

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

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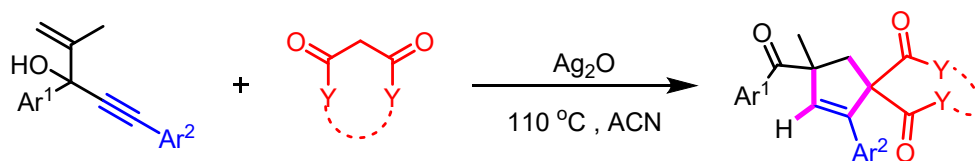
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1. General Information

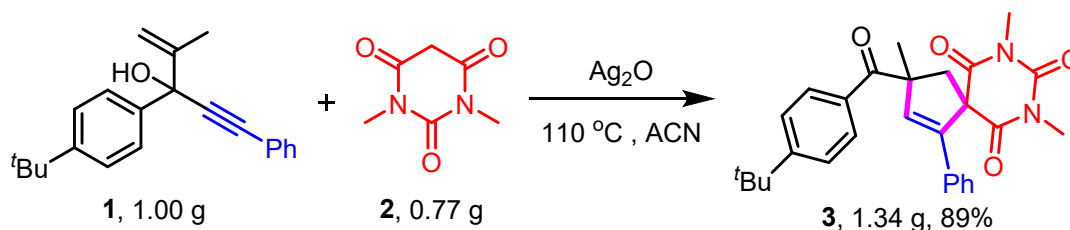
Commercially available reagents and solvents were of reagent grade quality without any further purification. Analytical thin-layer chromatography (TLC) was performed on 0.2 mm coated silica gel plates (HSGF 254) and visualized using a UV lamp (254 nm). Flash column chromatography was performed using silicycle silica gel (200-300 mesh). ^1H 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 °C 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

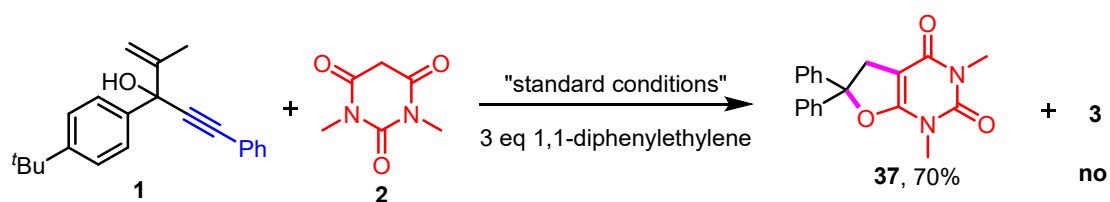


In a 35 mL oven-dried pressure sealed tube, a mixture of 1,4-enyne **1** (1.00 g, 3.29 mmol), 1,3-dimethylbarbituric acid **2** (0.77 g, 4.94 mmol), Ag₂O (1.51 g, 6.58 mmol) and acetonitrile (10 mL) was heated to 110 °C for 6h. Thereafter, the reaction mixture was quenched with saturated solution of NH₄Cl (100 mL) and extracted with EtOAc (100 mL). The organic layer was collected, dried over anhydrous Na₂SO₄ 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%).

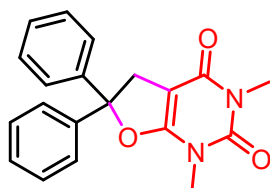
4. Mechanistic Studies

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), Ag₂O (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 NH₄Cl (30 mL) and extracted with EtOAc (30 mL). The organic layer was collected, dried over anhydrous Na₂SO₄ 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%).

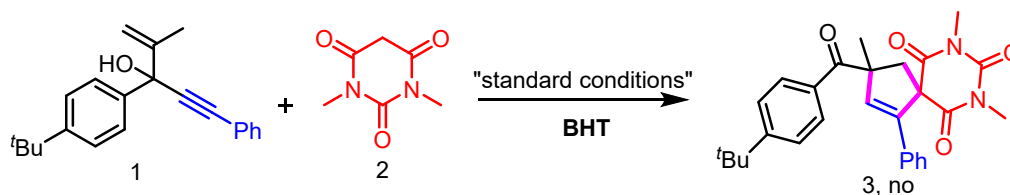


37

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; ¹H NMR (400 MHz, CDCl₃) δ 7.40 - 7.31 (m, 10H), 3.81 (s, 2H), 3.48 (s, 3H), 3.31 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) 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 C₂₀H₁₈N₂O₃Na [M+Na]⁺ calcd 357.1210, found 357.1211.

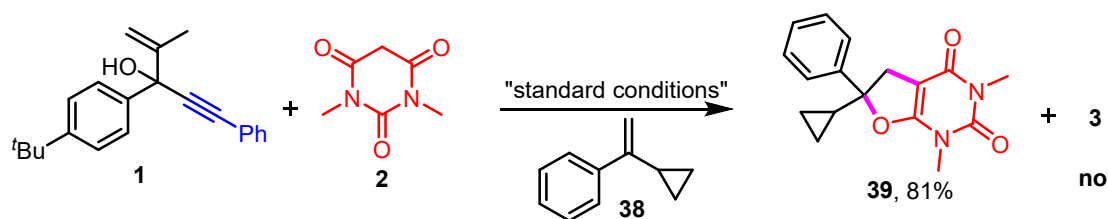
4-1-2: BHT (butylated hydroxytoluene) was added



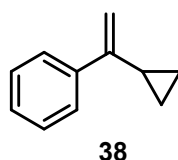
In an 15 mL oven-dried pressure sealed tube, a mixture of 1,4-enyne **1** (304.2 mg, 1 mmol), 1,3-dimethylbarbituric acid **2** (234.1 mg, 1.5 mmol), Ag₂O (459.6 mg, 2 mmol), BHT (661.1 mg, 3 mmol) and acetonitrile (3 mL) was heated to 110 °C for 6h. There was no spirocyclic compound **3** detected.

4-2) Radical clock experiment

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

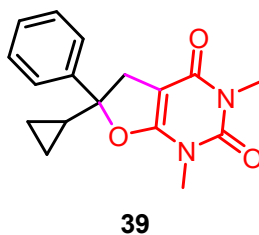


In a 15 mL oven-dried pressure sealed tube, a mixture of 1,4-enyne **1** (304.2 mg, 1 mmol), 1,3-dimethylbarbituric acid **2** (234.1 mg, 1.5 mmol), Ag₂O (459.6 mg, 2 mmol), radical probe **38** (432.3 mg, 3 mmol) and acetonitrile (3 mL) was heated to 110 °C for 6h. Then, the reaction mixture was quenched with saturated solution of NH₄Cl (30 mL) and extracted with EtOAc (30 mL). The organic layer was collected, dried over anhydrous Na₂SO₄ 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.



(1-cyclopropylvinyl) benzene (38):²

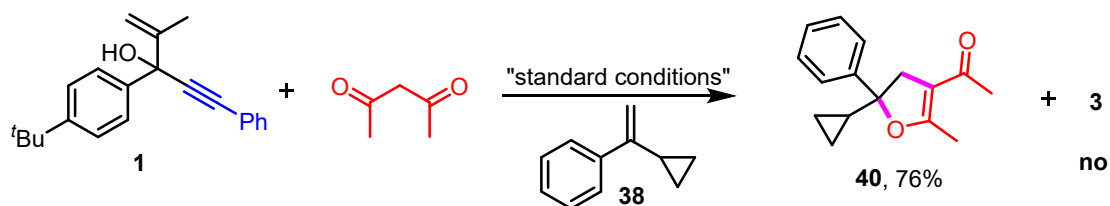
colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.81 - 7.72 (m, 2H), 7.52 - 7.46 (m, 2H), 7.45 - 7.39 (m, 1H), 5.47 (s, 1H), 5.12 (s, 1H), 1.85 - 1.75 (m, 1H), 1.01 - 0.95 (m, 2H), 0.79 - 0.72 (m, 2H).



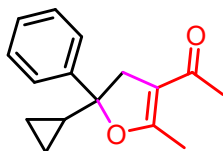
6-cyclopropyl-1,3-dimethyl-6-phenyl-5,6-dihydrofuro[2,3-*d*]pyrimidine-2,4(1*H*,3*H*)-dione (39):

White solid (362.2 mg, 81%); Eluent: petroleum ether/ethyl acetate 4:1; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (101 MHz, CDCl₃) 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 C₁₇H₁₈N₂O₃Na [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), Ag₂O (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 NH₄Cl (30 mL) and extracted with EtOAc (30 mL). The organic layer was collected, dried over anhydrous Na₂SO₄ 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%).

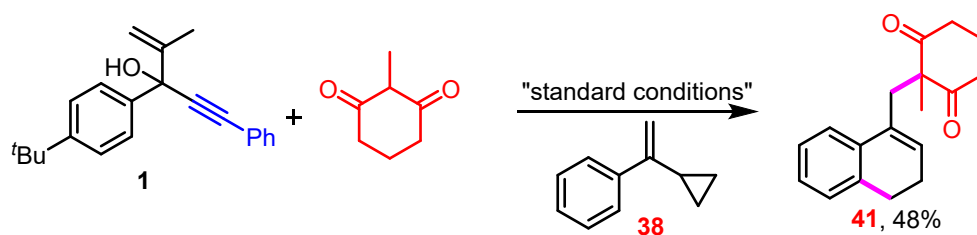


40

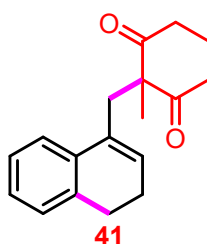
1-(5-cyclopropyl-2-methyl-5-phenyl-4,5-dihydrofuran-3-yl)ethan-1-one (40):

Yellow oil (276.0 mg, 76%); Eluent: petroleum ether/ethyl acetate 15:1; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (101 MHz, CDCl₃) 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 C₁₆H₁₉O₂ [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), Ag₂O (459.6 mg, 2 mmol), radical clock vinylcyclopropane substrate **38** (540.3 mg, 3 mmol) and acetonitrile (3 mL) was heated to 110 °C for 6 h. There was no spirocyclic compound **3** detected. Thereafter, the reaction mixture was quenched with saturated solution of NH₄Cl (20 mL) and extracted with EtOAc (20 mL). The organic layer was collected, dried over anhydrous Na₂SO₄ 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%).

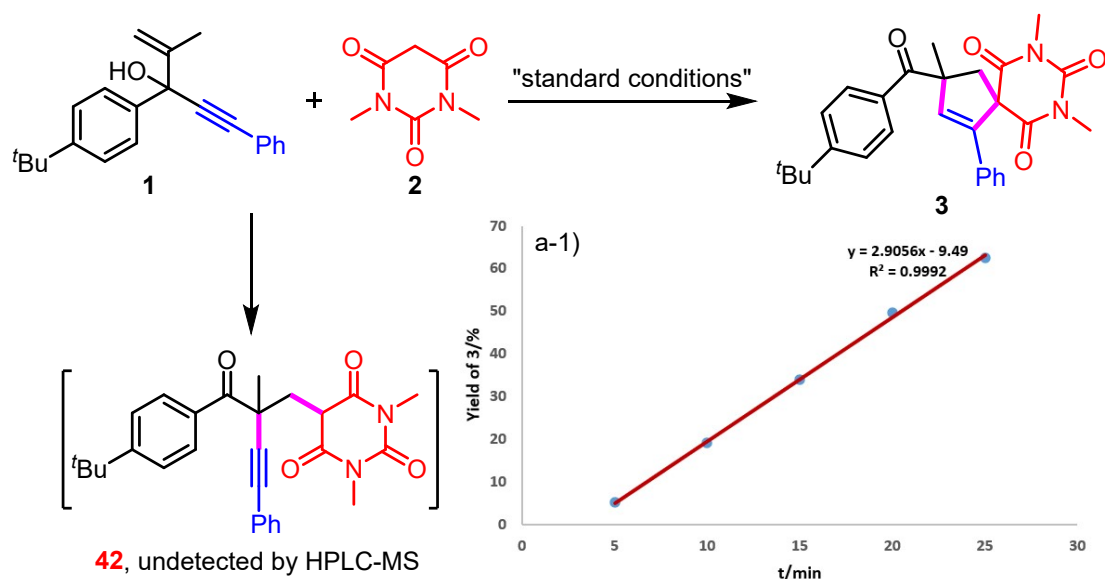


2-((3,4-dihydronaphthalen-1-yl)methyl)-2-methylcyclohexane-1,3-dione (**41**):

Yellow oil (128.7 mg, 48%); Eluent: petroleum ether/ethyl acetate 5:1; ¹H NMR (400 MHz, CDCl₃): 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); ¹³C NMR (101 MHz, CDCl₃): 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 C₁₈H₂₀O₂Na [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), Ag₂O (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

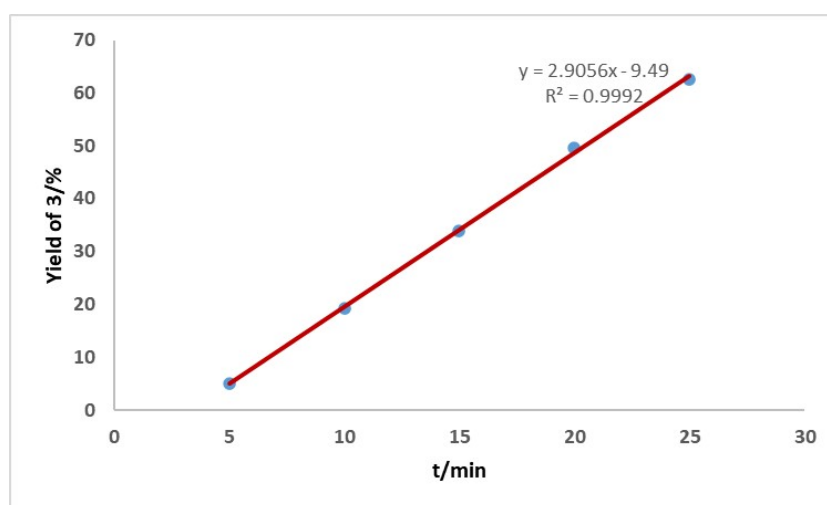
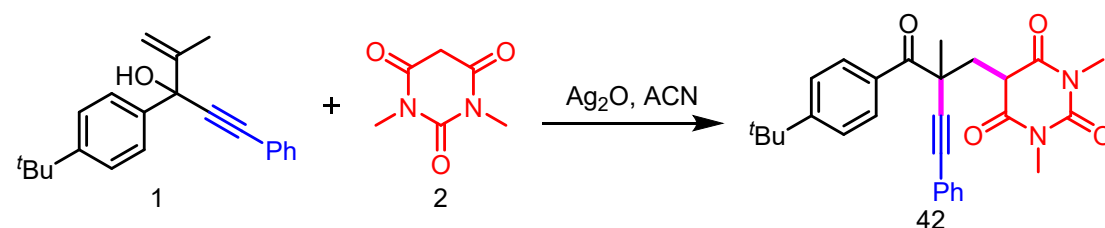


Figure S1 The yield of **3** at different reaction times

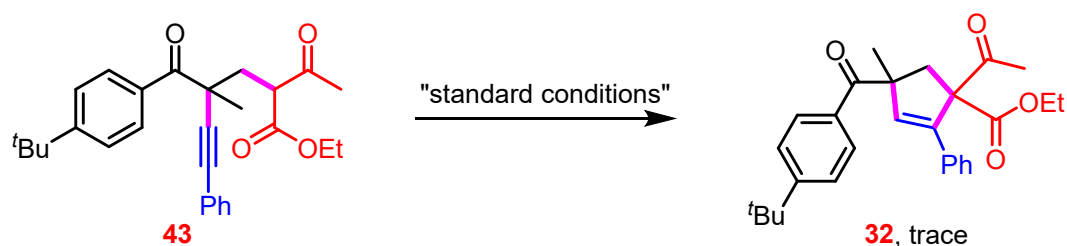
Table S1 Monitoring the migration product formation at lower temperature



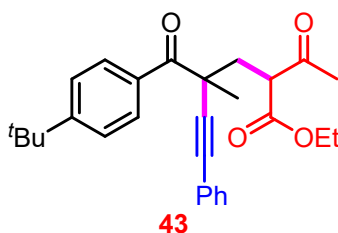
Monitoring 42 by HRMS				
Entry	Temperature (°C)			
		10 min	30 min	2 h
1	90	undetected	undetected	undetected
2	70	undetected	undetected	undetected
3	50	undetected	undetected	undetected

Reaction conditions: **1** (1 mmol, 304.2 mg), **2** (1.5 mmol, 234.1 mg), Ag₂O (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), Ag₂O (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.

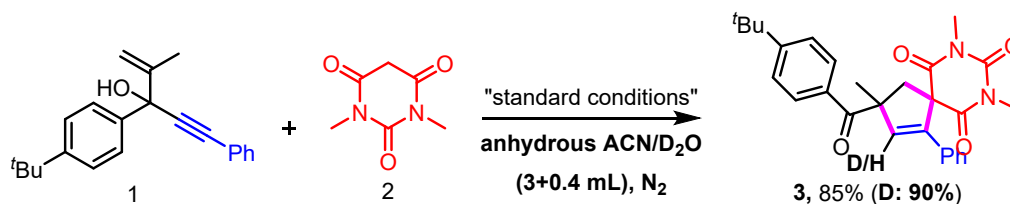


ethyl 2-acetyl-4-(4-(*tert*-butyl)benzoyl)-4-methyl-6-phenylhex-5-ynoate (43):

Yellow oil; Eluent: petroleum ether/ethyl acetate 20:1; ^1H 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 $\text{C}_{28}\text{H}_{32}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ calcd 455.2193, found 455.2198.

4-4) Isotope labeling experiments:

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 $^\circ\text{C}$. 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%).

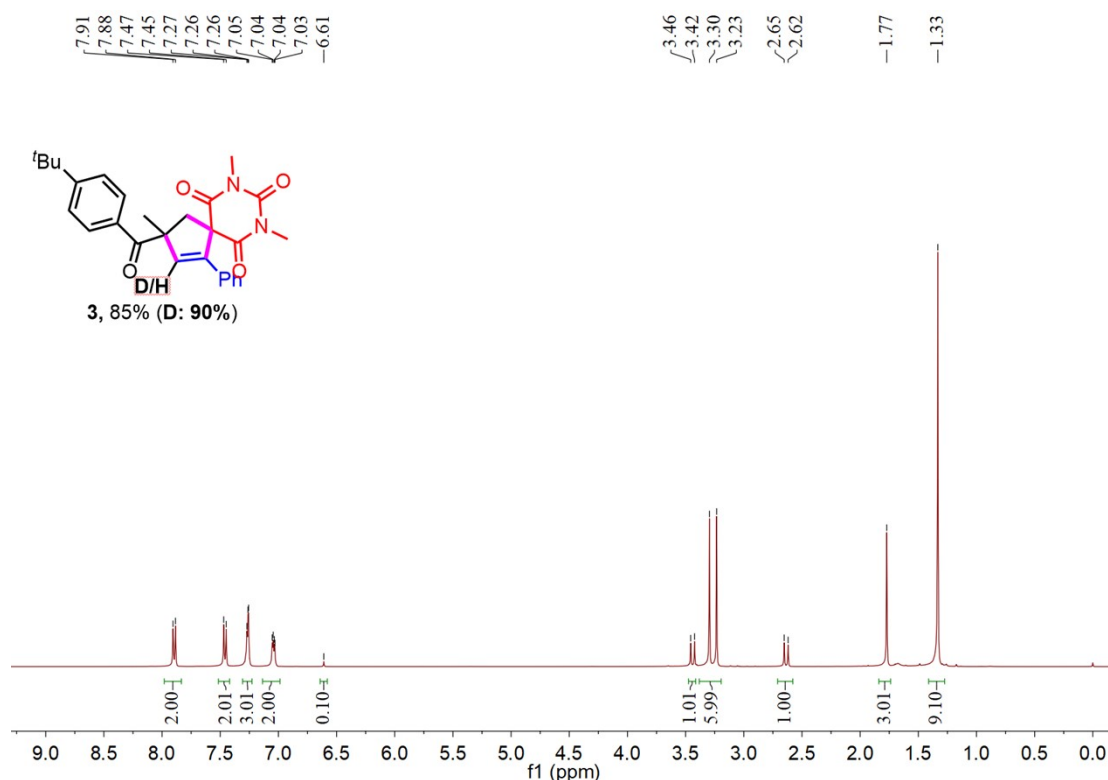
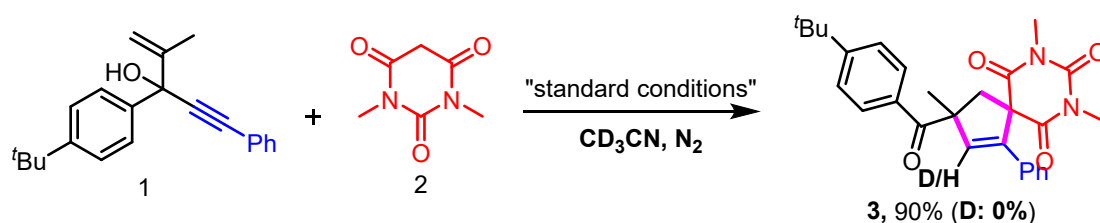


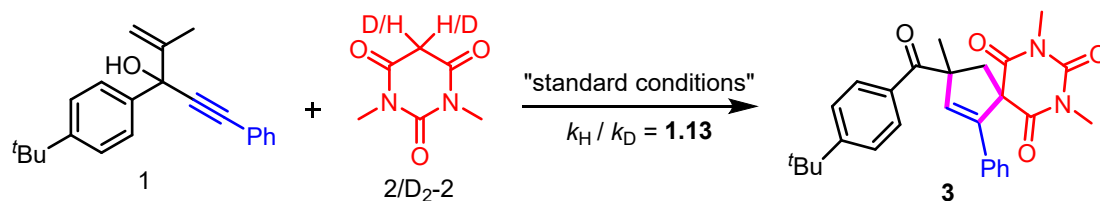
Figure S2 ^1H NMR analysis of electrochemically generated **3**/[D]-**3**

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 $^\circ\text{C}$. 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 **D₂-2** (234.1 mg or 237.1 mg, 1.5 mmol), Ag₂O (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

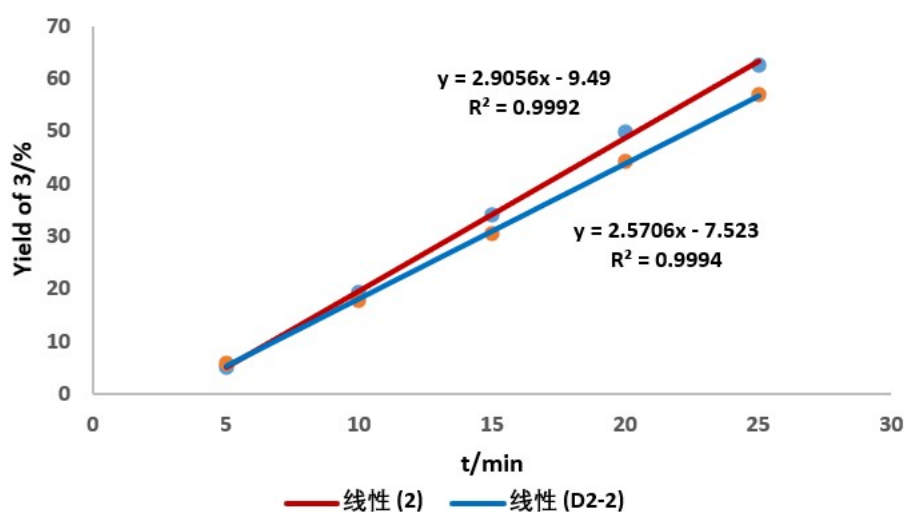
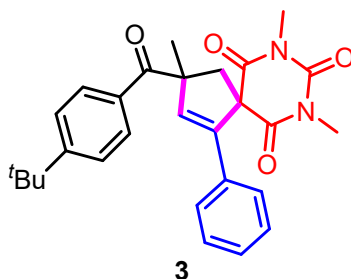


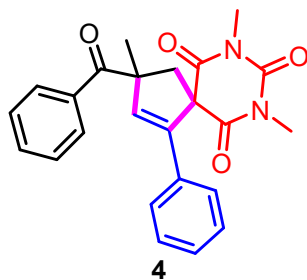
Figure S3 Parallel experiment of **2** and **D₂-2**

5. Characterization Data for Final Products



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

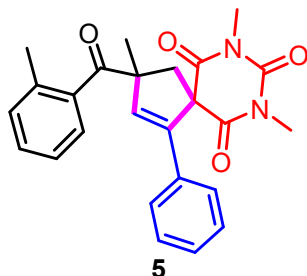
Yellow solid (421.6 mg, 92%); Eluent: petroleum ether/ethyl acetate 10:1; ^1H NMR (400 MHz, CDCl_3): δ 7.90 (dt, J = 8.5, 2.0 Hz, 2H), 7.46 (dt, J = 8.5, 2.1 Hz, 2H), 7.29 - 7.23 (m, 3H), 7.08 - 7.01 (m, 2H), 6.62 (s, 1H), 3.44 (d, J = 13.4 Hz, 1H), 3.29 (s, 3H), 3.23 (s, 3H), 2.64 (d, J = 13.4 Hz, 1H), 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 $\text{C}_{28}\text{H}_{30}\text{N}_2\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ calcd 481.2098, found 481.2104.



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

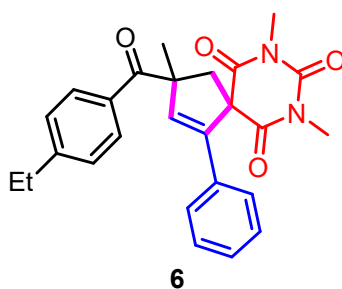
Yellow solid (349.9 mg, 87%); Eluent: petroleum ether/ethyl acetate 10:1; ^1H NMR (400 MHz, CDCl_3): δ 7.92 - 7.88 (m, 2H), 7.50 (tt, J = 7.3, 2.5 Hz, 1H), 7.43 (t, J = 7.4 Hz, 2H), 7.29 - 7.23 (m, 3H), 7.06 - 7.00 (m, 2H), 6.55 (s, 1H), 3.43 (d, J = 13.4 Hz, 1H), 3.28 (s, 3H), 3.22 (s, 3H), 2.64 (d, 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.



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

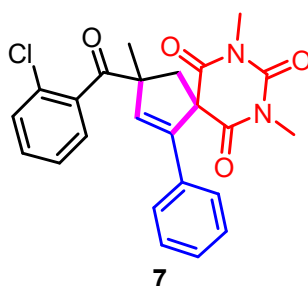
Yellow solid (366.2 mg, 88%); Eluent: petroleum ether/ethyl acetate 10:1; 1H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, $J = 7.6$ Hz, 1H), 7.32 - 7.22 (m, 5H), 7.19 (t, $J = 7.5$ Hz, 1H), 7.04 - 6.98 (m, 2H), 6.28 (s, 1H), 3.46 (d, $J = 13.6$ Hz, 1H), 3.29 (s, 3H), 3.27 (s, 3H), 2.49 (d, $J = 13.6$ Hz, 1H), 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.



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

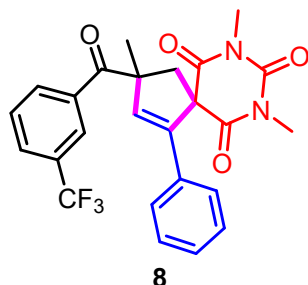
Yellow solid (387.2 mg, 90%); Eluent: petroleum ether/ethyl acetate 10:1; 1H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, $J = 7.4$ Hz, 2H), 7.49 (tt, $J = 7.3, 2.5$ Hz, 1H), 7.43 (tt, $J = 7.4, 1.0$ Hz, 2H), 7.09 (d, $J = 8.0$ Hz, 2H), 6.95 (d, $J = 8.0$ Hz, 2H), 6.53 (s, 1H), 3.42 (d, $J = 13.4$ Hz, 1H), 3.30 (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 $\text{C}_{26}\text{H}_{26}\text{N}_2\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ calcd 453.1785, found 453.1788.



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

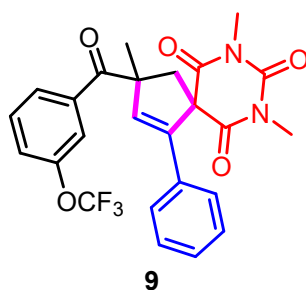
Yellow solid (392.5 mg, 90%); Eluent: petroleum ether/ethyl acetate 10:1; ^1H NMR (400 MHz, CDCl_3): δ 7.57 (dd, $J = 7.5, 1.7$ Hz, 1H), 7.42 (d, $J = 8.7$ Hz, 1H), 7.34 (td, $J = 7.7, 1.7$ Hz, 1H), 7.31 - 7.24 (m, 4H), 7.03 - 6.96 (m, 2H), 6.19 (s, 1H), 3.46 (d, $J = 13.6$ Hz, 1H), 3.30 (s, 3H), 3.27 (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 $\text{C}_{24}\text{H}_{21}\text{ClN}_2\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ calcd 459.1082, found 459.1089.



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

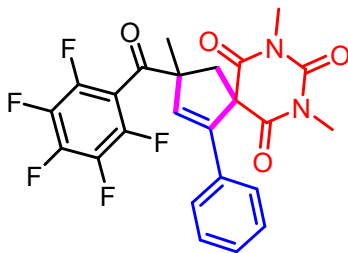
Yellow solid (409.0 mg, 87%); Eluent: petroleum ether/ethyl acetate 10:1; ^1H NMR

(400 MHz, CDCl₃): 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); ¹³C NMR (101 MHz, CDCl₃): 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; ¹⁹F NMR (376 MHz, CDCl₃): δ -62.62. HRMS (ESI-TOF) Calcd for C₂₅H₂₁F₃N₂O₄Na [M+Na]⁺ calcd 493.1346, found 493.1357.



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

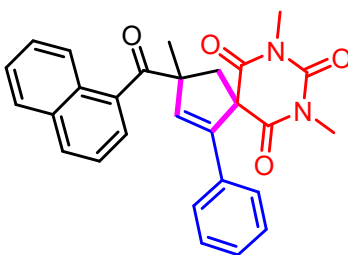
Yellow solid (398.6 mg, 82%); Eluent: petroleum ether/ethyl acetate 8:1; ¹H NMR (400 MHz, CDCl₃): δ 7.85 (d, J = 7.8 Hz, 1H), 7.75 (s, 1H), 7.48 (t, J = 8.0 Hz, 1H), 7.36 (d, J = 9.2 Hz, 1H), 7.30 - 7.23 (m, 3H), 7.05 - 6.98 (m, 2H), 6.46 (s, 1H), 3.40 (d, J = 13.4 Hz, 1H), 3.28 (s, 3H), 3.23 (s, 3H), 2.66 (d, J = 13.4 Hz, 1H), 1.75 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): 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; ¹⁹F NMR (376 MHz, CDCl₃): δ -57.81. HRMS (ESI-TOF) Calcd for C₂₅H₂₁F₃N₂O₅Na [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; ^1H 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 $\text{C}_{24}\text{H}_{17}\text{F}_5\text{N}_2\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ calcd 515.1001, found 515.1014.

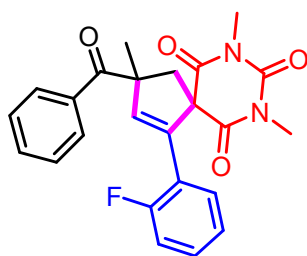


11

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; ^1H 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,

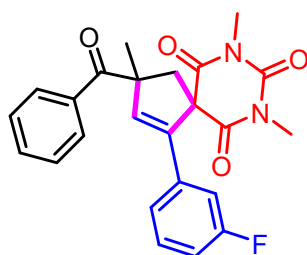
140.58, 137.86, 137.33, 133.65, 133.27, 130.25, 130.08, 128.82, 128.57, 128.35, 127.19, 126.40, 126.26, 125.65, 124.88, 124.28, 65.12, 63.34, 47.39, 29.11, 26.85; HRMS (ESI-TOF) Calcd for $C_{28}H_{24}N_2O_4Na$ $[M+Na]^+$ calcd 475.1628, found 475.1637.



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; 1H 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.

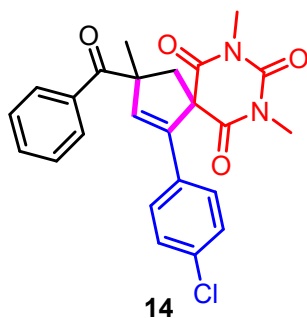


13

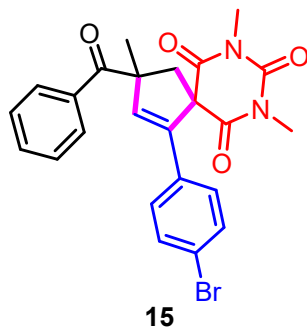
3-benzoyl-1-(3-fluorophenyl)-3,7,9-trimethyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-

trione (13):

Yellow solid (368.7 mg, 88%); Eluent: petroleum ether/ethyl acetate 10:1; ^1H 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 $\text{C}_{24}\text{H}_{21}\text{FN}_2\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ calcd 443.1378, found 443.1378.

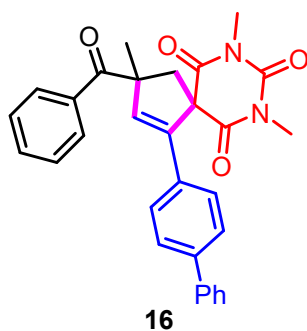
**3-benzoyl-1-(4-chlorophenyl)-3,7,9-trimethyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (14):**

Yellow solid (396.9 mg, 91%); Eluent: petroleum ether/ethyl acetate 10:1; ^1H 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 $\text{C}_{24}\text{H}_{21}\text{ClN}_2\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ calcd 459.1082, found 459.1076.



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

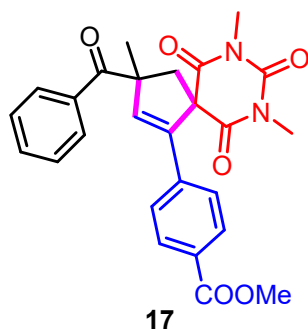
Yellow solid (422.5 mg, 88%); Eluent: petroleum ether/ethyl acetate 10:1; ^1H NMR (400 MHz, CDCl_3): δ 7.79 (dt, J = 8.6, 2.2 Hz, 2H), 7.58 (dt, J = 8.6, 1.7 Hz, 2H), 7.29 - 7.25 (m, 3H), 7.04 - 6.98 (m, 2H), 6.48 (s, 1H), 3.38 (d, J = 13.4 Hz, 1H), 3.28 (s, 3H), 3.23 (s, 3H), 2.63 (d, J = 13.4 Hz, 1H), 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 $\text{C}_{24}\text{H}_{21}\text{BrN}_2\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ calcd 503.0577, found 503.0586.



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):

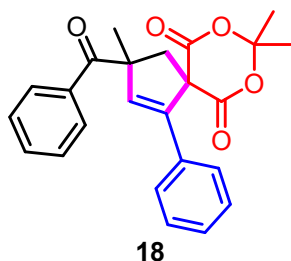
Yellow solid (377.8 mg, 79%); Eluent: petroleum ether/ethyl acetate 15:1; ^1H NMR (400 MHz, CDCl_3): δ 7.94 - 7.88 (m, 2H), 7.56 - 7.48 (m, 5H), 7.46 - 7.38 (m, 4H), 7.33 (tt, J = 7.3, 2.1 Hz, 1H), 7.12 (d, J = 8.2 Hz, 2H), 6.65 (s, 1H), 3.44 (d, J = 13.3 Hz, 1H), 3.33 (s, 3H), 3.27 (s, 3H), 2.62 (d, 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.



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

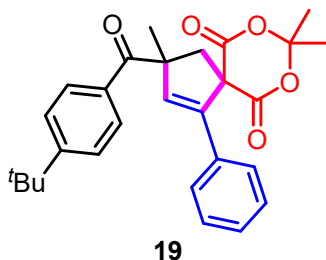
Yellow solid (331.3 mg, 72%); Eluent: petroleum ether/ethyl acetate 8:1; 1H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 7.8 Hz, 2H), 7.89 (d, J = 7.9 Hz, 2H), 7.51 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.12 (d, J = 8.2 Hz, 2H), 6.72 (s, 1H), 3.88 (s, 3H), 3.43 (d, J = 13.4 Hz, 1H), 3.31 (s, 3H), 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.



