

[Cp*RhCl₂]₂-Catalyzed Alkyne Hydroamination to 1,2-Dihydroquinolines

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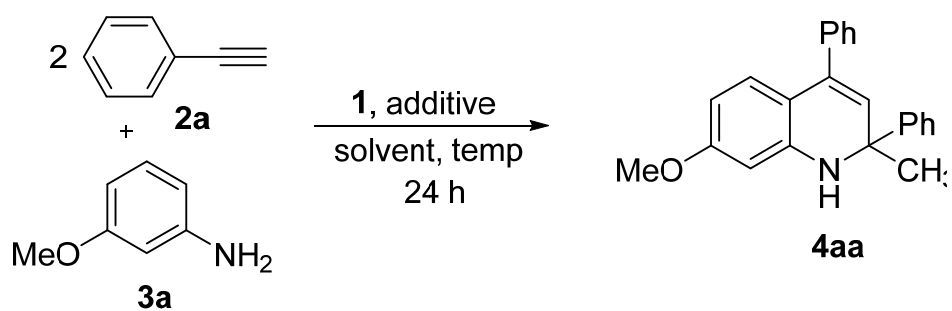
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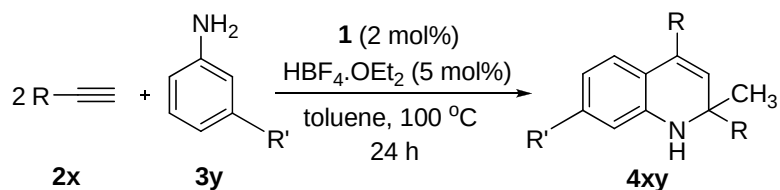
Table S9. Crystal and refinement data for **4aa** and **4ga**.

Table S1. Optimisation study for the reaction **2a** + **3a** → **4aa**.

Entry	1 (mol %)	Additive (mol %)	solvent	T (°C)	Isolated yield (%)
1	(2)	NH ₄ PF ₆ (5)	Toluene	40	-
2	(2)	NH ₄ PF ₆ (5)	Toluene	100	55
3	(3)	NH ₄ PF ₆ (6)	Toluene	150	55
4	(5)	NH ₄ PF ₆ (10)	Toluene	100	65
5	(2)	NH ₄ PF ₆ (12)	Toluene	100	58
6	(2)	HBF ₄ (5)	Toluene	100	86
7	(2)	TFA (5)	Toluene	100	70
8	(1)	HBF ₄ (2)	Toluene	100	75
9	(2)	-	Toluene	100	-
10	-	HBF ₄ (5)	Toluene	100	-
11	(2)	NBu ₄ PF ₆ (5)	Toluene	100	-
12	(2)	HBF ₄ (5)	DCE	80	78
13	(2)	HBF ₄ (5)	THF	40	-
14	(2)	HBF ₄ (5)	IPA	80	-
15	(2)	HBF ₄ (5)	MeOH	60	-

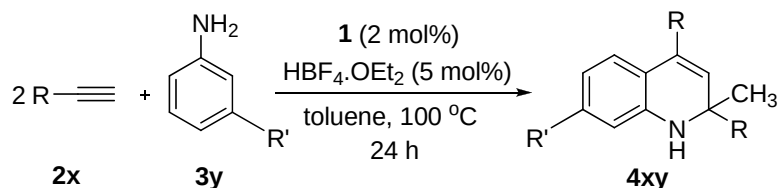
Conditions: **3a** (1.0 mmol), **2a** (2.1 mmol), **1**/ additive in a solvent (3 mL), heated for 24 h.

Table S2. Compound identification table for alkynes and anilines.



x	R		x	R		y	R'
a	Ph		m	Cl-3-C ₆ H ₄		a	OMe
b	CH ₃ -3-C ₆ H ₄		n	Cl-4-C ₆ H ₄		b	OEt
c	CH ₃ -4-C ₆ H ₄		o	F-3-C ₆ H ₄		c	O ⁿ Pr
d	CH ₃ (CH ₂) ₃ -4-C ₆ H ₄		p	F-4-C ₆ H ₄		d	O ⁱ Pr
e	^t Bu-4-C ₆ H ₄		q	-(CH ₂) ₂ CH ₃		e	O(CH ₂) ₃ CH ₃
f	CH ₃ (CH ₂) ₄ -4-C ₆ H ₄		r	-(CH ₂) ₃ CH ₃		f	O(CH ₂) ₅ CH ₃
g	HOCH ₂ -4-C ₆ H ₄		s	-(CH ₂) ₄ CH ₃		g	OCH ₂ Ph
h	HO-3-C ₆ H ₄		t	-(CH ₂) ₅ CH ₃		h	OCH ₂ -(<i>p</i> -tolyl)
i	CH ₃ O-3-C ₆ H ₄		u	-(CH ₂) ₇ CH ₃		i	3,5-(OCH ₃) ₂
j	CH ₃ O-4-C ₆ H ₄		v	-(CH ₂) ₉ CH ₃		j	Me
k	PhO-4-C ₆ H ₄		w	-(CH ₂) ₂ Ph		k	H
l	Br-4-C ₆ H ₄						

Table S3. Substrate scope study for the formation of 1,2-dihydroquinoline from the reaction of alkyne with aniline.



Entry	Alkyne (2x) R=	Aniline (3y) R'=	Product, yield (%)
1	Ph (2a)	OMe (3a)	4aa, 86
2	CH ₃ -3-C ₆ H ₄ (2b)	OMe (3a)	4ba, 89
3	CH ₃ -4-C ₆ H ₄ (2c)	OMe (3a)	4ca, 83
4	CH ₃ (CH ₂) ₃ -4-C ₆ H ₄ (2d)	OMe (3a)	4da, 79
5	^t Bu-4-C ₆ H ₄ (2e)	OMe (3a)	4ea, 78
6	CH ₃ (CH ₂) ₅ -4-C ₆ H ₄ (2f)	OMe (3a)	4fa, 87
7	HOCH ₂ -4-C ₆ H ₄ (2g)	OMe (3a)	4ga, 73
8	HO-3-C ₆ H ₄ (2h)	OMe (3a)	4ha, 71
9	CH ₃ O-3-C ₆ H ₄ (2i)	OMe (3a)	4ia, 91
10	CH ₃ O-4-C ₆ H ₄ (2j)	OMe (3a)	4ja, 89
11	PhO-4-C ₆ H ₄ (2k)	OMe (3a)	4ka, 83
12	Br-4-C ₆ H ₄ (2l)	OMe (3a)	4la, 71
13	Cl-3-C ₆ H ₄ (2m)	OMe (3a)	4ma, 70
14	Cl-4-C ₆ H ₄ (2n)	OMe (3a)	4na, 75
15	F-3-C ₆ H ₄ (2o)	OMe (3a)	4oa, 71
16	F-4-C ₆ H ₄ (2p)	OMe (3a)	4pa, 85
17	-(CH ₂) ₂ CH ₃ (2q)	OMe (3a)	4qa, 73
18	-(CH ₂) ₃ CH ₃ (2r)	OMe (3a)	4ra, 74
19	-(CH ₂) ₄ CH ₃ (2s)	OMe (3a)	4sa, 78
20	-(CH ₂) ₅ CH ₃ (2t)	OMe (3a)	4ta, 72
21	-(CH ₂) ₇ CH ₃ (2u)	OMe (3a)	4ua, 71
22	-(CH ₂) ₉ CH ₃ (2v)	OMe (3a)	4va, 75
23	-(CH ₂) ₂ Ph (2w)	OMe (3a)	4wa, 79
24	Ph (2a)	OEt (3b)	4ab, 83
25	Ph (2a)	OPr (3c)	4ac, 82
26	Ph (2a)	O ⁱ Pr (3d)	4ad, 79
27	Ph (2a)	O(CH ₂) ₃ CH ₃ (3e)	4ae, 81
28	Ph (2a)	O(CH ₂) ₅ CH ₃ (3f)	4af, 76
29	Ph (2a)	OCH ₂ Ph (3g)	4ag, 80
30	Ph (2a)	OCH ₂ -(<i>p</i> -tolyl) (3h)	4ah, 84
31	Ph (2a)	3,5-(OCH ₃) ₂ (3i)	4ai, 72
32	-(CH ₂) ₃ CH ₃ (2r)	Me (3j)	4rj, 48
33	-(CH ₂) ₃ CH ₃ (2r)	H (3k)	4rk, 34
34	Ph (2a)	H (3k)	4ak, 29

