Supporting Information for

Iron–Catalyzed Alkylation of *α*–oxo Ketene Dithioacetals

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Experimental procedures and analytical data

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1. General considerations

The solvents were dried and distilled prior to use by the literature methods. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker DRX–400 spectrometer and all chemical shift values refer to δ_{TMS} = 0.00 ppm or $CDCl_3$ ($\delta(^{1}H)$, 7.26 ppm; $\delta(^{13}C)$, 77.16 ppm). X–ray Crystallographic analysis was achieved by the Analysis Center, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. The HRMS analysis was obtained on a Waters GC-TOF CA156 mass spectrometer. All the melting points were uncorrected. Analytical TLC plates, Sigma-Aldrich silica gel 60_{F200} were viewed by UV light (254 nm). Column chromatographic purifications were performed on SDZF silica gel 160. All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. $Fe(OTf)_3$ was purchased from Sinopharm Chemical Reagent Co. Ltd. Ketene dithioacetals **1a**,[1] **1b**,[2] **1c**,[3] **1d**,[4] **1e**–**1k**,[3] **1m**–**1o**,[3] **1p**–**1q**,[5] **1r**,[3] **1s**,[6] **1t**,[7] **1u**,[8] 1-(1,3-dithiolan-2-ylidene)propan–2–one,[1] 4,4–bis(ethylthio)but–3–en–2–one and 4,4–bis(methyl–thio)but–3–en–2–one[5] were prepared as reported. The spectroscopic features of known compounds **4a**,[9] **6a**,[6] and **6c**[6] are in good agreement with those reported in the literatures.

References

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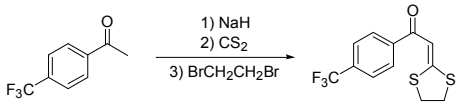
2. Experimental procedures

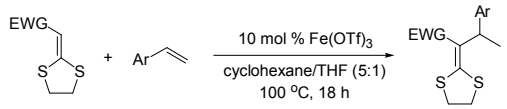
2.1. A typical procedure for the synthesis of α-oxo ketene dithioacetals (1)



1l, 37%

Synthesis of 2-(1,3-dithiolan-2-ylidene)-1-(4-(trifluoromethyl)phenyl)-ethanone (1l): 1,2-Dibromoethane (3.8 mL, 44 mmol) was added dropwise to a stirred mixture of 4'-(trifluoromethyl)acetophenone (5.7 g, 30 mmol), NaH (3.2 g, 60% in oil, 80 mmol), CS_2 (3.6 mL, 60 mmol), and 3 mL DMF in 48 mL toluene at 0 ^oC. The reaction was complete within 24 h by TLC monitoring. The resulting mixture was poured into 50 g of ice water, extracted with CH_2Cl_2 (3×15 mL). The combined organic phase was dried over anhydrous Na_2SO_4, and filtered. All the volatiles were removed under reduced pressure and the resultant residue was purified by recrystallization at –20 °C, affording **1l** as a yellow solid (3.2 g, 37%). M. p.: 117-118 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 and 7.62 (d each, J = 8.1 Hz, 2:2 H, aromatic CH), 7.24 (s, 1 H, C*H*=C-S), 3.36 (m, 4 H, $C(SCH_2)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 184.3 (C=O), 170.4 ($C(SCH_2)_2$), 141.0 (Cq, *p*-C of $CF_3C_6H_4$), 133.0 (q, J = 32.6 Hz, Cq, *i*-C of $CF_3C_6H_4$), 128.0 (*m*-CH of $CF_3C_6H_4$), 125.4 (q, J = 3.7 Hz, *o*-CH of $CF_3C_6H_4$), 123.7 (q, J = 271 Hz, Cq, CF_3), 107.6 (*C*H=C-S), 38.9 and 35.5 ($C(SCH_2)_2$). HRMS Calcd for $C_{12}H_9F_3ONaS_2$ $[M+Na]^+$: 312.9945; Found: 312.9953.

2.2. A typical procedure for iron–catalyzed alkylation of 1 with styrenes

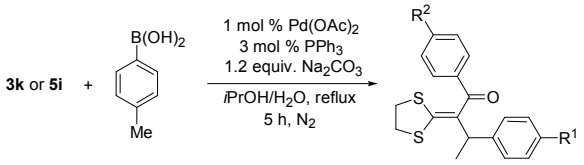


1 2 3

Synthesis of 3a (EWG = PhCO, Ar = Ph): Under a nitrogen atmosphere, a mixture of $Fe(OTf)_3$ (25 mg, 0.05 mmol), 2-(1,3-dithiolan-2-ylidene)-1-phenylethanone (**1a**) (111 mg, 0.5 mmol), styrene (62 mg, 0.6 mmol), and cyclohexane/THF (5:1, v/v, 2 mL) was stirred at 100 °C for 18 h in a 25-mL sealed tube. After cooled to ambient temperature, the mixture was filtered through a short pad of celite and rinsed with 20 mL CH_2Cl_2. The combined filtrate was concentrated

under reduced pressure and the resulting residue was purified by flash column chromatography on silica gel (petroleum ether (60-90 ^{o}C)/ethyl acetate = 10:1, v/v) to afford **3a** as a yellow solid (124 mg, 76%).

2.3. A typical procedure for palladium–catalyzed arylation of 3k and 5i with *p*-tolylboronic acid



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Arylation of 3k with *p*-tolylboronic acid: Under a nitrogen atmosphere, a mixture of **3k** (102 mg, 0.25 mmol) and *p*-tolylboronic acid (51 mg, 0.375 mmol) in *iso*–propanol (1 mL) was stirred at ambient temperature for 30 min, followed by addition of PPh_3 (2 mg, 0.0075 mmol), $Pd(OAc)_2$ (0.6 mg, 0.025 mmol), 0.15 mL of 2 M Na_2CO_3 (0.3 mmol), and 90 μL deionized water. The mixture was heated to reflux for 5 h. The resultant reaction mixture was cooled to ambient temperature, filtered through a short pad of celite, and rinsed with 20 mL CH_2Cl_2. The combined filtrate was evaporated all the volatiles under reduced pressure. The resulting residue was purified by column chromatography on silica gel (eluent:petroleum ether (60-90 °C)/ethyl acetate = 30:1, v/v) to afford the target product **7a** as a pale yellow solid (59 mg, 56%).

2.4. X-Ray crystallographic studies

The X-ray crystallographic studies of compound **6e** was carried out on a SMART APEX diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package. The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers CCDC 988290. Copies of this information may be obtained free of charge from The Director, CCDC,

12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit @ccdc.cam.ac.uk or www: http://www. ccdc.cam.ac.uk).

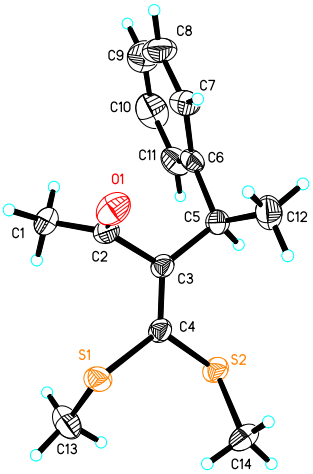


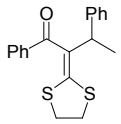
Figure 1. Molecular structure of **6e.**

Table 1. Crystal data and structure refinement for **6e**.

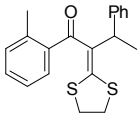
Identification code	cd213561
Empirical formula	$C_{14}H_{18}OS_2$
Formula weight	266.40
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 7.2689(9) A alpha = 90 deg.
	b = 11.4438(14) A beta = 96.396(2) deg.
	c = 17.560(2) A gamma = 90 deg.
Volume	1451.6(3) A^3
Z, Calculated density	4, 1.219 Mg/m^3
Absorption coefficient	0.350 mm^-1
F(000)	568
Crystal size	0.211 x 0.175 x 0.121 mm
Theta range for data collection	2.13 to 26.00 deg.
Limiting indices	-8<=h<=8, -12<=k<=14, -21<=l<=21
Reflections collected / unique	8448 / 2843 [R(int) = 0.0526]
Completeness to theta = 26.00	99.9 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.54533
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2843 / 0 / 159
Goodness-of-fit on F^2	1.066
Final R indices [I>2sigma(I)]	R1 = 0.0459, wR2 = 0.1139

R indices (all data)	R1 = 0.0528, wR2 = 0.1194
Extinction coefficient	0.018(3)
Largest diff. peak and hole	0.302 and -0.309 e.A^-3

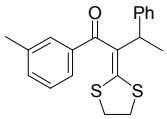
3. Analytical data



2-(1,3-Dithiolan-2-ylidene)-1,3-diphenylbutan-1-one (3a): Yield, 76%. Pale yellow solid, m. p.: 103-105 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (m, 2 H, aromatic CH), 7.46 (t, 1 H, aromatic CH), 7.39-7.35 (m, 4 H, aromatic CH), 7.28 (t, 2 H, aromatic CH), 7.18 (t, 1 H, aromatic CH), 4.32 (q, 1 H, C*H*CH_3), 3.27-3.18 (m, 4 H, $C(SCH_2)_2$), 1.65 (d, *J* = 7.2 Hz, 3 H, CHC*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.6 (Cq, C=O), 151.7 (Cq, *C*$(SCH_2)_2$), 143.3, 139.0, and 129.7 (Cq), 131.7, 128.6, 128.3, 128.1, 127.7, and 126.1 (aromatic CH), 44.8 (*C*HCH_3), 38.6 and 37.2 ($C(SCH_2)_2$), 18.0 (CH*C*H_3). HRMS Calcd for $C_{19}H_{18}ONaS_2$ $[M+Na]^+$: 349.0697; Found: 349.0687.

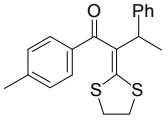


2-(1,3-Dithiolan-2-ylidene)-3-phenyl-1-o-tolylbutan-1-one (3b): Yield, 68%. Pale yellow solid, m. p.: 101-103 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26, 7.17, and 7.11 (m each, 5:2:2 H, aromatic CH), 4.32 (q, 1 H, C*H*CH_3), 3.30-3.19 (m, 4 H, $C(SCH_2)_2$), 2.28 (s, 3 H, CH_3), 1.62 (d, *J* = 7.2 Hz, 3 H, CHC*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.9 (C=O), 161.6 (Cq, *C*$(SCH_2)_2$), 143.1, 140.6, 135.8, and 130.3 (Cq each), 130.8, 129.3, 128.1, 127.7, 126.5, 126.0, and 125.3 (aromatic CH), 42.6 (*C*HCH_3), 38.5 and 36.9 ($C(SCH_2)_2$), 19.6 (CH*C*H_3), 16.5 (CH_3). HRMS Calcd for $C_{20}H_{20}OS_2$ $[M]^+$: 340.0956; Found: 340.0965.

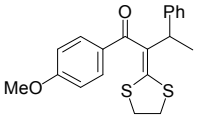


2-(1,3-Dithiolan-2-ylidene)-3-phenyl-1-m-tolylbutan-1-one (3c): Yield, 66%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.36 and 7.29-7.22 (m each, 4:4 H, aromatic CH), 7.18 (t, 1 H, aromatic CH), 4.31 (q, 1 H, C*H*CH_3), 3.31-3.19 (m, 4 H, $C(SCH_2)_2$), 2.34 (s, 3 H, CH_3), 1.62 (d, *J* = 7.2 Hz, 3 H, CHC*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.9 (Cq, C=O), 151.5 (Cq, *C*$(SCH_2)_2$), 143.4, 139.0, 138.1, and

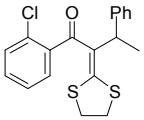
129.9 (Cq), 132.5, 129.1, 128.1, 127.7, 126.1, and 125.9 (aromatic CH), 44.7 (*C*HCH$_3$), 38.6 and 37.2 (C(S*C*H$_2$)$_2$), 21.4 (CH$_3$), 17.9 (CH*C*H$_3$). HRMS Calcd for $C_{20}H_{20}OS_2$ $[M]^+$: 340.0956; Found: 340.0955.



2-(1,3-Dithiolan-2-ylidene)-3-phenyl-1-p-tolylbutan-1-one (3d): Yield, 68%. White solid, m. p.: 108-109 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 and 7.38 (d each, *J* = 8.0 and 7.6 Hz, 2:2 H, aromatic CH), 7.26 (t, 2 H, aromatic CH), 7.17 (d, *J* = 7.6 Hz, 3 H, aromatic CH), 4.25 (q, *J* = 7.2 Hz, 1 H, C*H*CH$_3$), 3.31-3.15 (m, 4 H, C(SCH$_2$)$_2$), 2.37 (s, 3 H, CH$_3$), 1.61 (d, *J* = 7.2 Hz, 3 H, CHC*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.7 (Cq, C=O), 148.7 (Cq, *C*(SCH$_2$)$_2$), 143.5, 142.9, 136.0, and 130.1 (Cq), 129.23, 129.17, 128.2, 127.8, and 126.2 (aromatic CH), 45.3 (*C*HCH$_3$), 38.7 and 37.3 (C(S*C*H$_2$)$_2$), 21.7 (CH$_3$), 18.3 (CH*C*H$_3$). HRMS Calcd for $C_{20}H_{20}OS_2$ $[M]^+$: 340.0956; Found: 340.0961.

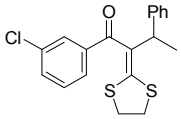


2-(1,3-Dithiolan-2-ylidene)-1-(4-methoxyphenyl)-3-phenylbutan-1-one (3e): Yield, 61%. Pale yellow solid, m. p.: 65-67 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 and 6.85 (d each, *J* = 8.7 Hz, 2:2 H, aromatic CH), 7.39 (d, *J* = 7.6 Hz), 7.26 (t, *J* = 7.6 Hz), and 7.16 (t) (2:2:1 H, aromatic CH), 4.21 (t, 1 H, C*H*CH$_3$), 3.83 (s, 3 H, OCH$_3$), 3.31.30 and 3.21 (m each, 2:2 H, C(SCH$_2$)$_2$), 1.60 (d, *J* = 7.2 Hz, 3 H, CHC*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.0 (Cq, C=O), 163.2 (Cq, *i*-C of C_6H_4OMe), 145.5 (Cq, *C*(SCH$_2$)$_2$), 143.6, 130.9, and 130.3 (Cq), 131.8, 128.2, 127.9, 126.3, and 113.7 (aromatic CH), 55.5 (OCH$_3$), 45.9 (*C*HCH$_3$), 38.7 and 37.4 (C(S*C*H$_2$)$_2$), 18.7 (CH*C*H$_3$). HRMS Calcd for $C_{20}H_{20}O_2S_2$ $[M]^+$: 356.0905; Found: 356.0901.

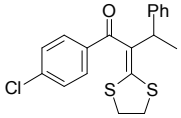


1-(2-Chlorophenyl)-2-(1,3-dithiolan-2-ylidene)-3-phenylbutan-1-one (3f): Yield, 66%. White solid, m. p.: 149-150 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.9 Hz, 1 H, aromatic CH), 7.25 (m, 5 H, aromatic CH), 7.17 (t, 2 H, aromatic CH), 7.06 (d, *J* = 7.1 Hz, 1 H, aromatic CH), 4.22 (q, 1 H, C*H*CH$_3$), 3.23 (m, 4 H,

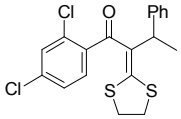
$C(SCH_2)_2$), 1.60 (d, J = 7.2 Hz, 3 H, CHCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 191.5 (Cq, C=O), 166.1 (Cq, $C(SCH_2)_2$), 142.8, 140.4, 130.6, and 129.1 (Cq), 130.0, 129.8, 128.1, 127.7, 127.4, 126.6, and 126.0 (aromatic CH), 41.5 (CHCH$_3$), 38.3 and 37.1 (C(SCH$_2$)$_2$), 15.8 (CHCH$_3$). HRMS Calcd for $C_{19}H_{17}OClS_2$ $[M]^+$: 360.0409; Found: 360.0402.



1-(3-Chlorophenyl)-2-(1,3-dithiolan-2-ylidene)-3-phenylbutan-1-one (3g): Yield, 70%. Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.48, 7.40, and 7.28 (m each, 1:2:5 H, aromatic CH), 7.17 (t, 1 H, aromatic CH), 4.29 (q, 1 H, CHCH$_3$), 3.27 (m, 4 H, $C(SCH_2)_2$), 1.62 (d, J = 7.2 Hz, 3 H, CHCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 193.9 (Cq, C=O), 154.2 (Cq, $C(SCH_2)_2$), 143.0, 141.0, 134.4, and 129.3 (Cq), 131.4, 129.6, 128.4, 128.2, 127.6, 126.4, and 126.3 (aromatic CH), 44.5 (CHCH$_3$), 38.7 and 37.1 (C(SCH$_2$)$_2$), 17.7 (CHCH$_3$). HRMS Calcd for $C_{19}H_{17}OClS_2$ $[M]^+$: 360.0409; Found: 360.0414.

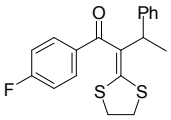


1-(4-Chlorophenyl)-2-(1,3-dithiolan-2-ylidene)-3-phenylbutan-1-one (3h): Yield, 68%. Pale yellow solid, m. p.: 107-108 ^{o}C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 and 7.35 (m each, 2:4 H, aromatic CH), 7.29 and 7.20 (t each, 2:1 H, aromatic CH), 4.30 (q, 1 H, CHCH$_3$), 3.36-3.21 (m, 4 H, $C(SCH_2)_2$), 1.65 (d, J = 7.2 Hz, 3 H, CHCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 194.5 (Cq, C=O), 151.6 (Cq, $C(SCH_2)_2$), 143.1, 138.1, 137.3, and 129.6 (Cq), 130.2, 128.7, 128.3, 127.7, and 126.3 (aromatic CH), 45.1 (CHCH$_3$), 38.7 and 37.3 (C(SCH$_2$)$_2$), 18.0 (CHCH$_3$). HRMS Calcd for $C_{19}H_{17}OClS_2$ $[M]^+$: 360.0409; Found: 360.0406.

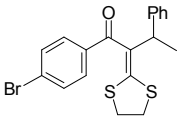


1-(2,4-Dichlorophenyl)-2-(1,3-dithiolan-2-ylidene)-3-phenylbutan-1-one (3i): Yield, 68%. Pale yellow solid, m. p.: 133-134 ^{o}C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 1.7 Hz, 1 H, aromatic CH), 7.23 and 7.15 (m each, 4:2 H, aromatic CH), 6.93 (d, J = 8.2 Hz, 1 H, aromatic CH), 4.22 (q, 1 H, CHCH$_3$), 3.34-3.19 (m, 4 H, $C(SCH_2)_2$), 1.58 (d, J = 7.2 Hz, 3 H, CHCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ

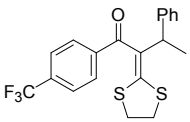
190.4 (Cq, C=O), 166.6 (Cq, *C*(SCH_2)$_2$), 142.6, 138.9, 135.2, 131.7, and 129.0 (Cq), 129.7, 128.4, 128.2, 127.7, 127.0, and 126.1 (aromatic CH), 41.8 (*C*HCH_3), 38.4 and 37.1 (C(S*C*H_2)$_2$), 16.0 (CH*C*H_3). HRMS Calcd for $C_{19}H_{16}OCl_2S_2$ $[M]^+$: 394.0020; Found: 394.0019.



2-(1,3-Dithiolan-2-ylidene)-1-(4-fluorophenyl)-3-phenylbutan-1-one (3j): Yield, 66%. Pale yellow solid, m. p.: 119-120 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.64, 7.26, and 7.02 (t each, 2:2:2 H, aromatic CH), 7.35 (d, *J* = 7.3 Hz, 2 H, aromatic CH), 7.17 (m, 1 H, aromatic CH), 4.26 (q, 1 H, C*H*CH_3), 3.27 (m, 4 H, C(SCH_2)$_2$), 1.62 (d, *J* = 7.0 Hz, 3 H, CHC*H*$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 194.4 (Cq, C=O), 165.1 (d, *J* = 252 Hz, Cq, *i*-C of C_6H_4F), 149.9 (Cq, *C*(SCH_2)$_2$), 143.1 and 129.7 (Cq each), 134.9 (d, *J* = 2.8 Hz, Cq, *p*-C of C_6H_4F), 131.4 (d, *J* = 9.0 Hz, CH, *m*-C of C_6H_4F), 128.2, 127.7, and 126.3 (aromatic CH), 115.5 (d, *J* = 21.8 Hz, CH, *o*-C of C_6H_4F), 45.3 (*C*HCH$_3$), 38.7 and 37.2 (C(S*C*H_2)$_2$), 18.1 (CH*C*H_3). HRMS Calcd for $C_{19}H_{17}OFS_2$ $[M]^+$: 344.0705; Found: 344.0713.

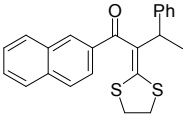


1-(4-Bromophenyl)-2-(1,3-dithiolan-2-ylidene)-3-phenylbutan-1-one (3k): Yield, 80%. Pale yellow solid, m. p.: 90-91 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (m, 4 H, aromatic CH), 7.33 (d, *J* = 7.6 Hz, 2 H, aromatic CH), 7.26 and 7.17 (t each, 2:1 H, aromatic CH), 4.27 (q, 1 H, C*H*CH_3), 3.24 (m, 4 H, C(SCH_2)$_2$), 1.62 (d, *J* = 7.2 Hz, 3 H, CHC*H*$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 194.4 (Cq, C=O), 152.0 (Cq, *C*(SCH_2)$_2$), 143.0, 137.6, 129.3, and 126.6 (Cq), 131.5, 130.2, 128.2, 127.6, and 126.2 (aromatic CH), 44.9 (*C*HCH$_3$), 38.6 and 37.1 (C(S*C*H_2)$_2$), 17.9 (CH*C*H_3). HRMS Calcd for $C_{19}H_{17}OBrS_2$ $[M]^+$: 403.9904; Found: 403.9910.

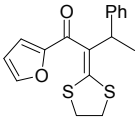


2-(1,3-Dithiolan-2-ylidene)-3-phenyl-1-(4-(trifluoromethyl)phenyl)butan-1-one (3l): Yield, 81%. Pale yellow solid, m. p.: 75-76 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.63-7.58 (m, 4 H, aromatic CH), 7.32 (d, *J* = 7.6 Hz), 7.26 (t), and 7.18 (t) (2:2:1 H, aromatic CH), 4.36 (q, 1 H, C*H*CH_3), 3.21 (m, 4 H, C(SCH_2)$_2$), 1.66 (d, *J* = 7.2 Hz, 3

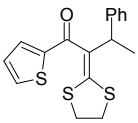
H, CHCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 193.7 (Cq, C=O), 156.2 (Cq, *C*$(SCH_2)_2$), 142.72, 142.66, and 128.9 (Cq each), 132.2 (q, *J* = 32.2 Hz, Cq, *i*-C of $CF_3C_6H_4$), 123.6 (q, *J* = 271 Hz, Cq, CF_3), 128.1, 128.0, 127.3, and 126.0 (aromatic CH), 125.0 (q, *J* = 3.5 Hz, *o*-CH of $CF_3C_6H_4$), 44.0 (*C*HCH$_3$), 38.4 and 36.8 (C(S*C*H$_2$)$_2$), 17.3 (CH*C*H$_3$). HRMS Calcd for $C_{20}H_{17}F_3OS_2$ $[M]^+$: 394.0673; Found: 394.0677.



2-(1,3-Dithiolan-2-ylidene)-1-(naphthalen-2-yl)-3-phenylbutan-1-one (3m): Yield, 77%. Pale yellow solid, m. p.: 105-107 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (br, 1 H, aromatic CH), 7.80 (m, 4 H, aromatic CH), 7.53 (m, 2 H, aromatic CH), 7.42 (d, *J* = 7.7 Hz, 2 H, aromatic CH), 7.28 and 7.18 (t each, 2:1 H, aromatic CH), 4.37 (q, 1 H, C*H*CH$_3$), 3.23 (m, 4 H, C$(SCH_2)_2$), 1.67 (d, *J* = 7.2 Hz, 3 H, CHC*H*$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 195.7 (Cq, C=O), 150.8 (Cq, *C*$(SCH_2)_2$), 143.4, 136.1, 135.1, 132.6, and 130.1 (Cq), 130.5, 129.4, 128.3, 128.2, 128.0, 127.8, 126.5, 126.3, and 124.8 (aromatic CH), 45.2 (*C*HCH$_3$), 38.7 and 37.2 (C(S*C*H$_2$)$_2$), 18.2 (CH*C*H$_3$). HRMS Calcd for $C_{23}H_{20}OS_2$ $[M]^+$: 376.0956; Found: 376.0958.

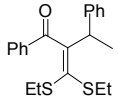


2-(1,3-Dithiolan-2-ylidene)-1-(furan-2-yl)-3-phenylbutan-1-one (3n): Yield, 55%. Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (s), 6.98 (d, *J* = 3.4 Hz), and 6.43 (m), (1:1:1 H, aromatic CH), 7.37 (d, *J* = 7.7 Hz), 7.27 (t), and 7.18 (t) (2:2:1 H, aromatic CH), 4.50 (q, 1 H, C*H*CH$_3$), 3.25 (m, 4 H, C$(SCH_2)_2$), 1.67 (d, *J* = 7.2 Hz, 3 H, CHC*H*$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 181.7 (Cq, C=O), 152.8 (Cq, *C*$(SCH_2)_2$), 143.2 and 129.3 (Cq each), 146.0, 128.2, 127.8, 126.2, 118.8, and 112.1 (aromatic CH), 43.2 (*C*HCH$_3$), 37.9 and 37.5 (C(S*C*H$_2$)$_2$), 17.4 (CH*C*H$_3$). HRMS Calcd for $C_{17}H_{16}O_2S_2$ $[M]^+$: 316.0592; Found: 316.0596.

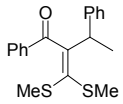


2-(1,3-Dithiolan-2-ylidene)-3-phenyl-1-(thiophen-2-yl)butan-1-one (3o): Yield, 68%. Pale yellow solid, m. p.: 93-95 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 4.9 and 0.7 Hz), 7.44 (dd, *J* = 3.7 and 0.8 Hz), and 7.00 (dd, *J* = 4.7and 4.0 Hz) (1:1:1

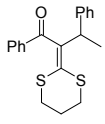
H, aromatic CH), 7.40 (d, J = 7.5 Hz), 7.27 (t), and 7.18 (t) (2:2:1 H, CH of Ph), 4.30 (q, 1 H, C*H*CH_3), 3.35-3.20 (m, 4 H, $C(SCH_2)_2$), 1.63 (d, J = 7.2 Hz, 3 H, CHC*H*$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 187.7 (Cq, C=O), 147.4 (Cq, *C*$(SCH_2)_2$), 144.4, 143.2, and 130.2 (Cq), 133.9, 133.8, 128.3, 127.84, 127.81, and 126.4 (aromatic CH), 45.3 (*C*HCH$_3$), 38.4 and 37.5 (C(S*C*H$_2$)$_2$), 18.5 (CH*C*H$_3$). HRMS Calcd for $C_{17}H_{16}OS_3$ $[M]^+$: 332.0363; Found: 332.0365.



2-(Bis(ethylthio)methylene)-1,3-diphenylbutan-1-one (3p): Yield, 55%. Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.6 Hz, 2 H, aromatic CH), 7.42 (t, 1 H, aromatic CH), 7.28 (m, 4 H, aromatic CH), 7.17 and 7.08 (t each, 2:1 H, aromatic CH), 4.82 (q, 1 H, C*H*CH_3), 2.84 and 2.60 (m each, 2:2 H, 2×SC*H*$_2$CH$_3$), 1.51 (d, J = 7.3 Hz, 3 H, CHC*H*$_3$), 1.32 and 0.99 (t each, 3:3 H, 2×SCH$_2$C*H*$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 196.5 (Cq, C=O), 153.1 (Cq, *C*$(SCH_2CH_3)_2$), 143.0, 137.7, and 130.5 (Cq each), 132.6, 129.2, 128.3, 128.2, 128.1, and 126.5 (aromatic CH), 43.8 (*C*HCH$_3$), 28.2 and 27.2 (S*C*H$_2$CH$_3$), 19.8 (CH*C*H$_3$), 15.6 and 14.2 (SCH$_2$*C*H$_3$). HRMS Calcd for $C_{21}H_{24}OS_2$ $[M]^+$: 356.1269; Found: 356.1265.

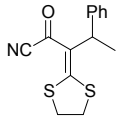


2-(Bis(methylthio)methylene)-1,3-diphenylbutan-1-one (3q): Yield, 58%. White solid, m. p.: 62-64 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.6 Hz, 2 H, aromatic CH), 7.42 (t, 1 H, aromatic CH), 7.26 (m, 4 H, aromatic CH), 7.13 (t each, 2:1 H, aromatic CH), 4.76 (q, 1 H, C*H*CH_3), 2.33 and 2.02 (s each, 3:3 H, 2×SCH$_3$), 1.51 (d, J = 7.3 Hz, 3 H, CHC*H*$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 196.0 (Cq, C=O), 150.9 (Cq, *C*SCH$_3$), 142.8, 137.6, and 133.3 (Cq), 132.6, 129.0, 128.3, 128.2, 128.1, and 126.5 (aromatic CH), 43.8 (*C*HCH$_3$), 19.4 (CH*C*H$_3$), 17.0 and 16.4 (CH$_3$). HRMS Calcd for $C_{19}H_{20}OS_2$ $[M]^+$: 328.0956; Found: 328.0954.

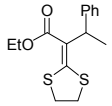


2-(1,3-Dithian-2-ylidene)-1,3-diphenylbutan-1-one (3r): Yield, 23%. Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.7 Hz, 2 H, aromatic CH), 7.45 (t, 1 H, aromatic CH), 7.32 (m, 4 H, aromatic CH), 7.19 and 7.10 (t each, 2:1 H, aromatic CH), 4.51 (q, 1 H, C*H*CH_3), 3.02 (m) and 2.72 (t) (2:2 H,

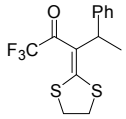
C(SCH_2CH$_2$CH_2S)), 2.11 (m, 2 H, C(SCH$_2$CH_2CH$_2$S), 1.50 (d, J = 7.2 Hz, 3 H, CHCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.6 (Cq, C=O), 143.1, 142.8, 137.9, and 131.2 (Cq), 132.8, 129.2, 128.3, 128.2, 128.0, and 126.4 (aromatic CH), 42.6 (*C*HCH$_3$), 29.7 and 29.2 (C(S*C*H$_2$CH$_2$*C*H$_2$S)), 24.3 C(SCH$_2$*C*H$_2$CH$_2$S), 19.2 (CH*C*H$_3$). HRMS Calcd for $C_{20}H_{20}ONaS_2$ $[M+Na]^+$: 363.0853; Found: 363.0860.



2-(1,3-Dithiolan-2-ylidene)-3-phenylbutanenitrile (3s): Yield, 75%. White solid, m. p.: 73-75 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 and 7.25 (m each, 4:1 H, aromatic CH), 3.74 (q, 1 H, C*H*CH$_3$), 3.46 (m, 4 H, C(SCH$_2$)$_2$), 1.57 (d, J = 7.1 Hz, 3 H, CHCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.4 (Cq, *C*(SCH$_2$)$_2$), 142.8 and 118.1 (Cq), 102.0 (Cq, CN), 128.7, 127.1, and 127.0 (aromatic CH), 44.1 (*C*HCH$_3$), 39.4 and 38.2 (C(S*C*H$_2$)$_2$), 20.5 (CH*C*H$_3$). HRMS Calcd for $C_{13}H_{13}NS_2$ $[M]^+$: 247.0489; Found: 247.0489.

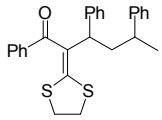


Ethyl 2-(1,3-dithiolan-2-ylidene)-3-phenylbutanoate (3t): Yield, 80%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (m, 4 H, aromatic CH), 7.19 (t, J = 6.8 Hz, 1 H, aromatic CH), 4.36 (q, 1 H, C*H*CH$_3$), 4.06 (q, 2 H, C*H*$_2$CH$_3$), 3.44-3.39 (m, 4 H, C(SCH$_2$)$_2$), 1.66 (d, J = 7.1 Hz, 3 H, CHCH_3), 1.07 (t, 3 H, CH$_2$CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.2 (Cq, C=O), 159.3 (*C*(SCH$_2$)$_2$), 144.1 and 121.3 (Cq), 127.8, 127.1, and 125.7 (aromatic CH), 60.1 (*C*H$_2$CH$_3$), 43.7 (*C*HCH$_3$), 38.9 and 36.5 (C(S*C*H$_2$)$_2$), 16.7 (CH*C*H$_3$), 14.0 (COOCH$_2$*C*H$_3$). HRMS Calcd for $C_{15}H_{18}O_2NaS_2$ $[M]^+$: 317.0646; Found: 317.0652.

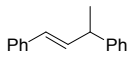


3-(1,3-Dithiolan-2-ylidene)-1,1,1-trifluoro-4-phenylpentan-2-one (3u): Yield, 33%. Pale yellow solid, m. p.: 104-106 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 4 H, aromatic CH), 7.26 (m, 1 H, aromatic CH), 4.61 (q, 1 H, C*H*CH$_3$), 3.25 (m, 4 H, CH$_2$CH$_2$), 1.76 (d, J = 7.2 Hz, 3 H, CHCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.5 (Cq, *C*(S(CH$_2$)$_2$)), 175.4 (q, J = 33 Hz, Cq, C=O), 141.8 (Cq, *i*-C of Ph), 124.0 (Cq), 128.2, 127.8, and 126.2 (aromatic CH), 117.9 (q, J = 289 Hz, Cq, CF_3), 37.7 and

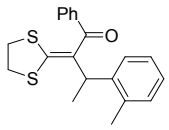
37.5 (CH_2CH_2), 37.08 (q, J = 2.9 Hz, CHCH$_3$), 14.7 (CHCH$_3$). HRMS Calcd for $C_{14}H_{13}F_3ONaS_2$ $[M+Na]^+$: 341.0258; Found: 341.0270.



