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Substrate Switched Dual Functionalization of Alkenes: Catalyst-free Synthetic Route for β-hydroxy and β-keto Thioethers

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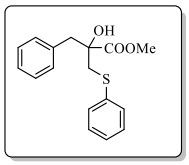
General information:

All chemicals were procured from commercial suppliers and used without further purification. Alkenes **1** & **4** were prepared following the known procedure.[1] NMR spectra were recorded on a Jeol resonance-400 instrument using $CDCl_3$ as solvent. Chemical shifts are reported in parts per million (ppm) and referenced to the residual solvent resonance. Coupling constant (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, dd = double doublet, q = quartet, m = multiplet. HRMS data were collected on Waters - Xevo G2S QTof with UPLC H-Class Ultra Performance Liquid chromatography - mass spectrometry (LC-MS) facility.

General Procedure for Table 1

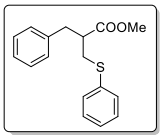
To a stirred solution of methyl 2-benzylacrylate **1a** (1.0 mmol, 0.176 g) and thiophenol **2a** (2.0 mmol, 0.220g) were added oxidant. Then the reaction mixture was stirred at room temperature till the complete conversion of methyl 2-benzylacrylate **1a**. The solvent was then evaporated and crude thus obtained was purified *via* column chromatography (silica gel, 2% EtOAc in hexanes) to afford the corresponding products **3a** as white solid.

Representative example of Table 1 (Entry 16): Methyl 2-benzyl-2-hydroxy-3-(phenylthio) propanoate (3a)



Methyl 2-benzylacrylate **1a** (1.0 mmol, 0.176 g) and thiophenol **2a** (2.0 mmol, 0.220g) were mixed in an open flask, silica gel (1.0 g, 60-120 mesh) was then added reaction mixture. The reaction mixture was kept under open air at room temperature without stirring. After complete conversion of alkene **1a**, the residue was purified *via* column chromatography (silica gel, 2% EtOAc in hexanes) to afford the corresponding products **3a** as white solid. Yield: 0.256 g, 85%; M.P.: 53 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.99 & 3.07 (ABq, 2H, J = 13.6 Hz), 3.25-3.47 (m*, 6H), 7.15-7.27 (m, 8H), 7.38-7.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.50, 44.32, 51.99, 77.81, 126.29, 126.64, 127.78, 128.41, 129.63, 130.36, 134.66, 135.23, 173.62; HRMS (ESI) exact mass calcd for $C_{17}H_{18}O_3S$ + Na (M + Na), 325.0874; Found: 325.0876. *This multiplet contains one singlet for three protons, one singlet for one proton and dABq for two protons.

Methyl 2-benzyl-3-(phenylthio)propanoate (3a')

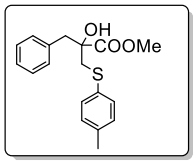


Colourless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.91-2.97 (m, 2H), 3.01-3.07 (m, 2H), 3.17-3.22 (m, 1H), 3.61 (s, 3H),7.13-7.15 (m, 2H), 7.20-7.31 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 35.01, 37.67, 47.44, 51.88, 126.57, 126.75, 128.62, 129.05, 129.07, 130.03, 135.45, 138.29, 174.32; HRMS (ESI) exact mass calcd for $C_{17}H_{18}O_2S$ + Na (M + Na) 309.0925; Found: 309.0928

General procedure for Table 2

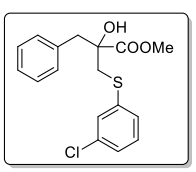
Alkenes **1** (1.0 mmol) and benzenethiols **2** (2.0 mmol) were mixed in an open flask, silica gel (1.0 g, 60-120 mesh) was then added reaction mixture. The reaction mixture was kept under open air at room temperature without stirring for 12 h. The residue was purified *via* column chromatography (silica gel, 2% EtOAc in hexanes) to afford the corresponding products **3.**

Methyl 2-benzyl-2-hydroxy-3-(*p*-tolylthio)propanoate (3b)



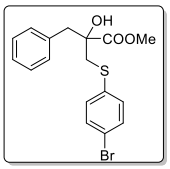
The title compound was prepared following the general procedure for Table 2, using methyl 2-benzylacrylate **1a** (1.0 mmol, 0.176 g) and 4-methylbenzenethiol **2b** (2.0 mmol, 0.248 g), providing **3b** as white solid. Yield: 0.259 g, 82%; M.P.: 64 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.29 (s, 3H), 2.98 & 3.06 (ABq, 2H, J = 13.6 Hz), 3.21-3.43 (m*, 3H), 3.47 (s, 3H), 7.07 (d, 2H, J = 8.0 Hz), 7.16 (dd, 2H, J = 7.6 &2.0 Hz), 7.21- 7.27 (m, 3H), 7.30 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.90, 44.44, 44.62, 52.27, 78.21, 126.92, 128.07, 129.49, 129.94, 131.30, 131.77, 135.02, 136.80, 173.97; HRMS (ESI) exact mass calcd for $C_{18}H_{20}O_3S$ + Na (M + Na), 339.1031; Found: 339.1022.* This multiplet contains one singlet for one proton and dABq for two protons.

Methyl 2-benzyl-3-((3-chlorophenyl)thio)-2-hydroxypropanoate (3c)



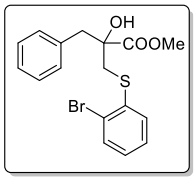
The title compound was prepared following the general procedure for Table 2, using methyl 2-benzylacrylate **1a** (1.0 mmol, 0.176 g) and 3-chlorobenzenethiol **2c** (2.0 mmol, 0.288 g), providing **3c** as white solid. Yield: 0.295 g, 88%; M.P.: 63 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.00 & 3.07 (ABq, 2H, J = 13.2 Hz), 3.27 & 3.43 (dABq, 2H, J = 64.4 & 13.2 Hz), 3.46 (s, 1H), 3.52 (s, 3H), 7.13-7.17 (m, 4H), 7.21-7.26 (m, 4H), 7.38 (d, 1H, J = 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.83, 45.32, 53.09, 78.86, 127.15, 127.68, 128.79, 130.27, 130.35, 130.57, 134.96, 135.47, 138.59, 174.49; HRMS (ESI) exact mass calcd for $C_{17}H_{17}ClO_3S$ + Na (M + Na), 359.0485.; Found: 359.0487.

Methyl 2-benzyl-3-((4-bromophenyl)thio)-2-hydroxypropanoate (3d)



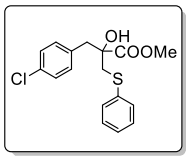
The title compound was prepared following the general procedure for Table 2, using methyl 2-benzylacrylate **1a** (1.0 mmol, 0.176 g) and 4-bromobenzenethiol **2d** (2.0 mmol, 0.378 g), providing **3d** as white solid. Yield: 0.327 g, 86%; M.P.: 90 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.98 & 3.06 (ABq, 2H, J = 13.6 Hz), 3.24 & 3.40 (dABq, 2H, J = 64.0 & 13.6 Hz), 3.42 (s, 1H), 3.51 (s, 3H), 7.14-7.16 (m, 2H), 7.21-7.27 (m, 5H), 7.34-7.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.66, 44.79, 52.54, 78.39, 120.53, 127.12, 128.23, 130.00, 131.80, 132.09, 134.90, 135.08, 173.96; HRMS (ESI) exact mass calcd for $C_{17}H_{17}BrO_3S$ + Na (M + Na), 402.9979.; Found: 402.9974.

Methyl 2-benzyl-3-((2-bromophenyl)thio)-2-hydroxypropanoate (3e)



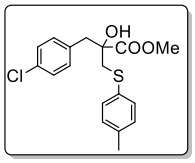
The title compound was prepared following the general procedure for Table 2, using methyl 2-benzylacrylate **1a** (1.0 mmol, 0.176 g) and 2-bromobenzenethiol **2e** (2.0 mmol, 0.378 g), providing **3e** as white solid. Yield: 0.320 g, 84%; M.P.: 66 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.96 & 3.02 (ABq, 2H, J = 13.6 Hz), 3.23 & 3.40 (dABq, 2H, J = 68.0 & 13.6 Hz), 3.38 (s, 1H), 3.48 (s, 3H), 6.96 (td, 1H, J = 8.0 & 1.2 Hz), 7.09-7.20 (m, 6H), 7.37 (dd, 1H, J = 8.0 & 1.6 Hz), 7.45 (dd, 1H, J = 8.0 & 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 42.47, 44.51, 52.27, 77.94, 125.12, 126.74, 127.26, 127.38, 127.85, 129.66, 130.94, 132.64, 134.58, 136.40, 173.58; HRMS (ESI) exact mass calcd for $C_{17}H_{17}BrO_3S$ + Na (M + Na), 402.9979.; Found: 402.9971.

Methyl 2-(4-chlorobenzyl)-2-hydroxy-3-(phenylthio)propanoate (3f)



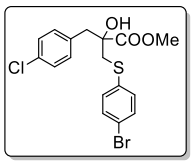
The title compound was prepared following the general procedure for Table 2, using methyl 2-(4-chlorobenzyl) **1b** (1.0 mmol, 0.210 g) and thiophenol **2a** (2.0 mmol, 0.220 g), providing **3f** as colourless liquid. Yield: 0.295 g, 88%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.97 & 3.03 (ABq, 2H, J =13.6 Hz), 3.23-3.46 (m*, 5H), 3.52 (s, 1H), 7.11 (d, 2H, J = 8.0 Hz), 7.17-7.28 (m, 5H), 7.39-7.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.97, 44.15, 52.62, 78.17, 126.96, 128.44, 129.01, 130.98, 131.56, 133.09, 133.82, 135.59, 173.98; HRMS (ESI) exact mass calcd for $C_{17}H_{17}ClO_3S$ + Na (M + Na), 359.0485; Found: 359.0489. * This multiplet contains one singlet for three protons and dABq for two protons.

Methyl 2-(4-chlorobenzyl)-2-hydroxy-3-(*p*-tolylthio)propanoate (3g)



The title compound was prepared following the general procedure for Table 2, using methyl 2-(4-chlorobenzyl) **1b** (1.0 mmol, 0.210 g) and 4-methylbenzenethiol **2b** (2.0 mmol, 0.248 g), providing **3g** as white solid. Yield: 0.287 g, 82%; M.P.: 95 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.30 (s, 3H), 2.96 & 3.02 (ABq, 2H, J = 13.6 Hz), 3.20 & 3.40 (dABq, 2H, J = 80.0 & 13.6 Hz), 3.45 (s, 3H), 3.48 (s, 1H), 7.07-7.12 (m, 4H), 7.20-7.22 (m, 2H), 7.29-7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.15, 43.98, 44.79, 52.59, 78.25, 128.42, 129.78, 131.55, 131.61, 131.84, 133.06, 133.87, 137.15, 174.01; HRMS (ESI) exact mass calcd for $C_{18}H_{19}ClO_3S$ + Na (M + Na), 373.0641; Found: 373.0645.

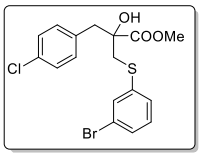
Methyl 3-((4-bromophenyl)thio)-2-(4-chlorobenzyl)-2-hydroxypropanoate(3h)



The title compound was prepared following the general procedure for Table 2, using methyl 2-(4-chlorobenzyl) **1b** (1.0 mmol, 0.210 g) and 4-bromobenzenethiol **2d** (2.0 mmol, 0.378 g), providing **3h** as white solid. Yield: 0.323 g, 78%; M.P.: 96 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.96 & 3.02 (ABq, 2H, J = 13.6 Hz), 3.22 & 3.39 (dABq, 2H, J = 66.4 & 13.6 Hz), 3.47 (s, 1H), 3.50 (s, 3H), 7.09 (d, 2H, J = 8.4 Hz), 7.20-7.26 (m, 4H), 7.36 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.95, 44.06, 52.78,

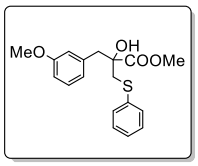
78.35, 120.82, 128.49, 131.50, 132.00, 132.34, 133.18, 133.62, 135.01, 173.92; HRMS (ESI) exact mass calcd for $C_{17}H_{16}BrClO_3S$ + Na (M + Na), 436.9590; Found: 436.9585.

Methyl 3-((3-bromophenyl)thio)-2-(4-chlorobenzyl)-2-hydroxypropanoate (3i)



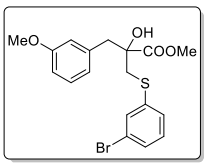
The title compound was prepared following the general procedure for Table 2, using methyl 2-(4-chlorobenzyl) **1b** (1.0 mmol, 0.210 g) and 3-bromobenzenethiol **2f** (2.0 mmol, 0.378 g), providing **3i** as colourless liquid. Yield: 0.307 g, 74%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.94 & 3.00 (ABq, 2H, J = 13.6 Hz), 3.21 & 3.38 (dABq, 2H, J = 67.2 & 13.6 Hz), 3.48 (s, 4H), 7.05-7.09 (m, 3H), 7.18 (d, 2H, J = 8.4 Hz), 7.27 (dd, 2H, 8.0 & 1.6 Hz), 7.49 (t, 1H, J = 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 43.66, 44.07, 52.86, 78.28, 122.77, 128.55, 129.06, 129.83, 130.30, 131.55, 132.85, 133.24, 133.64, 138.25, 173.93 HRMS (ESI) exact mass calcd for $C_{17}H_{16}BrClO_3S$ + Na (M + Na), 436.9590; Found: 436.9587.

Methyl 2-hydroxy-2-(3-methoxybenzyl)-3-(phenylthio)propanoate (3j)



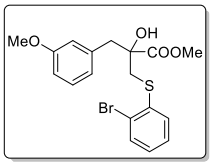
The title compound was prepared following the general procedure for Table 2, using methyl 2-(3-methoxybenzyl)acrylate **1c** (1.0 mmol, 0.206 g) and thiophenol **2a** (2.0 mmol, 0.220 g), providing **3j** as white solid. Yield: 0.285 g, 86%; M.P.: 58 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.99 & 3.07 (ABq, 2H, J = 13.6), 3.29 & 3.47 (dABq, 2H, J = 67.6 & 13.6 Hz), 3.47 (s, 3H), 3.50 (s, 1H), 3.75 (s, 3H), 6.75-6.79 (m, 3H), 7.15-7.21 (m, 2H), 7.25-7.28 (m, 2H), 7.41-7.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.03, 44.88, 52.55, 55.21, 78.34, 112.63, 115.94, 122.52, 126.84, 128.98, 129.27, 130.89, 135.86, 136.76, 159.50, 174.16; HRMS (ESI) exact mass calcd for $C_{18}H_{20}O_4S$ + Na (M + Na), 355.0980; Found: 355.0986.

Methyl 3-((3-bromophenyl) thio)-2-hydroxy-2-(3-methoxybenzyl)propanoate (3k)



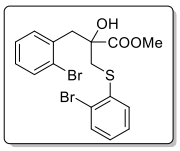
The title compound was prepared following the general procedure for Table 2, using methyl 2-(3-methoxybenzyl)acrylate **1c** (1.0 mmol, 0.206 g) and 3-bromobenzenethiol **2f** (2.0 mmol, 0.378 g), providing **3k** as colourless liquid. Yield: 0.312 g, 76%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.97 & 3.05 (ABq, 2H, J = 13.6 Hz), 3.26 & 3.42 (dABq, 2H, J = 61.2 & 13.6 Hz), 3.47 (s, 1H), 3.53 (s, 3H), 3.73 (s, 3H), 6.72-6.76 (m, 3H), 7.07-7.17 (m, 2H), 7.27-7.31 (m, 2H), 7.53 (t, 1H, J = 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.33, 44.78, 52.57, 55.05, 78.25, 112.50, 115.75, 122.29, 122.53, 128.77, 129.16, 129.50, 130.07, 132.56, 136.38, 138.32, 159.35, 173.90, HRMS (ESI) exact mass calcd for $C_{18}H_{19}BrO_4S$ + Na (M + Na), 433.0085.; Found: 433.0083.

Methyl 3-((2-bromophenyl) thio)-2-hydroxy-2-(3-methoxybenzyl)propanoate(3l)



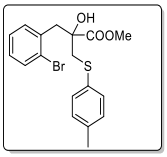
The title compound was prepared following the general procedure for Table 2, using methyl 2-(3-methoxybenzyl)acrylate **1c** (1.0 mmol, 0.206 g) and 2-bromobenzenethiol **2e** (2.0 mmol, 0.378 g), providing **3l** as colourless liquid. Yield: 0.304 g, 74%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.98 & 3.04 (ABq, 2H, J = 13.6 Hz), 3.27 & 3.43 (dABq, 2H, J = 63.6 & 13.6 Hz), 3.45 (s, 1H), 3.53 (s, 3H), 3.71 (s, 3H), 6.71-6.75 (m, 3H), 6.98-7.02 (m, 1H), 7.11-7.21 (m, 2H), 7.42 (dd, 1H, J = 8.0 & 1.2 Hz), 7.50 (dd, 1H, J = 8.0 & 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 42.83, 44.89, 52.65, 55.06, 78.28, 112.52, 115.74, 122.32, 125.46, 127.64, 127.75, 129.15, 131.29, 133.00, 136.44, 136.79, 159.35, 173.93; HRMS (ESI) exact mass calcd for $C_{18}H_{19}BrO_4S$ + Na (M + Na), 433.0085; Found: 433.0087.

Methyl 2-(2-bromobenzyl)-3-((2-bromophenyl)thio)-2-hydroxypropanoate (3m)



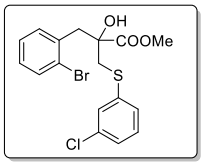
The title compound was prepared following the general procedure for Table 2, using methyl 2-(2-bromobenzyl) **1d** (1.0 mmol, 0.255 g) and 2-bromobenzenethiol **2e** (2.0 mmol, 0.378 g), providing **3m** as white solid. Yield: 0.404 g, 88%; M.P.: 56 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.25-3.33 (m 3H,), 3.55-3.59 (m, 5H), 7.03 (td, 1H, J = 2.0 & 7.6 Hz), 7.08 (td, 1H, J = 2.0 & 7.6 Hz), 7.20-7.24 (m, 2H), 7.38 (dd, 1H, J = 2.0 & 8.0 Hz), 7.42 (dd, 1H, J = 2.0 & 8.0 Hz), 7.51-7.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 42.12, 43.06, 52.58, 77.32, 125.09, 125.14, 126.85, 127.29, 127.37, 128.38, 130.85, 132.08, 132.53, 132.66, 134.35, 136.44, 173.80; HRMS (ESI) exact mass calcd for $C_{17}H_{16}Br_2O_3S$ + Na (M + Na), 480.9085; Found: 480.9079.

Methyl 2-(2-bromobenzyl)-2-hydroxy-3-(*p*-tolylthio)propanoate (3n)



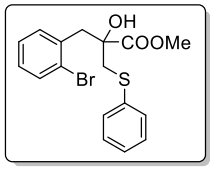
The title compound was prepared following the general procedure for Table 2, using methyl 2-(2-bromobenzyl) **1d** (1.0 mmol, 0.255 g) and 4-methylbenzenethiol **2b** (2.0 mmol, 0.248 g), providing **3n** as colourless liquid. Yield: 0.323 g, 82%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.30 (s, 3H), 3.20-3.31 (m, 3H), 3.50-3.61 (m, 5H), 7.05-7.09 (m, 3H), 7.22 (td, 1H, J = 7.6 & 0.8 Hz), 7.32 (d, 2H, J = 8.0 Hz), 7.41 (dd, 1H, J = 7.6 & 1.6 Hz), 7.52 (dd, 1H, J = 8.0 & 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.98, 43.13, 44.06, 52.55, 77.63, 125.48, 127.12, 128.56, 129.55, 131.26, 131.87, 132.35, 132.77, 134.89, 136.74, 174.17; HRMS (ESI) exact mass calcd for $C_{18}H_{19}BrO_3S$ + Na (M + Na), 417.0136; Found: 417.0131.

Methyl 2-(2-bromobenzyl)-3-((3-chlorophenyl) thio)-2-hydroxypropanoate (3o)



The title compound was prepared following the general procedure for Table 2, using methyl 2-(2-bromobenzyl) **1d** (1.0 mmol, 0.255 g) and 3-chlorobenzenethiol **2c** (2.0 mmol, 0.288 g), providing **3o** as colourless liquid. Yield: 0.307 g, 74%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.24-3.30 (m, 3H), 3.52-3.57 (m, 5H), 7.05-7.26 (m, 5H), 7.36-7.39 (m, 2H), 7.51 (d, 1H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): 43.02, 43.44, 53.00, 77.86, 125.65, 126.74, 127.39, 128.32, 128.90, 129.82, 129.95, 132.55, 133.05, 134.57, 134.83, 138.20, 174.28; HRMS (ESI) exact mass calcd for $C_{17}H_{16}BrClO_3S$ + Na (M + Na), 436.9590; Found: 436.9589.

Methyl 2-(2-bromobenzyl)-2-hydroxy-3-(phenylthio)propanoate (3p)



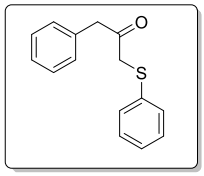
The title compound was prepared following the general procedure for Table 2, using methyl 2-(2-bromobenzyl) **1d** (1.0 mmol, 0.255 g) and thiophenol **2a** (2.0 mmol, 0.220 g), providing **3p** as colourless liquid. Yield: 0.342 g, 90%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.23-3.32 (m, 3H), 3.49-3.60 (m, 5H), 7.07

(td, 1H, *J* = 8.0 & 1.6 Hz), 7.18-7.27 (m, 4H), 7.40-7.41 (m, 3H), 7.52 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.36. 43.61, 52.80, 77.78, 125.69, 126.82, 127.35, 128.81, 128.99, 130.82, 132.55, 133.00, 135.04, 135.82, 174.35; HRMS (ESI) exact mass calcd for $C_{17}H_{17}BrO_3S$ + Na (M + Na), 402.9979.; Found: 402.9971

General procedure for Table 3

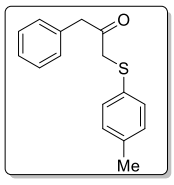
Alkenes **4** (1.0 mmol) and benzenethiols **2** (2.0 mmol) were mixed in a flask and then silica gel (1.0 g, 60-120 mesh) was added in to this reaction mixture. The reaction mixture was kept under open air at room temperature for 12 hour. The residue was purified *via* column chromatography (silica gel, 5 % EtOAc in hexanes) to afford the corresponding β-keto thioethers **5**.

1-Phenyl-3-(phenylthio)propan-2-one (5a)



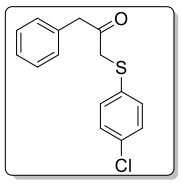
The title compound was prepared following the general procedure for Table 3, using 2-benzylacrylonitrile **4a** (1.0 mmol, 0.143 g) and benzenethiol **2a** (2.0 mmol, 0.220 g), providing **5a** as colourless liquid. Yield: 0.213 g, 88%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.70 (s, 2H), 3.89 (s, 2H), 7.17-7.34 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.30, 47.81, 127.20, 127.44, 129.03, 129.41, 129.78, 129.96, 133.91, 134.82, 203.05; HRMS (ESI) exact mass calcd for $C_{15}H_{14}OS$ + K (M + K), 281.0402; Found: 281.0407.

1-Phenyl-3-(*p*-tolylthio)propan-2-one (5b)



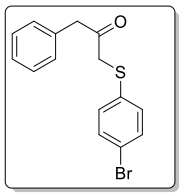
The title compound was prepared following the general procedure for Table 3, using 2-benzylacrylonitrile **4a** (1.0 mmol, 0.143 g) and 4-methylbenzenethiol **2b** (2.0 mmol, 0.248 g), providing **5b** as pale yellow liquid. Yield: 0.220 g, 86%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.27 (s, 3H), 3.60 (s, 2H), 3.82 (s, 2H), 7.04 (d, 2H, *J* = 8.0 Hz), 7.13 (d, 2H, *J* = 7.6 Hz) 7.20-7.29 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.21, 43.88, 47.66, 127.27, 128.88, 129.71, 130.11, 130.78, 130.89, 133.93, 137.43, 202.95; HRMS (ESI) exact mass calcd for $C_{16}H_{16}OS$+ K (M + K), 295.0559; Found: 295.0566

1-((4-Chlorophenyl)thio)-3-phenylpropan-2-one (5c)



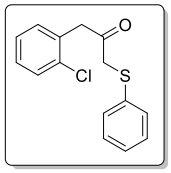
The title compound was prepared following the general procedure for Table 3, using 2-benzylacrylonitrile **4a** (1.0 mmol, 0.143 g) and 4-chlorobenzenethiol **2g** (2.0 mmol, 0.288 g), providing **5c** as pale yellow liquid Yield: 0.224 g, 81%, ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.65 (s, 2H), 3.85 (s, 2H), 7.15 (d, 2H, J = 6.8 Hz), 7.21 (s, 3H) 7.24-7.32 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.23, 47.78, 127.39, 128.94, 129.36, 129.57, 131.24, 133.07, 133.19, 133.54, 202.43; HRMS (ESI) exact mass calcd for $C_{15}H_{13}ClOS$+ K (M + K), 315.0013; Found: 315.0008

1-((4-Bromophenyl)thio)-3-phenylpropan-2-one (5d)



The title compound was prepared following the general procedure for Table 3, using 2-benzylacrylonitrile **4a** (1.0 mmol, 0.143 g) and 4-bromobenzenethiol **2d** (2.0 mmol, 0.378 g), providing **5d** as white solid. Yield: 0.250 g, 78%; M.P.: 65 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.64 (s, 2H), 3.83 (s, 2H), 7.10-7.15 (m, 4H), 7.22-7.36 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.04, 47.78, 121.06, 127.40, 128.95, 129.58, 131.32, 132.28, 133.53, 133.81, 202.38.; HRMS (ESI) exact mass calcd for $C_{15}H_{13}BrOS$ + K (M + K), 358.9508; Found: 358.9515

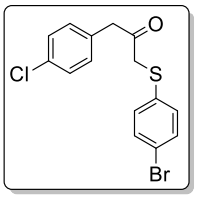
1-(2-Chlorophenyl)-3-(phenylthio)propan-2-one (5e)



The title compound was prepared following the general procedure for Table 3, using 2-(2-chlorobenzyl)acrylonitrile **4b** (1.0 mmol, 0.177 g) and benzenethiol **2a** (2.0 mmol, 0.220 g), providing **5e** as colour less liquid. Yield: 0.229 g, 83%, ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.75 (s, 2H), 4.01 (s, 2H), 7.13-7.22 (m, 4H), 7.25-7.29 (m, 2H), 7.33-7.36 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.69, 45.52,

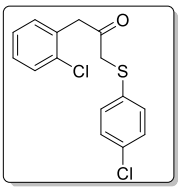
127.05, 127.11, 128.89, 129.27, 129.64, 129.75, 131.96, 132.49, 134.52, 134.74, 203.72.; HRMS (ESI) exact mass calcd for $C_{15}H_{13}ClOS$ + K (M + K), 315.0013; Found: 315.0017

1-((4-Bromophenyl)thio)-3-(4-chlorophenyl)propan-2-one (5f)



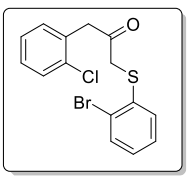
The title compound was prepared following the general procedure for Table 3, using 2-(4-chlorobenzyl)acrylonitrile **4f** (1.0 mmol, 0.177 g) and 4-bromobenzenethiol **2d** (2.0 mmol, 0.378 g), providing **5f** as colour white solid Yield: 0.277 g, 86%, M.P 68 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.64 (s, 2H), 3.82 (s, 2H), 7.06 (d, 2H, J = 8.0 Hz), 7.14 (d, 2H, J = 8.4 Hz), 7.26 (d, 2H, J = 8.4 Hz), 7.36 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.23, 46.72, 121.26, 129.00, 130.93, 131.40, 131.93, 132.34, 133.35, 133.52, 201.92; HRMS (ESI) exact mass calcd for $C_{15}H_{12}BrClOS$ + K (M + K), 392.9118; Found: 392.9121

1-(2-Chlorophenyl)-3-((4-chlorophenyl)thio)propan-2-one (5g)



The title compound was prepared following the general procedure for Table 3, using 2-(2-chlorobenzyl)acrylonitrile **4b** (1.0 mmol, 0.177 g) and 4-chlorobenzenethiol **2g** (2.0 mmol, 0.288 g), providing **5g** as pale yellow liquid. Yield: 0.270 g, 87%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.72 (s, 2H), 3.99 (s, 2H), 7.14-7.16 (m, 1H), 7.17-7.27 (m, 6H), 7.34-7.36 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.73, 45.59, 127.18, 129.00, 129.37, 129.68, 131.18, 131.92, 132.27, 133.15, 133.20, 134.46, 202.31; HRMS (ESI) exact mass calcd for $C_{15}H_{12}Cl_2OS$ + K (M + K), 348.9623; Found: 348.9628

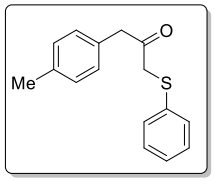
1-((2-Bromophenyl)thio)-3-(2-chlorophenyl)propan-2-one (5h)



The title compound was prepared following the general procedure for Table 3, using 2-(2-chlorobenzyl)acrylonitrile **4b** (1.0 mmol, 0.177 g) and 2-bromobenzenethiol **2e** (2.0 mmol, 0.378 g),

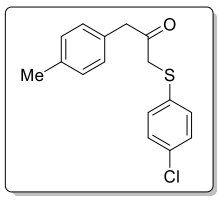
providing **5h** as white solid. Yield: 0.298 g, 84%; M.P 62 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.79 (s, 2H), 4.04 (s, 2H), 7.04 (td, 1H, *J* = 1.2 & 8.0 Hz), 7.15-7.28 (m, 5H), 7.34-7.37 (m, 1H) 7.54 (dd, 1H, *J* = 8.0 & 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 42.69, 45.59, 123.90, 127.17, 127.75, 128.18, 128.98, 129.23, 129.66, 132.00, 132.33, 133.27, 134.50, 136.04, 201.41; HRMS (ESI) exact mass calcd for $C_{15}H_{12}BrClOS$ + K (M + K), 392.9118; Found: 392.9114

1-(Phenylthio)-3-(*p*-tolyl)propan-2-one (5i)



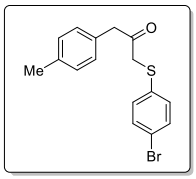
The title compound was prepared following the general procedure for Table 3, using 2-(4-methylbenzyl)acrylonitrile **4c** (1.0 mmol, 0.157 g) and benzenethiol **2a** (2.0 mmol, 0.220 g), providing **5i** as pale yellow liquid. Yield: 0.218 g, 85%, ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (s, 3H), 3.67 (s, 2H), 3.82 (s, 2H), 7.05 (d, 2H, *J* = 8.0 Hz), 7.11 (d, 2H, *J* = 8.0 Hz), 7.17-7.32 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.22, 43.05, 47.36, 127.01, 129.26, 129.51, 129.62, 129.80, 130.70, 134.80, 136.95, 203.18.; HRMS (ESI) exact mass calcd for $C_{16}H_{16}OS$ + K (M + K), 295.0559; Found: 295.0548

1-((4-Chlorophenyl)thio)-3-(*p*-tolyl)propan-2-one (5j)



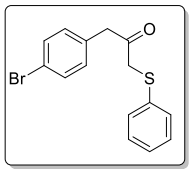
The title compound was prepared following the general procedure for Table 3, using 2-(4-methylbenzyl)acrylonitrile **4c** (1.0 mmol, 0.157 g) and 4-chlorobenzenethiol **2g** (2.0 mmol, 0.288 g), providing **5j** as colour less liquid. Yield: 0.244 g, 84%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (s, 3H), 3.65 (s, 2H), 3.80 (s, 2H), 7.04 (d, 2H, *J* = 8.0 Hz), 7.11 (d, 2H, *J* = 7.6 Hz), 7.19-7.23 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.18, 43.10, 47.47, 129.33, 129.44, 129.65, 130.45, 131.21, 133.11, 133.20, 137.07, 202.68; HRMS (ESI) exact mass calcd for $C_{16}H_{15}ClOS$ + K (M + K), 329.0169; Found: 329.0159

1-((4-Bromophenyl)thio)-3-(*p*-tolyl)propan-2-one (5k)



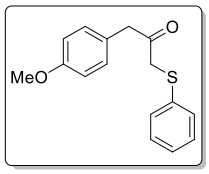
The title compound was prepared following the general procedure for Table 3, using 2-(4-methylbenzyl)acrylonitrile **4c** (1.0 mmol, 0.157 g) 4-bromobenzenethiol **2d** (2.0 mmol, 0.378 g), providing **5k** as white solid. Yield: 0.294 g, 88%, M.P. 63 ^{o}C; ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3H), 3.67 (s, 2H), 3.81 (s, 2H), 7.06 (d, 2H, J = 8.0 Hz), 7.12-7.15 (m, 4H), 7.36 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.21, 42.92, 47.48, 120.98, 129.45, 129.66, 130.44, 131.29, 132.24, 133.95, 137.07, 202.65; HRMS (ESI) exact mass calcd for $C_{16}H_{15}BrOS$ + K (M + K), 372.9664; Found: 372.9673

