Supporting Information

Quantifying the enamine-type nucleophilic reactivity of α-aryl vinyl azides

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Data storage system:

Folder and file names CGxxx and PTxxx refer to individual experiments and are identical to those in this Supporting Information.

Folder "products":

Electronic files of NMR, IR, and HRMS data of vinyl azides **1a**-**1i** (Section 2) and of amides **3a**-**3c** (Section 3) are collected in the folder "products".

Folder "kinetics":

Electronic files of kinetic studies of the reactions of vinyl azides **1** with benzhydrylium ions **2** (Section 4) are collected in the folder "kinetics".

The folders in "kinetics" contain

- txt files with absorbance vs. time data [raw data]
- exp files used for the k_{obs} determination [evaluated data]
- pdf files with results of the k_{obs} determination [evaluated data].

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1. General

Commercial reagents and dry solvents (stored over molecular sieves) were used without further purification as purchased from Sigma-Aldrich or Acros Organics. Dichloromethane was dried over CaH_2, diethyl ether was dried over sodium and distilled. For thin-layer chromatography, silica gel plates with F-254 fluorescence indicator (Merck) were used. Purification by flash column chromatography was performed using Merck silica gel 60 (0.040–0.063 mm) with freshly distilled solvents.

Melting points were acquired using Büchi Melting Point B-560 devices and are not corrected.

Nuclear magnetic resonance (NMR) spectra were recorded on 400 and 600 MHz spectrometers. Residual solvent signals were used as internal reference (δ_H 7.26 ppm, δ_C 77.16 ppm for $CDCl_3$; δ_H 5.32 ppm, δ_C 53.84 ppm for CD_2Cl_2).[S1] NMR signals were assigned based on information from additional 2D NMR experiments (COSY, gHSQC, gHMBC).

Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum BX-59343 instrument with a Smiths Detection DuraSamplIR II Diamond ATR sensor or a Bruker Tensor 27 FT-IR instrument with a "Platinum" Diamond ATR sensor for detection in the range 4500–600 cm^{-1} as a film for liquids or neat for solids.

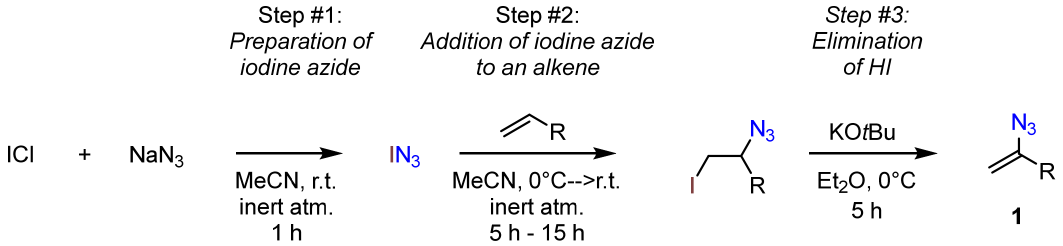
High resolution (HRMS) mass spectra were recorded on a Thermo Exploris 120, a Thermo Finnigan LTQ FT Ultra, or a Thermo Finnigan LTQ Orbitrap XL instrument. For ionization of the samples, electrospray ionization (ESI) was applied.

(S1) G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179.

2. Synthesis of Vinyl Azides **1a-1i**

General Procedure (*GP*):

Vinyl azides **1** were synthesized in a one-pot three-step procedure in analogy to the procedure reported in ref.[S2]

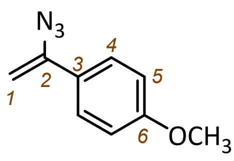


Step #1: Iodine monochloride (1.1 equiv.) was added to a flame-dried Schlenk flask and dissolved in MeCN (8 mL) under nitrogen atmosphere. Sodium azide (2.0 equiv.) was added to the orange-brown acetonitrile solution under room temperature, and the resulting suspension was stirred for 1 h at room temperature.

Step #2: To the reaction mixture from Step #1, a solution of the alkene (1.0 equiv., dissolved in 8 mL CH_2Cl_2) was added slowly at 0°C. Then, the mixture was allowed to warm up to room temperature while it was stirred overnight. The reaction mixture was quenched with aq. sat. $Na_2S_2O_3$ solution, and the organic materials were extracted three times with diethyl ether (3 × 20 mL). The combined organic phases were washed with brine and dried over $MgSO_4$. After evaporation of volatiles, the resulting crude materials were used immediately and without further purification for Step #3.

Step #3: The crude material from Step #2 was dissolved in diethyl ether (16 mL) under argon atmosphere. Then, KO*t*Bu was added in portions at 0°C. The suspension was stirred for 5 h at 0 °C (ice cooling). Subsequently, the reaction mixture was filtered through Celite, and the solvent was removed under reduced pressure. The resulting crude product was purified by flash column chromatography (silica gel, *n*-pentane or *n*-pentane/EtOAc mixtures) to give the vinyl azides **1**.

1-(1-Azidovinyl)-4-methoxybenzene (1a) was synthesized according to *GP* from iodine monochloride (0.23 mL, 0.72 g, 4.4 mmol), sodium azide (0.52 g, 8.0 mmol), 1-methoxy-4-vinylbenzene (0.54 g, 4.0 mmol), and KO*t*Bu (0.70 g, 6.2 mmol). The crude product was purified by flash column chromatography (silica gel, *n*-pentane:EtOAc 98:2) and recrystallized (*n*-pentane, −24°C) to give **1a** (0.280 g, 40%) as a light-yellow solid.



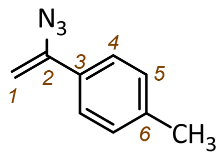
1a (CG715_2F1)

(S2) Y.-F. Wang, M. Hu, H. Hayashi, B. Xing, S. Chiba, *Org. Lett.*, 2016, **18**, 992-995.

NMR spectroscopic data agree with those reported in ref. S3.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.50 (d, *J* = 8.9 Hz, 2 H, 4-H), 6.88 (d, *J* = 9.0 Hz, 2 H, 5-H), 5.32 (d, *J* = 2.3 Hz, 1 H, 1-H^b), 4.86 (d, *J* = 2.3 Hz, 1 H, 1-H^a), 3.82 ppm (s, 3 H, 6-OCH_3).

1-(1-Azidovinyl)-4-methylbenzene (1b) was synthesized according to *GP* from iodine monochloride (1.14 g, 7.0 mmol), sodium azide (0.82 g, 13 mmol), 1-methyl-4-vinylbenzene (0.59 g, 5.0 mmol), and KO*t*Bu (0.67 g, 6.0 mmol). The crude product was purified by flash column chromatography (silica gel, *n*-pentane/EtOAc = 98:2) to afford **1b** (0.36 g, 45%) as a light-yellow solid.



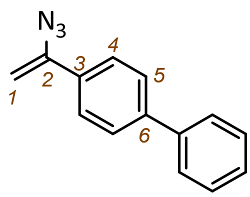
1b (PT176/PT211)

The NMR spectroscopic data agree with those reported in ref. S4.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.46 (d, *J* = 8.3 Hz, 2 H, 4-H), 7.17 (d, *J* = 7.9 Hz, 2 H, 5-H), 5.39 (d, *J* = 2.3 Hz, 1 H, 1-H^b), 4.91 (d, *J* = 2.3 Hz, 1 H, 1-H^a), 2.37 ppm (s, 3 H, 6-CH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): *δ* 145.1, 139.3, 131.6, 129.3, 125.6, 97.3, 21.4 ppm.

4-(1-Azidovinyl)-1,1'-biphenyl (1c) was synthesized according to *GP* from iodine monochloride (0.45 g, 2.8 mmol), sodium azide (0.41 g, 6.3 mmol), 4-vinyl-1,1'-biphenyl (0.45 g, 2.5 mmol), and KO*t*Bu (0.42 g, 3.7 mmol). The crude product was purified by flash column chromatography (silica gel, *n*-pentane) to afford **1c** (0.30 g, 54%) as a light-yellow solid.



1c (PT293)

The NMR spectroscopic data agree with those reported in ref. S4.

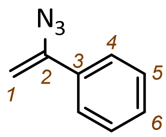
^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.66–7.62 (m, 2 H), 7.62–7.57 (m, 4 H), 7.47–7.42 (m, 2 H), 7.39–7.34 (m, 1 H), 5.49 (d, *J* = 2.5 Hz, 1 H, 1-H^b), 4.99 (d, *J* = 2.5 Hz, 1 H, 1-H^a) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): *δ* 144.8, 142.0, 140.5, 133.3, 129.0, 127.8, 127.3, 127.2, 126.1, 98.0 ppm.

(S3) P. Gu, Y. Su, X.-P. Wu, J. Sun, W. Liu, P. Xue, R. Li, *Org. Lett.*, 2012, **14**, 2246-2249.

(S4) Z. Liu, P. Liao, X. Bi, *Org. Lett.*, 2014, **16**, 3668-3671.

(1-Azidovinyl)benzene (1d) was synthesized according to *GP* from iodine monochloride (0.23 mL, 0.72 g, 4.4 mmol), sodium azide (0.52 g, 8.0 mmol), styrene (0.42 g, 4.0 mmol), and KO*t*Bu (0.70 g, 6.2 mmol). The crude product was purified by flash column chromatography (silica gel, *n*-pentane) to give **1d** (0.32 g, 55%) as a light-yellow oil.

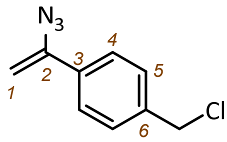


1d (CG677_1)

NMR spectroscopic data agree with those reported in ref. S4.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58–7.54 (m, 2 H, 4-H), 7.39–7.35 (m, 3 H, 5-H and 6-H), 5.44 (d, J = 2.3 Hz, 1 H, 1-H^a), 4.96 ppm (d, J = 2.4 Hz, 1 H, 1-H^b).

1-(1-Azidovinyl)-4-(chloromethyl)benzene (1e) was synthesized according to *GP* from iodine monochloride (1.85 g, 11.4 mmol), sodium azide (1.62 g, 25 mmol), 1-(chloromethyl)-4-vinylbenzene (1.38 g, 9.0 mmol), and KO*t*Bu (1.35 g, 12 mmol). The crude product was purified by flash column chromatography (silica gel, *n*-pentane/EtOAc = 98:2) to afford **1e** (0.98 g, 56%) as a brown liquid.

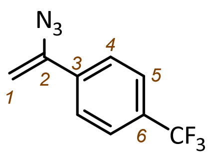


1e (PT237)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8.4 Hz, 2 H, 4-H), 7.38 (d, J = 8.5 Hz, 2 H, 5-H), 5.46 (d, J = 2.5 Hz, 1 H, 1-H^b), 4.98 (d, J = 2.6 Hz, 1 H, 1-H^a), 4.59 ppm (s, 2 H, 6-CH_2Cl).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 144.6, 138.4, 134.5, 128.8, 126.0, 98.5, 45.8 ppm.

