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Enantioselective olefin epoxidation using novel biphenyl and binaphthyl azepines and azepinium salts

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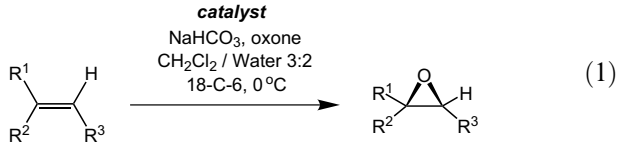
Abstract—Homologous biphenyl and (diastereomeric) binaphthyl tertiary azepines and quaternary iminium salts were prepared from (*S*)- and (*R*)-3,3-dimethylbutan-2-amine. Both the amines and iminium ions behave as effective catalysts for the enantioselective epoxidation of unfunctionalized olefins (ee up to 87%).

1. Introduction

Chiral nonracemic epoxides are useful precursors in synthetic chemistry, and frequent structures in natural products, often related to their biological activities (Eq. 1).[1] A few efficient catalytic methods currently exist for their preparation from olefins and many of them are based on transition metals such as the Katsuki–Sharpless or Katsuki–Jacobsen protocols.[2] In recent years, much effort has been devoted to the development of organocatalyzed epoxidation conditions that afford metal-free procedures; the catalysts being perhydrate, dioxirane, oxaziridine, or oxoammonium moieties as well as ammonium or oxaziridinium salts.[3]



(1)

Oxaziridinium ions are attractive alternatives to the commonly used dioxiranes.[4] These organic salts are effective oxygen transfer reagents towards nucleophilic substrates and electron-rich unfunctionalized olefins in particular. Moreover, the propensity of iminium ions to react with an Oxone® triple salt to generate the oxaziridinium species renders the development of catalytic processes possible.[5] Several successful enantioselective variants of the reaction have already been reported,[6–9] among which are studies using biphenyl **1i** and **2i**,[10–12] and binaphthyl **3i** and **4i** iminium salts (Fig. 1);[13] compounds [**3i**][X] and [**4i**][X] being some of the most effective iminium salt catalysts to date (ee up to 95%).[14]

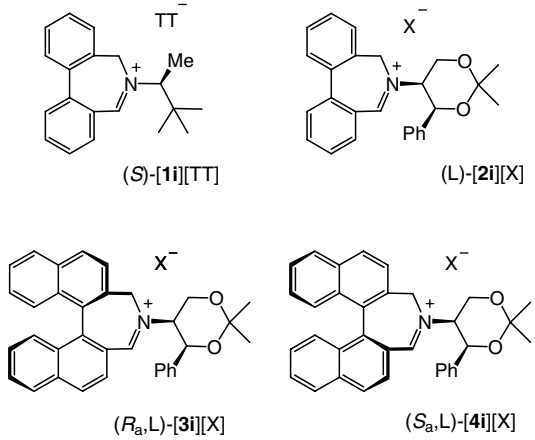


Figure 1. Selected nonracemic iminium salts and their absolute configuration, X^- symbolizes a lipophilic noncoordinating anion (BPh_4^- or TRISPHAT—abbreviated TT).

In compounds **1i** and **2i**, the stereocontrol over the reaction is provided by the exocyclic chiral appendages derived from enantiopure 3,3-dimethylbutan-2-amine **5** [(*S*)- or

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(*R*)-enantiomers] and L-acetonamine **6**, respectively (Fig. 2).[15] Significantly, with **1i** and **2i**, similar levels of reactivity and enantioselectivity were obtained indicating that amines **5** and **6** display similar stereochemical efficiency (ee up to 80% and 79%, respectively).[12]

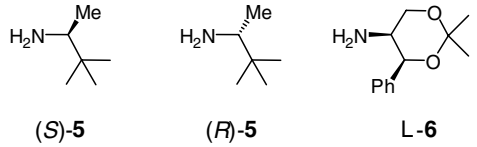


Figure 2. Nonracemic amines used as chiral auxiliaries.

Compounds **3i** and **4i** are diastereomers that incorporate both a configurationally rigid binaphthyl core and L-acetonamine as stereogenic elements. In this case, the *atropos* binaphthyl core has a predominant stereochemical influence. The enantioselectivity of the epoxidation reaction is controlled by the configuration of the biaryl moiety rather than the exocyclic appendage.[13] Essentially identical ee values are obtained in the reactions of prochiral olefins in the presence of diastereomeric **3i** and **4i** in favor of epoxides of opposite configurations.

