VERSITA

Chemical Papers 67 (1) 40–50 (2013)
DOI: 10.2478/s11696-012-0238-z

ORIGINAL PAPER

Substituted homoallenyl aldehydes and their derivatives. Part 2: Azines

Juraj Galeta, Stanislav Man, Aneta Valoušková, Milan Potáček*

Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

Received 21 March 2012; Revised 7 June 2012; Accepted 11 June 2012

Dedicated to Professor Štefan Toma on the occasion of his 75th birthday

This paper deals with the preparation of a variously substituted non-symmetrical azine set. The starting molecule for their preparation was a protected hydrazone. The protection was performed applying Zwierzak's method. This procedure is based on the transfer of hydrazine to diethylhydrazidophosphate, which reacts with aldehydes to produce protected hydrazones. In the second step of the procedure, under the action of sodium hydride, the addition of another aldehyde affords non-symmetrical azines in the reaction with the protected hydrazine. The procedure was shown to be a useful and effective method. In this, the second part of our study, we present results devoted to the preparation and full identification of non-symmetrical azines.

Keywords: allenyl, azine, aldehyde, hydrazone, deprotonation, non-symmetrical

Introduction

The preparation of protected hydrazones is the first part of azine synthesis by Zwierzak's method (Zwierzak & Sulewska, 1976; Koziara et al., 1986). We used this method with some changes to the synthetic pathway (Galeta et al., 2013) and we report here on the success of the second step, in which protected hydrazones under the treatment of sodium hydride react with the submitted aldehyde to produce non-symmetrical azines. Our targets were azines containing an allenyl skeleton (Schweizer & Lee, 1984; Schweizer et al., 1987). Syntheses of numerous organic compounds with biological activity have been based on the allenyl synthon (Zimmer, 1993; Brandsma, 2001; Brandsma & Nedolya, 2004; Krause & Hashmi, 2004; Brandsma, 2004; Brasholz et al., 2009). In the past, symmetrical azines were used in the preparation of fused cyclic compounds in intra-molecular criss-cross cycloaddition reactions (Zachová et al., 2005) leading to four fused five-membered rings and for research into their interesting transformations when treated with electrophiles (Galeta & Potáček, 2012; Zachová et al., 2006, 2009). Non-symmetrical azines serve as educts for the preparation of fused tricyclic heterocyclic systems by combined intra-intermolecular criss-cross cycloaddition (Galeta et al., 2009, 2011; Man et al., 2002, 2004, 2005).

Experimental

Unless stated otherwise, all reagents were purchased from commercial (Sigma–Aldrich, USA) supplier and used as received. Diethyl ether and toluene were distilled from sodium/benzophenone prior to use. All reactions were carried out under a dry argon atmosphere and monitored by TLC (Merck F_{254} silica gel; Merck, Germany). Products were separated by liquid chromatography with a Horizon HPFC System (Biotage, Sweden) fitted with Biotage Si 12+M and Si 25+M columns. FTIR spectra were recorded with a GENESIS ATI (Unicam, UK) spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker Avance 300 spectrometer (Bruker, USA) op-

*Corresponding author, e-mail: potacek@chemi.muni.cz

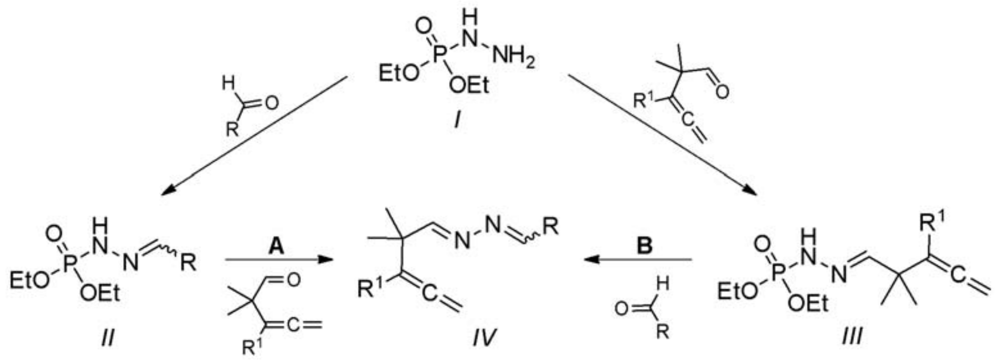

Fig. 1. Two synthetic approaches leading to non-symmetrical allenyl azines *IV*.

Table 1. Collection of non-symmetrical allenyl azines *IVa–IVax*

Compound	R^1	R	Yield/%	Reaction time/h
IVa	1-Adamantyl	H	69	24
IVb	TMS	H	86	3
IVc	H	1-Adamantyl	87	1
IVd	Me	1-Adamantyl	77	0.5
IVe	Pyrrol	1-Adamantyl	88	8
IVf	Morph	1-Adamantyl	65	6.5
IVg	1-Adamantyl	1-Adamantyl	77	1
IVh	Phenyl	1-Adamantyl	56	24
IVi	H	2-Furyl	83	1
IVj	Me	2-Furyl	91	1
IVk	TMS	2-Furyl	83	8.5
IVl	H	2-Thiophenyl	87	1
IVm	Me	2-Thiophenyl	90	1
IVn	TMS	2-Thiophenyl	76	5
IVo	H	*p*-Me_2N-Ph	86	2
IVp	H	*p*-MeO-Ph	79	2
IVq	Me	*p*-MeO-Ph	84	2
IVr	Et	*p*-MeO-Ph	86	2
IVs	H	*p*-Tolyl	89	2
IVt	Me	*p*-Tolyl	87	2
IVu	Et	*p*-Tolyl	87	2
IVv	H	Phenyl	82	2
IVw	Me	Phenyl	83	2
IVx	Et	Phenyl	90	2
IVy	1-Adamantyl	Phenyl	95	2
IVz	Phenyl	Phenyl	63	1
IVaa	H	*p*-Cl-Ph	83	2
IVab	Me	*p*-Cl-Ph	83	2
IVac	Et	*p*-Cl-Ph	81	2
IVad	H	*p*-NO_2-Ph	76	2
IVae	Me	*p*-NO_2-Ph	74	2
IVaf	Et	*p*-NO_2-Ph	78	2
IVag	Morph	*p*-NO_2-Ph	46	5
IVah	H	1-Naphthyl	65	4
IVai	Me	1-Naphthyl	86	1
IVaj	TMS	1-Naphthyl	81	6.5
IVak	H	9-Anthryl	76	3
IVal	Me	9-Anthryl	90	2
IVam	TMS	9-Anthryl	75	10
IVan	*p*-MeO-Ph	Et	82	1
IVao	*p*-MeO-Ph	Bn	76	1
IVap	*p*-Tolyl	Et	85	1
IVaq	*p*-Tolyl	Pr	73	5
IVar	*p*-Tolyl	*i*Pr	70	2
IVas	*p*-Tolyl	Bn	72	2
IVat	Phenyl	Et	82	2
IVau	Phenyl	Pr	71	4.5
IVav	Phenyl	*i*Pr	83	4
IVaw	*p*-O_2N-Ph	*i*Pr	81	2
IVax	*p*-O_2N-Ph	Bn	82	2

Pyrrol – pyrrolidinomethyl; Morph – morpholinomethyl.

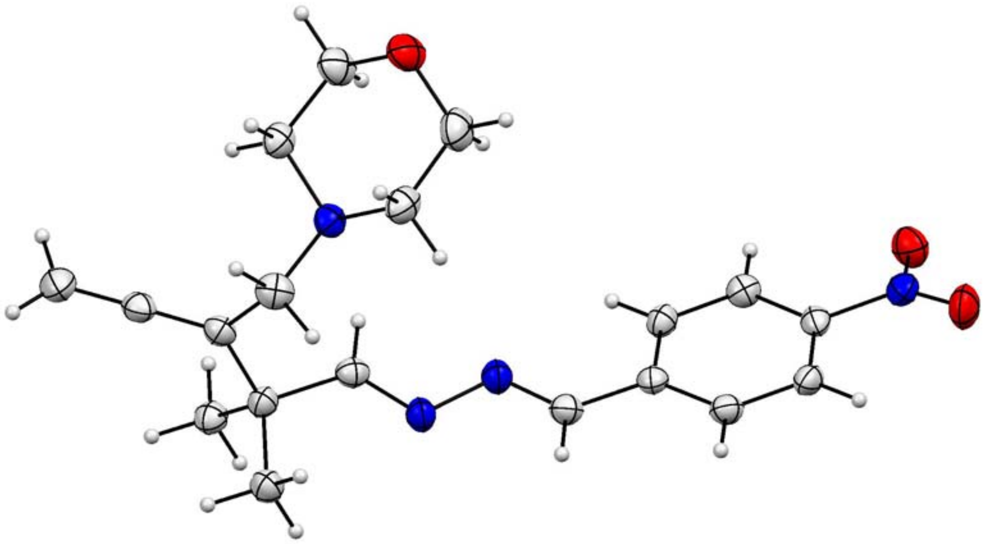

Fig. 2. ORTEP representation of allenyl azine *IVag* shown at 50 % probability level (blue – N, red – O).

Table 2. Characterisation data of five allenyl azines *IV*

Compound	Formula	M_r	w_i(calc.)/% w_i(found)/%			M.p.
			C	H	N	°C
IVq	$C_{16}H_{20}N_2O$	256.34	74.97 74.82	7.86 7.81	10.93 11.20	44–48
IVt	$C_{16}H_{20}N_2$	240.34	79.96 80.13	8.39 8.67	11.66 11.44	–
IVw	$C_{15}H_{18}N_2$	226.32	79.61 79.92	8.02 7.92	12.38 12.20	–
IVab	$C_{15}H_{17}ClN_2$	260.76	69.09 69.27	6.57 6.82	10.74 10.56	–
IVae	$C_{15}H_{17}N_3O_2$	271.31	66.40 66.39	6.32 6.29	15.49 15.17	75–78

erating at frequencies of 300.13 MHz (for ^{1}H NMR) and 75.47 MHz (for ^{13}C NMR) with $CDCl_3$ as solvent. Tetramethylsilane (δ 0.00) or $CDCl_3$ (δ 7.27) served as internal standards for ^{1}H NMR spectra, and $CDCl_3$ (δ 77.23) for ^{13}C NMR spectra. MS data were obtained on a Fisons Instruments TRIO 1000 spectrometer (Fisons Instruments, UK) at 70 eV in the electron impact (EI) mode. Elemental analyses were performed with a Perkin–Elmer CHN 2400 apparatus (Perkin–Elmer, USA). X-ray diffraction data were collected on a Kuma KM-4 four-circle CCD (Kuma Diffraction, Poland) diffractometer and corrected for Lorentz and polarisation effects. The structures were resolved by direct methods and refined by full-matrix least-squares methods using the SHELXTL program package (Bruker AXS, 1997). Hydrogen atoms were placed in calculated idealised positions.

