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# Palladium-catalyzed Regioselective Synthesis of Mono and Bis(arylthiol) Alkene from Propargyl Carbonate and Thiophenol

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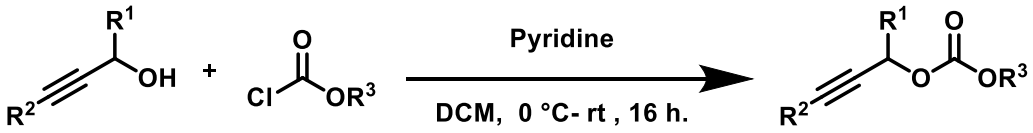
## 1. General experimental

Unless otherwise noted, all materials including solvents and reagents were obtained from commercial suppliers and were used without further purification. All dry reactions were carried out under argon or nitrogen atmosphere in dried glassware. All work-up and purification were carried out with reagent-grades solvents in air. Analytical TLC was performed using 2.5 × 5 cm plates coated with a 0.25 mmol thickness of silica gel (60F-254); visualization was accomplished under UV lamp. NMR spectra were recorded on 400 MHz spectrometer for $^{1}H$ NMR 100 MHz for $^{13}C$ NMR spectroscopy and chemical shift for $^{1}H$ NMR and $^{13}C$ NMR are expressed in parts per million(ppm) relative to the solvent. Chemical shifts are reported relative to the residual signals of either tetramethyl silane in $CDCl_3$ or deuterated DMSO for $^{1}H$ and $^{13}C$ NMR spectroscopy. $^{1}H$ and $^{13}C$ NMR chemical shift assignments are based on two-dimensional NMR experiments including $^{1}H$-COSY, NOESY, HSQC and HMBC. All $^{13}C$ spectra are $^{1}H$ decoupled. NMR data is represented as follows chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, m = multiplet, app. dd, = apparent doublet of doublets, app. t = apparent triplet), coupling constant (J) in Hertz (Hz), integration. HRMS were recorded by using Q-TOF mass spectrometer. Mass spectra were recorded using electron spray ionization (ESI-MS) using argon FAB gas. Column chromatography was performed with silica gel (100-200 mesh) as the stationary state. All reaction was monitored by TLC.

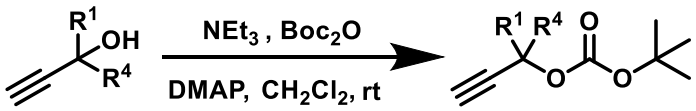
## 2. Synthetic Details

### General Procedure 1 (GP1) for the preparation of 1a, 1c-1d and 1k-1l:




As per literature procedure[1] a 250 ml schlenk flask was placed under an argon atmosphere and charged with functionalised propargyl alcohol (1 equiv.) and 0.2 M DCM, then stirred for 5 min at rt. After that pyridine (2 equiv.) was added to the solution and the mixture was stirred for 15 min. The solution was then cooled to 0ºC using an ice water bath followed by the dropwise addition of functionalised chloroformate (2 equiv.) over few mins. Then resulting mixture was allowed to stir for 1h at 0ºC and warmed to rt and stirred for 16 h. The reaction was quenched with the saturated solution of ammonium chloride and extracted into DCM and washed with water then brine. The crude product was dried over sodium sulphate and concentrated under reduced pressure. Then the liquid product (1a, 1c-1d and 1k-1l) was obtained by column- chromatography.

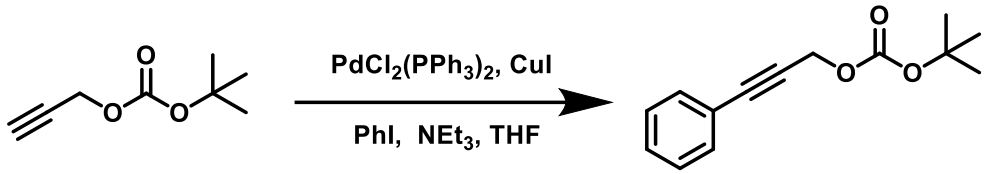
### General Procedure 2 (GP2) for the preparation of 1b, 1e, 1g and 1i-1j:




According to the literature procedure[2] to a solution of alcohol (1 equiv.) in DCM (0.5 M) was added $NEt_3$ (1.1 equiv.), $Boc_2O$ (1 equiv.) and DMAP (0.05 equiv.). The mixture was stirred

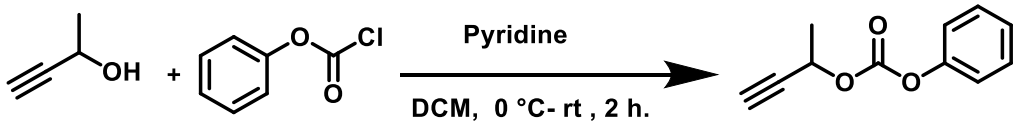
at rt and followed periodically by TLC. Upon completion, the reaction was quenched with water and extracted twice with diethyl ether. The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The crude was purified by flash column chromatography (silica gel, petroleum ether/diethyl ether) to give the protected alcohol (1b, 1e, 1g and 1i-1j).

**Procedure 1 (P1) for the preparation of 1h:**[3]



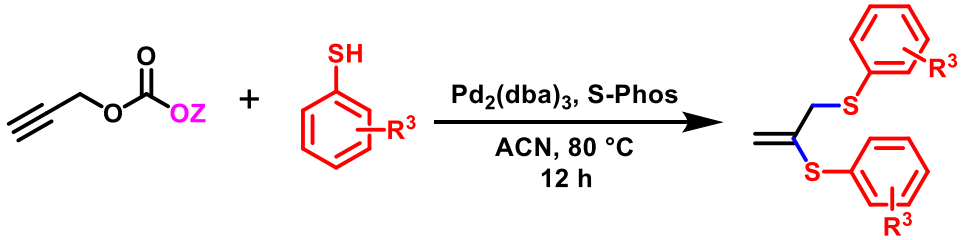

To a solution of alkyne (1 equiv.) in THF (0.1 M), PhI (1.2 equiv.), $PdCl_2(PPh_3)_2$ (0.03 equiv.), CuI (0.05 equiv.) and $NEt_3$ (10 equiv.) were successively added. The reaction mixture was allowed to react at rt overnight. Upon completion, it was diluted with diethyl ether and filtered through silica, and the filtrate was concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether/diethyl ether) to afford the desired product (1h).

**Procedure 2 (P2) for the preparation of 1f:**



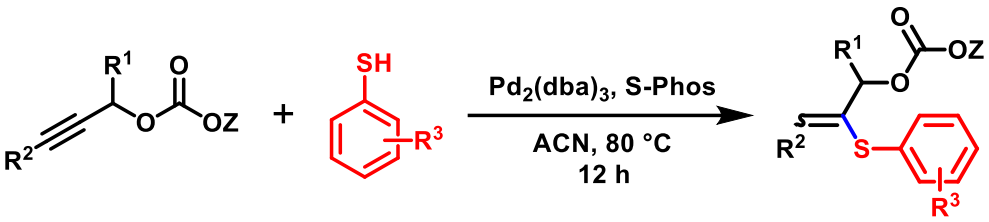

As per literature procedure[4] a 250 ml schlenk flask was placed under an argon atmosphere and charged with but-3-yn-2-ol (1 equiv.) and 0.2 M DCM, then stirred for 5 min at rt. After that pyridine (2 equiv.) was added to the solution and the mixture was stirred for 15 min. The solution was then cooled to 0ºC using an ice water bath followed by the dropwise addition of phenyl chloroformate (2 equiv.) over few mins. Then resulting mixture was allowed to stir for 1h at 0ºC and warmed to rt and stirred for an additional hour. The reaction was quenched with the saturated solution of ammonium chloride and extracted into DCM and washed with water then brine. The crude product was dried over sodium sulphate and concentrated under reduced pressure. Then the colourless liquid product (1f) was obtained through column-chromatography.

**General Procedure 3 (GP3) for the preparation of 3a-3g & 8a:**



A Schlenk tube equipped with a stir bar was evacuated, backfilled with nitrogen and charged with substrate (2.0 mmol), $Pd_2(dba)_3$ (2 mol%) and S-phos (5 mol%) before propargyl carbonate (1.1 mmol) in acetonitrile (0.2 M with respect to the substrate) was added. The reaction was stirred at 80ºC in an oil bath for 12 h. The suspension was filtered through a Celite pad and the resulting solution was concentrated in vacuo and the crude product was purified by flash column chromatography.

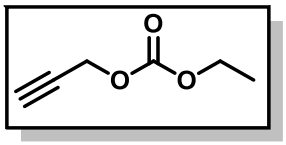
**General Procedure 4 (GP4) for the preparation of 4a-4z',4a' & 4i':**




A Schlenk tube equipped with a stir bar was evacuated, backfilled with nitrogen and charged with substrate (1.0 mmol), $Pd_2(dba)_3$ (2 mol%) and S-phos (5 mol%) before propargyl carbonate (1.1 mmol) in acetonitrile (0.2 M with respect to the substrate) was added. The reaction was stirred at 80ºC in an oil bath for 12 h. The suspension was filtered through a Celite pad and the resulting solution was concentrated in vacuo and the crude product was purified by flash column chromatography to produce the products 4a- 4z'& 4a'.

**3. Experimental section:**

**Ethyl prop-2-yn-1-yl carbonate (1a)**



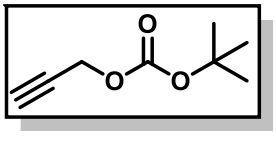

Colourless liquid. Synthesised by GP1 (87%).

**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 4.72 (d, *J* = 2.34 Hz, 2H), 4.23 (q, *J* = 7.13 Hz, 2H), 2.55 (t, *J* = 2.44 Hz, 1H), 1.32 (t, *J* = 7.08 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 154.47, 75.49, 64.48, 63.67, 54.97, 14.12.

**HRMS** (m/z): calculated for $C_6H_9O_3$ $[M + H]^+$, 129.0546; found, 129.0538.

**Tert-butyl prop-2-yn-1-yl carbonate (1b)**[3]

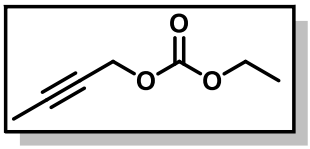



Pale yellow liquid. Synthesised by GP2 (91%).

**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 4.66 (d, *J* = 2.53 Hz, 2H), 2.49 (t, *J* = 2.44 Hz, 1H), 1.49 (s, 9H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 152.73, 82.98, 77.38, 75.18, 54.28, 27.68.

**But-2-yn-1-yl ethyl carbonate (1c)**[1]

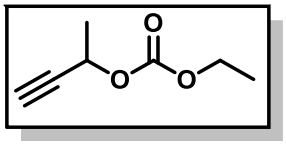


Colourless liquid. Synthesised by GP1 (95%).

**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 4.68-4.67 (m, 2H), 4.21 (q, *J* = 7.14 Hz, 2H), 1.86-1.84 (m, 3H), 1.30 (t, *J* = 7.12 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 154.52, 83.46, 72.65, 63.99, 55.62, 13.94, 3.18.

**But-3-yn-2-yl ethyl carbonate (1d)**[5]

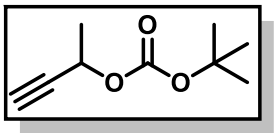


Yellow liquid. Synthesised by GP1 (97%).

**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 5.27 (dq, *J* = 2.14 Hz, *J* = 6.70 Hz, 1H), 4.19 (q, *J* = 7.16 Hz, 2H), 2.48 (d, *J* = 2.14 Hz, 1H), 1.52 (d, *J* = 6.75 Hz, 3H), 1.29 (t, *J* = 7.15 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 154.12, 81.45, 73.64, 64.26, 63.69, 21.86, 14.17.

**But-3-yn-2-yl tert-butyl carbonate (1e)**



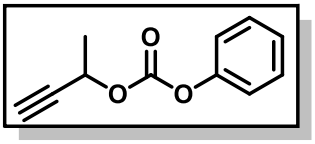
Yellow liquid. Synthesised by GP2 (93%).

**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 5.19 (dq, *J* = 2.10 Hz, *J* = 6.73 Hz, 1H), 2.44 (d, *J* = 2.12 Hz, 1H), 1.49 (d, *J* = 6.72 Hz, 3H), 1.45 (s, 9H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 152.37, 82.67, 81.76, 73.31, 62.76, 27.69, 21.19.

**HRMS** (m/z): calculated for $C_9H_{15}O_3$ $[M + H]^+$, 171.1016; found, 171.1023.

**But-3-yn-2-yl phenyl carbonate (1f)**



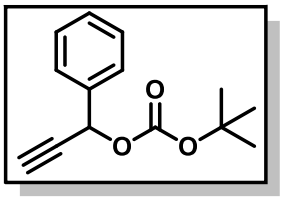
Colourless liquid. Synthesised by P2 (94%).

**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 7.40-7.33 (m, 2H), 7.24-7.15 (m, 3H), 5.37 (dq, *J* = 2.12 Hz, *J* = 6.73 Hz, 1H), 2.53 (d, *J* = 2.14 Hz, 1H), 1.60 (d, *J* = 6.72 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$):** δ = 152.71, 151.05, 129.50, 126.14, 120.99, 81.00, 74.33, 64.85, 21.22.

**HRMS** (m/z): calculated for $C_{11}H_{11}O_3$ $[M + H]^+$, 191.0703; found, 191.0708.

**Tert-butyl (1-phenylprop-2-yn-1-yl) carbonate (1g)**[3]

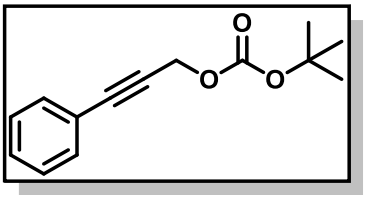


Colourless liquid. Synthesised by GP2 (88%).

**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 7.55-7.53 (m, 2H), 7.40-7.34 (m, 3H), 6.23 (d, *J* = 2.29, 1H), 2.68 (d, *J* = 2.32 Hz, 1H), 1.48 (s, 9H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 152.47, 136.25, 129.15, 128.69, 127.70, 83.16, 80.04, 76.00, 68.21, 27.76.

**Tert-butyl (3-phenylprop-2-yn-1-yl) carbonate (1h)**[3]

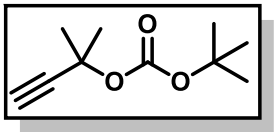


Colourless liquid. Synthesised by P1 (76%).

**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 7.45-7.43 (m, 2H), 7.33-7.27 (m, 3H), 4.89 (s, 2H), 1.50 (s, 9H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 152.88, 131.85, 128.72, 128.27, 122.19, 86.84, 82.88, 82.65, 55.26, 27.73.

**Tert-butyl (2-methylbut-3-yn-2-yl) carbonate (1i)**[3]

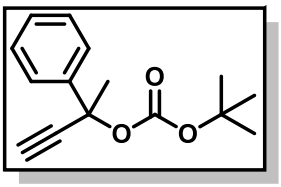


Colourless liquid. Synthesised by GP2 (89%).

**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 2.54 (s, 1H), 1.69 (s, 6H), 1.49 (s, 9H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 151.35, 84.47, 82.22, 72.81, 72.41, 28.86, 27.79.

**Tert-butyl (2-phenylbut-3-yn-2-yl) carbonate (1j)**[6]

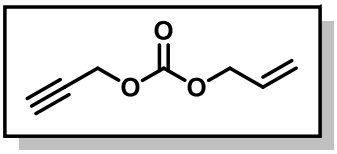


Colourless liquid. Synthesised by GP2 (90%).

**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 7.60-7.58 (m, 2H), 7.37-7.33 (m, 2H), 7.31-7.27 (m, 1H), 2.81 (s, 1H), 1.88 (s, 3H), 1.40 (s, 9H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 150.88, 142.19, 128.39, 127.96, 124.68, 82.83, 82.63 75.70, 32.59, 27.71.

**Allyl prop-2-yn-1-yl carbonate (1k)**



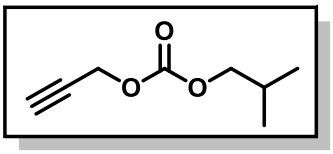
Colourless liquid. Synthesised by GP1 (95%).

**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 5.98-5.88 (m, 1H), 5.39-5.35 (m, 1H), 5.29-5.26 (m, 1H), 4.73(d, *J* = 2.47 Hz, 2H), 4.67-4.64 (m, 2H), 2.54 (t, *J* = 2.45 Hz, 1H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ =154.34, 131.26, 119.04, 75.65, 68.83, 55.21.

**HRMS** (m/z): calculated for $C_7H_9O_3$ $[M + H]^+$, 141.0546; found, 141.0532.

**Isobutyl prop-2-yn-1-yl carbonate (1l)**



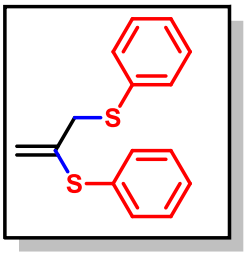
Colourless liquid. Synthesised by GP1 (90%).

**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 4.72 (d, *J* = 2.45 Hz, 2H), 3.96 (d, *J* = 6.67 Hz, 2H), 2.53 (t, *J* = 2.46 Hz, 1H), 2.03-1.93 (m, 1H), 0.96 (d, *J* = 6.74 Hz, 6H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ =154.67, 75.52, 74.54, 73.89, 55.06, 27.73, 18.79.

**HRMS** (m/z): calculated for $C_8H_{13}O_3$ $[M + H]^+$, 157.0859; found, 157.0847.

**Prop-2-ene-1,2-diylbis(phenylsulfane) (3a)**



Pale yellow oil. Synthesised by GP3 (76%).

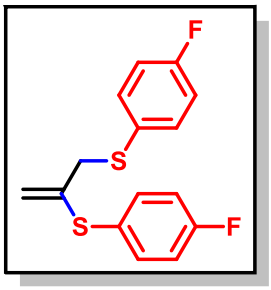
**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 7.42-7.41 (m, 2H), 7.34-7.27 (m, 6H), 7.24 (s, 1H), 7.22-7.17 (m, 1H), 5.37 (s, 1H), 5.07 (s, 1H), 3.65 (s, 2H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 141.13, 133.09, 132.69, 130.76, 130.35, 129.24, 128.84, 128.02, 126.61, 116.94, 40.21.

**IR** ν ($cm^{-1}$)**:** 3740, 3419, 2921, 1635, 1068, 738, 688.

**HRMS** (m/z): calculated for $C_{15}H_{15}S_2$ $[M + H]^+$, 259.0610; found, 259.0618.

**Prop-2-ene-1,2-diylbis((4-fluorophenyl)sulfane) (3b)**




Pale yellow oil. Synthesised by GP3 (82%).

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ = 7.42-7.35 (m, 4H), 7.05-6.96 (m, 4H), 5.17 (s, 1H), 4.88 (s, 1H), 3.56 (s, 2H).

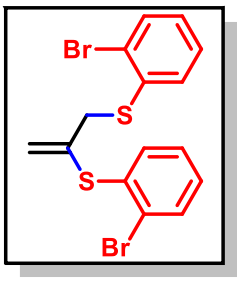
**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 164.15 (d, $J_{C-F}$ = 249.17 Hz), 163.50 (d, $J_{C-F}$ = 248.14 Hz), 161.67 (d, $J_{C-F}$ = 249.17 Hz), 161.08 (d, $J_{C-F}$ = 248.14 Hz), 141.91, 135.90 (d, $J_{C-F}$ = 8.43 Hz), 135.82 (d, $J_{C-F}$ = 8.43 Hz), 133.87 (d, $J_{C-F}$ = 8.18 Hz), 133.79 (d, $J_{C-F}$ = 8.18 Hz), 130.17 (d, $J_{C-F}$ = 3.28 Hz), 130.14 (d, $J_{C-F}$ = 3.28 Hz), 127.40 (d, $J_{C-F}$ = 3.99 Hz), 127.37 (d, $J_{C-F}$ = 3.99 Hz), 116.57 (d, $J_{C-F}$ = 27.79 Hz), 116.36 (d, $J_{C-F}$ = 27.79 Hz), 116.08 (d, $J_{C-F}$ = 21.84 Hz), 115.86 (d, $J_{C-F}$ = 21.84 Hz), 115.45, 41.49.

**$^{19}$F NMR (376 MHz, $CDCl_3$):** -112.59 (s, 1F), -114.37 (s, 1F).

**IR** ν ($cm^{-1}$): 3838, 3436, 2064, 1635, 1065, 668.

**HRMS** (m/z): calculated for $C_{15}H_{13}F_2S_2$ $[M + H]^+$, 295.0421; found, 295.0422.

**Prop-2-ene-1,2-diylbis((2-bromophenyl)sulfane) (3c)**




Colourless oil. Synthesised by GP3 (84%).

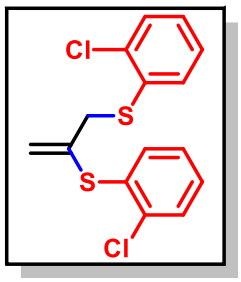
**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ = 7.62-7.60 (m, 1H), 7.55-7.53 (m, 1H), 7.44-7.42 (m, 1H), 7.30-7.21 (m, 3H), 7.15-7.12 (m, 1H), 7.06-7.02 (m, 1H), 5.58 (s, 1H), 5.17 (s, 1H), 3.71 (s, 2H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 138.41, 136.63, 134.22, 133.73, 133.60, 133.02, 130.13, 129.23, 128.04, 127.73, 127.46, 127.31, 124.60, 119.38, 38.85.

**IR** ν ($cm^{-1}$): 3433, 2921, 1634, 1444, 1105, 742.

**HRMS** (m/z): calculated for $C_{15}H_{13}Br_2S_2$ $[M + H]^+$, 416.8820; found 416.8824.

**Prop-2-ene-1,2-diylbis((2-chlorophenyl)sulfane) (3d)**




Colourless oil. Synthesised by GP3 (85%).

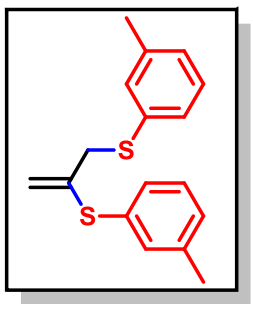
**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 7.45-7.42 (m, 2H), 7.37-7.35 (m, 1H), 7.33-7.30 (m, 1H), 7.24-7.20 (m, 2H), 7.19-7.11 (m, 2H), 5.52 (s, 1H), 5.13 (s, 1H), 3.71 (s, 2H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ =138.46, 136.95, 134.63, 134.50, 134.07, 132.02, 130.68, 130.26, 129.71, 129.24, 127.46, 127.37, 127.07, 118.76, 38.54.

**IR** ν ($cm^{-1}$): 3430, 2922, 1633, 1450, 1034, 744.

**HRMS** (m/z): calculated for $C_{15}H_{13}Cl_2S_2$ $[M + H]^+$, 326.9830; found, 326.9837.

**Prop-2-ene-1,2-diylbis(m-tolylsulfane) (3e)**




Pale yellow oil. Synthesised by GP3 (65%).

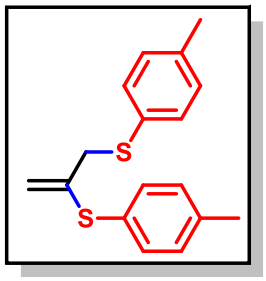
**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 7.25-7.24 (m, 1H), 7.22-7.20 (m, 2H), 7.15-7.13 (m, 3H), 7.12-7.09 (m, 1H), 7.01-6.99 (m, 1H), 5.39 (s, 1H), 5.10 (s, 1H), 3.65 (s, 2H), 2.32 (s, 3H), 2.30 (s, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ =141.17, 139.07, 138.57, 135.50, 133.58, 132.39, 130.77, 130.03, 129.03, 128.82, 128.67, 127.39, 127.10, 116.87, 40.05, 21.31, 21.25.

**IR** ν ($cm^{-1}$): 3839, 3740, 3422, 2921, 1634, 1064, 771.

**HRMS** (m/z): calculated for $C_{17}H_{19}S_2$ $[M + H]^+$, 287.0923; found, 287.0932.

**Prop-2-ene-1,2-diylbis(p-tolylsulfane) (3f)**



Colourless oil. Synthesised by GP3 (68%).

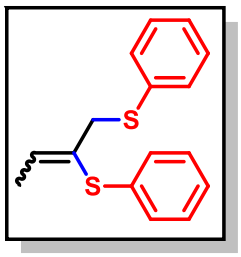
**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 7.33-7.30 (m, 2H), 7.26-7.25 (m, 2H), 7.14-7.12 (m, 2H), 7.08-7.05 (m, 2H), 5.24 (s, 1H), 4.95 (s, 1H), 3.59 (s, 2H), 2.34 (s, 3H), 2.31 (s, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ =142.01, 138.32, 136.76, 133.67, 132.39, 131.96, 131.07, 130.01, 129.59, 115.28, 40.77, 21.17, 21.05.

**IR** ν ($cm^{-1}$): 3432, 2921, 2316, 1634, 1490, 1091, 804.

**HRMS** (m/z): calculated for $C_{17}H_{19}S_2$ $[M + H]^+$, 287.0923; found, 287.0928.

**But-2-ene-1,2-diylbis(phenylsulfane) (3g)**



Pale yellow oil. Synthesised by GP3 (56%).

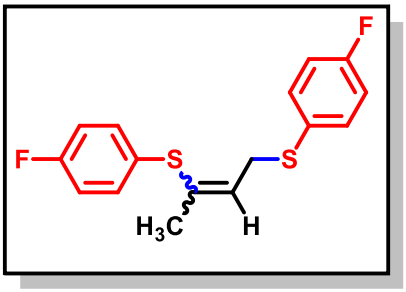
**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 7.33-7.26 (m, 5H), 7.25-7.15 (m, 5H), 6.11 (q, *J* = 6.76 Hz 1H), 3.62 (s, 2H), 1.85 (d, *J* = 6.79 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 136.14, 134.77, 134.25, 130.90, 130.60, 129.84, 129.13, 128.88, 126.58, 126.46, 42.01, 15.91.

**IR** ν ($cm^{-1}$): 3394, 2920, 1456, 1068.

**HRMS** (m/z): calculated for $C_{16}H_{17}S_2$ $[M + H]^+$, 273.0766; found, 273.0765.

**But-2-ene-1,3-diylbis((4-fluorophenyl)sulfane) (8a)**




Colourless oil. Synthesised by GP3 (62%).

**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 7.38-7.35 (m, 2H), 7.25-7.21 (m, 2H), 7.01-6.97 (m, 4H), 5.56 (qt, *J* = 8.00 Hz, *J* = 1.24 Hz, 1H), 3.49 (d, *J* = 7.98 Hz, 2H), 1.64 (s, 3H).

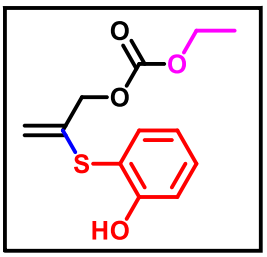
**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 163.79 (d, $J_{C\text{-}F}$ = 248.20 Hz), 163.64 (d, $J_{C\text{-}F}$ = 247.87 Hz), 161.30 (d, $J_{C\text{-}F}$ = 248.20 Hz), 161.18 (d, $J_{C\text{-}F}$ = 247.87 Hz), 134.79, 134.69 (d, $J_{C\text{-}F}$ = 5.03 Hz), 134.64 (d, $J_{C\text{-}F}$ = 5.03 Hz), 134.61 (d, $J_{C\text{-}F}$ = 5.14 Hz), 134.56 (d, $J_{C\text{-}F}$ = 5.14 Hz), 130.03 (d, $J_{C\text{-}F}$ = 4.12 Hz), 129.99 (d, $J_{C\text{-}F}$ = 4.12 Hz), 128.26 (d, $J_{C\text{-}F}$ = 2.64 Hz), 128.24 (d, $J_{C\text{-}F}$ = 2.64 Hz), 125.20, 116.31 (d, $J_{C\text{-}F}$ = 21.87 Hz), 116.09 (d, $J_{C\text{-}F}$ = 21.87 Hz), 116.05 (d, $J_{C\text{-}F}$ = 21.70 Hz), 115.83 (d, $J_{C\text{-}F}$ = 21.70 Hz), 34.31, 17.38.

**$^{19}$F NMR (376 MHz, $CDCl_3$):** -113.67 (s, 1F), -114.19 (s, 1F).

**IR** ν ($cm^{-1}$): 3379, 2920, 1384, 1225, 1080.

**HRMS** (m/z): calculated for $C_{16}H_{15}F_2S_2$ $[M + H]^+$, 309.0578; found, 309.0574.

**Ethyl (2-((2-hydroxyphenyl)thio)allyl) carbonate (4a)**




Pale yellow oil. Synthesised by GP4 (82%).

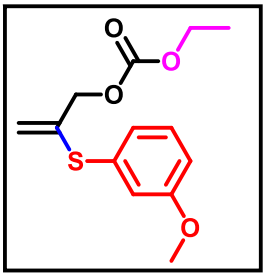
**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ = 7.47-7.44 (m, 1H), 7.36-7.32 (m, 1H), 7.03-7.01 (m, 1H), 6.94-6.89 (m, 1H), 6.39 (s, 1H), 5.41 (s, 1H), 4.97 (s, 1H), 4.64 (s, 2H), 4.22 (q, *J* = 7.13 Hz, 2H), 1.32 (t, *J* = 7.13 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 157.14, 154.69, 138.39, 136.61, 132.40, 121.20, 115.71, 115.04, 114.55, 68.36, 64.47, 14.25.

**IR** ν ($cm^{-1}$): 3396, 2923, 1743, 1647, 1382, 1260, 1020, 767.

**HRMS** (m/z): calculated for $C_{12}H_{15}O_4S$ $[M + H]^+$, 255.0686; found, 255.0682.

**Ethyl (2-((3-methoxyphenyl)thio)allyl) carbonate (4b)**



Yellow oil. Synthesised by GP4 (74%).

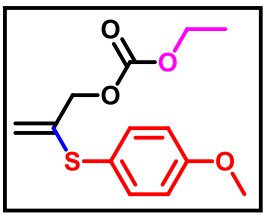
**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ = 7.23-7.21 (m, 1H), 7.01-6.97 (m, 2H), 6.83-6.81 (m, 1H), 5.60 (s, 1H), 5.39 (s, 1H), 4.65 (s, 2H), 4.20 (q, *J* = 7.12 Hz, 2H), 3.80 (s, 3H), 1.31 (t, *J* = 7.14 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 160.07, 154.67, 138.30, 130.04, 124.15, 118.63, 116.95, 113.92, 68.33, 64.30, 55.33, 14.24.

**IR** ν ($cm^{-1}$): 3391, 2921, 1617, 1383, 1051, 771.

**HRMS** (m/z): calculated for $C_{13}H_{17}O_4S$ $[M + H]^+$, 269.0842; found, 269.0835.

**Ethyl (2-((4-methoxyphenyl)thio)allyl) carbonate (4c)**



Pale yellow oil. Synthesised by GP4 (70%).

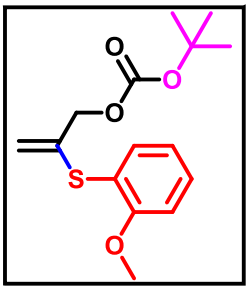
**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ = 7.42-7.39 (m, 2H), 6.89-6.87 (m, 2H), 5.39 (s, 1H), 5.05 (s, 1H), 4.63 (s, 2H), 4.23-4.18 (q, *J* = 7.14 Hz, 2H), 3.81 (s, 3H), 1.31 (t, *J* = 7.13 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 160.15, 154.73, 140.69, 135.67, 121.74, 114.95, 114.42, 68.48, 64.27, 55.35, 14.26.

**IR** ν ($cm^{-1}$): 3407, 2924, 1743, 1383, 1246, 1021, 753.

**HRMS** (m/z): calculated for $C_{13}H_{17}O_4S$ $[M + H]^+$, 269.0842; found, 269.0840.

**Tert-butyl (2-((2-methoxyphenyl)thio)allyl) carbonate (4d)**




Colourless oil. Synthesised by GP4 (72%).

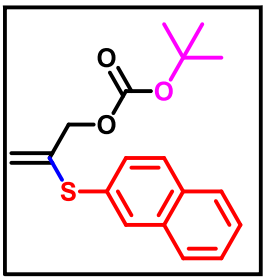
**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ = 7.40-7.38 (m, 1H), 7.30-7.25 (m, 1H), 6.95-6.88 (m, 2H), 5.55 (s, 1H), 5.27 (s, 1H), 4.59 (s, 2H), 3.86 (s, 3H), 1.48 (s, 9H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 158.41, 153.00, 137.89, 133.35, 129.47, 121.50, 121.30, 120.43, 117.29, 111.18, 82.38, 67.68, 55.90, 27.76.

**IR** ν ($cm^{-1}$): 3781, 3409, 2921, 2854, 2042, 1739, 1616, 1582, 1465, 1374, 1251, 1155, 1093, 1029, 943, 855, 751, 673, 578, 497.

**HRMS** (m/z): calculated for $C_{15}H_{21}O_4S$ $[M + H]^+$, 297.1155; found, 297.1155.

**Tert-butyl (2-(naphthalen-2-ylthio)allyl) carbonate (4e)**




Colourless oil. Synthesised by GP4 (74%).

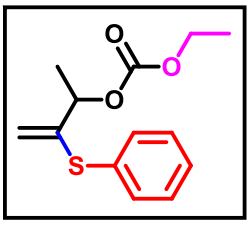
**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ = 7.93 (s, 1H), 7.82-7.76 (m, 3H), 7.49-7.47 (m, 3H), 5.59 (s, 1H), 5.35 (s, 1H), 4.62 (s, 2H), 1.47 (s, 9H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 152.98, 138.99, 133.76, 132.65, 131.44, 129.62, 129.30, 128.90, 127.74, 127.55, 126.63, 126.52, 117.83, 67.80, 27.74.

**IR** ν ($cm^{-1}$): 3391, 2923, 2854, 1743, 1646, 1381, 1275, 1160, 745.

**HRMS** (m/z): calculated for $C_{18}H_{21}O_3S$ $[M + H]^+$, 317.1206; found, 317.1213.

**Ethyl (3-(phenylthio)but-3-en-2-yl) carbonate (4f)**



Pale yellow oil. Synthesised by GP4 (88%).

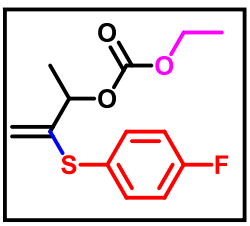
**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ = 7.47-7.45 (m, 2H), 7.36-7.27 (m, 3H), 5.52 (s, 1H), 5.22 (q, *J* = 6.56 Hz, 1H), 5.07 (s, 1H), 4.18 (q, *J* = 7.11 Hz, 2H), 1.51 (d, *J* = 6.57 Hz, 3H), 1.30 (t, *J* = 7.14 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 154.19, 145.26, 132.97, 132.22, 129.25, 128.01, 114.77, 75.60, 64.04, 20.27, 14.25.

**IR** ν ($cm^{-1}$): 3381, 2923, 1744, 1379, 1257, 1068, 771.

**HRMS** (m/z): calculated for $C_{13}H_{17}O_3S$ $[M + H]^+$, 253.0893; found, 253.0902.

**Ethyl (3-((4-fluorophenyl)thio)but-3-en-2-yl) carbonate (4g)**



Yellow oil. Synthesised by GP4 (88%).

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ = 7.47-7.43 (m, 2H), 7.06-7.02 (m, 2H), 5.46 (s, 1H), 5.20 (q, *J* = 6.55 Hz, 1H), 4.96 (s, 1H), 4.18 (q, *J* = 7.19 Hz, 2H), 1.50 (d, *J* = 6.59 Hz, 3H), 1.30 (t, *J* = 7.18 Hz, 3H).

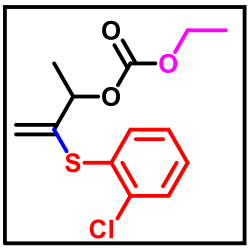
**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 164.11 (d, $J_{C\text{-}F}$ = 248.56 Hz), 161.64 (d, $J_{C\text{-}F}$ = 248.56 Hz), 154.17, 145.88, 135.65 (d, $J_{C\text{-}F}$ = 8.38 Hz), 135.57 (d, $J_{C\text{-}F}$ = 8.38 Hz), 127.03 (d, $J_{C\text{-}F}$ = 3.49 Hz), 126.99 (d, $J_{C\text{-}F}$ = 3.49 Hz), 116.58 (d, $J_{C\text{-}F}$ = 22.11 Hz), 116.36 (d, $J_{C\text{-}F}$ = 22.11 Hz), 113.67, 75.46, 64.06, 20.24, 14.23.

**$^{19}$F NMR (376 MHz, $CDCl_3$):** -112.85 (s, 1F).

**IR** ν ($cm^{-1}$): 3383, 2984, 1745, 1590, 1488, 1377, 1258, 1069, 831.

**HRMS** (m/z): calculated for $C_{13}H_{16}FO_3S$ $[M + H]^+$, 271.0799; found, 271.0804.

**3-((2-chlorophenyl)thio)but-3-en-2-yl ethyl carbonate (4h)**



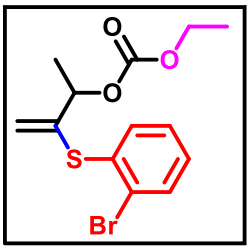

Yellow oil. Synthesised by GP4 (90%).

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ = 7.52-7.50 (m, 1H), 7.42-7.40 (m, 1H), 7.25-7.20 (m, 2H), 5.65 (s, 1H), 5.22 (q, *J* = 6.56 Hz, 1H), 5.15 (s, 1H), 4.19 (q, *J* = 7.13 Hz, 2H), 1.53 (d, *J* = 6.58 Hz, 3H), 1.30 (t, *J* = 7.15 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 154.18, 142.88, 136.06, 133.59, 132.05, 130.15, 128.91, 127.34, 117.43, 75.50, 64.09, 20.21, 14.26.

**HRMS** (m/z): calculated for $C_{13}H_{16}ClO_3S$ $[M + H]^+$, 287.0503; found, 287.0519.

**3-((2-bromophenyl)thio)but-3-en-2-yl ethyl carbonate (4i)**



Colourless oil. Synthesised by GP4 (92%).

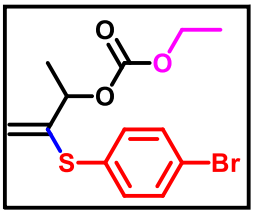
**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 7.60-7.58 (m, 1H), 7.52-7.50 (m, 1H), 7.30-7.26 (m, 1H), 7.14-7.10 (m, 1H), 5.68 (s, 1H), 5.22 (q, *J* = 6.53 Hz, 1H), 5.18 (s, 1H), 4.19 (q, *J* = 7.12 Hz, 2H), 1.53 (d, *J* = 6.52 Hz, 3H), 1.31 (t, *J* = 7.18 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 154.19, 143.02, 134.28, 133.46, 133.25, 128.88, 127.99, 126.25, 117.90, 75.46, 64.11, 20.25, 14.27.

**IR** ν ($cm^{-1}$): 3391, 2926, 1744, 1615, 1446, 1378, 1258, 1023, 753.

**HRMS** (m/z): calculated for $C_{13}H_{16}BrO_3S$ $[M + H]^+$, 330.9998; found, 330.9987.

**3-((4-bromophenyl)thio)but-3-en-2-yl ethyl carbonate (4j)**




Pale yellow oil. Synthesised by GP4 (90%).

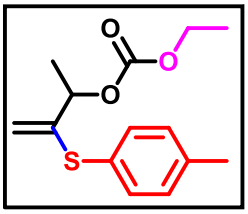
**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 7.47-7.43 (m, 2H), 7.33-7.29 (m, 2H), 5.57 (s, 1H), 5.19 (q, *J* = 6.57 Hz, 1H), 5.15 (s, 1H), 4.17 (q, *J* = 7.15 Hz, 2H), 1.49 (d, *J* = 6.56 Hz, 3H), 1.30 (t, *J* = 7.16 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 154.15, 144.48, 134.05, 132.37, 131.71, 122.16, 116.35, 75.47, 64.11, 20.21, 14.25.

**IR** ν ($cm^{-1}$): 3388, 1743, 1382, 1259, 1066, 765.

**HRMS** (m/z): calculated for $C_{13}H_{16}BrO_3S$ $[M + H]^+$, 330.9998; found, 330.9995.

**Ethyl (3-(p-tolylthio)but-3-en-2-yl) carbonate (4k)**




Colourless oil. Synthesised by GP4 (60%).

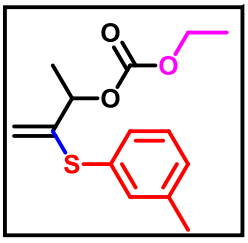
**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 7.35 (d, *J* = 8.09 Hz, 2H), 7.15 (d, *J* = 7.94 Hz, 2H), 5.43 (s, 1H), 5.21 (q, *J* = 6.58 Hz, 1H), 4.95 (s, 1H), 4.18 (q, *J* = 7.08 Hz, 2H), 2.34 (s, 3H), 1.51 (d, *J* = 6.54 Hz, 3H), 1.30 (t, *J* = 7.13 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 146.06, 138.38, 133.62, 130.08, 128.18, 113.04, 75.58, 64.02, 21.18, 20.31, 14.26.

**IR** ν ($cm^{-1}$): 3386, 2922, 1633, 1383, 1060, 770.

**HRMS** (m/z): calculated for $C_{14}H_{19}O_3S$ $[M + H]^+$, 267.1049; found, 267.1061.

**Ethyl (3-(m-tolylthio)but-3-en-2-yl) carbonate (4l)**



Colourless oil. Synthesised by GP4 (65%).

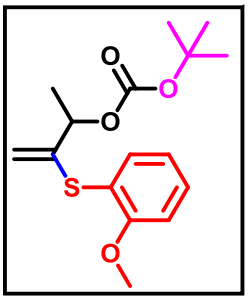
**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 7.28-7.20 (m, 3H), 7.11-7.09 (m, 1H), 5.50 (s, 1H), 5.22 (q, *J* = 6.54 Hz, 1H), 5.05 (s, 1H), 4.18 (q, *J* = 7.18 Hz, 2H), 2.33 (s, 3H), 1.51 (d, *J* = 6.56 Hz, 3H), 1.30 (t, *J* = 7.10 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 154.19, 145.41, 139.11, 133.58, 131.79, 130.02, 129.06, 128.87, 114.40, 75.61, 64.02, 21.21, 20.31, 14.25.

**IR** ν ($cm^{-1}$): 3396, 1744, 1383, 1258, 1058, 771.

**HRMS** (m/z): calculated for $C_{14}H_{19}O_3S$ $[M + H]^+$, 267.1049; found, 267.1055.

**Tert-butyl (3-((2-methoxyphenyl)thio)but-3-en-2-yl) carbonate (4m)**



Pale yellow oil. Synthesised by GP4 (78%).

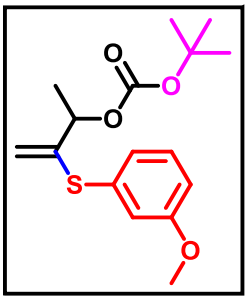
**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 7.45-7.43 (m, 1H), 7.31-7.27 (m, 1H), 6.95-6.88 (m, 2H), 5.49 (s, 1H), 5.17 (q, *J* = 6.55 Hz, 1H), 4.99 (s, 1H), 3.85 (s, 3H), 1.50 (d, *J* = 6.55 Hz, 3H), 1.48 (s, 9H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 158.60, 152.56, 144.38, 134.35, 129.62, 121.23, 120.58, 114.06, 111.25, 82.13, 74.76, 55.89, 27.81, 20.34.

**IR** ν ($cm^{-1}$): 3380, 2927, 1739, 1580, 1471, 1375, 1266, 1161, 1085, 761.

**HRMS** (m/z): calculated for $C_{16}H_{23}O_4S$ $[M + H]^+$, 311.1312; found, 311.1327.

**Tert-butyl (3-((3-methoxyphenyl)thio)but-3-en-2-yl) carbonate (4n)**




Pale yellow oil. Synthesised by GP4 (80%).

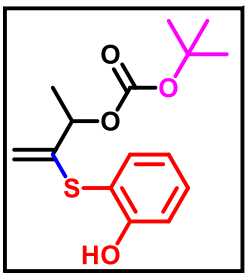
**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 7.25-7.18 (m, 1H), 7.08-7.00 (m, 2H), 6.83-6.74 (m, 1H), 5.54 (s, 1H), 5.17 (q, *J* = 6.58 Hz, 1H), 5.14 (s, 1H), 3.80 (s, 3H), 1.48 (d, *J* = 6.54 Hz, 3H), 1.48 (s, 9H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ =160.03, 152.53, 145.09, 133.71, 129.96, 124.65, 117.29, 115.27, 114.12, 82.25, 74.65, 55.31, 27.80, 20.29.

**IR** ν ($cm^{-1}$): 3380, 2928, 1740, 1585, 1380, 1261, 1160, 1087, 773.

**HRMS** (m/z): calculated for $C_{16}H_{23}O_4S$ $[M + H]^+$, 311.1312; found, 311.1316.

**Tert-butyl (3-((2-hydroxyphenyl)thio)but-3-en-2-yl) carbonate (4o)**



Yellow oil. Synthesised by GP4 (84%).

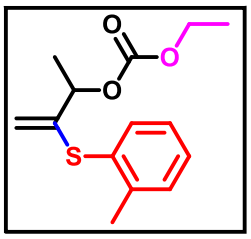
**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ = 7.46-7.44 (m, 1H), 7.36-7.32 (m, 1H), 7.03-7.01 (m, 1H), 6.94-6.89 (m, 1H), 6.44 (s, 1H), 5.31 (m, 1H), 5.18 (q, *J* = 6.57 Hz, 1H), 4.61 (s, 1H), 1.52-1.50 (m, 12H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 157.16, 152.87, 144.83, 136.78, 132.28, 121.07, 115.82, 114.70, 110.29, 82.78, 74.85, 27.79, 20.37.

**IR** ν ($cm^{-1}$): 3413, 2923, 1737, 1382, 1264, 1160, 1090, 767.

**HRMS** (m/z): calculated for $C_{15}H_{21}O_4S$ $[M + H]^+$, 297.1155; found, 297.1159.

**Ethyl (3-(o-tolylthio)but-3-en-2-yl) carbonate (4p)**




Yellow oil. Synthesised by GP4 (66%).

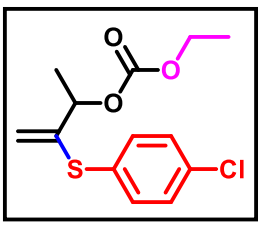
**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ = 7.49 (d, *J* = 7.44 Hz.,1H), 7.26-7.25 (m, 2H), 7.20-7.16 (m, 1H), 5.36 (s, 1H), 5.26-5.22 (q, *J* = 6.55 Hz, 1H), 4.65 (s, 1H), 4.22-4.17 (q, *J* = 7.12 Hz, 2H), 2.40 (s, 3H), 1.54 (d, *J* = 6.55 Hz, 3H), 1.31 (t, *J* = 7.12 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 154.23, 145.15, 141.74, 135.29, 130.76, 130.32, 129.03, 126.78, 111.13, 75.74, 64.05, 20.36, 14.27.

**IR** ν ($cm^{-1}$): 3417, 2924, 1744, 1630, 1379, 1256, 1054, 766.

**HRMS** (m/z): calculated for $C_{14}H_{19}O_3S$ $[M + H]^+$, 267.1049; found, 267.1042.

**3-((4-chlorophenyl)thio)but-3-en-2-yl ethyl carbonate (4q)**




Yellow oil. Synthesised by GP4 (88%).

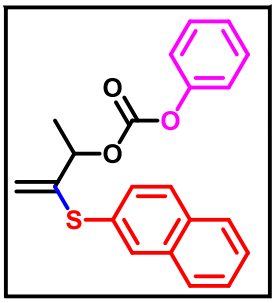
**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ = 7.39-7.37 (m, 2H), 7.31-7.29 (m, 2H), 5.56 (s, 1H), 5.22-5.17 (q, *J* = 6.53 Hz, 1H), 5.12 (s, 1H), 4.20-4.14 (m, 2H), 1.50 (d, *J* = 6.53 Hz, 3H), 1.30 (t, *J* = 7.14 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 154.16, 144.74, 134.17, 133.97, 130.92, 129.44, 115.90, 75.48, 64.11, 20.21, 14.23.

**IR** ν ($cm^{-1}$): 3425, 2926, 1744, 1634, 1381, 1257, 1076, 821.

**HRMS** (m/z): calculated for $C_{13}H_{16}ClO_3S$ $[M + H]^+$, 287.0503; found, 287.0508.

**3-(naphthalen-2-ylthio)but-3-en-2-yl phenyl carbonate (4r)**



Colourless oil. Synthesised by GP4 (70%).

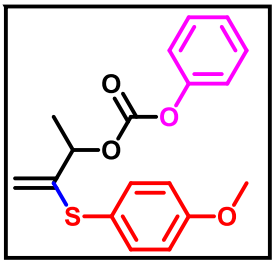
**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ = 7.99 (s, 1H), 7.81-7.77 (m, 2H), 7.52-7.47 (m, 2H), 7.39-7.34 (m, 3H), 7.28-7.18 (m, 3H), 7.14-7.12 (m, 3H), 5.63 (s, 1H), 5.41-5.36 (m, 1H), 5.18 (s, 1H), 1.64-1.61 (m, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 152.72, 151.05, 144.76, 133.80, 132.76, 132.19, 129.81, 129.50, 129.45, 129.01, 127.77, 127.62, 126.65, 126.15, 126.01, 121.03, 120.99, 115.69, 64.85, 20.24.

**IR ν ($cm^{-1}$):** 3401, 2924, 1759, 1383, 1250, 1078, 759.

**HRMS** (m/z): calculated for $C_{21}H_{19}O_3S$ $[M + H]^+$, 351.1049; found, 351.1052.

**3-((4-methoxyphenyl)thio)but-3-en-2-yl phenyl carbonate (4s)**



Colourless oil. Synthesised by GP4 (73%).

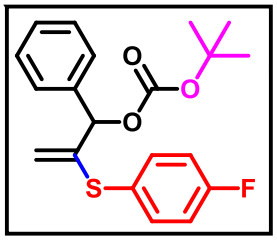
**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ = 7.40-7.36 (m, 5H), 7.28-7.18 (m, 4H), 6.83 (s, 1H), 6.82 (s, 1H), 5.40 (q, *J* = 6.72 Hz, 1H), 3.79 (s, 3H), 1.63 (d, *J* = 6.72 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 159.94, 152.71, 151.04, 132.68, 129.50, 128.46, 126.14, 120.98, 114.63, 64.84, 55.37, 21.23.

**IR** ν ($cm^{-1}$): 3403, 2922, 1384, 1218, 1062, 770.

**HRMS** (m/z): calculated for $C_{18}H_{19}O_4S$ $[M + H]^+$, 331.0999; found, 331.1004.

**Tert-butyl (2-((4-fluorophenyl)thio)-1-phenylallyl) carbonate (4t)**




Colourless oil. Synthesised by GP4 (70%).

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ = 7.56-7.54 (m, 1H), 7.41-7.32 (m, 7H), 7.03-6.99 (m, 1H), 6.02 (s, 1H), 5.56 (s, 1H), 5.10 (s, 1H), 1.47 (s, 9H).

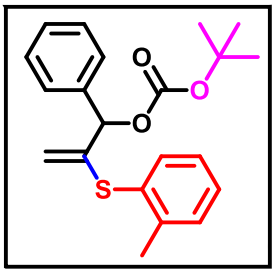
**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 164.09 (d, $J_{C-F}$ = 248.51 Hz), 161.62 (d, $J_{C-F}$ = 248.51 Hz), 152.42, 144.82, 135.68 (d, $J_{C-F}$ = 8.38 Hz), 135.60 (d, $J_{C-F}$ = 8.38 Hz), 129.15, 128.69, 128.43, 127.70, 127.42, 127.24 (d, $J_{C-F}$ = 2.68 Hz), 127.22 (d, $J_{C-F}$ = 2.68 Hz), 116.51 (d, $J_{C-F}$ = 21.94 Hz), 116.29 (d, $J_{C-F}$ = 21.94 Hz), 114.91, 82.69, 79.27, 27.76.

**$^{19}$F NMR (376 MHz, $CDCl_3$):** -112.92 (s, 1F).

**IR** ν ($cm^{-1}$): 3406, 2923, 1741, 1382, 1258, 1157, 1079, 755.

**HRMS** (m/z): calculated for $C_{20}H_{22}FO_3S$ $[M + H]^+$, 361.1268; found, 361.1274.

**Tert-butyl (1-phenyl-2-(o-tolylthio)allyl) carbonate (4u)**



Pale yellow oil. Synthesised by GP4 (72%).

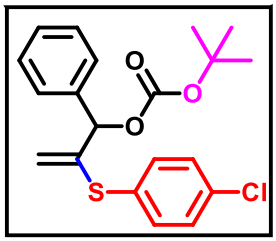
**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ = 7.44-7.30 (m, 7H), 7.26-7.13 (m, 3H), 6.05 (s, 1H), 5.45 (s, 1H), 4.79 (s, 1H), 2.26 (s, 3H), 1.47 (s, 9H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 152.48, 144.26, 141.87, 137.56, 135.38, 130.71, 130.51, 129.00, 128.48, 128.36, 127.35, 126.71, 112.28, 82.59, 79.44, 27.80, 20.31.

**IR** ν ($cm^{-1}$): 3420, 1742, 1626, 1458, 1376, 1263, 1159, 1083, 875, 760.

**HRMS** (m/z): calculated for $C_{21}H_{25}O_3S$ $[M + H]^+$, 357.1519; found, 357.1522.

**Tert-butyl (2-((4-chlorophenyl)thio)-1-phenylallyl) carbonate (4v)**



Pale yellow oil. Synthesised by GP4 (68%).

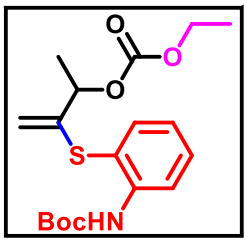
**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ = 7.37-7.31 (m, 6H), 7.30-7.28 (m, 3H), 6.01 (s, 1H), 5.65 (s, 1H), 5.24 (s, 1H), 1.46 (s, 9H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ =152.40, 143.76, 137.21, 134.02, 131.12, 129.39, 128.62, 128.44, 127.70, 127.44, 116.91, 79.29, 75.97, 27.77.

**IR** ν ($cm^{-1}$): 3411, 1741, 1383, 1259, 1158, 1085.

**HRMS** (m/z): calculated for $C_{20}H_{22}ClO_3S$ $[M + H]^+$, 377.0973; found, 377.0978.

**Tert-butyl (2-((3-((ethoxycarbonyl)oxy)but-1-en-2-yl)thio)phenyl)carbamate (4w)**




Colourless oil. Synthesised by GP4 (55%).

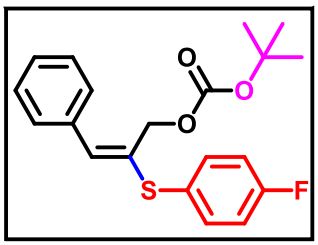
**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ = 8.17 (d, *J* = 8.04 Hz, 1H), 7.54-7.48 (m, 1H), 7.44 (s, 1H), 7.41- 7.37 (m, 1H), 7.04- 7.00 (m, 1H), 5.31 (s, 1H), 5.28-5.23 (q, *J* = 6.49 Hz, 1H), 4.58 (s, 1H), 4.24-4.18 (m, 2H), 1.57-1.55 (m, 3H), 1.51 (s, 9H), 1.32 (t, *J* = 7.14 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ =154.19, 144.46, 140.65, 136.83, 131.15, 123.13, 119.31, 117.04, 110.53, 80.68, 75.52, 64.17, 28.28, 20.40, 14.26.

**IR** ν ($cm^{-1}$): 3780, 3397, 2920, 1736, 1638, 1508, 1453, 1382, 1254, 1073, 948, 755, 668.

**HRMS** (m/z): calculated for $C_{18}H_{26}NO_5S$ $[M + H]^+$, 368.1526; found, 368.1528.

**Tert-butyl (2-((4-fluorophenyl)thio)-3-phenylallyl) carbonate (4x)**




Pale yellow oil. Synthesised by GP4 (72%).

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ = 7.60 (d, *J* = 7.73 Hz, 2H), 7.39-7.34 (m, 4H), 7.30-7.27 (m, 1H), 7.02 (s, 1H), 7.00-6.96 (m, 2H), 4.59 (s, 2H), 1.47 (s, 9H).

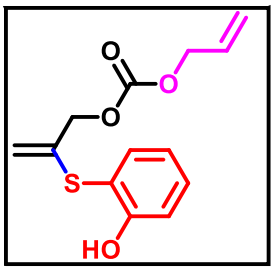
**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 163.45 (d, $J_{C-F}$ = 248.17 Hz), 161.48 (d, $J_{C-F}$ = 248.17 Hz), 152.91, 135.34, 134.32, 133.72 (d, $J_{C-F}$ = 8.12 Hz), 133.66 (d, $J_{C-F}$ = 8.12 Hz), 129.50, 129.20, 128.16, 128.12, 127.78 (d, $J_{C-F}$ = 3.46 Hz), 127.75 (d, $J_{C-F}$ = 3.46 Hz), 116.36 (d, $J_{C-F}$ = 22.21 Hz), 116.18 (d, $J_{C-F}$ = 22.21 Hz), 82.49, 69.16, 27.76.

**$^{19}$F NMR (376 MHz, $CDCl_3$):** -113.84 (s, 1F).

**IR** ν ($cm^{-1}$): 3778, 3399, 3300, 2921, 2853, 1757, 1590, 1246, 1171, 1090, 1028, 918, 825, 756, 682, 526.

**HRMS** (m/z): calculated for $C_{20}H_{22}FO_3S$ $[M + H]^+$, 361.1268; found, 361.1276.

**Allyl (2-((2-hydroxyphenyl)thio)allyl) carbonate (4y)**




Colourless oil. Synthesised by GP4 (65%).

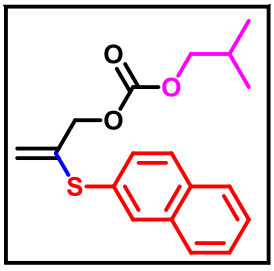
**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 7.47-7.32 (m, 2H), 7.04-6.92 (m, 2H), 6.38 (s, 1H), 5.99-5.89 (m, 1H), 5.41-5.27 (m, 3H), 4.98 (s, 1H), 4.66 (s, 4H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ =157.14, 154.52, 138.27, 136.62, 132.43, 131.35, 121.22, 119.17, 115.71, 115.17, 68.83, 68.55.

**IR** ν ($cm^{-1}$): 3777, 3417, 2923, 1744, 1627, 1458, 1384, 1254, 1101, 767.

**HRMS** (m/z): calculated for $C_{13}H_{15}O_4S$ $[M + H]^+$, 267.0686; found, 267.0681.

**Isobutyl (2-(naphthalen-2-ylthio)allyl) carbonate (4z)**




Colourless oil. Synthesised by GP4 (63%).

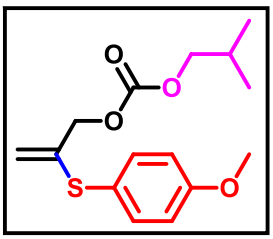
**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 7.94-7.93 (m, 1H), 7.82-7.76 (m, 3H), 7.50-7.47 (m, 3H), 5.61 (s, 1H), 5.37 (s, 1H), 4.69 (s, 2H), 3.91-3.90 (d, *J* = 6.72 Hz, 2H), 1.99-1.92 (m, 1H), 0.94-0.93 (d, *J* = 6.73 Hz, 6H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 154.89, 138.79, 133.77, 132.68, 131.47, 129.52, 129.27, 128.94, 127.76, 127.55, 126.66, 126.56, 118.17, 74.37, 68.53, 27.77, 18.86.

**IR** ν ($cm^{-1}$): 3835, 3737, 3388, 2923, 2856, 2350, 1747, 1617, 1456, 1384, 1250, 1153, 1064, 816, 747, 476.

**HRMS** (m/z): calculated for $C_{18}H_{21}O_3S$ $[M + H]^+$, 317.1206; found, 317.1204.

**Isobutyl (2-((4-methoxyphenyl)thio)allyl) carbonate (4z')**



Colourless oil. Synthesised by GP4 (75%).

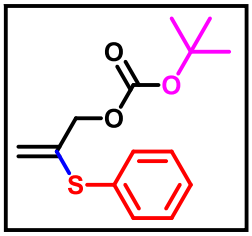
**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 7.41-7.38 (m, 2H), 6.89-6.81 (m, 2H), 5.39 (s, 1H), 5.06(s, 1H), 4.63 (s, 2H), 3.93 (d, *J* = 6.72 Hz, 2H), 3.80 (s, 3H), 2.03-1.93 (m, 1H), 0.95 (d, *J* = 6.72 Hz, 6H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ =160.14, 154.92, 140.72, 135.66, 132.66, 121.75, 114.94, 114.40, 74.33, 68.50, 55.34, 27.78, 18.88.

**IR** ν ($cm^{-1}$): 3917, 3777, 3413, 2924, 2304, 1744, 1598, 1490, 1459, 1383, 1247, 1101, 1032, 827, 765, 628.

**HRMS** (m/z): calculated for $C_{15}H_{21}O_4S$ $[M + H]^+$, 297.1155; found, 297.1164.

**Tert-butyl (2-(phenylthio)allyl) carbonate (4a')**



Colourless oil. Synthesised by GP4 (86%).

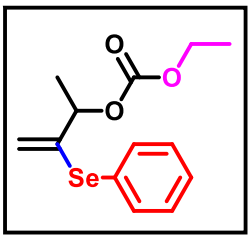
**$^1$H NMR (400 MHz, $CDCl_3$):** δ = 7.45-7.42 (m, 2H), 7.35-7.28 (m, 3H), 5.55 (s, 1H), 5.29 (s, 1H), 4.58 (s, 2H), 1.48 (s, 9H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 152.99, 139.07, 132.37, 132.27, 129.26, 127.89, 117.47, 82.49, 67.69, 27.76.

**IR** ν ($cm^{-1}$): 3782, 2921, 1740, 1382, 1260, 1070.

**HRMS** (m/z): calculated for $C_{14}H_{19}O_3S$ $[M + H]^+$, 267.1049; found, 267.1057.

**Ethyl (3-(phenylselanyl)but-3-en-2-yl) carbonate (7)**



Pale yellow oil. The compound (7) was Synthesized by follow the same procedure GP4 (75%).

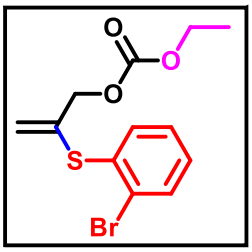
**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ = 7.58-7.56 (m, 2H), 7.31-7.29 (m, 3H), 5.84 (s, 1H), 5.27-5.23 (m, 2H), 4.19-4.13 (m, 2H), 1.49 (d, *J* = 6.54 Hz, 3H), 1.29 (t, *J* = 7.14 Hz, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ =154.15, 142.35, 134.59, 132.46, 129.35, 128.20, 128.04, 118.31, 115.66, 64.03, 20.52, 14.25.

**IR** ν ($cm^{-1}$): 3781, 3397, 2921, 2854, 1742, 1603, 1449, 1381, 1256, 1154, 1063, 1026, 883, 831, 739, 689.

**HRMS** (m/z): calculated for $C_{13}H_{17}O_3Se$ $[M + H]^+$, 301.0337; found, 301.0335.

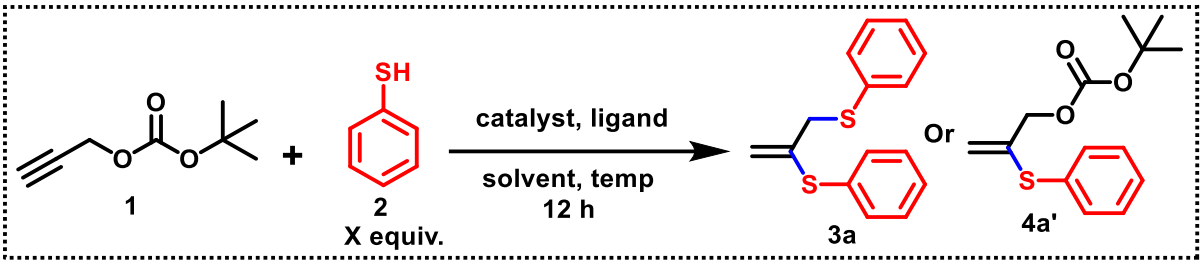
**Ethyl (2-((2-bromophenyl)thio)allyl) carbonate (4i')**



Colourless oil. Synthesised by GP4.

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ = 7.60-7.57 (m, 1H), 7.44-7.42 (m, 1H), 7.30-7.26 (m, 1H), 7.14- 7.09 (m, 1H), 5.76 (s, 1H), 5.47 (s, 1H), 4.66 (s, 1H), 4.21 (q, *J* = 7.16 Hz, 2H), 1.32 (t, *J* = 7.14 Hz, 3H).

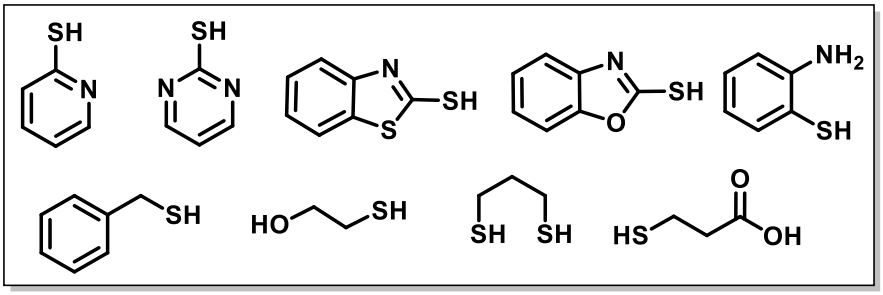
**Table 1. Optimization of the reaction conditions**[a]



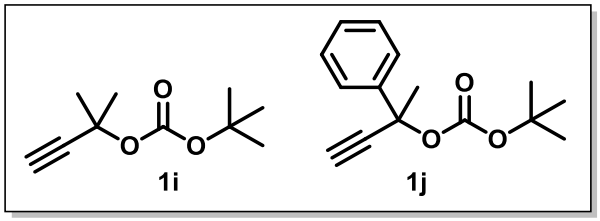

| Entry | Catalyst | ligand | solvent | X(equiv) | Temp. | Yield[b] (%) |
|---|---|---|---|---|---|---|
| 1. | $Pd_2(dba)_3$ | dppb | DMF | 2 | 80ºC | 52 |
| 2. | $Pd(OAc)_2$ | dppb | DMF | 2 | 80ºC | n.r. |
| 3. | $Pd(PPh_3)_4$ | dppb | DMF | 2 | 80ºC | 40 |
| 4. | $Ni(Cod)_2$ | dppb | DMF | 2 | 80ºC | 22 |
| 5. | $Pd_2(dba)_3$ | dppb | ACN | 2 | 80ºC | 63 |
| 6. | $Pd_2(dba)_3$ | dppe | ACN | 2 | 80ºC | 54 |
| 7. | $Pd_2(dba)_3$ | none | ACN | 2 | 80ºC | 30 |
| 8. | $Pd_2(dba)_3$ | Xantphos | ACN | 2 | 80ºC | 64 |
| 9. | $Pd_2(dba)_3$ | X-phos | ACN | 2 | 80ºC | 66 |
| **10.** | **$Pd_2(dba)_3$** | **S-phos** | **ACN** | **2** | **80°C** | **76** |
| 11. | $Pd_2(dba)_3$ | Me-phos | ACN | 2 | 80ºC | 72 |
| 12. | $Pd_2(dba)_3$ | S-phos | Toluene | 2 | 110ºC | 62 |
| 13. | $Pd_2(dba)_3$ | S-phos | 1,4-dioxane | 2 | 100ºC | 70 |
| 14[c]. | $Pd_2(dba)_3$ | S-phos | ACN | 1 | 80ºC | 86[d] |

[a]**Reaction Conditions:** propargyl carbonate (1.1 mmol), thiophenol (2.0 mmol), catalyst (2 mol%), ligand (5 mol%), 0.2 M, 12 h. [b]Determined by $^1$H NMR, [c]propargyl carbonate (1.1 mmol), thiophenol (1.0 mmol), catalyst (2 mol%), ligand (5 mol%), 0.2 M, 80ºC, 12 h. [d]4a' formed.

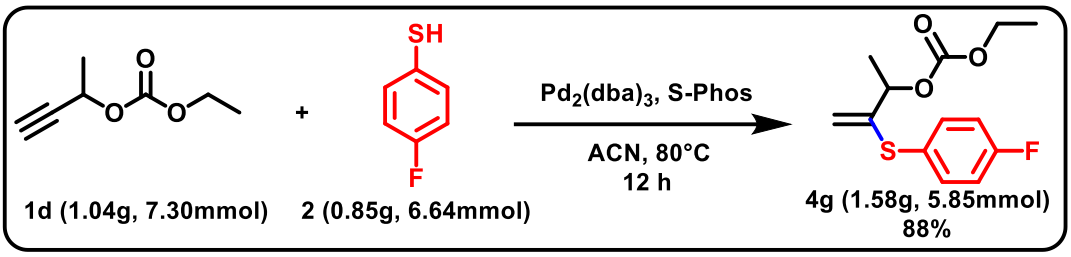
## Unreactive thiols



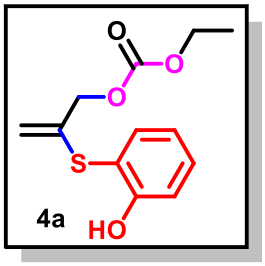

## Unreactive propargyl carbonates



**Gram scale synthesis**




**Confirmation of structure 4a through 1-D & 2-D NMR spectrum**



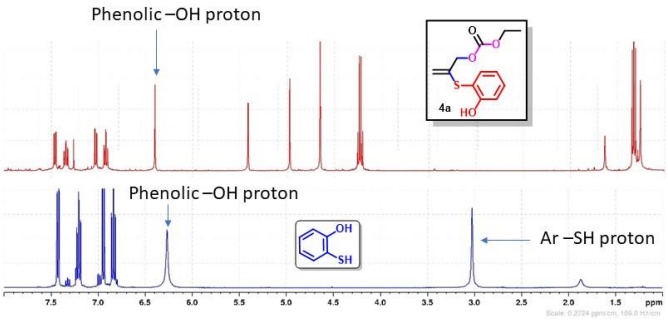




**Fig 1: comparison of $^{1}$H NMR between SM (2-mercapto phenol) and product (4a).**

mono(arylthiol) alkene (**4a**) having free –OH group was observed in a higher yield by using 2-mercapto phenol as a nucleophile. The structure **4a** was identified by 1D and 2D NMR spectrum. We have performed $^{1}$H NMR of 2-mercapto phenol (blue colour spectrum) and our compound **4a** (red colour spectrum). **(Fig 1)**. For 2-mercapto phenol, the phenolic -OH proton comes around δ value 6.26 (s, 1H) and -SH proton around δ 3.02 (s, 1H). In our compound **4a**, there are no peak around δ vale 3.00-4.00, that proves -SH proton is not present in this compound. In 2-mercapto phenol, the phenolic -OH proton is coming around δ value 6.26 and

after formation of mono(arylthiol) alkene (**4a**) that proton is coming in the same region (δ value 6.39). In compound **4a**, δ value 6.39 in proton

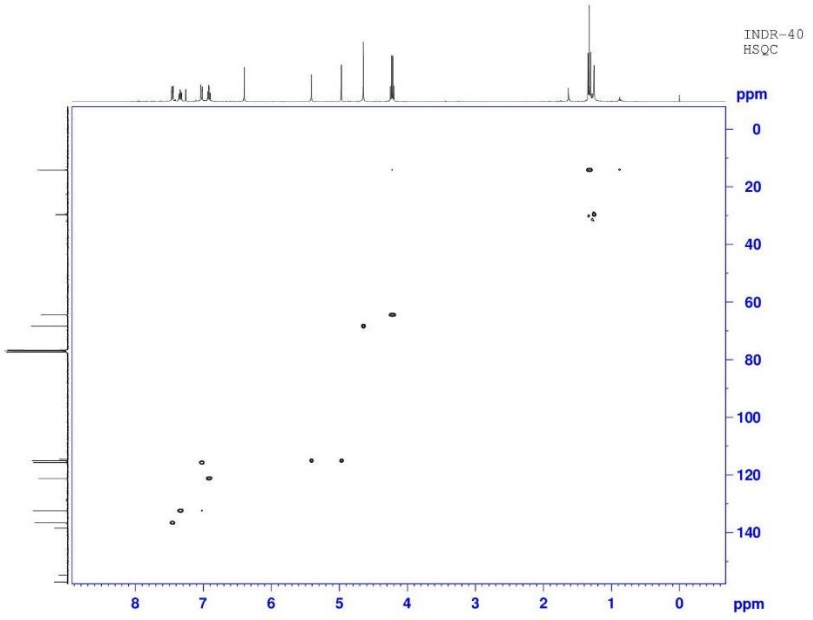



**Fig 2: 2D HSQC spectrum of product (4a).**

NMR corresponds no carbon which show in HSQC spectrum **(Fig 2)**, that proves this is phenolic -OH proton. In our novel methodology, mono(arylthiol) alkenes were formed via newly C-S bond formation through single attack by soft thio nucleophile without any decarboxylation. The phenolic -OH does not react as a nucleophile in our case, that may be more electronegativity of O than S. Another point is that why phenolic -OH group does not react as a second nucleophile by using 2-mercapto phenol as substrate, whereas external thiol attack as a second nucleophile by using 2 equiv. of thiophenol, and intramolecular -SH group attack as a second nucleophile when 2-mercapto thiophenol is used instead of 2-mercapto phenol. This may be -SH group of thiophenol is more reactive as compare to aromatic -OH group.

**Confirmation of structure 4g for mono(arylthiol) alkene product through 1-D & 2-D NMR spectrum**

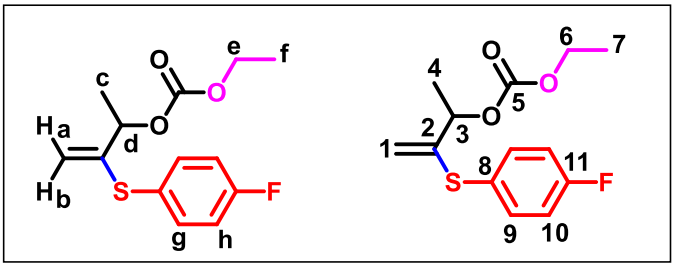



**Fig 3: Protons and carbon numbering of compound (4g).**

The structure **4g** for mono(arylthiol) alkene product was identified and all protons and carbons are assigned by using 1D (1H and 13C) and 2D NMR (COSY, NOESY, HSQC, HMBC) spectrum. In aromatic region two **g** protons are most downfilded, which comes around 7.47-7.43 (m, 2H). After that, two remaining aromatic protons (**h**) are appeared at 7.06-7.02 (m, 2H). Two olefinic protons are identified by NOESY and HSQC. In NOESY spectrum has some weak correlation between δ value 5.46 and δ value 5.20 and strong correlation between δ value 5.46 and δ value 4.96. In HSQC spectrum shows δ value 5.46 and 4.96 corresponds same carbon. That proves 5.46 (s, 1H) is proton **a**, 5.20 (q, *J* = 6.55 Hz, 1H) is proton **d** and 4.96 (s, 1H) is proton **b**. In 1H spectrum same J values and coupling nature shows that 1.50 is coming doublet for 3H **c** protons, 4.18 (q, *J* = 7.19 Hz, 2H) for **e** protons and 1.30 (t, *J* = 7.18 Hz, 3H) for **f** protons. All carbons of compound 4g are assigned by DEPT, HSQC and HMBC spectrum.

