Rhodium-Catalyzed Intermolecular Hydroarylation of Internal Alkynes with 
N-1-Phenylbenzotriazoles

Supporting Information

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General Remarks

$^1$H-NMR spectra were recorded on a Bruker AVIII-400 spectrometer. Chemical shifts (in ppm) were referenced to tetramethylsilane ($\delta = 0$ ppm) in CDCl$_3$ as an internal standard. $^{13}$C-NMR spectra were obtained by using the same NMR spectrometers and calibrated with CDCl$_3$ ($\delta = 77.0$ ppm). Mass spectra were recorded using an Agilent 5975 GC-MS. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.
Experimental Procedures

Typical procedure

A sealed tube was charged with substrate 1 (0.2 mmol), 2 (0.3 mmol), RhCl(PPh₃)₃ (0.005 mmol), AgOTf (0.01 mmol) in mesitylene (1.6 mL). The mixture was stirred at 160 °C under N₂ for 12 h. Then, the reaction was cooled down to room temperature, diluted with ethyl acetate (50 mL), filtered, and dried under vaccum. The crude product was purified by column chromatography on silica gel to obtain the desired products 3 (petroleum ether:ethyl acetate = 20:1).
Analytical Data for Compounds 3

1) 1-(2-((E)-1,2-Diphenylvinyl)phenyl)-1H-benzo[d][1,2,3]triazole (3aa)

The reaction of 1-phenyl-1H-benzo[d][1,2,3]triazole (1a, 0.2 mmol, 39 mg), diphenylacetylene (2a, 0.3 mmol, 53.5 mg), RhCl(PPh₃)₃ (0.005 mmol, 4.6 mg), AgOTf (0.01 mmol, 2.6 mg) in mesitylene (1.6 mL) under typical procedure afforded 73 mg (98%) of 3aa as solid. m.p.: 129-130 °C; ¹H NMR (CDCl₃, 400 MHz): δ = 7.88 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 7.3 Hz, 1H), 7.64 (t, J = 7.3 Hz, 1H), 7.56 (t, J = 7.3 Hz, 1H), 7.42 (d, J = 7.3 Hz, 1H), 7.37-7.16 (m, 3H), 7.15-7.07 (m, 3H), 7.02-6.96 (m, 2H), 6.84 (s, 1H), 6.81-6.66 (m, 3H), 6.52 (d, J = 7.2 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 145.2, 142.2, 139.7, 137.9, 136.6, 134.5, 133.5, 131.8, 131.5, 129.9, 129.2, 128.7, 128.6, 127.8, 127.6, 127.5, 127.02, 127.0, 126.9, 123.5, 119.4, 110.1 ppm; IR (KBr): νmax = 1612, 1593, 1502, 1504, 1458, 1271, 1072, 1007, 785, 767, 758, 748, 706, 698 cm⁻¹; MS (70 eV): m/z (%) 271.1 (M⁺, 100); HRMS m/z (ESI) calcd for C₂₆H₂₀N₃ (M + H)⁺: 374.1652, found 374.1643.

Figure S1. ORTEP drawing of 3aa

2) 1-(4-Methyl-2-((E)-1,2-diphenylvinyl)phenyl)-1H-benzo[d][1,2,3]triazole (3ba)
The reaction of 1-(4-methylphenyl)-1H-benzo[d][1,2,3]triazole (1b, 0.2 mmol, 41.9 mg), diphenylacetylene (2a, 0.3 mmol, 53.5 mg), RhCl(PPh₃)₃ (0.005 mmol, 4.6 mg), AgOTf (0.01 mmol, 2.6 mg) in mesitylene (1.6 mL) under typical procedure afforded 75 mg (97%) of 3ba as solid. m.p.: 150-151 °C; ¹H NMR (CDCl₃, 400 MHz): δ = 7.85 (d, J = 8.4 Hz, 1H), 7.55 (s, 1H), 7.39-7.15 (m, 6H), 7.09-7.02 (m, 3H), 6.97-6.91 (m, 2H), 6.8 (s, 1H), 6.78-6.68 (m, 3H), 6.52 (d, J = 8.0 Hz, 1H), 2.54 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ = 145.1, 141.9, 140.1, 139.8, 138.0, 136.7, 133.6, 132.3, 132.0, 131.2, 129.23, 129.20, 128.6, 127.8, 127.7, 127.5, 127.4, 126.9, 126.8, 123.4, 119.3, 110.1, 21.2 ppm; IR (KBr): νmax = 1501, 1444, 1273, 1066, 833, 768, 752, 717, 700 cm⁻¹; HRMS m/z (ESI) calcd for C₂₇H₂₂N₃ (M + H)⁺: 388.1808, found 388.1803.

3) 1-(4-Methoxy-2-((E)-1,2-diphenylvinyl)phenyl)-1H-benzo[d][1,2,3]triazole (3ca)

The reaction of 1-(4-methoxyphenyl)-1H-benzo[d][1,2,3]triazole (1c, 0.2 mmol, 45.1 mg), diphenylacetylene (2a, 0.3 mmol, 53.5 mg), RhCl(PPh₃)₃ (0.005 mmol, 4.6 mg), AgOTf (0.01 mmol, 2.6 mg) in mesitylene (1.6 mL) under typical procedure afforded 72 mg (89%) of 3ca as solid. m.p.: 132-133 °C; ¹H NMR (CDCl₃, 400 MHz): δ = 7.86 (d, J = 8.0 Hz, 1H), 7.39-7.18 (m, 4H), 7.18-7.12 (m, 1H), 7.11-7.01 (m, 4H), 6.99-6.89 (m, 2H), 6.83 (s, 1H), 6.80-6.66 (m, 3H), 6.53 (d, J = 6.8 Hz, 2H), 3.96 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ = 160.5, 145.1, 143.7, 139.7, 137.7, 136.5,
133.8, 131.5, 129.3, 129.2, 128.9, 128.6, 127.8, 127.5, 127.4, 127.1, 126.9, 123.4, 119.3, 116.9, 113.7, 110.1, 55.7 ppm; IR (KBr): \( \nu_{\text{max}} = 1610, 1571, 1502, 1453, 1284, 1249, 1216, 1068, 750, 699 \text{ cm}^{-1} \); HRMS m/z (ESI) calcd for C\(_{27}\)H\(_{22}\)N\(_3\)O (M + H): 404.1757, found 404.1748.