General procedures for preparation of non-symmetrical allenyl azines IV from hydrazones II and III

A mixture of protected allenyl hydrazone *III* (2 mmol) and paraformaldehyde (4 mmol, eq. CH_2O) in toluene (10 mL) was slowly added to a suspension of NaH (72 mg, 3 mmol) in diethyl ether (10 mL) at 5–10 °C. Next, the reaction mixture was stirred at laboratory temperature, the solution was filtered and the residue washed with diethyl ether (3 × 10 mL). The combined organic phases were pre-concentrated in a vacuum and the crude product purified by liquid chromatography (Et_2O) to give a colourless solid *IVa* (370 mg, 69 %). Azine *IVb* with trimethylsilyl (TMS) group was purified by vacuum distillation using a Kugelrohr apparatus (≈ 35 Pa, 60 °C) to give a colourless viscous oil (358 mg, 86 %).

Table 3. Spectral data of newly prepared compounds

Compound	Spectral data
IVa	IR, $\tilde{\nu}$/cm^{-1}: 1092, 1183, 1216, 1359, 1382, 1449, 1683, 1936 (=C=), 2849, 2897, 2926, 2967 ^{1}H NMR ($CDCl_3$), δ: 1.35 (s, 6H, 2 × CH_3), 1.60–1.68 (m, 6H, Ad), 1.70–1.78 (m, 6H, Ad), 1.94 (bs, 3H, Ad), 4.77 (s, 2H, =CH_2), 6.96 (d, 1H, ^{2}J = 13.5 Hz, N=CH_2), 7.38 (d, 1H, ^{2}J = 13.5 Hz, N=CH_2), 7.73 (s, 1H, HC=N) ^{13}C NMR ($CDCl_3$), δ: 27.6 (2 × CH_3), 29.1 (CH, Ad), 36.7 (CH_2, Ad), 36.8 (C, Ad), 40.8 (C), 43.1 (CH_2, Ad), 78.1 (=CH_2), 118.4 (=C—Ad), 149.2 (N=CH_2), 171.6 (HC=N), 207.6 (=C=) MS, m/z (%): 270 (M^+, 1), 255 (28), 135 (100), 107 (10)
IVb	^{1}H NMR ($CDCl_3$), δ: 0.14 (s, 9H, Si—CH_3), 1.32 (s, 6H, 2 × CH_3), 4.48 (s, 2H, =CH_2), 6.96 (d, 1H, ^{2}J = 13.5 Hz, N=CH_2), 7.38 (d, 1H, ^{2}J = 13.5 Hz, N=CH_2), 7.65 (s, 1H, HC=N) ^{13}C NMR ($CDCl_3$), δ: 0.9 (Si—CH_3), 26.4 (2 × CH_3), 41.0 (C), 71.4 (=CH_2), 101.8 (=C—Si), 149.6 (N=CH_2), 170.5 (HC=N), 209.6 (=C=)
IVc	IR, $\tilde{\nu}$/cm^{-1}: 1045, 1218, 1452, 1643, 1954 (=C=), 2850, 2907, 2968, 3020 ^{1}H NMR ($CDCl_3$), δ: 1.26 (s, 6H, 2 × CH_3), 1.65–1.82 (m, 12H, Ad), 2.04 (bs, 3H, Ad), 4.82 (d, 2H, ^{4}J = 6.7 Hz, =CH_2), 5.25 (t, 1H, ^{4}J = 6.7 Hz, HC=C), 7.53 (s, 1H, HC—Ad), 7.67 (s, 1H, HC=N) ^{13}C NMR ($CDCl_3$), δ: 25.6 (2 × CH_3), 28.1 (CH, Ad), 36.9 (CH_2, Ad), 38.0 (C, Ad), 39.7 (C), 39.8 (CH_2, Ad), 77.7 (=CH_2), 97.5 (H$\underline{C}$=C), 168.4 (HC—Ad), 171.0 (HC=N), 207.1 (=C=) MS, m/z (%): 270 (M^+, 56), 255 (30), 213 (16), 135 (100), 108 (70), 94 (43), 79 (42), 67 (30), 41 (20)
IVd	IR, $\tilde{\nu}$/cm^{-1}: 1046, 1218, 1452, 1642, 1953 (=C=), 2850, 2906, 2976, 3017 ^{1}H NMR ($CDCl_3$), δ: 1.28 (s, 6H, 2 × CH_3), 1.71 (t, 3H, ^{5}J = 3.1 Hz, =C—CH_3), 1.76–1.82 (m, 12H, Ad), 2.07 (bs, 3H, Ad), 4.73 (q, ^{5}J = 3.1 Hz, 2H, =CH_2), 7.53 (s, 1H, HC—Ad), 7.61 (s, 1H, HC=N) ^{13}C NMR ($CDCl_3$), δ: 15.4 (=C—$\underline{C}H_3$), 24.4 (2 × CH_3), 28.1 (CH, Ad), 36.9 (CH_2, Ad), 39.6 (C, Ad), 39.8 (CH_2, Ad), 40.1 (C), 76.0 (=CH_2), 103.5 (=$\underline{C}$—CH_3), 167.9 (HC—Ad), 170.6 (HC=N), 206.5 (=C=) MS, m/z (%): 284 (M^+, 2), 149 (98), 135 (95), 123 (73), 108 (100), 93 (51), 79 (61), 67 (66), 55 (24), 41 (30)
IVe	IR, $\tilde{\nu}$/cm^{-1}: 1048, 1116, 1220, 1321, 1345, 1385, 1452, 1519, 1642, 1954 (=C=), 2796, 2851, 2907, 2970, 3019 ^{1}H NMR ($CDCl_3$), δ: 1.30 (s, 6H, 2 × CH_3), 1.70–1.71 (m, 4H, pyrrol.), 1.74–1.81 (m, 12H, Ad), 2.05 (bs, 3H, Ad), 2.49–2.53 (m, 4H, N—CH_2), 3.07–3.12 (m, 2H, N—CH_2), 4.85–5.02 (m, 2H, =CH_2), 7.48 (s, 1H, HC—Ad), 7.64 (s, 1H, HC=N) ^{13}C NMR ($CDCl_3$), δ: 23.8 (2 × CH_2), 24.8 (2 × CH_3), 28.1 (CH, Ad), 36.9 (CH_2, Ad), 39.7 (C, Ad), 39.8 (CH_2, Ad), 40.3 (C), 54.2 (2 × CH_2), 55.2 (=C—$\underline{C}H_2$), 78.1 (=CH_2), 107.4 (=$\underline{C}$—CH_2), 168.0 (HC—Ad), 169.9 (HC=N), 206.6 (=C=) MS, m/z (%): 354 (M^+, 1), 191 (100), 122 (92), 84 (90), 70 (22), 42 (17)
IVf	IR, $\tilde{\nu}$/cm^{-1}: 1005, 1117, 1218, 1308, 1346, 1384, 1454, 1643, 1953 (=C=), 2763, 2808, 2849, 2904, 2965 ^{1}H NMR ($CDCl_3$), δ: 1.29 (s, 6H, 2 × CH_3), 1.68–1.81 (m, 12H, Ad), 2.04 (bs, 3H, Ad), 2.41 (m, 4H, N—CH_2), 2.93 (t, 2H, ^{5}J = 2.3 Hz, =C—CH_2), 3.69 (m, 4H, O—CH_2), 4.85 (t, 2H, ^{5}J = 2.3 Hz, =CH_2), 7.52 (s, 1H, HC—Ad), 7.74 (s, 1H, HC=N) ^{13}C NMR ($CDCl_3$), δ: 25.0 (2 × CH_3), 28.1 (CH, Ad), 36.9 (CH_2, Ad), 39.7 (C, Ad), 39.9 (CH_2, Ad), 40.1 (C), 53.6 (N—CH_2), 58.5 (=C—$\underline{C}H_2$), 67.1 (O—CH_2), 77.3 (=CH_2), 105.4 (=$\underline{C}$—CH_2), 168.8 (HC—Ad), 170.4 (HC=N), 207.5 (=C=) MS, m/z (%): 369 (M^+, 1), 207 (100), 122 (62), 100 (89), 79 (24), 56 (22)
IVg	IR, $\tilde{\nu}$/cm^{-1}: 1044, 1100, 1314, 1360, 1451, 1642, 1937 (=C=), 2850, 2901 ^{1}H NMR ($CDCl_3$), δ: 1.39 (s, 6H, 2 × CH_3), 1.63–1.96 (m, 24H, Ad), 1.99 (bs, 3H, Ad), 2.08 (bs, 3H, Ad), 4.80 (s, 2H, =CH_2), 7.55 (s, 1H, HC—Ad), 7.73 (s, 1H, HC=N) ^{13}C NMR ($CDCl_3$), δ: 27.8 (2 × CH_3), 28.1 (CH, Ad), 29.2 (CH, Ad), 36.5 (C, Ad), 36.9 (2 × CH_2, Ad), 39.8 (C, Ad), 39.9 (CH_2, Ad), 40.8 (C), 43.1 (CH_2, Ad), 78.0 (=CH_2), 118.7 (=C—Ad), 169.8 (HC—Ad), 170.0 (HC=N), 207.8 (=C=) MS, m/z (%): 404 (M^+, 1), 389 (26), 269 (42), 228 (10), 135 (100)
IVh	IR, $\tilde{\nu}$/cm^{-1}: 1032, 1127, 1220, 1362, 1451, 1600, 1641, 1942 (=C=), 2849, 2907, 2971 ^{1}H NMR ($CDCl_3$), δ: 1.35 (s, 6H, 2 × CH_3), 1.70–1.85 (m, 12H, Ad), 2.10 (bs, 3H, Ad), 4.96 (s, 2H, =CH_2), 7.22–7.39 (m, 5H, Ph), 7.48 (s, 1H, HC—Ad), 7.80 (s, 1H, HC=N) ^{13}C NMR ($CDCl_3$), δ: 25.6 (2 × CH_3), 28.0 (CH, Ad), 36.8 (CH_2, Ad), 36.9 (C, Ad), 39.7 (CH_2, Ad), 40.4 (C), 77.6 (=CH_2), 111.3 (=C–Ph), 126.9 (CH), 128.0 (2 × CH), 128.7 (2 × CH), 136.0 (C), 168.3 (HC—Ad), 170.3 (HC=N), 208.2 (=C=) MS, m/z (%): 346 (M^+, 100), 305 (13), 291 (78), 189 (18), 135 (35), 83 (16)
IVi	IR, $\tilde{\nu}$/cm^{-1}: 1018, 1082, 1150, 1272, 1306, 1363, 1385, 1475, 1635, 1644, 1955 (=C=), 2868, 2931, 2971, 3120 ^{1}H NMR ($CDCl_3$), δ: 1.27 (s, 6H, 2 × CH_3), 4.81 (d, 2H, ^{4}J = 6.7 Hz, =CH_2), 5.26 (t, 1H, ^{4}J = 6.7 Hz, HC=C), 6.48 (dd, 1H, ^{3}J = 3.4 Hz, ^{3}J = 1.8 Hz, Ar), 6.81 (d, 1H, ^{3}J = 3.4 Hz, Ar), 7.54 (d, 1H, ^{3}J = 1.8 Hz, Ar), 7.92 (s, 1H, HC=N), 8.33 (s, 1H, HC—Ar) ^{13}C NMR ($CDCl_3$), δ: 25.7 (2 × CH_3), 38.3 (C), 77.9 (=CH_2), 97.3 (H$\underline{C}$=C), 112.2 (CH), 116.0 (CH), 145.6 (CH), 149.6 (C), 150.3 (HC—Ar), 171.3 (HC=N), 207.1 (=C=)

