Supporting Information for:

Palladium-Catalyzed Dearomative Arylalkynylation of Indoles

Ren-Rong Liu, Teng-Fei Xu, Yong-Gang Wang, Bin Xiang, Jian-Rong Gao, and Yi-Xia Jia*

College of Chemical Engineering, Zhejiang University of Technology, Chaowang Road 18#, Hangzhou 310014, China

Email: yxjia@zjut.edu.cn

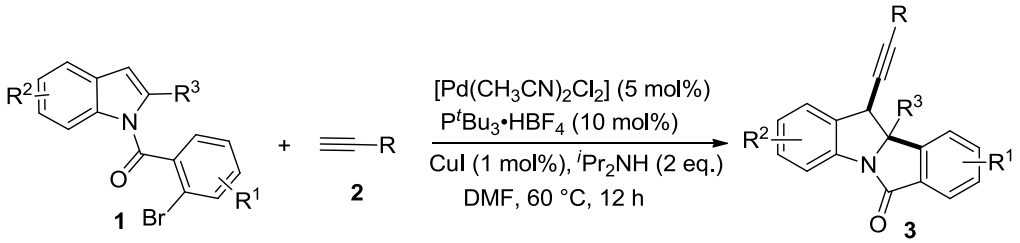
Contents:

1. General information

Reactions and manipulations involving organometallic or moisture sensitive compounds were carried out under dry nitrogen and glassware heated with heating gun prior to use. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE III 500MHz with TMS as internal standard. Anhydrous THF and toluene were freshly distilled over Na and benzophenone. Anhydrous DMF, DMA, and CH_3CN were freshly distilled over calcium hydride. Melting points were measured on a Büchi Melting Point B-545 apparatus and uncorrected. Commercial reagents were used as received without further purification unless otherwise noticed. HRMS were recorded on Agilent 6210 LCT (EI source) or Waters Xevo Q-Tof Mass Spectrometer (ESI source). Column chromatography was carried out using silica gel (200-300 mesh). Substrates **1** were synthesized according to the literature procedure and were known compounds.[1]

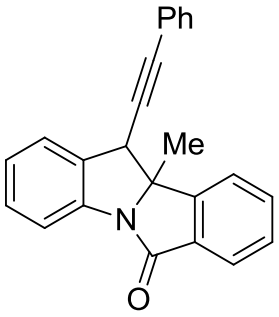
[1] Shen, C.; Liu, R.-R.; Fan, R.-J.; Li, Y.-L.; Xu, T.-F.; Gao, J.-R.; Jia, Y.-X. *J. Am. Chem. Soc.* **2015**, *137*, 4936.

2. Palladium-catalyzed dearomative arylalkynylation of indole



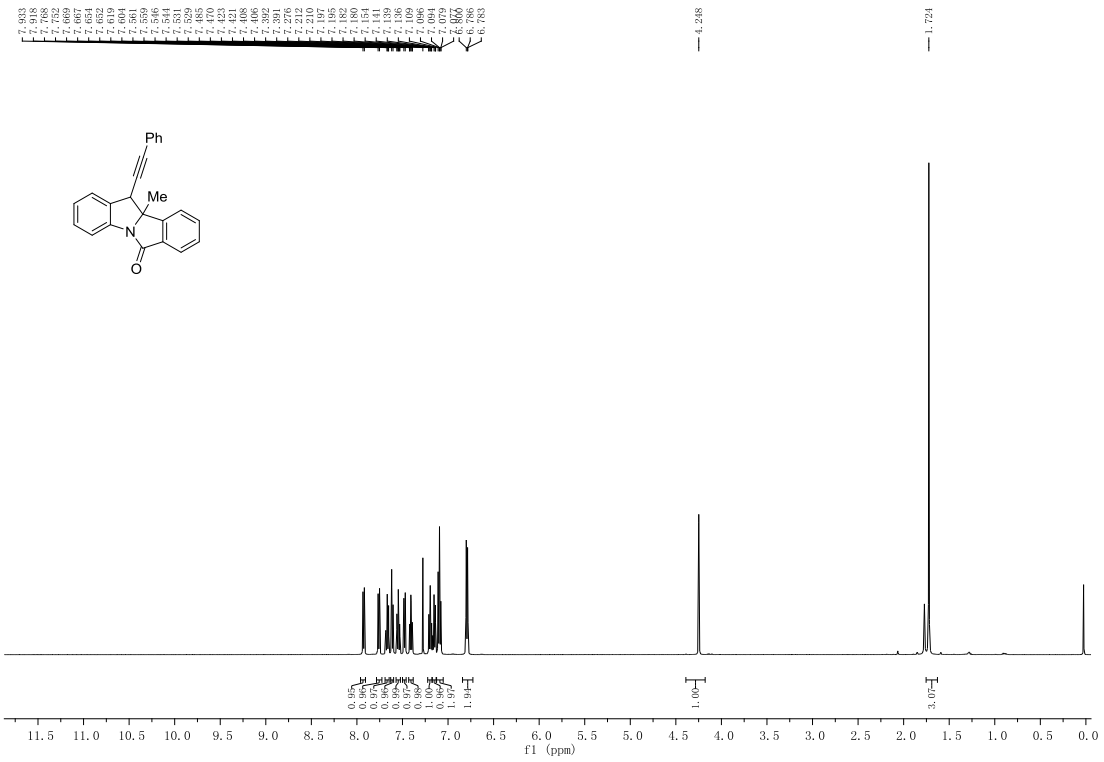
To a dried Schlenk tube were added $Pd(CH_3CN)_2Cl_2$ (2.6 mg, 0.01 mmol), $P^tBu_3 \cdot HBF_4$ (5.8 mg, 0.02 mmol), and $^iPr_2NH$ (0.4 mmol) under N_2, after which 2.0 mL DMF was introduced via a syringe and the resulting mixture was stirred at room temperature for 0.5 h. To the above mixture were subsequently added **1** (0.2 mmol), **2** (0.3 mmol), and CuI (0.002 mmol) under N_2. The Schlenk tube was then sealed by Teflon cap and the mixture was stirred at 60 ^oC for 12 h. The solvent was then removed under vacuum and the residue was purified by chromatography on silica gel, eluting with ethyl/petroleum ether 1:10 (v/v) to afford the products **3**.

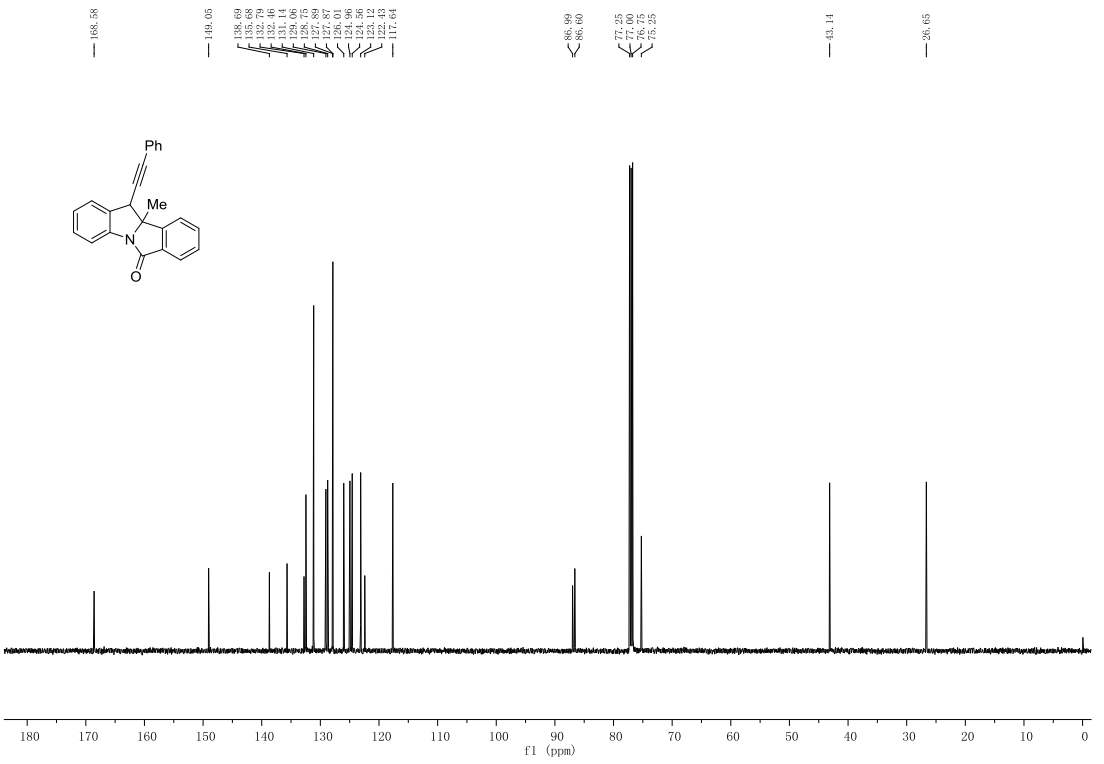
10b-Methyl-11-(phenylethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3aa**)



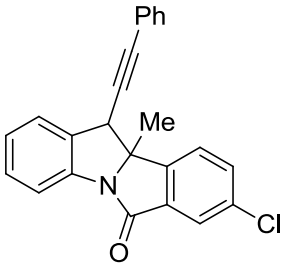
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 55.6 mg, 82% yield, m.p. 147−150 ℃; ^1H NMR (500 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.5 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.67 (td, *J* = 7.5, 1.0 Hz, 1H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.54 (td, *J* = 7.5, 1.0 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.41 (td, *J* = 7.5, 1.0 Hz, 1H), 7.20 (td, *J* = 7.5, 1.0 Hz, 1H), 7.14−7.17 (m, 1H), 7.08−7.11 (m, 2H), 6.78−6.80 (m, 2H), 4.25 (s, 1H), 1.72 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.6, 149.1, 138.7, 135.7, 132.8, 132.5, 131.1, 129.1, 128.8, 127.89,

127.87, 126.0, 125.0, 124.6, 123.1, 122.4, 117.6, 87.0, 86.6, 75.3, 43.1, 26.7. HRMS *m/z* (ESI+): Calculated for $C_{24}H_{18}NO$ ($[M+H]^+$): 336.1383, Found 336.1414.

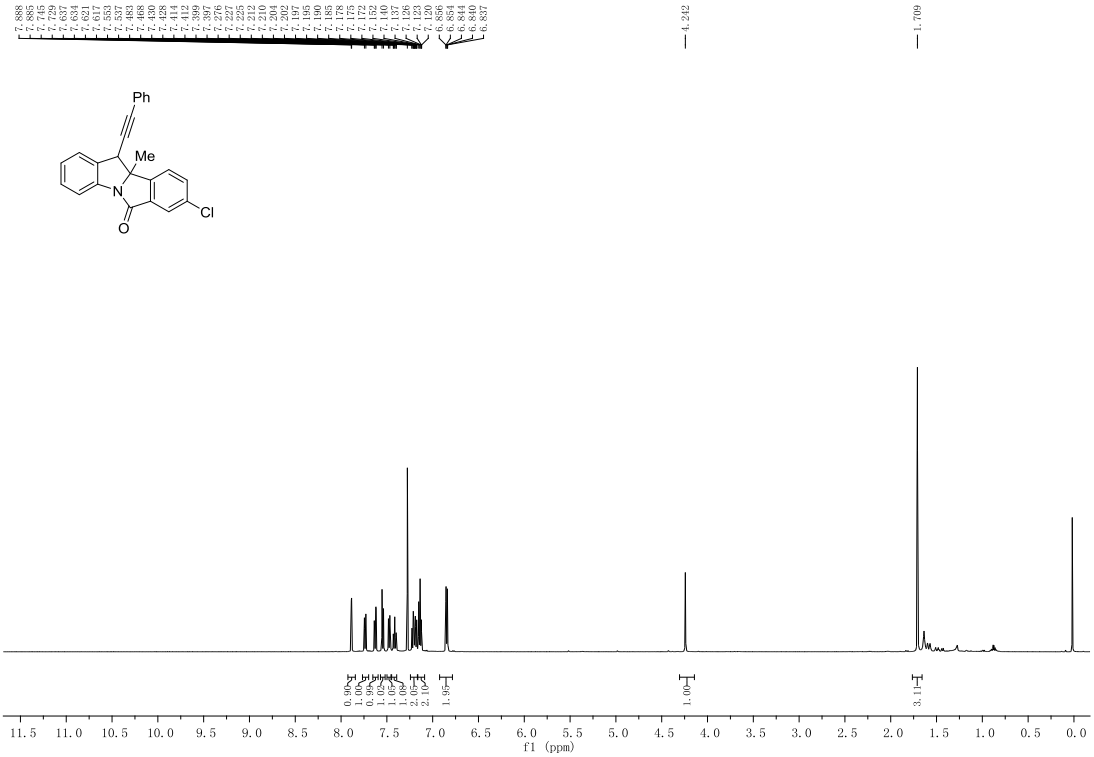


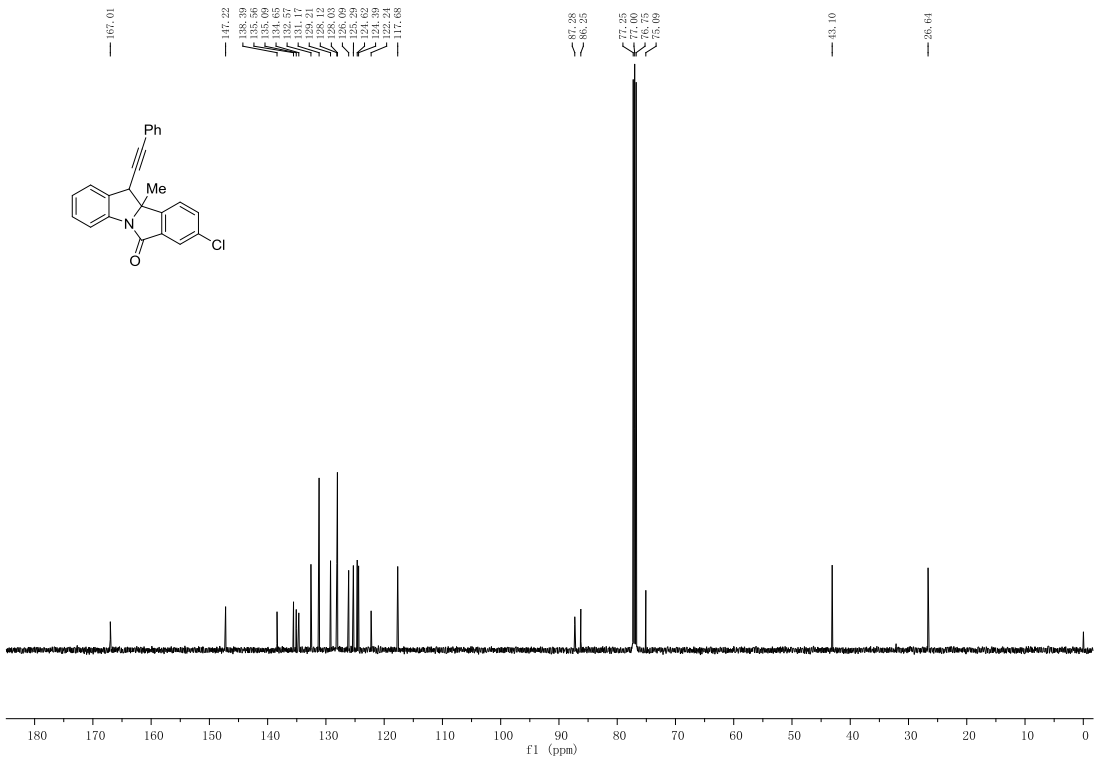


8-Chloro-10b-methyl-11-(phenylethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3ba**)

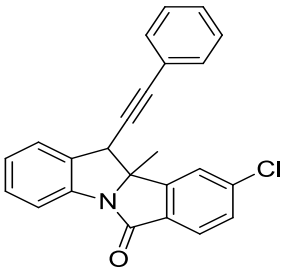


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 53.5 mg, 72% yield, m.p. 108−111 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (d, *J* = 1.5 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.63 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.41 (td, *J* = 7.5, 1.0 Hz, 1H), 7.17−7.23 (m, 2H), 7.12−7.15 (m, 2H), 6.84−6.86 (m, 2H), 4.24 (s, 1H), 1.71 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.0, 147.2, 138.4, 135.6, 135.1, 134.7, 132.6, 131.2, 129.2, 128.1, 128.0, 126.1, 125.3, 124.6, 124.4, 122.2, 117.7, 87.3, 86.3, 75.1, 43.1, 26.6. HRMS *m/z* (ESI+): Calculated for $C_{24}H_{17}ClNO$ ($[M+H]^+$): 370.0993, Found 370.0980.



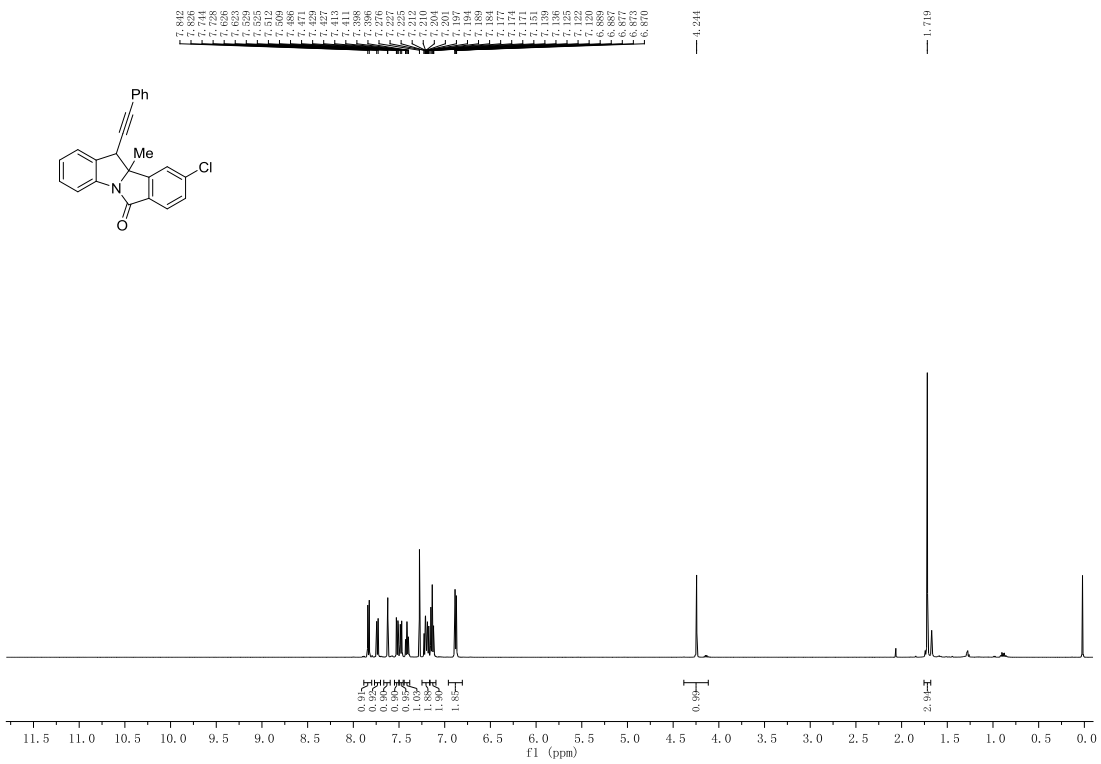


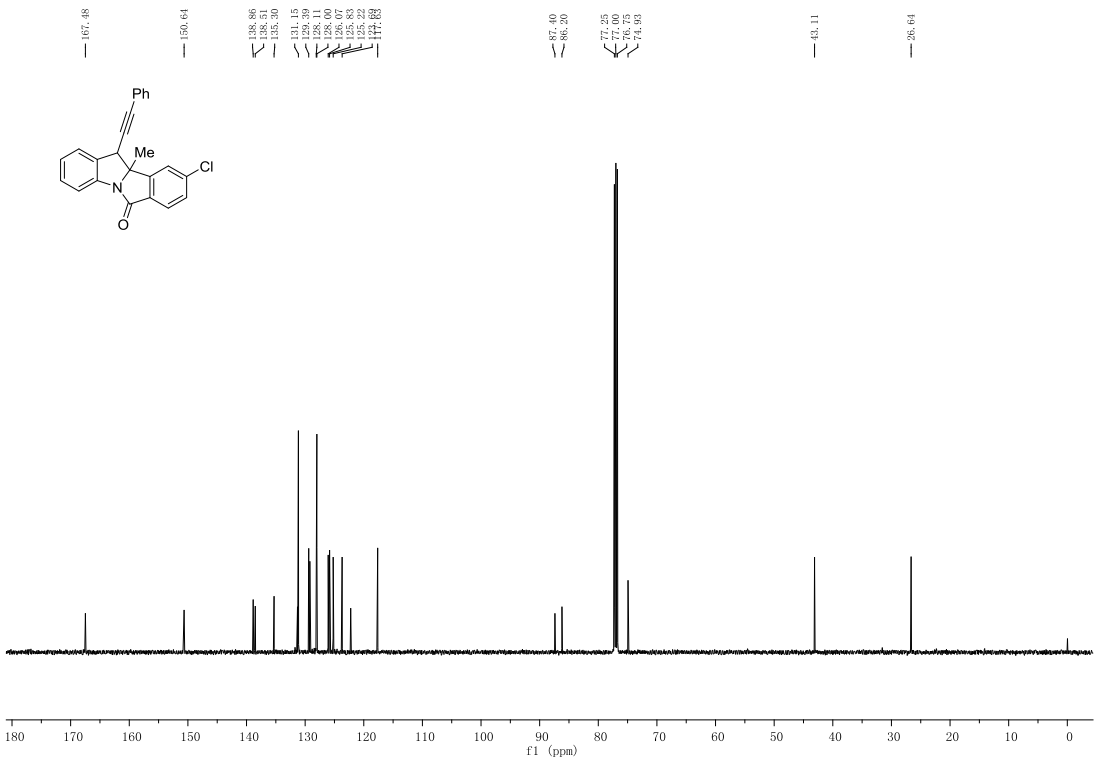
9-Chloro-10b-methyl-11-(phenylethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3ca**)



