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Supporting Information

Base-Promoted Hydride Transfer: Thermodynamics, Kinetics and Synthetic Applications

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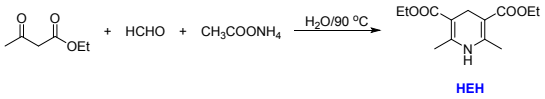
1 General Information

All chemicals were purchased from commercial sources and used as received unless otherwise noted. ^{1}H, ^{13}C NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts are reported in ppm with the solvent residual as the internal standard ($CDCl_3$, δ: 7.26 ppm; DMSO, δ: 2.50 ppm; acetonitrile-d_3, δ: 1.94 ppm). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constant (Hz), and integration. HRMS spectra were recorded on an Orbitrap analyzer. UV-vis spectra were recorded on a Hitachi U-3900H spectrometer.

2 Synthesis of Hydride Donors

2.1 Preparation of diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (HEH)[1]



HEH

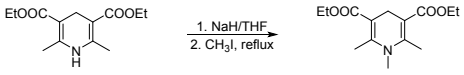
To a 250 ml round-bottom flask was added formaldehyde (37% aqueous solution, 3.75 ml, 50 mmol, 1.0 eqiv), ammonium acetate (7.7g, 100 mmol, 2.0 eqiv), ethyl acetoacetate (25.4 ml, 200 mmol, 4.0 eqiv) and 100 ml water. The flask was equipped with a reflux condenser and heated to 90 °C for 2 hours with vigorously stirring. The formed yellow small balls were filtered and washed with cold water and ethanol. The solid was recrystallized from ethanol two times to afford the Hantzsch esters as small needles (10.5 g, 41 mmol, 83% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.39 (brs, 1H), 4.15 (q, *J* = 7.1 Hz, 4H), 3.24 (s, 2H), 2.17 (s, 6H), 1.26 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.2, 145.0, 99.6, 59.8, 24.9, 19.2, 14.6.

The spectral data are in agreement with those reported in literature.[1]

2.2 Preparation of diethyl 1,2,6-trimethyl-1,4-dihydropyridine-3,5-dicarboxylate (N-Me HEH)[2]



N-Me HEH

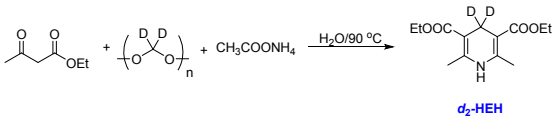
To a 250 ml flame-dried round-bottom flask was added NaH (0.36 g, 12 mmol, 1.2 eqiv) and dry THF 60 ml under Ar. The flask was cooled with ice-water bath and Hantzsch esters (2.53 g, 10 mmol, 1.0 eqiv) was added slowly. After 30 minutes, MeI (1.25 ml, 20 mmol, 2.0 eqiv) with 10 ml THF was added and the reaction mixture was heated to reflux for 2 hours. After cooling to room temperature, aqueous Na_2CO_3 was added to the flask to quench the MeI. The THF was distilled out and the mixture was extracted with diethyl ether. The ether layer was collected and concentrated. Recrystallization from ethanol afforded small needles (1.44 g, 54% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.18 (qd, *J* = 7.1, 3.6 Hz, 4H), 3.15 (d, *J* = 1.6 Hz, 4H), 2.44 – 2.32 (m, 5H), 1.29 (td, *J* = 7.1, 1.2 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.0, 150.6, 101.5, 59.7, 33.8, 23.9, 15.9, 14.4.

The spectral data are in agreement with those reported in literature.[3]

2.3 Preparation of diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate-4,4-d_2 (d_2-HEH)[4]



d_2-HEH

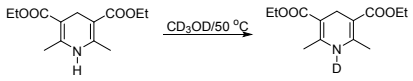
To a 250 ml round-bottom flask was added paraformaldehyde-d_2 (1 g, 31 mmol, 1.0 eqiv), ammonium acetate (4.8 g, 62 mmol, 2.0 eqiv), ethyl acetoacetate (16.3 g, 125 mmol, 4.0 eqiv) and 100 ml water. The mixture was heated to 90 °C for 2 hours with vigorously stirring. The formed precipitate was filtered and recrystallized from ethanol to afford small needles (6.12 g, 77% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.33 (brs, 1H), 4.15 (q, *J* = 7.1 Hz, 4H), 2.18 (s, 6H), 1.27 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.2, 145.0, 99.5, 61.6, 59.8, 19.2, 14.6.

The spectral data are in agreement with those reported in literature.[4]

2.4 Preparation of diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate-1-*d* (N-D HEH)[2]



N-D HEH

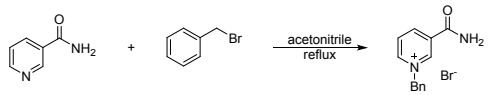
The solution of Hantzsch esters (253 mg, 10 mmol) in 5 ml of CD_3OH was stirred under Ar overnight. After evaporation of the solvent, light green power was obtained (250 mg, 98% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.15 (q, *J* = 7.1 Hz, 4H), 3.25 (s, 2H), 2.18 (d, *J* = 1.0 Hz, 6H), 1.27 (t, *J* = 7.1 Hz, 6H).

The spectral data are in agreement with those reported in literature.[2]

3 Synthesis of Hydride Acceptors

3.1 Preparation of 1-benzyl-3-carbamoylpyridin-1-ium bromide (BNA^+)[5]



BNA^+

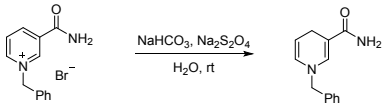
Nicotinamide (3.57 g, 29 mmol, 1.0 eqiv) was dissolved in 40 ml acetonitrile in a 100 ml round-bottom flask and benzyl bromide (5 g, 29 mmol, 1.0 eqiv) was added. The flask was equipped with a reflux condenser and heated to reflux for 8 hours, after which time a white precipitate formed. The reaction mixture was cooled to room temperature and the precipitate was filtered and washed with cold acetonitrile. The filtrate was dried under high vacuum over P_2O_5 and afforded target compound as white powder (8.11 g, 95% yield).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.65 (t, *J* = 1.5 Hz, 1H), 9.31 (dt, *J* = 6.1, 1.3 Hz, 1H), 8.98 (dt, *J* = 8.2, 1.4 Hz, 1H), 8.60 (s, 1H), 8.29 (dd, *J* = 8.1, 6.1 Hz, 1H), 8.19 (s, 1H), 7.65 – 7.52 (m, 2H), 7.51 – 7.36 (m, 3H), 5.93 (s, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 162.6, 146.3, 144.7, 143.8, 134.0, 133.9, 129.4, 129.2, 129.0, 128.2, 63.4.

The spectral data are in agreement with those reported in literature.[6]

3.2 Preparation of 1-benzyl-1,4-dihydropyridine-3-carboxamide (BNAH)[5]

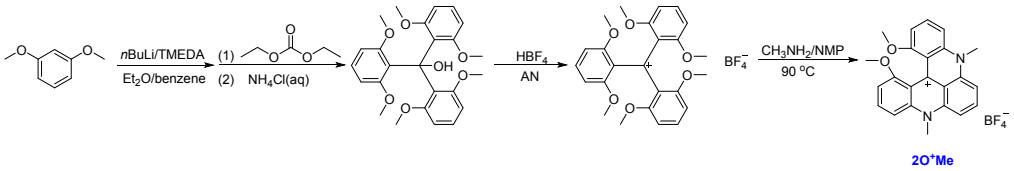


To a 250 ml round-bottom flask was added BNA^+ (2.93 g, 10 mmol, 1.0 eqiv), $NaHCO_3$ (4.2 g, 50 mmol, 5.0 eqiv) and distilled water (60 ml). $Na_2S_2O_4$ (8.7 g, 50 mmol, 5.0 eqiv) was added in small portions and the reaction mixture was stirred at room temperature in the dark for 3 hours. The precipitate was filtered, washed with cold water, recrystallized, and dried under high vacuum over P_2O_5 to afford target compound as yellow plates (1.15 g, 54% yield).

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.38 (dd, J = 8.3, 6.2 Hz, 2H), 7.30 (td, J = 7.3, 6.7, 1.7 Hz, 3H), 6.96 (d, J = 1.7 Hz, 1H), 5.84 (dd, J = 8.1, 1.7 Hz, 1H), 5.54 (s, 2H), 4.71 (dt, J = 8.1, 3.4 Hz, 1H), 4.30 (s, 2H), 3.05 (d, J = 1.7 Hz, 1H).

The spectral data are in agreement with those reported in literature.[5]

3.3 Preparation of 1,13-dimethoxy-5,9-dimethyl-5,9-dihydro-13*bH*-quinolino[2,3,4-*kl*]acridin-13*b*-ylium tetrafluoroborate ($2O^+Me$)[7]



To a flame-dried round-bottom flask was added 1,2-dimethoxybenzene (9.67 g, 70 mmol, 3.5 eqiv), TMEDA (8.13 g, 70 mmol, 3.5 eqiv), and 35 ml dry benzene under Ar. The flask was immersed in an acetone/liquid nitrogen bath to cool down to -78 °C for 30 minutes. Then *n*-BuLi (28 ml, 2.5 M) was added dropwise. The reaction mixture was warmed to room temperature very slowly and then cool down to -78 °C again. Diethyl carbonate (2.36 g, 20 mmol, 1.0 eqiv) dissolved in 20 ml dry benzene was added slowly and the mixture was stirred overnight. The flask was equipped with a reflux condenser and heated to reflux for 2 hours. The benzene was distilled out and the residue extracted with ethyl acetate. The crude product was used in the next step without further purification.

The crude product was dissolved in ethanol and aqueous HBF_4 was added slowly, the reaction mixture turned deep blue immediately. The solution was diluted with petroleum ether and precipitate formed. After filtration, the solid was recrystallization from acetonitrile/diethyl ether, dried under vacuum over P_2O_5 to afford target compound (1.3 g, two step yield: 12.5%).

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.62 (t, J = 8.5 Hz, 3H), 6.59 (d, J = 8.5 Hz, 6H), 3.54 (s, 18H).

^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 182.6, 163.7, 143.2, 126.4, 106.0, 57.4.

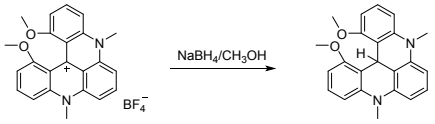
To a 100 ml round-bottom flask was added tris(2,6-dimethoxyphenyl)methylium tetrafluoroborate (812 mg, 1.6 mmol), methylamine solution in ethanol (4.6 g, 30% wt), and NMP (30 ml). The reaction mixture was heated to 90 °C for 2 hours and cooled to room temperature. Addition of water and small amount of HBF_4 solution afforded target compound as precipitate, which was filtered, recrystallized from acetonitrile/diethyl ether, dried over P2O5 under high vacuum. The desired product was obtained as dark green powder (500 mg, 70% yield).

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 8.07 (t, J = 8.5 Hz, 1H), 7.95 – 7.77 (m, 2H), 7.41 (dd, J = 8.8, 6.5 Hz, 4H), 6.90 (d, J = 8.0 Hz, 2H), 4.04 (s, 6H), 3.71 (s, 6H).

^{13}C NMR (101 MHz, CD_3CN) δ 160.1, 143.6, 142.9, 140.2, 137.8, 137.1, 119.8, 113.9, 108.5, 105.8, 104.1, 56.4, 38.2.

The spectral data are in agreement with those reported in literature.[7d, 7e]

3.4 Preparation of 1,13-dimethoxy-5,9-dimethyl-9,13*b*-dihydro-5*H*-quinolino[2,3,4-*kl*]acridine (2OHMe)[7d]



2O⁺Me 2OHMe

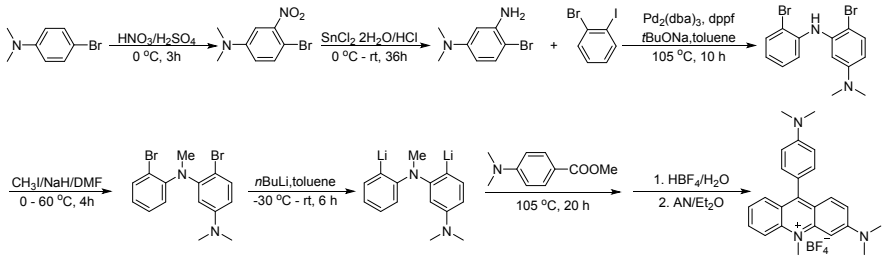
$NaBH_4$ (37 mg, 1 mmol, 3.0 eqiv) was slowly added to a solution of 2O$^+$Me (150 mg, 0.34 mmol, 1.0 eqiv) in CH_3OH (20 ml). After 20 minutes, the mixture was concentrated in vacuo, and the crude residue was purified by flash column chromatography (petroleum/ethyl acetate 20:1) to afford product as white solid (110 mg, 91% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 (t, *J* = 8.2 Hz, 1H), 7.10 (q, *J* = 7.9 Hz, 2H), 6.71 (dd, *J* = 8.1, 0.9 Hz, 1H), 6.59 – 6.44 (m, 6H), 4.74 (s, 1H), 3.74 (s, 3H), 3.48 (s, 3H), 3.43 (s, 3H), 3.31 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.1, 157.2, 146.9, 146.0, 142.2, 139.8, 127.7, 126.5, 125.7, 117.5, 111.4, 111.3, 106.6, 106.1, 105.5, 105.2, 103.8, 101.3, 56.3, 55.4, 34.5, 33.4, 32.6.