2-(1,3-Dithiolan-2-ylidene)-1,3,5-triphenylhexan-1-one (4a): *Diastereomer I* – Pale yellow solid, m. p.: 128-130 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 7.3 Hz, 2 H, aromatic CH), 7.40 (t, 1 H, aromatic CH), 7.27, 7.19, and 7.11 (m each, 6:3:3 H, aromatic CH), 3.82 (dd, J = 9.6 and 5.8 Hz, 1 H, CHCH$_2$CHCH$_3$), 3.27-3.08 (m, 4 H, C(SCH$_2$)$_2$), 2.64 (m, 1 H, CH$_2$CHCH$_3$), 2.43 and 2.29 (m each, 1:1 H, CHCH_2CHCH$_3$), 1.24 (d, J = 6.9 Hz, 3 H, CH$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 196.4 (Cq, C=O), 146.9 (Cq, C(SCH$_2$)$_2$), 146.8, 141.5, 138.3, and 129.41 (Cq), 132.3, 129.36, 128.7, 128.4, 128.34, 128.25, 127.4, 126.5, and 126.1 (aromatic CH), 50.6 (CHCH$_2$CHCH$_3$), 41.8 (CH$_2C$HCH$_3$), 38.9 (CHCH$_2$CH), 37.5 and 37.1 (C(SCH$_2$)$_2$), 22.7 (CH$_3$). *Diastereomer II* – Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 7.2 Hz, 2 H, aromatic CH), 7.44 (t, 1 H, aromatic CH), 7.29 and 7.20 (m each, 7:5 H, aromatic CH), 4.05 (t, 1 H, CHCH$_2$CHCH$_3$), 3.29 (m, 4 H, C(SCH$_2$)$_2$), 2.78 (m, 1 H, CH$_2$CHCH$_3$), 2.40 (t, 2 H, CHCH_2CH), 1.28 (d, J = 6.9 Hz, 3 H, CH$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 196.0 (Cq, C=O), 150.2 (Cq, C(SCH$_2$)$_2$), 147.4, 142.1, 138.7, and 128.6 (Cq), 132.1, 129.2, 128.5, 128.32, 128.26, 127.3, 126.4, and 126.0 (aromatic CH), 50.3 (CHCH$_2$CHCH$_3$), 41.4 (CH$_2C$HCH$_3$), 38.9 (CHCH$_2$CH), 37.8 and 37.1 (C(SCH$_2$)$_2$), 22.6 (CH$_3$). HRMS Calcd for $C_{27}H_{26}OS_2$ $[M]^+$: 430.1425; Found: 430.1436.

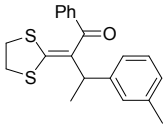


(*E*)-But-1-ene-1,3-diyldibenzene (4b):[9] Colorless liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (m, 3 H, aromatic CH), 7.30 and 7.22 (m each, 5:2 H, aromatic CH), 6.42 (m, 2 H, CH=CH), 3.66 (m, 1 H, CHCH$_3$), 1.49 (d, J = 7.0 Hz, 3 H, CHCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 145.8 and 137.7 (Cq), 135.4, 128.65, 128.62, 127.4, 127.2, 126.4, and 126.3 (CH), 42.7 (CHCH$_3$), 21.4 (CHCH$_3$).

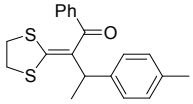


2-(1,3-Dithiolan-2-ylidene)-1-phenyl-3-o-tolylbutan-1-one (5a): Yield, 70%. Pale yellow solid, m. p.: 74-76 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.1 Hz,

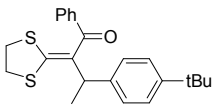
2 H, aromatic CH), 7.46 and 7.35 (t each, 1:3 H, aromatic CH), 7.07 (m, 3 H, aromatic CH), 4.26 (q, 1 H, C*H*CH_3), 3.36-3.21 (m, 4 H, C(SC*H*$_2$)$_2$), 2.42 (s, 3 H, CH_3), 1.64 (d, *J* = 7.2 Hz, 3 H, CHC*H*$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 196.2 (Cq, C=O), 147.2 (Cq, *C*(SCH$_2$)$_2$), 141.3, 138.7, 136.2, and 129.6 (Cq), 132.2, 129.9, 128.9, 128.3, 127.5, 126.3, and 126.0 (aromatic CH), 42.8 (*C*HCH$_3$), 39.0 and 37.2 (C(S*C*H$_2$)$_2$), 19.8 (CH_3), 18.7 (CH*C*H$_3$). HRMS Calcd for $C_{20}H_{20}OS_2$ $[M]^+$: 340.0956; Found: 340.0963.



2-(1,3-Dithiolan-2-ylidene)-1-phenyl-3-m-tolylbutan-1-one (5b): Yield, 70%. Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.2 Hz, 2 H, aromatic CH), 7.46 and 7.36 (t each, 1:2 H, aromatic CH), 7.16 and 6.99 (m each, 3:1 H, aromatic CH), 4.27 (q, 1 H, C*H*CH_3), 3.32-3.20 (m, 4 H, C(SC*H*$_2$)$_2$), 2.32 (s, 3 H, CH_3), 1.62 (d, *J* = 7.2 Hz, 3 H, CHC*H*$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 195.7 (Cq, C=O), 151.5 (Cq, *C*(SCH$_2$)$_2$), 143.2, 139.1, 137.6, and 130.0 (Cq), 131.7, 128.7, 128.5, 128.3, 128.0, 126.9, and 124.8 (aromatic CH), 44.7 (*C*HCH$_3$), 38.6 and 37.2 (C(S*C*H$_2$)$_2$), 21.6 (CH_3), 18.0 (CH*C*H$_3$). HRMS Calcd for $C_{20}H_{20}OS_2$ $[M]^+$: 340.0956; Found: 340.0951.

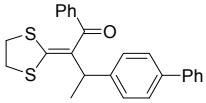


2-(1,3-Dithiolan-2-ylidene)-1-phenyl-3-p-tolylbutan-1-one (5c): Yield, 54%. Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (m), 7.46 (t), and 7.36 (t) (2:1:2 H, aromatic CH), 7.25 and 7.08 (d each, *J* = 7.8 and 7.9 Hz, 2:2 H, aromatic CH), 4.25 (q, 1 H, C*H*CH_3), 3.32-3.18 (m, 4 H, C(SC*H*$_2$)$_2$), 2.30 (s, 3 H, CH_3), 1.59 (d, *J* = 7.2 Hz, 3 H, CHC*H*$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 195.8 (Cq, C=O), 151.7 (Cq, *C*(SCH$_2$)$_2$), 140.3, 139.1, 135.7, and 130.1 (Cq), 131.8, 129.0, 128.8, 128.4, and 127.7 (aromatic CH), 44.4 (*C*HCH$_3$), 38.6 and 37.3 (C(S*C*H$_2$)$_2$), 21.1 (*C*H$_3$C$_6$H$_4$), 18.1 (CH*C*H$_3$). HRMS Calcd for $C_{20}H_{20}OS_2$ $[M]^+$: 340.0956; Found: 340.0954.

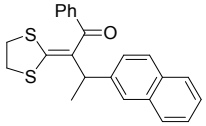


3-(4-*Tert*-butylphenyl)-2-(1,3-dithiolan-2-ylidene)-1-phenylbutan-1-one (5d): Yield, 49%. Pale yellow solid, m. p.: 67-69 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (m, 2 H, aromatic CH), 7.43 and 7.33 (t each, 1:2 H, aromatic CH), 7.26 (m, 4 H,

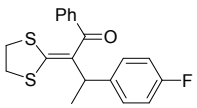
aromatic CH), 4.27 (q, 1 H, C*H*CH_3), 3.33-3.20 (m, 4 H, C(SCH_2)$_2$), 1.61 (d, *J* = 7.2 Hz, 3 H, CHC*H*$_3$), 1.30 (s, 9 H, *t*Bu). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 195.9 (Cq, C=O), 151.3 (Cq, *C*(SCH_2)$_2$), 148.9, 140.1, 139.1, and 130.1 (Cq), 131.6, 128.6, 128.2, 127.3, and 125.0 (aromatic CH), 44.4 (*C*HCH$_3$), 38.6 and 37.1 (C(S*C*H$_2$)$_2$), 34.4 (Cq, *C*(CH$_3$)$_3$), 31.4 (C(*C*H$_3$)$_3$), 17.8 (CH*C*H$_3$). HRMS Calcd for $C_{23}H_{26}OS_2$ $[M]^+$: 382.1425; Found: 382.1426.



3-(Biphenyl-4-yl)-2-(1,3-dithiolan-2-ylidene)-1-phenylbutan-1-one (5e): Yield, 52%. Pale yellow solid, m. p.: 97-99 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.65, 7.60 and 7.53 (d each, *J* = 7.4, 7.4, and 8.2 Hz, 2:2:2 H, aromatic CH), 7.40 (m, 8 H, aromatic CH), 4.35 (q, 1 H, C*H*CH_3), 3.25 (m, 4 H, C(SCH_2)$_2$), 1.67 (d, *J* = 7.2 Hz, 3 H, CHC*H*$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 195.8 (Cq, C=O), 151.9 (Cq, *C*(SCH_2)$_2$), 142.5, 141.0, 139.1, 139.0, and 129.8 (Cq), 131.8, 128.76, 128.75, 128.4, 128.2, 127.1, 127.0, and 126.9 (aromatic CH), 44.6 (*C*HCH$_3$), 38.2 and 37.2 (C(S*C*H$_2$)$_2$), 18.1 (CH*C*H$_3$). HRMS Calcd for $C_{25}H_{22}OS_2$ $[M]^+$: 402.1112; Found: 402.1120.

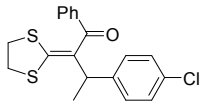


2-(1,3-Dithiolan-2-ylidene)-3-(naphthalen-2-yl)-1-phenylbutan-1-one (5f): Yield, 53%. Pale yellow solid, m. p.: 107-108 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (m, 4 H, aromatic CH), 7.66 (m, 2 H, aromatic CH), 7.55 (d, *J* = 8.5 Hz, 1 H, aromatic CH), 7.44 (m, 3 H, aromatic CH), 7.35 (t, 2 H, aromatic CH), 4.47 (q, 1 H, C*H*CH_3), 3.21 (m, 4 H, C(SCH_2)$_2$), 1.75 (d, 3 H, CHC*H*$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 195.7 (Cq, C=O), 152.8 (Cq, *C*(SCH_2)$_2$), 140.8, 139.1, 133.4, 132.2, and 129.6 (Cq), 131.8, 128.6, 128.4, 128.0, 127.8, 127.6, 126.8, 126.0, 125.8, and 125.4 (aromatic CH), 44.8 (*C*HCH$_3$), 38.6 and 37.2 (C(S*C*H$_2$)$_2$), 18.0 (CH*C*H$_3$). HRMS Calcd for $C_{23}H_{20}OS_2$ $[M]^+$: 376.0956; Found: 376.0963.

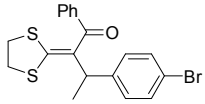


2-(1,3-Dithiolan-2-ylidene)-3-(4-fluorophenyl)-1-phenylbutan-1-one (5g): Yield, 73%. Pale yellow solid, m. p.: 88-90 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.61-7.59 (m, 2 H, aromatic CH), 7.47 (t, 1 H, aromatic CH), 7.34 and 6.93 (m each, 4:2 H,

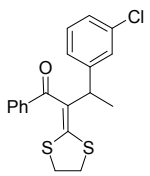
aromatic CH), 4.23 (q, 1 H, C*H*CH_3), 3.33-3.19 (m, 4 H, C($SCH_2)_2$), 1.59 (d, *J* = 7.2 Hz, 3 H, CHC*H*$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 195.7 (Cq, C=O), 161.3 (Cq and d, *J* = 243 Hz, C-F), 151.4 (Cq, *C*($SCH_2)_2$), 139.0 (d, *J* = 3 Hz, Cq, *p*-C of FC_6H_4), 138.9 and 129.6 (Cq), 131.9, 128.7, and 128.4 (aromatic CH), 129.2 (d, *J* = 7.8 Hz, *m*-CH of F-C_6H_4), 114.8 (d, *J* = 21 Hz, *o*-CH of F-C_6H_4), 44.3 (*C*HCH_3), 38.7 and 37.2 (C(S*C*$H_2)_2$), 18.3 (CH*C*H_3). HRMS Calcd for $C_{19}H_{17}FOS_2$ $[M]^+$: 344.0705; Found: 344.0709.



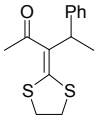
3-(4-Chlorophenyl)-2-(1,3-dithiolan-2-ylidene)-1-phenylbutan-1-one (5h): Yield, 69%. Pale yellow solid, m. p.: 73-74 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.62-7.60 (m, 2 H, aromatic CH), 7.47 and 7.37 (t each, 1:2 H, aromatic CH), 7.30 and 7.22 (d each, *J* = 8.4 and 8.5 Hz, 2:2 H, aromatic CH), 4.23 (q, 1 H, C*H*CH_3), 3.32-3.18 (m, 4 H, C($SCH_2)_2$), 1.58 (d, *J* = 7.2 Hz, 3 H, CHC*H*$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 195.6 (Cq, C=O), 152.2 (Cq, *C*($SCH_2)_2$), 142.0, 138.9, 131.9, and 129.3 (Cq), 132.0, 129.2, 128.7, 128.5, and 128.3 (aromatic CH), 44.3 (*C*HCH_3), 38.8 and 37.2 (C(S*C*$H_2)_2$), 18.1 (CH*C*H_3). HRMS Calcd for $C_{19}H_{17}OClS_2$ $[M]^+$: 360.0413; Found: 360.0409.



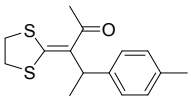
3-(4-Bromophenyl)-2-(1,3-dithiolan-2-ylidene)-1-phenylbutan-1-one (5i): Yield, 51%. Pale yellow solid, m. p.: 84-86 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.62-7.60 (m, 2 H, aromatic CH), 7.47 (t, 1 H, aromatic CH), 7.38 (m, 4 H, aromatic CH), 7.24 (d, *J* = 8.4 Hz, 2 H, aromatic CH), 4.20 (q, 1 H, C*H*CH_3), 3.25 (m, 4 H, C($SCH_2)_2$), 1.57 (d, *J* = 7.2 Hz, 3 H, CHC*H*$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 195.5 (Cq, C=O), 152.3 (Cq, *C*($SCH_2)_2$), 142.5, 138.9, 129.2, and 120.0 (Cq), 132.0, 131.2, 129.6, 128.7, and 128.5 (aromatic CH), 44.4 (*C*HCH_3), 38.8 and 37.2 (C(S*C*$H_2)_2$), 18.1 (CH*C*H_3). HRMS Calcd for $C_{19}H_{17}BrOS_2$ $[M]^+$: 403.9904; Found: 403.9907.



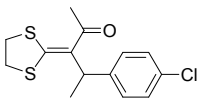
3-(3-Chlorophenyl)-2-(1,3-dithiolan-2-ylidene)-1-phenylbutan-1-one (5j): Yield, 22%. Yellow oil. 1H NMR (400 MHz, CDCl3) δ 7.60 (m, 2 H, aromatic CH), 7.47 (t, 1 H, aromatic CH), 7.34 (m, 3 H, aromatic CH),7.23 (d, *J* = 7.5 Hz, 1 H, aromatic CH), 7.16 (m, 2 H, aromatic CH), 4.24 (q, 1 H, C*H*CH_3), 3.26 (m, 4 H, C$(SCH_2)_2$), 1.58 (d, *J* = 7.2 Hz, 3 H, CHC*H*$_3$). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$) δ 195.5 (Cq, C=O), 152.8 (Cq, *C*$(SCH_2)_2$), 145.6, 139.0, 134.1, and 129.1 (Cq each), 131.9, 129.4, 128.7, 128.5, 128.0, 126.4, and 126.1 (aromatic CH), 44.6 (*C*HCH_3), 38.9 and 37.3 (C(S*C*$H_2)_2$), 17.9 ($CHCH_3$). HRMS Calcd for $C_{19}H_{17}OClS_2$ $[M]^+$: 360.0409; Found: 360.0410.



3-(1,3-Dithiolan-2-ylidene)-4-phenylpentan-2-one (6a):[6] Yield, 81%. Pale yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 (m, 5 H, aromatic CH), 4.53 (q, 1 H, C*H*CH_3), 3.35 (m, 4 H, C$(SCH_2)_2$), 1.88 (s, 3 H, $COCH_3$), 1.67 (d, *J* = 7.3 Hz, 3 H, CHC*H*$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 195.3 (Cq, C=O), 161.9 (Cq, *C*$(SCH_2)_2$), 143.3 and 129.7 (Cq), 128.5, 126.9, and 126.3 (aromatic CH), 42.7 (*C*HCH_3), 39.0 and 35.9 (C(S*C*$H_2)_2$), 28.7 (CO*C*H_3), 16.4 (CH*C*H_3).

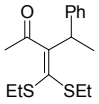


3-(1,3-Dithiolan-2-ylidene)-4-p-tolylpentan-2-one (6b): Yield, 52%. Pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.15 and 7.11 (d each, *J* = 8.2 Hz, 2:2 H, aromatic CH), 4.48 (q, 1 H, C*H*CH_3), 3.33 (m, 4 H, C(SC*H*$_2)_2$), 2.32 (s, 3 H, CH_3), 1.88 (s, 3 H, CH_3CO), 1.65 (d, *J* = 7.3 Hz, 3 H, CHC*H*$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 195.2 (Cq, C=O), 161.6 (Cq, *C*$(SCH_2)_2$), 140.1, 135.6, and 129.7 (Cq), 129.1 and 126.7 (aromatic CH), 42.2 (C*H*CH_3), 38.8 and 35.8 (C(S*C*$H_2)_2$), 28.6 (*C*H_3CO), 21.0 (CH_3), 16.4 (CH*C*H_3). HRMS Calcd for $C_{15}H_{18}OS_2$ $[M]^+$: 278.0799; Found: 278.0804.

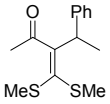


4-(4-Chlorophenyl)-3-(1,3-dithiolan-2-ylidene)pentan-2-one (6c):[6] Yield, 58%. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.27 and 7.19 (d each, *J* = 8.2 Hz, 2:2 H, aromatic CH), 4.46 (q, 1 H, C*H*CH_3), 3.39-3.30 (m, 4 H, C$(SCH_2)_2$), 1.90 (s, 3 H, CH_3CO), 1.65 (d, *J* = 7.2 Hz, 3 H, CHC*H*$_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 194.9 (Cq, C=O), 162.4 (Cq, *C*$(SCH_2)_2$), 141.9, 132.1, and 129.2 (Cq), 128.6 and

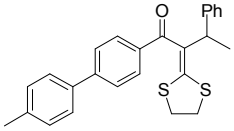
128.4 (aromatic CH), 42.1 (*C*HCH$_3$), 39.0 and 36.0 (C(S*C*H$_2$)$_2$), 28.7 (CH$_3$CO), 16.5 (CH*C*H$_3$).



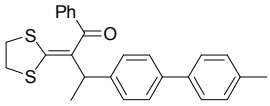
3-(Bis(ethylthio)methylene)-4-phenylpentan-2-one (6d): Yield, 36%. Colorless liquid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.28 (m) and 7.20 (t) (4:1 H, aromatic CH), 4.74 (q, 1 H, C*H*CH$_3$), 2.88-2.65 (m, 4 H, 2×SCH$_2$), 1.83 (s, 3 H, COCH$_3$), 1.49 (d, *J* = 7.2 Hz, 3 H, CHC*H*$_3$), 1.27 and 1.21 (t each, 3:3 H, 2×SCH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 204.7 (Cq, C=O), 157.7 (Cq, *C*SCH$_2$CH$_3$), 142.2 (Cq), 128.6, 127.8, and 126.8 (aromatic CH), 42.6 (*C*HCH$_3$), 32.5 (CO*C*H$_3$), 27.7 and 27.1 (S*C*H$_2$), 18.2 (CH*C*H$_3$), 15.3 and 14.5 (SCH$_2$*C*H$_3$). HRMS Calcd for C$_{16}$H$_{22}$ONaS$_2$ [M+Na]$^+$: 317.1010; Found: 317.1012.



3-(Bis(methylthio)methyl)-4-phenylpentan-2-one (6e): Yield, 32%. White solid, m. p.: 66-68 ^{o}C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.25 (m, 5 H, aromatic CH), 4.64 (q, 1 H, C*H*CH$_3$), 2.33 and 2.25 (s each, 3:3 H, 2×SCH$_3$), 1.86 (s, 3 H, CH$_3$CO), 1.49 (d, *J* = 7.2 Hz, 3 H, CHC*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 204.4 (Cq, C=O), 155.3 (Cq, *C*SCH$_3$), 142.1 and 130.3 (Cq), 128.6, 127.8, and 126.8 (aromatic CH), 42.7 (*C*HCH$_3$), 32.2 (*C*H$_3$CO), 18.2 (CH*C*H$_3$), 17.4 and 16.5 (SCH$_3$). HRMS Calcd for C$_{14}$H$_{18}$OS$_2$ [M]$^+$: 266.0799; Found: 266.0806.

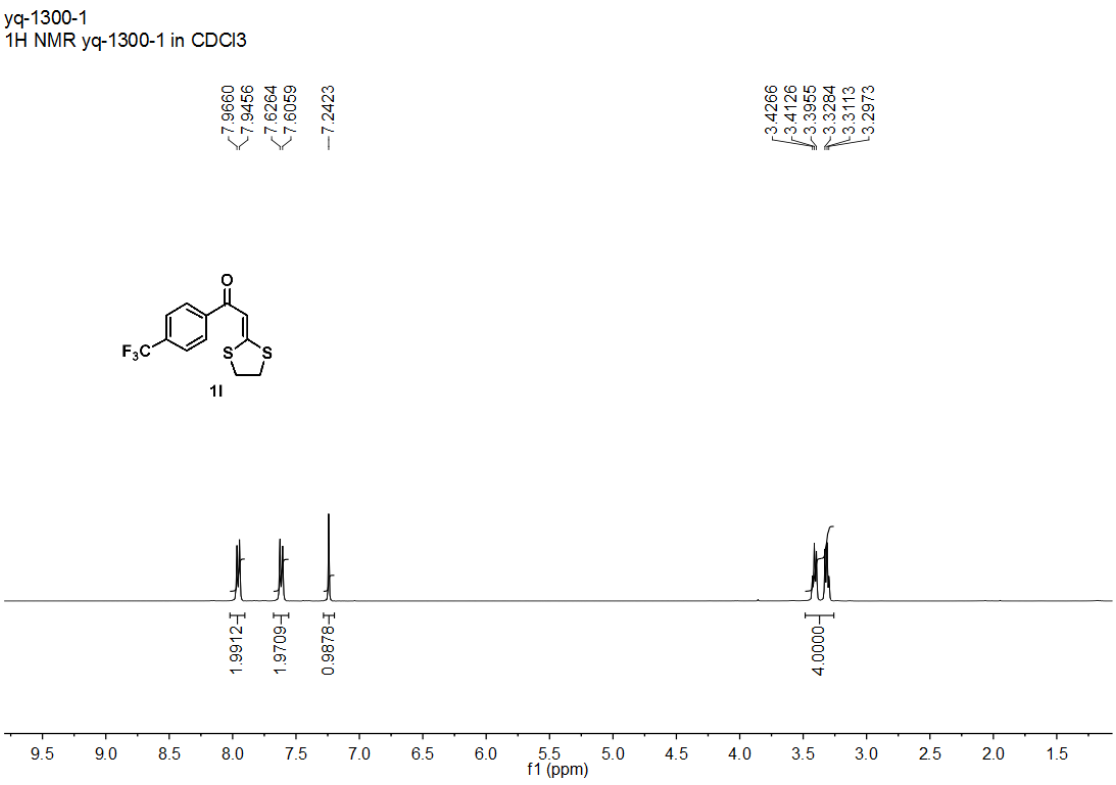


2-(1,3-Dithiolan-2-ylidene)-1-(4'-methylbiphenyl-4-yl)-3-phenylbutan-1-one (7a): Yield, 64%. Pale yellow solid, m. p.: 152-154 ^{o}C. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.72 (m, 2 H, aromatic CH), 7.59, 7.52, and 7.41 (d each, *J* = 8.3, 7.9, and 7.5 Hz, 2:2:2 H, aromatic CH), 7.28 (m, 4 H, aromatic CH), 7.19 (t, 1 H, aromatic CH), 4.32 (q, 1 H, C*H*CH$_3$), 3.26 (m, 4 H, C(SCH$_2$)$_2$), 2.41 (s, 3 H, CH$_3$), 1.66 (d, *J* = 7.2 Hz, 3 H, CHC*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ 195.5 (C=O), 150.2 (Cq, *C*(SCH$_2$)$_2$), 144.6, 143.4, 138.0, 137.2, and 130.0 (Cq), 129.7, 129.5, 128.3, 127.9, 127.1, 126.8, and 126.3 (aromatic CH), 45.1 (*C*HCH$_3$), 38.7 and 37.3 (C(S*C*H$_2$)$_2$), 21.3 (CH$_3$), 18.2 (CH*C*H$_3$). HRMS Calcd for C$_{26}$H$_{24}$ONaS$_2$ [M+Na]$^+$: 439.1166; Found: 439.1156.

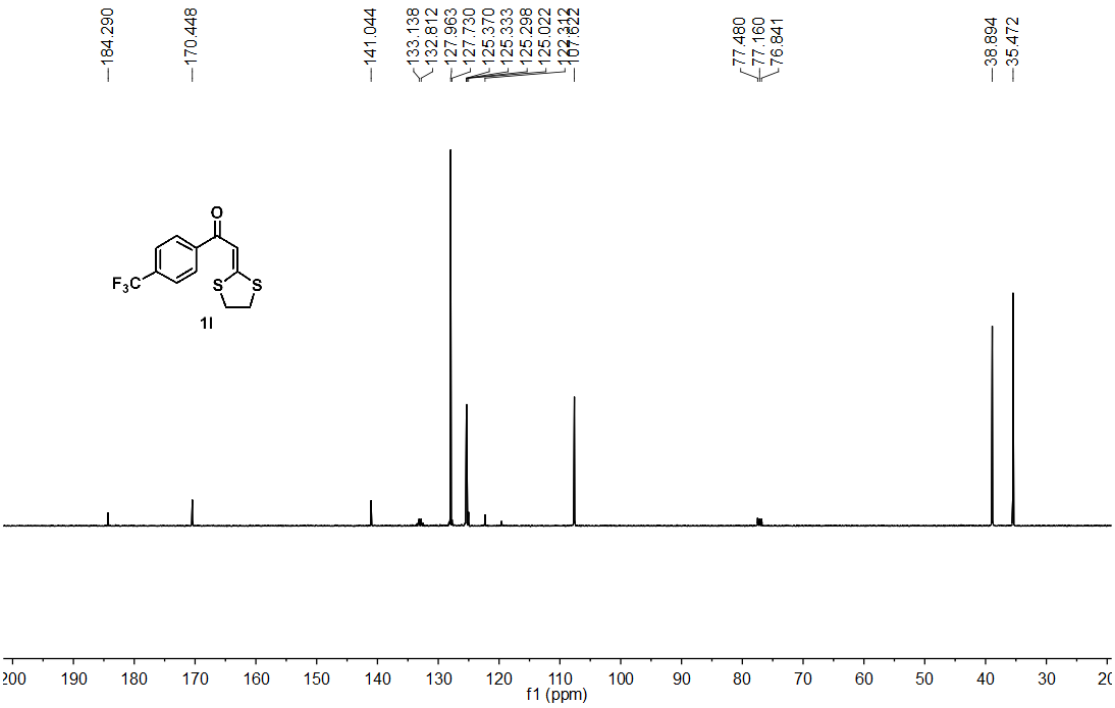


2-(1,3-Dithiolan-2-ylidene)-3-(4'-methylbiphenyl-4-yl)-1-phenylbutan-1-one (7b): Yield, 56%. Pale yellow solid, m. p.: 136-138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.3 Hz, 2 H, aromatic CH), 7.47 (m, 7 H, aromatic CH), 7.37 (t, 2 H, aromatic CH), 7.25 (d, *J* = 7.9 Hz, 2 H, aromatic CH), 4.35 (q, 1 H, C*H*CH_3), 3.28 (m, 4 H, C$(SCH_2)_2$), 2.41 (s, 3 H, CH_3), 1.67 (d, *J* = 7.2 Hz, 3 H, CHC*H*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.8 (Cq, C=O), 152.0 (*C*$(SCH_2)_2$), 142.2, 139.1, 138.9, 138.2, 136.8, and 129.8 (Cq), 131.8, 129.5, 128.7, 128.4, 128.1, 126.9, and 126.7 (aromatic CH), 44.6 (*C*HCH_3), 38.7 and 37.2 (C(S*C*$H_2)_2$), 21.2 (CH_3), 18.0 (CH*C*H_3). HRMS Calcd for $C_{26}H_{24}ONaS_2$ $[M+Na]^+$: 439.1166; Found: 439.1154.