1-(1-Azidovinyl)-4-(trifluoromethyl)benzene (1f) was synthesized according to *GP* from iodine monochloride (0.59 g, 3.6 mmol), sodium azide (0.49 g, 7.5 mmol), 1-(trifluoromethyl)-4-vinylbenzene (0.52 g, 3.0 mmol), and KO*t*Bu (0.50 g, 4.5 mmol). The crude product was purified by flash column chromatography (silica gel, *n*-pentane) to give **1f** (0.35 g, 55%) as a light brown liquid.



1f (PT280)

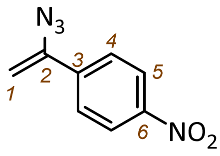
NMR spectroscopic data agree with those reported in ref. S5.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 8.3 Hz, 2 H, 4-H), 7.61 (d, J = 8.4 Hz, 2 H, 5-H), 5.55 (d, J = 2.8 Hz, 1 H, 1-H^b), 5.07 (d, J = 2.8 Hz, 1 H, 1-H^a) ppm.

(S5) N. S. Y. Loy, S. Kim, C.-M. Park, *Org. Lett.*, 2015, **17**, 395-397.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 144.1, 137.7 (br), 131.1 (q, $^2J_{C,F}$ = 32.6 Hz), 126.0, 125.6 (q, $^3J_{C,F}$ = 3.9 Hz), 124.1 (q, $^1J_{C,F}$ = 272.2 Hz), 99.7 ppm.

1-(1-Azidovinyl)-4-nitrobenzene (1g) was synthesized according to *GP* from iodine monochloride (0.92 g, 5.7 mmol), sodium azide (0.81 g, 13 mmol), 1-nitro-4-vinylbenzene (0.74 g, 5.0 mmol), and KO*t*Bu (0.67 g, 6.0 mmol). The crude product was purified by flash column chromatography (silica gel, *n*-pentane) and recrystallized (*n*-pentane/Et_2O mixture, −24°C) to give **1g** (0.44 g, 46%) as a light yellow solid.



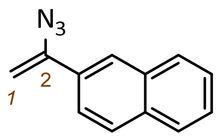
1g (PT212)

The NMR spectroscopic data agree with those reported in ref. S4.

^1H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 8.9 Hz, 2 H, 4-H), 7.74 (d, J = 8.9 Hz, 2 H, 5-H), 5.64 (d, J = 3.0 Hz, 1 H, 1-H^b), 5.16 ppm (d, J = 3.0 Hz, 1 H, 1-H^a).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 148.2, 143.5, 140.3, 126.5, 123.9, 101.2 ppm.

2-(1-Azidovinyl)naphthalene (1h) was synthesized according to *GP* from iodine monochloride (2.27 g, 14 mmol), sodium azide (1.62 g, 25 mmol), 2-vinylnaphthalene (1.54 g, 10 mmol), and KO*t*Bu (1.35 g, 12 mmol). The crude product was purified by flash column chromatography (silica gel, *n*-pentane) to give **1h** (1.09 g, 56%) as a light yellow solid.



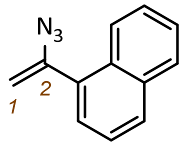
1h (PT206/23112025-pratch-2-Naphth)

NMR spectroscopic data agree with those reported in ref. S3.

^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 1.9 Hz, 1 H), 7.88–7.81 (m, 3 H), 7.67 (dd, J = 8.7 Hz, 1.9 Hz, 1 H), 7.53–7.48 (m, 2 H), 5.60 (d, J = 2.6 Hz, 1 H), 5.07 ppm (d, J = 2.5 Hz, 1 H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 145.1, 133.6, 133.2, 131.6, 128.7, 128.3, 127.7, 126.8, 126.6, 125.1, 123.2, 98.4 ppm.

1-(1-Azidovinyl)naphthalene (1i) was synthesized according to *GP* from iodine monochloride (0.19 mL, 0.58 g, 3.6 mmol), sodium azide (0.42 g, 6.5 mmol), 1-vinylnaphthalene (0.50 g, 3.2 mmol), and KO*t*Bu (0.56 g, 5.0 mmol). The crude product was purified by flash column chromatography (silica gel, *n*-pentane) to give **1i** (0.210 g, 34%) as a light-yellow oil.



1i (CG743)

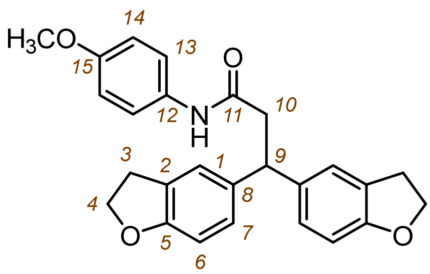
NMR spectroscopic data agree with those reported in refs. S4, S6.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 8.2 Hz, 1 H), 7.90–7.88 (m, 2 H), 7.59–7.46 (m, 4 H), 5.25 (d, J = 1.1 Hz, 1 H, 1-H^a), 4.94 ppm (d, J = 1.0 Hz, 1 H, 1-H^b).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 144.6, 133.7, 133.1, 130.9, 129.8, 128.6, 127.1, 127.0, 126.4, 125.3, 125.1, 104.1 ppm.

3. Amides 3a-3c from Reactions of Benzhydrylium Ions (2) with Vinyl Azides (1)

3,3-Bis(2,3-dihydrobenzofuran-5-yl)-N-(4-methoxyphenyl)propanamide (3a) was prepared by mixing a solution of **2c** [preformed at −20°C in 8 mL CH_2Cl_2 from Ar_2CH-OH (30.0 mg, 0.11 mmol) by addition of $HBF_4{\cdot}Et_2O$ (16.7 µl, 0.12 mmol)] with the vinyl azide **1a** (21.5 mg, 0.12 mmol, dissolved in 2 mL CH_2Cl_2) under nitrogen atmosphere at −20°C. After 30 min the reaction was quenched by addition of aqueous hydrochloric acid. The reaction mixture was extracted with dichloromethane (3 × 10 mL), and the combined organic phases were washed with brine (10 mL) and dried (over $MgSO_4$). Then, volatiles were removed under reduced pressure. The crude product was purified by column chromatography (basic Al_2O_3, eluent: *n*-pentane:EtOAc:NEt_3 50:49:1) to give **3a** as a colorless oil (26.0 mg, 57%).



3a (CG718F1)

R_f (*n*-pentane/EtOAc/NEt_3 50:49:1, basic Al_2O_3, UV) = 0.6

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.18 (d, J = 9.1 Hz, 2 H, 13-H), 7.06 (s, 2 H, 1-H), 7.01 (s, 1 H, NH), 7.00 (d, J = 8.2 Hz, 2 H, 7-H), 6.78 (d, J = 8.9 Hz, 2 H, 14-H), 6.70 (d, J = 8.2 Hz, 2 H, 6-H), 4.52 (t, J = 8.7 Hz, 4 H, 4-H), 4.48 (t, J = 7.8 Hz, 1 H, 9-H), 3.75 (s, 3 H, 15-OCH_3), 3.12 (t, J = 8.7 Hz, 4 H, 3-H), 2.96 ppm (d, J = 7.8 Hz, 2 H, 10-H).

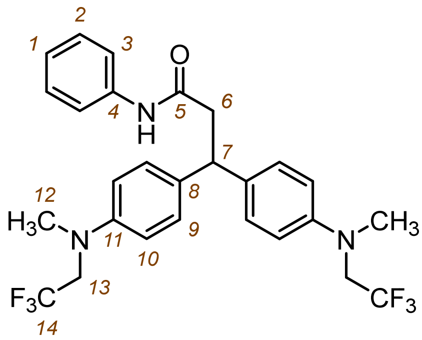
(S6) Y.-F. Wang, K. K. Toh, J.-Y. Lee, S. Chiba, *Angew. Chem. Int. Ed.*, 2011, **50**, 5927-5931.

$^{13}C\{^1H\}$ **NMR** (151 MHz, $CDCl_3$): δ 169.8 (C_q, C-11), 158.8 (C_q, C-5), 156.5 (C_q, C-15), 136.3 (C_q, C-8), 130.8 (C_q, C-12), 127.6 (C_q, C-2), 127.0 (CH, C-7), 124.5 (CH, C-1), 122.1 (CH, C-13), 114.1 (CH, C-14), 109.3 (CH, C-6), 71.4 (CH_2, C-4), 55.6 (CH_3, 15-OCH_3), 46.6 (CH, C-9), 44.9 (CH_2, C-10), 29.9 ppm (CH_2, C-3).

HRMS (pos. ESI): *m/z* calcd for $C_{26}H_{26}NO_4^+$ [M + H$^+$]: 416.1856; found: 416.1854.

IR (film, ATR): $\tilde{\nu}$ 3294, 2957, 2896, 1651, 1603, 1541, 1510, 1490, 1239, 1102, 1033, 982, 943, 828, 730 cm^{-1}.

3,3-Bis(4-(methyl(2,2,2-trifluoroethyl)amino)phenyl)-*N*-phenylpropanamide (3b) was prepared by mixing a solution **2e** [preformed in 8 mL CH_2Cl_2 from Ar_2CH-OH (33.0 mg, 0.081 mmol) by addition of $HBF_4 \cdot Et_2O$ (12 µl, 0.089 mmol) at −20°C] with the vinyl azide **1d** (13.0 mg, 0.089 mmol, dissolved in 2 mL CH_2Cl_2) under nitrogen atmosphere at −20°C. After 60 min the reaction was quenched by addition of aqueous hydrochloric acid. The reaction mixture was extracted with dichloromethane (3 × 10 mL), and the combined organic phases were washed with brine (10 mL) and dried (over $MgSO_4$). Then, volatiles were removed under reduced pressure. The crude product was purified by column chromatography (basic Al_2O_3, eluent: *n*-pentane:EtOAc:NEt_3 70:28:2 and silica/*n*-pentane:EtOAc:NEt_3 70:28:2) to give **3b** as a white solid (18.0 mg, 42%); m.p. 138°C.



3b (CG734_1)

R_f (*n*-pentane/EtOAc/NEt_3 70:28:2, basic Al_2O_3, UV) = 0.45

^1H **NMR** (400 MHz, CD_2Cl_2): δ 7.31 (d, J = 7.1 Hz, 2 H, 3-H), 7.27–7.23 (m, 2 H, 2-H), 7.15 (d, J = 8.8 Hz, 4 H, 9-H), 7.07–7.04 (m, 2 H, 1-H, 4-NH), 6.74 (d, J = 8.9 Hz, 4 H, 10-H), 4.44 (t, J = 7.8 Hz, 1 H, 7-H), 3.84 (q, $J_{H,F}$ = 9.1 Hz, 4 H, 13-H), 3.00–2.99 ppm (m, 8 H, 6-H and 12-H).

