

Supporting information for

Electrocatalytic Stereoselective Transformation of Aldehydes and Two Molecules of Pyrazolin-5-ones into (*R,*R**)-Bis(spiro-2,4-dihydro-3*H*-pyrazol-3-one)cyclopropanes**

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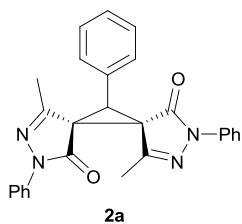
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1. General Information

All melting points were measured with a Gallenkamp melting point apparatus and are uncorrected. ¹H and ¹³C NMR spectra were recorded with a Bruker Avance II-300 spectrometer at ambient temperature in CDCl₃ solutions. Chemical shifts values are given in δ scale relative to Me₄Si. IR spectra were registered with a Bruker ALPHA-T FT-IR spectrometer in KBr pellets. High-resolution mass spectrometry (HRMS) (electrospray ionisation, ESI) was measured on a Bruker micrOTOF II instrument; external or internal calibration was done with an Electrospray Calibrant Solution (Fluka). Mass-spectra (EI = 70 eV) were obtained directly with a Finnigan MAT INCOS 50 spectrometer. All starting materials were obtained from commercial sources and used without purification.

2. Typical electrolysis procedure

A solution of 3-methyl-1-phenyl-2-pyrazoline-5-one **4** (10 mmol), aldehyde **3** (5 mmol) and sodium iodide (0.45 g, 3 mmol) in 20 mL of methanol was electrolyzed in an undivided cell equipped with a magnetic stirrer, a graphite anode and an iron cathode at 20 °C under a constant current density of 100 mA cm⁻² (*I* = 500 mA, electrodes square 5 cm²) until 2.5 F mol⁻¹ of electricity was passed (process time 40 min). After the electrolysis was finished, the reaction mixture was gently concentrated to one fifth of initial volume (*ca.* 4 mL) to crystallize the solid product, which was then filtered out, rinsed with an ice-cold methanol (2 × 2 mL), and dried under reduced pressure.



(5*R,6*R**) 4,10-Dimethyl-2,8,11-triphenyl-2,3,8,9-tetraazadispiro**

[4.0.4.1]undeca-3,9-diene-1,7-dione (2a) (known compound, see: S. Devi,

A. Nayak and A. S. Mitra, *J. Indian Chem. Soc.*, 1984, **61**, 640): white solid;

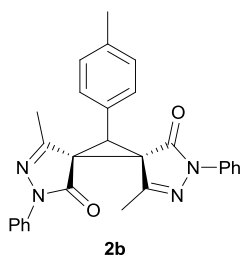
yield 1.63 g (75%); mp 166–168 °C; ¹H NMR (300 MHz, CDCl₃): 2.10 (s,

3 H, CH₃), 2.45 (s, 3 H, CH₃), 4.45 (s, 1 H, CH), 7.20–7.27 (m, 4 H, Ph),

7.38–7.49 (m, 7 H, Ph), 7.90 (d, *J* = 8.1 Hz, 2 H, Ph), 7.95 (d, *J* = 8.1 Hz, 2 H, Ph); ¹³C NMR (75

MHz, CDCl₃): 18.2, 20.1, 42.9, 50.1, 51.1, 118.8 (4C), 125.3, 125.4, 127.8, 128.4 (2C), 128.6,

128.7 (2C), 128.8 (2C), 129.7 (2C), 137.6, 137.7, 155.1, 155.8, 165.4, 167.5.



(5*R,6*R**) 11-(4-Methylphenyl)-4,10-dimethyl-2,8-diphenyl-2,3,8,9-**

tetraazadispiro-[4.0.4.1]undeca-3,9-diene-1,7-dione (2b) (known

compound, see: M. N. Elinson, A. N. Vereshchagin, E. O. Tretyakova, I. S.

