

**Diastereoselective Synthesis of Spiro[carbazole-3,5'-pyrimidines] and
Spiro[carbazole-3,1'-cyclohexanes] via Four-component Reaction**

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Supporting Information

Figures of the Single crystal structures	s2-s5
Single crystal data	s6-s9
General procedure for the reactions	s10-s11
^1H and $^{13}\text{C}\{1\text{H}\}$ NMR spectra of all compounds	s12 –s115

Single crystals were grown by slow evaporation of concentrated solution in CHCl₃ / DCM / EtOH (compounds **1a**, **1b**, **1c**, **1e**, **1m**, **1k'**, **2o**, **2o'**, **3b** and **4g**) in glass vials, which were then sealed by plugs with needles on them.

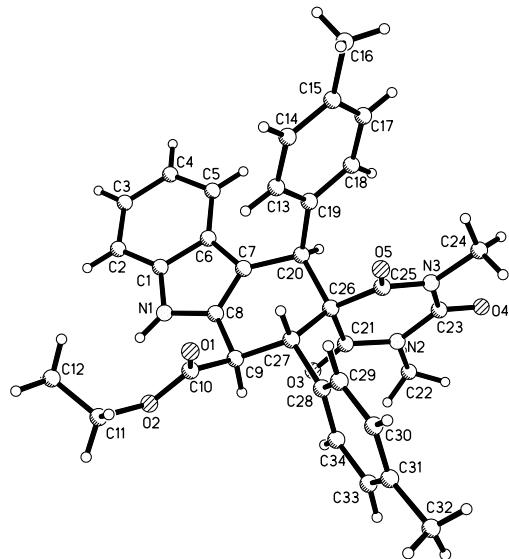


Fig. S1 ORTEP drawing (30%) of the crystal structure of **1a**

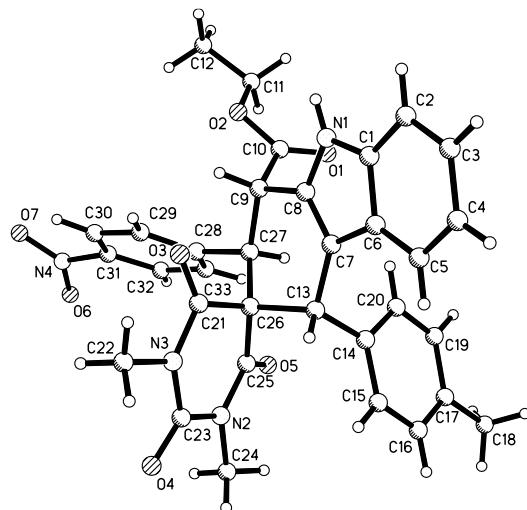


Fig. S2 ORTEP drawing (30%) of the crystal structure of **1b**

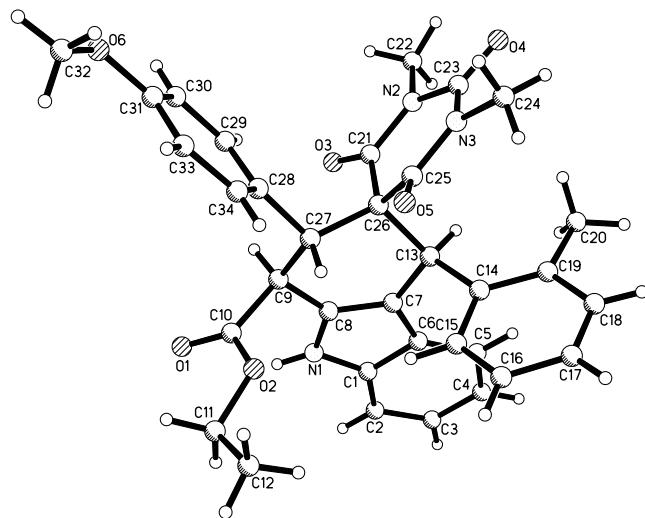


Fig. S3 ORTEP drawing (30%) of the crystal structure of **1c**

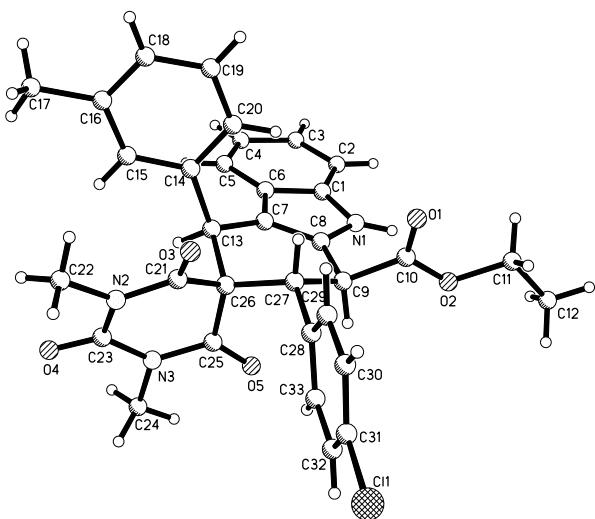


Fig. S4 ORTEP drawing (30%) of the crystal structure of **1e**

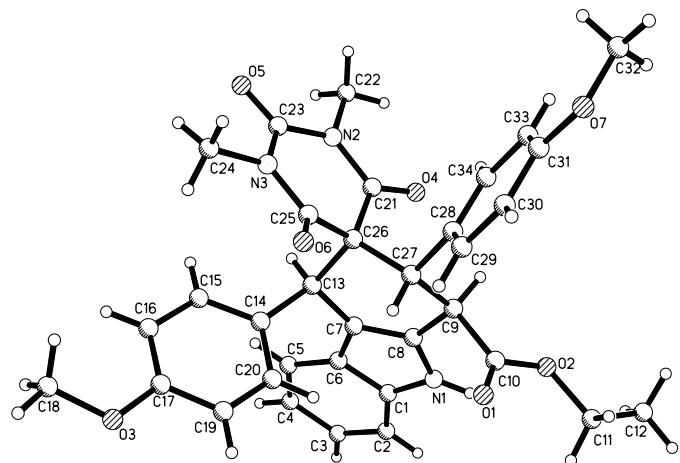


Fig. S5 ORTEP drawing (30%) of the crystal structure of **1m**

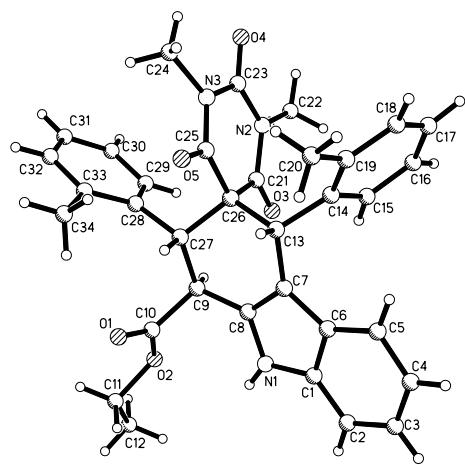


Fig. S6 ORTEP drawing (30%) of the crystal structure of **1k'**

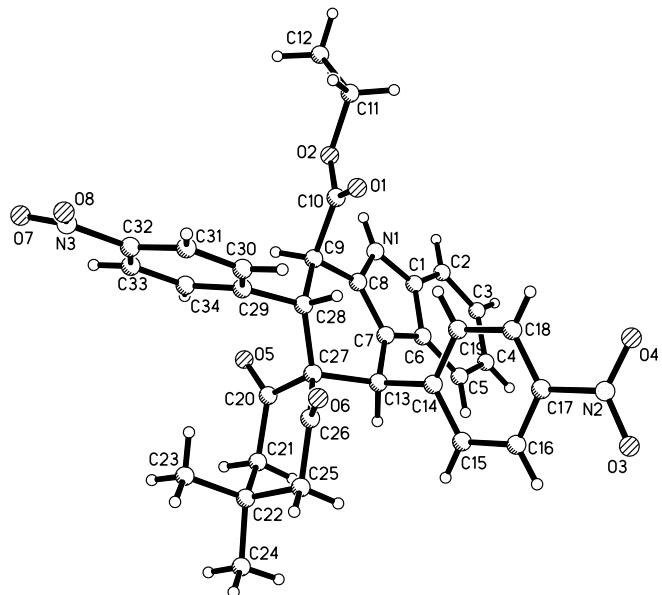


Fig. 7 ORTEP drawing (30%) of the crystal structure of **2o**

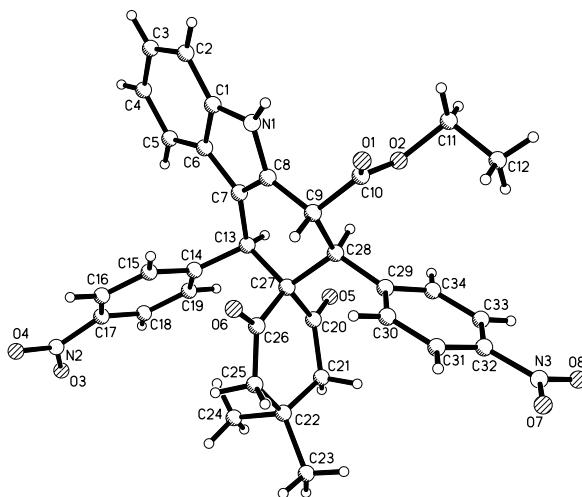


Fig. S8 ORTEP drawing (30%) of the crystal structure of **2o'**

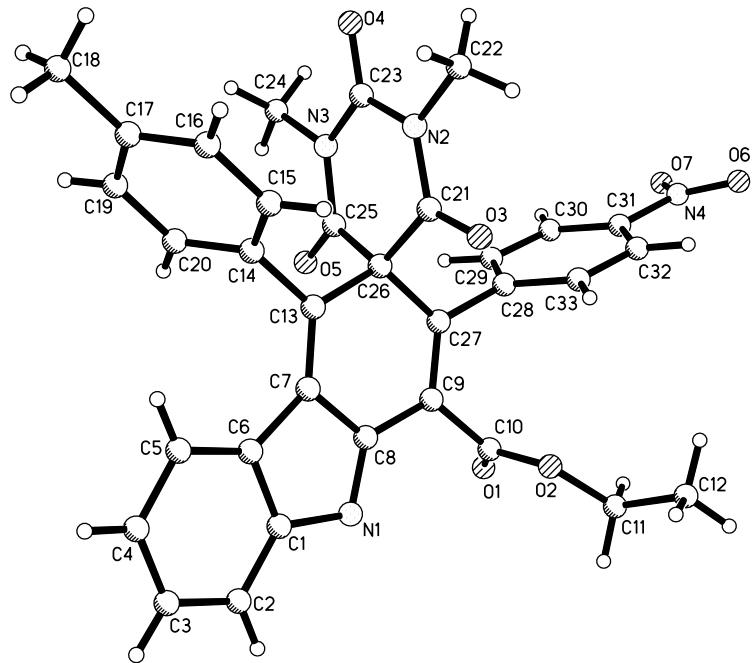


Fig. S9 ORTEP drawing (30%) of the crystal structure of **3b**

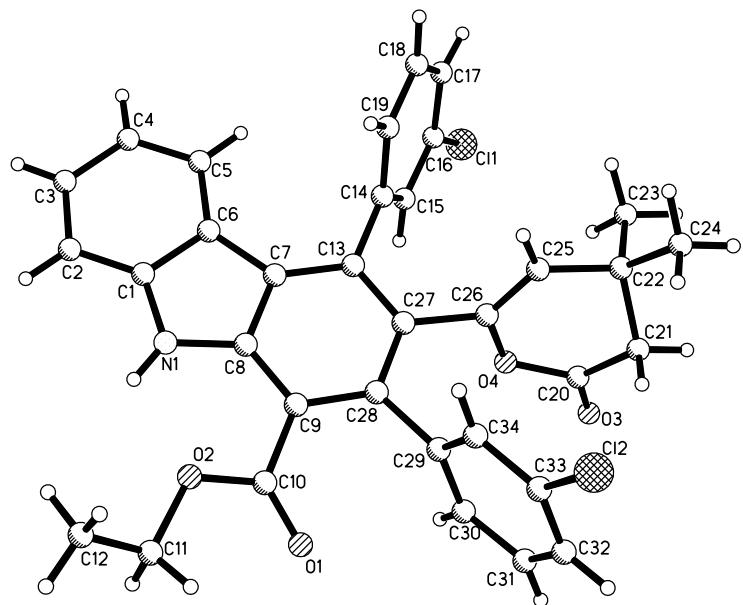


Fig.S10 ORTEP drawing (30%) of the crystal structure of **4g**

Table S1The single crystal date of compounds **1a**, **1b**, **1c**

Phase	1a	1b	1c
Empirical formula	C ₃₄ H ₃₃ N ₃ O ₅	C ₃₃ H ₃₀ N ₄ O ₇	C ₃₄ H ₃₃ N ₃ O ₆
Formula weight	563.63	594.61	579.63
Temperature/K	296(2) K	296(2) K	296(2) K
Wavelength/ Å	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P2(1)/n
<i>a</i> /Å	10.0138(5)	12.1728(16)	11.3100(8)
<i>b</i> /Å	11.7765(6)	13.4083(18)	9.5077(6)
<i>c</i> /Å	12.7363(6)	22.278(3)	27.4588(19)
α (°)	84.6324(15)	86.724(4)	90
β (°)	78.1330(15)	89.748(4)	96.138(3)
γ (°)	84.1528(16)	78.705(4)	90
<i>V</i> (Å ³)	1458.14(13)	3559.7(8)	2935.8(3)
<i>Z</i>	2	4	4
Calculated density (g·cm ⁻³)	1.284	1.109	1.311
Absorption coefficient(mm ⁻¹)	0.087	0.079	0.091
<i>F</i> (000)	596	1248	1224
θ range / (°)	2.086 to 25.998 deg.	1.931 to 25.998 deg.	2.268 to 25.998
Limiting indices	-12<=h<=12, -14<=k<=14, -15<=l<=15	-15<=h<=14, -16<=k<=16, -27<=l<=27	-13<=h<=13, -10<=k<=11, -33<=l<=33
Reflections collected/unique	20829 / 5718 [R(int) = 0.0311]	47241 / 13916 [R(int) = 0.1627]	26618 / 5756 [R(int) = 0.0744]
Completeness to theta	99.6 %	99.5 %	99.9 %
Max. and min. transmission	0.7456 and 0.6875	0.7456 and 0.5936	0.7456 and 0.6830
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data/restraints/parameters	5718 / 0 / 384	13916 / 0 / 801	5756 / 0 / 404
Goodness-of-fit on <i>F</i> ²	1.028	1.020	1.020
Final <i>R</i> indices[I>2sigma(I)]	R1 = 0.0512, wR2 = 0.1208	R1 = 0.0987, wR2 = 0.2202	R1 = 0.0625, wR2 = 0.1231
<i>R</i> indices (all data)	R1 = 0.0792, wR2 = 0.1367	R1 = 0.2259, wR2 = 0.2709	R1 = 0.1611, wR2 = 0.1568
Largest diff. peak and hole /(e · Å ⁻³)	0.218 and -0.265	0.606 and -0.342	0.185 and -0.164

Table S1The single crystal date of compounds **1e**, **1m**, **1k'**

Phase	1e	1m	1k'
Empirical formula	C ₃₃ H ₃₀ ClN ₃ O ₅	C ₃₄ H ₃₃ N ₃ O ₇	C ₃₄ H ₃₃ N ₃ O ₅
Formula weight	584.05	595.63	563.63
Temperature/K	296(2) K	296(2) K	296(2) K
Wavelength/ Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/n	P2(1)/c
<i>a</i> /Å	8.6348(3)	8.8520(7)	17.6658(12)
<i>b</i> /Å	17.8206(7)	18.3198(15)	12.4540(8)
<i>c</i> /Å	18.8901(8)	18.4779(17)	26.766(2)
α (°)	90	90	90
β (°)	94.7464(13)	95.474(3)	95.226(2)
γ (°)	90	90	90
<i>V</i> (Å ³)	2896.8(2)	2982.8(4)	5864.3(7)
<i>Z</i>	4	4	8
Calculated density (g·cm ⁻³)	1.339	1.326	1.277
Absorption coefficient(mm ⁻¹)	0.179	0.094	0.086
<i>F</i> (000)	1224	1256	2384
θ range / (°)	2.164 to 25.997 deg.	2.214 to 25.998	1.528 to 25.999 deg.
Limiting indices	-10<=h<=9, -21<=k<=21, -20<=l<=23	-10<=h<=10, -22<=k<=22, -20<=l<=22	-21<=h<=21, -15<=k<=15, -32<=l<=33
Reflections collected/unique	27001 / 5683 [R(int) = 0.0352]	27845 / 5836 [R(int) = 0.1304]	59155 / 11530 [R(int) = 0.1698]
Completeness to theta	99.6 %	99.8 %	99.9 %
Max. and min. transmission	0.7456 and 0.7042	0.7456 and 0.5371	0.7456 and 0.6887
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data/restraints/parameters	5683 / 48 / 383	5836 / 0 / 402	11530 / 396 / 767
Goodness-of-fit on <i>F</i> ²	1.034	1.004	1.022
Final <i>R</i> indices[I>2sigma(I)]	R1 = 0.0487, wR2 = 0.1118	R1 = 0.0681, wR2 = 0.1163	R1 = 0.1063, wR2 = 0.2190
<i>R</i> indices (all data)	R1 = 0.0792, wR2 = 0.1278	R1 = 0.2193, wR2 = 0.1593	R1 = 0.2613, wR2 = 0.2918
Largest diff. peak and hole (e · Å ⁻³)	0.328 and -0.516	0.197 and -0.188	0.527 and -0.702

Table S2The single crystal date of compounds **2o**, **2o'**

Phase	2o	2o'
Empirical formula	C ₃₄ H ₃₁ N ₃ O ₈	C ₃₄ H ₃₁ N ₃ O ₈
Formula weight	609.62	609.62
Temperature/K	296(2) K	296(2) K
Wavelength/ Å	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/n	P-1
<i>a</i> /Å	13.3152(19)	10.8318(6)
<i>b</i> /Å	11.0682(15)	11.4013(7)
<i>c</i> /Å	20.681	15.4837(8)
α (°)	90.000(4)	105.432(2)
β (°)	96.176(4)	103.175(2)
γ (°)	90	103.079(2)
<i>V</i> (Å ³)	3030.2(6)	1708.79(17)
<i>Z</i>	4	2
Calculated density (g·cm ⁻³)	1.336	1.185
Absorption coefficient(mm ⁻¹)	0.096	0.085
<i>F</i> (000)	1280	640
θ range / (°)	2.090 to 25.999 -16<=h<=16, -13<=k<=13, -25<=l<=20	1.946 to 25.999 -13<=h<=13, -14<=k<=14, -19<=l<=17
Limiting indices		
Reflections collected/unique	23239 / 5934 [R(int) = 0.2259]	17530 / 6537 [R(int) = 0.0475]
Completeness to theta	99.5 %	97.3 %
Max. and min. transmission	0.7456 and 0.6561	0.7456 and 0.6729
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data/restraints/parameters	5934 / 23 / 421	6537 / 205 / 478
Goodness-of-fit on <i>F</i> ²	1.117	1.024
Final <i>R</i> indices[I>2sigma(I)]	R1 = 0.1208, wR2 = 0.2225	R1 = 0.0946, wR2 = 0.2299
<i>R</i> indices (all data)	R1 = 0.1741, wR2 = 0.2476	R1 = 0.1818, wR2 = 0.2804
Largest diff. peak and hole /(e · Å ⁻³)	0.324 and -0.341	0.563 and -0.857

Table S3The single crystal date of compounds **3b**, **4g**

Phase	3b	4g
Empirical formula	C ₃₃ H ₂₆ N ₄ O ₇	C ₃₄ H ₂₇ Cl ₂ NO ₄
Formula weight	590.58	584.46
Temperature/K	273(2) K	296(2) K
Wavelength/ Å	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
<i>a</i> /Å	8.9596(5)	10.7954(11)
<i>b</i> /Å	9.3710(6)	11.0062(10)
<i>c</i> /Å	19.8144(11)	13.5566(12)
α (°)	99.2210(18)	68.256(3)
β (°)	100.1718(17)	87.382(3)
γ (°)	96.4144(19)	86.599(3)
<i>V</i> (Å ³)	1599.44(16)	1493.0(2)
<i>Z</i>	2	2
Calculated density (g·cm ⁻³)	1.226	1.300
Absorption coefficient(mm ⁻¹)	0.088	0.256
<i>F</i> (000)	616	608
θ range / (°)	2.125 to 25.995	2.053 to 25.996
Limiting indices	-10<=h<=11, -11<=k<=11, -24<=l<=24	-13<=h<=13, -13<=k<=13, -16<=l<=16
Reflections collected/unique	22802 / 6250	21316 / 5862
	[R(int) = 0.0351]	[R(int) = 0.0432]
Completeness to theta	99.5 %	99.8 %
Max. and min. transmission	0.7456 and 0.6860	0.7456 and 0.6956
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data/restraints/parameters	6250 / 15 / 402	5862 / 0 / 373
Goodness-of-fit on <i>F</i> ²	1.015	1.034
Final <i>R</i> indices[I>2sigma(I)]	R1 = 0.0602, wR2 = 0.1498	R1 = 0.0788, wR2 = 0.2039
<i>R</i> indices (all data)	R1 = 0.0960, wR2 = 0.1709	R1 = 0.1288, wR2 = 0.2348
Largest diff. peak and hole (e · Å ⁻³)	0.424 and -0.347	1.021 and -0.567

Experimental section

Unless noted, the commercial reagents and solvents were used without further purification.

Melting points were recorded with a micromelting point apparatus and are uncorrected. IR spectra were recorded using a Bruker Tensor 27 spectrometer (KBr disc). The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded with a Varian 400 spectrometer at 400 or 100 MHz. High-resolution mass spectra (HRMS) were recorded in ESI mode using a MicroTOF mass spectrometer. Single-crystal X-ray data were collected with a Bruker Smart APEX-2 CCD diffractometer. All reactions were monitored by thin-layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were monitored by observation under UV light (254 and 365 nm).

1. General procedures for the Synthesis of functionalized spiro[carbazole-3,5'-pyrimidines]

spiro[carbazole-2,4'-pyrazoles] via three-component reaction: A mixture of indole-2-acetate (0.5 mmol), aldehyde (0.6 mmol) and 2-arylidene-1,3'-dimethylbarbituric acid (0.5 mmol) in dry toluene (6.0 mL) was stirred at 110°C for three hours. After removing the solvent by evaporating at reduced pressure, the residue was subjected to column chromatography with ethyl acetate and light petroleum (V/V=1:5-1:8) to give pure **1a-1j** and **1a'-1j'**.

2. General procedures for the Synthesis of functionalized spiro[carbazole-3,5'-pyrimidines]

spiro[carbazole-2,4'-pyrazoles] via four-component reaction: A mixture of indole-2-acetate (0.5 mmol), aldehyde (1.0 mmol) and 1,3'-dimethylbarbituric acid (0.5 mmol) in dry toluene (6.0 mL) was stirred at 110°C for three hours. After removing the solvent by evaporating at reduced pressure, the residue was subjected to column chromatography with ethyl acetate and light petroleum (V/V=1:5-1:8) to give pure **1k-1r** and **1k'-1r'**.

3. General procedures for the Synthesis of functionalized spiro[carbazole-3,1'-cyclohexanes]

via four-component reaction: A mixture of indole-2-acetate (0.5 mmol), aromatic aldehyde (1.0 mmol) and cyclohexane-1,3-dione or dimedone (0.5 mmol) in dry toluene (6.0 mL) was stirred at 110°C for three hours. After removing the solvent by evaporating at reduced pressure, the residue was subjected to column chromatography with ethyl acetate and light petroleum (V/V=1:4-1:8) to give pure **2a-2o** and **2a'-2o'**.

4. General procedures for the Synthesis of functionalized spiro[carbazole-3,5'-pyrimidines]

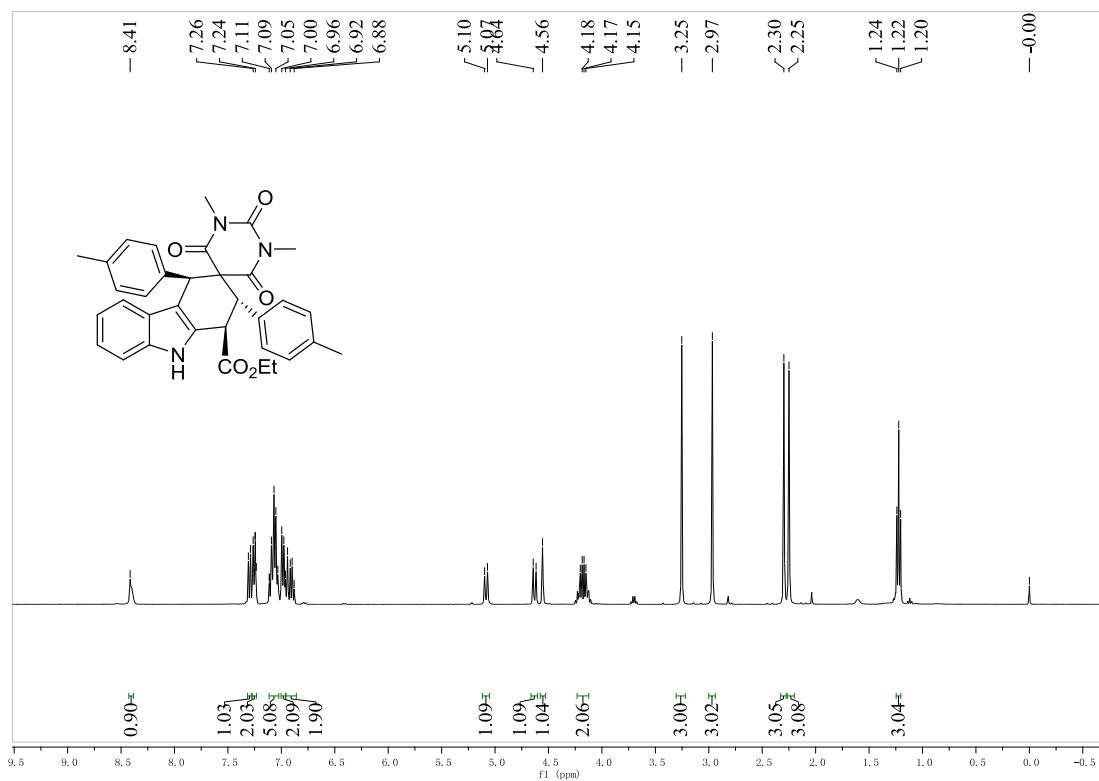
3a-3d: A mixture of indole-2-acetate (0.5 mmol), aldehyde (0.6 mmol) and 2-arylidene-1,3'-dimethylbarbituric acid (0.5 mmol) in dry toluene (6.0 mL) was stirred at 110°C for three hours. After removing the solvent by evaporating at reduced pressure, DDQ (1.0 mmol) and acetonitrile (10. 0 mL) was added. The suspension was stirred at room temperature for four hours. Then, the solvent was removed at reduced pressure. The residue was subjected to column chromatography with ethyl acetate and light petroleum (V/V=1:3 ~ 1:6) to give pure product **3a-3d**.

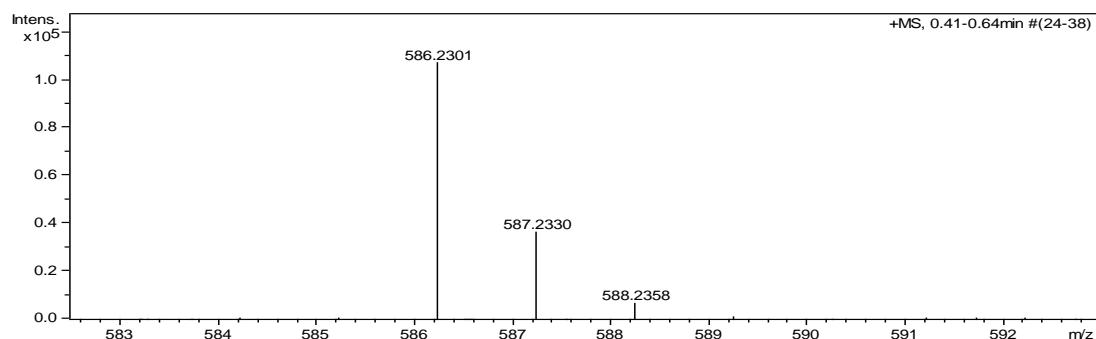
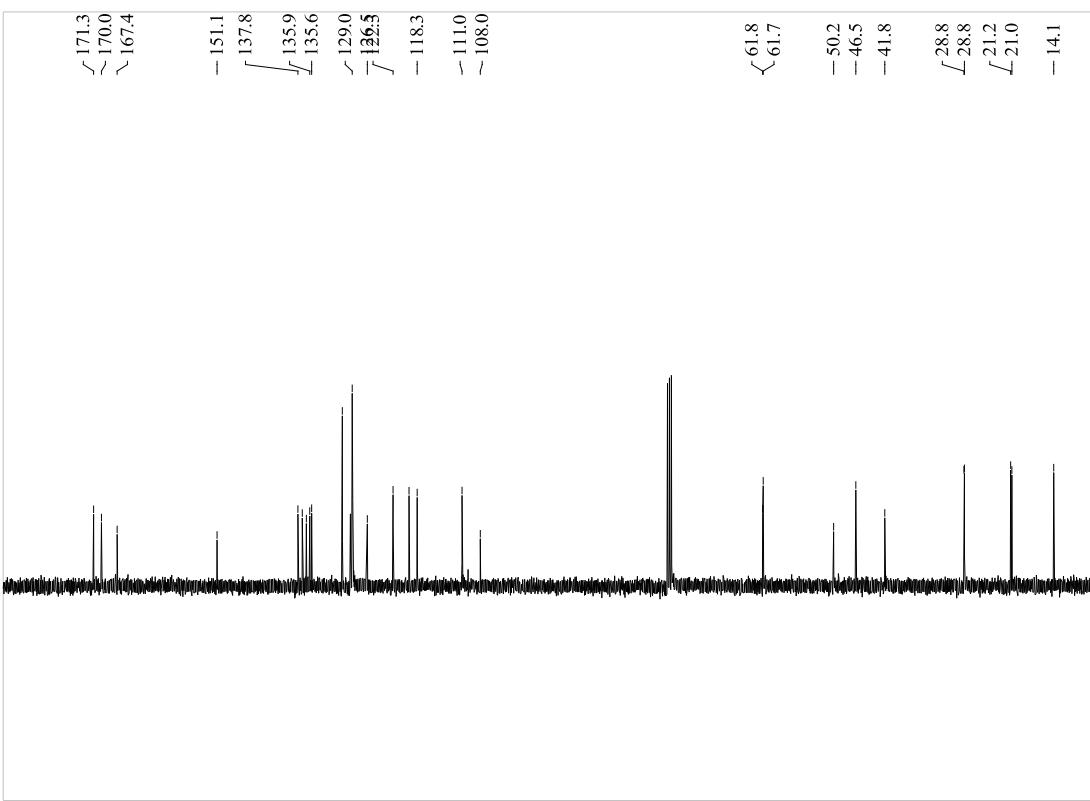
5. General procedures for the Synthesis of functionalized δ-valerolactone-substituted carbazoles **4a-4g:** A mixture of indole-2-acetate (0.5 mmol), aromatic aldehyde (1.0 mmol) and cyclohexane-1,3-dione or dimedone (0.5 mmol) in dry toluene (6.0 mL) was stirred at 110°C for three hours. After removing the solvent by evaporating at reduced pressure, DDQ (1.0 mmol) and acetonitrile (10. 0 mL) was added. The suspension was stirred at room temperature for four hours. Then, the solvent was removed at reduced pressure. The residue was subjected to column chromatography with ethyl acetate and light petroleum (V/V=1:3 ~ 1:6) to give pure product **4a-4g**.

Ethyl

*rel-(1*R*,2*S*,4*R*)-1',3'-dimethyl-2',4',6'-trioxo-2,4-di-*p*-tolyl-1,1',2,3',4,4',6',9-octahydro-2'H-spiro[carbazole-3,5'-pyrimidine]-1-carboxylate (1a):*

yellow solid, 70%, m.p. 206-208 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.42 (s, 1H, NH), 7.29 (d, J = 8.4 Hz, 1H, ArH), 7.26-7.23 (m, 2H, ArH), 7.11-7.03 (m, 5H, ArH), 6.99-6.96 (m, 2H, ArH), 6.94-6.88 (m, 2H, ArH), 5.08 (d, J = 10.8 Hz, 1H, CH), 4.63 (d, J = 10.8 Hz, 1H, CH), 4.56 (s, 1H, CH), 4.17 (q, J = 7.2 Hz, 2H, CH_2), 3.25 (s, 3H, CH_3), 2.97 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 1.22 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (400 MHz, CDCl_3) δ : 171.2, 169.9, 167.4, 151.0, 137.8, 137.1, 136.4, 135.9, 135.5, 130.5, 128.9, 126.4, 122.2, 119.6, 118.3, 110.9, 107.9, 61.7, 61.6, 50.1, 46.5, 41.7, 28.8, 28.7, 21.1, 20.9, 14.1; IR(KBr) ν : 3350, 3245, 3167, 3055, 2932, 2852, 2812, 1852, 1666, 1632, 1544, 1432, 1325, 1207, 1132, 1109, 978, 923, 856, 742 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{34}\text{H}_{33}\text{N}_3\text{O}_5([\text{M}+\text{Na}]^+)$: 586.2312, found: 586.2301.

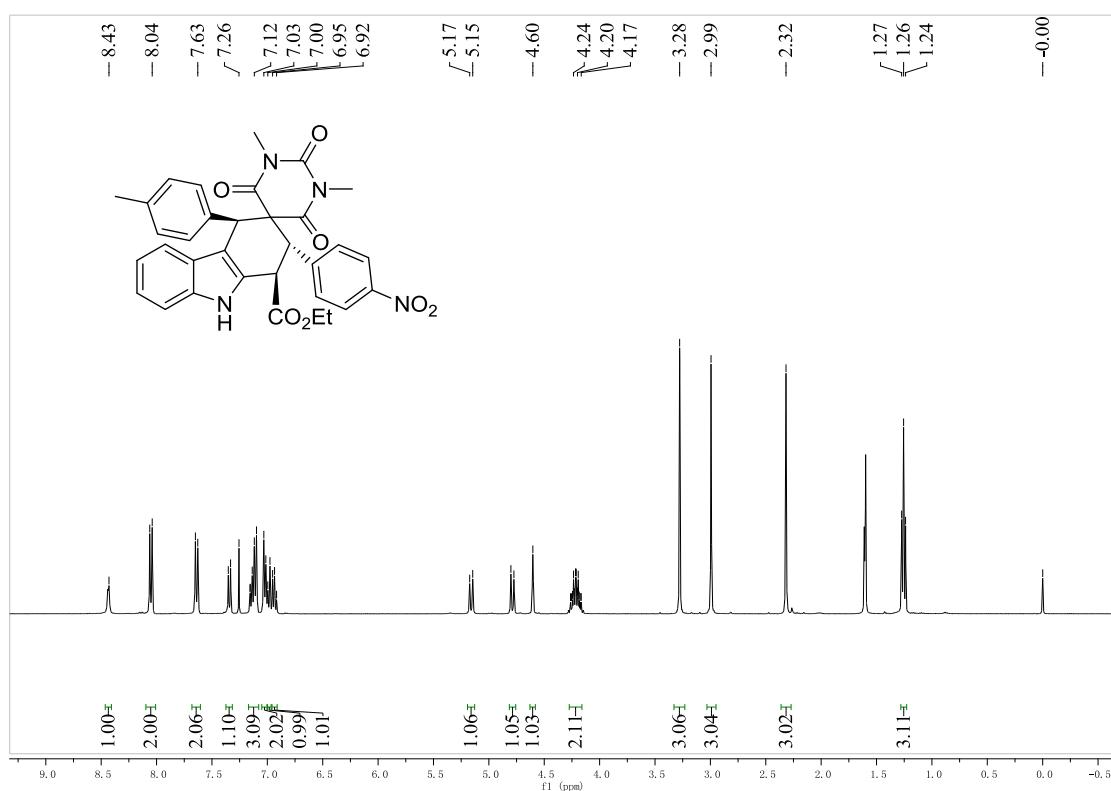


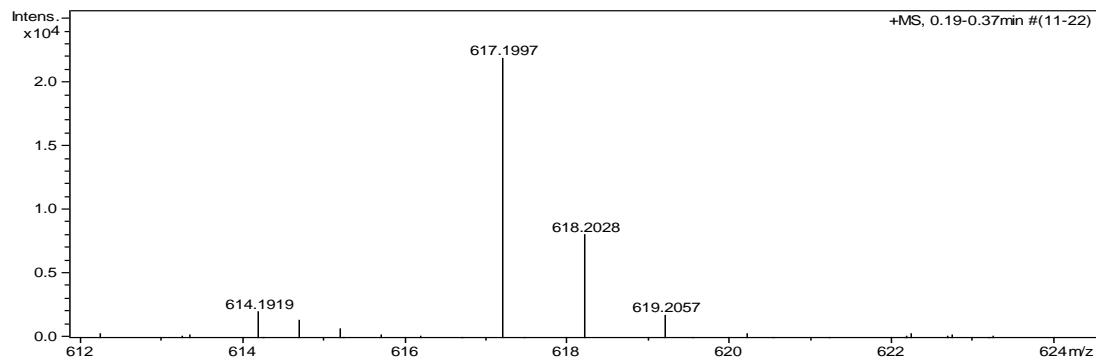
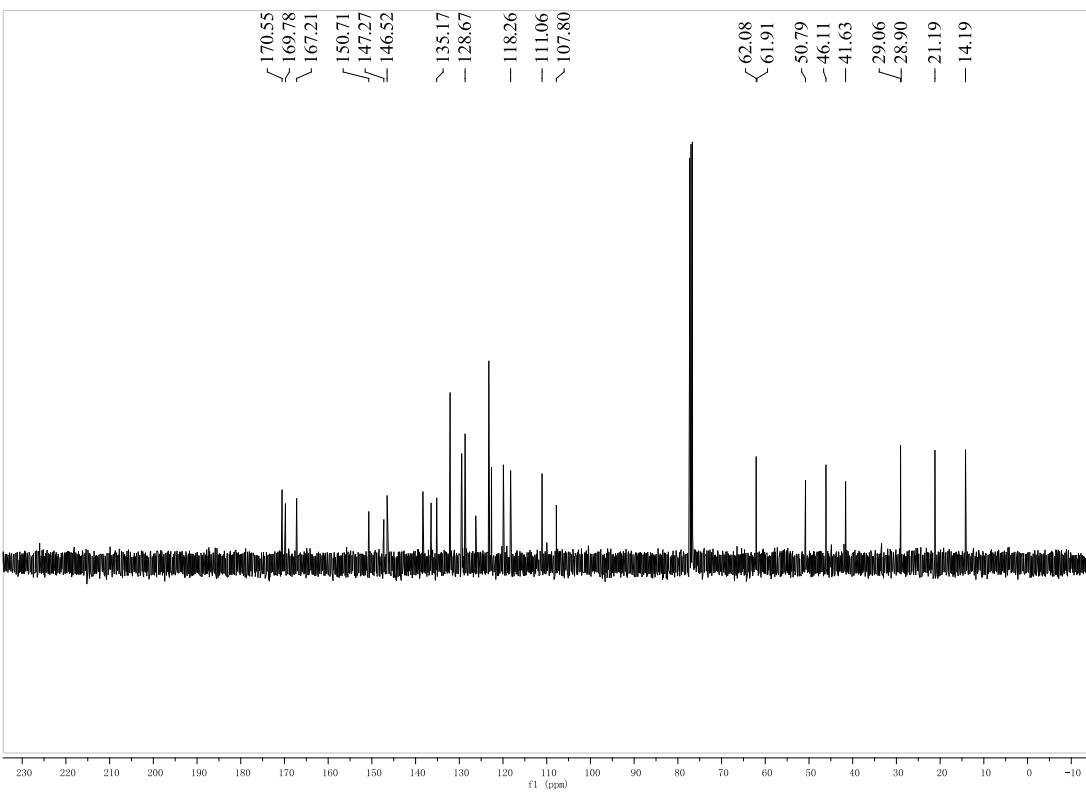


Ethyl

*rel-(1*R*,2*S*,4*R*)-1',3'-dimethyl-2-(4-nitrophenyl)-2',4',6'-trioxo-4-(*p*-tolyl)-1,1',2,3',4,4',6',9-octahydro-2'H-spiro[carbazole-3,5'-pyrimidine]-1-carboxylate (1b):*

yellow solid, 58%, m.p. 210-214 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.43 (s, 1H, NH), 8.05 (d, J = 8.8 Hz, 2H, ArH), 7.26-7.23 (m, 2H, ArH), 7.11-7.03 (m, 5H, ArH), 6.99-6.96 (m, 2H, ArH), 6.95-6.92 (m, 2H, ArH), 5.16 (d, J = 10.8 Hz, 1H, CH), 4.63 (d, J = 10.8 Hz, 1H, CH), 4.60 (s, 1H, CH), 4.20 (q, J = 7.2 Hz, 2H, CH_2), 3.28 (s, 3H, CH_3), 2.99 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 1.26 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (400 MHz, CDCl_3) δ : 170.5, 169.7, 167.2, 150.7, 147.2, 146.5, 138.3, 136.4, 135.1, 132.1, 129.4, 128.6, 123.2, 122.6, 119.9, 118.2, 111.0, 107.7, 62.0, 61.9, 50.7, 46.1, 41.6, 29.0, 28.9, 21.1, 14.1; IR(KBr) ν : 3390, 3275, 3234, 3167, 3049, 2932, 2852, 2836, 2014, 1853, 1672, 1613, 1554, 1489, 1367, 1289, 1145, 1112, 980, 923, 834, 742 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{33}\text{H}_{30}\text{N}_4\text{O}_7$ ([M+Na] $^+$): 617.2007, found: 617.1997.

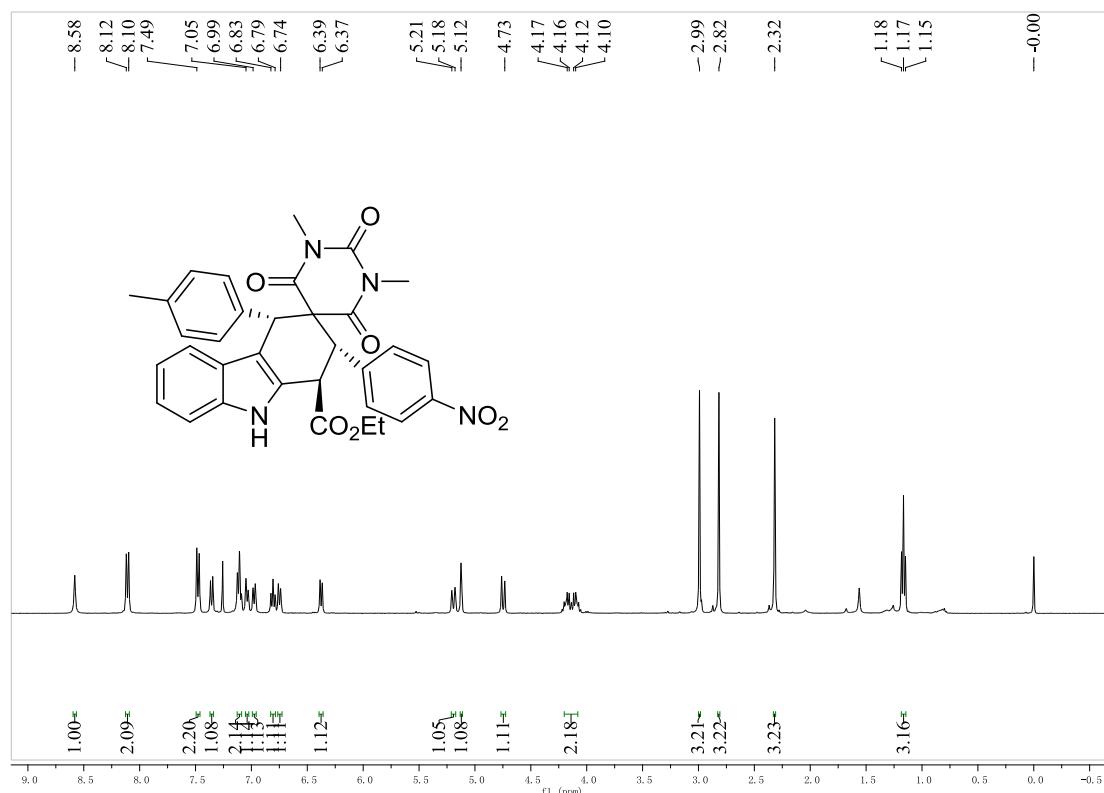


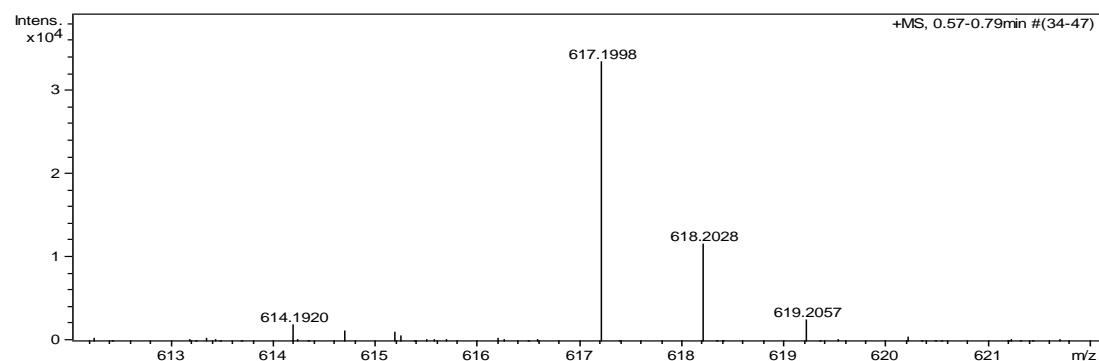
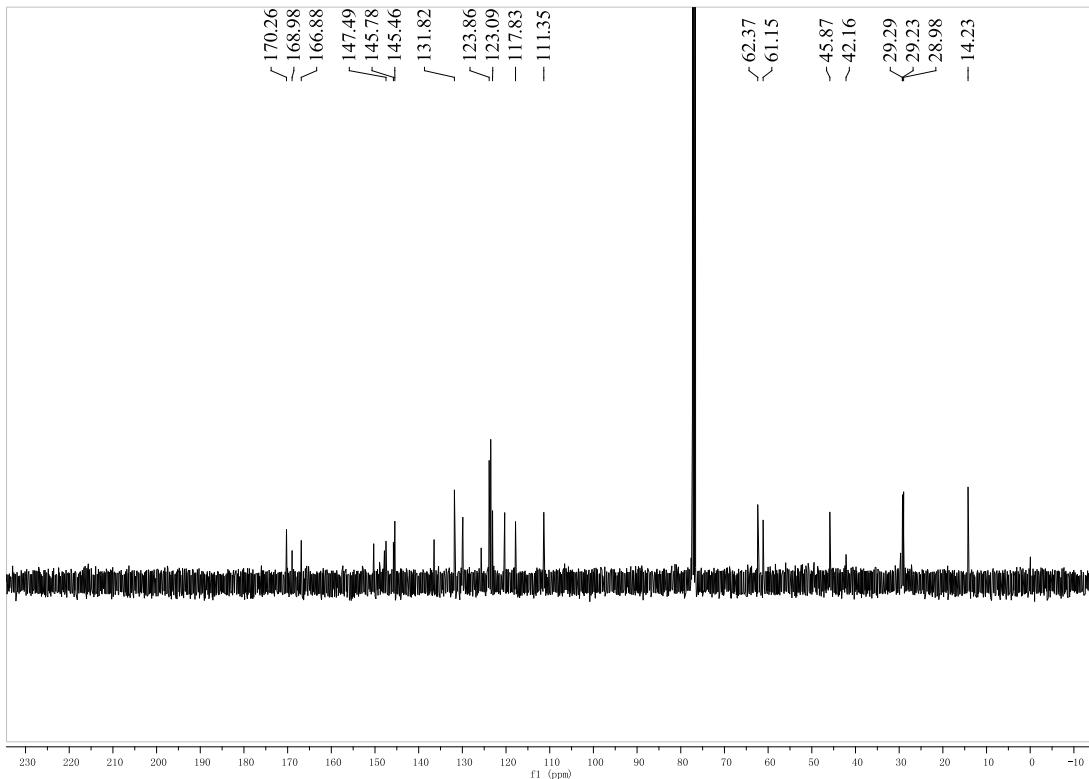


Ethyl

*rel-(1*R*,2*S*,4*S*)-1',3'-dimethyl-2-(4-nitrophenyl)-2',4',6'-trioxo-4-(*p*-tolyl)-1,1',2,3',4,4',6',9-octahydro-2'H-spiro[carbazole-3,5'-pyrimidine]-1-carboxylate (1b'):*

yellow solid, 7%, m.p. 216–218 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.58 (s, 1H, NH), 8.11 (d, J = 8.8 Hz, 2H, ArH), 7.48 (d, J = 8.8 Hz, 2H, ArH), 7.35 (d, J = 8.0 Hz, 2H, ArH), 7.11 (d, J = 7.6 Hz, 2H, ArH), 7.04 (d, J = 8.0 Hz, 1H, ArH), 6.98 (d, J = 8.0 Hz, 1H, ArH), 6.81 (t, J = 7.6 Hz, 1H, ArH), 6.75 (d, J = 8.0 Hz, 1H, ArH), 6.38 (d, J = 8.0 Hz, 1H, ArH), 5.19 (d, J = 7.6 Hz, 1H, CH), 5.13 (s, 1H, CH), 4.15 (d, J = 7.6 Hz, 1H, CH), 4.13 (q, J = 7.2 Hz, 2H, CH_2), 2.99 (s, 3H, CH_3), 2.82 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 1.17 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (400 MHz, CDCl_3) δ : 170.2, 168.9, 166.8, 150.2, 147.8, 147.4, 145.7, 145.4, 136.4, 131.8, 129.9, 129.8, 125.6, 123.8, 123.5, 123.0, 120.3, 117.8, 111.3, 62.3, 61.1, 45.8, 42.1, 29.6, 29.2, 29.2, 28.9, 14.2; IR(KBr) ν : 3372, 3260, 3182, 3042, 2976, 2832, 2806, 1844, 1672, 1643, 1521, 1416, 1373, 1268, 1172, 1132, 978, 924, 856, 742 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{33}\text{H}_{30}\text{N}_4\text{O}_7(\text{M}+\text{Na})^+$: 617.2007, found: 617.1998.

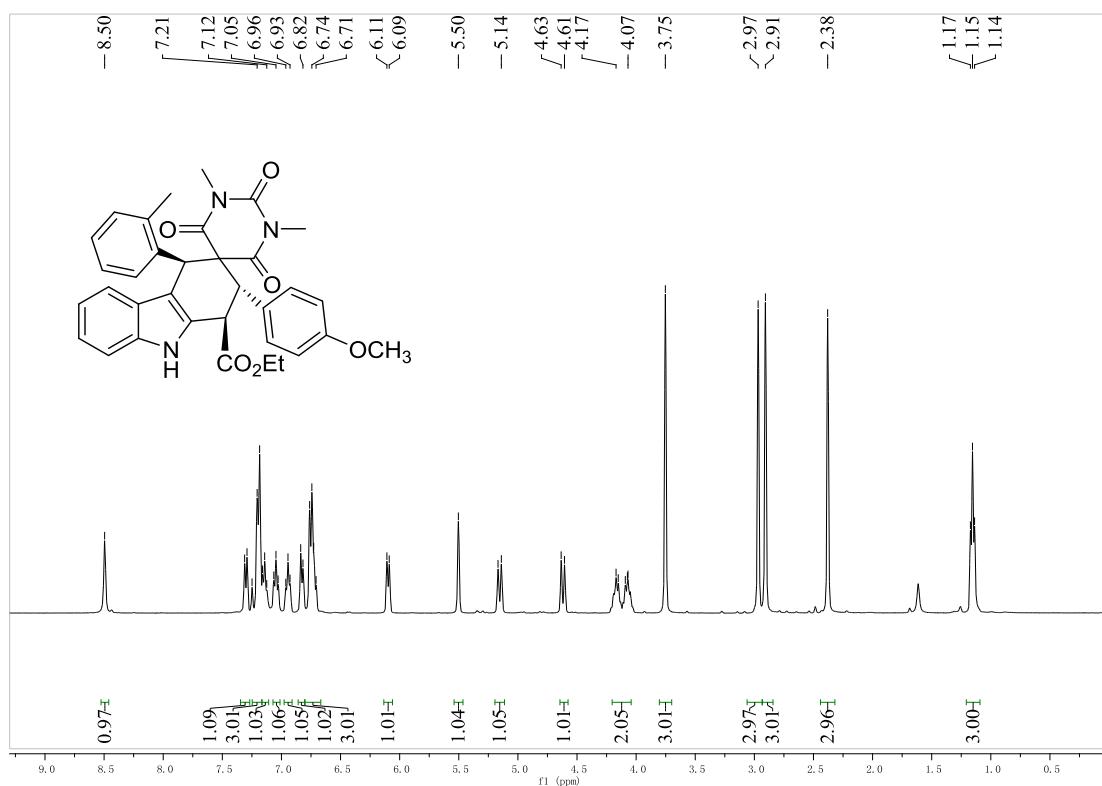


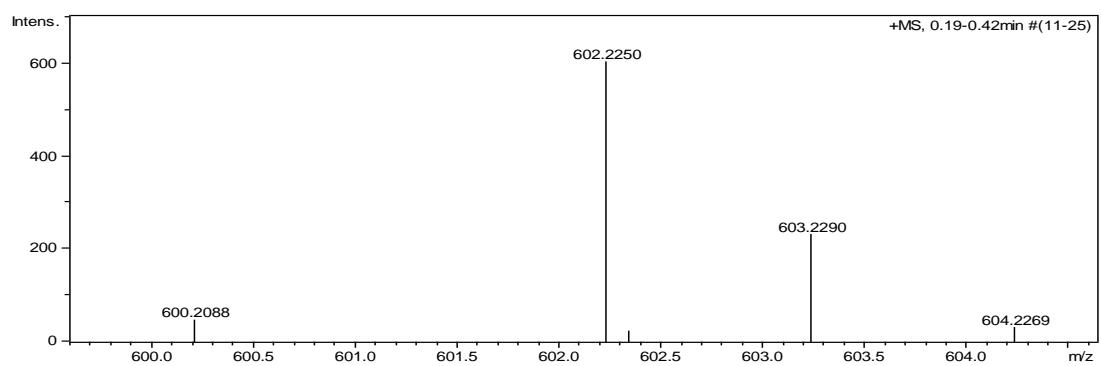
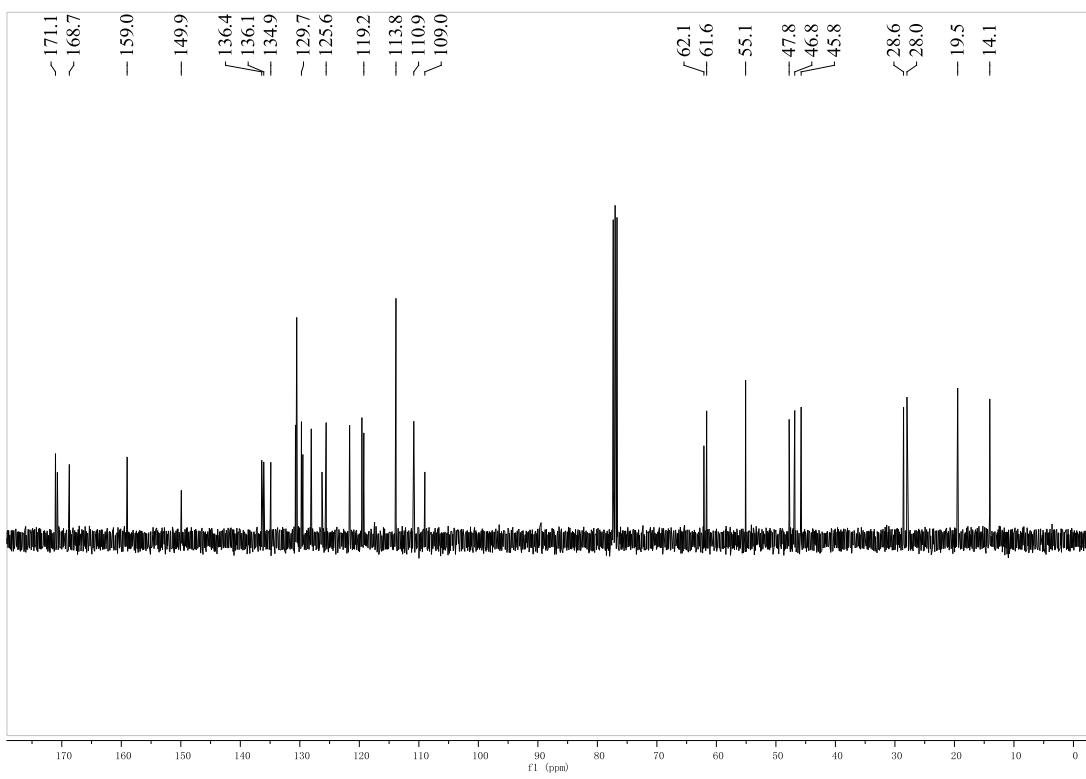


Ethyl

*rel-(1*R*,2*S*,4*R*)-2-(4-methoxyphenyl)-1',3'-dimethyl-2',4',6'-trioxo-4-(*o*-tolyl)-1,1',2,3',4,4',6',9'-octahydro-2'H-spiro[carbazole-3,5'-pyrimidine]-1-carboxylate (1c):*

yellow solid, 61%, m.p. 200-203 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.49 (s, 1H, NH), 7.31-7.29 (m, 1H, ArH), 7.21-7.19 (m, 3H, ArH), 7.16-7.13 (m, 1H, ArH), 7.05 (t, J = 7.2 Hz, 1H, ArH), 6.95 (t, J = 7.2 Hz, 1H, ArH), 6.84-6.82 (m, 1H, ArH), 6.76-6.71 (m, 3H, ArH), 6.11-6.09 (m, 1H, ArH), 5.50 (s, 1H, CH), 5.15 (d, J = 11.2 Hz, 1H, CH), 4.62 (d, J = 11.2 Hz, 1H, CH), 4.09 (q, J = 7.2 Hz, 2H, CH_2), 3.75 (s, 3H, OCH_3), 2.97 (s, 3H, CH_3), 2.91 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 1.16 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (400 MHz, CDCl_3) δ : 171.0, 168.7, 159.0, 149.9, 136.4, 136.0, 134.8, 130.7, 130.6, 130.5, 129.7, 129.4, 128.0, 126.2, 125.5, 121.6, 119.5, 119.2, 113.8, 110.8, 108.9, 62.1, 61.6, 55.0, 47.7, 46.8, 45.7, 28.5, 27.9, 19.4, 14.0; IR(KBr) ν : 3335, 3272, 3196, 3056, 2942, 2871, 2821, 2066, 1831, 1655, 1621, 1547, 1435, 1321, 1249, 1112, 1107, 932, 956, 843, 762 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{34}\text{H}_{33}\text{N}_3\text{O}_6$ ([M+Na] $^+$): 602.2262, found: 602.2250.

