Supporting Information

Regioselective Functionalization of Sulfenamides: S-Arylation with Cyclic Diaryl λ^3-Bromanes and λ^3-Chloranes

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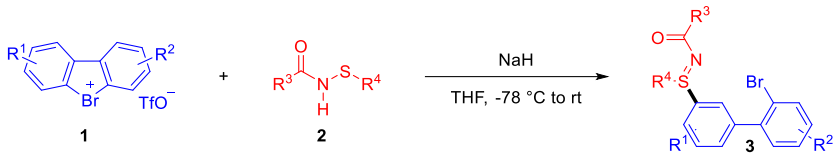
General remarks

All the chemicals that are not mentioned in the subsequent parts were purchased from Bidepharm, Energy Chemical, Aladdin, Macklin or TCI and used without further purification. For column chromatography, flash column and TLC (SiO_2, 60M, pore size 0.04-0.063 mm) were used. The TLC-glass-plates consisted of a 0.25 mm layer of silica 60 with Fluorescence indicator UV254. TLCs were checked under UV-light (254 nm or 365 nm) and stained with an aq. $KMnO_4$-solution. All ^{1}H, ^{13}C, ^{19}F NMR spectra were measured with a BRUKER Avance 400 spectrometer. The chemical shift of each signal was registered in ppm. For ^{1}H and ^{13}C measurements, the chemical shift refers to TMS, showing a signal at 0 ppm. As an internal standard, the remaining protons or respectively the carbons of the corresponding deuterated solvent were used ($CDCl_3$, 7.26 ppm (^{1}H-NMR), 77.16 ppm (^{13}C-NMR)). High-resolution mass spectra (HRMS) were reported from Bruker ultrafleXtreme MALDI TOF/TOF or Bruker autoflex maX MALDI-TOF(TOF) instrument with an ESI source. A chromatographic purification was performed before each measurement.

General procedure for sulfilimines synthesis

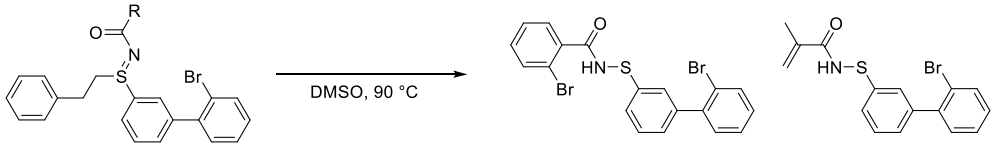


To a reaction vial equipped with a stirring bar was charged with the diaryl λ^3-bromane (or diaryl λ^3-chlorane) **1** (0.1 mmol, 1.0 eq.) and sulfenamide **2** (0.1 mmol, 1.0 eq.). Dry THF (1.5 mL) was added and the reaction vial was stirred at -78 °C. NaH (0.2 mmol, 2.0 eq) was then added in one portion. Afterwards, the reaction was transferred to room temperature. The reaction was monitored by TLC and stopped after 2 hours. Water (1 mL) was slowly added and the mixture was extracted with ethyl acetate (3 times). The combined organic layers were washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography using silica gel with ethyl acetate in petroleum ether as the eluent.

Scale-up synthesis

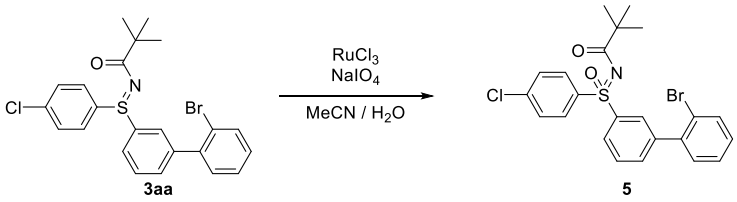
To a reaction vial equipped with a stirring bar was charged with diaryl λ^3-bromane **1a** (1.0 mmol, 1.0 eq.) and sulfenamide **2a** (1.0 mmol, 1.0 eq.). Dry tetrahydrofuran (15 mL) was added and the reaction vial was stirred at -78 °C. NaH (2.0 mmol, 2.0 eq) was then added in one portion. Afterwards, the reaction was transferred to room temperature and stirred. The reaction was monitored by TLC and stopped when it completed. Water (10 mL) was slowly added and the mixture was extracted with ethyl acetate (3 times). The combined organic layers were washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography using silica gel with ethyl acetate in petroleum ether (EtOAc : PE = 2 : 8) as the eluent. (0.44 g for **3aa**, 92% yield).

Synthesis of compound 4



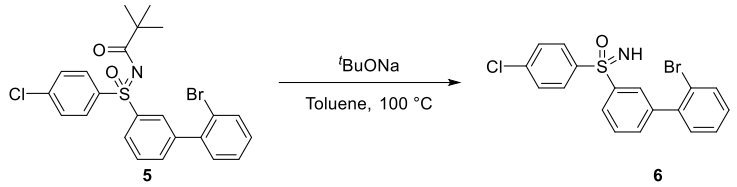
A 25 mL oven-dried Schlenk tube equipped with a N_2 balloon was charged with **3ay** (56.7 mg, 0.10 mmol, 1.0 equiv) or **3az** (45.2 mg, 0.10 mmol, 1.0 equiv) and anhydrous DMSO (1.0 mL, 0.1 M) at room temperature. Then the reaction mixture was heated at 90 °C in an oil bath for 14 h. After cooling to room temperature, water was added and the mixture was extracted with ethyl acetate (3 times). The combined organic layers were washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure. The crude products were purified by column chromatography to give **4a** in 72% yield (33.3 mg) as a paint yellow oil and **4b** in 74% yield (25.8 mg) as a colorless oil by column chromatography (EtOAc : PE = 1 : 9).

Synthesis of compound 5



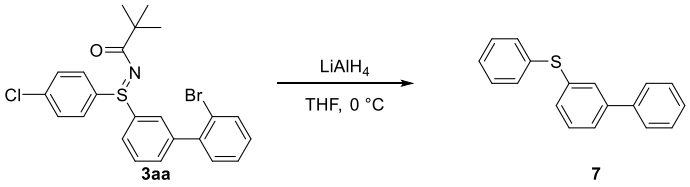
To a solution of **3aa** (47.6 mg, 0.1 mmol, 1.0 equiv.) in MeCN (1.5 mL) was added the solution of $NaIO_4$ (32.1 mg, 0.15mmol, 1.5 equiv.) in H_2O (2.5 mL), and $RuCI_3$ (0.2 mg, 0.001 mmol, 0.01 equiv.) was then added. The reaction mixture was stirred at 0℃ in an ice bath for 4 hours. After completion of reaction as monitored by TLC analysis, the mixture was extracted with CH_2Cl_2 (3 times). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified directly by flash column chromatography on silica gel (EtOAc : PE = 1 : 4) to give the corresponding product **5** as a colorless oil (45.6 mg, 91% yield).

Synthesis of compound 6



To a stirred solution of **5** (49.2 mg, 0.1 mmol, 1 equiv.) in toluene (1 mL) under N_2 was added ^{t}BuONa (13.5 mg, 0.1 mmol, 1.4 equiv.). The reaction mixture was stirred at 100 °C for 12 h. The reaction mixture was quenched with H_2O and filtered through a pad of celite using ethyl acetate as eluent. The combined filtrates were washed with brine, and the combined organics were dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purification by flash column chromatography on silica gel (EtOAc : PE = 1 : 4) to afford the corresponding product **6** (38.2 mg, 94%,) as a colorless oil.

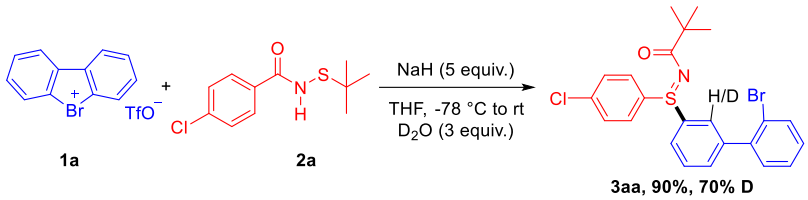
Synthesis of compound 7



To a solution of **3aa** (47.6 mg. 0.1 mmol, 1.0 equiv) in dry THF (1.0 mL, 0.1 M) was added $LiAlH_4$ (11.4 mg. 0.3 mmol, 3,0 equiv) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 24 hours. The reaction was quenched with aqueous ammonium chloride at 0 °C, and then the mixture was filtered through a pad of celite using ethyl acetate as eluent. The combined organics were washed with brine, dried over Na_2SO_4, and concentrated under reduced

pressure. The residue was purification by flash column chromatography on silica gel (PE) to afford the product **7** (24.8 mg, 95% yield) as a colorless oil.

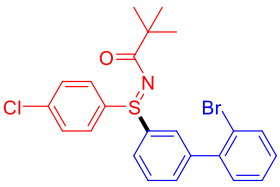
Deuterated labelling experiment



1a **2a** **3aa, 90%, 70% D**

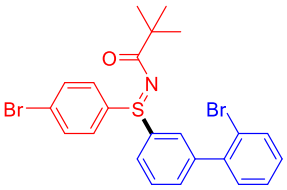
To a reaction vial equipped with a stirring bar was charged dry THF (1.5 mL) and D_2O (0.3 mmol, 3.0 eq). NaH (0.5 mmol, 5.0 eq) was then added in one portion. The reaction vial was stirred at room temperature for 10 min. Then diaryl λ^3-bromane **1a** (0.1 mmol, 1.0 eq.) and sulfenamide **2a** (0.1 mmol, 1.0 eq.) were added. The reaction was monitored by TLC until reaction completed. Water (1 mL) was slowly added and the mixture was extracted with ethyl acetate (3 times). The combined organic layers were washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography using silica gel with ethyl acetate in petroleum ether as the eluent to afford the product **3aa** in 90% yield with 70% deuterium incorporation.

N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)pivalamide (3aa)



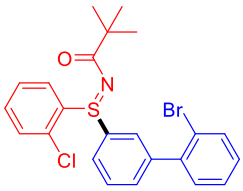
Yield: 47.1mg, 99%. Yellow oil. Purified by column chromatography on silica gel (EtOAc : PE = 2 : 8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 – 7.75 (m, 2H), 7.76 – 7.69 (m, 2H), 7.66 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.47 – 7.41 (m, 2H), 7.38 (td, *J* = 7.5, 1.2 Hz, 1H), 7.30 – 7.21 (m, 2H), 1.29 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 190.4, 142.6, 140.6, 138.1, 136.2, 135.5, 133.4, 132.8, 131.1, 130.0, 129.61, 129.59, 129.0, 128.6, 127.7, 126.5, 122.3, 40.3, 28.7. **HRMS** [ESI]: m/z calculated for $C_{23}H_{21}BrClNOS$ $[M+H]^+$ 474.0289, found 474.0287. IR (thin film): ν_{max} 2949, 1576, 1475, 1389, 1305, 1191, 1090, 1012, 755 cm^{-1}.

N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-bromophenyl)-l4-sulfaneylidene)pivalamide (3ab)



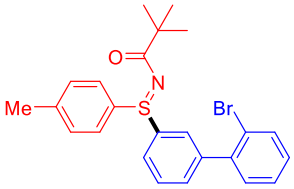
Yield: 49.5 mg, 95%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 2 : 8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.82 – 7.74 (m, 2H), 7.69 – 7.62 (m, 3H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.57 – 7.50 (m, 2H), 7.38 (td, *J* = 7.5, 1.2 Hz, 1H), 7.31 – 7.22 (m, 2H), 1.29 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 190.4, 142.6, 140.6, 136.14, 136.06, 133.4, 133.0, 132.9, 131.1, 129.6, 129.6, 129.1, 128.6, 127.7, 126.6, 126.4, 122.3, 40.3, 28.7. **HRMS** [ESI]: m/z calculated for: $C_{23}H_{21}Br_2NOS$ $[M+H]^+$ 517.9783, found 517.9797. IR (thin film): ν_{max} 2949, 2861, 1575, 1459, 1305, 1192, 1008, 755, 494 cm^{-1}.

N-((2'-bromo-[1,1'-biphenyl]-3-yl)(2-chlorophenyl)-l4-sulfaneylidene)pivalamide (3ac)



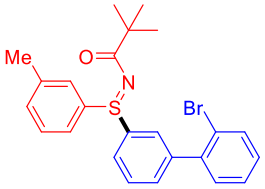
Yield: 41 mg, 86%. Faint yellow oil. Purified by column chromatography on silica gel (EtOAc : PE = 2 : 8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.89 – 7.82 (m, 2H), 7.65 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.48 – 7.39 (m, 3H), 7.37 (td, *J* = 7.5, 1.2 Hz, 1H), 7.28 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.22 (td, *J* = 7.7, 1.8 Hz, 1H), 1.29 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 190.2, 142.3, 140.6, 135.4, 135.1, 134.0, 133.4, 132.8, 132.7, 131.2, 130.5, 129.5, 129.4, 129.3, 128.3, 128.0, 127.7, 127.6, 122.3, 40.3, 28.7. **HRMS** [ESI]: m/z calculated for $C_{23}H_{21}BrClNOS$ $[M+H]^+$ 474.0289, found 474.0287. IR (thin film): ν_{max} 2949, 2862, 1577, 1458, 1303, 1189, 754, 692, 455 cm^{-1}.

N-((2'-bromo-[1,1'-biphenyl]-3-yl)(p-tolyl)-l4-sulfaneylidene)pivalamide (3ad)



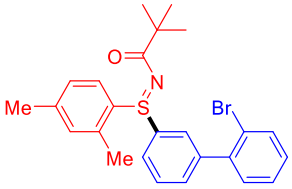
Yield: 20 mg, 44%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 2 : 8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.79 (t, *J* = 1.6 Hz, 1H), 7.76 (dt, *J* = 7.0, 2.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 3H), 7.54 – 7.47 (m, 2H), 7.37 (td, *J* = 7.5, 1.2 Hz, 1H), 7.30 – 7.20 (m, 4H), 2.36 (s, 3H), 1.29 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 190.2, 142.4, 142.3, 140.8, 136.8, 133.5, 133.4, 132.4, 131.2, 130.5, 129.5, 129.4, 128.5, 127.72, 127.68, 126.5, 122.3, 40.3, 28.7, 21.5. **HRMS** [ESI]: m/z calculated for $C_{24}H_{24}BrNOS$ $[M+H]^+$ 454.0835, found 454.0841. IR (thin film): ν_{max} 2948, 1569, 1458, 1305, 1192, 1017, 755, 694, 511 cm^{-1}.

N-((2'-bromo-[1,1'-biphenyl]-3-yl)(m-tolyl)-l4-sulfaneylidene)pivalamide (3ae)



Yield: 21.4 mg, 47%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 2 : 8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.85 – 7.75 (m, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.54 – 7.47 (m, 2H), 7.36 (dt, *J* = 13.3, 7.9 Hz, 2H), 7.30 – 7.21 (m, 3H), 2.37 (s, 3H), 1.30 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 190.3, 142.3, 140.8, 139.9, 136.7, 136.5, 133.4, 132.6, 132.5, 131.2, 129.6, 129.5, 129.4, 128.6, 127.9, 127.7, 126.6, 124.7, 122.3, 40.3, 28.7, 21.5. **HRMS** [ESI]: m/z calculated for $C_{24}H_{24}BrNOS$ $[M+H]^+$ 454.0835, found 454.0836. IR (thin film): ν_{max} 2949, 2923, 2861, 1570, 1476, 1388, 1305, 1192, 755 cm^{-1}.

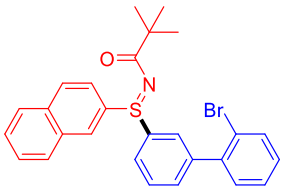
N-((2'-bromo-[1,1'-biphenyl]-3-yl)(2,4-dimethylphenyl)-l4-sulfaneylidene)pivalamide (3af)



Yield: 20.2 mg, 43%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 2 : 8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 – 7.69 (m, 3H), 7.66 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.37 (td, *J* = 7.5, 1.3 Hz, 1H), 7.28 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.23 (td, *J* = 7.7, 1.8 Hz, 1H), 7.14 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.05 (s, 1H), 2.58 (s, 3H), 2.32 (s, 3H), 1.27 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 190.0, 142.2, 142.2, 140.8, 138.4, 136.0, 133.4, 132.2, 132.0, 131.9, 131.2, 129.4, 129.3, 128.9, 128.5, 127.7, 127.4, 127.0, 122.4, 40.2, 28.7, 21.3, 19.4. **HRMS** [ESI]: m/z calculated for

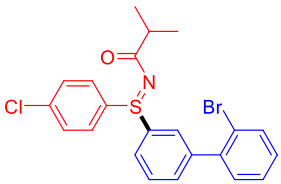
$C_{25}H_{26}BrNOS$ $[M+H]^+$ 468.0991, found 468.0998. IR (thin film): ν_{max} 2923, 2856, 1574, 1558, 1306, 1192, 756, 694, 617 cm^{-1}.

N-((2'-bromo-[1,1'-biphenyl]-3-yl)(naphthalen-2-yl)-l4-sulfaneylidene)pivalamide (3ag)



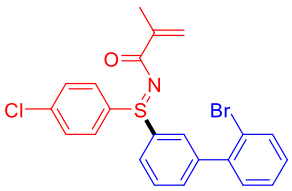
Yield: 40.2 mg, 82%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 2 : 8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.38 (s, 1H), 7.90 (dd, *J* = 8.9, 3.6 Hz, 2H), 7.87 – 7.81 (m, 3H), 7.70 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.54 – 7.46 (m, 2H), 7.39 – 7.32 (m, 1H), 7.27 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.21 (td, *J* = 7.6, 1.8 Hz, 1H), 1.33 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 190.4, 142.4, 140.7, 136.4, 134.5, 133.7, 133.4, 132.8, 132.6, 131.2, 130.2, 129.47, 129.46, 129.0, 128.7, 128.6, 128.5, 128.0, 127.7, 127.4, 126.6, 122.8, 122.4, 40.4, 28.8. **HRMS** [ESI]: m/z calculated for $C_{27}H_{24}BrNOS$ $[M+H]^+$ 490.0835, found 490.0838. IR (thin film): ν_{max} 2948, 2923, 1569, 1458, 1303, 1190, 1017, 753, 476 cm^{-1}.

N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)isobutyramide (3ah)



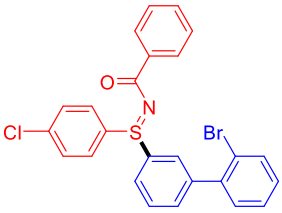
Yield: 37.7 mg, 82%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 2 : 8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.79 – 7.73 (m, 2H), 7.73 – 7.68 (m, 2H), 7.67 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.48 – 7.42 (m, 2H), 7.38 (td, *J* = 7.5, 1.3 Hz, 1H), 7.31 – 7.21 (m, 2H), 2.76 (hept, *J* = 6.9 Hz, 1H), 1.21 (d, *J* = 6.9 Hz, 6H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 188.9, 142.7, 140.5, 138.3, 135.6, 134.9, 133.4, 133.0, 131.1, 130.1, 129.7, 129.6, 129.2, 128.7, 127.7, 126.8, 122.3, 36.6, 20.6. **HRMS** [ESI]: m/z calculated for $C_{22}H_{19}BrClNOS$ $[M+H]^+$ 460.0132, found 460.0135. IR (thin film): ν_{max} 2963, 2866, 1580, 1459, 1224, 1089, 1012, 755, 507 cm^{-1}.

N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)methacrylamide (3ai)



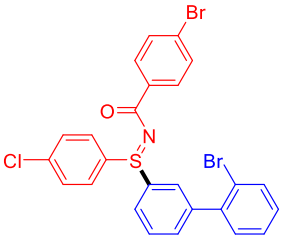
Yield: 40.8 mg, 89%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 2 : 8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.86 – 7.78 (m, 2H), 7.78 – 7.71 (m, 2H), 7.66 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.49 – 7.42 (m, 2H), 7.38 (td, *J* = 7.5, 1.2 Hz, 1H), 7.31 – 7.21 (m, 2H), 6.14 (s, 1H), 5.37 (t, *J* = 1.9 Hz, 1H), 2.07 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 178.5, 142.7, 141.8, 140.5, 138.3, 135.7, 135.0, 133.4, 133.0, 131.1, 130.1, 129.7, 129.6, 129.2, 128.9, 127.8, 126.8, 122.3, 121.1, 19.6. **HRMS** [ESI]: m/z calculated for $C_{22}H_{17}BrClNOS$ $[M+H]^+$ 457.9976, found 457.9973. IR (thin film): ν_{max} 2920, 1549, 1458, 1311, 1189, 1090, 1011, 692, 508 cm^{-1}.

N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)benzamide (3aj)



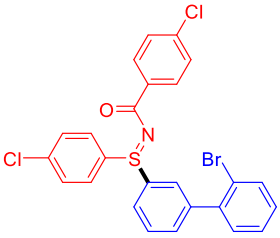
Yield: 44 mg, 89%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 2 : 8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.28 – 8.21 (m, 2H), 7.91 – 7.85 (m, 2H), 7.84 – 7.78 (m, 2H), 7.67 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.47 (t, *J* = 7.7 Hz, 3H), 7.43 – 7.35 (m, 3H), 7.30 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.27 – 7.22 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 176.7, 142.8, 140.5, 138.4, 136.1, 135.7, 135.0, 133.4, 133.1, 131.2, 131.1, 130.2, 129.74, 129.65, 129.2, 129.0, 128.9, 127.9, 127.8, 126.8, 122.3. **HRMS** [ESI]: m/z calculated for $C_{25}H_{17}BrClNOS$ $[M+H]^+$ 493.9976, found 493.9972. IR (thin film): ν_{max} 1595, 1556, 1474, 1322, 1393, 1012, 713, 692, 506 cm^{-1}.

4-bromo-N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)benzamide (3ak)



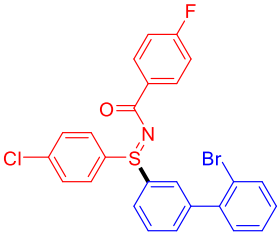
Yield: 48.9 mg, 85%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 2 : 8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 8.5 Hz, 2H), 7.91 – 7.87 (m, 1H), 7.85 (dt, *J* = 7.0, 2.1 Hz, 1H), 7.82 – 7.76 (m, 2H), 7.67 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.54 – 7.45 (m, 4H), 7.38 (td, *J* = 7.5, 1.3 Hz, 1H), 7.30 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.27 – 7.22 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 175.7, 142.8, 140.4, 138.6, 135.4, 135.1, 134.7, 133.4, 133.3, 131.13, 131.06, 130.7, 130.2, 129.8, 129.7, 129.2, 128.9, 127.8, 126.8, 125.8, 122.3. **HRMS** [ESI]: m/z calculated for $C_{25}H_{16}Br_2ClNOS$ $[M+H]^+$ 571.9081, found 571.9070. IR (thin film): ν_{max} 2925, 1591, 1319, 1011, 756, 693, 616, 507, 459 cm^{-1}.

N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)-4-chlorobenzamide (3al)



Yield: 43.4 mg, 82%. Colourless oil. Purified by column chromatography on sili ca gel (EtOAc : PE = 2 : 8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.21 – 8.14 (m, 2H), 7.91 – 7.87 (m, 1H), 7.85 (dt, *J* = 6.9, 2.1 Hz, 1H), 7.82 – 7.76 (m, 2H), 7.66 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.50 – 7.44 (m, 2H), 7.40 – 7.33 (m, 3H), 7.31 – 7.21 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 175.6, 142.8, 140.4, 138.6, 137.2, 135.4, 134.8, 134.6, 133.4, 133.2, 131.1, 130.4, 130.2, 129.8, 129.7, 129.2, 128.9, 128.1, 127.8, 126.8, 122.3. **HRMS** [ESI]: m/z calculated for $C_{25}H_{16}BrCl_2NOS$ $[M+H]^+$ 527.9586, found 527.9576. IR (thin film): ν_{max} 2852, 1591, 1553, 1317, 1089, 1013, 758, 692, 506 cm^{-1}.

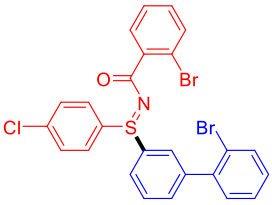
N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)-4-fluorobenzamide (3am)



Yield: 48.5 mg, 94%. Faint yellow oil. Purified by column chromatography on silica gel (EtOAc : PE = 2 : 8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.29 – 8.19 (m, 2H), 7.89 (d, *J* = 1.7 Hz, 1H), 7.86 (dt, *J* = 7.0, 2.1 Hz, 1H), 7.82 – 7.76 (m, 2H), 7.67 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.61 – 7.53 (m, 2H), 7.50 – 7.44 (m, 2H), 7.38 (td, *J* = 7.4, 1.2 Hz, 1H), 7.32 – 7.21 (m, 2H), 7.06 (t, *J* = 8.7 Hz, 2H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 175.65, 164.79 (d, *J* = 250.2 Hz), 142.8, 140.4, 138.5, 135.5, 134.9, 133.4, 133.2, 132.4 (d, *J* = 2.9 Hz), 131.3, 131.2, 131.1,

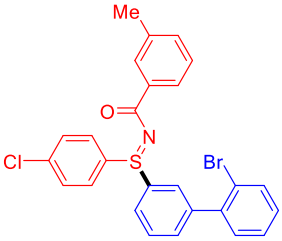
130.2, 129.7 (d, *J* = 9.9 Hz), 129.2, 128.9, 127.8, 126.8, 122.3, 114.7 (d, *J* = 21.5 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.58. **HRMS** [ESI]: m/z calculated for $C_{25}H_{16}BrClFNOS$ $[M+Na]^+$ 511.9881, found 511.9873. IR (thin film): ν_{max} 2924, 1607, 1561, 1320, 1148, 1012, 766, 691, 504 cm^{-1}.

2-bromo-N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)benzamide (3an)



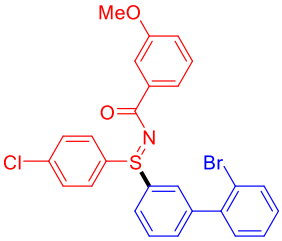
Yield: 50.9 mg, 89%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 2 : 8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.92 – 7.89 (m, 1H), 7.88 – 7.80 (m, 3H), 7.73 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.66 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.61 – 7.54 (m, 3H), 7.52 – 7.46 (m, 2H), 7.38 (td, *J* = 7.5, 1.3 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.22 (dtd, *J* = 19.2, 7.7, 1.8 Hz, 2H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 178.0, 142.9, 140.4, 139.4, 138.7, 135.0, 134.1, 133.43, 133.37, 133.3, 131.2, 130.3, 130.2, 129.8, 129.7, 129.5, 129.0, 127.8, 127.1, 127.0, 122.3, 120.5. **HRMS** [ESI]: m/z calculated for $C_{25}H_{16}Br_2ClNOS$ $[M+H]^+$ 571.9081, found 571.9073. IR (thin film): ν_{max} 2921, 2851, 1582, 1556, 1315, 1141, 1011, 715, 692 cm^{-1}.

N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)-3-methylbenzamide (3ao)



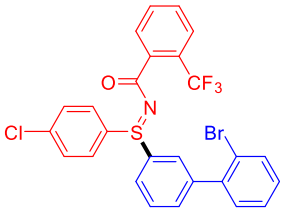
Yield: 47.4 mg, 93%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 2 : 8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 7.9 Hz, 2H), 7.91 – 7.84 (m, 2H), 7.83 – 7.77 (m, 2H), 7.66 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.49 – 7.44 (m, 2H), 7.37 (td, *J* = 7.5, 1.2 Hz, 1H), 7.29 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.27 – 7.18 (m, 3H), 2.38 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 176.8, 142.7, 141.3, 140.5, 138.3, 135.8, 135.1, 133.4, 133.1, 131.2, 130.1, 129.7, 129.6, 129.2, 129.0, 128.9, 128.6, 127.8, 126.8, 122.3, 21.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -108.44. **HRMS** [ESI]: m/z calculated for $C_{26}H_{19}BrClNOS$ $[M+Na]^+$ 529.9952, found 529.9949. IR (thin film): ν_{max} 2919, 1592, 1458, 1318, 1295, 1172, 1011, 754, 505 cm^{-1}.

N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)-3-methoxybenzamide (3ap)



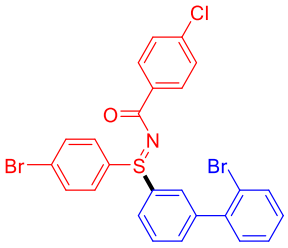
Yield: 43.2 mg, 82%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 2 : 8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 – 7.85 (m, 3H), 7.83 – 7.79 (m, 2H), 7.78 – 7.75 (m, 1H), 7.66 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.50 – 7.44 (m, 2H), 7.37 (td, *J* = 7.5, 1.2 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.26 – 7.21 (m, 1H), 7.02 (dd, *J* = 8.2, 2.6 Hz, 1H), 3.84 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 176.5, 159.3, 142.8, 140.4, 138.4, 137.6, 135.6, 134.9, 133.4, 133.2, 131.2, 130.2, 129.8, 129.7, 129.2, 128.9, 127.8, 126.9, 122.3, 121.6, 117.5, 113.4, 55.4. **HRMS** [ESI]: m/z calculated for $C_{26}H_{19}BrClNO_2S$ $[M+H]^+$ 524.0081, found 524.0073. IR (thin film): ν_{max} 2934, 1561, 1459, 1307, 1235, 1011, 831, 754, 504 cm^{-1}.

N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)-2-(trifluoromethyl) benzamide (3aq)



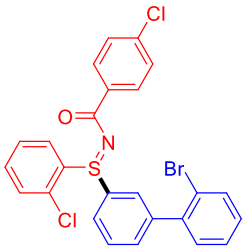
Yield: 46.7 mg, 83%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 2 : 8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.87 – 7.82 (m, 2H), 7.82 – 7.75 (m, 3H), 7.69 – 7.64 (m, 2H), 7.61 – 7.56 (m, 2H), 7.55 – 7.43 (m, 4H), 7.38 (td, *J* = 7.5, 1.3 Hz, 1H), 7.30 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.26 – 7.21 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 178.2, 142.9, 140.4, 138.7, 138.0 (d, *J* = 2.2 Hz), 134.8, 133.9, 133.4, 133.3, 131.5, 131.1, 130.2, 129.8, 129.7, 129.4, 129.02, 128.97, 127.8, 127.4, 127.0, 126.3 (q, *J* = 5.3 Hz), 124.0 (q, *J* = 273.6 Hz), 122.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.50. **HRMS** [ESI]: m/z calculated for $C_{26}H_{16}BrClF_3NOS$ $[M+H]^+$ 561.9849, found 561.9843. IR (thin film): ν_{max} 2923, 1592, 1313, 1164, 1053, 756, 692, 596, 505 cm^{-1}.

N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-bromophenyl)-l4-sulfaneylidene)-4-chlorobenzamide (3ar)



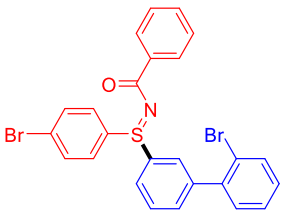
Yield: 50.8 mg, 88%. White solid. Purified by column chromatography on silica gel (EtOAc : PE = 2 : 8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.23 – 8.14 (m, 2H), 7.89 (d, *J* = 2.0 Hz, 1H), 7.85 (dt, *J* = 6.9, 2.2 Hz, 1H), 7.76 – 7.69 (m, 2H), 7.69 – 7.61 (m, 3H), 7.60 – 7.53 (m, 2H), 7.41 – 7.33 (m, 3H), 7.32 – 7.21 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 175.6, 142.8, 140.4, 137.2, 135.4, 135.3, 134.6, 133.4, 133.3, 133.2, 131.1, 130.4, 129.8, 129.7, 129.3, 128.9, 128.1, 127.8, 126.91, 126.85, 122.3. **HRMS** [ESI]: m/z calculated for $C_{25}H_{16}Br_2ClNOS$ $[M+H]^+$ 571.9081, found 571.9080. IR (thin film): ν_{max} 1591, 1552, 1459, 1317, 1165, 1008, 757, 723, 502 cm^{-1}.

N-((2'-bromo-[1,1'-biphenyl]-3-yl)(2-chlorophenyl)-l4-sulfaneylidene)-4-chlorobenzamide (3as)



Yield: 43.4 mg, 82%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 2 : 8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.21 – 8.14 (m, 2H), 7.91 – 7.87 (m, 1H), 7.85 (dt, *J* = 6.9, 2.1 Hz, 1H), 7.82 – 7.76 (m, 2H), 7.67 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.50 – 7.44 (m, 2H), 7.41 – 7.33 (m, 3H), 7.29 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.27 – 7.22 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 175.6, 142.8, 140.4, 138.6, 137.2, 135.4, 134.8, 134.6, 133.4, 133.2, 131.1, 130.4, 130.2, 129.8, 129.7, 129.2, 128.9, 128.1, 127.8, 126.8, 122.3. **HRMS** [ESI]: m/z calculated for $C_{25}H_{16}BrCl_2NOS$ $[M+H]^+$ 527.9586, found 527.9584. IR (thin film): ν_{max} 2924, 1591, 1552, 1318, 1088, 1012, 757, 690, 505 cm^{-1}.

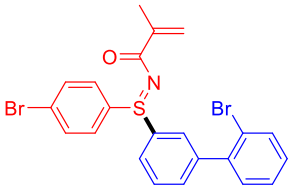
N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-bromophenyl)-l4-sulfaneylidene)benzamide (3at)



Yield: 44.2 mg, 82%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 2 : 8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.28 – 8.22 (m, 2H), 7.92 – 7.89 (m, 1H), 7.87 (dt, *J* = 6.8, 2.1 Hz, 1H), 7.77 – 7.71 (m, 2H), 7.68 – 7.60 (m, 3H), 7.59 – 7.53 (m, 2H), 7.48 – 7.43 (m, 1H), 7.43 – 7.35 (m, 3H), 7.29 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.26 – 7.21 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*)

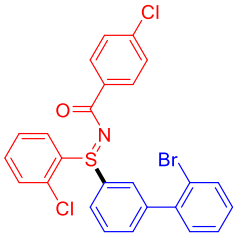
δ 176.7, 142.8, 140.4, 136.1, 135.7, 135.6, 133.4, 133.2, 133.1, 131.2, 131.1, 129.8, 129.7, 129.3, 129.0, 128.9, 127.9, 127.8, 126.9, 126.8, 122.3. **HRMS** [ESI]: m/z calculated for $C_{25}H_{17}Br_2NOS$ $[M+H]^+$ 537.9470, found 537.9463. IR (thin film): ν_{max} 1594, 1554, 1322, 1293, 1066, 1007, 712, 691, 499 cm^{-1}.

N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-bromophenyl)-l4-sulfaneylidene)methacrylamide (3au)



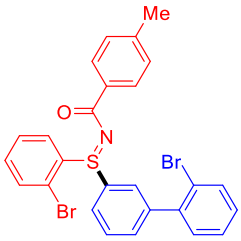
Yield: 41.2 mg, 82%. Faint yellow oil. Purified by column chromatography on silica gel (EtOAc : PE = 2 : 8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.85 – 7.82 (m, 1H), 7.80 (dt, *J* = 6.7, 2.2 Hz, 1H), 7.70 – 7.64 (m, 3H), 7.61 (d, *J* = 8.7 Hz, 2H), 7.58 – 7.51 (m, 2H), 7.38 (td, *J* = 7.5, 1.2 Hz, 1H), 7.29 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.27 – 7.21 (m, 1H), 6.13 (d, *J* = 1.1 Hz, 1H), 5.37 (t, *J* = 1.8 Hz, 1H), 2.07 (s 3H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 178.5, 142.7, 141.7, 140.5, 135.64, 135.56, 133.4, 133.1, 131.1, 129.7, 129.6, 129.3, 128.9, 127.8, 126.8, 126.7, 122.3, 121.1, 19.6. **HRMS** [ESI]: m/z calculated for $C_{22}H_{17}Br_2NOS$ $[M+Na]^+$ 523.9290, found 523.9291. IR (thin film): ν_{max} 2919, 1556, 1459, 1312, 1193, 1066, 1007, 755, 693 cm^{-1}.

N-((2'-bromo-[1,1'-biphenyl]-3-yl)(2-chlorophenyl)-l4-sulfaneylidene)-4-chlorobenzamide (3av)



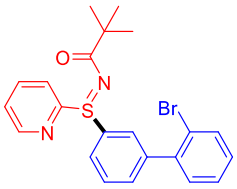
Yield: 42.4 mg, 80%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 2 : 8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.22 – 8.15 (m, 3H), 7.94 – 7.87 (m, 2H), 7.65 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.51 – 7.44 (m, 3H), 7.40 – 7.33 (m, 3H), 7.29 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.27 – 7.21 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 175.4, 142.5, 140.5, 137.2, 134.8, 134.7, 134.1, 133.9, 133.4, 133.2, 133.0, 131.2, 130.7, 130.4, 129.8, 129.6, 129.5, 128.4, 128.3, 128.1, 127.9, 127.8, 122.4. **HRMS** [ESI]: m/z calculated for $C_{25}H_{16}BrCl_2NOS$ $[M+H]^+$ 527.9586, found 527.9579. IR (thin film): ν_{max} 2922, 1587, 1550, 1457, 1322, 1289, 1089, 1014, 757 cm^{-1}.

N-((2'-bromo-[1,1'-biphenyl]-3-yl)(2-bromophenyl)-l4-sulfaneylidene)-4-methylbenzamide (3aw)



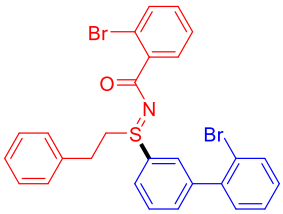
Yield: 42 mg, 74%. White solid. Purified by column chromatography on silica gel (EtOAc : PE = 2 : 8). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.18 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.14 (d, *J* = 7.9 Hz, 2H), 7.93 (d, *J* = 8.5 Hz, 2H), 7.63 (ddd, *J* = 9.6, 8.1, 1.2 Hz, 2H), 7.56 – 7.49 (m, 3H), 7.36 (t, *J* = 7.1 Hz, 2H), 7.29 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.25 – 7.16 (m, 3H), 2.38 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 176.6, 142.4, 141.3, 140.6, 136.4, 135.1, 133.8, 133.42, 133.39, 133.1, 133.0, 131.2, 130.0, 129.5, 129.4, 129.0, 128.9, 128.8, 128.6, 128.1, 127.7, 123.1, 122.4, 21.6. **HRMS** [ESI]: m/z calculated for $C_{26}H_{19}Br_2NOS$ $[M+H]^+$ 551.9627, found 551.9621. IR (thin film): ν_{max} 2958, 2925, 2855, 1722, 1590, 1270, 1118, 1019, 754 cm^{-1}.

(S,Z)-N-((2'-bromo-[1,1'-biphenyl]-3-yl)(pyridin-2-yl)-l4-sulfaneylidene)pivalamide (3ax)



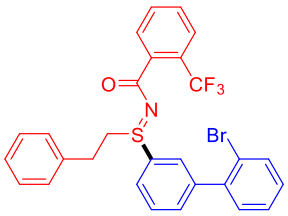
Yield: 20.3 mg, 46%. Pale yellow oil. Purified by column chromatography on silica gel (EtOAc : PE = 3 : 7). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.59 – 8.53 (m, 1H), 8.14 – 8.09 (m, 1H), 7.96 – 7.83 (m, 3H), 7.65 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.40 – 7.32 (m, 2H), 7.28 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.25 – 7.20 (m, 1H), 1.34 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 190.5, 157.9, 150.3, 142.2, 140.8, 138.4, 135.4, 133.4, 132.8, 131.2, 129.4, 129.1, 128.9, 127.6, 127.2, 125.3, 122.3, 121.4, 40.4, 28.7. **HRMS** [ESI]: m/z calculated for $C_{22}H_{21}BrN_2OS$ $[M+H]^+$ 441.0631, found 441.0646. IR (thin film): ν_{max} 2964, 2863, 1571, 1422, 1191, 1084, 756, 694, 471 cm^{-1}.

2-bromo-N-((2'-bromo-[1,1'-biphenyl]-3-yl)(phenethyl)-l4-sulfaneylidene)benzamide (3ay)



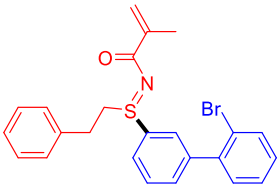
Yield: 47.9 mg, 84%. Faint yellow oil. Purified by column chromatography on silica gel (EtOAc : PE = 3 : 7). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 – 7.85 (m, 2H), 7.71 – 7.61 (m, 4H), 7.58 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.40 (td, *J* = 7.4, 1.2 Hz, 1H), 7.35 – 7.27 (m, 5H), 7.26 – 7.23 (m, 1H), 7.22 – 7.17 (m, 3H), 3.63 – 3.55 (m, 1H), 3.48 – 3.41 (m, 1H), 3.20 – 3.12 (m, 1H), 3.10 – 3.01 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 178.4, 155.1, 149.4, 142.9, 140.5, 140.0, 137.5, 133.4, 133.3, 133.1, 131.2, 130.1, 129.8, 129.7, 129.0, 128.6, 128.4, 127.7, 127.2, 127.1, 126.6, 122.4, 120.3, 51.2, 29.6. **HRMS** [ESI]: m/z calculated for $C_{27}H_{21}Br_2NOS$ $[M+H]^+$ 565.9783, found 565.9778. IR (thin film): ν_{max} 2923, 1692, 1571, 1458, 1324, 1027, 753, 696, 451 cm^{-1}.