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

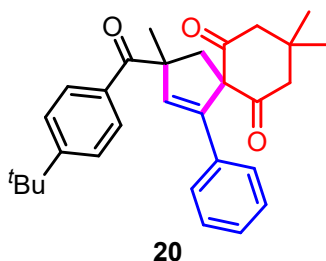
Yellow solid (327.7 mg, 84%); Eluent: petroleum ether/ethyl acetate 20:1; 1H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 7.2 Hz, 2H), 7.51 (t, J = 7.3 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.31 - 7.25 (m, 3H), 7.20 (dd, J = 7.6, 2.0 Hz, 2H), 6.70 (s, 1H), 3.57 (d,

$J = 13.3$ 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 $\text{C}_{24}\text{H}_{22}\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$ calcd 413.1359, found 413.1361.



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

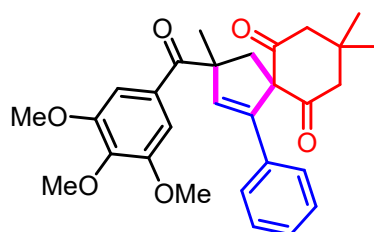
Yellow solid (383.7 mg, 86%); Eluent: petroleum ether/ethyl acetate 20:1; ^1H NMR (400 MHz, CDCl_3): δ 7.91 (dt, $J = 8.6, 1.8$ Hz, 2H), 7.46 (dt, $J = 8.6, 1.7$ Hz, 2H), 7.31 - 7.20 (m, 5H), 6.77 (s, 1H), 3.59 (d, $J = 13.3$ Hz, 1H), 2.62 (d, $J = 13.3$ Hz, 1H), 1.83 (s, 3H), 1.78 (s, 6H), 1.33 (s, 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 $\text{C}_{28}\text{H}_{30}\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$ calcd 469.1985, found 469.1993.



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; ^1H 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

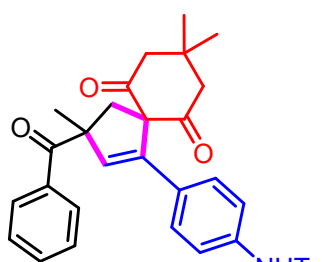
- 7.20 (m, 3H), 7.16 (dd, $J = 7.7, 1.8$ Hz, 2H), 6.47 (s, 1H), 3.40 (d, $J = 12.9$ Hz, 1H), 2.83 (dd, $J = 37.6, 15.2$ Hz, 2H), 2.45 (ddd, $J = 15.2, 8.0, 2.1$ Hz, 2H), 2.29 (d, $J = 13.0$ Hz, 1H), 1.60 (s, 3H), 1.32 (s, 9H), 1.13 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 208.07, 206.71, 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 $\text{C}_{30}\text{H}_{34}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 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):

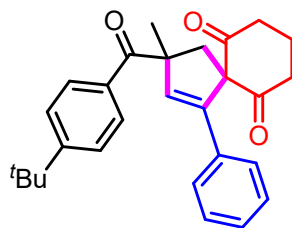
Yellow solid (304.8 mg, 64%); Eluent: petroleum ether/ethyl acetate 8:1; ^1H NMR (400 MHz, CDCl_3): δ 7.29 - 7.23 (m, 5H), 7.19 (dd, $J = 7.5, 2.0$ Hz, 2H), 6.42 (s, 1H), 3.90 (s, 3H), 3.88 (s, 6H), 3.24 (d, $J = 13.1$ Hz, 1H), 2.81 (dd, $J = 15.0, 6.2$ Hz, 2H), 2.50 (dd, $J = 15.1, 2.1$ Hz, 1H), 2.44 (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 $\text{C}_{29}\text{H}_{32}\text{O}_6\text{Na}$ $[\text{M}+\text{Na}]^+$ 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):

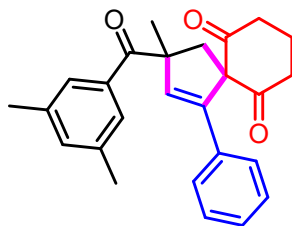
Yellow solid (372.0 mg, 67%); Eluent: petroleum ether/ethyl acetate 5:1; ^1H NMR (400 MHz, DMSO- d_6): δ 7.90 (d, J = 7.4 Hz, 2H), 7.64 (d, J = 8.2 Hz, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 6.94 (s, 4H), 6.59 (s, 1H), 3.24 – 3.02 (m, 4H), 2.33 (q, J = 11.6, 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 $\text{C}_{33}\text{H}_{33}\text{NSO}_5\text{Na}$ $[\text{M}+\text{Na}]^+$ 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):

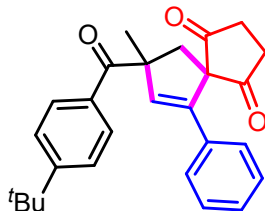
Yellow oil (306.5 mg, 74%); Eluent: petroleum ether/ethyl acetate 15:1; ^1H NMR (400 MHz, CDCl_3): δ 7.90 (dt, J = 8.5, 1.9 Hz, 2H), 7.44 (dt, J = 8.5, 1.8 Hz, 2H), 7.26 - 7.16 (m, 3H), 7.09 - 7.01 (m, 2H), 6.70 (s, 1H), 3.34 (d, J = 13.1 Hz, 1H), 2.88 (dddd, J = 26.5, 15.7, 10.0, 5.4 Hz, 2H), 2.75 - 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 $\text{C}_{28}\text{H}_{30}\text{O}_3$ $[\text{M}+\text{Na}]^+$ calcd 437.2087, found 437.2094.



24

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

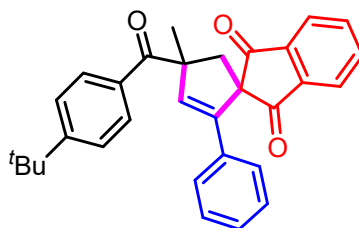
Yellow oil (254.9 mg, 66%); Eluent: petroleum ether/ethyl acetate 15:1; ^1H NMR (400 MHz, CDCl_3): δ 7.51 (s, 2H), 7.27 - 7.20 (m, 3H), 7.13 (s, 1H), 7.07 - 7.01 (m, 2H), 6.62 (s, 1H), 3.30 (d, $J = 13.1$ Hz, 1H), 2.95 - 2.80 (m, 2H), 2.75 - 2.60 (m, 2H), 2.35 (s, 6H), 2.20 (d, $J = 13.1$ Hz, 2H), 2.05 - 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 $\text{C}_{26}\text{H}_{26}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 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):

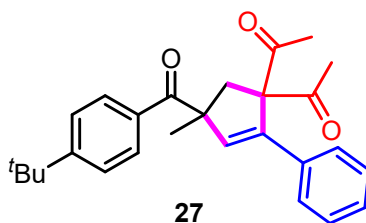
Yellow oil (256.1 mg, 64%); Eluent: petroleum ether/ethyl acetate 15:1; ^1H NMR (400 MHz, CDCl_3): δ 7.94 (dt, $J = 8.6, 1.8$ Hz, 2H), 7.46 (dt, $J = 8.6, 1.8$ Hz, 2H), 7.29 - 7.23 (m, 3H), 7.06 - 6.99 (m, 2H), 6.56 (s, 1H), 3.08 (d, $J = 13.2$ Hz, 1H), 2.93 - 2.82 (m, 2H), 2.81 - 2.68 (m, 2H), 2.26 (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 $\text{C}_{27}\text{H}_{28}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 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):

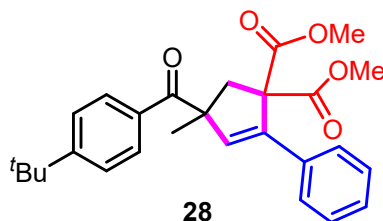
5-Yellow solid (354.1 mg, 79%); Eluent: petroleum ether/ethyl acetate 20:1; ^1H NMR (400 MHz, CDCl_3): δ 8.06 - 7.96 (m, 4H), 7.91 - 7.84 (m, 2H), 7.47 (dt, $J = 8.6, 2.0$ Hz, 2H), 7.13 - 7.07 (m, 3H), 7.02 - 6.97 (m, 2H), 6.75 (s, 1H), 3.17 (d, $J = 13.4$ Hz, 1H), 2.38 (d, $J = 13.4$ Hz, 1H), 1.82 (s, 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 $\text{C}_{31}\text{H}_{28}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ calcd 471.1931, found 471.1936.



27

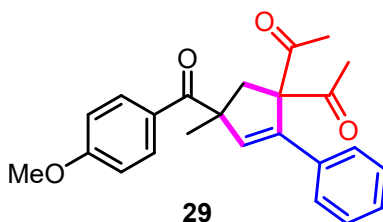
1,1'-(4-(4-(*tert*-butyl)benzoyl)-4-methyl-2-phenylcyclopent-2-ene-1,1-diyl)bis(ethan-1-one) (27):

Yellow oil (245.4 mg, 61%); Eluent: petroleum ether/ethyl acetate 15:1; ^1H 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 $\text{C}_{27}\text{H}_{30}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ calcd 425.2087, found 425.2084.



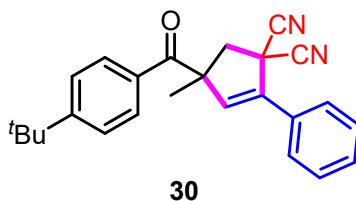
dimethyl 4-(4-(*tert*-butyl)benzoyl)-4-methyl-2-phenylcyclopent-2-ene-1,1-dicarboxylate (28):

Yellow oil (295.3 mg, 68%); Eluent: petroleum ether/ethyl acetate 10:1; ^1H 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 $\text{C}_{27}\text{H}_{30}\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$ calcd 457.1985, found 457.1987.



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

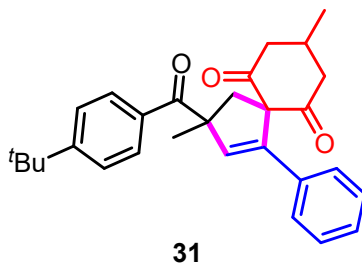
Yellow oil (263.3 mg, 70%); Eluent: petroleum ether/ethyl acetate 8:1; ^1H NMR (400 MHz, CDCl_3): δ 7.95 (dt, J = 8.9, 2.0 Hz, 2H), 7.34 - 7.22 (m, 6H), 6.94 (dt, J = 8.9, 1.9 Hz, 2H), 6.74 (s, 1H), 3.87 (s, 3H), 3.38 (d, J = 14.0 Hz, 1H), 2.61 (d, J = 14.0 Hz, 1H), 2.18 (d, J = 15.7 Hz, 6H), 1.63 (s, 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 $\text{C}_{24}\text{H}_{24}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$ calcd 399.1567, found 399.1558.



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; ^1H 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 $\text{C}_{25}\text{H}_{24}\text{N}_2\text{O}[\text{M}+\text{Na}]^+$ calcd 391.1781, found 391.1786.

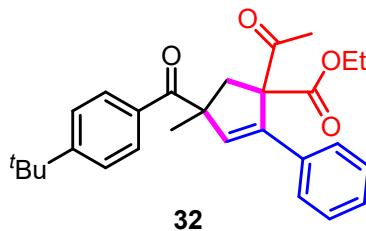


3-(4-(*tert*-butyl)benzoyl)-3,8-dimethyl-1-phenylspiro[4.5]dec-1-ene-6,10-dione

(31):

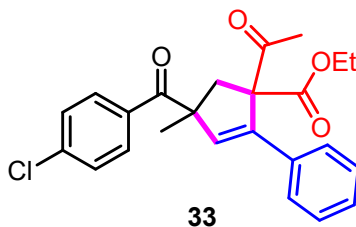
Yellow oil (359.7 mg, 84%, $dr = 2.3:1$); Eluent: petroleum ether/ethyl acetate 15:1; ^1H NMR (400 MHz, CDCl_3) δ 7.87 - 7.77 (m, 2H), 7.36 (d, $J = 8.5$ Hz, 2H), 7.18 - 7.09 (m, 3H), 7.02 - 6.93 (m, 2H), 6.62 (s, 0.3H), 6.56 (s, 0.7H), 3.25 (d, $J = 13.0$ Hz, 1H), 2.88 (dddd, $J = 35.5, 17.0, 4.5, 2.0$ 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

C₂₉H₃₂O₃Na [M+Na]⁺ calcd 451.2244, found 451.2248.



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

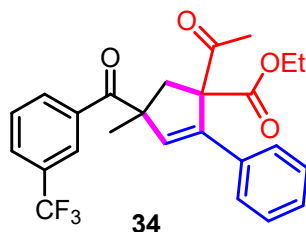
Yellow oil (315.3 mg, 65%, *dr* = 7.9:1); Eluent: petroleum ether/ethyl acetate 10:1; ¹H NMR (400 MHz, CDCl₃): δ 7.87 (dt, *J* = 8.5, 1.8 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.41 - 7.36 (m, 2H), 7.31 - 7.23 (m, 3H), 6.61 (s, , 1H), 4.23 - 4.06 (m, 2H), 3.29 (d, *J* = 13.6 Hz, 1H), 2.86 (d, *J* = 13.6 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); ¹³C NMR (101 MHz, CDCl₃): 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 C₂₈H₃₂O₄Na [M+Na]⁺ calcd 455.2193, found 455.2188.



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

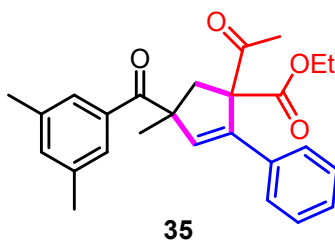
Yellow oil (278.9 mg, 68%, *dr* = 1.5:1); Eluent: petroleum ether/ethyl acetate 10:1; ¹H NMR (400 MHz, Chloroform-d) δ 7.44 - 7.39 (m, 1H), 7.36 - 7.31 (m, 2H), 7.29 - 7.23 (m, 6H), 6.18 (s, 0.6H), 6.15 (s, 0.4H), 4.23 - 3.99 (m, 2H), 3.46 (d, *J* = 11.6 Hz, 0.4H), 3.27 (d, *J* = 13.8 Hz, 0.6H), 2.73 (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); ¹³C NMR (101 MHz, CDCl₃): 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.



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

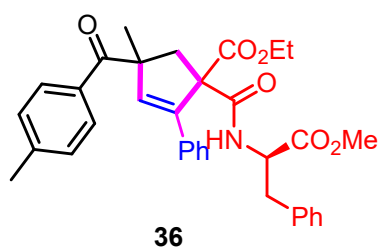
Yellow oil (315.3 mg, 71%, *dr* = 6.9:1); Eluent: petroleum ether/ethyl acetate 10:1; 1H NMR (400 MHz, $CDCl_3$): δ 8.13 (s, 1H), 8.07 (d, J = 7.9 Hz, 1H), 7.77 (d, J = 7.7 Hz, 1H), 7.58 (t, J = 7.8 Hz, 1H), 7.38 - 7.33 (m, 2H), 7.29 - 7.26 (m, 3H), 6.42 (d, J = 14.7 Hz, 1H), 4.25 - 4.05 (m, 2H), 3.30 (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 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.



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; 1H 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 $\text{C}_{27}\text{H}_{30}\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$ calcd 427.1880, found 427.1889.



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; ^1H 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 $\text{C}_{34}\text{H}_{35}\text{NO}_6\text{Na}$ $[\text{M}+\text{Na}]^+$ 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.

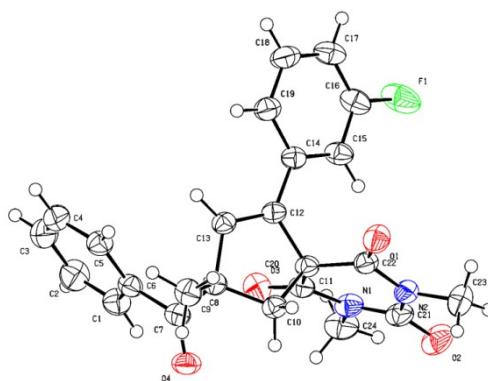


Figure S4 Structure of **13** by X-Ray crystallographic (CCDC = 2207175)

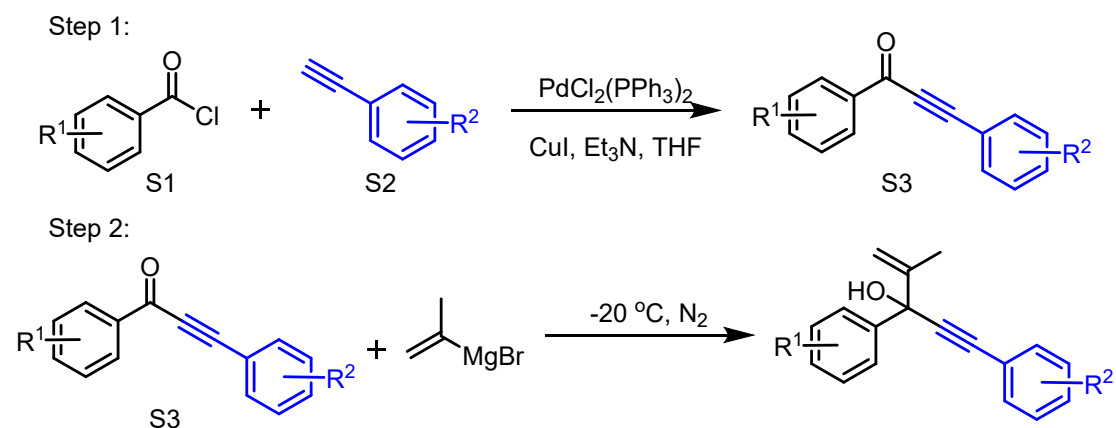
Table S2 Crystal data and structure refinement for **13**

Empirical formula	C ₂₄ H ₂₁ FN ₂ O 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
ρ calc/g/cm ³	1.391
μ /mm ⁻¹	0.537
F(000)	880.0
Crystal size/mm ³	0.12 × 0.1 × 0.1

Radiation	GaK α ($\lambda = 1.34139$)
2 Θ range for data collection/ $^\circ$	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 [$R_{\text{int}} = 0.0558$, $R_{\text{sigma}} = 0.0470$]
Data/restraints/parameters	4434/0/283
Largest diff. peak/hole / e $\text{\AA}^{-3}$	0.20/-0.34

7. Synthesis of Substrates

7.1) the synthesis of 1,4-enynes



Step 1:^{3,4}

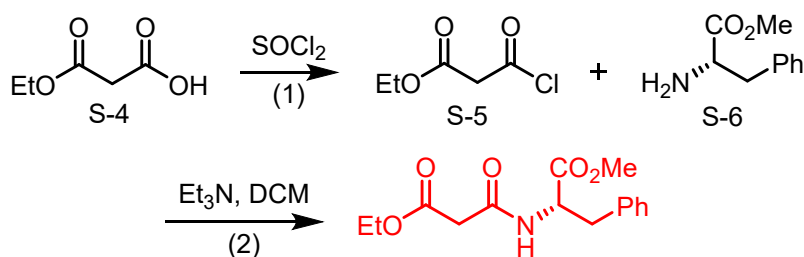
A mixture of $\text{Pd}(\text{PPh}_3)\text{Cl}_2$ (2 mol%, 0.2 mmol), CuI (4 mol%, 0.4 mmol), Et_3N (1.5 equiv, 15 mmol) and acyl chloride **S1** (1.2 equiv, 12 mmol) were dissolved in 20 mL anhydrous tetrahydrofuran (THF) and stirred for 10 minutes at room temperature under argon conditions. Then, terminal 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

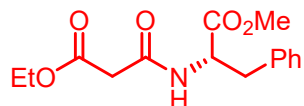
Compound **S3** was dissolved in 10 mL anhydrous tetrahydrofuran. Then, isopropenylmagnesium bromide (10 mL, 1 mol/L in THF) was added to the solution above dropwise at $-20\text{ }^\circ\text{C}$ and stirred for 10 mins under argon. The reaction was then moved to room temperature for another 6 hours. 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 amide⁶



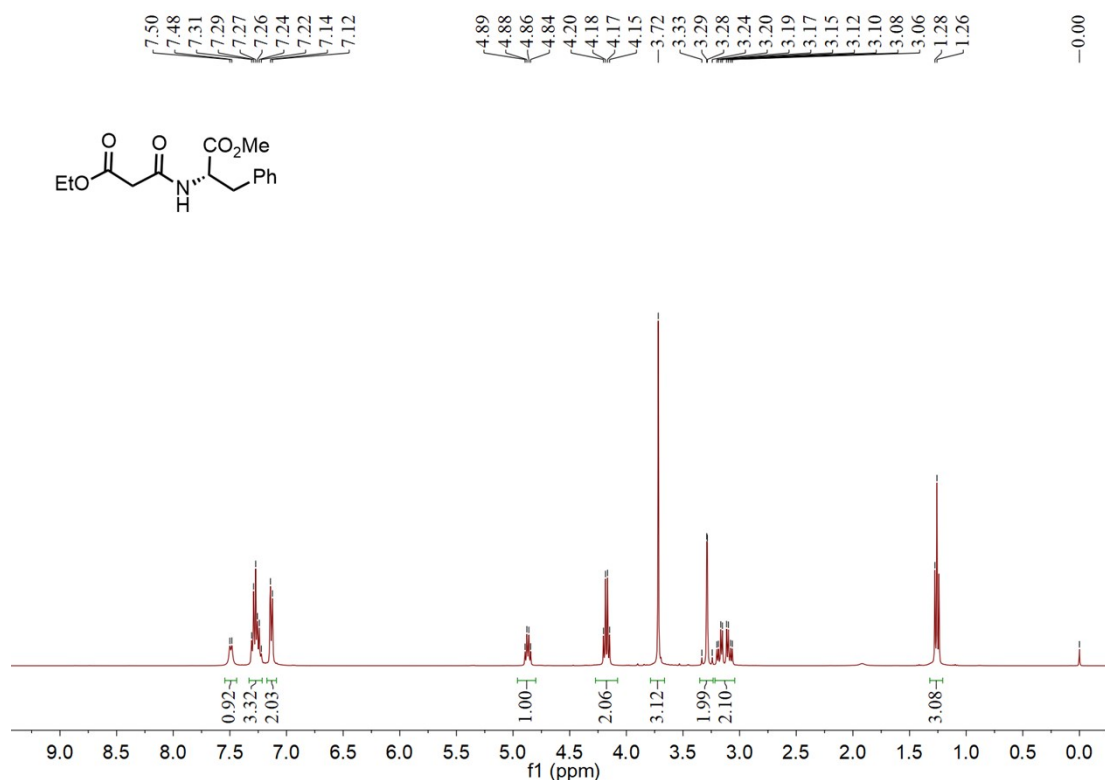
Commercially available 3-ethoxy-3-oxopropanoic acid **S-4** (1.32 g, 10 mmol) was dissolved in 10 mL CH_2Cl_2 in an oven dried 50 mL round bottom flask equipped with stir bar and SOCl_2 (1.30 g, 11 mmol) were added at RT. The reaction mixture was stirred for the 1 h to give acyl chloride **S-5**. D-Phenylalanine 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 $0\text{ }^\circ\text{C}$. The mixture was slowly warmed to room temperature and continued to stir for 4 h. The reaction

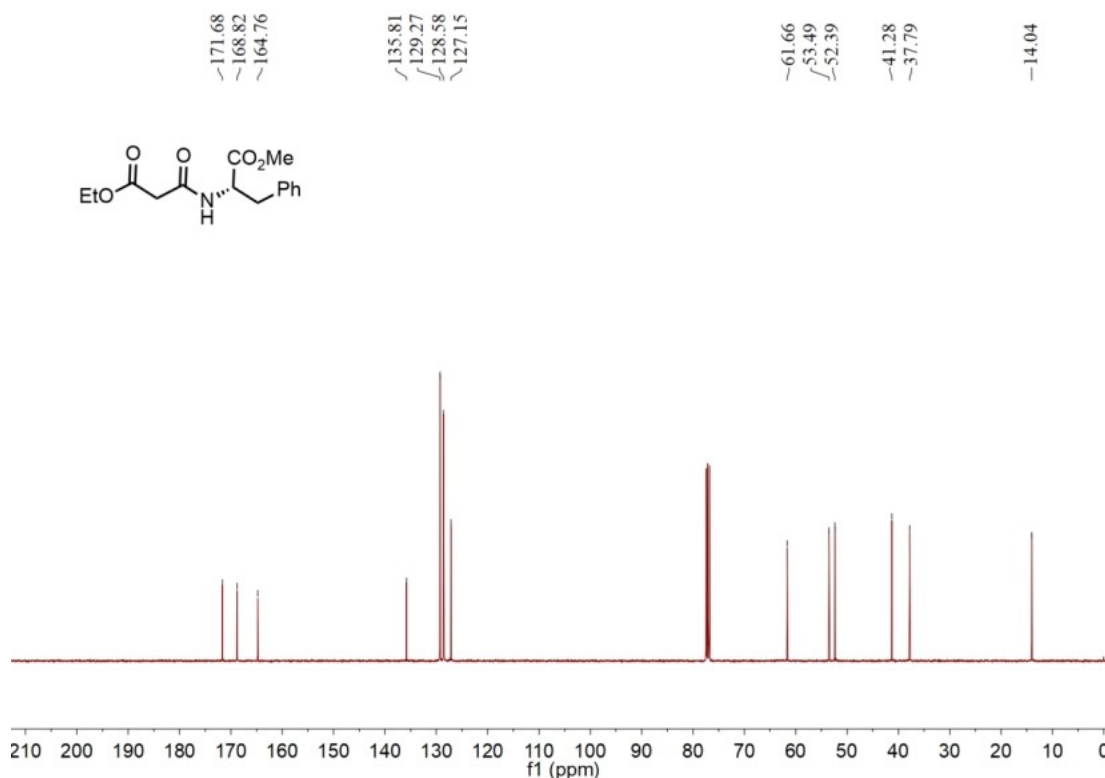
mixture was then poured into 1 N HCl/CH₂Cl₂ and extracted with CH₂Cl₂, dried over Na₂SO₄ and concentrated. The crude product was purified by chromatography on silica gel with petroleum ether/ethyl acetate (1:1) as the eluent to obtain chiral amide product (1.96 g, 67%).



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; ¹H NMR (400 MHz, CDCl₃): 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); ¹³C NMR (101 MHz, CDCl₃): 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 C₁₅H₁₉NO₅Na [M+Na]⁺ calcd 316.1155, found 316.1171.





8. References

- [1] Qian, C. Y.; Nishino, H.; Kurosawa, K.; Korp, J. D., Manganese(II) acetate-Mediated Double 2-Hydroperoxyalkylations of Barbituric Acid and Its Derivatives. *The Journal of Organic Chemistry* 1993, 58, 4448-4451.
- [2] Cao, J.; Lv, D.; Yu, F.; Chiou, M.-F.; Li, Y.; Bao, H., Regioselective Three-Component Synthesis of Vicinal Diamines via 1,2-Diamination of Styrenes. *Organic Letters* 2021, 23, 3184-3189.
- [3] Le Foulher, V.; Chen, Y.; Gandon, V.; Bizet, V.; Salomé, C.; Fessard, T.; Liu, F.; Houk, K. N.; Blanchard, N., Activating Pyrimidines by Pre-distortion for the General Synthesis of 7-Aza-indazoles from 2-Hydrazonylpyrimidines via Intramolecular Diels-Alder Reactions. *Journal of the American Chemical Society* 2019, 141, 15901-15909.
- [4] Qi, H.; Chi, D.; Chen, S., Pd-Catalyzed C-H Functionalization of Indole-Containing Alkene-Tethered Aryl Halides with Alkynes To Construct Indole Alkaloid

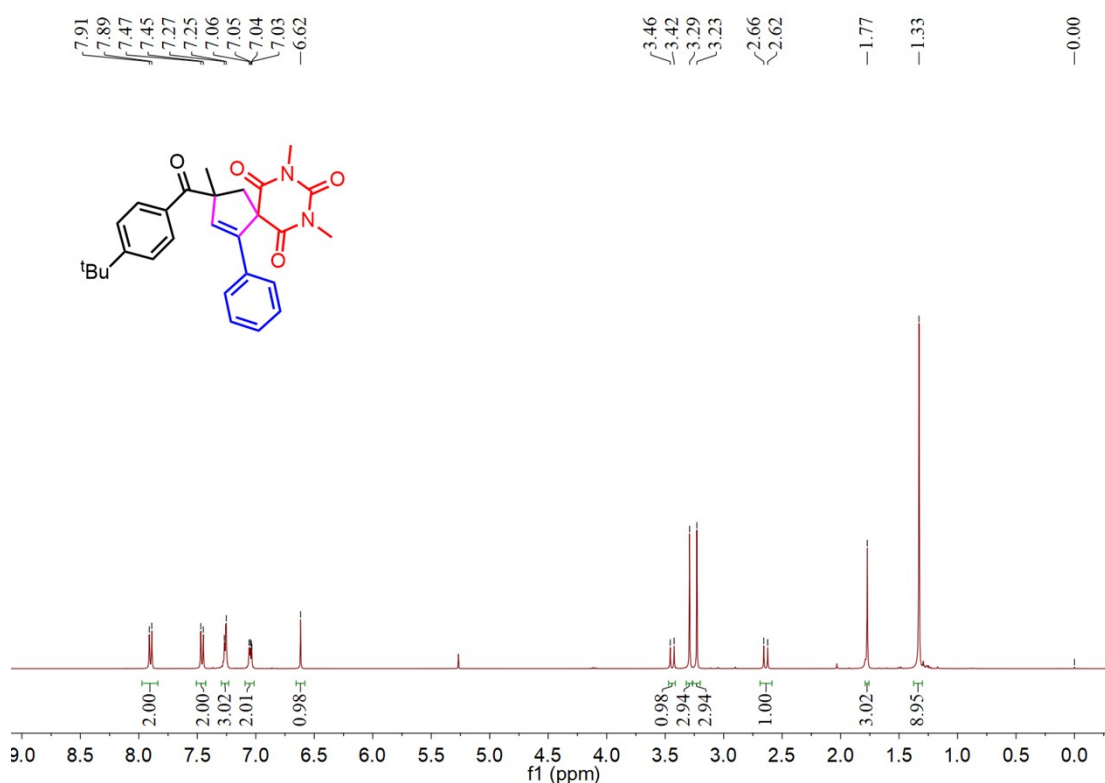
Scaffolds. Organic Letters 2022, 24, 2910-2914.

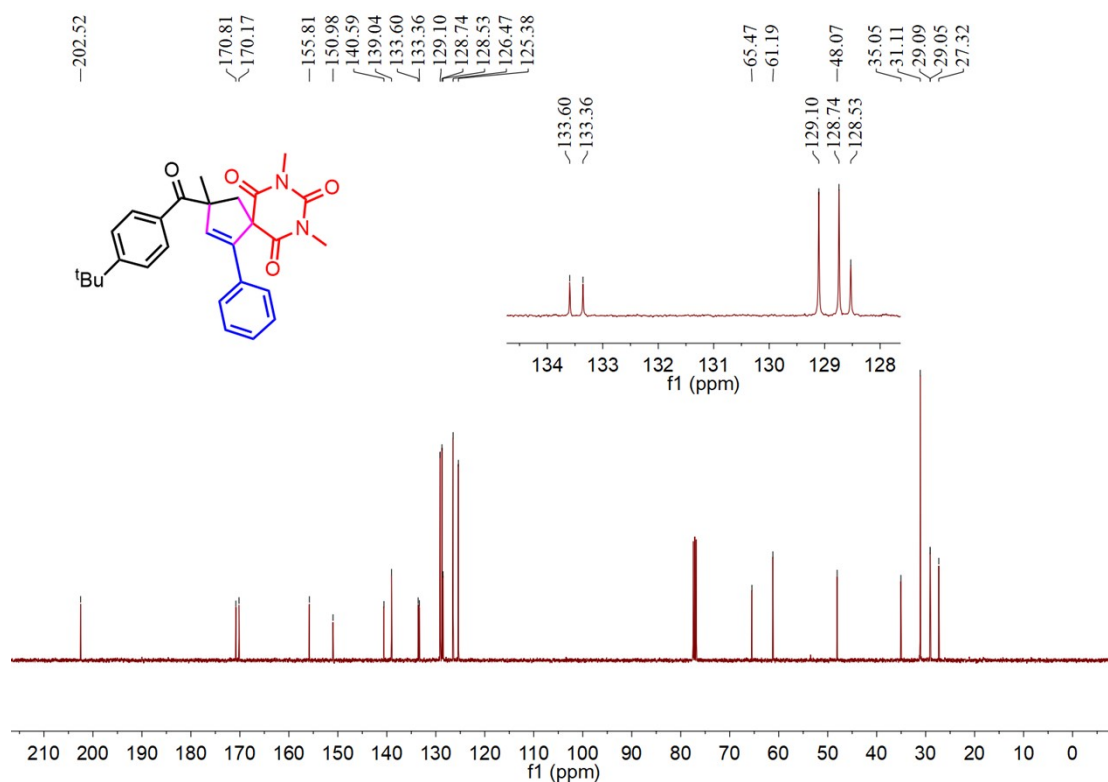
[5] Zhao, Q.; Hao, W.-J.; Shi, H.-N.; Xu, T.; Tu, S.-J.; Jiang, B., Photocatalytic Annulation-Alkynyl Migration Strategy for Multiple Functionalization of Dual Unactivated Alkenes. Organic Letters 2019, 21, 9784-9789.

[6] Poncet, J.; Jouin, P.; Castro, B.; Nicolas, L.; Boutar, M.; Gaudemer, A., Tetramic Acid Chemistry .1. Reinvestigation of Racemization During the Stnthesis of Tetramic Acids via Dieckmann Cyclization. Journal of the Chemical Society-Perkin Transactions 1 1990, 611-616.