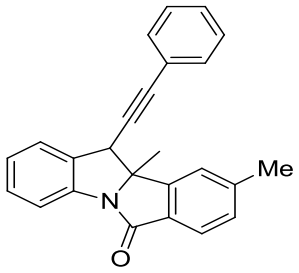
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 51.0 mg, 69% yield, m.p. 162−165 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 1.5 Hz, 1H), 7.52 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.41 (td, *J* = 7.5, 1.0 Hz, 1H), 7.17−7.23 (m, 2H), 7.12−7.15 (m, 2H), 6.87−6.89 (m, 2H), 4.24 (s, 1H), 1.72 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.5, 150.6, 138.9, 138.5, 135.3, 131.3, 131.2, 129.4, 129.2, 128.1, 128.0, 126.1, 125.8, 125.2, 123.7, 122.2, 117.6, 87.4, 86.2, 74.9, 43.1,

26.6. HRMS *m/z* (ESI+): Calculated for $C_{24}H_{17}ClNO$ ($[M+H]^+$): 370.0993, Found 370.0977.

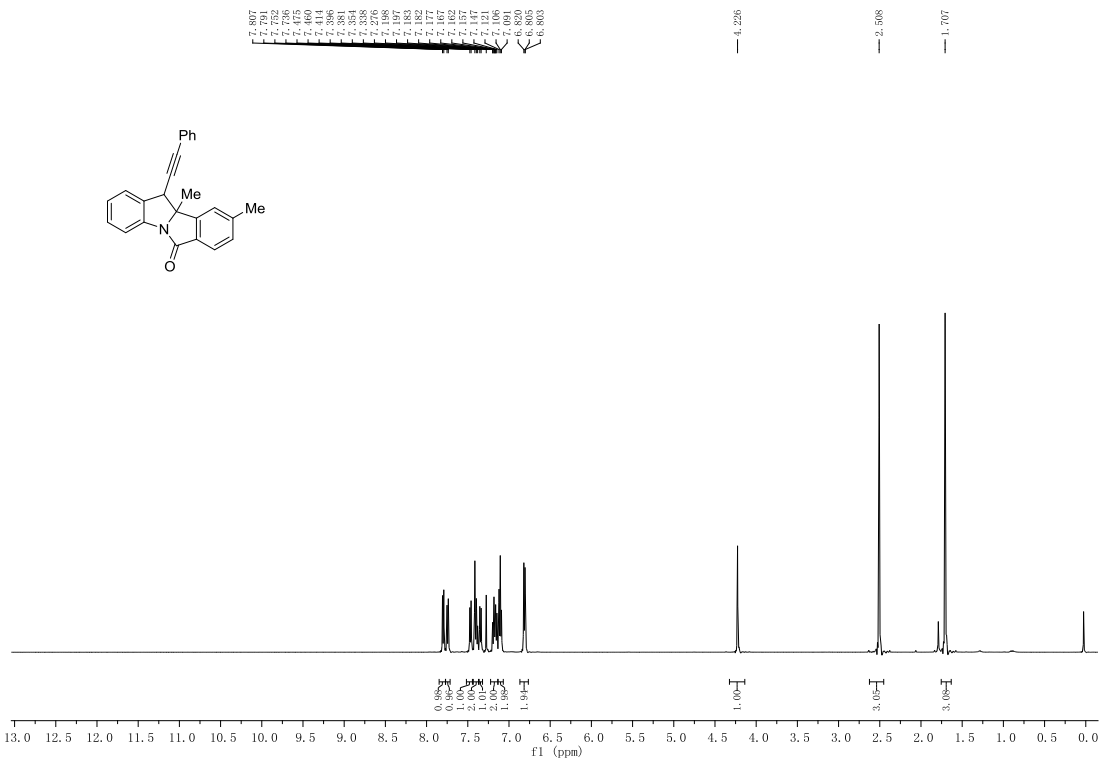




9,10b-Dimethyl-11-(phenylethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3da**)



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 59.0 mg, 84% yield, m.p. 165–167 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.38–7.41 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.15–7.20 (m, 2H), 7.11 (t, *J* = 7.5 Hz, 2H), 6.80–6.82 (m, 2H), 4.23 (s, 1H), 2.51 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.8, 149.5, 143.3, 138.9, 135.5, 131.1, 130.2, 129.7, 129.0, 127.9, 126.0, 124.8, 124.4, 123.6, 122.6, 117.6, 86.9, 86.8, 75.0, 43.1, 26.8, 22.0. HRMS *m/z* (ESI+): Calculated for $C_{25}H_{20}NO$ ($[M+H]^+$): 350.1539, Found 350.1566.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7.197
7.183
7.172
7.171
7.167
7.162
7.157
7.147
7.121
7.106
7.091
6.820
6.805
6.803
4.226
2.508
1.707
Ph
Me
Me
N
O
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0.96
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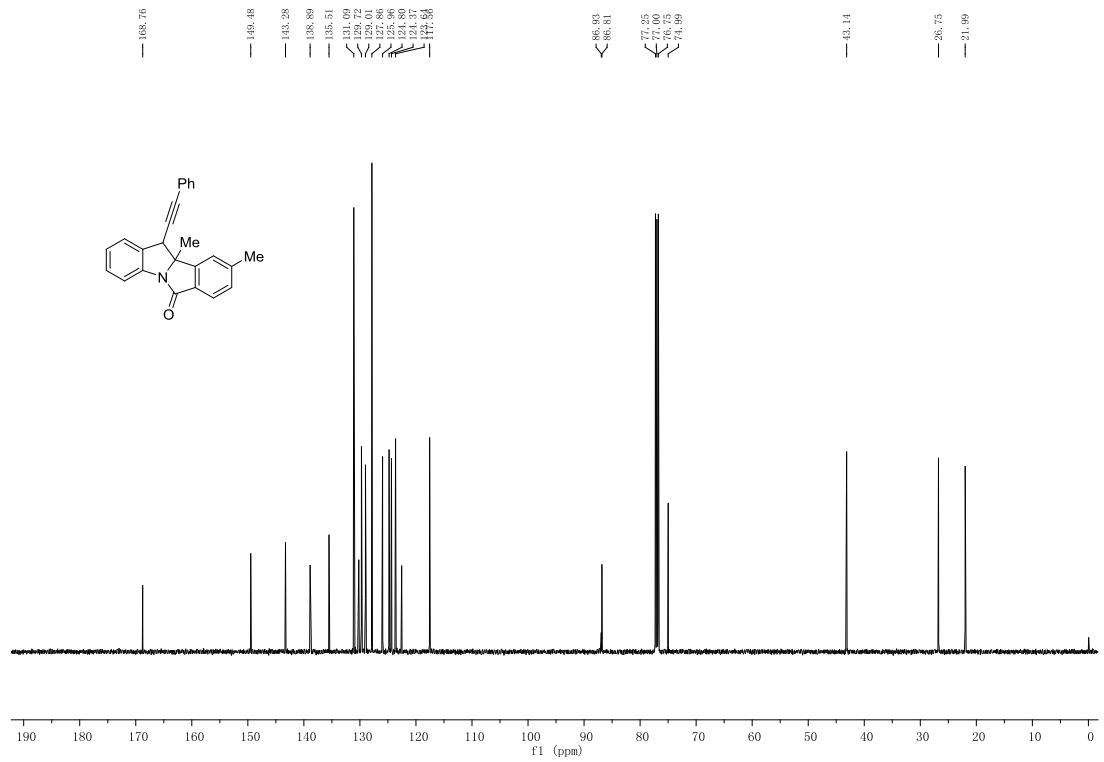
2.00
1.01
2.00
1.99
1.94
1.00
3.05
3.08
f1 (ppm)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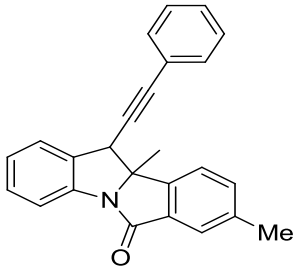
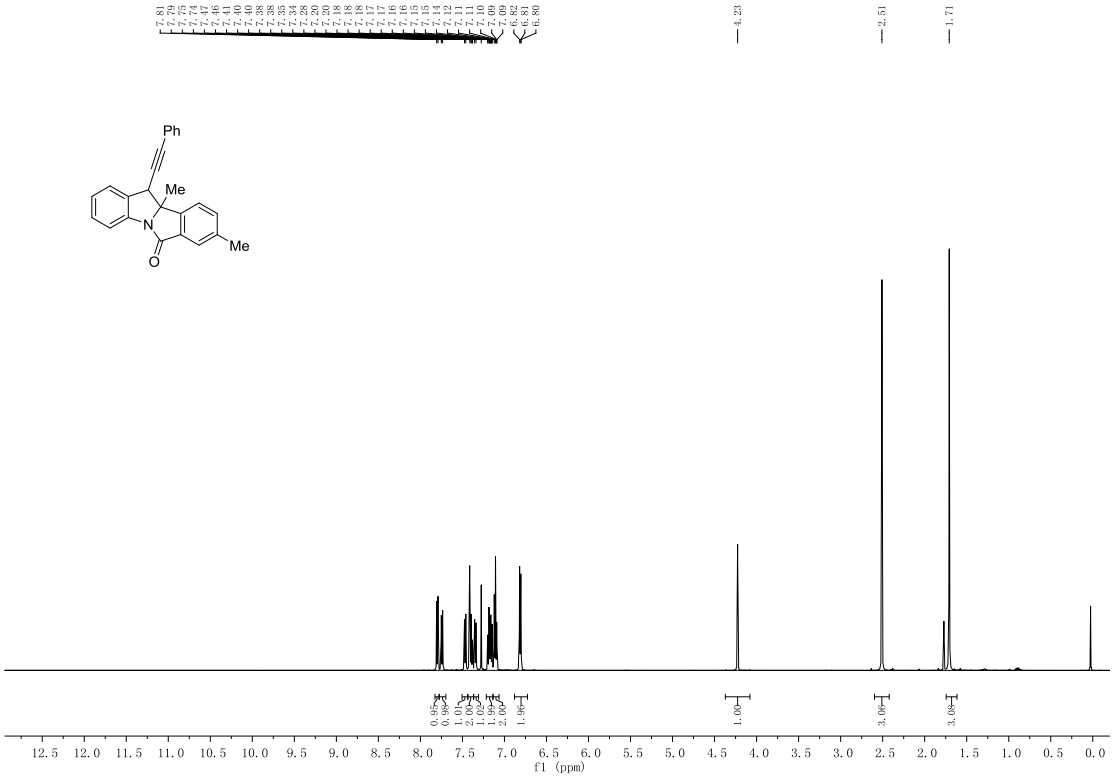
117.56
86.93
86.81
77.25
77.00
76.75
74.99
43.14
26.75
21.99
Ph
Me
Me
N
O
f1 (ppm)

8,10b-Dimethyl-11-(phenylethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3ea**)



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 58.3 mg, 83% yield, m.p. 161−164 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.38−7.41 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.15−7.20 (m, 2H), 7.09−7.12 (m, 2H), 6.80−6.82 (m, 2H), 4.23 (s, 1H), 2.51 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.8, 149.5, 143.3, 138.9, 135.6, 131.2, 130.3, 129.8, 129.0, 127.87, 127.86, 126.0, 124.8, 124.5, 123.6, 122.6, 117.6, 86.9, 86.8, 75.0, 43.2, 26.8, 22.0. HRMS *m/z* (ESI+): Calculated for $C_{25}H_{20}NO$ ($[M+H]^+$): 350.1539, Found 350.1549.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7.75
7.74
7.47
7.46
7.41
7.40
7.38
7.38
7.35
7.34
7.28
7.20
7.20
7.18
7.18
7.17
7.17
7.17
7.16
7.16
7.15
7.15
7.14
7.12
7.11
7.10
7.09
7.09
6.82
6.81
6.80
4.23
2.51
1.71
Ph
Me
N
O
Me
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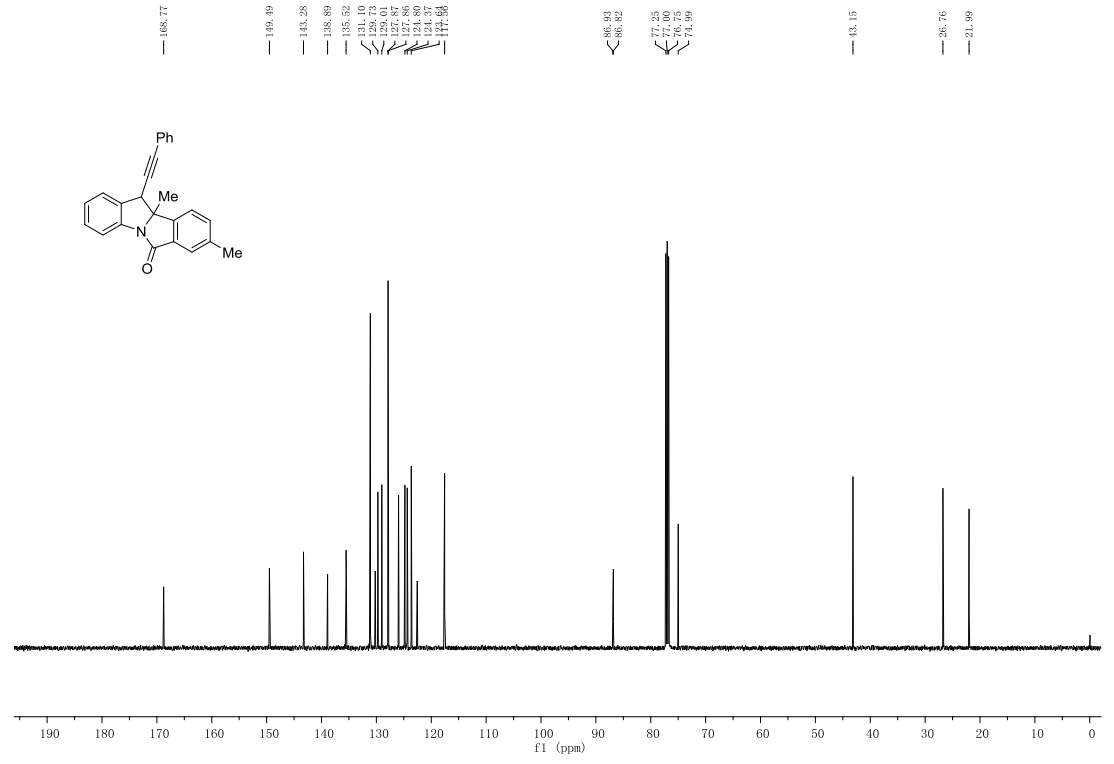
0.98
1.01
2.00
1.02
1.94
2.00
1.96
1.00
3.06
3.08
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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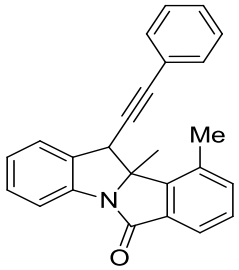
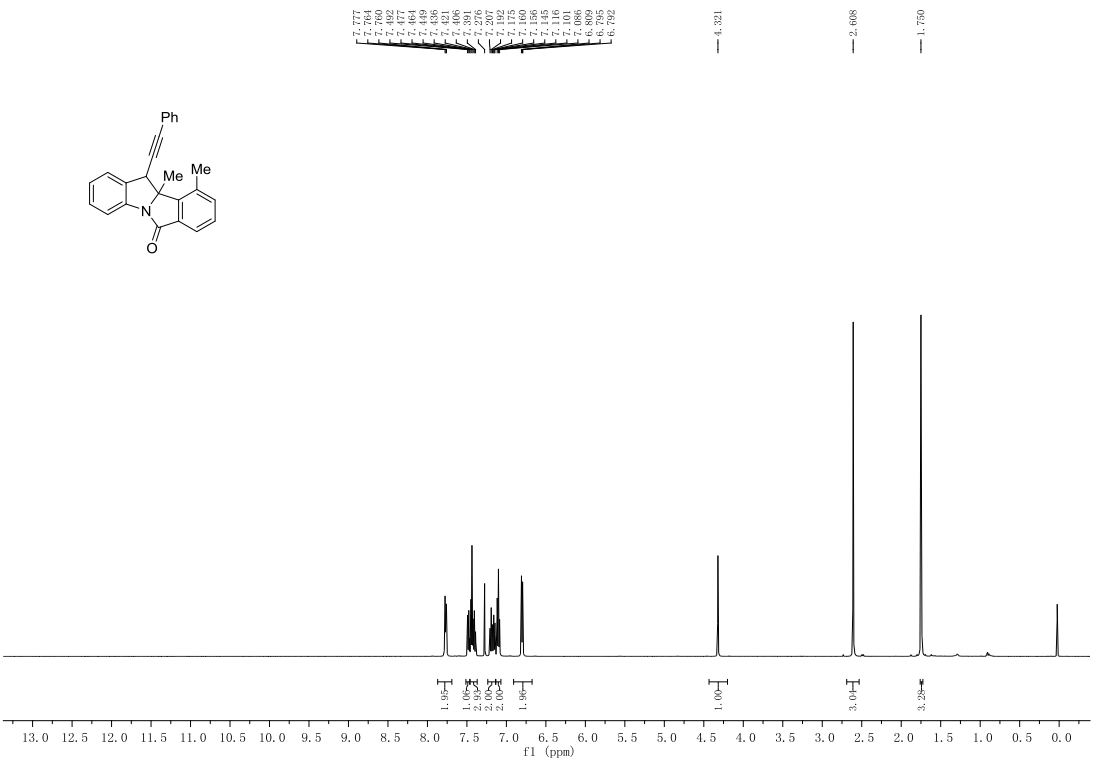
117.54
86.93
86.82
77.25
77.00
76.75
74.99
43.15
26.76
21.89
Ph
Me
N
O
Me
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

10,10b-Dimethyl-11-(phenylethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3fa**)



