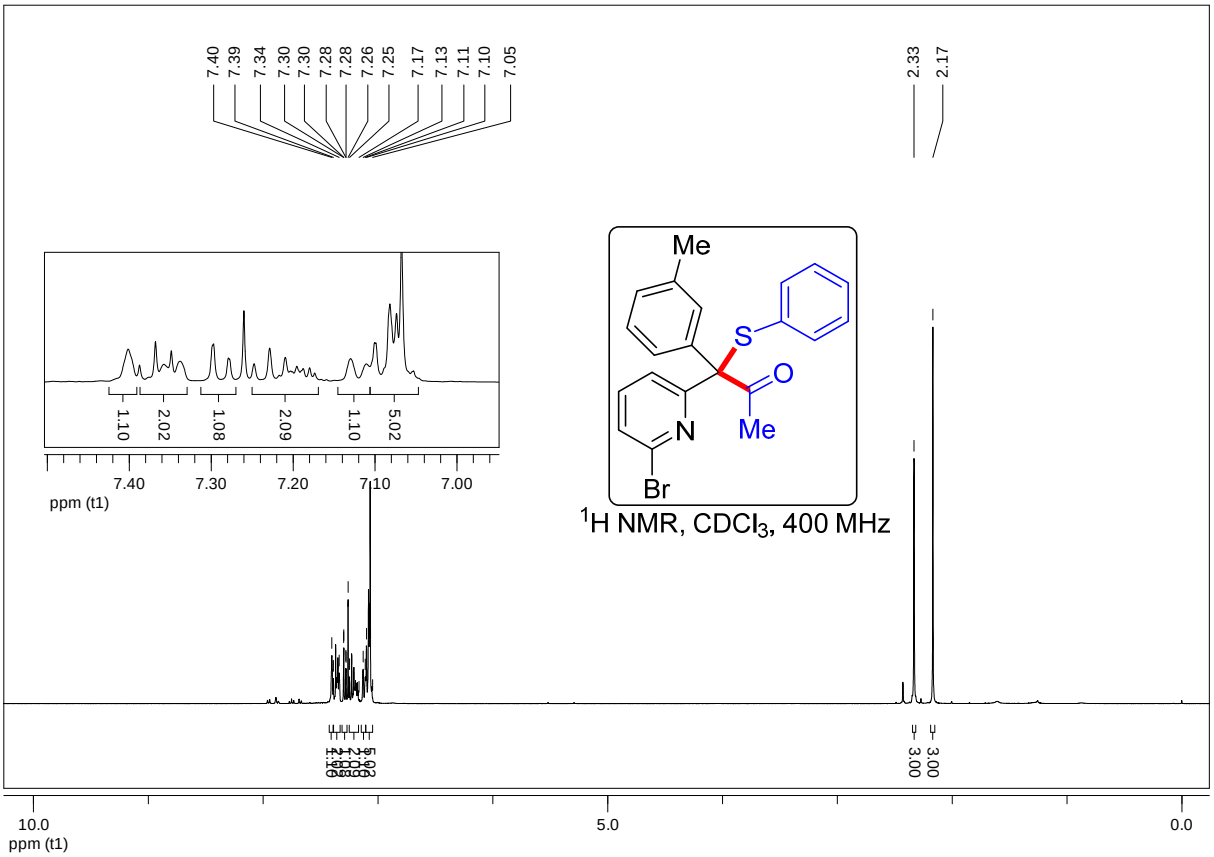


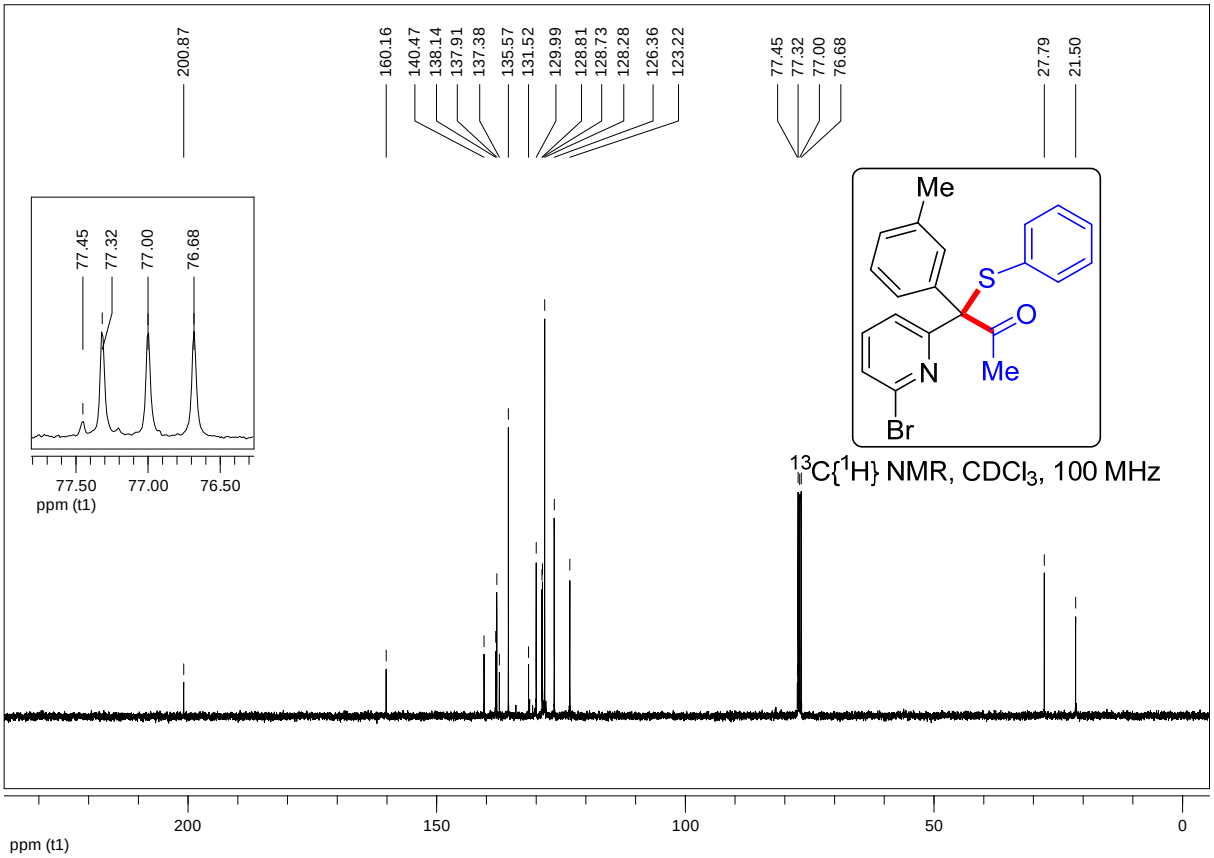
^{1}H NMR, $CDCl_3$, 400 MHz



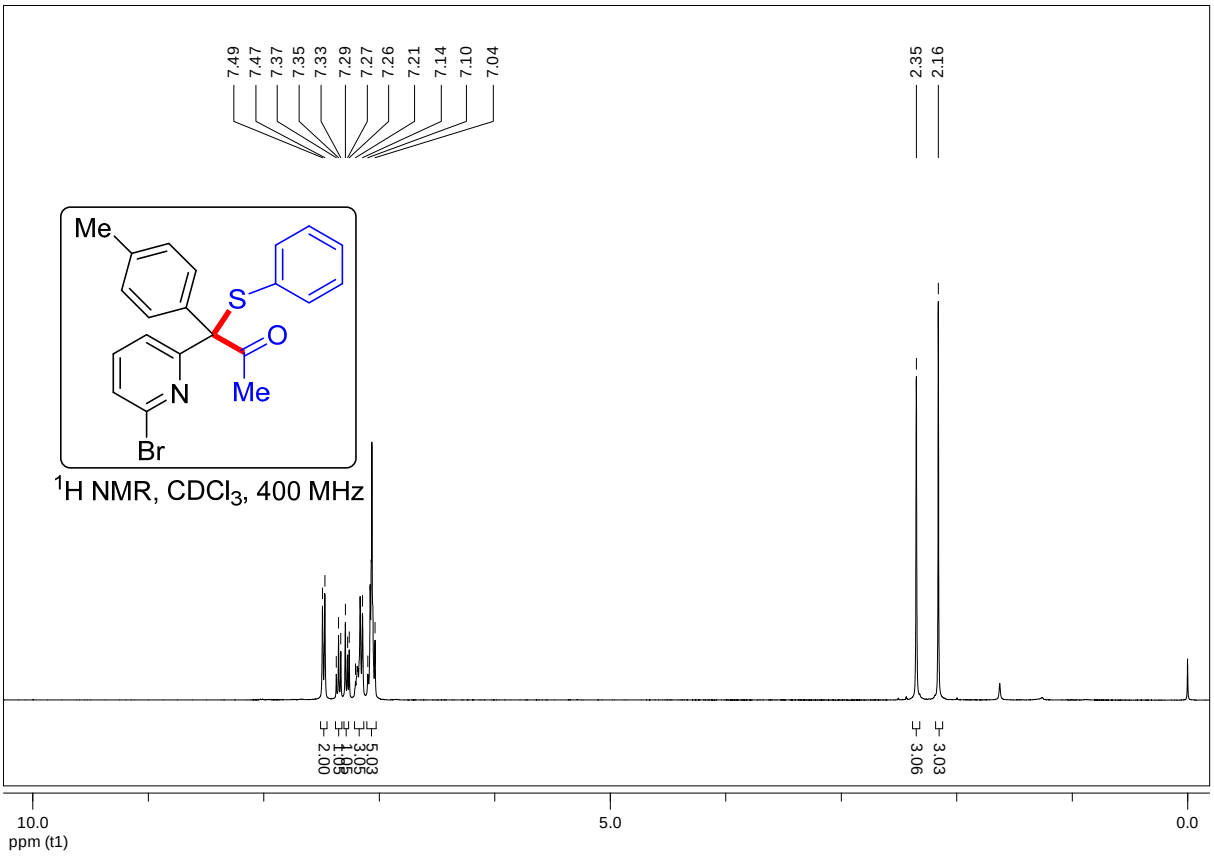
$^{13}C\{^{1}H\}$ NMR, $CDCl_3$, 100 MHz

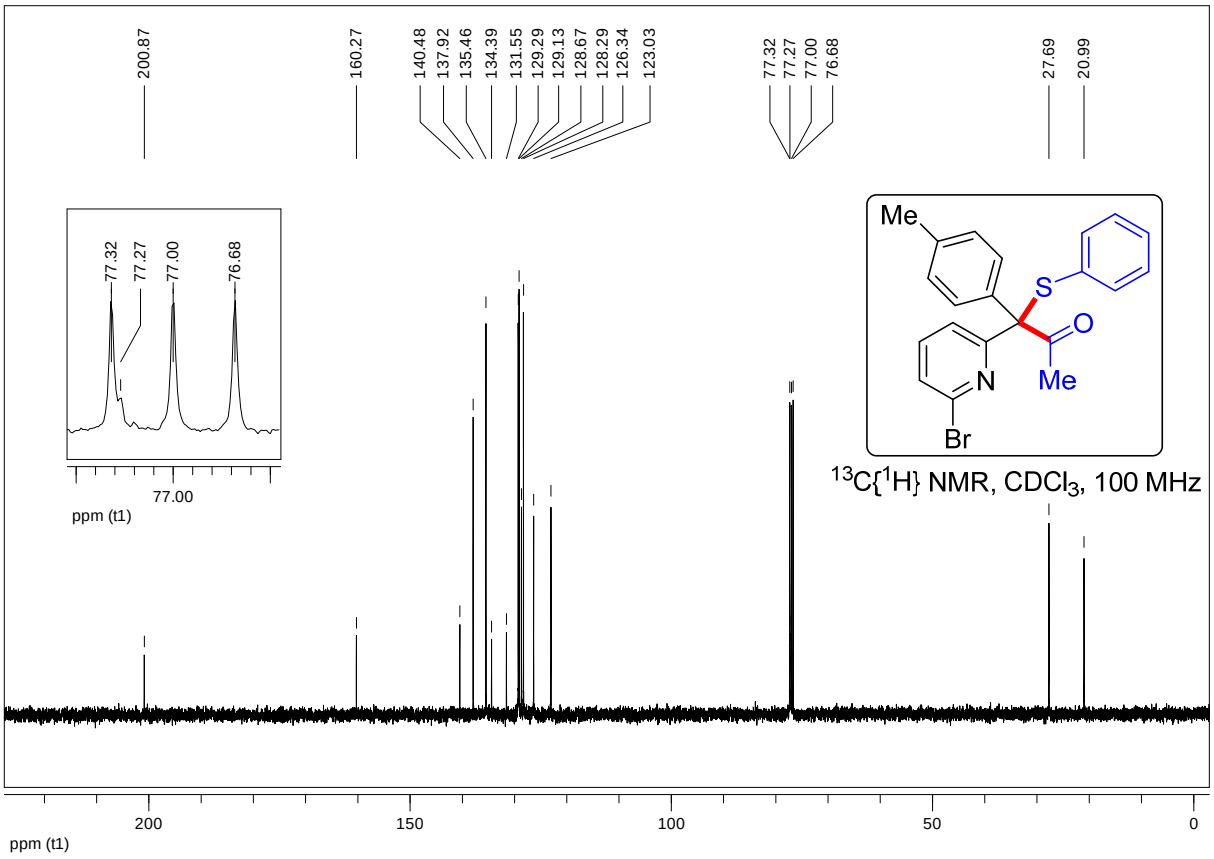
1-(6-bromopyridin-2-yl)-1-phenyl-1-(m-tolylthio)propan-2-one (3ba)