1-(4-Bromophenyl)-3-(phenylthio)propan-2-one (5l)



The title compound was prepared following the general procedure for Table 3, using 2-(4-bromobenzyl)acrylonitrile **4e** (1.0 mmol, 0.222 g) and benzenethiol **2a** (2.0 mmol, 0.220 g), providing **5l** as colourless liquid. Yield: 0.263 g, 82%, ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.66 (s, 2H), 3.82 (s, 2H), 7.00 (d, 2H, J = 8.4 Hz), 7.19-7.31 (m, 5H), 7.40 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 43.35, 46.68, 121.32, 127.22, 129.31, 129.90, 131.34, 131.89, 132.67, 134.37, 203.30; HRMS (ESI) exact mass calcd for $C_{15}H_{13}BrOS$ + K (M + K), 358.9508; Found: 358.9514

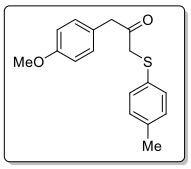
1-(4-Methoxyphenyl)-3-(phenylthio)propan-2-one (5m)



The title compound was prepared following the general procedure for Table 3, using 2-(4-methoxybenzyl)acrylonitrile **4d** (1.0 mmol, 0.173 g) and benzenethiol **2a** (2.0 mmol, 0.220 g), providing **5m** as colour less liquid. Yield: 0.250 g, 92%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.67 (s, 2H), 3.77 (s, 3H), 3.79 (s, 2H), 6.84 (d, 2H, J = 8.8 Hz), 7.07 (d, 2H, J = 8.4 Hz), 7.19-7.32 (m, 5H); ^{13}C NMR (100 MHz,

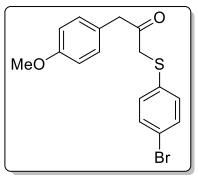
$CDCl_3$): δ 43.00, 46.84, 55.35, 114.33, 125.76, 127.00, 129.26, 129.76, 130.67, 134.80, 158.87, 203.31.; HRMS (ESI) exact mass calcd for $C_{16}H_{16}O_2S$ + K (M + K), 311.0508; Found: 311.0518

1-(4-Methoxyphenyl)-3-(p-tolylthio)propan-2-one (5n)



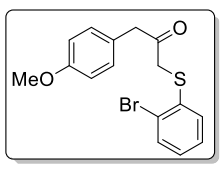
The title compound was prepared following the general procedure for Table 3, using 2-(4-methoxybenzyl)acrylonitrile **4d** (1.0 mmol, 0.173 g) and 4-methylbenzenethiol **2b** (2.0 mmol, 0.248 g), providing **5n** as colour less liquid. Yield: 0.257 g, 90%, ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (s, 3H), 3.63 (s, 2H), 3.77 (s, 3H), 3.79 (s, 2H), 6.84 (d, 2H, J = 8.4 Hz), 7.07-7.09 (m, 4H), 7.24 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.18, 43.68, 46.79, 55.33, 114.30, 125.87, 130.07, 130.69, 130.72, 130.95, 137.35, 158.84, 203.33.; HRMS (ESI) exact mass calcd for $C_{17}H_{18}O_2S$ + K (M + K), 325.0665; Found: 325.0671

1-((4-Bromophenyl)thio)-3-(4-methoxyphenyl)propan-2-one (5o)



The title compound was prepared following the general procedure for Table 3, using 2-(4-methoxybenzyl)acrylonitrile **4d** (1.0 mmol, 0.173 g) and 4-bromobenzenethiol **2d** (2.0 mmol, 0.378 g), providing **5o** as white solid. Yield: 0.309 g, 88%; M.P. 66 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.64 (s, 2H), 3.77 (s, 5H), 6.83 (d, 2H, J = 8.4 Hz), 7.06(d, 2H, J = 8.4 Hz), 7.13 (d, 2H, J = 8.8 Hz). 7.35 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 42.85; 46.94, 55.35, 114.36, 120.98, 125.47, 130.59, 131.27, 132.24, 133.91, 158.93, 202.78; HRMS (ESI) exact mass calcd for $C_{16}H_{15}BrO_2S$ + K (M + K), 388.9613; Found: 388.9608

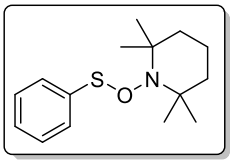
1-((2-Bromophenyl)thio)-3-(4-methoxyphenyl)propan-2-one (5p)



The title compound was prepared following the general procedure for Table 3, using 2-(4-methoxybenzyl)acrylonitrile **4d** (1.0 mmol, 0.173 g), and 2-bromobenzenethiol **2e** (2.0 mmol, 0.378 g),

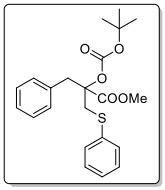
providing **5p** as colourless liquid Yield: 0.277 g, 79%, ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.70 (s, 2H), 3.77 (s, 3H), 3.82 (s, 2H), 6.83 (d, 2H, J = 8.4 Hz), 7.01-7.05 (m, 1H), 7.09 (d, 2H, J = 8.8 Hz). 7.18-7.20 (m, 2H), 7.52 (d, 1H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 41.93, 46.87, 55.36, 114.36, 123.92, 125.52, 127.68, 128.11, 129.20, 130.64, 133.24, 136.06, 158.90, 203.02; HRMS (ESI) exact mass calcd for $C_{16}H_{15}BrO_2S$ + K (M + K), 388.9613; Found: 388.9608

2,2,6,6-Tetramethyl-1-((phenylthio)oxy)piperidine (6)

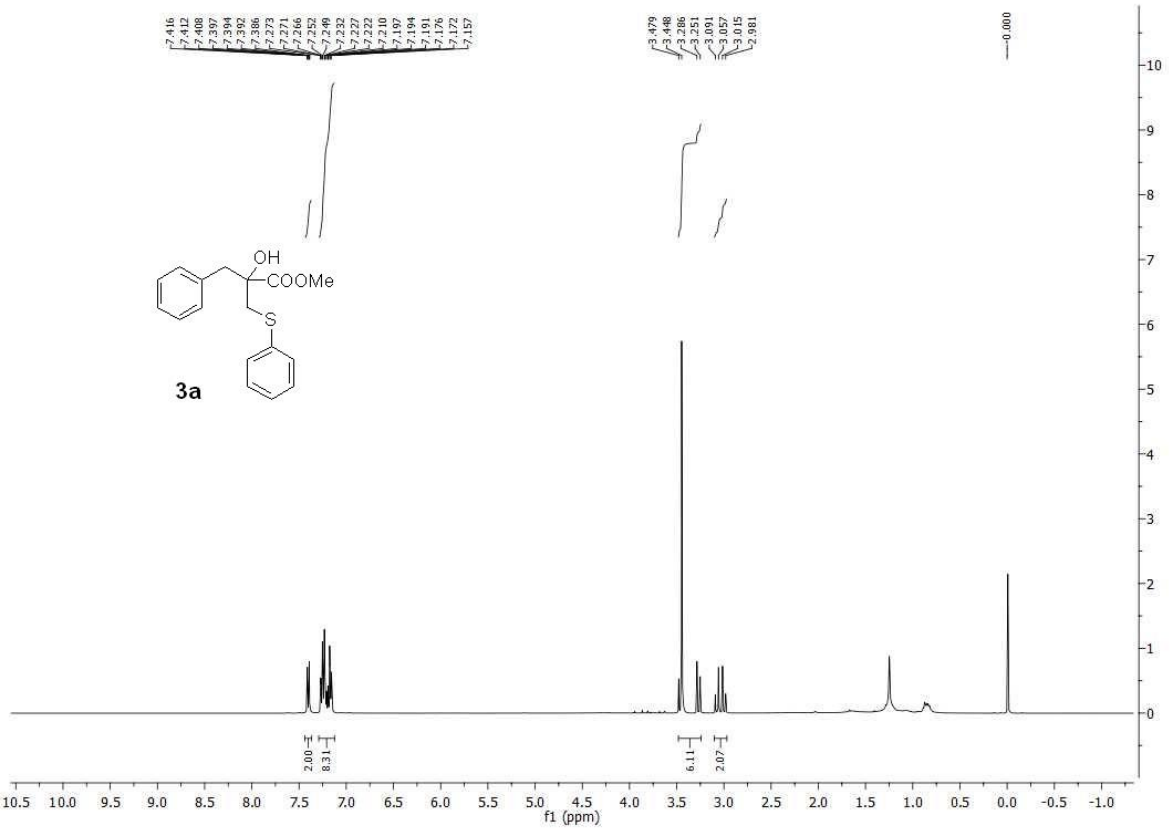


^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (s, 3H), 1.50-1.66 (m, 15H), 7.36-7.46 (m, 3H), 7.67-7.69 (m, 2H); HRMS (ESI) exact mass calcd for $C_{15}H_{23}NOS$ + Na (M + Na), 288.1398; Found: 288.1392

2-Benzyl-1-(methylperoxy)-3-(phenylthio)-1λ^2-propan-2-yl tert-butyl carbonate (7)



^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (s, 9H), 3.35 (dd, 2H, J = 14.0 & 1.6 Hz), 3.55 (s, 3H), 3.58-3.66 (m, 2H), 7.11-7.13 (m, 2H), 7.21-7.30 (m, 7H), 7.42-7.44 (m, 2H).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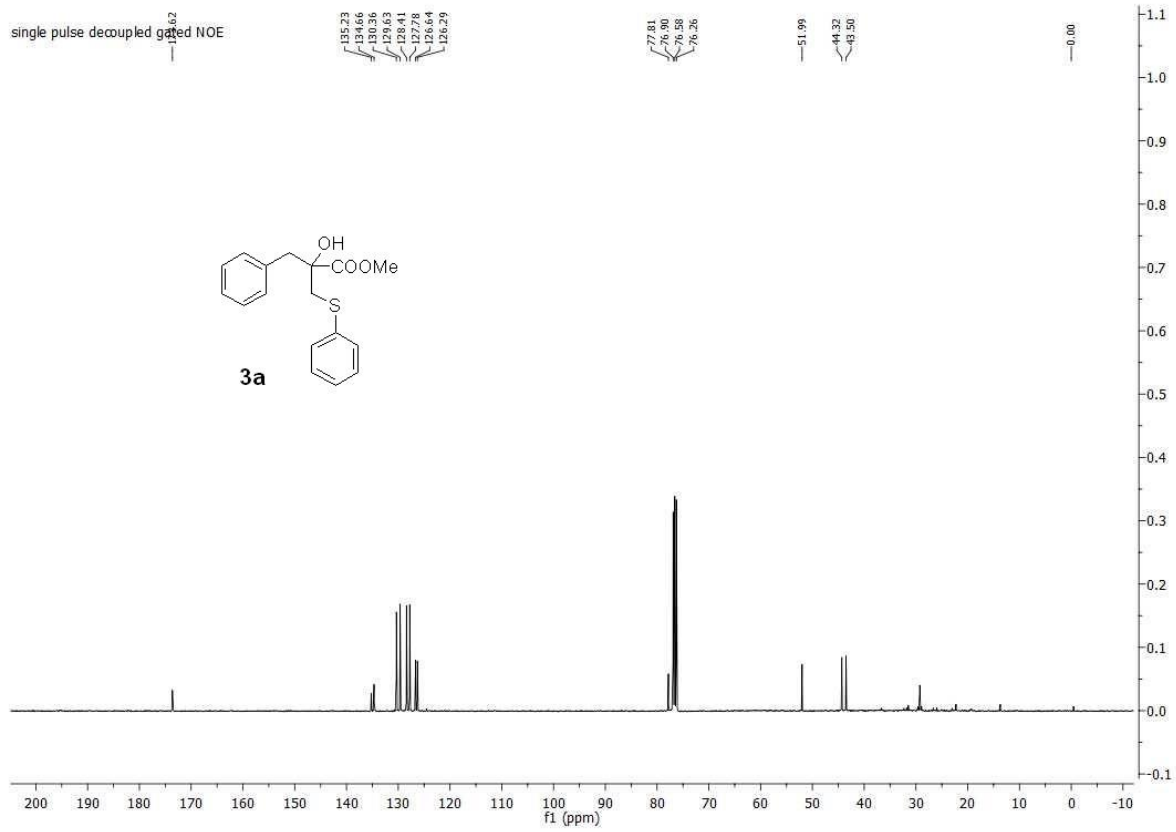
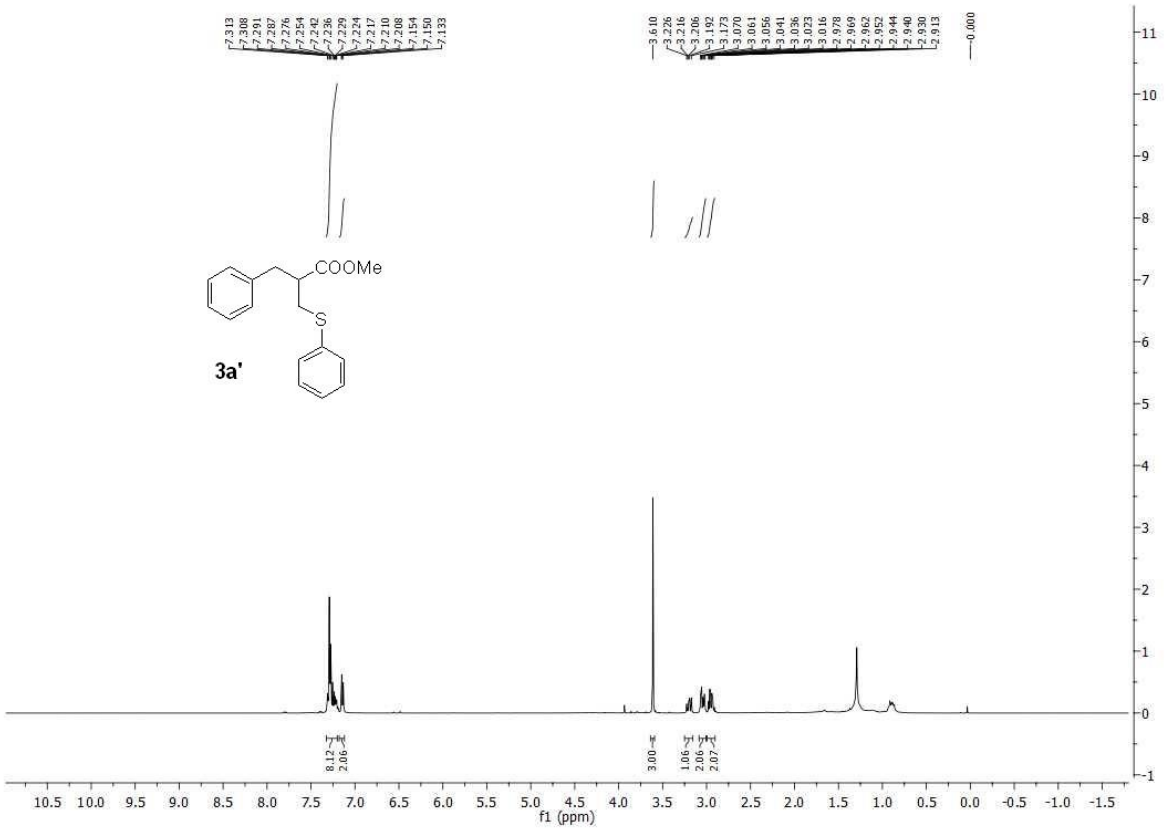
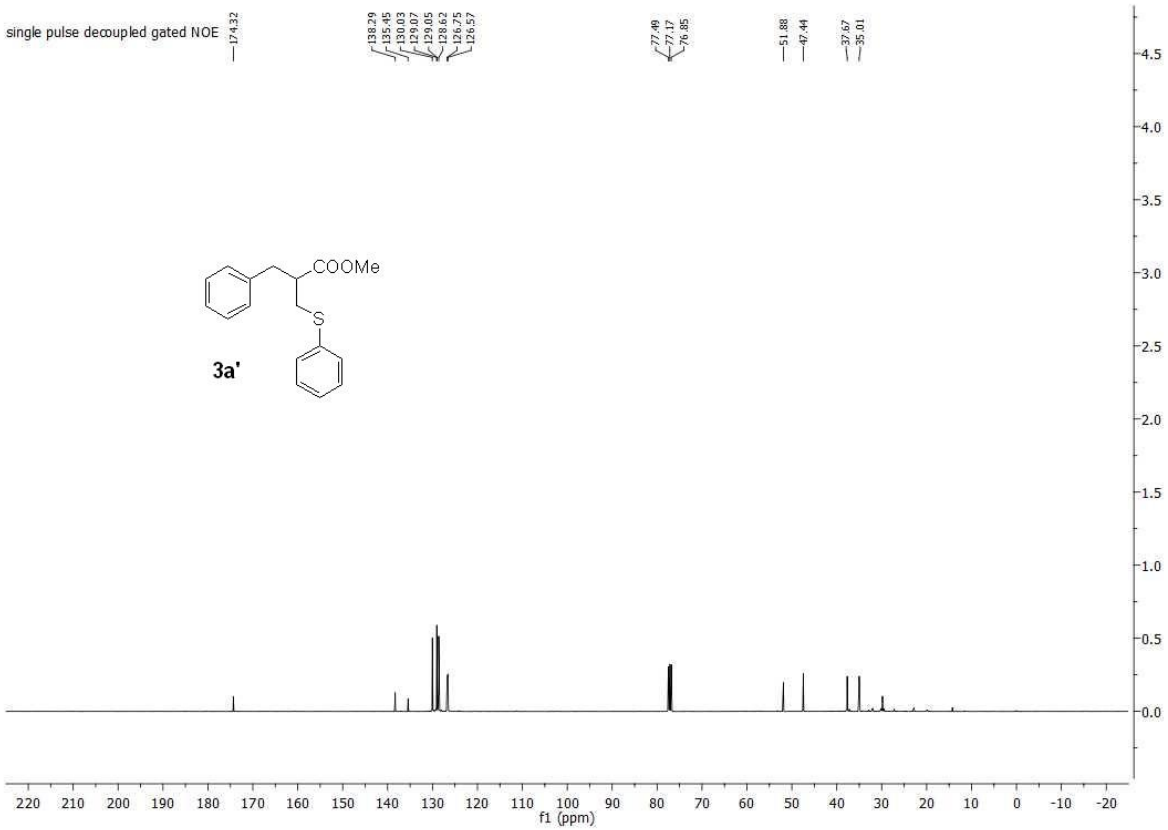
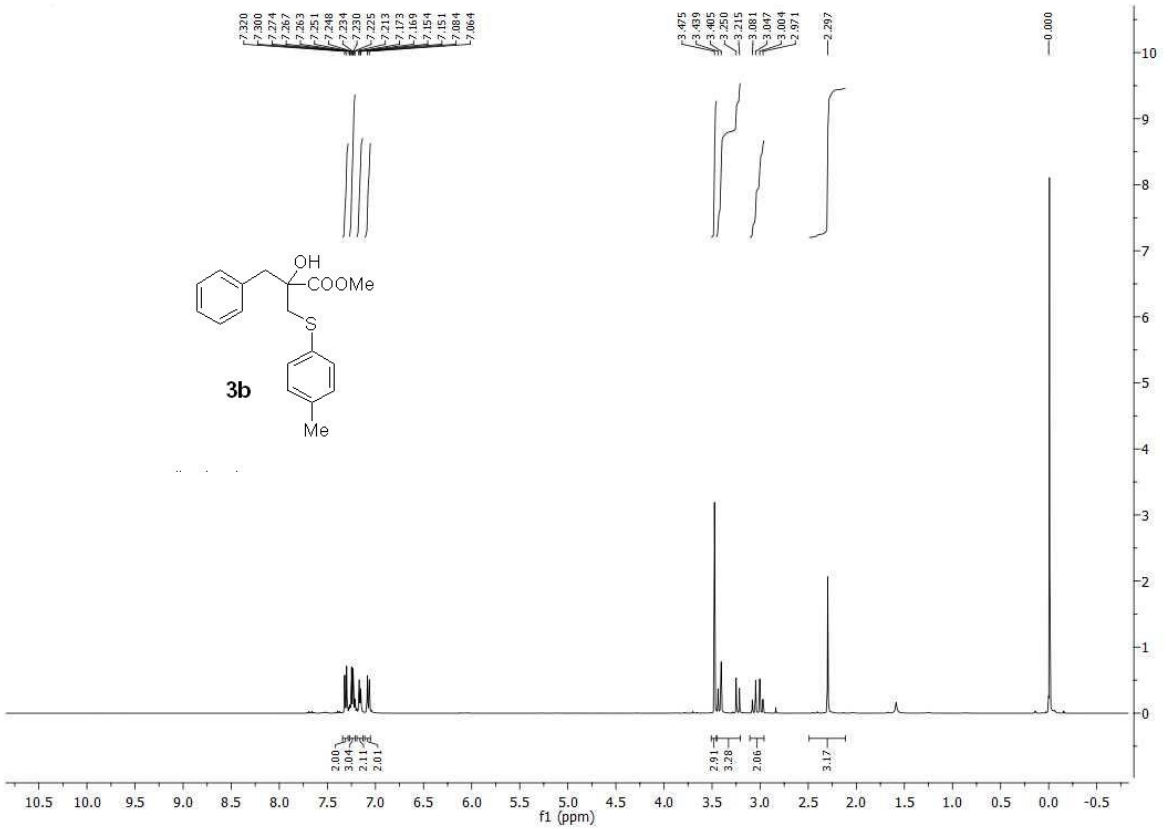
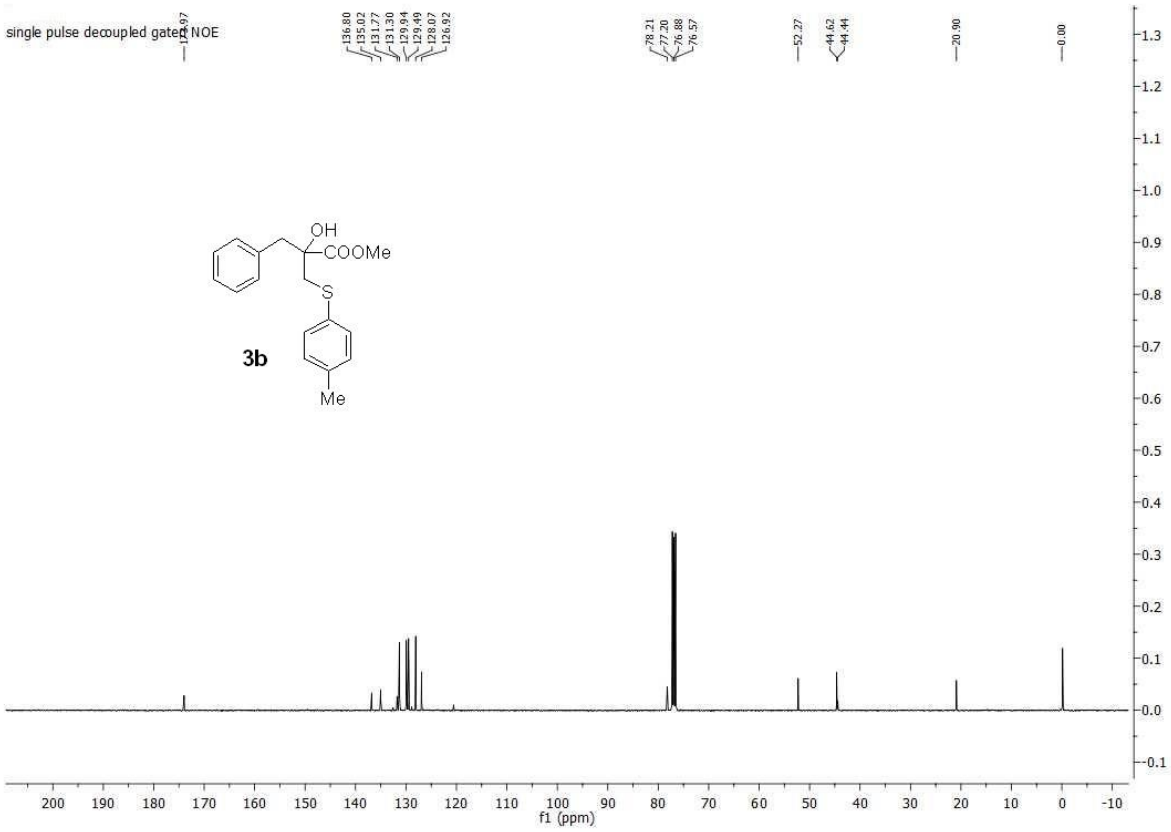
7.412
7.408
7.397
7.394
7.392
7.386
7.273
7.271
7.266
7.252
7.249
7.232
7.227
7.222
7.210
7.197
7.194
7.191
7.176
7.172
7.157
3.479
3.448
3.286
3.251
3.091
3.057
3.015
2.981
0.000
OH
COOMe
S
3a
2.00
8.31
6.11
2.07
f1 (ppm)

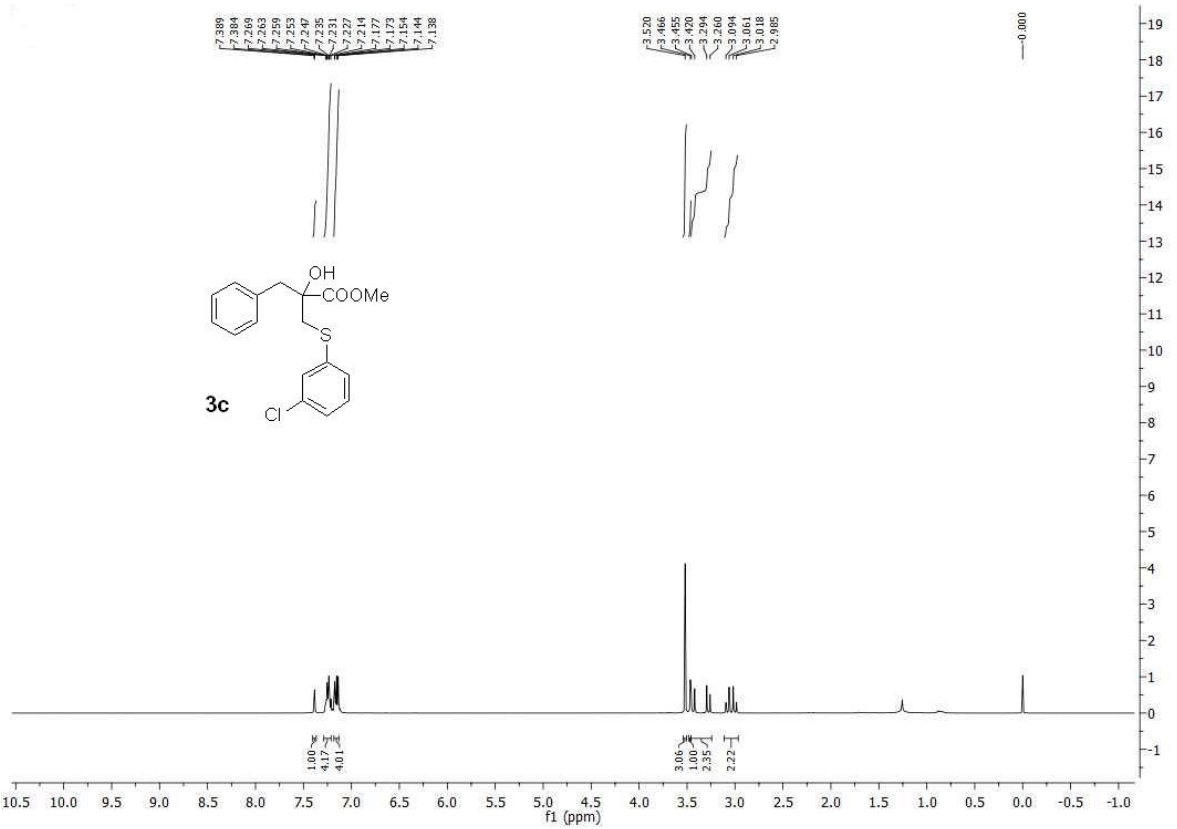

single pulse decoupled gated NOE
135.23
134.66
130.36
129.63
128.41
127.78
126.64
126.29
77.81
76.90
76.58
76.26
51.99
44.32
43.50
0.00
OH
COOMe
S
3a
f1 (ppm)


COOMe
S
3a'
f1 (ppm)


single pulse decoupled gated NOE
COOMe
S
3a'
f1 (ppm)