4) 1-(2-((E)-1,2-Diphenylvinyl)-4-(trifluoromethoxy)phenyl)-1H-beno[d][1,2,3]triazole (3da)

![Diagram of 3da]

The reaction of 1-(4-(trifluoromethoxy)phenyl)-1H-benzo[d][1,2,3]triazole (1d, 0.2 mmol, 55.8 mg), diphenylacetylene (2a, 0.3 mmol, 53.5 mg), RhCl(PPh\(_3\))\(_3\) (0.005 mmol, 4.6 mg), AgOTf (0.01 mmol, 2.6 mg) in mesitylene (1.6 mL) under typical procedure afforded 87 mg (95%) of 3da as solid. m.p.: 126-127 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta = 7.89 \) (d, \( J = 6.0 \text{ Hz}, 1\text{H} \)), 7.62 (s, 1H), 7.51-7.38 (m, 2H), 7.37-7.15 (m, 3H), 7.14-7.04 (m, 3H), 7.01-6.92 (m, 2H), 6.86 (s, 1H), 6.82-6.67 (m, 3H), 6.51 (d, \( J = 7.6 \text{ Hz}, 2\text{H} \)); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \( \delta = 149.9, 145.2, 144.3, 138.5, 137.1, 136.1, 133.5, 132.9, 132.6, 129.3, 129.2, 128.6, 127.9, 127.7, 127.42, 127.37, 127.2, 123.9, 123.7, 120.5, 120.4 (q, \( J_{\text{C-F}} = 257.6 \text{ Hz} \)), 119.6 ppm; IR (KBr): \( \nu_{\text{max}} = 1503, 1453, 1256, 1220, 1169, 1068, 738, 698 \text{ cm}^{-1} \); HRMS m/z (ESI) calcd for C\(_{27}\)H\(_{19}\)F\(_3\)N\(_3\)O (M + H): 458.1475, found 458.1466.

5) 1-(4-(Trifluoromethyl)-2-((E)-1,2-diphenylvinyl)phenyl)-1H-benzo[d][1,2,3]triazole (3ea)

![Diagram of 3ea]

The reaction of 1-(4-(trifluoromethyl)phenyl)-1H-benzo[d][1,2,3]triazole (1e, 0.2
mmol, 52.6 mg), diphenylacetylene (2a, 0.3 mmol, 53.5 mg), RhCl(PPh₃)₃ (0.005 mmol, 4.6 mg), AgOTf (0.01 mmol, 2.6 mg) in mesitylene (1.6 mL) under **typical procedure** afforded 80 mg (91%) of 3ea as solid. m.p.: 119-120 °C; ¹H NMR (CDCl₃, 400 MHz): δ = 8.03 (s, 1H), 7.96-7.86 (m, 1H), 7.82 (d, J = 7.2 Hz, 1H), 7.55 (d, J = 7.2 Hz, 1H), 7.41-7.15 (m, 3H), 7.14-7.04 (m, 3H), 7.02-6.94 (m, 2H), 6.91 (s, 1H), 6.82-6.65 (m, 3H), 6.49 (d, J = 6.8 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 145.3, 143.0, 138.6, 137.5, 137.1, 136.1, 133.3, 132.8, 132.3, 131.9, 129.3, 128.8 (d, J_C-F = 3.6 Hz), 128.6, 128.2, 127.9, 127.7, 127.51, 127.47, 127.3, 125.6 (d, J_C-F = 3.2 Hz), 123.6 (q, J_C-F = 271 Hz), 119.7, 109.8 ppm; IR (KBr): ν_max = 1609, 1508, 1491, 1445, 1431, 1246, 1167, 1131, 1120, 1075, 1058, 860, 724, 694 cm⁻¹; HRMS m/z (ESI) calcd for C₂₇H₁₉F₃N₃ (M + H)⁺: 442.1526, found 442.1521.

6) 1-(4-Ethoxycarbonyl)-2-((E)-1,2-diphenylvinyl)phenyl)-1H-benzo[d][1,2,3]triazole (3fa)

![3fa]

The reaction of 1-(4-ethoxycarbonylphenyl)-1H-benzo[d][1,2,3]triazole (1f, 0.2 mmol, 53.5 mg), diphenylacetylene (2a, 0.3 mmol, 53.5 mg), RhCl(PPh₃)₃ (0.005 mmol, 4.6 mg), AgOTf (0.01 mmol, 2.6 mg) in mesitylene (1.6 mL) under **typical procedure** afforded 85 mg (95%) of 3fa as solid. m.p.: 110-111 °C; ¹H NMR (CDCl₃, 400 MHz): δ = 8.44 (s, 1H), 8.23 (d, J = 6.8 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.50 (d, J = 7.6 Hz, 1H), 7.40-7.15 (m, 3H), 7.13-7.05 (m, 3H), 7.03-6.97 (m, 2H), 6.95 (s, 1H), 6.80-6.61 (m, 3H), 6.48 (d, J = 6.8 Hz, 2H), 4.49 (q, J = 7.2 Hz, 2H), 1.47 (t, J = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ = 165.4, 145.2, 142.2, 139.0, 138.0, 137.3, 136.3, 133.2, 133.0, 132.2, 131.8, 129.7, 129.2, 128.5, 127.8, 127.6, 127.5, 127.3, 127.2, 127.0, 123.7, 119.5, 109.9, 61.5, 14.2 ppm; IR (KBr): ν_max = 1720, 1599, 1495, 1448, 1299, 1279, 1242, 1229, 1122, 1053, 765, 752, 699 cm⁻¹; HRMS m/z
(ESI) calcd for C_{29}H_{24}N_{3}O_{2} (M + H)^+: 446.1863, found 446.1858.