Table S5. Amount of reagent used, product formed, and HRMS data for products. All experiments carried out using **3a** (123 mg, 1 mmol), alkyne (2.1 mmol) and **1** (12 mg, 0.02 mmol).

	Alkyne	Product (mg, %)	HRMS: [M+H] ⁺ Found (calc)		Alkyne	Product (mg, %)	HRMS: [M+H] ⁺ Found (calc)
1	C ₆ H ₅ CCH (230 μ l, 2.1 mmol)	C ₂₃ H ₂₁ NO, 4aa (281 mg, 86%)	328.1710 (328.1701)	13	3-Cl-C ₆ H ₄ CCH (257 μ l, 2.1 mmol)	C ₂₃ H ₁₉ Cl ₂ NO, 4ma (276 mg, 70%)	396.0926 (396.0922)
2	3-CH ₃ -C ₆ H ₄ CCH (270 μ l, 2.1 mmol)	C ₂₅ H ₂₅ NO, 4ba (316 mg, 89%)	356.2024 (356.2014)	14	4-Cl-C ₆ H ₄ CCH (285 mg, 2.1 mmol)	C ₂₃ H ₁₉ Cl ₂ NO, 4na (296 mg, 75%)	396.0916 (396.0922)
3	4-CH ₃ -C ₆ H ₄ CCH (266 μ l, 2.1 mmol)	C ₂₅ H ₂₅ NO, 4ca (294 mg, 83%)	356.2016 (356.2014)	15	3-F-C ₆ H ₄ CCH (242 μ l, 2.1 mmol)	C ₂₃ H ₁₉ F ₂ NO, 4oa (257 mg, 71%)	364.1514 (364.1513)
4	4-C ₄ H ₉ -C ₆ H ₄ CCH (332 mg, 2.1 mmol)	C ₃₁ H ₃₇ NO, 4da (347 mg, 79%)	440.2957 (440.2953)	16	4-F-C ₆ H ₄ CCH (240 μ l, 2.1 mmol)	C ₂₃ H ₁₉ F ₂ NO, 4pa (308 mg, 85%)	364.1518 (364.1513)
5	4- ^t Bu-C ₆ H ₄ CCH (378 μ l, 2.1 mmol)	C ₃₁ H ₃₇ NO, 4ea (342 mg, 78%)	440.2951 (440.2953)	17	CH ₃ (CH ₂) ₂ CCH (207 μ l, 2.1 mmol)	C ₁₇ H ₂₅ NO, 4qa (189 mg, 73%)	260.2019 (260.2014)
6	4-C ₅ H ₁₁ -C ₆ H ₄ CCH (361 mg, 2.1 mmol)	C ₃₃ H ₄₁ NO, 4fa (406 mg, 87%)	468.3274 (468.3266)	18	CH ₃ (CH ₂) ₃ CCH (241 μ l, 2.1 mmol)	C ₁₉ H ₂₉ NO, 4ra (212 mg, 74%)	288.2328 (288.2327)
7	4-HOCH ₂ -C ₆ H ₄ CCH (277 mg, 2.1 mmol)	C ₂₅ H ₂₅ NO ₃ , 4ga (282 mg, 73%)	388.1931 (388.1913)	19	CH ₃ (CH ₂) ₄ CCH (275 μ l, 2.1 mmol)	C ₂₁ H ₃₃ NO, 4sa (245 mg, 78%)	316.2662 (316.2640)
8	3-HO-C ₆ H ₄ CCH (288 μ l, 2.1 mmol)	C ₂₃ H ₂₁ NO ₃ , 4ha (255 mg, 71%)	360.1602 (360.1600)	20	CH ₃ (CH ₂) ₅ CCH (294 μ l, 2.1 mmol)	C ₂₃ H ₃₇ NO, 4ta (247 mg, 72%)	344.2948 (344.2953)
9	3-CH ₃ O-C ₆ H ₄ CCH (266 μ l, 2.1 mmol)	C ₂₅ H ₂₅ NO ₃ , 4ia (352 mg, 91%)	388.1912 (388.1913)	21	CH ₃ (CH ₂) ₇ CCH (379 μ l, 2.1 mmol)	C ₂₇ H ₄₅ NO, 4ua (283 mg, 71%)	400.3579 (400.3579)
10	4-CH ₃ OC ₆ H ₄ CCH (272 μ l, 2.1 mmol)	C ₂₅ H ₂₅ NO ₃ , 4ja (344 mg, 89%)	388.1906 (388.1913)	22	CH ₃ (CH ₂) ₉ CCH (448 μ l, 2.1 mmol)	C ₃₁ H ₅₃ NO, 4va (341 mg, 75%)	456.4205 (456.4205)
11	4-PhO-C ₆ H ₄ CCH (379 μ l, 2.1 mmol)	C ₃₅ H ₂₉ NO ₃ , 4ka (424 mg, 83%)	512.2231 (512.2226)	23	PhCH ₂ CH ₂ CCH (295 μ l, 2.1 mmol)	C ₂₇ H ₂₉ NO, 4wa (302 mg, 79%)	384.2326 (384.2327)
12	4-Br-C ₆ H ₄ CCH (378 mg, 2.1 mmol)	C ₂₃ H ₁₉ Br ₂ NO, 4la (342 mg, 71%)	483.9899 (483.9912)				

Table S6. Amount of reagent used, product formed, and HRMS data for products. All experiments carried out using arylamine (1 mmol), alkyne (2.1 mmol) and **1** (12 mg, 0.02 mmol).