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ = 7.47-7.43 (m, 2H, **g**), 7.06-7.02 (m, 2H, **h**), 5.46 (s, 1H, **a**), 5.20 (q, *J* = 6.55 Hz, 1H, **d**), 4.96 (s, 1H, **b**), 4.18 (q, *J* = 7.19 Hz, 2H, **e**), 1.50 (d, *J* = 6.59 Hz, 3H, **c**), 1.30 (t, *J* = 7.18 Hz, 3H, **f**).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 164.11 (d, $J_{C\text{-}F}$ = 248.56 Hz, **C11**), 161.64 (d, $J_{C\text{-}F}$ = 248.56 Hz), 154.17 (**C5**), 145.88 (**C2**), 135.65 (d, $J_{C\text{-}F}$ = 8.38 Hz, **C9**), 135.57 (d, $J_{C\text{-}F}$ = 8.38 Hz), 127.03 (d, $J_{C\text{-}F}$ = 3.49 Hz, **C8**), 126.99 (d, $J_{C\text{-}F}$ = 3.49 Hz), 116.58 (d, $J_{C\text{-}F}$ = 22.11 Hz, **C10**), 116.36 (d, $J_{C\text{-}F}$ = 22.11 Hz,), 113.67 (**C1**), 75.46 (**C3**), 64.06 (**C6**), 20.24 (**C4**), 14.23 (**C7**).

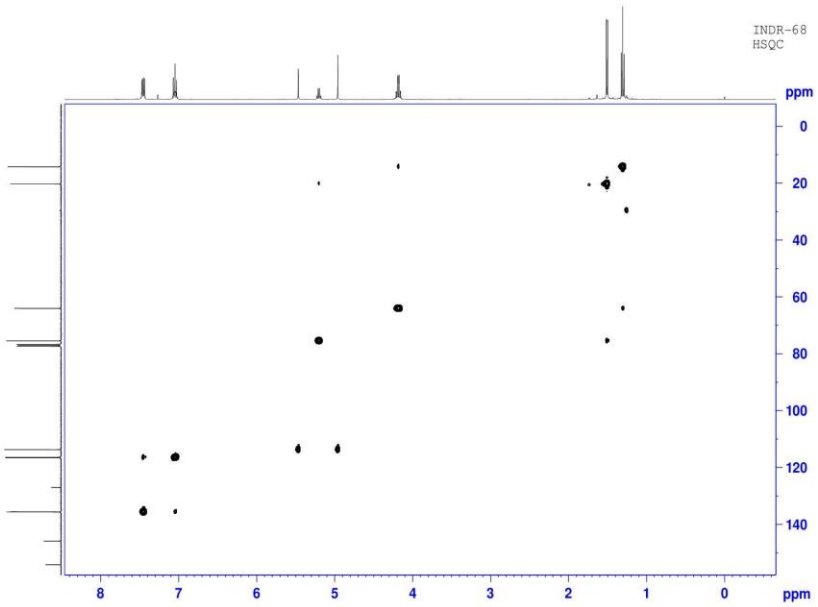



**Fig 4: 2D HSQC spectrum of product (4g).**

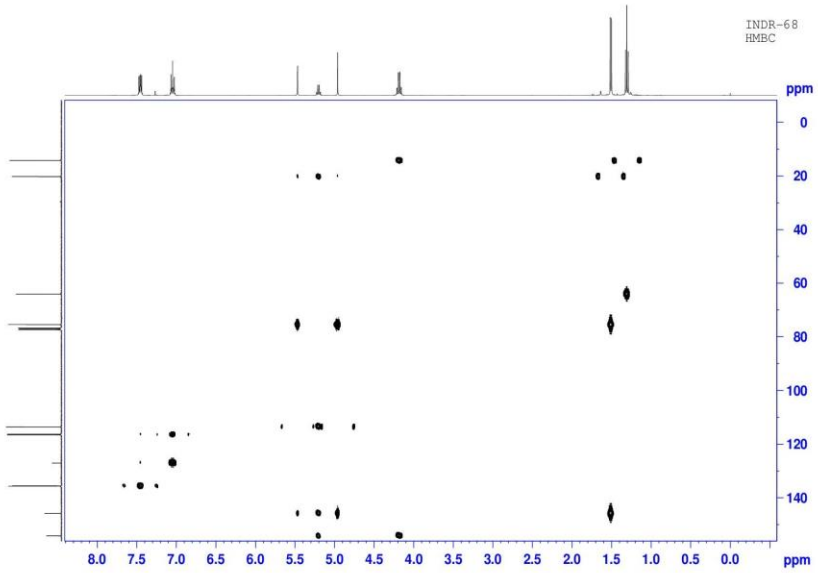



**Fig 5: 2D HMBC spectrum of product (4g).**

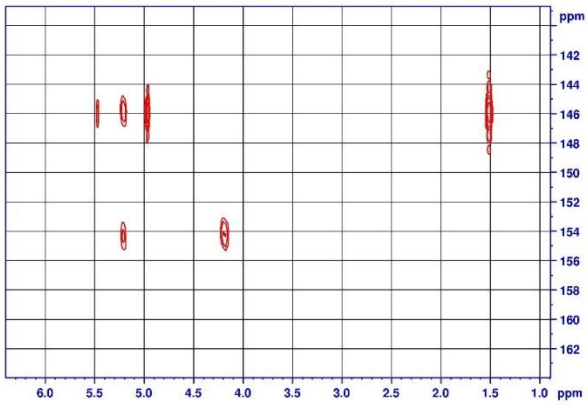



**Fig 6: Magnified 2D HMBC Spectrum of 4g.**

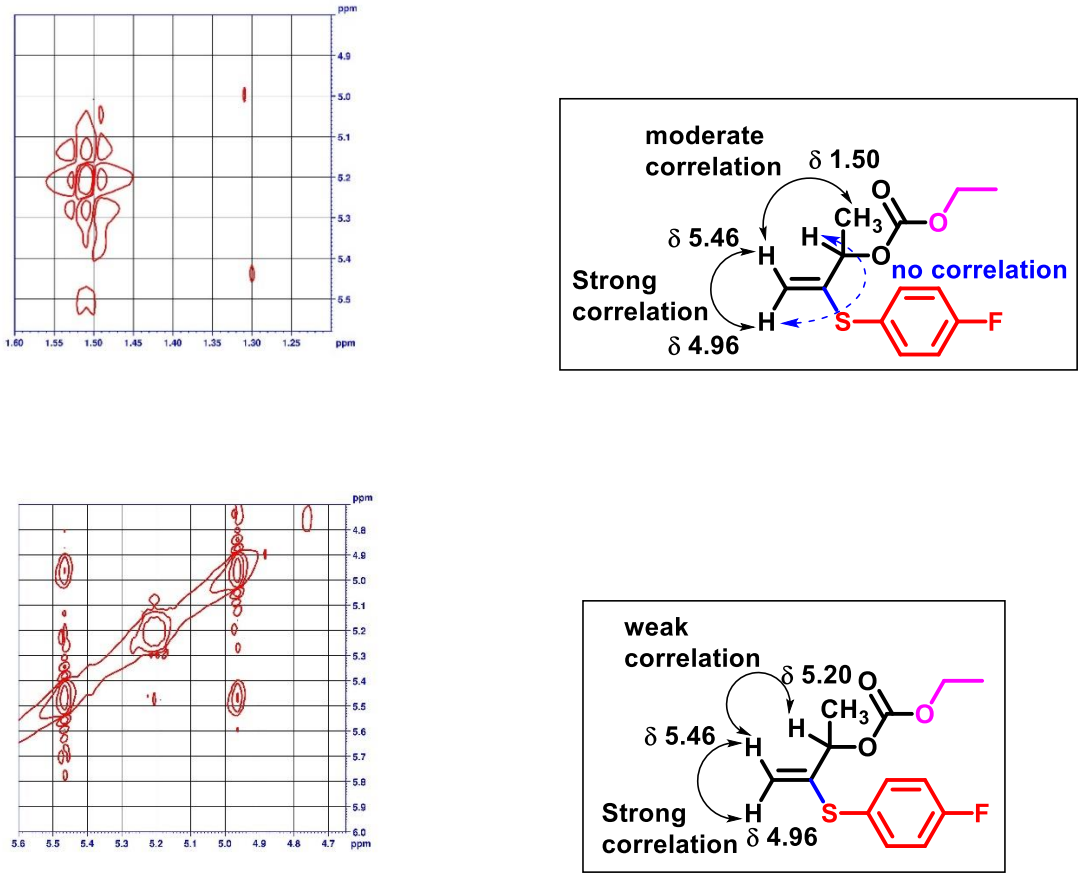



**Fig 7: Magnified 2D NOESY Spectrum of 4g.**

**Confirmation of structure 3a for bis(arylthiol) alkene product with literature-known compound[7] through 1-D NMR spectrum**

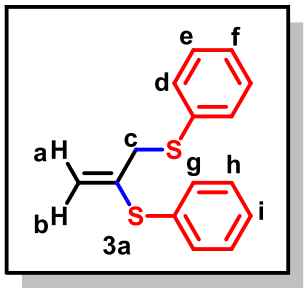



**Fig 8: Protons numbering of compound (3a).**

Our reported spectral data as follow

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ = 7.42-7.41 (m, 2H, **d,e,f,g,h,i**), 7.34-7.27 (m, 6H, **d,e,f,g,h,i**), 7.24 (s, 1H, **d,e,f,g,h,i**), 7.22-7.17 (m, 1H, **d,e,f,g,h,i**), 5.37 (s, 1H, **a,b**), 5.07 (s, 1H, **a,b**), 3.65 (s, 2H, **c**).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 141.13, 133.09, 132.69, 130.76, 130.35, 129.24, 128.84, 128.02, 126.61, 116.94, 40.21.

The same compound was reported by Cohen group[7] (Org. Lett., 2006, 8 (10), 2087-2090). The spectral data of this compound which reported in their manuscript are shown below.

**$^{1}$H NMR (300 MHz, $CDCl_3$):** δ = 3.66 (s, 2H), 5.08 (s, 1H), 5.38 (s, 1H), 7.17-7.44 (m, 10H).

**$^{13}$C NMR (75.5 MHz, $CDCl_3$):** δ = 141.1, 135.7, 133.1, 132.7, 130.3, 129.2, 128.8, 128.0, 126.6, 116.9, 40.2.

**Confirmation of structure 8a through 1-D & 2-D NMR spectrum**

The structure **8a** (1,3-dithiolated product) was identified and all protons and carbons are assigned by using 1D (1H and 13C) and 2D NMR (COSY, NOESY, HSQC, HMBC) spectrum. All assigned protons and carbons are mentioned below.

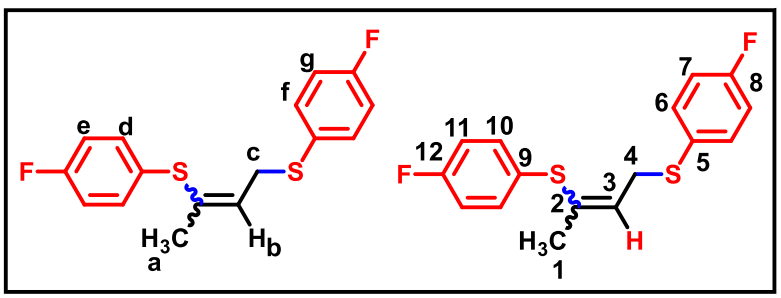
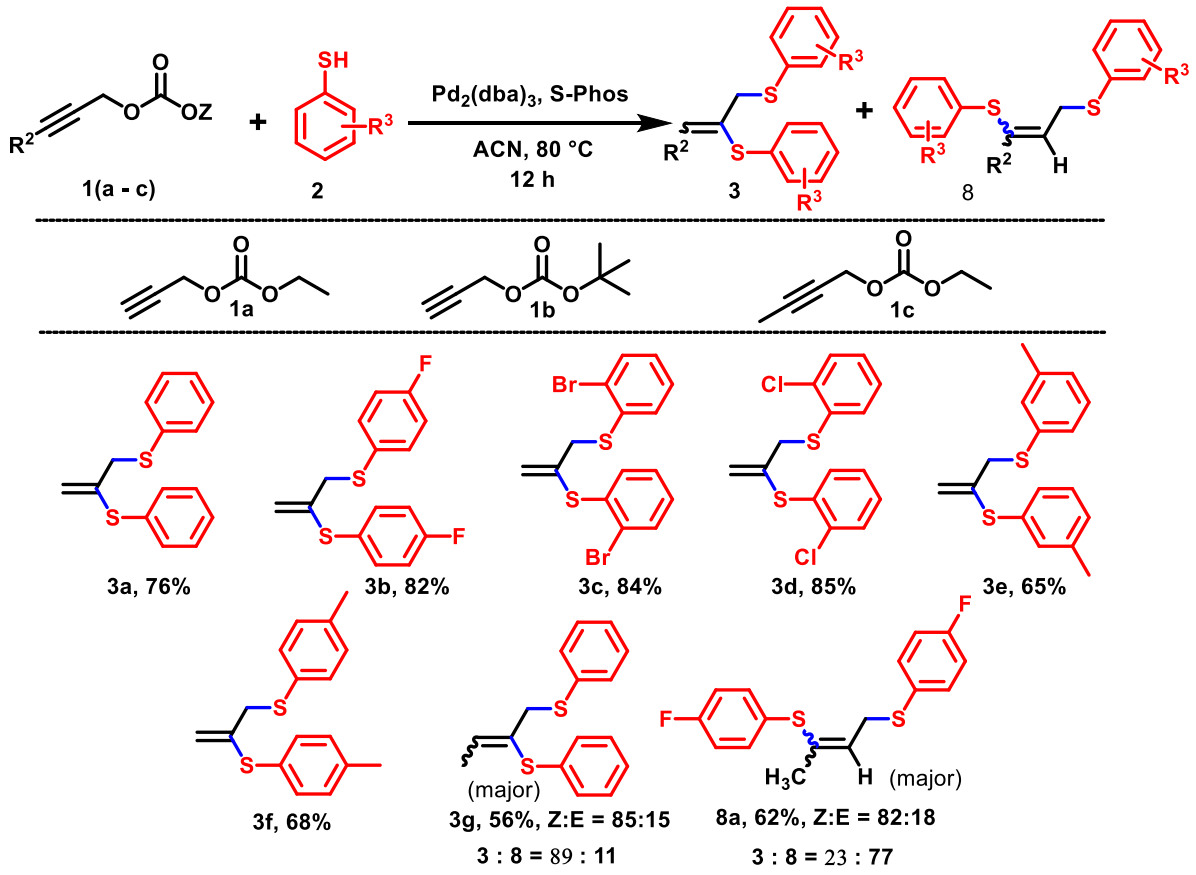


**Fig 9: Protons and carbon numbering of compound (8a).**

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ = 7.38-7.35 (m, 2H, **d,e,f,g**), 7.25-7.21 (m, 2H, **d,e,f,g**), 7.01-6.97 (m, 4H, **d,e,f,g**), 5.56 (qt, *J* = 8.00 Hz, *J* = 1.24 Hz, 1H, **b**), 3.49 (d, *J* = 7.98 Hz, 2H, **c**), 1.64 (s, 3H, **a**).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ = 163.79 (d, $J_{C-F}$ = 248.20 Hz, **C8, C12**), 163.64 (d, $J_{C-F}$ = 247.87 Hz, **C8, C12**), 161.30 (d, $J_{C-F}$ = 248.20 Hz), 161.18 (d, $J_{C-F}$ = 247.87 Hz), 134.79 (**C2**), 134.69 (d, $J_{C-F}$ = 5.03 Hz, **C6, C7, C10, C11**), 134.64 (d, $J_{C-F}$ = 5.03 Hz), 134.61 (d, $J_{C-F}$ = 5.14 Hz, **C6, C7, C10, C11**), 134.56 (d, $J_{C-F}$ = 5.14 Hz), 130.03 (d, $J_{C-F}$ = 4.12 Hz, **C5, C9**), 129.99 (d, $J_{C-F}$ = 4.12 Hz), 128.26 (d, $J_{C-F}$ = 2.64 Hz, **C5, C9**), 128.24 (d, $J_{C-F}$ = 2.64 Hz), 125.20 (**C3**), 116.31 (d, $J_{C-F}$ = 21.87 Hz, **C6, C7, C10, C11**), 116.09 (d, $J_{C-F}$ = 21.87 Hz), 116.05 (d, $J_{C-F}$ = 21.70 Hz, **C6, C7, C10, C11**), 115.83 (d, $J_{C-F}$ = 21.70 Hz), 34.31 (**C4**), 17.38 (**C1**).

**Scheme S1** Substrates scope for Tsuji-Trost-type substitution [a]




[a]**Reaction Conditions:** propargyl carbonate (1.1 mmol), thiophenol (2.0 mmol), catalyst (2 mol%), ligand (5 mol%), 0.2 M, 12 h.

Without any substitution on terminal alkyne of propargyl carbonate, there was no possibility formation of regioisomer **8**. When the methyl group was present in the terminal alkyne of

propargylic carbonate (**1c**), two types of regioisomers were found and the yield of products (**3g** & **8a**) were comparatively poor.

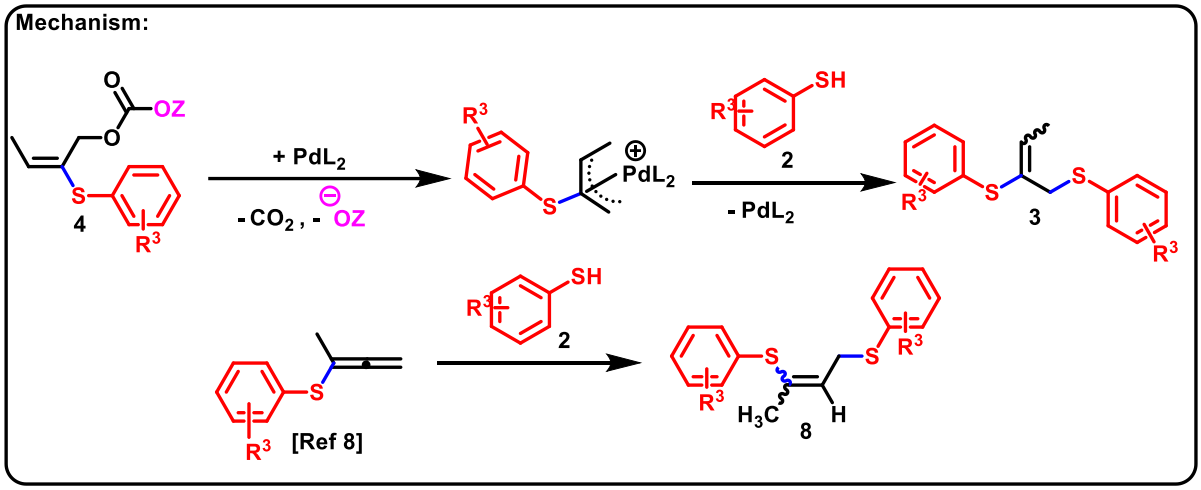



**Fig 10: Plausible reaction mechanism of formation of regioisomer 3 and 8.**

By using normal thiophenol as nucleophile with the reaction of **1c**, the geminal disulfide **3g** was formed. Surprisingly electron withdrawing group containing thiophenol reacted with **1c** to produce another regioisomer **8a** as a major product. The probable reaction mechanism are shown in Fig. 10.

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8. C. Q. O'Broin, P. J. Guiry, *J. Org. Chem.*, 2020, **85**, 10321-10333.

# Palladium-catalyzed Regioselective Synthesis of Mono and Bis(arylthiol) Alkene from Propargyl Carbonate and Thiophenol.

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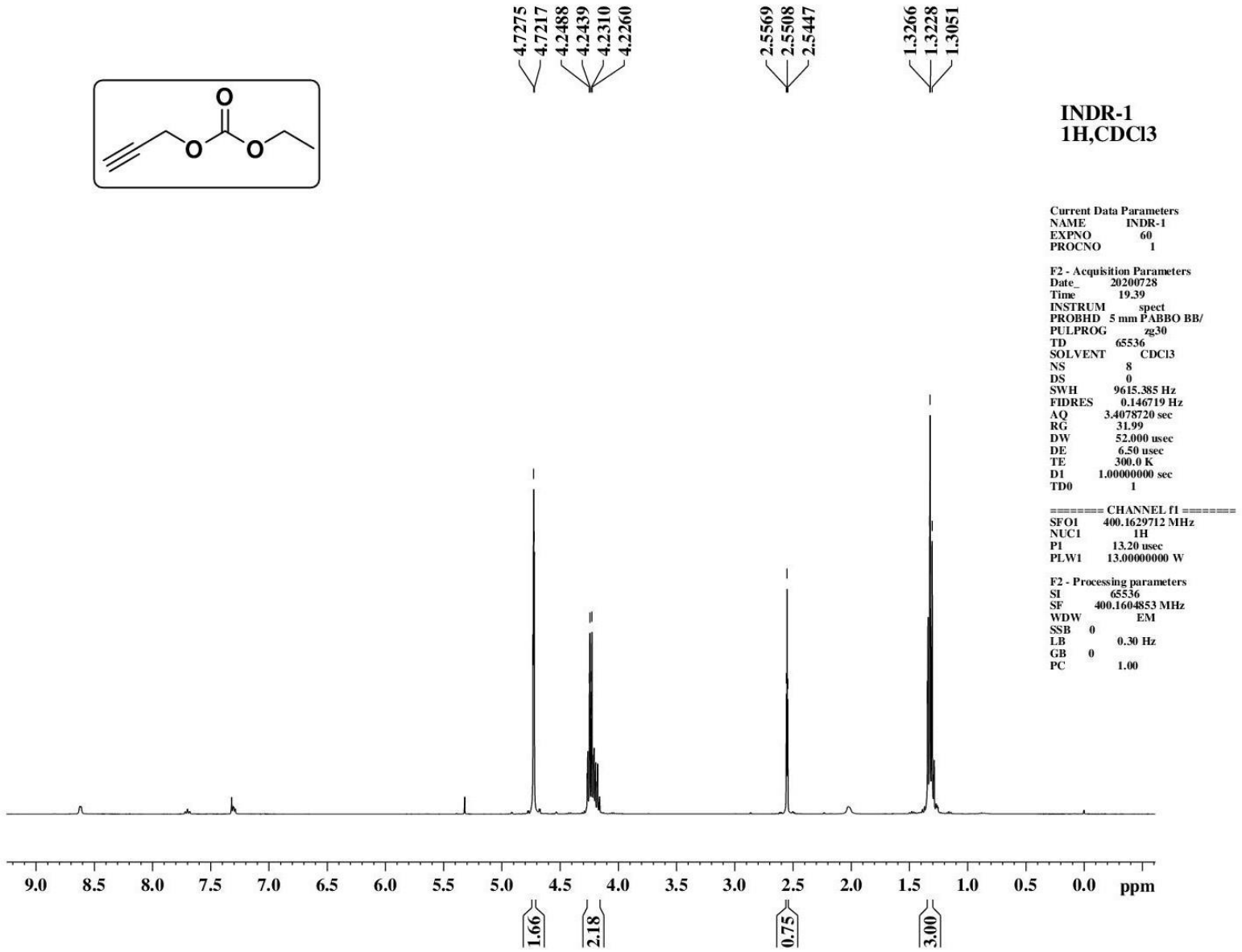