Table 3. (continued)

Compound	Spectral data
IVj	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1017, 1083, 1109, 1150, 1274, 1372, 1456, 1479, 1636, 1952 (=C=), 2869, 2930, 2973, 3119 ^{1}H NMR ($CDCl_3$), δ: 1.27 (s, 6H, 2 × CH_3), 1.68 (t, 3H, ^5J = 3.0 Hz, =C—CH_3), 4.70 (q, 2H, ^5J = 3.0 Hz, =CH_2), 6.49 (dd, 1H, ^3J = 3.3 Hz, ^3J = 1.7 Hz, Ar), 6.82 (d, 1H, ^3J = 3.3 Hz, Ar), 7.55 (d, 1H, ^3J = 1.7 Hz, Ar), 7.88 (s, 1H, HC=N), 8.34 (s, 1H, HC—Ar) ^{13}C NMR ($CDCl_3$), δ: 15.3 (=C—$\underline{C}H_3$), 24.4 (2 × CH_3), 40.4 (C), 76.1 (=CH_2), 103.4 (=$\underline{C}$—CH_3), 112.2 (CH), 116.0 (CH), 145.6 (CH), 149.6 (C), 150.1 (HC—Ar), 171.2 (HC=N), 206.4 (=C=)
IVk	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1018, 1083, 1155, 1250, 1306, 1362, 1383, 1465, 1480, 1636, 1896, 1923 (=C=), 2870, 2898, 2936, 2963, 3108 ^{1}H NMR ($CDCl_3$), δ: 0.13 (s, 9H, Si—CH_3), 1.34 (s, 6H, 2 × CH_3), 4.47 (s, 2H, =CH_2), 6.50 (dd, 1H, ^3J = 3.4 Hz, ^3J = 1.8 Hz, Ar), 6.82 (d, 1H, ^3J = 3.4 Hz, Ar), 7.55 (d, 1H, ^3J = 1.8 Hz, Ar), 7.91 (s, 1H, HC=N), 8.34 (s, 1H, HC—Ar) ^{13}C NMR ($CDCl_3$), δ: 0.9 (Si—CH_3), 26.5 (2 × CH_3), 41.0 (C), 71.4 (=CH_2), 101.8 (=C—Si), 112.2 (CH), 115.9 (CH), 145.5 (CH), 149.7 (C), 150.0 (HC—Ar), 172.2 (HC=N), 209.6 (=C=)
IVl	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1046, 1143, 1213, 1363, 1426, 1457, 1583, 1614, 1630, 1954 (=C=), 2866, 2927, 2968, 3077 ^{1}H NMR ($CDCl_3$), δ: 1.30 (s, 6H, 2 × CH_3), 4.85 (d, 2H, ^4J = 6.7 Hz, =CH_2), 5.29 (t, 1H, ^4J = 6.7 Hz, HC=C), 7.09 (dd, 1H, ^3J = 5.0 Hz, ^3J = 3.7 Hz, Ar), 7.37 (d, 1H, ^3J = 3.7 Hz, Ar), 7.44 (d, 1H, ^3J = 5.0 Hz, Ar), 7.89 (s, 1H, HC=N), 8.64 (s, 1H, HC—Ar) ^{13}C NMR ($CDCl_3$), δ: 25.7 (2 × CH_3), 38.3 (C), 77.9 (=CH_2), 97.4 (H$\underline{C}$=C), 127.8 (CH), 129.8 (CH), 132.2 (CH), 139.0 (C), 155.3 (HC—Ar), 170.6 (HC=N), 207.2 (=C=)
IVm	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1046, 1108, 1214, 1427, 1454, 1581, 1630, 1952 (=C=), 2867, 2927, 2972 ^{1}H NMR ($CDCl_3$), δ: 1.29 (s, 6H, 2 × CH_3), 1.70 (t, 3H, ^5J = 3.1 Hz, =C—CH_3), 4.71 (q, 2H, ^5J = 3.1 Hz, =CH_2), 7.04–7.10 (m, 1H, Ar), 7.34–7.38 (m, 1H, Ar), 7.40–7.44 (m, 1H, Ar), 7.82 (s, 1H, HC=N), 8.63 (s, 1H, HC—Ar) ^{13}C NMR ($CDCl_3$), δ: 15.4 (=C—$\underline{C}H_3$), 24.5 (2 × CH_3), 40.4 (C), 76.1 (=CH_2), 103.4 (=$\underline{C}$—CH_3), 127.8 (CH), 129.7 (CH), 132.1 (CH), 139.1 (C), 155.1 (HC—Ar), 170.4 (HC=N), 206.5 (=C=) MS, m/z (%): 232 (M^+, 1), 220 (100), 192 (35), 147 (24), 110 (46), 96 (32), 70 (29)
IVn	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1046, 1173, 1213, 1250, 1362, 1383, 1427, 1462, 1583, 1632, 1897, 1922 (=C=), 2869, 2897, 2933, 2965, 3058, 3076 ^{1}H NMR ($CDCl_3$), δ: 0.16 (s, 9H, Si—CH_3), 1.37 (s, 6H, 2 × CH_3), 4.49 (s, 2H, =CH_2), 7.09 (dd, 1H, ^3J = 4.9 Hz, ^3J = 3.7 Hz, Ar), 7.38 (d, 1H, ^3J = 3.7 Hz, Ar), 7.44 (d, 1H, ^3J = 4.9 Hz, Ar), 7.87 (s, 1H, HC=N), 8.64 (s, 1H, HC—Ar) ^{13}C NMR ($CDCl_3$), δ: 0.8 (Si—CH_3), 26.4 (2 × CH_3), 40.9 (C), 71.2 (=CH_2), 101.6 (=C—Si), 127.6 (CH), 129.5 (CH), 131.9 (CH), 139.0 (C), 154.8 (HC—Ar), 171.3 (HC=N), 209.4 (=C=)
IVo	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1180, 1366, 1527, 1610, 1953 (=C=), 2809, 2866, 2923, 2977, 3201 ^{1}H NMR ($CDCl_3$), δ: 1.29 (s, 6H, 2 × CH_3), 2.98 (s, 6H, N—CH_3), 4.82 (d, 2H, ^4J = 6.6 Hz, =CH_2), 5.30 (t, 1H, ^4J = 6.6 Hz, HC=C), 6.66 (d, 2H, ^3J = 8.8 Hz, Ar), 7.62 (d, 2H, ^3J = 8.8 Hz, Ar), 7.88 (s, 1H, HC=N), 8.41 (s, 1H, HC—Ar) ^{13}C NMR ($CDCl_3$), δ: 25.8 (2 × CH_3), 38.1 (C), 40.2 (N—CH_3), 77.7 (=CH_2), 97.6 (H$\underline{C}$=C), 111.7 (CH), 121.7 (C), 130.1 (CH), 152.4 (C), 161.8 (HC—Ar), 168.6 (HC=N), 207.1 (=C=) MS, m/z (%): 255 (M^+, 16), 254 (24), 240 (35), 146 (100), 94 (44)
IVp	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1032, 1168, 1252, 1512, 1608, 1633, 1954 (=C=), 2837, 2868, 2931, 2966, 3035, 3072 ^{1}H NMR ($CDCl_3$), δ: 1.31 (s, 6H, 2 × CH_3), 3.83 (s, 3H, O—CH_3), 4.84 (d, 2H, ^4J = 6.7 Hz, =CH_2), 5.30 (t, 1H, ^4J = 6.7 Hz, HC=C), 6.92 (d, 2H, ^3J = 8.9 Hz, Ar), 7.71 (d, 2H, ^3J = 8.9 Hz, Ar), 7.88 (s, 1H, HC=N), 8.44 (s, 1H, HC—Ar) ^{13}C NMR ($CDCl_3$), δ: 25.8 (2 × CH_3), 38.2 (C), 55.5 (O—CH_3), 77.8 (=CH_2), 97.6 (H$\underline{C}$=C), 114.4 (CH), 126.9 (C), 130.2 (CH), 160.9 (HC—Ar), 162.2 (C), 169.8 (HC=N), 207.2 (=C=) MS, m/z (%): 243 (M^+ + 1, 45), 241 (67), 227 (100), 211 (25), 134 (50), 108 (56), 94 (58)
IVq	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1030, 1254, 1512, 1608, 1628, 1954 (=C=), 2837, 2866, 2927, 2978, 3045, 3076 ^{1}H NMR ($CDCl_3$), δ: 1.30 (s, 6H, 2 × CH_3), 1.71 (t, 3H, ^5J = 3.0 Hz, =C—CH_3), 3.84 (s, 3H, O—CH_3), 4.72 (q, 2H, ^5J = 3.0 Hz, =CH_2), 6.93 (d, 2H, ^3J = 8.9 Hz, Ar), 7.71 (d, 2H, ^3J = 8.9 Hz, Ar), 7.81 (s, 1H, HC=N), 8.44 (s, 1H, HC—Ar) ^{13}C NMR ($CDCl_3$), δ: 15.5 (=C—$\underline{C}H_3$), 24.5 (2 × CH_3), 40.4 (C), 55.5 (O—CH_3), 76.1 (=CH_2), 103.6 (=$\underline{C}$—CH_3), 114.4 (CH), 127.0 (C), 130.2 (CH), 160.7 (HC—Ar), 162.2 (C), 169.6 (HC=N), 206.6 (=C=) MS, m/z (%): 257 (M^+ + 1, 25), 255 (27), 241 (100), 225 (12), 211 (25), 134 (27), 122 (40), 108 (65)
IVr	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1032, 1168, 1252, 1512, 1608, 1633, 1952 (=C=), 2839, 2872, 2931, 2968, 3035, 3072 ^{1}H NMR ($CDCl_3$), δ: 1.00 (t, 3H, ^3J = 7.3 Hz, H_3C—CH_2), 1.31 (s, 6H, 2 × CH_3), 1.90–2.03 (m, 2H, H_3C—C$\underline{H_2}$), 3.84 (s, 3H, O—CH_3), 4.85 (t, 2H, ^5J = 4.0 Hz, =CH_2), 6.93 (d, 2H, ^3J = 8.9 Hz, Ar), 7.71 (d, 2H, ^3J = 8.9 Hz, Ar), 7.81 (s, 1H, HC=N), 8.44 (s, 1H, HC—Ar) ^{13}C NMR ($CDCl_3$), δ: 12.7 ($H_3\underline{C}$—CH_2), 20.5 (H_3C—$\underline{C}H_2$), 24.7 (2 × CH_3), 40.6 (C), 55.5 (O—CH_3), 78.9 (=CH_2), 110.7 (=C—Et), 114.4 (CH), 127.0 (C), 130.2 (CH), 160.7 (HC—Ar), 162.1 (C), 169.8 (HC=N), 205.9 (=C=) MS, m/z (%): 271 (M^+ + 1, 72), 255 (100), 241 (36), 227 (16), 134 (46), 122 (83), 107 (36)