To the best of our knowledge, for these dinaphthylazepinium systems, with the exception of (−)-isopinocamphenylamine which leads to less selective catalysts than those derived from L-(+)-acetonamine,[13] no other chiral exocyclic appendages have been reported to date. In view of our results with **1i** and **2i**, it was debatable whether binaphthyl iminium ions **7i** and **8i** derived from 3,3-dimethylbutan-2-amine **5** (Fig. 3) would display similar or better levels of selectivity to that of salts **3i** and **4i** and whether the biaryl core would still predominate in the stereocontrol.

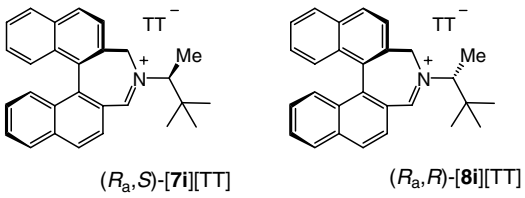


Figure 3. Binaphthyl iminium salts [**7i**][TT] and [**8i**][TT] derived from (*S*)-**5** and (*R*)-**5**, respectively, TT = TRISPHAT.

Furthermore and maybe more importantly, as we have recently demonstrated that azepine precursors to iminium ions **2i**, **3i**, and **4i** are essentially as effective catalysts for the enantioselective epoxidation of prochiral olefins as their unsaturated derivatives,[16] we wondered whether azepines **1a** (Fig. 4), **7a** and **8a** (Scheme 1) would behave similarly and also display effective enantioselective oxidation abilities.

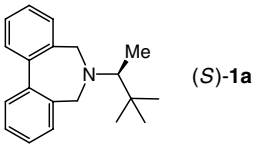
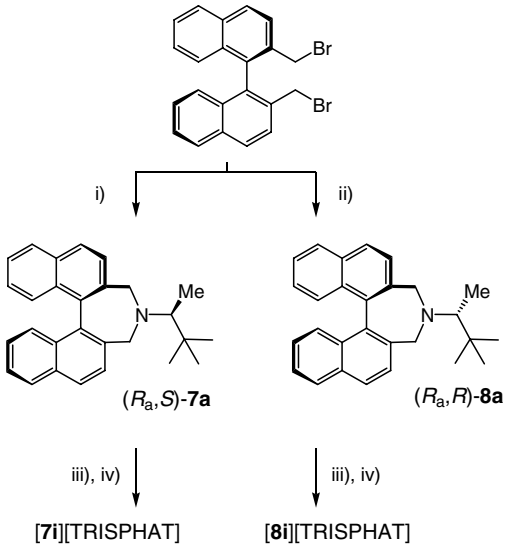


Figure 4. Azepine precursor **1a** to azepinium catalyst **1i**.



Scheme 1. Reagents and conditions: (i) (*S*)-**5** (1.2 equiv), K_2CO_3 (4.0 equiv), CH_3CN, reflux, 72%; (ii) (*R*)-**5** (1.2 equiv), K_2CO_3 (4.0 equiv), CH_3CN, reflux; 76%; (iii) NBS (1.1 equiv), $CHCl_3$, 20 °C; (iv) $[Et_2NH_2]$-[TRISPHAT] (1.2 equiv), chromatography (basic Al_2O_3, CH_2Cl_2) (two steps), 86–88%.

Herein, we report that tertiary amines **1a**, **7a**, and **8a**, and iminium cations **7i** and **8i** behave as efficient catalysts for the enantioselective epoxidation of unfunctionalized alkenes (ee up to 87%).

2. Results and discussion

The preparation of azepine **1a** and its derived iminium salt [**1i**][TRISPHAT] has been previously reported.[12]

For the synthesis of the novel binaphthyl derivatives **7a**, **8a**, **7i**, and **8i**, a short three steps protocol was developed using the known (R_a)-2,2′-bis(bromomethyl)-1,1′-binaphthyl as the starting material and standard reactions (Scheme 1):[16] (i) an alkylation with (*S*)-**5** or (*R*)-**5** to afford diastereomeric amines **7a** and **8a** (72% and 76% respectively); (ii) subsequent eliminations with *N*-bromosuccinimide to form the iminium salts; and (iii) ion pair metatheses with an ammonium TRISPHAT salt to afford the final products [**7i**][TRISPHAT] and [**8i**][TRISPHAT] (86% and 88% respectively, two steps).[17]

One set of epoxidation conditions (CH_2Cl_2/$NaHCO_3$/18-crown-6/H_2O) and five different prochiral di- and tri-substituted unfunctionalized alkenes **9**–**13** (Fig. 5) were selected for the study. The results are reported in Tables 1 and 2 for biphenyl **1a** and **1i** and binaphthyls **7a**, **8a**, **7i** and **8i** catalysts, respectively.

