A General and Efficient Approach to 2*H*-Indazoles and 1*H*-Pyrazoles Through Copper-catalyzed Intramolecular N-N Bond Formation under Mild Conditions

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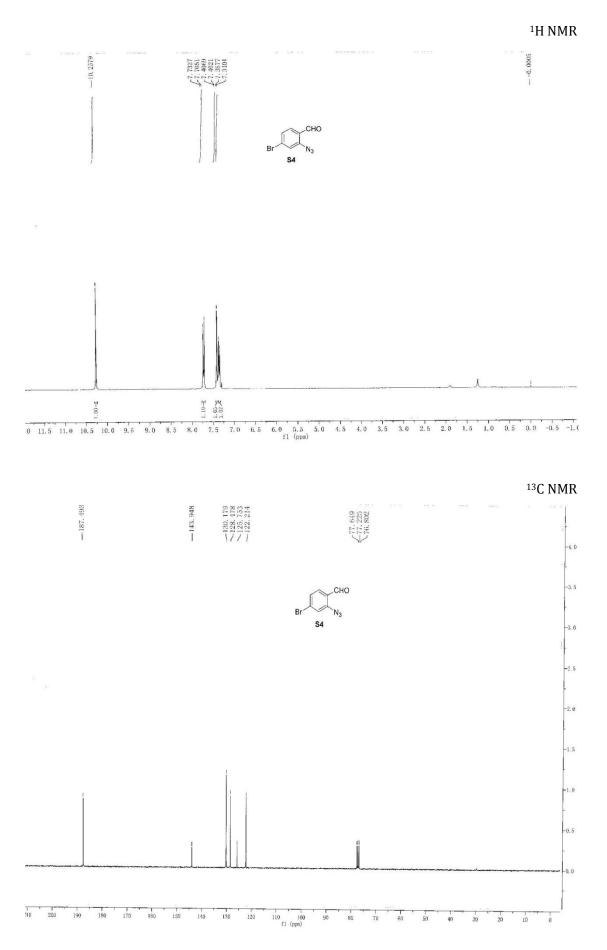
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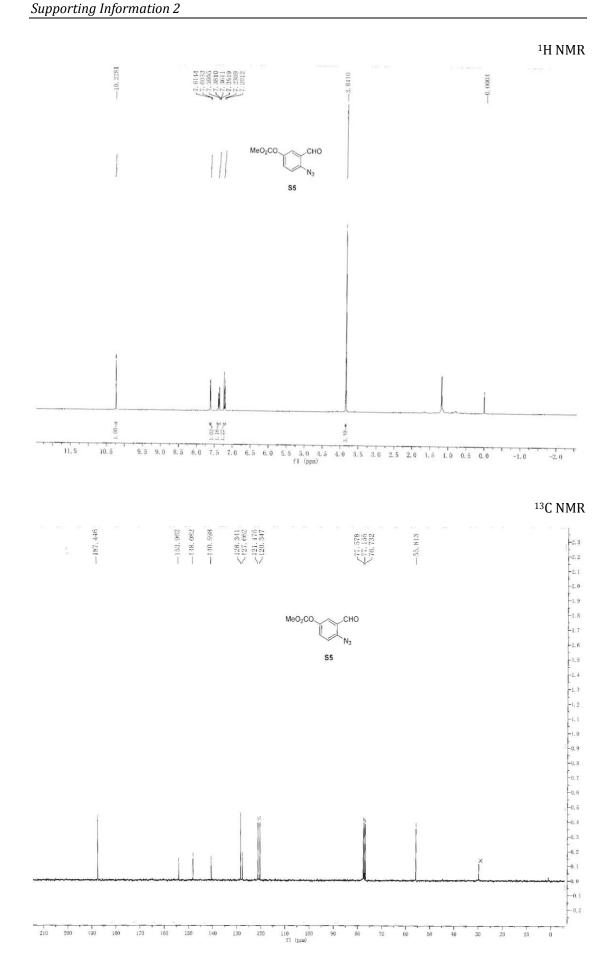
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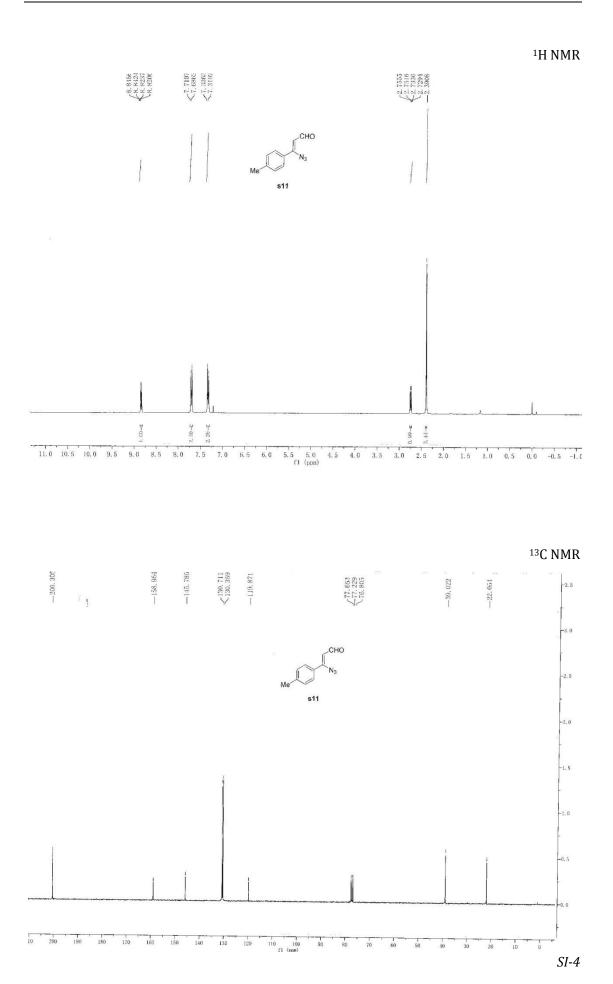
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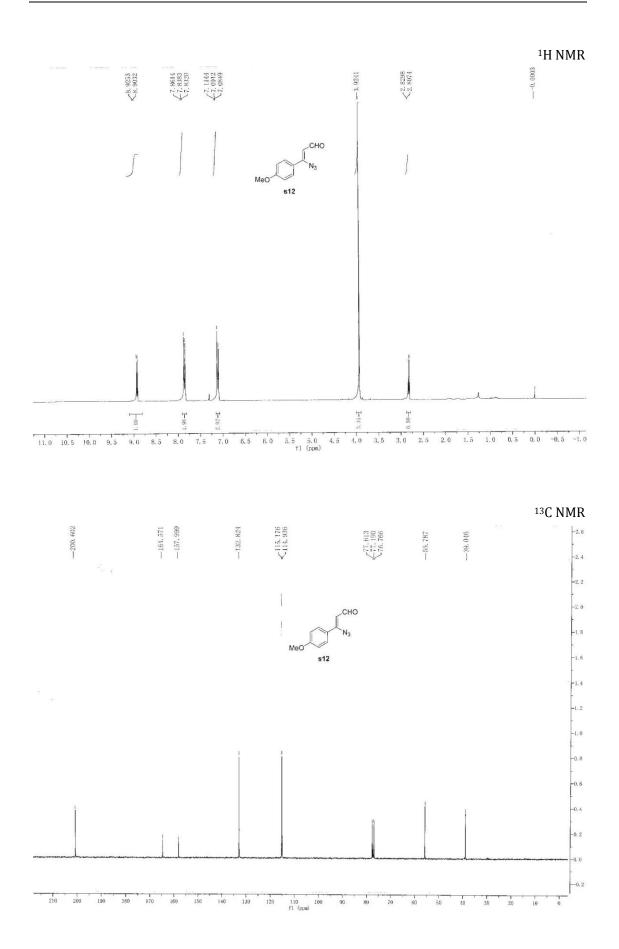


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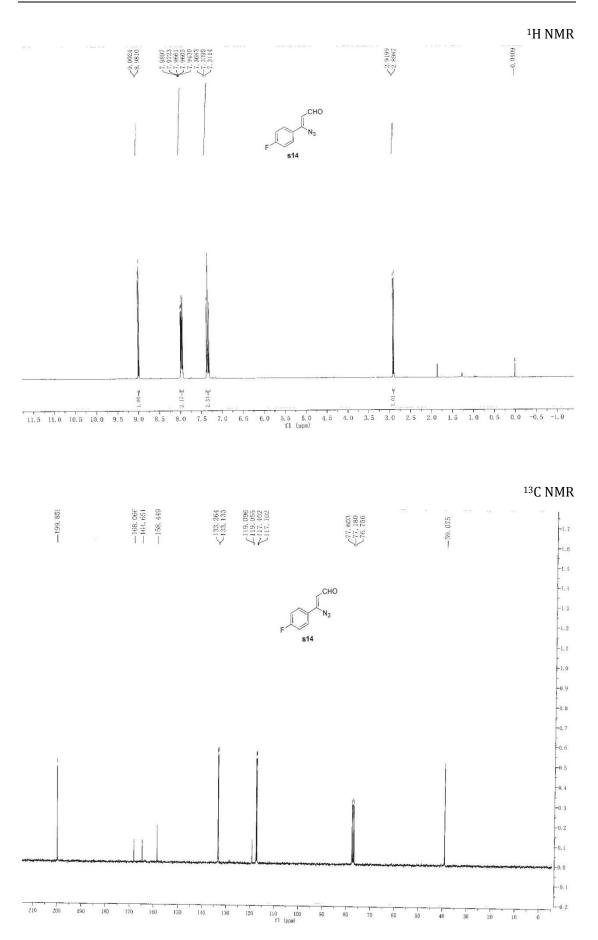
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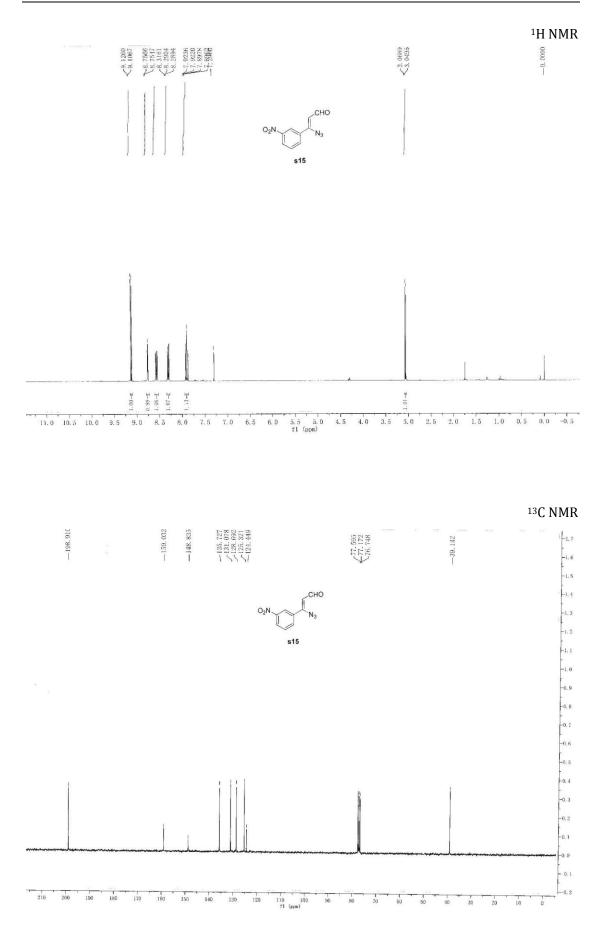
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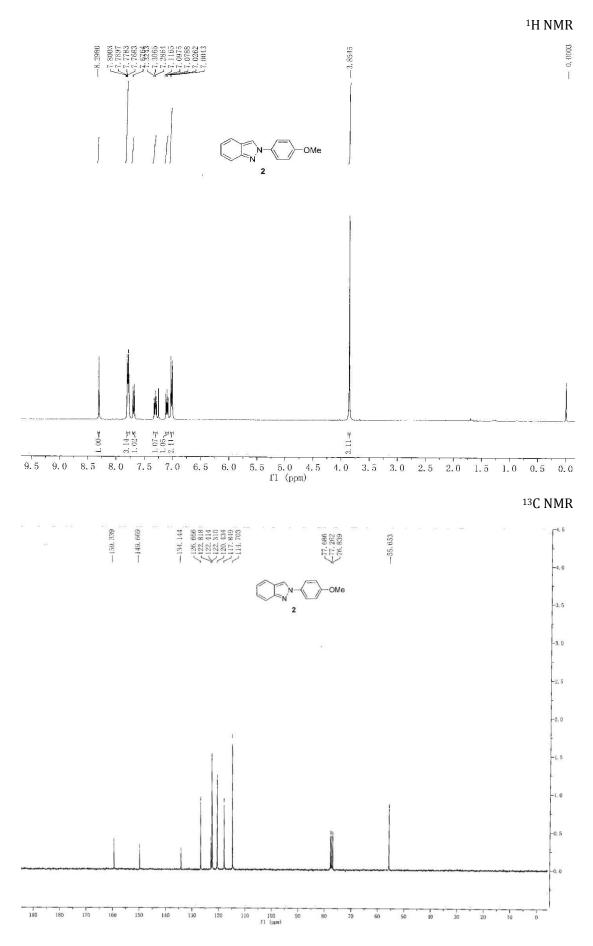


