INTRAMOLECULAR KETENIMINE-KETENIMINE [2+2] AND [4+2] CYCLOADDITIONS

Mateo Alajarín,^{*a} Baltasar Bonillo,^a Pilar Sánchez-Andrada,^a Ángel Vidal,^a
Delia Bautista^b

^a *Departamento de Química Orgánica, Facultad de Química, Universidad de Murcia,
Campus de Espinardo, 30100, Murcia, Spain*

^b *Servicio Universitario de Instrumentación Científica, Universidad de Murcia, Campus de
Espinardo, 30100, Murcia, Spain*

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General Methods

All melting points are uncorrected. Infrared (IR) spectra were recorded neat or as Nujol emulsions. ^1H NMR spectra were recorded in CDCl_3 at 300 or 400 MHz. ^{13}C NMR spectra were recorded in CDCl_3 at 75 or 100 MHz. The chemical shifts are expressed in ppm, relative to Me_4Si at $\delta = 0.00$ ppm for ^1H , while the chemical shifts for ^{13}C are reported relative to the resonance of CDCl_3 $\delta = 77.10$ ppm or $\text{DMSO}-d_6$ $\delta = 35.35$ ppm. Mass spectra were determined at an ionizing voltage of 70 eV.

Materials: 2-Azidobenzyl chloride **7a**,¹ 2-azido-3-methylbenzyl chloride **7b**,² 2-azido-5-bromobenzyl bromide **7c**,³ 2-azido-5-chlorobenzyl chloride **7d**,² 2-azido-5-methylbenzyl chloride **7e**,⁴ 3-azido-2-bromomethylnaphthalene **7f**,³ 1,2-bis(azidomethyl)benzene **1**,⁵ bis(iminophosphorane) **13**,⁶ and diphenylketene⁷ were prepared following published experimental procedures.

Preparation of 2,2'-bis(azidomethyl)biphenyl **4**

To a solution of 2,2'-bis(bromomethyl)biphenyl (10 mmol) in DMSO (30 mL) NaN_3 (1.62 g, 25 mmol) was added. The reaction mixture was stirred at room temperature for 12 h. Then, water (100 mL) was added and the resulting suspension was extracted with diethyl ether (3 x 75 mL). The combined organic layers were washed with water (3 x 100 mL) and brine (100 mL), and dried over anhydrous MgSO_4 . The solvent was removed under reduced pressure and the resulting material was chromatographed on a silica gel column using hexanes/diethyl ether (10:1, v/v) as eluent. Yield 96%; colorless oil; IR (neat) 2096 (vs), 1477 (s), 1448 (s), 1344 (s), 1257 (vs), 1194 (m), 1007 (w), 949 (w), 887 (w), 873 (m), 758 (vs) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 4.06 (d, 2 H, $J = 13.6$ Hz), 4.13 (d, 2 H, $J = 13.6$ Hz), 7.20-7.24 (m, 2 H), 7.36-7.49 (m, 6 H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 52.6, 128.3, 128.4, 129.3, 130.2, 133.7 (s), 139.6 (s); MS (EI, 70 eV) m/z (rel int) 208 ($\text{M}^+ - 2 \text{N}_2$, 12), 180 (100). Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{N}_6$ (264.29): C, 63.62; H, 4.58; N, 31.80. Found: C, 63.44; H, 4.55; N, 31.95.

Preparation of dinitriles **3** and **6**

To a solution of the corresponding bis(azide) **1** or **4** (2 mmol) in anhydrous toluene (20 mL) triphenylphosphine (1.05 g, 4 mmol) was added in five portions. The reaction mixture was stirred at room temperature, under nitrogen, for 12 h. Then, a solution of diphenylketene (0.78 g, 4 mmol) in anhydrous toluene (5 mL) was added, and after stirring at room temperature for

30 min the reaction mixture was heated at reflux temperature for 2 h. After cooling, the solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column using hexanes/diethyl ether (7:3, v/v) as eluent.