N-((2'-bromo-[1,1'-biphenyl]-3-yl)(phenethyl)-l4-sulfaneylidene)-2-(trifluoromethyl)benzamide (3az)



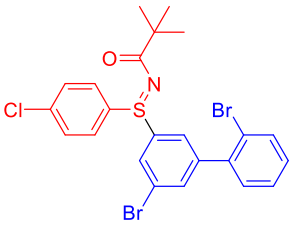
Yield: 51.7 mg, 93%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 3 : 7). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.88 – 7.81 (m, 2H), 7.74 – 7.66 (m, 3H), 7.65 – 7.60 (m, 2H), 7.54 (td, *J* = 7.5, 1.2 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.40 (td, *J* = 7.5, 1.3 Hz, 1H), 7.35 – 7.28 (m, 3H), 7.26 – 7.22 (m, 1H), 7.21 – 7.16 (m, 2H), 3.65 – 3.56 (m, 1H), 3.45 – 3.36 (m, 1H), 3.15 – 2.98 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 178.5, 142.9, 140.5, 138.4 (d, *J* = 1.7 Hz), 137.5, 133.6, 133.3, 133.0, 131.6, 131.2, 129.7 (d, *J* = 2.7 Hz), 129.4, 129.0, 128.8, 128.6, 128.4, 127.8, 127.6, 127.3, 127.2, 126.6, 126.3 (q, *J* = 5.2 Hz), 124.1 (q, *J* = 273.4 Hz), 122.3, 51.2, 29.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.51. **HRMS** [ESI]: m/z calculated for $C_{28}H_{21}BrF_3NOS$ $[M+H]^+$ 556.0552, found 556.0544. IR (thin film): ν_{max} 2924, 2832, 1735, 1550, 1305, 1185, 1195, 759, 690 cm^{-1}.

N-((2'-bromo-[1,1'-biphenyl]-3-yl)(phenethyl)-l4-sulfaneylidene)methacrylamide (3aa')



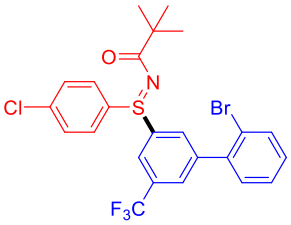
Yield: 35 mg, 77%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 3 : 7). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.82 – 7.79 (m, 1H), 7.77 (dt, *J* = 6.6, 2.2 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.42 – 7.37 (m, 1H), 7.34 – 7.26 (m, 4H), 7.25 – 7.21 (m, 1H), 7.18 – 7.12 (m, 2H), 6.08 (d, *J* = 2.3 Hz, 1H), 5.34 (t, *J* = 2.0 Hz, 1H), 3.53 – 3.45 (m, 1H), 3.39 – 3.31 (m, 1H), 3.08 – 3.00 (m, 1H), 2.98 – 2.90 (m, 1H), 2.06 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 178.8, 142.7, 142.0, 140.6, 137.8, 133.9, 133.3, 133.1, 131.2, 129.6, 128.9, 128.6, 128.2, 127.7, 127.0, 126.4, 126.2, 122.4, 120.4, 50.8, 29.4, 19.7. **HRMS** [ESI]: m/z calculated for $C_{24}H_{22}BrNOS$ $[M+H]^+$ 452.0678, found 452.0670. IR (thin film): ν_{max} 2921, 1668, 1630, 1433, 1155, 1017, 755, 696, 616 cm^{-1}.

N-((4-chlorophenyl)(2',5'-dibromo-[1,1'-biphenyl]-3-yl)-l4-sulfaneylidene)pivalamide (3ba)



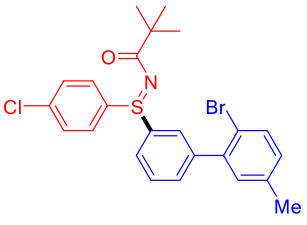
Yield: 53.3 mg, 96%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 1 : 9). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 – 7.88 (m, 1H), 7.75 – 7.70 (m, 3H), 7.68 – 7.63 (m, 2H), 7.46 (dd, *J* = 8.1, 1.2 Hz, 2H), 7.40 – 7.36 (m, 1H), 7.28 – 7.23 (m, 2H), 1.29 (s, 9H). **^{13}C{^{1}H} NMR** δ 190.6, 144.1, 139.2, 138.5, 138.2, 135.7, 134.8, 133.5, 131.0, 130.2, 130.1, 129.0, 128.8, 127.9, 127.3, 123.3, 122.1, 40.3, 28.6. **HRMS** [ESI]: m/z calculated for $C_{23}H_{20}Br_2ClNOS$ $[M+Na]^+$ 573.9213, found 573.9226. IR (thin film): ν_{max} 2962, 1575, 1475, 1390, 1306, 1191, 1090, 828, 752 cm^{-1}.

N-((2'-bromo-5'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene) pivalamide (3ca)



Yield: 44 mg, 81%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 1 : 9). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.98 (d, *J* = 1.7 Hz, 1H), 7.79 – 7.72 (m, 3H), 7.72 – 7.67 (m, 1H), 7.51 – 7.45 (m, 2H), 7.45 – 7.39 (m, 1H), 7.29 (t, *J* = 7.3 Hz, 2H), 1.30 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 190.7, 143.4, 139.1, 138.7, 138.0, 134.5, 133.6, 132.3 (d, *J* = 33.5 Hz), 131.7, 131.0, 130.4, 130.3, 129.6 (q, *J* = 3.4 Hz), 129.1, 128.0, 123.1 (q, *J* = 273.2 Hz), 122.9 (q, *J* = 3.7 Hz), 122.1, 40.4, 28.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.67. **HRMS** [ESI]: m/z calculated for $C_{24}H_{20}BrClF_3NOS$ $[M+Na]^+$ 563.9982, found 563.9976. IR (thin film): ν_{max} 2964, 2868, 1576, 1476, 1337, 1175, 1135, 1094, 757 cm^{-1}.

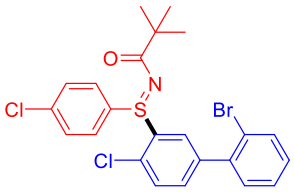
N-((2'-bromo-5'-methyl-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)pivalamide (3da)



Yield: 38 mg, 77% (*m* / *o* = 1.0 : 0.5). Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 1 : 9). Major: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 – 7.74 (m, 2H), 7.74 – 7.69 (m, 3H), 7.58 (d, *J* = 12.8 Hz, 1H), 7.43 (d, *J* = 8.6 Hz, 3H), 7.10 (d, *J* = 2.2 Hz, 1H), 7.05 (dd, *J* = 8.2, 2.1 Hz, 1H), 2.33 (s, 3H), 1.29 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 190.4, 142.7, 139.9, 138.0, 137.7, 136.1, 135.5, 133.1, 132.8, 131.9, 130.4, 130.0, 129.6, 129.0, 128.6, 126.4,

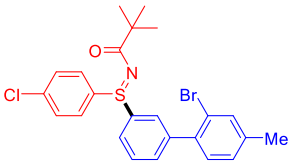
118.8, 40.3, 28.7, 20.9. **HRMS** [ESI]: m/z calculated for $C_{24}H_{23}BrClNOS$ $[M+H]^+$ 488.0445, found 488.0447. IR (thin film): ν_{max} 2934, 1561, 1459, 1307, 1011, 831, 754, 692, 504 cm^{-1}.

N-((2'-bromo-4'-chloro-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)pivalamide (3ea)



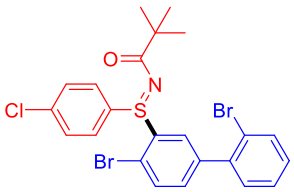
Yield: 40.5 mg, 79% (*m* / *o* = 1.0 : 0.4). Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 1 : 9). Major: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.20 – 8.15 (m, 1H), 7.83 – 7.75 (m, 2H), 7.73 – 7.68 (m, 1H), 7.48 – 7.46 (m, 1H), 7.45 – 7.38 (m, 3H), 7.29 – 7.26 (m, 2H), 7.21 – 7.16 (m, 1H), 1.25 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 190.3, 141.2, 139.9, 138.4, 134.3, 133.8, 133.6, 131.0, 130.3, 130.0, 129.9, 129.83, 129.78, 129.0, 127.9, 125.2, 122.2, 40.3, 28.6. **HRMS** [ESI]: m/z calculated for $C_{23}H_{20}BrCl_2NOS$ $[M+H]^+$ 507.9899, found 507.9898. IR (thin film): ν_{max} 2962, 1575, 1475, 1389, 1304, 1189, 1093, 758, 513 cm^{-1}.

N-((2'-bromo-4'-methyl-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)pivalamide (3fa)



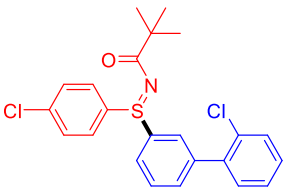
Yield: 26 mg, 53% (*m* / *o* = 1.0 : 0.94). Yellow oil. Purified by column chromatography on silica gel (EtOAc : PE = 1 : 9). Mixture: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 1.9 Hz, 1H), 7.79 (q, *J* = 1.3 Hz, 1H), 7.75 (dt, *J* = 6.5, 2.4 Hz, 1H), 7.73 – 7.70 (m, 2H), 7.67 (td, *J* = 6.6, 1.7 Hz, 3H), 7.53 – 7.48 (m, 3H), 7.43 (dd, *J* = 8.6, 3.0 Hz, 5H), 7.37 (td, *J* = 7.5, 1.2 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.28 – 7.22 (m, 2H), 7.17 (d, *J* = 2.1 Hz, 2H), 2.65 (s, 3H), 2.38 (s, 3H), 1.29 (s, 9H), 1.25 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 190.4, 190.2, 142.6, 140.7, 140.5, 139.9, 138.0, 137.8, 137.6, 136.0, 135.5, 134.6, 134.4, 133.8, 133.4, 132.9, 132.7, 131.2, 131.1, 130.8, 130.02, 129.95, 129.54, 129.51, 129.3, 129.0, 128.63, 128.55, 128.3, 127.7, 126.3, 126.5, 122.4, 122.0, 40.3, 40.2, 28.7, 20.8, 19.2. **HRMS** [ESI]: m/z calculated for $C_{24}H_{23}BrClNOS$ $[M+H]^+$ 488.0445, found 488.0456. IR (thin film): ν_{max} 2942, 2859, 1578, 1475, 1389, 1305, 1191, 1091, 1012 cm^{-1}.

N-((4-chlorophenyl)(2',4'-dibromo-[1,1'-biphenyl]-3-yl)-l4-sulfaneylidene)pivalamide (3ga)



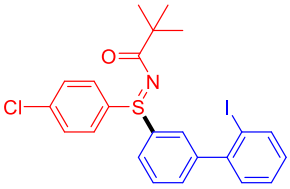
Yield: 30.1 mg, 54% (*m* / *o* = 1.0 : 0.7). Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 1 : 9). Major **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 2.2 Hz, 1H), 7.86 – 7.76 (m, 3H), 7.54 – 7.47 (m, 1H), 7.44 – 7.41 (m, 2H), 7.32 – 7.38 (m, 2H), 7.23 – 7.17 (m, 2H), 1.25 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 190.3, 141.8, 139.9, 138.3, 134.2, 134.0, 133.6, 131.0, 130.7, 130.0, 129.9, 129.84, 129.79, 129.5, 127.89, 127.86, 122.4, 40.2, 28.6. **HRMS** [ESI]: m/z calculated for $C_{23}H_{20}Br_2ClNOS$ $[M+H]^+$ 573.9213, found 573.9223. IR (thin film): ν_{max} 2948, 2923, 2861, 1574, 1475, 1449, 1303, 1189, 1012 cm^{-1}.

N-((2'-chloro-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)pivalamide (3ha)



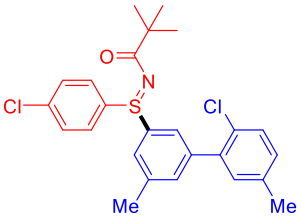
Yield: 34.8 mg, 80%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 1 : 9). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 (s, 1H), 7.77 (dt, *J* = 6.7, 2.1 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 6.9 Hz, 2H), 7.50 – 7.47 (m, 1H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.28 (m, 3H), 1.29 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 190.4, 141.0, 138.5, 138.1, 136.3, 135.5, 132.9, 132.3, 131.2, 130.2, 130.1, 129.6, 129.4, 128.9, 128.5, 127.2, 126.5, 40.3, 28.7. **HRMS** [ESI]: m/z calculated for $C_{23}H_{21}Cl_2NOS$ $[M+H]^+$ 430.0794, found 430.079. IR (thin film): ν_{max} 2923, 1576, 1475, 1389, 1305, 1192, 1091, 755, 508 cm^{-1}.

(R,E)-N-((4-chlorophenyl)(2'-iodo-[1,1'-biphenyl]-3-yl)-l4-sulfaneylidene)pivalamide (3ia)



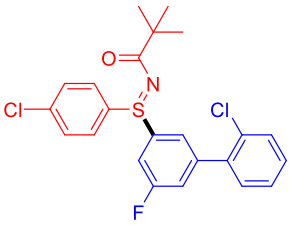
Yield: 16.7 mg, 32%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 1 : 9). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.95 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.79 (dt, *J* = 8.0, 1.5 Hz, 1H), 7.76 – 7.69 (m, 3H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.47 – 7.38 (m, 4H), 7.28 – 7.25 (m, 1H), 7.07 (td, *J* = 7.7, 1.7 Hz, 1H), 1.29 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 190.4, 145.6, 144.6, 139.8, 138.0, 136.0, 135.5, 132.7, 130.0, 129.6, 129.6, 129.1, 128.6, 128.5, 126.6, 98.1, 40.3, 28.7. **HRMS** [ESI]: m/z calculated for $C_{23}H_{21}ClINOS$ $[M+H]^+$ 522.0150, found 522.0155. IR (thin film): ν_{max} 2962, 2924, 1576, 1475, 1389, 1305, 1190, 1091, 754 cm^{-1}.

N-((2'-chloro-5,5'-dimethyl-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)pivalamide (3ja)



Yield: 37.6 mg, 82%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 1 : 9). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.74 – 7.68 (m, 2H), 7.62 (t, *J* = 1.6 Hz, 1H), 7.54 (td, *J* = 1.7, 0.9 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.35 – 7.31 (m, 2H), 7.13 – 7.07 (m, 2H), 2.43 (s, 3H), 2.35 (s, 3H), 1.29 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 190.4, 141.0, 139.9, 138.3, 137.9, 137.0, 136.0, 135.5, 133.8, 131.8, 130.0, 129.9, 129.2, 128.9, 126.7, 125.7, 40.3, 28.7, 21.5, 20.8. **HRMS** [ESI]: m/z calculated for $C_{25}H_{25}Cl_2NOS$ $[M+H]^+$ 458.1107, found 458.1103. IR (thin film): ν_{max} 2949, 1576, 1389, 1305, 1191, 1089, 1011, 813, 694 cm^{-1}.

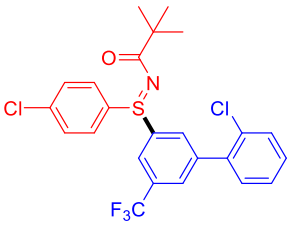
N-((2'-chloro-5'-fluoro-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)pivalamide (3ka)



Yield: 36.0 mg, 80%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 1 : 9). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.59 (s, 1H), 7.53 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.47 (dd, *J* = 7.0, 5.2 Hz, 3H), 7.34 (dt, *J* = 7.4, 3.7 Hz, 2H), 7.31 – 7.26 (m, 2H), 1.30 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 190.58, 162.54 (d, *J* = 252.7 Hz), 142.9 (d, *J* = 8.0 Hz), 138.49, 138.48 (d, *J* = 7.5 Hz), 137.3 (d, *J* = 1.9 Hz), 134.9, 132.2, 131.1, 130.4, 130.2, 129.9, 128.9, 127.3, 124.4 (d, *J* = 3.3 Hz), 120.3 (d, *J* = 22.5 Hz), 113.3 (d, *J* = 24.8 Hz), 40.3, 28.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -108.67. **HRMS** [ESI]: m/z calculated for $C_{23}H_{20}Cl_2FNOS$

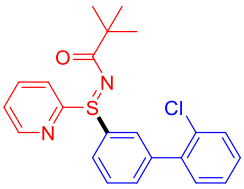
$[M+H]^+$ 448.0700, found 448.0702. IR (thin film): ν_{max} 2925, 1579, 1476, 1411, 1308, 1185, 1091, 1012, 757 cm^{-1}.

N-((2'-chloro-5'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene) pivalamide (3la)



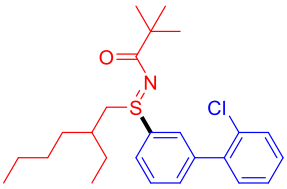
Yield: 35.0 mg, 70%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 1 : 9). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.02 (dt, *J* = 10.7, 1.8 Hz, 2H), 7.80 (d, *J* = 1.6 Hz, 1H), 7.78 – 7.73 (m, 2H), 7.53 – 7.45 (m, 3H), 7.38 (dd, *J* = 5.9, 3.5 Hz, 2H), 7.31 (dd, *J* = 5.9, 3.6 Hz, 1H), 1.30 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 190.7, 141.8, 138.7, 138.1, 137.1, 134.5, 132.3 (q, *J* = 33.5 Hz), 132.2, 131.6, 131.1, 130.42, 130.36, 130.2, 129.6 (q, *J* = 3.5 Hz), 129.0, 127.5, 123.1 (q, *J* = 273.3 Hz), 122.9 (q, *J* = 3.8 Hz), 40.4, 28.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.68. **HRMS** [ESI]: m/z calculated for $C_{24}H_{20}Cl_2F_3NOS$ $[M+Na]^+$ 520.0487, found 520.0479. IR (thin film): ν_{max} 2964, 2926, 2864, 1576, 1477, 1337, 1175, 1136, 757 cm^{-1}.

(S,Z)-N-((2'-chloro-[1,1'-biphenyl]-3-yl)(pyridin-2-yl)-l4-sulfaneylidene)pivalamide(3ma)



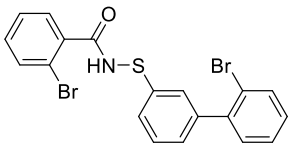
Yield: 20.0 mg, 50%. Pale yellow oil. Purified by column chromatography on silica gel (EtOAc : PE = 3:7). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.59 – 8.53 (m, 1H), 8.12 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.96 – 7.83 (m, 3H), 7.59 – 7.49 (m, 2H), 7.48 – 7.43 (m, 1H), 7.37 – 7.28 (m, 4H), 1.35 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 190.5, 157.9, 150.3, 140.6, 138.8, 138.4, 135.5, 132.9, 132.4, 131.3, 130.2, 129.2, 129.2, 128.8, 127.12, 127.09, 125.3, 121.4, 40.4, 28.7. **HRMS** [ESI]: m/z calculated for $C_{22}H_{21}ClN_2OS$ $[M+Na]^+$ 419.0955, found 419.0976. IR (thin film): ν_{max} 2968, 2925, 1572, 1422, 1306, 1191, 1084, 756, 694 cm^{-1}.

N-((1R,E)-(2'-chloro-[1,1'-biphenyl]-3-yl)(2-ethylhexyl)-l4-sulfaneylidene)pivalamide (3na)



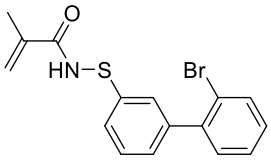
Yield: 36.5 mg, 84%, 1 : 1 d.r. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 1 : 9). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 2.0 Hz, 1H), 7.73 (dq, *J* = 6.6, 2.3 Hz, 1H), 7.58 (d, *J* = 6.6 Hz, 2H), 7.49 (dd, *J* = 7.1, 2.7 Hz, 1H), 7.37 – 7.30 (m, 3H), 3.21 (ddd, *J* = 12.7, 8.6, 6.7 Hz, 1H), 2.82 (ddd, *J* = 12.7, 6.6, 4.3 Hz, 1H), 1.77 – 1.64 (m, 1H), 1.55 – 1.35 (m, 4H), 1.25 (s, 13H), 0.94 – 0.80 (m, 6H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 190.5, 190.4, 140.9, 138.8, 135.9, 135.8, 132.9, 132.9, 132.3, 131.2, 130.1, 129.5, 129.3, 127.9, 127.8, 127.2, 126.1, 126.0, 55.0, 54.9, 40.03, 40.00, 35.1, 35.0, 32.5, 32.2, 28.7, 28.4, 28.4, 25.8, 25.5, 22.8, 22.7, 14.0, 10.5, 10.4. **HRMS** [ESI]: m/z calculated for $C_{25}H_{34}ClNOS$ $[M+H]^+$ 432.2122, found 432.2146. IR (thin film): ν_{max} 2960, 2860, 1575, 1459, 1308, 1196, 1037, 756, 697 cm^{-1}.

2-bromo-N-((2'-bromo-[1,1'-biphenyl]-3-yl)thio)benzamide (4a)



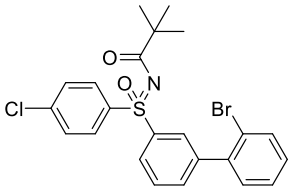
Yield: 33.3 mg, 72%. Paint yellow oil. Purified by column chromatography on silica gel (EtOAc : PE = 1 : 9). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.71 – 7.55 (m, 3H), 7.52 – 7.42 (m, 2H), 7.42 – 7.28 (m, 5H), 7.22 (dt, *J* = 7.5, 3.9 Hz, 2H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 169.3, 142.0, 141.7, 137.7, 136.6, 133.6, 133.1, 132.1, 131.2, 129.9, 129.1, 128.7, 128.5, 127.7, 127.5, 127.0, 125.3, 122.4, 119.3. **HRMS** [ESI]: m/z calculated for $C_{19}H_{13}Br_2NOS$ $[M+H]^+$ 461.9157, found 461.9149. IR (thin film): ν_{max} 2923, 2852, 1660, 1429, 1242, 1113, 751, 694, 448 cm^{-1}.

N-((2'-bromo-[1,1'-biphenyl]-3-yl)thio)methacrylamide (4b)



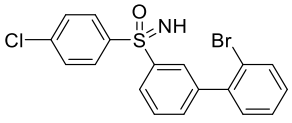
Yield: 25.8 mg, 74%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 1 : 9). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.65 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.40 – 7.28 (m, 5H), 7.26 – 7.18 (m, 2H), 7.07 (s, 1H), 5.80 (s, 1H), 5.50 (d, *J* = 1.7 Hz, 1H), 2.04 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 169.9, 141.9, 141.7, 139.7, 138.4, 133.2, 131.2, 129.1, 128.7, 128.1, 127.5, 126.2, 124.5, 122.4, 121.5, 19.2. **HRMS** [ESI]: m/z calculated for $C_{16}H_{14}BrNOS$ $[M+H]^+$ 348.0052, found 348.0046. IR (thin film): ν_{max} 2852, 1668, 1628, 1458, 1432, 1156, 1017, 754, 696 cm^{-1}.

N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)(oxo)-l6-sulfaneylidene)pivalamide (5)



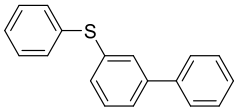
Yield: 45.6 mg, 91%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 1 : 9). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 1.7 Hz, 1H), 7.99 (dt, *J* = 7.3, 1.9 Hz, 1H), 7.94 – 7.88 (m, 2H), 7.68 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.51 – 7.46 (m, 2H), 7.40 (td, *J* = 7.5, 1.1 Hz, 1H), 7.32 – 7.24 (m, 2H), 1.28 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 188.0, 142.4, 140.2, 139.9, 139.4, 138.7, 134.3, 133.5, 131.2, 129.8, 129.7, 129.4, 129.0, 128.7, 127.8, 126.6, 122.3, 41.8, 27.7. **HRMS** [ESI]: m/z calculated for $C_{23}H_{21}BrClNO_2S$ $[M+H]^+$ 490.0238, found 490.0228. IR (thin film): ν_{max} 2969, 2867, 1645, 1391, 1286, 1165, 1086, 855, 750 cm^{-1}.

(2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)(imino)-l6-sulfanone (6)



Yield: 38.2 mg, 94%. Colourless oil. Purified by column chromatography on silica gel (EtOAc : PE = 1 : 9). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.12 – 7.09 (m, 1H), 8.06 – 7.98 (m, 3H), 7.68 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.62 – 7.52 (m, 2H), 7.49 – 7.43 (m, 2H), 7.38 (td, *J* = 7.5, 1.2 Hz, 1H), 7.30 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.25 (dd, *J* = 7.8, 6.0 Hz, 1H), 3.15 (s, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 142.9, 142.2, 141.8, 140.5, 139.4, 133.8, 133.4, 131.2, 129.6, 129.54, 129.47, 129.1, 129.0, 127.7, 126.9, 122.4. **HRMS** [ESI]: m/z calculated for $C_{18}H_{13}BrClNOS$ $[M+H]^+$ 405.9663, found 405.9655. IR (thin film): ν_{max} 2740, 1672, 1621, 1436, 1239, 1104, 1013, 751, 544 cm^{-1}.

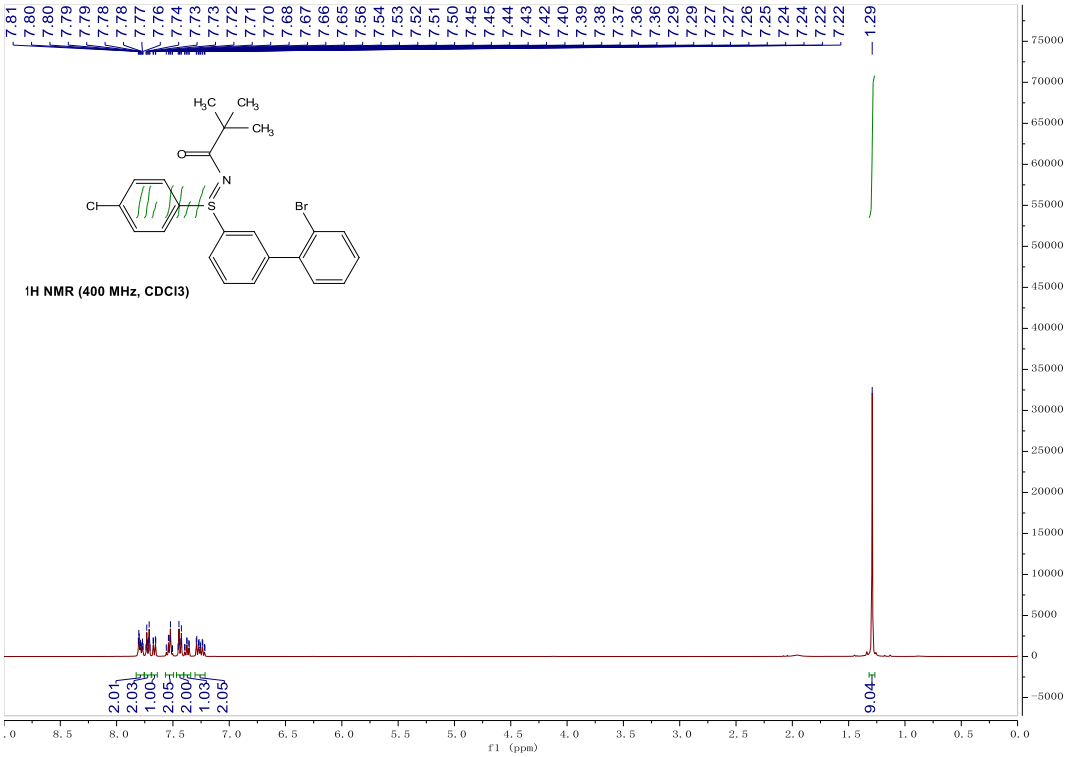
(2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)sulfane (7)

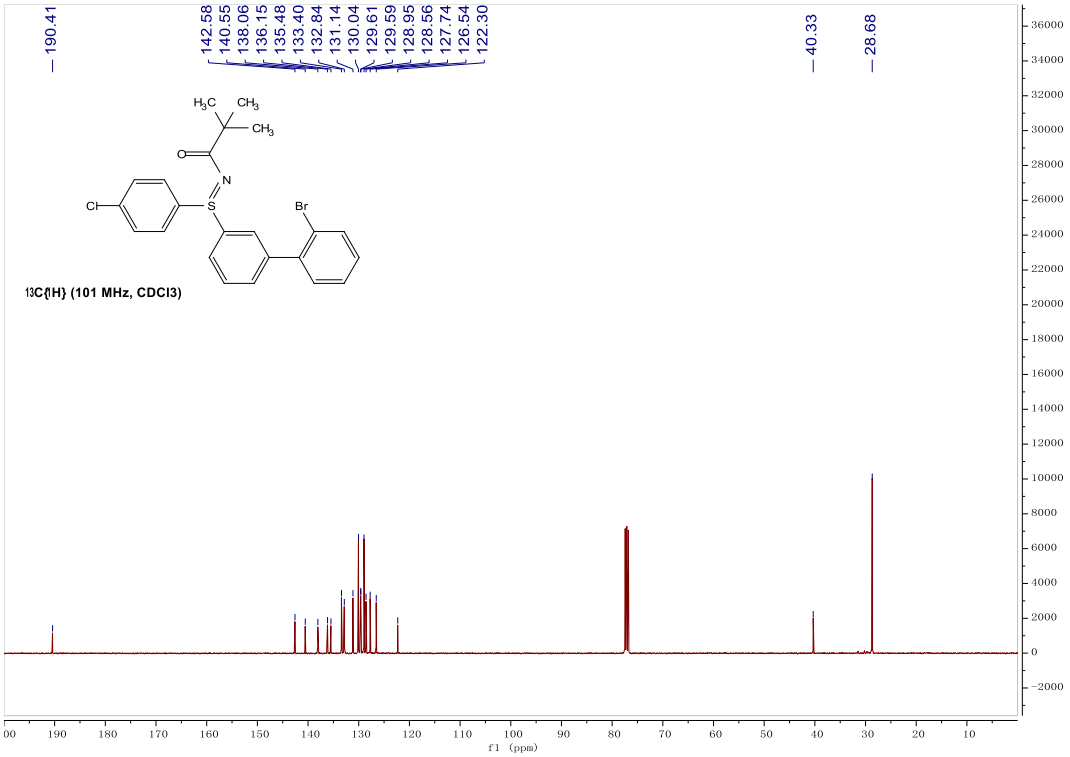


Yield: 24.8 mg, 95%. Colourless oil. Purified by column chromatography on silica gel (PE). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.59 (t, *J* = 1.8 Hz, 1H), 7.56 – 7.52 (m, 2H), 7.47 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.45 – 7.34 (m, 6H), 7.33 – 7.24 (m, 4H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 142.3, 140.4, 136.4, 135.6, 131.1, 129.7, 129.60, 129.55, 129.3, 128.8, 127.6, 127.2, 127.1, 125.9. **HRMS** [ESI]: m/z calculated for $C_{18}H_{12}S$ $[M+H]^+$ 263.0889, found 263.0885. IR (thin film): ν_{max} 2922, 1587, 1474, 1439, 1398, 1090, 754, 697, 614 cm^{-1}.

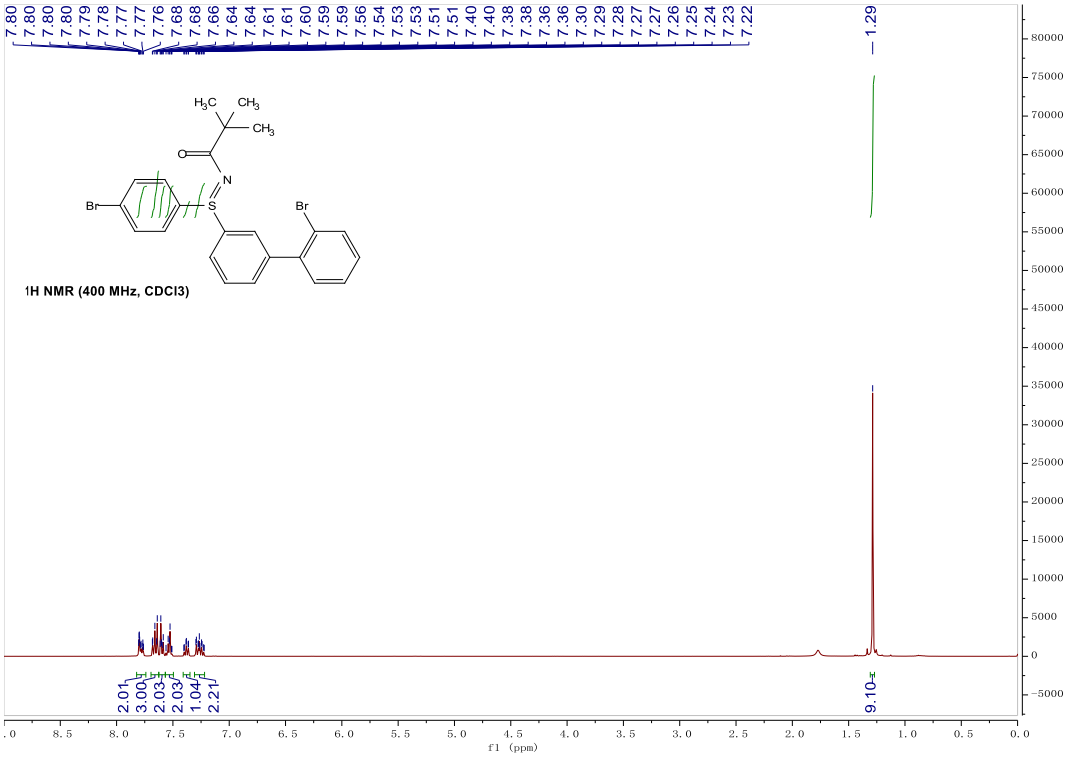
Copies of NMR spectra

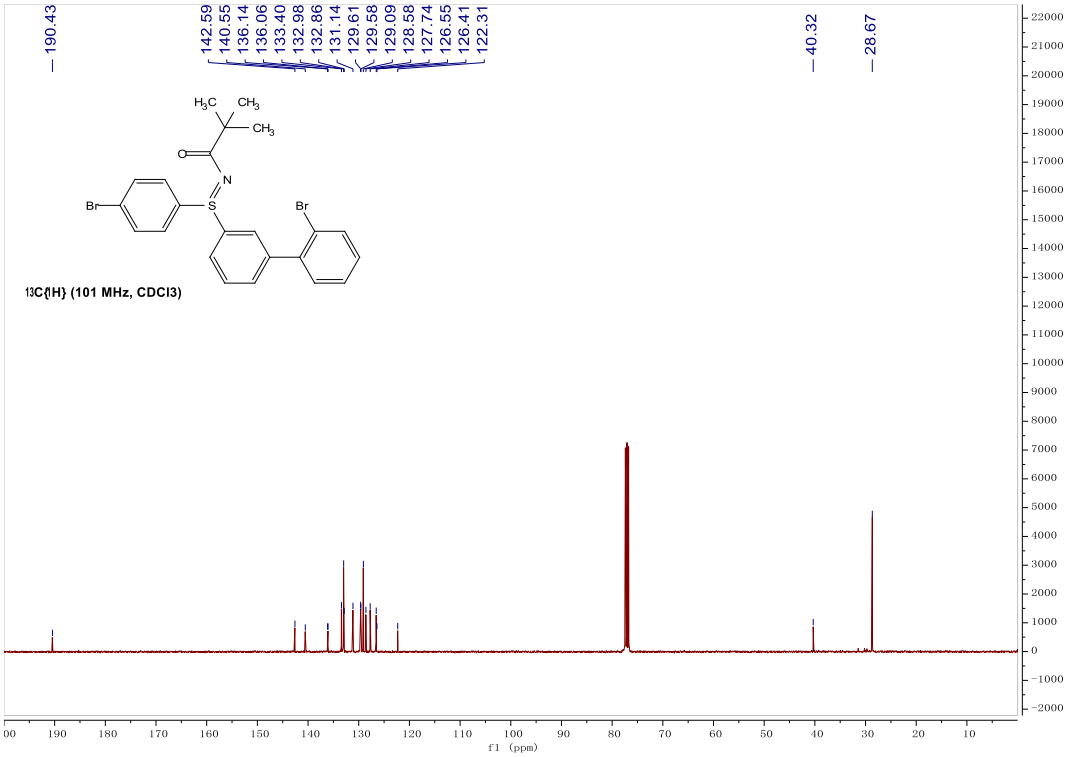
N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)pivalamide (3aa)



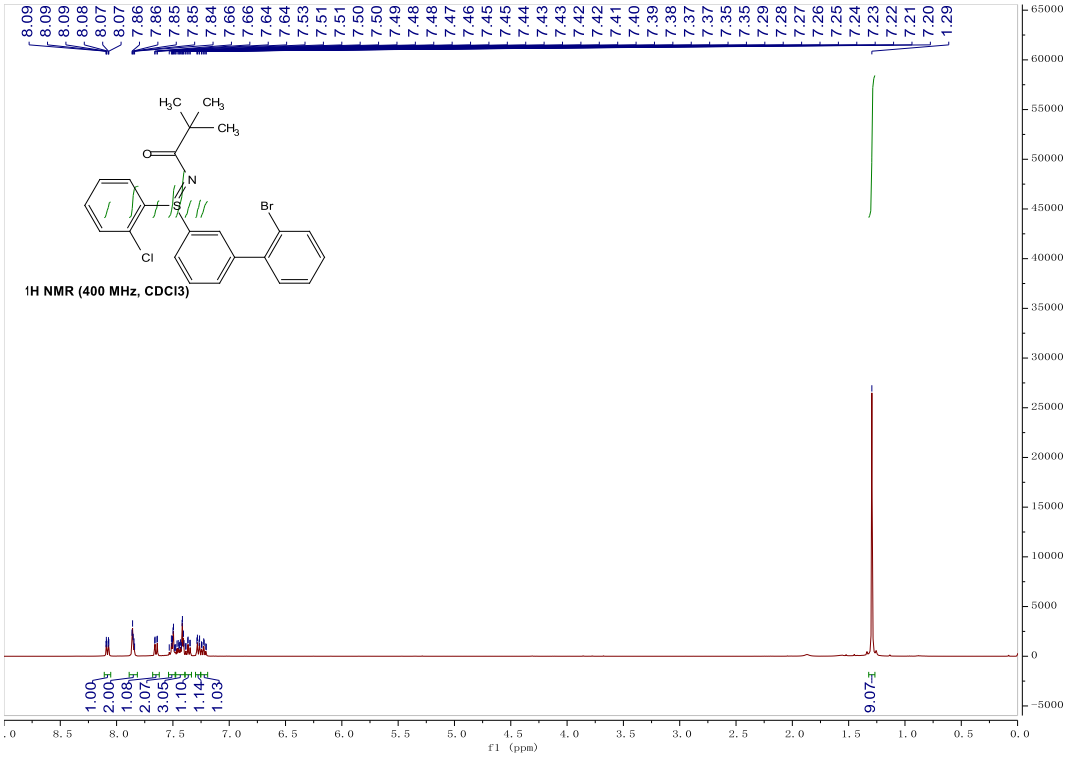


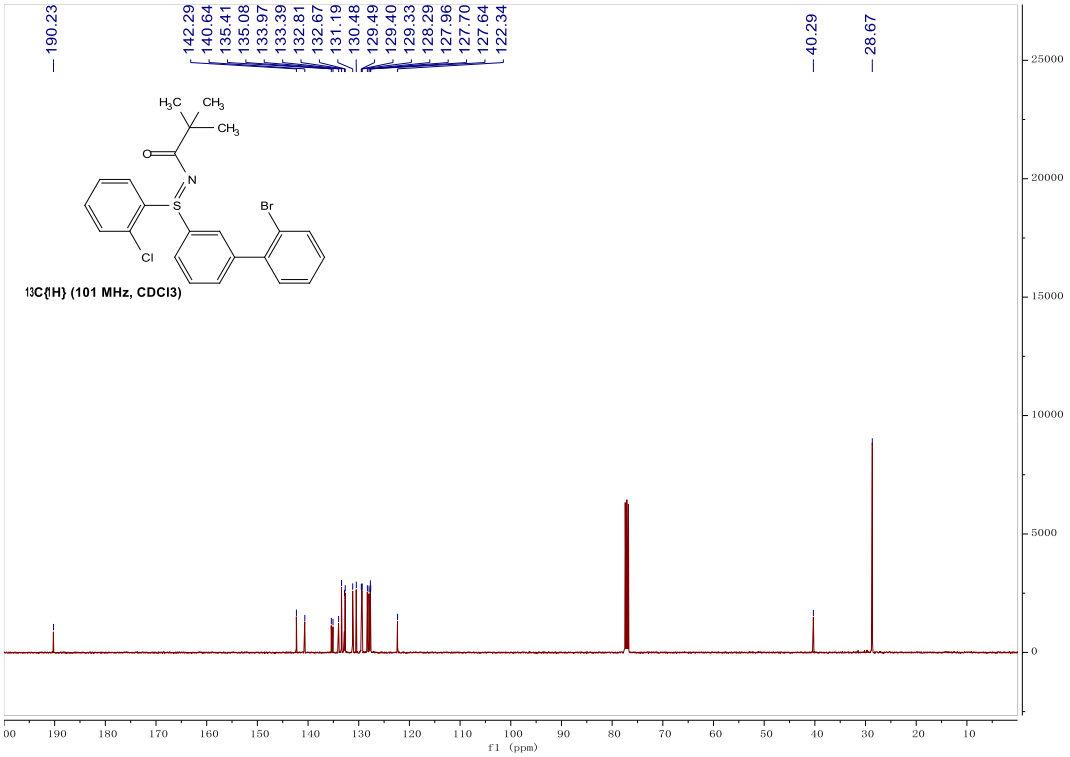
N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-bromophenyl)-l4-sulfaneylidene)pivalamide (3ab)