S/No	Alkyne	Aniline	Product (mg, %)	HRMS: [M+H] ⁺ Found (calc)
1	PhCCH (230 μ l, 2.1 mmol)	3-C ₂ H ₅ O-C ₆ H ₄ NH ₂ (137 mg, 1.0 mmol)	C ₂₄ H ₂₃ NO, 4ab (283 mg, 83%)	342.1862 (342.1858)
2	PhCCH (230 μ l, 2.1 mmol)	3-C ₃ H ₇ O-C ₆ H ₄ NH ₂ (151 mg, 1.0 mmol)	C ₂₅ H ₂₅ NO, 4ac (291 mg, 82%)	356.2012 (356.2014)
3	PhCCH (230 μ l, 2.1 mmol)	3-(CH ₃) ₂ CHO-C ₆ H ₄ NH ₂ (151 mg, 1.0 mmol)	C ₂₅ H ₂₅ NO, 4ad (280 mg, 79%)	356.2019 (356.2014)
4	PhCCH (230 μ l, 2.1 mmol)	3-C ₄ H ₉ O-C ₆ H ₄ NH ₂ (165 mg, 1.0 mmol)	C ₂₆ H ₂₇ NO, 4ae (298 mg, 81%)	370.2171 (370.2171)
5	PhCCH (230 μ l, 2.1 mmol)	3-C ₆ H ₁₃ O-C ₆ H ₄ NH ₂ (193 mg, 1.0 mmol)	C ₂₈ H ₃₁ NO, 4af (301 mg, 76%)	398.2483 (398.2484)
6	PhCCH (230 μ l, 2.1 mmol)	3-PhCH ₂ O-C ₆ H ₄ NH ₂ (199 mg, 1.0 mmol)	C ₂₉ H ₂₅ NO, 4ag (322 mg, 80%)	404.2021 (404.2014)
7	PhCCH (230 μ l, 2.1 mmol)	3-(4-tolyl)-CH ₂ O-C ₆ H ₄ NH ₂ (213 mg, 1.0 mmol)	C ₃₀ H ₂₇ NO, 4ah (350 mg, 84%)	418.2174 (418.2171)
8	PhCCH (230 μ l, 2.1 mmol)	3,5-CH ₃ O-C ₆ H ₃ NH ₂ (153 mg, 1.0 mmol)	C ₂₄ H ₂₃ NO ₂ , 4ai (257 mg, 72%)	358.1805 (358.1807)
9	CH ₃ (CH ₂) ₃ CCH (241 μ l, 2.1 mmol)	3-CH ₃ -C ₆ H ₃ NH ₂ (107 mg, 1.0 mmol)	C ₁₉ H ₂₉ N, 4rj (130 mg, 48%)	272.2373 (272.2378)
10	CH ₃ (CH ₂) ₃ CCH (241 μ l, 2.1 mmol)	C ₆ H ₅ NH ₂ (93 mg, 1.0 mmol)	C ₁₈ H ₂₇ N, 4rk (87 mg, 34%)	258.2221 (258.2222)
11	PhCCH (230 μ l, 2.1 mmol)	C ₆ H ₅ NH ₂ (93 mg, 1.0 mmol)	C ₂₂ H ₁₉ N, 4ak (86 mg, 29%)	297.1521 (297.1517)

Table S7. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data for 3-alkoxyanilines.

	^1H NMR data	$^{13}\text{C}\{^1\text{H}\}$ NMR data
3b	1.41 (t, $^3J_{\text{HH}} = 7.1$, 3H, CH ₃), 3.60 (s, 2H, NH ₂) 4.00 (q, $^3J_{\text{HH}} = 7.1$, 2H, OCH ₂), 6.25-6.30 (m, 2H, aromatic), 6.34 (dd, $^3J_{\text{HH}} = 8.2$, 2.3, 1H, aromatic), 7.07 (t, $^3J_{\text{HH}} = 8.0$, 1H, aromatic).	14.93 (CH ₃), 63.23 (OCH ₂), 101.65, 104.57, 107.86 and 130.11 (aromatic CH), 147.92 and 160.13 (aromatic C).
3c	1.04 (t, $^3J_{\text{HH}} = 7.3$, 3H, CH ₃), 1.75-1.84 (m, 2H, CH ₂), 3.66 (s, 2H, NH ₂), 3.89 (t, $^3J_{\text{HH}} = 6.6$, 2H, OCH ₂), 6.25-6.35 (m, 3H, aromatic), 7.06 (t, $^3J_{\text{HH}} = 8.0$, 1H, aromatic).	10.67 (CH ₃), 22.74 (CH ₂), 69.42 (OCH ₂), 101.79, 104.73, 107.87 and 130.17 (aromatic CH), 147.91 and 160.42 (aromatic C).
3d	1.33 (d, $^3J_{\text{HH}} = 6.4$, 6H, 2×CH ₃), 3.64 (s, 2H, NH ₂) 4.50 (sep, $^3J_{\text{HH}} = 6.4$, 1H, CH), 6.24-6.34 (m, 3H, aromatic), 7.05 (t, $^3J_{\text{HH}} = 8.0$, 1H, aromatic).	22.29 (CH ₃), 69.73 (OCH), 103.19, 106.00, 107.90 and 130.20 (aromatic CH), 147.96 and 159.18 (aromatic C).
3e²	0.97 (t, $^3J_{\text{HH}} = 7.3$, 3H, CH ₃), 1.44-1.53 (m, 2H, CH ₂), 1.71-1.78 (m, 2H, CH ₂), 3.64 (s, 2H, NH ₂), 3.92 (t, $^3J_{\text{HH}} = 6.4$, 2H, OCH ₂), 6.24-6.34 (m, 3H, aromatic), 7.05 (t, $^3J_{\text{HH}} = 8.0$, 1H, aromatic).	14.04 (CH ₃), 19.45 and 31.55 (CH ₂), 67.64 (OCH ₂), 101.85, 104.80, 107.90 and 130.21 (aromatic CH), 147.91 and 160.50 (aromatic C).
3f	0.91 (t, $^3J_{\text{HH}} = 6.9$, 3H, CH ₃), 1.31-1.35 (m, 4H, 2×CH ₂), 1.44 (q, $^3J_{\text{HH}} = 7.8$, 2H, CH ₂), 1.75 (q, $^3J_{\text{HH}} = 6.9$, 2H, CH ₂), 3.63 (s, 2H, NH ₂), 3.91 (t, $^3J_{\text{HH}} = 6.6$, 2H, OCH ₂), 6.24-6.33 (m, 3H, aromatic), 7.04 (t, $^3J_{\text{HH}} = 8.0$, 1H, aromatic).	14.25 (CH ₃), 22.82, 25.95, 29.48 and 31.80 (CH ₂), 67.99 (OCH ₂), 101.89, 104.85, 107.92 and 130.24 (aromatic CH), 147.91 and 160.53 (aromatic C).
3g³	3.65 (s, 2H, NH ₂), 5.03 (s, 2H, OCH ₂), 6.30-6.42 (m, 3H, aromatic), 7.07 (t, $^3J_{\text{HH}} = 8.0$, 1H, aromatic), 7.25-7.44 (m, 5H, aromatic).	70.02 (OCH ₂), 102.22, 105.06, 108.39, 127.64, 128.06, 128.74 and 130.33 (aromatic CH), 137.43, 147.98 and 160.21 (aromatic C).
3h	2.40 (s, 3H, CH ₃), 3.66 (s, 2H, NH ₂), 5.01 (s, 2H, OCH ₂), 6.32-6.45 (m, 3H, aromatic), 7.10 (t, $^3J_{\text{HH}} = 8.0$, 1H, aromatic), 7.23 (d, $^3J_{\text{HH}} = 8.2$, 2H, aromatic), 7.35 (d, $^3J_{\text{HH}} = 7.8$, 2H, aromatic).	21.36 (CH ₃), 69.90 (OCH ₂), 102.18, 105.03, 108.27, 127.75, 129.38, and 130.25 (aromatic CH), 134.34, 137.77, 147.95 and 160.23 (aromatic C).

Table S8. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data for **4** & **5**.