Bushmarinov and G. I. Nikishin *Synthesis*, 2011, 3015): white solid; yield:

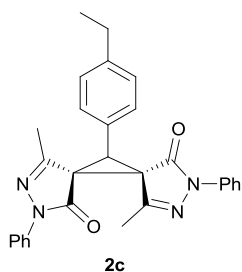
1.70 g (76%); mp 135–137 °C; ¹H NMR (300 MHz, CDCl₃): 2.10 (s, 3 H,

CH₃), 2.38 (s, 3 H, CH₃), 2.54 (s, 3 H, CH₃), 4.40 (s, 1 H, CH), 7.08–7.48

(m, 10 H, Ph), 7.90 (d, *J* = 8.6 Hz, 2 H, Ph), 7.94 (d, *J* = 8.6 Hz, 2 H, Ph); ¹³C NMR (75 MHz,

CDCl₃): 18.2, 20.2, 21.2, 42.9, 50.2, 51.2, 118.8 (4C), 124.8, 125.2, 125.4, 128.7 (2C), 128.8 (2C),

129.2 (2C), 129.6 (2C), 137.7, 137.8, 138.4, 155.2, 155.9, 165.4, 167.6.



(5*R,6*R**) 11-(4-Ethylphenyl)-4,10-dimethyl-2,8-diphenyl-2,3,8,9-**

tetraazadispiro-[4.0.4.1]undeca-3,9-diene-1,7-dione (2c) (known

compound, see: M. N. Elinson, A. N. Vereshchagin, E. O. Tretyakova, I. S.

Bushmarinov and G. I. Nikishin *Synthesis*, 2011, 3015): white solid; yield:

1.85 g (80%); mp 146–148 °C; ¹H NMR (300 MHz, CDCl₃): 1.27 (t, *J* =

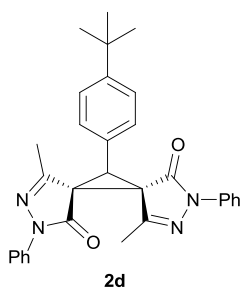
7.5 Hz, 3 H, CH₃), 2.12 (s, 3 H, CH₃), 2.55 (s, 3 H, CH₃), 2.70 (q, *J* = 7.5 Hz,

2 H, CH₂) 4.43 (s, 1 H, CH), 7.13 (d, *J* = 7.8 Hz, 2 H, Ph), 7.20–7.50 (m, 8 H, Ph), 7.90 (d, *J* =

8.4 Hz, 2 H, Ph), 7.95 (d, *J* = 8.4 Hz, 2 H, Ph); ¹³C NMR (75 MHz, CDCl₃): 15.1, 18.2, 20.1, 28.4,

42.9, 50.2, 51.3, 118.8 (4C), 125.0, 125.2, 125.3, 127.9 (2C), 128.7 (2C), 128.8 (2C), 129.7 (2C),

137.7, 137.8, 144.7, 155.2, 155.8, 165.5, 167.6



(5*R,6*R**) 11-(4-*t*-Butylphenyl)-4,10-dimethyl-2,8-diphenyl-2,3,8,9-**

tetraazadispiro-[4.0.4.1]undeca-3,9-diene-1,7-dione (2d): white solid;

yield: 1.91 g (78%); mp 164–166 °C. ¹H NMR (300 MHz, CDCl₃): 1.32 (s,

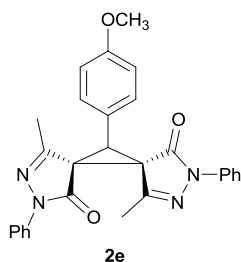
9H, *t*-Bu), 2.08 (s, 3H, CH₃), 2.53 (s, 3H, CH₃), 4.39 (s, 1H, CH), 7.17–7.25

(m, 4H, Ar), 7.37–7.46 (m, 6H, Ar), 7.87–7.94 (m, 4H, Ar). ¹³C NMR (75

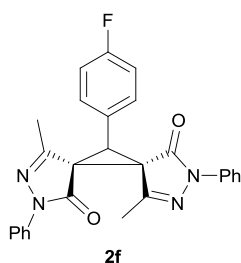
MHz, CDCl₃): 18.4, 20.3, 31.4 (3C), 34.8, 42.9, 50.4, 51.6, 119.1 (2C), 119.2