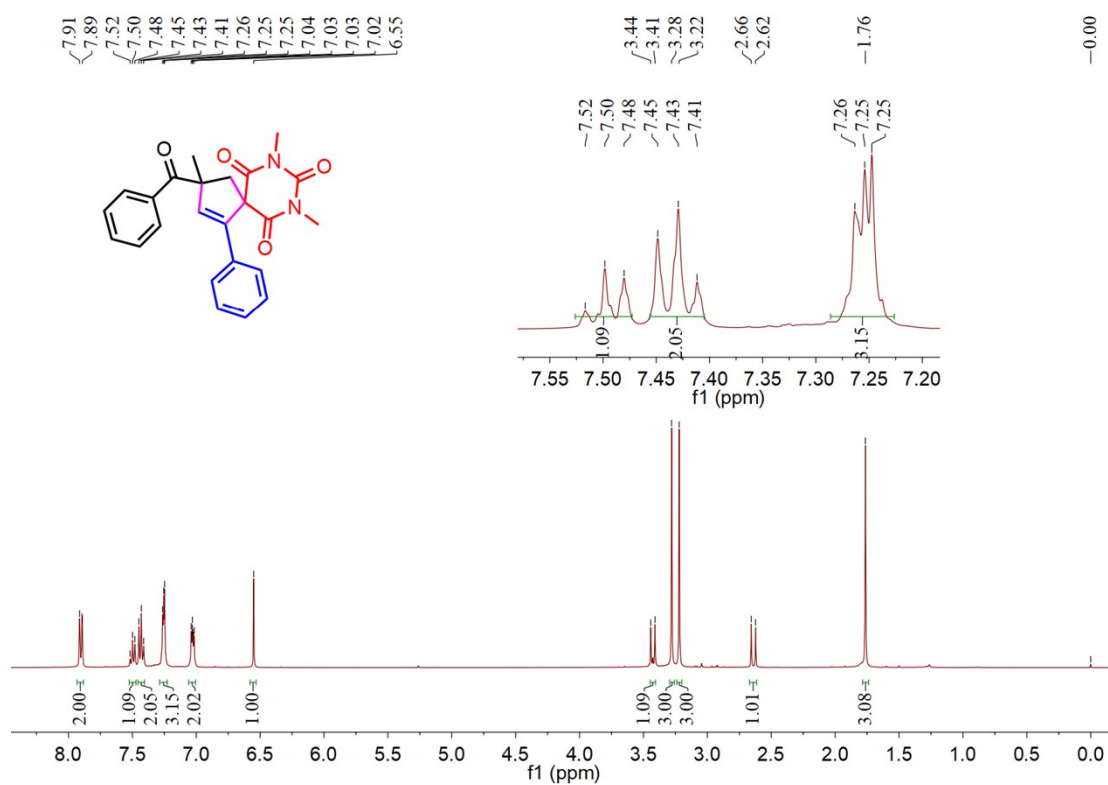
9. NMR Spectra for Spirocyclic Products and Intermediates of Mechanistic Studies

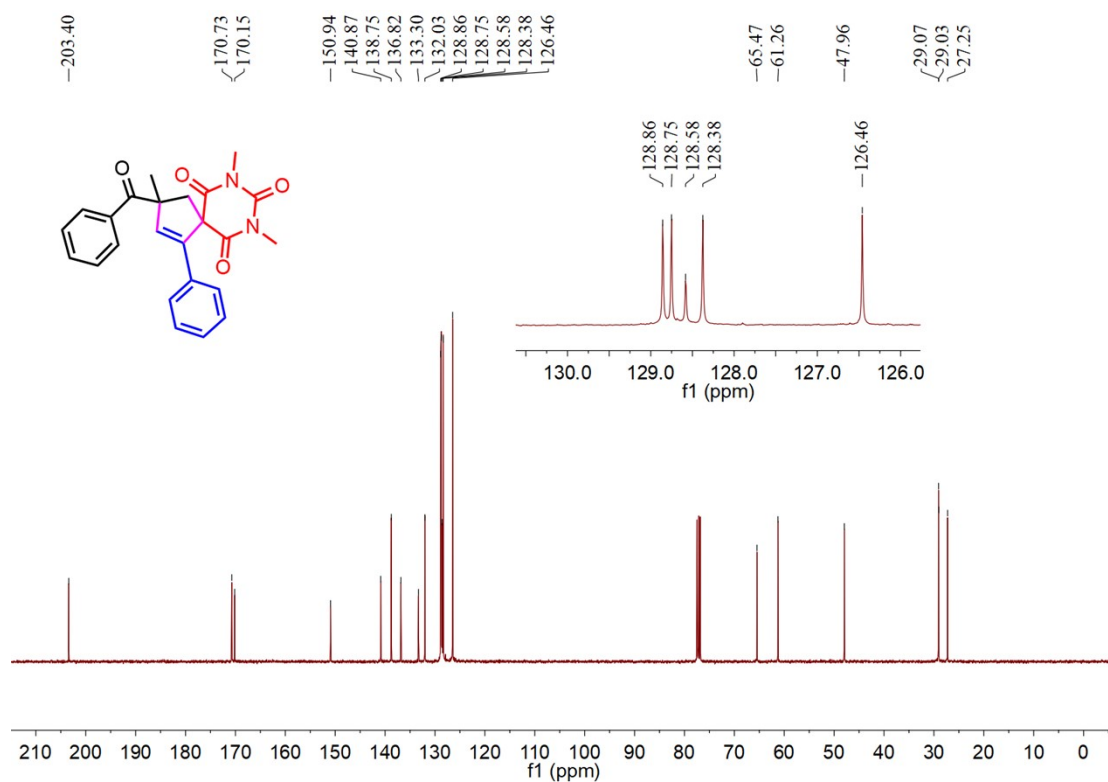
3-(4-(*tert*-butyl)benzoyl)-3,7,9-trimethyl-1-phenyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (3):



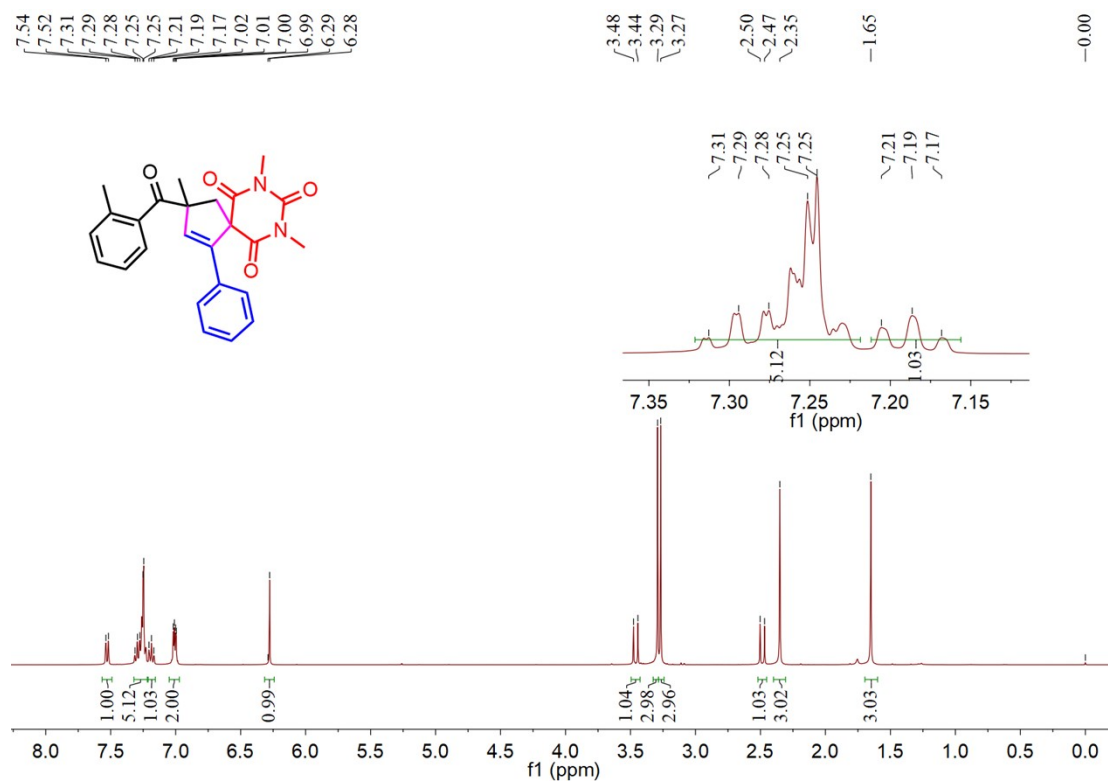


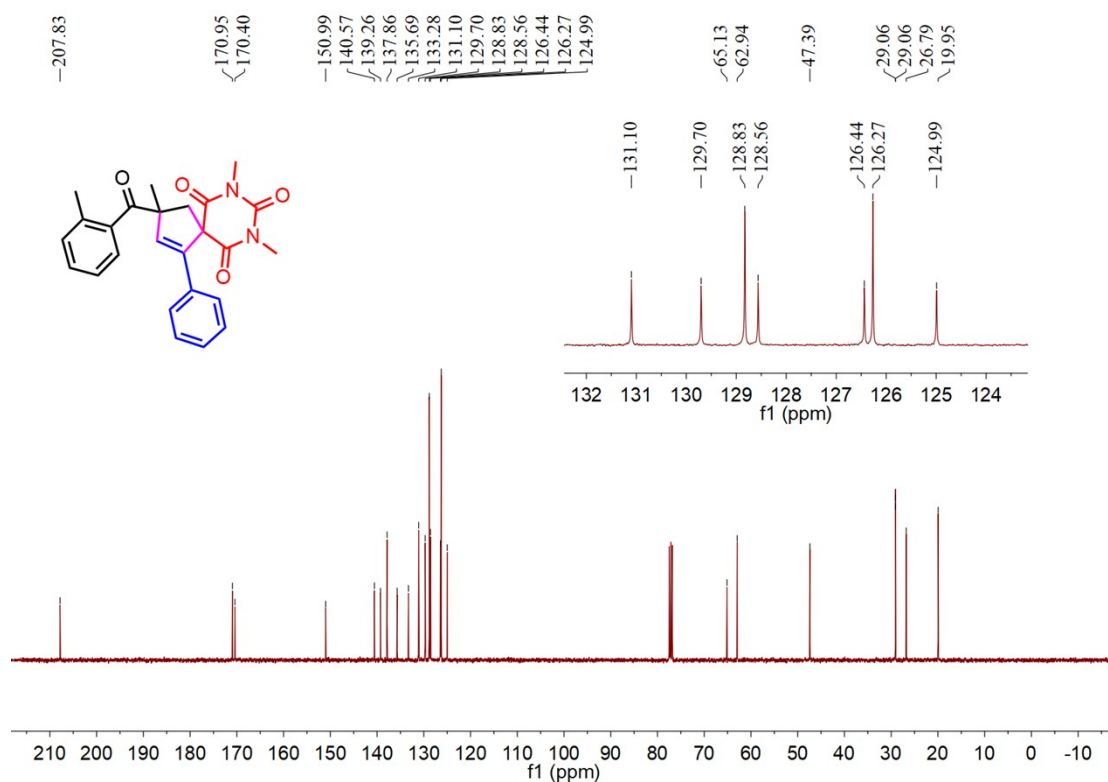
3-benzoyl-3,7,9-trimethyl-1-phenyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (4):



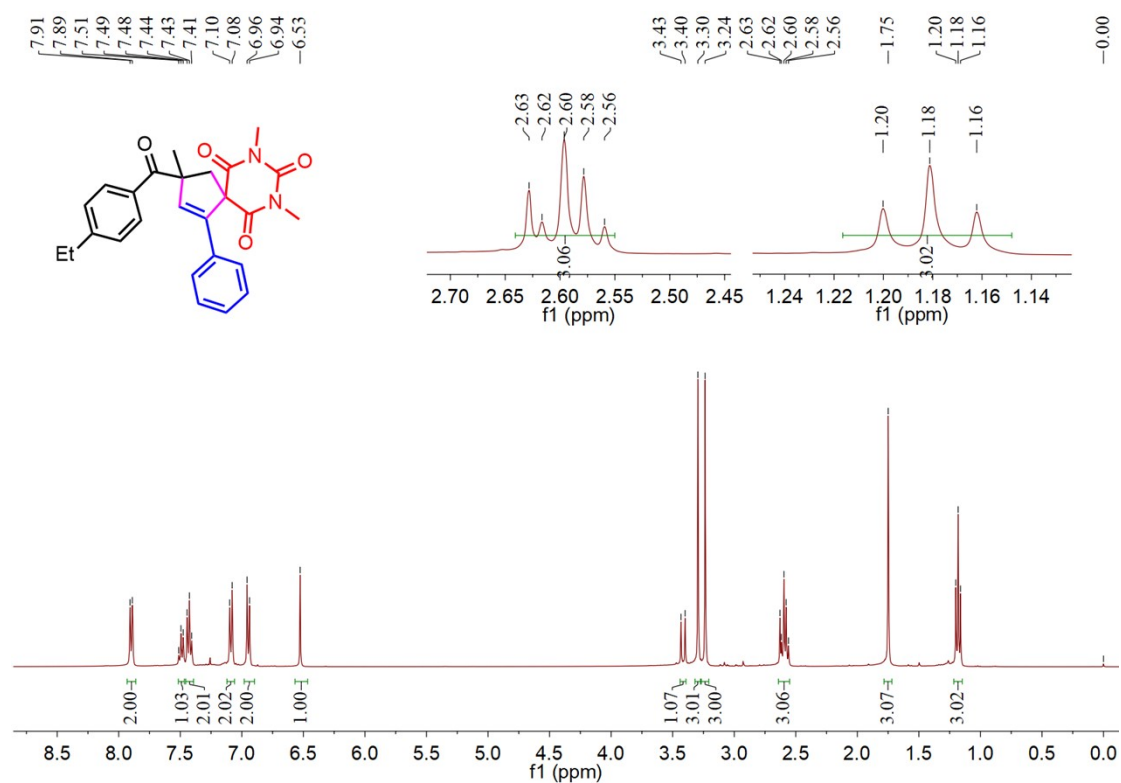


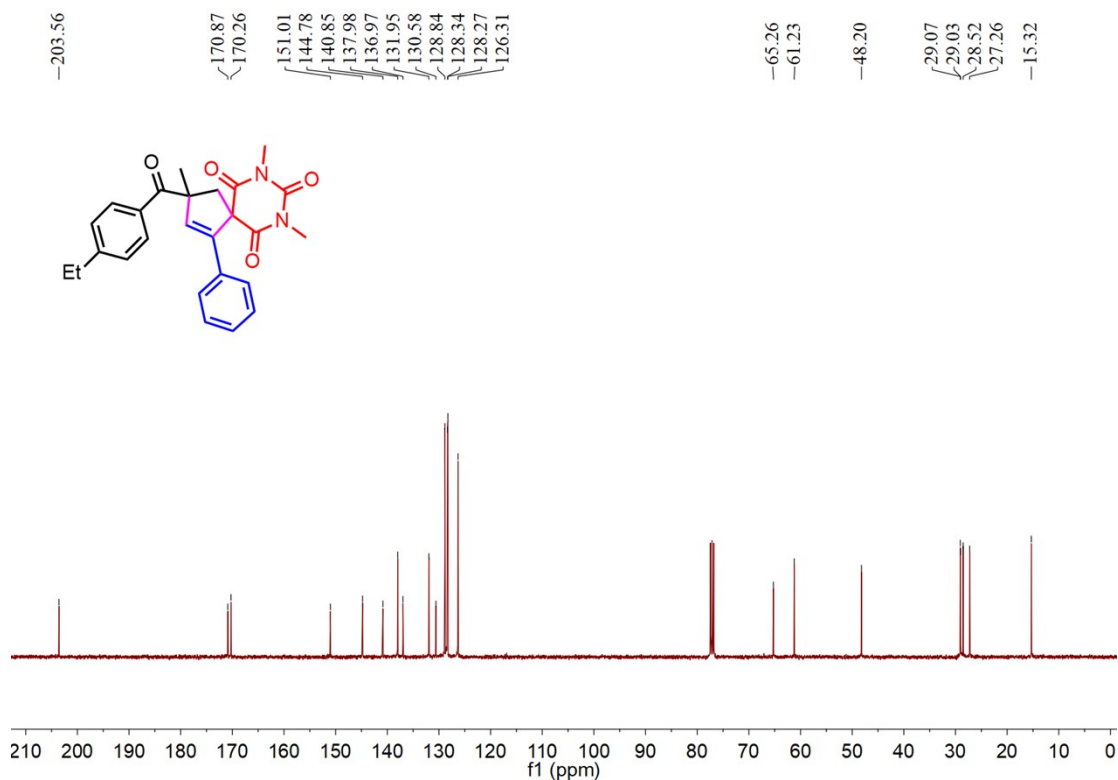
3,7,9-trimethyl-3-(2-methylbenzoyl)-1-phenyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (5):



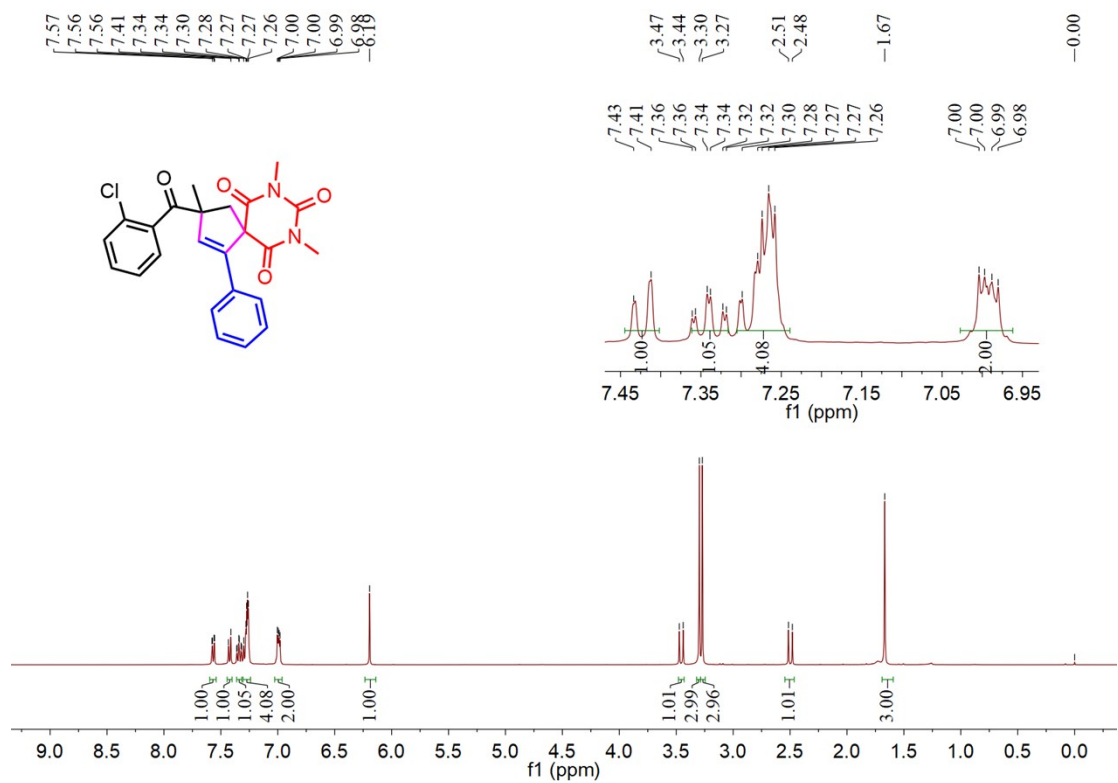


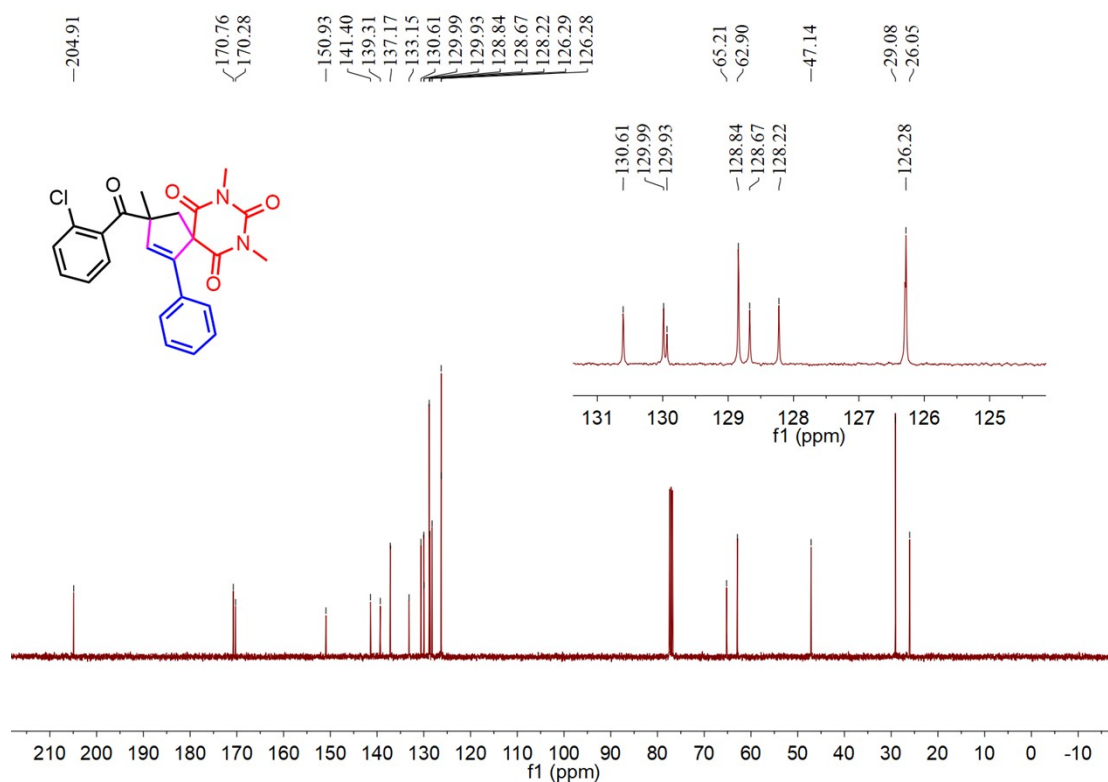
3-(4-ethylbenzoyl)-3,7,9-trimethyl-1-phenyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (6):



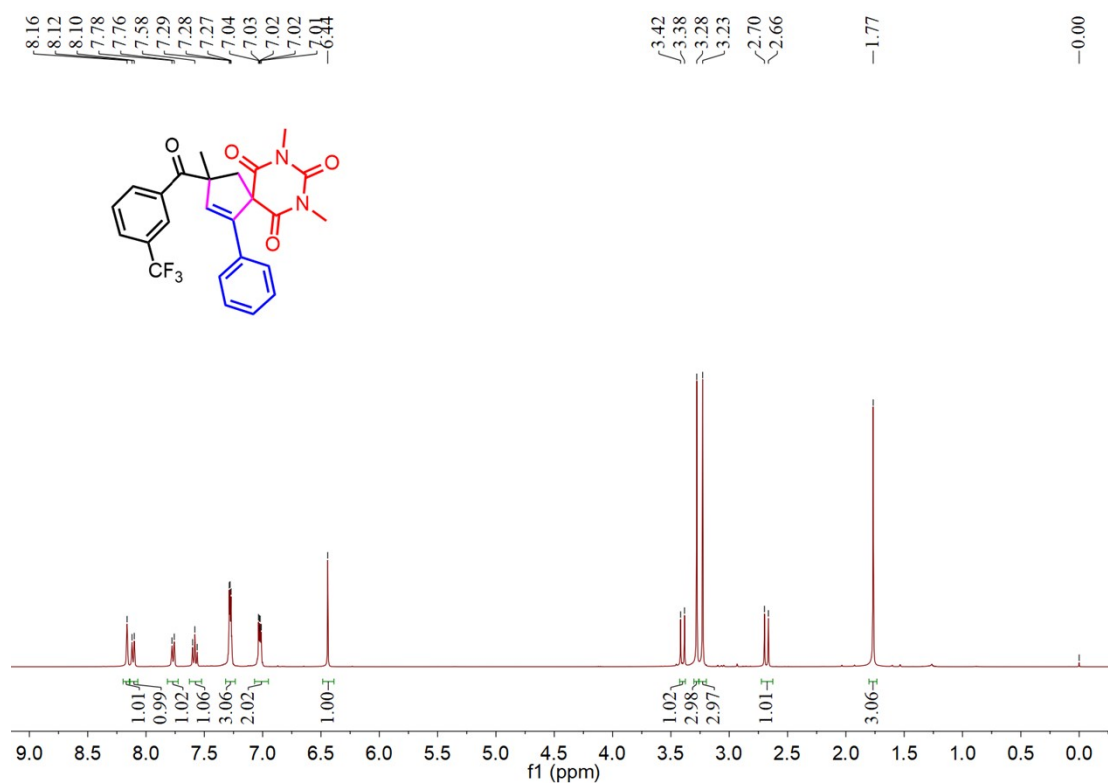


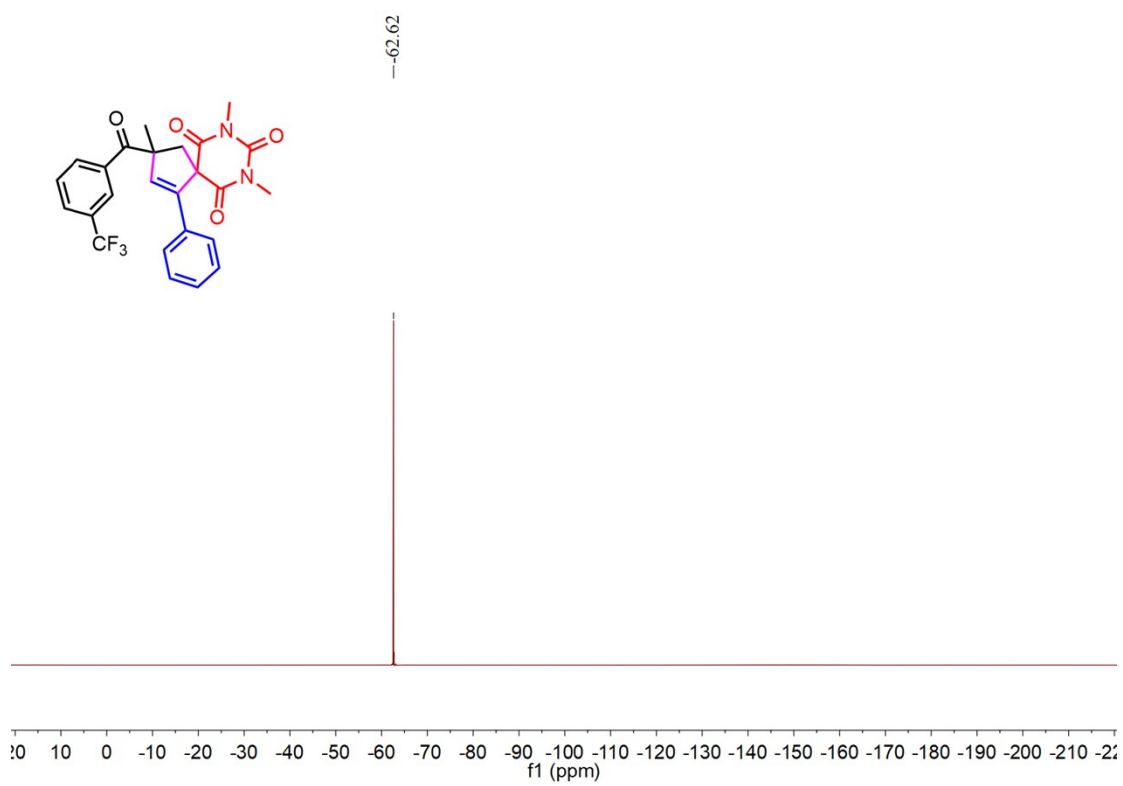
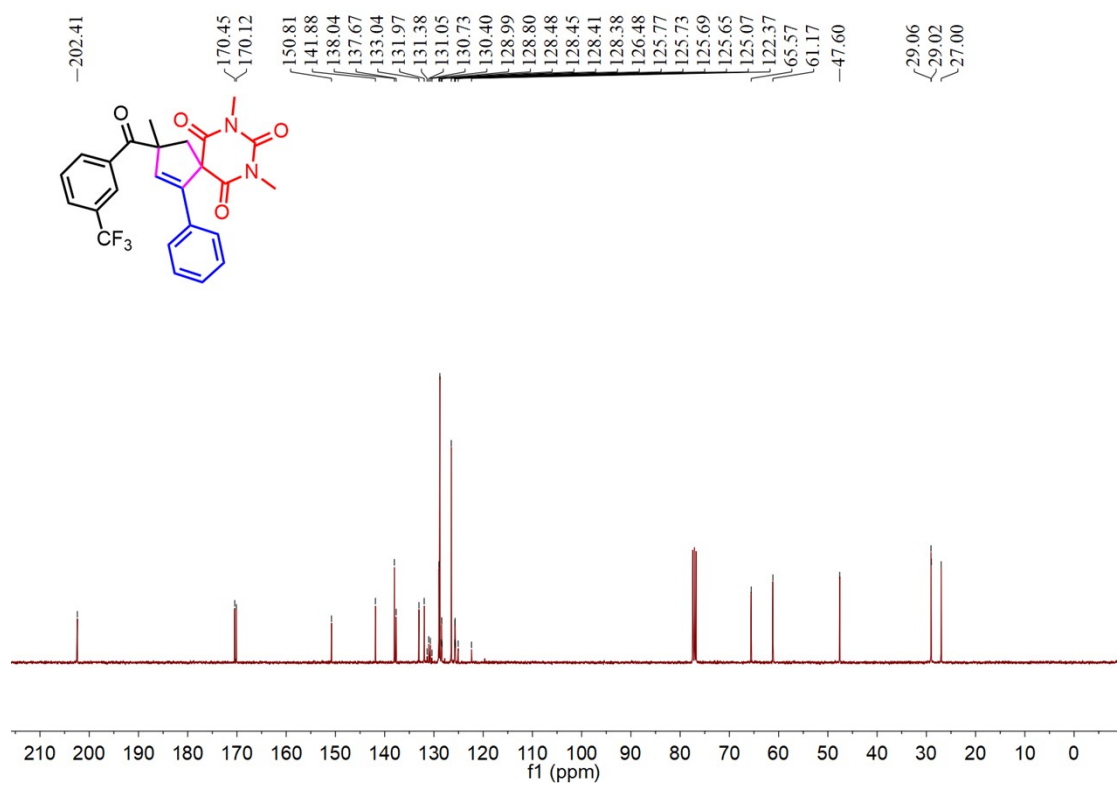
3-(2-chlorobenzoyl)-3,7,9-trimethyl-1-phenyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (7):



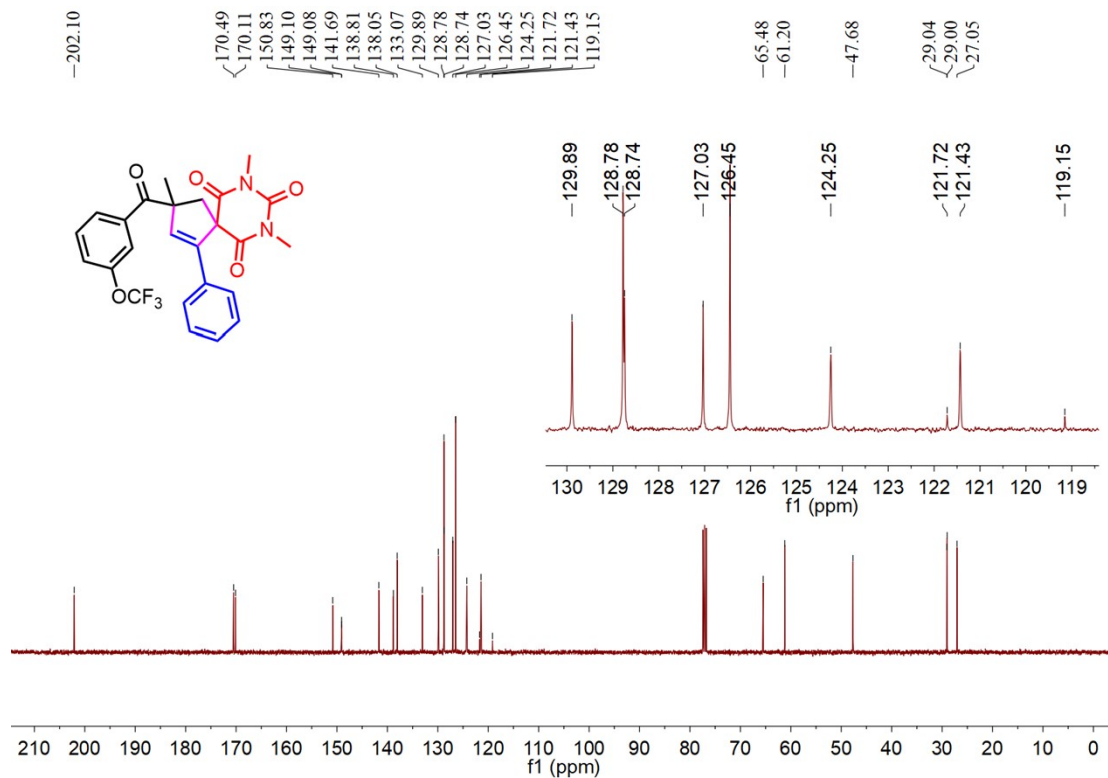
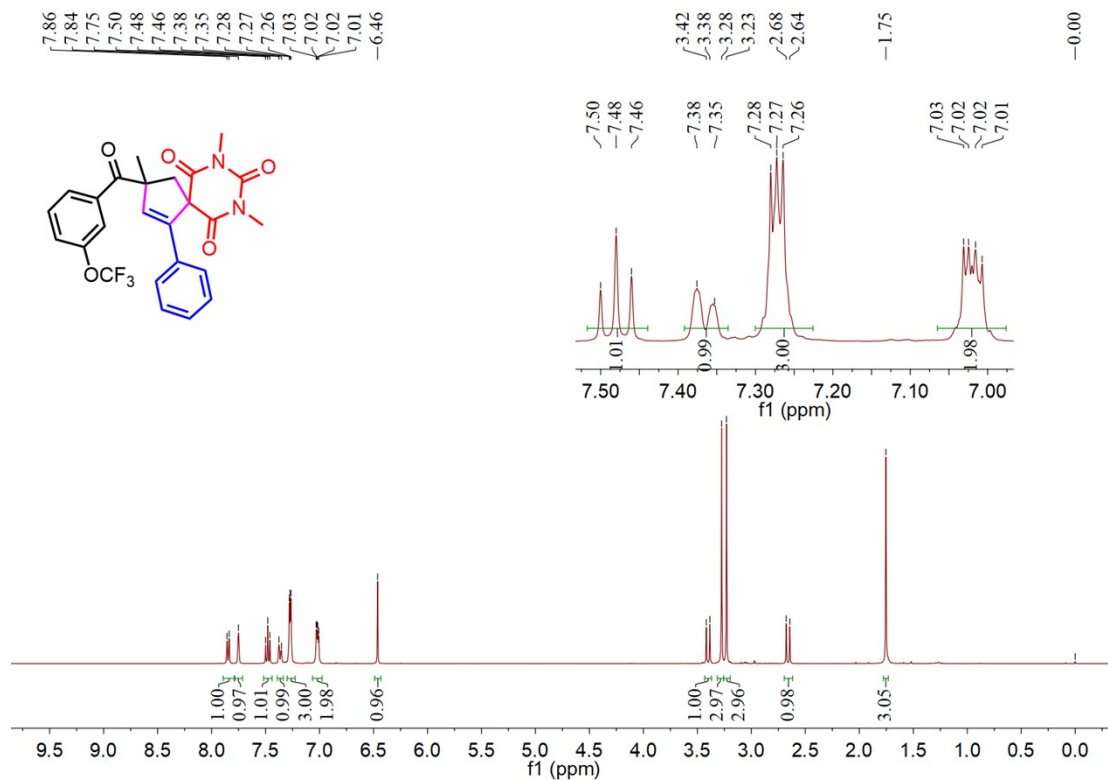


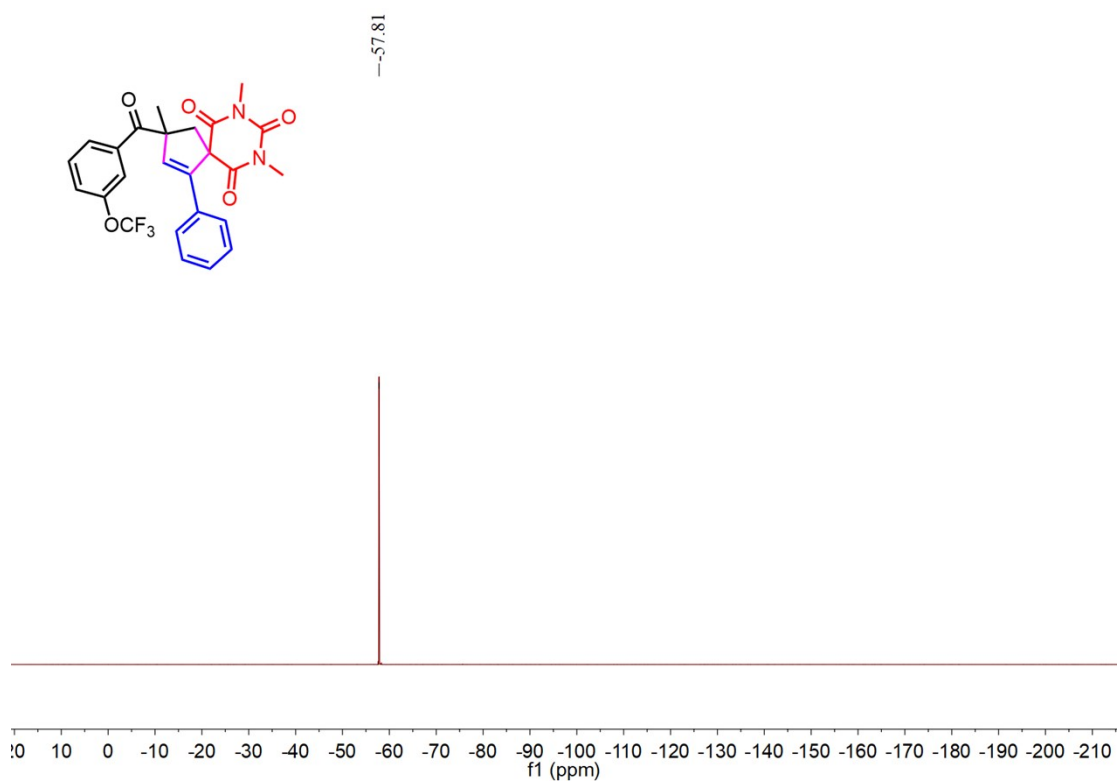
3,7,9-trimethyl-1-phenyl-3-(3-(trifluoromethyl)benzoyl)-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (8):