**Fig.S1** $^{1}$H NMR Spectrum of **1a**

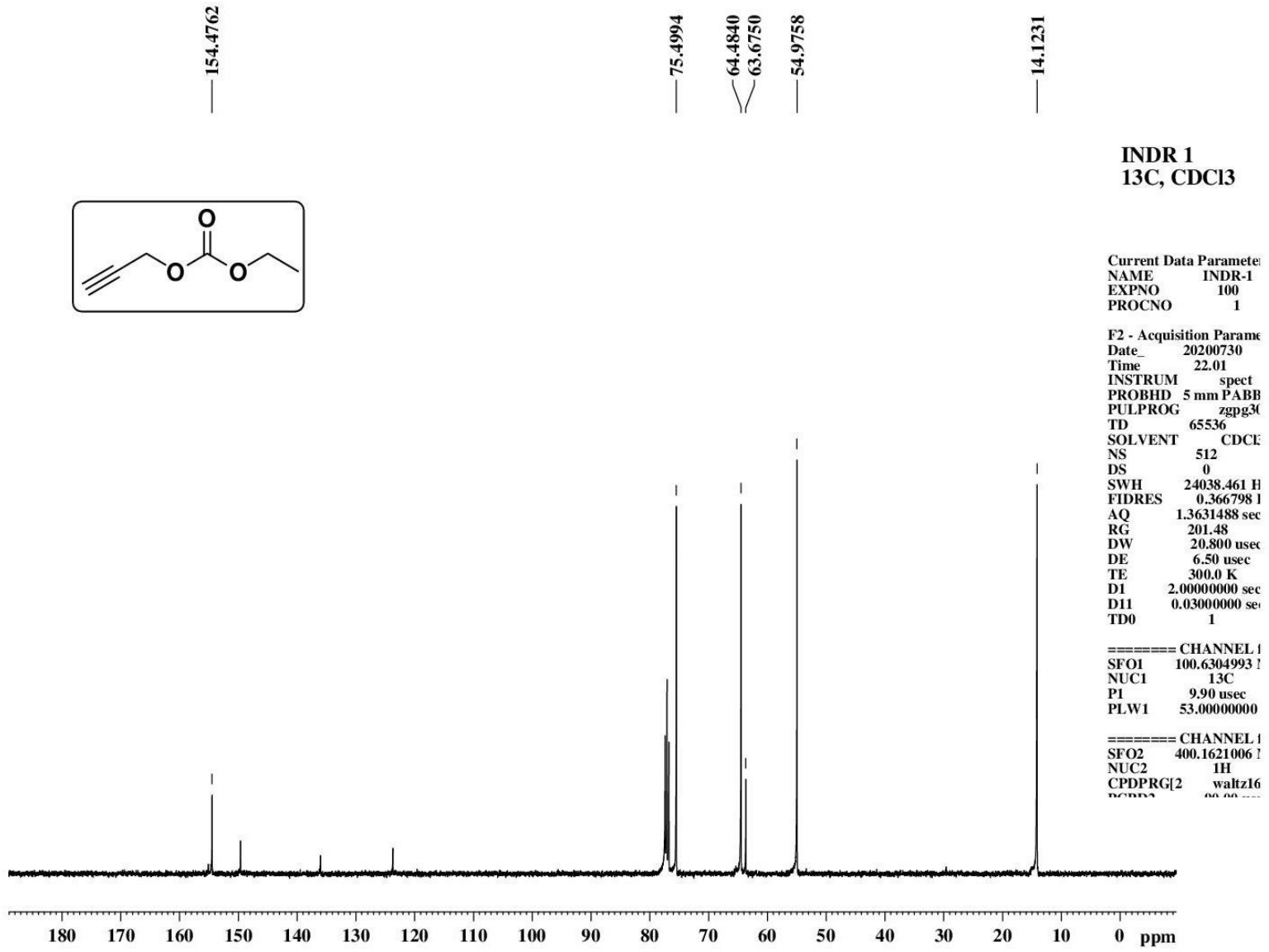



**Fig.S2** $^{13}$C NMR Spectrum of **1a**

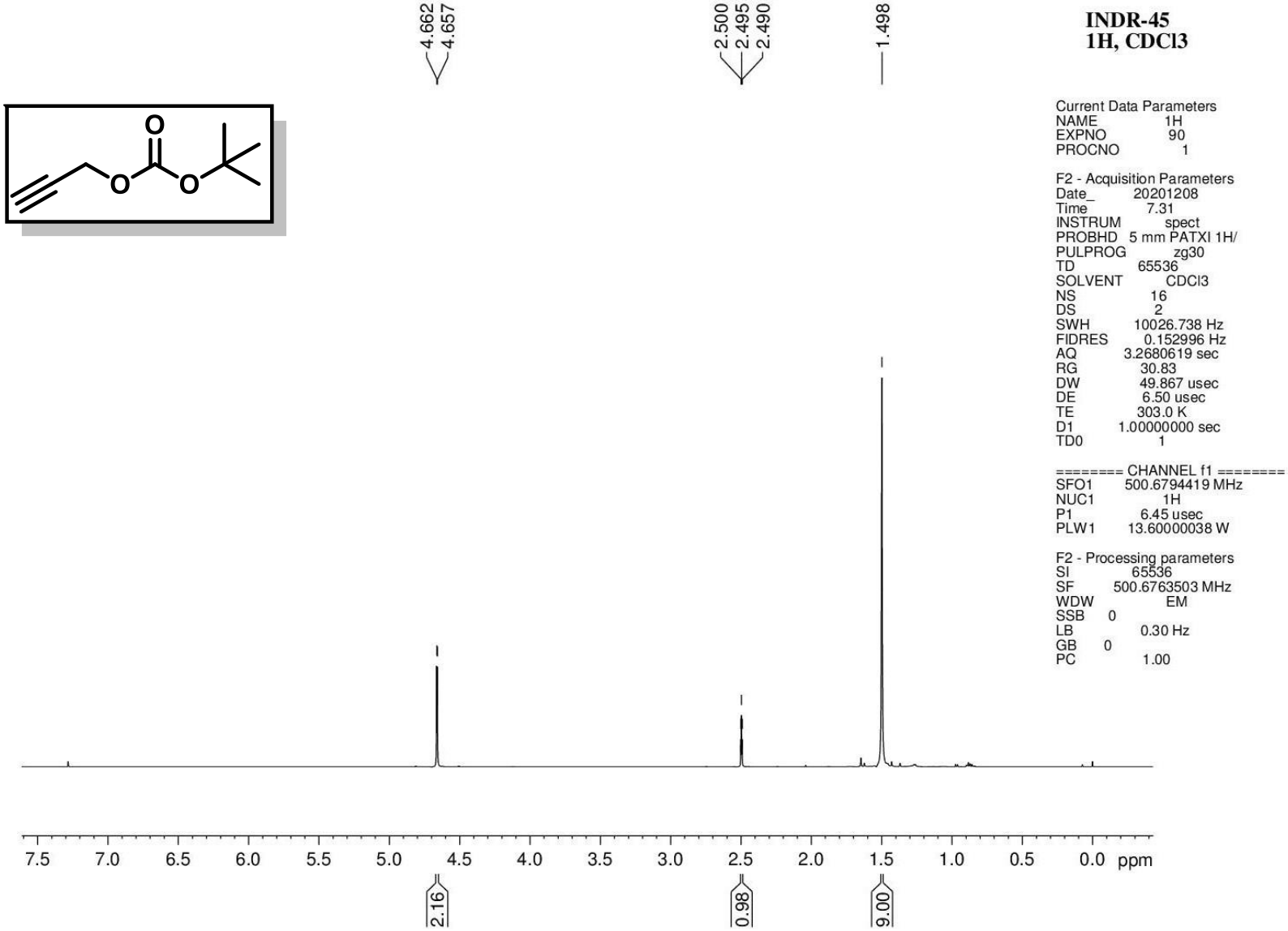



**Fig.S3** $^{1}$H NMR Spectrum of **1b**

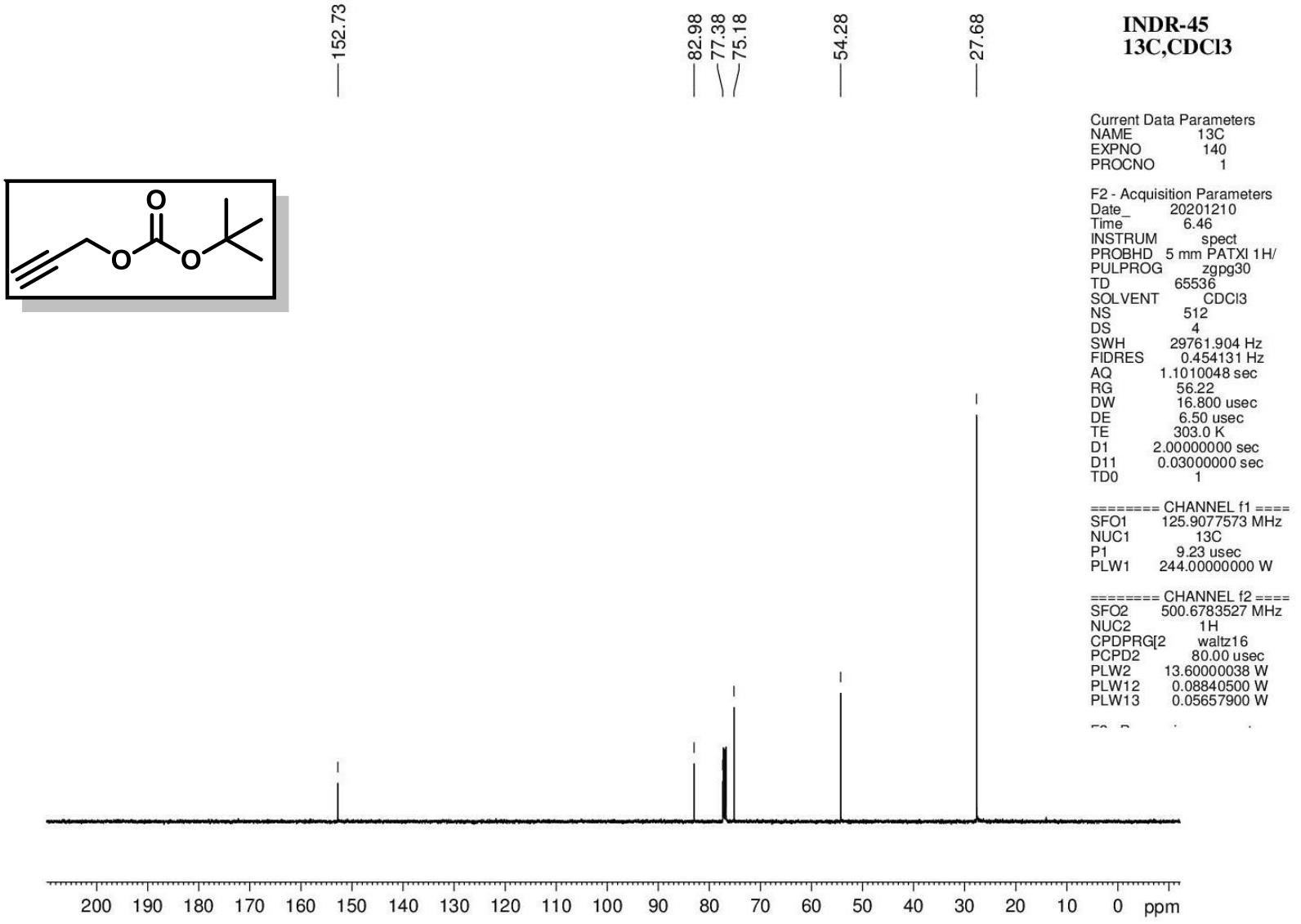



**Fig.S4** $^{13}$C NMR Spectrum of **1b**

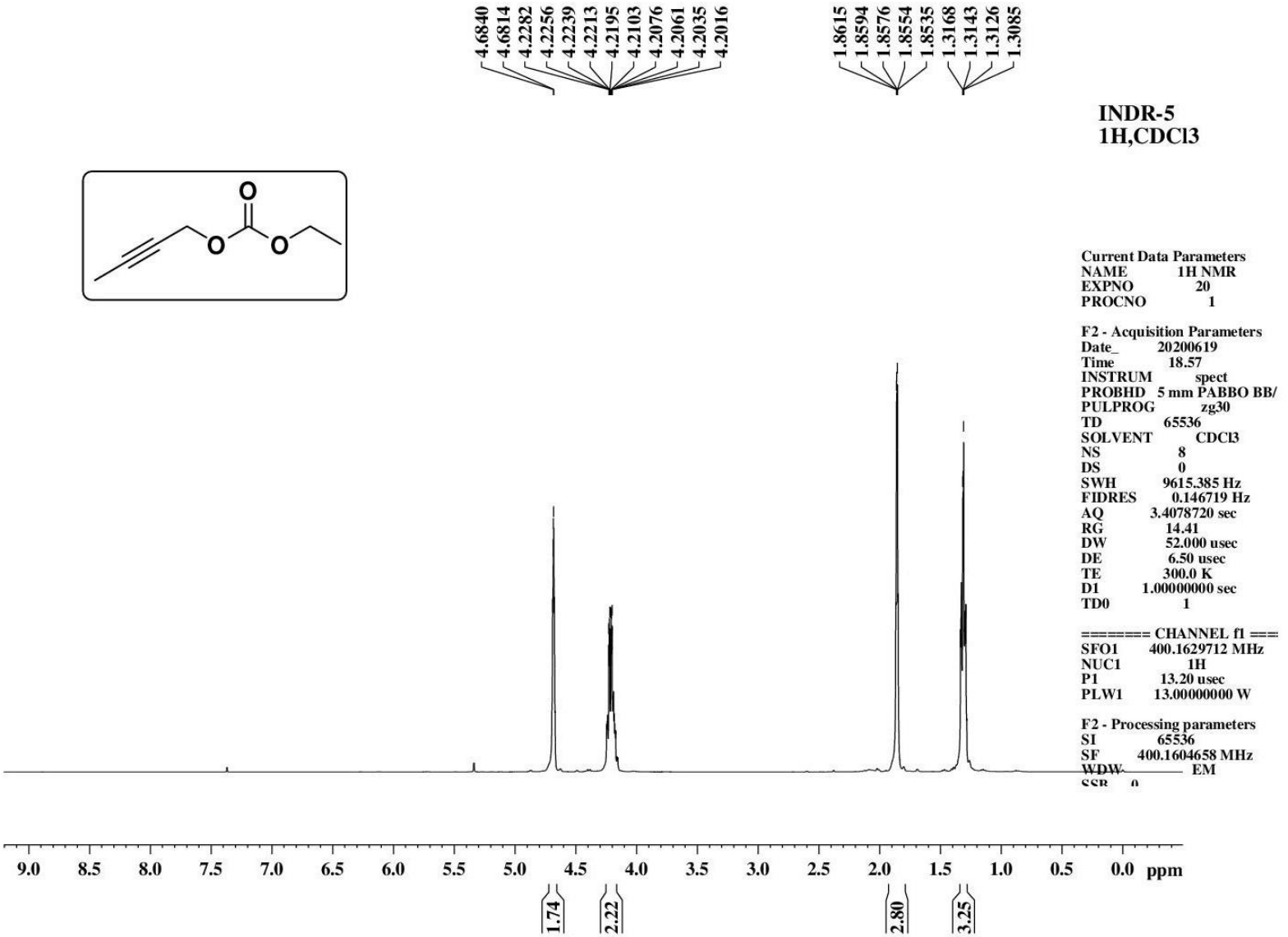



**Fig.S5** $^{1}$H NMR Spectrum of **1c**

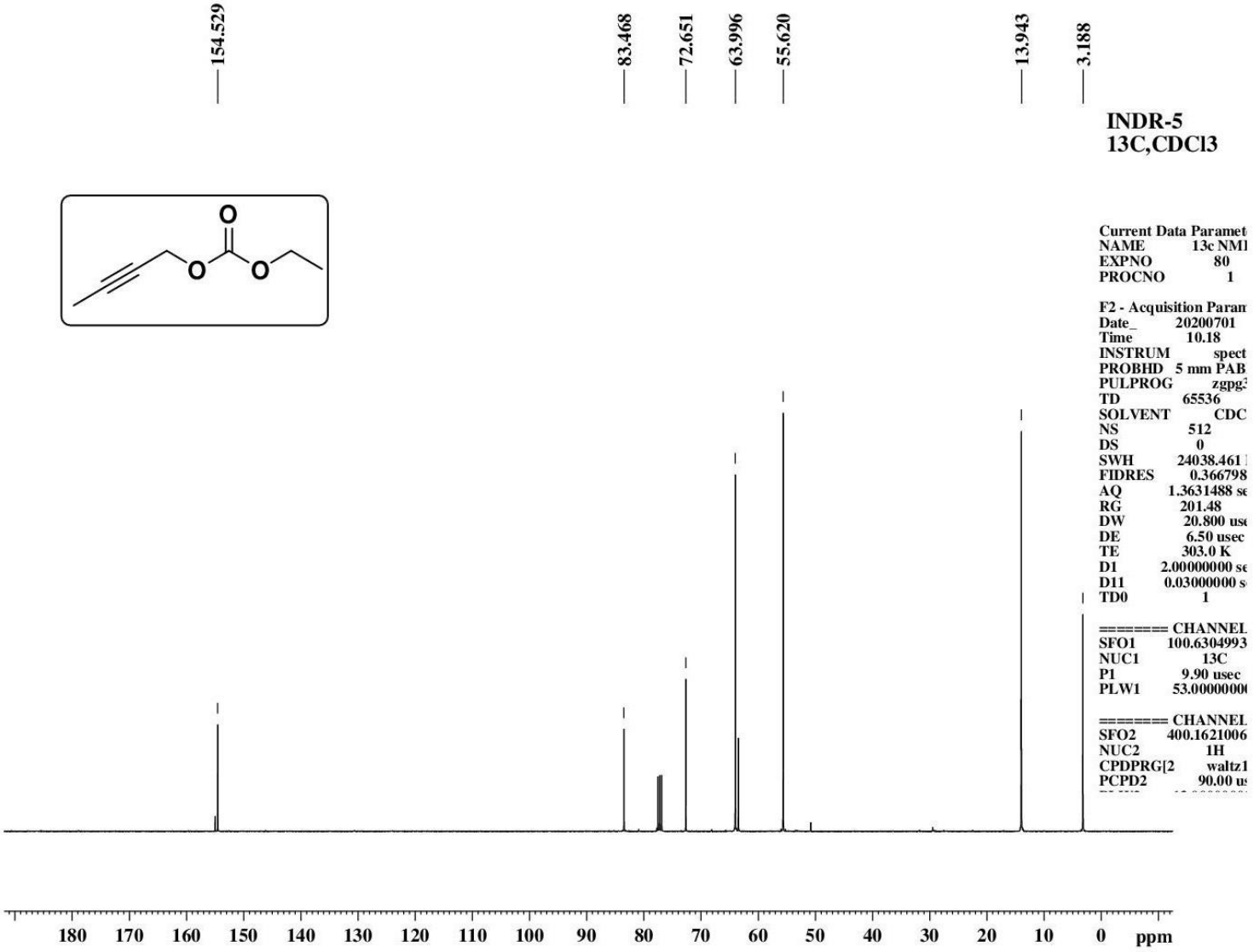



**Fig.S6** $^{13}$C NMR Spectrum of **1c**

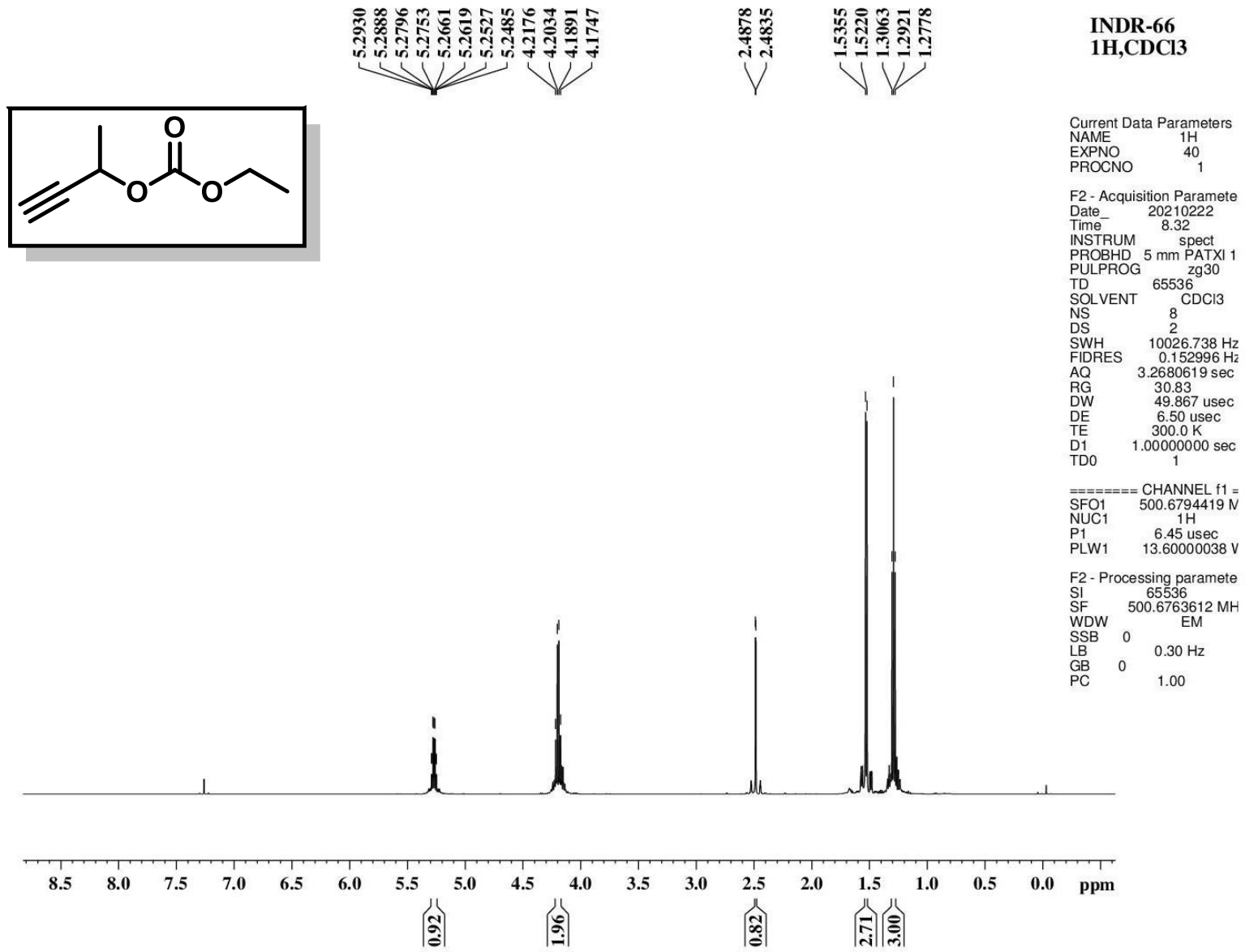



**Fig.S7** $^{1}$H NMR Spectrum of **1d**

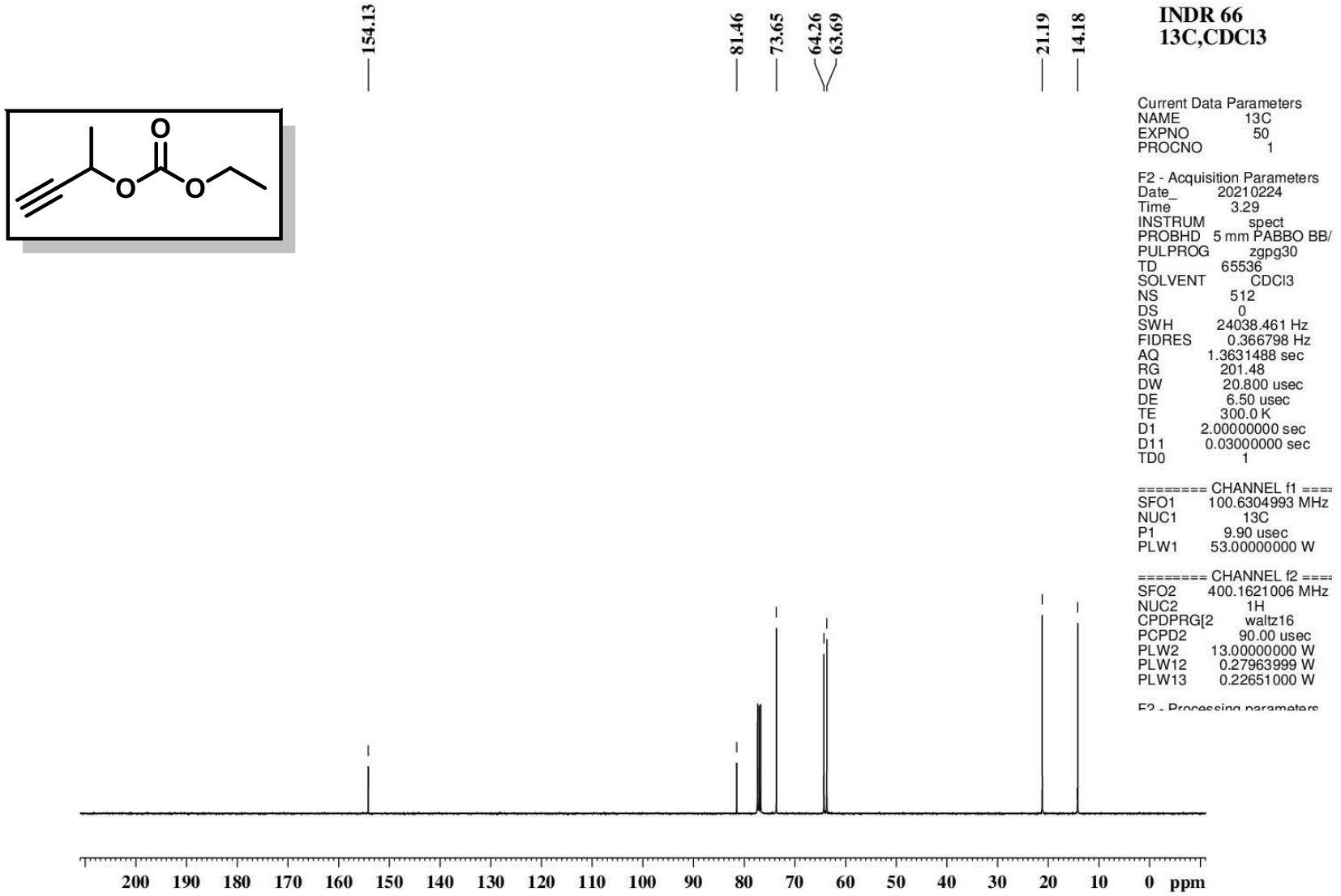



**Fig.S8** $^{13}$C NMR Spectrum of **1d**

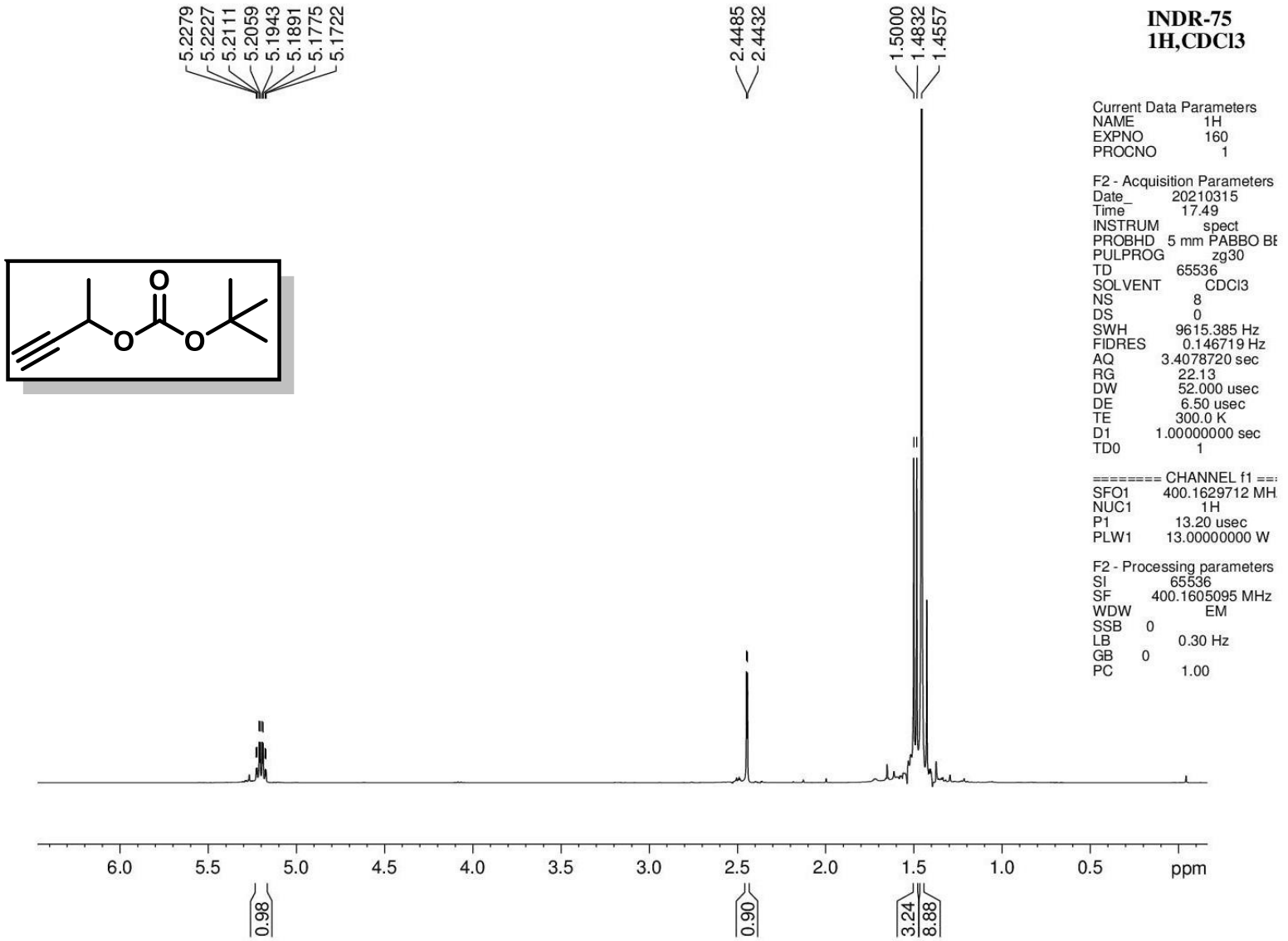



**Fig.S9** $^{1}$H NMR Spectrum of **1e**

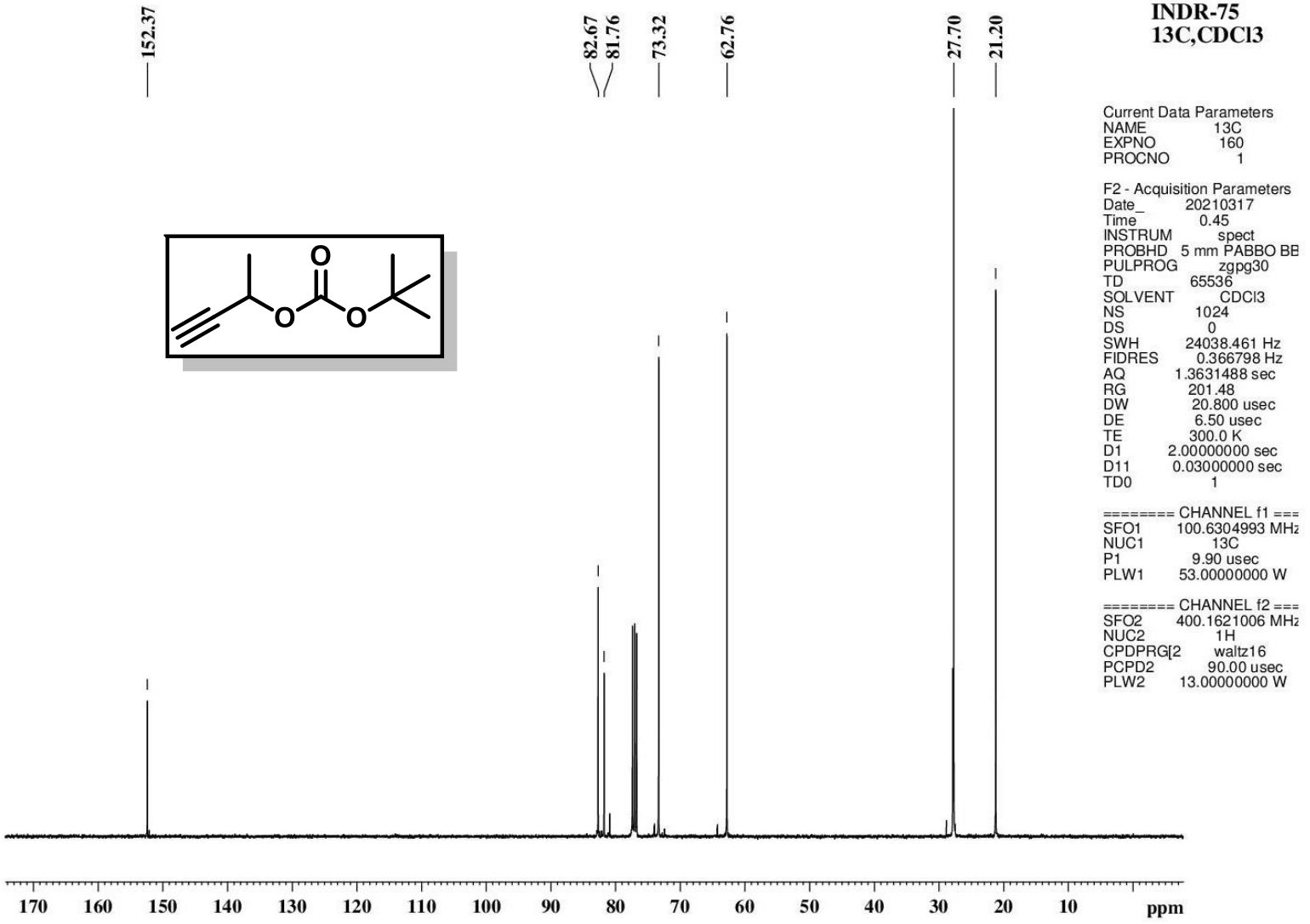



**Fig.S10** $^{13}$C NMR Spectrum of **1e**

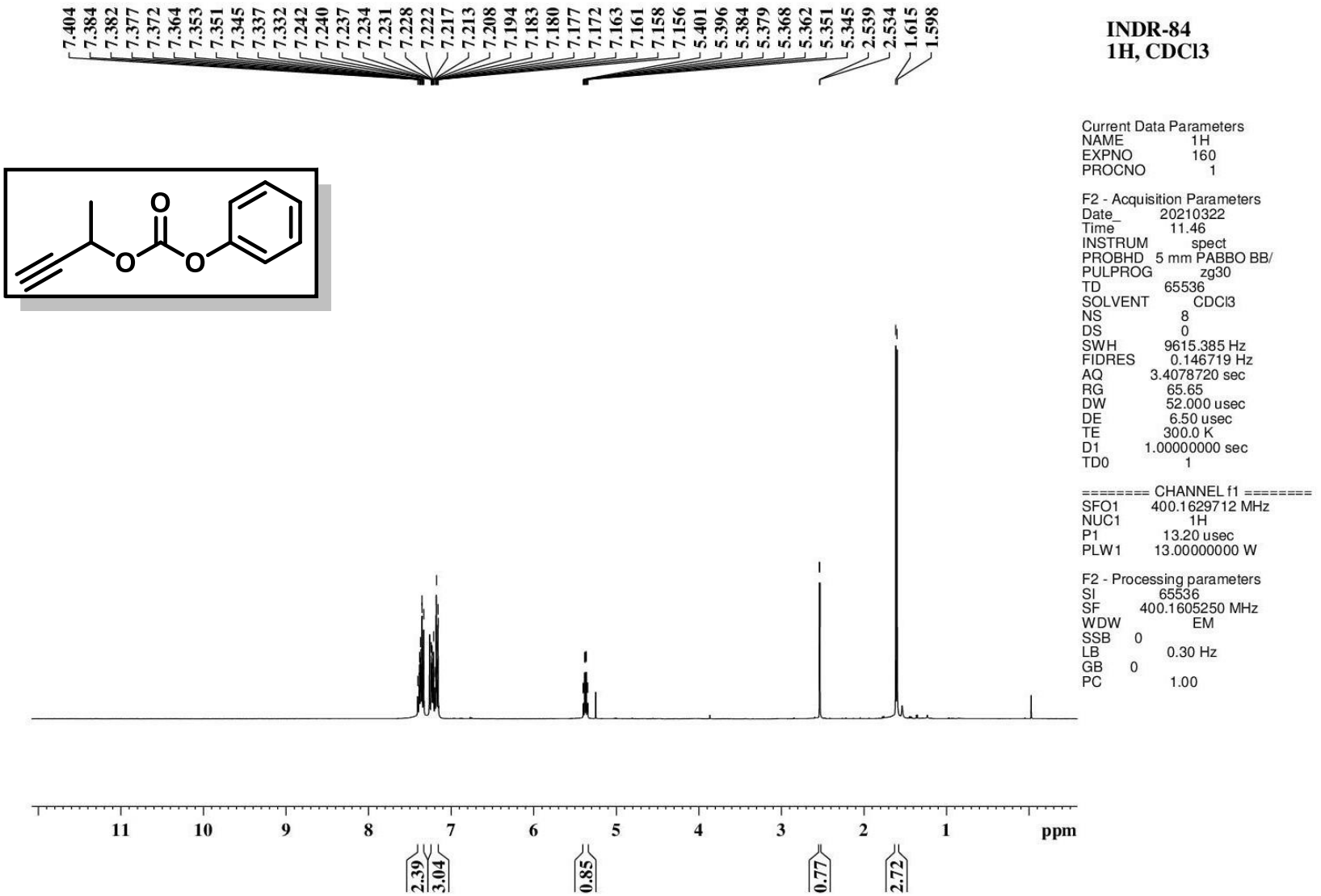



**Fig.S11** $^{1}$H NMR Spectrum of **1f**

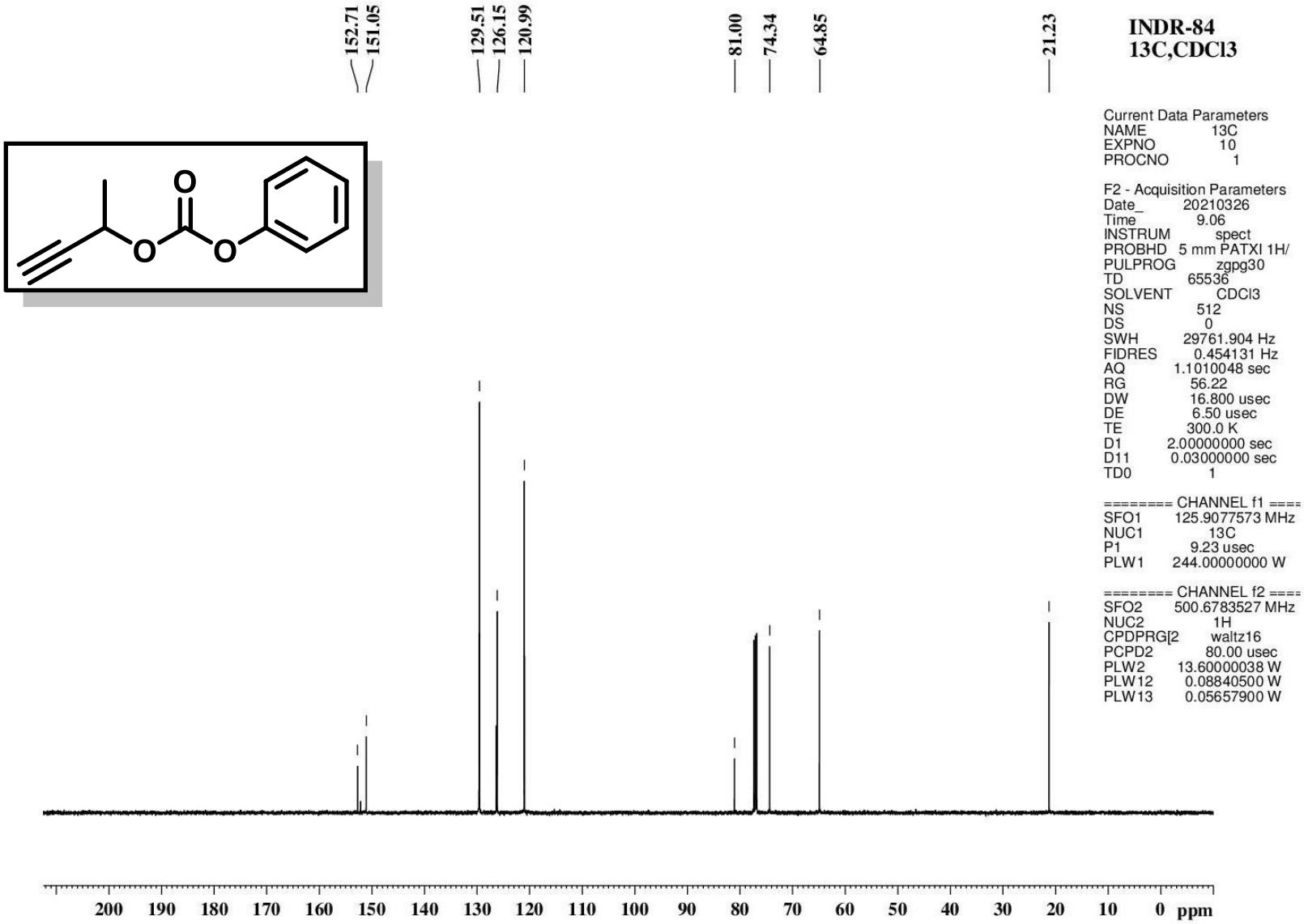



**Fig.S12** $^{13}$C NMR Spectrum of **1f**

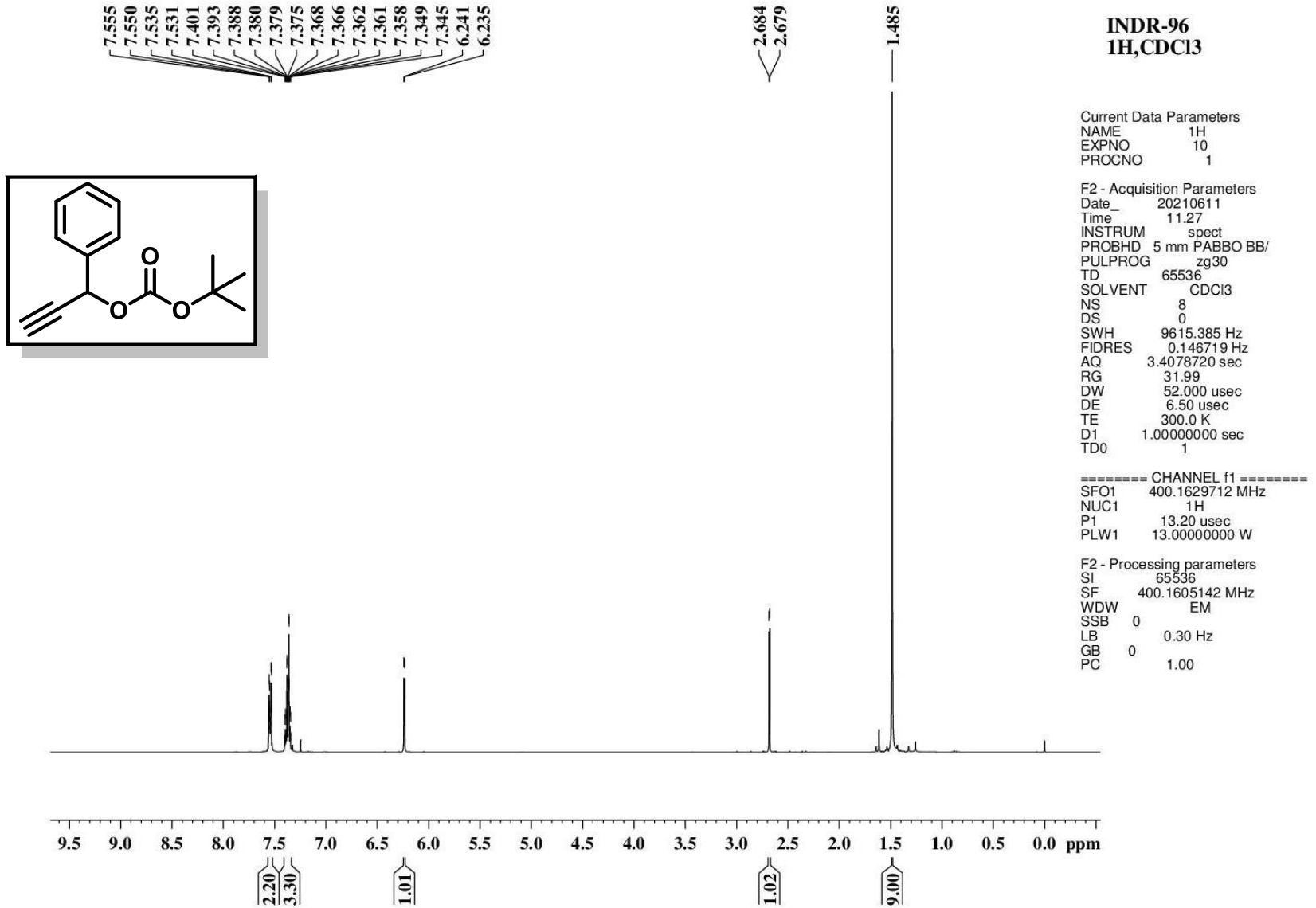



**Fig.S13** $^{1}$H NMR Spectrum of **1g**

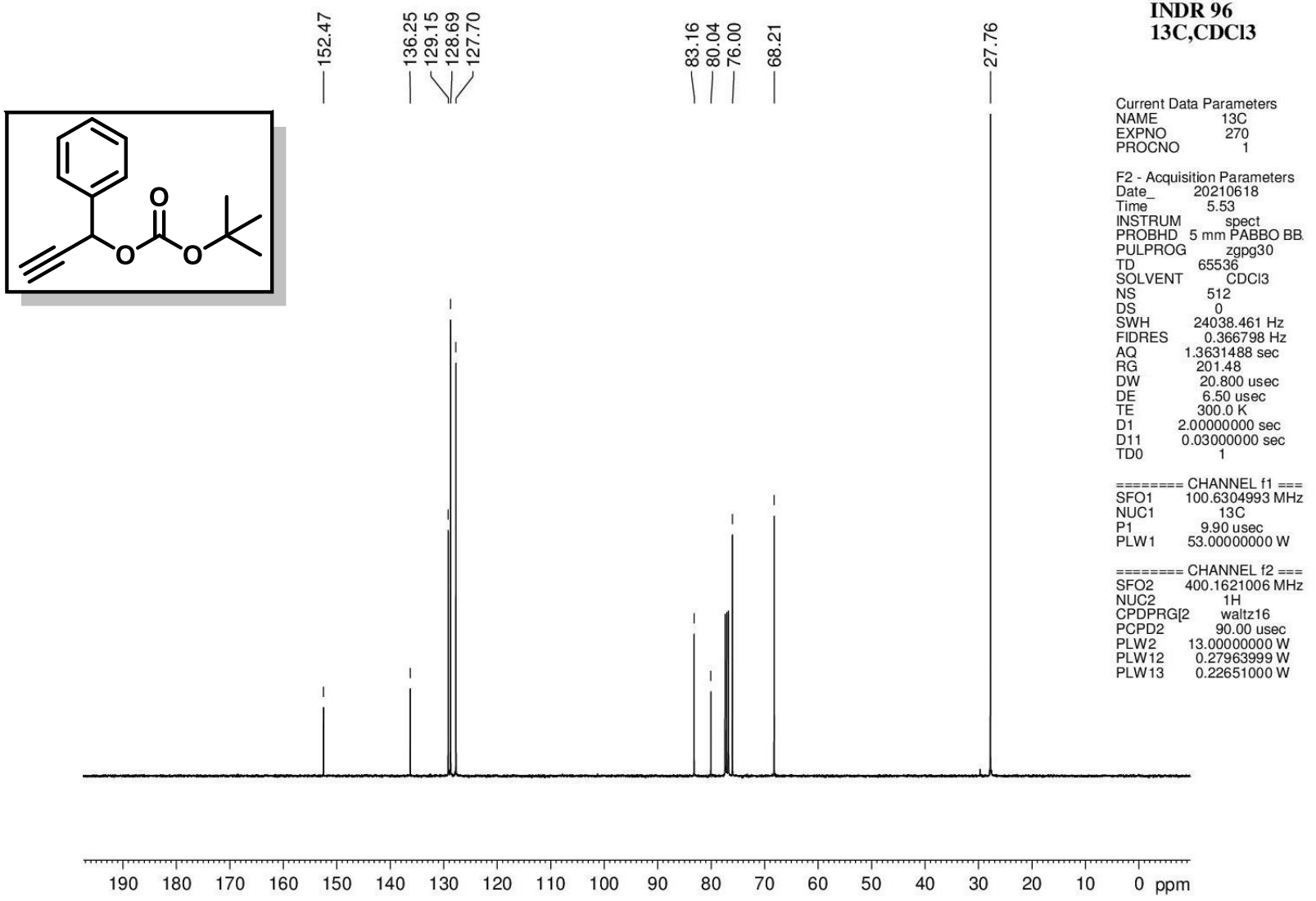



**Fig.S14** $^{13}$C NMR Spectrum of **1g**

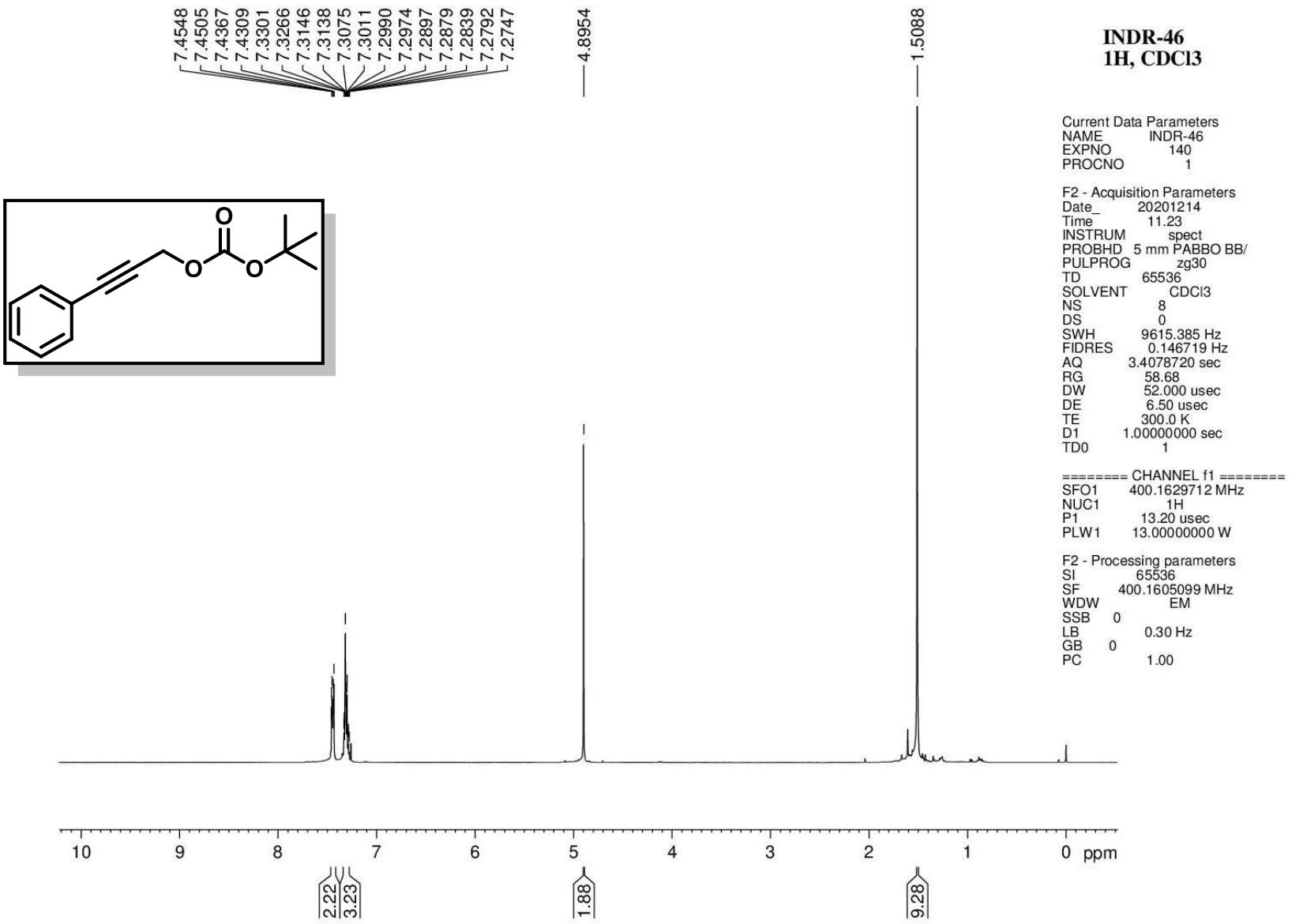



**Fig.S15** $^{1}$H NMR Spectrum of **1h**

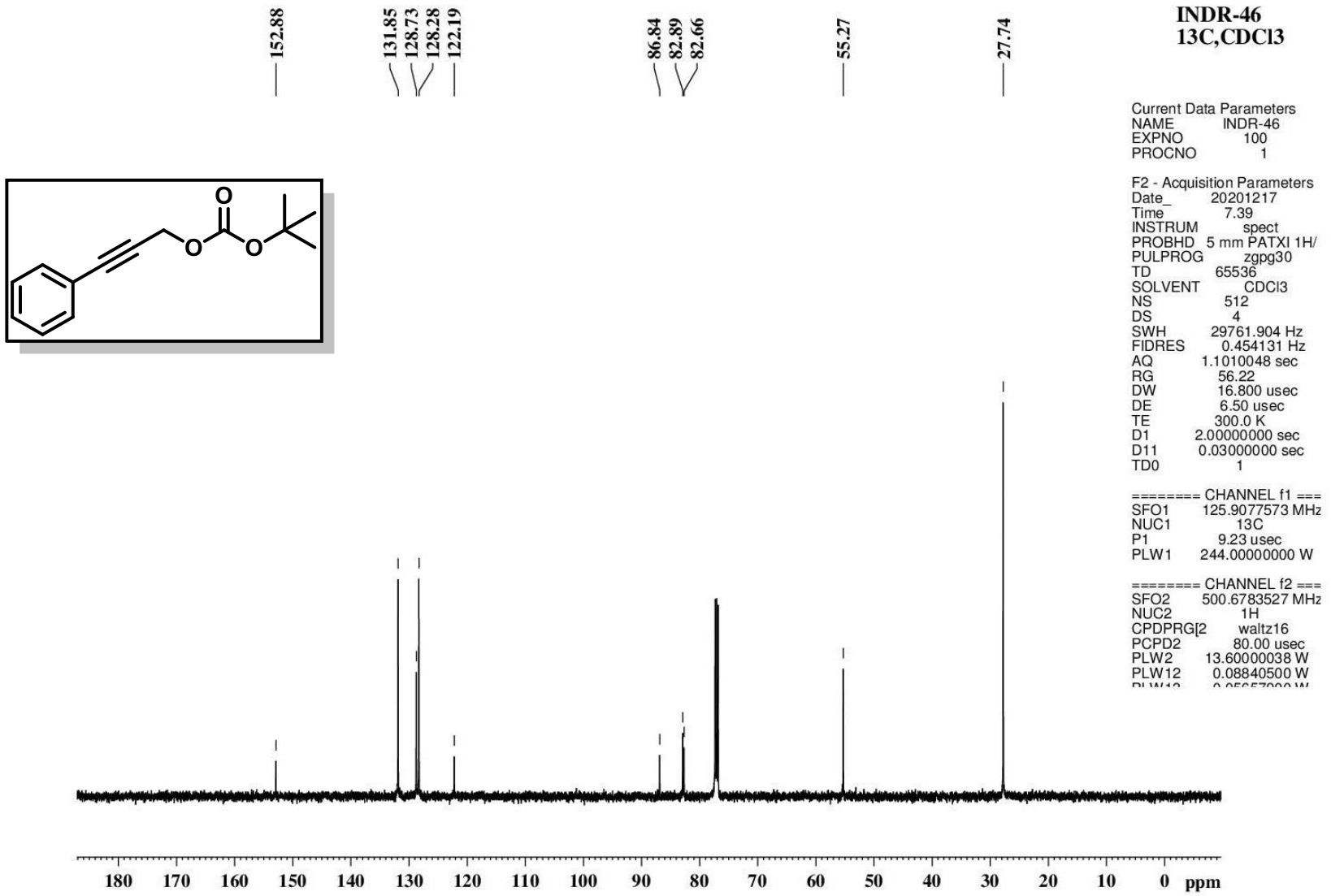



**Fig.S16** $^{13}$C NMR Spectrum of **1h**

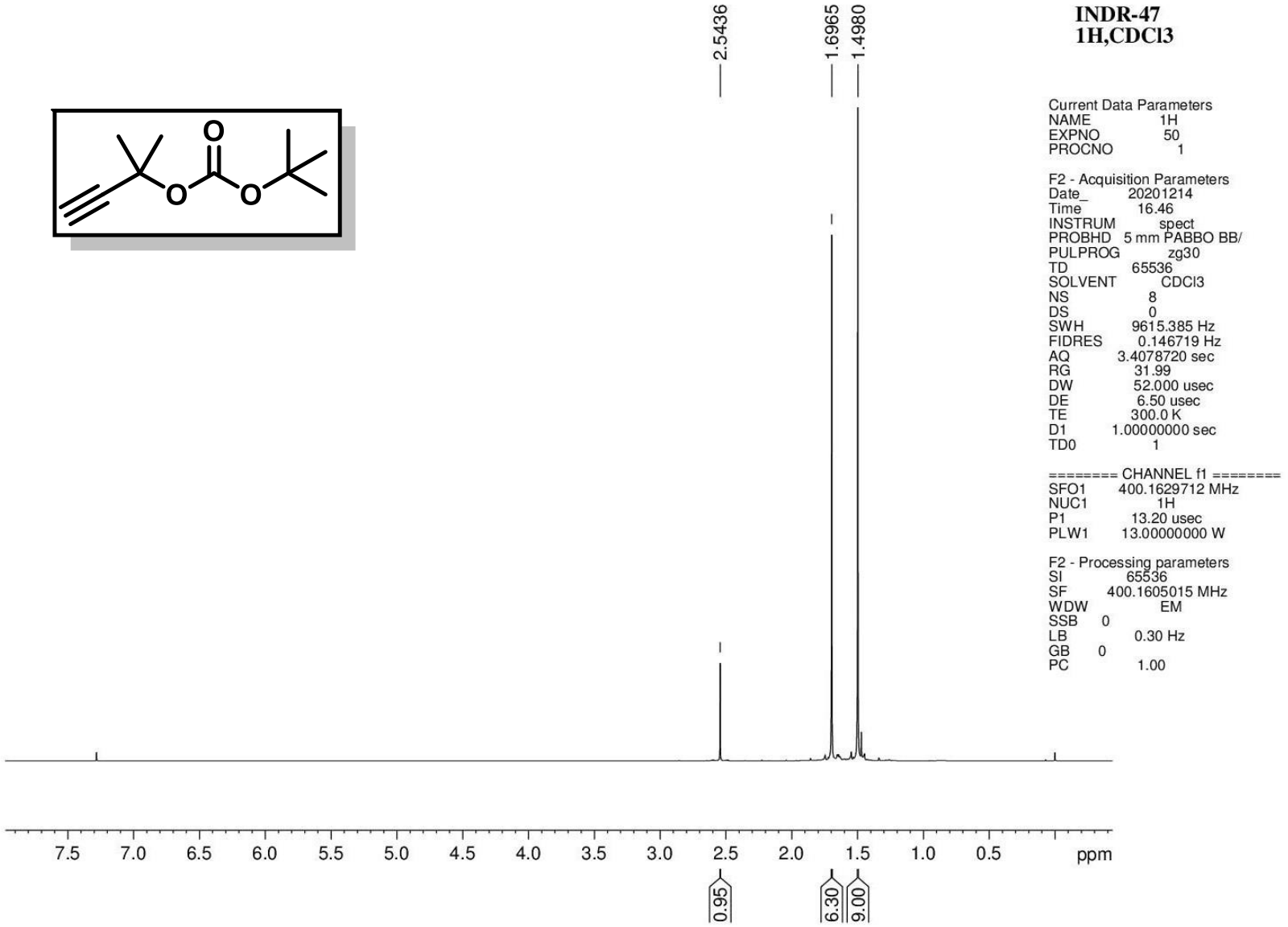



**Fig.S17** $^{1}$H NMR Spectrum of **1i**

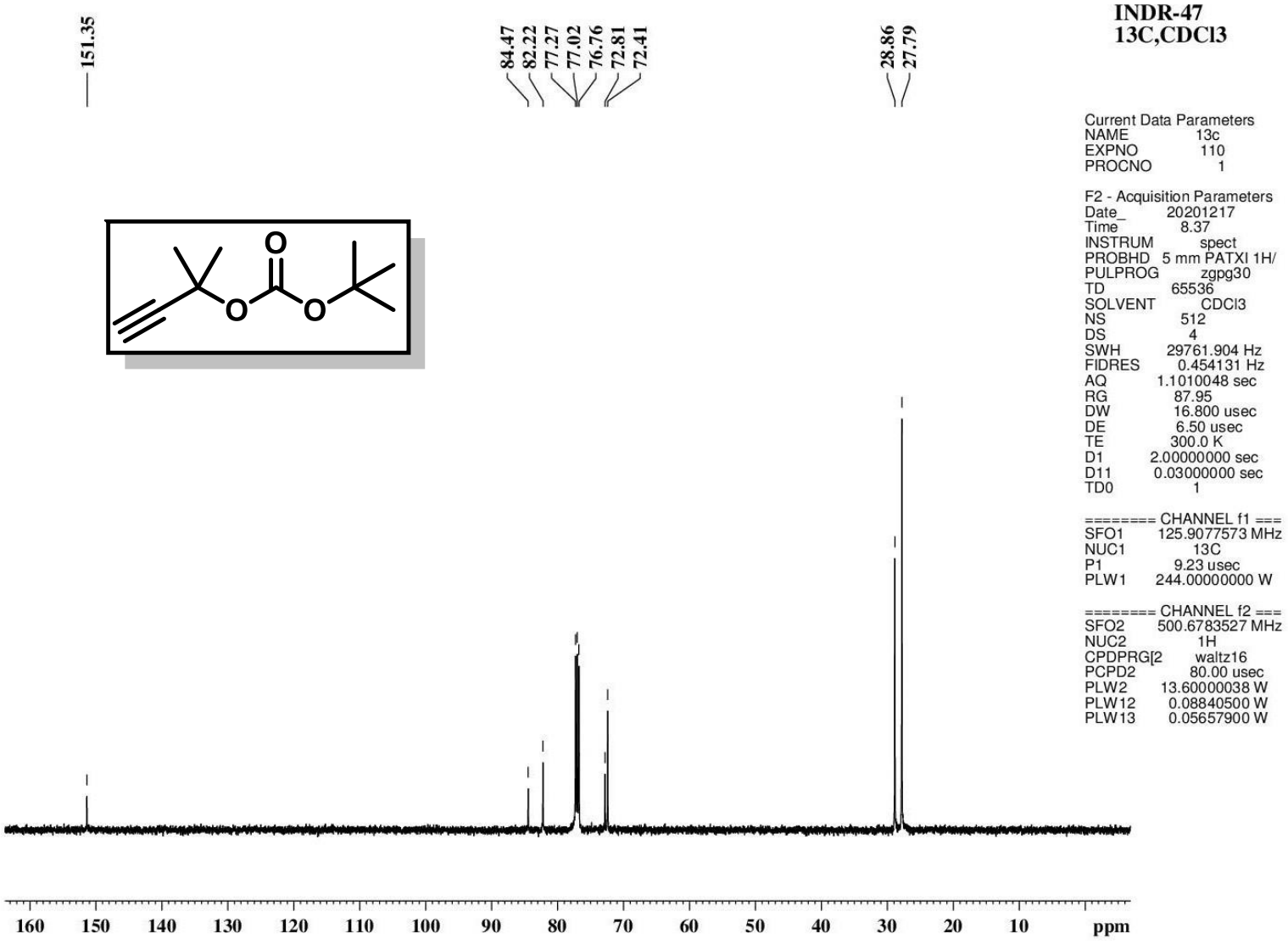



**Fig.S18** $^{13}$C NMR Spectrum of **1i**

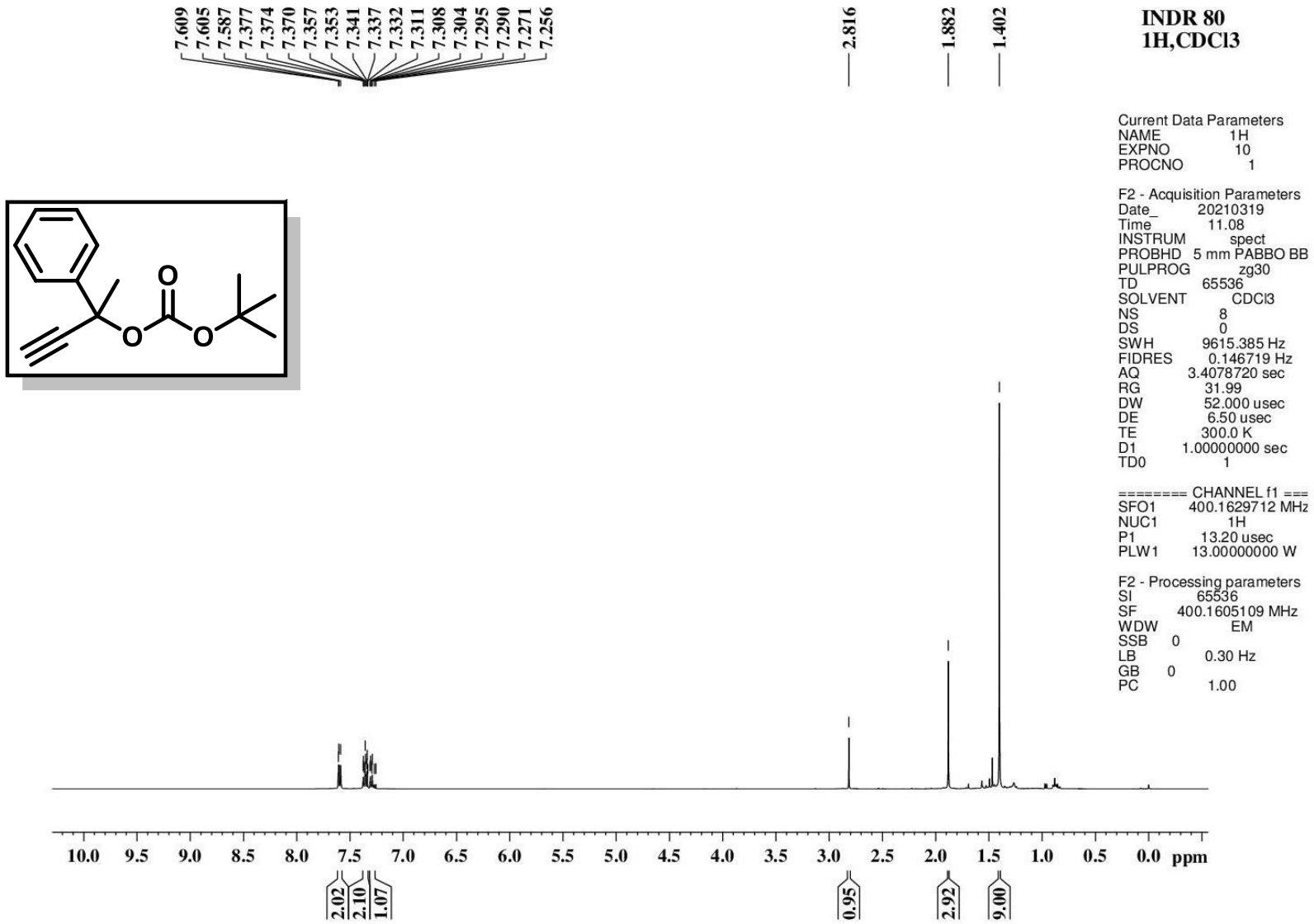



**Fig.S19** $^{1}$H NMR Spectrum of **1j**

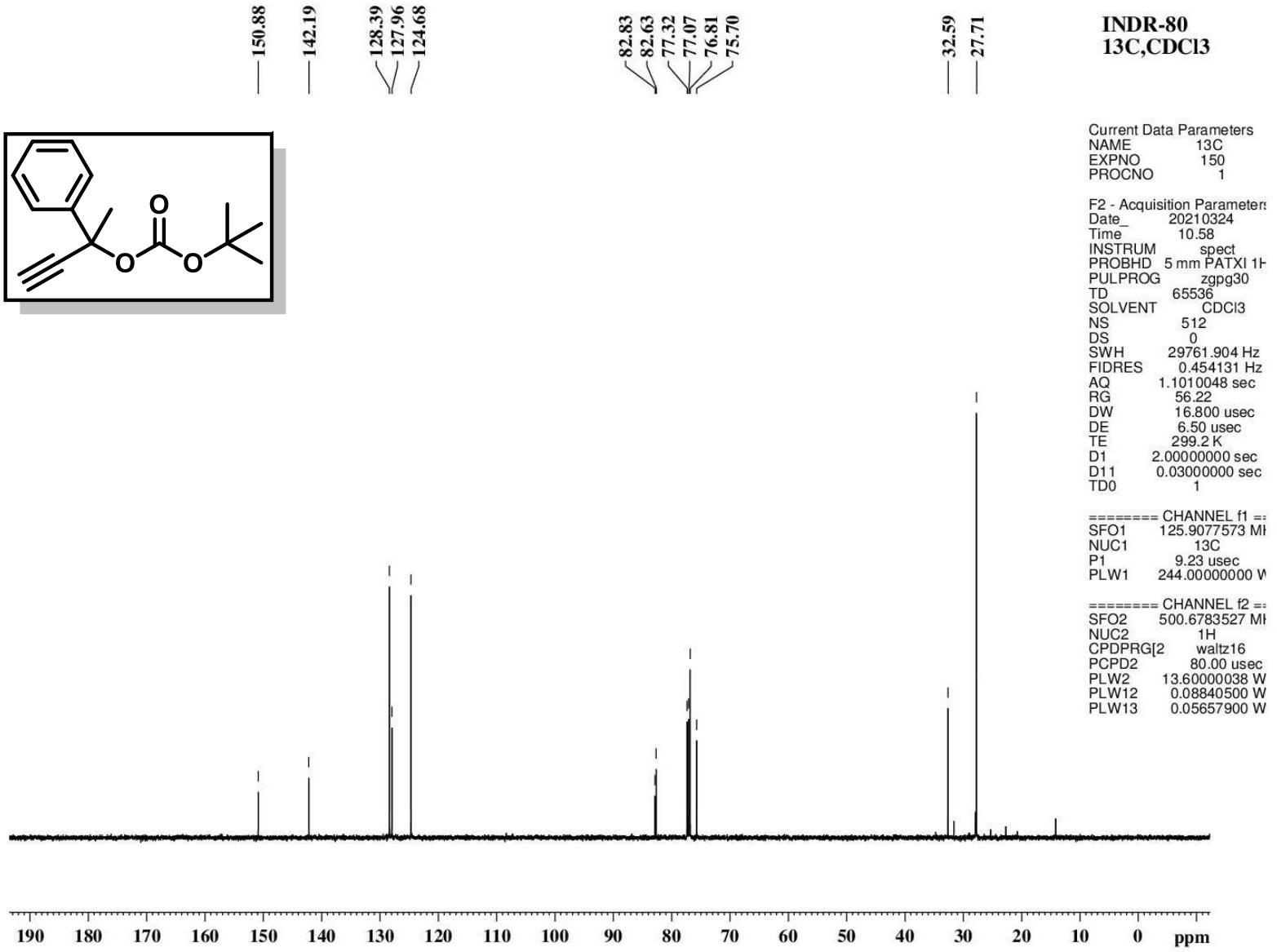



**Fig.S20** $^{13}$C NMR Spectrum of **1j**

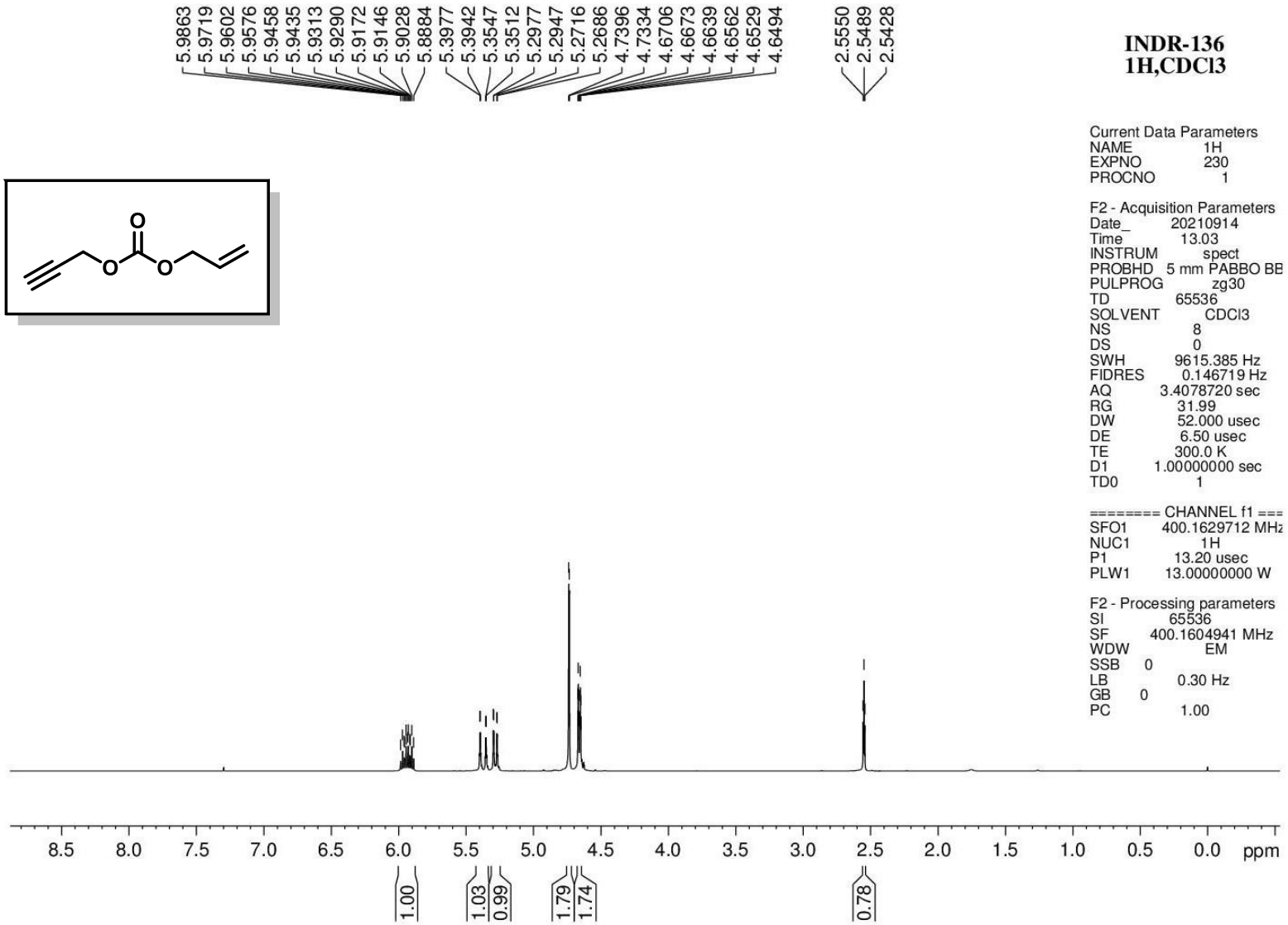



**Fig.S21** $^{1}$H NMR Spectrum of **1k**

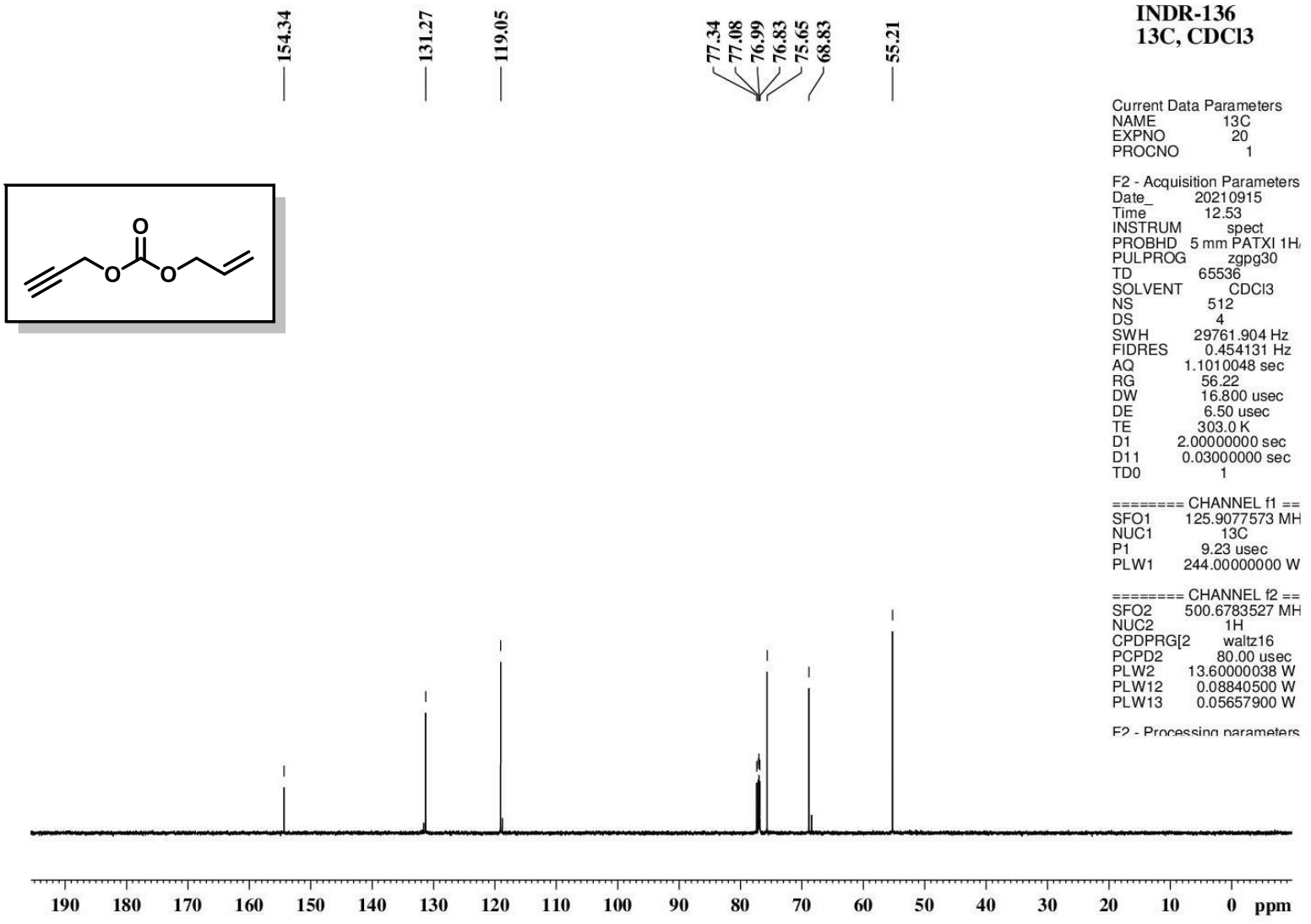



**Fig.S22** $^{13}$C NMR Spectrum of **1k**

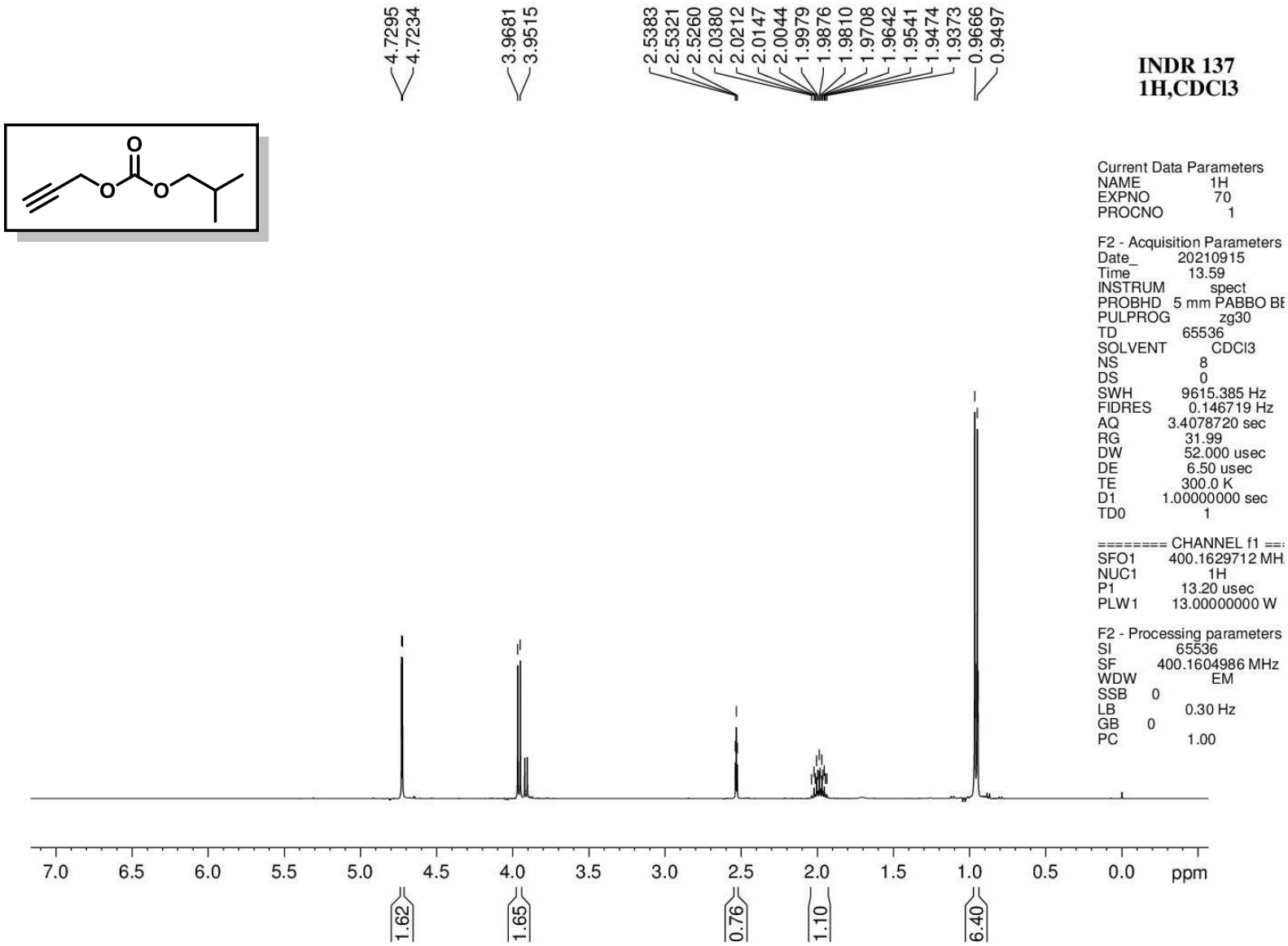



**Fig.S23** $^{1}$H NMR Spectrum of **1l**

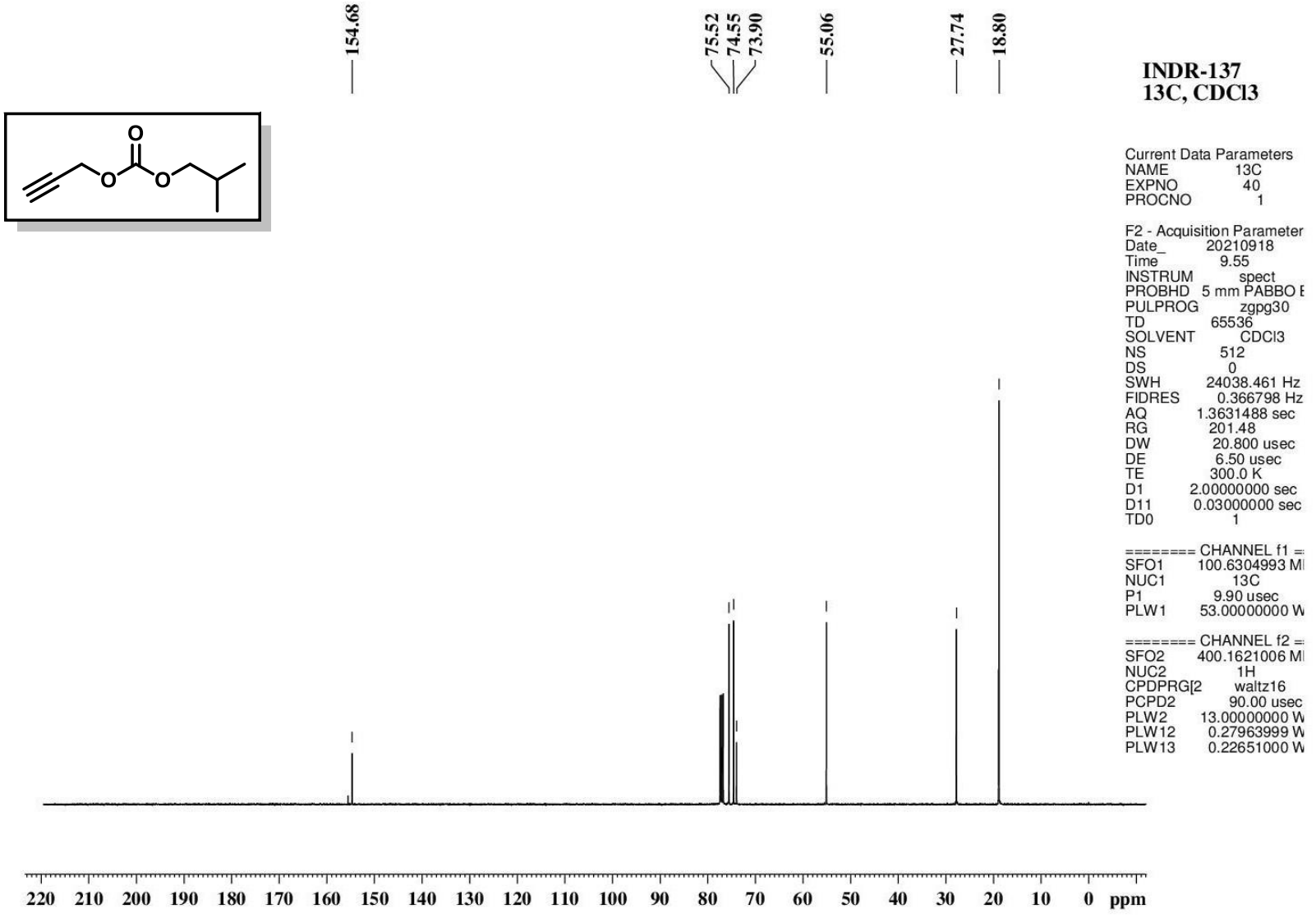



**Fig.S24** $^{13}$C NMR Spectrum of **1l**

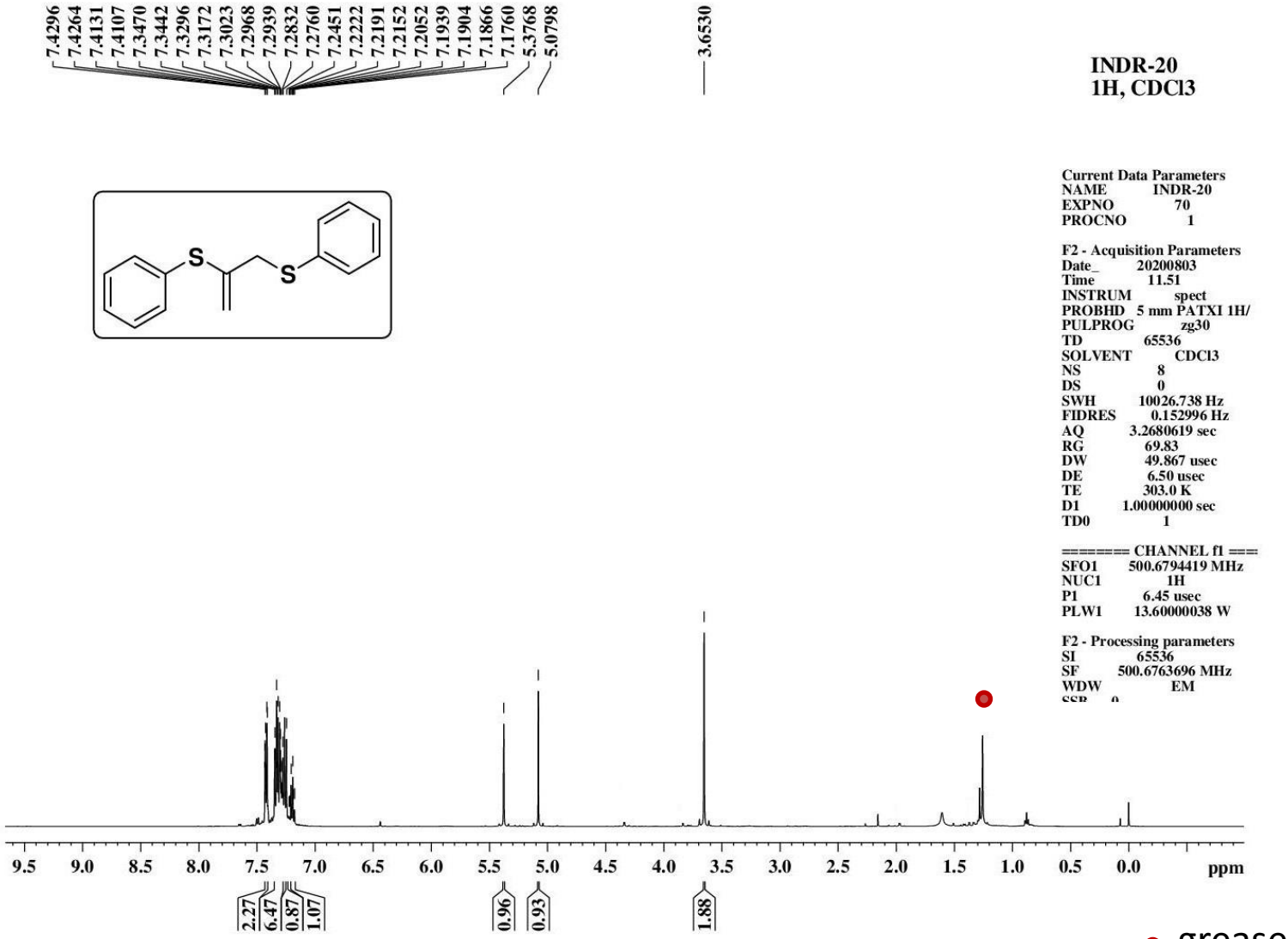



**Fig.S25** $^{1}$H NMR Spectrum of **3a**

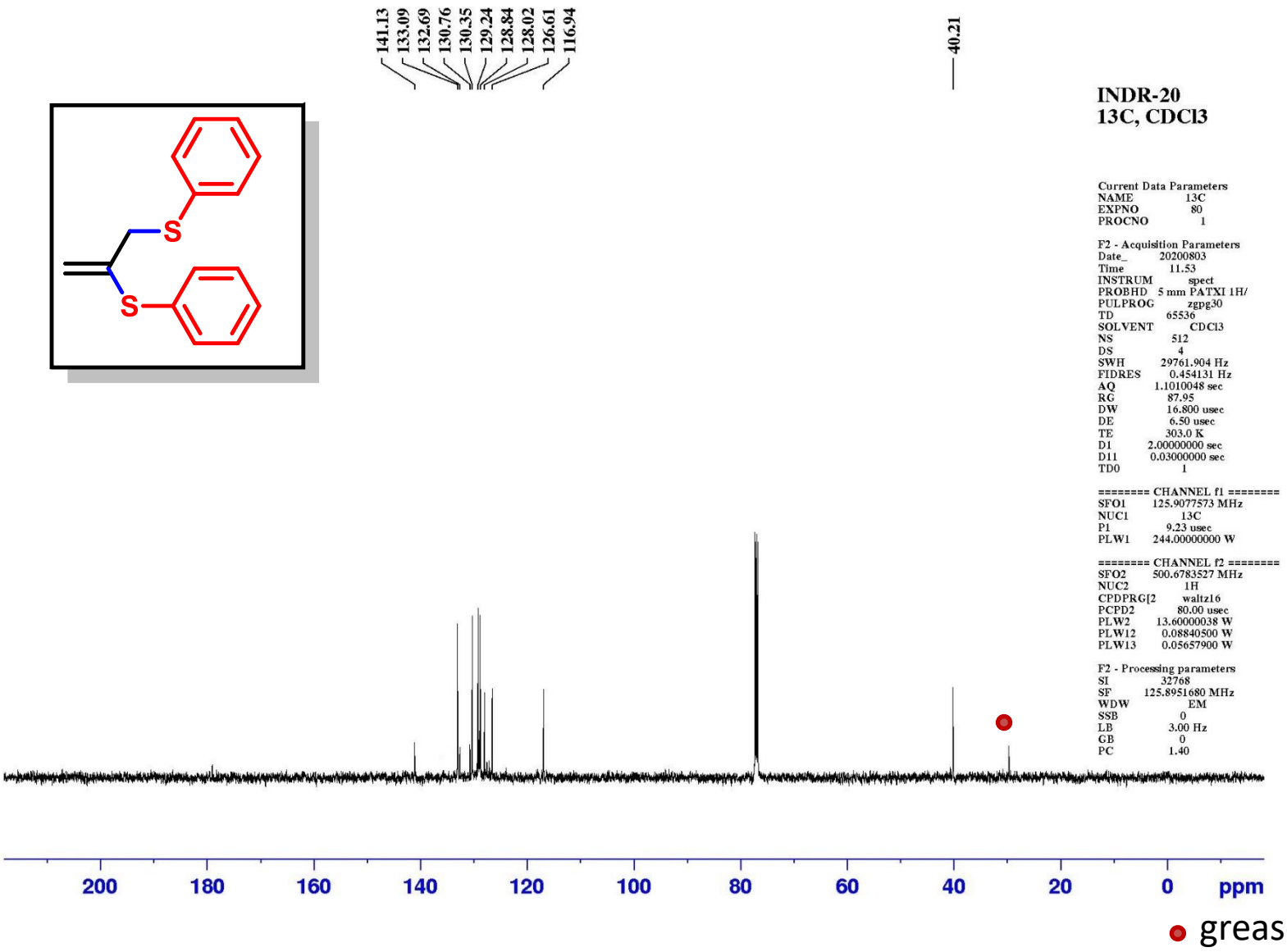



**Fig.S26** $^{13}$C NMR Spectrum of **3a**

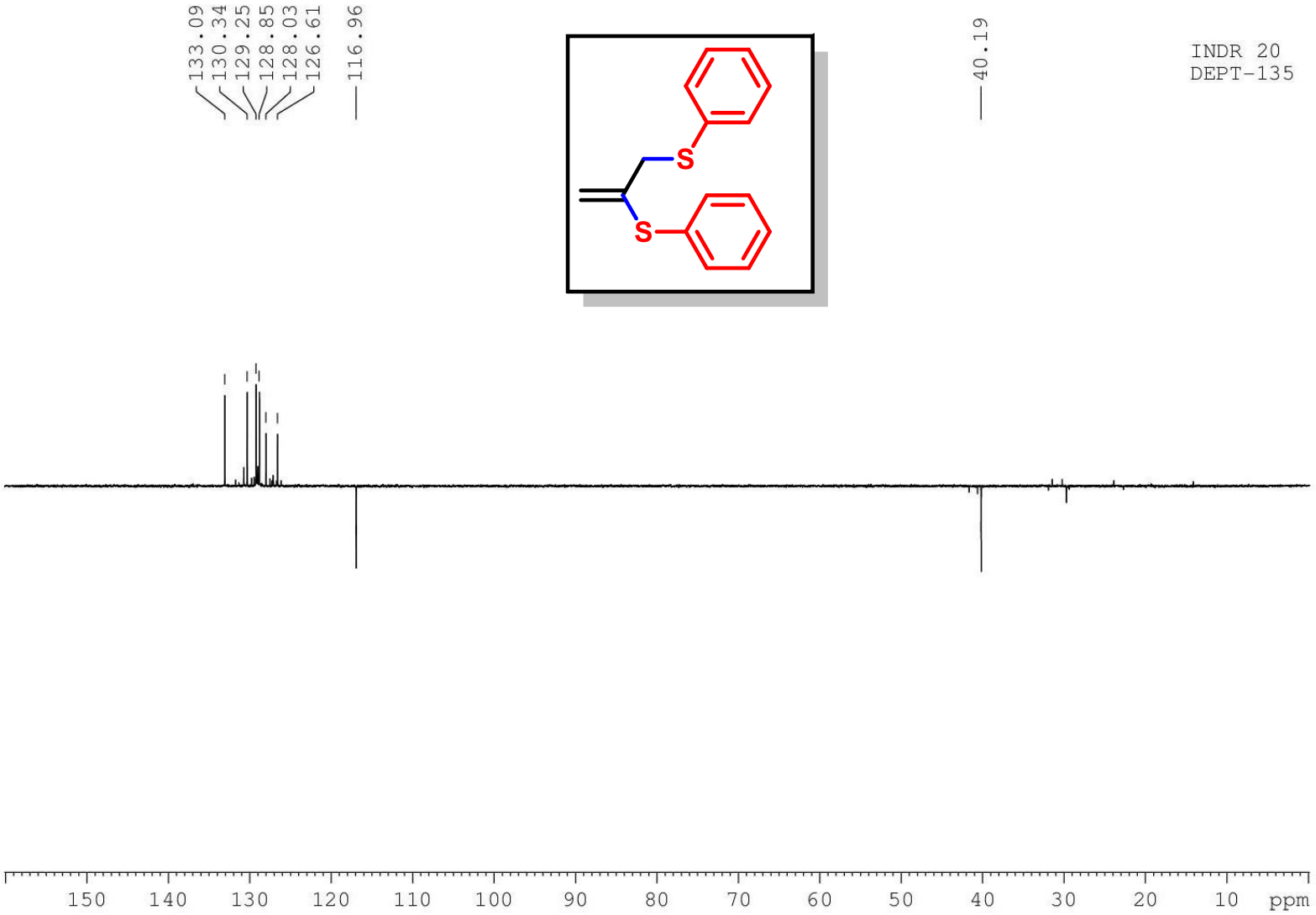



**Fig.S27** DEPT-135 Spectrum of **3a**

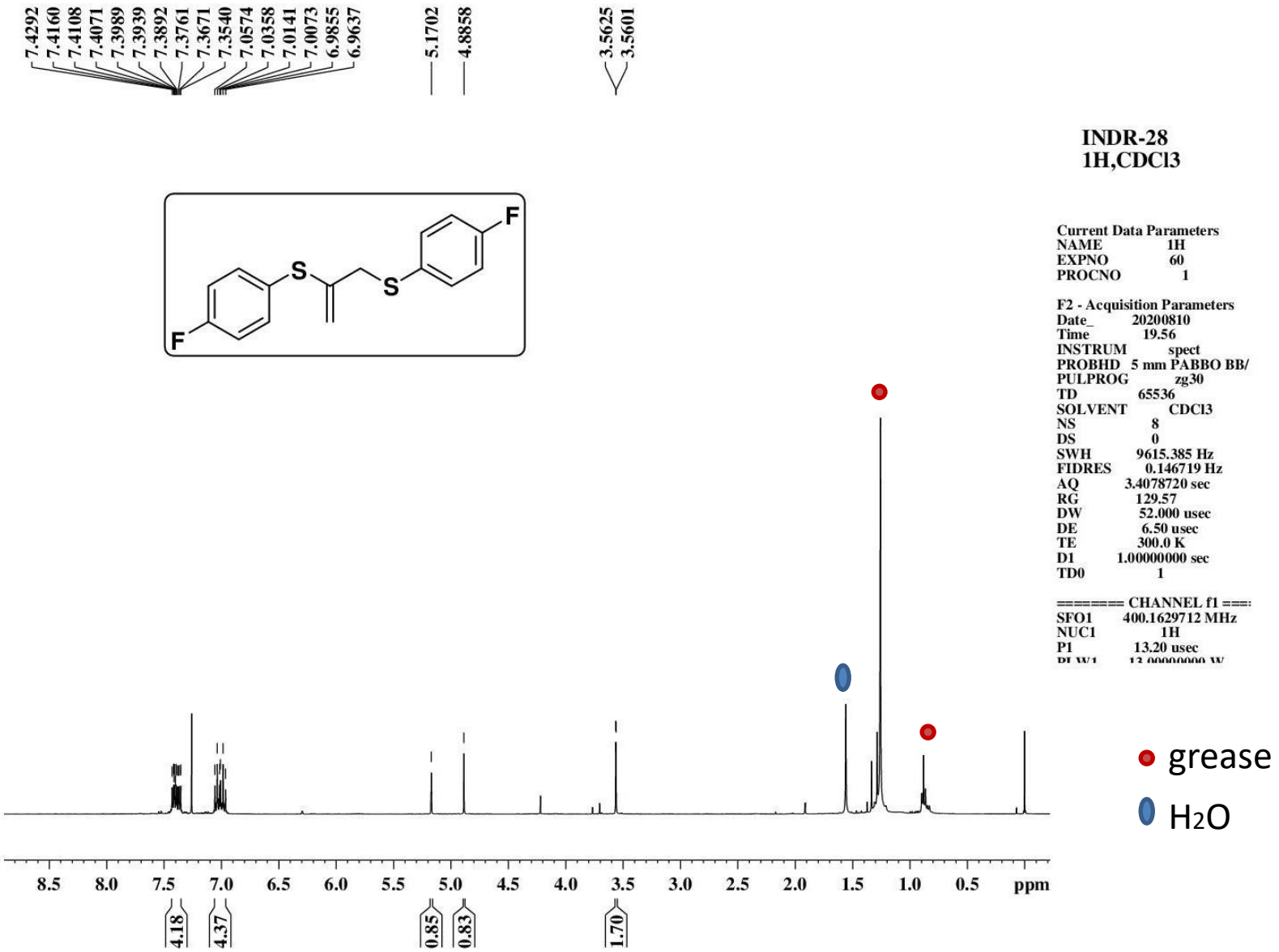