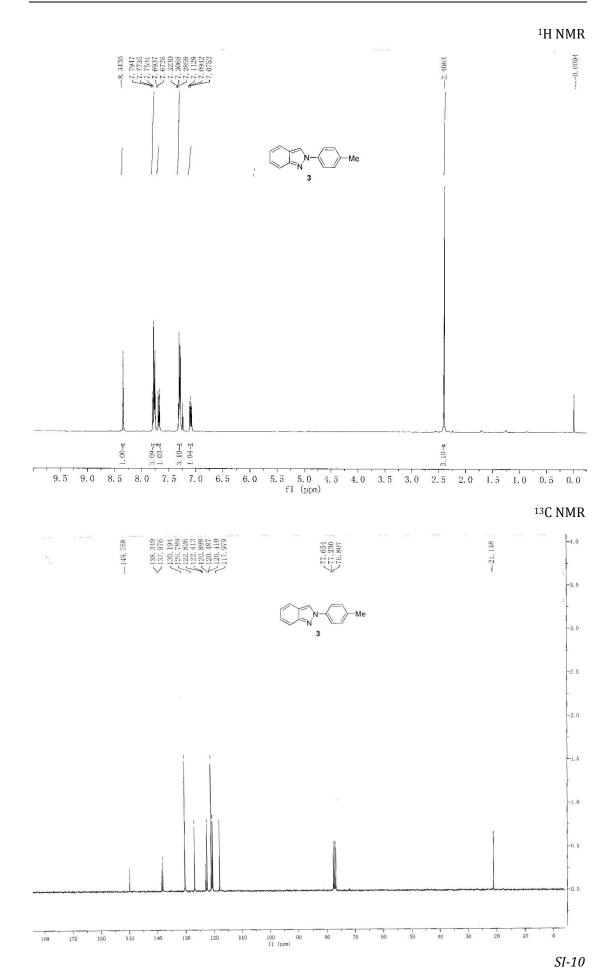
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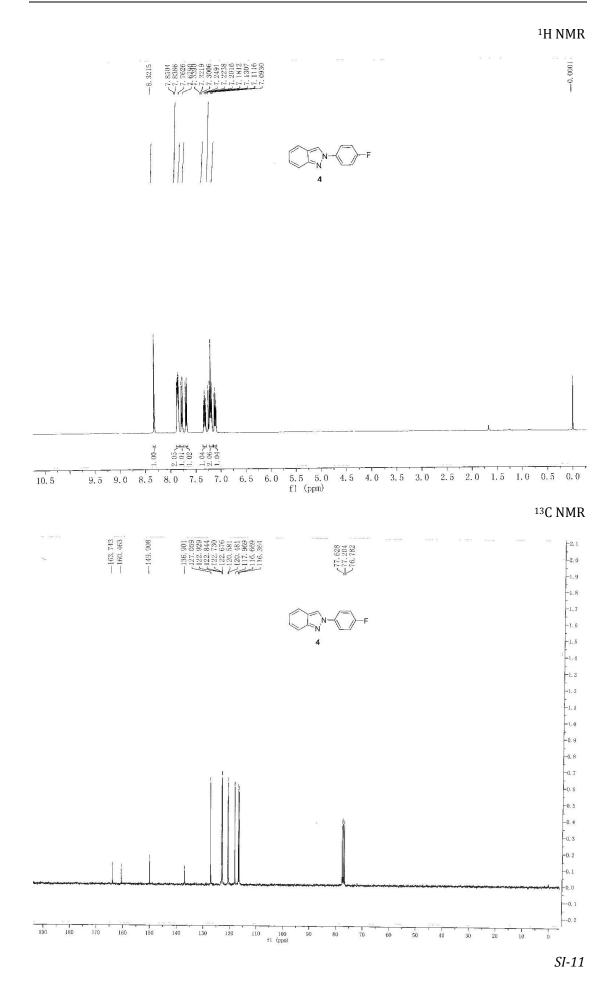
^{1}H NMR 9, 1046 9, 1046 9, 0850 8, 4967 8, 4965 8, 4734 8, 4677 8, 1617 8, 1515 8, 1515 8, 1515 8, 1515 8, 1515 8, 1515 8, 1515 $<_{3.0543}^{3.0543}$ СНО N₃ O₂N s13 2, 19 Å I-00 18-I 1.0 10.5 10.0 9.5 9.0 8.5 7.5 2.5 2.0 8.0 7.0 6.5 5.5 5.0 f1 (ppm) 4.5 4.0 3.5 3. 0 0.5 0.0 -0.5 -1.0 6.0 1.5 1.0 ¹³C NMR ~131,549 -128,032 -124,773 -159.216 -39.228 $\underbrace{ < 77.566} 77.142 \\ 76.719 \\ 76.719 \\ 76.719 \\ 76.719 \\ 700 \\$ -2.0 -1.9 -1.8 1.7 СНО 1.6 -1.5 O₂N² -1.4 s13 -1.3 -1.2 -1.1 -1.0 -0.9 -0.8 -0.7 -0.6 -0.5 -0.4 -0.3 -0.2 -0.1 -0.0 - 0. T -0.2 210 200 190 180 170 160 150 140 130 120 110 100 f1 (рыя) 90 80 70 60 50 30 40 20 10