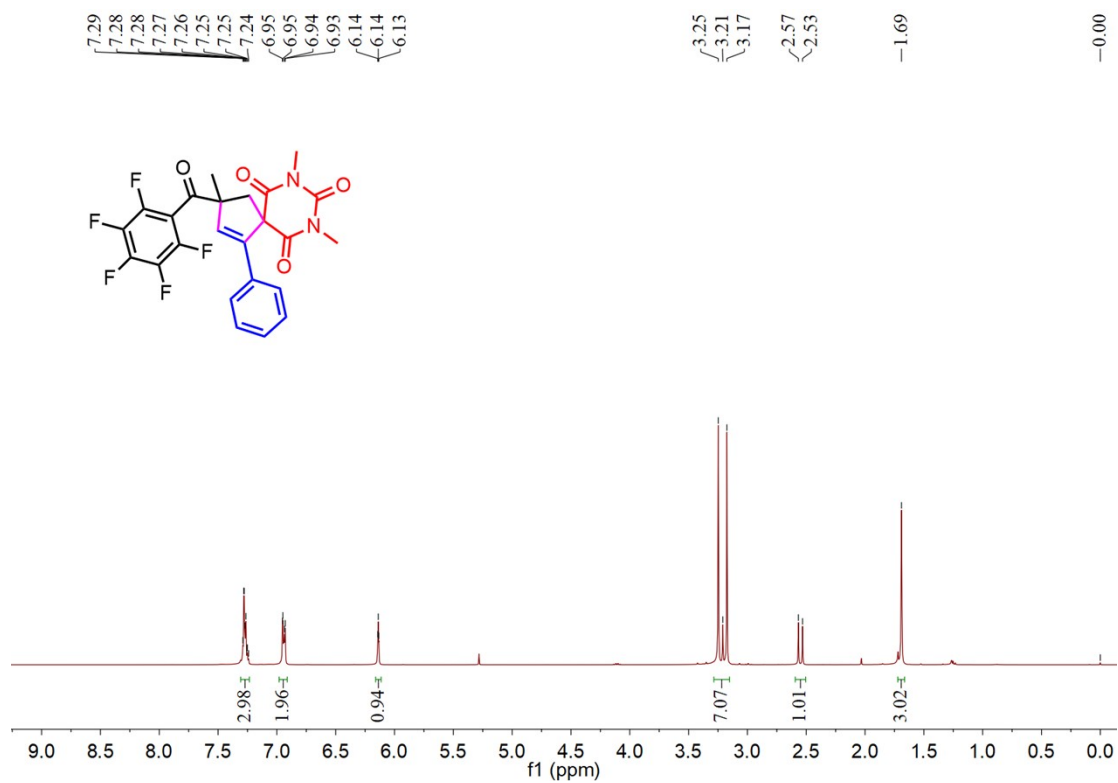


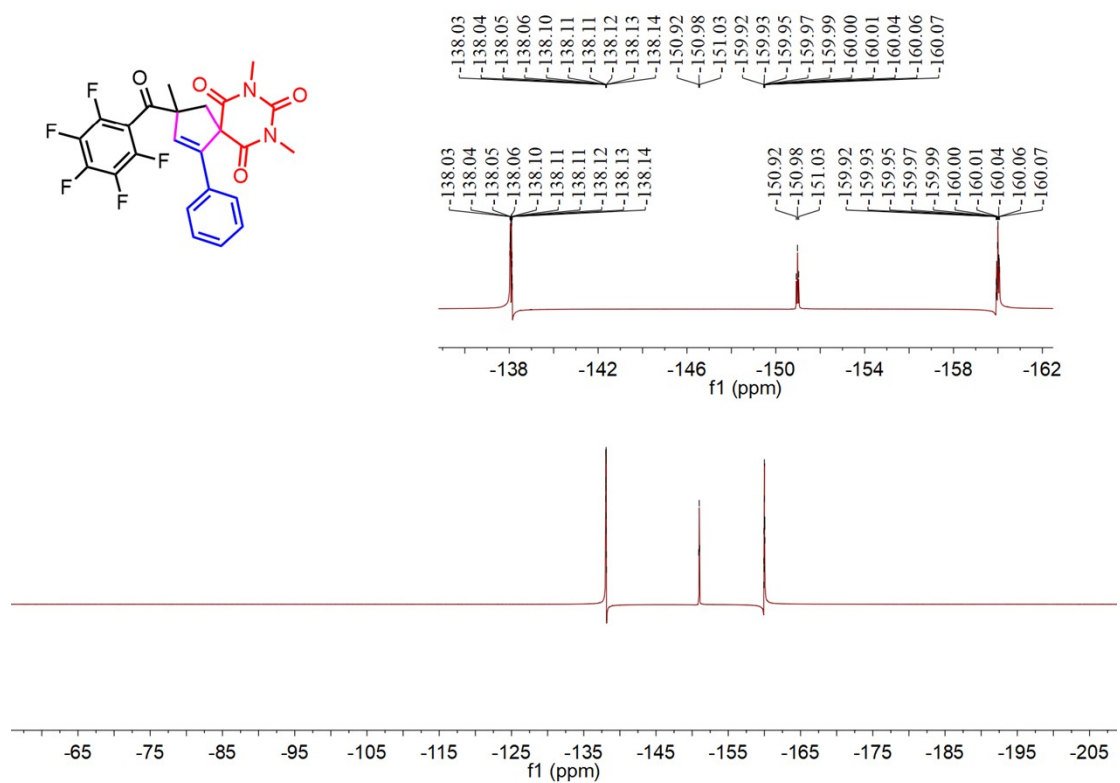
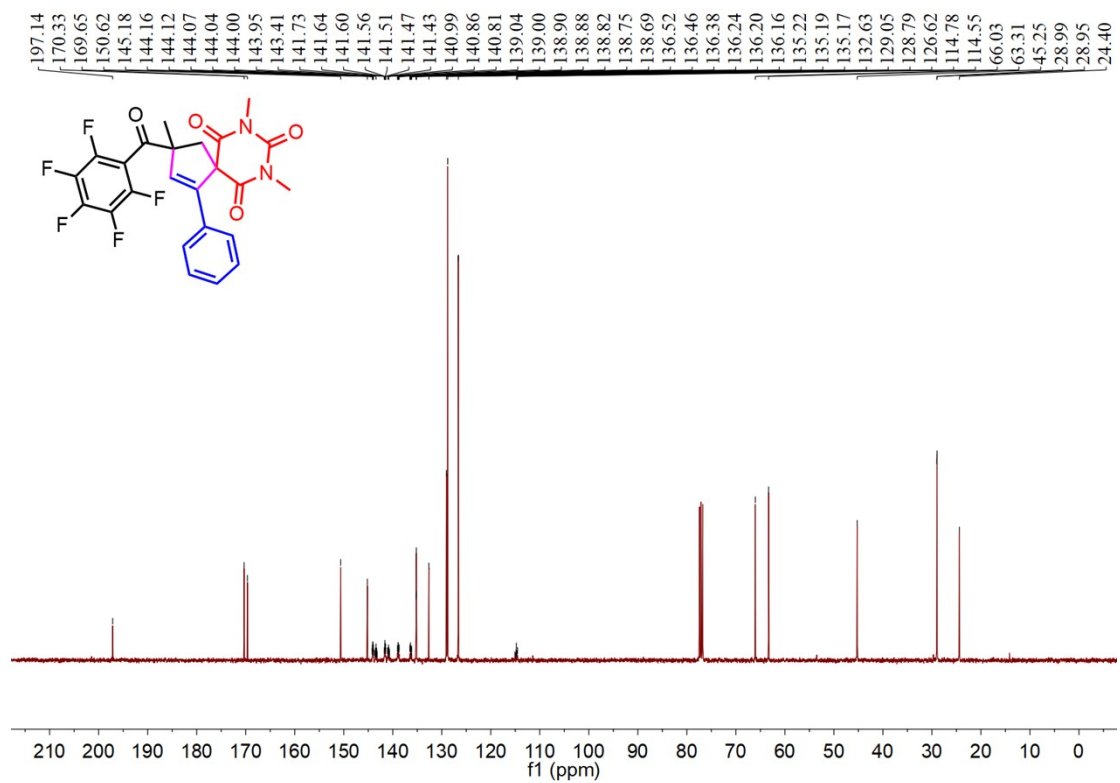
3,7,9-trimethyl-1-phenyl-3-(3-(trifluoromethoxy)benzoyl)-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (9):



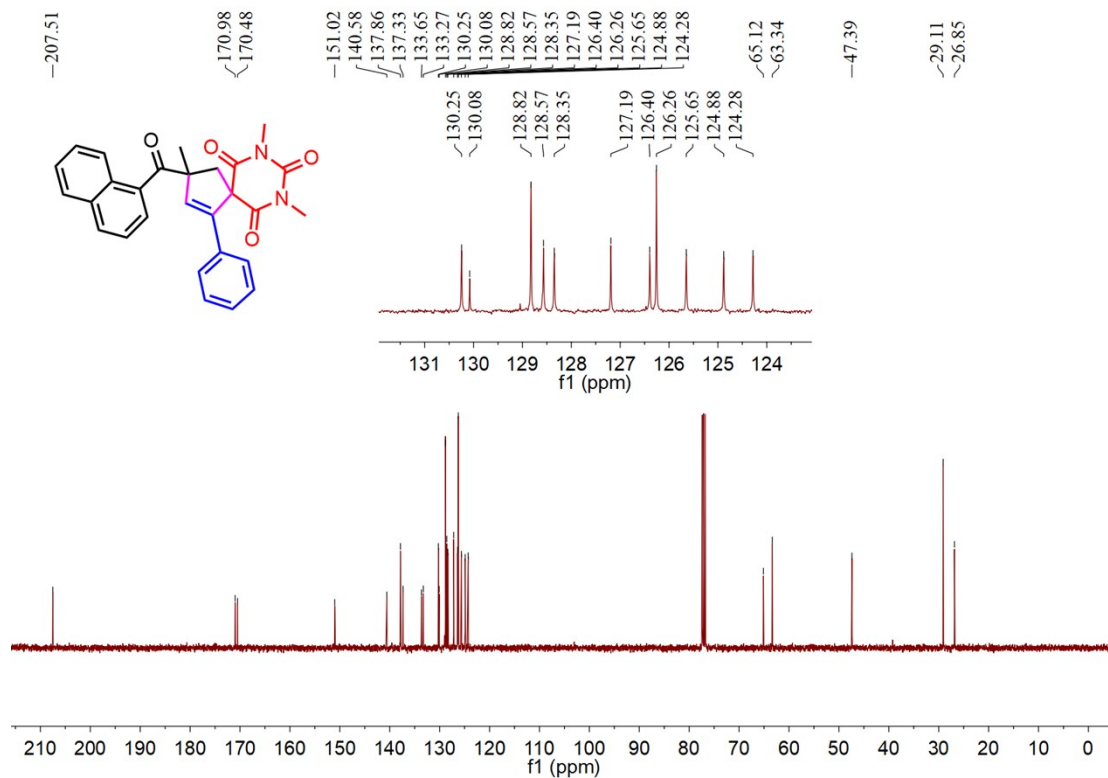
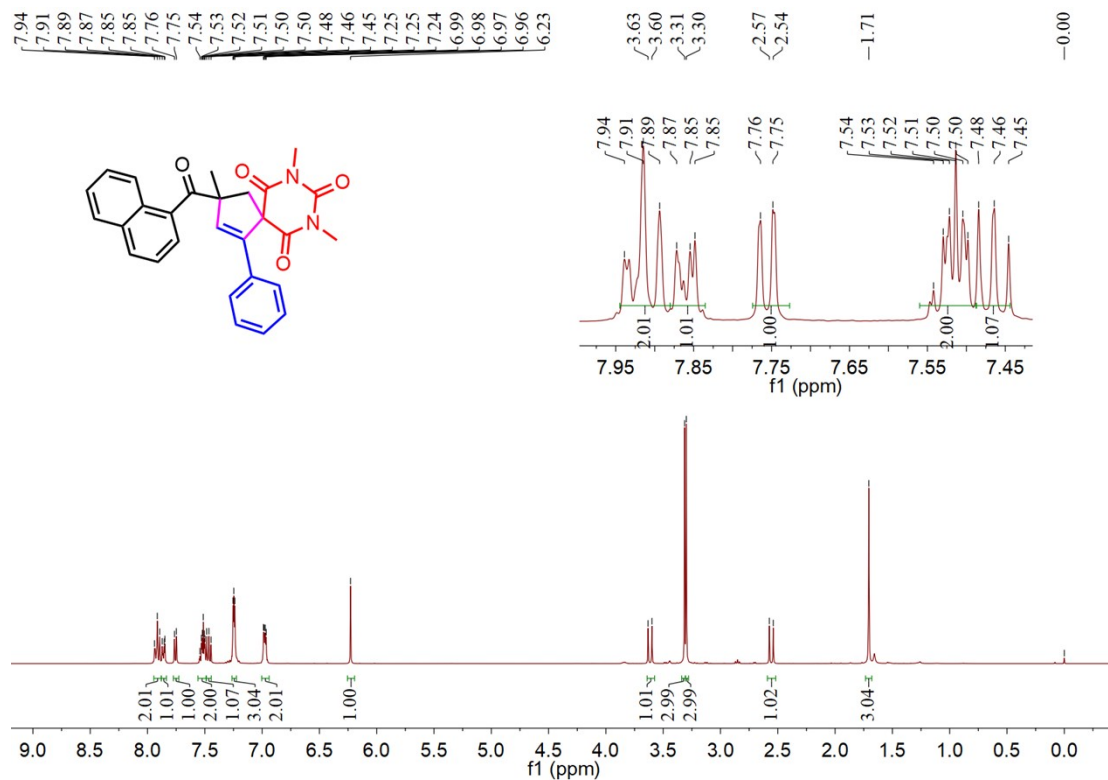


3,7,9-trimethyl-3-(perfluorobenzoyl)-1-phenyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (10):

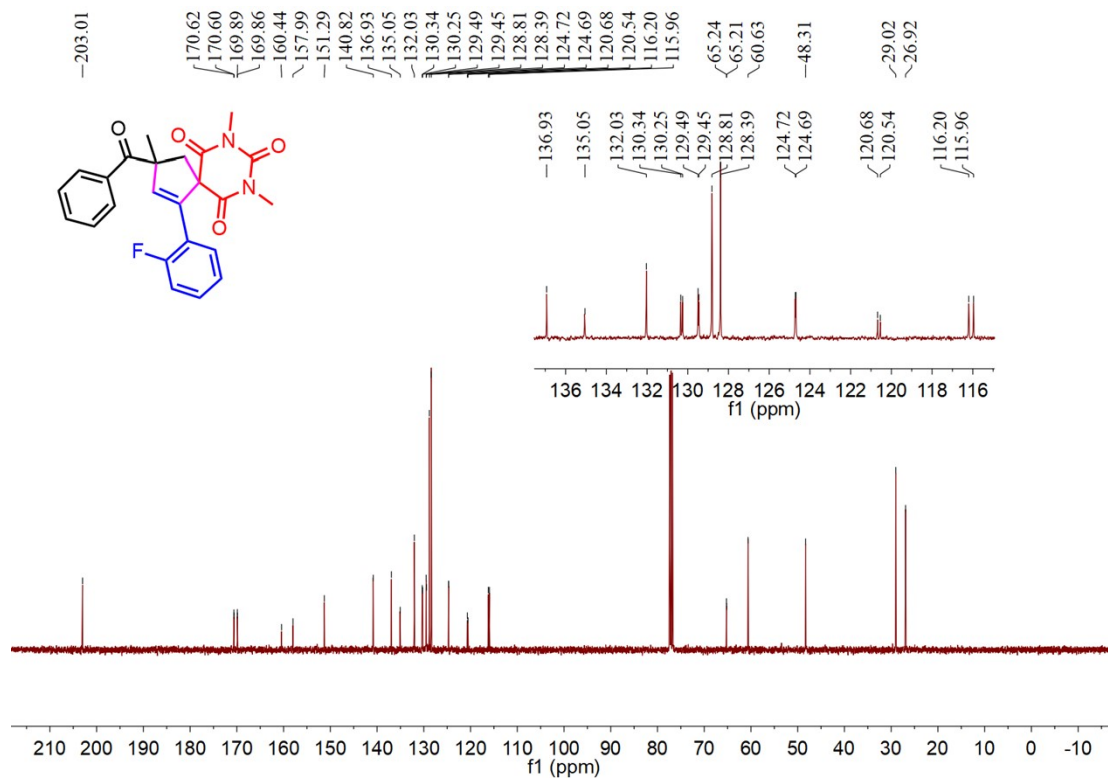
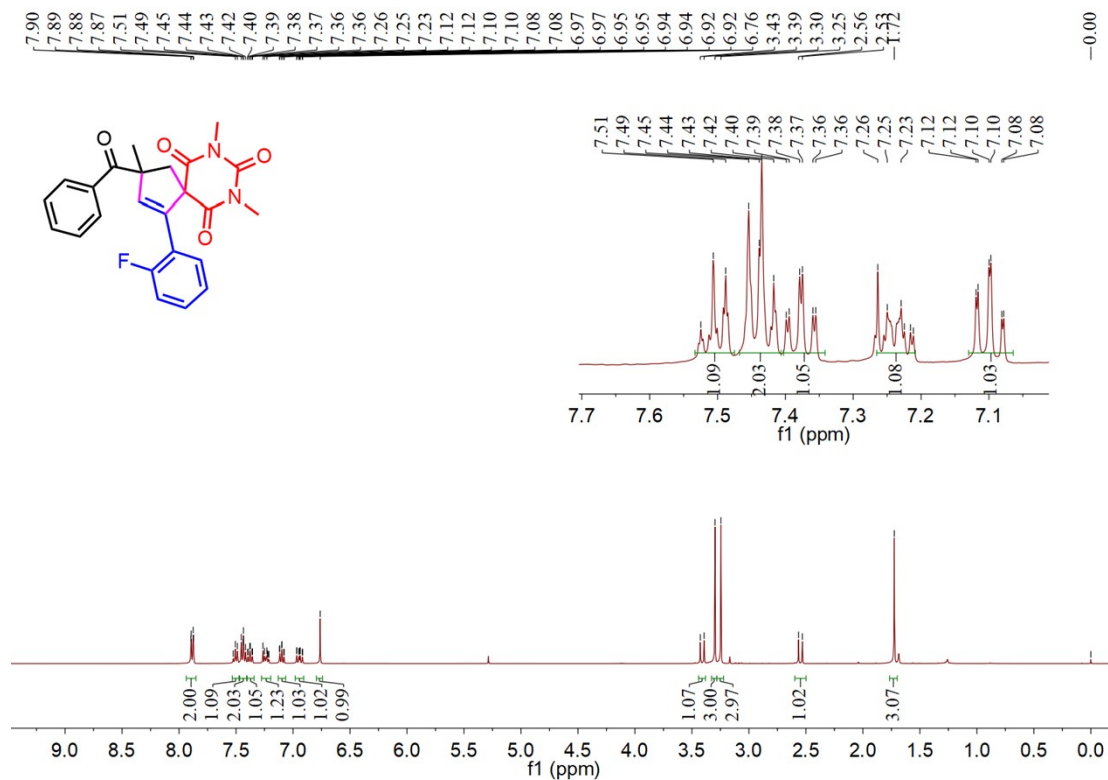


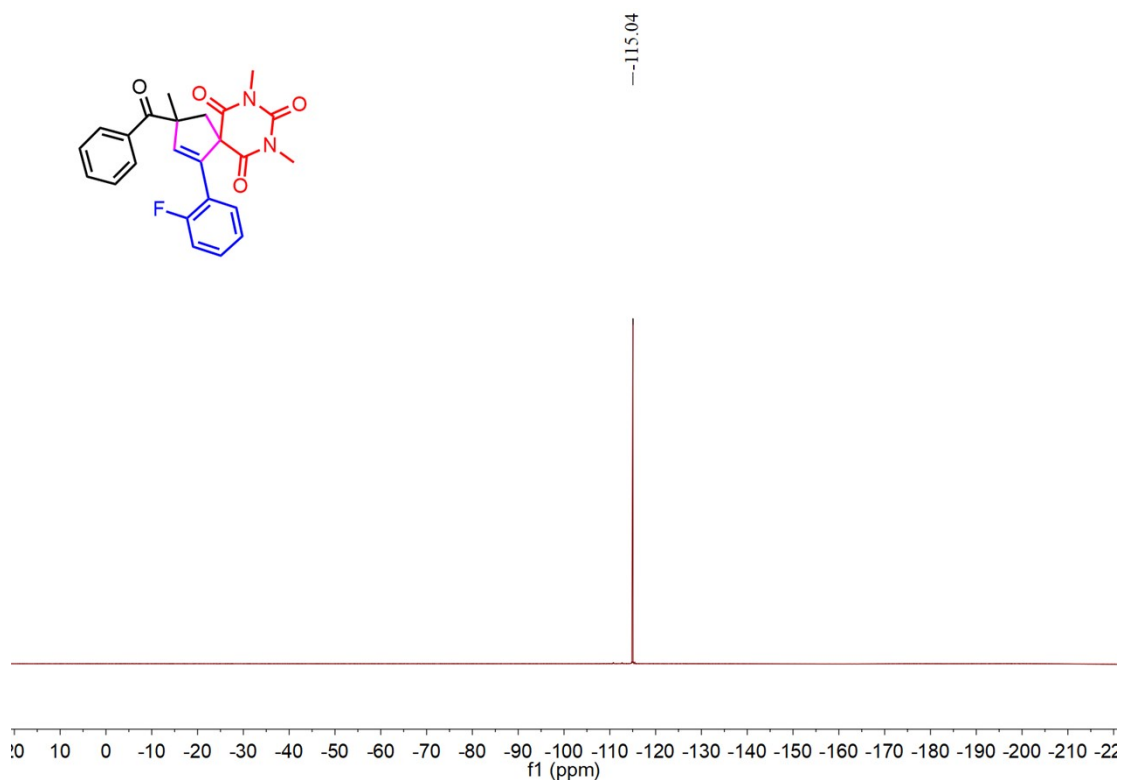


3-(1-naphthoyl)-3,7,9-trimethyl-1-phenyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (11):

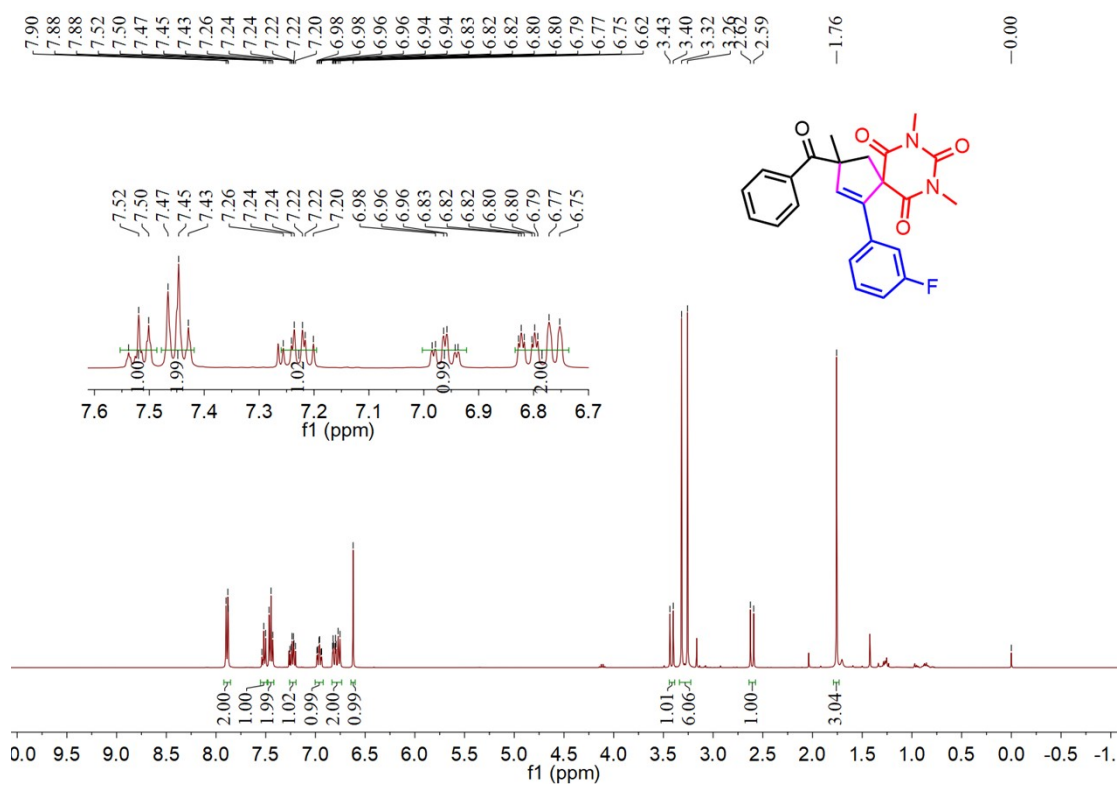


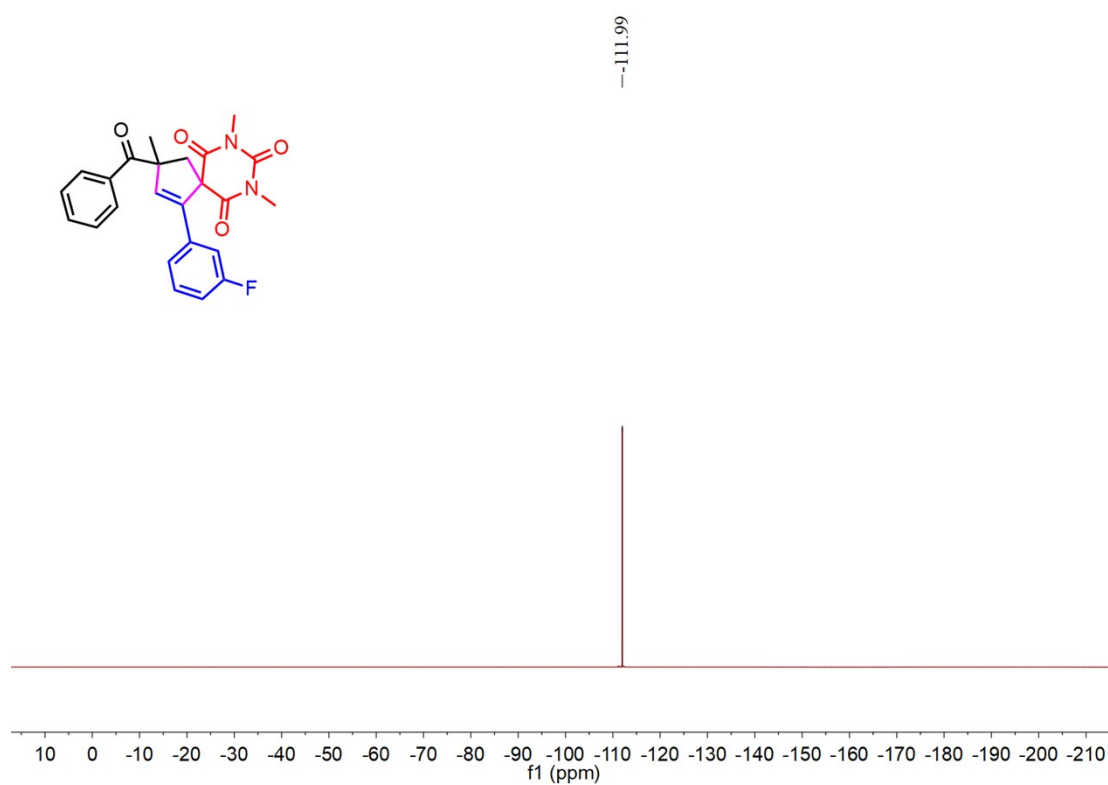
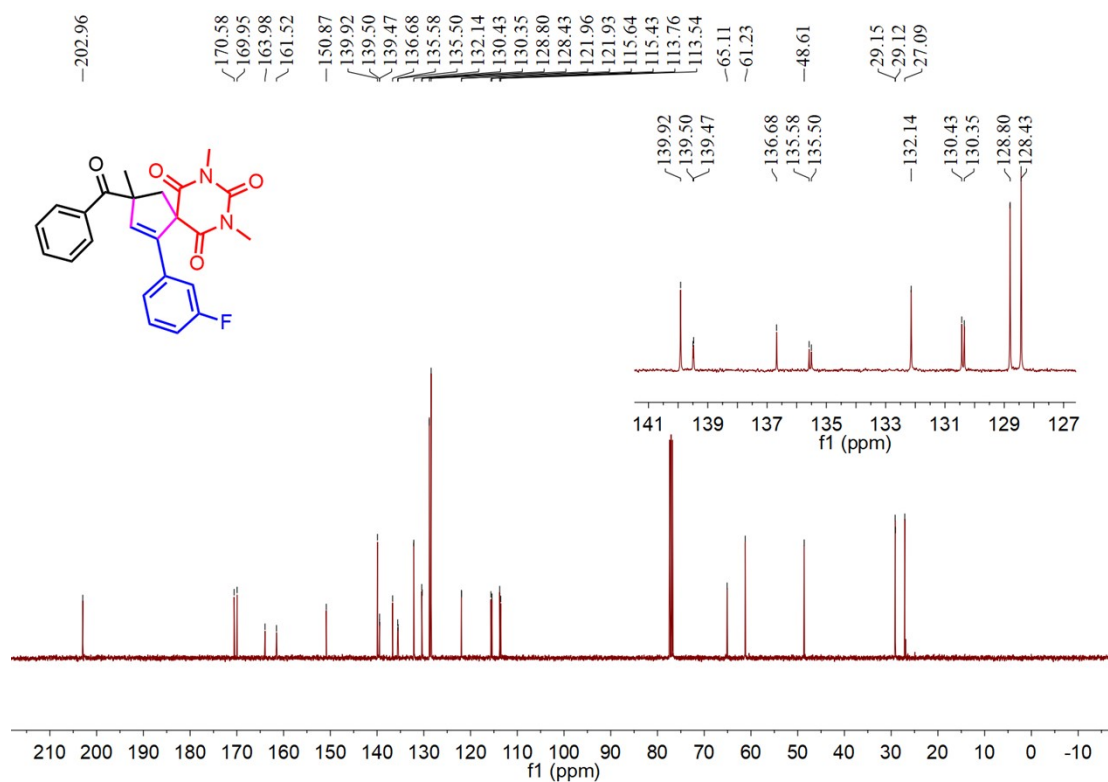
3-benzoyl-1-(2-fluorophenyl)-3,7,9-trimethyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (12):



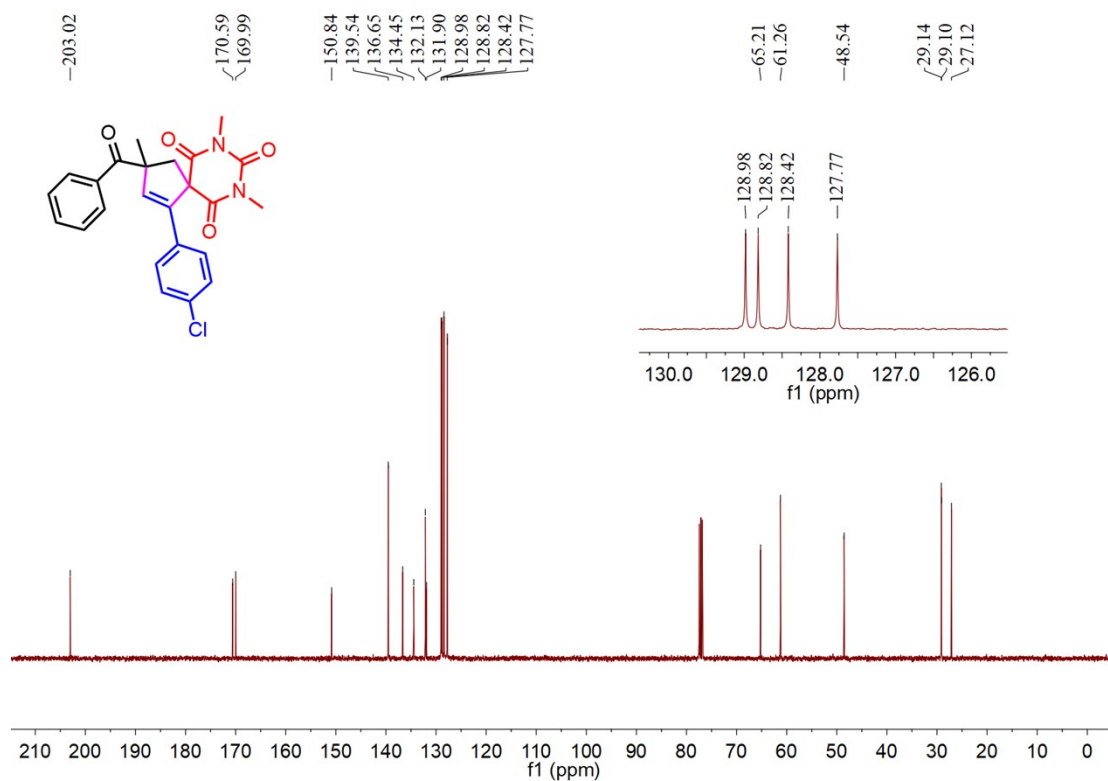
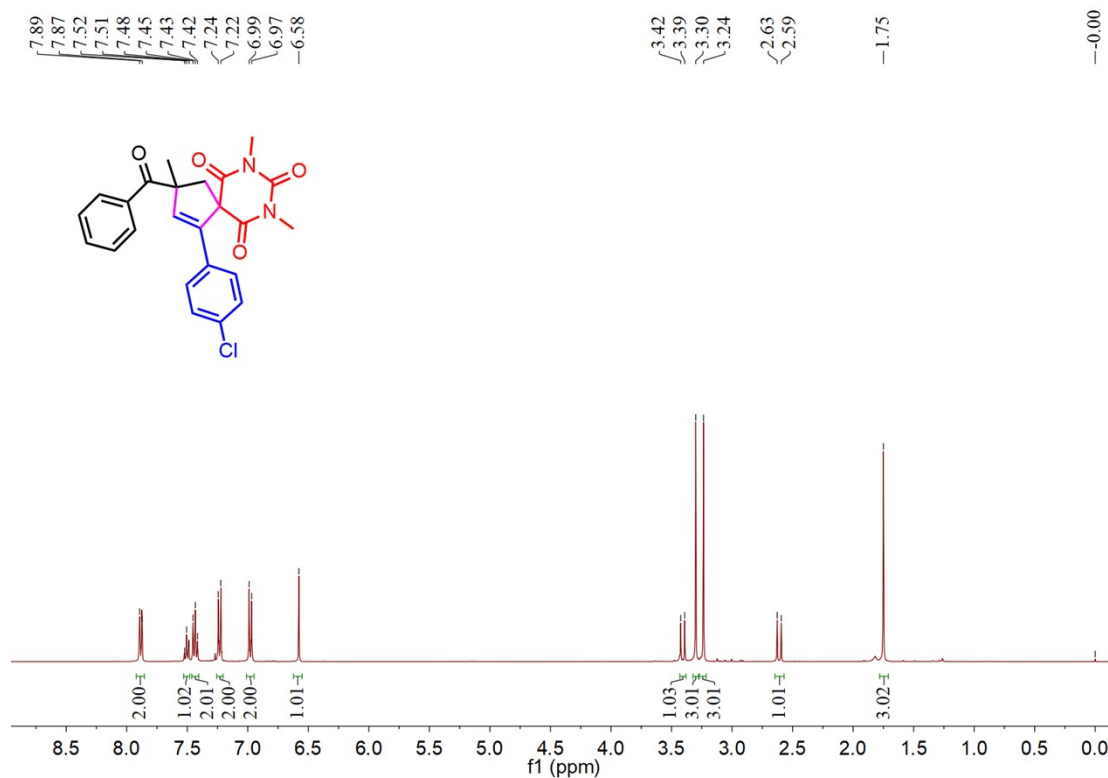


3-benzoyl-1-(3-fluorophenyl)-3,7,9-trimethyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (13):