(2C), 124.9, 125.4, 125.5, 125.6 (2C), 128.9 (2C), 129.0 (2C), 129.6, 137.8, 137.9, 151.9, 155.5,

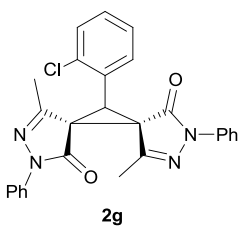
156.1, 165.7, 167.9. IR (KBr): $\nu = 2963, 2866, 1707, 1499, 1394, 1363, 1275, 1129, 754, 687 \text{ cm}^{-1}$. MS, m/z , %: 490 (M^+ , 21), 357 (10), 318 (46), 261 (14), 232 (5), 185 (27), 155 (20), 128 (24), 91 (47), 77 (100). HRMS (ESI): 513.2249 [$M+Na$] $^+$, calcd for $C_{31}H_{30}N_4NaO_2$: 513.2261.



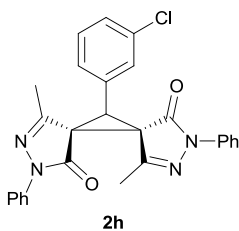
(5R*,6R*) 11-(4-Methoxyphenyl)-4,10-dimethyl-2,8-diphenyl-2,3,8,9-tetraazadi-spiro[4.0.4.1]undeca-3,9-diene-1,7-dione (2e) (known compound, see: M. N. Elinson, A. N. Vereshchagin, E. O. Tretyakova, I. S. Bushmarinov and G. I. Nikishin *Synthesis*, 2011, 3015): white solid; yield: 1.51 g (65%); mp 145–147 °C; 1H NMR (300 MHz, $CDCl_3$): 2.10 (s, 3 H, CH_3), 2.52 (s, 3 H, CH_3), 2.60 (s, 3 H, CH_3), 4.10 (s, 1 H, CH), 6.87 (d, $J = 8.0$ Hz, 1 H, Ph), 6.97 (t, $J = 7.2$ Hz, 1 H, Ph), 7.10–7.50 (m, 8 H, Ph), 7.86 (d, $J = 7.8$ Hz, 2 H, Ph), 7.94 (d, $J = 7.8$ Hz, 2 H, Ph).



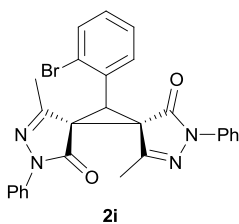
(5R*,6R*) 11-(4-Fluorophenyl)-4,10-dimethyl-2,8-diphenyl-2,3,8,9-tetraazadispiro-[4.0.4.1]undeca-3,9-diene-1,7-dione (2f): white solid; yield: 1.54 g (68%); mp 147–149 °C. 1H NMR (300 MHz, $CDCl_3$): 2.11 (s, 3H, CH_3), 2.54 (s, 3H, CH_3), 4.40 (s, 1H, CH), 7.06–7.12 (m, 2H, Ar), 7.19–7.28 (m, 4H, Ar), 7.40–7.48 (m, 4H, Ar), 7.88–7.95 (m, 4H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): 18.3, 20.2, 42.1, 50.1, 51.2, 115.7 (d, $^2J_{C-F} = 21.9$ Hz, 2C), 118.9 (4C), 123.8 (d, $^4J_{C-F} = 3.3$ Hz, 1C), 125.4, 125.5, 128.8 (2C), 128.9 (2C), 131.6 (d, $^3J_{C-F} = 8.3$ Hz, 2C), 137.7, 137.8, 154.8, 155.8, 162.7 (d, $^1J_{C-F} = 249$ Hz, 1C), 165.4, 167.5. IR (KBr): $\nu = 2985, 1721, 1711, 1597, 1513, 1500, 1367, 1293, 1130, 759 \text{ cm}^{-1}$. MS, m/z , %: 452 (M^+ , 6), 319 (6), 280 (12), 223 (3), 185 (23), 146 (20), 128 (17), 91 (33), 77 (100), 51 (25). HRMS (ESI): 475.1531 [$M+Na$] $^+$, calcd for $C_{27}H_{21}FN_4O_2$: 475.1541.