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 58.0 mg, 82% yield, m.p. 134−138 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76−7.77 (m, 2H), 7.46−7.49 (m, 1H), 7.39−7.45 (m, 3H), 7.15−7.21 (m, 2H), 7.10 (t, *J* = 7.5 Hz, 2H), 6.79−6.81 (m, 2H), 4.32 (s, 1H), 2.61 (s, 3H), 1.75 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.9, 147.0, 138.1, 135.5, 134.3, 133.4, 133.2, 131.2, 129.1, 129.0, 127.9, 126.0, 124.9, 122.5, 122.3, 117.3, 86.2, 86.1, 75.6, 42.3, 24.8, 18.8. HRMS *m/z* (ESI+): Calculated for $C_{25}H_{20}NO$ ($[M+H]^+$): 350.1539, Found 350.1524.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7.477
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7.406
7.391
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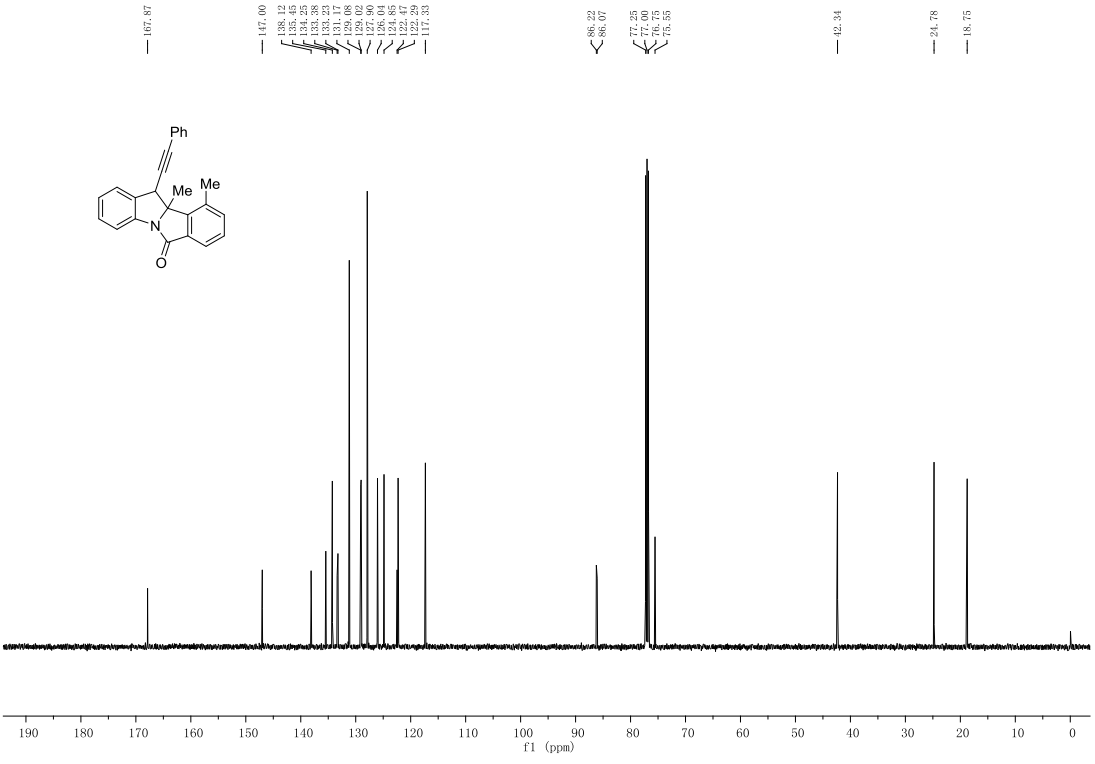
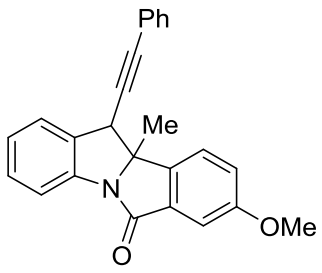
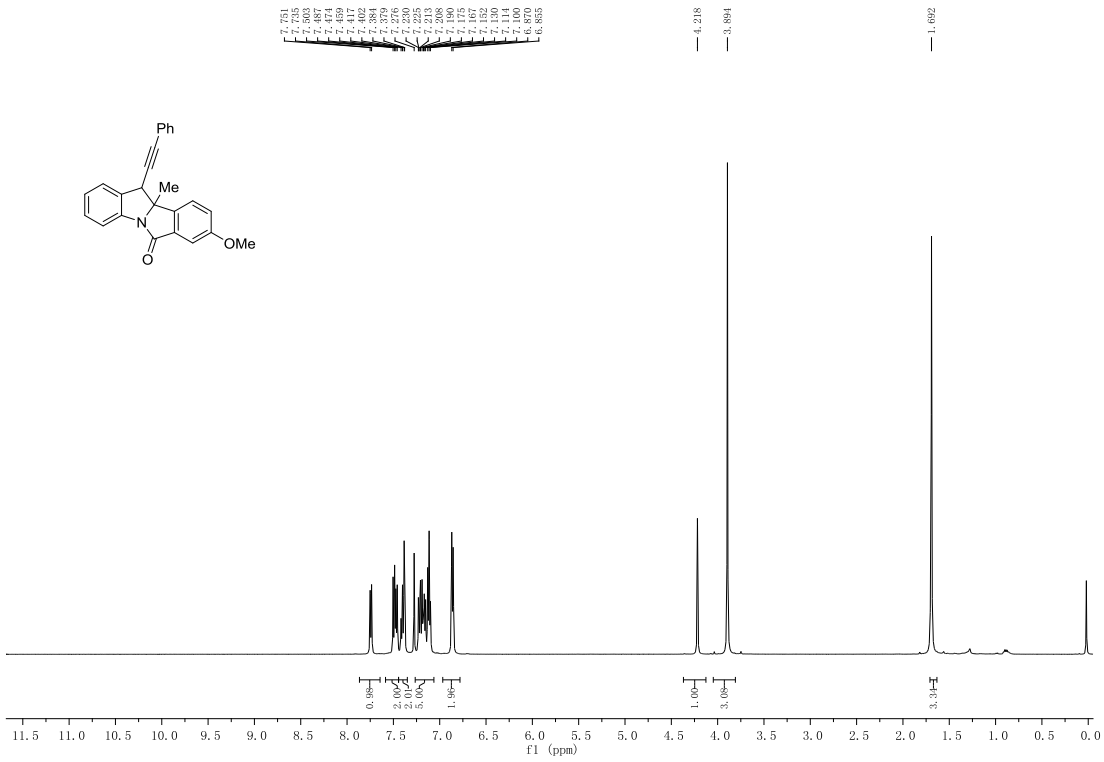
7.192
7.175
7.160
7.156
7.145
7.116
7.101
7.086
6.809
6.795
6.792
4.321
2.608
1.750
Ph
Me
Me
N
O
1.95
1.08
2.92
2.00
2.00
1.96
1.00
3.04
3.29
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


167.87
147.00
138.12
135.45
134.25
133.38
133.23
131.17
129.08
129.02
127.90
126.84
124.85
122.47
122.29
117.33
86.22
86.07
77.25
77.00
76.75
75.55
42.34
24.78
18.75
Ph
Me
Me
N
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

8-Methoxy-10b-methyl-11-(phenylethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3ga**)



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 57.0 mg, 78% yield, m.p. 101−104 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.46−7.50 (m, 2H), 7.38−7.42 (m, 2H), 7.10−7.23 (m, 5H), 6.86 (d, *J* = 7.5 Hz, 2H), 4.22 (s, 1H), 3.89 (s, 3H), 1.69 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.5, 160.5, 141.5, 138.7, 135.9, 134.2, 131.2, 129.0, 127.9, 126.0, 124.9, 124.0, 122.5, 120.8, 117.6, 107.1, 86.9, 86.7, 74.9, 55.7, 43.2, 26.8. HRMS *m/z* (ESI+): Calculated for $C_{25}H_{20}NO_2$ ($[M+H]^+$): 366.1489, Found 366.1461.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7.459
7.417
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7.379
7.276
7.230
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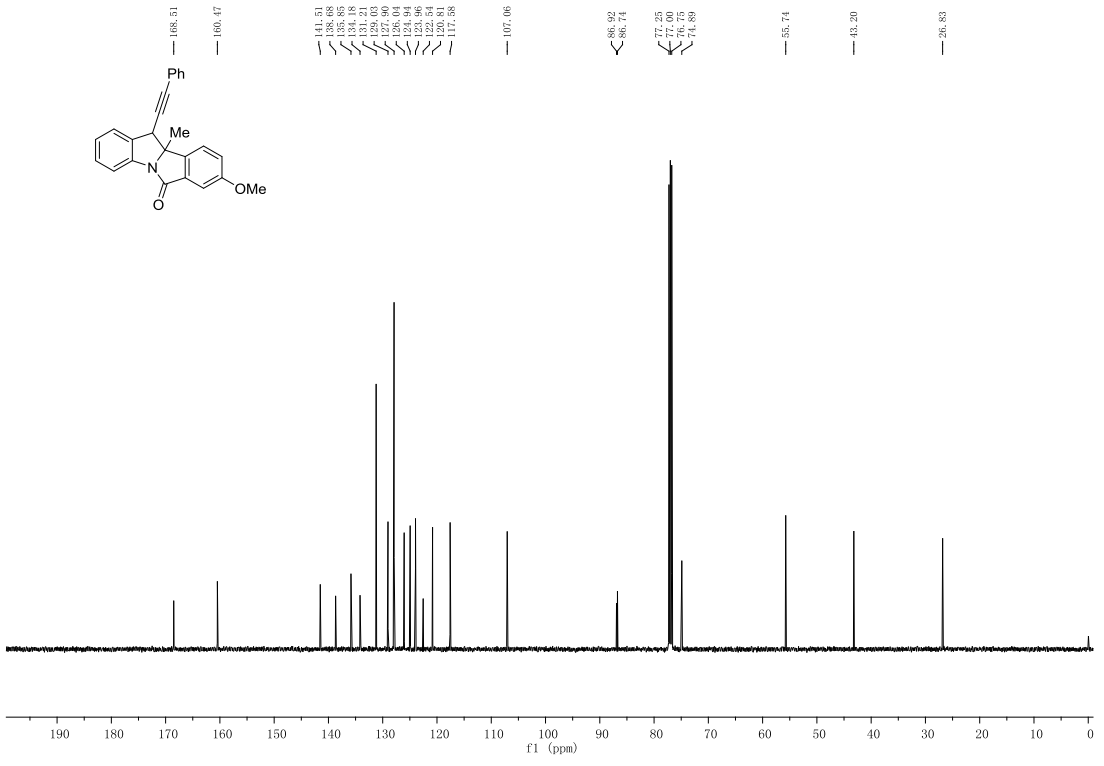
7.213
7.208
7.190
7.175
7.167
7.152
7.130
7.114
7.100
6.870
6.855
4.218
3.894
1.692
Ph
Me
N
O
OMe
0.98
2.04
2.01
5.00
1.98
1.00
3.08
3.34
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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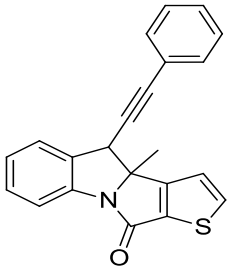
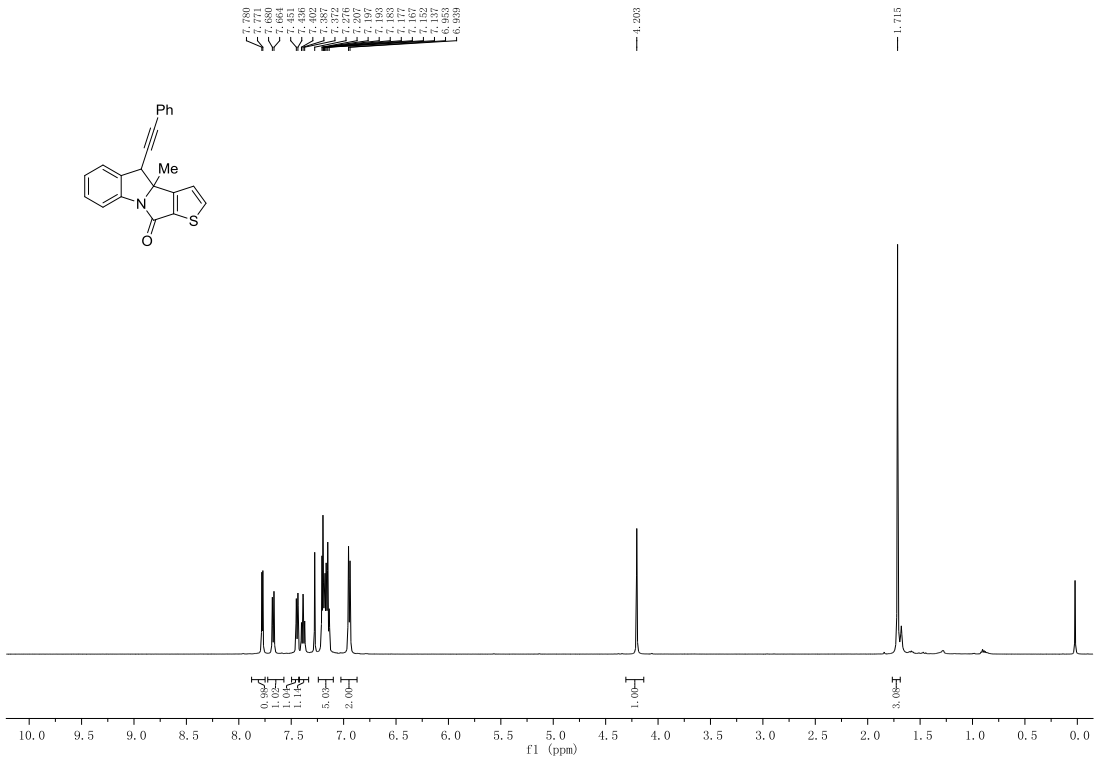
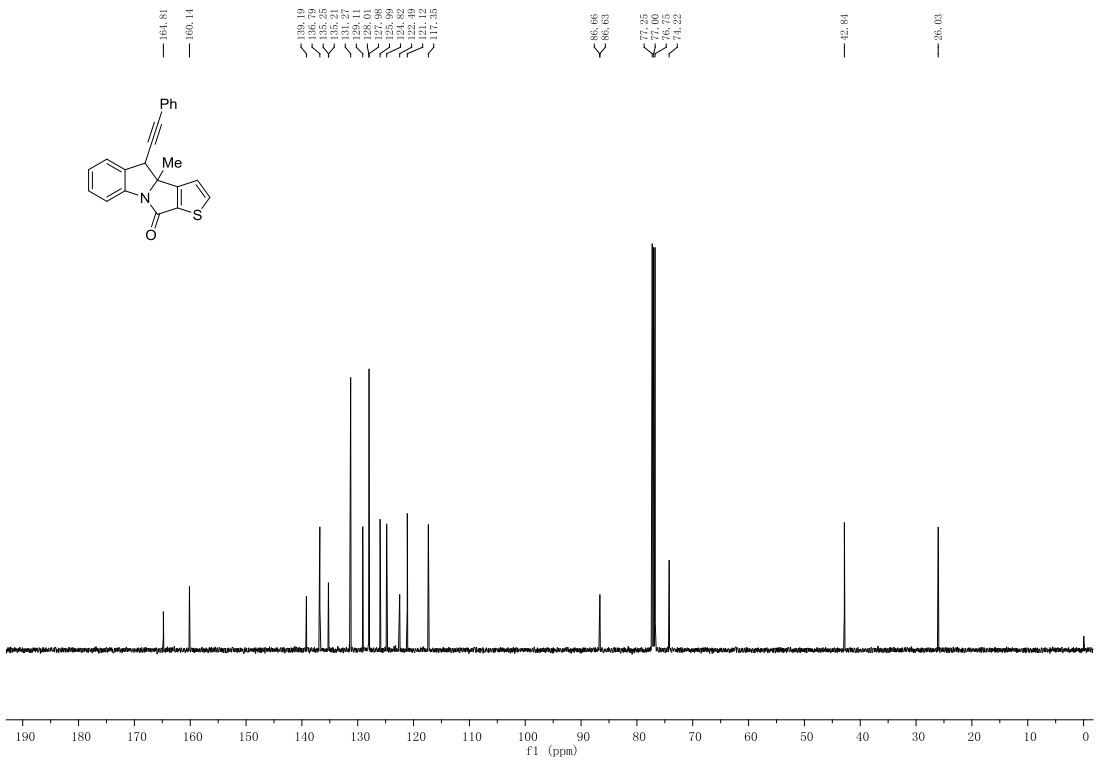
77.25
77.00
76.75
74.80
55.74
43.20
26.83
Ph
Me
N
O
OMe
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3b-Methyl-4-(phenylethynyl)-3b,4-dihydro-10H-thieno[3',2':3,4]pyrrolo[1,2-a]indol-10-one (**3ha**)

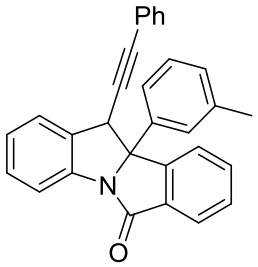


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 31.5 mg, 47% yield, m.p. 148–150 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, *J* = 4.5 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.14–7.20 (m, 5H), 6.95 (d, *J* = 7.0 Hz, 2H), 4.20 (s, 1H), 1.71 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.8, 160.1, 139.2, 136.8, 135.3, 135.2, 131.3 129.1, 128.01, 127.98, 126.0, 124.8, 122.5, 121.1, 117.4, 86.7, 86.6, 74.2, 42.8, 26.0. HRMS *m/z* (ESI+): Calculated for $C_{22}H_{16}NOS$ ($[M+H]^+$): 342.0947, Found 342.0958.

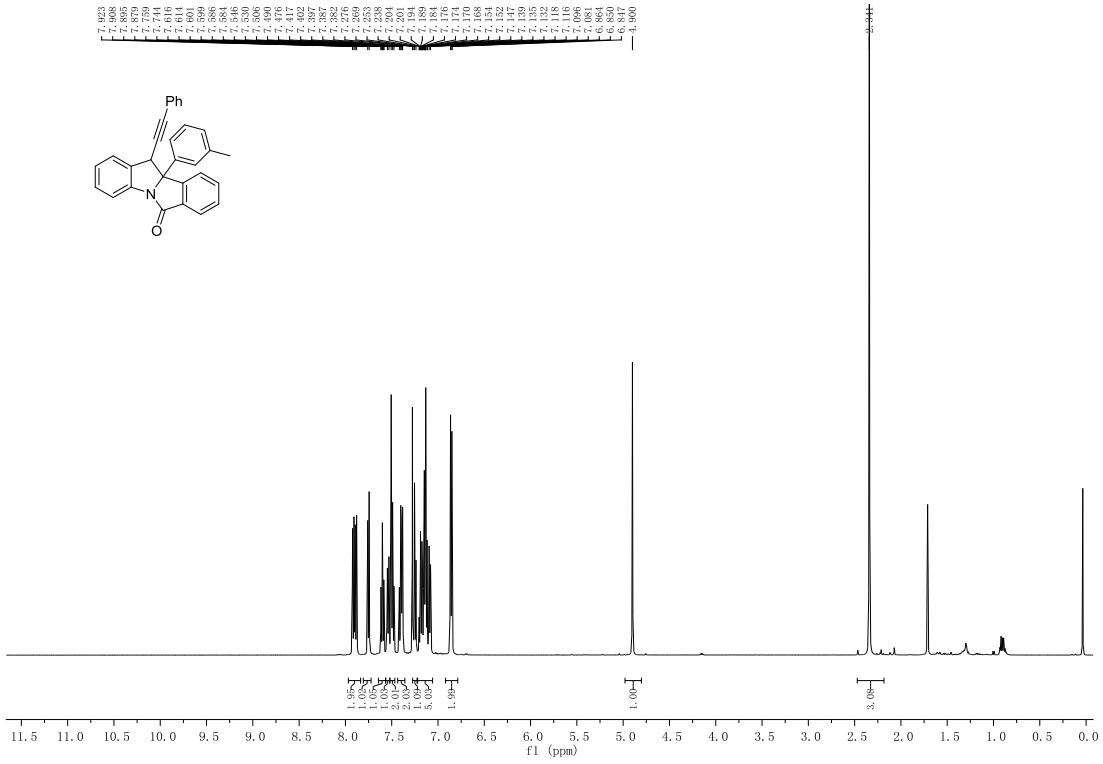

7.780
7.771
7.680
7.664
7.451
7.436
7.402
7.387
7.372
7.276
7.207
7.197
7.193
7.183
7.177
7.167
7.152
7.137
6.953
6.939
4.203
1.715
Ph
Me
N
S
O
0.98
1.05
1.00
1.14
5.05
2.00
1.00
3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

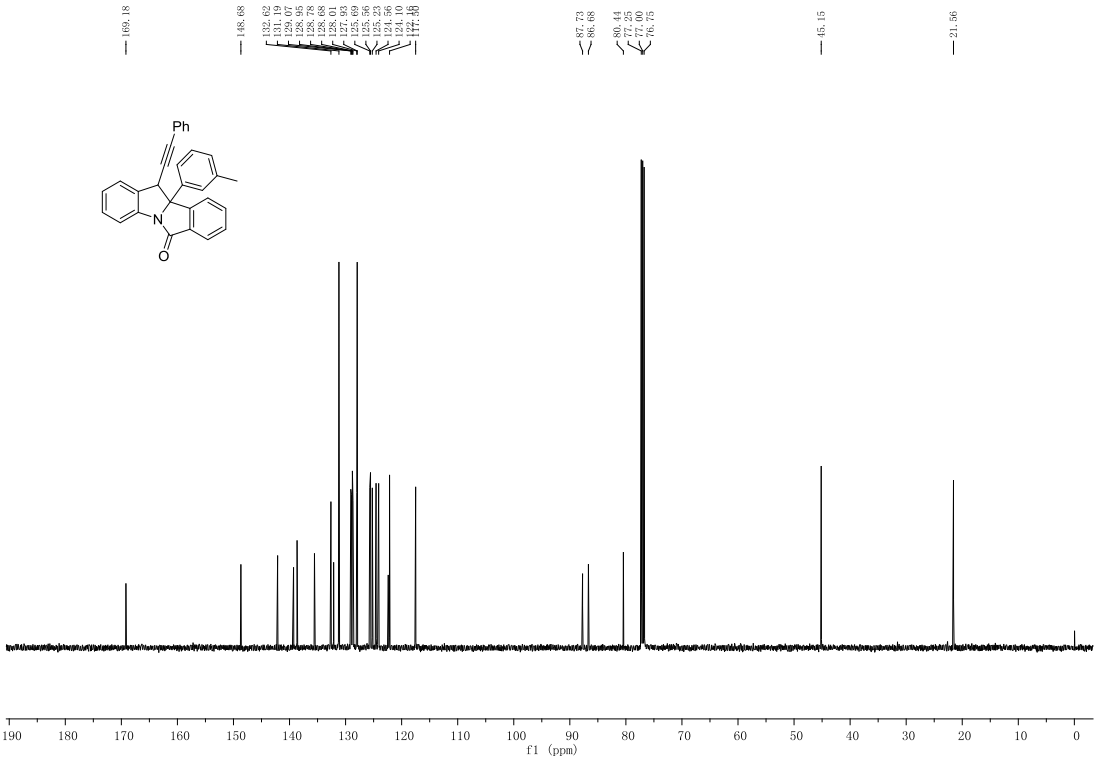

164.81
160.14
139.19
136.79
135.25
135.21
131.27
131.11
128.01
127.98
125.99
123.82
122.49
121.12
117.35
86.66
86.63
77.25
77.00
76.75
74.22
42.84
26.03
Ph
Me
N
S
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

11-(Phenylethynyl)-10b-(*m*-tolyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3ia**)

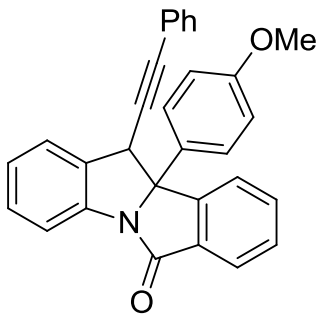


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 60.0 mg, 73% yield, m.p. 147−150 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (dd, *J* = 14.5, 8.0 Hz, 2H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.60 (td, *J* = 7.5, 1.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.38−7.42 (m, 2H), 7.44−7.36 (m, 2H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.08−7.20 (m, 5H), 6.85−6.86 (m, 2H), 4.90 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.2, 148.7, 142.1, 139.3, 138.7, 135.6, 132.6, 132.1, 131.2, 129.1, 129.0, 128.8, 128.7, 128.0, 127.9, 125.7, 125.6, 125.2, 124.6, 124.1, 122.4, 122.2, 117.5, 87.7, 86.7, 80.4, 45.2, 21.6. HRMS *m/z* (ESI+): Calculated for $C_{30}H_{22}NO$ ($[M+H]^+$): 412.1696, Found 412.1662.