OH
COOMe
S
3b
Me
f1 (ppm)


single pulse decoupled gated NOE
OH
COOMe
S
3b
Me
f1 (ppm)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7.384
7.269
7.263
7.259
7.253
7.247
7.235
7.231
7.227
7.214
7.177
7.173
7.154
7.144
7.138
3.520
3.466
3.455
3.420
3.294
3.260
3.094
3.061
3.018
2.985
0.000
OH
COOMe
S
Cl
3c
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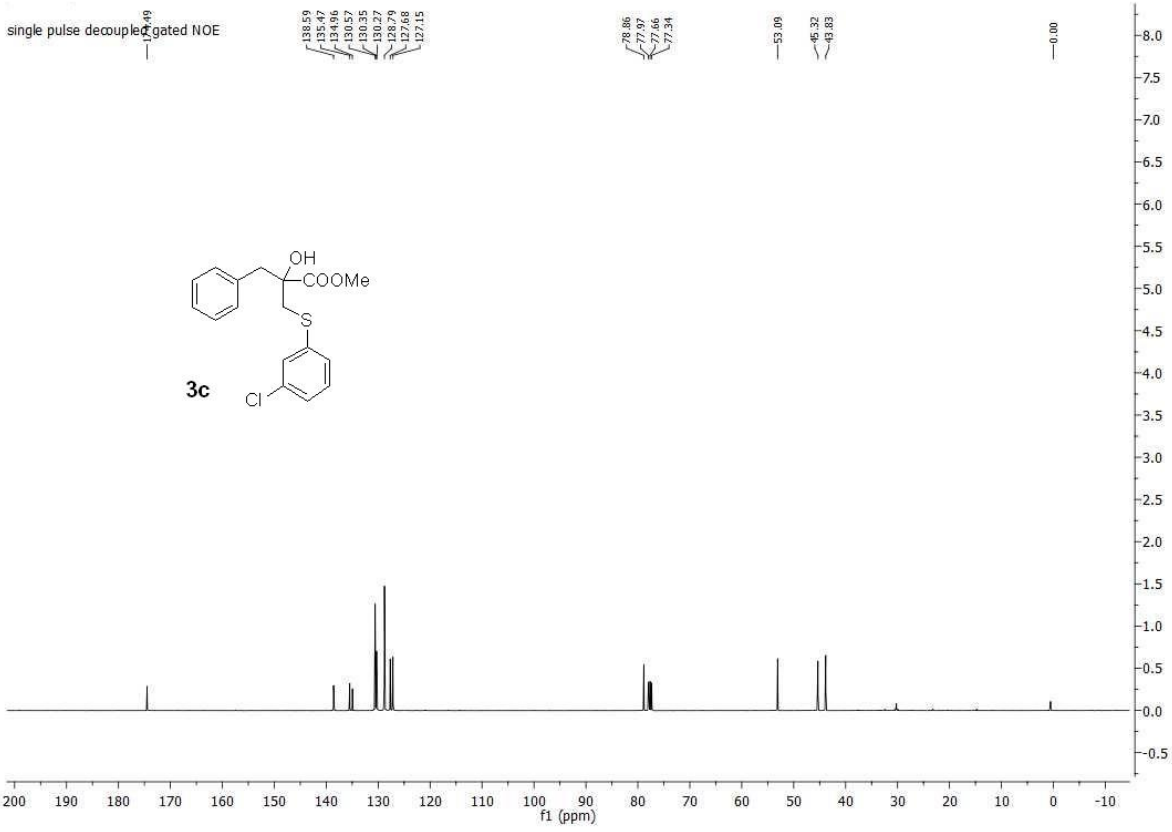
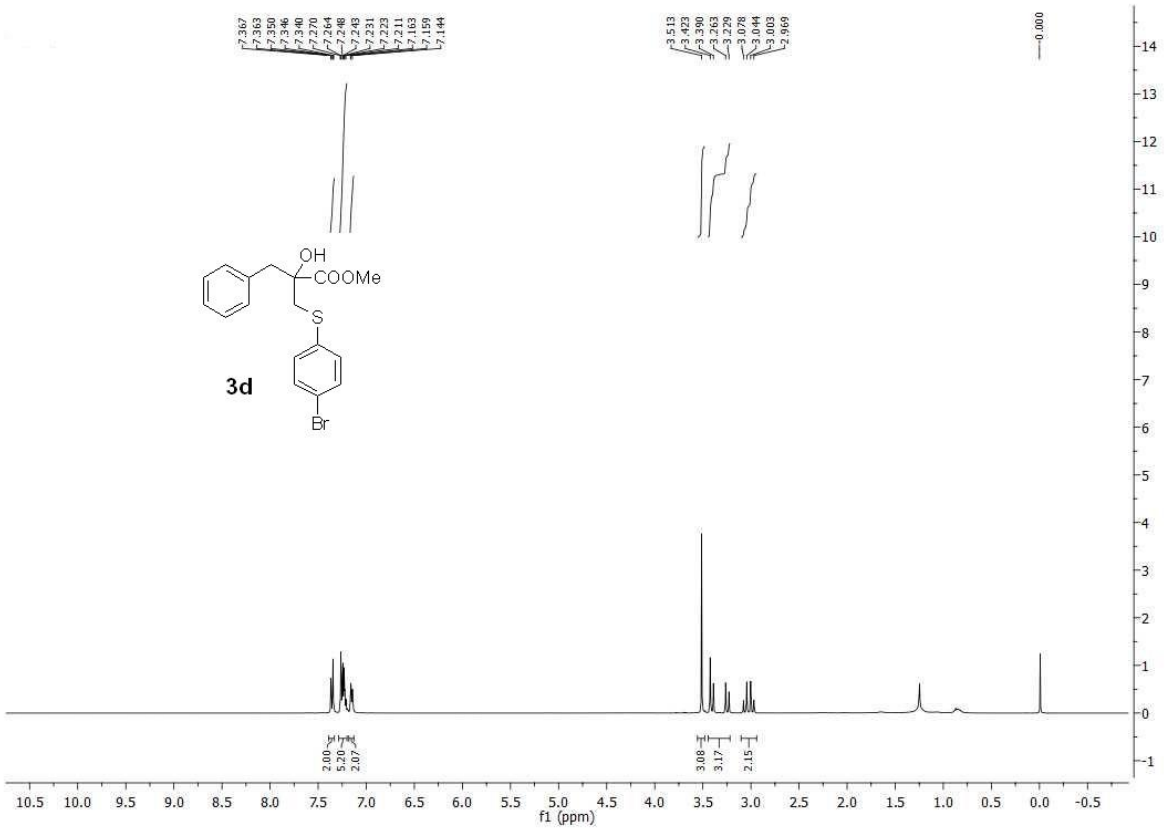
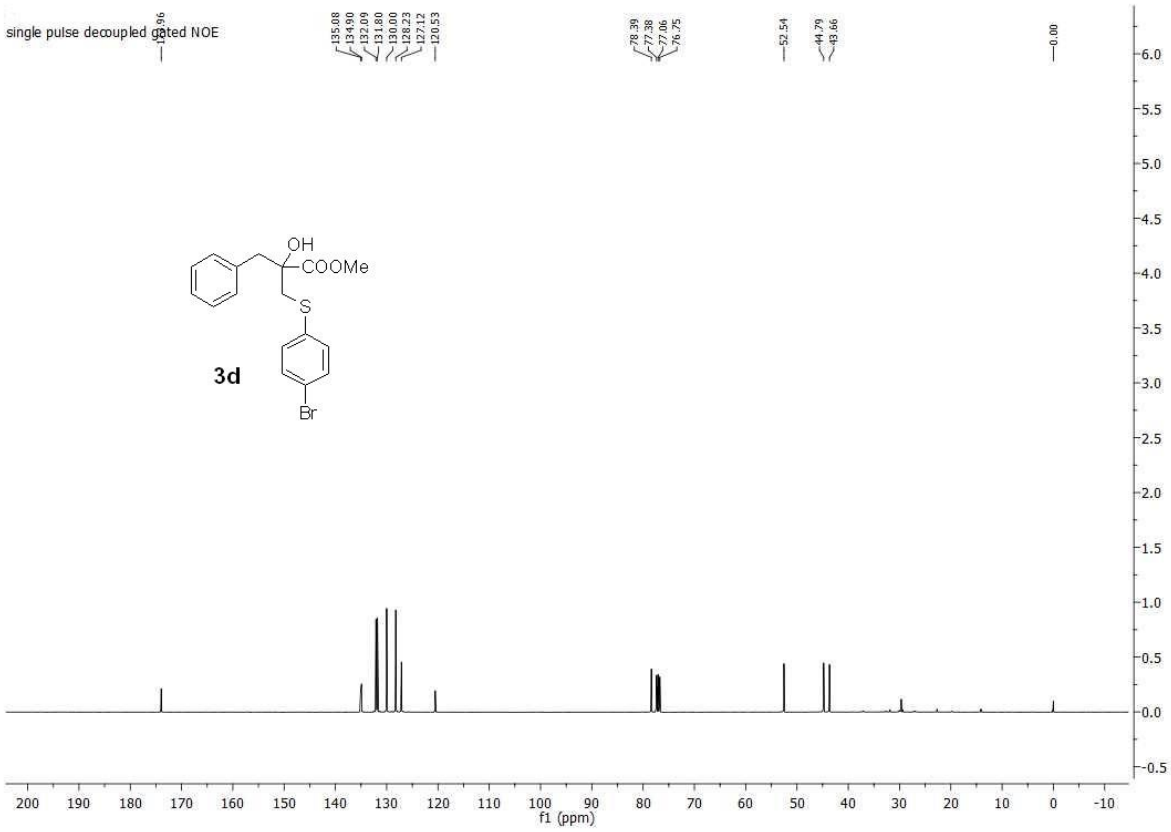
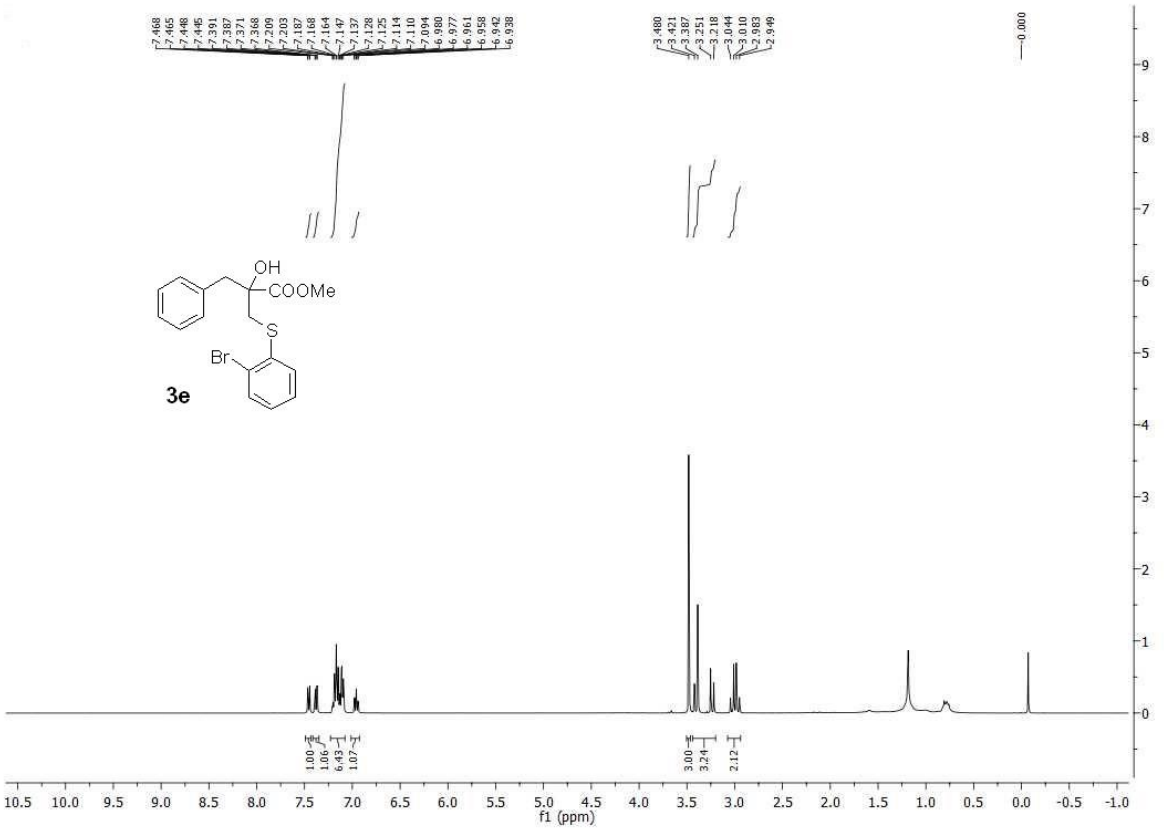
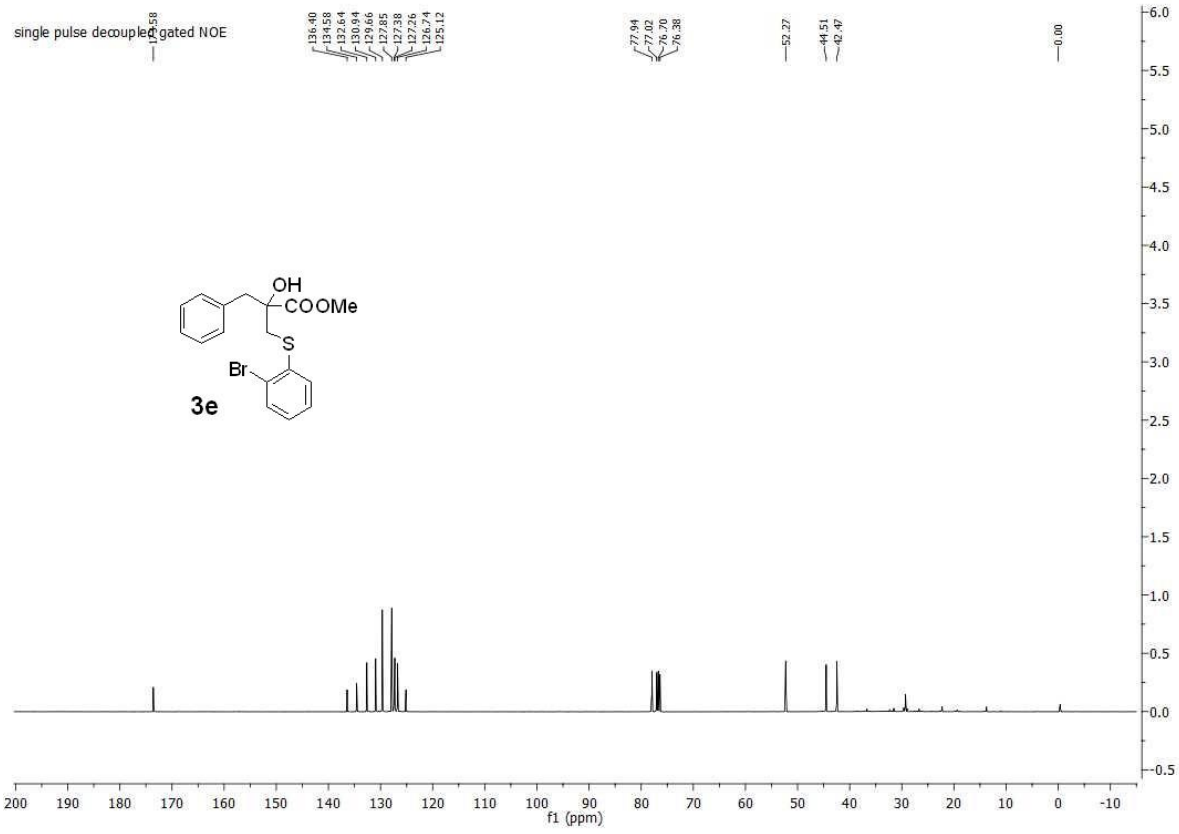
4.17
4.01
3.06
1.00
2.35
2.22
f1 (ppm)

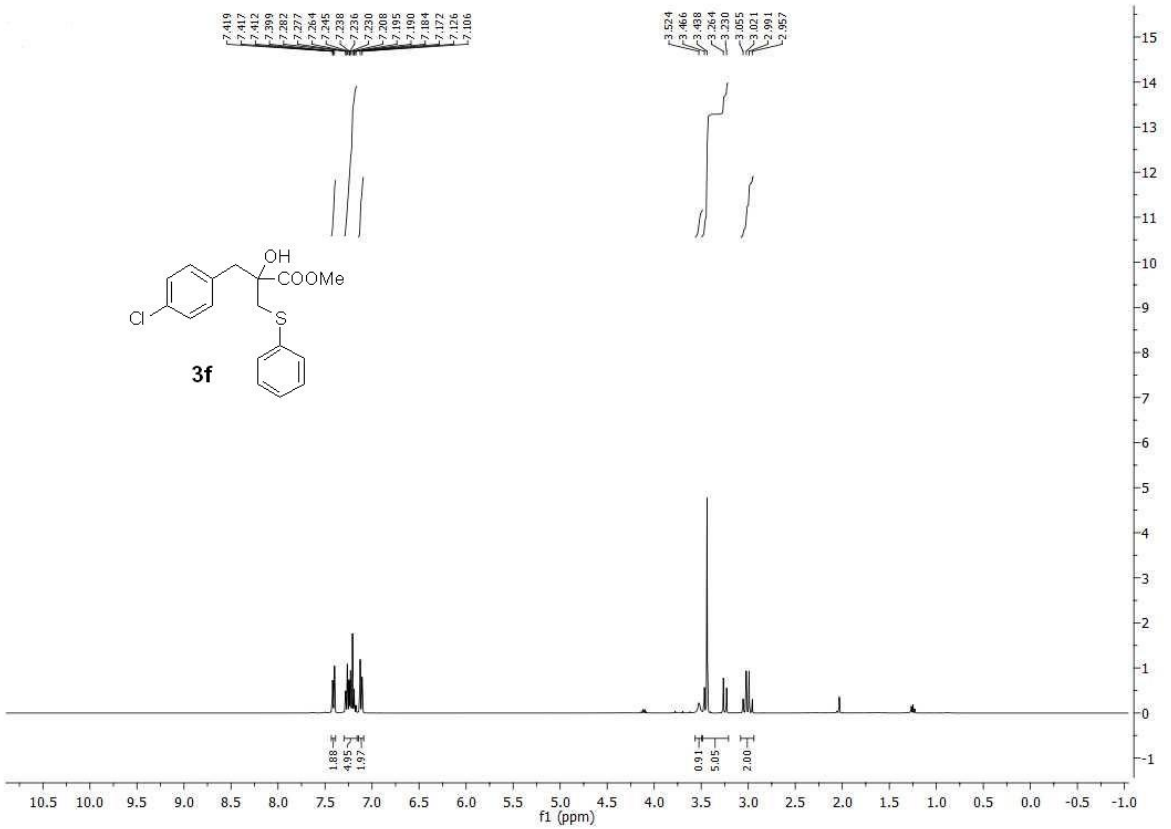

single pulse decoupled gated NOE
174.49
138.59
135.47
134.96
130.57
130.35
130.27
128.79
127.68
127.15
78.86
77.97
77.66
77.34
53.09
45.32
43.83
0.00
OH
COOMe
S
Cl
3c
f1 (ppm)


OH
COOMe
S
Br
3d
f1 (ppm)


single pulse decoupled gated NOE
OH
COOMe
S
Br
3d
f1 (ppm)


OH
COOMe
S
Br
3e
f1 (ppm)


single pulse decoupled gated NOE
OH
COOMe
S
Br
3e
f1 (ppm)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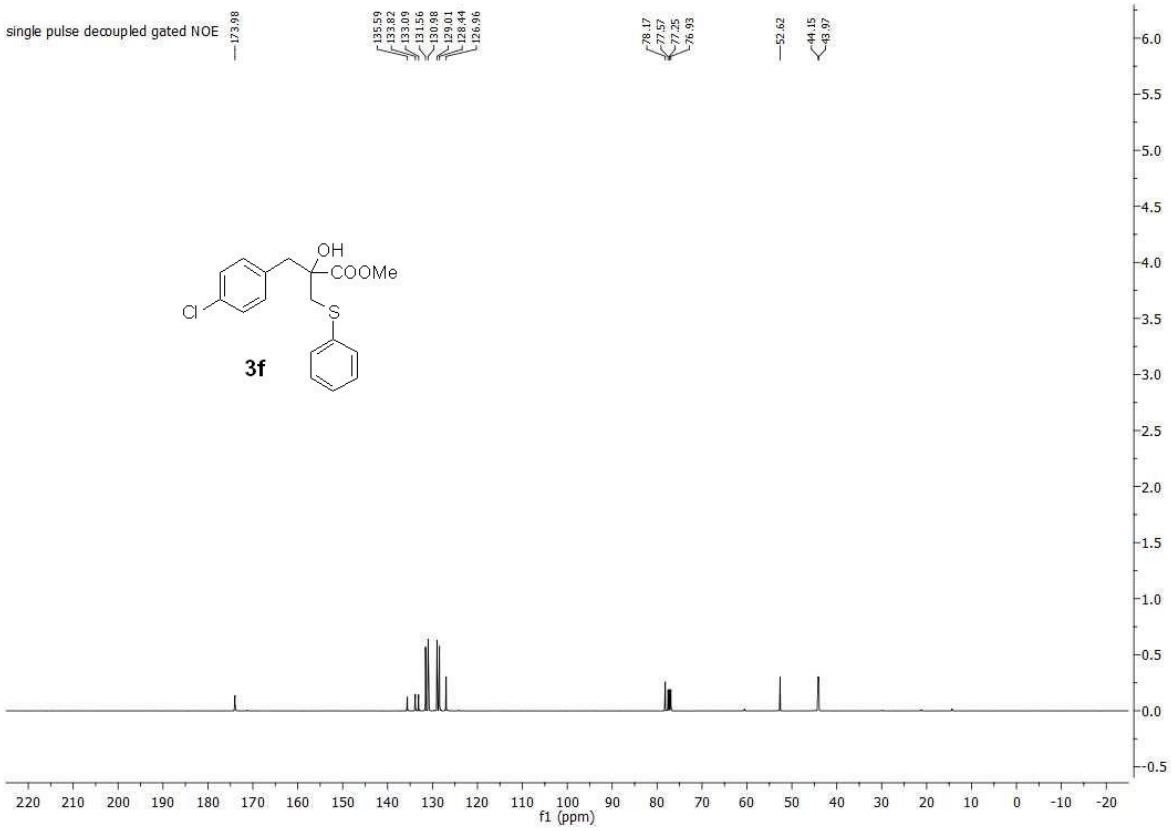
7.282
7.277
7.264
7.245
7.238
7.236
7.230
7.208
7.195
7.190
7.184
7.172
7.126
7.106
3.524
3.466
3.438
3.264
3.230
3.055
3.021
2.991
2.957
OH
COOMe
Cl
S
3f
1.88
4.95
1.97
0.91
5.05
2.00
f1 (ppm)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133.82
133.09
131.56
130.98
129.01
128.44
126.96
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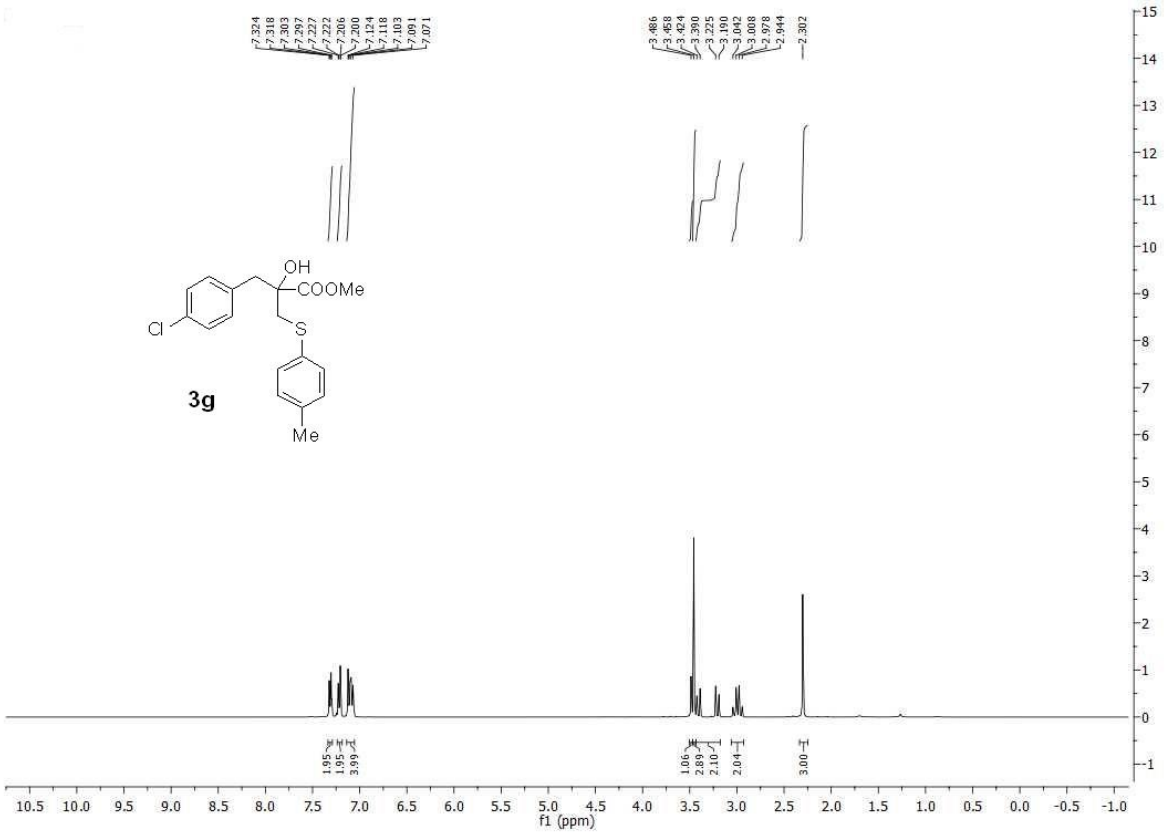
77.57
77.25
76.93
52.62
44.15
43.97
OH
COOMe
Cl
S
3f
f1 (ppm)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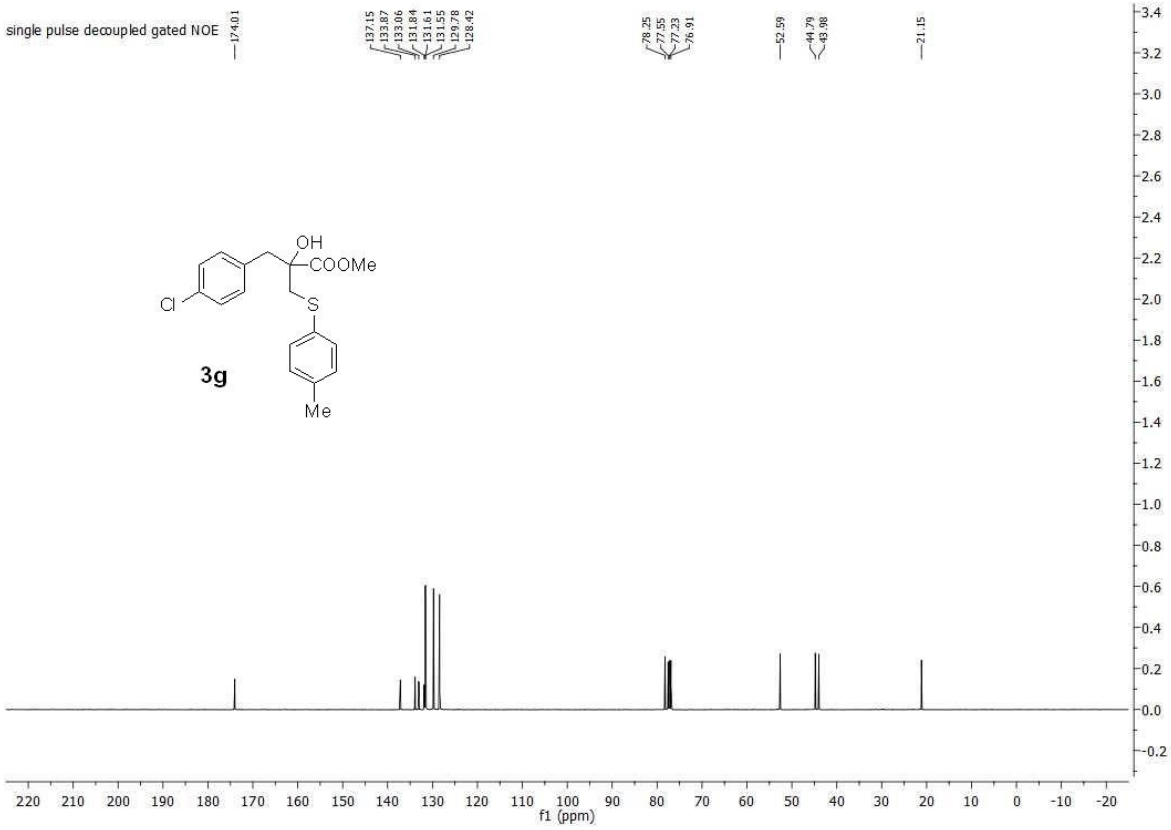
7.227
7.222
7.206
7.200
7.124
7.118
7.103
7.091
7.071
3.486
3.458
3.424
3.390
3.225
3.190
3.042
3.008
2.978
2.944
2.302
OH
COOMe
Cl
S
Me
3g
1.95
1.95
3.99
1.06
2.89
2.10
2.04
3.00
f1 (ppm)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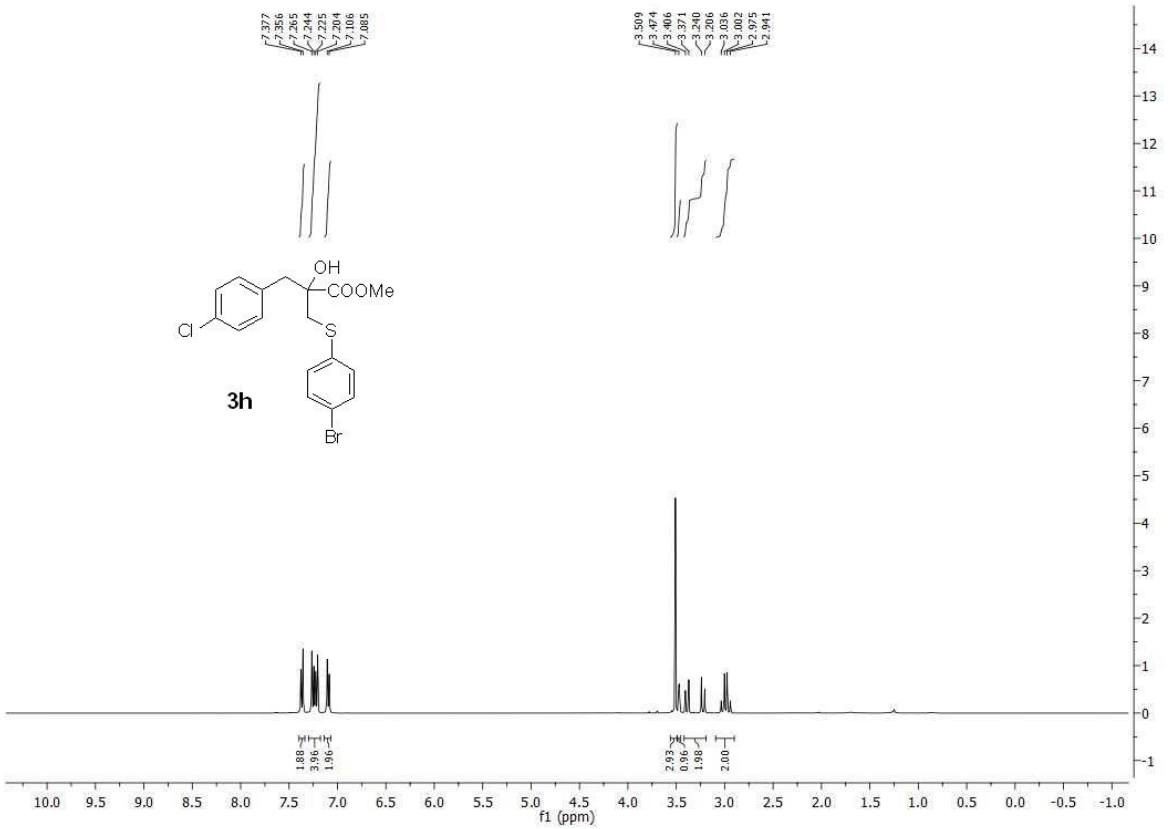
133.06
131.84
131.61
131.55
129.78
128.42
78.25
77.55
77.23
76.91
52.59
44.79
43.98
21.15
OH
COOMe
Cl
S
Me
3g
f1 (ppm)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7.265
7.244
7.225
7.204
7.106
7.085
3.509
3.474
3.406
3.371
3.240
3.206
3.036
3.002
2.975
2.941
OH
COOMe
Cl
S
Br
3h
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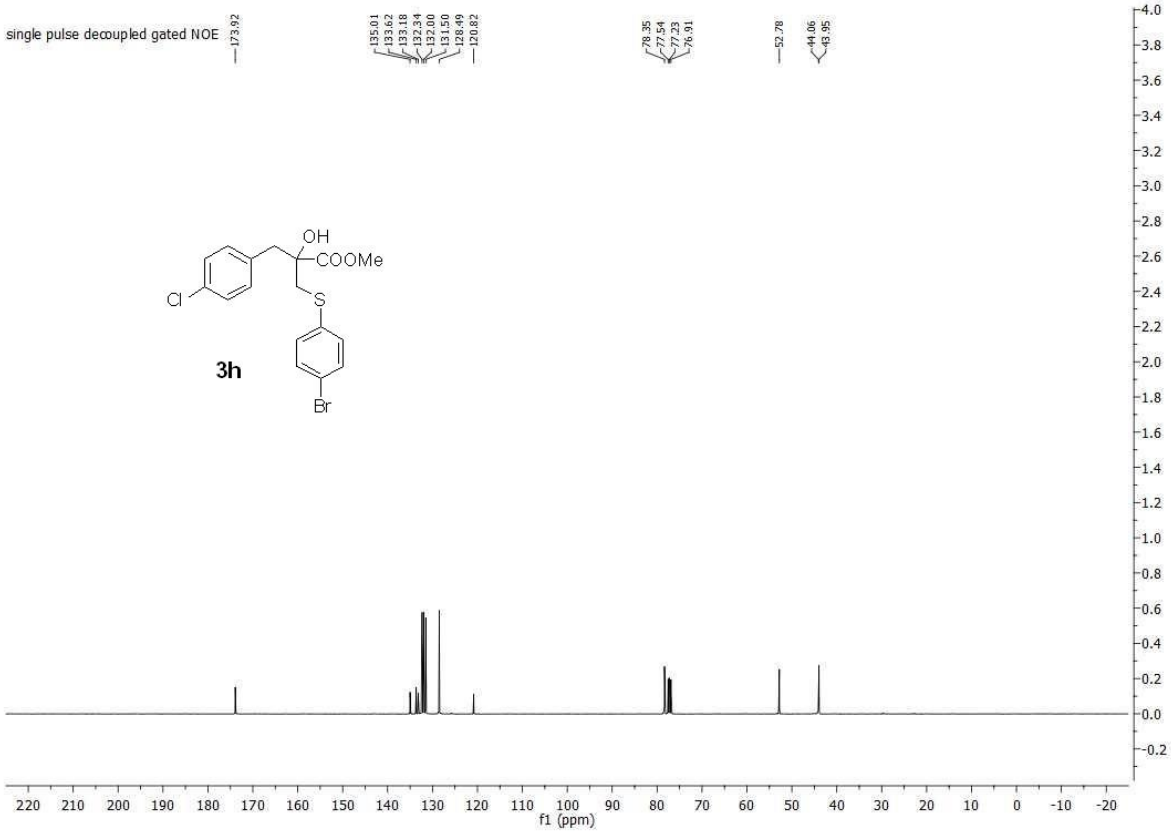
3.96
1.96
2.93
0.96
1.98
2.00
f1 (ppm)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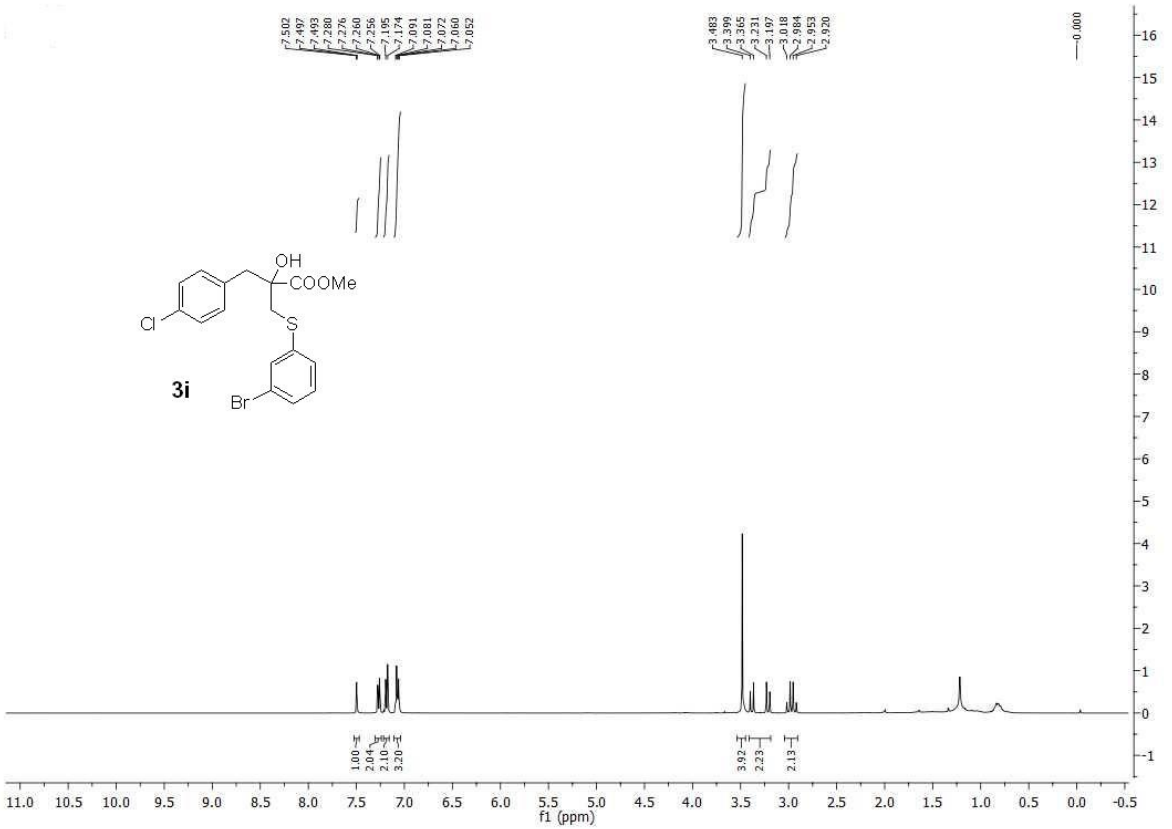
133.62
133.18
132.34
132.00
131.50
128.49
120.82
78.35
77.54
77.23
76.91
52.78
44.06
43.95
OH
COOMe
Cl
S
Br
3h
f1 (ppm)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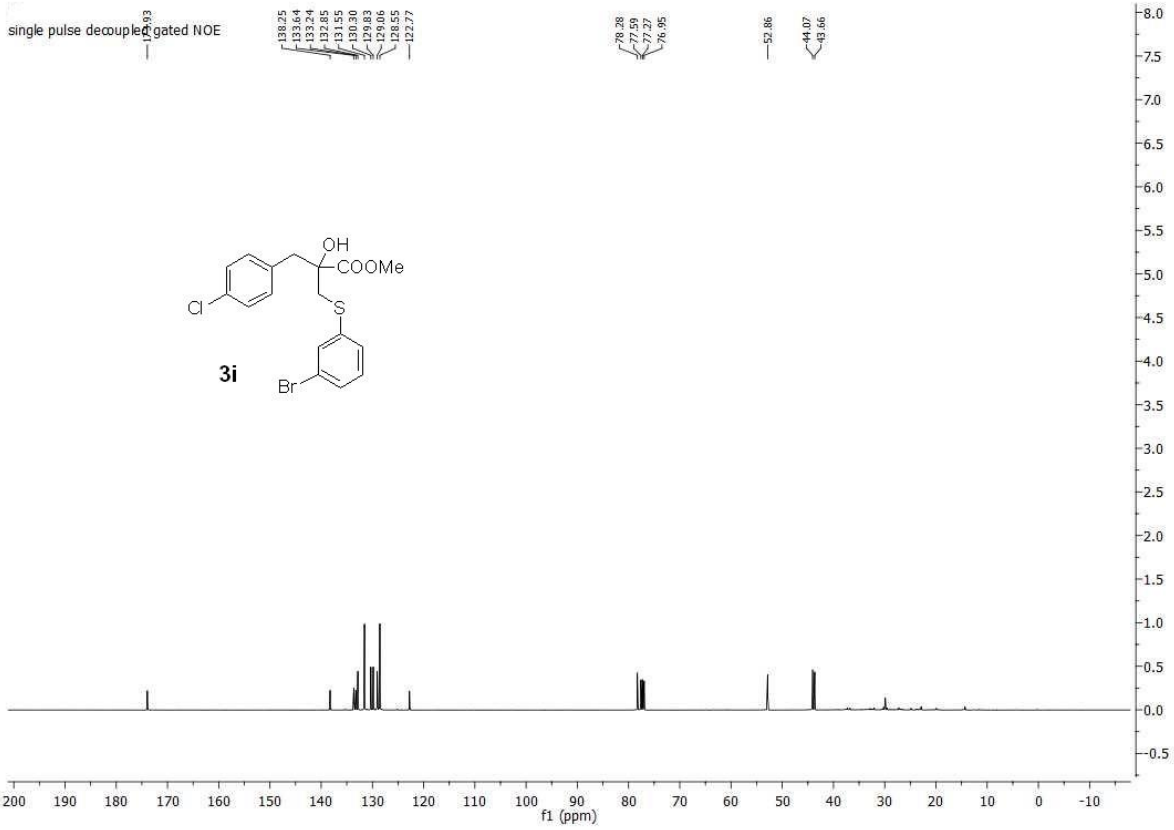
7.091
7.081
7.072
7.060
7.052
3.483
3.399
3.365
3.231
3.197
3.018
2.984
2.953
2.920
0.000
OH
COOMe
Cl
S
Br
3i
1.00
2.04
2.10
3.20
3.92
2.23
2.13
f1 (ppm)