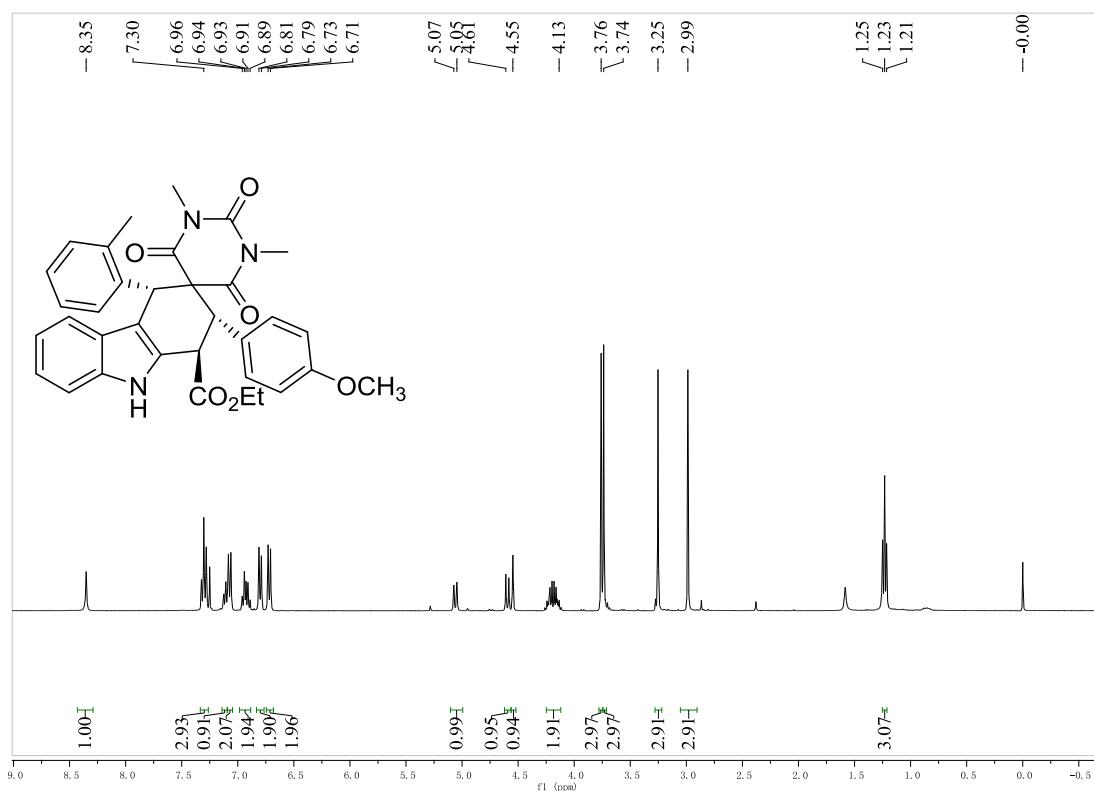


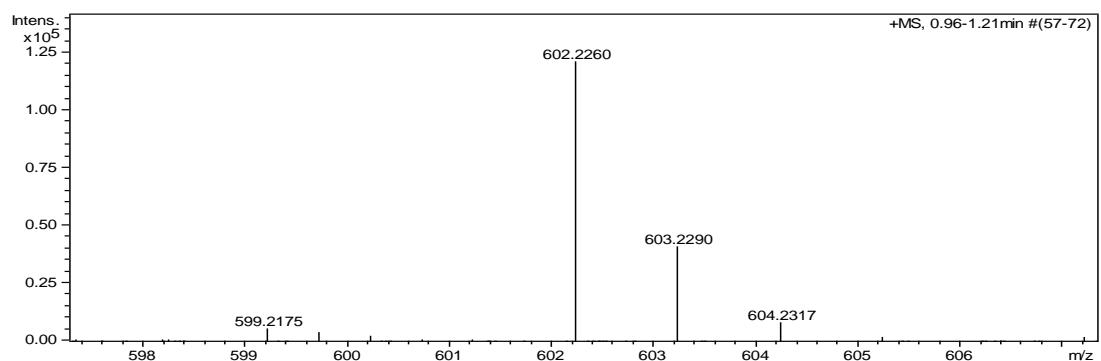
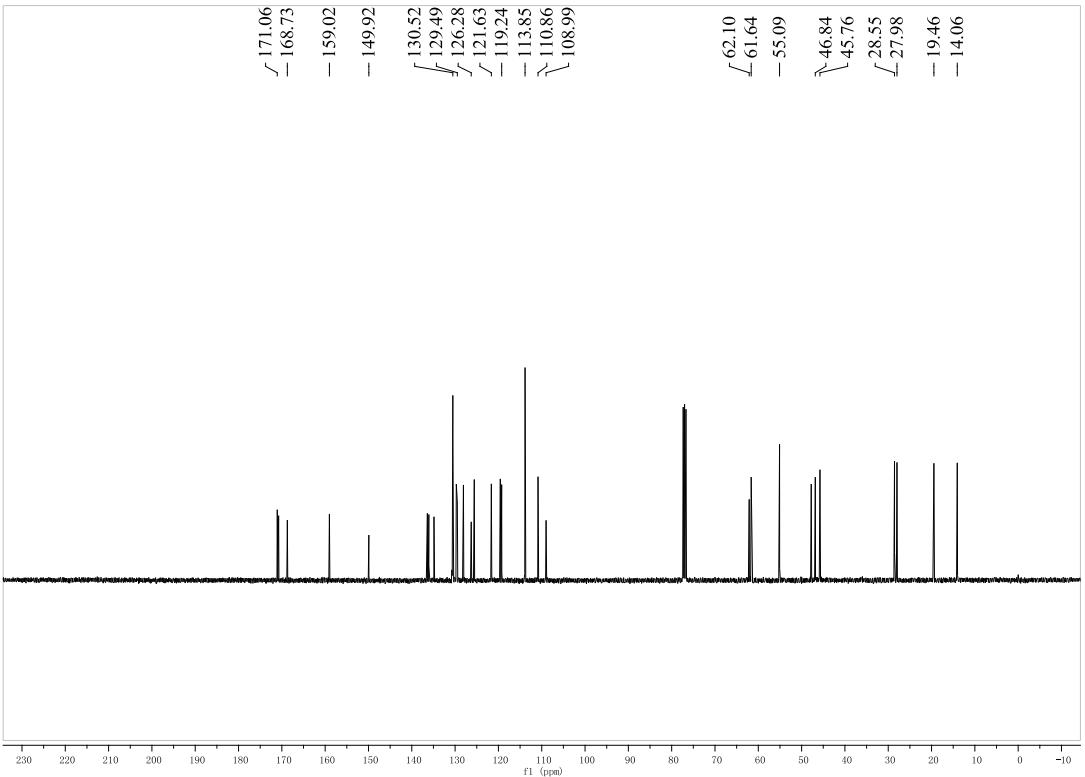


Ethyl

*re-(1*R*,2*S*,4*S*)-2-(4-methoxyphenyl)-1',3'-dimethyl-2',4',6'-trioxo-4-(*o*-tolyl)-1,1',2,3',4,4',6',9'-octahydro-2'H-spiro[carbazole-3,5'-pyrimidine]-1-carboxylate (1c')*:

yellow solid, 12.1%, m.p. 216-218 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.35 (s, 1H, NH), 7.30 (t, *J* = 8.8 Hz, 3H, ArH), 7.11 (d, *J* = 6.8 Hz, 1H, ArH), 7.07 (d, *J* = 8.8 Hz, 2H, ArH), 6.96-6.89 (m, 2H, ArH), 6.80 (d, *J* = 8.4 Hz, 2H, ArH), 6.72 (d, *J* = 8.8 Hz, 2H, ArH), 5.06 (d, *J* = 10.8 Hz, 1H, CH), 4.60 (d, *J* = 10.8 Hz, 1H, CH), 4.55 (s, 1H, CH), 4.18 (q, *J* = 7.2 Hz, 2H, CH₂), 3.76 (s, 3H, OCH₃), 3.74 (s, 3H, CH₃), 3.25 (s, 3H, CH₃), 2.98 (s, 3H, CH₃), 1.23 (t, *J* = 7.2 Hz, 3H, CH₃); ¹³C NMR (400 MHz, CDCl₃) δ: 171.0, 168.7, 159.0, 149.9, 136.4, 136.0, 134.8, 130.7, 130.6, 130.5, 129.7, 129.4, 128.0, 126.2, 125.5, 121.6, 119.5, 119.2, 113.8, 110.8, 108.9, 62.1, 61.6, 55.0, 47.7, 46.8, 45.7, 28.5, 27.9, 19.4, 14.0; IR(KBr) ν: 3362, 3306, 3184, 3042, 2913, 2855, 2809, 2100, 1845, 1642, 1603, 1547, 1442, 1376, 1251, 1134, 1157, 972, 962, 832, 759 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₄H₃₃N₃O₆([M+Na]⁺): 602.2262, found: 602.2260.

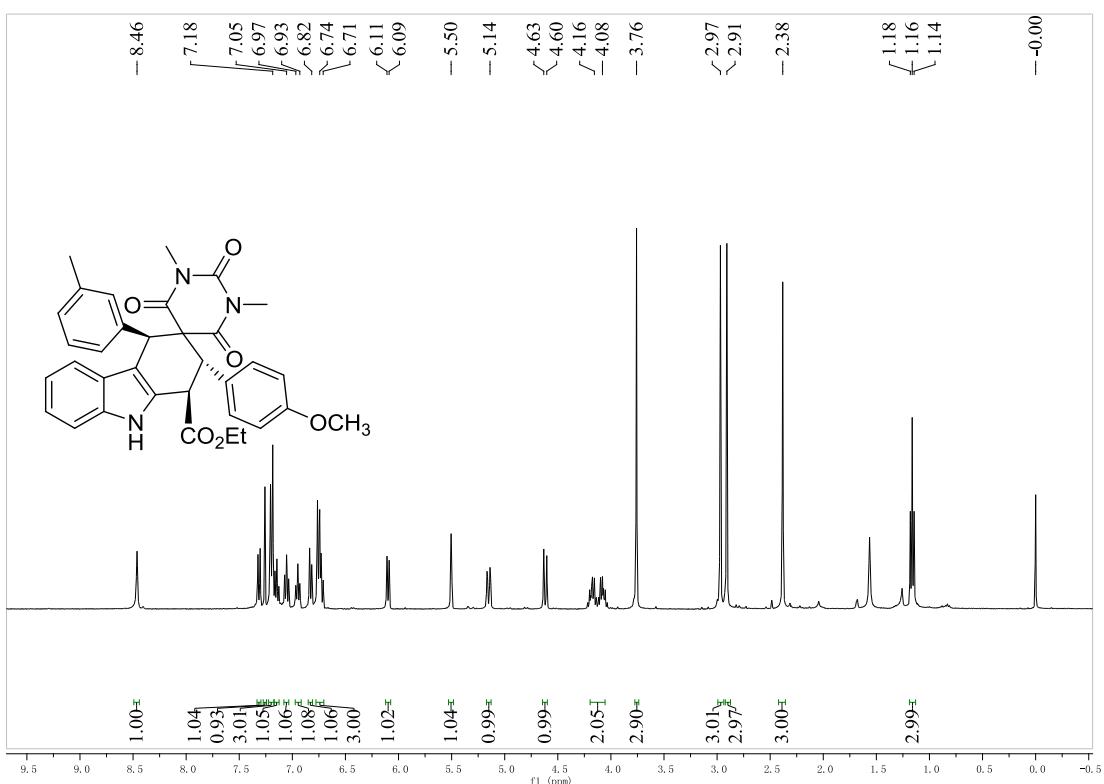


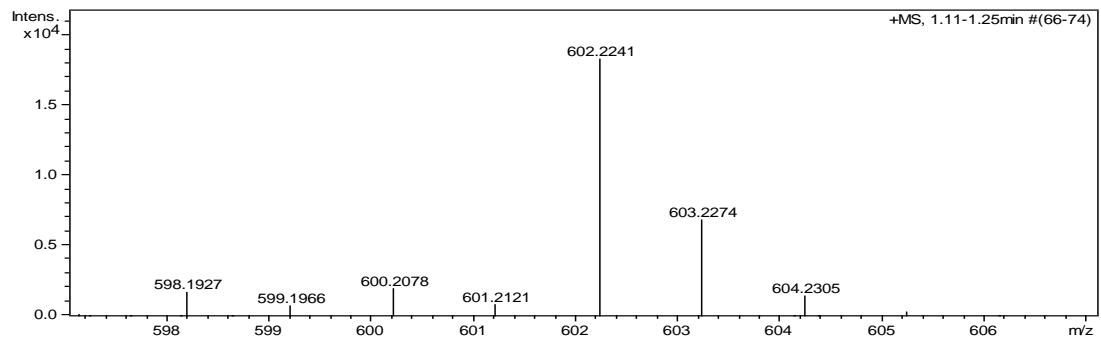
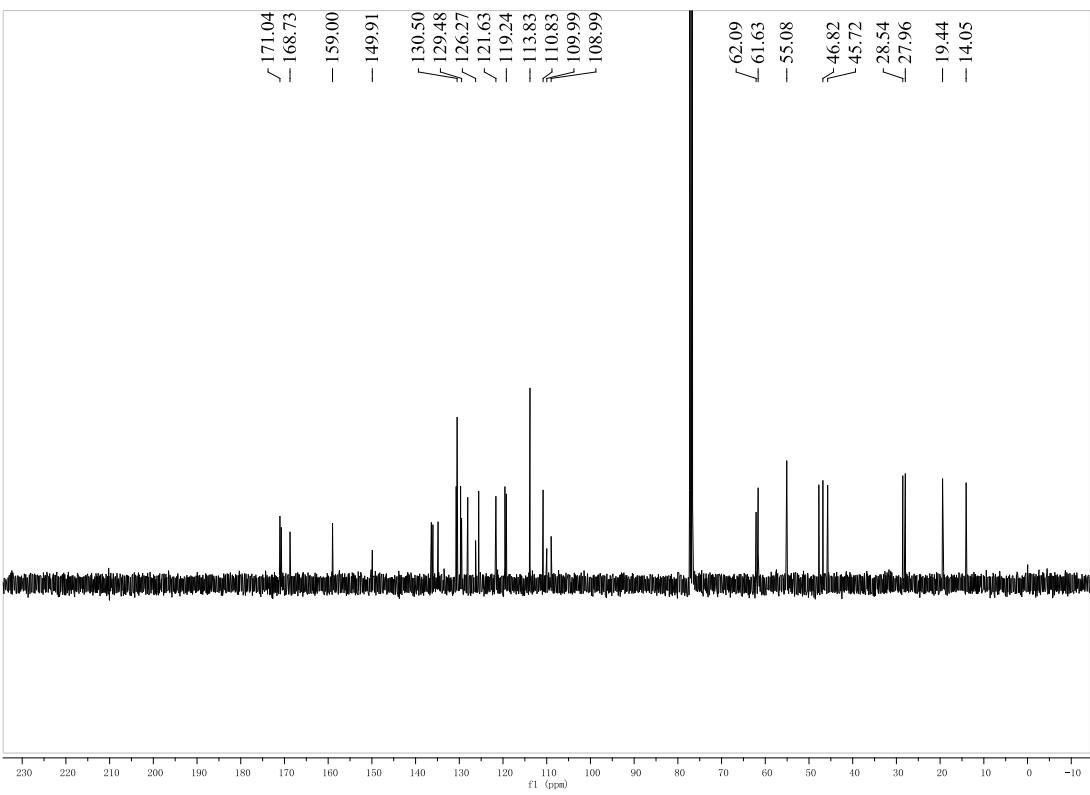


Ethyl

*rel-(1*R*,2*S*,4*R*)-2-(4-methoxyphenyl)-1',3'-dimethyl-2',4',6'-trioxo-4-(*m*-tolyl)-1,1',2,3',4,4',6',9'-octahydro-2'H-spiro[carbazole-3,5'-pyrimidine]-1-carboxylate (1d):*

yellow solid, 70%, m.p. 205-209 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.46 (s, 1H, NH), 7.31 (d, *J* = 8.4 Hz, 1H, ArH), 7.26-7.25 (m, 1H, ArH), 7.19 (d, *J* = 8.4 Hz, 3H, ArH), 7.15 (t, *J* = 7.6 Hz, 1H, ArH), 7.05 (t, *J* = 7.6 Hz, 1H, ArH), 6.95 (t, *J* = 7.6 Hz, 1H, ArH), 6.82 (d, *J* = 8.4 Hz, 1H, ArH), 6.76-6.71 (m, 3H, ArH), 6.09 (d, *J* = 8.4 Hz, 1H, ArH), 5.51 (s, 1H, CH), 5.15 (d, *J* = 11.2 Hz, 1H, CH), 4.62 (d, *J* = 11.2 Hz, 1H, CH), 4.12 (q, *J* = 6.8 Hz, 2H, CH₂), 3.76 (s, 3H, OCH₃), 2.97 (s, 3H, CH₃), 2.91 (s, 3H, CH₃), 2.38 (s, 3H, CH₃), 1.16 (t, *J* = 6.8 Hz, 3H, CH₃); ¹³C NMR (400 MHz, CDCl₃) δ: 171.0, 168.7, 159.0, 149.9, 136.3, 136.0, 134.8, 130.7, 130.5, 130.5, 129.7, 129.4, 128.0, 126.2, 125.5, 121.6, 119.5, 119.2, 113.8, 110.8, 109.9, 108.9, 62.0, 61.6, 55.0, 47.7, 46.8, 45.7, 28.5, 27.9, 19.4, 14.0; IR(KBr) v: 3348, 3321, 3207, 3176, 3055, 2972, 2846, 2813, 2102, 1855, 1638, 1621, 1536, 1476, 1332, 1278, 1164, 1143, 946, 911, 854, 763 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₄H₃₃N₃O₆([M+Na]⁺): 602.2262, found: 602.2241.

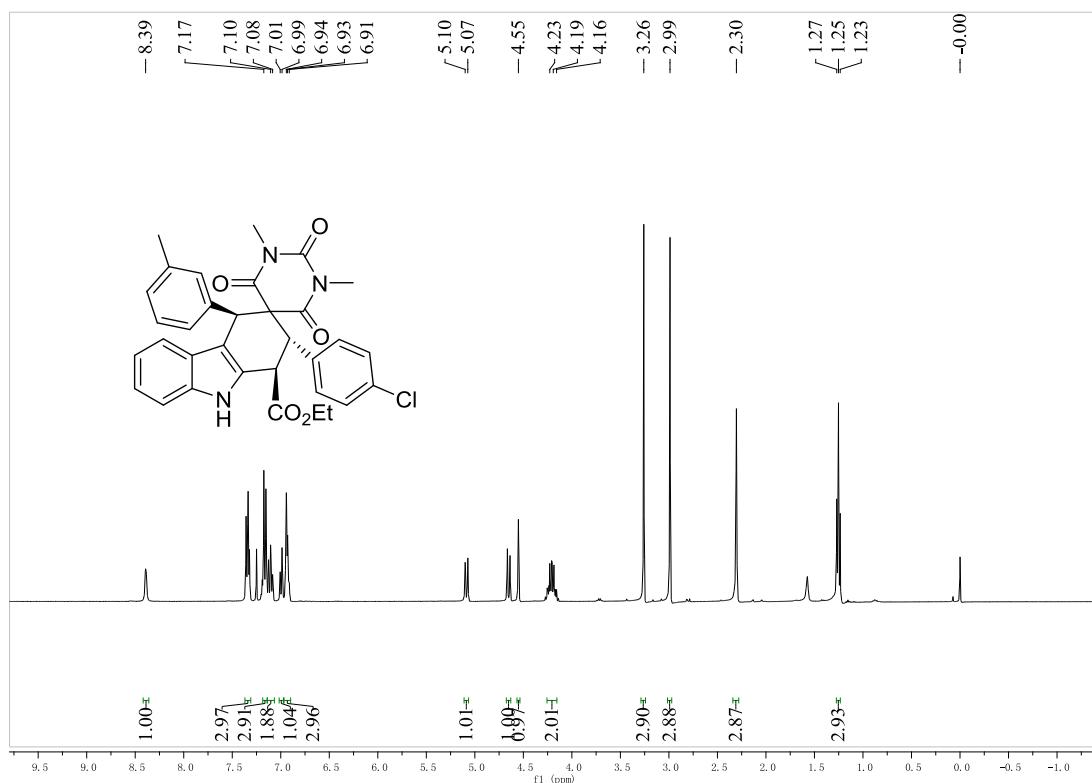


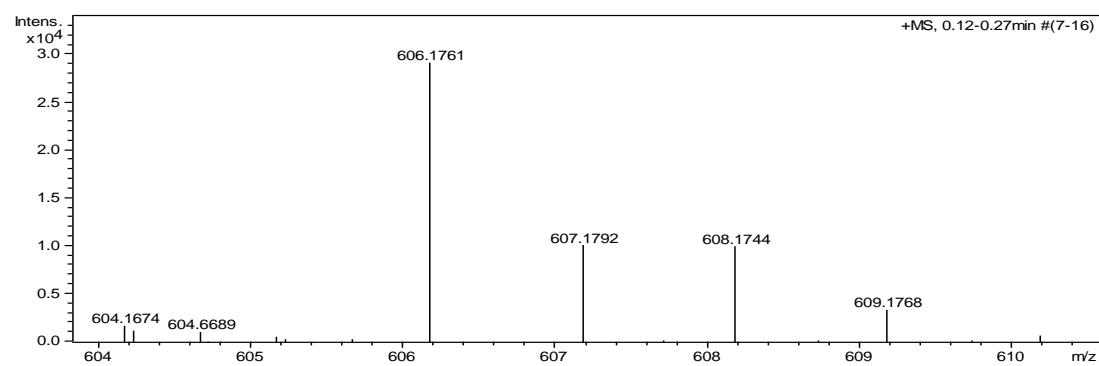
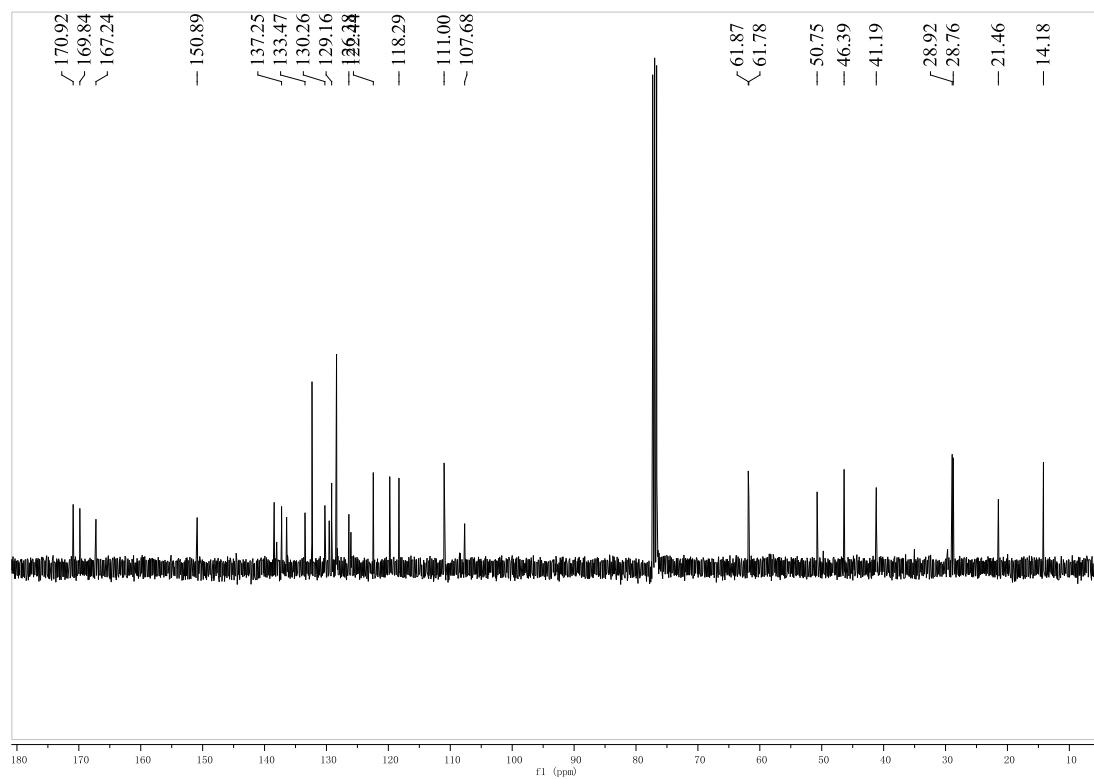


Ethyl

rel-(1*R*,2*S*,4*R*)-2-(4-chlorophenyl)-1',3'-dimethyl-2',4',6'-trioxo-4-(*m*-tolyl)-1,1',2,3',4,4',6',9-octahydro-2'H-spiro[carbazole-3,5'-pyrimidine]-1-carboxylate (1e):

yellow solid, 60%, m.p. 211-213 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.39 (s, 1H, NH), 7.36-7.32 (m, 3H, ArH), 7.18-7.15 (m, 3H, ArH), 7.13-7.08 (m, 2H, ArH), 7.01-6.99 (m, 1H, ArH), 6.94-6.91 (m, 3H, ArH), 5.09 (d, *J* = 10.8 Hz, 1H, CH), 4.65 (d, *J* = 10.8 Hz, 1H, CH), 4.55 (s, 1H, CH), 4.21 (q, *J* = 6.8 Hz, 2H, CH₂), 3.26 (s, 3H, CH₃), 2.99 (s, 3H, CH₃), 2.31 (s, 3H, CH₃), 1.25 (t, *J* = 6.8 Hz, 3H, CH₃); ¹³C NMR (400 MHz, CDCl₃) δ: 170.9, 169.8, 167.2, 150.8, 138.4, 137.2, 136.4, 133.4, 132.3, 130.2, 129.5, 129.1, 128.3, 126.3, 122.4, 119.7, 118.2, 111.0, 107.6, 61.8, 61.7, 50.7, 46.3, 41.1, 28.9, 28.7, 21.4, 14.1; IR(KBr) ν: 3327, 3306, 3267, 3152, 3072, 2989, 2832, 2813, 2145, 1802, 1645, 1621, 1578, 1445, 1324, 1245, 1147, 1129, 952, 933, 862, 792 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₃H₃₀ClN₃O₅([M+Na]⁺): 606.1766, found: 606.1761.

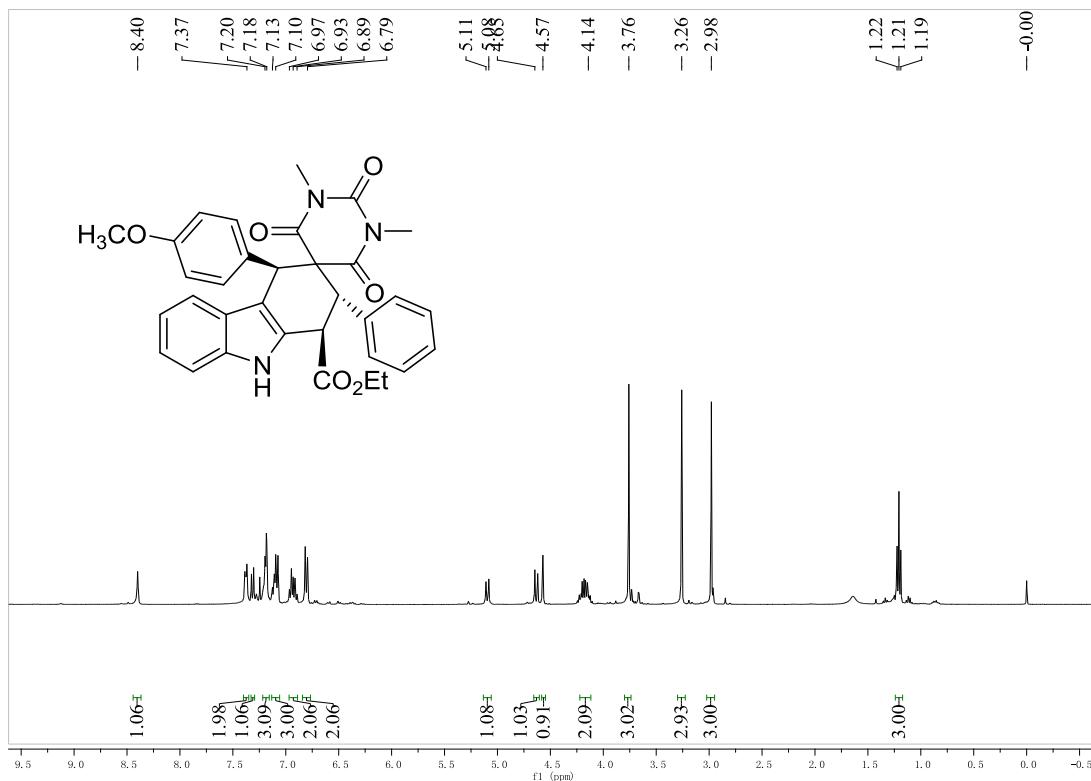


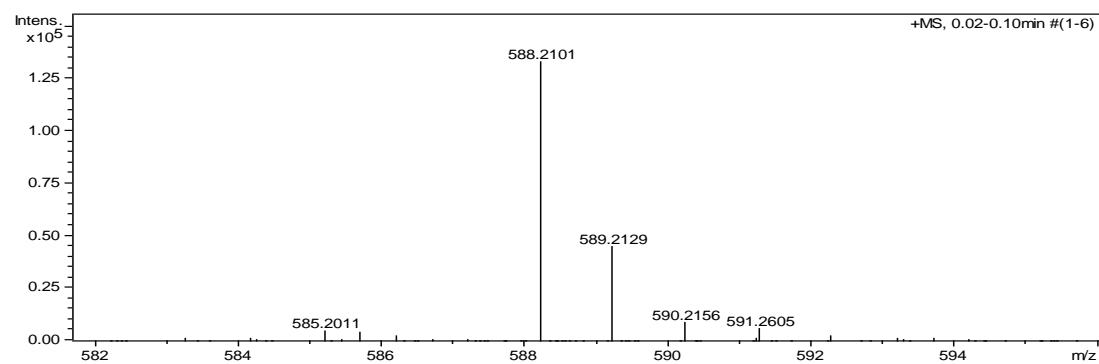
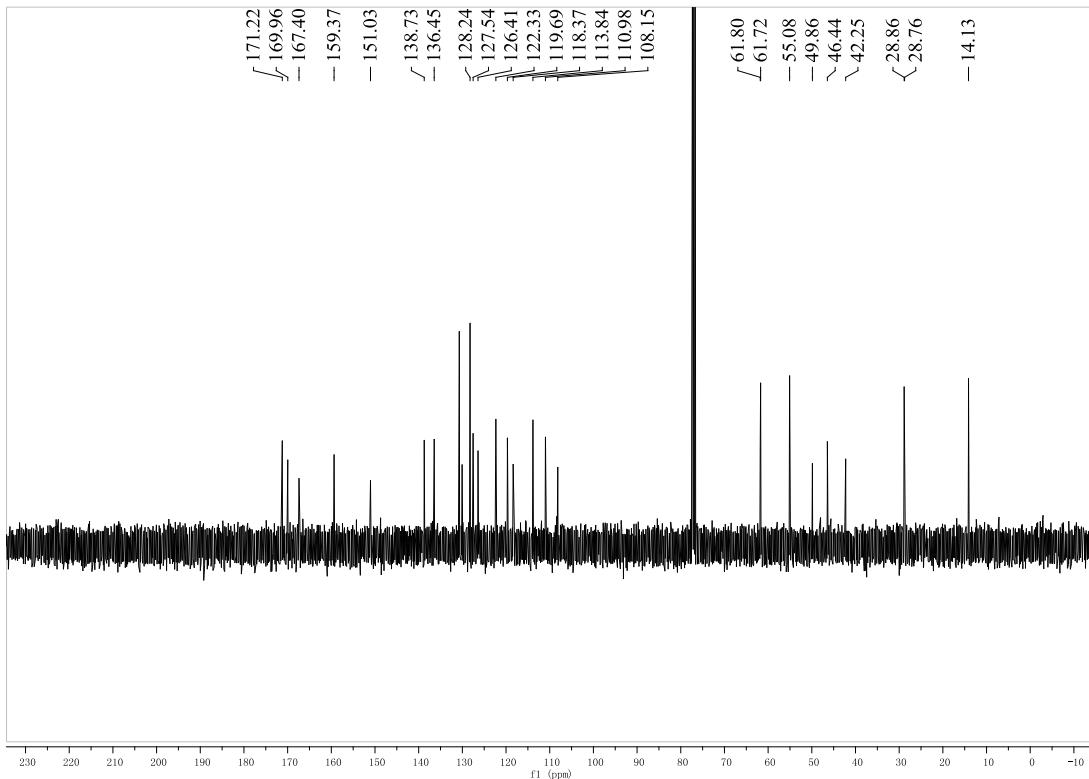


Ethyl

rel-(*1R,2S,4R*)-4-(4-methoxyphenyl)-1',3'-dimethyl-2',4',6'-trioxo-2-phenyl-1,1',2,3',4,4',6',9'-octahydro-2'H-spiro[carbazole-3,5'-pyrimidine]-1-carboxylate (**1f**):

yellow solid, 70%, m.p. 204-206 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.40 (s, 1H, NH), 7.39-7.37 (m, 2H, ArH), 7.31 (d, J = 8.0 Hz, 1H, ArH), 7.21-7.18 (m, 3H, ArH), 7.13-7.07 (m, 3H, ArH), 6.97-6.89 (m, 2H, ArH), 6.80 (d, J = 8.0 Hz, 2H, ArH), 5.09 (d, J = 10.8 Hz, 1H, CH), 4.63 (d, J = 10.8 Hz, 1H, CH), 4.57 (s, 1H, CH), 4.17 (q, J = 7.2 Hz, 2H, CH_2), 3.76 (s, 3H, OCH_3), 3.26 (s, 3H, CH_3), 2.98 (s, 3H, CH_3), 1.21 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (400 MHz, CDCl_3) δ : 171.2, 169.9, 167.3, 159.3, 151.0, 138.7, 136.4, 130.7, 130.7, 130.4, 130.0, 128.2, 127.5, 126.4, 122.3, 119.6, 118.3, 113.8, 110.9, 108.1, 61.8, 61.7, 55.0, 49.8, 46.4, 42.2, 28.8, 28.7, 14.1; IR(KBr) ν : 3362, 3348, 3213, 3162, 3078, 2963, 2832, 2814, 2162, 1873, 1642, 1613, 1566, 1481, 1365, 1262, 1178, 1137, 952, 921, 862, 782 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{33}\text{H}_{31}\text{N}_3\text{O}_6([\text{M}+\text{Na}]^+)$: 588.2105, found: 588.2101.

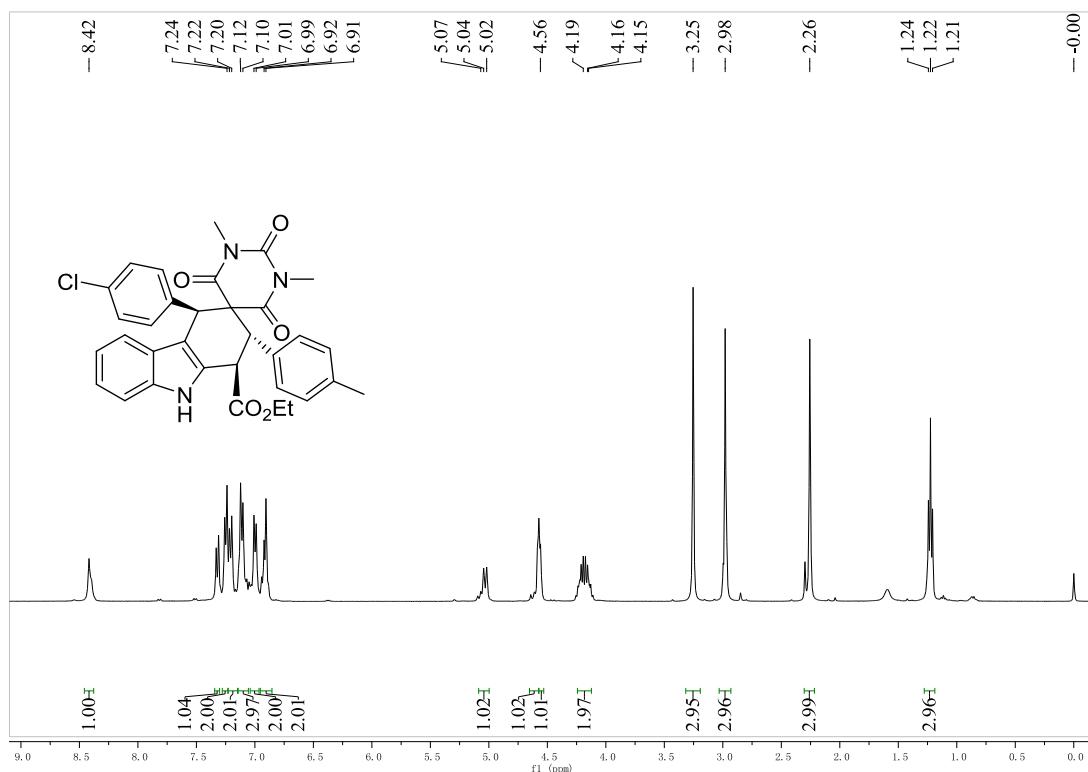


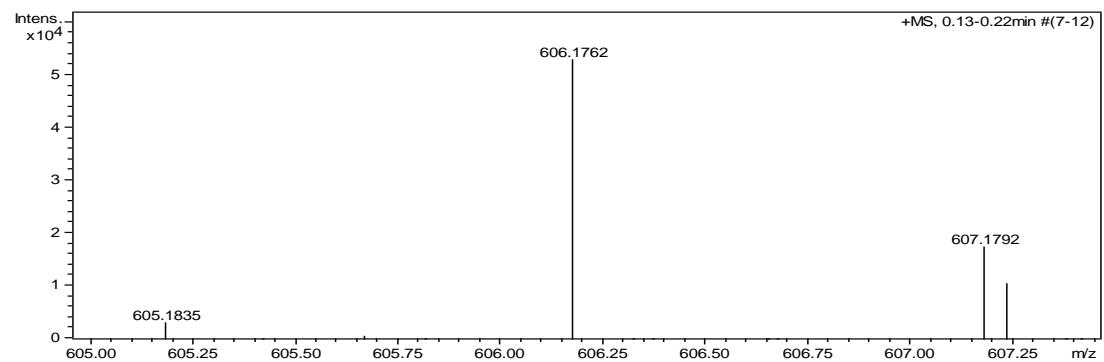
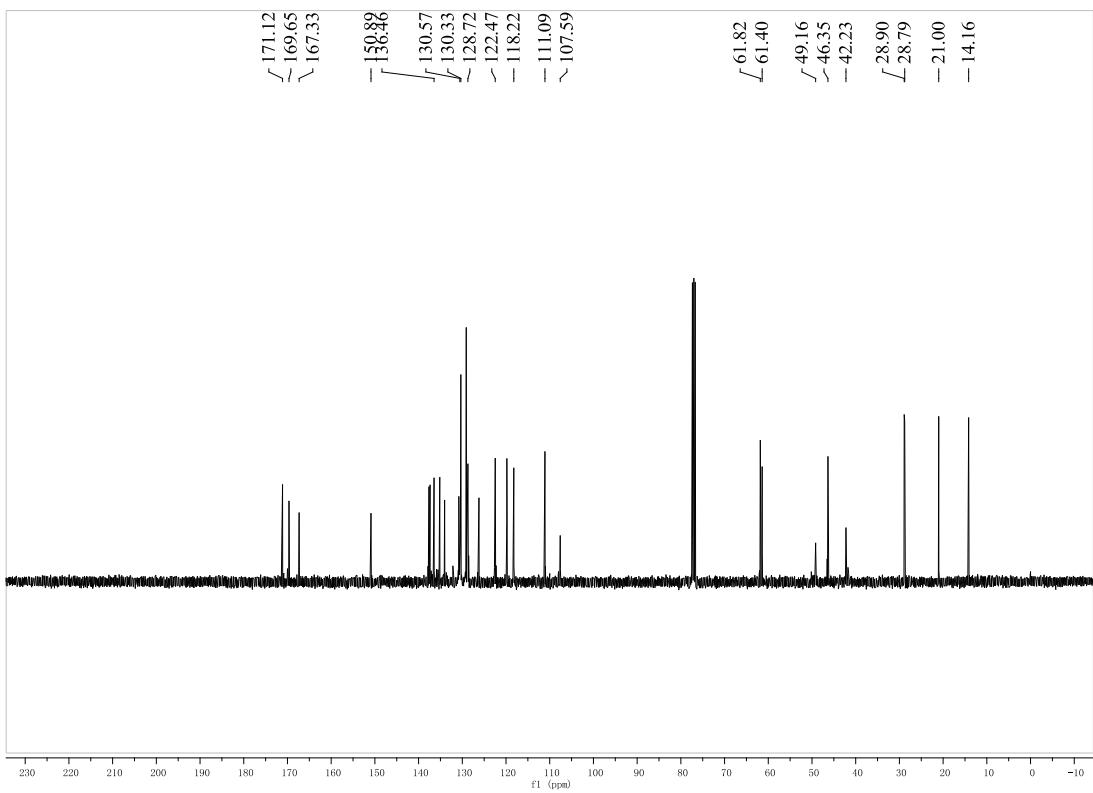


Ethyl

rel-(*1R,2S,4R*)-4-(4-chlorophenyl)-1',3'-dimethyl-2',4',6'-trioxo-2-(*p*-tolyl)-1,1',2,3',4,4',6',9-octahydro-2'H-spiro[carbazole-3,5'-pyrimidine]-1-carboxylate (**1g**):

yellow solid, 75%, m.p. 206-210 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.42 (s, 1H, NH), 7.32 (d, J = 8.0 Hz, 1H, ArH), 7.24 (d, J = 8.0 Hz, 2H, ArH), 7.20 (d, J = 8.0 Hz, 1H, ArH), 7.12-7.10 (m, 3H, ArH), 7.01-6.99 (m, 2H, ArH), 6.92-6.91 (m, 2H, ArH), 5.07-5.02 (m, 1H, CH), 4.64-4.58 (m, 1H, CH), 4.57-4.56 (m, 1H, CH), 4.17 (q, J = 7.2 Hz, 2H, CH_2), 3.25 (s, 3H, CH_3), 2.98 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 1.23 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (400 MHz, CDCl_3) δ : 171.1, 169.6, 167.3, 150.8, 137.6, 137.3, 136.4, 135.1, 134.0, 130.7, 130.5, 130.3, 130.3, 129.0, 128.7, 126.1, 122.4, 119.8, 118.2, 111.0, 107.5, 61.8, 61.4, 49.1, 46.3, 42.2, 28.9, 28.7, 21.0, 14.1; IR(KBr) ν : 3323, 3307, 3264, 3153, 3042, 2982, 2832, 2855, 2172, 1842, 1673, 1643, 1521, 1455, 1367, 1272, 1183, 1142, 952, 963, 872, 746 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{33}\text{H}_{30}\text{ClN}_3\text{O}_5$ ([M+Na] $^+$): 606.1766, found: 606.1762.

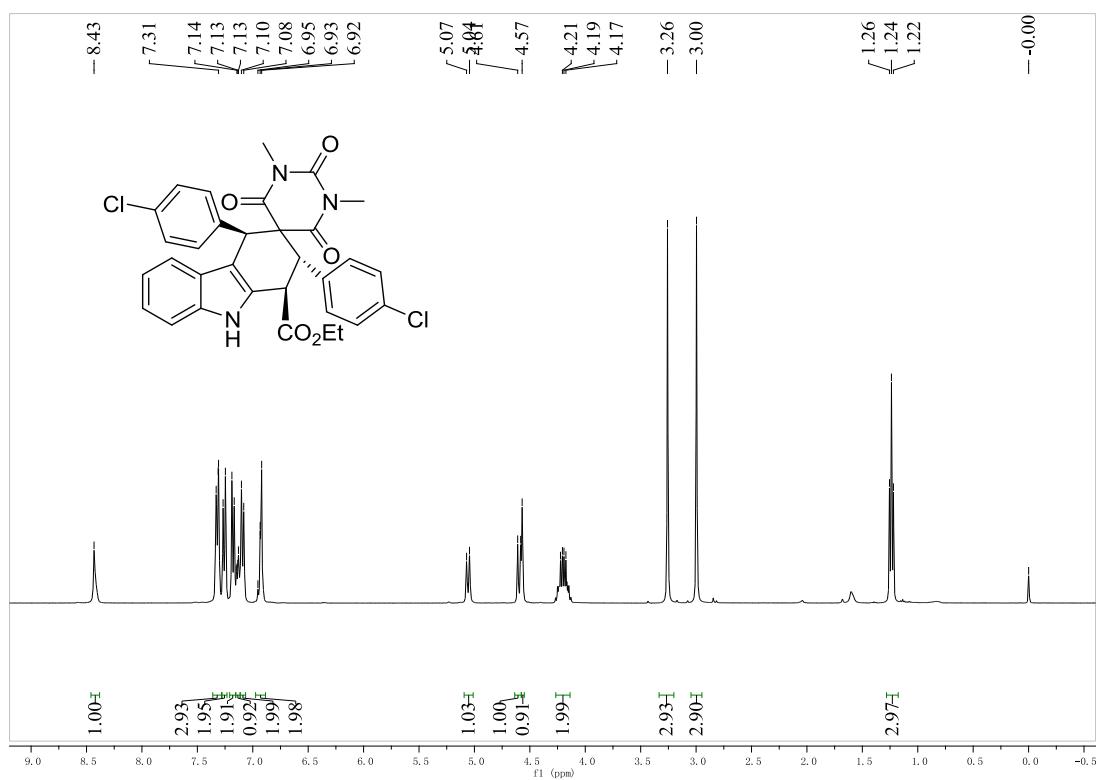


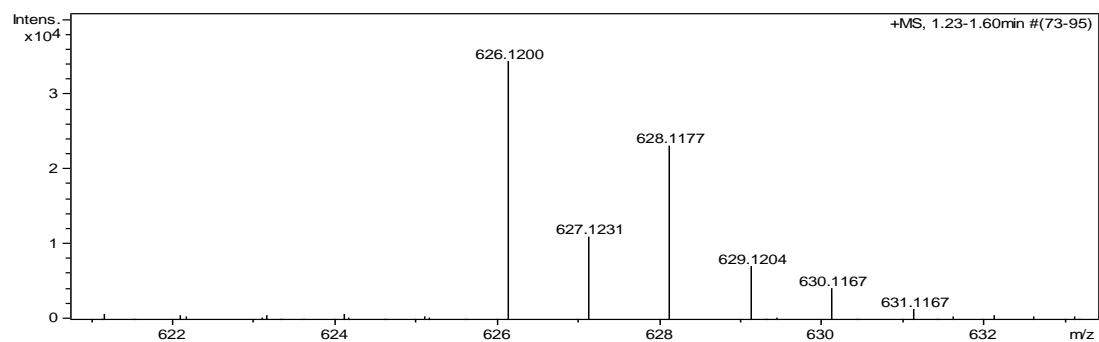
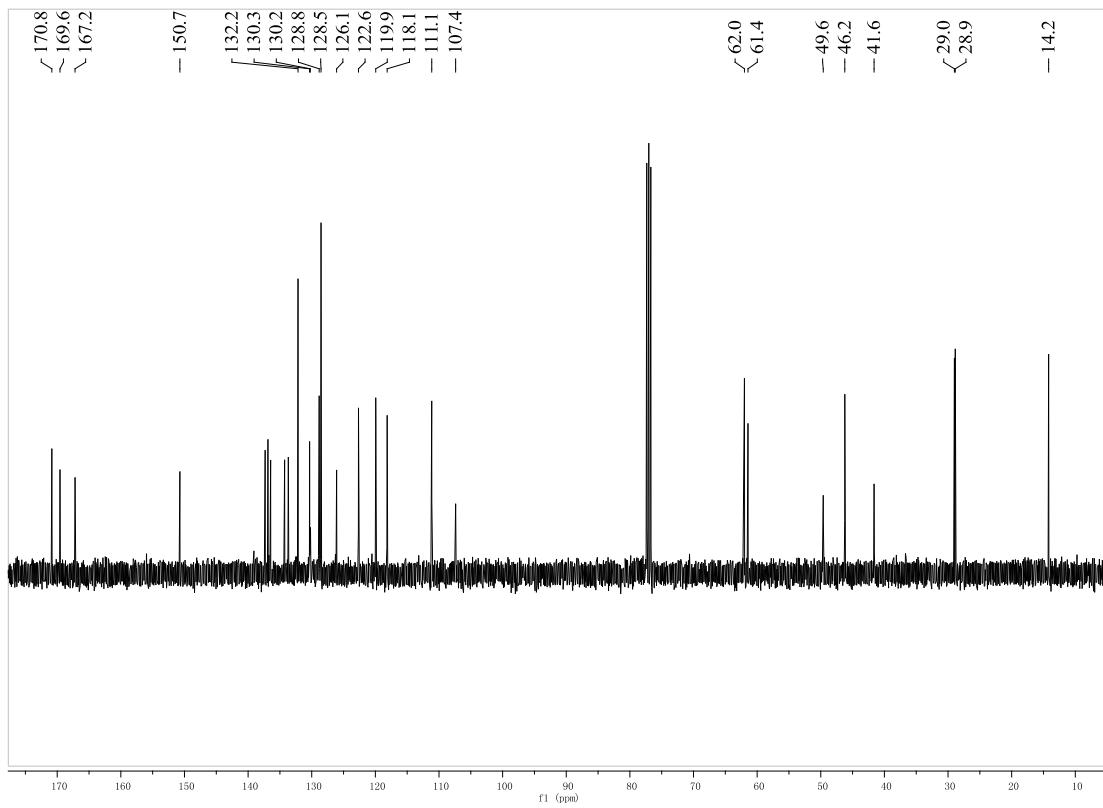


Ethy

*rel-(1*R*,2*S*,4*R*)-2,4-bis(4-chlorophenyl)-1',3'-dimethyl-2',4',6'-trioxo-1,1',2,3',4,4',6',9-octahydro-2'H-spiro[carbazole-3,5'-pyrimidine]-1-carboxylate (1h):*

yellow solid, 68%, m.p. 212-214 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.43 (s, 1H, NH), 7.31 (d, J = 8.4 Hz, 3H, ArH), 7.25 (d, J = 8.4 Hz, 2H, ArH), 7.17 (d, J = 8.0 Hz, 2H, ArH), 7.15-7.13 (m, 1H, ArH), 7.09 (d, J = 8.0 Hz, 2H, ArH), 6.95-6.92 (m, 2H, ArH), 5.06 (d, J = 10.4 Hz, 1H, CH), 4.59 (d, J = 10.4 Hz, 1H, CH), 4.57 (s, 1H, CH), 4.20 (q, J = 7.2 Hz, 2H, CH_2), 3.26 (s, 3H, CH_3), 3.00 (s, 3H, CH_3), 1.24 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (400 MHz, CDCl_3) δ : 170.8, 169.5, 167.1, 150.7, 137.3, 136.8, 136.4, 134.2, 133.6, 132.1, 130.3, 130.2, 128.8, 128.5, 126.0, 122.6, 119.9, 118.1, 111.1, 107.3, 61.9, 61.4, 49.6, 46.2, 41.6, 29.0, 28.8, 14.1; IR(KBr) ν : 3379, 3321, 3265, 3178, 3045, 2978, 2864, 2832, 2187, 1839, 1655, 1632, 1576, 1462, 1348, 1267, 1178, 1132, 976, 948, 862, 755 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{32}\text{H}_{27}\text{Cl}_2\text{N}_3\text{O}_5([\text{M}+\text{Na}]^+)$: 626.1220, found: 606.1200.