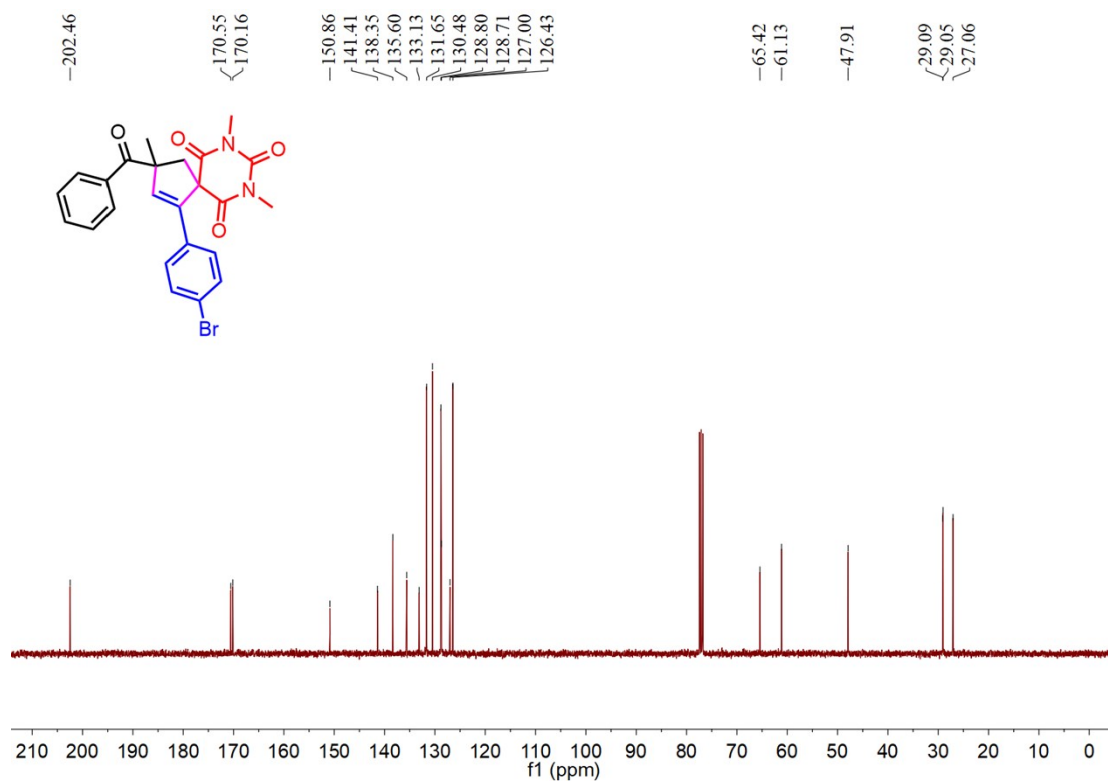
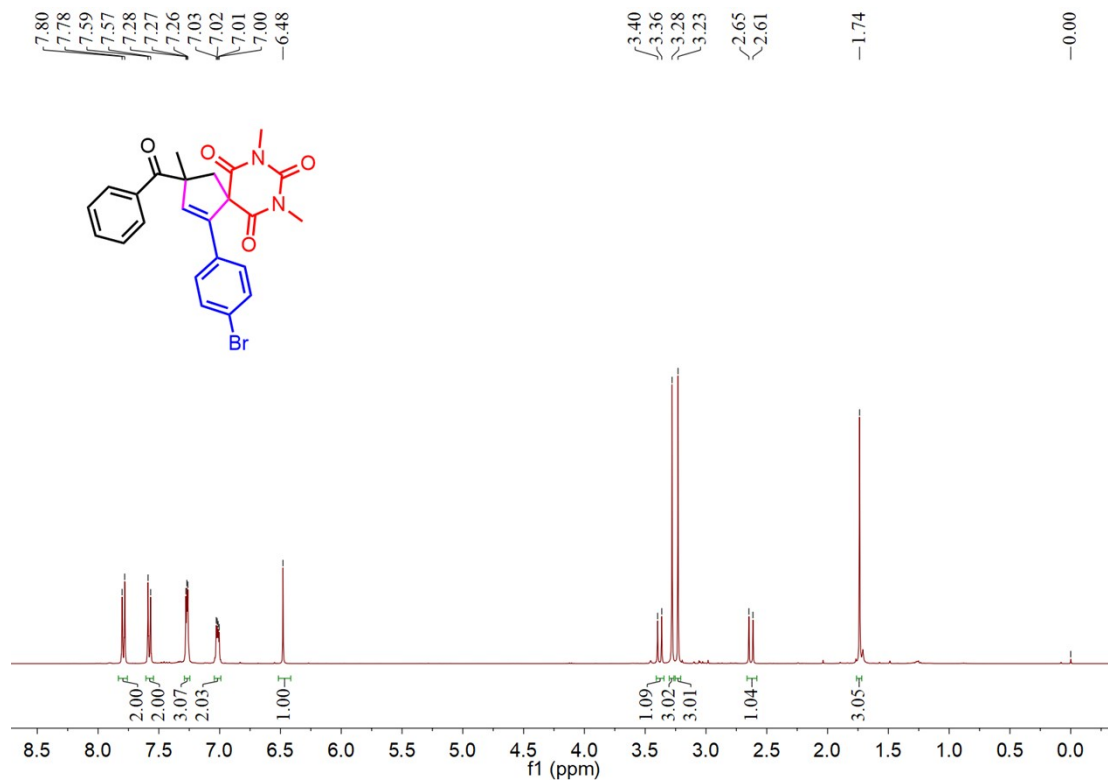


3-benzoyl-1-(4-chlorophenyl)-3,7,9-trimethyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (14):

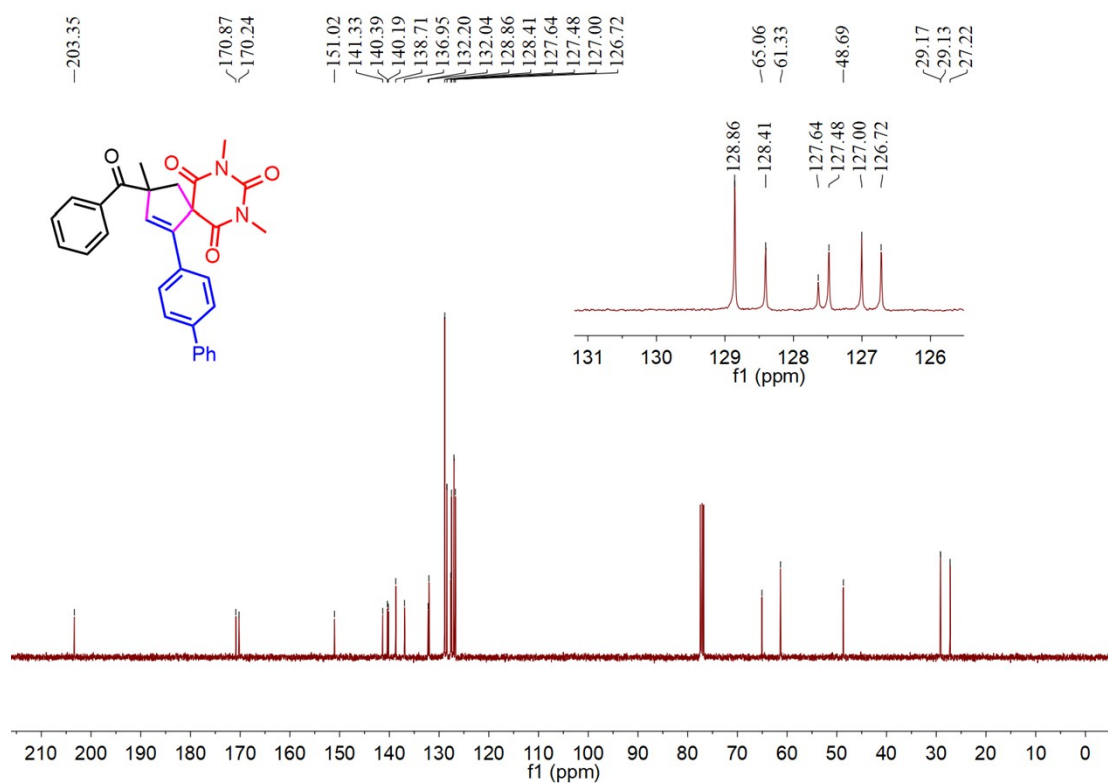
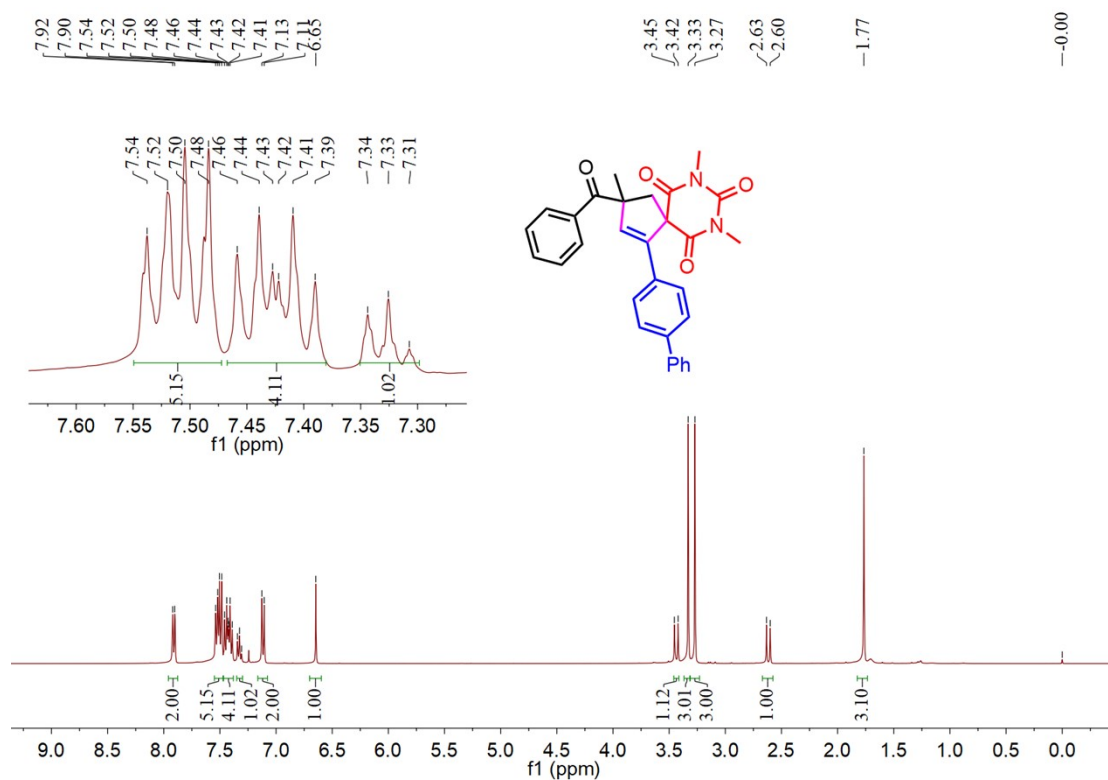


3-benzoyl-1-(4-bromophenyl)-3,7,9-trimethyl-7,9-diazaspiro[4.5]dec-1-ene-

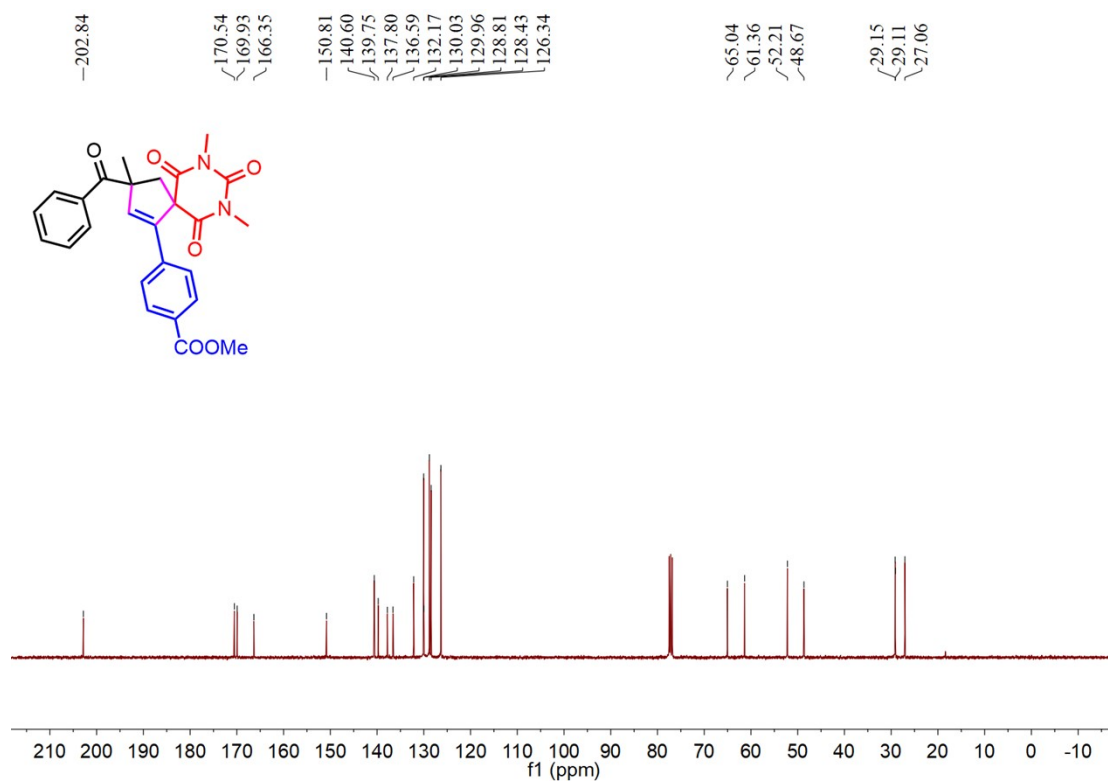
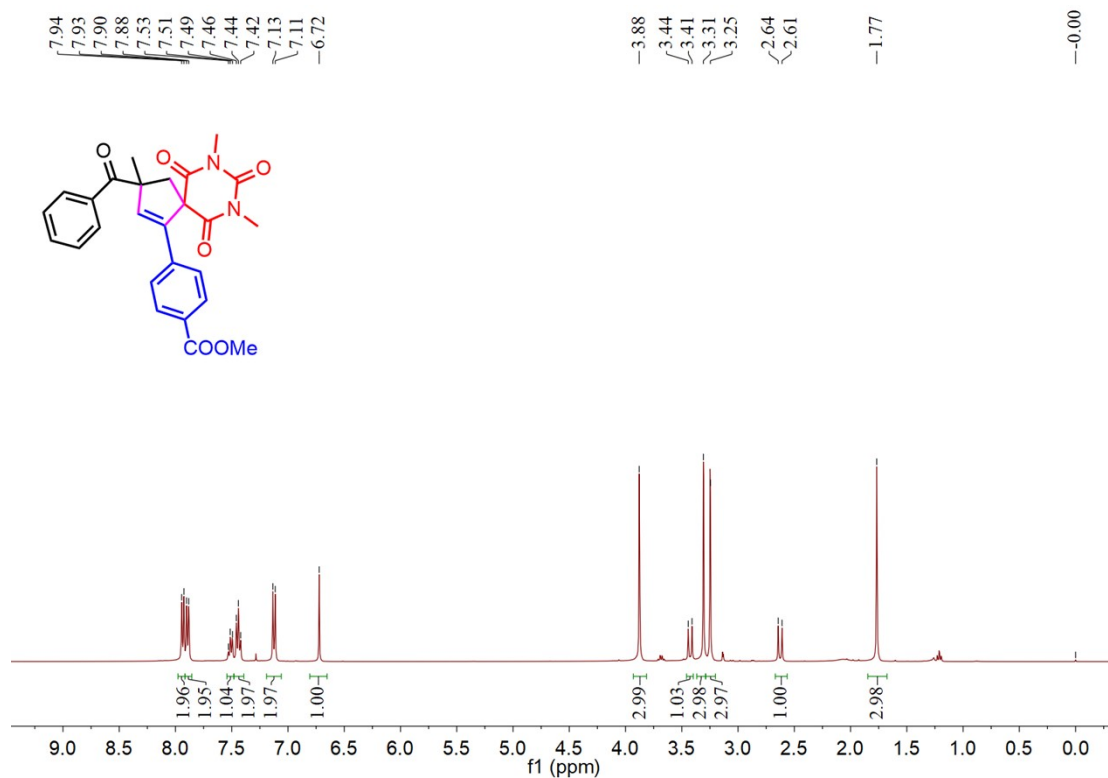
6,8,10-trione (15):



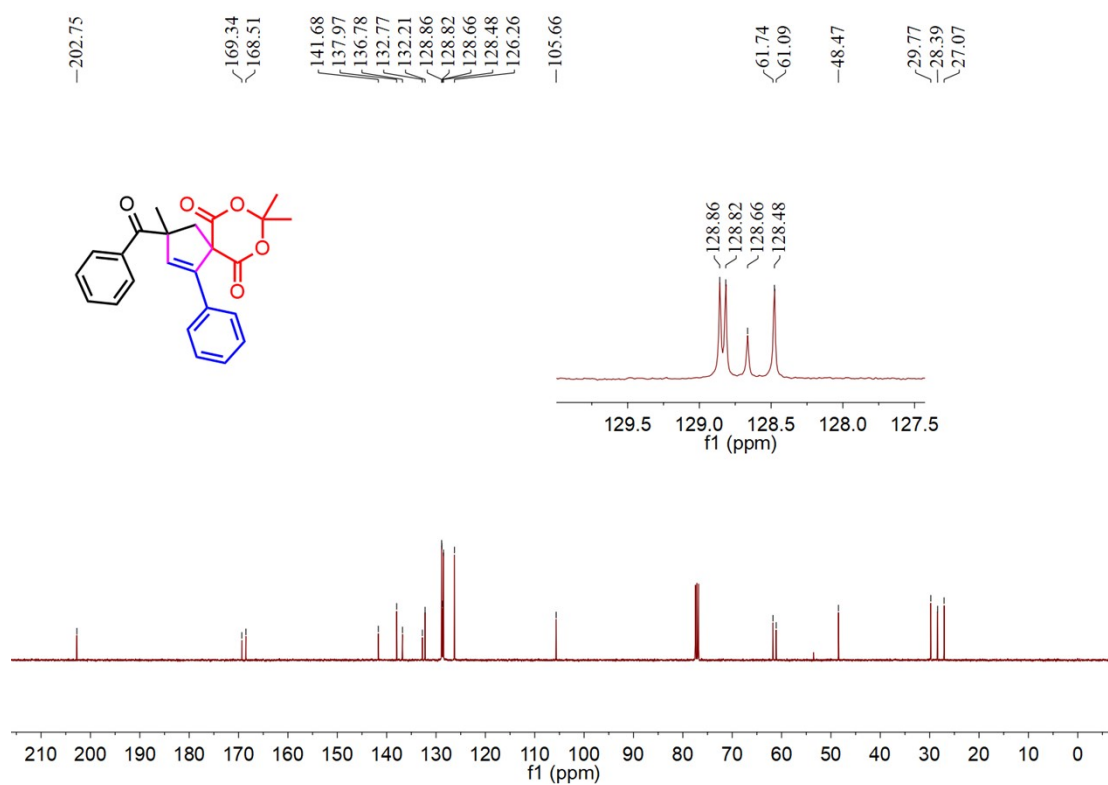
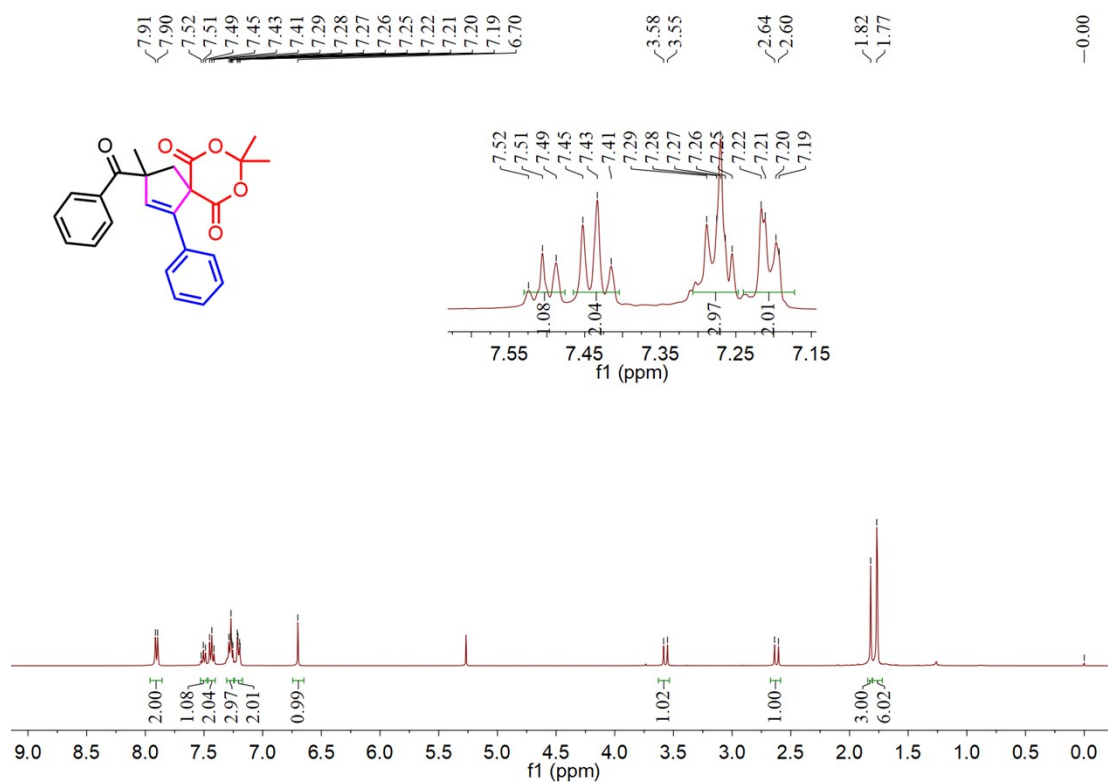
1-([1,1'-biphenyl]-4-yl)-3-benzoyl-3,7,9-trimethyl-7,9-diazaspiro[4.5]dec-1-ene-6,8,10-trione (16):



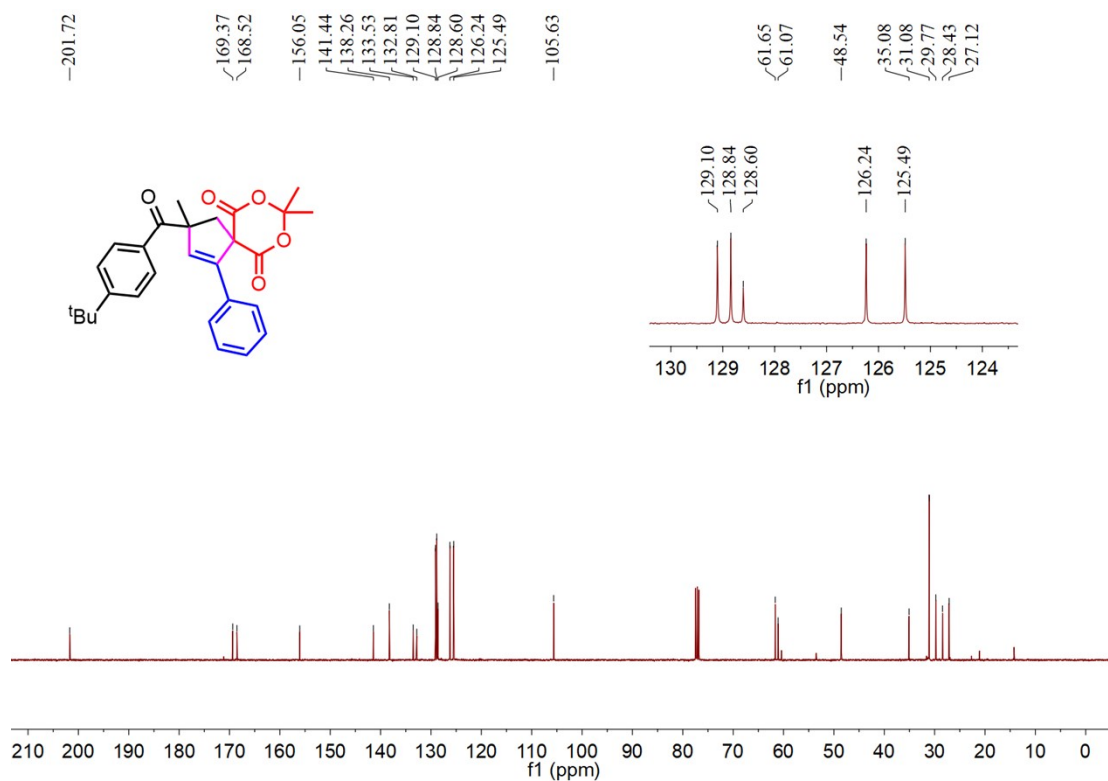
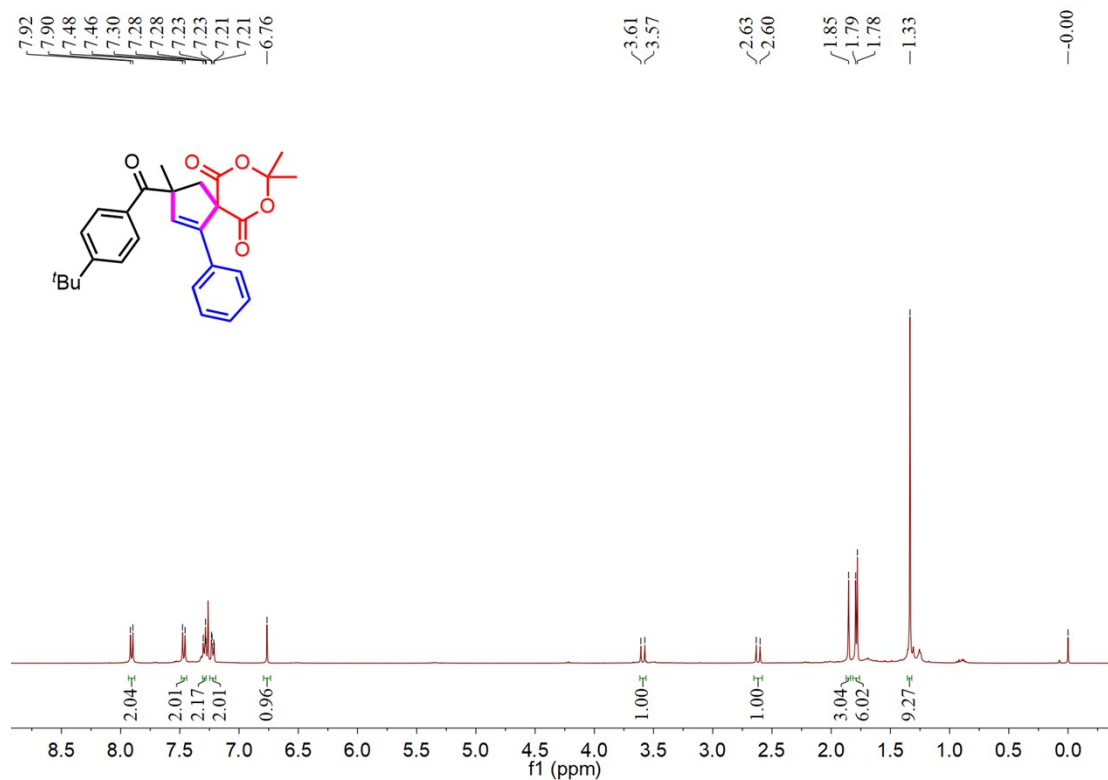
methy14-(3-benzoyl-3,7,9-trimethyl-6,8,10-trioxo-7,9-diazaspiro[4.5]dec-1-en-1-yl)benzoate (17):



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

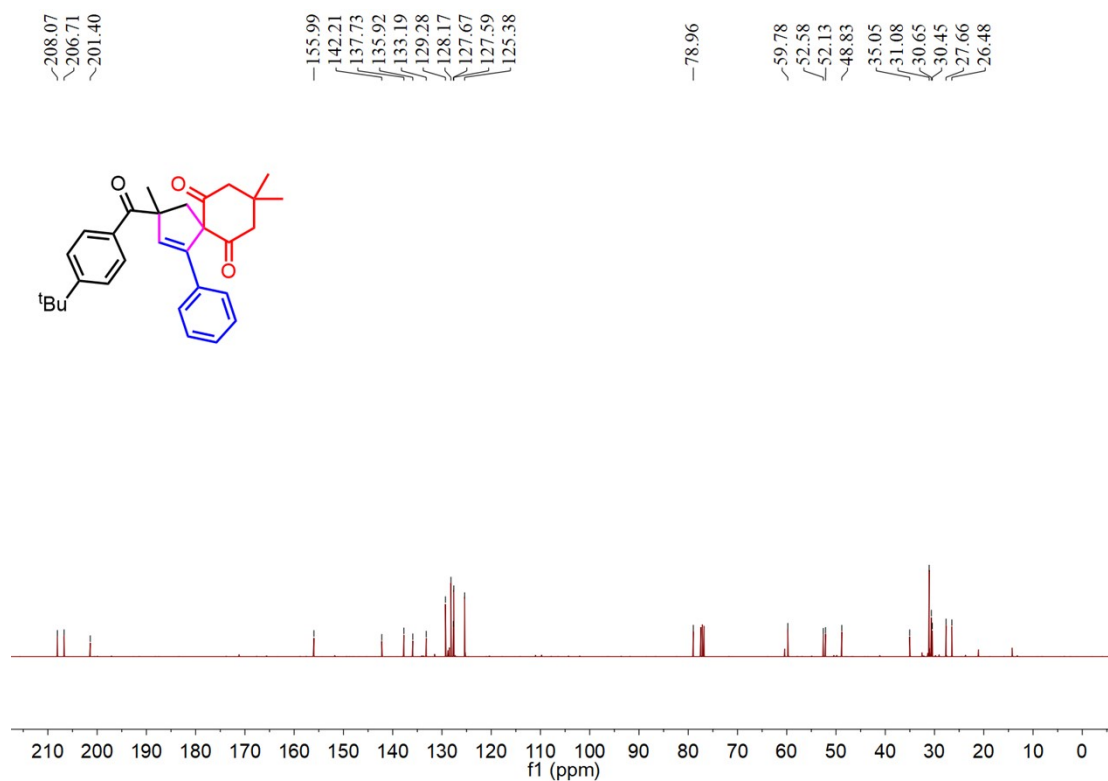
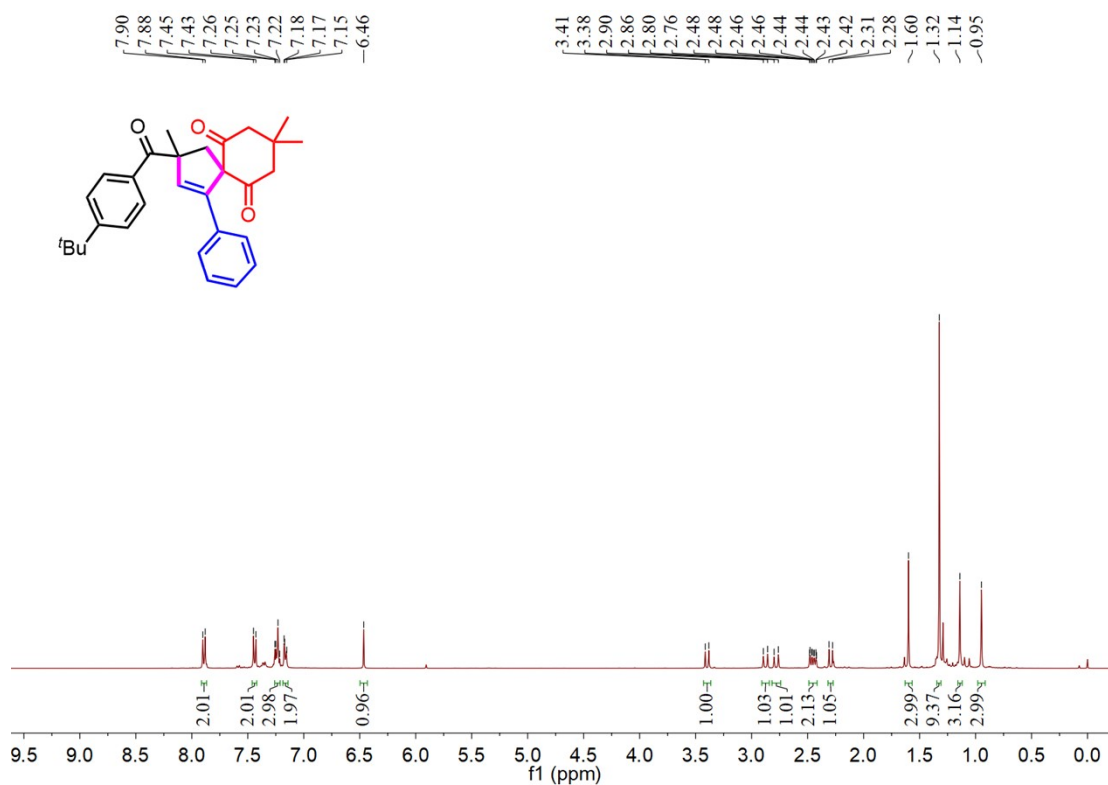


3-(4-(*tert*-butyl)benzoyl)-3,8,8-trimethyl-1-phenyl-7,9-dioxaspiro[4.5]dec-1-ene-6,10-dione (19):

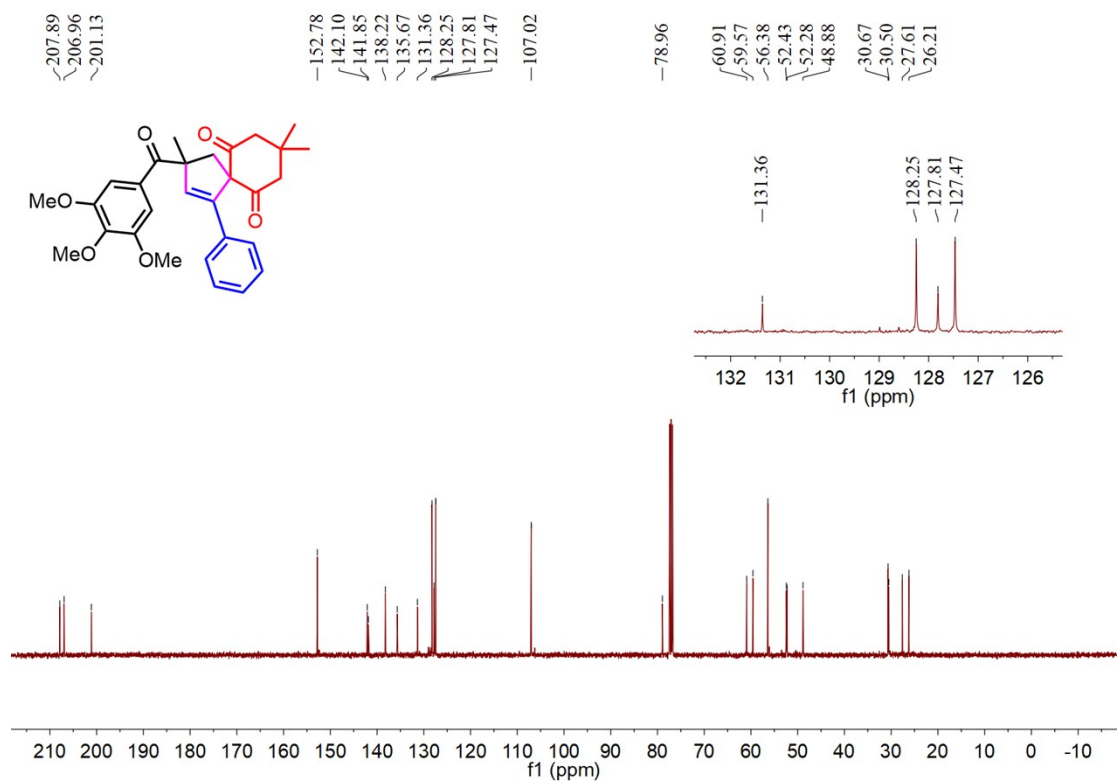
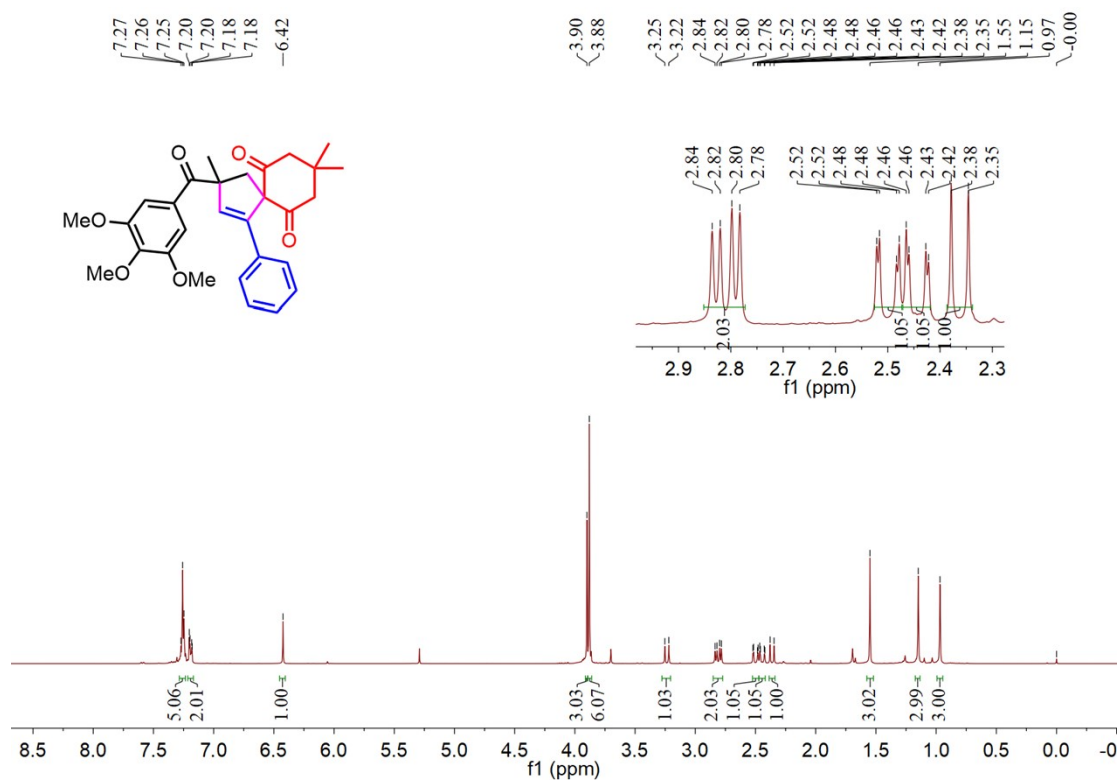