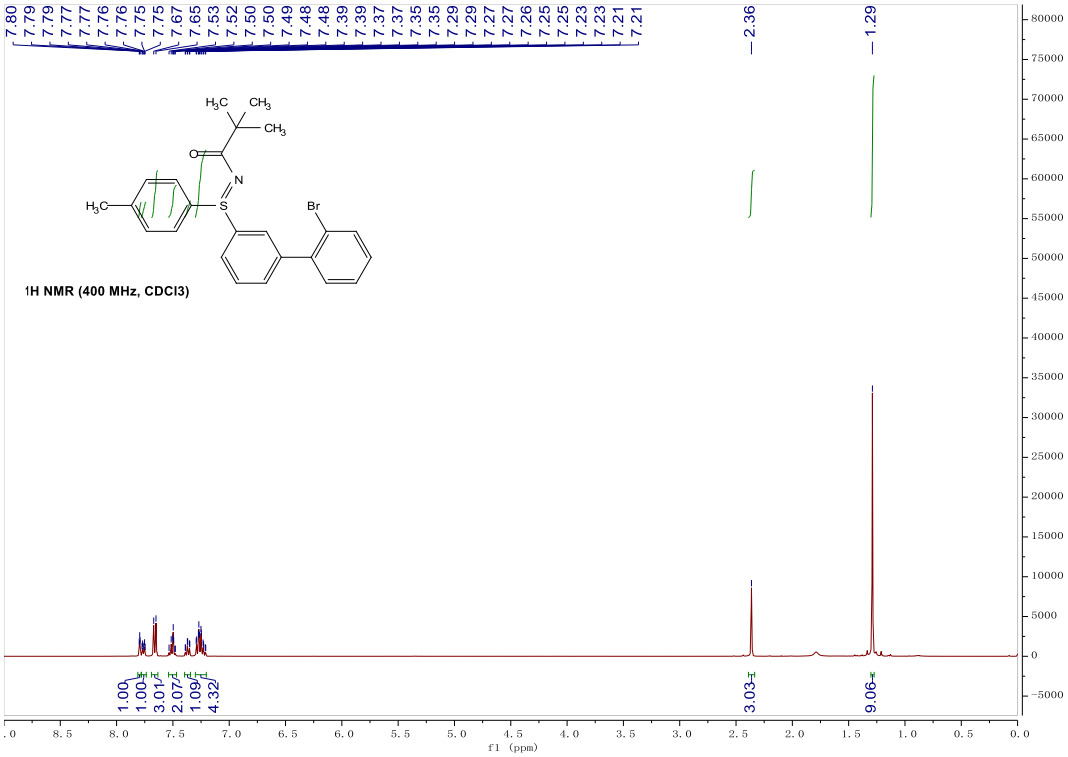


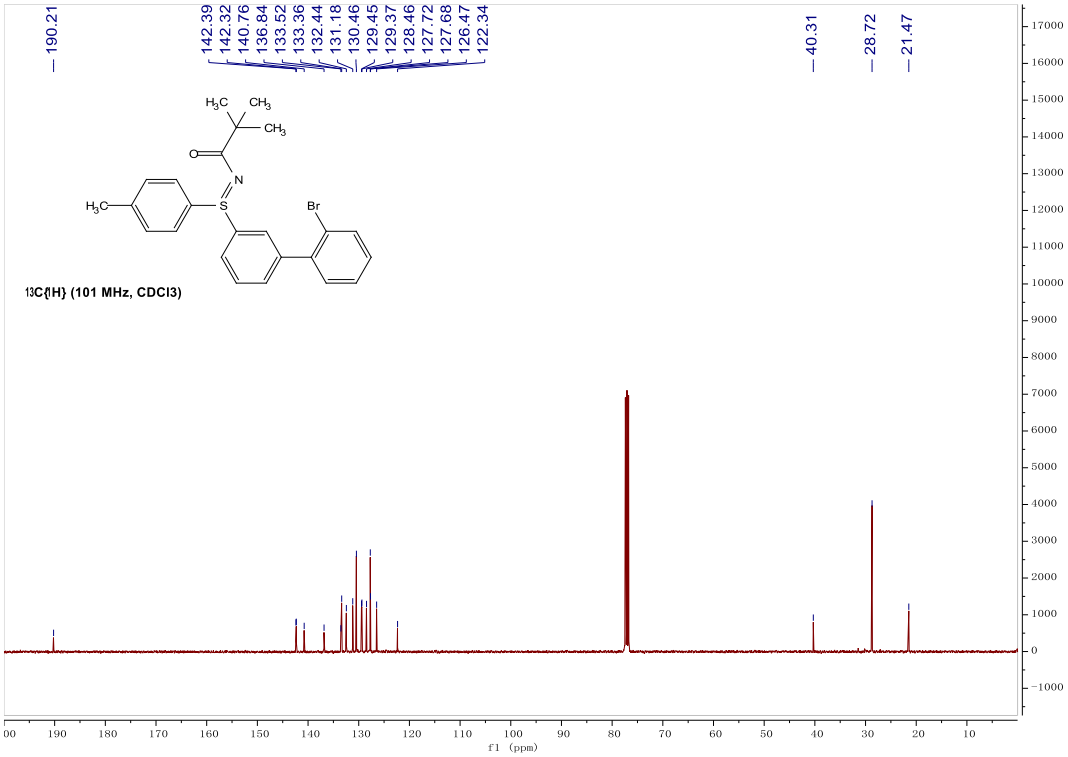
N-((2'-bromo-[1,1'-biphenyl]-3-yl)(2-chlorophenyl)-l4-sulfaneylidene)pivalamide (3ac)



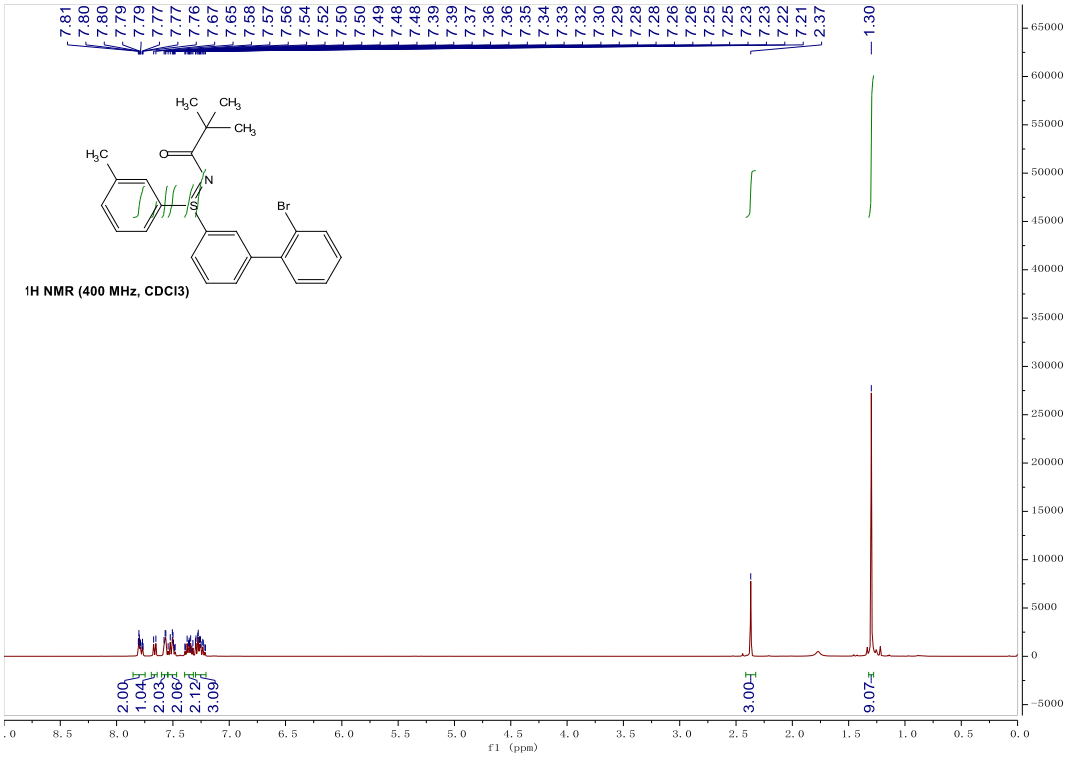


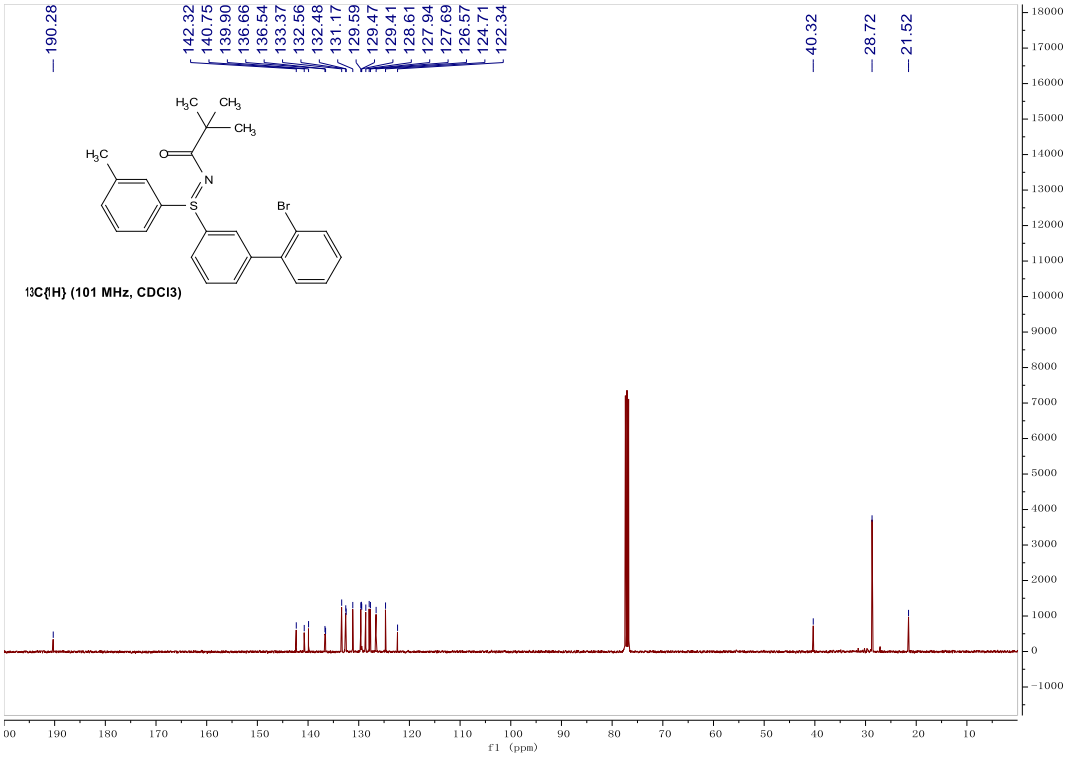
N-((2'-bromo-[1,1'-biphenyl]-3-yl)(p-tolyl)-l4-sulfaneylidene)pivalamide (3ad)



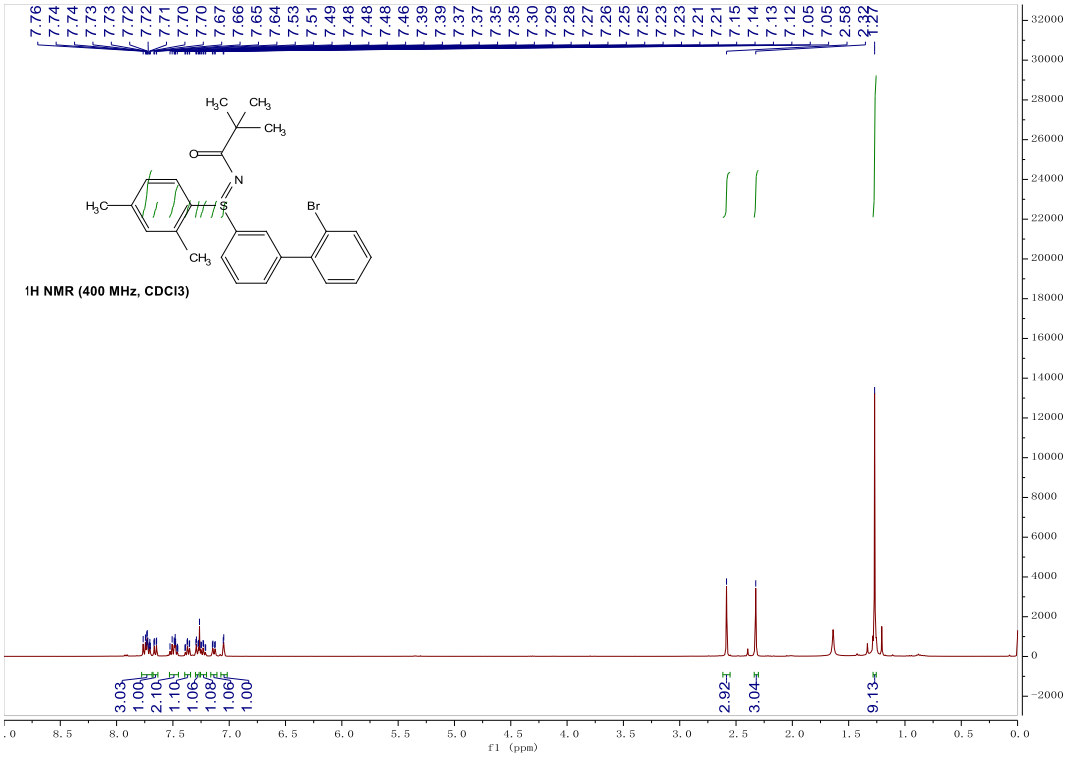


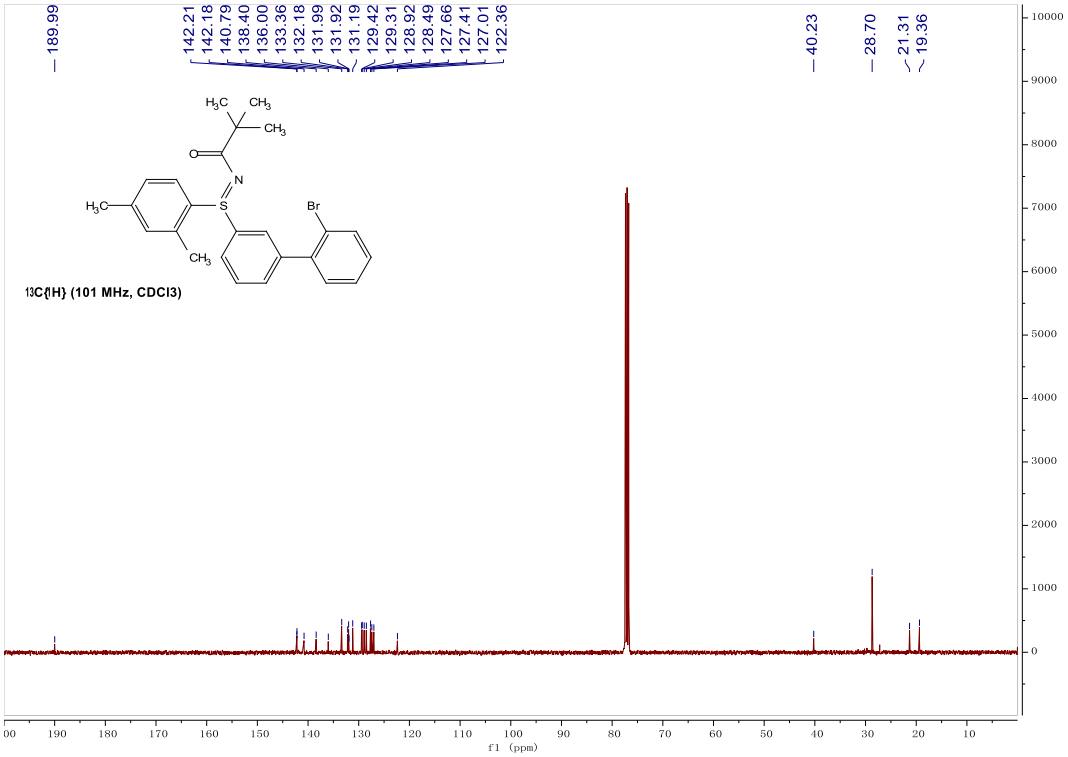
N-((2'-bromo-[1,1'-biphenyl]-3-yl)(m-tolyl)-l4-sulfaneylidene)pivalamide (3ae)



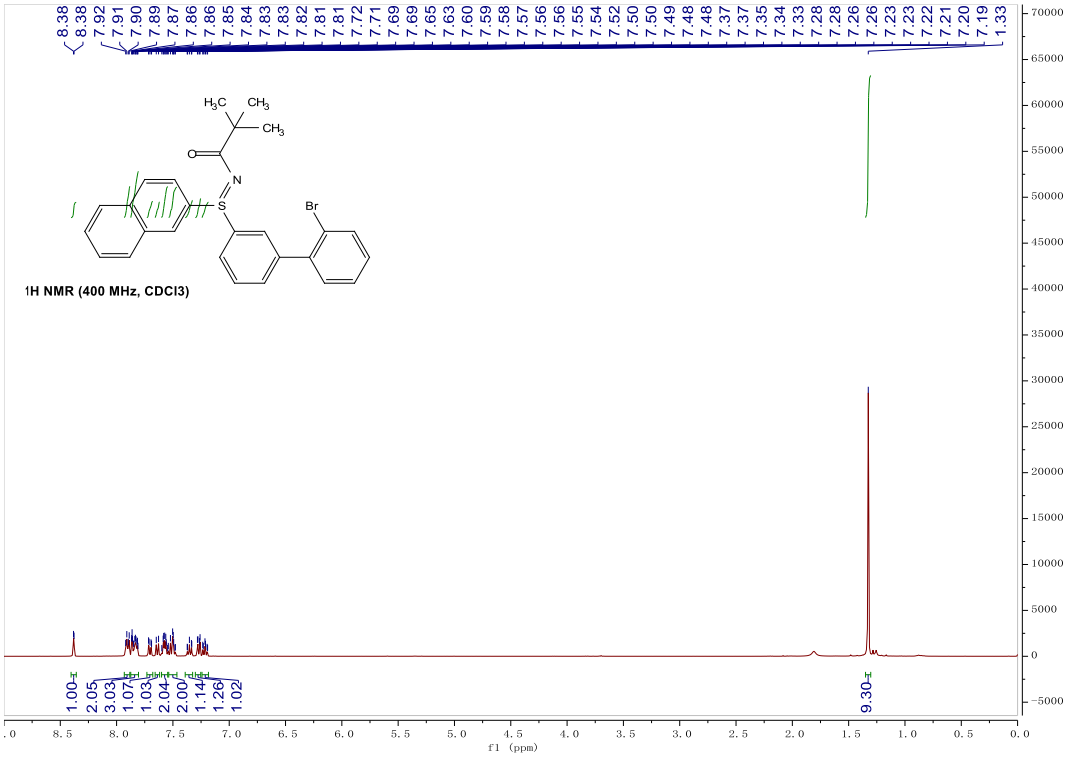


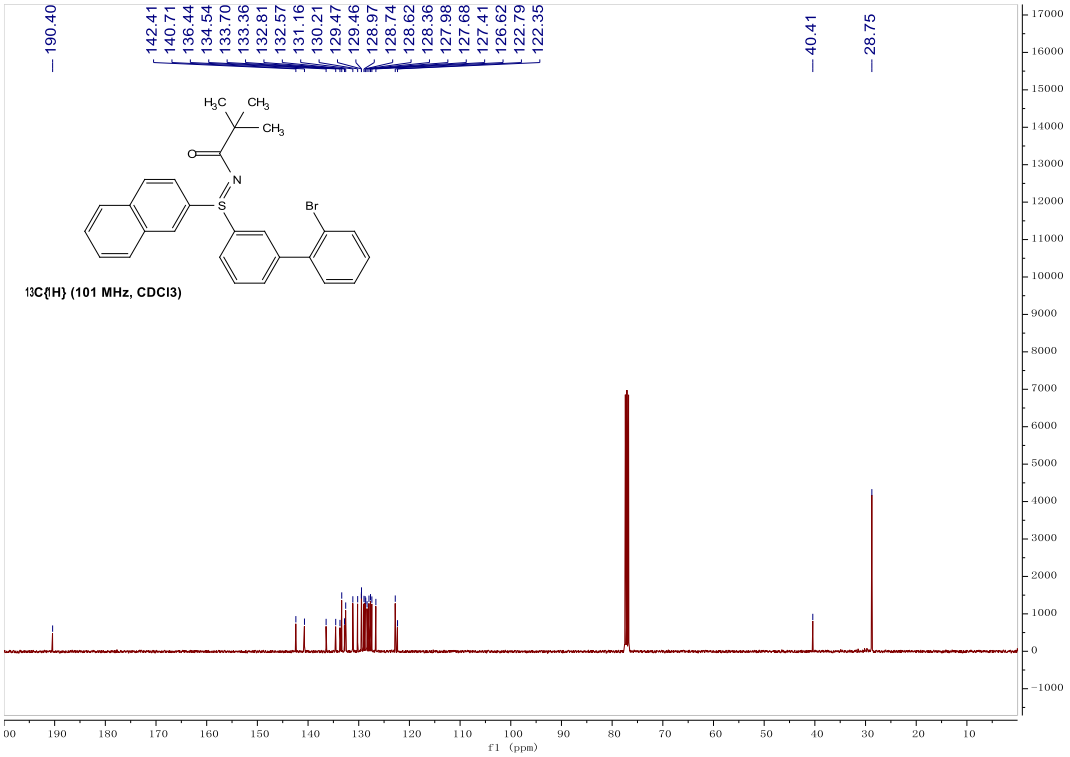
N-((2'-bromo-[1,1'-biphenyl]-3-yl)(2,4-dimethylphenyl)-l4-sulfaneylidene)pivalamide (3af)



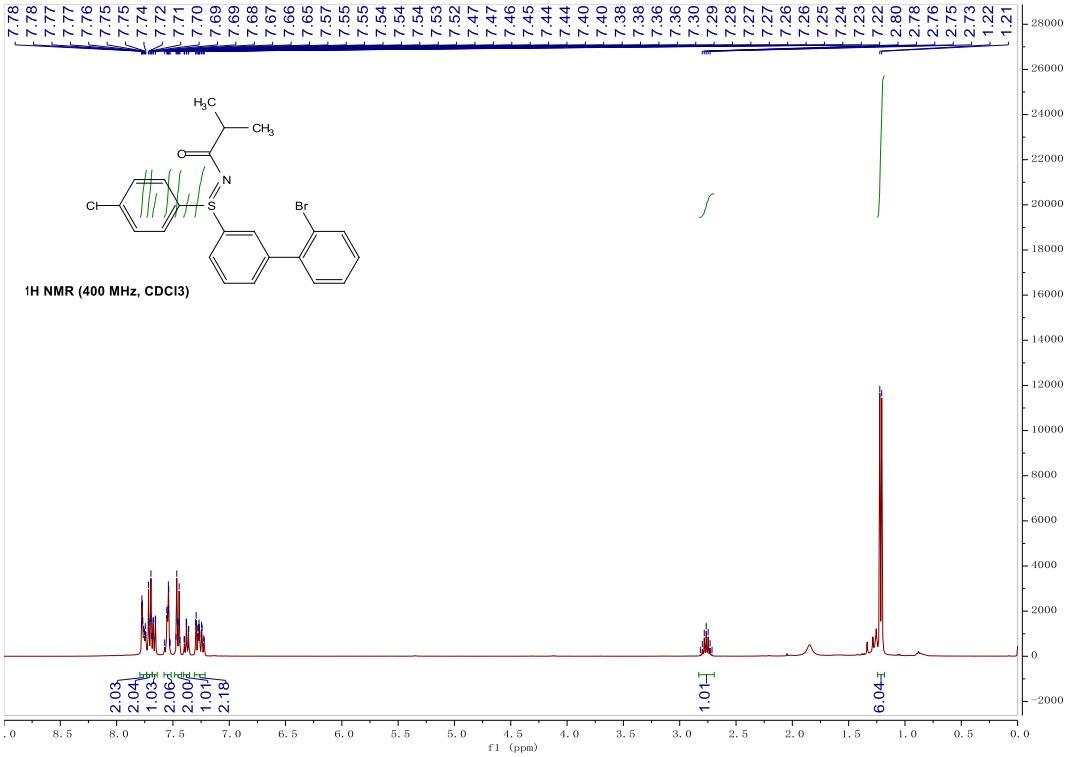


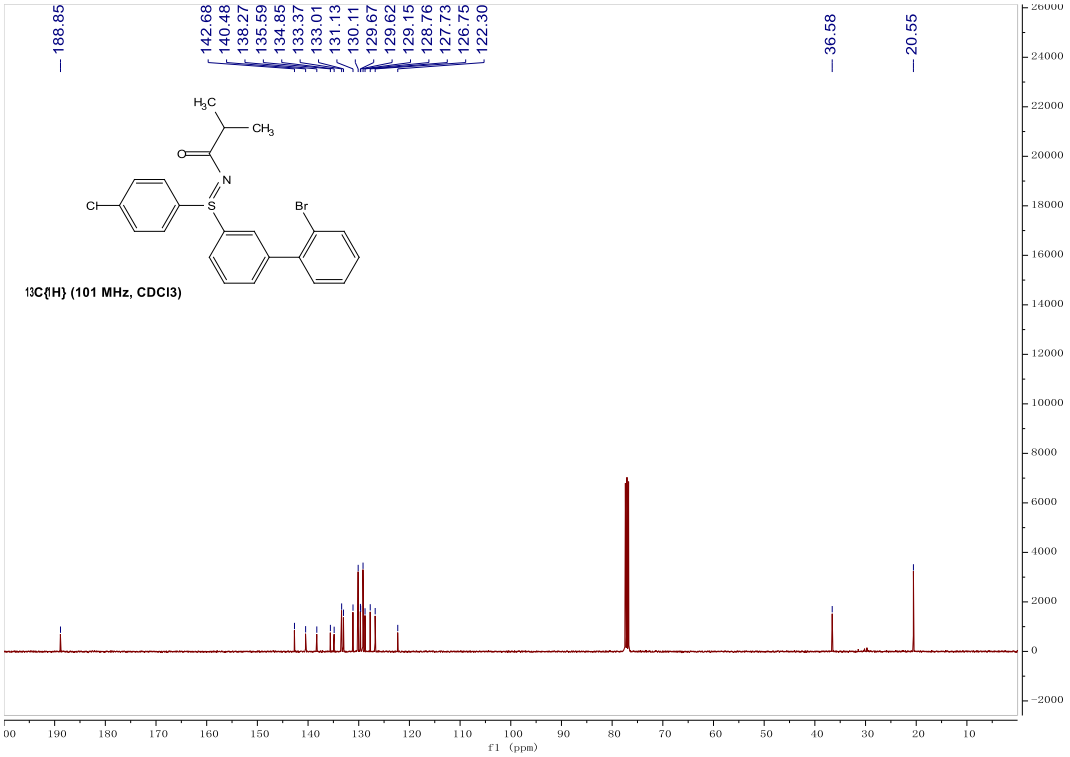
N-((2'-bromo-[1,1'-biphenyl]-3-yl)(naphthalen-2-yl)-l4-sulfaneylidene)pivalamide (3ag)



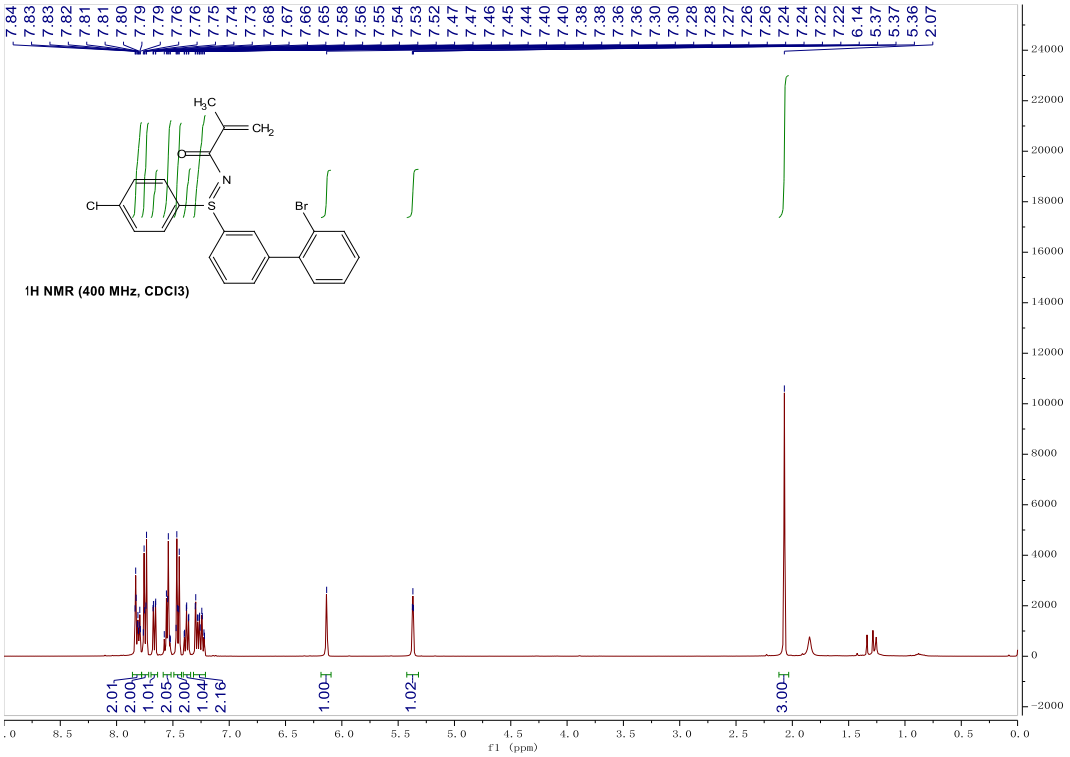


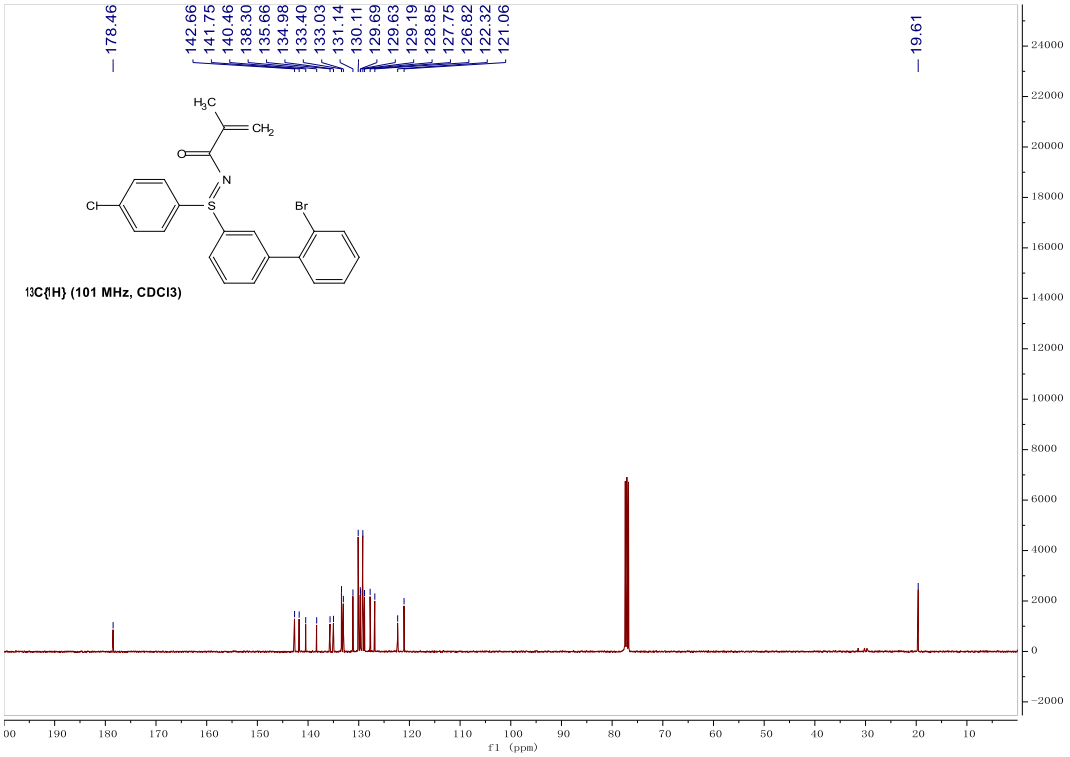
N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)isobutyramide (3ah)



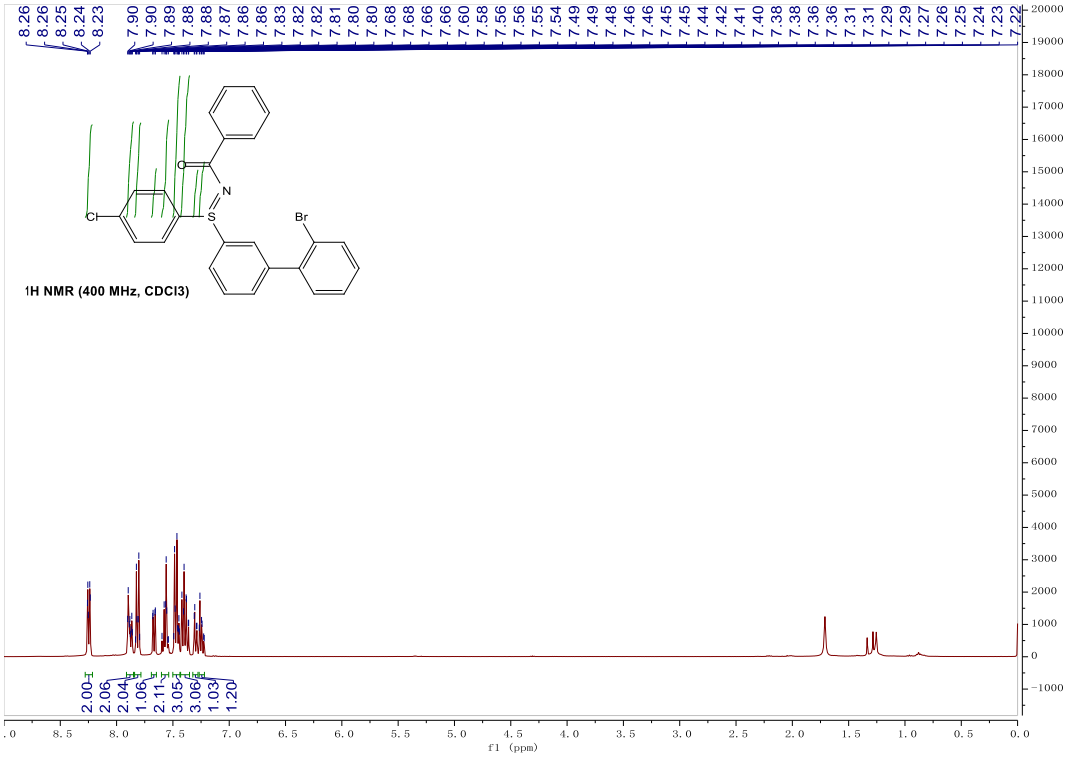


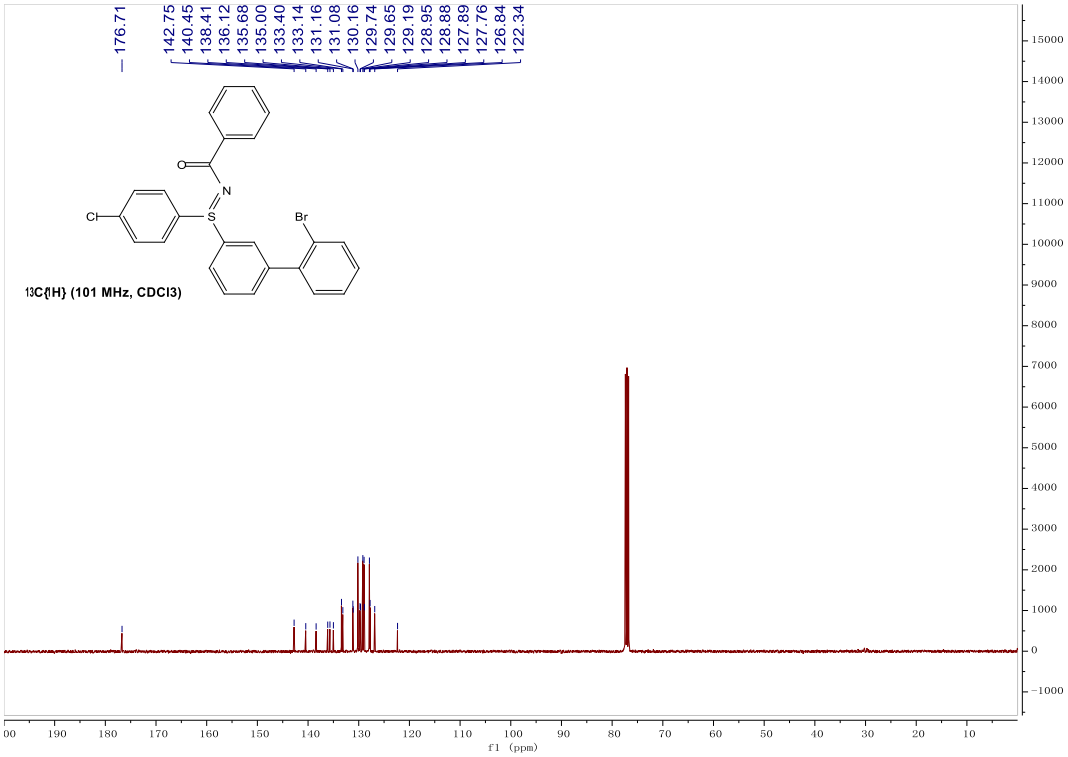
N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)methacrylamide (3ai)



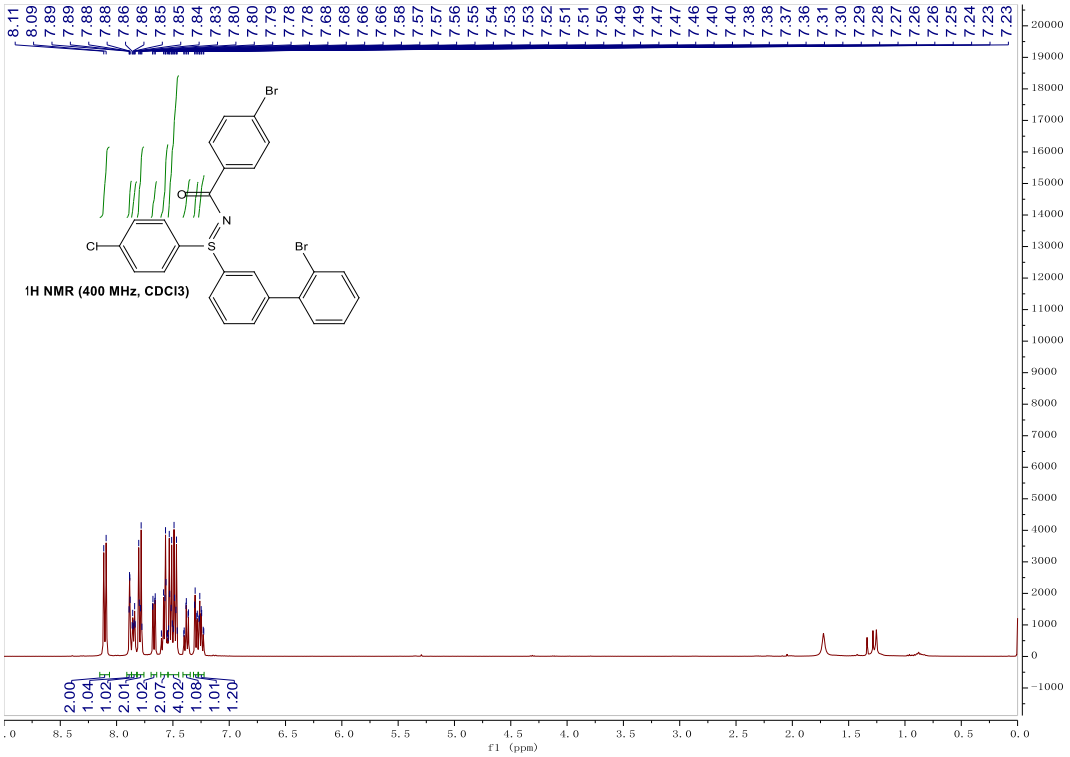


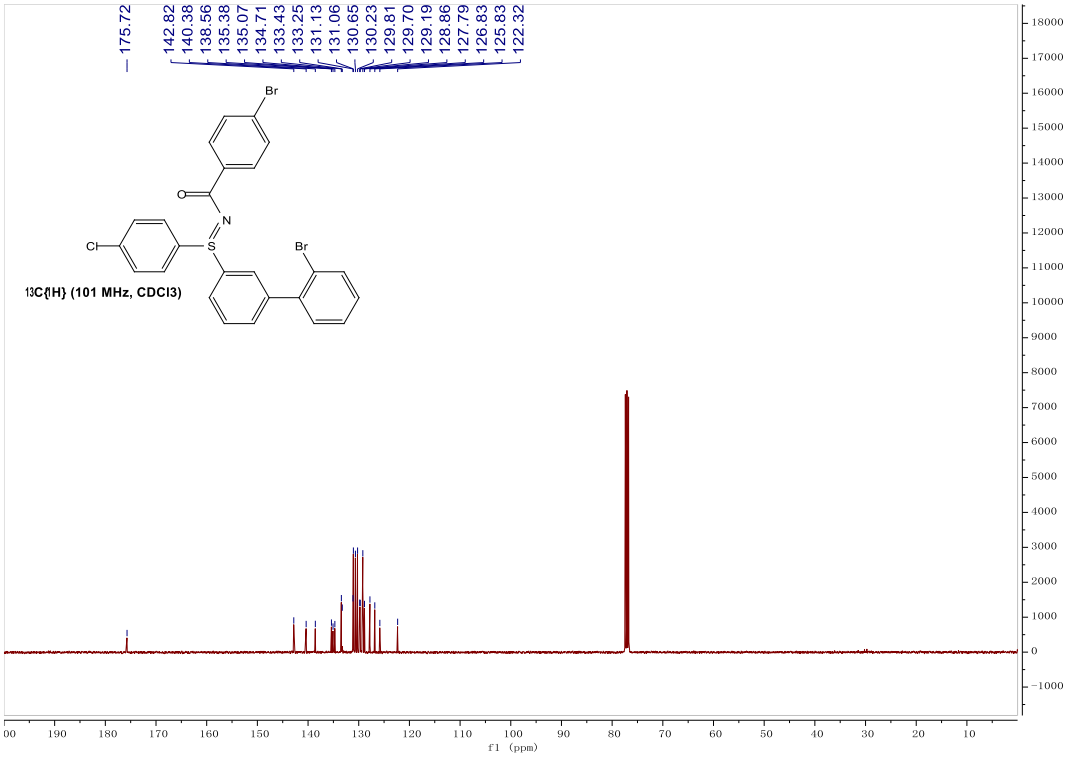
N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)benzamide (3aj)



