Intramolecular trapping of the spiro radicals to unusual cyclization products from the usual migration substrates

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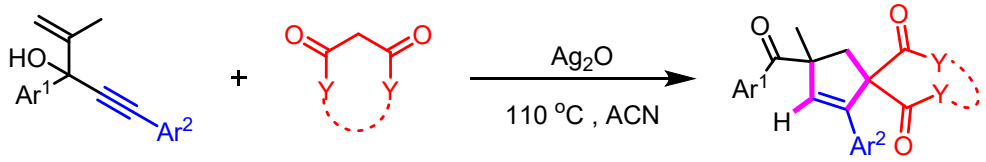
1. General Information

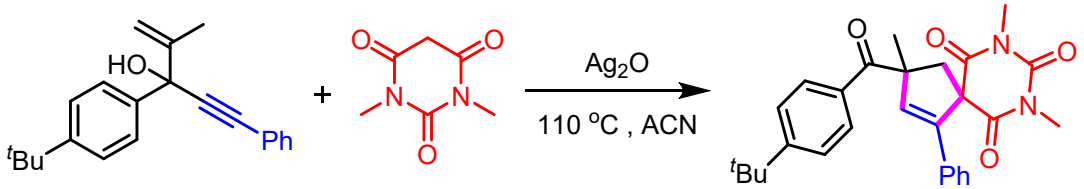
Commercially available reagents and solvents were of reagent grade quality without any further purification. Analytical thin-layer chromatography (TLC) was performed on 0.2 mm coated silica gel plates (HSGF 254) and visualized using a UV lamp (254 nm). Flash column chromatography was performed using silicycle silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR were recorded on magnet system 400'54 ascend purchased from Bruker Biospin AG. ESI-MS spectra were recorded on Agilent Q-TOF 6520.

2. General Procedure for Intramolecular Trapping of the Spiro Radicals to Unusual Spirocyclic Products



In an 15 mL oven-dried pressure sealed tube, a mixture of 1,4-enyne (1 mmol), 1,3-dicarbonyl compound (1.5 mmol, 1.5 equiv), Ag_2O (2 mmol, 2 equiv) and acetonitrile (3 mL) was heated to 110 ℃ for 6h. Thereafter, the reaction mixture was quenched with saturated solution of NH_4Cl (30 mL) and extracted with EtOAc (30 mL). The organic layer was collected, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The corresponding spirocyclic compound was isolated by column chromatography on silica gel using petroleum ether and EtOAc as eluent.

3. Gram-Scale Synthesis of 3



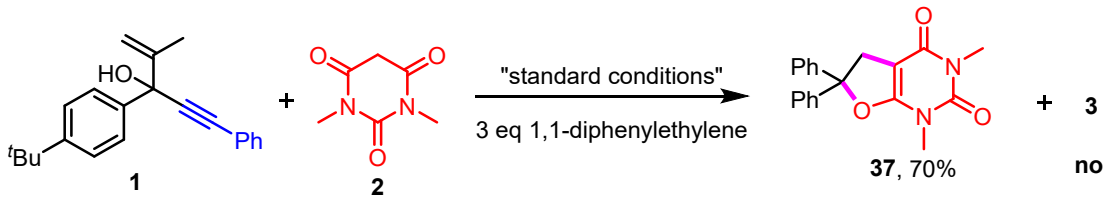
1, 1.00 g **2**, 0.77 g **3**, 1.34 g, 89%

In a 35 mL oven-dried pressure sealed tube, a mixture of 1,4-enyne **1** (1.00 g, 3.29 mmol), 1,3-dimethylbarbituric acid **2** (0.77 g, 4.94 mmol), Ag_2O (1.51 g, 6.58 mmol) and acetonitrile (10 mL) was heated to 110 °C for 6h. Thereafter, the reaction mixture was quenched with saturated solution of NH_4Cl (100 mL) and extracted with EtOAc (100 mL). The organic layer was collected, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as the eluent to obtain spirocyclic compound **3** (1.34 g, 89%).

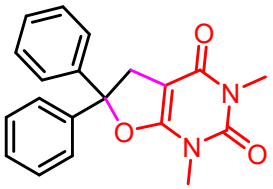
4. Mechanistic Studies

4-1) Radical-trapping experiments

4-1-1: 1,1-diphenylethylene was added



In an 15 mL oven-dried pressure sealed tube, a mixture of 1,4-enyne **1** (304.2 mg, 1 mmol), 1,3-dimethylbarbituric acid **2** (234.1 mg, 1.5 mmol), Ag_2O (459.6 mg, 2 mmol), 1,1-diphenyl ethylene (540.3 mg, 3 mmol) and acetonitrile (3 mL) was heated to 110 °C for 6h. There was no spirocyclic compound **3** was detected based on TLC analysis. However, a new by-product was detected. Then, the reaction mixture was quenched with saturated solution of NH_4Cl (30 mL) and extracted with EtOAc (30 mL). The organic layer was collected, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (4:1) as the eluent to obtain the radical trapping product **37** (280.7 mg, 70%).

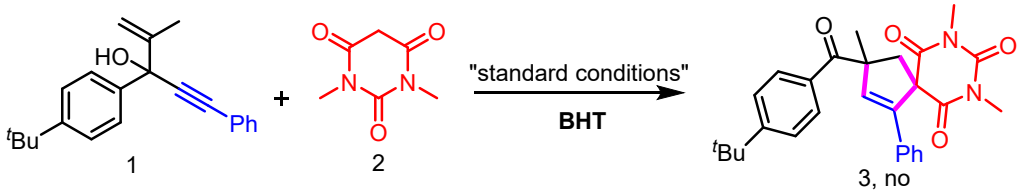


37

1,3-dimethyl-6,6-diphenyl-5,6-dihydrofuro[2,3-*d*]pyrimidine-2,4(1*H*,3*H*)-dione (37):[1]

White solid (280.7 mg, 70%); Eluent: petroleum ether/ethyl acetate 4:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.31 (m, 10H), 3.81 (s, 2H), 3.48 (s, 3H), 3.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.23, 160.15, 151.74, 142.96, 128.66, 128.43, 125.73, 97.69, 85.97, 40.67, 29.70, 28.08; HRMS (ESI-TOF) Calcd for $C_{20}H_{18}N_2O_3Na$ $[M+Na]^+$ calcd 357.1210, found 357.1211.

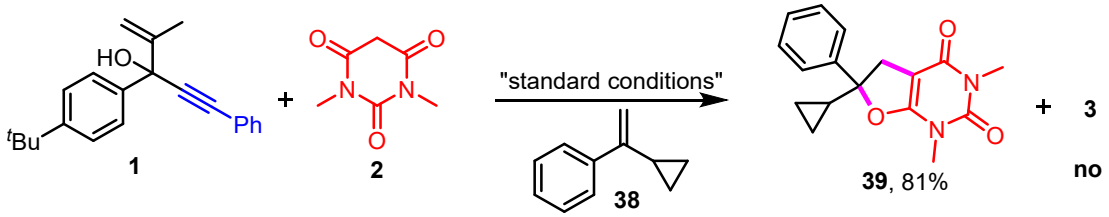
4-1-2: BHT (butylated hydroxytoluene) was added



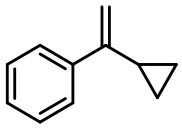
In an 15 mL oven-dried pressure sealed tube, a mixture of 1,4-enyne **1** (304.2 mg, 1 mmol), 1,3-dimethylbarbituric acid **2** (234.1 mg, 1.5 mmol), Ag_2O (459.6 mg, 2 mmol), BHT (661.1 mg, 3 mmol) and acetonitrile (3 mL) was heated to 110 °C for 6h. There was no spirocyclic compound **3** detected.

4-2) Radical clock experiment

4-2-1: 1,3-Dimethylbarbituric acid **2** was involved



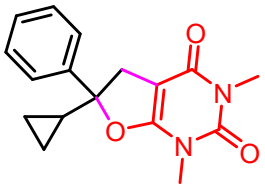
In a 15 mL oven-dried pressure sealed tube, a mixture of 1,4-enyne **1** (304.2 mg, 1 mmol), 1,3-dimethylbarbituric acid **2** (234.1 mg, 1.5 mmol), Ag_2O (459.6 mg, 2 mmol), radical probe **38** (432.3 mg, 3 mmol) and acetonitrile (3 mL) was heated to 110 °C for 6h. Then, the reaction mixture was quenched with saturated solution of NH_4Cl (30 mL) and extracted with EtOAc (30 mL). The organic layer was collected, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (4:1) as the eluent to obtain the radical trapping product **39** (362.2 mg, 81%). No target product **3** was detected.



38

(1-cyclopropylvinyl) benzene (38):[2]

colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 - 7.72 (m, 2H), 7.52 - 7.46 (m, 2H), 7.45 - 7.39 (m, 1H), 5.47 (s, 1H), 5.12 (s, 1H), 1.85 - 1.75 (m, 1H), 1.01 - 0.95 (m, 2H), 0.79 - 0.72 (m, 2H).

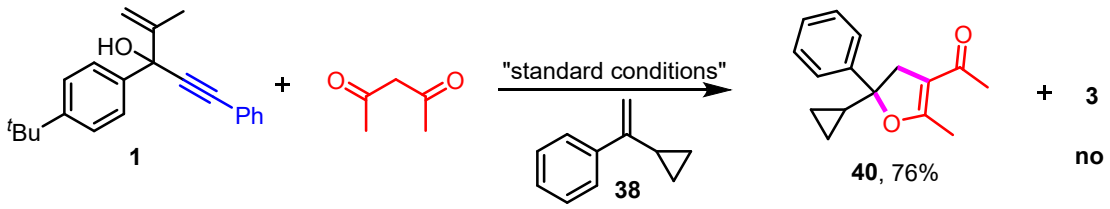


39

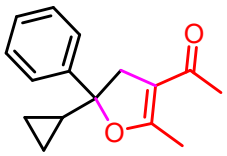
6-cyclopropyl-1,3-dimethyl-6-phenyl-5,6-dihydrofuro[2,3-*d*]pyrimidine-2,4(1*H*,3*H*)-dione (39):

White solid (362.2 mg, 81%); Eluent: petroleum ether/ethyl acetate 4:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 - 7.21 (m, 5H), 3.35 (s, 3H), 3.23 (s, 3H), 3.21 - 3.11 (m, 2H), 1.48 - 1.40 (m, 1H), 0.62 - 0.48 (m, 2H), 0.44 - 0.30 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.61, 158.38, 149.79, 140.89, 126.49, 126.20, 123.01, 95.70, 83.91, 35.81, 27.61, 26.06, 18.98, -0.00, -0.38; HRMS (ESI-TOF) Calcd for $C_{17}H_{18}N_2O_3Na$ $[M+Na]^+$ calcd 321.1210, found 321.1212.

4-2-2: Acetylacetone was involved



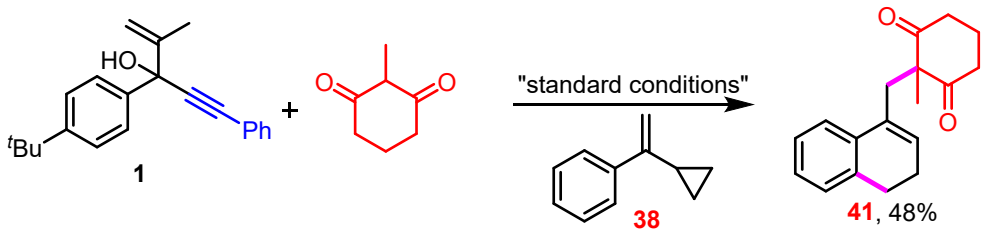
In a 15 mL oven-dried pressure sealed tube, a mixture of 1,4-enyne **1** (304.2 mg, 1 mmol), acetylacetone (150.1 mg, 1.5 mmol), Ag_2O (459.6 mg, 2 mmol), radical probe **38** (432.3 mg, 3 mmol) and acetonitrile (3 mL) was heated to 110 °C for 6h. There was no spirocyclic compound **3** obtained according to TLC analysis. The reaction mixture was quenched with saturated solution of NH_4Cl (30 mL) and extracted with EtOAc (30 mL). The organic layer was collected, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (15:1) as the eluent to obtain the radical trapping product **40** (276.0 mg, 76%).



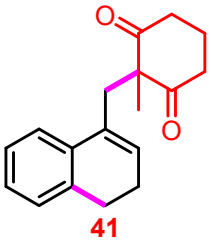
40

1-(5-cyclopropyl-2-methyl-5-phenyl-4,5-dihydrofuran-3-yl)ethan-1-one (40): Yellow oil (276.0 mg, 76%); Eluent: petroleum ether/ethyl acetate 15:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 - 7.32 (m, 4H), 7.28 (tt, J = 6.2, 1.3 Hz, 1H), 3.14 (s, 2H), 2.30 (s, 3H), 2.19 (s, 3H), 1.42 - 1.34 (m, 1H), 0.60 - 0.52 (m, 1H), 0.49 - 0.42 (m, 2H), 0.42 - 0.35 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.78, 164.86, 143.80, 126.64, 125.77, 123.30, 110.52, 88.47, 41.16, 27.80, 19.85, 13.40, -0.00, -0.52. HRMS (ESI-TOF) Calcd for $C_{16}H_{19}O_2$ $[M+H]^+$ calcd 243.1380, found 243.1382.

4-2-3: 2-Methylcyclohexane-1,3-dione was involved



In a 15 mL oven-dried and pressure sealed tube, a mixture of 1,4-enyne **1** (304.2 mg, 1 mmol), 2-methylcyclohexane-1,3-dione (189.1 mg, 1.5 mmol), Ag_2O (459.6 mg, 2 mmol), radical clock vinylcyclopropane substrate **38** (540.3 mg, 3 mmol) and acetonitrile (3 mL) was heated to 110 ℃ for 6 h. There was no spirocyclic compound **3** detected. Thereafter, the reaction mixture was quenched with saturated solution of NH_4Cl (20 mL) and extracted with EtOAc (20 mL). The organic layer was collected, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (5:1) as the eluent to obtain the radical trapping product **41** (128.7 mg, 48%).

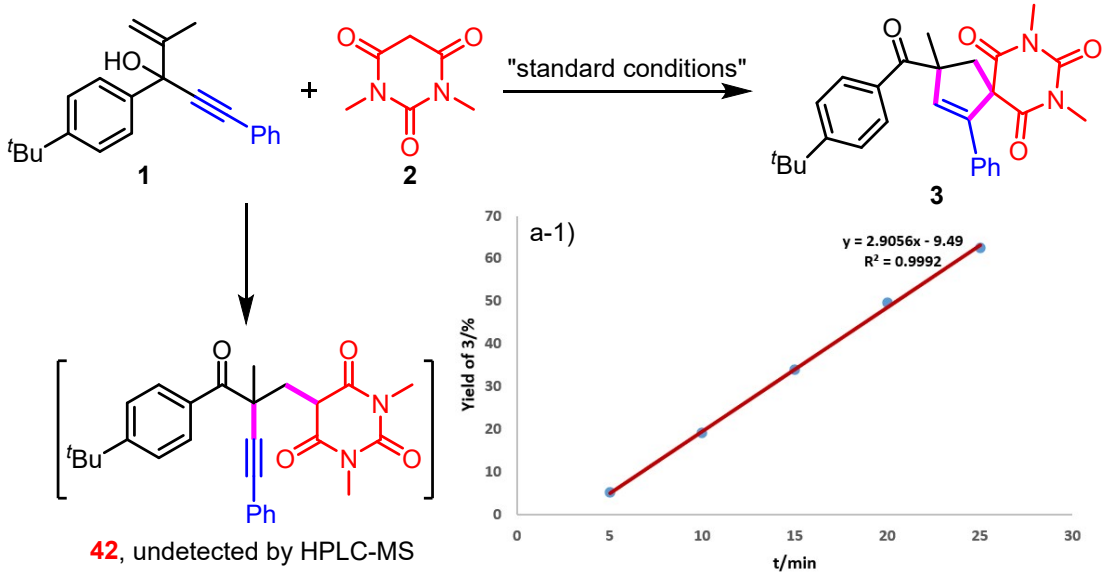


2-((3,4-dihydronaphthalen-1-yl)methyl)-2-methylcyclohexane-1,3-dione (**41**):

Yellow oil (128.7 mg, 48%); Eluent: petroleum ether/ethyl acetate 5:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 - 7.08 (m, 2H), 7.08 - 7.01 (m, 2H), 5.79 - 5.63 (m, 1H), 3.58 (s, 0.2H), 2.91 (s, 1.8H), 2.60 (t, J = 7.9 Hz, 2H), 2.52 - 2.39 (m, 2H), 2.35 - 2.26 (m, 2H), 2.15 - 2.06 (m, 2H), 1.83 - 1.75 (m, 1H), 1.74 - 1.63 (m, 1H), 1.21 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 211.32, 136.33, 134.07, 132.57, 129.73, 127.66, 127.13, 126.42, 123.35, 64.42, 40.83, 39.45, 28.38, 23.13, 21.72, 16.96; HRMS (ESI): m/z for $C_{18}H_{20}O_2Na$ $[M+Na]^+$ calcd 291.1356, found 291.1410.

4-3) Verification experiments of intermediates

4-3-1: monitoring of the migration product **42**



In a 15 mL oven-dried pressure sealed tube, a mixture of 1,4-enyne **1** (304.2 mg, 1 mmol), 1,3-dimethylbarbituric acid **2** (234.1 mg, 1.5 mmol), Ag_2O (459.6 mg, 2 mmol), and acetonitrile (3 mL) was heated to 110 °C. Aliquots of 0.1 mL were removed from the cell every 5 minutes and the yields of the product were determined by HPLC analysis with **3** as the external standard.

Time [min]	5	10	15	20	25
Yield of **3** (%)	5.11	19.21	33.96	49.67	62.52

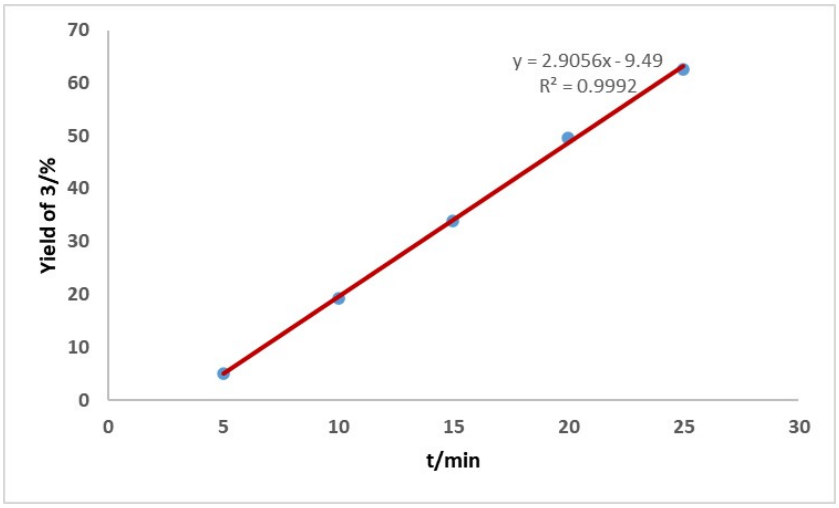
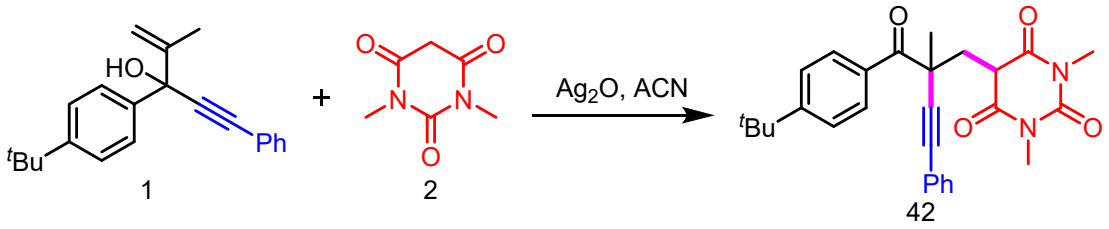


Figure S1 The yield of **3** at different reaction times

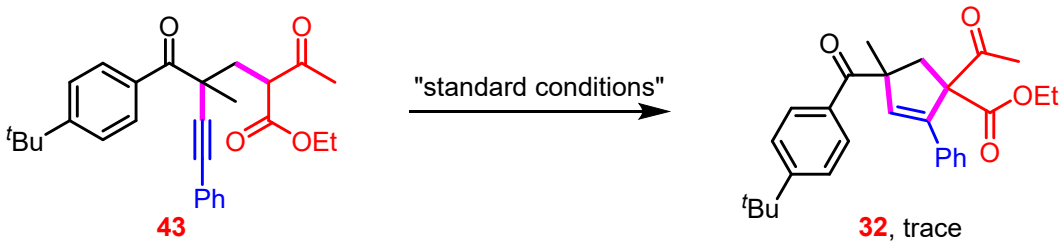
Table S1 Monitoring the migration product formation at lower temperature



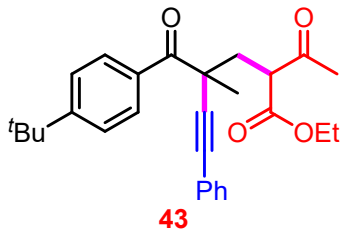
Entry	Temperature (°C)	Monitoring **42** by HRMS		
		10 min	30 min	2 h
1	90	undetected	undetected	undetected
2	70	undetected	undetected	undetected
3	50	undetected	undetected	undetected

Reaction conditions: **1** (1 mmol, 304.2 mg), **2** (1.5 mmol, 234.1 mg), Ag_2O (2 mmol, 463.5 mg), ACN (3 mL).

4-3-2: Verification experiments using migration product **43** as the starting material



In a 15 mL oven-dried pressure sealed tube, a mixture of migration product **43** (304.2 mg, 1 mmol), Ag_2O (459.6 mg, 2 mmol), and acetonitrile (3 mL) was heated to 110 °C for 6 h. However, only trace amounts of corresponding product **32** was detected.



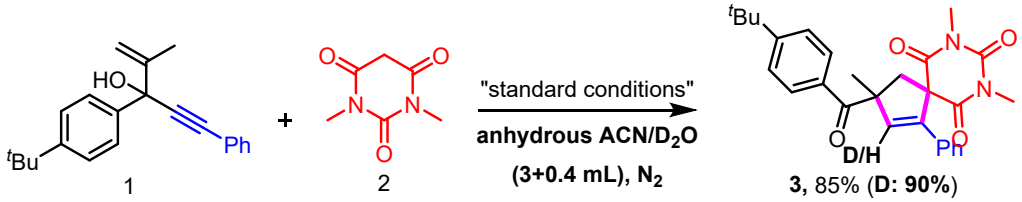
43

ethyl 2-acetyl-4-(4-(*tert*-butyl)benzoyl)-4-methyl-6-phenylhex-5-ynoate (43):

Yellow oil; Eluent: petroleum ether/ethyl acetate 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.38 - 7.33 (m, 2H), 7.32 - 7.27 (m, 3H), 4.20 - 3.98 (m, 2H), 3.81 (q, *J* = 5.7 Hz, 1H), 2.92 - 2.81 (m, 1H), 2.42 (dt, *J* = 14.1, 6.8 Hz, 1H), 2.31 (d, *J* = 48.3 Hz, 3H), 1.67 (s, 3H), 1.34 (s, 9H), 1.25 - 1.11 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 202.78, 197.77, 169.72, 156.70, 132.06, 131.42, 130.01, 128.47, 128.32, 125.15, 122.67, 90.86, 87.14, 61.53, 57.23, 45.84, 36.97, 35.13, 31.08, 29.47, 26.97, 13.91; HRMS (ESI): m/z for $C_{28}H_{32}O_4Na$ $[M+Na]^+$ calcd 455.2193, found 455.2198.

4-4) Isotope labeling experments:

4-4-1: 0.4 mL D_2O was added



In a 15 mL oven-dried pressure sealed tube, a mixture of 1,4-enyne **1** (304.2 mg, 1 mmol), 1,3-dimethylbarbituric acid **2** (234.1 mg, 1.5 mmol), Ag_2O (459.6 mg, 2 mmol), anhydrous acetonitrile (3 mL) and D_2O (0.4 mL) was heated to 110 °C. Thereafter, the reaction mixture was quenched with saturated solution of NH_4Cl (30 mL) and extracted with EtOAc (30 mL). The organic layer was collected, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as the eluent to obtain the isotope labeling product **3** and **D-3** (390.3 mg, 85%) (D: 90%).

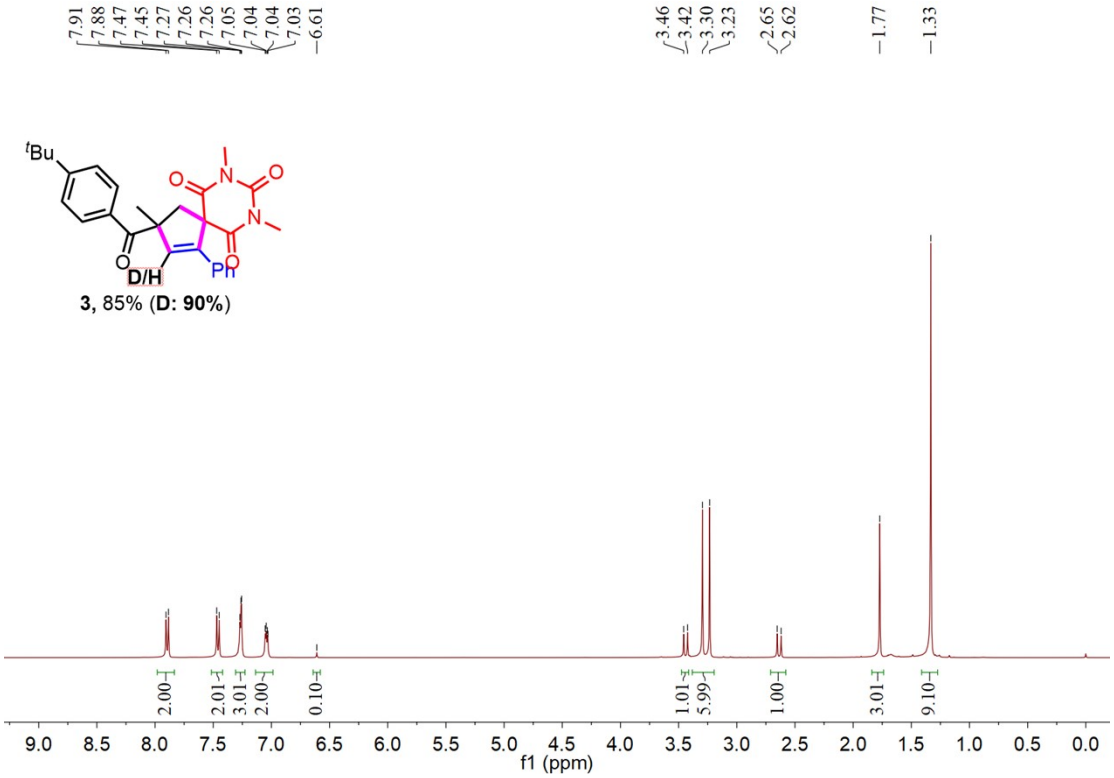
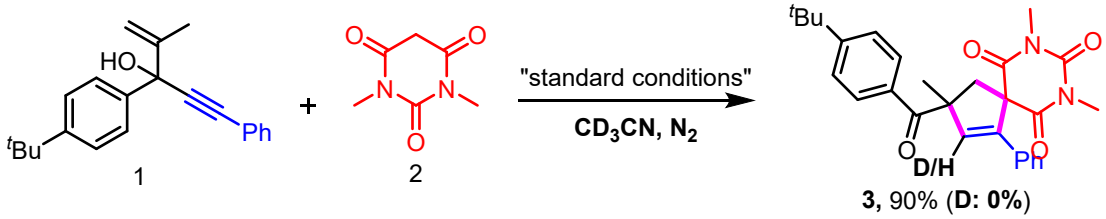


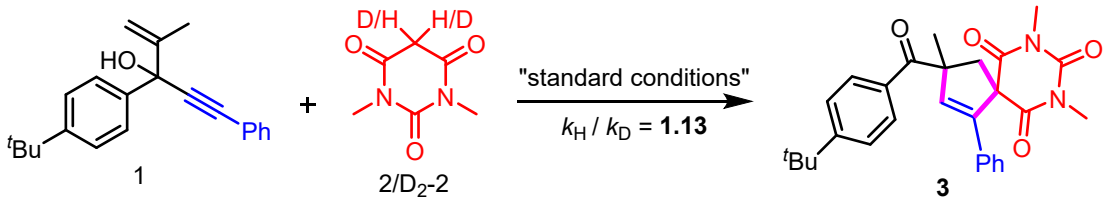
Figure S2 ^{1}H NMR analysis of electrochemically generated **3**/**[D]-3**

4-4-2: CD_3CN was used



In a 15 mL oven-dried pressure sealed tube, a mixture of 1,4-enyne **1** (304.2 mg, 1 mmol), 1,3-dimethylbarbituric acid **2** (234.1 mg, 1.5 mmol), Ag_2O (459.6 mg, 2 mmol) and CD_3CN (3 mL) was heated to 110 °C. Thereafter, the reaction mixture was quenched with saturated solution of NH_4Cl (30 mL) and extracted with EtOAc (30 mL). The organic layer was collected, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as the eluent to obtain the isotope labeling product **3** (412.4 mg, 90%) (D: 0%).

4-5) KIE experiments:



In a 15 mL oven-dried pressure sealed tube, a mixture of 1,4-enyne **1** (304.2 mg, 1 mmol), 1,3-dimethylbarbituric acid **2** or 1,3-dimethylbarbituric acid **D_2-2** (234.1 mg or 237.1 mg, 1.5 mmol), Ag_2O (459.6 mg, 2 mmol) and acetonitrile (3 mL) was heated to 110 °C. Aliquots of 0.1 mL were removed from the cell every 5 minutes and the yields of the product were determined by HPLC analysis with **3** as the external standard.

	Time [min]	5	10	15	20	25
Yield of **3** (%)	2 was used	5.11	19.21	33.96	49.67	62.52
	D_2-2 was used	5.87	17.70	30.52	44.21	56.88

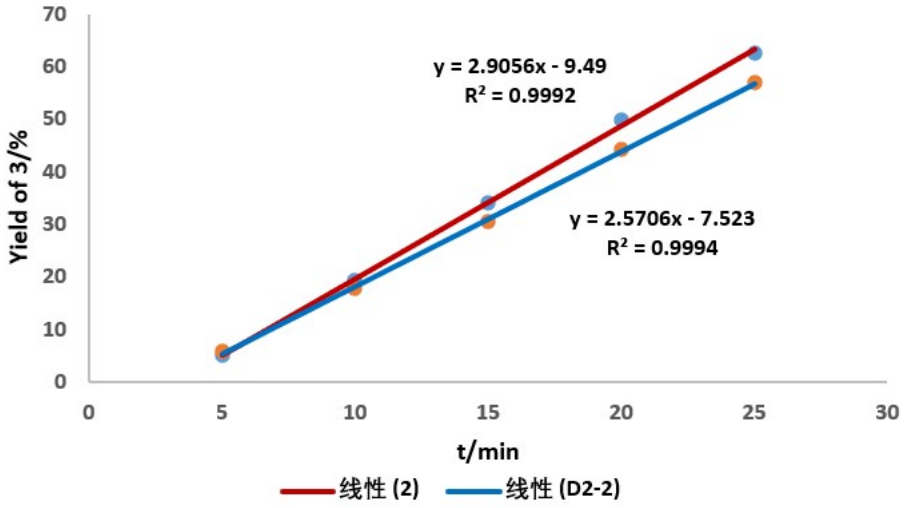
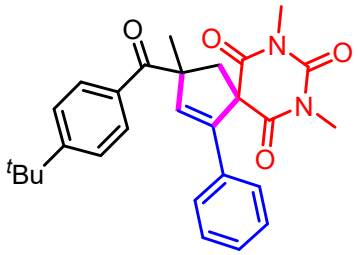


Figure S3 Parallel experiment of **2** and **D_2-2**

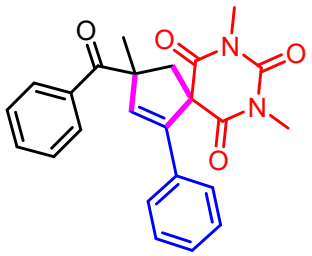
5. Characterization Data for Final Products



3

3-(4-(*tert*-butyl)benzoyl)-3,7,9-trimethyl-1-phenyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (3):

Yellow solid (421.6 mg, 92%); Eluent: petroleum ether/ethyl acetate 10:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.46 (dt, *J* = 8.5, 2.1 Hz, 2H), 7.29 - 7.23 (m, 3H), 7.08 - 7.01 (m, 2H), 6.62 (s, 1H), 3.44 (d, *J* = 13.4 Hz, 1H), 3.29 (s, 3H), 3.23 (s, 3H), 2.64 (d, *J* = 13.4 Hz, 1H), 1.77 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 202.52, 170.81, 170.17, 155.81, 150.98, 140.59, 139.04, 133.60, 133.36, 129.10, 128.74, 128.53, 126.47, 125.38, 65.47, 61.19, 48.07, 35.05, 31.11, 29.09, 29.05, 27.32; HRMS (ESI-TOF) Calcd for $C_{28}H_{30}N_2O_4Na$ $[M+Na]^+$ calcd 481.2098, found 481.2104.

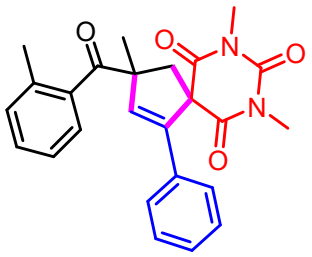


4

3-benzoyl-3,7,9-trimethyl-1-phenyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (4):

Yellow solid (349.9 mg, 87%); Eluent: petroleum ether/ethyl acetate 10:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 - 7.88 (m, 2H), 7.50 (tt, *J* = 7.3, 2.5 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.29 - 7.23 (m, 3H), 7.06 - 7.00 (m, 2H), 6.55 (s, 1H), 3.43 (d, *J* = 13.4 Hz, 1H), 3.28 (s, 3H), 3.22 (s, 3H), 2.64 (d, *J* = 13.4 Hz, 1H), 1.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 203.40, 170.73, 170.15, 150.94, 140.87, 138.75, 136.82, 133.30, 132.03, 128.86, 128.75, 128.58, 128.38, 126.46, 65.47, 61.26, 47.96, 29.07, 29.03,

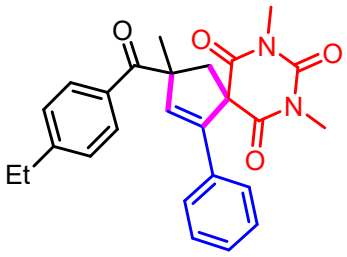
27.25; HRMS (ESI-TOF) Calcd for $C_{24}H_{22}N_2O_4Na$ $[M+Na]^+$ calcd 425.1472, found 425.1478.



5

3,7,9-trimethyl-3-(2-methylbenzoyl)-1-phenyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (5):

Yellow solid (366.2 mg, 88%); Eluent: petroleum ether/ethyl acetate 10:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 7.6 Hz, 1H), 7.32 - 7.22 (m, 5H), 7.19 (t, J = 7.5 Hz, 1H), 7.04 - 6.98 (m, 2H), 6.28 (s, 1H), 3.46 (d, J = 13.6 Hz, 1H), 3.29 (s, 3H), 3.27 (s, 3H), 2.49 (d, J = 13.6 Hz, 1H), 2.35 (s, 3H), 1.65 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.83, 170.95, 170.40, 150.99, 140.57, 139.26, 137.86, 135.69, 133.28, 131.10, 129.70, 128.83, 128.56, 126.44, 126.27, 124.99, 65.13, 62.94, 47.39, 29.07, 29.06, 26.79, 19.95; HRMS (ESI-TOF) Calcd for $C_{25}H_{24}N_2O_4Na$ $[M+Na]^+$ calcd 439.1628, found 439.1637.

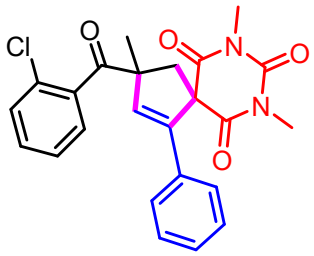


6

3-(4-ethylbenzoyl)-3,7,9-trimethyl-1-phenyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (6):

Yellow solid (387.2 mg, 90%); Eluent: petroleum ether/ethyl acetate 10:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 7.4 Hz, 2H), 7.49 (tt, J = 7.3, 2.5 Hz, 1H), 7.43 (tt, J = 7.4, 1.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 8.0 Hz, 2H), 6.53 (s, 1H), 3.42 (d, J = 13.4 Hz, 1H), 3.30 (s, 3H), 3.24 (s, 3H), 2.64 - 2.55 (m, 3H), 1.75 (s, 3H),

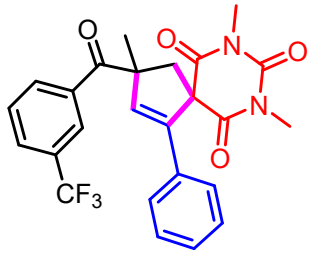
1.18 (t, J = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 203.56, 170.87, 170.26, 151.01, 144.78, 140.85, 137.98, 136.97, 131.95, 130.58, 128.84, 128.34, 128.27, 126.31, 65.26, 61.23, 48.20, 29.07, 29.03, 28.52, 27.26, 15.32; HRMS (ESI-TOF) Calcd for $C_{26}H_{26}N_2O_4Na$ $[M+Na]^+$ calcd 453.1785, found 453.1788.



7

3-(2-chlorobenzoyl)-3,7,9-trimethyl-1-phenyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (7):

Yellow solid (392.5 mg, 90%); Eluent: petroleum ether/ethyl acetate 10:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (dd, J = 7.5, 1.7 Hz, 1H), 7.42 (d, J = 8.7 Hz, 1H), 7.34 (td, J = 7.7, 1.7 Hz, 1H), 7.31 - 7.24 (m, 4H), 7.03 - 6.96 (m, 2H), 6.19 (s, 1H), 3.46 (d, J = 13.6 Hz, 1H), 3.30 (s, 3H), 3.27 (s, 3H), 2.50 (d, J = 13.6 Hz, 1H), 1.67 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.91, 170.76, 170.28, 150.93, 141.40, 139.31, 137.17, 133.15, 130.61, 129.99, 129.93, 128.84, 128.67, 128.22, 126.29, 126.28, 65.21, 62.90, 47.14, 29.08, 26.05; HRMS (ESI-TOF) Calcd for $C_{24}H_{21}ClN_2O_4Na$ $[M+Na]^+$ calcd 459.1082, found 459.1089.