single pulse decoupled gated NOE
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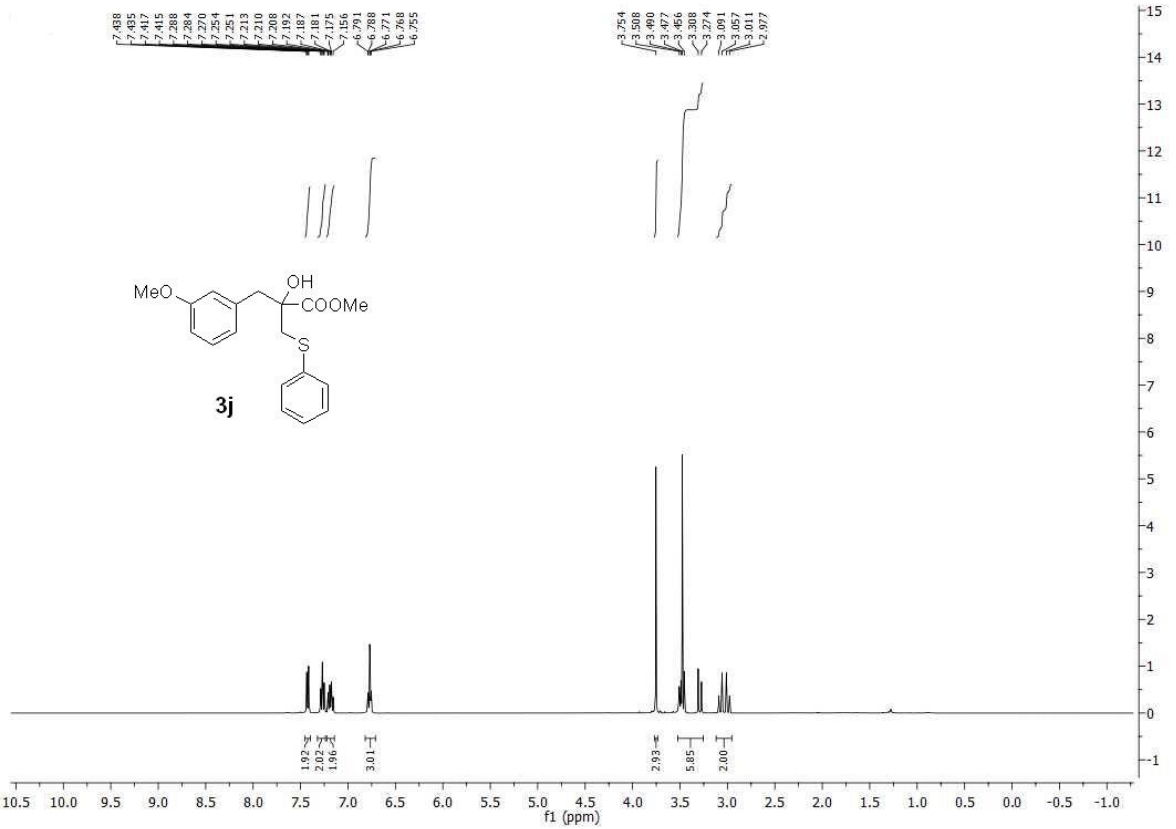
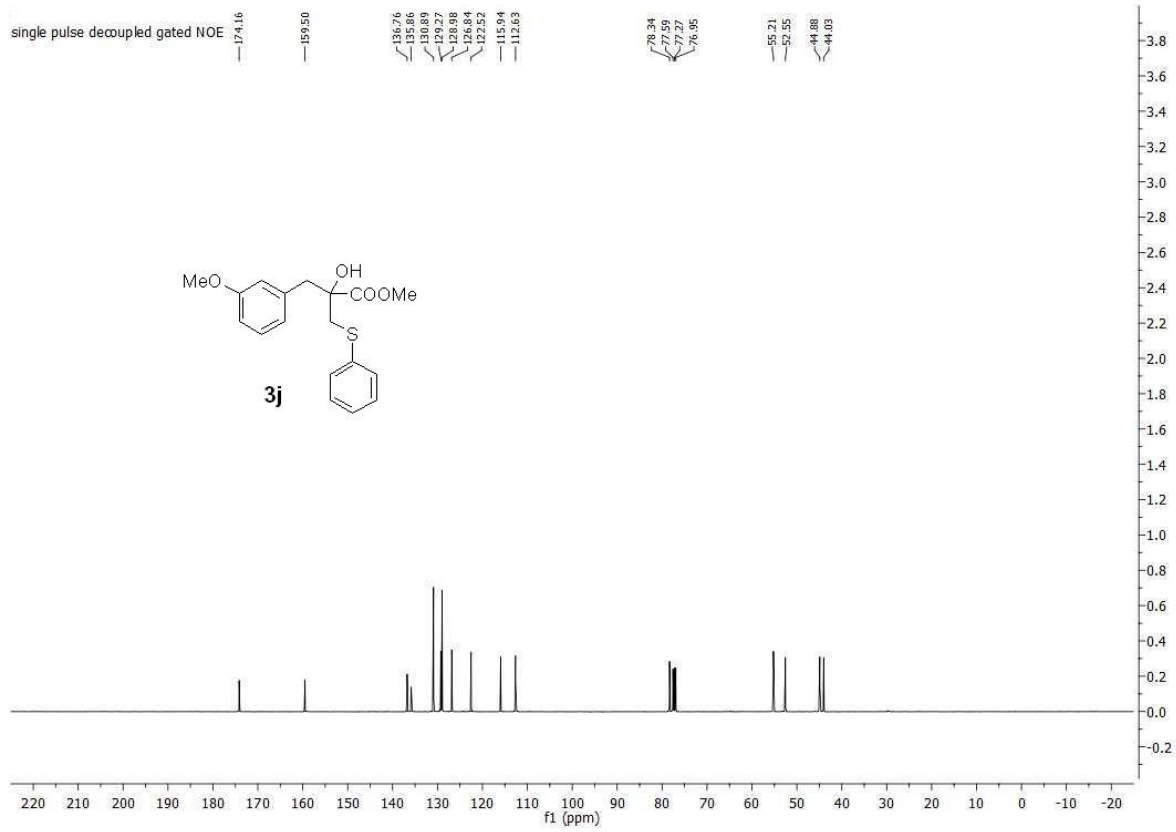
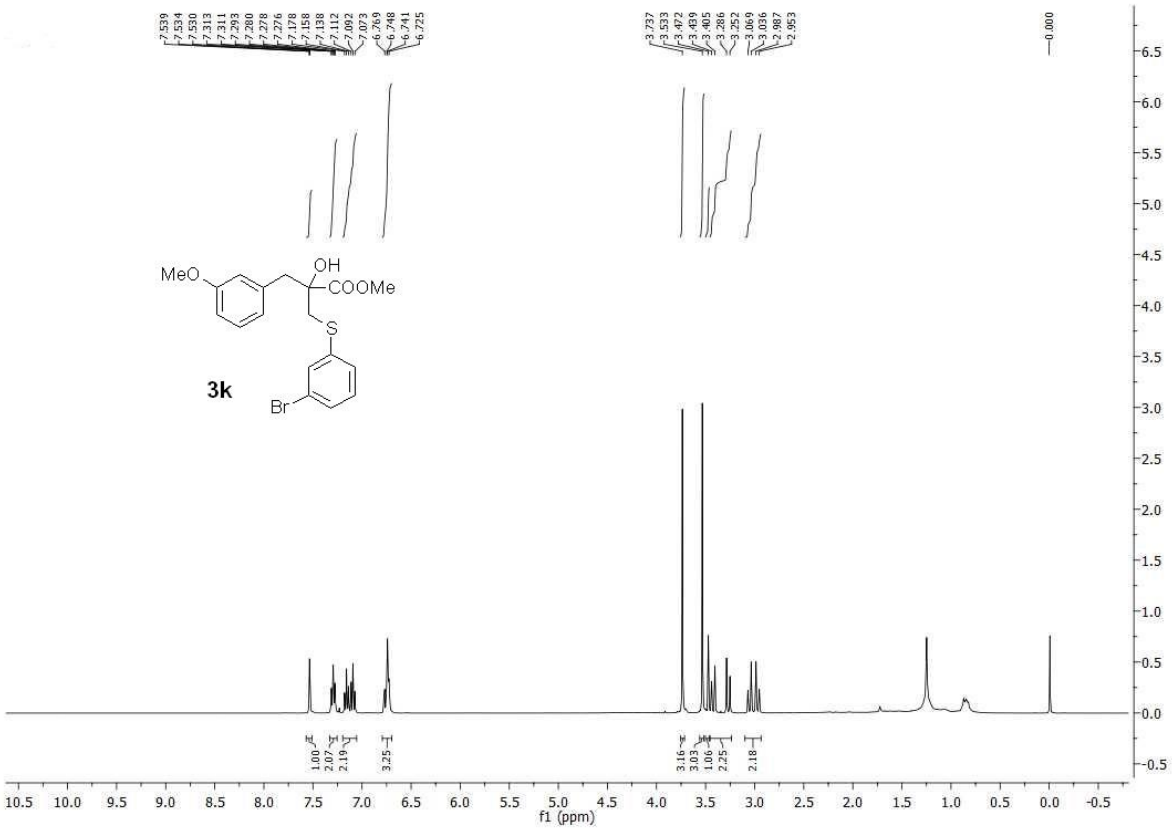
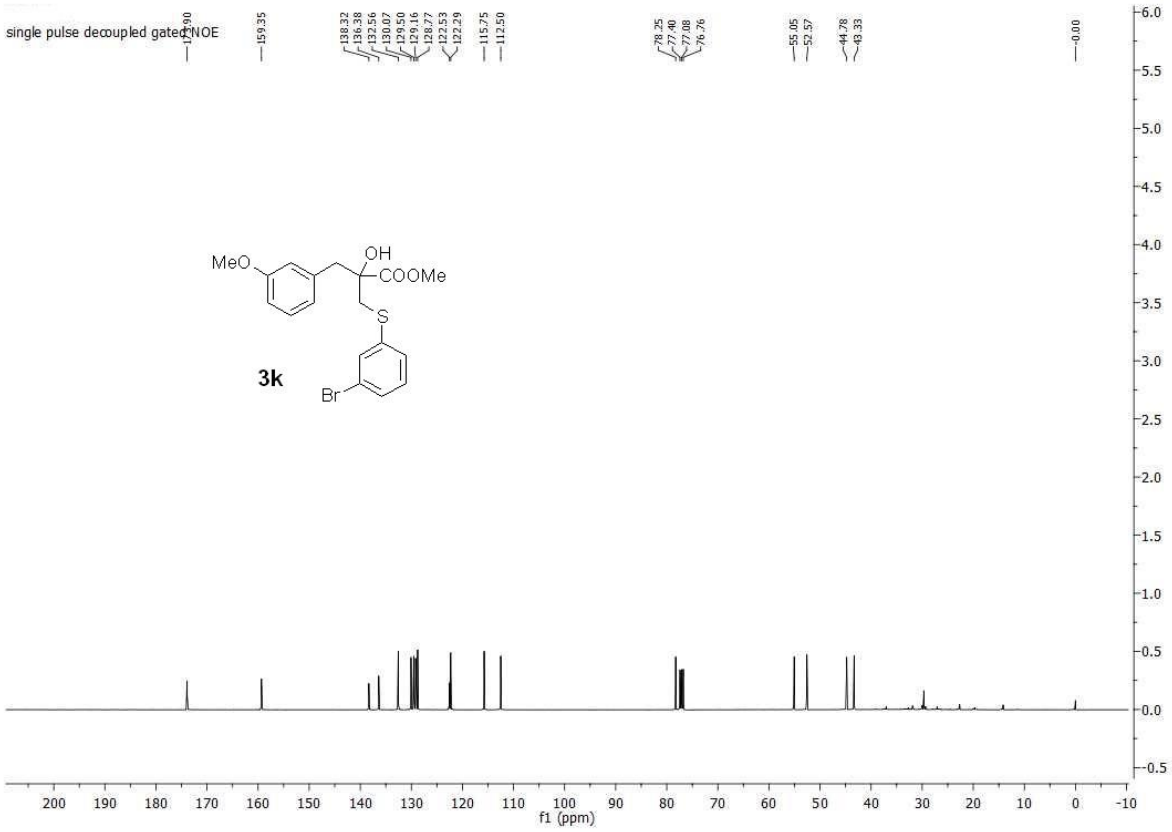
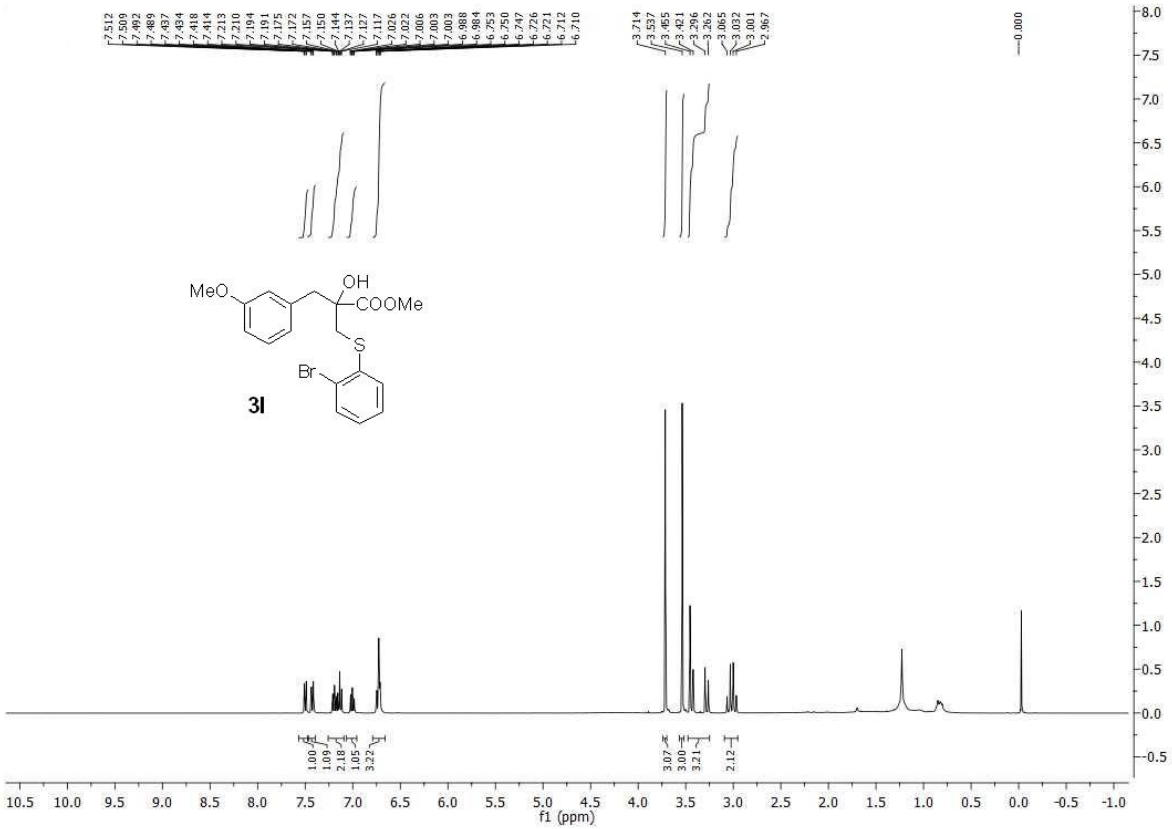
133.64
133.24
132.85
131.55
130.30
129.83
129.06
128.55
122.77
79.28
77.59
77.27
76.95
52.86
44.07
43.66
OH
COOMe
Cl
S
Br
3i
f1 (ppm)


MeO
OH
COOMe
S
3j
f1 (ppm)


single pulse decoupled gated NOE
MeO
OH
COOMe
S
3j
f1 (ppm)


MeO
OH
COOMe
S
Br
3k
f1 (ppm)


single pulse decoupled gated NOE
MeO
OH
COOMe
S
Br
3k
f1 (ppm)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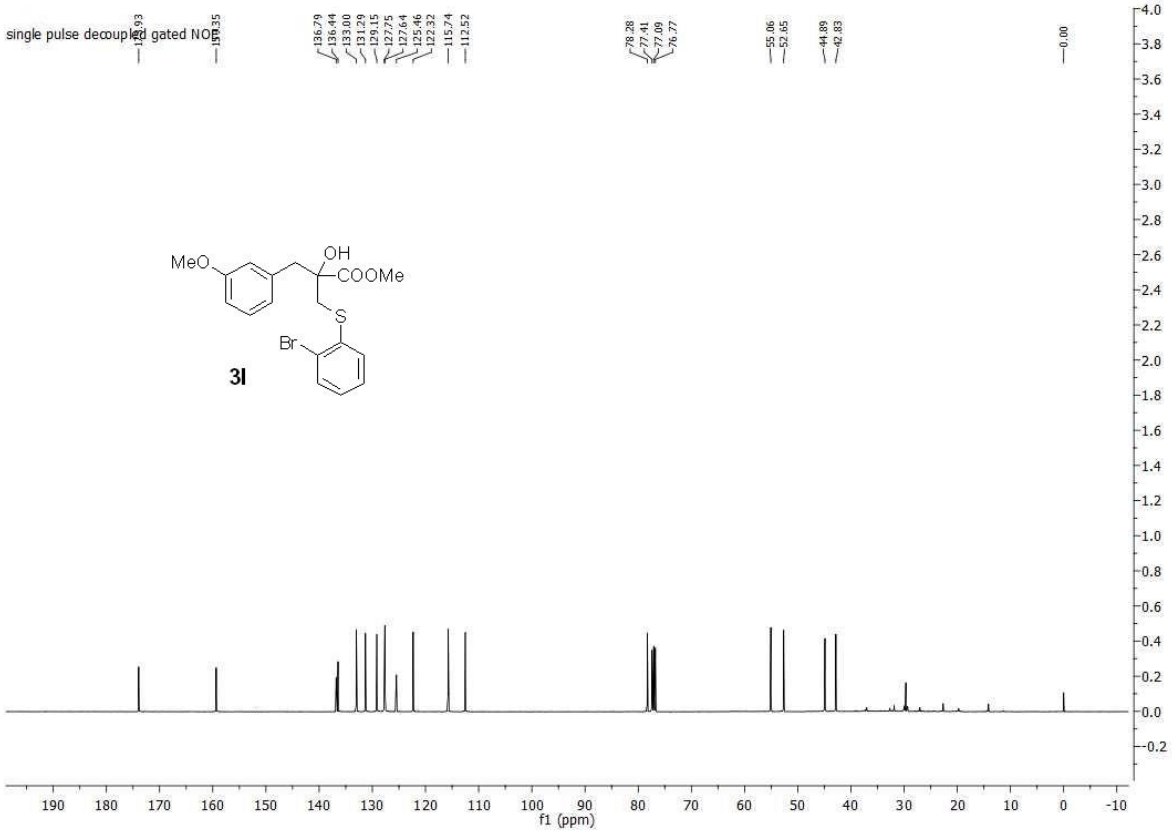
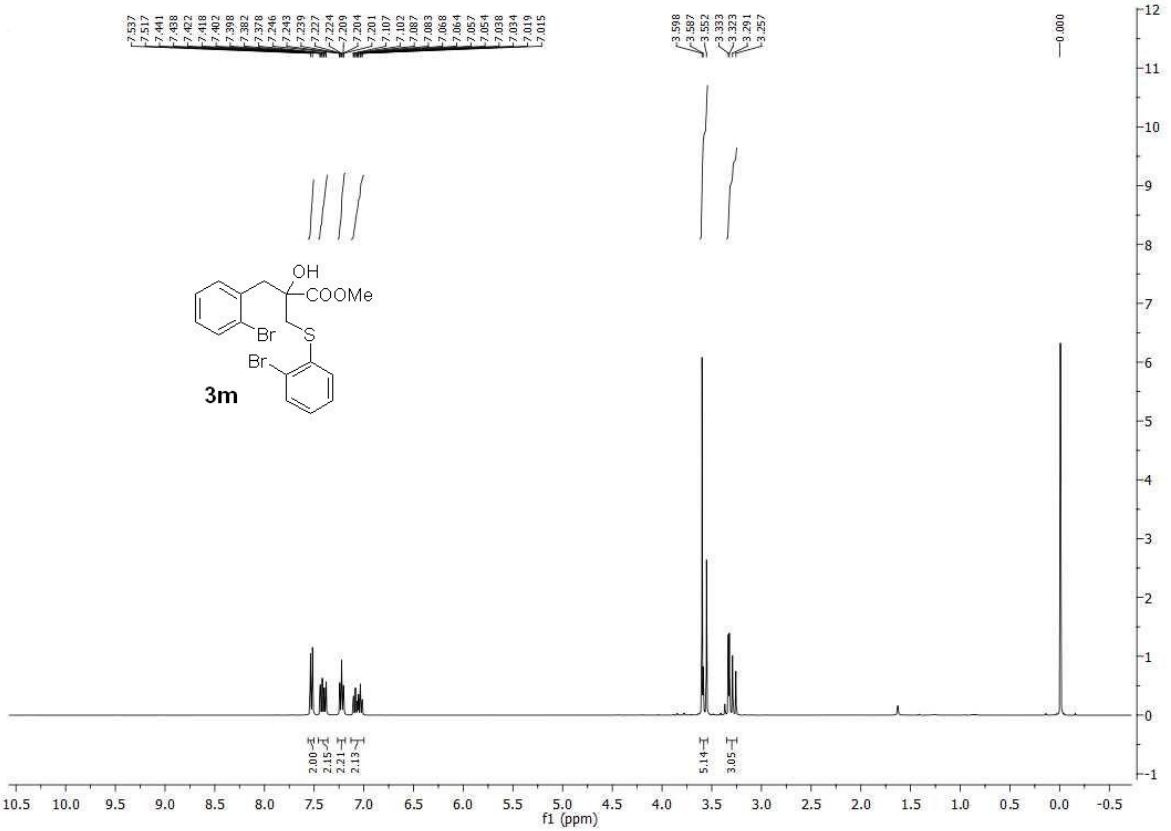
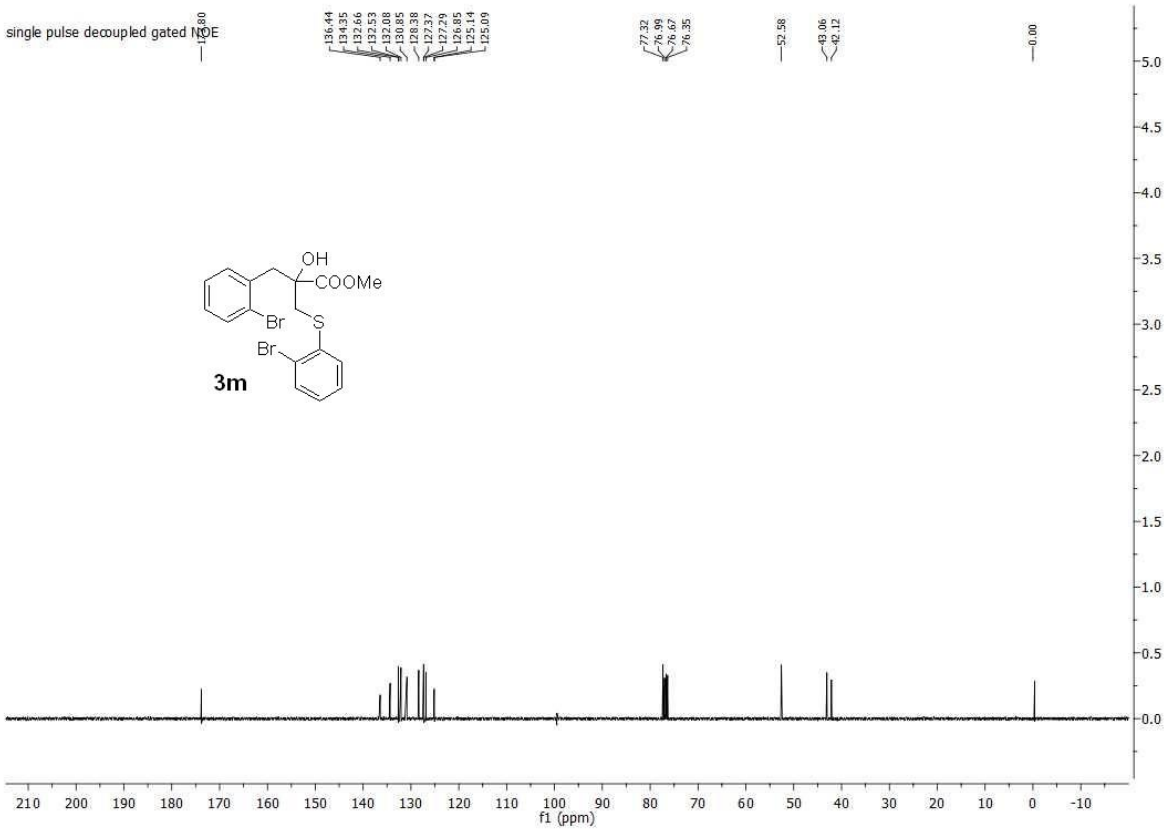
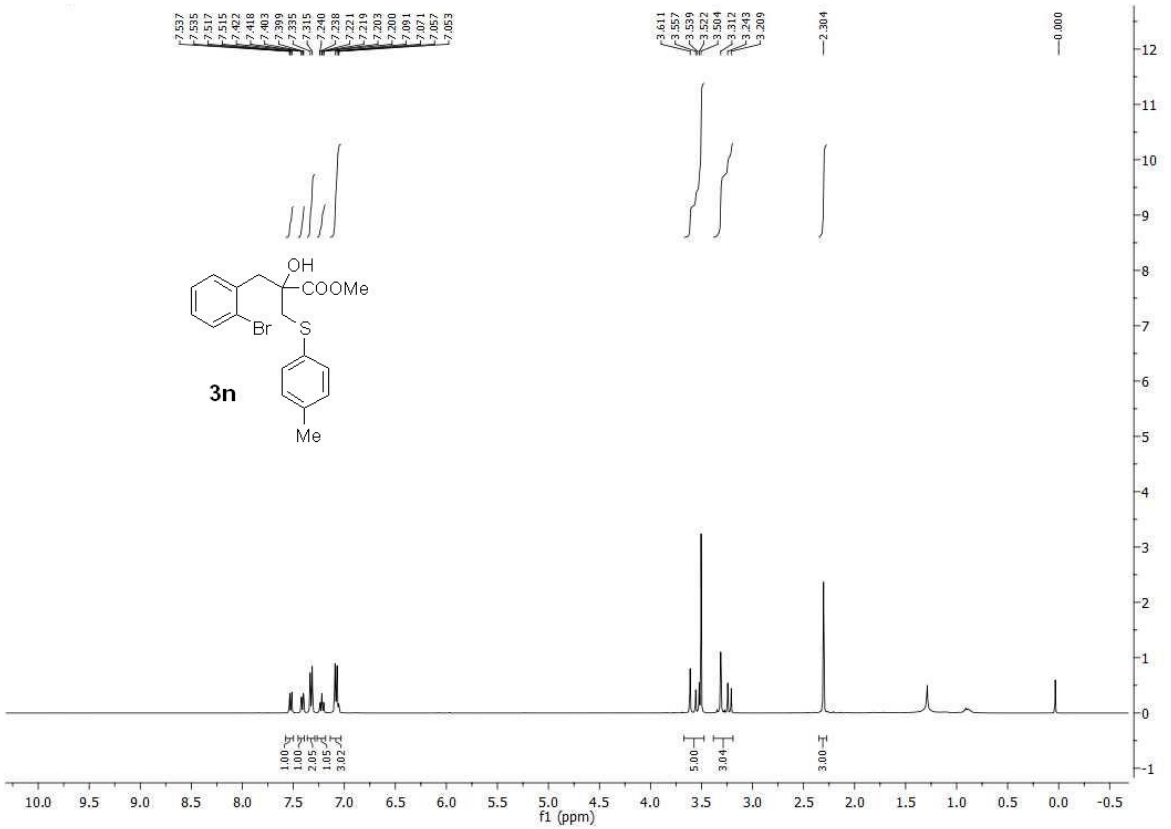
OH
COOMe
S
Br
3l
f1 (ppm)


single pulse decoupled gated NOE
MeO
OH
COOMe
S
Br
3l
f1 (ppm)