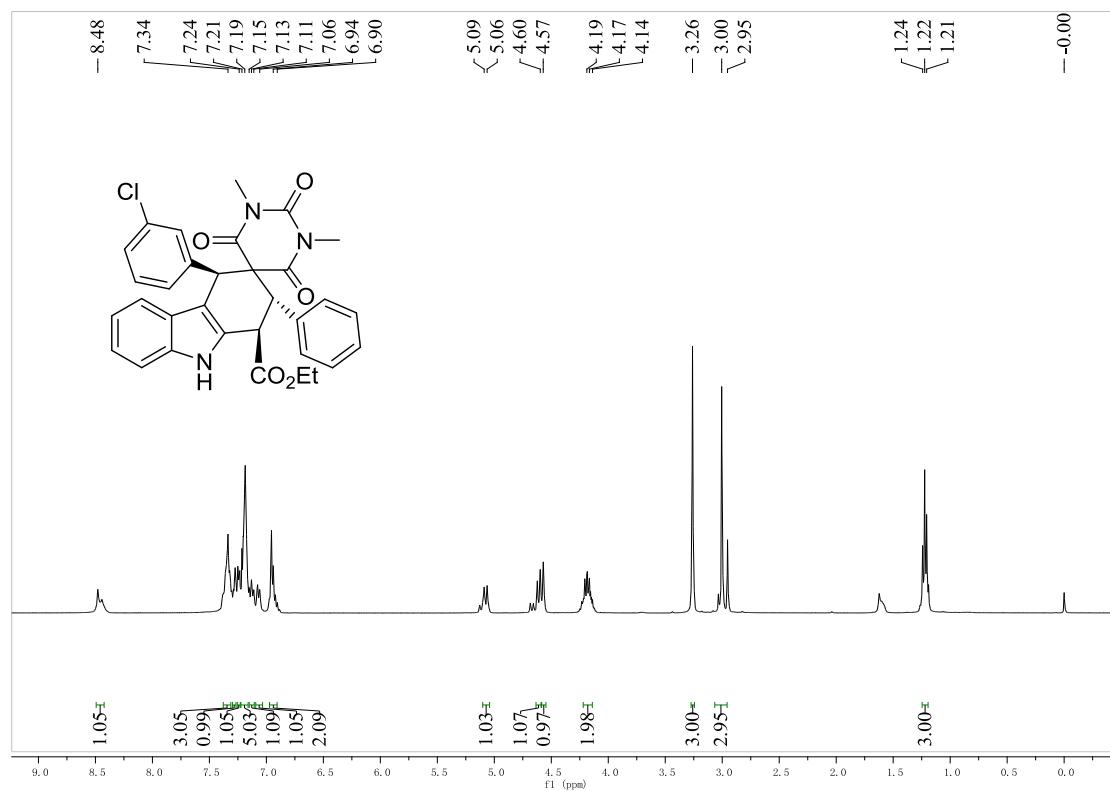


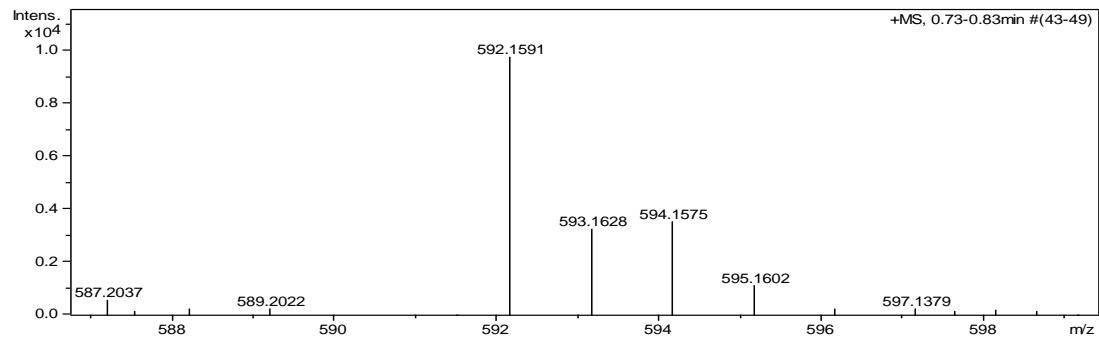
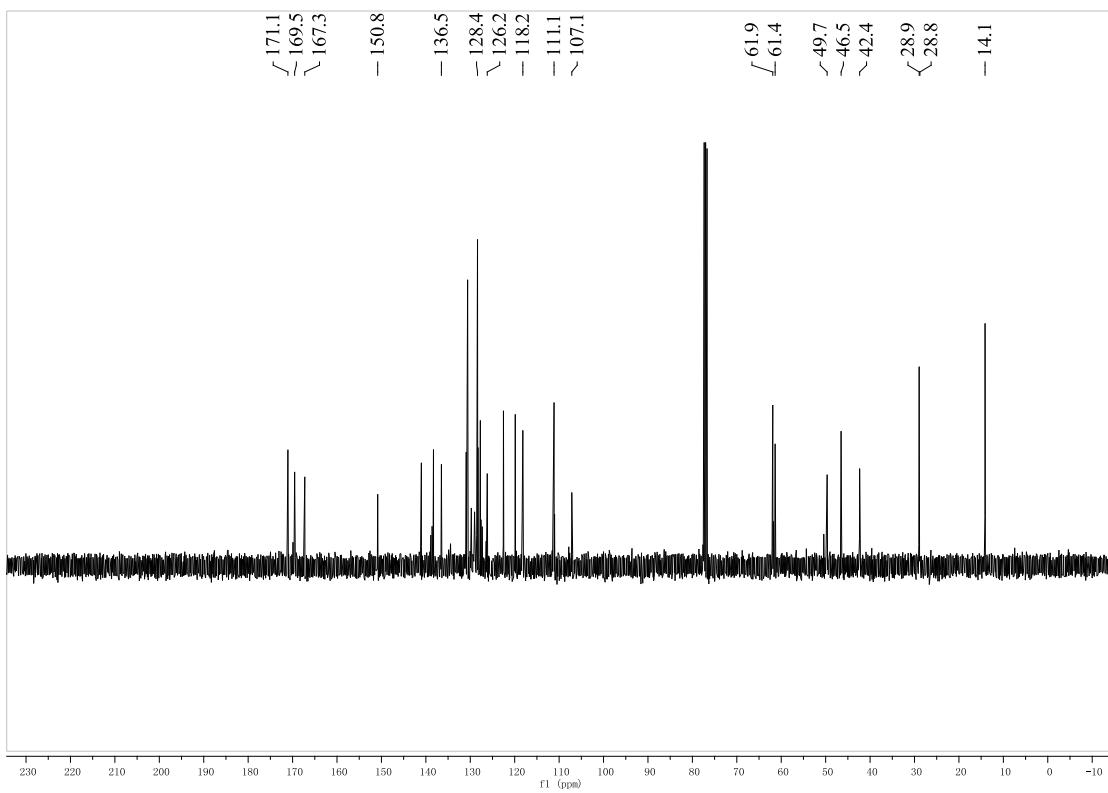


Ethyl

rel-(1*R*,2*S*,4*R*)-4-(3-chlorophenyl)-1',3'-dimethyl-2',4',6'-trioxo-2-phenyl-1,1',2,3',4,4',6',9-octahydro-2'H-spiro[carbazole-3,5'-pyrimidine]-1-carboxylate (**1i**):

yellow solid, 76%, m.p. 216-219 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.48 (s, 1H, NH), 7.38-7.30 (m, 3H, ArH), 7.29-7.28 (m, 1H, ArH), 7.25-7.23 (m, 1H, ArH), 7.22-7.19 (m, 5H, ArH), 7.15-7.11 (m, 1H, ArH), 7.08-7.06 (m, 1H, ArH), 6.96-6.91 (m, 2H, ArH), 5.08 (d, J = 10.8 Hz, 1H, CH), 4.61 (d, J = 10.8 Hz, 1H, CH), 4.57 (s, 1H, CH), 4.18 (q, J = 7.2 Hz, 2H, CH_2), 3.26 (s, 3H, CH_3), 3.01 (s, 3H, CH_3), 1.22 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (400 MHz, CDCl_3) δ : 171.0, 169.5, 167.2, 150.8, 141.0, 138.2, 136.4, 130.9, 130.7, 130.5, 128.4, 128.3, 128.2, 127.7, 126.1, 122.5, 119.8, 118.1, 111.1, 107.1, 61.9, 61.3, 49.6, 46.5, 42.3, 28.9, 28.7, 14.1; IR(KBr) ν : 3362, 3308, 3242, 3163, 3055, 2932, 2845, 2816, 2134, 1832, 1643, 1617, 1532, 1473, 1365, 1248, 1162, 1146, 982, 948, 872, 780 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{32}\text{H}_{28}\text{ClN}_3\text{O}_5([\text{M}+\text{Na}]^+)$: 592.1610, found: 592.1591.

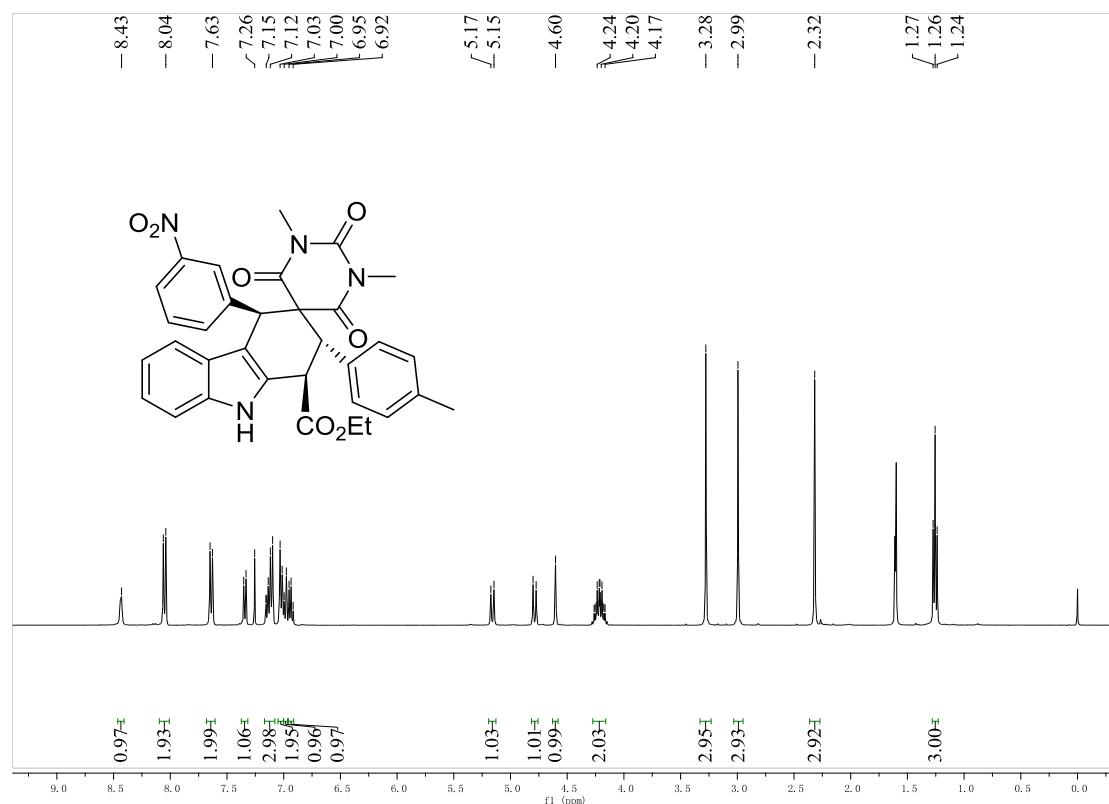


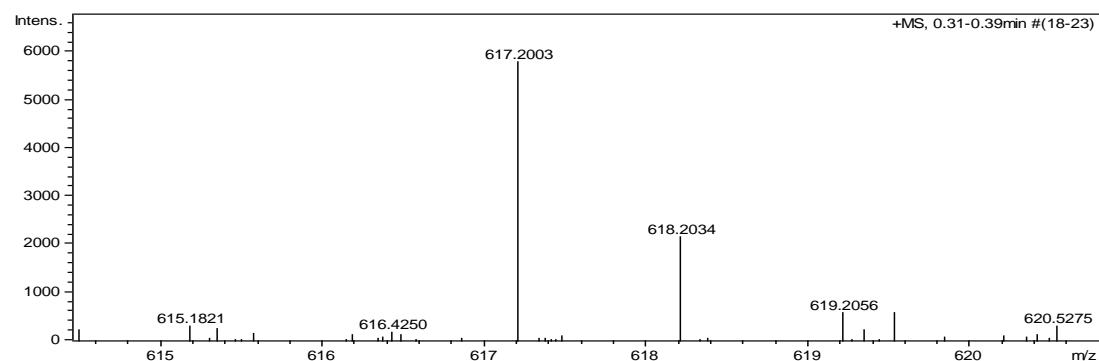
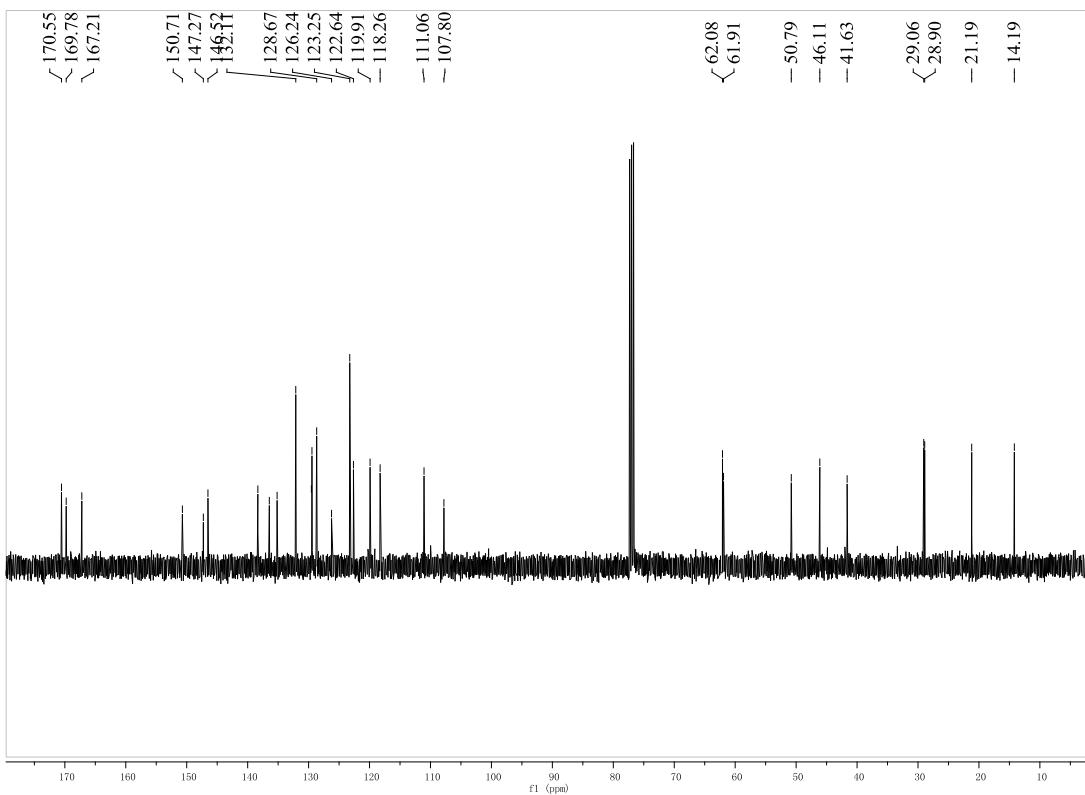


Ethyl

*rel-(1*R*,2*S*,4*S*)-1',3'-dimethyl-4-(3-nitrophenyl)-2',4',6'-trioxo-2-(*p*-tolyl)-1,1',2,3',4,4',6',9-octahydro-2'H-spiro[carbazole-3,5'-pyrimidine]-1-carboxylate (1j):*

yellow solid, 73%, m.p. 211-213 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.43 (s, 1H, NH), 8.05 (d, J = 8.8 Hz, 2H, ArH), 7.64 (d, J = 8.8 Hz, 2H, ArH), 7.34 (d, J = 8.8 Hz, 1H, ArH), 7.16-7.09 (m, 3H, ArH), 7.02 (d, J = 7.2 Hz, 2H, ArH), 6.98 (d, J = 7.2 Hz, 1H, ArH), 6.95-6.92 (m, 1H, ArH), 5.16 (d, J = 10.8 Hz, 1H, CH), 4.78 (d, J = 10.8 Hz, 1H, CH), 4.60 (s, 1H, CH), 4.21 (d, J = 7.2 Hz, 2H, CH_2), 3.28 (s, 3H, CH_3), 2.99 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 1.26 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (400 MHz, CDCl_3) δ : 170.5, 169.7, 167.2, 150.7, 147.2, 146.5, 138.3, 136.4, 135.1, 132.1, 129.5, 129.4, 128.6, 126.2, 123.2, 122.6, 119.9, 118.2, 111.0, 107.7, 62.0, 61.9, 50.7, 46.1, 41.6, 29.0, 28.9, 21.1, 14.1; IR(KBr) ν : 3364, 3321, 3278, 3168, 3055, 2962, 2872, 2844, 2132, 1847, 1617, 1601, 1532, 1431, 1333, 1241, 1162, 1142, 972, 931, 872, 782 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{33}\text{H}_{30}\text{N}_4\text{O}_7$ ([M+Na] $^+$): 617.2007, found: 617.2003.

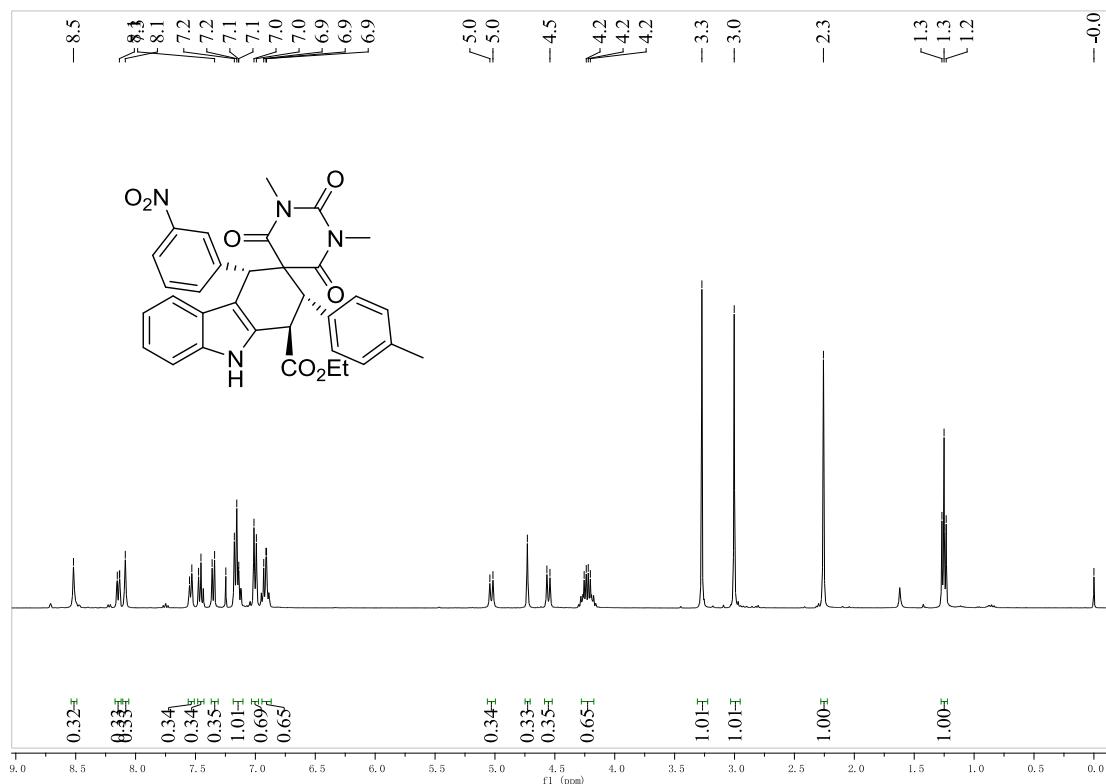


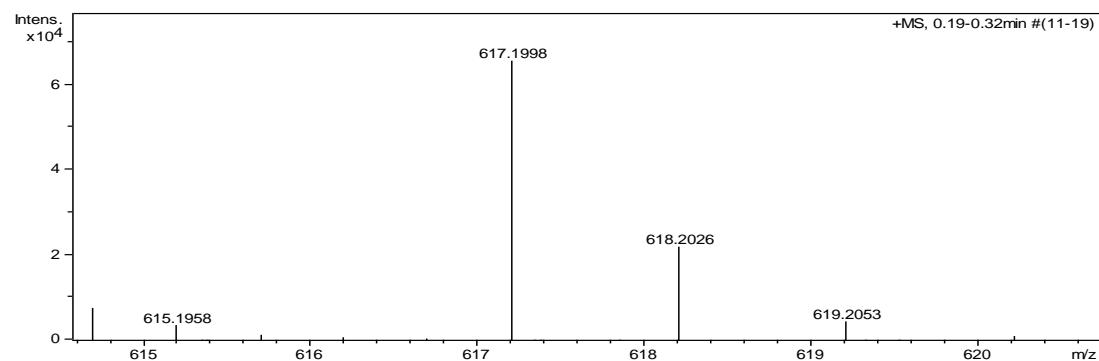
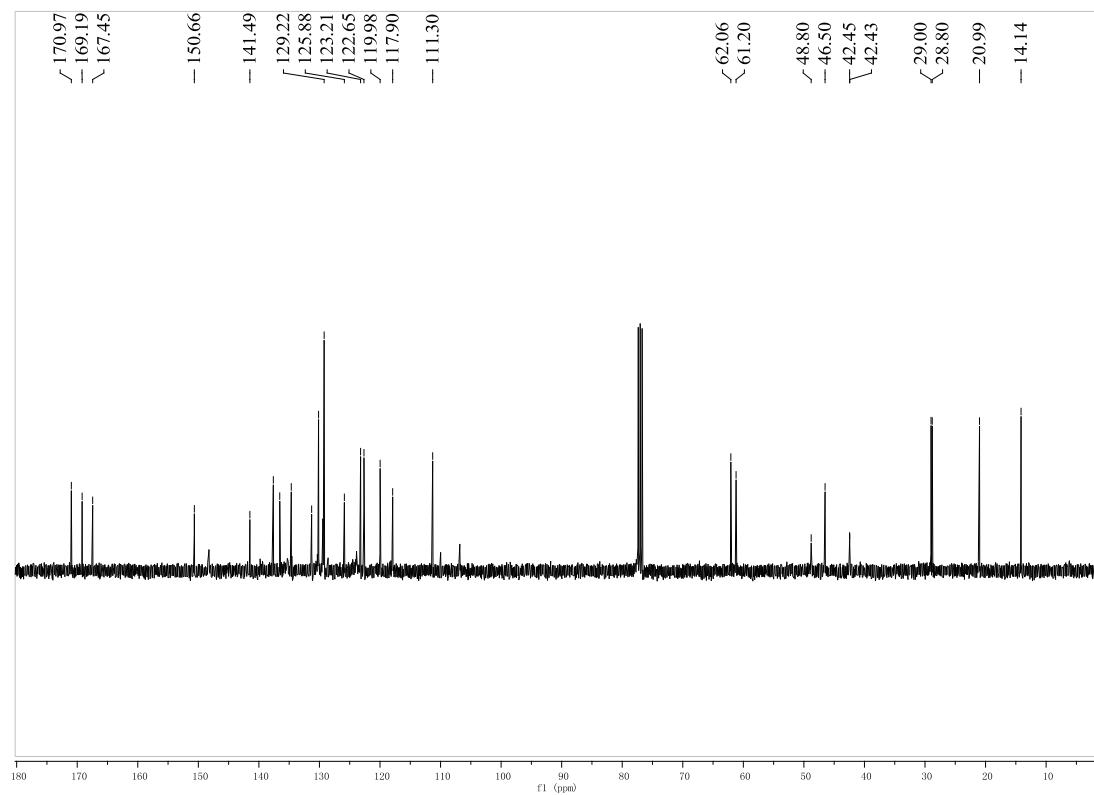


Ethy

rel-(1*R*,2*S*,4*R*)-1',3'-dimethyl-4-(3-nitrophenyl)-2',4',6'-trioxo-2-(*p*-tolyl)-1,1',2,3',4,4',6',9-octahydro-2'H-spiro[carbazole-3,5'-pyrimidine]-1-carboxylate (1j'):

yellow solid, 9%, m.p. 220-222 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.52 (s, 1H, NH), 8.14 (d, *J* = 8.0 Hz, 1H, ArH), 8.09 (s, 1H, ArH), 7.54 (d, *J* = 8.0 Hz, 1H, ArH), 7.47-7.44 (m, 1H, ArH), 7.35 (d, *J* = 8.0 Hz, 1H, ArH), 7.18-7.12 (m, 3H, ArH), 7.00 (d, *J* = 8.0 Hz, 2H, ArH), 6.95-6.89 (m, 2H, ArH), 5.03 (d, *J* = 10.4 Hz, 1H, CH), 4.73 (s, 1H, CH), 4.55 (d, *J* = 10.4 Hz, 1H, CH), 4.22 (q, *J* = 7.2 Hz, 2H, CH₂), 3.27 (s, 3H, CH₃), 3.00 (s, 3H, CH₃), 2.26 (s, 3H, CH₃), 1.25 (t, *J* = 7.2 Hz, 3H, CH₃); ¹³C NMR (400 MHz, CDCl₃) δ: 170.9, 169.1, 167.4, 150.6, 141.4, 137.6, 136.5, 134.6, 131.2, 130.1, 129.2, 125.8, 123.2, 122.6, 119.9, 117.9, 111.3, 62.0, 61.2, 48.7, 46.5, 42.4, 42.4, 29.0, 28.8, 20.9, 14.1; IR(KBr) ν: 3378, 3314, 3255, 3172, 3046, 2978, 2856, 2832, 2114, 1856, 1632, 1642, 1577, 1438, 1348, 1255, 1179, 1135, 980, 952, 889, 779 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₃H₃₀N₄O₇([M+Na]⁺): 617.2007, found: 617.1998.

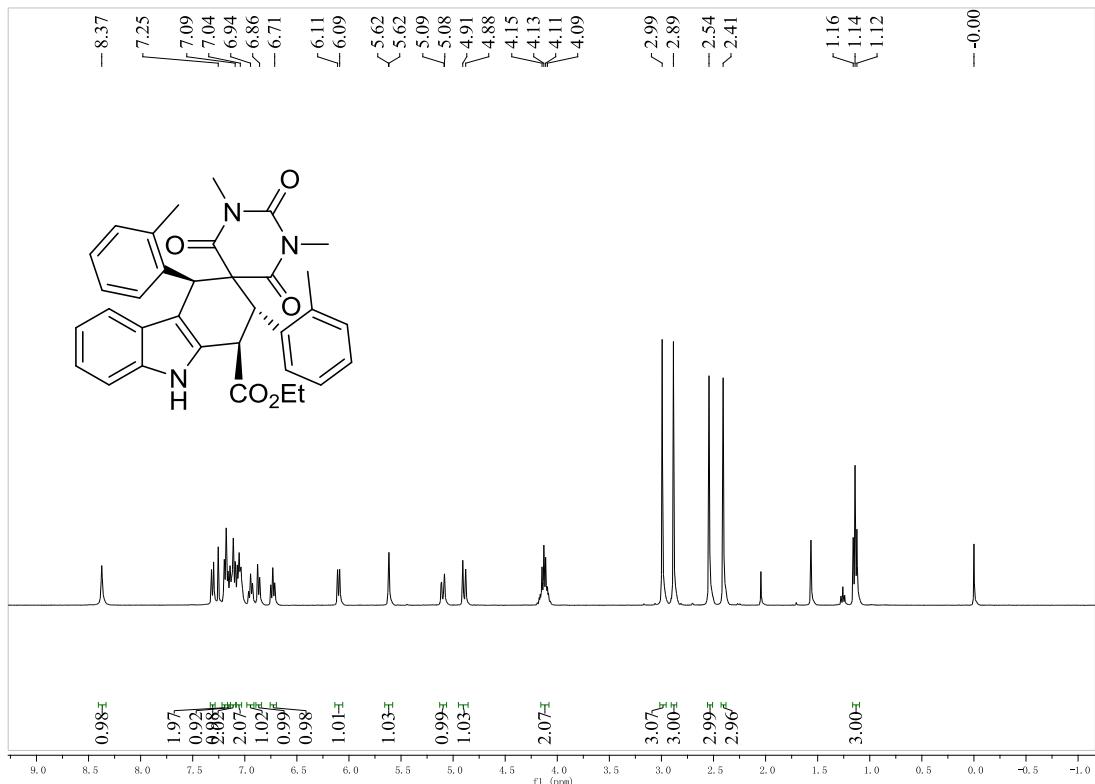


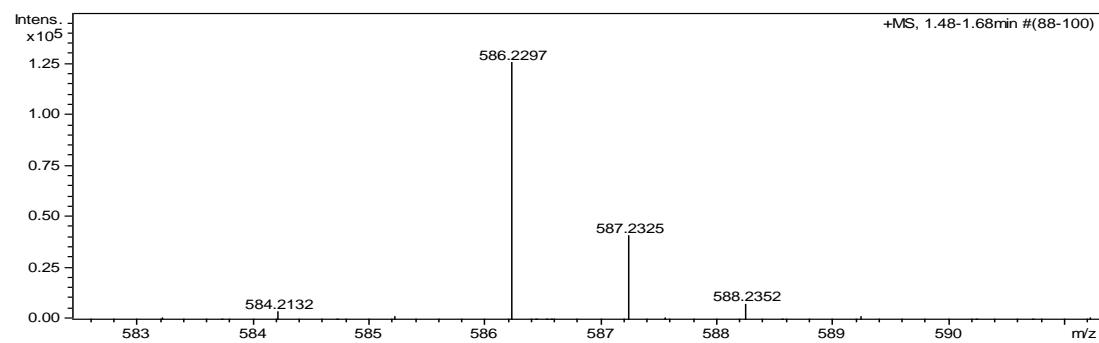
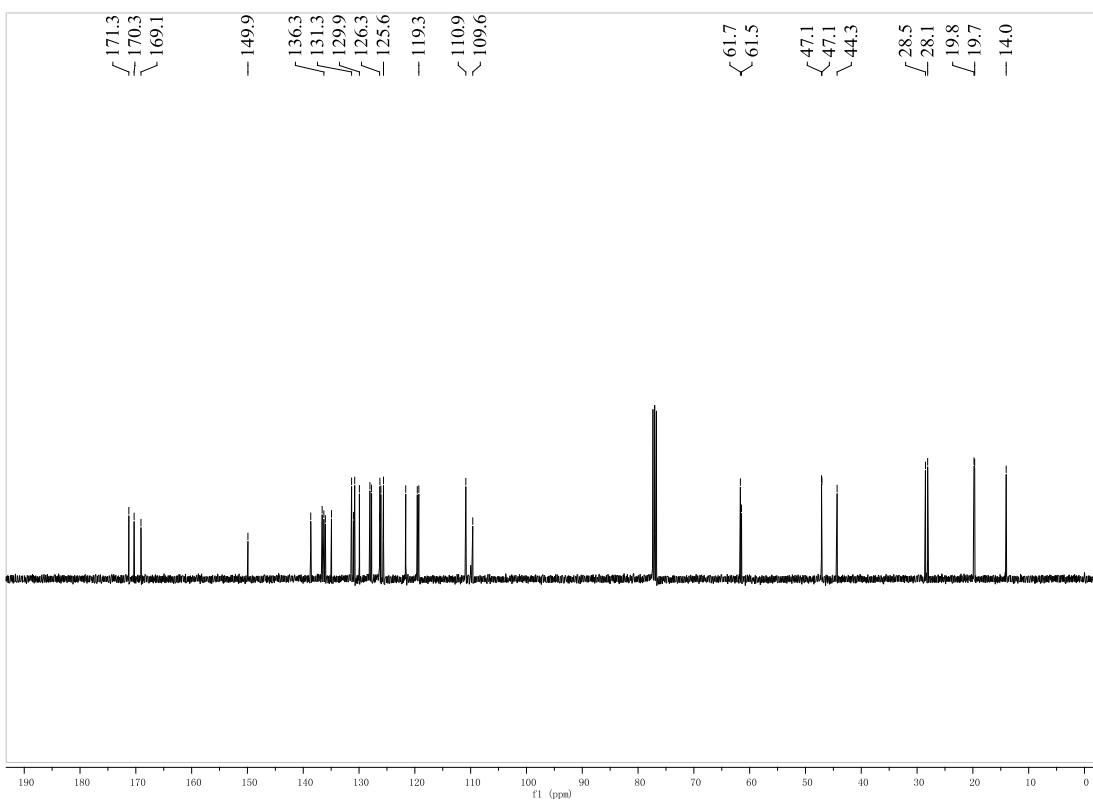


Ethyl

rel-(*1R,2S,4R*)-1',3'-dimethyl-2',4',6'-trioxo-2,4-di-*o*-tolyl-1,1',2,3',4,4',6',9-octahydro-2'H-spiro[carbazole-3,5'-pyrimidine]-1-carboxylate (1k'):

yellow solid, 71%, m.p. 203-206 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.37 (s, 1H, NH), 7.31 (d, J = 8.4 Hz, 1H, ArH), 7.18 (t, J = 7.2 Hz, 1H, ArH), 7.15 (d, J = 7.2 Hz, 1H, ArH), 7.13-7.09 (m, 2H, ArH), 7.07-7.04 (m, 2H, ArH), 6.95 (t, J = 7.2 Hz, 1H, ArH), 6.86 (d, J = 8.0 Hz, 1H, ArH), 6.73 (t, J = 7.2 Hz, 1H, ArH), 6.09 (d, J = 8.0 Hz, 1H, ArH), 5.61 (d, J = 1.6 Hz, 1H, CH), 5.10 (dd, J_1 = 11.2 Hz, J_2 = 2.0 Hz, 1H, CH), 4.89 (d, J = 11.2 Hz, 1H, CH), 4.11 (q, J = 7.2 Hz, 2H, CH_2), 2.99 (s, 3H, CH_3), 2.88 (s, 3H, CH_3), 2.54 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 1.14 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (400 MHz, CDCl_3) δ : 171.2, 170.3, 169.0, 149.9, 138.6, 136.6, 136.3, 136.0, 134.9, 131.3, 130.9, 130.7, 129.9, 128.0, 127.7, 126.3, 126.2, 126.0, 125.6, 121.6, 119.5, 119.2, 110.8, 109.6, 61.6, 61.4, 47.1, 47.0, 44.3, 28.5, 28.1, 19.8, 19.6, 14.0; IR(KBr) ν : 3382, 3245, 3163, 3023, 2918, 2832, 2152, 1873, 1655, 1631, 1542, 1428, 1317, 1295, 1167, 1145, 956, 923, 872, 745 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{34}\text{H}_{33}\text{N}_3\text{O}_5$ ([M+Na] $^+$): 586.2312, found: 586.2297.

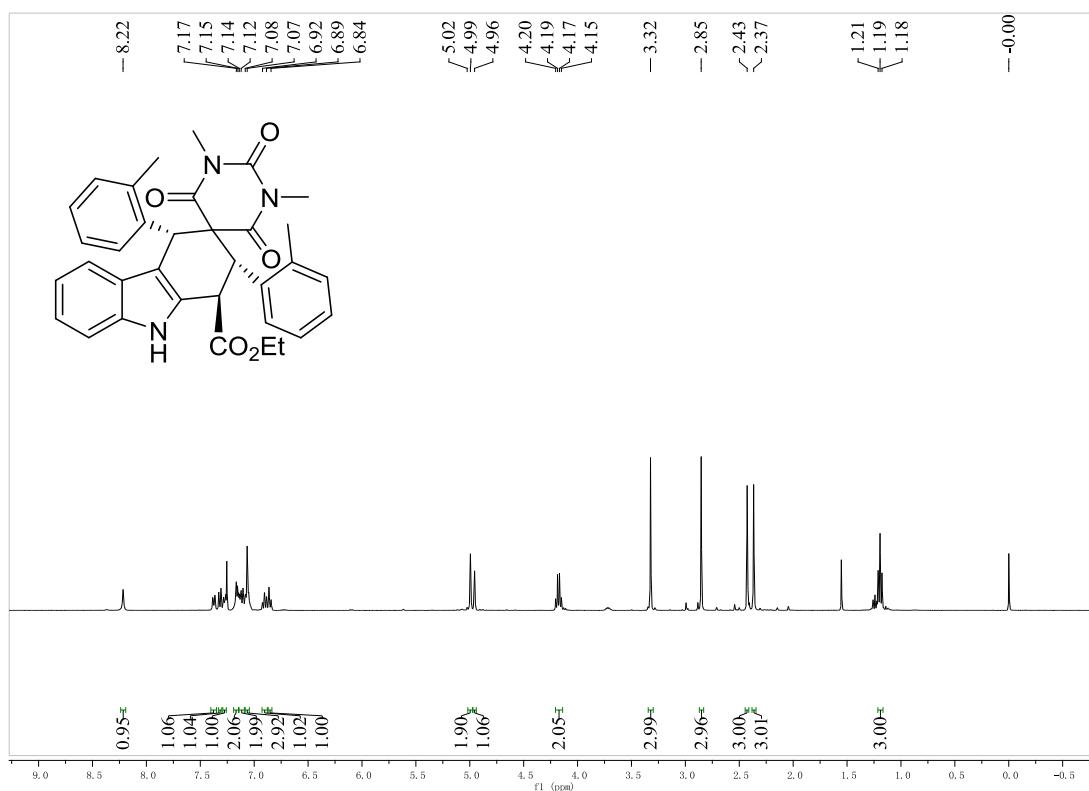


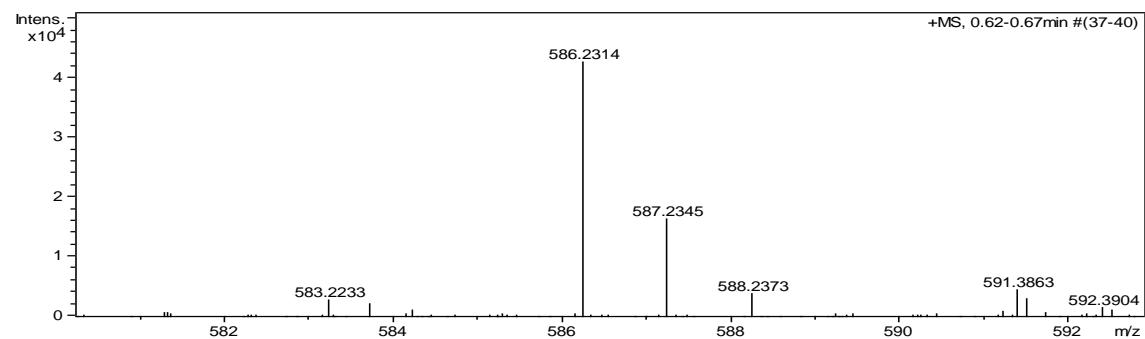
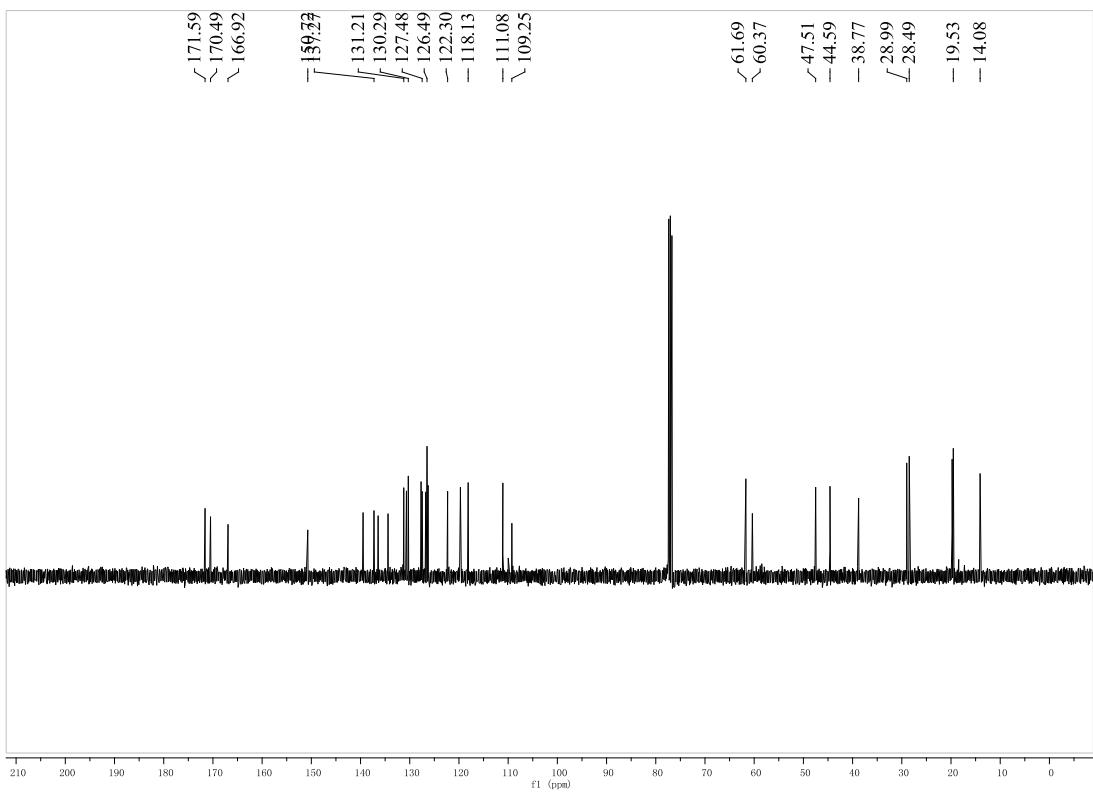


Ethyl

*rel-(1*R*,2*S*,4*S*)-1',3'-dimethyl-2',4',6'-trioxo-2,4-di-*o*-tolyl-1,1',2,3',4,4',6',9-octahydro-2'H-spiro[carbazole-3,5'-pyrimidine]-1-carboxylate (1k')*:

yellow solid, 9%, m.p. 211-214 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.22 (s, 1H, NH), 7.37 (d, *J* = 8.4 Hz, 1H, ArH), 7.31 (d, *J* = 8.4 Hz, 1H, ArH), 7.28-7.26 (m, 1H, ArH), 7.17-7.15 (m, 2H, ArH), 7.14-7.10 (m, 2H, ArH), 7.08-7.05 (m, 3H, ArH), 6.91 (t, *J* = 7.6 Hz, 1H, ArH), 6.85 (d, *J* = 7.6 Hz, 1H, ArH), 5.02-4.99 (m, 2H, CH), 4.96 (s, 1H, CH), 4.17 (q, *J* = 7.2 Hz, 2H, CH₂), 3.32 (s, 3H, CH₃), 2.85 (s, 3H, CH₃), 2.43 (s, 3H, CH₃), 2.37 (s, 3H, CH₃), 1.19 (t, *J* = 7.2 Hz, 3H, CH₃); ¹³C NMR (400 MHz, CDCl₃) δ: 171.5, 170.4, 166.9, 150.7, 139.4, 137.2, 137.2, 136.4, 134.4, 131.3, 131.2, 130.6, 130.2, 127.7, 127.4, 126.7, 126.4, 126.2, 122.3, 119.7, 118.1, 111.0, 109.2, 61.6, 60.3, 47.5, 44.5, 38.7, 28.9, 28.4, 19.7, 19.5, 14.0; IR(KBr) ν: 3379, 3251, 3148, 3033, 2973, 2864, 2173, 1849, 1667, 1618, 1537, 1471, 1365, 1288, 1173, 1151, 982, 907, 866, 755 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₄H₃₃N₃O₅ ([M+Na]⁺): 586.2312, found: 586.2314.

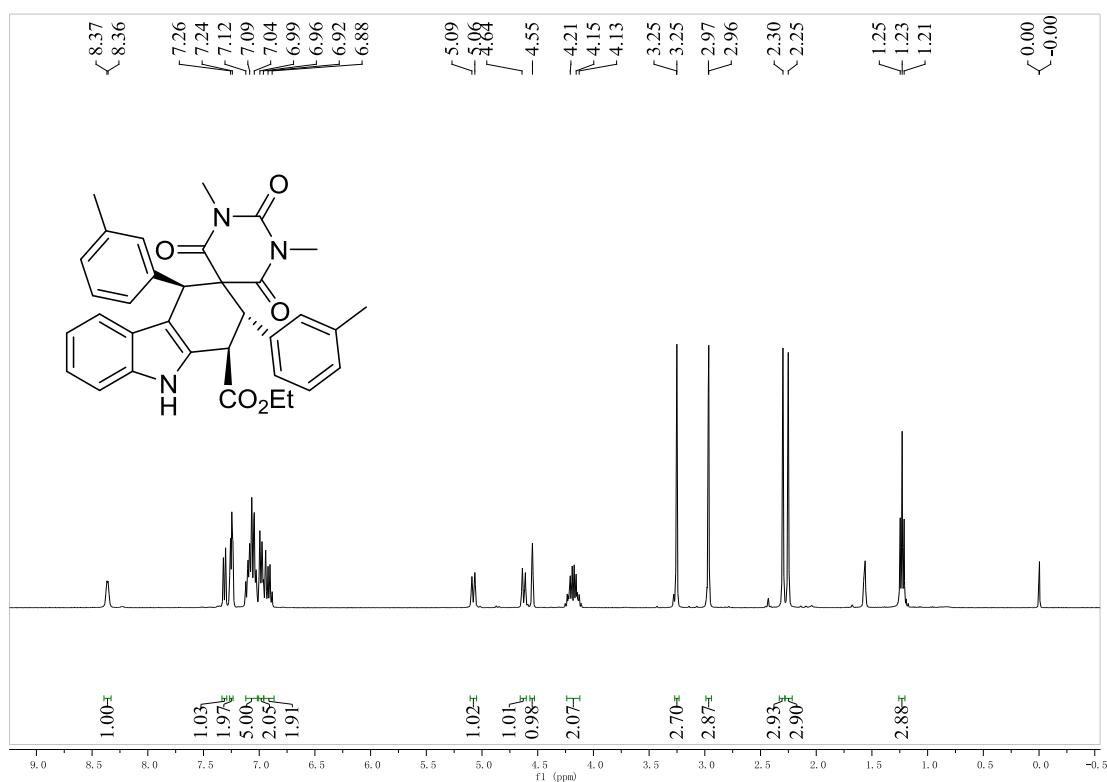


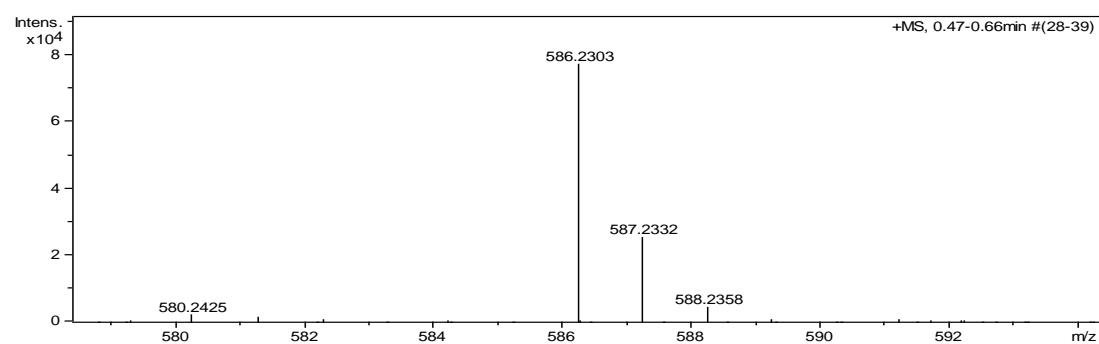
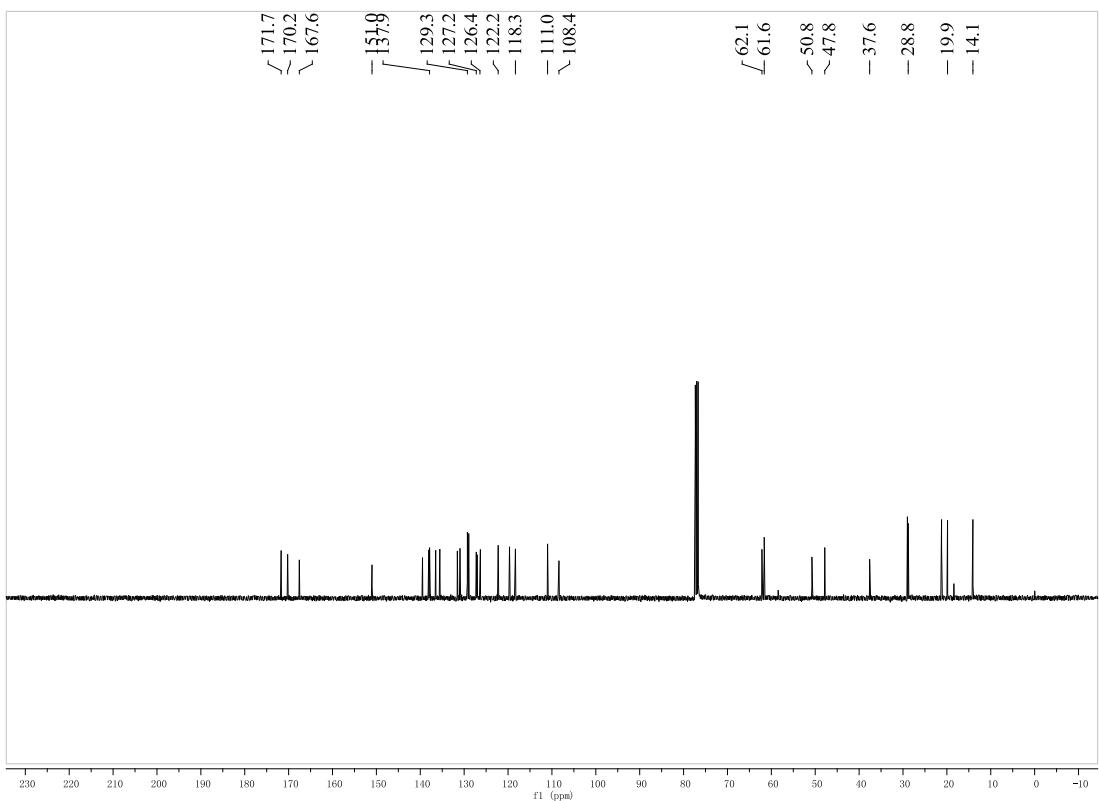


Ethyl

*rel-(1*R*,2*S*,4*R*)-1',3'-dimethyl-2',4',6'-trioxo-2,4-di-*m*-tolyl-1,1',2,3',4,4',6',9-octahydro-2'H-spiro[carbazole-3,5'-pyrimidine]-1-carboxylate (1l):*

yellow solid, 77%, m.p. 201-204 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.36 (s, 1H, NH), 7.31 (d, J = 8.0 Hz, 1H, ArH), 7.26-7.24 (m, 2H, ArH), 7.12-7.03 (m, 5H, ArH), 6.99-6.96 (m, 2H, ArH), 6.94-6.88 (m, 2H, ArH), 5.08 (d, J = 10.4 Hz, 1H, CH), 4.62 (d, J = 10.4 Hz, 1H, CH), 4.55 (s, 1H, CH), 4.17 (q, J = 7.2 Hz, 2H, CH_2), 3.25 (s, 3H, CH_3), 2.97 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 1.23 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (400 MHz, CDCl_3) δ : 171.7, 170.2, 167.5, 150.9, 139.4, 138.0, 137.8, 136.4, 135.5, 131.5, 130.9, 129.2, 128.9, 127.2, 127.0, 126.4, 126.3, 122.2, 119.6, 118.3, 110.9, 108.3, 62.1, 61.6, 50.7, 47.8, 37.6, 28.9, 28.8, 21.2, 19.8, 14.0; IR(KBr) ν : 3371, 3213, 3148, 3056, 2972, 2846, 2133, 1892, 1665, 1641, 1572, 1435, 1326, 1287, 1155, 1123, 942, 913, 865, 738 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{34}\text{H}_{33}\text{N}_3\text{O}_5$ ([M+Na] $^+$): 586.2312, found: 586.2303.