Table 3. (continued)

Compound	Spectral data
IVs	IR, $\tilde{\nu}$/cm^{-1}: 1109, 1176, 1306, 1458, 1635, 1954 (=C=), 2868, 2929, 2968, 3026, 3051 ^{1}H NMR ($CDCl_3$), δ: 1.31 (s, 6H, 2 × CH_3), 2.38 (s, 3H, Ph—CH_3), 4.84 (d, 2H, ^4J = 6.7 Hz, =CH_2), 5.30 (t, 1H, ^4J = 6.7 Hz, HC=C), 7.21 (d, 2H, ^3J = 8.1 Hz, Ar), 7.65 (d, 2H, ^3J = 8.1 Hz, Ar), 7.88 (s, 1H, HC=N), 8.45 (s, 1H, HC—Ar) ^{13}C NMR ($CDCl_3$), δ: 21.8 (Ph—CH_3), 25.8 (2 × CH_3), 38.3 (C), 77.9 (=CH_2), 97.5 (H$\underline{C}$=C), 128.6 (CH), 129.7 (CH), 131.5 (C), 141.6 (C), 161.3 (HC—Ar), 170.0 (HC=N), 207.2 (=C=) MS, m/z (%): 227 (M^+ + 1, 100), 211 (72), 118 (13), 108 (37), 94 (39)
IVt	IR, $\tilde{\nu}$/cm^{-1}: 1109, 1176, 1306, 1454, 1635, 1954 (=C=), 2868, 2928, 2971, 3026, 3049 ^{1}H NMR ($CDCl_3$), δ: 1.30 (s, 6H, 2 × CH_3), 1.71 (t, 3H, ^5J = 3.0 Hz, =C—CH_3), 2.38 (s, 3H, Ph—CH_3), 4.72 (q, 2H, ^5J = 3.0 Hz, =CH_2), 7.21 (d, 2H, ^3J = 8.1 Hz, Ar), 7.66 (d, 2H, ^3J = 8.1 Hz, Ar), 7.82 (s, 1H, HC=N), 8.45 (s, 1H, HC—Ar) ^{13}C NMR ($CDCl_3$), δ: 15.5 (=C—$\underline{C}H_3$), 21.8 (Ph—CH_3), 24.5 (2 × CH_3), 40.4 (C), 76.1 (=CH_2), 103.5 (=$\underline{C}$—CH_3), 128.5 (CH), 129.7 (CH), 131.5 (C), 141.6 (C), 161.0 (HC—Ar), 169.8 (HC=N), 206.5 (=C=) MS, m/z (%): 240 (M^+, 20), 225 (100), 122 (38), 108 (100), 91 (85)
IVu	IR, $\tilde{\nu}$/cm^{-1}: 1176, 1306, 1458, 1635, 1950 (=C=), 2873, 2931, 2970, 3026, 3049 ^{1}H NMR ($CDCl_3$), δ: 1.00 (t, 3H, ^3J = 7.4 Hz, $\underline{H_3}$C—CH_2), 1.31 (s, 6H, 2 × CH_3), 1.89–2.03 (m, 2H, H_3C—C$\underline{H_2}$), 2.38 (s, 3H, Ph—CH_3), 4.85 (t, 2H, ^5J = 4.0 Hz, =CH_2), 7.21 (d, 2H, ^3J = 7.9 Hz, Ar), 7.65 (d, 2H, ^3J = 7.9 Hz, Ar), 7.81 (s, 1H, HC=N), 8.45 (s, 1H, HC—Ar) ^{13}C NMR ($CDCl_3$), δ: 12.7 ($H_3\underline{C}$—CH_2), 20.5 (H_3C—$\underline{C}H_2$), 21.8 (Ph—CH_3), 24.7 (2 × CH_3), 40.6 (C), 78.9 (=CH_2), 110.7 (=C—Et), 128.6 (CH), 129.7 (CH), 131.6 (C), 141.6 (C), 161.0 (HC—Ar), 170.1 (HC=N), 205.9 (=C=) MS, m/z (%): 255 (M^+ + 1, 84), 239 (100), 122 (91), 109 (46), 91 (63)
IVv	IR, $\tilde{\nu}$/cm^{-1}: 1448, 1635, 1954 (=C=), 2868, 2929, 2968, 3028, 3060 ^{1}H NMR ($CDCl_3$), δ: 1.31 (s, 6H, 2 × CH_3), 4.84 (d, 2H, ^4J = 6.6 Hz, =CH_2), 5.30 (t, 1H, ^4J = 6.6 Hz, HC=C), 7.35–7.47 (m, 3H, Ph), 7.72–7.82 (m, 2H, Ph), 7.88 (s, 1H, HC=N), 8.47 (s, 1H, HC—Ph) ^{13}C NMR ($CDCl_3$), δ: 25.8 (2 × CH_3), 38.3 (C), 77.9 (=CH_2), 97.5 (H$\underline{C}$=C), 128.6 (2 × CH), 128.9 (2 × CH), 131.2 (CH), 134.2 (C), 161.1 (HC—Ph), 170.3 (HC=N), 207.2 (=C=) MS, m/z (%): 213 (M^+ + 1, 100), 197 (35), 77 (48)
IVw	IR, $\tilde{\nu}$/cm^{-1}: 1109, 1448, 1637, 1955 (=C=), 2870, 2929, 3026, 3062 ^{1}H NMR ($CDCl_3$), δ: 1.31 (s, 6H, 2 × CH_3), 1.72 (t, 3H, ^5J = 3.0 Hz, =C—CH_3), 4.73 (q, 2H, ^5J = 3.0 Hz, =CH_2), 7.38–7.46 (m, 3H, Ph), 7.73–7.80 (m, 2H, Ph), 7.82 (s, 1H, HC=N), 8.47 (s, 1H, HC—Ph) ^{13}C NMR ($CDCl_3$), δ: 15.5 (=C—$\underline{C}H_3$), 24.5 (2 × CH_3), 40.4 (C), 76.1 (=CH_2), 103.5 (=$\underline{C}$—CH_3), 128.6 (2 × CH), 128.9 (2 × CH), 131.2 (CH), 134.3 (C), 160.9 (HC—Ph), 170.0 (HC=N), 206.5 (=C=) MS, m/z (%): 225 (M^+ + 1, 38), 211 (88), 122 (42), 108 (74), 77 (100)
IVx	IR, $\tilde{\nu}$/cm^{-1}: 1448, 1635, 1952 (=C=), 2870, 2933, 2968, 3062 ^{1}H NMR ($CDCl_3$), δ: 1.00 (t, 3H, ^3J = 7.4 Hz, $\underline{H_3}$C—CH_2), 1.31 (s, 6H, 2 × CH_3), 1.90–2.03 (m, 2H, H_3C—C$\underline{H_2}$), 4.85 (t, 2H, ^5J = 4.0 Hz, =CH_2), 7.34–7.47 (m, 3H, Ph), 7.71–7.79 (m, 2H, Ph), 7.81 (s, 1H, HC=N), 8.47 (s, 1H, HC—Ph) ^{13}C NMR ($CDCl_3$), δ: 12.7 ($H_3\underline{C}$—CH_2), 20.5 (H_3C—$\underline{C}H_2$), 24.7 (2 × CH_3), 40.7 (C), 79.0 (=CH_2), 110.7 (=C—Et), 128.6 (2 × CH), 128.9 (2 × CH), 131.2 (CH), 134.3 (C), 160.9 (HC—Ph), 170.4 (HC=N), 205.9 (=C=) MS, m/z (%): 240 (M^+, 14), 225 (78), 211 (34), 122 (58), 77 (100)
IVy	IR, $\tilde{\nu}$/cm^{-1}: 1032, 1127, 1220, 1362, 1451, 1600, 1641, 1942 (=C=), 2849, 2907, 2971 ^{1}H NMR ($CDCl_3$), δ: 1.35 (s, 6H, 2 × CH_3), 1.70–1.85 (m, 12H, Ad), 2.10 (bs, 3H, Ad), 4.96 (s, 2H, =CH_2), 7.22–7.39 (m, 5H, Ph), 7.48 (s, 1H, HC—Ad), 7.80 (s, 1H, HC=N) ^{13}C NMR ($CDCl_3$), δ: 25.6 (2 × CH_3), 28.0 (CH, Ad), 36.8 (CH_2, Ad), 36.9 (C, Ad), 39.7 (CH_2, Ad), 40.4 (C), 77.6 (=CH_2), 111.6 (=C—Ad), 126.9 (CH), 128.0 (2 × CH), 128.7 (2 × CH), 134.2 (C), 168.3 (HC—Ad), 170.3 (HC=N), 208.2 (=C=) MS, m/z (%): 346 (M^+, 100), 305 (13), 291 (78), 189 (18), 135 (35), 83 (16)
IVz	IR, $\tilde{\nu}$/cm^{-1}: 1472, 1482, 1609, 1625, 1927 (=C=), 2932, 3037, 3057 ^{1}H NMR ($CDCl_3$), δ: 1.33 (s, 6H, 2 × CH_3), 4.93 (s, 2H, =CH_2), 7.11–7.25 (m, 6H, Ph), 7.31–7.33 (m, 2H, Ph), 7.67–7.70 (m, 2H, Ph), 7.96 (s, 1H, HC=N), 8.38 (s, 1H, HC—Ph) ^{13}C NMR ($CDCl_3$), δ: 25.6 (2 × CH_3), 40.6 (C), 77.7 (=CH_2), 116.6 (=C—Ph), 126.9 (2 × CH), 128.0 (2 × CH), 128.3 (2 × CH), 128.6 (2 × CH), 130.9 (CH), 132.8 (CH), 134.0 (C), 135.9 (C), 160.6 (HC—Ph), 170.4 (HC=N), 208.2 (=C=)
IVaa	IR, $\tilde{\nu}$/cm^{-1}: 1092, 1491, 1635, 1954 (=C=), 2868, 2929, 2970, 3030, 3055 ^{1}H NMR ($CDCl_3$), δ: 1.31 (s, 6H, 2 × CH_3), 4.85 (d, 2H, ^4J = 6.6 Hz, =CH_2), 5.29 (t, 1H, ^4J = 6.6 Hz, HC=C), 7.39 (d, 2H, ^3J = 8.3 Hz, Ar), 7.70 (d, 2H, ^3J = 8.3 Hz, Ar), 7.87 (s, 1H, HC=N), 8.43 (s, 1H, HC—Ar) ^{13}C NMR ($CDCl_3$), δ: 25.7 (2 × CH_3), 38.3 (C), 78.0 (=CH_2), 97.4 (H$\underline{C}$=C), 129.3 (CH), 129.7 (CH), 132.7 (C), 137.2 (C), 159.8 (HC—Ar), 170.7 (HC=N), 207.2 (=C=) MS, m/z (%): 247 (M^+, 16), 245 (20), 231 (21), 139 (28), 135 (26), 111 (61), 108 (95), 94 (100)