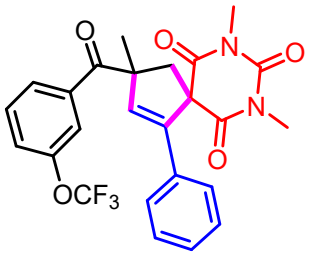


8

3,7,9-trimethyl-1-phenyl-3-(3-(trifluoromethyl)benzoyl)-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (8):

Yellow solid (409.0 mg, 87%); Eluent: petroleum ether/ethyl acetate 10:1; ^{1}H NMR

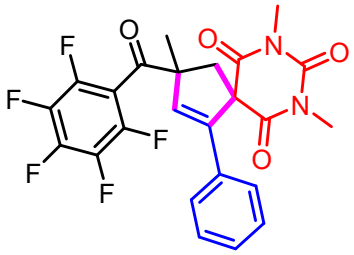
(400 MHz, $CDCl_3$): δ 8.16 (s, 1H), 8.11 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.32 - 7.24 (m, 3H), 7.07 - 6.95 (m, 2H), 6.44 (s, 1H), 3.40 (d, *J* = 13.4 Hz, 1H), 3.28 (s, 3H), 3.23 (s, 3H), 2.68 (d, *J* = 13.4 Hz, 1H), 1.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 202.41, 170.45, 170.12, 150.81, 141.88, 138.04, 137.67, 133.04, 131.97, 130.89 (q, *J* = 32.8 Hz), 128.99, 128.80, 128.43 (q, *J* = 3.5 Hz), 126.48, 125.71 (q, *J* = 3.7 Hz), 125.07, 122.37, 65.57, 61.17, 47.60, 29.06, 29.02, 27.00; ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.62. HRMS (ESI-TOF) Calcd for $C_{25}H_{21}F_3N_2O_4Na$ $[M+Na]^+$ calcd 493.1346, found 493.1357.



9

3,7,9-trimethyl-1-phenyl-3-(3-(trifluoromethoxy)benzoyl)-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (9):

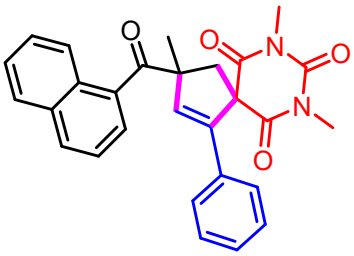
Yellow solid (398.6 mg, 82%); Eluent: petroleum ether/ethyl acetate 8:1; ^1H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.8 Hz, 1H), 7.75 (s, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 9.2 Hz, 1H), 7.30 - 7.23 (m, 3H), 7.05 - 6.98 (m, 2H), 6.46 (s, 1H), 3.40 (d, *J* = 13.4 Hz, 1H), 3.28 (s, 3H), 3.23 (s, 3H), 2.66 (d, *J* = 13.4 Hz, 1H), 1.75 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 202.10, 170.49, 170.11, 150.83, 149.10, 149.08, 141.69, 138.81, 138.05, 133.07, 129.89, 128.78, 128.74, 127.03, 126.45, 124.25, 121.72, 121.43, 119.15, 65.48, 61.20, 47.68, 29.04, 29.00, 27.05; ^{19}F NMR (376 MHz, $CDCl_3$): δ -57.81. HRMS (ESI-TOF) Calcd for $C_{25}H_{21}F_3N_2O_5Na$ $[M+Na]^+$ calcd 509.1295, found 509.1300.



10

3,7,9-trimethyl-3-(perfluorobenzoyl)-1-phenyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (10):

Yellow solid (398.6 mg, 81%); Eluent: petroleum ether/ethyl acetate 10:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 - 7.23 (m, 3H), 6.97 - 6.91 (m, 2H), 6.14 (t, *J* = 1.9 Hz, 1H), 3.28 - 3.16 (m, 7H), 2.55 (d, *J* = 14.1 Hz, 1H), 1.69 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.14, 170.33, 169.65, 150.62, 145.18, 144.24 - 143.91 (m), 143.65 - 143.10 (m), 141.86 - 141.34 (m), 141.09 - 140.51 (m), 139.15 - 138.65 (m), 136.62 - 136.05 (m), 135.21 (t, *J* = 2.7 Hz), 132.63, 129.05, 128.79, 126.62, 115.07 - 114.38 (m), 66.03, 63.31, 45.25, 28.99, 28.95, 24.40; ^{19}F NMR (376 MHz, $CDCl_3$) : δ -137.99 - -138.15 (m), -150.90 - -151.06 (m), -159.90 - -160.12 (m); HRMS (ESI-TOF) Calcd for $C_{24}H_{17}F_5N_2O_4Na$ $[M+Na]^+$ calcd 515.1001, found 515.1014.

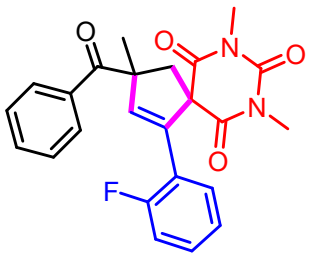


11

3-(1-naphthoyl)-3,7,9-trimethyl-1-phenyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (11):

Yellow solid (352.7 mg, 78%); Eluent: petroleum ether/ethyl acetate 15:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 - 7.88 (m, 2H), 7.88 - 7.84 (m, 1H), 7.76 (d, *J* = 6.4 Hz, 1H), 7.56 - 7.49 (m, 2H), 7.49 - 7.44 (m, 1H), 7.26 - 7.22 (m, 3H), 7.01 - 6.94 (m, 2H), 6.23 (s, 1H), 3.62 (d, *J* = 13.6 Hz, 1H), 3.31 (s, 3H), 3.30 (s, 3H), 2.56 (d, *J* = 13.6 Hz, 1H), 1.71 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 207.51, 170.98, 170.48, 151.02,

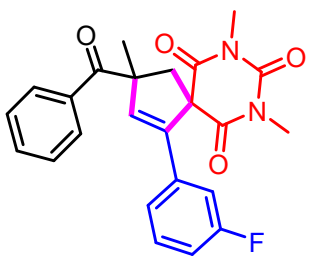
140.58, 137.86, 137.33, 133.65, 133.27, 130.25, 130.08, 128.82, 128.57, 128.35, 127.19, 126.40, 126.26, 125.65, 124.88, 124.28, 65.12, 63.34, 47.39, 29.11, 26.85; HRMS (ESI-TOF) Calcd for $C_{28}H_{24}N_2O_4Na$ $[M+Na]^+$ calcd 475.1628, found 475.1637.



12

3-benzoyl-1-(2-fluorophenyl)-3,7,9-trimethyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (12):

Yellow solid (364.5 mg, 87%); Eluent: petroleum ether/ethyl acetate 10:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 - 7.85 (m, 2H), 7.51 (tt, *J* = 7.3, 2.2 Hz, 1H), 7.47 - 7.41 (m, 2H), 7.38 (td, *J* = 7.9, 1.7 Hz, 1H), 7.27 - 7.21 (m, 1H), 7.10 (td, *J* = 7.6, 1.1 Hz, 1H), 6.94 (ddd, *J* = 11.9, 8.3, 1.0 Hz, 1H), 6.76 (s, 1H), 3.41 (d, *J* = 13.2 Hz, 1H), 3.30 (s, 3H), 3.25 (s, 3H), 2.55 (d, *J* = 13.2 Hz, 1H), 1.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 203.01, 170.62, 170.60, 169.89, 169.86, 160.44, 157.99, 151.29, 140.82, 136.93, 135.05, 132.03, 130.34, 130.25, 129.49, 129.45, 128.81, 128.39, 124.72, 124.69, 120.68, 120.54, 116.20, 115.96, 65.24, 65.21, 60.63, 48.31, 29.02, 26.92; HRMS (ESI-TOF) Calcd for $C_{24}H_{21}FN_2O_4Na$ $[M+Na]^+$ calcd 443.1378, found 443.1381.

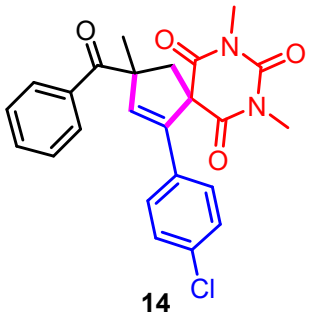


13

3-benzoyl-1-(3-fluorophenyl)-3,7,9-trimethyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-

trione (13):

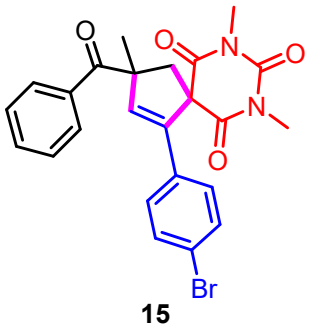
Yellow solid (368.7 mg, 88%); Eluent: petroleum ether/ethyl acetate 10:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 - 7.85 (m, 2H), 7.52 (tt, *J* = 7.3, 1.1 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.27 - 7.19 (m, 1H), 6.96 (td, *J* = 8.2, 2.2 Hz, 1H), 6.81 (dt, *J* = 9.9, 2.1 Hz, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 6.62 (s, 1H), 3.42 (d, *J* = 13.4 Hz, 1H), 3.29 (d, *J* = 24.1 Hz, 6H), 2.61 (d, *J* = 13.4 Hz, 1H), 1.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 202.96, 170.58, 169.95, 163.98, 161.52, 150.87, 139.92, 139.50, 139.47, 136.68, 135.58, 135.50, 132.14, 130.43, 130.35, 128.80, 128.43, 121.96, 121.93, 115.64, 115.43, 113.76, 113.54, 65.11, 61.23, 48.61, 29.15, 29.12, 27.09; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.99; HRMS (ESI-TOF) Calcd for $C_{24}H_{21}FN_2O_4Na$ $[M+Na]^+$ calcd 443.1378, found 443.1378.



14

3-benzoyl-1-(4-chlorophenyl)-3,7,9-trimethyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (14):

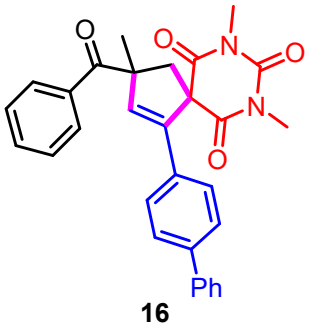
Yellow solid (396.9 mg, 91%); Eluent: petroleum ether/ethyl acetate 10:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 - 7.86 (m, 2H), 7.53 - 7.48 (m, 1H), 7.43 (tt, *J* = 7.4, 1,6 Hz, 2H), 7.23 (dt, *J* = 8.5, 2.5 Hz, 2H), 6.98 (dt, *J* = 8.5, 2.6 Hz, 2H), 6.58 (s, 1H), 3.41 (d, *J* = 13.4 Hz, 1H), 3.30 (s, 3H), 3.24 (s, 3H), 2.61 (d, *J* = 13.4 Hz, 1H), 1.75 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 203.02, 170.59, 169.99, 150.84, 139.54, 136.65, 134.45, 132.13, 131.90, 128.98, 128.82, 128.42, 127.77, 65.21, 61.26, 48.54, 29.14, 29.10, 27.12; HRMS (ESI-TOF) Calcd for $C_{24}H_{21}ClN_2O_4Na$ $[M+Na]^+$ calcd 459.1082, found 459.1076.



15

3-benzoyl-1-(4-bromophenyl)-3,7,9-trimethyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (15):

Yellow solid (422.5 mg, 88%); Eluent: petroleum ether/ethyl acetate 10:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (dt, *J* = 8.6, 2.2 Hz, 2H), 7.58 (dt, *J* = 8.6, 1.7 Hz, 2H), 7.29 - 7.25 (m, 3H), 7.04 - 6.98 (m, 2H), 6.48 (s, 1H), 3.38 (d, *J* = 13.4 Hz, 1H), 3.28 (s, 3H), 3.23 (s, 3H), 2.63 (d, *J* = 13.4 Hz, 1H), 1.74 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 202.46, 170.55, 170.16, 150.86, 141.41, 138.35, 135.60, 133.13, 131.65, 130.48, 128.80, 128.71, 127.00, 126.43, 65.42, 61.13, 47.91, 29.09, 29.05, 27.06; HRMS (ESI-TOF) Calcd for $C_{24}H_{21}BrN_2O_4Na$ $[M+Na]^+$ calcd 503.0577, found 503.0586.

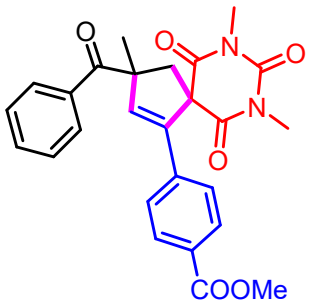


16

1-([1,1'-biphenyl]-4-yl)-3-benzoyl-3,7,9-trimethyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (16):

Yellow solid (377.8 mg, 79%); Eluent: petroleum ether/ethyl acetate 15:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 - 7.88 (m, 2H), 7.56 - 7.48 (m, 5H), 7.46 - 7.38 (m, 4H), 7.33 (tt, *J* = 7.3, 2.1 Hz, 1H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.65 (s, 1H), 3.44 (d, *J* = 13.3 Hz, 1H), 3.33 (s, 3H), 3.27 (s, 3H), 2.62 (d, *J* = 13.4 Hz, 1H), 1.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 203.35, 170.87, 170.24, 151.02, 141.33, 140.39, 140.19, 138.71,

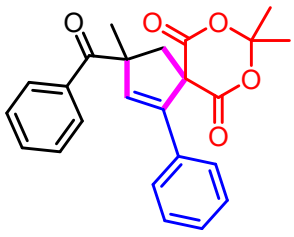
136.95, 132.20, 132.04, 128.86, 128.41, 127.64, 127.48, 127.00, 126.72, 65.06, 61.33, 48.69, 29.17, 29.13, 27.22; HRMS (ESI-TOF) Calcd for $C_{30}H_{26}N_2O_4Na$ $[M+Na]^+$ calcd 501.1785, found 501.1796.



17

methyl4-(3-benzoyl-3,7,9-trimethyl-6,8,10-trioxo-7,9-diazaspiro[4.5]dec-1-en-1-yl)benzoate (17):

Yellow solid (331.3 mg, 72%); Eluent: petroleum ether/ethyl acetate 8:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.8 Hz, 2H), 7.89 (d, *J* = 7.9 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.72 (s, 1H), 3.88 (s, 3H), 3.43 (d, *J* = 13.4 Hz, 1H), 3.31 (s, 3H), 3.25 (s, 3H), 2.63 (d, *J* = 13.4 Hz, 1H), 1.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 202.84, 170.54, 169.93, 166.35, 150.81, 140.60, 139.75, 137.80, 136.59, 132.17, 130.03, 129.96, 128.81, 128.43, 126.34, 65.04, 61.36, 52.21, 48.67, 29.15, 29.11, 27.06; HRMS (ESI-TOF) Calcd for $C_{26}H_{24}N_2O_6Na$ $[M+Na]^+$ calcd 483.1527, found 483.1534.

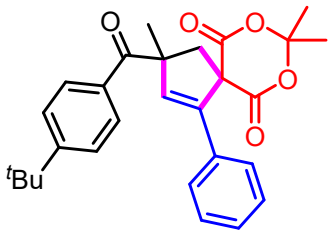


18

3-benzoyl-3,8,8-trimethyl-1-phenyl-7,9-dioxaspiro[4.5]dec-1-ene-6,10-dione (18):

Yellow solid (327.7 mg, 84%); Eluent: petroleum ether/ethyl acetate 20:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.2 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.31 - 7.25 (m, 3H), 7.20 (dd, *J* = 7.6, 2.0 Hz, 2H), 6.70 (s, 1H), 3.57 (d,

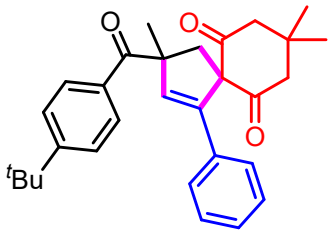
J = 13.3 Hz, 1H), 2.62 (d, *J* = 13.3 Hz, 1H), 1.82 (s, 3H), 1.77 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 202.75, 169.34, 168.51, 141.68, 137.97, 136.78, 132.77, 132.21, 128.86, 128.82, 128.66, 128.48, 126.26, 105.66, 61.74, 61.09, 48.47, 29.77, 28.39, 27.07; HRMS (ESI-TOF) Calcd for $C_{24}H_{22}O_5Na$ $[M+Na]^+$ calcd 413.1359, found 413.1361.



19

3-(4-(*tert*-butyl)benzoyl)-3,8,8-trimethyl-1-phenyl-7,9-dioxaspiro[4.5]dec-1-ene-6,10-dione (19):

Yellow solid (383.7 mg, 86%); Eluent: petroleum ether/ethyl acetate 20:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (dt, *J* = 8.6, 1.8 Hz, 2H), 7.46 (dt, *J* = 8.6, 1.7 Hz, 2H), 7.31 - 7.20 (m, 5H), 6.77 (s, 1H), 3.59 (d, *J* = 13.3 Hz, 1H), 2.62 (d, *J* = 13.3 Hz, 1H), 1.83 (s, 3H), 1.78 (s, 6H), 1.33 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 201.72, 169.37, 168.52, 156.05, 141.44, 138.26, 133.53, 132.81, 129.10, 128.84, 128.60, 126.24, 125.49, 105.63, 61.65, 61.07, 48.54, 35.08, 31.08, 29.77, 28.43, 27.12; HRMS (ESI-TOF) Calcd for $C_{28}H_{30}O_5Na$ $[M+Na]^+$ calcd 469.1985, found 469.1993.

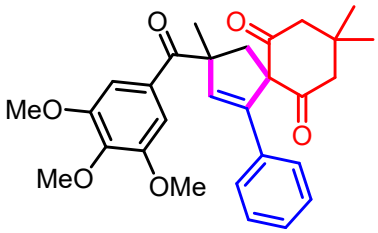


20

3-(4-(*tert*-butyl)benzoyl)-3,8,8-trimethyl-1-phenylspiro[4.5]dec-1-ene-6,10-dione (20):

Yellow oil (393.6 mg, 89%); Eluent: petroleum ether/ethyl acetate 25:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (dt, *J* = 8.5, 1.8 Hz, 2H), 7.44 (d, *J* = 8.5, 1.7 Hz, 2H), 7.27

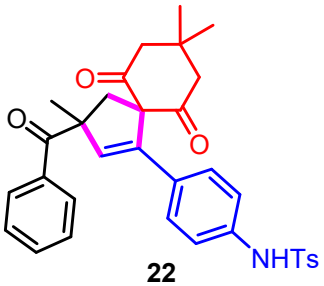
- 7.20 (m, 3H), 7.16 (dd, *J* = 7.7, 1.8 Hz, 2H), 6.47 (s, 1H), 3.40 (d, *J* = 12.9 Hz, 1H), 2.83 (dd, *J* = 37.6, 15.2 Hz, 2H), 2.45 (ddd, *J* = 15.2, 8.0, 2.1 Hz, 2H), 2.29 (d, *J* = 13.0 Hz, 1H), 1.60 (s, 3H), 1.32 (s, 9H), 1.13 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 208.07, 206.71, 201.40, 155.99, 142.21, 137.73, 135.92, 133.19, 129.28, 128.17, 127.67, 127.59, 125.38, 78.96, 59.78, 52.58, 52.13, 48.83, 35.05, 31.08, 30.65, 30.45, 27.66, 26.48; HRMS (ESI-TOF) Calcd for $C_{30}H_{34}O_3Na$ $[M+Na]^+$ calcd 465.2400, found 465.2407



21

3,8,8-trimethyl-1-phenyl-3-(3,4,5-trimethoxybenzoyl)spiro[4.5]dec-1-ene-6,10-dione (21):

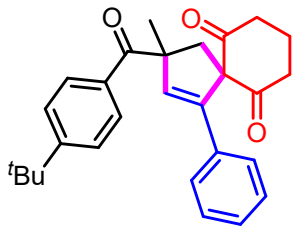
Yellow solid (304.8 mg, 64%); Eluent: petroleum ether/ethyl acetate 8:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 - 7.23 (m, 5H), 7.19 (dd, *J* = 7.5, 2.0 Hz, 2H), 6.42 (s, 1H), 3.90 (s, 3H), 3.88 (s, 6H), 3.24 (d, *J* = 13.1 Hz, 1H), 2.81 (dd, *J* = 15.0, 6.2 Hz, 2H), 2.50 (dd, *J* = 15.1, 2.1 Hz, 1H), 2.44 (dd, *J* = 15.0, 2.1 Hz, 1H), 2.36 (d, *J* = 13.1 Hz, 1H), 1.55 (s, 3H), 1.15 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 207.89, 206.96, 201.13, 152.78, 142.10, 141.85, 138.22, 135.67, 131.36, 128.25, 127.81, 127.47, 107.02, 78.96, 60.91, 59.57, 56.38, 52.43, 52.28, 48.88, 30.67, 30.50, 27.61, 26.21; HRMS (ESI-TOF) Calcd for $C_{29}H_{32}O_6Na$ $[M+Na]^+$ calcd 499.2091, found 499.2097.



22

N-(4-(3-benzoyl-3,8,8-trimethyl-6,10-dioxospiro[4.5]dec-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (22):

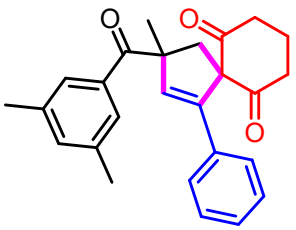
Yellow solid (372.0 mg, 67%); Eluent: petroleum ether/ethyl acetate 5:1; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.90 (d, *J* = 7.4 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.94 (s, 4H), 6.59 (s, 1H), 3.24 – 3.02 (m, 4H), 2.33 (q, *J* = 11.6, 9.8 Hz, 6H), 1.41 (s, 3H), 1.14 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 208.24, 206.69, 202.05, 143.75, 141.40, 137.11, 136.29, 136.20, 136.18, 132.30, 129.67, 129.00, 128.44, 128.42, 127.20, 120.67, 78.85, 59.81, 52.46, 51.91, 49.15, 30.70, 30.58, 27.50, 26.30, 21.51; HRMS (ESI-TOF) Calcd for $C_{33}H_{33}NSO_5Na$ $[M+Na]^+$ calcd 578.1972, found 578.1955.



23

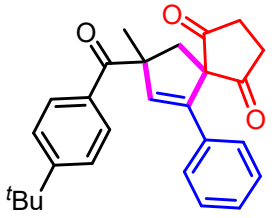
3-(4-(*tert*-butyl)benzoyl)-3-methyl-1-phenylspiro[4.5]dec-1-ene-6,10-dione (23):

Yellow oil (306.5 mg, 74%); Eluent: petroleum ether/ethyl acetate 15:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (dt, *J* = 8.5, 1.9 Hz, 2H), 7.44 (dt, *J* = 8.5, 1.8 Hz, 2H), 7.26 - 7.16 (m, 3H), 7.09 - 7.01 (m, 2H), 6.70 (s, 1H), 3.34 (d, *J* = 13.1 Hz, 1H), 2.88 (dddd, *J* = 26.5, 15.7, 10.0, 5.4 Hz, 2H), 2.75 - 2.63 (m, 2H), 2.22 (d, *J* = 13.3 Hz, 2H), 1.99 (dt, *J* = 14.5, 4.8 Hz, 1H), 1.59 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 208.53, 206.87, 201.33, 155.98, 141.71, 136.23, 134.17, 133.35, 129.27, 128.40, 127.72, 126.61, 125.40, 78.26, 60.41, 48.25, 38.95, 38.32, 35.05, 31.08, 26.45, 17.31; HRMS (ESI-TOF) Calcd for $C_{28}H_{30}O_3$ $[M+Na]^+$ calcd 437.2087, found 437.2094.



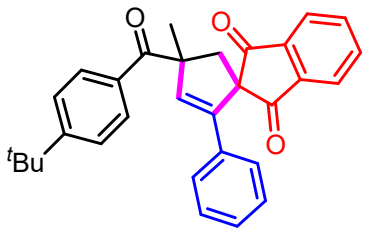
24

3-(3,5-dimethylbenzoyl)-3-methyl-1-phenylspiro[4.5]dec-1-ene-6,10-dione (24): Yellow oil (254.9 mg, 66%); Eluent: petroleum ether/ethyl acetate 15:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (s, 2H), 7.27 - 7.20 (m, 3H), 7.13 (s, 1H), 7.07 - 7.01 (m, 2H), 6.62 (s, 1H), 3.30 (d, *J* = 13.1 Hz, 1H), 2.95 - 2.80 (m, 2H), 2.75 - 2.60 (m, 2H), 2.35 (s, 6H), 2.20 (d, *J* = 13.1 Hz, 2H), 2.05 - 1.94 (m, 1H), 1.58 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 208.56, 206.85, 202.65, 141.77, 137.99, 136.57, 136.33, 134.30, 133.86, 128.40, 127.72, 126.79, 126.65, 78.36, 60.58, 48.15, 38.95, 38.37, 26.42, 21.33, 17.29; HRMS (ESI-TOF) Calcd for $C_{26}H_{26}O_3Na$ $[M+Na]^+$ calcd 409.1774, found 409.1779.



25

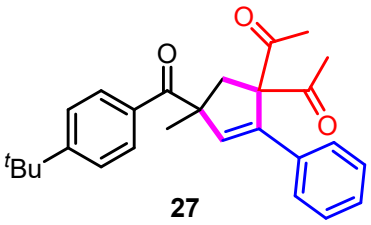
8-(4-(*tert*-butyl)benzoyl)-8-methyl-6-phenylspiro[4.4]non-6-ene-1,4-dione (25): Yellow oil (256.1 mg, 64%); Eluent: petroleum ether/ethyl acetate 15:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (dt, *J* = 8.6, 1.8 Hz, 2H), 7.46 (dt, *J* = 8.6, 1.8 Hz, 2H), 7.29 - 7.23 (m, 3H), 7.06 - 6.99 (m, 2H), 6.56 (s, 1H), 3.08 (d, *J* = 13.2 Hz, 1H), 2.93 - 2.82 (m, 2H), 2.81 - 2.68 (m, 2H), 2.26 (d, *J* = 13.2 Hz, 1H), 1.72 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 214.22, 213.41, 202.04, 156.00, 141.29, 139.24, 133.91, 133.33, 129.32, 128.69, 128.31, 126.79, 125.35, 71.74, 60.87, 45.93, 36.04, 35.06, 31.08, 27.38; HRMS (ESI-TOF) Calcd for $C_{27}H_{28}O_3Na$ $[M+Na]^+$ calcd 423.1931, found 423.1935.



26

4-(4-(*tert*-butyl)benzoyl)-4-methyl-2-phenylspiro[cyclopentane-1,2'-inden]-2-ene-1',3'-dione (26):

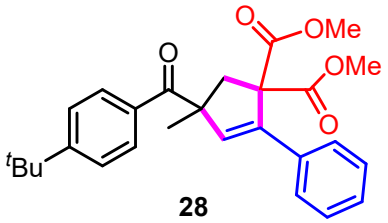
5-Yellow solid (354.1 mg, 79%); Eluent: petroleum ether/ethyl acetate 20:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 - 7.96 (m, 4H), 7.91 - 7.84 (m, 2H), 7.47 (dt, *J* = 8.6, 2.0 Hz, 2H), 7.13 - 7.07 (m, 3H), 7.02 - 6.97 (m, 2H), 6.75 (s, 1H), 3.17 (d, *J* = 13.4 Hz, 1H), 2.38 (d, *J* = 13.4 Hz, 1H), 1.82 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 202.54, 202.00, 201.70, 155.93, 141.81, 141.73, 140.96, 140.29, 136.16, 133.91, 133.53, 129.43, 128.52, 128.05, 126.47, 125.35, 123.83, 68.81, 60.60, 46.05, 35.07, 31.10, 27.49; HRMS (ESI-TOF) Calcd for $C_{31}H_{28}O_3Na$ $[M+Na]^+$ calcd 471.1931, found 471.1936.



27

1,1'-(4-(4-(*tert*-butyl)benzoyl)-4-methyl-2-phenylcyclopent-2-ene-1,1-diyl)bis(ethan-1-one) (27):

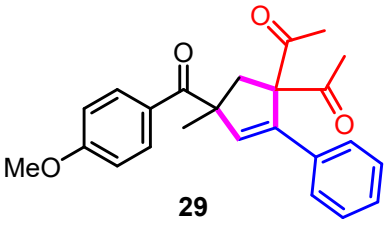
Yellow oil (245.4 mg, 61%); Eluent: petroleum ether/ethyl acetate 15:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (dt, *J* = 8.6, 1.9 Hz, 2H), 7.47 (dt, *J* = 8.6, 1.8 Hz, 2H), 7.32 - 7.23 (m, 5H), 6.75 (s, 1H), 3.40 (d, *J* = 14.1 Hz, 1H), 2.60 (d, *J* = 14.1 Hz, 1H), 2.20 (s, 3H), 2.16 (s, 3H), 1.64 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 207.34, 207.20, 201.59, 156.37, 142.38, 137.27, 134.33, 132.81, 129.15, 128.56, 128.24, 127.21, 125.53, 80.06, 59.98, 43.95, 35.10, 31.06, 28.21, 27.49, 26.58; HRMS (ESI-TOF) Calcd for $C_{27}H_{30}O_3Na$ $[M+Na]^+$ calcd 425.2087, found 425.2084.



28

dimethyl4-(4-(*tert*-butyl)benzoyl)-4-methyl-2-phenylcyclopent-2-ene-1,1-dicarboxylate (28):

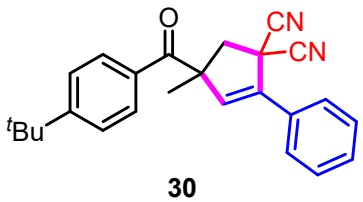
Yellow oil (295.3 mg, 68%); Eluent: petroleum ether/ethyl acetate 10:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (dt, *J* = 8.5, 1.8 Hz, 2H), 7.40 - 7.33 (m, 4H), 7.24 - 7.17 (m, 3H), 6.48 (s, 1H), 3.65 (s, 3H), 3.55 (s, 3H), 3.41 (d, *J* = 13.5 Hz, 1H), 2.78 (d, *J* = 13.5 Hz, 1H), 1.53 (s, 3H), 1.26 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 201.86, 171.79, 171.32, 156.05, 141.56, 138.06, 134.61, 133.17, 129.20, 128.04, 127.89, 127.59, 125.37, 67.67, 59.26, 52.86, 52.77, 46.93, 35.06, 31.08, 30.93, 25.68; HRMS (ESI-TOF) Calcd for $C_{27}H_{30}O_5Na$ $[M+Na]^+$ calcd 457.1985, found 457.1987.



29

1,1'-(4-(4-methoxybenzoyl)-4-methyl-2-phenylcyclopent-2-ene-1,1-diyl)bis(ethan-1-one) (29):

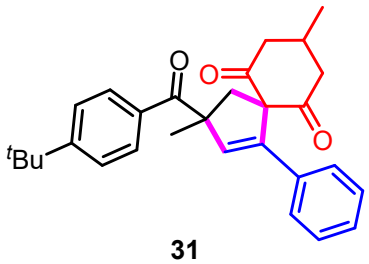
Yellow oil (263.3 mg, 70%); Eluent: petroleum ether/ethyl acetate 8:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (dt, *J* = 8.9, 2.0 Hz, 2H), 7.34 - 7.22 (m, 6H), 6.94 (dt, *J* = 8.9, 1.9 Hz, 2H), 6.74 (s, 1H), 3.87 (s, 3H), 3.38 (d, *J* = 14.0 Hz, 1H), 2.61 (d, *J* = 14.0 Hz, 1H), 2.18 (d, *J* = 15.7 Hz, 6H), 1.63 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 207.32, 207.19, 200.25, 163.09, 142.20, 137.54, 134.35, 131.62, 128.55, 128.22, 127.95, 127.21, 113.76, 80.10, 59.75, 55.51, 44.08, 28.25, 27.46, 26.68; HRMS (ESI-TOF) Calcd for $C_{24}H_{24}O_4Na$ $[M+Na]^+$ calcd 399.1567, found 399.1558.



30

4-(4-(*tert*-butyl)benzoyl)-4-methyl-2-phenylcyclopent-2-ene-1,1-dicarbonitrile (30):

White solid (191.5 mg, 52%); Eluent: petroleum ether/ethyl acetate 20:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (dt, *J* = 8.5, 1.8 Hz, 2H), 7.67 - 7.61 (m, 2H), 7.51 (dt, *J* = 8.5 1.7 Hz, 2H), 7.47 7.39 (m, 3H), 6.85 (s, 1H), 3.66 (d, *J* = 13.8 Hz, 1H), 3.02 (d, *J* = 13.8 Hz, 1H), 1.80 (s, 3H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.95, 157.25, 138.42, 135.83, 131.90, 130.32, 129.81, 129.15, 129.13, 126.48, 125.88, 115.74, 114.55, 60.46, 48.42, 39.62, 35.22, 31.03, 25.64; HRMS (ESI-TOF) Calcd for $C_{25}H_{24}N_2ONa$ $[M+Na]^+$ calcd 391.1781, found 391.1786.

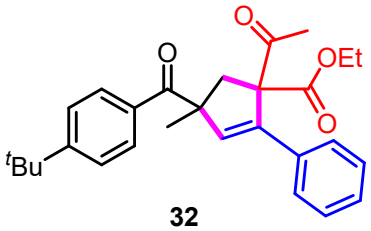


31

3-(4-(*tert*-butyl)benzoyl)-3,8-dimethyl-1-phenylspiro[4.5]dec-1-ene-6,10-dione (31):

Yellow oil (359.7 mg, 84%, *dr* = 2.3:1); Eluent: petroleum ether/ethyl acetate 15:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 - 7.77 (m, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.18 - 7.09 (m, 3H), 7.02 - 6.93 (m, 2H), 6.62 (s, 0.3H), 6.56 (s, 0.7H), 3.25 (d, *J* = 13.0 Hz, 1H), 2.88 (dddd, *J* = 35.5, 17.0, 4.5, 2.0 Hz, 1.3H), 2.74 - 2.61 (m, 0.7H), 2.55 (dd, *J* = 27.1, 12.7 Hz, 0.7H), 2.47 - 2.35 (m, 1H), 2.30 - 2.19 (m, 1.3H), 2.14 (t, *J* = 13.0, 1H), 1.52 (s, 2.1H), 1.50 (s, 0.9H), 1.24 (s, 9H), 1.11 (d, *J* = 6.4 Hz, 0.9H), 1.02 (d, *J* = 6.6 Hz, 2.1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.66, 207.09, 201.46, 155.93, 142.05, 136.99, 134.64, 133.42, 129.26, 128.37, 127.75, 126.90, 125.38, 77.63, 60.39, 47.73, 46.98, 46.26, 35.05, 31.09, 26.51, 24.47, 21.13; HRMS (ESI-TOF) Calcd for

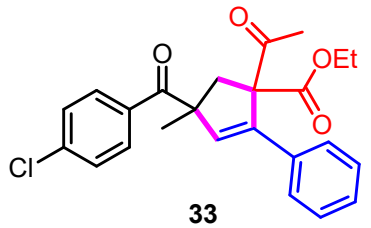
$C_{29}H_{32}O_3Na$ $[M+Na]^+$ calcd 451.2244, found 451.2248.



32

ethyl1-acetyl-4-(4-(*tert*-butyl)benzoyl)-4-methyl-2-phenylcyclopent-2-ene-1-carboxylate (32):

Yellow oil (315.3 mg, 65%, *dr* = 7.9:1); Eluent: petroleum ether/ethyl acetate 10:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (dt, *J* = 8.5, 1.8 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.41 - 7.36 (m, 2H), 7.31 - 7.23 (m, 3H), 6.61 (s, , 1H), 4.23 - 4.06 (m, 2H), 3.29 (d, *J* = 13.6 Hz, 1H), 2.86 (d, *J* = 13.6 Hz, 1H), 2.20 (s, 3H), 1.65 (s, 3H), 1.33 (d, *J* = 3.4 Hz, 9H), 1.11 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 204.54, 201.75, 171.73, 156.18, 142.35, 137.37, 134.73, 132.96, 129.18, 128.08, 127.94, 127.75, 125.43, 74.30, 61.74, 59.46, 45.14, 35.07, 31.07, 27.10, 26.10, 13.82; HRMS (ESI-TOF) Calcd for $C_{28}H_{32}O_4Na$ $[M+Na]^+$ calcd 455.2193, found 455.2188.

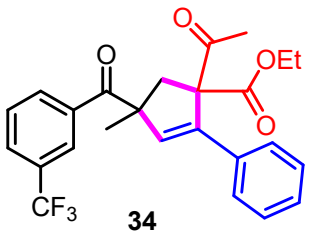


33

ethyl-1-acetyl-4-(4-chlorobenzoyl)-4-methyl-2-phenylcyclopent-2-ene-1-carboxylate (33):

Yellow oil (278.9 mg, 68%, *dr* = 1.5:1); Eluent: petroleum ether/ethyl acetate 10:1; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.44 - 7.39 (m, 1H), 7.36 - 7.31 (m, 2H), 7.29 - 7.23 (m, 6H), 6.18 (s, 0.6H), 6.15 (s, 0.4H), 4.23 - 3.99 (m, 2H), 3.46 (d, *J* = 11.6 Hz, 0.4H), 3.27 (d, *J* = 13.8 Hz, 0.6H), 2.73 (d, *J* = 13.9 Hz, 0.6H), 2.44 (d, *J* = 14.2 Hz, 0.4H), 2.22 (s, 1.2H), 2.17 (s, 1.8H), 1.53 (s, 1.8H), 1.51 (s, 1.2H), 1.12 - 1.02 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 205.52, 204.38, 171.50, 143.72, 139.57, 135.27, 134.52, 130.52, 129.93, 128.15, 127.72, 127.35, 126.50, 74.54, 61.79, 61.34, 43.13,

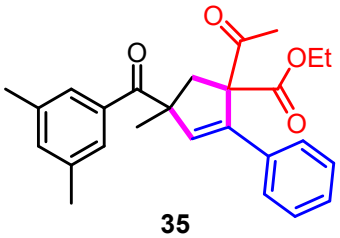
27.05, 24.38, 13.79; HRMS (ESI-TOF) Calcd for $C_{24}H_{23}ClO_4Na$ $[M+Na]^+$ calcd 433.1177, found 433.1179.



34

ethyl-1-acetyl-4-methyl-2-phenyl-4-(3-(trifluoromethyl)benzoyl)cyclopent-2-ene-1-carboxylate (34):

Yellow oil (315.3 mg, 71%, *dr* = 6.9:1); Eluent: petroleum ether/ethyl acetate 10:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (s, 1H), 8.07 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.38 - 7.33 (m, 2H), 7.29 - 7.26 (m, 3H), 6.42 (d, *J* = 14.7 Hz, 1H), 4.25 - 4.05 (m, 2H), 3.30 (d, *J* = 13.7 Hz, 1H), 2.81 (d, *J* = 13.7 Hz, 1H), 2.22 (s, 3H), 1.65 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.08, 201.26, 171.48, 143.71, 136.85, 136.21, 134.54, 132.03, 129.06, 128.83 - 128.65 (m), 128.25, 128.18, 128.14, 127.82, 125.80 (q, *J* = 3.9 Hz), 74.36, 61.88, 59.45, 44.99, 27.41, 25.75, 13.77; ^{19}F NMR (376 MHz, $CDCl_3$) : δ -62.79; HRMS (ESI-TOF) Calcd for $C_{25}H_{23}F_3O_4Na$ $[M+Na]^+$ calcd 467.1441, found 467.1454.

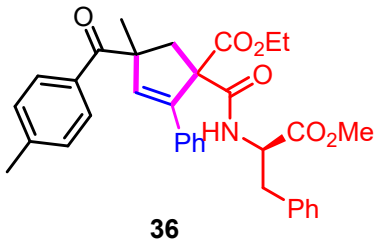


35

ethyl-1-acetyl-4-(3,5-dimethylbenzoyl)-4-methyl-2-phenylcyclopent-2-ene-1-carboxylate (35):

Yellow oil (242.5 mg, 60%, *dr* = 1.3:1); Eluent: petroleum ether/ethyl acetate 10:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 15.0 Hz, 2H), 7.42 - 7.35 (m, 2H), 7.30 - 7.23 (m, 3H), 7.14 (d, *J* = 3.9 Hz, 1H), 6.55 (s, 0.56H), 6.46 (s, 0.44H), 4.24 - 4.00 (m, 2H), 3.50 (d, *J* = 13.8 Hz, 0.44H), 3.27 (d, *J* = 13.6 Hz, 0.56H), 2.85 (d, *J* = 13.6 Hz,

0.56H), 2.56 (d, J = 13.8 Hz, 0.44H), 2.34 (s, 6H), 2.25 (s, 1.32H), 2.18 (s, 1.68H), 1.63 (s, 1.68H), 1.55 (s, 1.32H), 1.10 (t, J = 7.1 Hz, 1.68H), 1.02 (t, J = 7.1 Hz, 1.32H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.96, 203.35, 171.73, 142.40, 138.02, 137.90, 136.20, 134.80, 134.00, 128.08, 127.95, 127.78, 126.70, 74.39, 61.74, 59.59, 45.16, 27.10, 26.00, 21.34, 13.81; HRMS (ESI-TOF) Calcd for $C_{27}H_{30}O_5Na$ $[M+Na]^+$ calcd 427.1880, found 427.1889.