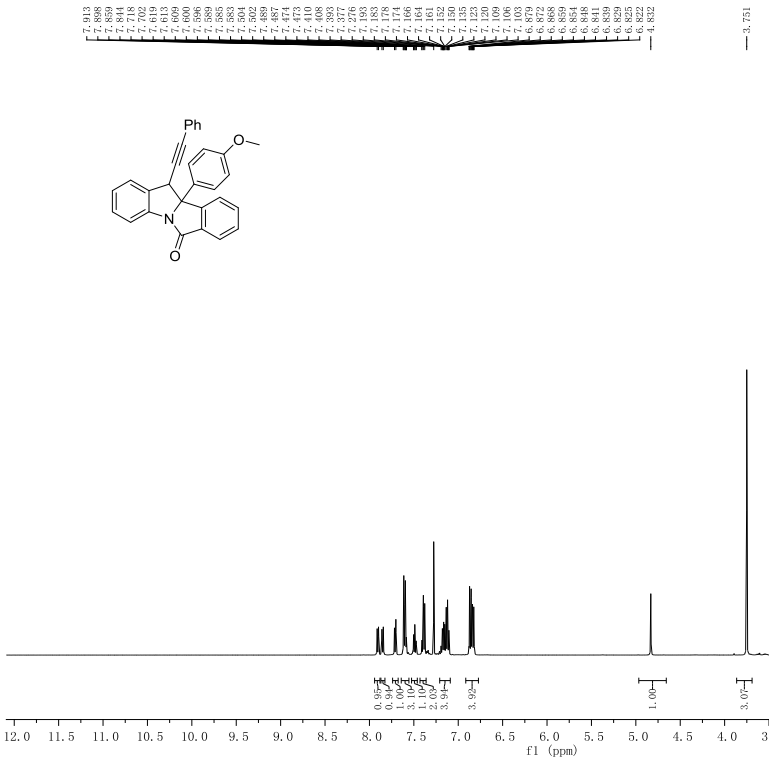

Ph
N
O
f1 (ppm)

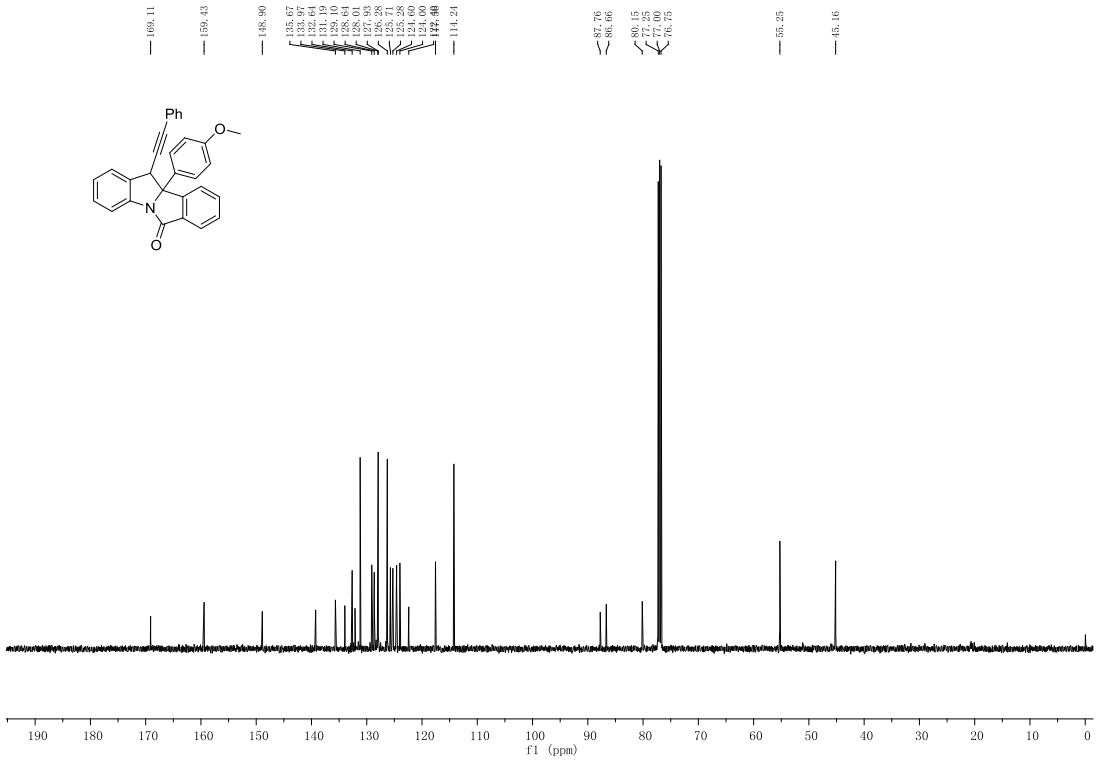

Ph
N
O
f1 (ppm)

10b-(4-Methoxyphenyl)-11-(phenylethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3ja**)

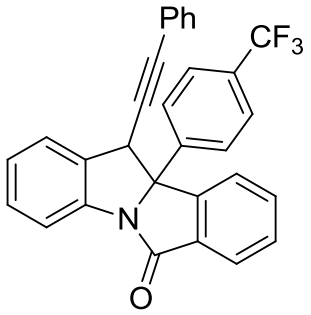


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 51.2 mg, 60% yield, m.p. 112−115 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.5 Hz, 1H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.58−7.62 (m, 3H), 7.49 (td, *J* = 7.5, 1.5 Hz, 1H), 7.38−7.41 (m, 2H), 7.10−7.19 (m, 4H), 6.82−6.88 (m, 4H), 4.83 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.1, 159.4, 148.9, 139.2, 135.7, 134.0, 132.6, 132.1, 131.2, 129.1, 128.6, 128.0, 127.9, 126.3, 125.7, 125.3, 124.6, 124.0, 122.4, 117.6, 114.2, 87.8, 86.7, 80.2, 55.3, 45.2. HRMS *m/z* (ESI+): Calculated for $C_{30}H_{22}NO_2$ ($[M+H]^+$): 428.1645, Found 428.1611.

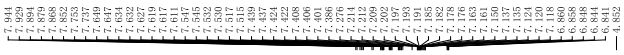

7.913
7.898
7.859
7.844
7.718
7.702
7.619
7.613
7.604
7.600
7.596
7.589
7.585
7.583
7.504
7.502
7.489
7.487
7.474
7.473
7.410
7.408
7.393
7.377
7.276
7.193
7.183
7.178
7.174
7.166
7.164
7.161
7.152
7.150
7.135
7.123
7.120
7.109
7.106
7.103
6.879
6.872
6.868
6.859
6.854
6.848
6.841
6.839
6.829
6.825
6.822
4.832
3.751
Ph
O
N
O
0.95
0.94
1.00
3.10
1.10
2.03
3.94
3.92
1.00
3.07
12.0 11.5 11.0 10.5 10.0 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
f1 (ppm)

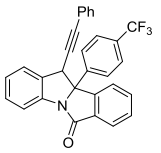

169.11
159.43
148.90
135.67
133.97
132.64
131.19
129.10
128.64
128.01
127.93
126.28
125.71
125.28
124.60
124.00
114.24
87.76
86.66
80.15
77.25
77.00
76.75
55.25
45.16
Ph
O
N
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

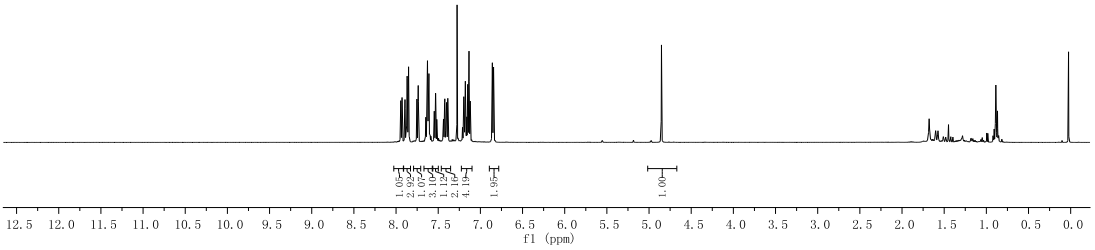
11-(Phenylethynyl)-10b-(4-(trifluoromethyl)phenyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3ka**)

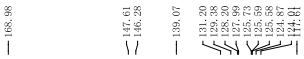


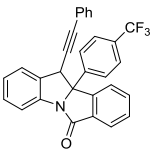
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 71.6 mg, 77% yield, m.p. 86–90 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.5 Hz, 1H), 7.85–7.89 (m, 3H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.61–7.65 (m, 3H), 7.53 (td, *J* = 7.5, 1.0 Hz, 1H), 7.39–7.44 (m, 2H), 7.12–7.21 (m, 4H), 6.84–6.86 (m, 2H), 4.85 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.0, 147.6, 146.3, 139.1, 135.0, 132.9, 132.2, 131.2, 130.5 (q, *J* = 32.5 Hz), 129.4, 129.2, 128.2, 128.0, 126.0 (q, *J* = 3.8 Hz), 125.7, 125.59, 125.58, 124.9, 124.0, 122.7, 122.2, 117.6, 88.2, 86.0, 80.2, 45.3. HRMS *m/z* (ESI+): Calculated for $C_{30}H_{19}F_3NO$ ($[M+H]^+$): 466.1413, Found 466.1432.

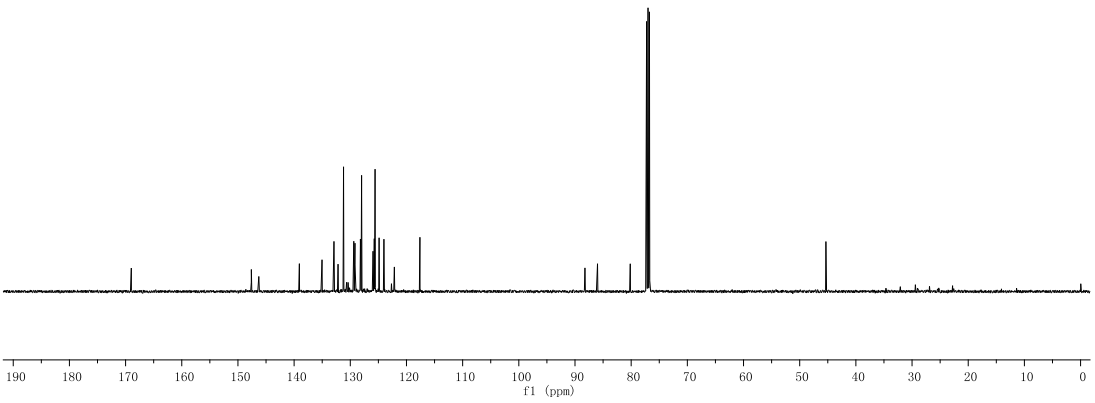



Ph
CF3
N
O

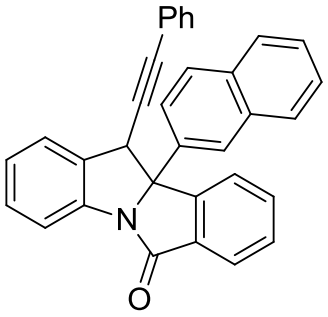

1.05
2.05
3.10
1.12
2.10
4.19
1.95
1.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



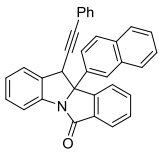

Ph
CF3
N
O

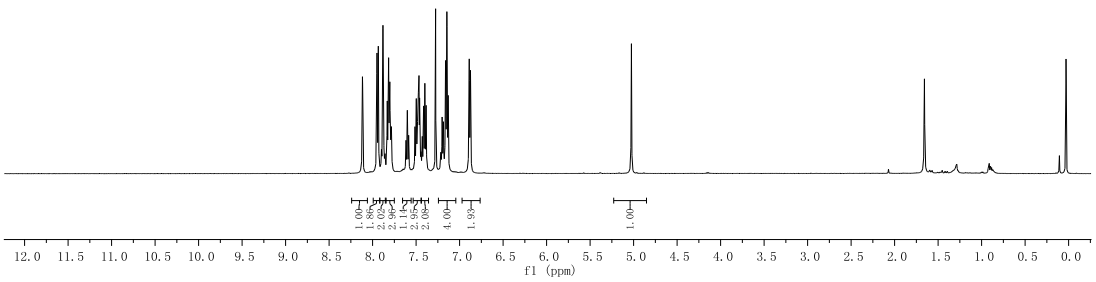

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

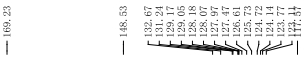
10b-(Naphthalen-2-yl)-11-(phenylethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3la**)

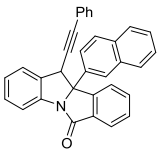


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 65.2 mg, 73% yield, m.p. 177−180 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.86−7.90 (m, 2H), 7.78−7.83 (m, 3H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.44−7.51 (m, 3H), 7.39−7.43 (m, 2H), 7.13−7.22 (m, 4H), 6.88 (d, *J* = 7.0 Hz, 2H), 5.03 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.2, 148.5, 139.3, 139.2, 135.5, 133.0, 132.9, 132.7, 132.2, 131.2, 129.2, 129.1, 128.8, 128.2, 128.1, 128.0, 127.5, 126.6, 126.5, 125.7, 125.3, 124.7, 124.1, 123.8, 123.1, 122.4, 117.6, 87.8, 86.6, 80.6, 45.0. HRMS *m/z* (ESI+): Calculated for $C_{33}H_{22}NO$ ($[M+H]^+$): 448.1696, Found 448.1692.


Ph
N
O

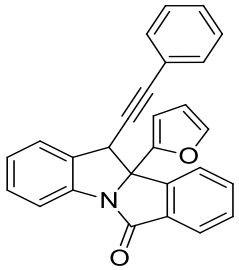

1.00
1.98
2.02
2.96
1.14
2.95
2.06
4.00
1.93
1.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



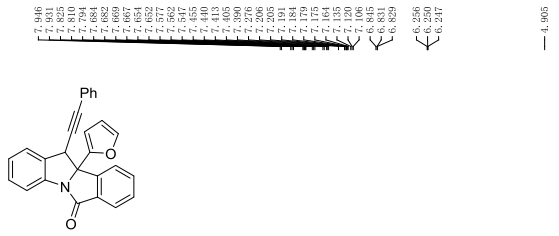

Ph
N
O

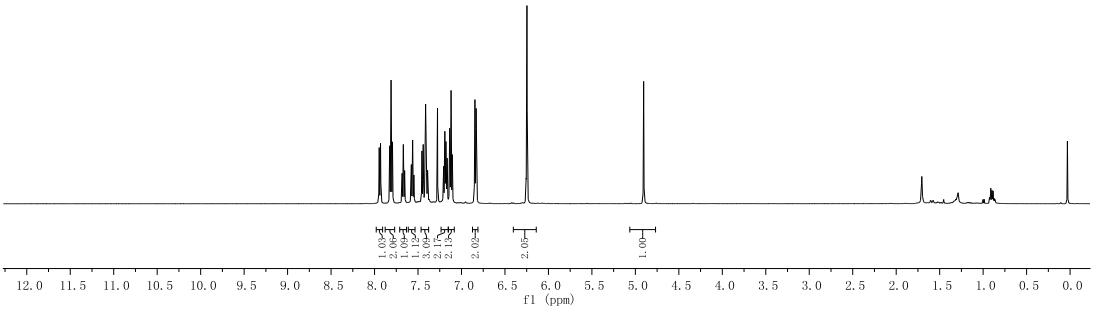
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

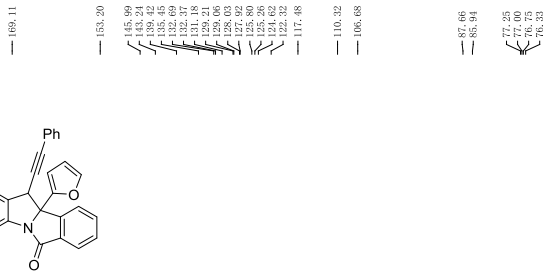
10b-(Furan-2-yl)-11-(phenylethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3ma**)

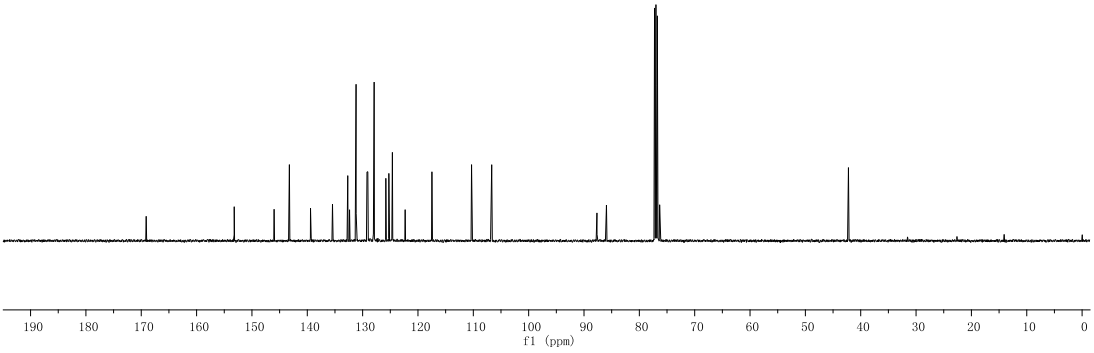


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 59.0 mg, 76% yield, m.p. 131−134 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (d, *J* = 7.5 Hz, 1H), 7.81 (t, *J* = 8.0 Hz, 2H), 7.67 (td, *J* = 7.5, 1.0 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.39−7.46 (m, 3H), 7.16−7.21 (m, 2H), 7.12 (t, *J* = 7.5 Hz, 2H), 6.83−6.85 (m, 2H), 6.25−6.26 (m, 2H), 4.91 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.1, 153.2, 146.0, 143.2, 139.4, 135.5, 132.7, 132.4, 131.2, 129.2, 129.1, 128.0, 127.9, 125.8, 125.3, 124.6, 122.3, 117.5, 110.3, 106.7, 87.7, 85.9, 76.3, 42.2. HRMS *m/z* (ESI+): Calculated for $C_{27}H_{18}NO_2$ ($[M+H]^+$): 388.1332, Found 388.1331.