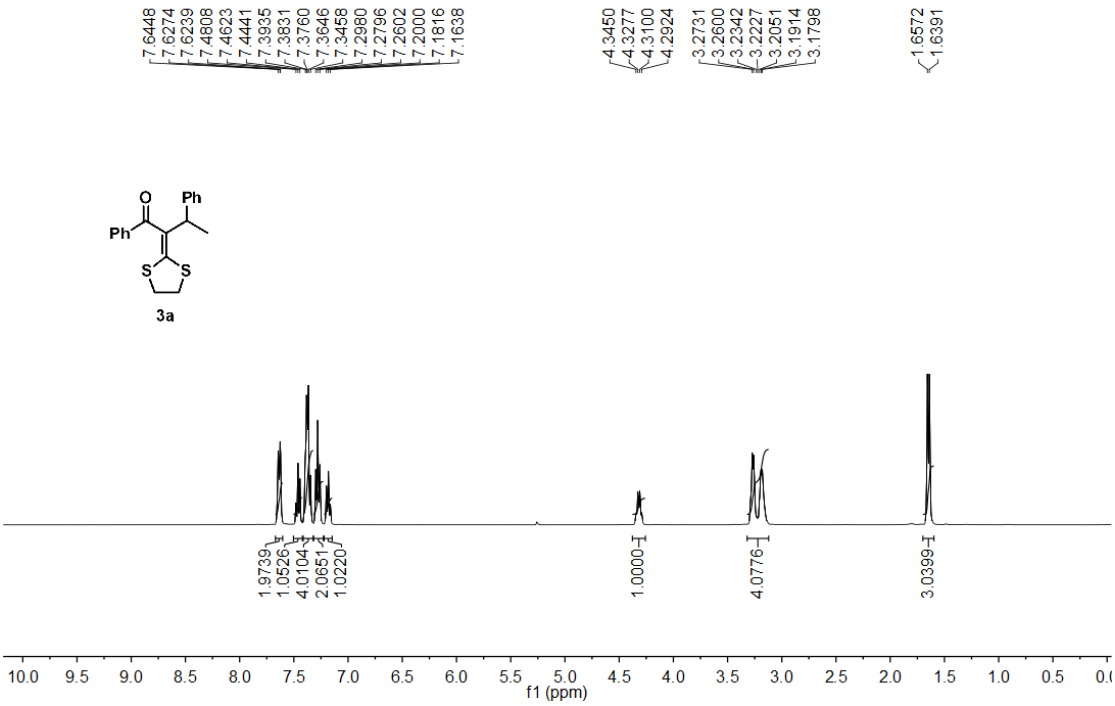
4. Copies of NMR spectra



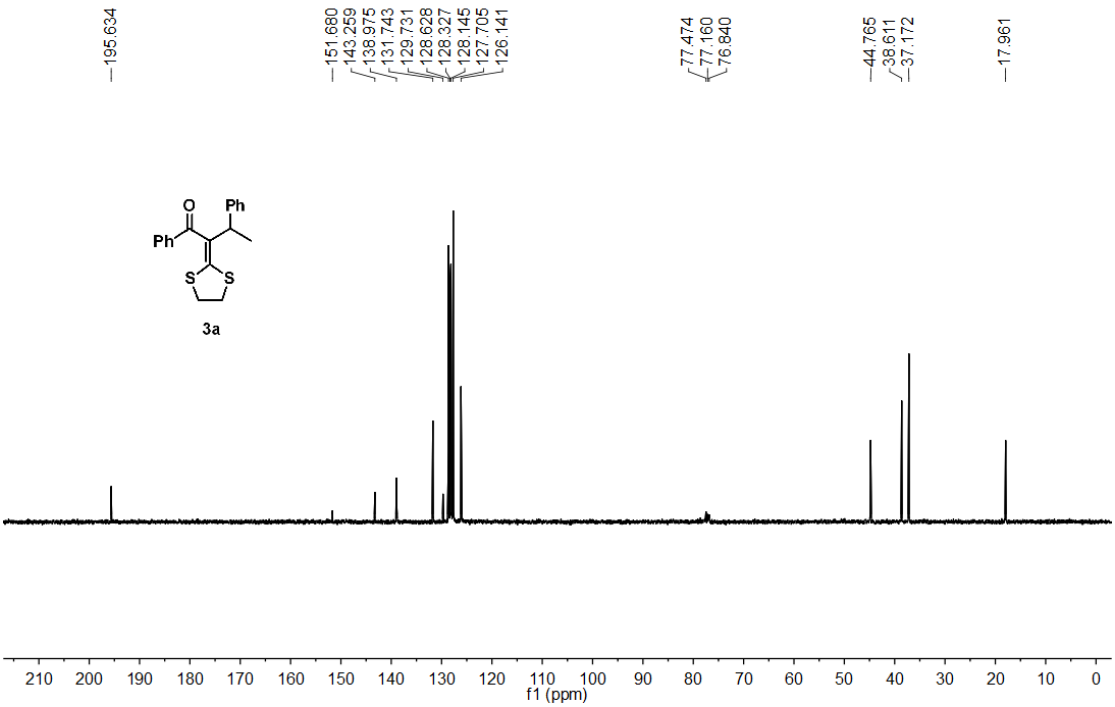
yq-1300
13C NMR yq-1300 CDCl3



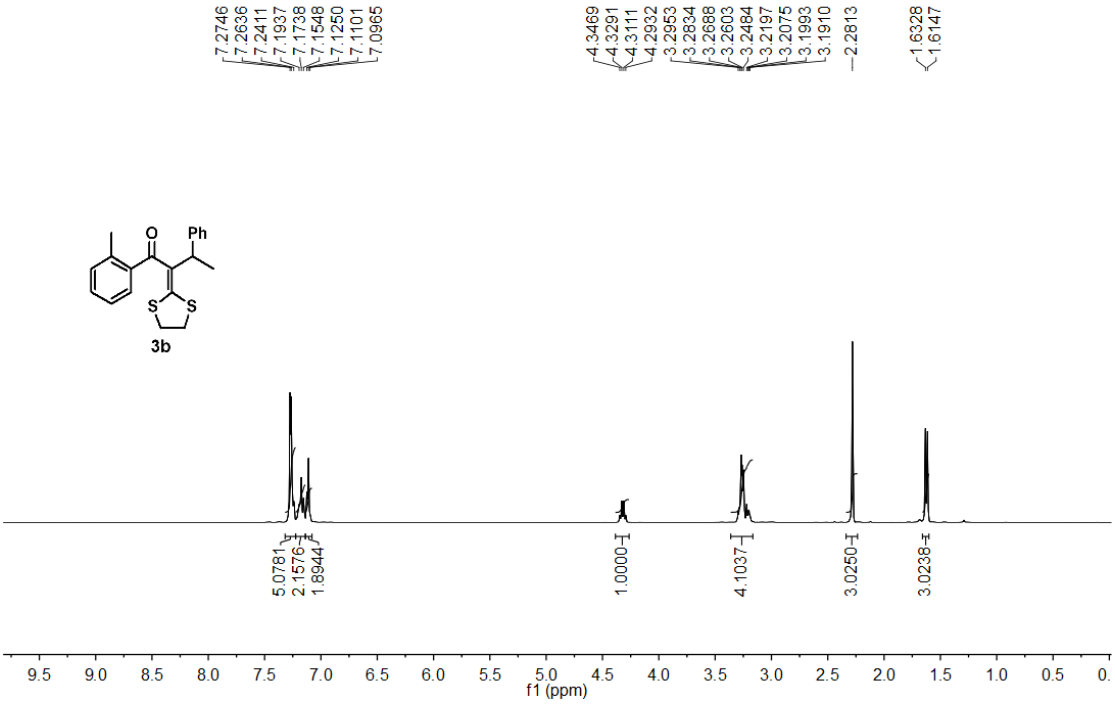
yq-130625
1H NMR yq-130625 in CDCl3



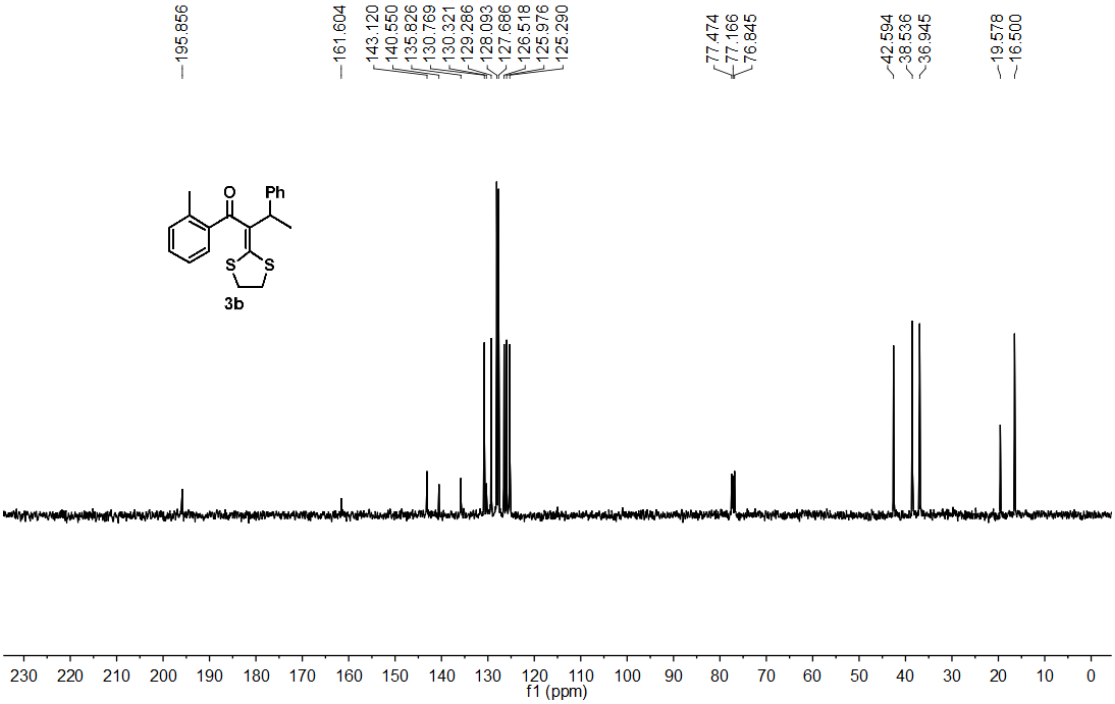
yq-130625
13C NMR yq-130625 CDCl3



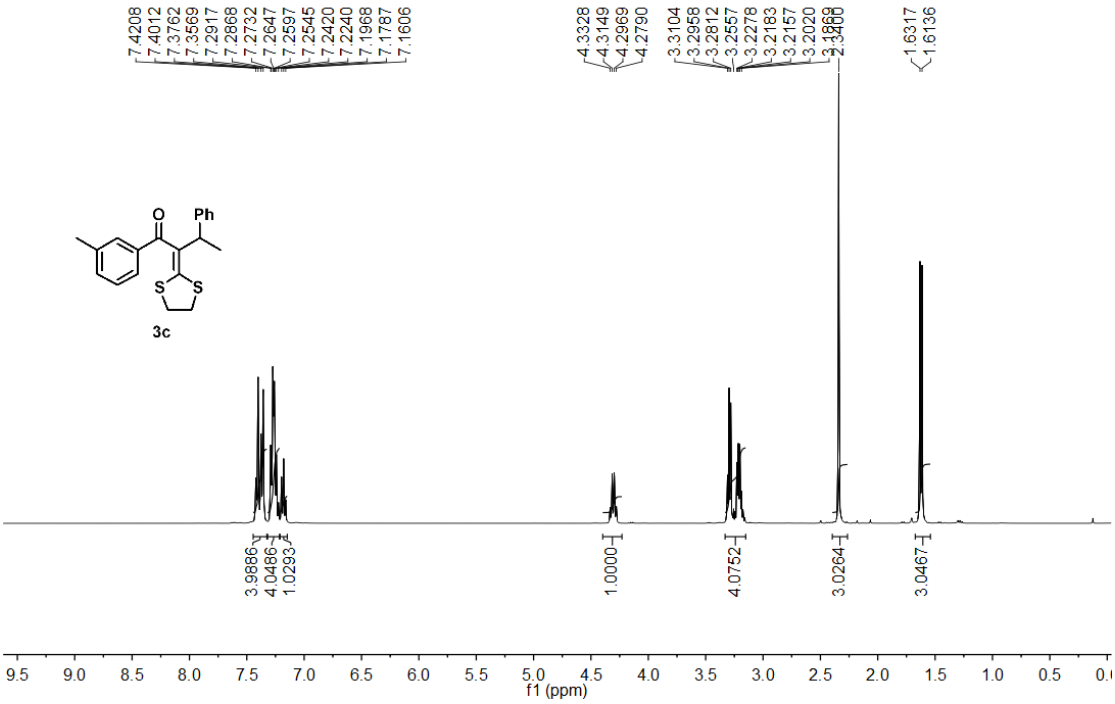
yq-1312-2
1H NMR yq-1312-2 in CDCl3



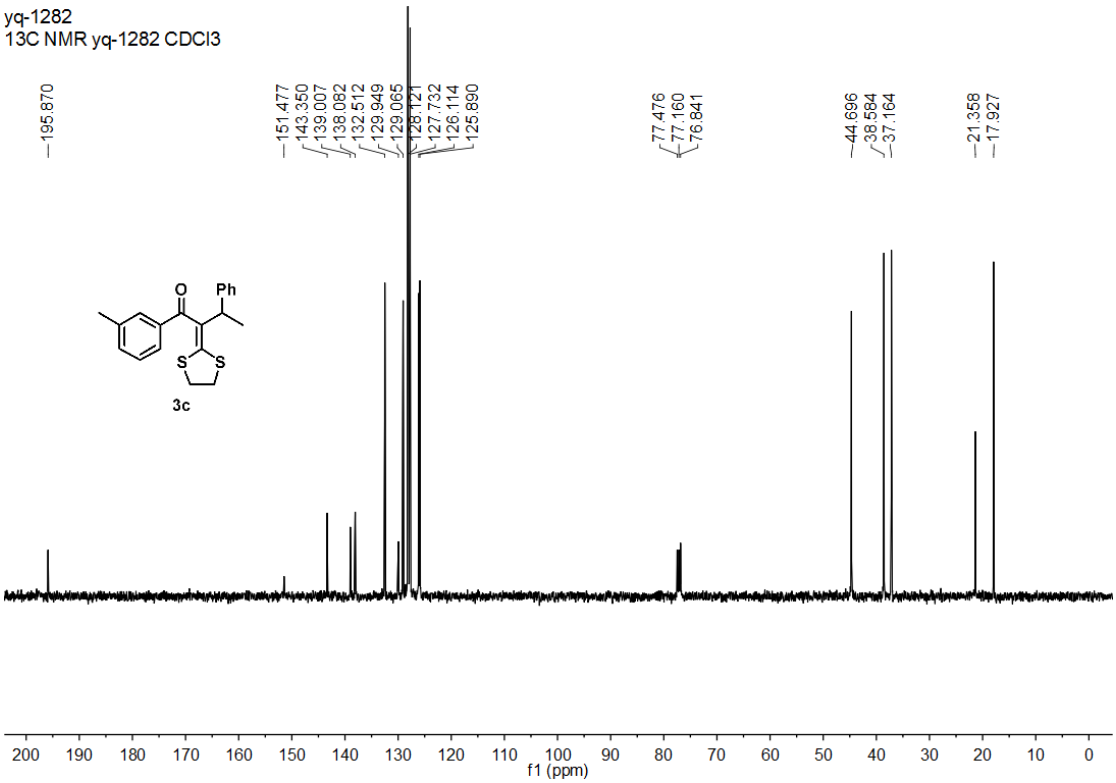
yq-1312-2
13C NMR yq-1312-2 CDCl3



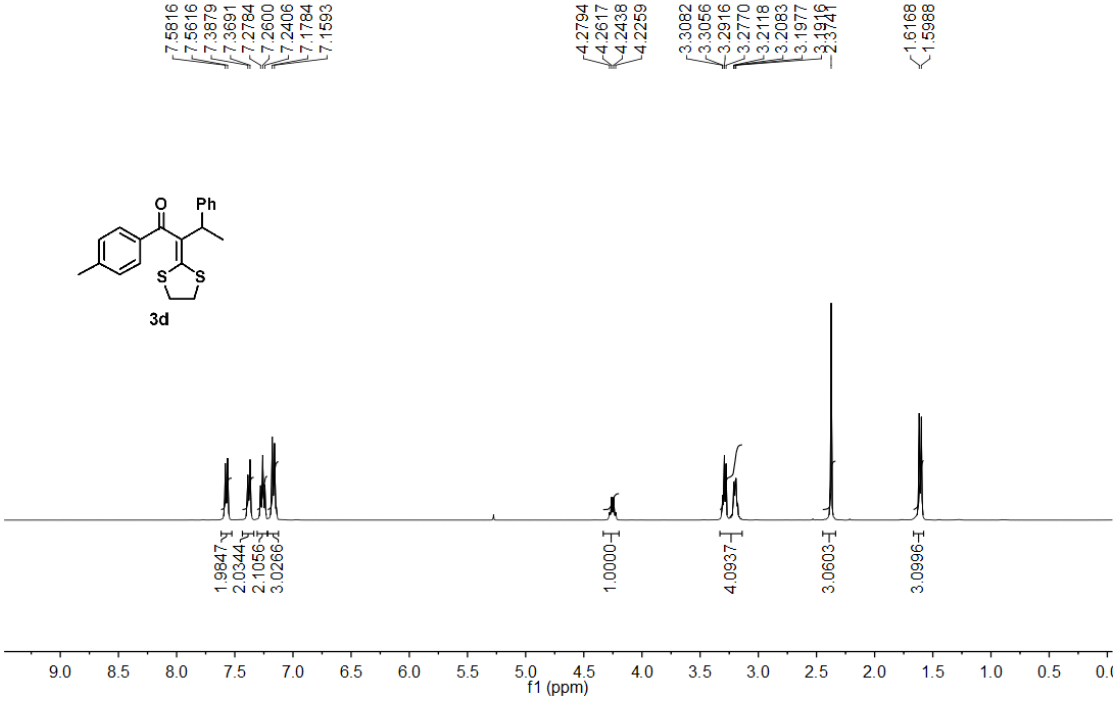
yq-1282
1H NMR yq-1282 in CDCl3



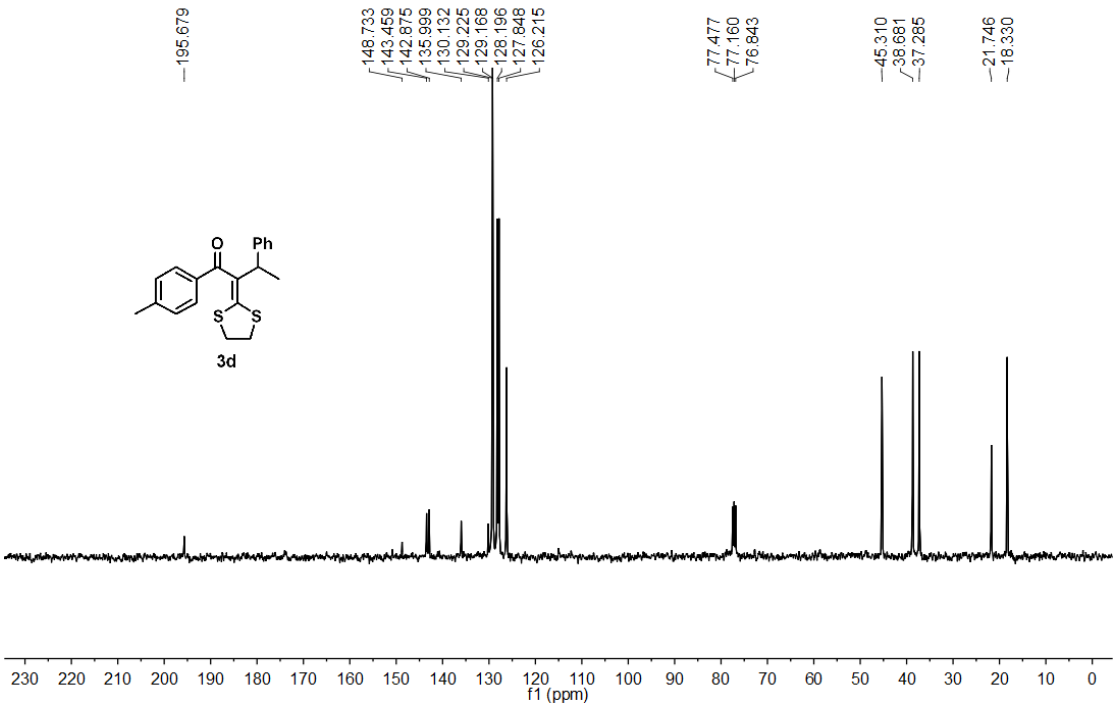
yq-1282
13C NMR yq-1282 CDCl3



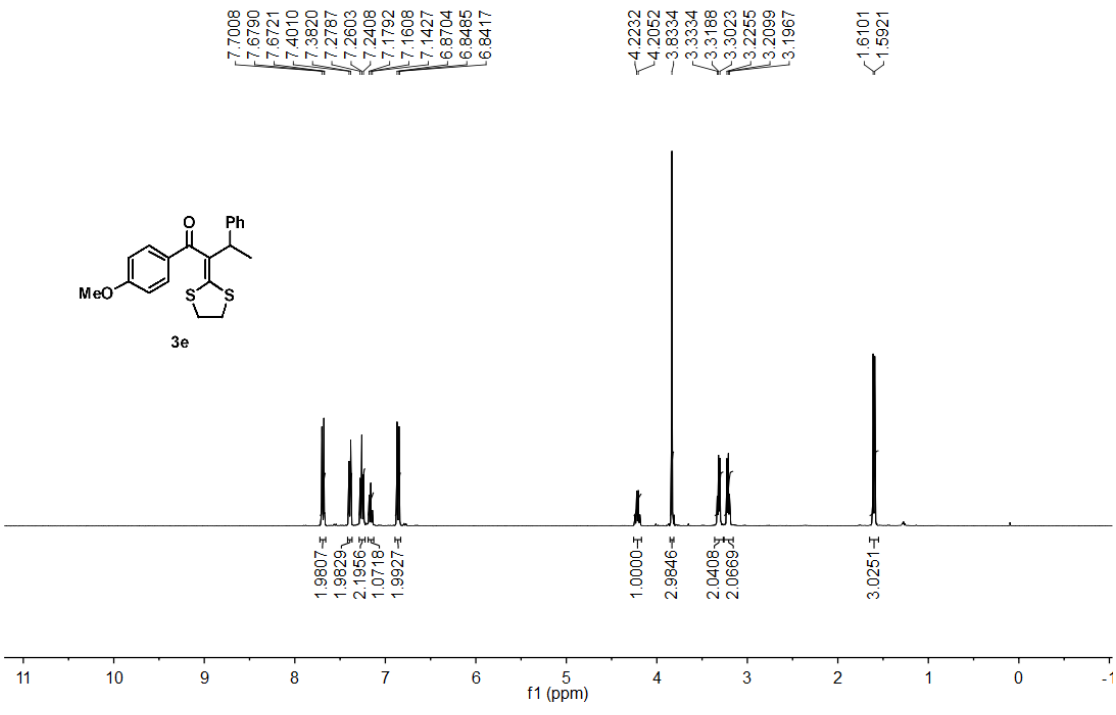
yq-1283
1H NMR yq-1283 in CDCl3



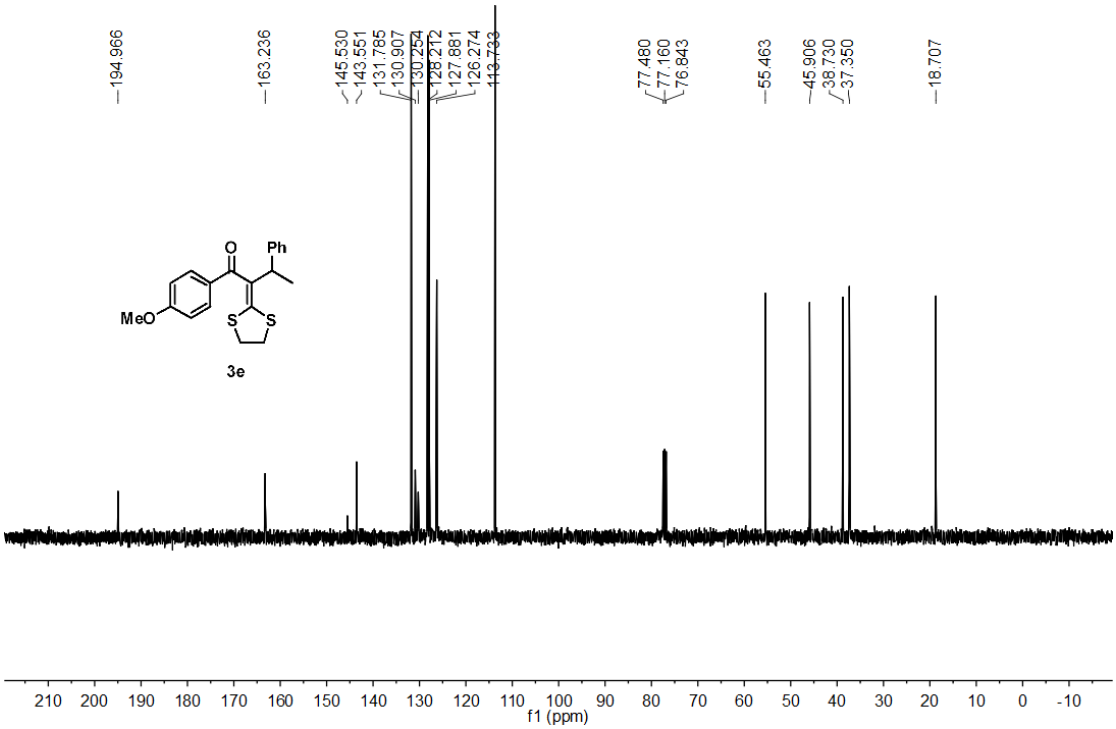
yq-1283
13C NMR yq-1283 CDCl3



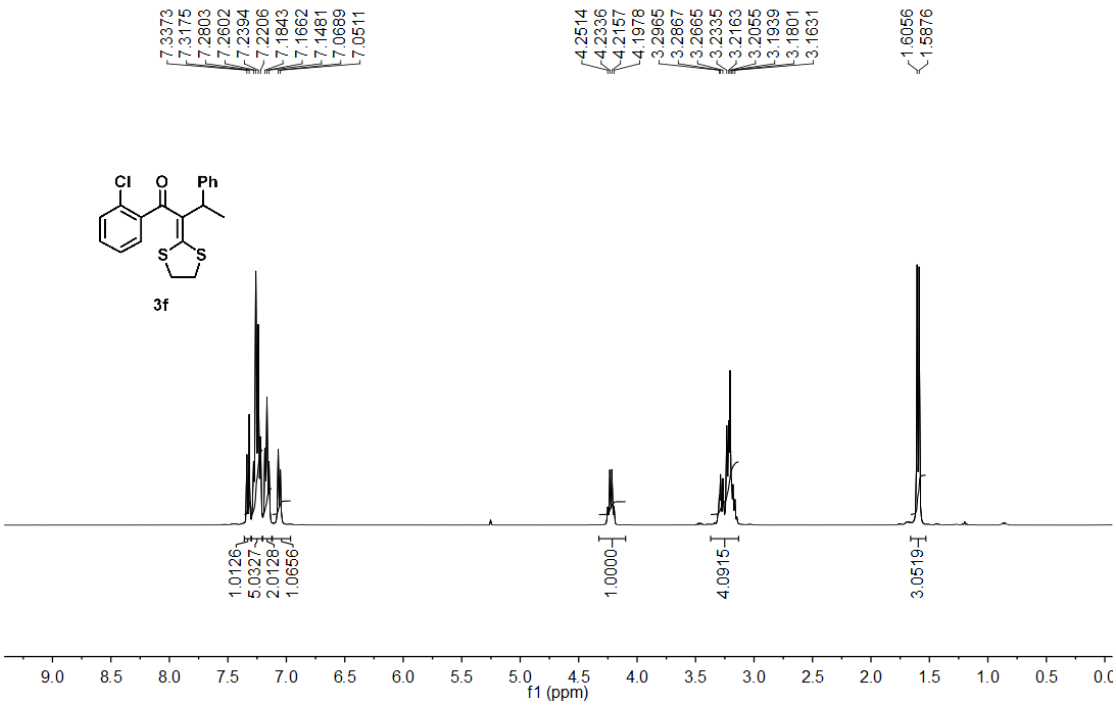
yq-1203-7
1H NMR (yq-1203-7 in CDCl3)



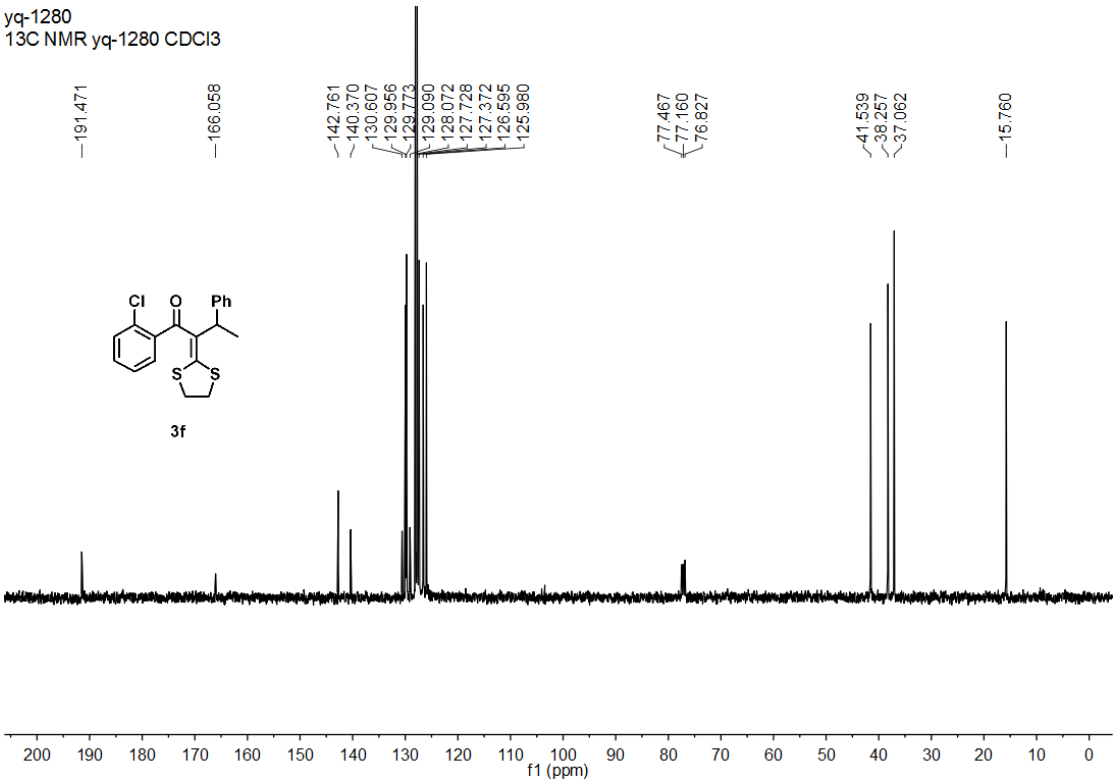
yq-1203-6
13C NMR (yq-1203-6 in CDCl3)