36

methyl 1-(((*R*)-1-methoxy-1-oxo-3-phenylpropan-2-yl)carbamoyl)-4-methyl-4-(4-methylbenzoyl)-2-phenylcyclopent-2-ene-1-carboxylate (36):

white solid (62.6 mg, 26%, *dr* = 4.3:1); Eluent: petroleum ether/ethyl acetate 2:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 - 7.68 (m, 2H), 7.61 (dd, J = 13.8, 7.6 Hz, 1H), 7.21 - 7.12 (m, 7H), 7.11 - 7.03 (m, 3H), 7.00 - 6.89 (m, 2H), 6.51 (s, 1H), 4.87 - 4.67 (m, 1H), 4.15 - 3.92 (m, 2H), 3.63 - 3.45 (s, 3H), 3.22 - 3.14 (m, 0.4H), 3.03 - 2.88 (m, 1.6H), 2.75 - 2.59 (m, 1H), 2.32 (s, 3H), 1.51 (s, 3H), 1.04 - 0.80 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 203.03, 173.41, 171.53, 169.99, 142.96, 141.06, 138.08, 136.05, 134.26, 133.36, 129.50, 129.29, 129.11, 129.05, 128.47, 128.18, 127.80, 126.92, 66.64, 62.05, 59.68, 53.63, 52.16, 48.15, 37.83, 26.42, 21.62, 13.72; HRMS (ESI): m/z for $C_{34}H_{35}NO_6Na$ $[M+Na]^+$ calcd 576.2357, found 576.2368.

6. X-ray Crystallography Studies of Compound 13

Single crystal suitable for X-ray diffraction was obtained by slow evaporation of a saturated solution of compound **13** (cyclohexane/CH_2Cl_2) in a loosely capped vial.

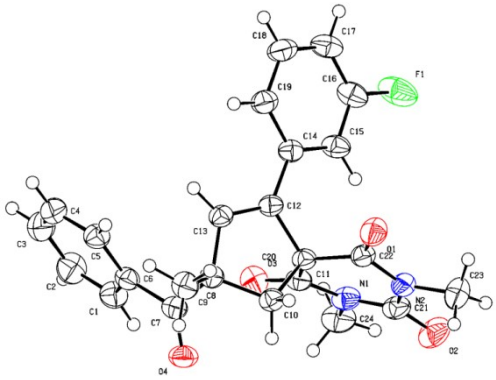


Figure S4 Structure of **13** by X-Ray crystallographic (CCDC = 2207175)

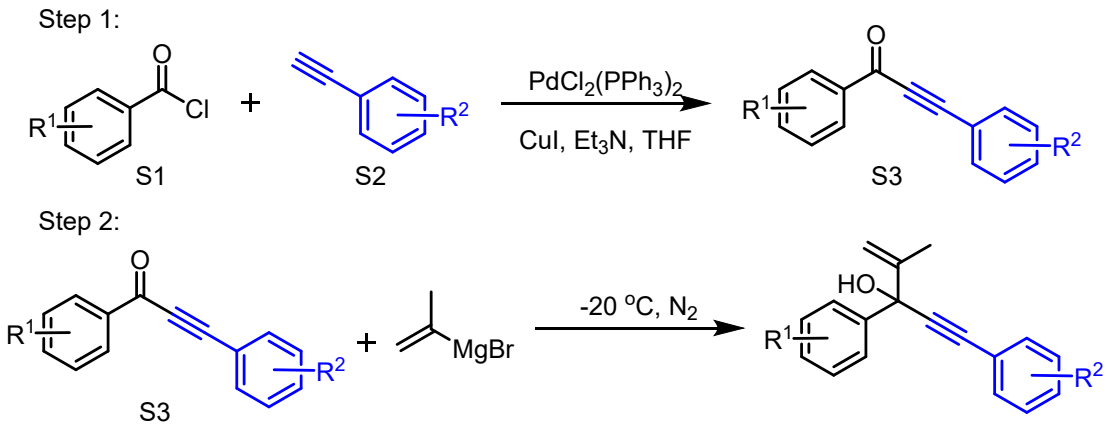
Table S2 Crystal data and structure refinement for **13**

Empirical formula	$C_{24}H_{21}FN_2O_4$
Formula weight	420.43
Temperature/K	193.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.8055(7)
b/Å	11.8006(9)
c/Å	19.3349(15)
α/°	90
β/°	91.749(4)°
γ/°	90
Volume/Å^3	2008.2(3)
Z	4
ρcalcg/cm^3	1.391
μ/mm^{-1}	0.537
F(000)	880.0
Crystal size/mm^3	0.12 × 0.1 × 0.1

Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	7.96 to 120.764
Index ranges	$-8 \leq h \leq 11$, $-15 \leq k \leq 14$, $-24 \leq l \leq 23$
Reflections collected	15972
Independent reflections	4434 [R_{int} = 0.0558, R_{sigma} = 0.0470]
Data/restraints/parameters	4434/0/283
Largest diff. peak/hole / e Å^{-3}	0.20/-0.34

7. Synthesis of Substrates

7.1) the synthesis of 1,4-enynes



Step 1:[3,4]

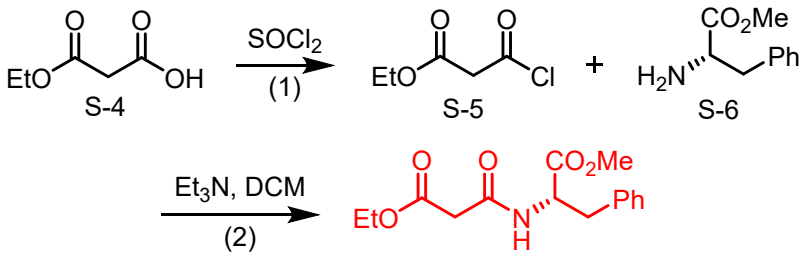
A mixture of $Pd(PPh_3)Cl_2$ (2 mol%, 0.2 mmol), CuI (4 mol%, 0.4 mmol), Et_3N (1.5 equiv, 15 mmol) and acyl chloride **S1** (1.2 equiv, 12 mmol) were dissolved in 20 mL anhydrous tetrahydrofuran (THF) and stirred for 10 minutes at room temperature under argon conditions. Then, terminal alkyne **S2** (1.0 equiv, 10 mmol) was added to the reaction vial by dropwise and stirred for overnight. Then, the reaction solution was diluted with ethyl acetate (150 mL) and washed with brine (150 mL) and H_2O

(150 mL). The separated organic layer was dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to obtain a crude product, which was separated by column chromatography (eluent: petroleum ether 100/1) to give the desired product **S-3**.

Step 2:[5]

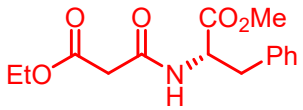
Compound **S3** was dissolved in 10 mL anhydrous tetrahydrofuran. Then, isopropenylmagnesium bromide (10 mL, 1 mol/L in THF) was added to the solution above dropwise at -20 °C and stirred for 10 mins under argon. The reaction was then moved to room temperature for another 6 hours. After the completion of the reaction determined by TLC, the reaction mixture was quenched by adding aqueous saturated solution of NH_4Cl (80 mL) and extracted with ethyl acetate (2×60 mL). The organic phase was dried over Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to obtain a crude product, which was separated by column chromatography (eluent: petroleum ether 5/1) to give the desired product.

7.2) the synthesis of chiral amide[6]



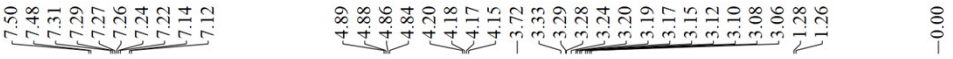
Commercially available 3-ethoxy-3-oxopropanoic acid **S-4** (1.32 g, 10 mmol) was dissolved in 10 mL CH_2Cl_2 in an oven dried 50 mL round bottom flask equipped with stir bar and $SOCl_2$ (1.30 g, 11 mmol) were added at RT. The reaction mixture was stirred for the 1 h to give acyl chloride **S-5**. D-Phenylalanine methyl ester hydrochloride **S-6** (2.16 g, 10 mmol) and Et_3N (1.32 g, 30 mmol) was dissolved in 10 mL CH_2Cl_2 in another oven dried 50 mL round bottom flask stirred for the 10 min then it was added to the prepared acyl chloride **S-5** dropwise at 0 °C. The mixture was slowly warmed to room temperature and continued to stir for 4 h. The reaction

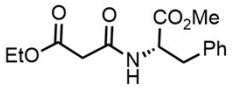
mixture was then poured into 1 N HCl/CH_2Cl_2 and extracted with CH_2Cl_2, dried over Na_2SO_4 and concentrated. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (1:1) as the eluent to obtain chiral amide product (1.96 g, 67%).

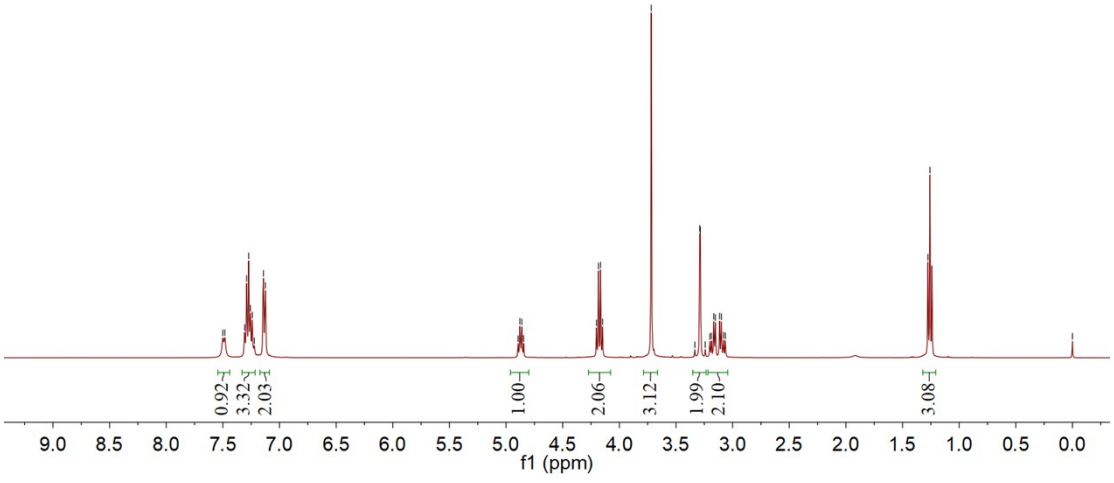


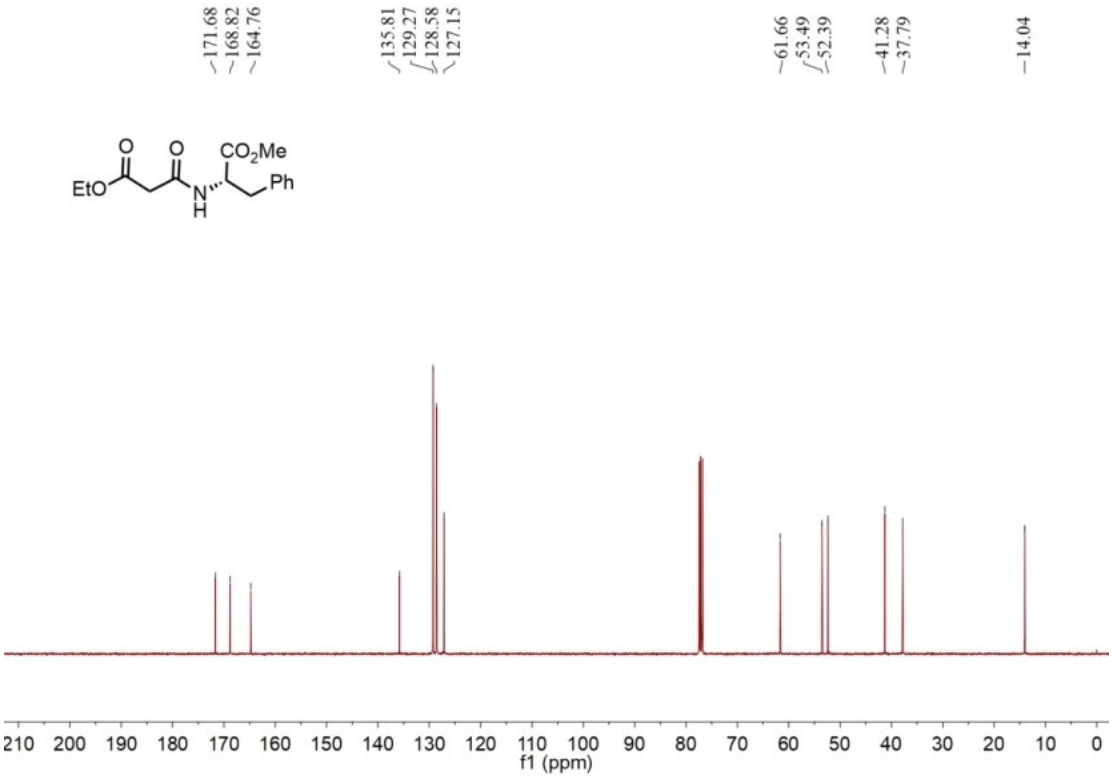
ethyl (*R*)-3-((1-methoxy-1-oxo-3-phenylpropan-2-yl)amino)-3-oxopropanoate:

White solid (1.96 g, 67%); Eluent: petroleum ether/ethyl acetate 1:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.0 Hz, 1H), 7.33 - 7.21 (m, 3H), 7.13 (d, *J* = 7.0 Hz, 2H), 4.87 (q, *J* = 6.3 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.72 (s, 3H), 3.29 (d, *J* = 2.0 Hz, 2H), 3.22 - 3.04 (m, 2H), 1.27 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.68, 168.82, 164.76, 135.81, 129.27, 128.58, 127.15, 61.66, 53.49, 52.39, 41.28, 37.79, 14.04; HRMS (ESI): m/z for $C_{15}H_{19}NO_5Na$ $[M+Na]^+$ calcd 316.1155, found 316.1171.









8. References

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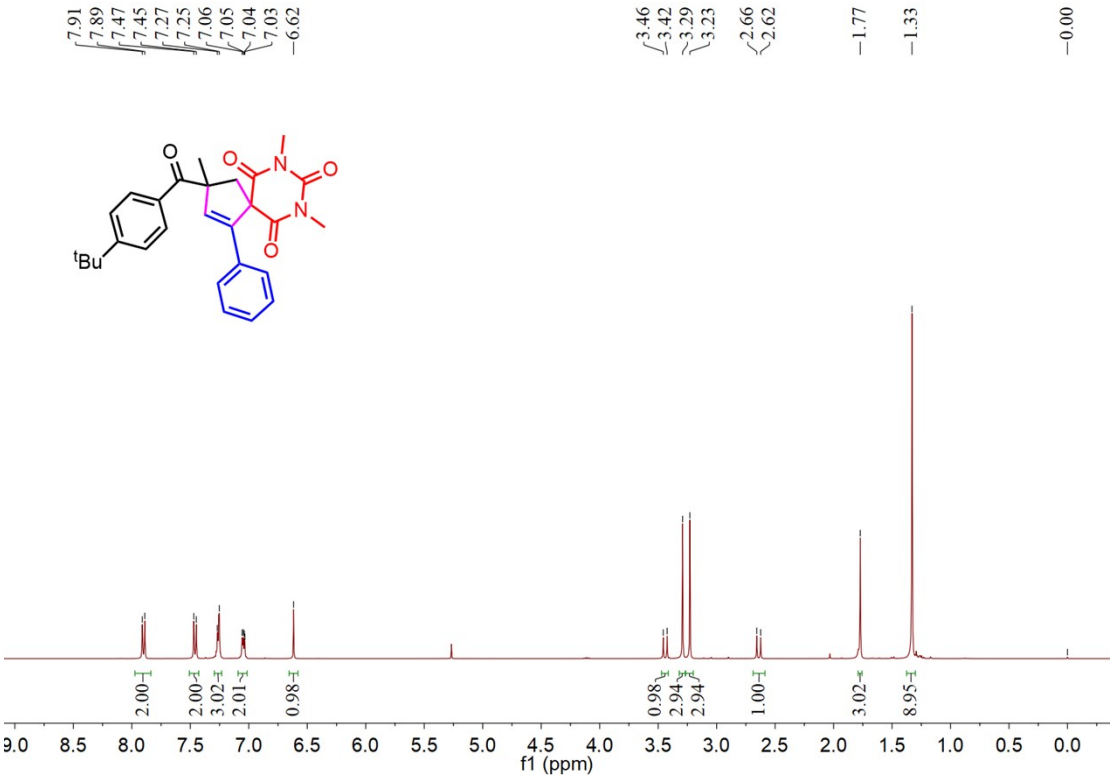
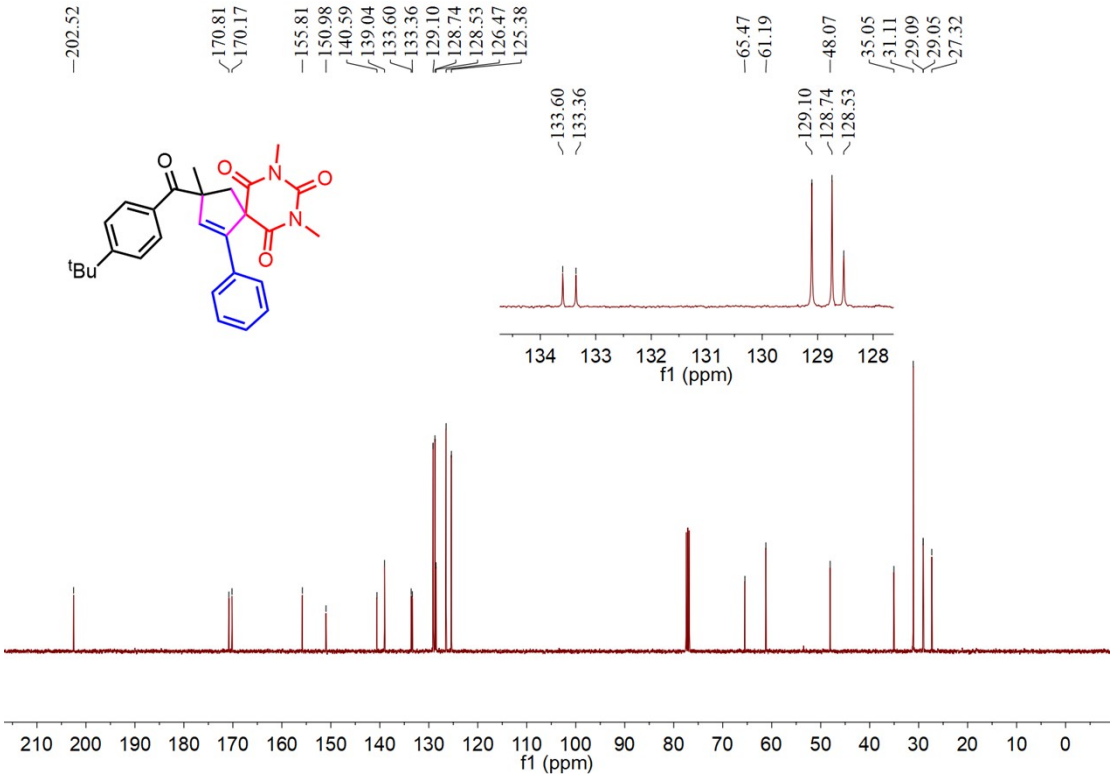
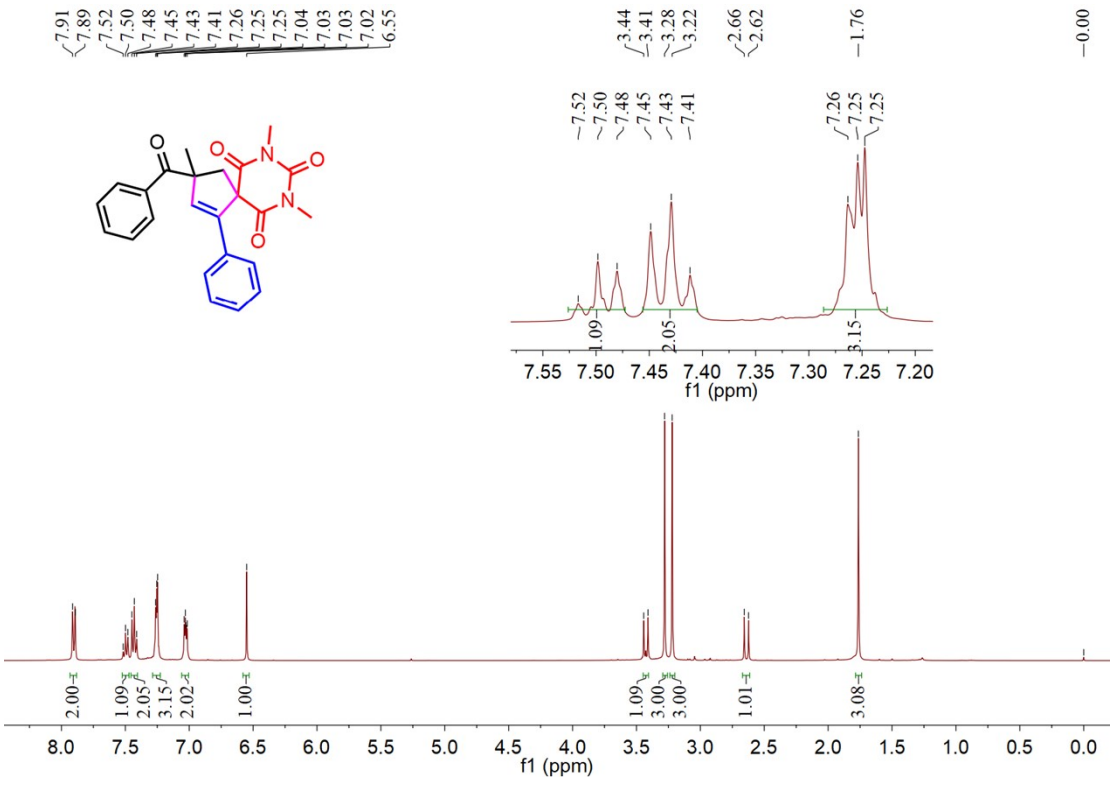
9. NMR Spectra for Spirocyclic Products and Intermediates of Mechanistic Studies

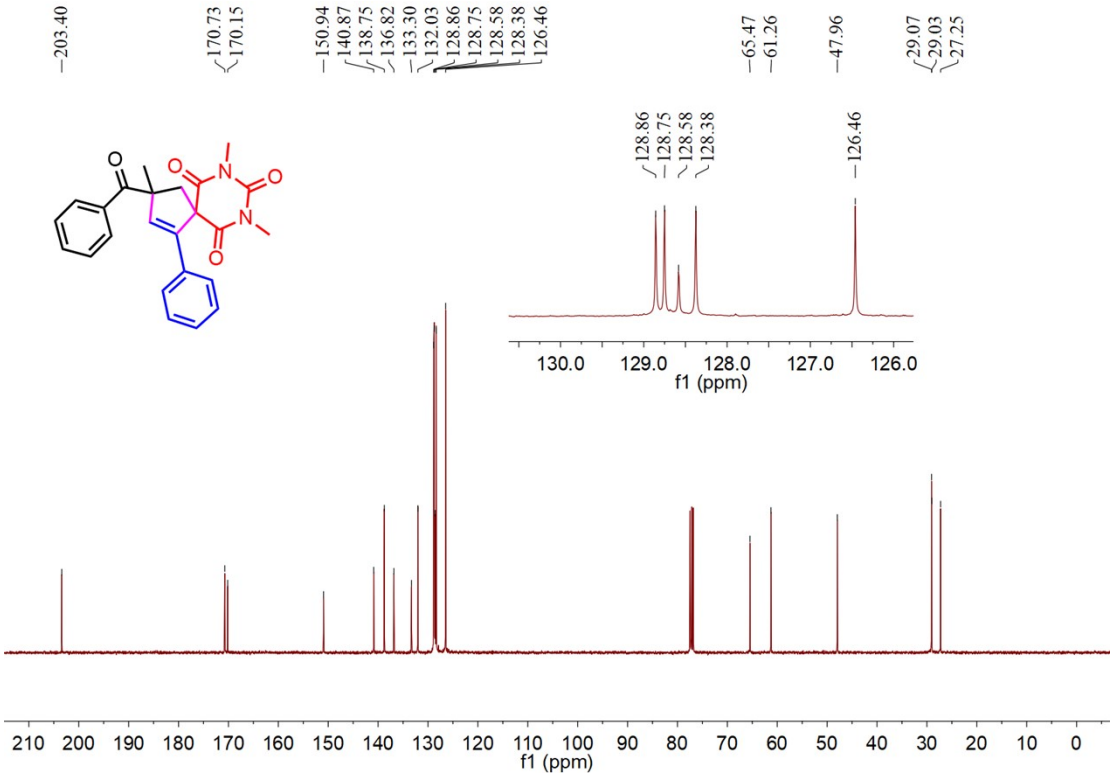
3-(4-(*tert*-butyl)benzoyl)-3,7,9-trimethyl-1-phenyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (3):



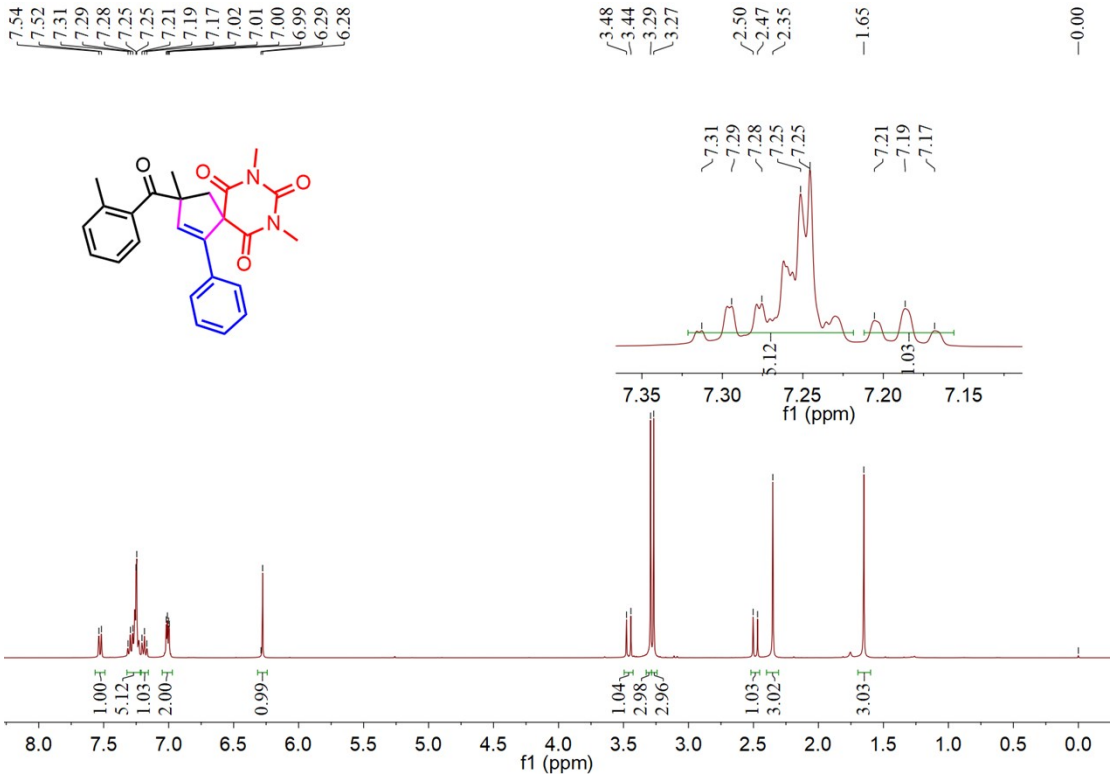


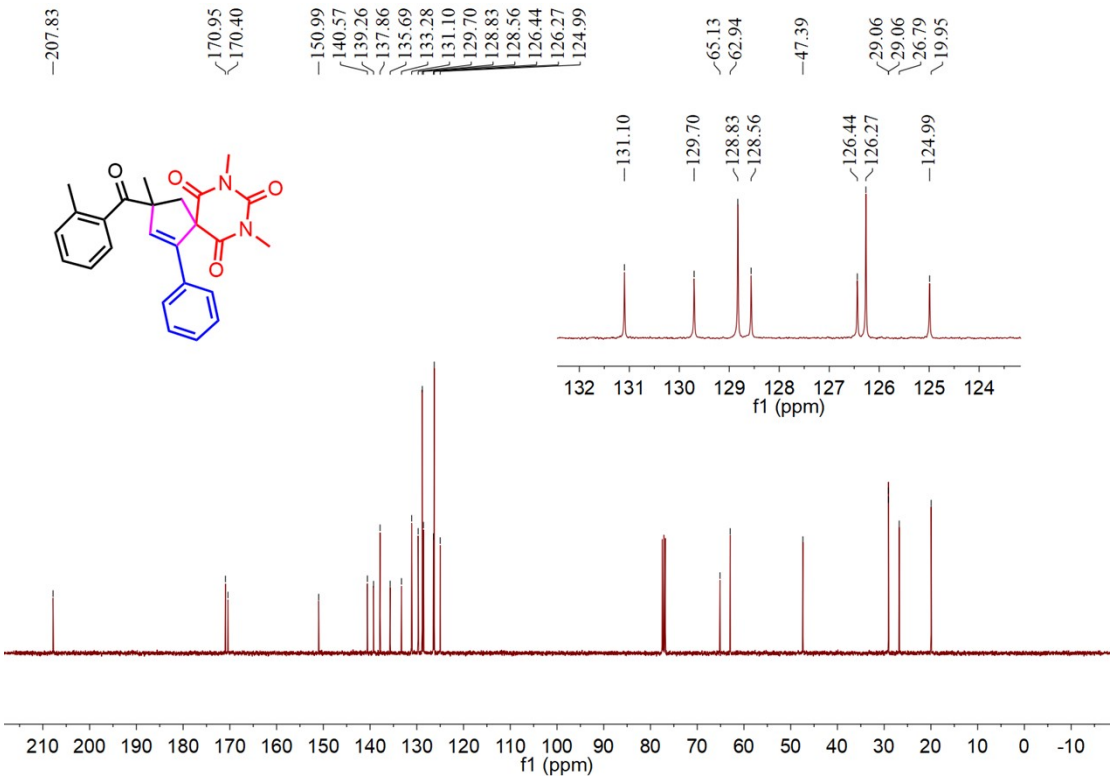
3-benzoyl-3,7,9-trimethyl-1-phenyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (4):



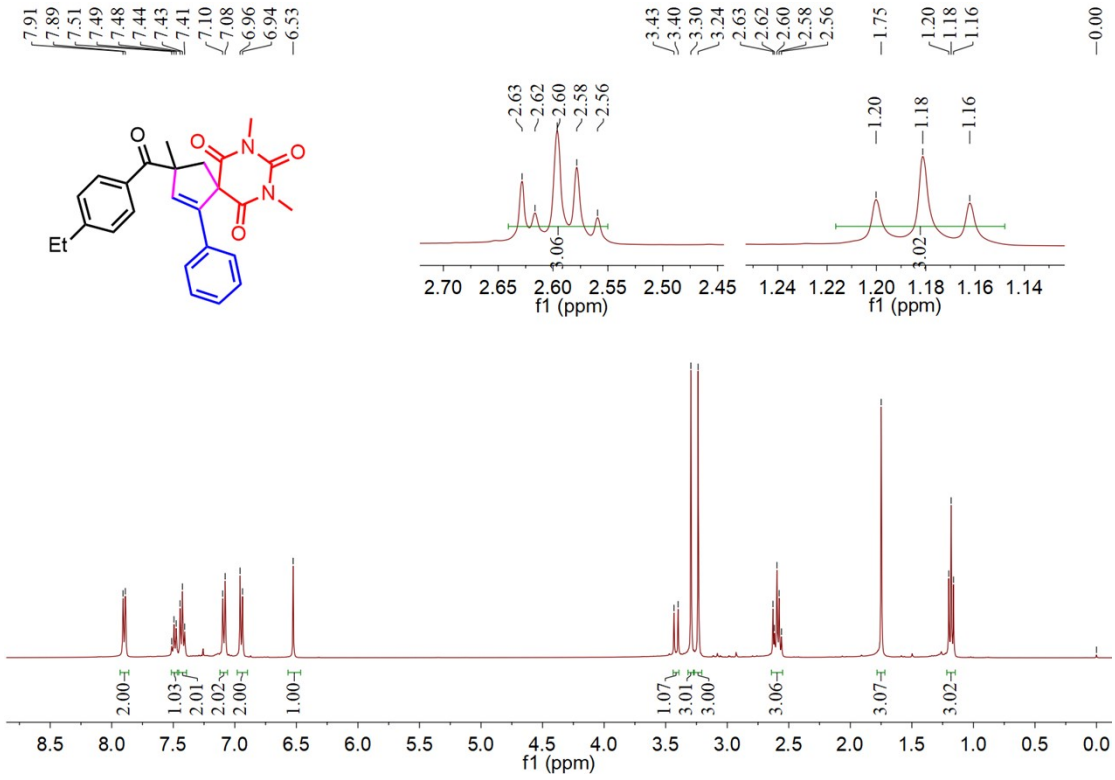


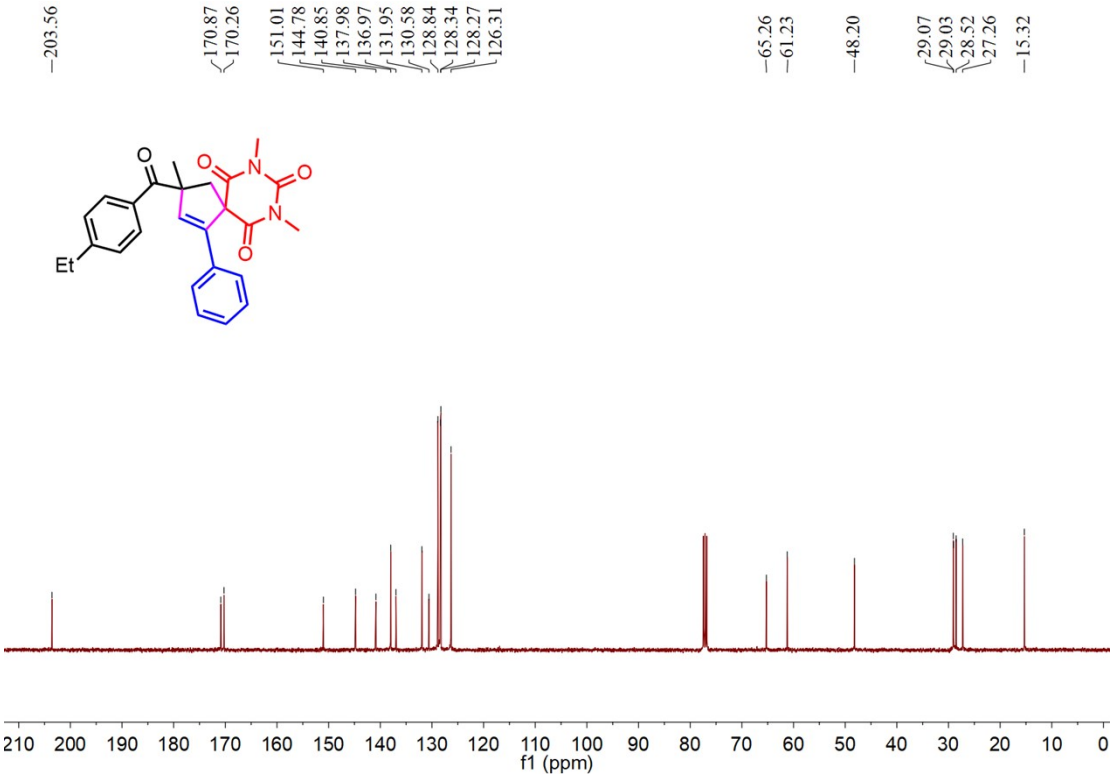
3,7,9-trimethyl-3-(2-methylbenzoyl)-1-phenyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (5):