Dinitrile 3: yield 51%; mp 237 °C (colorless prism, diethyl ether); IR (Nujol) 2261 (m), 2229 (m), 1600 (s), 1490 (vs), 1334 (m), 1241 (m), 1184 (m), 1159 (m), 1089 (m), 1032 (s), 1001 (m), 774 (vs), 757 (vs), 698 (vs) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 3.02 (s, 4 H), 6.84-6.87 (m, 2 H), 7.09-7.13 (m, 10 H), 7.28-7.35 (m, 12 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 40.3, 52.5 (s), 122.0 (s), 127.2, 127.7, 128.1, 128.7, 131.9, 134.3 (s), 140.2 (s); MS (EI, 70 eV) m/z (rel int) 488 (M^+ , 5), 296 (100). Anal. Calcd for $\text{C}_{36}\text{H}_{28}\text{N}_2$ (488.63): C, 88.49; H, 5.78; N, 5.73. Found: C, 88.15; H, 5.89; N, 5.88.

Dinitrile 6: yield 47%; mp 193 °C (colorless prism, diethyl ether); IR (Nujol) 2239 (m), 1599 (w), 1493 (s), 1448 (w), 1097 (s), 1031 (w), 750 (s), 696 (vs) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 3.46 (d, 2 H, $J = 14.2$ Hz), 3.56 (d, 2 H, $J = 14.2$ Hz), 6.61 (d, 2 H, $J = 7.2$ Hz), 6.95 (d, 4 H, $J = 7.2$ Hz), 7.07-7.23 (m, 12 H), 7.29-7.31 (m, 10 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 40.7, 52.0 (s), 122.6 (s), 127.2, 127.3, 127.4, 127.7, 128.1, 128.7, 128.9, 129.3, 131.0, 132.8 (s), 139.8 (s), 140.4 (s), 141.3 (s); MS (EI, 70 eV) m/z (rel int) 564 (M^+ , 20), 435 (100). Anal. Calcd for $\text{C}_{42}\text{H}_{32}\text{N}_2$ (564.73): C, 89.33; H, 5.71; N, 4.96. Found: C, 89.15; H, 5.89; N, 4.91.

Preparation of diazides 8

To a solution of the corresponding 2-azidobenzyl bromide or 2-azidobenzyl chloride **7** (10 mmol) in DMSO (30 mL) NaN_3 (0.81 g, 12.5 mmol) was added. The reaction mixture was stirred at room temperature for 12 h. Then, water (100 mL) was added and the resulting suspension was extracted with diethyl ether (3 x 75 mL). The combined organic layers were washed with water (3 x 100 mL) and brine (100 mL), and dried over anhydrous MgSO_4 . The solvent was removed under reduced pressure and the resulting material was chromatographed on a silica gel column using hexanes/diethyl ether as eluent.

2-Azidobenzylazide 8a: eluent for column chromatography, hexanes/diethyl ether (10:0.1, v/v); yield 50%; colorless oil; IR (neat) 2120 (vs), 1583 (vs), 1487 (vs), 1450 (vs), 1348 (vs), 1299 (vs), 1163 (m), 1148 (m), 1099 (m), 882 (m), 755 (vs) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 4.31 (s, 2 H), 7.14 (td, 1 H, $J = 7.5, 1.1$ Hz), 7.18-7.20 (m, 1 H), 7.30-7.32 (m, 1 H),

7.36-7.40 (m, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 50.2, 118.3, 125.0, 126.7 (s), 129.9, 130.4, 138.6 (s); MS (EI, 70 eV) m/z (rel int) 174 (M^+ , 5), 90 (100). Anal. Calcd for $\text{C}_7\text{H}_6\text{N}_6$ (174.16): C, 48.27; H, 3.47; N, 48.25. Found: C, 48.12; H, 3.42; N, 48.46.

2-Azido-3-methylbenzylazide 8b: eluent for column chromatography, hexanes/diethyl ether (10:0.1, v/v); yield 49%; colorless oil; IR (neat) 2144 (vs), 1593 (m), 1466 (vs), 1434 (vs), 1345 (vs), 1302 (vs), 1168 (m), 1132 (m), 1082 (m), 1037 (w), 972 (w), 870 (m), 820 (m), 780 (vs), 755 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 2.45 (s, 3 H), 4.39 (s, 2 H), 7.09-7.18 (m, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 18.0, 51.4, 126.1, 128.1, 129.1 (s), 131.9, 133.1 (s), 136.9 (s); MS (EI, 70 eV) m/z (rel int) 188 (M^+ , 5), 103 (100). Anal. Calcd for $\text{C}_8\text{H}_8\text{N}_6$ (188.19): C, 51.06; H, 4.28; N, 44.66. Found: C, 50.84; H, 4.35; N, 44.78.