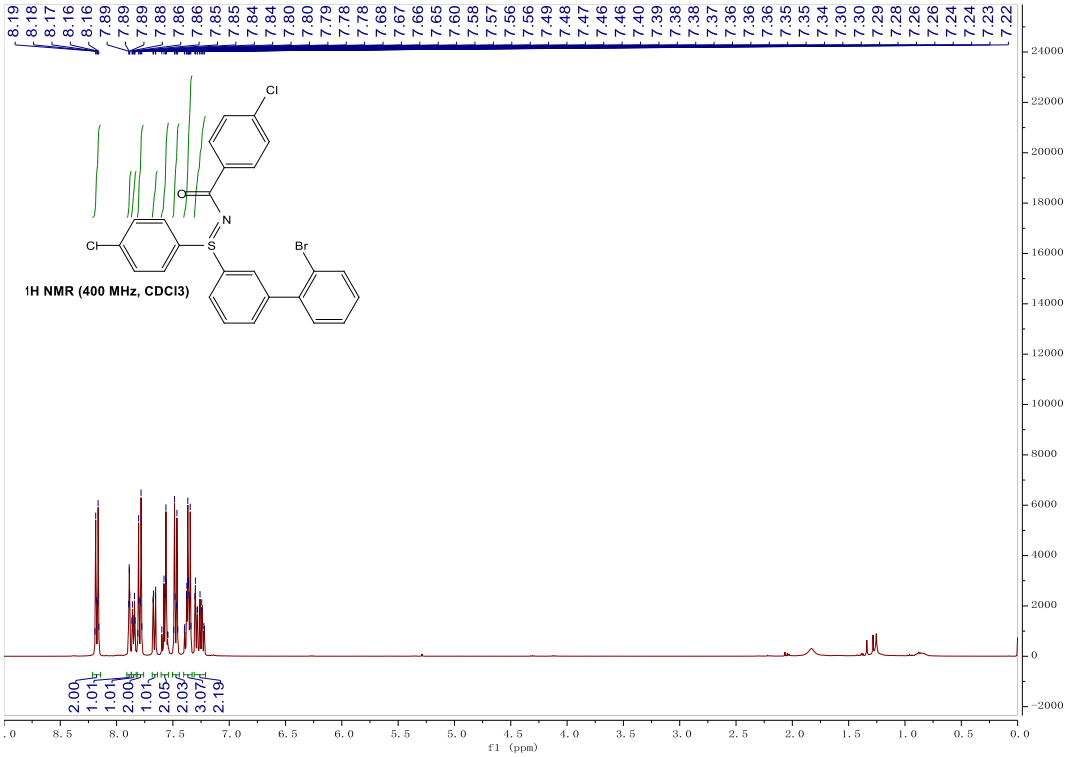


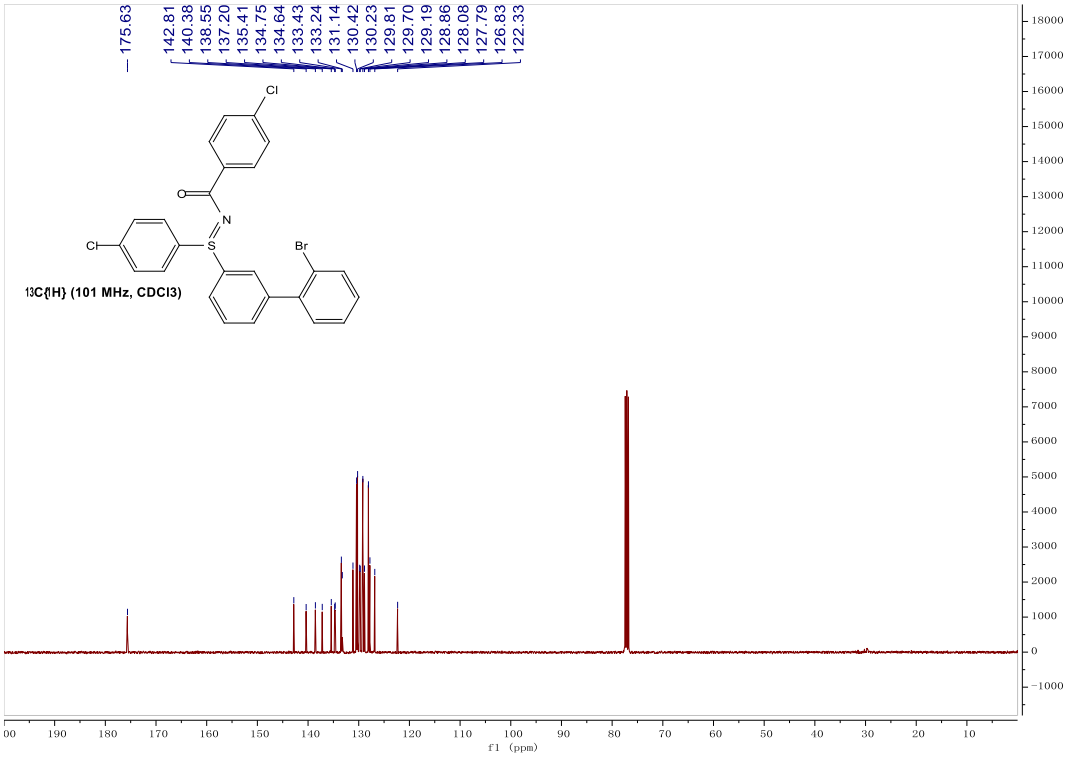
4-bromo-N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)benzamide (3ak)



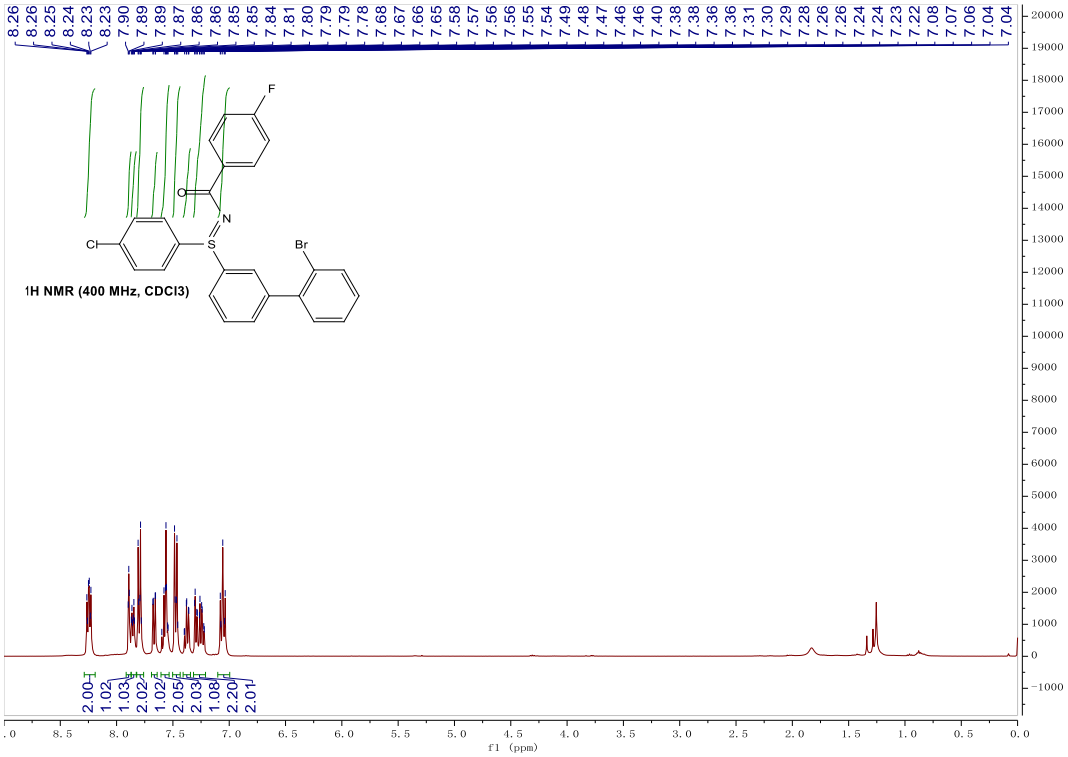


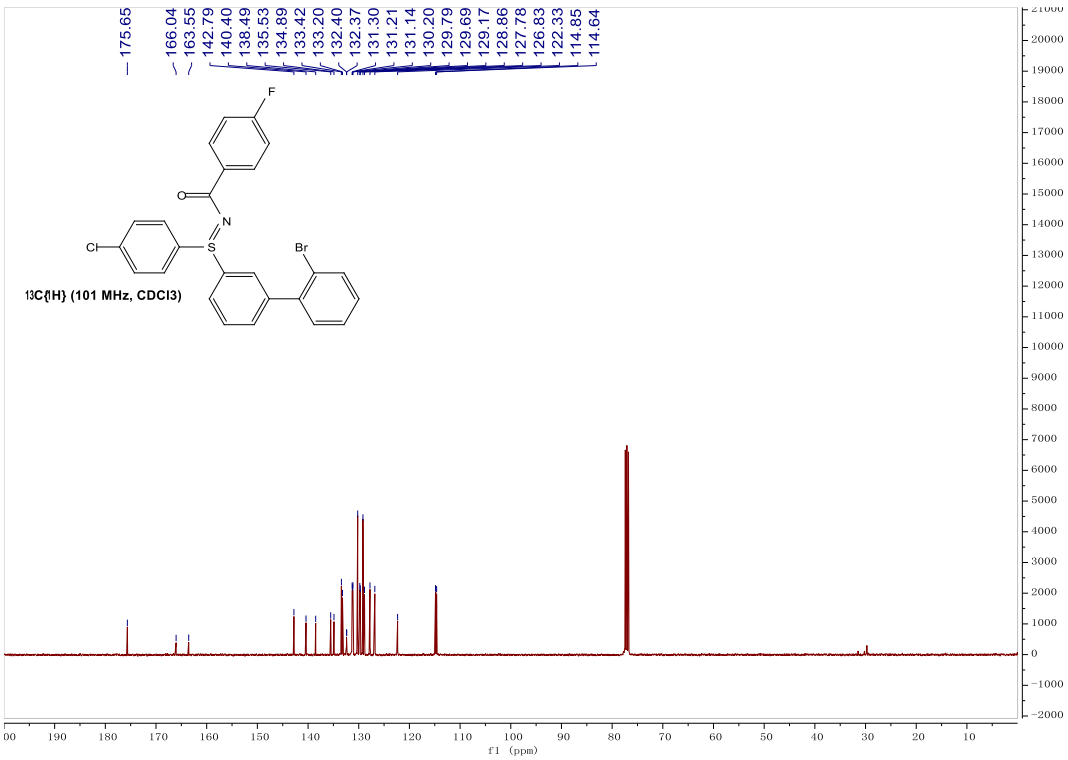
N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)-4-chlorobenzamide (3al)

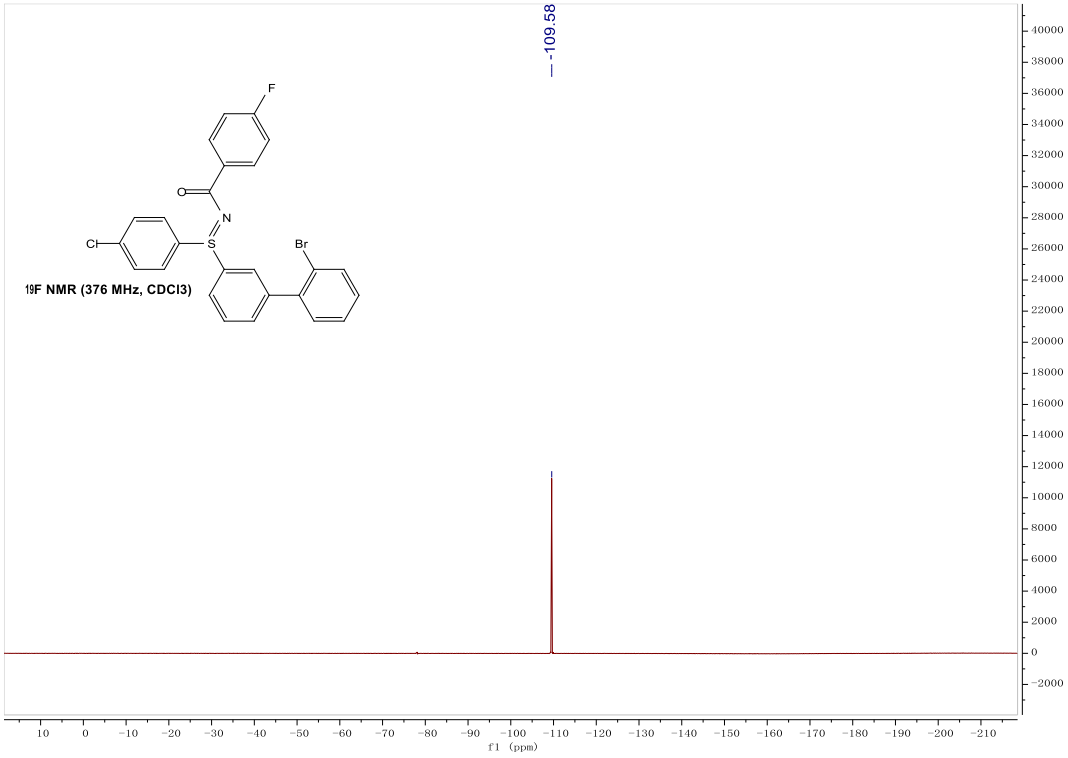




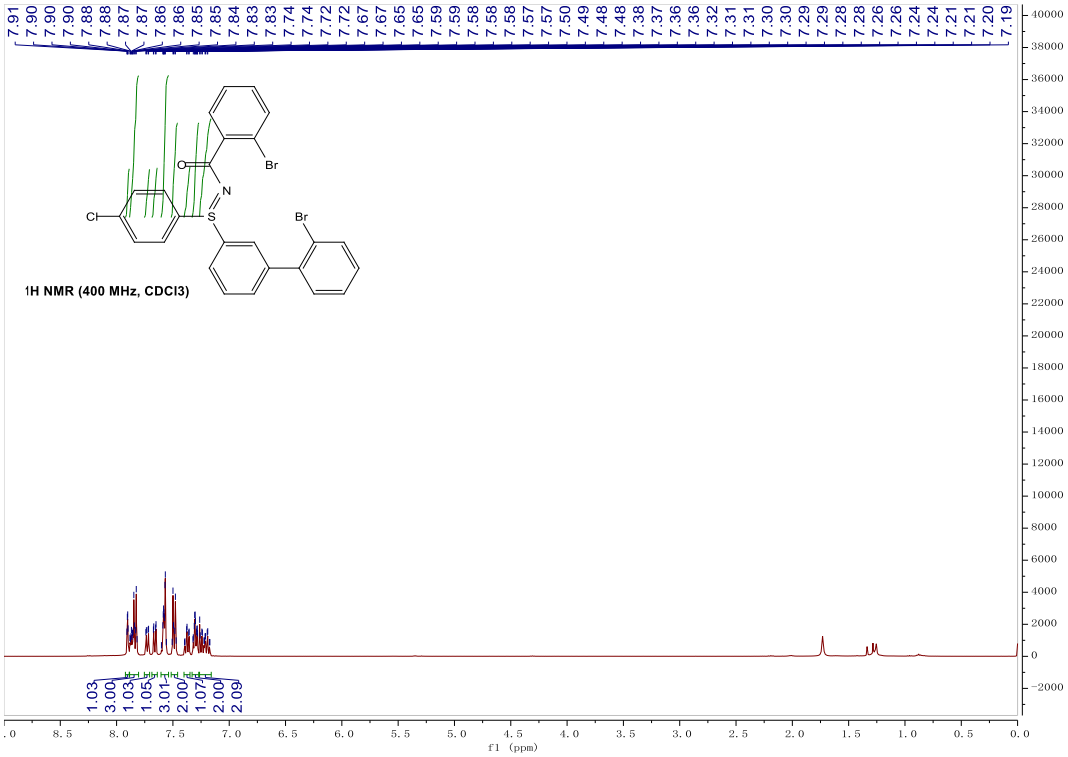
N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)-4-fluorobenzamide (3am)

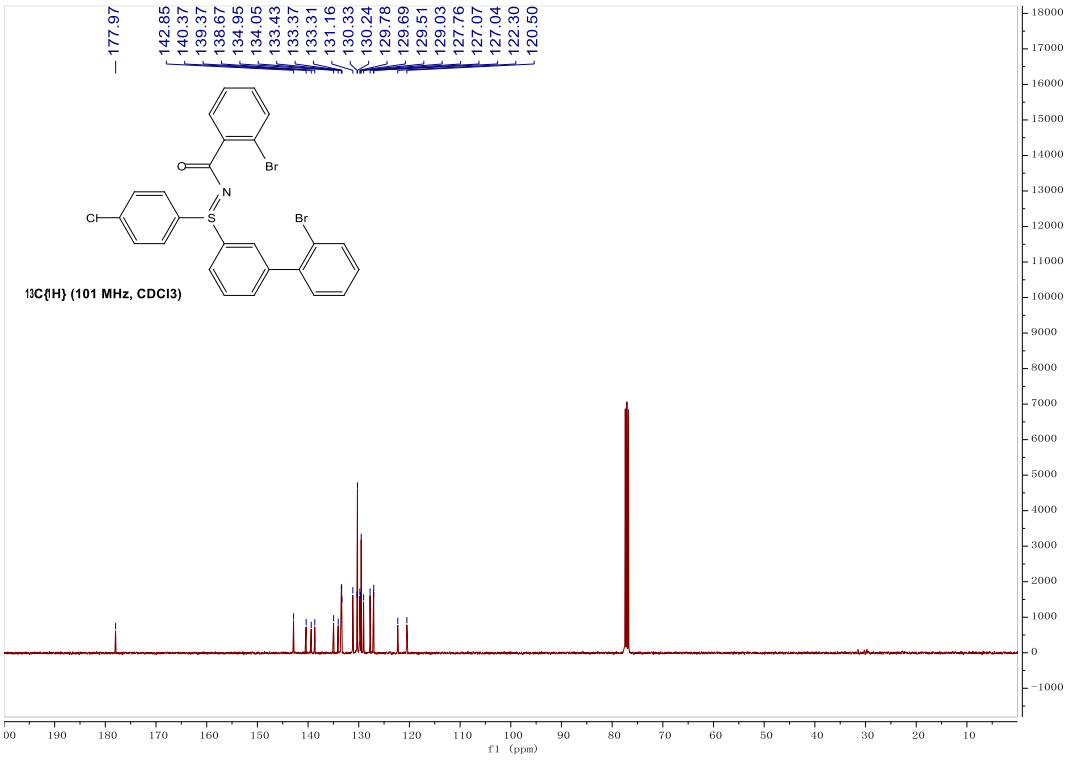




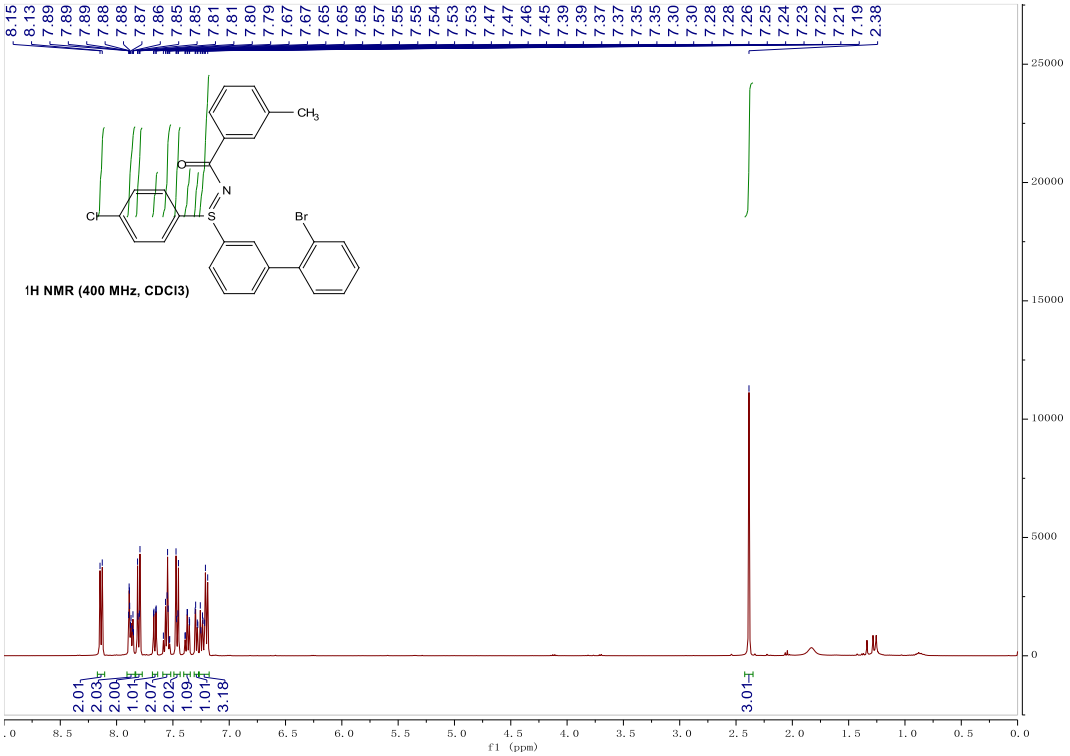


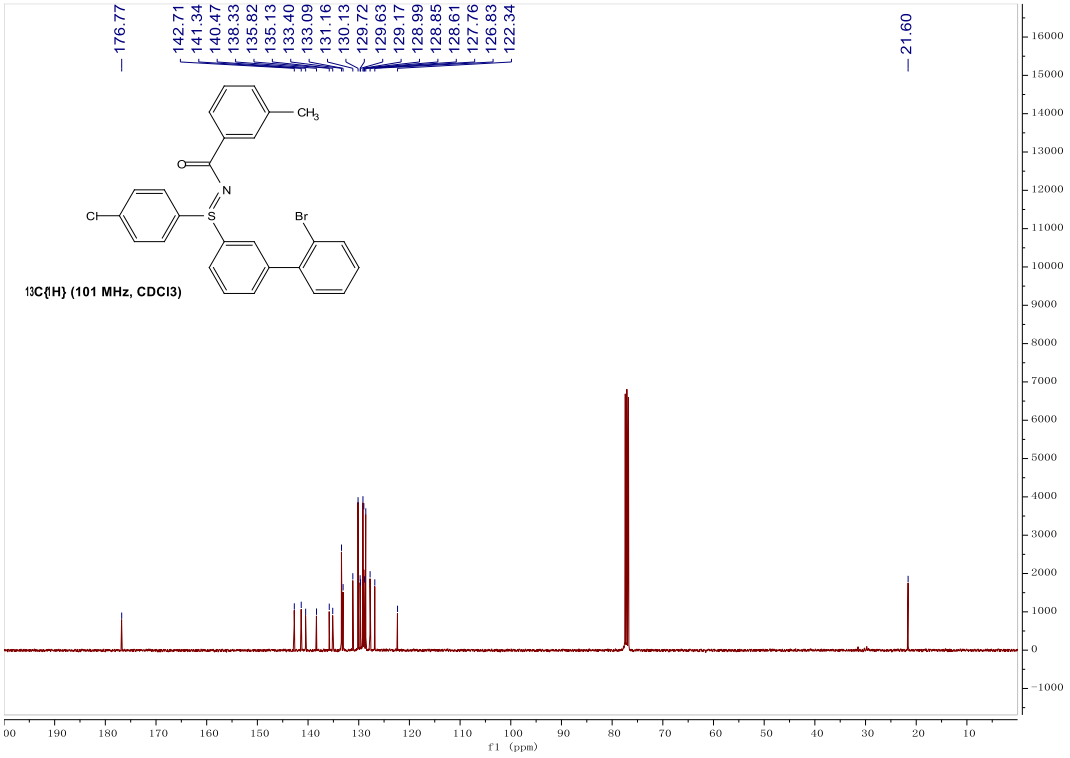
2-bromo-N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)benzamide (3an)



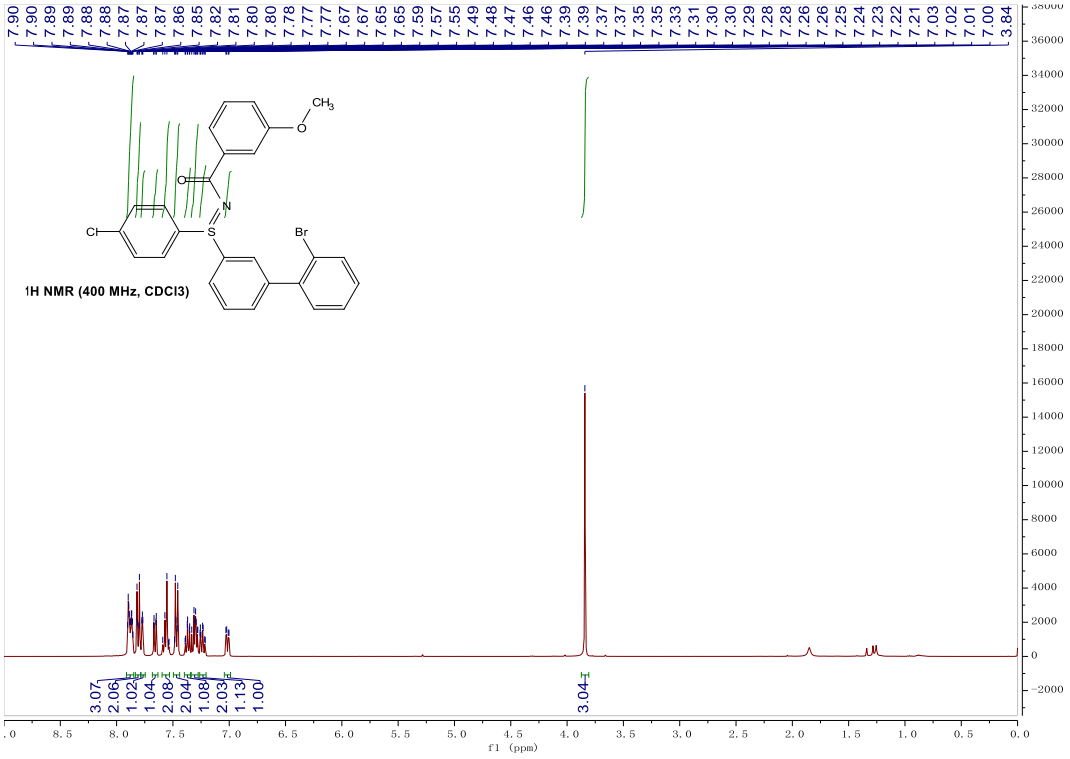


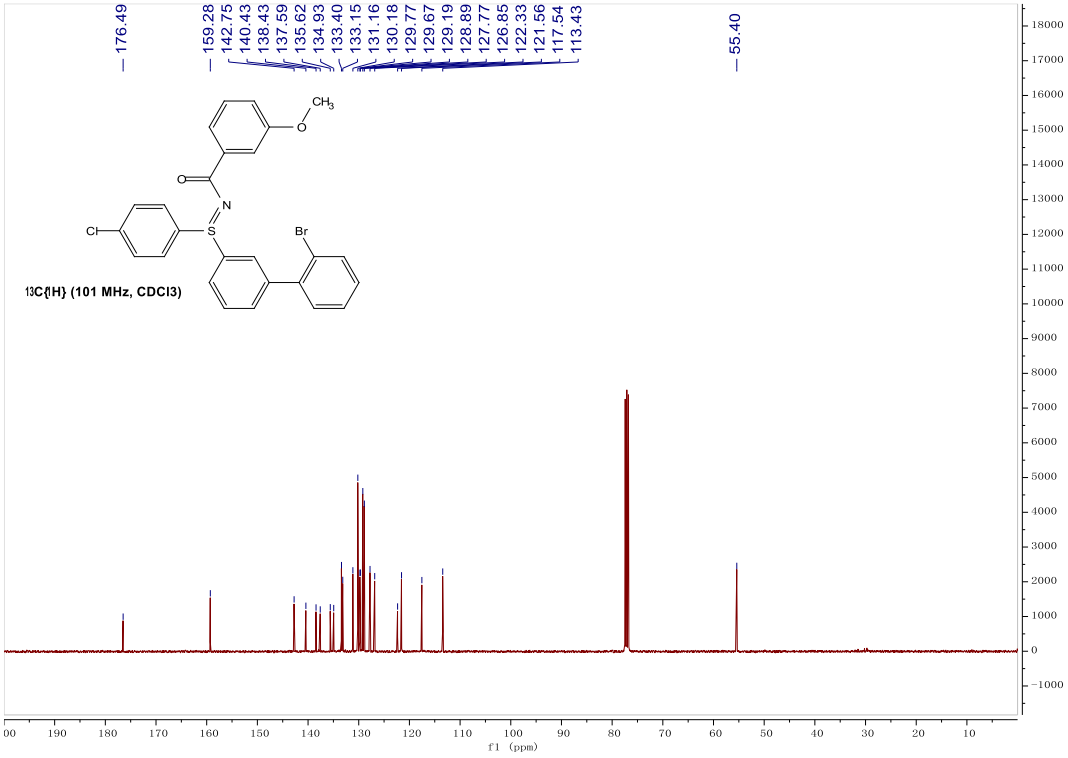
N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)-3-methylbenzamide (3ao)



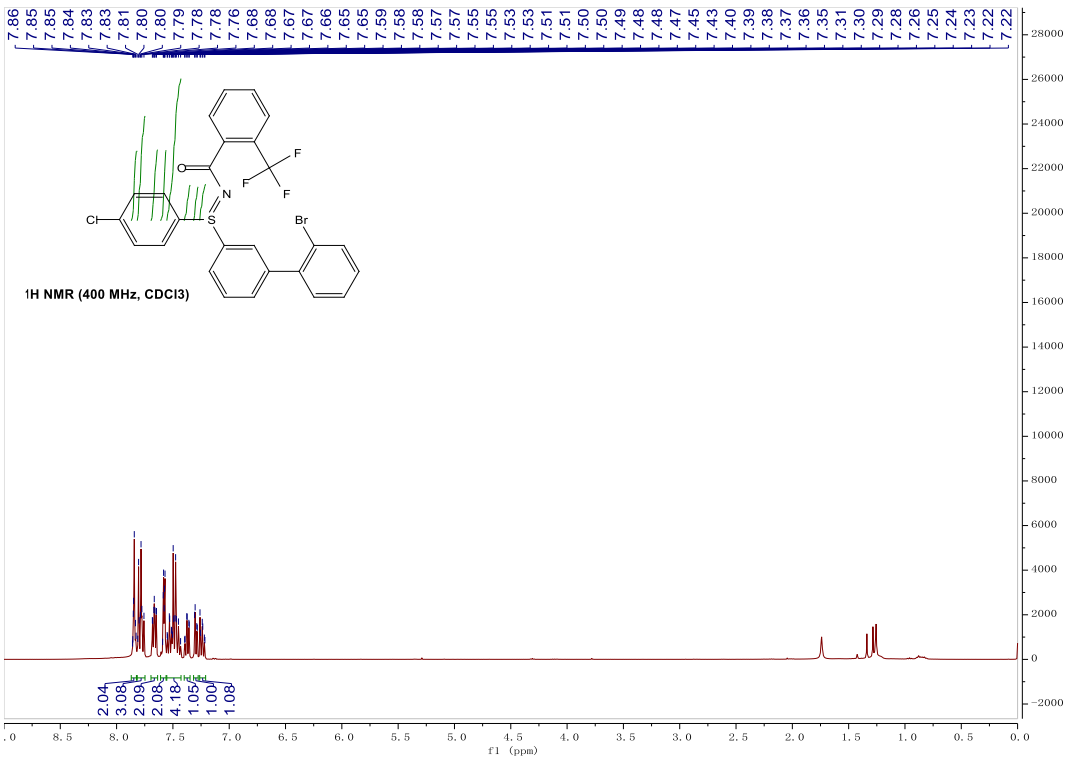


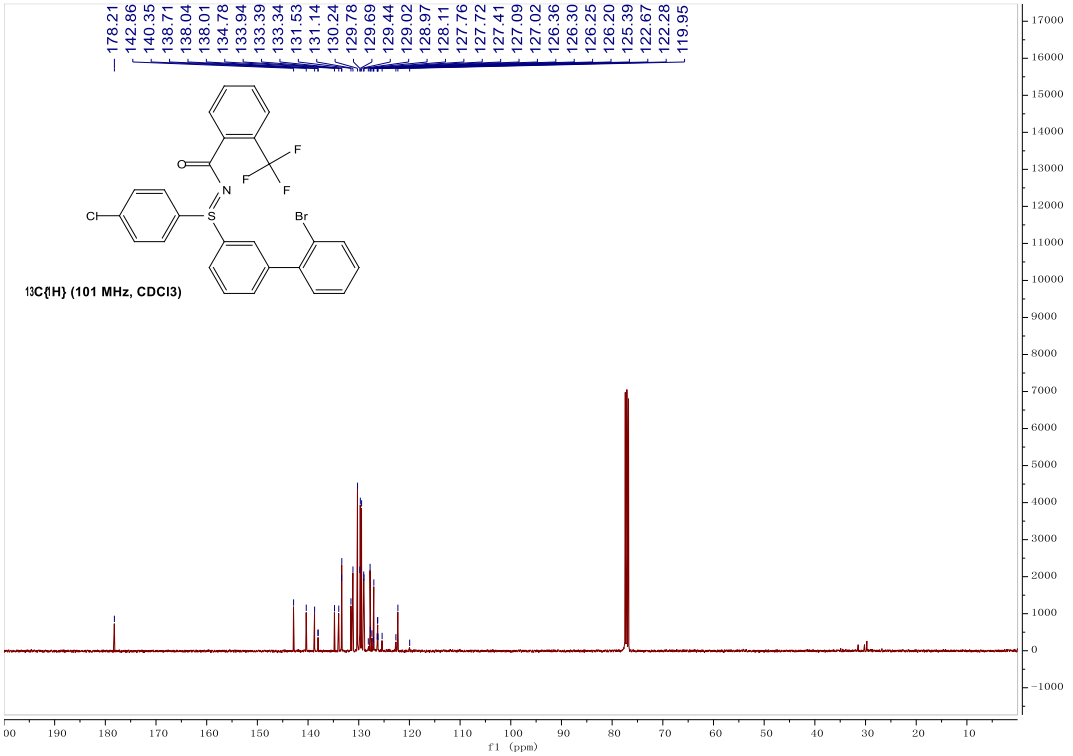
N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)-3-methoxybenzamide (3ap)





N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)-2-(trifluoromethyl)benzamide (3aq)

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129.78
129.69
129.44
129.02
128.97
128.11
127.76
127.72
127.41
127.09
127.02
126.36
126.30
126.25
126.20
125.39
122.67
122.28
119.95
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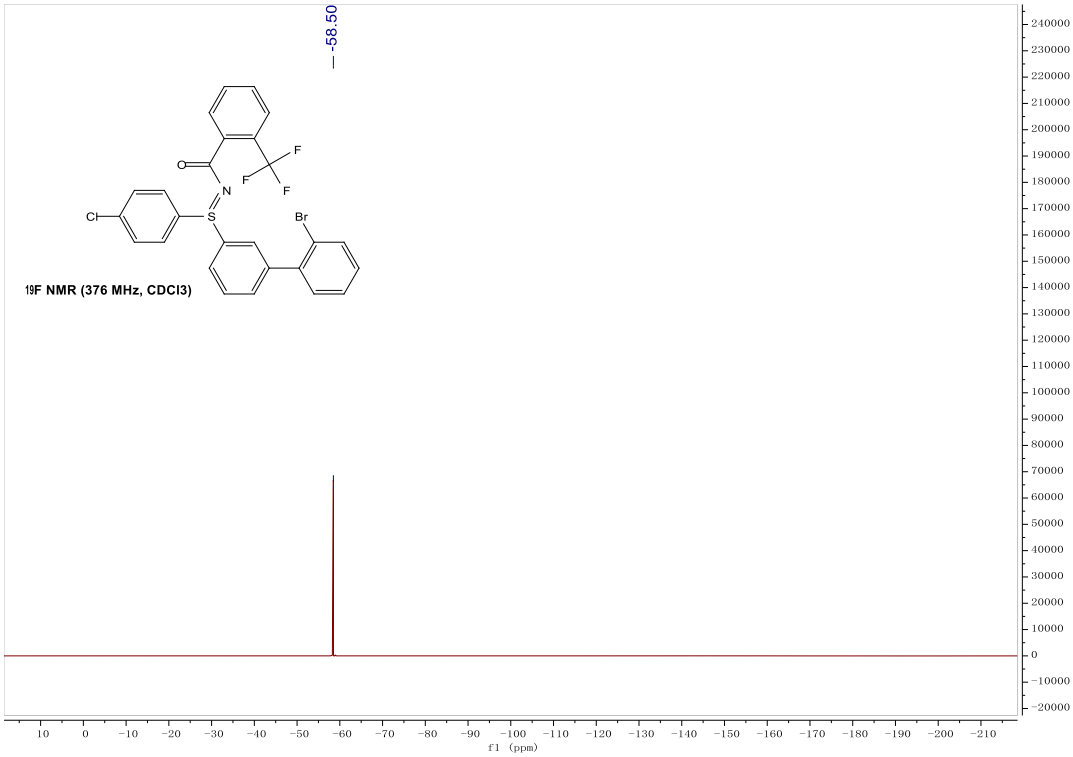
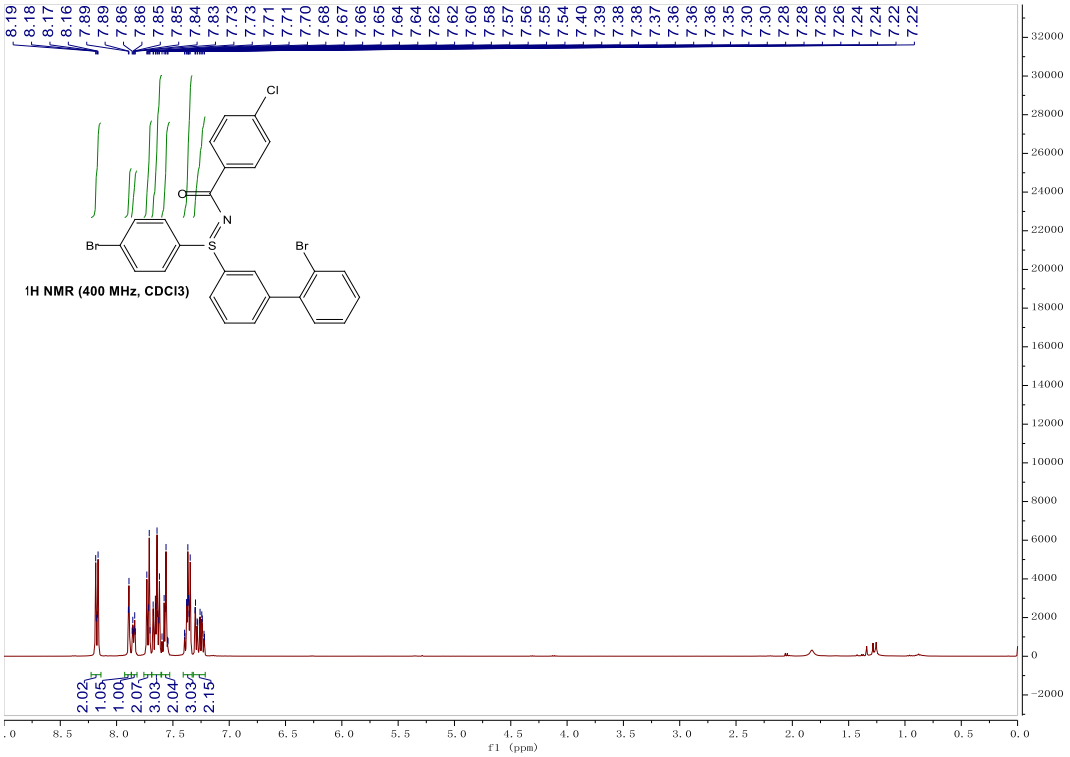
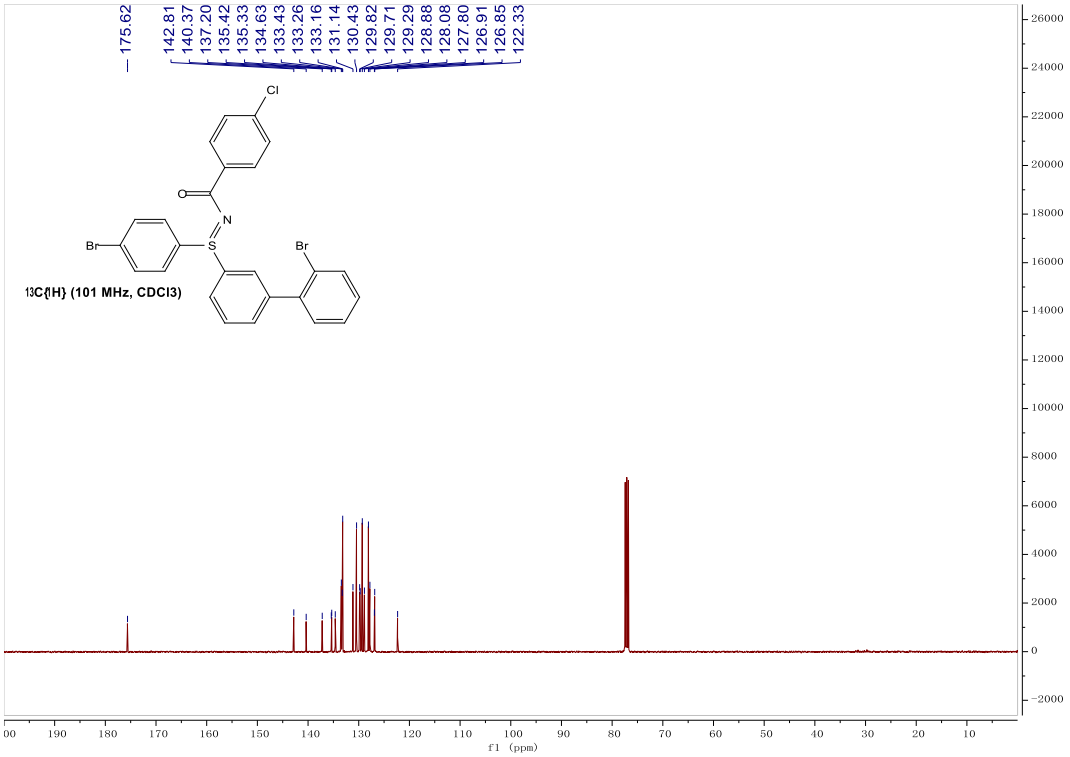
N
S
F
F
F
Cl
Br
13C{1H} (101 MHz, CDCl3)
f1 (ppm)