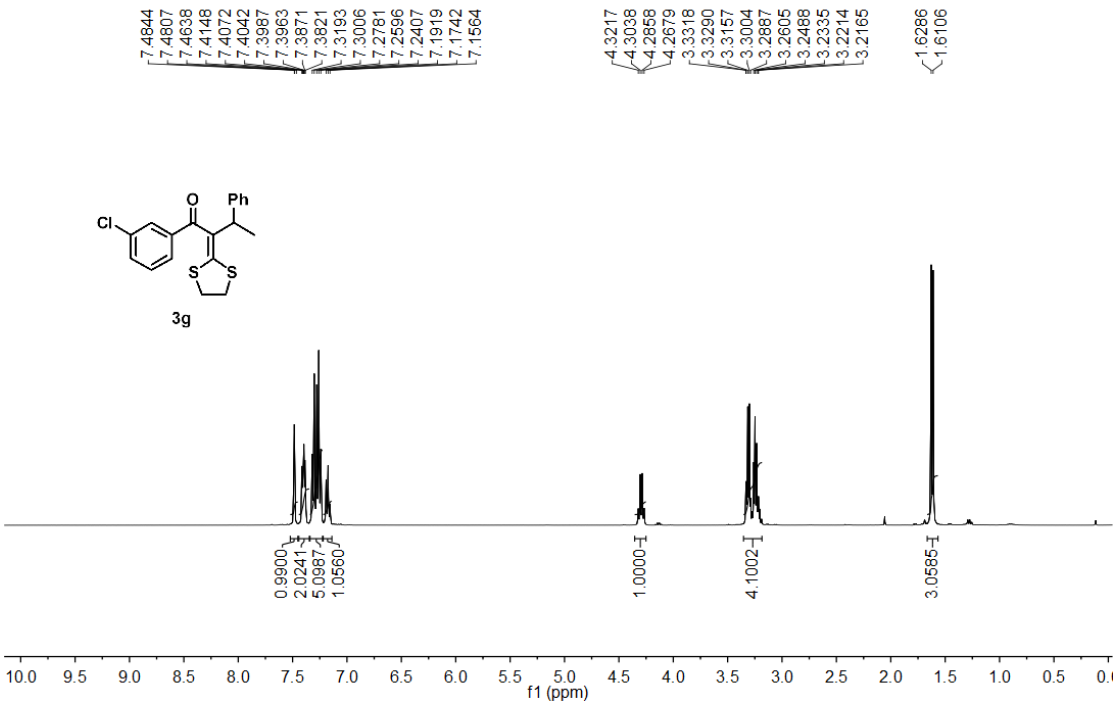
yq-1280
1H NMR yq-1280 in CDCl3



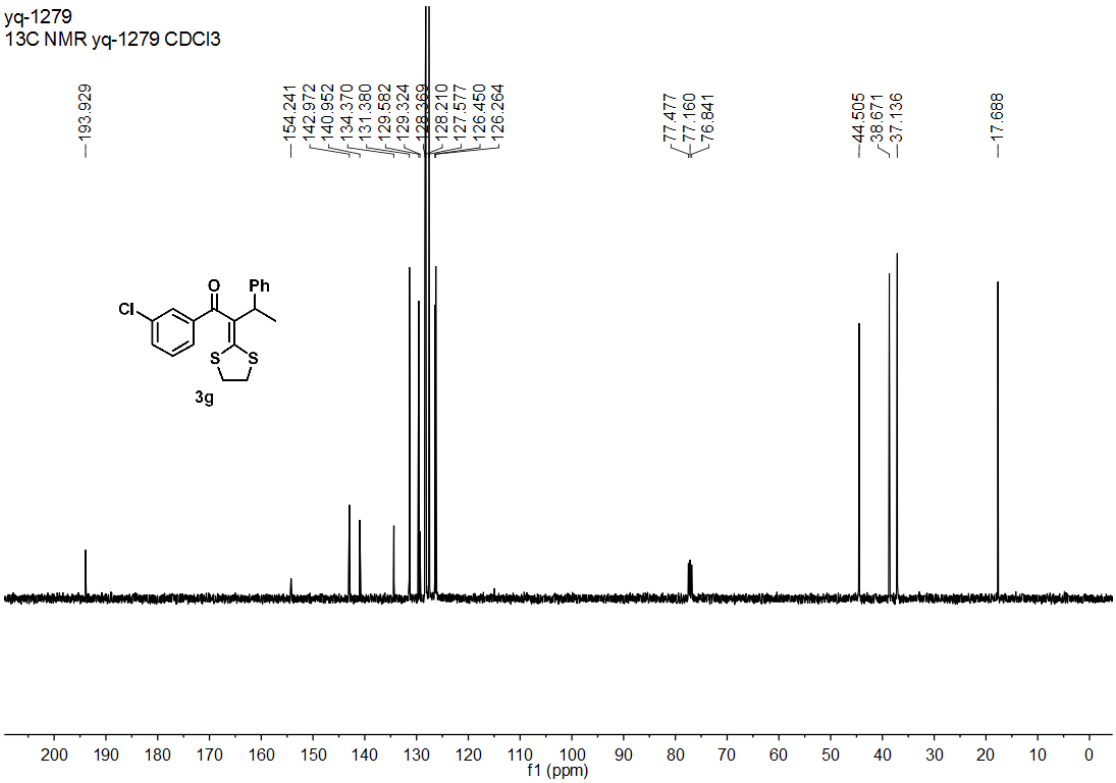
yq-1280
13C NMR yq-1280 CDCl3



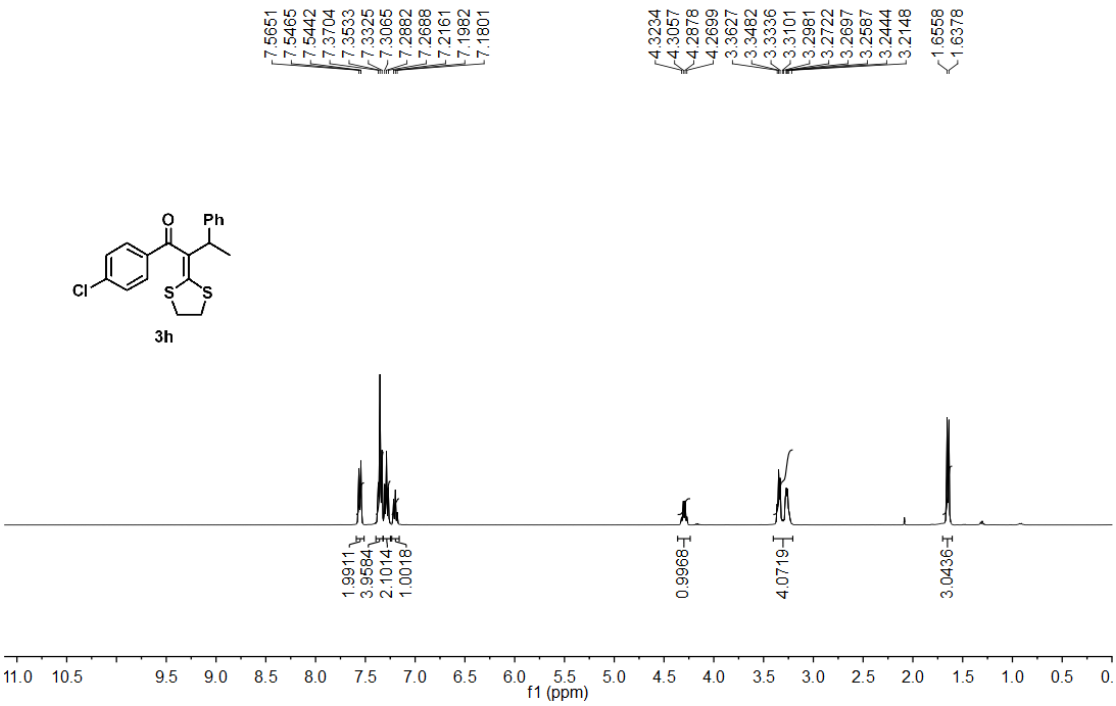
yq-1279
1H NMR yq-1279 in cdcl3



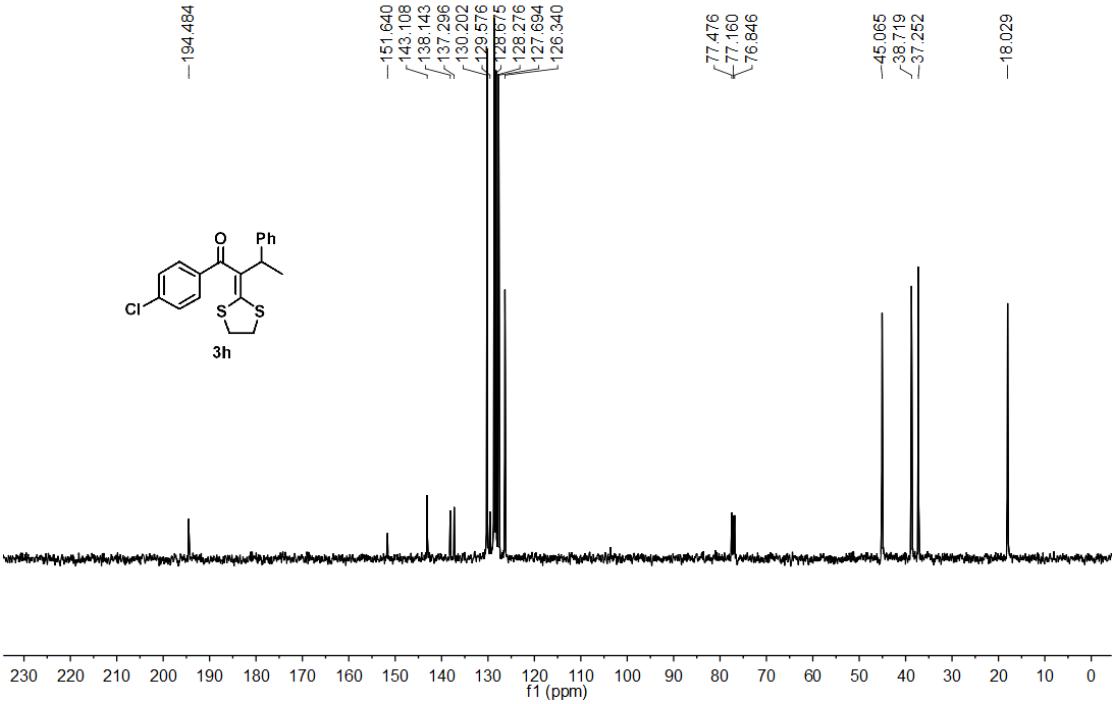
yq-1279
13C NMR yq-1279 CDCl3



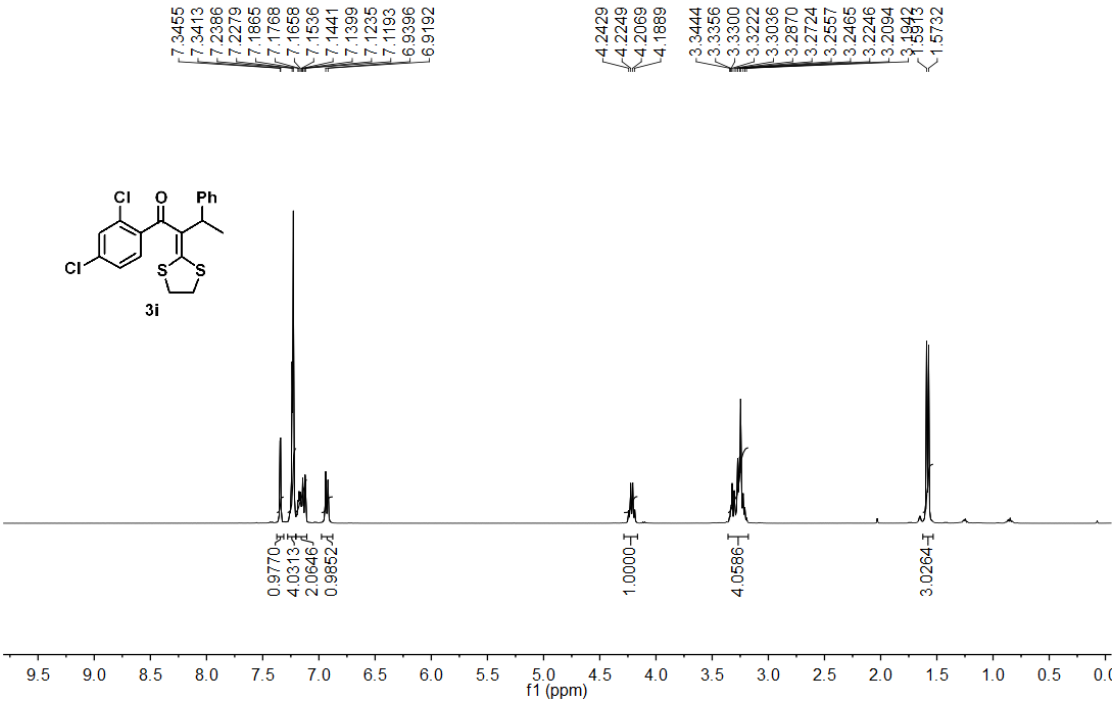
yq-1267-1
1H NMR yq-1267-1 in CDCl3



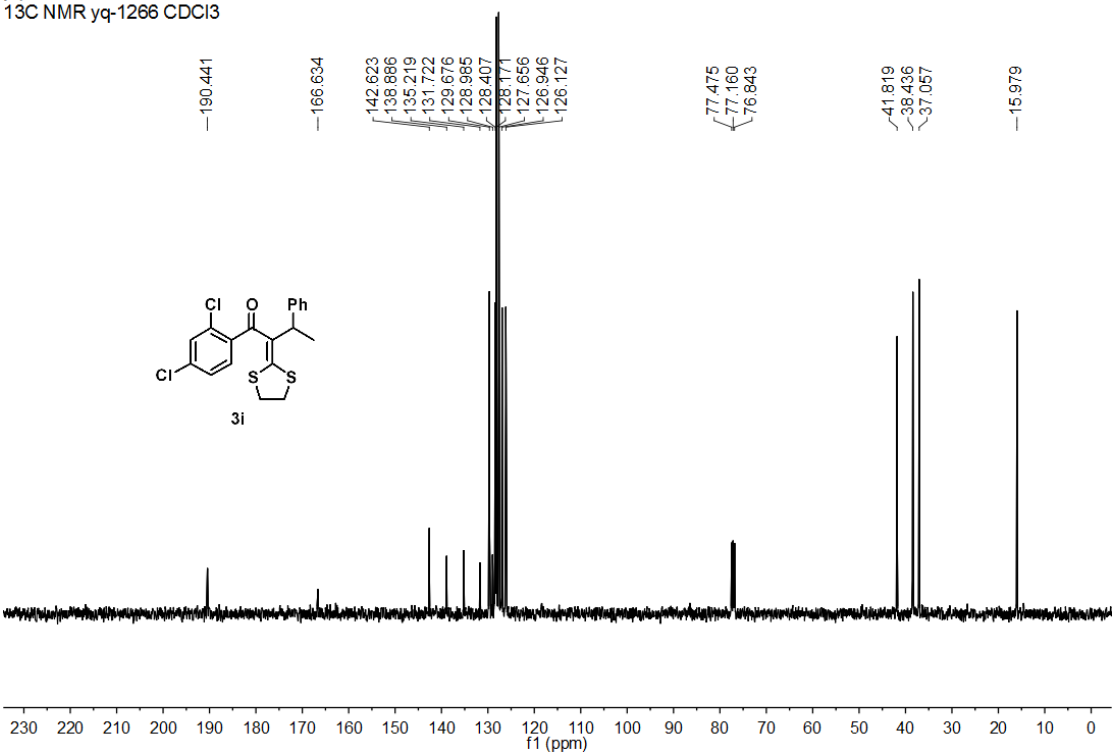
yq-1267-1
13C NMR yq-1267-1 CDCl3



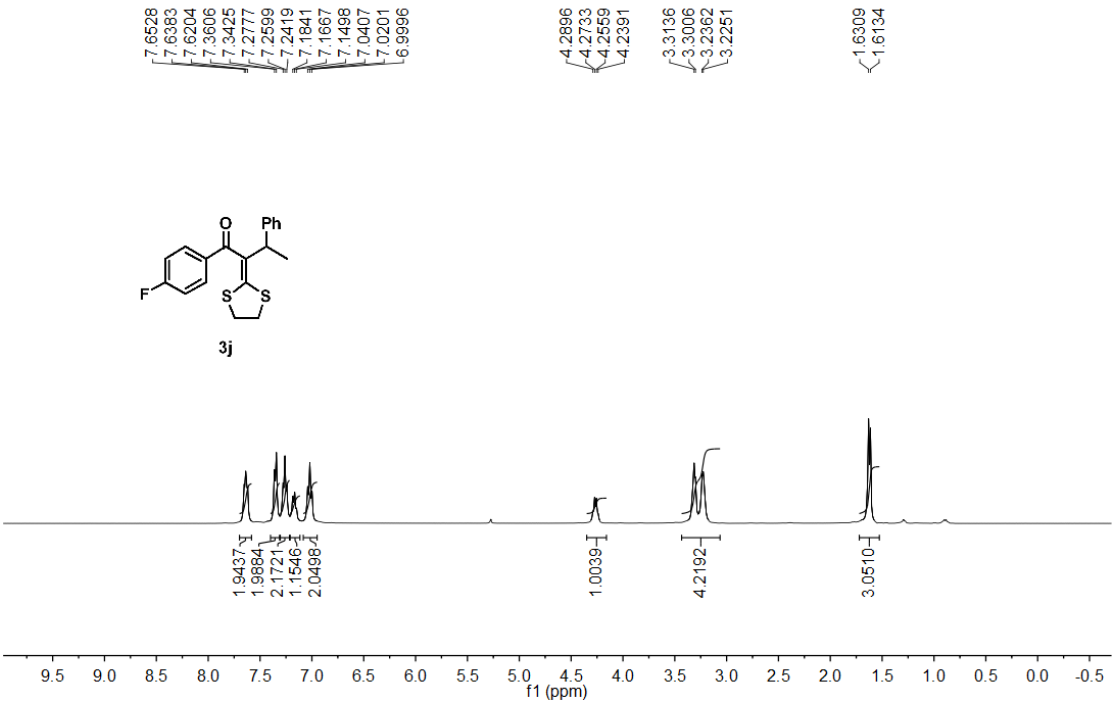
yq-1266
1H NMR yq-1266 in CDCl3



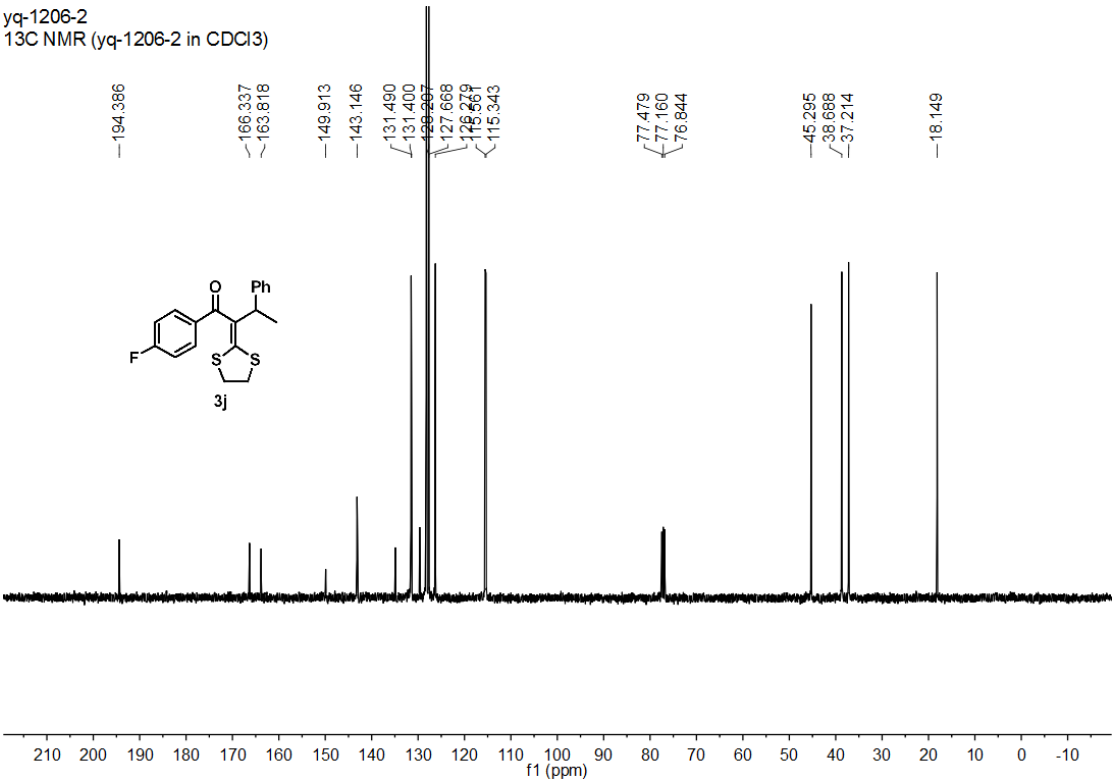
yq-1266
13C NMR yq-1266 CDCl3



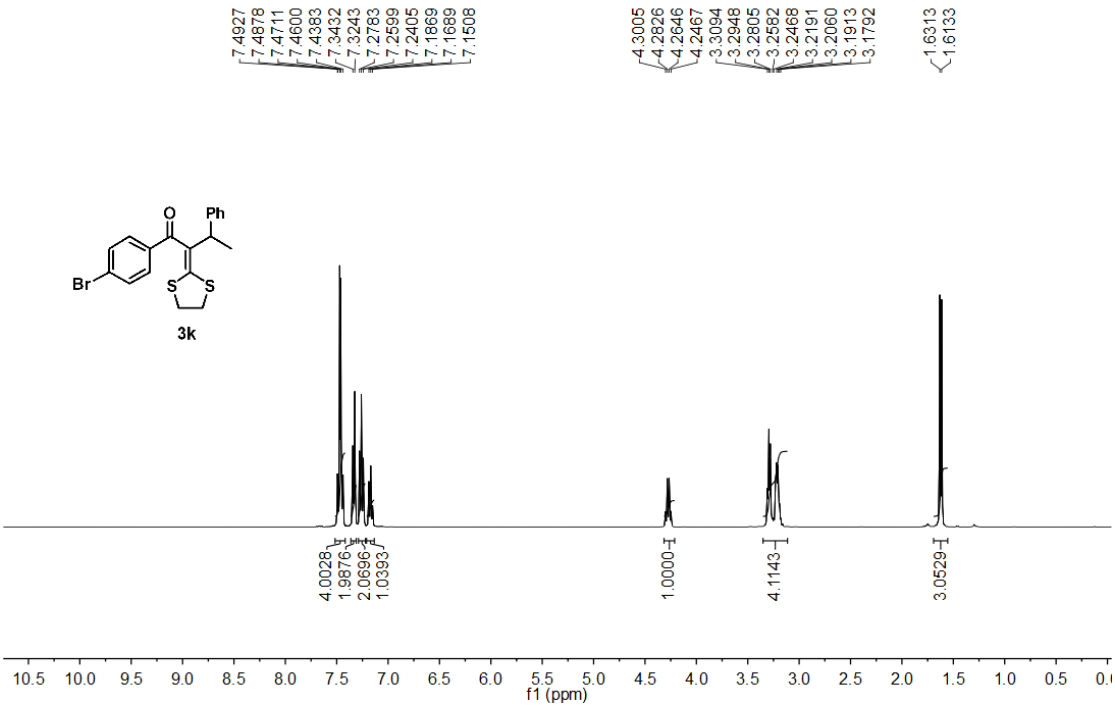
yq-1206-2
1H NMR (yq-1206-2 in CDCl3)



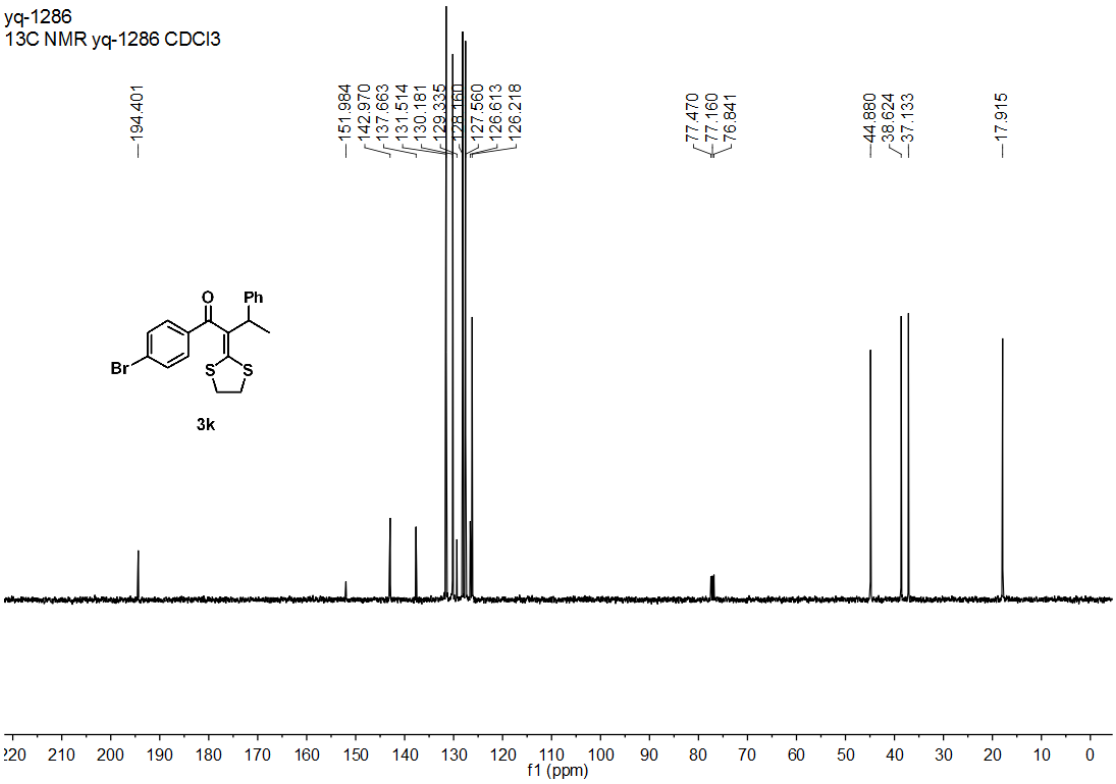
yq-1206-2
13C NMR (yq-1206-2 in CDCl3)



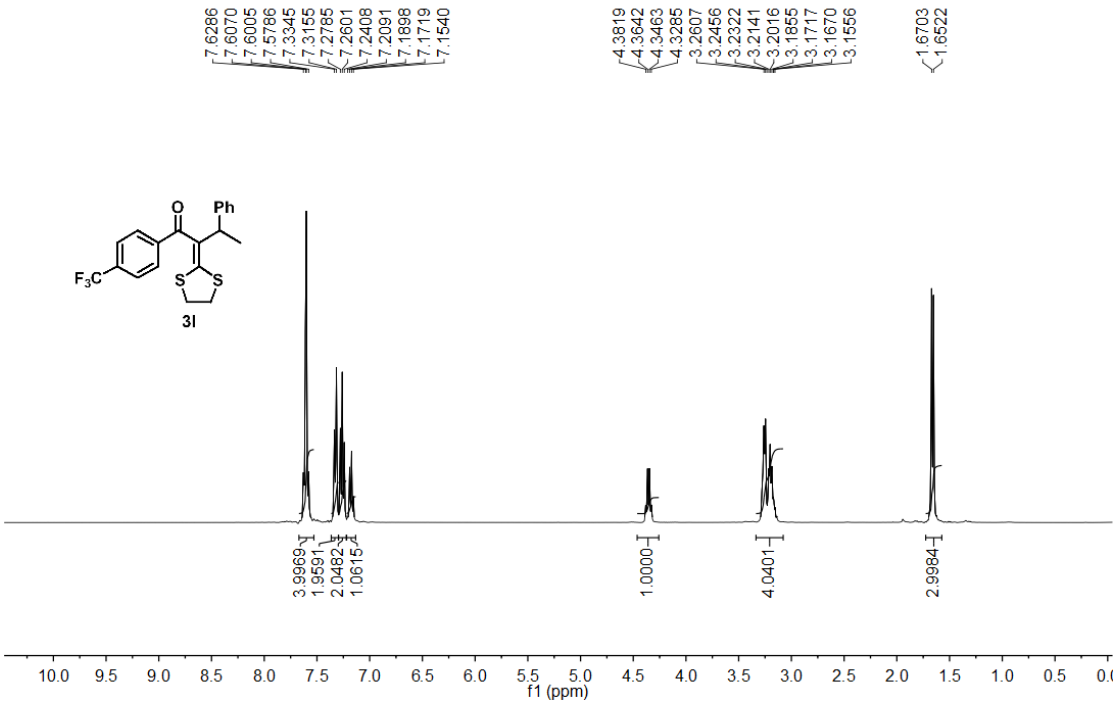
yq-1286
1H NMR yq-1286 in CDCl3



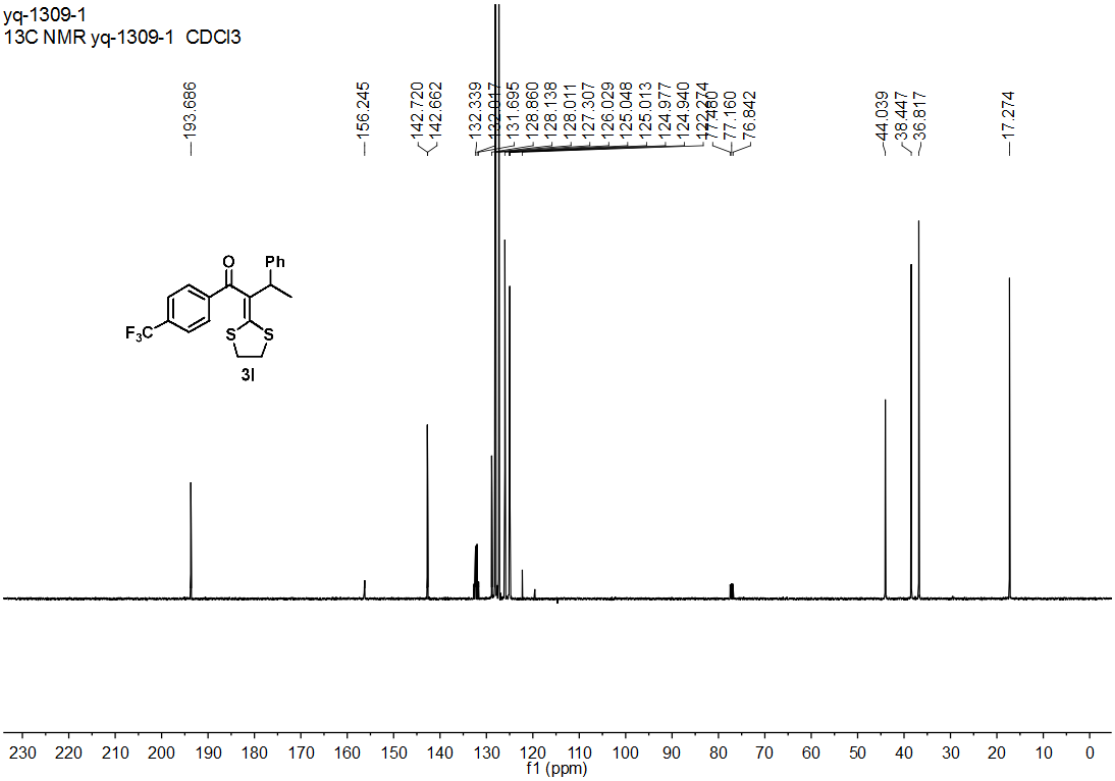
yq-1286
13C NMR yq-1286 CDCl3



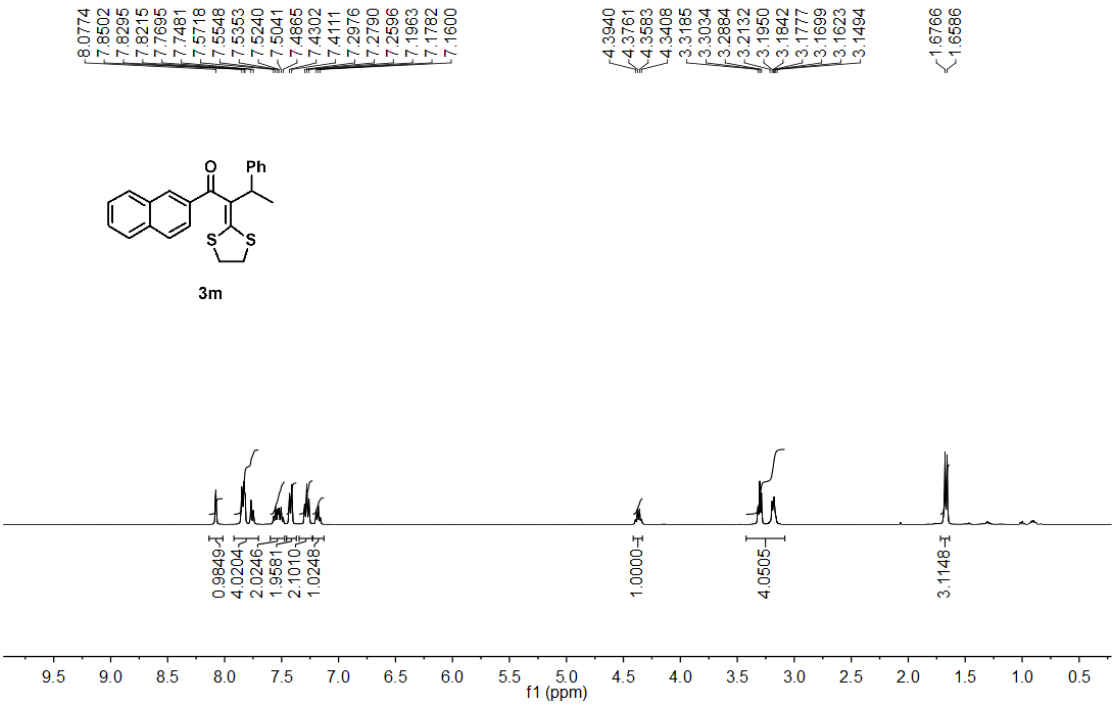
yq-1309-1
1H NMR yq-1309-1 in CDCl3



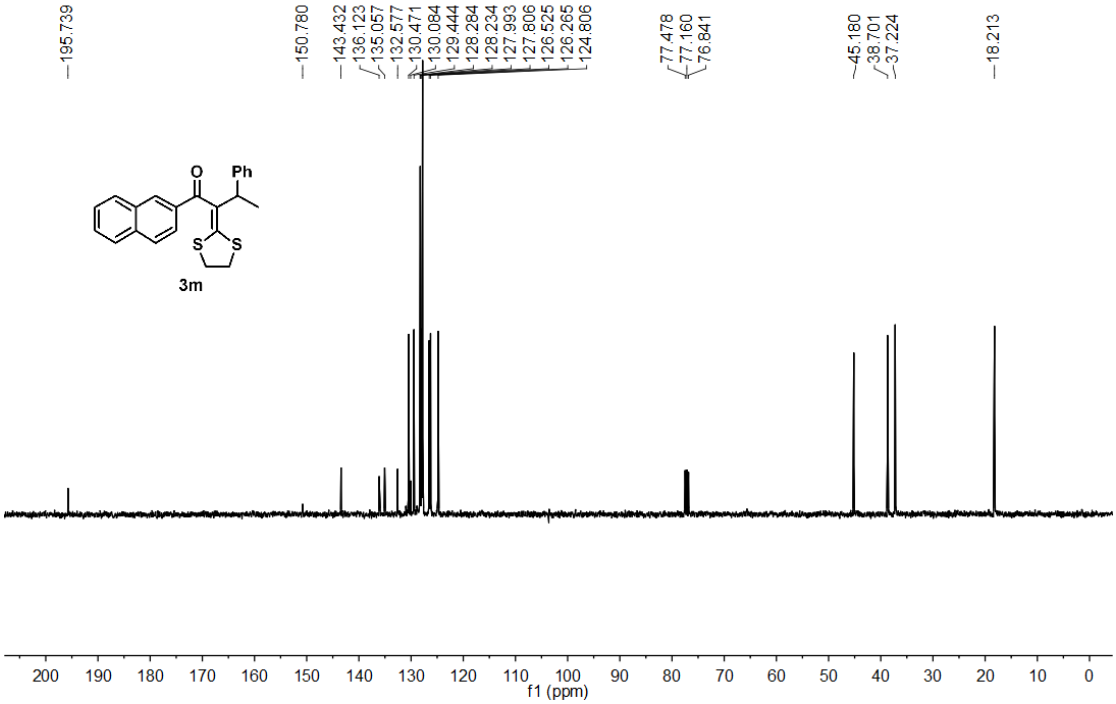
yq-1309-1
13C NMR yq-1309-1 CDCl3



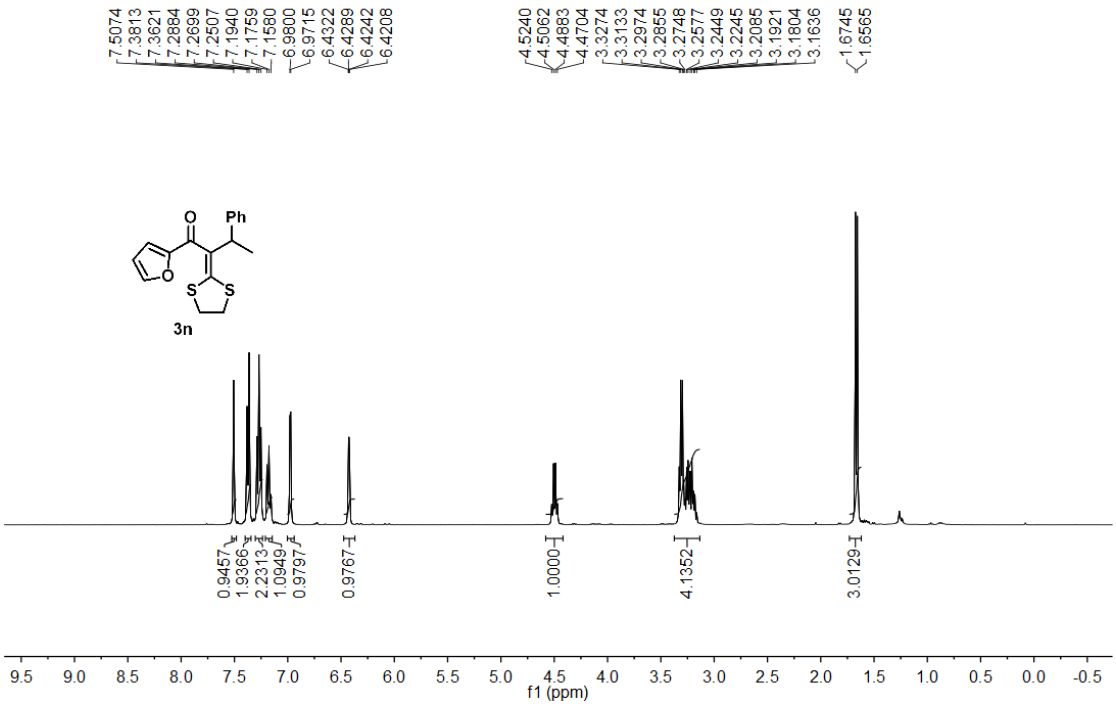
yq-1293
1H NMR yq-1293 in CDCl3



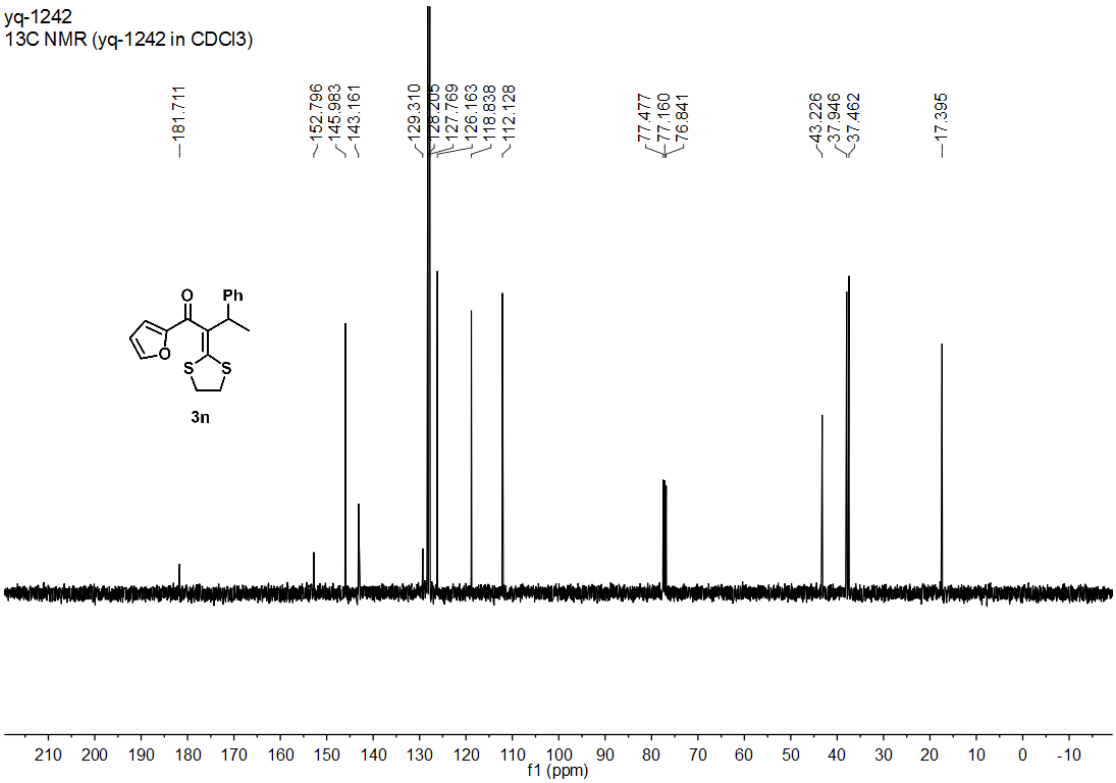
yq-1293
13C NMR yq-1293 CDCl3



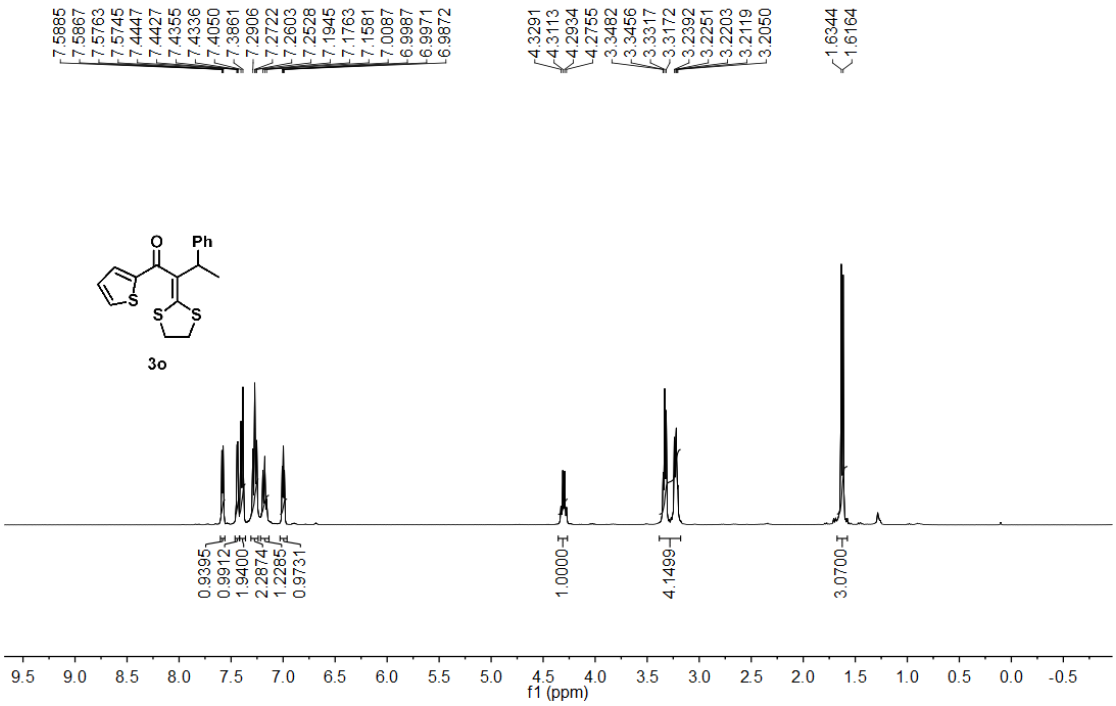
yq-1242
1H NMR (yq-1242 in CDCl3)