2-Azido-5-bromobenzylazide 8c: eluent for column chromatography, hexanes/diethyl ether (10:0.1, v/v); yield 78%; colorless oil; IR (neat) 2101 (vs), 1575 (s), 1479 (vs), 1402 (vs), 1342 (vs), 1274 (vs), 1191 (vs), 1155 (vs), 1102 (vs), 888 (s), 856 (s), 811 (vs), 669 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 4.29 (s, 2 H), 7.04-7.07 (m, 1 H), 7.46-7.50 (m, 2 H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 49.8, 117.8 (s), 119.9, 128.8 (s), 132.6, 133.0, 137.6 (s); MS (EI, 70 eV) m/z (rel int) 254 ($\text{M}^+ + 2$, 5), 252 (M^+ , 5), 89 (100). Anal. Calcd for $\text{C}_7\text{H}_5\text{BrN}_6$ (253.06): C, 33.22; H, 1.99; N, 33.21. Found: C, 33.18; H, 1.93; N, 33.05.

2-Azido-5-chlorobenzylazide 8d: eluent for column chromatography, hexanes/diethyl ether (10:0.1, v/v); yield 40%; colorless oil; IR (neat) 2120 (vs), 1577 (m), 1483 (vs), 1438 (s), 1409 (s), 1348 (s), 1303 (vs), 1193 (s), 1153 (s), 1111 (vs), 907 (m), 866 (m), 813 (vs) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz) δ 4.29 (s, 2 H), 7.09-7.12 (m, 1H), 7.31-7.35 (m, 2 H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 49.8, 119.5, 128.5 (s), 129.6, 130.1, 130.3 (s), 137.0 (s); MS (EI, 70 eV) m/z (rel int) 210 ($\text{M}^+ + 2$, 2), 208 (M^+ , 7), 89 (100). Anal. Calcd for $\text{C}_7\text{H}_5\text{ClN}_6$ (208.61): C, 40.30; H, 2.41; N, 40.28. Found: C, 40.27; H, 2.29; N, 40.11.

2-Azido-5-methylbenzylazide 8e: eluent for column chromatography, hexanes/diethyl ether (10:0.1, v/v); yield 59%; colorless oil; IR (neat) 2128 (vs), 1585 (m), 1498 (vs), 1450 (m), 1344 (s), 1297 (vs), 1160 (s), 1095 (w), 865 (m), 813 (vs) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 2.33 (s, 3 H), 4.27 (s, 2 H), 7.08 (d, 1 H, $J = 8.1$ Hz), 7.11-7.12 (m, 1 H), 7.17-7.19 (m, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 20.8, 50.3, 118.3, 126.4 (s), 130.5, 131.1, 134.9 (s), 135.8

(s); MS (EI, 70 eV) m/z (rel int) 188 (M^+ , 11), 104 (100). Anal. Calcd for $C_8H_8N_6$ (188.19): C, 51.06; H, 4.28; N, 44.66. Found: C, 50.87; H, 4.39; N, 44.64.

3-Azido-2-azidomethylnaphthalene 8f: eluent for column chromatography, hexanes/diethyl ether (9:1, v/v); yield 96%; mp 57 °C (colorless prism, diethyl ether); IR (Nujol) 2104 (vs), 1624 (s), 1596 (s), 1503 (s), 1330 (s), 1282 (vs), 1071 (s), 889 (s), 868 (vs), 841 (s), 754 (vs), 723 (vs), 695 (s) cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ 4.33 (s, 2 H), 7.36-7.39 (m, 1 H), 7.40 (s, 1 H), 7.44 (td, 1 H, $J = 6.9, 1.3$ Hz), 7.64-7.66 (m, 2 H), 7.21 (dd, 1 H, $J = 8.1, 0.7$ Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 50.7, 115.6, 125.8, 126.1 (s), 126.3, 127.2, 127.8, 129.5, 130.6 (s), 133.6 (s), 136.4 (s); MS (EI, 70 eV) m/z (rel int) 224 (M^+ , 9), 140 (100). Anal. Calcd for $C_{11}H_8N_6$ (224.22): C, 58.92; H, 3.60; N, 37.48. Found: C, 58.69; H, 3.55; N, 37.67.