Significantly, amine **1a** behaves as an effective catalyst essentially performing as well as iminium **1i** in terms of conversions; enantiomeric excesses were however globally lower with the azepine moiety. Ee values up to 70% and 80% were nevertheless obtained with olefin **10** as substrate and catalysts **1a** and [**1i**][TRISPHAT], respectively. With the exception of alkene **13**, nonracemic epoxides of

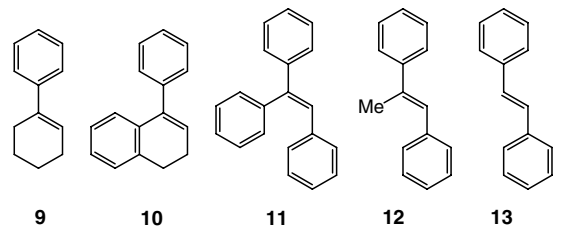


Figure 5. Prochiral di- and tri-substituted alkenes.

analogous absolute configurations were isolated from the reactions with **1a** and [**1i**][TRISPHAT]; the result with *trans*-stilbene that sees an inversion in the sense of induction is, at the moment, unexplained.

As mentioned, olefins **9**–**13** were also treated with substoichiometric amounts (5 mol %) of **7a**, **8a**, [**7i**][TRISPHAT] and [**8i**][TRISPHAT]. The results are reported in Table 2; all four derivatives behaved as catalysts. Careful analysis of the data reveals a number of subtleties but some general trends can be found.

If one compares the selectivity of the diastereomeric catalysts together—that is, **7a** with **8a**, and **7i** with **8i**—one generally observes analogous levels of stereoinduction in the (R_a,*S*) and (R_a,*R*) series with, to the exception of olefin **11**, slightly better ee with the (R_a,*R*)-configurated catalysts **8a** and **8i**. An identical sense of induction was obtained for the nonracemic epoxides in all examples. This indicates that the binaphthyl framework is (again[13,16]) a more effective chiral auxiliary than 3,3-dimethylbutan-2-amine, since the configuration of the epoxides does not change with opposite absolute configuration of the chiral appendage.

This general lack of 'matched'/'mismatched' distinction, as far as enantiomeric excesses are concerned, does not apply to conversions. Catalyst **7i** performed better than **8i**. Amine **7a** also catalyzed the reaction better than **8a** (e.g., olefin **10**, **7a**: 100% vs **8a**: 44%). As such, the 'matched' catalysts in terms of selectivity (ee values) are 'mismatched' in terms of conversions.

Comparing the selectivity of the homologous amine and iminium salts—that is, **7a** with **7i**, and **8a** with **8i**—it can be seen that the amines and iminium salts induce the same sense of stereoselective induction into the nonracemic epoxides; the iminium cations leading to (slightly) better enantiomeric excesses, in particular in the case of olefin **13** (e.g., ee: **7i**: 30% vs **7a**: 3%).

3. Conclusion

Commercially available (*S*)- and (*R*)-3,3-dimethylbutan-2-amine **5** lead, in only two or three steps, to effective amine and iminium catalysts for the enantioselective epoxidation of prochiral unfunctionalized olefins. Although the exocyclic auxiliary is not the predominant force for stereocontrol of the reaction in the diastereomeric series, it has, unlike (−)-isopinocamphenylamine,[13] no detrimental influence on the enantioselectivity. It promotes, under biphasic CH_2Cl_2/water conditions, even better ee values than L-acetonamine derived catalysts (e.g., olefin **10**, ee: **8a**: 86% vs **3a**: 78% and **8i**: 87% vs **3i**: 69%).[16]

It is also noteworthy that the amines and iminium ions lead to such similar enantiomeric excess values. It is, therefore, reasonable to consider a single mechanistic pathway for the two processes.[18] Investigations are currently underway to