The spectral data are in agreement with those reported in literature.[7d]

3.5 Preparation of 3-(dimethylamino)-9-(4-(dimethylamino)phenyl)-10-methylacridin-10-ium tetrafluoroborate (p3-Acr$^+$)



p3-Acr+

Hydride acceptor p3-Acr$^+$ was synthesized according to modified literature procedure:[8]

To a 500 ml round-bottom flask was added 4-bromo-*N*,*N*-dimethylaniline (25 g, 125 mmol), H_2SO_4 (50 ml) and the flask was immersed in an ice-water bath for 30 minutes. HNO_3 (8 ml, 150 mmol) was added slowly to the reaction mixture. The ice-water bath was maintained for another 1 hour then the mixture was warmed to rt for 3 hours until TLC indicated complete conversion of starting material. The reaction mixture was poured into ice-water carefully and neutralized with NaOH until orange precipitate formed. The solid was filtered, washed with large amount of water and used in the next step without further purification.

The obtained orange solid (~ 125 mmol) was dissolved in HCl (100 ml) and cooled with ice-water bath. $SnCl_2 \bullet H_2O$ (85 g, 375 mmol, 3.0 eqiv) was dissolved in HCl and added into the reaction mixture slowly. The mixture was stirred for 2 days and TLC indicated complete conversion of starting material. The mixture was diluted with water and filtered. The filtrate was neutralized with NaOH and extracted with ethyl acetate. The organic layers was combined and filtered through a short pad of silica gel. Evaporation of solvent afforded product as yellow solid (22.3 g, 83% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 8.7 Hz, 1H), 6.20 – 6.08 (m, 2H), 4.25 (s, 2H), 2.91 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.0, 144.4, 132.5, 105.2, 99.8, 97.0, 40.6.

To a flame-dried, round-bottom flask was added 4-bromo-N^1,N^1-dimethylbenzene-1,3-diamine (3.9 g, 18 mmol), 1-bromo-2-iodobenzene (5.1 g, 18 mmol), *t*BuONa (2.6 g, 27 mmol), $Pd_2(dba)_3$ (411 mg, 0.45 mmol), dppf (498 mg, 0.9 mmol), and dry toluene (25 ml) under Ar. The mixture was heated to 105 °C and stirred overnight. The mixture was cooled to rt and quenched with water, extracted with ethyl acetate and purified by flash column chromatography (petroleum ether/ ethyl acetate 40:1 to 20:1). The product was obtained as white solid (5.45 g, 82% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.40 (d, *J* = 8.9 Hz, 1H), 7.36 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.22 (ddd, *J* = 8.4, 7.4, 1.5 Hz, 1H), 6.82 (ddd, *J* = 8.0, 7.3, 1.6 Hz, 1H), 6.69 (d, *J* = 2.9 Hz, 1H), 6.37 (s, 1H), 6.31 (dd, *J* = 8.9, 2.9 Hz, 1H), 2.91 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.7, 140.7, 140.0, 133.2, 133.1, 128.1, 121.9, 117.5, 113.8, 108.2, 103.2, 101.6, 40.7.

HRMS (ESI): calcd $C_{14}H_{15}Br_2N_2^+$ 370.9576, found 370.9564.

To a flame-dried, round-bottom flask was added the above obtained solid (5.45 g, 14.7 mmol, 1.0 eqiv), KH (736 mg, 18.4 mmol, 1.25 eqiv), and dry DMF (40 ml). The mixture was heated to 60 °C for 30 minutes then CH_3I (2.61 g, 18.4 mmol, 1.25 eqiv) was added. The mixture was stirred for 6 hours and cooled to rt. The mixture was quenched with aqueous $NaHCO_3$, diluted with water and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column chromatography (petroleum ether/ethyl acetate 40:1 to 20:1). The target compound was obtained as beige oil which solidified overnight as white solid (5.65 g, 98% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.39 – 7.29 (m, 1H), 7.28 – 7.17 (m, 1H), 7.02 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.97 – 6.89 (m, 1H), 6.34 (d, *J* = 7.0 Hz, 2H), 3.23 (s, 3H), 2.88 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.8, 149.0, 149.0, 134.3, 134.3, 128.1, 124.6, 124.0, 120.5, 109.4, 108.3, 106.6, 41.4, 40.7.

HRMS (ESI): calcd $C_{15}H_{17}Br_2N_2^+$ 384.9732, found 384.9724.

To a flame-dried, round-bottom flask was added 4-bromo-N^3-(2-bromophenyl)-N^1,N^1,N^3-trimethylbenzene-1,3-diamine (1 g, 2.6 mmol, 1.0 eqiv) and dry toluene (30 ml). The flask was immersed in an acetonitrile/liquid nitrogen bath for 30 minutes then *n*BuLi (2.38 ml, 2.4 M, 2.2 eqiv) was added dropwise. The mixture was slowly warmed to rt and stirred for 2 hours. Methyl 4-(dimethylamino)benzoate (350 mg, 1.95 mmol, 0.8 eqiv) was dissolved in dry toluene (20 ml) and added slowly. The reaction mixture was heated to 105 °C and stirred overnight. The mixture was cooled to rt, quenched with aqueous HBF_4, and extracted with dichloromethane. The organic layers were combined, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash column chromatography (CH_2Cl_2/CH_3OH 30:1). Recrystallization from acetonitrile/diethyl ether twice afforded product as brown powder (210 mg, 24% yield).

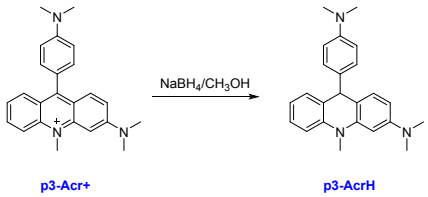
^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 8.17 (d, *J* = 9.0 Hz, 1H), 8.03 (ddd, *J* = 8.8, 6.9, 1.5 Hz, 1H), 7.90 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.76 (d, *J* = 9.8 Hz, 1H), 7.58 – 7.49 (m, 1H), 7.34 (dd, *J* = 9.9, 2.4 Hz, 1H), 7.29 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 2.3 Hz, 1H), 4.32 (s, 3H), 3.34 (s, 6H), 3.09 (s, 6H).

^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 158.0, 157.3, 152.4, 145.7, 141.6, 136.1, 133.3, 132.5,

131.2, 125.5, 124.5, 121.6, 121.0, 118.6, 117.7, 112.5, 93.0, 41.3, 40.4, 37.6.

HRMS (ESI): calcd $C_{24}H_{26}N_3^+$ 356.2121, found 356.2117.

3.6 Preparation of 9-(4-(dimethylamino)phenyl)-N,N,10-trimethyl-9,10-dihydroacridin-3-amine (p3-AcrH)



$NaBH_4$ (49 mg, 1.3 mmol, 3.0 eqiv) was slowly added to a solution of p3-Acr^+ (190 mg, 0.43 mmol, 1.0 eqiv) in CH_3OH (20 ml). After 20 minutes, the mixture was concentrated in vacuo, and the crude residue was purified by flash column chromatography (petroleum/ethyl acetate 10:1) to afford product as oily residue (96 mg, 62% yield), which easily turned red when exposed to air.

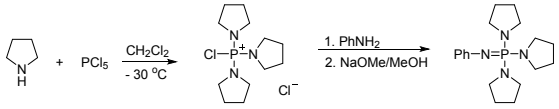
^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.18 (d, J = 7.4 Hz, 2H), 7.00 (dd, J = 8.7, 4.5 Hz, 2H), 6.93 – 6.81 (m, 3H), 6.57 (d, J = 8.7 Hz, 2H), 6.42 – 6.30 (m, 2H), 4.99 (s, 1H), 3.39 (s, 3H), 2.92 (s, 6H), 2.79 (s, 6H).

^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 151.7, 150.5, 143.9, 143.5, 136.1, 129.8, 129.3, 129.2, 128.4, 127.8, 121.2, 117.3, 113.7, 113.6, 106.6, 98.6, 47.4, 41.1, 41.0, 33.7.

HRMS (ESI): calcd $C_{24}H_{28}N_3^+$ 358.2278, found 358.2268.

4 Synthesis of Super Bases[9]

4.1 Preparation of (phenylimino)tripyrrolidinophosphorane



Phosphorous pentachloride (10.4 g, 50 mmol) was stirred in dry dichloromethane (75 ml) and immersed in a dry-ice bath under Ar protection. Pyrrolidine (12.4 ml, 150 mmol) was added dropwise while maintaining the mixture below -30 °C. Triethylamine (28 ml, 200 mmol) was added slowly and kept temperature under -30 °C. The mixture was slowly warm up and stirred for another 2 hours The triethylamine hydrochloride was filtered and the filtrate was concentrated in vacuo. Then dry THF (50 ml) was added to the residue. The mixture was cooled to -10 °C, then aniline (5.12 g, 55 mmol) was mixed with triethylamine (7.5 ml, 55mmol) and added dropwise over 30 minutes. After addition, the mixture was heated to 60 °C for 40 minutes then stirred at room temperature overnight. The triethylamine hydrochloride was filtered and THF was removed in vacuo. The residue was slurred in ethyl acetate and dried to afford white solid (10 g, 60% yield).

The above obtained white solid (2.6 g, 7.0 mmol) was dissolved in dry acetonitrile (20 ml), freshly prepared CH_3OK (from KH and CH_3OH) was added and white precipitate formed immediately. The solid was filtered and filtrate was concentrated in vacuo. The residue was extracted with petroleum ether/ethyl acetate (1:1, v/v) and combined. Evaporation of solvent afforded product as white solid (2.3 g, 98%).

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 6.97 (t, J = 7.1 Hz, 2H), 6.64 (d, J = 7.9 Hz, 2H), 6.48 (t, J = 7.2 Hz, 1H), 3.25 – 3.03 (m, 12H), 1.87 – 1.70 (m, 12H).

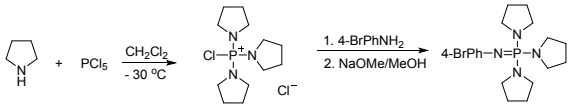
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 153.5, 129.4, 123.6, 123.4, 116.3, 47.5, 47.5, 27.1,

27.0.

^{31}P NMR (162 MHz, Acetonitrile-d_3) δ 8.0.

The spectral data are in agreement with those reported in literature.[9b]

4.2 Preparation of (4-bromophenylimino)tripyrrolidinophosphorane



Synthesized from phosphorous pentachloride, pyrrolidine, and 4-bromoanaline. Product was obtained as light yellow solid (3.0 g, two step yield 60%).

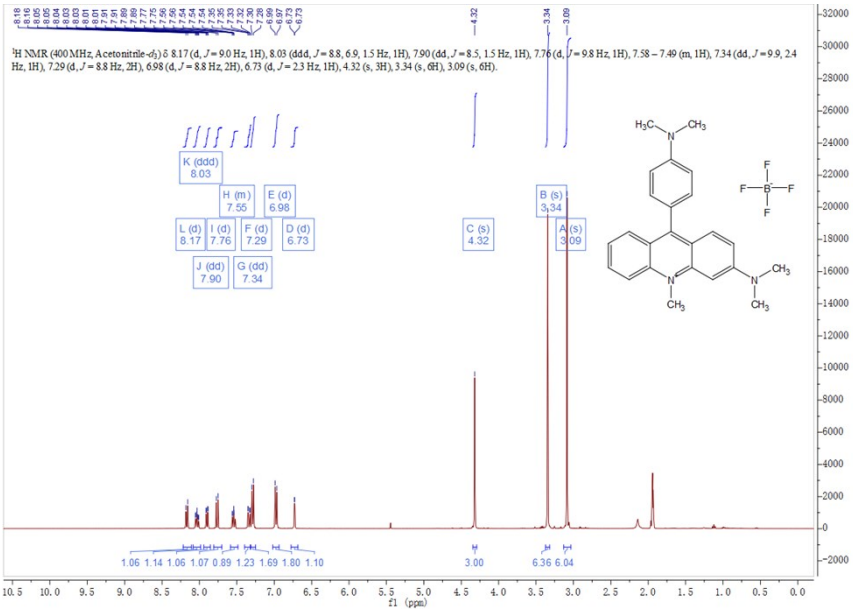
^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.05 (dd, J = 8.5, 1.2 Hz, 2H), 6.55 (d, J = 8.5 Hz, 2H), 3.22 – 3.05 (m, 12H), 1.87 – 1.71 (m, 12H).