(5R*,6R*) 11-(2-Chlorophenyl)-4,10-dimethyl-2,8-diphenyl-2,3,8,9-tetraazadispiro-[4.0.4.1]undeca-3,9-diene-1,7-dione (2g) (known compound, see: M. N. Elinson, A. N. Vereshchagin, E. O. Tretyakova, I. S. Bushmarinov and G. I. Nikishin *Synthesis*, 2011, 3015): yellowish solid; yield: 1.76 g (75%); mp 169–171 °C; 1H NMR (300 MHz, $CDCl_3$): 2.15 (s, 3 H, CH_3), 2.55 (s, 3 H, CH_3), 4.25 (s, 1 H, CH), 7.20–7.50 (m, 10 H, Ph), 7.85 (d, $J = 8.1$ Hz, 2 H, Ph), 7.94 (d, $J = 8.1$ Hz, 2 H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): 18.1, 20.1, 41.6, 50.3, 50.7, 118.9 (2C), 119.1 (2C), 125.4, 125.5, 126.5 (2C), 128.8 (2C), 128.9 (2C), 129.7, 130.0, 131.7, 135.1, 137.7, 137.8, 154.8, 155.6, 165.4, 167.3.

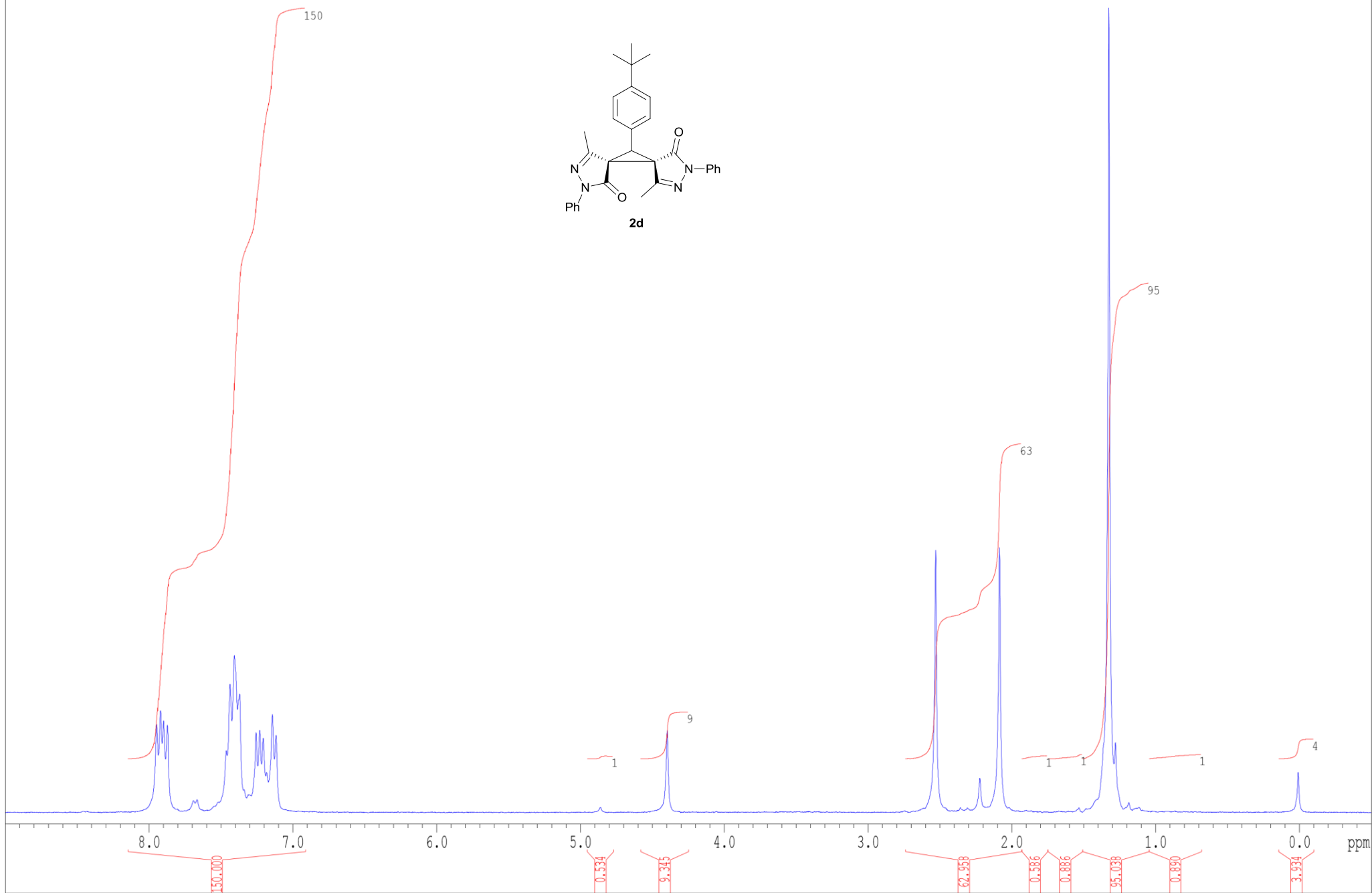
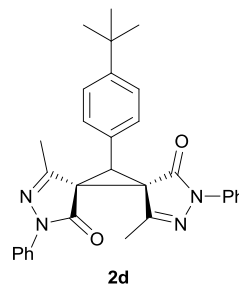