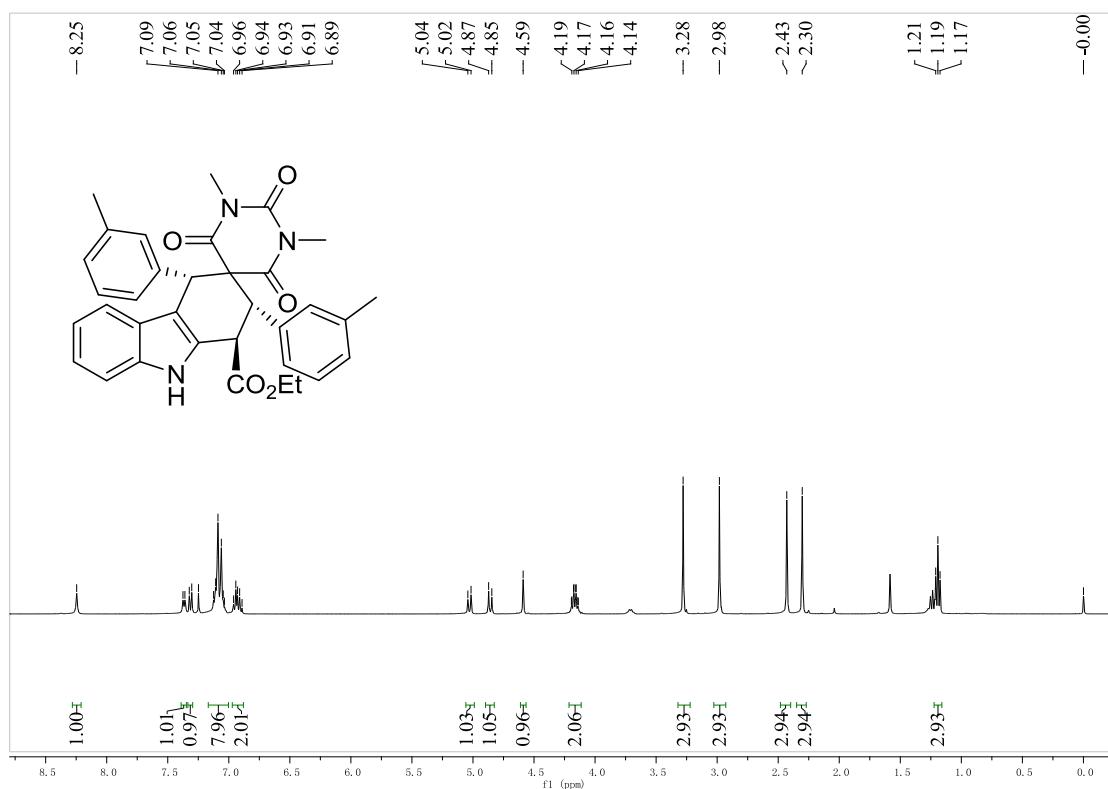


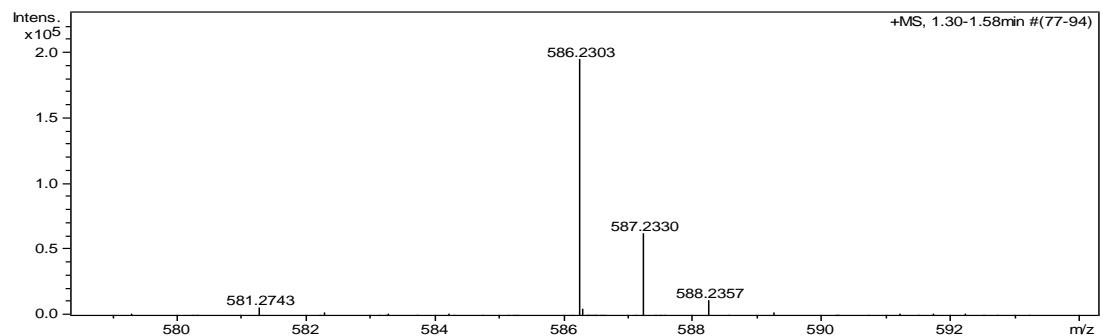
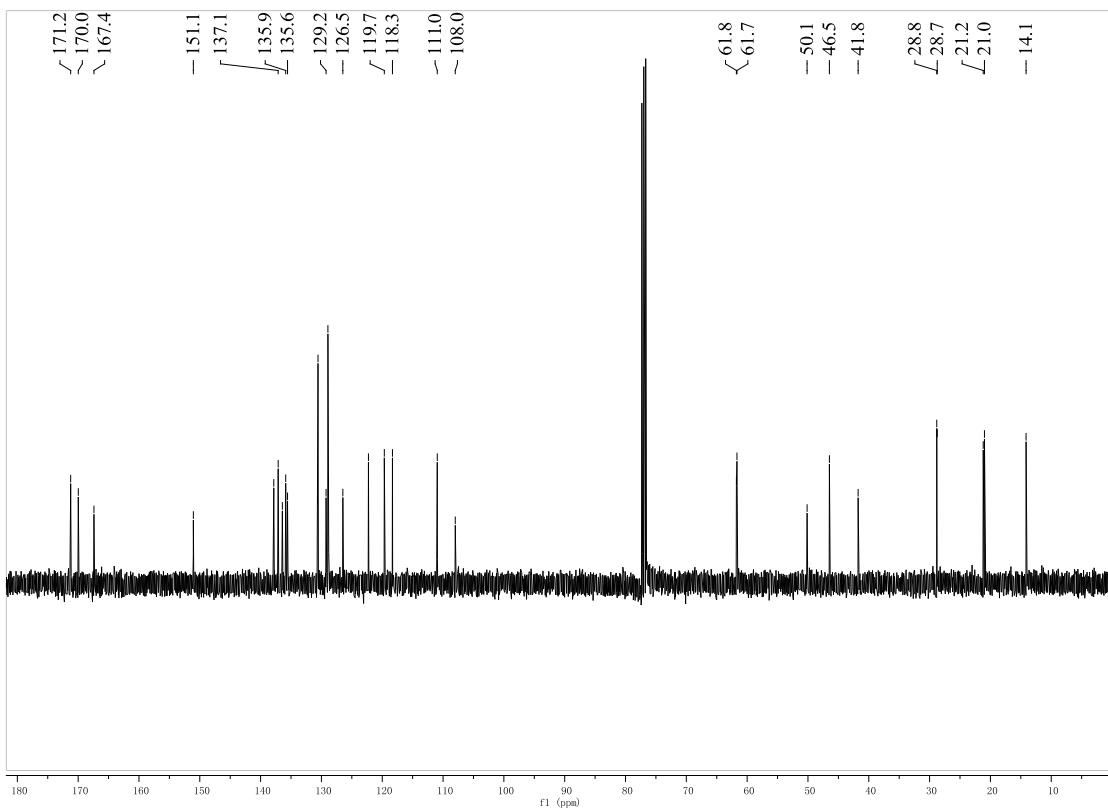


Ethyl

*rel-(1*R*,2*S*,4*S*)-1',3'-dimethyl-2',4',6'-trioxo-2,4-di-*m*-tolyl-1,1',2,3',4,4',6',9-octahydro-2'H-spiro[carbazole-3,5'-pyrimidine]-1-carboxylate (1l')*:

yellow solid, 6%, m.p. 213-215 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.25 (s, 1H, NH), 7.36 (d, J = 6.4 Hz, 1H, ArH), 7.31 (d, J = 6.4 Hz, 1H, ArH), 7.12-7.04 (m, 8H, ArH), 6.96-6.89 (m, 2H, ArH), 5.03 (d, J = 10.4 Hz, 1H, CH), 4.86 (d, J = 10.4 Hz, 1H, CH), 4.59 (s, 1H, CH), 4.17 (q, J = 6.8 Hz, 2H, CH_2), 3.28 (s, 3H, CH_3), 2.98 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 1.19 (t, J = 6.8 Hz, 3H, CH_3); ^{13}C NMR (400 MHz, CDCl_3) δ : 171.2, 169.9, 167.4, 151.0, 137.8, 137.1, 136.4, 135.8, 135.5, 130.6, 130.5, 129.2, 128.9, 128.8, 126.4, 122.2, 119.6, 118.3, 110.9, 107.9, 61.7, 61.6, 50.1, 46.4, 41.7, 28.8, 28.7, 21.1, 20.9, 14.1; IR(KBr) ν : 3359, 3278, 3154, 3066, 2965, 2852, 2148, 1876, 1642, 1612, 1565, 1487, 1345, 1245, 1123, 1111, 999, 945, 865, 742 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{34}\text{H}_{33}\text{N}_3\text{O}_5$ ([M+Na] $^+$): 586.2312, found: 586.2303.

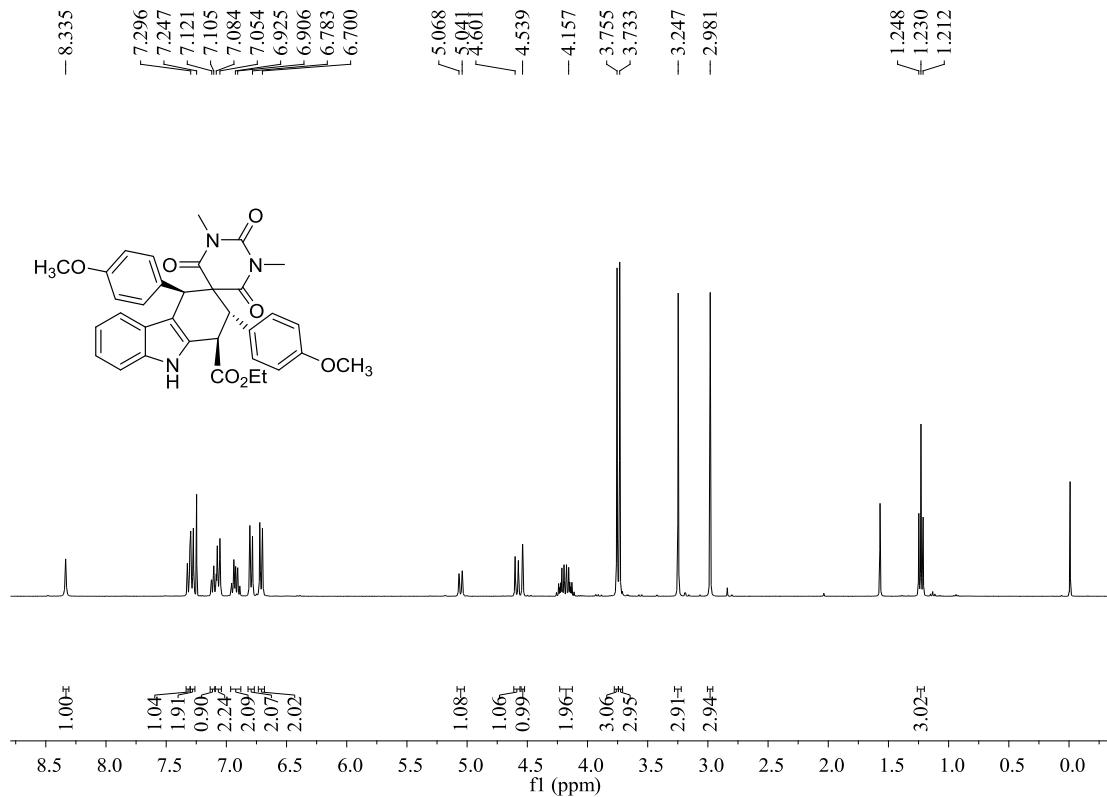


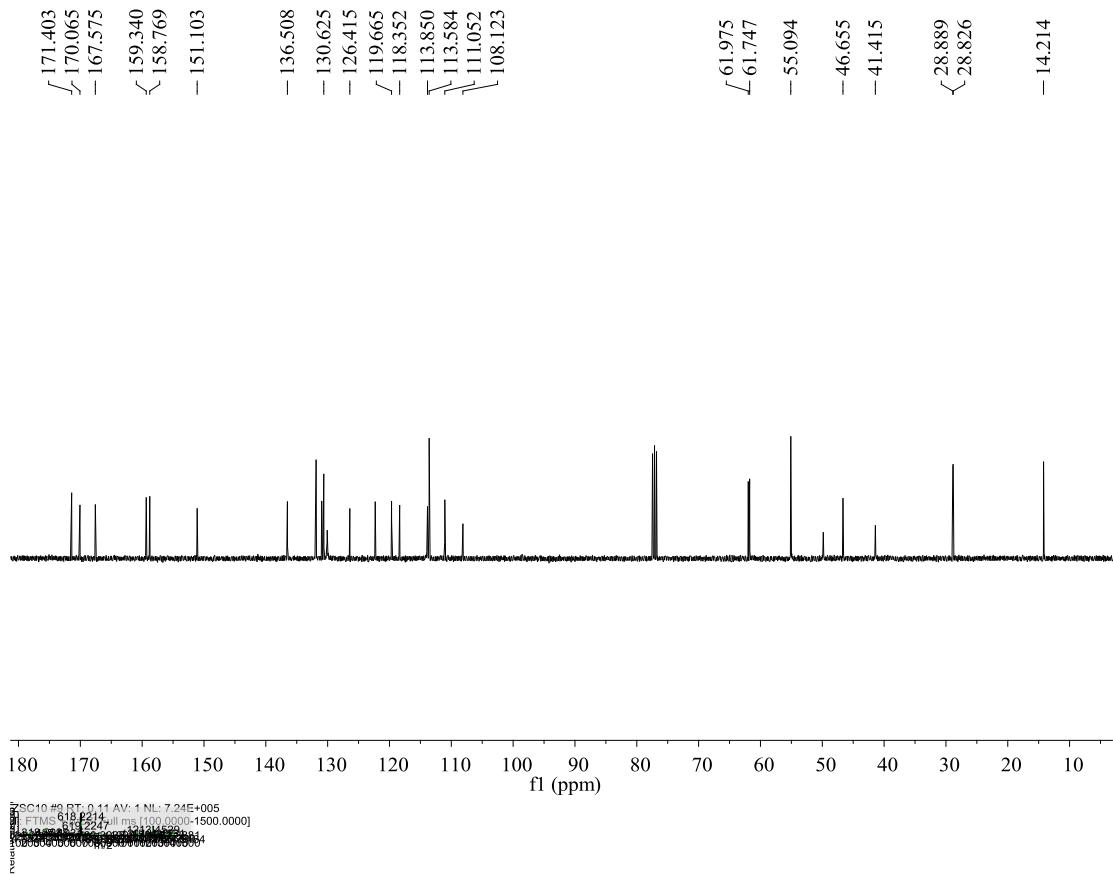


Ethyl

*rel-(1*R*,2*S*,4*R*)-2,4-bis(4-methoxyphenyl)-1',3'-dimethyl-2',4',6'-trioxo-1,1',2,3',4,4',6',9-octahydro-2'H-spiro[carbazole-3,5'-pyrimidine]-1-carboxylate (1m):*

yellow solid, 75%, m.p. 201-204 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.34 (s, 1H, NH), 7.32 (d, *J* = 8.0 Hz, 1H, ArH), 7.29 (d, *J* = 8.8 Hz, 2H, ArH), 7.13-7.06 (m, 3H, ArH), 6.96-6.90 (m, 2H, ArH), 6.80 (d, *J* = 8.8 Hz, 2H, ArH), 6.72 (d, *J* = 8.8 Hz, 2H, ArH), 5.06 (d, *J* = 10.8 Hz, 1H, CH), 4.59 (d, *J* = 10.8 Hz, 1H, CH), 4.55 (s, 1H, CH), 4.19 (q, *J* = 7.2 Hz, 2H, CH₂), 3.76 (s, 3H, OCH₃), 3.74 (s, 3H, OCH₃), 3.26 (s, 3H, CH₃), 2.99 (s, 3H, CH₃), 1.24 (t, *J* = 7.2 Hz, 3H, CH₃); ¹³C NMR (400 MHz, CDCl₃) δ: 171.4, 170.0, 167.5, 159.3, 158.7, 151.1, 136.5, 131.8, 130.9, 130.6, 126.4, 122.3, 119.6, 118.3, 113.8, 113.5, 111.0, 108.1, 61.9, 61.7, 55.1, 55.0, 49.8, 46.6, 41.4, 28.8, 28.8, 14.2; IR(KBr) ν: 3345, 3267, 3132, 3017, 2960, 2833, 2140, 1873, 1641, 1601, 1514, 1411, 1372, 1255, 1146, 1137, 967, 941, 871, 765 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₄H₃₃N₃O₇ ([M+Na]⁺): 618.2211, found: 618.2214.

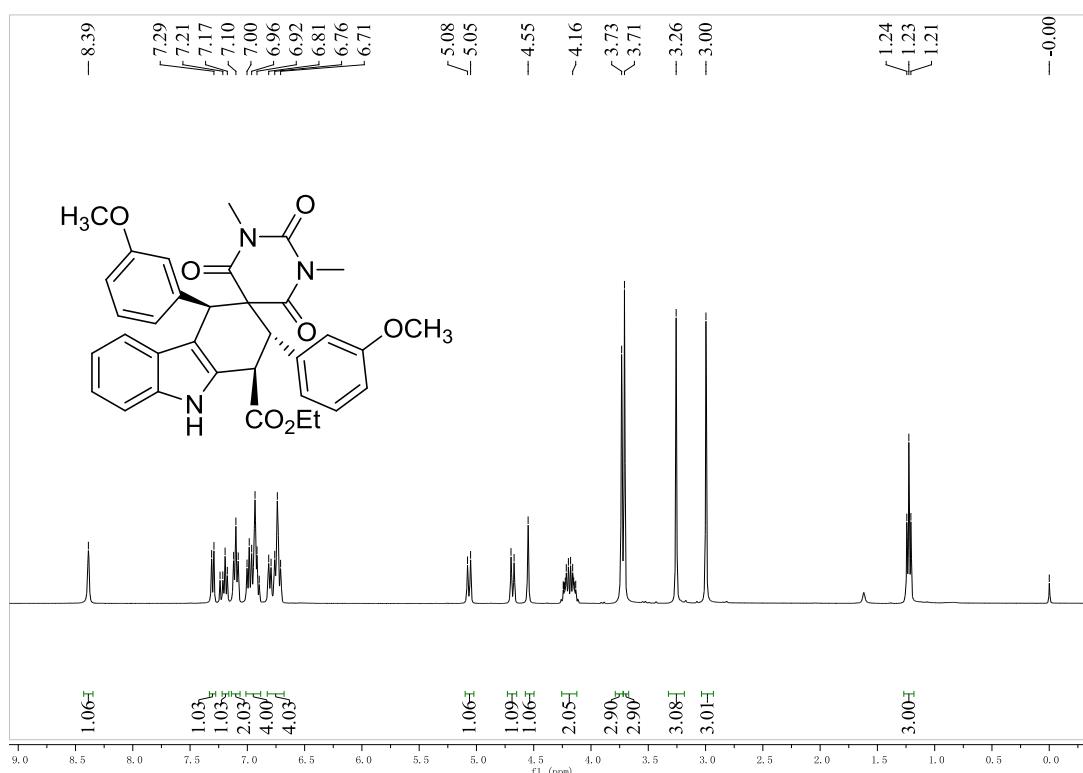


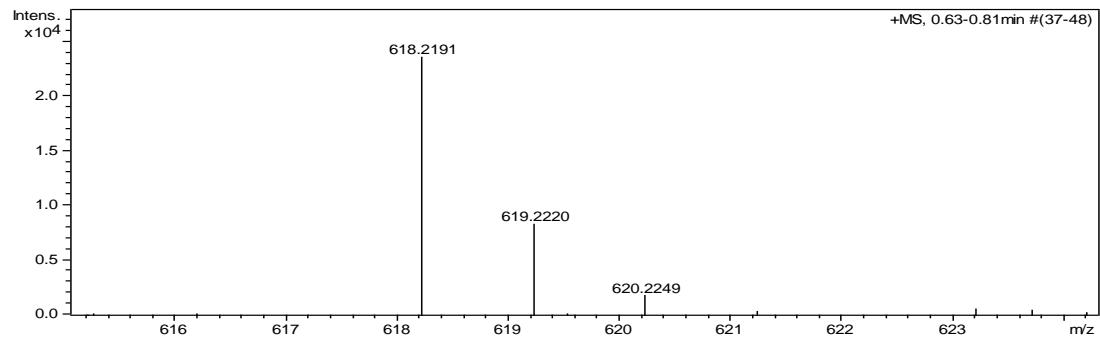
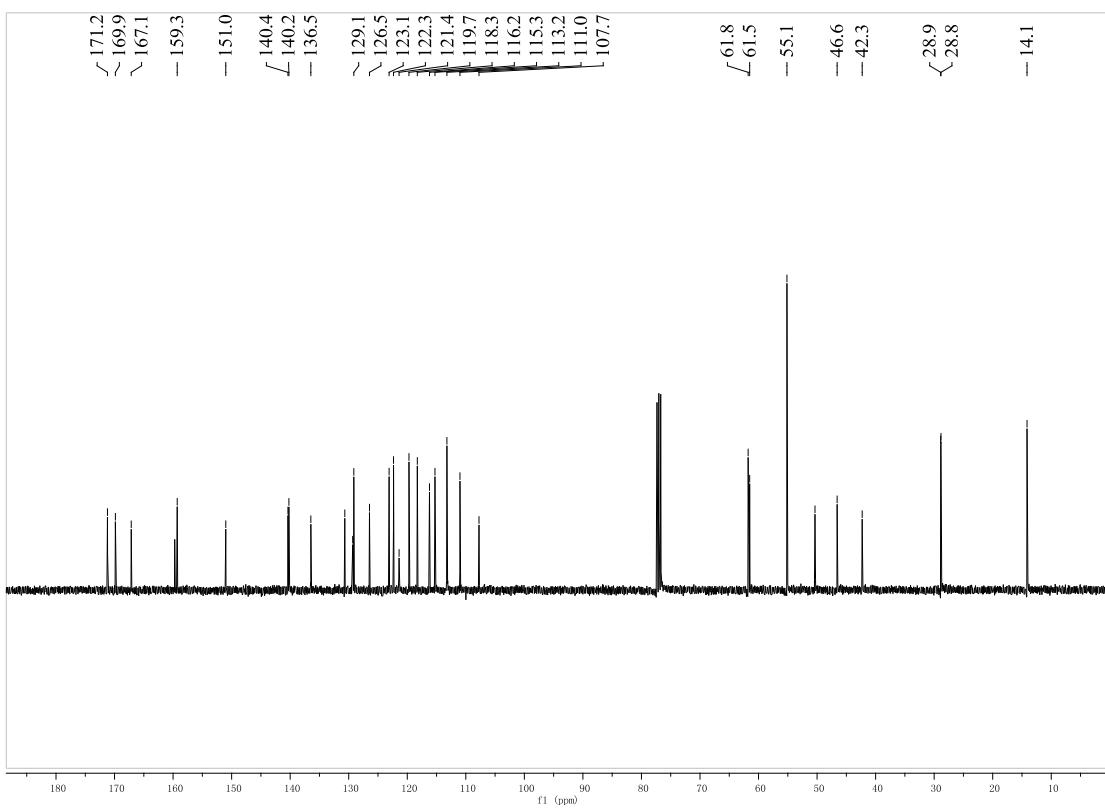


Ethyl

*rel-(1*R*,2*S*,4*R*)-2,4-bis(3-methoxyphenyl)-1',3'-dimethyl-2',4',6'-trioxo-1,1',2,3',4,4',6',9-octahydro-2'H-spiro[carbazole-3,5'-pyrimidine]-1-carboxylate (1n):*

yellow solid, 70%, m.p. 209-213 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.39 (s, 1H, NH), 7.30 (d, J = 8.0 Hz, 1H, ArH), 7.19 (t, J = 8.0 Hz, 1H, ArH), 7.10 (t, J = 8.0 Hz, 2H, ArH), 7.00-6.90 (m, 4H, ArH), 6.81-6.71 (m, 4H, ArH), 5.07 (d, J = 10.4 Hz, 1H, CH), 4.68 (d, J = 10.8 Hz, 1H, CH), 4.55 (s, 1H, CH), 4.18 (q, J = 7.2 Hz, 2H, CH_2), 3.73 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.26 (s, 3H, CH_3), 3.00 (s, 3H, CH_3), 1.23 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (400 MHz, CDCl_3) δ : 171.2, 169.8, 167.1, 151.0, 140.3, 140.2, 136.4, 130.6, 129.3, 129.1, 126.4, 123.1, 122.3, 121.3, 119.7, 118.2, 116.2, 115.2, 113.2, 111.0, 107.7, 61.7, 61.5, 55.1, 50.3, 46.5, 42.2, 28.8, 28.8, 14.1; IR(KBr) ν : 3372, 3264, 3138, 3072, 2946, 2831, 2172, 1862, 1655, 1638, 1571, 1467, 1352, 1261, 1178, 1121, 973, 952, 834, 721 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{34}\text{H}_{33}\text{N}_3\text{O}_7$ ([M+Na] $^+$): 618.2211, found: 618.2191.

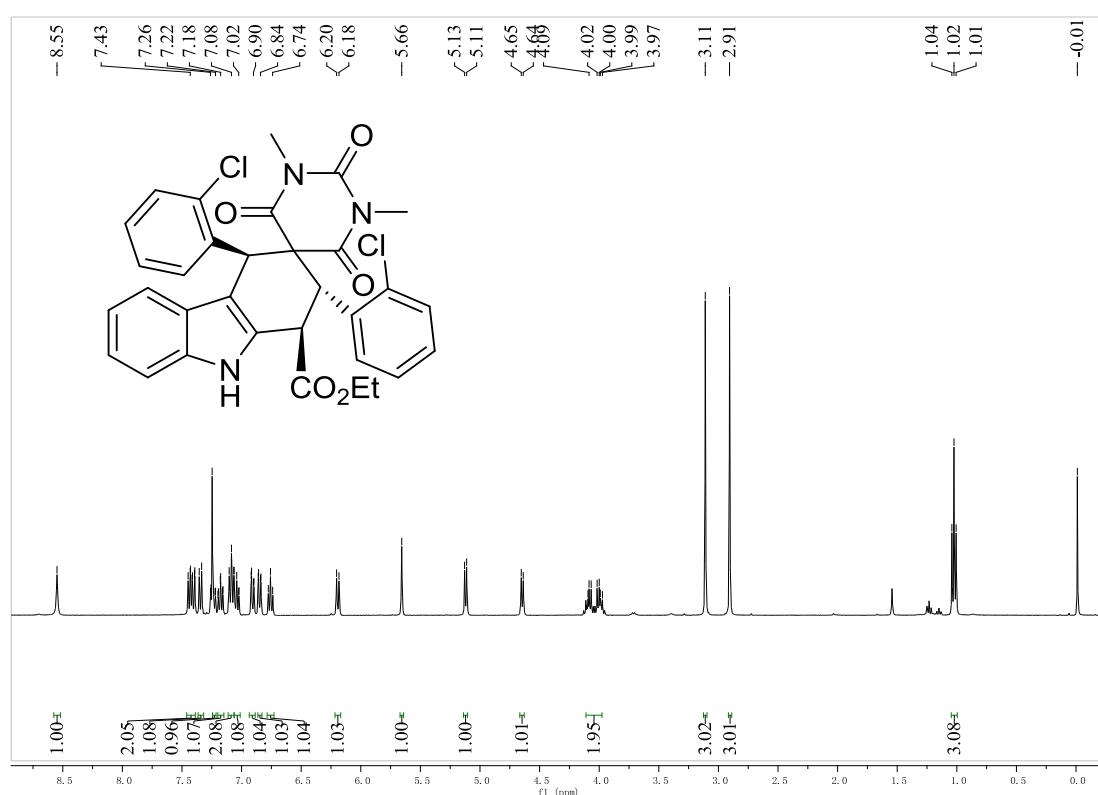


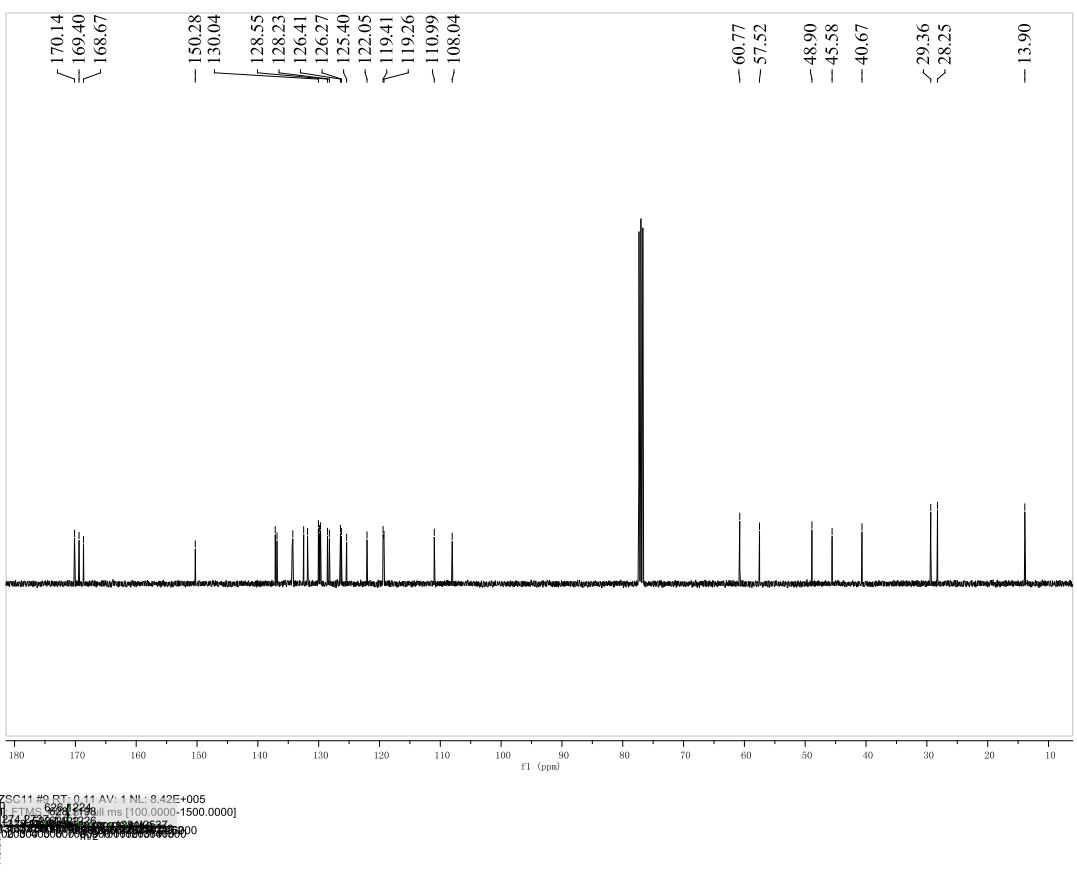


Ethyl

*rel-(1*R*,2*R*,4*R*)-2,4-bis(2-chlorophenyl)-1',3'-dimethyl-2',4',6'-trioxo-1,1',2,3',4,4',6',9-octahydroro-2'H-spiro[carbazole-3,5'-pyrimidine]-1-carboxylate (1o):*

yellow solid, 72%, m.p. 214-216 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.55 (s, 1H, NH), 7.45-7.39 (m, 2H, ArH), 7.34 (d, J = 8.4 Hz, 1H, ArH), 7.26-7.22 (m, 1H, ArH), 7.20-7.16 (m, 1H, ArH), 7.09 (t, J = 7.6 Hz, 2H, ArH), 7.04 (t, J = 8.4 Hz, 1H, ArH), 6.91 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H, ArH), 6.85 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H, ArH), 6.76 (t, J = 7.2 Hz, 1H, ArH), 6.19 (d, J = 8.0 Hz, 1H, ArH), 5.66 (s, 1H, CH), 5.12 (d, J = 6.8 Hz, 1H, CH), 4.64 (d, J = 10.8 Hz, 1H, CH), 4.04 (q, J = 7.2 Hz, 2H, CH_2), 3.11 (s, 3H, CH_3), 2.91 (s, 3H, CH_3), 1.02 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (400 MHz, CDCl_3) δ : 170.1, 169.3, 168.6, 150.2, 137.1, 136.8, 134.2, 132.4, 131.8, 130.0, 129.8, 129.6, 128.5, 128.2, 126.4, 126.2, 125.4, 122.0, 119.4, 119.2, 110.9, 108.0, 60.7, 57.5, 48.9, 45.5, 40.6, 29.3, 28.2, 13.8; IR(KBr) ν : 3341, 3257, 3103, 2941, 2856, 2143, 1817, 1643, 1622, 1556, 1454, 1367, 1249, 1165, 1148, 945, 912, 864, 751 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{32}\text{H}_{27}\text{Cl}_2\text{N}_3\text{O}_5$ ([M+Na] $^+$): 626.1220, found: 626.1224.



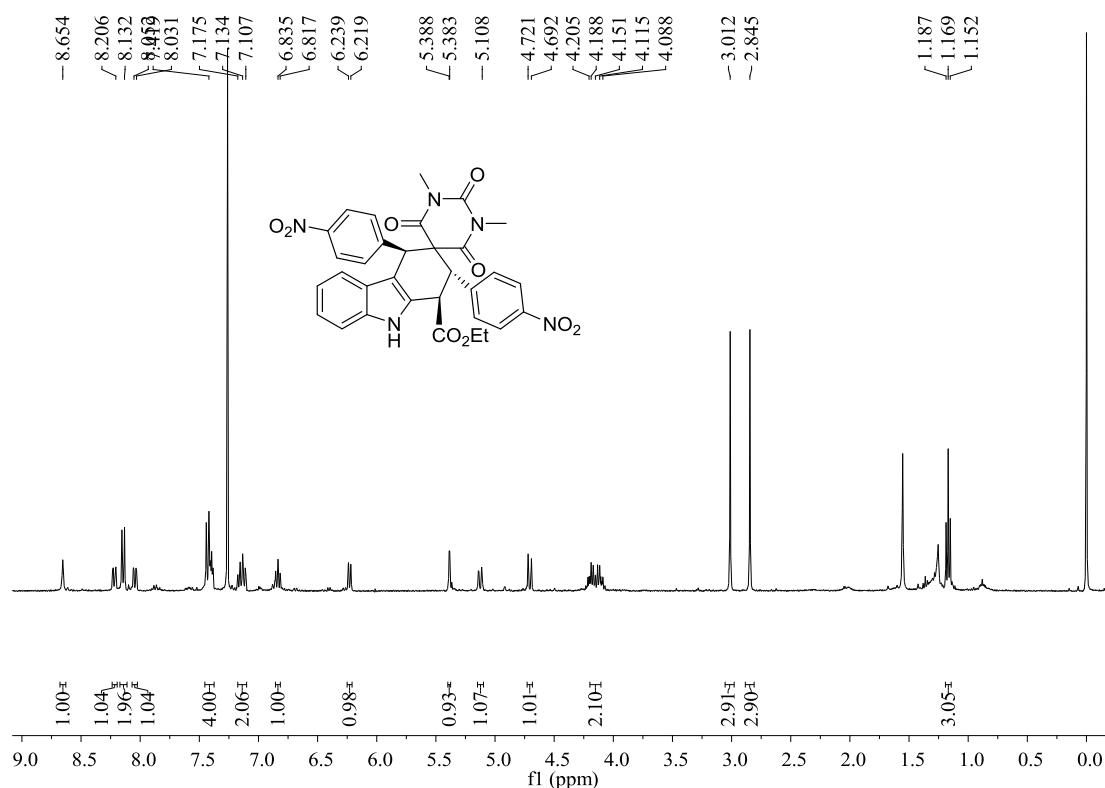


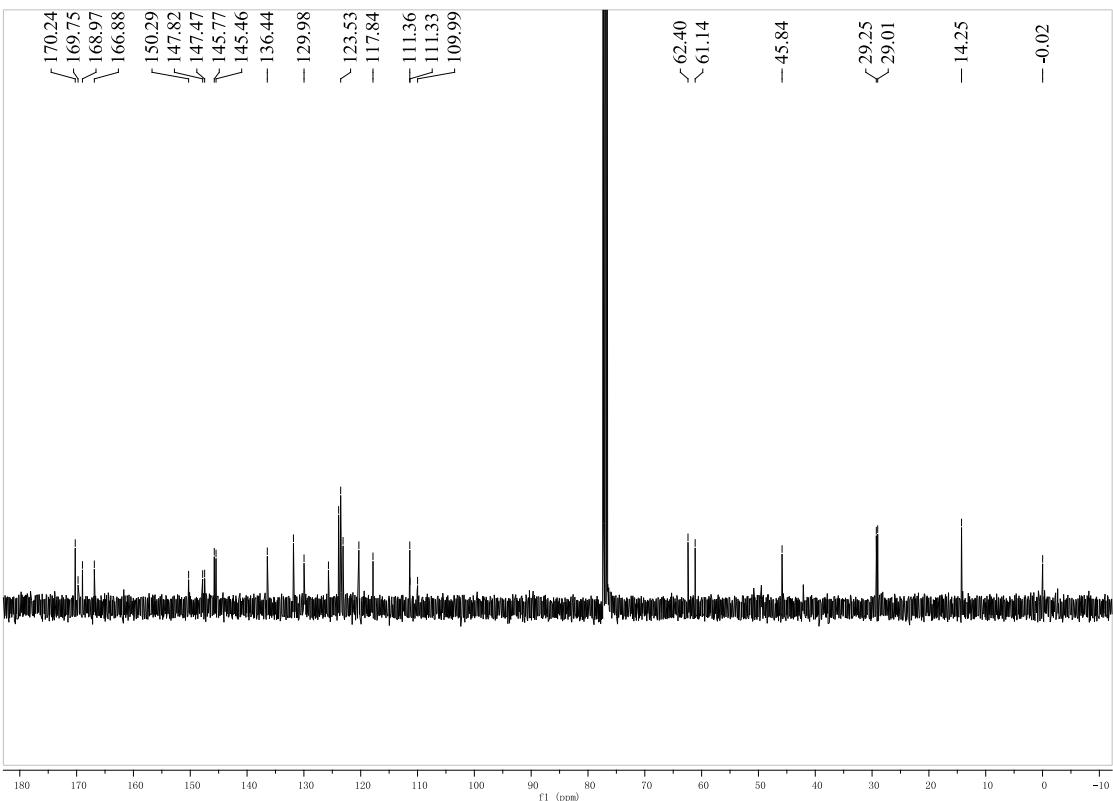
Ethyl

*rel-(1*R*,2*S*,4*R*)-1',3'-dimethyl-2,4-bis(4-nitrophenyl)-2',4',6'-trioxo-1,1',2,3',4,4',6',9-octahydr*

o-2'H-spiro[carbazole-3,5'-pyrimidine]-1-carboxylate (1p):

yellow solid, 63%, m.p. 206-209 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.65 (s, 1H, NH), 8.22 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.4 Hz, 1H, ArH), 8.14 (d, *J* = 8.4 Hz, 2H, ArH), 8.04 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.4 Hz, 1H, ArH), 7.44-7.40 (m, 4H, ArH), 7.17-7.11 (m, 2H, ArH), 6.84 (t, *J* = 8.0 Hz, 1H, ArH), 6.22 (d, *J* = 8.0 Hz, 1H, ArH), 5.38 (d, *J* = 2.0 Hz, 1H, CH), 5.12 (dd, *J*₁ = 10.6 Hz, *J*₂ = 2.0 Hz, 1H, CH), 4.71 (d, *J* = 10.6 Hz, 1H, CH), 4.15 (q, *J* = 7.2 Hz, 2H, CH₂), 3.01 (s, 3H, CH₃), 2.84 (s, 3H, CH₃), 1.17 (t, *J* = 7.2 Hz, 3H, CH₃); ¹³C NMR (400 MHz, CDCl₃) δ: 170.2, 169.7, 168.9, 166.8, 150.2, 147.8, 147.4, 145.7, 145.4, 136.4, 131.8, 129.9, 125.6, 123.8, 123.5, 123.1, 120.3, 117.8, 111.3, 111.3, 109.9, 62.4, 61.1, 45.8, 29.2, 29.0, 14.2; IR(KBr) ν: 3342, 3255, 3167, 3041, 2951, 2841, 2163, 1826, 1661, 1643, 1565, 1432, 1355, 1248, 1163, 1153, 963, 948, 827, 761 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₂H₂₇N₅O₉ ([M+H]⁺): 678.1701, found: 678.1703.



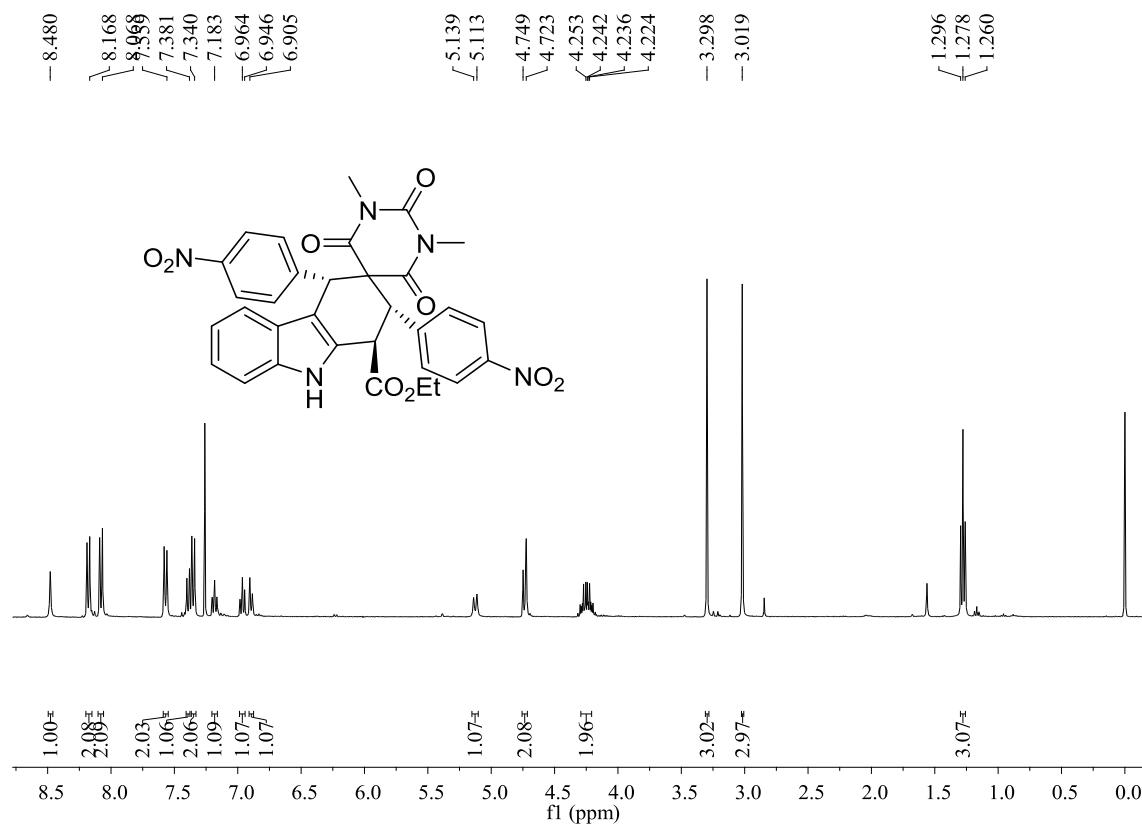


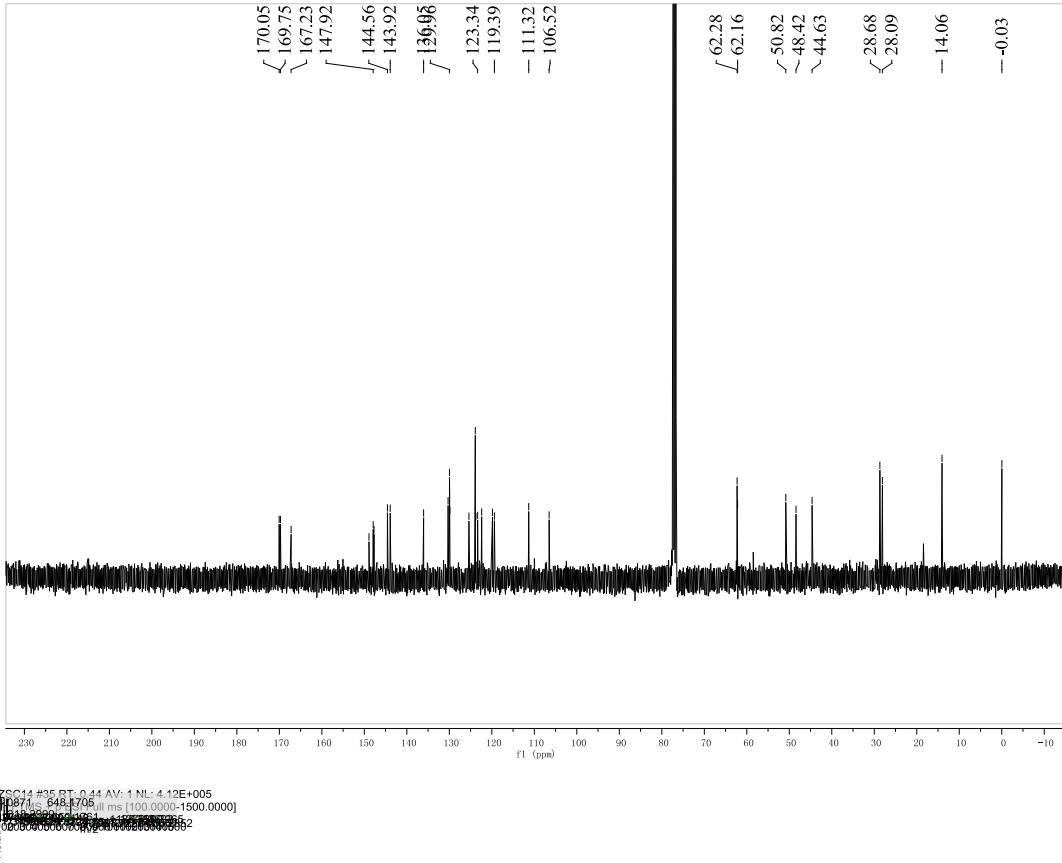
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P22.022.648.1703 ms [100.0000-1500.0000]
P23.022.648.1703 ms [100.0000-1500.0000]

Ethyl

*rel-(1*R*,2*S*,4*S*)-1',3'-dimethyl-2,4-bis(4-nitrophenyl)-2',4',6'-trioxo-1,1',2,3',4,4',6',9-octahydr
o-2'H-spiro[carbazole-3,5'-pyrimidine]-1-carboxylate (1p')*:

yellow solid, 9%, m.p. 209–213 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.48 (s, 1H, NH), 8.17 (d, *J* = 8.8 Hz, 2H, ArH), 8.08 (d, *J* = 8.8 Hz, 2H, ArH), 7.57 (d, *J* = 8.8 Hz, 2H, ArH), 7.39 (d, *J* = 8.4 Hz, 1H, ArH), 7.35 (d, *J* = 8.8 Hz, 2H, ArH), 7.18 (t, *J* = 8.0 Hz, 1H, ArH), 6.96 (t, *J* = 7.2 Hz, 1H, ArH), 6.89 (d, *J* = 8.0 Hz, 1H, ArH), 5.12 (d, *J* = 10.4 Hz, 1H, CH), 4.75 (d, *J* = 10.4 Hz, 1H, CH), 4.72 (s, 1H, CH), 4.24 (q, *J* = 7.2 Hz, 2H, CH₂), 3.30 (s, 3H, CH₃), 3.02 (s, 3H, CH₃), 1.28 (t, *J* = 7.2 Hz, 3H, CH₃); ¹³C NMR (400 MHz, CDCl₃) δ: 170.0, 169.7, 167.2, 148.9, 147.9, 147.7, 144.5, 143.9, 136.0, 130.2, 129.9, 129.9, 129.8, 125.3, 123.8, 123.7, 123.3, 122.3, 119.8, 119.3, 111.3, 106.5, 62.3, 62.2, 50.8, 48.4, 44.6, 28.6, 28.0, 14.0; IR(KBr) ν: 3342, 3241, 3167, 3041, 2938, 2841, 2163, 1826, 1661, 1631, 1565, 1432, 1355, 1248, 1178, 1153, 963, 948, 827, 761 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₂H₂₇N₅O₉ ([M+Na]⁺): 648.1701, found: 648.1705.



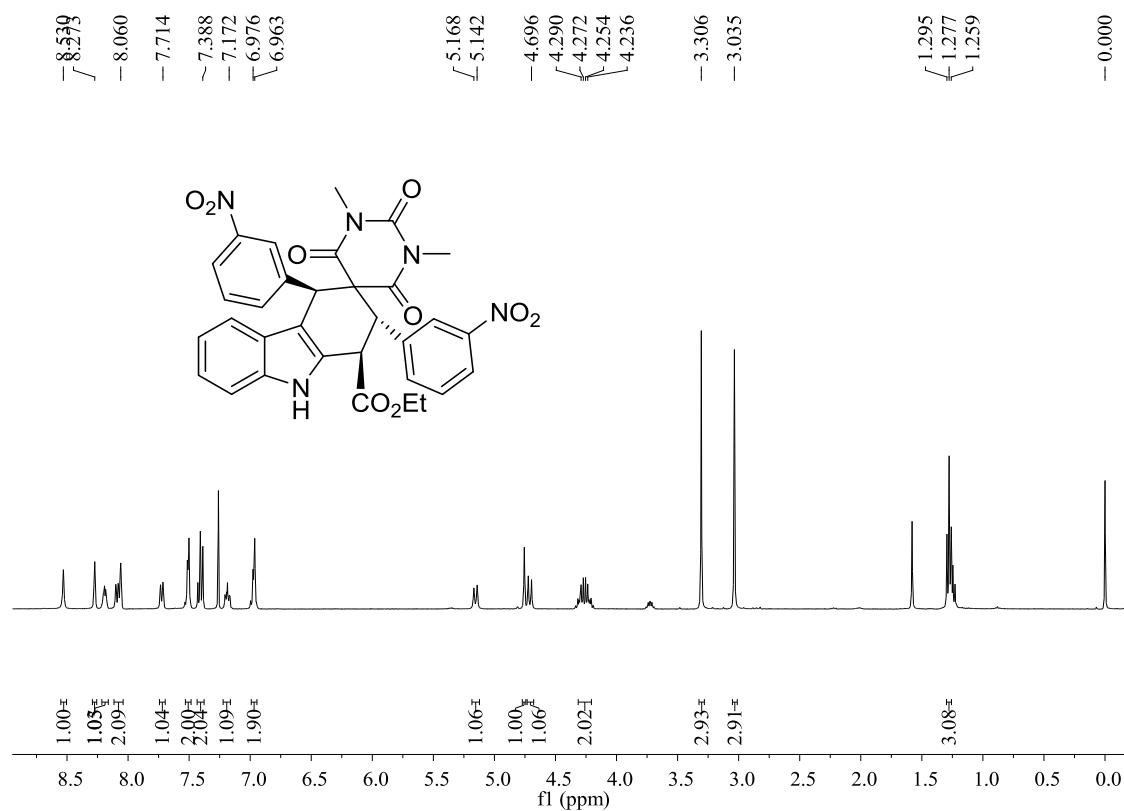


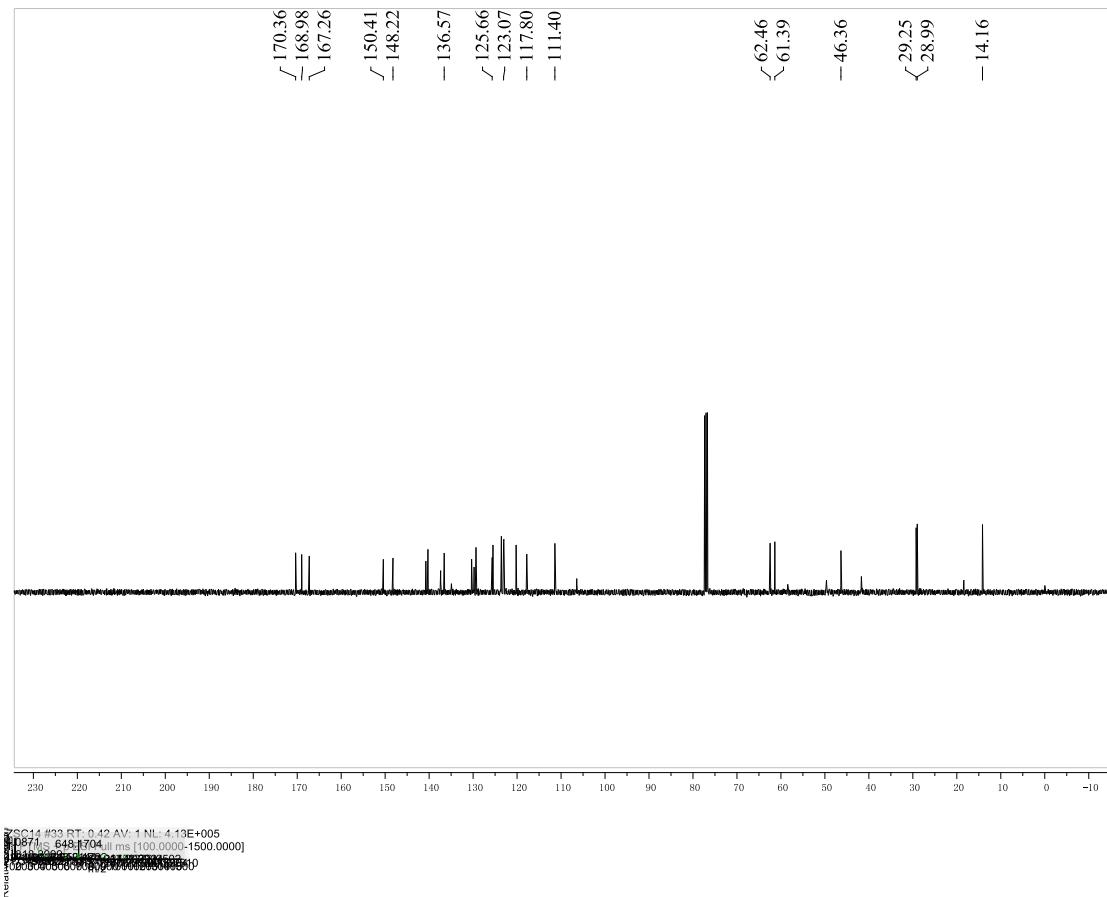
Ethyl

*rel-(1*R*,2*S*,4*R*)-1',3'-dimethyl-2,4-bis(3-nitrophenyl)-2',4',6'-trioxo-1,1',2,3',4,4',6',9-octahydr*

o-2'H-spiro[carbazole-3,5'-pyrimidine]-1-carboxylate (1q):

yellow solid, 63%, m.p. 221-224 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.53 (s, 1H, NH), 8.27 (s, 1H, ArH), 8.20-8.18 (m, 1H, ArH), 8.10-8.06 (m, 2H, ArH), 7.72 (d, *J* = 8.0 Hz, 1H, ArH), 7.52-7.50 (m, 2H, ArH), 7.41 (t, *J* = 8.0 Hz, 2H, ArH), 7.21-7.17 (m, 1H, ArH), 6.98-6.96 (m, 2H, ArH), 5.15 (d, *J* = 10.4 Hz, 1H, CH), 4.76 (s, 1H, CH), 4.71 (d, *J* = 10.4 Hz, 1H, CH), 4.26 (q, *J* = 7.2 Hz, 2H, CH₂), 3.31 (s, 3H, CH₃), 3.04 (s, 3H, CH₃), 1.28 (t, *J* = 7.2 Hz, 3H, CH₃); ¹³C NMR (400 MHz, CDCl₃) δ: 170.3, 168.9, 167.2, 150.4, 148.2, 140.7, 140.2, 137.3, 136.5, 130.3, 129.7, 129.3, 125.6, 125.4, 123.5, 123.0, 123.0, 120.2, 117.7, 111.4, 62.4, 61.3, 46.3, 29.2, 28.9, 14.1; IR(KBr) ν: 3369, 3244, 3157, 3032, 2934, 2857, 2163, 1843, 1631, 1611, 1562, 1483, 1346, 1231, 1159, 1146, 933, 902, 846, 751 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₂H₂₇N₅O₉ ([M+Na]⁺): 648.1701, found: 648.1704.