**Fig.S28** $^{1}$H NMR Spectrum of **3b**

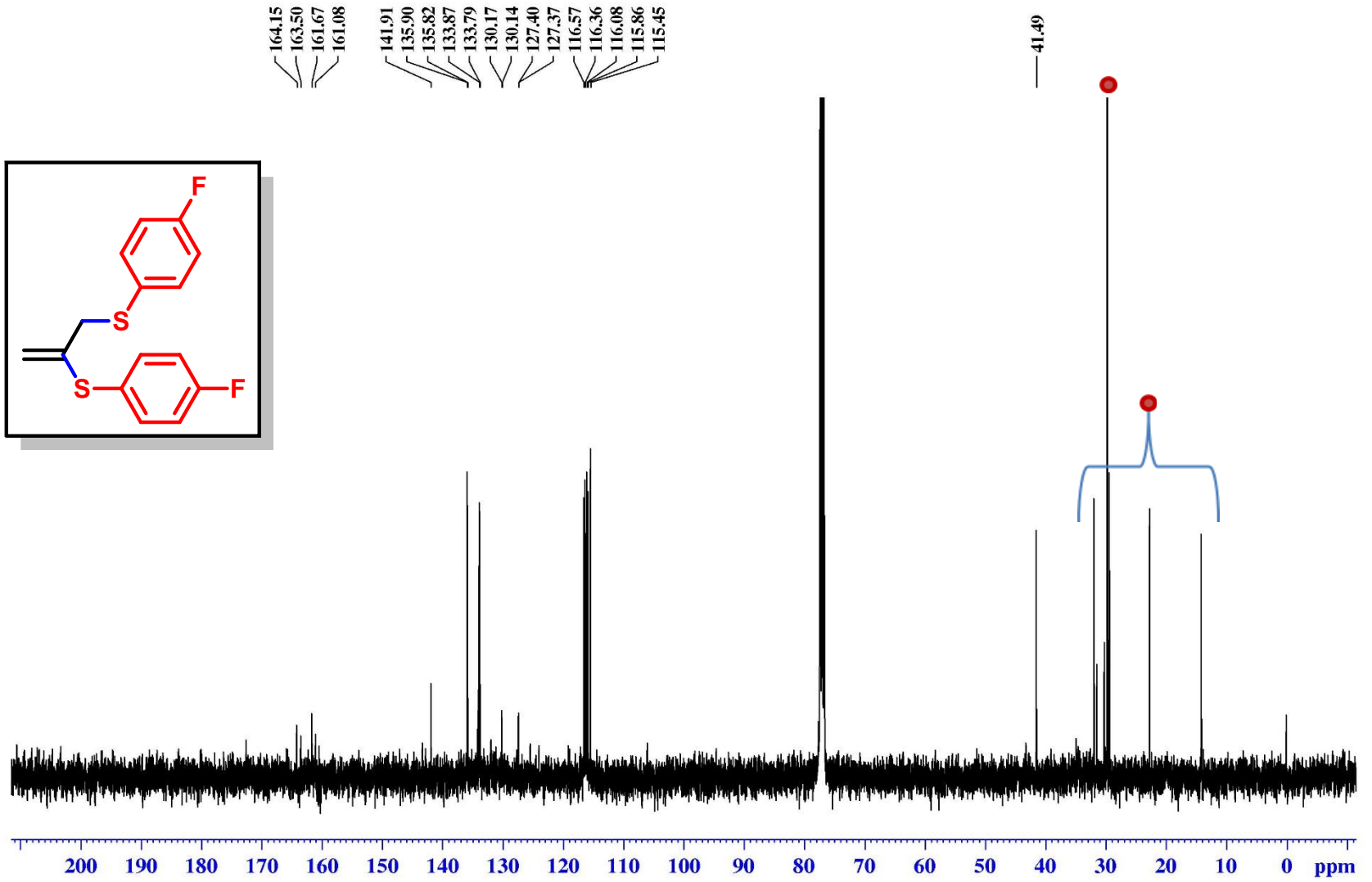



**Fig.S29** $^{13}$C NMR Spectrum of **3b**

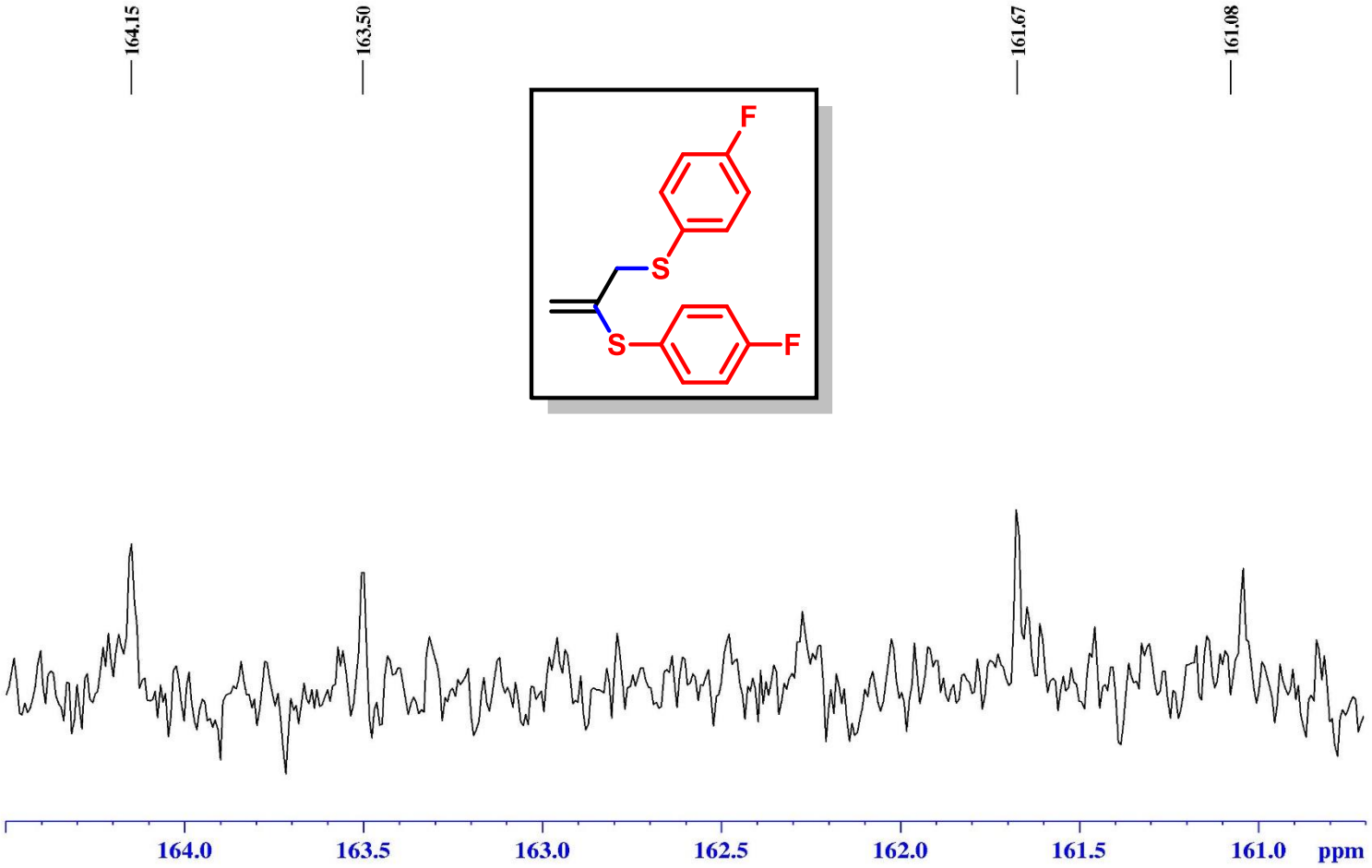



**Fig.S30** $^{13}$C NMR Spectrum of **3b** (magnified region between 164.5-160.7)


**Fig.S31** $^{19}$F NMR Spectrum of **3b**

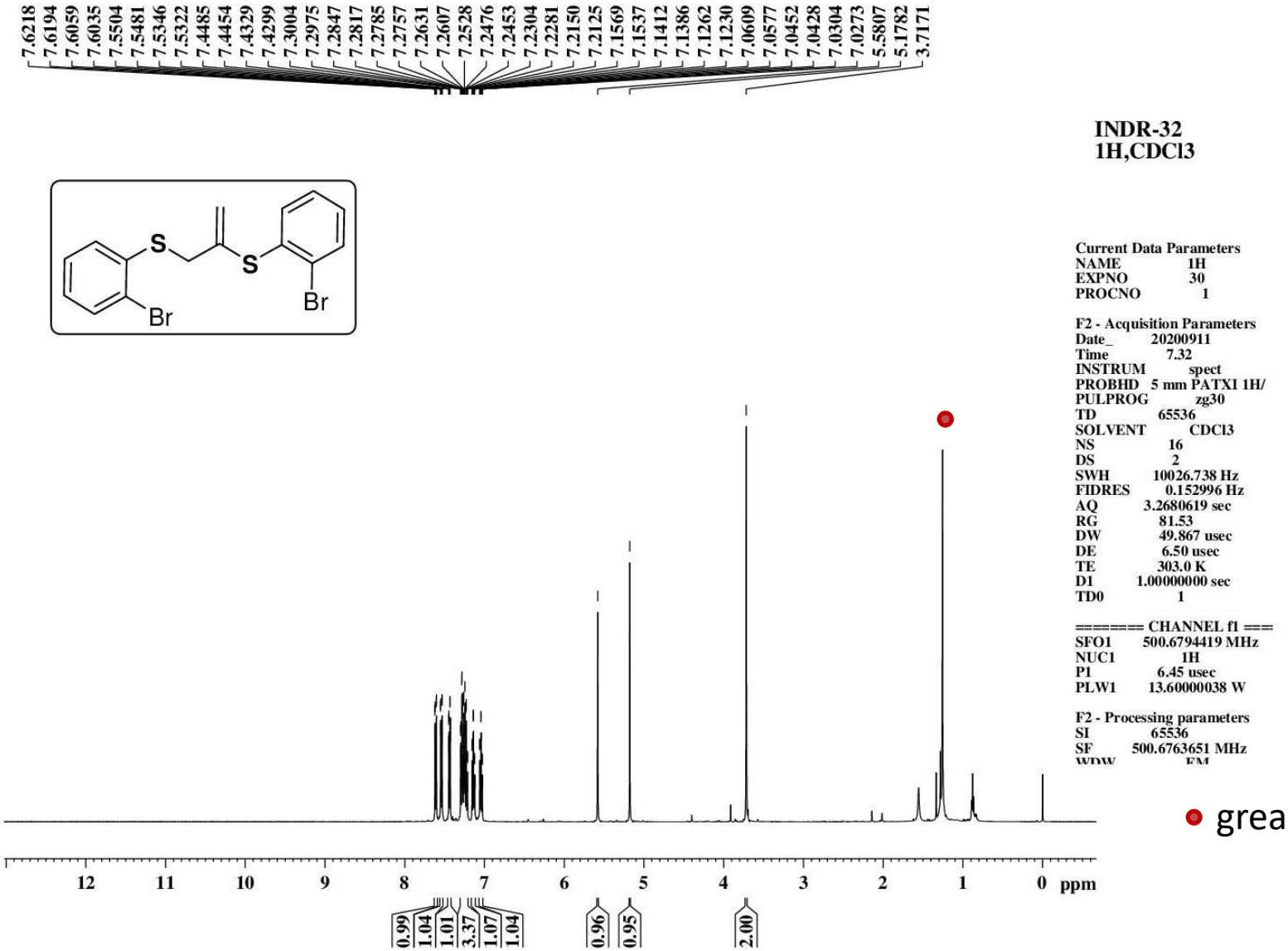



**Fig.S32** $^{1}$H NMR Spectrum of **3c**

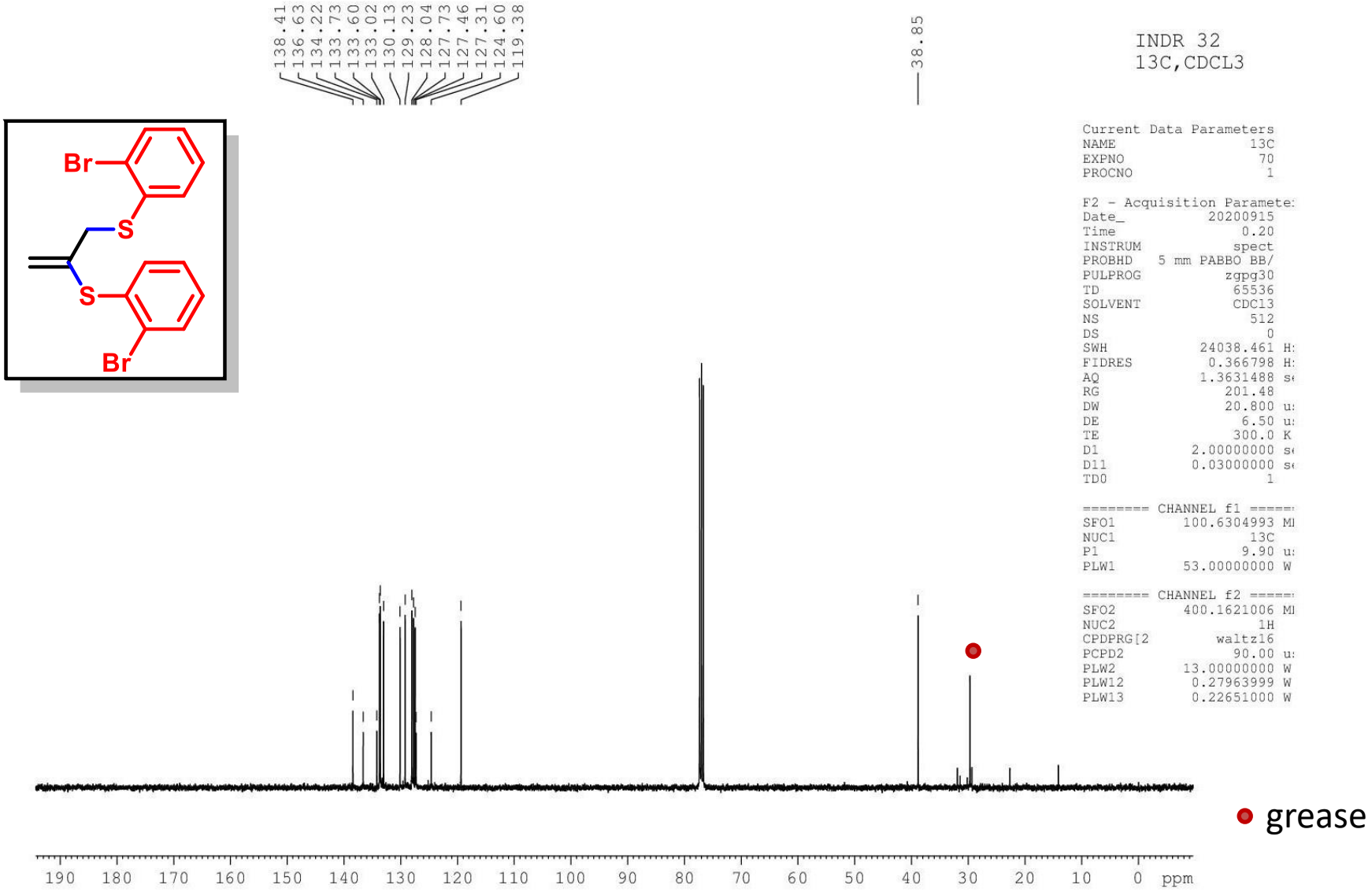



**Fig.S33** $^{13}$C NMR Spectrum of **3c**

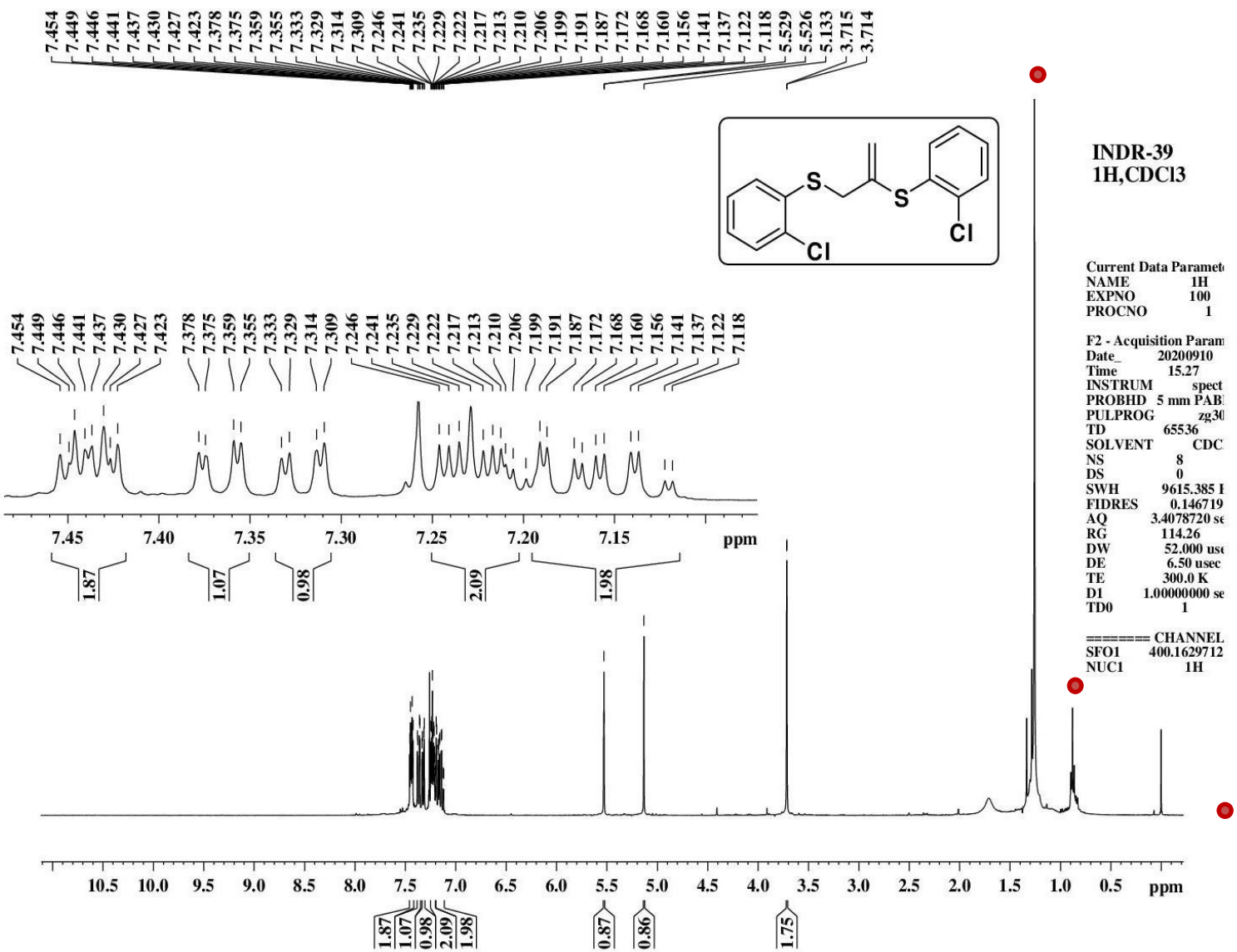



**Fig.S34** $^{1}$H NMR Spectrum of **3d**

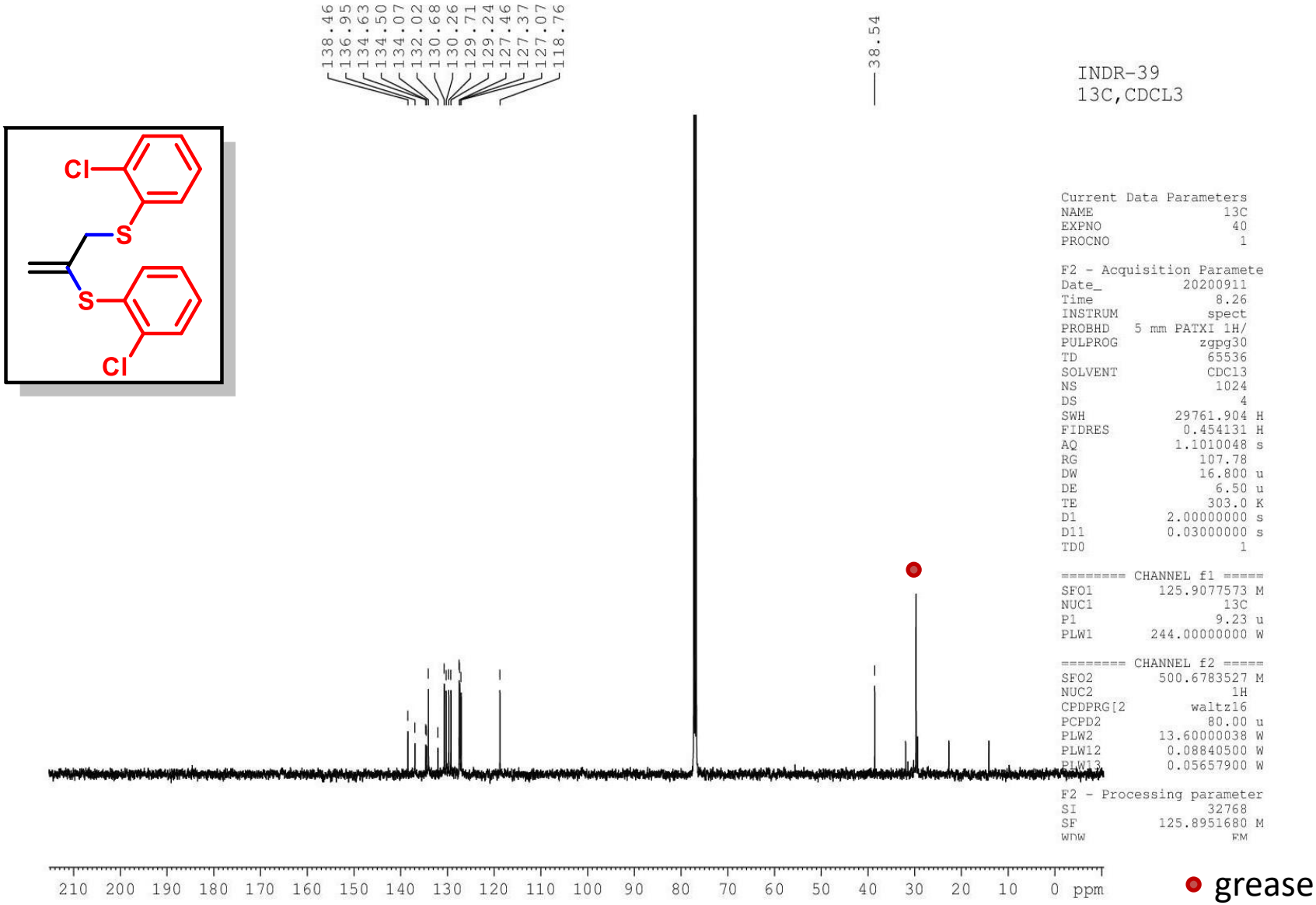



**Fig.S35** $^{13}$C NMR Spectrum of **3d**

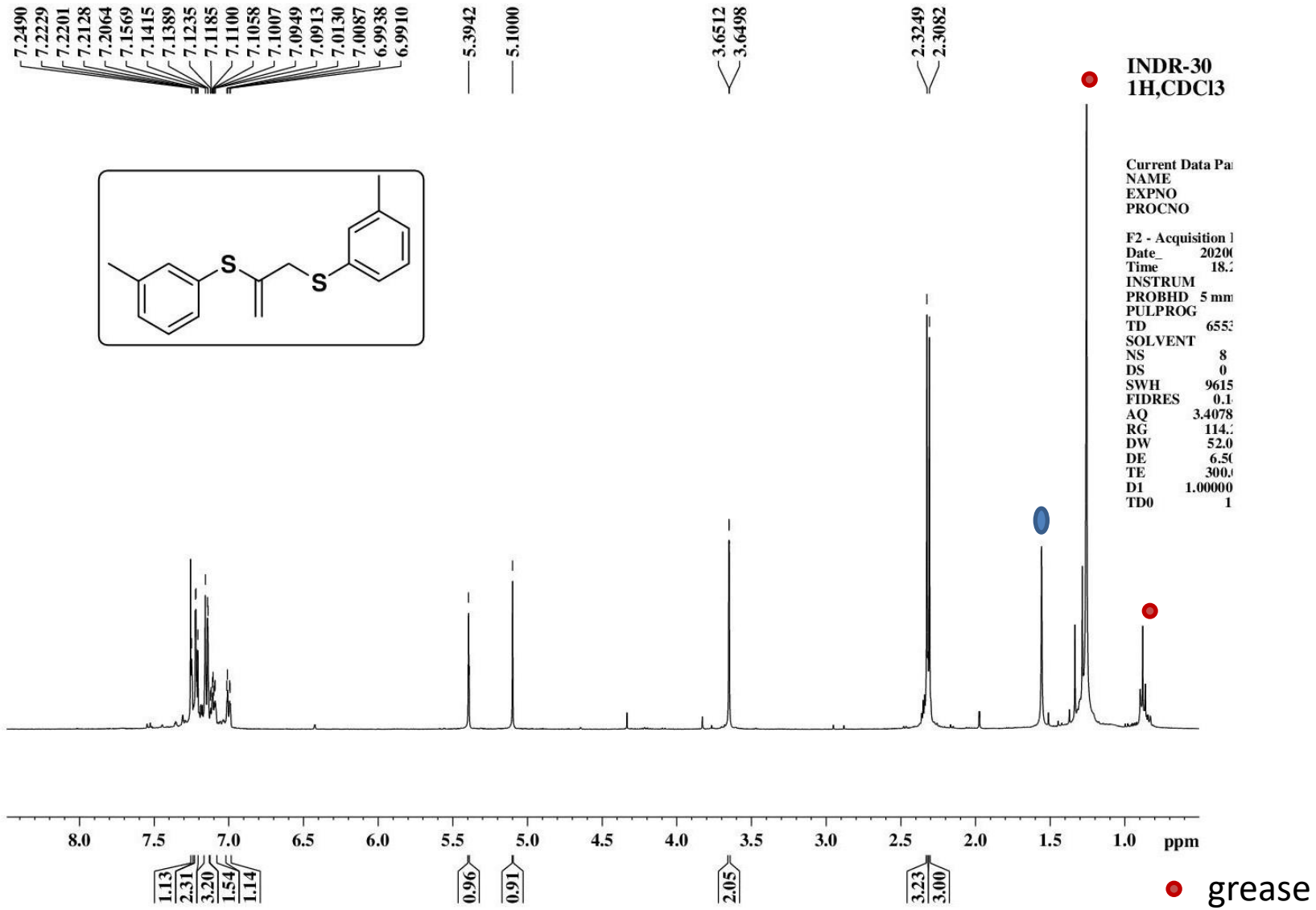



**Fig.S36** $^{1}$H NMR Spectrum of **3e**

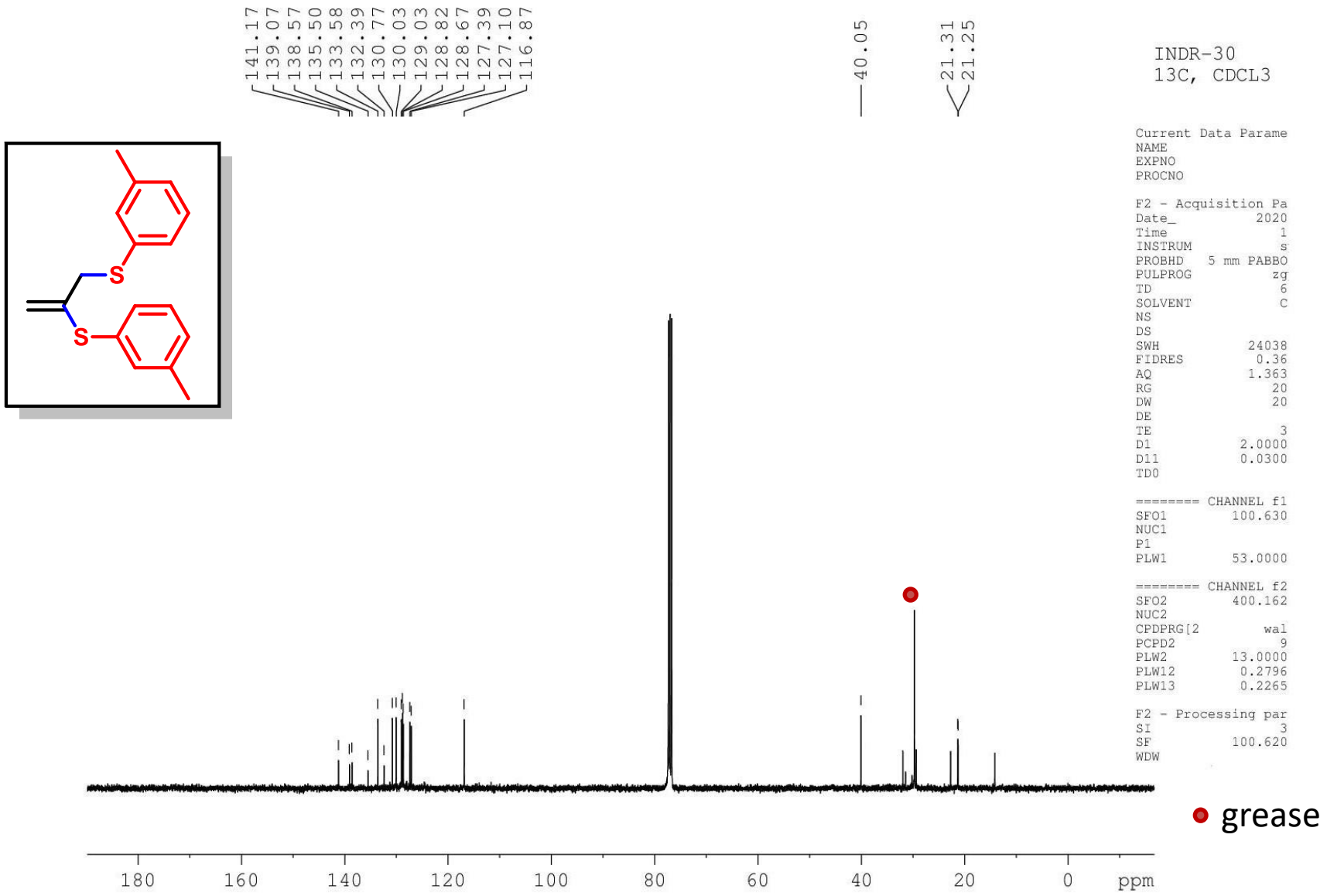



**Fig.S37** $^{13}$C NMR Spectrum of **3e**

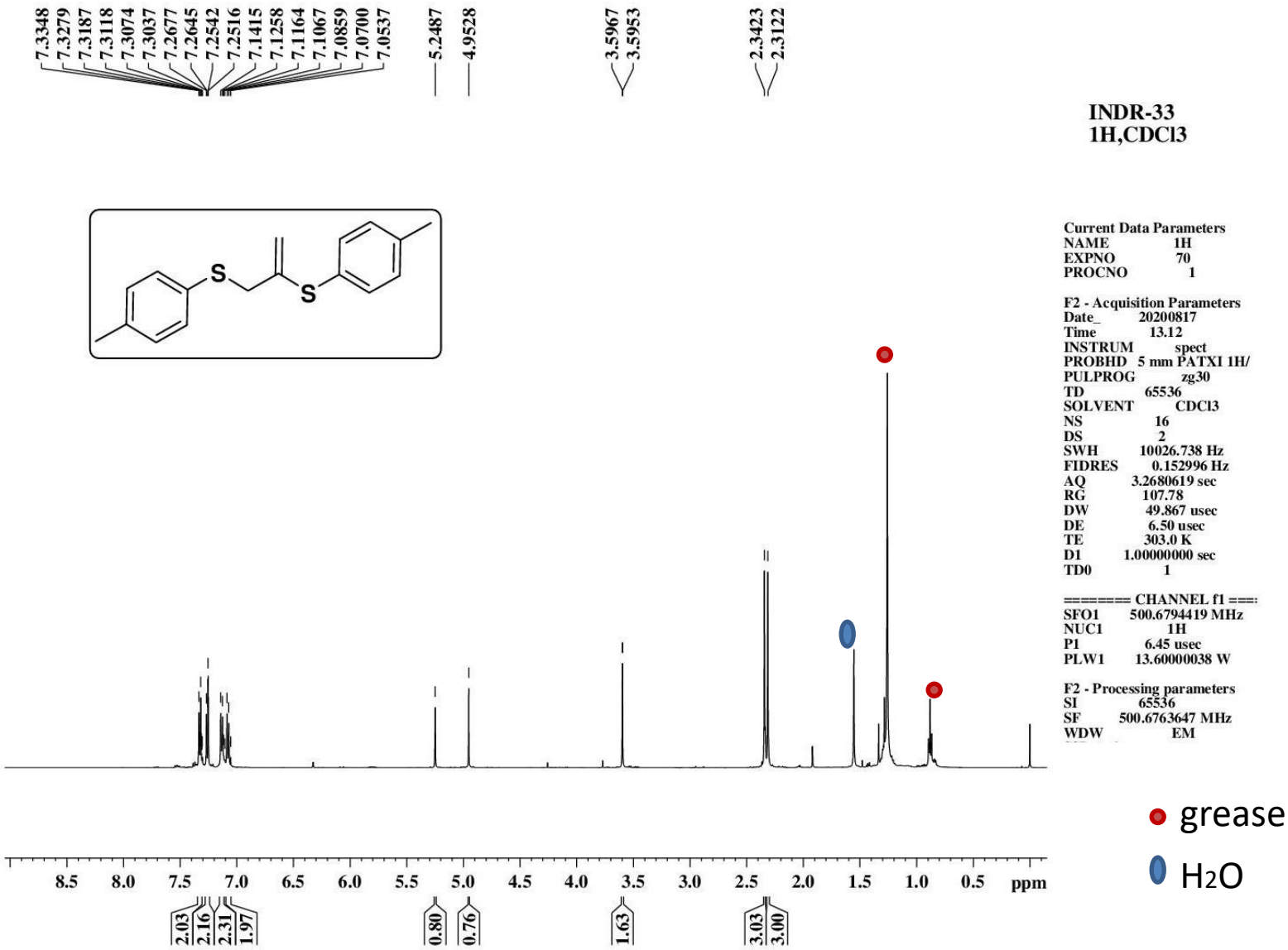



**Fig.S38** $^{1}$H NMR Spectrum of **3f**

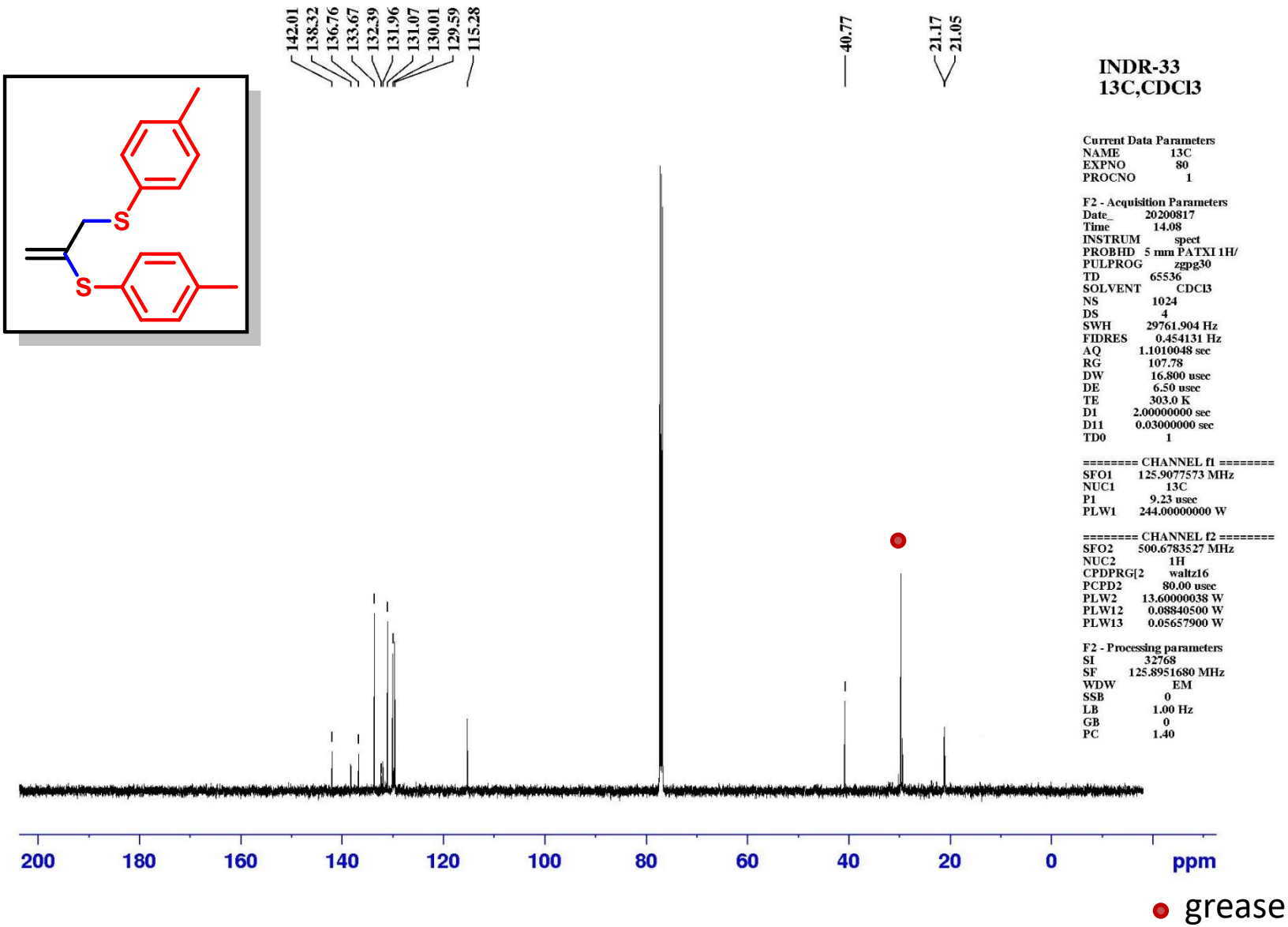



**Fig.S39** $^{13}$C NMR Spectrum of **3f**

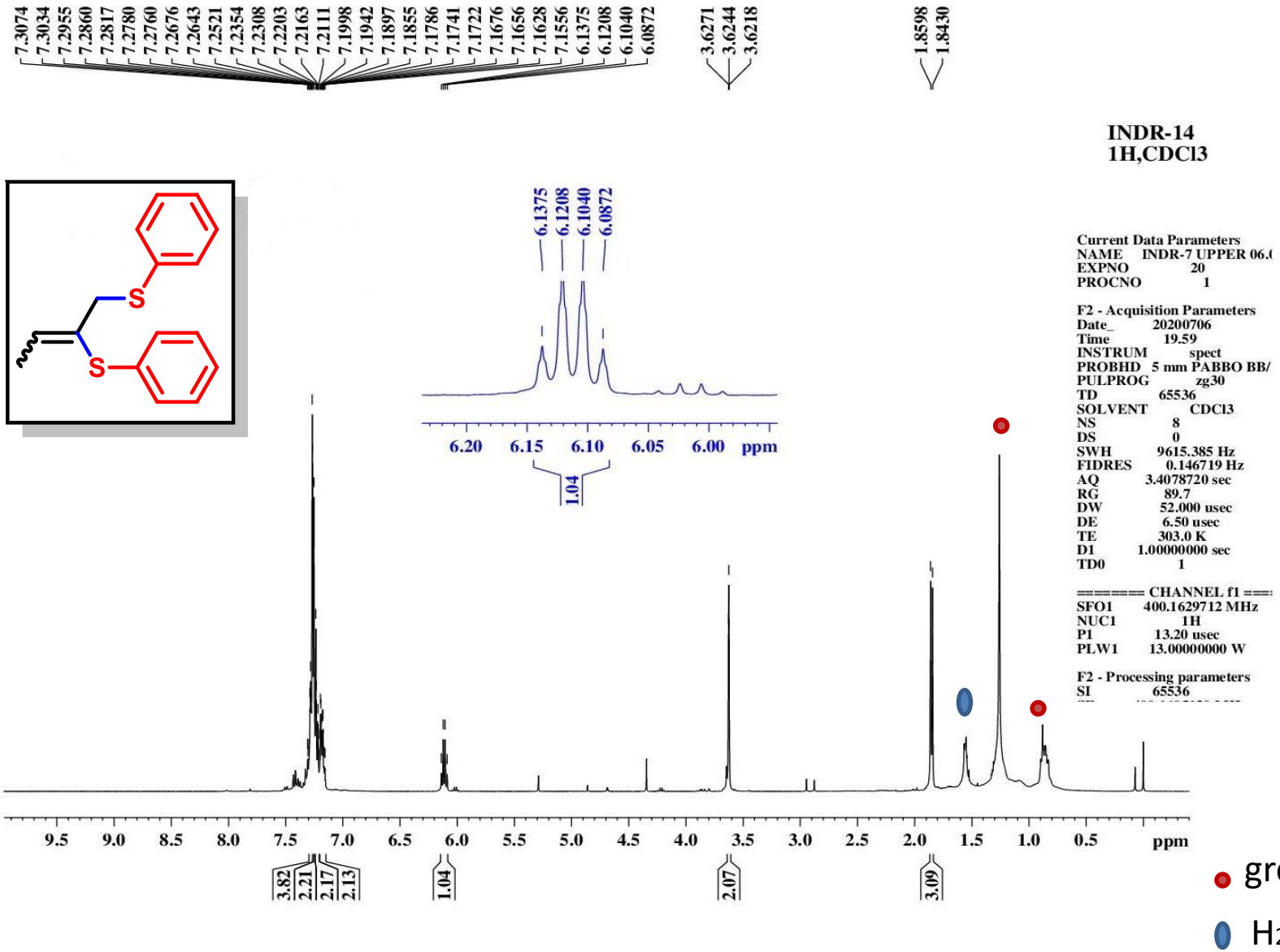



**Fig.S40** $^{1}$H NMR Spectrum of **3g**

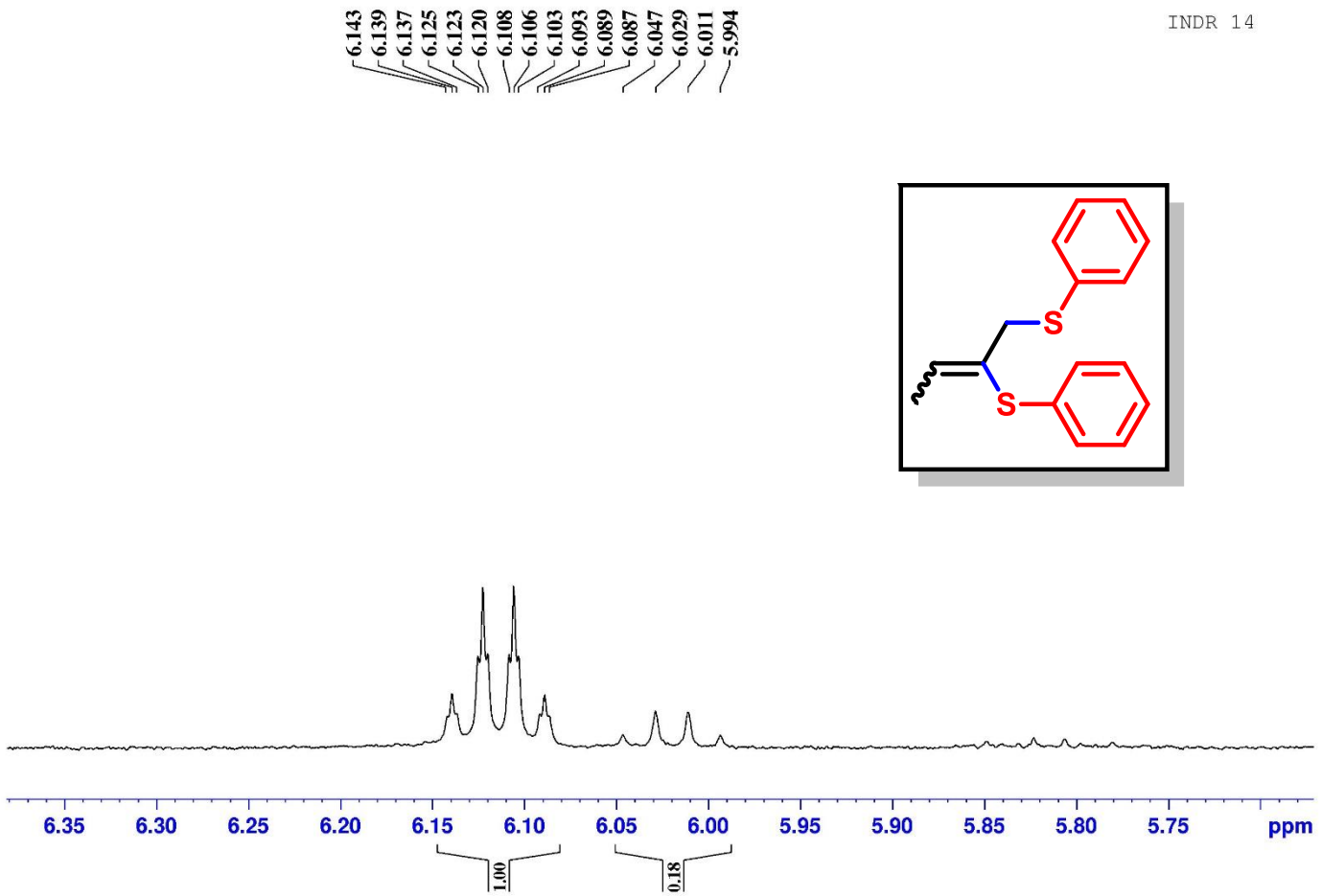



**Fig.S41** $^{1}$H NMR Spectrum of isomeric mixture of **3g** ( magnified region between 6.35-5.75)

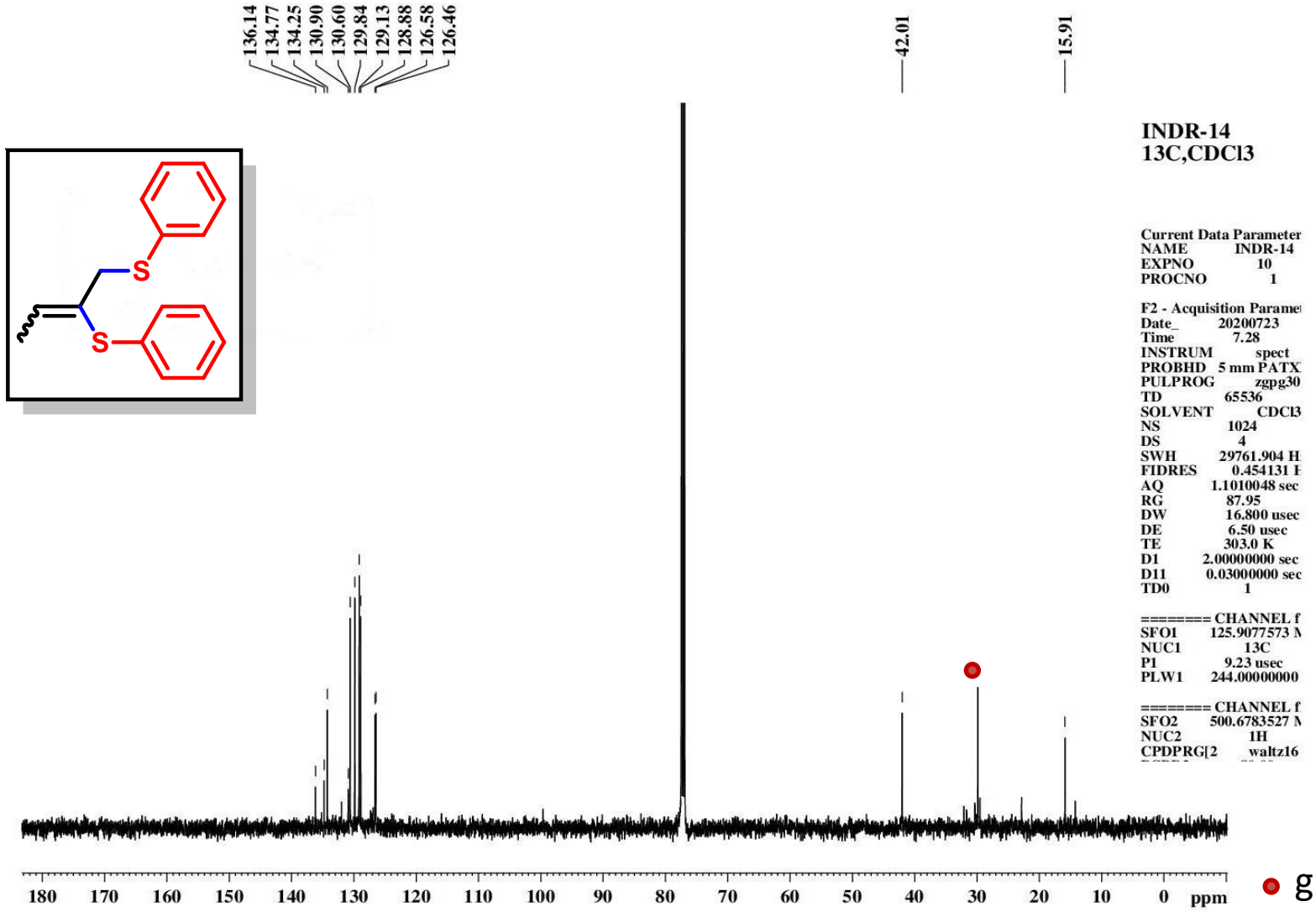



**Fig.S42** $^{13}$C NMR Spectrum of **3g**

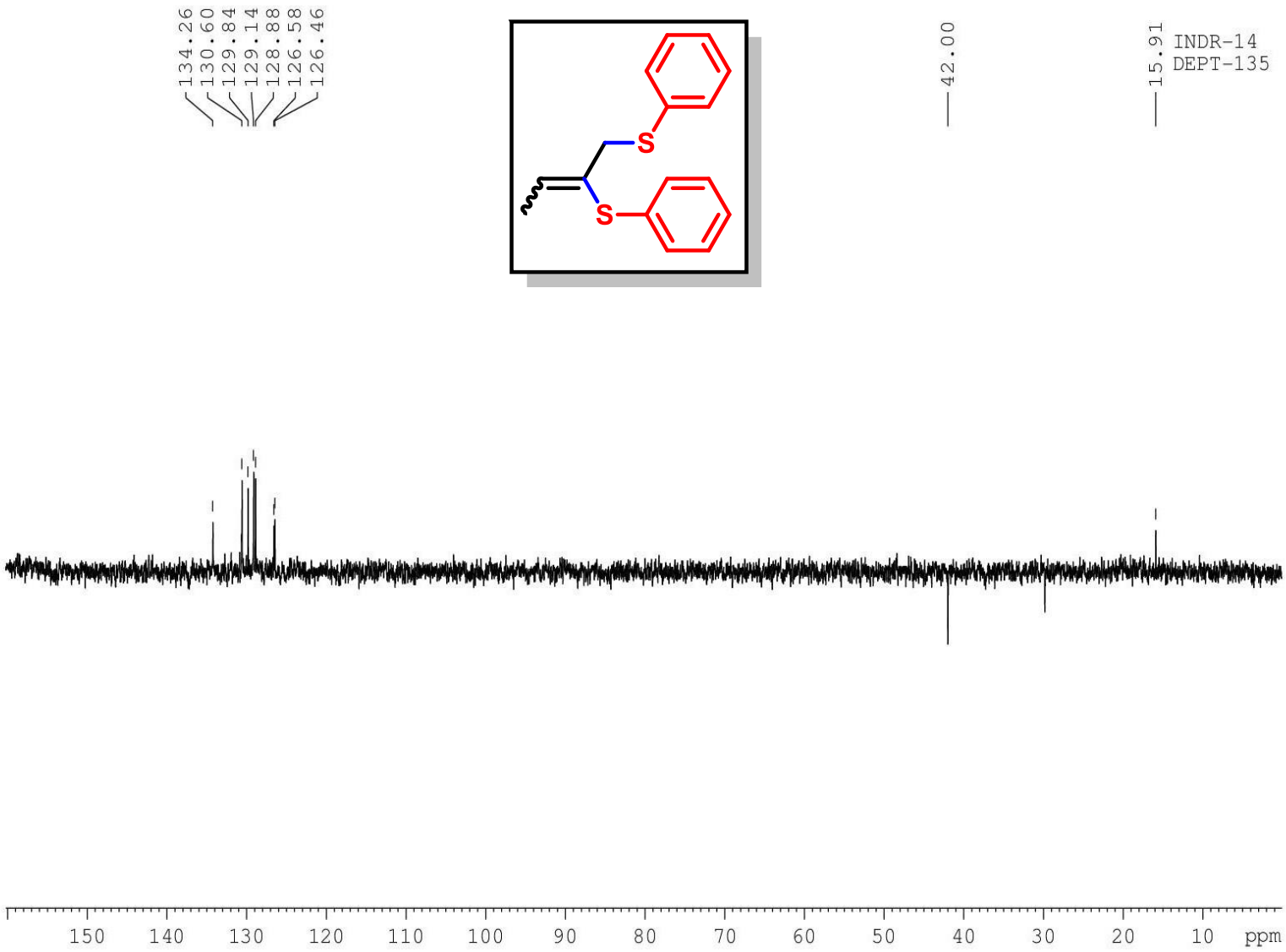



**Fig.S43** DEPT-135 Spectrum of **3g**

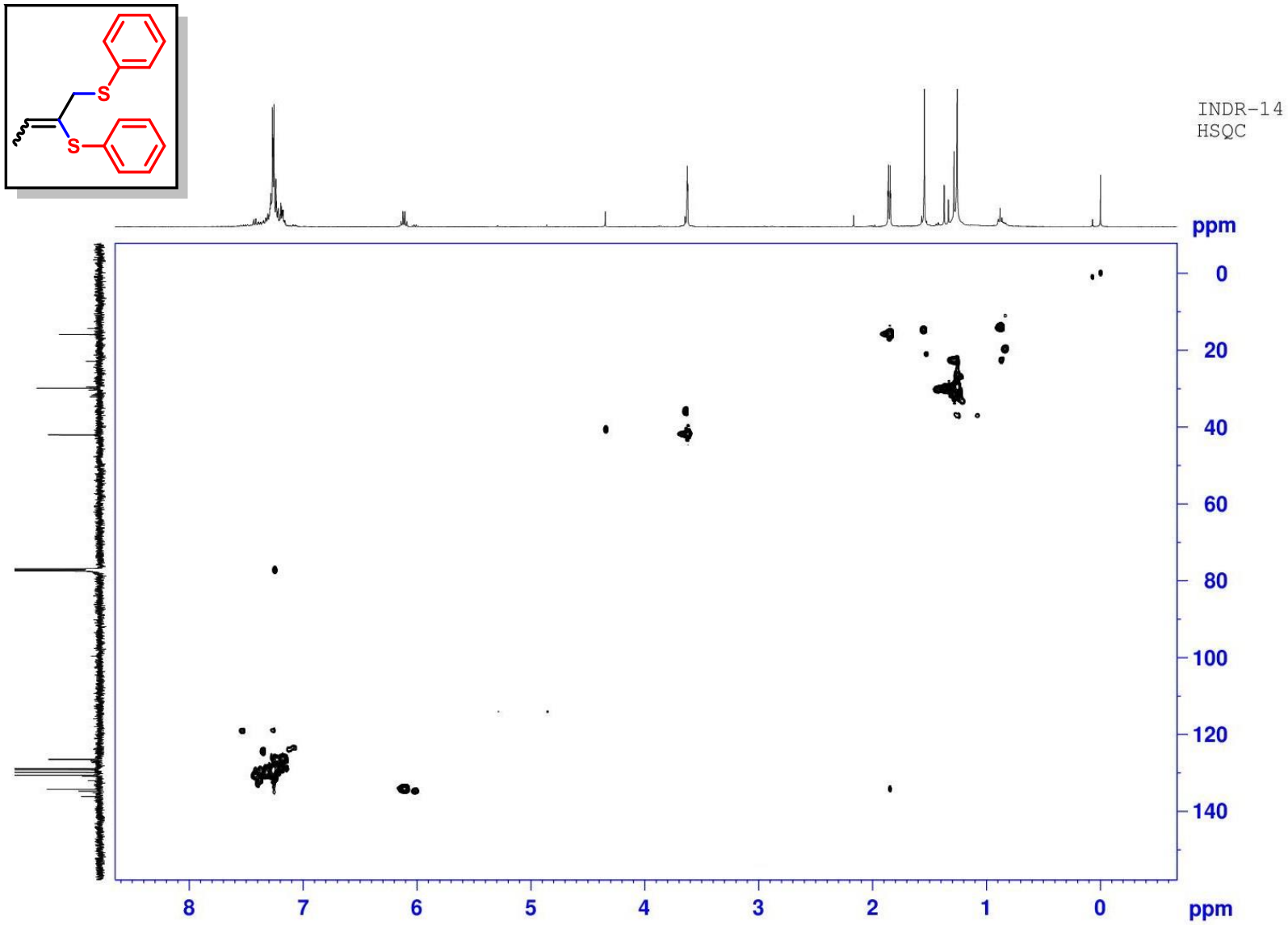



**Fig.S44** HSQC Spectrum of **3g**

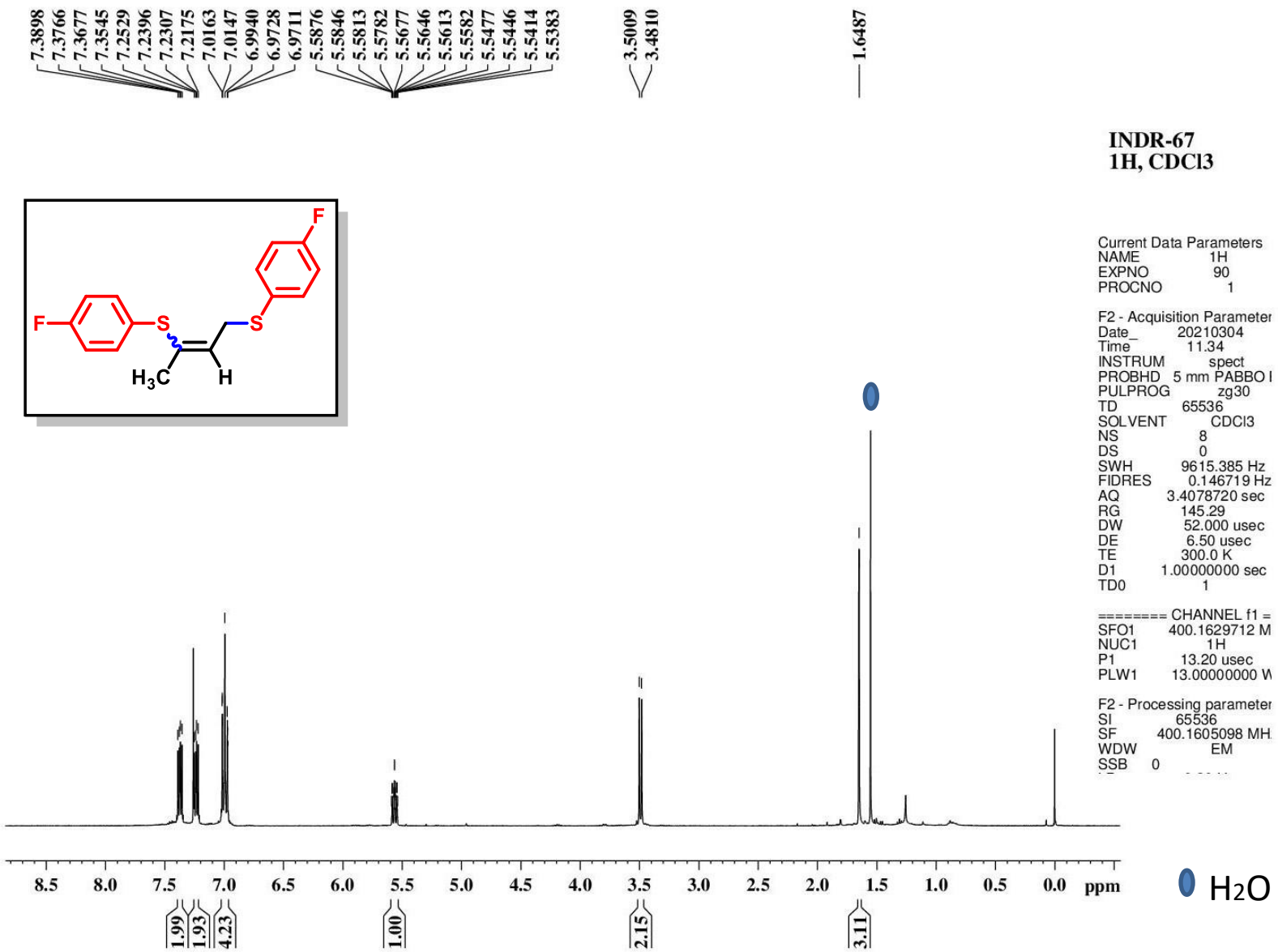



**Fig.S45** $^{1}$H NMR Spectrum of **8a**

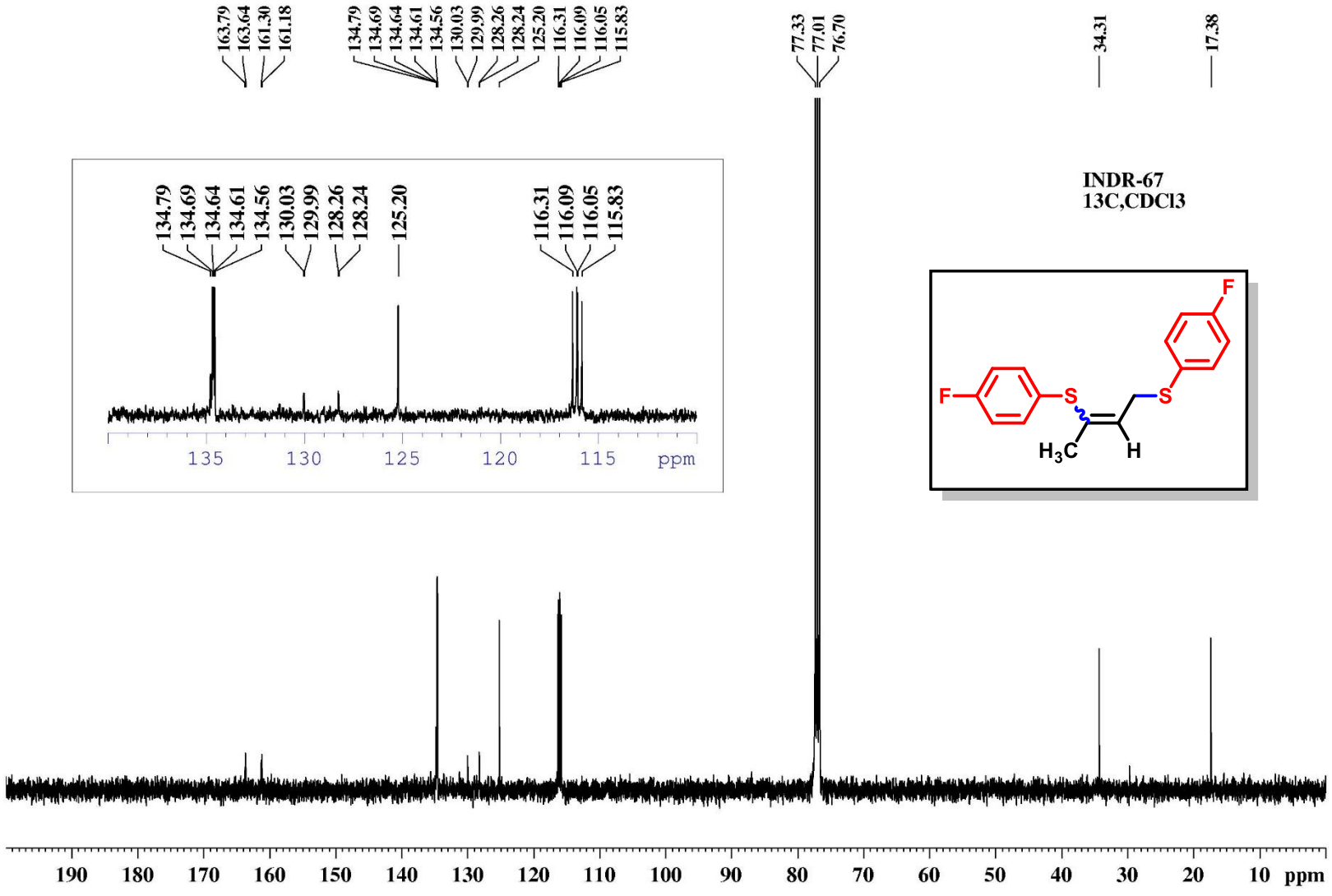



**Fig.S46** $^{13}$C NMR Spectrum of **8a**

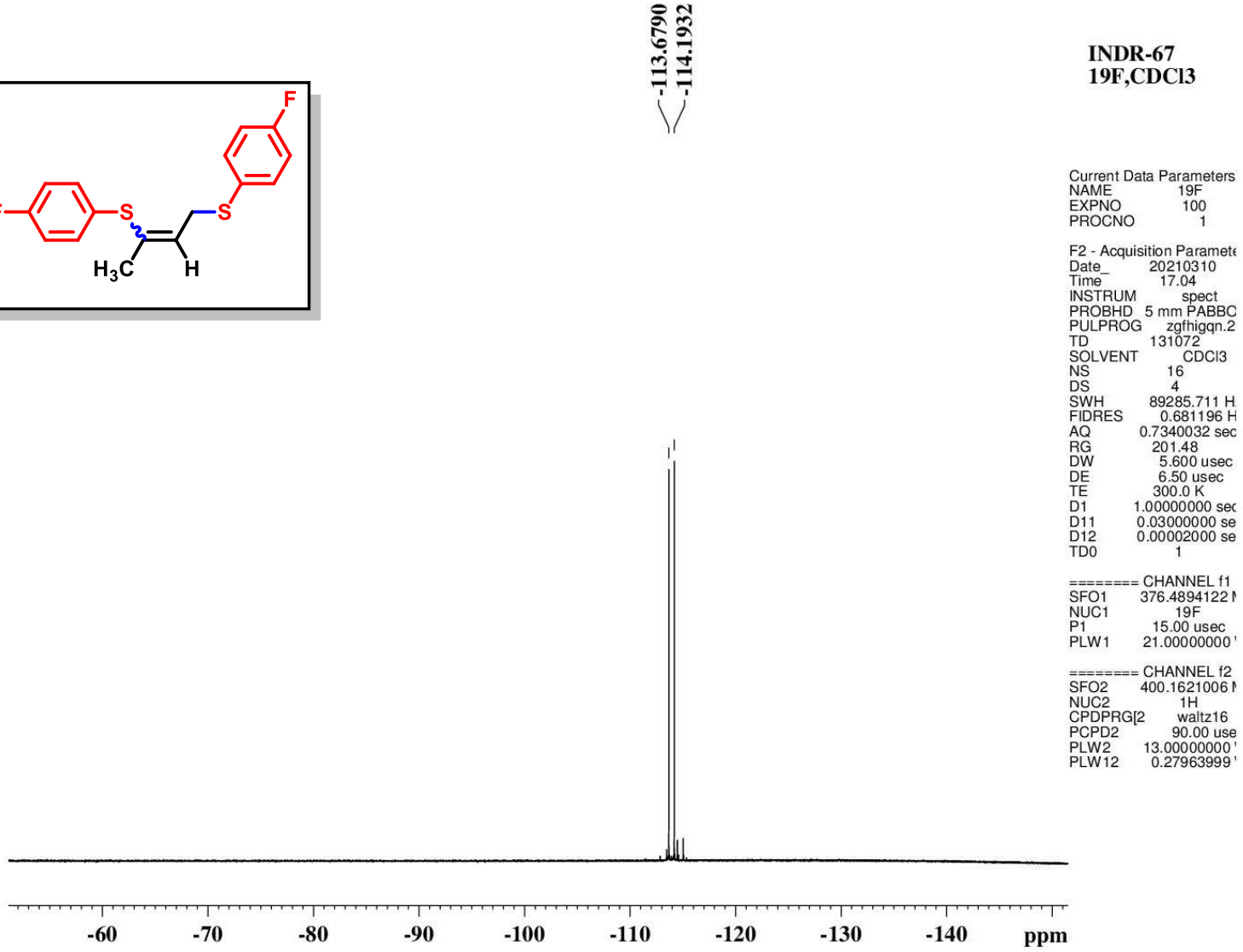



**Fig.S47** $^{19}$F NMR Spectrum of **8a**

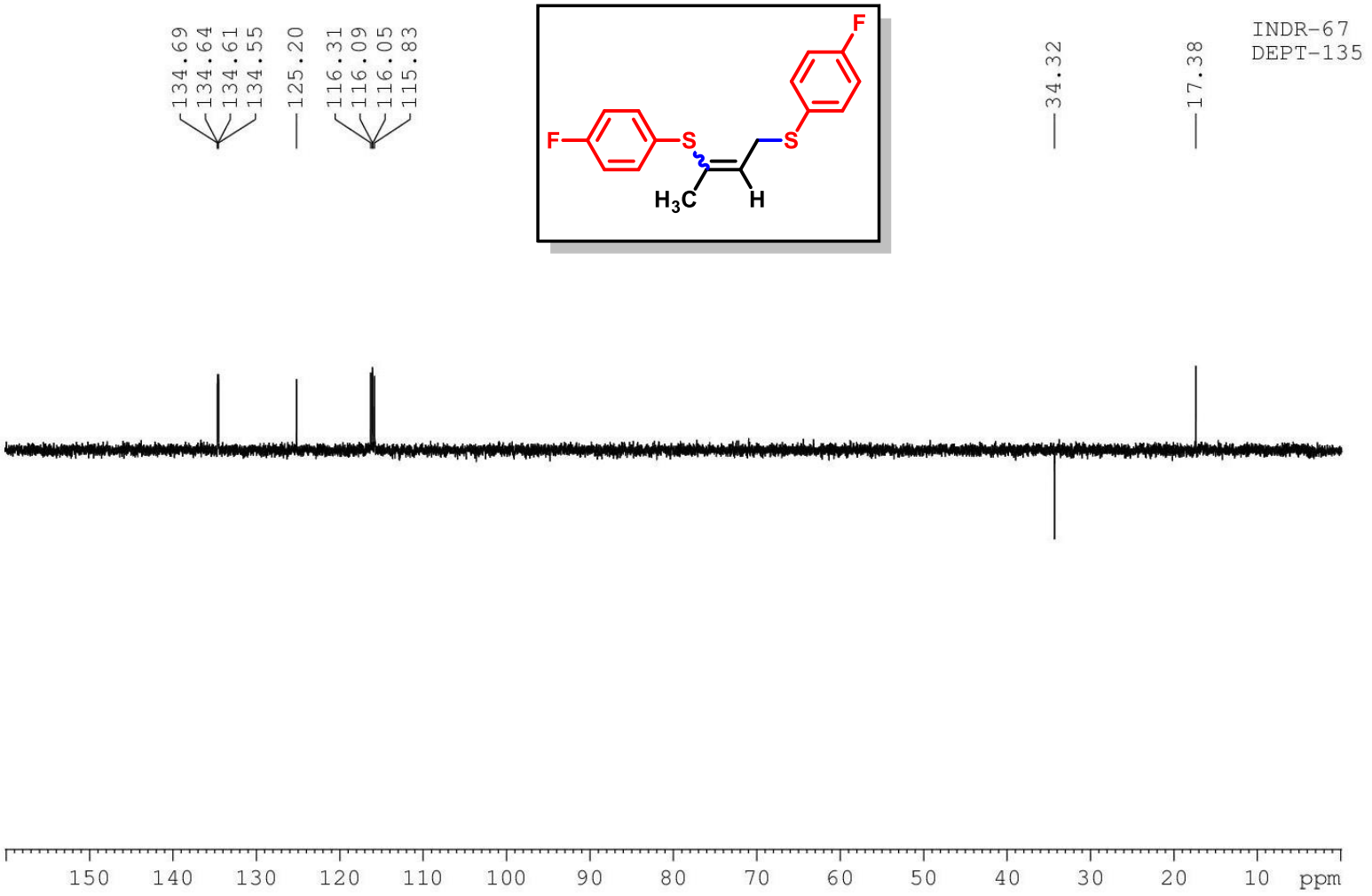



**Fig.S48** DEPT-135 Spectrum of **8a**

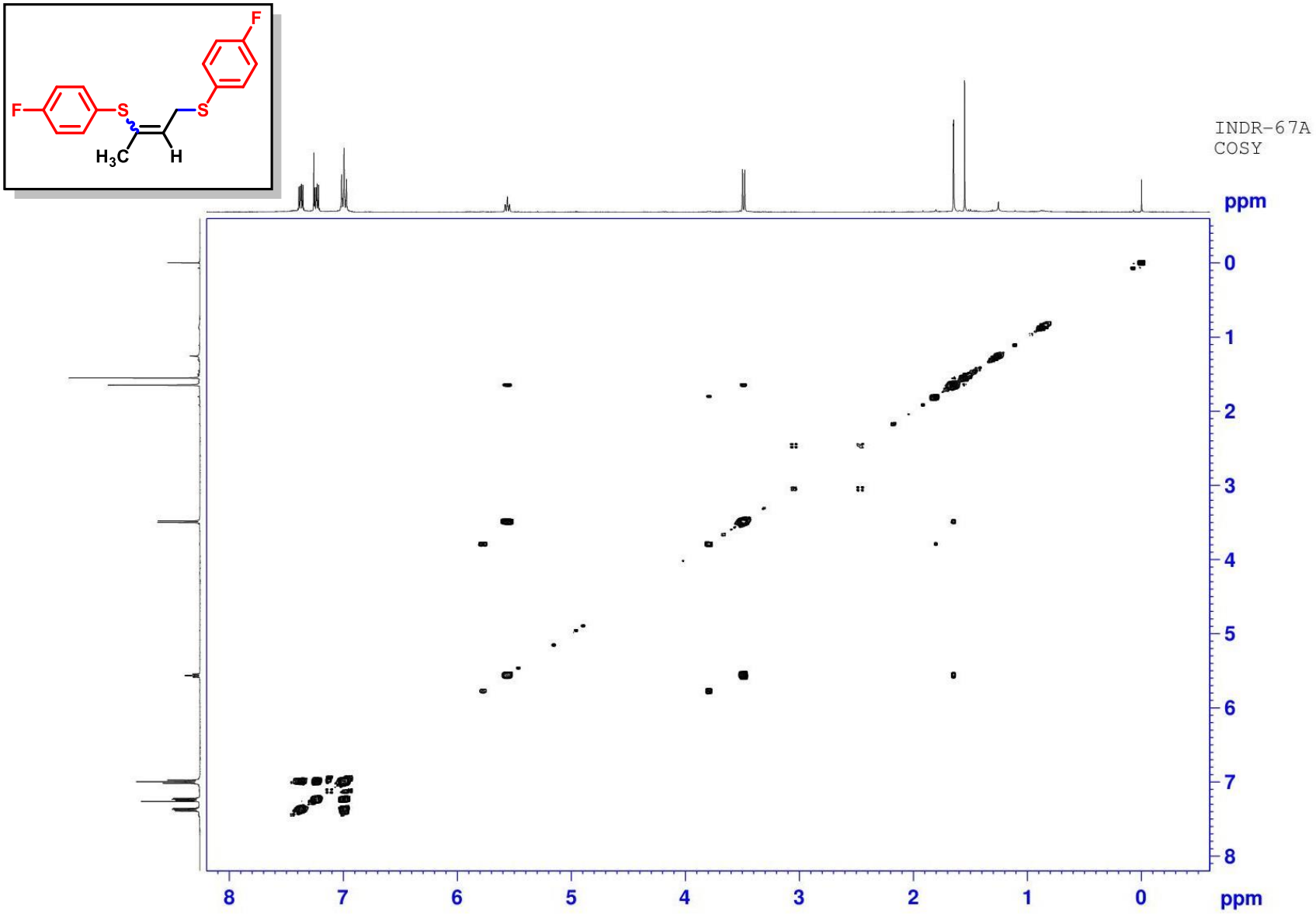



**Fig.S49** COSY Spectrum of **8a**

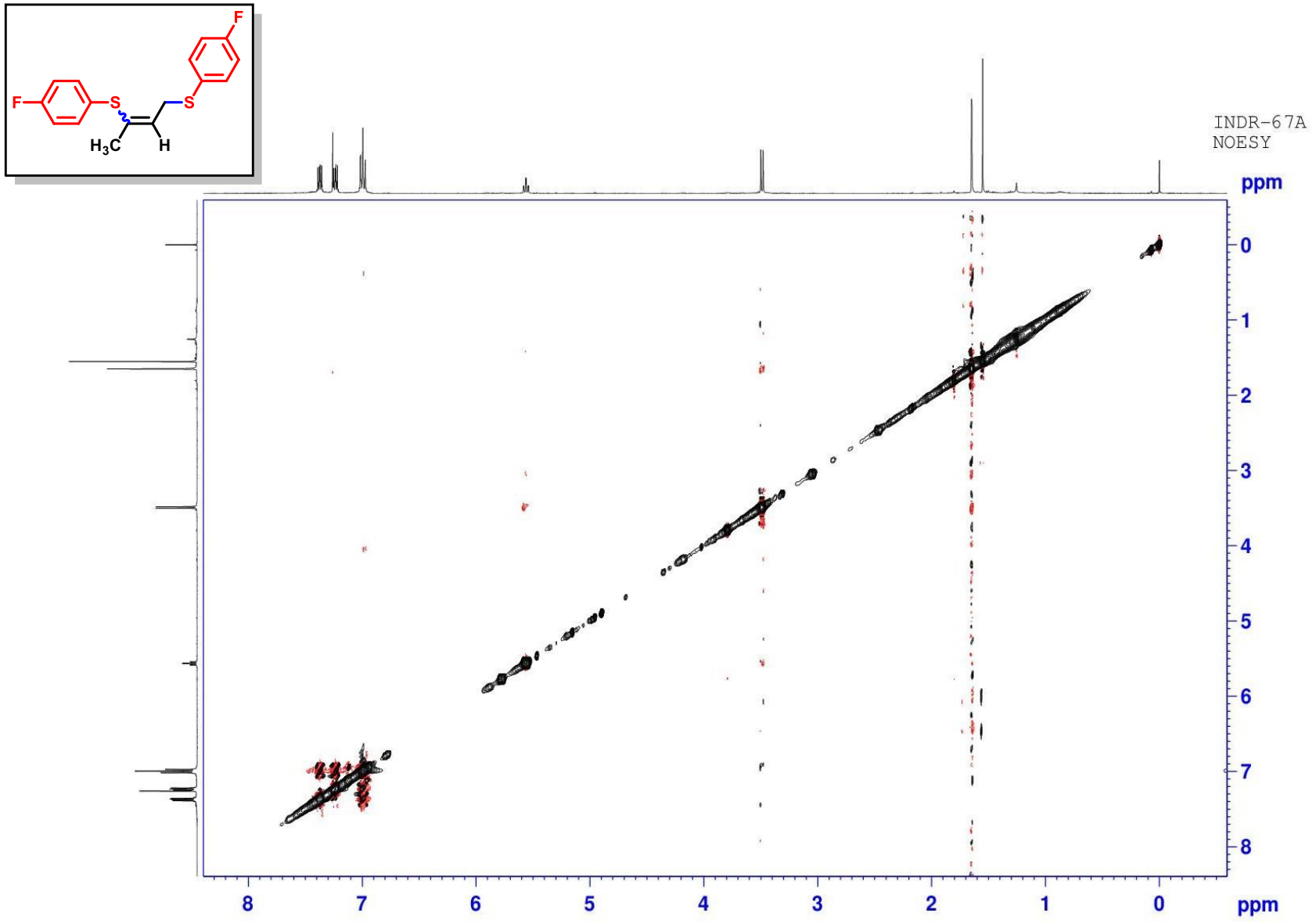



**Fig.S50** NOESY Spectrum of **8a**

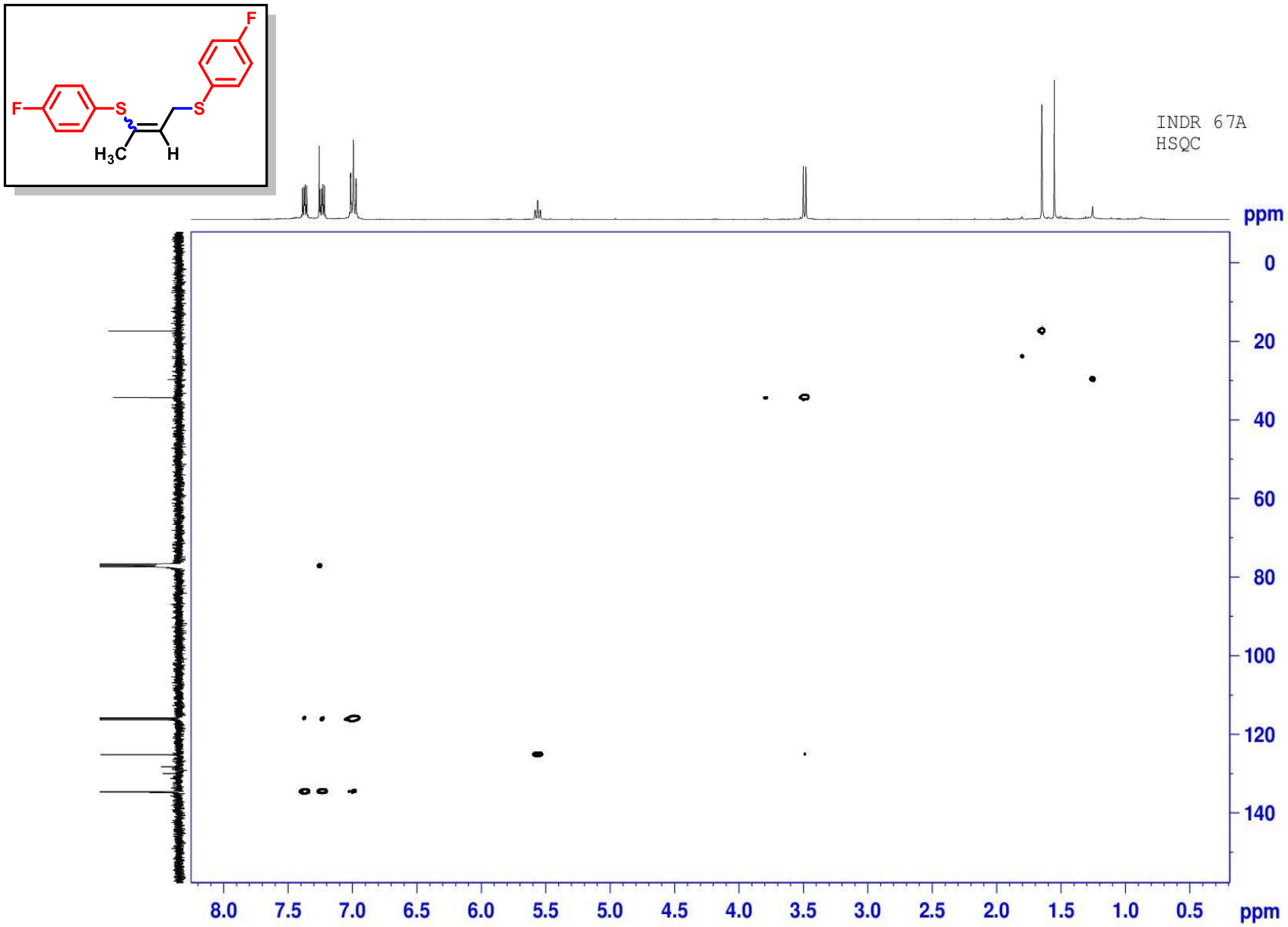



**Fig.S51** HSQC Spectrum of **8a**

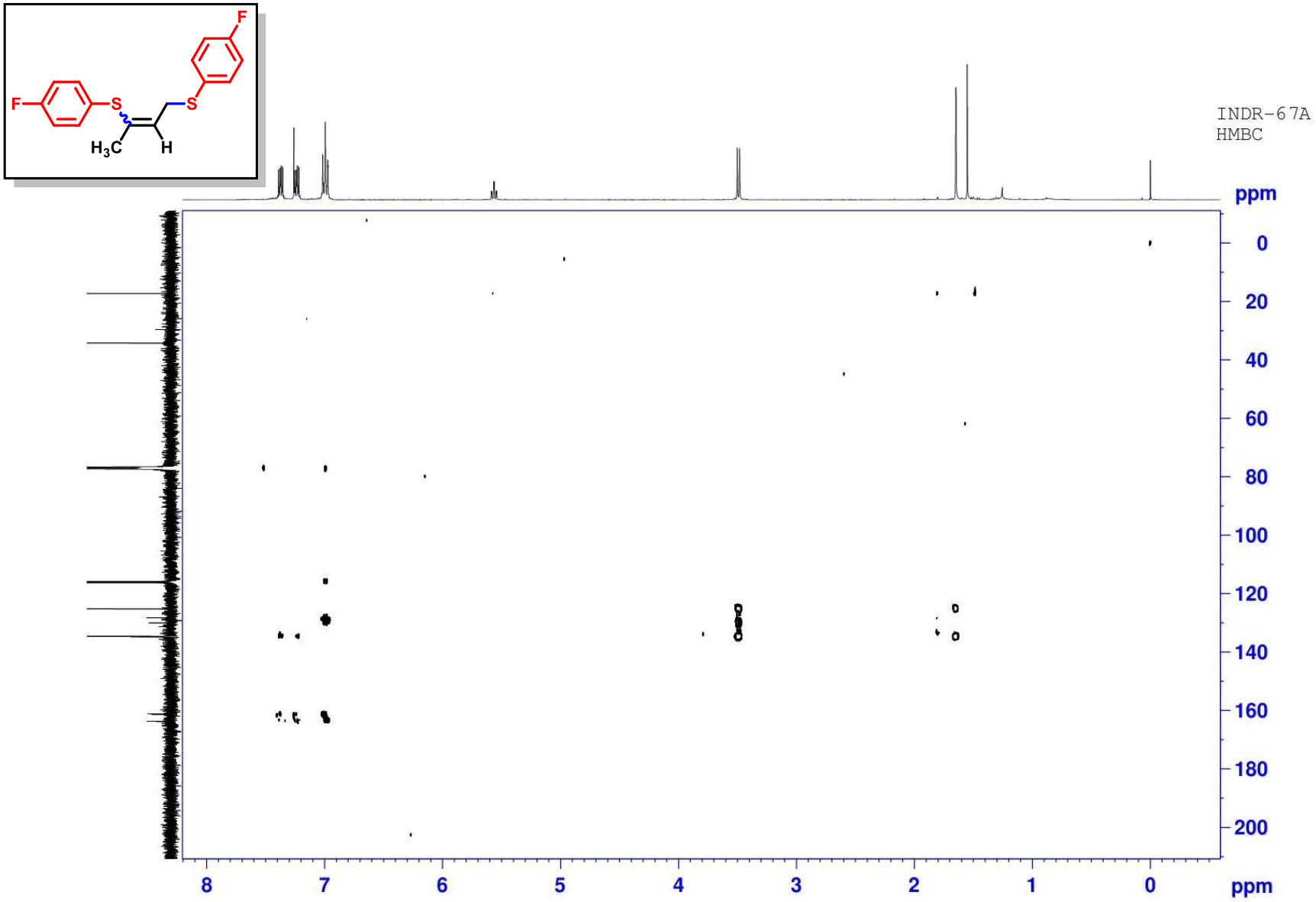



**Fig.S52** HMBC Spectrum of **8a**

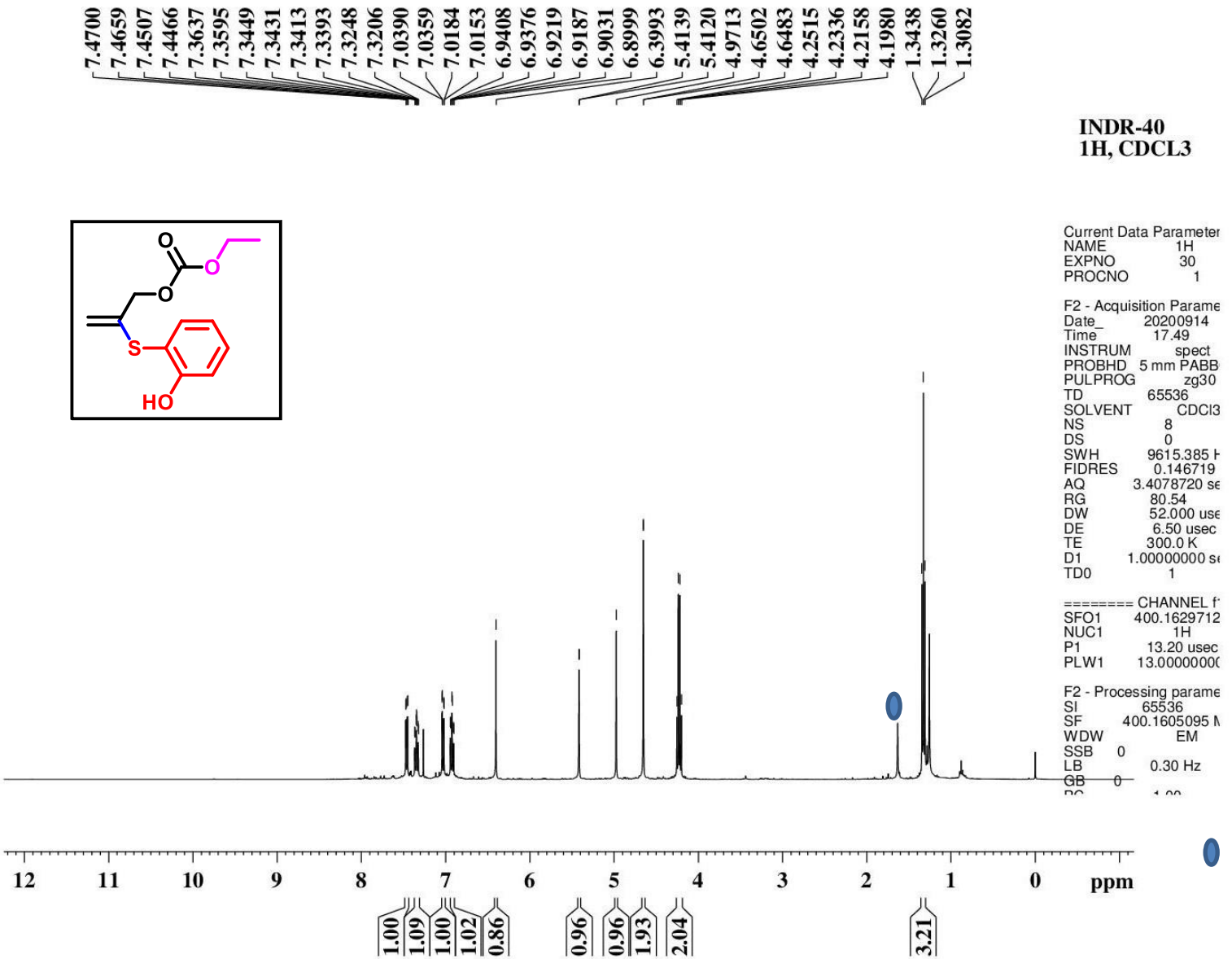



**Fig.S53** $^{1}$H NMR Spectrum of **4a**

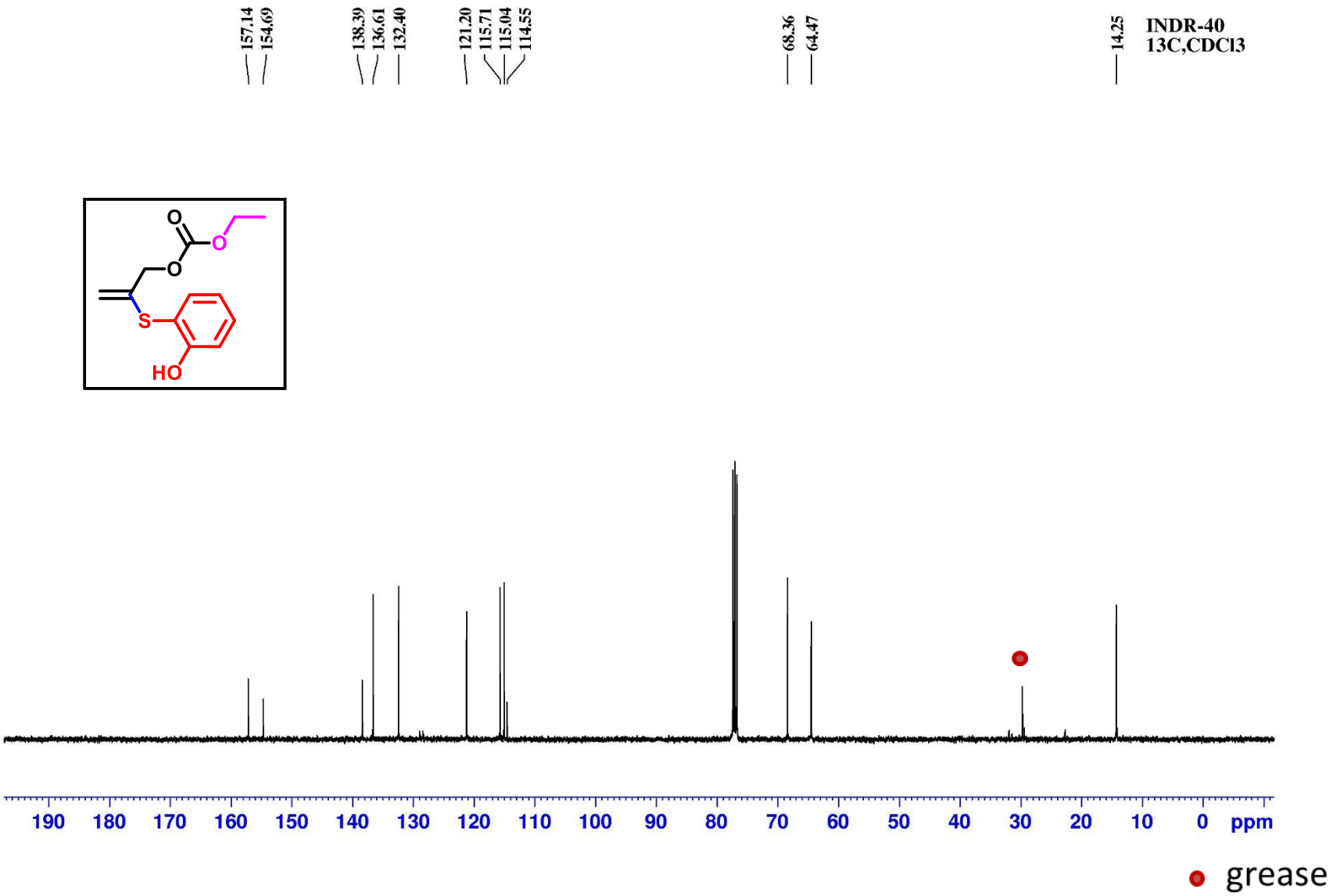



**Fig.S54** $^{13}$C NMR Spectrum of **4a**

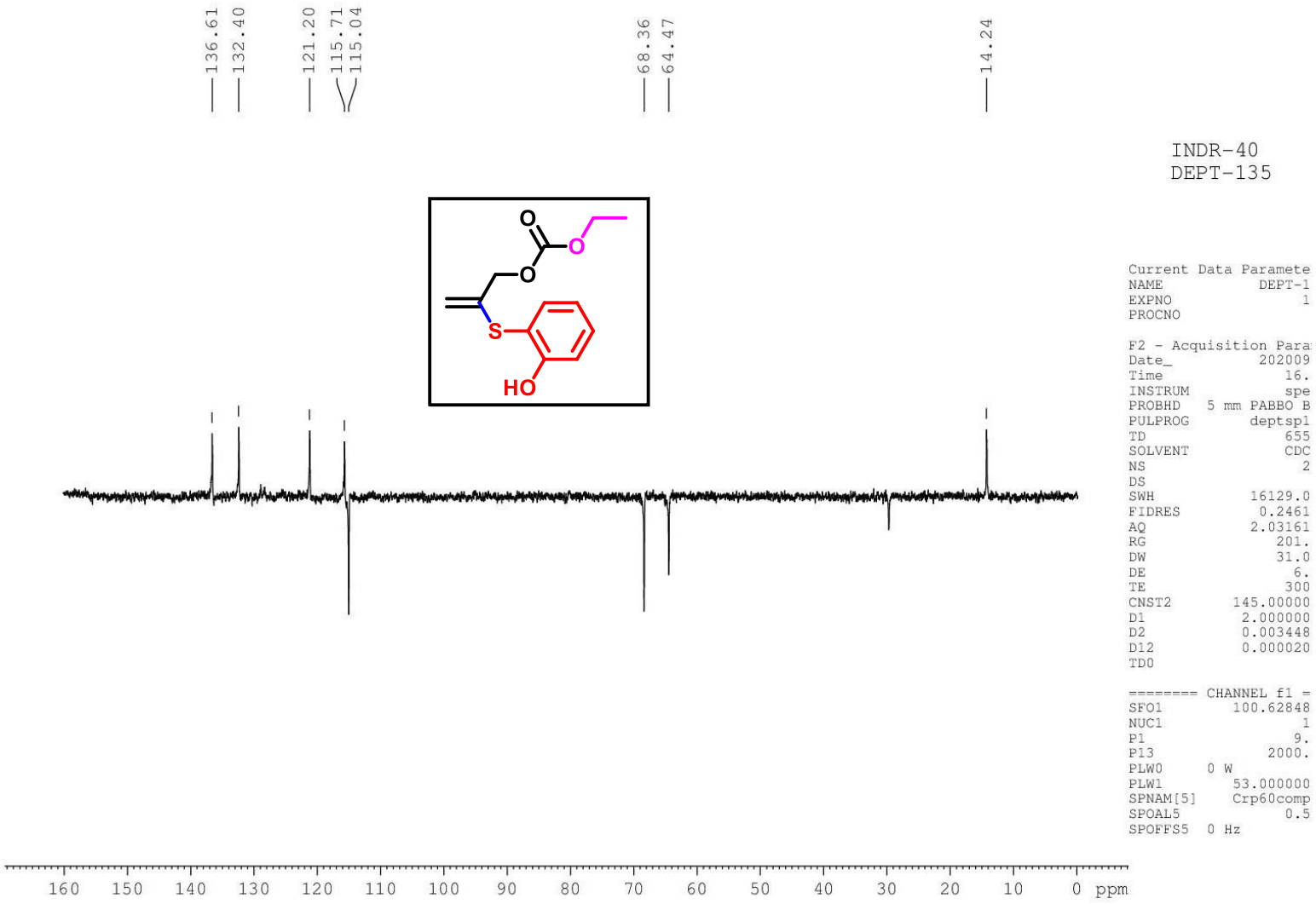
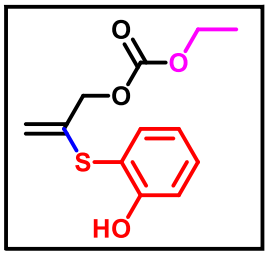