(5R*,6R*) 11-(3-Chlorophenyl)-4,10-dimethyl-2,8-diphenyl-2,3,8,9-tetraazadispiro-[4.0.4.1]undeca-3,9-diene-1,7-dione (2h) (known compound, see: M. N. Elinson, A. N. Vereshchagin, E. O. Tretyakova, I. S. Bushmarinov and G. I. Nikishin *Synthesis*, 2011, 3015): yellowish solid; yield: 1.64 g (70%); mp 157–158 °C; ¹H NMR (300 MHz, CDCl₃): 2.13 (s, 3 H, CH₃), 2.52 (s, 3 H, CH₃), 4.39 (s, 1 H, CH), 7.10 (d, *J* = 6.9 Hz, 1 H, Ph), 7.20–7.45 (m, 9 H, Ph), 7.89 (d, *J* = 7.8 Hz, 2 H, Ph), 7.95 (d, *J* = 7.8 Hz, 2 H, Ph); ¹³C NMR (75 MHz, CDCl₃): 18.2, 20.1, 42.0, 49.8, 50.8, 118.8 (4C), 125.4, 125.5, 128.0, 128.8 (4C), 128.9, 129.7, 129.8, 130.0, 134.3, 137.6, 137.7, 154.5, 155.5, 165.1, 167.2.



(5R*,6R*) 11-(2-Bromophenyl)-4,10-dimethyl-2,8-diphenyl-2,3,8,9-tetraazadispiro-[4.0.4.1]undeca-3,9-diene-1,7-dione (2i) (known compound, see: M. N. Elinson, A. N. Vereshchagin, E. O. Tretyakova, I. S. Bushmarinov and G. I. Nikishin *Synthesis*, 2011, 3015): white solid; yield: 1.95 g (76%); mp 154–155°C; ¹H NMR (300 MHz, CDCl₃): 2.13 (s, 3 H, CH₃), 2.51 (s, 3 H, CH₃), 4.38 (s, 1 H, CH), 7.13–7.53 (m, 10 H, Ph), 7.87 (d, *J* = 7.9 Hz, 2 H, Ph), 7.93 (d, *J* = 7.9 Hz, 2 H, Ph);

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167.86
165.74

156.13
155.47
151.90

137.93
137.88
129.61
129.04
128.97
125.61
125.52
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119.05