	^1H NMR data	$^{13}\text{C}\{^1\text{H}\}$ NMR data
4aa ⁴	1.77 (s, 3H, CH ₃), 3.76 (s, 3H, CH ₃), 4.23 (bs, 1H, NH), 5.52 (s, 1H, =CH), 6.14-6.16 (m, 2H, aromatic), 6.82-6.85 (m, 1H, aromatic), 7.22-7.26 (m, 1H, aromatic), 7.34-7.37 (m, 7H, aromatic), 7.57 (d, $^3J_{\text{HH}}=7.8$, 2H, aromatic).	30.35 (CH ₃), 55.33 (C), 57.38 (OCH ₃), 98.94, 102.76, 114.22, 125.53, 126.83, 126.99, 127.47, 127.51, 128.35, 128.61, 129.15, 135.56, 139.83, 144.76, 149.06 and 160.77 (C&CH, aromatic & alkene).
4ba	1.84 (s, 3H, CH ₃), 2.46 & 2.47 (s, 6H, 2xCH ₃ , Ar-CH ₃), 3.83 (s, 3H, OCH ₃), 4.30 (bs, 1H, NH), 5.61 (s, 1H, =CH), 6.22-6.26 (m, 2H, aromatic), 6.97 (d, $^3J_{\text{HH}}=8.2$, 1H, aromatic), 7.15 (d, $^3J_{\text{HH}}=7.3$, 1H, aromatic), 7.22-7.37 (m, 5H, aromatic), 7.46 (d, $^3J_{\text{HH}}=8.2$, 1H, aromatic), 7.48 (s, 1H, aromatic).	21.54 & 21.81 (Ar-CH ₃), 30.21 (CH ₃), 55.18 (C), 57.24 (OCH ₃), 98.85, 102.55, 114.13, 122.60, 126.15, 126.32, 126.73, 127.40, 127.63, 128.14, 128.41, 129.71, 135.36, 137.81, 137.98, 139.75, 144.71, 149.01 and 160.62 (C&CH, aromatic & alkene).
4ca ⁴	1.81 (s, 3H, CH ₃), 2.40 & 2.46 (s, 6H, 2xCH ₃ , Ar-CH ₃), 3.81 (s, 3H, OCH ₃), 4.28 (bs, 1H, NH), 5.58 (s, 1H, =CH), 6.19-6.23 (m, 2H, aromatic), 6.94 (d, $^3J_{\text{HH}}=8.2$, 1H, aromatic), 7.21-7.27 (m, 4H, aromatic), 7.34 (d, $^3J_{\text{HH}}=8.2$, 2H, aromatic), 7.52 (d, $^3J_{\text{HH}}=8.2$, 2H, aromatic).	21.08 & 21.32 (Ar-CH ₃), 30.30 (CH ₃), 55.19 (C), 56.98 (OCH ₃), 98.86, 102.57, 114.29, 125.40, 126.67, 127.37, 128.95, 129.17, 135.21, 136.41, 136.87, 137.04, 144.78, 146.19 and 160.59 (C&CH, aromatic & alkene).
4da	0.95-1.01 (m, 6H, 2xCH ₃), 1.37-1.46 (m, 4H, 2xCH ₂), 1.59-1.71 (m, 4H, 2xCH ₂), 1.78 (s, 3H, CH ₃), 2.60-2.69 (m, 4H, 2xCH ₂), 3.78 (s, 3H, OCH ₃), 4.23 (bs, 1H, NH), 5.53 (s, 1H, =CH), 6.14-6.19 (m, 2H, aromatic), 6.91 (d, $^3J_{\text{HH}}=8.7$, 1H, aromatic), 7.18-7.26 (m, 4H, aromatic), 7.32 (d, $^3J_{\text{HH}}=7.8$, 2H, aromatic), 7.50 (d, $^3J_{\text{HH}}=8.2$, 2H, aromatic).	14.14 and 14.16 (CH ₃), 22.58(CH ₂), 30.23 (CH ₃), 33.77, 33.83, 35.33 and 35.57 (CH ₂), 55.26 (C), 57.12 (OCH ₃), 98.83, 102.56, 114.27, 125.45, 126.79, 127.42, 128.31, 128.53, 128.95, 135.16, 137.09, 141.52, 142.12, 144.80, 146.37 and 160.62 (C&CH, aromatic & alkene).
4ea	1.36 (s, 9H, 3xCH ₃), 1.40 (s, 9H, 3xCH ₃), 1.80 (s, 3H, CH ₃), 3.79 (s, 3H, OCH ₃), 4.24 (bs, 1H, NH), 5.54 (s, 1H, =CH), 6.15-6.20 (m, 2H, aromatic), 6.95 (d, $^3J_{\text{HH}}=8.2$, 1H, aromatic), 7.34-7.44 (m, 6H, aromatic), 7.54 (d, $^3J_{\text{HH}}=7.8$, 2H, aromatic).	30.17, 31.51 and 31.57 (CH ₃), 34.54 and 34.69 (C), 55.24 (C), 57.04 (OCH ₃), 98.79, 102.57, 114.20, 125.15, 125.25, 125.40, 126.84, 127.44, 128.71, 135.03, 136.84, 144.80, 146.06, 149.65, 150.29 and 160.61 (C&CH, aromatic & alkene).
4fa	0.93-0.98 (m, 6H, 2xCH ₃), 1.37-1.42 (m, 8H, 4xCH ₂), 1.64-1.72 (m, 4H, 2xCH ₂), 1.79 (s, 3H, CH ₃), 2.61-2.70 (m, 4H, 2xCH ₂), 3.78 (s, 3H, OCH ₃), 4.24 (bs, 1H, NH), 5.54 (s, 1H, =CH), 6.15-6.19 (m, 2H, aromatic), 6.92 (d, $^3J_{\text{HH}}=8.2$, 1H, aromatic), 7.18-7.26 (m, 4H, aromatic), 7.32 (d, $^3J_{\text{HH}}=7.8$, 2H, aromatic), 7.51 (d, $^3J_{\text{HH}}=8.2$, 2H, aromatic).	14.19 (CH ₃), 22.69 (CH ₂), 30.19 (CH ₃), 31.29, 31.34, 31.70, 35.59 and 35.82 (CH ₂), 55.21 (C), 57.08 (OCH ₃), 98.80, 102.52, 114.22, 125.42, 126.76, 127.37, 128.26, 128.48, 128.60, 128.73, 128.91, 135.12, 137.05, 141.51, 142.12, 144.77, 146.34 and 160.58 (C&CH, aromatic & alkene).

Table S8. Continued.....