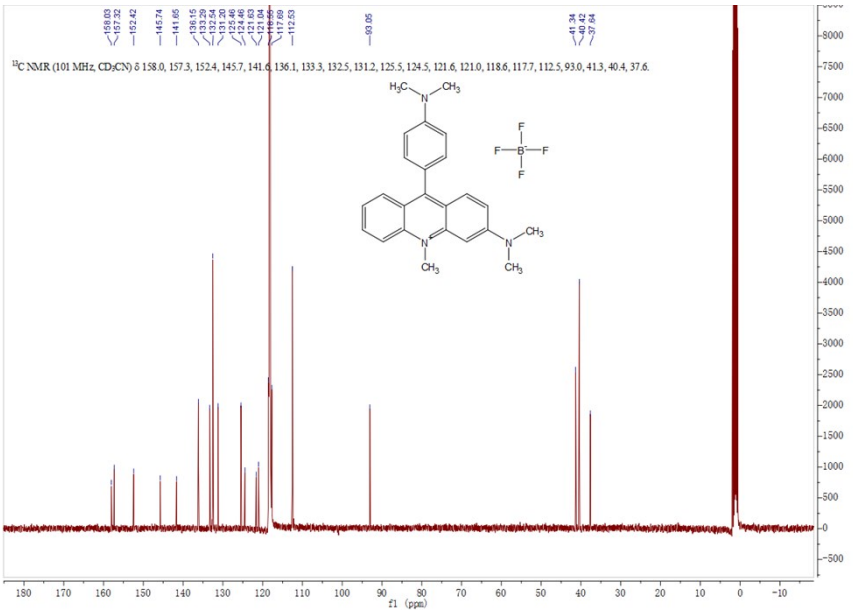
^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 153.0, 132.0, 125.2, 125.1, 107.1, 47.5, 47.5, 27.1, 27.0.

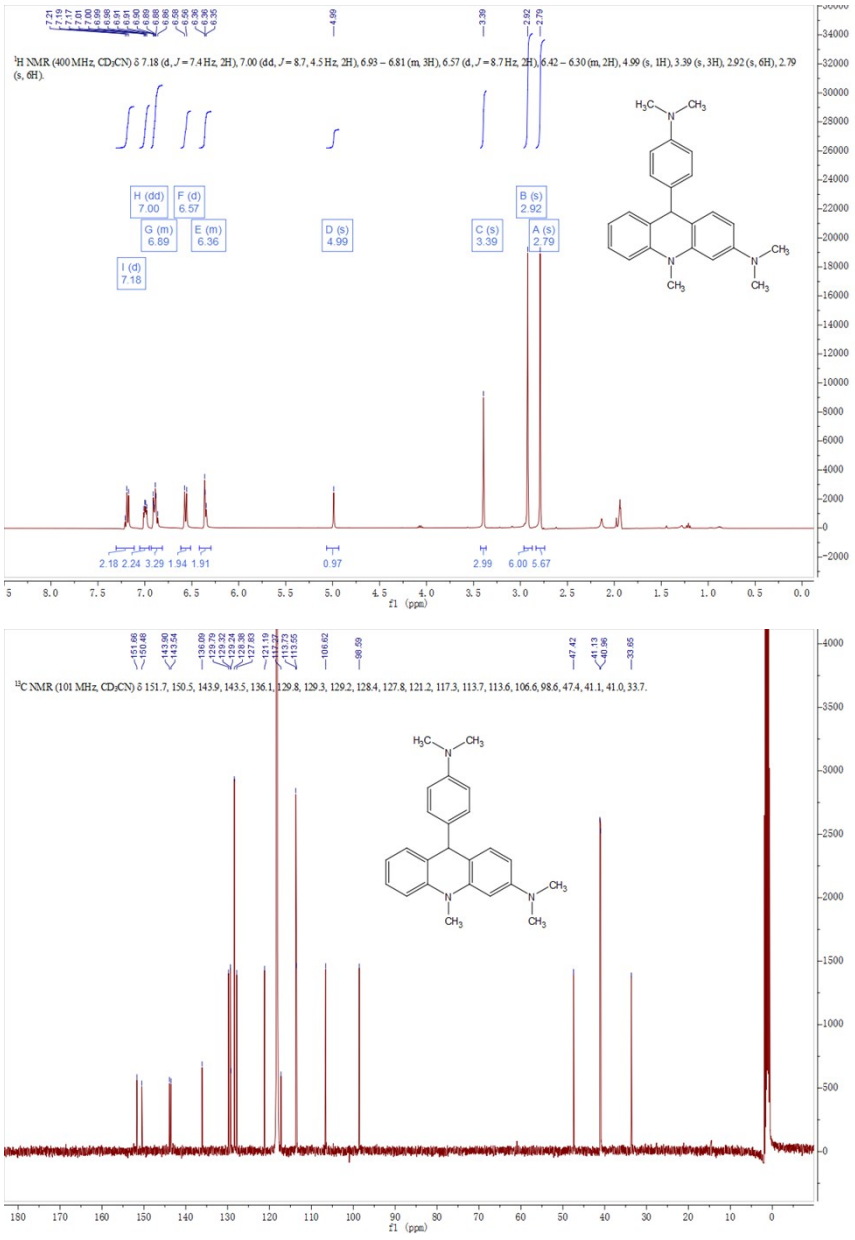
^{31}P NMR (162 MHz, Acetonitrile-d_3) δ 9.1.

The spectral data are in agreement with those reported in literature.[9b]

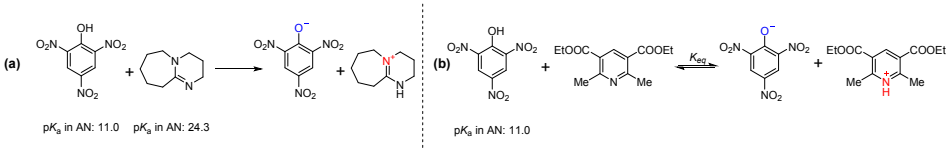
5 ^{1}H and ^{13}C NMR Spectra







6 pK_{aH} Measurement of Hantzsch Pyridine in Acetonitrile



Scheme S1 pK_{aH} determination of diethyl Hantzsch pyridine in acetonitrile: (a) determination of molar extinction coefficient (b) pK_{aH} determination using picric acid as indicator

General Information: Acetonitrile (purity > 99.9%, Super Dry, water ≤ 30 ppm) was purchased from J&K Scientific. Picric acid was recrystallized three time prior to use. Hantzsch pyridine was purified by flash column chromatography.

The pK_{aH} determination was performed in a two-step procedure that was modified according to literature[10]: (a) The molar extinction coefficient of picric acid anion at certain region of UV-vis was determined by titrating a solution of base (DBU) with a solution picric acid and monitoring the

absorbance change. The molar extinction coefficient could be calculated by plotting the absorbance against the concentration of picric acid anion (Figure S1). (b) Several aliquots of the Hantzsch pyridine solution with known concentration were then added to a certain amount of picric acid solution, and the absorbance of picric acid anion was recorded at the same wavelength where molar extinction coefficient was determined (Figure S2). The concentration of picric acid anion could be calculated according to Beer's Law. The concentration of the other three species could be calculated according to the conservation of charge and mass, thus the pK_{aH} of Hantzsch pyridine was determined for each aliquot added.

The choice of wavelength should have little influence on the result. To make sure the reproducibility and accuracy, we choose the region from 450nm to 470nm to calculate the molar extinction coefficient and pK_{aH}. This method was verified by measuring 3-acetylpyridine whose pK_a in acetonitrile was reported to be 10.8 in literature.

At least two independent runs were carried out to measuring the pK_{aH} of Hantzsch pyridine in acetonitrile. According to these measurements, the pK_{aH} of Hantzsch pyridine in acetonitrile is assigned to be 10.4.

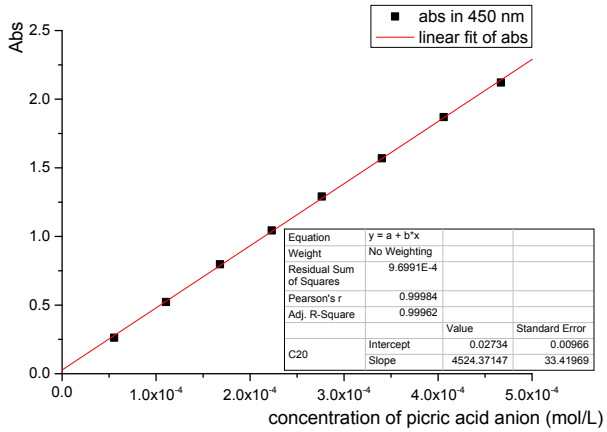


Figure S1 Determination of molar extinction coefficient of picric acid anion at 450 nm.

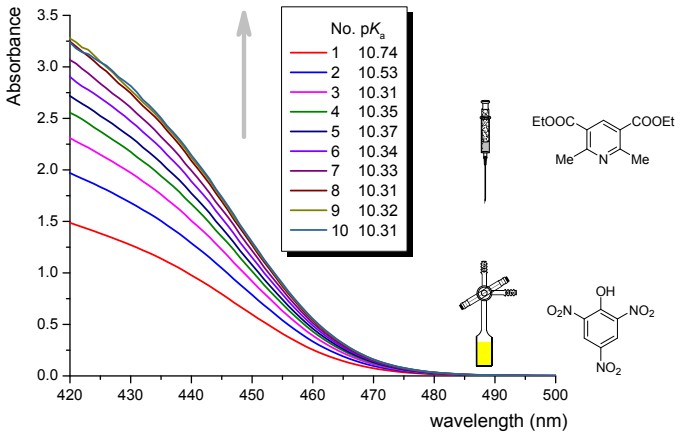


Figure S2 UV-vis spectra of pK_a determination using picric acid as indicator.

7 UV-vis Spectra of Hydride Acceptors and Stability Tests

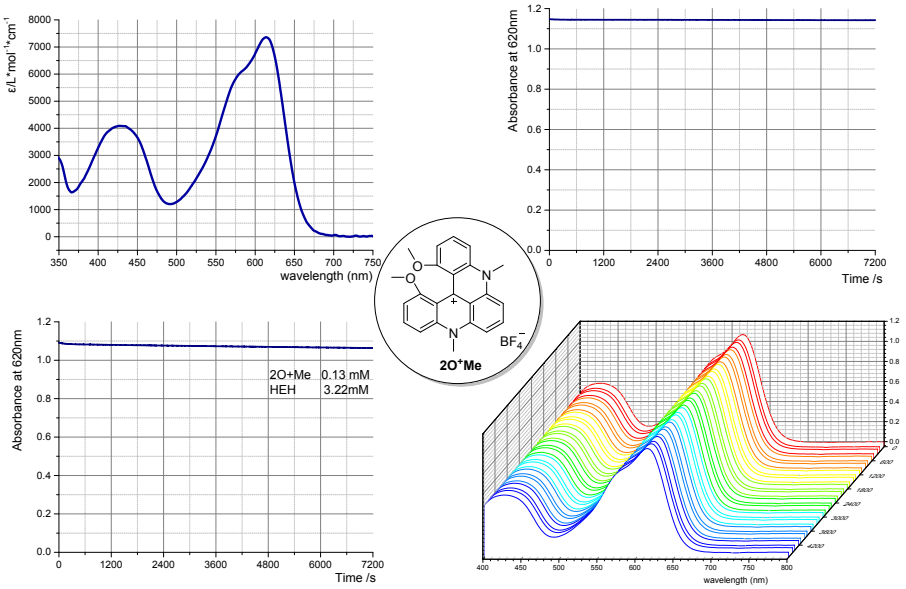


Figure S3 UV-vis spectra and stabilities test of 2O⁺Me.

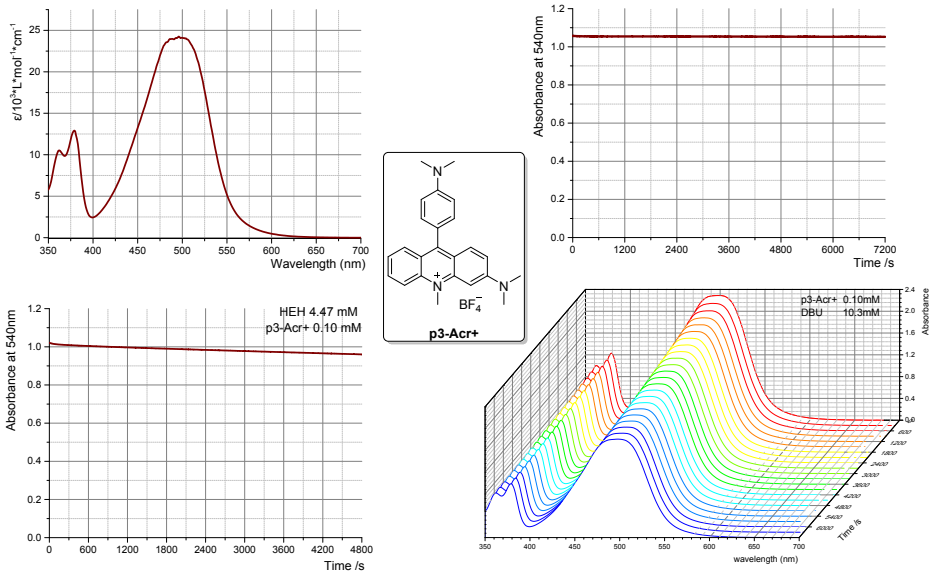


Figure S4 UV-vis spectra and stabilities test of p3-Acr⁺.