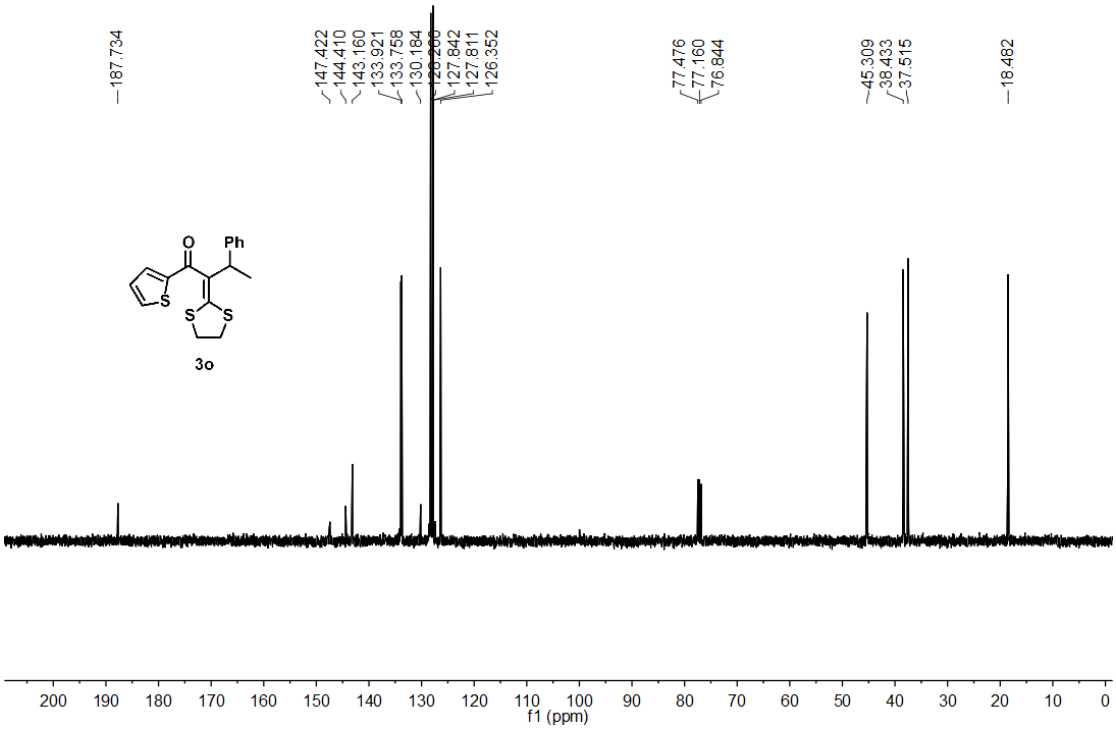
yq-1242
13C NMR (yq-1242 in CDCl3)



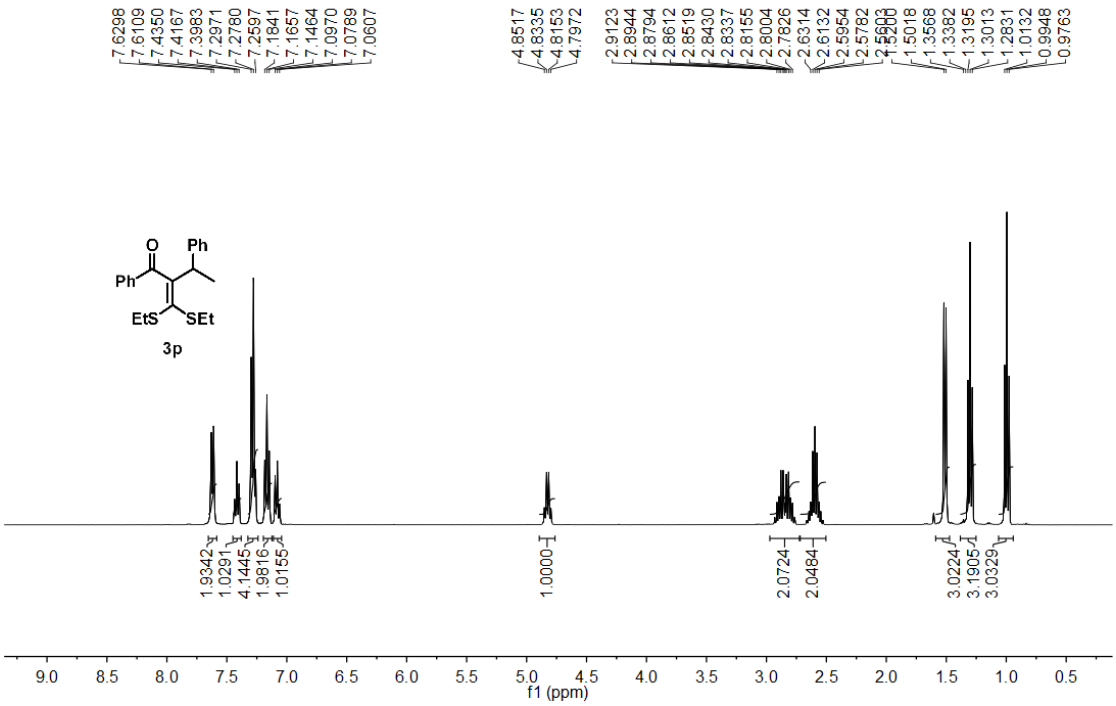
yq-1228
1H NMR (yq-1228 in CDCl3)



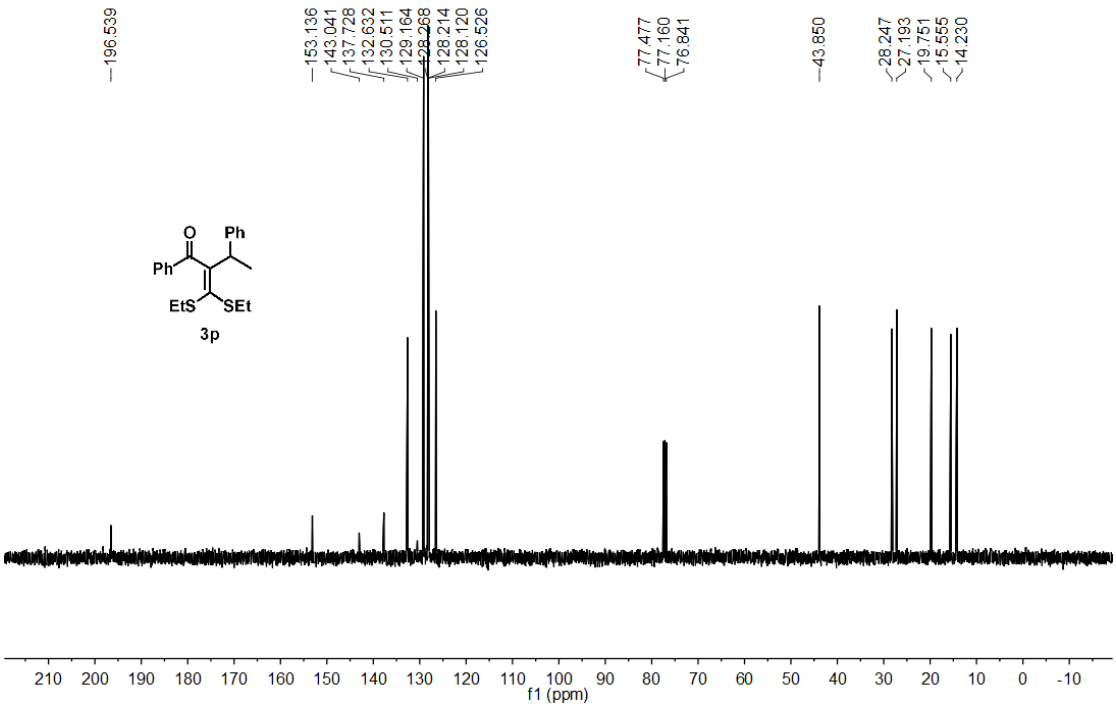
yq-1228
13C NMR (yq-1228 in CDCl3)



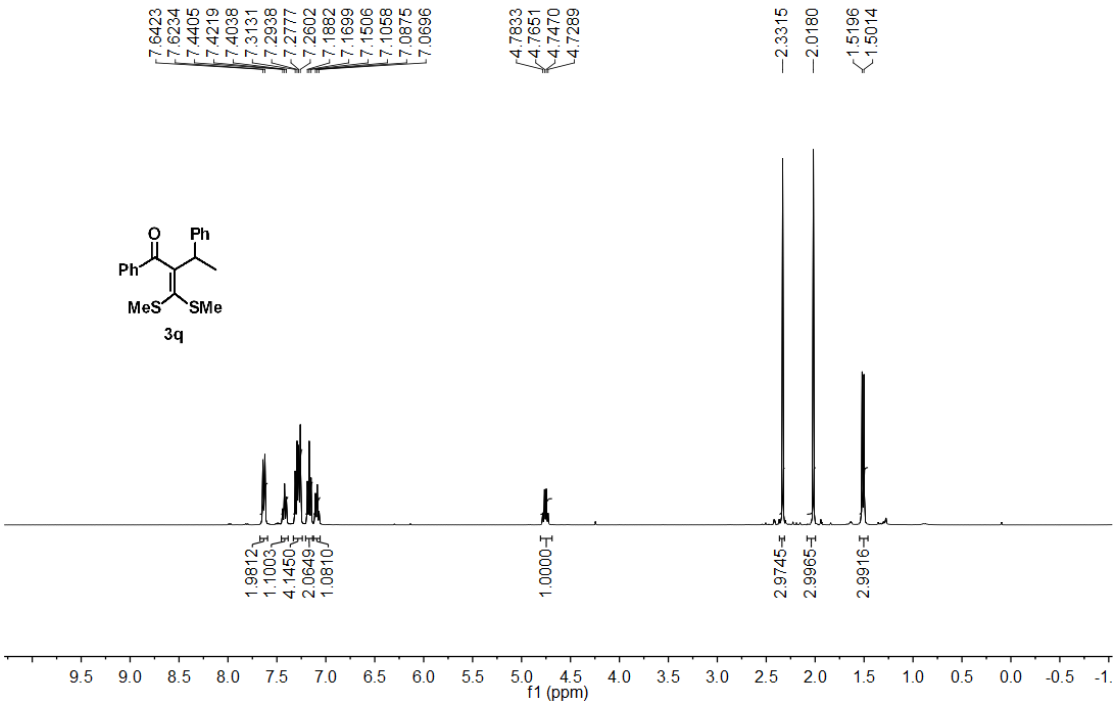
yq-1219-3
1H NMR (yq-1219-3 in CDCl3)



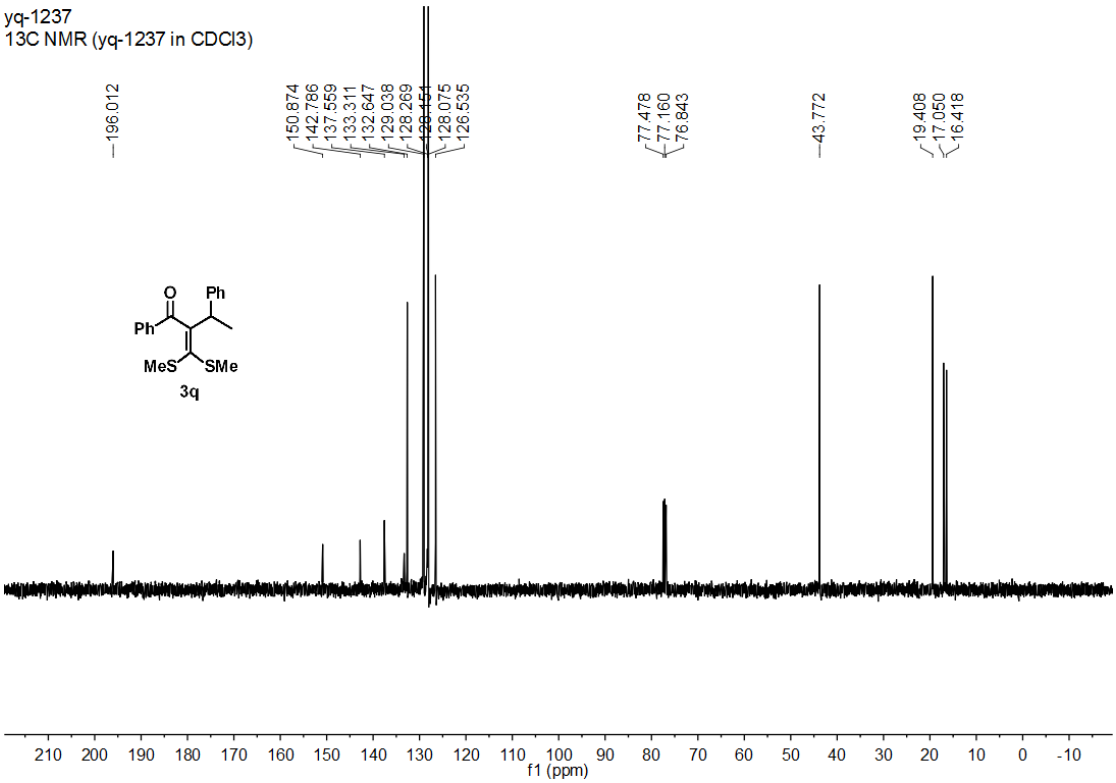
yq-1219-3
13C NMR (yq-1219-3 in CDCl3)



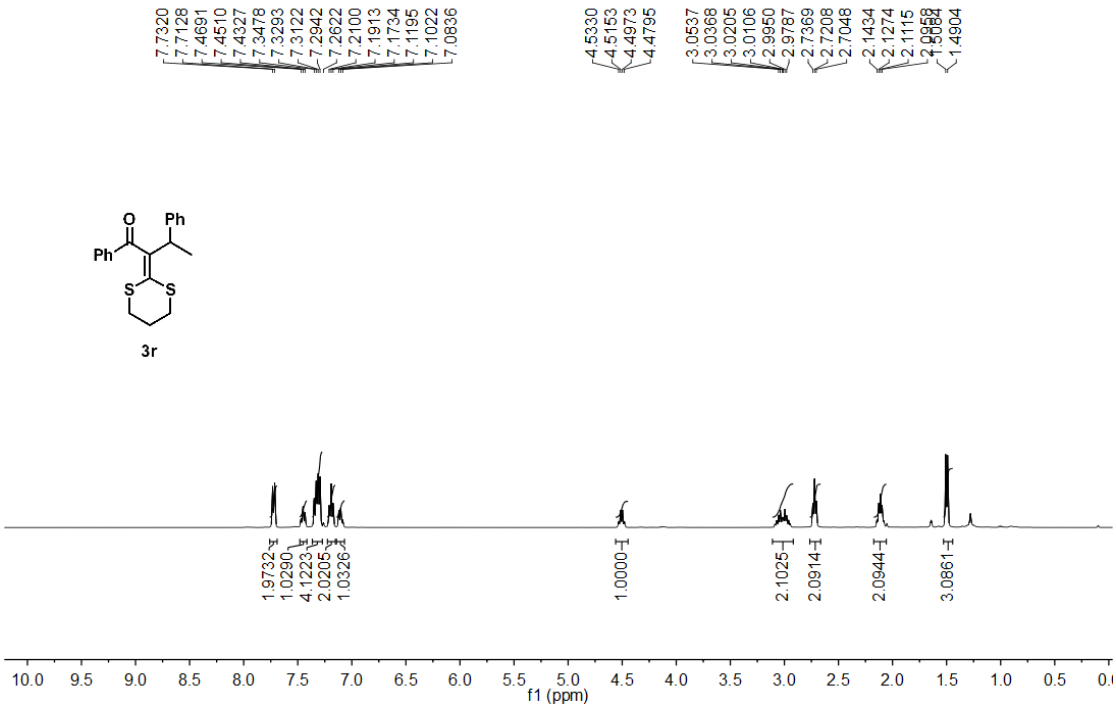
yq-1237
1H NMR (yq-1237 in CDCl3)



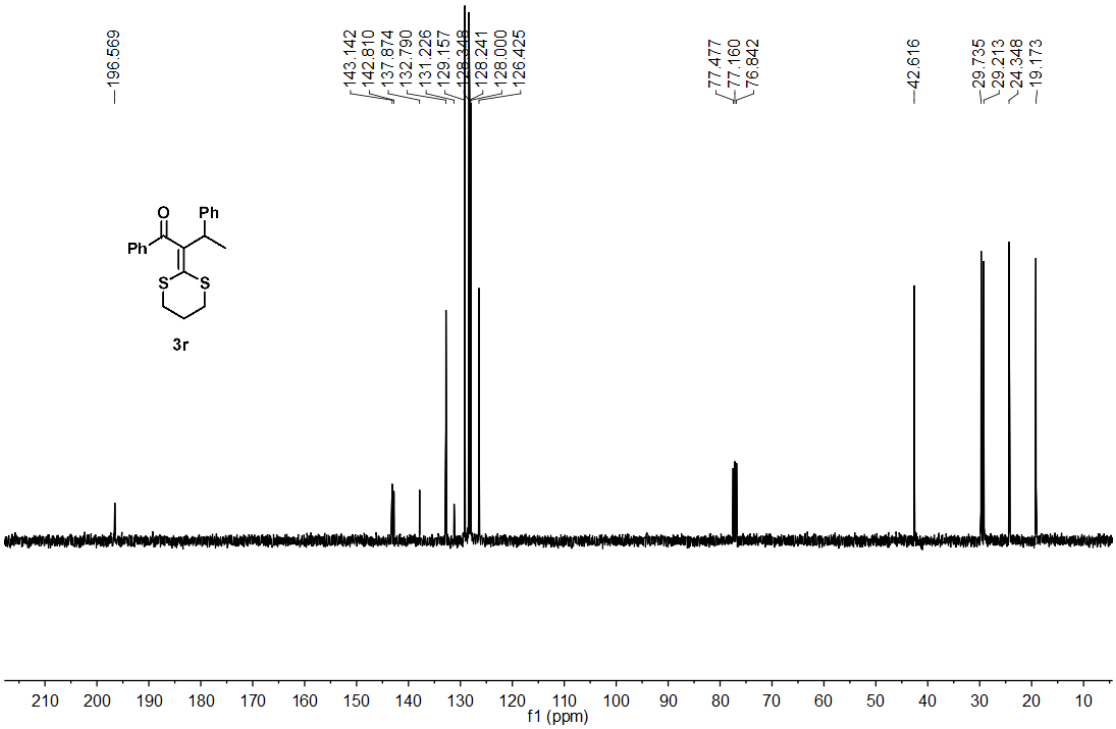
yq-1237
13C NMR (yq-1237 in CDCl3)



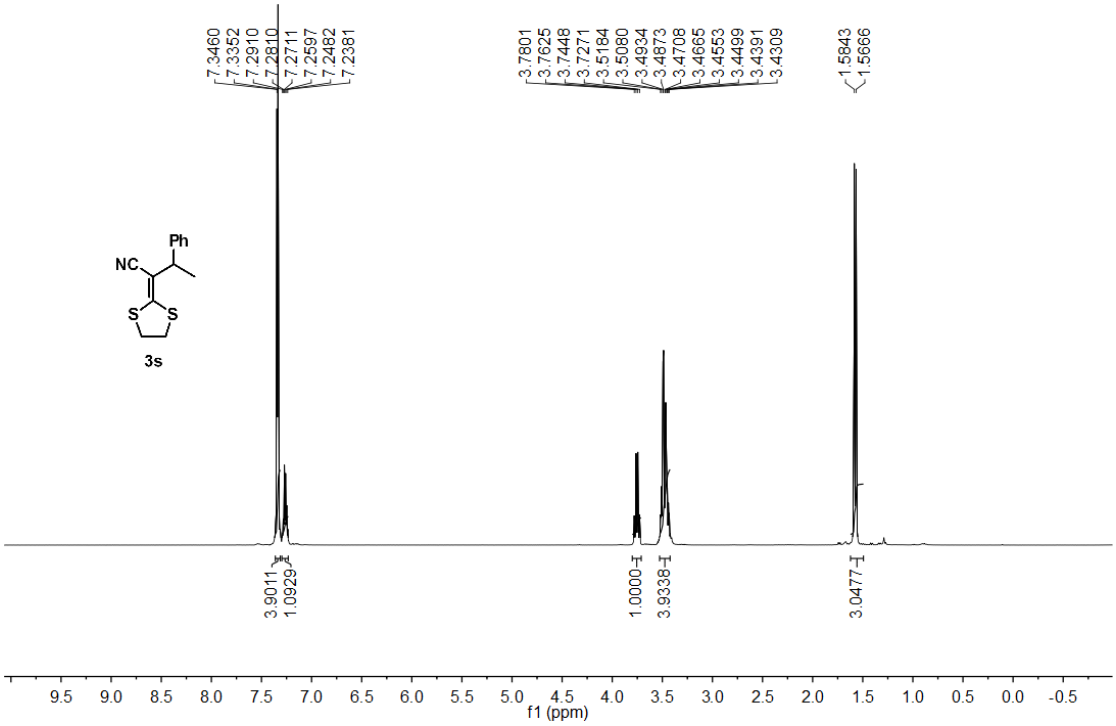
yq-1256-3
1H NMR yq-1256-3 in CDCl3



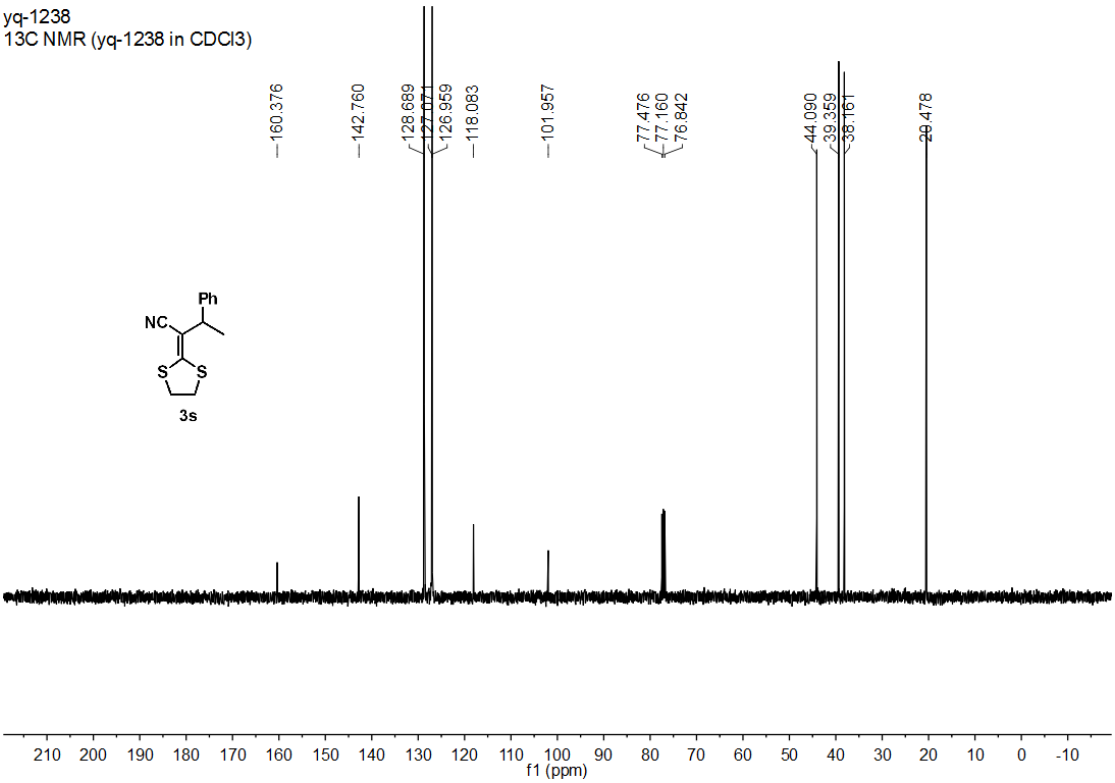
yq-1256-3
13C NMR yq-1256-3 CDCl3



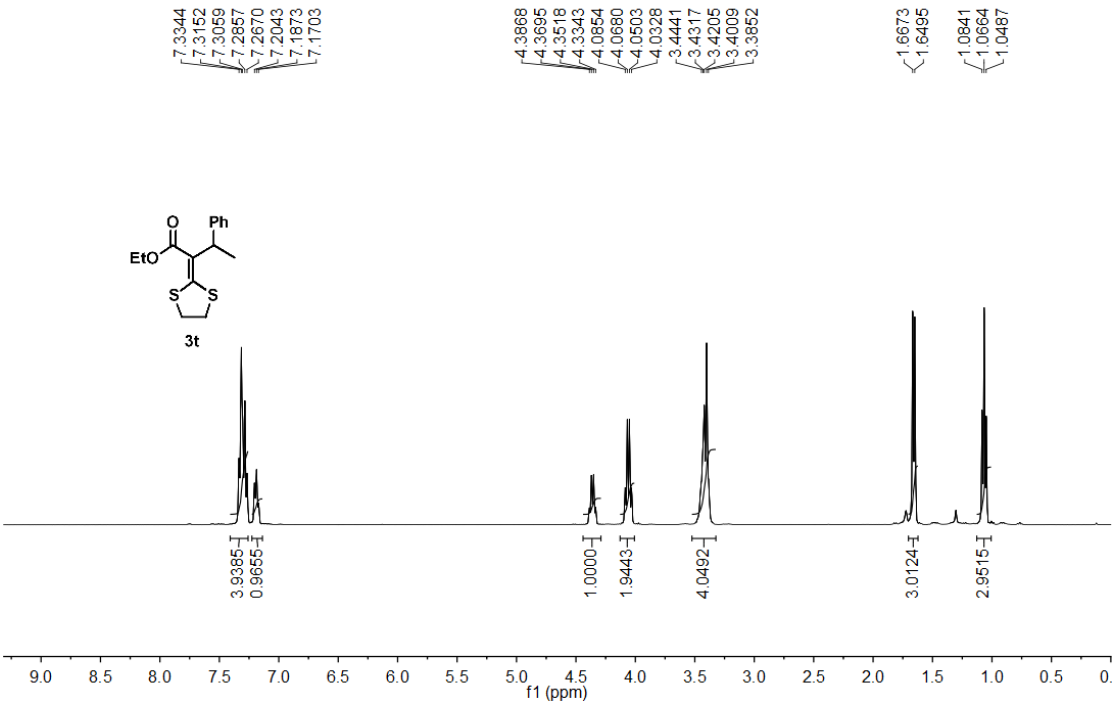
yq-1238
1H NMR (yq-1238 in CDCl3)



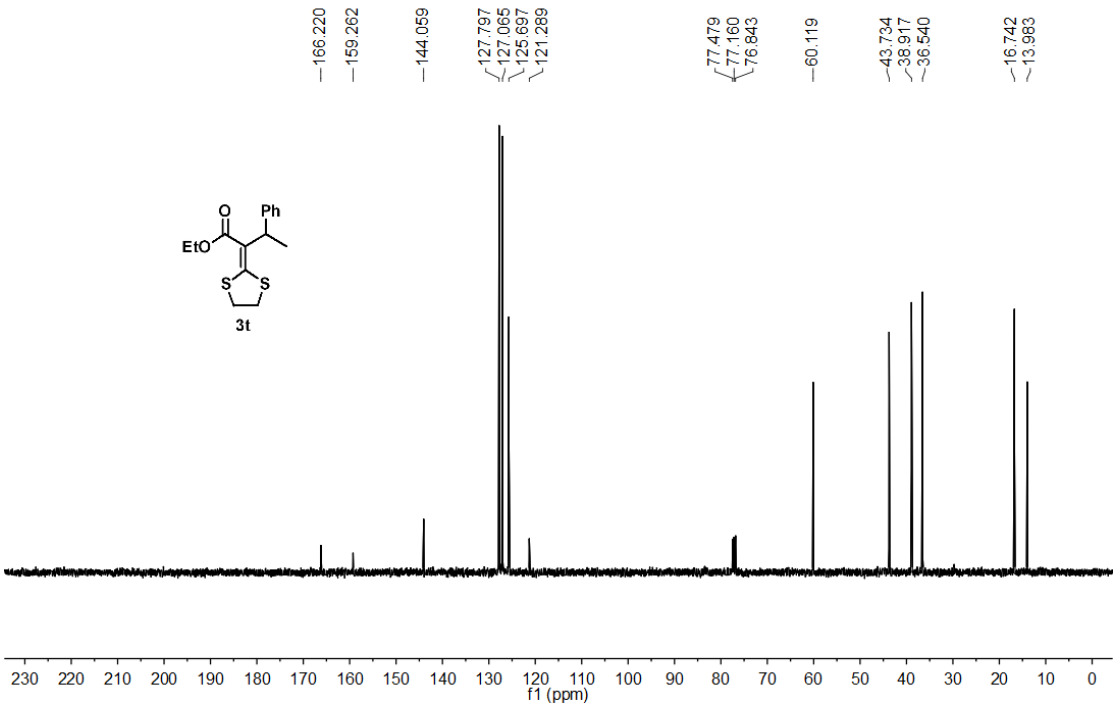
yq-1238
13C NMR (yq-1238 in CDCl3)