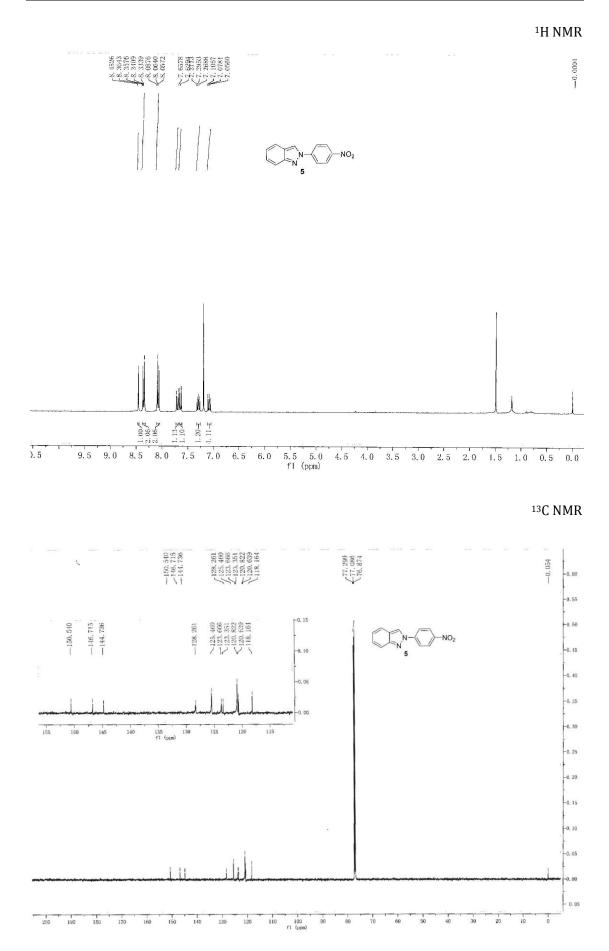




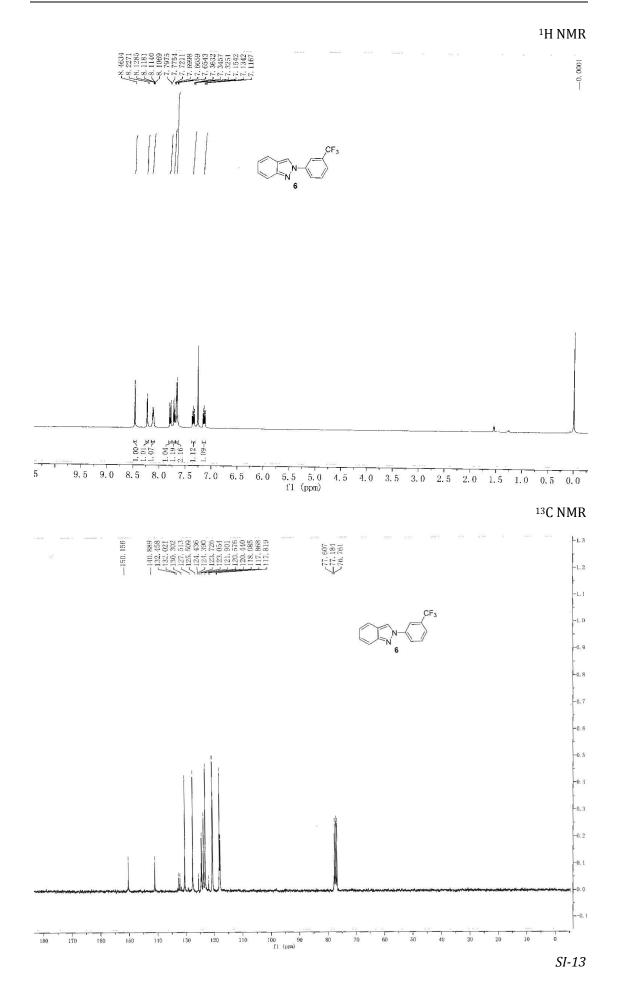


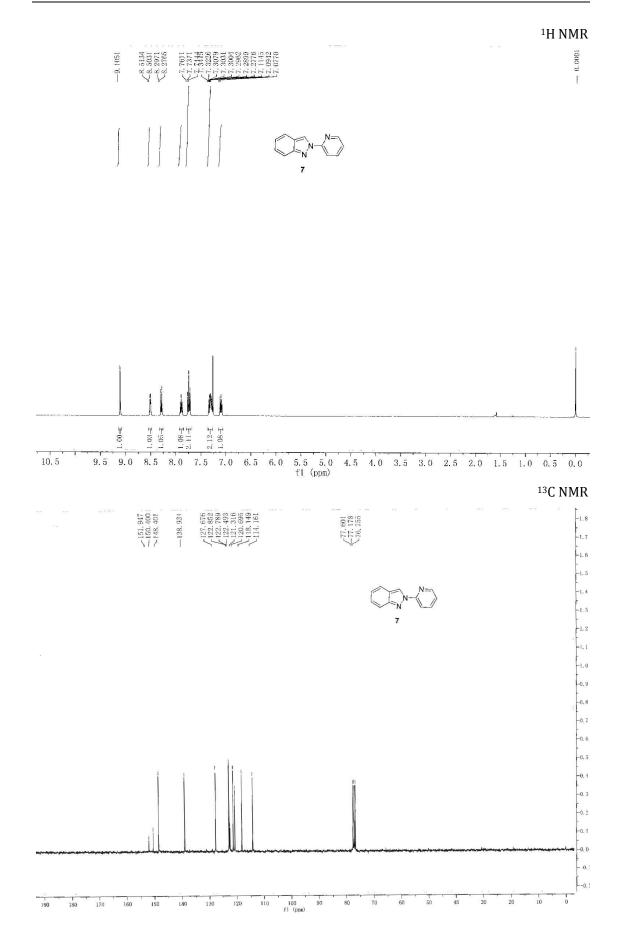


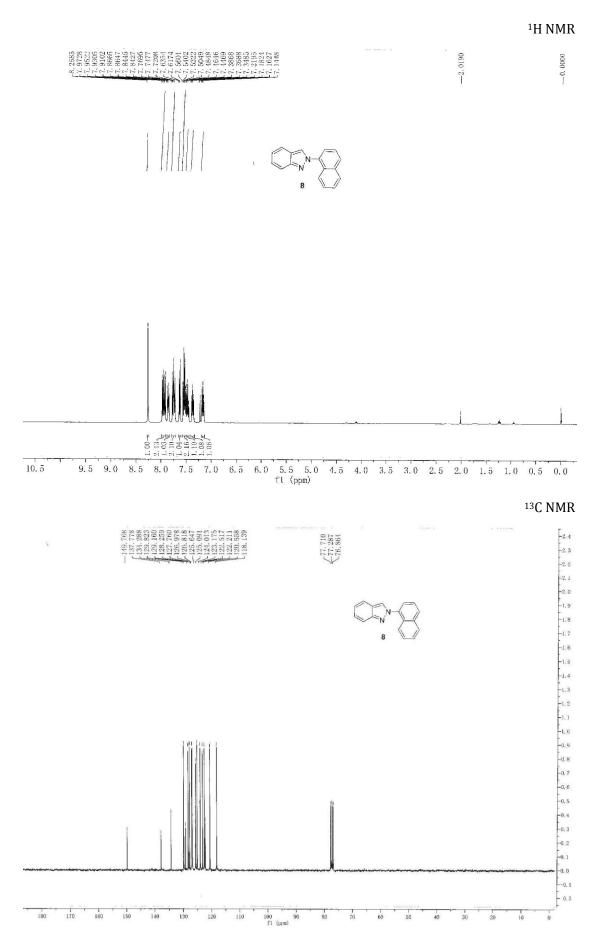




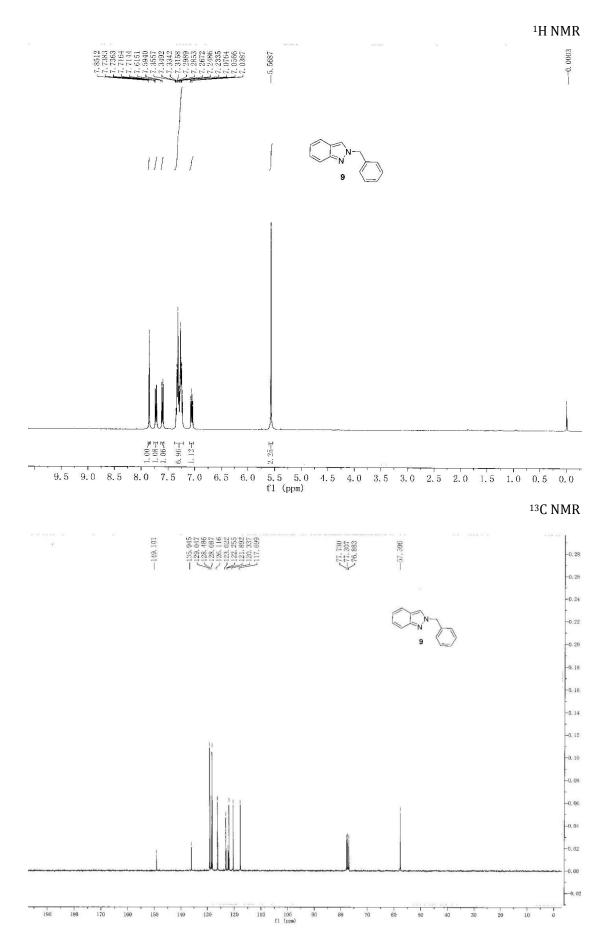
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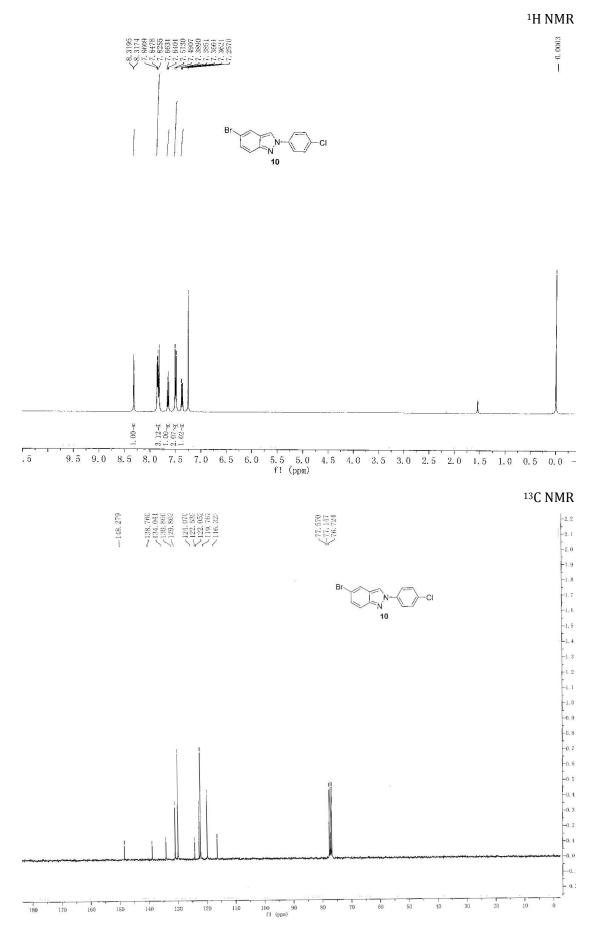