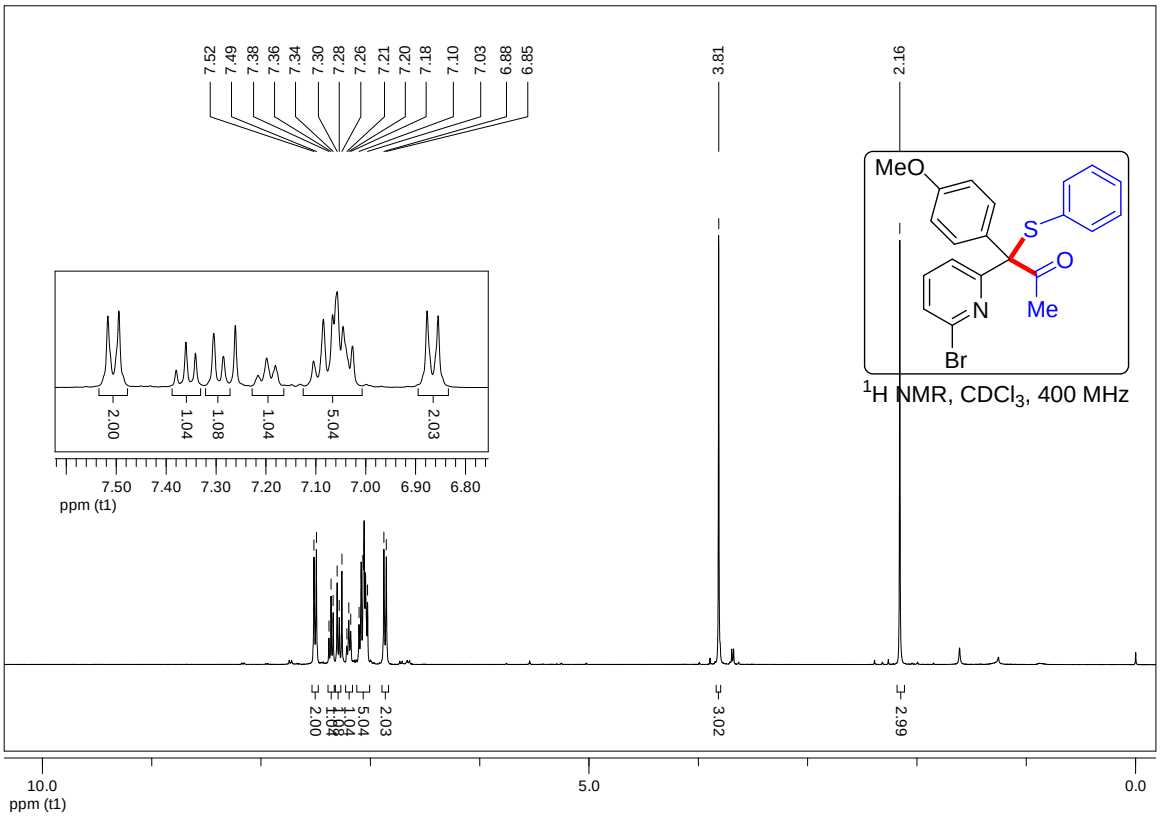


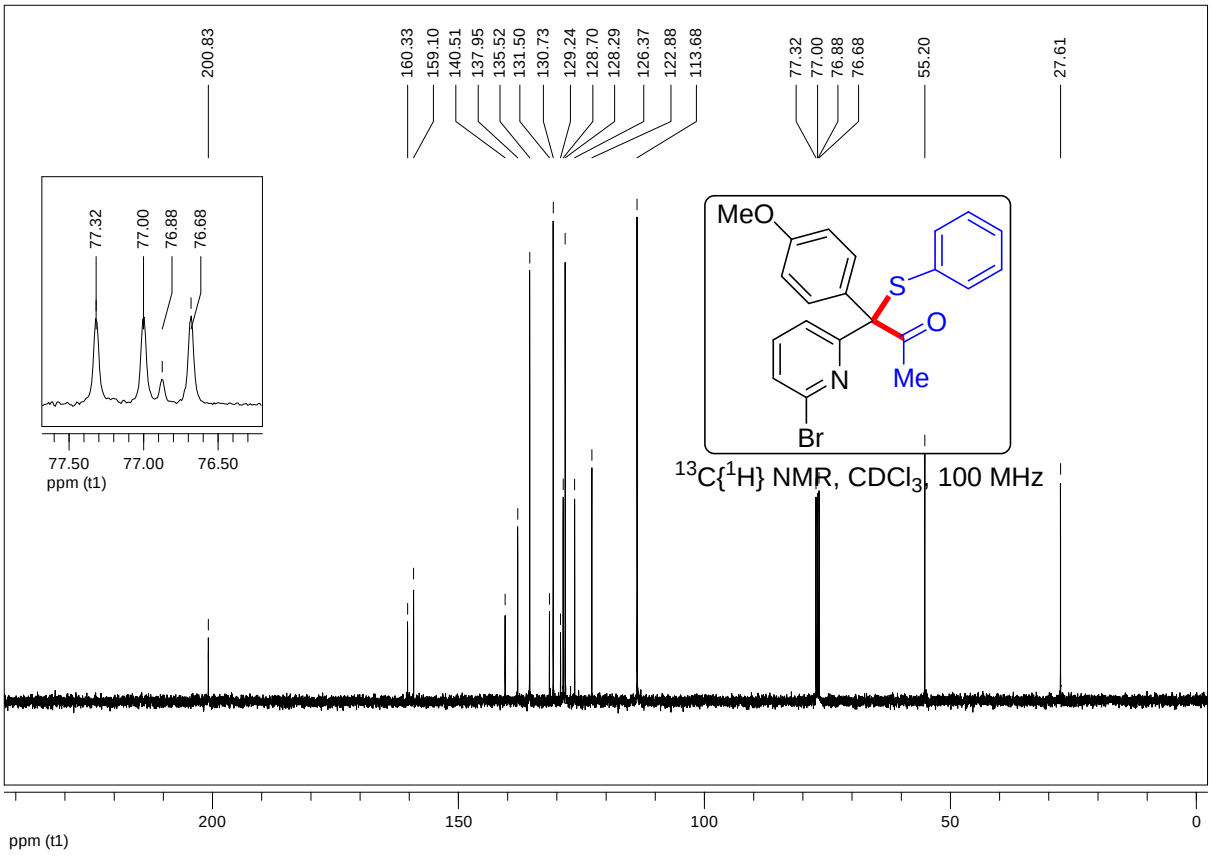
1-(6-bromopyridin-2-yl)-1-phenyl-1-(p-tolylthio)propan-2-one (3ca)



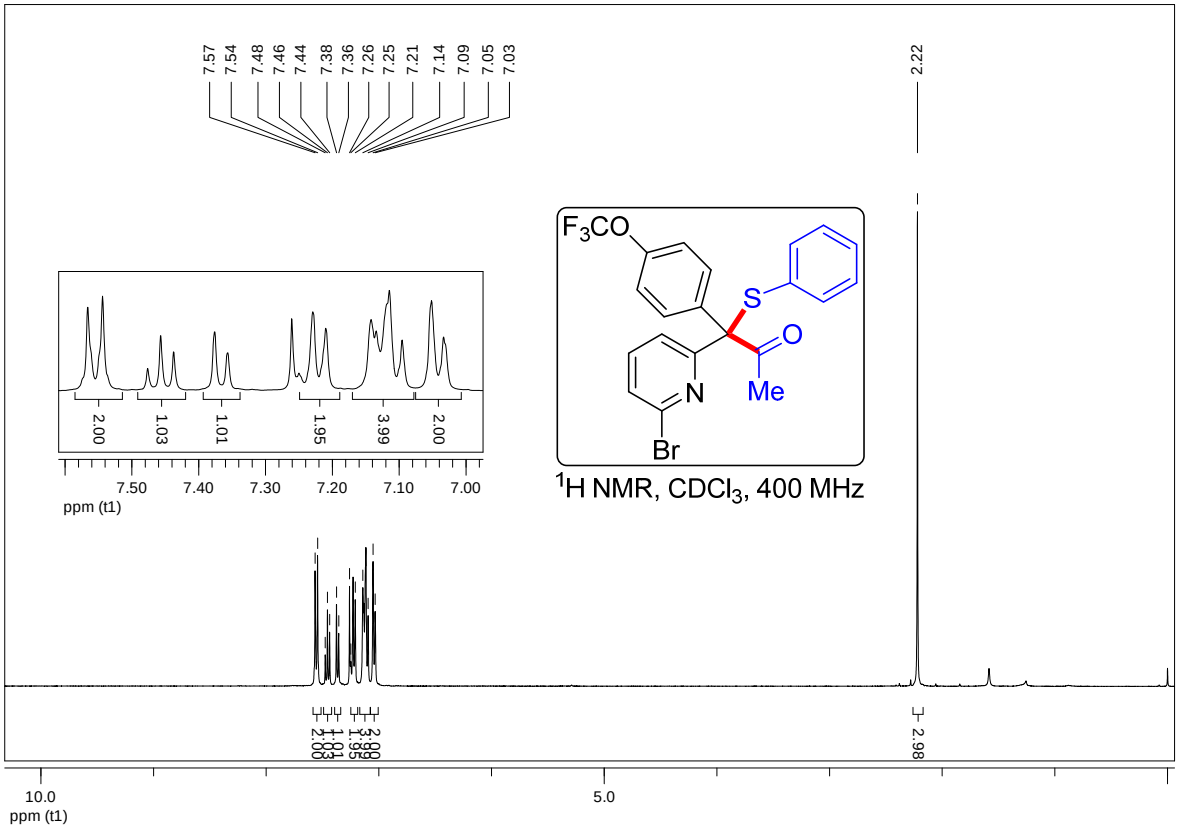


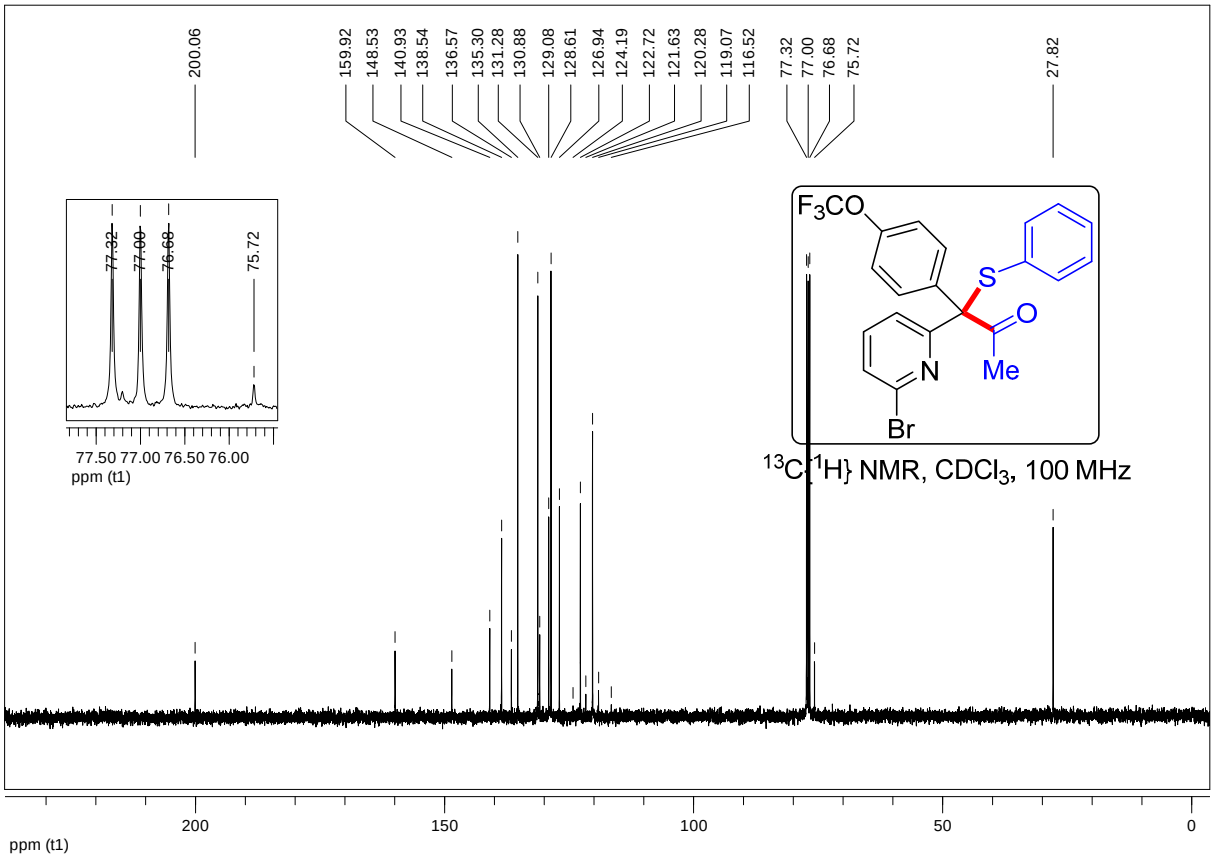
1-(6-bromopyridin-2-yl)-1-((4-methoxyphenyl)thio)-1-phenylpropan-2-one (3da)