8 Hydride Transfer Method for Hydricity Determinations

The hydride affinity of compound p3-Acr⁺ in acetonitrile was determined by the hydride transfer method using BNAH as reference, whose hydricity was previously reported in acetonitrile (ΔG_{H^-} = 59 kcal/mol). The hydride transfer reaction between p3-Acr⁺ and BNAH was monitored by NMR spectrometer and the reaction underwent cleanly over 7 days in acetonitrile-d_3 (Figure S5). The reaction equilibrium constant was obtained by integration of ^{1}H NMR spectrum. With the calculated K_{eq} to be 29.1, the free energy for hydride transfer between p3-Acr⁺ and BNAH in acetonitrile was 2.0 kcal/mol. However, because the BNAH in the reaction was almost consumed

completely, it is expected that the hydricity of p3-AcrH in acetonitrile is larger than 61.0 kcal/mol.

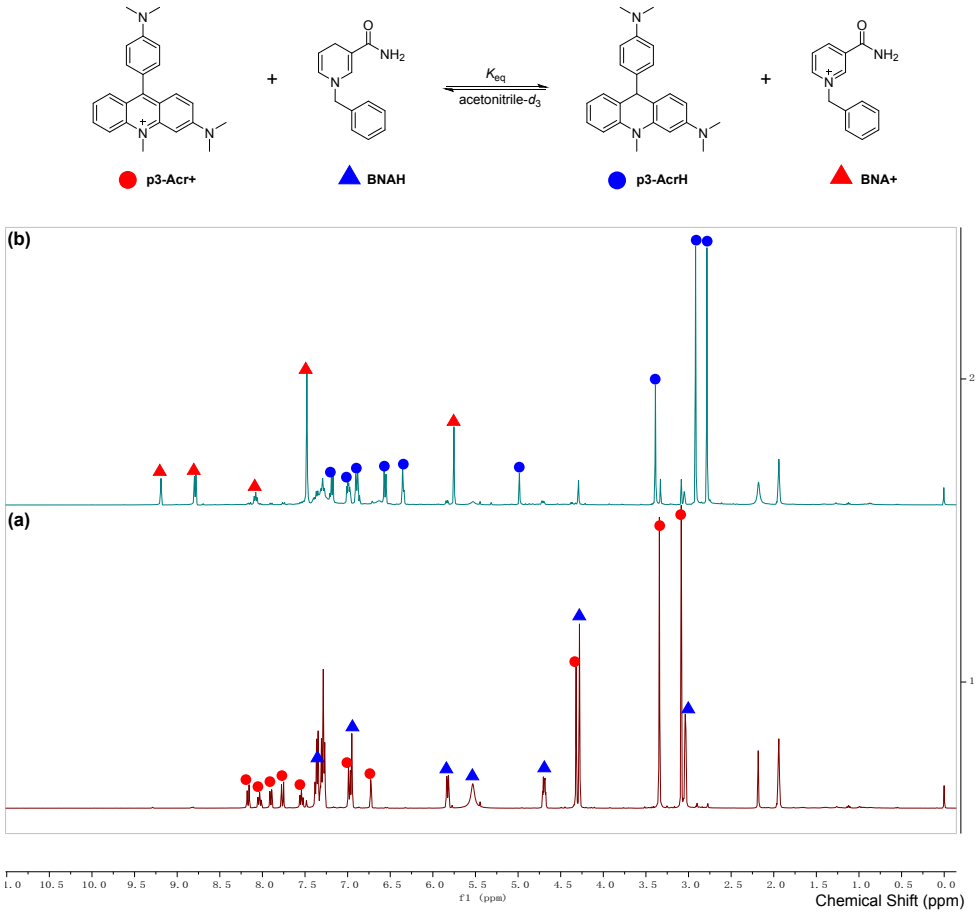
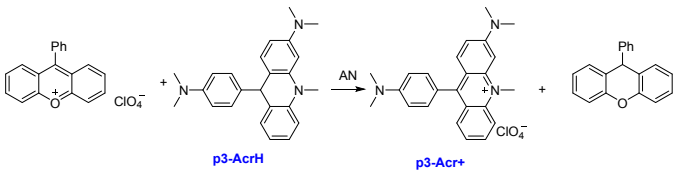


Figure S5 Hydride transfer method for determination of p3-Acr$^+$ using BNAH as reference.

9 Isothermal Titration Calorimetry (ITC) Experiment for Hydricity Determinations



The titration experiments were carried out on a MicroCal VP-ITC isothermal titration calorimeter in acetonitrile at 298 K. The heat of reaction was determined following 10-20 automatic injections from a syringe containing $PhXn^+ClO_4^-$ solution into the reaction cell containing hydride donor solution. Time interval between every two injections was set 200-300 seconds. The reaction heat was obtained by integration of each peak except the first one. The reaction heat for the hydride transfer reaction of p3-AcrH with $PhXn^+ClO_4^-$ was 26.0 ± 0.6 kcal/mol, which was the average values of at least three independent runs.

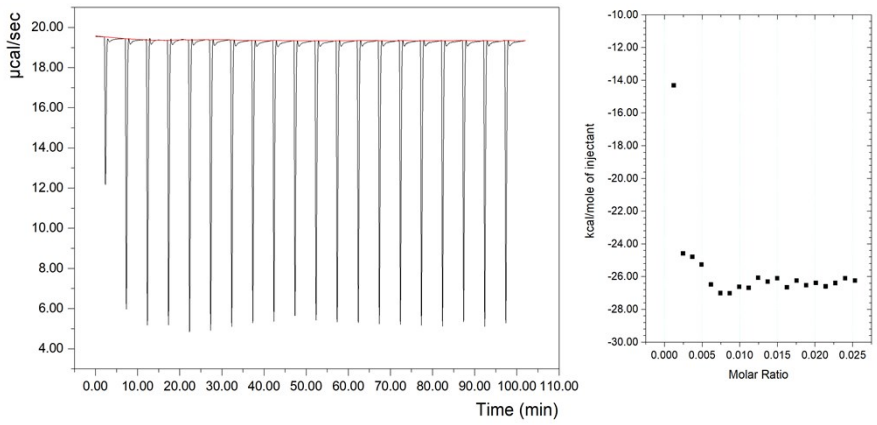
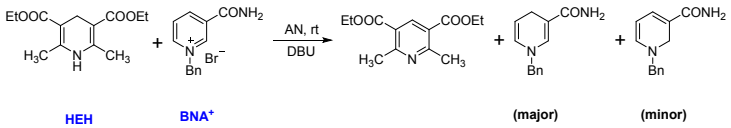


Figure S6 Isothermal titration calorimetry (ITC) for the reaction heat of p3-AcrH with 9-phenylxanthylium cation ($PhXn^+ClO4^-$) in acetonitrile at 298 K.

10 Base-Promoted Hydride Transfer Reactions

10.1 BPHyT reaction of HEH and BNA^+



To a 100 ml round bottom flask was added Hantzsch ester (512.0 mg, 2.0 mmol), BNA^+ (595 mg, 2.0 mmol,), DBU (378 mg, 2.5 mmol) and acetonitrile (25 ml) under Ar. The mixture was stirred for 2 hours at room temperature. Flash column chromatography afforded 2,6-dimethylpyridine-3,5-dicarboxylate (400 mg) as white solid. BNA^+ was reduced as 1,4- and 1,2-isomers which could not be separated by flash column chromatography. Unreacted Hantzsch esters was recovered (110 mg).

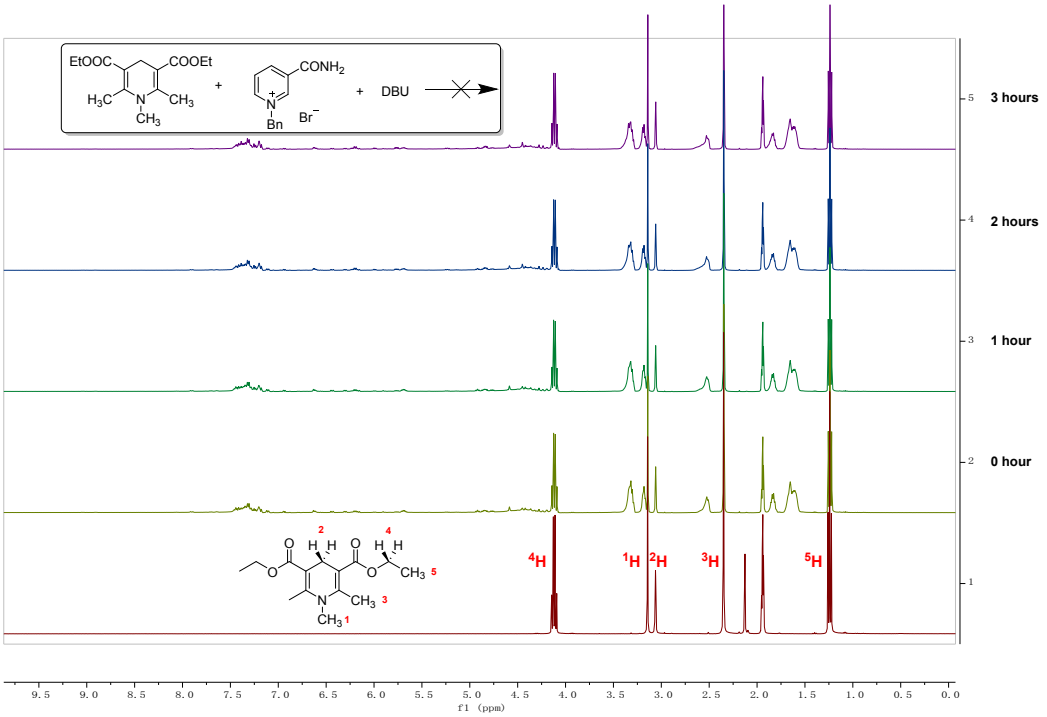
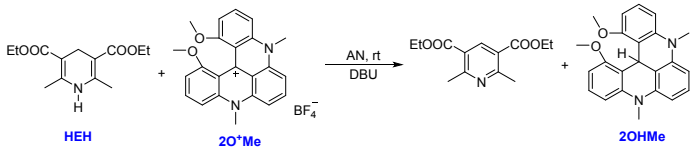


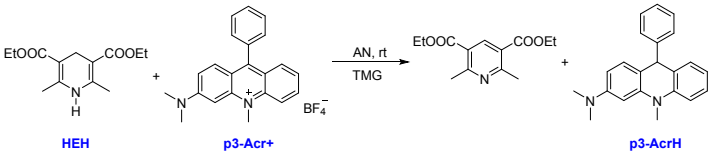
Figure S7 ^{1}H NMR spectra of BPHyT reaction between *N*-Me-HEH and BNA$^+$.

10.2 BPHyT reaction of HEH and 2O$^+$Me



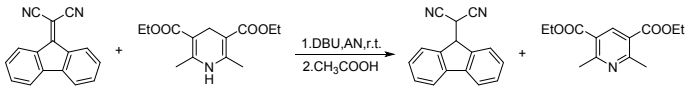
To a reaction tube was added Hantzsch ester (126.6 mg, 0.5 mmol, 5.0 eqiv), 2O$^+$Me (44.4 mg, 0.1 mmol, 1.0 eqiv), DBU (152.2 mg, 1 mmol, 10.0 eqiv) and acetonitrile (5 ml) under Ar. The mixture was stirred for 30 minutes at room temperature and TLC indicated complete conversion of 2O$^+$Me. Flash column chromatography afforded 2,6-dimethylpyridine-3,5-dicarboxylate (22.3 mg) and 2OHMe (30.4 mg, 85% yield) as a white solid. Unreacted Hantzsch esters was recovered (91.0 mg).

10.3 BPHyT reaction of HEH and p3-Acr$^+$



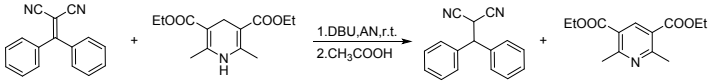
To a reaction tube was added Hantzsch ester (126.6 mg, 0.5 mmol, 5.0 eqiv), p3-Acr$^+$ (44.4 mg, 0.1 mmol, 1.0 eqiv), TMG (115 mg, 1 mmol, 10.0 eqiv) and acetonitrile (5 ml) under Ar. The mixture was stirred for 10 minutes at room temperature and TLC indicated complete conversion of p3-Acr$^+$. Flash column chromatography afforded 2,6-dimethylpyridine-3,5-dicarboxylate (23.0 mg) and p3-AcrH (31.1 mg, 87% yield) as a white solid. Unreacted Hantzsch esters was recovered (89 mg).

10.4 BPHyT reaction of HEH and 2-(9H-fluoren-9-ylidene)malononitrile



To a reaction tube was added Hantzsch ester (50.6 mg, 0.2 mmol, 1.0 eqiv), 2-(9*H*-fluoren-9-ylidene)malononitrile (46.0 mg, 0.2 mmol, 1.0 eqiv), DBU (30.4 mg, 0.2 mmol, 1.0 eqiv) and acetonitrile (5.0 ml) under Ar. The mixture was stirred until TLC indicated complete conversion of starting material. Flash column chromatography afforded 2-(9*H*-fluoren-9-yl)malononitrile (36 mg, 77% yield) as a white solid.