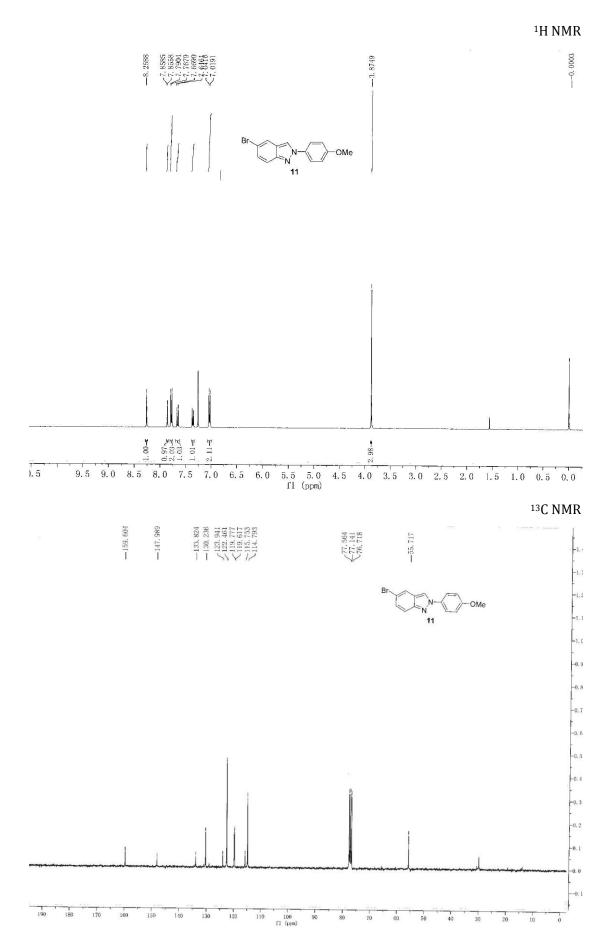




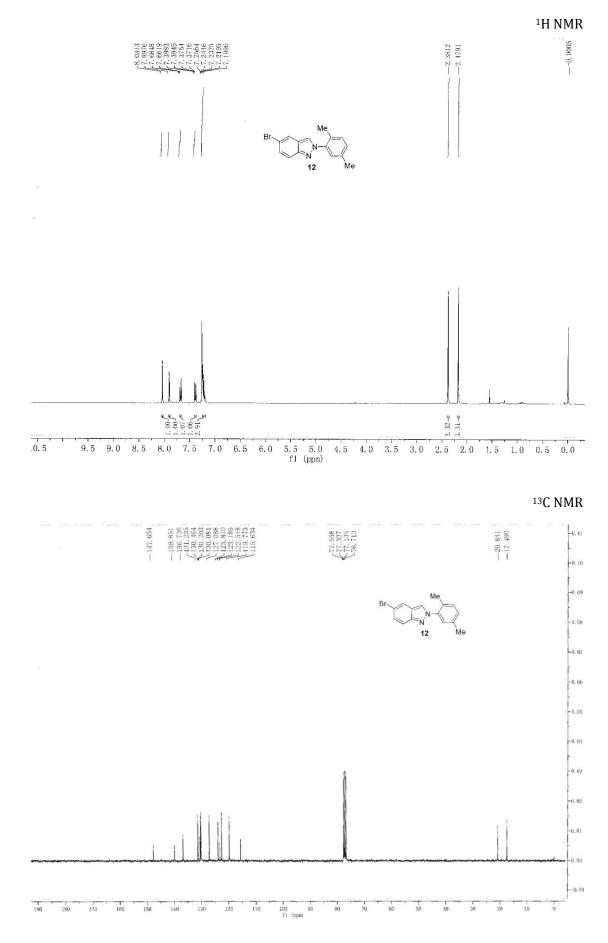


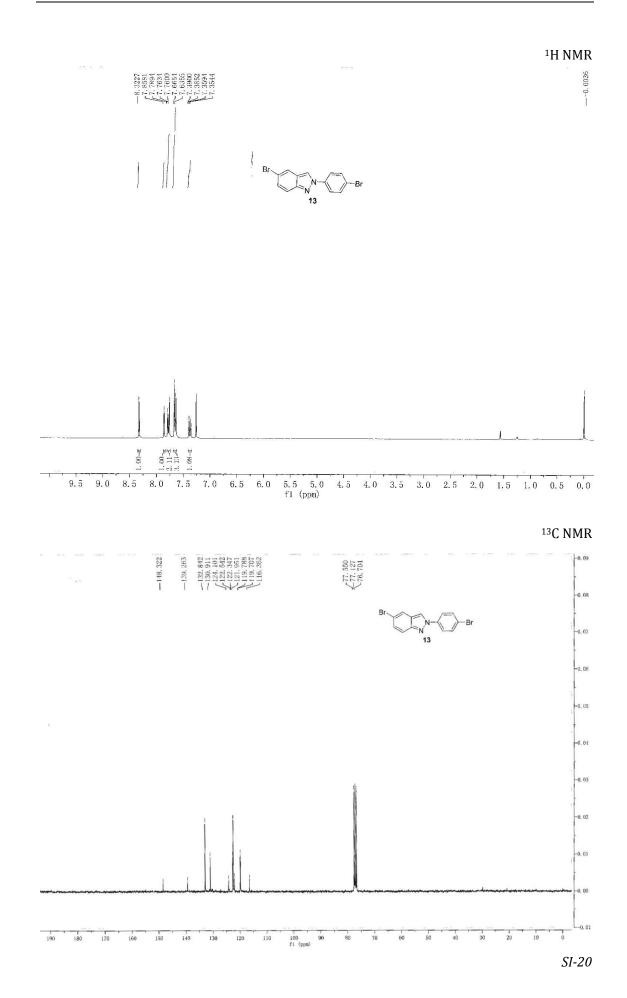


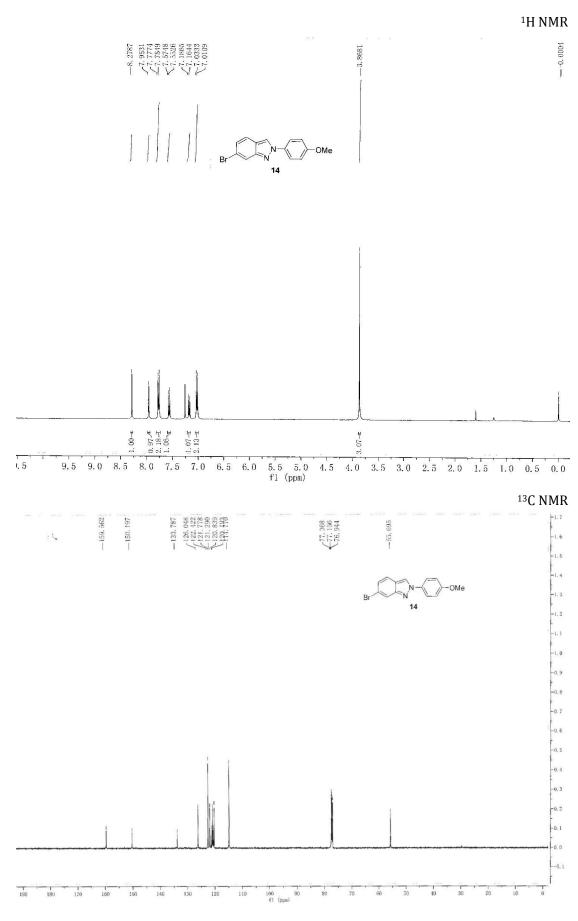


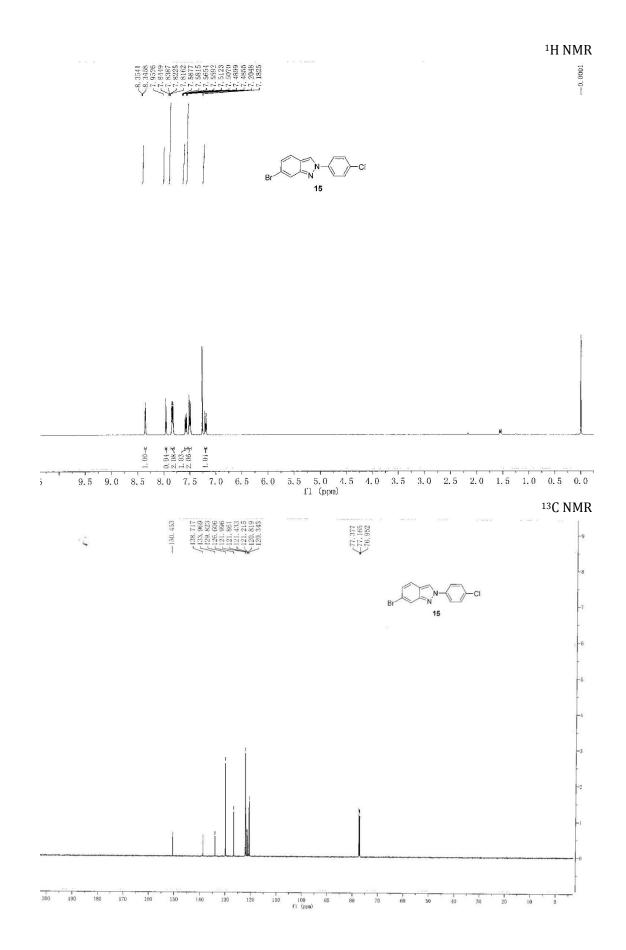


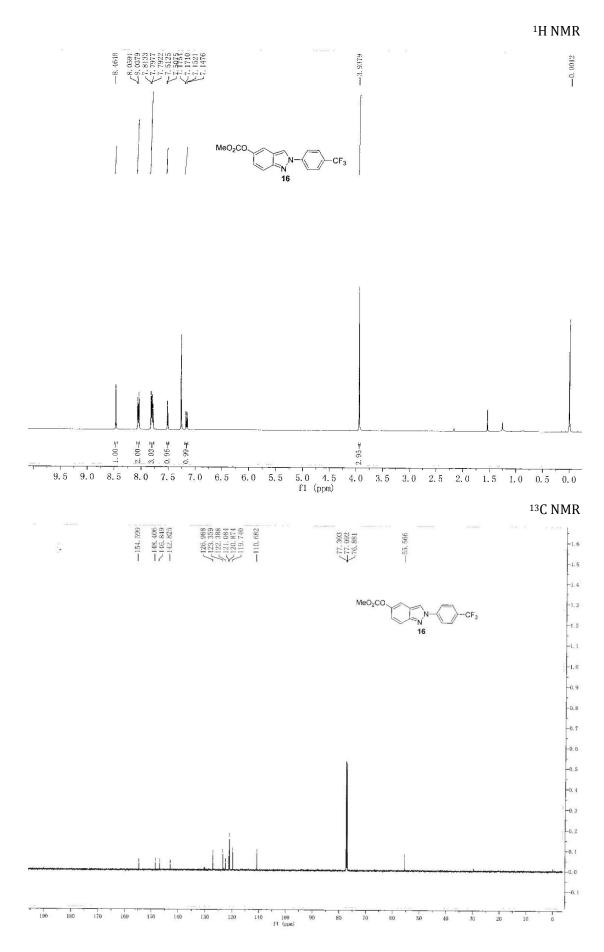
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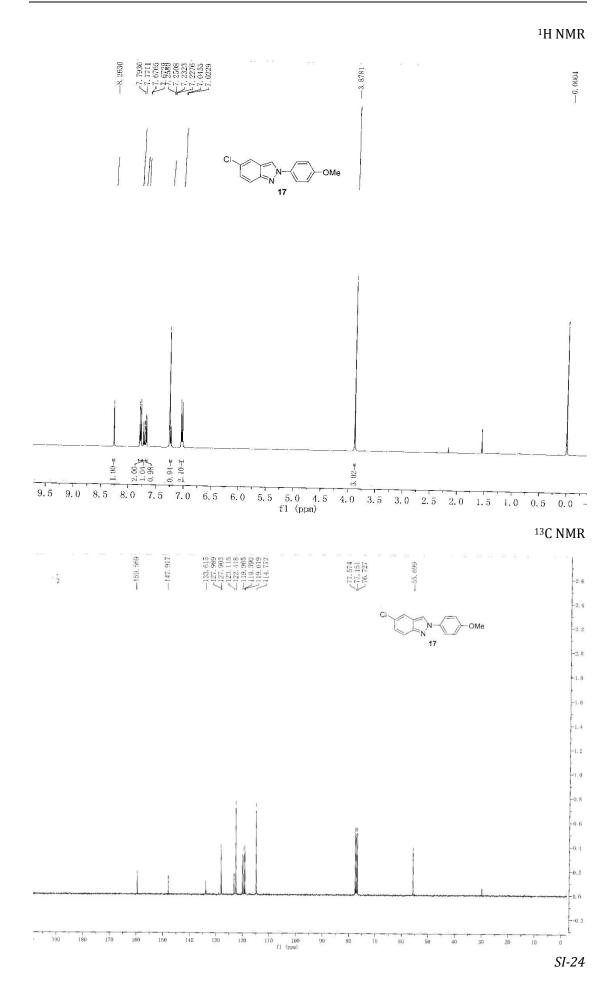