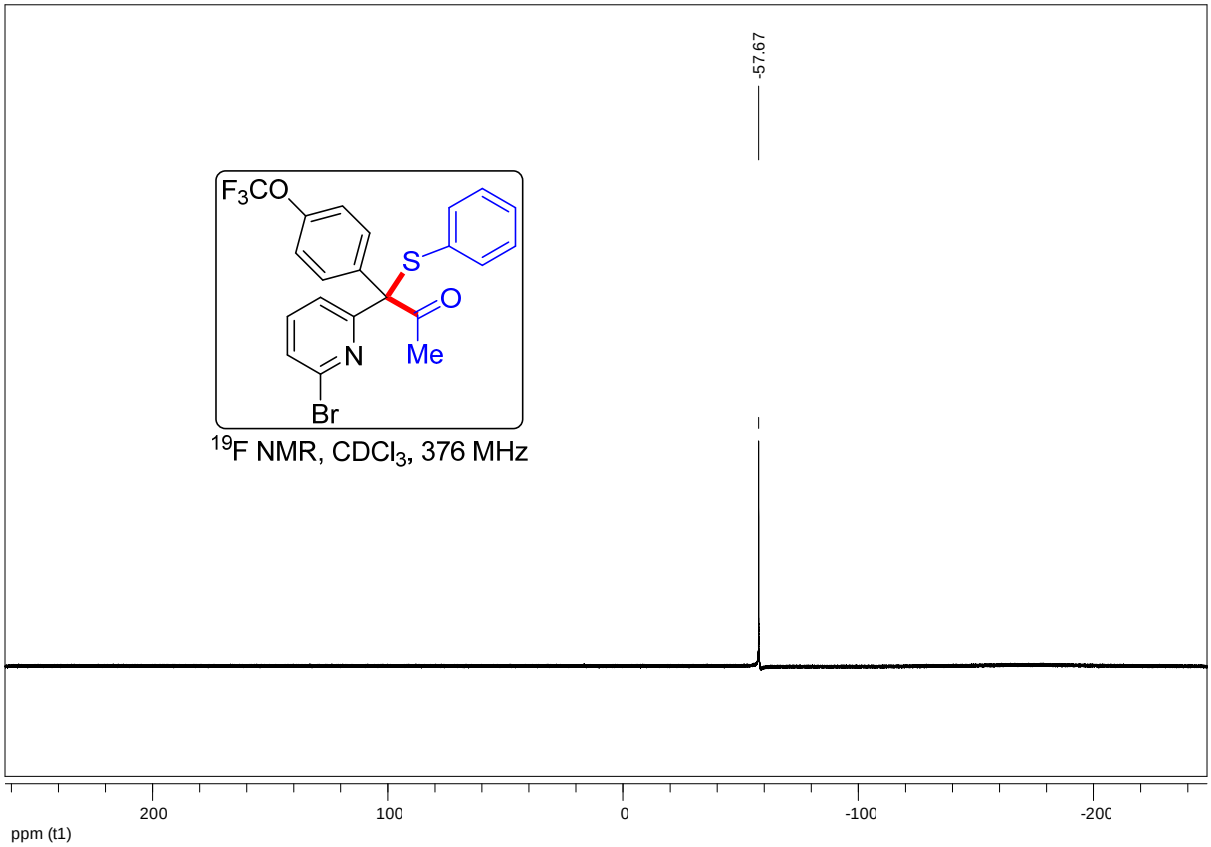




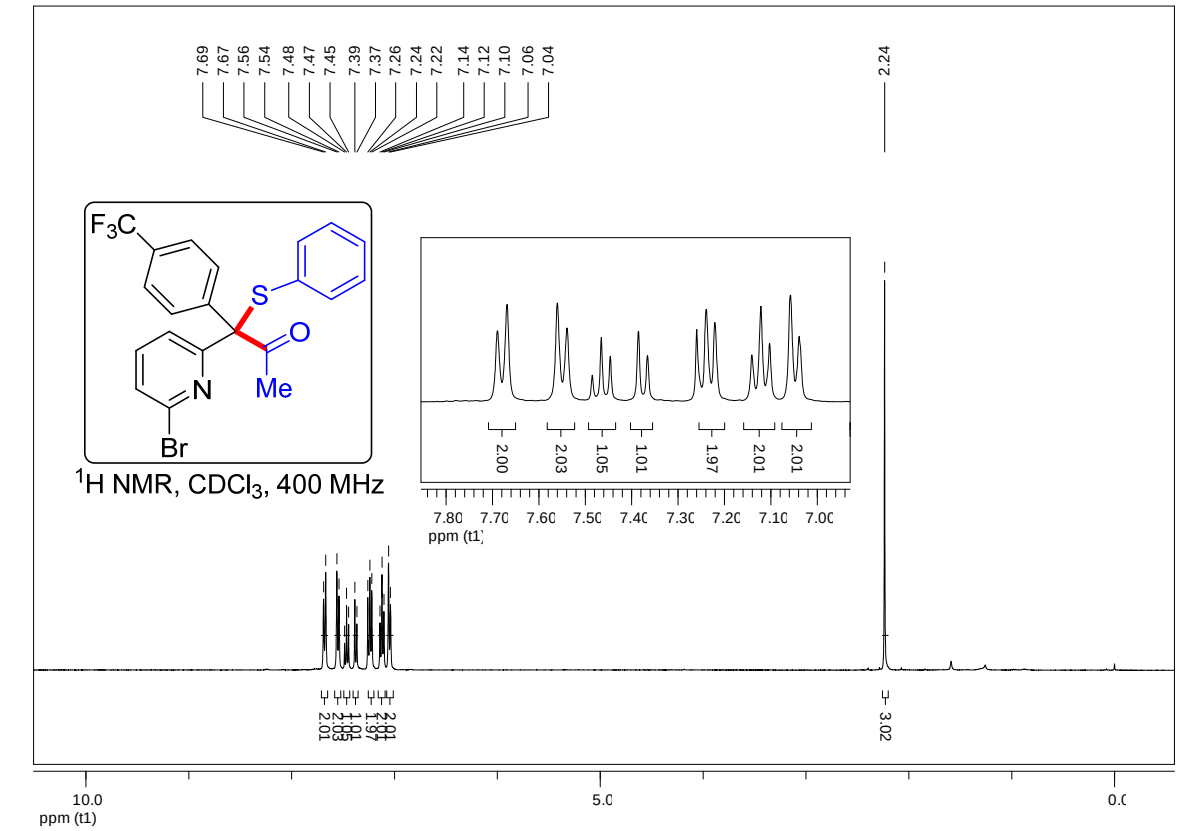
1-(6-bromopyridin-2-yl)-1-phenyl-1-((4-(trifluoromethoxy)phenyl)thio)propan-2-one (3ea)

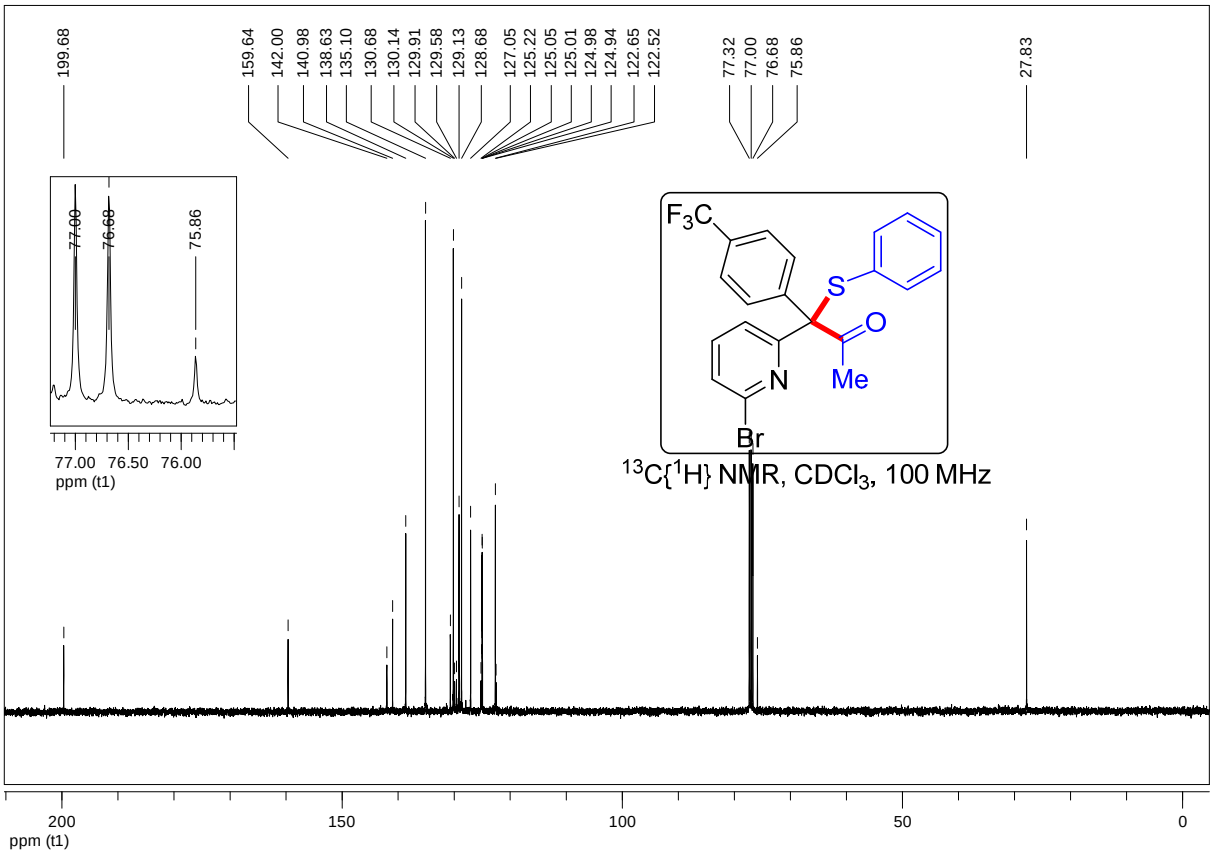


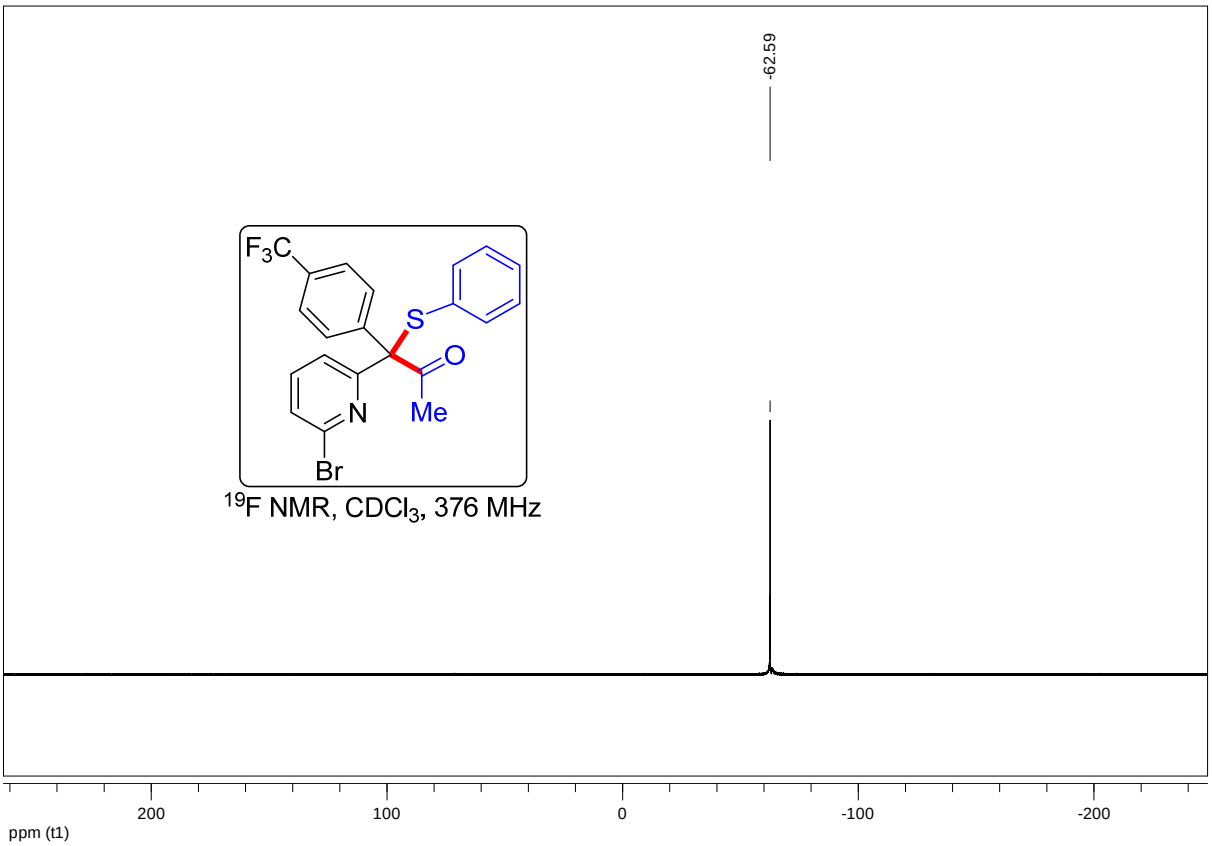



-57.67
F3CO
S
O
N
Me
Br
19F NMR, CDCl3, 376 MHz
200
100
0
-100
-200
ppm (t1)