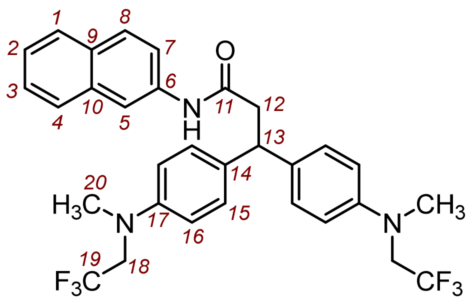
$^{13}C\{^1H\}$ **NMR** (101 MHz, CD_2Cl_2): δ 169.9 (C_q, C-5), 147.7 (C_q, C-11), 138.4 (C_q, C-4), 134.3 (C_q, C-8), 129.2 (CH, C-2), 128.6 (CH, C-9), 126.2 (C_q, q, $^1J_{C,F}$ = 282.9 Hz, C-14), 124.4 (CH, C-1), 120.2 (CH, C-3), 113.3 (CH, q, $^5J_{C,F}$ = 0.9 Hz, C-10), 54.6 (CH_2, q, $^2J_{C,F}$ = 32.3 Hz, C-13), 45.9 (CH, C-7), 44.7 (CH_2, C-6), 39.5 ppm (CH_3, q, $^4J_{C,F}$ = 1.0 Hz, C-12).

^{19}F **NMR** (376 MHz, CD_2Cl_2): δ −70.96 ppm (t, $J_{F,H}$ = 9.1 Hz, CF_3).

HRMS (pos. ESI): *m/z* calcd for $C_{27}H_{27}F_6N_3NaO^+$ [M + Na$^+$]: 541.1951; found: 541.1963.

IR (neat, ATR): $\tilde{\nu}$ 3257, 2917, 1658, 1602, 1552, 1517, 1371, 1264, 1159, 1139, 1093, 987, 821, 807, 759, 694, 657 cm^{-1}.

3,3-Bis(4-(methyl(2,2,2-trifluoroethyl)amino)phenyl)-*N*-(naphthalen-2-yl)propanamide (3c) was obtained by dissolving preformed **2e** (20 mg, 0.042 mmol in 5.0 mL) in dichloromethane (5.0 mL) at –40 °C. After 10 min of stirring, a dichloromethane solution of the vinyl azide **1h** (9.0 mg, 0.046 mmol in 2.0 mL) and water (2 mg, 0.084 mmol) were added. The reaction mixture was stirred for 4 h at –40 °C under a nitrogen atmosphere (the reaction progress was monitored by thin layer chromatography). Upon completion, aqueous ammonia (2 M) was added. The phases were separated, and the aqueous phase was extracted with dichloromethane (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, eluent: *n*-pentane/EtOAc 70:30) to afford **3c** as a white solid (13.0 mg, 55%); m.p. 146°C.



3c (PT337)

R_f (*n*-pentane/EtOAc 70:30, SiO_2, UV) = 0.40

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 2.2 Hz, 1 H), 7.75–7.69 (m, 3 H), 7.45–7.35 (m, 2 H), 7.18–7.16 (m, 5 H), 7.03 (s, 1 H, NH), 6.74 (d, J = 8.8 Hz, 4 H, 16-H), 4.49 (t, J = 7.7 Hz, 1 H, 13-H), 3.81 (q, $J_{H,F}$ = 8.9 Hz, 4 H, 18-H), 3.07 (d, J = 7.8 Hz, 2 H, 12-H), 3.01 ppm (s, 6 H, 20-H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 170.1 (C_q, C-11), 147.4 (C_q), 135.2 (C_q), 133.9 (C_q), 133.7 (C_q), 130.7 (C_q), 128.7 (CH), 128.6 (CH), 127.7 (CH), 127.6 (CH), 126.6 (CH), 125.4 (C_q, q, $^1J_{C,F}$ = 282 Hz, CF_3, C-19), 125.1 (CH), 120.0 (CH), 116.8 (CH), 113.1 (CH), 54.5 (CH_2, q, $^2J_{C,F}$ = 32.5 Hz, 18-H), 45.8 (CH, C-13), 45.1 (CH_2, C-12), 39.3 ppm (CH_3, C-20).

^{19}F NMR (376 MHz, $CDCl_3$): δ –70.50 ppm (t, $J_{F,H}$ = 8.9 Hz, CF_3)**.**

HRMS (pos. ESI): *m/z* calcd for $C_{31}H_{29}F_6N_3NaO^+$ [M + Na^+]: 596.2107; found: 596.2106.

IR (film, ATR): $\tilde{\nu}$ 3294, 2923, 1655, 1611, 1551, 1518, 1371, 1264, 1160, 1146, 1094, 987, 815, 658 cm^{-1}.

4. Kinetics of the Reactions of Benzhydrylium Ions (2) with Vinyl Azides (1)

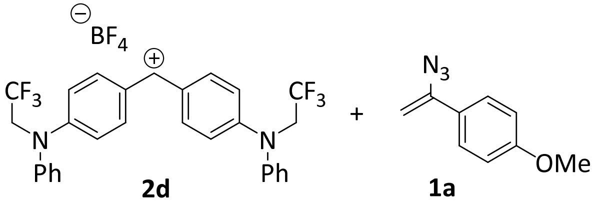
Solutions for kinetic measurements were prepared by using dry dichloromethane (Sigma-Aldrich, for HPLC, ≥ 99.8%), which was stirred for two weeks over sulfuric acid (96%), separated, washed, and distilled over CaH_2 and then kept under an atmosphere of dry nitrogen. Cyrene™ was purchased (Sigma-Aldrich, ≥98.5% by GC) and used without further purification.

The kinetics of the reactions of the vinyl azides **1** with benzhydrylium ions **2** were followed photometrically at the absorbance maxima of the colored benzhydrylium ions by using UV-Vis spectroscopy. For fast reactions, AppliedPhotophysics SX.20 stopped-flow instruments were used. The kinetics of slower reactions were followed by using a conventional J&M TIDAS diode array spectrophotometer, controlled by TIDASDAQ3 (v3) software and connected to a Hellma 661.502-QX quartz Suprasil immersion probe (light path d = 5 mm) via fiber optic cables and standard SMA connectors. The temperature (20.0 ± 0.2 °C) in all kinetic experiments was maintained constant by using circulating bath cryostats. The vinyl azides **1** were used in at least 2.5-fold excess over the benzhydrylium ions **2** (that is, $[\mathbf{2}]_0 << [\mathbf{1}]_0$) to ensure pseudo-first order reaction conditions. Least squares-fitting of the mono-exponential decay function

$$A_t = A_0 \exp(-k_{obs}t) + C$$

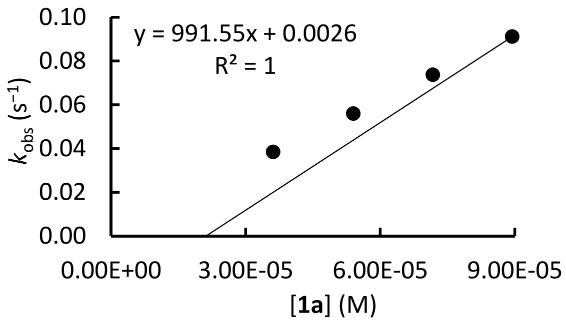
to the time-dependent experimental absorbances A_t was used to calculate the first-order rate constants k_{obs} (s^{-1}) at four to five different nucleophile concentrations (k_{obs} at only three [**1c**] and [**1f**] were determined for the reactions of **2c** with **1c** and **1f**, respectively). Subsequently, the second-order rate constants k_2^{exp} (M^{-1} s^{-1}) of the bimolecular reactions were calculated as the slopes of the linear correlations of k_{obs} vs $[\mathbf{1}]_0$, the initial concentrations of the vinyl azides.

1a + **2d** in CH_2Cl_2 (conventional photometry, detection at λ = 601 nm)



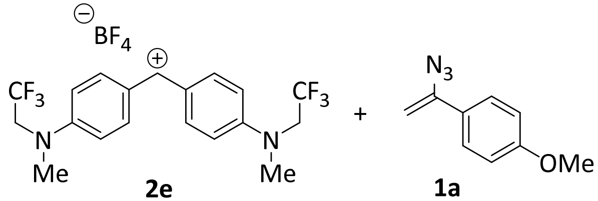
2d **1a** CG739

[**2d**]$_0$ (M)	[**1a**]$_0$ (M)	k_{obs} (s^{-1})
8.24×10^{-6}	3.61×10^{-5}	3.84×10^{-2}
7.86×10^{-6}	5.40×10^{-5}	5.60×10^{-2}
7.99×10^{-6}	7.17×10^{-5}	7.37×10^{-2}
8.21×10^{-6}	8.94×10^{-5}	9.12×10^{-2}



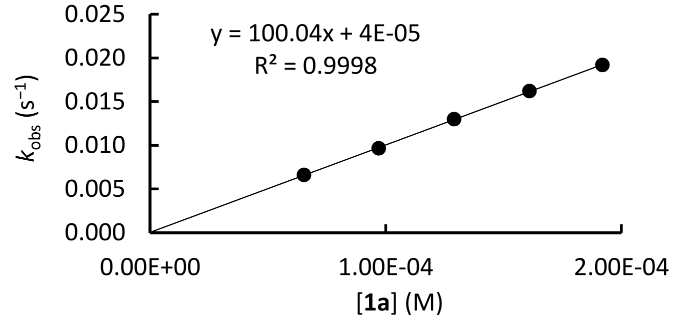
k_2 = (9.92 ± 0.02) × 10^2 M^{-1} s^{-1}

1a + **2e** in CH_2Cl_2 (conventional photometry, detection at λ = 593 nm)



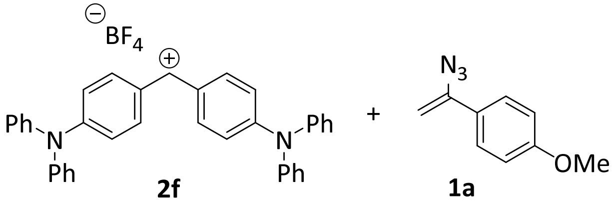
2e **1a** CG740

[**2e**]$_0$ (M)	[**1a**]$_0$ (M)	k_{obs} (s^{-1})
7.55×10^{-6}	6.53×10^{-5}	6.60×10^{-3}
8.52×10^{-6}	9.70×10^{-5}	9.65×10^{-3}
8.36×10^{-6}	1.29×10^{-4}	1.30×10^{-2}
8.33×10^{-6}	1.61×10^{-4}	1.62×10^{-2}
8.55×10^{-6}	1.92×10^{-4}	1.92×10^{-2}



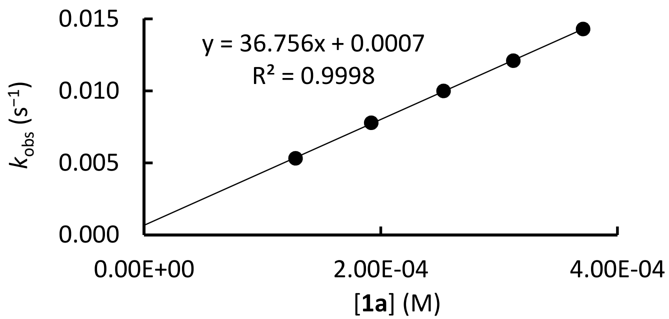
k_2 = (1.00 ± 0.01) × 10^2 M^{-1} s^{-1}