Preparation of bis(iminophosphoranes) 9

To a solution of 2-azidobenzylazide **8** (5 mmol) in anhydrous diethyl ether (25 mL) triphenylphosphine (2.64 g, 10 mmol) was added in five portions. The reaction mixture was stirred, under nitrogen, at room temperature for 12 h, and the precipitated solid was filtered and dried.

Bis(iminophosphoranes) **9** were used immediately in the following step without further purification because of their rapid decomposition in solution and in the solid state.

Bis(iminophosphorane) 9a ($R^1 = R^2 = R^3 = H$): yield 81%.

Bis(iminophosphorane) 9b ($R^1 = R^2 = H, R^3 = CH_3$): yield 52%.

Bis(iminophosphorane) 9c ($R^1 = Br, R^2 = R^3 = H$): yield 79%.

Bis(iminophosphorane) 9d ($R^1 = Cl, R^2 = R^3 = H$): yield 96%.

Bis(iminophosphorane) 9e ($R^1 = CH_3, R^2 = R^3 = H$): yield 63%.

Bis(iminophosphorane) 9f ($R^1-R^2 = C_6H_4, R^3 = H$): yield 72%.

Analytical and spectroscopic data of compounds 11b-f

4-Methyl-2,2-diphenyl-1-diphenylmethylenidene-1,2-dihydroazeto[2,1-*b*]quinazoline 11b:

eluent for column chromatography, hexanes/diethyl ether (9:1, v/v); yield 77%; mp 190 °C (colorless prism, diethyl ether/*n*-pentane); IR (Nujol) 1714 (vs), 1632 (vs), 1594 (vs), 1492 (vs), 1291 (m), 1239 (m), 1194 (s), 1127 (vs), 1105 (vs), 1076 (s), 1036 (s), 1024 (m), 1004 (w), 939 (w), 853 (w), 827 (w), 784 (s), 763 (vs), 725 (s), 698 (vs), 664 (s) cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 2.33 (s, 3 H), 4.20 (s, 2 H), 6.52 (d, 1 H, *J* = 7.4 Hz), 6.67-6.70 (m, 2 H), 6.83 (t, 1 H, *J* = 7.5 Hz), 6.95-7.04 (m, 4 H), 7.20-7.34 (m, 15 H); ¹³C NMR (CDCl₃, 100 MHz) δ 20.3, 46.2, 70.4 (s), 112.8 (s), 119.2 (s), 122.4, 122.6, 124.4, 125.2, 125.5, 125.7, 125.8, 126.2, 126.5, 127.7, 127.8, 128.8, 132.1 (s), 136.3 (s), 136.4 (s), 136.6 (s), 137.9 (s), 143.1 (s), 159.3 (s); MS (EI, 70eV) *m/z* (rel int) 488.63 (M⁺, 46), 296 (100). Anal. Calcd for C₃₆H₂₈N₂ (488.63): C, 88.49; H, 5.77; N, 5.73. Found: C, 88.23; H, 5.79; N, 5.84.

6-Bromo-2,2-diphenyl-1-diphenylmethylenidene-1,2-dihydroazeto[2,1-*b*]quinazoline 11c:

eluent for column chromatography, hexanes/diethyl ether (9:1, v/v); yield 78%; mp 234 °C (colorless prism, diethyl ether/*n*-pentane); IR (Nujol) 1716 (vs), 1638 (vs), 1593 (vs), 1328 (m), 1286 (m), 1267 (m), 1199 (s), 1174 (m), 1131 (vs), 1115 (vs), 1097 (s), 1033 (m), 865 (s), 826 (s), 785 (s), 768 (s), 758 (vs), 726 (s), 702 (vs), 662 (s) cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 4.18 (s, 2 H), 6.70-6.73 (m, 2 H), 6.85 (d, 1 H, *J* = 2.2 Hz), 6.96-7.06 (m, 4 H), 7.21-7.37 (m, 16 H); ¹³C NMR (CDCl₃, 75 MHz) δ 44.3, 70.0 (s), 115.2 (s), 117.5 (s), 123.1 (s), 126.7, 127.6, 127.8, 127.9 (s), 128.0, 128.5, 128.6, 129.7, 129.8, 131.0, 131.5, 138.1 (s), 138.4 (s), 138.7 (s), 145.1 (s), 164.5 (s); MS (EI, 70 eV) *m/z* (rel int) 554 (M⁺ + 2, 14), 552 (M⁺, 14), 200 (100). Anal. Calcd for C₃₅H₂₅BrN₂ (553.50): C, 75.95; H, 4.55; N, 5.06. Found: C, 75.87; H, 4.37; N, 4.94.