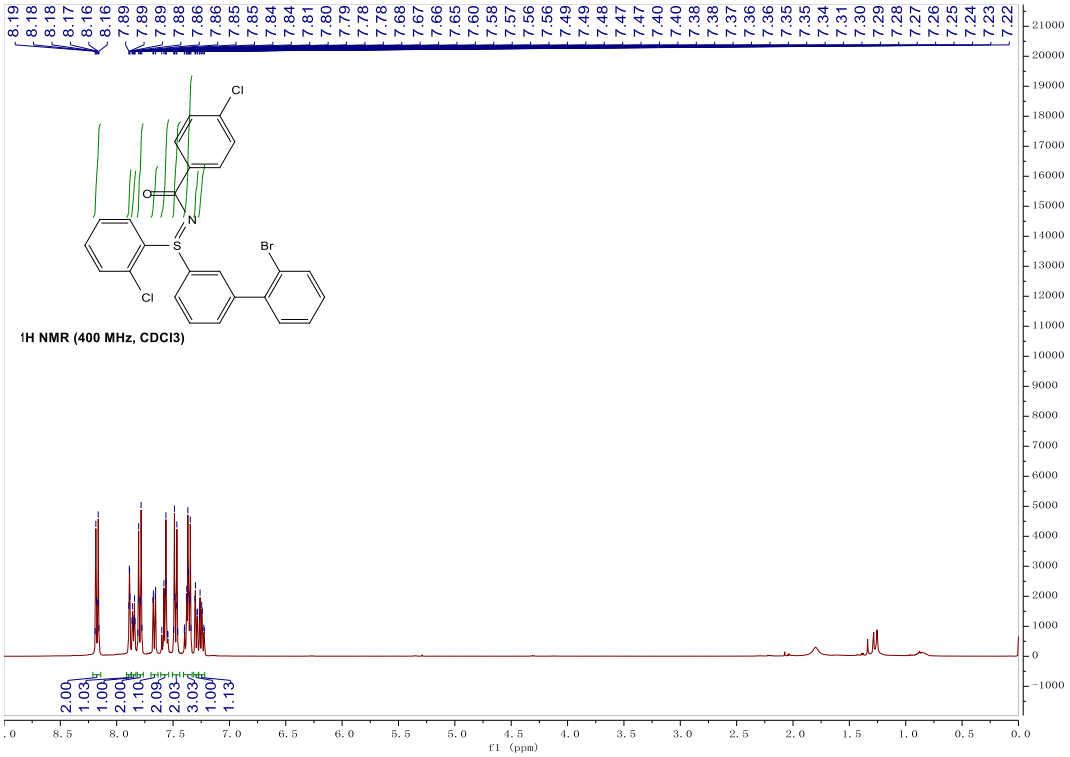

-58.50
O
N
S
F
F
F
Cl
Br
19F NMR (376 MHz, CDCl3)
f1 (ppm)

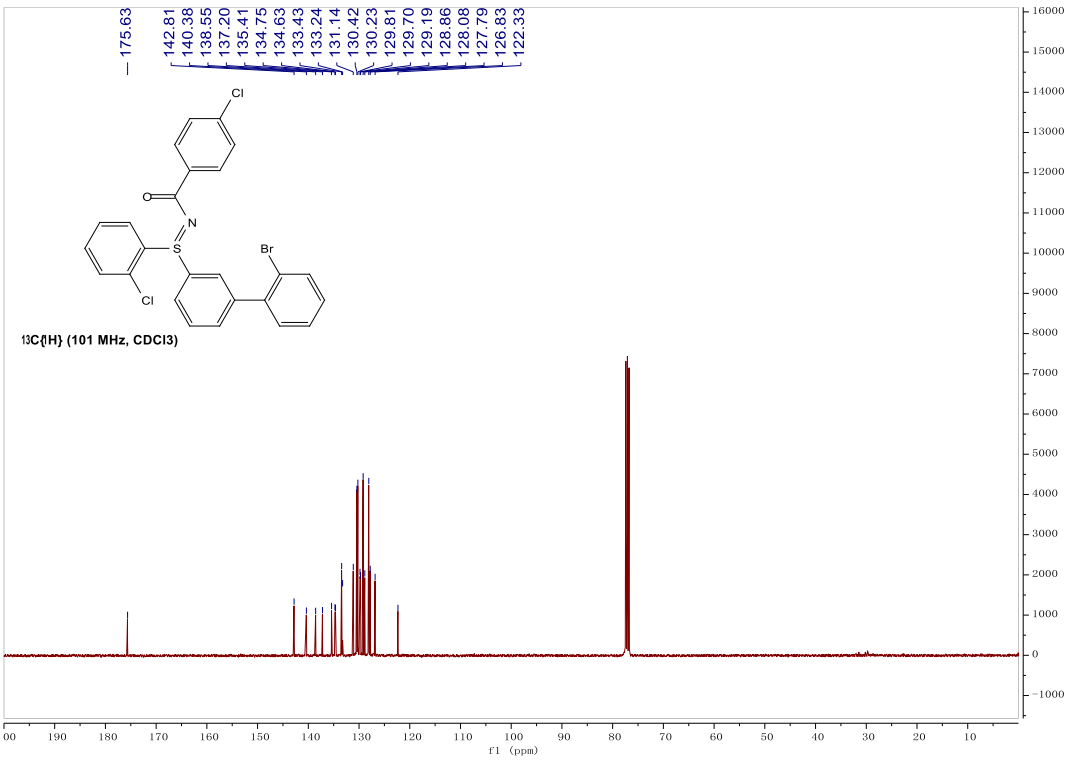
N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-bromophenyl)-l4-sulfaneylidene)-4-chlorobenzamide (3ar)



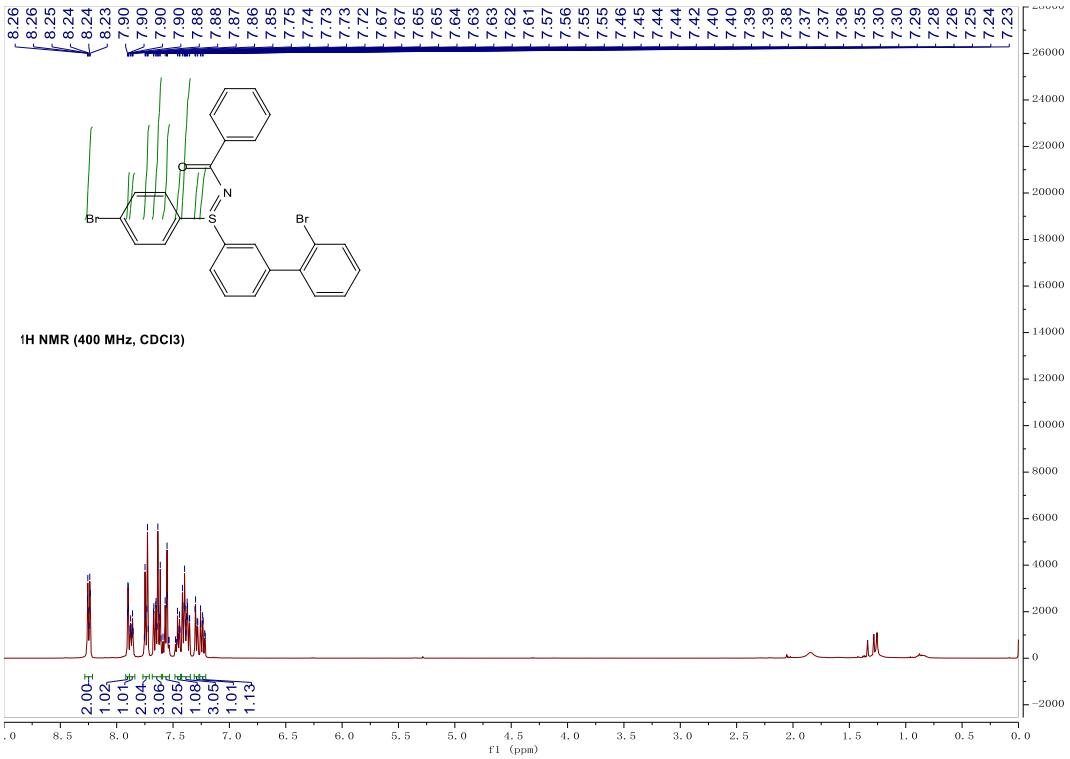


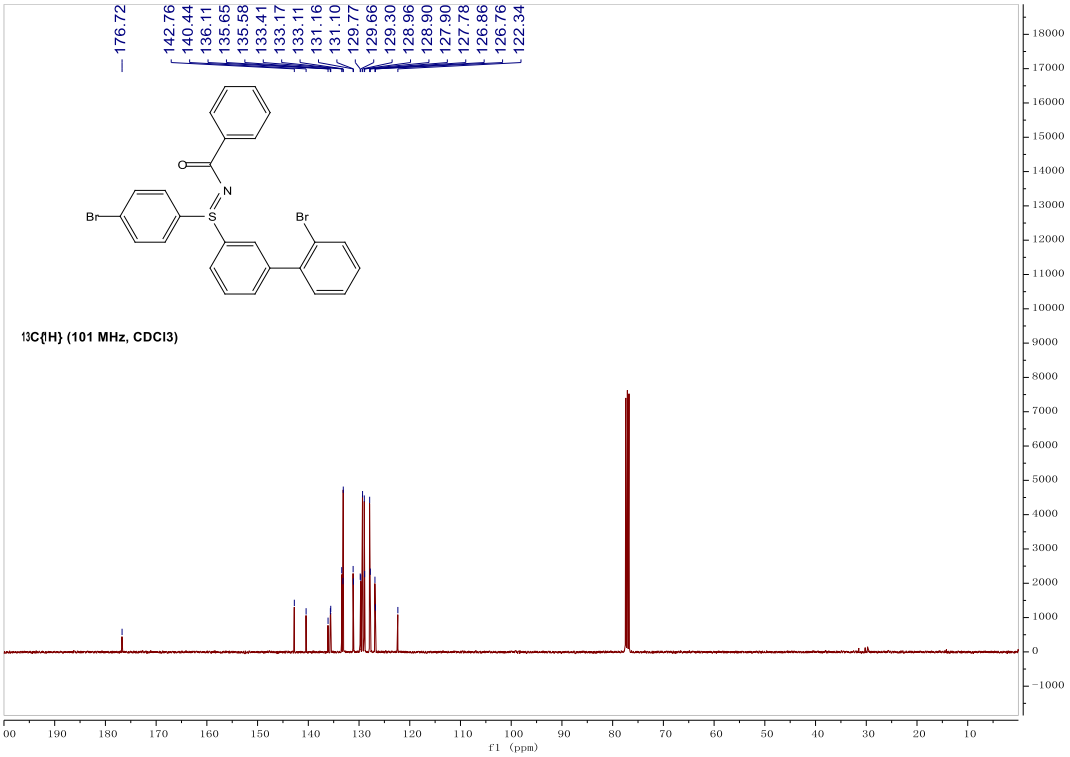
N-((2'-bromo-[1,1'-biphenyl]-3-yl)(2-chlorophenyl)-l4-sulfaneylidene)-4-chlorobenzamide (3as)



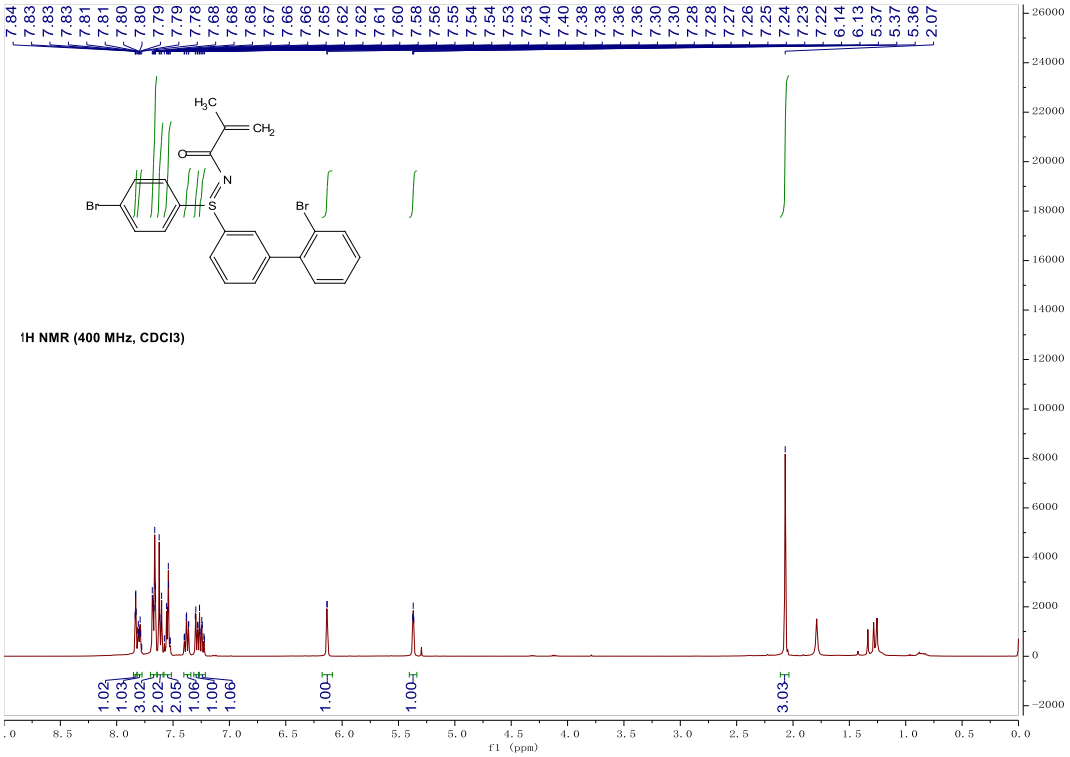


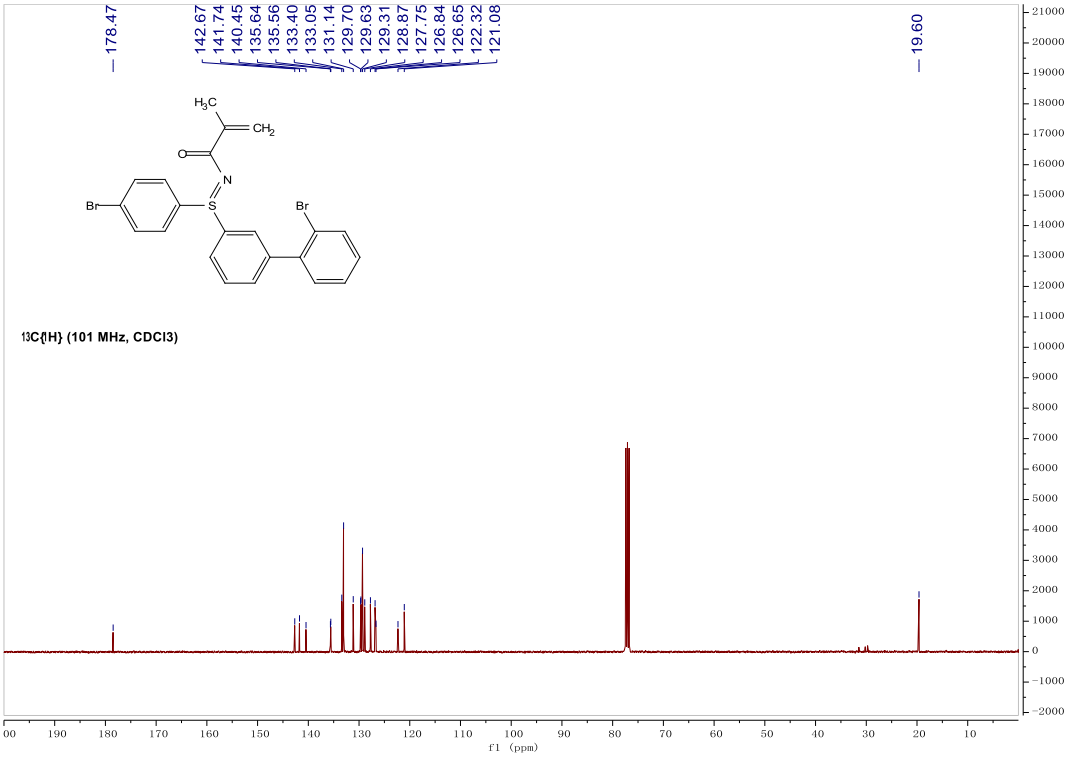
N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-bromophenyl)-l4-sulfaneylidene)benzamide (3at)



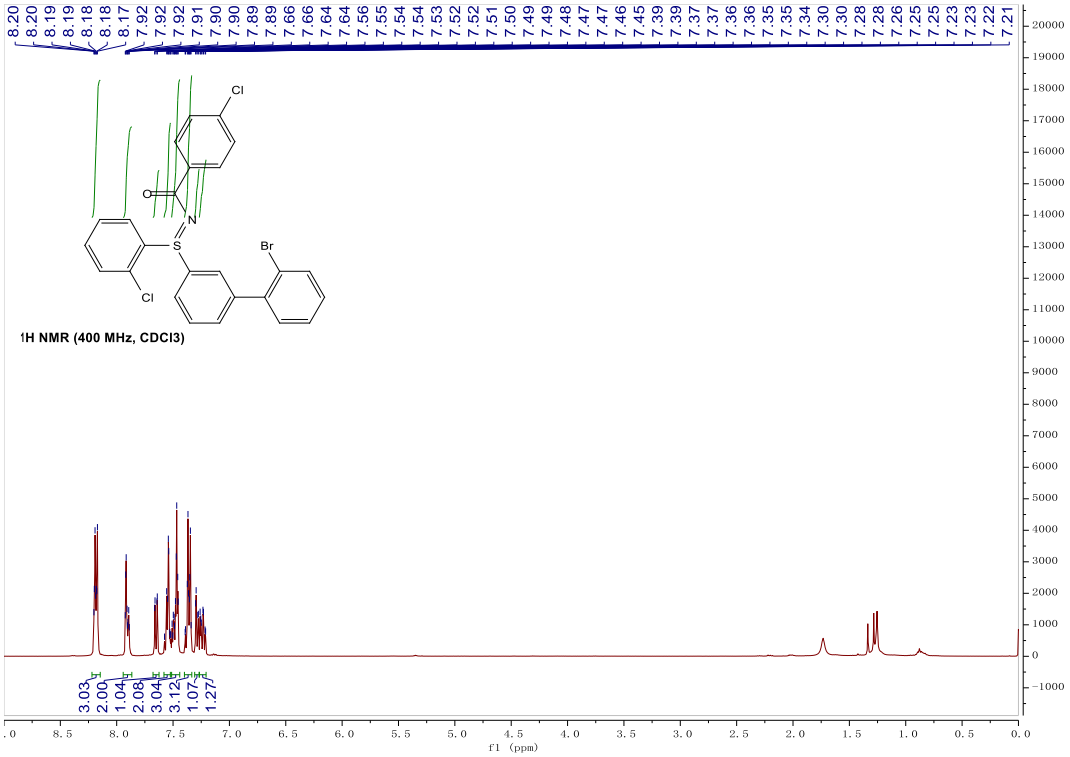


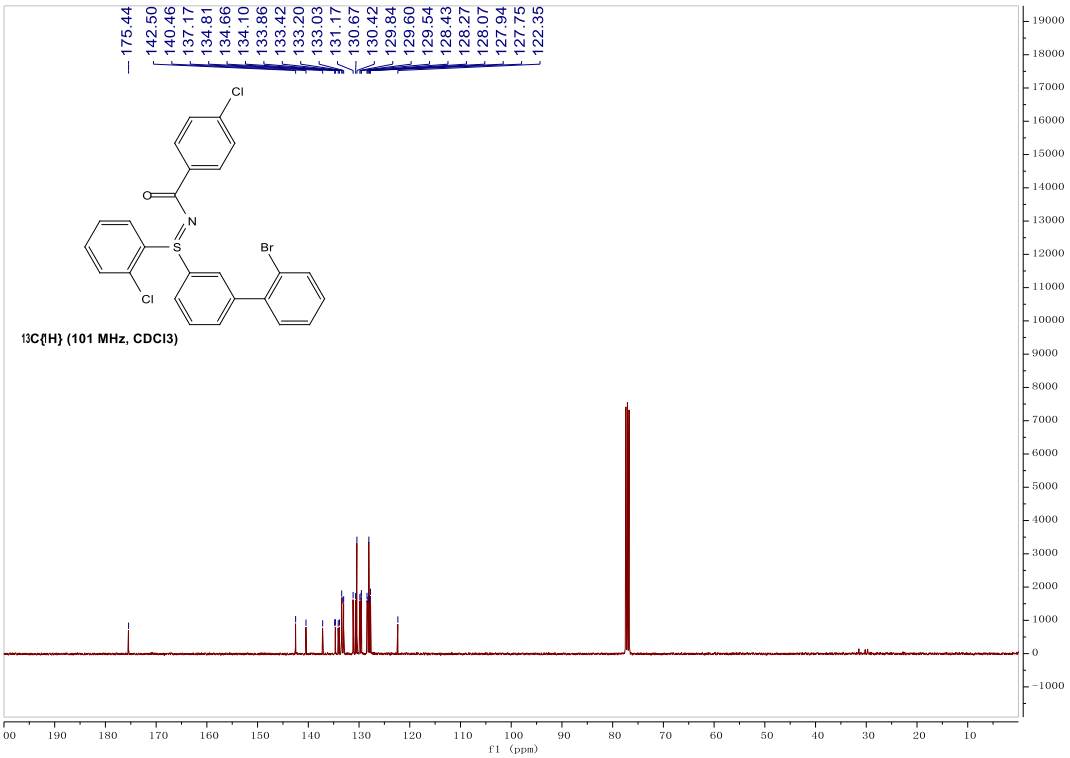
N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-bromophenyl)-l4-sulfaneylidene)methacrylamide (3au)



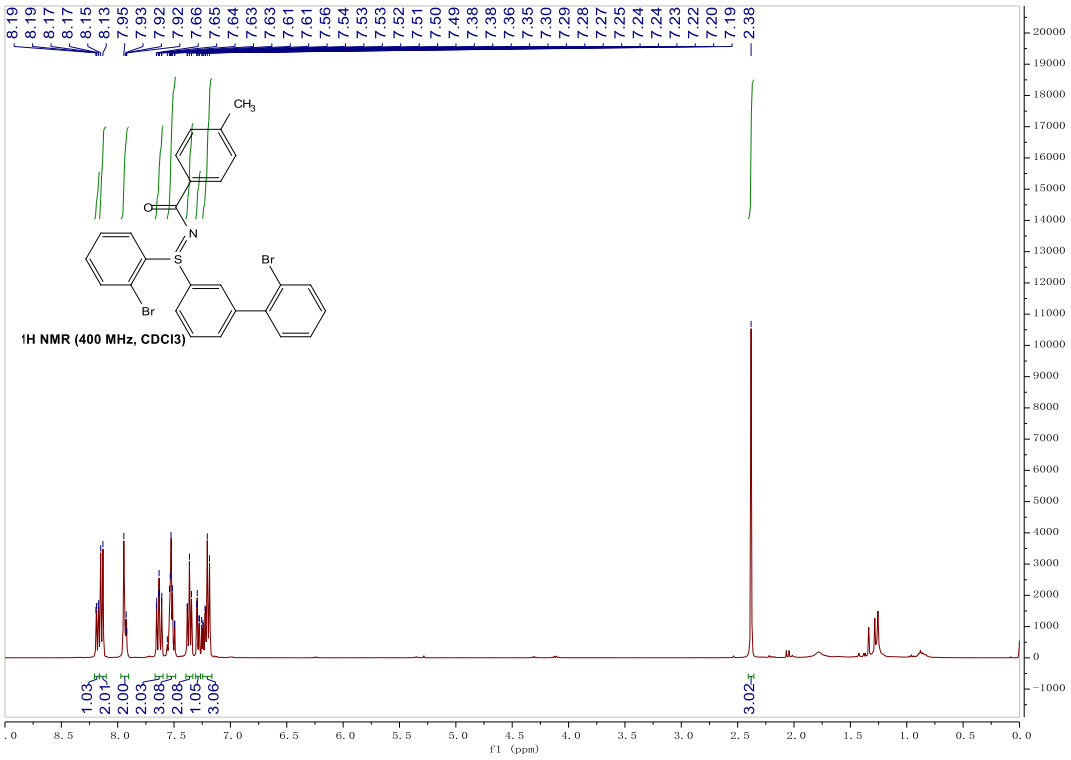


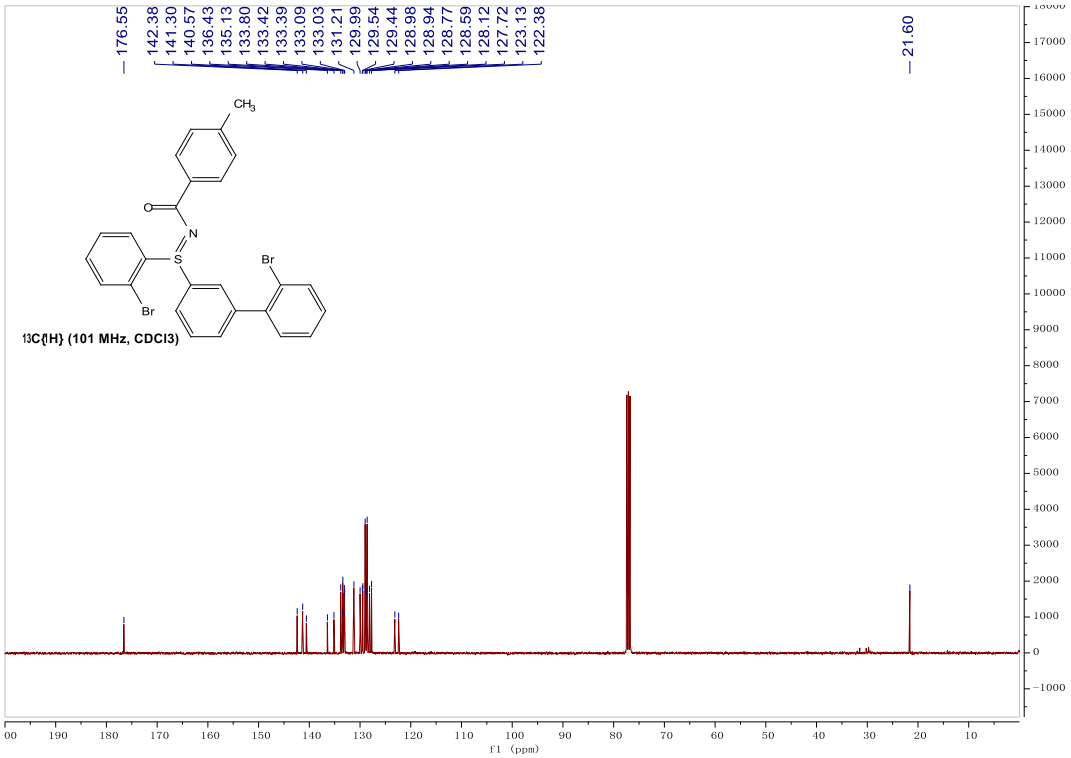
N-((2'-bromo-[1,1'-biphenyl]-3-yl)(2-chlorophenyl)-l4-sulfaneylidene)-4-chlorobenzamide (3av)



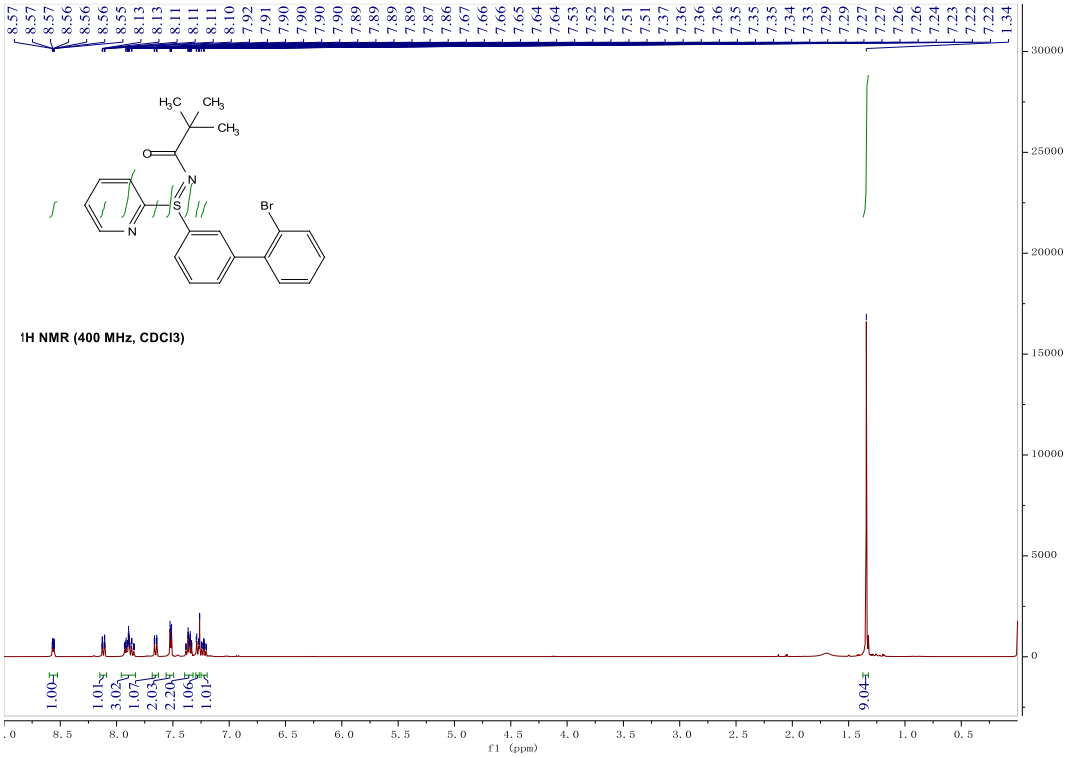


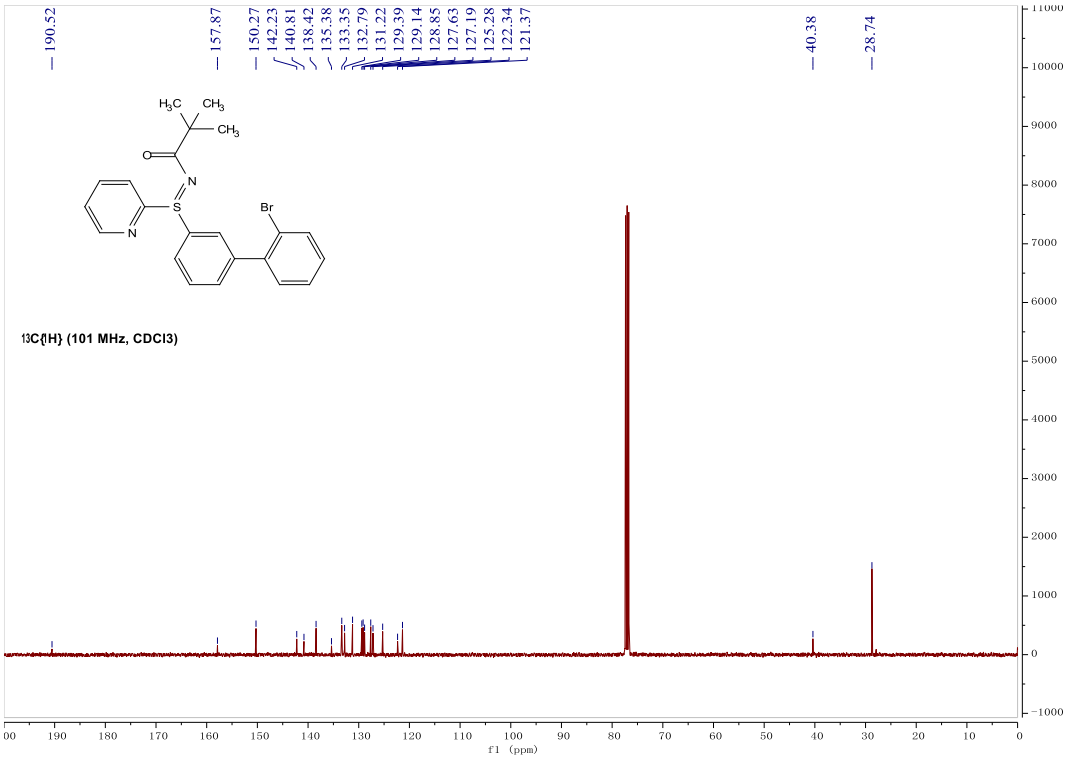
N-((2'-bromo-[1,1'-biphenyl]-3-yl)(2-bromophenyl)-l4-sulfaneylidene)-4-methylbenzamide (3aw)



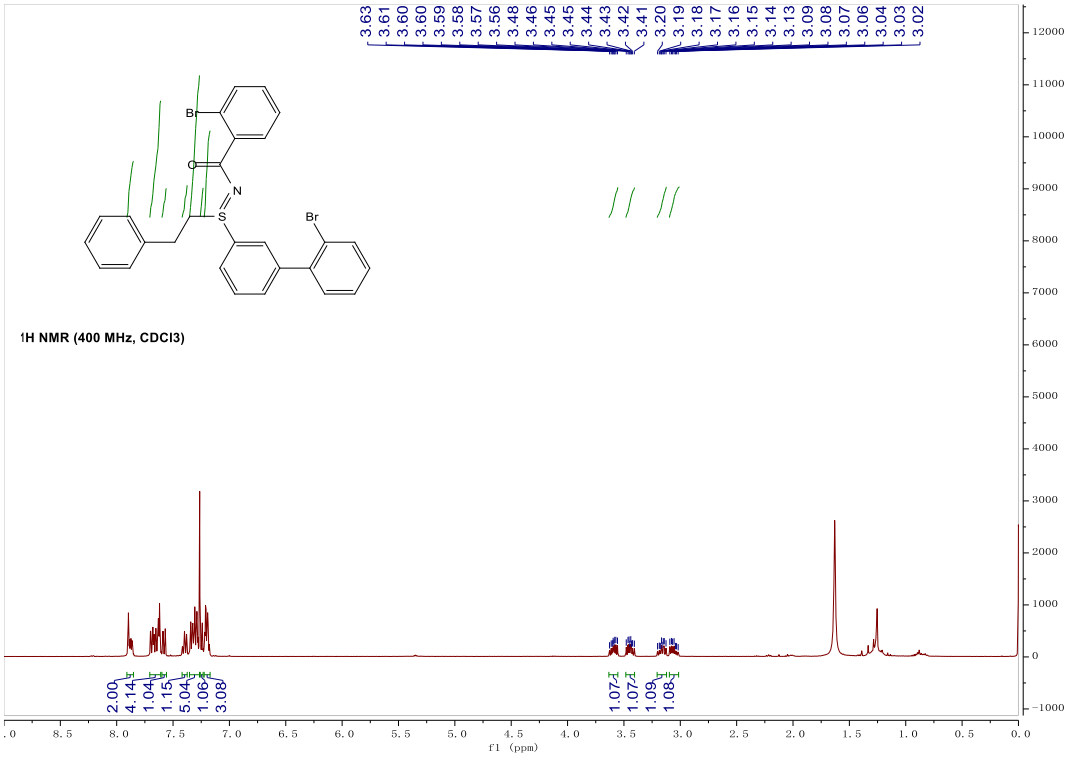


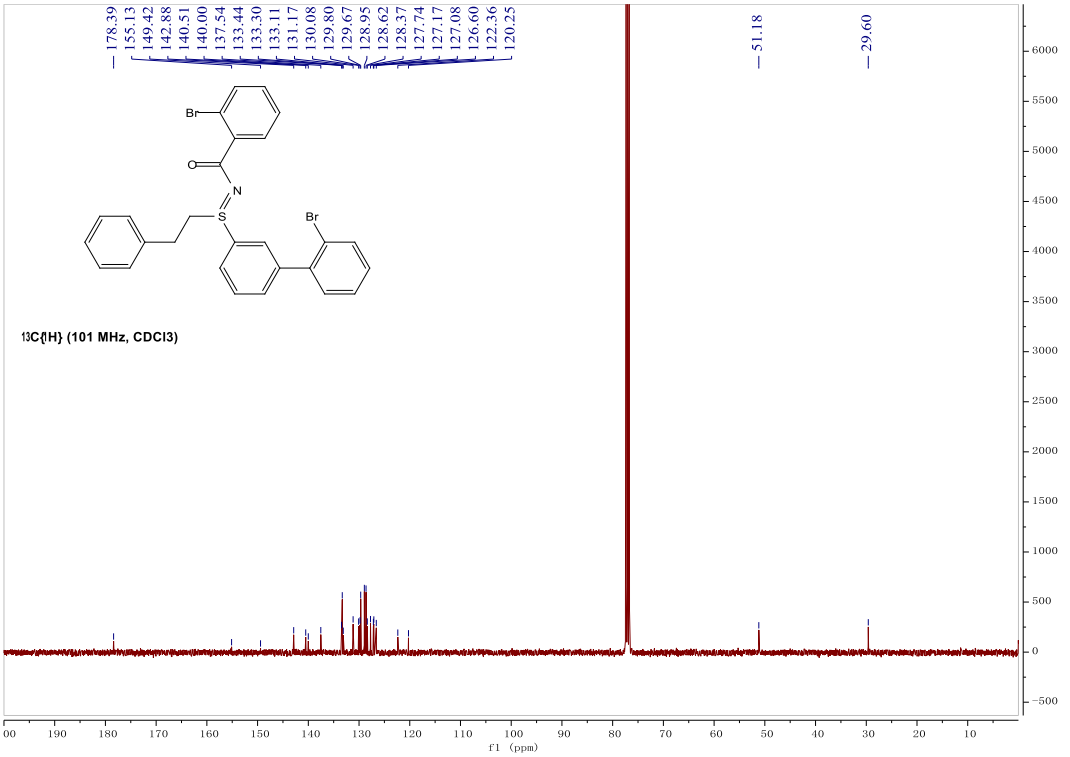
(S,Z)-N-((2'-bromo-[1,1'-biphenyl]-3-yl)(pyridin-2-yl)-l4-sulfaneylidene)pivalamide (3ax)



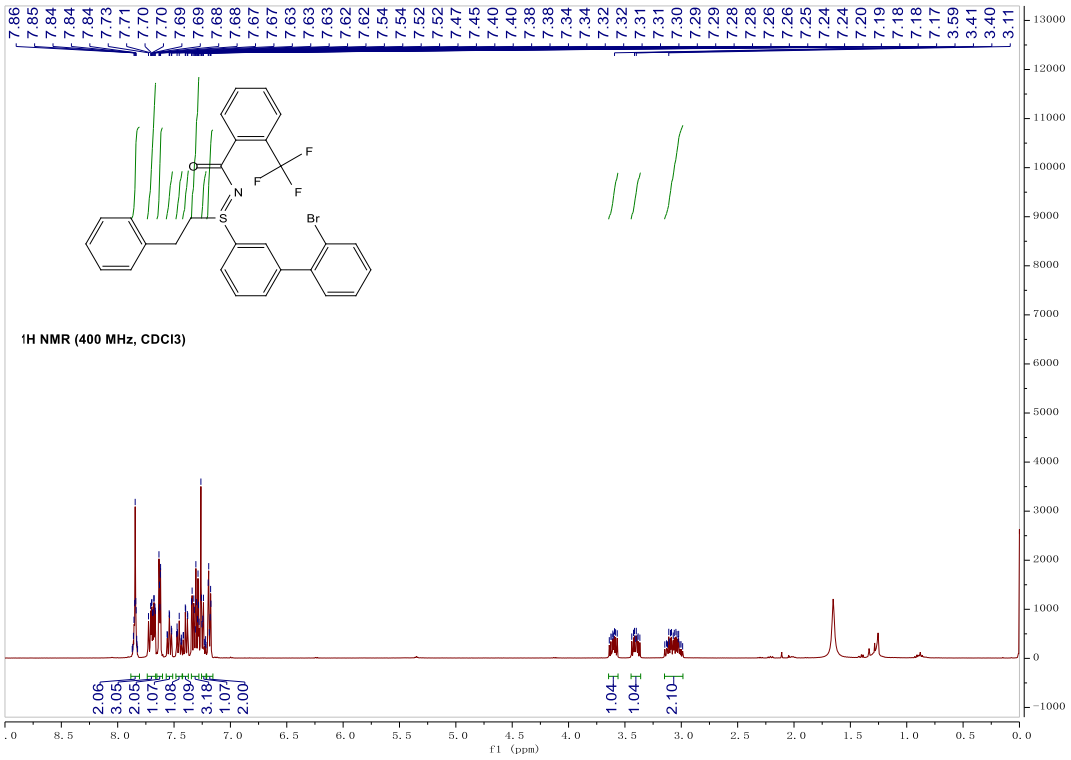


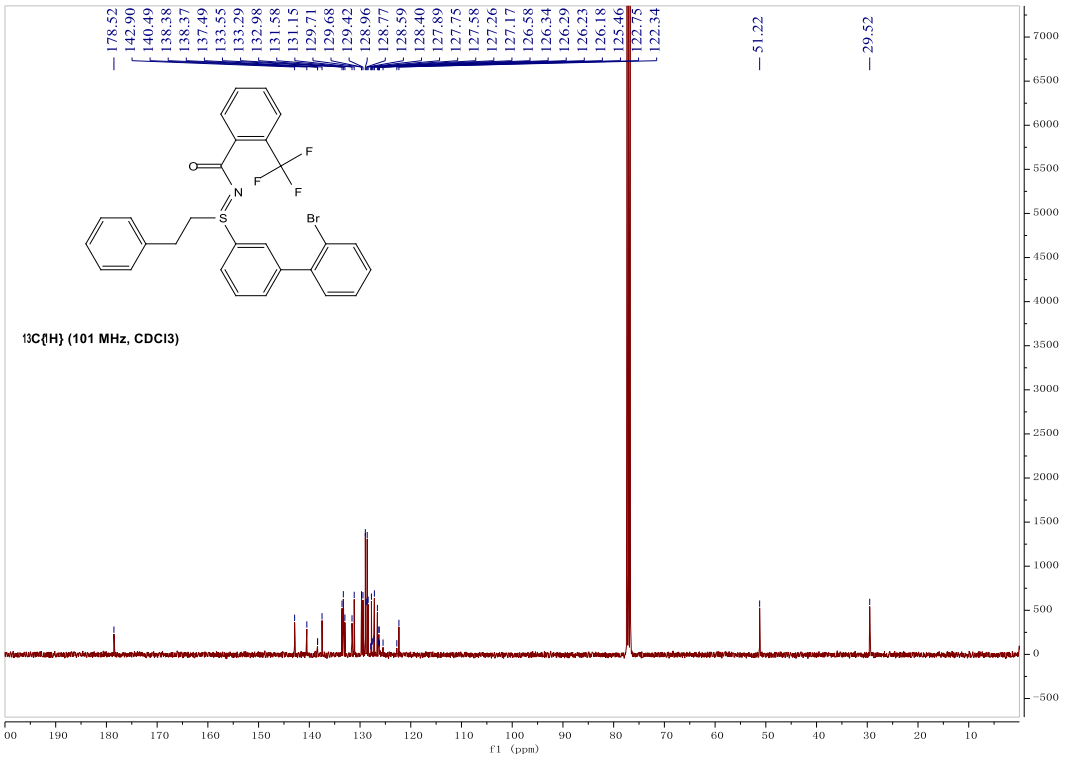
2-bromo-N-((2'-bromo-[1,1'-biphenyl]-3-yl)(phenethyl)-l4-sulfaneylidene)benzamide (3ay)