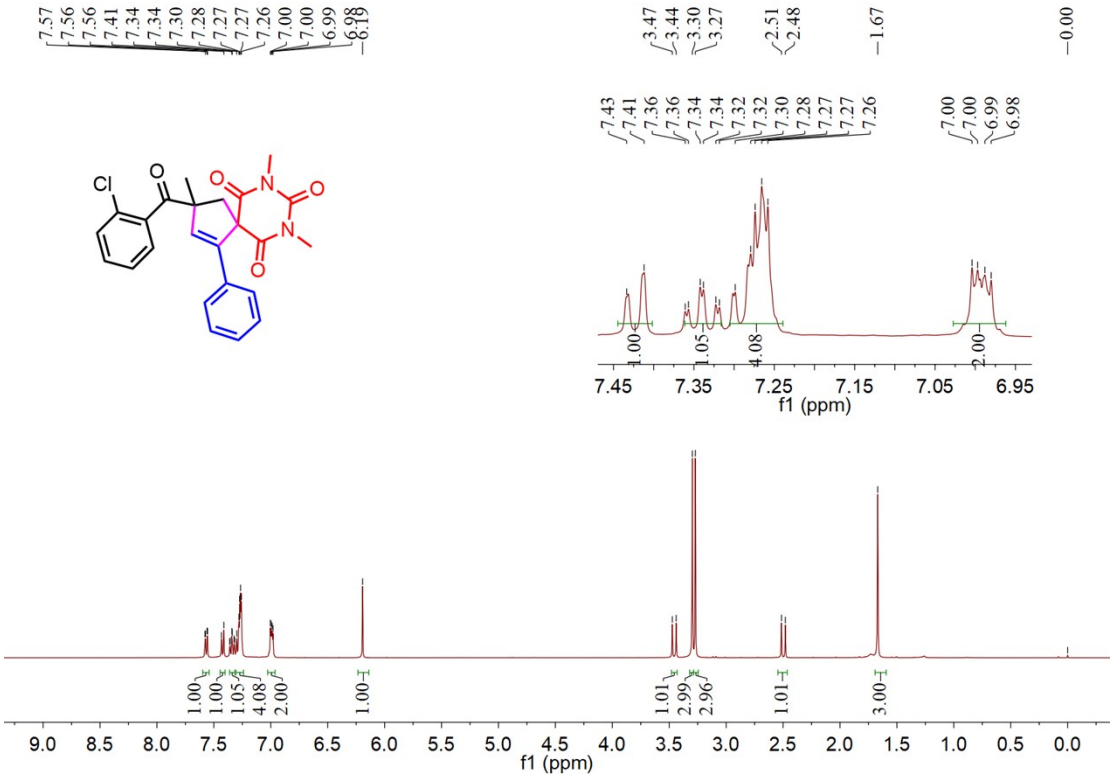


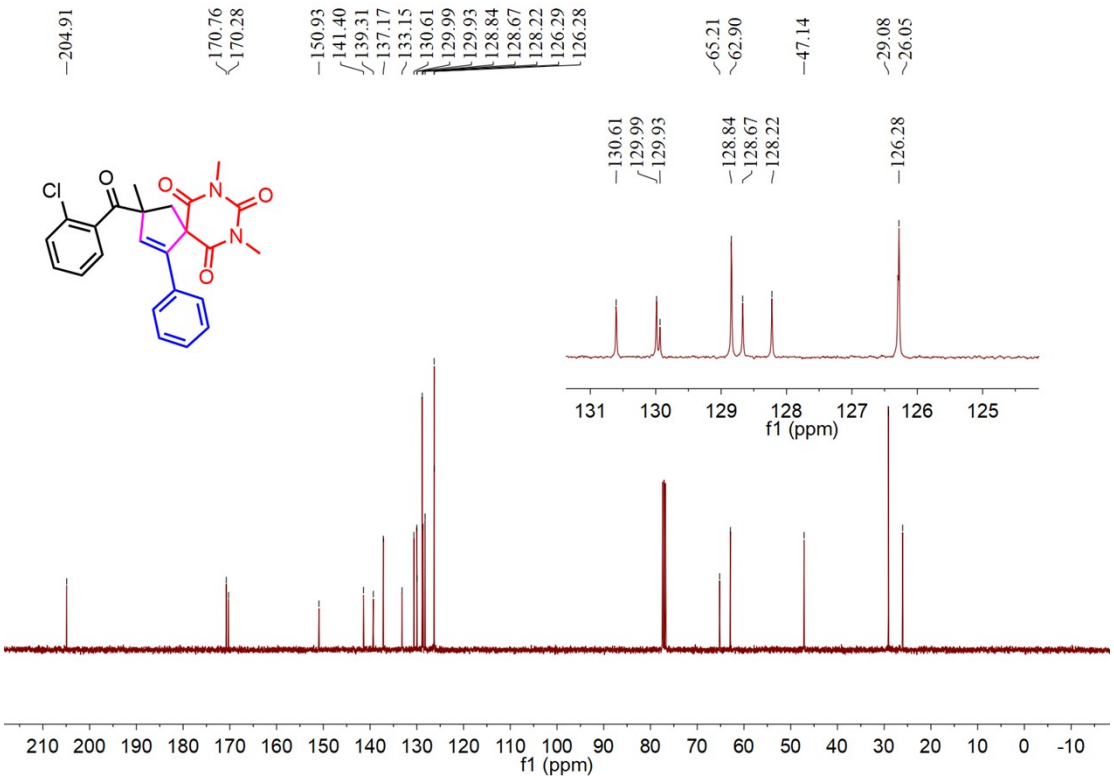
3-(4-ethylbenzoyl)-3,7,9-trimethyl-1-phenyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (6):



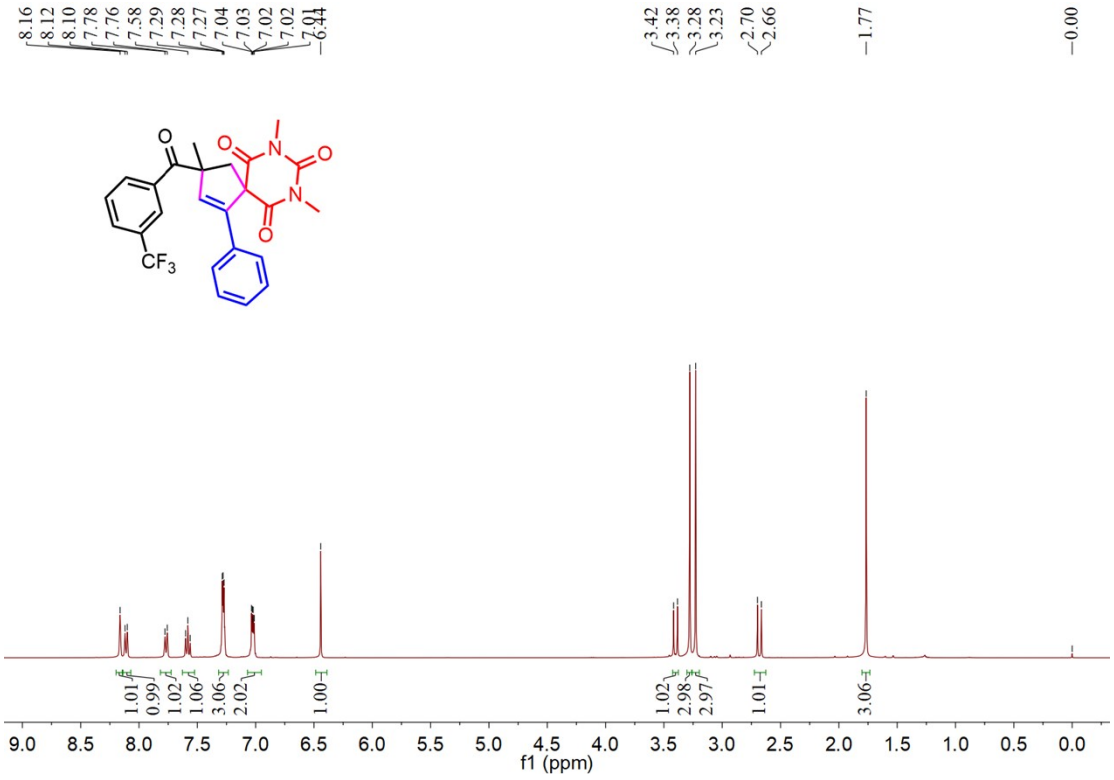


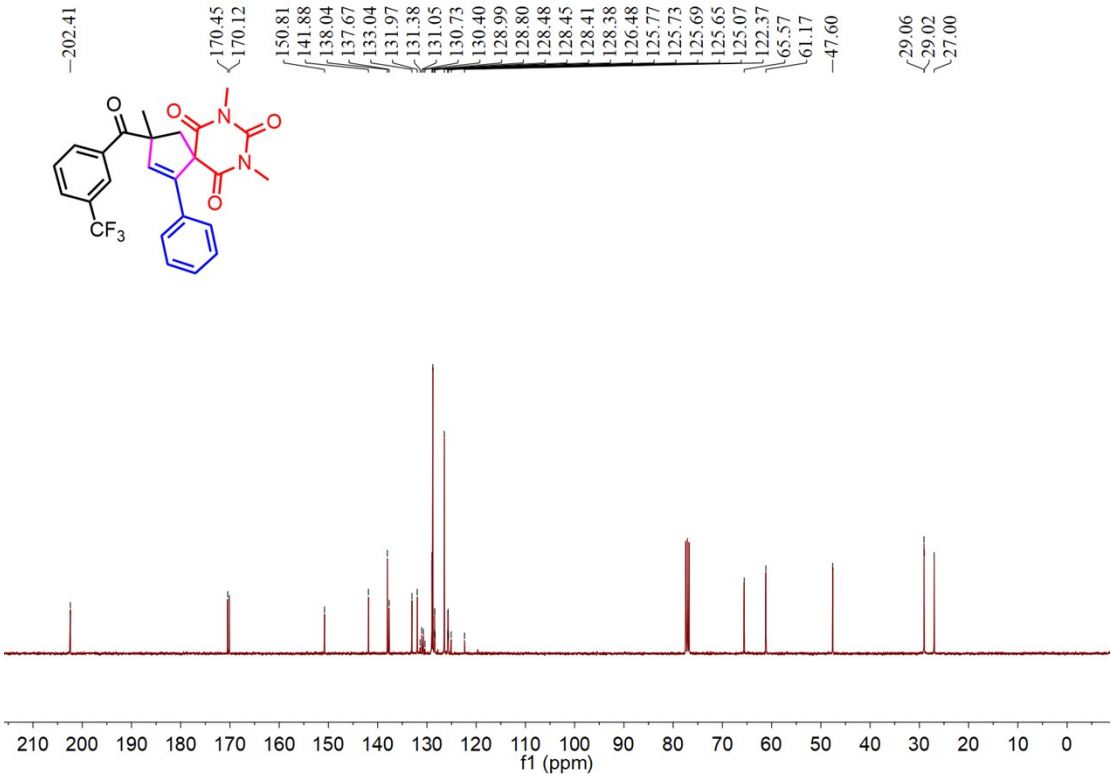
3-(2-chlorobenzoyl)-3,7,9-trimethyl-1-phenyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (7):





3,7,9-trimethyl-1-phenyl-3-(3-(trifluoromethyl)benzoyl)-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (8):

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29.02
27.00
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N
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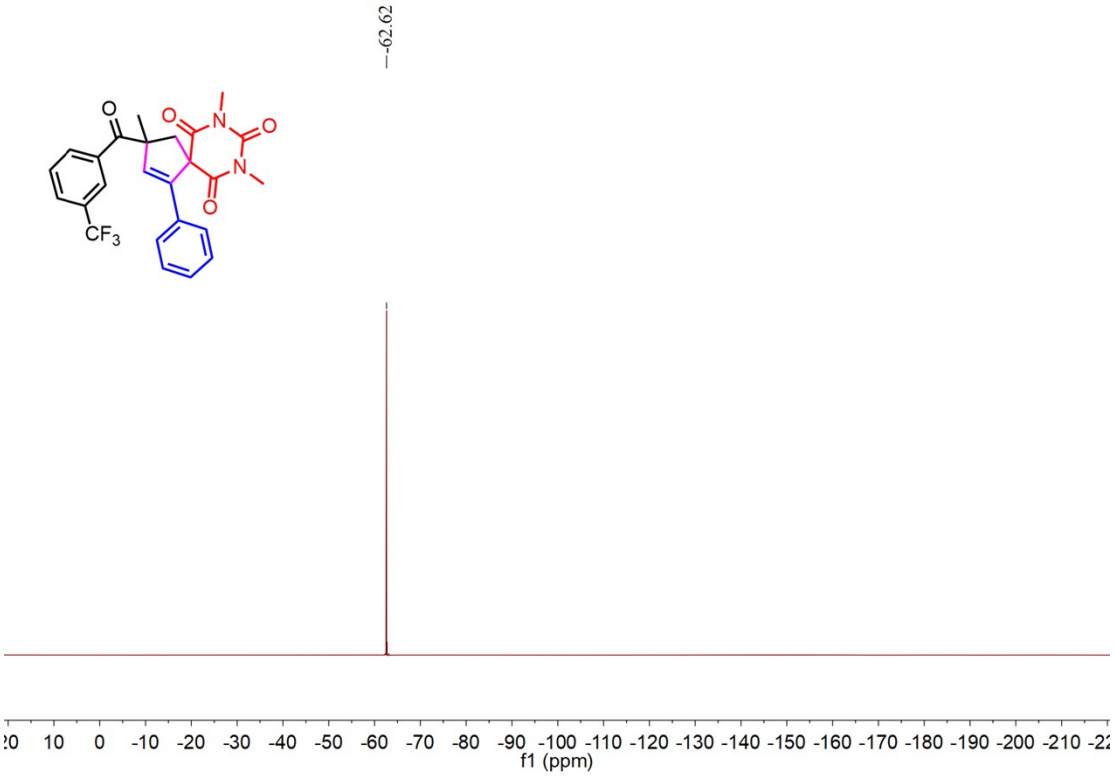
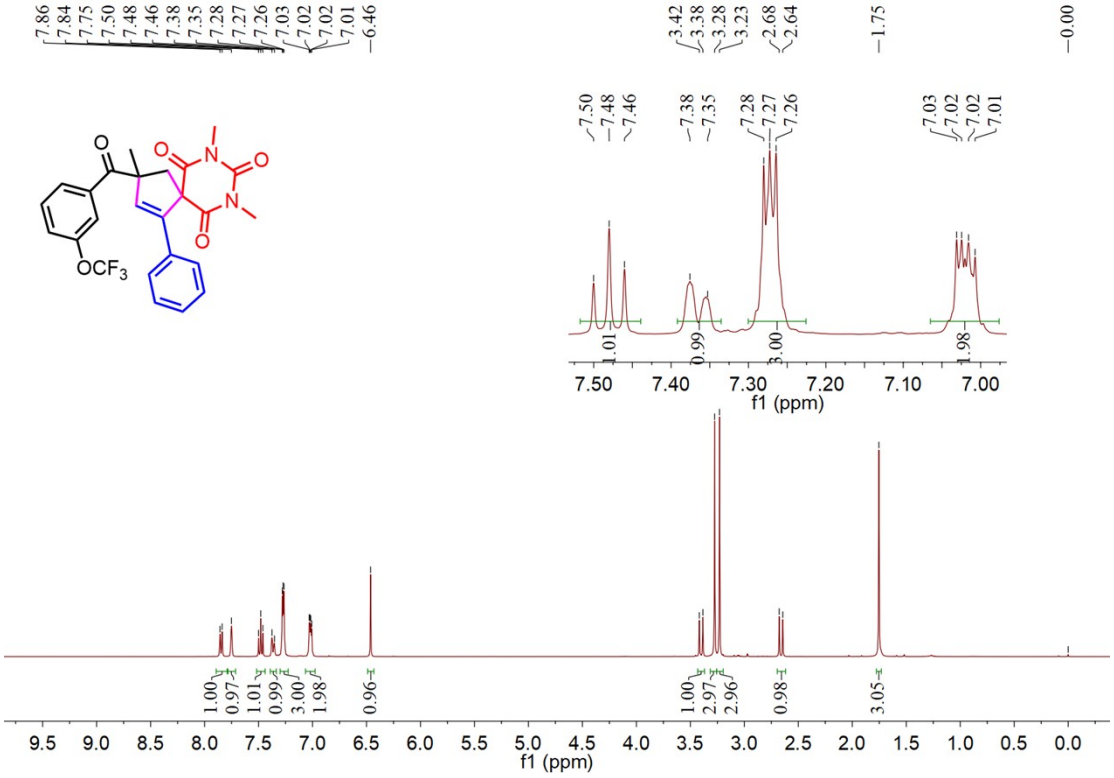
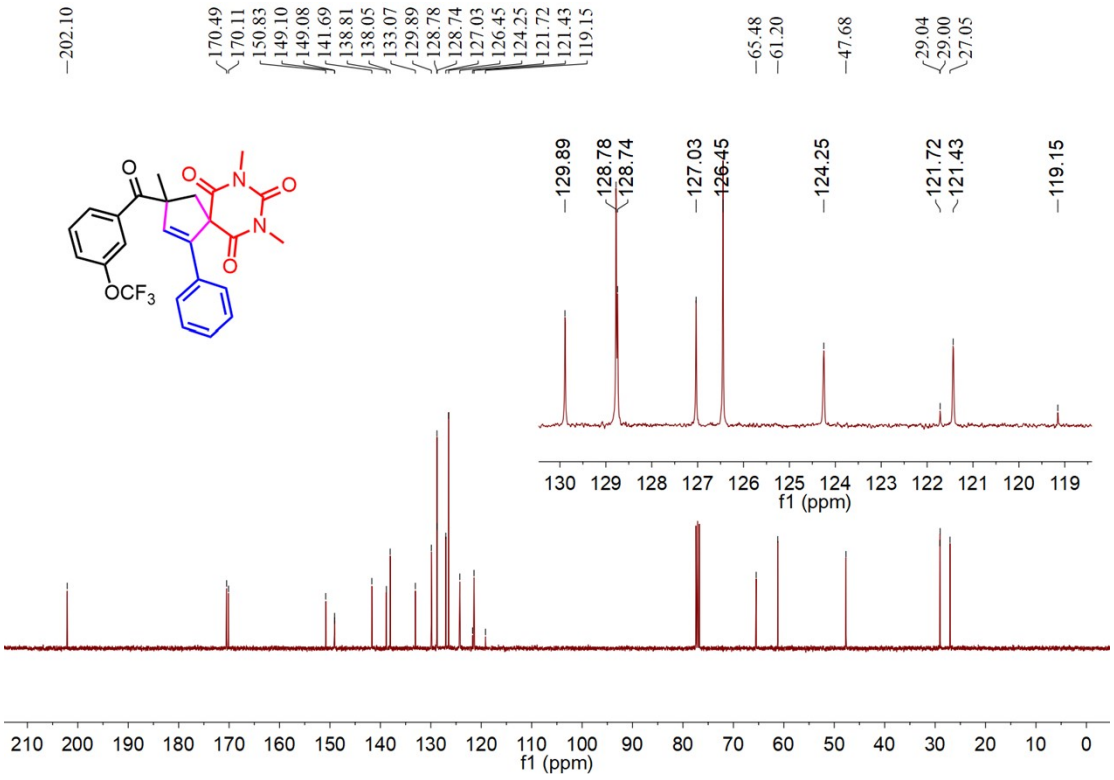
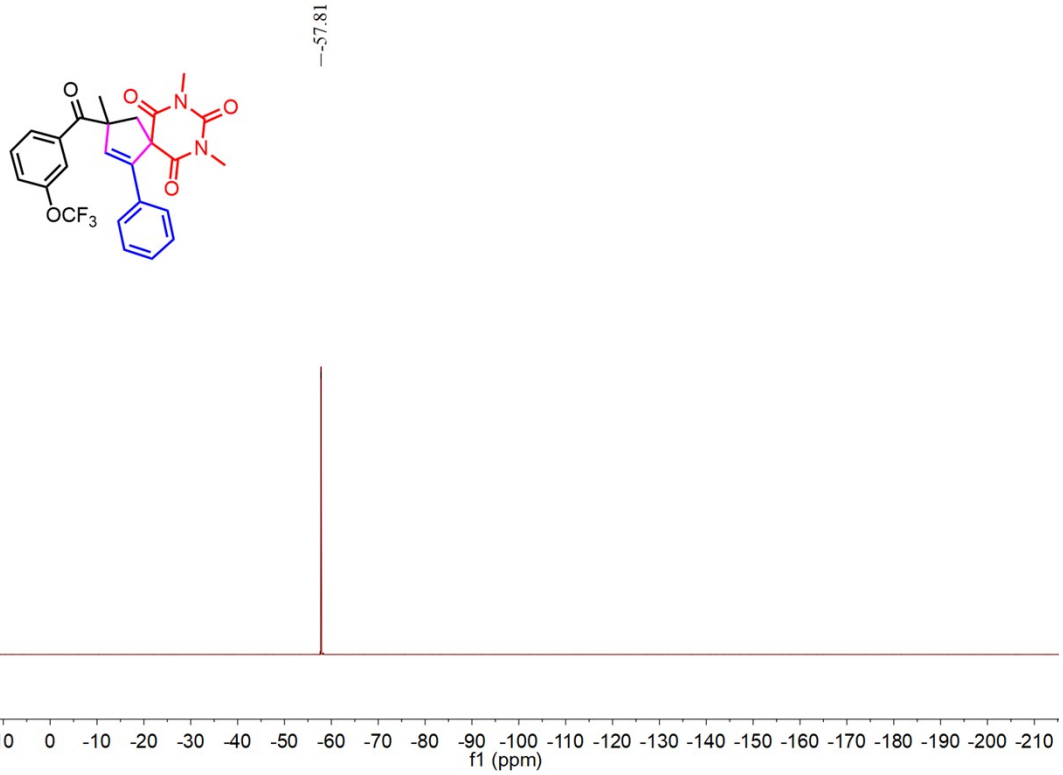
O
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-62.62
O
N
O
N
O
O
CF3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)

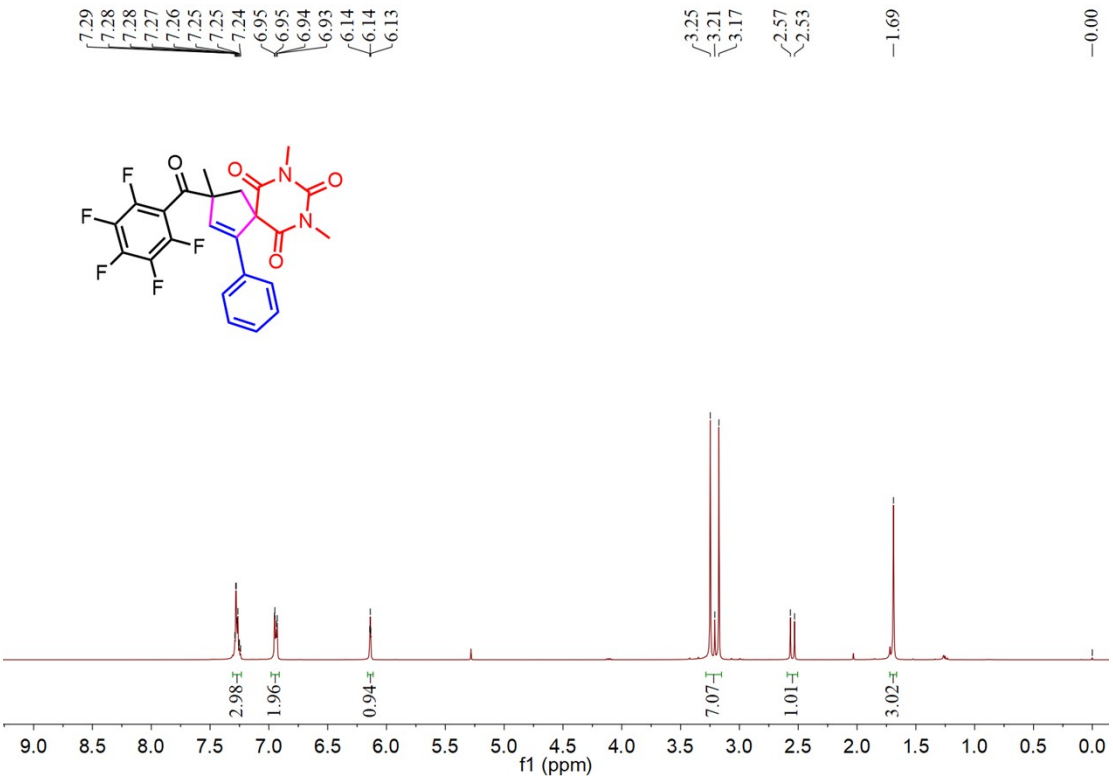
3,7,9-trimethyl-1-phenyl-3-(3-(trifluoromethoxy)benzoyl)-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (9):

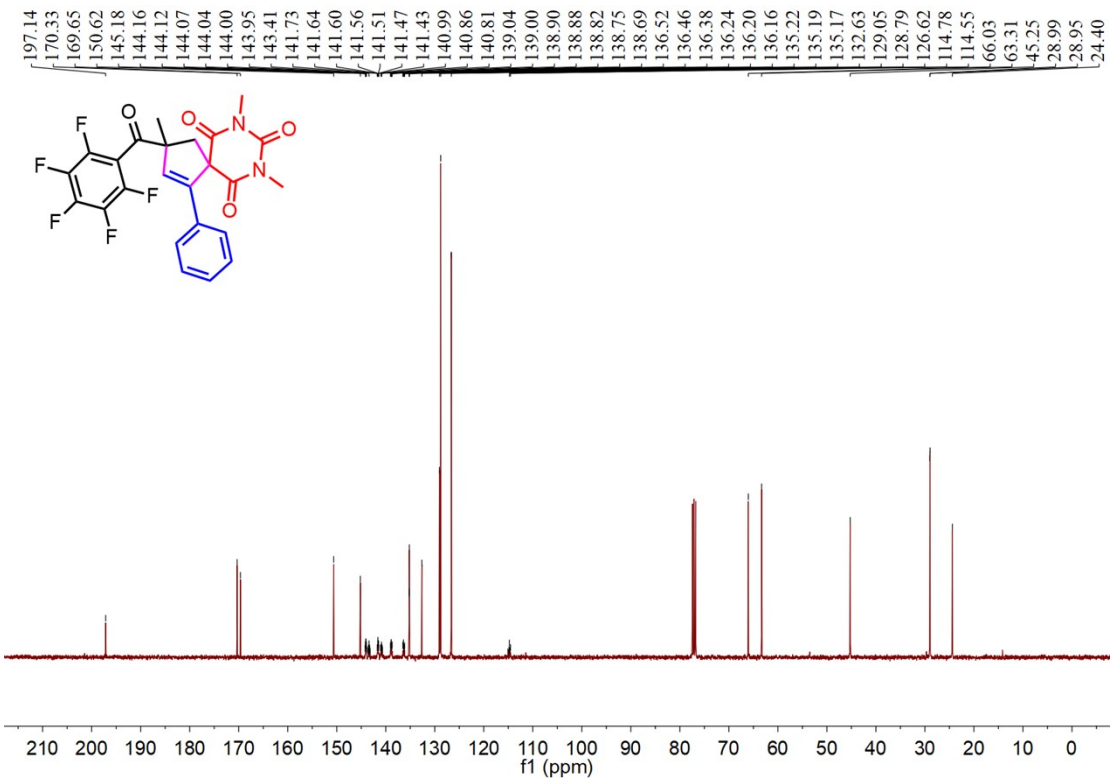


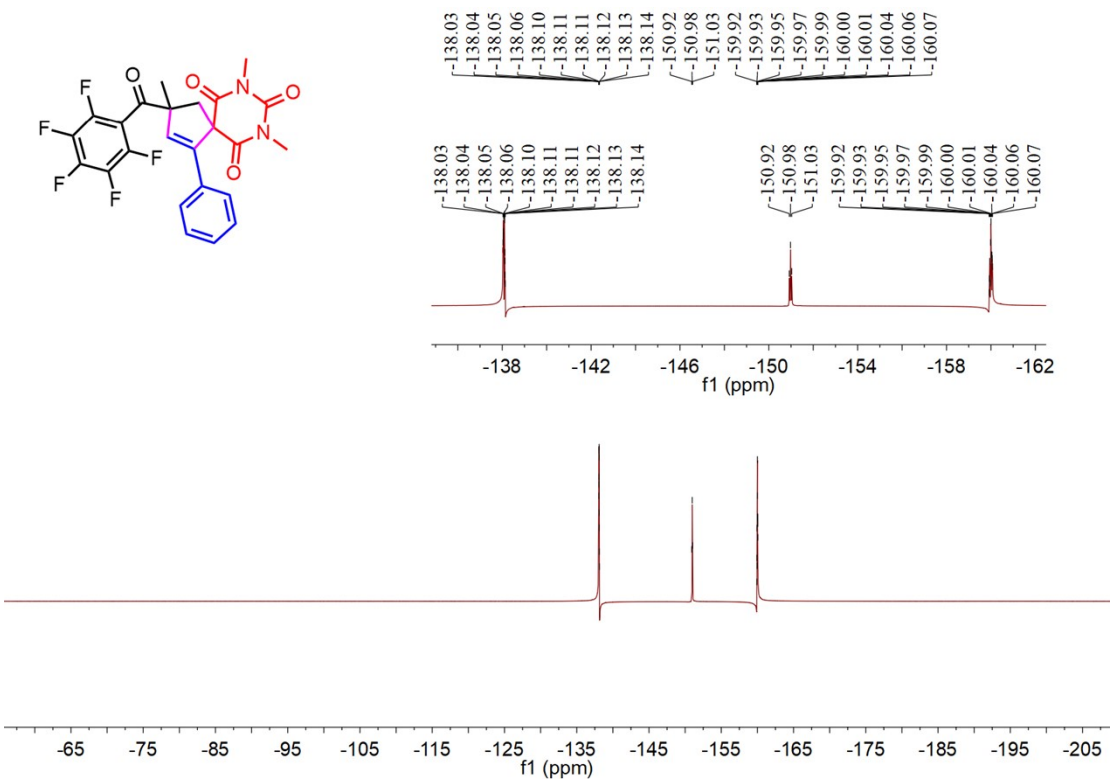




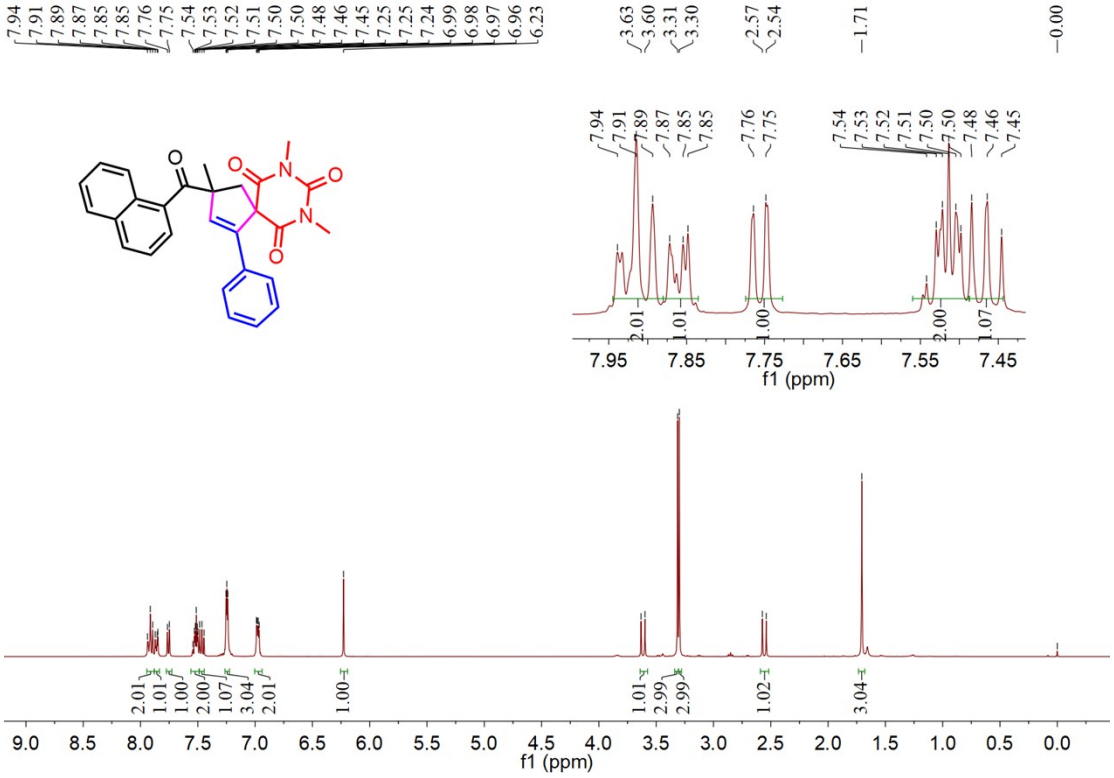
3,7,9-trimethyl-3-(perfluorobenzoyl)-1-phenyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (10):

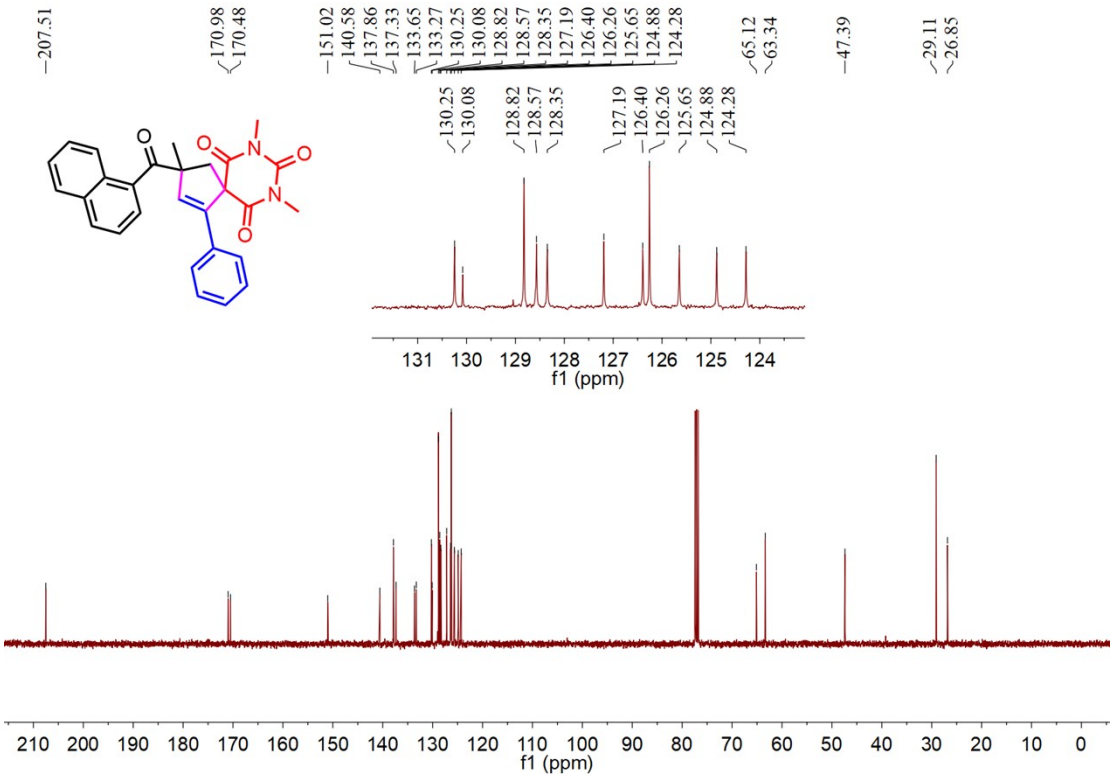



197.14
170.33
169.65
150.62
145.18
144.16
144.12
144.07
144.04
144.00
143.95
143.41
141.73
141.64
141.60
141.56
141.51
141.47
141.43
140.99
140.86
140.81
139.04
139.00
138.90
138.88
138.82
138.75
138.69
136.52
136.46
136.38
136.24
136.20
136.16
135.22
135.19
135.17
132.63
129.05
128.79
126.62
114.78
114.55
66.03
63.31
45.25
28.99
28.95
24.40
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

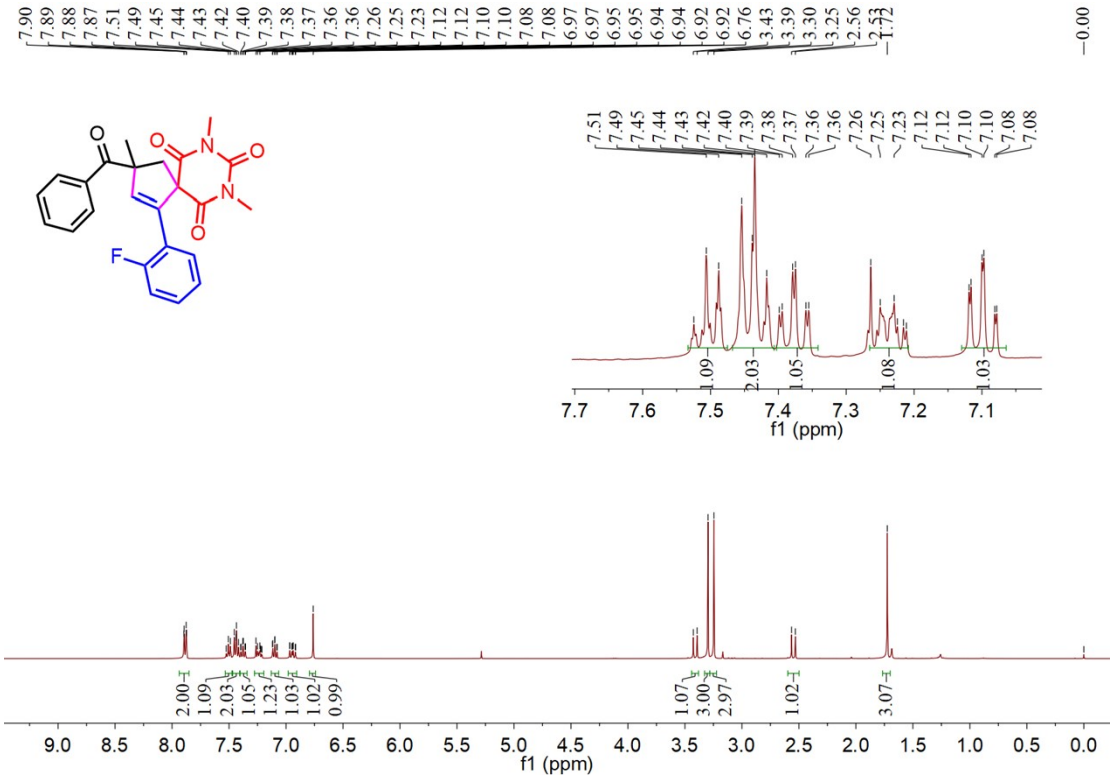

138.03
138.04
138.05
138.06
138.10
138.11
138.11
138.12
138.13
138.14
150.92
150.98
151.03
159.92
159.93
159.95
159.97
159.99
160.00
160.01
160.04
160.06
160.07
-138 -142 -146 -150 -154 -158 -162
f1 (ppm)
-65 -75 -85 -95 -105 -115 -125 -135 -145 -155 -165 -175 -185 -195 -205
f1 (ppm)

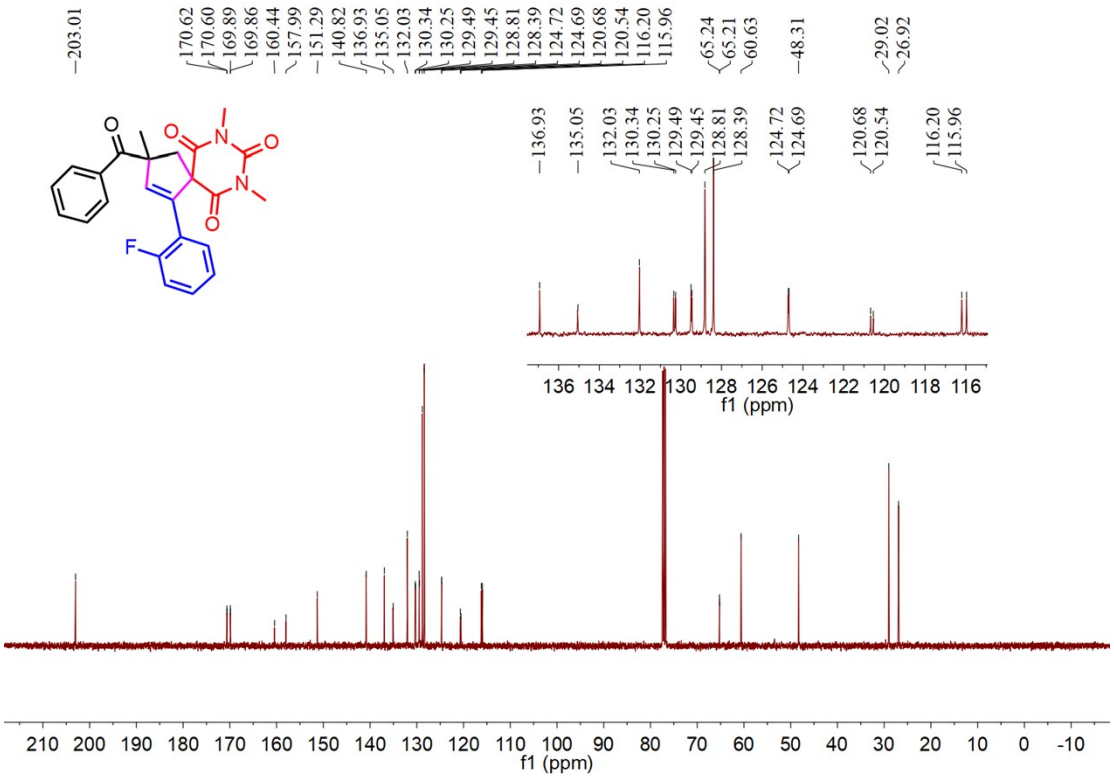
3-(1-naphthoyl)-3,7,9-trimethyl-1-phenyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (11):