Table 3. (continued)

Compound	Spectral data
IVab	IR, $\tilde{\nu}$/cm^{-1}: 1092, 1490, 1635, 1954 (=C=), 2868, 2931, 2974, 3029, 3051 ^{1}H NMR (CDCl$_3$), δ: 1.30 (s, 6H, 2 × CH$_3$), 1.71 (t, 3H, ^{5}J = 3.0 Hz, =C—CH$_3$), 4.73 (q, 2H, ^{5}J = 3.0 Hz, =CH$_2$), 7.39 (d, 2H, ^{3}J = 8.4 Hz, Ar), 7.70 (d, 2H, ^{3}J = 8.4 Hz, Ar), 7.81 (s, 1H, HC=N), 8.43 (s, 1H, HC—Ar) ^{13}C NMR (CDCl$_3$), δ: 15.4 (=C—$\underline{\text{C}}$H$_3$), 24.4 (2 × CH$_3$), 40.5 (C), 76.2 (=CH$_2$), 103.4 (=$\underline{\text{C}}$—CH$_3$), 129.3 (CH), 129.7 (CH), 132.8 (C), 137.2 (C), 159.6 (HC—Ar), 170.5 (HC=N), 206.6 (=C=) MS, m/z (%): 261 (M^{+}, 100), 259 (22), 245 (76), 138 (24), 122 (62), 108 (100), 93 (36)
IVac	IR, $\tilde{\nu}$/cm^{-1}: 1090, 1491, 1635, 1950 (=C=), 2872, 2931, 2970, 3030, 3051 ^{1}H NMR (CDCl$_3$), δ: 1.00 (t, 3H, ^{3}J = 7.3 Hz, $\underline{\text{H}}_3$C—CH$_2$), 1.31 (s, 6H, 2 × CH$_3$), 1.89–2.02 (m, 2H, H$_3$C—C$\underline{\text{H}}_2$), 4.86 (t, 2H,^{5}J = 4.0 Hz, =CH$_2$), 7.39 (d, 2H, ^{3}J = 8.4 Hz, Ar), 7.70 (d, 2H, ^{3}J = 8.4 Hz, Ar), 7.80 (s, 1H, HC=N), 8.43 (s, 1H, HC—Ar) ^{13}C NMR (CDCl$_3$), δ: 12.7 (H$_3\underline{\text{C}}$—CH$_2$), 20.5 (H$_3$C—$\underline{\text{C}}$H$_2$), 24.7 (2 × CH$_3$), 40.7 (C), 79.0 (=CH$_2$), 110.6 (=C—Et), 129.3 (CH), 129.7 (CH), 132.8 (C), 137.2 (C), 159.6 (HC—Ar), 170.8 (HC=N), 205.9 (=C=) MS, m/z (%): 275 (M^{+}, 32), 248 (11), 165 (100), 138 (46), 111 (63), 89 (55)
IVad	IR, $\tilde{\nu}$/cm^{-1}: 1108, 1340, 1518, 1598, 1634, 1950 (=C=), 2867, 2931, 2971, 3043, 3092, 3129 ^{1}H NMR (CDCl$_3$), δ: 1.32 (s, 6H, 2 × CH$_3$), 4.87 (d, 2H, ^{4}J = 6.6 Hz, =CH$_2$), 5.29 (t, 1H, ^{4}J = 6.6 Hz, HC=C), 7.89 (s, 1H, HC=N), 7.93 (d, 2H, ^{3}J = 8.9 Hz, Ar), 8.27 (d, 2H, ^{3}J = 8.9 Hz, Ar), 8.50 (s, 1H, HC—Ar) ^{13}C NMR (CDCl$_3$), δ: 25.7 (2 × CH$_3$), 38.5 (C), 78.1 (=CH$_2$), 97.2 (H$\underline{\text{C}}$=C), 124.2 (CH), 129.1 (CH), 140.1 (C), 149.3 (C), 158.3 (HC—Ar), 171.6 (HC=N), 207.3 (=C=) MS, m/z (%): 256 (M^{+}, 38), 242 (80), 195 (20), 108 (76), 94 (100), 79 (64)
IVae	IR, $\tilde{\nu}$/cm^{-1}: 1107, 1343, 1520, 1602, 1631, 1951 (=C=), 2865, 2927, 2971, 3051, 3081, 3108 ^{1}H NMR (CDCl$_3$), δ: 1.32 (s, 6H, 2 × CH$_3$), 1.72 (t, 3H, ^{5}J = 3.0 Hz, =C—CH$_3$), 4.74 (q, 2H, ^{5}J = 3.0 Hz, =CH$_2$), 7.83 (s, 1H, HC=N), 7.93 (d, 2H,^{3}J = 8.8 Hz, Ar), 8.27 (d, 2H, ^{3}J = 8.8 Hz, Ar), 8.50 (s, 1H, HC—Ar) ^{13}C NMR (CDCl$_3$), δ: 15.4 (=C—$\underline{\text{C}}$H$_3$), 24.3 (2 × CH$_3$), 40.6 (C), 76.3 (=CH$_2$), 103.2 (=$\underline{\text{C}}$—CH$_3$), 124.1 (CH), 129.1 (CH), 140.1 (C), 149.3 (C), 158.1 (HC—Ar), 171.4 (HC=N), 206.5 (=C=) MS, m/z (%): 271 (M^{+}, 4), 270 (19), 256 (100), 210 (33), 122 (55), 108 (58)
IVaf	IR, $\tilde{\nu}$/cm^{-1}: 1103, 1342, 1521, 1601, 1633, 1949 (=C=), 2856, 2871, 2931, 2969, 3046, 3103 ^{1}H NMR (CDCl$_3$), δ: 1.01 (t, 3H, ^{3}J = 7.3 Hz, $\underline{\text{H}}_3$C—CH$_2$), 1.32 (s, 6H, 2 × CH$_3$), 1.89–2.03 (m, 2H, H$_3$C—C$\underline{\text{H}}_2$), 4.87 (t, 2H, ^{5}J = 4.0 Hz, =CH$_2$), 7.83 (s, 1H, HC=N), 7.93 (d, 2H, ^{3}J = 8.6 Hz, Ar), 8.27 (d, 2H, ^{3}J = 8.6 Hz, Ar), 8.50 (s, 1H, HC—Ar) ^{13}C NMR (CDCl$_3$), δ: 12.7 (H$_3\underline{\text{C}}$—CH$_2$), 20.5 (H$_3$C—$\underline{\text{C}}$H$_2$), 24.6 (2 × CH$_3$), 40.8 (C), 79.1 (=CH$_2$), 110.4 (=C—Et), 124.1 (CH), 129.1 (CH), 140.1 (C), 149.3 (C), 158.1 (HC—Ar), 171.7 (HC=N), 205.9 (=C=) MS, m/z (%): 285 (M^{+}, 3), 284 (10), 270 (100), 256 (33), 224 (23), 136 (25), 122 (66), 107 (42)
IVag	^{1}H NMR (CDCl$_3$), δ: 1.36 (s, 6H, 2 × CH$_3$), 2.39–2.47 (m, 4H, N—CH$_2$), 2.96–3.00 (m, 2H, =C—CH$_2$), 3.61–3.68 (m, 4H, O—CH$_2$), 4.84–4.88 (m, 2H, =CH$_2$), 7.93 (d, 2H, ^{3}J = 8.1 Hz, Ar), 7.96 (s, 1H, HC=N), 8.28 (d, 2H, ^{3}J = 8.1 Hz, Ar), 8.50 (s, 1H, HC—Ar) ^{13}C NMR (CDCl$_3$), δ: 24.9 (2 × CH$_3$), 40.2 (C), 53.6 (N—CH$_2$), 58.7 (=C—$\underline{\text{C}}$H$_2$), 67.2 (O—CH$_2$), 77.5 (=CH$_2$), 105.3 (=$\underline{\text{C}}$—CH$_2$), 124.2 (CH), 129.0 (CH), 140.2 (C), 149.3 (C), 157.8 (HC—Ar), 172.5 (HC=N), 207.6 (=C=)
IVah	IR, $\tilde{\nu}$/cm^{-1}: 1240, 1319, 1338, 1464, 1510, 1578, 1633, 1954 (=C=), 2868, 2927, 2970, 3053 ^{1}H NMR (CDCl$_3$), δ: 1.44 (s, 6H, 2 × CH$_3$), 4.94 (d, 2H, ^{4}J = 6.8 Hz, =CH$_2$), 5.43 (t, 1H, ^{4}J = 6.8 Hz, HC=C), 7.47–7.67 (m, 3H, Ar), 7.84–8.00 (m, 2H, Ar), 8.00–8.09 (m, 1H, Ar), 8.10 (s, 1H, HC=N), 8.85–8.97 (m, 1H, Ar), 9.21 (s, 1H, HC—Ar) ^{13}C NMR (CDCl$_3$), δ: 25.8 (2 × CH$_3$), 38.3 (C), 77.9 (=CH$_2$), 97.5 (H$\underline{\text{C}}$=C), 124.7 (CH), 125.3 (CH), 126.3 (CH), 127.3 (CH), 128.8 (CH), 129.1 (CH), 129.7 (C), 131.5 (C), 131.7 (CH), 134.0 (C), 160.9 (HC—Ar), 170.3 (HC=N), 207.2 (=C=) MS, m/z (%): 262 (M^{+}, 24), 247 (71), 234 (17), 192 (30), 153 (75), 139 (34), 127 (100), 108 (73), 94 (96), 79 (47), 67 (65), 53 (41), 41 (54)
IVai	IR, $\tilde{\nu}$/cm^{-1}: 1109, 1240, 1317, 1338, 1371, 1456, 1512, 1576, 1633, 1951 (=C=), 2868, 2927, 2972, 3045 ^{1}H NMR (CDCl$_3$), δ: 1.36 (s, 6H, 2 × CH$_3$), 1.75 (t, 3H, ^{5}J = 3.1 Hz, =C—CH$_3$), 4.74 (q, 2H, ^{5}J = 3.1 Hz, =CH$_2$), 7.45–7.65 (m, 3H, Ar), 7.81–7.94 (m, 2H, Ar), 7.95 (s, 1H, HC=N), 7.95–8.02 (m, 1H, Ar), 8.78–8.89 (m, 1H, Ar), 9.14 (s, 1H, HC—Ar) ^{13}C NMR (CDCl$_3$), δ: 15.5 (=C—$\underline{\text{C}}$H$_3$), 24.5 (2 × CH$_3$), 40.5 (C), 76.2 (=CH$_2$), 103.6 (=$\underline{\text{C}}$—CH$_3$), 124.8 (CH), 125.5 (CH), 126.3 (CH), 127.4 (CH), 128.9 (CH), 129.1 (CH), 129.8 (C), 131.6 (C), 131.7 (CH), 134.1 (C), 160.7 (HC—Ar), 170.3 (HC=N), 206.6 (=C=) MS, m/z (%): 277 (M^{+} + 1, 30), 261 (35), 245 (31), 229 (39), 149 (17), 122 (87), 108 (100), 95 (27), 79 (24), 67 (50), 55 (32), 41 (25)
IVaj	IR, $\tilde{\nu}$/cm^{-1}: 1022, 1173, 1214, 1249, 1315, 1339, 1362, 1383, 1406, 1461, 1511, 1577, 1633, 1896, 1924 (=C=), 2898, 2932, 2965, 3053 ^{1}H NMR (CDCl$_3$), δ: 0.24 (s, 9H, Si—CH$_3$), 1.48 (s, 6H, 2 × CH$_3$), 4.56 (s, 2H, =CH$_2$), 7.50–7.67 (m, 3H, Ar), 7.87–7.99 (m, 2H, Ar), 8.00–8.04 (m, 1H, Ar), 8.05 (s, 1H, HC=N), 8.89 (d, 1H, ^{3}J = 8.4 Hz, Ar), 9.20 (s, 1H, HC—Ar) ^{13}C NMR (CDCl$_3$), δ: 1.0 (Si—CH$_3$), 26.6 (2 × CH$_3$), 41.1 (C), 71.5 (=CH$_2$), 102.0 (=C—Si), 124.8 (CH), 125.5 (CH), 126.3 (CH), 127.4 (CH), 128.9 (CH), 129.1 (CH), 130.0 (C), 131.7 (CH), 134.1 (C), 160.6 (HC—Ar), 171.4 (HC=N), 209.6 (=C=)