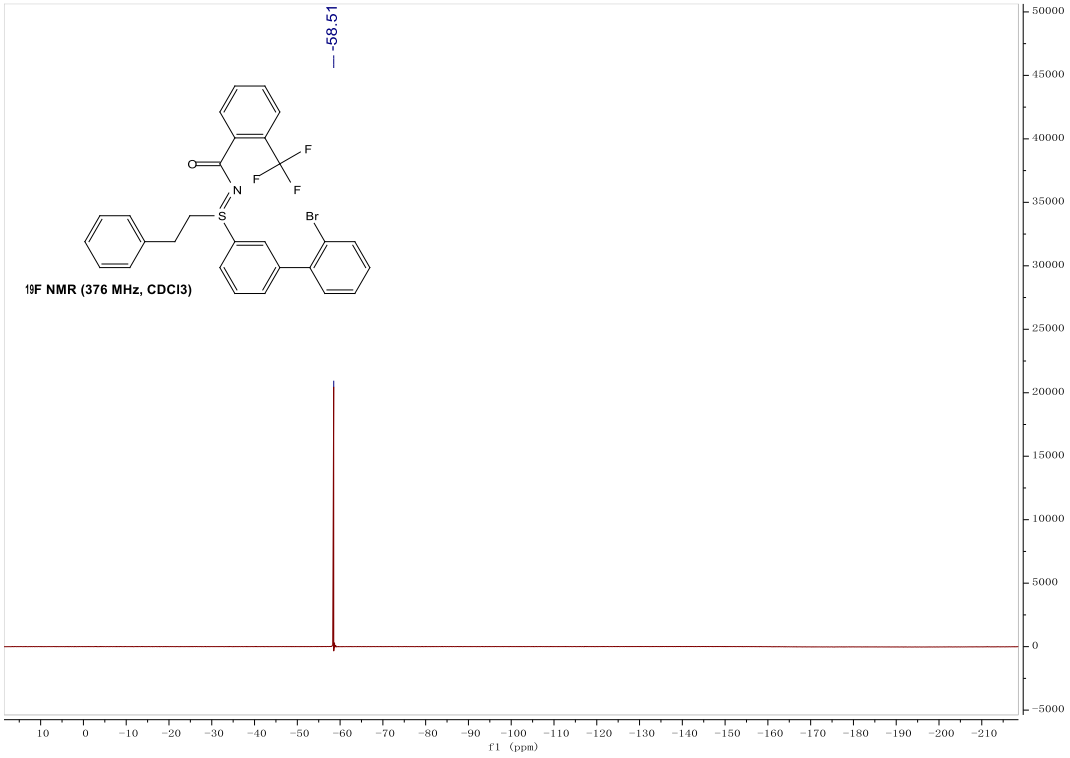




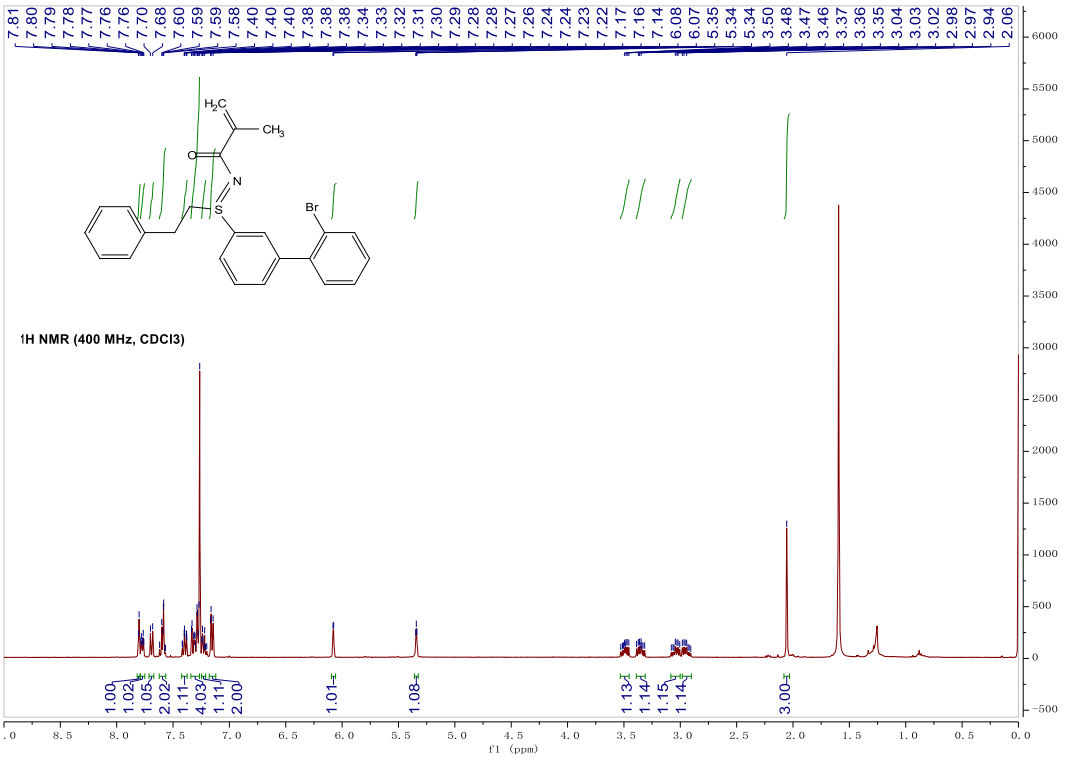
N-((2'-bromo-[1,1'-biphenyl]-3-yl)(phenethyl)-l4-sulfaneylidene)-2-(trifluoromethyl)benzamide (3az)

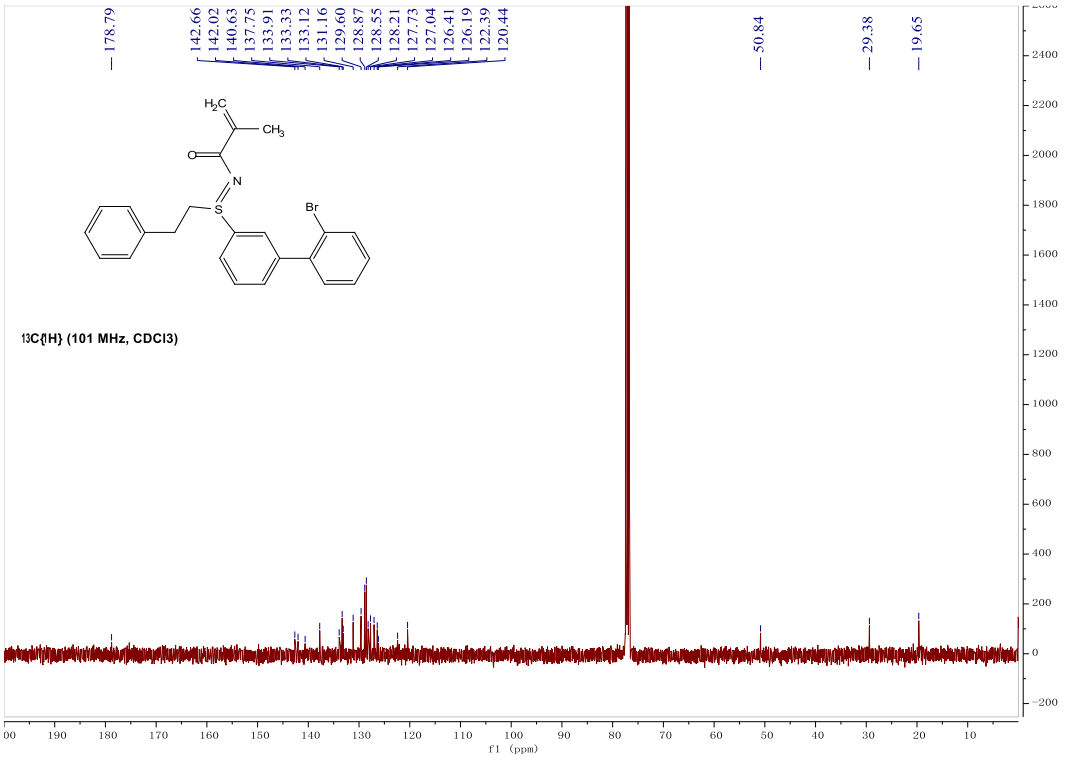




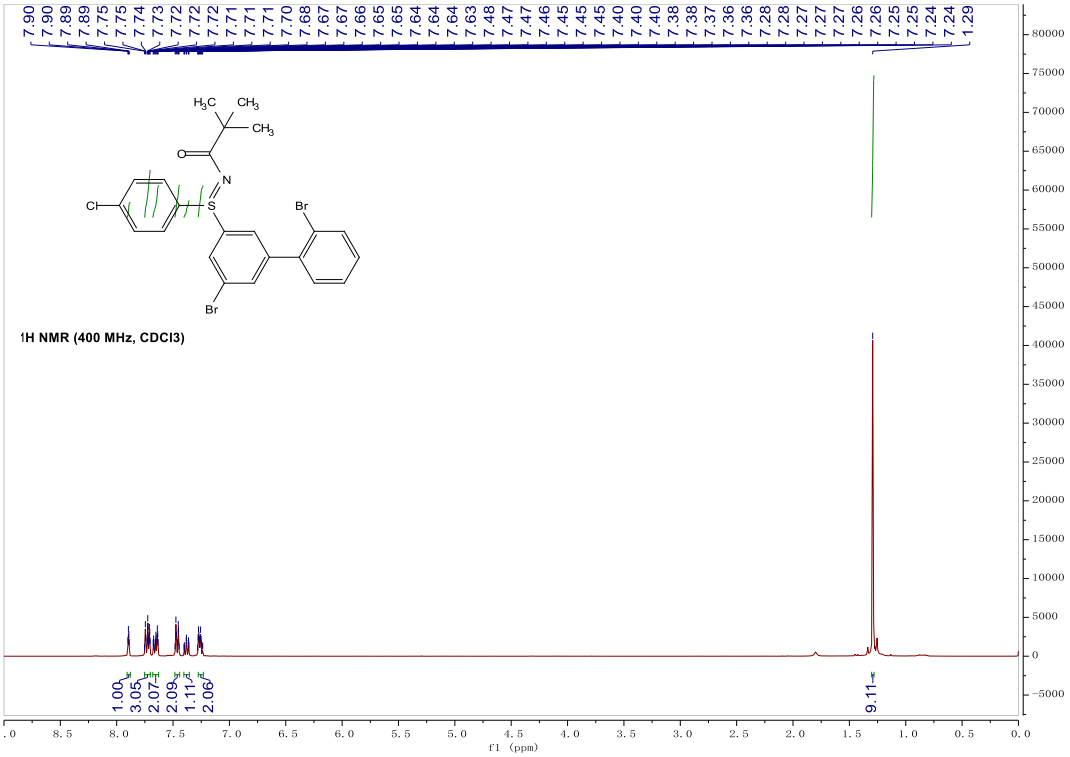


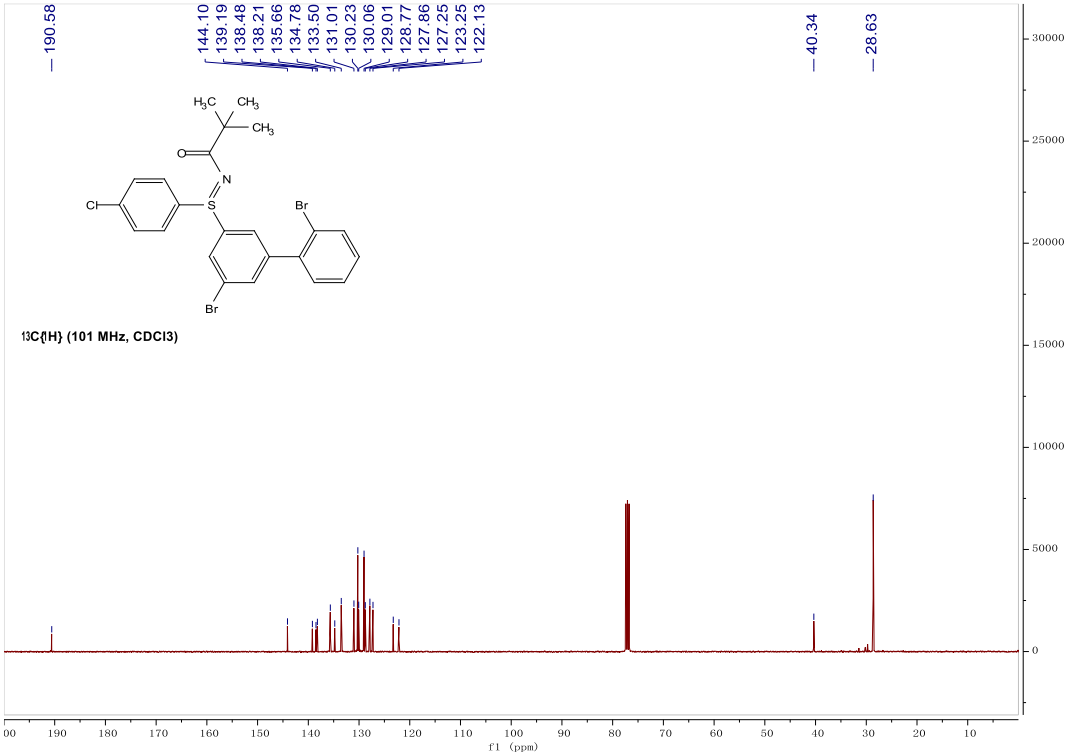
N-((2'-bromo-[1,1'-biphenyl]-3-yl)(phenethyl)-l4-sulfaneylidene)methacrylamide (3aa')



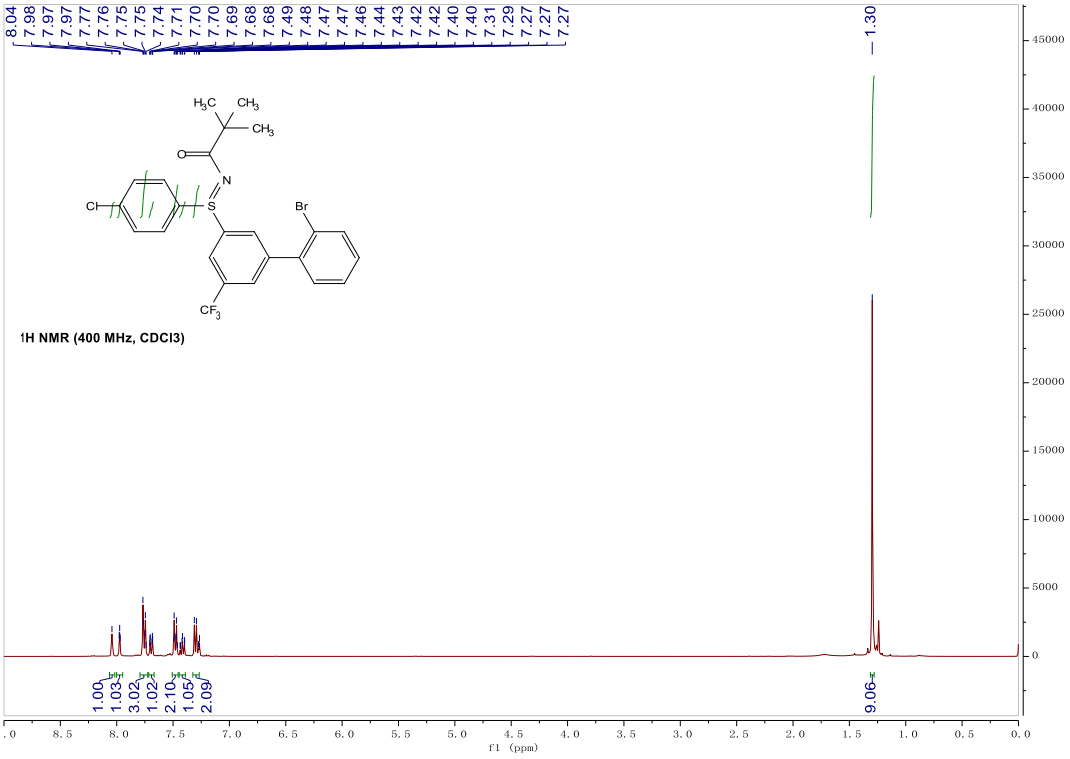


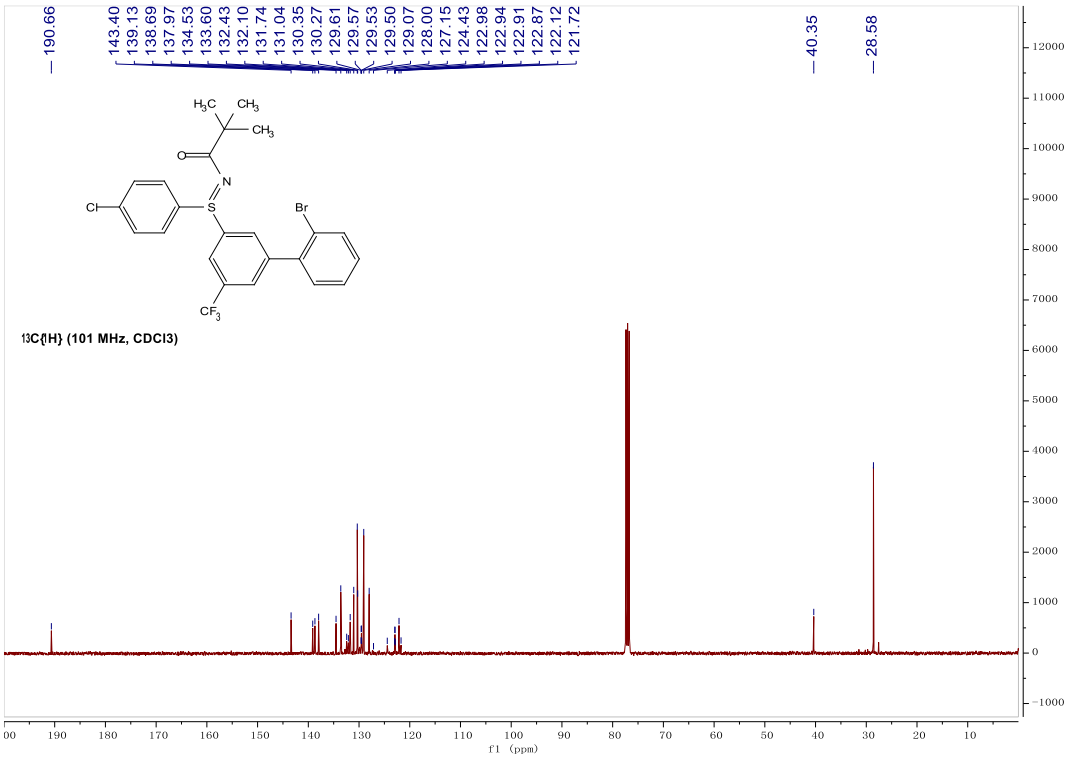
N-((4-chlorophenyl)(2',5'-dibromo-[1,1'-biphenyl]-3-yl)-l4-sulfaneylidene)pivalamide (3ba)





N-((2'-bromo-5'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)pivalamide (3ca)

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122.12
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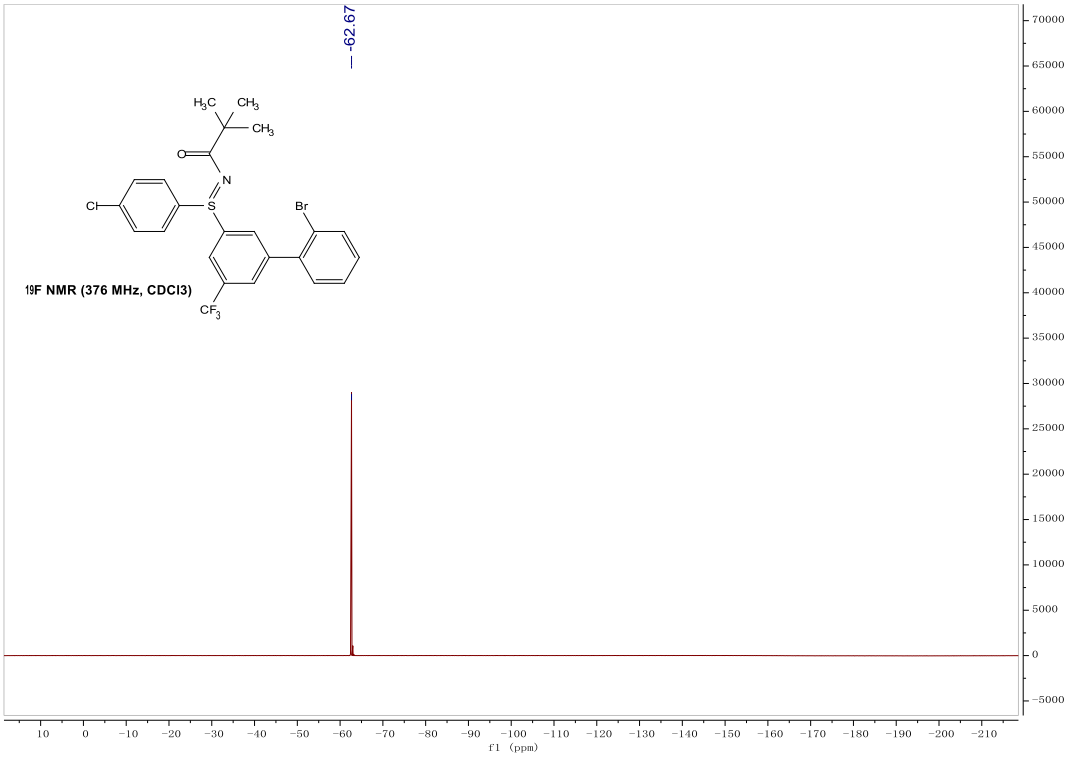
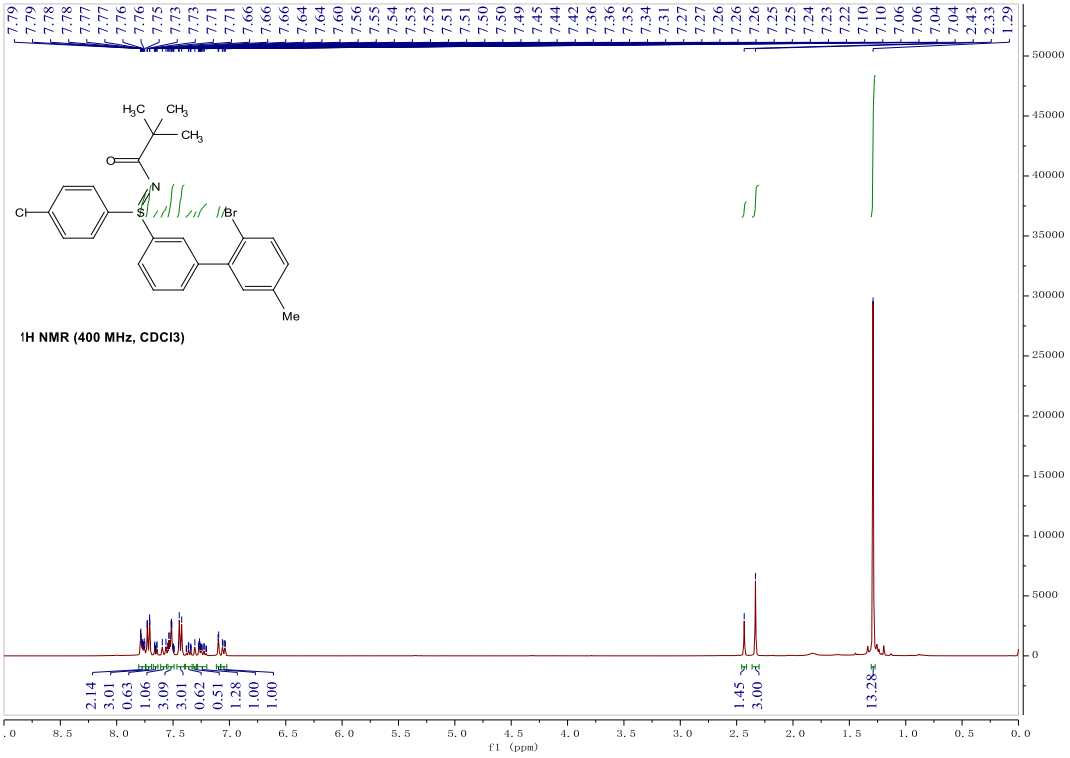
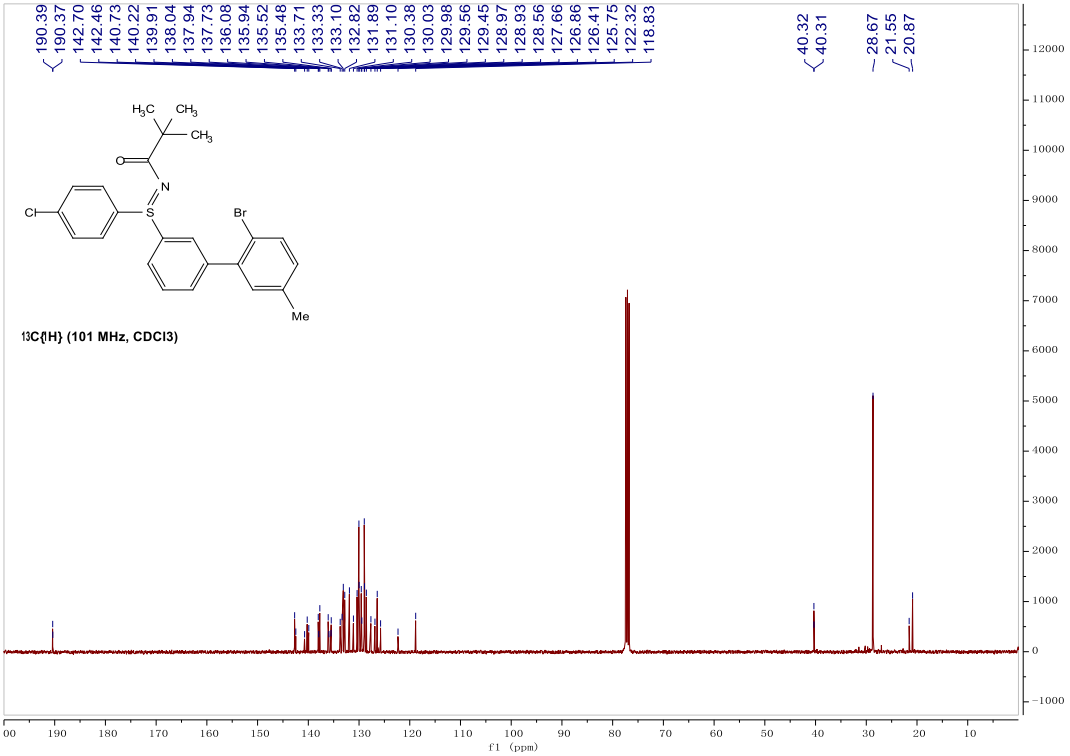
f1 (ppm)

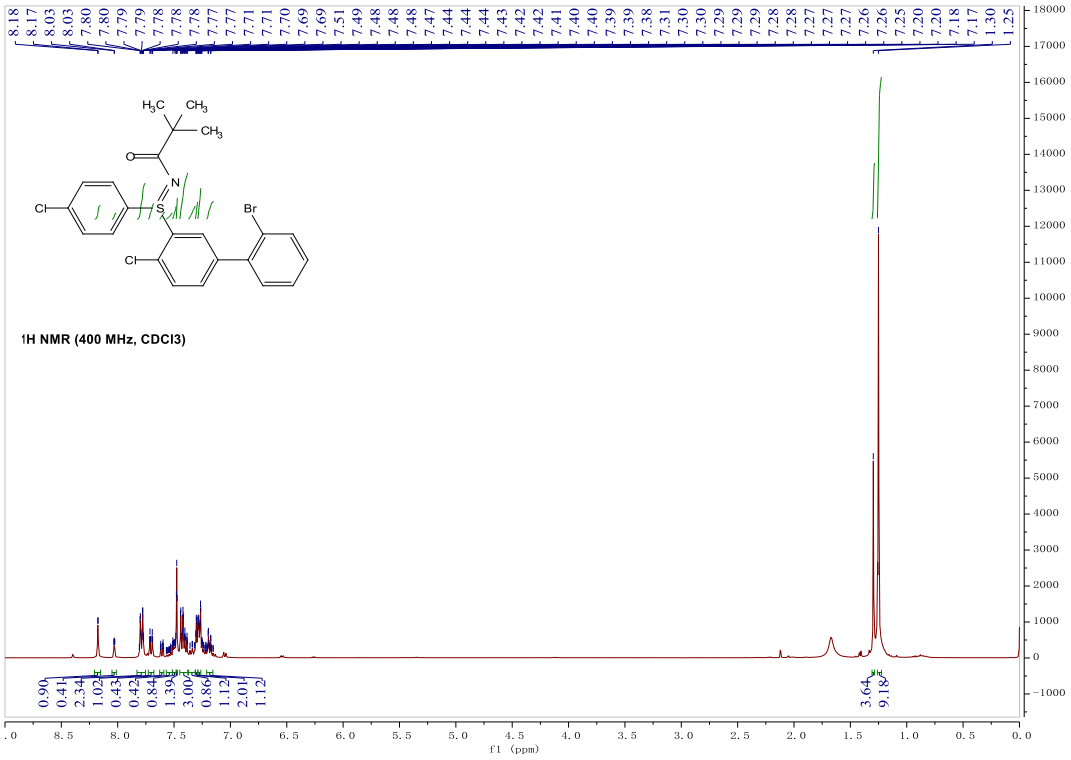

-62.67
19F NMR (376 MHz, CDCl3)
f1 (ppm)

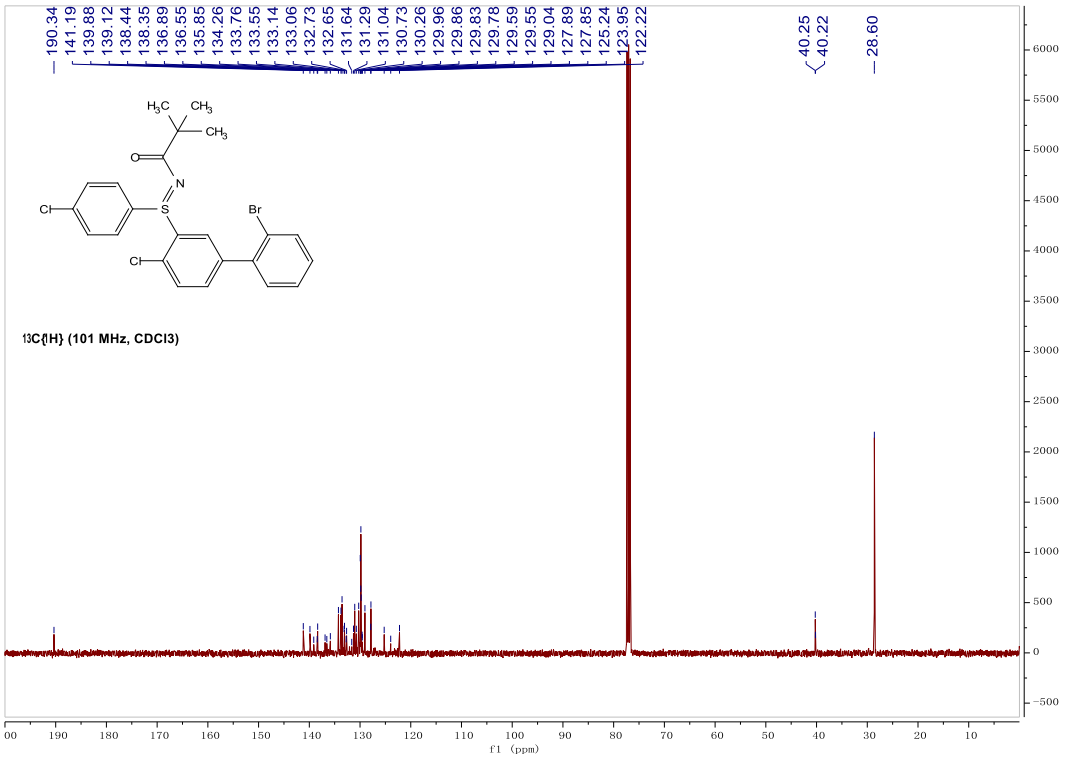
N-((2'-bromo-5'-methyl-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)pivalamide (3da)



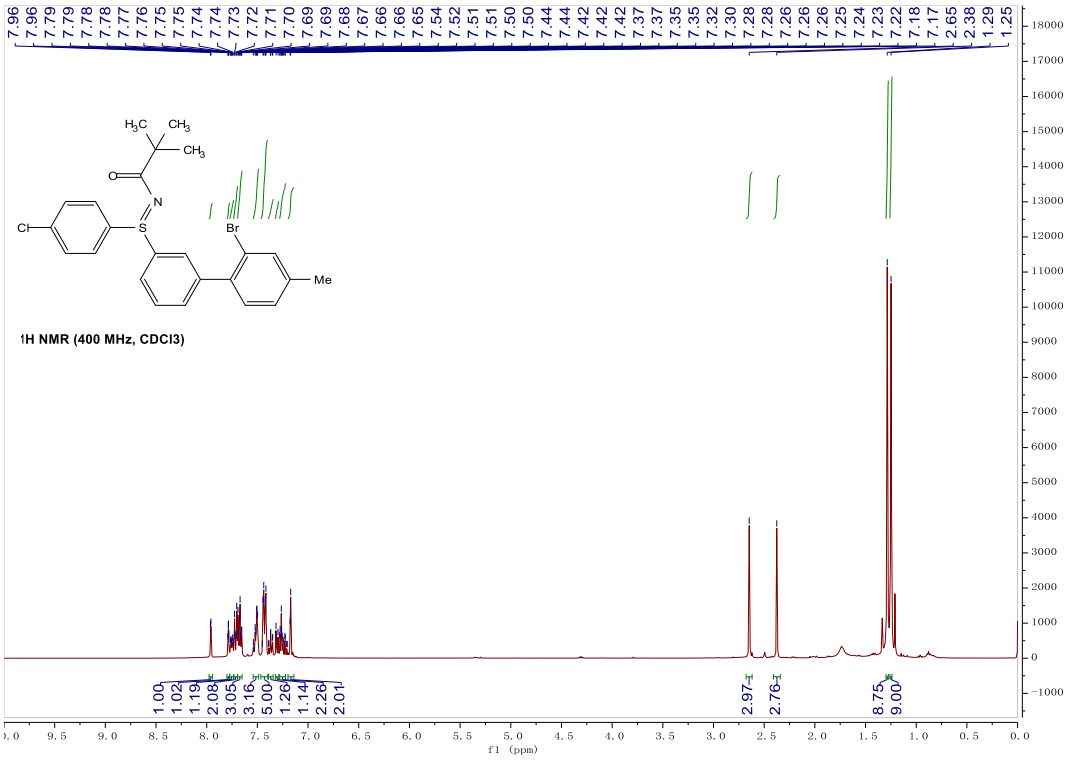


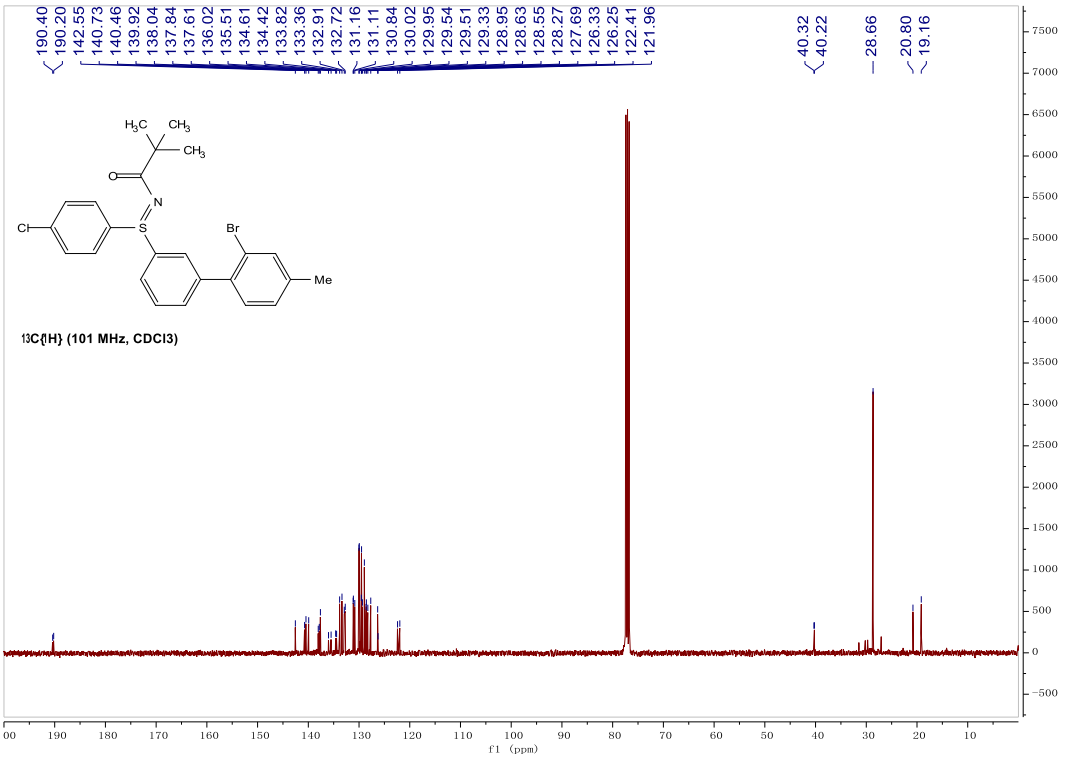
N-((2'-bromo-4'-chloro-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)pivalamide (3ea)