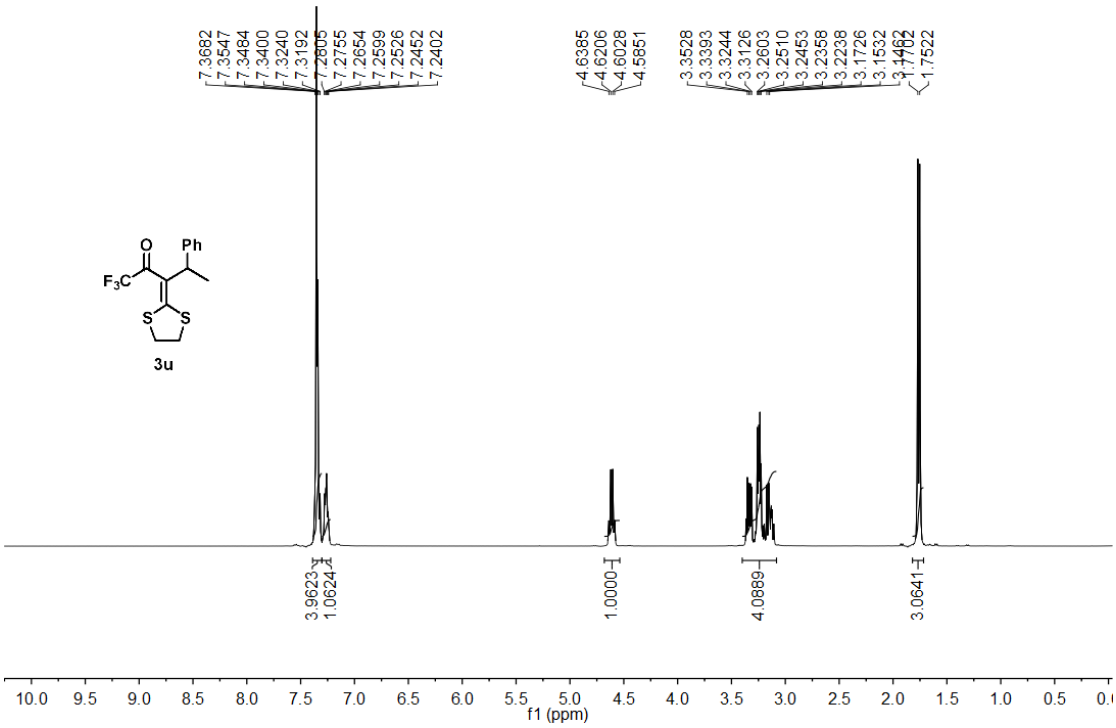
yq-1406
1H NMR yq-1406 in CDCl3



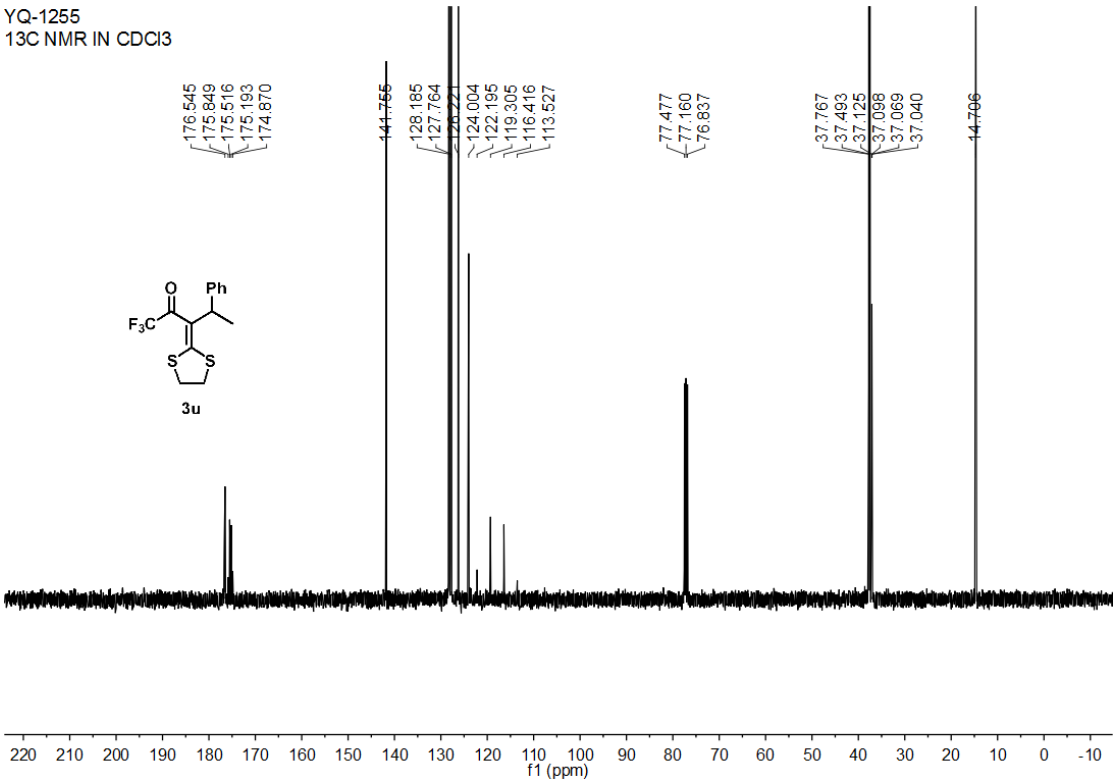
yq-1406
13C NMR yq-1406 CDCl3



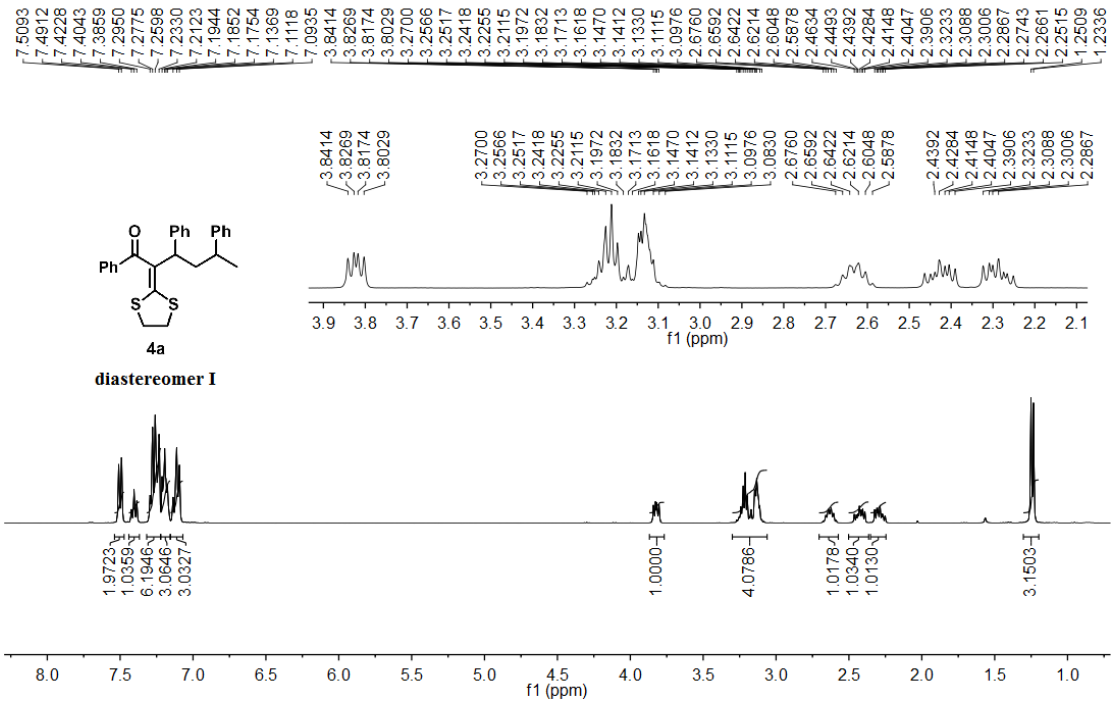
yq-1255
1H NMR yq-1255 in CDCl3



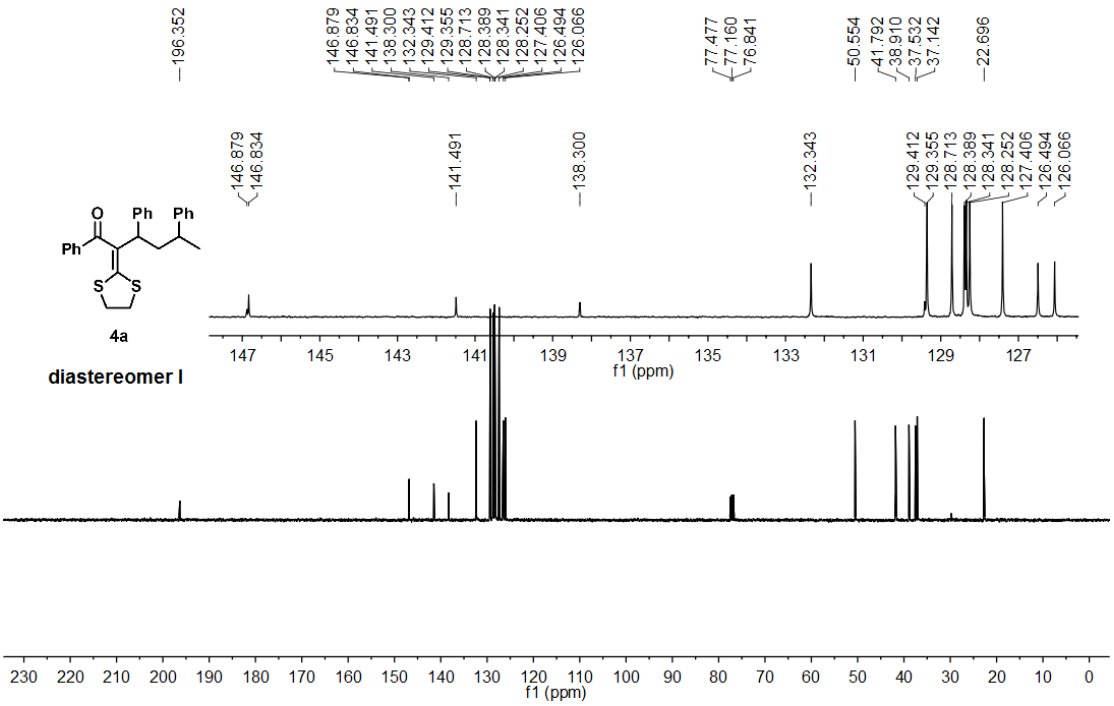
YQ-1255
13C NMR IN CDCl3



yq-1244-1-2
1H NMR yq-1244-1-2 in CDCl3



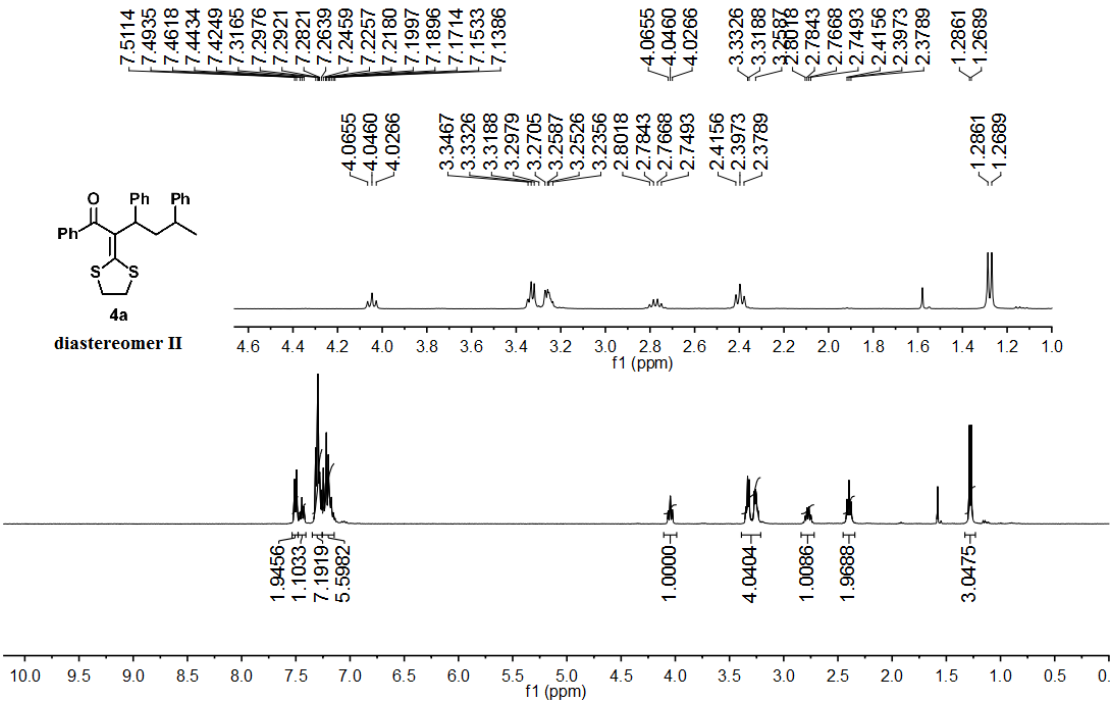
yq-1244-1
13C NMR yq-1244-1 CDCl3



4a

diastereomer I

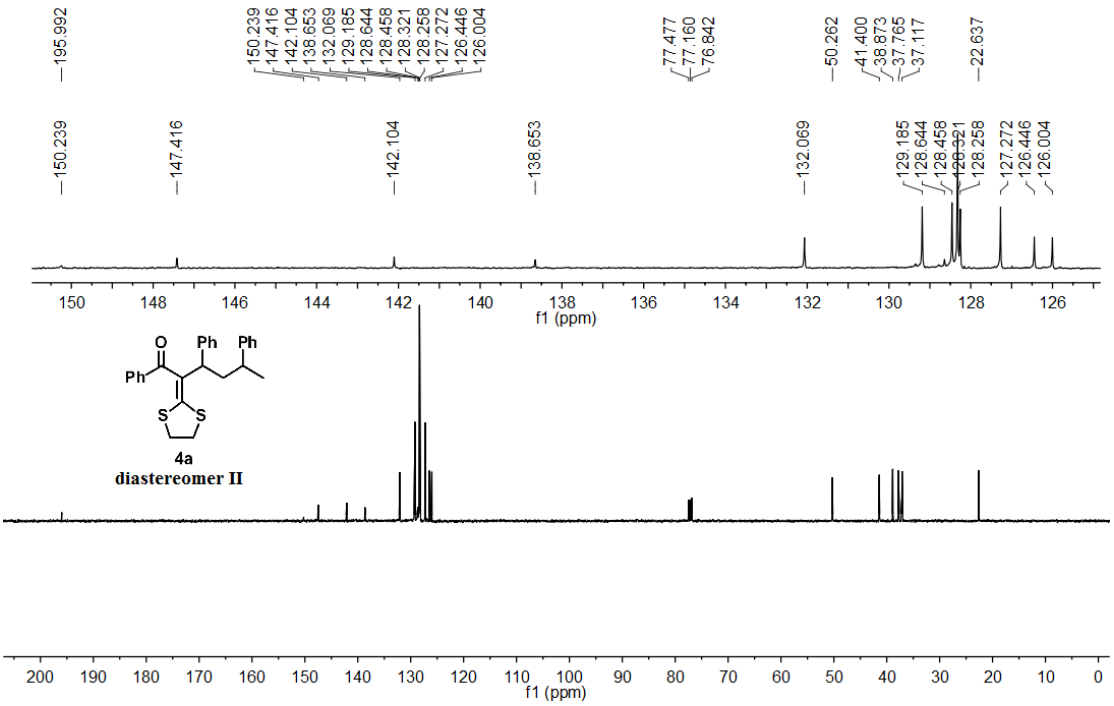
yq-1244-2-2
1H NMR yq-1244-2-2 in CDCl3



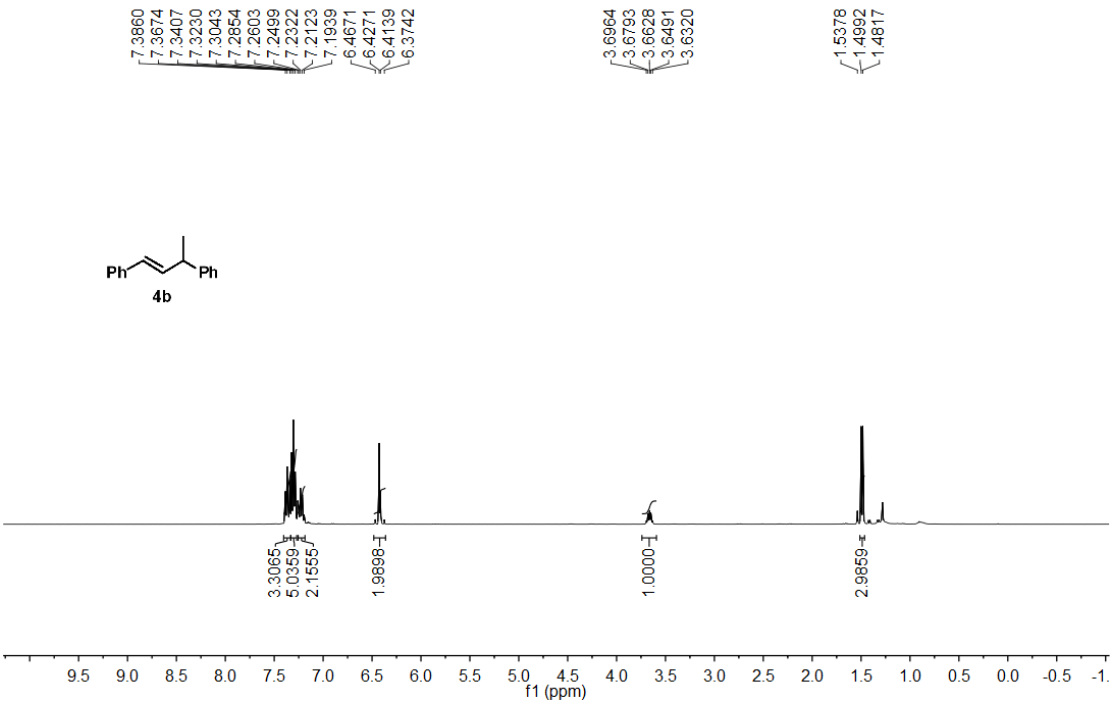
4a

diastereomer II

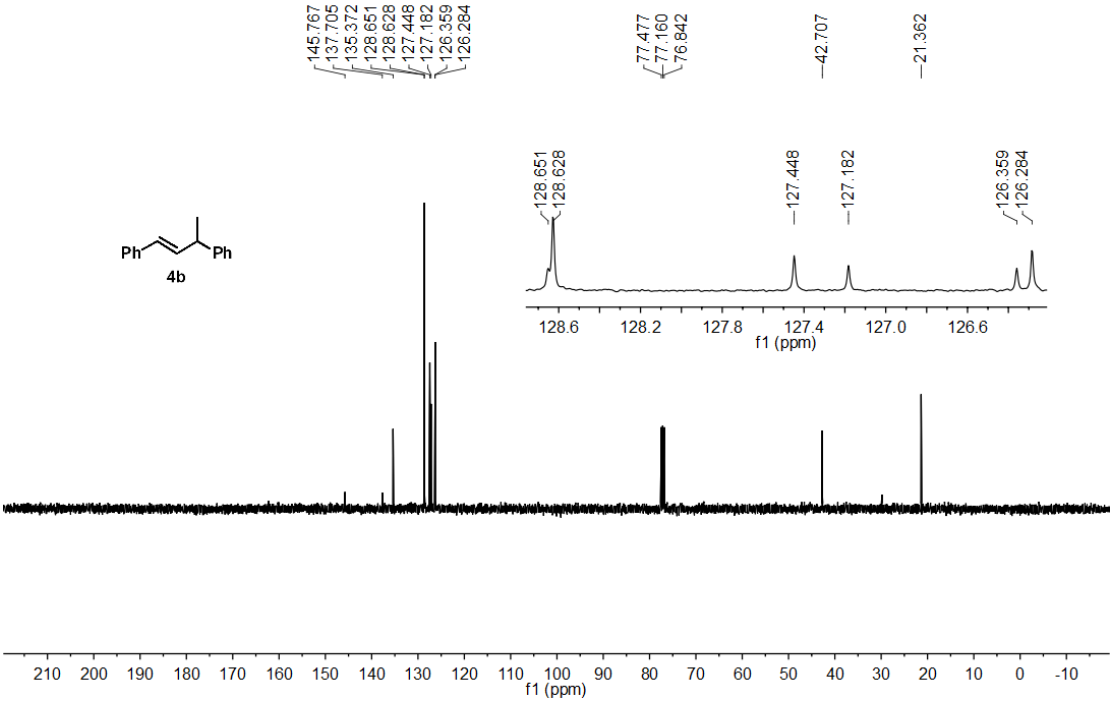
yq-1244-2-2
13C NMR yq-1244-2-2 CDCl3



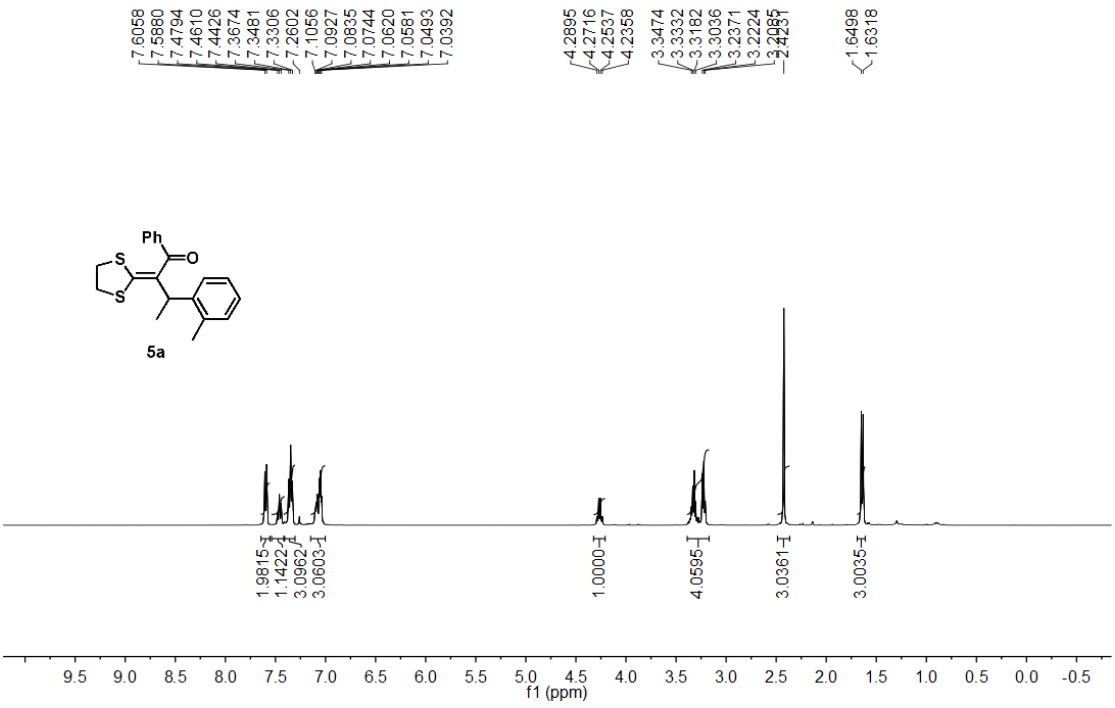
yq1031
1H NMR (yq1031 in CDCl3)



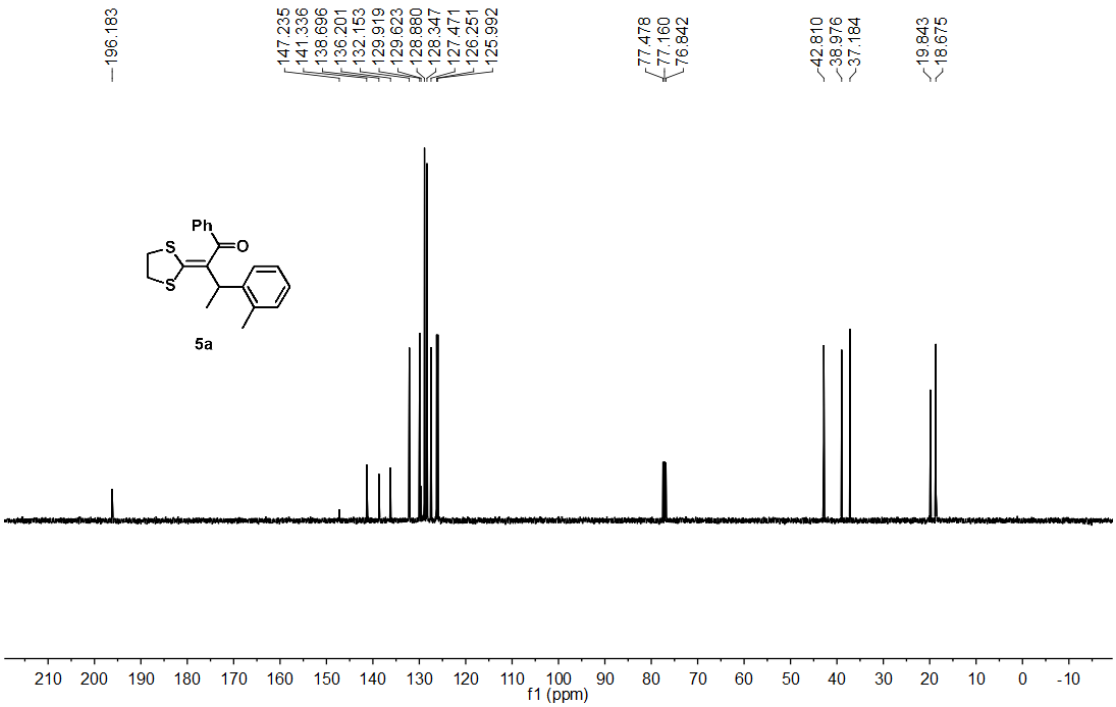
yq1031
13C NMR (yq1031 in CDCl3)



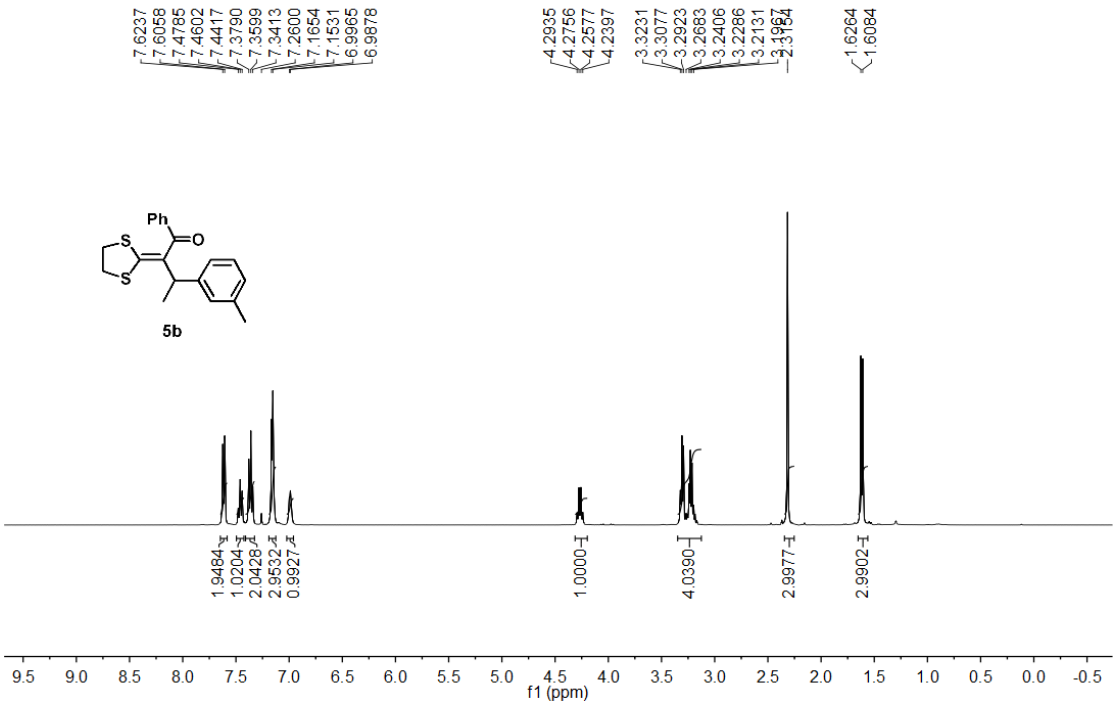
yq-1236
1H NMR (yq-1236 in CDCl3)



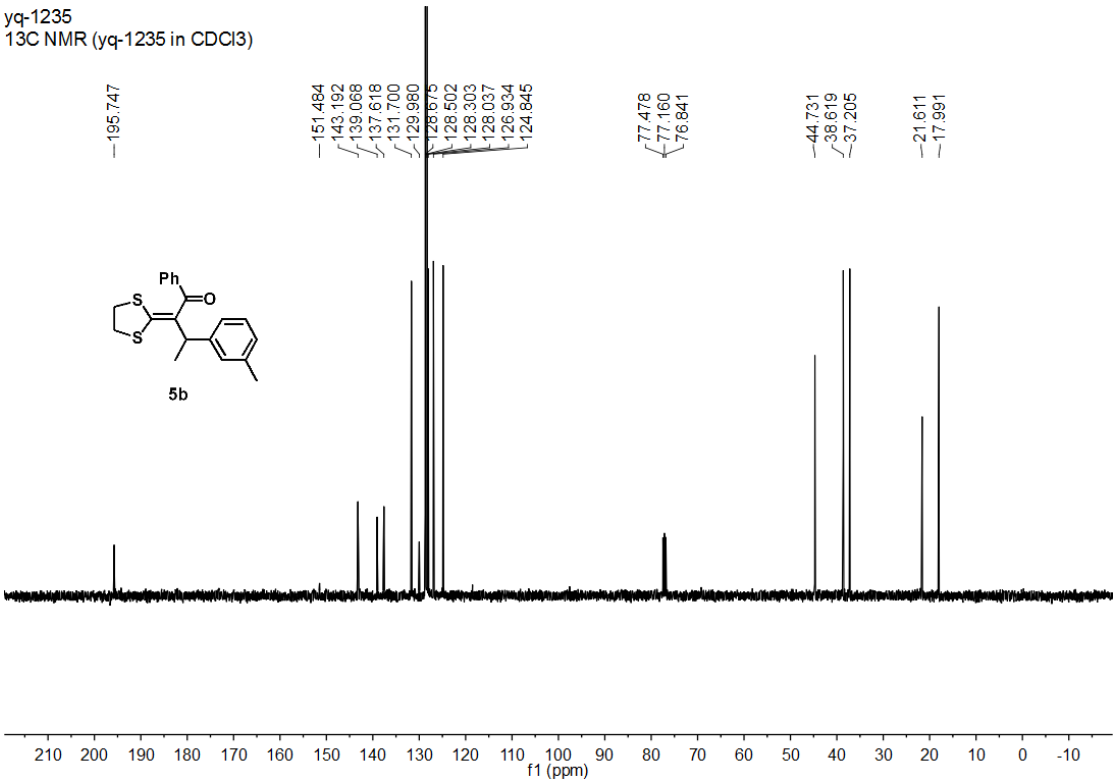
yq-1236
13C NMR (yq-1236 in CDCl3)



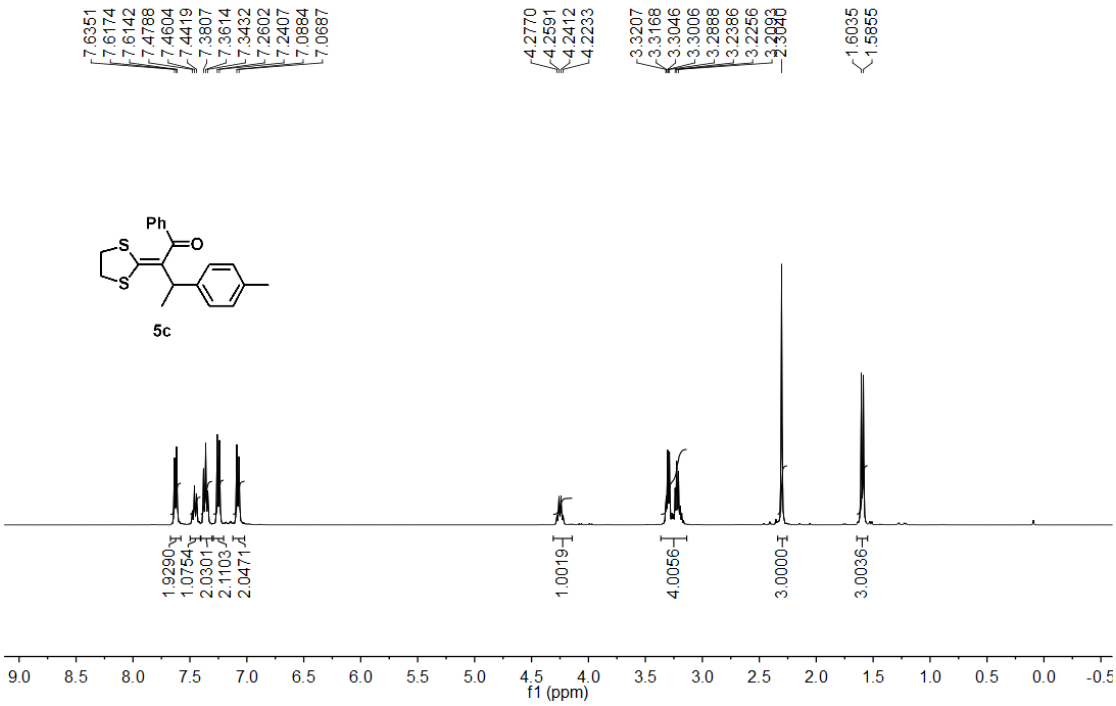
yq-1235
1H NMR (yq-1235 in CDCl3)



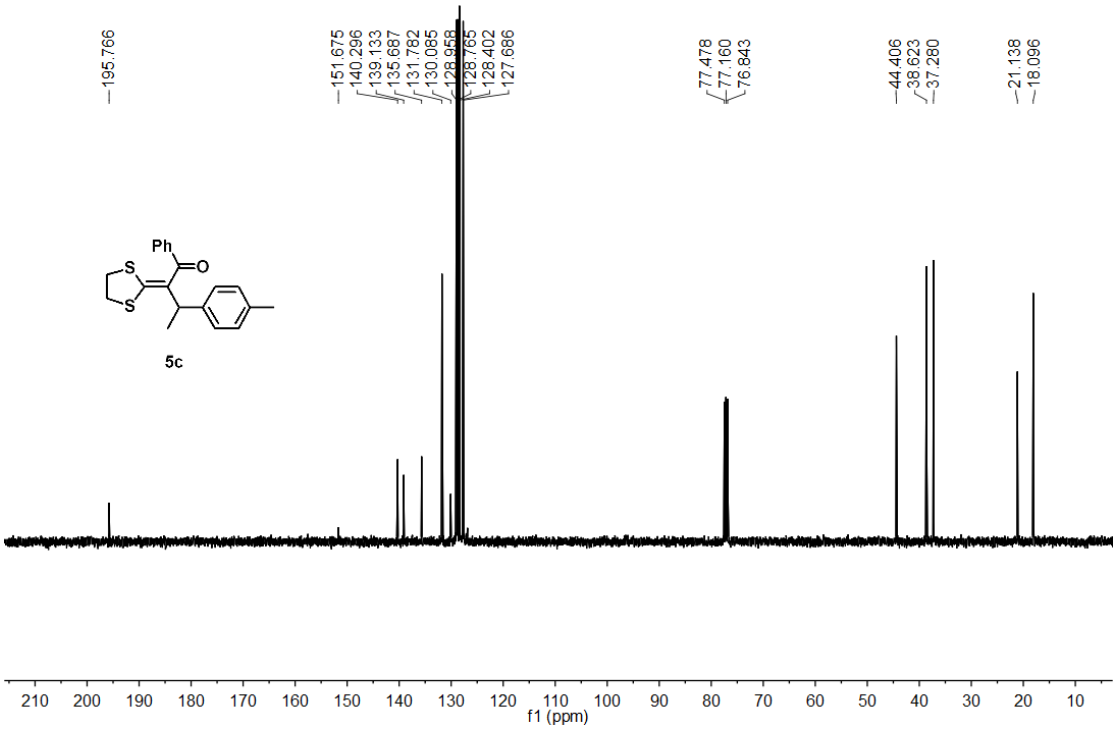
yq-1235
13C NMR (yq-1235 in CDCl3)



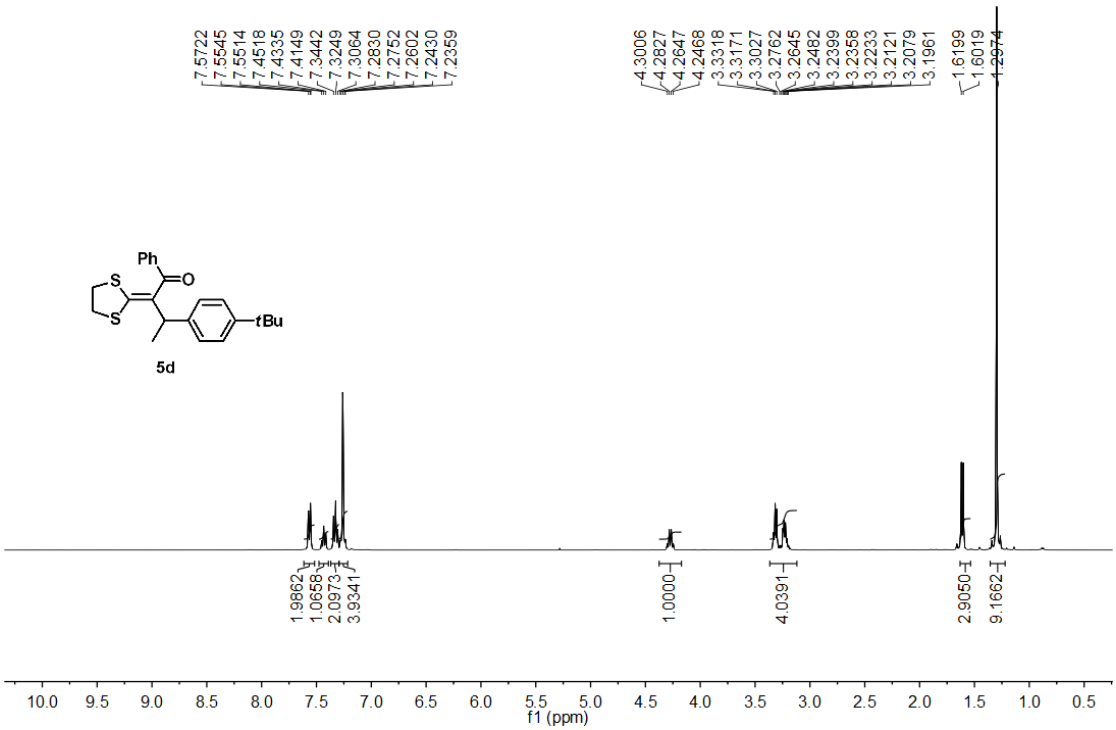
yq-1223
1H NMR (yq-1223 in CDCl3)