Table 3. (continued)

Compound	Spectral data
IVak	IR, $\tilde{\nu}$/cm^{-1}: 1159, 1257, 1444, 1454, 1520, 1632, 1954 (=C=), 2867, 2929, 2970, 3051 ^{1}H NMR ($CDCl_3$), δ: 1.45 (s, 6H, 2 × CH_3), 4.94 (d, 2H, ^4J = 6.6 Hz, =CH_2), 5.45 (t, 1H, ^4J = 6.6 Hz, HC=C), 7.45–7.65 (m, 4H, Ant), 7.98–8.10 (m, 2H, Ant), 8.13 (s, 1H, HC=N), 8.53 (s, 1H, Ant), 8.64–8.75 (m, 2H, Ant), 9.72 (s, 1H, HC—Ant) ^{13}C NMR ($CDCl_3$), δ: 25.9 (2 × CH_3), 38.5 (C), 78.0 (=CH_2), 97.6 (H$\underline{\text{C}}$=C), 125.4 (2 × CH), 125.6 (2 × CH), 127.1 (2 × CH), 129.1 (2 × CH), 130.5 (CH), 130.7 (C), 131.5 (C), 160.7 (HC—Ant), 170.9 (HC=N), 207.3 (=C=) MS, m/z (%): 312 (M^+, 64), 297 (27), 203 (100), 176 (27), 108 (15), 94 (90), 79 (18), 67 (14), 53 (14), 41 (22)
IVal	IR, $\tilde{\nu}$/cm^{-1}: 1109, 1215, 1444, 1632, 1952 (=C=), 2868, 2927, 2974, 3051, 3082 ^{1}H NMR ($CDCl_3$), δ: 1.42 (s, 6H, 2 × CH_3), 1.81 (t, 3H, ^5J = 3.0 Hz, =C—$\underline{\text{C}}H_3$), 4.77 (q, 2H, ^5J = 3.0 Hz, =CH_2), 7.45–7.65 (m, 4H, Ant), 8.00–8.04 (m, 1H, Ant), 8.05 (s, 1H, HC=N), 8.05–8.08 (m, 1H, Ant), 8.55 (s, 1H, Ant), 8.64–8.71 (m, 2H, Ant), 9.71 (s, 1H, HC—Ant) ^{13}C NMR ($CDCl_3$), δ: 15.6 (=C—$\underline{\text{C}}H_3$), 24.6 (2 × CH_3), 40.6 (C), 76.2 (=CH_2), 103.6 (=$\underline{\text{C}}$—CH_3), 125.4 (2 × CH), 125.6 (2 × CH), 127.2 (2 × CH), 129.2 (2 × CH), 130.5 (CH), 130.8 (C), 131.6 (C), 160.1 (HC—Ant), 170.7 (HC=N), 206.6 (=C=) MS, m/z (%): 327 (M^+ + 1, 19), 312 (18), 203 (100), 176 (32), 108 (58), 67 (10)
IVam	IR, $\tilde{\nu}$/cm^{-1}: 1021, 1160, 1249, 1306, 1362, 1444, 1519, 1632, 1896, 1924 (=C=), 2869, 2898, 2930, 2965, 3029, 3052, 3082 ^{1}H NMR ($CDCl_3$), δ: 0.28 (s, 9H, Si—CH_3), 1.52 (s, 6H, 2 × CH_3), 4.58 (s, 2H, =CH_2), 7.49–7.54 (m, 2H, Ant), 7.55–7.61 (m, 2H, Ant), 8.04 (d, 2H, ^3J = 8.3 Hz, Ant), 8.12 (s, 1H, HC=N), 8.53 (bs, 1H, Ant), 8.65–8.69 (m, 2H, Ant), 9.71 (s, 1H, HC—Ant) ^{13}C NMR ($CDCl_3$), δ: 1.1 (Si—CH_3), 26.6 (2 × CH_3), 41.3 (C), 71.5 (=CH_2), 102.0 (=C—Si), 125.4 (2 × CH), 125.5 (2 × CH), 127.1 (2 × CH), 129.1 (2 × CH), 130.3 (CH), 130.7 (C), 131.5 (C), 160.2 (HC—Ant), 171.9 (HC=N), 209.7 (=C=)
IVan	IR, $\tilde{\nu}$/cm^{-1}: 1035, 1180, 1245, 1290, 1384, 1461, 1509, 1606, 1646, 1940 (=C=), 2836, 2935, 2969 ^{1}H NMR ($CDCl_3$), δ: 1.14 (t, 3H, ^3J = 7.6 Hz, CH_2—C$\underline{\text{H}}_3$), 1.32 (s, 6H, 2 × CH_3), 2.35 (dq, 2H, ^3J = 7.6 Hz, ^3J = 5.1 Hz, C$\underline{\text{H}}_2$—CH_3), 3.80 (s, 3H, OCH_3), 4.98 (s, 2H, =CH_2), 6.97 (d, 2H, ^3J = 8.7 Hz, Ar), 7.68 (d, 2H, ^3J = 8.7 Hz, Ar), 7.72 (s, 1H, HC=N), 7.80 (t, 1H, ^3J = 5.1 Hz, =C$\underline{\text{H}}$—CH_2) ^{13}C NMR ($CDCl_3$), δ: 10.5 (CH_2—$\underline{\text{C}}H_3$), 25.6 (2 × CH_3), 26.1 ($\underline{\text{C}}H_2$—CH_3), 39.9 (C), 55.4 (OCH_3), 77.5 (=CH_2), 109.5 (=C—Ar), 115.5 (2 × CH), 130.4 (2 × CH), 139.0 (C), 151.3 (C), 165.8 (=$\underline{\text{C}}$H—CH_2), 170.9 (HC=N), 208.8 (=C=)
IVao	IR, $\tilde{\nu}$/cm^{-1}: 1035, 1180, 1245, 1288, 1454, 1509, 1606, 1643, 1941 (=C=), 2834, 2931, 2969, 3029 ^{1}H NMR ($CDCl_3$), δ: 1.35 (s, 6H, 2 × CH_3), 3.68 (d, 2H, ^3J = 5.8 Hz, =CH—C$\underline{\text{H}}_2$), 3.79 (s, 3H, OCH_3), 4.99 (s, 2H, =CH_2), 7.07 (d, 2H, ^3J = 8.1 Hz, Ar), 7.33–7.45 (m, 5H, Ph), 7.62 (d, 2H, ^3J = 8.1 Hz, Ar), 7.75 (s, 1H, HC=N), 7.84 (t, 1H, ^3J = 5.8 Hz, =C$\underline{\text{H}}$—CH_2) ^{13}C NMR ($CDCl_3$), δ: 24.3 (CH_2), 25.2 (2 × CH_3), 39.5 (C), 55.4 (OCH_3), 77.6 (=CH_2), 109.5 (=C—Ar), 114.9 (CH), 127.5 (C), 128.5 (CH), 128.9 (CH), 129.1 (CH), 129.5 (CH), 131.3 (C), 152.2 (C), 162.4 (=$\underline{\text{C}}$H—CH_2), 170.8 (HC=N), 209.2 (=C=)
IVap	IR, $\tilde{\nu}$/cm^{-1}: 1032, 1210, 1388, 1466, 1512, 1649, 1942 (=C=), 2878, 2922, 2966 ^{1}H NMR ($CDCl_3$), δ: 1.15 (t, 3H, ^3J = 7.2 Hz, CH_2—C$\underline{\text{H}}_3$), 1.35 (s, 6H, 2 × CH_3), 2.30 (dq, 2H, ^3J = 7.2 Hz, ^3J = 5.2 Hz, C$\underline{\text{H}}_2$—CH_3), 2.40 (s, 3H, Ph—CH_3), 5.01 (s, 2H, =CH_2), 7.20 (d, 2H, ^3J = 8.0 Hz, Ar), 7.67 (d, 2H, ^3J = 8.0 Hz, Ar), 7.70 (s, 1H, HC=N), 7.76 (t, 1H, ^3J = 5.1 Hz, =C$\underline{\text{H}}$—CH_2) ^{13}C NMR ($CDCl_3$), δ: 10.4 (CH_2—$\underline{\text{C}}H_3$), 22.0 (Ph—CH_3), 25.3 (2 × CH_3), 25.9 ($\underline{\text{C}}H_2$—CH_3), 39.5 (C), 77.4 (=CH_2), 111.8 (=C—Ar), 128.5 (2 × CH), 129.4 (2 × CH), 131.0 (C), 137.3 (C), 165.2 (=$\underline{\text{C}}$H—CH_2), 169.9 (HC=N), 207.8 (=C=)
IVaq	IR, $\tilde{\nu}$/cm^{-1}: 1014, 1106, 1346, 1382, 1465, 1600, 1940 (=C=), 2873, 2933, 2967 ^{1}H NMR ($CDCl_3$), δ: 1.20 (t, 3H, ^3J = 7.1 Hz, CH_2—C$\underline{\text{H}}_3$), 1.38 (s, 6H, 2 × CH_3), 1.60–1.68 (m, 2H, CH_2), 1.76–1.83 (m, 2H, CH_2), 2.34 (s, 3H, Ph—CH_3), 5.00 (s, 2H, =CH_2), 7.24 (d, 2H, ^3J = 8.2 Hz, Ar), 7.63 (s, 1H, HC=N), 7.65 (d, 2H, ^3J = 8.2 Hz, Ar), 7.81 (t, 1H, ^3J = 5.3 Hz, =C$\underline{\text{H}}$—CH_2) ^{13}C NMR ($CDCl_3$), δ: 13.9 (CH_2—$\underline{\text{C}}H_3$), 19.8 ($\underline{\text{C}}H_2$—CH_3), 21.7 (Ph—CH_3), 23.0 (CH_2), 25.4 (2 × CH_3), 40.0 (C), 77.4 (=CH_2), 110.5 (=C—Ar), 128.3 (2 × CH), 129.5 (2 × CH), 131.0 (C), 137.4 (C), 165.7 (=$\underline{\text{C}}$H—CH_2), 169.9 (HC=N), 207.4 (=C=)
IVar	IR, $\tilde{\nu}$/cm^{-1}: 1021, 1110, 1383, 1464, 1510, 1644, 1940 (=C=), 2870, 2928, 2967 ^{1}H NMR ($CDCl_3$), δ: 1.09 (d, 6H, ^3J = 7.0 Hz, 2 × CH_3), 1.35 (s, 6H, 2 × CH_3), 2.35 (s, 3H, Ph—CH_3), 2.38–2.52 (m, 1H, CH), 4.99 (s, 2H, =CH_2), 7.22 (d, 2H, ^3J = 8.1 Hz, Ar), 7.60 (d, 2H, ^3J = 8.1 Hz, Ar), 7.64 (s, 1H, HC=N), 7.70 (d, 1H, ^3J = 5.7 Hz, =C$\underline{\text{H}}$—CH) ^{13}C NMR ($CDCl_3$), δ: 19.8 (2 × CH_3), 25.6 (2 × CH_3), 30.1 (CH), 40.9 (C), 77.4 (=CH_2), 110.7 (=C—Ar), 128.3 (2 × CH), 129.7 (2 × CH), 130.8 (C), 136.7 (C), 165.8 (=$\underline{\text{C}}$H—CH), 169.0 (HC=N), 207.1 (=C=)