1a + **2f** in CH_2Cl_2 (conventional photometry, detection at λ = 674 nm)



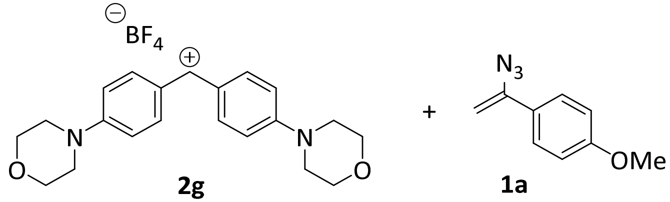
CG741

[**2f**]$_0$ (M)	[**1a**]$_0$ (M)	k_{obs} (s^{-1})
1.05×10^{-5}	1.28×10^{-4}	5.32×10^{-3}
1.04×10^{-5}	1.92×10^{-4}	7.79×10^{-3}
1.02×10^{-5}	2.53×10^{-4}	1.00×10^{-2}
1.01×10^{-5}	3.12×10^{-4}	1.21×10^{-2}
9.88×10^{-6}	3.71×10^{-4}	1.43×10^{-2}



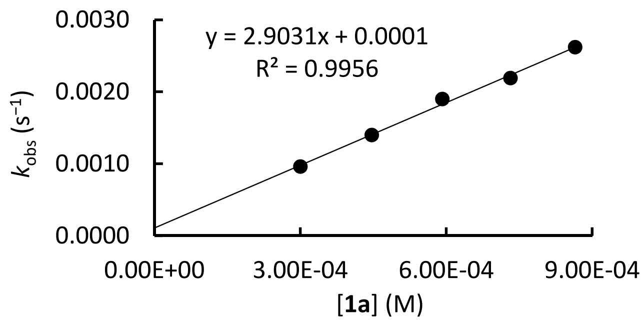
$k_2 = (3.68 \pm 0.03) \times 10^1$ M^{-1} s^{-1}

1a + **2g** in CH_2Cl_2 (conventional photometry, detection at λ = 620 nm)



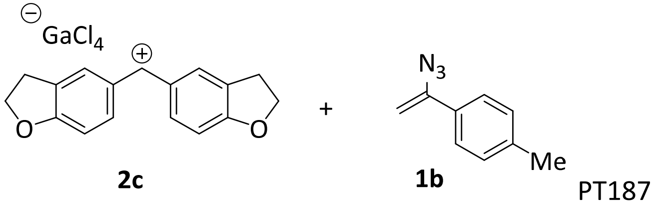
CG742

[**2g**]$_0$ (M)	[**1a**]$_0$ (M)	k_{obs} (s^{-1})
7.65×10^{-6}	3.00×10^{-4}	9.62×10^{-4}
7.72×10^{-6}	4.47×10^{-4}	1.40×10^{-3}
7.62×10^{-6}	5.92×10^{-4}	1.90×10^{-3}
7.33×10^{-6}	7.32×10^{-4}	2.19×10^{-3}
7.10×10^{-6}	8.65×10^{-4}	2.62×10^{-3}

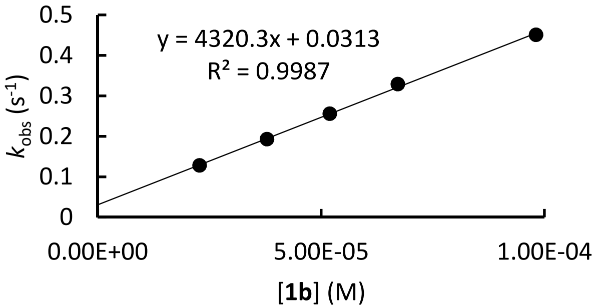


$k_2 = (2.90 \pm 0.11)$ M^{-1} s^{-1}

1b + **2c** in CH_2Cl_2 (conventional photometry, detection at λ = 535 nm)

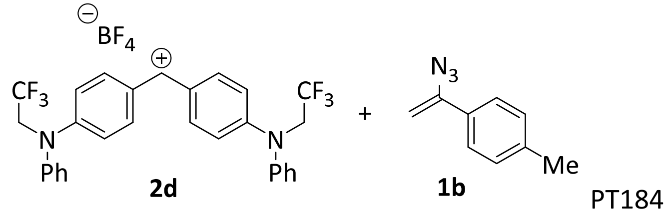


[**2c**]$_0$ (M)	[**1b**]$_0$ (M)	k_{obs} (s^{-1})
7.60×10^{-6}	2.28×10^{-5}	0.128
7.58×10^{-6}	3.79×10^{-5}	0.193
7.42×10^{-6}	5.19×10^{-5}	0.256
7.46×10^{-6}	6.72×10^{-5}	0.329
7.55×10^{-6}	9.81×10^{-5}	0.451

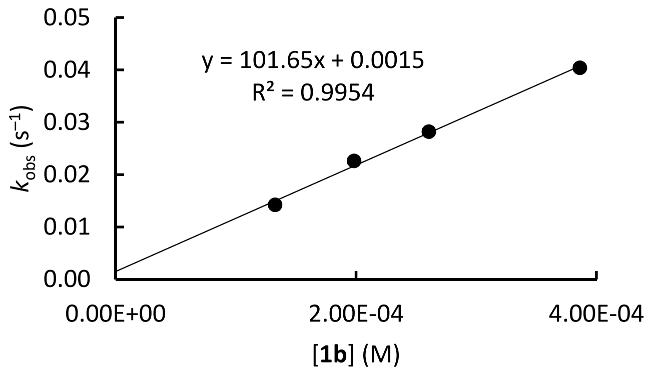


k_2 = (4.32 ± 0.09) × 10^3 M^{-1} s^{-1}

1b + **2d** in CH_2Cl_2 (conventional photometry, detection at λ = 601 nm)

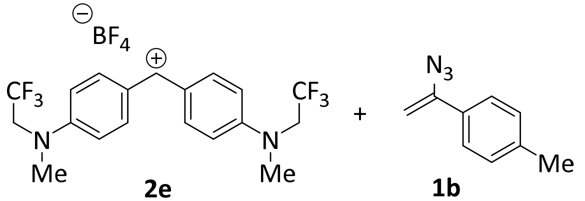


[**2d**]$_0$ (M)	[**1b**]$_0$ (M)	k_{obs} (s^{-1})
1.33×10^{-5}	1.33×10^{-4}	1.42×10^{-2}
1.32×10^{-5}	1.98×10^{-4}	2.26×10^{-2}
1.30×10^{-5}	2.61×10^{-4}	2.82×10^{-2}
1.29×10^{-5}	3.86×10^{-4}	4.04×10^{-2}



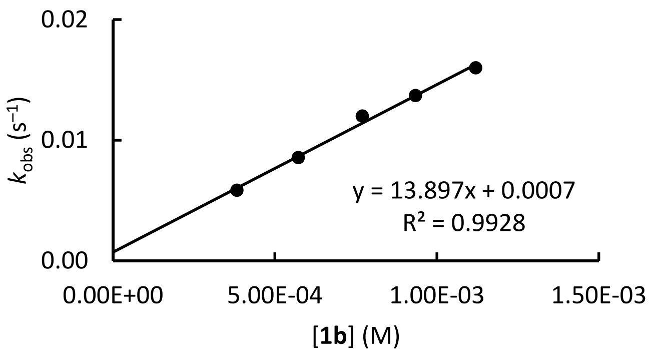
k_2 = (1.02 ± 0.05) × 10^2 M^{-1} s^{-1}

1b + **2e** in CH_2Cl_2 (conventional photometry, detection at λ = 593 nm)



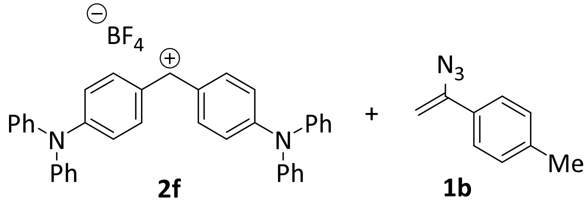
2e **1b** PT185

[**2e**]$_0$ (M)	[**1b**]$_0$ (M)	k_{obs} (s^{-1})
9.58×10^{-6}	3.83×10^{-4}	5.84×10^{-3}
9.53×10^{-6}	5.72×10^{-4}	8.56×10^{-3}
9.62×10^{-6}	7.70×10^{-4}	1.20×10^{-2}
9.34×10^{-6}	9.34×10^{-4}	1.37×10^{-2}
9.30×10^{-6}	1.12×10^{-3}	1.60×10^{-2}



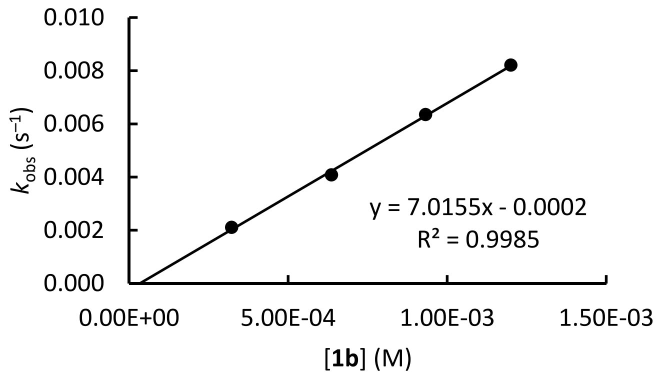
k_2 **= (1.39 ± 0.07) × 10**^{1} **M**$^{-1}$ **s**$^{-1}$

1b + **2f** in CH_2Cl_2 (conventional photometry, detection at λ = 672 nm)



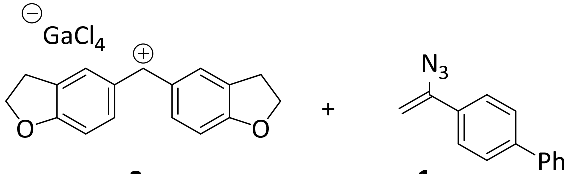
2f **1b** PT186

[**2f**]$_0$ (M)	[**1b**]$_0$ (M)	k_{obs} (s^{-1})
1.29×10^{-5}	3.22×10^{-4}	2.11×10^{-3}
1.27×10^{-5}	6.36×10^{-4}	4.08×10^{-3}
1.24×10^{-5}	9.32×10^{-4}	6.35×10^{-3}
1.20×10^{-5}	1.20×10^{-3}	8.21×10^{-3}



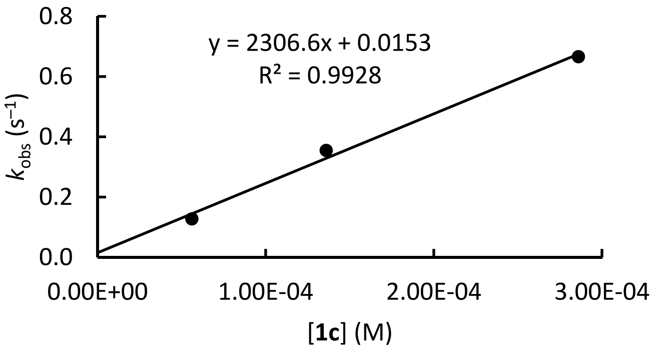
k_2 **= (7.02 ± 0.02) M**$^{-1}$ **s**$^{-1}$