**Fig.S55** DEPT-135 Spectrum of **4a**



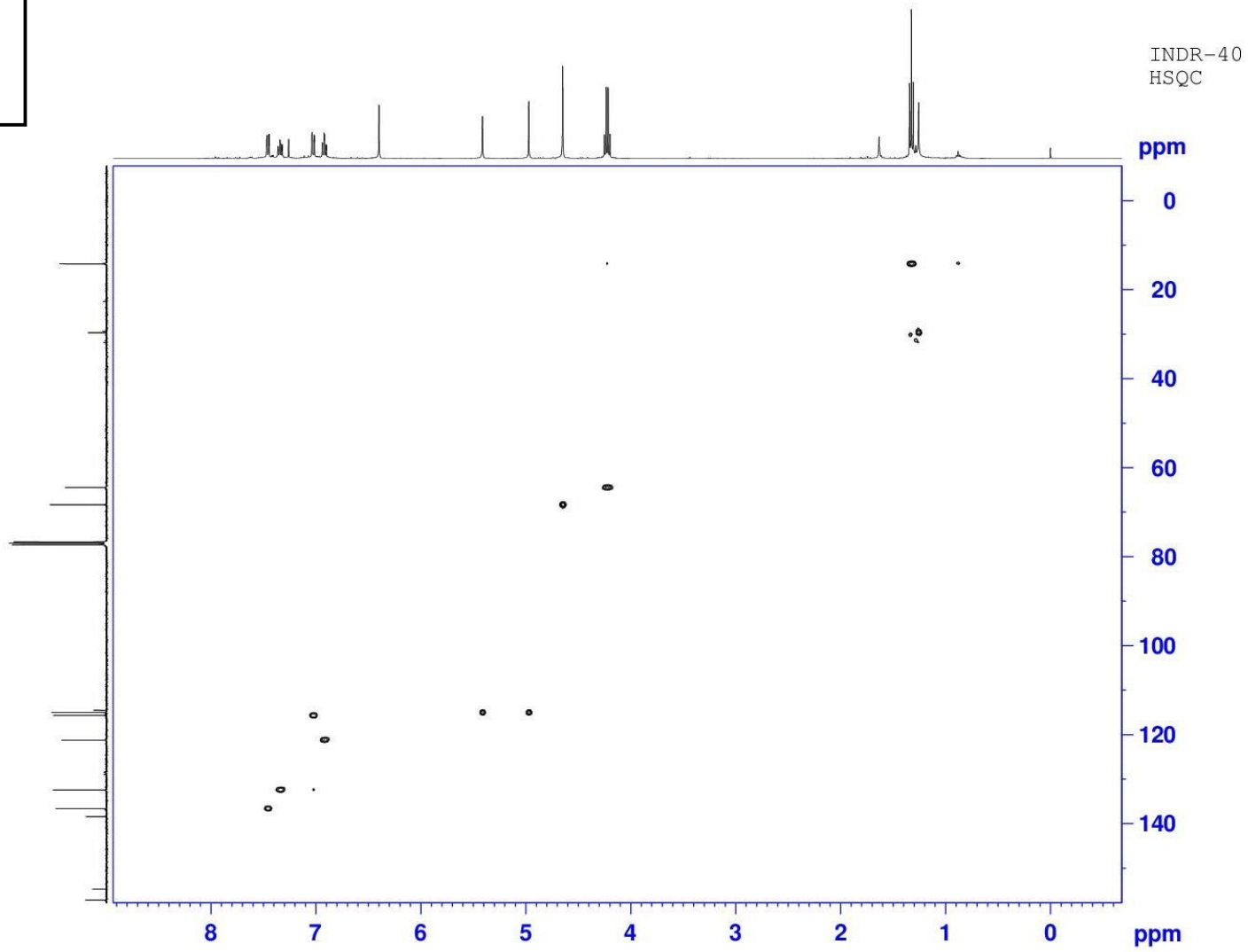




**Fig.S56** HSQC Spectrum of **4a**

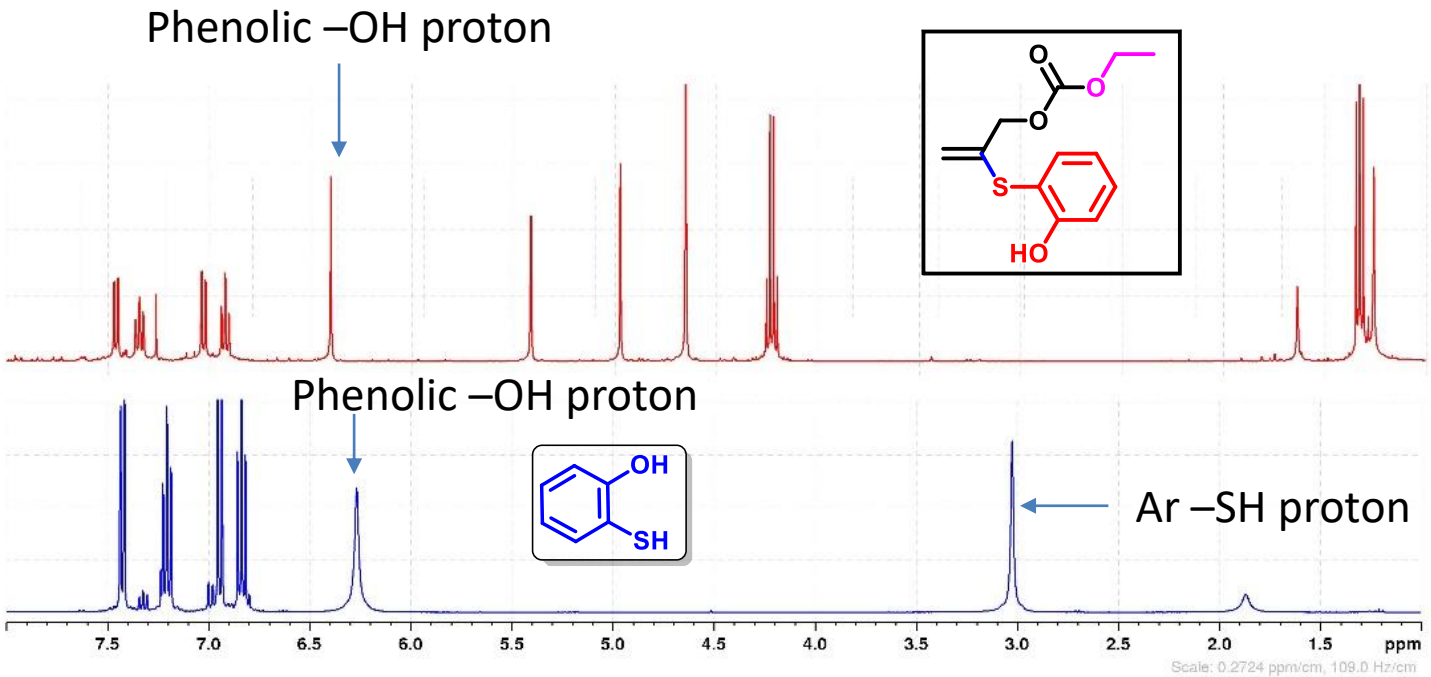



**Fig.S57 comparison of 1H NMR between SM (2-mercapto phenol) and product (4a).**

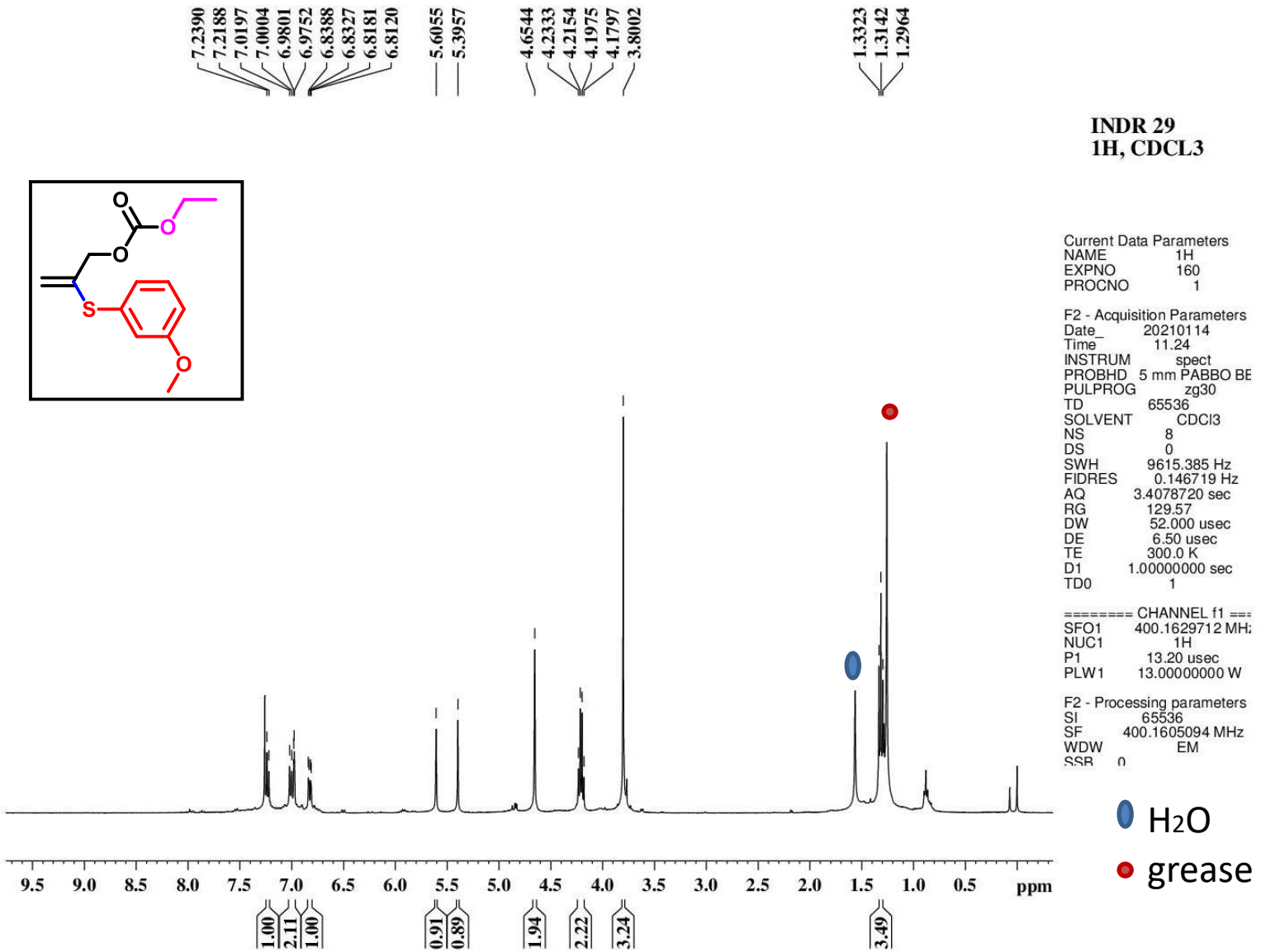



**Fig.S58** $^{1}$H NMR Spectrum of **4b**

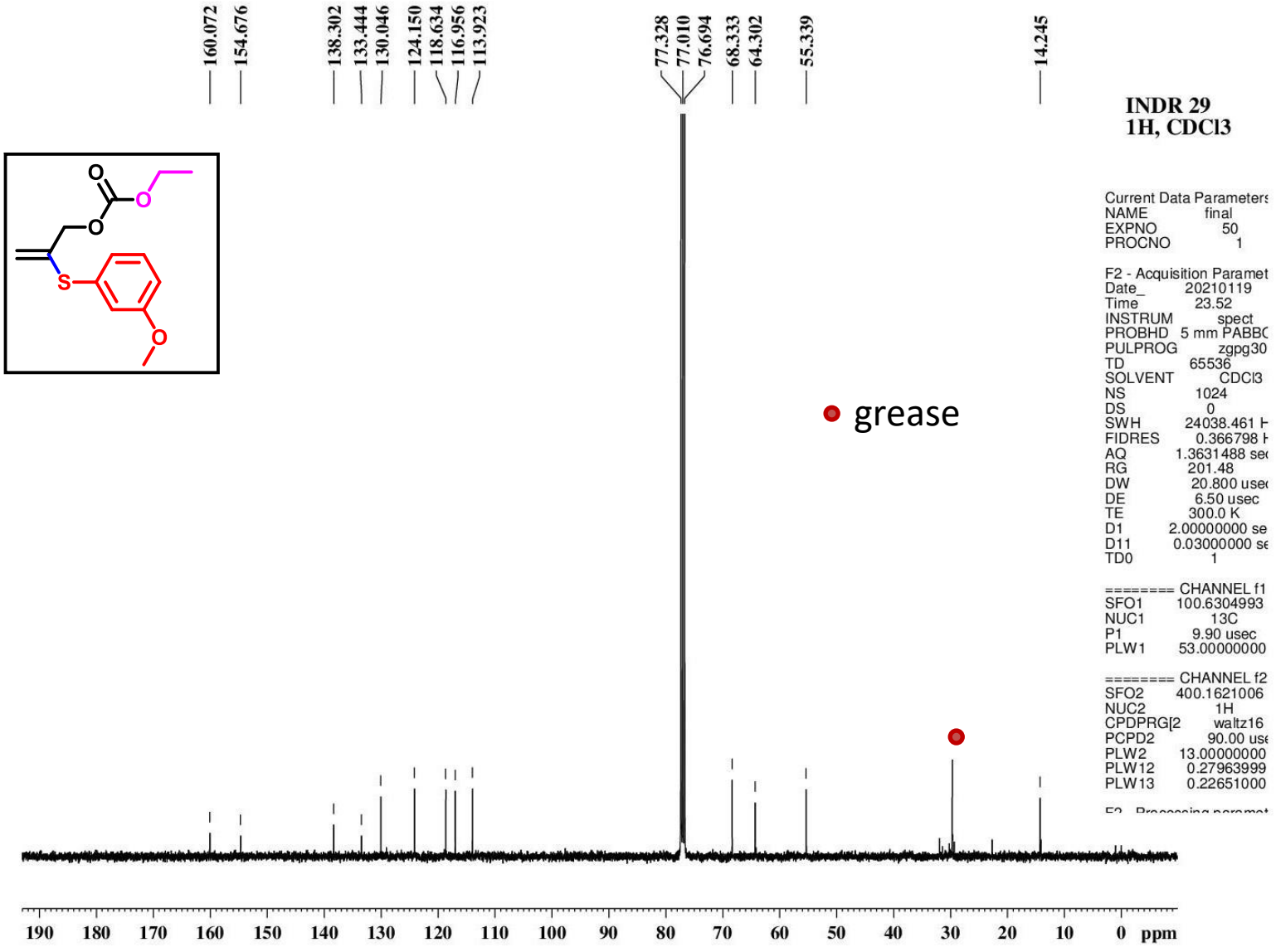



**Fig.S59** $^{13}$C NMR Spectrum of **4b**

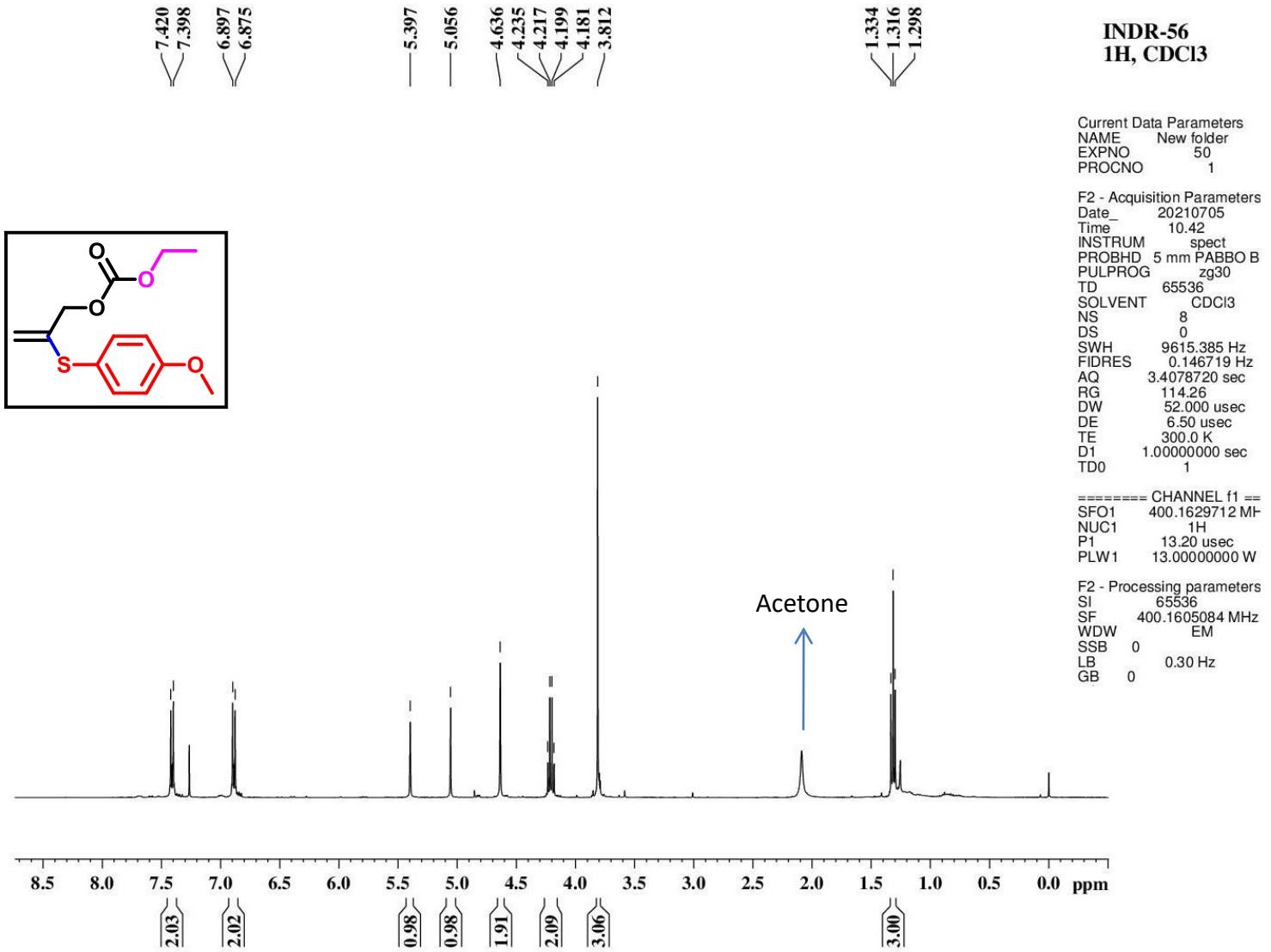



**Fig.S60** $^{1}$H NMR Spectrum of **4c**

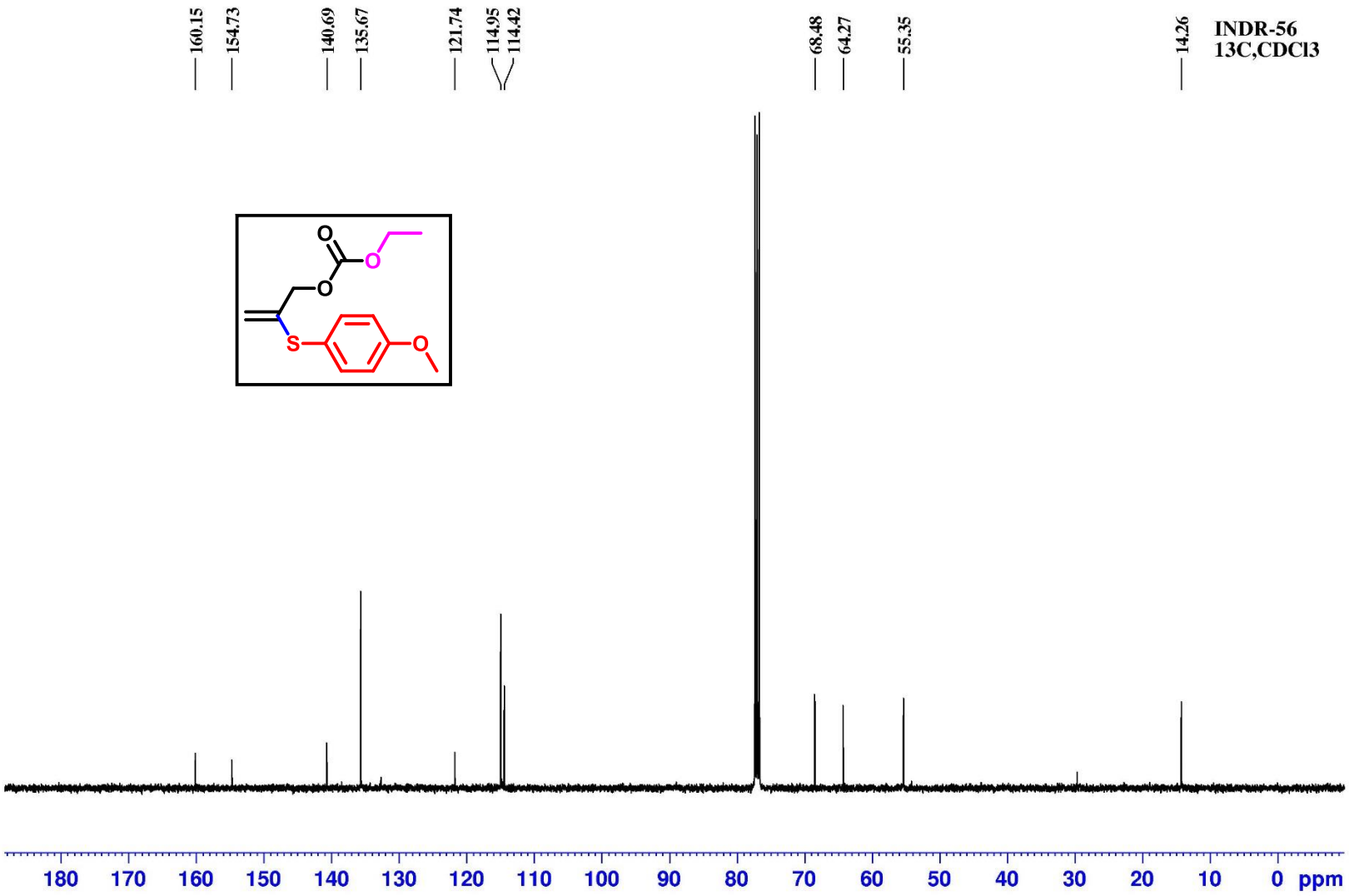



**Fig.S61** $^{13}$C NMR Spectrum of **4c**

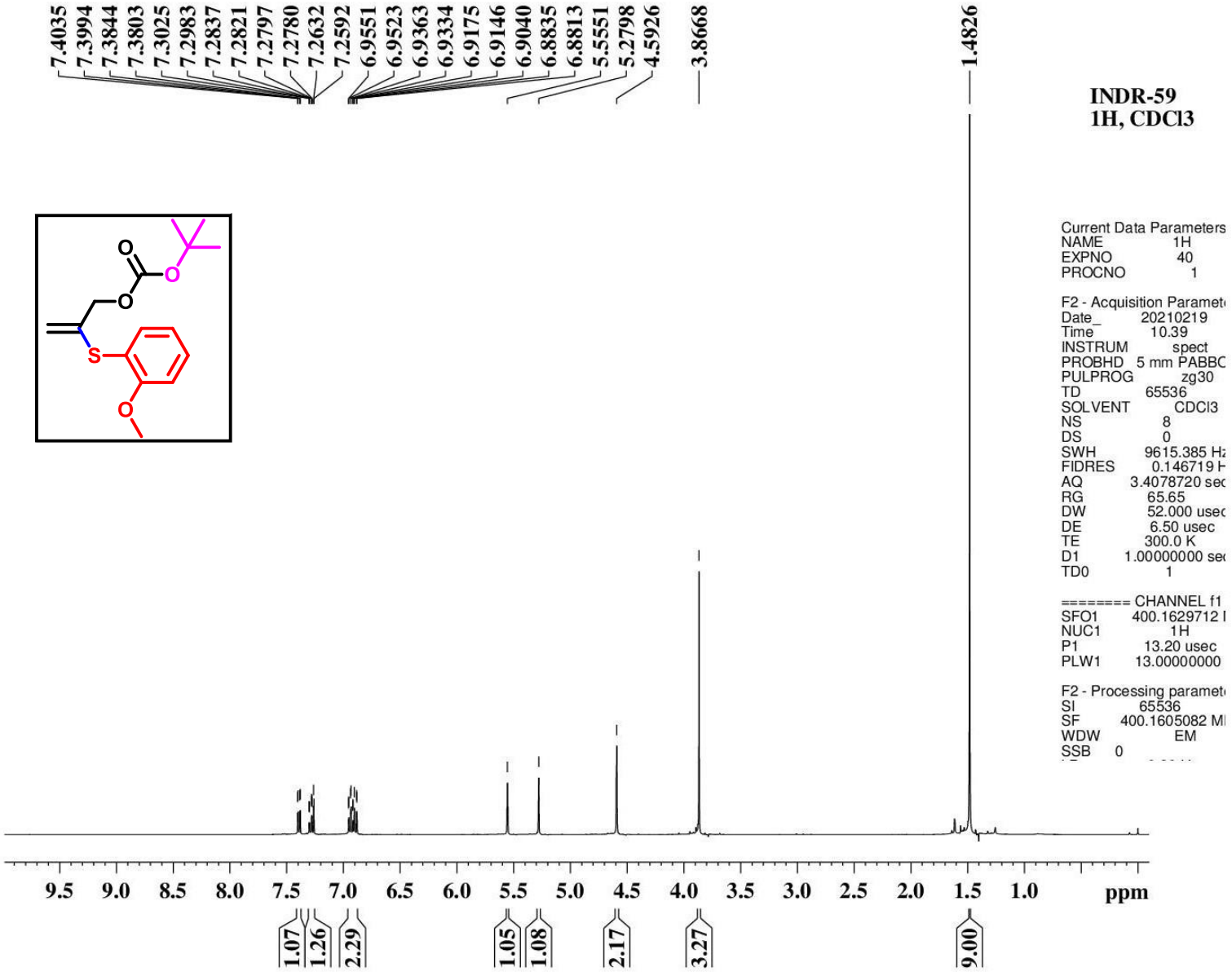



**Fig.S62** $^{1}$H NMR Spectrum of **4d**

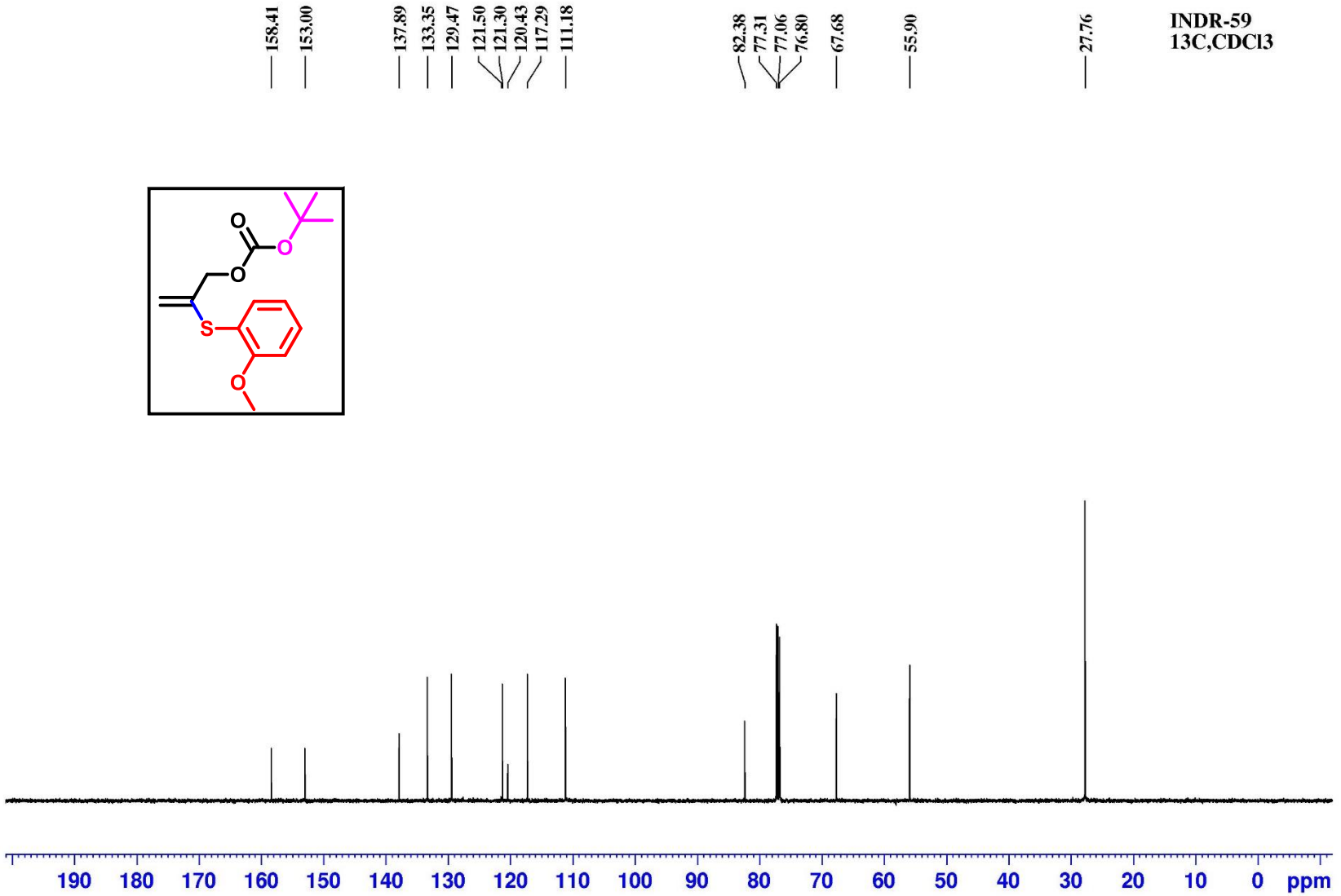



**Fig.S63** $^{13}$C NMR Spectrum of **4d**

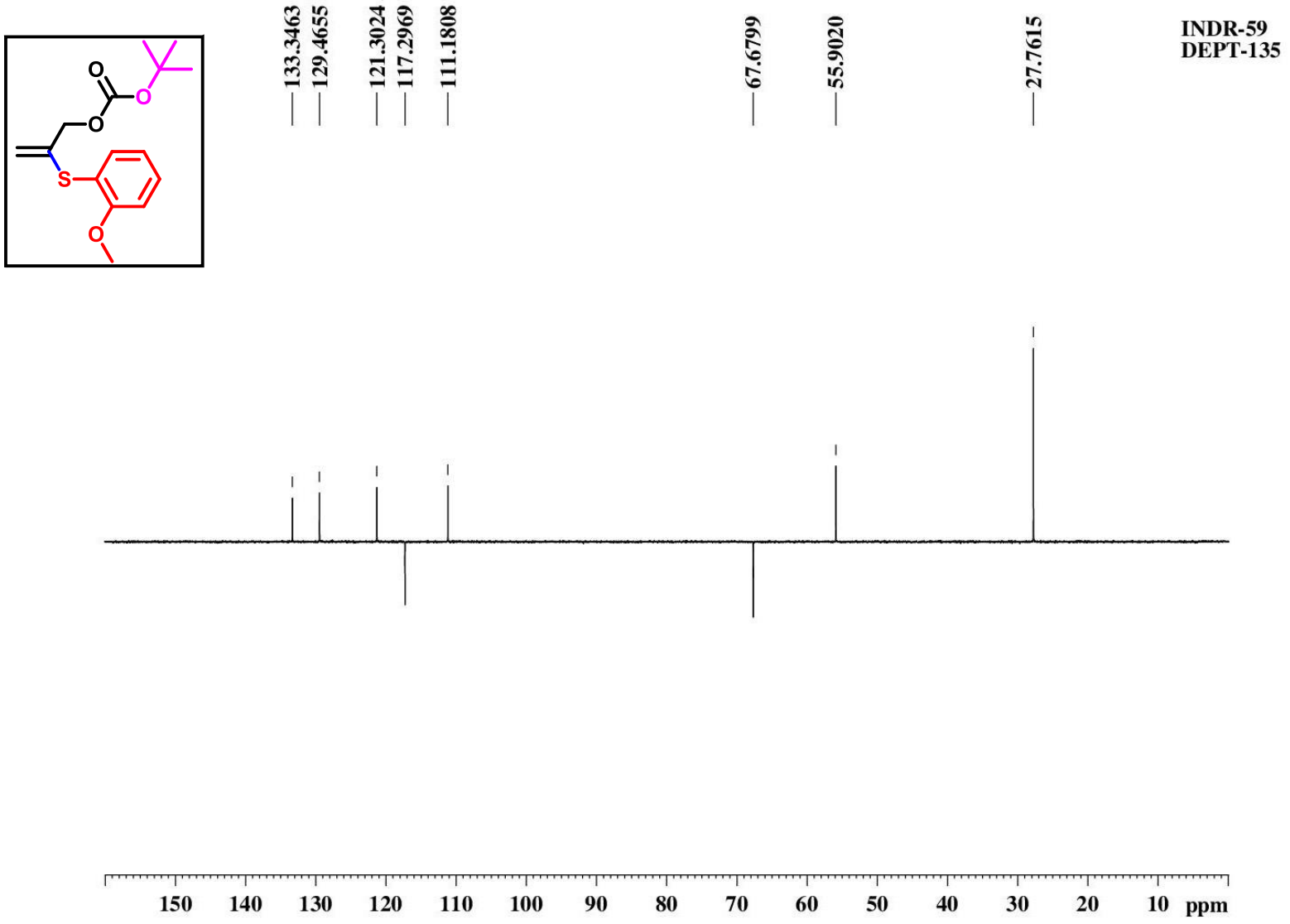



**Fig.S64** DEPT-135 Spectrum of **4d**

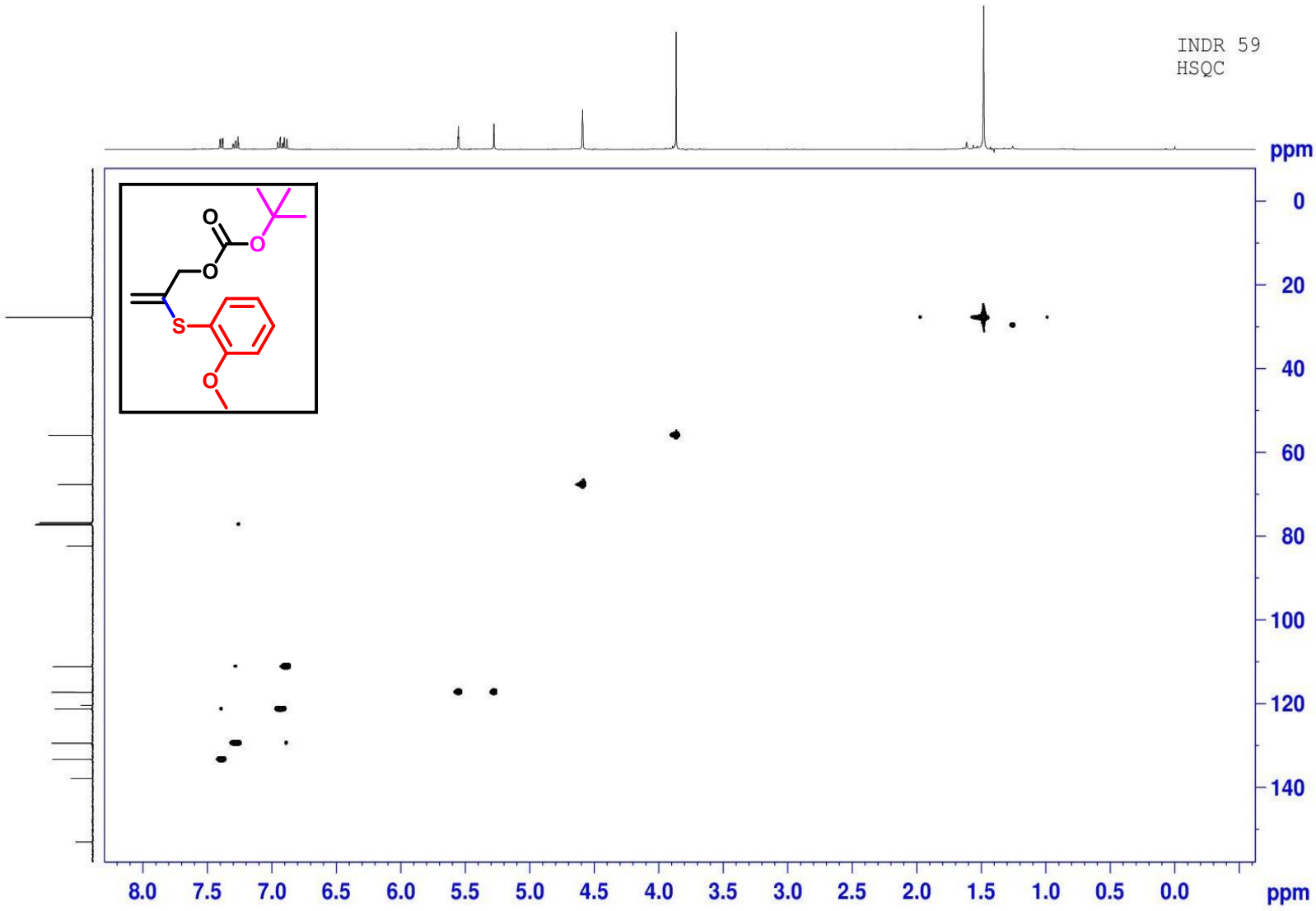



**Fig.S65** HSQC Spectrum of **4d**

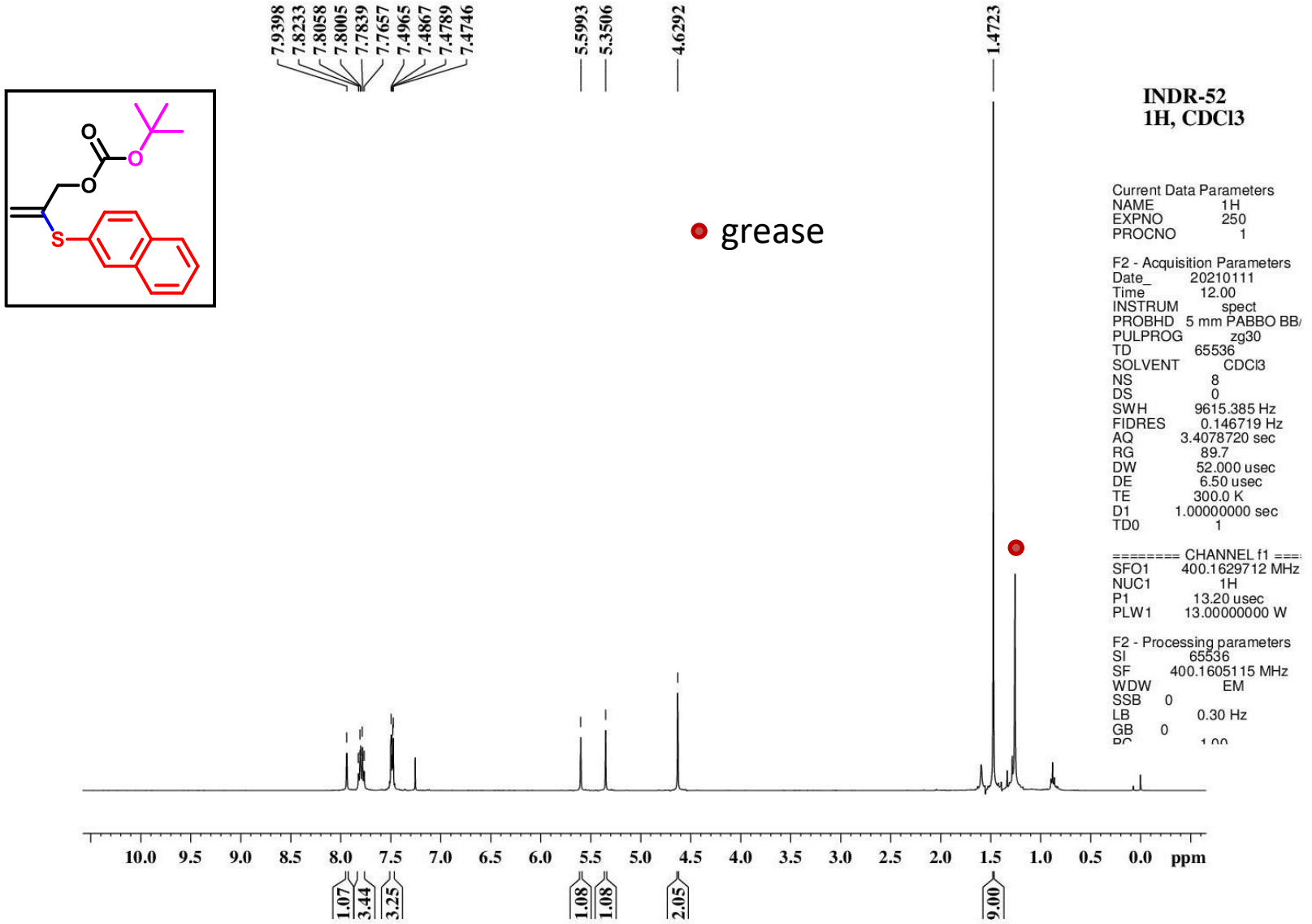



**Fig.S66** $^{1}$H NMR Spectrum of **4e**

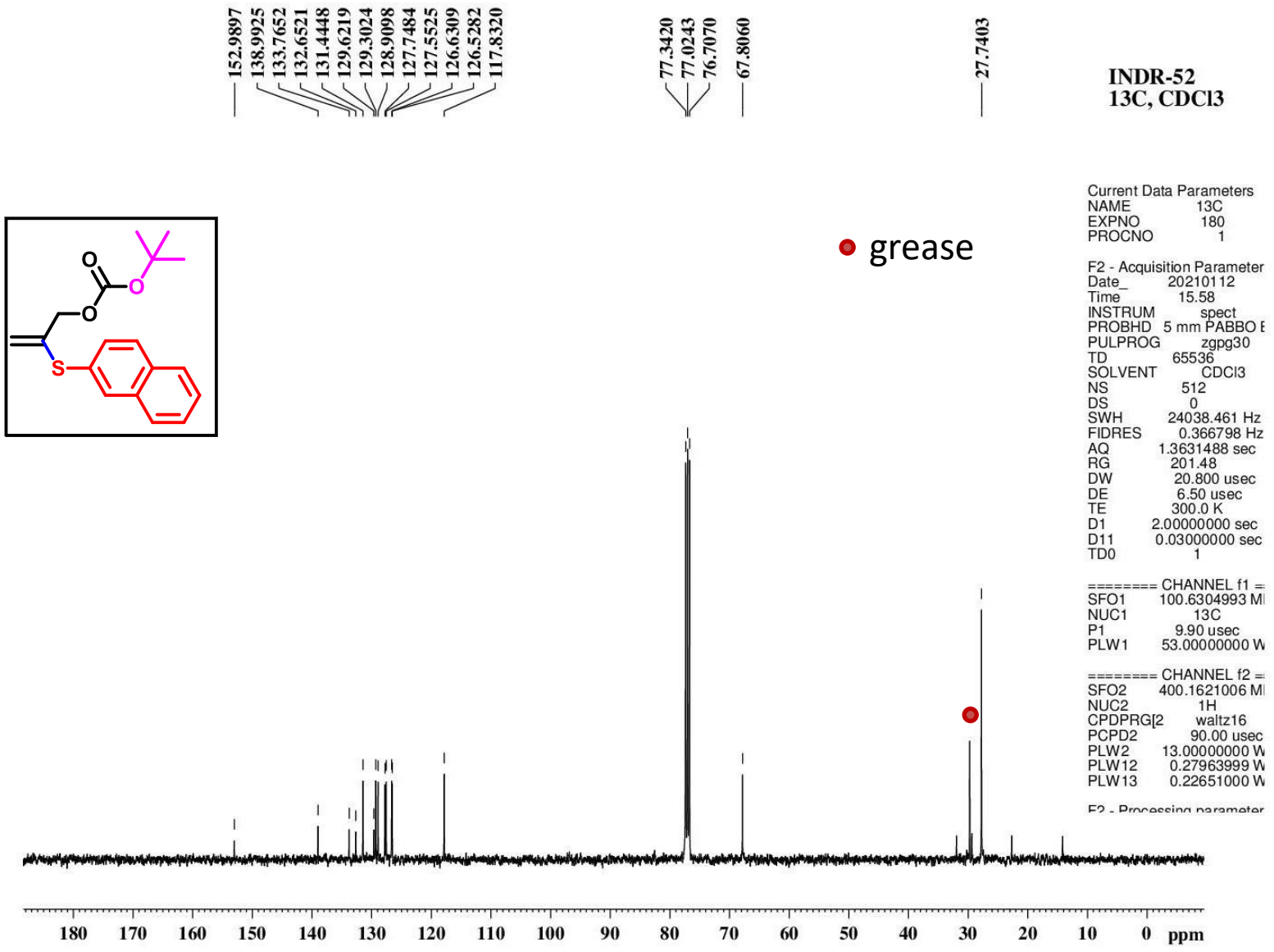



**Fig.S67** $^{13}$C NMR Spectrum of **4e**

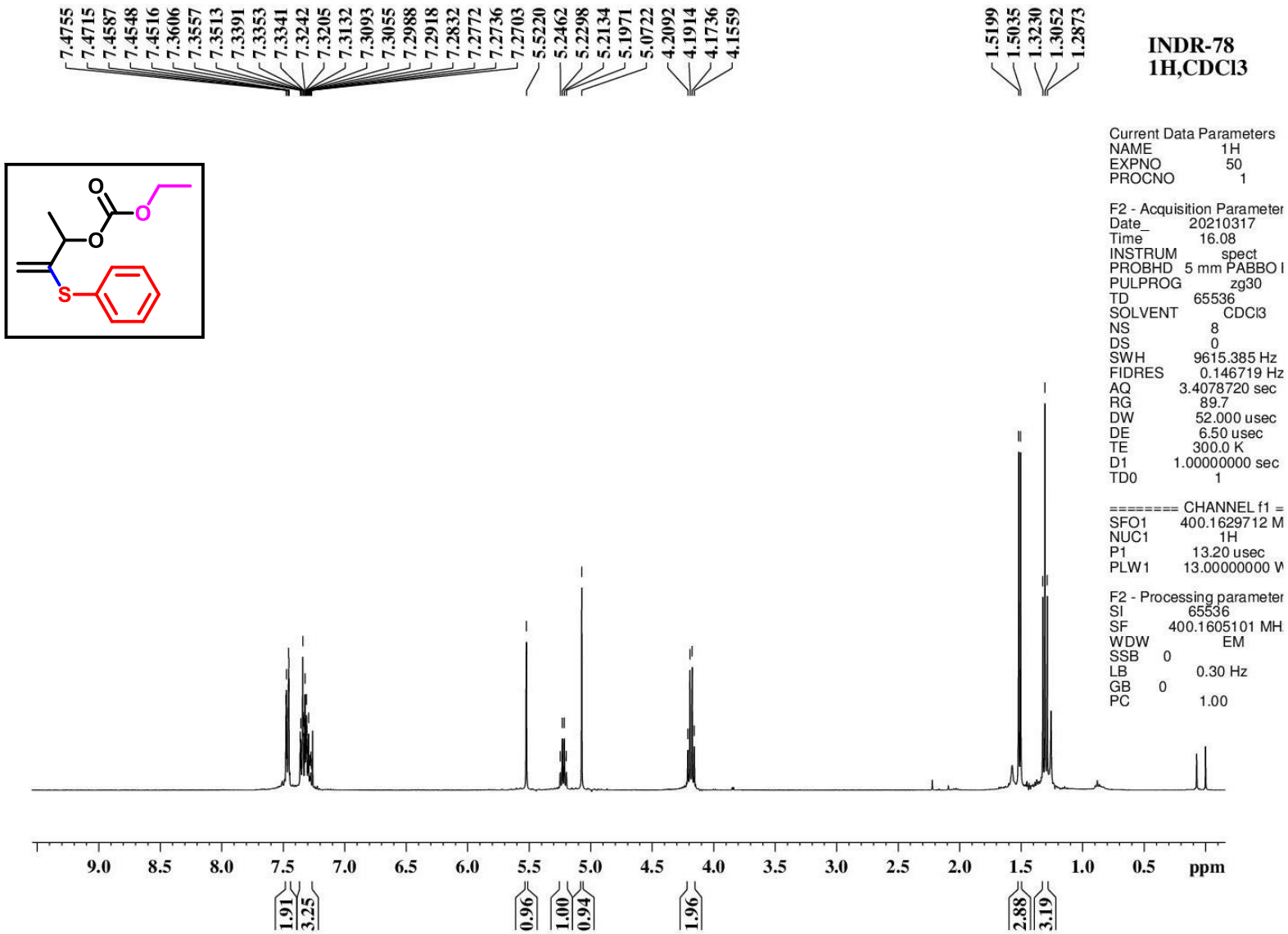



**Fig.S68** $^{1}$H NMR Spectrum of **4f**

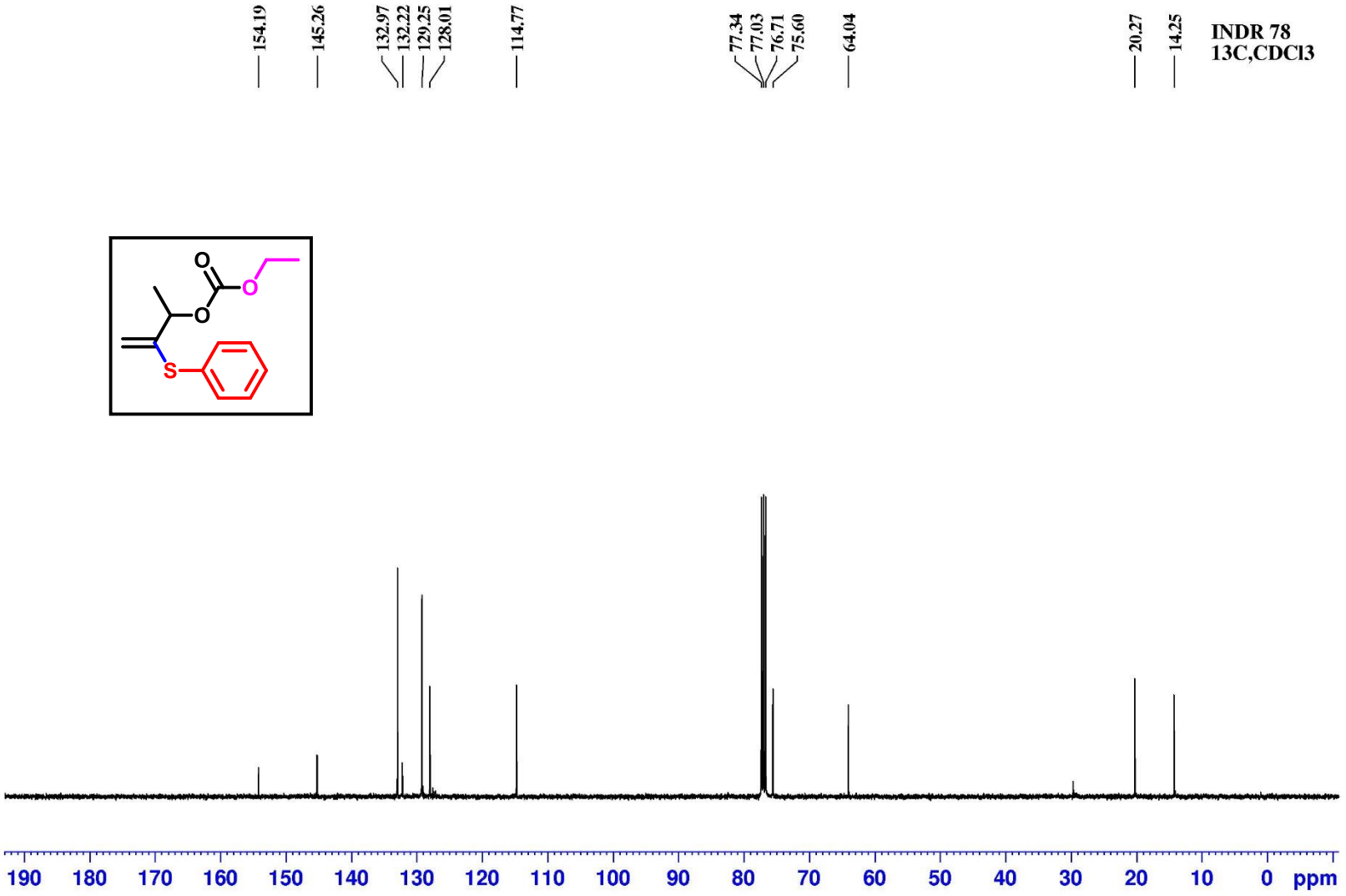



**Fig.S69** $^{13}$C NMR Spectrum of **4f**

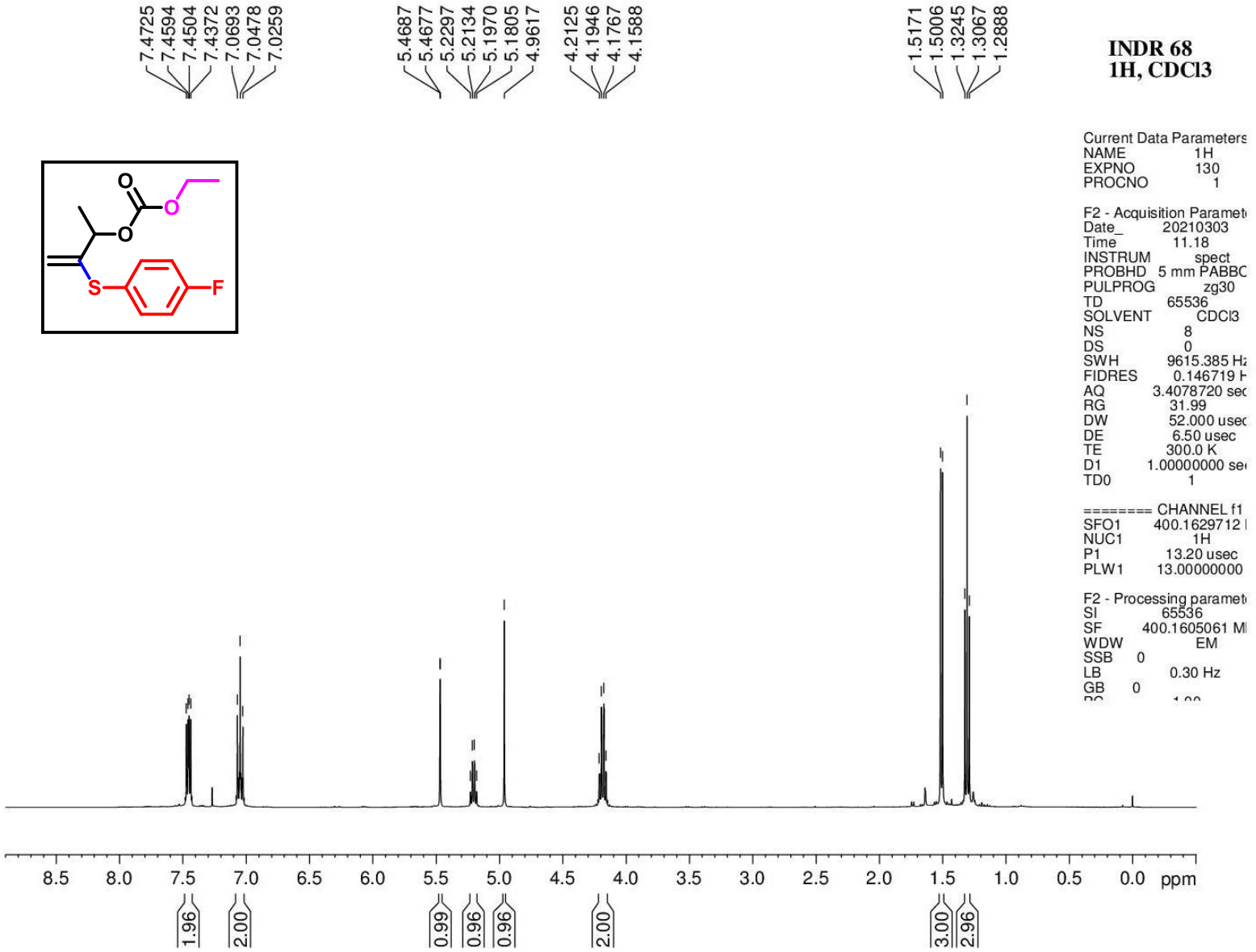



**Fig.S70** $^{1}$H NMR Spectrum of **4g**

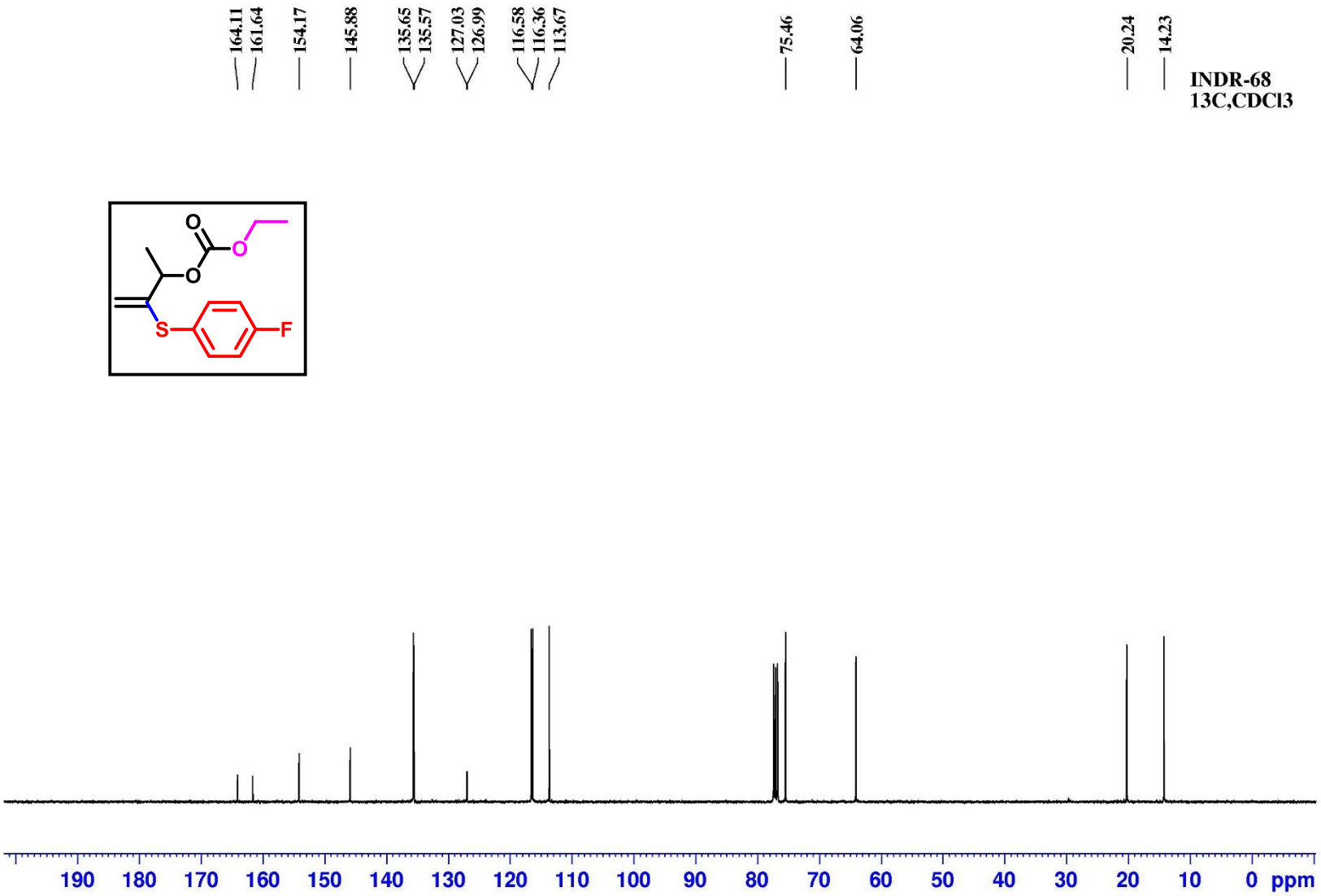



**Fig.S71** $^{13}$C NMR Spectrum of **4g**

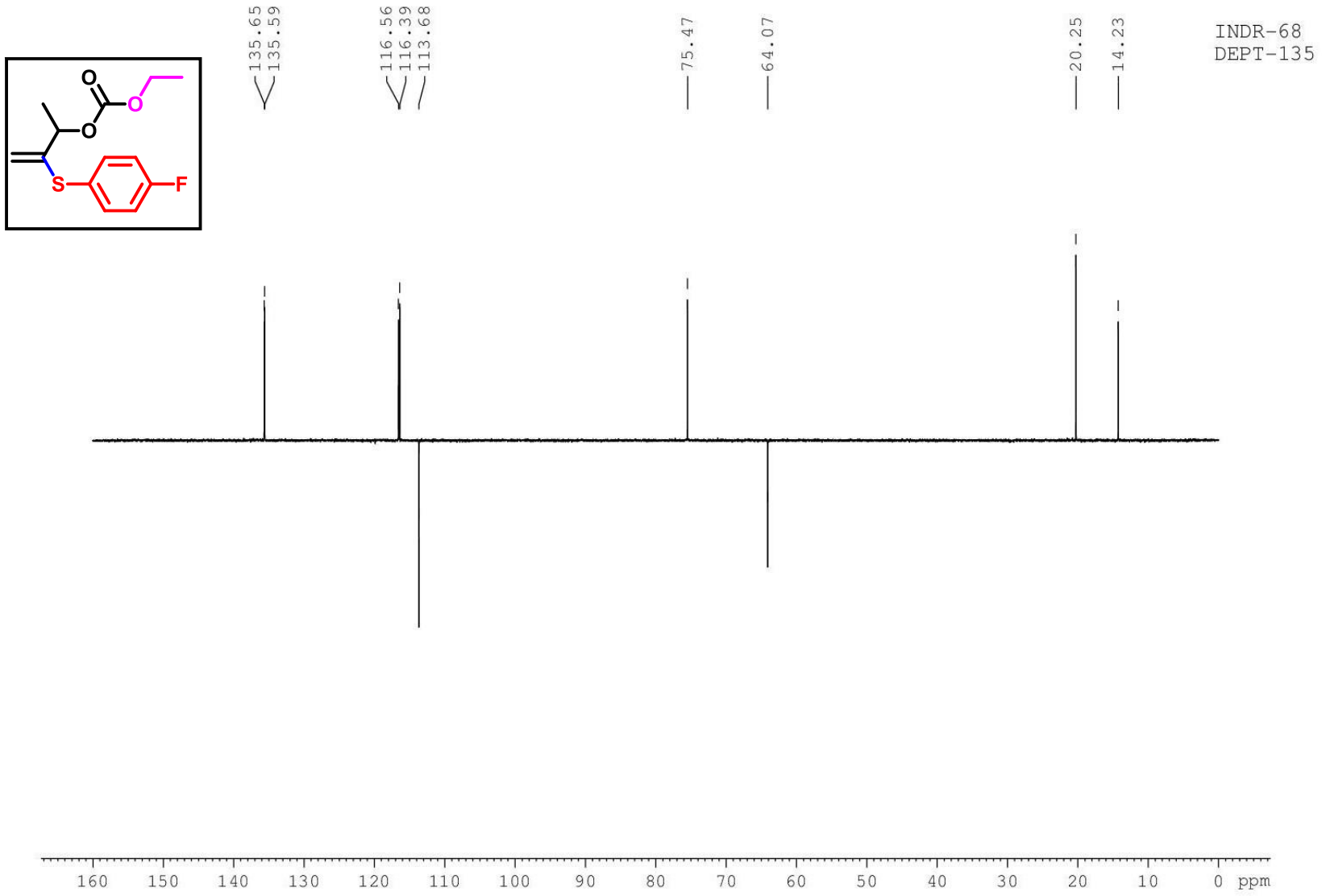



**Fig.S72** DEPT-135 Spectrum of **4g**

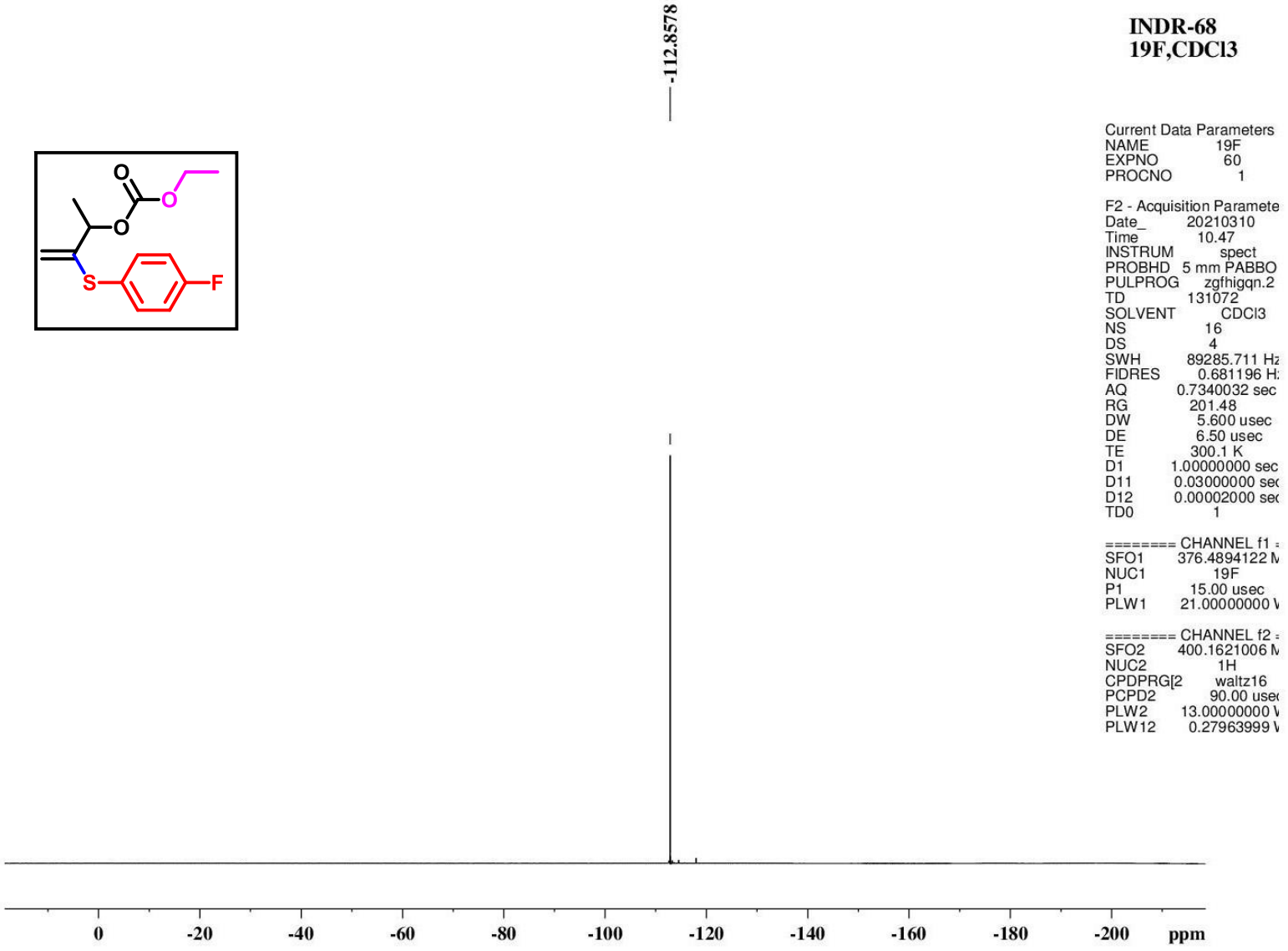



**Fig.S73** $^{19}$F NMR Spectrum of **4g**

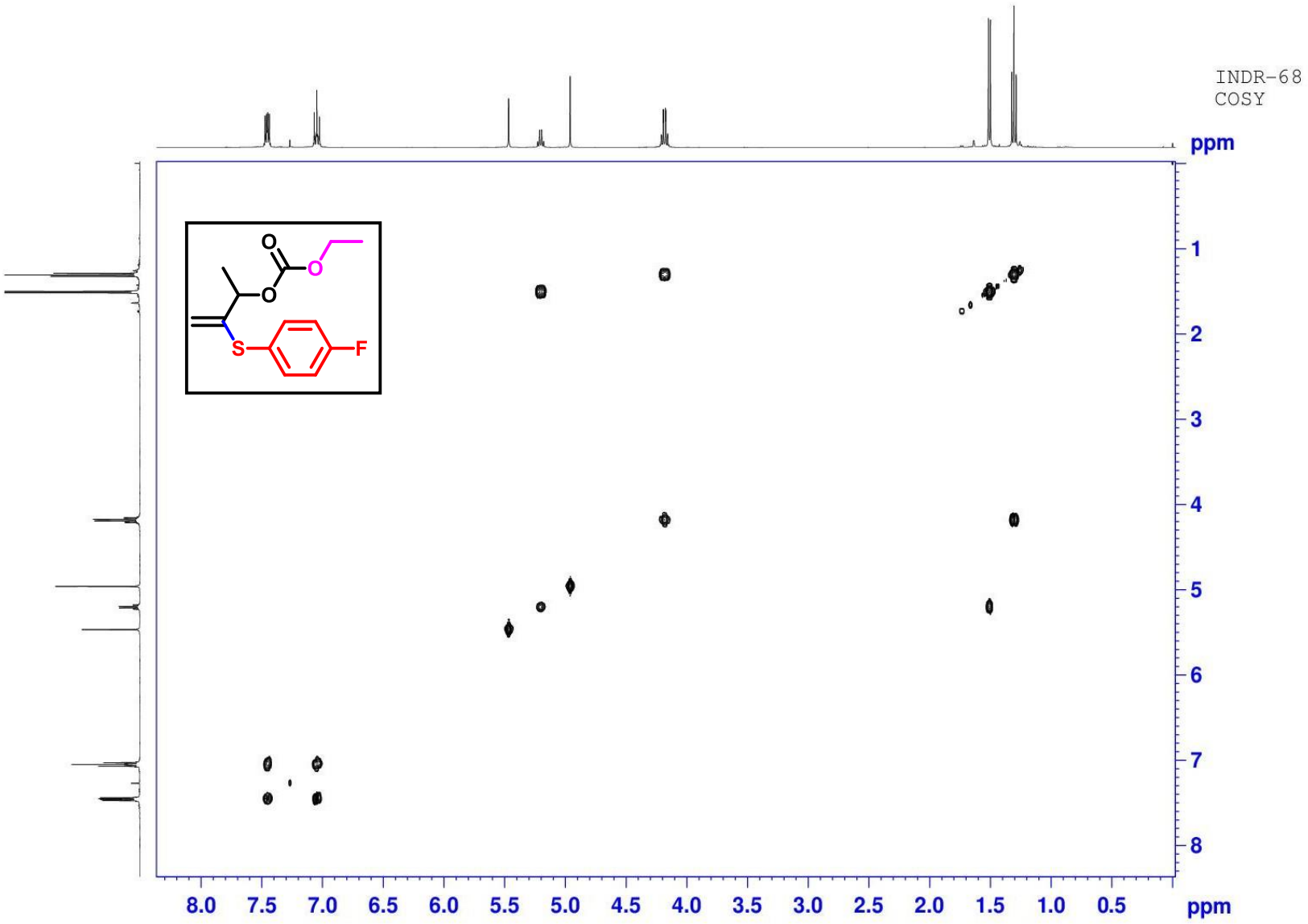



**Fig.S74** COSY Spectrum of **4g**

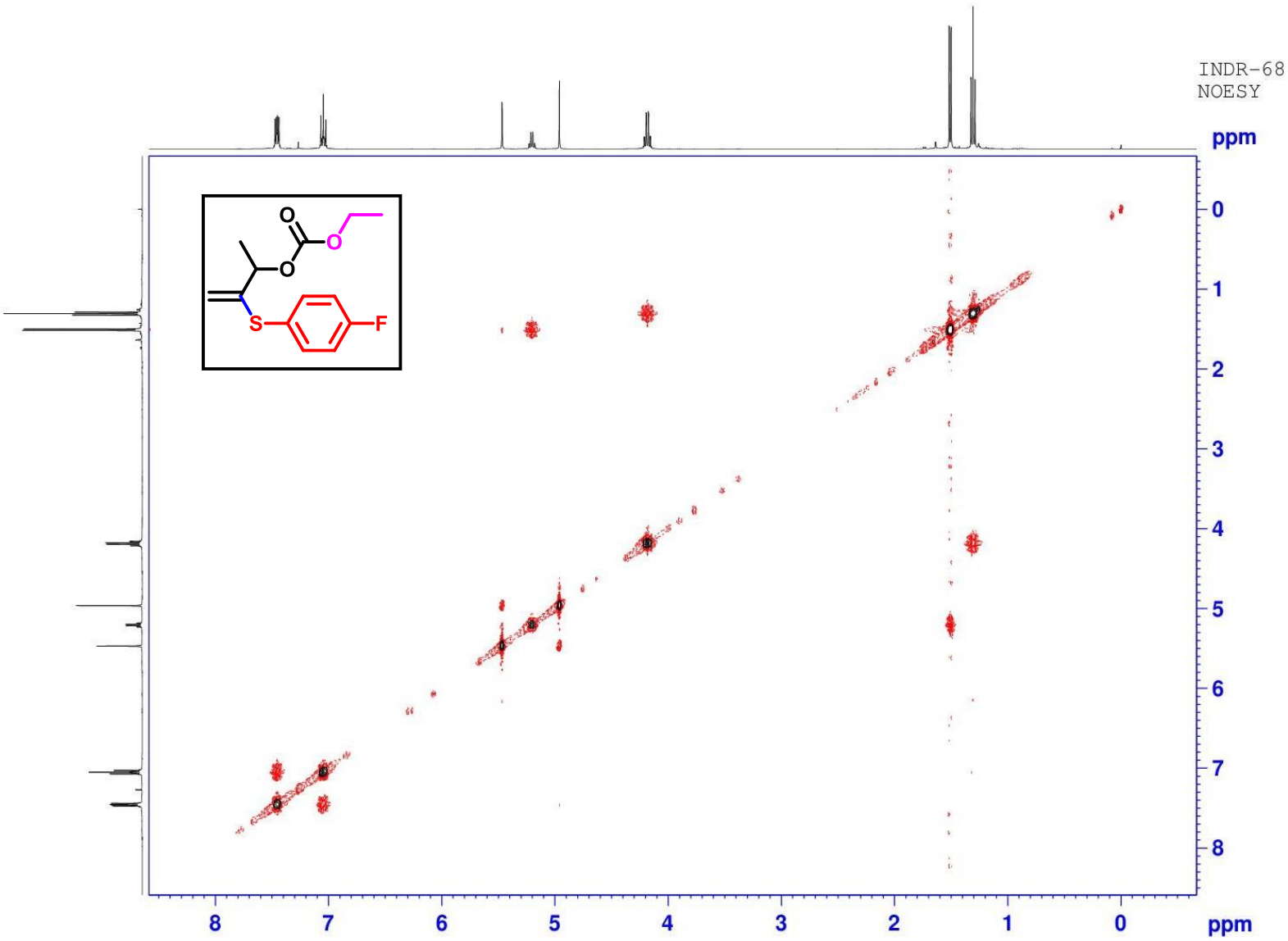



**Fig.S75** NOESY Spectrum of **4g**

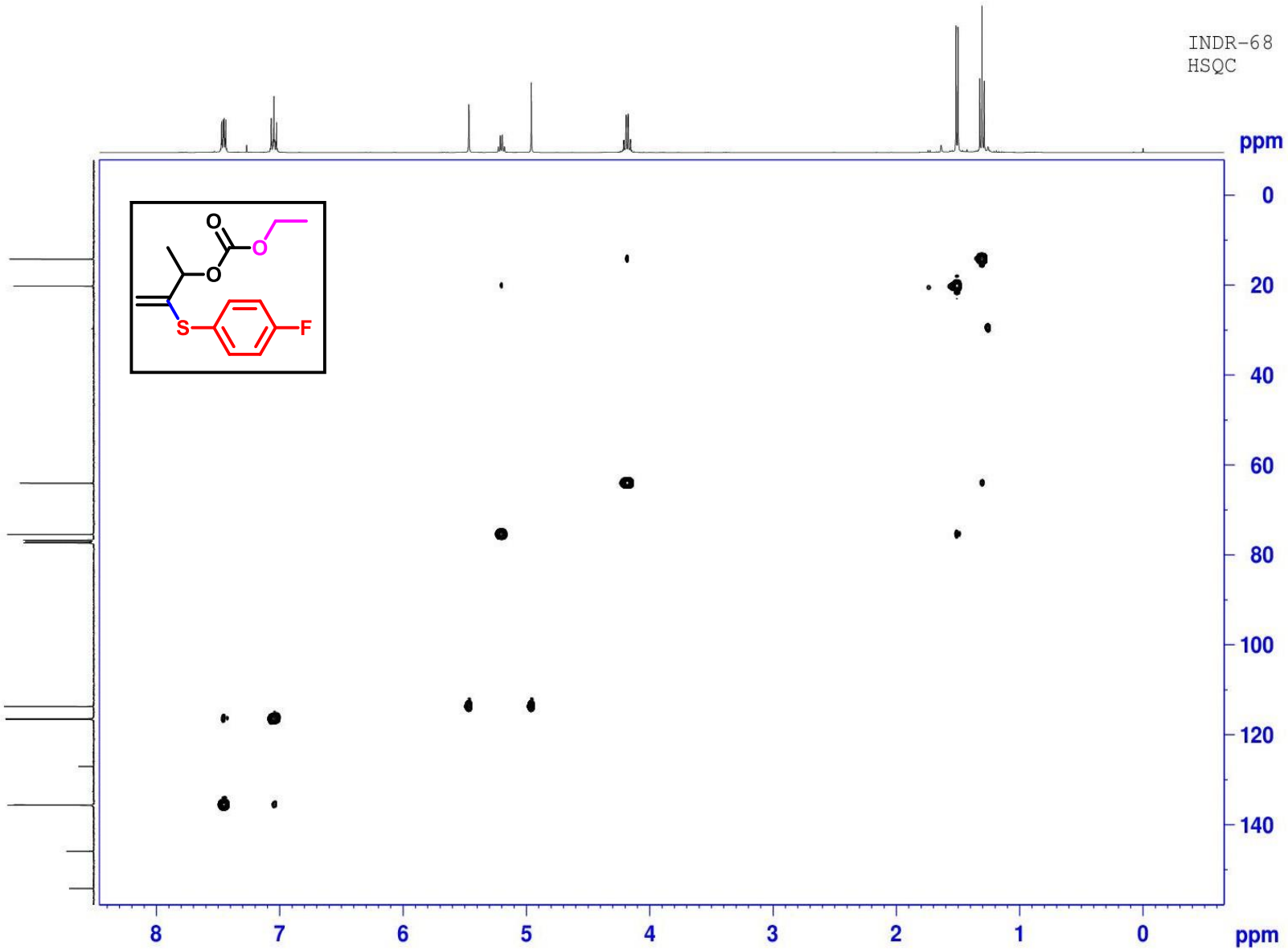



**Fig.S76** HSQC Spectrum of **4g**

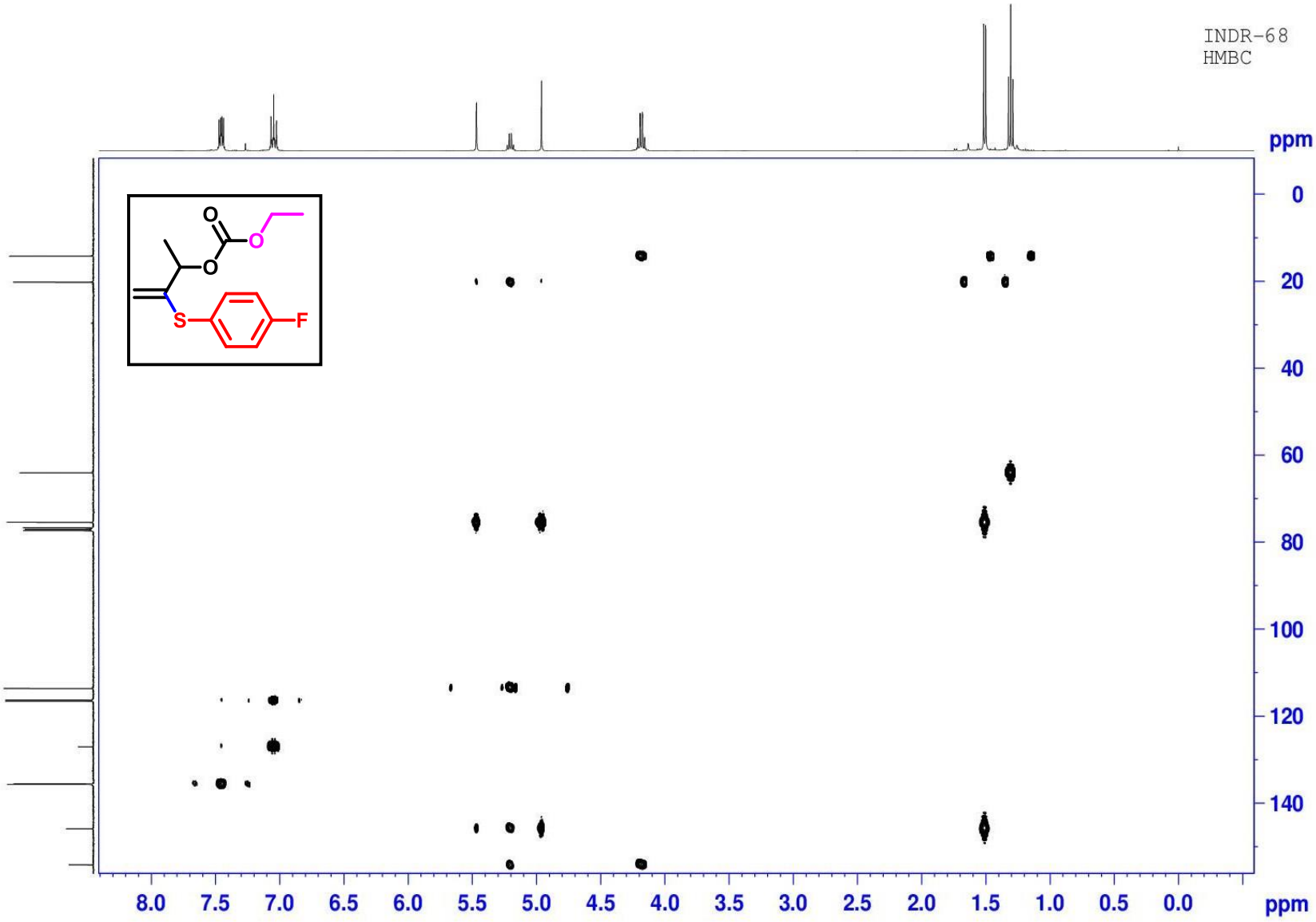