OH
COOMe
Br
S
Br
3m
f1 (ppm)


single pulse decoupled gated NOE
OH
COOMe
Br
S
Br
3m
f1 (ppm)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7.399
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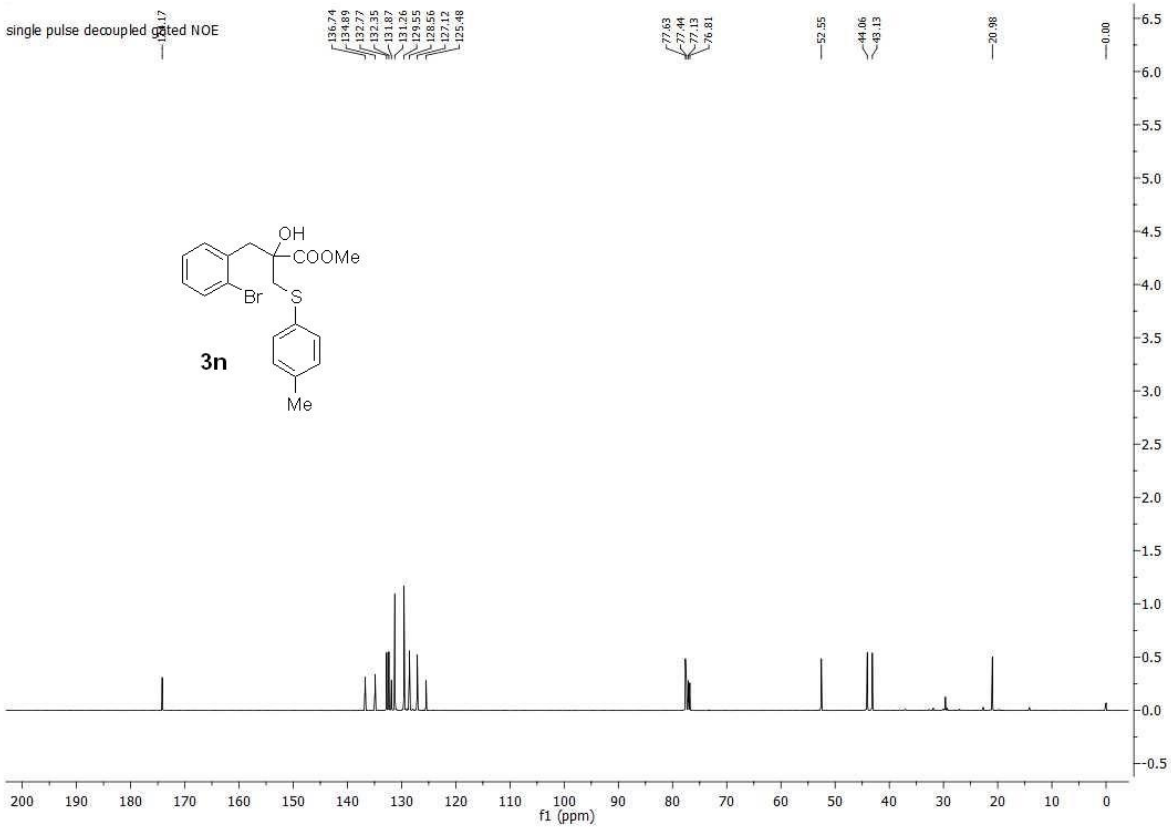
7.315
7.240
7.238
7.221
7.219
7.203
7.200
7.091
7.071
7.067
7.053
3.611
3.557
3.539
3.522
3.504
3.312
3.243
3.209
2.304
0.000
OH
COOMe
Br
S
3n
Me
1.00
1.00
2.05
1.05
3.02
5.00
3.04
3.00
f1 (ppm)


single pulse decoupled gated NOE
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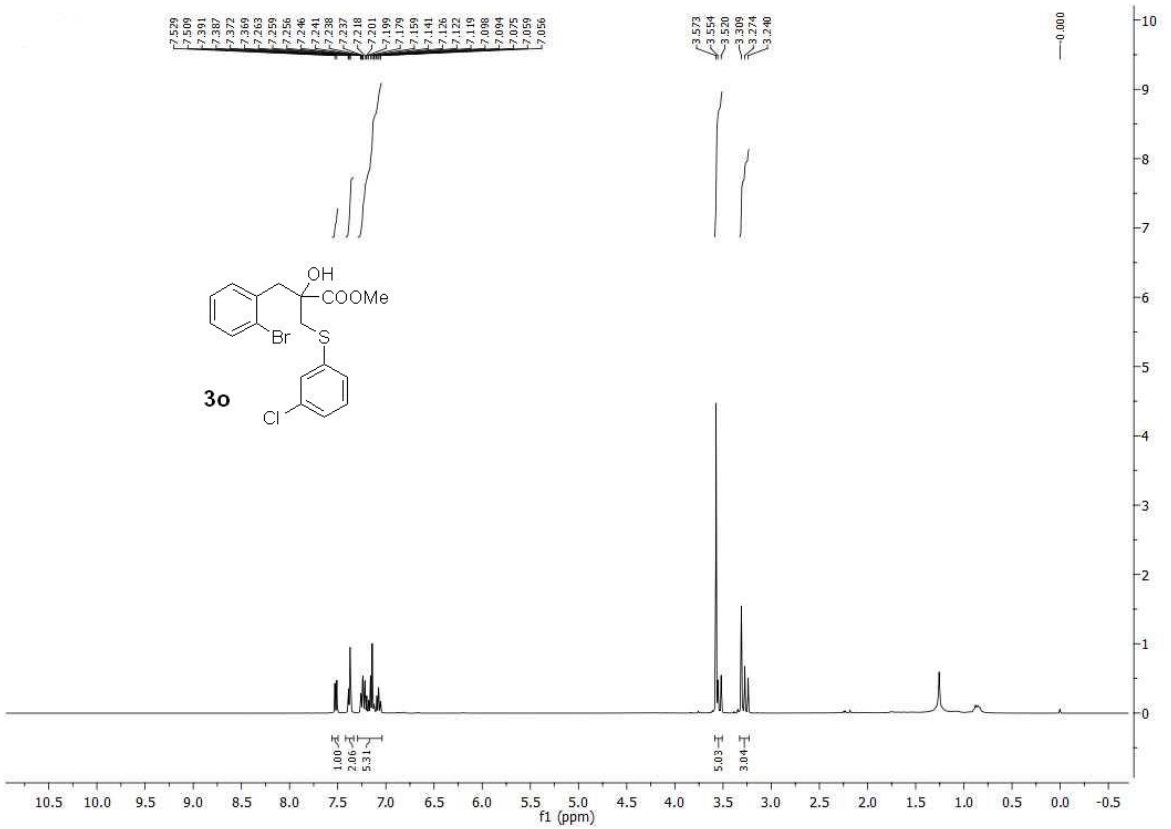
129.55
128.56
127.12
125.48
77.63
77.44
77.13
76.81
52.55
44.06
43.13
20.98
0.00
OH
COOMe
Br
S
3n
Me
f1 (ppm)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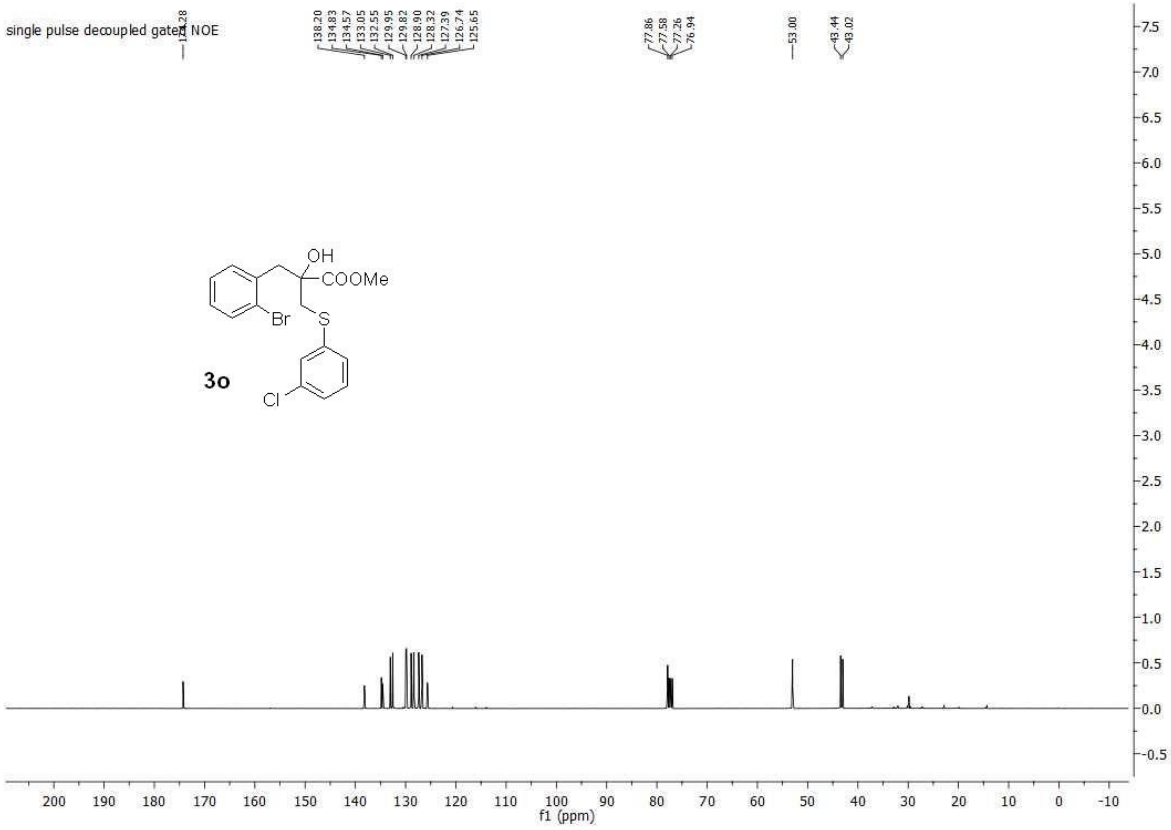
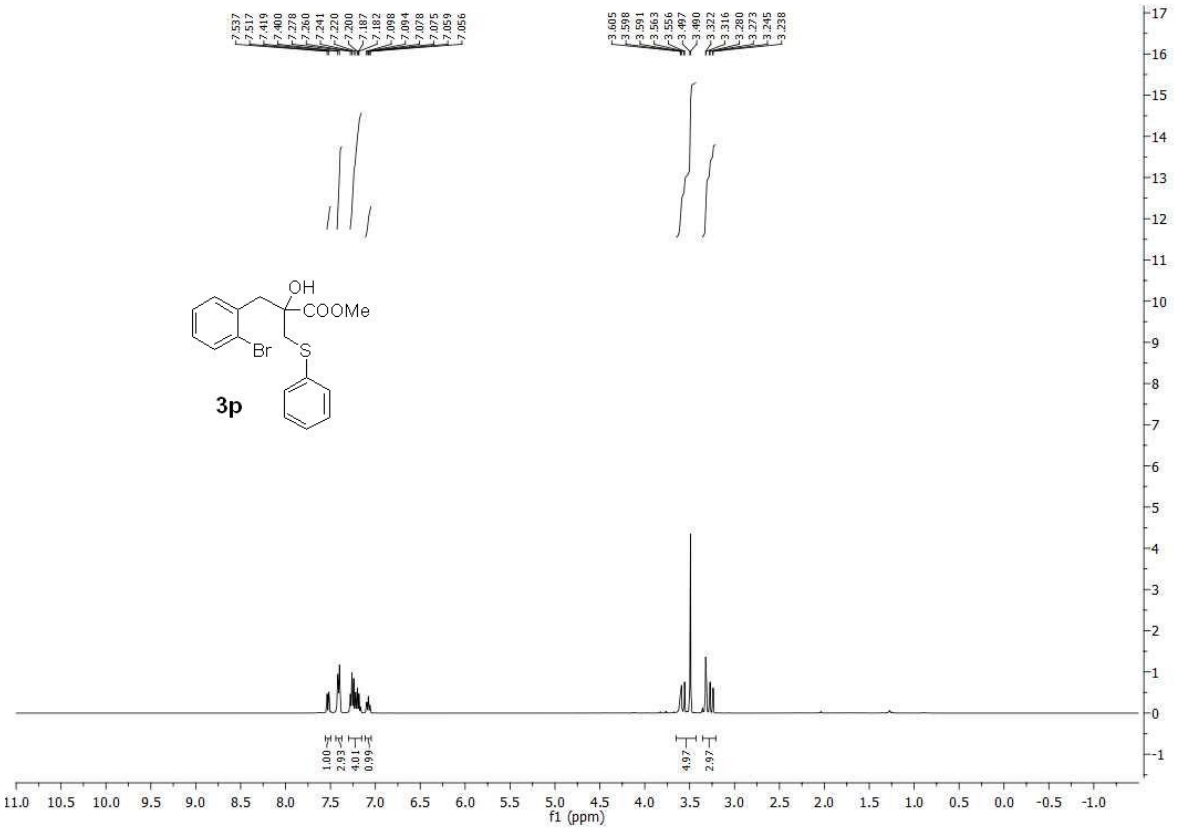
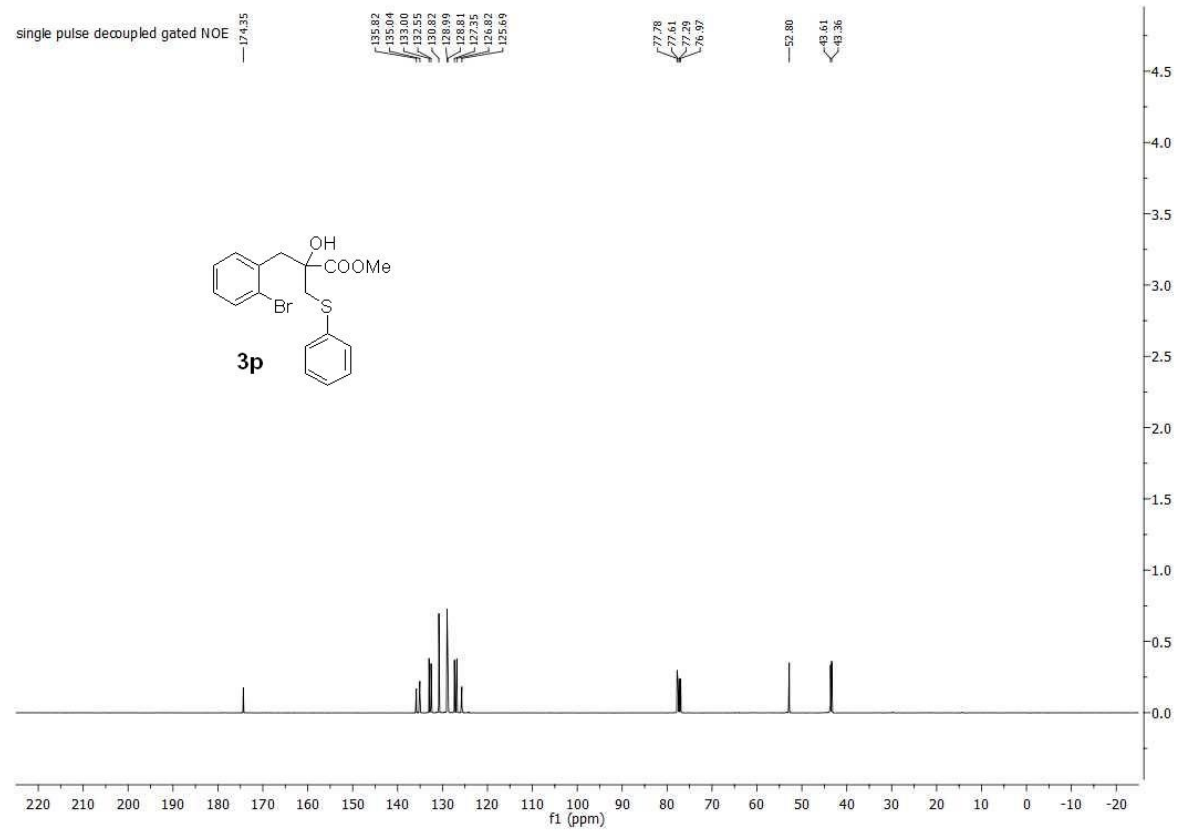
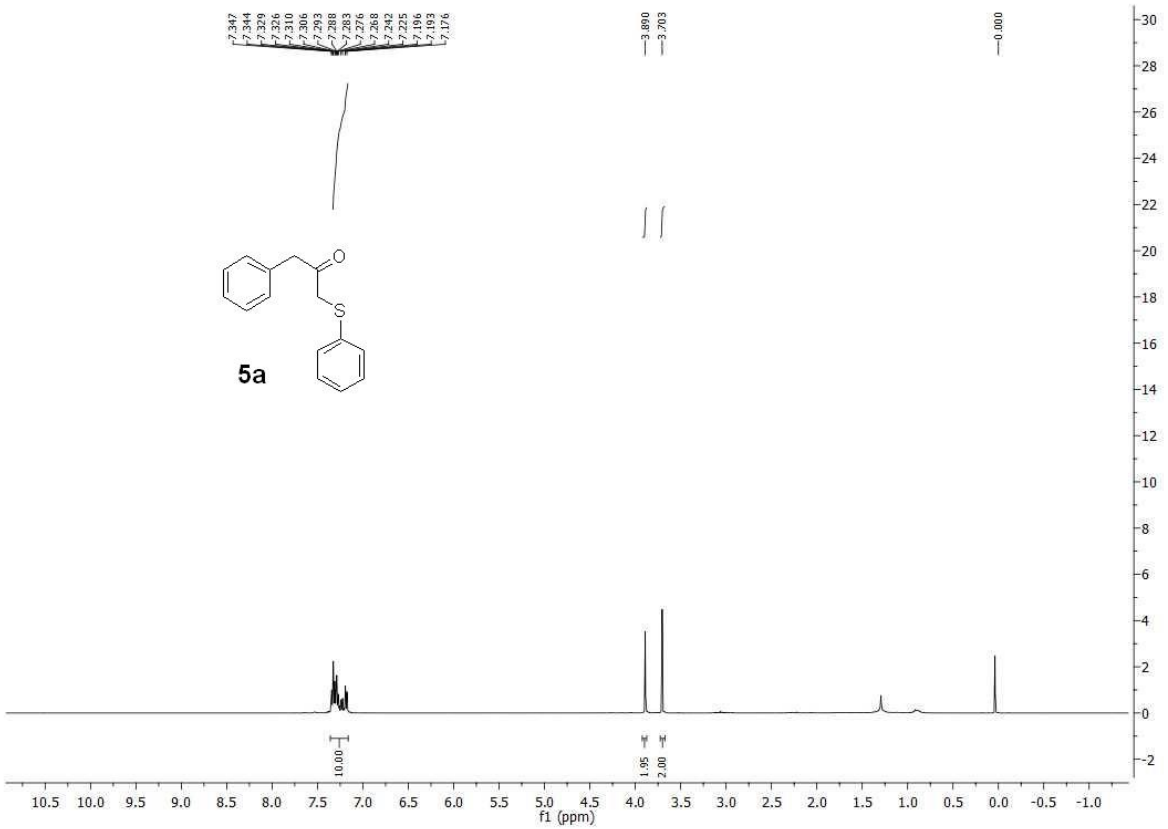
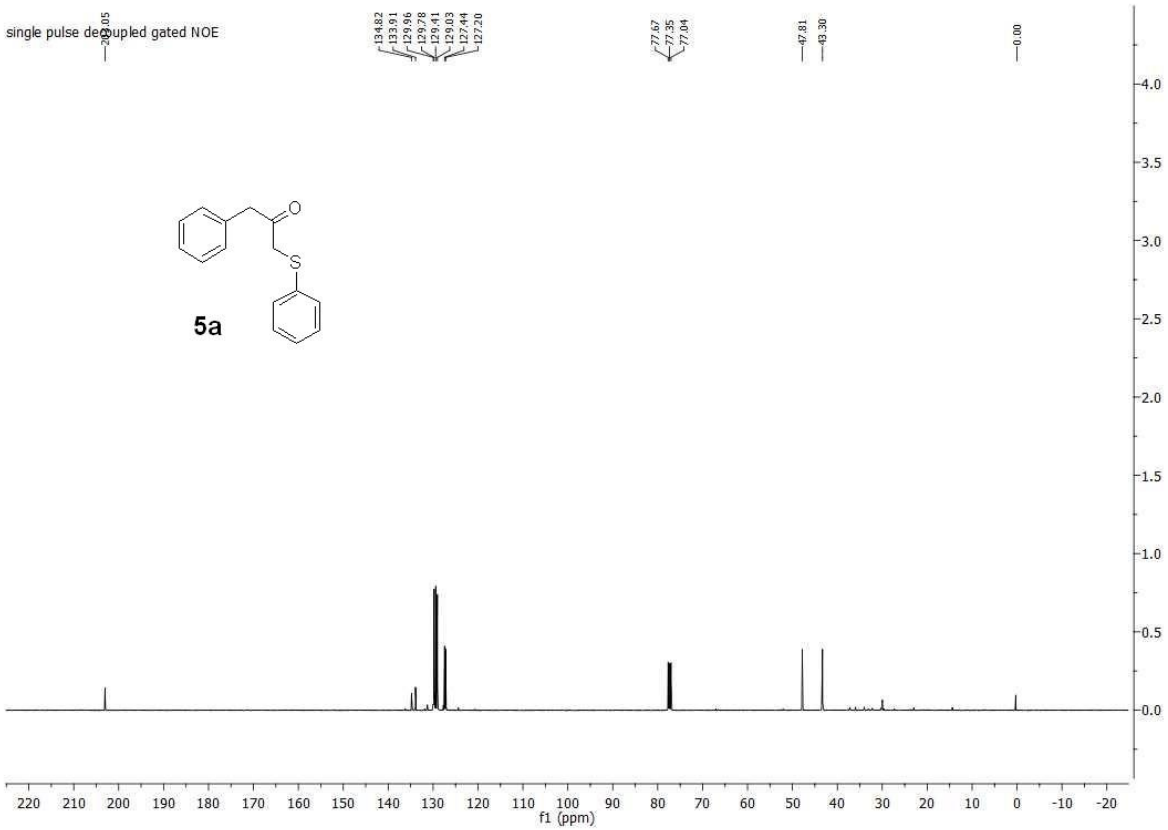
7.238
7.237
7.218
7.201
7.199
7.179
7.159
7.141
7.126
7.122
7.119
7.098
7.094
7.075
7.059
7.056
3.573
3.554
3.520
3.309
3.274
3.240
0.000
OH
COOMe
Br
S
Cl
3o
1.00
2.06
5.31
5.03
3.04
f1 (ppm)

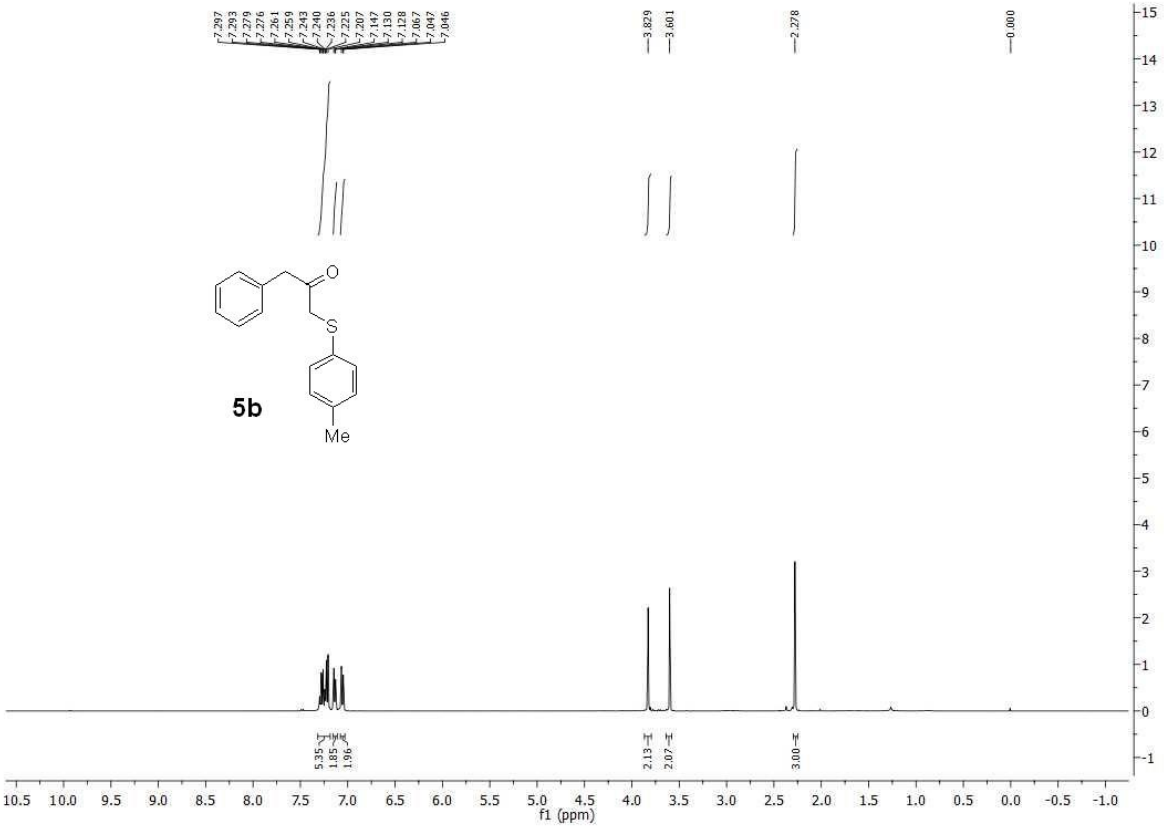

single pulse decoupled gated NOE
138.20
134.83
134.57
133.05
132.55
129.95
129.82
128.90
128.32
127.39
126.74
125.65
77.86
77.58
77.26
76.94
53.00
43.44
43.02
OH
COOMe
Br
S
Cl
3o
f1 (ppm)

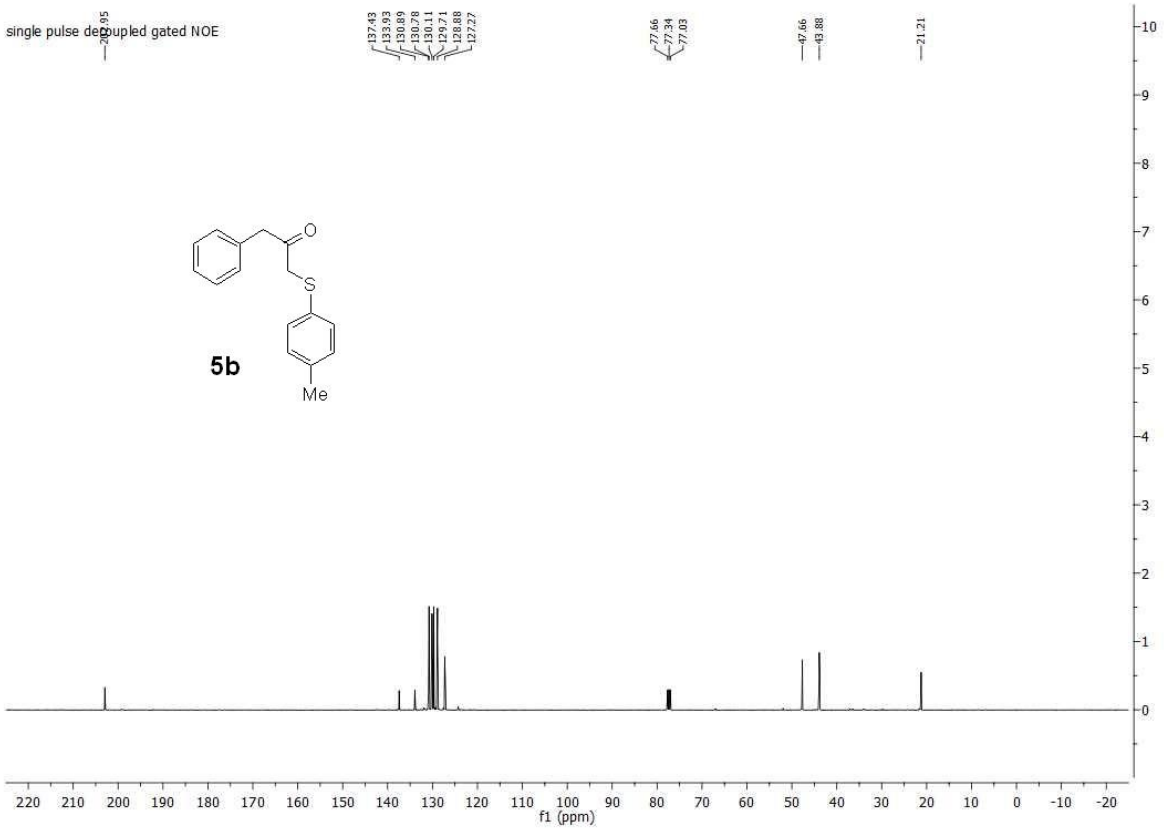

7.537
7.517
7.419
7.400
7.278
7.260
7.241
7.220
7.200
7.187
7.182
7.098
7.094
7.078
7.075
7.059
7.056
3.605
3.598
3.591
3.563
3.556
3.497
3.480
3.322
3.316
3.280
3.273
3.245
3.238
OH
COOMe
Br
S
3p
1.00
2.93
4.01
0.99
4.97
2.97
f1 (ppm)


single pulse decoupled gated NOE
174.35
135.82
135.04
133.00
132.55
130.82
128.99
128.81
127.35
126.82
125.69
77.78
77.61
77.29
76.97
52.80
43.61
43.36
OH
COOMe
Br
S
3p
f1 (ppm)


7.347
7.344
7.329
7.326
7.310
7.306
7.293
7.288
7.283
7.276
7.268
7.242
7.225
7.196
7.193
7.176
3.890
3.703
0.000
O
S
5a
10.00
1.95
2.00
f1 (ppm)


single pulse decoupled gated NOE
197.05
134.82
133.91
129.96
129.78
129.41
129.03
127.44
127.20
77.67
77.35
77.04
47.81
43.30
0.00
O
S
5a
f1 (ppm)