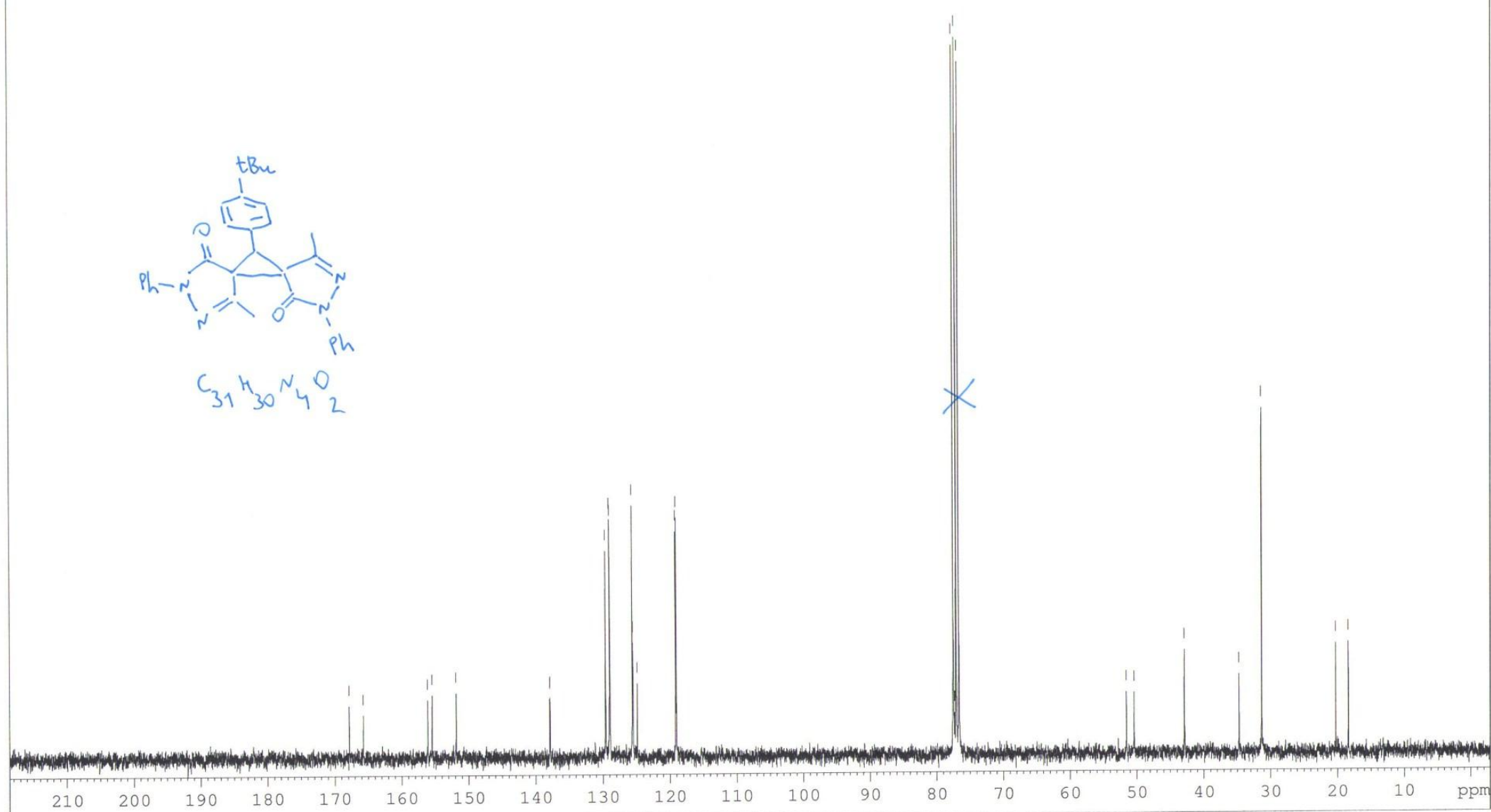
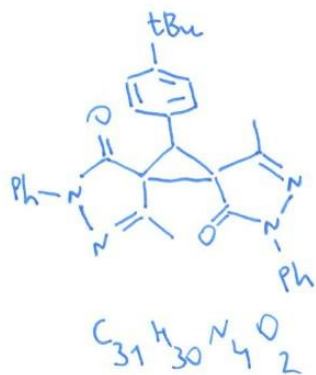
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