Table 3. (continued)

Compound	Spectral data
IVas	IR, $\tilde{\nu}$/cm^{-1}: 1023, 1119, 1384, 1460, 1517, 1621, 1942 (=C=), 2872, 2936, 2969 ^{1}H NMR (CDCl$_3$), δ: 1.34 (s, 6H, 2 × CH$_3$), 2.31 (s, 3H, Ph—CH$_3$), 3.66 (d, 2H, ^3J = 5.9 Hz, =CH—C$\underline{\text{H}}_2$), 4.96 (s, 2H, =CH$_2$), 7.21 (d, 2H, ^3J = 8.4 Hz, Ar), 7.30–7.42 (m, 5H, Ph), 7.58 (d, 2H, ^3J = 8.4 Hz, Ar), 7.61 (s, 1H, HC=N), 7.88 (t, 1H, ^3J = 5.9 Hz, =C$\underline{\text{H}}$—CH$_2$) ^{13}C NMR (CDCl$_3$), δ: 24.0 (CH$_2$), 25.6 (2 × CH$_3$), 39.3 (C), 77.9 (=CH$_2$), 110.1 (=C—Ar), 127.5 (C), 128.5 (CH), 128.7 (CH), 128.9 (CH), 129.1 (CH), 129.5 (CH), 131.3 (C), 137.7 (C), 162.4 (=$\underline{\text{C}}$H—CH$_2$), 170.1 (HC=N), 207.9 (=C=)
IVat	IR, $\tilde{\nu}$/cm^{-1}: 1047, 1126, 1383, 1492, 1597, 1646, 1941 (=C=), 2880, 2934, 2974 ^{1}H NMR (CDCl$_3$), δ: 1.35 (s, 6H, 2 × CH$_3$), 1.52 (t, 3H, ^3J = 7.5 Hz, CH$_2$—C$\underline{\text{H}}_3$), 2.36 (dq, 2H, ^3J = 7.5 Hz, ^3J = 5.1 Hz, C$\underline{\text{H}}_2$—CH$_3$), 4.99 (s, 2H, =CH$_2$), 7.25–7.30 (m, 2H, Ph), 7.79–7.83 (m, 3H, Ph), 7.84 (t, 1H, ^3J = 5.1 Hz, =C$\underline{\text{H}}$—CH$_2$), 7.87 (s, 1H, HC=N) ^{13}C NMR (CDCl$_3$), δ: 10.4 (CH$_2$—$\underline{\text{C}}$H$_3$), 25.3 (2 × CH$_3$), 25.9 ($\underline{\text{C}}$H$_2$—CH$_3$), 40.1 (C), 77.4 (=CH$_2$), 116.8 (=C—Ph), 127.7 (2 × CH), 127.8 (CH), 128.5 (2 × CH), 137.0 (C), 165.2 (=$\underline{\text{C}}$H—CH$_2$), 168.9 (HC=N), 207.9 (=C=)
IVau	IR, $\tilde{\nu}$/cm^{-1}: 1016, 1109, 1344, 1382, 1465, 1601, 1943 (=C=), 2877, 2939, 2964 ^{1}H NMR (CDCl$_3$), δ: 1.29 (t, 3H, ^3J = 7.1 Hz, CH$_2$—C$\underline{\text{H}}_3$), 1.36 (s, 6H, 2 × CH$_3$), 1.59–1.65 (m, 2H, CH$_2$), 1.68–1.71 (m, 2H, CH$_2$), 4.96 (s, 2H, =CH$_2$), 7.38 (t, 1H, ^3J = 5.0 Hz, =C$\underline{\text{H}}$—CH$_2$), 7.51–7.59 (m, 2H, Ph), 7.75–7.80 (m, 3H, Ph), 7.81 (s, 1H, HC=N) ^{13}C NMR (CDCl$_3$), δ: 13.9 (CH$_2$—$\underline{\text{C}}$H$_3$), 19.8 ($\underline{\text{C}}$H$_2$—CH$_3$), 23.0 (CH$_2$), 25.2 (2 × CH$_3$), 39.6 (C), 77.3 (=CH$_2$), 111.8 (=C—Ph), 127.3 (CH), 128.5 (2 × CH), 128.8 (2 × CH), 137.3 (C), 164.5 (=$\underline{\text{C}}$H—CH$_2$), 169.3 (HC=N), 207.8 (=C=)
IVav	IR, $\tilde{\nu}$/cm^{-1}: 1029, 1087, 1141, 1398, 1456, 1558, 1600, 1650, 1945 (=C=), 2925, 2971 ^{1}H NMR (CDCl$_3$), δ: 1.11 (d, 6H, ^3J = 7.0 Hz, 2 × CH$_3$), 1.38 (s, 6H, 2 × CH$_3$), 2.40–2.55 (m, 1H, CH), 5.02 (s, 2H, =CH$_2$), 7.43–7.49 (m, 2H, Ph), 7.52 (d, 1H, ^3J = 6.7 Hz, =C$\underline{\text{H}}$—CH), 7.69–7.74 (m, 3H, Ph), 7.85 (s, 1H, HC=N) ^{13}C NMR (CDCl$_3$), δ: 19.8 (2 × CH$_3$), 25.7 (2 × CH$_3$), 29.9 (CH), 40.3 (C), 77.8 (=CH$_2$), 111.7 (=C—Ph), 127.0 (CH), 128.2 (2 × CH), 128.8 (2 × CH), 136.5 (C), 165.8 (=$\underline{\text{C}}$H—CH), 169.0 (HC=N), 207.1 (=C=)
IVaw	IR, $\tilde{\nu}$/cm^{-1}: 1051, 1101, 1384, 1463, 1517, 1592, 1644, 1934 (=C=), 2871, 2921, 2960 ^{1}H NMR (CDCl$_3$), δ: 1.16 (d, 6H, ^3J = 7.1 Hz, 2 × CH$_3$), 1.40 (s, 6H, 2 × CH$_3$), 2.55–2.66 (m, 1H, =CH—C$\underline{\text{H}}$), 5.18 (s, 2H, =CH$_2$), 7.41 (d, 2H, ^3J = 8.8 Hz, Ar), 7.70 (s, 1H, HC=N), 7.84 (t, 1H, ^3J = 5.3 Hz, =C$\underline{\text{H}}$—CH), 8.14 (d, 2H, ^3J = 8.8 Hz, Ar) ^{13}C NMR (CDCl$_3$), δ: 19.8 (2 × CH$_3$), 26.7 (2 × CH$_3$), 29.3 (CH), 42.9 (C), 79.8 (=CH$_2$), 108.0 (=C—Ar), 123.2 (CH), 128.8 (CH), 141.0 (C), 146.8 (C), 163.6 (=$\underline{\text{C}}$H—CH), 170.9 (HC=N), 209.9 (=C=)
IVax	IR, $\tilde{\nu}$/cm^{-1}: 1027, 1113, 1347, 1382, 1467, 1511, 1620, 1932 (=C=), 2873, 2937, 2968 ^{1}H NMR (CDCl$_3$), δ: 1.37 (s, 6H, 2 × CH$_3$), 3.68 (d, 2H, ^3J = 5.5 Hz, =CH—C$\underline{\text{H}}_2$), 5.21 (s, 2H, =CH$_2$), 7.31–7.38 (m, 5H, Ph), 7.39 (d, 2H, ^3J = 8.9 Hz, Ar), 7.79 (s, 1H, HC=N), 7.84 (t, 1H, ^3J = 5.5 Hz, =C$\underline{\text{H}}$—CH$_2$), 8.10 (d, 2H, ^3J = 8.9 Hz, Ar) ^{13}C NMR (CDCl$_3$), δ: 24.6 (CH$_2$), 27.2 (2 × CH$_3$), 42.5 (C), 80.1 (=CH$_2$), 107.5 (=C—Ar), 123.8 (CH), 127.9 (CH), 128.5 (CH), 129.3 (CH), 130.1 (CH), 141.3 (C), 146.9 (C), 162.9 (=$\underline{\text{C}}$H—CH$_2$), 171.3 (HC=N), 210.2 (=C=)

Ad – 1-Adamantyl; Ant – 9-anthryl; Ph – phenyl.