1c + **2c** (generated in solution from $Ar_2CH{-}Cl$ + 3 equiv. $GaCl_3$) in CH_2Cl_2 (conventional photometry, detection at λ = 535 nm)



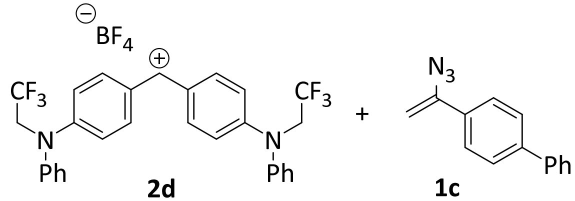
2c **1c** PT308

[**2c**]$_0$ (M)	[**1c**]$_0$ (M)	k_{obs} (s^{-1})
1.87×10^{-5}	5.62×10^{-5}	1.28×10^{-1}
1.94×10^{-5}	1.36×10^{-4}	3.55×10^{-1}
1.91×10^{-5}	2.86×10^{-4}	6.66×10^{-1}



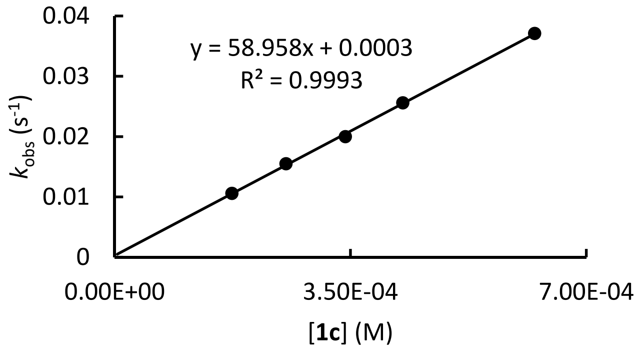
k_2 **= (2.31 ± 0.20) × 10^3 M^{-1} s^{-1}**

1c + **2d** in CH_2Cl_2 (conventional photometry, detection at λ = 601 nm)



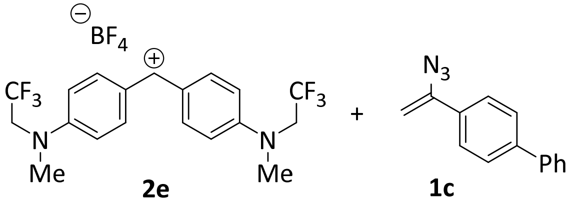
2d **1c** PT307

[**2d**]$_0$, (M)	[**1c**]$_0$, (M)	k_{obs}, (s^{-1})
8.71×10^{-6}	1.74×10^{-4}	1.06×10^{-2}
8.48×10^{-6}	2.55×10^{-4}	1.55×10^{-2}
8.56×10^{-6}	3.43×10^{-4}	2.00×10^{-2}
8.56×10^{-6}	4.28×10^{-4}	2.56×10^{-2}
8.56×10^{-6}	6.23×10^{-4}	3.71×10^{-2}



k_2 **= (5.90 ± 0.09) × 10^1 M^{-1} s^{-1}**

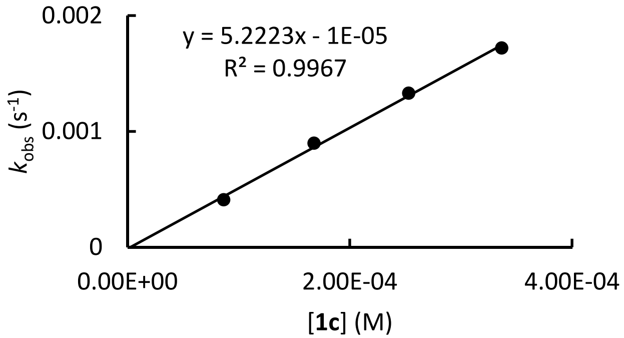
1c + **2e** in CH_2Cl_2 (conventional photometry, detection at λ = 593 nm)



PT316

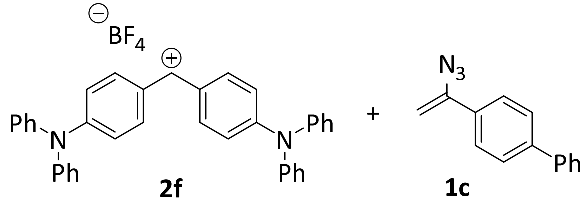
[**2e**]$_0$ (M)	[**1c**]$_0$ (M)	k_{obs} (s^{-1})
5.77×10^{-6}	8.65×10^{-5}	4.09×10^{-4}
5.59×10^{-6}	1.68×10^{-4}	8.97×10^{-4}
5.62×10^{-6}	2.53×10^{-4}	1.33×10^{-3}
5.61×10^{-6}	3.37×10^{-4}	1.72×10^{-3}

Only data from the first 35% of conversion were used to determine k_{obs}.



k_2 **= (5.22 ± 0.22) M^{-1} s^{-1}**

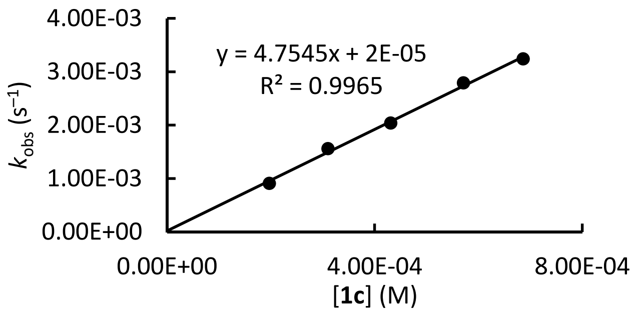
1c + **2f** in CH_2Cl_2 (conventional photometry, detection at λ = 672 nm)



PT315

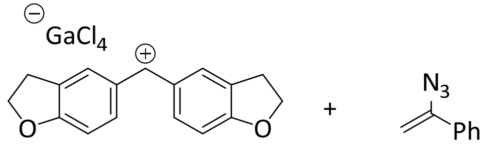
[**2f**]$_0$ (M)	[**1c**]$_0$ (M)	k_{obs} (s^{-1})
9.84×10^{-6}	1.97×10^{-4}	9.10×10^{-4}
9.70×10^{-6}	3.10×10^{-4}	1.56×10^{-3}
9.57×10^{-6}	4.31×10^{-4}	2.04×10^{-3}
9.51×10^{-6}	5.71×10^{-4}	2.79×10^{-3}
9.52×10^{-6}	6.86×10^{-4}	3.24×10^{-3}

Only data from the first half-life time were used to determine k_{obs}.



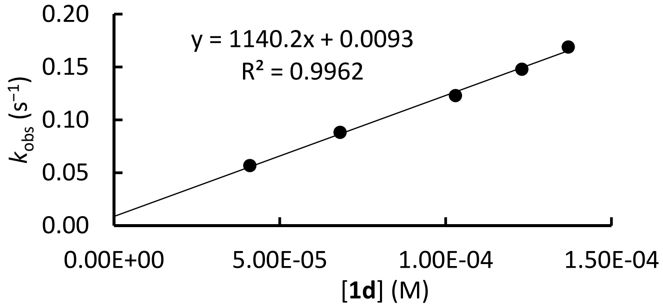
k_2 **= (4.75 ± 0.16) M^{-1} s^{-1}**

1d + **2c** (generated in CH_2Cl_2 solution from Ar_2CH-Cl + 3 equiv. $GaCl_3$) in dichloromethane (conventional photometry, detection at λ = 535 nm)



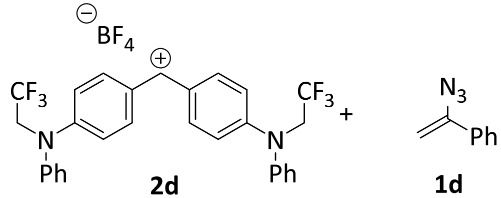
2c **1d** CG725

$[\mathbf{2c}]_0$ (M)	$[\mathbf{1d}]_0$ (M)	k_{obs} (s^{-1})
1.37×10^{-5}	4.10×10^{-5}	5.68×10^{-2}
1.36×10^{-5}	6.82×10^{-5}	8.83×10^{-2}
1.37×10^{-5}	1.03×10^{-4}	1.23×10^{-1}
1.37×10^{-5}	1.23×10^{-4}	1.48×10^{-1}
1.37×10^{-5}	1.37×10^{-4}	1.69×10^{-1}



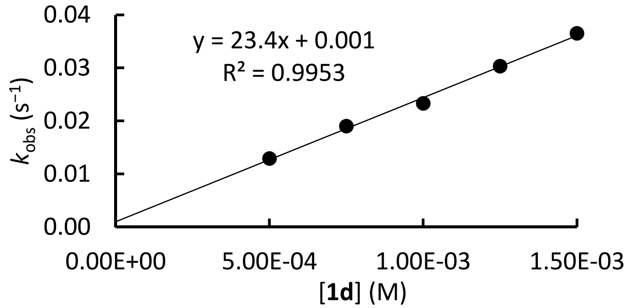
k_2 = **(1.14 ± 0.04) × 10³ M⁻¹ s⁻¹**

1d + **2d** in CH_2Cl_2 (stopped-flow method, detection at λ = 601 nm)



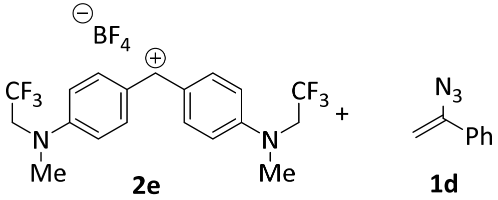
2d **1d** CG679

$[\mathbf{2d}]_0$ (M)	$[\mathbf{1d}]_0$ (M)	k_{obs} (s^{-1})
3.73×10^{-6}	5.00×10^{-4}	1.29×10^{-2}
3.10×10^{-6}	7.50×10^{-4}	1.90×10^{-2}
3.10×10^{-6}	1.00×10^{-3}	2.33×10^{-2}
3.02×10^{-6}	1.25×10^{-3}	3.03×10^{-2}
2.86×10^{-6}	1.50×10^{-3}	3.65×10^{-2}



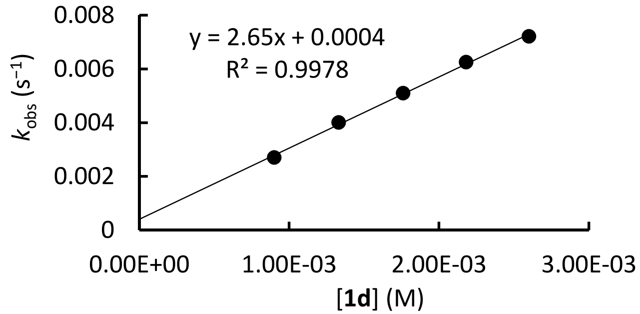
k_2 = **(2.34 ± 0.09) × 10¹ M⁻¹ s⁻¹**

1d + **2e** in CH_2Cl_2 (conventional photometry, detection at λ = 593 nm)