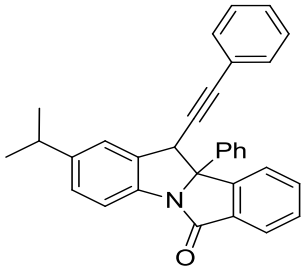

7.946
7.931
7.895
7.810
7.794
7.684
7.682
7.669
7.667
7.654
7.652
7.577
7.562
7.547
7.455
7.440
7.413
7.405
7.390
7.276
7.206
7.195
7.191
7.184
7.179
7.175
7.164
7.135
7.120
7.106
6.845
6.831
6.829
6.256
6.250
6.247
4.905
Ph
O
N
O


1.03
2.09
2.04
1.09
1.12
3.09
2.15
2.13
2.02
2.05
1.00
12.0 11.5 11.0 10.5 10.0 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
f1 (ppm)

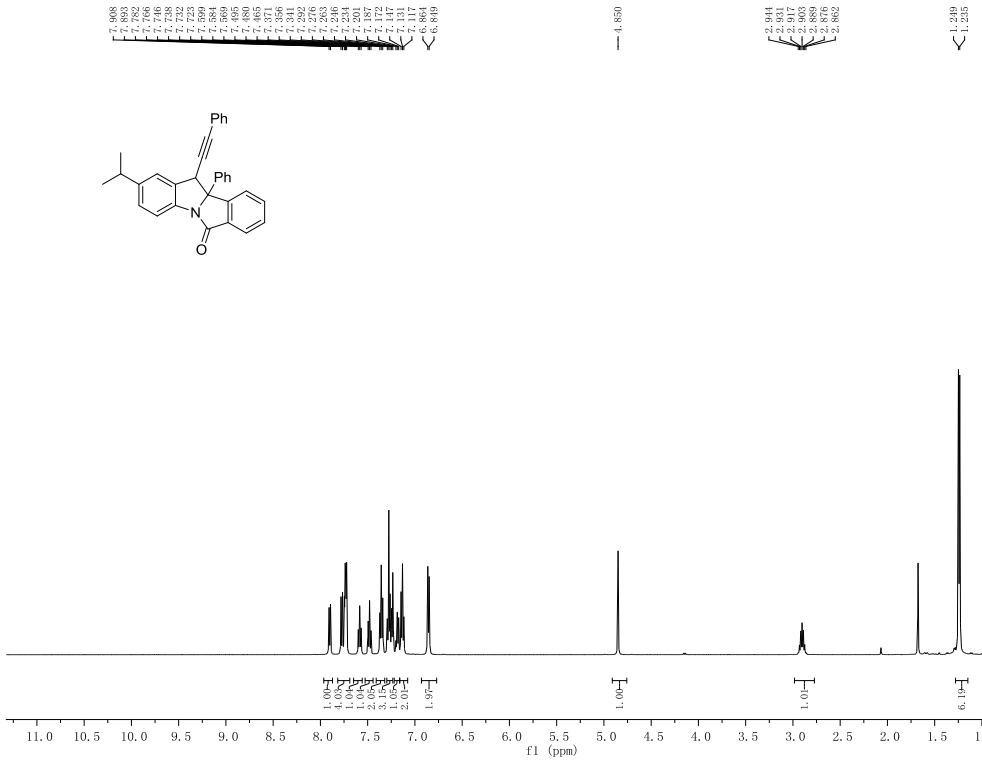

169.11
153.20
145.99
143.24
139.42
135.45
132.69
132.37
131.18
129.21
129.06
128.03
127.92
125.80
125.36
124.62
122.32
117.48
110.32
106.68
87.66
85.94
77.25
77.00
76.75
76.33
42.22
Ph
O
N
O

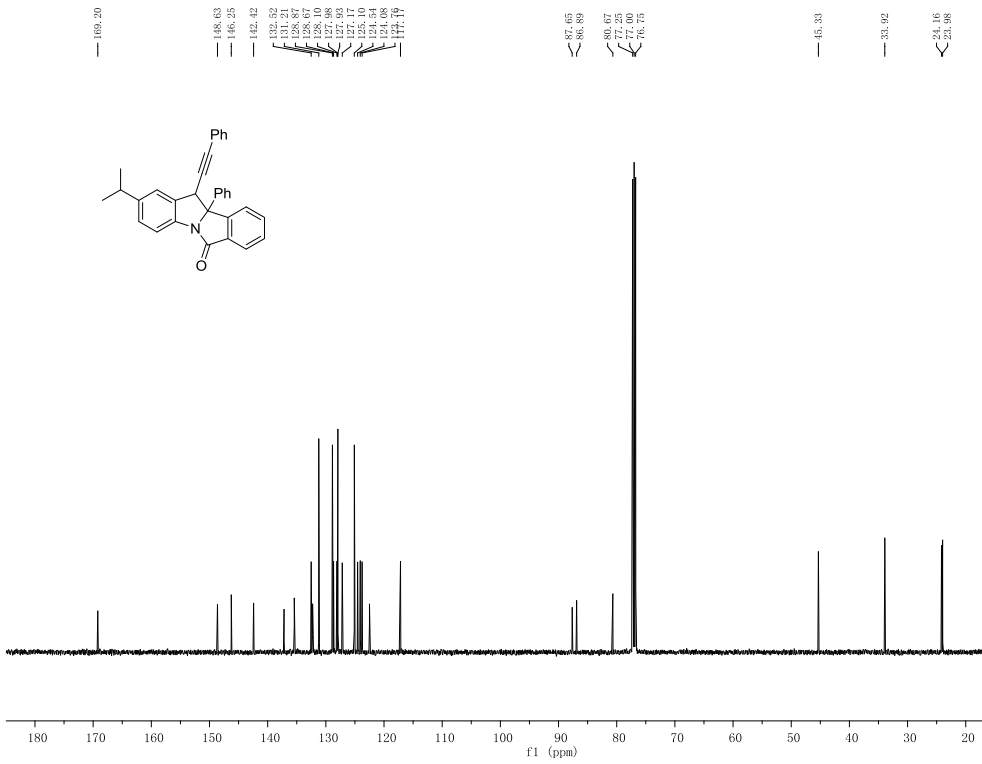

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2-Isopropyl-10b-phenyl-11-(phenylethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3na**)

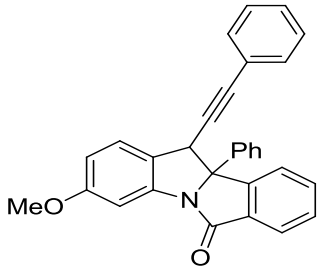


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 47.5 mg, 54% yield, m.p. 178–180 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.5 Hz, 1H), 7.72–7.78 (m, 4H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.23–7.29 (m, 3H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 7.5 Hz, 2H), 4.85 (s, 1H), 2.86–2.94 (m, 1H), 1.24 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.2, 148.6, 146.3, 142.4, 137.2, 135.4, 132.5, 132.3, 131.2, 128.9, 128.7, 128.1, 128.0, 127.9, 127.2, 125.1, 124.5, 124.1, 123.8, 122.5, 117.2, 87.7, 86.9, 80.7, 45.3, 33.9, 24.2, 24.0. HRMS *m/z* (ESI+): Calculated for $C_{32}H_{26}NO$ ($[M+H]^+$): 440.2009, Found 440.1992.

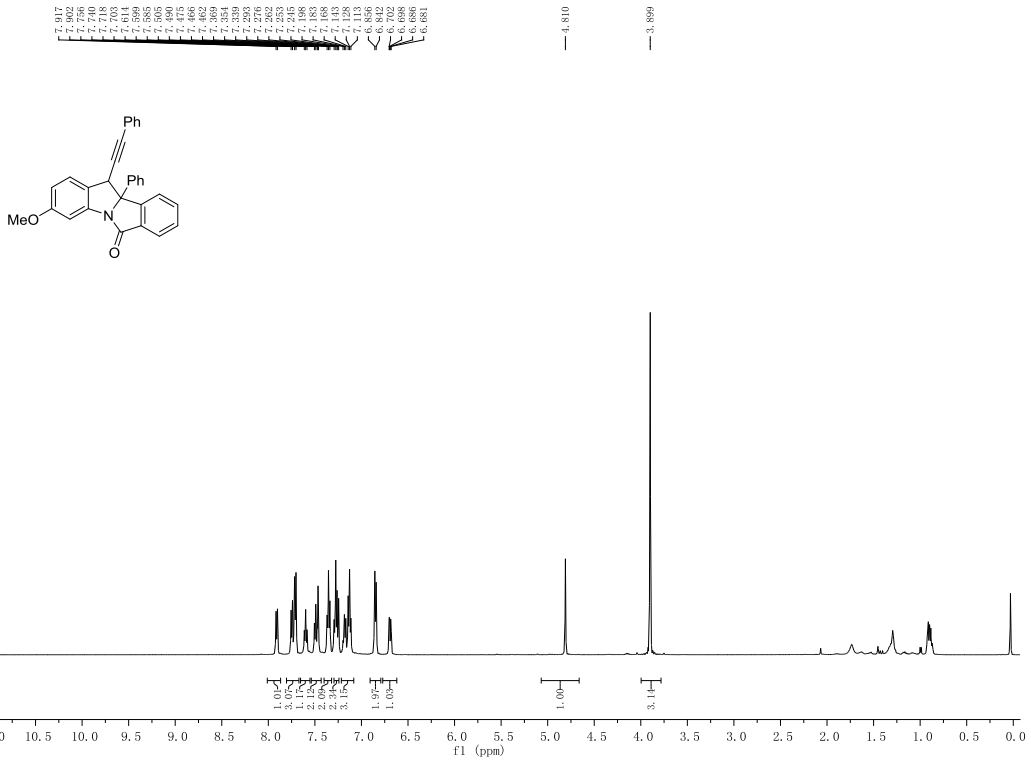

7.908
7.893
7.782
7.766
7.746
7.738
7.732
7.723
7.569
7.884
7.495
7.480
7.465
7.371
7.356
7.341
7.292
7.276
7.263
7.246
7.234
7.210
7.187
7.172
7.147
7.131
7.117
6.864
6.849
4.850
2.944
2.931
2.917
2.903
2.889
2.876
2.862
1.249
1.235
Ph
Ph
N
O
1.00
4.05
1.04
1.04
3.15
1.05
2.01
1.97
1.00
1.01
6.19
11.0 10.5 10.0 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
f1 (ppm)

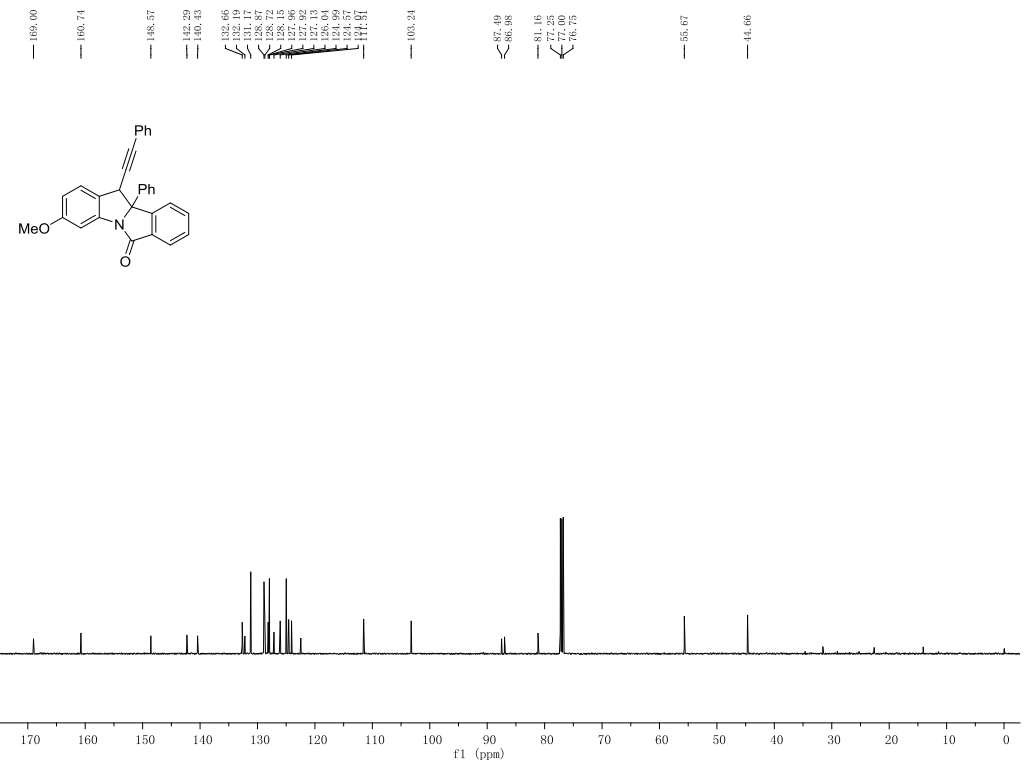

169.20
148.63
146.25
142.42
132.52
131.21
128.87
128.67
128.10
127.98
127.93
127.17
125.10
124.54
124.08
123.76
117.17
87.65
86.89
80.67
77.25
77.00
76.75
45.33
33.92
24.16
23.98
Ph
Ph
N
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3-Methoxy-10b-phenyl-11-(phenylethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3oa**)

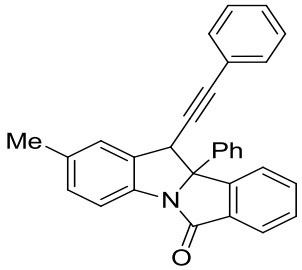


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 71.4 mg, 82% yield, m.p. 74–76 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.5 Hz, 1H), 7.70–7.76 (m, 3H), 7.60 (t, *J* = 7.0 Hz, 1H), 7.46–7.51 (m, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.25–7.29 (m, 2H), 7.11–7.20 (m, 3H), 6.85 (d, *J* = 7.0 Hz, 2H), 6.69 (dd, *J* = 8.5, 2.5 Hz, 1H), 4.81 (s, 1H), 3.90 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.0, 160.7, 148.6, 142.3, 140.4, 132.7, 132.2, 131.2, 128.9, 128.8, 128.2, 128.0, 127.9, 127.1, 126.0, 125.0, 124.6, 124.1, 122.5, 111.5, 103.2, 87.5, 87.0, 81.2, 55.7, 44.7. HRMS *m/z* (ESI+): Calculated for $C_{30}H_{22}NO_2$ ($[M+H]^+$): 428.1645, Found 428.1637.

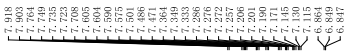

7.917
7.902
7.756
7.740
7.718
7.703
7.614
7.599
7.585
7.565
7.490
7.475
7.466
7.462
7.369
7.354
7.339
7.293
7.276
7.262
7.253
7.245
7.198
7.183
7.168
7.143
7.128
7.113
6.856
6.842
6.702
6.698
6.686
6.681
4.810
3.899
Ph
Ph
MeO
N
O
1.01
3.05
1.15
1.15
2.09
2.34
3.15
1.97
1.03
1.00
3.14
11.5 11.0 10.5 10.0 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
f1 (ppm)


169.00
160.74
148.57
142.29
140.43
132.66
132.19
131.17
128.87
128.72
128.15
127.96
127.92
127.13
126.04
124.99
124.57
111.97
103.24
87.49
86.98
81.16
77.35
77.00
76.75
55.67
44.66
Ph
Ph
MeO
N
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

2-Methyl-10b-phenyl-11-(phenylethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3pa**)



Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 51.8 mg, 63% yield, m.p. 192−195 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.5 Hz, 1H), 7.71−7.76 (m, 4H), 7.59 (t, *J* = 7.5, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.26−7.29 (m, 1H), 7.17−7.21 (m, 3H), 7.13 (t, *J* = 7.5 Hz, 2H), 6.85−6.86 (m, 2H), 4.83 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.1, 148.5, 142.2, 136.9, 135.6, 135.1, 132.5, 132.3, 131.2, 129.7, 128.9, 128.7, 128.1, 128.0, 127.9, 126.3, 125.1, 124.5, 124.0, 122.4, 117.2, 87.7, 86.7, 80.7, 45.3, 21.2. HRMS *m/z* (ESI+): Calculated for $C_{30}H_{22}NO$ ($[M+H]^+$): 412.1696, Found 412.1692.


7.918
7.903
7.764
7.749
7.735
7.723
7.708
7.605
7.604
7.590
7.575
7.501
7.488
7.471
7.364
7.349
7.333
7.298
7.276
7.272
7.257
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7.201
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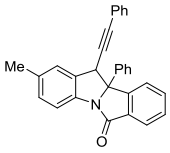
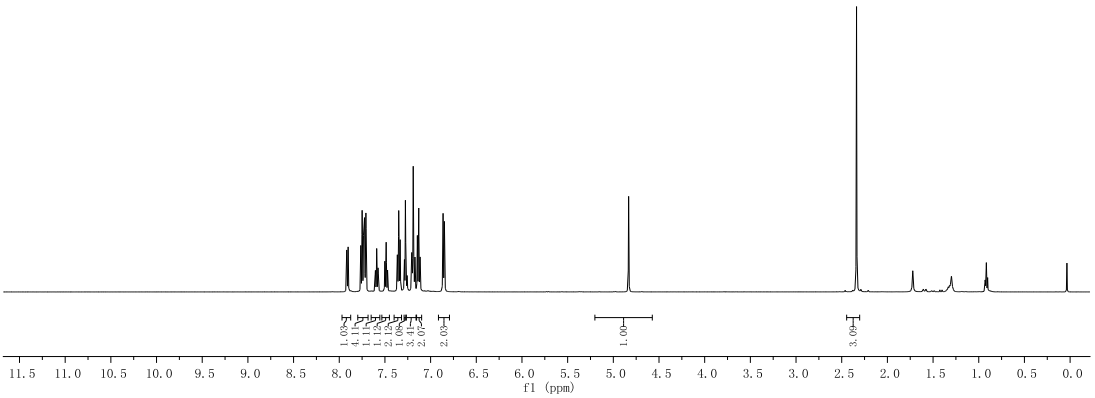
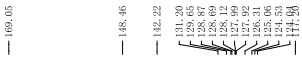
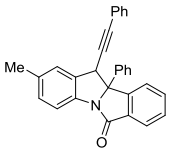
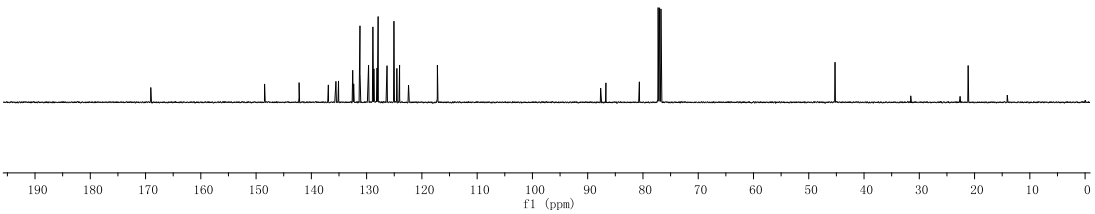
7.115
6.864
6.849
6.847
4.833
2.338


Ph
Me
Ph
N
O

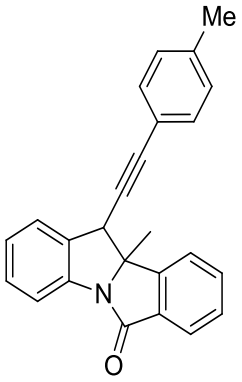

1.03
4.15
1.13
2.12
1.04
3.45
2.07
2.03
1.00
3.09
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


169.05
148.46
142.22
131.20
129.65
128.87
128.69
128.12
127.99
127.92
126.31
125.06
124.53
124.04
111.20
87.66
86.70
80.65
77.25
77.00
76.75
45.25
21.16

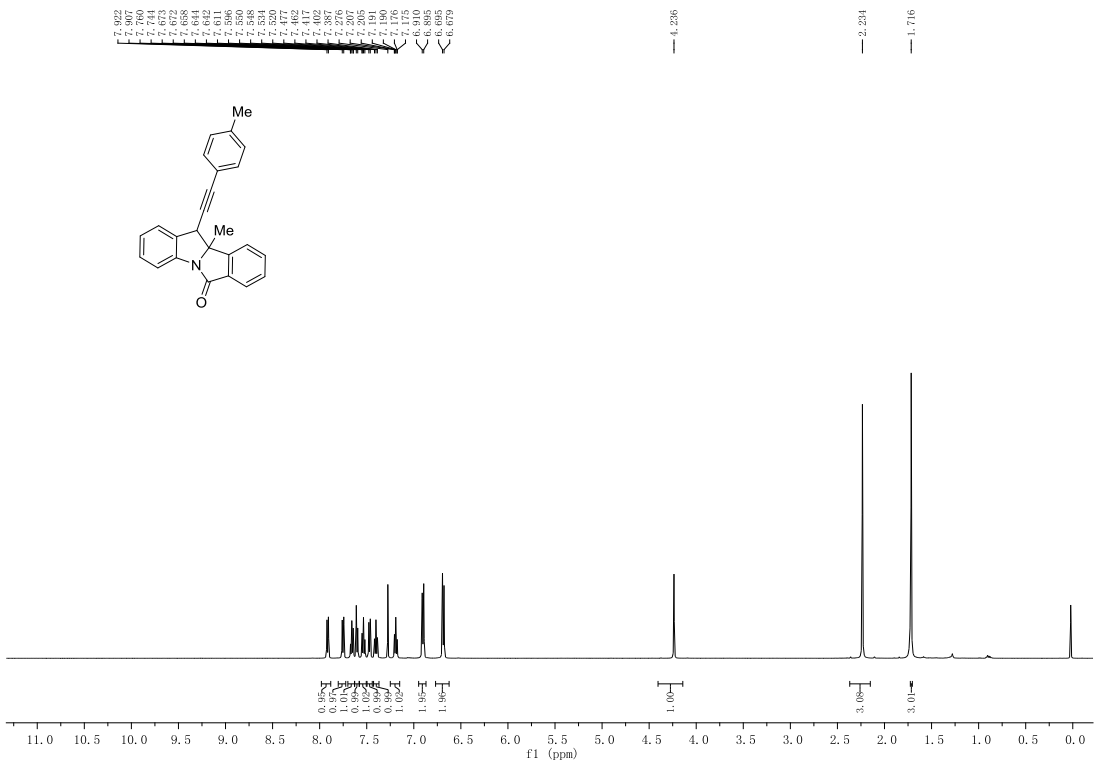

Ph
Me
Ph
N
O

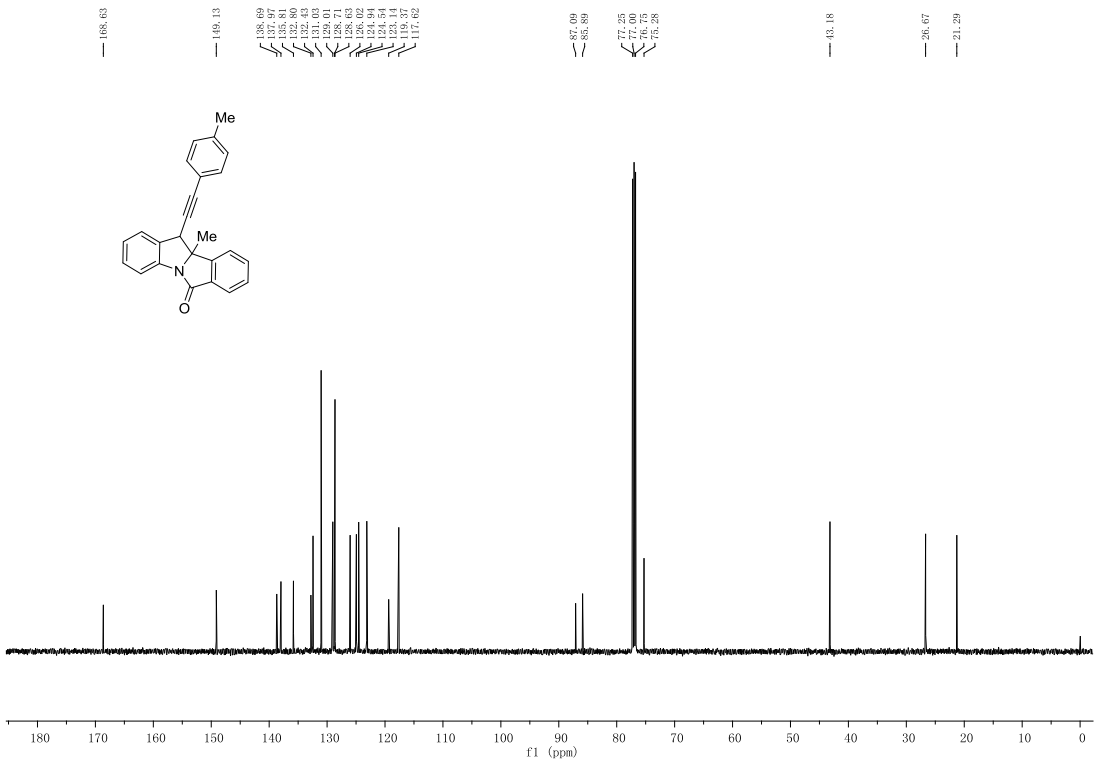

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

10b-Methyl-11-(*p*-tolylethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3ab**)

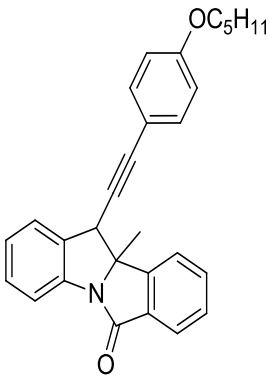


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 55.0 mg, 82% yield, m.p. 118–120 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.64–7.67 (m, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.52–7.55 (m, 1H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.19 (td, *J* = 7.5, 0.5 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 2H), 6.69 (d, *J* = 8.0 Hz, 2H), 4.24 (s, 1H), 2.23 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.6, 149.1, 138.7, 138.0, 135.8, 132.8, 132.4, 131.0, 129.0, 128.7, 128.6, 126.0, 124.9, 124.5, 123.1, 119.4, 117.6, 87.1, 85.9, 75.3, 43.2, 26.7, 21.3. HRMS *m/z* (ESI+): Calculated for $C_{25}H_{20}NO$ ($[M+H]^+$): 350.1539, Found 350.1558.