The procedure for the preparation of other azines *IVc*–*IVax* differed only in the amounts of reactants used. The reaction mixture contained 10.5 mmol of protected hydrazone *II* and 10 mmol of allenyl aldehyde. The desired azines were purified by filtering the crude product in petroleum ether through a short column of neutral alumina or by liquid chromatography (DCM).

Results and discussion

The investigation and preparation of non-symmetrical allenyl azines *IV* represents a major part of the work undertaken in our laboratory. The starting compounds *II* and *III* for their preparation were published in Part 1 (Galeta et al., 2013). Their preparation follows Zwierzak's procedure, in which protected hydrazine *I* reacts with carbonyl compounds forming protected hydrazones *II* or *III*. Their reaction in the presence of a strong base with a second aldehyde afforded the expected azines *IV*. Two reaction pathways (A and B) could be utilised (Fig. 1). The second pathway (B) served for derivatives with a hydrogen atom (R = H) because it was not possible to prepare hydrazone *II* after reaction with formaldehyde. Thus, we collected very differently substituted azines *IV* in high yields using a relatively easy and rapid procedure (Table 1).

For structural studies, we were able to prepare a crystal suitable for X-ray analysis. It clearly shows that the stereochemical arrangement in a heterodiene system is *trans* – *s-trans* – *trans* and that the allenyl group lies approximately in the extended plane defined by the heterodiene and *p*-nitrophenyl ring but is oriented in the opposite direction (Fig. 2).

Since thermal stress can initiate slow decomposition of compounds *IV*, elemental analyses of just five representatives were carried out (Table 2). It is

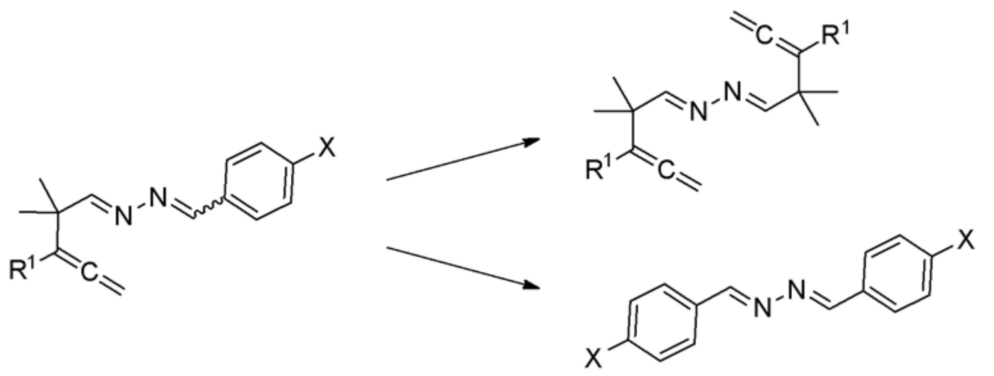

Fig. 3. Decomposition of aromatic aldazines.

worth noting here that aliphatic aldazines are some of the most stable derivatives. The stability of aromatic derivatives decreases with their increasing aromaticity. It was observed that decomposition mainly produced their symmetrical counterparts (Fig. 3) consisting of the same aldehyde segments bound to nitrogen atoms of the azine moiety. For this reason, handling them at ambient temperature was limited to the shortest time necessary. Spectral data of all newly prepared compounds are summarized in Table 3.

Conclusions

Detailed investigation of scope of preparation of non-symmetrical allenyl azines afforded 50 new derivatives, which can serve as very potent systems for subsequent cycloaddition reaction steps. Two possible pathways for their preparation and, alternatively, the degradation products of aromatic aldazines were discussed. The crystal structure of one product was also obtained and discussed.

Acknowledgements. The authors are grateful to Marek Nečas for crystallographic measurements. The research was supported by the Grant Agency of the Czech Republic, project No. 203/09/1345.

Supplementary data

Crystallographic data on the structure of azine *IVag* have been deposited in the Cambridge Crystallographic Data Centre, CCDC No. 871315. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Tel: +44 (0)1223 762911; e-mail: kamila@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

References

Brandsma, L. (2001). Unsaturated carbanions, heterocumulenes and thiocarbonyl compounds – new routes to heterocycles. *European Journal of Organic Chemistry*, *2001*, 4569–4581. DOI: 10.1002/1099-0690(200112)2001:24<4569::aid-ejoc 4569>3.0.CO;2-w.

Brandsma, L. (2004). *Synthesis of acetylenes, allenes and cumulenes: Methods and techniques*. Oxford, UK: Elsevier.

Brandsma, L., & Nedolya, N. A. (2004). Allenic compounds and isothiocyanates as key building units in the synthesis of heterocycles. *Synthesis*, *2004*, 735–745. DOI: 10.1055/s-2004-816005.

Brasholz, M., Reissig, H. U., & Zimmer, R. (2009). Sugars, alkaloids, and heteroaromatics: exploring heterocyclic chemistry with alkoxyallenes. *Accounts of Chemical Research*, *42*, 45–56. DOI: 10.1021/ar800011h.

Bruker AXS (1997). SHELXTL, Version 5.10. An integrated system for solving and refining crystal structures from diffraction data. Madison, WI, USA: Bruker AXS.

Galeta, J., Man, S., & Potáček, M. (2009). Non-symmetrical allenyl azines and their transformations leading to new heterocyclic skeletons. *ARKIVOC*, *2009*, *6*, 245–259.

Galeta, J., Man, S., Bouillon, J. P., & Potáček, M. (2011). Unexpected heterocyclic products from cycloaddition reactions of nonsymmetrical allenyl aldoketazines with substituted alkynes. *European Journal of Organic Chemistry*, *2011*, 392–398. DOI: 10.1002/ejoc.201001044.

Galeta, J., & Potáček, M. (2012). Substituted diazatetracyclo $[4.4.0.1^{3,10}.1^{5,8}]$dodecanes as stable caged proton sponges. *The Journal of Organic Chemistry*, *77*, 1010–1017. DOI: 10.1021/jo202235f.

Galeta, J., Man, S., & Potáček, M. (2013). Substituted homoallenyl aldehydes and their derivatives. Part 1: Homoallenyl aldehydes and protected hydrazones. *Chemical Papers*, *67*, 29–39. DOI: 10.2478/s11696-012-0215-6.

Koziara, A., Turski, K., & Zwierzak, A. (1986). A general synthesis of unsymmetrical azines via *N*-(diethoxyphosphinyl)-hydrazones. *Synthesis*, *1986*, 298–301. DOI: 10.1055/s-1986-31589.

Krause, N., & Hashmi, A. S. K. (2004). *Modern allene chemistry*. Weinheim, Germany: Wiley–VCH.

Man, S., Kulhánek, P., Potáček, M., & Nečas, M. (2002). New fused heterocycles by combined intra-intermolecular criss-cross cycloaddition of nonsymmetrical azines. *Tetrahedron Letters*, *43*, 6431–6433. DOI: 10.1016/s0040-4039(02)01378-3.

Man, S., Bouillon, J. P., Nečas, M., & Potáček, M. (2004). Combined intra-intermolecular criss-cross cycloaddition of a new fluorinated unsymmetrical allenylazine with alkynes. *Tetrahedron Letters*, *45*, 9419–9421. DOI: 10.1016/j.tetlet.2004.10.107.

Man, S., Nečas, M., Bouillon, J. P., Baillia, H., Harakat, D., & Potáček, M. (2005). New intra-intermolecular criss-cross cycloaddition of unsymmetrical allenylazines with alkynes leading to three fused five-membered heterocycles. *Tetrahedron*, *61*, 2387–2393. DOI: 10.1016/j.tet.2005.01.020.

Schweizer, E. E., & Lee, K. J. (1984). Reactions of azines. 8. Synthesis and thermal rearrangement of 1-oxo-3,4-diaza-2,4,6-heptatrienes and 1-oxo-3,4-diaza-2,4,6,7-octatetraenes (allenyl azines). *The Journal of Organic Chemistry*, *49*, 1959–1964. DOI: 10.1021/jo00185a025.

Schweizer, E. E., Hayes, J. E., Hirwe, S. N., & Rheingold, A. L. (1987). Reactions of azines. 9. Preparation of 4,5-dihydropyrazolo[1,5-a]pyridines, 6,7-dihydropyrazolo[1,5-a]pyridines, and pyrazolo[1,5-a]pyridines. *The Journal of Organic Chemistry*, *52*, 1319–1324. DOI: 10.1021/jo00383a028.

Zachová, H., Man, S., Nečas, M., & Potáček, M. (2005). Fused tetracyclic heterocycles by thermally initiated intramolecular criss-cross cycloaddition of 3-substituted homoallenylaldazines. *European Journal of Organic Chemistry*, *2005*, 2548–2557. DOI: 10.1002/ejoc.200400814.

Zachová, H., Marek, R., Man, S., Taraba, J., & Potáček, M. (2006). A new rearrangement of fused tetracyclic heterocycles in an acidic medium in the presence of $NaBH_3CN$. *Tetrahedron Letters*, *47*, 8157–8159. DOI: 10.1016/j.tetlet.2006.09.030.

Zachová, H., Man, S., Taraba, J., & Potáček, M. (2009). Rearrangement of fused tetracyclic heterocycles induced by alkyl halides and formation of a new type of 'proton sponge'. *Tetrahedron*, *65*, 792–797. DOI: 10.1016/j.tet.2008.11.057.

Zimmer, R. (1993). Alkoxyallenes – building blocks in organic synthesis. *Synthesis*, *1993*, 165–178. DOI: 10.1055/s-1993-25823.

Zwierzak, A., & Sulewska, A. (1976). Solid-liquid phase-transfer-catalysed phosphorylation of hydrazine. Preparation of dialkyl phosphorohydrazidates and N,N'-bis[dialkoxyphosphoryl]hydrazines. *Synthesis*, *1976*, 835–837. DOI: 10.1055/s-1976-25385.