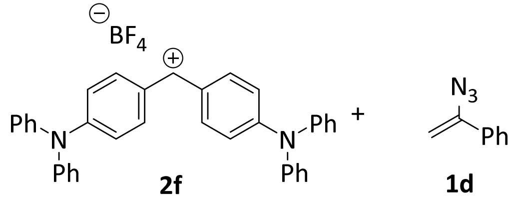
CG726

[**2e**]$_0$ (M)	[**1d**]$_0$ (M)	k_{obs} (s^{-1})
1.19×10^{-5}	9.00×10^{-4}	2.70×10^{-3}
1.24×10^{-5}	1.33×10^{-3}	4.01×10^{-3}
1.27×10^{-5}	1.76×10^{-3}	5.10×10^{-3}
1.27×10^{-5}	2.18×10^{-3}	6.25×10^{-3}
1.26×10^{-5}	2.60×10^{-3}	7.21×10^{-3}



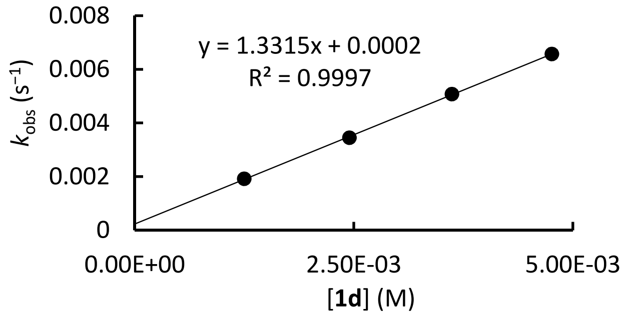
$\boldsymbol{k_2}$ **= (2.65 ± 0.07) M^{-1} s^{-1}**

1d + **2f** in CH_2Cl_2 (conventional photometry, detection at λ = 674 nm)



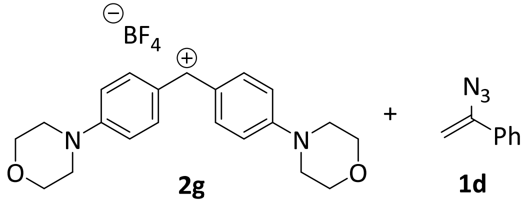
CG727

[**2f**]$_0$ (M)	[**1d**]$_0$ (M)	k_{obs} (s^{-1})
1.08×10^{-5}	1.25×10^{-3}	1.92×10^{-3}
1.08×10^{-5}	2.45×10^{-3}	3.45×10^{-3}
1.11×10^{-5}	3.62×10^{-3}	5.08×10^{-3}
1.03×10^{-5}	4.76×10^{-3}	6.57×10^{-3}



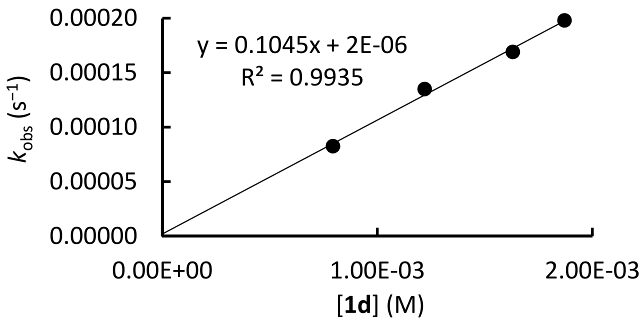
$\boldsymbol{k_2}$ **= (1.33 ± 0.02) M^{-1} s^{-1}**

1d + **2g** in CH_2Cl_2 (conventional photometry, detection at λ = 620 nm)



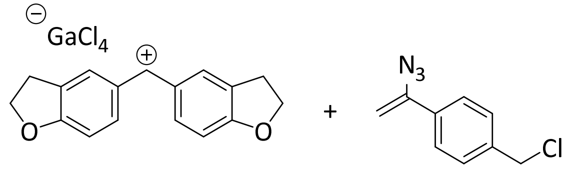
2g **1d** CG728

[**2g**]$_0$ (M)	[**1d**]$_0$ (M)	k_{obs} (s^{-1})
8.47×10^{-6}	7.94×10^{-4}	8.25×10^{-5}
7.71×10^{-6}	1.22×10^{-3}	1.35×10^{-4}
8.11×10^{-6}	1.63×10^{-3}	1.69×10^{-4}
8.22×10^{-6}	1.87×10^{-3}	1.98×10^{-4}



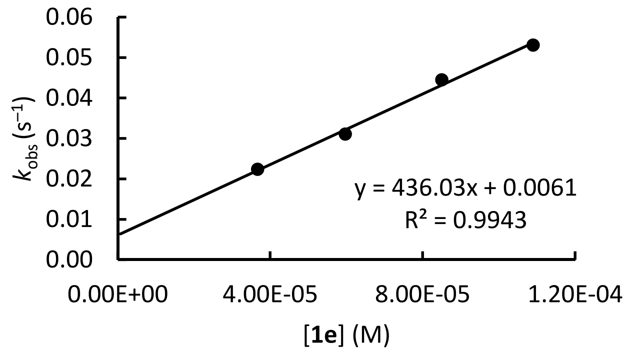
$\boldsymbol{k_2 = (1.05 \pm 0.06) \times 10^{-1}\ M^{-1}\ s^{-1}}$

1e + **2c** (generated in solution from $Ar_2CH{-}Cl$ + 3 equiv. $GaCl_3$) in CH_2Cl_2 (conventional photometry, detection at λ = 535 nm)



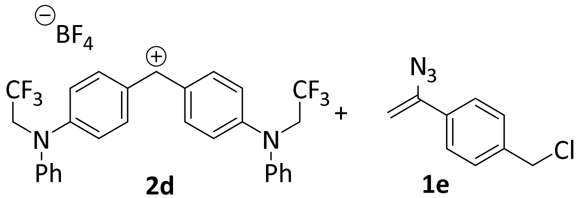
2c **1e** PT271

[**2c**]$_0$ (M)	[**1e**]$_0$ (M)	k_{obs} (s^{-1})
1.22×10^{-5}	3.67×10^{-5}	2.24×10^{-2}
1.19×10^{-5}	5.97×10^{-5}	3.11×10^{-2}
1.21×10^{-5}	8.50×10^{-5}	4.45×10^{-2}
1.21×10^{-5}	1.09×10^{-4}	5.31×10^{-2}



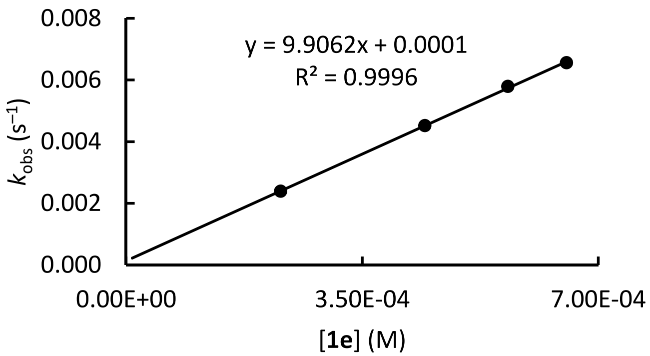
$\boldsymbol{k_2 = (4.36 \pm 0.23) \times 10^{2}\ M^{-1}\ s^{-1}}$

1e + **2d** in CH_2Cl_2 (conventional photometry, detection at λ = 601 nm)



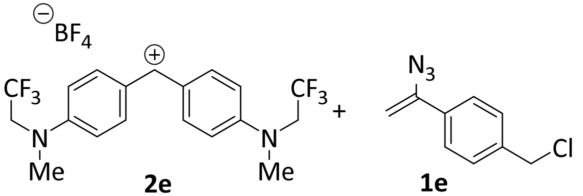
2d **1e** PT270

$[\mathbf{2d}]_0$ (M)	$[\mathbf{1e}]_0$ (M)	k_{obs} (s^{-1})
2.29×10^{-5}	2.29×10^{-4}	2.39×10^{-3}
2.22×10^{-5}	4.43×10^{-4}	4.52×10^{-3}
2.26×10^{-5}	5.66×10^{-4}	5.79×10^{-3}
2.18×10^{-5}	6.53×10^{-4}	6.56×10^{-3}



k_2 = (9.91 ± 0.15) M^{-1} s^{-1}

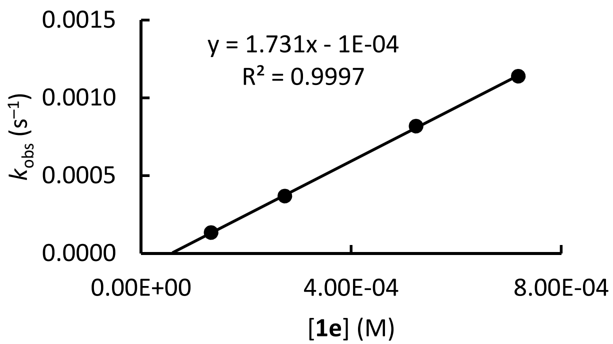
1e + **2e** in CH_2Cl_2 (conventional photometry, detection at λ = 593 nm)



2e **1e** PT272

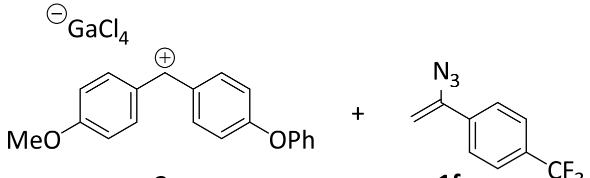
$[\mathbf{2e}]_0$ (M)	$[\mathbf{1e}]_0$ (M)	k_{obs} (s^{-1})
8.89×10^{-6}	1.33×10^{-4}	1.34×10^{-4}
9.13×10^{-6}	2.74×10^{-4}	3.68×10^{-4}
8.73×10^{-6}	5.24×10^{-4}	8.18×10^{-4}
8.65×10^{-6}	7.18×10^{-4}	1.14×10^{-3}

Only data from the first half-life time were used to determine k_{obs}.