7) 1-(4-Chloro-2-((E)-1,2-diphenylvinyl)phenyl)-1H-benzo[d][1,2,3]triazole (3ga)

The reaction of 1-(4-chlorophenyl)-1H-benzo[d][1,2,3]triazole (1g, 0.2 mmol, 45.9 mg), diphenylacetylene (2a, 0.3 mmol, 53.5 mg), RhCl(PPh_{3})_{3} (0.005 mmol, 4.6 mg), AgOTf (0.01 mmol, 2.6 mg) in mesitylene (1.6 mL) under **typical procedure** afforded 72 mg (88%) of 3ga as solid. m.p.: 165-166 °C; \(^1\)H NMR (CDCl_{3}, 400 MHz): δ = 7.86 (d, J = 7.6 Hz, 1H), 7.76 (s, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.42-7.13 (m, 4H), 7.13-7.01 (m, 3H), 7.00-6.90 (m, 2H), 6.85 (s, 1H), 6.82-6.65 (m, 3H), 6.52 (d, J = 6.4 Hz, 2H); \(^{13}\)C NMR (CDCl_{3}, 100 MHz): δ = 145.2, 143.8, 138.5, 137.3, 136.2, 135.8, 133.5, 133.1, 132.3, 131.6, 129.2, 128.9, 128.60, 128.57, 127.8, 127.6, 127.29, 127.26, 127.1, 123.6, 119.5, 109.8 ppm; IR (KBr): v_{max} = 1493, 1442, 1059, 752, 697 cm\(^{-1}\); HRMS m/z (ESI) calcd for C_{26}H_{19}ClN_{3} (M + H)^+: 408.1262, found 408.1258.

8) 1-(4-Fluoro-2-((E)-1,2-diphenylvinyl)phenyl)-1H-benzo[d][1,2,3]triazole (3ha)

The reaction of 1-(4-fluorophenyl)-1H-benzo[d][1,2,3]triazole (1h, 0.2 mmol, 42.6 mg), diphenylacetylene (2a, 0.3 mmol, 53.5 mg), RhCl(PPh_{3})_{3} (0.005 mmol, 4.6 mg), AgOTf (0.01 mmol, 2.6 mg) in mesitylene (1.6 mL) under **typical procedure** afforded 75 mg (96%) of 3ha as solid. m.p.: 139-140 °C; \(^1\)H NMR (CDCl_{3}, 400 MHz): δ = 7.86 (d, J = 7.2 Hz, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.43-7.36 (m, 1H), 7.35-7.20 (m, 3H), 7.19-7.12 (m, 1H), 7.12-7.02 (m, 3H), 6.98-6.87 (m, 2H), 6.82 (s, 1H), 6.80-6.69 (m, 3H), 6.53 (d, J = 7.2 Hz, 2H); \(^{13}\)C NMR (CDCl_{3}, 100 MHz): δ = 163.0
(d, $J_{C-F} = 249.9$ Hz), 145.1, 144.6 (d, $J_{C-F} = 7.9$ Hz), 138.6, 137.3, 136.1, 133.6, 132.3, 130.6, 129.5 (d, $J_{C-F} = 9.1$ Hz), 129.2, 128.6, 127.9, 127.7, 127.3, 127.2, 127.1, 123.6, 119.5, 118.6 (d, $J_{C-F} = 23.2$ Hz), 115.4 (d, $J_{C-F} = 22.7$ Hz), 109.8 ppm; IR (KBr): $\nu_{\text{max}} = 1606, 1581, 1504, 1445, 1269, 1182, 1067, 865, 750, 696$ cm$^{-1}$; HRMS m/z (ESI) calcd for C$_{26}$H$_{19}$F$_3$N$_3$ (M + H)$^+$: 392.1558, found 392.1564.

9) 1-(4-Phenyl-2-((E)-1,2-diphenylvinyl)phenyl)-1H-benzo[d][1,2,3]triazole (3ia)

The reaction of 1-(4-phenylphenyl)-1H-benzo[d][1,2,3]triazole (1i, 0.2 mmol, 54.3 mg), diphenylacetylene (2a, 0.3 mmol, 53.5 mg), RhCl(PPh$_3$)$_3$ (0.005 mmol, 4.6 mg), AgOTf (0.01 mmol, 2.6 mg) in mesitylene (1.6 mL) under typical procedure afforded 87 mg (97%) of 3ia as solid. m.p.: 101-102 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 8.05-7.95$ (d, $J = 1.6$ Hz, 1H), 7.88 (d, $J = 8.4$ Hz, 1H), 7.81-7.70 (m, 3H), 7.59-7.41 (m, 4H), 7.37-7.20 (m, 3H), 7.11-6.95 (m, 5H), 6.93 (s, 1H), 6.82-6.68 (m, 3H), 6.56 (d, $J = 6.8$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 145.3, 143.1, 142.6, 139.9, 139.7, 137.9, 136.7, 133.7, 131.8, 130.52, 130.51, 129.3, 129.0, 128.7, 128.2, 128.1, 127.9, 127.8, 127.6, 127.3, 127.2, 127.1, 127.0, 123.5, 119.5, 110.2 ppm; IR (KBr): $\nu_{\text{max}} = 1491, 1445, 1059, 784, 764, 743, 695$ cm$^{-1}$; HRMS m/z (ESI) calcd for C$_{32}$H$_{24}$N$_3$ (M + H)$^+$: 450.1965, found 450.1956.

10) 1-(5-Methoxy-2-((E)-1,2-diphenylvinyl)phenyl)-1H-benzo[d][1,2,3]triazole (3ja) and 1-(3-Methoxy-2-((E)-1,2-diphenylvinyl)phenyl)-1H-benzo[d][1,2,3]triazole (3ja')
The reaction of 1-(3-methoxyphenyl)-1H-benzo[d][1,2,3]triazole (1j, 0.2 mmol, 45.1 mg), diphenylacetylene (2a, 0.3 mmol, 53.5 mg), RhCl(PPh$_3$)$_3$ (0.005 mmol, 4.6 mg), AgOTf (0.01 mmol, 2.6 mg) in mesitylene (1.6 mL) under typical procedure afforded 58 mg (72%) of 3ja and 3ja’ as mixtures (2.78:1.00). HRMS m/z (ESI) calcd for C$_{27}$H$_{22}$N$_3$O (M + H)$^+$: 404.1757, found 404.1756.