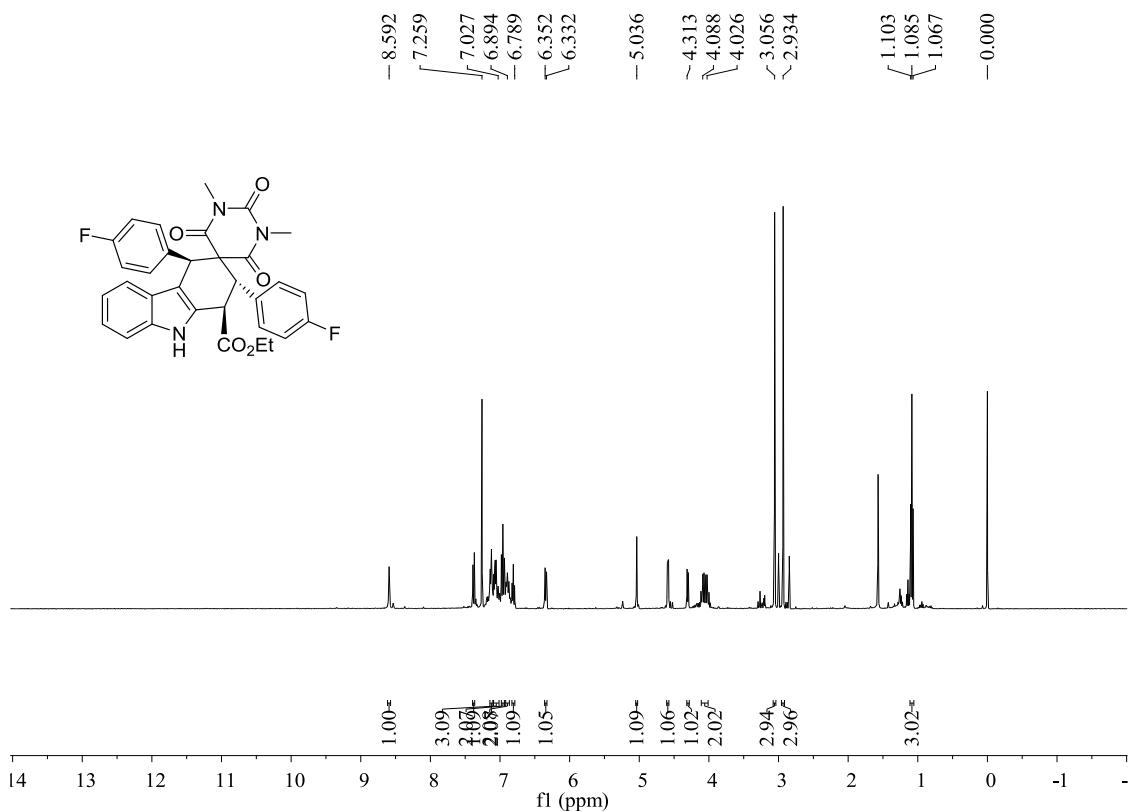


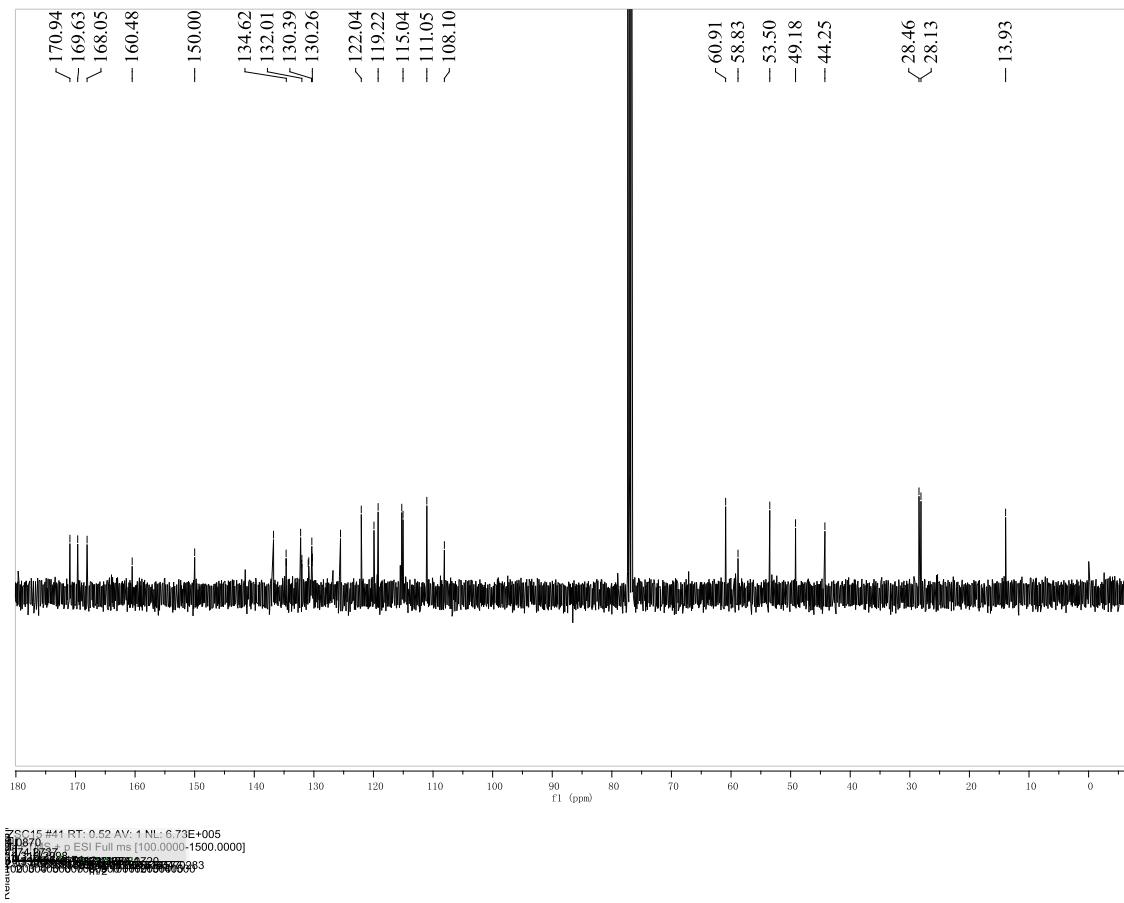


Ethy

rel-(1*R*,2*S*,4*R*)-2,4-bis(4-fluorophenyl)-1',3'-dimethyl-2',4',6'-trioxo-1,1',2,3',4,4',6',9-octahydrro-2'H-spiro[carbazole-3,5'-pyrimidine]-1-carboxylate (1r):

yellow solid, 65%, m.p. 212-214 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.59 (s, 1H, NH), 7.37 (d, *J* = 8.0 Hz, 1H, ArH), 7.13 (d, *J* = 7.2 Hz, 2H, ArH), 7.11-7.03 (m, 3H, ArH), 6.96 (t, *J* = 8.4 Hz, 2H, ArH), 6.89 (t, *J* = 8.4 Hz, 2H, ArH), 6.81 (t, *J* = 8.0 Hz, 1H, ArH), 6.34 (d, *J* = 8.0 Hz, 1H, ArH), 5.04 (s, 1H, CH), 4.58 (d, *J* = 6.8 Hz, 1H, CH), 4.30 (d, *J* = 6.8 Hz, 1H, CH), 4.05 (q, *J* = 7.2 Hz, 2H, CH₂), 3.06 (s, 3H, CH₃), 2.93 (s, 3H, CH₃), 1.08 (t, *J* = 7.2 Hz, 3H, CH₃); ¹³C NMR (400 MHz, CDCl₃) δ: 170.9, 169.6, 168.0, 160.4, 150.0, 136.7, 134.6, 134.6, 132.2, 132.0, 132.0, 130.9, 130.8, 130.3, 130.3, 130.2, 130.2, 125.5, 122.0, 119.9, 119.2, 115.2, 115.0, 111.0, 108.1, 60.9, 58.8, 53.5, 49.1, 44.2, 28.4, 28.1, 13.9; IR(KBr) ν: 3361, 3257, 3143, 3066, 2917, 2857, 2163, 1874, 1666, 1621, 1588, 1493, 1367, 1288, 1165, 1134, 951, 967, 855, 787 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₂H₂₇F₂N₃O₅ ([M+Na]⁺): 594.1811, found: 594.1812.

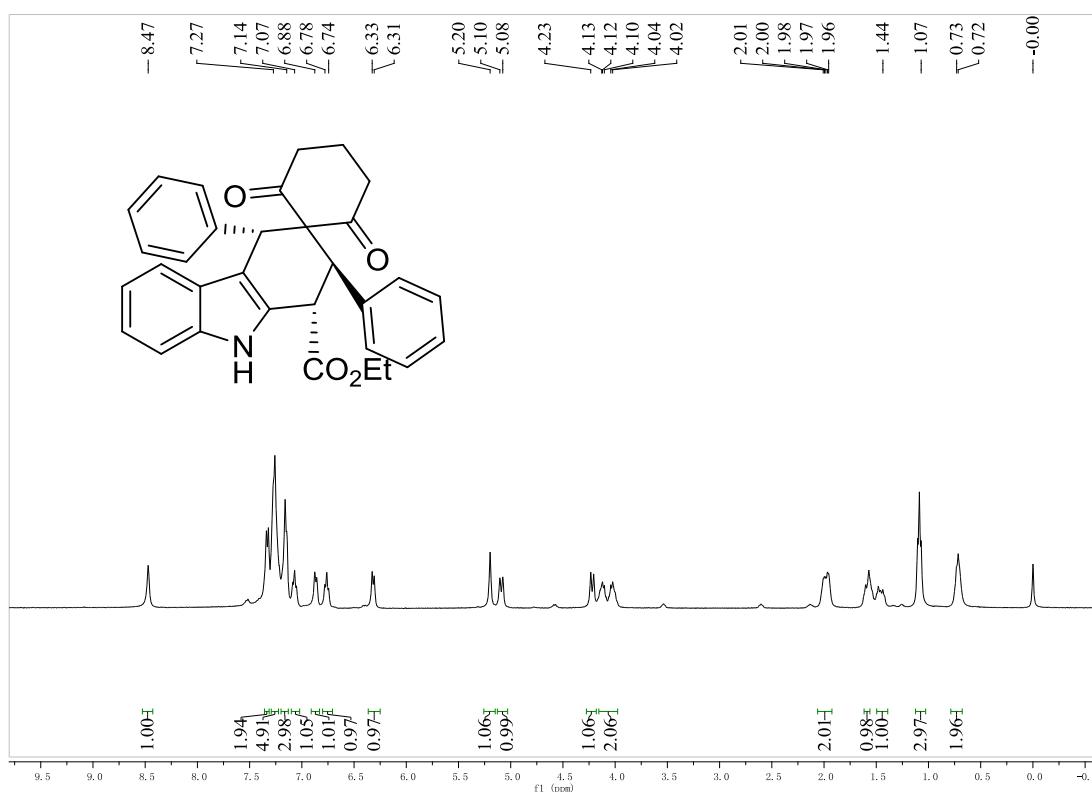


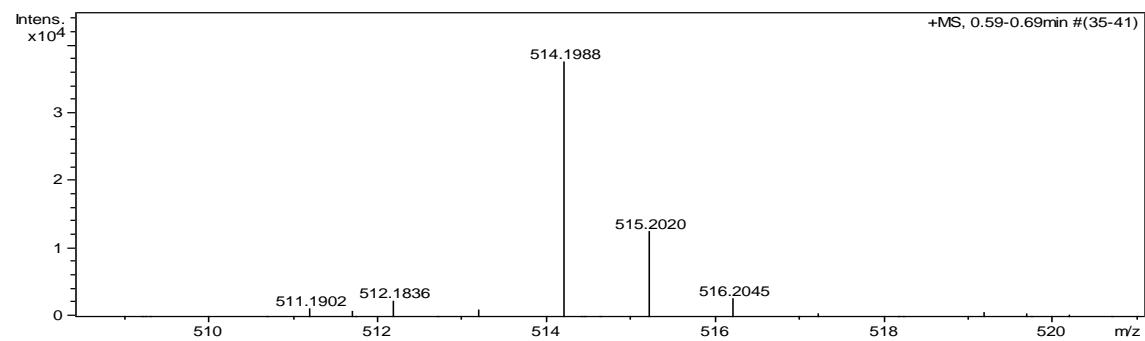
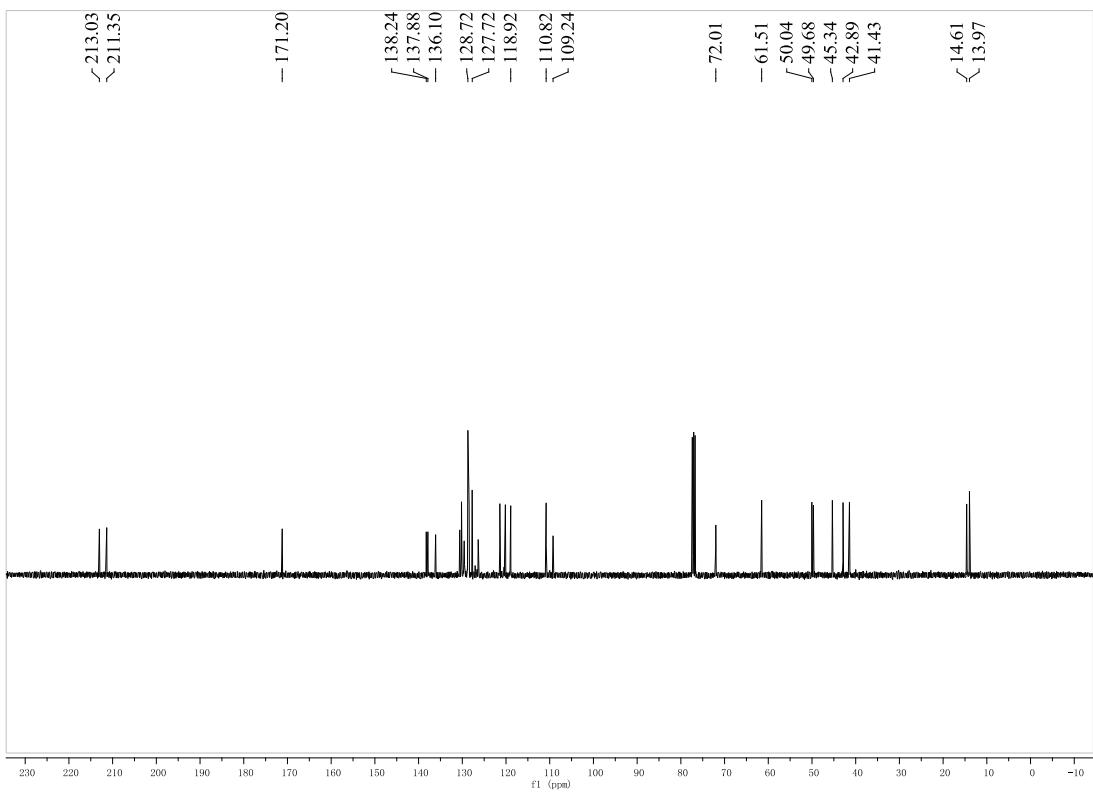


Ethyl

rel-(*1S,2R,4S*)-2',6'-dioxo-2,4-diphenyl-1,2,4,9-tetrahydrospiro[carbazole-3,1'-cyclohexane]-1-carboxylate (2a):

White solid, 76%, m.p. 175-178 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.47 (s, 1H, NH), 7.33 (d, J = 7.64 Hz, 2H, ArH), 7.27-7.22 (m, 5H, ArH), 7.16-7.15 (m, 3H, ArH), 7.07 (t, J = 7.2 Hz, 1H, ArH), 6.86 (d, J = 7.6 Hz, 1H, ArH), 6.76 (d, J = 7.2 Hz, 1H, ArH), 6.32 (d, J = 8.0 Hz, 1H, ArH), 5.20 (s, 1H, CH), 5.09 (d, J = 11.2 Hz, 1H, CH), 4.22 (d, J = 11.2 Hz, 1H, CH), 4.07 (q, J = 6.8 Hz, 2H, CH_2), 2.01-1.96 (m, 2H, CH_2), 1.60-1.54 (m, 1H, CH), 1.48-1.44 (m, 1H, CH), 1.09 (t, J = 6.8 Hz, 3H, CH_3), 0.73-0.71 (m, 2H, CH_2); ^{13}C NMR (400 MHz, CDCl_3) δ : 213.03, 211.34, 171.20, 138.24, 137.87, 136.10, 130.58, 130.18, 130.13, 129.56, 128.72, 128.60, 128.44, 127.74, 127.72, 126.36, 121.41, 120.14, 118.92, 110.82, 109.23, 72.00, 61.51, 50.03, 49.68, 45.34, 42.89, 41.42, 14.61, 13.97; IR (KBr) ν : 3407, 3164, 2977, 1853, 1746, 1631, 1613, 1555, 1431, 1317, 1300, 1285, 1184, 906, 867 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{32}\text{H}_{29}\text{NO}_4$ ([M+H] $^+$): 514.1989, found: 514.1988.

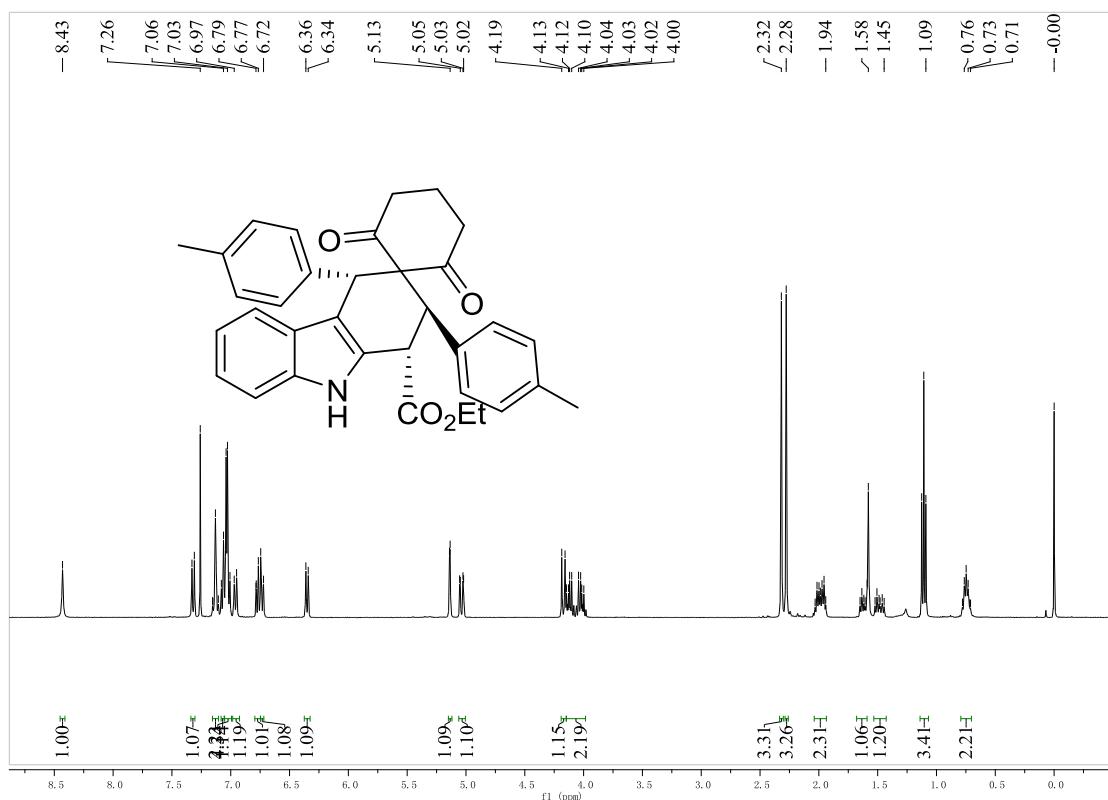


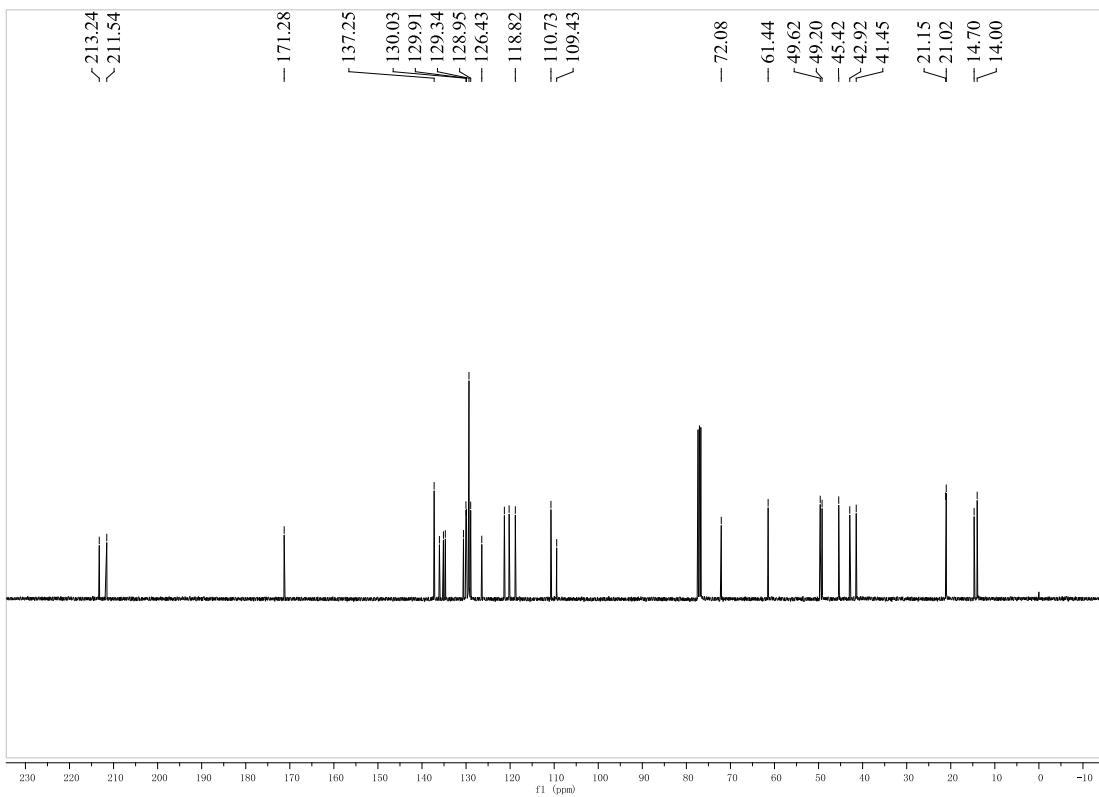


Ethyl

rel-(*1S,2R,4S*)-2',6'-dioxo-2,4-di-*p*-tolyl-1,2,4,9-tetrahydrospiro[carbazole-3,1'-cyclohexane]-1-carboxylate (2b):

White solid, 84%, m.p. 181-183 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.43 (s, 1H, NH), 7.32 (d, J = 8.4 Hz, 1H, ArH), 7.13 (t, J = 9.6 Hz, 2H, ArH), 7.07 (d, J = 7.2 Hz, 1H, ArH), 7.04-7.01 (m, 4H, ArH), 6.96 (d, J = 8.4 Hz, 1H, ArH), 6.77 (d, J = 7.2 Hz, 1H, ArH), 6.73 (d, J = 9.6 Hz, 1H, ArH), 6.35 (d, J = 8.0 Hz, 1H, ArH), 5.14 (d, J = 2.4 Hz, 1H, CH), 5.04 (dd, J_1 = 2.4 Hz, J_2 = 11.6 Hz, 1H, CH), 4.17 (d, J = 11.2 Hz, 1H, CH), 4.07 (q, J = 7.2 Hz, 2H, CH_2), 2.32 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.03-1.94 (m, 2H, CH_2), 1.65-1.59 (m, 1H, CH), 1.52-1.45 (m, 1H, CH), 1.11 (t, J = 7.2 Hz, 3H, CH_3), 0.78-0.71 (m, 2H, CH_2); ^{13}C NMR (400 MHz, CDCl_3) δ : 213.2, 211.5, 171.2, 137.2, 136.0, 135.1, 134.7, 130.5, 130.0, 129.9, 129.3, 128.9, 126.4, 121.3, 120.2, 118.8, 110.7, 109.4, 72.0, 61.4, 49.6, 49.2, 45.4, 42.9, 41.4, 21.1, 21.0, 14.7, 14.0; IR (KBr) ν : 3431, 3045, 2981, 1846, 1731, 1655, 1613, 1587, 1456, 1337, 1300, 1219, 1187, 845, 787 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{34}\text{H}_{33}\text{NO}_4$ ([M+H] $^+$): 520.2468, found: 520.2462.

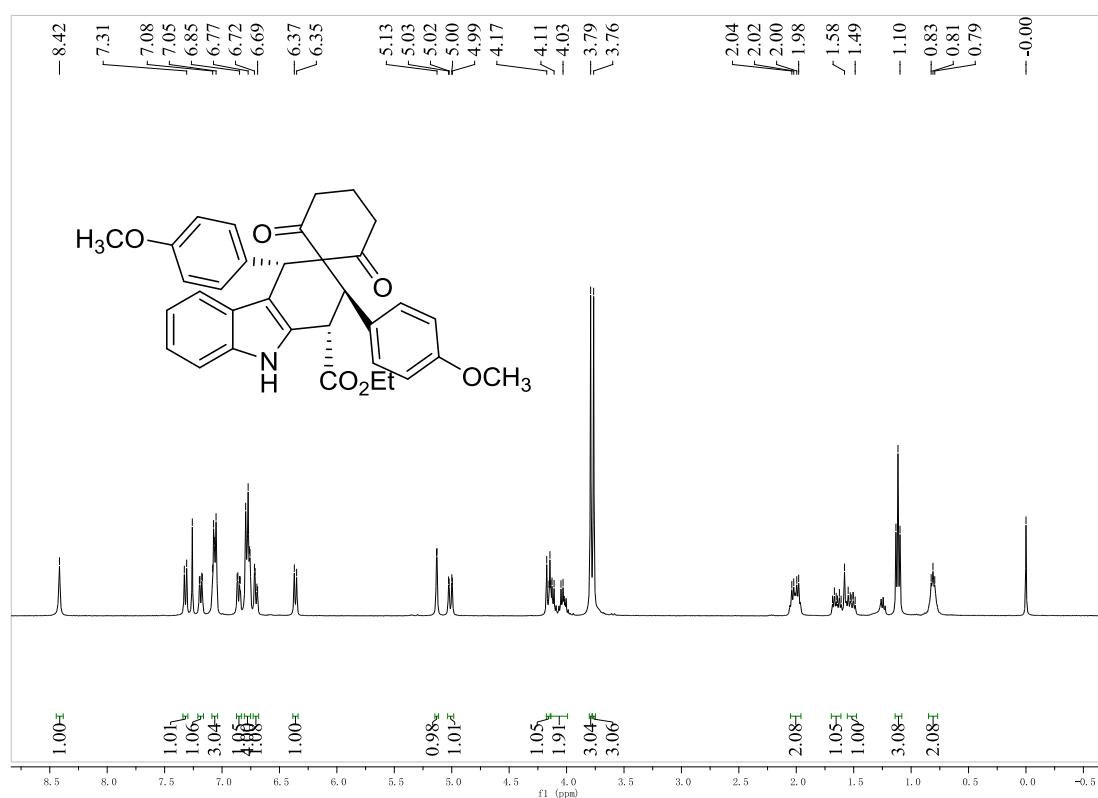


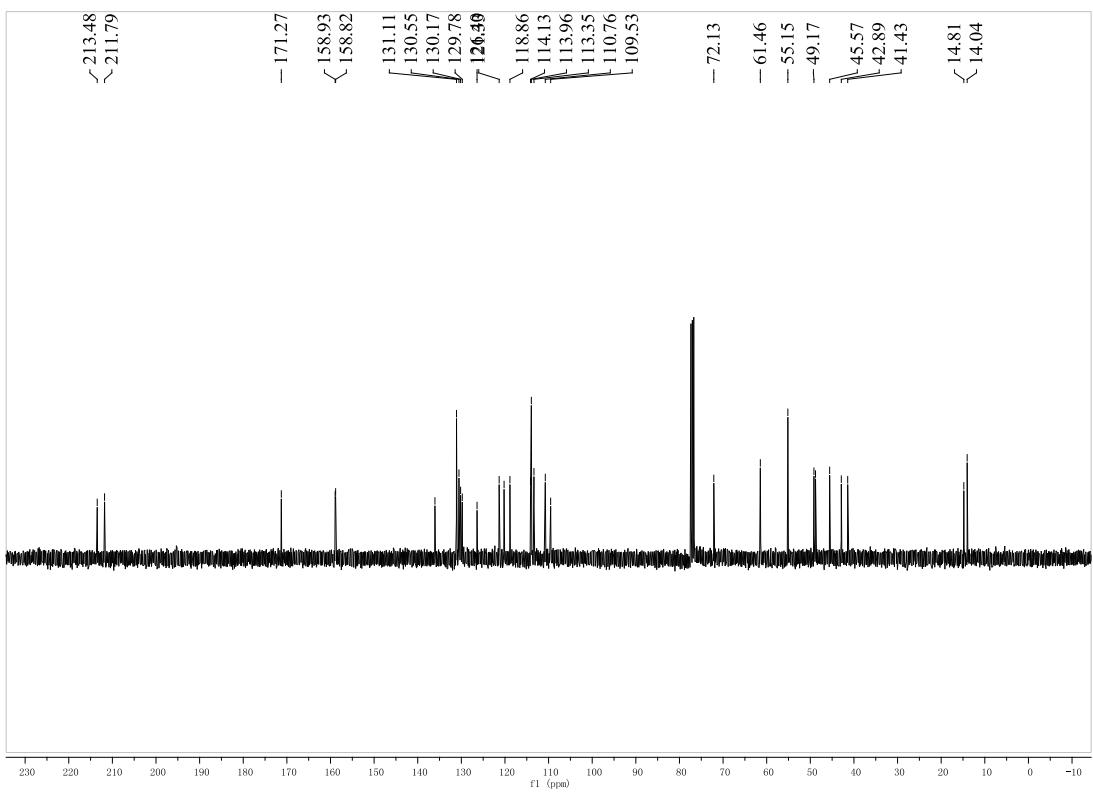


Ethyl

rel-(*1S,2R,4S*)-2,4-bis(4-methoxyphenyl)-2',6'-dioxo-1,2,4,9-tetrahydrospiro[carbazole-3,1'-cyclohexane]-1-carboxylate (2c):

white solid, 82%, m.p. 183-185 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.42 (s, 1H, NH), 7.31 (d, *J* = 8.4 Hz, 1H, ArH), 7.18 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.0 Hz, 1H, ArH), 7.08-7.05 (m, 3H, ArH), 6.85 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.0 Hz, 1H, ArH), 6.80-6.76 (m, 4H, ArH), 6.70 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.0 Hz, 1H, ArH), 6.36 (d, *J* = 8.0 Hz, 1H, ArH), 5.13 (d, *J* = 2.0 Hz, 1H, CH), 5.01 (dd, *J*₁ = 11.2 Hz, *J*₂ = 2.0 Hz, 1H, CH), 4.16 (d, *J* = 11.2 Hz, 1H, CH), 4.08 (q, *J* = 7.2 Hz, 2H, CH₂), 3.79 (s, 3H, OCH₃), 3.76 (s, 3H, OCH₃), 2.04-1.98 (m, 2H, CH₂), 1.69-1.61 (m, 1H, CH), 1.55-1.49 (m, 1H, CH), 1.12 (t, *J* = 7.2 Hz, 3H, CH₃), 0.83-0.80 (m, 2H, CH₂); ¹³C NMR (400 MHz, CDCl₃) δ: 213.4, 211.7, 171.2, 158.9, 158.8, 136.0, 131.1, 130.5, 130.1, 129.7, 126.4, 121.3, 120.2, 118.8, 114.1, 113.9, 113.3, 110.7, 109.5, 72.1, 61.4, 55.1, 49.1, 48.8, 45.5, 42.8, 41.4, 14.8, 14.0; IR (KBr) ν: 3451, 3145, 2978, 1906, 1732, 1656, 1617, 1509, 1487, 1355, 1341, 1279, 1164, 884, 762 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₄H₃₃NO₆([M+H]⁺): 552.2361, found: 552.2358.

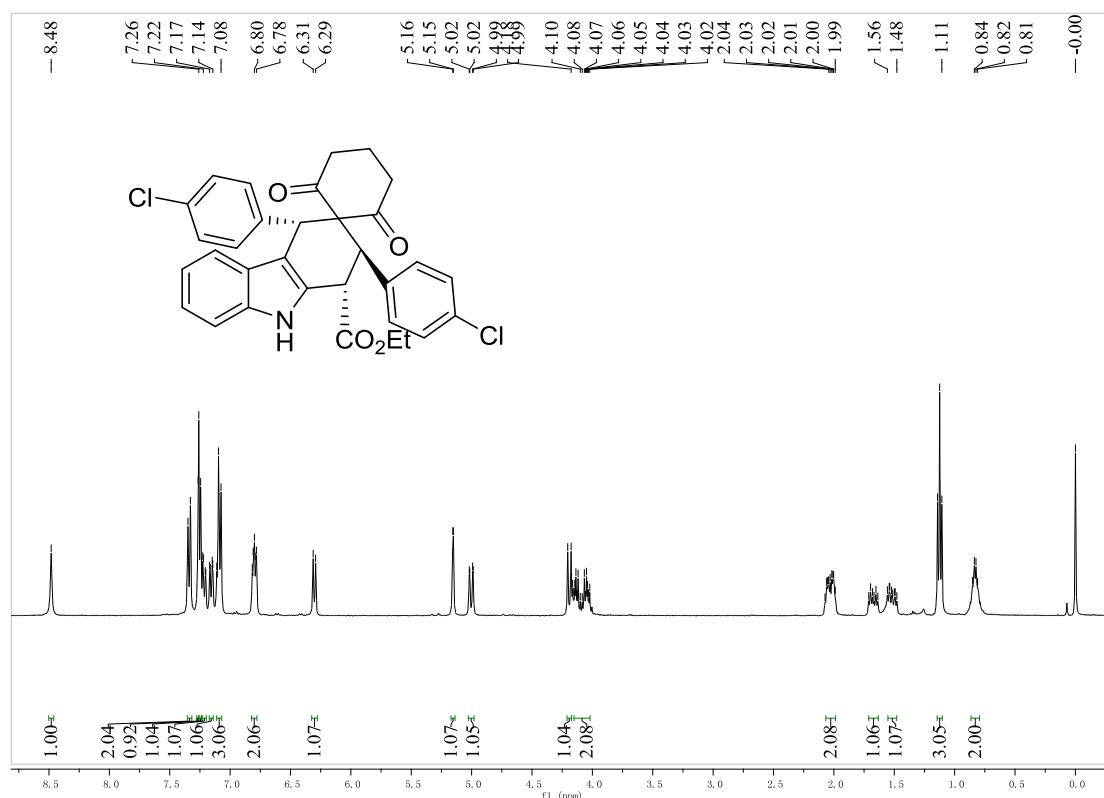


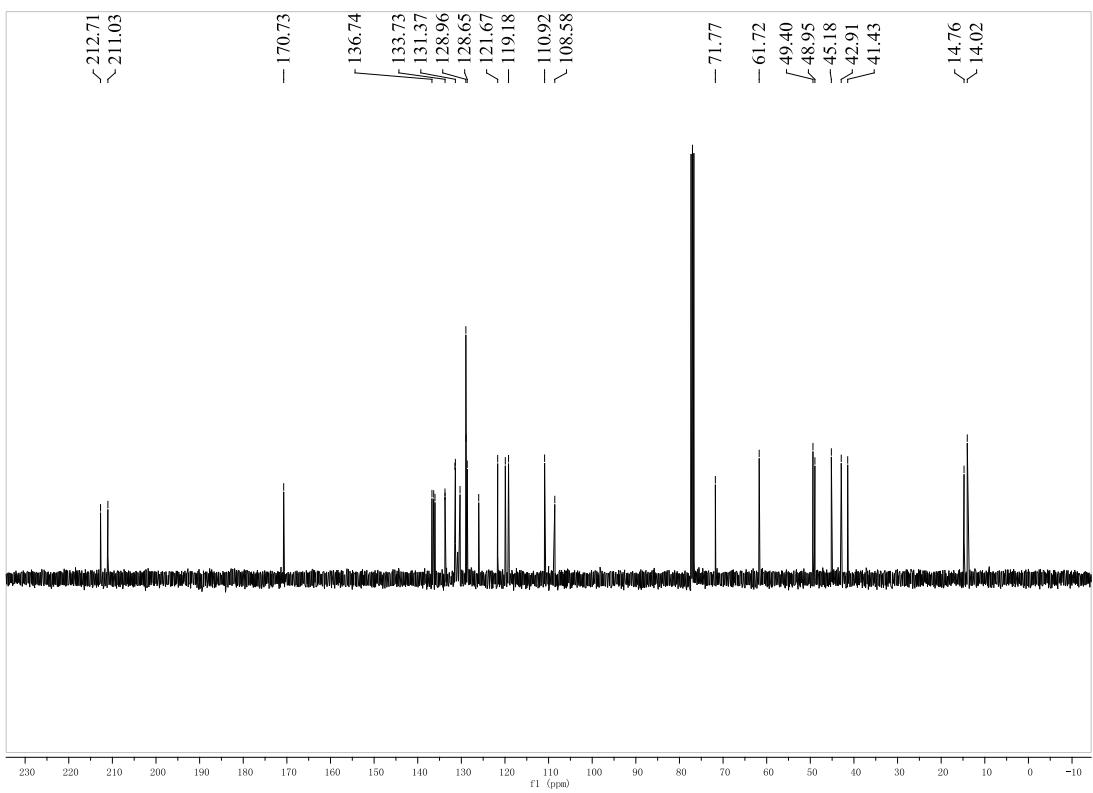


Ethyl

rel-(*1S,2R,4S*)-2,4-bis(4-chlorophenyl)-2',6'-dioxo-1,2,4,9-tetrahydrospiro[carbazole-3,1'-cyclohexane]-1-carboxylate (**2d**):

white solid, 80%, m.p. 190-192 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.48 (s, 1H, NH), 7.33 (d, *J* = 8.0 Hz, 2H, ArH), 7.27-7.26 (m, 1H, ArH), 7.26-7.24 (m, 1H, ArH), 7.21 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.0 Hz, 1H, ArH), 7.15 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.0 Hz, 1H, ArH), 7.11-7.08 (m, 3H, ArH), 6.82-6.78 (m, 2H, ArH), 6.30 (d, *J* = 8.0 Hz, 1H, ArH), 5.15 (d, *J* = 2.0 Hz, 1H, CH), 5.00 (dd, *J*₁ = 11.2 Hz, *J*₂ = 2.0 Hz, 1H, CH), 4.19 (d, *J* = 11.2 Hz, 1H, CH), 4.08 (q, *J* = 7.2 Hz, 2H, CH₂), 2.07-1.99 (m, 2H, CH₂), 1.71-1.64 (m, 1H, CH), 1.54-1.48 (m, 1H, CH), 1.12 (t, *J* = 7.2 Hz, 3H, CH₃), 0.85-0.81 (m, 2H, CH₂); ¹³C NMR (400 MHz, CDCl₃) δ: 212.7, 211.0, 170.7, 136.7, 136.3, 136.0, 133.7, 133.7, 131.4, 131.3, 130.3, 128.9, 128.9, 128.6, 126.0, 121.6, 119.9, 119.1, 110.9, 108.5, 71.7, 61.7, 49.3, 48.9, 45.1, 42.9, 41.4, 14.7, 14.0; IR (KBr) ν: 3431, 3045, 2966, 1868, 1771, 1643, 1637, 1554, 1478, 1321, 1301, 1266, 1145, 882, 761 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₂H₂₇Cl₂NO₄ ([M+Na]⁺): 582.1209, found: 582.1208.



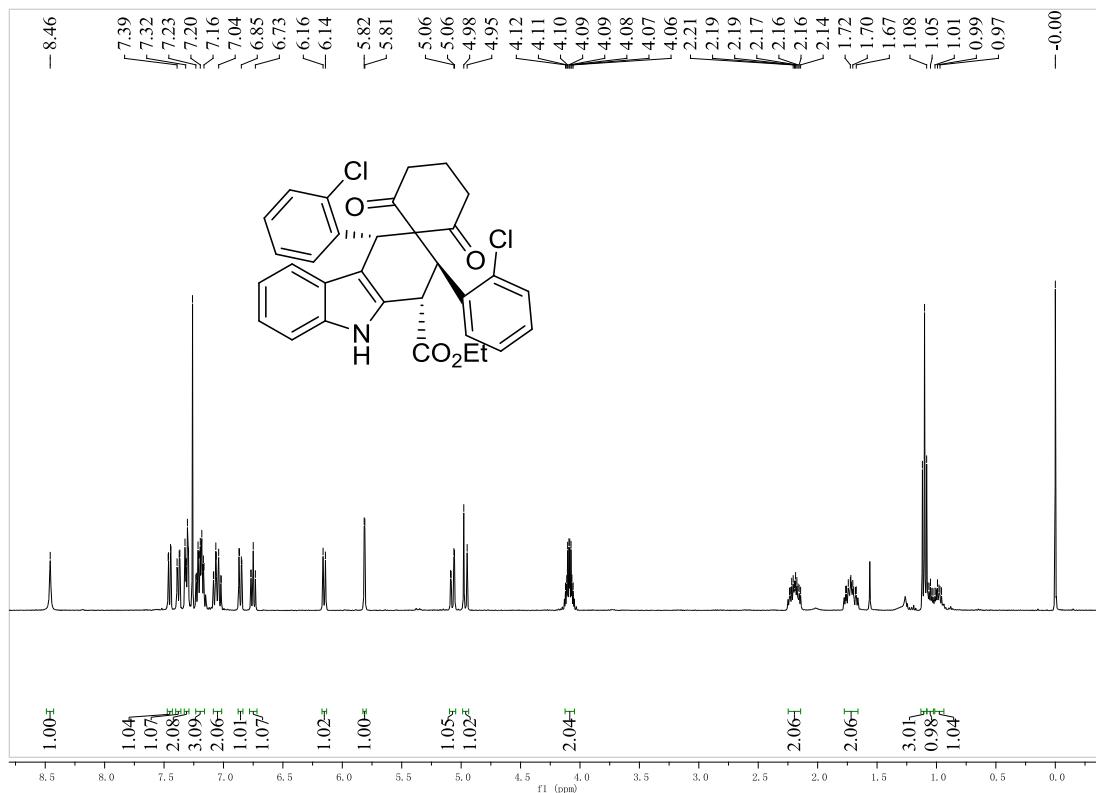


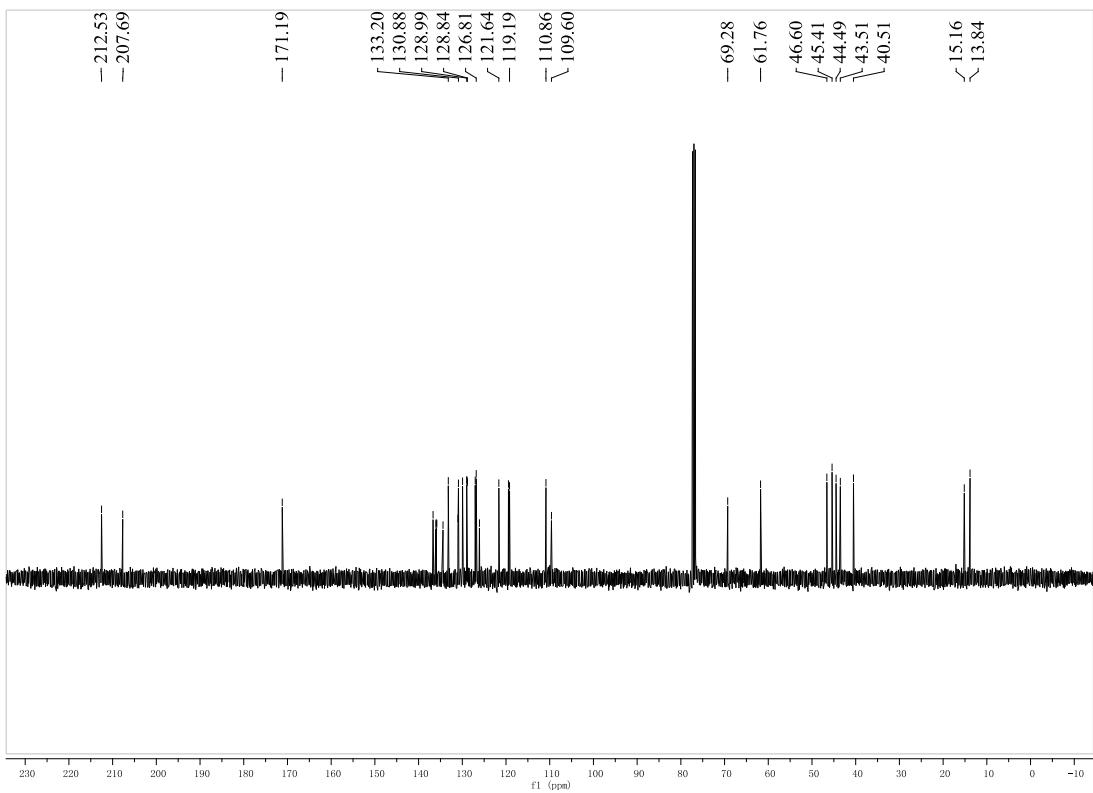
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0274575821298 null ms [100.0000-1500.0000]
0274575821298 null ms [100.0000-1500.0000]

Ethyl

rel-(*1S,2S,4S*)-2,4-bis(2-chlorophenyl)-2',6'-dioxo-1,2,4,9-tetrahydrospiro[carbazole-3,1'-cyclohexane]-1-carboxylate (**2e**):

white solid, 74%, m.p. 198-200 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.46 (s, 1H, NH), 7.45 (dd, *J*₁ = 8.0 Hz, *J*₂ = 0.8 Hz, 1H, ArH), 7.38 (dd, *J*₁ = 8.0 Hz, *J*₂ = 2.0 Hz, 1H, ArH), 7.32-7.29 (m, 2H, ArH), 7.23-7.16 (m, 3H, ArH), 7.09-7.02 (m, 2H, ArH), 6.86 (dd, *J*₁ = 8.0 Hz, *J*₂ = 2.0 Hz, 1H, ArH), 6.75 (t, *J* = 8.0 Hz, 1H, ArH), 6.15 (d, *J* = 8.0 Hz, 1H, ArH), 5.81 (d, *J* = 2.0 Hz, 1H, CH), 5.07 (dd, *J*₁= 11.2 Hz, *J*₂= 2.0 Hz, 1H, CH), 4.96 (d, *J* = 11.2 Hz, 1H, CH), 4.09 (q, *J* = 7.2 Hz, 2H, CH₂), 2.24-2.14 (m, 2H, CH₂), 1.77-1.68 (m, 2H, CH₂), 1.10 (t, *J* = 7.2 Hz, 3H, CH₃), 1.07-1.03 (m, 1H, CH), 1.01-0.96 (m, 1H, CH); ¹³C NMR (400 MHz, CDCl₃) δ: 212.5, 207.6, 171.1, 136.6, 136.0, 135.9, 135.8, 134.4, 133.2, 130.9, 130.8, 129.9, 128.9, 128.9, 128.8, 127.0, 126.8, 126.0, 121.6, 119.4, 119.1, 110.8, 109.6, 69.2, 61.7, 46.6, 45.4, 44.4, 43.5, 40.5, 15.1, 13.8; IR (KBr) ν: IR (KBr) ν: 3411, 3045, 2966, 1868, 1761, 1643, 1637, 1574, 1478, 1321, 1301, 1245, 1145, 890, 761 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₂H₂₇Cl₂NO₄([M+Na]⁺): 582.1209, found: 582.1208.

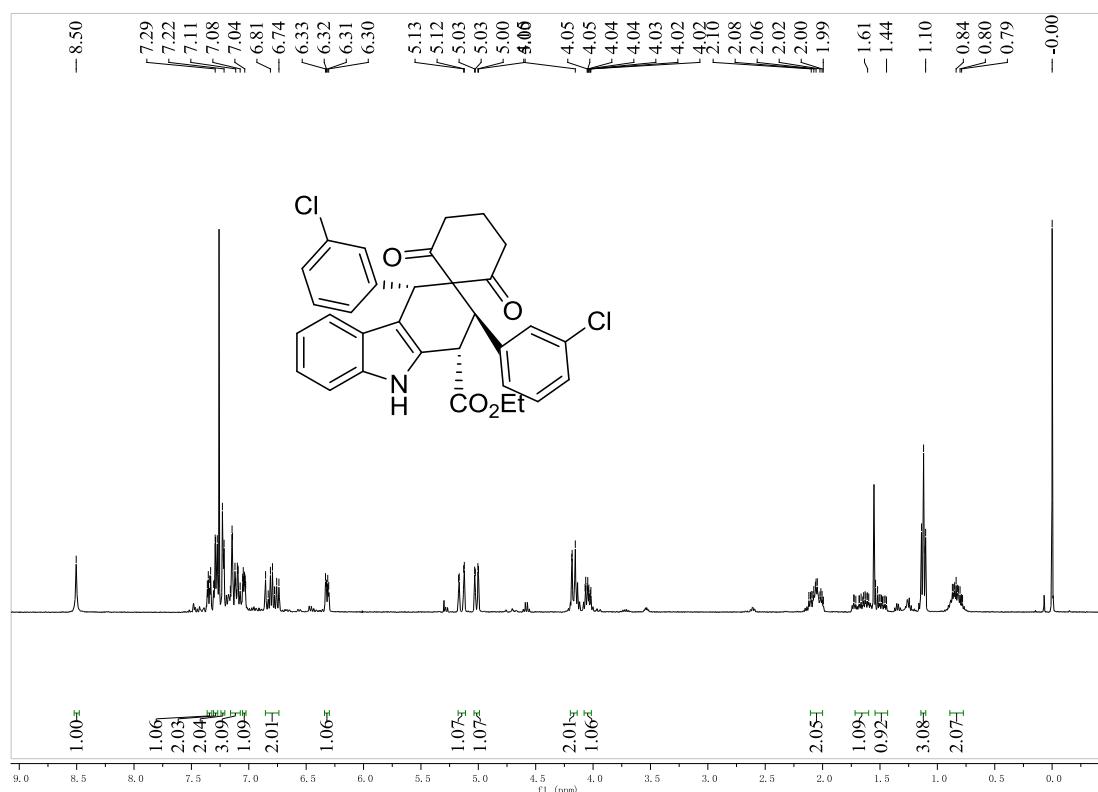


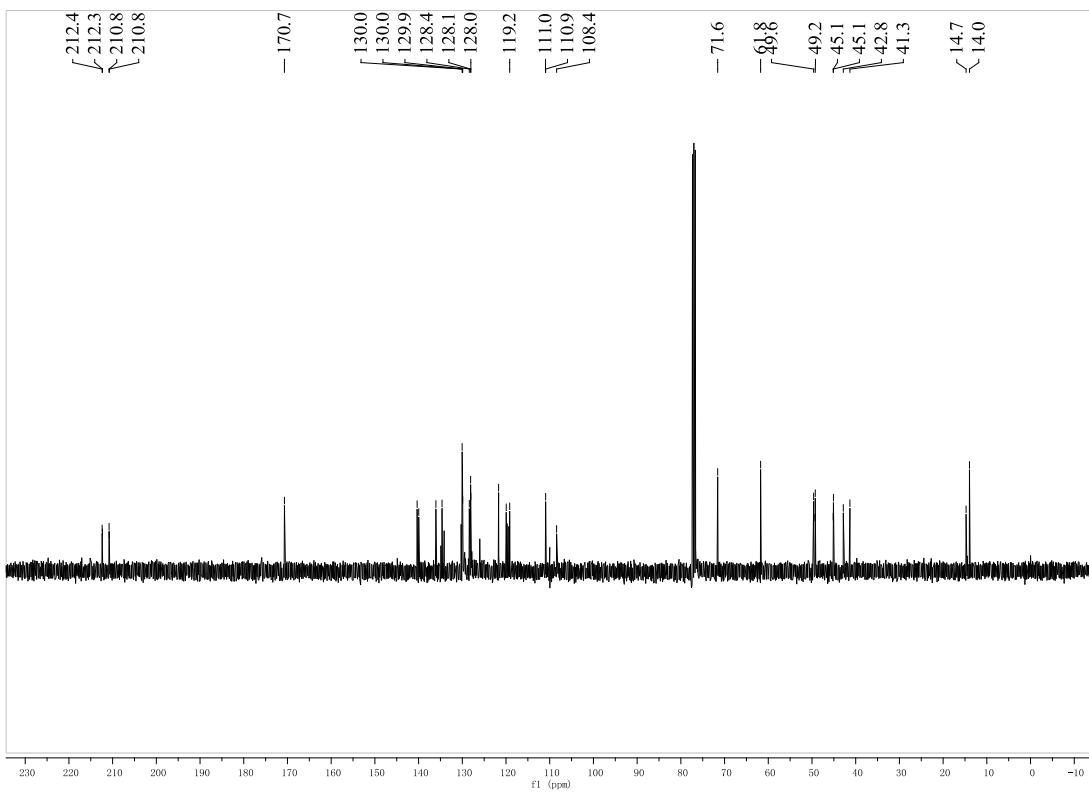


Ethyl

rel-(*1S,2R,4S*)-2,4-bis(3-chlorophenyl)-2',6'-dioxo-1,2,4,9-tetrahydrospiro[carbazole-3,1'-cyclohexane]-1-carboxylate (**2f**):

white solid, 66%, m.p. 196-198 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.50 (s, 1H, NH), 7.35 (dd, *J*₁ = 8.0 Hz, *J*₂ = 3.2 Hz, 1H, ArH), 7.31-7.29 (m, 2H, ArH), 7.23-7.22 (m, 2H, ArH), 7.16-7.08 (m, 3H, ArH), 7.05-7.03 (m, 1H, ArH), 6.85-6.74 (m, 2H, ArH), 6.32 (dd, *J*₁ = 8.0 Hz, *J*₂ = 3.2 Hz, 1H, ArH), 5.14 (dd, *J*₁ = 17.6 Hz, *J*₂ = 2.0 Hz, 1H, CH), 5.01 (dd, *J*₁ = 11.2 Hz, *J*₂ = 2.0 Hz, 1H, CH), 4.17 (q, *J* = 7.2 Hz, 2H, CH₂), 4.07-4.02 (m, 1H, CH), 2.11-2.01 (m, 2H, CH₂), 1.71-1.61 (m, 1H, CH), 1.54-1.44 (m, 1H, CH), 1.12 (t, *J* = 7.2 Hz, 3H, CH₃), 0.87-0.78 (m, 2H, CH₂); ¹³C NMR (400 MHz, CDCl₃) δ: 212.3, 212.3, 210.8, 210.7, 170.6, 140.3, 139.9, 136.0, 134.6, 130.0, 129.9, 129.9, 128.3, 128.0, 128.0, 121.6, 119.9, 119.1, 110.9, 110.9, 108.4, 71.5, 61.7, 49.6, 49.3, 49.2, 45.1, 45.0, 42.8, 41.3, 14.7, 13.9; IR (KBr) ν: 3420, 3045, 2976, 1842, 1764, 1643, 1611, 1538, 1478, 1321, 1301, 1266, 1145, 882, 770 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₂H₂₇Cl₂NO₄([M+Na]⁺): 582.1209, found: 582.1210.