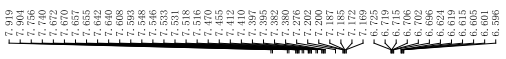

7.922
7.907
7.760
7.744
7.673
7.672
7.658
7.644
7.642
7.641
7.596
7.550
7.548
7.534
7.520
7.477
7.462
7.417
7.402
7.387
7.276
7.207
7.205
7.191
7.190
7.176
7.175
6.910
6.695
6.695
6.679
4.236
2.234
1.716
Me
Me
N
O
0.95
0.97
1.01
0.99
1.02
0.99
0.99
1.02
1.95
1.86
1.00
3.08
3.01
11.0 10.5 10.0 9.5 9.0 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
f1 (ppm)

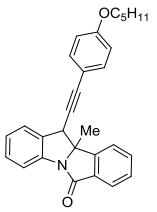

168.63
149.13
138.69
137.97
135.81
132.80
132.43
131.03
129.01
128.71
128.63
126.02
124.94
124.54
123.14
119.37
117.62
87.09
85.89
77.25
77.00
76.75
75.28
43.18
26.67
21.29
Me
Me
N
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

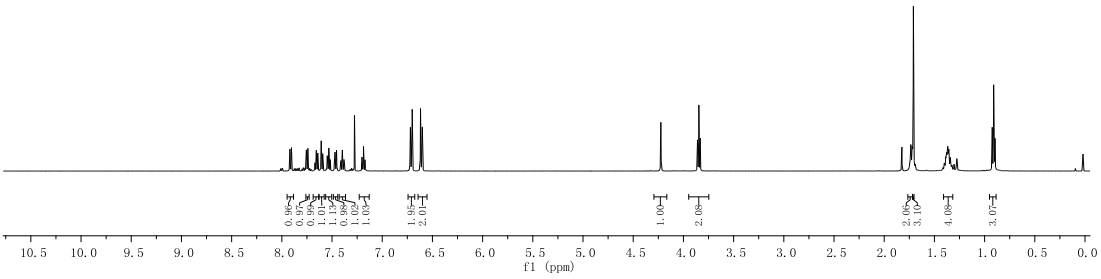
10b-Methyl-11-((4-(pentyloxy)phenyl)ethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3ac**)

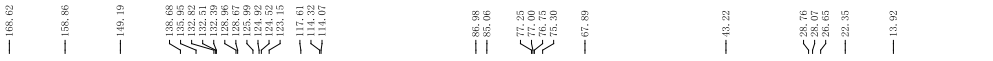


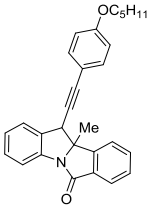
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 71.6 mg, 85% yield, m.p. 114−115 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.66 (td, *J* = 7.5, 1.0 Hz, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.53 (td, *J* = 7.5, 1.0 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.40 (td, *J* = 7.5, 1.0 Hz, 1H), 7.19 (td, *J* = 7.5, 1.0 Hz, 1H), 6.70−6.73 (m, 2H), 6.60 −6.62 (m, 2H), 4.22 (s, 1H), 3.85 (t, *J* = 6.5 Hz, 2H), 1.72−1.75 (m, 2H), 1.71 (s, 3H), 1.32−1.41 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.6, 158.9, 149.2, 138.7, 136.0, 132.8, 132.5, 132.4, 129.0, 128.7, 126.0, 124.9, 124.5, 123.2, 117.6, 114.3, 114.1, 87.0, 85.1, 75.3, 67.9, 43.2, 28.8, 28.1, 26.7, 22.4, 13.9. HRMS *m/z* (ESI+): Calculated for $C_{29}H_{28}NO_2$ ($[M+H]^+$): 422.2115, Found 422.2092.

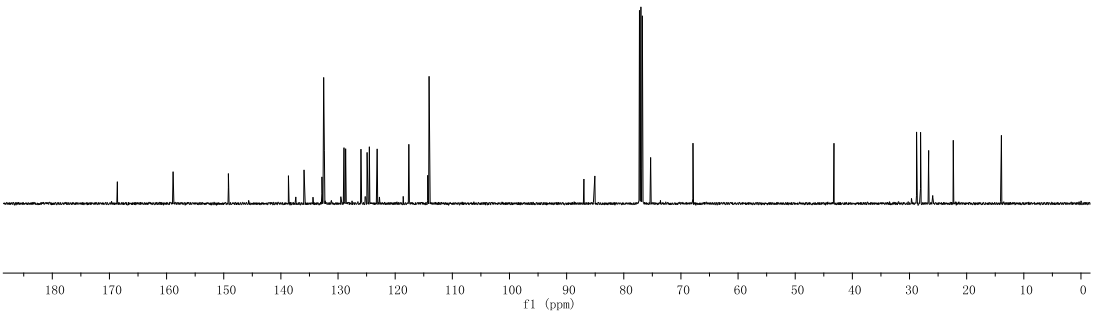



OC5H11
Me
N
O

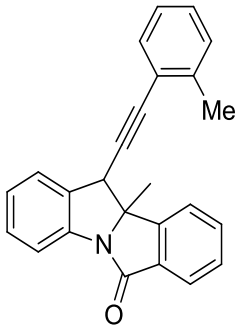

f1 (ppm)



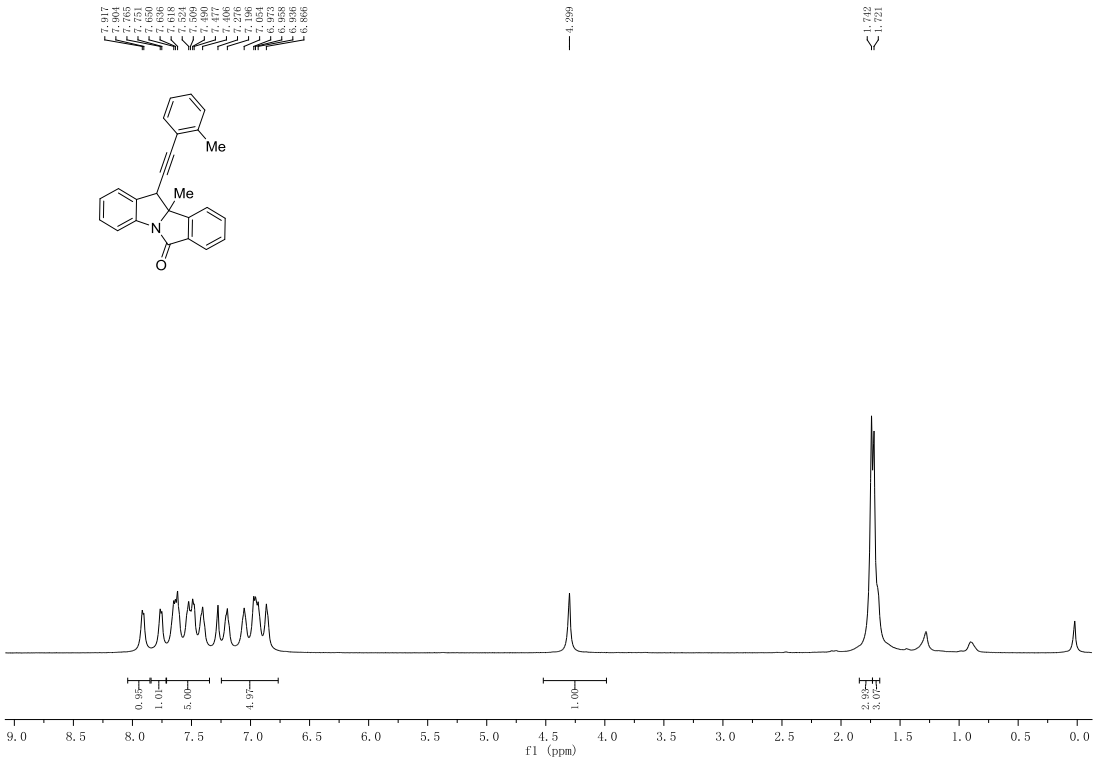

OC5H11
Me
N
O

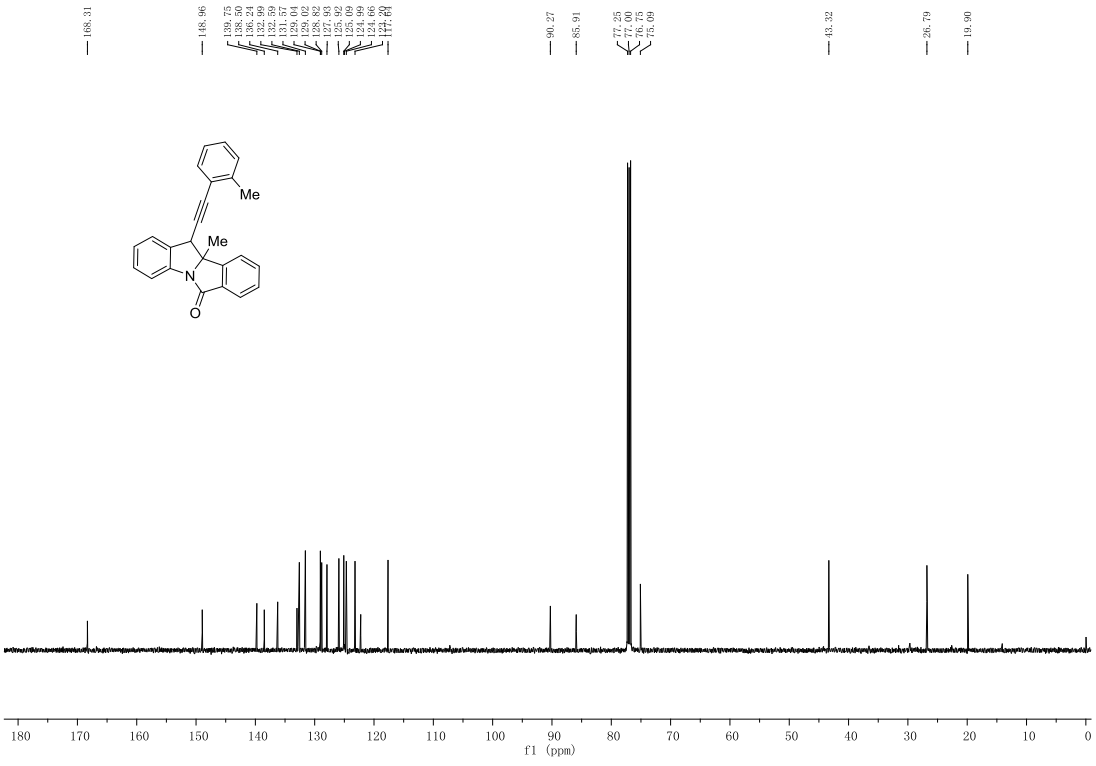

f1 (ppm)

10b-Methyl-11-(*o*-tolylethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3ad**)

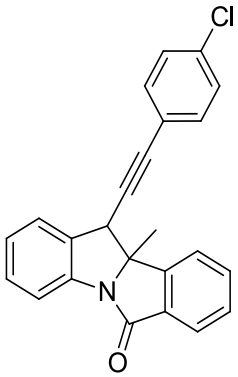


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 61.3 mg, 87% yield, m.p. 115−117 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, *J* = 6.5 Hz, 1H), 7.76 (d, *J* = 6.5 Hz, 1H), 7.41−7.65 (m, 5H), 6.87 −7.20 (m, 5H), 4.30 (s, 1H), 1.74 (s, 3H), 1.72 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.3, 149.0, 139.8, 138.5, 136.2, 133.0, 132.6, 131.6, 129.04, 129.02, 128.8, 127.9, 125.9, 125.1, 125.0, 124.7, 123.2, 122.2, 117.6, 90.3, 85.9, 75.1, 43.3, 26.8, 19.9. HRMS *m/z* (ESI+): Calculated for $C_{25}H_{20}NO$ ($[M+H]^+$): 350.1539, Found 350.1550.

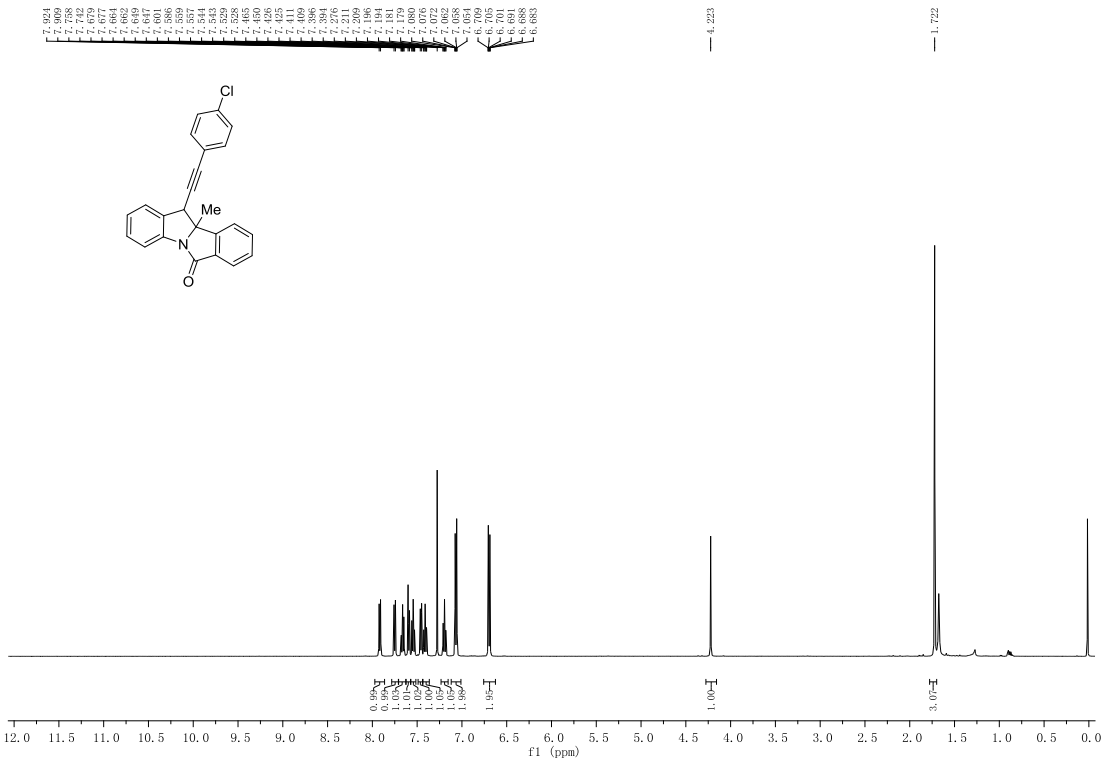

7.917
7.904
7.765
7.751
7.650
7.638
7.618
7.524
7.509
7.490
7.477
7.466
7.276
7.196
7.054
6.973
6.958
6.936
6.866
4.299
1.742
1.721
Me
Me
N
O
0.95
1.01
5.00
4.97
1.00
2.93
3.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

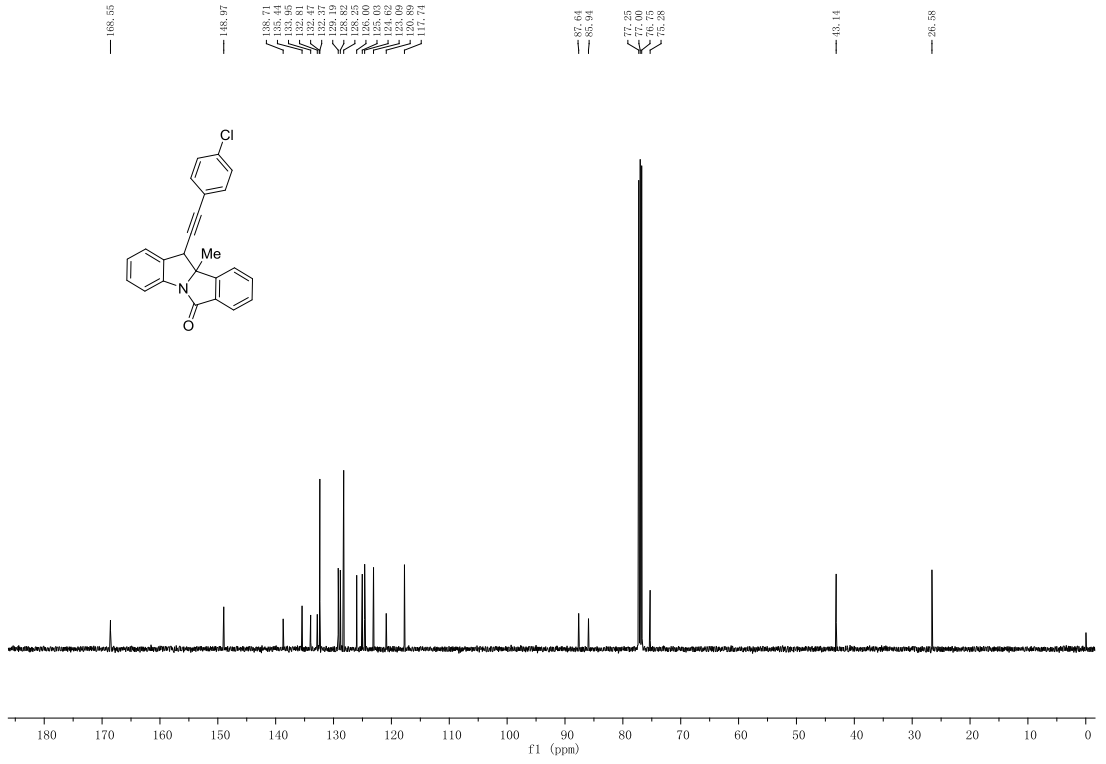

168.31
148.96
139.75
138.50
136.24
132.99
132.69
131.57
129.04
129.02
128.82
127.43
125.92
125.09
124.99
124.66
124.20
117.61
90.27
85.91
77.25
77.00
76.75
75.09
43.32
26.79
19.90
Me
Me
N
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

11-((4-Chlorophenyl)ethynyl)-10b-methyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3ae**)

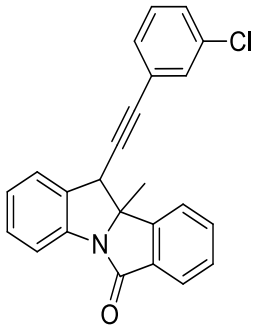


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 56.0 mg, 76% yield, m.p. 126–128 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.66 (td, *J* = 7.5, 1.0 Hz, 1H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.54 (td, *J* = 7.5, 0.5 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.41 (td, *J* = 7.5, 1.0 Hz, 1H), 7.20 (td, *J* = 7.5, 1.0 Hz, 1H), 7.05–7.08 (m, 2H), 6.68 –6.71 (m, 2H), 4.22 (s, 1H), 1.72 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.6, 149.0, 138.7, 135.4, 134.0, 132.8, 132.5, 132.4, 129.2, 128.8, 128.3, 126.0, 125.0, 124.6, 123.1, 120.9, 117.7, 87.6, 85.9, 75.3, 43.1, 26.6. HRMS *m/z* (ESI+): Calculated for $C_{24}H_{17}ClNO$ ($[M+H]^+$): 370.0993, Found 370.0988.