11) 1-(5-Methyl-2-((E)-1,2-diphenylvinyl)phenyl)-1H-benzo[d][1,2,3]triazole (3ka)

The reaction of 1-(3-methylphenyl)-1H-benzo[d][1,2,3]triazole (1k, 0.2 mmol, 41.9 mg), diphenylacetylene (2a, 0.3 mmol, 53.5 mg), RhCl(PPh$_3$)$_3$ (0.005 mmol, 4.6 mg), AgOTf (0.01 mmol, 2.6 mg) in mesitylene (1.6 mL) under typical procedure afforded 50 mg (65%) of 3ka as solid. m.p.: 139-140 °C; $^{1}H$ NMR (CDCl$_3$, 400 MHz): $\delta$ = 7.89 (d, $J$ = 7.6 Hz, 1H), 7.65 (d, $J$ = 7.6 Hz, 1H), 7.46 (d, $J$ = 8.4 Hz, 1H), 7.38-7.22 (m, 4H), 7.11-7.05 (m, 3H), 7.01-6.93 (m, 2H), 6.83 (s, 1H), 6.81-6.71 (m, 3H), 6.53 (d, $J$ = 7.6 Hz, 2H), 2.50 (s, 3H); $^{13}C$ NMR (CDCl$_3$, 100 MHz): $\delta$ = 145.2, 139.6, 139.2, 139.0, 138.1, 136.8, 134.4, 133.6, 131.6, 131.1, 130.6, 129.2, 128.7, 128.2, 127.8, 127.5, 127.0, 126.89, 126.85, 123.4, 119.4, 110.2, 20.9 ppm; IR (KBr): $\nu_{\text{max}}$ = 1507, 1493, 1459, 1445, 1271, 1072, 748, 721, 697 cm$^{-1}$; HRMS m/z (ESI) calcd for C$_{27}$H$_{22}$N$_3$ (M + H)$^+$: 388.1808, found 388.1801.

12) 1-(3,5-Dimethoxy-2-((E)-1,2-diphenylvinyl)phenyl)-1H-benzo[d][1,2,3]triazole (3la)
The reaction of 1-(3,5-dimethoxyphenyl)-1H-benzo[d][1,2,3]triazole (1l, 0.2 mmol, 51.1 mg), diphenylacetylene (2a, 0.3 mmol, 53.5 mg), RhCl(PPh₃)₃ (0.01 mmol, 9.3 mg), AgOTf (0.02 mmol, 5.1 mg) in mesitylene (1.6 mL) under typical procedure afforded 34 mg (39%) of 3la as solid. m.p.: 69-70 °C; ¹H NMR (CDCl₃, 400 MHz): δ = 7.91 (d, J = 8.4 Hz, 1H), 7.33-7.17 (m, 1H), 7.16-7.00 (m, 9H), 6.94-6.89 (m, 2H), 6.88-6.79 (m, 1H), 6.78-6.68 (m, 1H), 6.66-6.57 (m, 1H), 3.88 (s, 3H), 3.63 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ = 160.8, 159.8, 145.0, 142.1, 137.7, 136.8, 133.9, 133.4, 130.9, 128.3, 127.8, 127.7, 127.0, 126.9, 126.3, 123.2, 120.3, 119.2, 110.0, 103.8, 100.5, 56.0, 55.7 ppm; IR (KBr): νₑₓₘₐₓ = 1606, 1575, 1492, 1459, 1277, 1163, 1047, 1023, 745, 694 cm⁻¹; HRMS m/z (ESI) calcd for C₂₈H₂₄N₃O₂ (M + H)⁺: 434.1863, found 434.1856.

13) 5,6-Dimethyl-1-(2-((E)-1,2-diphenylvinyl)phenyl)-1H-benzo[d][1,2,3]triazole (3ma)

The reaction of 1-phenyl-5,6-dimethyl-1H-benzo[d][1,2,3]triazole (1m, 0.2 mmol, 44.7 mg), diphenylacetylene (2a, 0.3 mmol, 53.5 mg), RhCl(PPh₃)₃ (0.005 mmol, 4.6 mg), AgOTf (0.01 mmol, 2.6 mg) in mesitylene (1.6 mL) under typical procedure afforded 70 mg (87%) of 3ma as solid. m.p.: 181-182 °C; ¹H NMR (CDCl₃, 400 MHz): δ = 7.72 (d, J = 7.1 Hz, 1H), 7.66-7.58 (m, 2H), 7.54 (t, J = 7.1 Hz, 1H), 7.40 (d, J = 7.1 Hz, 1H), 7.12-7.02 (m, 3H), 7.00-6.89 (m, 3H), 6.86-6.68 (m, 4H), 6.52 (d, J = 7.2 Hz, 2H), 2.33 (s, 3H), 2.32 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ = 144.4,
142.1, 139.8, 138.1, 137.2, 136.7, 134.8, 133.1, 132.7, 131.6, 131.4, 129.7, 129.2, 128.7, 128.5, 127.8, 127.7, 126.9, 126.8, 118.4, 109.7, 20.5, 20.1 ppm; IR (KBr): \(\nu_{\text{max}} = 1496, 1443, 1245, 1104, 1058, 837, 770, 695\ \text{cm}^{-1}\); HRMS m/z (ESI) calcd for C\(_{28}\)H\(_{24}\)N\(_3\) (M + H)\(^+\): 402.1965, found 402.1967.