Table 1. Enantioselective epoxidation of olefins **9**–**13** using azepine **1a** and iminium salt [**1i**][TRISPHAT] as catalysts[a,b]

Alkene	Amine **1a**			Iminium salt [**1i**][TRISPHAT]		
	Conv. (%)	ee (%)	Conf.	Conv. (%)	ee (%)	Conf.
9	58	39	(−)-(*S*,*S*)	68	66	(−)-(*S*,*S*)
10	100	70	(+)-(1*R*,2*S*)	100	80	(+)-(1*R*,2*S*)
11	60	15	(+)-(*S*)	61	31	(+)-(*S*)
12	74	22	(−)-(*S*,*S*)	75	46	(−)-(*S*,*S*)
13	61	22	(+)-(*R*,*R*)	64	17	(−)-(*S*,*S*)

[a] 5 mol % of catalyst, 2.5 mol % 18-C-6, 1.1 equiv Oxone®, 4.0 equiv $NaHCO_3$, CH_2Cl_2/H_2O (3:2), 2 h, 0 °C. Average of at least two runs.
[b] The enantiomeric excesses were determined by CSP-GC (**9**, Chiraldex Hydrodex β-3P) or CSP-HPLC (**10**–**13**, CHIRALPAK®-IB, 0.5 ml min^{-1}, hexane–*i*-PrOH 95:5, λ 230 nm); the conversions using an internal standard (naphthalene).

Table 2. Enantioselective epoxidation of olefins **9**–**13** using azepines **7a** and **8a** and iminium salts [**7i**][TRISPHAT] and [**8i**][TRISPHAT] as catalysts[a,b]

Alkene	Amines						Iminium salts					
	7a			**8a**			[**7i**][TRISPHAT]			[**8i**][TRISPHAT]		
	Conv. (%)	ee (%)	Conf.	Conv. (%)	ee (%)	Conf.	Conv. (%)	ee (%)	Conf.	Conv. (%)	ee (%)	Conf.
9	70	74	(−)-(*S*,*S*)	43	86	(−)-(*S*,*S*)	67	84	(−)-(*S*,*S*)	48	86	(−)-(*S*,*S*)
10	100	81	(+)-(1*R*,2*S*)	44	86	(+)-(1*R*,2*S*)	85	86	(+)-(1*R*,2*S*)	61	87	(+)-(1*R*,2*S*)
11	56	37	(+)-(*S*)	50	26	(+)-(*S*)	82	38	(+)-(*S*)	62	29	(+)-(*S*)
12	70	49	(−)-(*S*,*S*)	23	59	(−)-(*S*,*S*)	75	61	(−)-(*S*,*S*)	54	61	(−)-(*S*,*S*)
13	87	3	(−)-(*S*,*S*)	28	14	(−)-(*S*,*S*)	98	30	(−)-(*S*,*S*)	75	30	(−)-(*S*,*S*)

[a] 5 mol % of catalyst, 2.5 mol % 18-C-6, 1.1 equiv Oxone®, 4.0 equiv $NaHCO_3$, CH_2Cl_2/H_2O (3:2), 2 h, 0 °C. Average of at least two runs.
[b] The enantiomeric excesses were determined by CSP-GC (**9**, Chiraldex Hydrodex β-3P) or CSP-HPLC (**10**–**13**, CHIRALPAK®-IB, 0.5 ml min^{-1}, hexane–*i*-PrOH 95:5, λ 230 nm); the conversions using an internal standard (naphthalene).

help understand the mechanism of the catalytic process with these particular tertiary azepines and azepinium salts.