4ga	1.60 (s, 3H, CH ₃), 3.59 (s, 3H, OCH ₃), 4.46 & 4.53 (s, 4H, 2xCH ₂), 5.49 (s, 1H, =CH), 5.97 (d, ³ J _{HH} =8.2, 1H, aromatic), 6.23 (s, 1H, aromatic), 6.60 (d, ³ J _{HH} =8.7, 1H, aromatic), 7.17-7.27 (m, 6H, aromatic), 7.43 (d, ³ J _{HH} =8.2, 2H, aromatic).	31.14 (CH ₃), 55.43 (C), 57.46 (OCH ₃), 64.95 (OCH ₂), 99.80, 103.44, 115.63, 126.29, 127.72, 127.88, 127.95, 129.85, 136.89, 140.21, 140.47, 141.63, 147.13, 149.84 and 161.89 (C&CH, aromatic & alkene).
4ha	1.62 (s, 3H, CH ₃), 3.66 (s, 3H, OCH ₃), 3.64 (bs, 1H, NH), 5.49 (s, 1H, =CH), 6.02 (d, ³ J _{HH} =8.7, 1H, aromatic), 6.25 (s, 1H, aromatic), 6.58 (d, ³ J _{HH} =7.3, 1H, aromatic), 6.69-6.75 (m, 4H, aromatic), 6.95 (d, ³ J _{HH} =7.3, 2H, aromatic), 7.06-7.15 (m, 2H, aromatic).	31.15 (CH ₃), 55.42 (C), 57.54 (OCH ₃), 99.65, 103.37, 113.53, 114.16, 115.16, 115.46, 116.72, 117.48, 121.24, 127.36, 127.95, 130.13, 130.18, 136.96, 142.75, 147.01, 152.53, 158.15 and 161.91 (C&CH, aromatic & alkene).
4ia	1.80 (s, 3H, CH ₃), 3.78, 3.82 & 3.84 (s, 9H, 3xOCH ₃), 4.38 (bs, 1H, NH), 5.61 (s, 1H, =CH), 6.19-6.22 (m, 2H, aromatic), 6.83 (d, ³ J _{HH} =8.0, 1H, aromatic), 6.94 (d, ³ J _{HH} =8.2, 2H, aromatic), 6.99-7.03 (m, 2H, aromatic), 7.18-7.19 (m, 2H, aromatic), 7.29-7.36 (m, 2H, aromatic).	30.15 (CH ₃), 55.06 (C), 55.14, 55.20 & 57.07 (OCH ₃), 98.76, 102.66, 111.52, 111.83, 112.91, 113.88, 114.45, 117.65, 121.42, 126.38, 127.26, 129.16, 129.42, 135.31, 141.07, 144.60, 150.58, 159.37 and 159.56, 160.55 (C&CH, aromatic & alkene).
4ja ⁴	1.77 (s, 3H, CH ₃), 3.77, 3.80 & 3.86 (s, 9H, 3xOCH ₃), 4.31 (bs, 1H, NH), 5.51 (s, 1H, =CH), 6.15-6.21 (m, 2H, aromatic), 6.90-6.97 (m, 5H, aromatic), 7.34 (d, ³ J _{HH} =8.2, 2H, aromatic), 7.52 (d, ³ J _{HH} =8.7, 2H, aromatic).	30.08 (CH ₃), 55.12 (C), 55.28 & 56.68 (OCH ₃), 98.77, 102.52, 113.61, 113.67, 114.27, 126.54, 126.63, 127.24, 130.08, 132.11, 134.65, 141.33, 144.76, 158.35, 158.97 and 160.53 (C&CH, aromatic & alkene).
4ka	1.76 (s, 3H, CH ₃), 3.76 (s, 3H, OCH ₃), 4.19 (bs, 1H, NH), 5.49 (s, 1H, =CH), 6.13-6.17 (m, 2H, aromatic), 6.87 (d, ³ J _{HH} =8.7, 1H, aromatic), 6.95-7.13 (m, 11H, aromatic), 7.31-7.37 (m, 6H, aromatic), 7.51 (d, ³ J _{HH} =8.7, 2H, aromatic).	30.20 (CH ₃), 55.19 (C), 56.99 (OCH ₃), 98.93, 102.81, 114.10, 118.63, 119.10, 123.46, 126.68, 126.98, 127.38, 129.89, 130.43, 134.70, 134.81, 143.87, 144.65, 156.22, 156.77, 157.24, 157.32 and 160.76 (C&CH, aromatic & alkene).
4la	1.72 (s, 3H, CH ₃), 3.76 (s, 3H, OCH ₃), 4.19 (bs, 1H, NH), 5.44 (s, 1H, =CH), 6.14-6.16 (m, 2H, aromatic), 6.76 (d, ³ J _{HH} =9.6, 1H, aromatic), 7.19 (d, ³ J _{HH} =7.8, 2H, aromatic), 7.38-7.49 (m, 6H, aromatic).	30.19 (CH ₃), 55.38 (C), 57.09 (OCH ₃), 99.12, 103.14, 113.75, 121.01, 121.63, 126.33, 127.31, 127.41, 130.78, 131.55, 131.68, 135.09, 138.50, 144.52, 147.93 and 161.01 (C&CH, aromatic & alkene).
4ma	1.74 (s, 3H, CH ₃), 3.77 (s, 3H, OCH ₃), 4.21 (bs, 1H, NH), 5.46 (s, 1H, =CH), 6.16-6.18 (m, 2H, aromatic), 6.78 (d, ³ J _{HH} =8.2, 1H, aromatic), 7.20-7.34 (m, 6H, aromatic), 7.42 (d, ³ J _{HH} =7.8, 1H, aromatic), 7.51 (s, 1H, aromatic).	30.21 (CH ₃), 55.37 (C), 57.30 (OCH ₃), 99.12, 103.24, 113.54, 123.80, 125.87, 126.41, 127.22, 127.34, 127.42, 127.77, 129.12, 129.65, 129.97, 134.25, 134.56, 141.44, 144.42, 150.95 and 161.04 (C&CH, aromatic & alkene).

Table S8. Continued.....