14) 5-Nitro-1-(2-((E)-1,2-diphenylvinyl)phenyl)-1H-benzo[d][1,2,3]triazole (3na)

![Chemical Structure](image)

The reaction of 1-phenyl-5-nitro-1H-benzo[d][1,2,3]triazole (1n, 0.2 mmol, 48.0 mg), diphenylacetylene (2a, 0.3 mmol, 53.5 mg), RhCl(PPh\(_3\))\(_3\) (0.005 mmol, 4.6 mg), AgOTf (0.01 mmol, 2.6 mg) in mesitylene (1.6 mL) under typical procedure afforded 31 mg (37%) of 3na as solid. m.p.: 147-148 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz):
\[\delta = 8.81\ (s, 1H), 8.18\ (d, J = 7.6 \text{ Hz}, 1H), 7.82\ (d, J = 7.47 \text{ Hz}, 1H), 7.71\ (t, J = 7.47 \text{ Hz}, 1H), 7.60\ (t, J = 7.47 \text{ Hz}, 1H), 7.40\ (d, J = 7.47 \text{ Hz}, 1H), 7.28-7.20\ (m, 2H), 7.15-7.02\ (m, 4H), 7.01-6.93\ (m, 2H), 6.90\ (s, 1H), 6.78-6.66\ (m, 2H), 6.50\ (d, J = 6.0 \text{ Hz}, 1H); \] \(^{13}\)C NMR (CDCl\(_3\), 100 MHz):
\[\delta = 144.5, 144.3, 142.6, 139.1, 137.9, 136.3, 136.2, 133.7, 132.3, 132.2, 130.9, 129.3, 129.0, 128.6, 128.0, 127.8, 127.6, 127.5, 127.2, 122.1, 116.8, 110.7\ \text{ppm}; \] IR (KBr): \(\nu_{\text{max}} = 1526, 1346, 1071, 801\ \text{cm}^{-1}\); HRMS m/z (ESI) calcd for C\(_{28}\)H\(_{19}\)N\(_3\)O\(_2\) (M + H)\(^+\): 419.1503, found 419.1502.

15) 6-Methoxy-1-(2-((E)-1,2-diphenylvinyl)phenyl)-1H-benzo[d][1,2,3]triazole (3oa) and 5-Methoxy-1-(2-((E)-1,2-diphenylvinyl)phenyl)-1H-benzo[d][1,2,3] triazole (3oa’)

![Chemical Structure](image)

The reaction of 1-phenyl-6 or 5-methoxy-1H-benzo[d][1,2,3]triazole 1o and 1o’
(1o/1o' = 2.57:1.00, 0.2 mmol, 45.1 mg), diphenylacetylene (2a, 0.3 mmol, 53.5 mg),
RhCl(PPh₃)₃ (0.005 mmol, 4.6 mg), AgOTf (0.01 mmol, 2.6 mg) in mesitylene (1.6 mL) under typical procedure afforded 43 mg (53%) of 3oa and 3oa’ as mixtures (2.23:1.00). HRMS m/z (ESI) calcd for C₂₇H₂₂N₃O (M + H)⁺: 404.1757, found 404.1749.

16) 6-Fluoro-1-(2-((E)-1,2-diphenylvinyl)phenyl)-1H-benzo[d][1,2,3] triazole (3pa) and 5-Fluoro-1-(2-((E)-1,2-diphenylvinyl)phenyl)-1H-benzo[d][1,2,3] triazole (3pa')

The reaction of 1-phenyl-5 or 6-fluoro-1H-benzo[d][1,2,3]triazole 1p and 1p’ (1p/1p’ = 1.50:1.00, 0.2 mmol, 42.6 mg), diphenylacetylene (2a, 0.3 mmol, 53.5 mg), RhCl(PPh₃)₃ (0.005 mmol, 4.6 mg), AgOTf (0.01 mmol, 2.6 mg) in mesitylene (1.6 mL) under typical procedure afforded 70 mg (89%) of 3pa and 3pa’ (1.83:1.00) as mixture. HRMS m/z (ESI) calcd for C₂₆H₁₉FN₃ (M + H)⁺: 392.1558, found 392.1556.

17) 6-(Trifluoromethyl)-1-(2-((E)-1,2-diphenylvinyl)phenyl)-1H-benzo[d][1,2,3] triazole (3qa) and 5-(Trifluoromethyl)-1-(2-((E)-1,2-diphenylvinyl)phenyl)-1H-benzo[d][1,2,3] triazole (3qa’)

The reaction of 1-phenyl-6 or 5-trifluoromethyl-1H-benzo[d][1,2,3]triazole 1q and
1q' (1q/1q' = 1.38:1.00, 0.15 mmol, 39.5 mg), diphenylacetylene (2a, 0.225 mmol, 40.1 mg), RhCl(PPh$_3$)$_3$ (0.00375 mmol, 3.5 mg), AgOTf (0.0075 mmol, 1.9 mg) in mesitylene (1.6 mL) under typical procedure afforded 46 mg (69%) of 3qa and 3qa' (1.52:1.00) as mixtures. HRMS m/z (ESI) calcd for C$_{27}$H$_{19}$F$_3$N$_3$ (M + H)$^+$: 442.1526, found 442.1527.

18) 1-(4-Methoxy-2-((E)-1,2-diphenylvinyl)phenyl)-1H-1,2,3-triazole (3ra)

The reaction of 1-(4-methoxyphenyl)-1H-[1,2,3]triazole (1n, 0.2 mmol, 35.0 mg), diphenylacetylene (2a, 0.3 mmol, 53.5 mg), RhCl(PPh$_3$)$_3$ (0.005 mmol, 4.6 mg), AgOTf (0.01 mmol, 2.6 mg) in mesitylene (1.6 mL) under N$_2$ for 50 h afforded 34 mg (48%) of 3ra as solid. m.p.: 143-144 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta =$ 7.50 (s, 2H), 7.42 (d, $J =$ 8.4 Hz, 1H), 7.14-6.92 (m, 12H), 6.59 (s, 1H), 3.87 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta =$ 159.8, 142.0, 139.5, 139.0, 137.1, 134.7, 132.6, 130.6, 129.8, 129.3, 127.84, 127.80, 127.72, 127.68, 127.1, 126.9, 116.5, 113.3, 55.6 ppm; IR (KBr): $\nu_{\text{max}} =$ 1607, 1575, 1504, 1462, 1421, 1294, 1205, 1061, 1028, 952, 810, 775, 699 cm$^{-1}$; HRMS m/z (ESI) calcd for C$_{23}$H$_{20}$N$_3$O (M + H)$^+$: 354.1601, found 354.1601.