4. Experimental

NMR spectra were recorded on Bruker AMX-400 at room temperature, unless otherwise stated. ^{1}H NMR: chemical shifts are given in ppm relative to Me_4Si with the solvent resonance used as the internal standard. ^{31}P NMR (162 MHz): chemical shifts are reported in ppm relative to H_3PO_4. ^{13}C NMR (100 MHz): chemical shifts are given in ppm relative to Me_4Si, with the solvent resonance used as the internal standard ($CDCl_3$ δ 77.0 ppm, DMSO-d_6 δ 39.5 ppm, CD_2Cl_2 δ 53.8). IR spectra were recorded with a Perkin–Elmer 1650 FT-IR spectrometer using a diamond ATR Golden Gate sampling. Melting points (Mp) were measured in open capillary tubes on a Stuart Scientific SMP3 melting point apparatus and are uncorrected. Electrospray mass spectra (ES-MS) were obtained on a Finnigan SSQ 7000 at the Department of Mass Spectroscopy of the University of Geneva. Optical rotations were measured on a JASCO P-1030 polarimeter in a thermostated (20 °C) 10.0 cm long microcell with high pressure lamps of sodium or mercury and are reported as follows: $[\alpha]_{\lambda}^{20}$ (c (g/100 ml), solvent). Chiral stationary phase (CSP) HPLC analyses were performed on an Agilent 1100 apparatus (binary pump, autosampler, column thermostat and diode array detector) and a DAICEL CHIRALPAK®-IB column (25 × 4.6 cm). CSP GC analysis was performed on a Hewlett–Packard 6890 GC chromatograph using a Hydrodex-β column (25 m × 0.25 mm, H_2, 40 psi). Retention times (t_R) are given in minutes (min).

4.1. Biphasic enantioselective epoxidation procedure

In a 10 ml flask equipped with a magnetic stirring bar, $NaHCO_3$ (67.0 mg, 0.80 mmol, 4.0 equiv) was added to 800 μl of water. Oxone® (132.0 mg, 0.21 mmol, 1.0 equiv) was then added and the solution stirred for 2 min until effervescence subsided. A solution (500 μl) of a 0.4 mol/l of the alkene (0.20 mmol, 1.0 equiv) and naphthalene (0.20 mmol, 1.0 equiv, internal reference) in CH_2Cl_2 was added and the resulting biphasic mixture cooled to 0 °C with a cryostatic bath. The catalyst (10.0 μmol, 5 mol %) in CH_2Cl_2 (500 μl) was added, followed by a solution of 18-crown-6 (1.0 mg, 5.0 μmol, 2.5 mol %) in CH_2Cl_2 (200 μl). The reaction mixture was then stirred at room temperature for 2 h.

4.2. (−)-(R_a)-4,5-Dihydro-3*H*-4-[(*S*)-3,3-dimethylbutan-2-yl]dinaphth[2,1-*c*;1′,2′-*e*]azepine or (R_a,*S*)-7a

In a 25 ml round bottomed flask containing a solution of (*S*)-3,3-dimethylbutan-2-amine (82.2 mg, 0.812 mmol) in acetonitrile (10 ml) was added (R_a)-2-(bromomethyl)-1-(2-(bromomethyl)naphthalen-1-yl)naphthalene (298.0 mg, 0.677 mmol) and potassium carbonate (374.3 mg, 2.708 mmol). The mixture was heated at reflux (80 °C) for circa 3 h (till the complete consumption of the starting material as monitored by TLC, SiO_2, and CH_2Cl_2) and concentrated in vacuo. The solid was directly purified by chromatography (SiO_2, CH_2Cl_2) to yield the desired compound as a yellow solid (185 mg, 72%).

Mp 174 °C; $[\alpha]_D^{20} = -272.4$ (c 0.10, MeOH); IR (neat) 3054, 2968, 2858, 2795, 1689, 1595, 1507, 1459, 1268, 1143, 1114 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (2d, 4H, $J = 8.1$ Hz), 7.58 (d, 2H, $J = 8.3$ Hz), 7.46–7.41 (m, 4H), 7.26–7.22 (m, 2H), 3.73 (d, 2H, $J = 12.4$ Hz), 3.53 (d, 2H, $J = 12.4$ Hz), 2.51 (q, 1H, $J = 7.1$ Hz), 1.13 (d, 3H, $J = 7.1$ Hz), 0.97 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.3 (C^{IV}), 134.9 (C^{IV}), 133.0 (C^{IV}), 131.5 (C^{IV}), 128.7 (CH), 128.6 (CH), 128.4 (CH), 127.8 (CH), 125.7 (CH), 125.4 (CH), 68.1 (CH), 54.3 (CH_2), 36.9 (C^{IV}), 27.3 (CH_3), 12.3 (CH_3); MS-ES (+) m/z (rel intensity) 479.5 (50), 412.5 (60), 396.3 (80), 379.3 (100, M), 294.1 (95, M−C_6H_{13}), 279.1 (100), 266.1 (97), 252.3 (75); HRMS (ESI) calcd for $C_{28}H_{30}N$ $[M+H]^+$ 380.2372, found 380.2367.