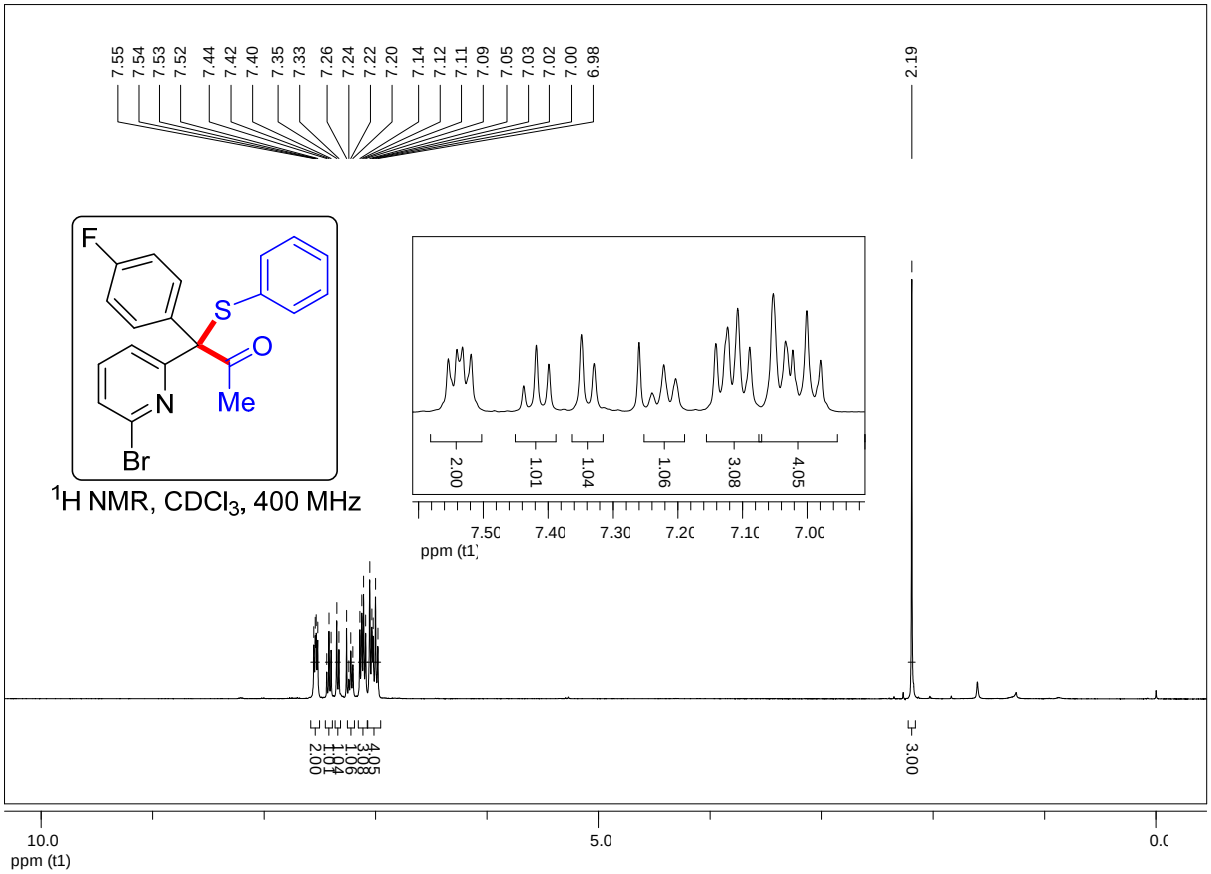
1-(6-bromopyridin-2-yl)-1-phenyl-1-((4-(trifluoromethyl)phenyl)thio)propan-2-one (3fa)

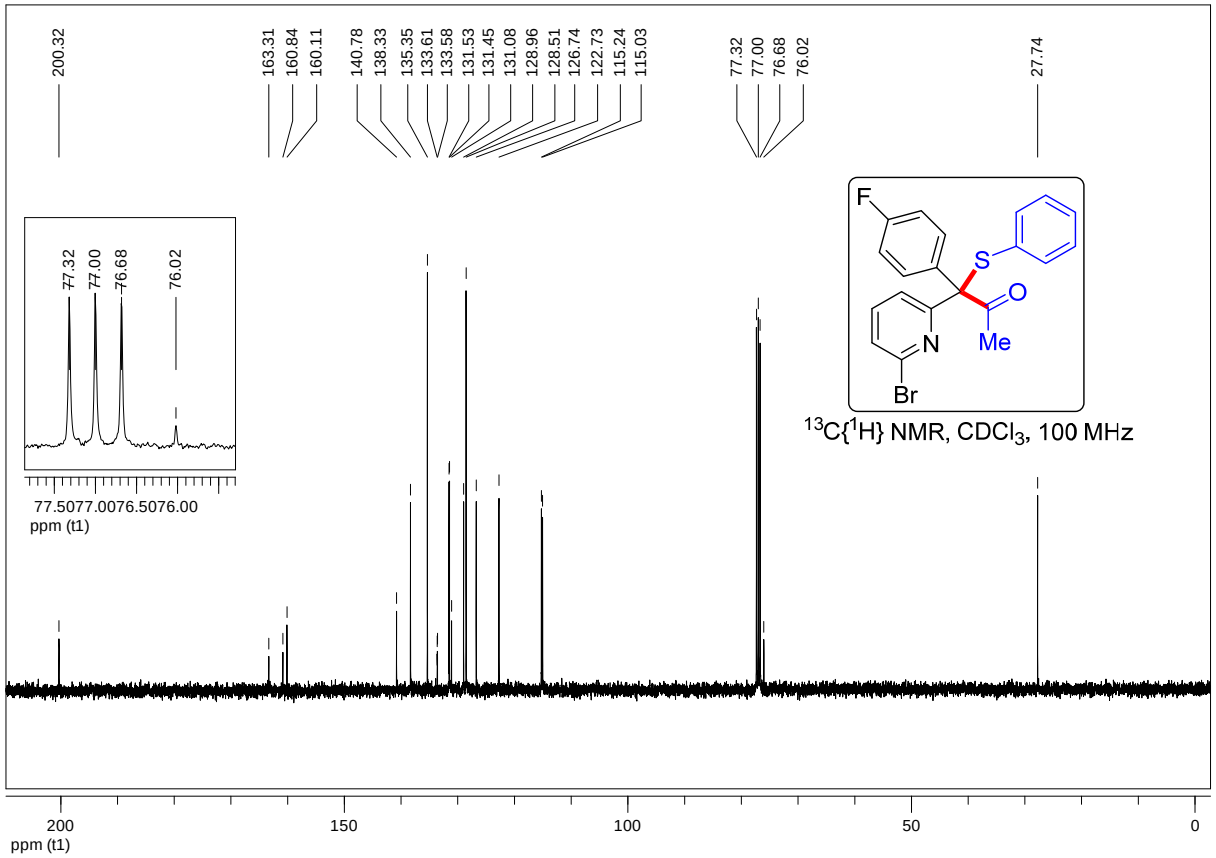


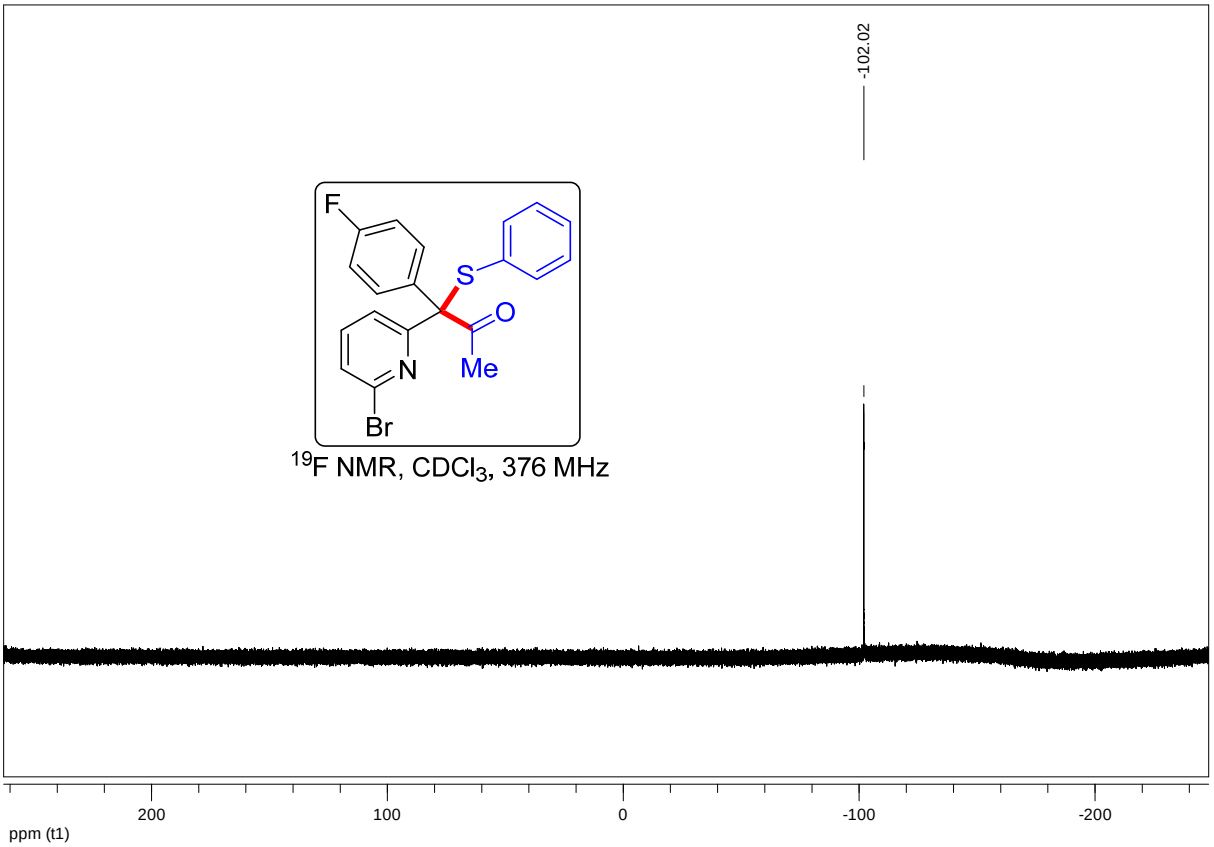



-62.59
F3C
S
O
N
Me
Br
19F NMR, CDCl3, 376 MHz
200
100
0
-100
-200
ppm (t1)

1-(6-bromopyridin-2-yl)-1-((4-fluorophenyl)thio)-1-phenylpropan-2-one (3ga)