19) 3-(2-((E)-1,2-Diphenylvinyl)phenyl)-3H-[1,2,3]triazolo[4,5-b]pyridine (3sa)

The reaction of 1-phenyl-1H-7-azabenzo[d][1,2,3]triazole (1s, 0.2 mmol, 39.2 mg), diphenylacetylene (2a, 0.3 mmol, 53.5 mg), RhCl(PPh$_3$)$_3$ (0.005 mmol, 4.6 mg), AgOTf (0.01 mmol, 2.6 mg) in mesitylene (1.6 mL) under typical procedure
afforded 65 mg (87%) of 3sa as solid. m.p.: 139-140 °C; 1H NMR (CDCl3, 400 MHz): 
δ = 8.58-8.46 (m, 1H), 8.18 (d, J = 8.4 Hz, 1H), 7.71 (d, J = 7.07 Hz, 1H), 7.63 (t, J = 7.07 Hz, 1H), 7.57 (t, J = 7.07 Hz, 1H), 7.48 (d, J = 7.07 Hz, 1H), 7.30-7.16 (m, 1H), 7.09-7.02 (m, 3H), 6.96-6.86 (m, 2H), 6.79 (s, 1H), 6.77-6.68 (m, 5H); 13C NMR (CDCl3, 100 MHz): δ = 150.2, 146.2, 142.5, 139.3, 138.3, 136.8, 136.2, 133.3, 131.7, 131.5, 130.2, 129.3, 128.6, 128.2, 128.0, 127.8, 127.5, 126.9, 126.7, 119.4 ppm; IR (KBr): νmax = 2156, 1589, 1496, 1455, 1259, 764, 701 cm⁻¹; HRMS m/z (ESI) calcd for C25H19N4 (M + H)⁺: 375.1604, found 375.1602.

20) 1-(2-((E)-1,2-Dip-tolylvinyl)phenyl)-1H-benzo[d][1,2,3]triazole (3ab)

The reaction of 1-phenyl-1H-benzo[d][1,2,3]triazole (1a, 0.2 mmol, 39.0 mg), bis(4-methylphenyl)acetylene (2b, 0.3 mmol, 61.9 mg), RhCl(PPh3)3 (0.005 mmol, 4.6 mg), AgOTf (0.01 mmol, 2.6 mg) in mesitylene (1.6 mL) under typical procedure afforded 77 mg (96%) of 3ab as solid. m.p.: 138-139 °C; 1H NMR (CDCl3, 400 MHz): δ = 7.90 (d, J = 7.6 Hz, 1H), 7.76 (d, J = 7.47 Hz, 1H), 7.65 (t, J = 7.47 Hz, 1H), 7.56 (t, J = 7.47 Hz, 1H), 7.43 (d, J = 7.47 Hz, 1H), 7.37-7.17 (m, 3H), 7.96-7.86 (m, 4H), 6.78 (s, 1H), 6.57 (d, J = 8.4 Hz, 2H), 6.46 (d, J = 8.0 Hz, 2H), 2.26 (s, 3H), 2.05 (s, 3H); 13C NMR (CDCl3, 100 MHz): δ = 145.3, 142.8, 138.8, 136.8, 136.6, 135.4, 134.6, 134.0, 133.6, 131.8, 131.2, 129.9, 129.2, 128.6, 128.5, 128.4, 128.3, 127.8, 126.9, 123.4, 119.4, 110.4, 21.1, 20.9 ppm; IR (KBr): νmax = 1509, 1458, 1271, 1065, 784, 741 cm⁻¹; HRMS m/z (ESI) calcd for C28H24N3 (M + H)⁺: 402.1965, found 402.1966.

21) 1-(2-((E)-1,2-Bis(4-fluorophenyl)vinyl)phenyl)-1H-benzo[d][1,2,3]triazole (3ac)
The reaction of 1-phenyl-1H-benzo[d][1,2,3]triazole (1a, 0.2 mmol, 39.0 mg), bis(4-fluorophenyl)acetylene (2c, 0.3 mmol, 64.3 mg), RhCl(PPh₃)₃ (0.005 mmol, 4.6 mg), AgOTf (0.01 mmol, 2.6 mg) in mesitylene (1.6 mL) under typical procedure afforded 72 mg (88%) of 3ac as solid. m.p.: 158-159 °C; ¹H NMR (CDCl₃, 400 MHz): δ = 7.89 (d, J = 8.8 Hz, 1H), 7.73 (d, J = 7.5 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.57 (t, J = 7.5 Hz, 1H), 7.43 (d, J = 7.5 Hz, 1H), 7.39 - 7.21 (m, 2H), 7.21 - 7.11 (m, 1H), 6.86 - 7.01 (m, 2H), 6.84 - 6.66 (m, 2H), 6.60 - 6.29 (m, 4H); ¹³C NMR (CDCl₃, 100 MHz): δ = 161.6 (d, J_C-F = 246.2 Hz), 161.5 (d, J_C-F = 246.0 Hz), 145.1, 141.9, 138.5, 134.4, 133.7 (d, J_C-F = 3.5 Hz), 133.4, 132.5 (d, J_C-F = 3.4 Hz), 131.7, 130.9, 130.8, 130.4 (d, J_C-F = 19 Hz), 130.2 (d, J_C-F = 22.5 Hz), 128.9, 127.6, 127.2, 123.7, 119.4, 114.9 (d, J_C-F = 21.4 Hz), 114.6 (d, J_C-F = 21.5 Hz), 109.9 ppm; IR (KBr): ν_max = 1599, 1507, 1459, 1223, 1158, 1068, 837, 788, 744 cm⁻¹; HRMS m/z (ESI) calcd for C₂₆H₁₈F₂N₃ (M + H)⁺: 410.1463, found 410.1457.