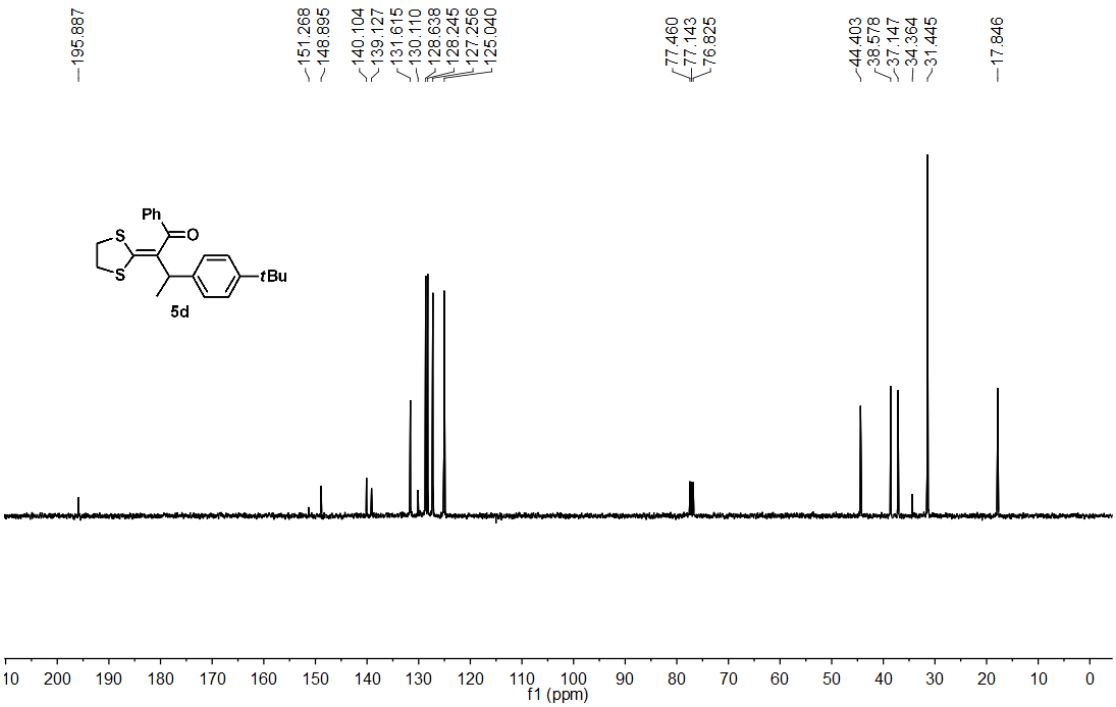
yq-1223-2
13C NMR (yq-1223-2 in CDCl3)



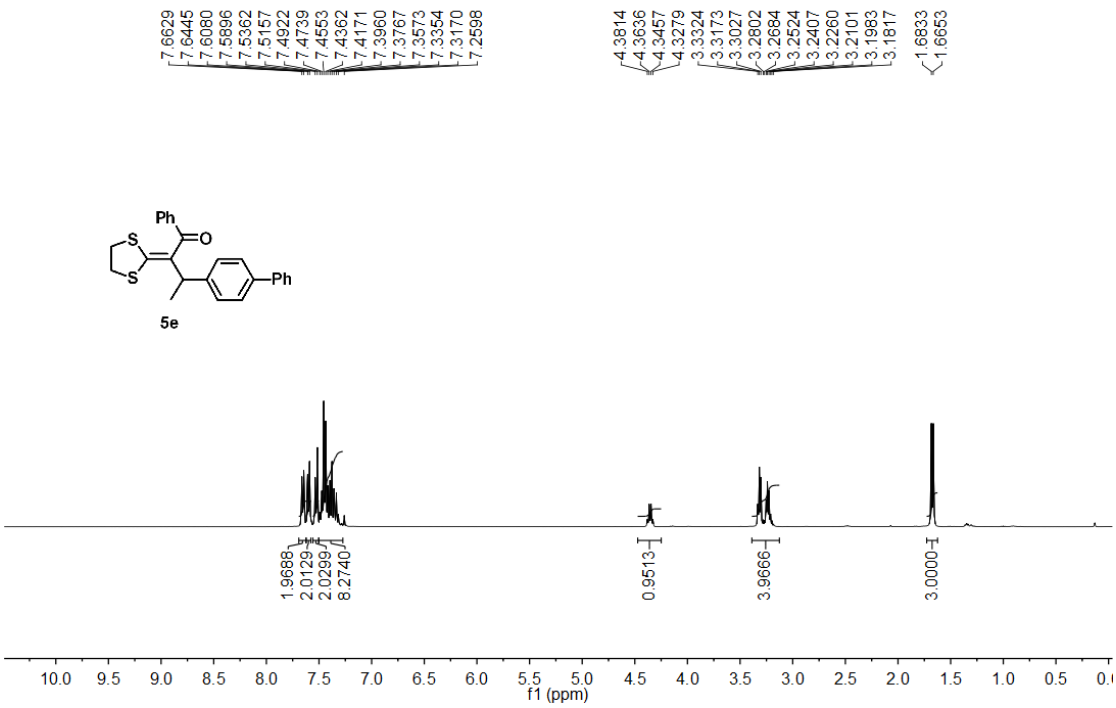
yq-1249
1H NMR yq-1249 in CDCl3



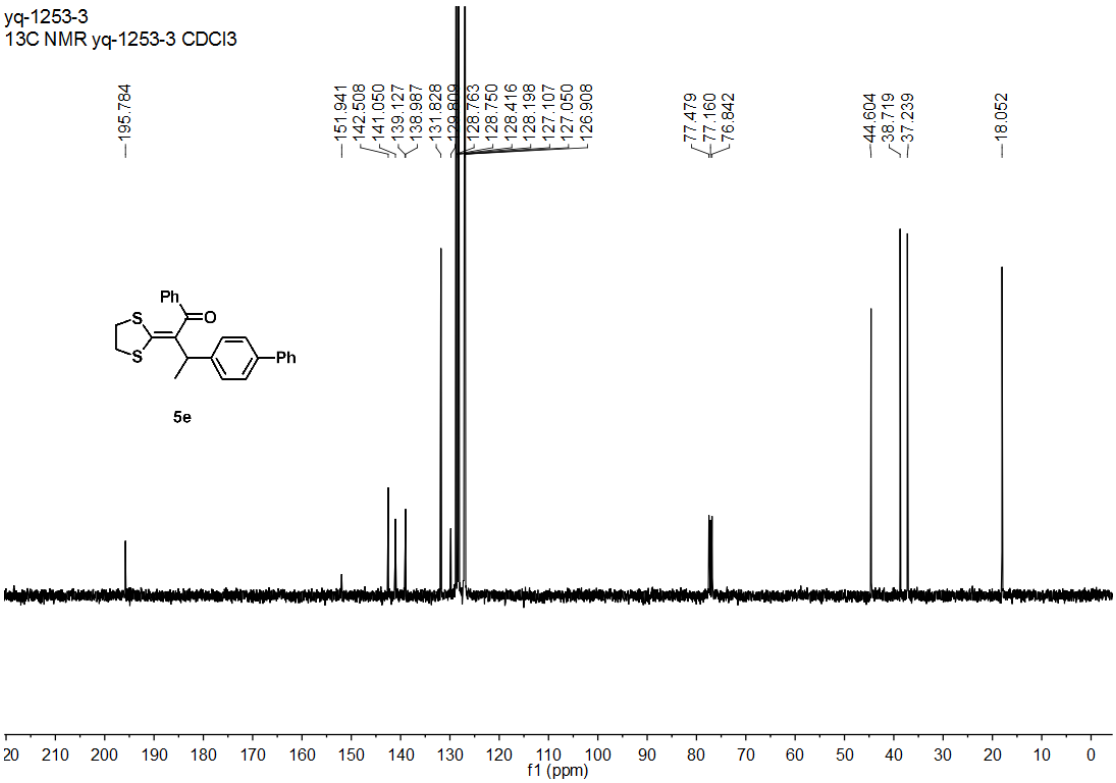
yq-1249
13C NMR yq-1249 CDCl3



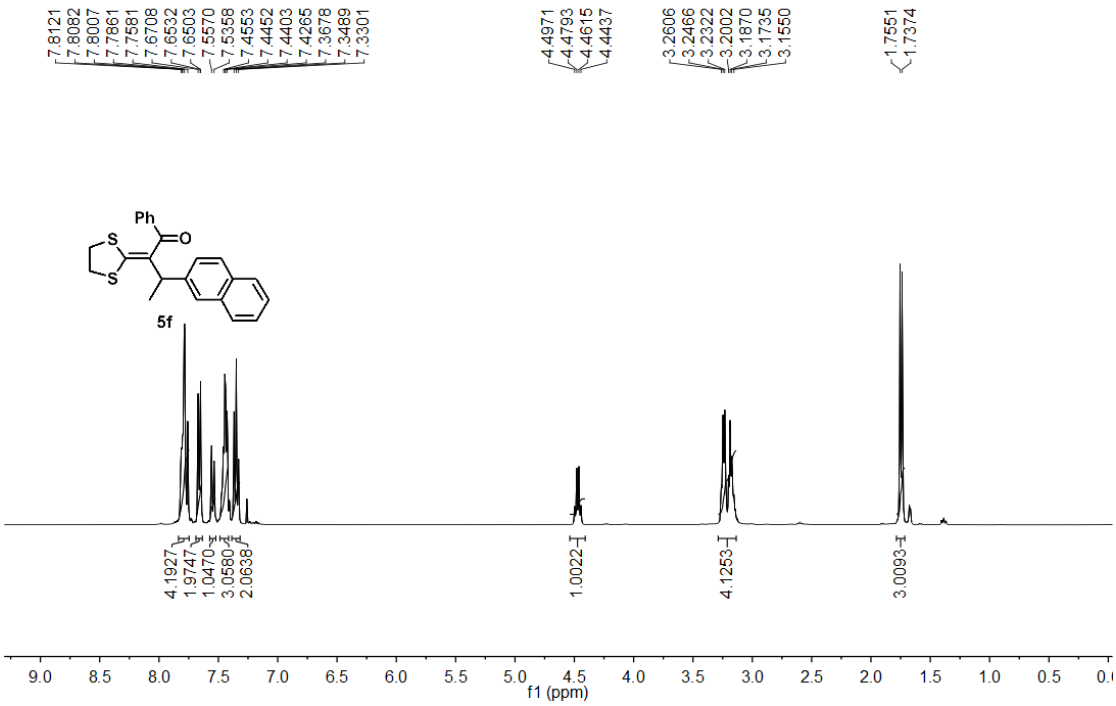
yq1253-2
1H NMR yq1253-2 in CDCl3



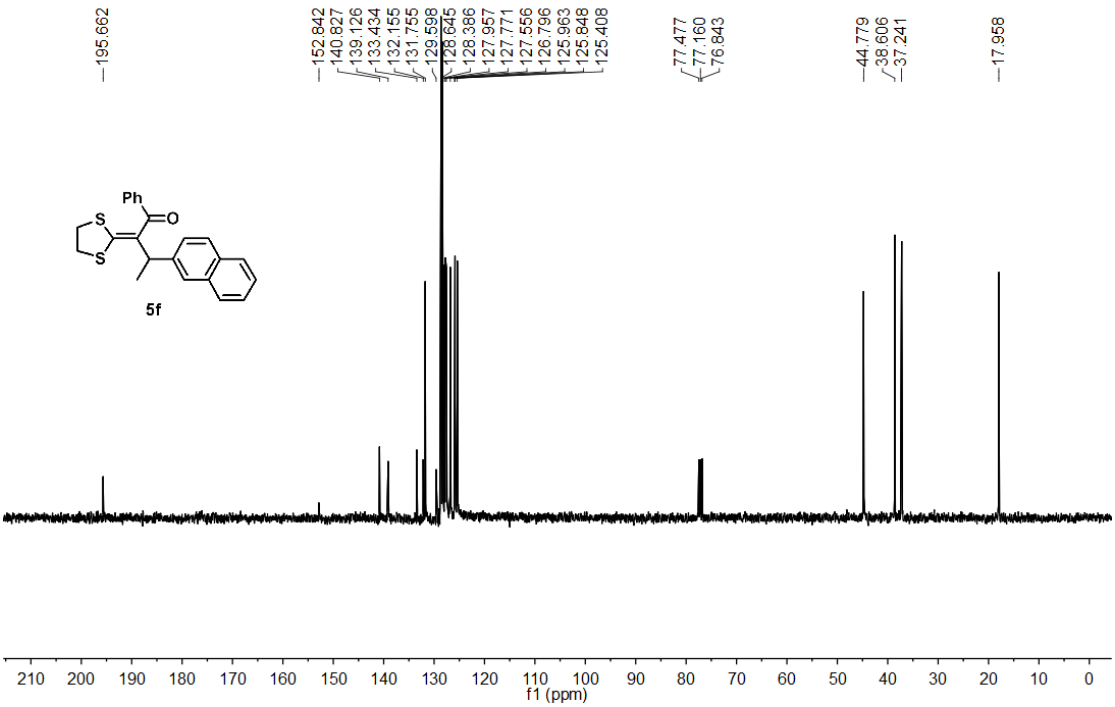
yq-1253-3
13C NMR yq-1253-3 CDCl3



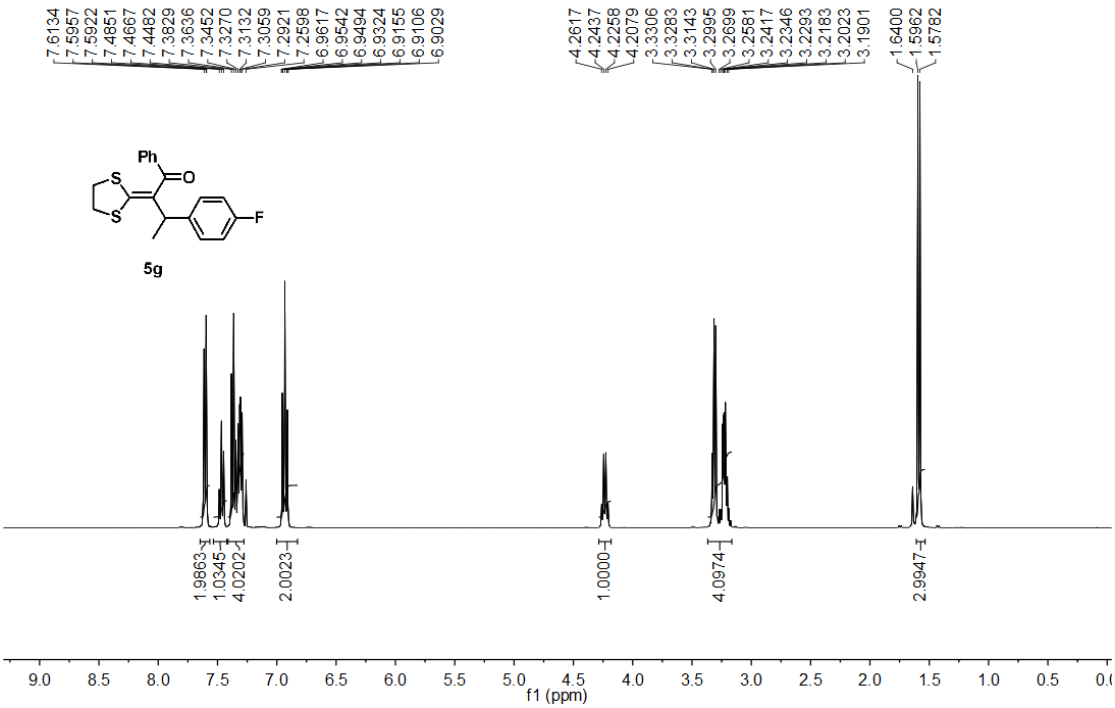
yq-1260-4
1H NMR yq-1260-4 in cdcl3



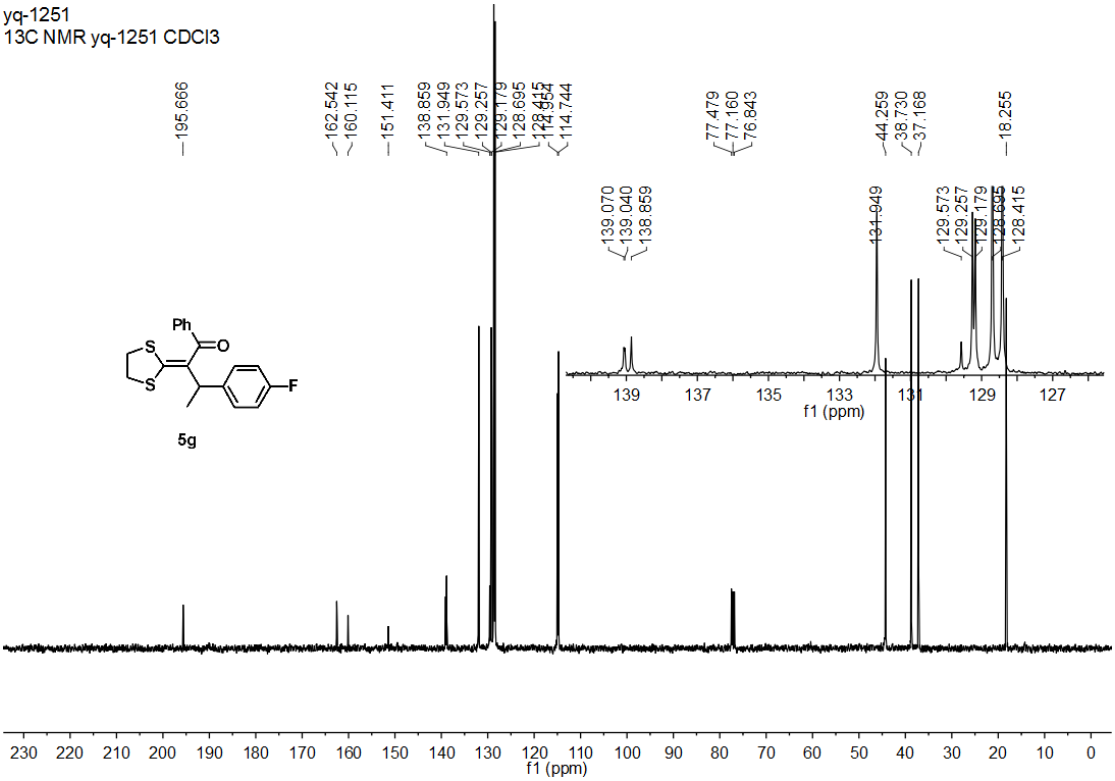
yq-1260-4
13C NMR yq-1260-4 CDCl3



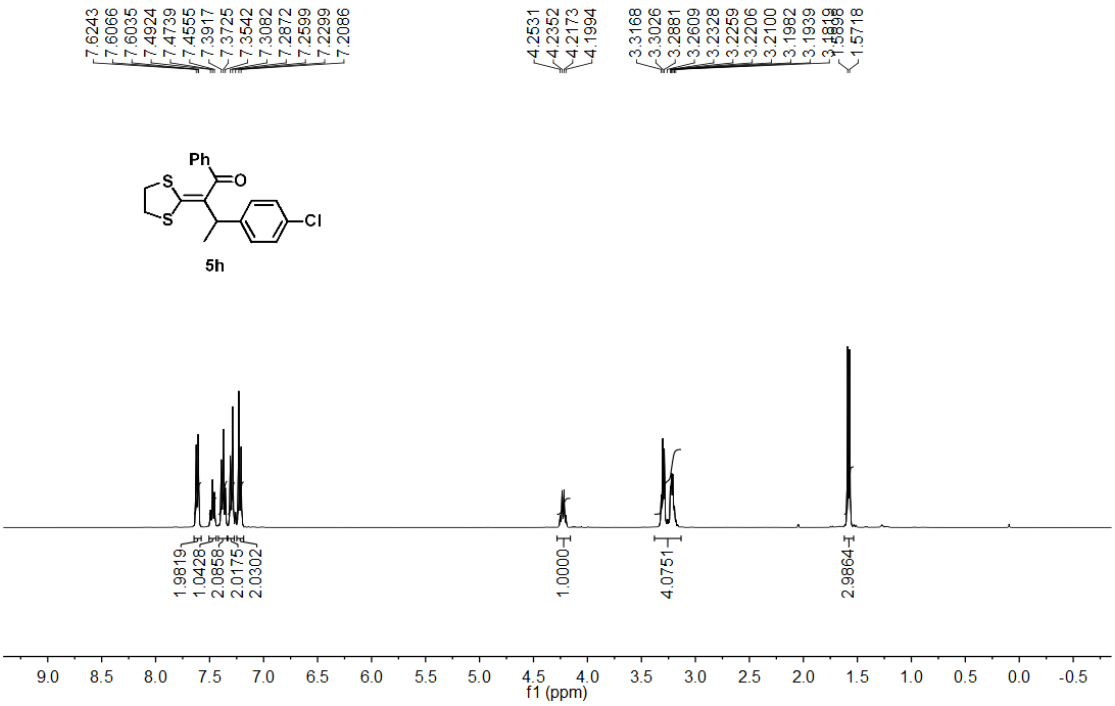
yq-1251-1
1H NMR yq-1251-1 in CDCl3



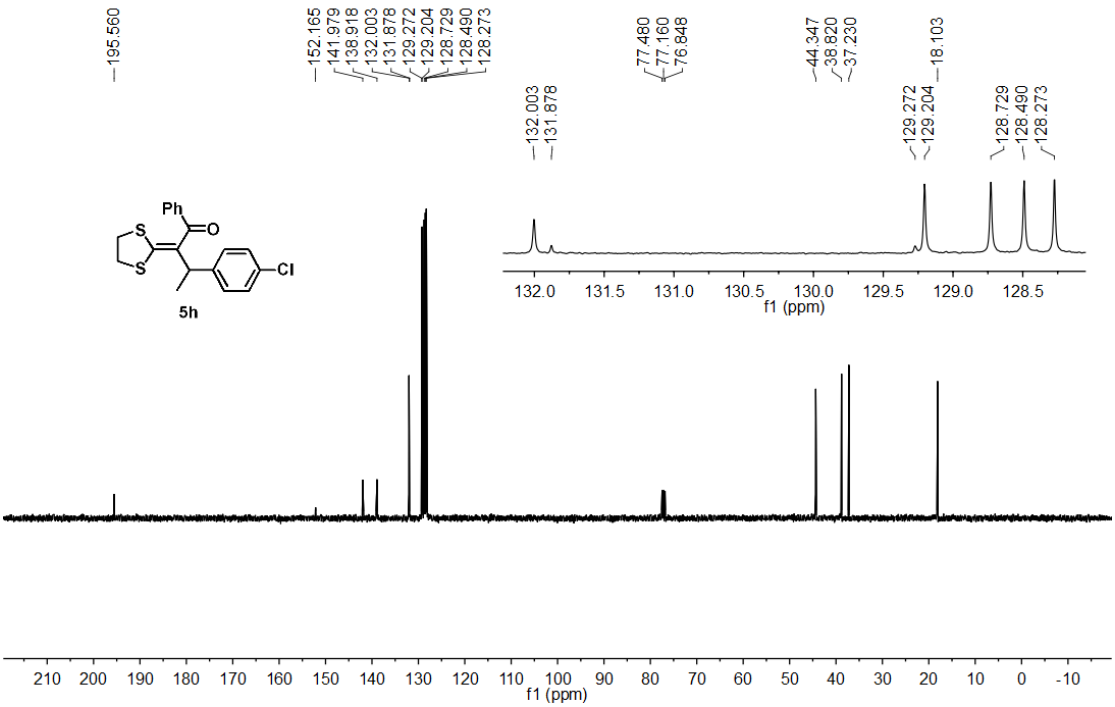
yq-1251
13C NMR yq-1251 CDCl3



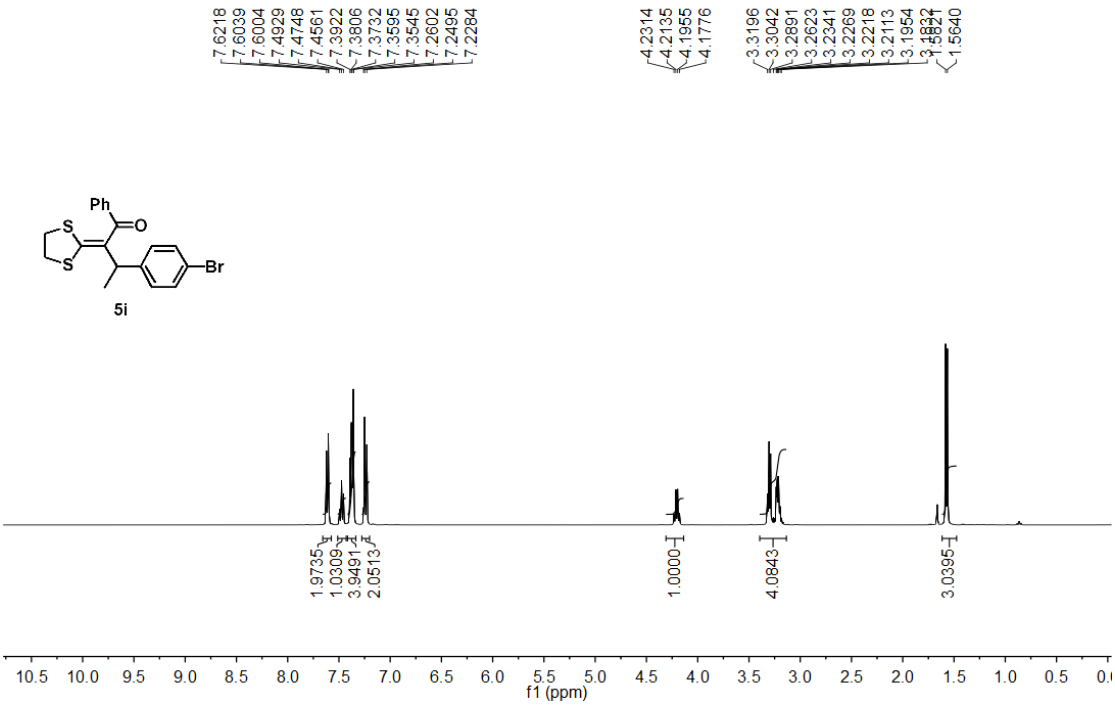
yq-1224
1H NMR (yq-1224 in CDCl3)



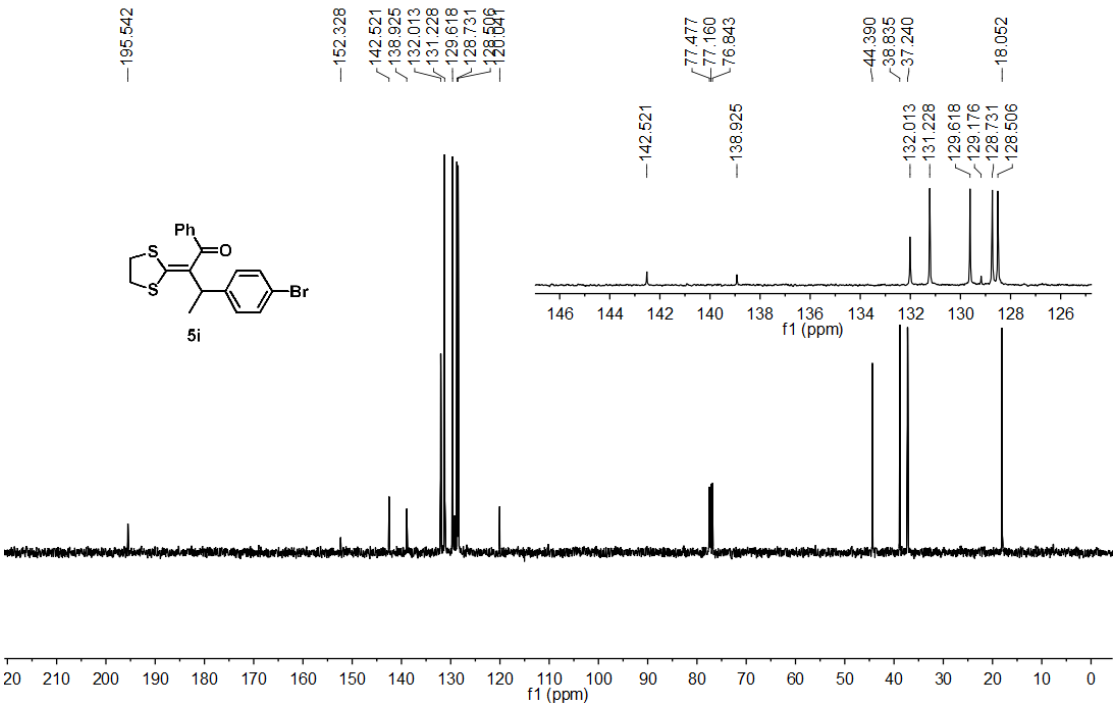
yq-1224
13C NMR (yq-1224 in CDCl3)