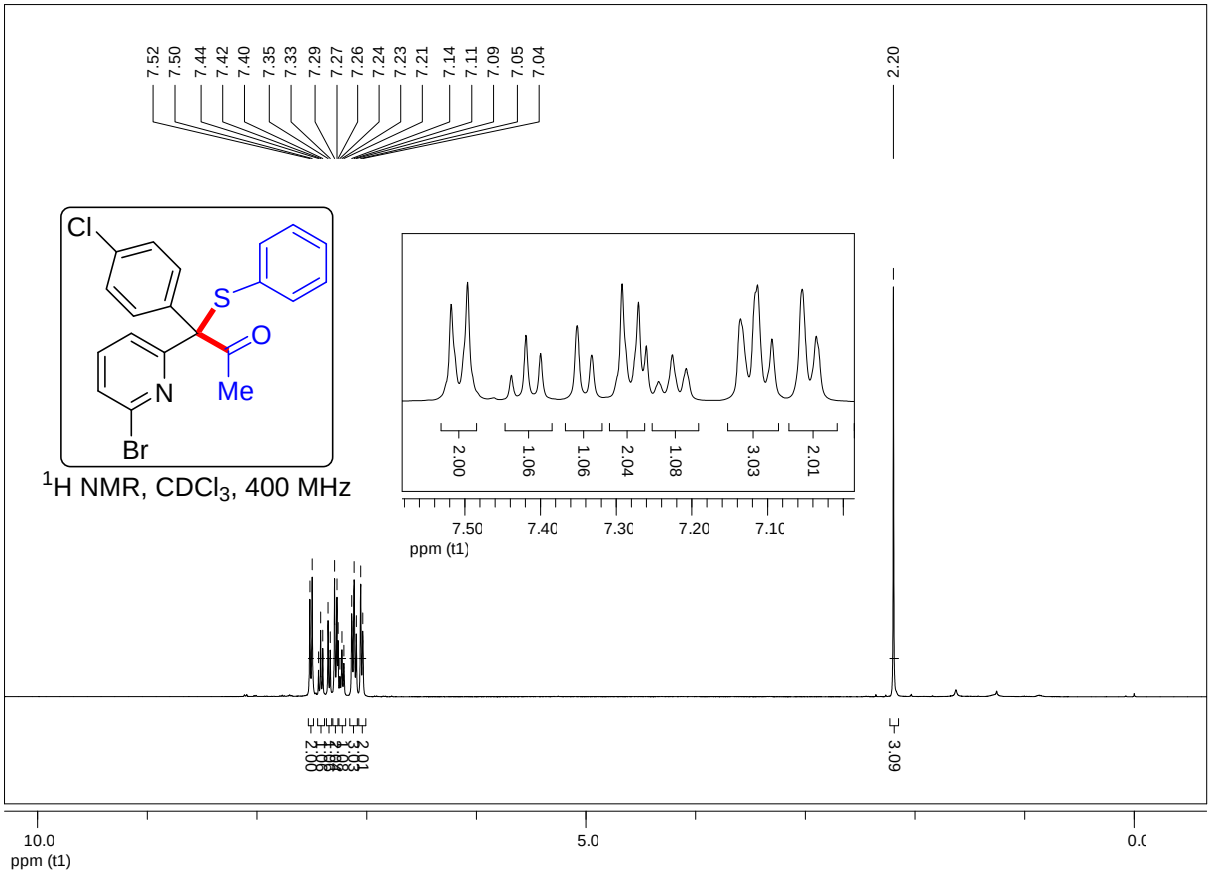




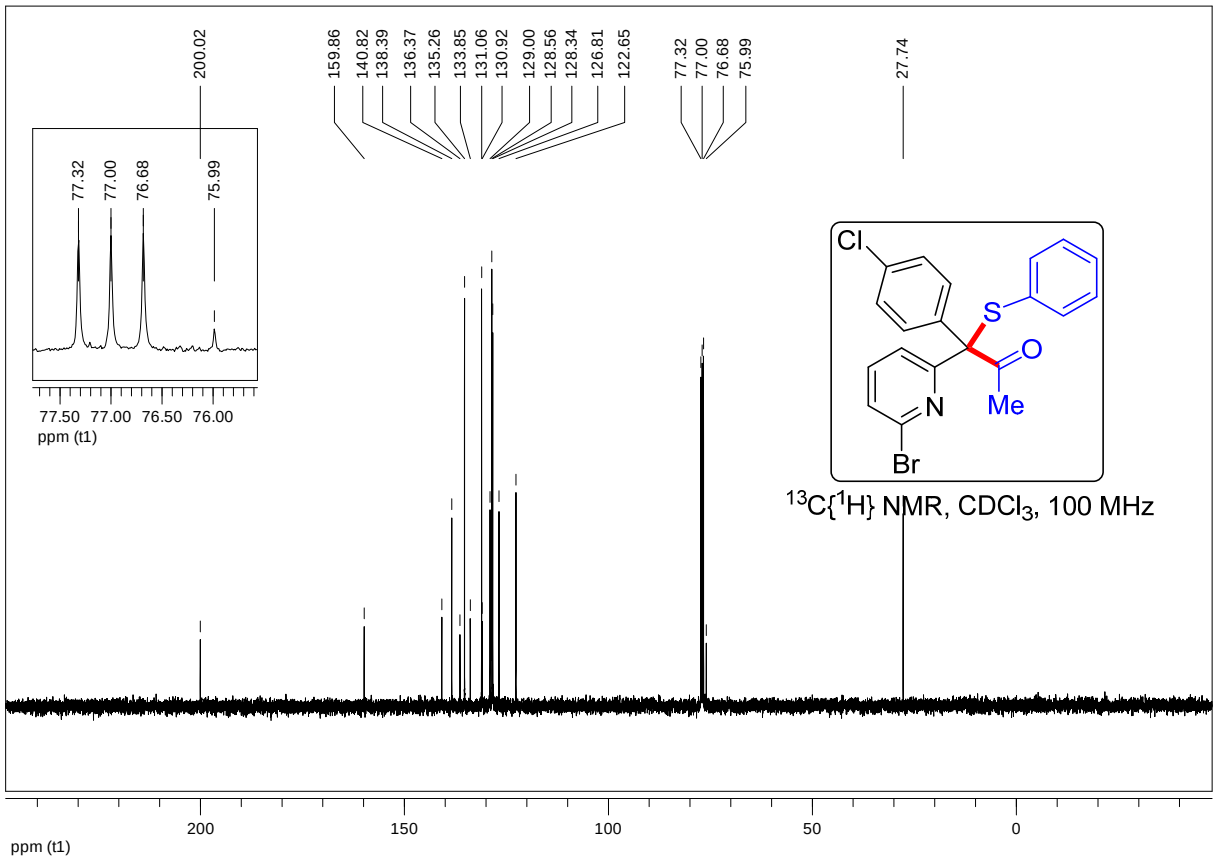


^{19}F NMR, $CDCl_3$, 376 MHz

1-(6-bromopyridin-2-yl)-1-((4-chlorophenyl)thio)-1-phenylpropan-2-one (3ha)

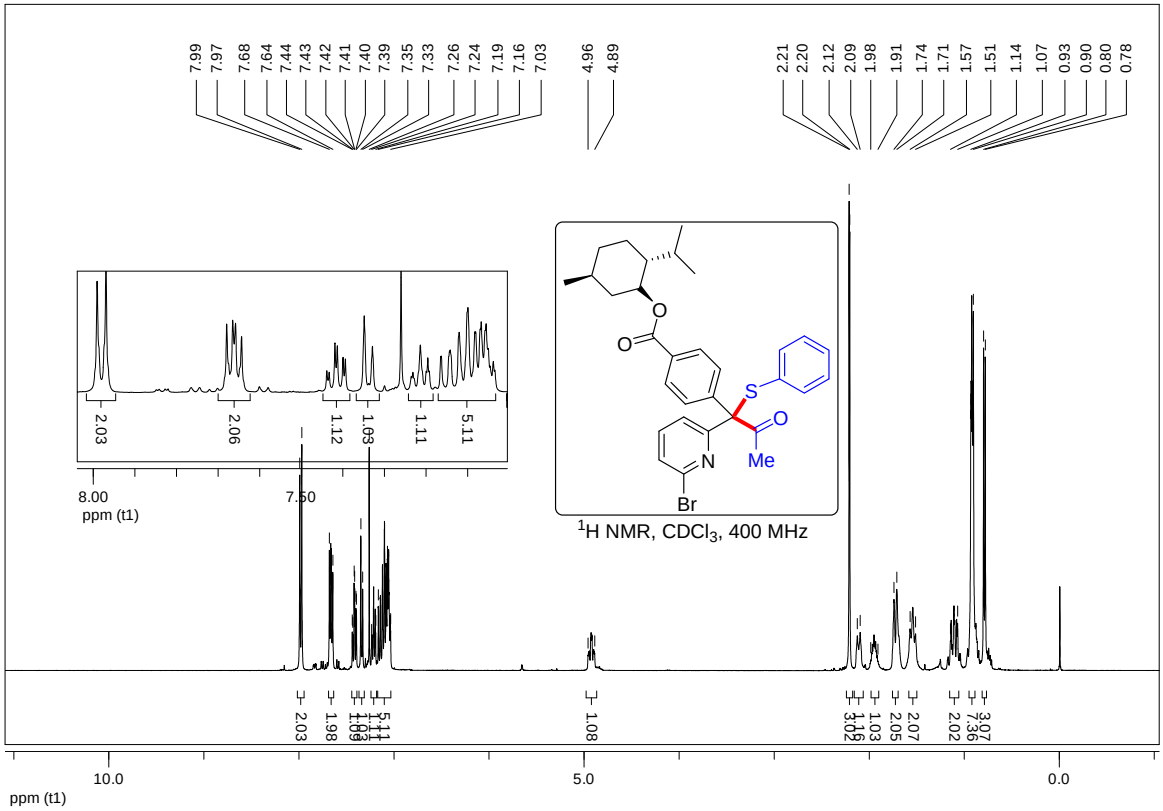


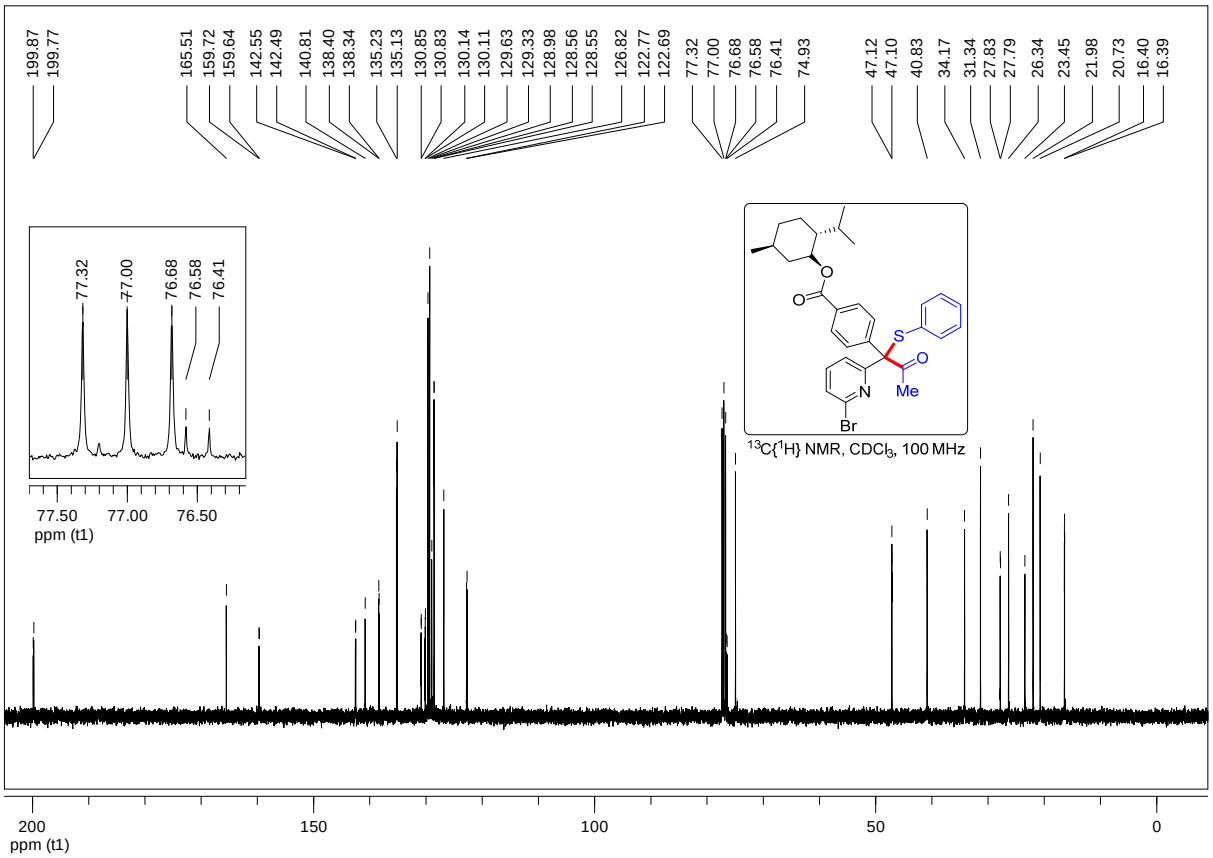
^{1}H NMR, $CDCl_3$, 400 MHz



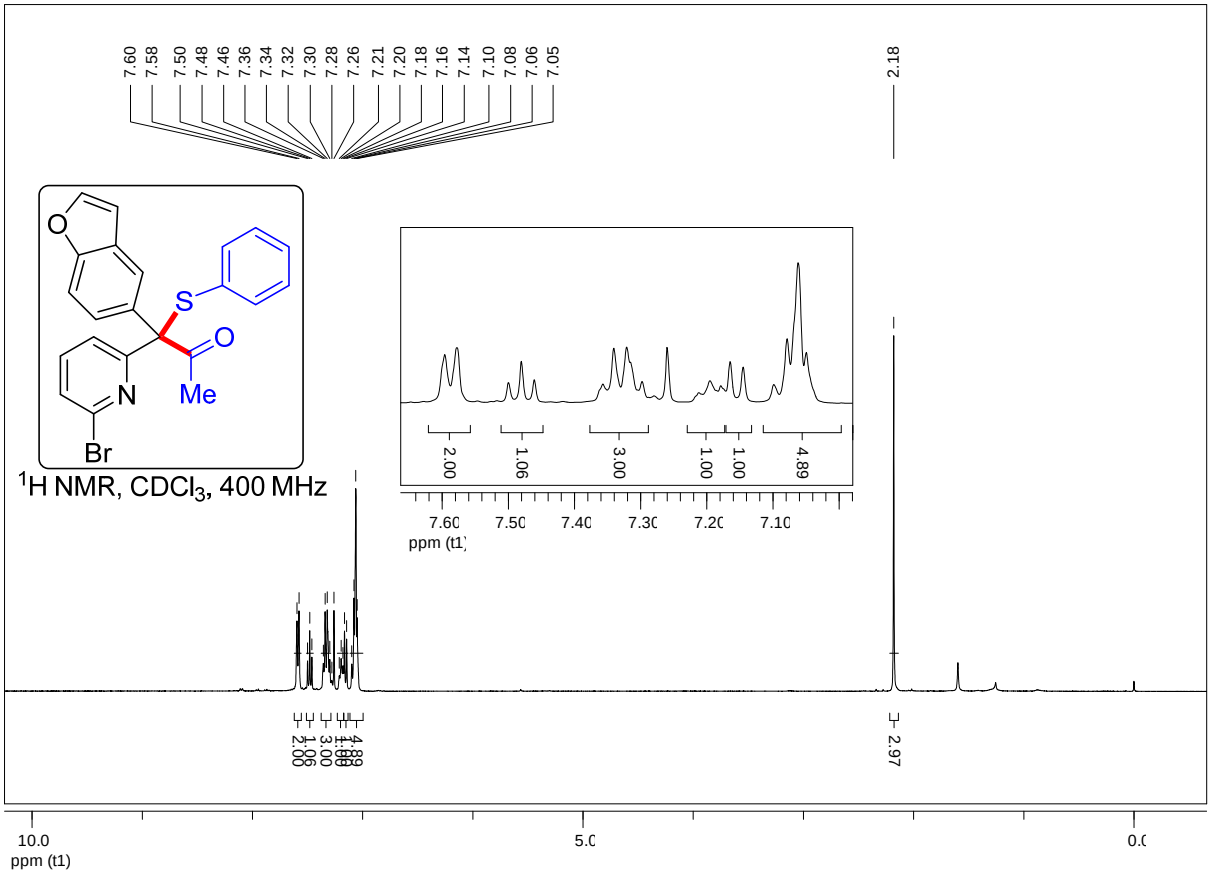
$^{13}C\{^{1}H\}$ NMR, $CDCl_3$, 100 MHz