7.297
7.293
7.279
7.276
7.261
7.259
7.243
7.240
7.236
7.225
7.207
7.147
7.130
7.128
7.067
7.047
7.046
3.829
3.601
2.278
0.000
O
S
Me
5b
5.35
1.85
1.96
2.13
2.07
3.00
f1 (ppm)


single pulse decoupled gated NOE
197.95
137.43
133.93
130.89
130.78
130.11
129.71
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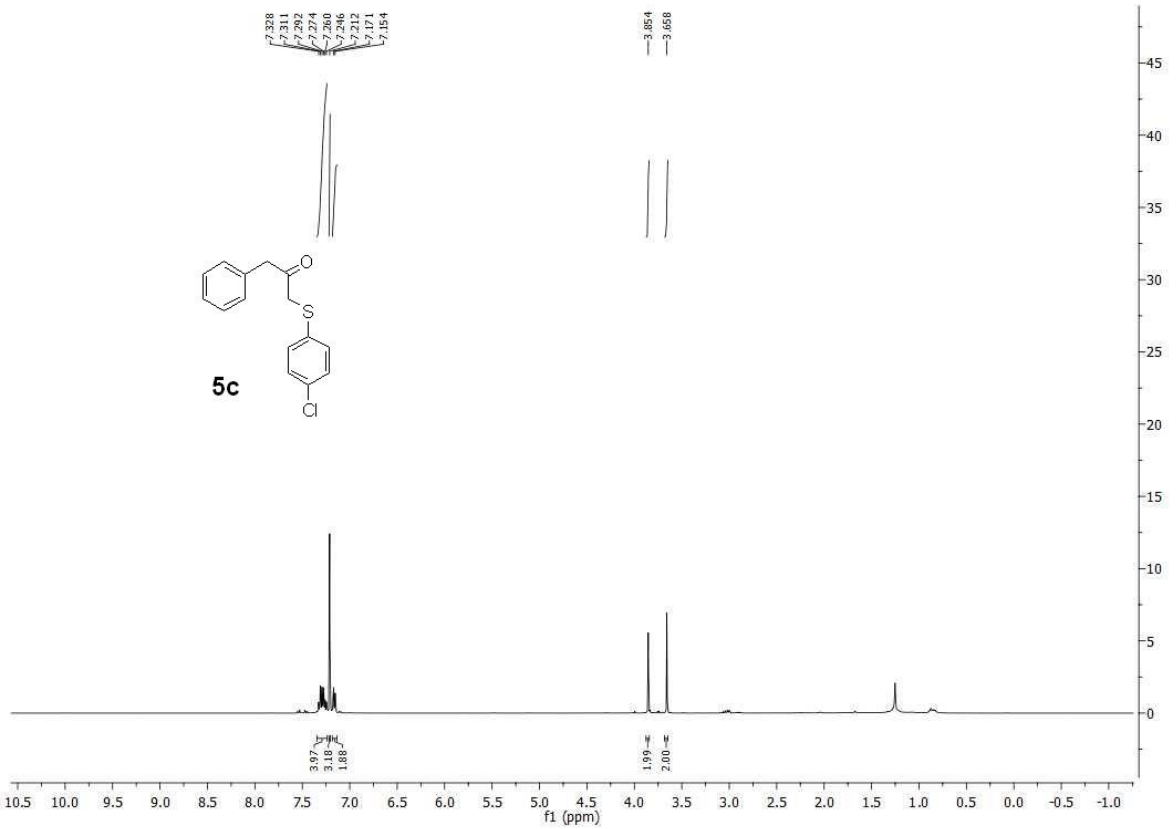
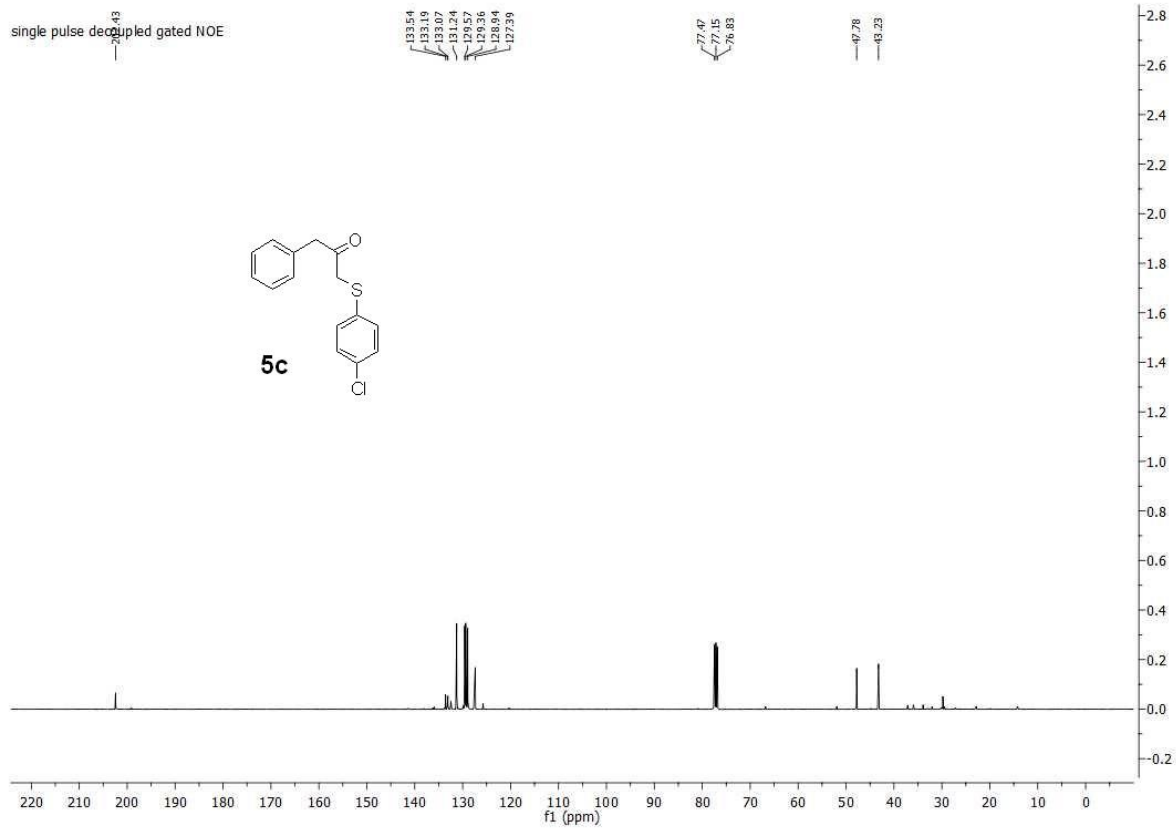
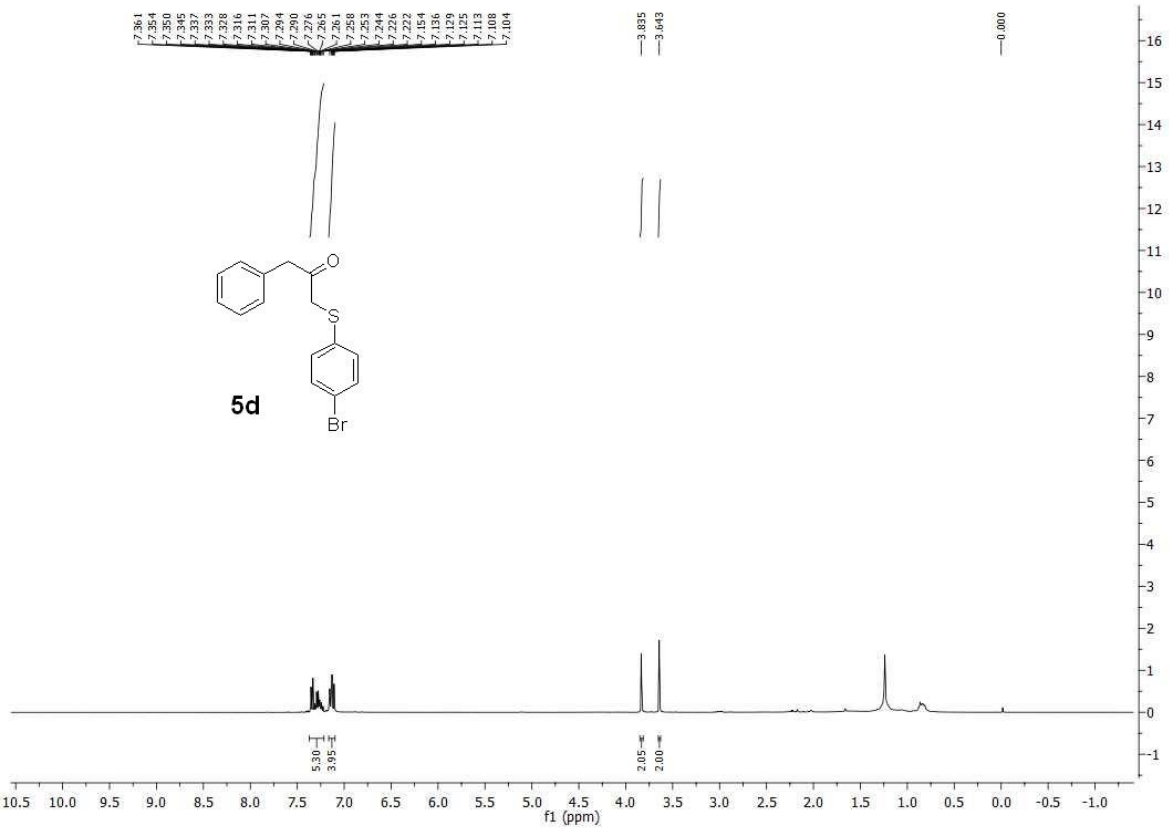
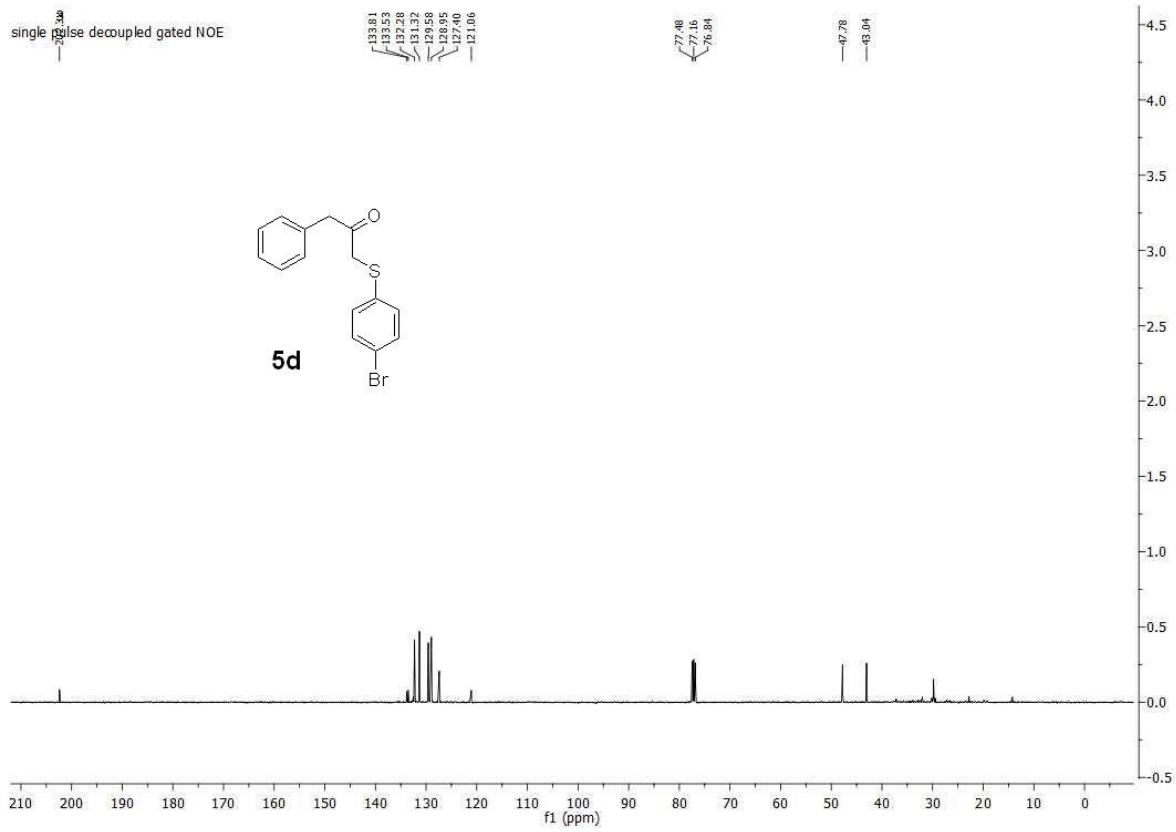
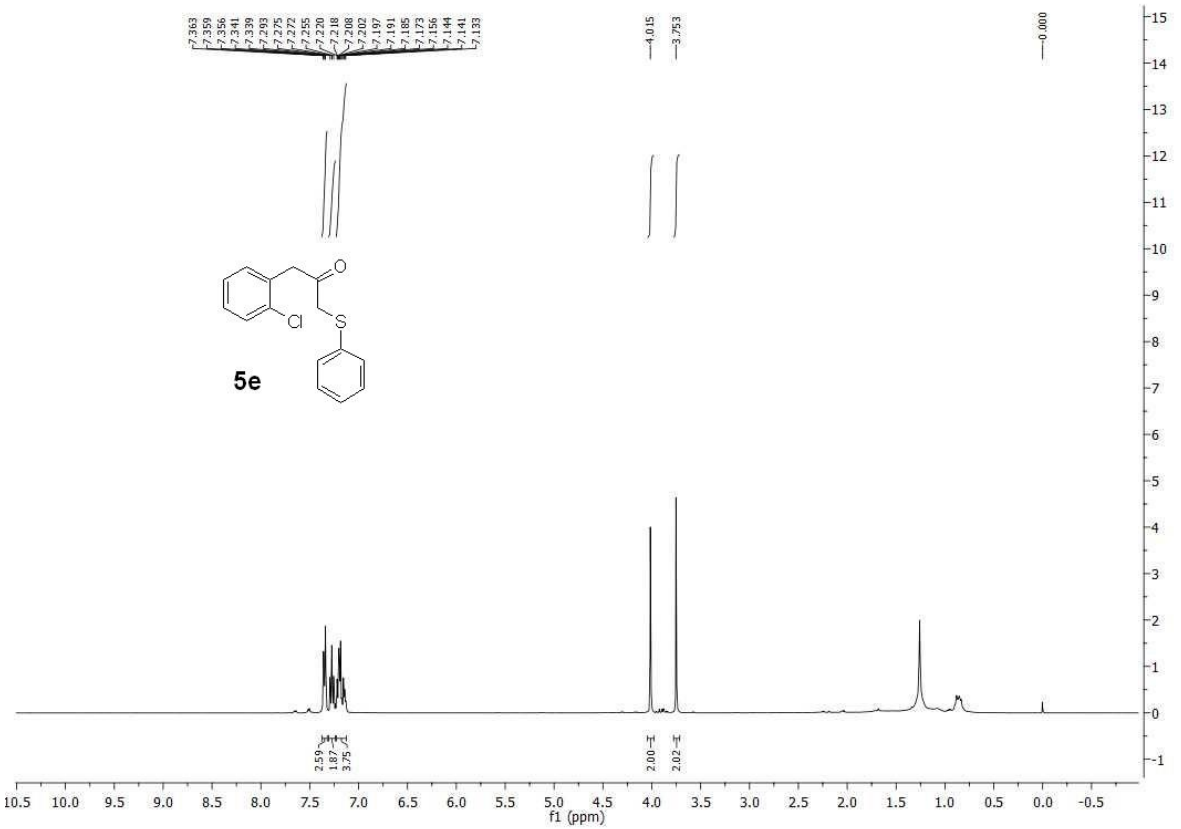
127.27
77.66
77.34
77.03
47.66
43.88
21.21
O
S
Me
5b
f1 (ppm)

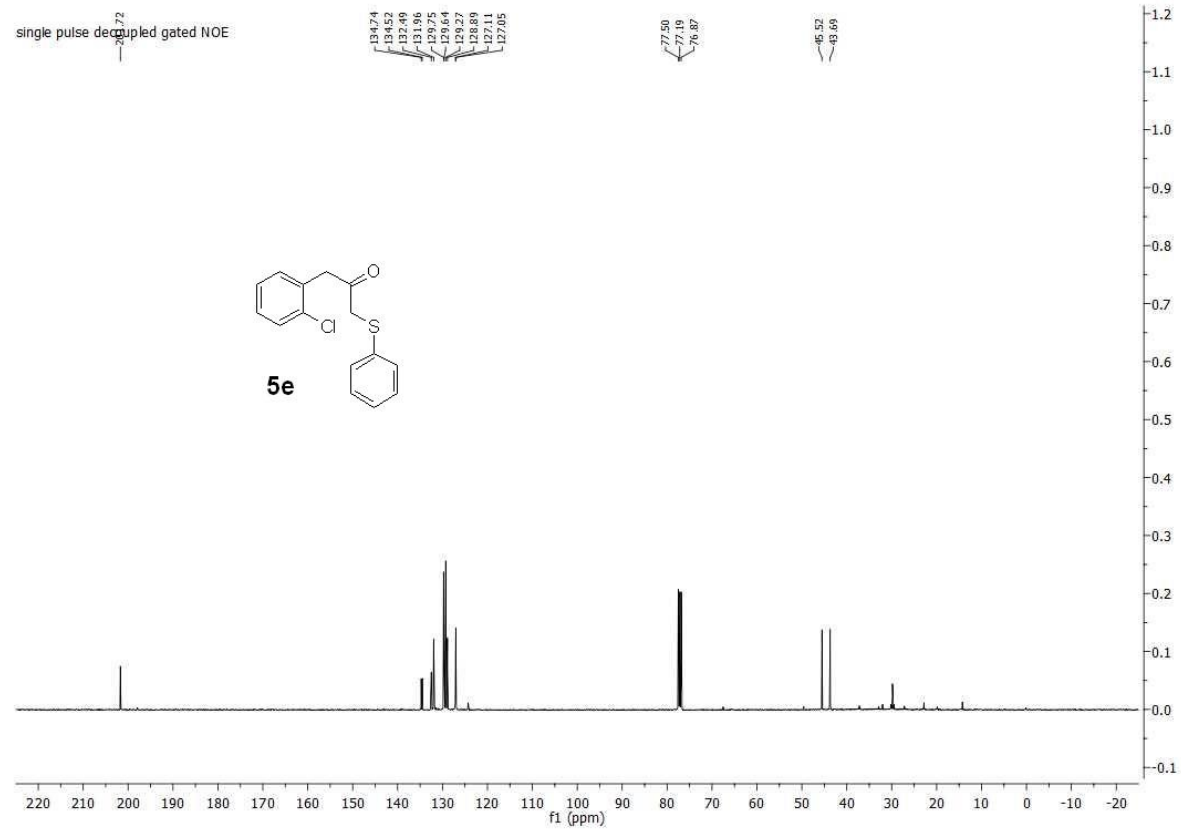

7.328
7.311
7.292
7.274
7.260
7.246
7.212
7.171
7.154
3.854
3.658
O
S
Cl
5c
3.97
3.18
1.88
1.99
2.00
f1 (ppm)

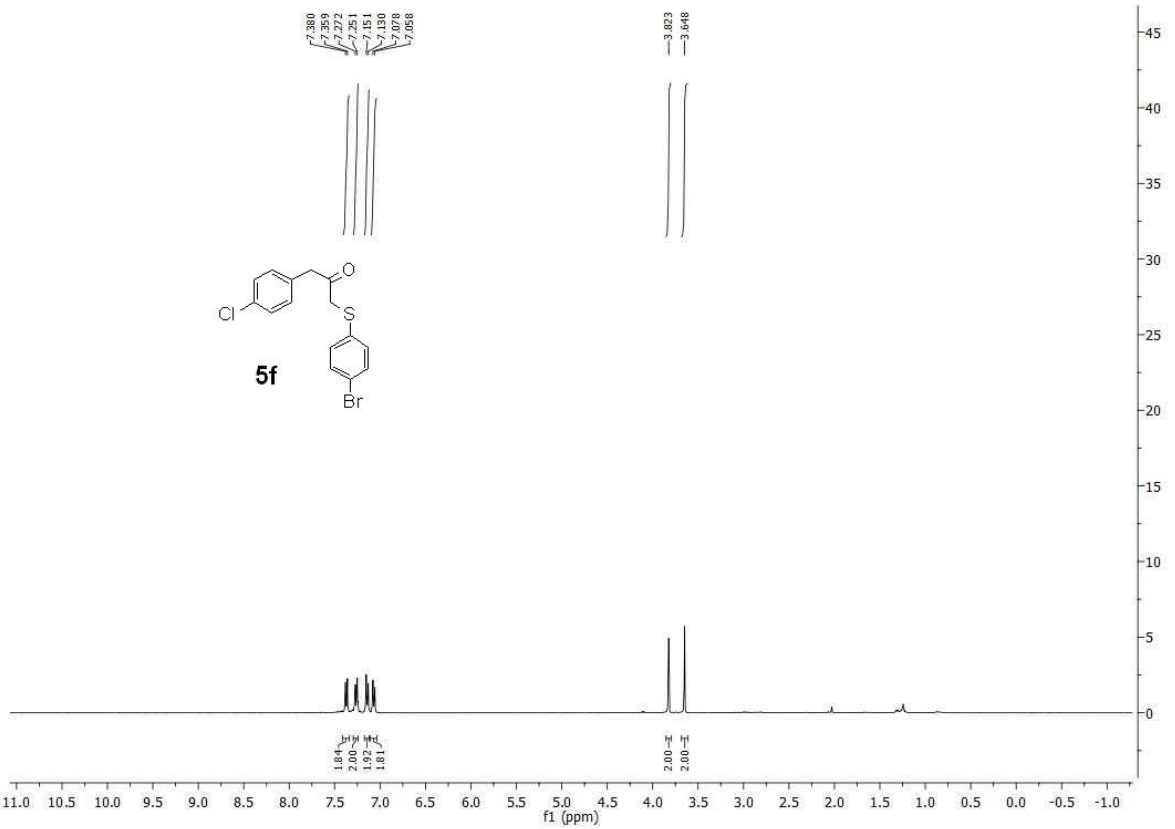

single pulse decoupled gated NOE
197.43
133.54
133.19
133.07
131.24
129.57
129.36
128.84
127.39
77.47
77.15
76.83
47.78
43.23
O
S
Cl
5c
f1 (ppm)

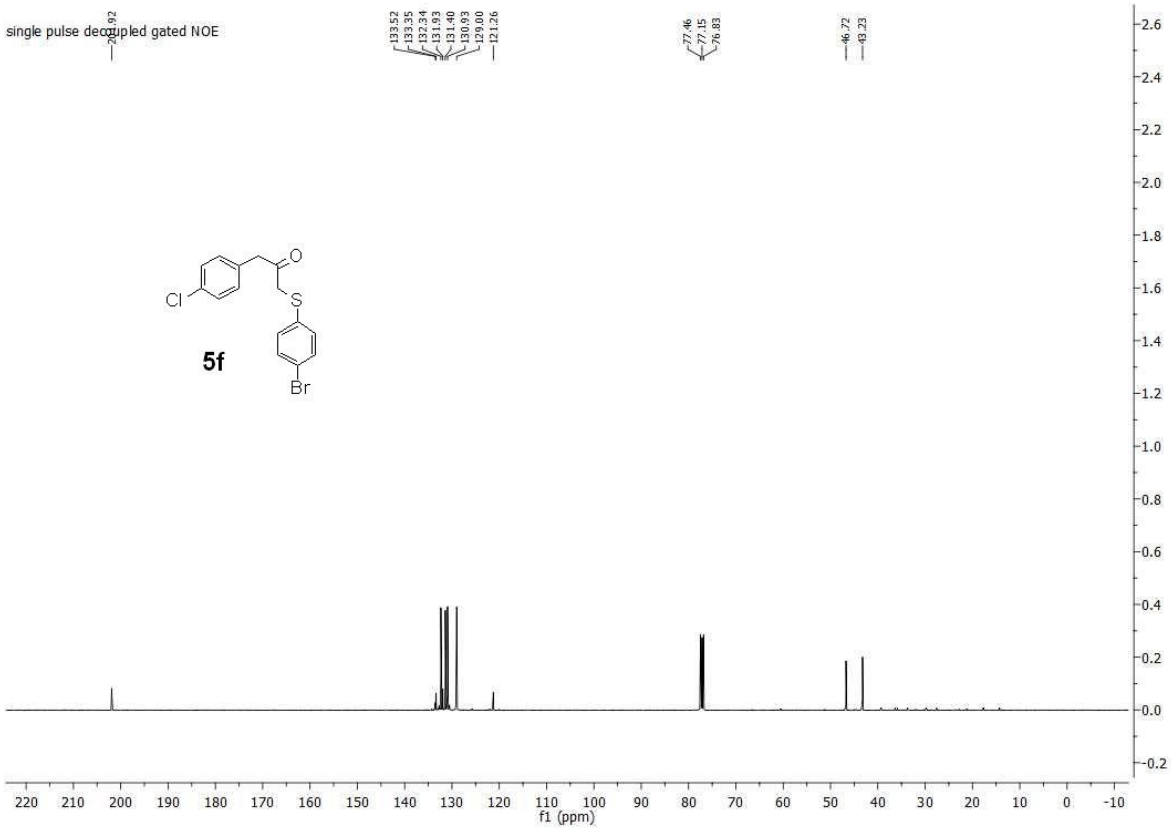

7.361
7.354
7.350
7.345
7.337
7.333
7.328
7.316
7.311
7.307
7.294
7.290
7.276
7.265
7.261
7.258
7.253
7.244
7.226
7.222
7.154
7.136
7.129
7.125
7.113
7.108
7.104
3.835
3.643
0.000
O
S
Br
5d
5.30
3.95
2.05
2.00
f1 (ppm)

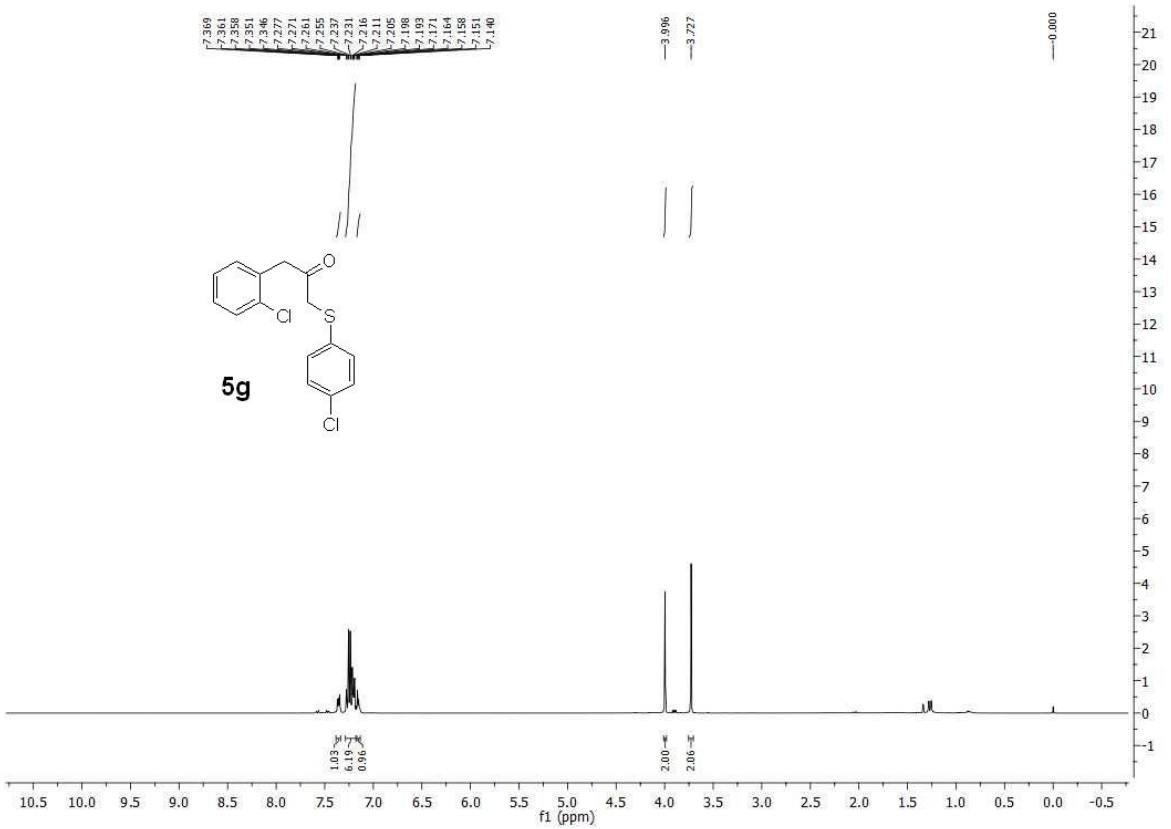

single pulse decoupled gated NOE
133.81
133.53
132.28
131.32
129.58
128.95
127.40
121.06
77.48
77.16
76.84
47.78
43.04
O
S
Br
5d
f1 (ppm)

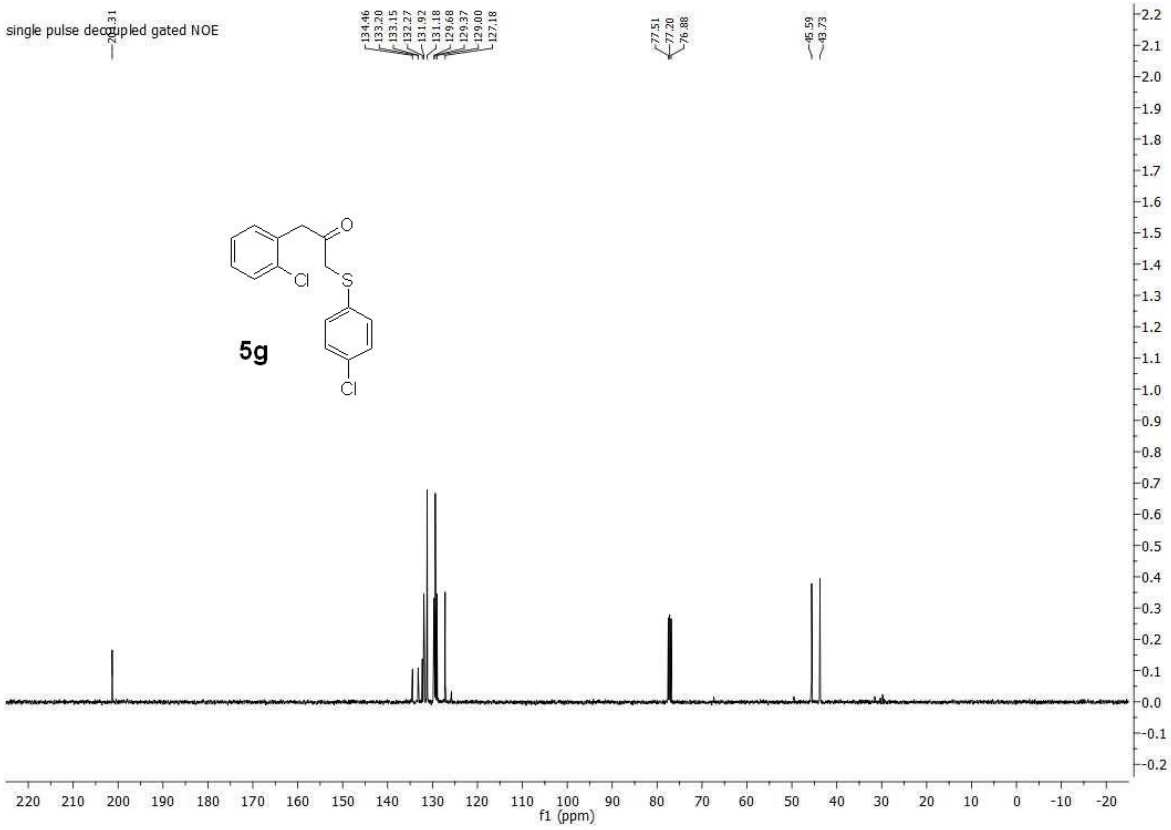

7.363
7.359
7.356
7.341
7.339
7.293
7.275
7.272
7.255
7.220
7.218
7.208
7.202
7.197
7.191
7.185
7.173
7.156
7.144
7.141
7.133
4.015
3.753
0.000
Cl
O
S
5e
2.59
1.87
3.75
2.00
2.02
f1 (ppm)

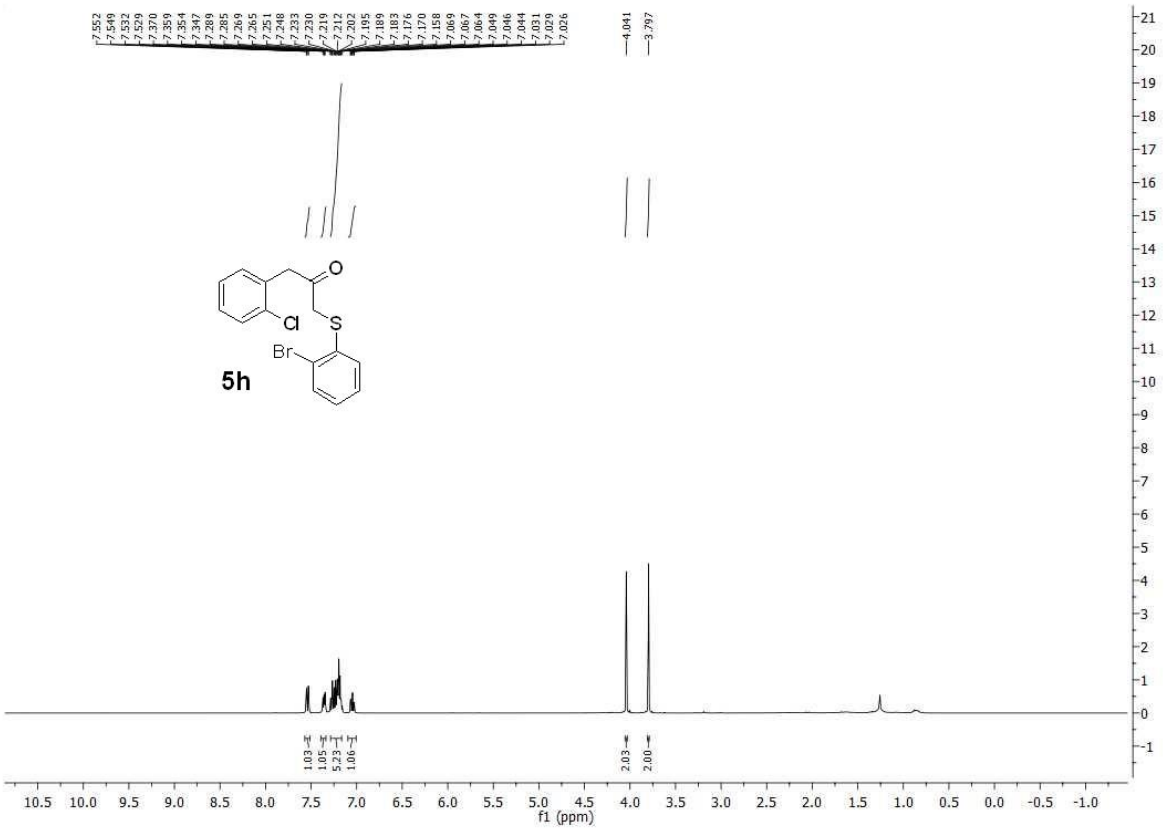

single pulse decoupled gated NOE
194.72
134.74
134.52
132.49
131.96
129.75
129.64
129.27
128.89
127.11
127.05
77.50
77.19
76.87
45.52
43.69
Cl
O
S
5e
f1 (ppm)