**Fig.S77** HMBC Spectrum of **4g**

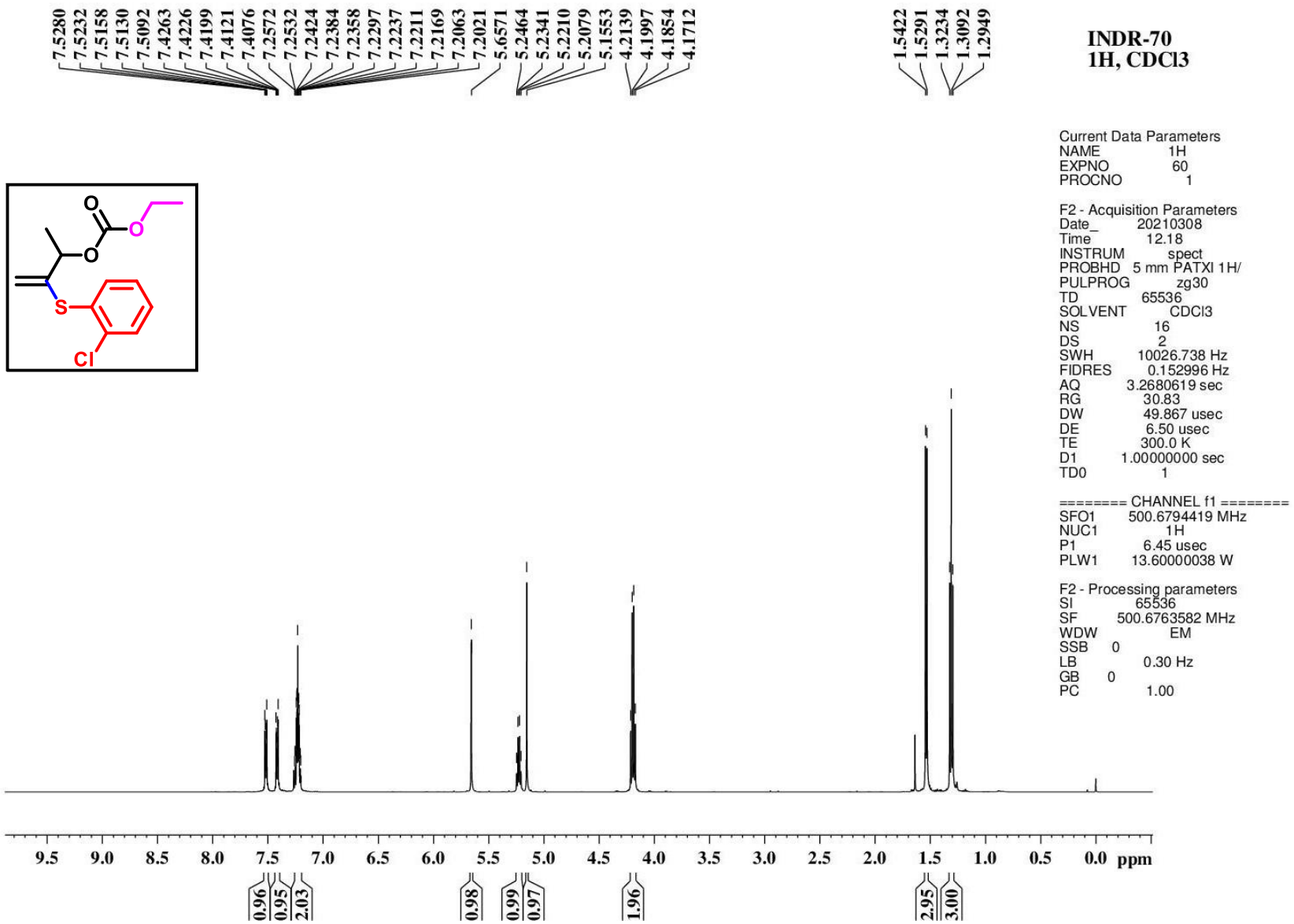



**Fig.S78** $^{1}$H NMR Spectrum of **4h**

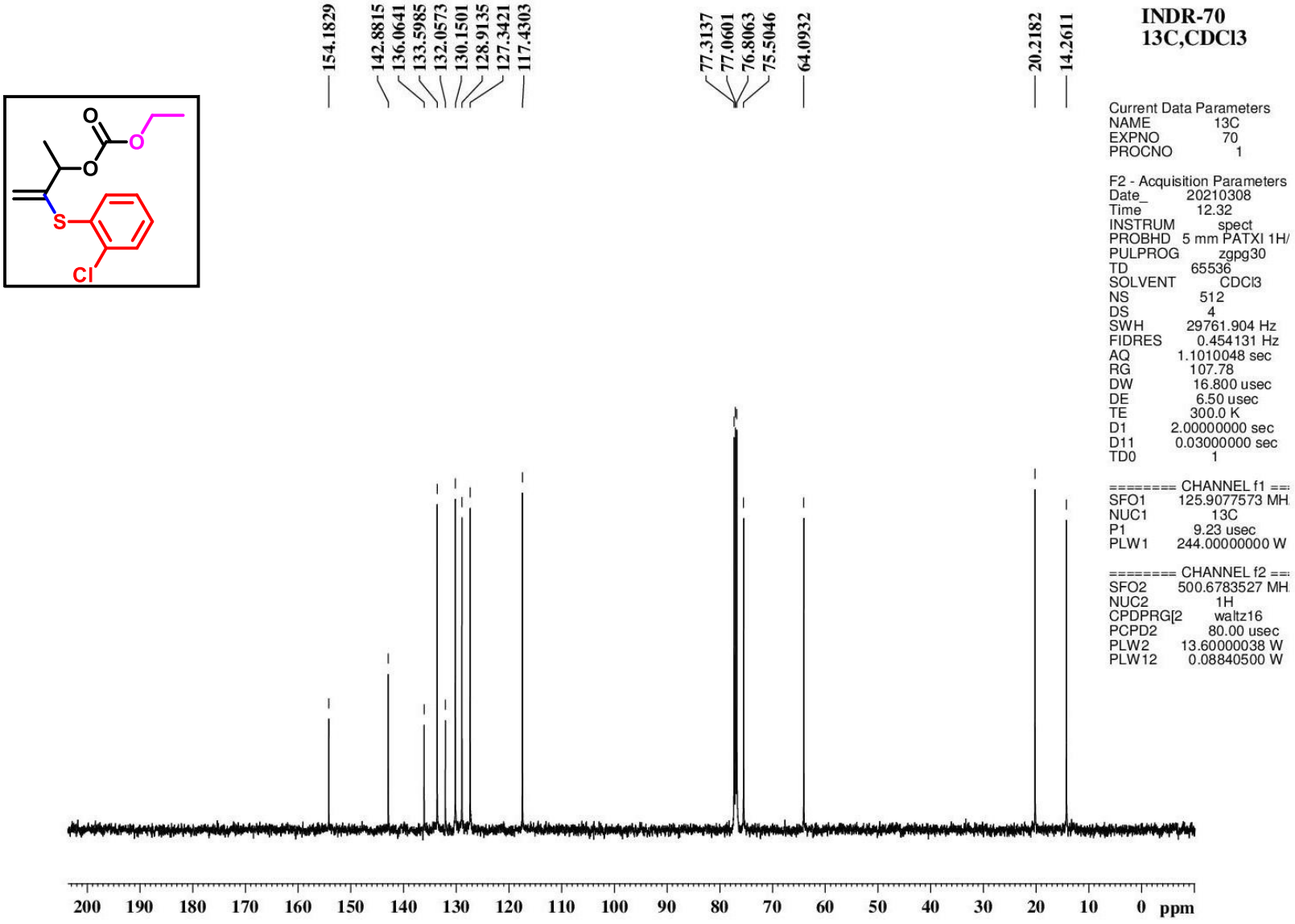



**Fig.S79** $^{13}$C NMR Spectrum of **4h**

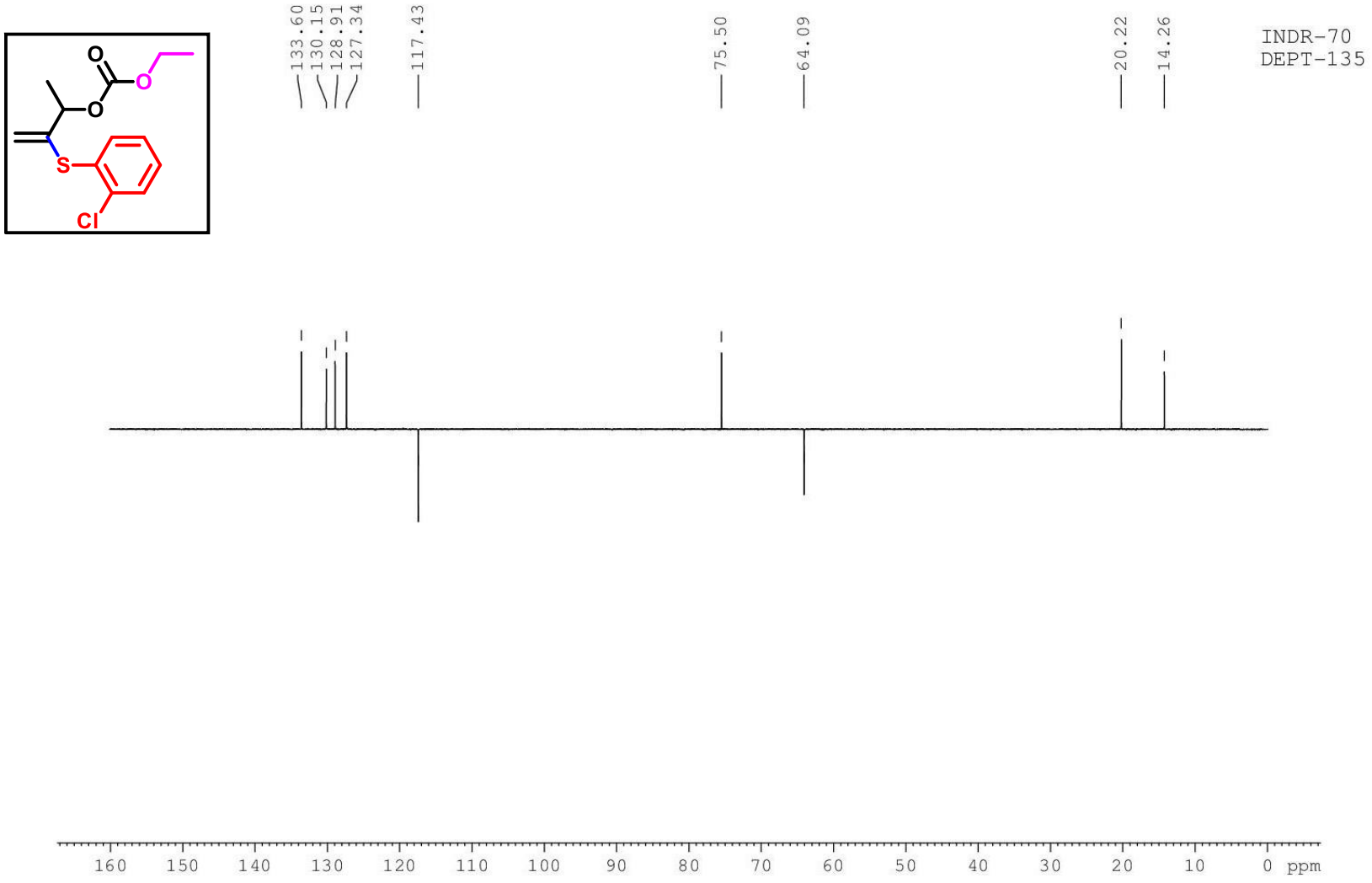



**Fig.S80** DEPT-135 Spectrum of **4h**

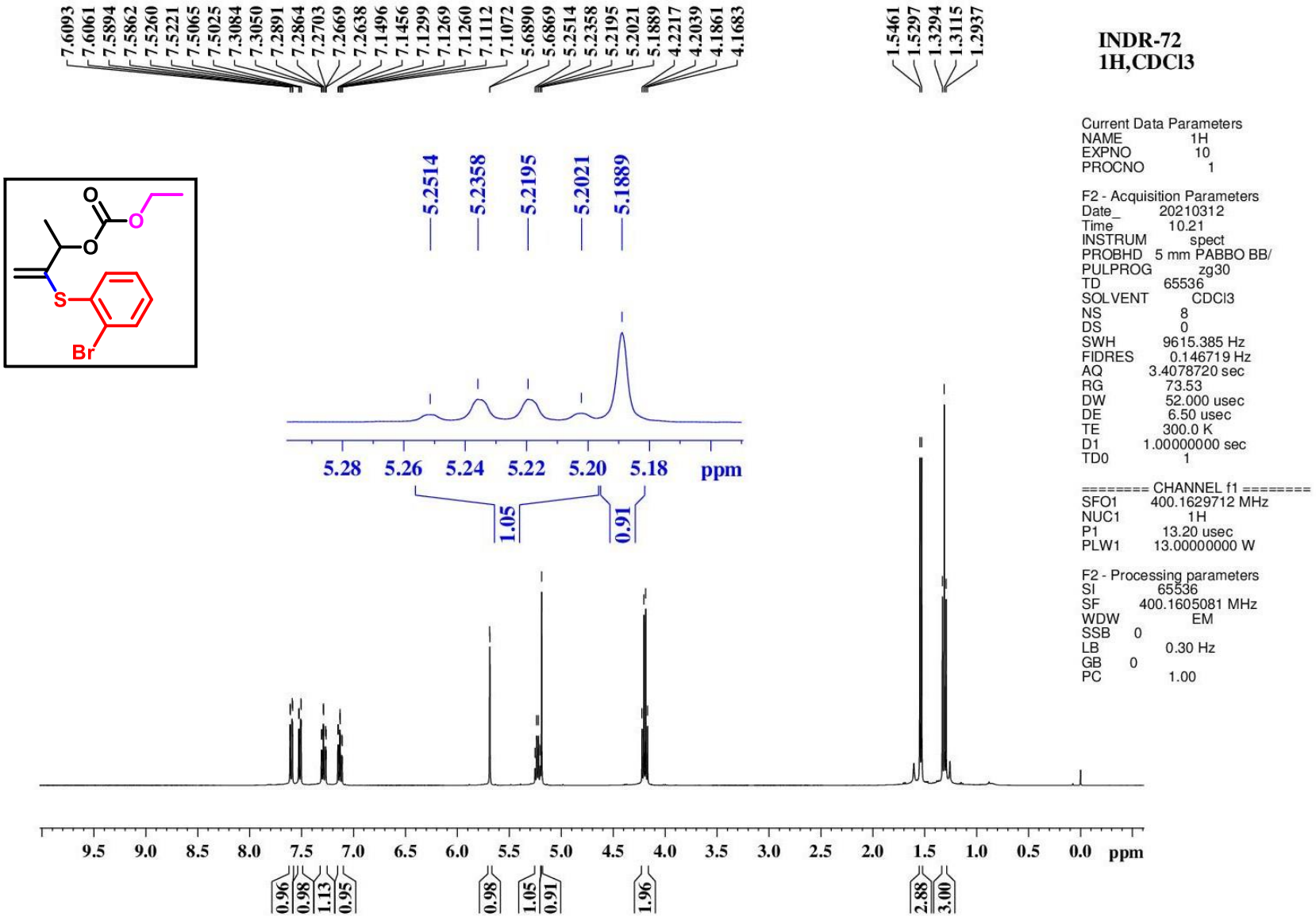



**Fig.S81** $^{1}$H NMR Spectrum of **4i**

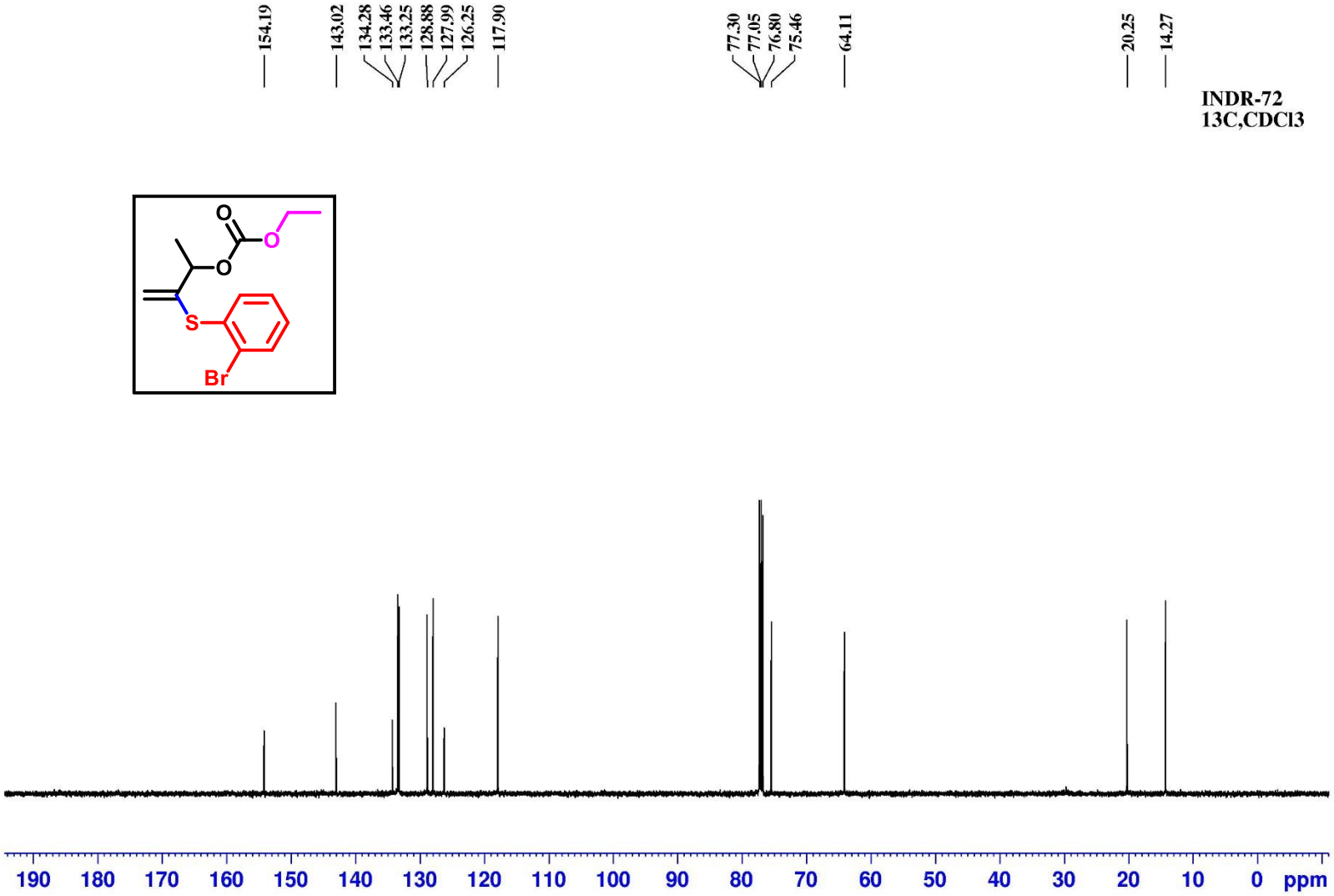



**Fig.S82** $^{13}$C NMR Spectrum of **4i**

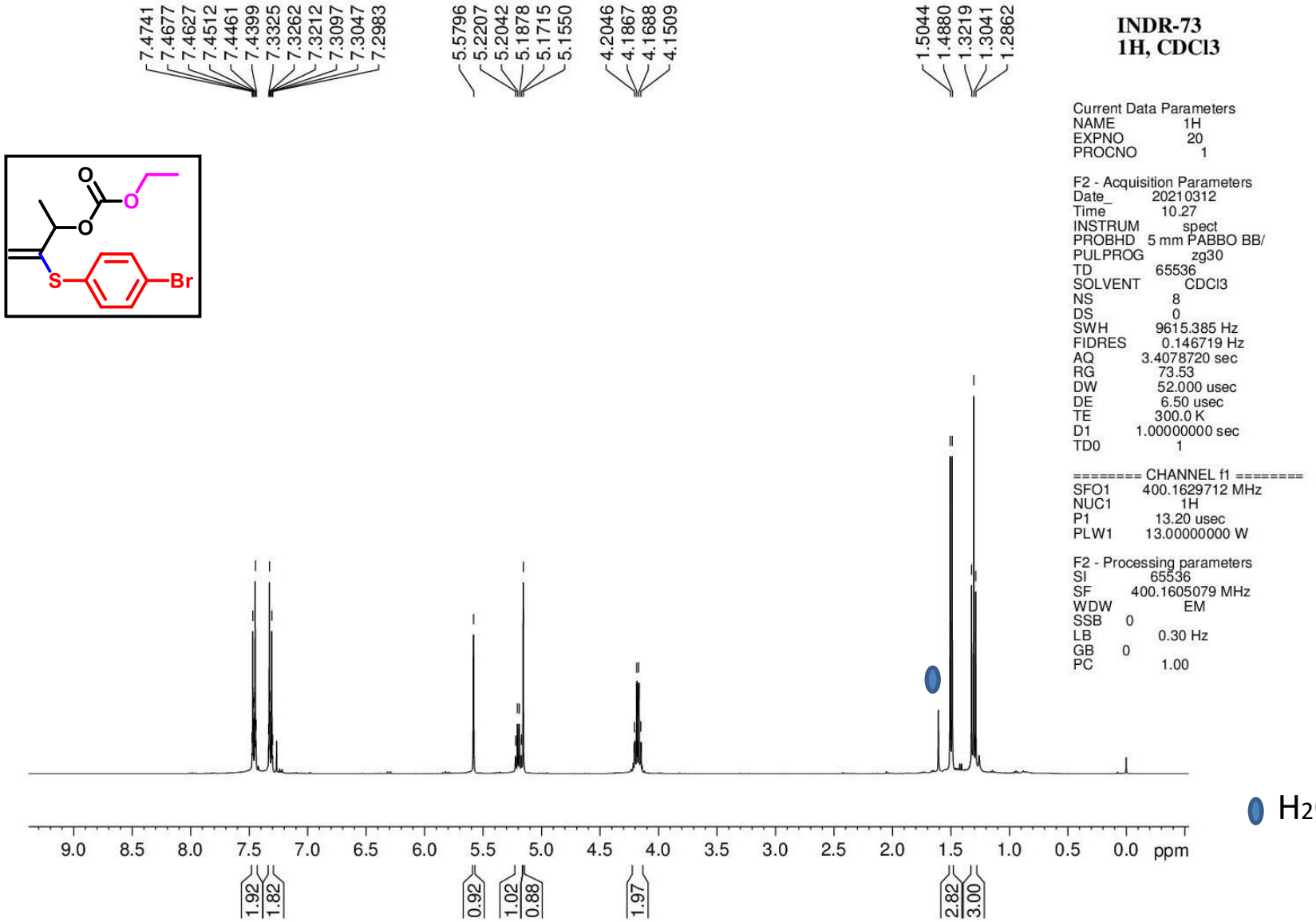



**Fig.S83** $^{1}$H NMR Spectrum of **4j**

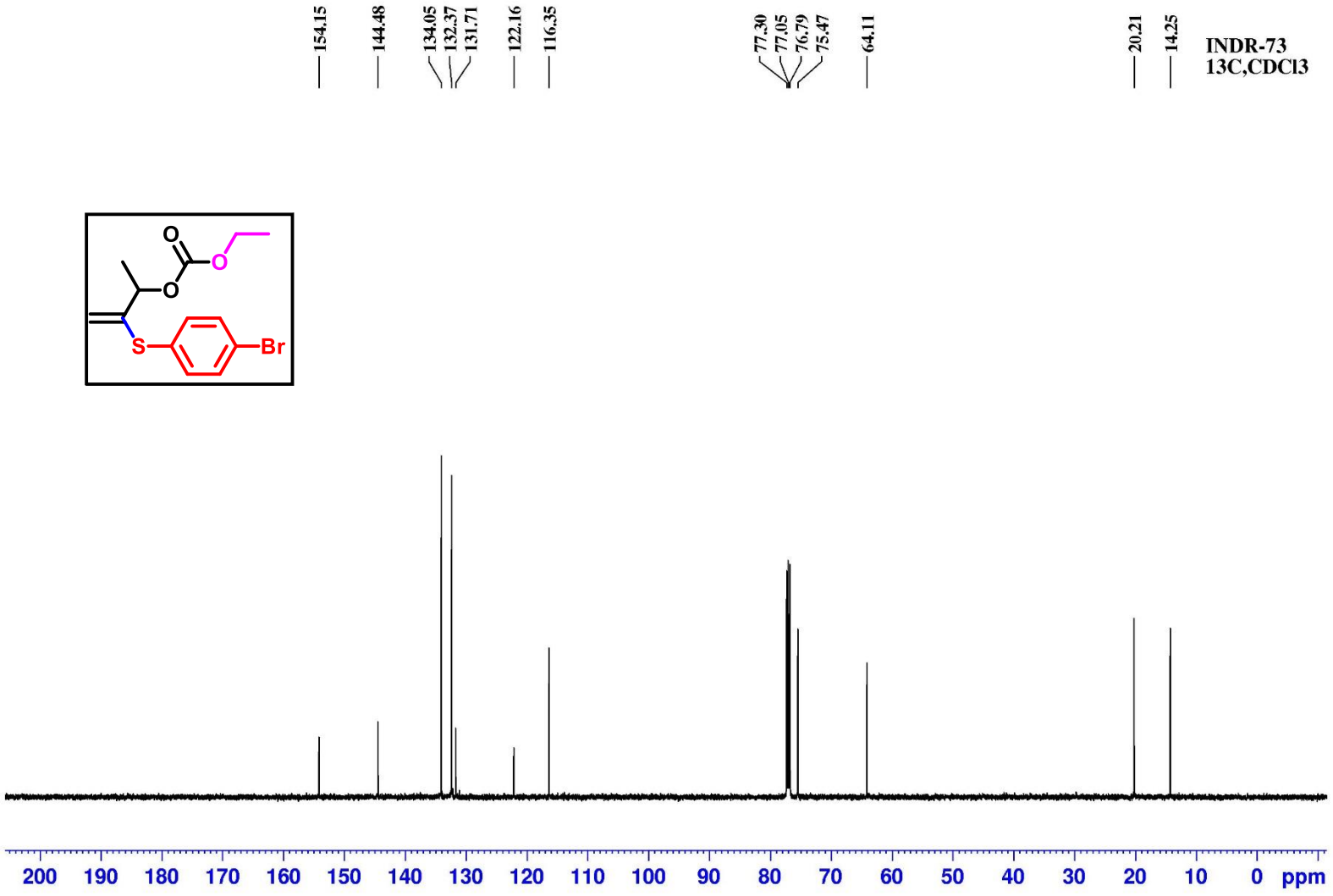



**Fig.S84** $^{13}$C NMR Spectrum of **4j**

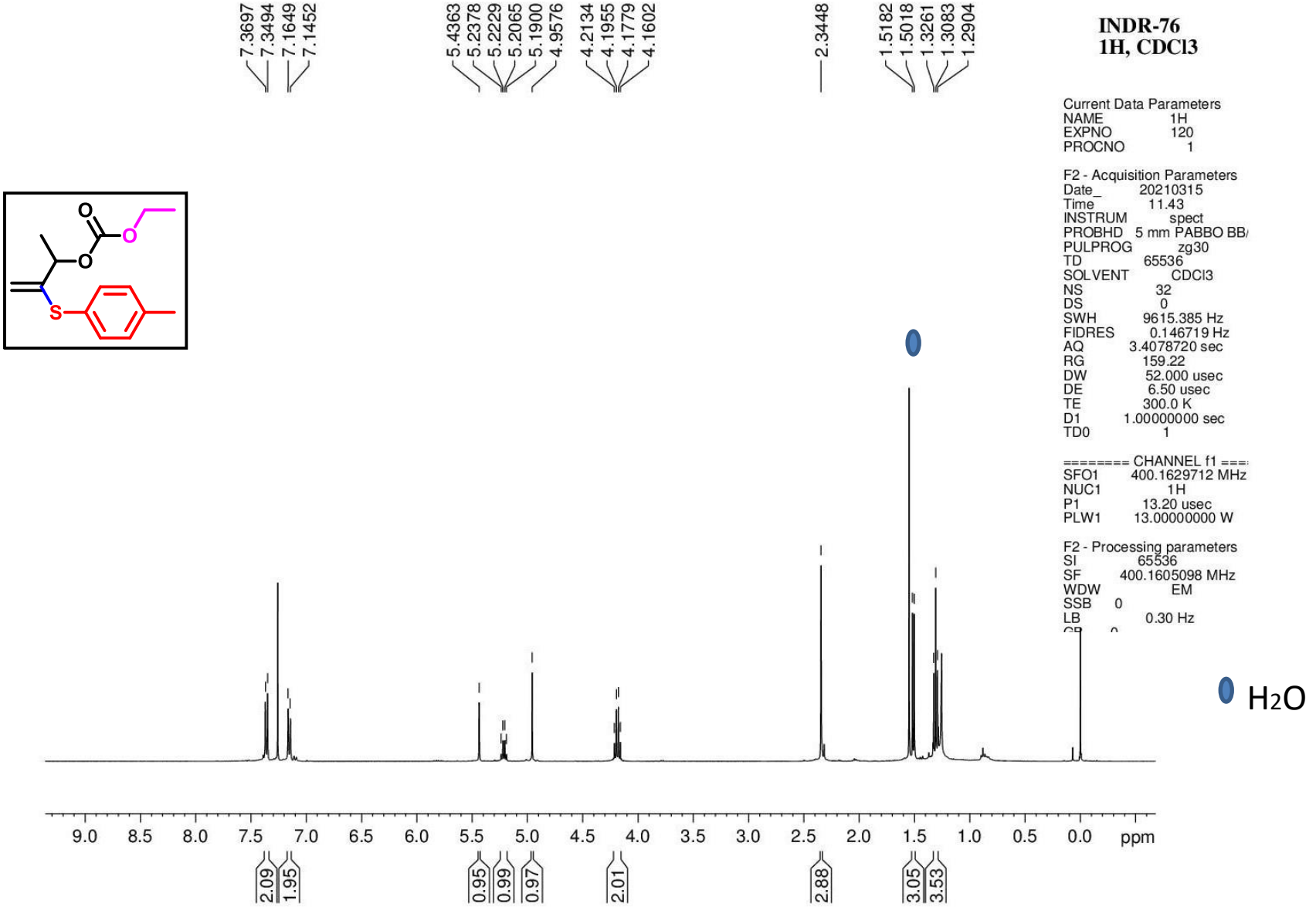



**Fig.S85** $^{1}$H NMR Spectrum of **4k**

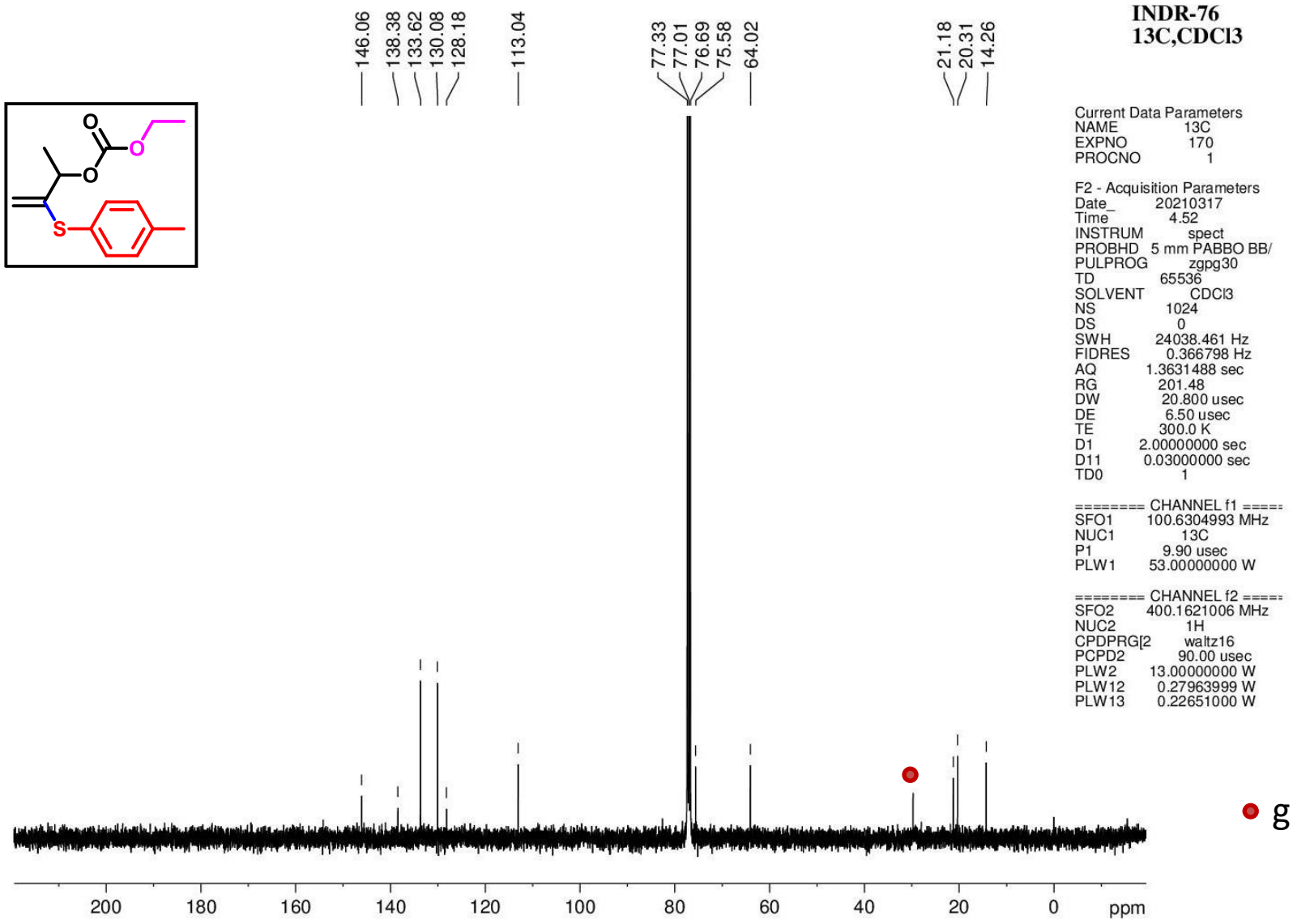



**Fig.S86** $^{13}$C NMR Spectrum of **4k**

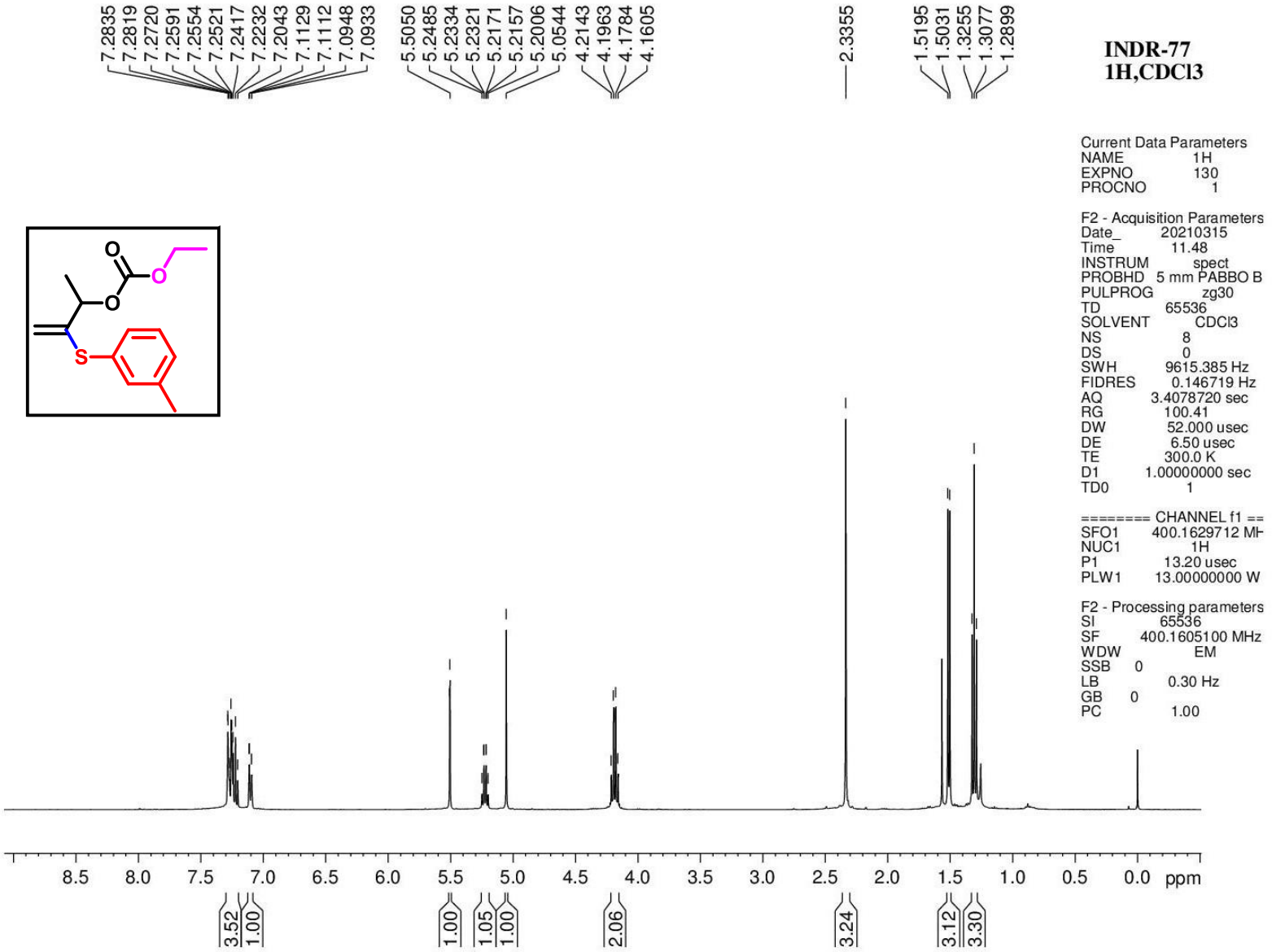



**Fig.S87** $^{1}$H NMR Spectrum of **4l**

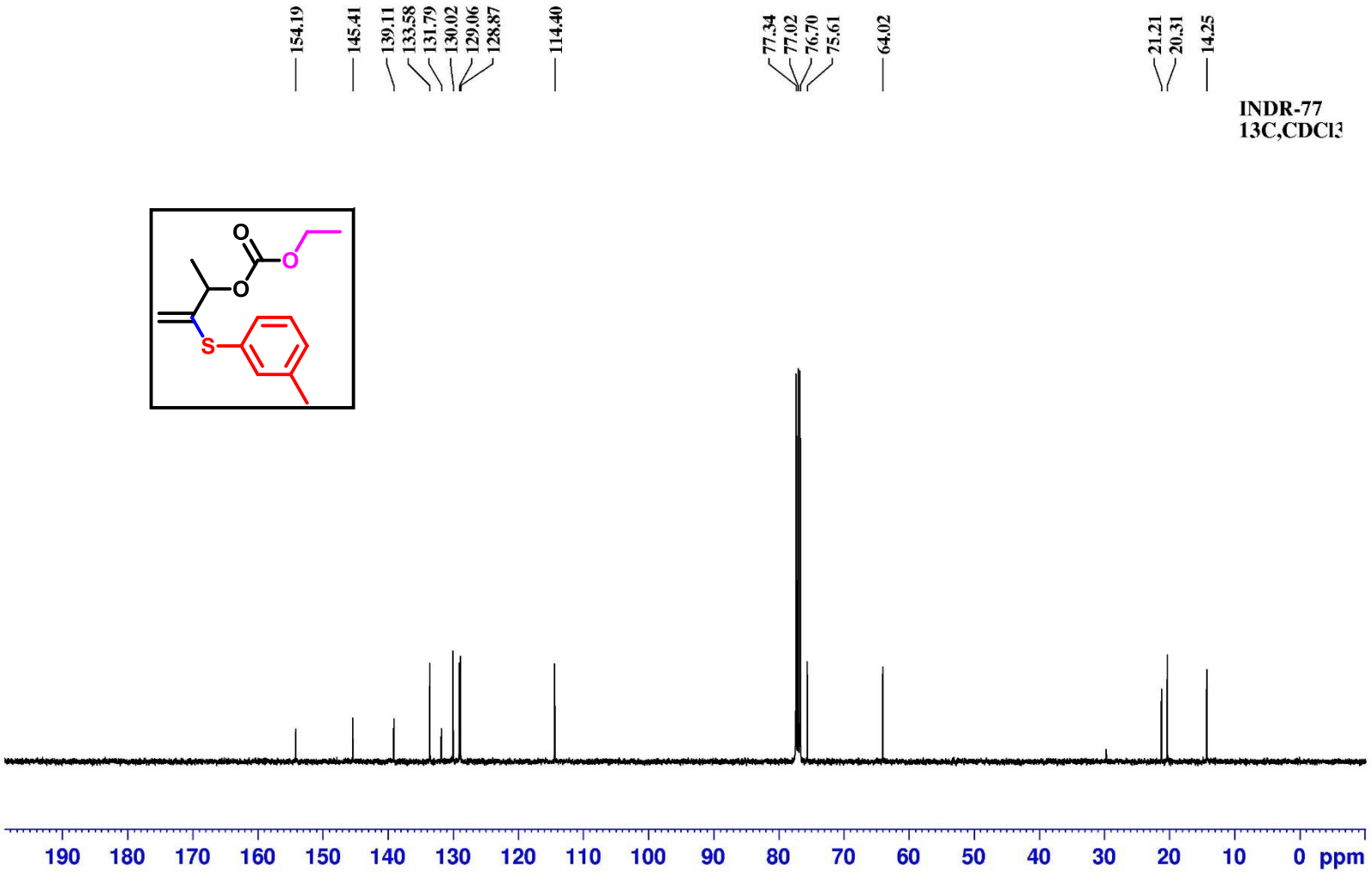



**Fig.S88** $^{13}$C NMR Spectrum of **4l**

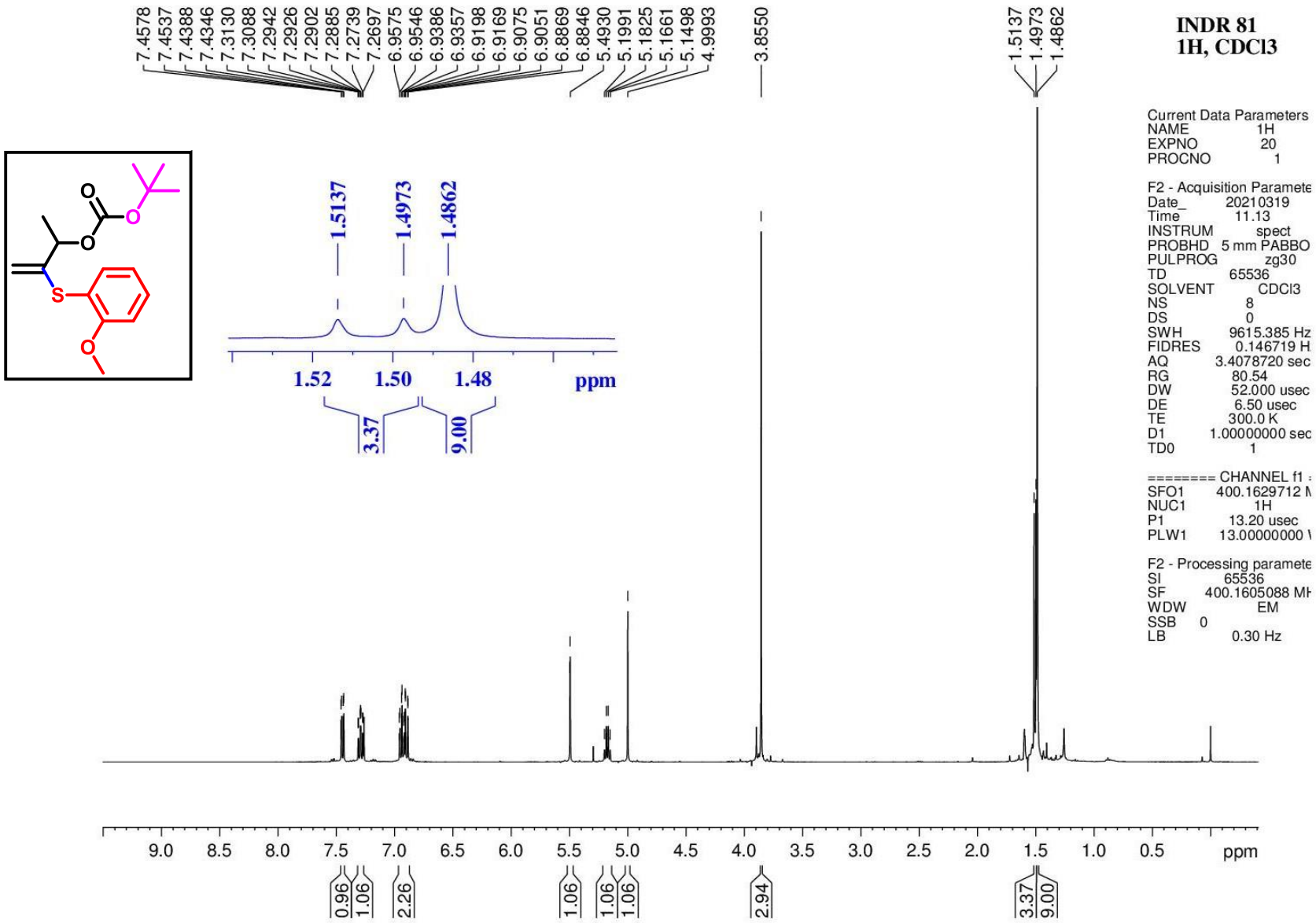



**Fig.S89** $^{1}$H NMR Spectrum of **4m**

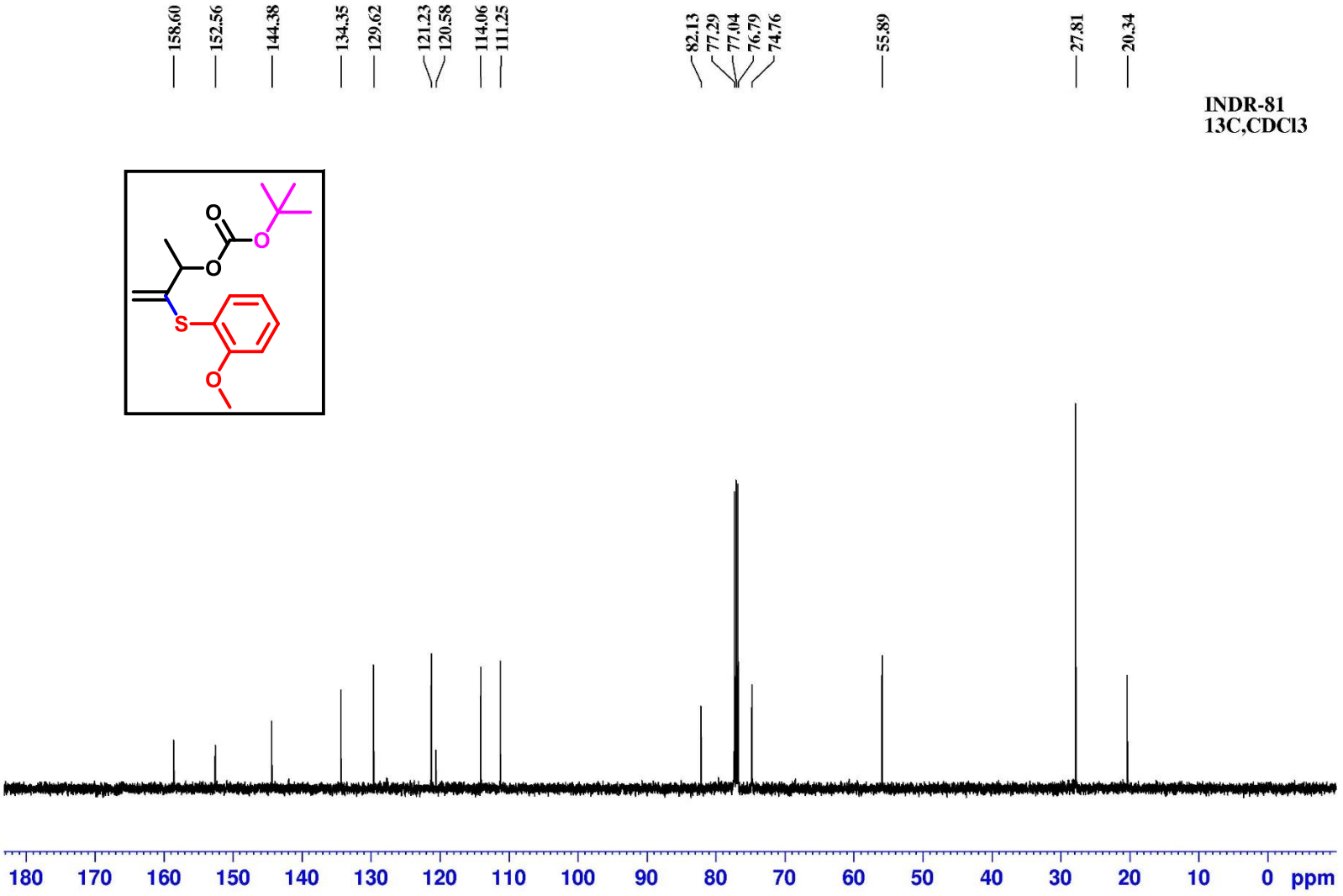



**Fig.S90** $^{13}$C NMR Spectrum of **4m**

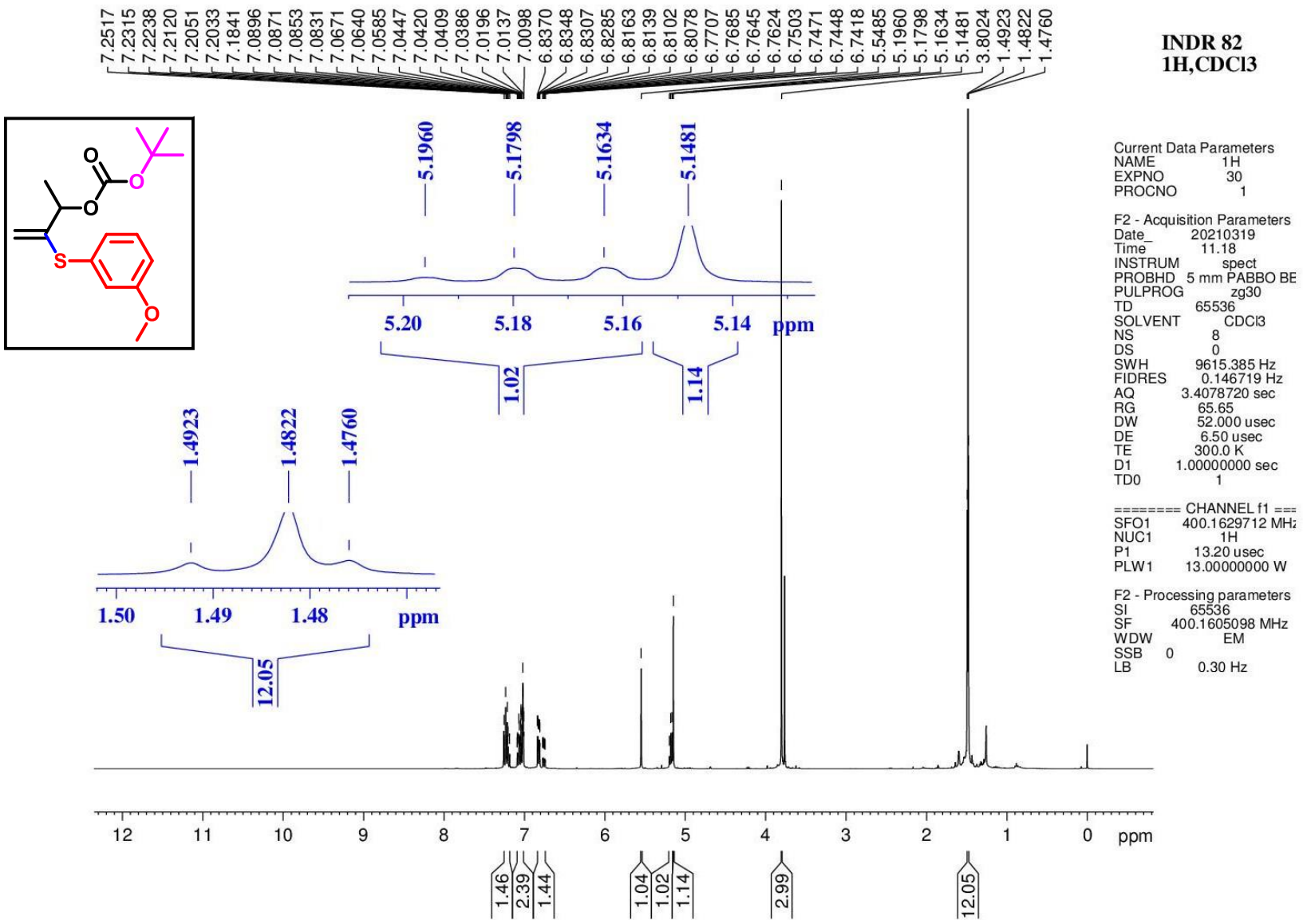



**Fig.S91** $^{1}$H NMR Spectrum of **4n**

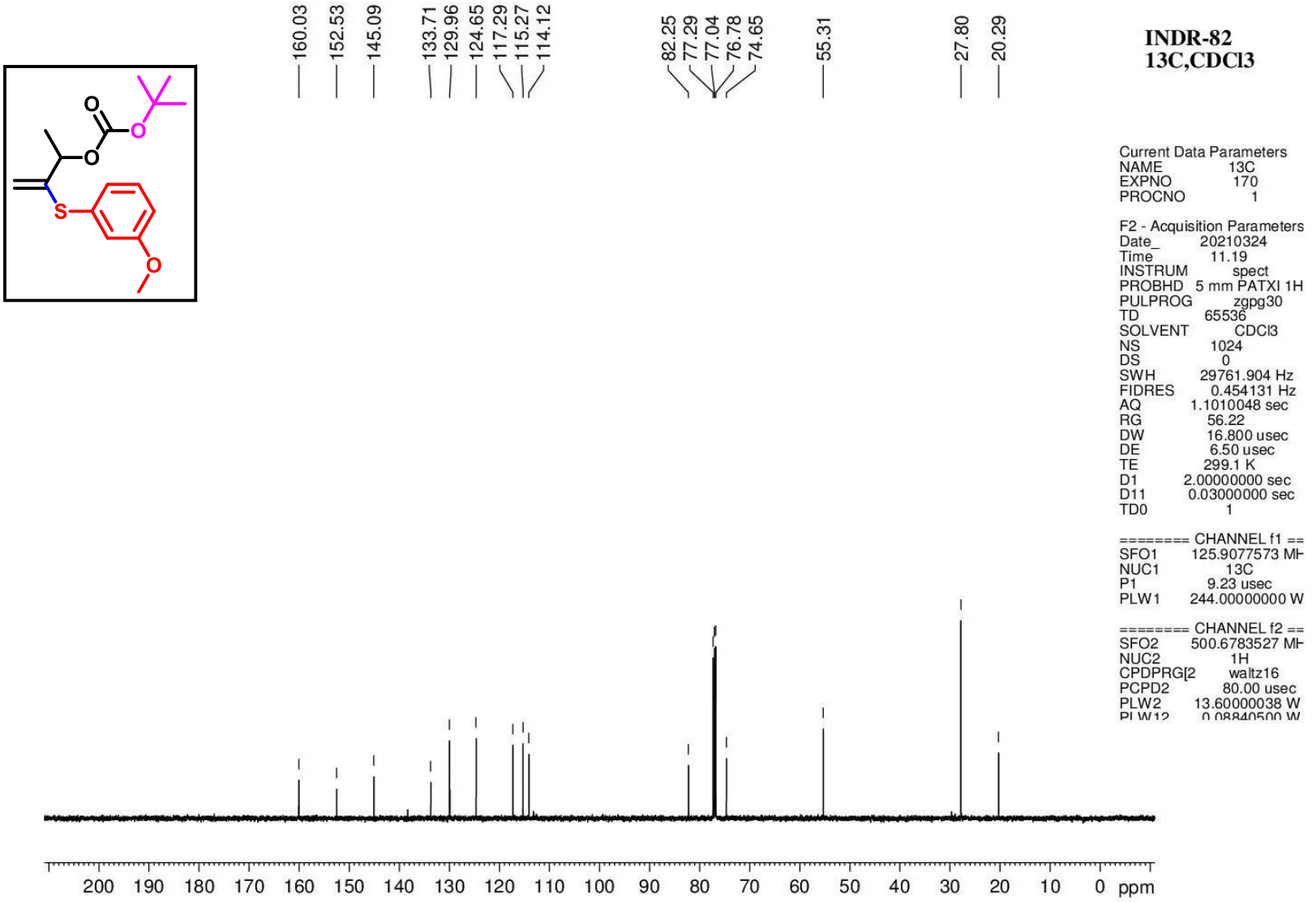



**Fig.S92** $^{13}$C NMR Spectrum of **4n**

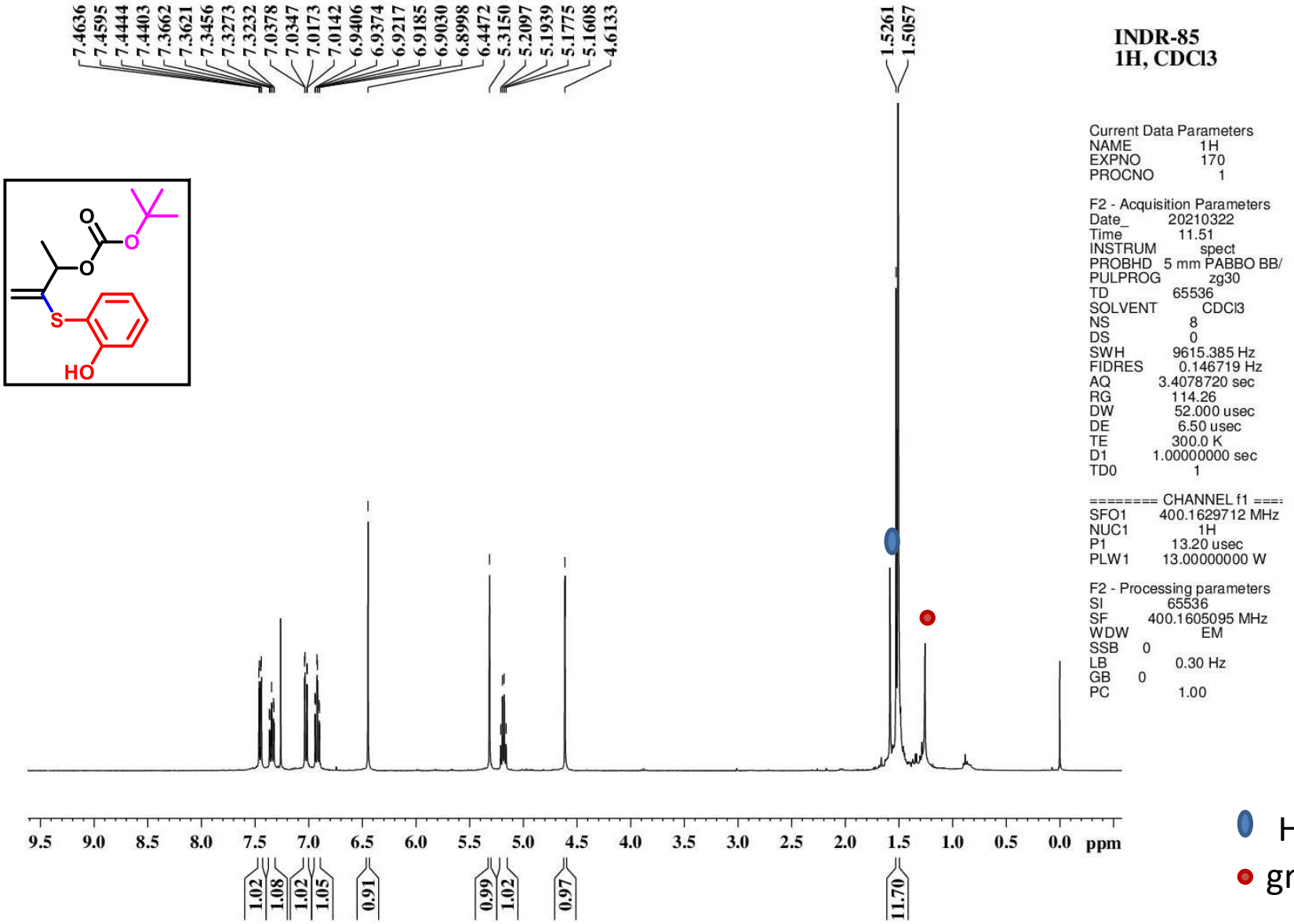



**Fig.S93** $^{1}$H NMR Spectrum of **4o**

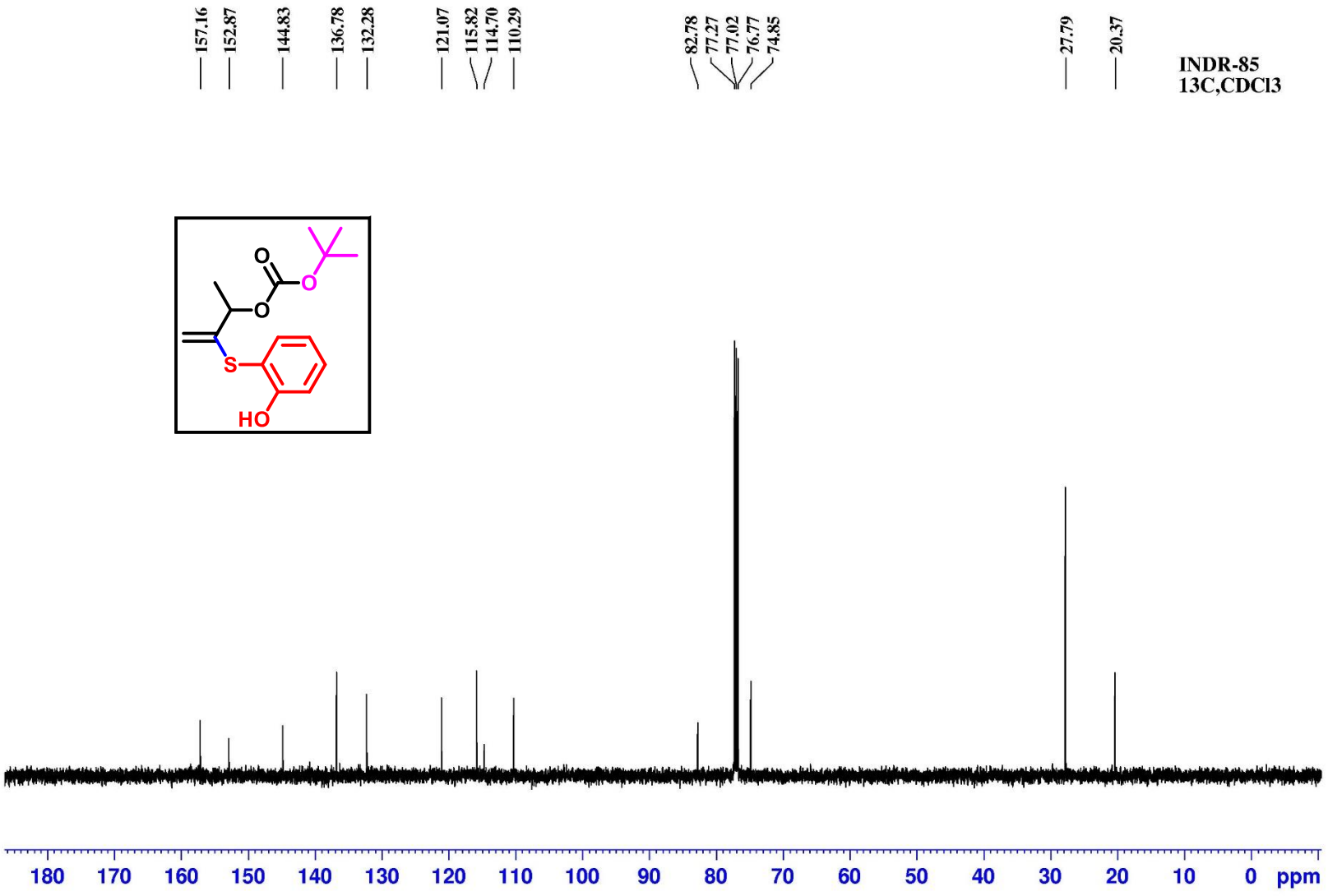



**Fig.S94** $^{13}$C NMR Spectrum of **4o**

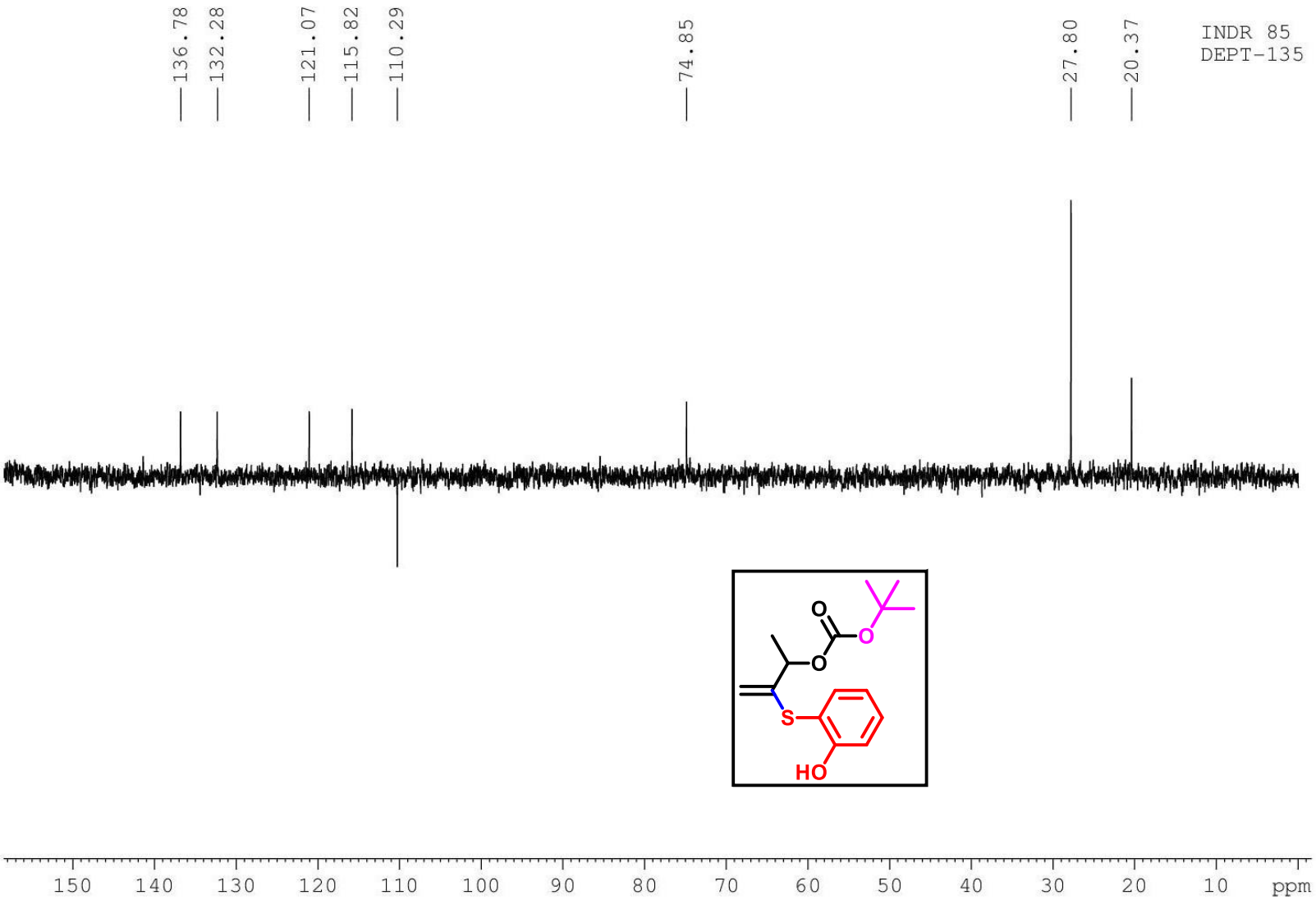



**Fig.S95** DEPT-135 Spectrum of **4o**

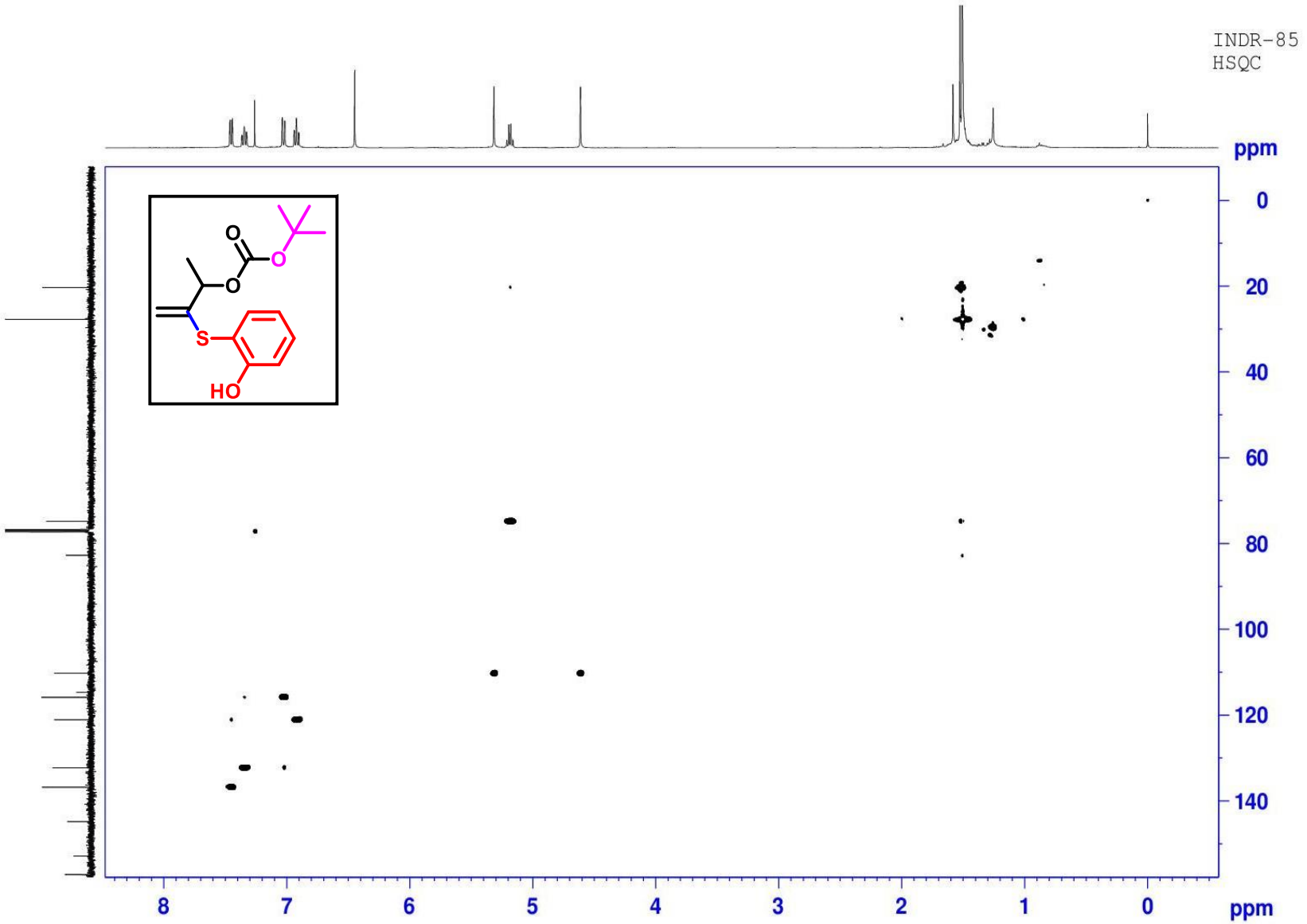



**Fig.S96** HSQC Spectrum of **4o**

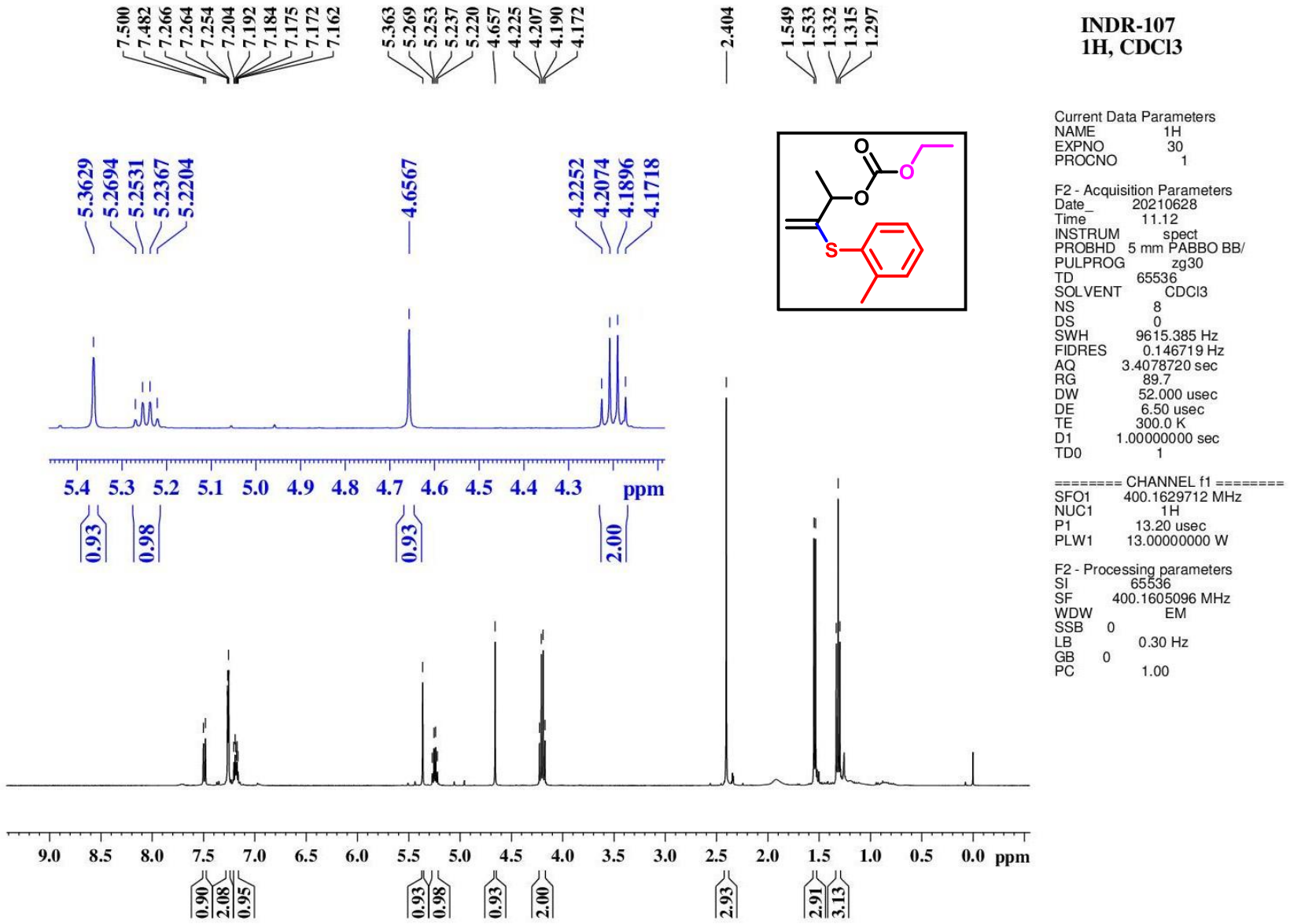



**Fig.S97** $^{1}$H NMR Spectrum of **4p**

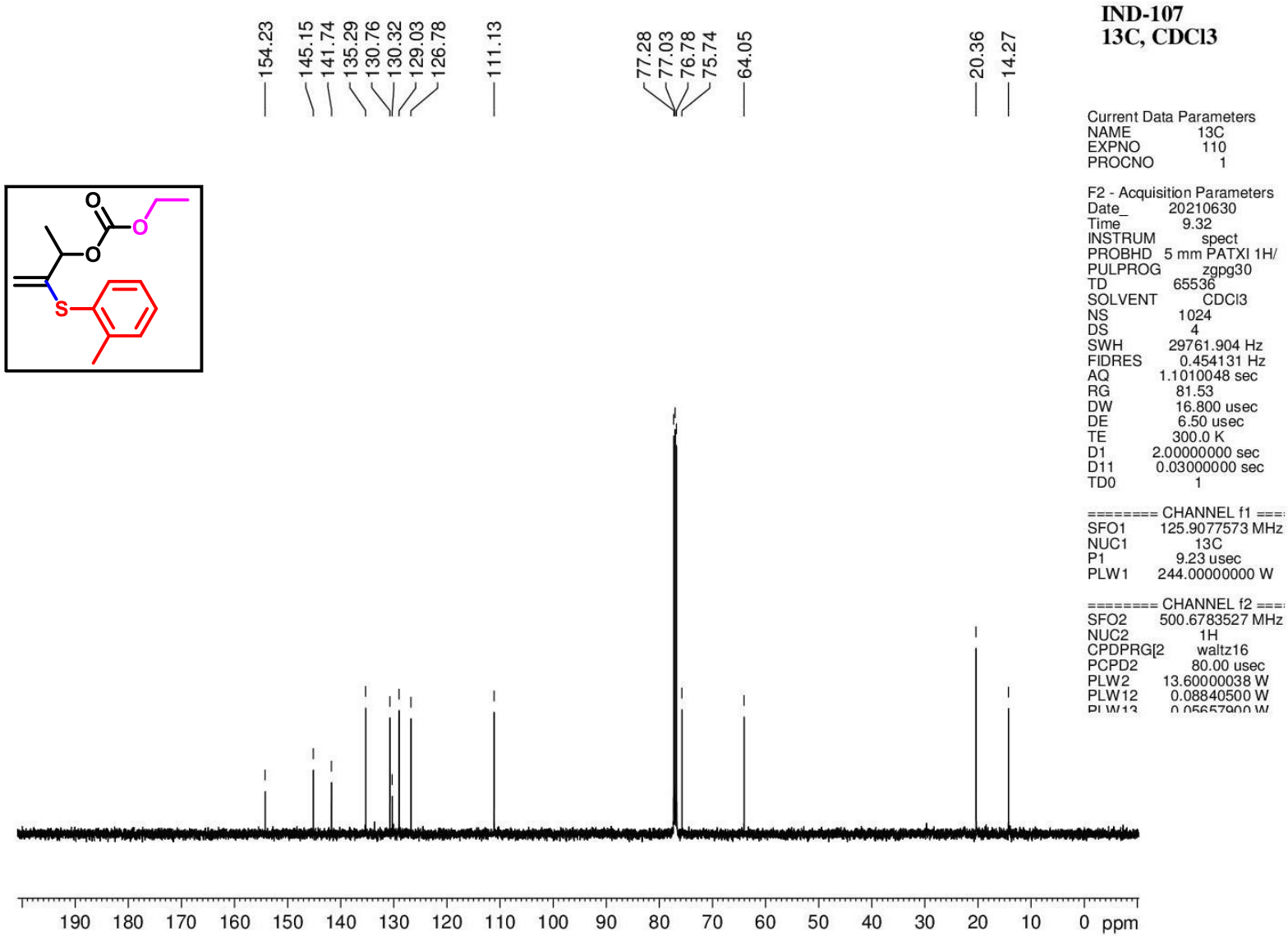



**Fig.S98** $^{13}$C NMR Spectrum of **4p**

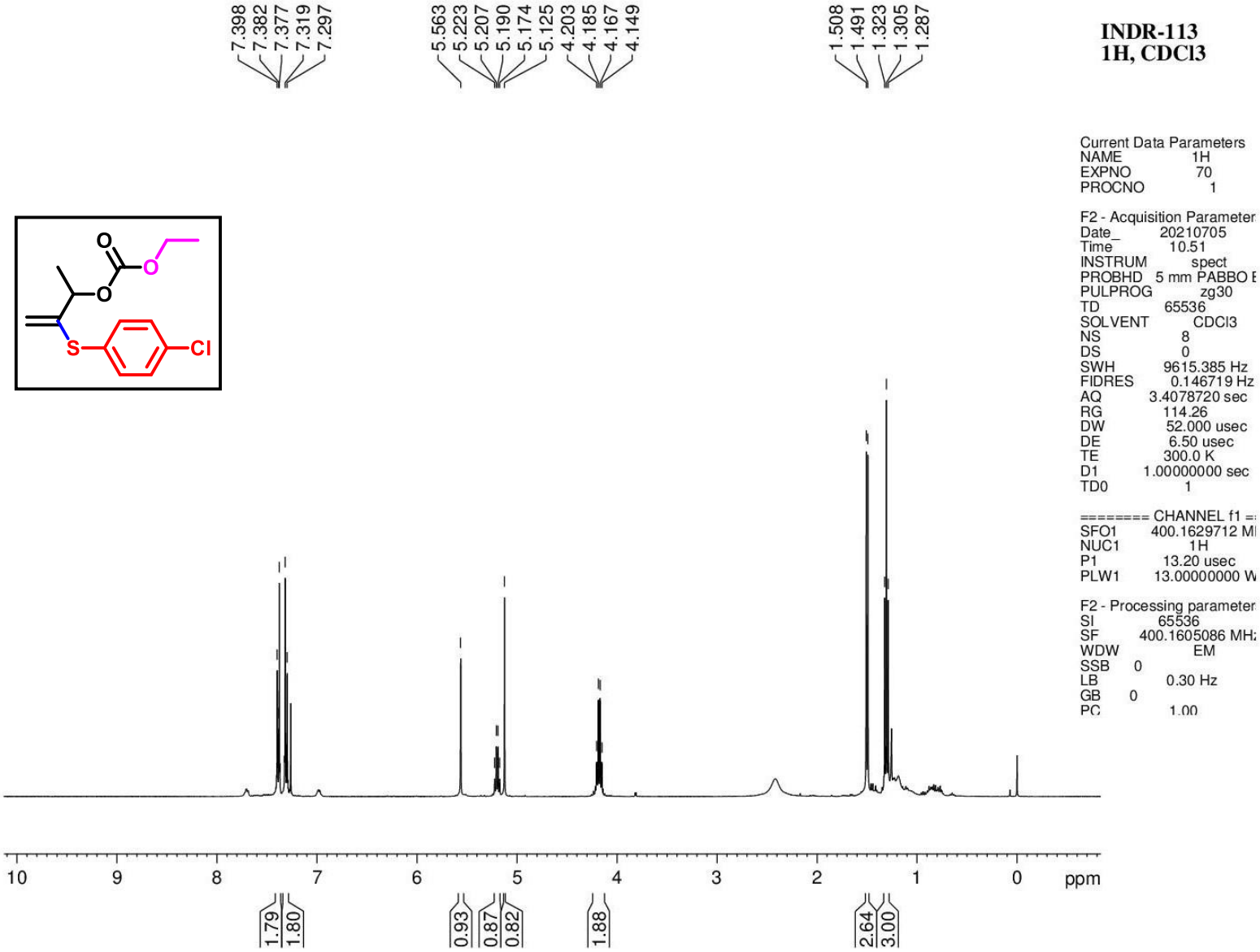



**Fig.S99** $^{1}$H NMR Spectrum of **4q**

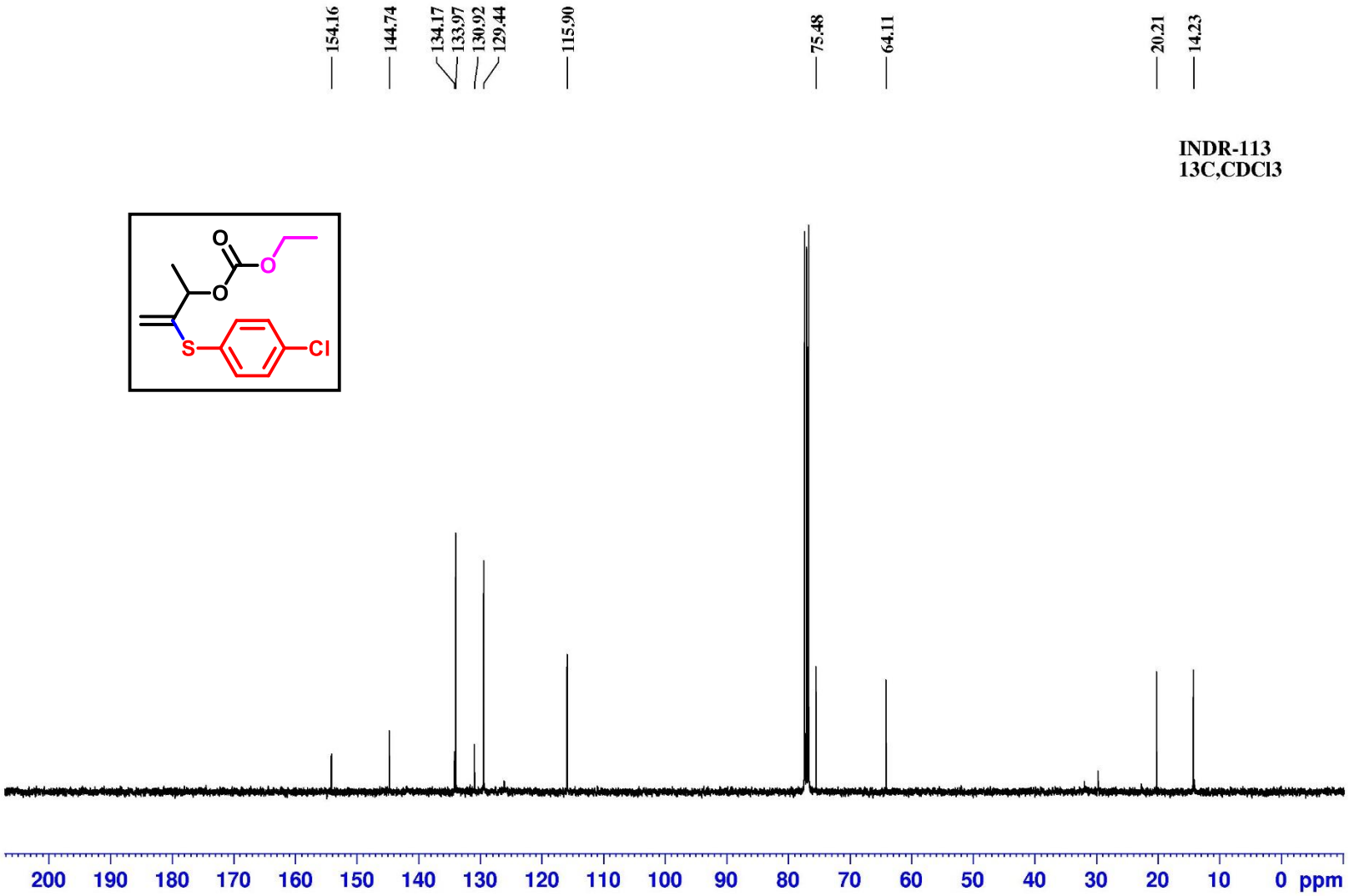