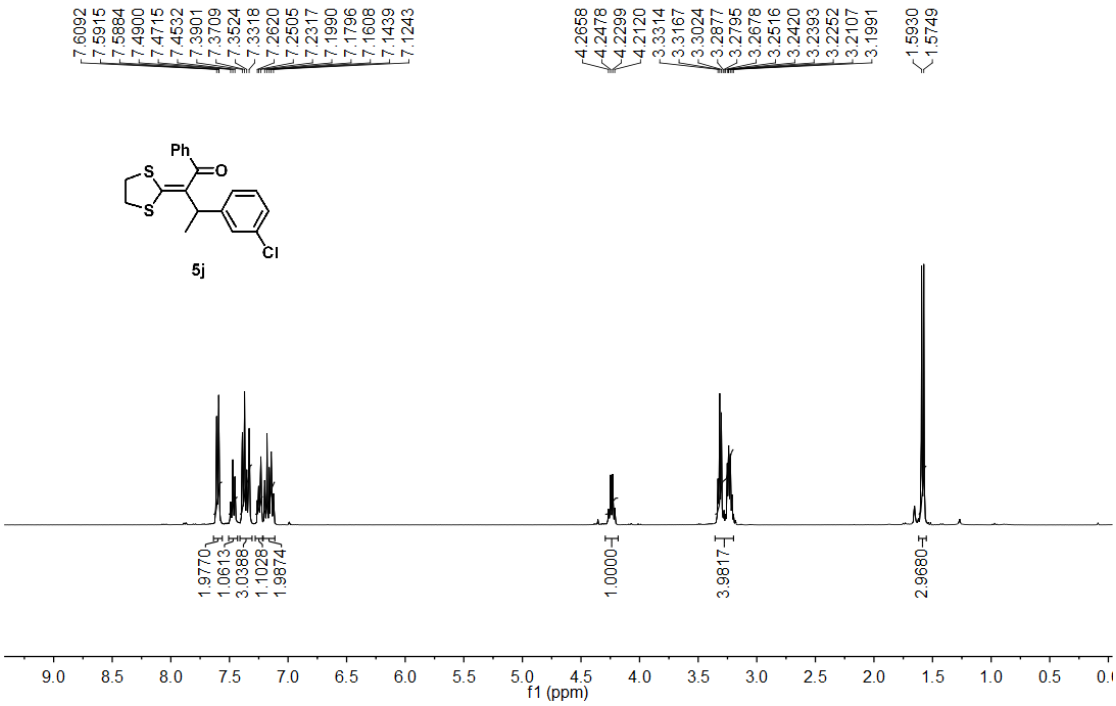
yq-1250
1H NMR yq-1250 in CDCl3



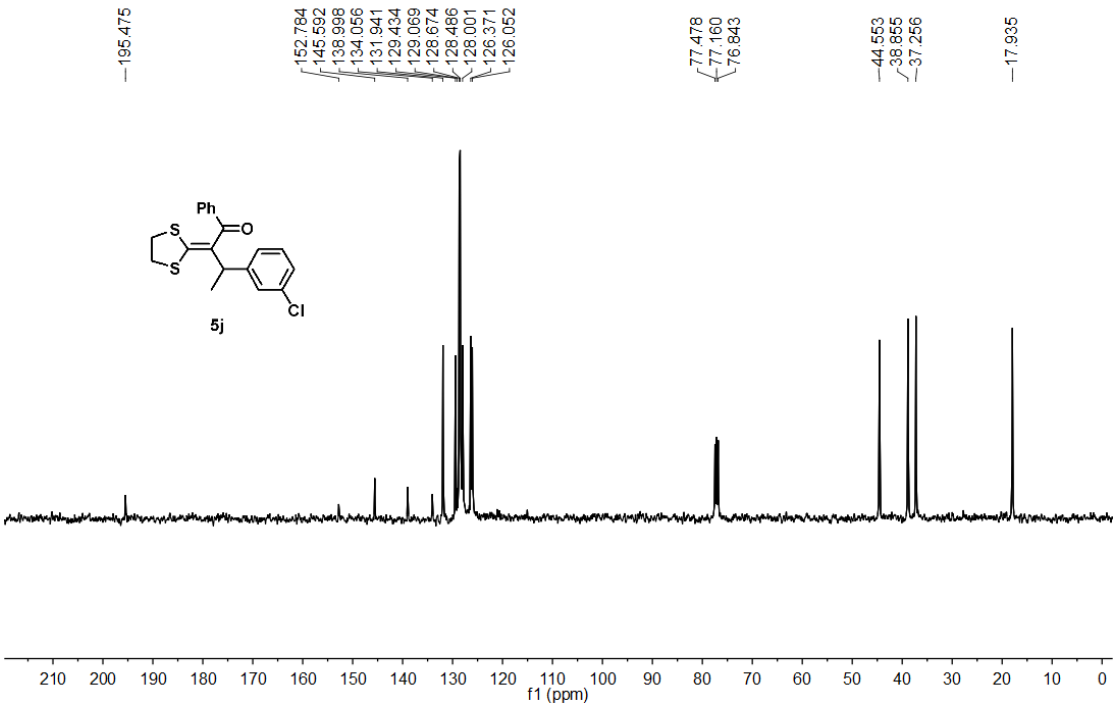
yq-1250
13C NMR yq-1250 CDCl3



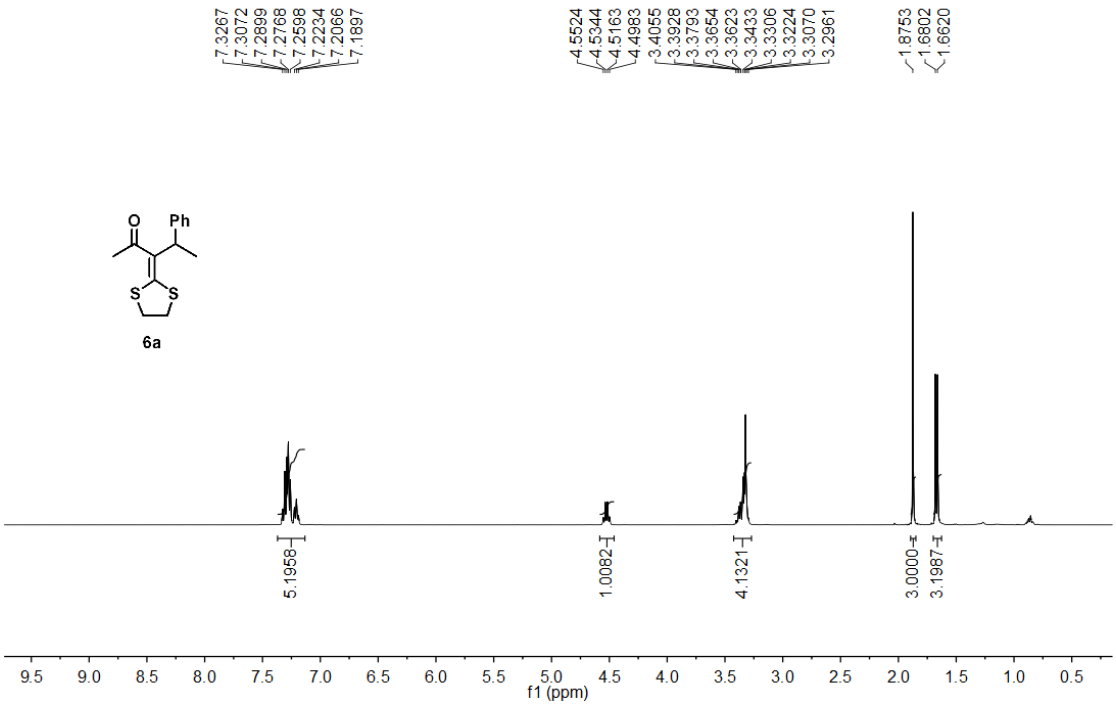
yq-1220-1
1H NMR yq-1220-1 in CDCl3



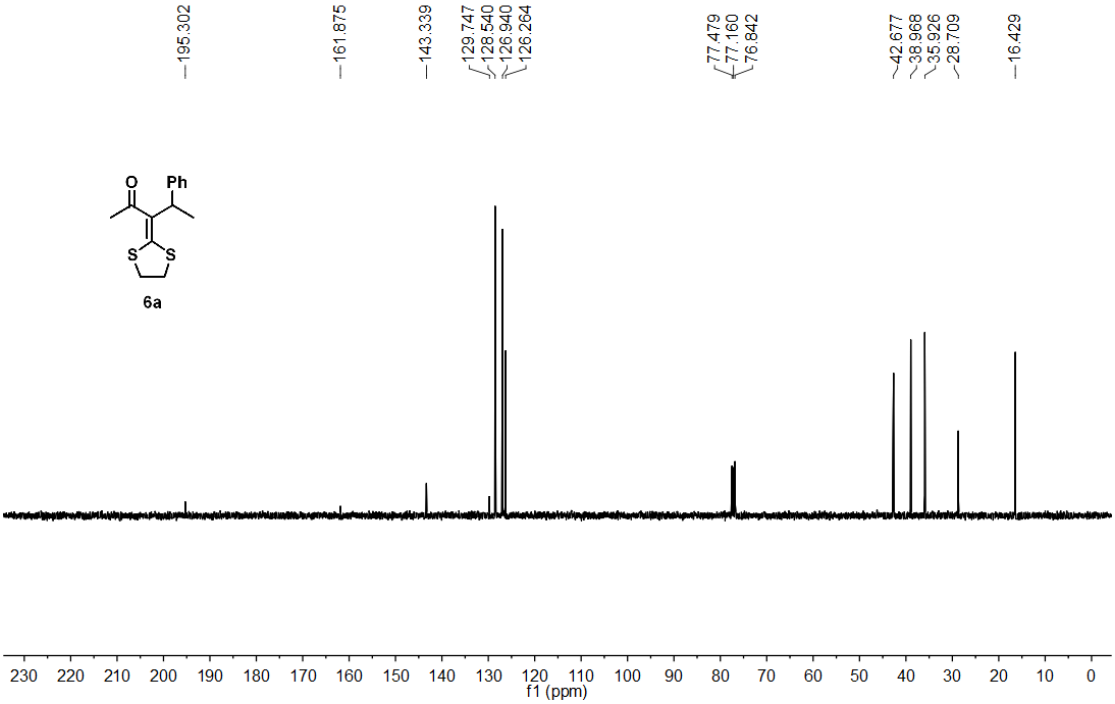
yq-1220-1
13C NMR yq-1220-1 CDCl3



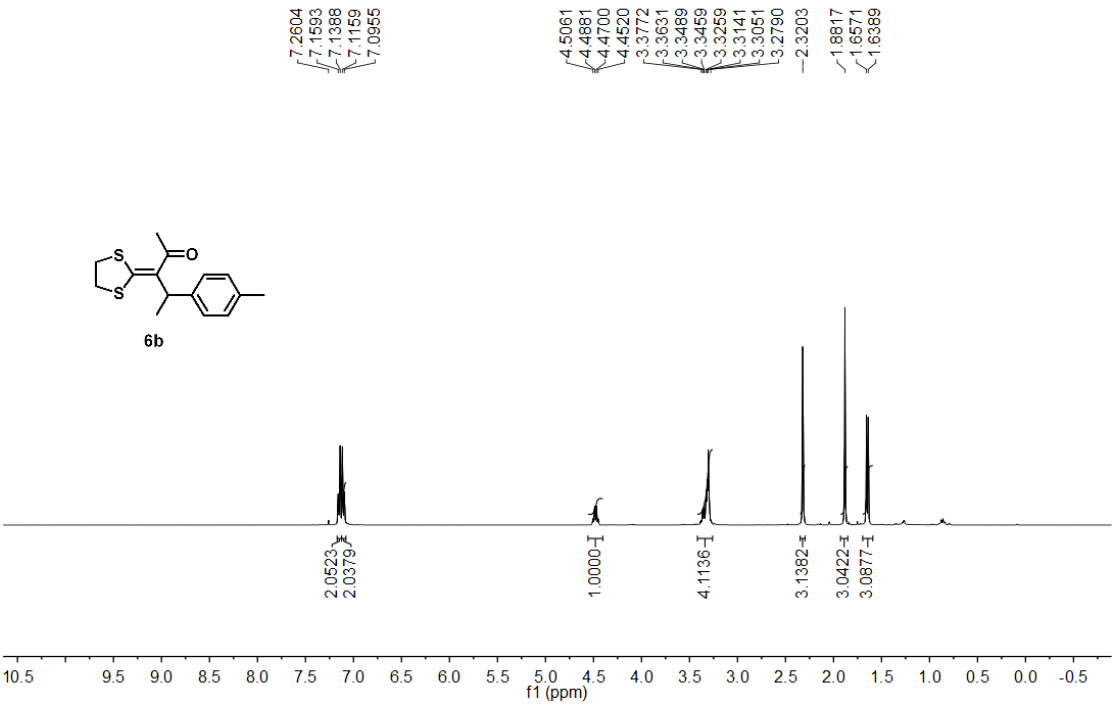
yq-130924
1H NMR yq-130924 in CDCl3



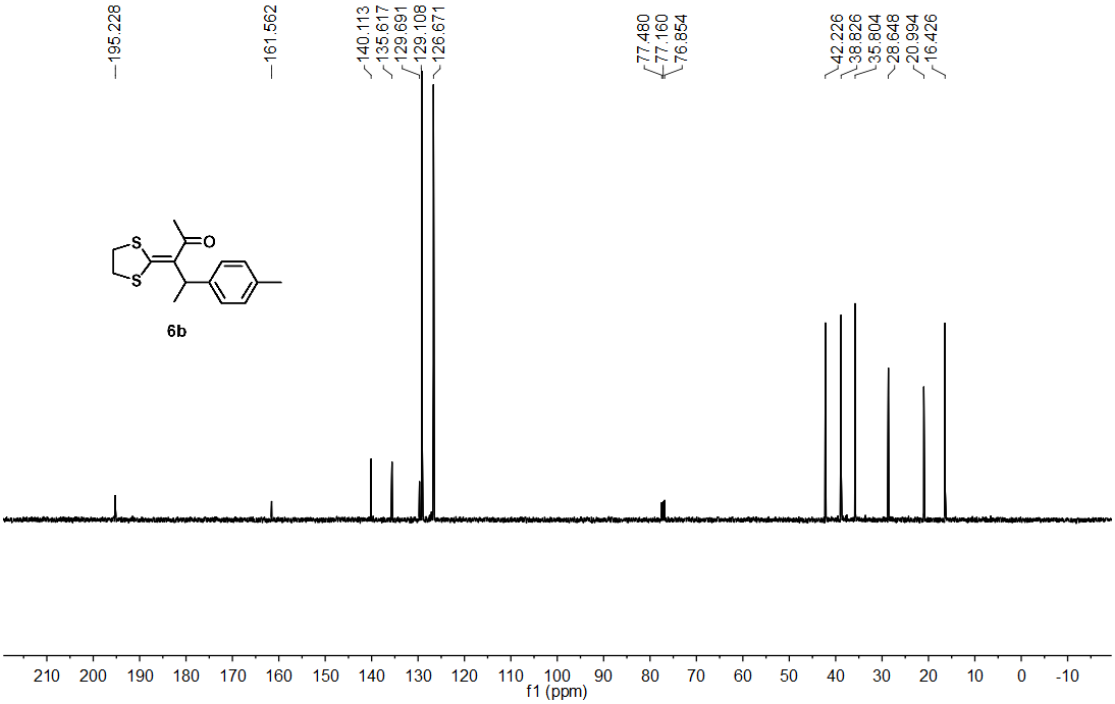
yq-130924
13C NMR yq-130924 CDCl3



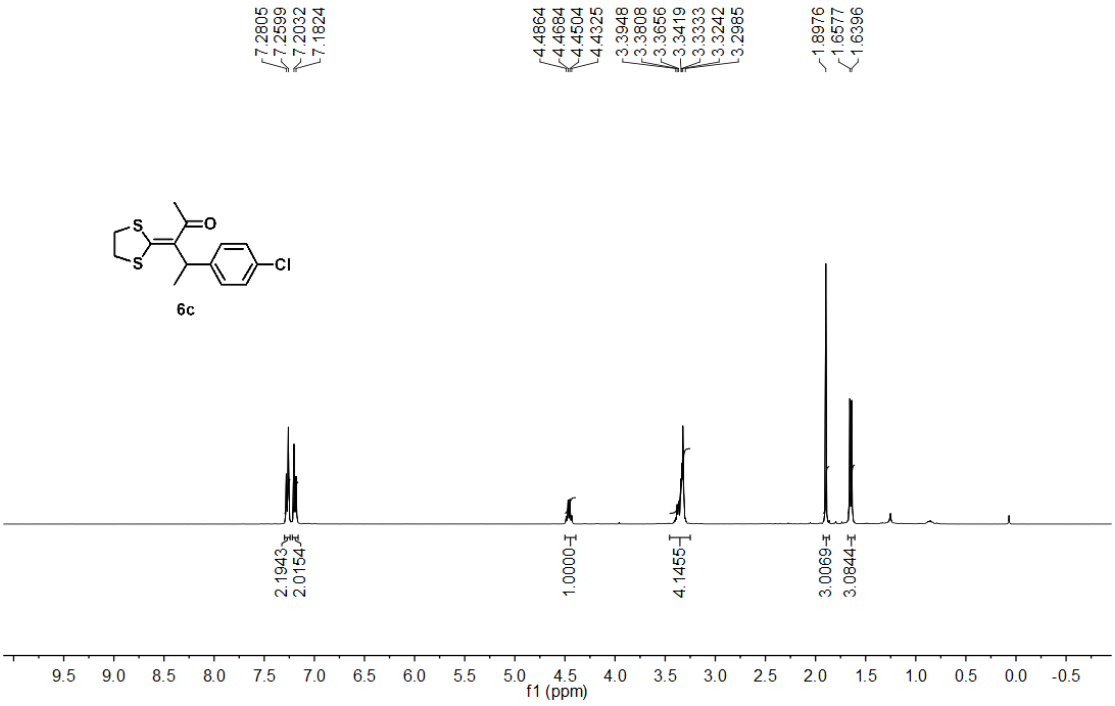
yq-1167
1H NMR (yq-1167 in CDCl3)



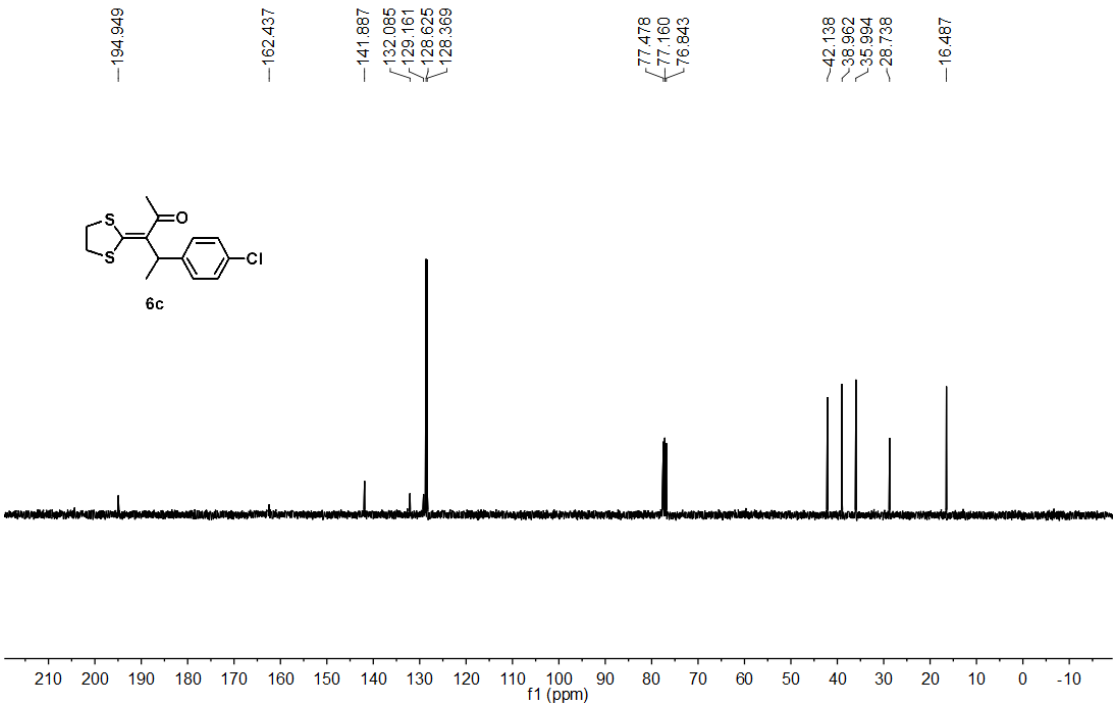
yq-1167
13C NMR (yq-1167 in CDCl3)



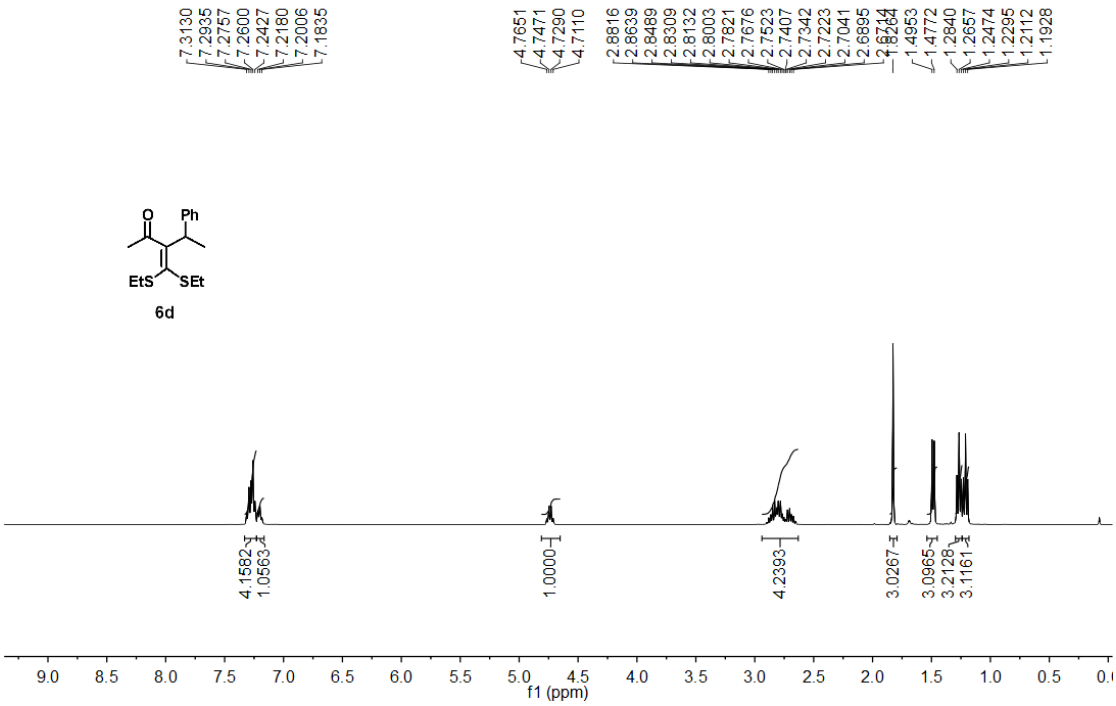
yq-1168
1H NMR (yq-1168 in CDCl3)



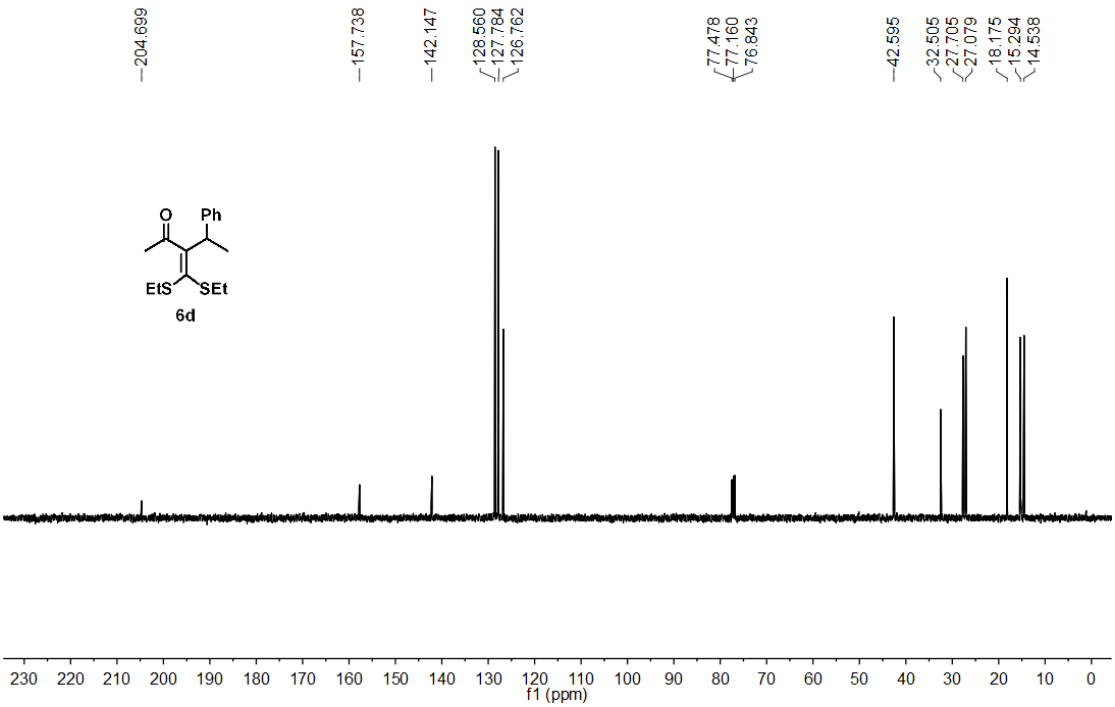
yq-1168
13C NMR (yq-1168 in CDCl3)



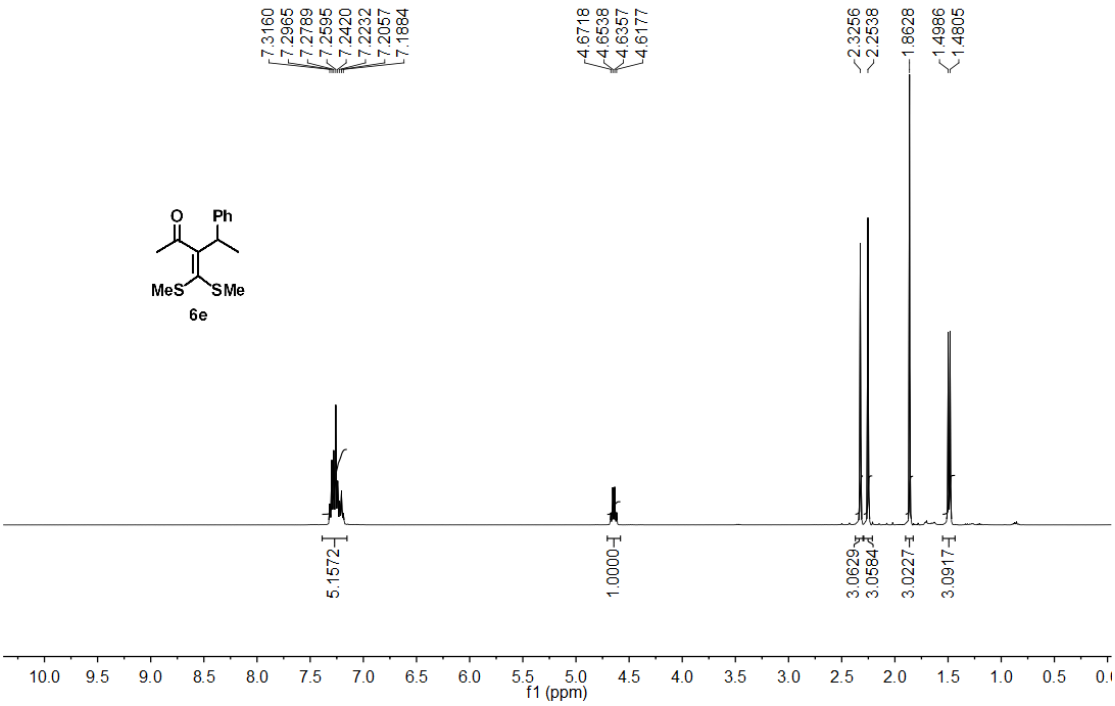
yq-1161-5
1H NMR yq-1161-5 in CDCl3

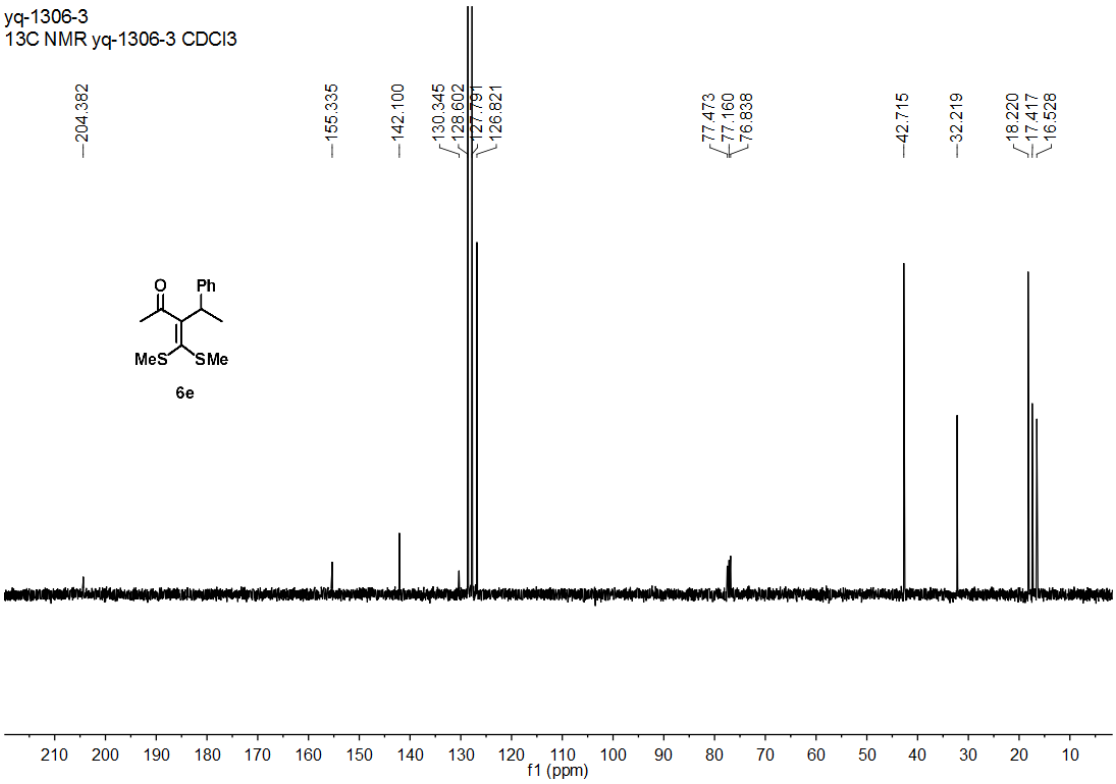


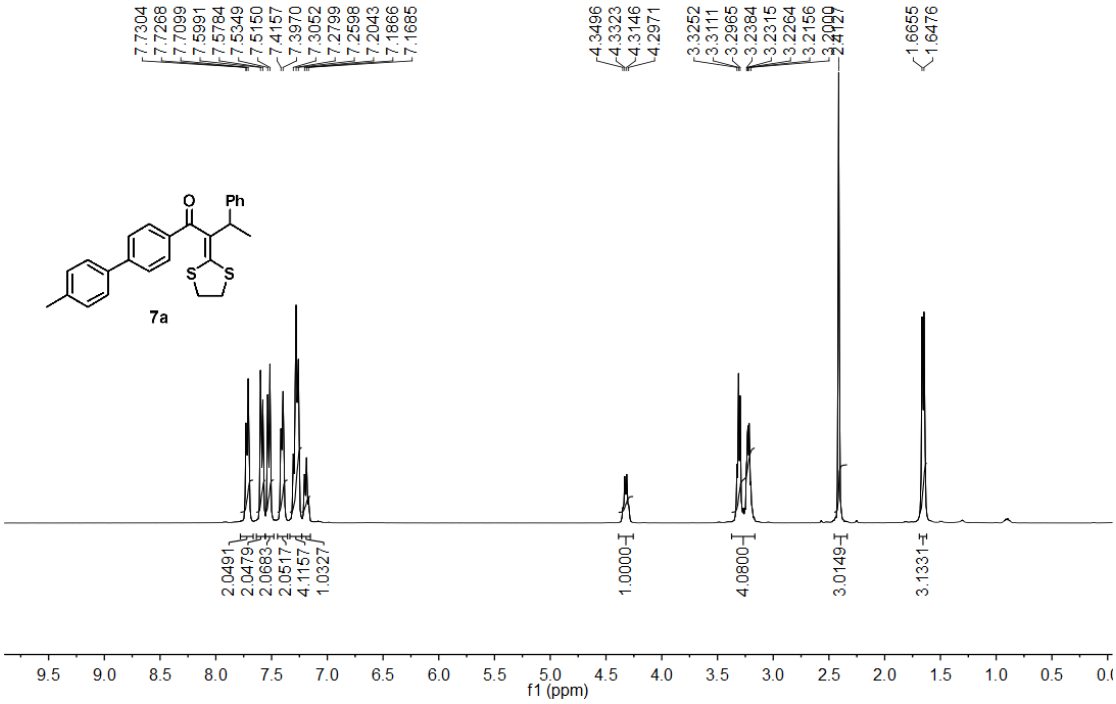
yq-1161-5
13C NMR yq-1161-5 CDCl3



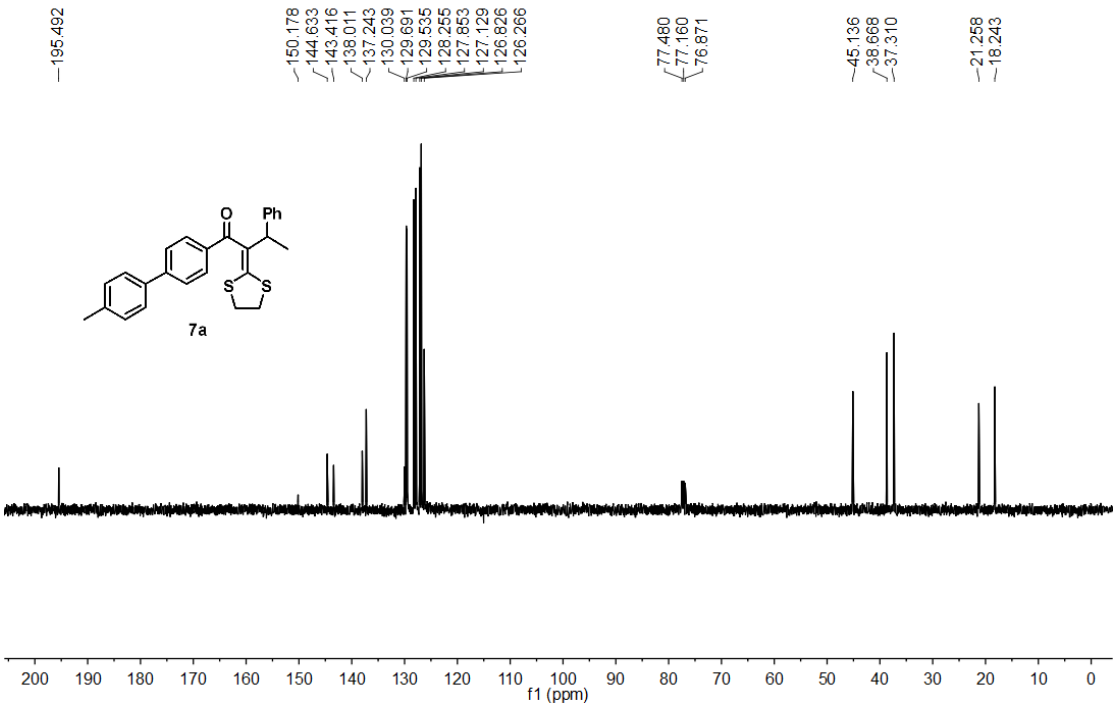
yq-1306-3
1H NMR yq-1306-3 in CDCl3



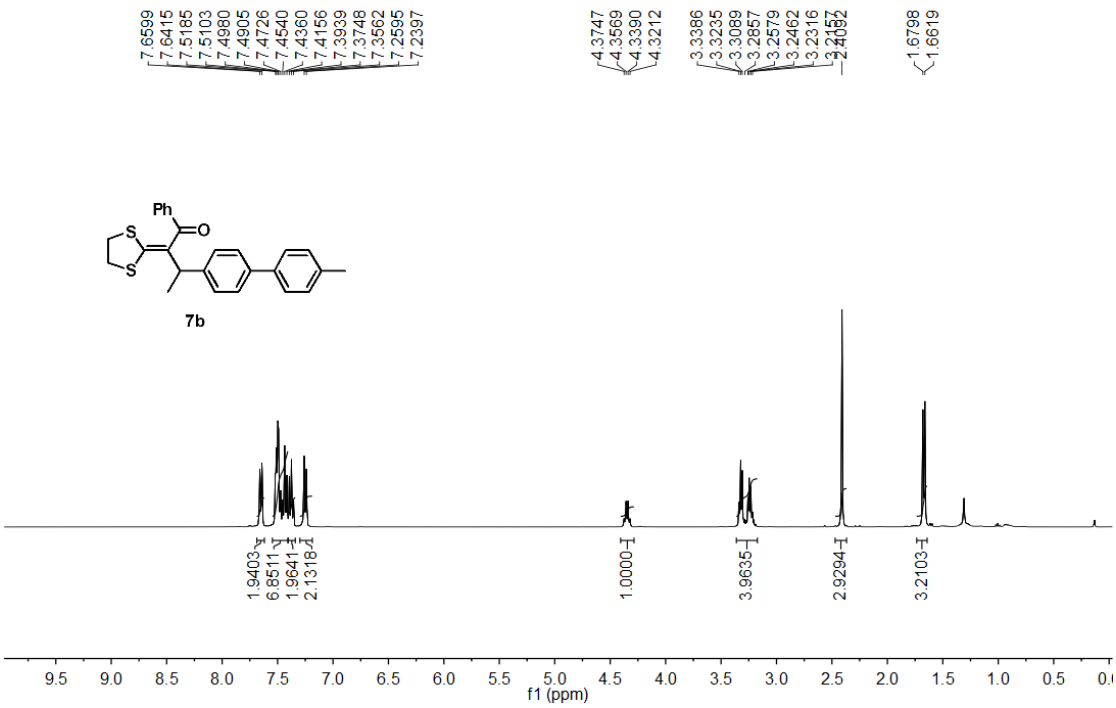

yq-1306-3
13C NMR yq-1306-3 CDCl3
204.382
155.335
142.100
130.345
128.602
127.791
126.821
77.473
77.160
76.838
42.715
32.219
18.220
17.417
16.528
O
Ph
MeS
SMe
6e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


yq-1331-3
1H NMR yq-1331-3 in CDCl3
7.7304
7.7268
7.7099
7.5991
7.5784
7.5349
7.5150
7.4157
7.3970
7.3052
7.2799
7.2598
7.2043
7.1866
7.1685
4.3496
4.3323
4.3146
4.2971
3.3252
3.3111
3.2965
3.2384
3.2315
3.2264
3.2156
3.2009
2.4127
1.6655
1.6476
O
Ph
S
S
7a
2.0491
2.0479
2.0683
2.0517
4.1157
1.0327
1.0000
4.0800
3.0149
3.1331
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

yq-1331-3
13C NMR yq-1331-3 CDCl3



yq-1356
1H NMR yq-1356 in CDCl3



yq-1356
13C NMR yq-1356 CDCl3