7.380
7.359
7.272
7.251
7.151
7.130
7.078
7.058
3.823
3.648
Cl
O
S
Br
5f
1.84
2.00
1.92
1.81
2.00
2.00
f1 (ppm)


single pulse decoupled gated NOE
133.52
133.35
132.34
131.93
131.40
130.93
129.00
121.26
77.46
77.15
76.83
46.72
43.23
Cl
O
S
Br
5f
f1 (ppm)


7.369
7.361
7.358
7.351
7.346
7.277
7.271
7.261
7.255
7.237
7.231
7.216
7.211
7.205
7.198
7.193
7.171
7.164
7.158
7.151
7.140
3.996
3.727
0.000
O
Cl
S
Cl
5g
1.03
6.19
0.96
2.00
2.06
f1 (ppm)


single pulse decoupled gated NOE
28.31
134.46
133.20
133.15
132.27
131.92
131.18
129.68
129.37
129.00
127.18
77.51
77.20
76.88
45.59
43.73
O
Cl
S
Cl
5g
f1 (ppm)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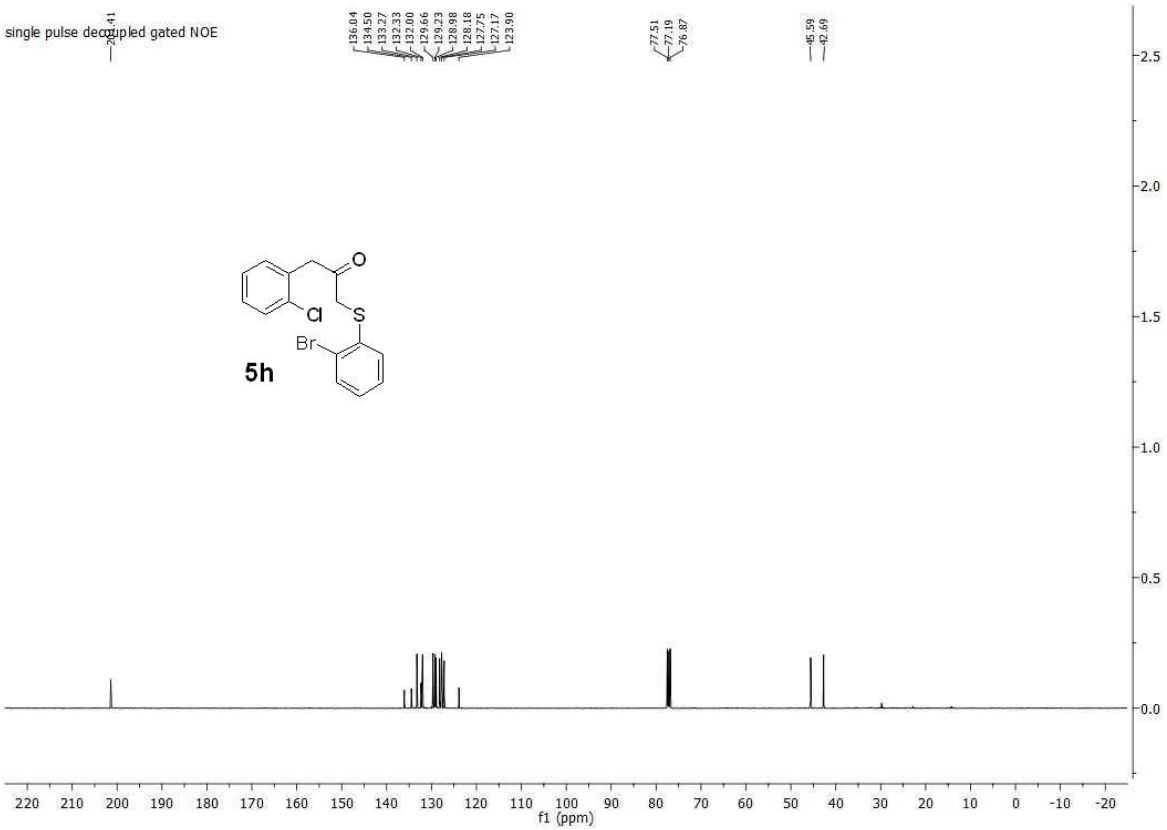
7.549
7.532
7.529
7.370
7.359
7.354
7.347
7.340
7.285
7.269
7.265
7.251
7.248
7.233
7.230
7.219
7.212
7.202
7.195
7.189
7.183
7.176
7.170
7.158
7.069
7.067
7.064
7.049
7.046
7.044
7.031
7.029
7.026
4.041
3.797
Cl
O
S
Br
5h
1.03
1.05
5.23
1.06
2.03
2.00
f1 (ppm)


single pulse decoupled gated NOE
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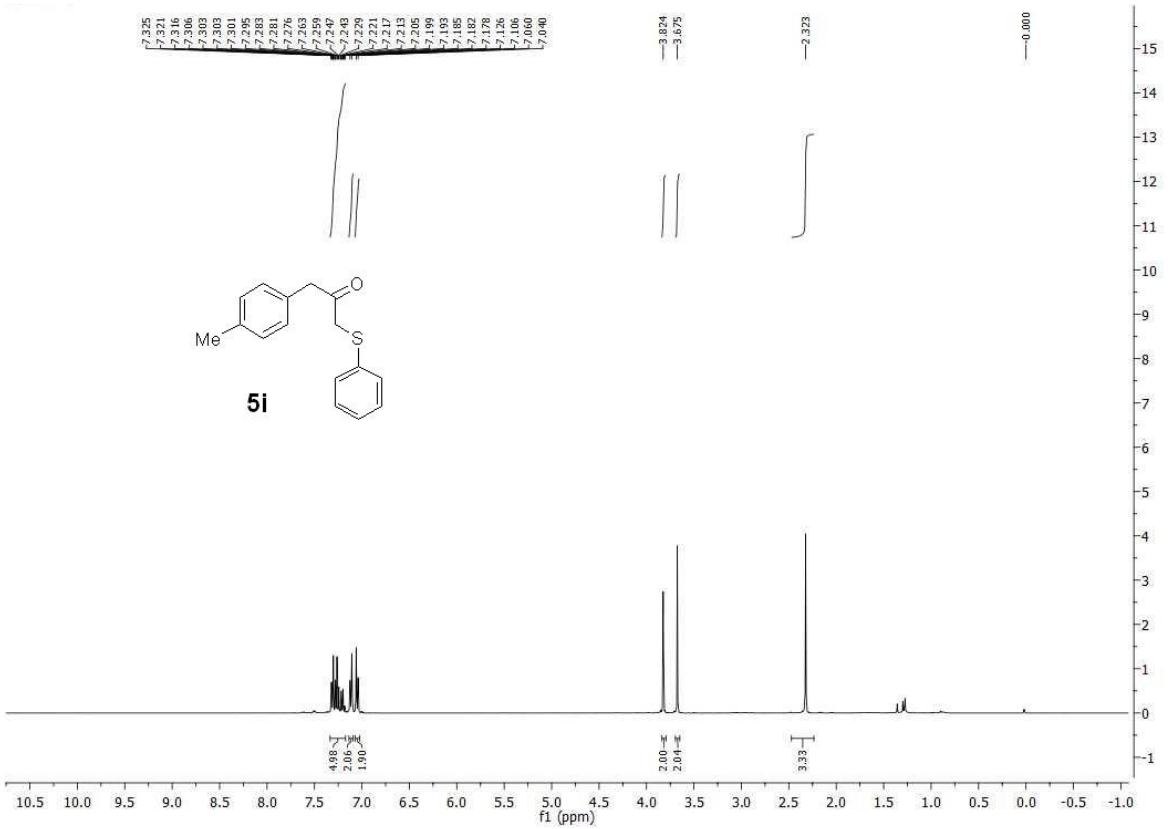
136.04
134.50
133.27
132.33
132.00
129.66
129.23
128.98
128.18
127.75
127.17
123.90
77.51
77.19
76.87
45.59
42.69
Cl
O
S
Br
5h
f1 (ppm)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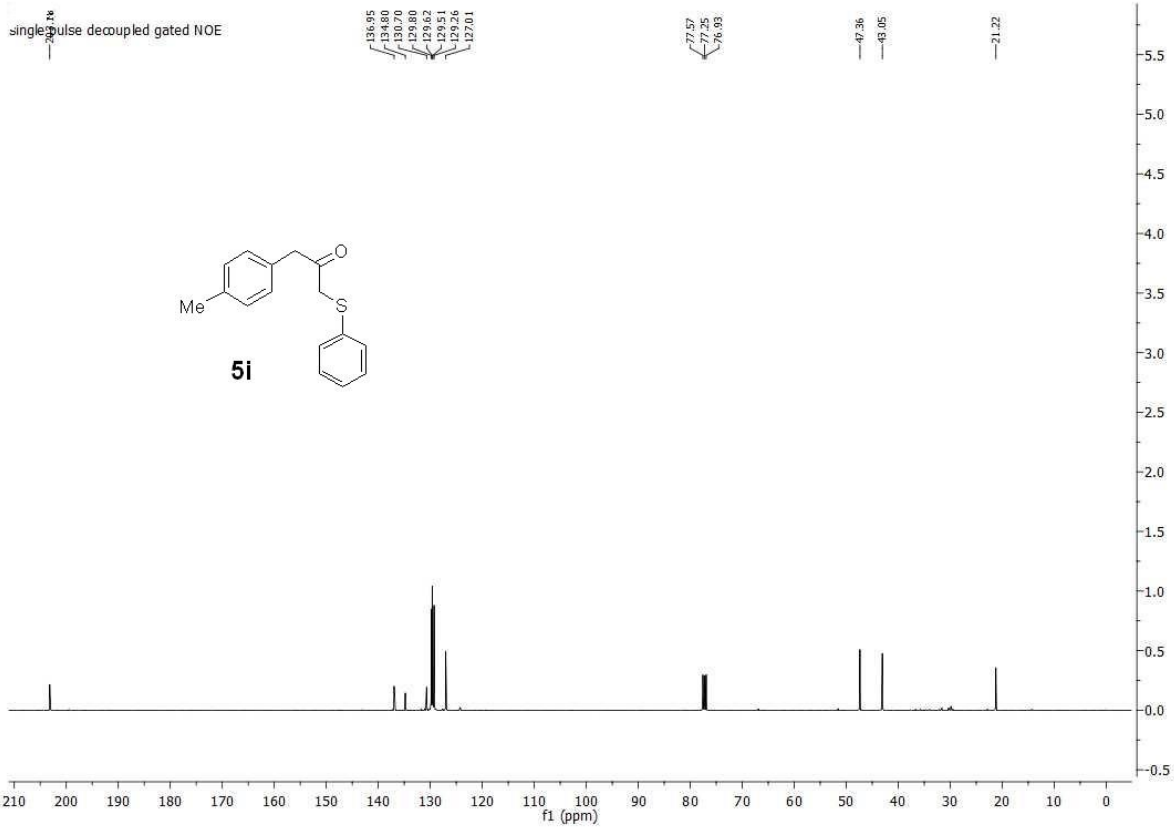
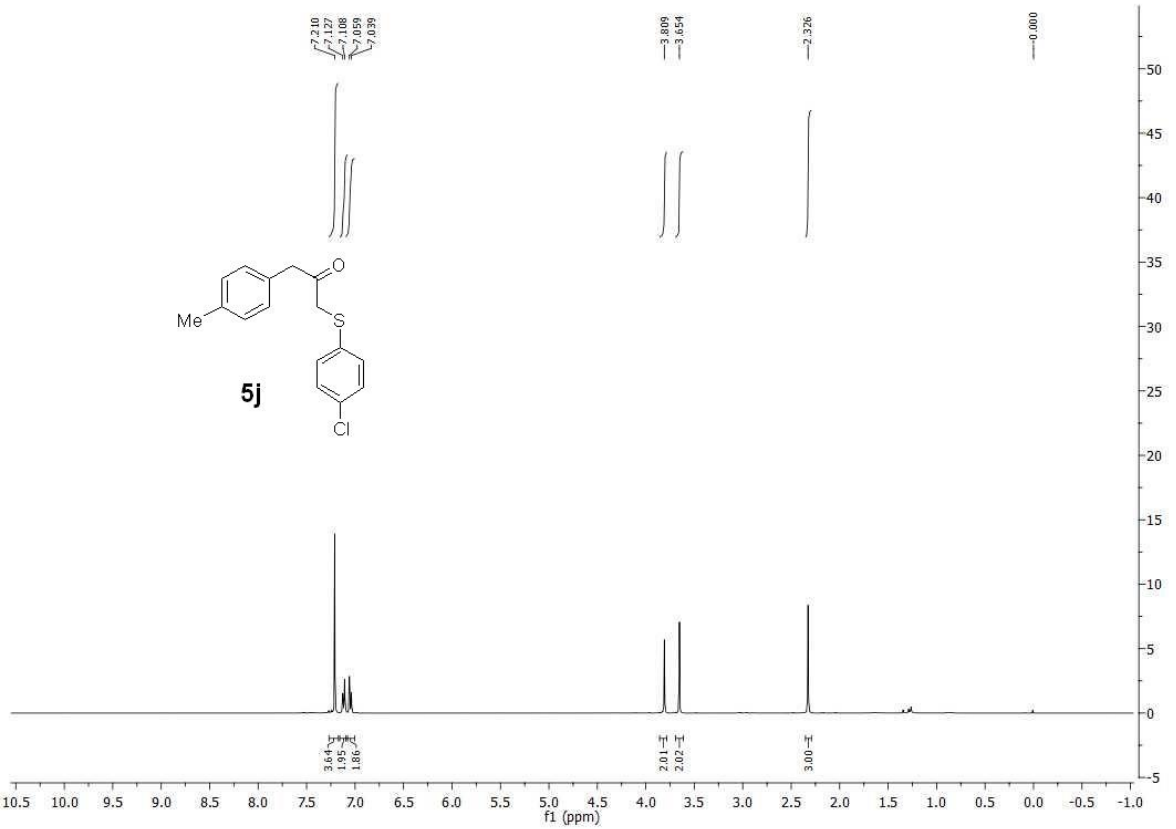
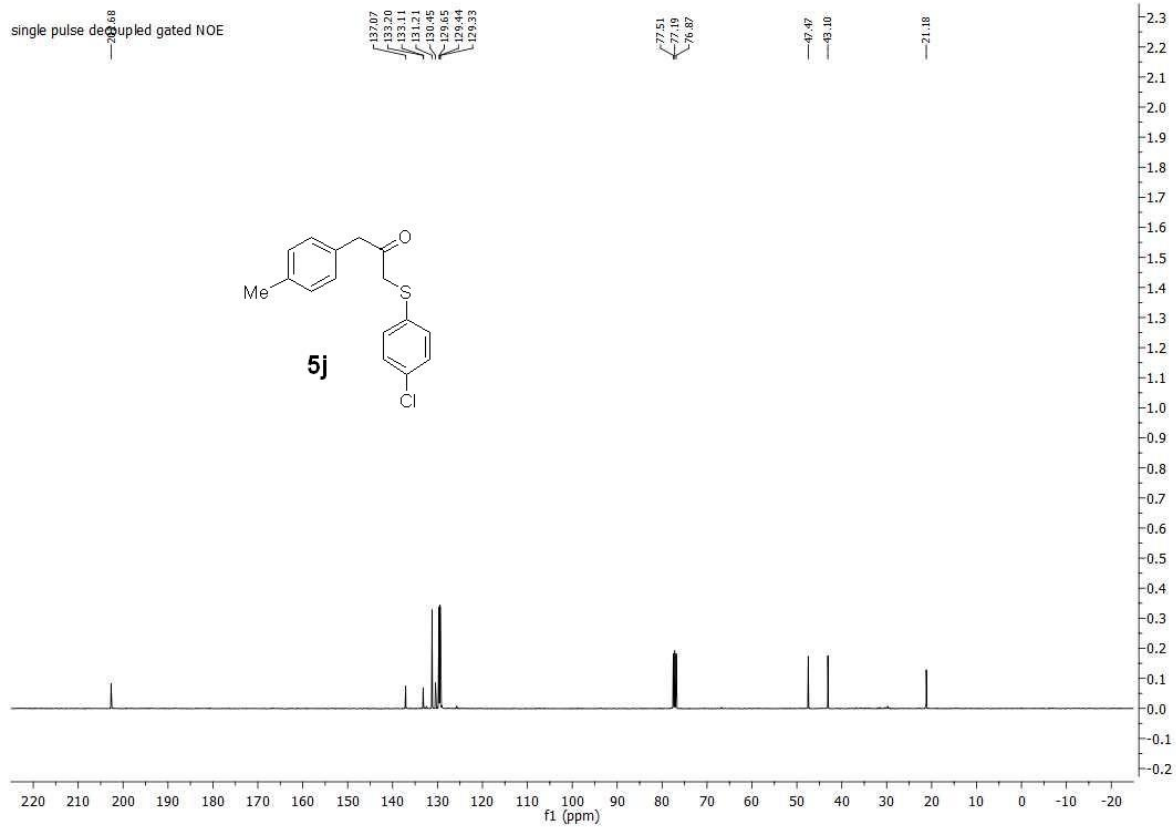
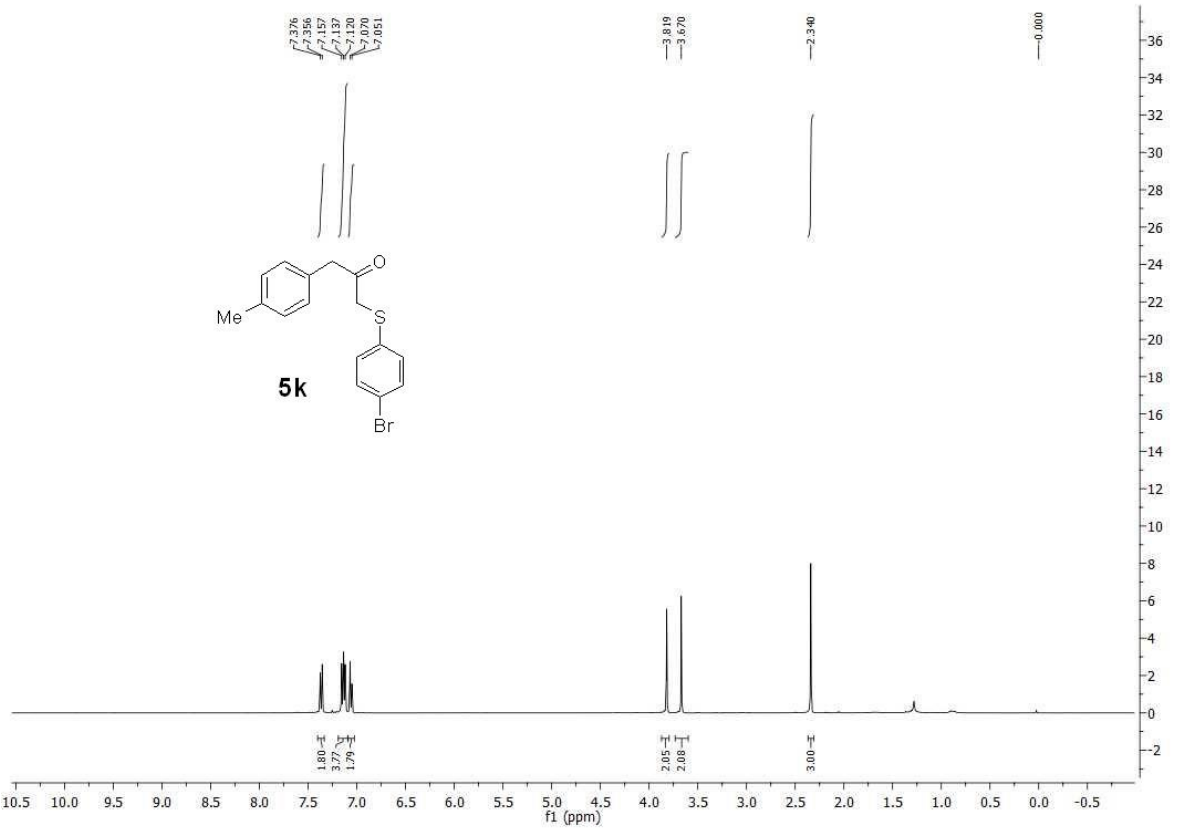
7.321
7.316
7.306
7.303
7.303
7.301
7.295
7.283
7.281
7.276
7.263
7.259
7.247
7.243
7.229
7.221
7.217
7.213
7.205
7.199
7.193
7.185
7.182
7.178
7.126
7.106
7.060
7.040
3.824
3.675
2.323
0.000
Me
O
S
5i
4.98
2.06
1.90
2.00
2.04
3.33
f1 (ppm)


single pulse decoupled gated NOE
136.95
134.80
130.70
129.80
129.62
129.51
129.26
127.01
77.57
77.25
76.93
47.36
43.05
21.22
Me
O
S
5i
f1 (ppm)


7.210
7.127
7.108
7.099
7.039
3.809
3.654
2.326
0.000
Me
O
S
Cl
5j
3.64
1.95
1.86
2.01
2.02
3.00
f1 (ppm)


single pulse decoupled gated NOE
197.68
137.07
133.20
133.11
131.21
130.45
129.65
129.44
129.33
77.51
77.19
76.87
47.47
43.10
21.18
Me
O
S
Cl
5j
f1 (ppm)


7.376
7.356
7.157
7.137
7.120
7.070
7.051
3.819
3.670
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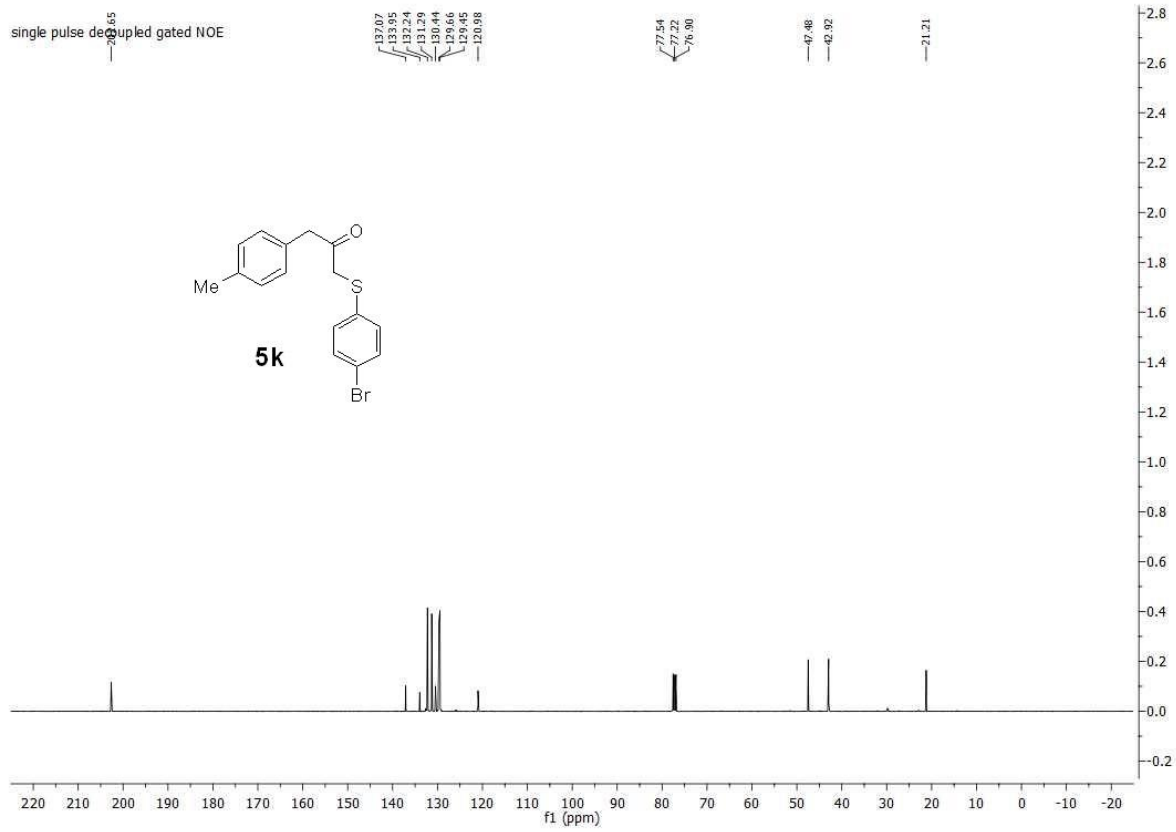
0.000
Me
O
S
Br
5k
1.80
3.77
1.79
2.05
2.08
3.00
f1 (ppm)


single pulse decoupled gated NOE
197.65
137.07
133.95
132.24
131.29
130.44
129.66
129.45
120.98
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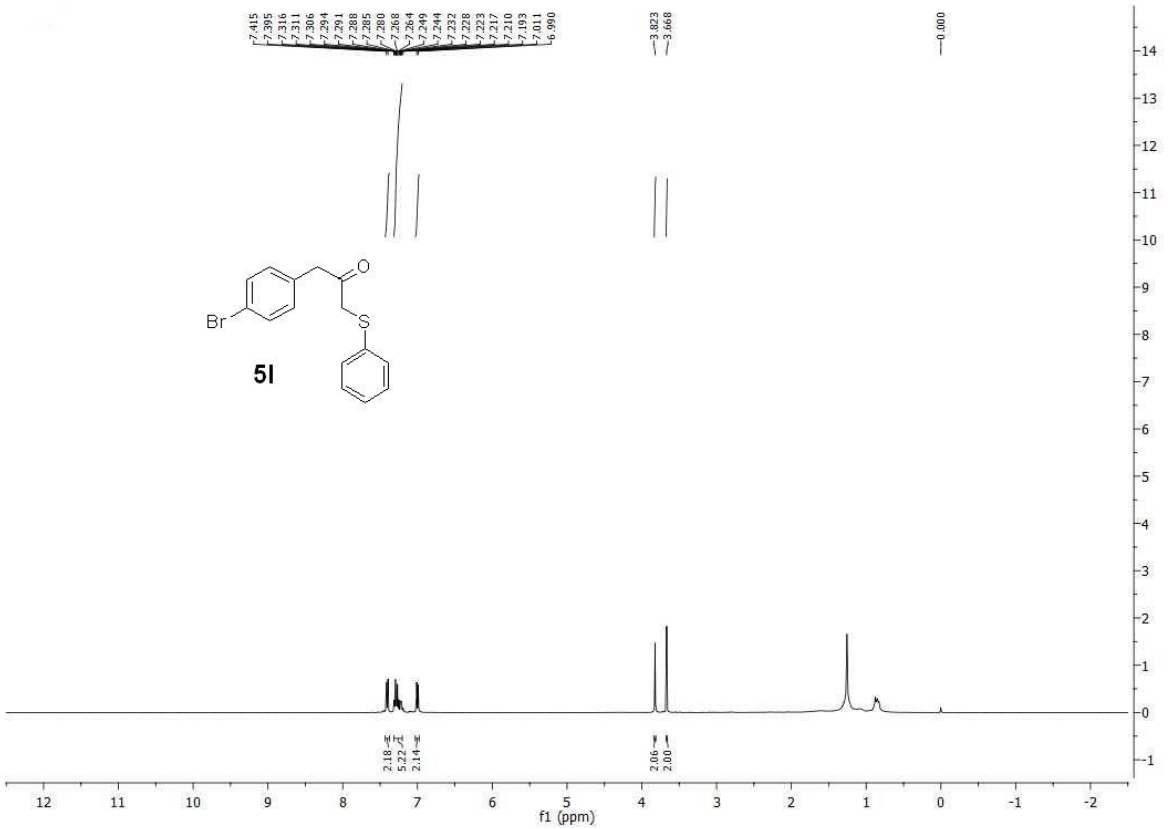
77.22
76.90
47.48
42.92
21.21
Me
O
S
Br
5k
f1 (ppm)