**Fig.S100** $^{13}$C NMR Spectrum of **4q**

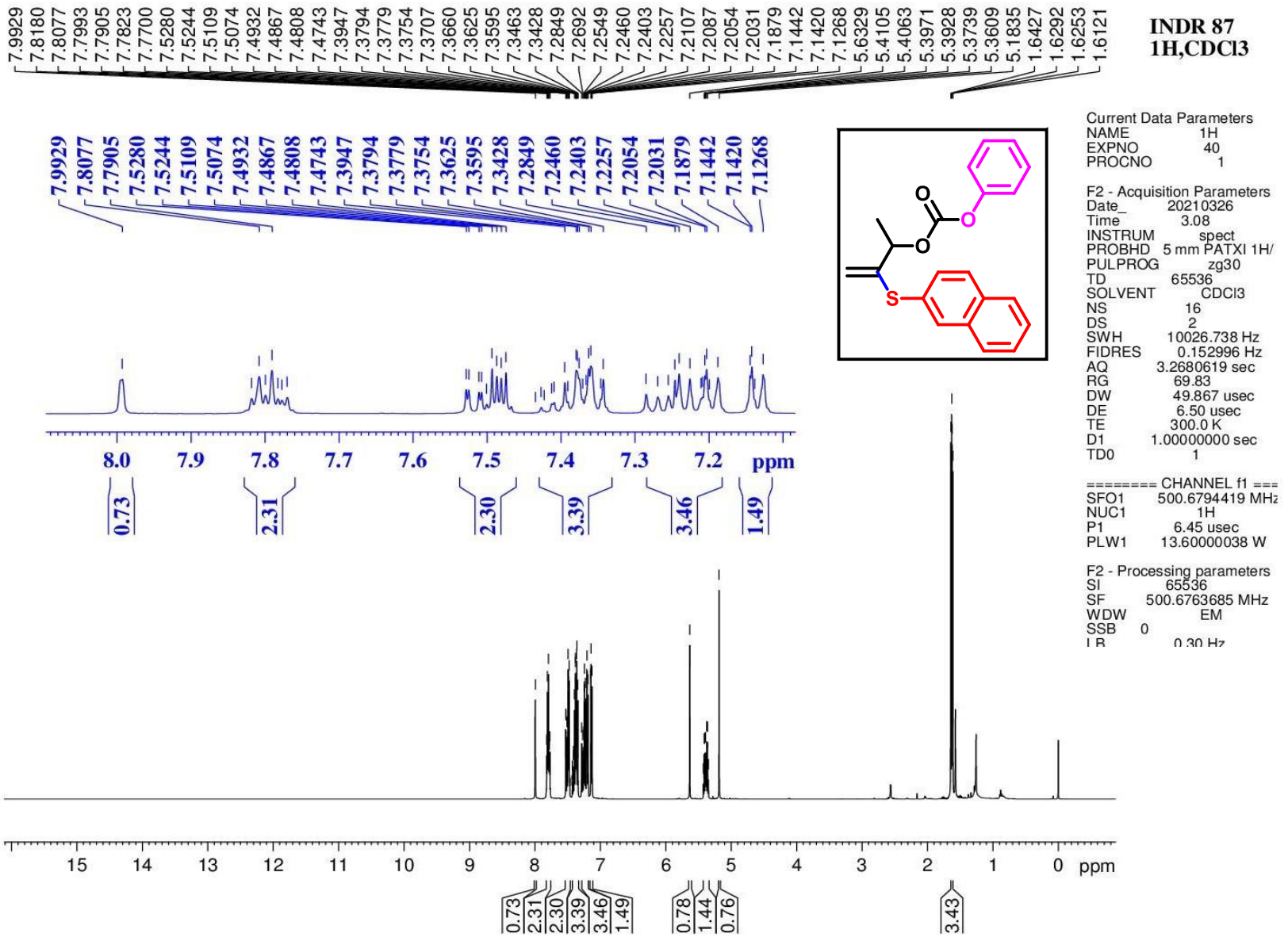



**Fig.S101** $^{1}$H NMR Spectrum of **4r**

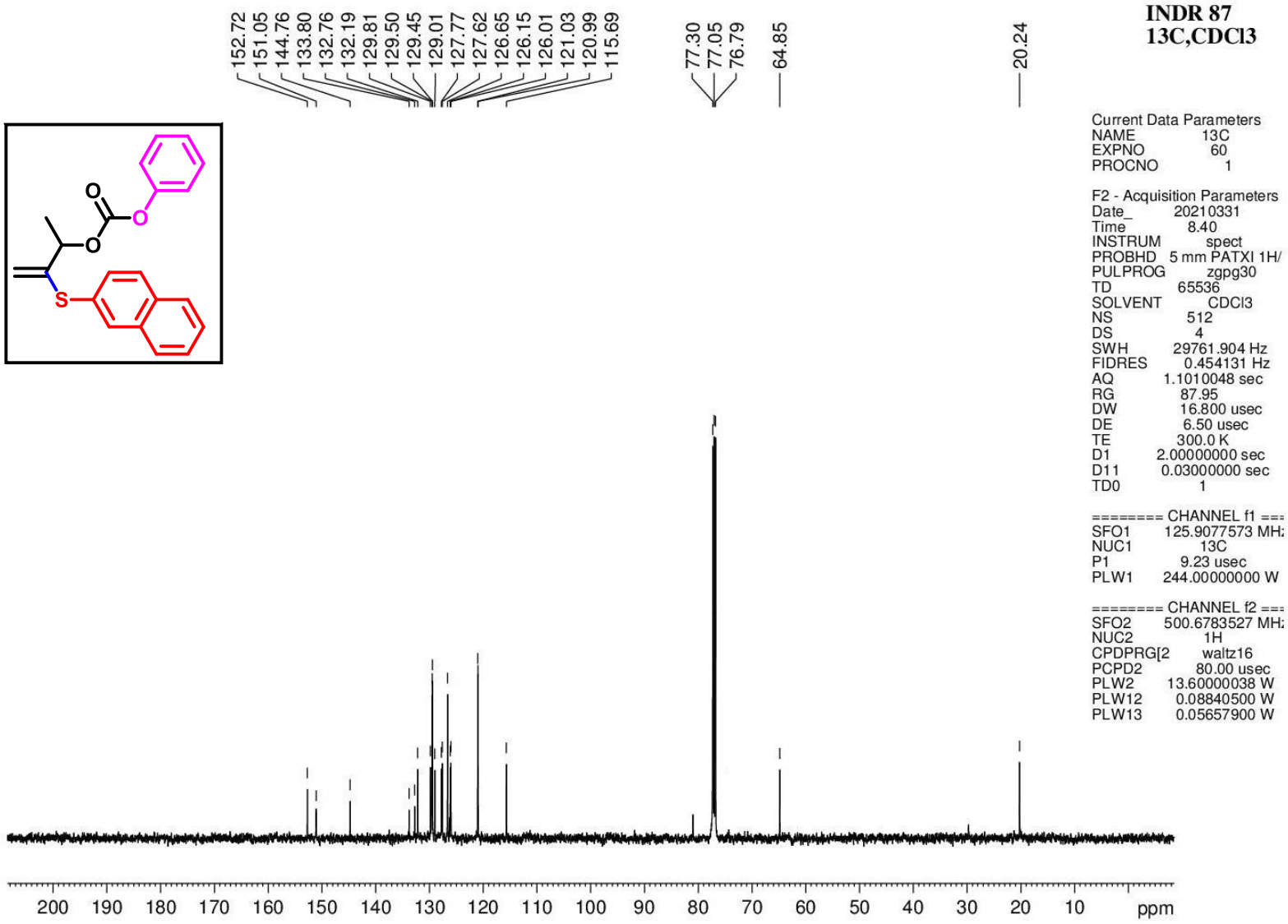



**Fig.S102** $^{13}$C NMR Spectrum of **4r**

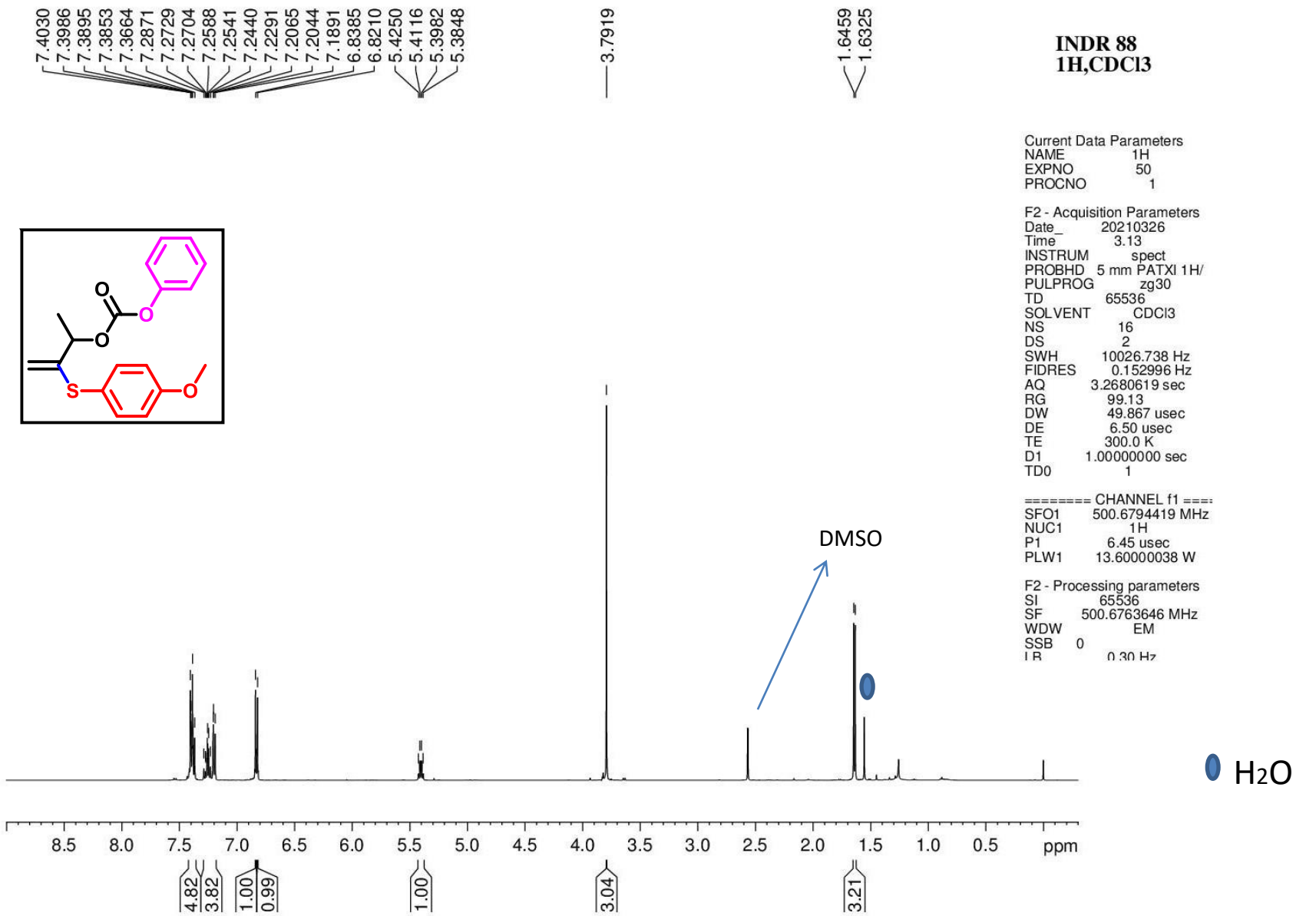



**Fig.S103** $^{1}$H NMR Spectrum of **4s**

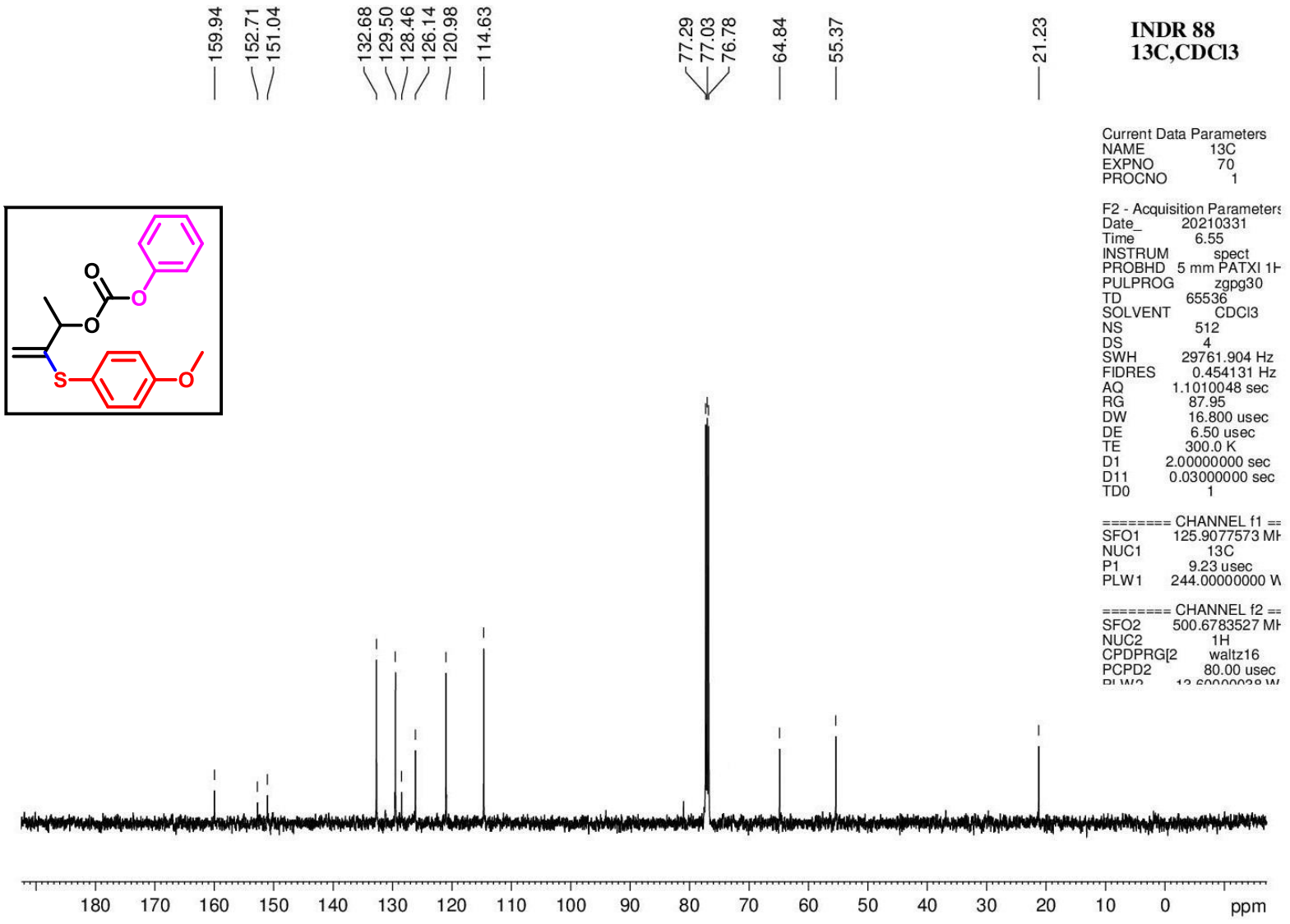



**Fig.S104** $^{13}$C NMR Spectrum of **4s**

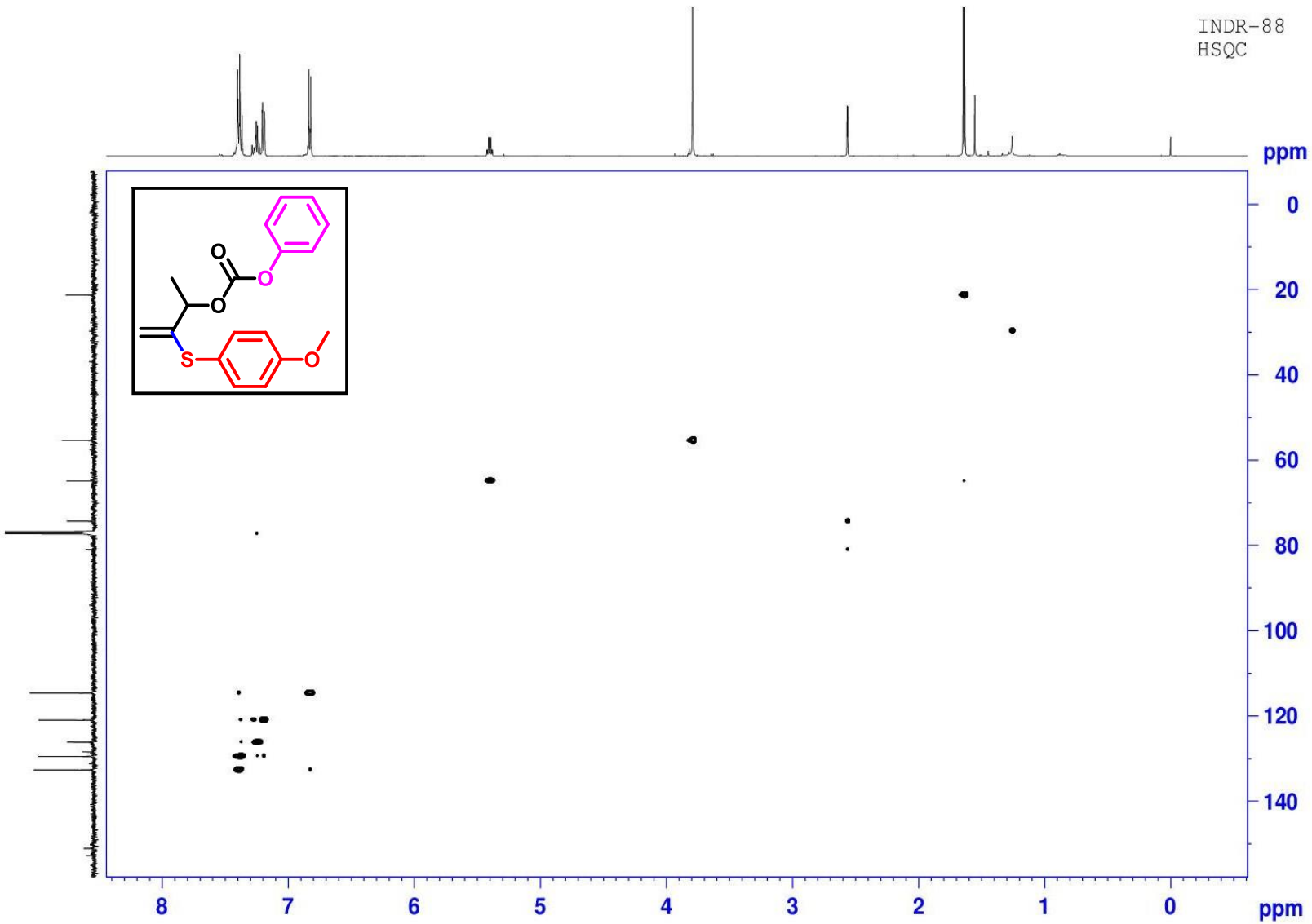



**Fig.S105** HSQC Spectrum of **4s**

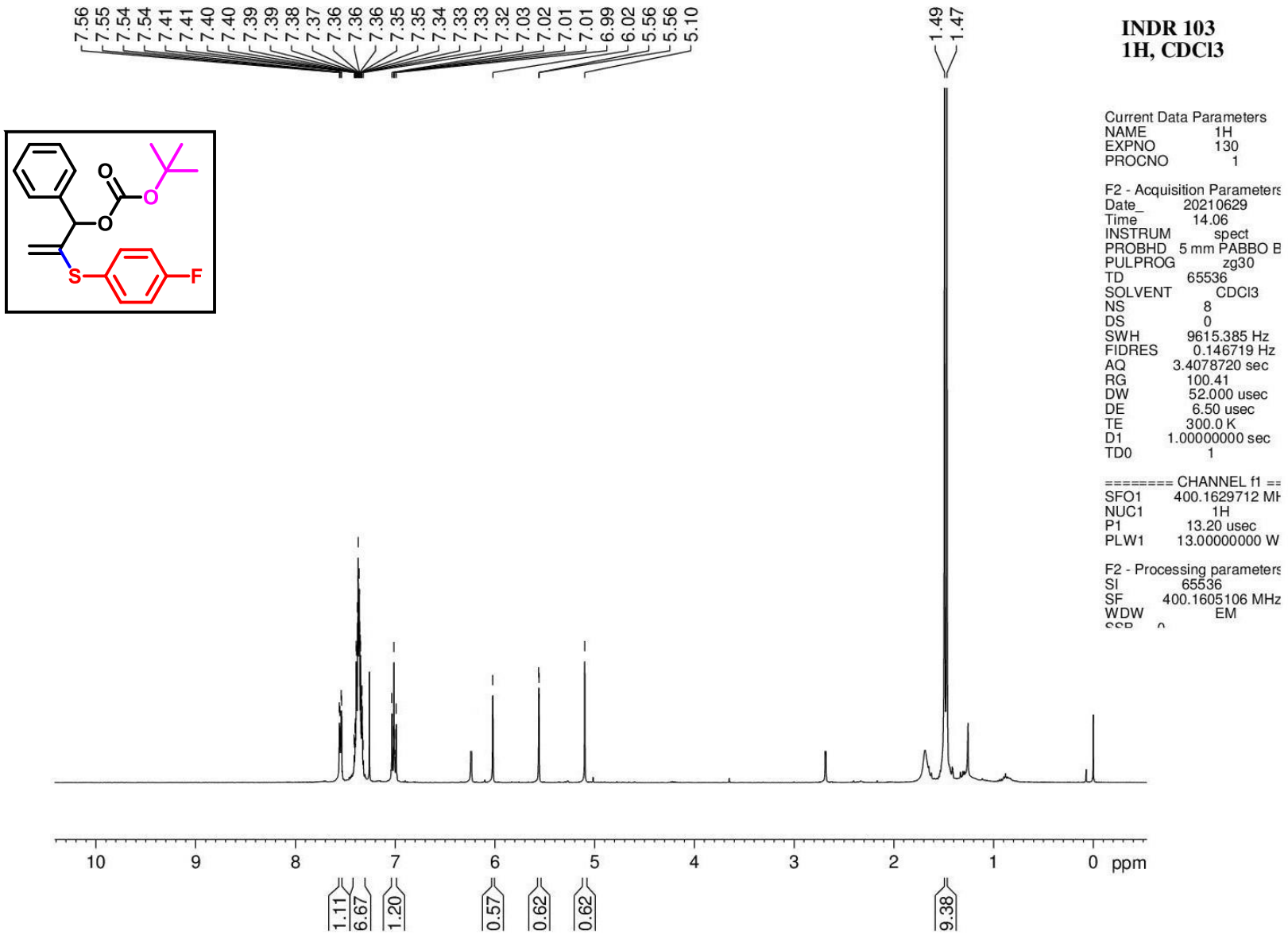



**Fig.S106** $^{1}$H NMR Spectrum of **4t**

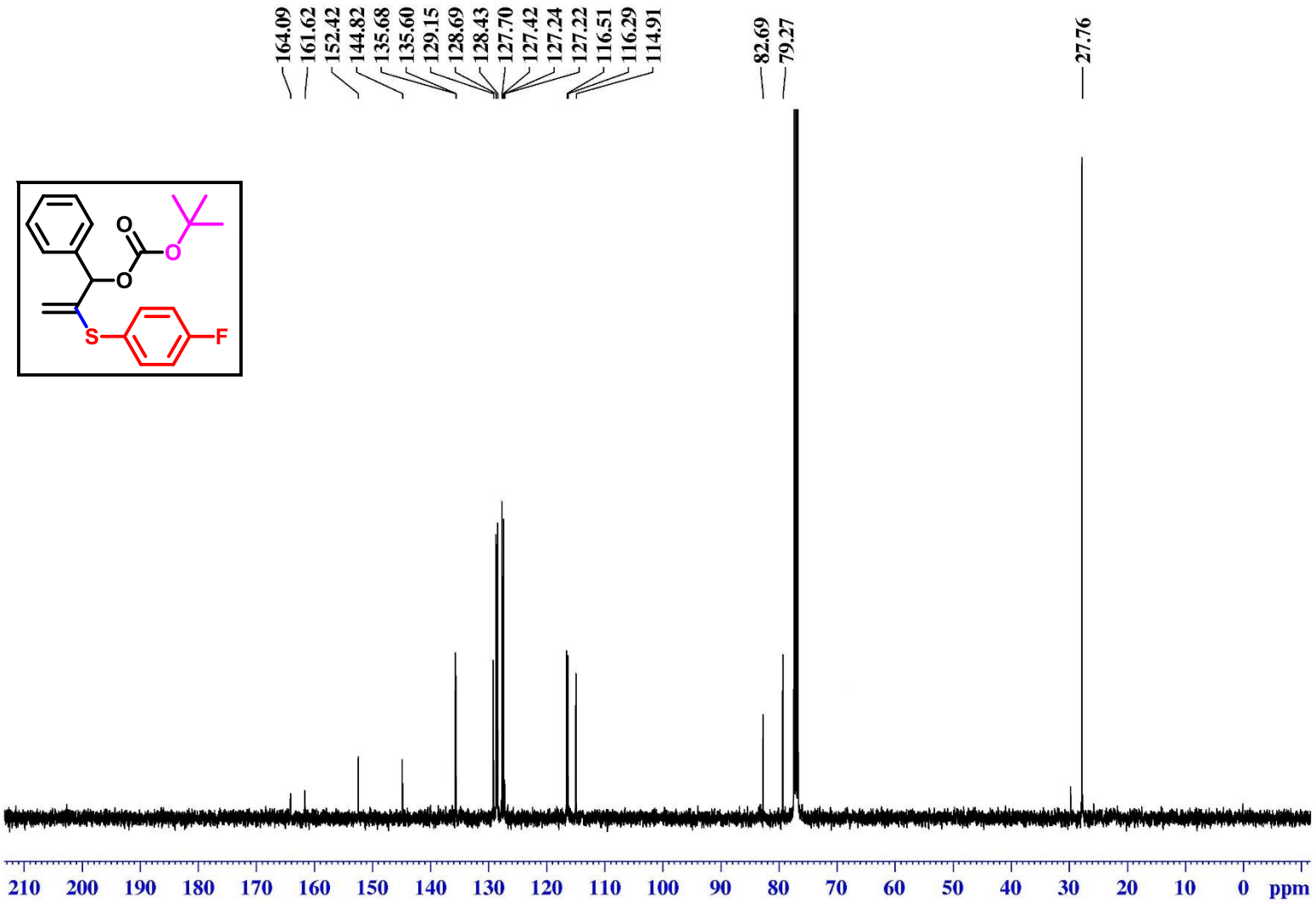



**Fig.S107** $^{13}$C NMR Spectrum of **4t**

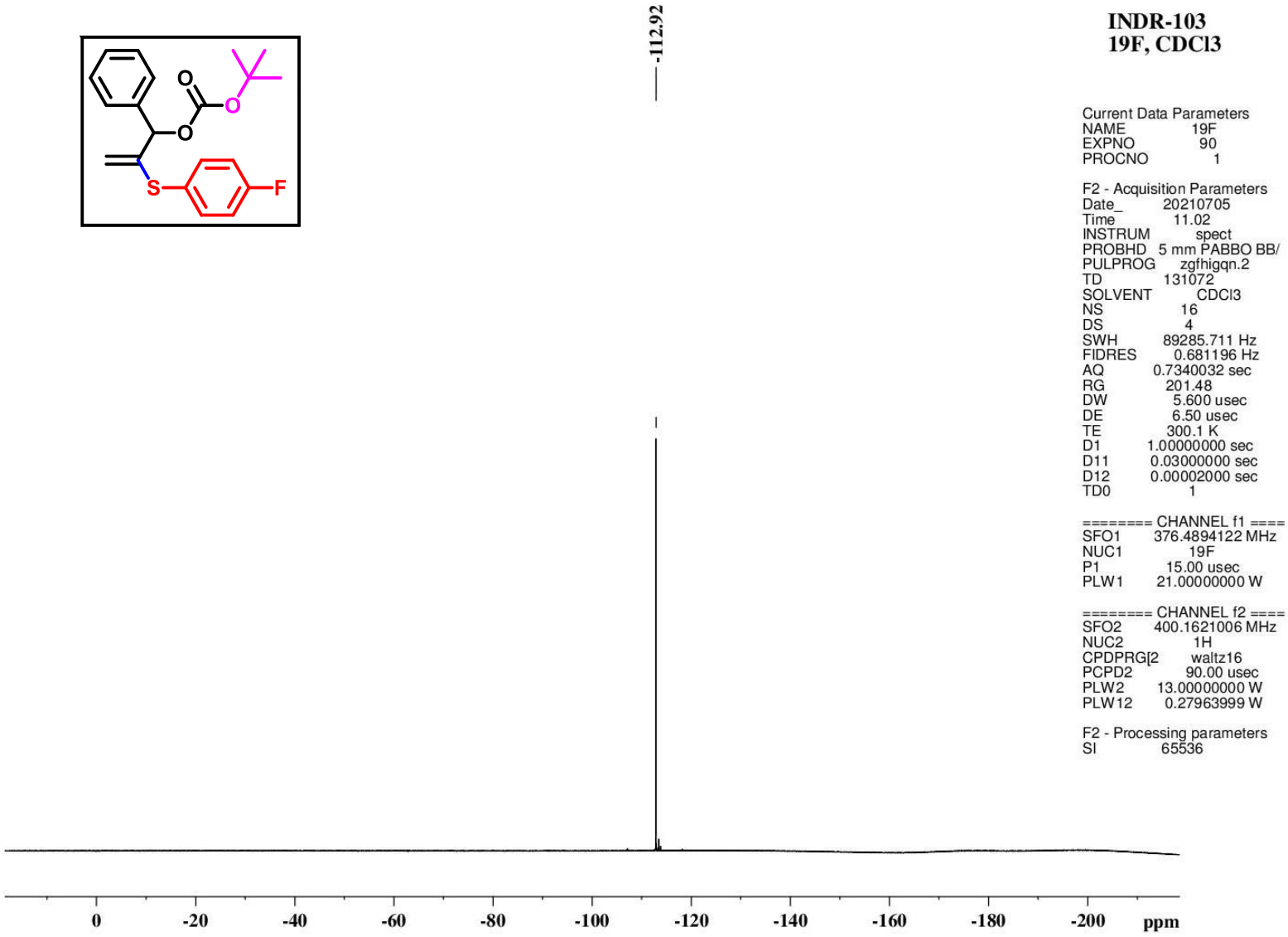



**Fig.S108** $^{19}$F NMR Spectrum of **4t**

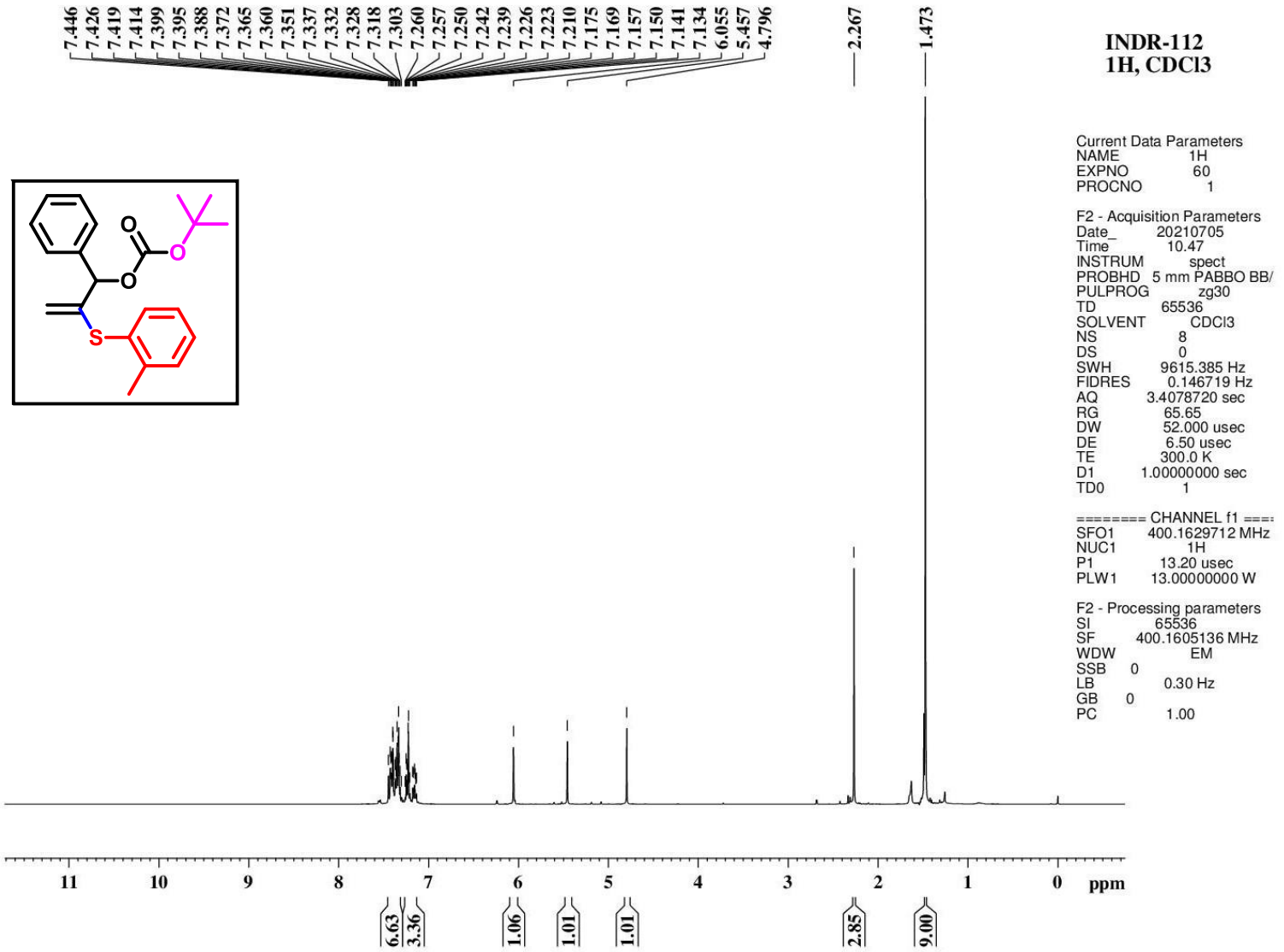



**Fig.S109** $^{1}$H NMR Spectrum of **4u**

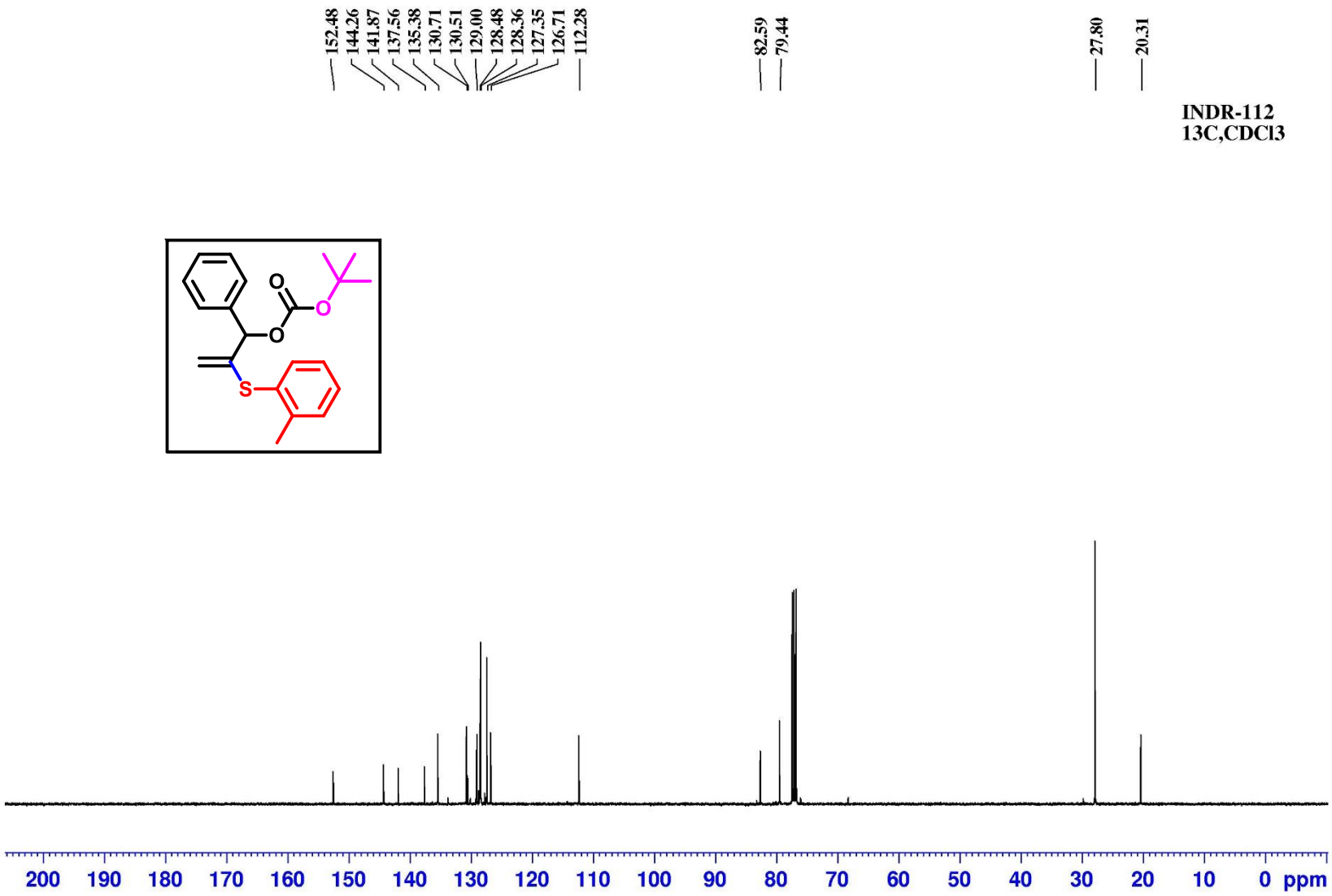



**Fig.S110** $^{13}$C NMR Spectrum of **4u**

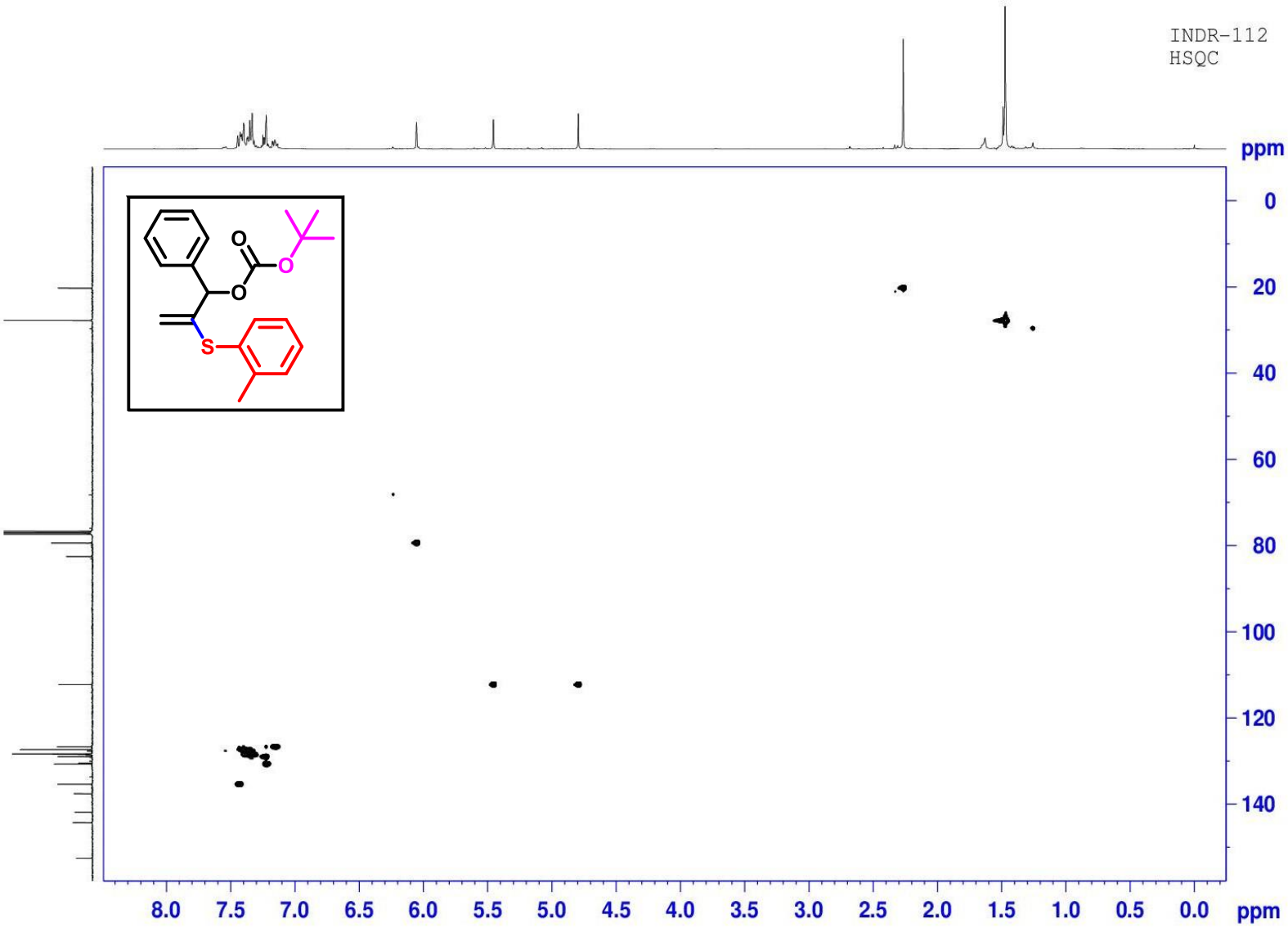



**Fig.S111** HSQC Spectrum of **4u**

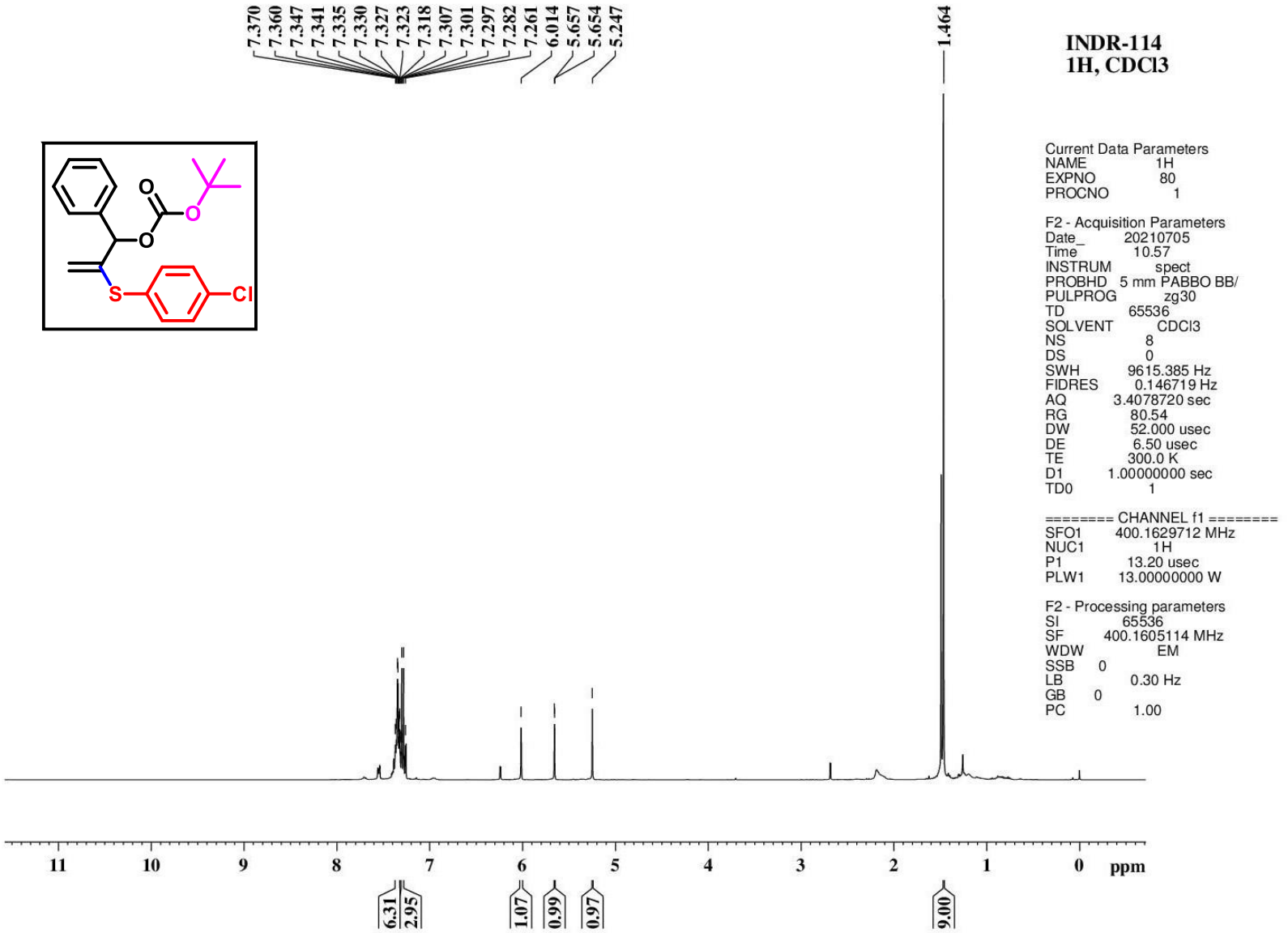



**Fig.S112** $^{1}$H NMR Spectrum of **4v**

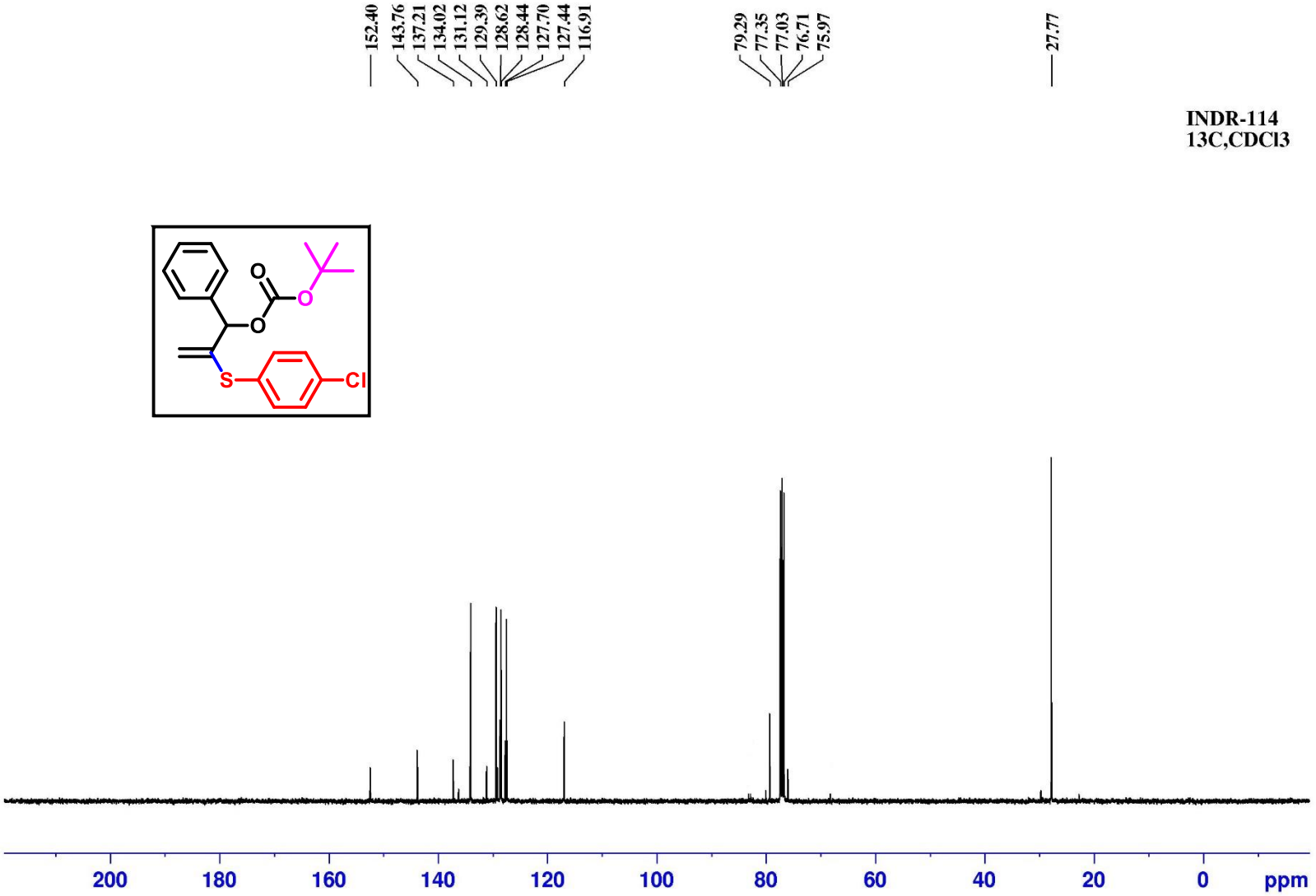



**Fig.S113** $^{13}$C NMR Spectrum of **4v**

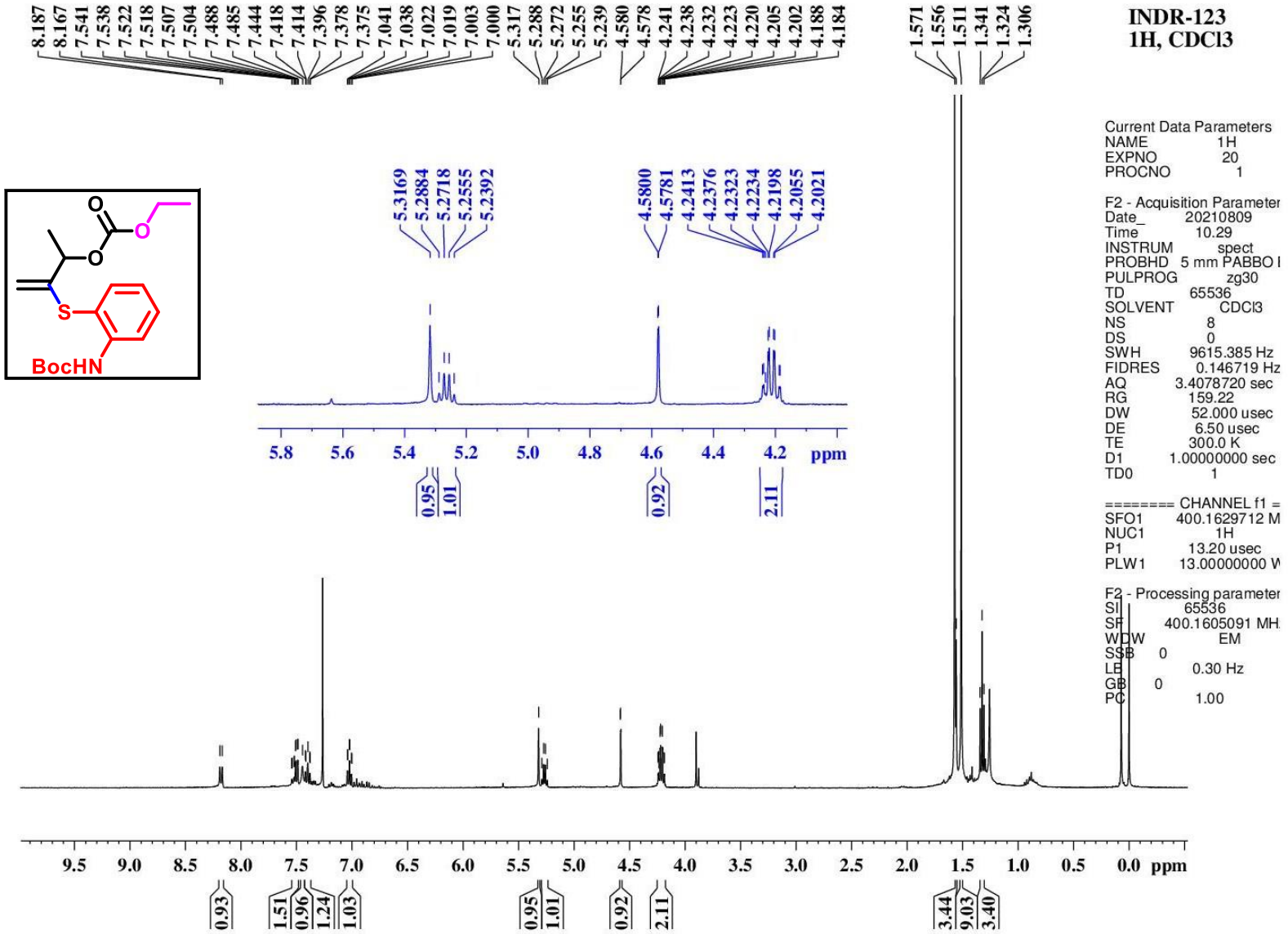



**Fig.S114** $^{1}$H NMR Spectrum of **4w**

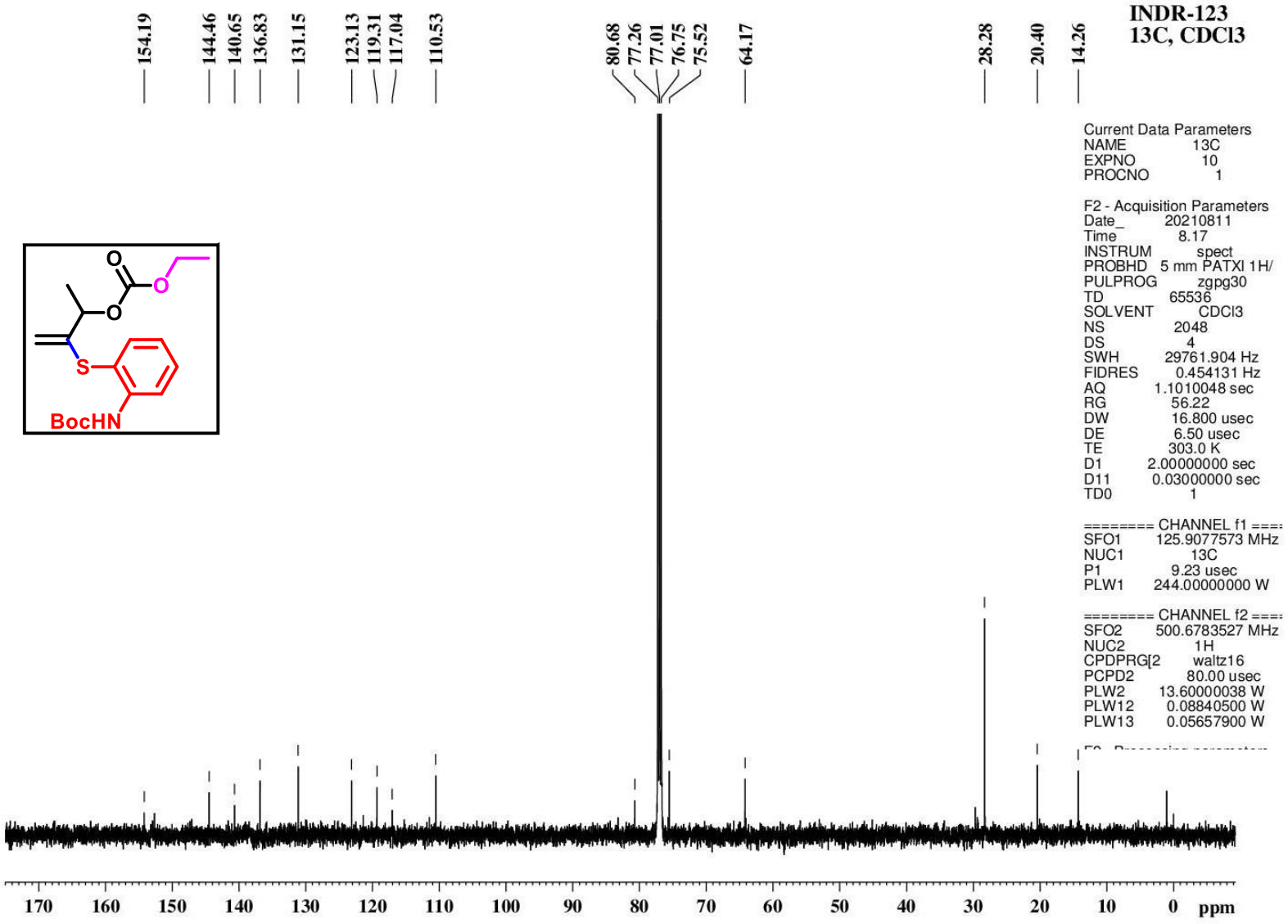



**Fig.S115** $^{13}$C NMR Spectrum of **4w**

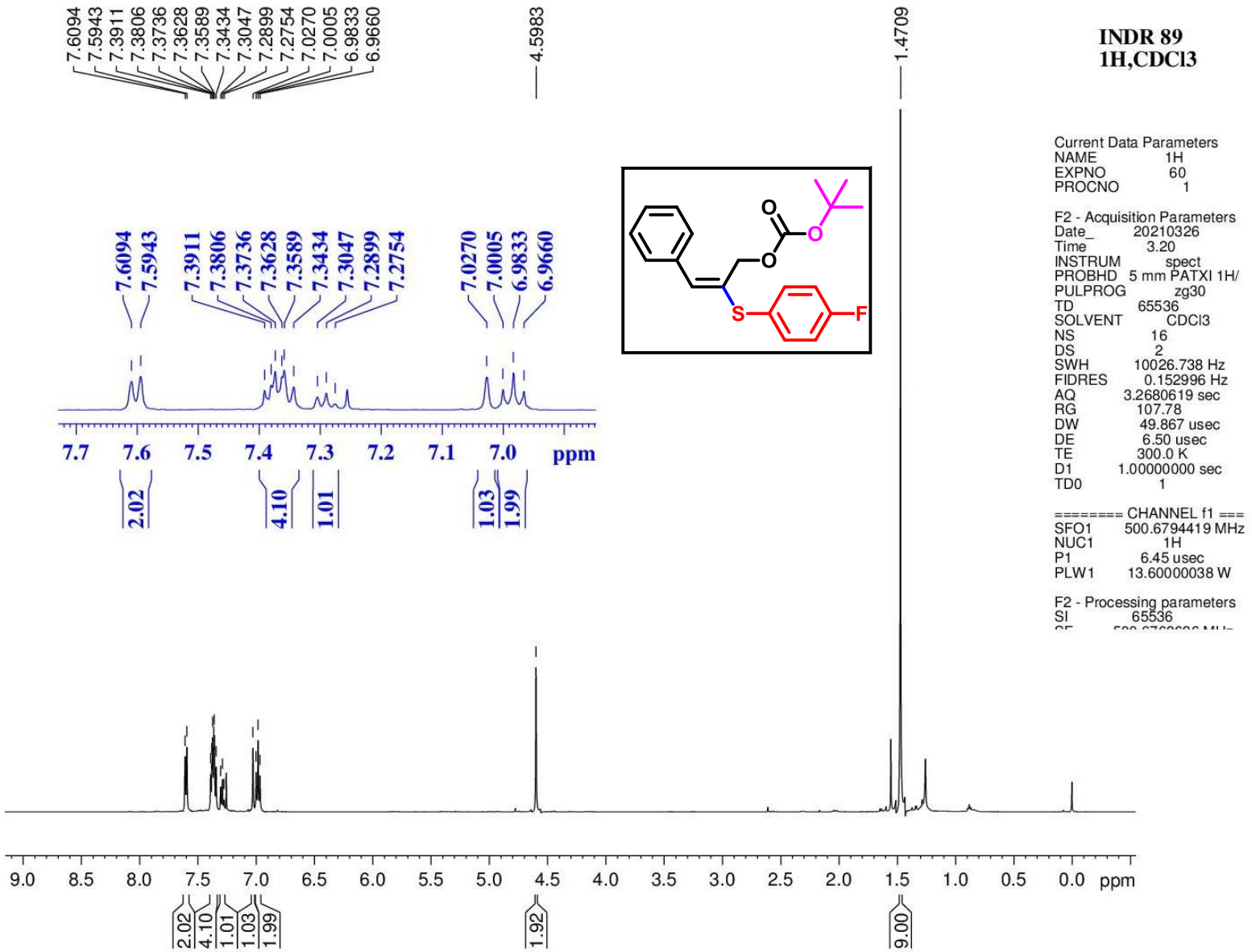



**Fig.S116** $^{1}$H NMR Spectrum of **4x**

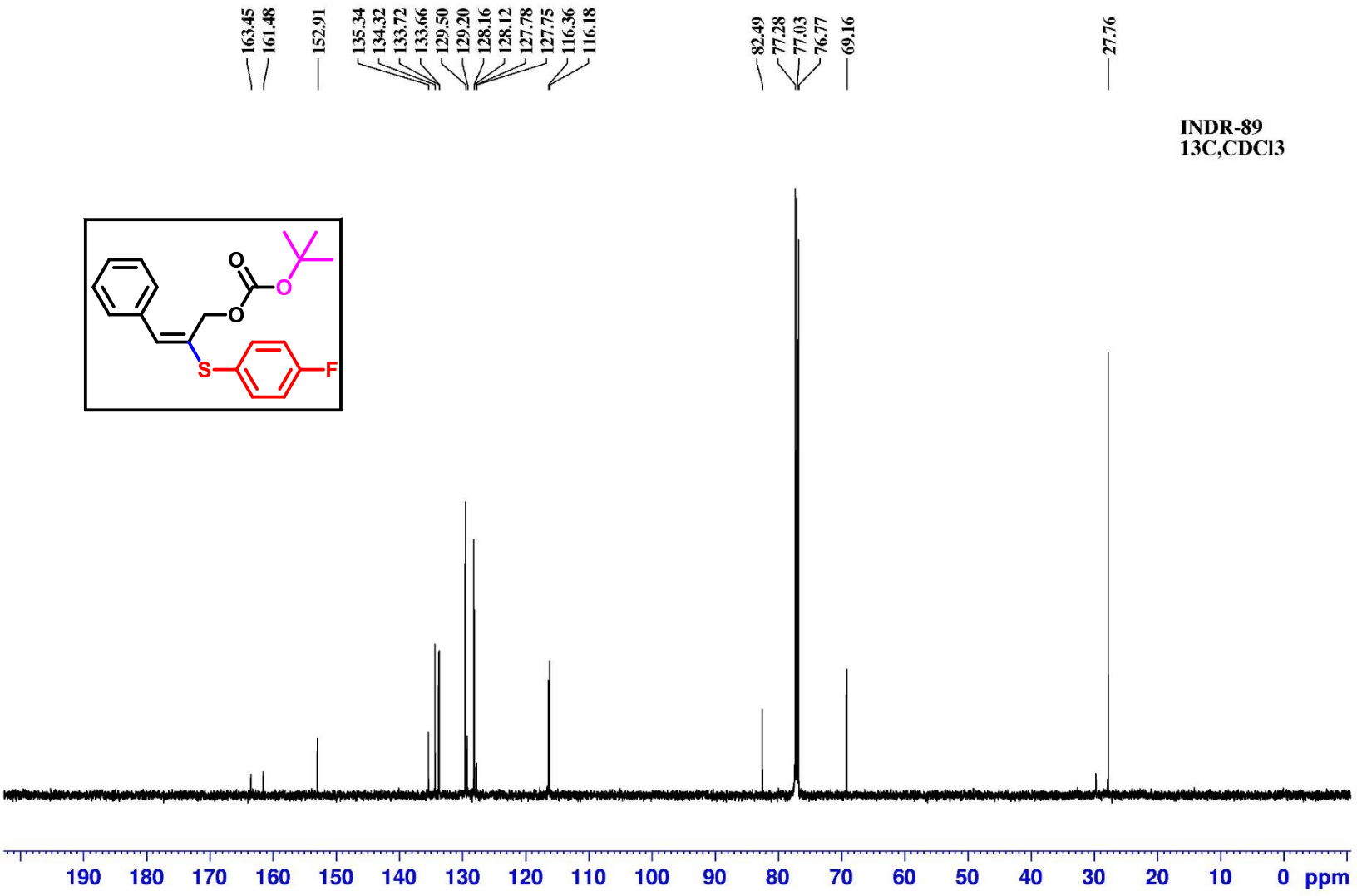



**Fig.S117** $^{13}$C NMR Spectrum of **4x**

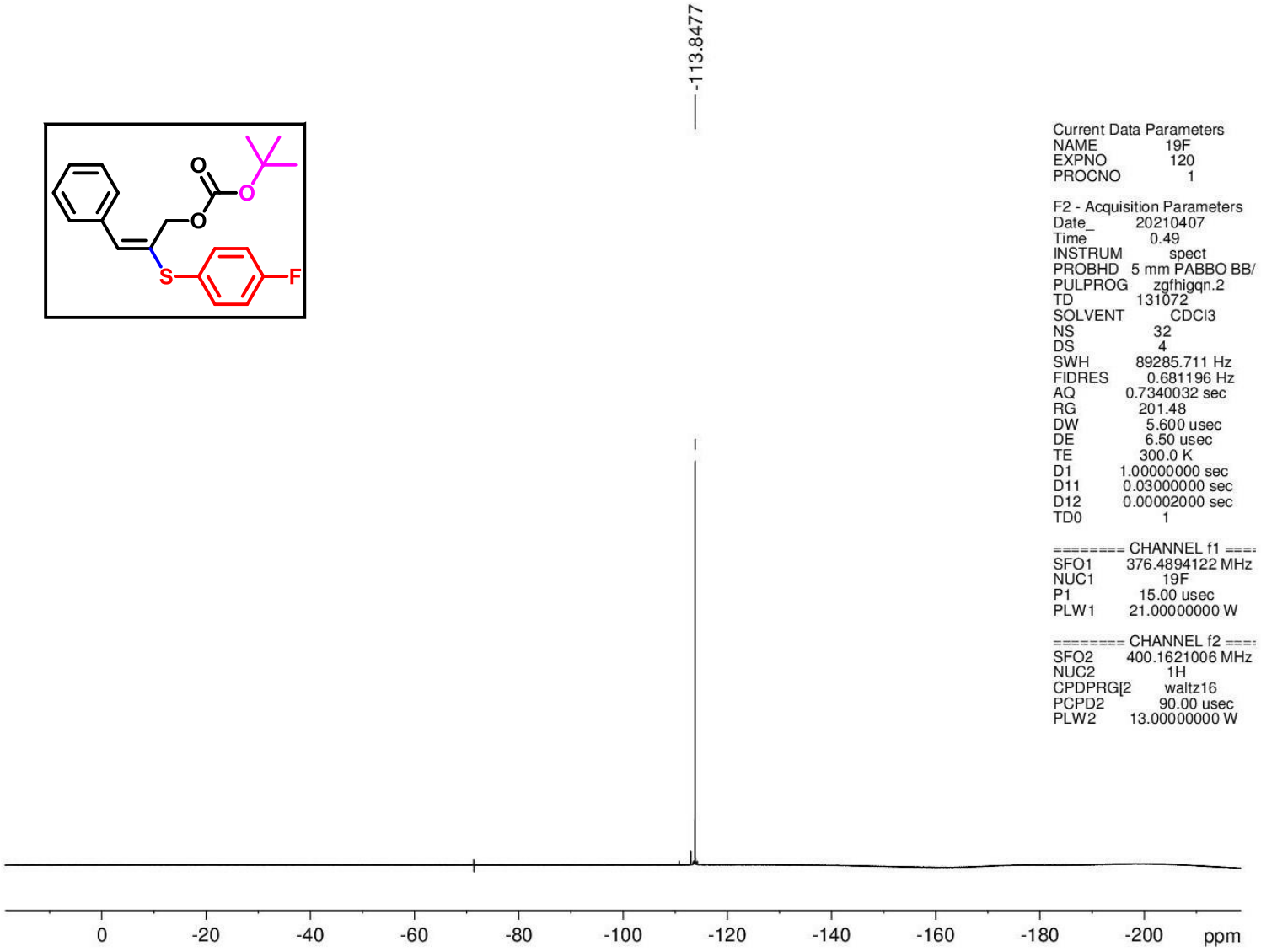



**Fig.S118** $^{19}$F NMR Spectrum of **4x**

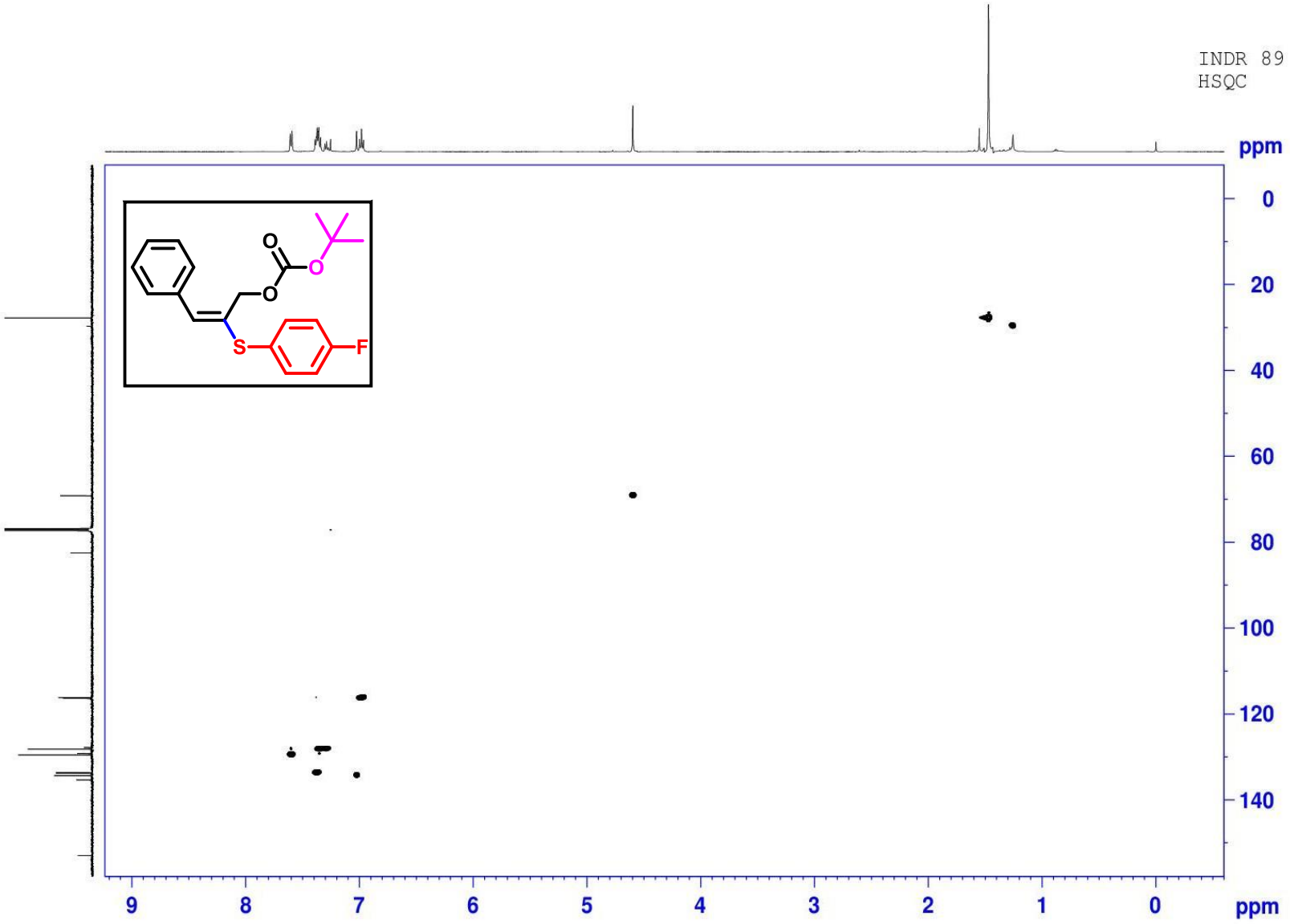



**Fig.S119** HSQC Spectrum of **4x**

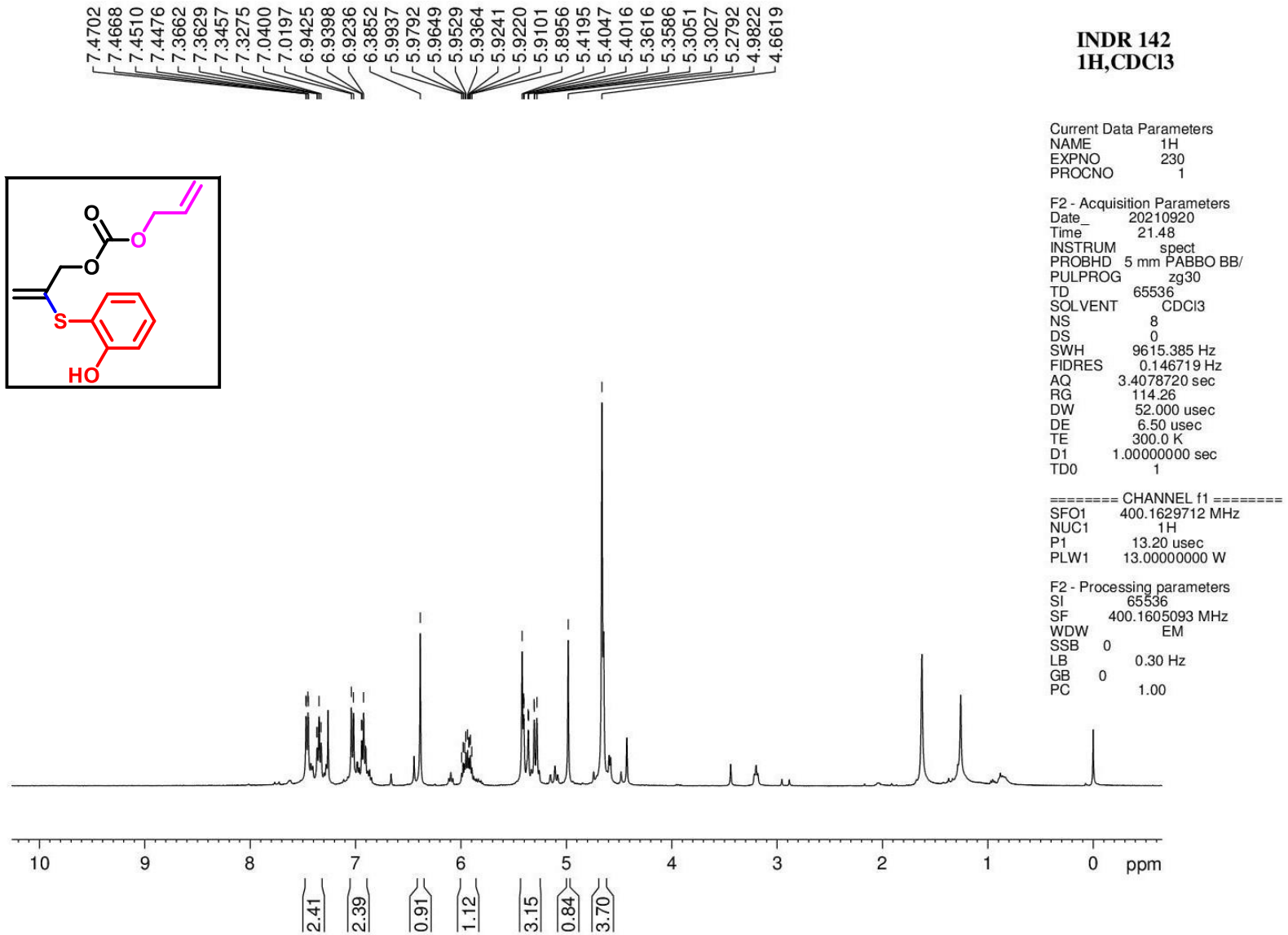



**Fig.S120** $^{1}$H NMR Spectrum of **4y**

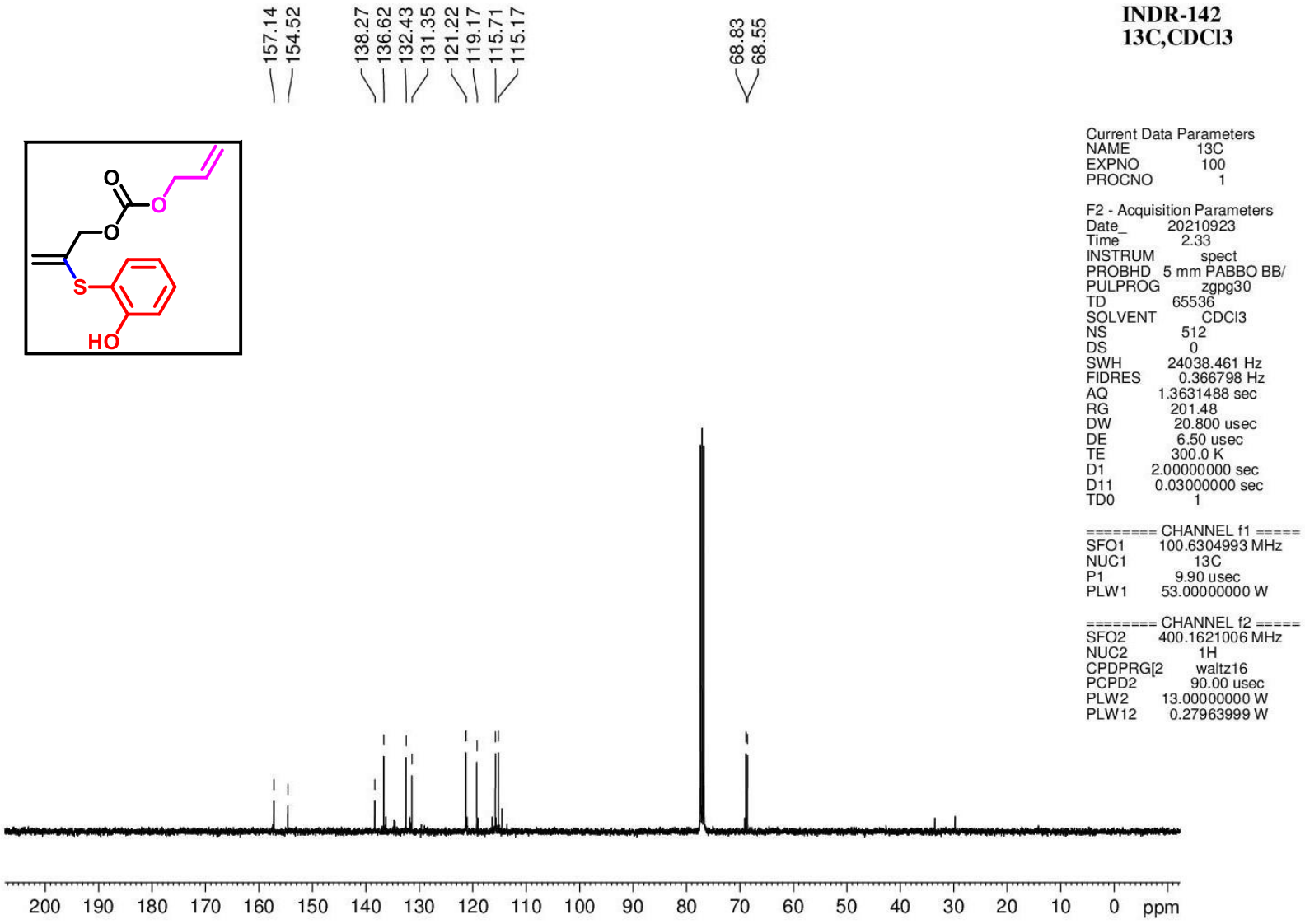



**Fig.S121** $^{13}$C NMR Spectrum of **4y**

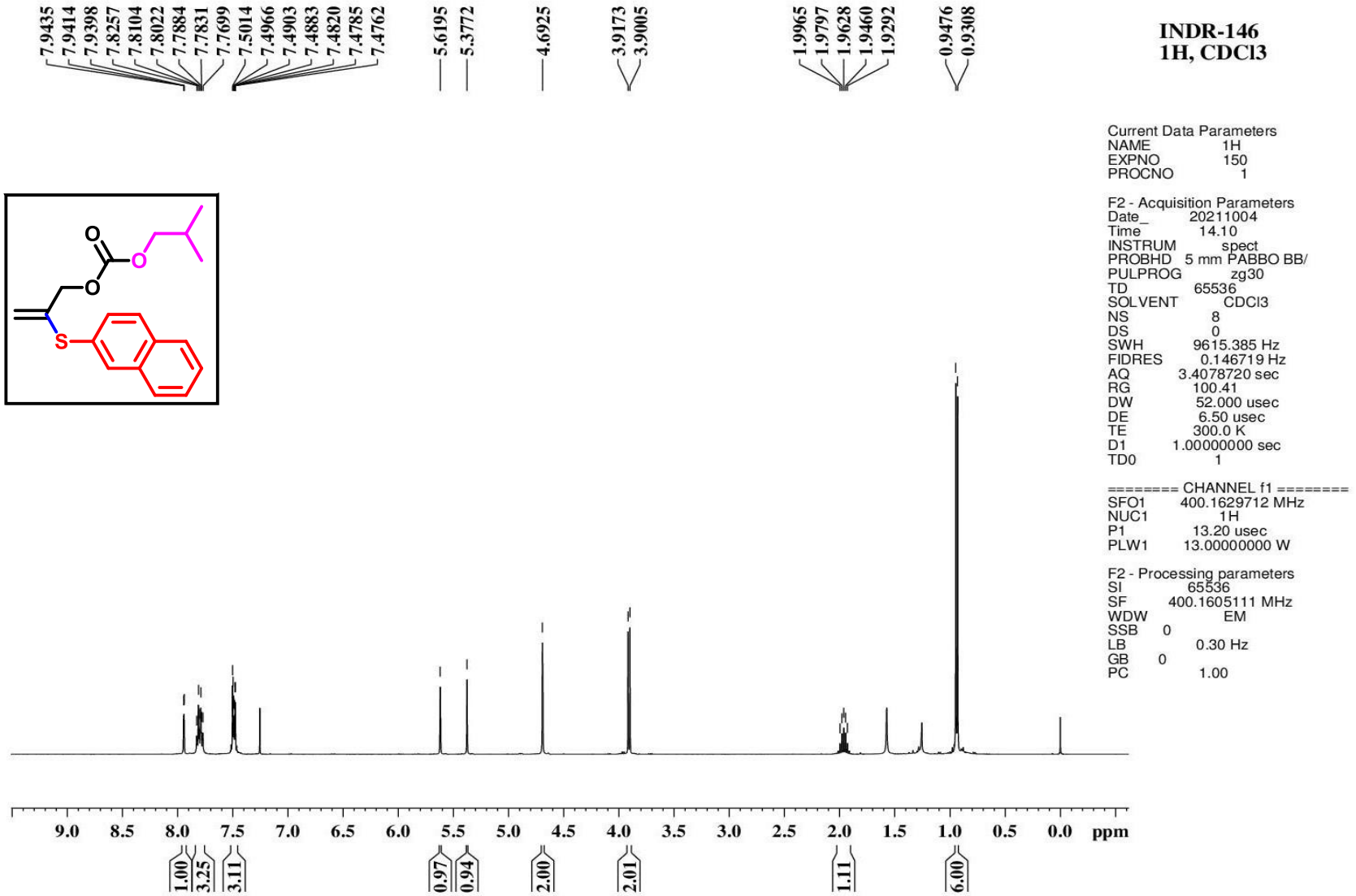