4.3. (−)-(R_a)-4,5-Dihydro-3*H*-4-[(*R*)-3,3-dimethylbutan-2-yl]dinaphth[2,1-*c*;1′,2′-*e*]azepine (R_a,*R*)-8a

Prepared in an analogous fashion to **7a** with (*R*)-**5** (82.2 mg) to afford **8a** as a yellow solid (195 mg, 76%). Mp 193 °C; $[\alpha]_D^{20} = -255.8$ (c 0.10, MeOH); IR (neat) 3052, 2957, 2866, 1592, 1457, 1377, 1357, 1109 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, 4H, $J = 8.1$ Hz), 7.55 (d, 2H, $J = 8.4$ Hz), 7.49 (d, 2H, $J = 8.6$ Hz), 7.45 (d, 2H, $J = 7.0$ Hz), 7.26 (m, 2H), 3.58 (d, 2H, $J = 12.1$ Hz), 3.52 (d, 2H, $J = 12.4$ Hz), 2.81 (q, 1H, $J = 7.1$ Hz), 0.97 (s, 9H), 0.84 (d, 3H, $J = 7.1$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.0 (C^{IV}), 134.6 (C^{IV}), 133.0 (C^{IV}), 131.3 (C^{IV}), 128.6 (CH), 128.3 (CH), 127.6 (CH), 127.5 (CH), 125.6 (CH), 125.2 (CH), 69.7 (CH), 53.4 (CH_2), 37.1 (C^{IV}), 27.3 (CH_3), 11.7 (CH_3); MS-ES (+) m/z (rel intensity) 394.3 (75), 379.3 (97, M), 294.3 (100, M−C_6H_{13}), 267.3 (95), 252.3 (20); HRMS (ESI) calcd for $C_{28}H_{30}N$ $[M+H]^+$ 380.2372, found 380.2337.

4.4. (−)-(R_a)-[(*S*)-3,3-Dimethylbutan-2-yl]-3*H*-4-azapinium-cyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene (*rac*)-tris(tetrachlorobenzenediolato)phosphate(V) [(R_a,*S*)-7i][*rac*-TRISPHAT]

To a solution of (R_a,*S*)-**7a** (115 mg, 0.303 mmol) in $CHCl_3$ (2.0 ml) was added NBS (59.3 mg, 0.333 mmol) as a solid. After 20 min of stirring at 20 °C (till complete consumption of the starting material as monitored by TLC, SiO_2, and CH_2Cl_2), was added a solution of [Et_2NH_2][*rac*-TRISPHAT] (296.0 mg, 0.364 mmol) in acetone (2.0 ml). After 2 min stirring, the mixture was evaporated to dryness. The desired salt was isolated after column chromatography (SiO_2, CH_2Cl_2) as an intense yellow solid (300 mg, 86%).

$R_f = 0.70$ (CH_2Cl_2/EtOAc 9:1). Mp 251 °C; $[\alpha]_D^{20} = -207.4$ (c 0.10, MeOH); IR (neat) 2959, 1611, 1590, 1548, 1445, 1388, 1302, 1235, 970, 818 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.98 (s, 1H), 8.13 (d, 1H, $J = 8.3$ Hz), 8.01 (d, 1H, $J = 8.3$ Hz), 7.95 (m, 3H), 7.74 (t, 1H, $J = 8.1$ Hz), 7.59 (d, 1H, $J = 8.3$ Hz), 7.56 (t, 1H, $J = 7.8$ Hz), 7.50 (d, 1H, $J = 8.6$ Hz), 7.40 (t, 1H, $J = 8.3$ Hz), 7.29 (d, 1H, $J = 8.6$ Hz), 7.07 (d, 1H, $J = 8.8$ Hz), 5.02 (d, 1H, $J = 13.1$ Hz), 4.56 (d, 1H, $J = 12.6$ Hz), 4.15 (q, 1H,