22) 1-(2-((E)-1,2-Di(naphthalen-1-yl)vinyl)phenyl)-1H-benzo[d][1,2,3]triazole (3ad)

The reaction of 1-phenyl-1H-benzo[d][1,2,3]triazole (1a, 0.2 mmol, 39.0 mg), bis(1-naphthyl)acetylene (2d, 0.3 mmol, 83.5 mg), RhCl(PPh₃)₃ (0.01 mmol, 9.3 mg), AgOTf (0.02 mmol, 5.1 mg) in mesitylene (1.6 mL) under typical procedure afforded 41 mg (43%) of 3ad as solid. m.p.: 105-106 °C; ¹H NMR (CDCl₃, 400 MHz):
\[ \delta = 8.21 \text{ (d, } J = 8.4 \text{ Hz, 1H), } 8.07 \text{ (d, } J = 8.0 \text{ Hz, 1H), } 7.83-7.65 \text{ (m, 4H), } 7.64-7.42 \text{ (m, 6H), } 7.30-7.19 \text{ (m, 2H), } 7.17-7.05 \text{ (m, 3H), } 7.05-6.93 \text{ (m, 1H), } 6.90-6.77 \text{ (m, 1H), } 6.76-6.66 \text{ (m, 1H), } 6.64-6.45 \text{ (m, 3H); } ^{13}\text{C NMR (CDCl}_3, 100 \text{ MHz): } \delta = 145.1, 143.2, 140.5, 135.4, 134.3, 133.9, 133.4, 133.3, 132.6, 132.1, 131.7, 131.0, 130.7, 128.7, 128.4, 128.2, 128.1, 127.6, 127.13, 127.09, 126.8, 126.2, 125.8, 125.4, 125.3, 125.0, 124.9, 124.8, 124.5, 123.4, 119.2, 109.10 \text{ ppm; IR (KBr): } v_{\text{max}} = 1498, 1273, 1063, 797, 777, 744 \text{ cm}^{-1}; \text{ HRMS m/z (ESI) calcd for } C_{34}H_{24}N_3 (M + H)^+: 474.1965, \text{ found } 474.1957. \\

23) 1-(2-((E)-1-Phenylprop-1-enyl)phenyl)-1H-benzo[d][1,2,3]triazole (3ae)

\[ \text{The reaction of 1-phenyl-1H-benzo[d][1,2,3]triazole (1a, 0.2 mmol, 39.0 mg), 1-phenyl-1-propyne (2e, 0.3 mmol, 37 } \mu \text{L), RhCl(PPh}_3)_3 (0.01 mmol, 9.3 mg), AgOTf (0.02 mmol, 5.1 mg) in mesitylene (1.6 mL) under typical procedure afforded 30 mg (48\%) of 3ae as liquid; } ^1\text{H NMR (CDCl}_3, 400 \text{ MHz): } \delta = 8.05-7.84 \text{ (m, 1H), } 7.69-7.46 \text{ (m, 3H), } 7.40-7.21 \text{ (m, 3H), } 7.18-7.01 \text{ (m, 1H), } 6.88-6.73 \text{ (m, 3H), } 6.63-6.44 \text{ (m, 2H), } 6.04 \text{ (d, } J = 6.8 \text{ Hz, 1H), } 1.68 \text{ (d, } J = 6.8 \text{ Hz, 3H); } ^{13}\text{C NMR (CDCl}_3, 100 \text{ MHz): } \delta = 145.2, 142.2, 139.4, 137.7, 134.4, 133.6, 131.6, 129.9, 128.3, 128.2, 128.1, 127.5, 127.2, 127.0, 126.4, 123.4, 119.4, 110.2, 15.3 \text{ ppm; IR (KBr): } v_{\text{max}} = 1496, 1458, 1441, 1274, 1185, 1062, 1006, 786, 765, 745, 701 \text{ cm}^{-1}; \text{ HRMS m/z (ESI) calcd for } C_{21}H_{18}N_3 (M + H)^+: 312.1495, \text{ found } 312.1503. \\

24) 1-(2-((E)-1-Phenylbut-1-enyl)phenyl)-1H-benzo[d][1,2,3]triazole (3af)

\[ \text{The reaction of 1-phenyl-1H-benzo[d][1,2,3]triazole (1a, 0.2 mmol, 39.0 mg),} \]
1-phenyl-1-butyn-1-phenyl-1-butyn (2f, 0.3 mmol, 43 µL), RhCl(PPh$_3$)$_3$ (0.01 mmol, 9.3 mg), AgOTf (0.02 mmol, 5.1 mg) in mesitylene (1.6 mL) under typical procedure afforded 43 mg (66%) of 3af as solid. m.p.: 77-78 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 7.93$ (d, $J = 8.0$ Hz, 1H), 7.66-7.55 (m, 2H), 7.55-7.45 (m, 1H), 7.44-7.23 (m, 3H), 7.22-7.13 (m, 1H), 6.97-6.81 (m, 3H), 6.64-6.50 (m, 2H), 5.83 (t, $J = 7.5$ Hz, 1H), 2.03 (m, $J = 7.5$ Hz, 2H), 0.84 (t, $J = 7.5$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 145.3, 142.1, 138.1, 137.8, 135.9, 134.5, 133.8, 131.7, 129.9, 128.3, 128.2, 127.7, 127.3, 127.0, 126.6, 123.5, 119.5, 110.4, 22.7, 14.0 ppm; IR (KBr): $\nu_{\text{max}} = 1613, 1497, 1458, 1444, 1272, 1062, 1005, 785, 773, 760, 743, 710$ cm$^{-1}$; HRMS m/z (ESI) calcd for C$_{22}$H$_{20}$N$_3$ (M + H)$^+$: 326.1652, found 326.1654.