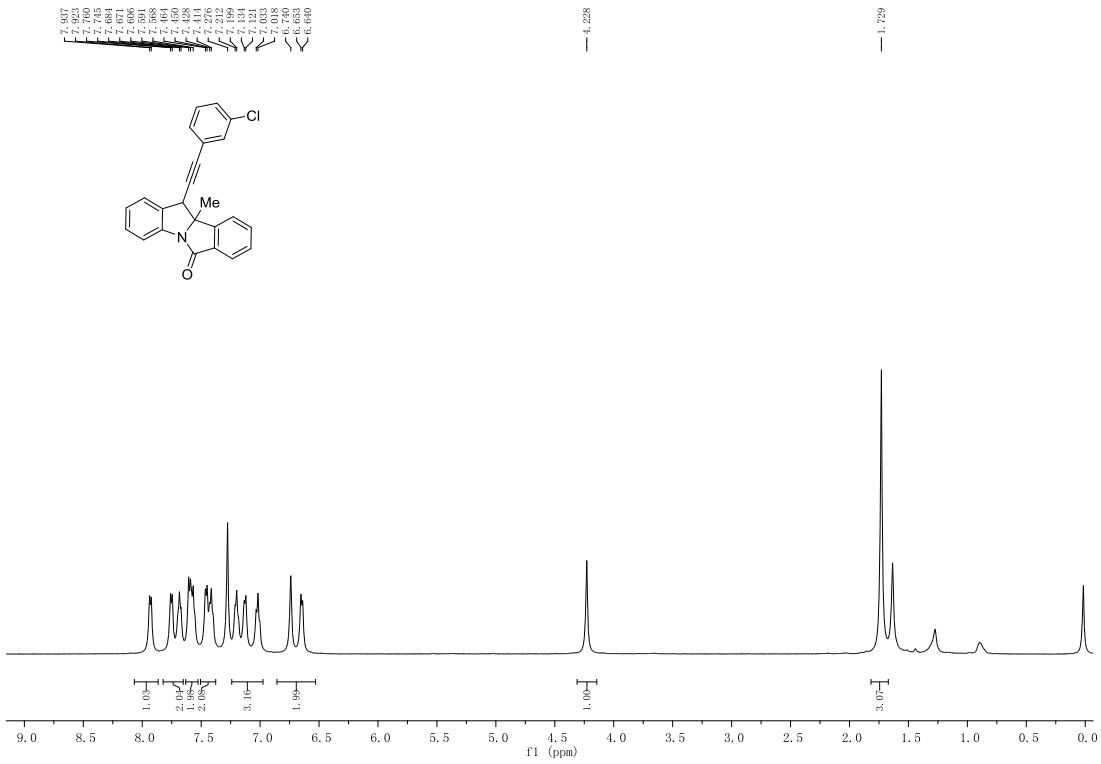

7.924
7.909
7.758
7.742
7.679
7.677
7.664
7.662
7.649
7.647
7.601
7.586
7.559
7.557
7.544
7.543
7.529
7.528
7.465
7.450
7.426
7.425
7.411
7.409
7.396
7.394
7.276
7.211
7.209
7.196
7.194
7.181
7.179
7.080
7.076
7.072
7.062
7.058
7.054
6.709
6.705
6.701
6.691
6.688
6.683
4.223
1.722
Cl
Me
N
O
0.95
0.99
1.03
1.01
1.02
1.04
1.05
1.05
1.98
1.95
1.00
3.07
12.0 11.5 11.0 10.5 10.0 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
f1 (ppm)

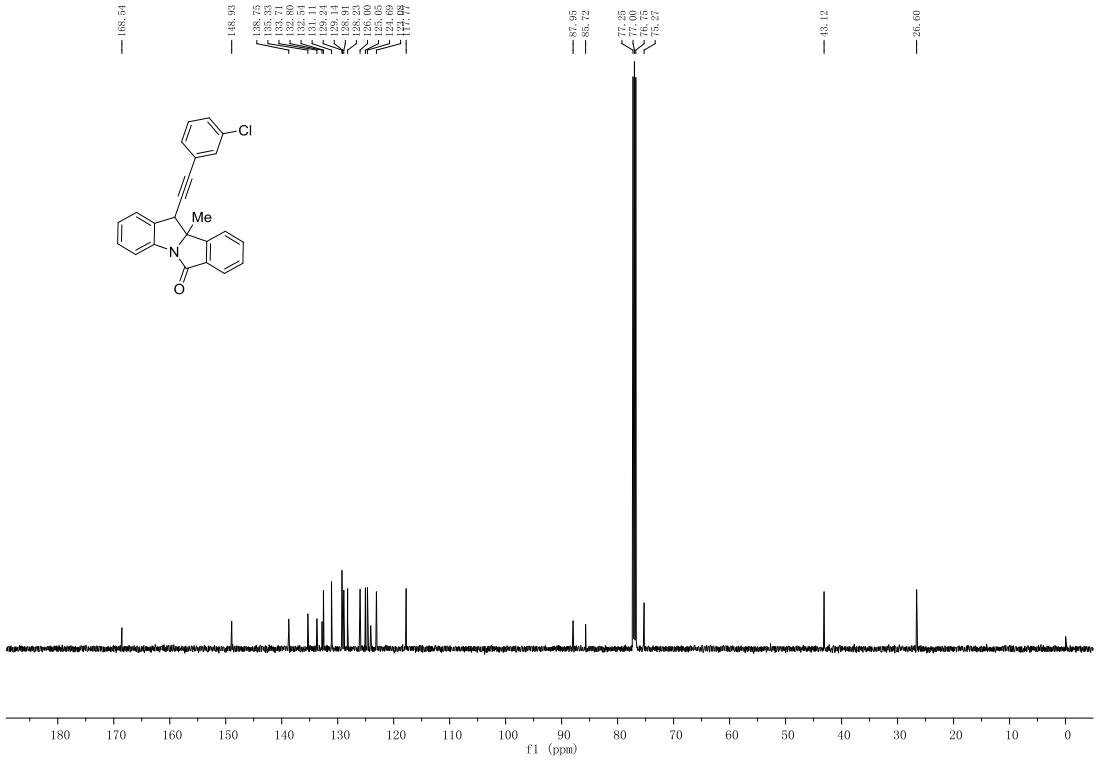

168.55
148.97
138.71
135.44
133.45
132.81
132.47
132.37
129.19
128.82
128.25
126.00
125.03
124.62
123.09
120.89
117.74
87.64
85.94
77.25
77.00
76.75
75.28
43.14
26.58
Cl
Me
N
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

11-((3-Chlorophenyl)ethynyl)-10b-methyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3af**)

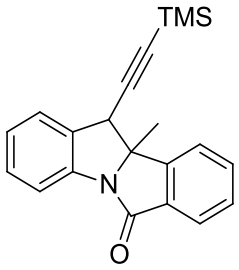


Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 55.0 mg, 75% yield, m.p. 115−118 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.0 Hz, 1H), 7.67−7.76 (m, 2H), 7.57−7.61 (m, 2H), 7.41−7.46 (m, 2H), 7.02−7.21 (m, 3H), 6.64−6.74 (m, 2H), 4.23 (s, 1H), 1.73 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.5, 148.9, 138.8, 135.3, 133.7, 132.8, 132.5, 131.1, 129.24, 129.23, 129.1, 128.9, 128.2, 126.0, 125.1, 124.7, 124.1, 123.1, 117.8, 88.0, 85.7, 75.3, 43.1, 26.6. HRMS *m/z* (ESI+): Calculated for $C_{24}H_{17}ClNO$ ($[M+H]^+$): 370.0993, Found 370.0983.

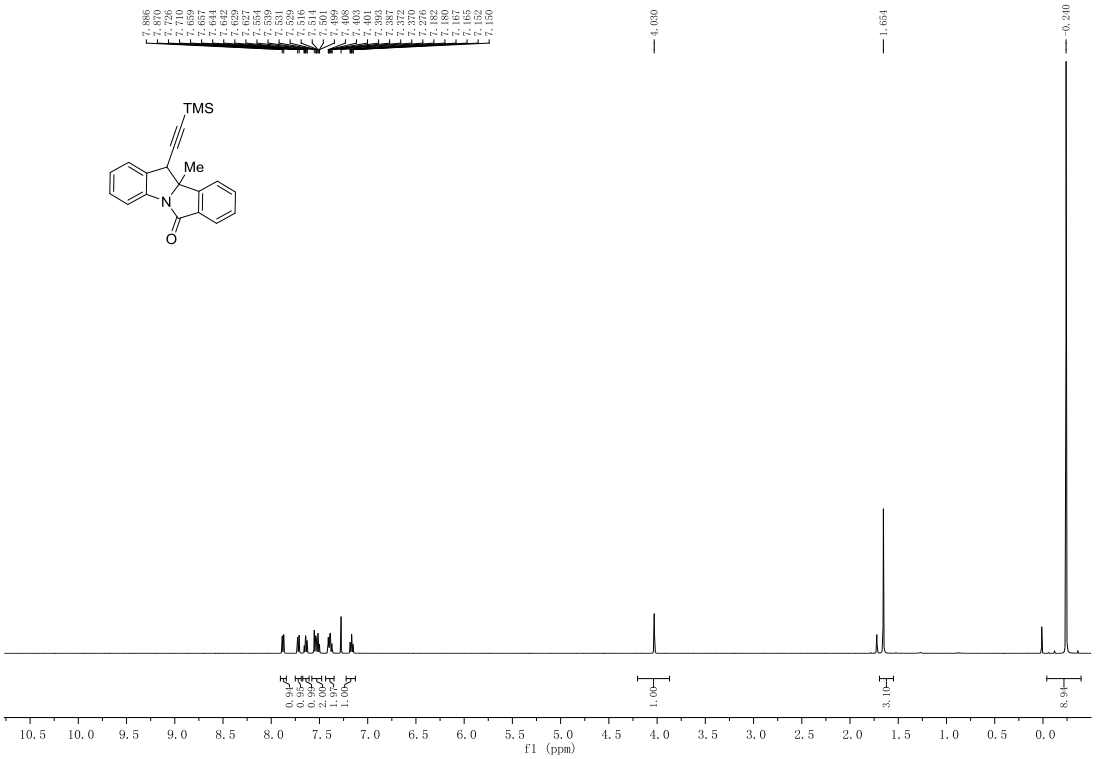

7.937
7.923
7.760
7.745
7.684
7.671
7.606
7.591
7.568
7.464
7.456
7.428
7.414
7.276
7.242
7.194
7.134
7.121
7.033
7.018
6.740
6.653
6.640
4.228
1.729
Cl
Me
N
O
1.03
2.04
1.08
2.05
3.16
1.99
1.00
3.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

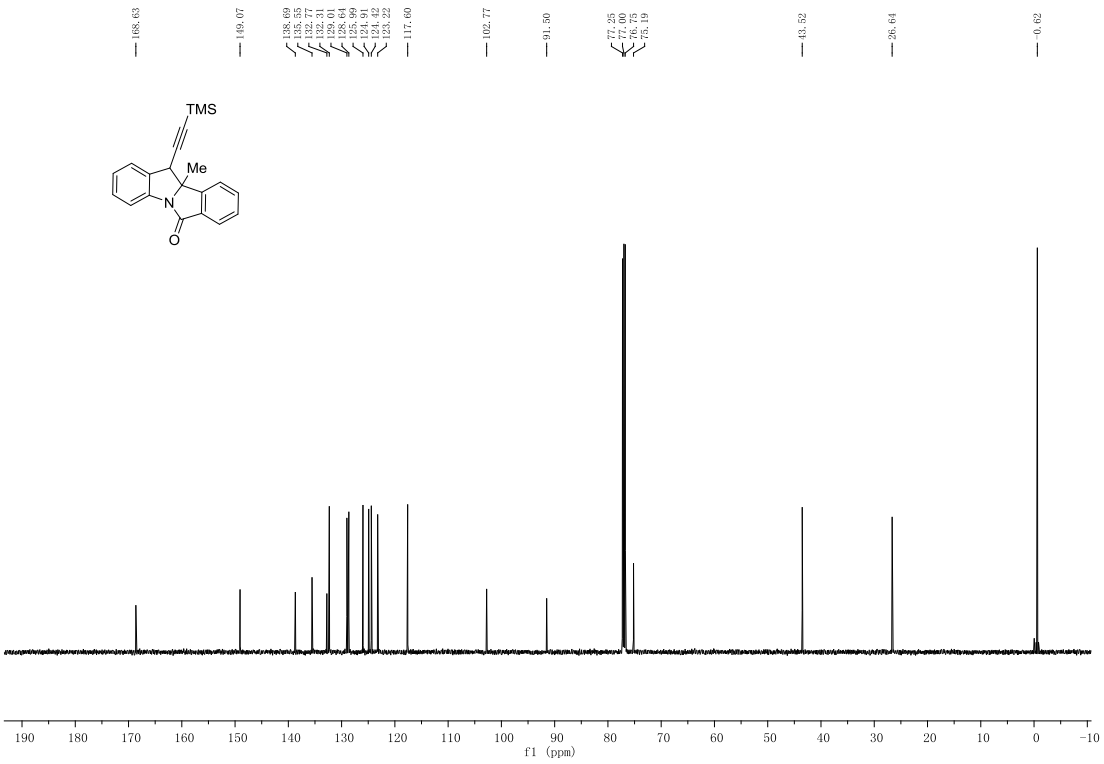

168.54
148.93
138.75
135.33
133.71
132.80
132.54
131.11
129.24
129.14
128.91
128.23
126.00
125.05
124.69
87.95
85.72
77.25
77.00
76.75
75.27
43.12
26.60
Cl
Me
N
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

10b-Methyl-11-((trimethylsilyl)ethynyl)-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**3ag**)



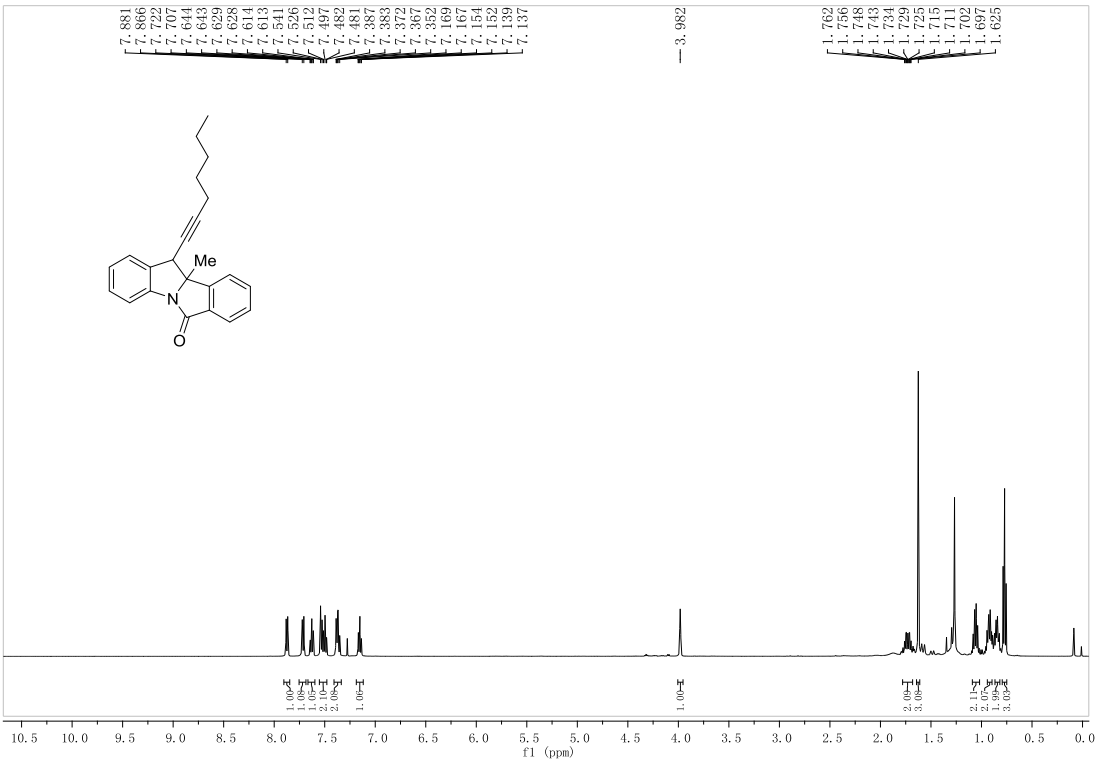
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v); white solid, 41.4 mg, 62% yield, m.p. 138−140 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.64 (td, *J* = 7.5, 1.0 Hz, 1H), 7.50−7.55 (m, 2H), 7.37−7.41 (m, 2H), 7.17 (td, *J* = 7.5, 1.0 Hz, 1H), 4.03 (s, 1H), 1.65 (s, 3H), -0.24 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.6, 149.1, 138.7, 135.6, 132.8, 132.3, 129.0, 128.6, 126.0, 124.9, 124.4, 123.2, 117.6, 102.8, 91.5, 75.2, 43.5, 26.6, -0.6. HRMS *m/z* (ESI+): Calculated for $C_{21}H_{22}NOSi$ ($[M+H]^+$): 332.1465, Found 332.1493.

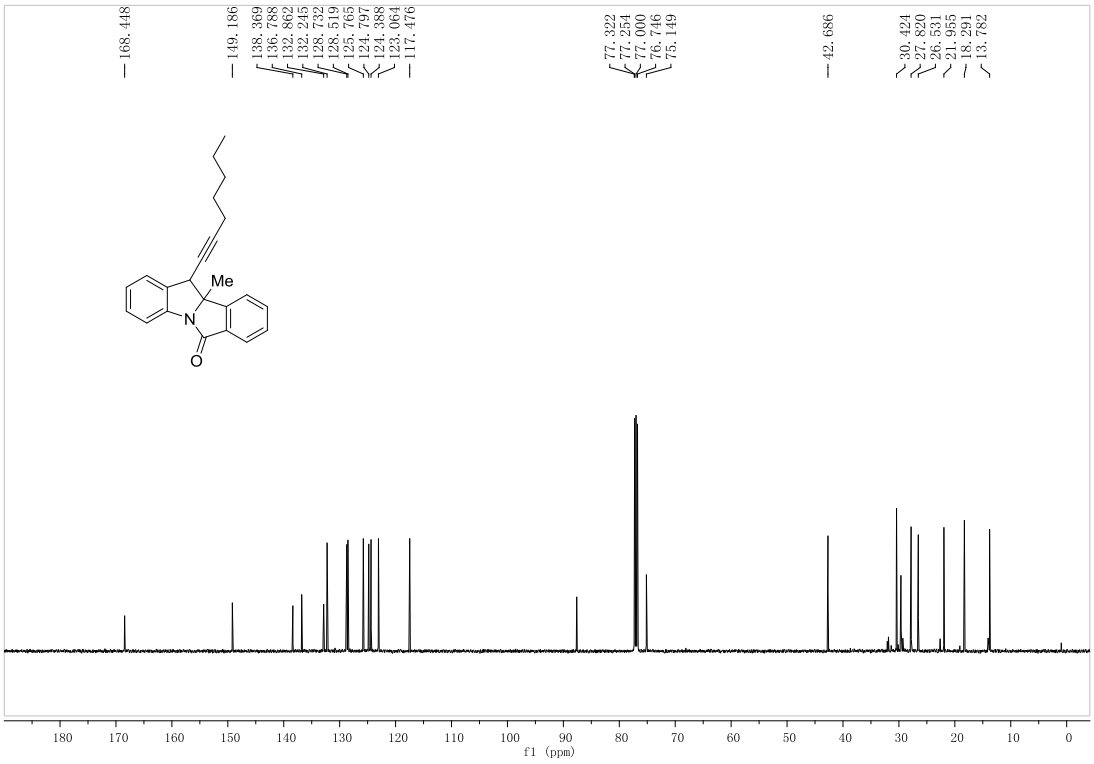

7.886
7.870
7.726
7.710
7.659
7.657
7.644
7.642
7.629
7.627
7.554
7.539
7.531
7.529
7.516
7.514
7.501
7.499
7.408
7.403
7.401
7.393
7.387
7.372
7.370
7.276
7.182
7.180
7.167
7.165
7.152
7.150
4.030
1.654
0.240
TMS
Me
N
O
0.94
0.96
0.99
2.00
1.97
1.00
1.00
3.10
8.94
f1 (ppm)


168.63
149.07
138.69
135.55
132.77
132.31
129.01
128.64
125.98
124.91
124.42
123.22
117.60
102.77
91.50
77.25
77.00
76.75
75.19
43.52
28.64
0.62
TMS
Me
N
O
f1 (ppm)

11-(Hept-1-yn-1-yl)-10b-methyl-10b,11-dihydro-6H-isoindolo[2,1-a]ind-ol-6-one (**3ah**)[2]

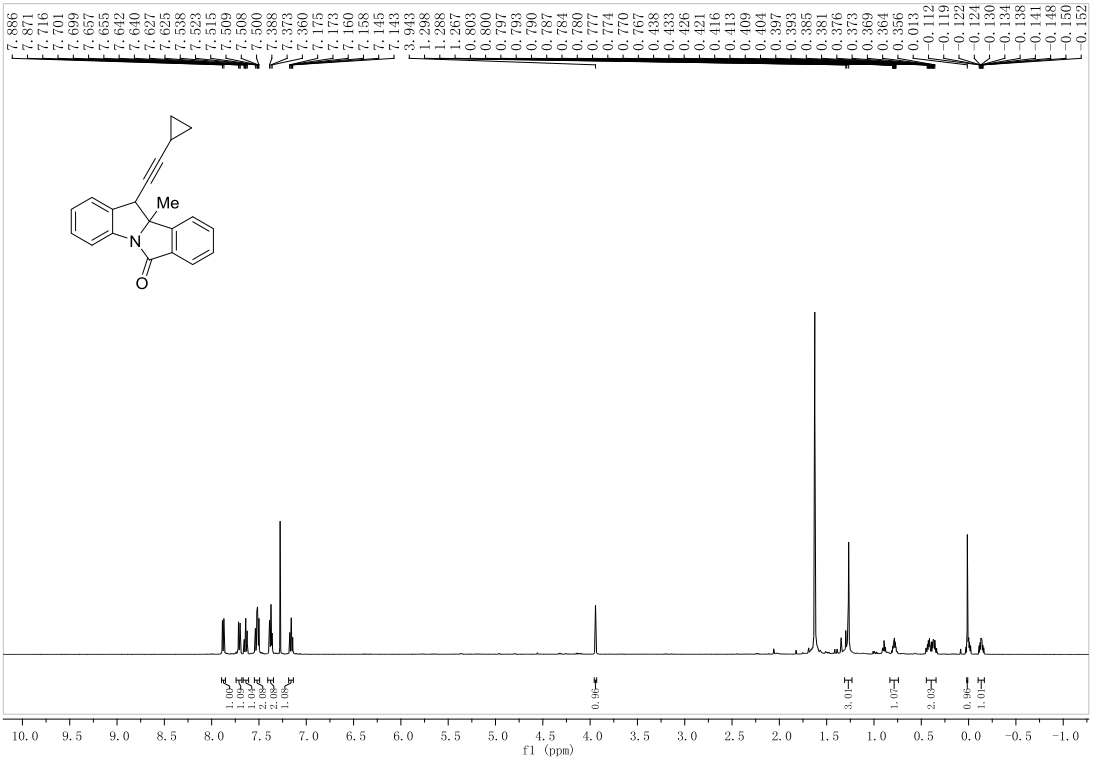
Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:20 (v/v); brown oil, 34.7 mg, 52% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.63 (td, *J* = 7.5, 0.9 Hz, 1H), 7.48–7.55 (m, 2H), 7.34–7.41 (m, 2H), 7.15 (td, *J* = 7.5, 0.8 Hz, 1H), 3.98 (s, 1H), 1.68–1.78 (m, 2H), 1.63 (s, 3H), 1.06 (dd, *J* = 14.6, 7.3 Hz, 2H), 0.90–0.94 (m, 2H), 0.82–0.87 (m, 2H), 0.77 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168. 5, 149.2, 138.4, 136.8, 132.9, 132.3, 128.7, 128.5, 125.8, 124.8, 124.4, 123.1, 117.5, 76.8, 75.2, 42.7, 30.4, 27.8, 26.5, 21.9, 18.3, 13.8.