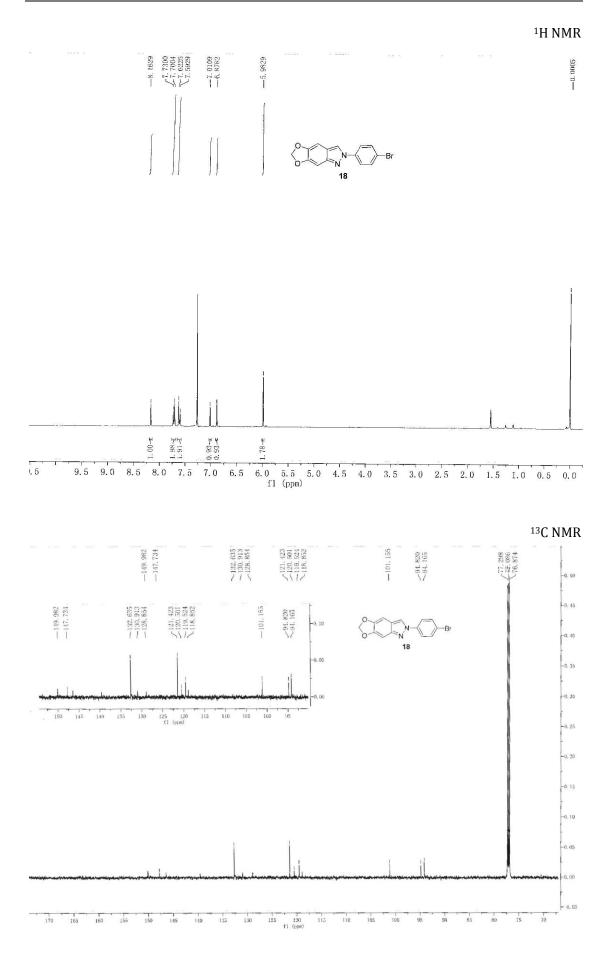


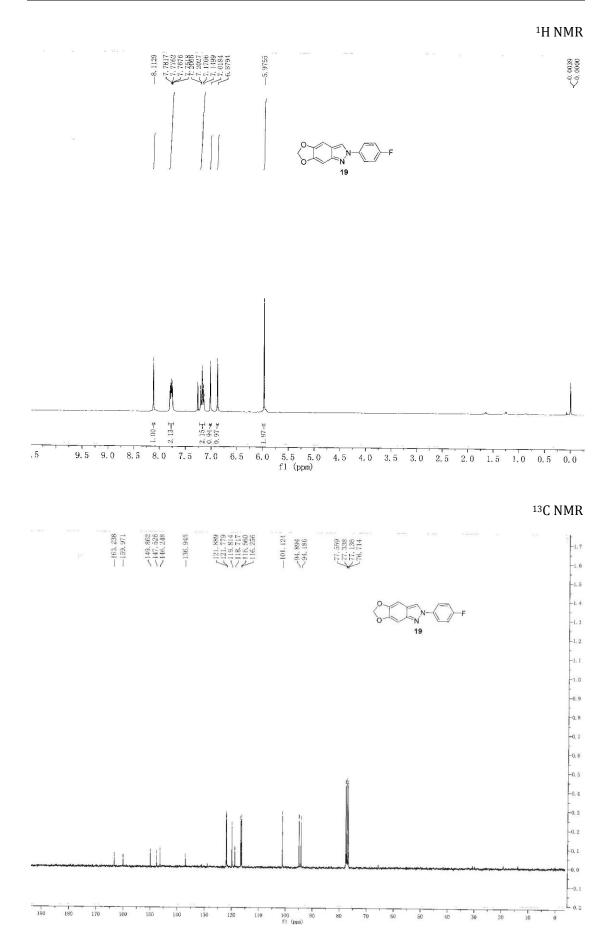


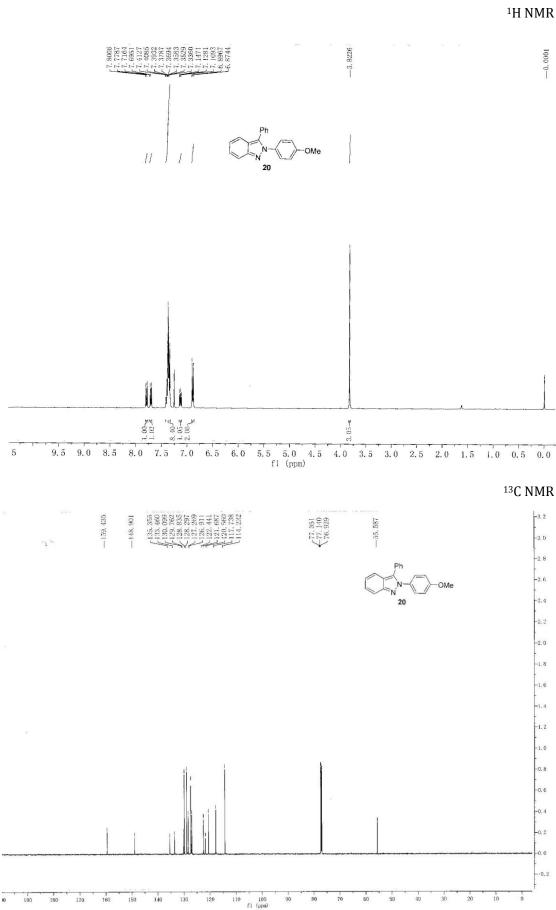


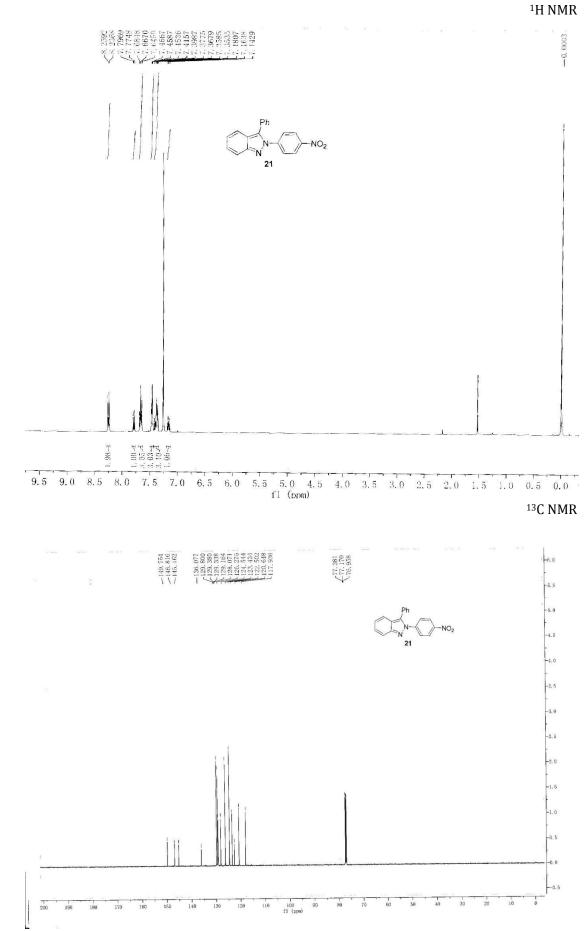




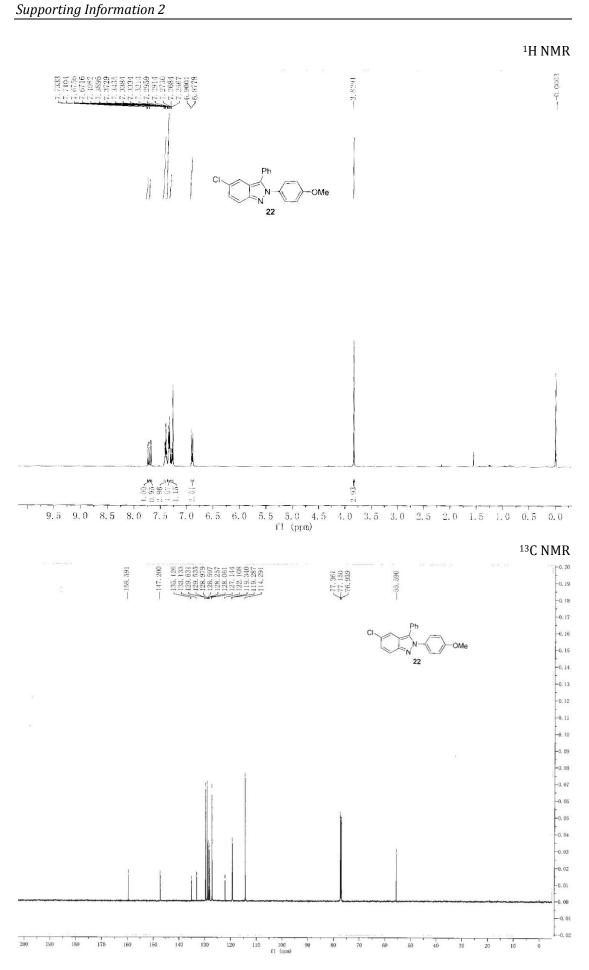


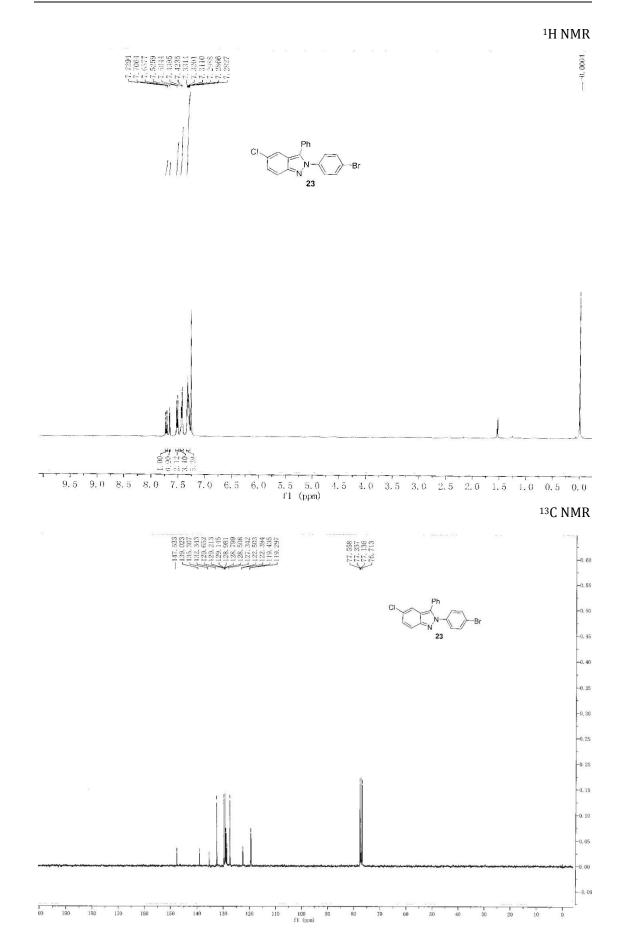












180

170

160

150

140

130

120

110

100 90 fl (ppm) 70

60

50

10

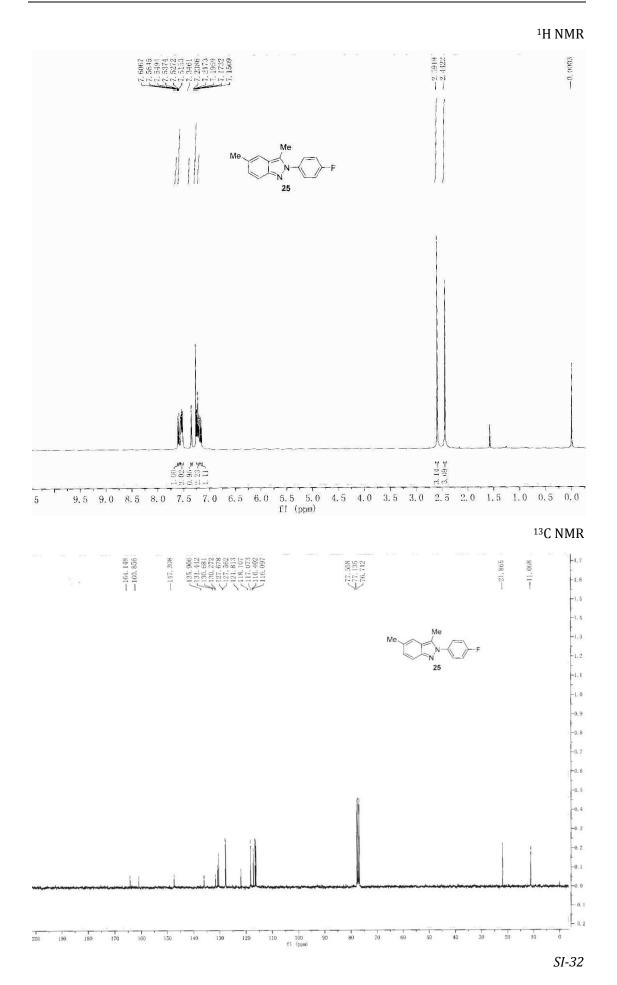
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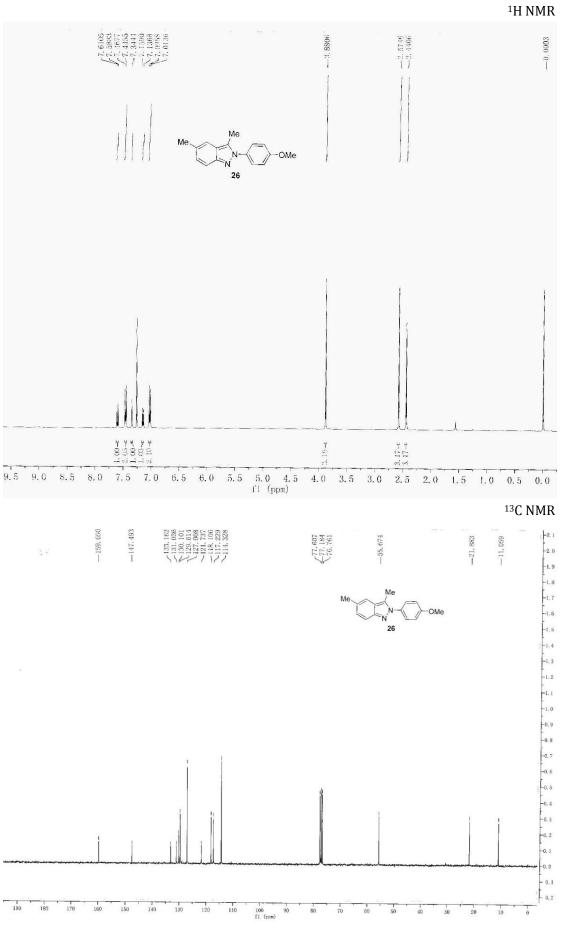
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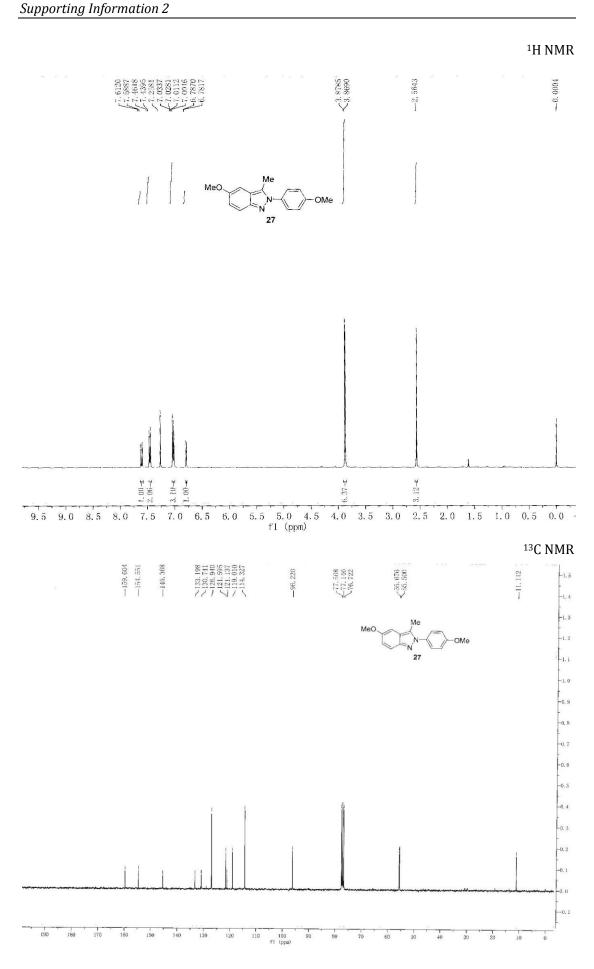
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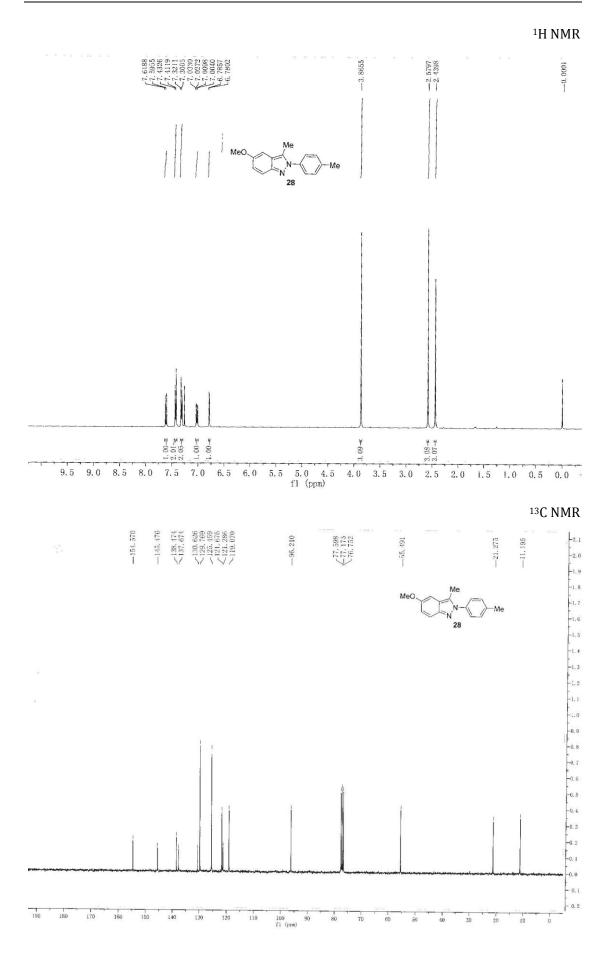
¹H NMR -2. 3838 -0,0003 1.1 Ph CI Me [] 24 02 -E er; 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 f1 (ppm) 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 13C NMR (112) 123 624 (137, 583 (137, 583 (129, 558 (129, 558 (129, 558 (129, 558 (129, 558 (128, 122) (129, 558 (128, 122) (129, 558 (128, 122) (128, 122) (128, 122) (129, 128) (129, -147.281 $\frac{\sqrt{77.562}}{\sqrt{76.716}}$ -21.273-1.4 -1.3 -1.2 -1.1 24 1.0 0.9 -0.8 -0.7 -0.6 -0.5 -0.4 0.3 -0. 2 -0.1 -0.0 -0.1