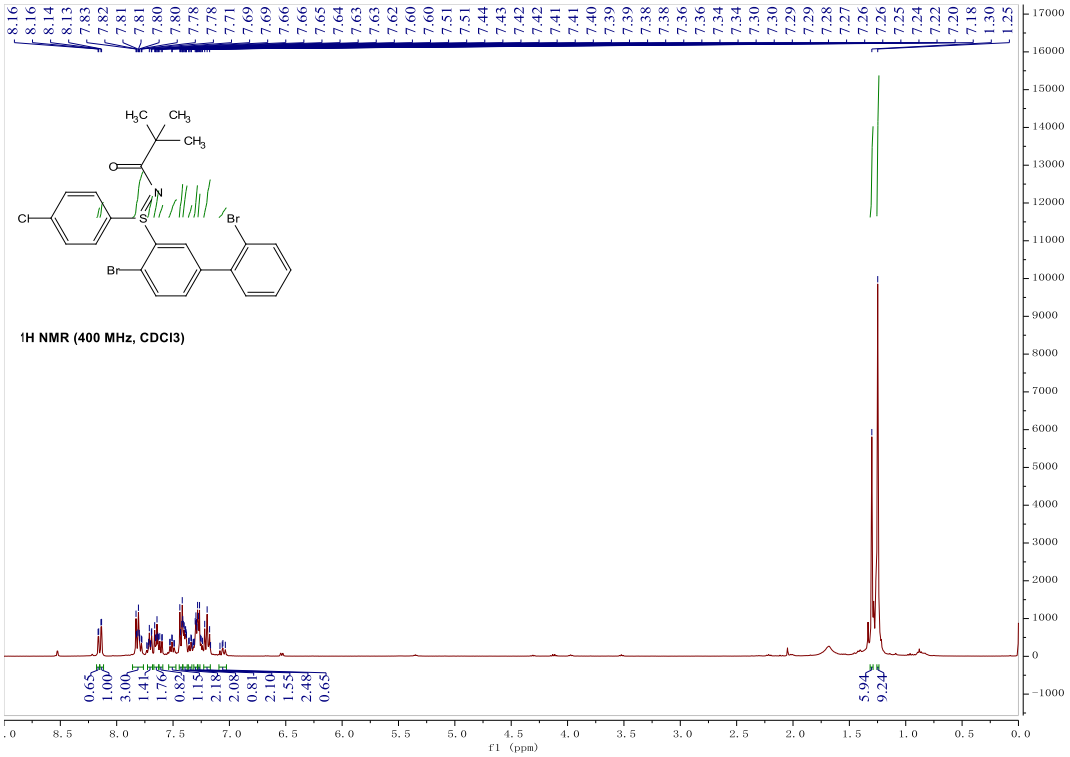


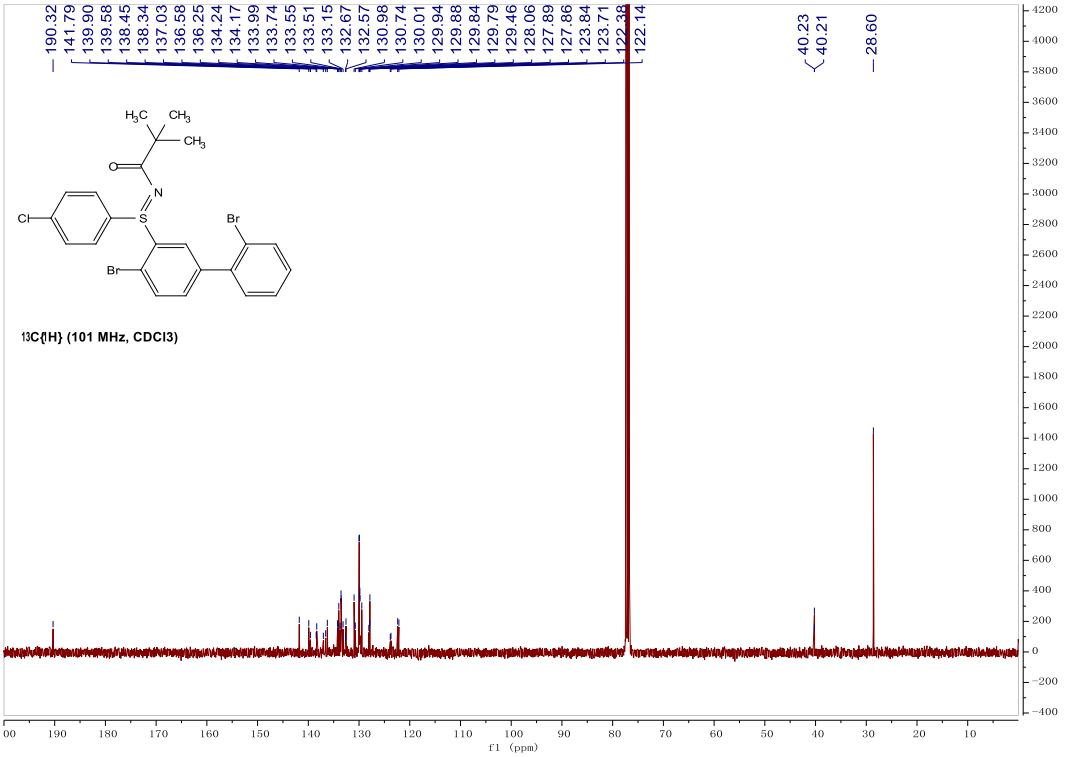
N-((2'-bromo-4'-methyl-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)pivalamide (3fa)



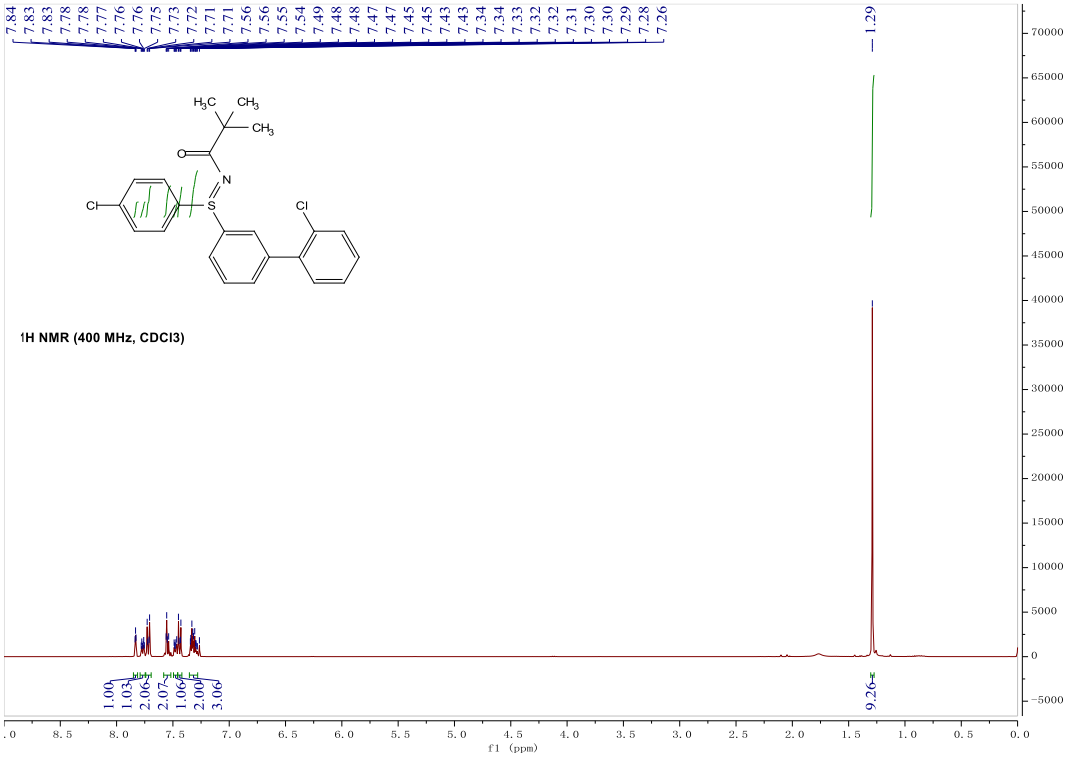


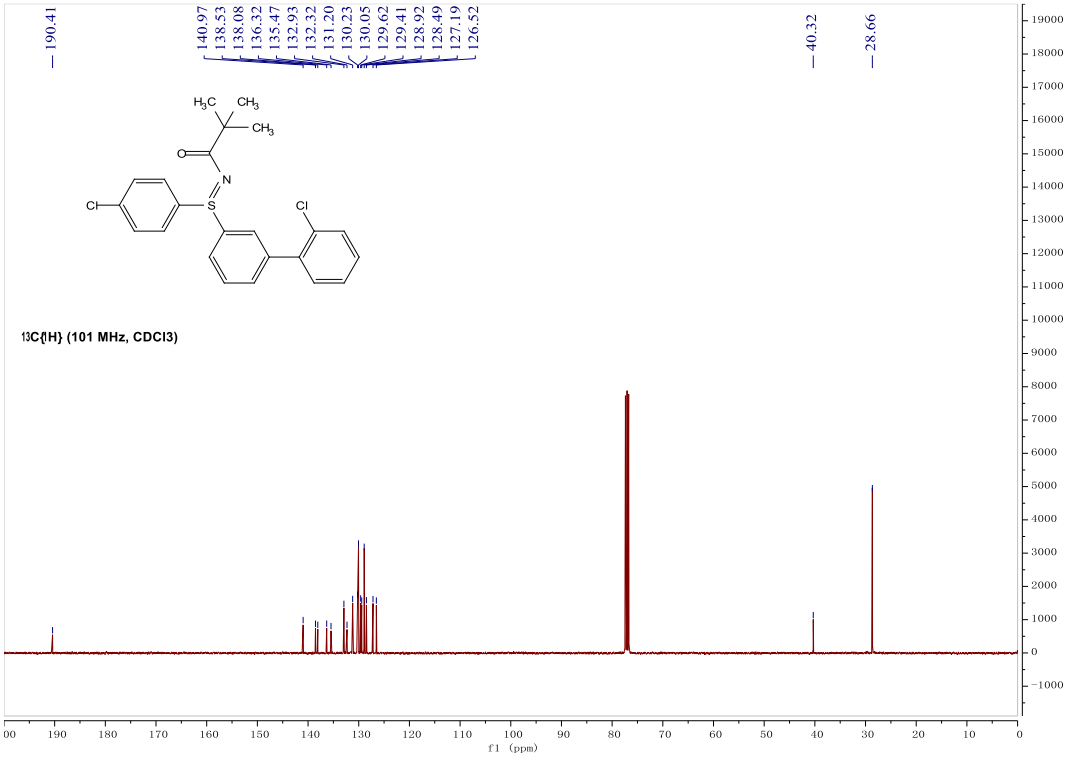
N-((4-chlorophenyl)(2',4'-dibromo-[1,1'-biphenyl]-3-yl)-l4-sulfaneylidene)pivalamide (3ga)



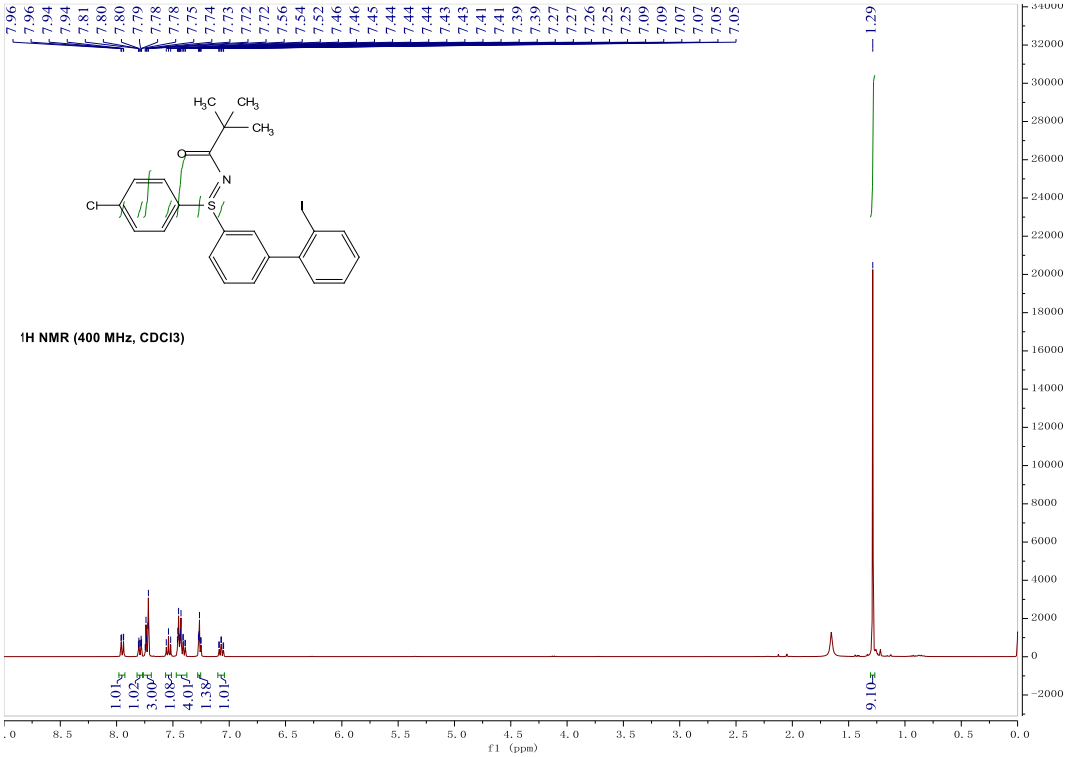


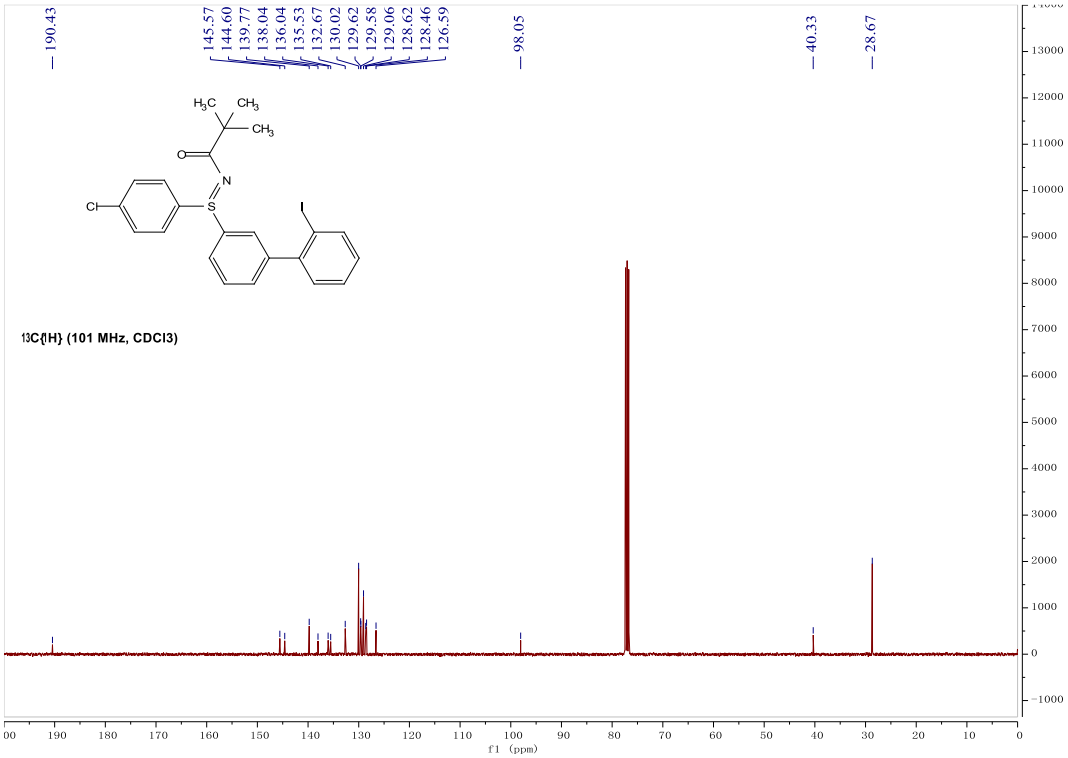
N-((2'-chloro-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)pivalamide (3ha)



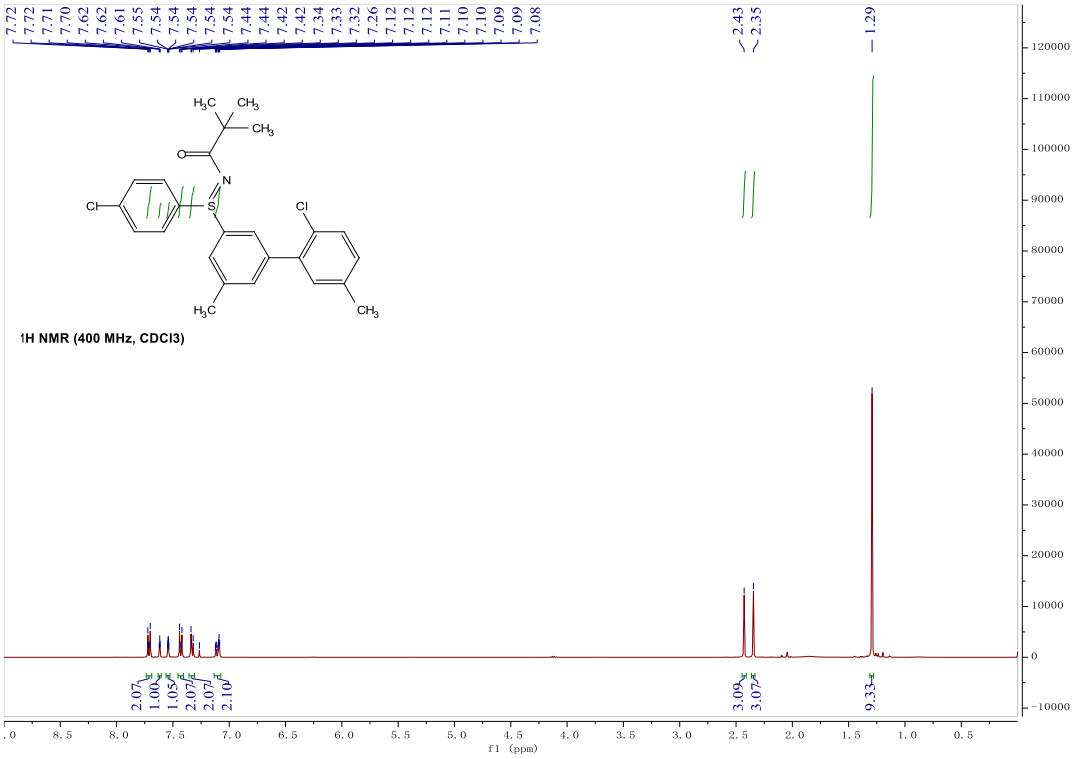


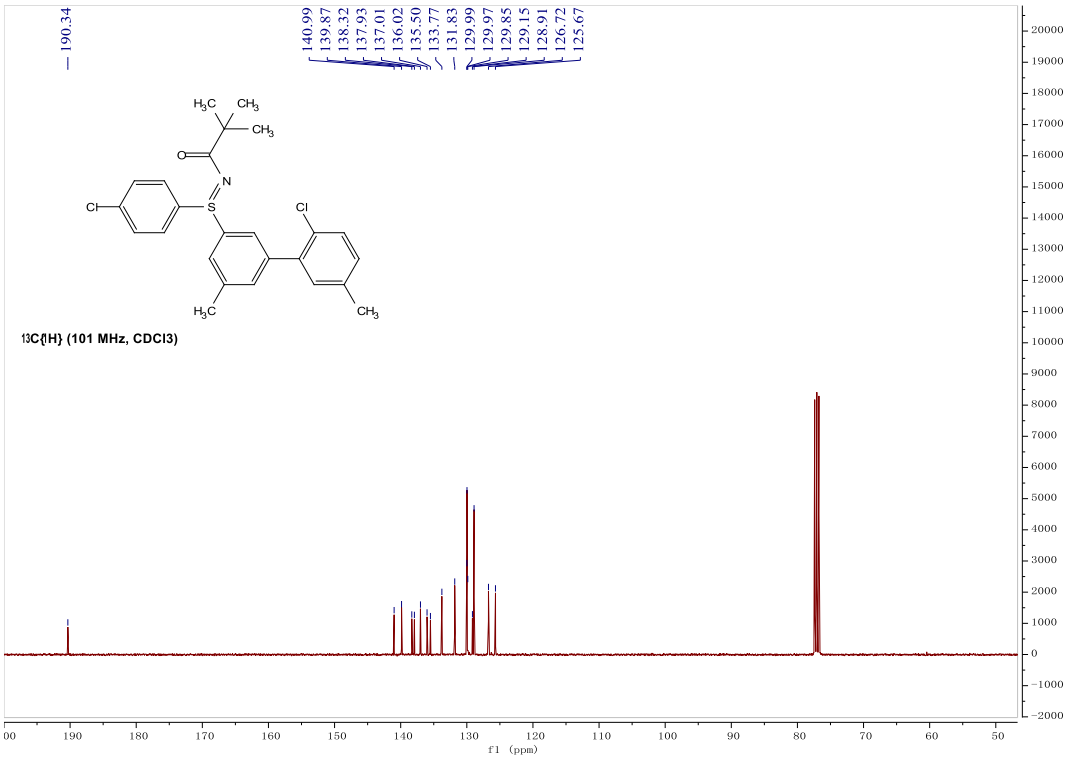
(R,E)-N-((4-chlorophenyl)(2'-iodo-[1,1'-biphenyl]-3-yl)-l4-sulfaneylidene)pivalamide (3ia)



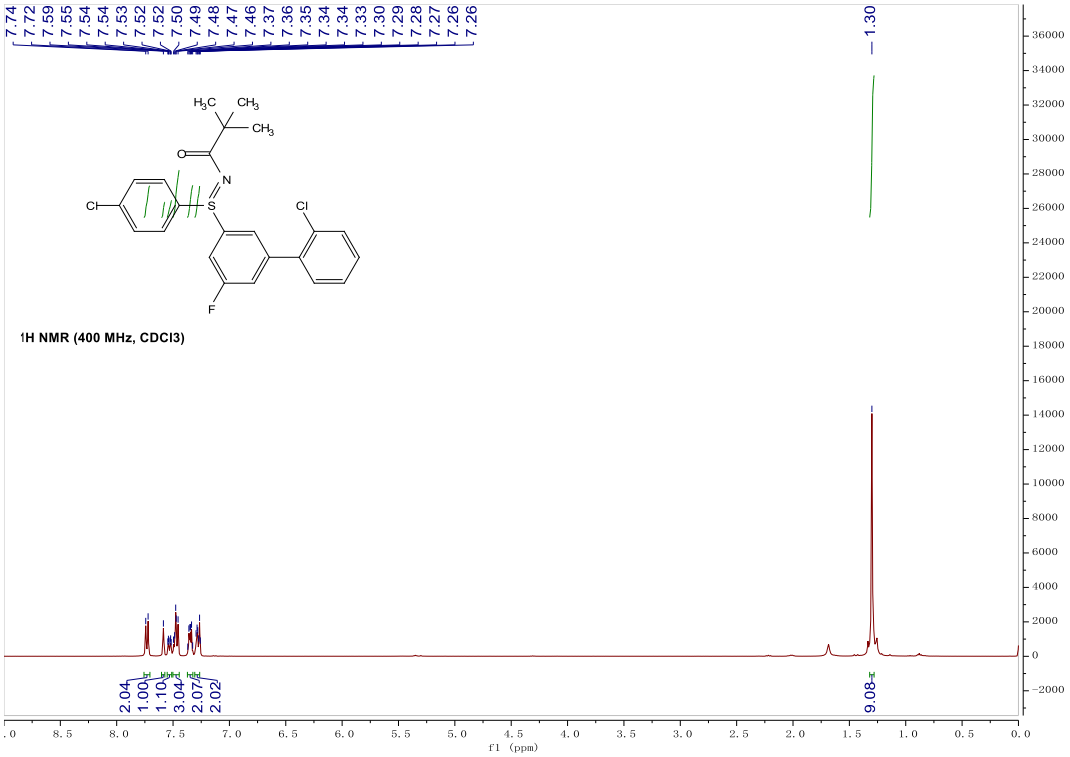


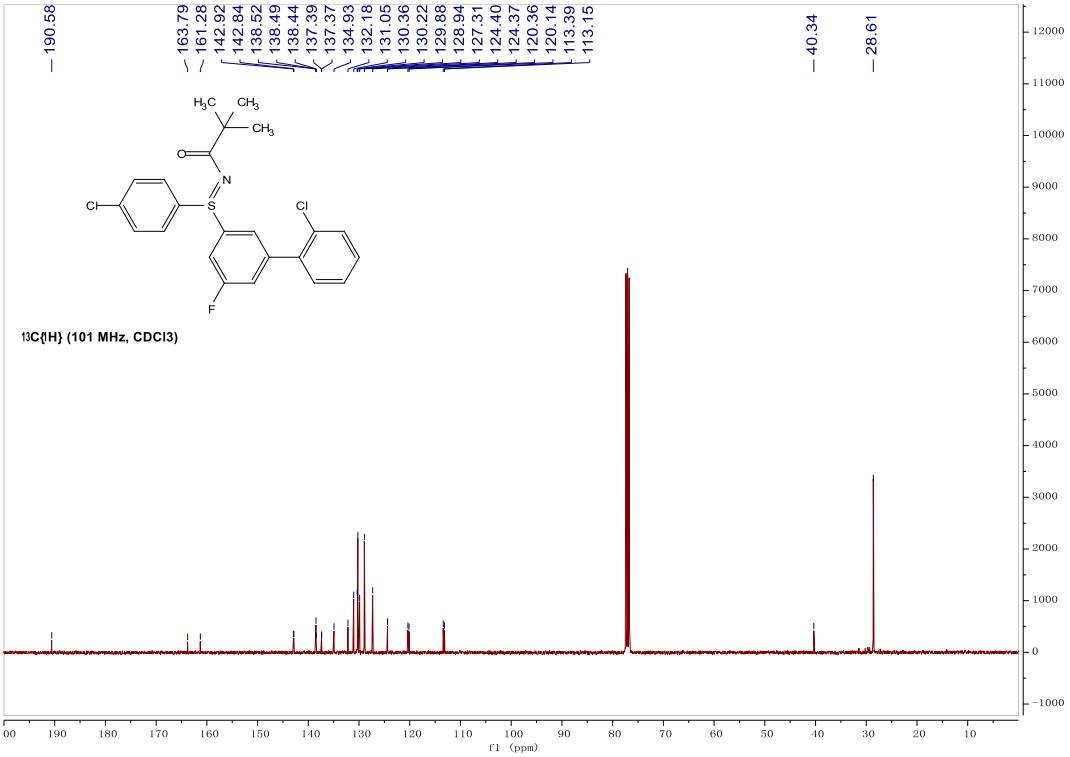
N-((2'-chloro-5,5'-dimethyl-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)pivalamide (3ja)

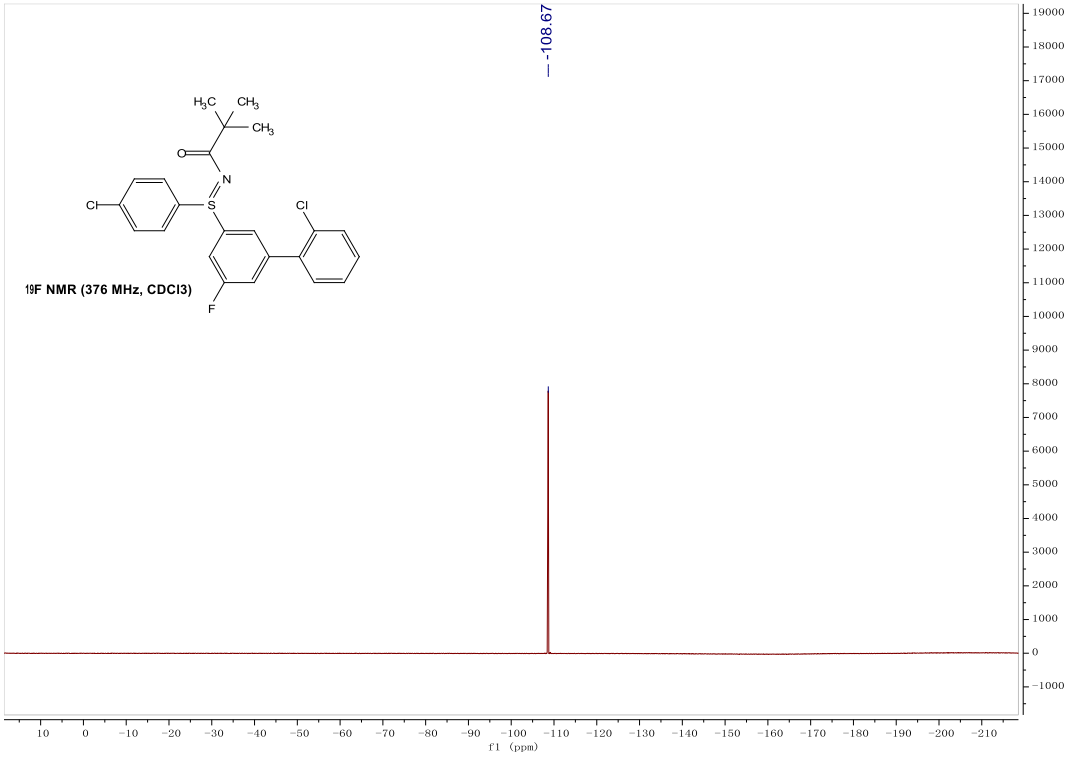




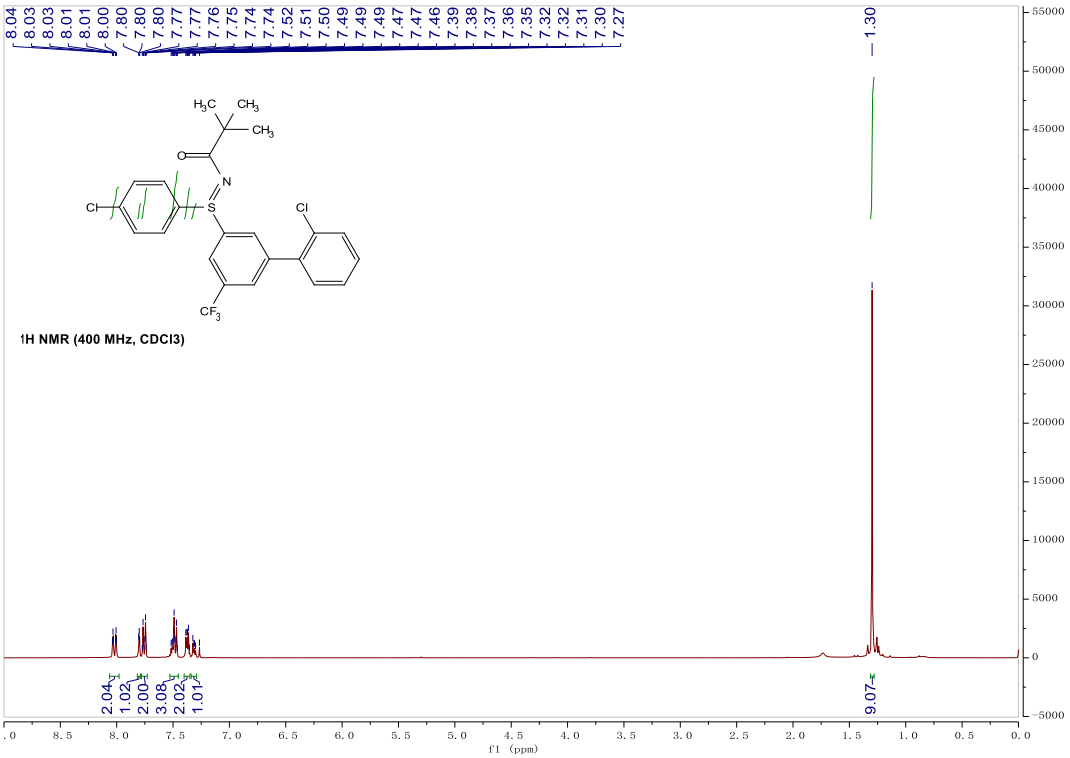
N-((2'-chloro-5'-fluoro-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)pivalamide (3ka)

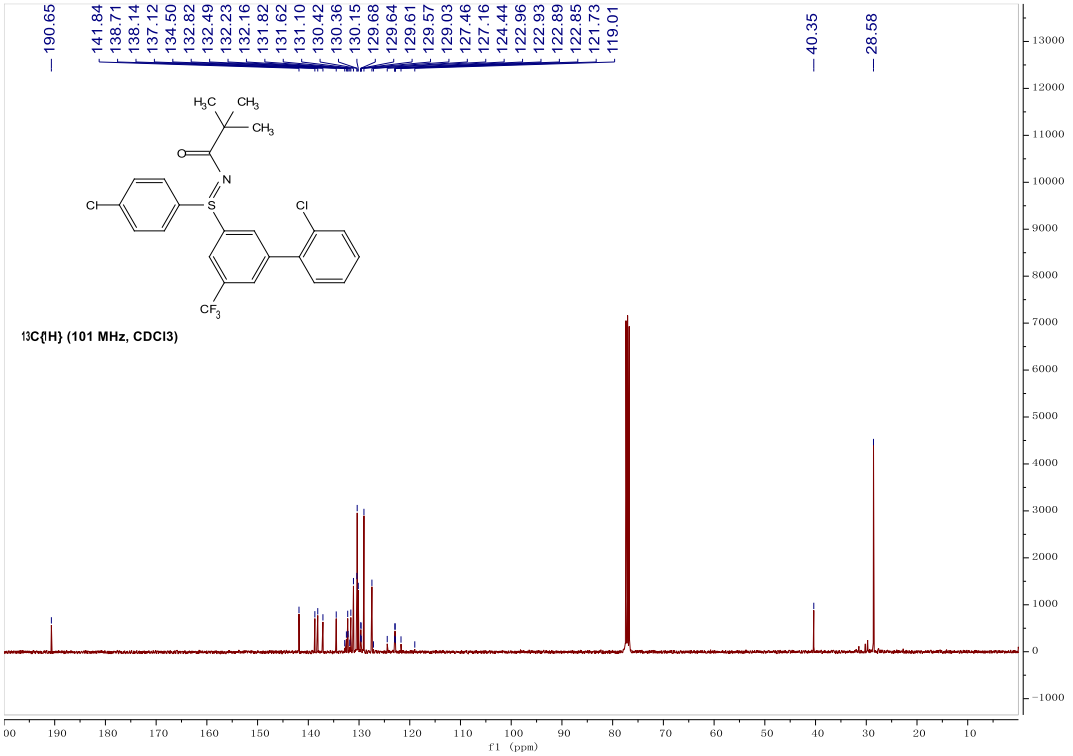


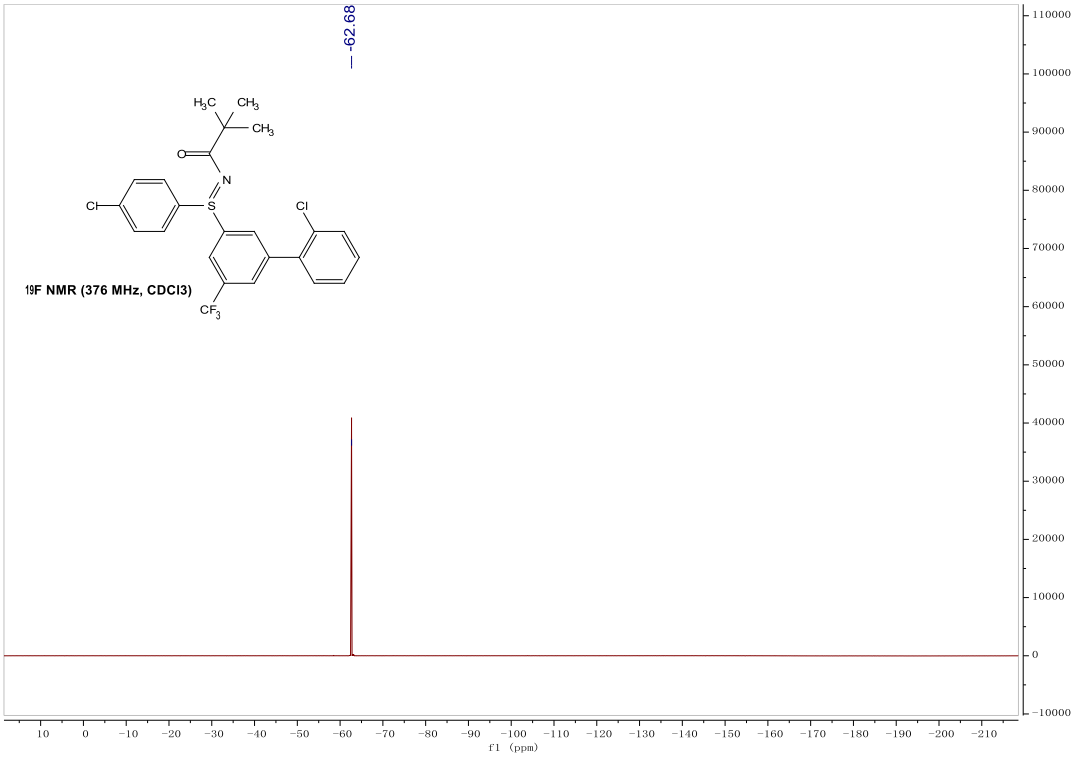




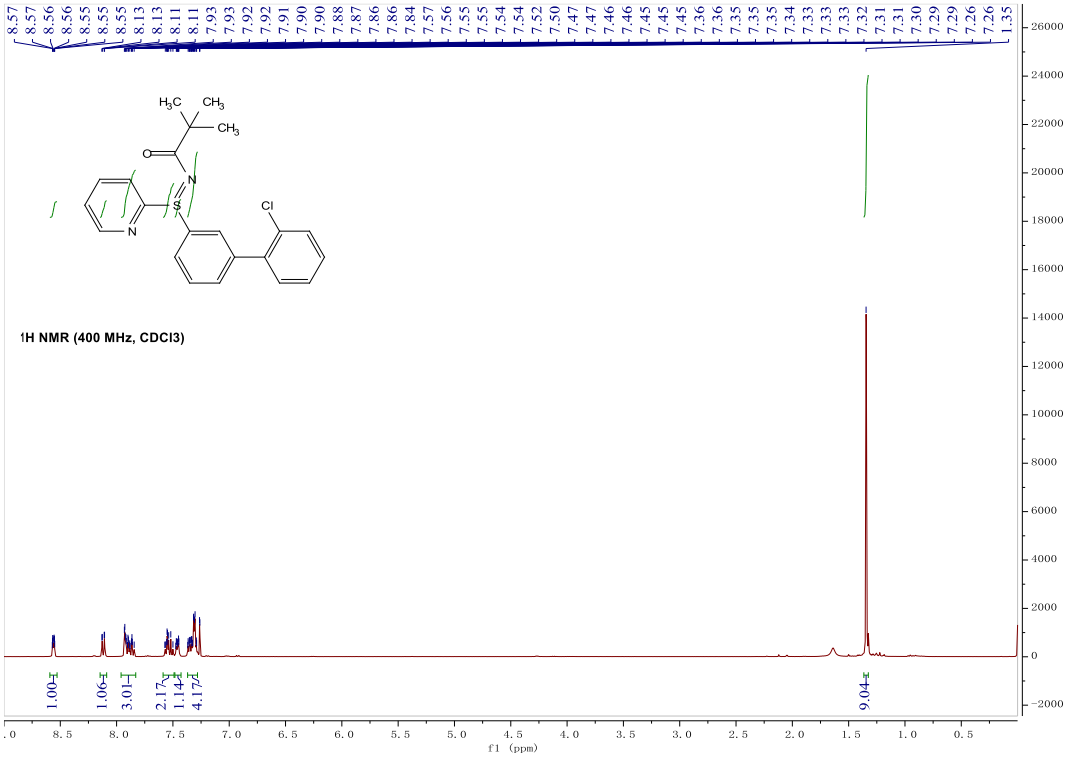
N-((2'-chloro-5'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene) pivalamide (3la)

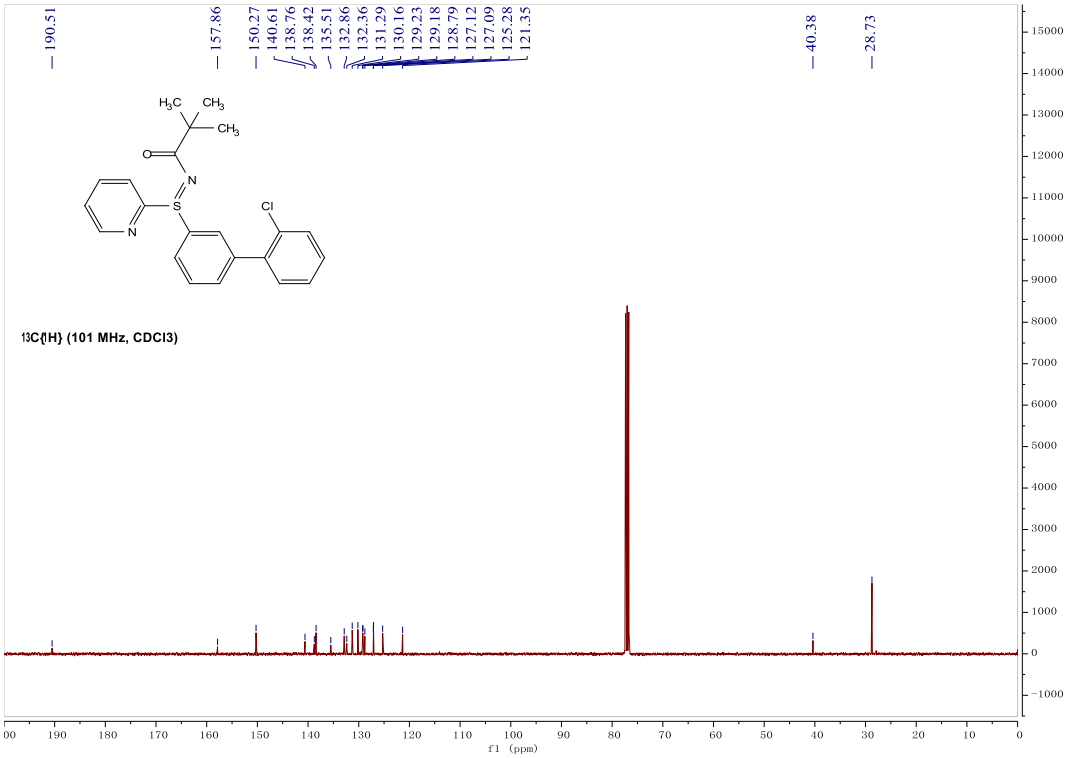



190.65
141.84
138.71
138.14
137.12
134.50
132.82
132.49
132.23
132.16
131.82
131.62
131.10
130.42
130.36
130.15
129.68
129.64
129.61
129.57
129.03
127.46
127.16
124.44
122.96
122.93
122.89
122.85
121.73
119.01
40.35
28.58
13C{1H} (101 MHz, CDCl3)
f1 (ppm)