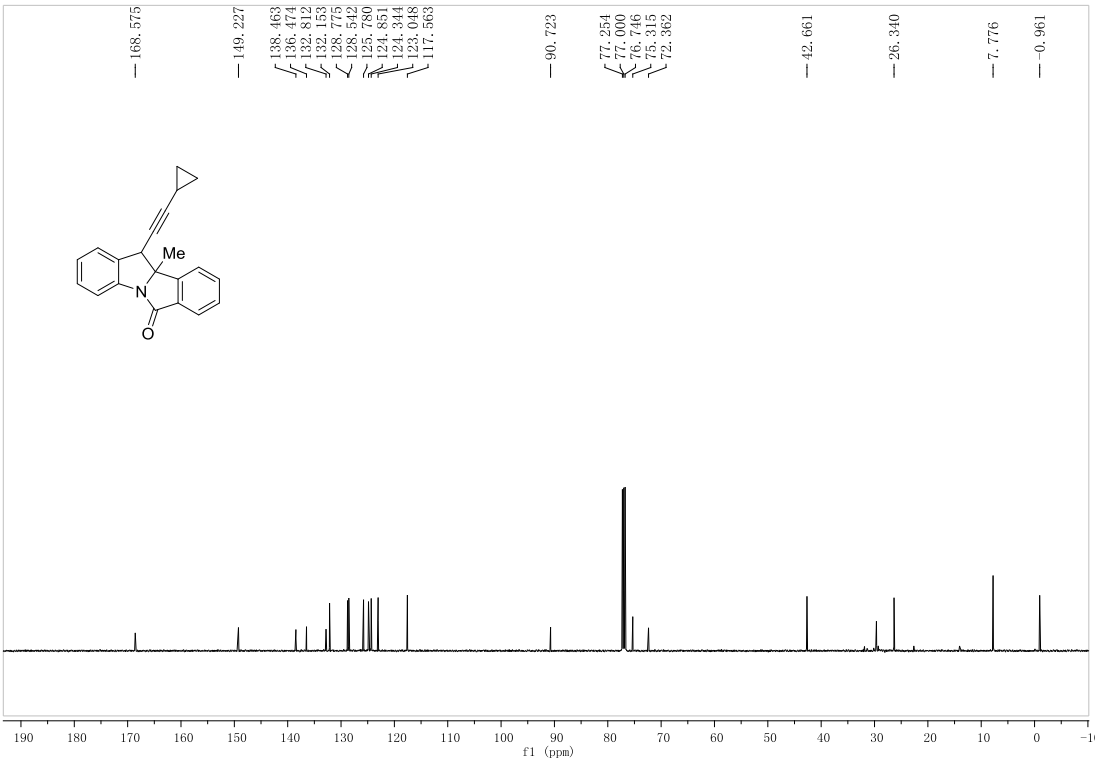



168.448
149.186
138.369
136.788
132.862
132.245
128.732
128.519
125.765
124.797
124.388
123.064
117.476
77.322
77.254
77.000
76.746
75.149
42.686
30.424
27.820
26.531
21.955
18.291
13.782
Me
N
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

11-(Cyclopropylethynyl)-10b-methyl-10b,11-dihydro-6H isoindolo[2,1-a]indol-6-one (**3ai**)[2]

Purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:20 (v/v); brown solid, 37.7 mg, 60% yield; m.p. 142-144 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, *J* = 7.6 Hz, 1H), 7.68–7.74 (m, 1H), 7.64 (td, *J* = 7.5, 1.0 Hz, 1H), 7.49–7.55 (m, 2H), 7.37 (t, *J* = 6.9 Hz, 2H), 7.16 (td, *J* = 7.5, 1.0 Hz, 1H), 3.94 (s, 1H), 1.23–1.31 (m, 3H), 0.74–0.83 (m, 1H), 0.34–0.45 (m, 2H), 0.01 (s, 1H), -0.17–-0.10 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.6, 149.2, 138.5, 136.5, 132.8, 132.2, 128.8, 128.5, 125.8, 124.9, 124.3, 123.1, 117.6, 90.7, 76.7, 75.3, 72.4, 42.7, 26.3, 7.8, -0.9.

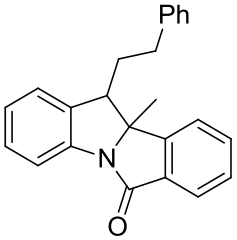




[2] S. Chen, X.-X. Wu, J. Wang, X.-H. Hao, Y. Xia, Y. Shen, H. Jing and Y.-M. Liang, *Org. lett.*, 2016, **18**, 4016.

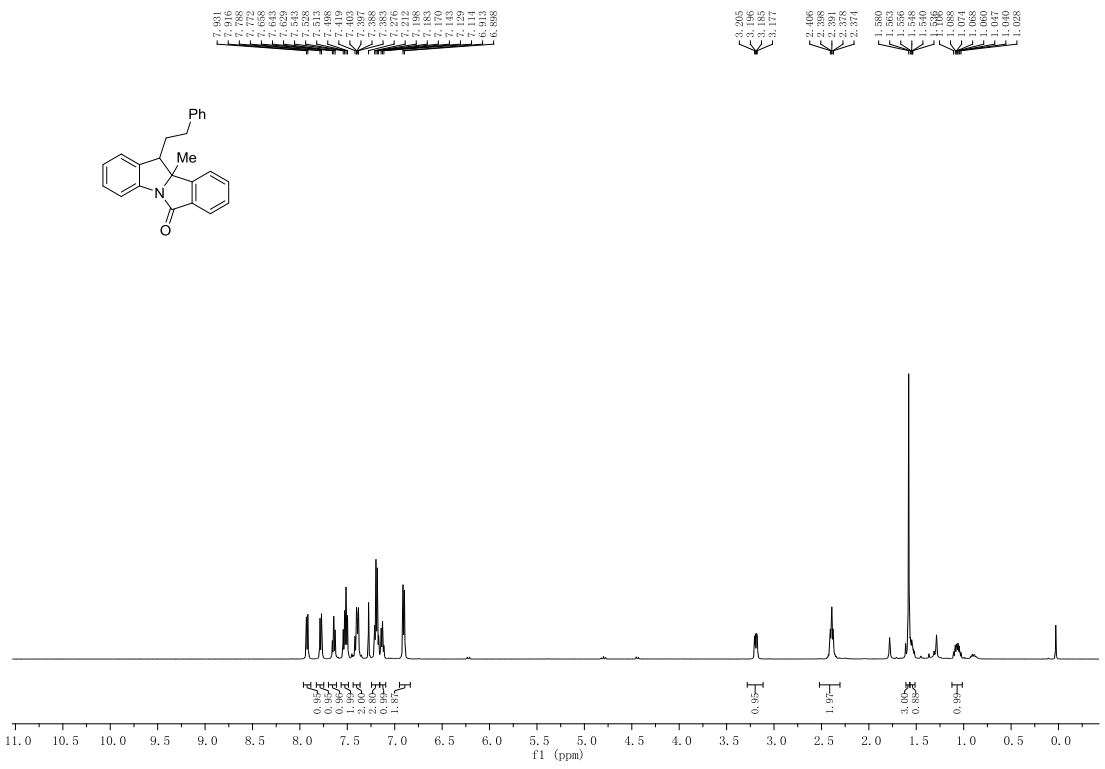
3. Synthetic transformations of products

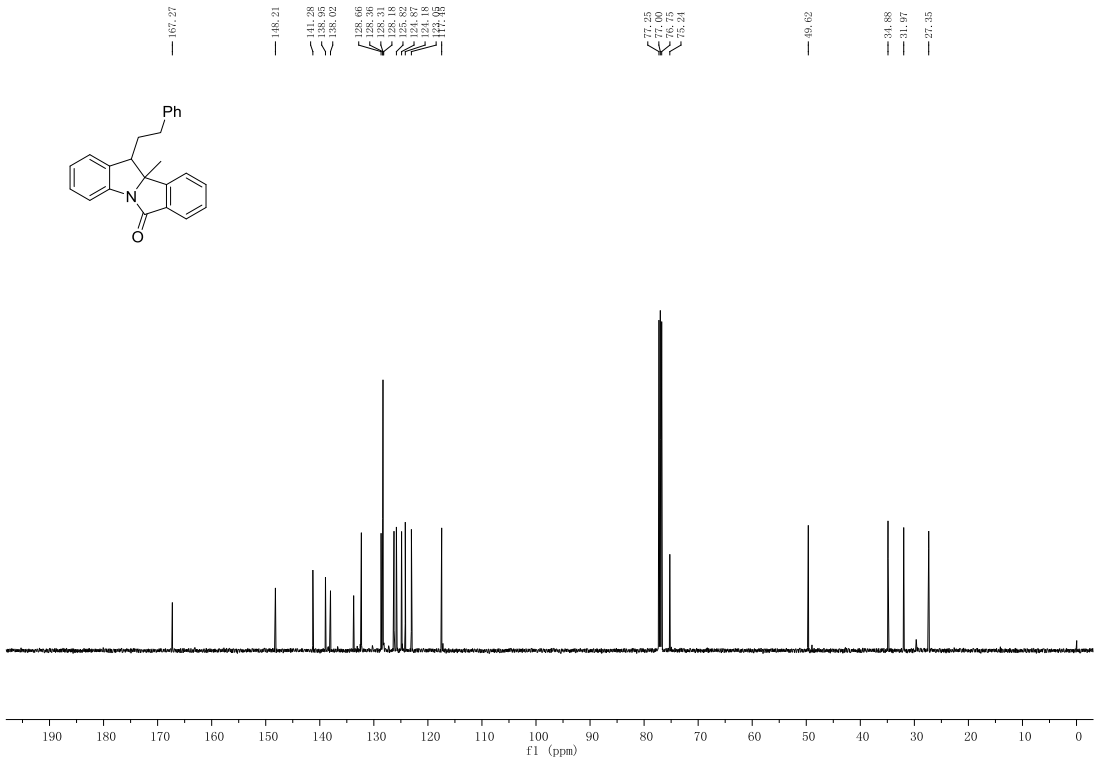
10b-Methyl-11-phenethyl-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**4**)



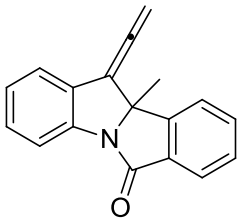
The mixture of Pd/C (5.0 mg, 0.0050 mmol, 10 mol%) and compound **3aa** (47.0 mg, 0.14 mmol, 1.0 eq) in EtOH (10.0 mL) was stirred with a hydrogen balloon at room temperature for 24 h. The resulting mixture was then filtered and washed with EtOH. After the solvent EtOH was removed under vacuum, the residue was purified by flash column chromatography on silica gel, eluting with ethyl acetate/petroleum

ether 1:10 (v/v) to give compound **4** (40.4 mg, 85%) as a white solid, m.p. 128–130 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.5 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.52 (dd, *J* = 15.0, 7.5 Hz, 2H), 7.38–7.42 (m, 2H), 7.17–7.21 (m, 3H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 7.5 Hz, 2H), 3.19 (dd, *J* = 9.5, 4.0 Hz, 1H), 2.37–2.41 (m, 2H), 1.58 (s, 3H), 1.52–1.56 (m, 1H), 1.03–1.11 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.3, 148.2, 141.3, 139.0, 138.0, 133.7, 132.3, 128.7, 128.4, 128.3, 128.2, 126.3, 125.8, 124.9, 124.2, 123.1, 117.5, 75.2, 49.6, 34.9, 32.0, 27.4. HRMS *m/z* (ESI+): Calculated for $C_{24}H_{22}NO$ ($[M+H]^+$): 340.1696, Found 340.1693.



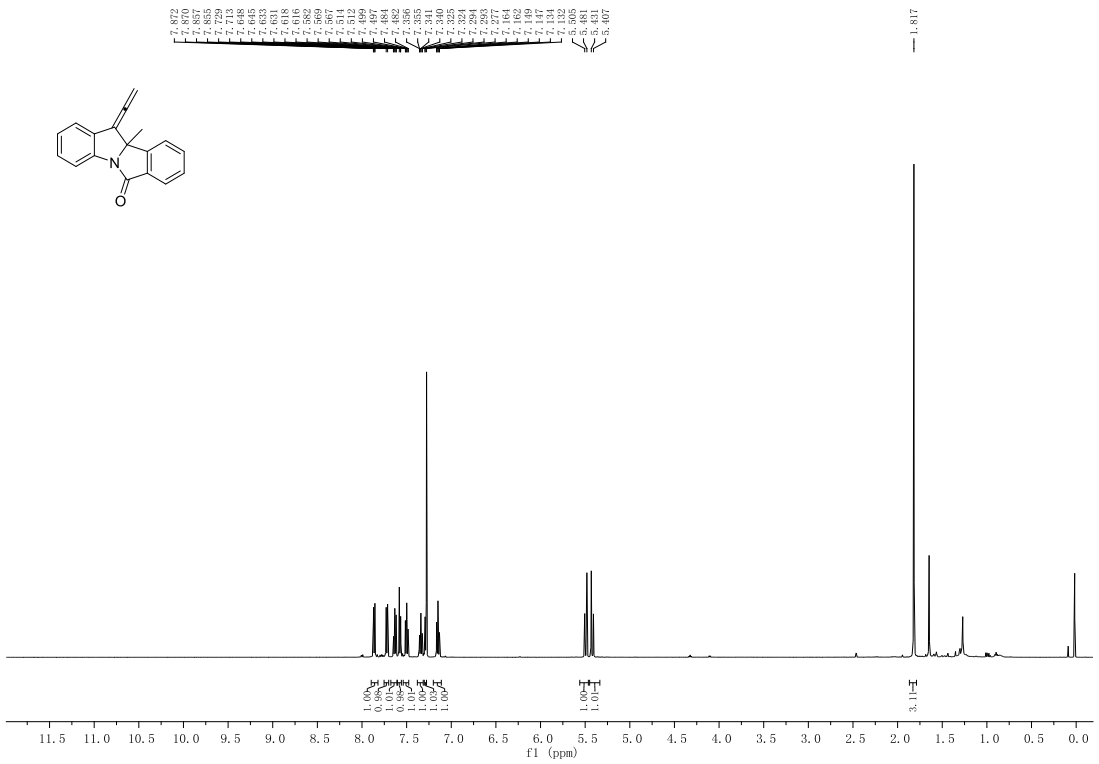


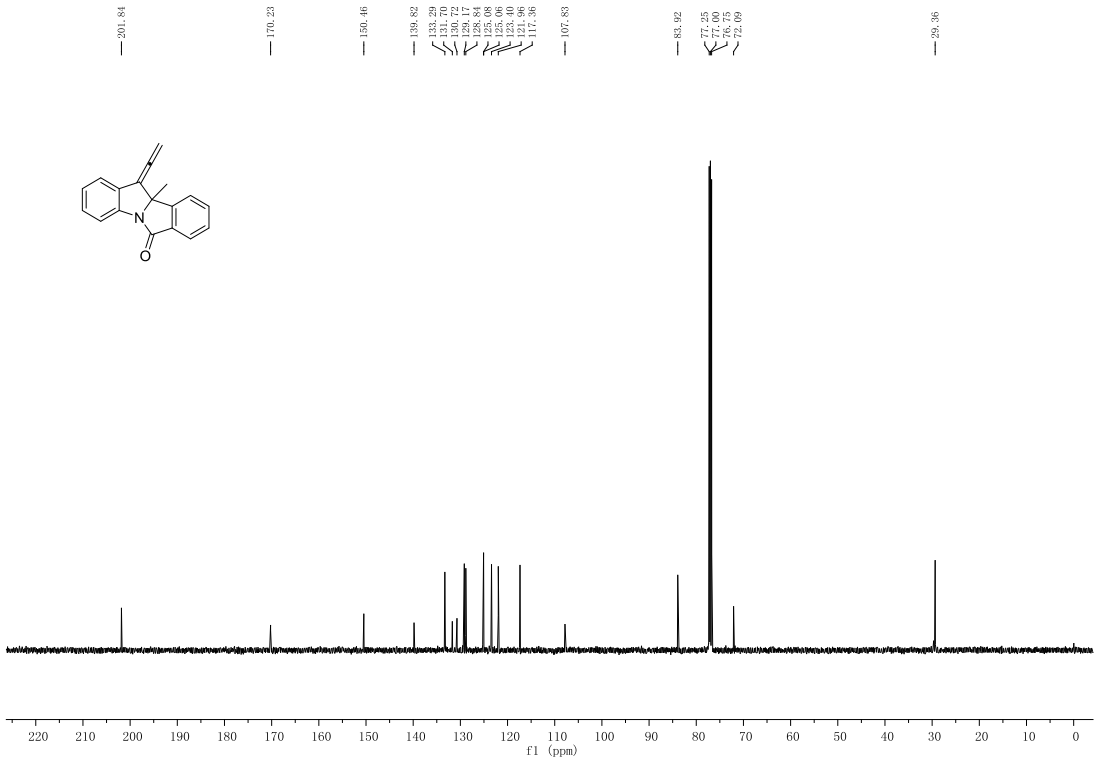
10b-Methyl-11-vinylidene-10b,11-dihydro-6H-isoindolo[2,1-a]indol-6-one (**5**)



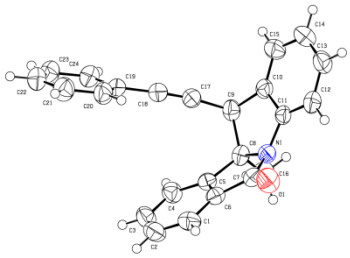
To a solution of compound **3ag** (33.2 mg, 0.10 mmol, 1.0 equiv) in THF (2 mL) was added tetrabutyl ammonium fluoride trihydrate (31.6 mg, 0.10 mmol, 1.0 equiv). The resulting mixture was then stirred at 0 ℃ for 3 h. After which, the mixture was concentrated and the residue was purified by flash column chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:10 (v/v) to give compound **5** (23.8 mg, 92%) as a white solid, m.p. 147−149 ℃; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86−7.87 (m, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.63 (td, *J* = 7.5, 1.0 Hz, 1H), 7.57−7.58 (m, 1H), 7.50 (td, *J* = 7.5, 1.0 Hz, 1H), 7.32−7.36 (m, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.15

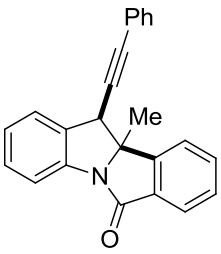
(td, *J* = 7.5, 1.0 Hz, 1H), 5.49 (d, *J* = 12.0 Hz, 1H), 5.42 (d, *J* = 12.0 Hz, 1H), 1.82 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.8, 170.2, 150.5, 139.8, 133.3, 131.7, 130.7, 129.2, 128.8, 125.08, 125.06, 123.4, 122.0, 117.4, 107.8, 83.9, 72.1, 29.4. HRMS *m/z* (ESI+): Calculated for $C_{18}H_{14}NO$ ($[M+H]^+$): 260.1070, Found 260.1067.





4. X-ray structural analysis of compound 3aa





Bond precision: C-C = 0.0041 A Wavelength=0.71073

Cell: a=15.3015(18) b=12.1976(10) c=9.6252(8)
alpha=90 beta=90 gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	1796.5(3)	1796.5(3)
Space group	P n a 21	P n a 21
Hall group	P 2c -2n	P 2c -2n
Moiety formula	C24 H17 N O	C24 H17 N O
Sum formula	C24 H17 N O	C24 H17 N O
Mr	335.39	335.39
Dx,g cm-3	1.240	1.240
Z	4	4
Mu (mm-1)	0.075	0.075
F000	704.0	704.0
F000'	704.28	
h,k,lmax	18,14,11	18,14,11
Nref	3291[1752]	1750
Tmin,Tmax	0.964,0.976	0.986,1.000
Tmin'	0.964	

Correction method= # Reported T Limits: Tmin=0.986 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.00/0.53 Theta(max)= 25.330

R(reflections)= 0.0376(1347) wR2(reflections)= 0.0824(1750)

S = 1.048 Npar= 236