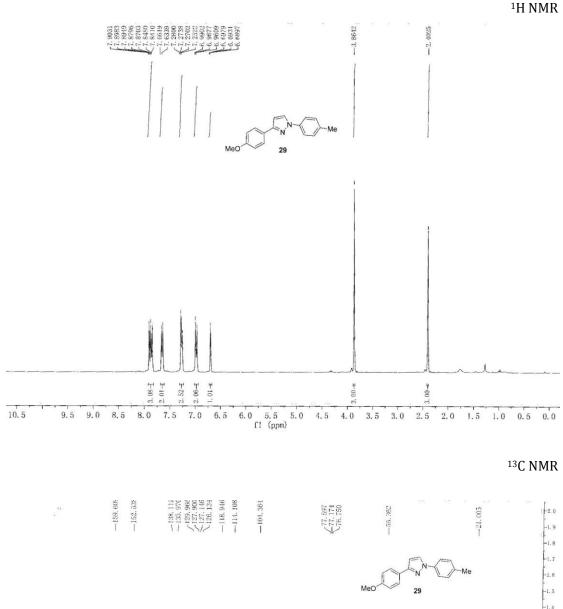


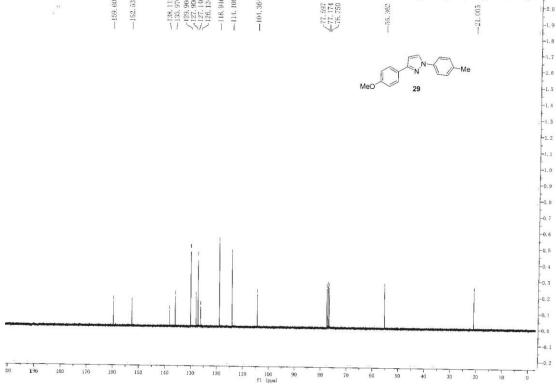


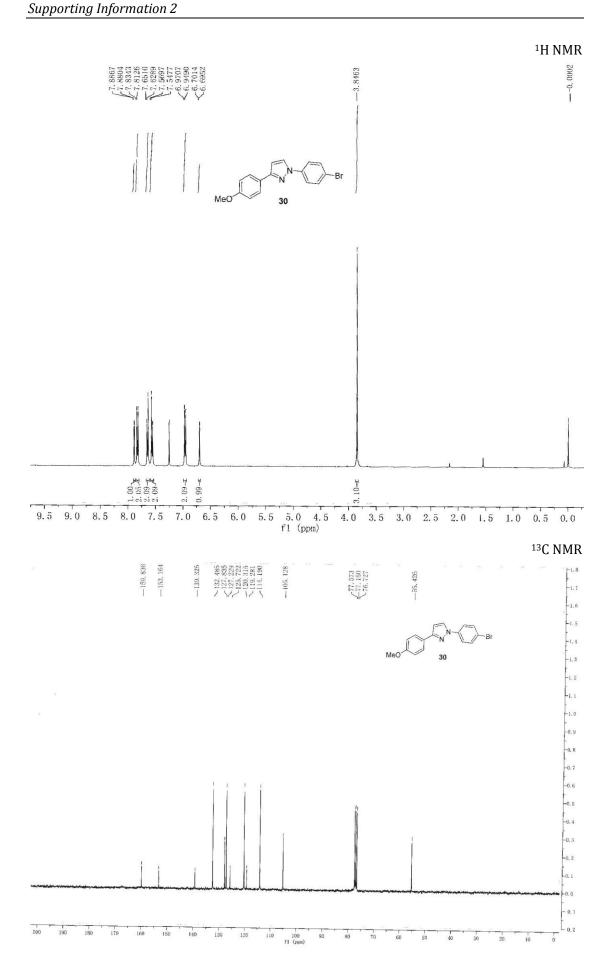
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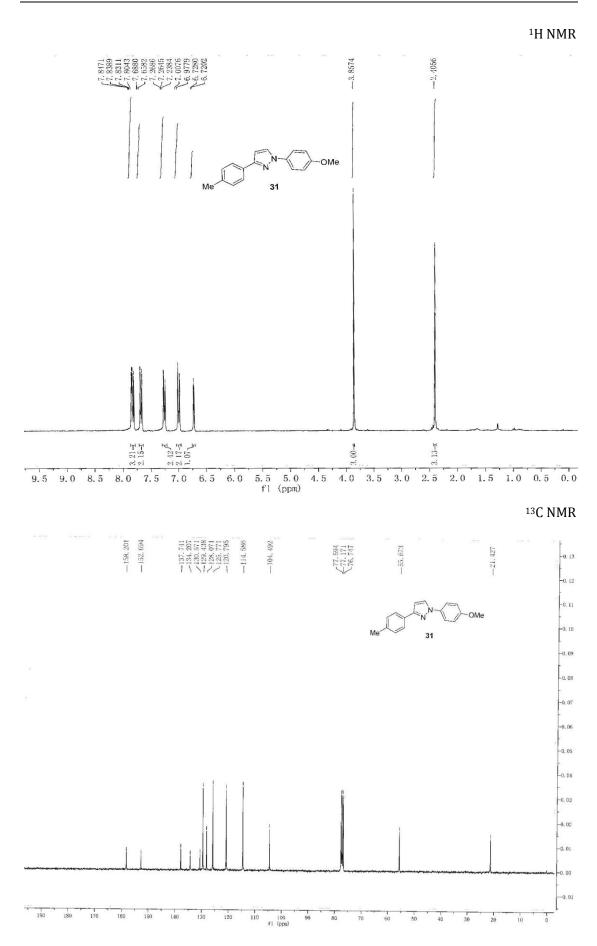