3-(4-(*tert*-butyl)benzoyl)-3,8,8-trimethyl-1-phenylspiro[4.5]dec-1-ene-6,10-dione

(20):



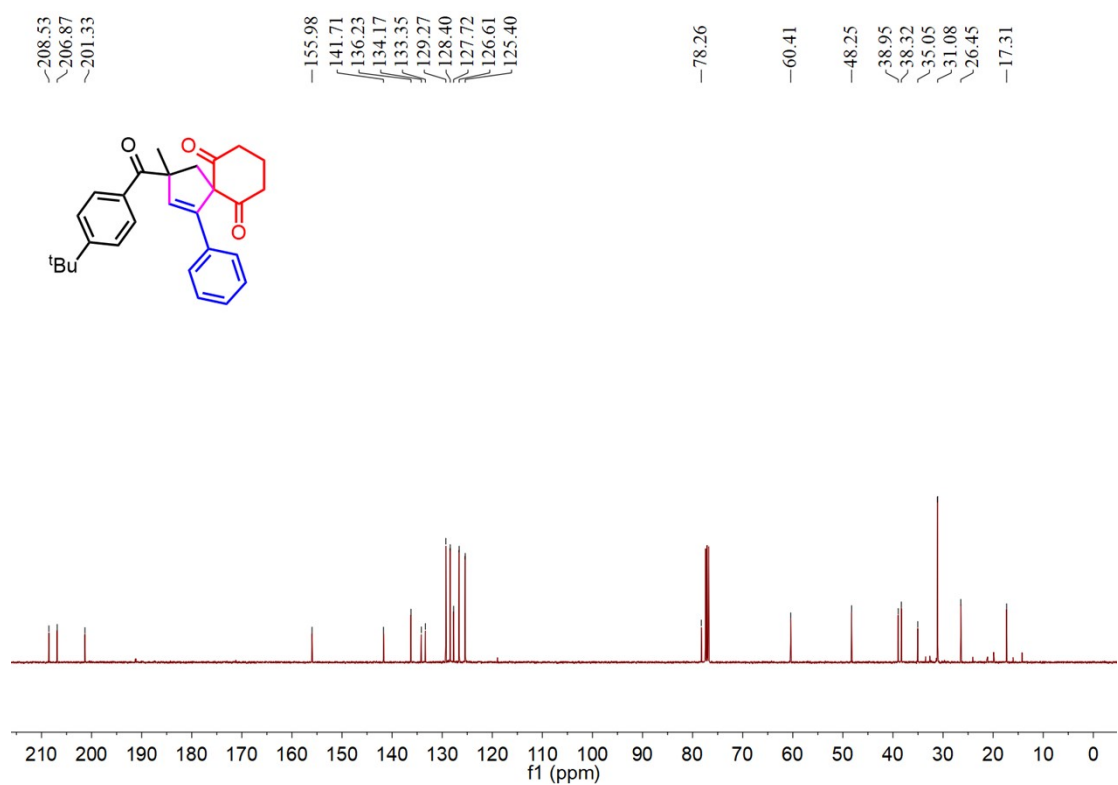
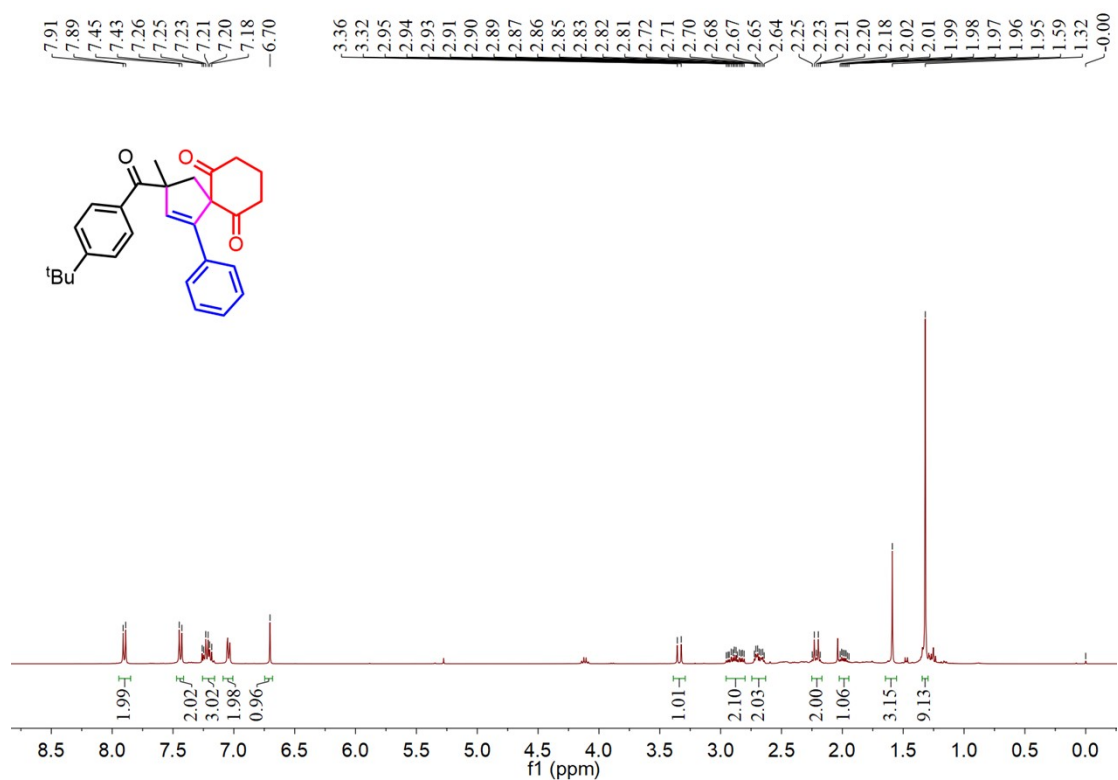
3,8,8-trimethyl-1-phenyl-3-(3,4,5-trimethoxybenzoyl)spiro[4.5]dec-1-ene-6,10-dione (21):



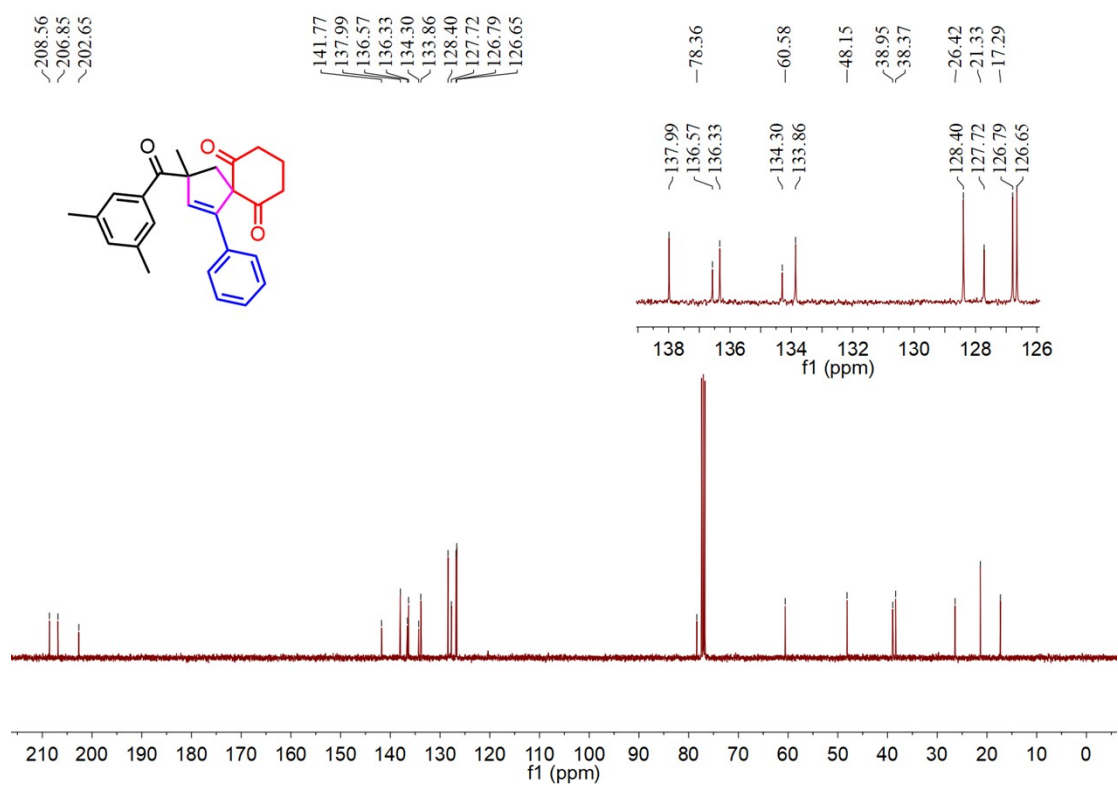
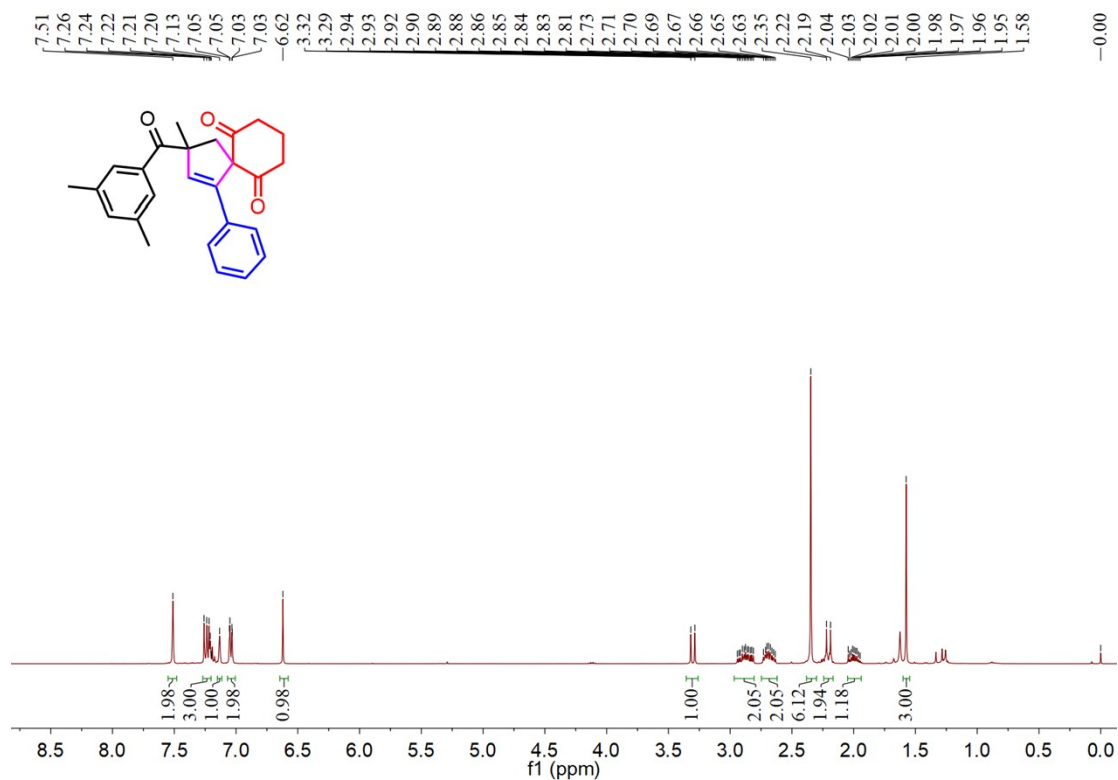
Chemical structure of compound 10 is shown. The ^1H NMR spectrum (CDCl₃) shows peaks at the following chemical shifts (ppm): 7.91, 7.89, 7.85, 7.63, 7.59, 7.57, 7.56, 7.49, 7.47, 7.45, 7.33, 7.30, 6.94, 6.59, 3.22, 3.19, 3.14, 3.10, 3.06, 2.50, 2.37, 2.36, 2.34, 2.32, 2.29, 1.41, 1.14, and 0.87. Integration values are provided below the peaks: 2.00, 2.00, 1.02, 2.09, 2.08, 4.05, 0.99, 4.12, 6.48, 3.08, 3.03, and 3.08.



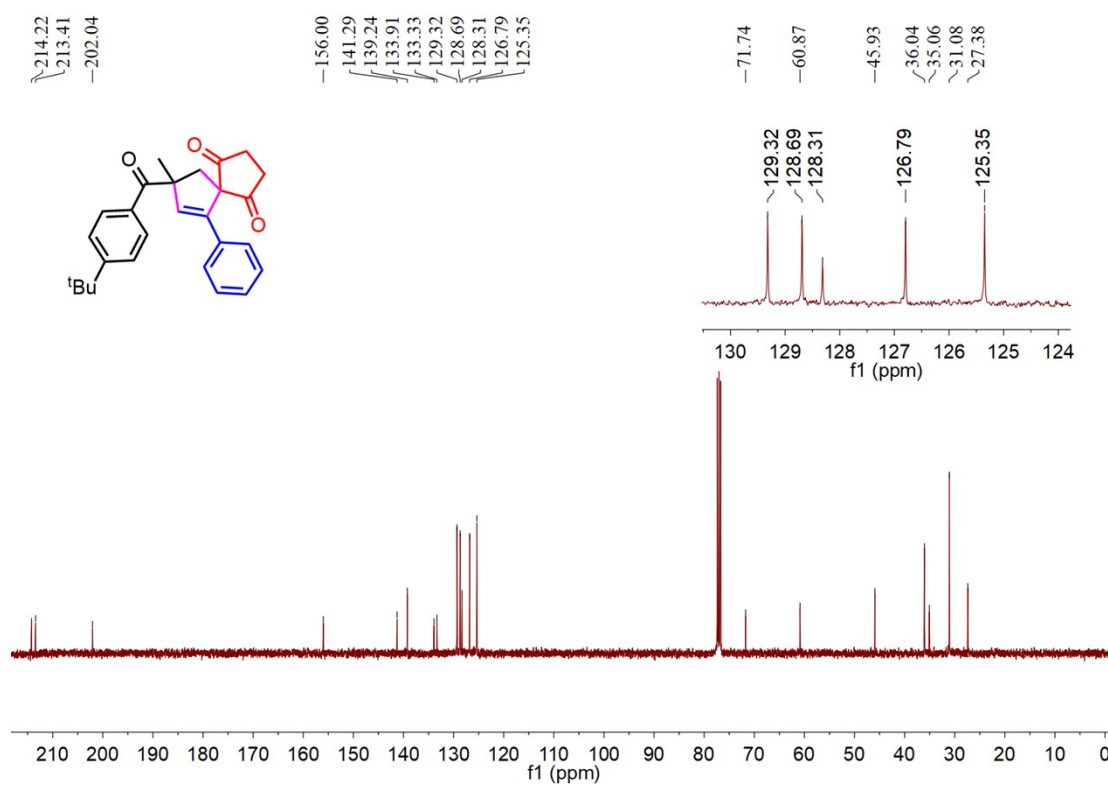
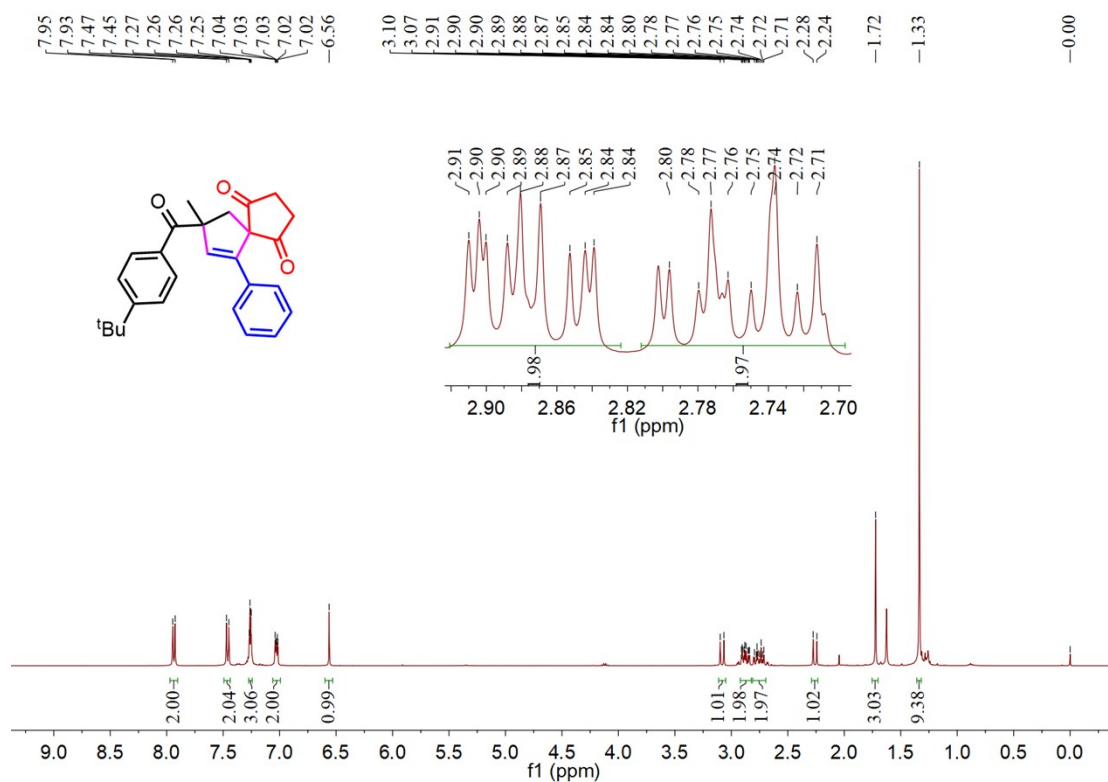
3-(4-(*tert*-butyl)benzoyl)-3-methyl-1-phenylspiro[4.5]dec-1-ene-6,10-dione (23):



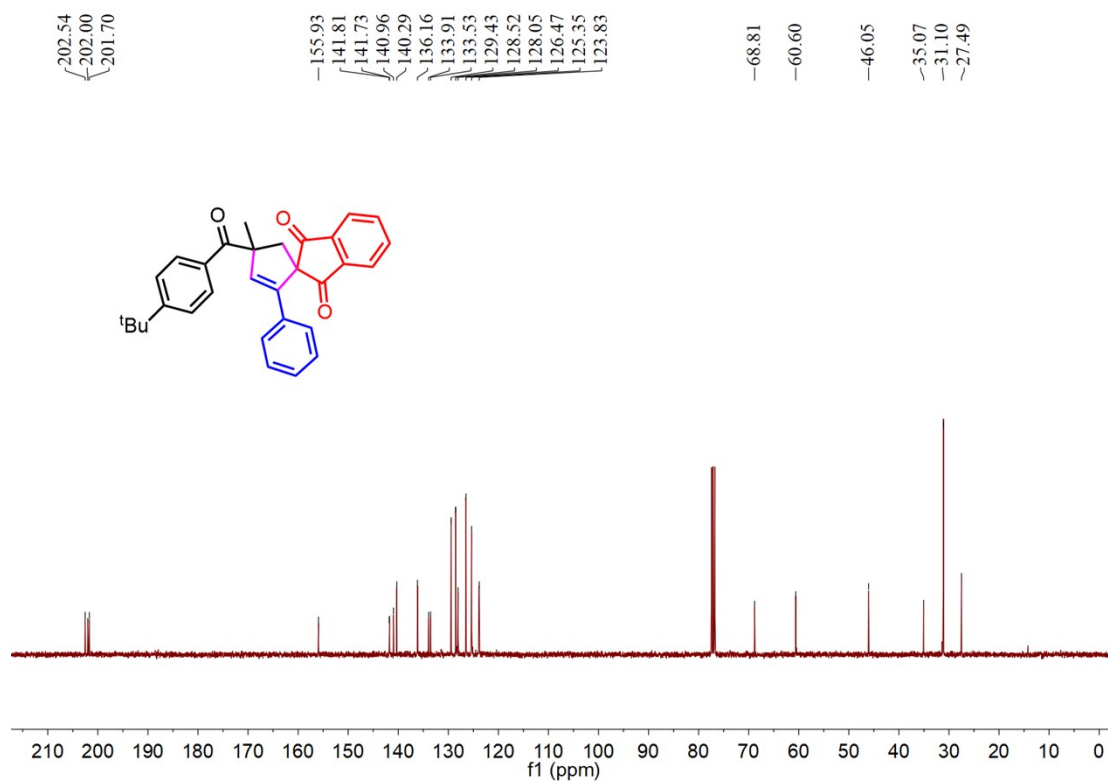
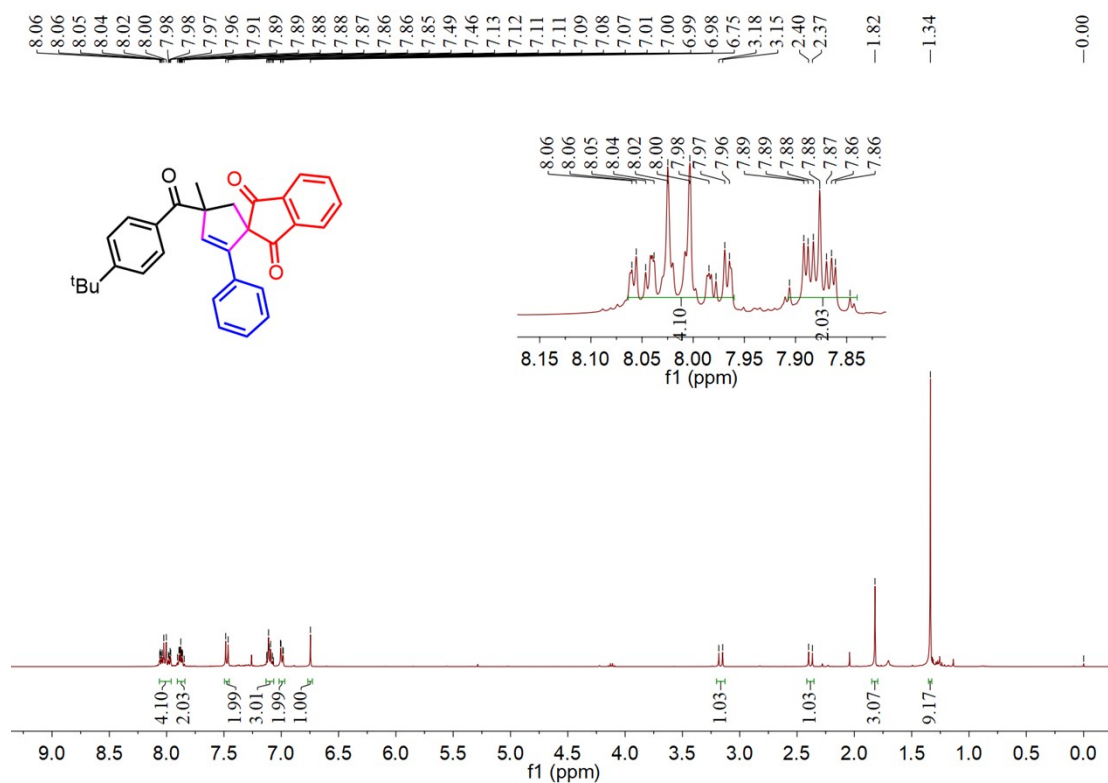
3-(3,5-dimethylbenzoyl)-3-methyl-1-phenylspiro[4.5]dec-1-ene-6,10-dione (24):



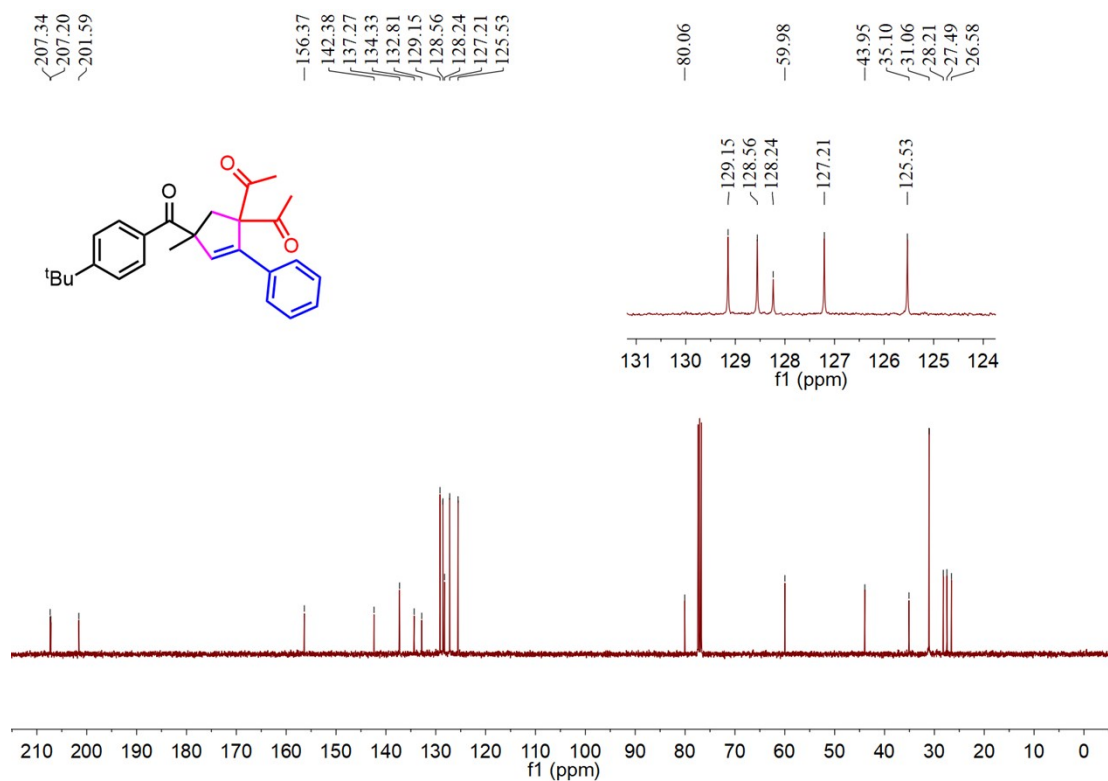
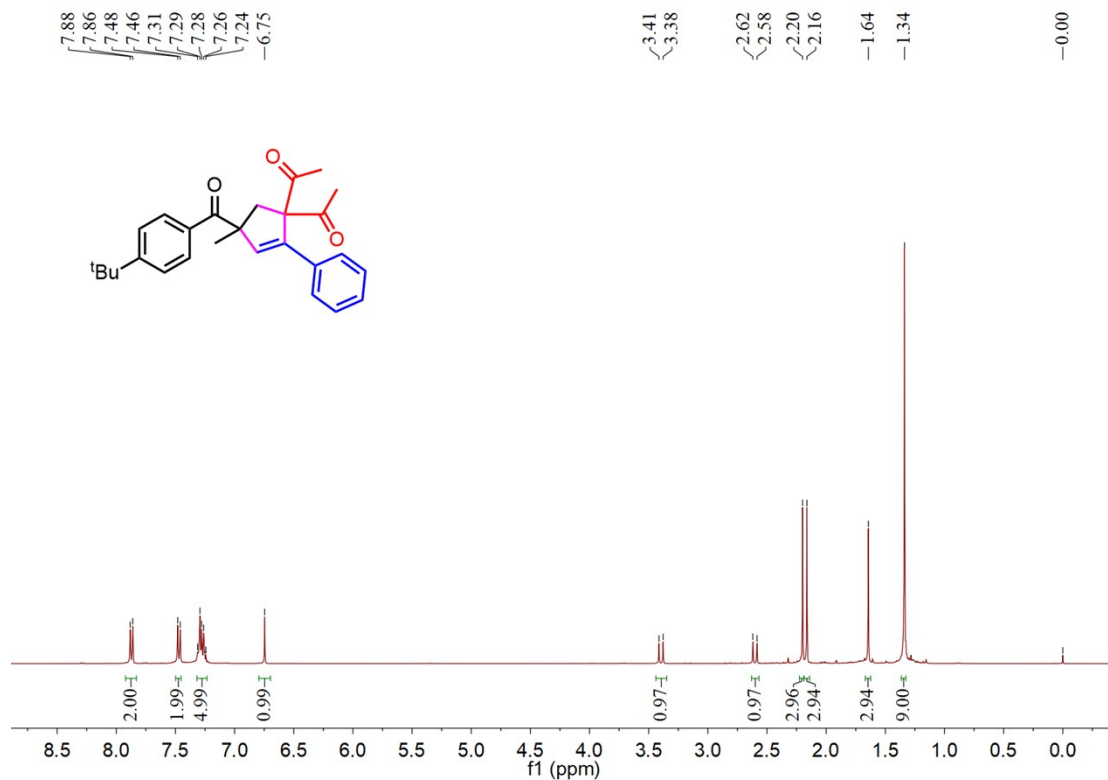
8-(4-(*tert*-butyl)benzoyl)-8-methyl-6-phenylspiro[4.4]non-6-ene-1,4-dione (25):



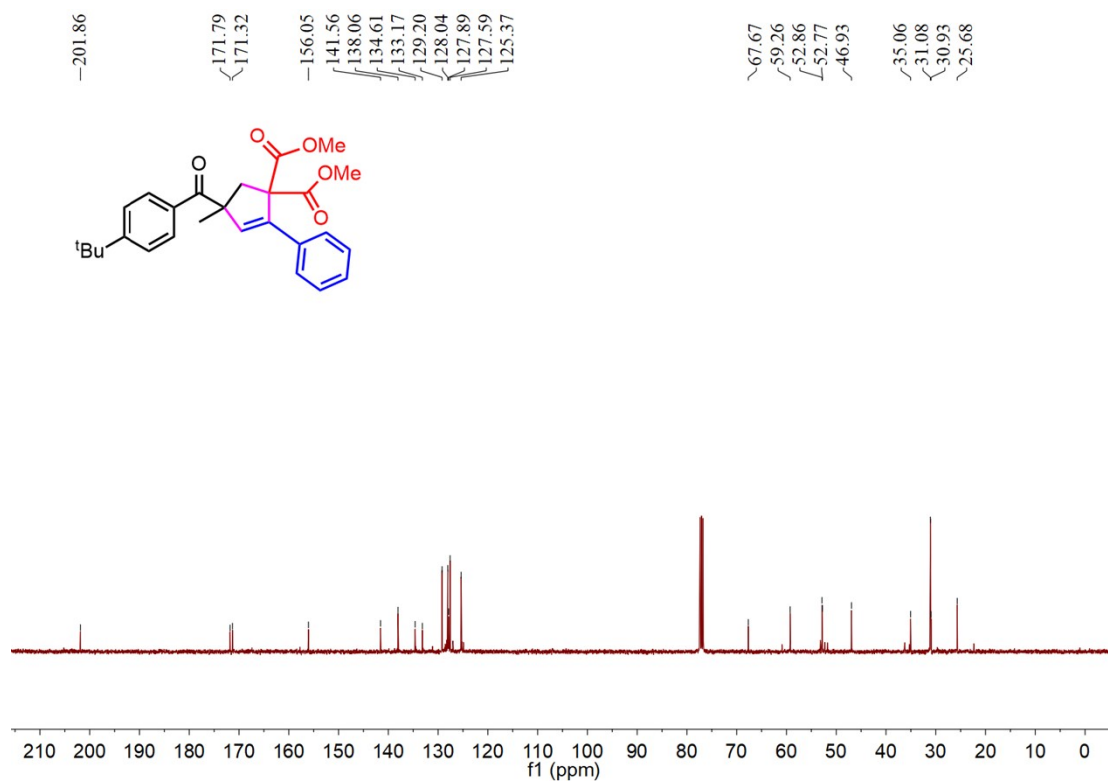
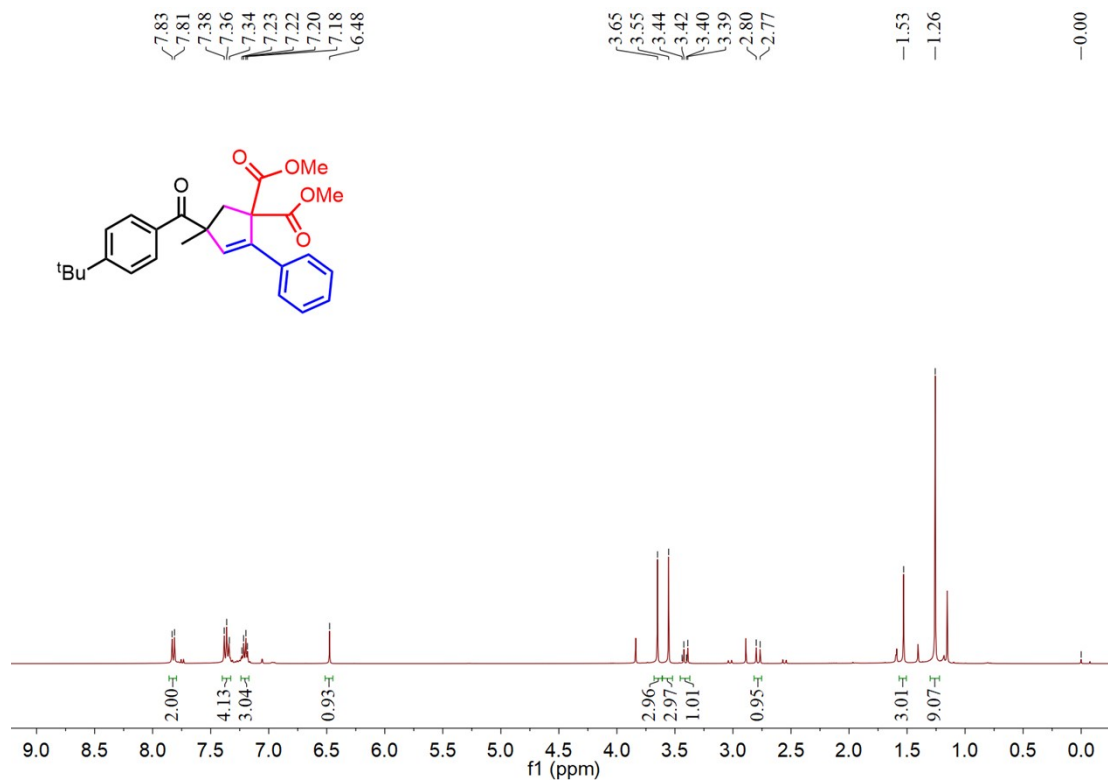
4-(4-(*tert*-butyl)benzoyl)-4-methyl-2-phenylspiro[cyclopentane-1,2'-inden]-2-ene-1',3'-dione (26):