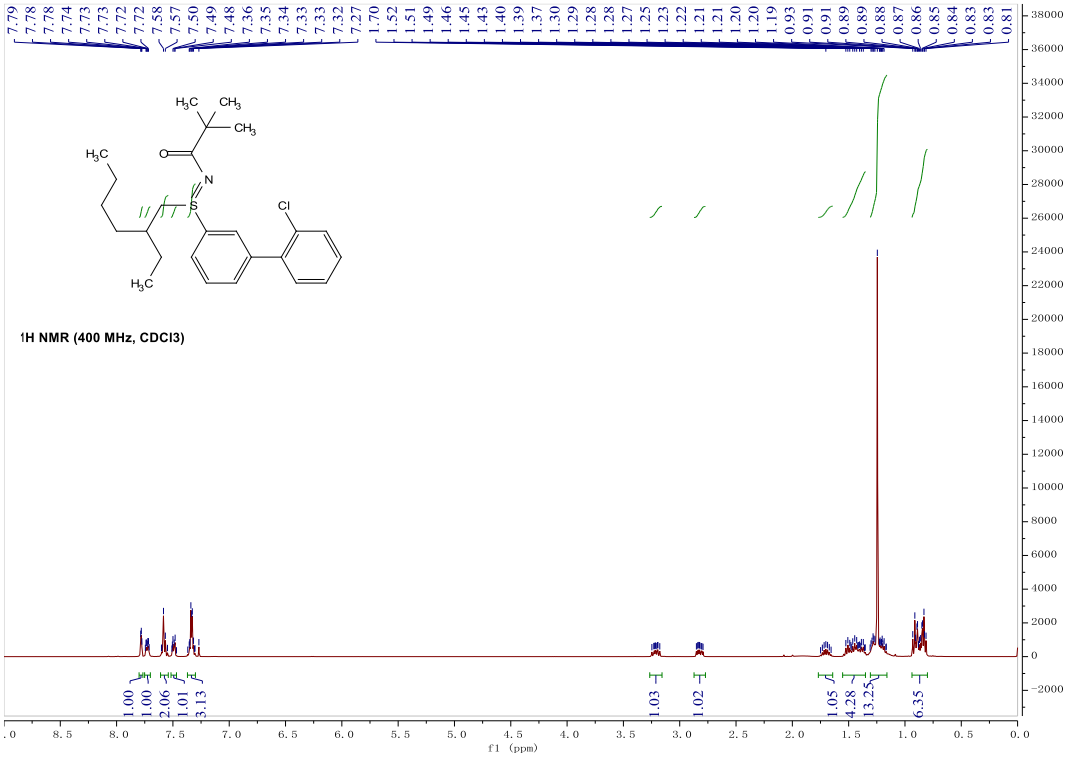

-62.68
19F NMR (376 MHz, CDCl3)
f1 (ppm)

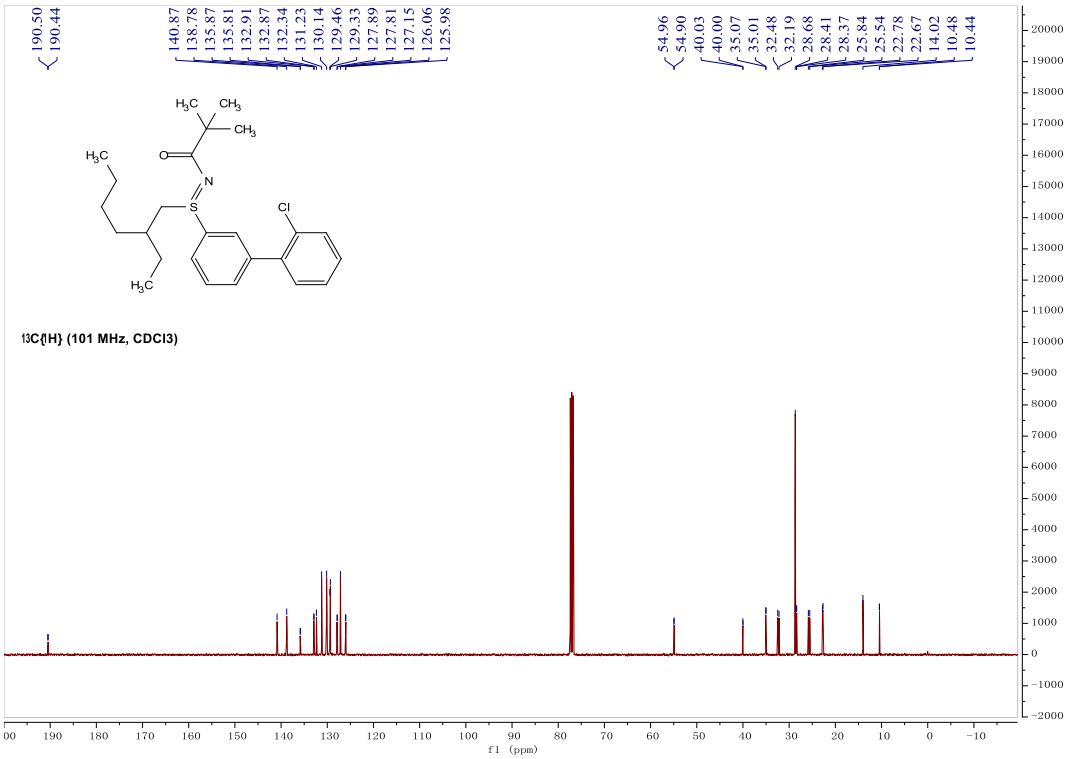
(S,Z)-N-((2'-chloro-[1,1'-biphenyl]-3-yl)(pyridin-2-yl)-l4-sulfaneylidene)pivalamide(3ma)



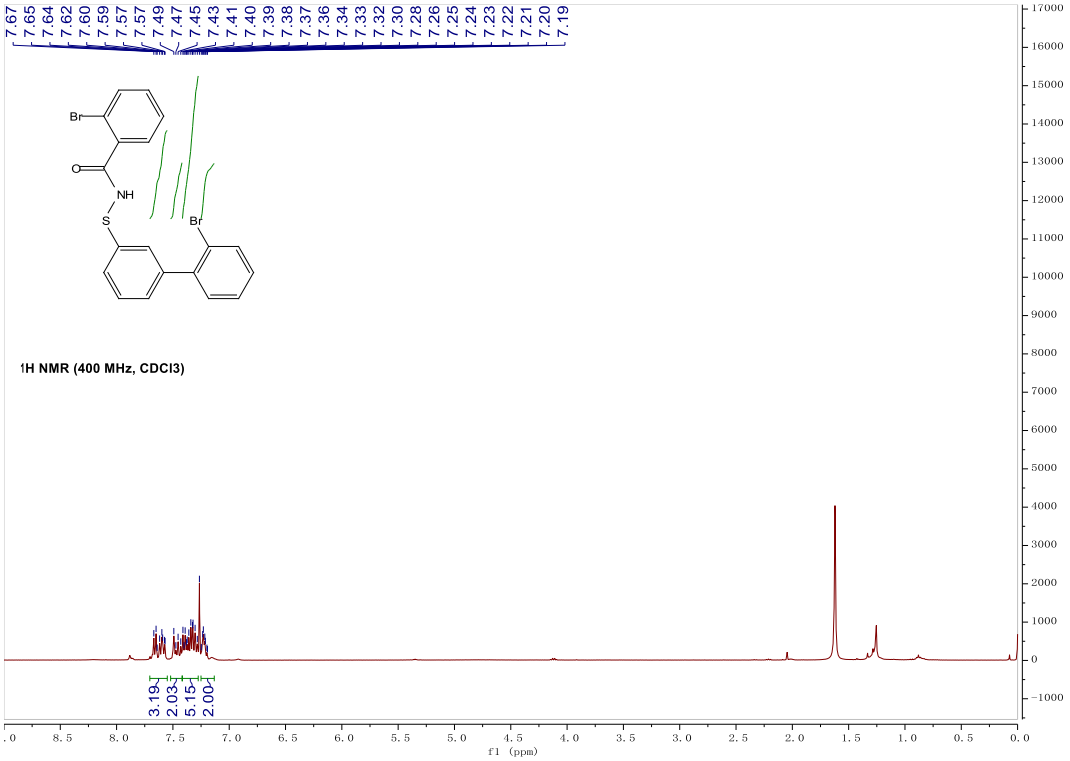


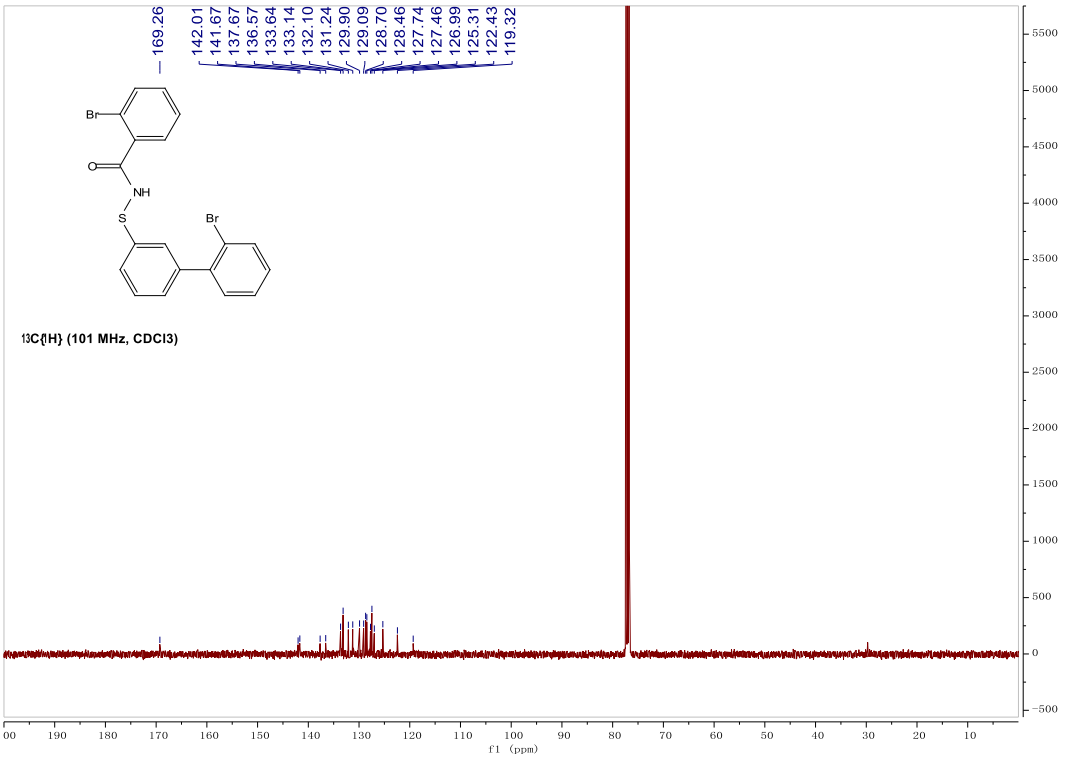
N-((1R,E)-(2'-chloro-[1,1'-biphenyl]-3-yl)(2-ethylhexyl)-l4-sulfaneylidene)pivalamide (3na)



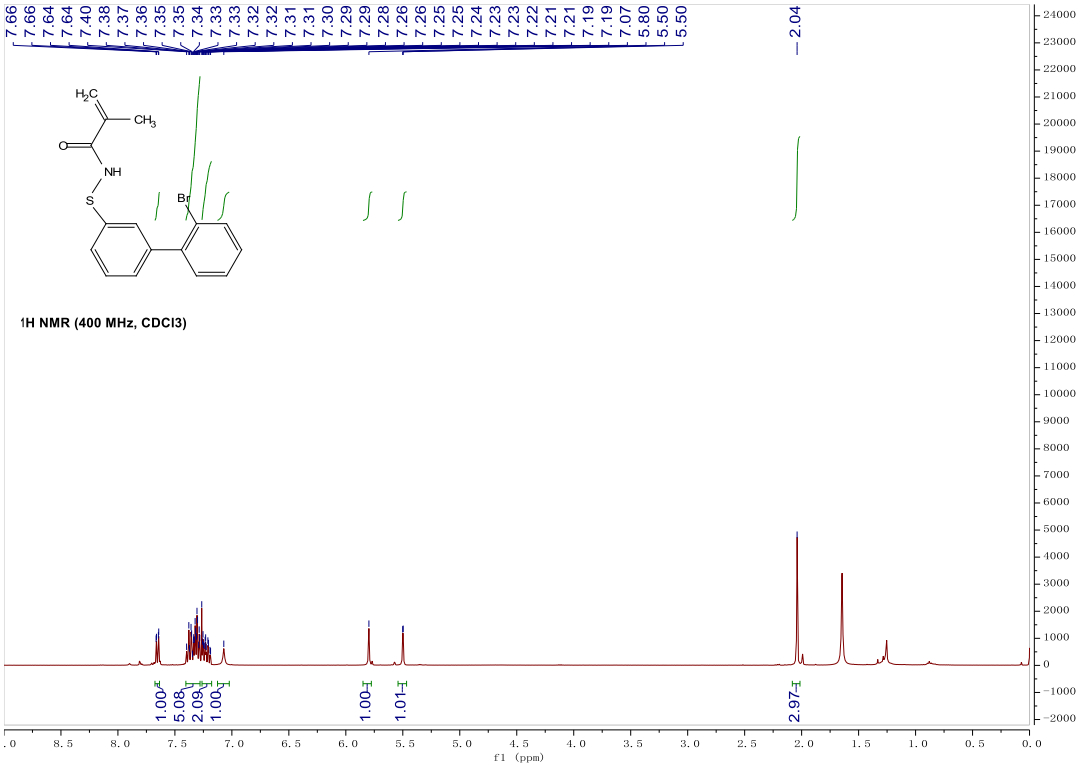


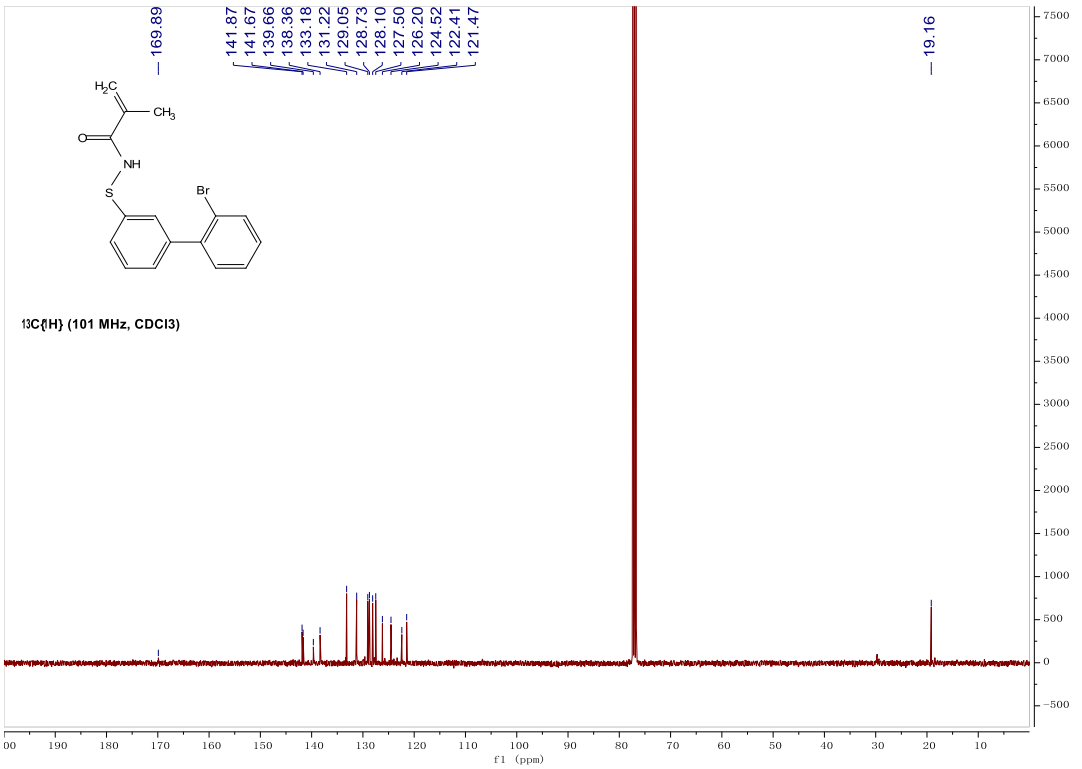
2-bromo-N-((2'-bromo-[1,1'-biphenyl]-3-yl)thio)benzamide (4a)



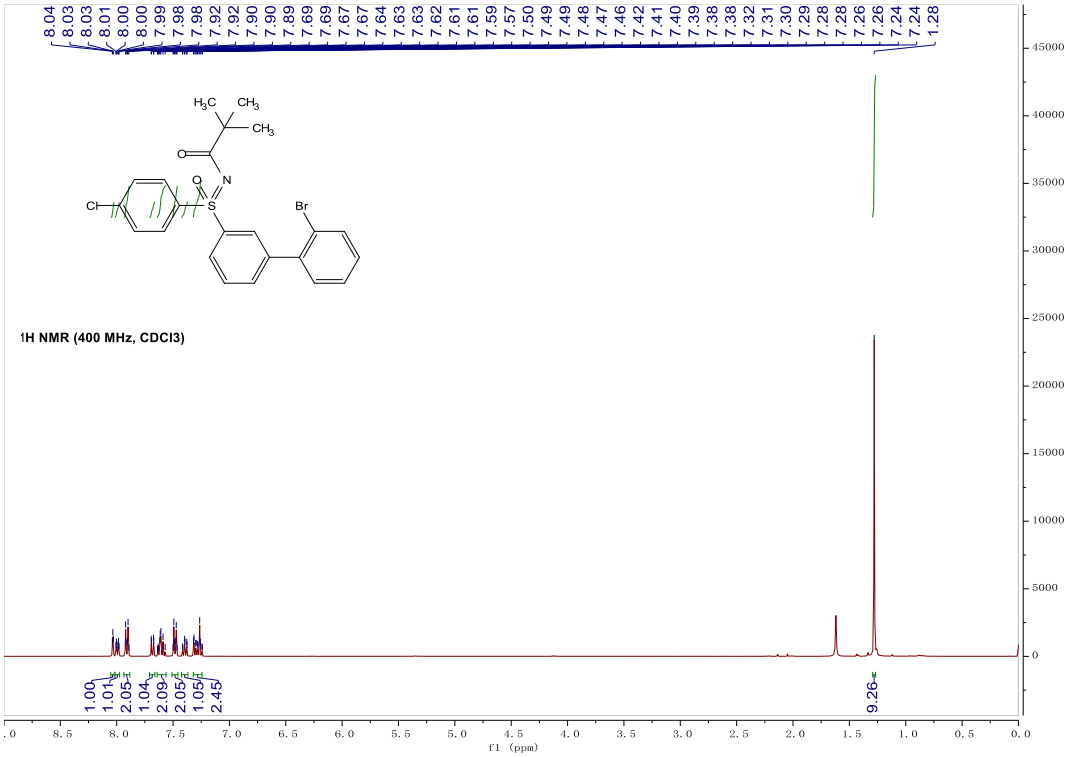


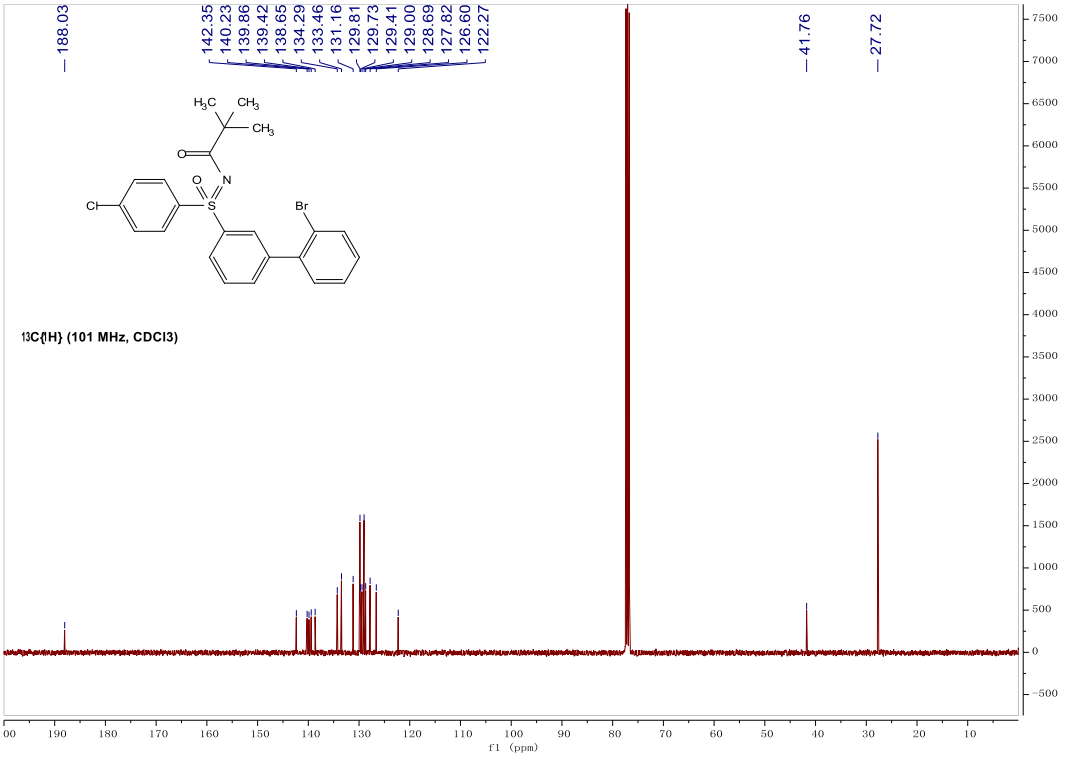
N-((2'-bromo-[1,1'-biphenyl]-3-yl)thio)methacrylamide (4b)



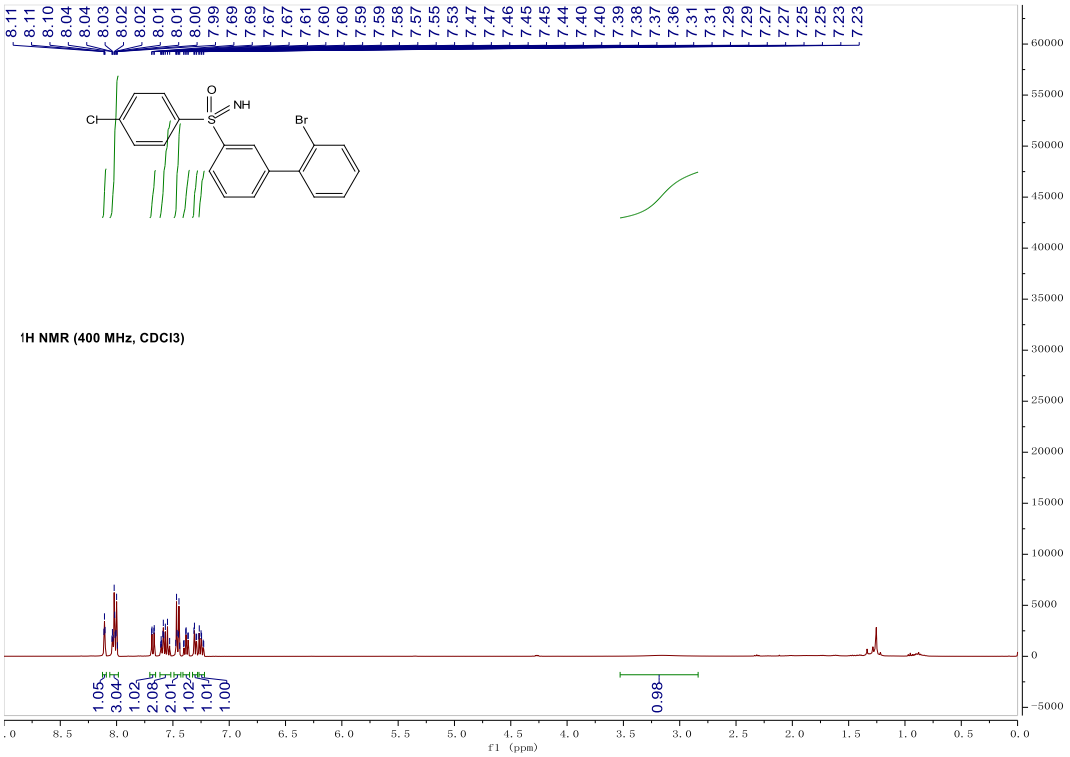


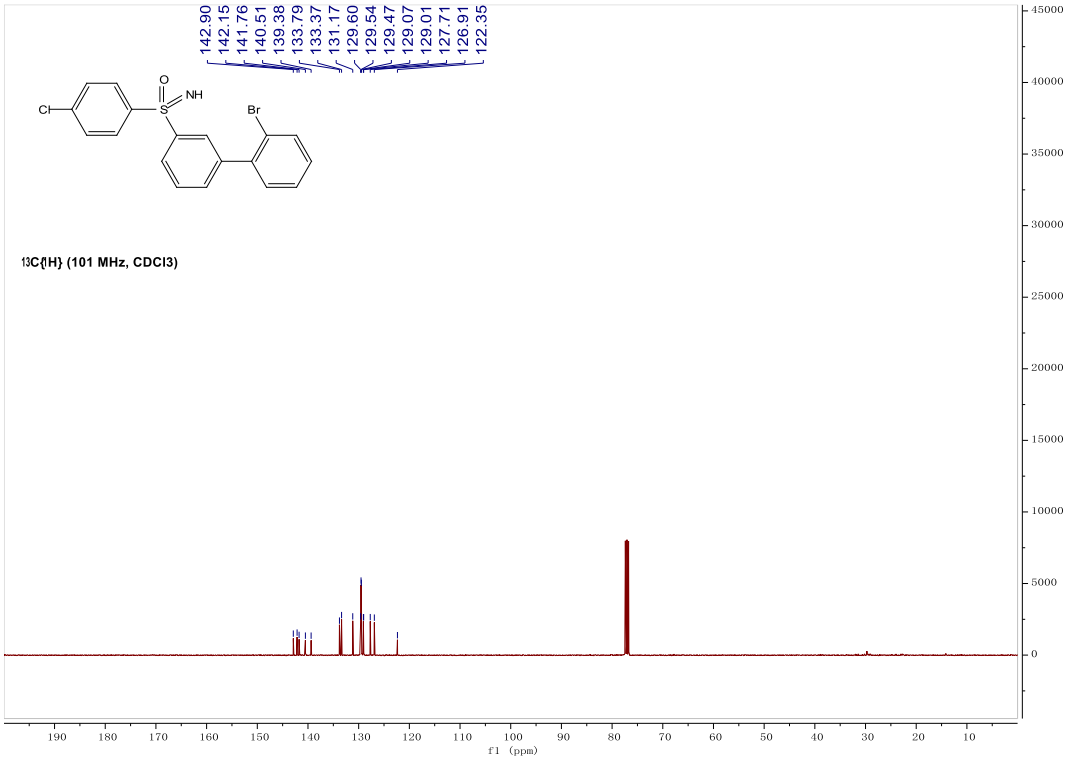
N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)(oxo)-l6-sulfaneylidene)pivalamide (5)



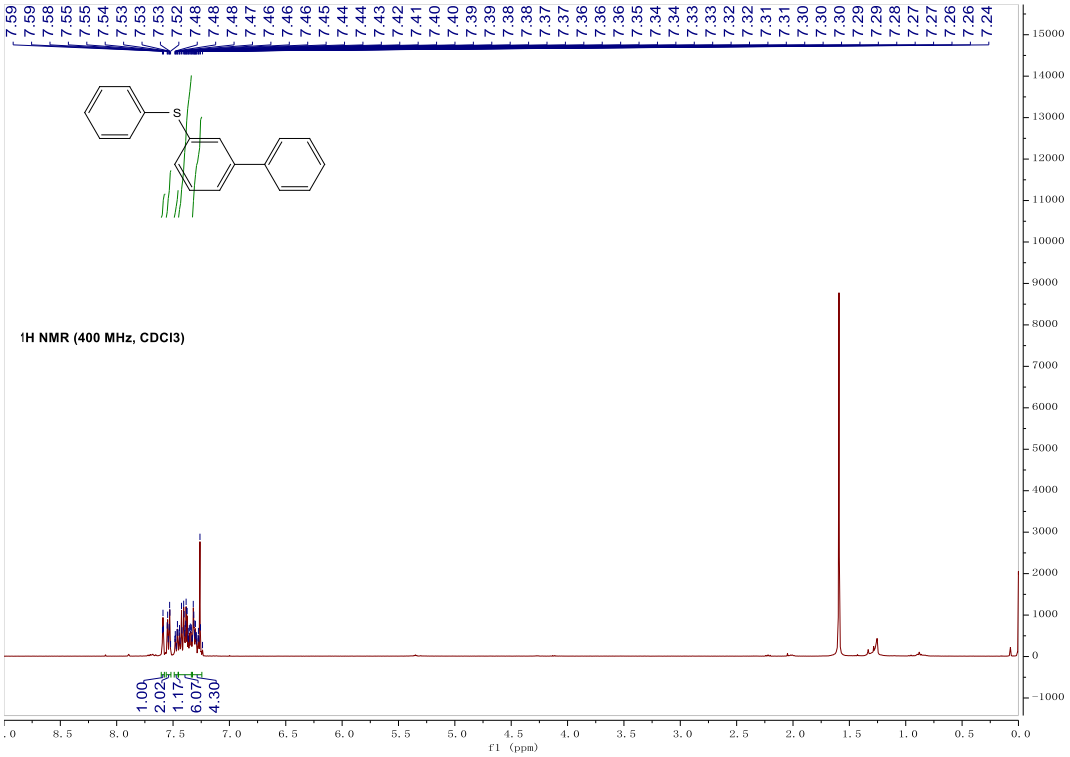


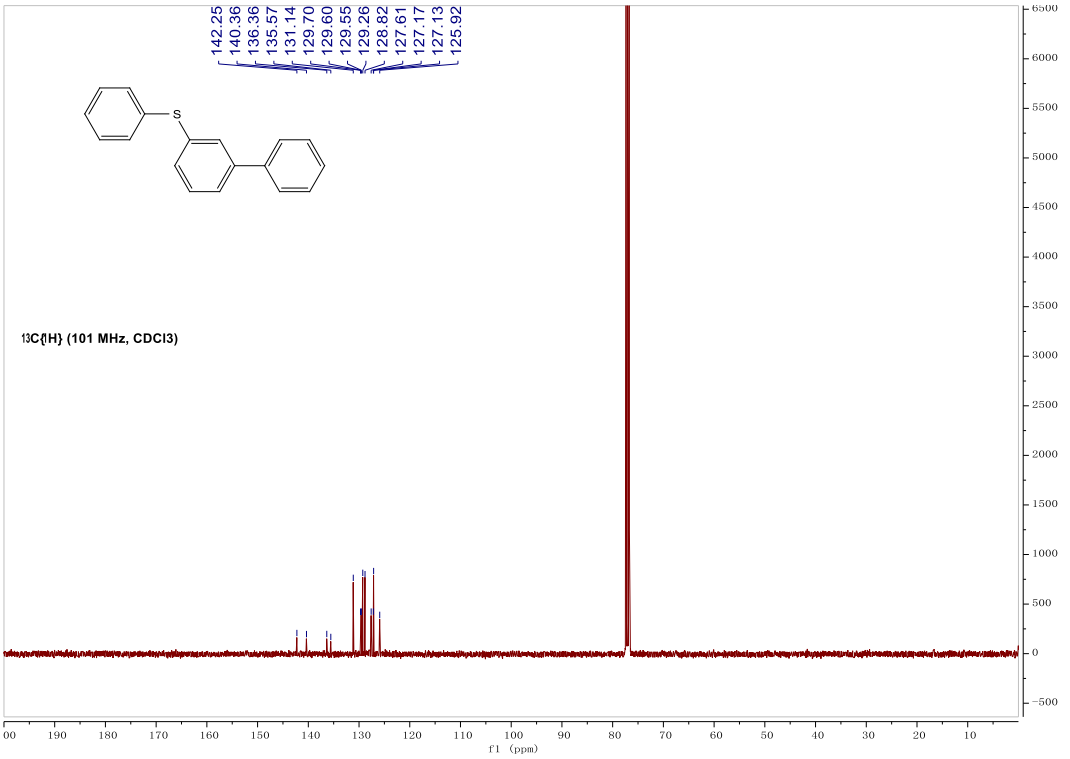
(2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)(imino)-l6-sulfanone (6)



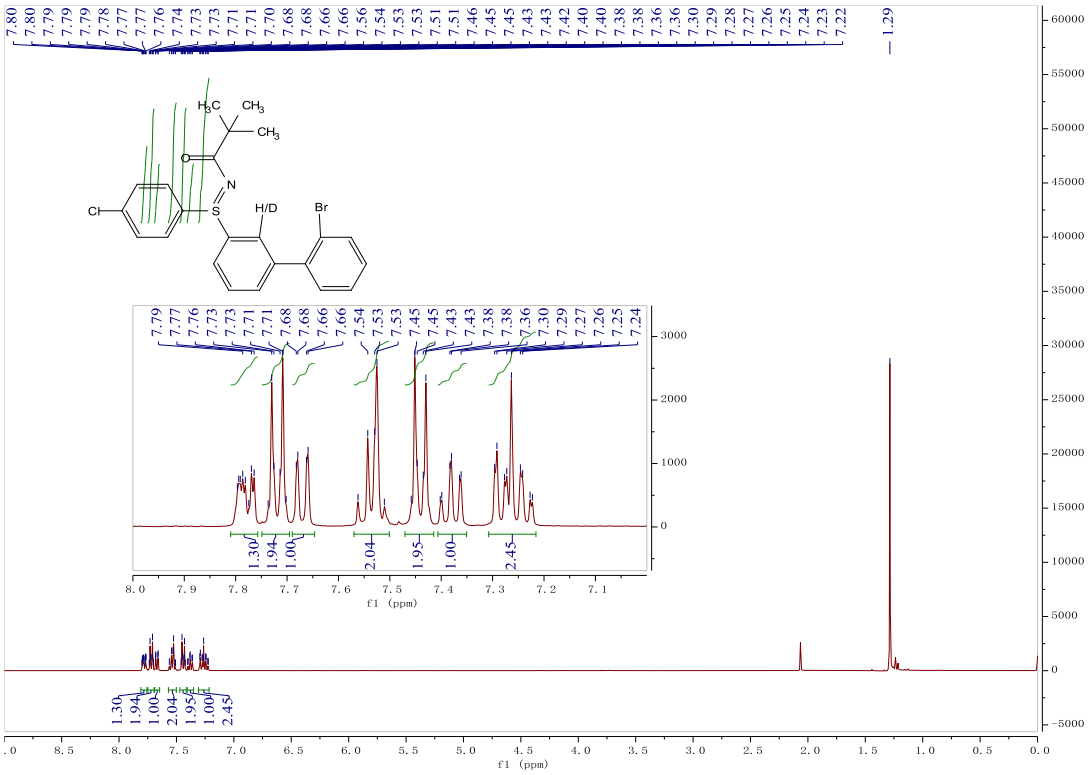


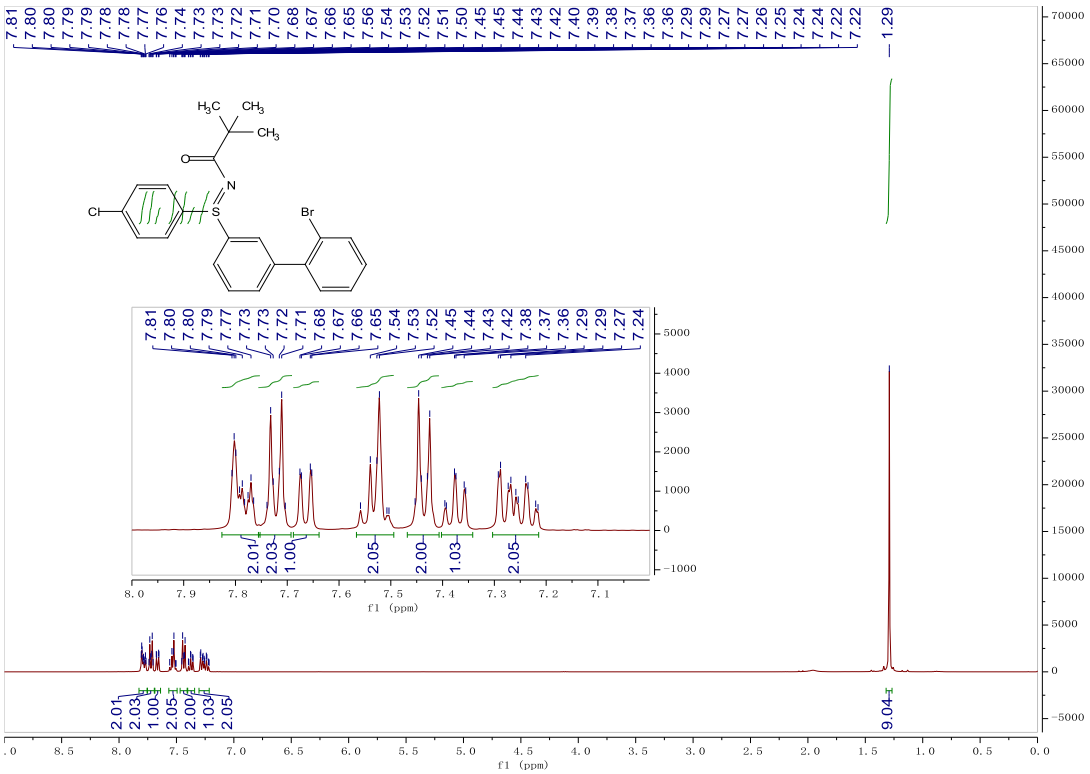
(2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)sulfane (7)





N-((2'-bromo-[1,1'-biphenyl]-3-yl)(4-chlorophenyl)-l4-sulfaneylidene)pivalamide (3aa-H/D)

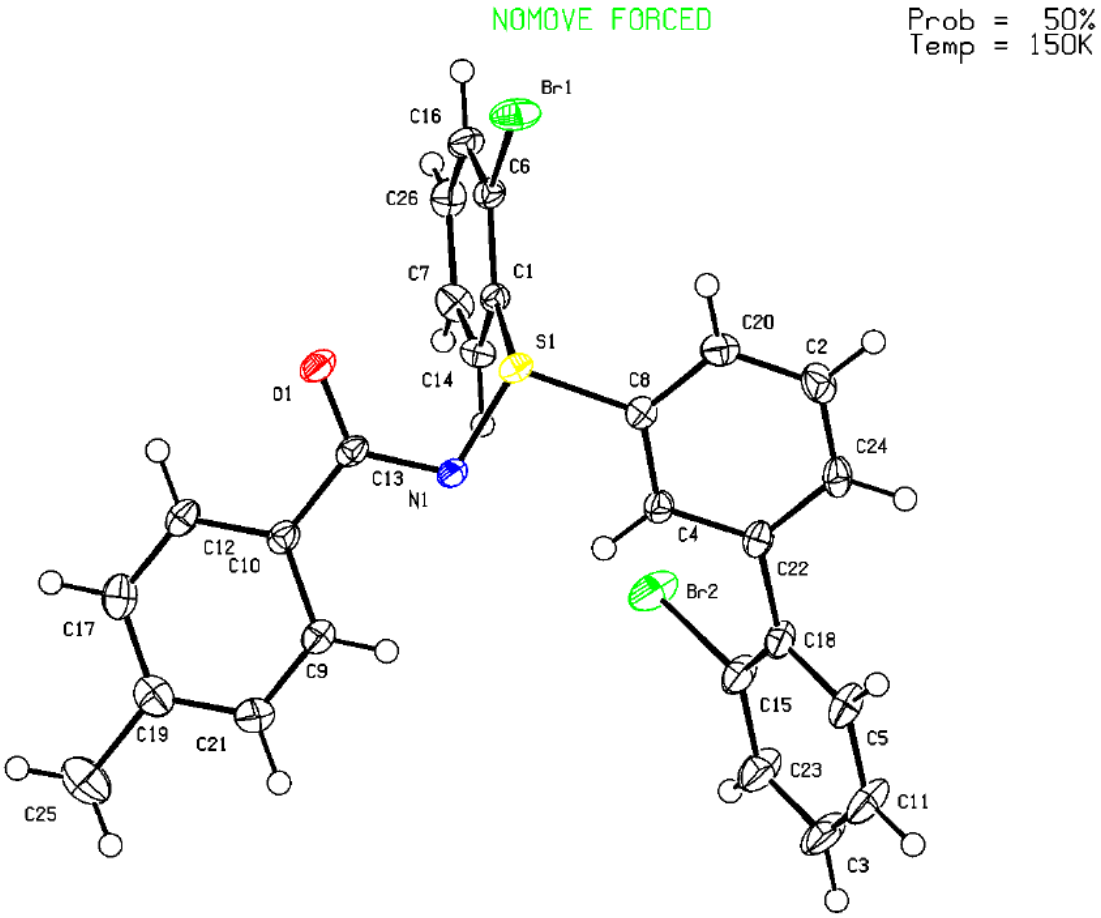




Crystal data and structure refinement for 3aw

Sample preparation: a pure solid sample was firstly dissolved in ethyl acetate in a vial at room temperature, and petroleum ether was added into the above solution slowly while keeping the sample completely dissolved. The vial was properly sealed with parafilm and kept at room temperature to allow the slow evaporation of the solvents until a single crystal was obtained.

Compound **3aw**: (The crystal structure of compound **3aw** has been deposited at the Cambridge Crystallographic Data Centre (**CCDC** 2465288). The data is available free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.)



X-ray crystallographic data of compounds **3aw**. The ellipsoid contour percent probability level is 50% in the caption of the thermal ellipsoid plot.

Crystal data and structure refinement for **3aw**.

Empirical formula	$C_{26}H_{19}Br_2NOS$
Formula weight	553.30
Temperature/K	150.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.23180(10)
b/Å	10.86210(10)
c/Å	13.1254(2)
α/°	78.4350(10)
β/°	79.2600(10)
γ/°	79.2680(10)
Volume/Å^3	1116.05(2)
Z	2
ρcalcg/cm^3	1.646
μ/mm-1	5.626
F(000)	552.0
Crystal size/mm^3	0.18 × 0.15 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.41 to 152.8
Index ranges	$-10 \leq h \leq 9$, $-13 \leq k \leq 13$, $-16 \leq l \leq 16$
Reflections collected	11932
Independent reflections	4427 [Rint = 0.0203, Rsigma = 0.0154]
Data/restraints/parameters	4427/0/281
Goodness-of-fit on F^2	1.098
Final R indexes [I>=2σ (I)]	R_1 = 0.0318, wR_2 = 0.0815
Final R indexes [all data]	R_1 = 0.0323, wR_2 = 0.0819