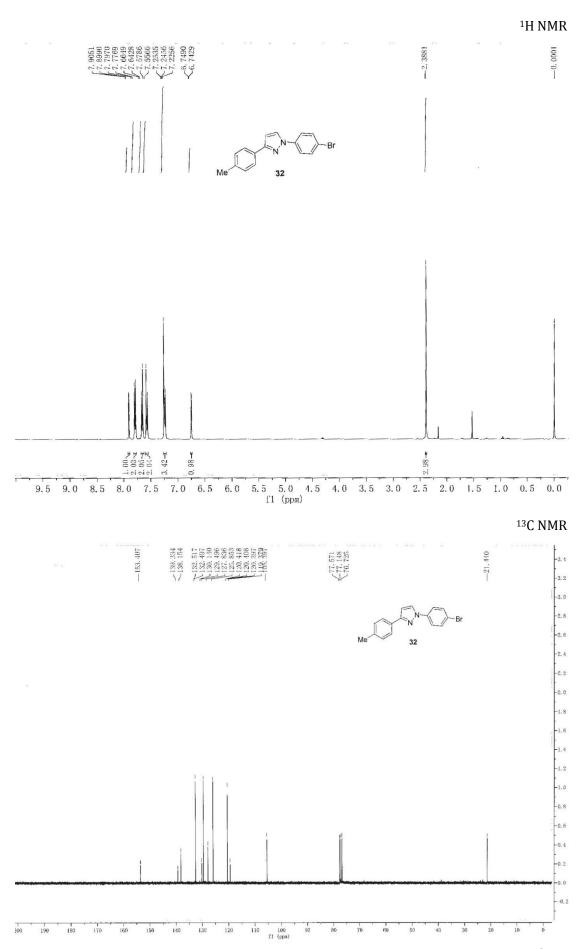


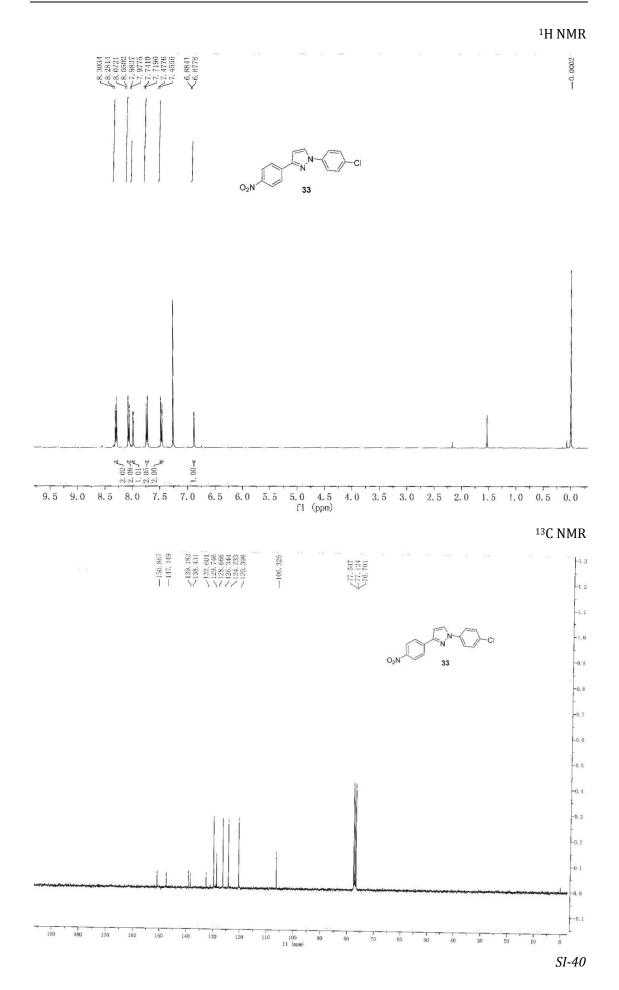


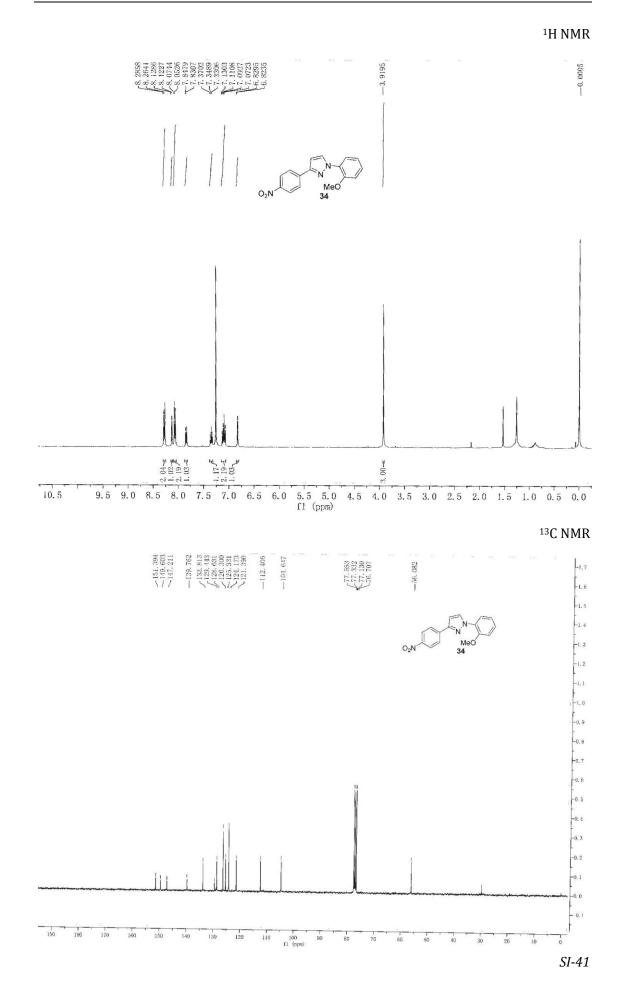


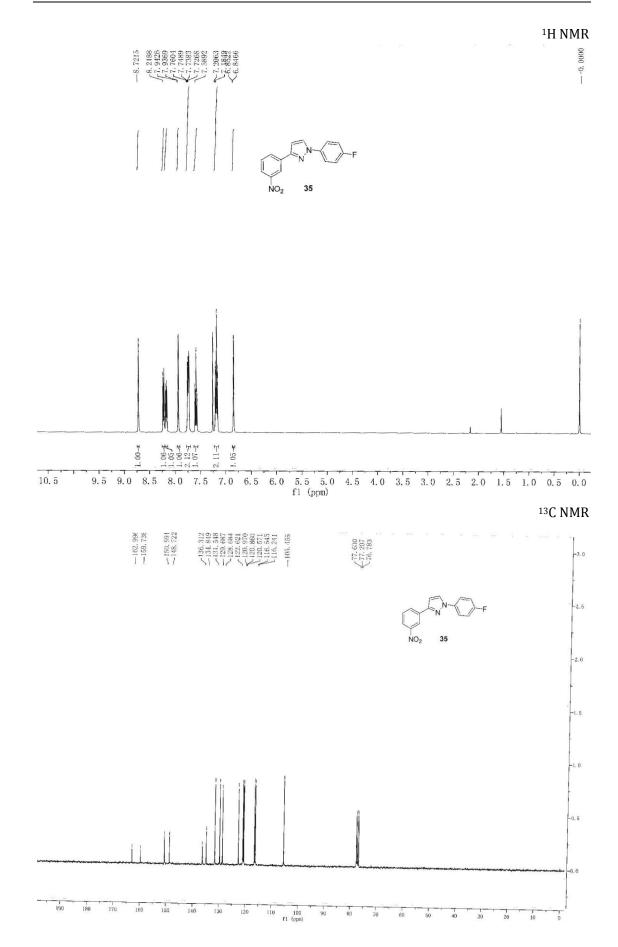


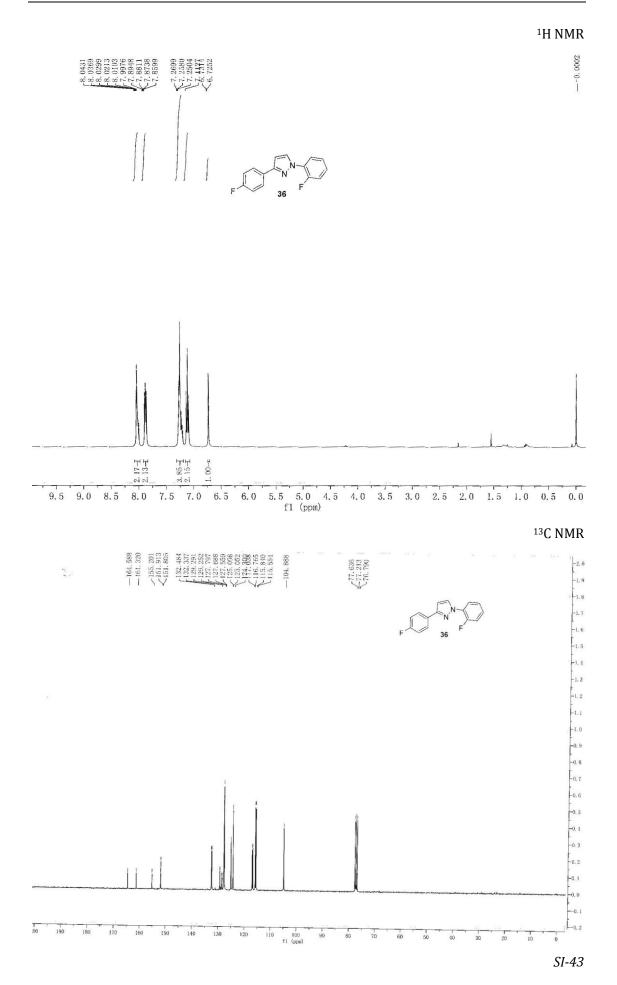


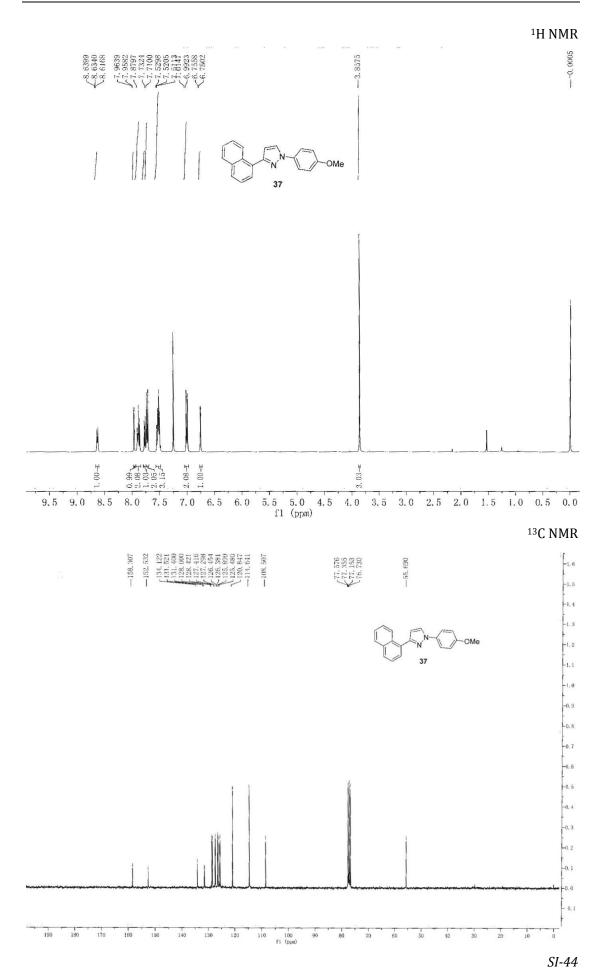




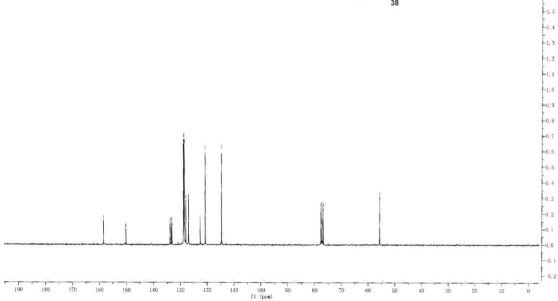








Supporting Information 2 -3. 8518 OMe 11 38 2.09 2.09 38 子 8.38 子 8.38 104 ~i 5.5 5.0 f1 (ppm) 2.5 2.0 1.5 3.5 3.0 1.0 0.5 0.0 9.5 8.0 7.5 7.0 6.0 4.5 4.0 9.0 8.5 6.5 100 -158.398447 148 821 882 662 933 933 933 933 933 933 933 933 631 631 631 $\frac{77.671}{77.248}$ -55.682 -150. -OMe N Ph 38