10.5 BPHyT reaction of HEH and 2-(diphenylmethylene)malononitrile

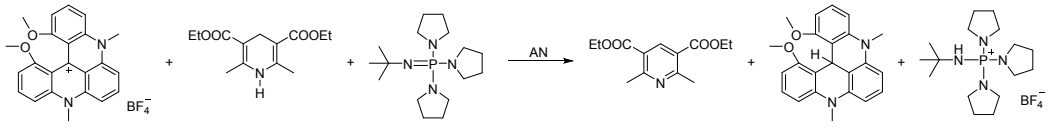


To a reaction tube was added Hantzsch ester (50.6 mg, 0.2 mmol, 1.0 eqiv), 2-(diphenylmethylene)malononitrile (46.0 mg, 0.2 mmol, 1.0 eqiv), DBU (30.4 mg, 0.2 mmol, 1.0 eqiv) and acetonitrile (5.0 ml) under Ar. The mixture was stirred until TLC indicated complete conversion of starting material. Flash column chromatography afforded 2-benzhydrylmalononitrile (38 mg, 82% yield) as a white solid.

11 Kinetic Experiments

Kinetic experiments were performed in acetonitrile using a Hitachi U-3900H spectrometer and a stopped-flow connected to a circulating bath to regulate the temperature of cell compartments. The hydride transfer reaction rate was measured at 293 K by monitoring the absorbance decrease of **2O$^+$Me** at 620 nm or **p3-Acr$^+$** at 540 nm under pseudo-first-order conditions (base and Hantzsch esters in over 20-fold excess). The pseudo-first-order rate constants were then converted to k_3 by linear correlation of k_{obs} against the concentration of bases and Hantzsch ester.

11.1 BPHyT reactions of 2O$^+$Me with Hantzsch esters and bases

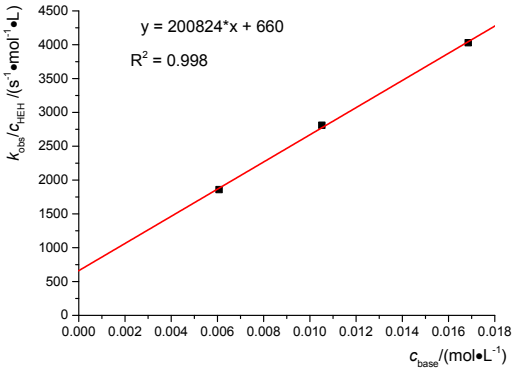


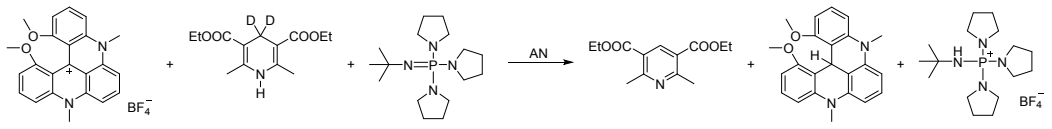
2O$^+$Me HEH tBuP1pyrr 2OHMe

Table S1 kinetics of the reaction of **2O$^+$Me** (1.26×10^{-4} mol^{-1} L^{-1}) with Hantzsch (HEH), *t*BuP1pyrr as base, λ = 620 nm.

No.	$[\mathbf{HEH}]_0$ / mol^{-1} L	$[\mathbf{Base}]_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	3.68×10^{-3}	6.07×10^{-3}	6.85
2	3.68×10^{-3}	1.05×10^{-2}	10.34
3	3.68×10^{-3}	1.68×10^{-2}	14.94

$k_3 = 2.00 \times 10^5$ L^2 mol^{-2} s^{-1}



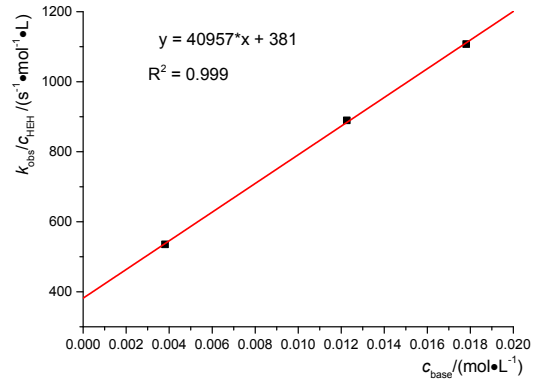


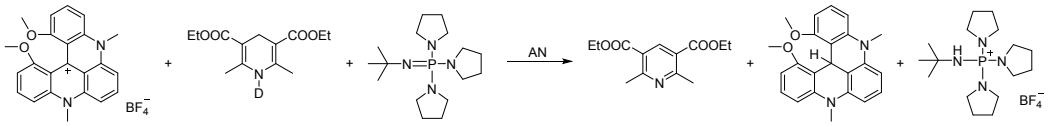
2O$^+$Me d_2-HEH tBuP1pyrr 2OHMe

Table S2 kinetics of the reaction of **2O$^+$Me** (1.26×10^{-4} mol^{-1} L^{-1}) with d_2-Hantzsch (d_2-HEH), *t*BuP1pyrr as base, λ = 620 nm.

No.	$[d_2\text{-}\mathbf{HEH}]_0$ / mol^{-1} L	$[\mathbf{Base}]_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	3.81×10^{-3}	5.39×10^{-3}	2.04
2	3.81×10^{-3}	1.23×10^{-2}	3.39
3	3.81×10^{-3}	1.78×10^{-2}	4.22

$k_3 = 4.10 \times 10^4$ L^2 mol^{-2} s^{-1}



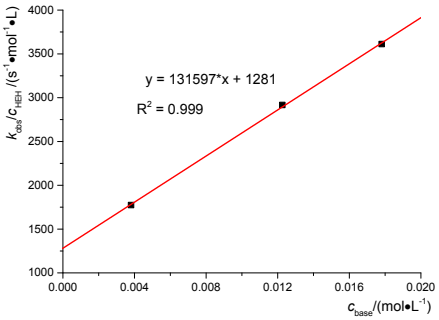


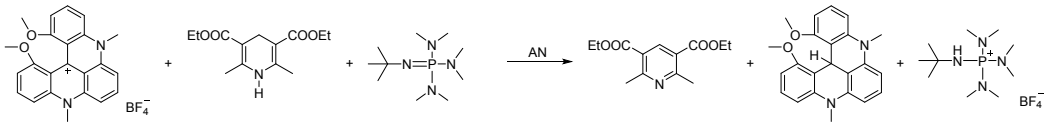
2O⁺Me **ND-HEH** **tBuP1pyrr** **2OHMe**

Table S3 kinetics of the reaction of **2O⁺Me** (1.26 × 10^{-4} mol^{-1} L^{-1}) with ND-Hantzsch (ND-HEH), *t*BuP1pyrr as base, λ = 620 nm.

No.	[ND-**HEH**]$_0$ / mol^{-1} L	[**Base**]$_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	4.07 × 10^{-3}	5.39 × 10^{-3}	7.22
2	4.07 × 10^{-3}	1.23 × 10^{-2}	11.87
3	4.07 × 10^{-3}	1.78 × 10^{-2}	14.70

k_3 = 1.32 × 10^5 L^2 mol^{-2} s^{-1}



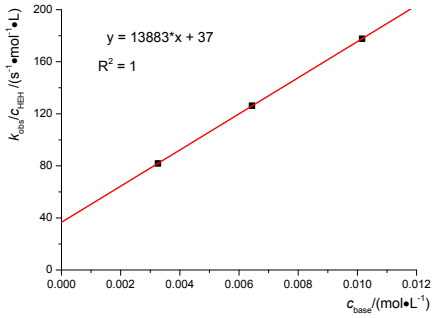


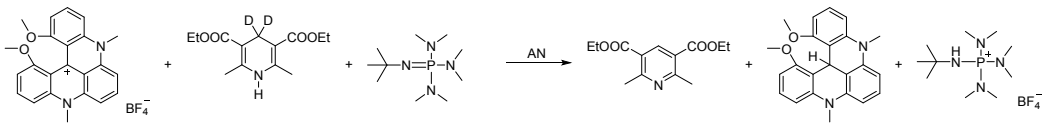
2O⁺Me **HEH** **tBuP1dma** **2OHMe**

Table S4 kinetics of the reaction of **2O⁺Me** (1.26 × 10^{-4} mol^{-1} L^{-1}) with Hantzsch (HEH), *t*BuP1dma as base, λ = 620 nm.

No.	[**HEH**]$_0$ / mol^{-1} L	[**Base**]$_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	3.58 × 10^{-3}	3.26 × 10^{-3}	0.29
2	3.58 × 10^{-3}	6.44 × 10^{-3}	0.45
3	3.58 × 10^{-3}	1.02 × 10^{-2}	0.64

k_3 = 1.39 × 10^4 L^2 mol^{-2} s^{-1}



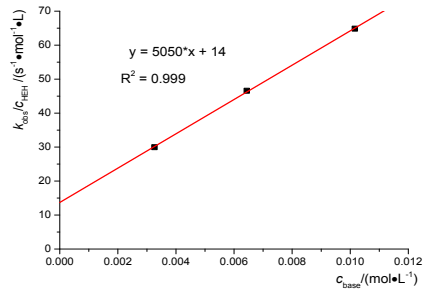


2O⁺Me **d_2-HEH** **tBuP1dma** **2OHMe**

Table S5 kinetics of the reaction of **2O⁺Me** (1.26 × 10^{-4} mol^{-1} L^{-1}) with d_2-Hantzsch (d_2-HEH), *t*BuP1dma as base, λ = 620 nm.

No.	[d_2-**HEH**]$_0$ / mol^{-1} L	[**Base**]$_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	3.67 × 10^{-3}	3.26 × 10^{-3}	0.11
2	3.67 × 10^{-3}	6.44 × 10^{-3}	0.17
3	3.67 × 10^{-3}	1.02 × 10^{-2}	0.24

k_3 = 5.05 × 10^3 L^2 mol^{-2} s^{-1}



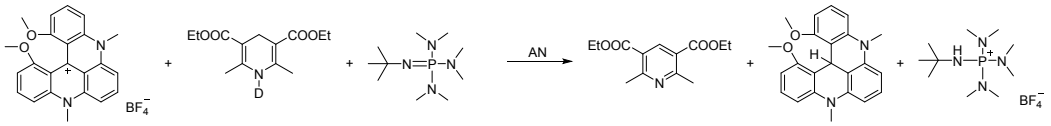
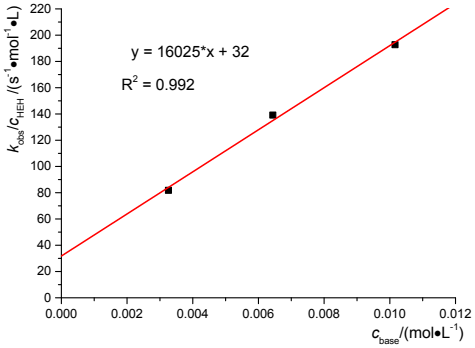


Table S6 kinetics of the reaction of **2O$^+$Me** (1.26 × 10^{-4} mol^{-1} L^{-1}) with ND-Hantzsch (ND-HEH), *t*BuP1dma as base, λ = 620 nm.

No.	[ND-**HEH**]$_0$ / mol^{-1} L	[**Base**]$_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	3.58 × 10^{-3}	3.26 × 10^{-3}	0.29
2	3.58 × 10^{-3}	6.44 × 10^{-3}	0.50
3	3.58 × 10^{-3}	1.02 × 10^{-2}	0.69

k_3 = 1.60 × 10^4 L^2 mol^{-2} s^{-1}



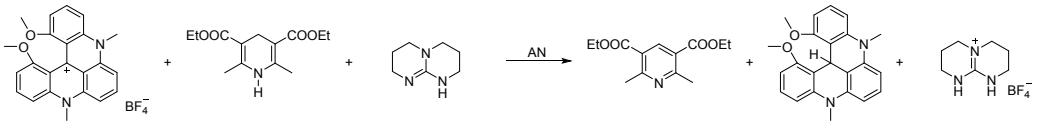


Table S7 kinetics of the reaction of **2O$^+$Me** (1.31 × 10^{-4} mol^{-1} L^{-1}) with Hantzsch (HEH), TBD as base, λ = 620 nm.

No.	[**HEH**]$_0$ / mol^{-1} L	[**Base**]$_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	3.38 × 10^{-3}	5.76 × 10^{-3}	5.36 × 10^{-2}
2	3.38 × 10^{-3}	1.23 × 10^{-2}	1.14 × 10^{-1}
3	3.38 × 10^{-3}	1.84 × 10^{-2}	1.66 × 10^{-1}

k_3 = 2.63 × 10^3 L^2 mol^{-2} s^{-1}

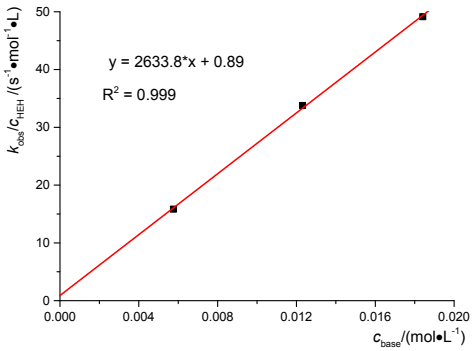
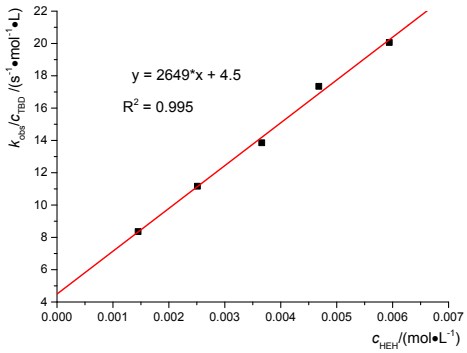


Table S8 kinetics of the reaction of **2O$^+$Me** (6.2 × 10^{-5} mol^{-1} L^{-1}) with Hantzsch (HEH), TBD as base, λ = 620 nm.