4na	1.73 (s, 3H, CH ₃), 3.76 (s, 3H, OCH ₃), 4.20 (bs, 1H, NH), 5.45 (s, 1H, =CH), 6.15-6.17 (m, 2H, aromatic), 6.77 (d, ³ J _{HH} =8.2, 1H, aromatic), 7.25-7.35 (m, 6H, aromatic), 7.46 (d, ³ J _{HH} =8.7, 2H, aromatic).	30.16 (CH ₃), 55.32 (C), 56.97 (OCH ₃), 99.09, 103.06, 113.76, 126.41, 126.91, 127.35, 128.54, 128.65, 130.39, 132.80, 133.41, 134.91, 138.01, 144.51, 147.37 and 160.93 (C&CH, aromatic & alkene).
4oa	1.74 (s, 3H, CH ₃), 3.76 (s, 3H, OCH ₃), 4.24 (bs, 1H, NH), 5.50 (s, 1H, =CH), 6.16-6.19 (m, 2H, aromatic), 6.82 (d, ³ J _{HH} =8.2, 1H, aromatic), 6.91-6.95 (m, 1H, aromatic), 7.00-7.08 (m, 1H, aromatic), 7.13 (d, ³ J _{HH} =7.3, 1H, aromatic), 7.22-7.35 (m, 4H, aromatic).	30.26 (CH ₃), 55.32 (C), 57.20 (OCH ₃), 99.11, 103.19, 112.73 (d, ² J _{CF} =23.0), 113.87 (d, ² J _{CF} =21.1), 114.49 (d, ² J _{CF} =21.1), 116.05 (d, ² J _{CF} =21.1), 121.01, 124.82, 126.39, 127.42, 129.86 (d, ³ J _{CF} =8.6), (d, ³ J _{CF} =7.7), 135.08, 141.86 (d, ³ J _{CF} =7.7), 144.51, 151.65 (d, ³ J _{CF} =5.8), 161.00, 162.83 (d, ¹ J _{CF} =246.2), 163.08 (d, ¹ J _{CF} =247.2) (C&CH, aromatic & alkene).
4pa	1.76 (s, 3H, CH ₃), 3.77 (s, 3H, OCH ₃), 4.21 (bs, 1H, NH), 5.46 (s, 1H, =CH), 6.15-6.19 (m, 2H, aromatic), 6.80 (d, ³ J _{HH} =8.7, 1H, aromatic), 7.00-7.09 (m, 4H, aromatic), 7.30-7.34 (m, 2H, aromatic), 7.50-7.54 (m, 2H, aromatic).	30.16 (CH ₃), 55.27 (C), 56.92 (OCH ₃), 98.98, 102.92, 113.97, 115.22 (d, ² J _{CF} =21.1), 126.62, 127.23, 127.24 (d, ² J _{CF} =18.2), 130.59, 130.66, 134.71, 135.55, 144.52, 144.77, 160.84, 161.77 (d, ¹ J _{CF} =246.2) and 162.37 (d, ¹ J _{CF} =247.2) (C&CH, aromatic & alkene).
4qa	0.90 (t, ³ J _{HH} =7.3, 3H, CH ₃), 0.97 (t, ³ J _{HH} =7.3, 3H, CH ₃), 1.23 (s, 3H, CH ₃), 1.34-1.49 (m, 4H, 2xCH ₂), 1.55-1.60 (m, 2H, CH ₂), 2.29-2.34 (m, 2H, CH ₂), 3.62 (bs, 1H, NH), 3.75 (s, 3H, OCH ₃), 5.09 (s, 1H, =CH), 6.00 (s, 1H, aromatic), 6.16 (d, ³ J _{HH} =8.5, 1H, aromatic), 6.99 (d, ³ J _{HH} =8.7, 1H, aromatic).	14.22, 14.72 and 17.75 (CH ₃), 22.65, 30.30, 34.34 and 46.93 (CH ₂), 54.79 (C), 55.19 (OCH ₃), 98.47, 101.89, 114.35, 124.36, 124.52, 132.58, 145.53 and 160.15 (C&CH, aromatic & alkene).
4ra ⁵	0.90 (t, ³ J _{HH} =6.8, 3H, CH ₃), 0.96 (t, ³ J _{HH} =7.3, 3H, CH ₃), 1.23 (s, 3H, CH ₃), 1.28-1.58 (m, 10H, 5xCH ₂), 2.32-2.37 (m, 2H, CH ₂), 3.61 (bs, 1H, NH), 3.74 (s, 3H, OCH ₃), 5.01 (s, 1H, =CH), 6.01 (s, 1H, aromatic), 6.18 (d, ³ J _{HH} =8.5, 1H, aromatic), 7.00 (d, ³ J _{HH} =8.7, 1H, aromatic).	14.17, 14.29 and 22.81 (CH ₃), 23.31, 26.63, 30.18, 30.76, 31.93 and 44.13 (CH ₂), 54.69(C), 55.16 (OCH ₃), 98.50, 101.89, 114.35, 124.22, 124.50, 132.80, 145.47 and 160.12 (C&CH, aromatic & alkene).
4sa	0.85 (t, ³ J _{HH} =6.8, 3H, CH ₃), 0.88 (t, ³ J _{HH} =6.9, 3H, CH ₃), 1.19 (s, 3H, CH ₃), 1.21-1.55 (m, 14H, 7xCH ₂), 2.26-2.32 (m, 2H, CH ₂), 3.58 (bs, 1H, NH), 3.72 (s, 3H, OCH ₃), 5.06 (s, 1H, =CH), 5.97 (s, 1H, aromatic), 6.14 (d, ³ J _{HH} =8.5, 1H, aromatic), 6.96 (d, ³ J _{HH} =8.7, 1H, aromatic).	14.29, 14.34, 22.79, 22.88, 24.20, 28.33, 30.22, 32.06, 32.26, 32.52 and 44.40 (CH ₃ &CH ₂), 54.80 (C), 55.25 (OCH ₃), 98.58, 101.96, 114.44, 124.32, 124.57, 132.91, 145.52 and 160.18 (C&CH, aromatic & alkene).

Table S8. Continued.....

4ta⁵	0.86 (t, $^3J_{HH}=6.8$, 3H, CH ₃), 0.89 (t, $^3J_{HH}=6.9$, 3H, CH ₃), 1.17 (s, 3H, CH ₃), 1.25-1.56 (m, 18H, 9xCH ₂), 2.28-2.34 (m, 2H, CH ₂), 3.59 (bs, 1H, NH), 3.74 (s, 3H, OCH ₃), 5.07 (s, 1H, =CH), 5.99 (s, 1H, aromatic), 6.15 (d, $^3J_{HH}=8.5$, 1H, aromatic), 6.97 (d, $^3J_{HH}=8.7$, 1H, aromatic).	14.30, 22.87, 22.91, 24.49, 28.59, 29.51, 29.99, 30.22, 31.97, 32.07, 32.28 and 44.46 (CH ₃ &CH ₂), 54.80 (C), 55.26 (OCH ₃), 98.57, 101.95, 114.44, 124.31, 124.57, 132.89, 145.51 and 160.17 (C&CH, aromatic & alkene).
4ua	0.88 (t, $^3J_{HH}=7.3$, 3H, CH ₃), 0.89 (t, $^3J_{HH}=6.9$, 3H, CH ₃), 1.22 (s, 3H, CH ₃), 1.26-1.59 (m, 26H, 13xCH ₂), 2.29-2.35 (m, 2H, CH ₂), 3.60 (bs, 1H, NH), 3.75 (s, 3H, OCH ₃), 5.08 (s, 1H, =CH), 6.00 (s, 1H, aromatic), 6.16 (d, $^3J_{HH}=8.5$, 1H, aromatic), 6.99 (d, $^3J_{HH}=8.2$, 1H, aromatic).	14.33, 22.91, 24.54, 28.63, 29.54, 29.58, 29.73, 29.84, 30.23, 30.34, 32.10, 32.13, 32.29 and 44.46 (CH ₃ &CH ₂), 54.80 (C), 55.23 (OCH ₃), 98.57, 101.95, 114.43, 124.30, 124.57, 132.89, 145.52 and 160.17 (C&CH, aromatic & alkene).
4va	0.88 (t, $^3J_{HH}=6.8$, 3H, CH ₃), 0.89 (t, $^3J_{HH}=7.3$, 3H, CH ₃), 1.21 (s, 3H, CH ₃), 1.24-1.57 (m, 34H, 17xCH ₂), 2.28-2.34 (m, 2H, CH ₂), 3.59 (bs, 1H, NH), 3.74 (s, 3H, OCH ₃), 5.07 (s, 1H, =CH), 5.99 (s, 1H, aromatic), 6.15 (d, $^3J_{HH}=8.5$, 1H, aromatic), 6.98 (d, $^3J_{HH}=8.2$, 1H, aromatic).	14.35, 22.91, 24.54, 28.63, 29.59, 29.77, 29.89, 30.24, 30.35, 32.14, 32.29 and 44.47 (CH ₃ &CH ₂), 54.81 (C), 55.25 (OCH ₃), 98.58, 101.95, 114.44, 124.33, 124.58, 132.89, 145.52 and 160.18 (C&CH, aromatic & alkene).
4wa	1.27 (s, 3H, CH ₃), 1.69-1.82 (m, 2H, CH ₂), 2.53-2.61 (m, 1H, CH ₂), 2.67-2.80 (m, 3H, CH ₂), 2.88-2.93 (m, 2H, CH ₂), 3.64 (bs, 1H, NH), 3.78 (s, 3H, OCH ₃), 5.08 (s, 1H, =CH), 6.02 (s, 1H, aromatic), 6.23 (d, $^3J_{HH}=8.5$, 1H, aromatic), 7.10 (d, $^3J_{HH}=8.7$, 1H, aromatic), 7.15-7.34 (m, 10H, aromatic).	30.53, 31.28, 34.14, 34.92 and 46.12 (CH ₃ &CH ₂), 55.00 (C), 55.26 (OCH ₃), 98.67, 102.24, 113.83, 124.22, 124.52, 125.78, 126.03, 128.50, 128.54, 128.72, 132.55, 142.25, 142.88, 145.46 and 160.37 (C&CH, aromatic & alkene).
4ab	1.43 (t, $^3J_{HH}=7.3$, 3H, CH ₃), 1.81 (s, 3H, CH ₃), 4.02 (q, $^3J_{HH}=7.3$, 2H, CH ₂), 4.26 (bs, 1H, NH), 5.57 (s, 1H, =CH), 6.17-6.20 (m, 2H, aromatic), 6.88 (d, $^3J_{HH}=9.6$, 1H, aromatic), 7.27 (t, $^3J_{HH}=7.3$, 1H, aromatic), 7.35-7.42 (m, 7H, aromatic), 7.61 (d, $^3J_{HH}=8.0$, 2H, aromatic).	15.04 & 30.31 (CH ₃), 57.30 (C), 63.37 (OCH ₂), 99.48, 103.34, 114.09, 125.48, 126.72, 126.91, 127.40, 127.46, 128.29, 128.54, 129.11, 135.57, 139.83, 144.73, 149.06 and 160.10 (aromatic C&CH).
4ac	1.03 (t, $^3J_{HH}=7.3$, 3H, CH ₃), 1.77 (s, 3H, CH ₃), 1.76-1.81 (m, 2H, CH ₂), 3.88 (t, $^3J_{HH}=6.9$, 2H, CH ₂), 4.21 (bs, 1H, NH), 5.52 (s, 1H, =CH), 6.13-6.16 (m, 2H, aromatic), 6.83 (d, $^3J_{HH}=9.2$, 1H, aromatic), 7.22-7.26 (m, 1H, aromatic), 7.32-7.37 (m, 7H, aromatic), 7.57 (d, $^3J_{HH}=8.5$, 2H, aromatic).	10.75 (CH ₃), 22.82 (CH ₂), 30.34 (CH ₂), 57.37 (C), 69.54 (OCH ₂), 99.53, 103.46, 114.09, 125.54, 126.72, 126.96, 127.43, 127.49, 128.32, 128.59, 129.15, 135.63, 139.89, 144.71, 149.09 and 160.35 (C&CH, aromatic & alkene).
4ad	1.33 (d, $^3J_{HH}=6.4$, 6H, 2xCH ₃), 1.77 (s, 3H, CH ₃), 4.19 (bs, 1H, NH), 4.47-4.53 (m, 1H, CH), 5.51 (s, 1H, =CH), 6.11-6.14 (m, 2H, aromatic), 6.82 (d, $^3J_{HH}=9.1$, 1H, aromatic), 7.23 (t, $^3J_{HH}=7.3$, 1H, aromatic), 7.31-7.37 (m, 7H, aromatic), 7.57 (d, $^3J_{HH}=7.8$, 2H, aromatic).	22.36 (CH ₃), 30.36 (CH), 57.37 (C), 69.77 (OCH), 100.76, 104.52, 114.00, 125.54, 126.74, 126.94, 127.42, 127.47, 128.31, 128.58, 129.14, 135.58, 139.87, 144.75, 149.12 and 159.07 (C&CH, aromatic & alkene).