6-Chloro-2,2-diphenyl-1-diphenylmethylenidene-1,2-dihydroazeto[2,1-*b*]quinazoline 11d:

eluent for column chromatography, hexanes/diethyl ether (4:1, v/v); yield 76%; mp 240 °C (colorless prism, diethyl ether/*n*-pentane); IR (Nujol) 1707 (s), 1625 (vs), 1209 (m), 1131 (m), 1115 (s), 1074 (m), 874 (m), 833 (w), 784 (w), 759 (m), 698 (vs) cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 4.18 (s, 2 H), 6.70-6.73 (m, 3 H), 6.96-7.08 (m, 5 H), 7.26-7.37 (m, 15 H); ¹³C NMR (CDCl₃, 75 MHz) δ 44.4, 70.0 (s), 115.2 (s), 122.7 (s), 126.7, 126.8, 127.5, 127.6, 127.8, 128.0, 128.5, 128.6, 129.8, 131.0, 138.2 (s), 138.4 (s), 138.7 (s), 140.8 (s), 145.1 (s), 164.4

(s); MS (EI, 70 eV) m/z (rel int) 510 ($M^+ + 2$, 9), 508 (M^+ , 23), 238 (100). Anal. Calcd for $C_{35}H_{25}ClN_2$ (509.05): C, 82.58; H, 4.95; N, 5.50. Found: C, 82.49; H, 4.79; N, 5.51.

6-Methyl-2,2-diphenyl-1-diphenylmethyldene-1,2-dihydroazeto[2,1-*b*]quinazoline 11e: eluent for column chromatography, hexanes/diethyl ether (7:3, v/v); yield 51%; mp 229 °C (colorless prism, diethyl ether/*n*-pentane); IR (Nujol) 1716 (s), 1642 (vs), 1609 (vs), 1201 (s), 1139 (s), 829 (m), 764 (s), 698 (vs) cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ 3.00 (s, 3 H), 4.19 (s, 2 H), 6.53-6.54 (m, 1 H), 6.70-6.73 (m, 2 H), 6.93-7.00 (m, 3 H), 7.02-7.07 (m, 2 H), 7.26-7.28 (m, 8 H), 7.32-7.34 (m, 7 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.9, 44.6, 70.0 (s), 114.4 (s), 120.9 (s), 126.1, 126.5, 127.3, 127.6, 127.7, 127.8, 127.9, 128.4, 128.5, 129.0, 129.9, 131.1, 134.7 (s), 138.5 (s), 138.7 (s), 139.0 (s), 139.5 (s), 145.6 (s), 163.5 (s); MS (EI, 70 eV) m/z (rel int) 488 (M^+ , 15), 218 (100). Anal. Calcd for $C_{36}H_{28}N_2$ (488.63): C, 88.49; H, 5.77; N, 5.73. Found: C, 88.27; H, 5.88; N, 5.80.

Compound 11f: eluent for column chromatography, hexanes/diethyl ether (7:3, v/v); yield 16%; mp 250 °C (colorless prism, diethyl ether/*n*-pentane); IR (Nujol) 1725 (w), 1646 (vs), 1618 (vs), 1598 (s), 1340 (m), 1207 (m), 1126 (s), 1086 (s), 1031 (w), 889 (m), 745 (s), 709 (m), 698 (vs) cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ 4.38 (s, 2 H), 6.74 (d, 2 H, $J = 7.1$ Hz), 6.97-7.04 (m, 2 H), 7.05-7.08 (m, 1 H), 7.19 (s, 1 H), 7.25 (s, 1 H), 7.29-7.42 (m, 16 H), 7.58-7.68 (m, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.8, 70.1 (s), 114.8 (s), 121.7 (s), 123.3, 125.3, 126.0, 126.2, 126.6, 127.0, 127.5, 127.6, 127.8, 128.0, 128.1, 128.5, 128.6, 129.9, 131.1, 131.2 (s), 133.9 (s), 138.5 (s), 138.6 (s), 139.0 (s), 139.6 (s), 145.5 (s), 164.2 (s); MS (EI, 70 eV) m/z (rel int) 524 (M^+ , 47), 254 (100). Anal. Calcd for $C_{39}H_{28}N_2$ (524.66): C, 89.28; H, 5.38; N, 5.34. Found: C, 89.11; H, 5.43; N, 5.44.