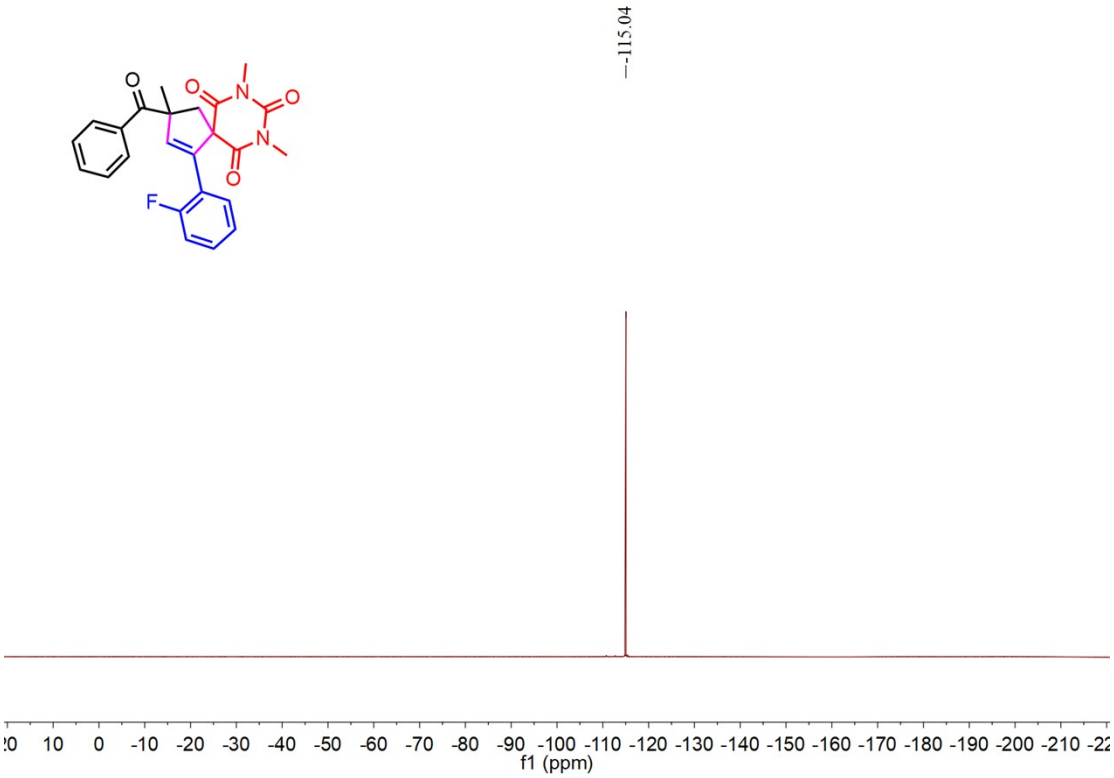




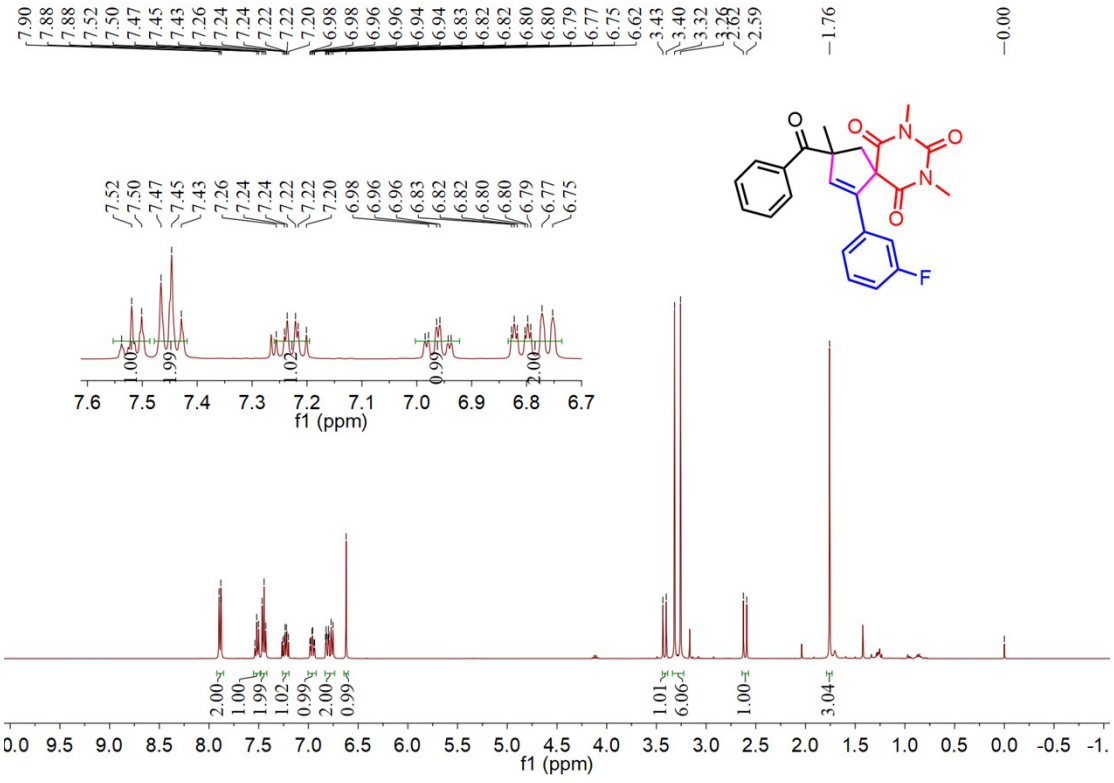
3-benzoyl-1-(2-fluorophenyl)-3,7,9-trimethyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (12):

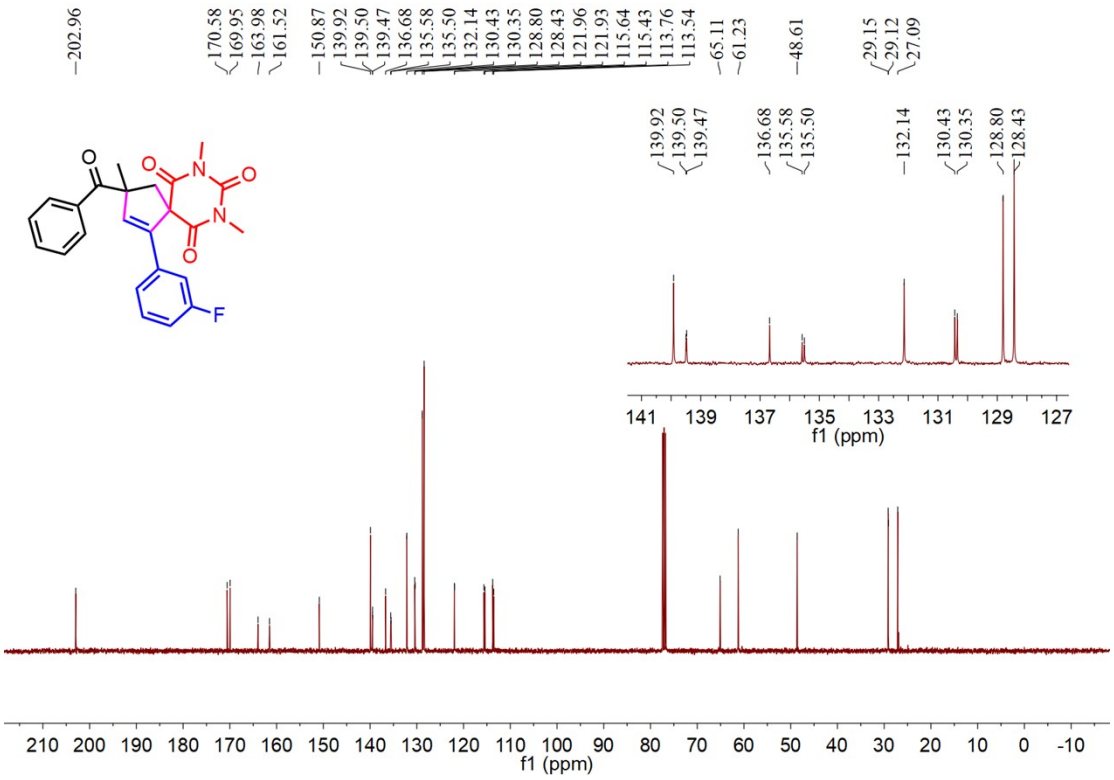


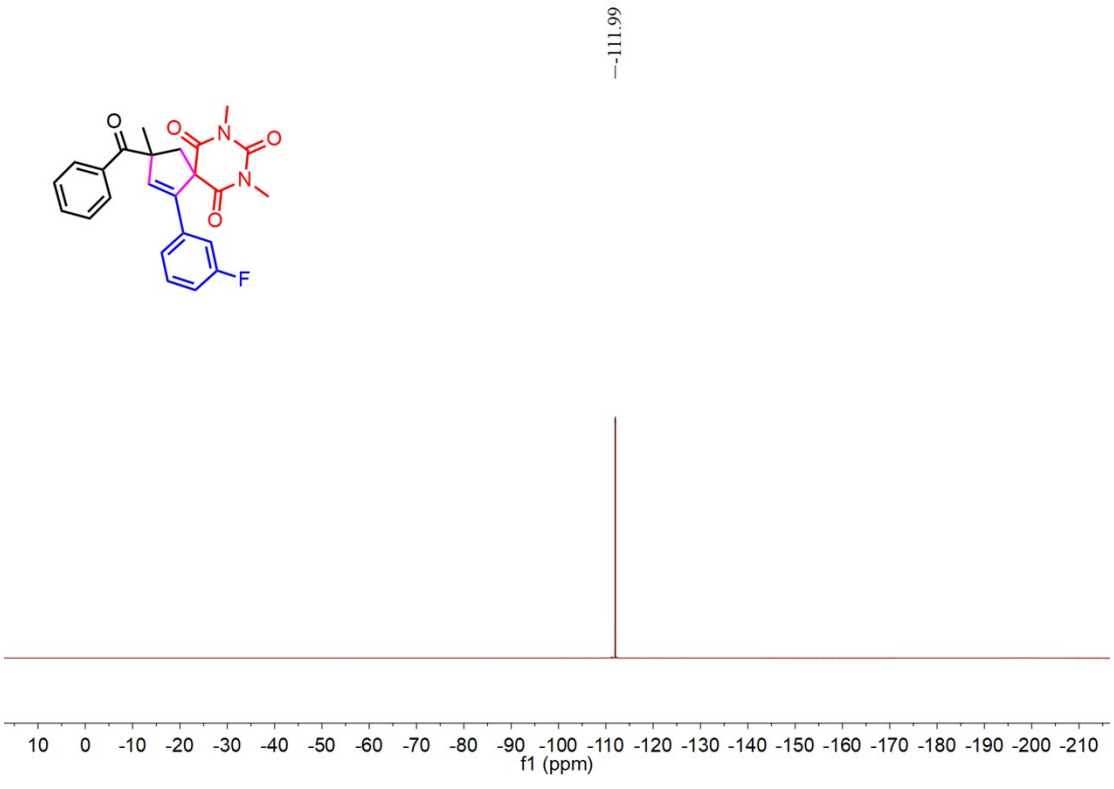




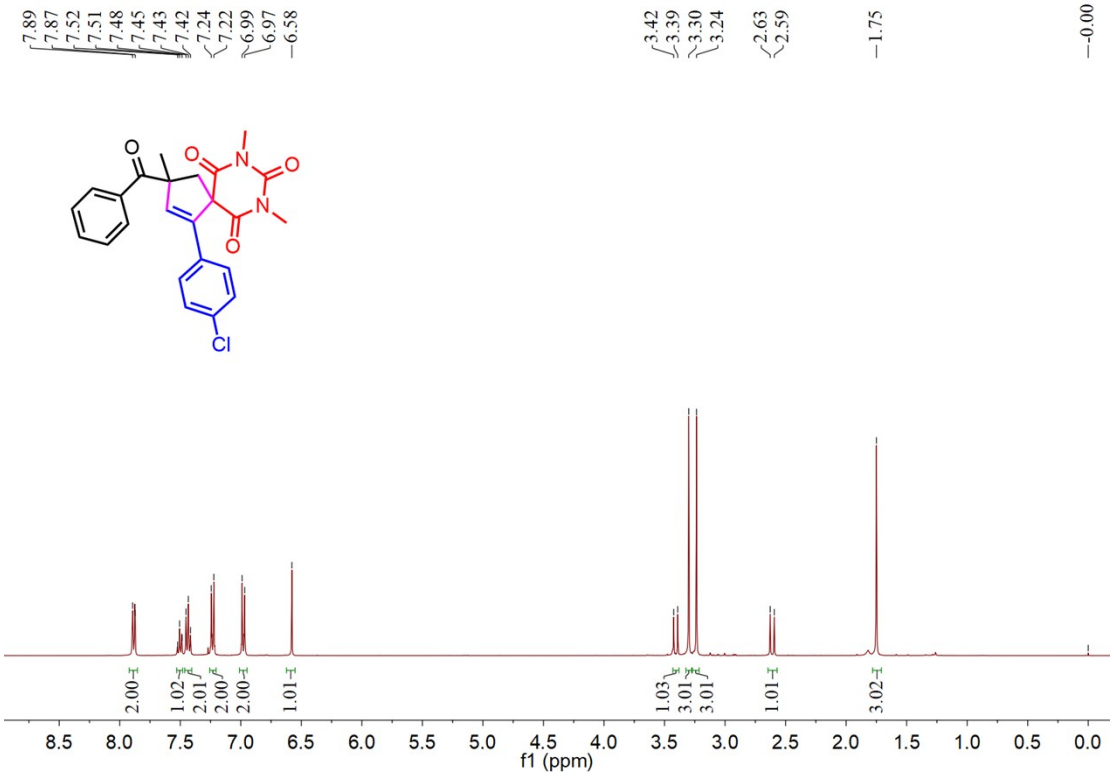
3-benzoyl-1-(3-fluorophenyl)-3,7,9-trimethyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (13):

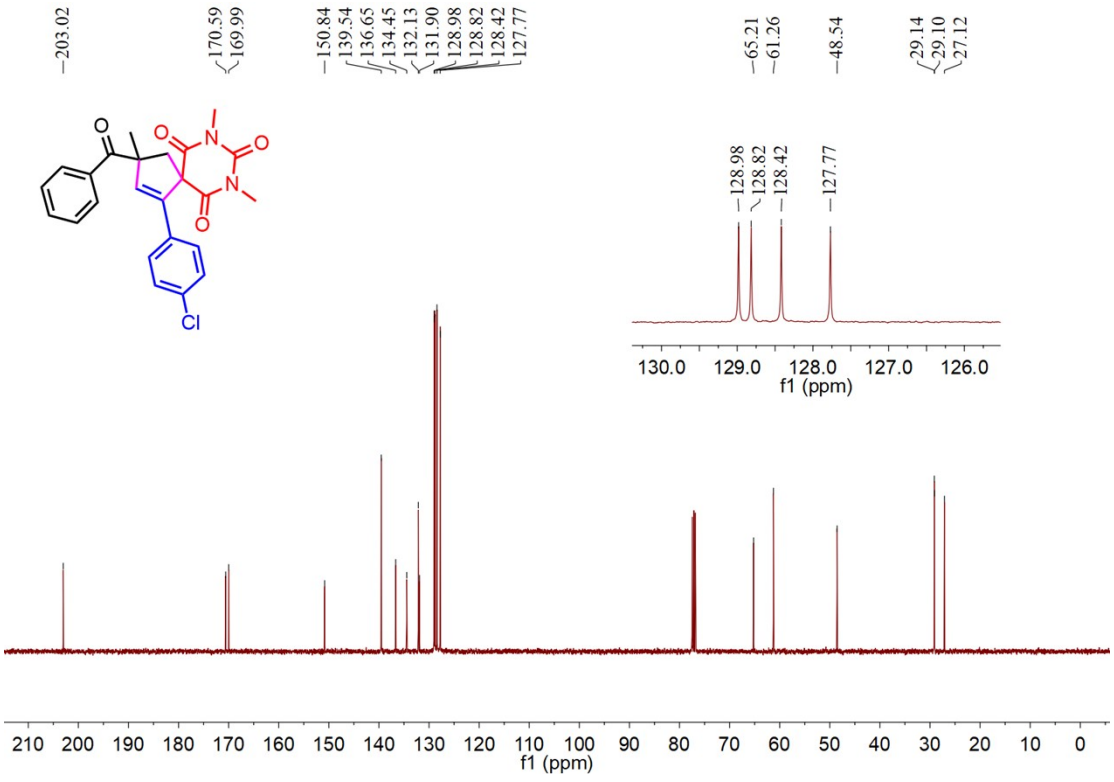



202.96
170.58
169.95
163.98
161.52
150.87
139.92
139.50
139.47
136.68
135.58
135.50
132.14
130.43
130.35
128.80
128.43
121.96
121.93
115.64
115.43
113.76
113.54
65.11
61.23
48.61
29.15
29.12
27.09
O
N
O
N
O
O
F
141 139 137 135 133 131 129 127
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

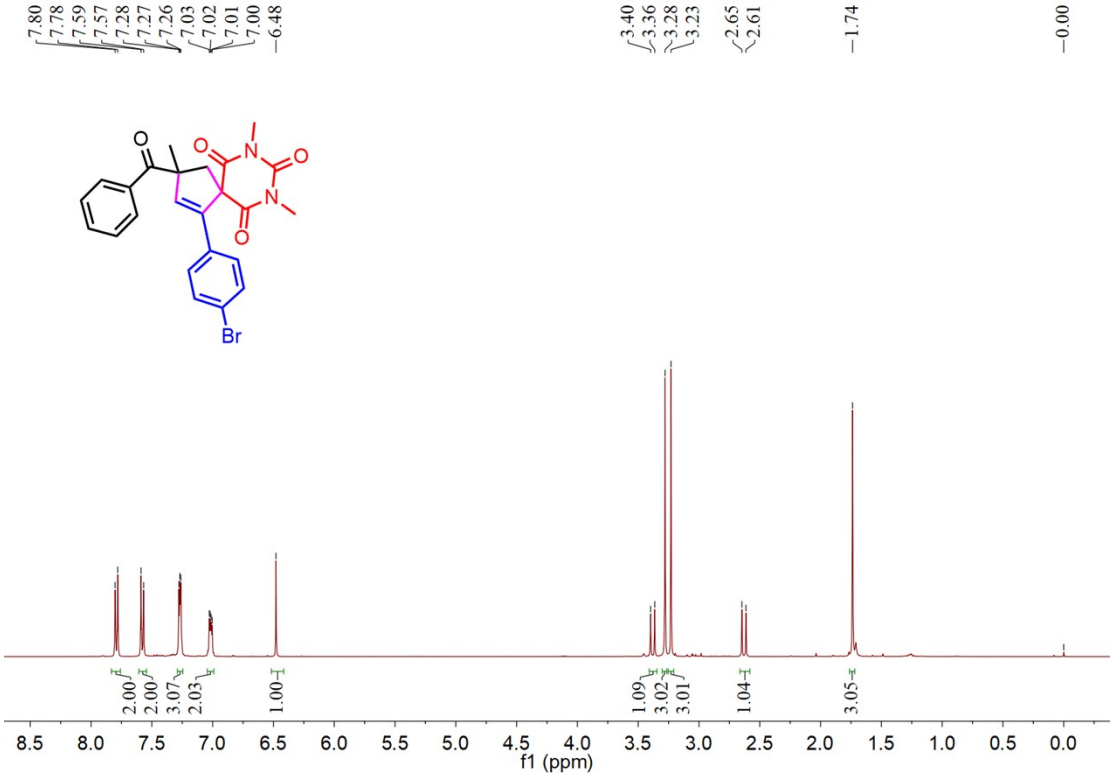

-111.99
O
N
O
N
O
O
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

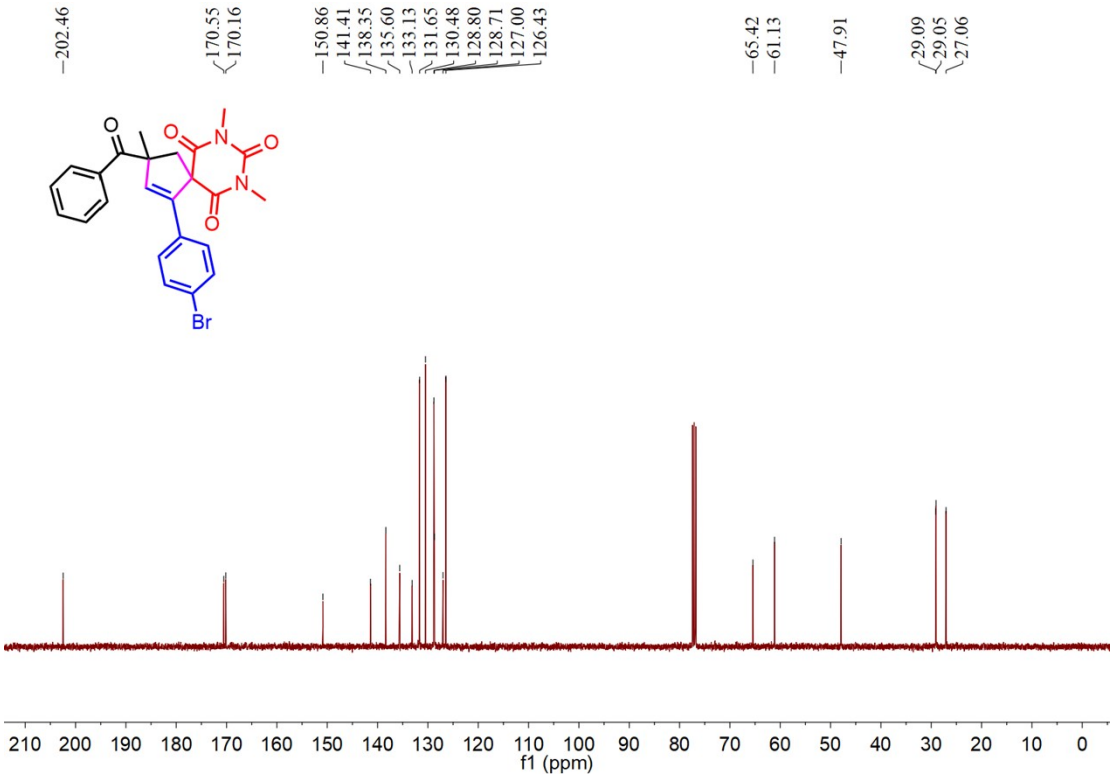
3-benzoyl-1-(4-chlorophenyl)-3,7,9-trimethyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (14):



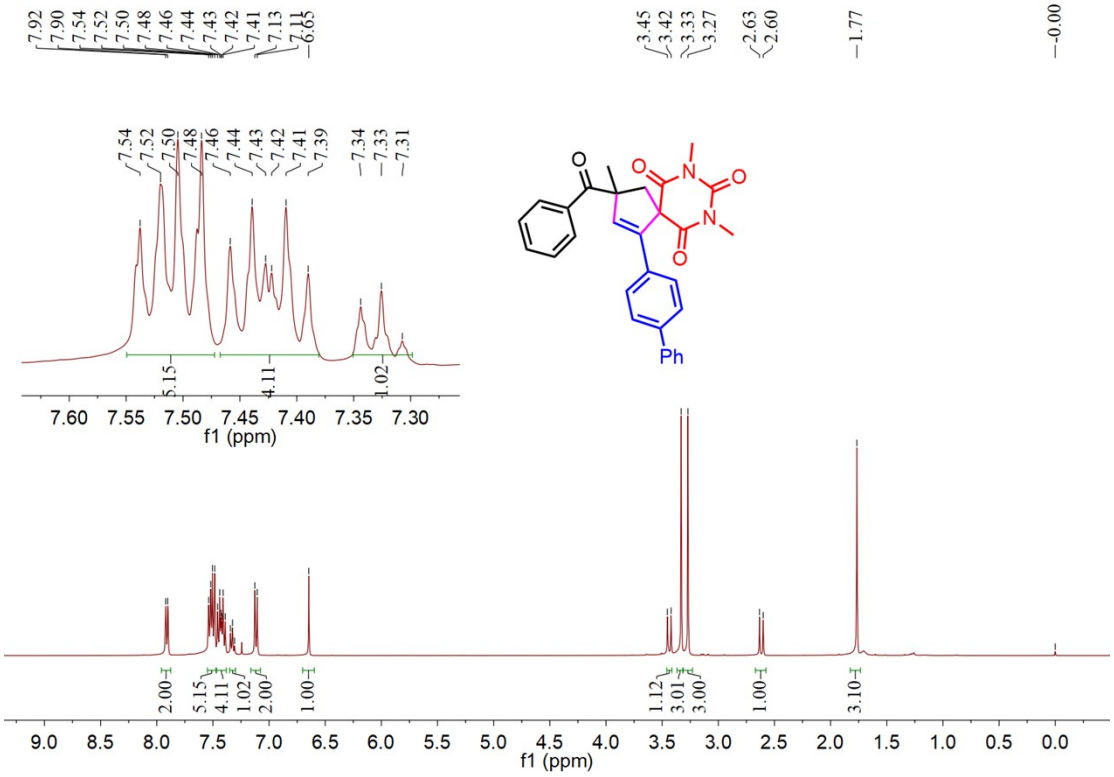


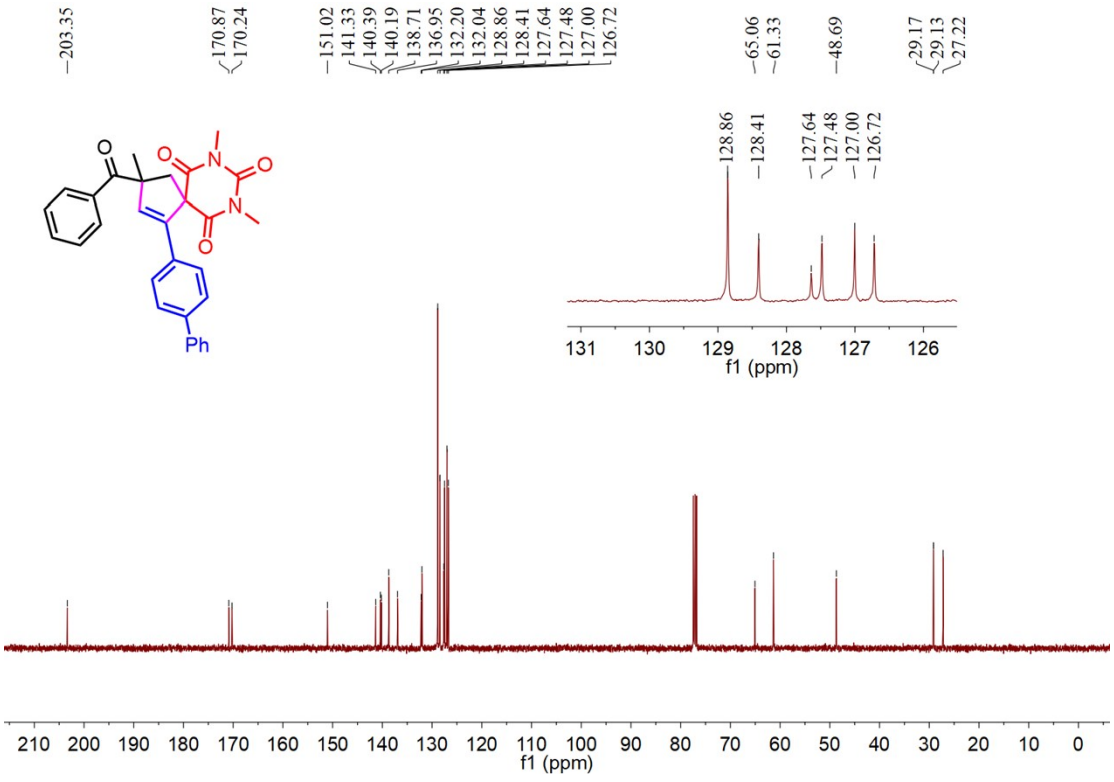
3-benzoyl-1-(4-bromophenyl)-3,7,9-trimethyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (15):



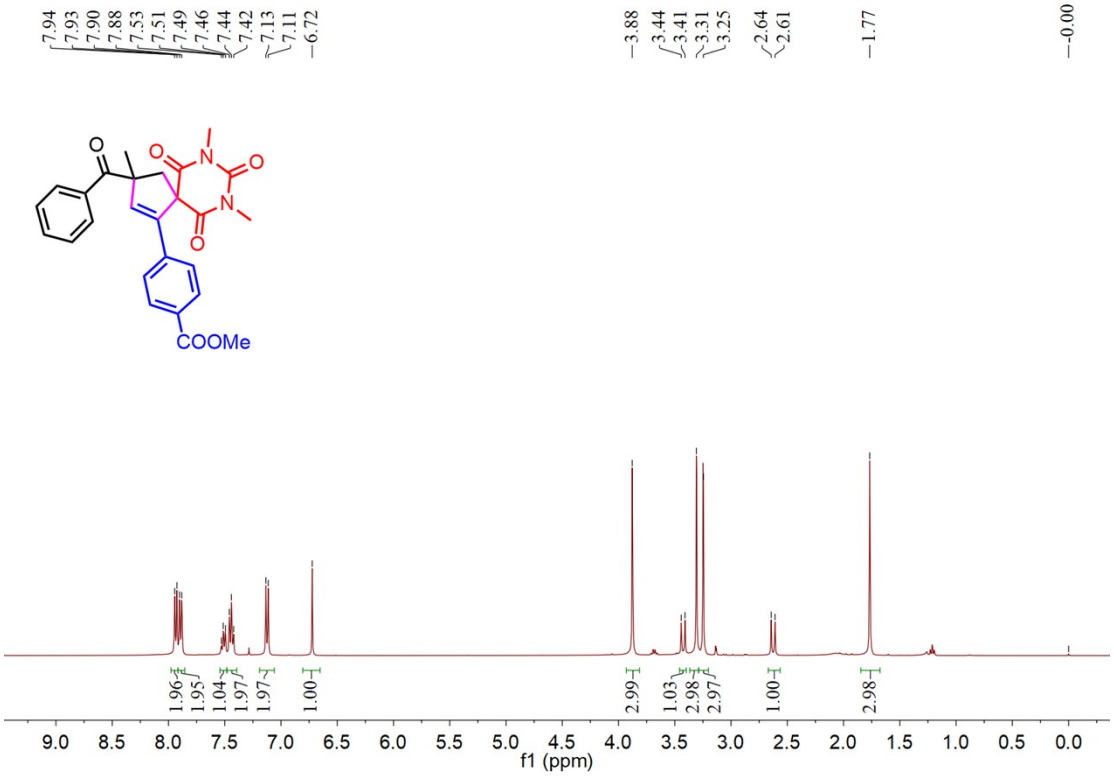


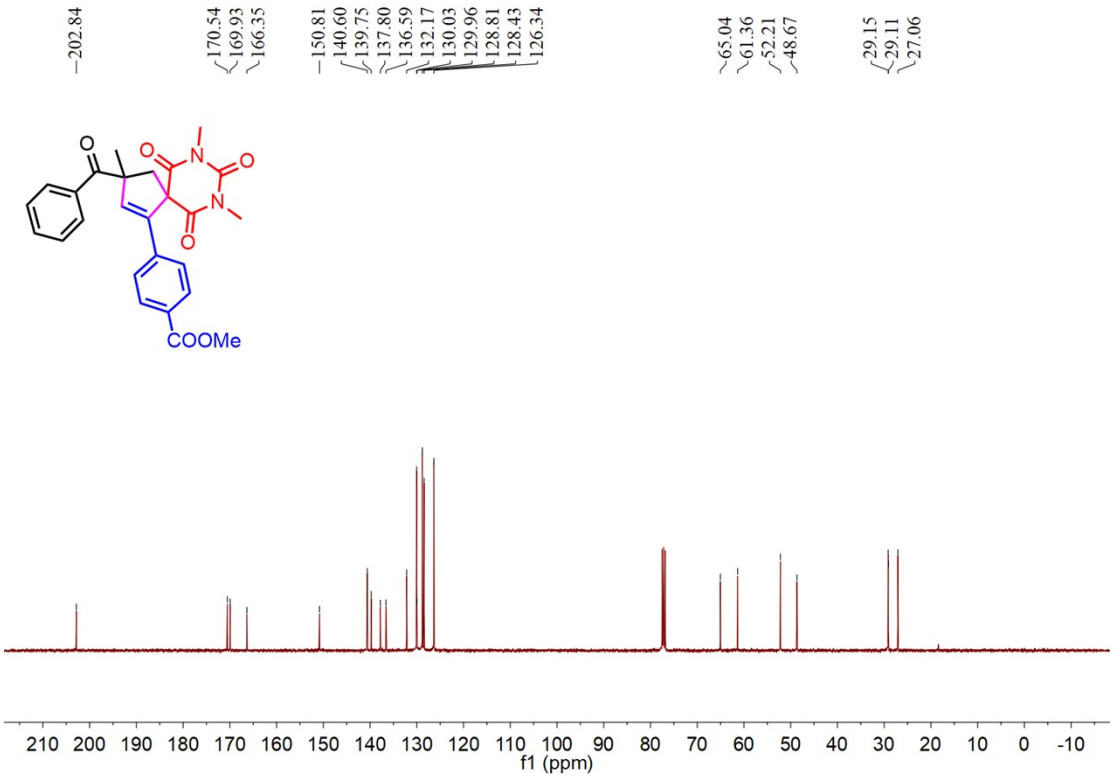
1-([1,1'-biphenyl]-4-yl)-3-benzoyl-3,7,9-trimethyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (16):



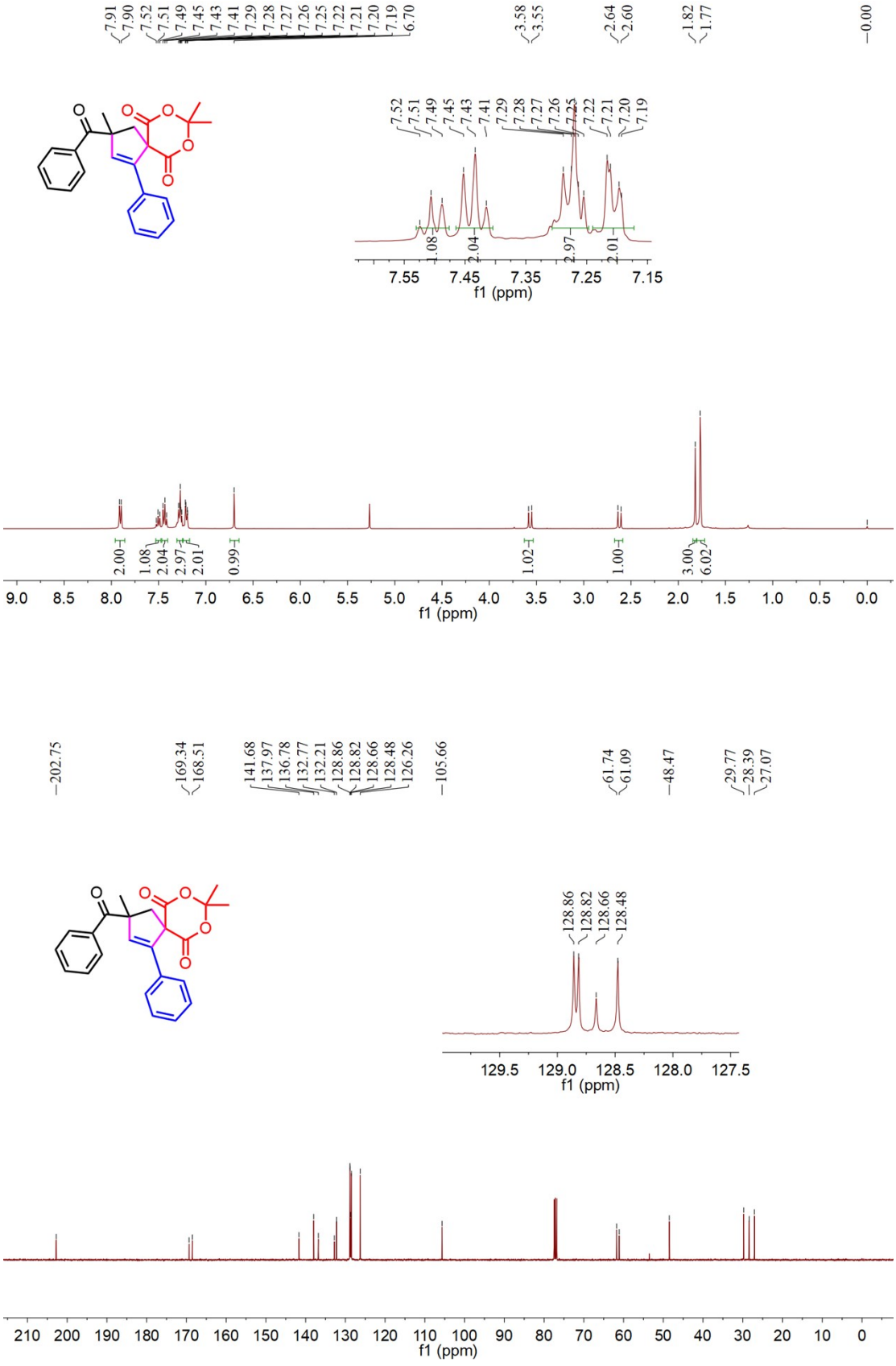


methyl4-(3-benzoyl-3,7,9-trimethyl-6,8,10-trioxo-7,9-diazaspiro[4.5]dec-1-en-1-yl)benzoate (17):