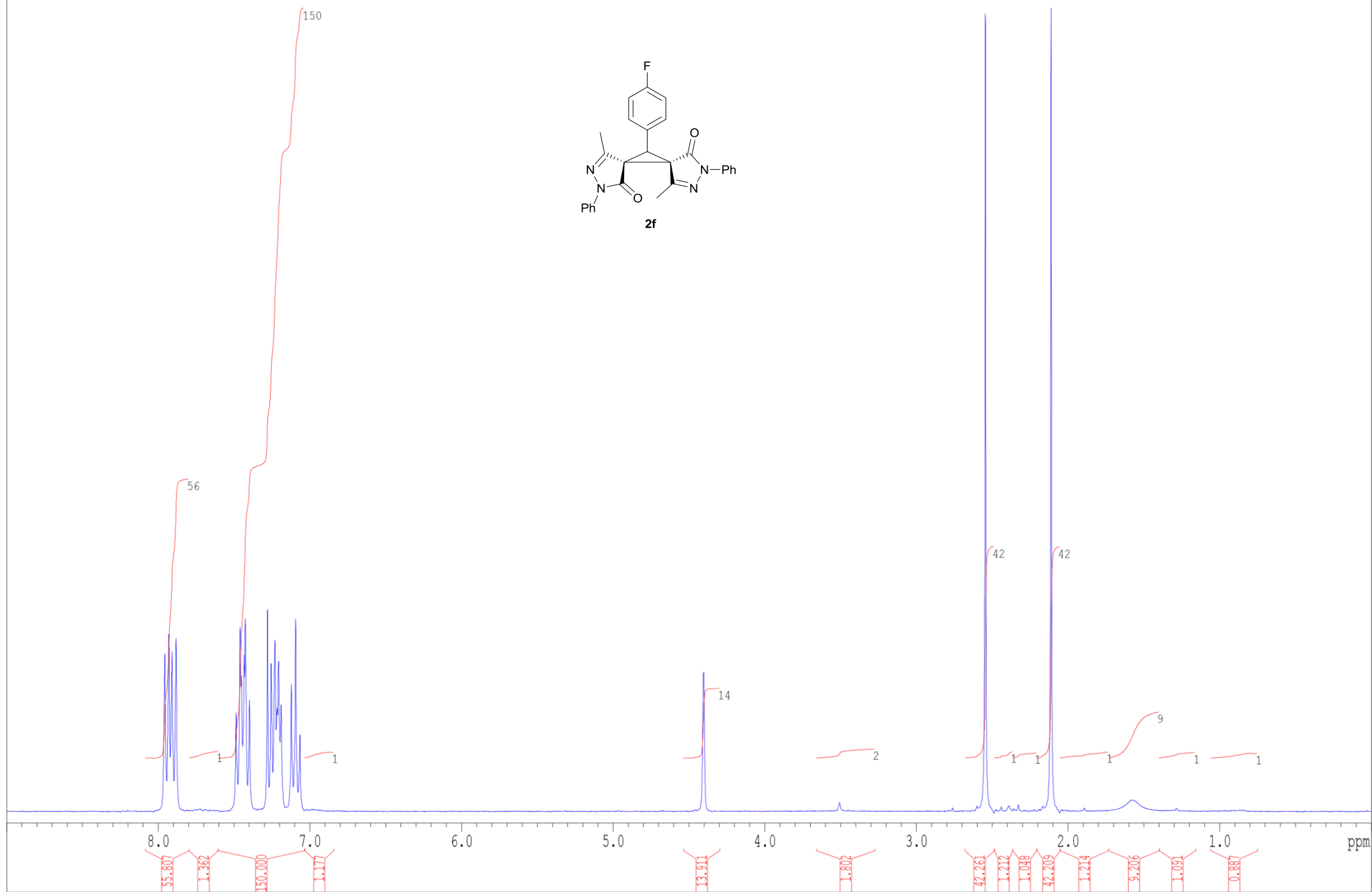
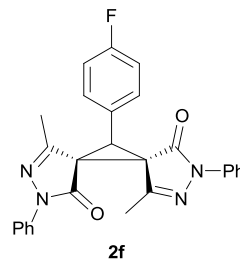
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