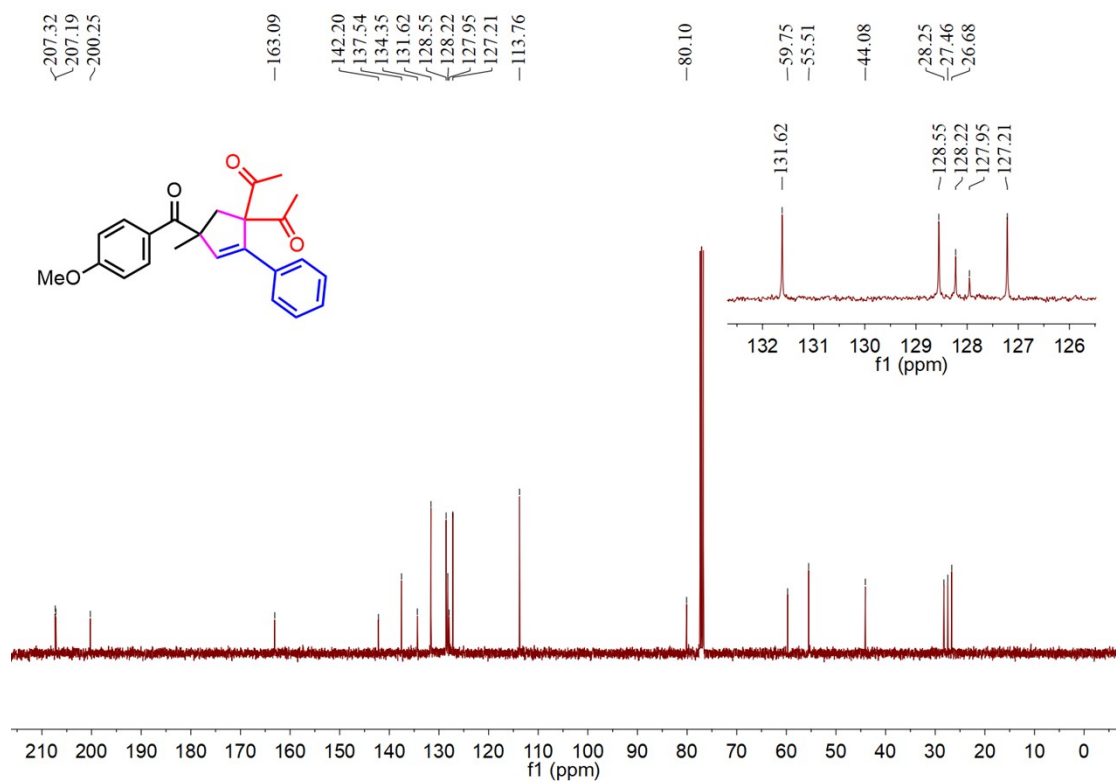
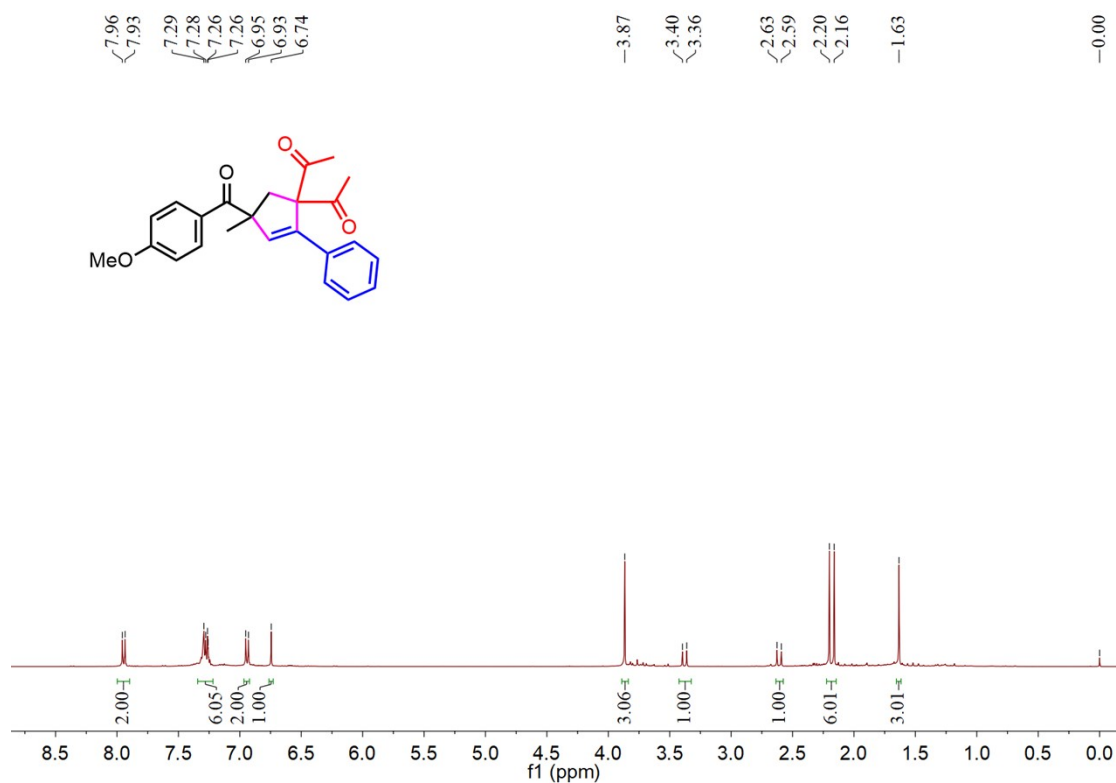
1,1'-(4-(4-(*tert*-butyl)benzoyl)-4-methyl-2-phenylcyclopent-2-ene-1,1'-diyl)bis(ethan-1-one) (27):



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

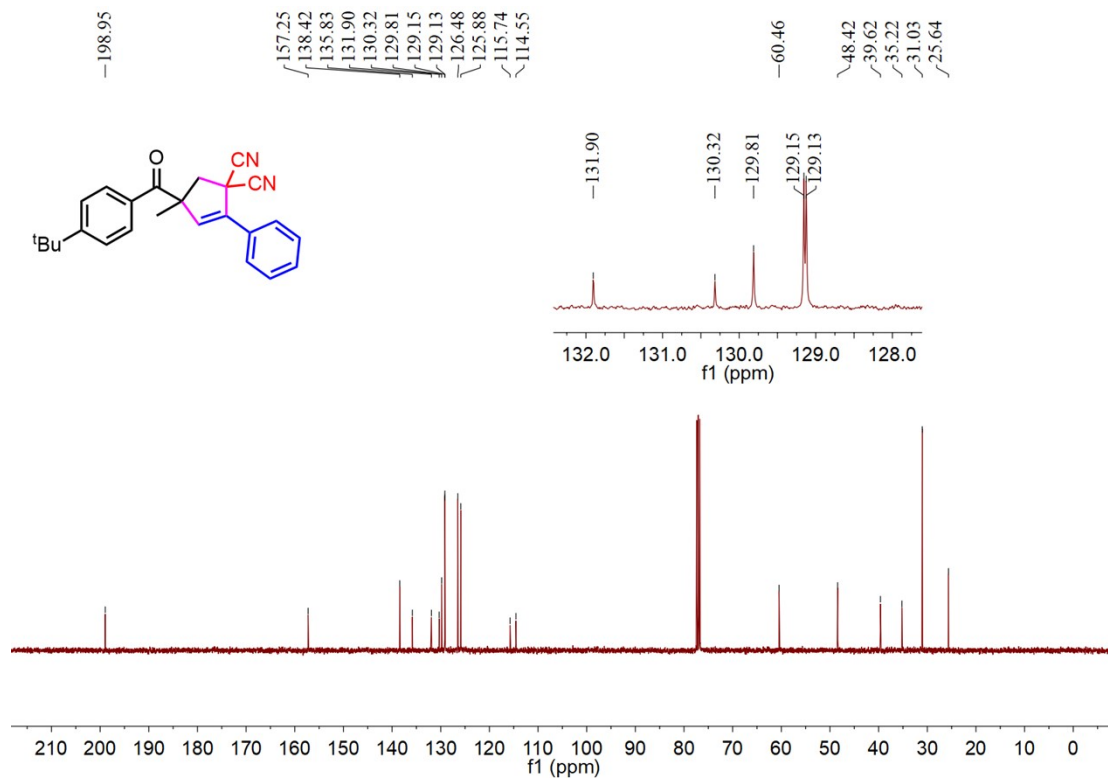
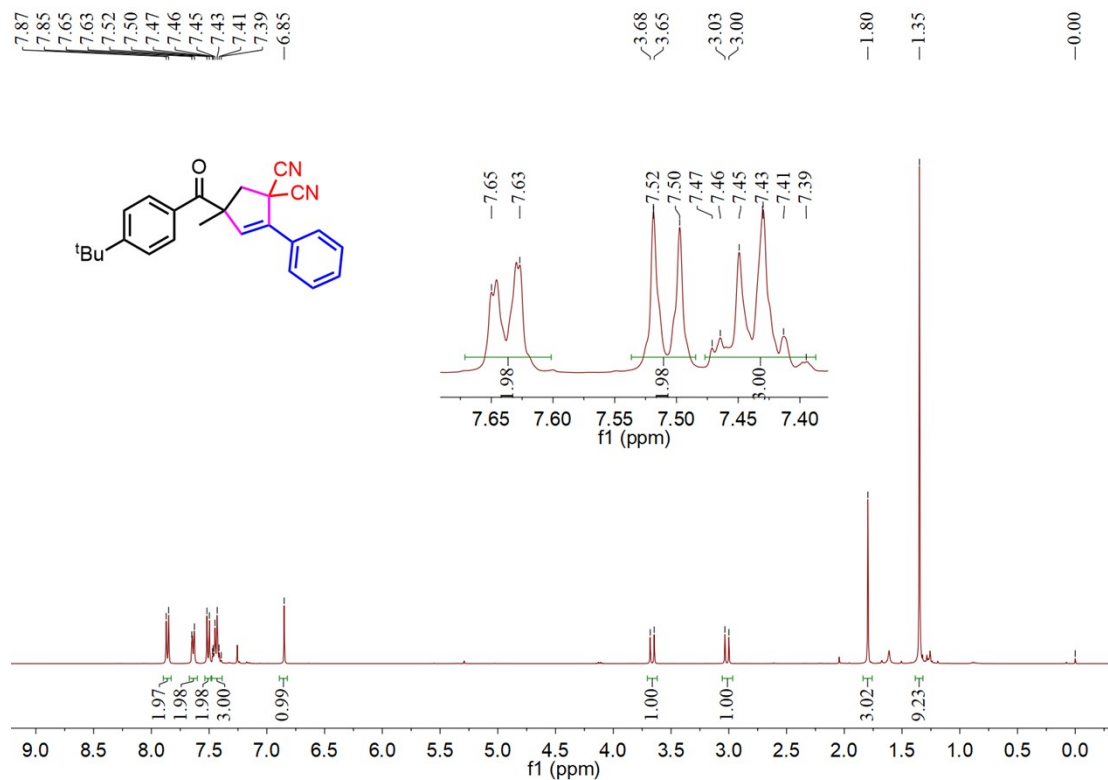


1,1'-(4-(4-methoxybenzoyl)-4-methyl-2-phenylcyclopent-2-ene-1,1-diyl)bis(ethan-1-one) (29):



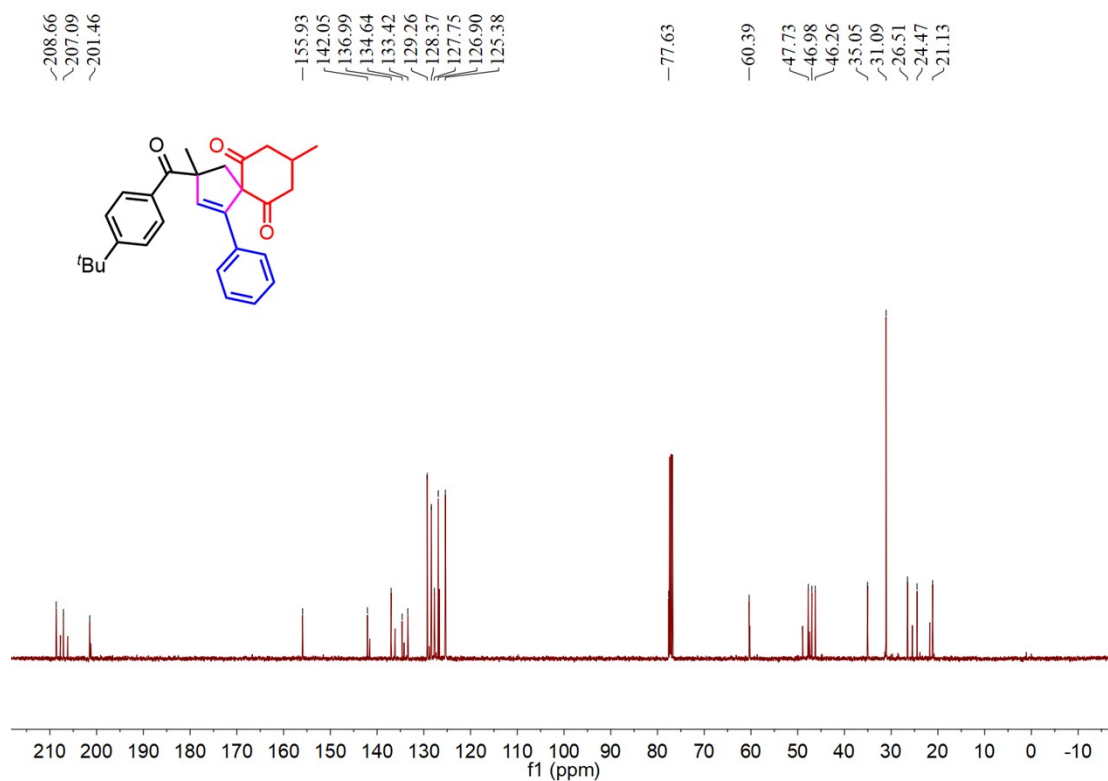
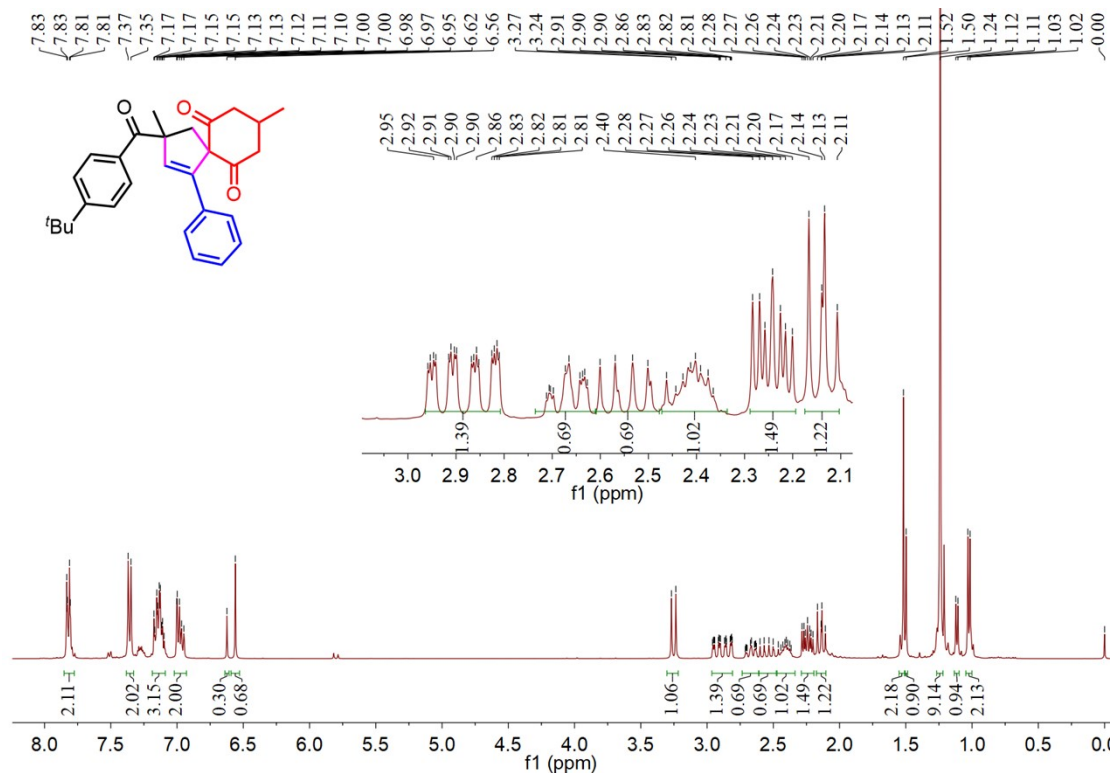
4-(4-(*tert*-butyl)benzoyl)-4-methyl-2-phenylcyclopent-2-ene-1,1-dicarbonitrile

(30):

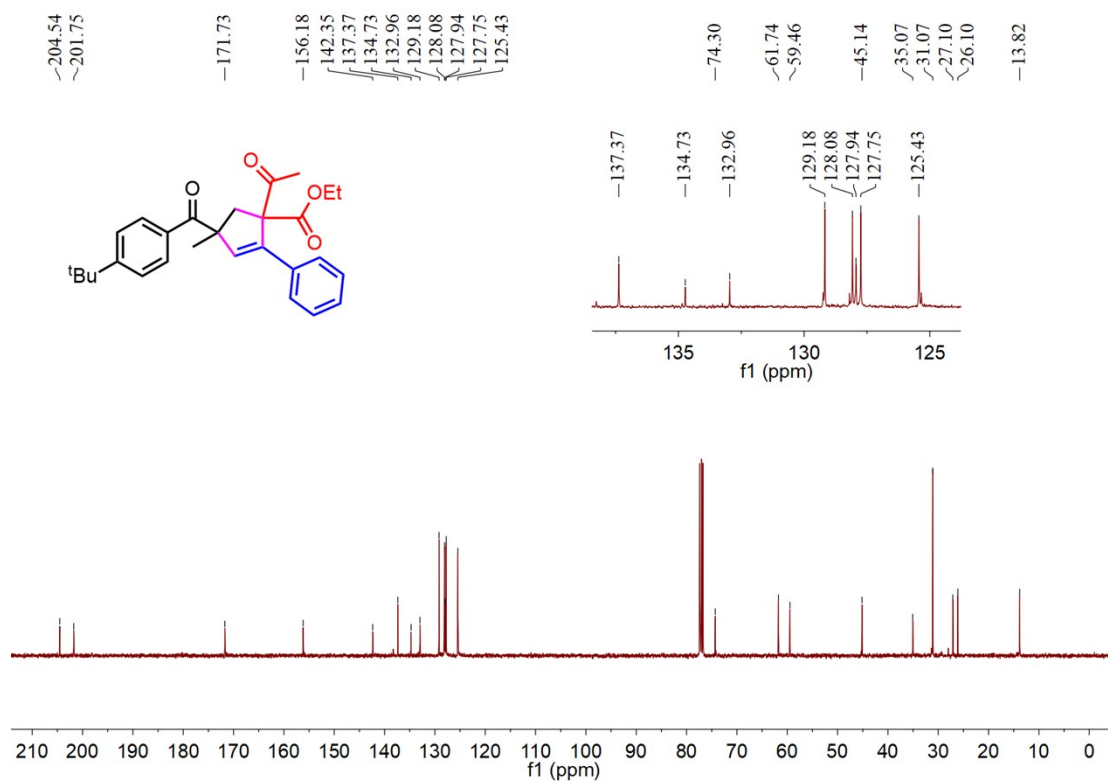
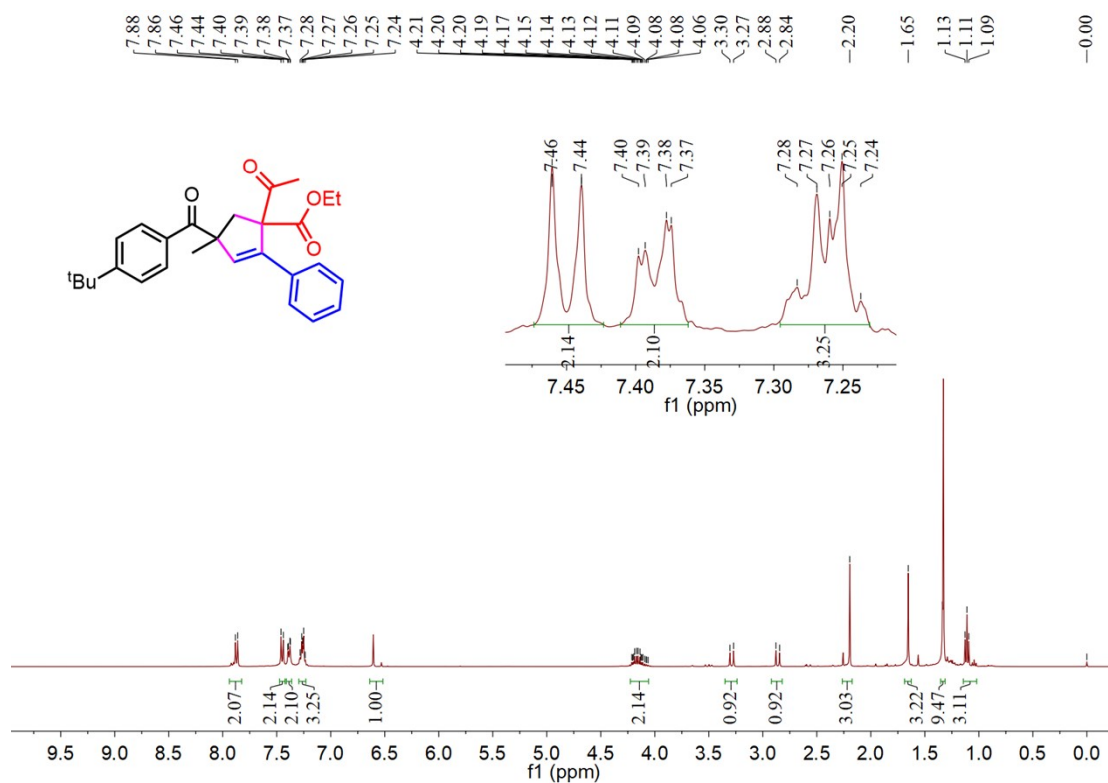


3-(4-(*tert*-butyl)benzoyl)-3,8-dimethyl-1-phenylspiro[4.5]dec-1-ene-6,10-dione

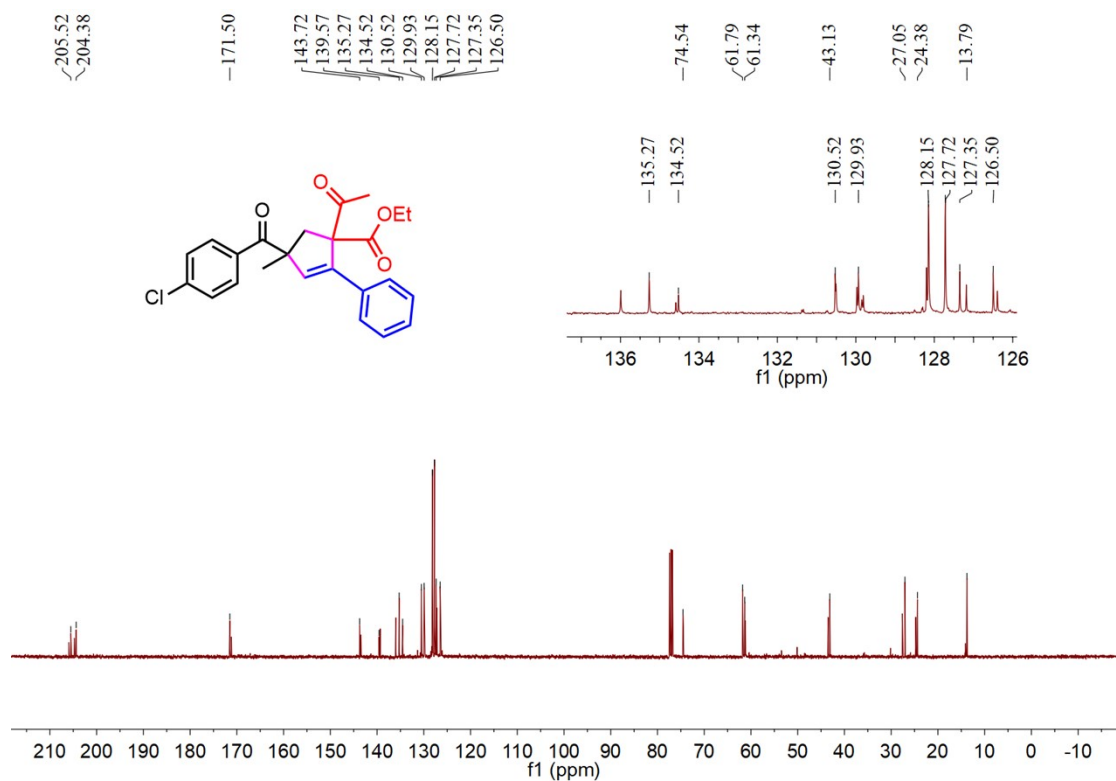
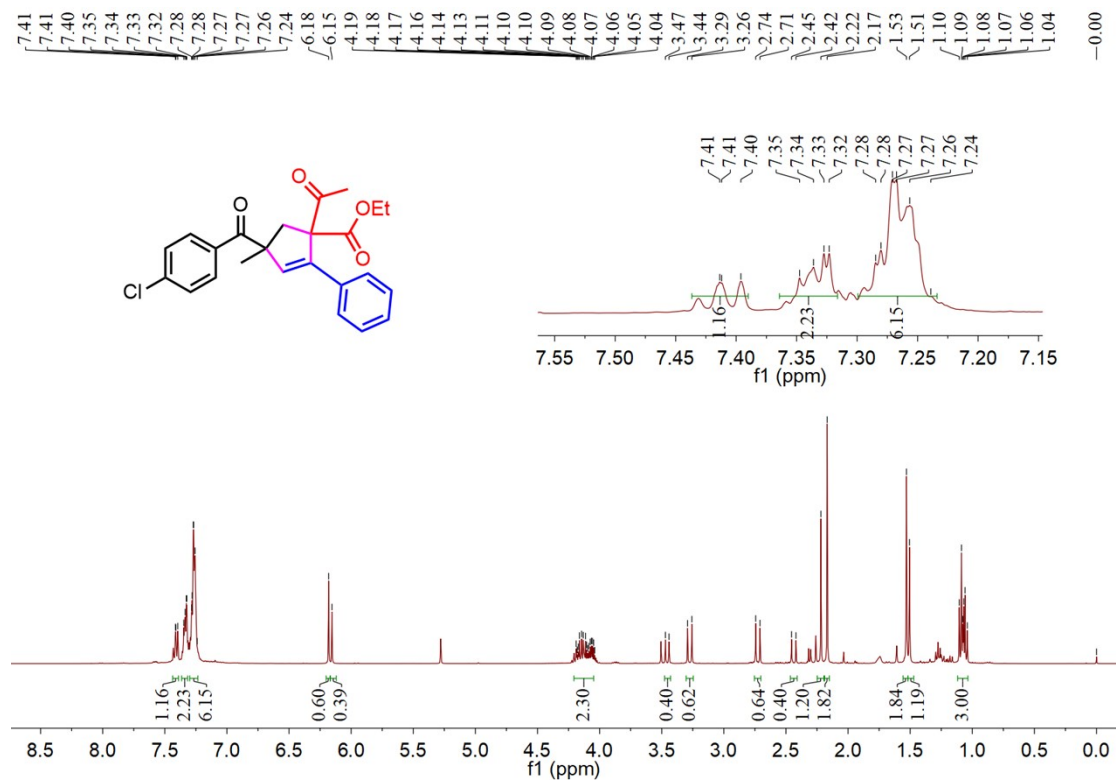
(31):



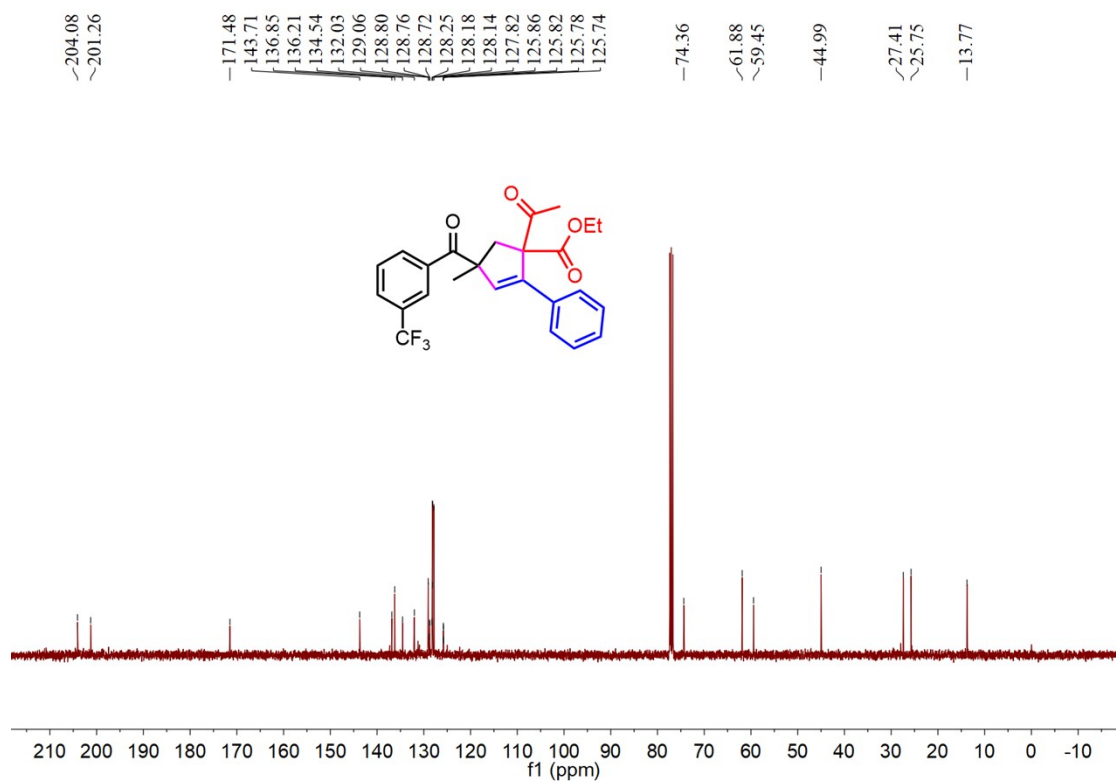
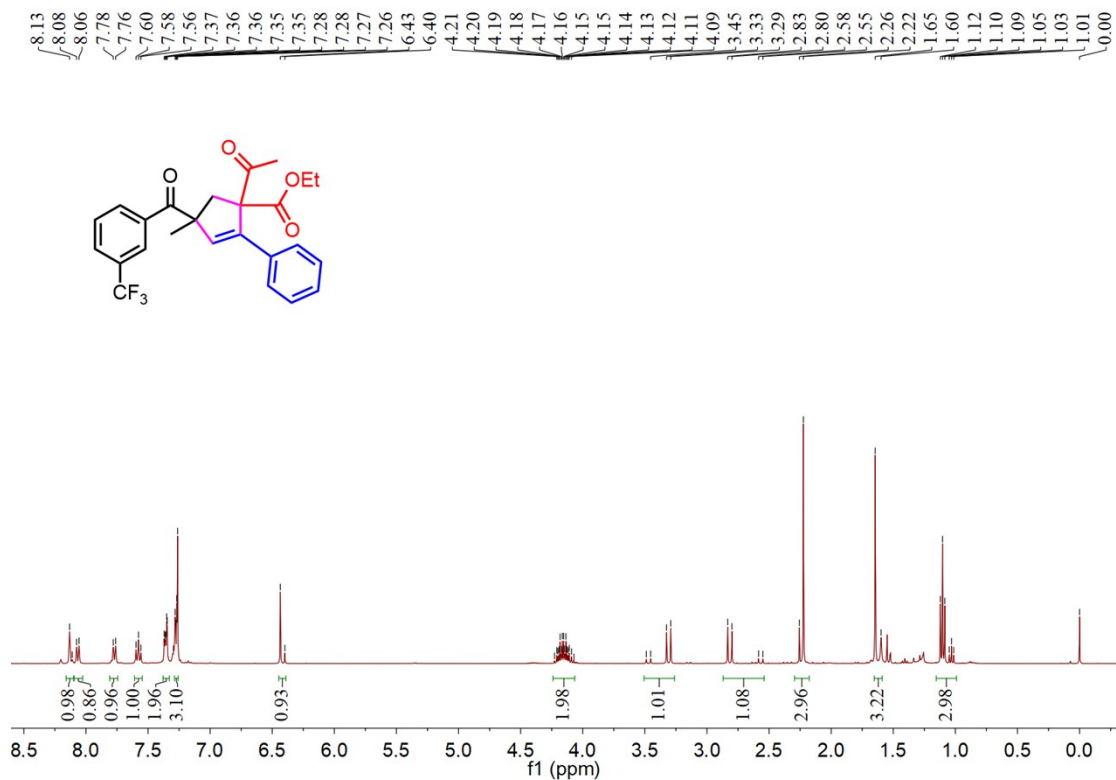
ethyl 1-acetyl-4-(4-(*tert*-butyl)benzoyl)-4-methyl-2-phenylcyclopent-2-ene-1-carboxylate (32):

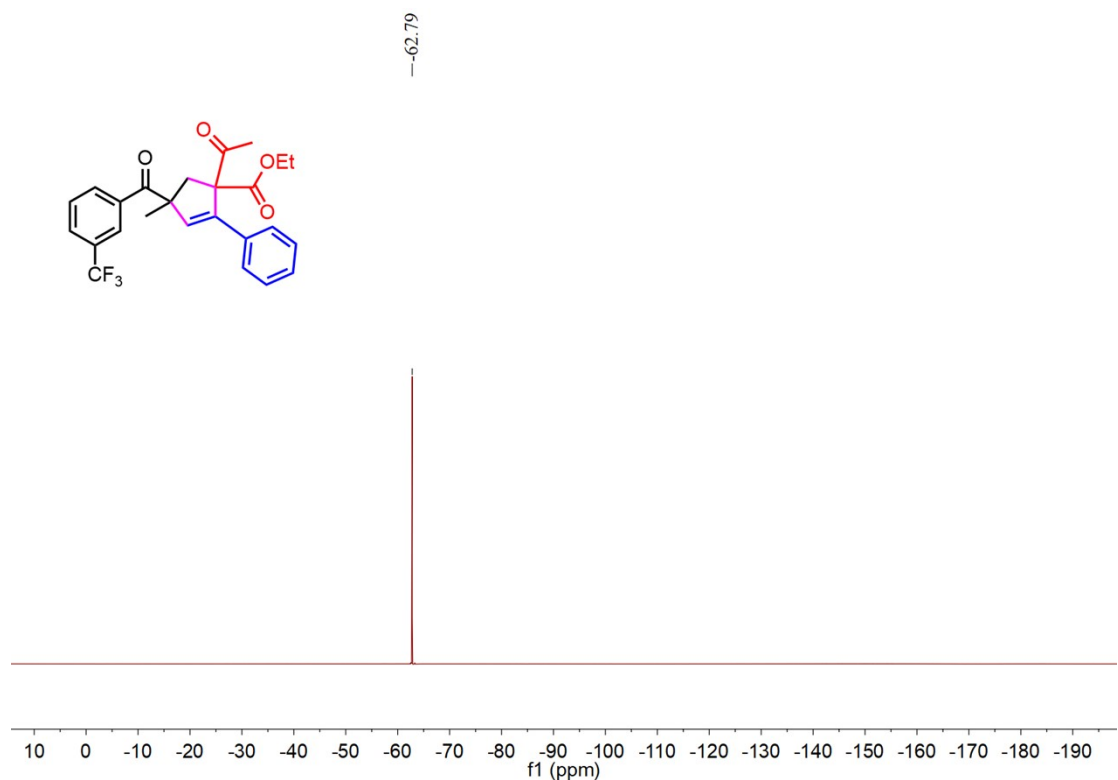


ethyl-1-acetyl-4-(4-chlorobenzoyl)-4-methyl-2-phenylcyclopent-2-ene-1-carboxylate (33):