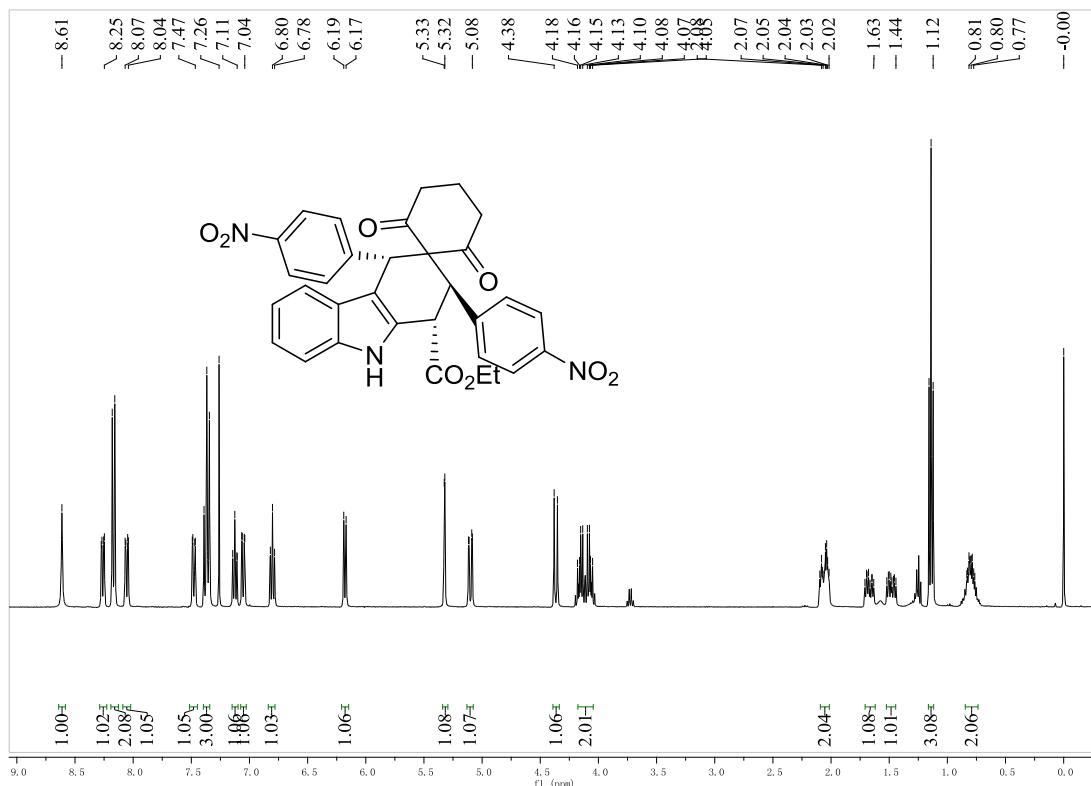


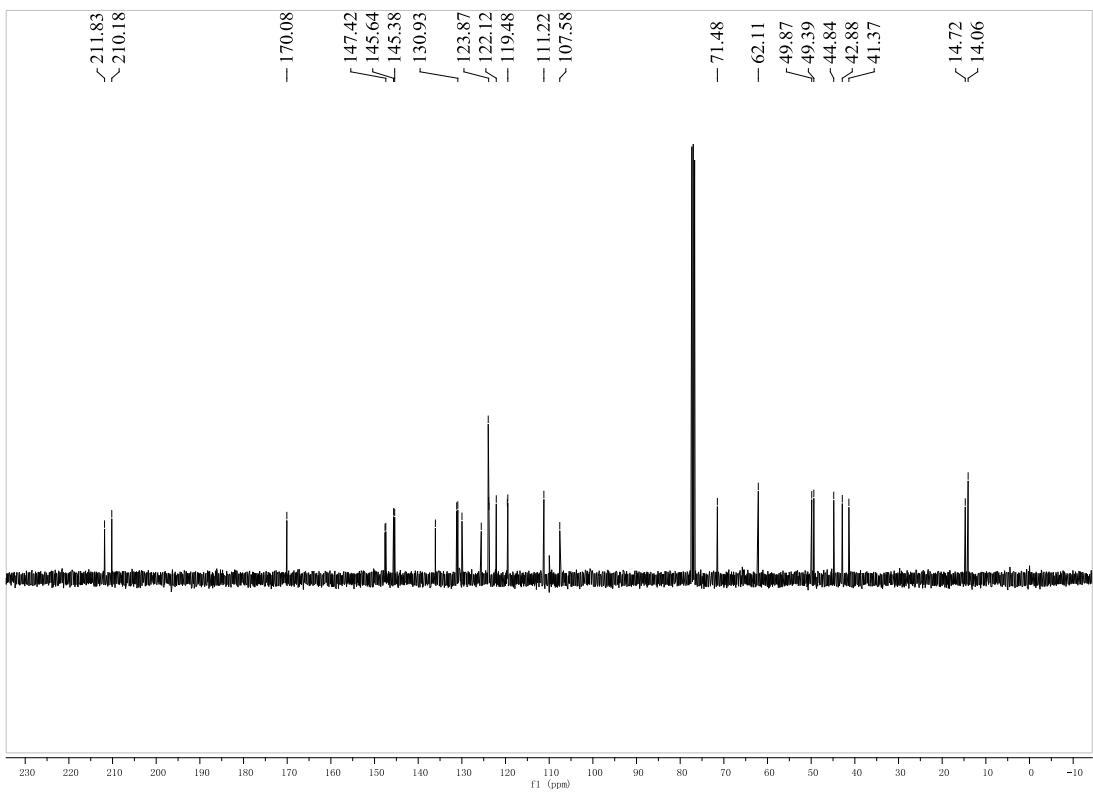
ZGC8_20210130103749 #10 RT: 0.12 AV: 1 NL: 6.41E+005
[FTMS, m/z 55-179, full, 1.23265e5000-1500.0000]
0.20000e0 0.50000e0 0.80000e0 1.00000e0 1.20000e0 1.40000e0

Ethyl

rel-(*1S,2R,4S*)-2,4-bis(4-nitrophenyl)-2',6'-dioxo-1,2,4,9-tetrahydrospiro[carbazole-3,1'-cyclohexane]-1-carboxylate (2g):

white solid, 76%, m.p. 203-205 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.61 (s, 1H, NH), 8.26 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.4 Hz, 1H, ArH), 8.17 (d, *J* = 8.8 Hz, 2H, ArH), 8.05 (dd, *J*₁ = 8.8 Hz, *J*₂ = 2.4 Hz, 1H, ArH), 7.48 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.0 Hz, 1H, ArH), 7.39-7.35 (m, 3H, ArH), 7.13 (t, *J* = 7.2 Hz, 1H, ArH), 7.05 (dd, *J*₁ = 8.8 Hz, *J*₂ = 2.0 Hz, 1H, ArH), 6.80 (t, *J* = 7.2 Hz, 1H, ArH), 6.18 (d, *J* = 8.0 Hz, 1H, ArH), 5.32 (d, *J* = 2.0 Hz, 1H, CH), 5.09 (dd, *J*₁ = 11.6 Hz, *J*₂ = 2.4 Hz, 1H, CH), 4.37 (d, *J* = 11.6 Hz, 1H, CH), 4.12 (q, *J* = 7.2 Hz, 2H, CH₂), 2.09-2.02 (m, 2H, CH₂), 1.71-1.63 (m, 1H, CH), 1.52-1.44 (m, 1H, CH), 1.14 (t, *J* = 7.2 Hz, 3H, CH₃), 0.83-0.77 (m, 2H, CH₂); ¹³C NMR (400 MHz, CDCl₃) δ: 211.8, 210.1, 170.0, 147.5, 147.4, 145.6, 145.3, 136.0, 131.1, 130.9, 129.9, 125.5, 123.9, 123.8, 123.7, 122.1, 119.5, 119.4, 111.2, 107.5, 71.4, 62.1, 49.8, 49.3, 44.8, 42.8, 41.3, 14.7, 14.0; IR (KBr) ν: 3471, 3000, 2941, 1932, 1816, 1690, 1631, 1507, 1471, 1345, 1300, 1241, 1131, 932, 817 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₂H₂₇N₃O₈([M+Na]⁺): 604.1690, found: 604.1684.

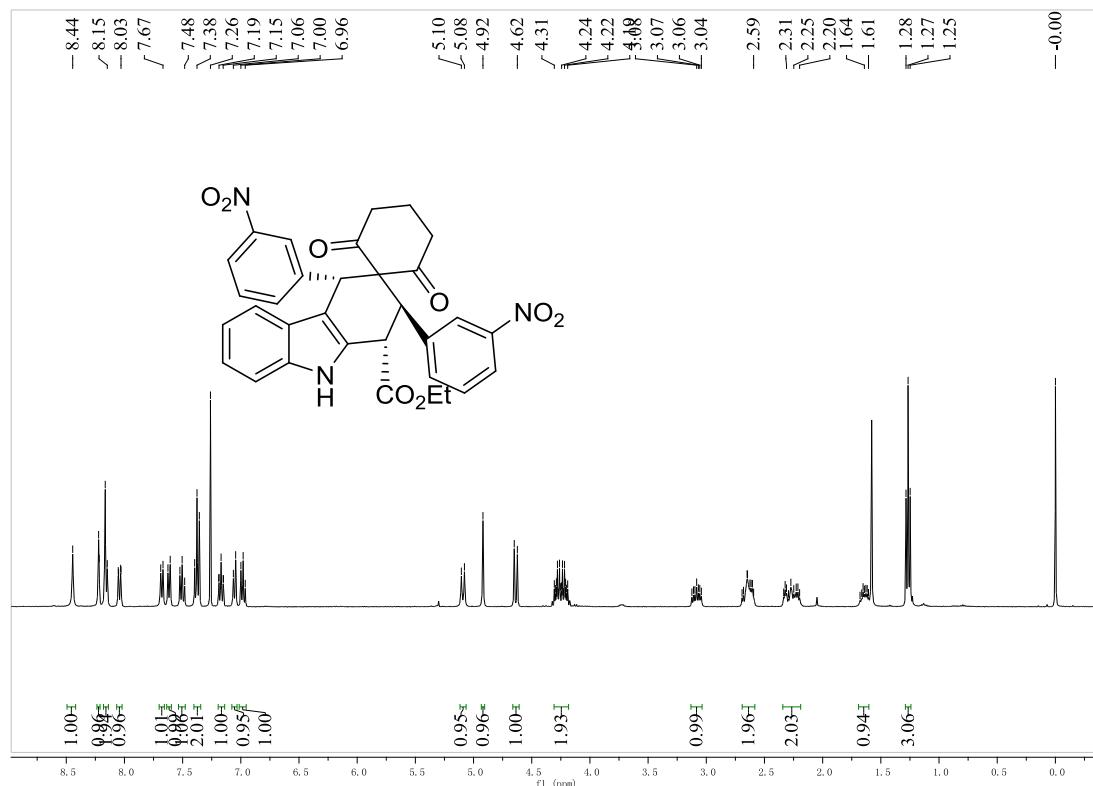


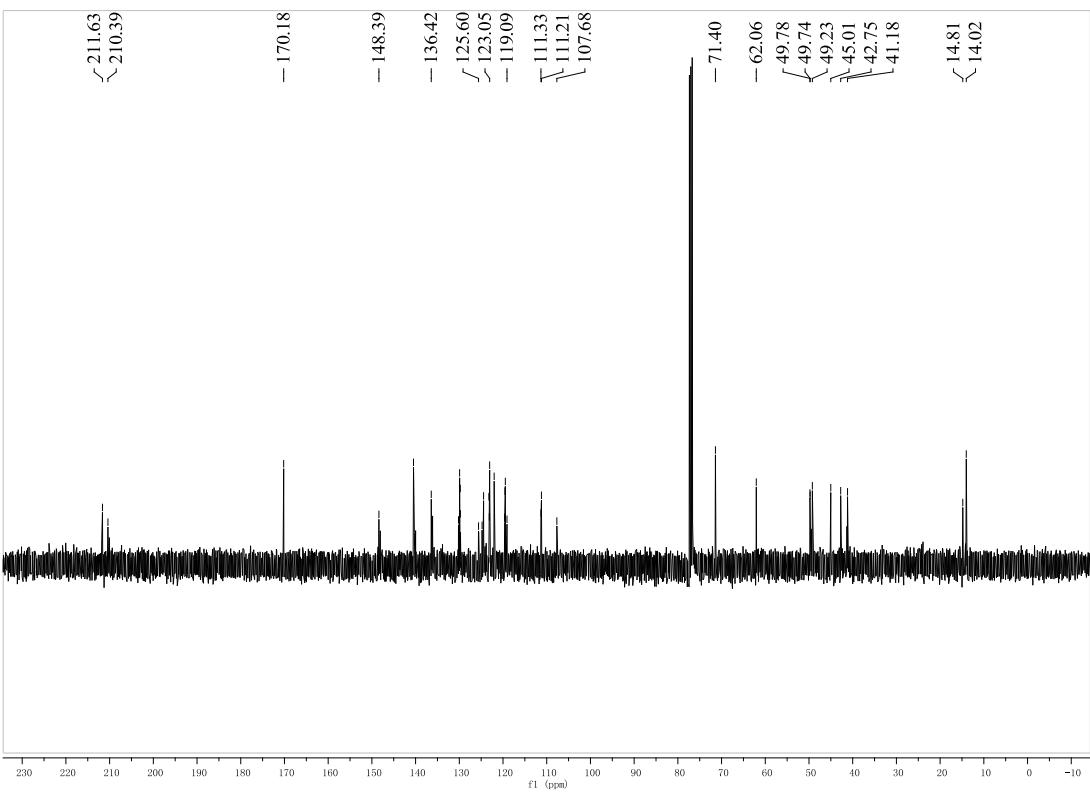


Ethyl

rel-(*1S,2R,4S*)-2,4-bis(3-nitrophenyl)-2',6'-dioxo-1,2,4,9-tetrahydrospiro[carbazole-3,1'-cyclohexane]-1-carboxylate (2h):

white solid, 62%, m.p. 213-215 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.45 (s, 1H, NH), 8.22-8.21 (m, 1H, ArH), 8.17-8.15 (m, 2H, ArH), 8.04 (dd, *J*₁ = 8.0 Hz, *J*₂ = 1.2 Hz, 1H, ArH), 7.67 (d, *J* = 7.6 Hz, 1H, ArH), 7.61 (d, *J* = 7.6 Hz, 1H, ArH), 7.50 (t, *J* = 8.0 Hz, 1H, ArH), 7.38 (t, *J* = 8.0 Hz, 2H, ArH), 7.17 (t, *J* = 8.0 Hz, 1H, ArH), 7.05 (d, *J* = 7.6 Hz, 1H, ArH), 6.98 (t, *J* = 7.6 Hz, 1H, ArH), 5.09 (d, *J* = 10.4 Hz, 1H, CH), 4.92 (s, 1H, CH), 4.63 (d, *J* = 10.4 Hz, 1H, CH), 4.25 (q, *J* = 7.2 Hz, 2H, CH₂), 3.12-3.04 (m, 1H, CH), 2.69-2.59 (m, 2H, CH₂), 2.34-2.20 (m, 2H, CH₂), 1.68-1.61 (m, 1H, CH), 1.27 (t, *J* = 7.2 Hz, 3H, CH₃); ¹³C NMR (400 MHz, CDCl₃) δ: 211.6, 210.3, 170.1, 148.3, 140.4, 136.4, 130.1, 129.9, 129.7, 129.7, 125.6, 124.7, 124.4, 123.2, 123.1, 123.0, 122.0, 119.6, 119.5, 119.4, 119.0, 111.3, 111.2, 107.6, 71.4, 62.0, 49.7, 49.7, 49.2, 45.0, 42.7, 41.1, 14.8, 14.0; IR (KBr) ν: 3459, 3010, 2941, 1932, 1816, 1690, 1653, 1507, 1462, 1345, 1331, 1248, 1131, 932, 817 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₂H₂₇N₃O₈([M+Na]⁺): 604.1690, found: 604.1688.



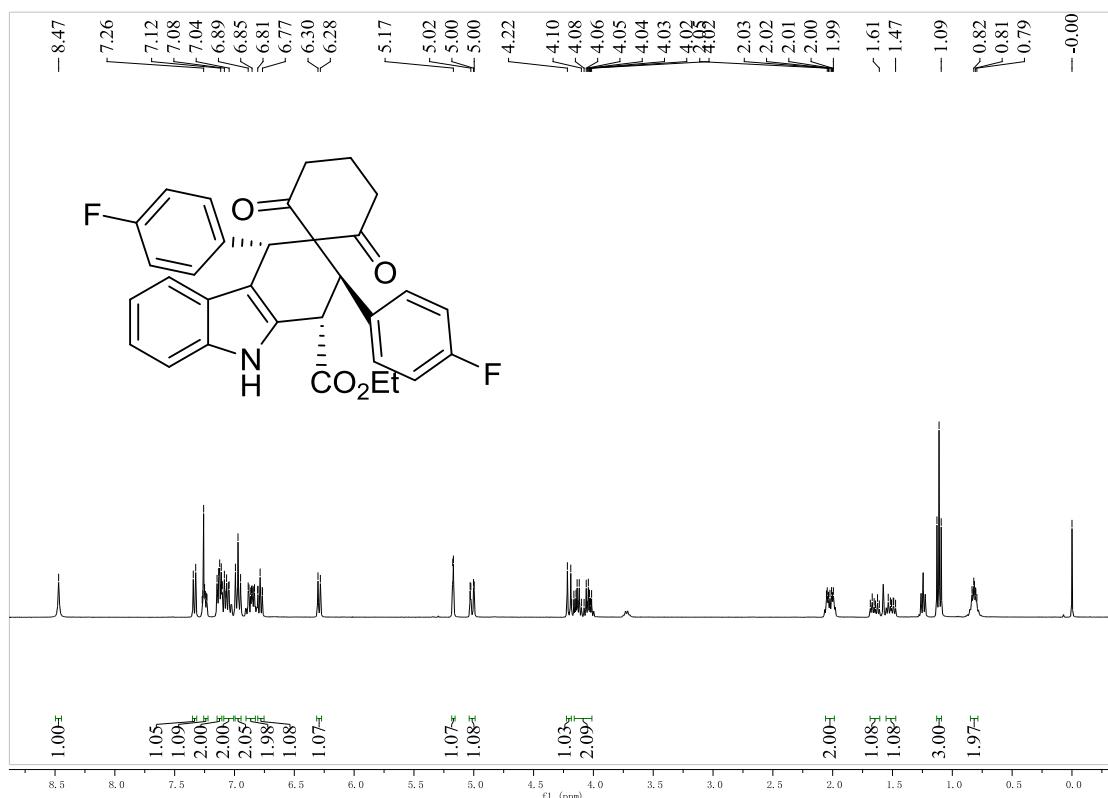


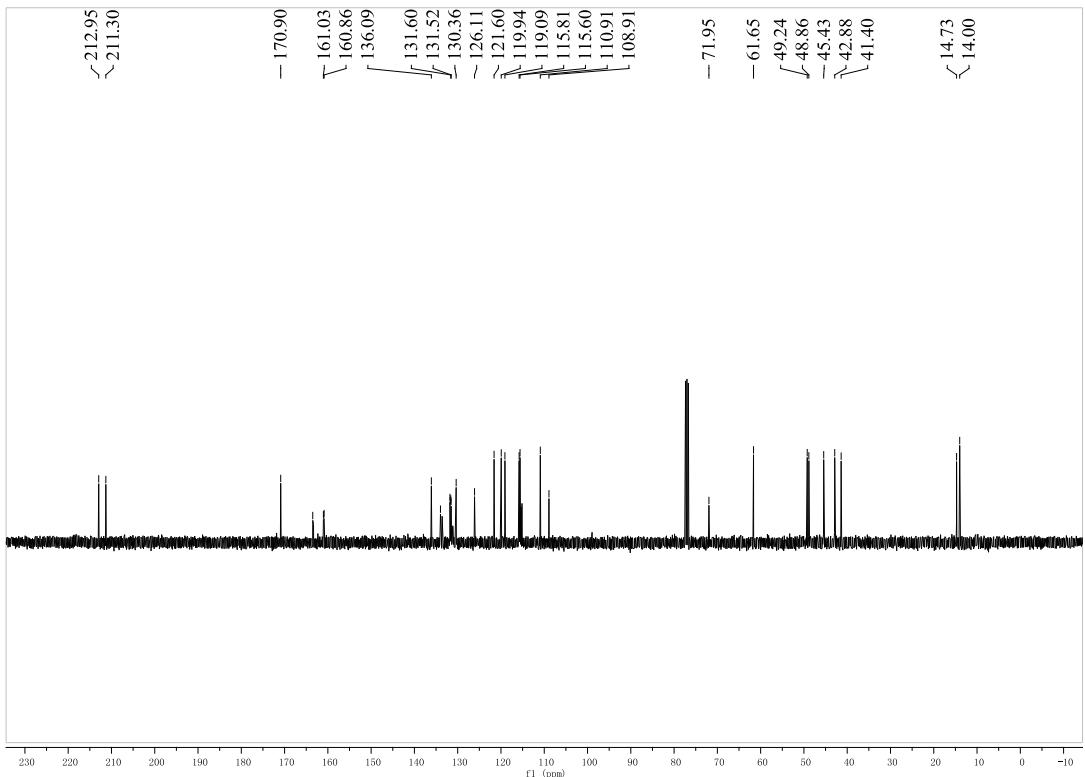
ZS07_20210130103451 #22 RT: 0.28 AV: 1 NL: 1.73E+006
1280.6 s, 1D ESI Full ms [100.0000-1500.0000]
10000 4000 3000 2000 1000 600 400 300 200 100

Ethyl

rel-(*1S,2R,4S*)-2,4-bis(4-fluorophenyl)-2',6'-dioxo-1,2,4,9-tetrahydrospiro[carbazole-3,1'-cyclohexane]-1-carboxylate (**2i**):

white solid, 70%, m.p. 184-186 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.47 (s, 1H, NH), 7.33 (d, *J* = 8.4 Hz, 1H, ArH), 7.26-7.23 (m, 1H, ArH), 7.15-7.11 (m, 2H, ArH), 7.09-7.05 (m, 2H, ArH), 6.97 (t, *J* = 8.2 Hz, 2H, ArH), 6.89-6.83 (m, 2H, ArH), 6.79 (t, *J* = 8.0 Hz, 1H, ArH), 6.29 (d, *J* = 8.0 Hz, 1H, ArH), 5.17 (d, *J* = 2.0 Hz, 1H, CH), 5.01 (dd, *J*₁ = 11.2 Hz, *J*₂ = 2.0 Hz, 1H, CH), 4.20 (d, *J* = 11.2 Hz, 1H, CH), 4.09 (q, *J* = 7.2 Hz, 2H, CH₂), 2.05-1.99 (m, 2H, CH₂), 1.69-1.61 (m, 1H, CH), 1.54-1.48 (m, 1H, CH), 1.11 (t, *J* = 7.2 Hz, 3H, CH₃), 0.84-0.80 (m, 2H, CH₂); ¹³C NMR (400 MHz, CDCl₃) δ: 212.9, 211.3, 170.8, 163.4, 161.0, 160.8, 136.0, 133.9, 131.7, 131.7, 131.5, 131.5, 130.3, 126.1, 121.5, 119.9, 119.0, 115.8, 115.5, 110.9, 108.9, 71.9, 61.6, 49.2, 48.8, 45.4, 42.8, 41.4, 14.7, 14.0; IR (KBr) ν: 3441, 3082, 2973, 1845, 1761, 1688, 1648, 1565, 1483, 1343, 1382, 1266, 1141, 863, 745 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₂H₂₈F₂NO₄([M+H]⁺): 528.1981, found: 528.1973.

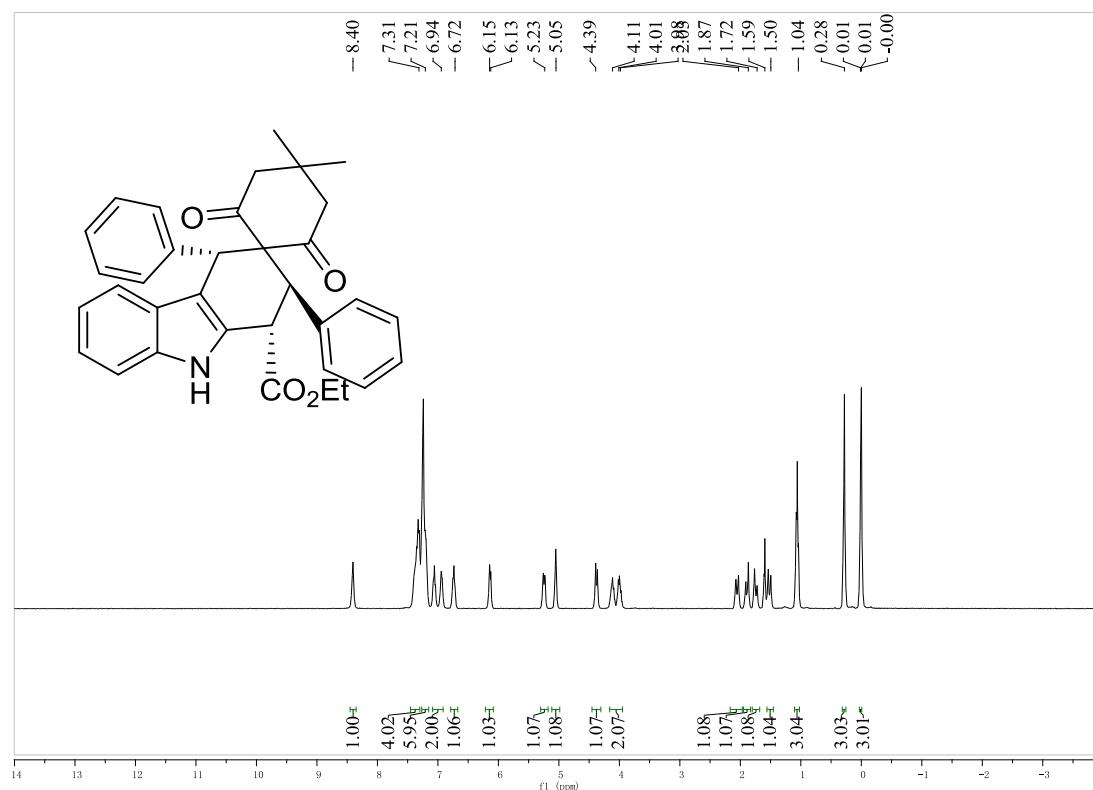


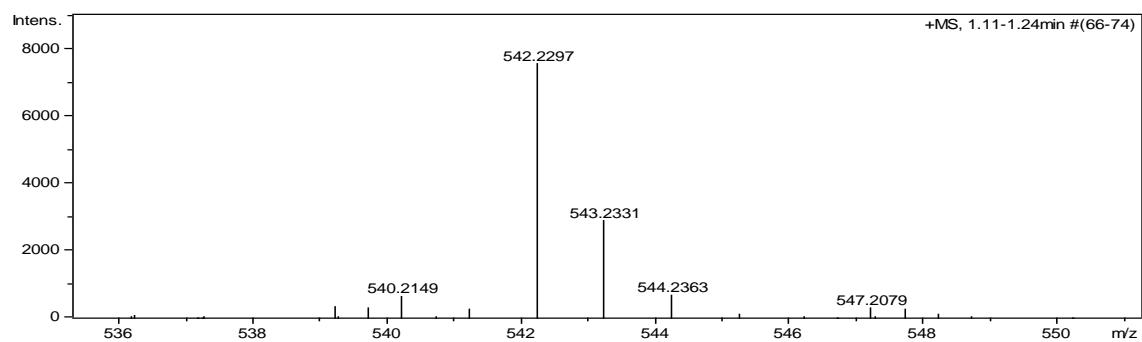
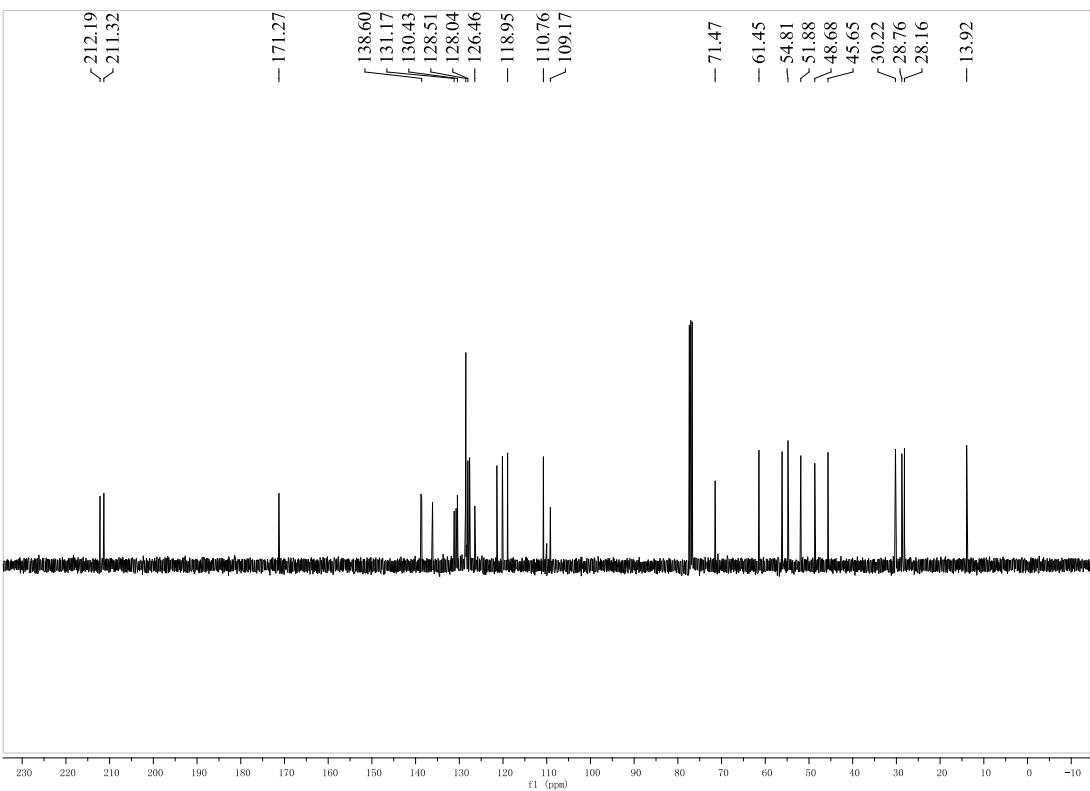


Ethyl

rel-(*1S,2R,4S*)-4',4'-dimethyl-2',6'-dioxo-2,4-diphenyl-1,2,4,9-tetrahydrospiro[carbazole-3,1'-cyclohexane]-1-carboxylate (**2j**):

white solid, 63%, m.p. 178-181 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.40 (s, 1H, NH), 7.39-7.31 (m, 4H, ArH), 7.27-7.20 (m, 6H, ArH), 7.08-6.93 (m, 2H, ArH), 6.75-6.72 (m, 1H, ArH), 6.15-6.13 (m, 1H, ArH), 5.24 (dd, *J*₁ = 10.8 Hz, *J*₂ = 2.4 Hz, 1H, CH), 5.04 (d, *J* = 2.4 Hz, 1H, CH), 4.37 (d, *J* = 10.8 Hz, 1H, CH), 4.06 (q, *J* = 7.2 Hz, 2H, CH₂), 2.05 (dd, *J*₁ = 17.2 Hz, *J*₂ = 1.6 Hz, 1H, CH), 1.88 (d, *J* = 17.2 Hz, 1H, CH), 1.74 (dd, *J*₁ = 16.4 Hz, *J*₂ = 1.6 Hz, 1H, CH), 1.52 (d, *J* = 16.4 Hz, 1H, CH), 1.06 (t, *J* = 7.2 Hz, 3H, CH₃), 0.28 (s, 3H, CH₃), 0.01 (s, 3H, CH₃); ¹³C NMR (400 MHz, CDCl₃) δ: 212.1, 211.3, 171.2, 138.7, 138.6, 136.1, 131.1, 130.7, 130.4, 128.5, 128.5, 128.3, 128.0, 127.6, 126.4, 121.4, 120.1, 118.9, 110.7, 109.1, 71.4, 61.4, 56.1, 54.8, 51.8, 48.6, 45.6, 30.2, 28.7, 28.1, 13.9; IR (KBr) ν: 3354, 3167, 3079, 2945, 1766, 1637, 1645, 1587, 1464, 1371, 1378, 1256, 1183, 967, 888 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₄H₃₃NO₄([M+Na]⁺): 542.2302, found: 542.2297.

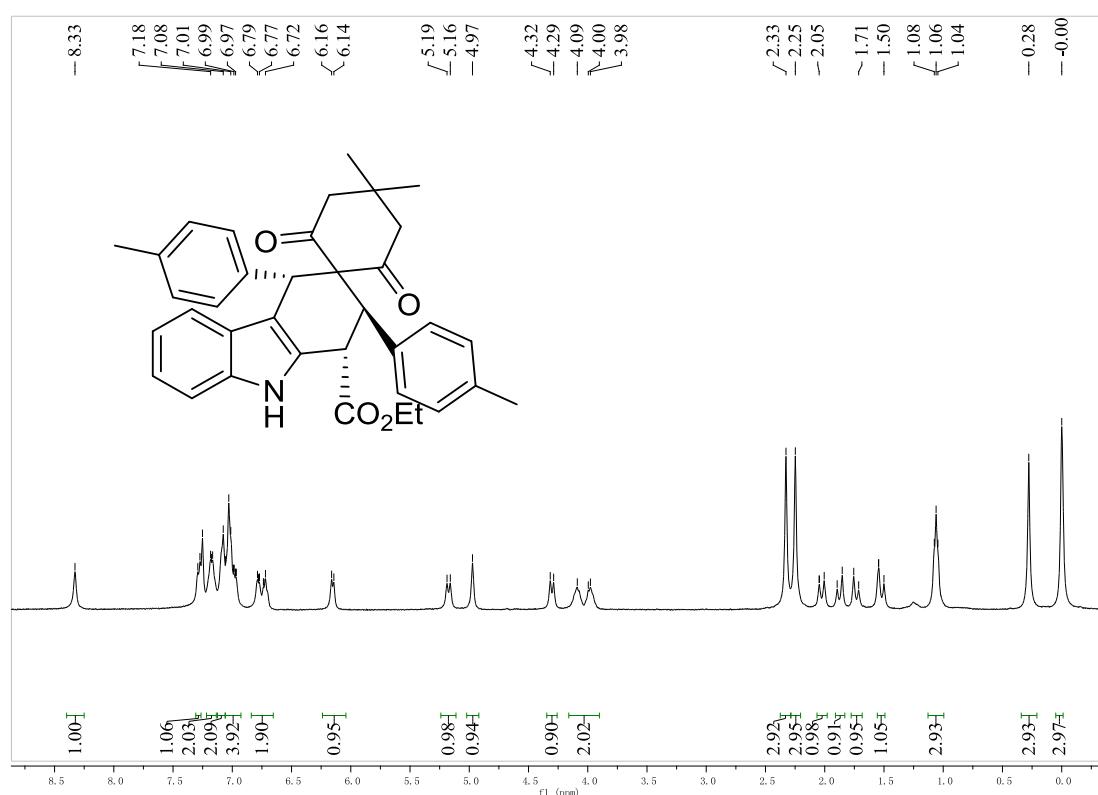


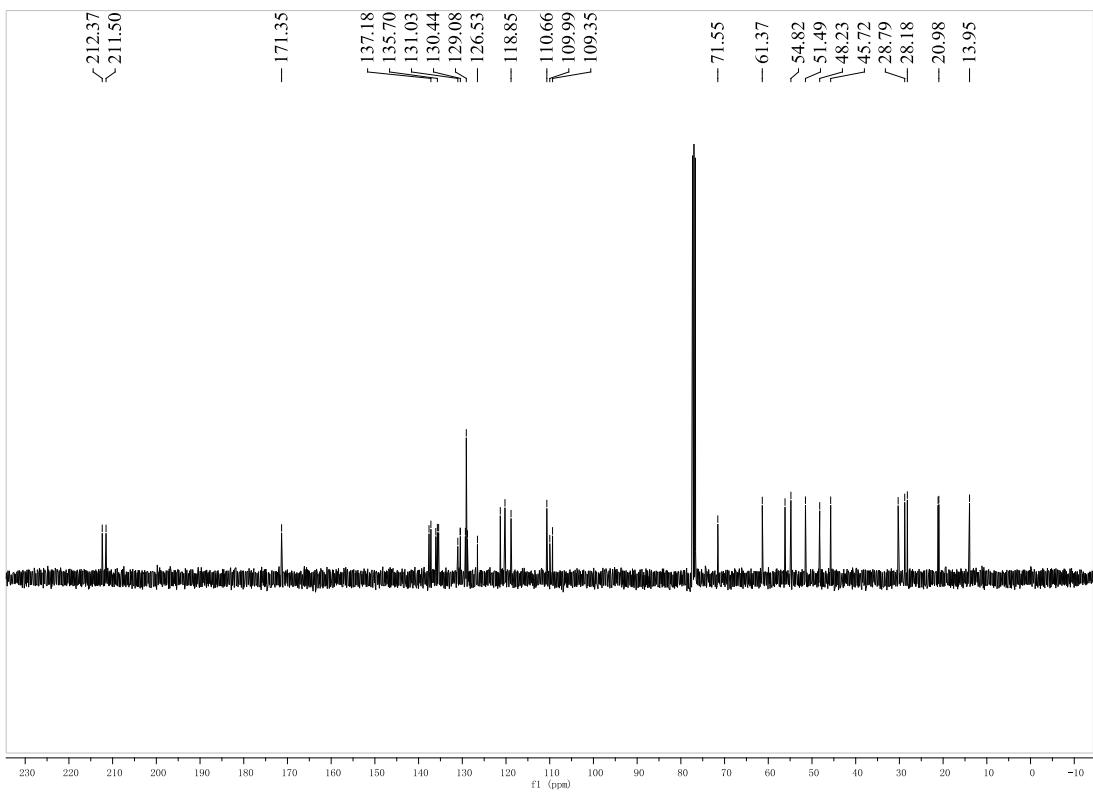


Ethyl

rel-(*1S,2R,4S*)-4',4'-dimethyl-2',6'-dioxo-2,4-di-p-tolyl-1,2,4,9-tetrahydrospiro[carbazole-3,1'-cyclohexane]-1-carboxylate (2k):

white solid, 63%, m.p. 178-181 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.33 (s, 1H, NH), 7.29-7.27 (m, 1H, ArH), 7.18-7.17 (m, 2H, ArH), 7.08-7.06 (m, 2H, ArH), 7.03-6.97 (m, 4H, ArH), 6.79-6.72 (m, 2H, ArH), 6.15 (d, *J* = 7.6 Hz, 1H, ArH), 5.17 (d, *J* = 11.2 Hz, 1H, CH), 4.97 (s, 1H, CH), 4.30 (d, *J* = 11.2 Hz, 1H, CH), 4.09 (q, *J* = 6.4 Hz, 2H, CH₂), 2.33 (s, 3H, CH₃), 2.25 (s, 3H, CH₃), 2.02 (d, *J* = 16.8 Hz, 1H, CH), 1.87 (d, *J* = 16.8 Hz, 1H, CH), 1.73 (d, *J* = 16.8 Hz, 1H, CH), 1.52 (d, *J* = 16.8 Hz, 1H, CH), 1.06 (t, *J* = 6.4 Hz, 3H, CH₃), 0.28 (s, 3H, CH₃), 0.10 (s, 3H, CH₃); ¹³C NMR (400 MHz, CDCl₃) δ: 212.3, 211.5, 171.3, 137.6, 137.1, 136.0, 135.7, 135.4, 131.0, 130.4, 130.4, 129.2, 129.0, 128.8, 126.5, 121.3, 120.2, 118.8, 110.6, 109.9, 109.3, 71.5, 61.3, 56.1, 54.8, 51.4, 48.2, 45.7, 30.2, 28.7, 28.1, 21.1, 20.9, 13.9; IR (KBr) ν: 3400, 3173, 3054, 2985, 1787, 1643, 1611, 1545, 1437, 1380, 1356, 1244, 1167, 932, 840 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₆H₃₇NO₄[M+Na]⁺: 570.2615, found: 570.2607.



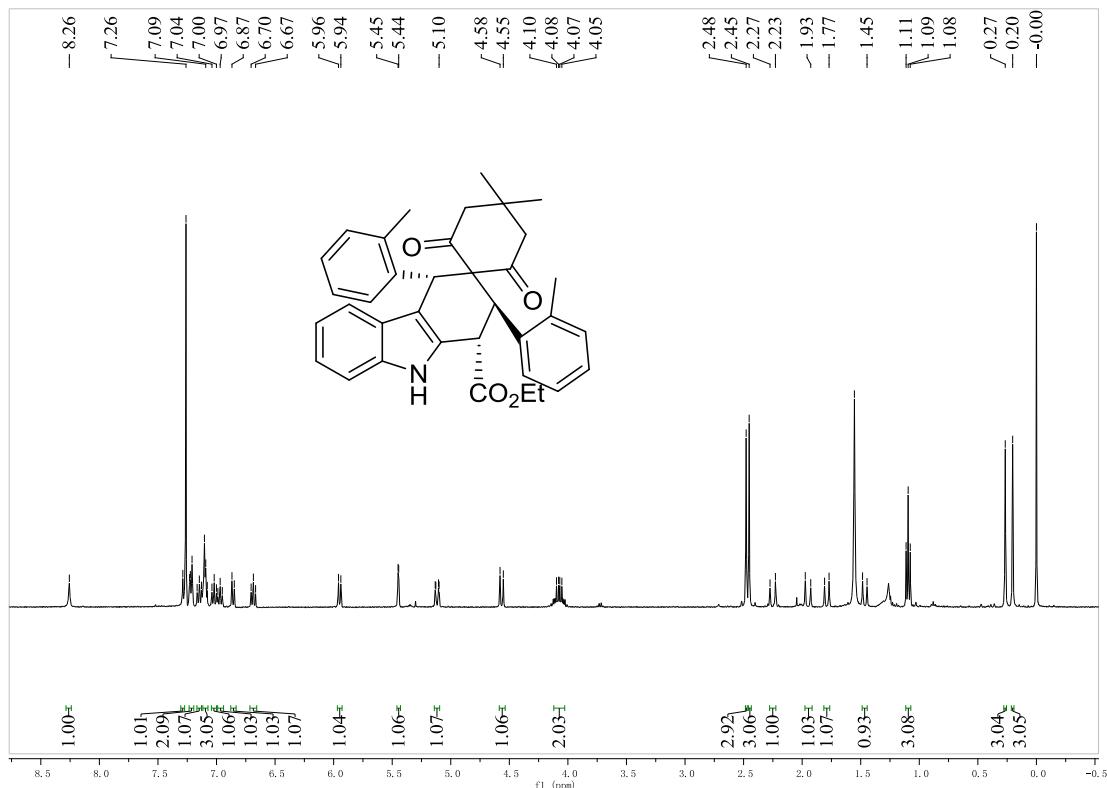


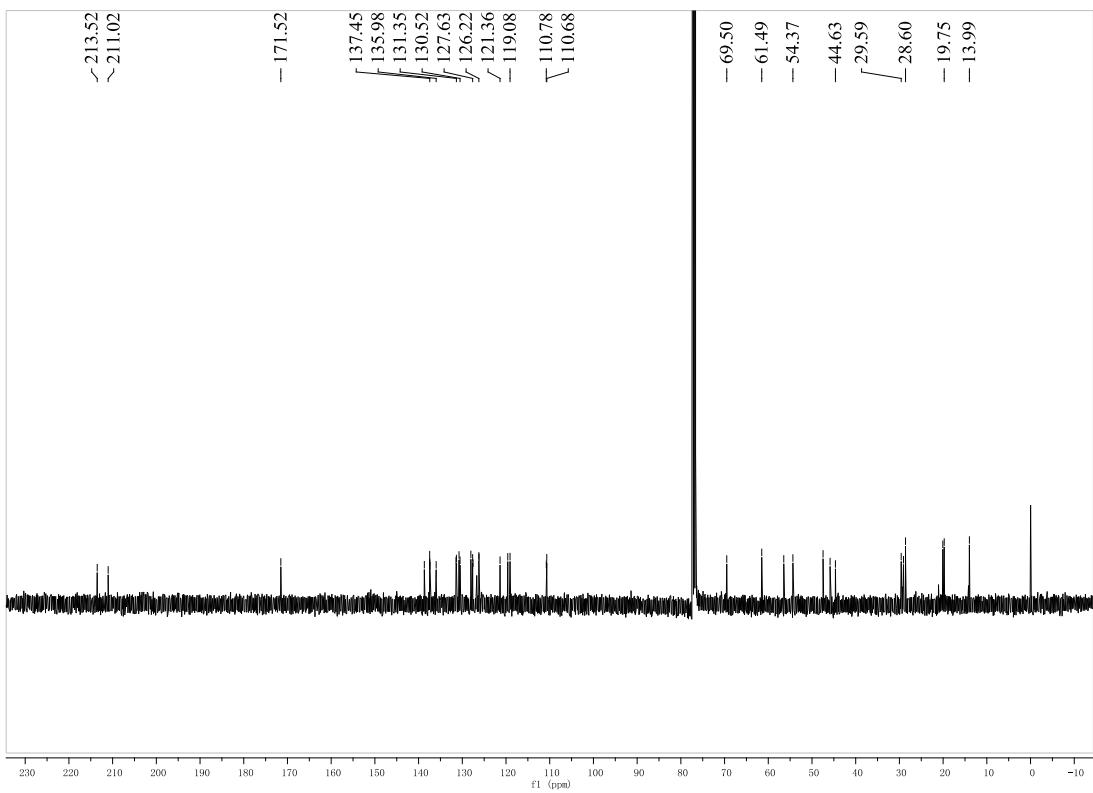
ZSC11_20210120104636 #21 RT: 0.26 AV: 1 NL: 1.12E+006
[1567015659 Full trace 1568-0000-1500.0000]
[1567015659 Full trace 1568-0000-1500.0000]
[1567015659 Full trace 1568-0000-1500.0000]
[1567015659 Full trace 1568-0000-1500.0000]
[1567015659 Full trace 1568-0000-1500.0000]

Ethyl

rel-(*1S,2R,4S*)-4',4'-dimethyl-2',6'-dioxo-2,4-di-*o*-tolyl-1,2,4,9-tetrahydrospiro[carbazole-3,1'-cyclohexane]-1-carboxylate (**2l**):

white solid, 53%, m.p. 181-183 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.26 (s, 1H, NH), 7.28-7.26 (m, 1H, ArH), 7.23-7.21 (m, 2H, ArH), 7.15 (t, *J* = 7.6 Hz, 1H, ArH), 7.10-7.08 (m, 3H, ArH), 7.02 (t, *J* = 7.6 Hz, 1H, ArH), 6.97 (t, *J* = 8.0 Hz, 1H, ArH), 6.85 (d, *J* = 8.0 Hz, 1H, ArH), 6.69 (t, *J* = 8.0 Hz, 1H, ArH), 5.94 (d, *J* = 8.0 Hz, 1H, ArH), 5.45 (d, *J* = 2.0 Hz, 1H, CH), 5.11 (dd, *J*₁ = 11.2 Hz, *J*₂ = 2.0 Hz, 1H, CH), 4.57 (d, *J* = 11.2 Hz, 1H, CH), 4.08 (q, *J* = 7.2 Hz, 2H, CH₂), 2.48 (s, 3H, CH₃), 2.45 (s, 3H, CH₃), 2.25 (d, *J* = 18.4 Hz, 1H, CH), 1.95 (d, *J* = 18.4 Hz, 1H, CH), 1.78 (d, *J* = 15.4 Hz, 1H, CH), 1.46 (d, *J* = 15.2 Hz, 1H, CH), 1.09 (t, *J* = 7.2 Hz, 3H, CH₃), 0.27 (s, 3H, CH₃), 0.20 (s, 3H, CH₃); ¹³C NMR (400 MHz, CDCl₃) δ: 213.5, 211.0, 171.5, 138.6, 137.4, 137.4, 135.9, 131.4, 130.7, 130.5, 128.0, 127.6, 126.1, 121.3, 119.5, 119.0, 110.7, 110.6, 69.5, 61.4, 56.4, 54.3, 47.4, 45.8, 44.6, 29.5, 29.0, 28.6, 20.0, 19.7, 13.9; IR (KBr) ν: 3413, 3155, 3081, 2961, 1766, 1651, 1630, 1543, 1466, 1358, 1318, 1260, 1141, 962, 860 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₆H₃₇NO₄([M+Na]⁺): 570.2615, found: 570.2607.

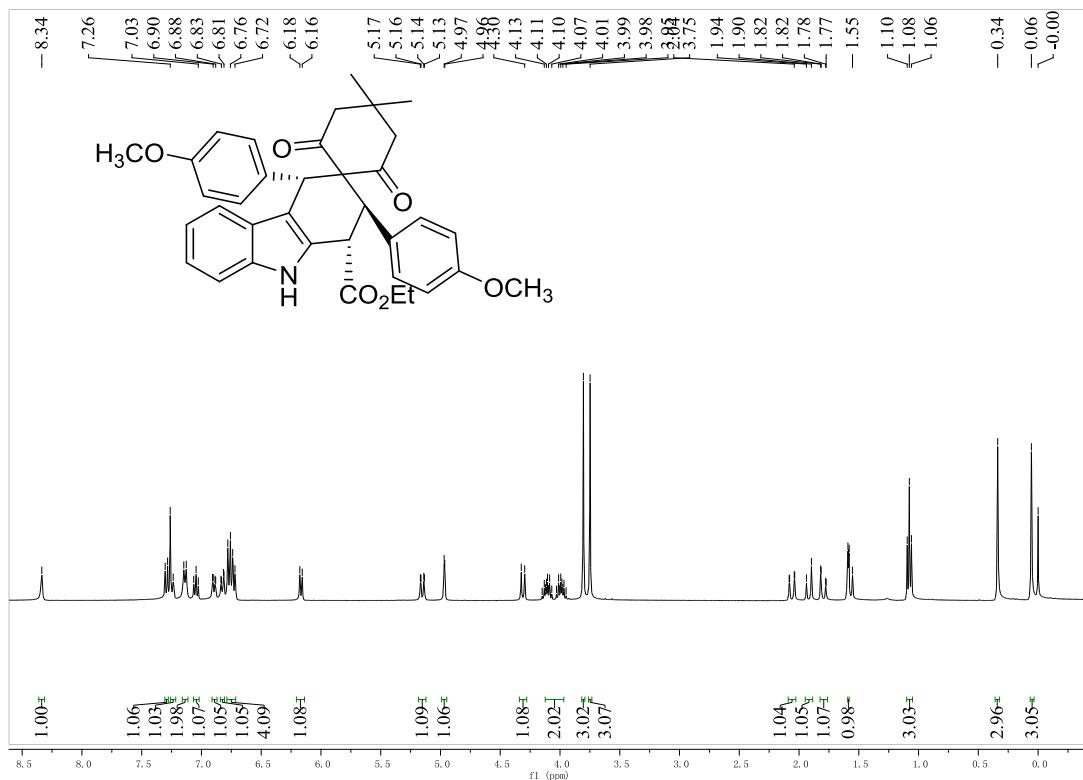


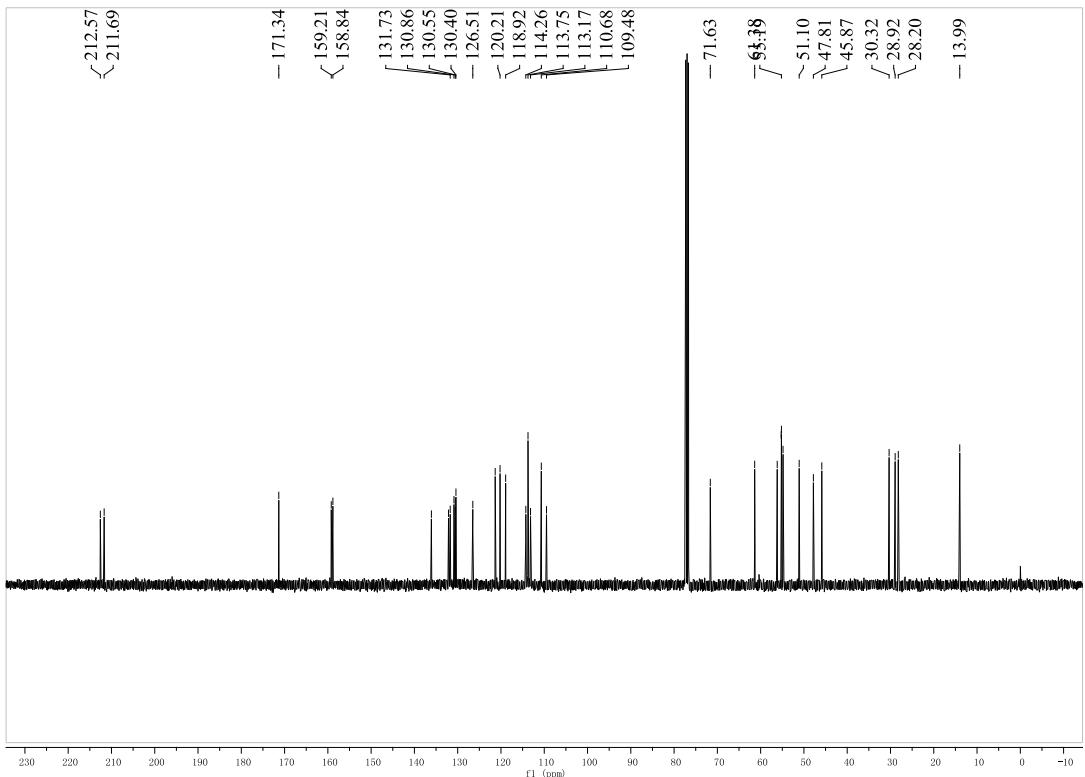


Ethyl

rel-(*1S,2R,4S*)-4',4'-dimethyl-2',6'-dioxo-2,4-di-*o*-tolyl-1,2,4,9-tetrahydrospiro[carbazole-3,1'-cyclohexane]-1-carboxylate (2m):

white solid, 61%, m.p. 177-179 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.34 (s, 1H, NH), 7.29 (d, J = 8.4 Hz, 1H, ArH), 7.26-7.24 (m, 1H, ArH), 7.13 (d, J = 8.4 Hz, 2H, ArH), 7.05 (t, J = 8.0 Hz, 1H, ArH), 6.89 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H, ArH), 6.82 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H, ArH), 6.78-6.72 (m, 4H, ArH), 6.16 (t, J = 7.6 Hz, 1H, ArH), 5.15 (dd, J_1 = 11.2 Hz, J_2 = 2.0 Hz, 1H, CH), 4.96 (d, J = 2.0 Hz, 1H, CH), 4.30 (d, J = 11.2 Hz, 1H, CH), 4.04 (q, J = 7.2 Hz, 2H, CH_2), 3.80 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 2.06 (dd, J_1 = 17.2 Hz, J_2 = 1.2 Hz, 1H, CH), 1.91 (d, J = 16.4 Hz, 1H, CH), 1.19 (dd, J_1 = 16.4 Hz, J_2 = 1.2 Hz, 1H, CH), 1.59-1.58 (m, 1H, CH), 1.08 (t, J = 7.2 Hz, 3H, CH_3), 0.34 (s, 3H, CH_3), 0.06 (s, 3H, CH_3); ^{13}C NMR (400 MHz, CDCl_3) δ : 212.5, 211.6, 171.3, 159.2, 158.8, 136.0, 132.1, 131.7, 130.8, 130.5, 130.4, 126.5, 121.3, 120.2, 118.9, 114.2, 113.7, 113.1, 110.6, 109.4, 71.6, 61.3, 56.1, 55.2, 55.1, 54.8, 51.0, 47.8, 45.8, 30.3, 28.9, 28.1, 13.9; IR (KBr) ν : 3410, 3058, 2966, 1871, 1736, 1654, 1646, 1578, 1432, 1364, 1300, 1247, 1157, 899, 765 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{36}\text{H}_{37}\text{NO}_6([\text{M}+\text{Na}]^+)$: 602.2513, found: 602.2507.