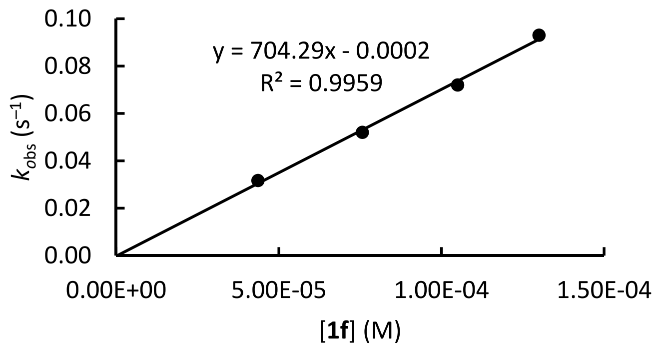
k_2 = (1.73 ± 0.02) M^{-1} s^{-1}

1f + **2a** (generated in solution from $Ar_2CH{-}Cl$ + 3 equiv. $GaCl_3$) in CH_2Cl_2
(conventional photometry, detection at λ = 516 nm)



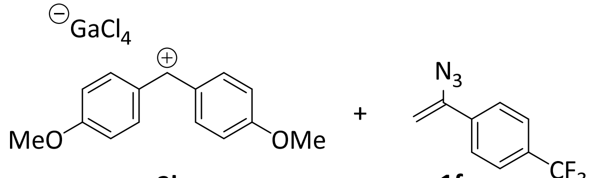
2a **1f** PT291

[**2a**]$_0$ (M)	[**1f**]$_0$ (M)	k_{obs} (s^{-1})
1.45×10^{-5}	4.36×10^{-5}	3.17×10^{-2}
1.48×10^{-5}	7.57×10^{-5}	5.20×10^{-2}
1.50×10^{-5}	1.05×10^{-4}	7.20×10^{-2}
1.44×10^{-5}	1.30×10^{-4}	9.30×10^{-2}



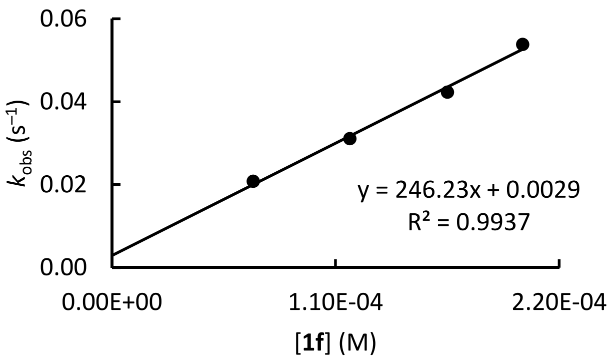
$\boldsymbol{k_2 = (7.04 \pm 0.32) \times 10^2\ M^{-1}\ s^{-1}}$

1f + **2b** (generated in solution from $Ar_2CH{-}Cl$ + 3 equiv. $GaCl_3$) in CH_2Cl_2
(conventional photometry, detection at λ = 512 nm)



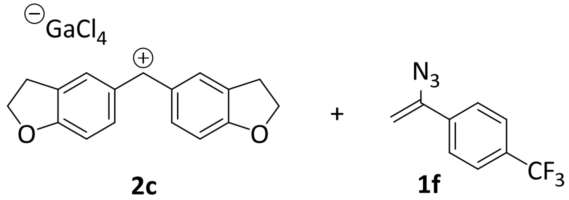
2b **1f** PT286

[**2b**]$_0$ (M)	[**1f**]$_0$ (M)	k_{obs} (s^{-1})
2.32×10^{-5}	6.95×10^{-5}	2.08×10^{-2}
2.29×10^{-5}	1.17×10^{-4}	3.11×10^{-2}
2.30×10^{-5}	1.65×10^{-4}	4.23×10^{-2}
2.27×10^{-5}	2.02×10^{-4}	5.38×10^{-2}



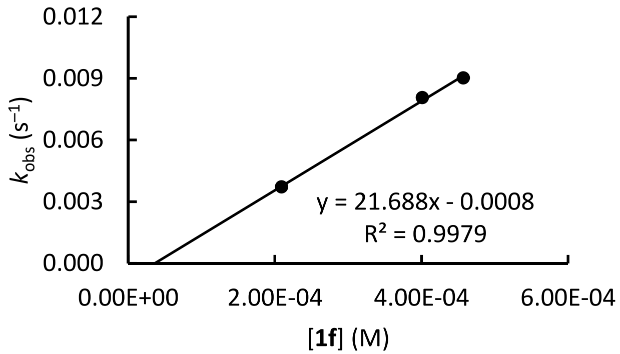
$\boldsymbol{k_2 = (2.46 \pm 0.14) \times 10^2\ M^{-1}\ s^{-1}}$

1f + **2c** (generated in solution from $Ar_2CH{-}Cl$ + 3 equiv. $GaCl_3$) in CH_2Cl_2
(conventional photometry, detection at λ = 535 nm)



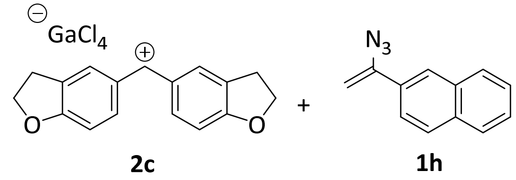
PT285

[**2c**]$_0$ (M)	[**1f**]$_0$ (M)	k_{obs} (s^{-1})
1.04×10^{-5}	2.09×10^{-4}	3.72×10^{-3}
1.00×10^{-5}	4.01×10^{-4}	8.06×10^{-3}
9.93×10^{-6}	4.57×10^{-4}	9.02×10^{-3}



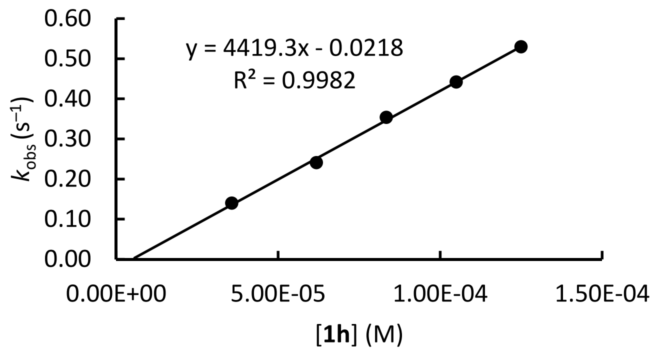
k_2 **= (2.17 ± 0.10) × 10^1 M^{-1} s^{-1}**

1h + **2c** (generated in solution from $Ar_2CH\text{-}Cl$ + 3 equiv. $GaCl_3$) in CH_2Cl_2
(conventional photometry, detection at λ = 535 nm)



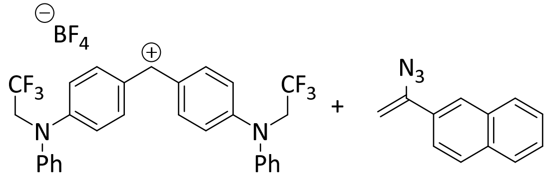
PT301

[**2c**]$_0$ (M)	[**1h**]$_0$ (M)	k_{obs} (s^{-1})
1.43×10^{-5}	3.57×10^{-5}	1.40×10^{-1}
1.55×10^{-5}	6.18×10^{-5}	2.41×10^{-1}
1.52×10^{-5}	8.34×10^{-5}	3.54×10^{-1}
1.50×10^{-5}	1.05×10^{-4}	4.42×10^{-1}
1.47×10^{-5}	1.25×10^{-4}	5.29×10^{-1}



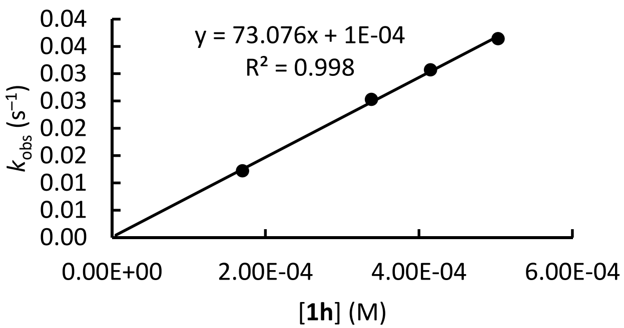
k_2 **= (4.42 ± 0.11) × 10^3 M^{-1} s^{-1}**

1h + **2d** in CH_2Cl_2 (conventional photometry, detection at λ = 601 nm)



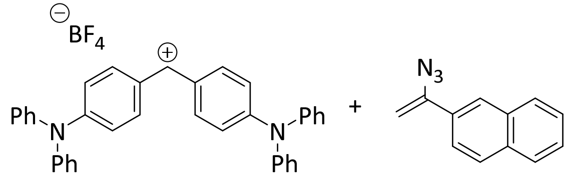
2d **1h** PT222

$[\mathbf{2d}]_0$ (M)	$[\mathbf{1h}]_0$ (M)	k_{obs} (s^{-1})
1.70×10^{-5}	1.70×10^{-4}	1.22×10^{-2}
1.69×10^{-5}	3.38×10^{-4}	2.53×10^{-2}
1.66×10^{-5}	4.15×10^{-4}	3.07×10^{-2}
1.68×10^{-5}	5.03×10^{-4}	3.64×10^{-2}



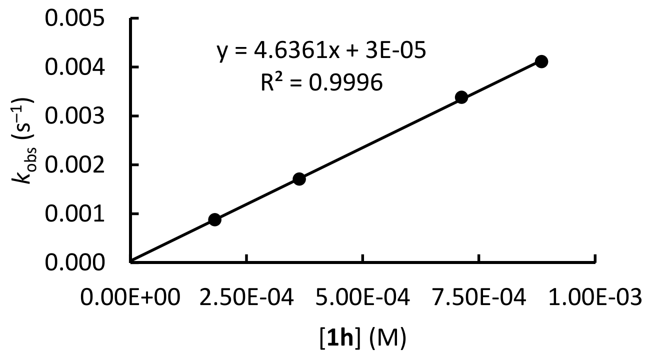
$k_2 = (7.31 \pm 0.23) \times 10^{1}\ M^{-1}\ s^{-1}$

1h + **2f** in CH_2Cl_2 (conventional photometry, detection at λ = 672 nm)



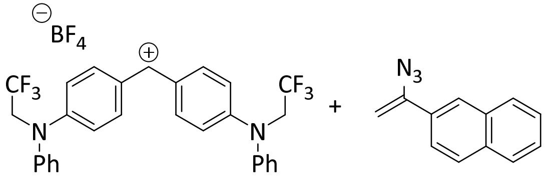
2f **1h** PT234

$[\mathbf{2f}]_0$ (M)	$[\mathbf{1h}]_0$ (M)	k_{obs} (s^{-1})
1.82×10^{-5}	1.82×10^{-4}	8.77×10^{-4}
1.82×10^{-5}	3.64×10^{-4}	1.71×10^{-3}
1.78×10^{-5}	7.13×10^{-4}	3.38×10^{-3}
1.77×10^{-5}	8.85×10^{-4}	4.11×10^{-3}



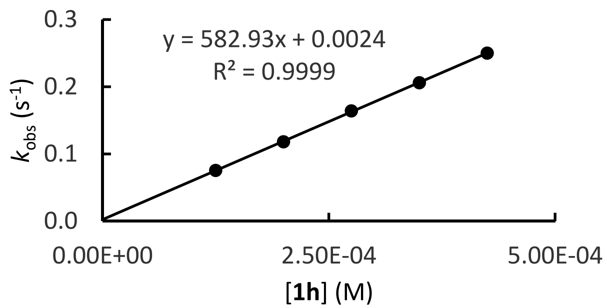
$k_2 = (4.64 \pm 0.06)\ M^{-1}\ s^{-1}$

1h + **2d** in Cyrene (stopped-flow, detection at λ = 601 nm)