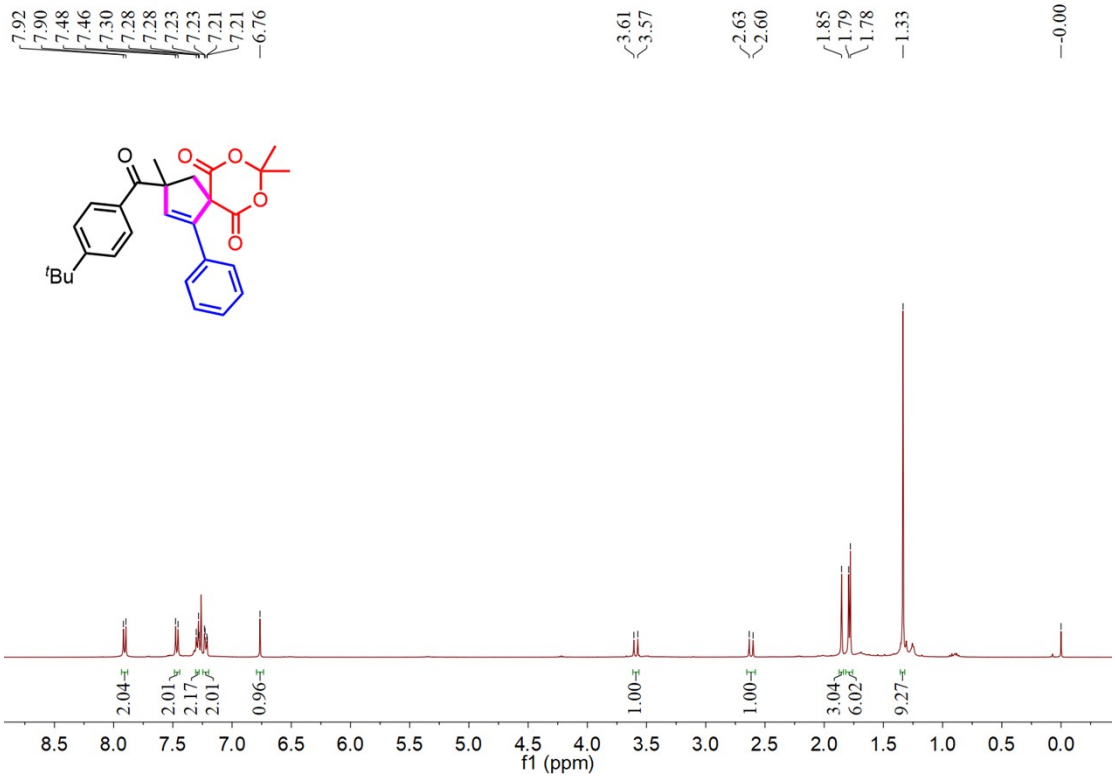


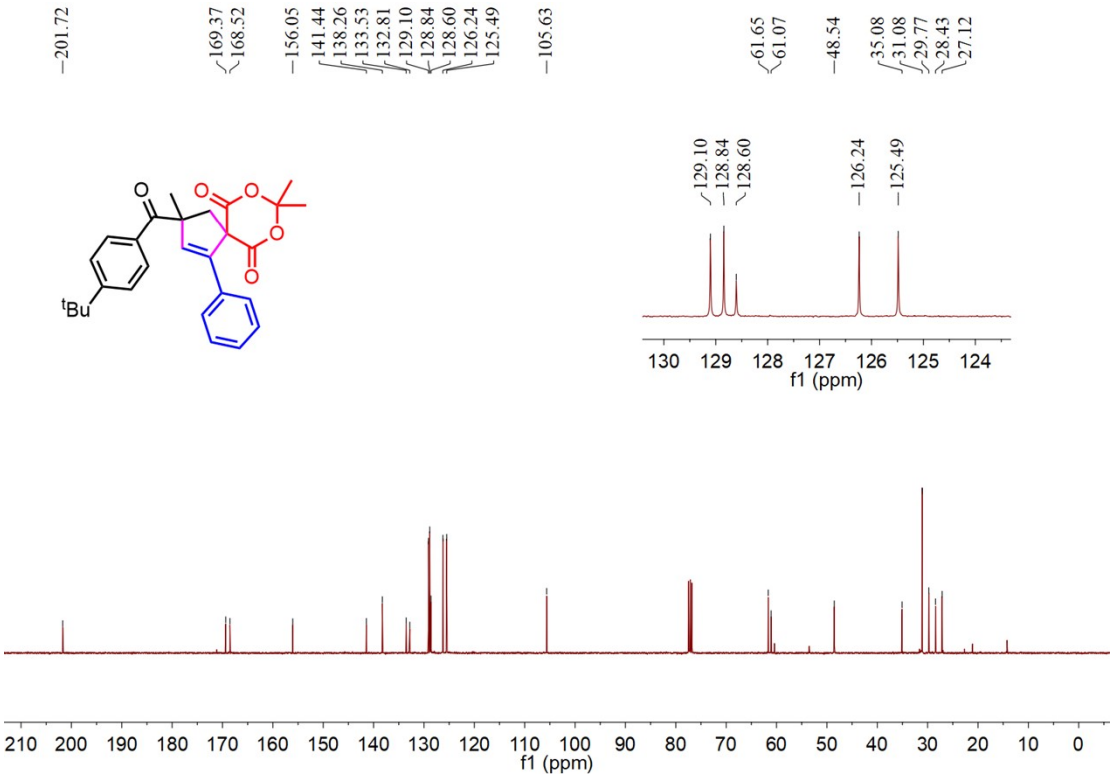


3-benzoyl-3,8,8-trimethyl-1-phenyl-7,9-dioxaspiro[4.5]dec-1-ene-6,10-dione (18):

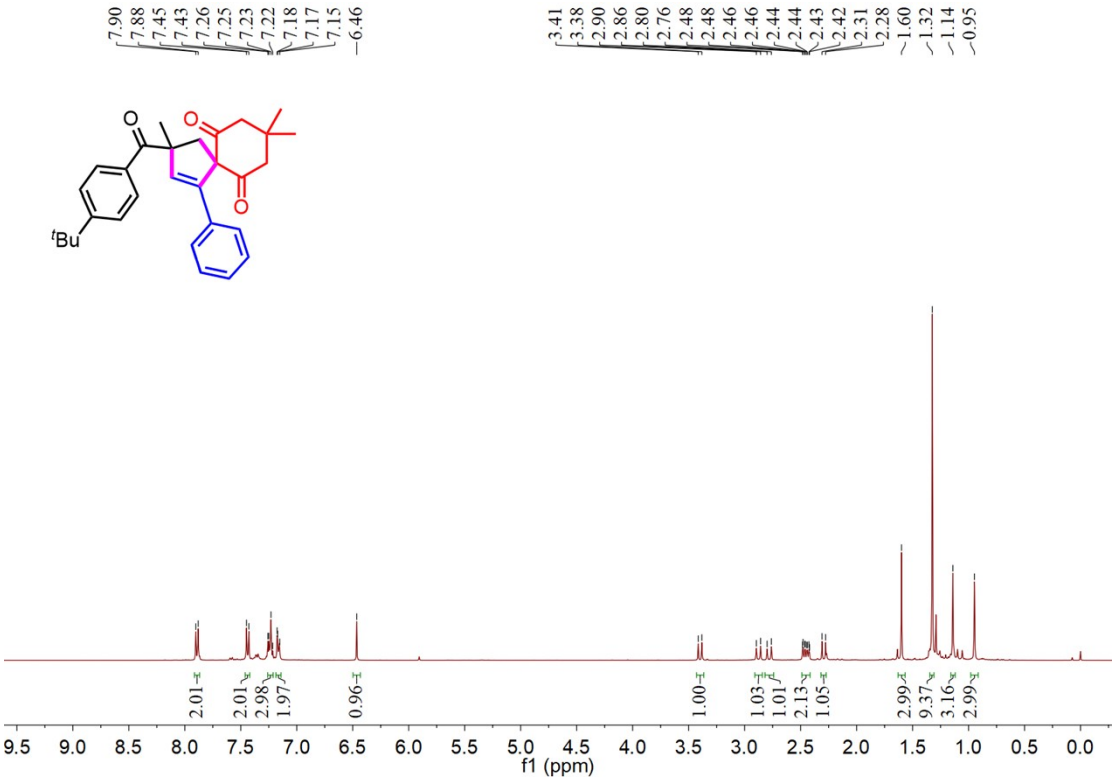


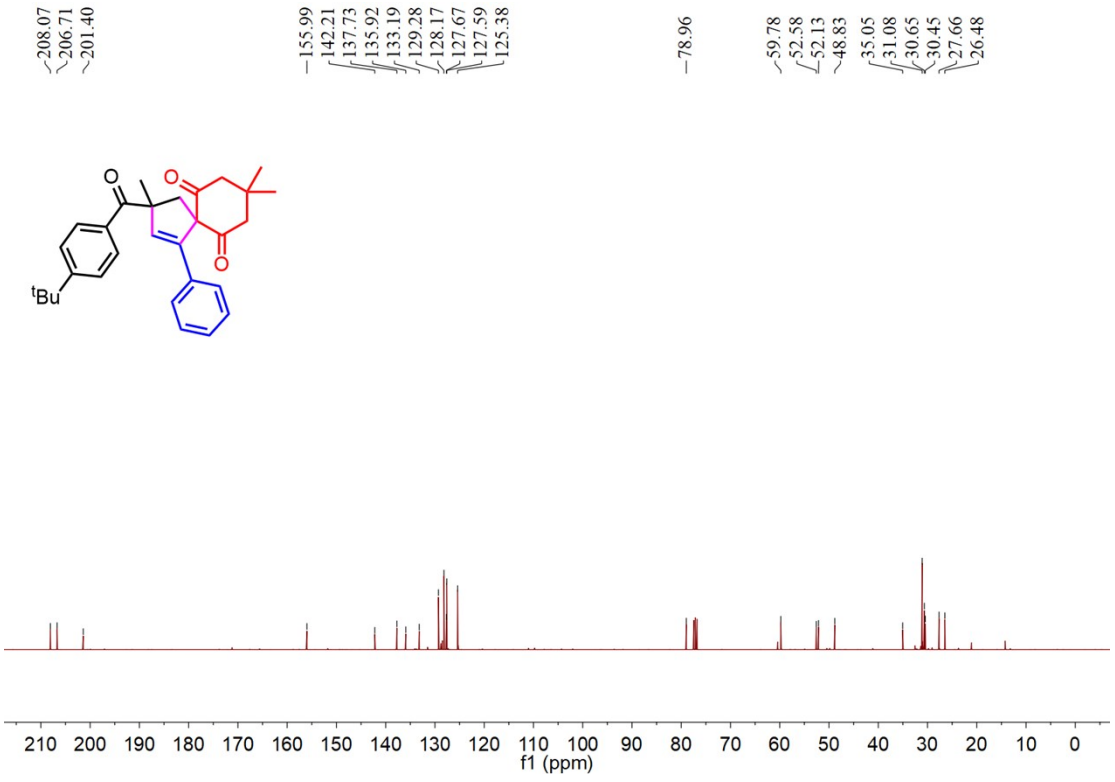
3-(4-(*tert*-butyl)benzoyl)-3,8,8-trimethyl-1-phenyl-7,9-dioxaspiro[4.5]dec-1-ene-6,10-dione (19):



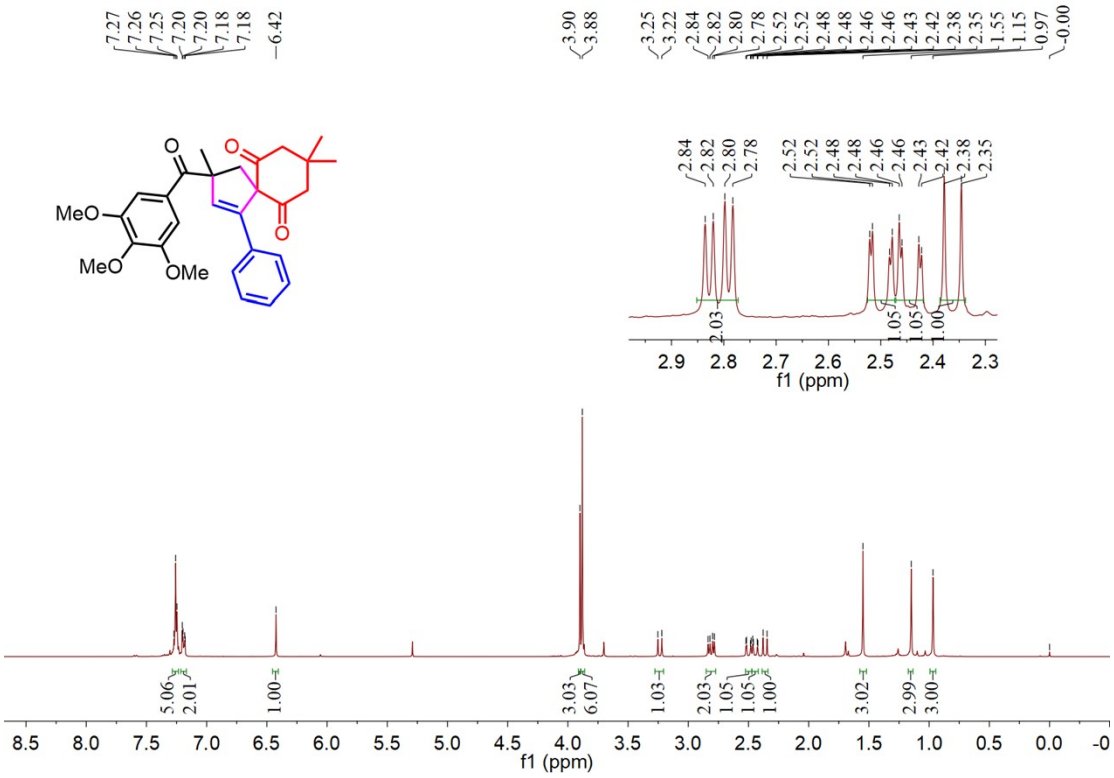


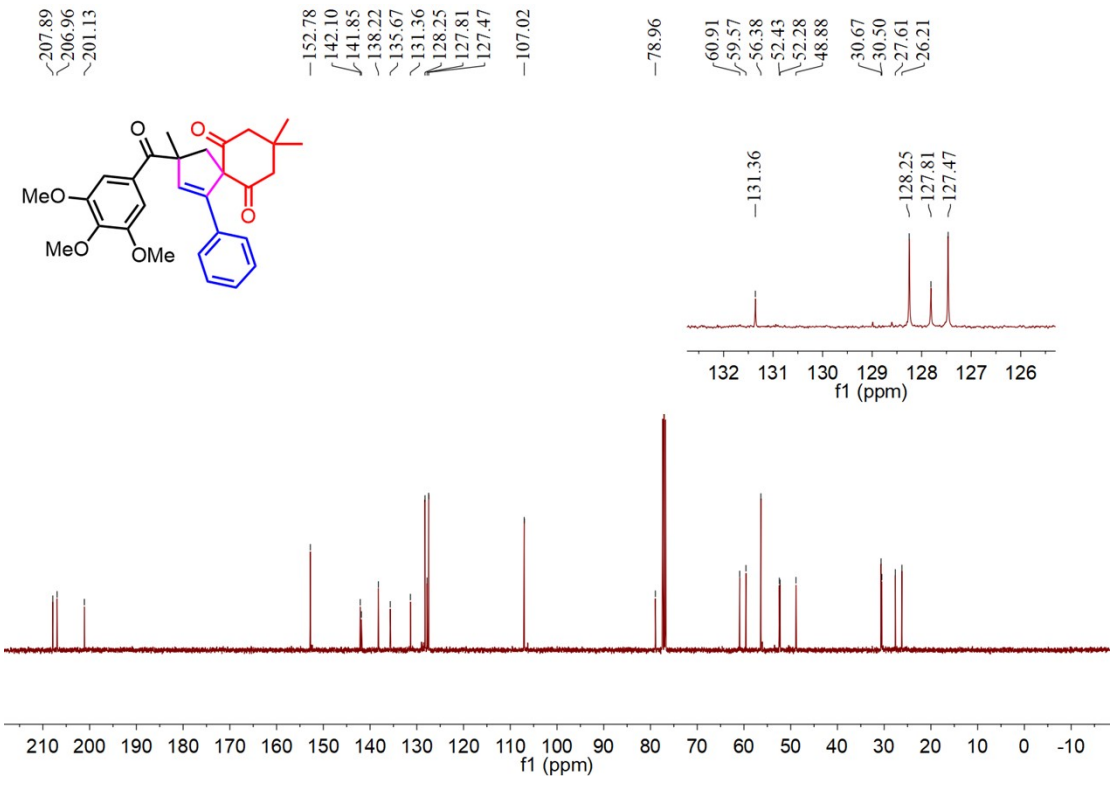
3-(4-(*tert*-butyl)benzoyl)-3,8,8-trimethyl-1-phenylspiro[4.5]dec-1-ene-6,10-dione (20):



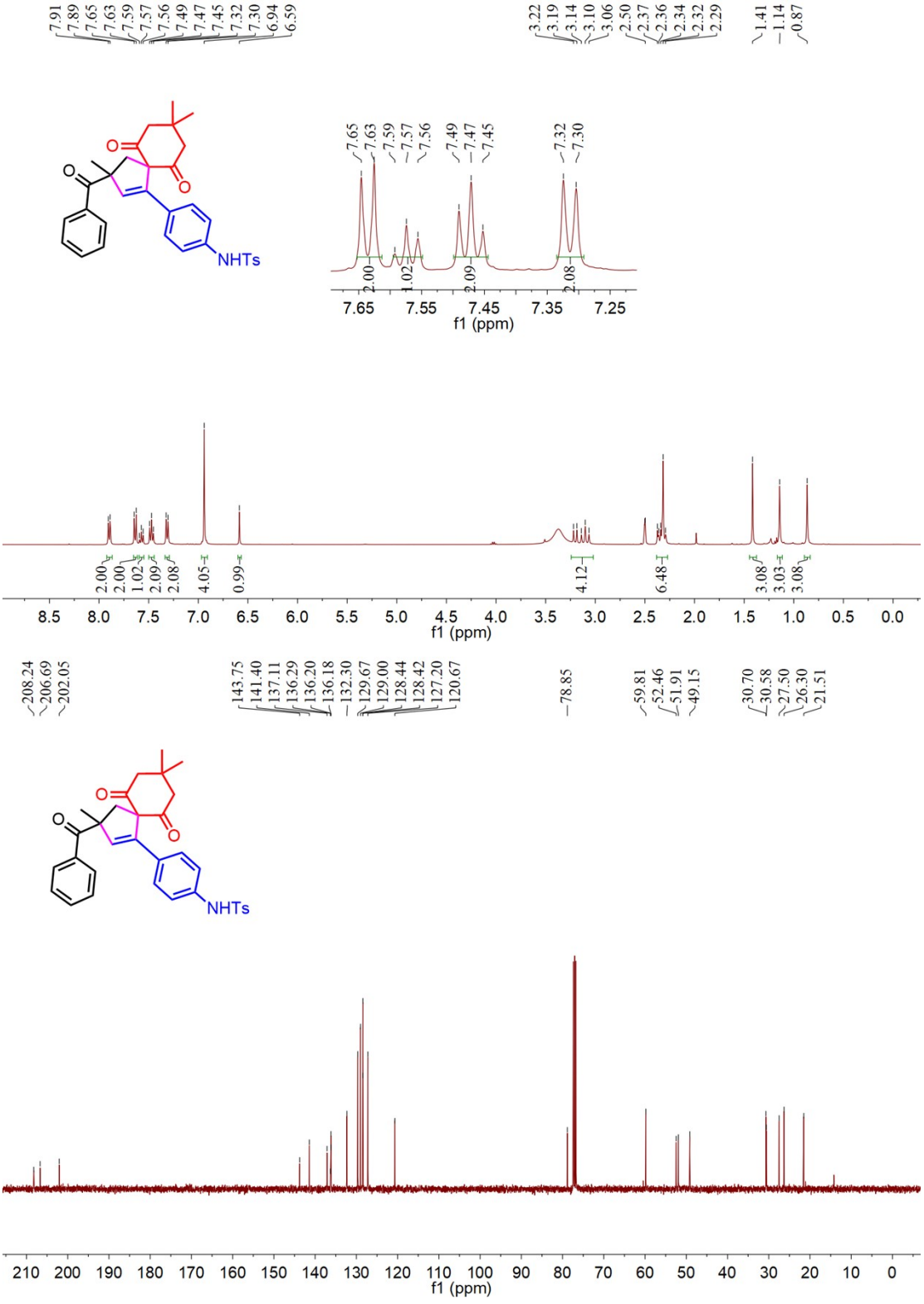


3,8,8-trimethyl-1-phenyl-3-(3,4,5-trimethoxybenzoyl)spiro[4.5]dec-1-ene-6,10-dione (21):

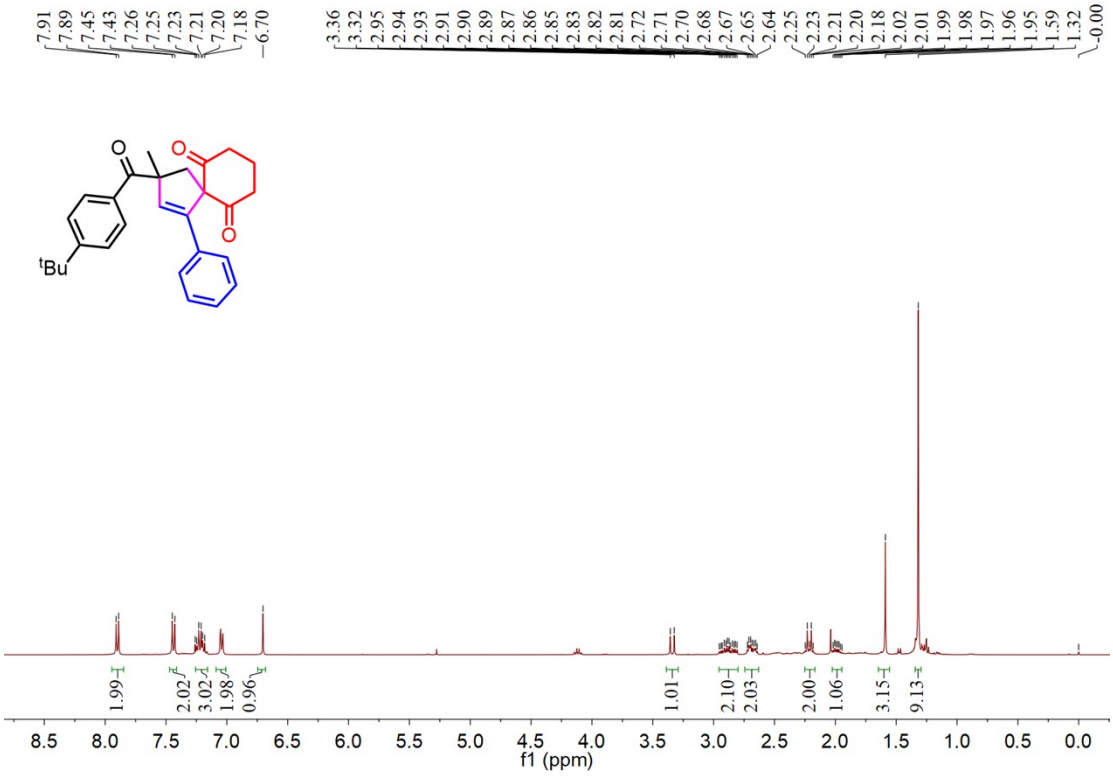


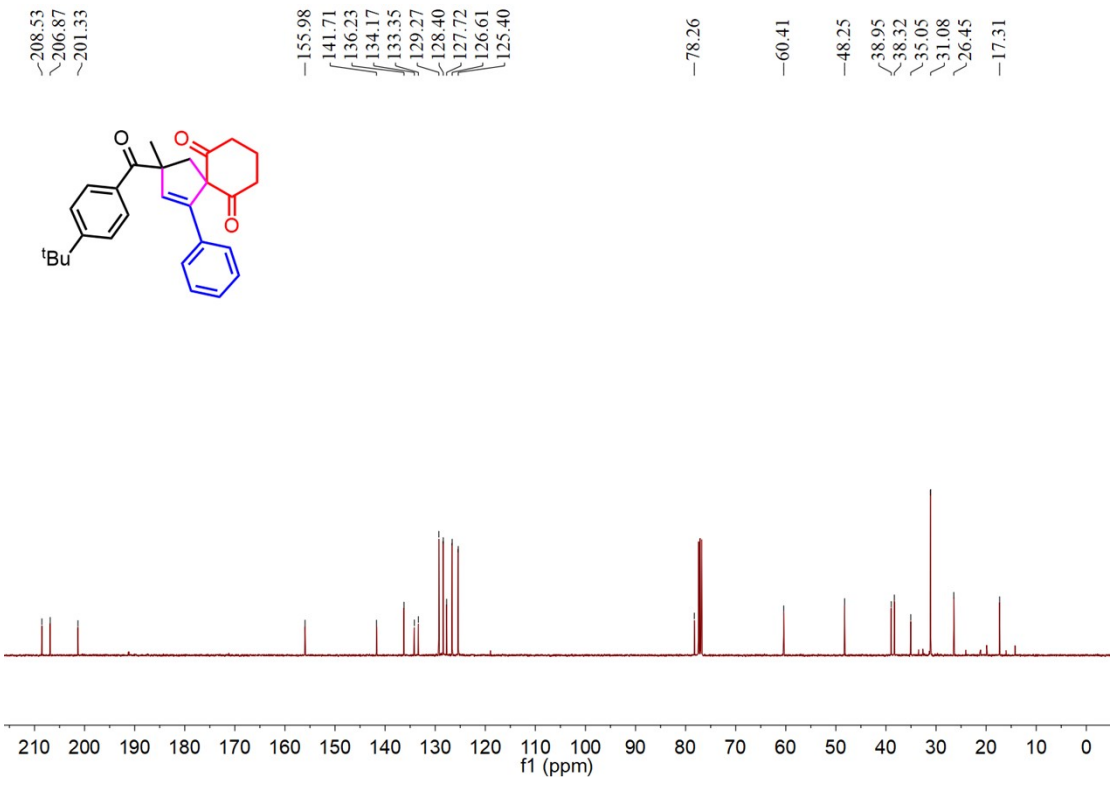


N-(4-(3-benzoyl-3,8,8-trimethyl-6,10-dioxospiro[4.5]dec-1-en-1-yl)phenyl)-4-methylbenzenesulfonamide (22):

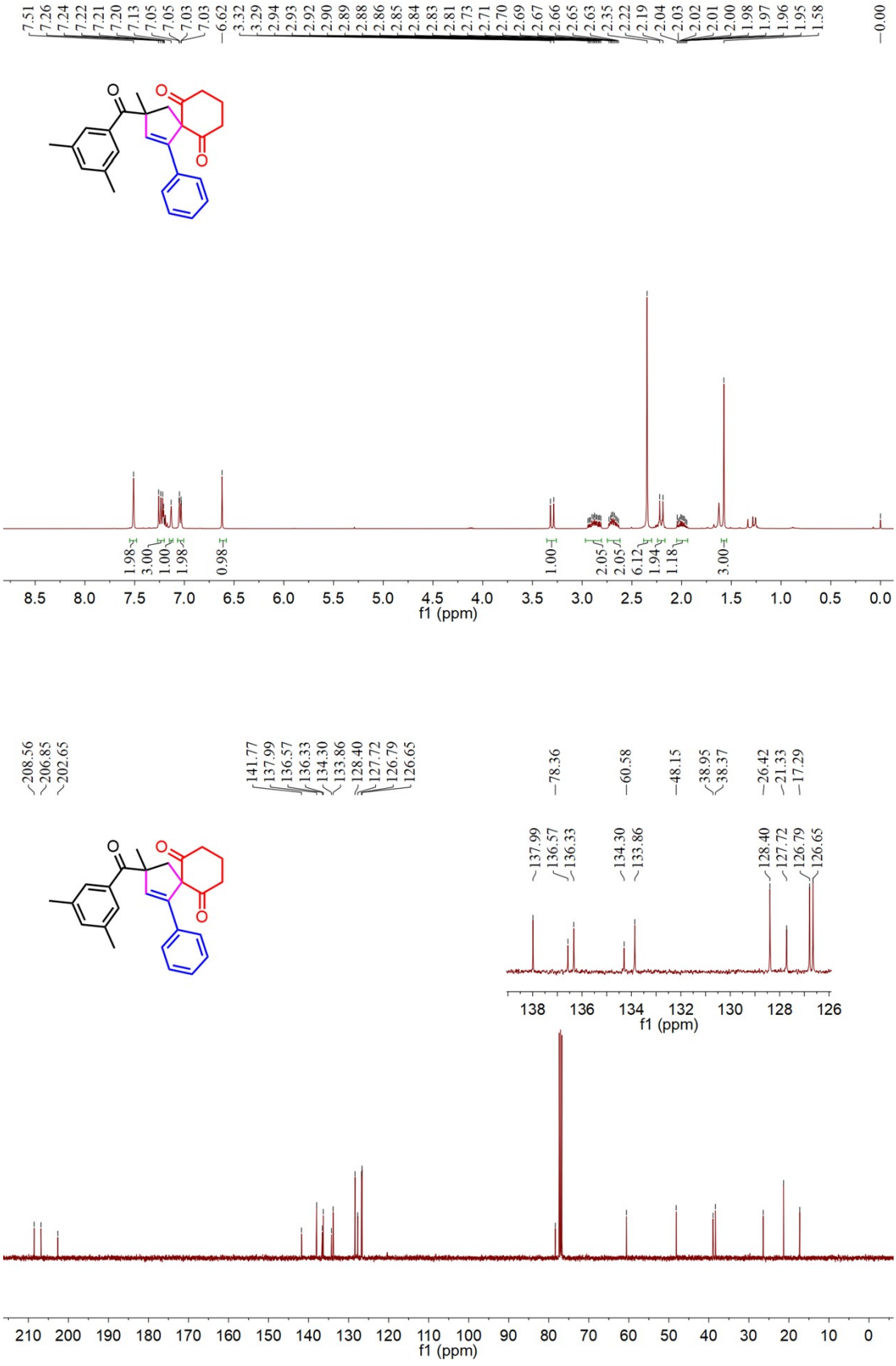


3-(4-(*tert*-butyl)benzoyl)-3-methyl-1-phenylspiro[4.5]dec-1-ene-6,10-dione (23):

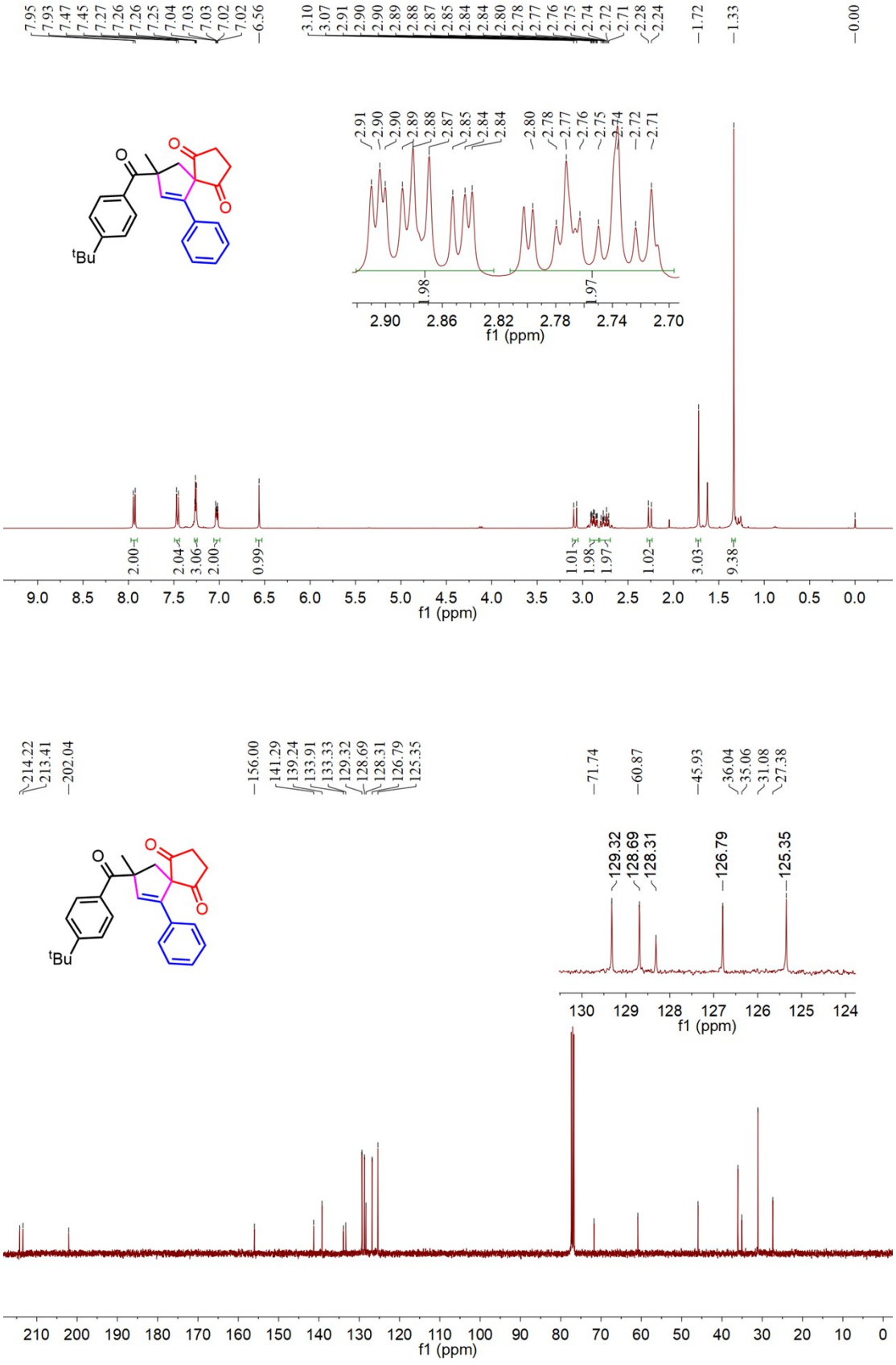




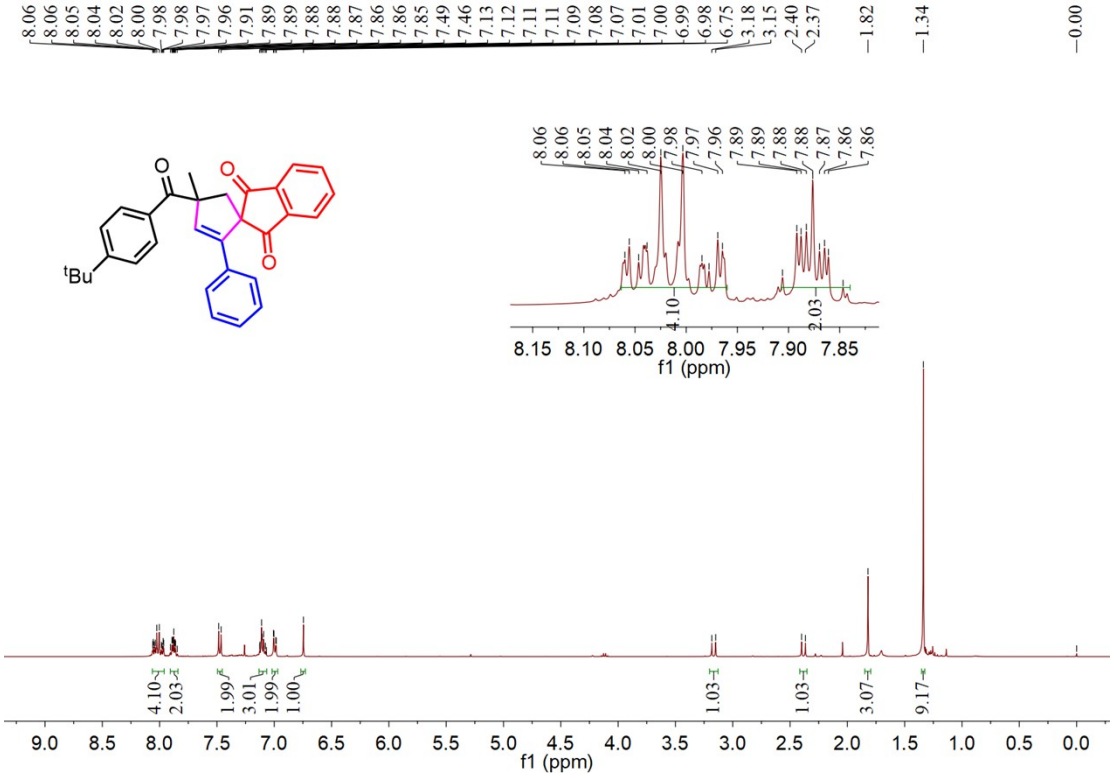
3-(3,5-dimethylbenzoyl)-3-methyl-1-phenylspiro[4.5]dec-1-ene-6,10-dione (24):

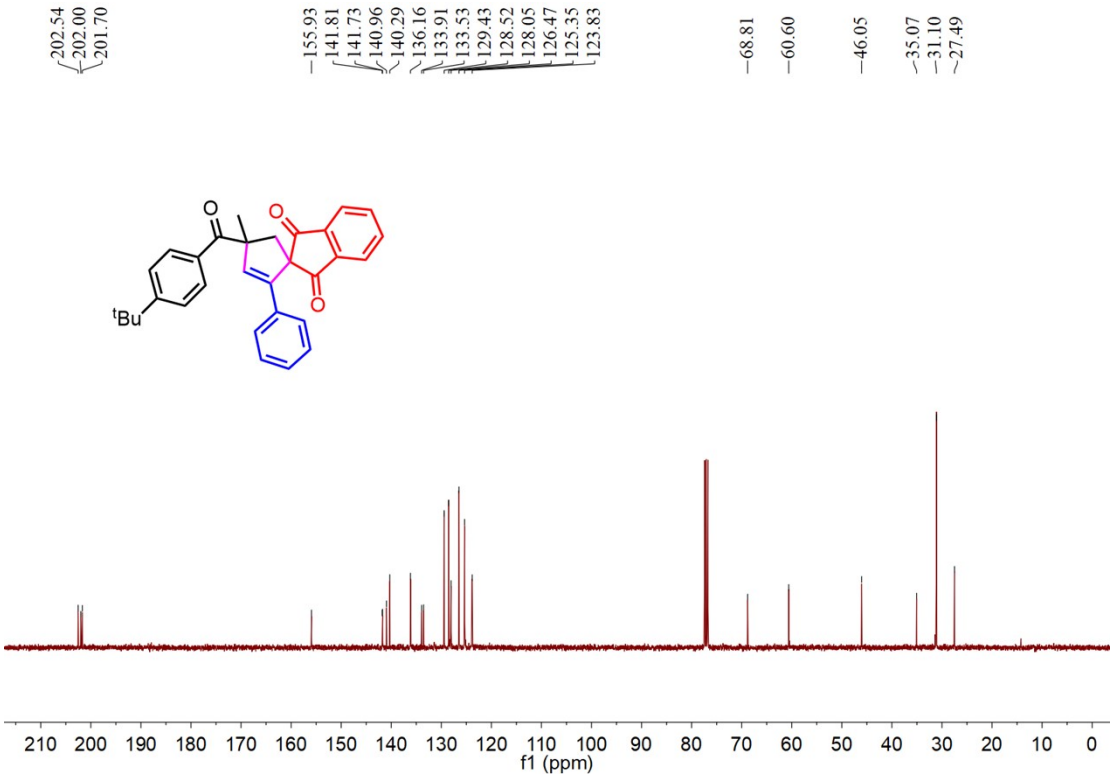


8-(4-(*tert*-butyl)benzoyl)-8-methyl-6-phenylspiro[4.4]non-6-ene-1,4-dione (25):