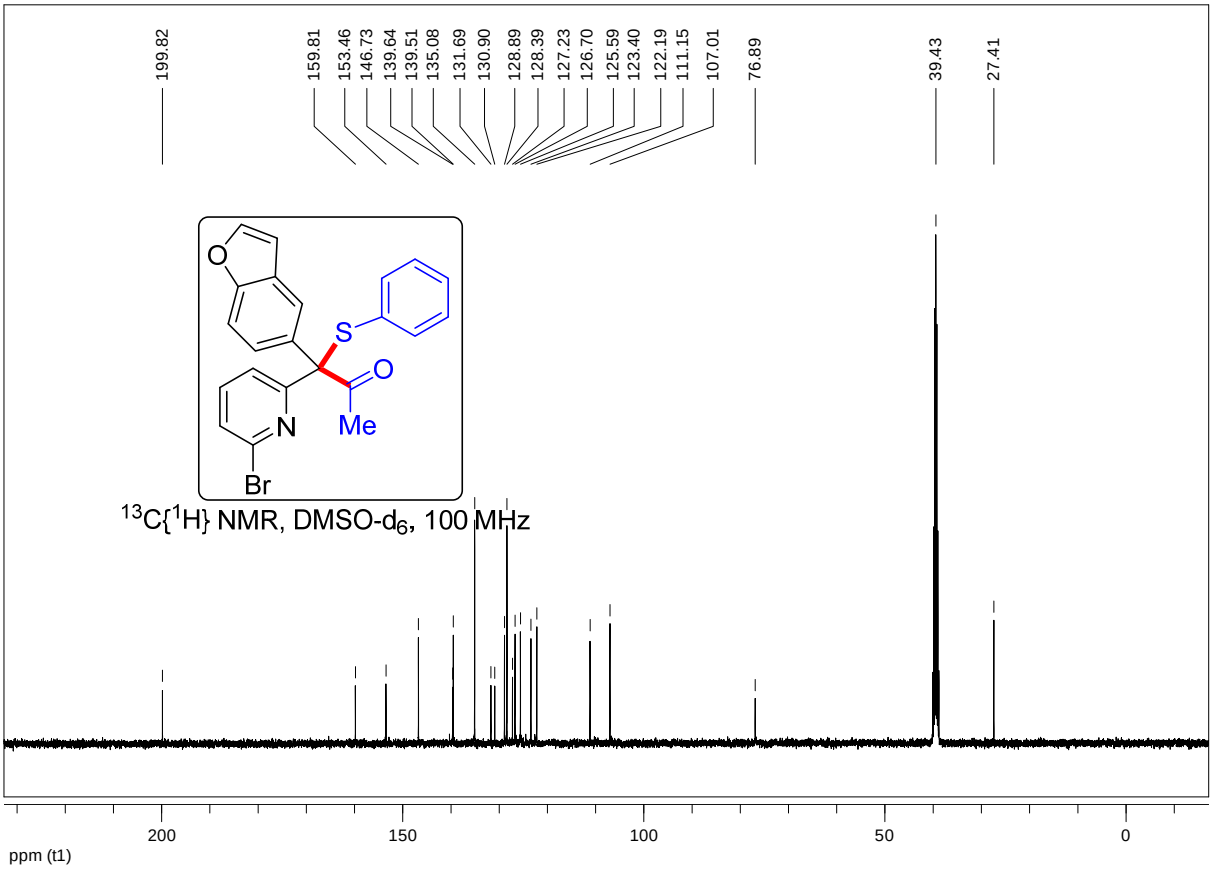
(1R,2R,5S)-2-isopropyl-5-methylcyclohexyl-4-(1-(6-bromopyridin-2-yl)-2-oxo-1-(phenylthio)propyl)benzoate (3ia)



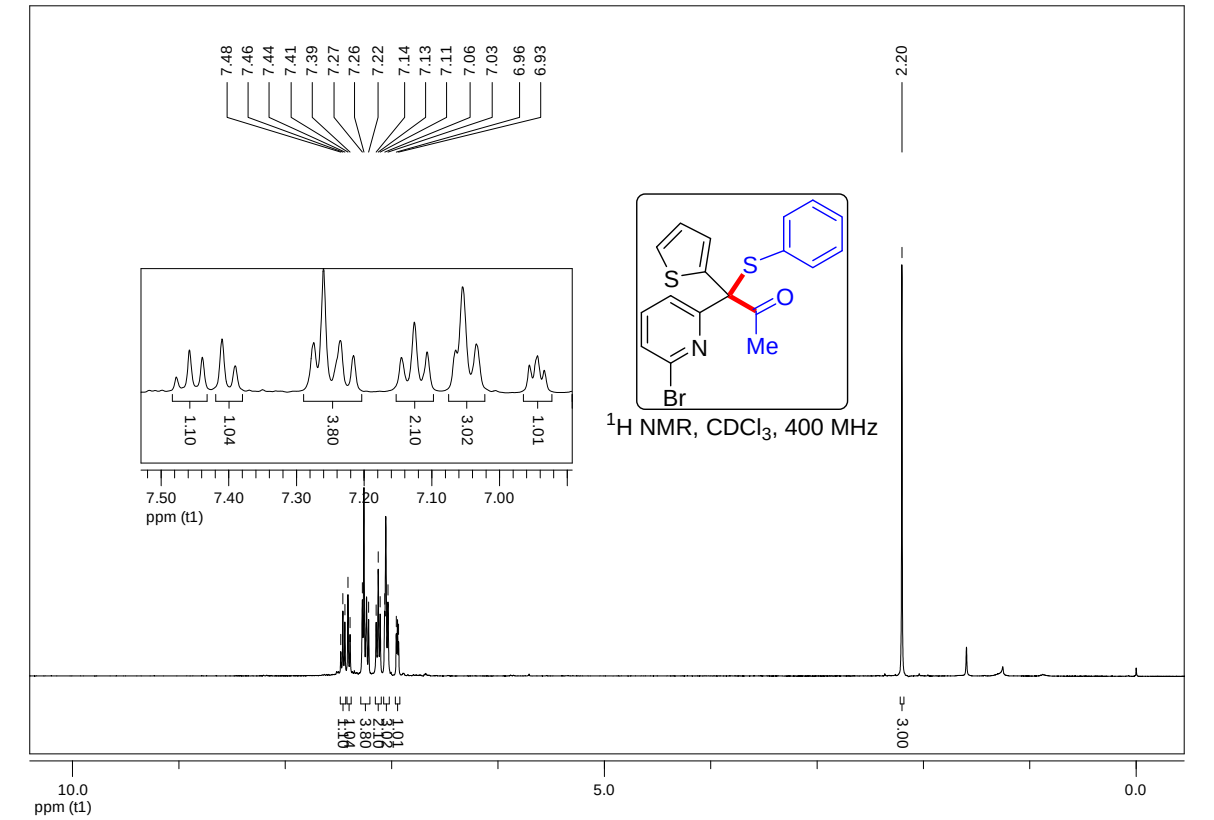


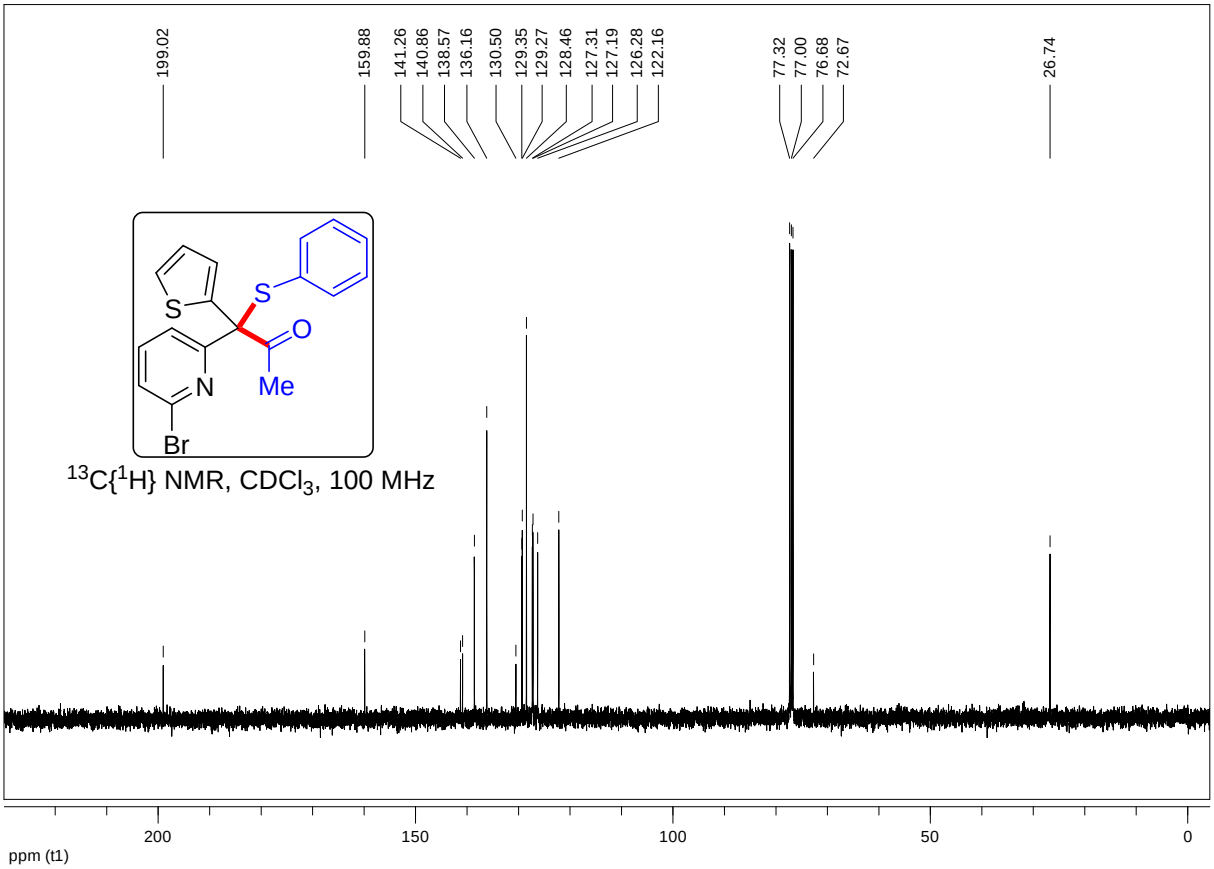
1-(benzofuran-7-yl)-1-(6-bromopyridin-2-yl)-1-(phenylthio)propan-2-one (3ja)



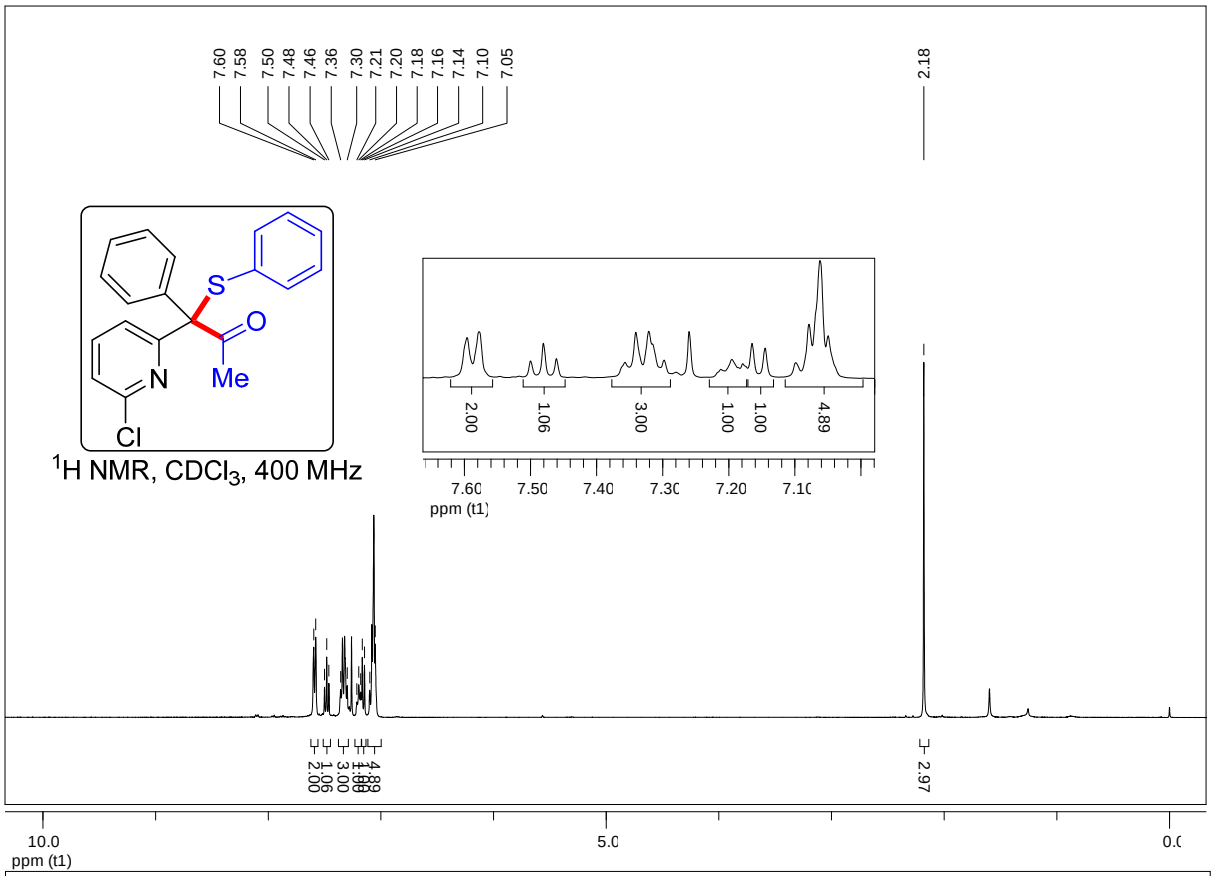


1-(6-bromopyridin-2-yl)-1-((4-chlorophenyl)thio)-1-(thiophen-2-yl)propan-2-one (3ka)