No.	[**HEH**]$_0$ / mol^{-1} L	[**Base**]$_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	1.45 × 10^{-3}	5.48 × 10^{-3}	4.58 × 10^{-2}
2	2.51 × 10^{-3}	5.48 × 10^{-3}	6.12 × 10^{-2}
3	3.66 × 10^{-3}	5.48 × 10^{-3}	7.59 × 10^{-2}
4	4.68 × 10^{-3}	5.48 × 10^{-3}	9.51 × 10^{-2}
5	5.94 × 10^{-3}	5.48 × 10^{-3}	1.10 × 10^{-1}

k_3 = 2.65 × 10^3 L^2 mol^{-2} s^{-1}



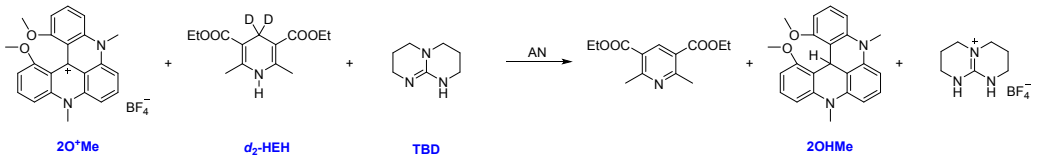
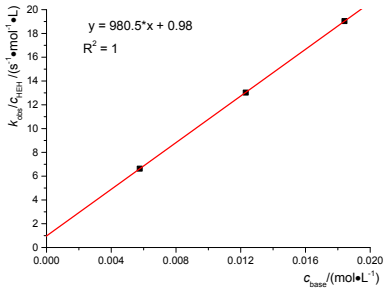


Table S9 kinetics of the reaction of **2O$^+$Me** (1.31×10^{-4} mol^{-1} L^{-1}) with d_2-Hantzsch (d_2-HEH), TBD as base, λ = 620 nm.

No.	$[d_2\text{-HEH}]_0$ / mol^{-1} L	$[\text{Base}]_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	3.76×10^{-3}	5.76×10^{-3}	2.49×10^{-2}
2	3.76×10^{-3}	1.23×10^{-2}	4.90×10^{-2}
3	3.76×10^{-3}	1.84×10^{-2}	7.16×10^{-2}

$k_3 = 9.80 \times 10^2$ L^2 mol^{-2} s^{-1}



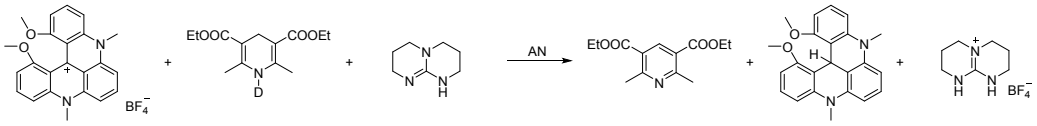
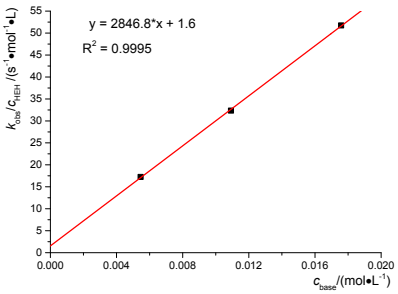


Table S10 kinetics of the reaction of **2O$^+$Me** (1.31×10^{-4} mol^{-1} L^{-1}) with ND-Hantzsch (ND-HEH), TBD as base, λ = 620 nm.

No.	$[\text{ND-HEH}]_0$ / mol^{-1} L	$[\text{Base}]_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	3.41×10^{-3}	5.76×10^{-3}	7.18×10^{-2}
2	3.41×10^{-3}	1.23×10^{-2}	1.34×10^{-1}
3	3.41×10^{-3}	1.84×10^{-2}	2.15×10^{-1}

$k_3 = 2.85 \times 10^3$ L^2 mol^{-2} s^{-1}



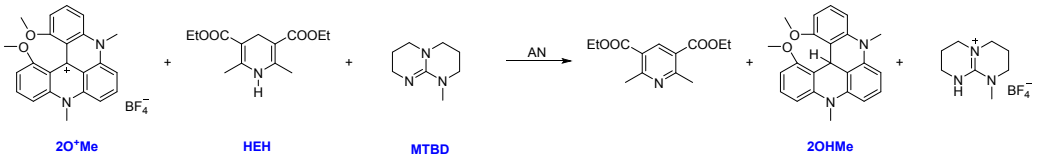
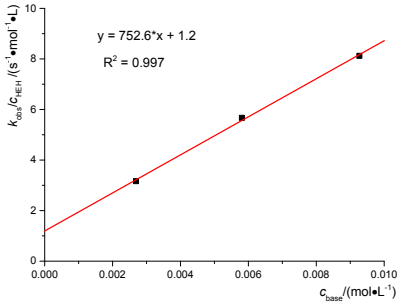


Table S11 kinetics of the reaction of **2O$^+$Me** (1.2×10^{-4} mol^{-1} L^{-1}) with Hantzsch (HEH), MTBD as base, λ = 620 nm.

No.	$[\text{HEH}]_0$ / mol^{-1} L	$[\text{Base}]_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	2.12×10^{-3}	2.69×10^{-3}	6.71×10^{-3}
2	2.12×10^{-3}	5.81×10^{-3}	1.20×10^{-2}
3	2.12×10^{-3}	9.27×10^{-3}	1.72×10^{-2}

$k_3 = 7.53 \times 10^2$ L^2 mol^{-2} s^{-1}



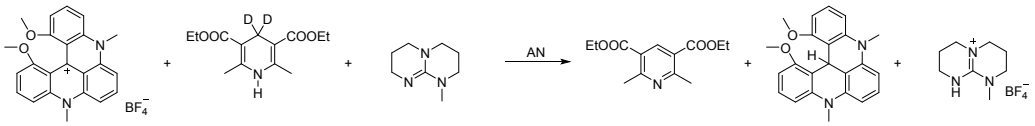
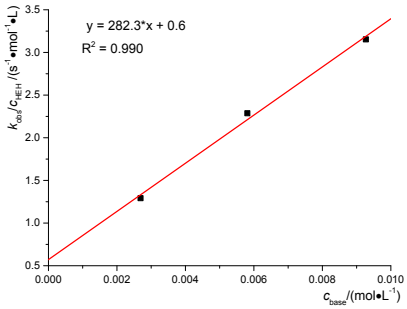


Table S12 kinetics of the reaction of **2O$^+$Me** (1.2×10^{-4} mol^{-1} L^{-1}) with d_2-Hantzsch (d_2-HEH), MTBD as base, λ = 620 nm.

No.	$[d_2\text{-HEH}]_0$ / mol^{-1} L	$[\text{Base}]_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	2.09×10^{-3}	2.69×10^{-3}	2.70×10^{-3}
2	2.09×10^{-3}	5.81×10^{-3}	4.78×10^{-3}
3	2.09×10^{-3}	9.27×10^{-3}	6.59×10^{-3}

$k_3 = 2.82 \times 10^2$ L^2 mol^{-2} s^{-1}



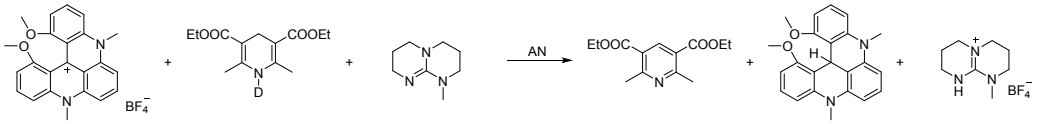
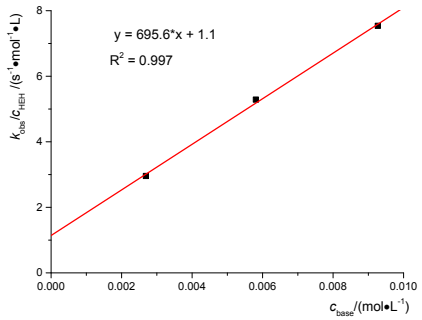


Table S13 kinetics of the reaction of **2O$^+$Me** (1.2×10^{-4} mol^{-1} L^{-1}) with ND-Hantzsch (ND-HEH), MTBD as base, λ = 620 nm.

No.	$[\text{ND-HEH}]_0$ / mol^{-1} L	$[\text{Base}]_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	2.30×10^{-3}	2.69×10^{-3}	6.80×10^{-3}
2	2.30×10^{-3}	5.81×10^{-3}	1.22×10^{-2}
3	2.30×10^{-3}	9.27×10^{-3}	1.73×10^{-2}

$k_3 = 6.96 \times 10^2$ L^2 mol^{-2} s^{-1}



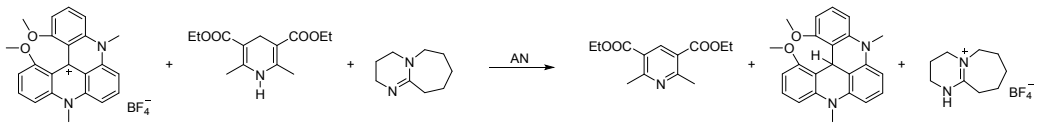
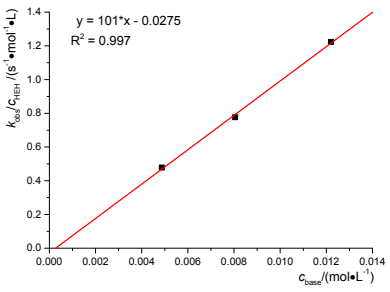


Table S14 kinetics of the reaction of **2O$^+$Me** (1.20×10^{-4} mol^{-1} L^{-1}) with Hantzsch (HEH), DBU as base, λ = 620 nm.

No.	$[\text{HEH}]_0$ / mol^{-1} L	$[\text{Base}]_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	2.55×10^{-3}	4.87×10^{-3}	1.23×10^{-3}
2	2.55×10^{-3}	8.05×10^{-3}	1.98×10^{-3}
3	2.64×10^{-3}	1.22×10^{-2}	3.23×10^{-3}

$k_3 = 1.00 \times 10^2$ L^2 mol^{-2} s^{-1}



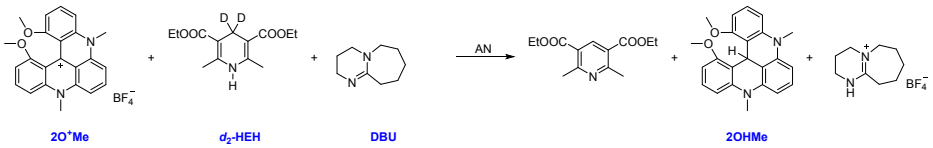
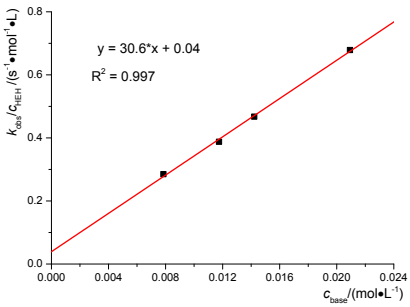


Table S15 kinetics of the reaction of **2O$^+$Me** (1.20×10^{-4} mol^{-1} L^{-1}) with d_2-Hantzsch (d_2-HEH), DBU as base, λ = 620 nm.

No.	[d_2-**HEH**]$_0$ / mol^{-1} L	[**Base**]$_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	2.78×10^{-3}	7.85×10^{-3}	7.91×10^{-4}
2	2.88×10^{-3}	1.18×10^{-2}	1.12×10^{-3}
3	2.88×10^{-3}	1.42×10^{-2}	1.35×10^{-3}
4	2.88×10^{-3}	2.09×10^{-2}	1.96×10^{-3}

$k_3 = 3.06 \times 10^1$ L^2 mol^{-2} s^{-1}



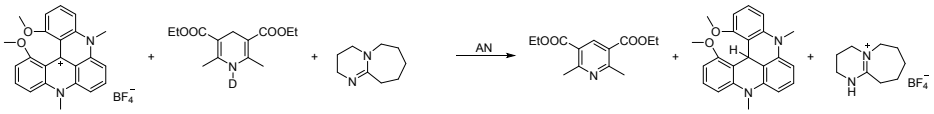
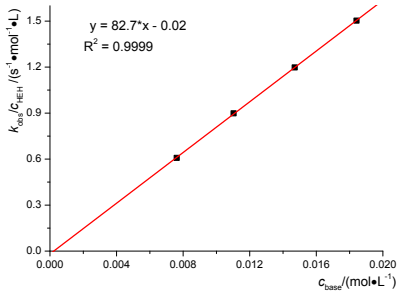


Table S16 kinetics of the reaction of **2O$^+$Me** (1.26×10^{-4} mol^{-1} L^{-1}) with ND-Hantzsch (ND-HEH), DBU as base, λ = 620 nm.