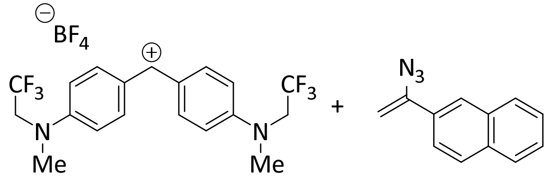
2d **1h** PT303

[**2d**]$_0$ (M)	[**1h**]$_0$ (M)	k_{obs} (s^{-1})
5.0×10^{-5}	1.25×10^{-4}	7.54×10^{-2}
5.0×10^{-5}	2.00×10^{-4}	1.18×10^{-1}
5.0×10^{-5}	2.75×10^{-4}	1.64×10^{-1}
5.0×10^{-5}	3.50×10^{-4}	2.06×10^{-1}
5.0×10^{-5}	4.25×10^{-4}	2.50×10^{-1}



k_2 = (5.83 ± 0.04) × 10^2 M^{-1} s^{-1}

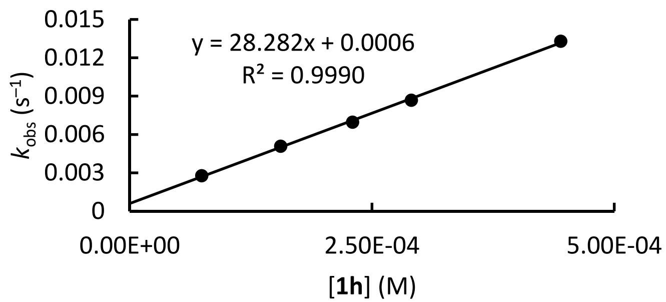
1h + **2e** in Cyrene (conventional photometry, detection at λ = 593 nm)



2e **1h** PT276

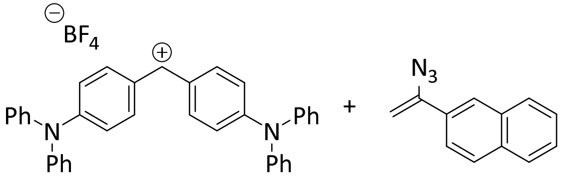
[**2e**]$_0$ (M)	[**1h**]$_0$ (M)	k_{obs} (s^{-1})
1.56×10^{-5}	7.43×10^{-5}	2.78×10^{-3}
1.53×10^{-5}	1.56×10^{-4}	5.08×10^{-3}
1.45×10^{-5}	2.30×10^{-4}	6.97×10^{-3}
1.48×10^{-5}	2.91×10^{-4}	8.69×10^{-3}
1.49×10^{-5}	4.45×10^{-4}	1.33×10^{-2}

Only data from the first half-life time were used to determine k_{obs}.



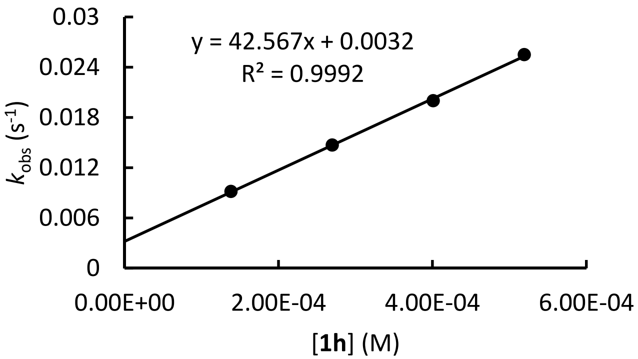
k_2 = (2.83 ± 0.05) × 10^1 M^{-1} s^{-1}

1h + **2f** in Cyrene (conventional photometry, detection at λ = 672 nm)



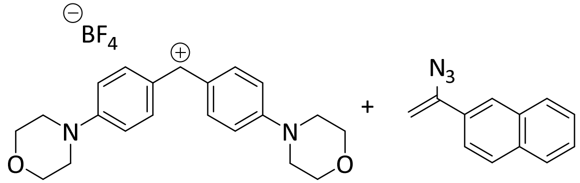
2f **1h** PT338

[**2f**]$_0$ (M)	[**1h**]$_0$ (M)	k_{obs} (s^{-1})
2.76×10^{-5}	1.38×10^{-4}	9.17×10^{-3}
2.70×10^{-5}	2.70×10^{-4}	1.47×10^{-2}
2.67×10^{-5}	4.01×10^{-4}	2.00×10^{-2}
2.60×10^{-5}	5.19×10^{-4}	2.55×10^{-2}



k_2 = (4.26 ± 0.09) × 10^1 M^{-1} s^{-1}

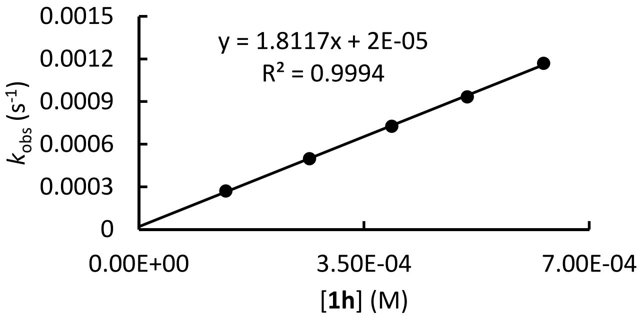
1h + **2g** in Cyrene (conventional photometry, detection at 620 nm)



2g **1h** PT330

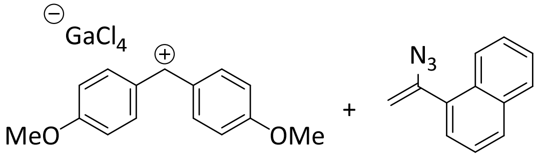
[**2g**]$_0$ (M)	[**1h**]$_0$ (M)	k_{obs} (s^{-1})
9.02×10^{-6}	1.35×10^{-4}	2.71×10^{-4}
8.84×10^{-6}	2.65×10^{-4}	4.98×10^{-4}
8.73×10^{-6}	3.93×10^{-4}	7.27×10^{-4}
8.51×10^{-6}	5.10×10^{-4}	9.34×10^{-4}
8.50×10^{-6}	6.29×10^{-4}	1.17×10^{-3}

Only data from the first half-life time were used to determine k_{obs}.



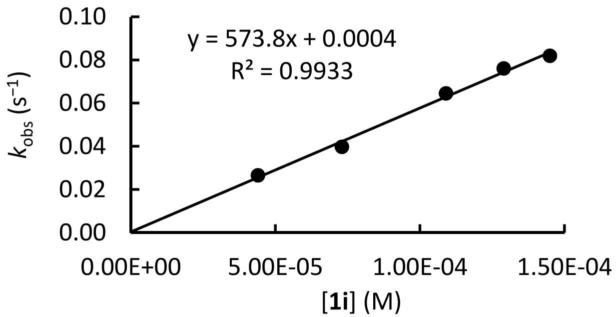
k_2 = (1.81 ± 0.03) M^{-1} s^{-1}

1i + **2b** (generated in solution from Ar_2CH-Cl + 3 equiv. $GaCl_3$) in CH_2Cl_2
(conventional photometry, detection at λ = 512 nm)



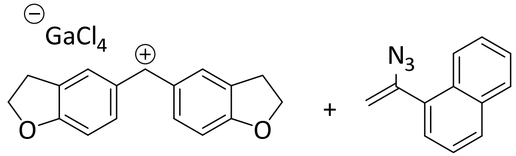
2b **1i** CG749

[**2b**]$_0$ (M)	[**1i**]$_0$ (M)	k_{obs} (s^{-1})
1.47×10^{-5}	4.40×10^{-5}	2.66×10^{-2}
1.46×10^{-5}	7.30×10^{-5}	3.98×10^{-2}
1.45×10^{-5}	1.09×10^{-4}	6.45×10^{-2}
1.44×10^{-5}	1.29×10^{-4}	7.61×10^{-2}
1.45×10^{-5}	1.45×10^{-4}	8.19×10^{-2}



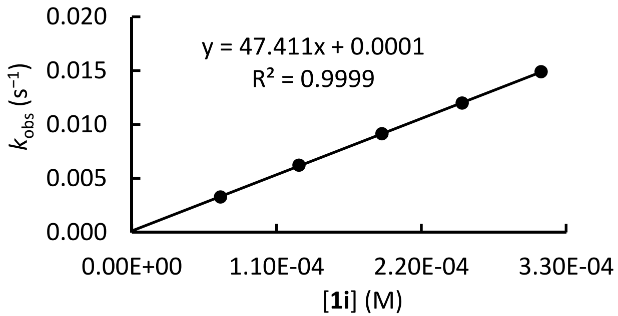
k_2 = (5.74 ± 0.27) × 10^2 M^{-1} s^{-1}

1i + **2c** (generated in solution from Ar_2CH-Cl + 3 equiv. $GaCl_3$) in CH_2Cl_2
(conventional photometry, detection at λ = 535 nm)



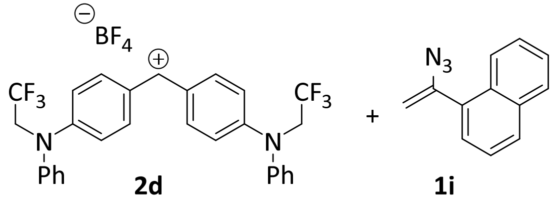
2c **1i** CG748

[**2c**]$_0$ (M)	[**1i**]$_0$ (M)	k_{obs} (s^{-1})
1.35×10^{-5}	6.74×10^{-5}	3.29×10^{-3}
1.27×10^{-5}	1.27×10^{-4}	6.24×10^{-3}
1.27×10^{-5}	1.90×10^{-4}	9.15×10^{-3}
1.26×10^{-5}	2.51×10^{-4}	1.20×10^{-2}
1.24×10^{-5}	3.11×10^{-4}	1.49×10^{-2}



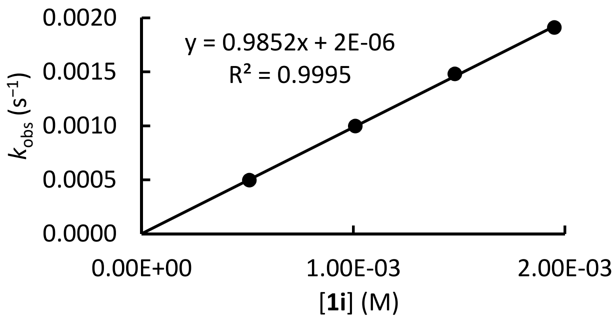
k_2 = (4.74 ± 0.03) × 10^1 M^{-1} s^{-1}

1i + **2d** in CH_2Cl_2 (conventional photometry, detection at λ = 601 nm)



2d **1i** CG747

[**2d**]$_0$ (M)	[**1i**]$_0$ (M)	k_{obs} (s^{-1})
9.26×10^{-6}	5.09×10^{-4}	4.97×10^{-4}
9.82×10^{-6}	1.01×10^{-3}	9.98×10^{-4}
9.96×10^{-6}	1.48×10^{-3}	1.48×10^{-3}
9.18×10^{-6}	1.95×10^{-3}	1.91×10^{-3}



$\boldsymbol{k_2}$ **= (9.85 ± 0.16) × 10^{-1} M^{-1} s^{-1}**

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