Table S8. Continued.....

4ae	0.97 (t, $^3J_{HH}=7.3$, 3H, CH ₃), 1.45-1.51 (m, 2H, CH ₂), 1.77 (s, 3H, CH ₃), 1.71-1.78 (m, 2H, CH ₂), 3.92 (t, $^3J_{HH}=6.4$, 2H, CH ₂), 4.20 (bs, 1H, NH), 5.51 (s, 1H, =CH), 6.12-6.14 (m, 2H, aromatic), 6.81 (d, $^3J_{HH}=7.8$, 1H, aromatic), 7.23 (t, $^3J_{HH}=6.4$, 1H, aromatic), 7.32-7.37 (m, 7H, aromatic), 7.57 (d, $^3J_{HH}=8.0$, 2H, aromatic).	14.08 (CH ₃), 19.47 (CH ₂), 30.35 (CH ₂), 31.57 (CH ₂), 57.37 (C), 67.71 (OCH ₂), 99.50, 103.45, 114.05, 125.54, 126.71, 126.97, 127.43, 127.49, 128.33, 128.60, 129.16, 135.62, 139.89, 144.73, 149.09 and 160.36(C&CH, aromatic & alkene).
4af	0.95 (t, $^3J_{HH}=6.4$, 3H, CH ₃), 1.37-1.47 (m, 6H, 3xCH ₂), 1.79 (s, 3H, CH ₃), 1.76-1.80 (m, 2H, CH ₂), 3.94 (t, $^3J_{HH}=6.9$, 2H, CH ₂), 4.23 (bs, 1H, NH), 5.53 (s, 1H, =CH), 6.16-6.17 (m, 2H, aromatic), 6.82-6.86 (m, 1H, aromatic), 7.25 (t, $^3J_{HH}=6.4$, 1H, aromatic), 7.32-7.39 (m, 7H, aromatic), 7.58 (d, $^3J_{HH}=8.2$, 2H, aromatic).	14.26 (CH ₃), 22.82, 25.94, 29.48 (CH ₂), 30.33 (CH ₂), 31.80 (CH ₂), 57.35 (C), 68.02 (OCH ₂), 99.50, 103.44, 114.04, 125.53, 126.70, 126.95, 127.42, 127.48, 128.32, 128.58, 129.15, 135.62, 139.88, 144.72, 149.10 and 160.35 (C&CH, aromatic & alkene).
4ag	1.76 (s, 3H, CH ₃), 4.21 (bs, 1H, NH), 5.01 (s, 2H, CH ₂), 5.51(s, 1H, =CH), 6.19-6.21 (m, 2H, aromatic), 6.82 (d, $^3J_{HH}=8.7$, 1H, aromatic), 7.21-7.25 (m, 1H, aromatic), 7.29-7.42 (m, 12H, aromatic), 7.55 (d, $^3J_{HH}=8.5$, 2H, aromatic).	30.37 (CH ₃), 57.42 (C), 70.07 (OCH ₂), 99.90, 103.68, 114.44, 125.56, 126.96, 127.01, 127.48, 127.54, 127.68, 128.16, 128.36, 128.62, 128.77, 129.16, 135.58, 137.35, 139.81, 144.65, 149.03 and 160.03 (C&CH, aromatic & alkene).
4ah	1.81 (s, 3H, CH ₃), 2.41 (s, 2H, CH ₂), 4.23 (bs, 1H, NH), 5.01 (s, 2H, CH ₂), 5.57 (s, 1H, =CH), 6.25-6.27 (m, 2H, aromatic), 6.89 (d, $^3J_{HH}=9.2$, 1H, aromatic), 7.24 (d, $^3J_{HH}=7.8$, 2H, aromatic), 7.28 (t, $^3J_{HH}=7.3$, 1H, aromatic), 7.34-7.41 (m, 9H, aromatic), 7.60 (d, $^3J_{HH}=7.8$, 2H, aromatic).	21.38, 30.31 (CH ₃), 57.34 (C), 69.93 (OCH ₂), 99.86, 103.65, 114.34, 125.52, 126.87, 126.95, 127.42, 127.48, 127.78, 128.32, 128.57, 129.12, 129.40, 134.26, 135.54, 137.79, 139.79, 144.70, 149.03 and 160.06 (C&CH, aromatic & alkene).
4ai⁵	1.68 (s, 3H, CH ₃), 3.29 (s, 3H, OCH ₃), 3.76 (s, 3H, OCH ₃), 4.35 (bs, 1H, NH), 5.53 (s, 1H, =CH), 5.79 (s, 1H, aromatic), 5.91 (s, 1H, aromatic), 7.17-7.31 (m, 8H, aromatic), 7.50 (d, $^3J_{HH}=5.3$, 2H, aromatic).	29.72 (CH ₃), 55.17 (C), 55.34 and 56.45 (OCH ₃), 90.11, 92.23, 104.07, 125.53, 126.28, 126.85, 127.32, 127.51, 128.25, 128.42, 134.99, 143.01, 146.66, 148.53, 158.15 and 161.35 (C&CH, aromatic & alkene).
4rj	0.88-0.96 (m, 6H, 2xCH ₃), 1.22 (s, 3H, CH ₃), 1.25-1.55 (m, 10H, 5xCH ₂), 2.22 (s, 3H, CH ₃), 2.31-2.37 (m, 2H, CH ₂), 3.65 (bs, 1H, NH), 5.15 (s, 1H, =CH), 6.26 (s, 1H, aromatic), 6.42 (d, $^3J_{HH}=7.3$, 1H, aromatic), 6.98 (d, $^3J_{HH}=7.8$, 1H, aromatic).	14.23, 14.35 and 21.51 (CH ₃), 22.87, 23.37, 26.72, 30.10, 30.83, 31.96 and 44.07 (CH ₂), 54.63(C), 113.70, 117.69, 118.17, 123.50, 125.75, 133.10, 138.24 and 144.03 (C&CH, aromatic & alkene).
4rk	0.88-0.97 (m, 6H, 2xCH ₃), 1.24 (s, 3H, CH ₃), 1.26-1.58 (m, 10H, 5xCH ₂), 2.35-2.39 (m, 2H, CH ₂), 3.58 (bs, 1H, NH), 5.21 (s, 1H, =CH), 6.42 (d, $^3J_{HH}=7.8$, 1H, aromatic), 6.60 (t, $^3J_{HH}=7.3$, 1H, aromatic), 6.96 (t, $^3J_{HH}=7.7$, 1H, aromatic), 7.09 (d, $^3J_{HH}=7.8$, 1H, aromatic).	14.22, 14.34 and 22.87 (CH ₃), 23.37, 26.71, 30.10, 30.78, 31.90 and 44.08 (CH ₂), 54.61(C), 112.97, 116.79, 120.64, 123.56, 126.74, 128.31, 133.18 and 144.13 (C&CH, aromatic & alkene).