No.	[ND-**HEH**]$_0$ / mol^{-1} L	[**Base**]$_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	3.32×10^{-3}	7.62×10^{-3}	1.97×10^{-3}
2	3.32×10^{-3}	1.10×10^{-2}	2.91×10^{-3}
3	3.32×10^{-3}	1.47×10^{-2}	3.88×10^{-3}
4	3.32×10^{-3}	1.84×10^{-2}	4.87×10^{-3}

$k_3 = 8.27 \times 10^1$ L^2 mol^{-2} s^{-1}



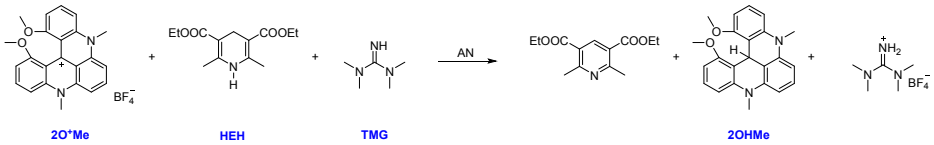
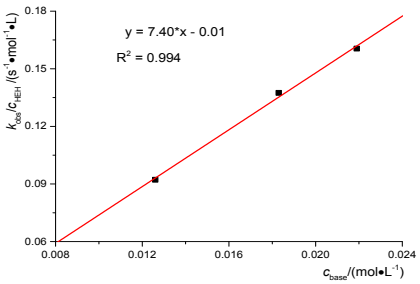


Table S17 kinetics of the reaction of **2O$^+$Me** (1.33×10^{-4} mol^{-1} L^{-1}) with Hantzsch (HEH), TMG as base, λ = 620 nm.

No.	[**HEH**]$_0$ / mol^{-1} L	[**Base**]$_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	3.47×10^{-3}	1.26×10^{-2}	3.20×10^{-4}
2	3.47×10^{-3}	1.83×10^{-2}	4.77×10^{-4}
3	3.47×10^{-3}	2.19×10^{-2}	5.57×10^{-4}

$k_3 = 7.4 \times 10^0$ L^2 mol^{-2} s^{-1}



11.2 BPHyT reactions of p3-Acr$^+$ with Hantzsch esters and bases

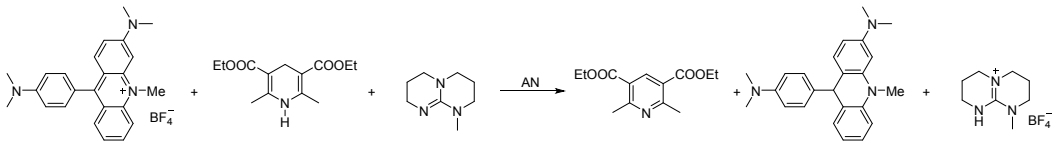
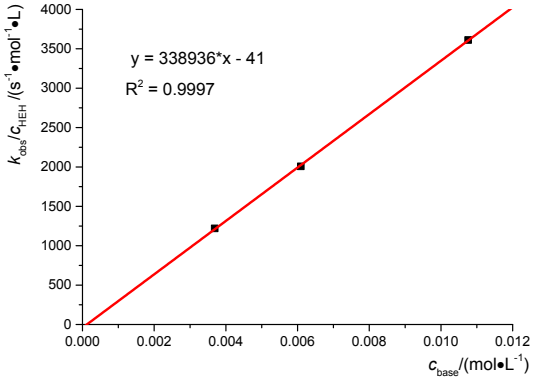


Table S18 kinetics of the reaction of **p3-Acr**$^+$ (1.10×10^{-4} mol^{-1} L^{-1}) with Hantzsch (HEH), MTBD as base, λ = 540 nm.

No.	$[\mathbf{HEH}]_0$ / mol^{-1} L	$[\mathbf{Base}]_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	2.36×10^{-3}	3.69×10^{-3}	2.88
2	2.36×10^{-3}	6.09×10^{-3}	4.74
3	2.36×10^{-3}	1.08×10^{-2}	8.52

$k_3 = 3.39 \times 10^5$ L^2 mol^{-2} s^{-1}



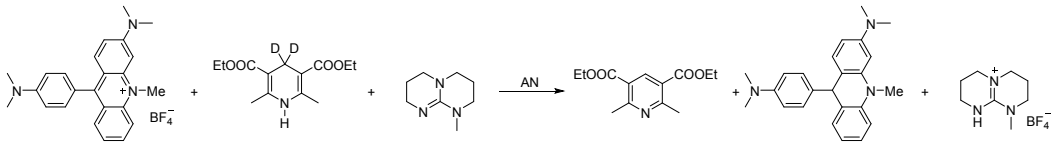
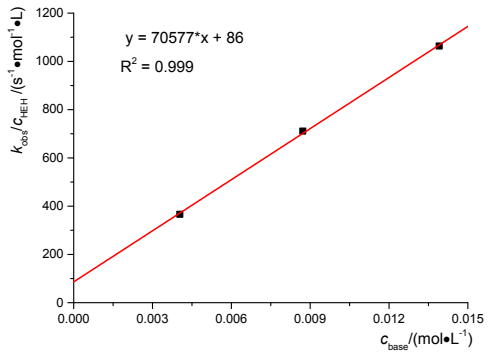


Table S19 kinetics of the reaction of **p3-Acr**$^+$ (1.10×10^{-4} mol^{-1} L^{-1}) with d_2-Hantzsch (d_2-HEH), MTBD as base, λ = 540 nm.

No.	$[d_2\text{-}\mathbf{HEH}]_0$ / mol^{-1} L	$[\mathbf{Base}]_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	3.80×10^{-3}	4.04×10^{-3}	1.39
2	3.80×10^{-3}	8.72×10^{-2}	2.70
3	3.80×10^{-3}	1.39×10^{-2}	4.04

$k_3 = 7.06 \times 10^4$ L^2 mol^{-2} s^{-1}



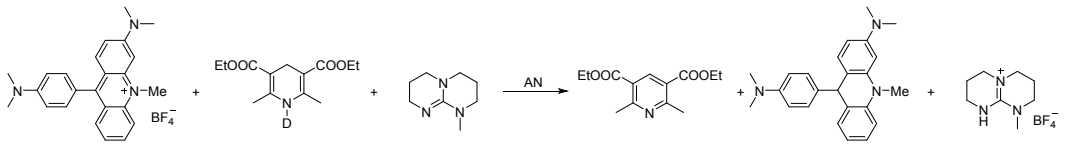
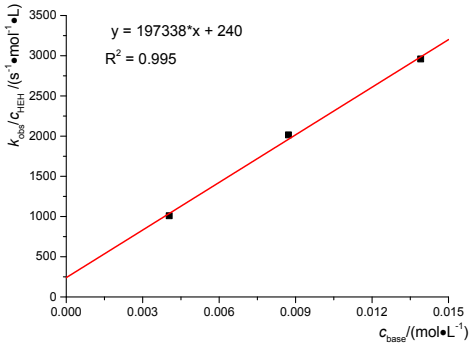


Table S20 kinetics of the reaction of **2O$^+$Me** (1.26×10^{-4} mol^{-1} L) with N-D-Hantzsch (ND-HEH), MTBD as base, λ = 540 nm.

No.	[ND-**HEH**]$_0$ / mol^{-1} L	[**Base**]$_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	3.82×10^{-3}	4.04×10^{-3}	3.86
2	3.82×10^{-3}	8.72×10^{-2}	7.70
3	3.82×10^{-3}	1.39×10^{-2}	11.31

$k_3 = 1.97 \times 10^5$ L^2 mol^{-2} s^{-1}



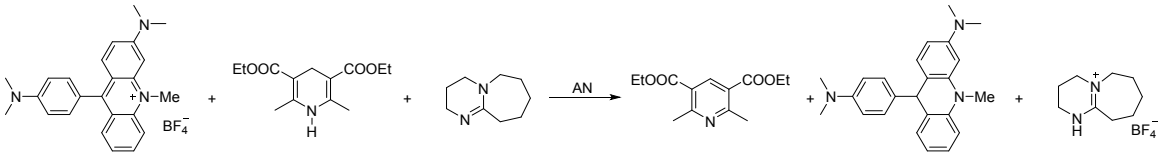
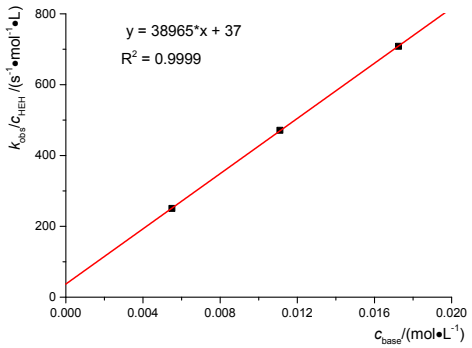


Table S21 kinetics of the reaction of **p3-Acr$^+$** (1.19×10^{-4} mol^{-1} L^{-1}) with Hantzsch (HEH), DBU as base, λ = 540 nm.

No.	[**HEH**]$_0$ / mol^{-1} L	[**Base**]$_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	2.58×10^{-3}	5.50×10^{-3}	0.65
2	2.58×10^{-3}	1.11×10^{-2}	1.22
3	2.58×10^{-3}	1.72×10^{-2}	1.83

$k_3 = 3.90 \times 10^4$ L^2 mol^{-2} s^{-1}



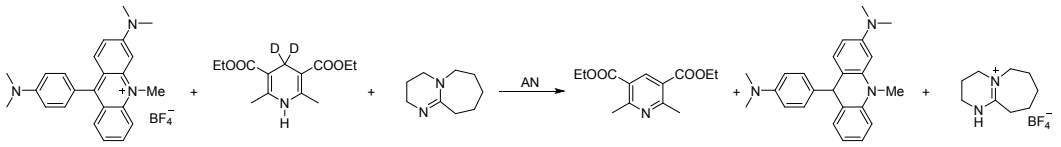
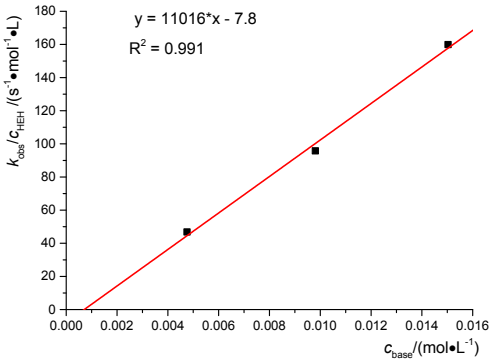


Table S22 kinetics of the reaction of **p3-Acr**$^+$ (1.52×10^{-4} mol^{-1} L^{-1}) with d_2-Hantzsch (d_2-HEH), DBU as base, λ = 540 nm.

No.	$[d_2\text{-HEH}]_0$ / mol^{-1} L	$[\text{Base}]_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	3.61×10^{-3}	4.76×10^{-3}	1.69×10^{-1}
2	3.61×10^{-3}	9.81×10^{-3}	3.46×10^{-1}
3	3.61×10^{-3}	1.50×10^{-2}	5.77×10^{-1}

$k_3 = 1.10 \times 10^4$ L^2 mol^{-2} s^{-1}



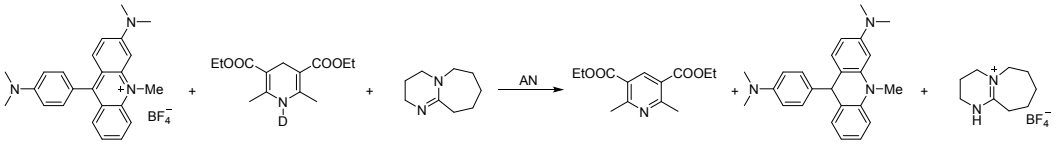
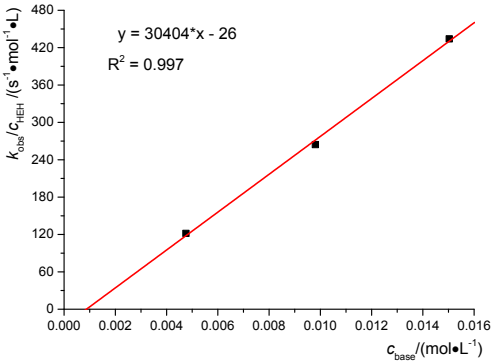


Table S23 kinetics of the reaction of **2O$^+$Me** (1.52×10^{-4} mol^{-1} L^{-1}) with ND-Hantzsch (ND-HEH), DBU as base, λ = 540 nm.