¹H NMR

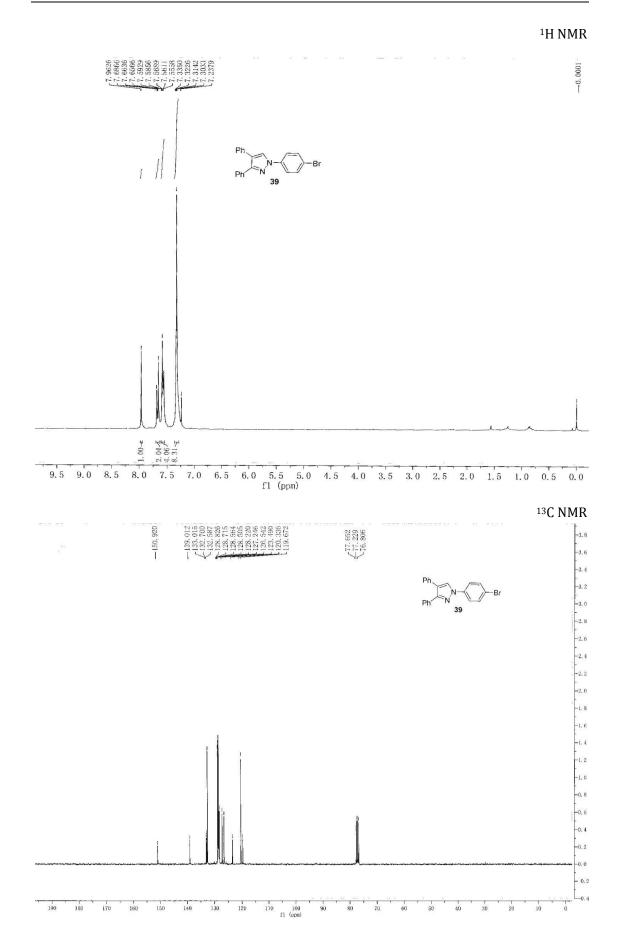
13C NMR

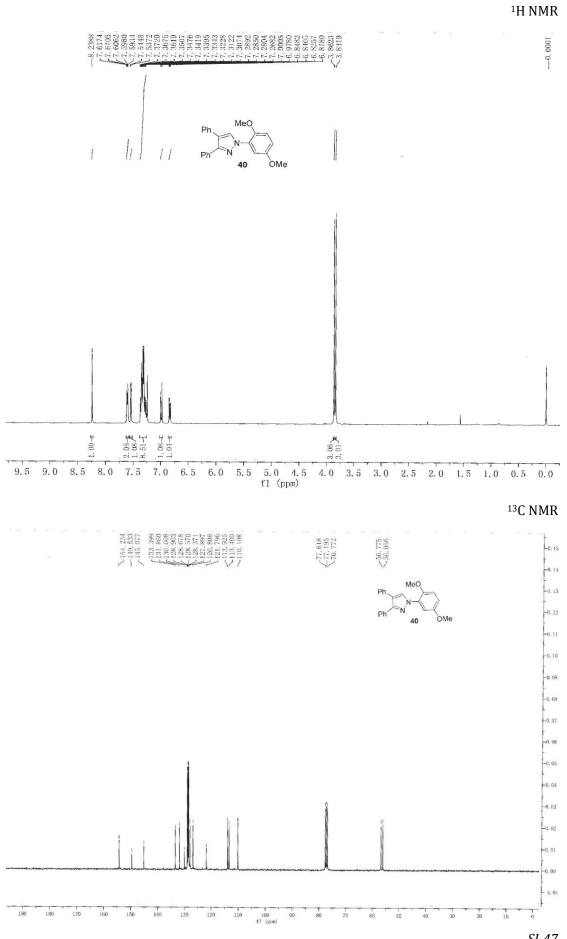
-2.2

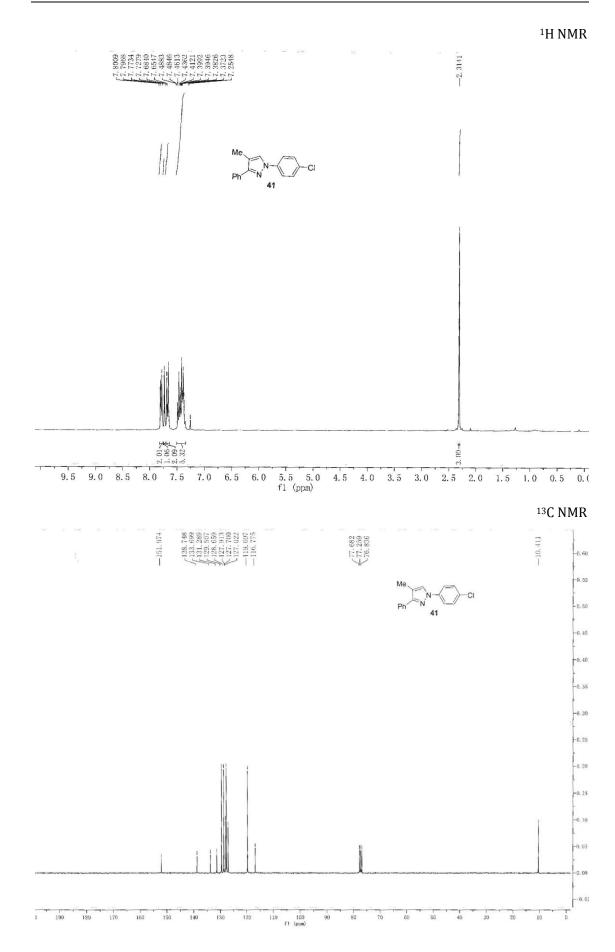
-2.1 -2.0 1.9 1.8 -1.7

-1.6

SI-45







SI-48

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 $\frac{1}{200}$

190 180 160

150 140 130 120

110 100 fl (ppm)

90 80 70

60

50

10 30 20 10 0

170

Supporting Information 2 ¹H NMR 7824 7639 6117 -3, 7720 : 57692576913681368398839883357-2.26849037 -0.001OMe 42 97 91 99 99 99 99 99 99 99 $3.00 \pm$ 95-1 02-1 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 fl (ppm) ¹³C NMR -158.014-151.156 $\begin{array}{c} 134.117 \\ 128.600 \\ 127.604 \\ 127.804 \\ 127.325 \\ -120.370 \\ -113.858 \\ -114.578 \end{array}$ -65.630 77.711 77.288 76.864 -10.395OMe N 42 -1.0 -3.5 -3.0 -2.5 -2.0 -1.5 -1.0

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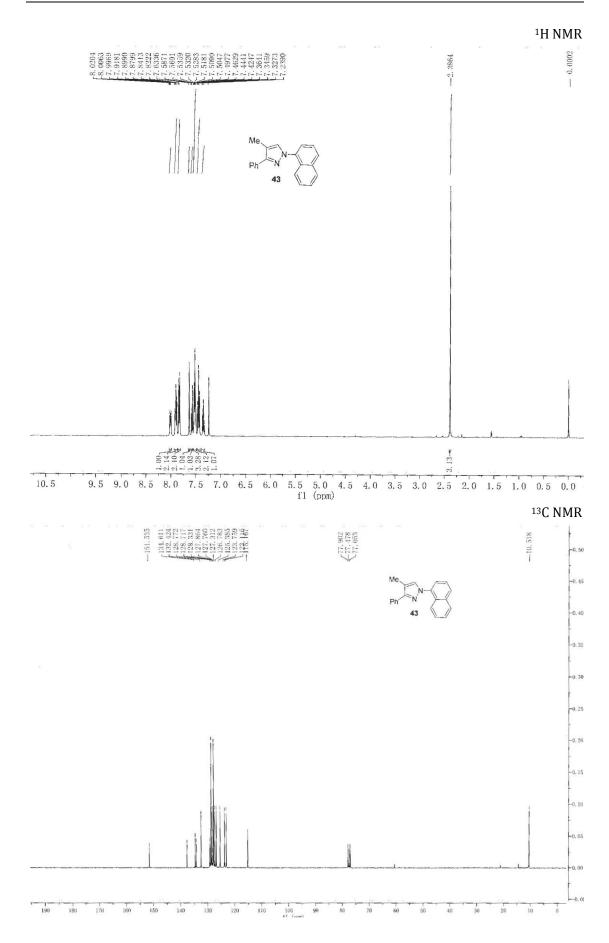
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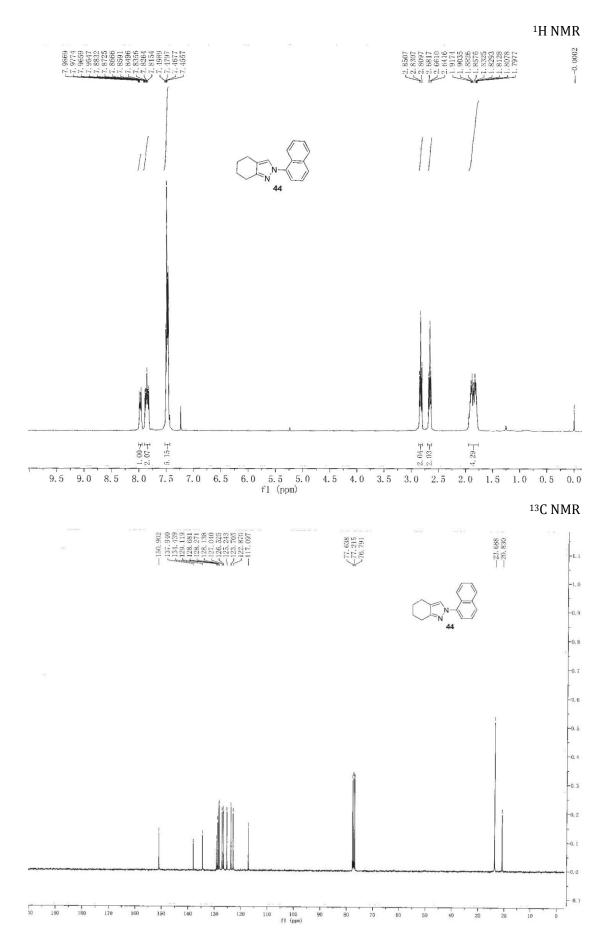
0.0

0.5

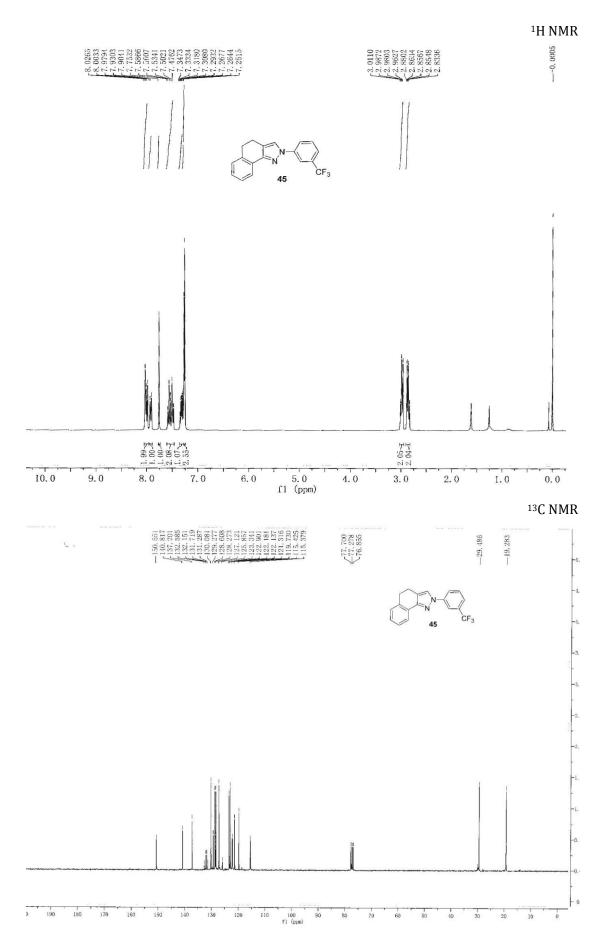
-5.0

-4.5





SI-51



$^{1}\mathrm{H}\,\mathrm{NMR}$ 7559 6314 6314 6093 4786 6435 1475 1435 1130 1130 1130 8739 8519 -8.2533 -5.7635 -3.9413 -0.0003o e MeO₂CO. OH N 48 1.06-1 2.12-1 0.98 ∉ 2.05 ∉ 0.92 ⊷ 100 0.95-I 2.95-≖ 10.5 7.0 6.5 6.0 5.5 5.0 fl (ppm) 9.5 9.0 8.5 8.0 7.5 $4.5 \ 4.0 \ 3.5 \ 3.0 \ 2.5 \ 2.0 \ 1.5 \ 1.0 \ 0.5 \ 0.0 \ -$ 13C NMR -3.2 -157.906 -154.605 ~147.264 648 454 192 072 142 486 619 40, 870 40, 593 40, 593 40, 315 40, 037 -39, 759 -39, 759 -39, 759 -39, 759 -132.608-55.941122. 122. 122. 116. -3.0 -2.8 -2.6 -132.608122.648 122.454 122.192 122.072 119.142 -116.486 -157.906 -147.264 -111.619 -154.605MeO₂CO -0.6 -2.4 OF N -2.2 -0.4 48 -2.0 -0, 2 -1.8 -0.0 -1.6 110 140 115 160 155 150 145 130 125 120 135 f1 (ppm) 1.4 -1.2 -1.0 -0.8 -0.6 -0.4 -0.2 -0. 0 - 0.2

130

140

150

190

180

170

160

120

110

100 fl (ppm)

90

80 70

0

20

40

50

60

30

10

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