Table S8. Continued.....

4ak ⁵	1.54 (s, 3H, CH ₃), 6.02 (bs, 1H, NH), 6.93 (t, ³ J _{HH} =7.3, 1H, aromatic), 7.07 (d, ³ J _{HH} =7.8, 2H, aromatic), 7.26-7.30 (m, 2H, aromatic), 7.36 (t, ³ J _{HH} =7.3, 1H, aromatic), 7.43-7.54 (m, 4H, aromatic), 7.67 (d, ³ J _{HH} =8.5, 3H, aromatic), 7.76 (s, 1H, alkene), 7.91 (d, ³ J _{HH} =8.2, 1H, aromatic), 8.02 (d, ³ J _{HH} =8.2, 1H, aromatic).	
5	3.65 (bs, 2H, NH), 3.79 (s, 3H, OCH ₃), 5.32 (d, ² J _{HH} =1.4 Hz, 1H, CH ₂), 5.74 (d, ² J _{HH} =1.4 Hz, 1H, CH ₂), 6.29 (s, 1H, aromatic), 6.38 (d, ³ J _{HH} =8.7 Hz, 1H, aromatic), 7.03 (d, ³ J _{HH} =8.2 Hz, 1H, aromatic), 7.28-7.33 (m, 3H, aromatic), 7.36-7.39 (m, 2H, aromatic).	55.36 (OCH ₃), 101.48, 104.44, 116.20, 120.83, 126.96, 128.23, 128.72, 132.01, 140.32, 144.80, 146.93 and 160.49 (C&CH, alkene & aromatic).
8b	1.69 (s, 6H, 2×CH ₃), 3.77 (s, 3H, OCH ₃), 3.79 (bs, 1H, NH), 6.38 (d, ³ J _{HH} =8.2, 1H, aromatic), 6.59 (d, ³ J _{HH} =8.2, 1H, aromatic), 6.67 (s, 1H, aromatic), 7.11 (t, ³ J _{HH} =8.2, 1H, aromatic), 7.27-7.30 (m, 3H, aromatic), 7.39-7.41 (m, 2H, aromatic).	30.79 (CH ₃), 48.91 (CMe ₂), 55.28 (OCH ₃), 82.88 and 93.48 (C≡C), 102.57, 104.32, 109.69, 123.42, 128.15, 128.38, 129.72, 131.76, 147.33 and 160.56 (C&CH, aromatic).
8c	1.68 (s, 6H, 2×CH ₃), 3.73 (bs, 1H, NH), 6.80 (t, ³ J _{HH} =7.3, 1H, aromatic), 7.01 (d, ³ J _{HH} =7.3, 2H, aromatic), 7.20 (t, ³ J _{HH} =7.3, 2H, aromatic), 7.25-7.28 (m, 3H, aromatic), 7.36-7.38 (m, 2H, aromatic).	30.80 (CH ₃), 49.00 (CMe ₂), 82.84 and 93.57 (C≡C), 117.11, 119.00, 123.45, 128.13, 128.37, 129.02, 131.76 and 145.98 (C&CH, aromatic).
4aa'	1.37 (s, 6H, 2×CH ₃), 3.76 (s, 3H, OCH ₃), 3.79 (bs, 1H, NH), 5.36 (s, 1H, alkene), 6.11-6.16 (m, 2H, aromatic), 6.82 (d, ³ J _{HH} =8.7, 1H, aromatic), 7.33-7.40 (m, 5H, aromatic).	30.80 (CH ₃), 52.16 (CMe ₂), 55.30 (OCH ₃), 99.32 and 102.74, 114.93, 127.24, 127.38, 127.78, 128.30, 129.12, 135.79, 140.08, 145.24 and 160.48 (C&CH, alkene & aromatic).

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Table S9. Crystal and refinement data for **4aa** and **4ga**.

Compound	4aa	4ga
Empirical formula	C ₂₃ H ₂₁ N O	C ₂₅ H ₂₅ N O ₃
Formula weight	327.41	387.46
Crystal system	Monoclinic	Triclinic
Space group	P2 ₁ /c	P $\bar{1}$
a, Å	5.9791(19)	9.9270(6)
b, Å	32.635(10)	12.9188(7)
c, Å	8.845(3)	16.2923(9)
α , deg	90	98.309(3)
β , deg	95.044(10)	104.241(3)
γ , deg	90	97.519(3)
Volume, Å ³	1719.2(9)	1973.54(19)
Z	4	4
Density (calculated), Mg/m ³	1.265	1.304
Absorption coefficient, mm ⁻¹	0.077	0.085
F(000)	696	824
Crystal size, mm ³	0.40 x 0.20 x 0.10	0.36 x 0.28 x 0.08
Reflections collected	18343	9693
Independent reflections	5106 [R(int) = 0.0454]	8056 [R(int) = 0.0630]
Max. and min. transmission	0.9924 and 0.9700	0.9932 and 0.9700
Data / restraints / parameters	5106 / 0 / 232	8056 / 182 / 575
Goodness-of-fit on F ²	1.092	1.102
Final R indices [I>2sigma(I)]	R1 = 0.0535, wR2 = 0.1468	R1 = 0.0594, wR2 = 0.1697
R indices (all data)	R1 = 0.0929, wR2 = 0.1758	R1 = 0.0924, wR2 = 0.1851
Largest diff. peak and hole, e.Å ⁻³	0.380 and -0.471	0.406 and -0.381