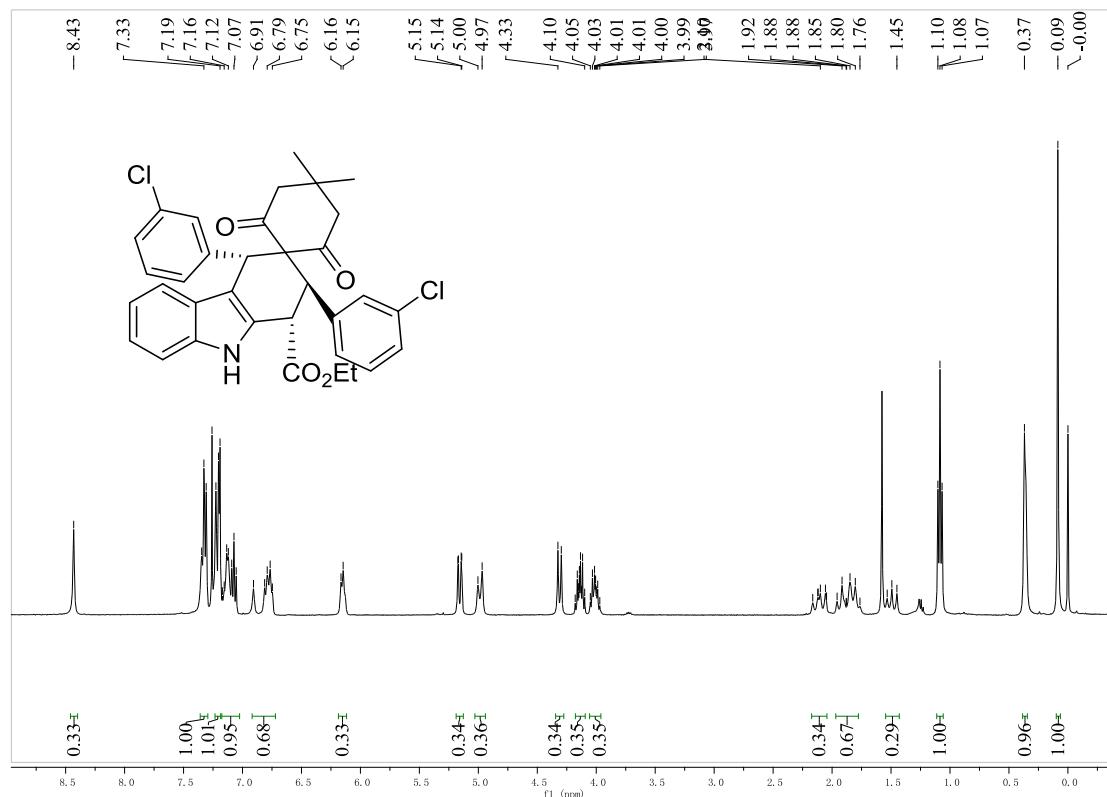


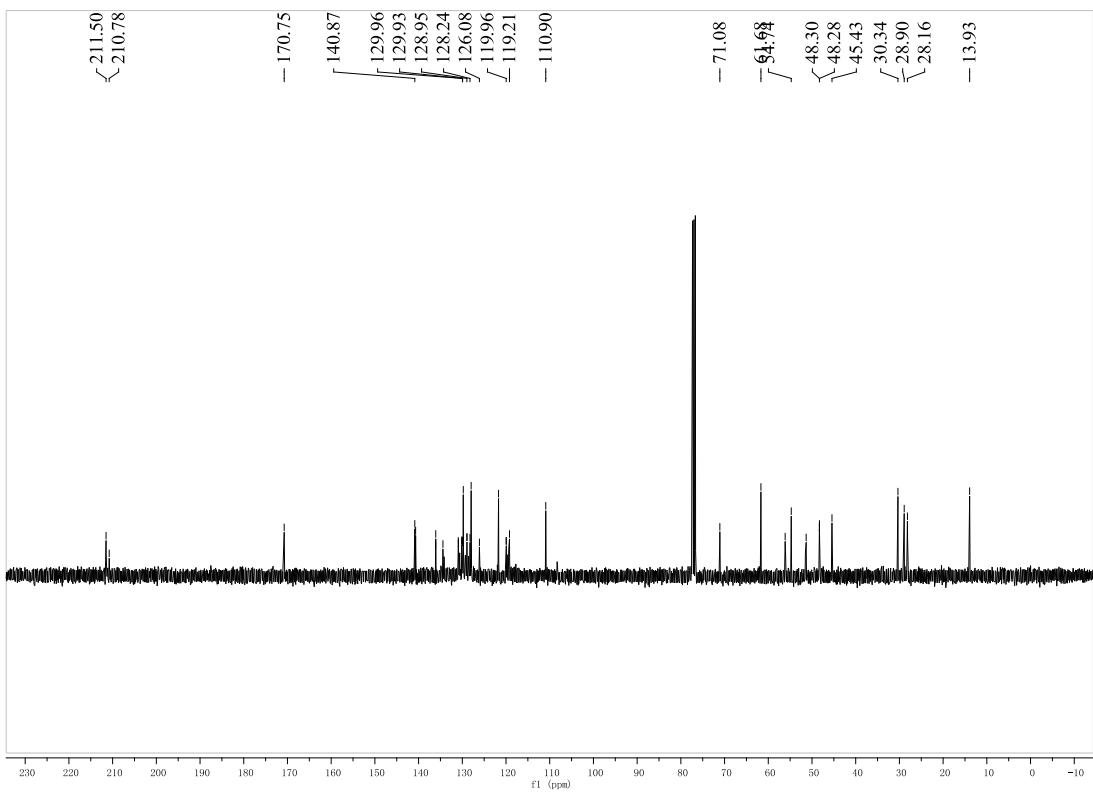
SC12_20210120104932 #34 RT: 0.43 AV: 1 NL: 1.01E+006
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[11845127, 11845127, 11845127]
[11845127, 11845127, 11845127]
[11845127, 11845127, 11845127]

Ethyl

rel-(1*S*,2*R*,4*S*)-2,4-bis(3-chlorophenyl)-4',4'-dimethyl-2',6'-dioxo-1,2,4,9-tetrahydrospiro[carbazole-3,1'-cyclohexane]-1-carboxylate (2n):

white solid, 50%, m.p. 190-193 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.43 (s, 1H, NH), 7.35-7.31 (m, 3H, ArH), 7.23-7.19 (m, 3H, ArH), 7.17-7.05 (m, 3H, ArH), 6.91-6.75 (m, 2H, ArH), 6.17-6.13 (m, 1H, ArH), 5.15 (dd, $J_1 = 11.2$ Hz, $J_2 = 2.0$ Hz, 1H, CH), 4.98 (d, $J = 14.4$ Hz, 1H, CH), 4.30 (d, $J = 11.2$ Hz, 1H, CH), 4.04 (q, $J = 7.2$ Hz, 2H, CH_2), 2.16-2.05 (m, 1H, CH), 1.96-1.76 (m, 2H, CH), 1.53-1.45 (m, 1H, CH), 1.09 (t, $J = 7.2$ Hz, 3H, CH_3), 0.37 (s, 3H, CH_3), 0.09 (s, 3H, CH_3); ^{13}C NMR (400 MHz, CDCl_3) δ : 211.5, 210.7, 170.7, 140.8, 140.6, 136.1, 136.0, 134.4, 130.9, 130.8, 130.1, 130.1, 129.9, 129.7, 128.9, 128.2, 127.9, 126.0, 121.7, 119.9, 119.2, 110.9, 71.0, 61.6, 56.1, 54.7, 51.3, 48.3, 48.2, 48.2, 45.4, 30.3, 28.9, 28.1, 13.9; IR (KBr) ν : 3433, 3051, 2963, 1841, 1766, 1680, 1631, 1531, 1445, 1317, 1290, 1241, 1164, 921, 854, 746 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{34}\text{H}_{31}\text{ClNO}_4$ ([M+Na] $^+$): 610.1522, found: 610.1515.

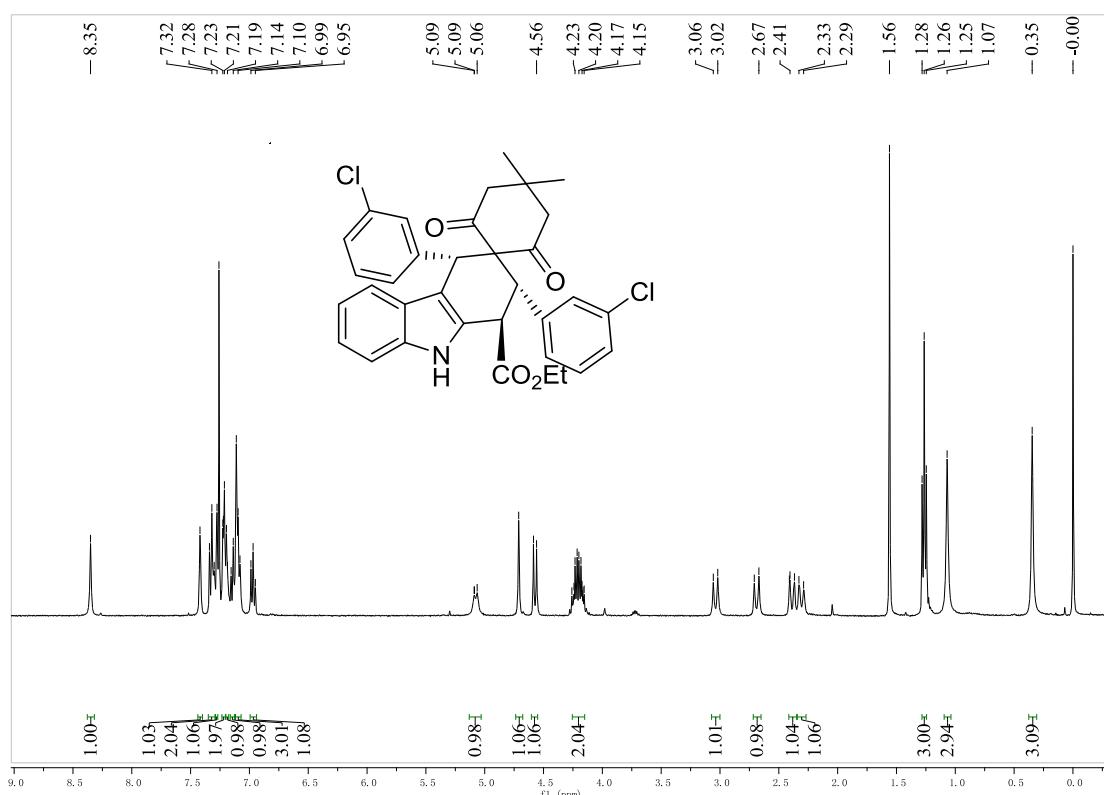


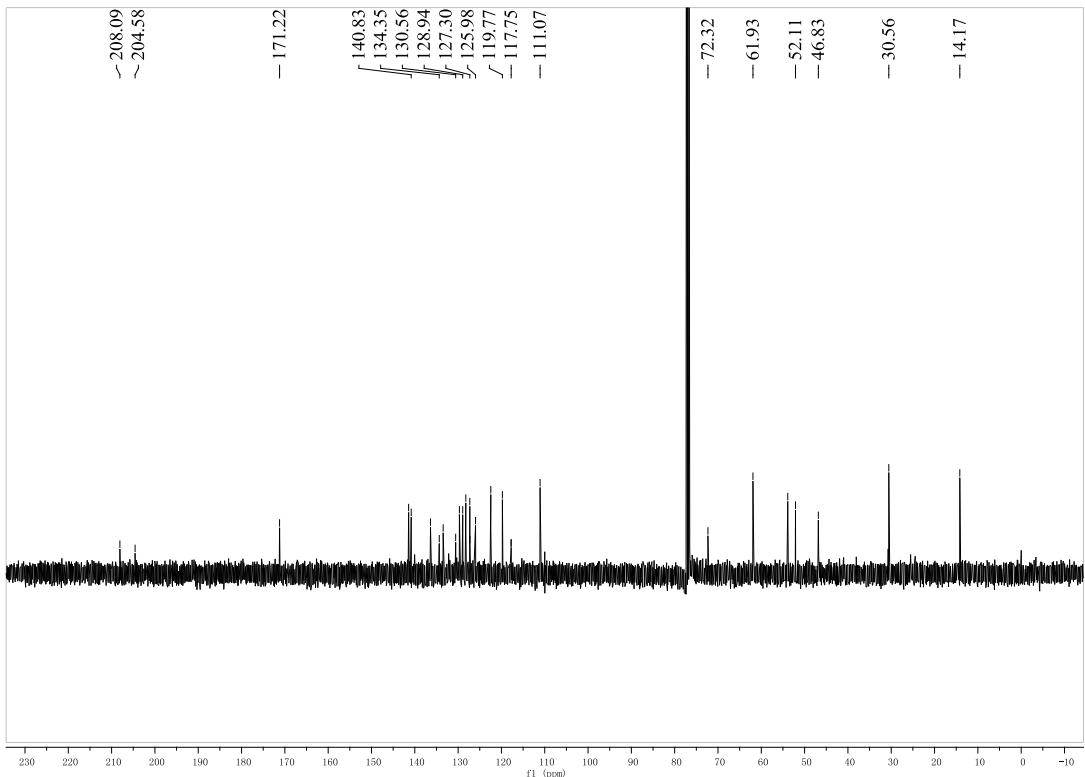


Ethyl

*re-(1*R*,2*S*,4*S*)-2,4-bis(3-chlorophenyl)-4',4'-dimethyl-2',6'-dioxo-1,2,4,9-tetrahydrospiro[carbazole-3,1'-cyclohexane]-1-carboxylate (2n'):*

white solid, 6%, m.p. 167-169 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.35 (s, 1H, NH), 7.42 (s, 1H, ArH), 7.34-7.30 (m, 2H, ArH), 7.27-7.26 (m, 2H, ArH), 7.23-7.21 (m, 2H, ArH), 7.20-7.19 (m, 2H, ArH), 7.14 (d, J = 7.2 Hz, 1H, ArH), 7.11-7.08 (m, 3H, ArH), 6.97 (t, J = 7.2 Hz, 1H, ArH), 5.07 (d, J = 10.4 Hz, 1H, CH), 4.71 (s, 1H, CH), 4.57 (d, J = 10.4 Hz, 1H, CH), 4.20 (q, J = 7.2 Hz, 2H, CH_2), 3.03 (d, J = 14.2 Hz, 1H, CH), 2.68 (d, J = 14.2 Hz, 1H, CH), 2.38 (d, J = 14.2 Hz, 1H, CH), 2.31 (d, J = 14.2 Hz, 1H, CH), 1.27 (t, J = 7.2 Hz, 3H, CH_3), 1.07 (s, 3H, CH_3), 0.35 (s, 3H, CH_3); ^{13}C NMR (400 MHz, CDCl_3) δ : 208.0, 204.5, 171.2, 141.4, 140.8, 136.3, 134.3, 133.4, 130.5, 129.7, 128.9, 128.2, 127.3, 127.2, 125.9, 122.4, 119.7, 117.7, 117.7, 111.0, 72.3, 61.9, 53.8, 52.1, 46.8, 30.5, 14.1; IR (KBr) ν : 3403, 3071, 2982, 1900, 1843, 1710, 1631, 1546, 1433, 1369, 1260, 1269, 1180, 951, 833, 767 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{34}\text{H}_{31}\text{ClNO}_4([\text{M}+\text{Na}]^+)$: 610.1522, found: 610.1519.



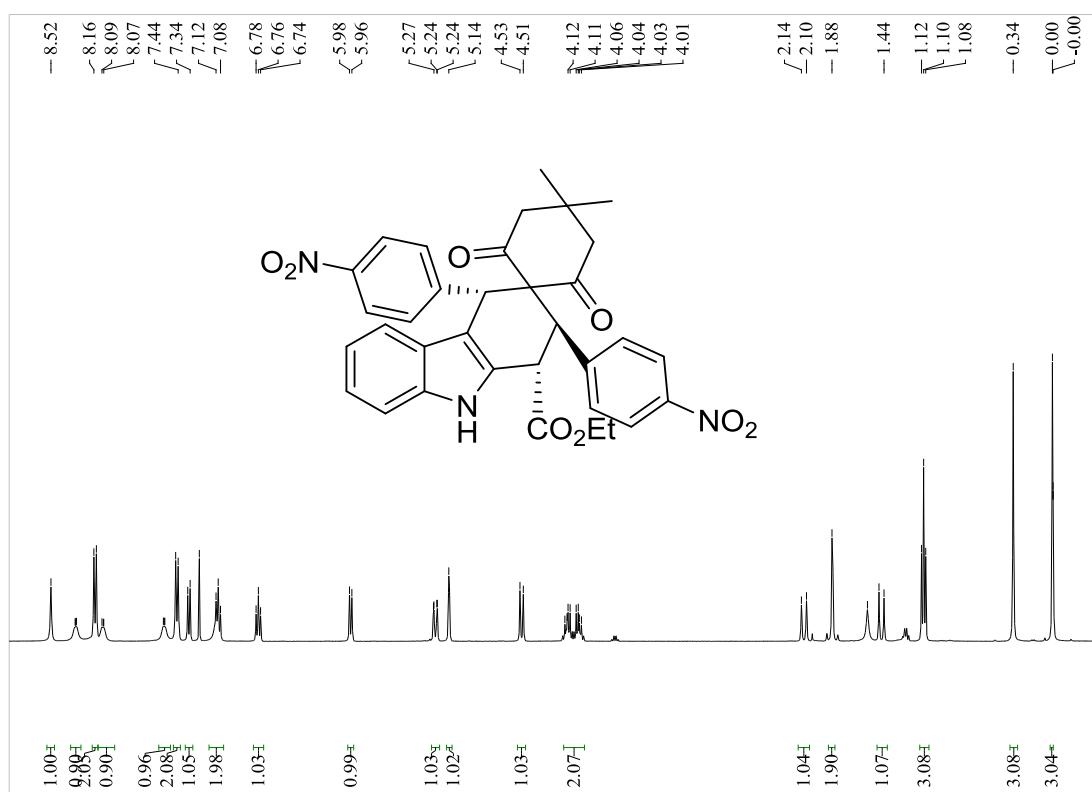


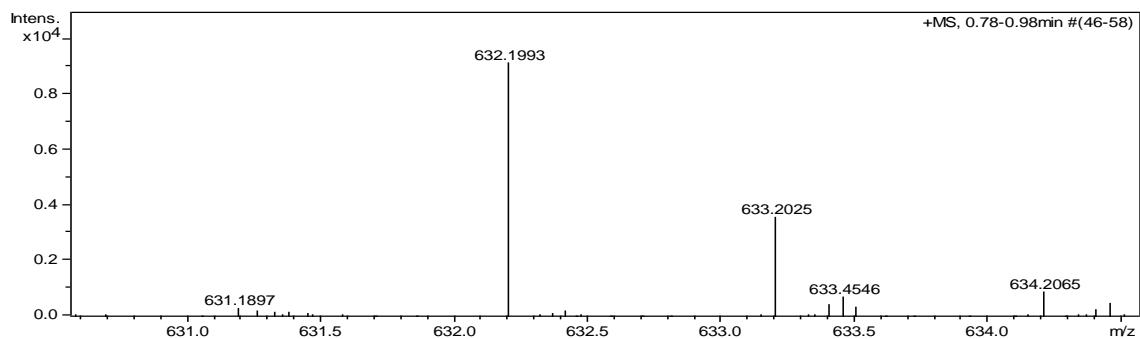
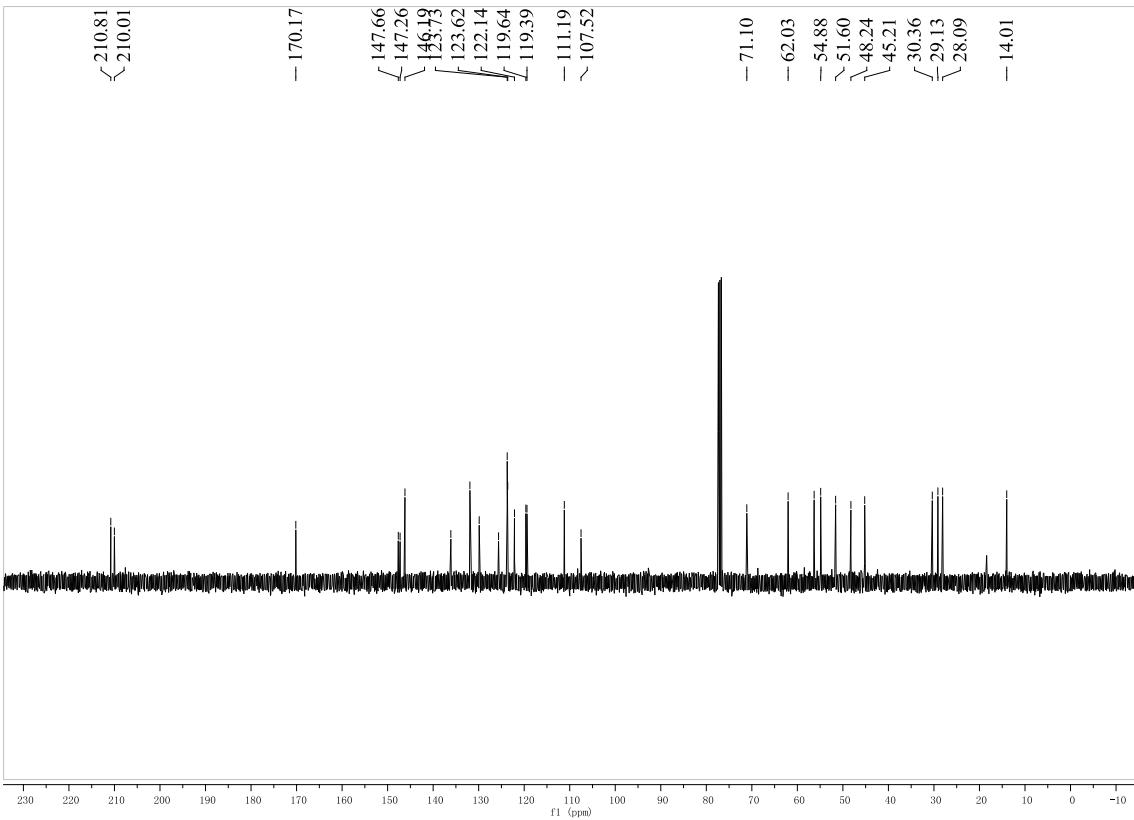
Z:\SC15_20210130105821 #28 RT: 0.35 AV: 1 NL: 6.63E+005
012387474927 ESI Full ms [100.0000-1500.0000]
[100.0000-1500.0000] 100.0000-1500.0000

Ethyl

rel-(*1S,2R,4S*)-4',4'-dimethyl-2,4-bis(4-nitrophenyl)-2',6'-dioxo-1,2,4,9-tetrahydrospiro[carba zole-3,1'-cyclohexane]-1-carboxylate (2o):

white solid, 51%, m.p. 190-193 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.52 (s, 1H, NH), 8.31-8.30 (m, 1H, ArH), 8.14 (d, *J* = 8.4 Hz, 2H, ArH), 8.08-8.07 (m, 1H, ArH), 7.56-7.55 (m, 1H, ArH), 7.44 (d, *J* = 8.4 Hz, 2H, ArH), 7.34 (d, *J* = 8.0 Hz, 1H, ArH), 7.11-7.08 (m, 2H, ArH), 6.75 (d, *J* = 8.0 Hz, 1H, ArH), 5.96 (d, *J* = 8.0 Hz, 1H, ArH), 5.24 (dd, *J*₁ = 11.2 Hz, *J*₂ = 1.6 Hz, 1H, CH), 5.13 (s, 1H, CH), 4.51 (d, *J* = 11.6 Hz, 1H, CH), 4.07 (q, *J* = 7.2 Hz, 2H, CH₂), 2.11 (d, *J* = 17.2 Hz, 1H, CH), 1.88-1.87 (m, 2H, CH₂), 1.46 (d, *J* = 17.2 Hz, 1H, CH), 1.09 (t, *J* = 7.2 Hz, 3H, CH₃), 0.33 (s, 3H, CH₃), 0.07 (s, 3H, CH₃); ¹³C NMR (400 MHz, CDCl₃) δ: 210.8, 210.0, 170.1, 147.6, 147.2, 146.1, 136.1, 131.9, 129.8, 125.6, 123.7, 123.6, 122.1, 119.6, 119.3, 111.1, 107.5, 71.1, 62.0, 56.3, 54.8, 51.6, 48.2, 45.2, 30.3, 29.1, 28.0, 14.0; IR (KBr) ν: 3454, 3078, 2967, 1884, 1772, 1681, 1645, 1587, 1454, 1367, 1331, 1267, 1148, 833, 782 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₄H₃₁N₃O₈ ([M+Na]⁺): 632.2003, found: 632.1993.

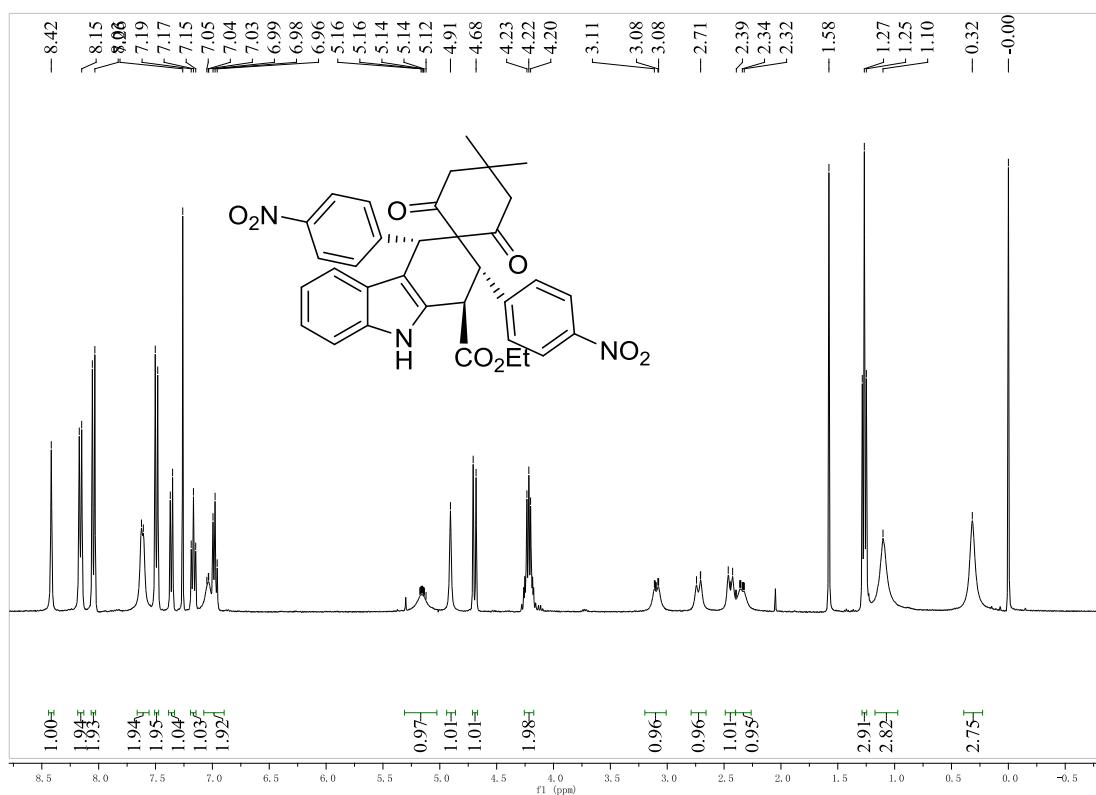


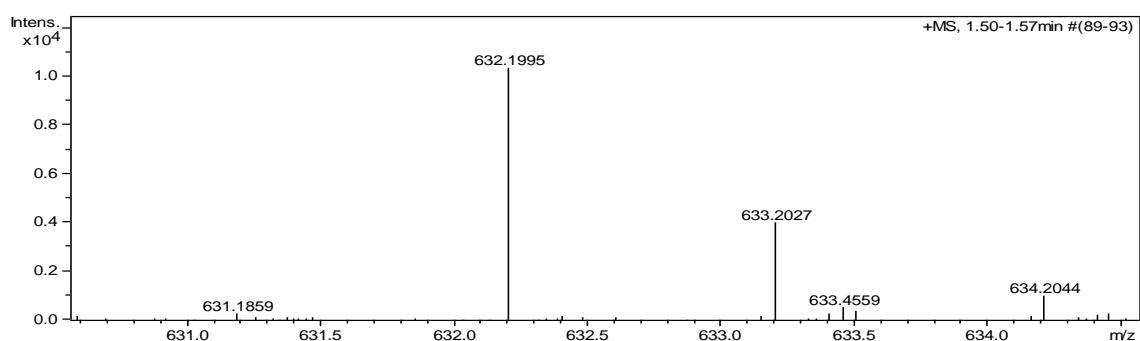
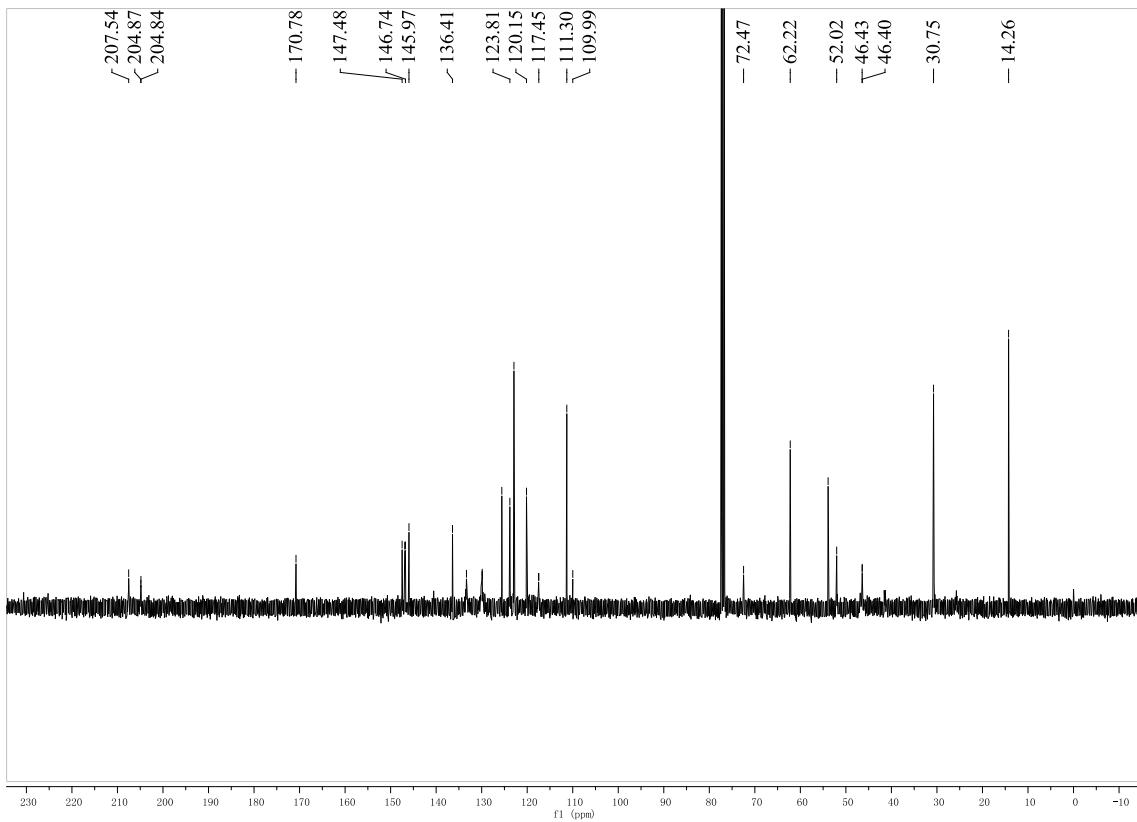


Ethyl

rel-(1*S*,2*R*,4*S*)-4',4'-dimethyl-2,4-bis(4-nitrophenyl)-2',6'-dioxo-1,2,4,9-tetrahydrospiro[carbazole-3,1'-cyclohexane]-1-carboxylate (20'):

white solid, 7%, m.p. 176-178 °C; ^1H NMR (400 MHz, CDCl_3) δ: 8.42 (s, 1H, NH), 8.16 (d, J = 8.4 Hz, 2H, ArH), 8.04 (d, J = 8.8 Hz, 2H, ArH), 7.62-7.61 (m, 2H, ArH), 7.49 (d, J = 8.4 Hz, 2H, ArH), 7.36 (d, J = 8.4 Hz, 1H, ArH), 7.17 (t, J = 7.6 Hz, 1H, ArH), 7.05-6.96 (m, 2H, ArH), 5.18-5.12 (m, 1H, ArH), 4.91 (s, 1H, CH), 4.69 (d, J = 10.4 Hz, 1H, CH), 4.21 (q, J = 7.2 Hz, 2H, CH_2), 3.10 (d, J = 14.4 Hz, 1H, CH), 2.71 (d, J = 14.4 Hz, 1H, CH), 2.45 (d, J = 14.4 Hz, 1H, CH), 2.36-2.32 (m, 1H, CH), 1.27 (t, J = 7.2 Hz, 3H, CH_3), 1.10 (s, 3H, CH_3), 0.32 (s, 3H, CH_3); ^{13}C NMR (400 MHz, CDCl_3) δ: 207.5, 204.8, 204.8, 170.7, 147.4, 146.9, 146.7, 145.9, 136.4, 133.3, 129.9, 129.8, 129.8, 125.5, 123.8, 122.9, 120.1, 117.5, 117.4, 111.2, 109.9, 72.4, 62.2, 53.9, 52.0, 46.4, 46.4, 30.7, 14.2; IR (KBr) ν: 3400, 3098, 2974, 1863, 1755, 1678, 1664, 1581, 1417, 1309, 1287, 1240, 1113, 854, 763 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{34}\text{H}_{31}\text{N}_3\text{O}_8([\text{M}+\text{Na}]^+)$: 632.2003, found: 632.1995.

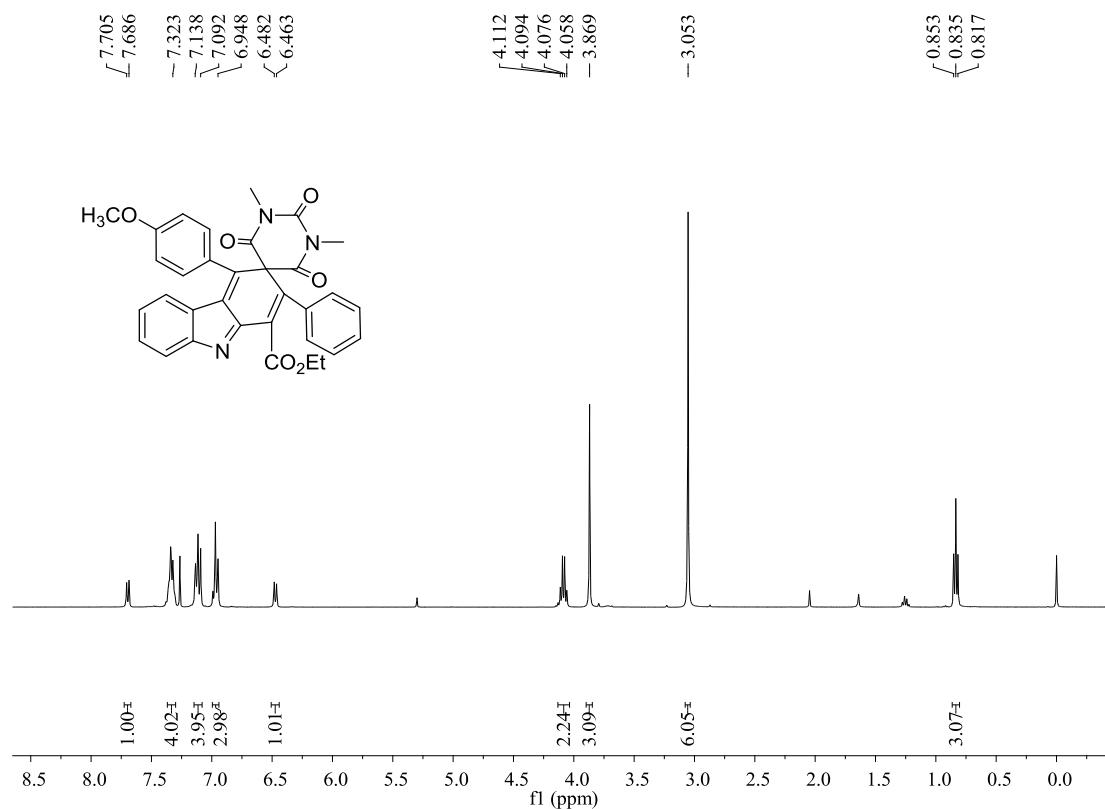


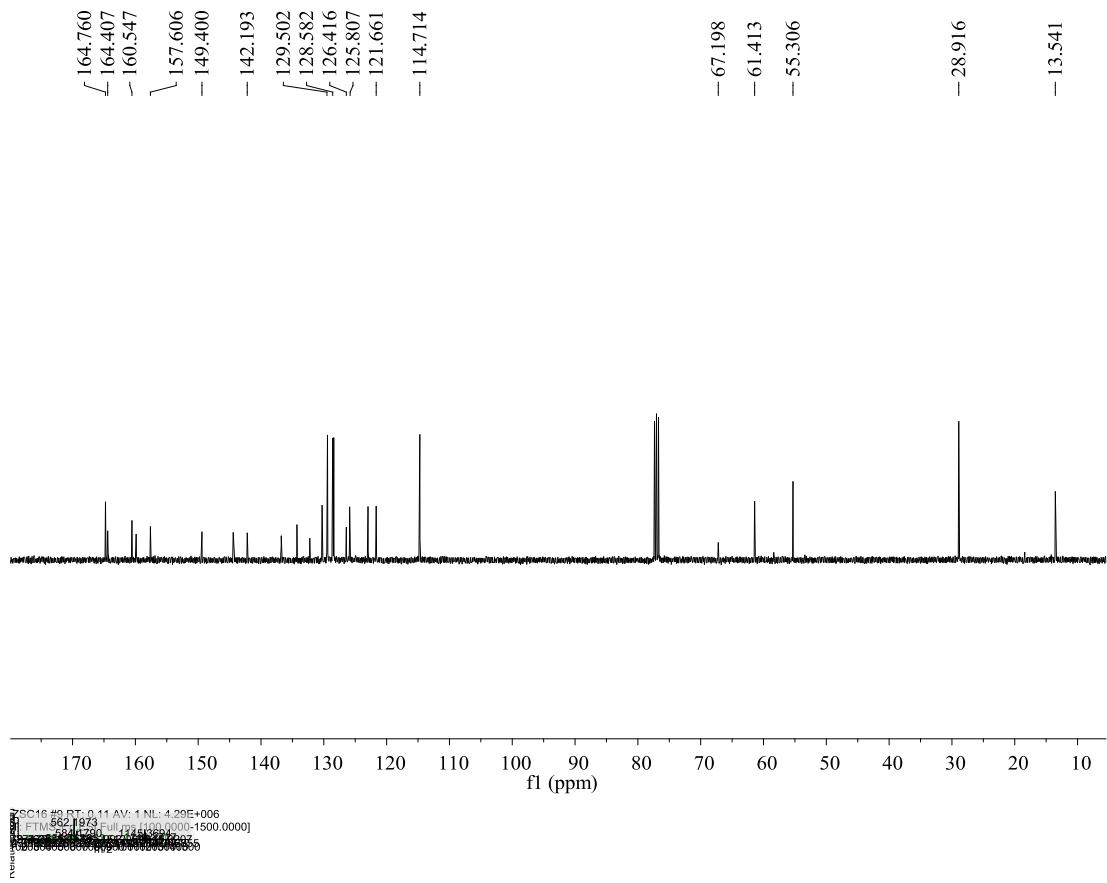


Ethyl

4-(4-methoxyphenyl)-1',3'-dimethyl-2',4',6'-trioxo-2-phenyl-1',3',4',6'-tetrahydro-2'H-spiro[c arbazole-3,5'-pyrimidine]-1-carboxylate (3a):

yellow solid, 70%, m.p. 209-213 °C; ¹H NMR (400 MHz, CDCl₃) δ: 7.69 (d, *J* = 7.6 Hz, 1H, ArH), 7.36-7.26 (m, 4H, ArH), 7.14-7.09 (m, 4H, ArH), 6.99-6.95 (m, 3H, ArH), 6.47 (d, *J* = 7.6 Hz, 1H, ArH), 4.08 (q, *J* = 7.2 Hz, 2H, CH₂), 3.84 (s, 3H, OCH₃), 3.05 (s, 3H, CH₃), 3.04 (s, 3H, CH₃), 0.84 (t, *J* = 7.2 Hz, 3H, CH₃); ¹³C NMR (400 MHz, CDCl₃) δ: 164.7, 164.4, 160.5, 159.8, 157.6, 149.3, 144.4, 142.1, 136.7, 134.2, 132.2, 130.2, 129.5, 129.4, 128.5, 128.4, 126.4, 125.8, 125.8, 122.9, 121.6, 114.7, 67.1, 61.4, 55.3, 28.9, 13.5; IR(KBr) ν: 3234, 3173, 3048, 2955, 2867, 2187, 1844, 1657, 1621, 1564, 1488, 1375, 1287, 1154, 1134, 951, 938, 821, 769 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₃H₂₇N₃O₆ ([M+H]⁺): 562.1973, found: 562.1973.

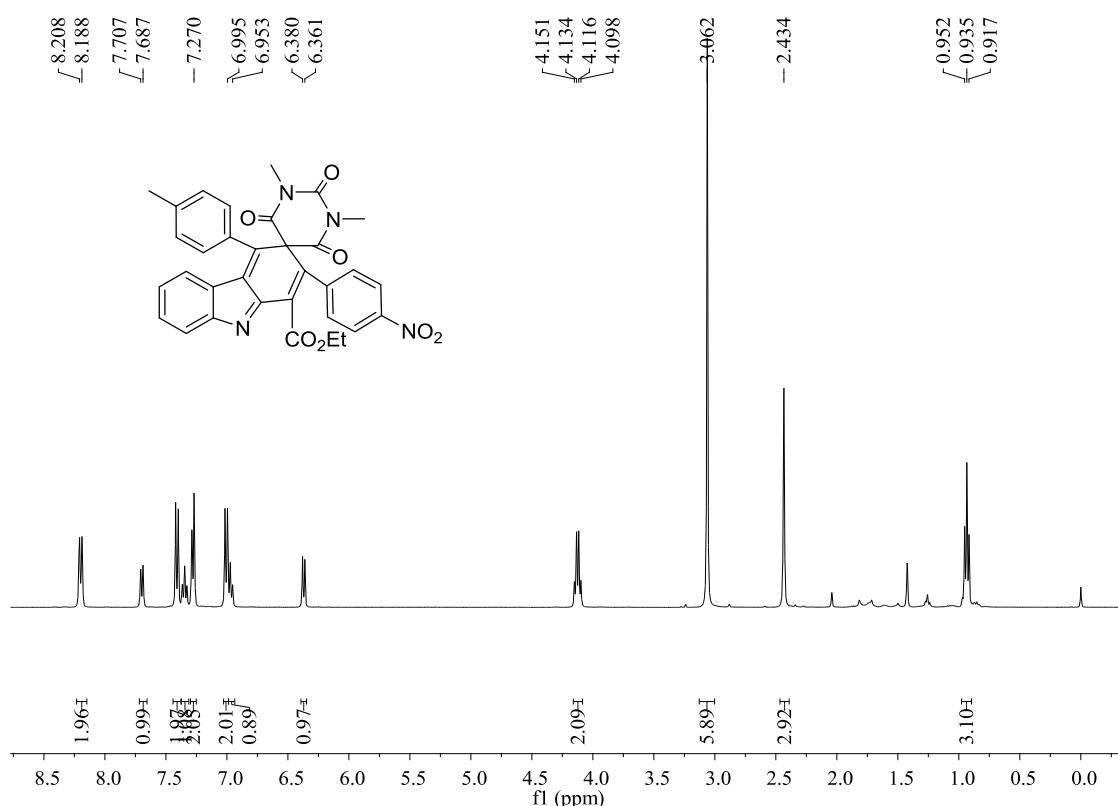


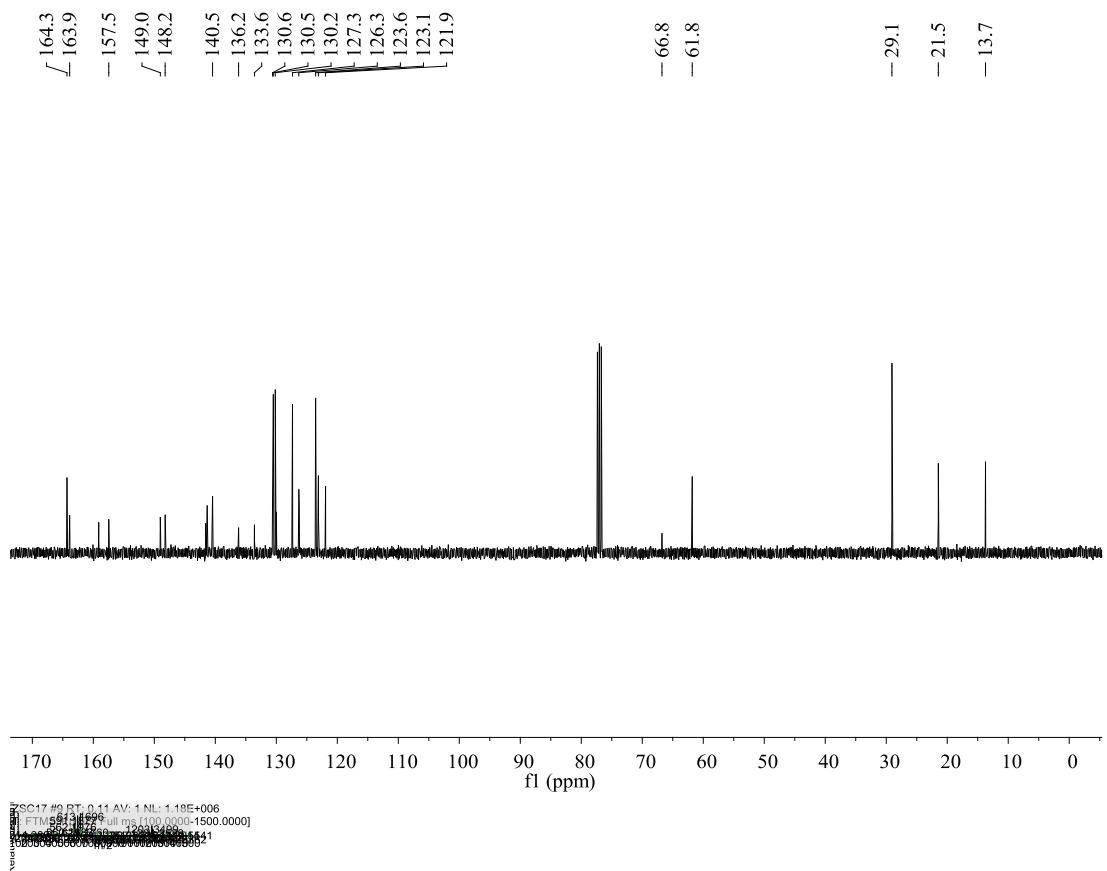


Ethy

1',3'-dimethyl-2-(4-nitrophenyl)-2',4',6'-trioxo-4-(*p*-tolyl)-1',3',4',6'-tetrahydro-2'H-spiro[carbazole-3,5'-pyrimidine]-1-carboxylate (3b):

yellow solid, 65%, m.p. 209-213 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.19 (d, *J* = 8.0 Hz, 2H, ArH), 7.69 (d, *J* = 8.0 Hz, 1H, ArH), 7.41 (d, *J* = 8.0 Hz, 2H, ArH), 7.35 (t, *J* = 7.6 Hz, 1H, ArH), 7.28 (d, *J* = 6.8 Hz, 2H, ArH), 7.00 (d, *J* = 8.0 Hz, 2H, ArH), 6.96 (d, *J* = 7.6 Hz, 1H, ArH), 6.37 (d, *J* = 7.6 Hz, 1H, ArH), 4.12 (q, *J* = 6.8 Hz, 2H, CH₂), 3.06 (s, 3H, CH₃), 3.05 (s, 3H, CH₃), 2.43 (s, 3H, CH₃), 0.94 (t, *J* = 6.8 Hz, 3H, CH₃); ¹³C NMR (400 MHz, CDCl₃) δ: 164.3, 163.8, 159.1, 157.4, 149.0, 148.2, 141.5, 141.3, 140.4, 136.1, 133.5, 130.5, 130.4, 130.1, 127.3, 126.3, 123.5, 123.0, 121.9, 66.7, 61.8, 29.0, 21.4, 13.7; IR(KBr) ν: 3245, 3182, 3065, 2988, 2867, 2167, 1836, 1647, 1654, 1565, 1488, 1332, 1225, 1158, 976, 952, 812, 721 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₃H₂₆N₄O₇ ([M+Na]⁺): 613.1694, found: 613.1696.

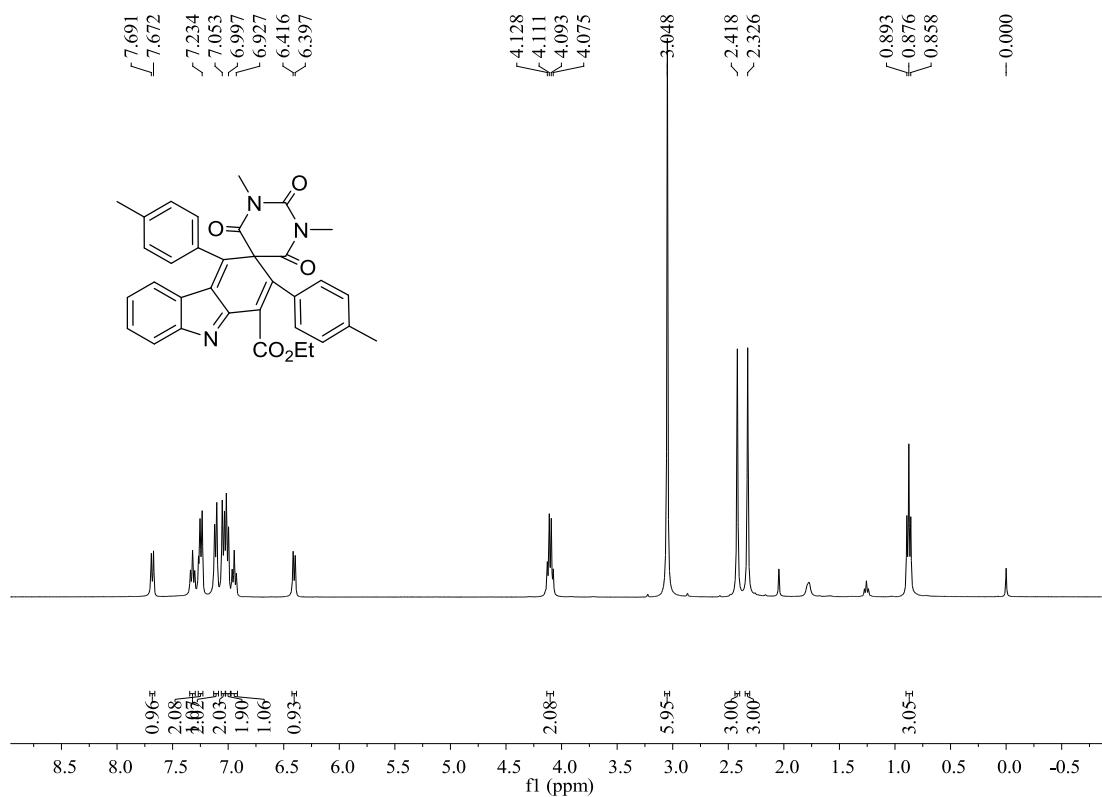


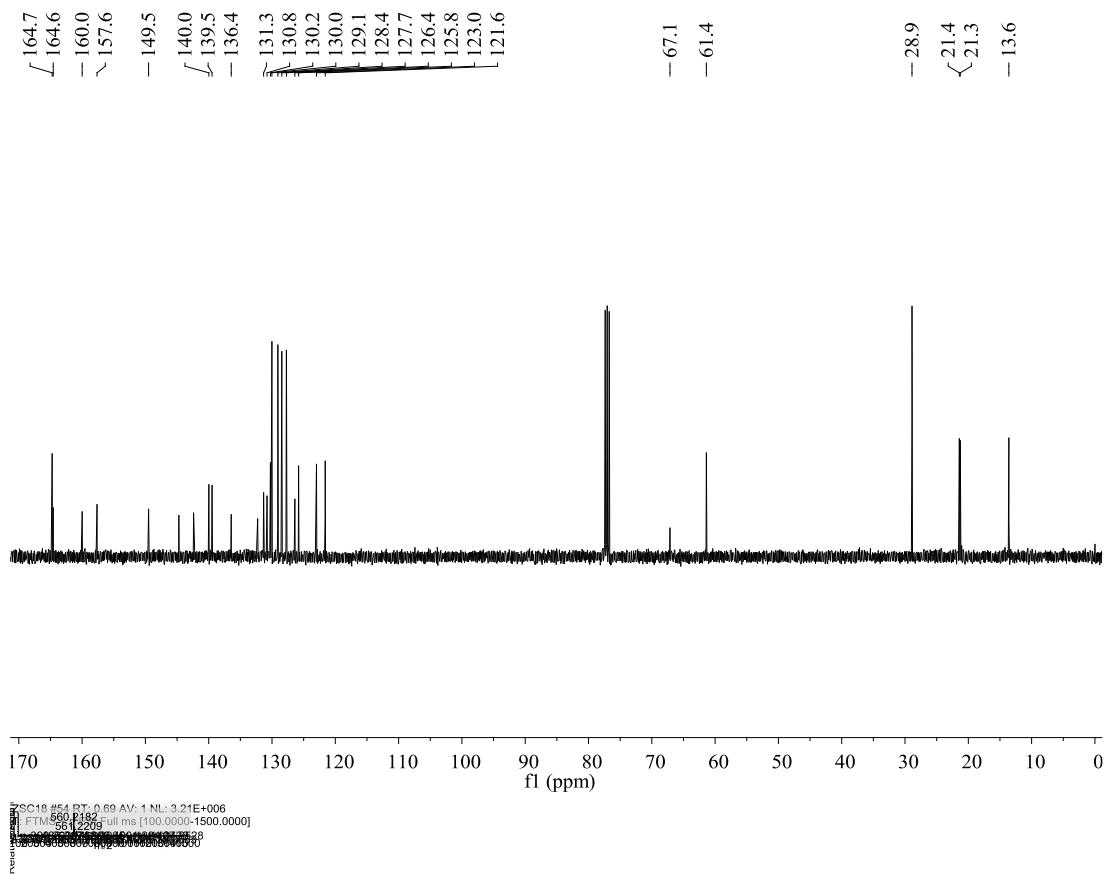


Ethyl

1',3'-dimethyl-2-(4-nitrophenyl)-2',4',6'-trioxo-4-(*p*-tolyl)-1',3',4',6'-tetrahydro-2'H-spiro[carbazole-3,5'-pyrimidine]-1-carboxylate (3c):

yellow solid, 73%, m.p. 209-213 °C; ¹H NMR (400 MHz, CDCl₃) δ: 7.68 (d, *J* = 7.6 Hz, 1H, ArH), 7.32 (t, *J* = 7.2 Hz, 1H, ArH), 7.27-7.23 (m, 2H, ArH), 7.11 (d, *J* = 8.0 Hz, 2H, ArH), 7.04 (d, *J* = 7.6 Hz, 2H, ArH), 7.00 (d, *J* = 8.0 Hz, 2H, ArH), 6.95 (t, *J* = 7.2 Hz, 1H, ArH), 6.40 (d, *J* = 7.6 Hz, 1H, ArH), 4.10 (q, *J* = 6.8 Hz, 2H, CH₂), 3.05 (s, 3H, CH₃), 3.04 (s, 3H, CH₃), 2.42 (s, 3H, CH₃), 2.33 (s, 3H, CH₃), 0.88 (t, *J* = 6.8 Hz, 3H, CH₃); ¹³C NMR (400 MHz, CDCl₃) δ: 164.7, 164.5, 159.9, 157.6, 149.4, 144.7, 142.3, 139.9, 139.4, 136.4, 132.2, 131.3, 130.7, 130.2, 130.0, 129.0, 128.4, 127.7, 126.3, 125.8, 122.9, 121.5, 67.1, 61.3, 28.8, 21.4, 21.2, 13.5; IR(KBr) ν: 3218, 3143, 3056, 2931, 2811, 2145, 1889, 1667, 1612, 1548, 1431, 1346, 1278, 1163, 1147, 982, 941, 878, 763 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₄H₂₉N₃O₅ ([M+H]⁺): 560.2180, found: 560.2182.