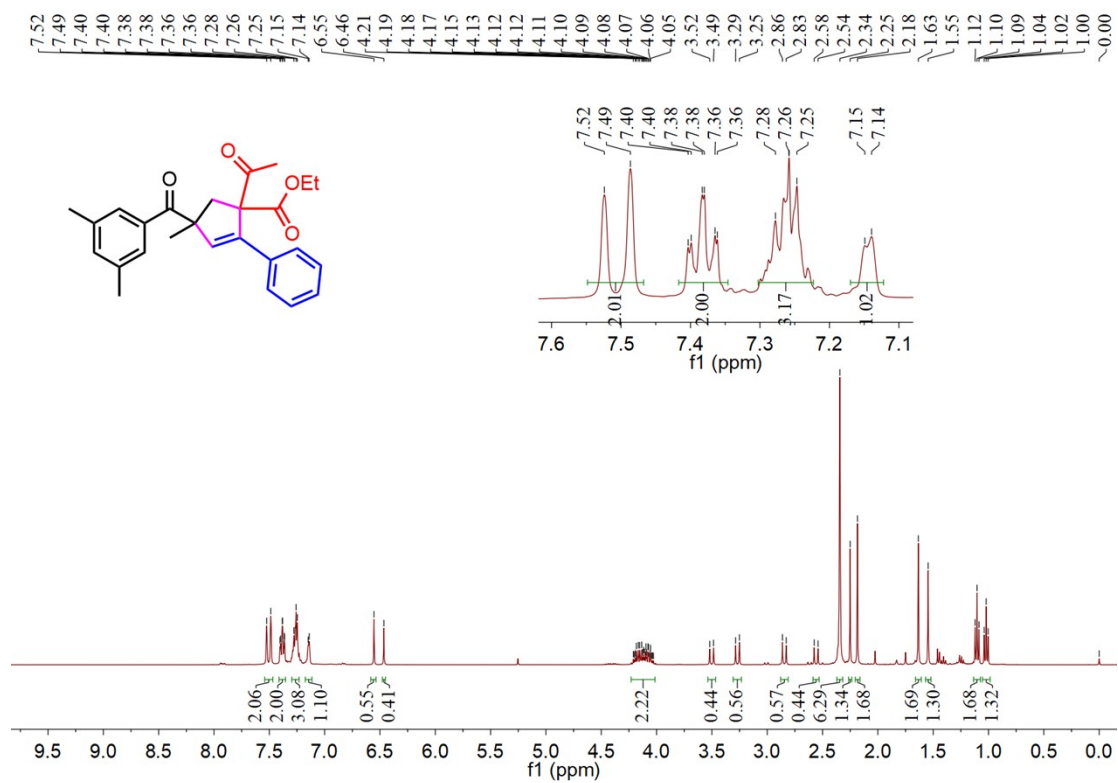


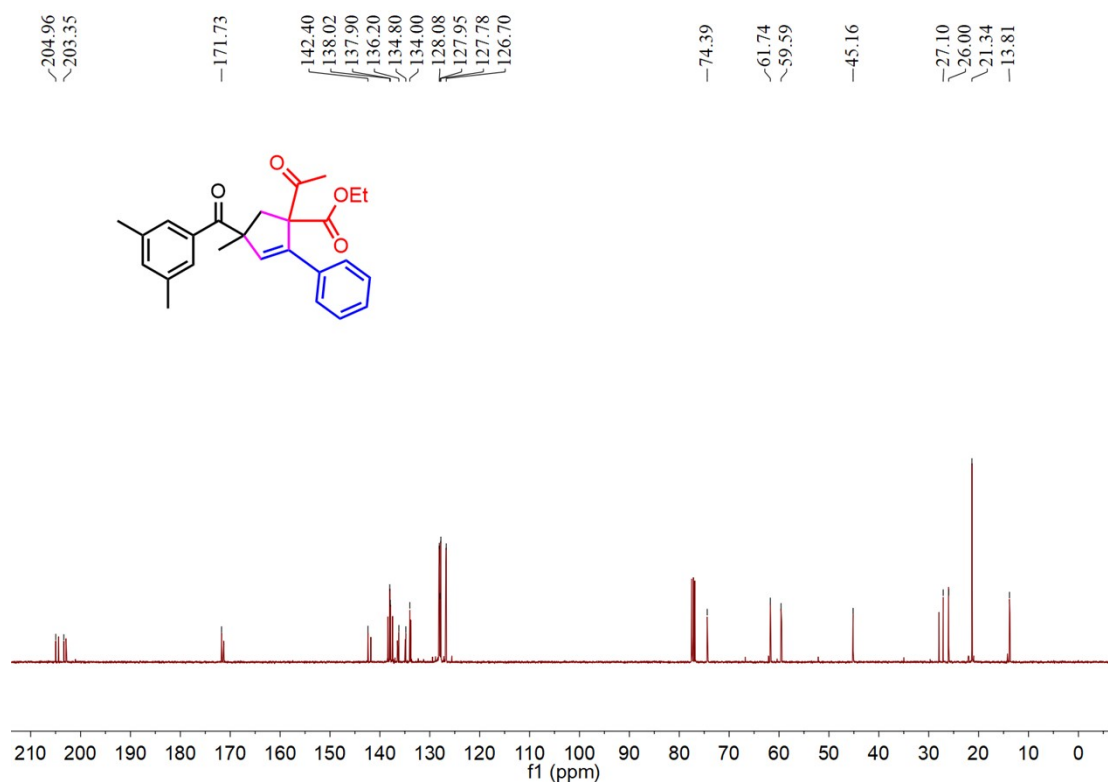
ethyl-1-acetyl-4-methyl-2-phenyl-4-(3-(trifluoromethyl)benzoyl)cyclopent-2-ene-1-carboxylate (34):



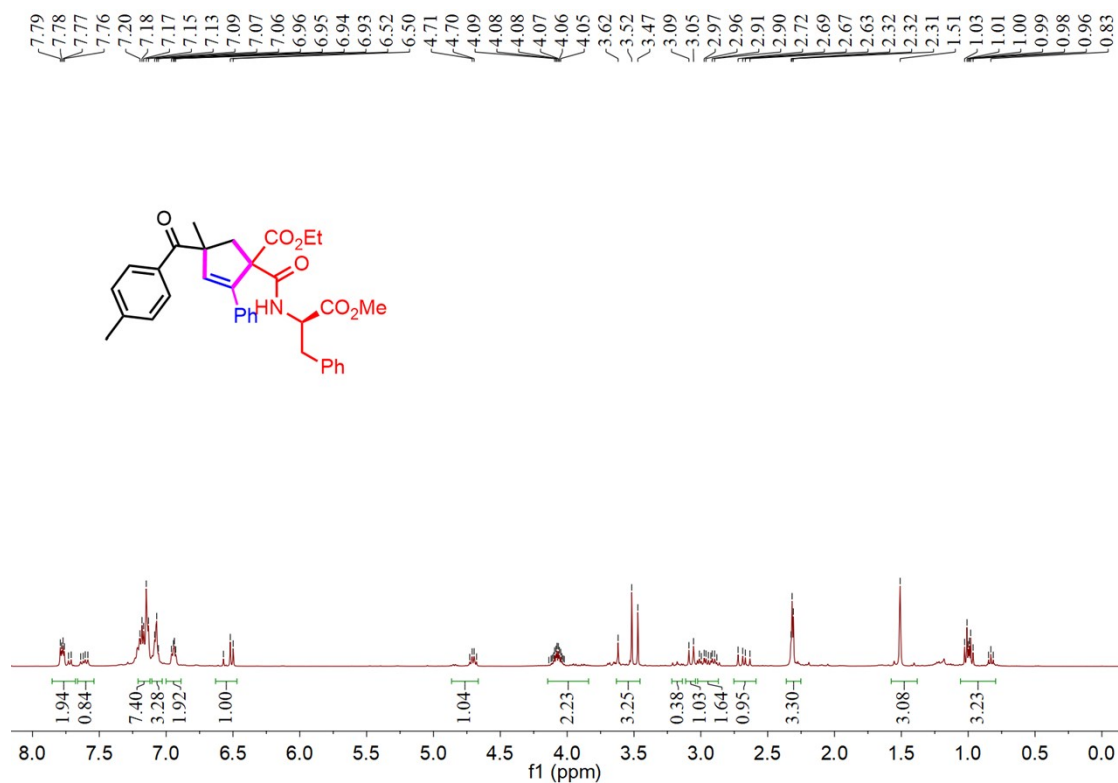


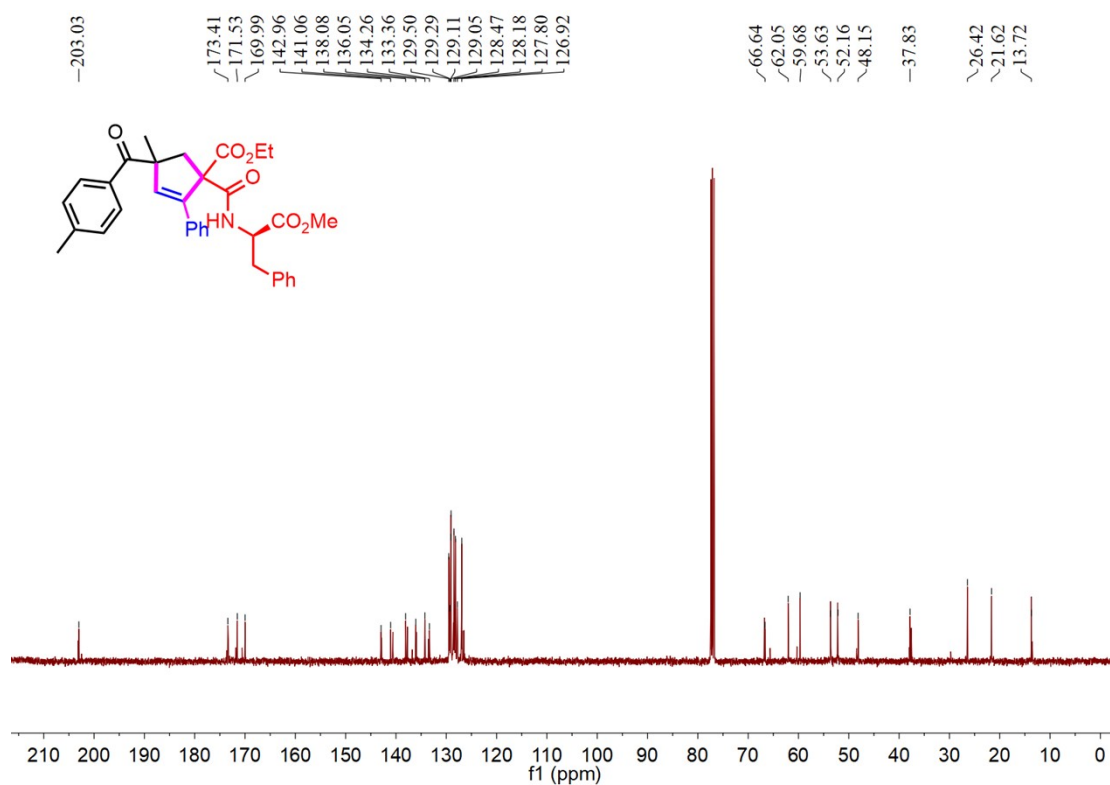
ethyl-1-acetyl-4-(3,5-dimethylbenzoyl)-4-methyl-2-phenylcyclopent-2-ene-1-carboxylate (35):



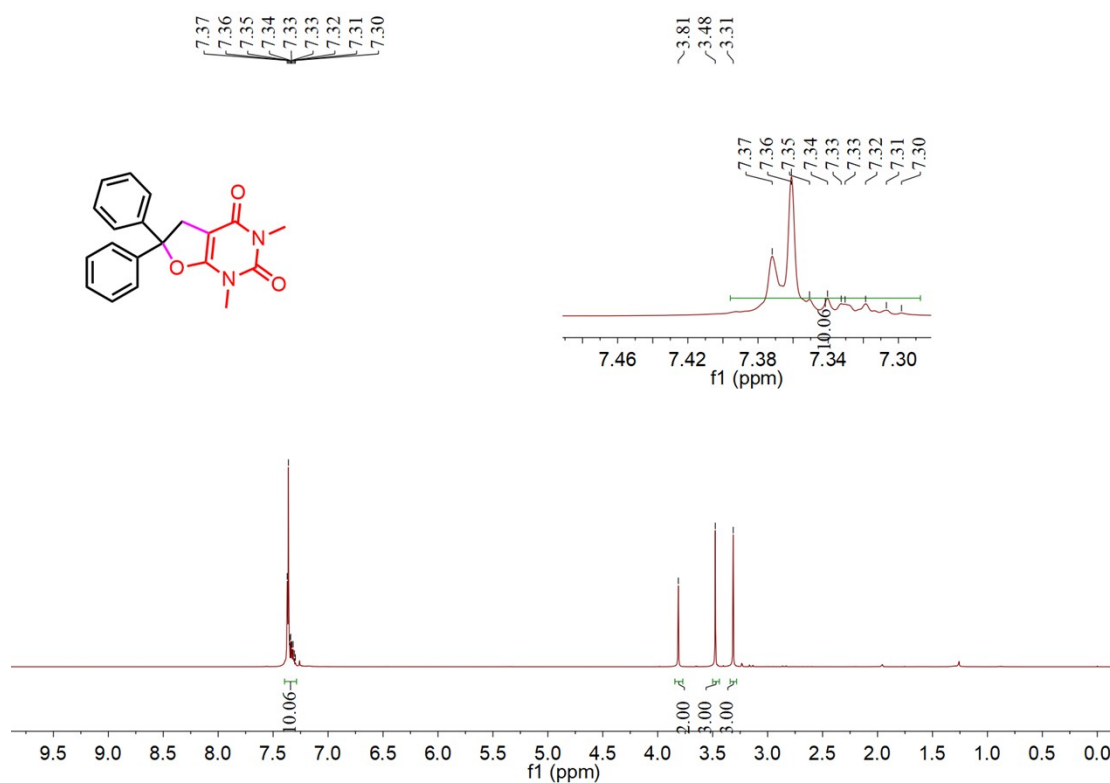


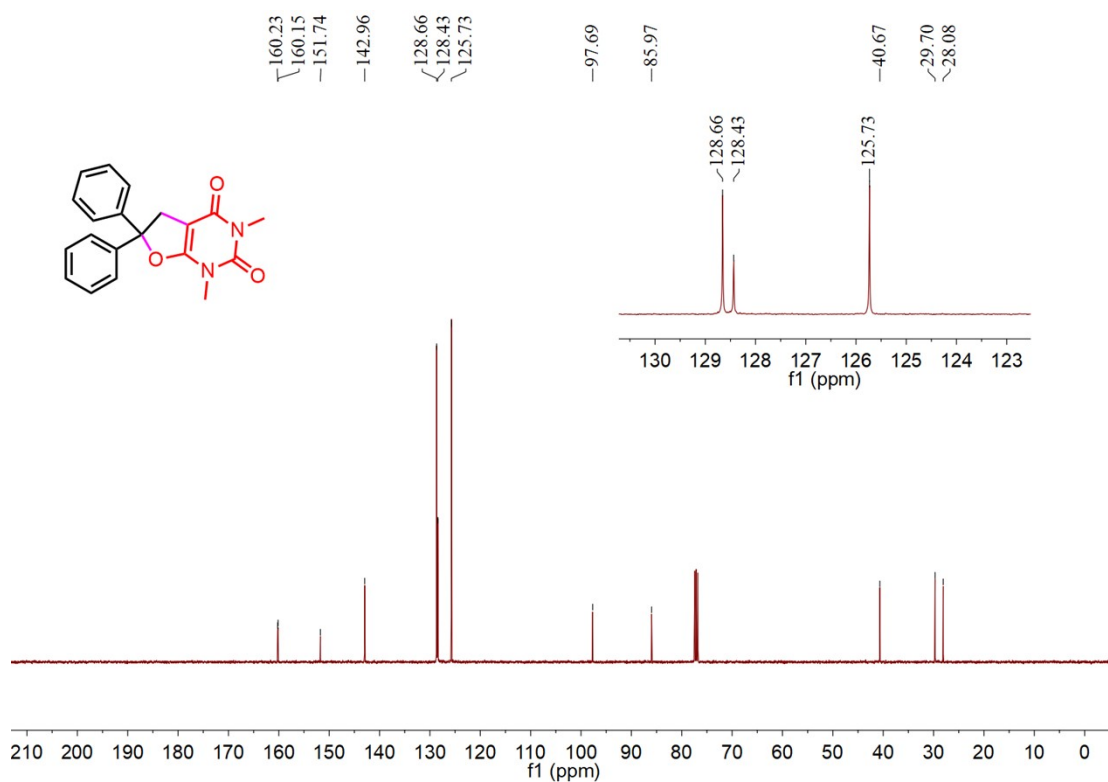
ethyl-4-methyl-4-(4-methylbenzoyl)-2-phenylcyclopent-2-ene-1-carboxylate (36):



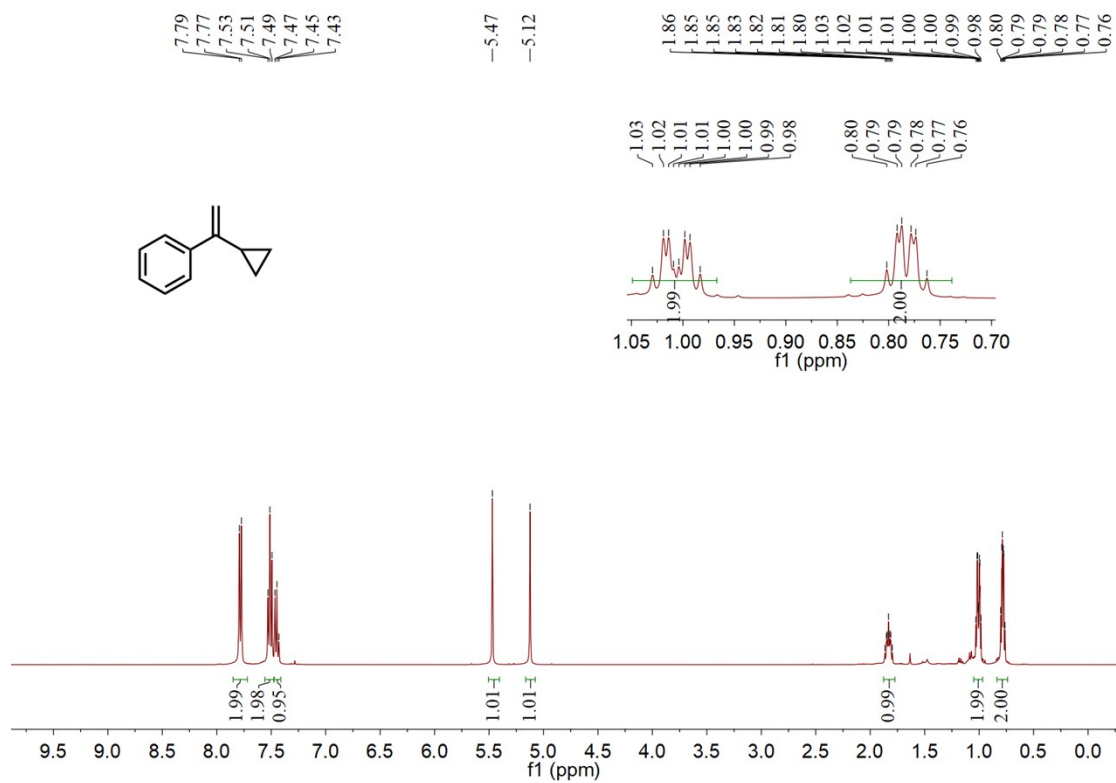


1,3-dimethyl-6,6-diphenyl-5,6-dihydrofuro[2,3-*d*]pyrimidine-2,4(1*H*,3*H*)-dione (37):

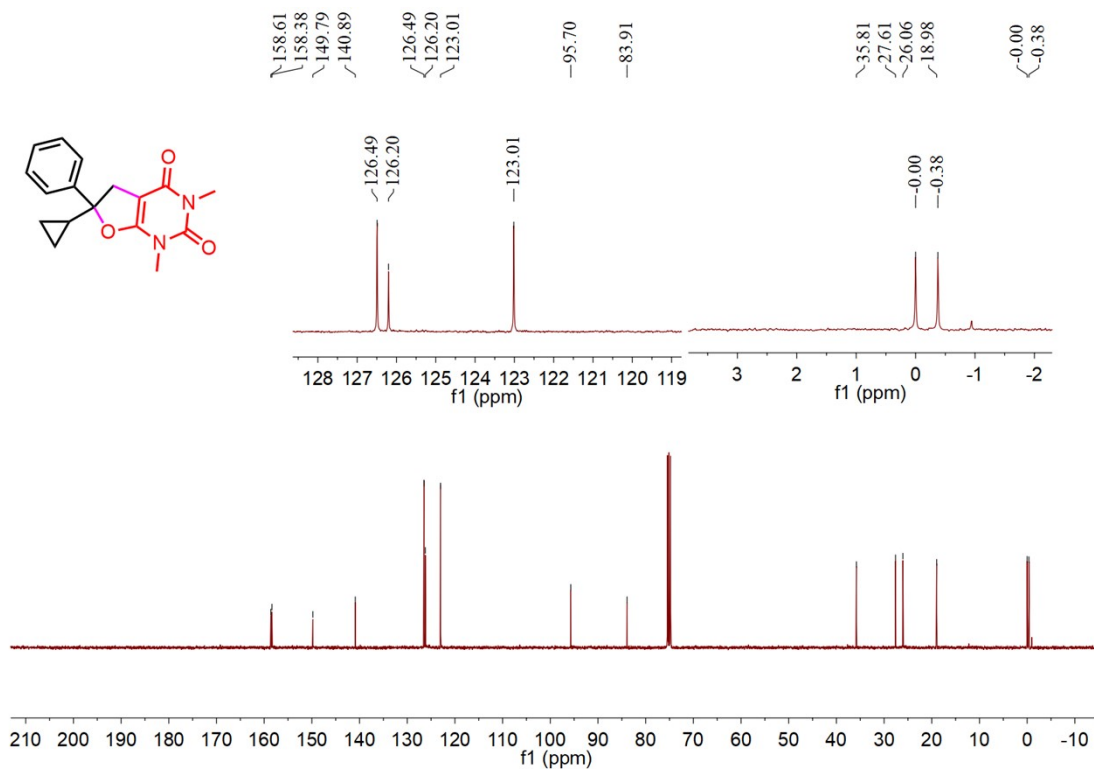
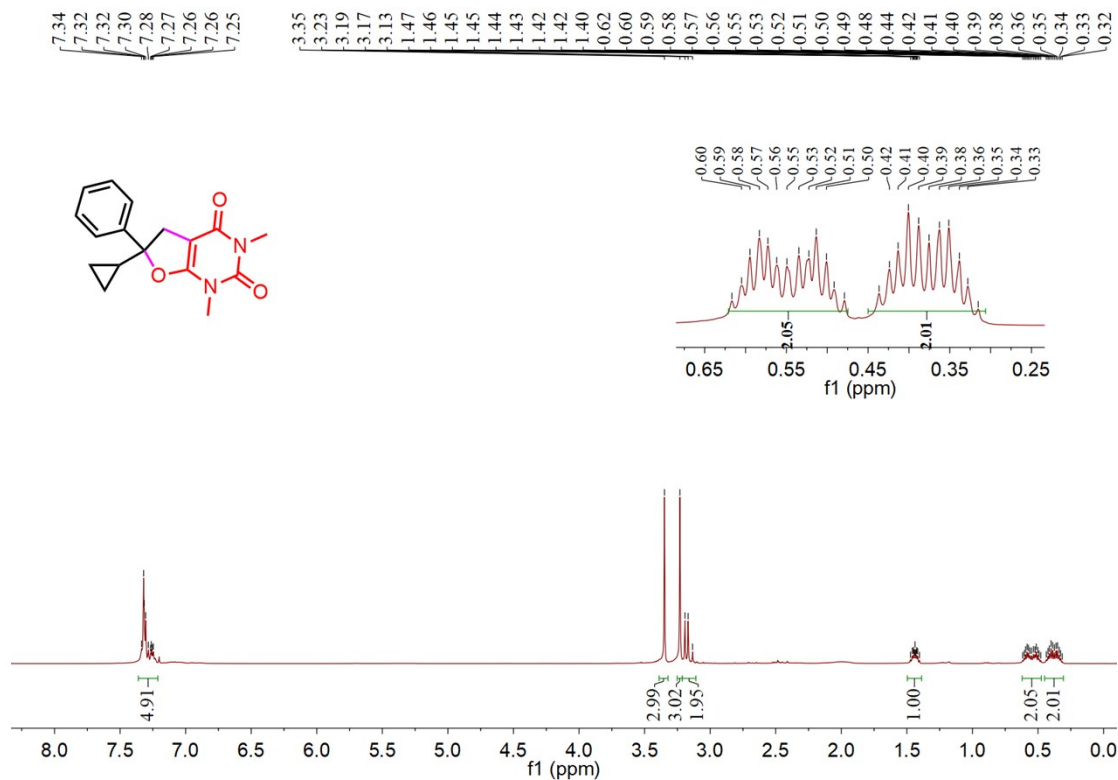




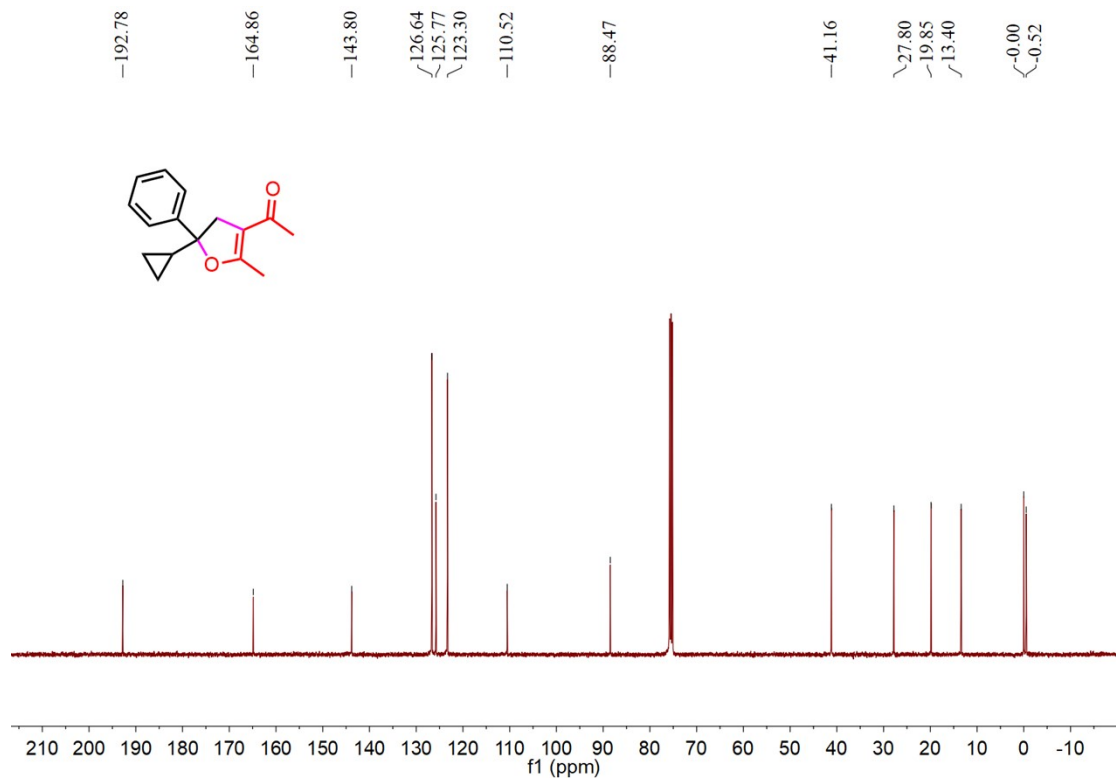
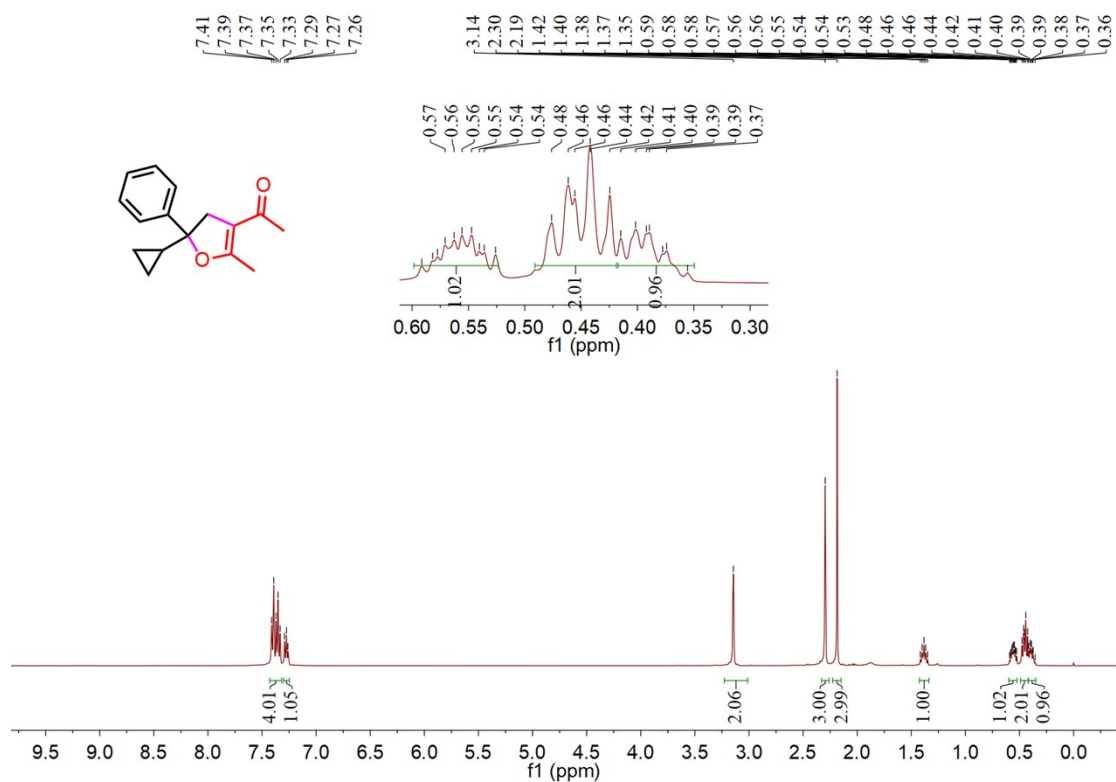
(1-cyclopropylvinyl) benzene (38):



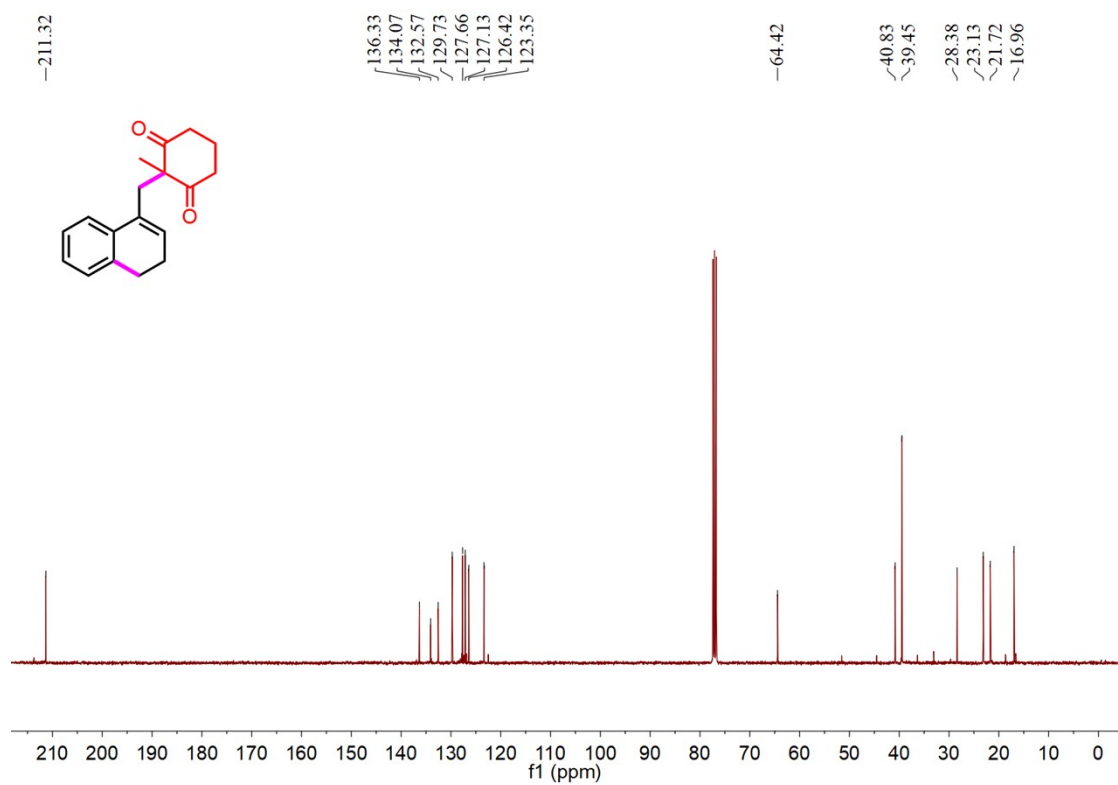
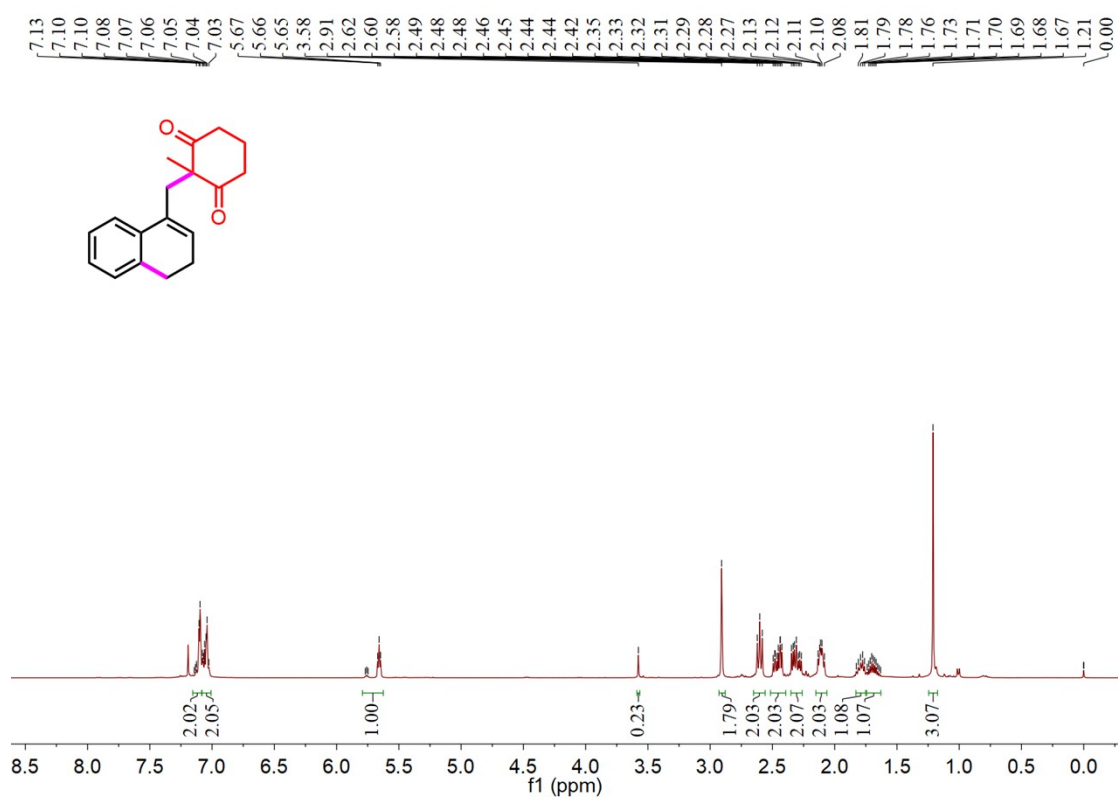
**6-cyclopropyl-1,3-dimethyl-6-phenyl-5,6-dihydrofuro[2,3-*d*]pyrimidine-
2,4(1*H*,3*H*)-dione (39):**



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):