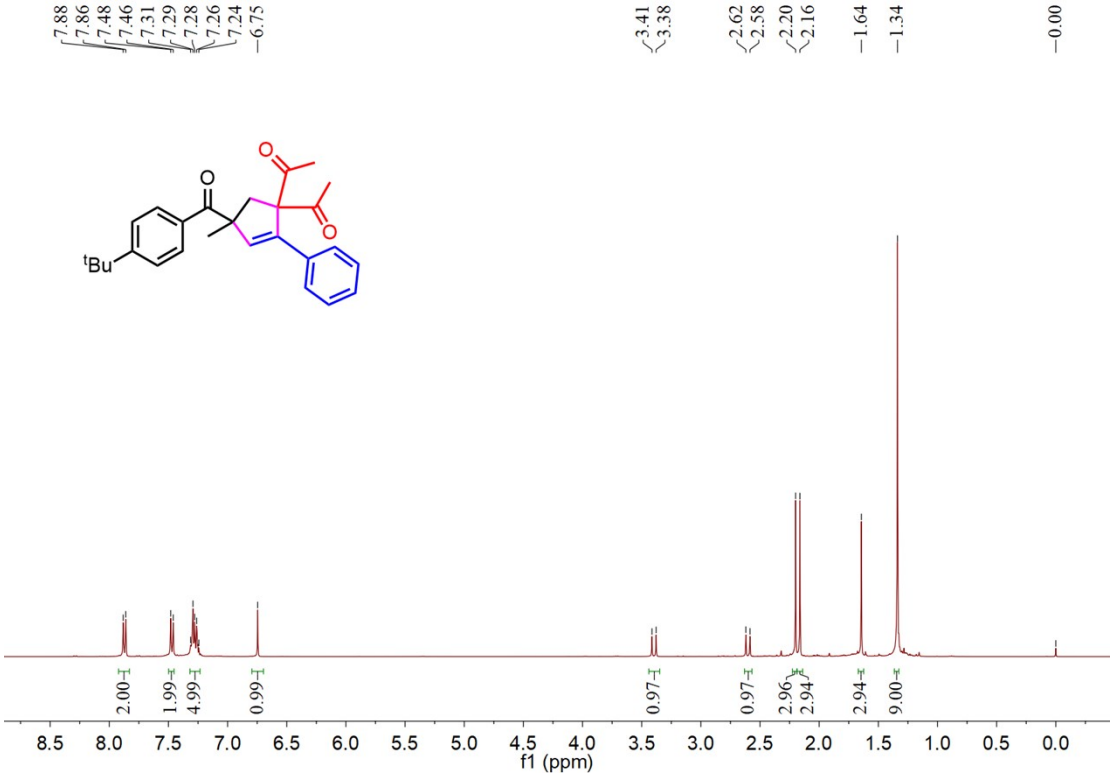


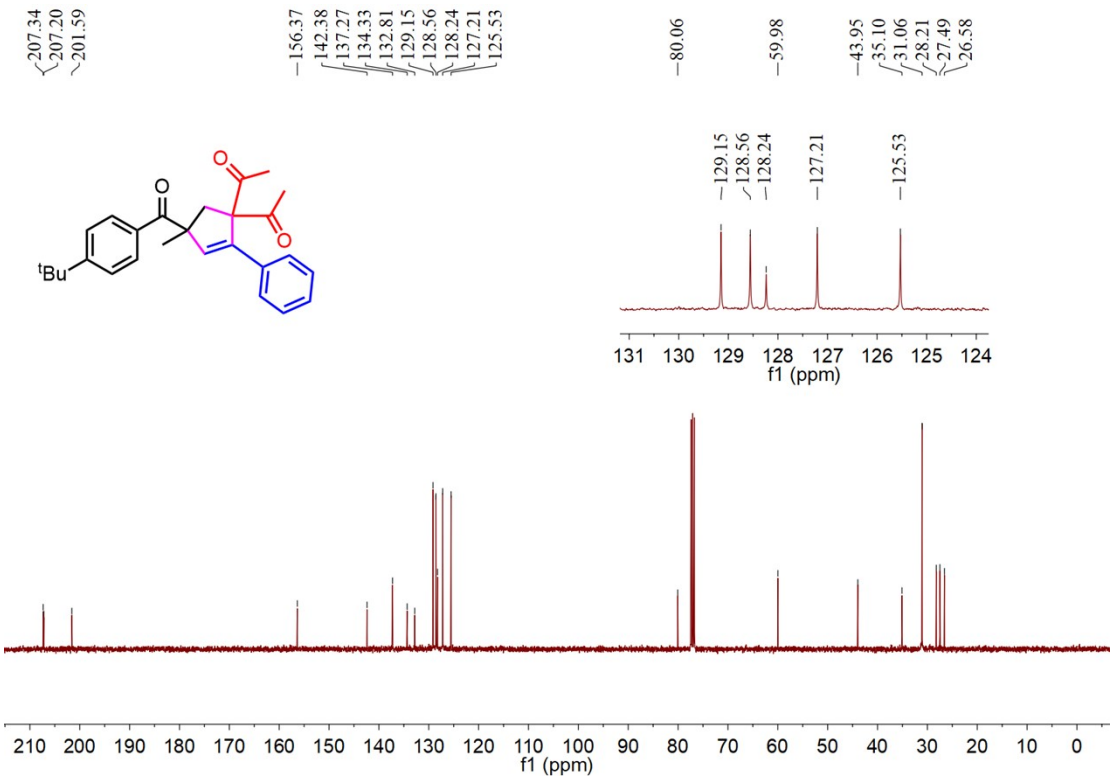
4-(4-(*tert*-butyl)benzoyl)-4-methyl-2-phenylspiro[cyclopentane-1,2'-inden]-2-ene-1',3'-dione (26):



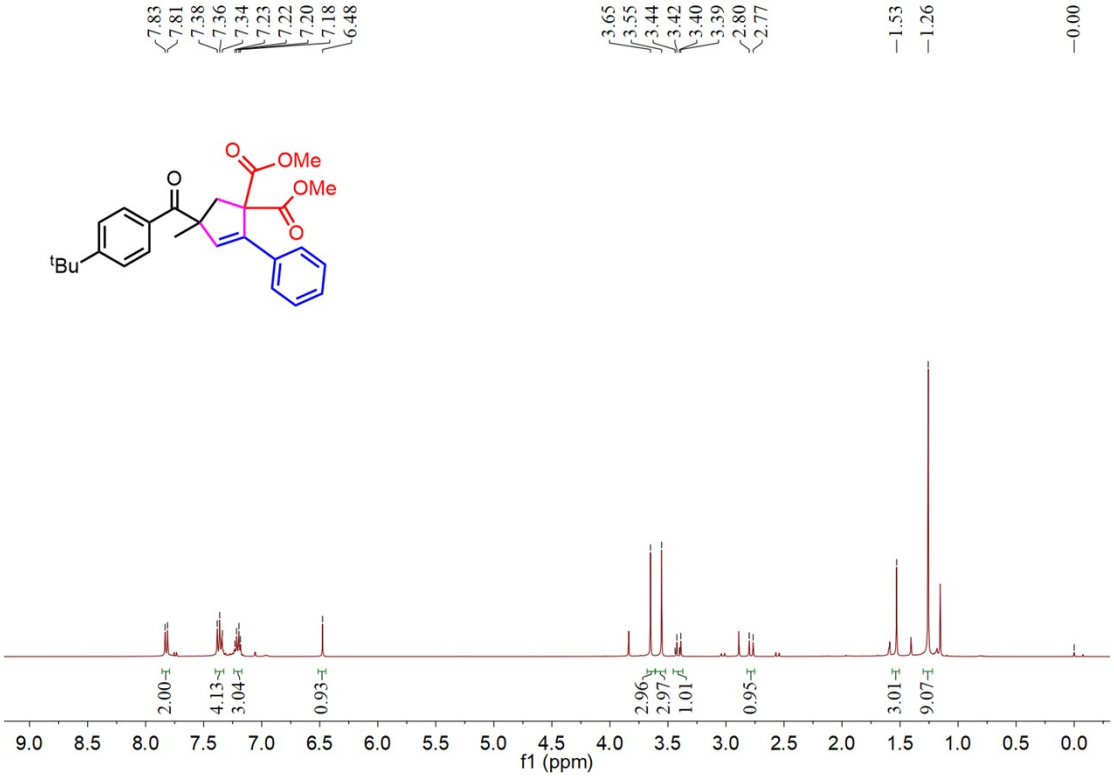


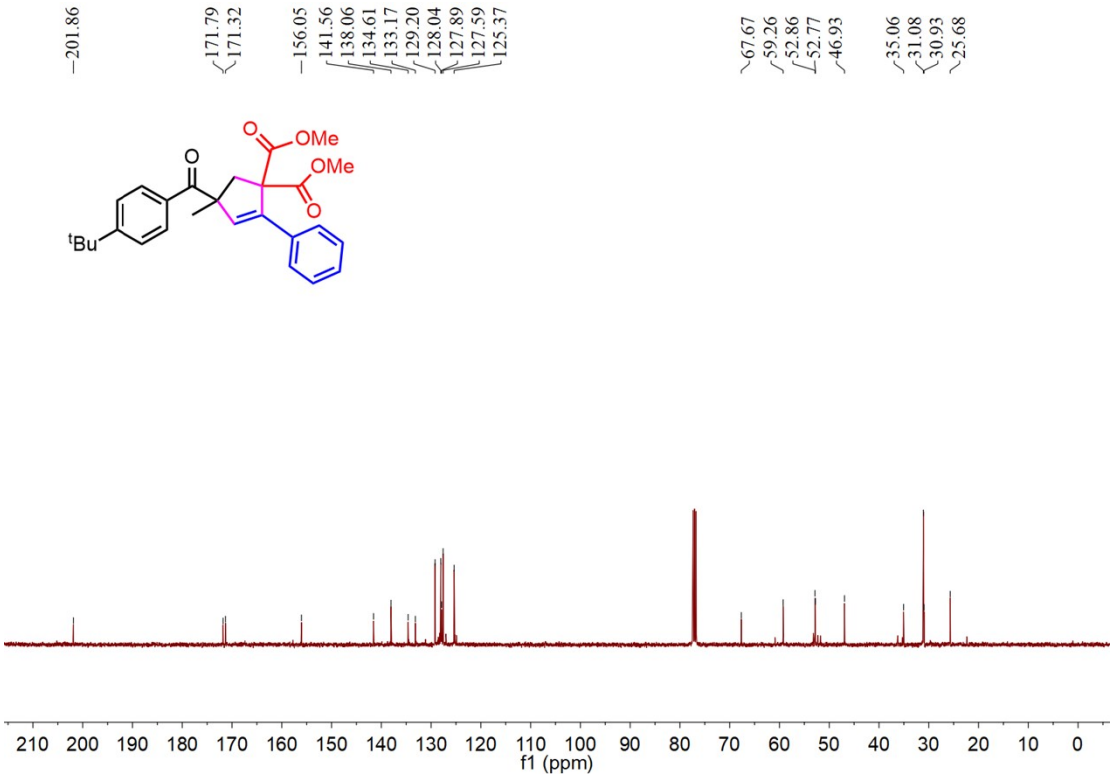
1,1'-(4-(4-(*tert*-butyl)benzoyl)-4-methyl-2-phenylcyclopent-2-ene-1,1-diyl)bis(ethan-1-one) (27):



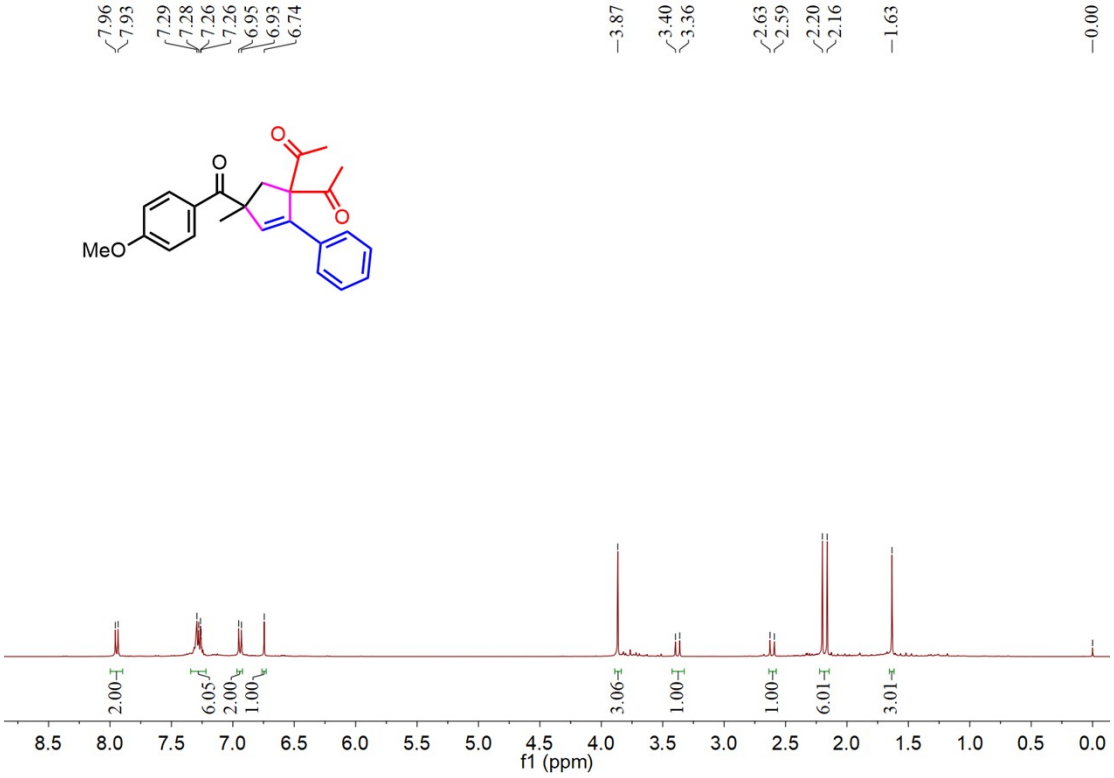


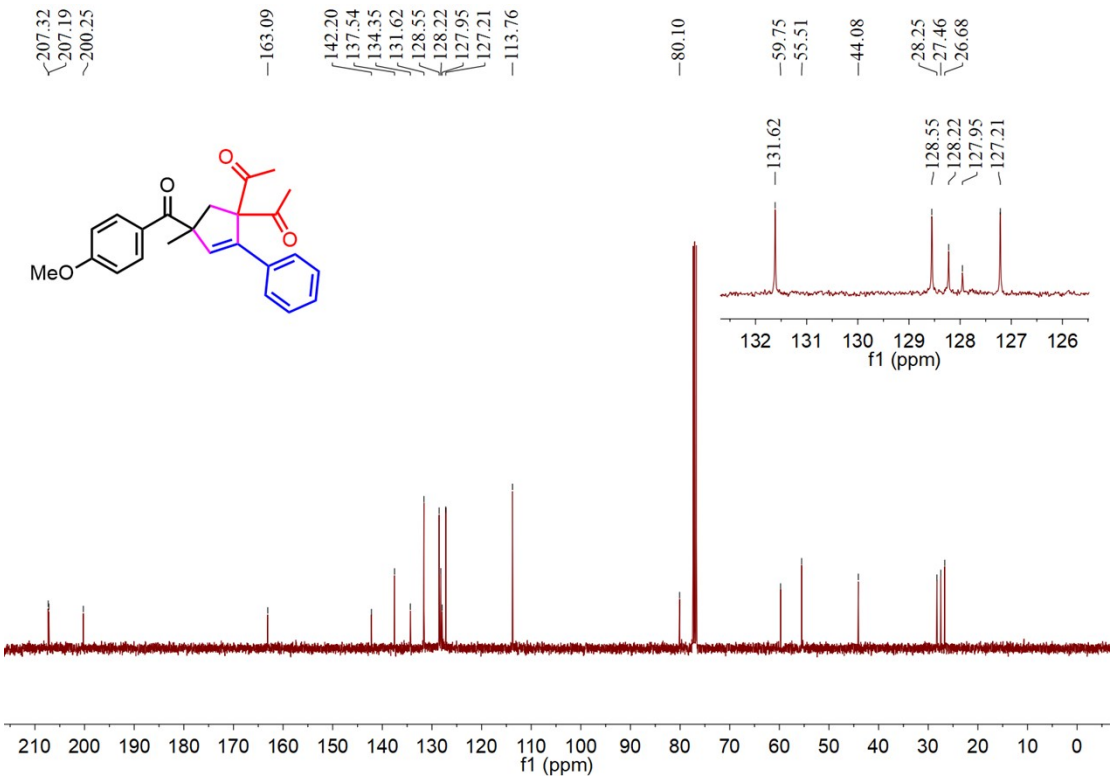
dimethyl4-(4-(*tert*-butyl)benzoyl)-4-methyl-2-phenylcyclopent-2-ene-1,1-dicarboxylate (28):



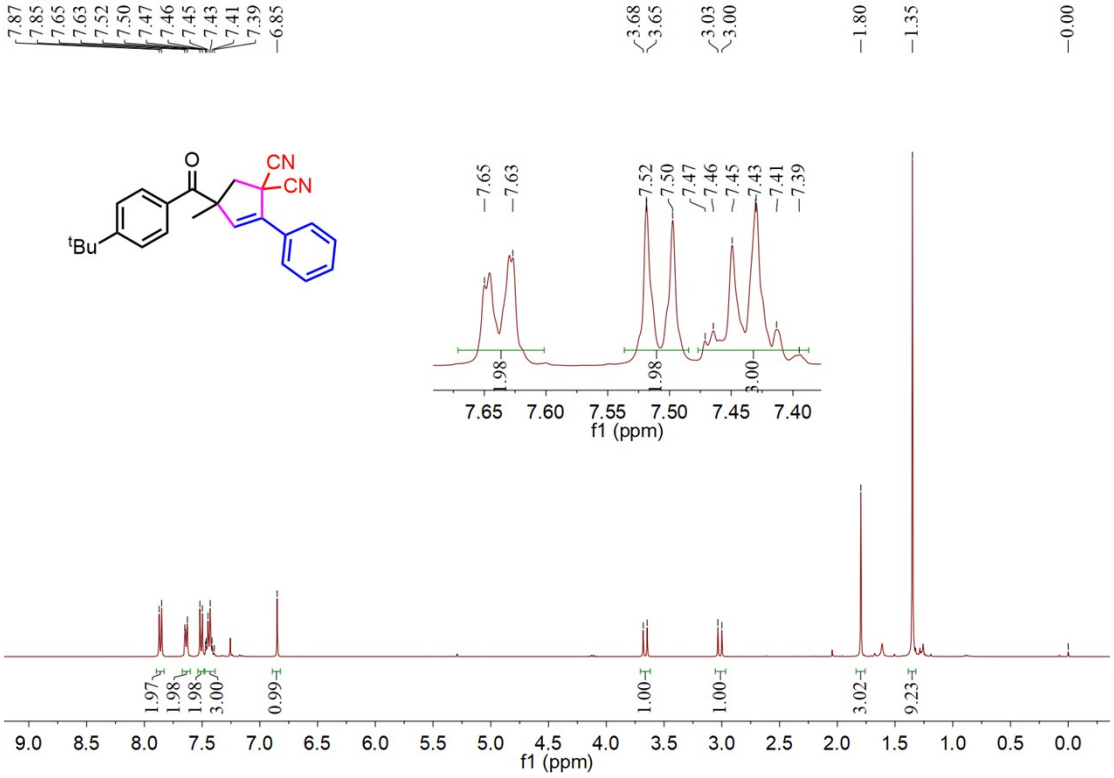


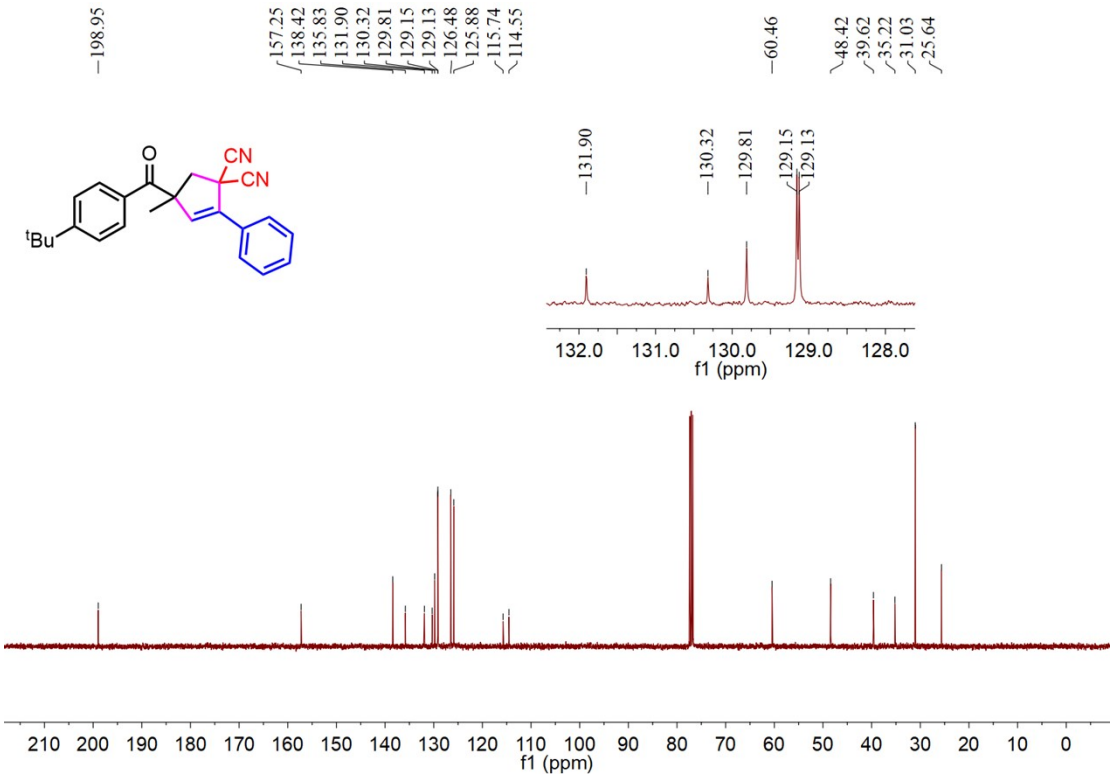
1,1'-(4-(4-methoxybenzoyl)-4-methyl-2-phenylcyclopent-2-ene-1,1-diyl)bis(ethan-1-one) (29):



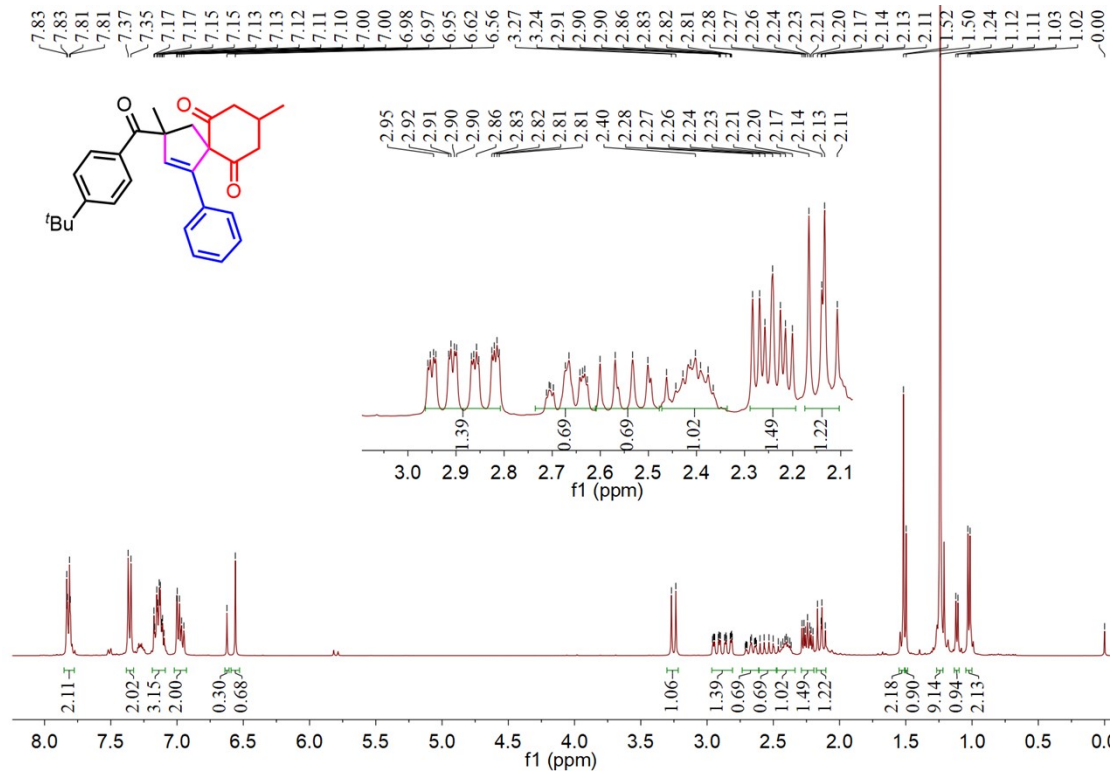


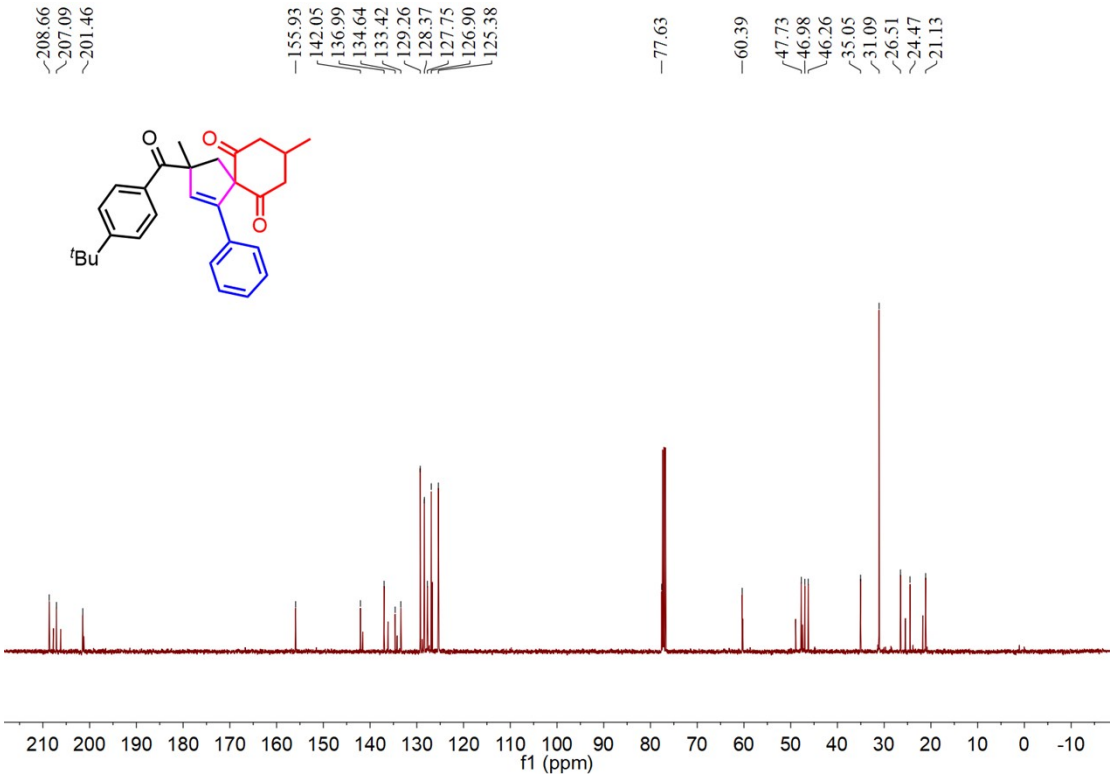
4-(4-(*tert*-butyl)benzoyl)-4-methyl-2-phenylcyclopent-2-ene-1,1-dicarbonitrile (30):



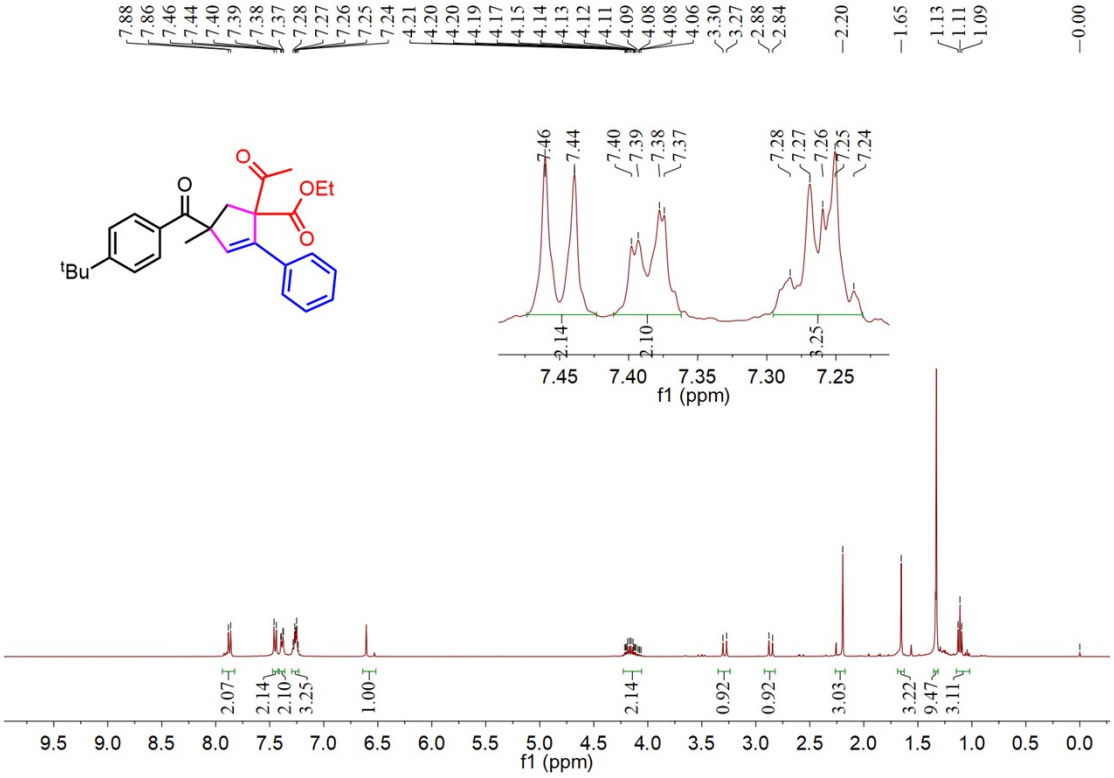


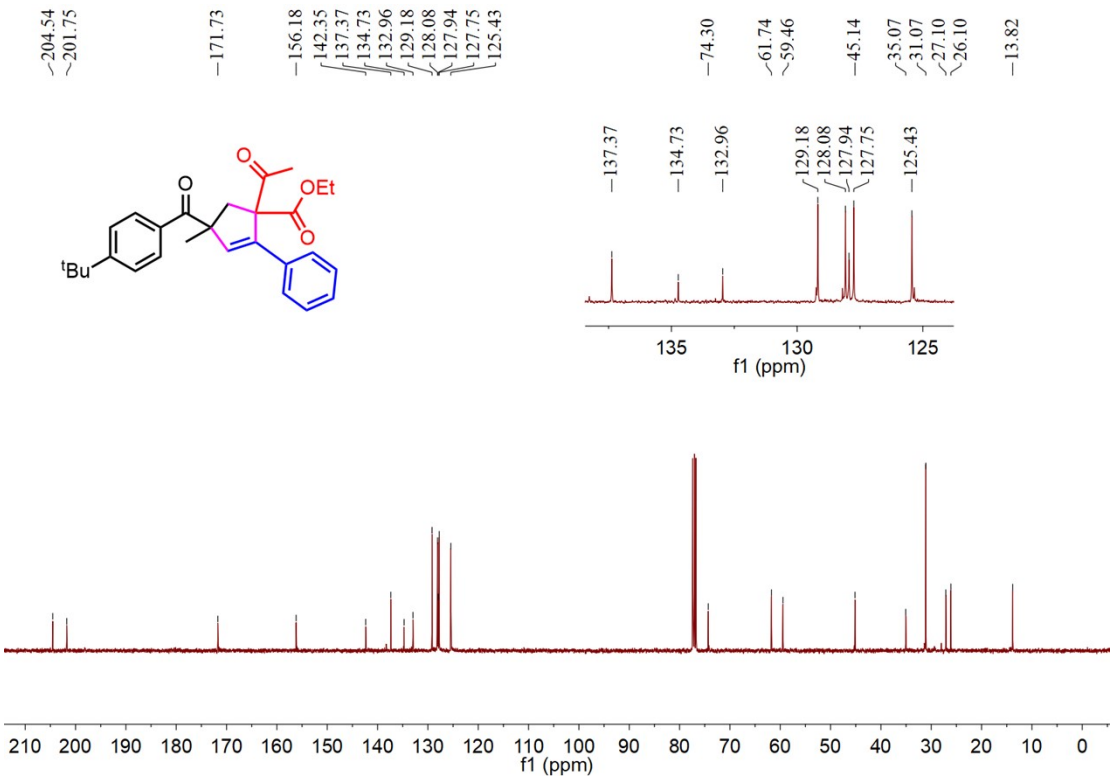
3-(4-(*tert*-butyl)benzoyl)-3,8-dimethyl-1-phenylspiro[4.5]dec-1-ene-6,10-dione (31):



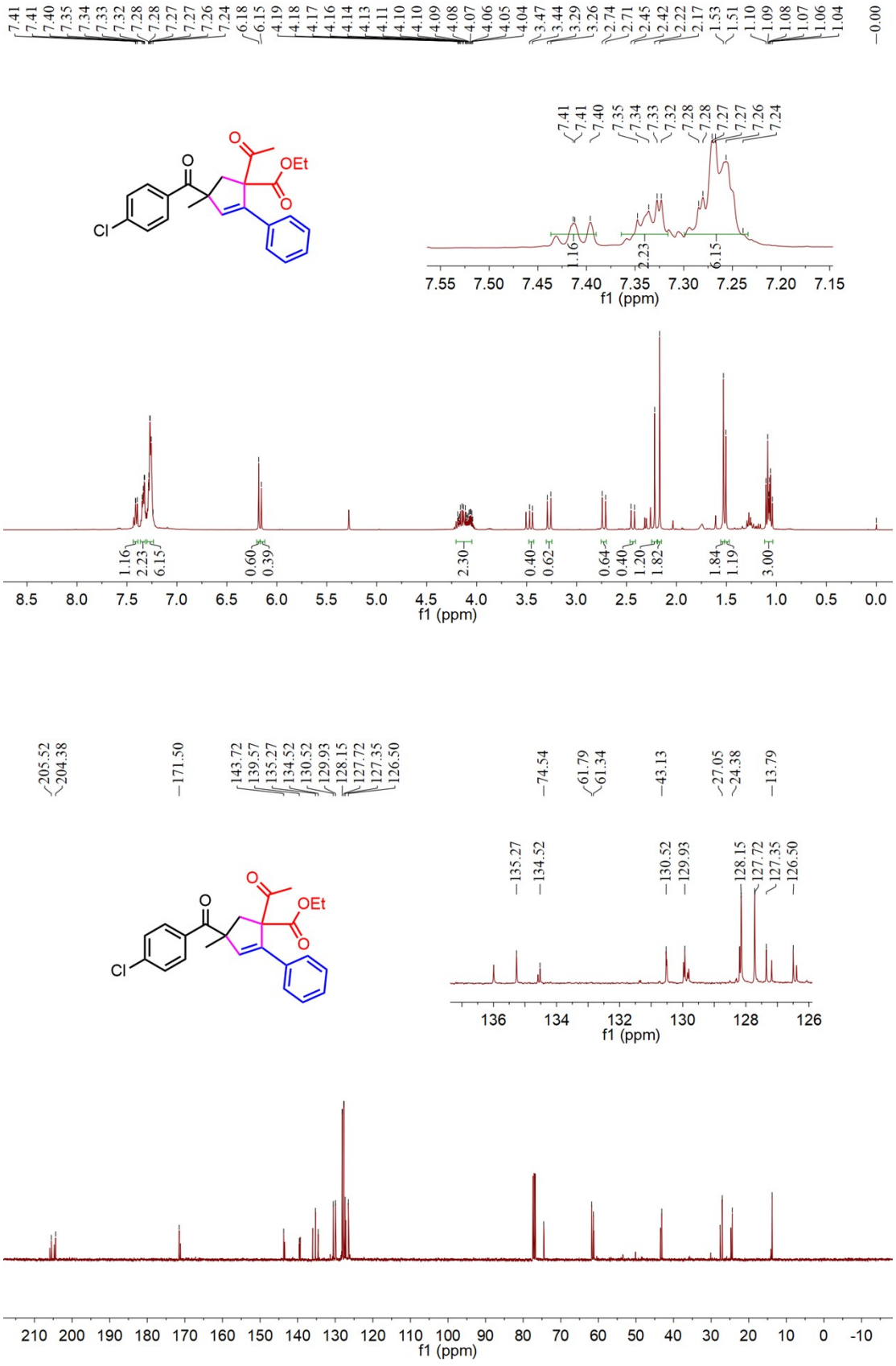


ethyl1-acetyl-4-(4-(*tert*-butyl)benzoyl)-4-methyl-2-phenylcyclopent-2-ene-1-carboxylate (32):