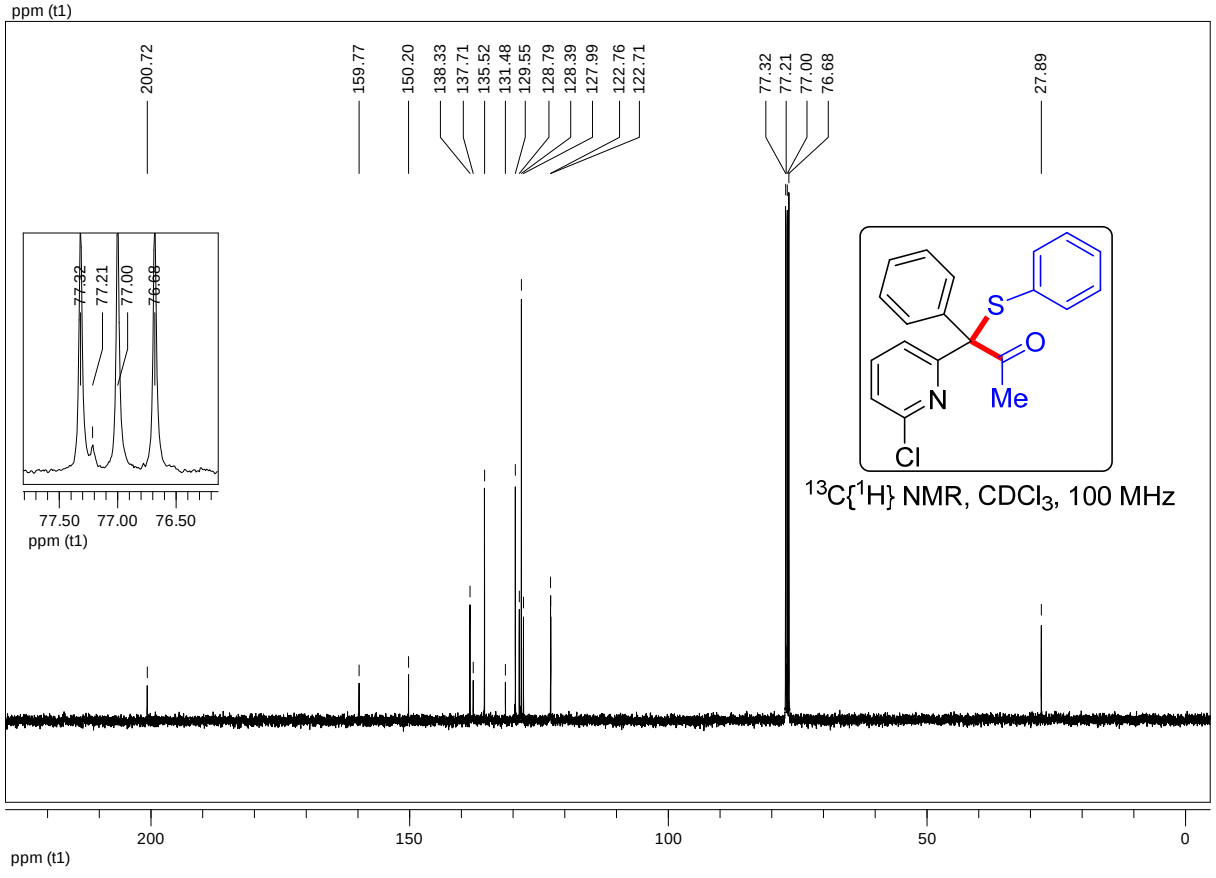




1-(6-chloropyridin-2-yl)-1-phenyl-1-(phenylthio)propan-2-one (3la)