7.415
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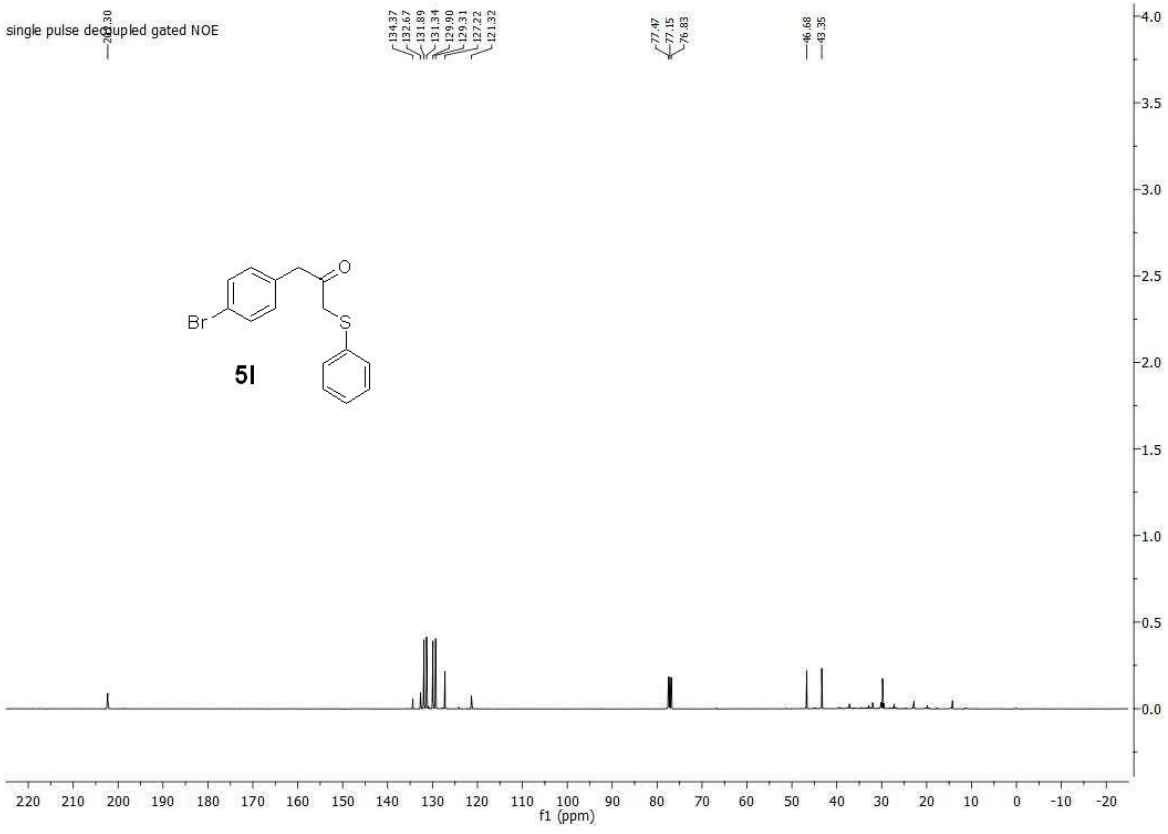
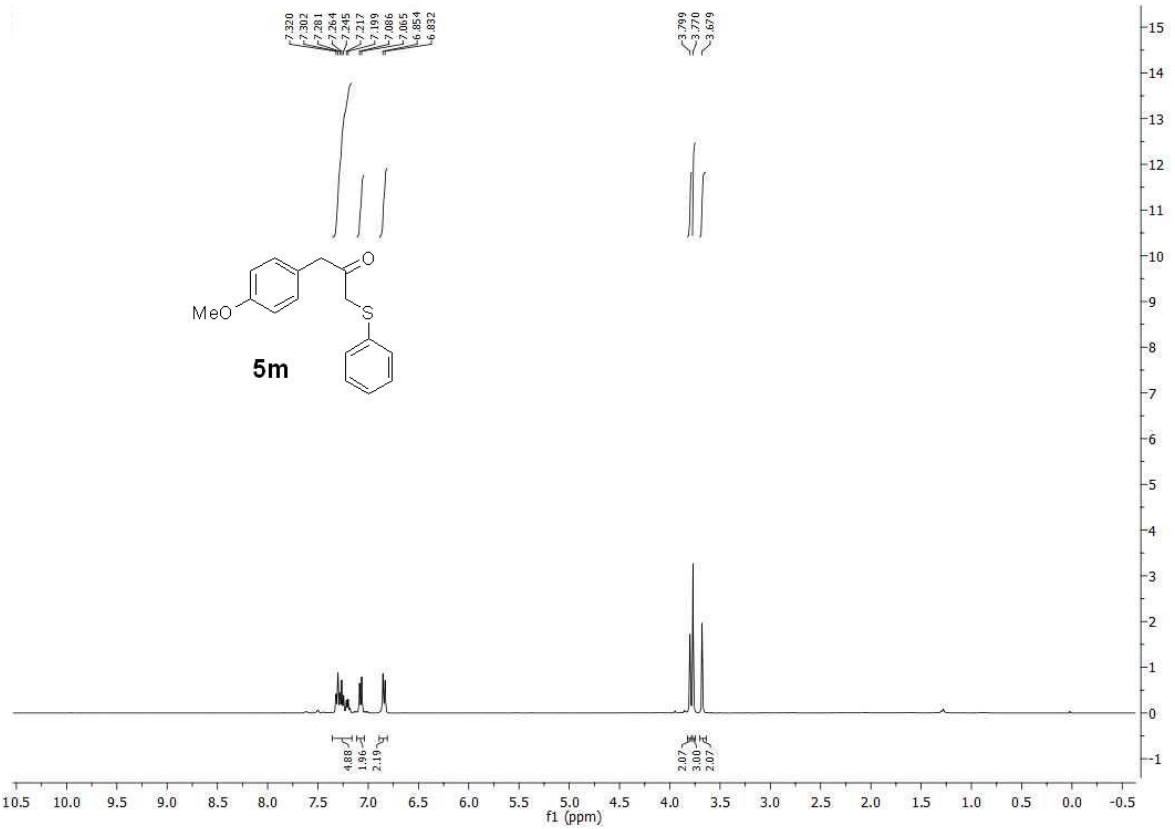
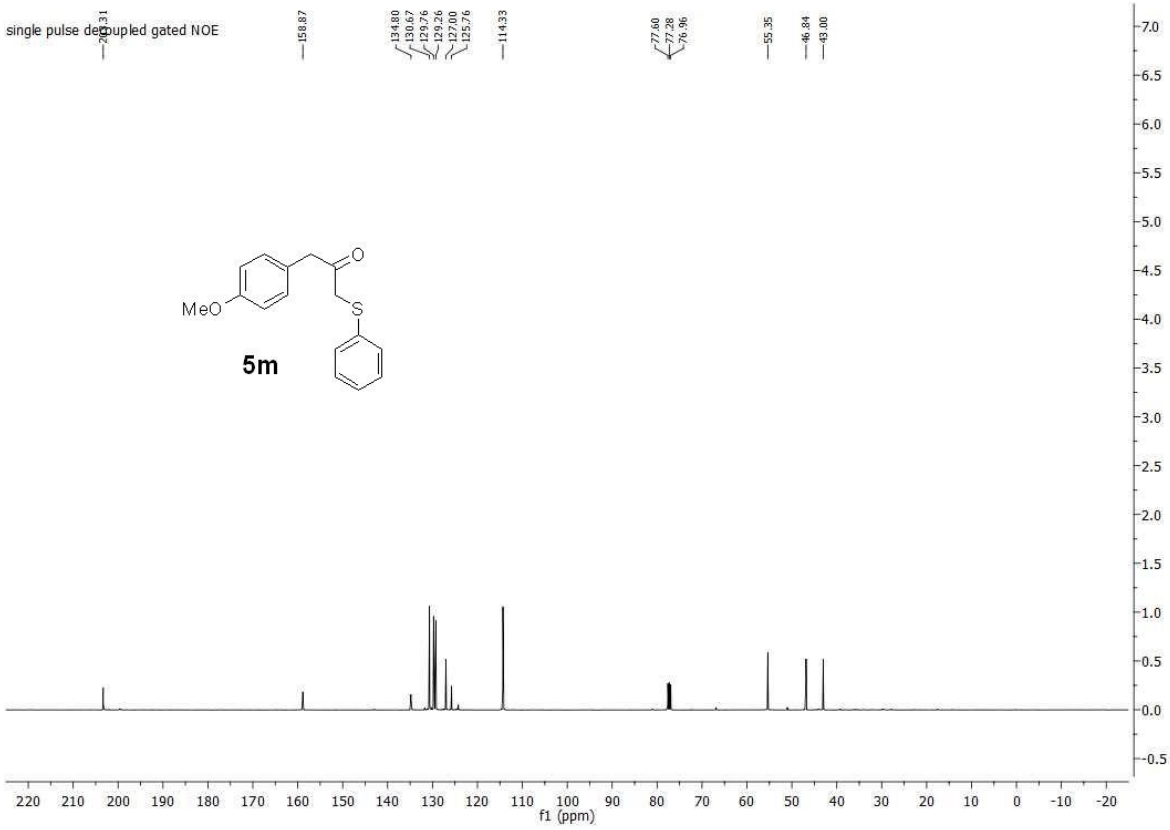
7.306
7.294
7.291
7.288
7.285
7.280
7.268
7.264
7.249
7.244
7.232
7.228
7.223
7.217
7.210
7.193
7.011
6.990
3.823
3.668
0.000
Br
O
S
5l
2.18
5.22
2.14
2.06
2.00
f1 (ppm)


single pulse decoupled gated NOE
200.30
134.37
132.67
131.89
131.34
129.90
129.31
127.22
121.32
77.47
77.15
76.83
46.68
43.35
Br
O
S
5l
f1 (ppm)


7.320
7.302
7.281
7.264
7.245
7.217
7.199
7.086
7.065
6.854
6.832
3.799
3.770
3.679
MeO
O
S
5m
4.88
1.96
2.19
2.07
3.00
2.07
f1 (ppm)


single pulse decoupled gated NOE
197.31
158.87
134.80
130.67
129.76
129.26
127.00
125.76
114.33
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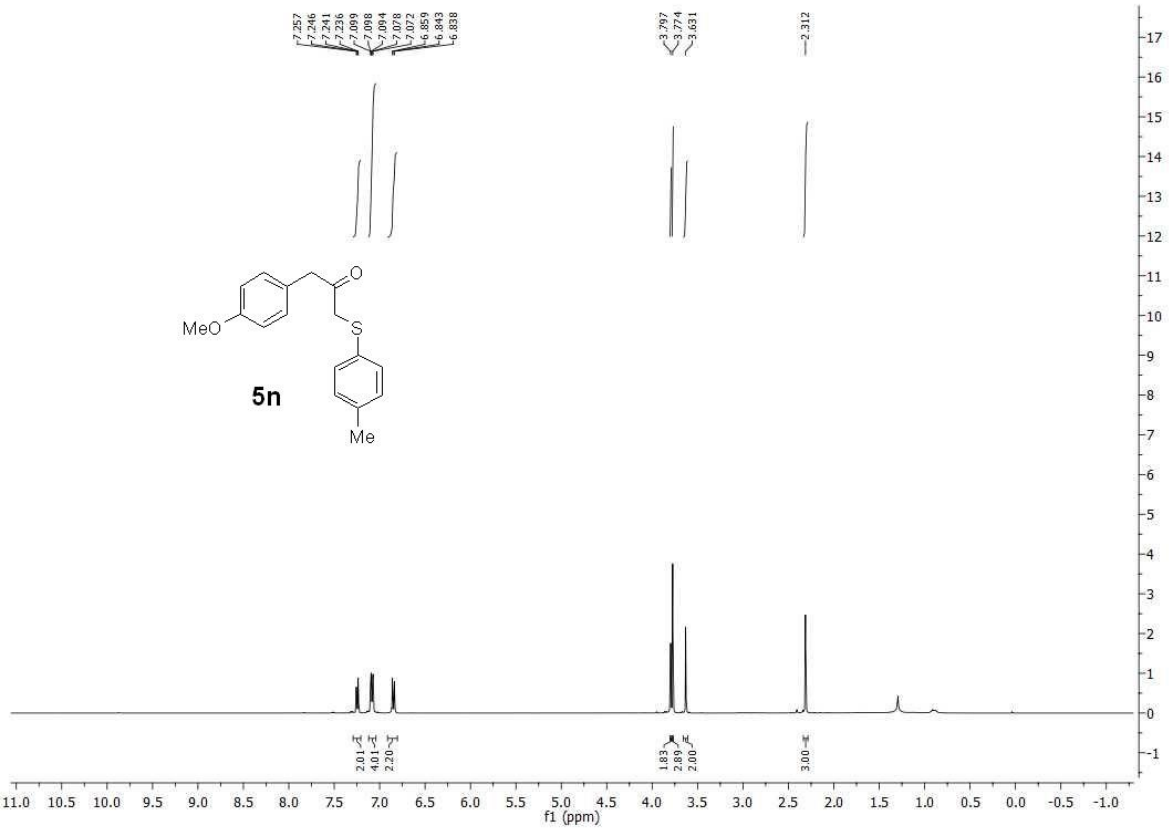
77.38
76.96
55.35
46.84
43.00
MeO
O
S
5m
f1 (ppm)


7.257
7.246
7.241
7.236
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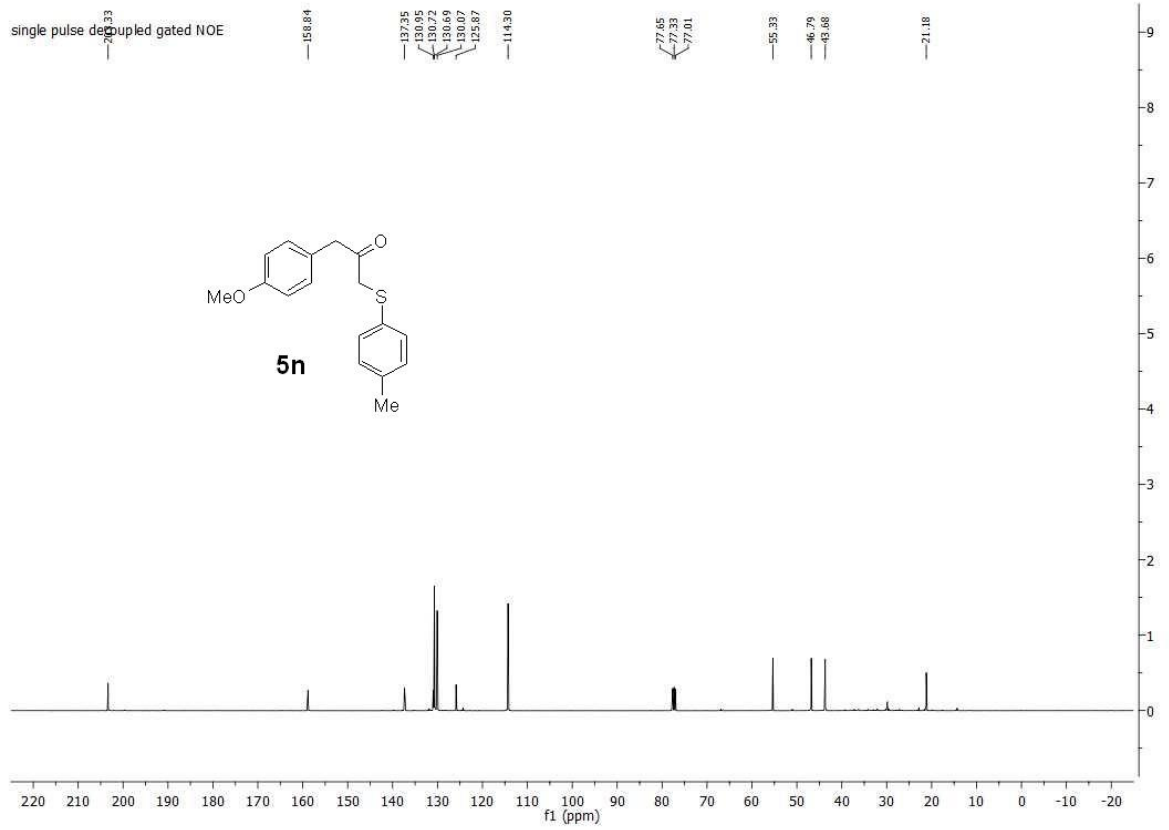
7.098
7.094
7.078
7.072
6.859
6.843
6.838
3.797
3.774
3.631
2.312
MeO
S
O
Me
5n
2.01
4.01
2.20
1.83
2.89
2.00
3.00
f1 (ppm)


single pulse decoupled gated NOE
158.84
137.35
130.95
130.72
130.69
130.07
125.87
114.30
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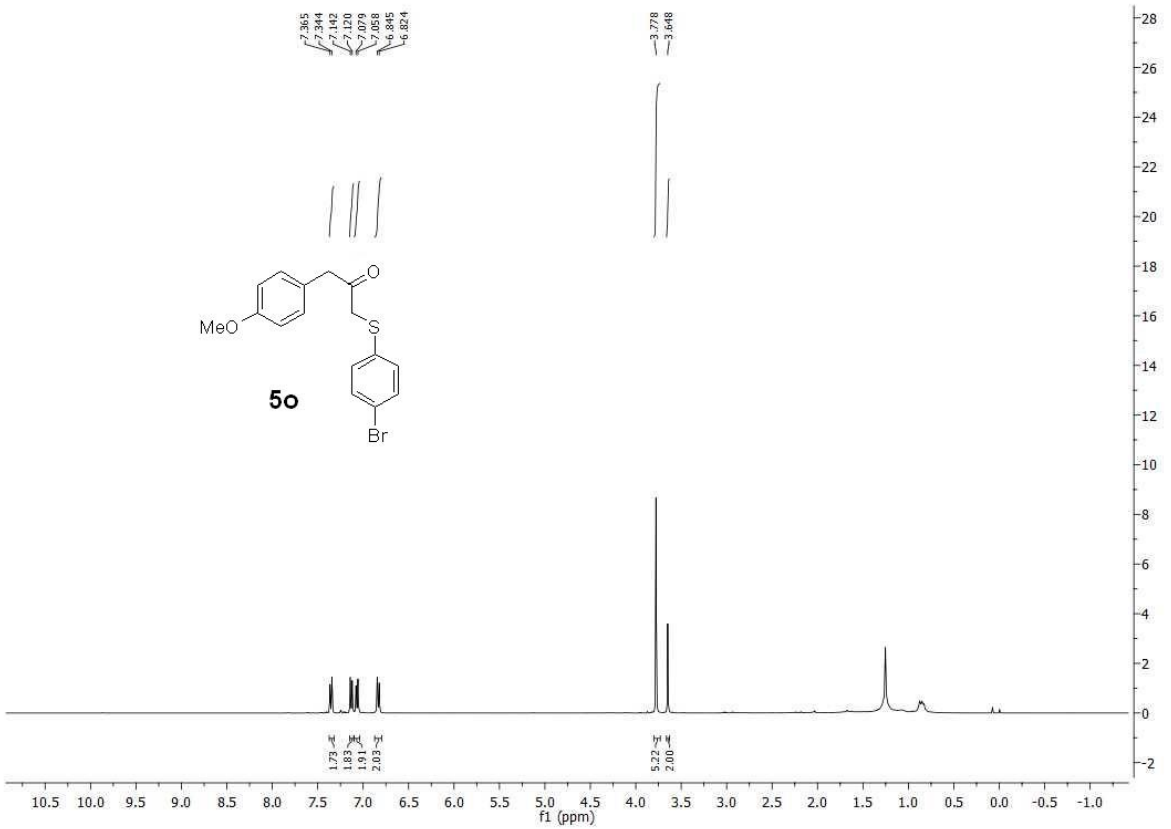
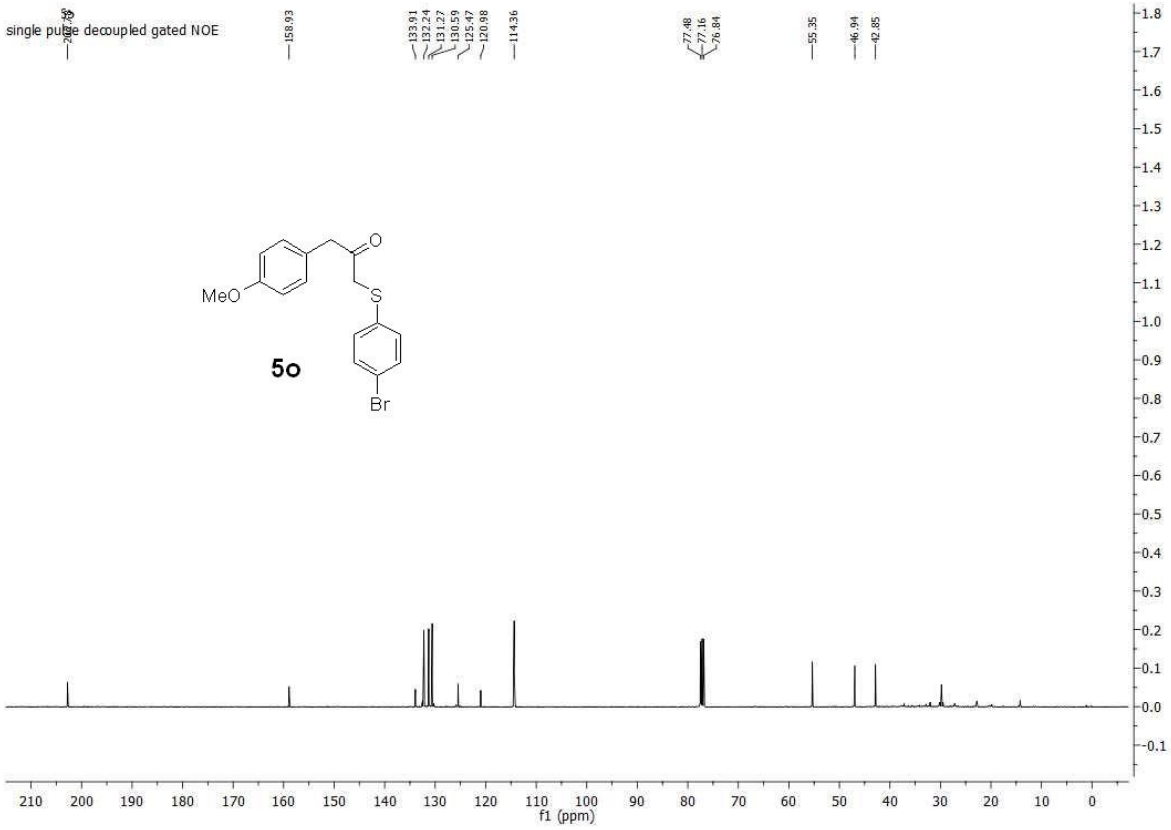
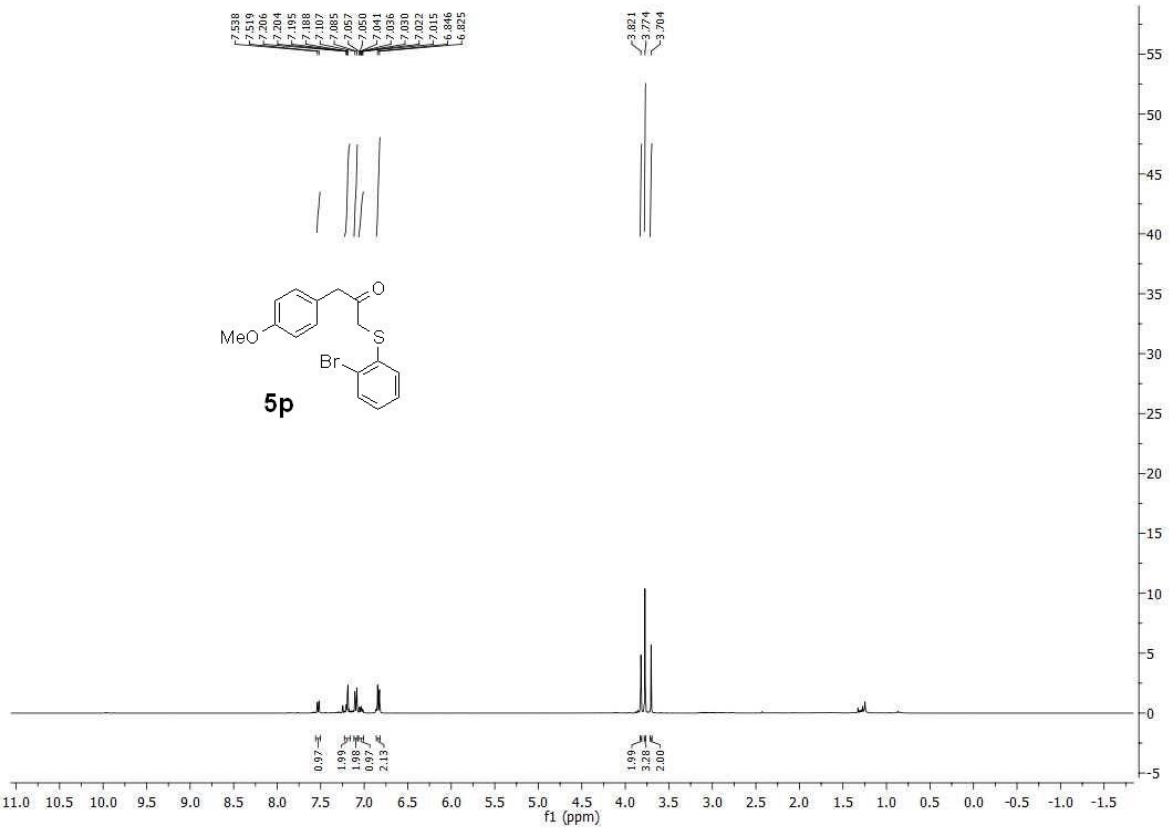
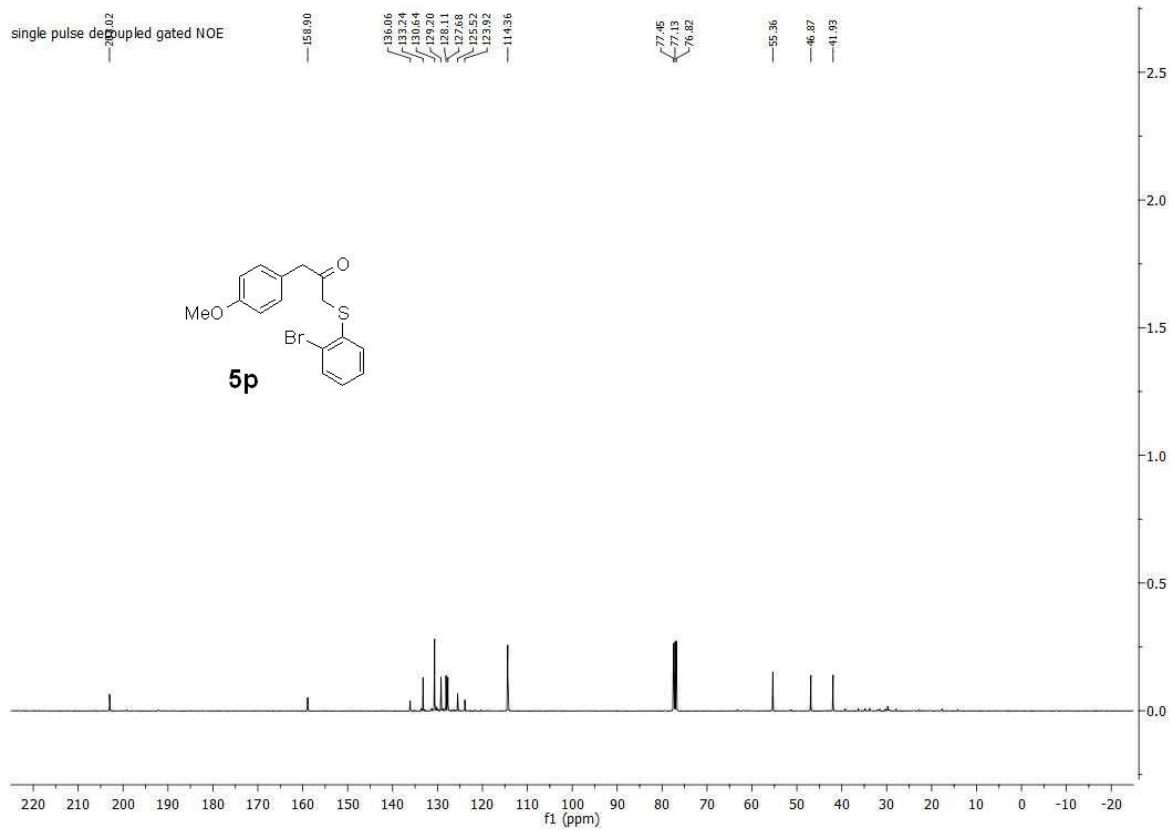
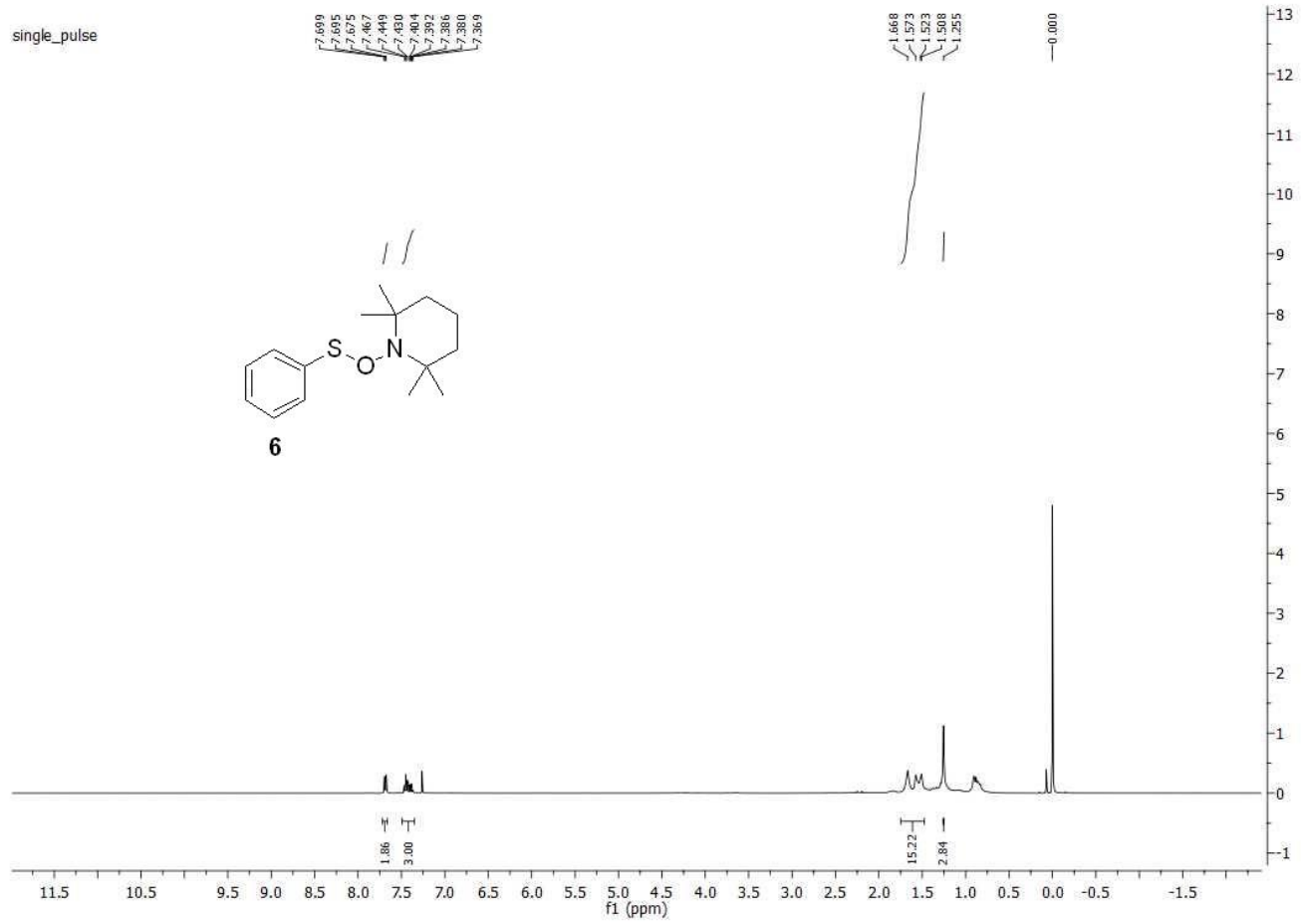
77.01
55.33
46.79
43.68
21.18
MeO
S
O
Me
5n
f1 (ppm)

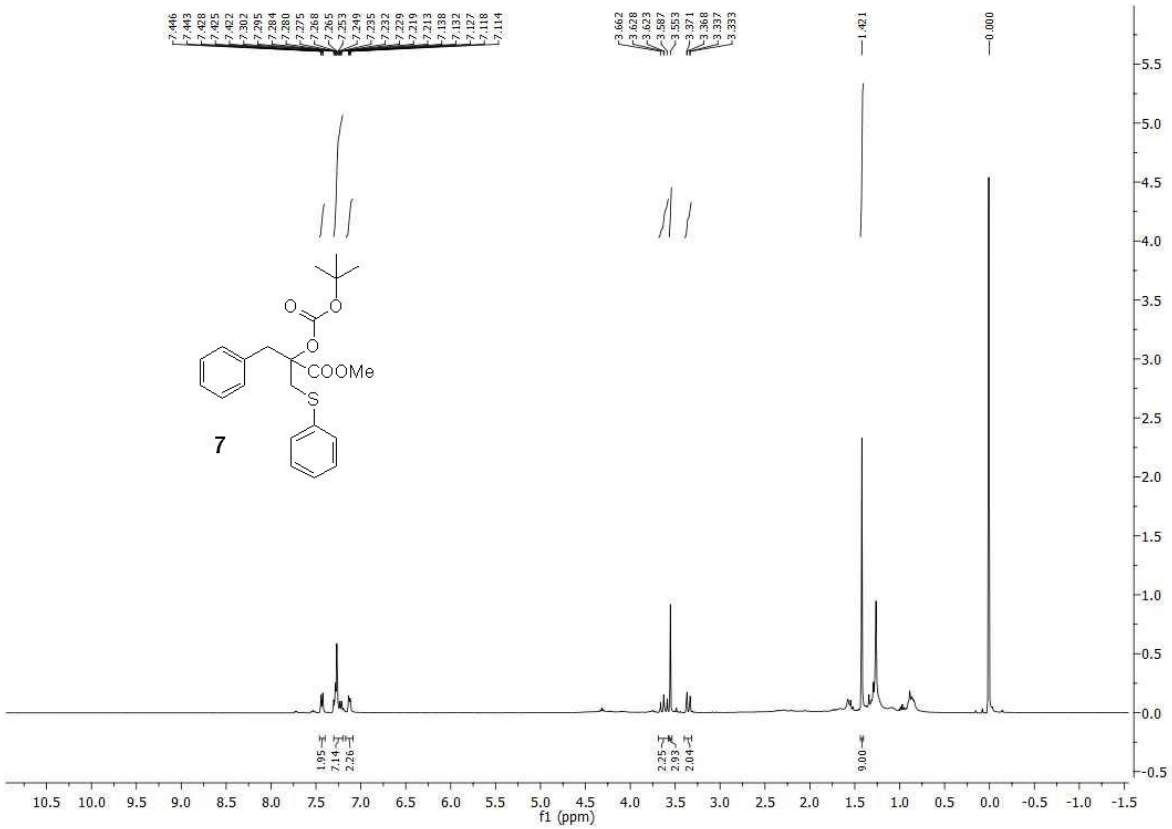

7.365
7.344
7.142
7.120
7.079
7.058
6.845
6.824
3.778
3.648
MeO
O
S
Br
5o
1.73
1.83
1.91
2.03
5.22
2.00
f1 (ppm)


single pulse decoupled gated NOE
158.93
133.91
132.24
131.27
130.59
125.47
120.98
114.36
77.48
77.16
76.84
55.35
46.94
42.85
MeO
O
S
Br
5o
f1 (ppm)


7.538
7.519
7.206
7.204
7.195
7.188
7.107
7.085
7.057
7.050
7.041
7.036
7.030
7.022
7.015
6.846
6.825
3.821
3.774
3.704
MeO
O
S
Br
5p
0.97
1.99
1.98
0.97
2.13
1.99
3.28
2.00
f1 (ppm)


single pulse decoupled gated NOE
200.02
158.90
136.06
133.24
130.64
129.20
128.11
127.68
125.52
123.92
114.36
77.45
77.13
76.82
55.36
46.87
41.93
MeO
O
S
Br
5p
f1 (ppm)


single_pulse
7.699
7.695
7.675
7.467
7.449
7.430
7.404
7.392
7.386
7.380
7.369
1.668
1.573
1.523
1.508
1.255
0.000
S
O
N
6
1.86
3.00
15.22
2.84
f1 (ppm)



Refernces

1. D. Basavaiah, K. R. Reddy and N. Kumaragurubaran, *Nat. Protoc.,* 2007, **2**, 2665