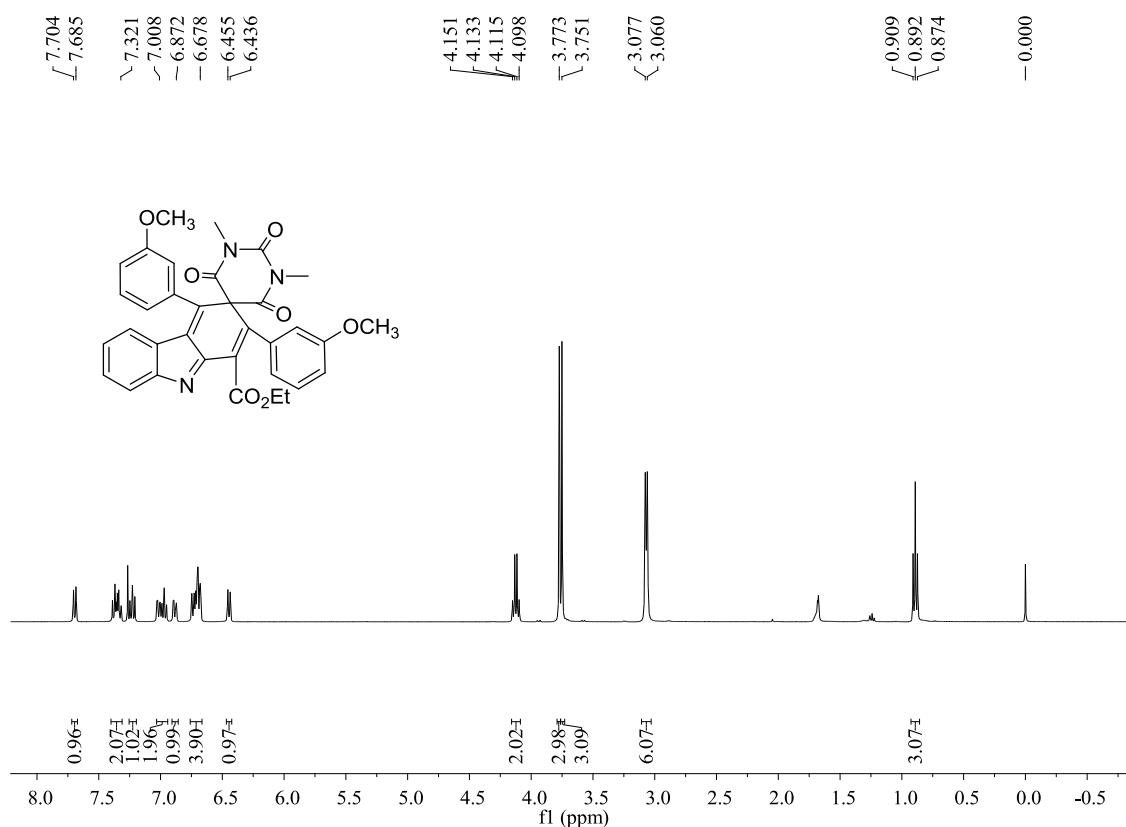


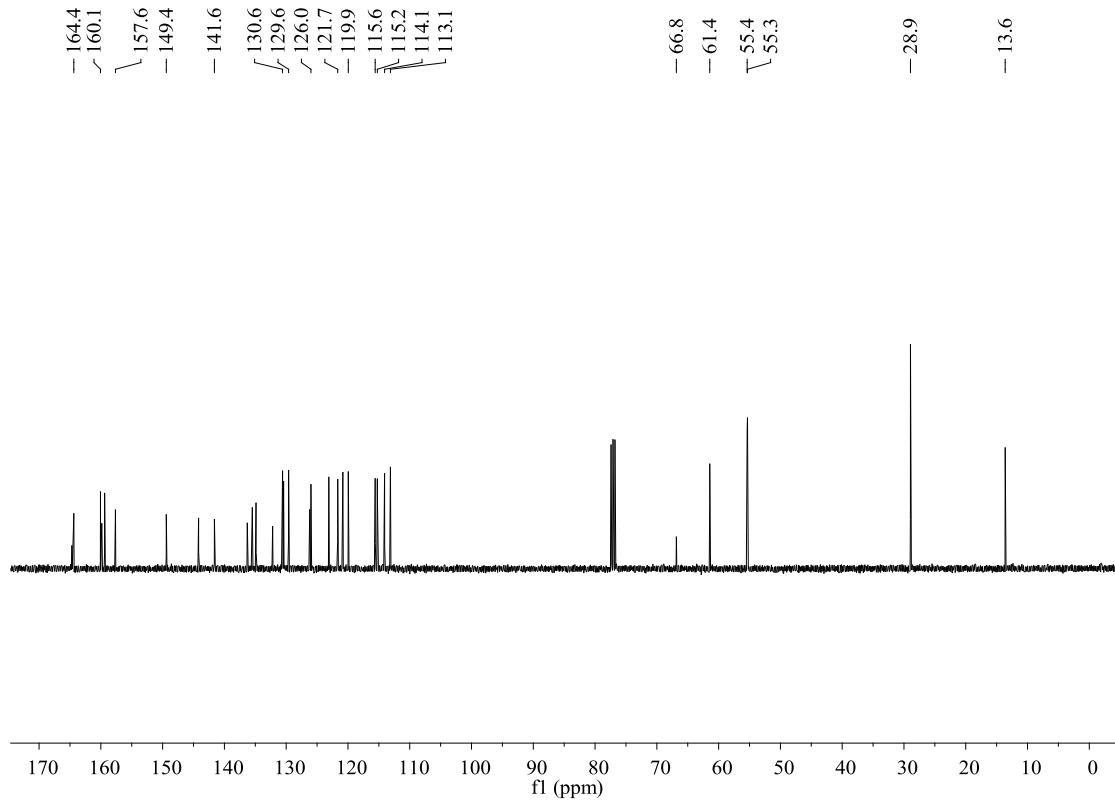


Ethy

2,4-bis(3-methoxyphenyl)-1',3'-dimethyl-2',4',6'-trioxo-1',3',4',6'-tetrahydro-2'H-spiro[carba zole-3,5'-pyrimidine]-1-carboxylate (3d):

yellow solid, 70%, m.p. 209-213 °C; ¹H NMR (400 MHz, CDCl₃) δ: 7.69 (d, *J* = 7.6 Hz, 1H, ArH), 7.39-7.32 (m, 2H, ArH), 7.23 (t, *J* = 8.0 Hz, 1H, ArH), 7.03-6.95 (m, 2H, ArH), 6.88 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.4 Hz, 1H, ArH), 6.75-6.68 (m, 4H, ArH), 6.44 (d, *J* = 7.6 Hz, 1H, ArH), 4.12 (q, *J* = 6.8 Hz, 2H, CH₂), 3.77 (s, 3H, OCH₃), 3.75 (s, 3H, OCH₃), 3.08 (s, 3H, CH₃), 3.06 (s, 3H, CH₃), 0.89 (t, *J* = 6.8 Hz, 3H, CH₃); ¹³C NMR (400 MHz, CDCl₃) δ: 164.3, 160.0, 159.3, 157.6, 149.4, 144.1, 141.6, 136.3, 135.4, 134.8, 132.1, 130.5, 130.4, 129.6, 126.1, 125.9, 123.0, 121.6, 120.8, 119.9, 115.5, 115.2, 114.0, 113.1, 66.8, 61.4, 55.3, 55.3, 28.9, 13.6; IR(KBr) v: 3217, 3142, 3064, 2917, 2833, 2165, 1849, 1631, 1611, 1548, 1433, 1346, 1271, 1164, 1131, 912, 888, 823, 764 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₄H₂₉N₃O₇ ([M+H]⁺): 592.2078, found: 592.2080.



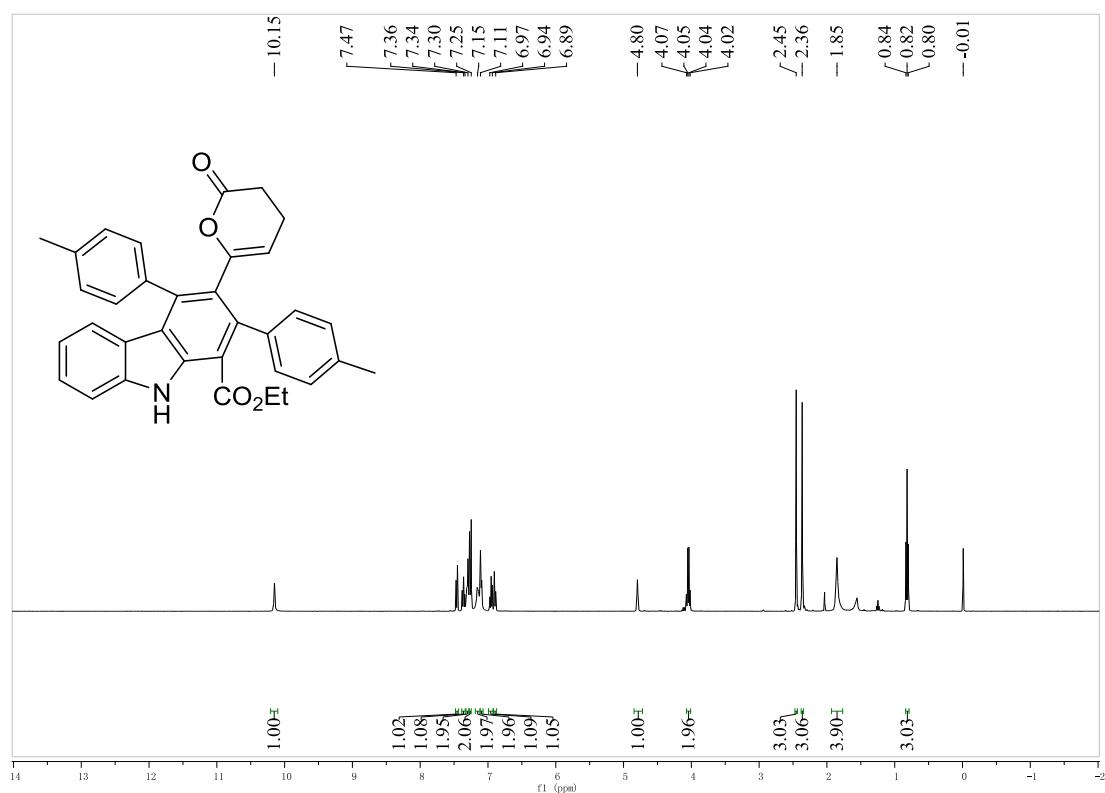


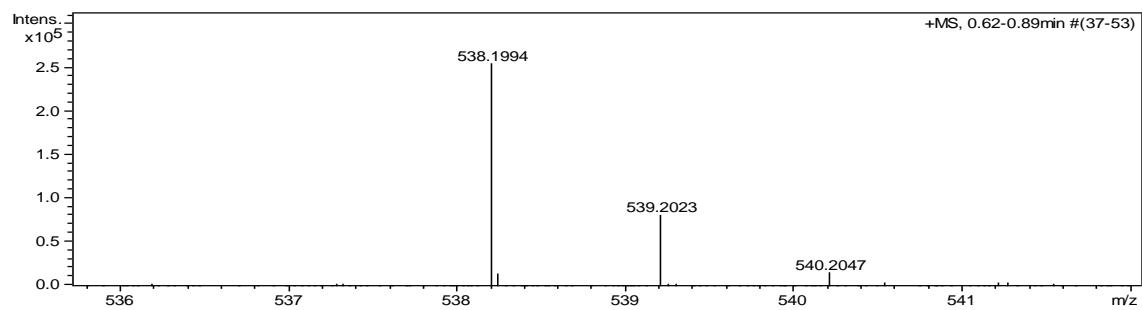
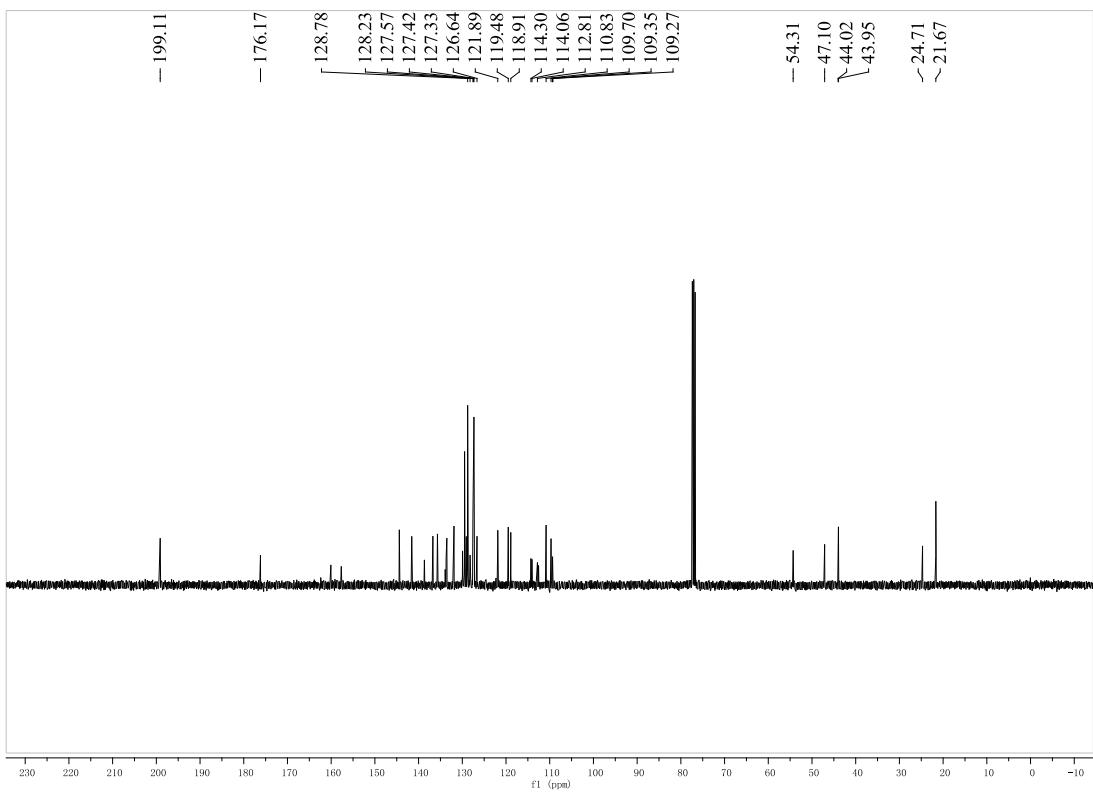
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592,2080
FTMS Full m/z[205-339] [100-1500.0000]
614,1895 199,8958
743,2080 152,1735 190
202,2080 203,2080 204,2080

6-(1-((Ethylperoxy)- λ^2 -methyl)-2,4-di-p-tolyl-9H-carbazol-3-yl)-3,4-dihydro-2H-pyran-2-one

(4a):

yellow solid, 70%, m.p. 196-199 °C; ^1H NMR (400 MHz, CDCl_3) δ : 10.15 (s, 1H, NH), 7.46 (d, J = 8.4 Hz, 1H, ArH), 7.36 (t, J = 8.4 Hz, 1H, ArH), 7.30 (d, J = 7.6 Hz, 2H, ArH), 6.95 (t, J = 8.0 Hz, 1H, ArH), 6.89 (d, J = 8.0 Hz, 1H, ArH), 4.81-4.80 (m, 1H, CH), 4.04 (q, J = 7.2 Hz, 2H, CH_2), 2.45 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 1.84-1.85 (m, 4H, CH), 0.82 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (400 MHz, CDCl_3) δ : 199.1, 176.1, 144.4, 141.5, 138.6, 138.6, 136.7, 135.6, 133.5, 131.9, 129.9, 129.4, 129.0, 128.7, 128.6, 127.5, 127.4, 127.3, 126.6, 121.8, 119.4, 118.9, 114.2, 114.0, 112.8, 112.5, 110.8, 109.6, 54.3, 47.1, 44.0, 43.9, 24.7, 21.6; IR (KBr) ν : 3411, 3251, 3054, 2973, 1864, 1755, 1682, 1617, 1567, 1456, 1387, 1356, 1278, 1171, 937, 854 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{34}\text{H}_{29}\text{NO}_4([\text{M}+\text{Na}]^+)$: 538.1989, found: 538.1994.

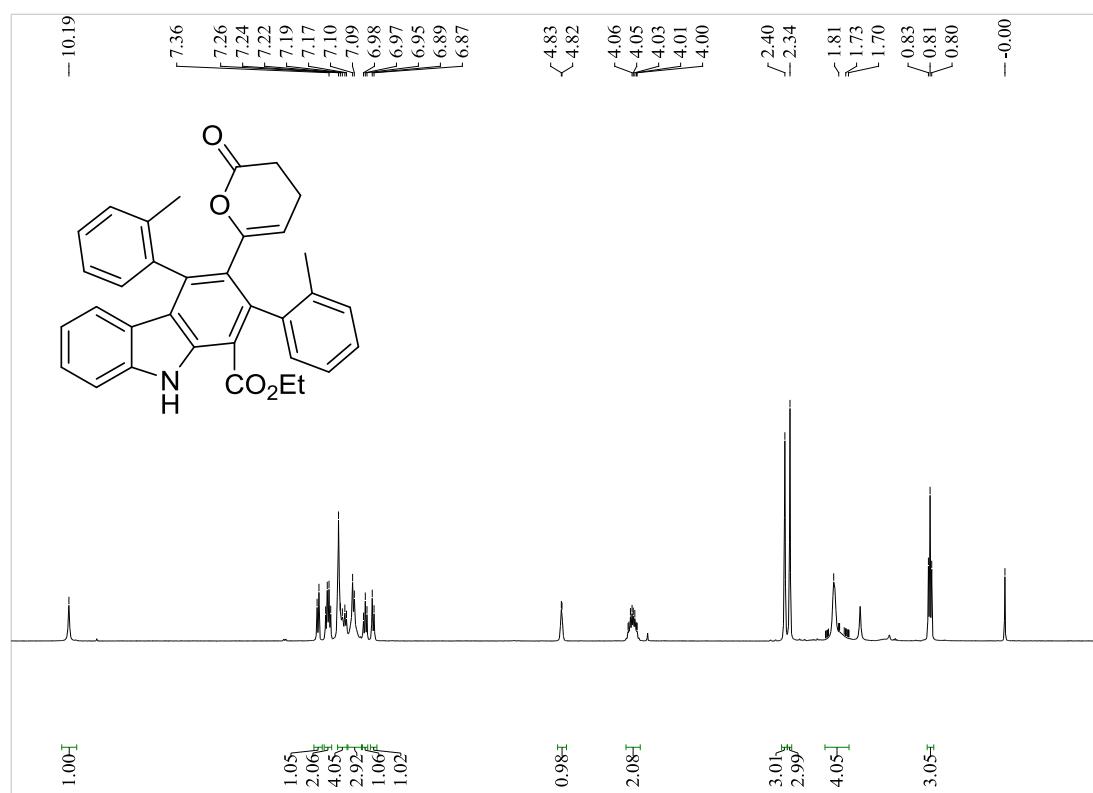


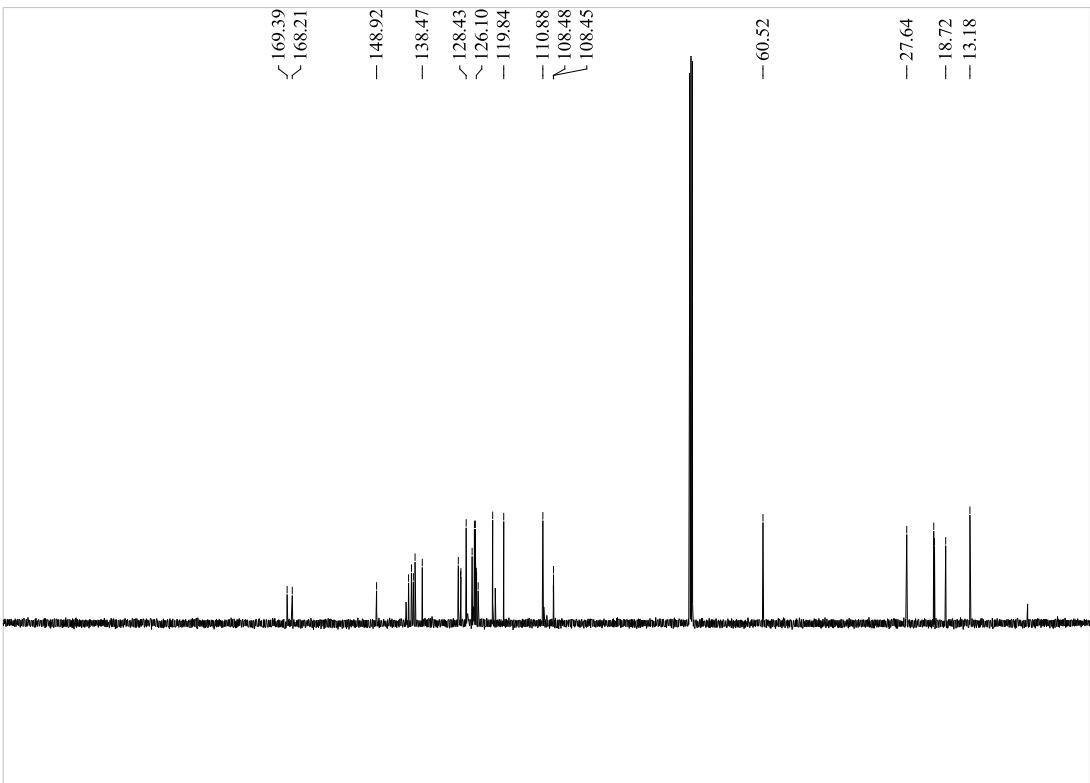


6-(1-((Ethylperoxy)- λ^2 -methyl)-2,4-di-*o*-tolyl-9*H*-carbazol-3-yl)-3,4-dihydro-2*H*-pyran-2-one

(4b):

yellow solid, 70%, m.p. 201-203 °C; ^1H NMR (400 MHz, CDCl_3) δ : 10.19 (s, 1H, NH), 7.48 (d, J = 8.4 Hz, 1H, ArH), 7.40-7.34 (m, 2H, ArH), 7.26-7.17 (m, 4H, ArH), 7.10-7.09 (m, 3H, ArH), 6.97 (t, J = 8.0 Hz, 1H, ArH), 6.88 (d, J = 8.0 Hz, 1H, ArH), 4.83 (d, J = 2.8 Hz, 1H, CH), 4.05 (q, J = 7.2 Hz, 2H, CH_2), 2.40 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 1.95-1.87 (m, 2H, CH_2), 1.81-1.70 (m, 2H, CH_2), 0.82 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (400 MHz, CDCl_3) δ : 169.3, 168.2, 148.9, 141.6, 140.9, 140.5, 140.1, 138.4, 130.2, 129.6, 129.6, 128.4, 127.0, 126.5, 126.3, 126.1, 126.0, 125.6, 122.3, 119.8, 110.8, 108.4, 108.4, 60.5, 27.6, 21.4, 21.2, 18.7, 13.1; IR (KBr) ν : 3471, 3055, 2961, 1832, 1740, 1655, 1637, 1583, 1471, 1350, 1301, 1261, 1185, 864, 768 cm^{-1} ; MS (*m/z*): HRMS (ESI) Calcd. for $\text{C}_{34}\text{H}_{29}\text{NO}_4([\text{M}+\text{Na}]^+)$: 538.1989, found: 538.1982.

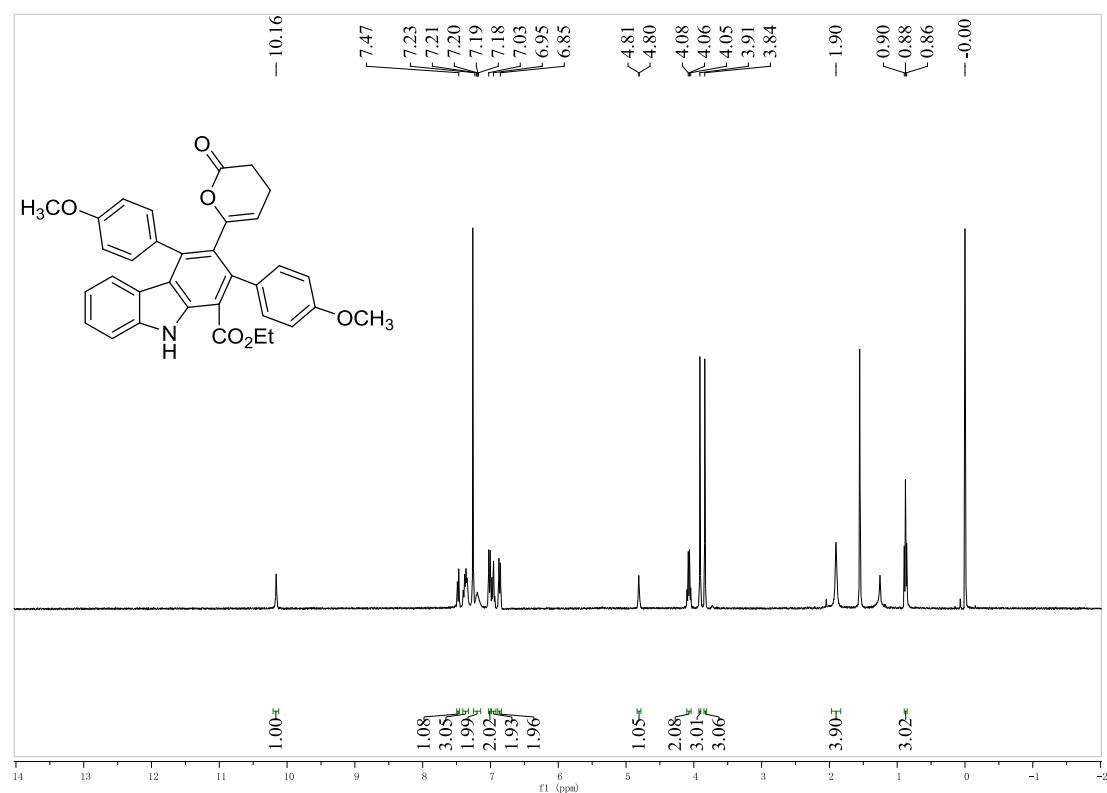


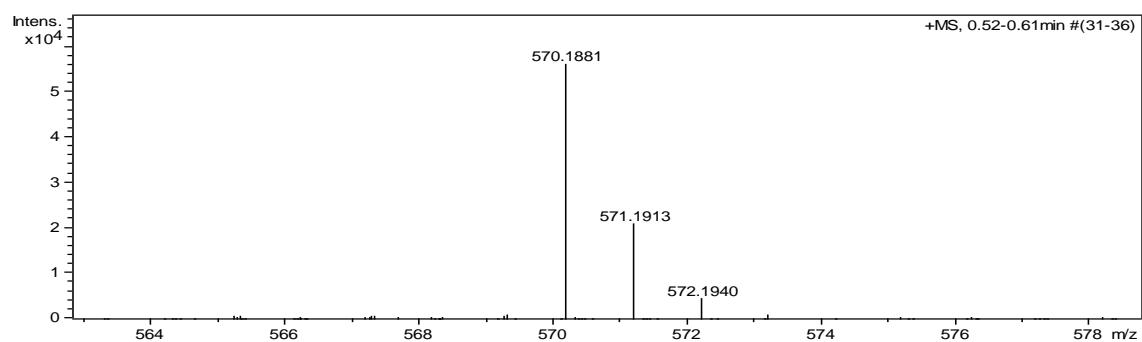
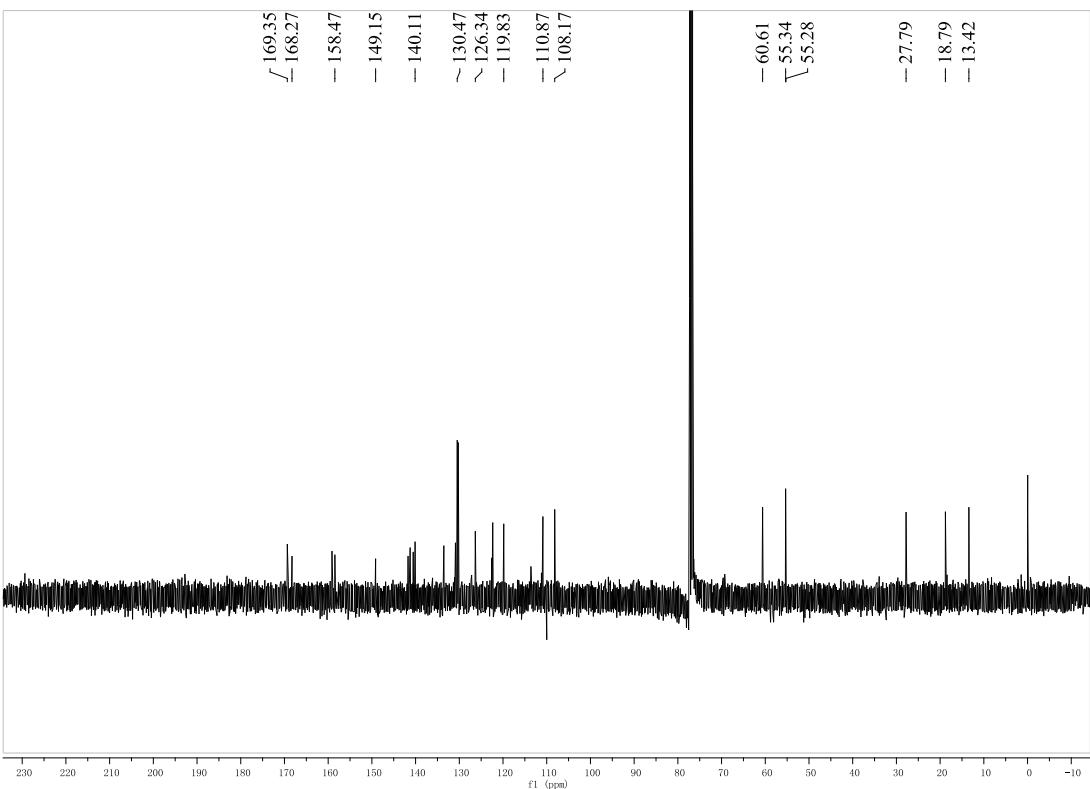


SC10_20210130104340 #53 RT: 0.67 AV: 1 NL: 1.48E+006
[1280.538, 1982.7] Full ms [100.0000-1500.0000]
[138.831, 1053.406]
[100.0000-1500.0000]
[100.0000-1500.0000]

6-(1-((Ethylperoxy)- λ^2 -methyl)-2,4-bis(4-methoxyphenyl)-9H-carbazol-3-yl)-3,4-dihydro-2H-pyran-2-one (4c):

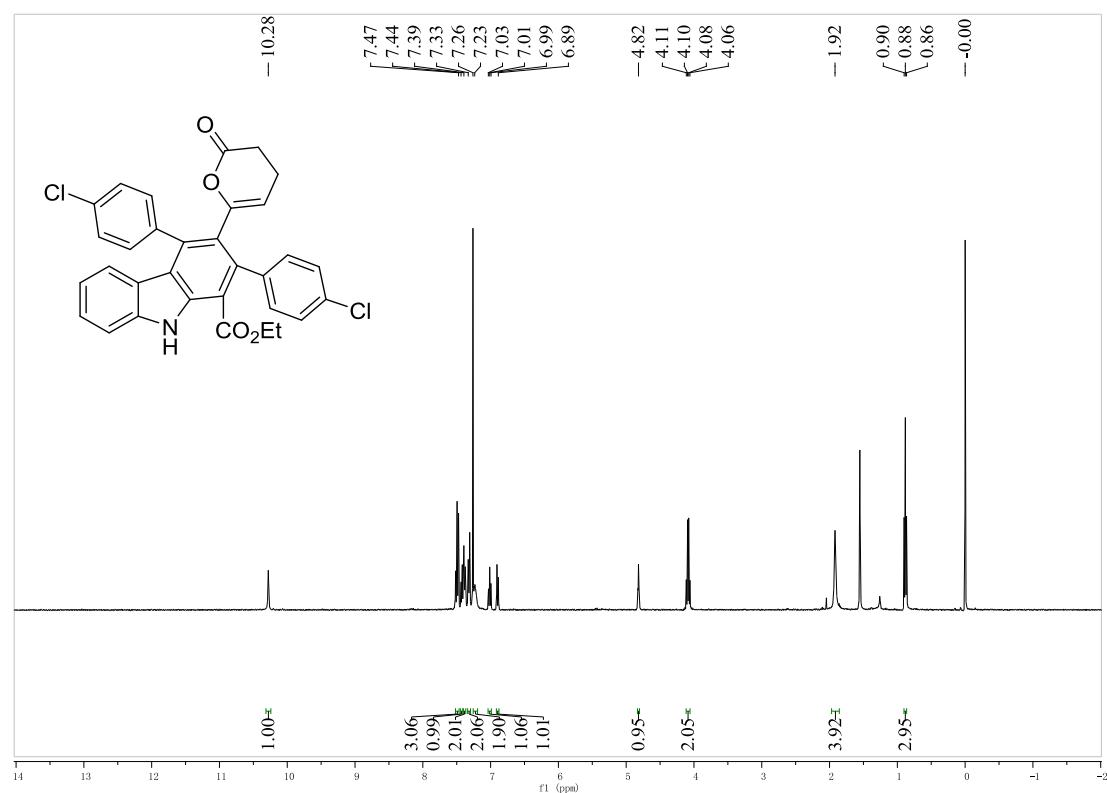
yellow solid, 61%, m.p. 206-209 °C; ^1H NMR (400 MHz, CDCl_3) δ : 10.16 (s, 1H, NH), 7.48 (d, J = 8.0 Hz, 1H, ArH), 7.40-7.34 (m, 3H, ArH), 7.23-7.17 (m, 2H, ArH), 7.01 (d, J = 8.8 Hz, 2H, ArH), 6.98-6.94 (m, 2H, ArH), 6.86 (d, J = 8.8 Hz, 2H, ArH), 4.83-4.81 (m, 1H, CH), 4.07 (q, J = 7.2 Hz, 2H, CH_2), 3.91 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 1.92-1.90 (m, 4H, CH), 0.88 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (400 MHz, CDCl_3) δ : 169.3, 168.2, 159.1, 158.4, 149.1, 141.2, 140.5, 140.1, 133.5, 130.8, 130.4, 130.2, 126.3, 122.3, 119.8, 110.8, 108.1, 60.6, 55.3, 55.2, 27.7, 18.7, 13.4; IR (KBr) ν : 3411, 3134, 2987, 1865, 1757, 1687, 1631, 1599, 1483, 1346, 1331, 1294, 1167, 887, 782 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{34}\text{H}_{29}\text{NO}_6([\text{M}+\text{Na}]^+)$: 570.1887, found: 570.1881.

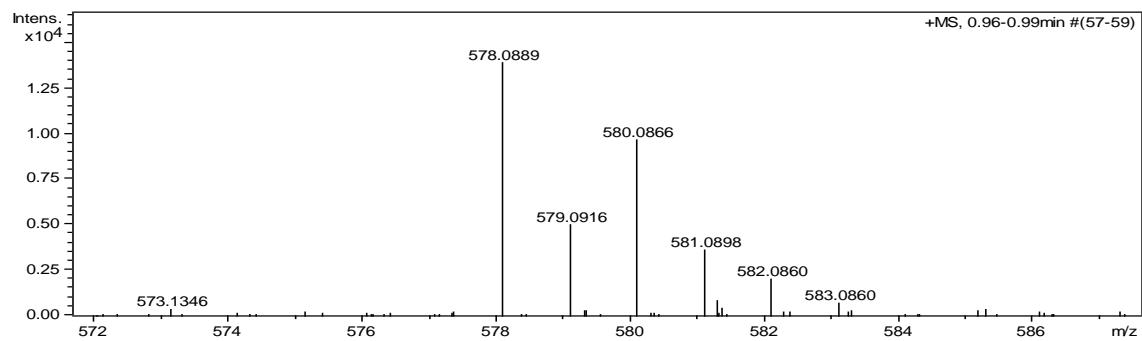
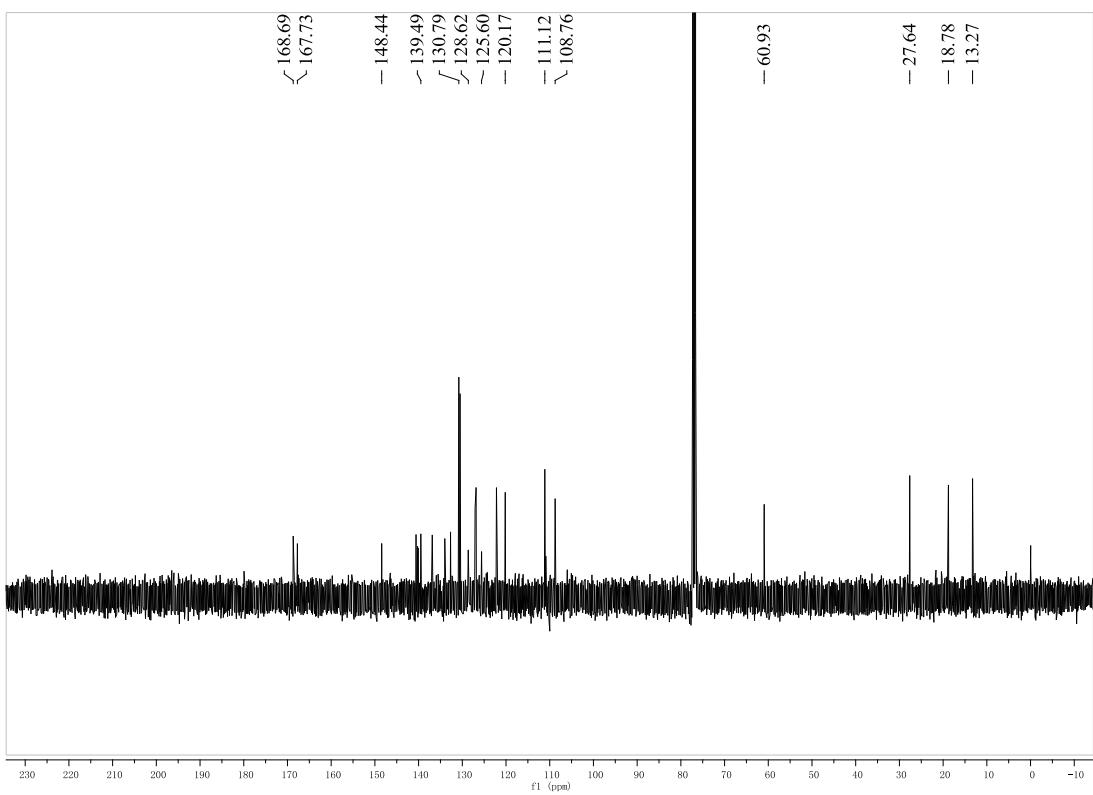




6-(2,4-bis(4-chlorophenyl)-1-((ethylperoxy)- λ^2 -methyl)-9H-carbazol-3-yl)-3,4-dihydro-2H-pyran-2-one (4d):

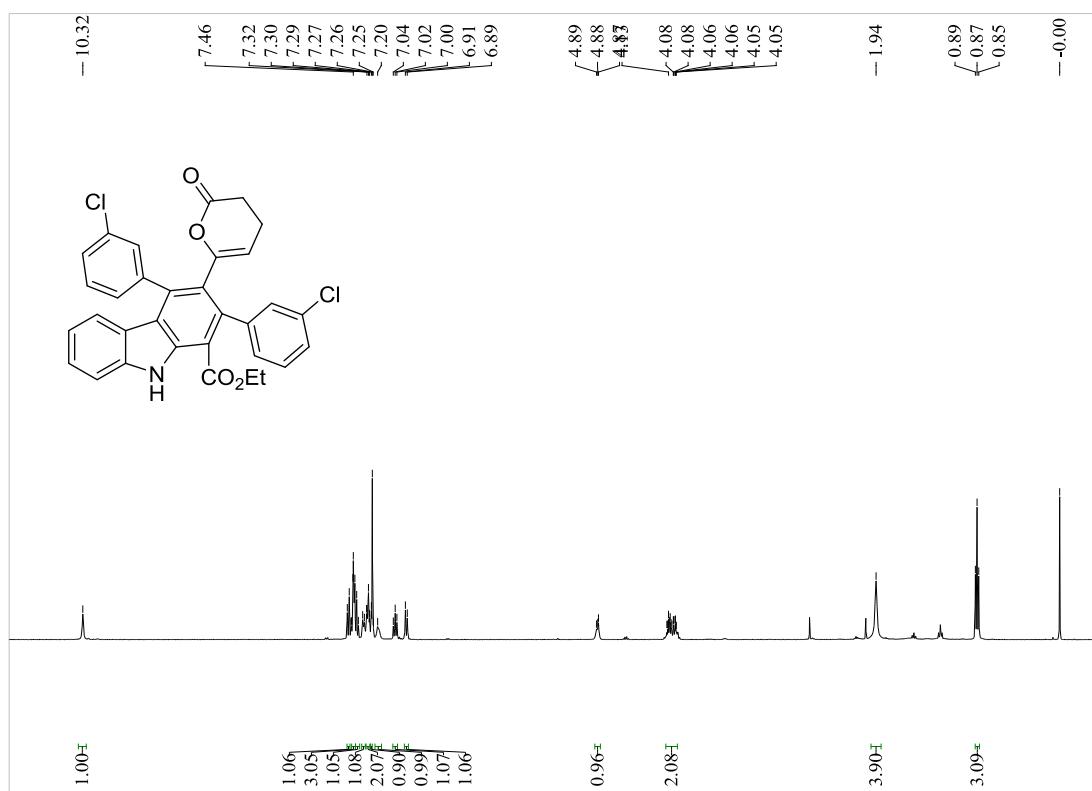
yellow solid, 54%, m.p. 217-220 °C; ^1H NMR (400 MHz, CDCl_3) δ : 10.28 (s, 1H, NH), 7.49 (t, J = 8.8 Hz, 3H, ArH), 7.42 (t, J = 7.2 Hz, 1H, ArH), 7.38 (d, J = 8.0 Hz, 2H, ArH), 7.32 (d, J = 8.4 Hz, 2H, ArH), 7.24-7.23 (m, 2H, ArH), 7.01 (t, J = 7.2 Hz, 1H, ArH), 6.89 (d, J = 8.0 Hz, 1H, ArH), 4.83-4.81 (m, 1H, CH), 4.08 (q, J = 7.2 Hz, 2H, CH_2), 1.92-1.91 (m, 4H, CH), 0.88 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (400 MHz, CDCl_3) δ : 168.6, 167.7, 148.4, 140.5, 140.5, 140.2, 140.0, 139.4, 136.8, 132.6, 130.7, 130.5, 128.6, 128.6, 127.0, 126.8, 125.5, 122.1, 122.0, 120.1, 111.1, 108.7, 60.9, 27.6, 18.7, 13.2; IR (KBr) ν : 3465, 3038, 2973, 1844, 1787, 1667, 1612, 1567, 1455, 1382, 1345, 1277, 1162, 887, 792 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{32}\text{H}_{23}\text{Cl}_2\text{NO}_4$ ([M+Na] $^+$): 578.0896, found: 578.0889.

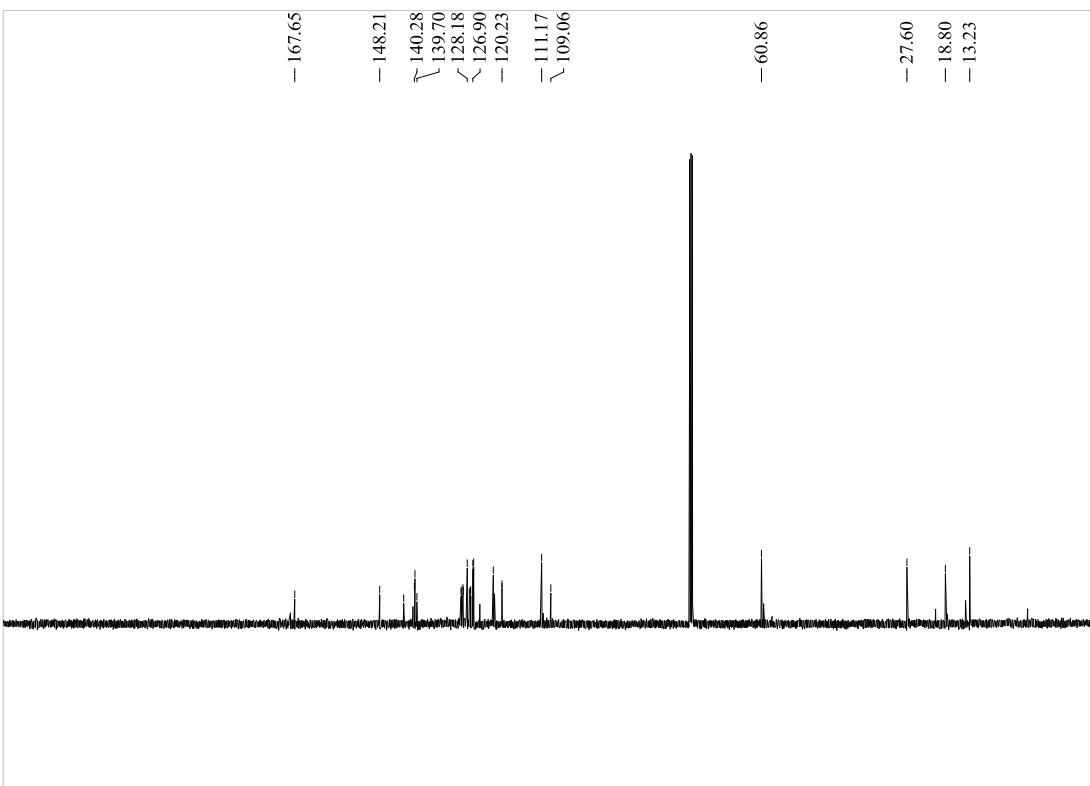




6-(2,4-bis(3-chlorophenyl)-1-((ethylperoxy)- λ^2 -methyl)-9*H*-carbazol-3-yl)-3,4-dihydro-2*H*-pyran-2-one (4e):

yellow solid, 62%, m.p. 198-200 °C; ^1H NMR (400 MHz, CDCl_3) δ : 10.32 (s, 1H, NH), 7.51 (d, J = 8.0 Hz, 1H, ArH), 7.47-7.44 (m, 3H, ArH), 7.41 (d, J = 7.2 Hz, 1H, ArH), 7.35 (d, J = 7.2 Hz, 1H, ArH), 7.32-7.29 (m, 2H, ArH), 7.27-7.26 (m, 1H, ArH), 7.20-7.19 (m, 1H, ArH), 7.02 (t, J = 7.2 Hz, 1H, ArH), 6.90 (d, J = 8.0 Hz, 1H, ArH), 4.87 (d, J = 2.8 Hz, 1H, CH), 4.09 (q, J = 7.2 Hz, 2H, CH_2), 1.98-1.93 (m, 2H, CH_2), 1.93-1.91 (m, 2H, CH_2), 0.87 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (400 MHz, CDCl_3) δ : 167.6, 148.2, 142.7, 140.2, 140.1, 139.7, 129.6, 129.4, 129.1, 129.0, 128.1, 127.6, 127.4, 127.3, 126.9, 126.7, 122.2, 120.2, 120.2, 111.1, 109.0, 60.8, 27.6, 18.7, 13.2; IR (KBr) ν : 3456, 3044, 2957, 1871, 1788, 1667, 1654, 1531, 1487, 1368, 1341, 1266, 1132, 887, 768 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{32}\text{H}_{23}\text{Cl}_2\text{N}_3\text{O}_4([\text{M}+\text{Na}]^+)$: 578.0896, found: 578.0896.

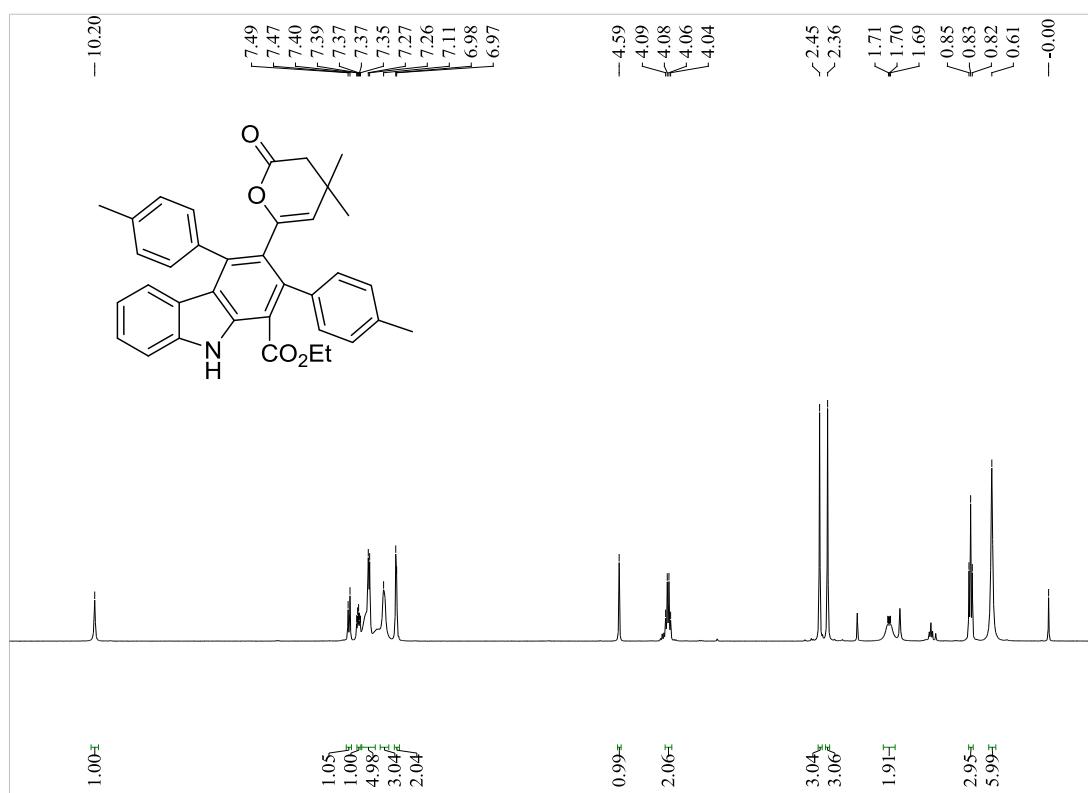


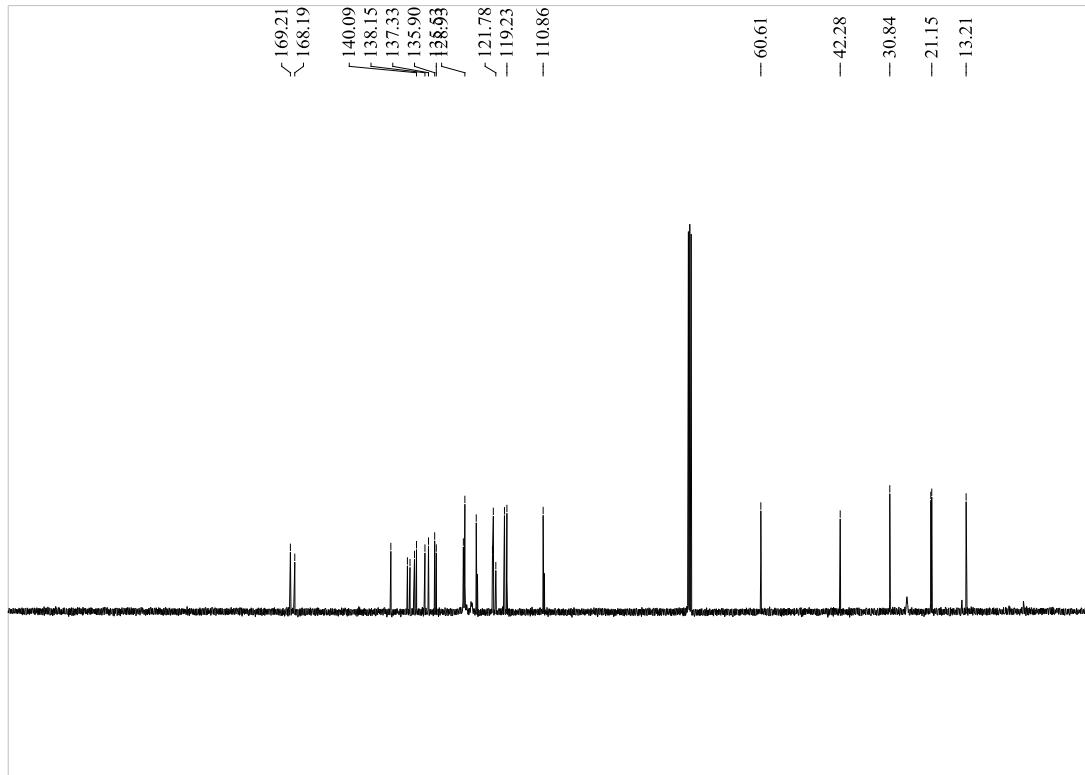


ZGC9_20210130104044 #14 RT: 0.17 AV: 1 NL: 3.35E+005
12857.1929 -SL Full.ms [100.0000-1500.0000]
12857.1929 -SL Full.ms [100.0000-1500.0000]
12857.1929 -SL Full.ms [100.0000-1500.0000]
12857.1929 -SL Full.ms [100.0000-1500.0000]

6-(1-((Ethylperoxy)- λ^2 -methyl)-2,4-di-p-tolyl-9H-carbazol-3-yl)-4,4-dimethyl-3,4-dihydro-2H-pyran-2-one (4f):

yellow solid, 63%, m.p. 200-203 °C; ^1H NMR (400 MHz, CDCl_3) δ : 10.20 (s, 1H, NH), 7.47 (d, J = 8.0 Hz, 1H, ArH), 7.40-7.36 (m, 1H, ArH), 7.27-7.26 (m, 5H, ArH), 7.11-7.10 (m, 3H, ArH), 6.97 (d, J = 8.0 Hz, 2H, ArH), 4.59 (s, 1H, CH), 4.06 (q, J = 7.2 Hz, 2H, CH_2), 2.45 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 1.72-1.70 (m, 1H, CH), 1.69-1.68 (m, 1H, CH), 0.83 (t, J = 7.2 Hz, 3H, CH_3), 0.61 (s, 3H, CH_3), 0.60 (s, 3H, CH_3); ^{13}C NMR (400 MHz, CDCl_3) δ : 169.2, 168.1, 146.0, 142.1, 141.5, 140.5, 140.0, 138.1, 137.3, 135.9, 135.5, 129.2, 128.9, 126.3, 122.5, 122.3, 121.7, 119.7, 119.2, 110.8, 60.6, 42.2, 30.8, 21.3, 21.1, 13.2; IR (KBr) ν : 3431, 3055, 2918, 1865, 1753, 1667, 1653, 1587, 1472, 1350, 1368, 1250, 1138, 862, 755 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{36}\text{H}_{33}\text{NO}_4$ ([M+Na] $^+$): 566.2302, found: 566.2297.





6-(2,4-Bis(3-chlorophenyl)-1-((ethylperoxy)-λ²-methyl)-9H-carbazol-3-yl)-4,4-dimethyl-3,4-di hydro-2H-pyran-2-one (4g):

yellow solid, 51%, m.p. 205-207 °C; ¹H NMR (400 MHz, CDCl₃) δ: 10.35 (s, 1H, NH), 7.51 (d, *J* = 8.0 Hz, 1H, ArH), 7.47-7.36 (m, 6H, ArH), 7.30 (d, *J* = 8.0 Hz, 2H, ArH), 7.19-7.17 (m, 1H, ArH), 7.05-6.98 (m, 2H, ArH), 4.66 (s, 1H, CH), 4.09 (q, *J* = 7.2 Hz, 2H, CH₂), 1.82-1.76 (m, 1H, CH), 1.75-1.74 (m, 1H, CH), 0.88 (t, *J* = 7.2 Hz, 3H, CH₃), 0.71 (s, 3H, CH₃), 0.64 (s, 3H, CH₃); ¹³C NMR (400 MHz, CDCl₃) δ: 168.3, 167.5, 142.7, 140.6, 140.3, 140.1, 140.0, 139.6, 129.7, 129.3, 128.0, 127.9, 127.6, 127.4, 126.9, 126.5, 125.2, 122.2, 121.9, 120.2, 120.0, 111.2, 60.8, 42.2, 31.0, 13.2; IR (KBr) ν: 3445, 3017, 2955, 1871, 1764, 1682, 1638, 1538, 1447, 1381, 1322, 1286, 1131, 855, 763 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₄H₂₇Cl₂NO₄([M+Na]⁺): 606.1209, found: 606.1202.