Analytical and spectroscopic data of compound 12

Compound 12: eluent for column chromatography, hexanes/diethyl ether (7:3, v/v); yield 61%; mp 160 °C (colorless prism, diethyl ether); IR (Nujol) 2223 (m), 2015 (vs), 1594 (vs), 1489 (vs), 1222 (m), 1154 (s), 1123 (w), 1080 (m), 1050 (w), 1030 (m), 960 (m), 910 (s), 875 (s), 850 (w), 760 (vs), 736 (s), 697 (vs) cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ 4.25 (d, 1 H, $J = 12.1$ Hz), 4.28 (d, 1 H, $J = 12.1$ Hz), 5.48 (s, 1 H), 7.10 (d, 1 H, $J = 7.5$ Hz), 7.19-7.34 (m, 17 H), 7.40-7.46 (m, 3 H), 7.47 (dd, 1 H, $J = 7.5, 1.3$ Hz), 7.65-7.68 (m, 1 H), 7.73-7.75 (m, 2

H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 34.9, 39.5, 77.7 (s), 119.8 (s), 128.5, 126.4, 126.5, 126.6, 127.4, 127.5, 127.8, 127.9, 128.1, 128.8, 129.0, 129.1, 129.3, 129.5, 131.0, 132.7 (s), 132.9 (s), 133.2 (s), 133.8 (s), 133.9 (s), 135.2 (s), 137.7 (s), 138.2 (s), 190.3 (s); MS (EI, 70eV) m/z (rel int) 524 (M^+ , 100). Anal. Calcd for $\text{C}_{39}\text{H}_{28}\text{N}_2$ (524.66): C, 89.28; H, 5.38; N, 5.34. Found: C, 89.00; H, 5.42; N, 5.47.

Analytical and spectroscopic data of compound 16

Compound 16: mp 241 °C (colorless prism, nitrobenzene); IR (Nujol) 3354 (s), 1660 (s), 1641 (m), 1595 (w), 1227 (m), 1159 (w), 1036 (w), 1004 (s), 973 (w), 947 (w), 870 (w), 771 (vs), 756 (vs), 727 (s), 700 (vs), 651 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 5.93 (ddd, 1 H, $J = 13.7, 7.9, 1.0$ Hz), 6.71-6.73 (m, 2 H), 6.77 (dd, 1 H, $J = 8.1, 1.0$ Hz), 6.83-6.97 (m, 8 H), 7.02-7.13 (m, 7 H), 7.18-7.26 (m, 4 H), 7.32-7.36 (m, 1 H), 7.49-7.53 (m, 1 H), 7.80 (dd, 1 H, $J = 7.8, 1.2$ Hz), 10.81 (s, 1 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 67.0 (s), 91.9 (s), 121.6, 122.5, 125.1, 125.6, 126.9, 127.2, 127.5, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6, 129.2, 129.3, 129.4 (s), 130.1, 130.4, 130.5, 131.2, 131.9, 136.7 (s), 137.3 (s), 139.8 (s), 142.4 (s), 144.4 (s), 147.4 (s), 149.0 (s), 169.1 (s), 170.3 (s); MS (EI, 70 eV) m/z (rel int) 568 (M^+ , 7), 536 (100). Anal. Calcd for $\text{C}_{40}\text{H}_{28}\text{N}_2\text{O}_2$ (568.67): C, 72.94; H, 4.96; N, 4.93. Found: C, 72.69; H, 4.99; N, 4.77.

Figure S1. X-Ray structure of **11d**

Figure S2. X-Ray structure of **16^a**

^a The phenyl groups at C14 and C(21) have been omitted and denoted simply as Ph for clarity.

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ppm

- 141.333
- 140.421
- 139.832
- 132.802
- 131.013
- 129.260
- 128.921
- 128.693
- 128.103
- 127.686
- 127.447
- 127.330
- 127.214
- 122.607

- 77.416
- 77.099
- 76.782

52.007

40.742

4.19

2.21

0.00

4.3801

-0.0002

ppm
190.298

138.186
133.820
133.237
132.739
130.983
129.479
129.264
129.062
129.012
128.777
128.100
127.905
127.827
127.512
127.462
126.618
126.548
126.513
120.854
119.818

77.709
77.420
77.103
76.786

39.480
34.879