**Fig.S122** $^{1}$H NMR Spectrum of **4z**

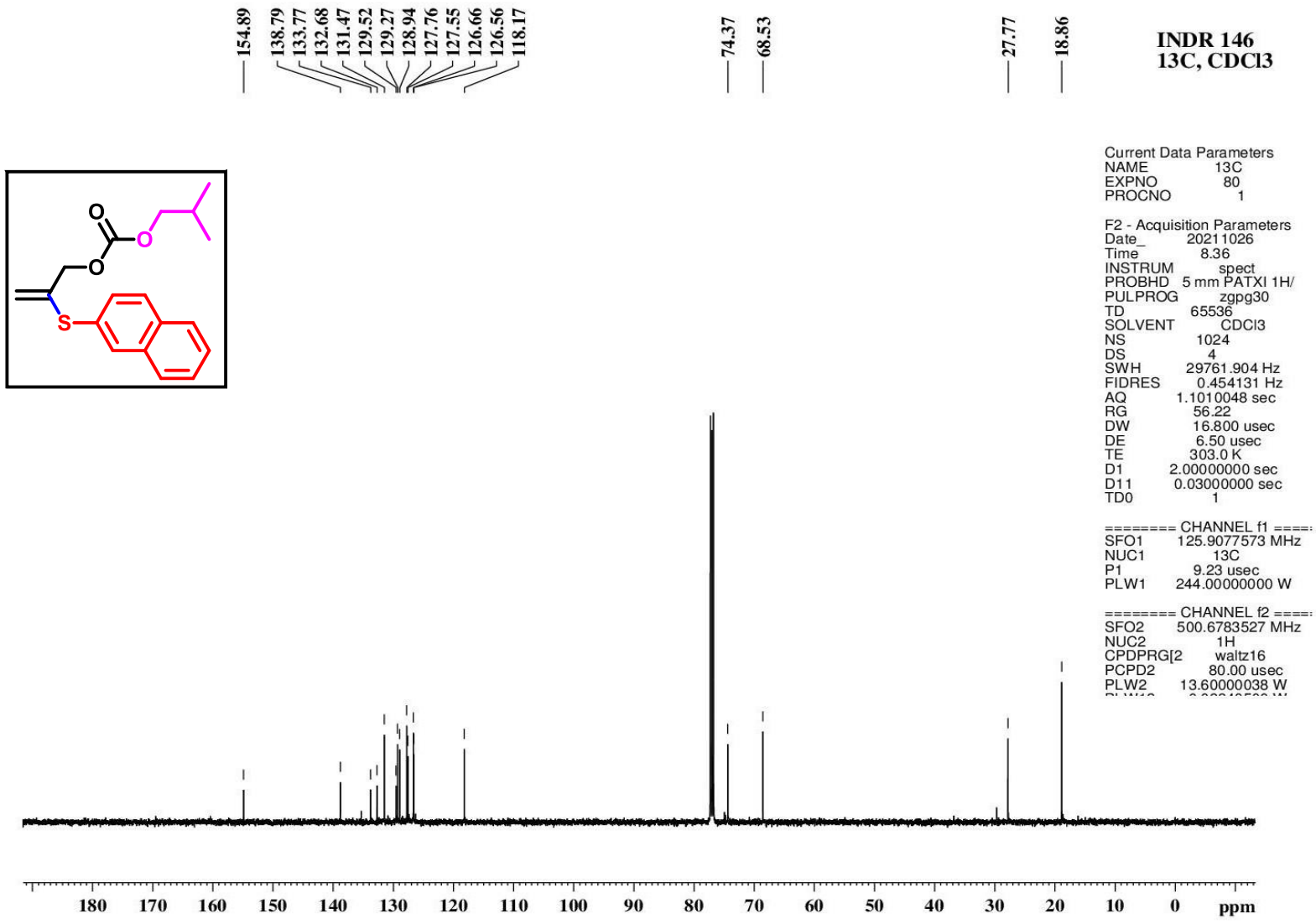



**Fig.S123** $^{13}$C NMR Spectrum of **4z**

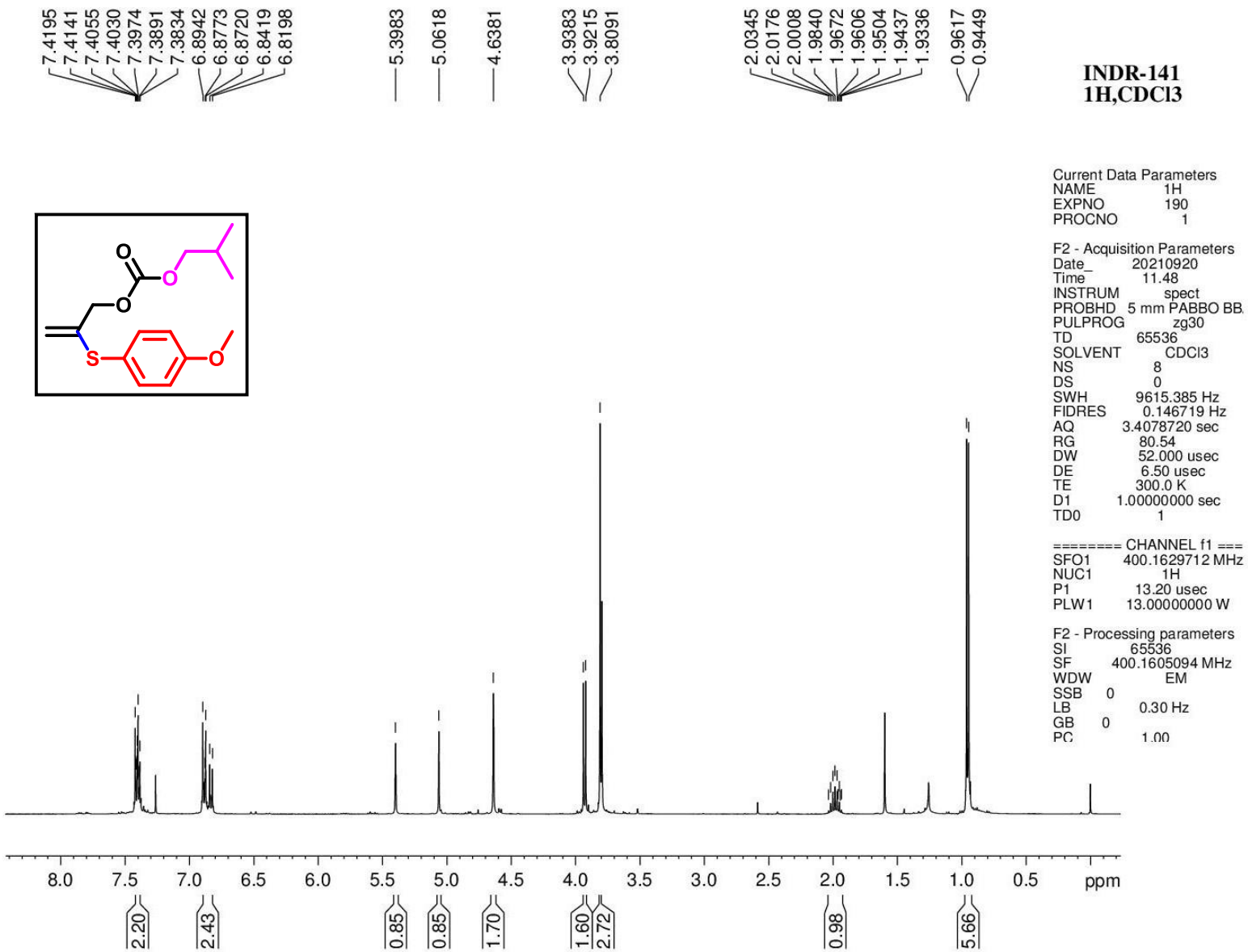





**Fig.S124** $^{1}$H NMR Spectrum of **4z'**

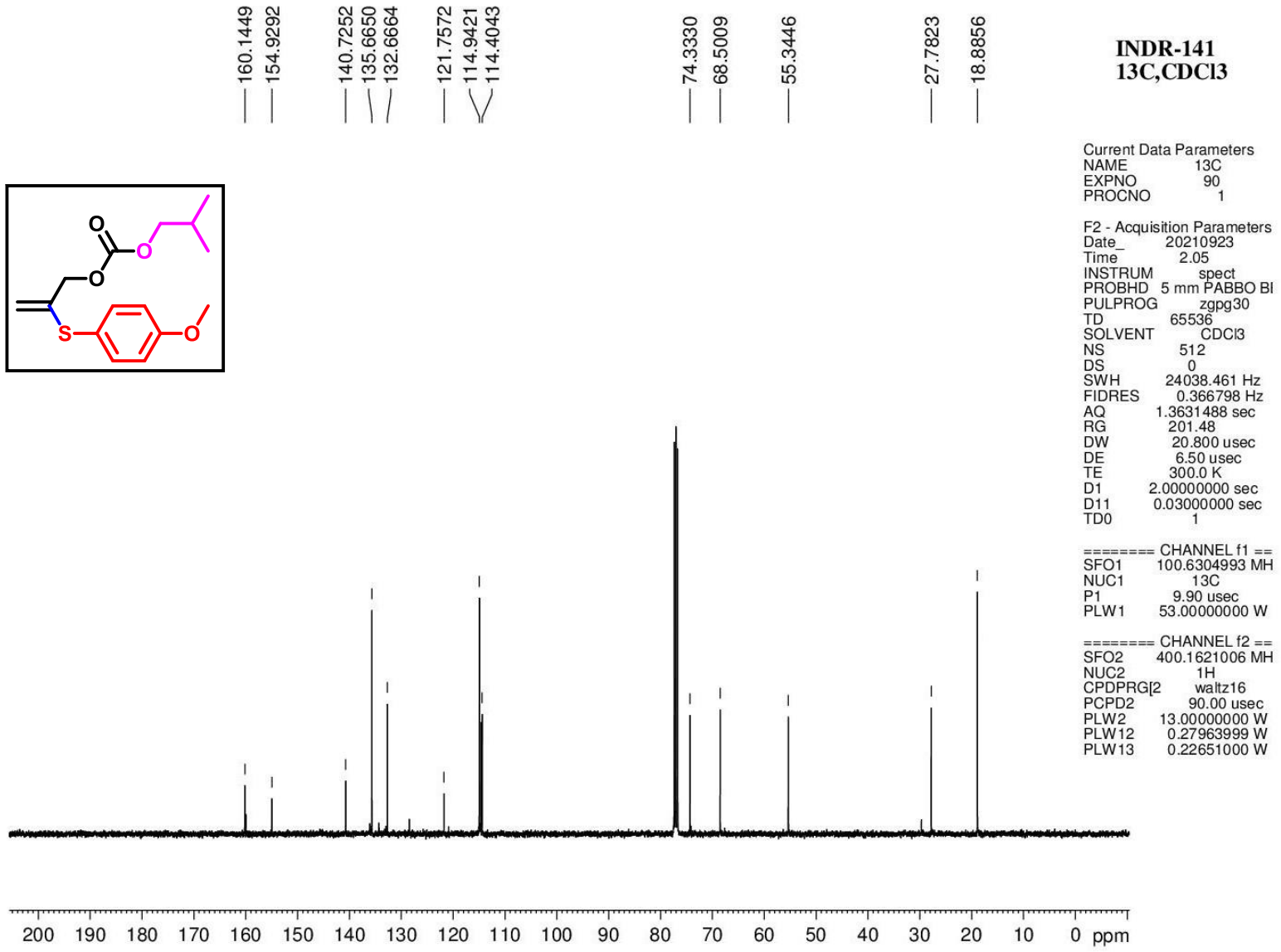



**Fig.S125** $^{13}$C NMR Spectrum of **4z'**

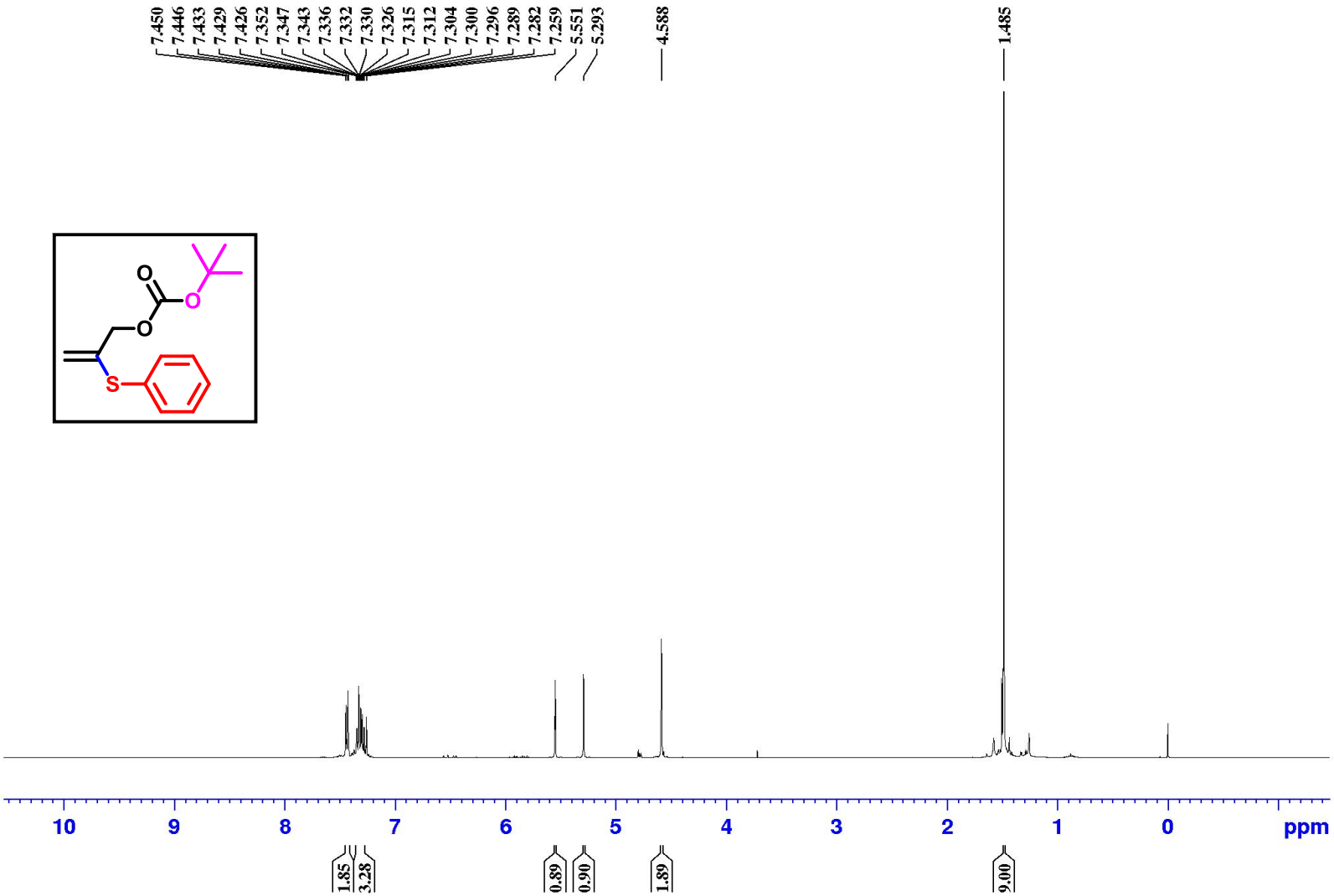



**Fig.S126** $^{1}$H NMR Spectrum of **4a'**

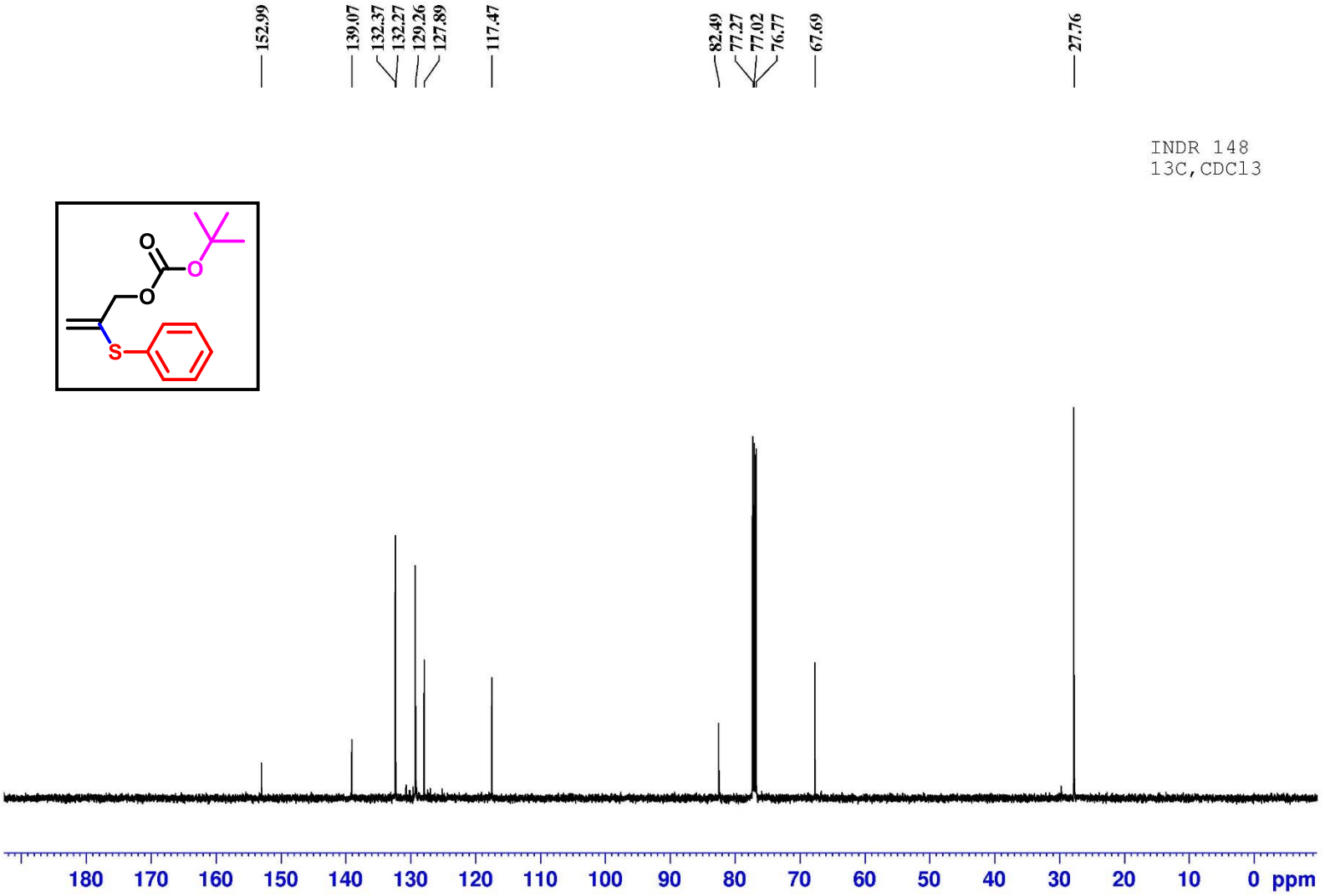



**Fig.S127** $^{13}$C NMR Spectrum of **4a'**

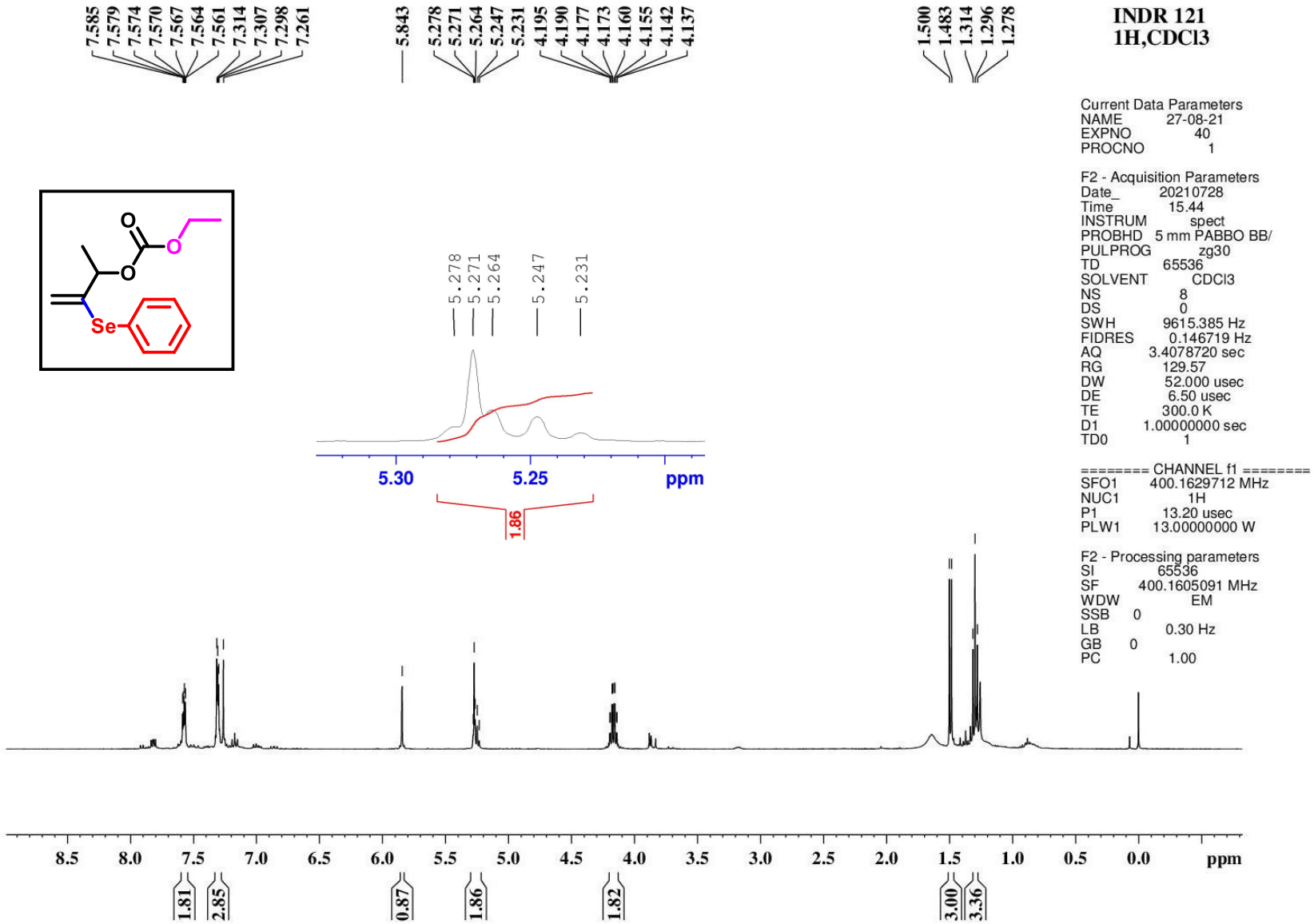



**Fig.S128** $^{1}$H NMR Spectrum of **7**

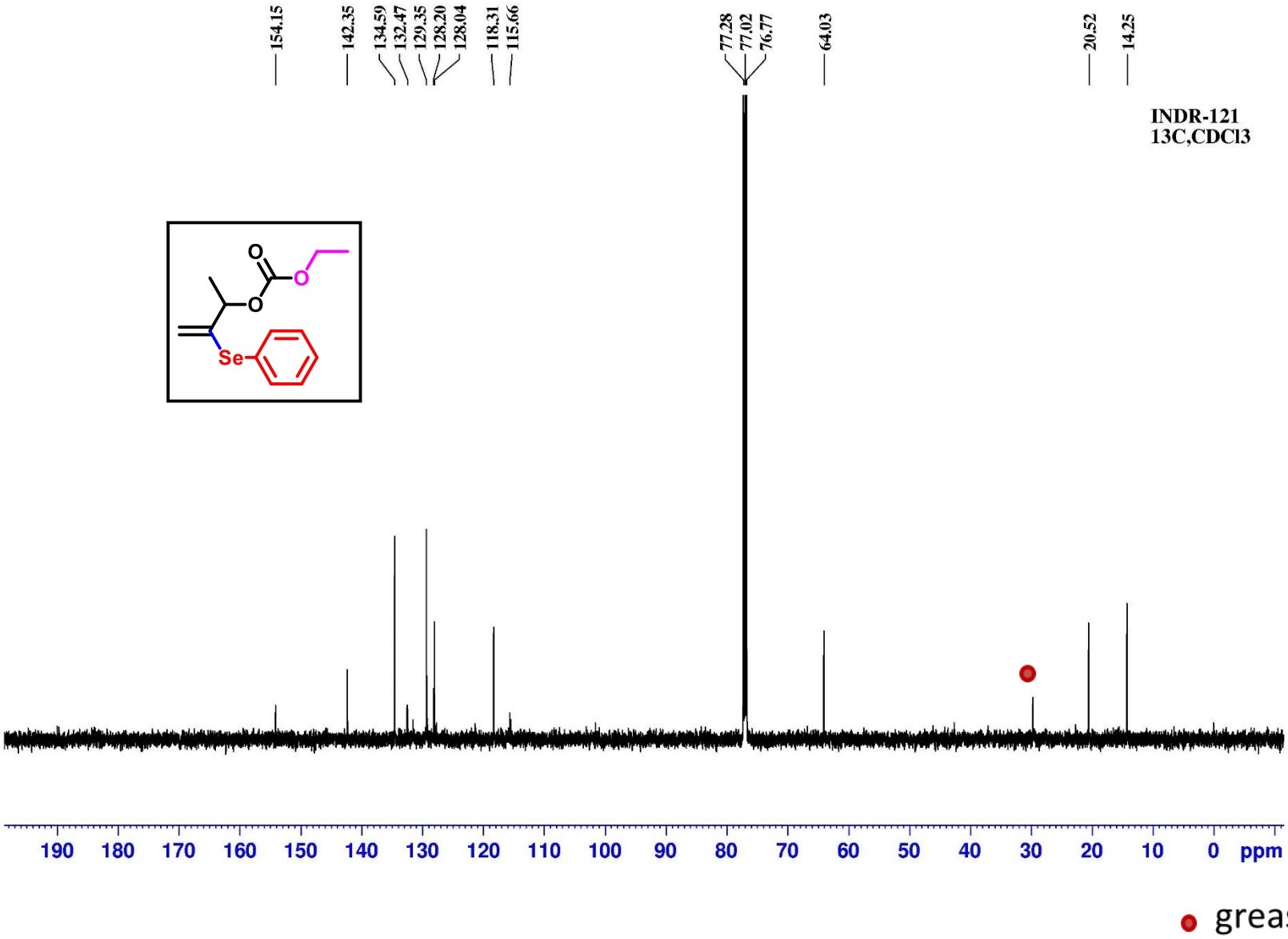



**Fig.S129** $^{13}$C NMR Spectrum of **7**

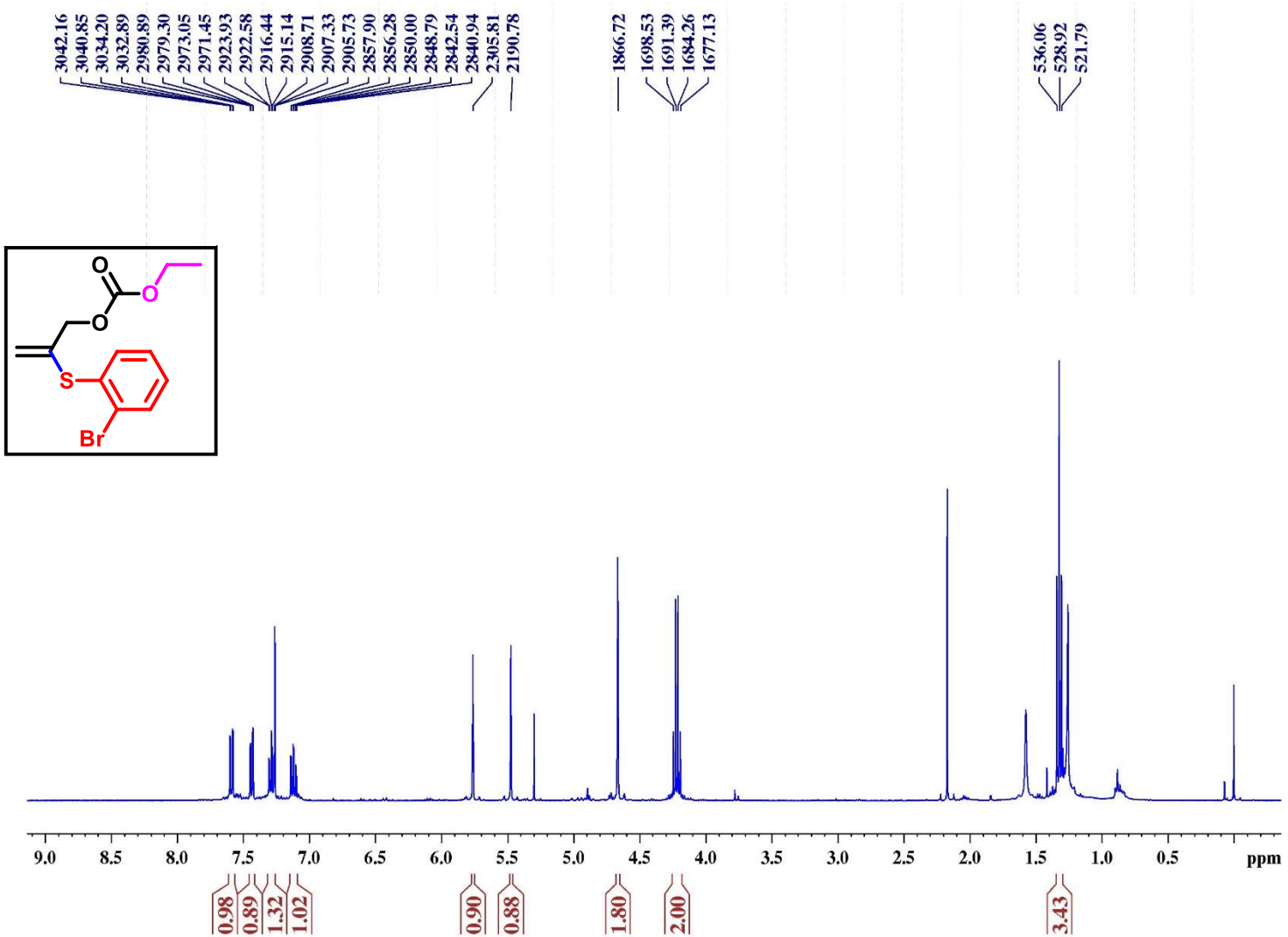



**Fig.S130** $^{1}$H NMR Spectrum of **4i'**

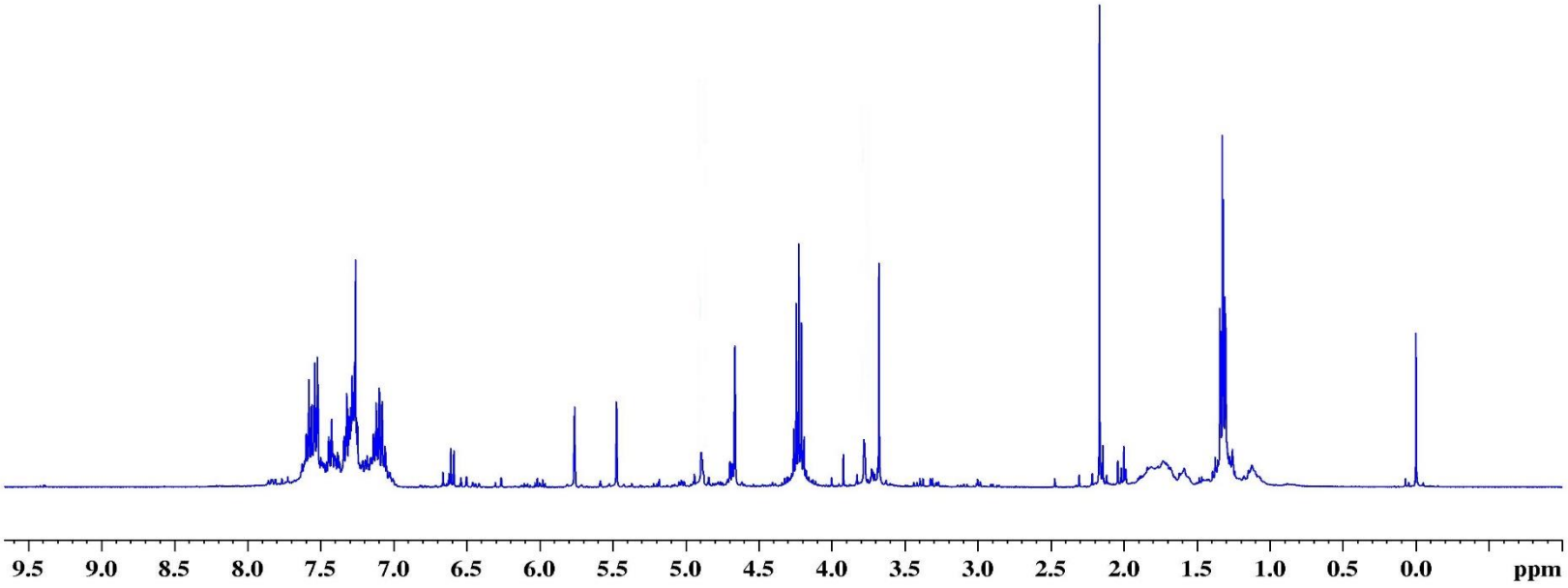



**Fig.S131** $^{1}$H NMR Spectrum (Crude) of the reaction between propargyl carbonate (1.1 mmol) and 2-bromothiophenol (1.0 mmol) for preparation of mono(arylthiol) alkene **4i'**

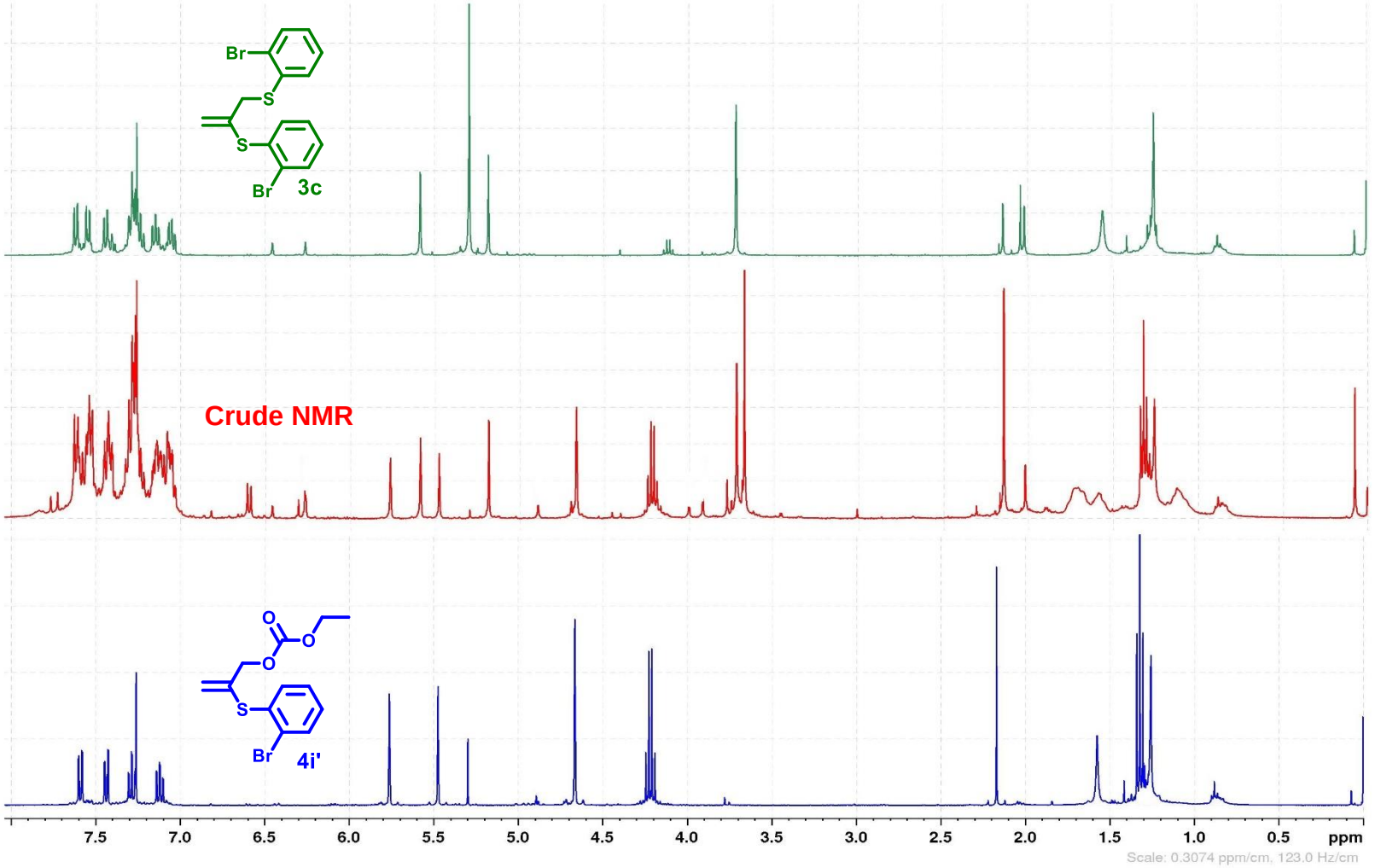



**Fig.S132** Comparison between crude $^{1}$H NMR Spectrum of the reaction between propargyl carbonate (1.0 mmol) and 2-bromothiophenol (1.5 mmol) under optimized reaction condition and $^{1}$H NMR of purified mono(arylthiol) alkene **4i'** as well as bis(arylthiol) alkene **3c**

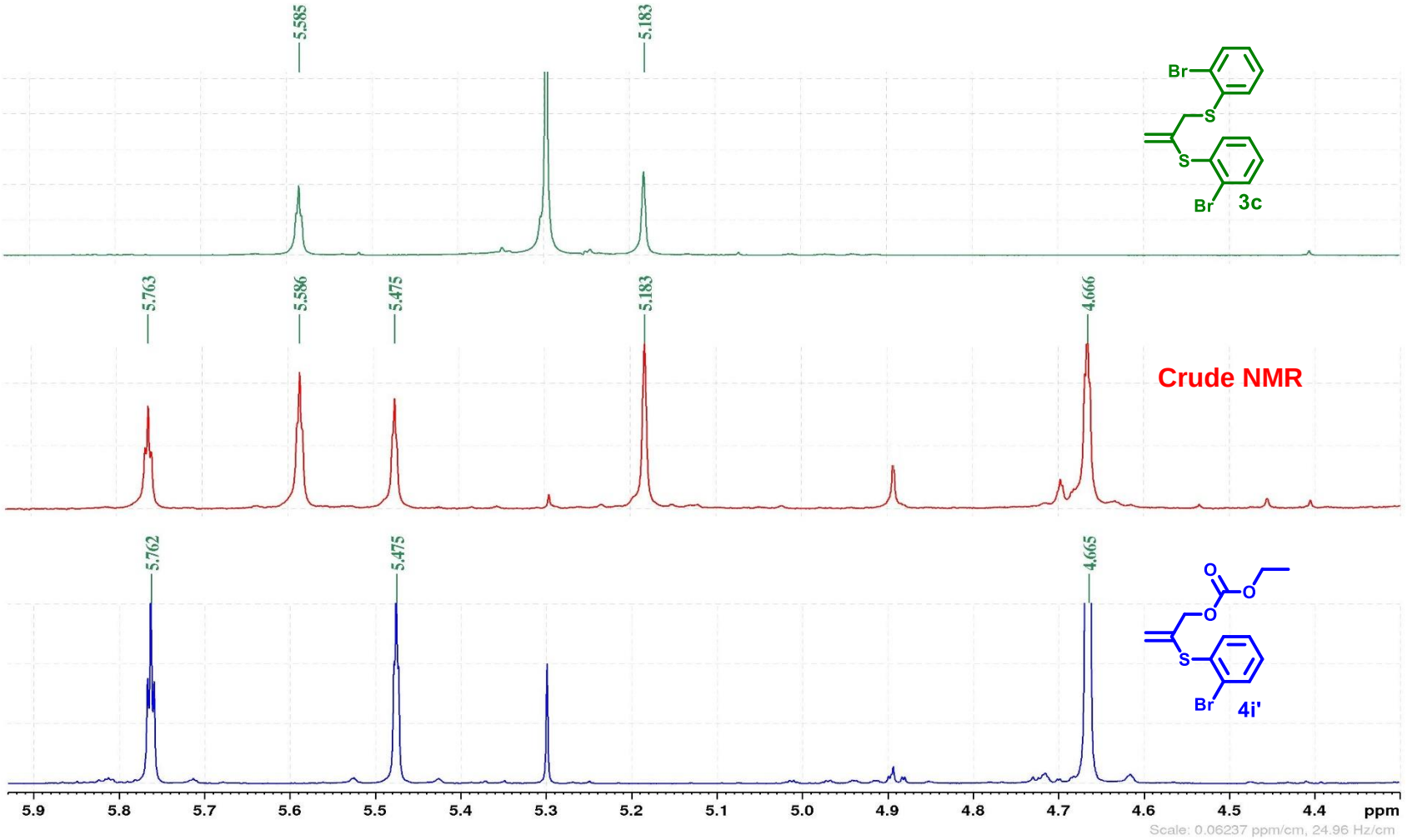



**Fig.S133** Magnified region of crude $^{1}$H NMR Spectrum of the reaction between propargyl carbonate (1.0 mmol) and 2-bromothiophenol (1.5 mmol) under optimized reaction condition and $^{1}$H NMR of purified mono(arylthiol) alkene **4i'** as well as bis(arylthiol) alkene **3c**

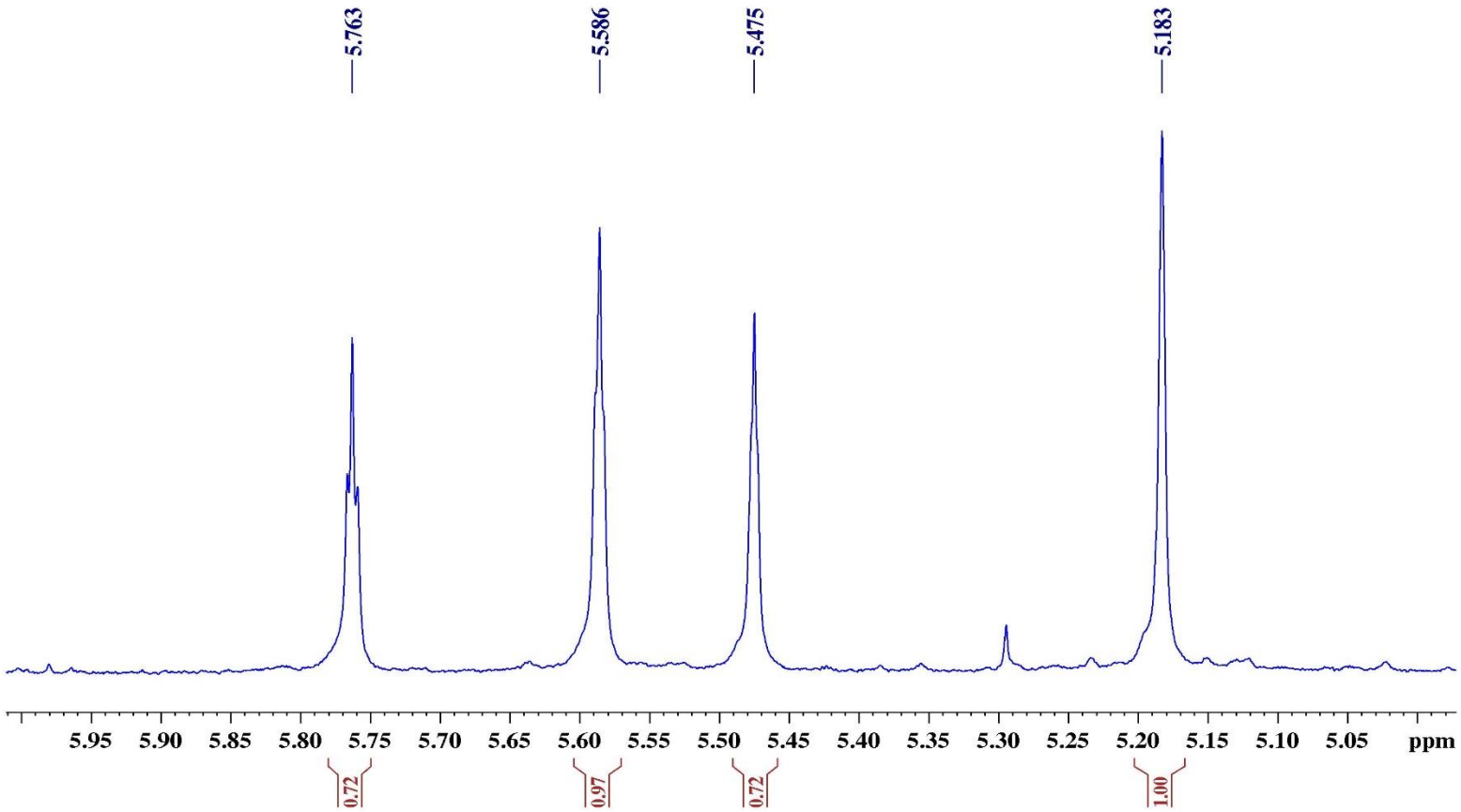



**Fig.S134** Distribution of products (**3c** and **4i'**) from magnified region of crude $^{1}$H NMR Spectrum of reaction mixture of propargyl carbonate (1.0 mmol) and 2-bromothiophenol (1.5 mmol) under optimized reaction condition