No.	$[\text{ND-HEH}]_0$ / mol^{-1} L	$[\text{Base}]_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	3.62×10^{-3}	4.76×10^{-3}	4.41×10^{-1}
2	3.62×10^{-3}	9.81×10^{-3}	9.57×10^{-1}
3	3.62×10^{-3}	1.50×10^{-2}	1.57×10^{0}

$k_3 = 3.04 \times 10^4$ L^2 mol^{-2} s^{-1}



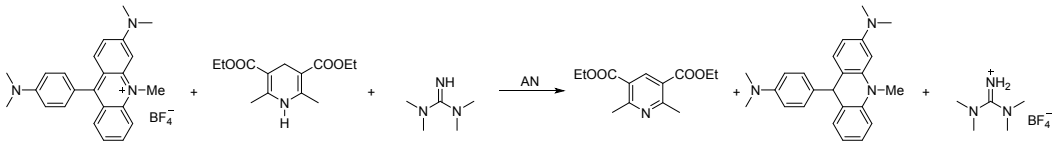
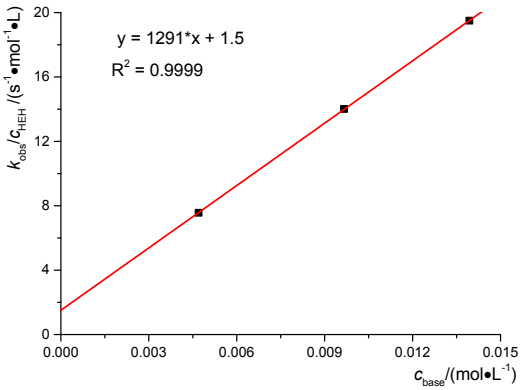


Table S24 kinetics of the reaction of **p3-Acr**$^+$ (1.21×10^{-4} mol^{-1} L^{-1}) with Hantzsch (HEH), TMG as base, λ = 540 nm.

No.	$[\mathbf{HEH}]_0$ / mol^{-1} L	$[\mathbf{Base}]_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	3.85×10^{-3}	4.70×10^{-3}	2.91×10^{-2}
2	3.85×10^{-3}	9.66×10^{-3}	5.39×10^{-2}
3	3.85×10^{-3}	1.39×10^{-2}	7.51×10^{-2}

$\boldsymbol{k_3 = 1.29 \times 10^3\ L^2\ mol^{-2}\ s^{-1}}$



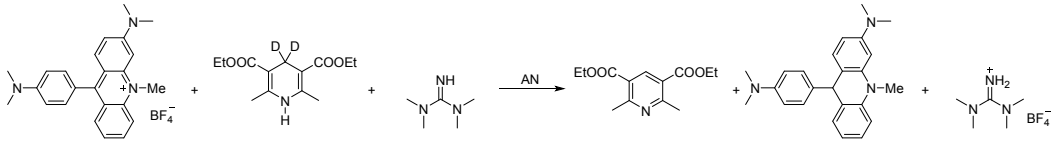
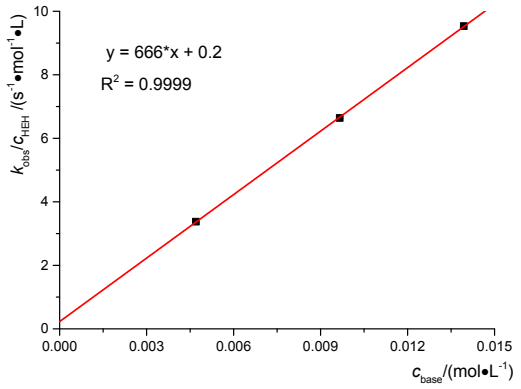


Table S25 kinetics of the reaction of **p3-Acr**$^+$ (1.21×10^{-4} mol^{-1} L^{-1}) with d_2-Hantzsch (d_2-HEH), TMG as base, λ = 540 nm.

No.	$[d_2\text{-}\mathbf{HEH}]_0$ / mol^{-1} L	$[\mathbf{Base}]_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	3.71×10^{-3}	4.70×10^{-3}	1.25×10^{-2}
2	3.71×10^{-3}	9.66×10^{-3}	2.46×10^{-2}
3	3.71×10^{-3}	1.39×10^{-2}	3.54×10^{-2}

$\boldsymbol{k_3 = 6.66 \times 10^2\ L^2\ mol^{-2}\ s^{-1}}$



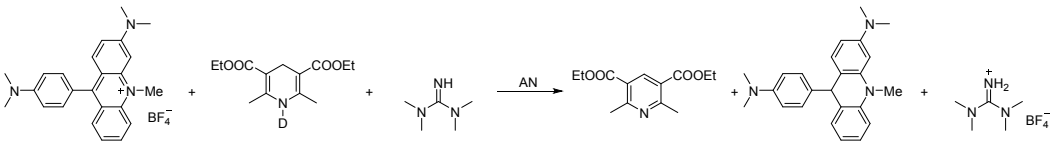
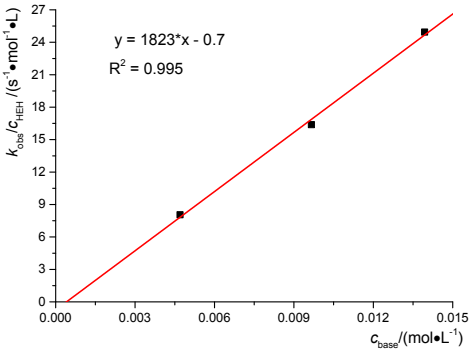


Table S26 kinetics of the reaction of **2O$^+$Me** (1.21×10^{-4} mol^{-1} L^{-1}) with ND-Hantzsch (ND-HEH), TMG as base, λ = 540 nm.

No.	[ND-**HEH**]$_0$ / mol^{-1} L	[**Base**]$_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	3.90×10^{-3}	4.70×10^{-3}	3.14×10^{-1}
2	3.90×10^{-3}	9.66×10^{-3}	6.39×10^{-1}
3	3.90×10^{-3}	1.39×10^{-2}	9.73×10^{0}

$k_3 = 1.82 \times 10^3$ L^2 mol^{-2} s^{-1}



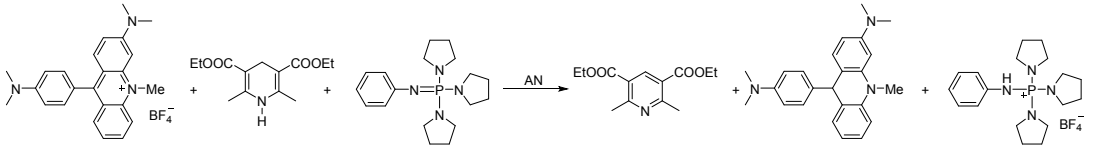
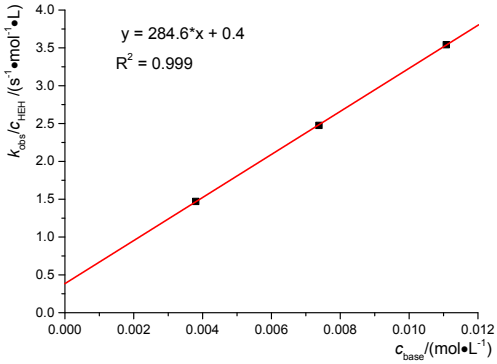


Table S27 kinetics of the reaction of **p3-Acr$^+$** (1.07×10^{-4} mol^{-1} L^{-1}) with Hantzsch (HEH), PhP1pyrr as base, λ = 540 nm.

No.	[**HEH**]$_0$ / mol^{-1} L	[**Base**]$_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	2.38×10^{-3}	3.80×10^{-3}	3.50×10^{-3}
2	2.38×10^{-3}	7.38×10^{-3}	5.89×10^{-3}
3	2.38×10^{-3}	1.11×10^{-2}	8.43×10^{-3}

$k_3 = 2.85 \times 10^2$ L^2 mol^{-2} s^{-1}



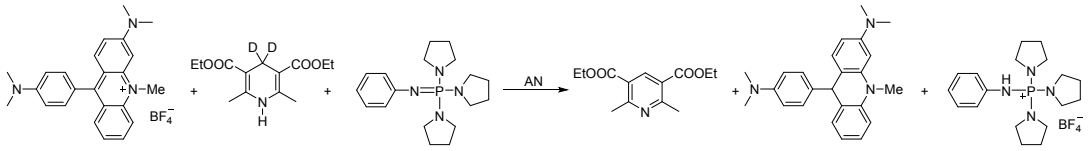
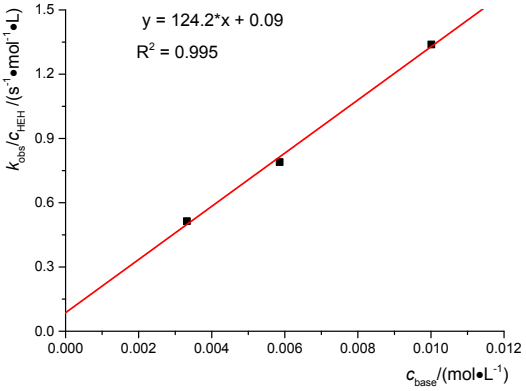


Table S28 kinetics of the reaction of **p3-Acr**$^+$ (1.07×10^{-4} mol^{-1} L^{-1}) with d_2-Hantzsch (d_2-HEH), PhP1pyrr as base, λ = 540 nm.

No.	[d_2-**HEH**]$_0$ / mol^{-1} L	[**Base**]$_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	2.51×10^{-3}	3.32×10^{-3}	1.30×10^{-3}
2	2.28×10^{-3}	5.86×10^{-3}	1.80×10^{-3}
3	2.51×10^{-3}	1.00×10^{-2}	3.36×10^{-3}

$k_3 = 1.24 \times 10^2$ L^2 mol^{-2} s^{-1}



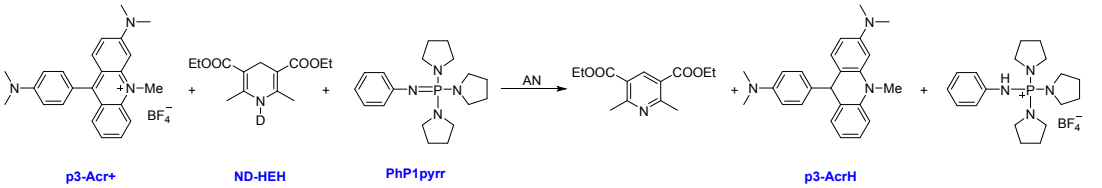
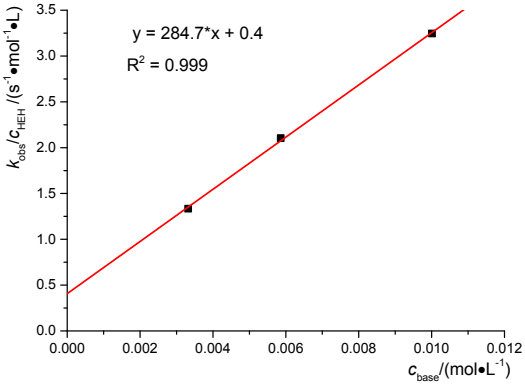


Table S29 kinetics of the reaction of **2O$^+$Me** (1.07×10^{-4} mol^{-1} L^{-1}) with ND-Hantzsch (ND-HEH), TMG as base, λ = 540 nm.

No.	[ND-**HEH**]$_0$ / mol^{-1} L	[**Base**]$_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	2.70×10^{-3}	3.32×10^{-3}	3.61×10^{-1}
2	2.70×10^{-3}	5.81×10^{-3}	5.69×10^{-1}
3	2.70×10^{-3}	1.00×10^{-2}	8.78×10^{0}

$k_3 = 2.85 \times 10^2$ L^2 mol^{-2} s^{-1}



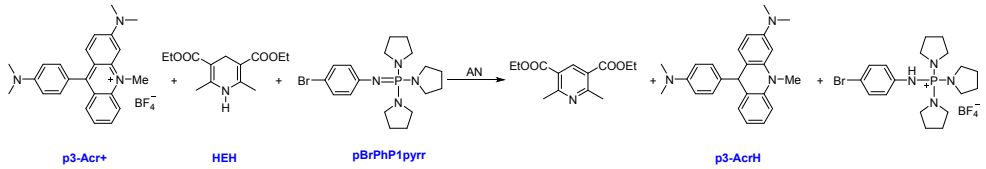
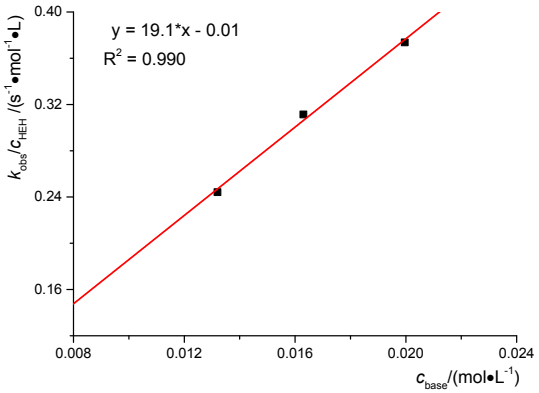


Table S30 kinetics of the reaction of **p3Acr**$^{+}$ (1.07×10^{-4} mol^{-1} L^{-1}) with Hantzsch (HEH), pBrPhP1pyrr as base, λ = 620 nm.

No.	$[\mathbf{HEH}]_0$ / mol^{-1} L	$[\mathbf{Base}]_0$ / mol^{-1} L	k_{obs}/ s^{-1}
1	2.40×10^{-3}	1.32×10^{-2}	5.86×10^{-4}
2	2.89×10^{-3}	1.63×10^{-2}	9.00×10^{-4}
3	2.89×10^{-3}	2.00×10^{-2}	1.08×10^{-3}

$k_3 = 1.90 \times 10^1$ L^2 mol^{-2} s^{-1}



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