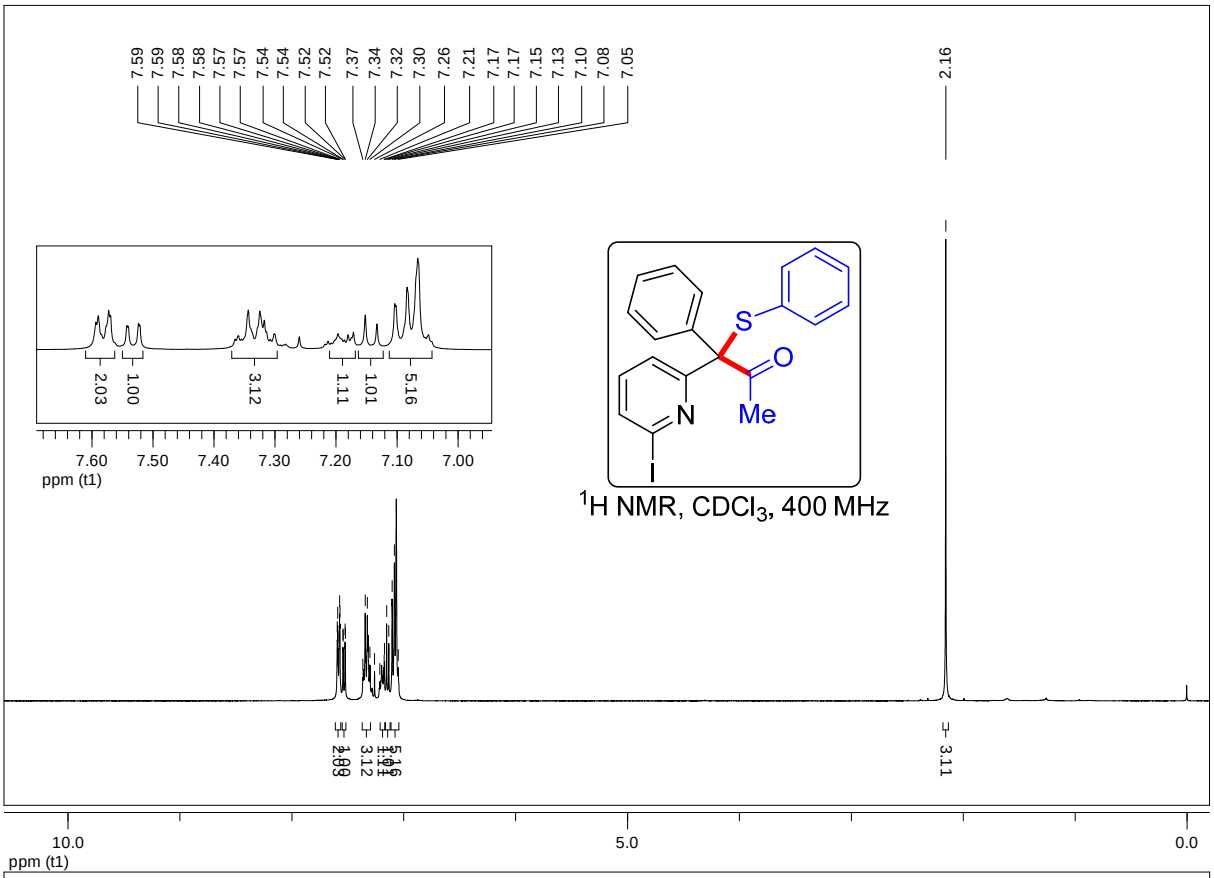


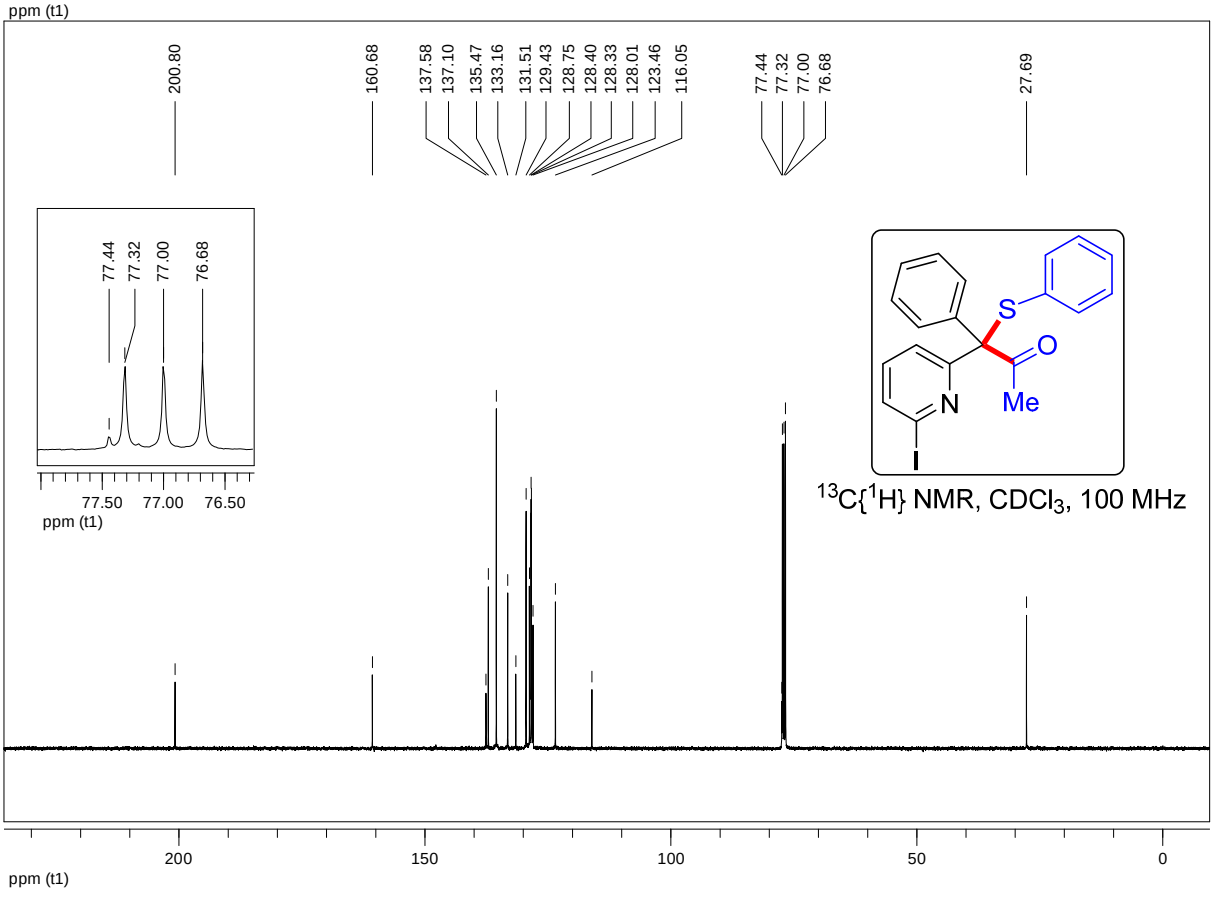
^{1}H NMR, $CDCl_3$, 400 MHz



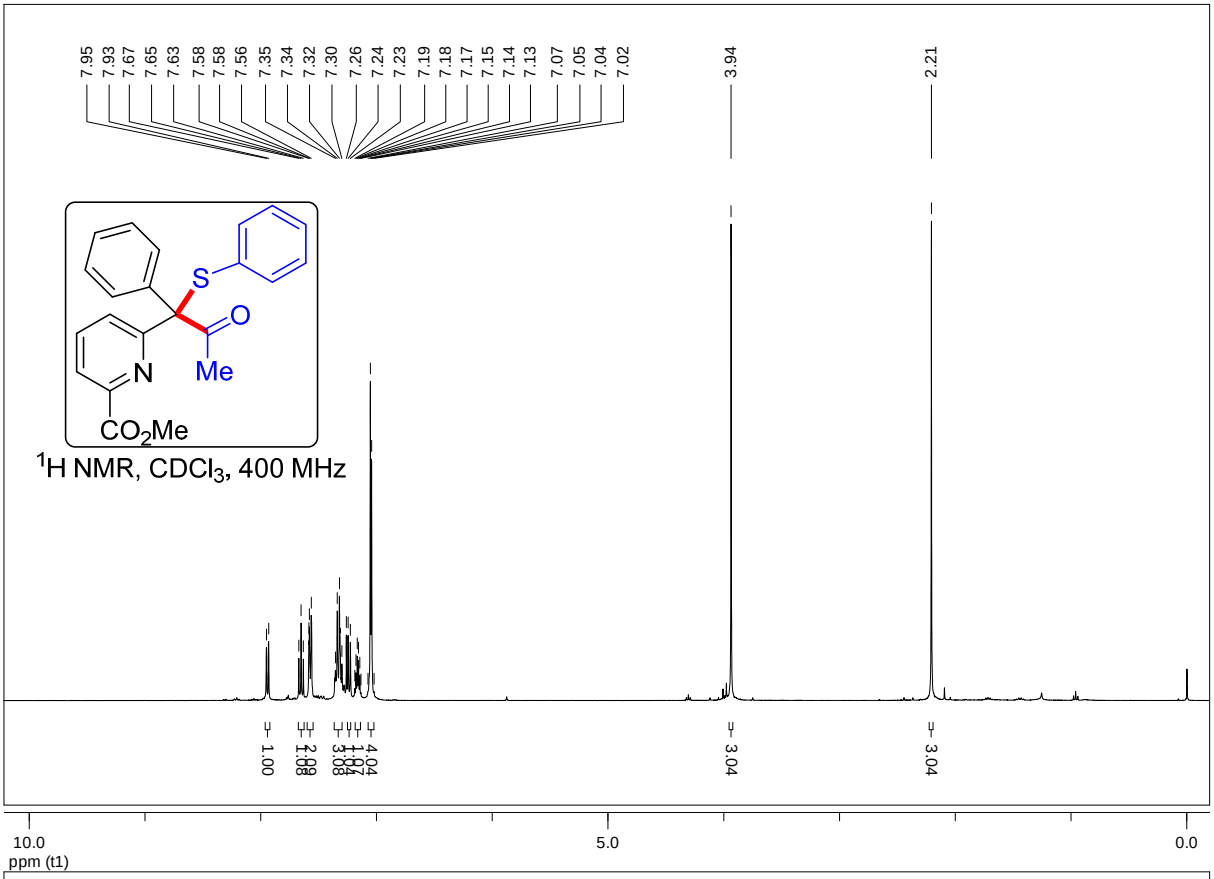
$^{13}C\{^{1}H\}$ NMR, $CDCl_3$, 100 MHz

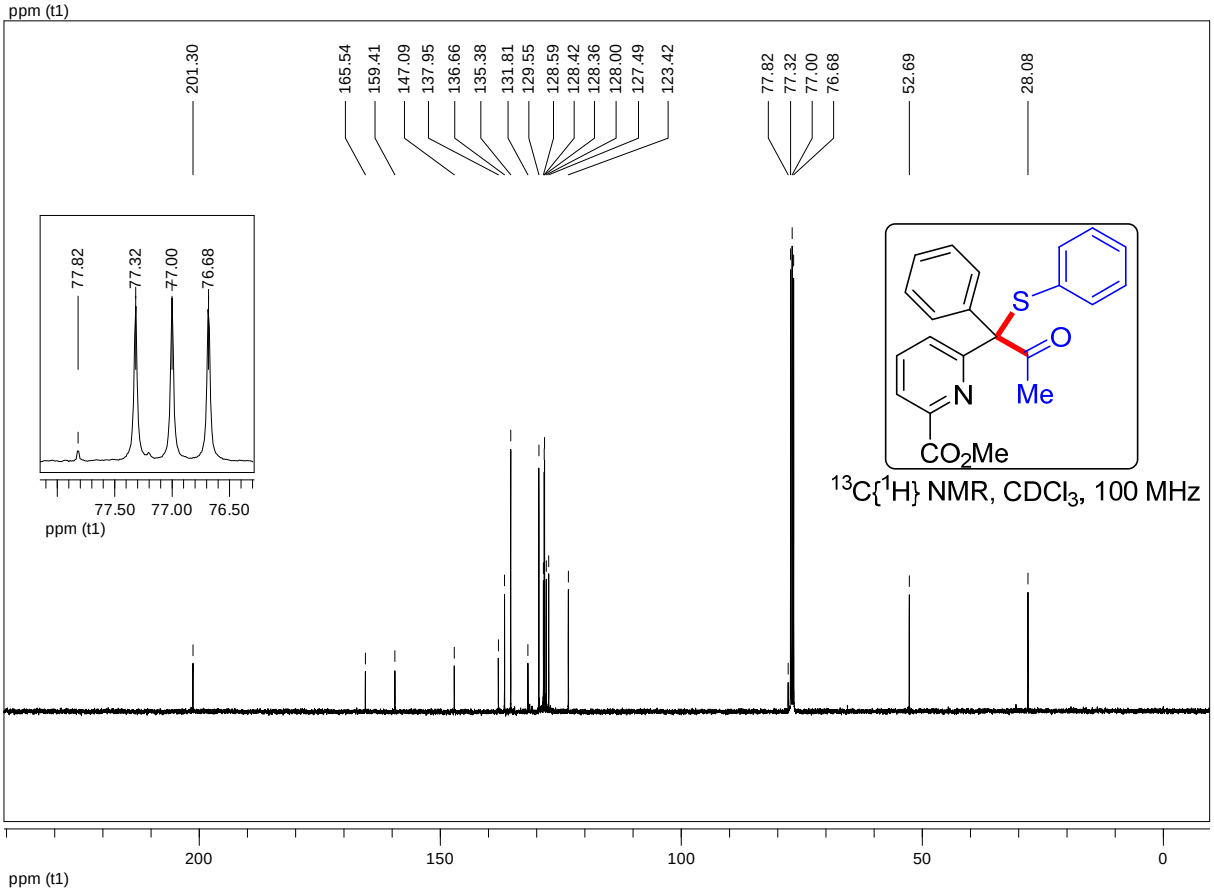
1-(6-iodopyridin-2-yl)-1-phenyl-1-(phenylthio)propan-2-one (3ma)



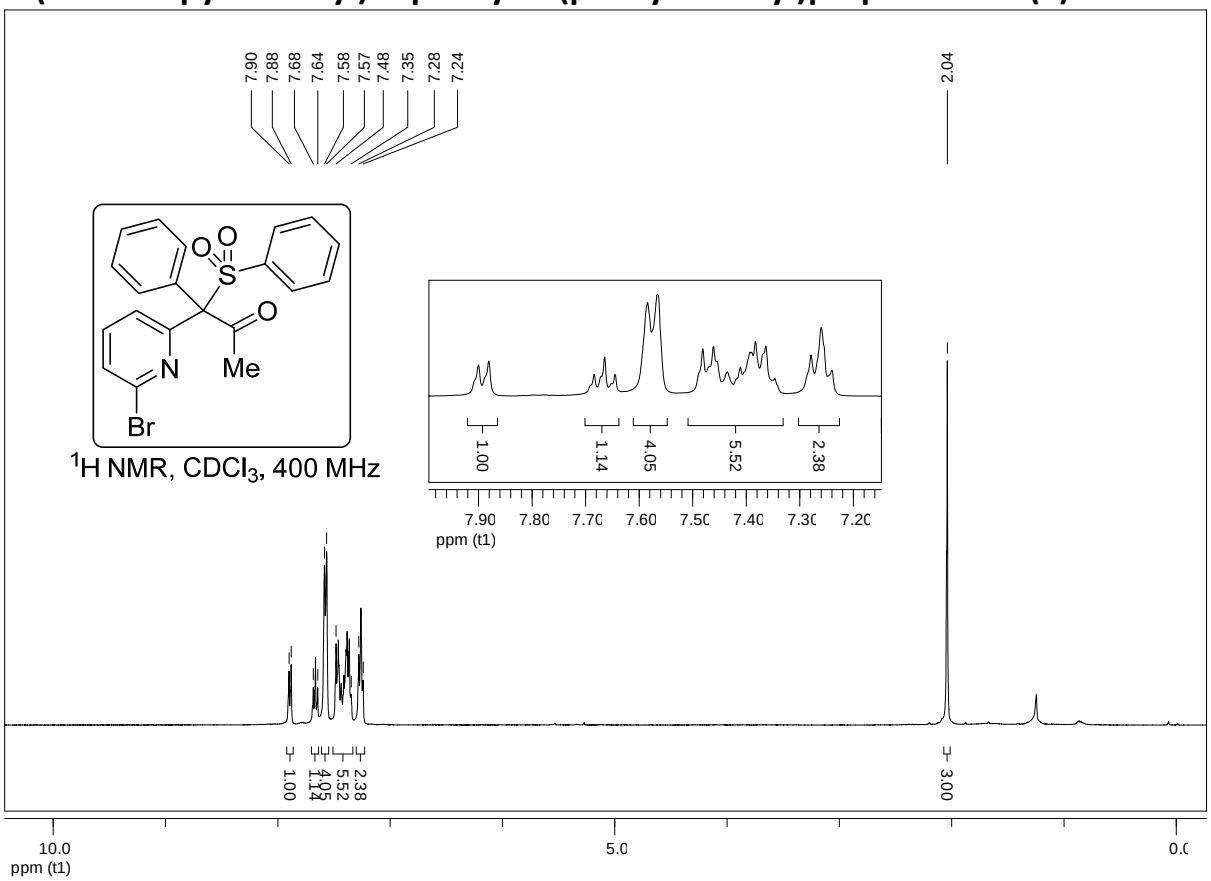


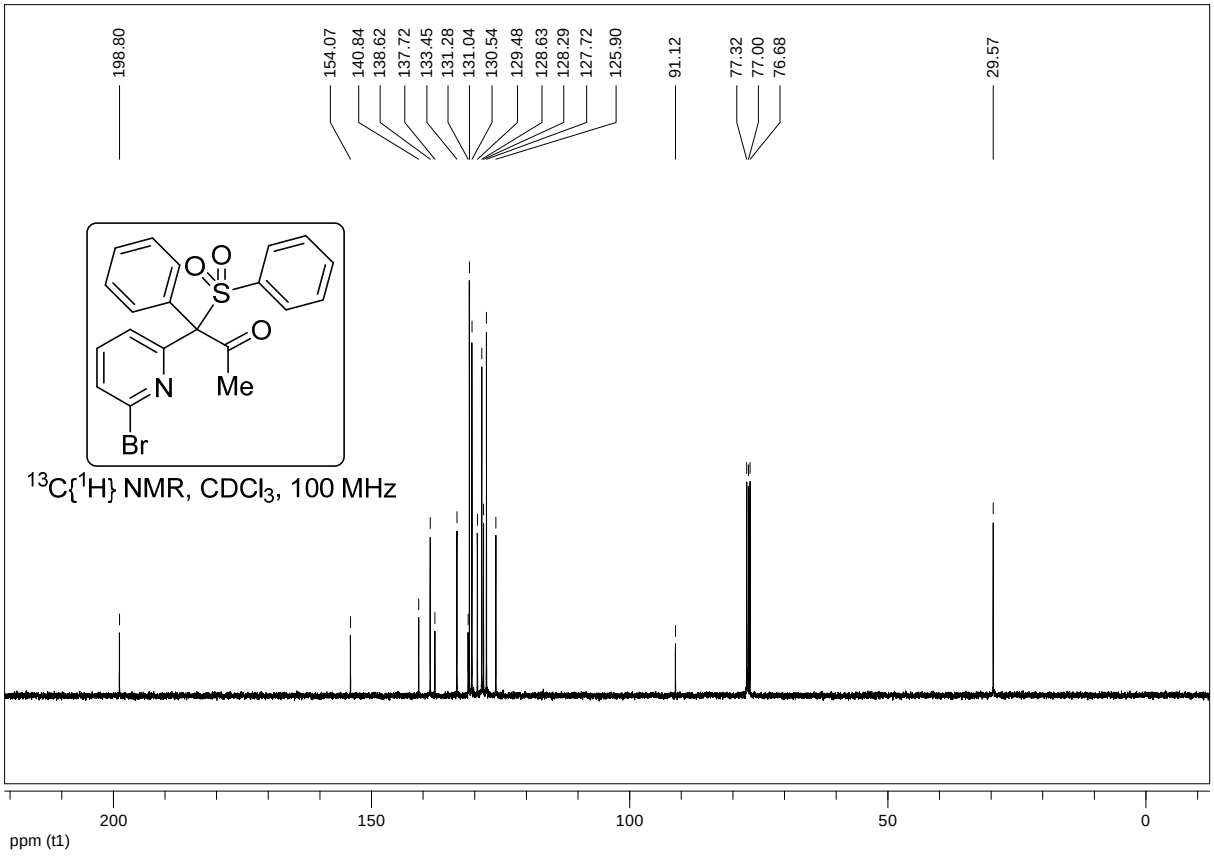
methyl 6-(2-oxo-1-phenyl-1-(phenylthio)propyl)picolinate (3na)





1-(6-bromopyridin-2-yl)-1-phenyl-1-(phenylsulfonyl)propan-2-one (4)





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[1] (a) Chuprakov, S.; Hwang, F. W.; Gevorgyan, V. *Angew. Chem.Int*. Ed. **2007**, 46, 4757; (b) Shi, Y.; Okuda, A. V.; Gevorgyan, V. *Angew. Chem.Int*. Ed. **2014**, 53, 14191; (c) Hirayama, T.;Ueda, S.; Tsurue, N.; Okuda, K.; Nagasawa, H. *Chem.-Eur. J*. **2014**, 20, 4156.

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