$J = 6.8$ Hz), 1.71 (d, 3H, $J = 6.6$ Hz), 1.09 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.8 (N=CH), 142.7 (C^{IV}), 142.2 (C^{IV}, TT, $J = 6.4$ Hz), 142.1 (C^{IV}, TT, $J = 5.5$ Hz), 135.9 (C^{IV}), 134.2 (C^{IV}), 134.1 (C^{IV}), 132.3 (CH), 132.1 (C^{IV}), 132.0 (C^{IV}), 131.7 (C^{IV}), 130.1 (CH), 129.7 (CH), 129.0 (CH), 128.9 (CH), 128.4 (CH), 128.1 (CH), 127.9 (CH), 127.5 (CH), 126.0 (CH), 125.6 (C^{IV}), 125.3 (CH), 122.9 (C^{IV}, TT), 122.8 (C^{IV}, TT), 114.2 (C^{IV}, TT, $J = 7.4$ Hz), 114.0 (C^{IV}, TT, $J = 7.4$ Hz), 79.7 (CH), 36.4 (C^{IV}), 29.9 (CH_2), 27.3 (CH_3), 14.2 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ −80.70, −80.75; MS-ES (+) *m/z* (rel intensity) 378.3 (100, M^+), 294.3 (70, $M-C_6H_{13}$), 267.5 (80). MS-ES (−) *m/z* (rel intensity) 768.3 (100, TRISPHAT); HRMS (ESI-positive) calcd for $C_{28}H_{28}N$ $[M]^+$ 378.2216, found 380.2227 and (ESI-negative) calcd for $C_{18}Cl_{12}O_6P$ $[M]^-$ 764.5666, found 764.5758.

4.5. (−)-(R_a)-[(*R*)-3,3-Dimethylbutan-2-yl]-3*H*-4-azapinium-cyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene (*rac*)-tris(tetrachlorobenzenediolato)phosphate(V) [(R_a,*R*)-8i][*rac*-TRISPHAT]

Prepared in an analogous fashion to [**7i**][TRISPHAT] with (R_a,*R*)-**8a** (103 mg) to afford [**8i**][TRISPHAT] as an intense yellow solid (275 mg, 88%). $R_f = 0.76$ (CH_2Cl_2). Mp 220 °C; $[\alpha]_D^{20} = -264.3$ (*c* 0.10, MeOH); IR (neat) 3052, 2957, 2866, 1592, 1457, 1377, 1357, 1109 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.35 (s, 1H), 8.14 (d, 1H, $J = 8.3$ Hz), 8.00 (d, 1H, $J = 8.1$ Hz), 7.75–7.64 (m, 4H), 7.57 (t, 1H, $J = 7.1$ Hz), 7.44–7.36 (m, 2H), 7.31 (d, 1H, $J = 8.6$ Hz), 7.10 (d, 1H, $J = 8.8$ Hz), 4.97 (d, 1H, $J = 13.6$ Hz), 4.66 (d, 1H, $J = 13.4$ Hz), 4.36 (q, 1H, $J = 6.6$ Hz), 1.65 (d, 3H, $J = 6.3$ Hz), 1.08 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.6 (N=CH), 142.6 (C^{IV}), 142.1 (C^{IV}, TT, $J = 6.4$ Hz), 135.8 (C^{IV}), 134.1 (C^{IV}), 134.0 (C^{IV}), 132.2 (C^{IV}), 132.0 (CH), 131.7 (C^{IV}), 131.3 (CH), 129.6 (CH), 129.3 (CH), 129.0 (CH), 128.8 (CH), 128.2 (CH), 127.9 (CH), 127.8 (CH), 126.1 (C^{IV}), 125.7 (CH), 123.1 (C^{IV}, TT), 123.0 (C^{IV}, TT), 114.2 (C^{IV}, TT, $J = 7.4$ Hz), 114.0 (C^{IV}, TT, $J = 7.4$ Hz), 77.3 (CH), 36.4 (C^{IV}), 29.9 (CH_2), 27.2 (CH_3), 14.4 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ −80.77, −80.81; MS-ES (+) *m/z* (rel intensity) 393.3 (33), 378.1 (100, M^+), 294.3 (90, $M-C_6H_{13}$), 267.3 (85), 252.3 (20). MS-ES (−) *m/z* (rel intensity) 768.3 (100, TRISPHAT); HRMS (ESI-positive) calcd for $C_{28}H_{28}N$ $[M]^+$ 378.2216, found 380.2245 and (ESI-negative) calcd for $C_{18}Cl_{12}O_6P$ $[M]^-$ 764.5666, found 764.5563.

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