251-(2-((1E,3E)-1,4-diphenylbuta-1,3-dien-2-yl)phenyl)-1H-benzo[d][1,2,3]triazole/1-(2-((1E,3E)-1,4-diphenylbuta-1,3-dienyl)phenyl)-1H-benzo[d][1,2,3]triazole

The reaction of 1-phenyl-1H-benzo[d][1,2,3]triazole (1a, 0.2 mmol, 39.0 mg), (E)-1,4-diphenylbuta-1-en-3-yne (2g, 0.3 mmol, 61.3 mg), RhCl(PPh$_3$)$_3$ (0.005 mmol, 4.6 mg), AgOTf (0.01 mmol, 2.6 mg) in mesitylene (1.6 mL) under typical procedure afforded 60 mg (75%) of 3ag and 3ag' (1.26:1.00) as a mixtures. HRMS m/z (ESI) calcd for C$_{28}$H$_{22}$N$_3$ (M + H)$^+$: 400.1808, found 400.1805.
Deuterium-Labeling Experiments

1) The reaction of 1a-d$_5$ (0.1 mmol, 20 mg), 2a (0.15 mmol, 26.7 mg), RhCl(PPh$_3$)$_3$ (0.0025 mmol, 2.3 mg), AgOTf (0.005 mmol, 1.3 mg), H$_2$O (0.5 mmol, 9 µL) in mesitylene (0.8 mL) at 160 °C under N$_2$ for 0.5 h afforded 3aa-d$_5$ (3 mg, 8%) with the recovery of 1a-d$_5$ (17 mg, 85%).
2) Kinetic Isotope Effect (KIE) Experiment:

(1) Intermolecular KIE

The reaction of 1a (0.1 mmol, 19.5 mg), 1a-\textit{d}_5 (0.1 mmol, 20.0 mg), 2a (0.3 mmol, 53.5 mg), RhCl(PPh\textsubscript{3})\textsubscript{3} (0.005 mmol, 4.6 mg), AgOTf (0.01 mmol, 2.6 mg) in mesitylene (1.6 mL) at 160 °C under N\textsubscript{2} for 0.5 h afforded 3aa and 3aa-\textit{d}_5 (3aa + 3aa-\textit{d}_5, 8 mg, 11%) with the ratio of 1.67:1.00 (3aa/3aa-\textit{d}_5), which was determined by \textsuperscript{1}H NMR.
(2) Intramolecular KIE

The reaction of 1a-d1 (0.2 mmol, 39.2 mg), 2a (0.3 mmol, 53.5 mg), RhCl(PPh3)₃ (0.005 mmol, 4.6 mg), AgOTf (0.01 mmol, 2.6 mg) in mesitylene (1.6 mL) at 160 °C under N₂ for 0.5 h afforded 3aa-d₁ and 3aa-d₁’ (3aa-d₁ + 3aa-d₁’, 21 mg, 28 %) with
the ratio of 2.10:1.00 (3aa-d_{1}/3aa-d_{1}').
Peking University Mass Spectrometry Sample Analysis Report

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Comment: ESI Positive

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Operator: Peking University

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Peking University Mass Spectrometry Sample Analysis Report

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Instrument: Bruker Apex IV FTMS
Operator: Peking University

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Peking University Mass Spectrometry Sample Analysis Report

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## Peking University Mass Spectrometry Sample Analysis Report

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Operator: Peking University

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Peking University Mass Spectrometry Sample Analysis Report

Analysis Info
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Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Peking University Mass Spectrometry Sample Analysis Report

Analysis Info
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Comment ESI Positive

Acquisition Date 6/26/2013 9:10:47 PM
Instrument Bruker Apex IV FTMS
Operator Peking University

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Peking University Mass Spectrometry Sample Analysis Report

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Peking University Mass Spectrometry Sample Analysis Report

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Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Peking University Mass Spectrometry Sample Analysis Report

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Operator: Peking University

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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The image contains a 1H NMR spectrum with chemical shifts marked, along with two molecular structures labeled as 3oa and 3oa'. The spectrum shows peaks at various ppm values, indicating the presence of different chemical environments. The ratio of the peaks is given as (2.23 : 1.00).
Peking University Mass Spectrometry Sample Analysis Report

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Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Peking University Mass Spectrometry Sample Analysis Report

Analysis Info
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Acquisition Date: 6/26/2013 9:15:00 PM
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Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

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<th>Score</th>
<th>m/z</th>
<th>err [mDa]</th>
<th>err [ppm]</th>
<th>mSigma</th>
<th>rdb</th>
<th>e^-</th>
<th>Conf</th>
<th>N-Rule</th>
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<td>354.16005</td>
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<td>C23 H20 N3 O</td>
<td>100.00</td>
<td>354.16009</td>
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<td>0.1</td>
<td>1.2</td>
<td>15.5</td>
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</table>
Peking University Mass Spectrometry Sample Analysis Report

Analysis Info
Analysis Name: 13060980_20130626_000019.d
Sample: 18
Comment: ESI Positive

Acquisition Date: 6/26/2013 9:05:08 PM
Instrument: Bruker Apex IV FTMS
Operator: Peking University

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Peking University Mass Spectrometry Sample Analysis Report

**Analysis Info**
- **Analysis Name**: 13060980_20130626_000021.d
- **Sample**: 20
- **Comment**: ESI Positive
- **Acquisition Date**: 6/26/2013 9:08:54 PM
- **Instrument**: Bruker Apex IV FTMS
- **Operator**: Peking University

**Graphic**
- M/z values: 326.16541, 312.15025, 342.16018, 358.15546, 374.16769, 386.28897
- Intensity
- Compound: 3af

**Table**
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<table>
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<th>#</th>
<th>Formula</th>
<th>Score</th>
<th>m/z</th>
<th>err (mDa)</th>
<th>err (ppm)</th>
<th>mSigma</th>
<th>rdb</th>
<th>e^-</th>
<th>N-Rule</th>
</tr>
</thead>
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<td>326.16541</td>
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<td>C22H20N3S</td>
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Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name: 13060960_20130626_000026.d
Sample: 25
Comment: ESI Positive

Acquisition Date: 6/26/2013 9:19:06 PM
Instrument: Bruker Apex IV FTMS
Operator: Peking University

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$K_H/K_D = 1.67$

3aa

3aa-d$_5$
3aa-\textit{d}_1/3aa-\textit{d}'_1=2.1:1