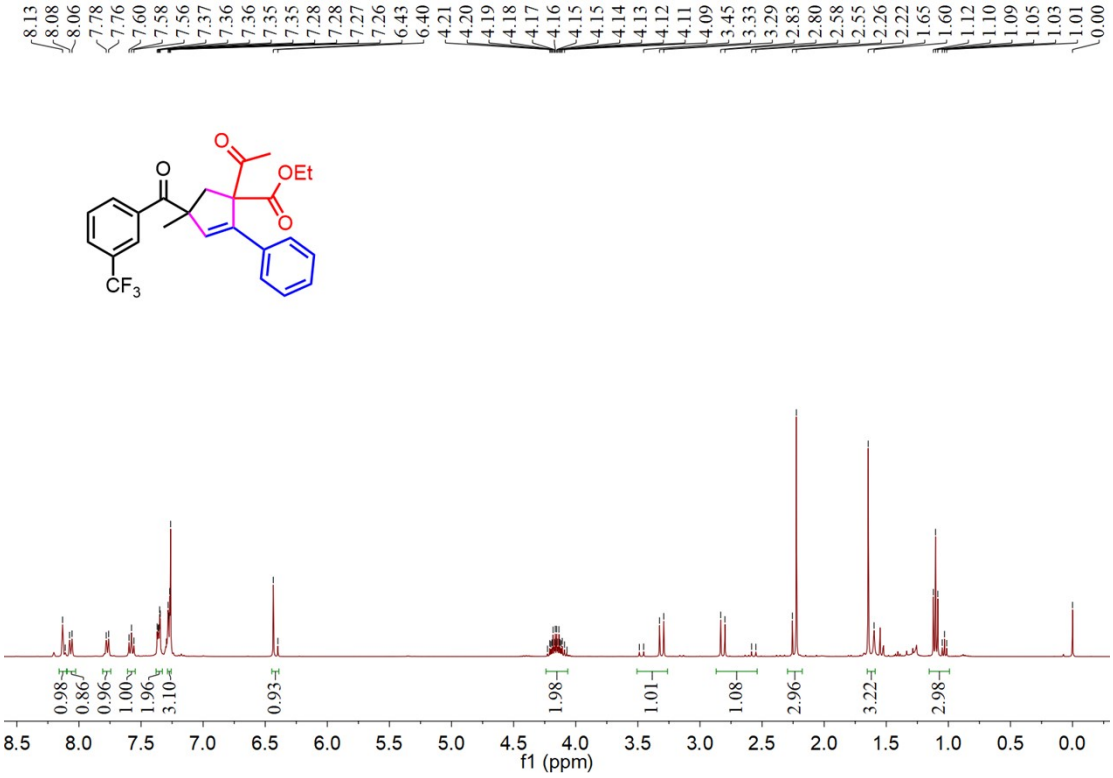


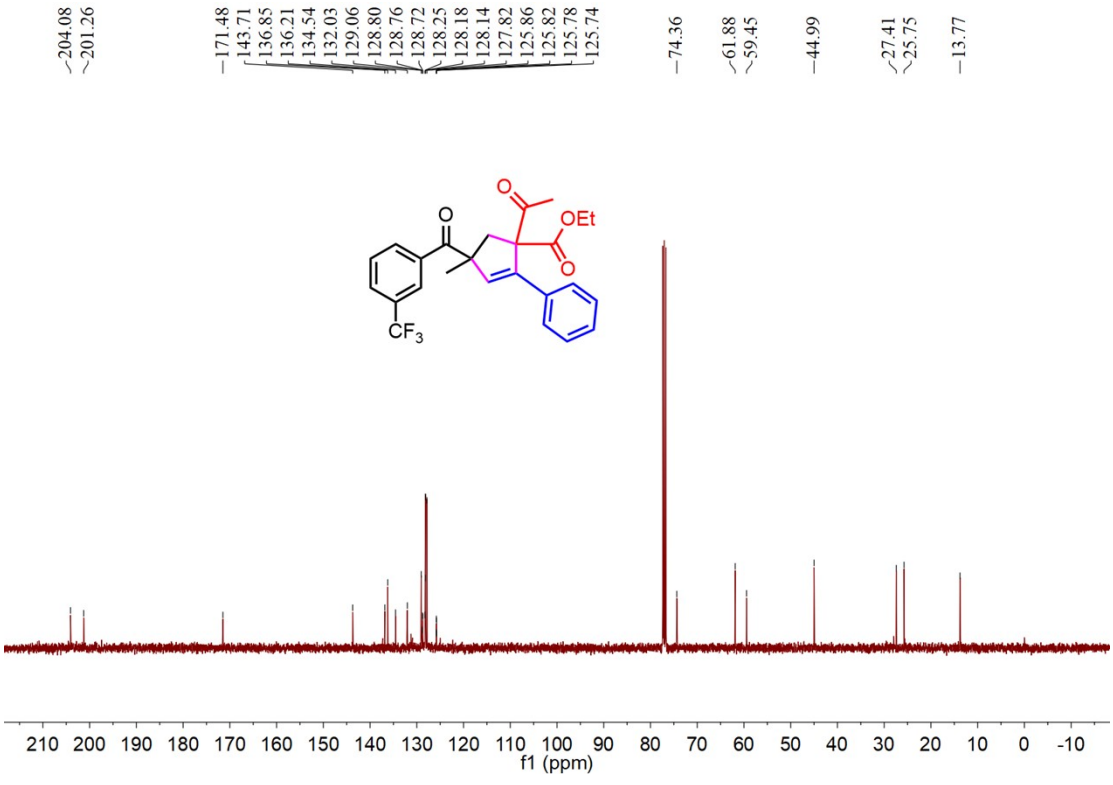


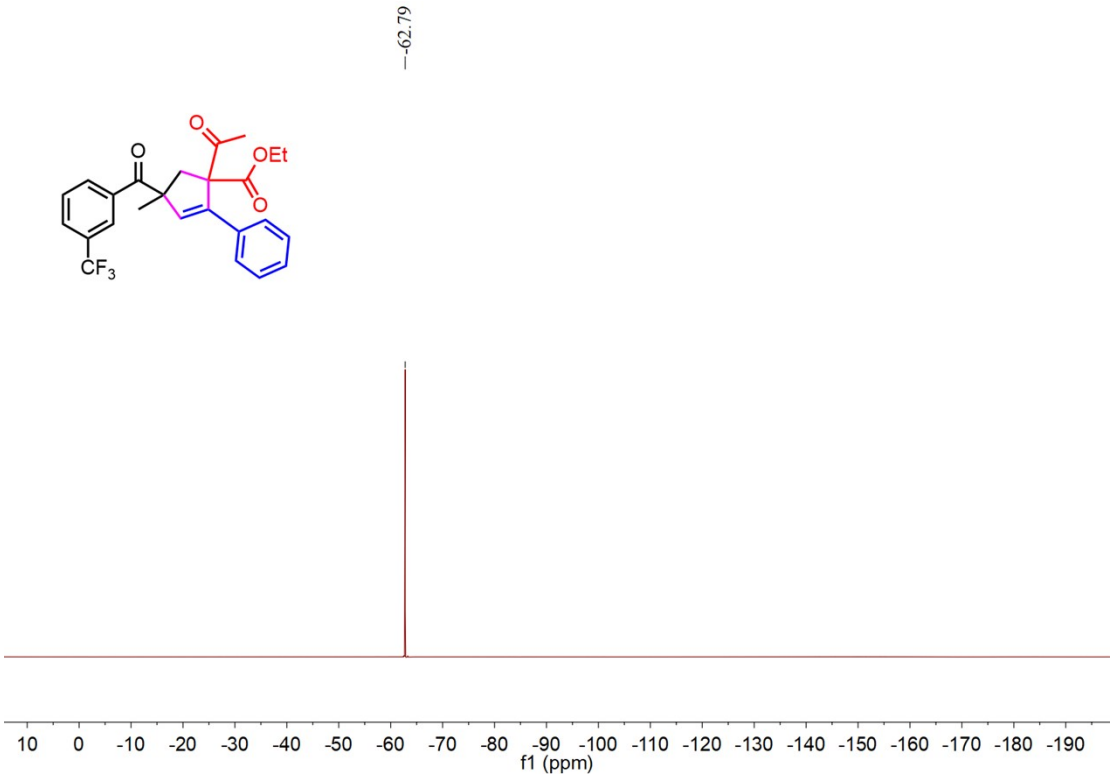
ethyl-1-acetyl-4-(4-chlorobenzoyl)-4-methyl-2-phenylcyclopent-2-ene-1-carboxylate (33):



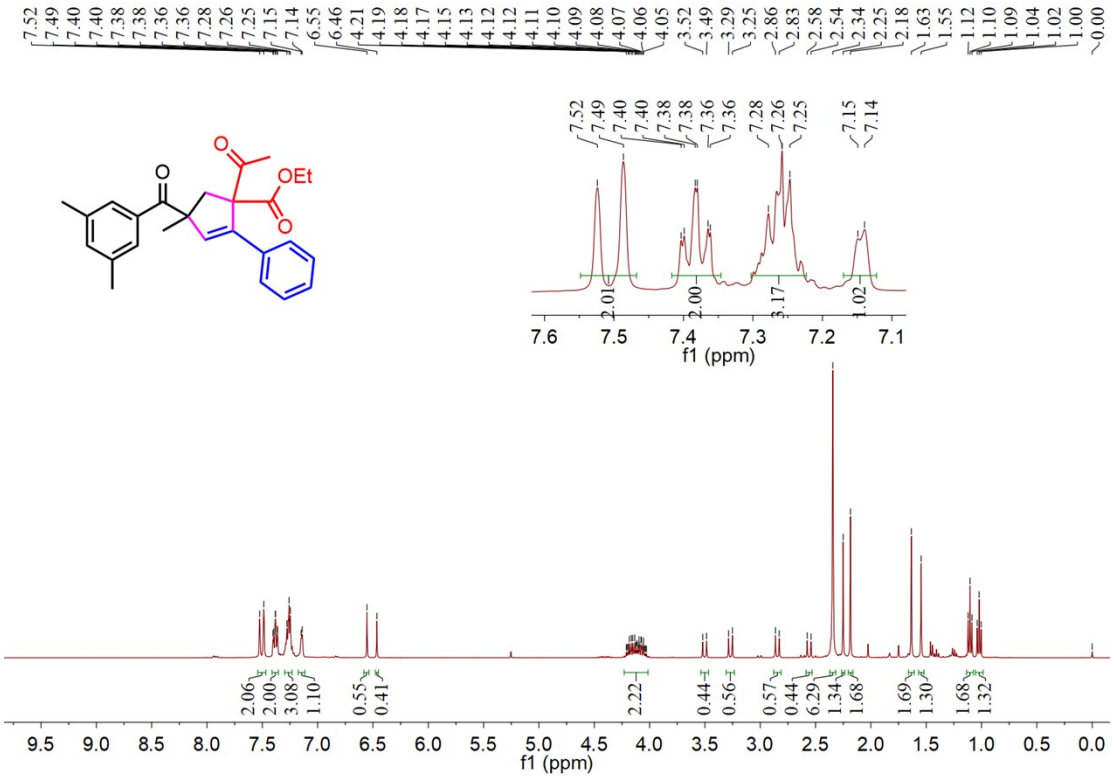
ethyl-1-acetyl-4-methyl-2-phenyl-4-(3-(trifluoromethyl)benzoyl)cyclopent-2-ene-1-carboxylate (34):

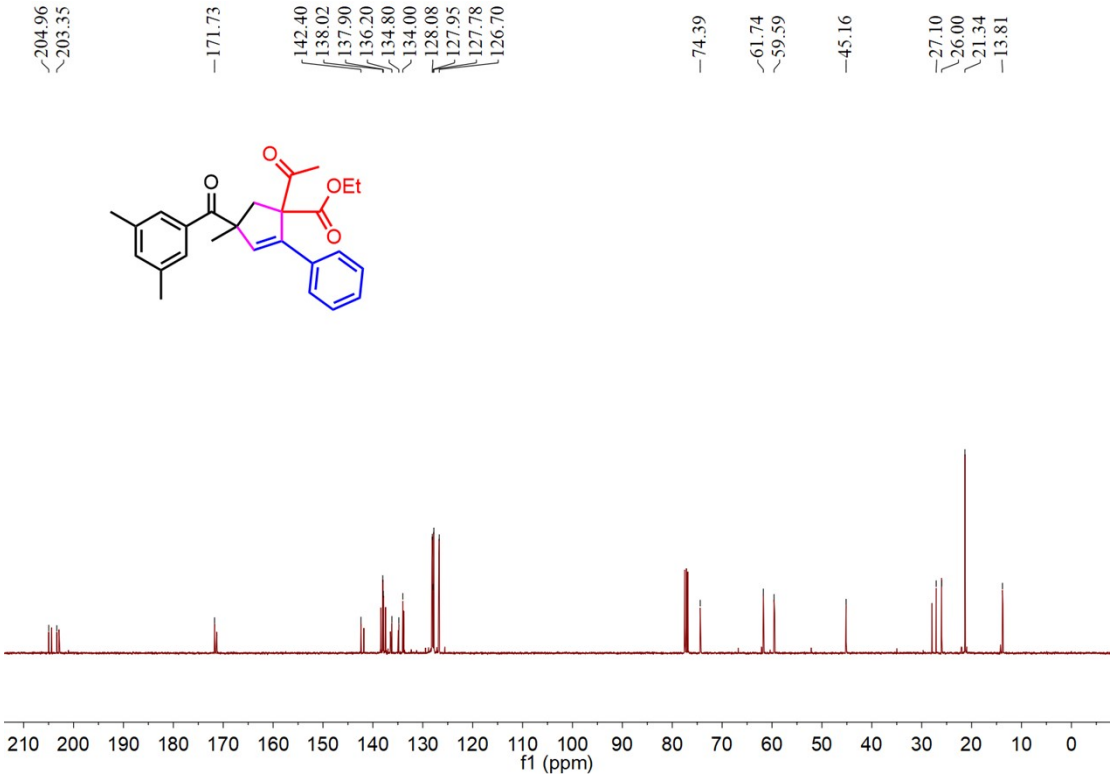




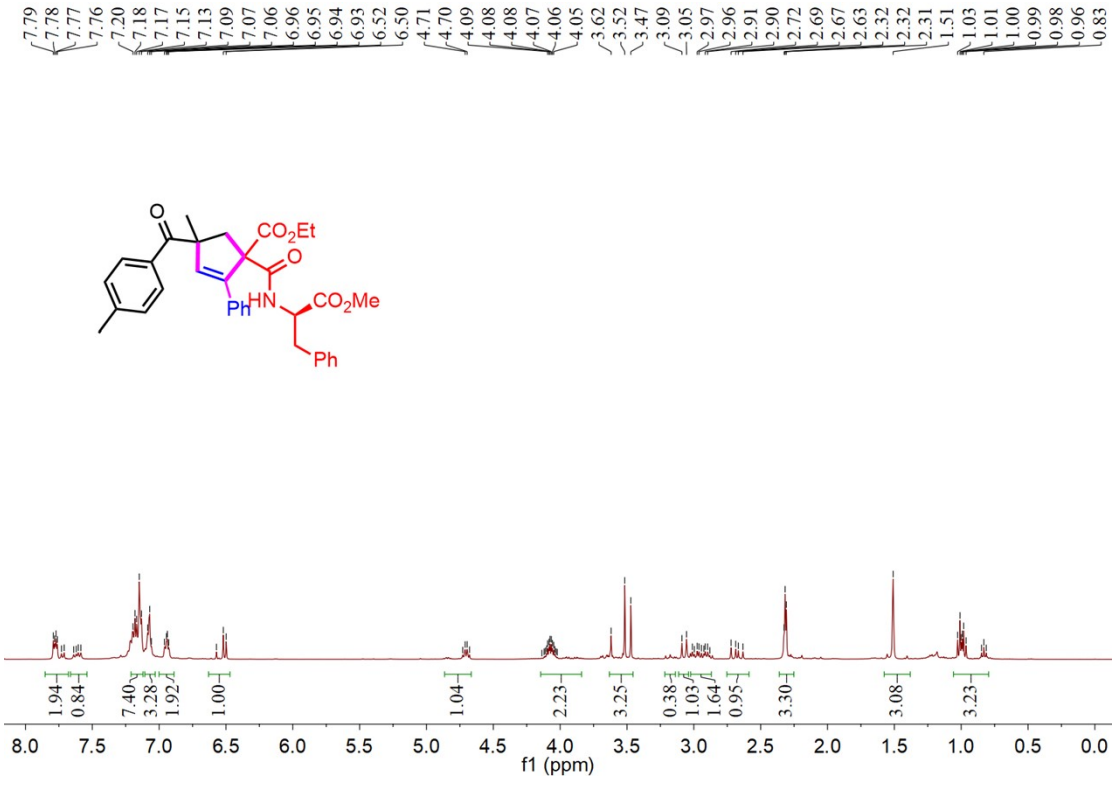


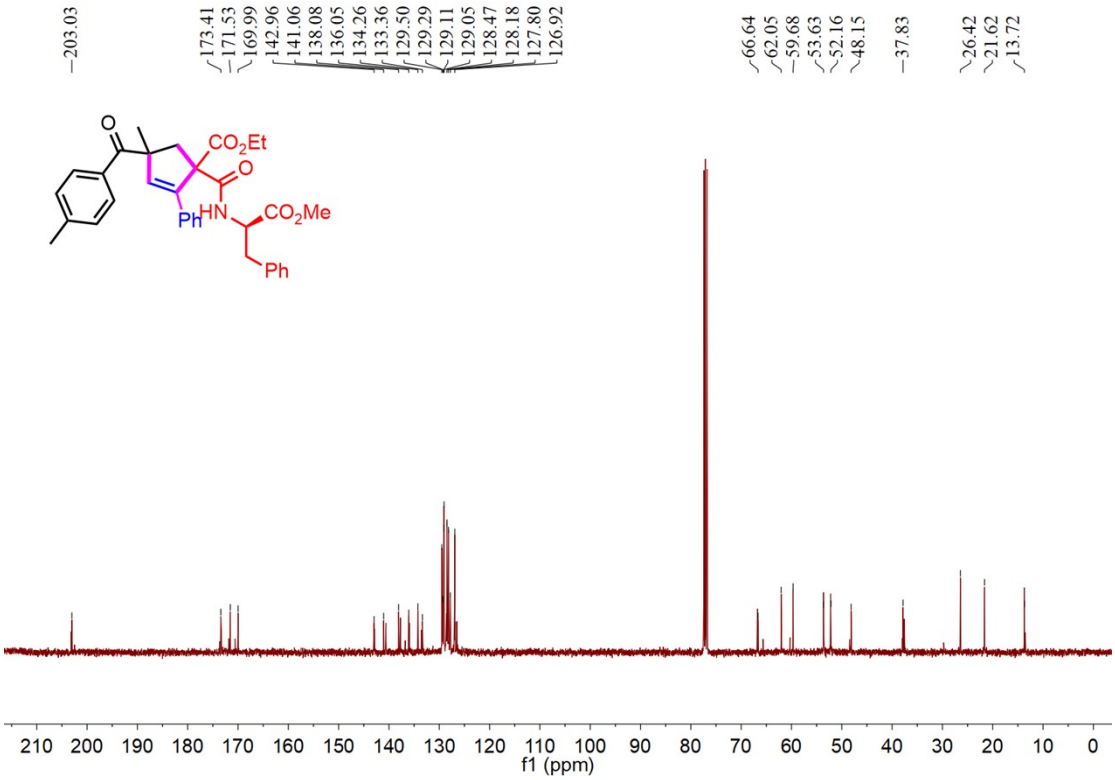
ethyl-1-acetyl-4-(3,5-dimethylbenzoyl)-4-methyl-2-phenylcyclopent-2-ene-1-carboxylate (35):



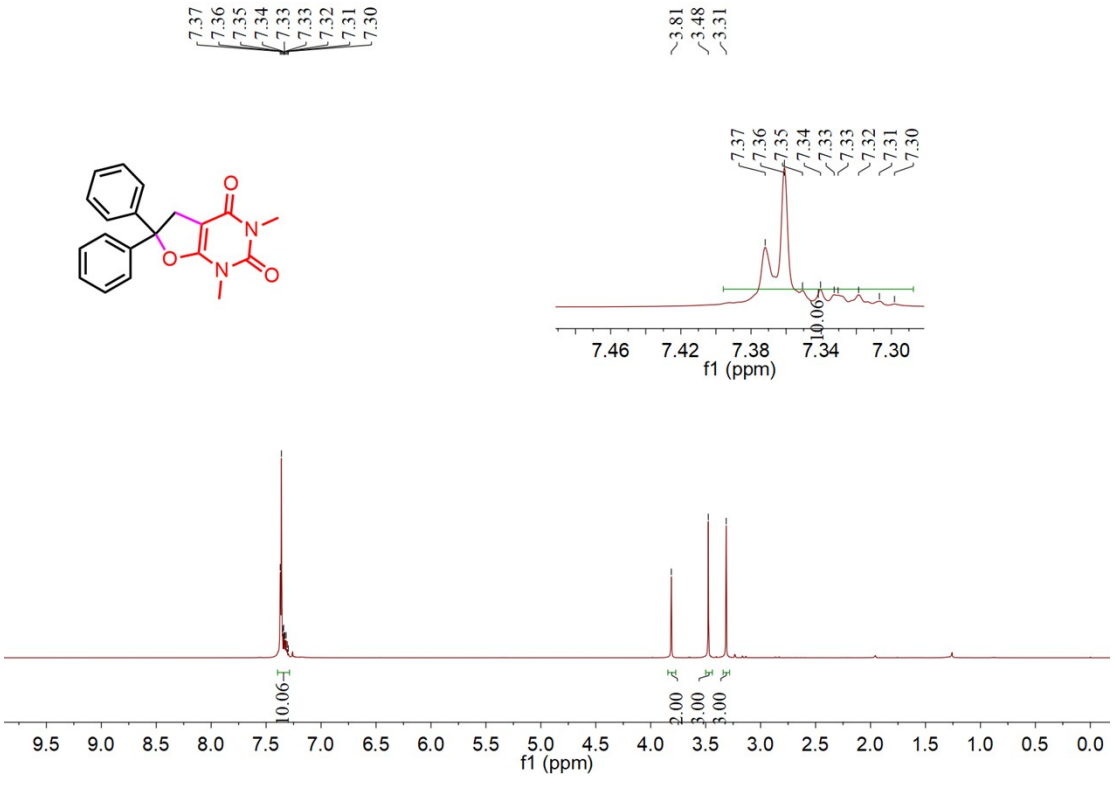


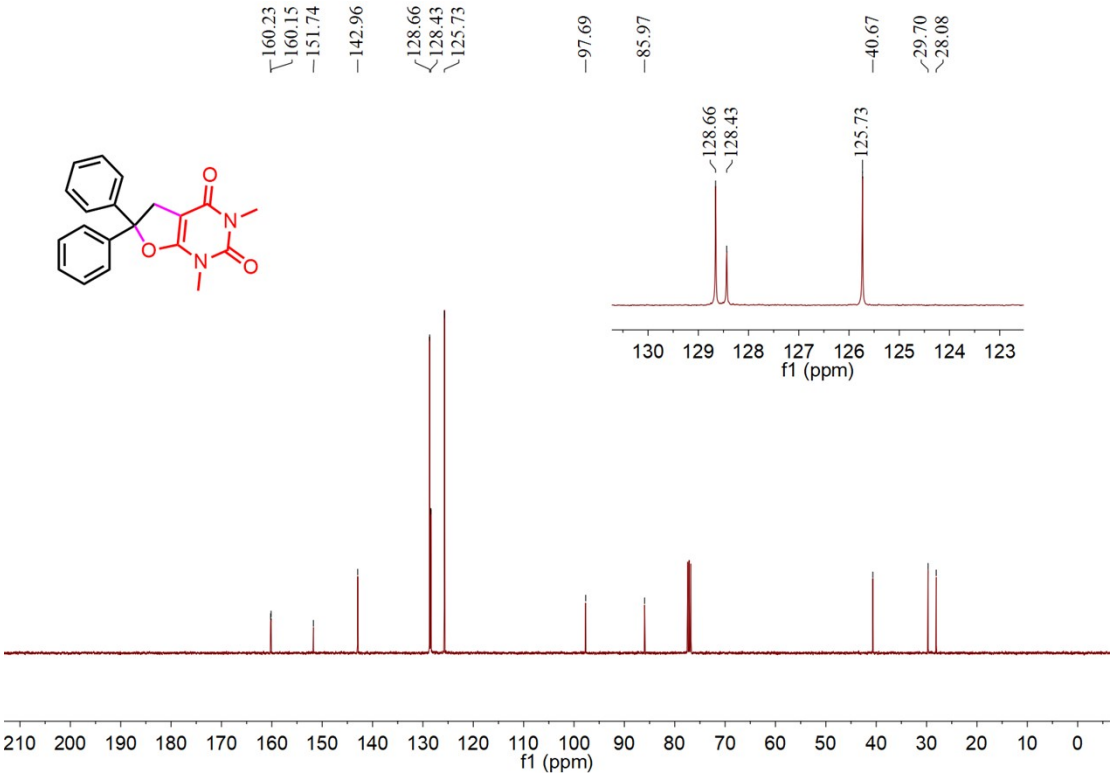
ethyl-(4R)-1-(((R)-1-methoxy-1-oxo-3-phenylpropan-2-yl)carbamoyl)-4-methyl-4-(4-methylbenzoyl)-2-phenylcyclopent-2-ene-1-carboxylate (36):



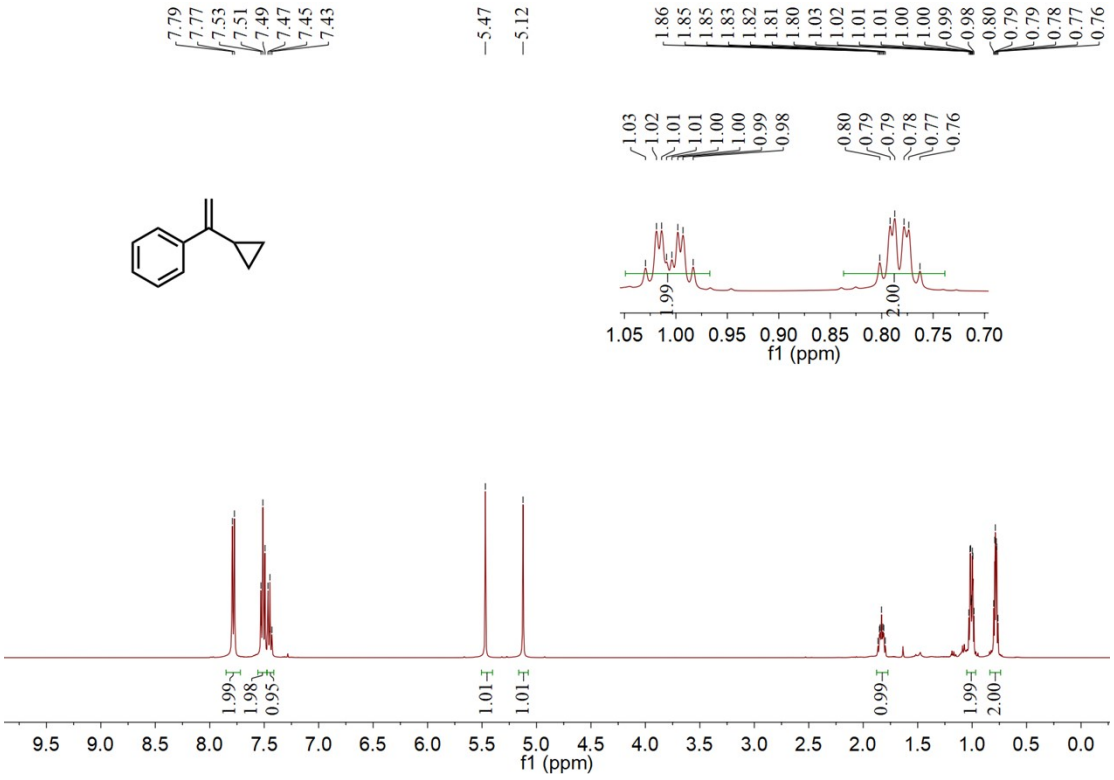


1,3-dimethyl-6,6-diphenyl-5,6-dihydrofuro[2,3-*d*]pyrimidine-2,4(1*H*,3*H*)-dione (37):

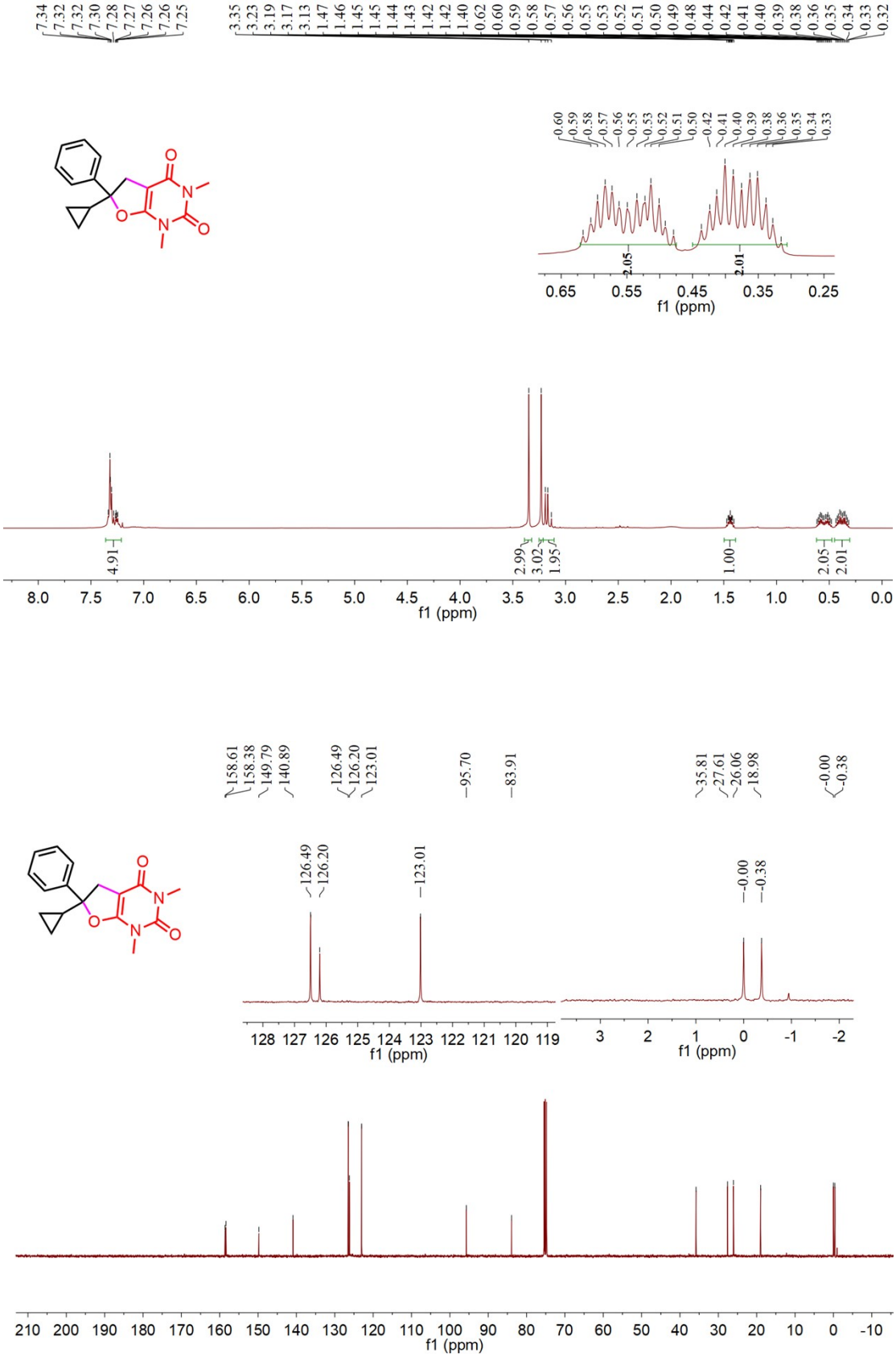




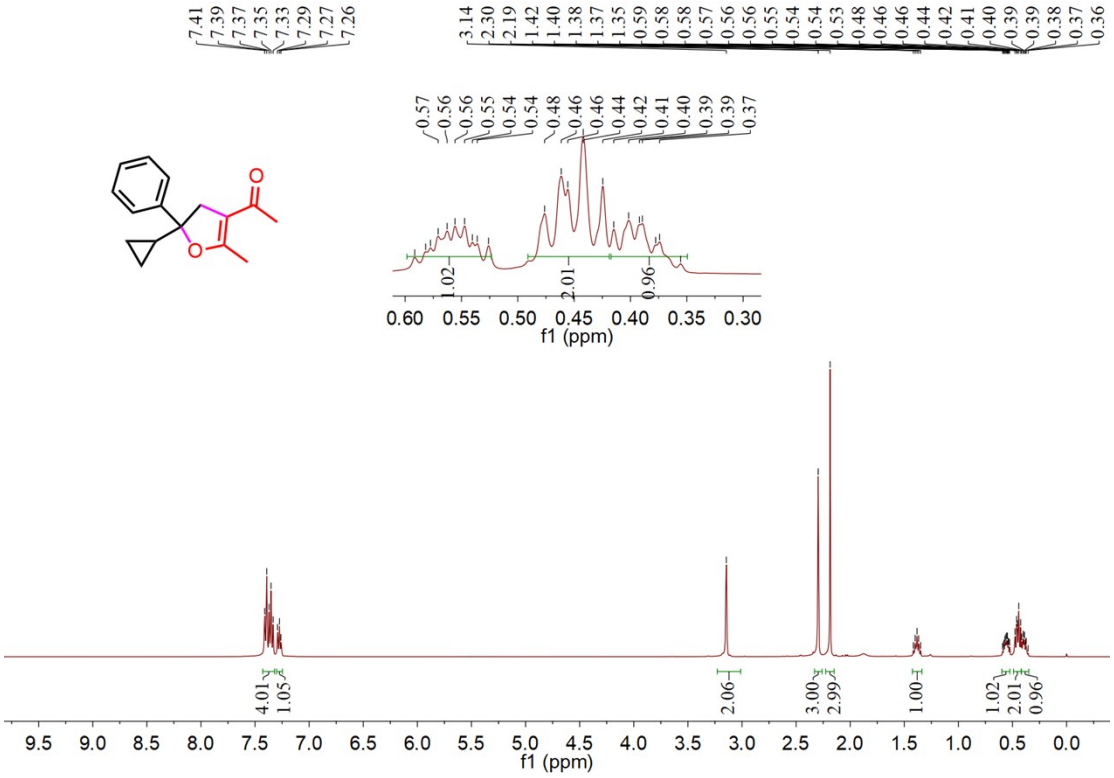
(1-cyclopropylvinyl) benzene (38):

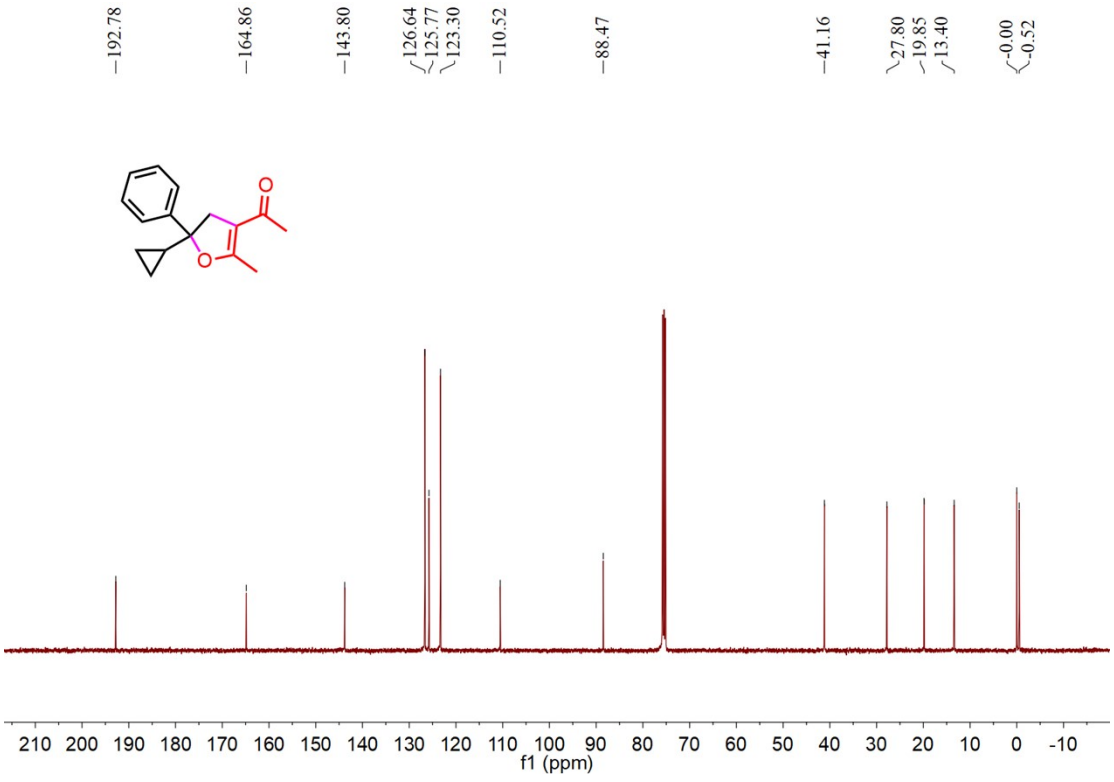


6-cyclopropyl-1,3-dimethyl-6-phenyl-5,6-dihydrofuro[2,3-*d*]pyrimidine-2,4(1*H*,3*H*)-dione (39):

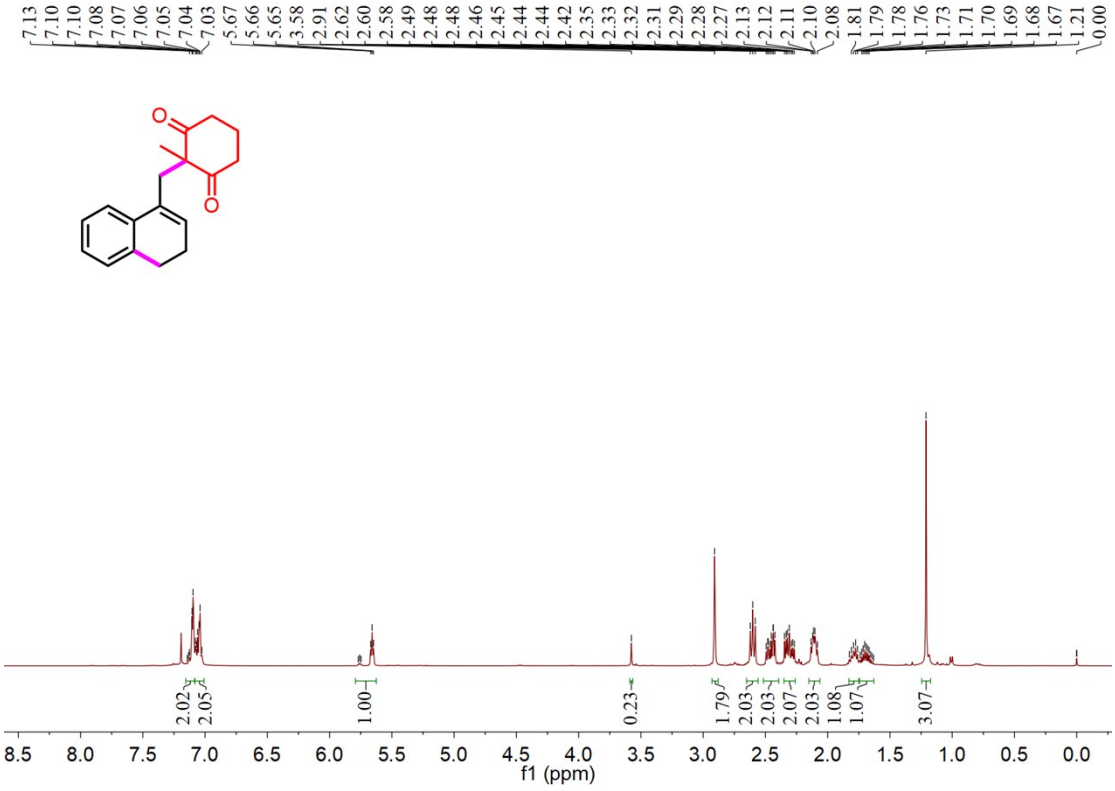


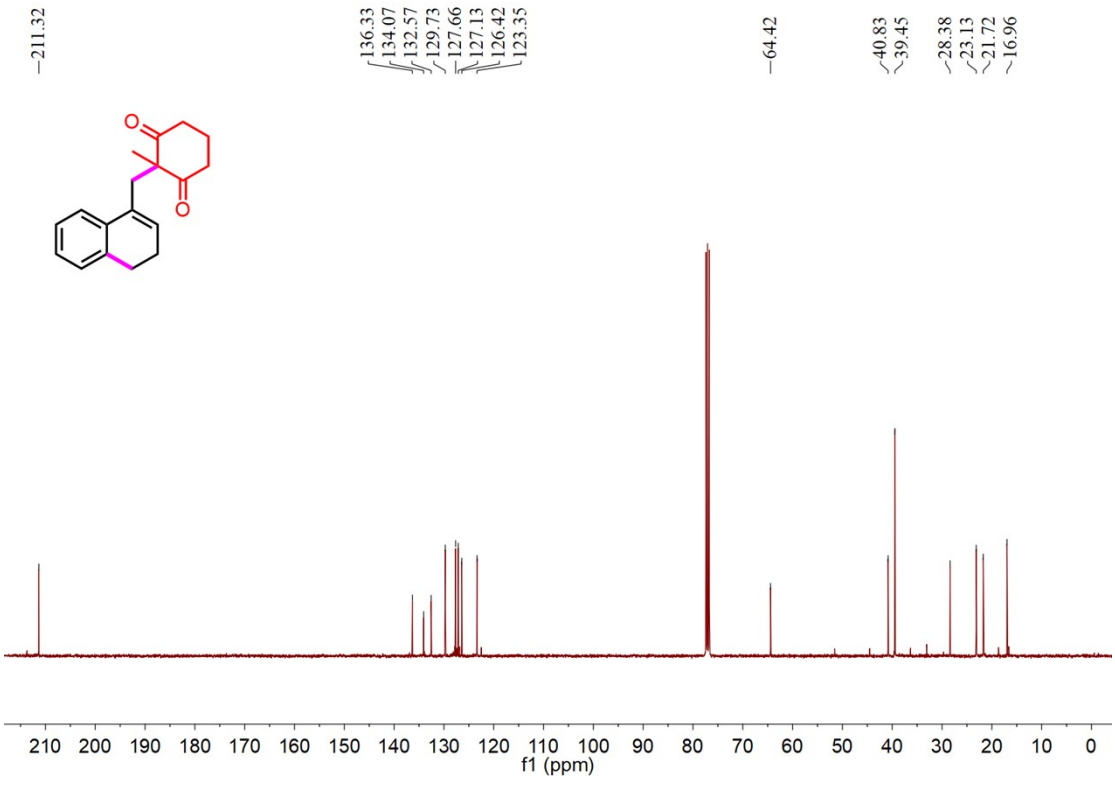
1-(5-cyclopropyl-2-methyl-5-phenyl-4,5-dihydrofuran-3-yl)ethan-1-one (**40**):





2-((3,4-dihydronaphthalen-1-yl)methyl)-2-methylcyclohexane-1,3-dione (**41**):





ethyl 2-acetyl-4-(4-(*tert*-butyl)benzoyl)-4-methyl-6-phenylhex-5-ynoate (43):